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Preparation of Allyltin Reagents Grafted on Solid Support: Clean and Easily Recyclable Reagents for Allylation of Aldehydes

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Abstract: The preparation of polymer-supported allyltin reagents was shown to be possible for both unfunctionalized and functionalized allyl units. These reagents were treated with aldehydes in the presence of cerium(III) or indium(III) salts to afford high yields of homoallylic alcohols, practically uncontaminated with organotin residues (less than 5 ppm). Some mechanism aspects are briefly discussed and the potential for regeneration and reuse of these supported reagents is pointed out.

Keywords: aldehydes · allylation · polymer-supported reagents · recycling · tin

Introduction

The development of new synthetic methods that are environmentally benign is of great interest today. One important strategy for this purpose involves the use of supported reagents or catalysts.[1] The immobilization of transition-metal catalysts and certain organometallic compounds, in order to control the pollution from these species at trace levels (a few ppm), has attracted a lot of attention, especially when compounds of biological or pharmaceutical interest are concerned. Moreover, immobilized reagents on polymer supports are particularly well suited for parallel and high-throughput syntheses, due to their well known properties of dispersal and removal from reaction mixtures.[2] Furthermore, the potential to recycle these polymer-bound reagents and catalysts also constitutes a highly desirable goal.[3] In this context, considerable efforts have been made to transfer the well established solution-phase reactions involving organometallic compounds or transition-metal complexes to solid supports. Accordingly, the use of supported reagents has recently been applied to free radical chemistry,[4] cross-coupling reactions,[5] olefin metathesis,[6] oxidation,[7] halogenation,[8] and reduction[9] reactions. In comparison, polymer-supported allylmetal reagents remain relatively unexplored, and in particular the preparation of polymer-supported allylstannanes[10] and their use in the allylation of aldehydes have not yet received much attention even though this polymer-supported chemistry should display major advantages in terms of ease of use, ease of removal of the tin residues from the desired products, and potential for recycling the supported tin reagents.

To the best of our knowledge, only a few examples of the use of immobilized allyltin reagents in allylation of aldehydes have been reported. Dumartin et al. have developed the polymer-supported dibutylallyltin reagent **1a**, synthesized by treatment of an allyl Grignard reagent with an iodotriorganostannylated resin,[11] whilst Cossy and Marshall have described the synthesis of the polymer-supported (α-alkoxycrotyl)tributyltin **2** by coupling a commercially available carboxylic polystyrene resin with an (α-hydroxycrotyl)-tributylstannane.[12] In both instances the authors pointed out that these new allylstannanes grafted onto polystyrene resin could be used for the allylation of aldehydes either with the aid of $BF_3{\cdot}OEt_2$ or through transmetalation with indium tribromide.[12] More recently, Gastaldi et al. have prepared soluble polyaromatic hydrocarbons (PAHs) bearing an allyltin unit **3** and have shown their usefulness in both radical and ionic allylations.[13] An allylstannane re-

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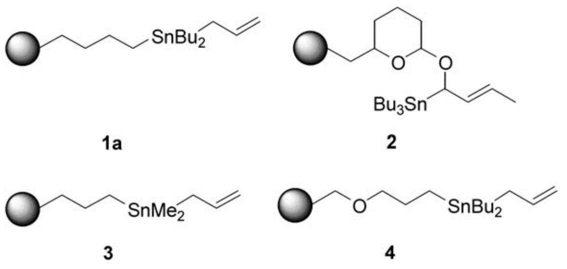
agent **4** grafted onto a soluble non-cross-linked polystyrene support was also obtained by Enholm and shown to be efficient in the free radical allylation reaction of organic halides[10] (Scheme 1).



Scheme 1.

In spite of the considerable improvements brought by these supported reagents, both for easy recovery of the products and for limitation of the tin contamination, further improvements can be reasonably suggested. In the case of the immobilized reagent **1a**, attachment of the scaffold was achieved by use of allylmagnesium reagents, which are incompatible with the presence of functionalities such as esters or nitriles, whilst in the case of the polymer-bound reagent **2**, the functional crotyltin unit is grafted to the solid support through an ether linkage instead of a tin–carbon linkage, a situation that may complicate the recycling of the reagents, due to the poor stabilities of α-hydroxyorganostannanes, and that might also make complete control of tin pollution more difficult.

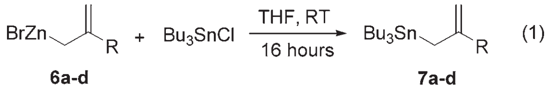
Finally, with soluble polymers, the separation and the isolation of the desired reaction products is usually less easy, because it is necessary to induce the precipitation of the macromolecular support with an appropriate solvent.[10,13] Thus, in view of the above remarks, and in conjunction with our recent involvement in the synthesis of polymer-supported organometallic reagents,[14] we investigated a new route to insoluble polymer-supported allylstannanes allowing the presence of functional groups on the allylic moiety. Here we describe a general and efficient route to immobilized allyltin reagents of type **1** by treatment of suitably substituted allylzinc reagents **6** with the resins **5** used as triorganostannyl halides (Scheme 2). We also evaluated the potential of these C-linked reagents **1a–d** in the allylation of a series of aldehydes, focusing both on the tin contamination in the isolated homoallylic alcohols and on the potential for recycling these new immobilized reagents.

Results and Discussion

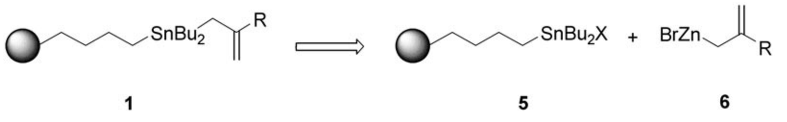
Preparation of the polymer-supported di-*n*-butylallyltin reagents of type 1a–d: The usual synthetic routes to allyltriorganotins in solution include treatment of triorganotin halides or triorganotin oxides with allylic Grignard reagents,[15] allyllithiums,[16] or allylzinc reagents.[17] Hydrostannation of either 1,2- or 1,3-dienes under free radical conditions or with palladium catalysis,[18,19] as well as stannylcupration of allenes,[20] have also been employed to obtain allyltins, but difficulties were encountered in controlling the regio- and/or the stereochemistry of the reactions. Tin hydrides have also been used to prepare allyltins from allylsulfones and related compounds.[21] While they are easy to carry out in terms of workup, the above preparations usually suffer from a lack of regio- and stereospecificity when γ-substituted allyl units are involved (mixture of isomers are obtained), although synthetic methods involving deprotonation reactions by organolithium reagents based either on crotyl carbamates in the presence of (−)-sparteine[22] or on chiral allylic substrates[23] have been reported to overcome these limitations satisfactorily in some cases. In practice, the problems encountered with the selectivity of the reactions can be more easily circumvented by the use of stannylanions, which can be used to achieve S_N2 reactions with allyl tosylates or chlorides[24] or 1,4-additions on α,β-enals. (*E*)- or (*Z*)-γ-oxygenated allyltins can also be selectively obtained through 1,4-additions of organocuprates to β-tributylstannylacroleine,[25] and in these series, when enantioenriched alkoxyallyltins are desired, the available highly enantioenriched α-oxygenated allyltins[26] can be stereospecifically isomerized into the γ-oxygenated isomers.[27]

Obviously, the use of stannyl anions should be of high interest for selectivity, but in a first step we needed to examine the use of more conventional reagents to establish the effective availability of supported allyltins and to evaluate their potential as recyclable allylation reagents. Initially then, to test compatibility with functional groups on the reagent, we decided to attempt direct coupling of organozinc reagents with triorganotin halides, a route that has not been extensively explored.[5d]

When carried out in liquid phase, the reactions between allylzinc reagents **6a–d**[28] and tributyltin chloride afforded the corresponding allyltins **7a–d** in fairly good isolated yields [Eq. (1)].

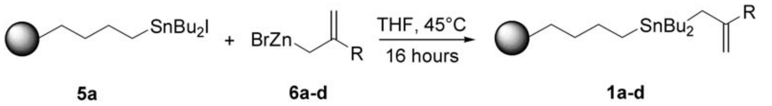


R = H (97%); Me (57%); COOEt (64%); CN (61%)



Scheme 2. Synthetic strategy.

These results suggest that it should be possible to synthesize a series of triorganoallyltin reagents grafted onto solid support by adding organozinc reagents **6** to a resin containing triorganotin halide units. For this purpose, we chose the already known polymer-supported triorganotin iodide **5a**,[9a–e,14] which seemed to be among the more suitable ones for our solid-phase applications because of its ease of formation and good loading (1.1 to 1.3 $mmol\,g^{-1}$). A series of immobilized triorganoallyltin reagents **1a–d** was thus prepared from polymer **5a** and appropriate allylzinc reagents **6a–d** [Eq. (2)]. The results are summarized in Table 1.



(2)

Table 1. Preparation of polymer-supported allyltin reagents **1a–d** with allylzincs.

Entry	Allylzinc **6**	Resin **1**	Conversion[a] [%]
1	**6a**: R = H	**1a**: R = H	94
2	**6b**: R = CH_3	**1b**: R = CH_3	88
3	**6c**: R = COOEt	**1c**: R = COOEt	75
4	**6d**: R = CN	**1d**: R = CN	53

[a] Conversion determined by ^{119}Sn MAS-NMR with use of an appropriate repetition time for quantitative analysis.

In a typical procedure, a solution of allylzinc **6a–d** in THF was added under argon to a mixture of solid-supported tin reagent **5a** in THF and the reaction mixture was stirred for 16 h at 45 °C before workup and filtration. The expected polymer-supported tin reagents **1a–d** were then successively washed with THF and absolute ethanol and were then dried under vacuum. The formation of the polymer-supported triorganoallyltin reagents **1a–d** was established through their IR spectra, each of which exhibits a well defined band around 1620 cm^{-1}, indicative of the C=C double bond of the allylic moiety. The presence of additional functionality on the allylic unit was also characterized by specific IR absorptions (band at 1720 cm^{-1} in the case of resin **1c** and weak band at 2200 cm^{-1} in the case of **1d**). Chemical information on the tin environment was also well established through solid-state ^{119}Sn MAS-NMR analysis, allowing us to ascertain the levels of conversion of resin **5a** to resins **1a–d**.[29,9c–d] Indeed, comparison of the relative intensities of the signal due to the polymer-supported triorganotin iodide **5a** with those due to the supported allyltins was indicative of the conversion rate of Sn−I (δ_{Sn} = +80.5 ppm) into Sn−Allyl (δ_{Sn} = −9.5 to −18.5 ppm) (reference: Ph_4Sn, δ_{Sn} = −121.1 ppm).[30] The complete disappearance of the signal due to **5a** in the case of polymer **1a** was regarded as evidence of a nearly quantitative conversion (Table 1, entry 1). For polymers **1b–d**, however, the presence of two typical signals at δ_{Sn} = +80.5 ppm and around δ_{Sn} = −15 ppm was indicative of incomplete conversion (Table 1, entries 2–4).

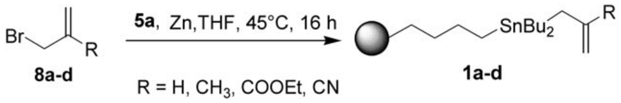
Table 2. One-pot synthesis of polymer-supported allyltins **1a–d**.

Entry	Allyl halide **8**	Resin **1**	Conversion[a] [%]	δ ^{119}Sn MAS-NMR	Tin loading[b] [$mmol\,g^{-1}$]
1	**8a**: R = H	**1a**: R = H	100	−18.5	1.41
2	**8b**: R = CH_3	**1b**: R = CH_3	95	−17.5	1.11
3	**8c**: R = COOEt	**1c**: R = COOEt	99	−12.1	1.23
4	**8d**: R = CN	**1d**: R = CN	94	−9.5	1.19

[a] Conversion determined by ^{119}Sn MAS-NMR spectroscopy. [b] Tin loading determined by elemental analysis.

In an effort to improve these results, we turned our attention to Tagliavini's procedure, which involves the one-pot synthesis of triorgano- and diorganoallyltins through a zinc-promoted coupling reaction between allyl bromide and R_3SnX (X = Cl, I, OH, etc.), Bu_2SnCl_2, or $(Bu_2SnCl)_2O$ in the presence of air and water.[17,31] We have confirmed its efficiency for the synthesis of **7a** and **7b** (81 and 88 % yields, respectively) and have shown its possible extension to functionalized allyl halides for the synthesis of **7c** and **7d** (87 and 91 % yields) by treatment of suitable allyl bromides with Bu_3SnCl and zinc powder in a THF/H_2O (NH_4Cl-saturated) mixture. The allylation of resin **5a** over 16 h under similar experimental conditions was also investigated, but ^{119}Sn MAS-NMR analysis of the collected resin particles (successively washed with THF and absolute ethanol and dried under vacuum) revealed a failure of this strategy to provide polymer-supported allyltins **1a–d**. The starting resin **5a** was recovered except in the case of **1c** (R = COOEt), in which a low conversion (30 %) was observed. This result may be explained by the large amount of water in THF, which is incompatible with the polystyrene resin:[32] the pore structure cannot fill with the co-solvent, preventing access of the organozinc reagents to the polymer network.

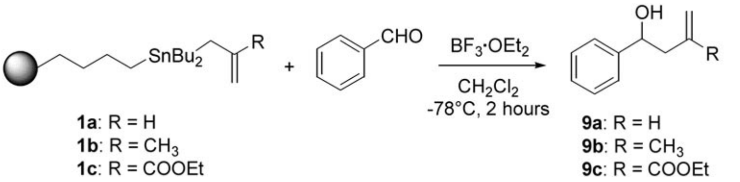
Accordingly, the reaction was subsequently achieved at 45 °C in anhydrous THF. These experimental conditions, much more favorable for a good swelling of resin **5a**, allowed the desired reaction with a high level of conversion, as determined by solid-state ^{119}Sn NMR (Scheme 3). As can be seen in Table 2 (entries 1–4), this method appears to be highly efficient for the preparation of the series of polymer-supported allyltins **1a–d**. Moreover, our procedure does not require prior preparation of the allylzinc reagents **6a–d**, so the polymer-supported allyltins **1a–d** are directly obtained



Scheme 3.

in a one-pot process with nearly quantitative loading as determined by solid state ^{119}Sn NMR (1.1–1.4 mmol g^{-1}).

Allylation reactions between aldehydes and polymer-supported allyltriorganotins 1a–d: The grafting rates and the natures of the substituents around tin being well established in supported allyltins **1a–d**, we therefore checked their efficiency in the allylation reactions of various aldehydes. Initially we carried out the allylation reaction with benzaldehyde in the presence of resins **1a–c** and $BF_3 \cdot OEt_2$ as Lewis acid promoter under anhydrous conditions [Eq. (3)]. For this purpose, resin **1a–c**, benzaldehyde, and CH_2Cl_2 were placed in a flask under argon and $BF_3 \cdot OEt_2$ (3 equiv) was added dropwise at −78 °C. The results are summarized in Table 3.



(3)

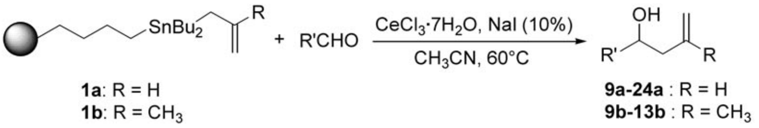
Table 3. Allylation of benzaldehyde in the presence of resins **1a–c** and with $BF_3 \cdot OEt_2$ as a Lewis acid promoter.

Entry	Resin **1**	Homoallylic alcohols **9**	Conversion[a] [%]	Yields[b] [%]
1	**1a**	**9a**	≈100	61
2	**1b**	**9b**	92	67
3	**1c**	**9c**	≈100	83

[a] Conversion determined by GC. [b] Yield of isolated pure compound after column chromatography on silica gel.

After stirring for 2 h at −78 °C and subsequent quenching with a mixture of THF/H_2O (1:1 v/v), the conversion rates of the crude homoallylic alcohols **9** were comparable to those obtained with soluble allyltins. It is worth noting that the reaction is unaffected by the presence of the ester function in the β-position (Table 3, entry 3).

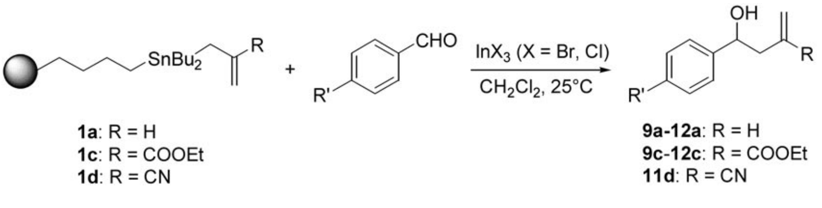
While this first approach had proved acceptable, improvements were sought to make the methodology amenable to automated parallel synthesis. The strictly anhydrous conditions and the low temperatures required with the use of $BF_3 \cdot OEt_2$ to promote the allylation of aldehydes are unsuitable for easy handling and manipulation, so we devoted our efforts to finding experimental conditions that would allow allylation reactions without the use of anhydrous solvents, inert atmosphere, and low temperature. $CeCl_3 \cdot 7H_2O$ seemed to be an attractive candidate for use as a Lewis acid in our solid-phase application in this context, due to its water tolerance and ready availability at low cost. Among the numerous methodologies[33] that employ cerium(III) derivatives for transferring nucleophile moieties to electrophilic centers, the allylation of aldehydes promoted by the $CeCl_3 \cdot 7H_2O$/NaI (10 %) system as a Lewis acid appeared to be a possible route,[34] so we examined the efficiency of this system in acetonitrile for the allylation of a series of aldehydes with resins **1a–d** [Eq. (4)].



(4)

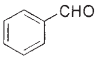
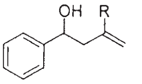
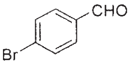
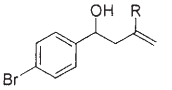
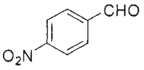
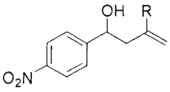
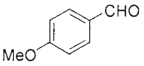
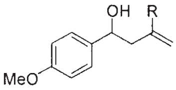
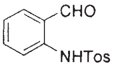
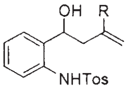
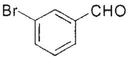
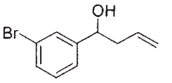
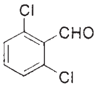
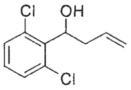
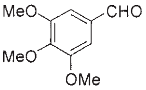
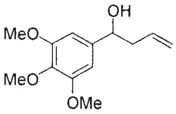
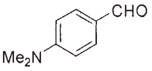
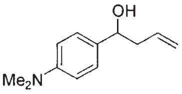
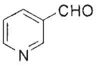
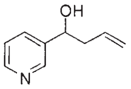
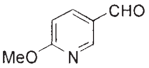
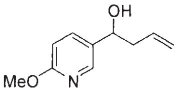
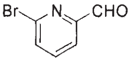
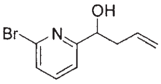
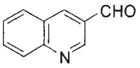
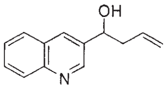
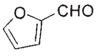
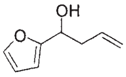
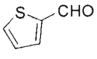
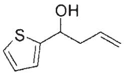
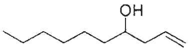
The reactions were conducted by heating a mixture of resin **1a–d** in acetonitrile containing the aldehyde and the $CeCl_3 \cdot 7H_2O$/NaI (10 %) combination (in suitable tubes for parallel synthesis equipment, with use of ellipsoidal stirring) at 60 °C for 24 to 48 h (Table 4). Good yields were obtained with the resins **1a** and **1b** whatever the nature of the aldehydes, while functionalized allyltin resins **1c** and **1d** appear to be nearly unreactive under these experimental conditions, a result that might be due either to insufficient Lewis acid character of the hydrated cerium salt or to competitive chelation on the β-functional group.

To circumvent the lack of reactivity of **1c** and **1d** in allylation promoted by cerium(III) salts, we investigated the use of other Lewis acids to promote this reaction and found that the use of indium(III) bromide or chloride [Eq. (5)] was also efficient, as attested by the results shown in Table 5 and consistently with previous reports concerning reactions achieved in liquid phase.[35] Good yields were uniformly obtained with $InBr_3$ as a promoter in this series, and $InCl_3$ was shown to have nearly the same efficiency when tested on two examples.



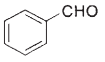
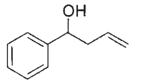
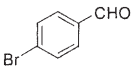
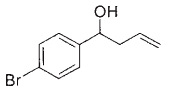
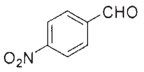
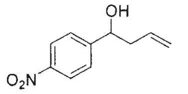
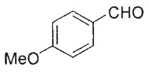
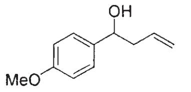
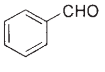
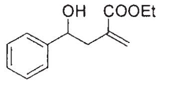
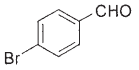
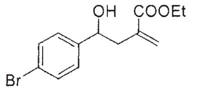
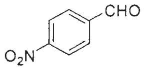
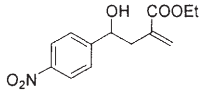
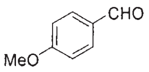
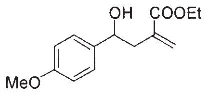
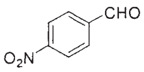
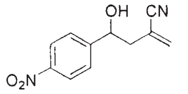
(5)

Table 4. Allylation of a series of aldehydes with resins **1a** and **1b** in the presence of $CeCl_3{\cdot}7H_2O$/NaI (10%) as a promoter.

Entry	Aldehyde	Product	Time [h]	Yield[a] [%]	Sn[b] [ppm]	Ce[c] [ppm]
1		 **9a**: R = H	30	95	3.8 ± 0.2	< 0.10
		9b: R = Me	36	90		
2		 **10a**: R = H	24	99	1.6 ± 0.1	< 0.10
		10b: R = Me	24	91	2.8 ± 0.2	0.28 ± 0.02
3		 **11a**: R = H	30	97	2.5 ± 0.2	< 0.10
		11b: R = Me	30	92		
4		 **12a**: R = H	48	82	3.3 ± 0.2	< 0.10
		12b: R = Me	48	78		
5		 **13a**: R = H	48	83	1.1 ± 0.1	0.11 ± 0.01
		13b: R = Me	48	89		
6		 **14a**	30	85		
7		 **15a**	48	93	6.0 ± 0.3	0.16 ± 0.01
8		 **16a**	60	74		
9		 **17a**	48	77		
10		 **18a**	48	86	1.0 ± 0.1	< 0.10
11		 **19a**	62	88		
12		 **20a**	60	85		
13		 **21a**	96	68	1.9 ± 0.3	< 0.10
14		 **22a**	48	87		
15		 **23a**	48	89	1.7 ± 0.1	< 0.10
16		 **24a**	48	82		

[a] Yield of isolated product after column chromatography. [b] Quantification of tin residues in the homoallylic alcohols determined by ICP-MS (average of three runs). [c] Quantification of cerium residues in the homoallylic alcohols determined by ICP-MS (average of three runs).

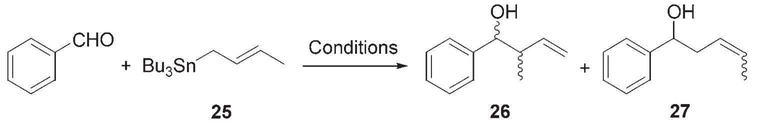
Table 5. Allylation of aldehydes with resins **1a, 1c,** and **1d** with $InBr_3$ or $InCl_3$ as a promoter.

Entry	Resin **1**	Aldehyde	Product		Yields[a] [%]
1	**1a**			**9a**	94
2	**1a**			**10a**	99 97[b]
3	**1a**			**11a**	95[c]
4	**1a**			**12a**	84
5	**1c**			**9c**	91
6	**1c**			**10c**	96 93[b]
7	**1c**			**11c**	92
8	**1c**			**12c**	72
9	**1d**			**11d**	73

[a] Yield of isolated product after column chromatography with use of $InBr_3$ as a promoter unless mentioned otherwise. [b] Reaction carried out with $InCl_3$. [c] The amount of tin residues in the product **11a** was measured by ICP-MS and found to be 1.1 ± 0.1 ppm.

Discussion of mechanism: From these different results, whatever the natures of the functional groups borne either by the supported allyltin reagent or by the aldehyde substrate, it appears that supported allyltins, in the presence of appropriate Lewis acids, can act as efficient allylation reagents. Furthermore, it is noteworthy that experimental conditions involving cerium(III) or indium(III) halides are compatible for applications in automated parallel synthesis. At this level, the question might be the real usefulness of the supported allyltins, since the effective species might be allylcerium or allylindium reagents resulting from a transmetallation reaction.[12,35]

Since allylcerium or allylindium species should react through a six-membered cyclic transition state,[35] in contrast with an open, acyclic transition state when allyltriorganotins are allowed to react with the aldehyde/Lewis acid complex,[36] the stereochemistry of the reactions involving simple γ-substituted allylmetals should be indicative of the nature of the involved mechanism. Thus, the crotylstannation of benzaldehyde under the experimental conditions used for the reactions involving supported allyltriorganotins afforded a mixture of branched and linear homoallylic alcohols **26** and **27** [Eq. (6)].



25 26 27 (6)

While **26** had been obtained as a single product with a strong preference for the *syn* isomer (*syn*/*anti* 82:18) from the reaction carried out in the presence of boron trifluoride (as would be expected from the opened transition state),[36] the reactions performed in the presence of $CeCl_3{\cdot}7H_2O$ or in the presence of $InCl_3$ or $InBr_3$ afforded mixtures of **26** and **27**. The major isomer, however, was *syn*-**26** (*syn*/*anti* 70:30 to 84:16), which is consistent with an opened transition state, because the six-membered transition state should mainly give the *anti* isomer. Furthermore, with cerium or indium salts, the linear adduct **27** was obtained mainly as the *Z* isomer, a trend that might be explained by a partial isomerization of crotyltributyltin into the less stable, but more reactive, 3-tributylstannyl-but-1-ene before addition to the aldehyde (Lewis acids facilitate this equilibrium). It is of interest to note that opposite stereochemical trends were observed by Loh in allylation reactions performed with crotyl bromide and metals in aqueous media (an *anti* preference being the main stereochemical trend for the branched isomers, while linear ones were obtained with high *E* stereoselectivity).[37] In a very closely related area, reactions between crotyltributyltins and aldehydes in the presence of carboxylic acids were recently reported by Zhao and Li. In this case, a strong preference for the linear isomer **27** was observed, but the proposed mechanism can hardly account for the very high *Z* stereoselectivity.[38]

In summary, our stereochemical results are consistent with a mechanism in which the effective allylating species should be allyltins, which should react with aldehydes linked to BF_3, $InCl_3$, or $InBr_3$. It suggests that these salts are acting mainly (or exclusively) as simple Lewis acids (without transmetalation of the organotin reagent) under our experimental conditions (those used for studies involving supported allyltins). The mechanistic aspects of these reactions, which can be strongly affected by the natures of the solvent and the additives and more generally by the experimental conditions, will be discussed in detail elsewhere.

Investigations of Sn and Ce contamination in the obtained homoallylic alcohols: The ^{13}C NMR and ^{1}H NMR spectra of the isolated homoallylic alcohols indicated no meaningful contamination by organotin residues. This observation was subsequently confirmed by ICP-MS analysis, which showed low or insignificant tin contamination (<5 ppm). Moreover, cerium residues were also quantified as below 1 ppm by ICP emission analysis of the crude homoallylic alcohols when this Lewis acid was used as a promoter. At this stage, complete validation of the method required the potential to recycle the recovered polymer-supported tin reagents at the end of the allylation reactions. For this purpose, the resin particles recovered at the end of the three different allylation processes were washed with THF and absolute ethanol, dried under vacuum, and characterized by IR and ^{119}Sn MAS-NMR spectroscopy before being regenerated and reused. As an example, in the ^{119}Sn MAS-NMR spectra of the resins recovered at the end of the reactions promoted either by $CeCl_3{\cdot}7H_2O/NaI$ (10%) or $InBr_3$, the signals at +147 and +133 ppm are indicative of the regeneration of the polymer-supported tin halides **5b** and **5c** (Figure 1).[39] That these organotin halides had been isolated was further evidenced by elemental analysis (cf: Experimental Section). In the case of the $BF_3{\cdot}OEt_2$-promoted allylation reactions, the recovered resins were less easily characterized and the ^{119}Sn MAS-NMR spectra of these resins only showed very ill-defined noisy signals, so the clear identification of the expected distannoxane-type species was impossible, an observation consistent with previous reports in the literature.[40] In spite of this, the obtained resin was amenable to regeneration (vide infra).

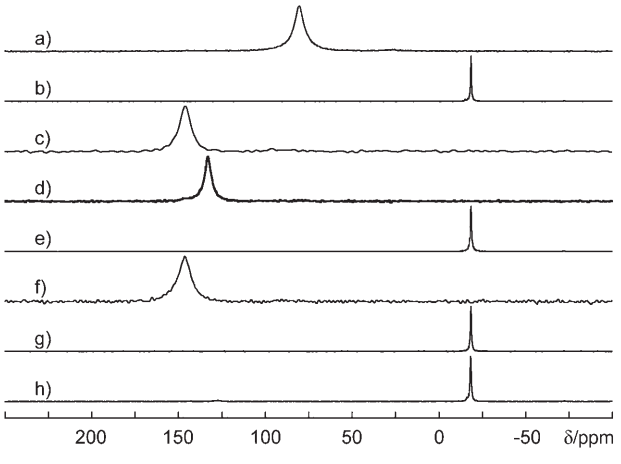


Figure 1. Solid-state ^{119}Sn MAS-NMR spectra of polymer-supported organotin reagents. a) Polymer **5a**, $\delta(Sn) = +80$ ppm. b) Polymer **1a**, $\delta(Sn) = -18.5$ ppm, obtained from **5a**. c) Polymer **5b** obtained after the first allylstannation mediated by $CeCl_3{\cdot}7H_2O/NaI$ (10%), $\delta(Sn) = +147$ ppm. d) Polymer **5c** obtained after the $InBr_3$-mediated allylstannation, $\delta(Sn) = +133$ ppm. e) Polymer **1a** obtained after the first recycling from **5b** with allylmagnesium chloride, $\delta(Sn) = -18.5$ ppm. f) Polymer **5b** obtained after the second allylstannation mediated by $CeCl_3{\cdot}7H_2O/NaI$ (10%), $\delta(Sn) = +147$ ppm. g) Polymer **1a** obtained after the second recycling from **5b** with allylmagnesium chloride, $\delta(Sn) = -18.5$ ppm. h) Polymer **1a** obtained after the fourth recycling from **5b** with allylmagnesium chloride, $\delta(Sn) = -18.5$ ppm.

Reuse of the organotin resins: The three different types of resins recovered after the allylation reactions were regenerated and reused. The recovered resins were allylated by the previously described one-pot procedure with allyl bromide and Zn (vide supra, Scheme 3) or by treatment with allylmagnesium bromide, with the regeneration of the polymer-supported allyltin reagents **1a–d** being checked by ^{119}Sn MAS-NMR spectroscopy.

It is worth noting that zinc or/and magnesium salts are retained in the polymeric matrix, together with oxygenated solvents, but without prohibitive effects on the regeneration and further use of supported allyltins (cf. Experimental Section). Accordingly, the reactivities of the regenerated resins **1a–d** were evaluated in the allylation of benzaldehyde. Table 6 shows the functional group capacity values, together with the yields of homoallylic alcohols obtained after one to five regeneration cycles with resin **1a**. The recycled resin **1a** gave similarly high reactivity in subsequent reactions. For each cycle, we recorded ^{119}Sn MAS-NMR spectra before and after reaction in order to check the recyclability, and in all cases the regenerated allyltin **1a** displayed the same spectrum as the first generated allyltin **1a**, with a unique signal at −18.5 ppm (see Figure 1b). Similarly, after the reactions the recovered resins each displayed a unique signal indicative of a tin halide moiety (Sn−Br or Sn−Cl depending on the nature of the Lewis acid used; see Figure 1c and d). We additionally checked the presence of tin residues in the final products by ICP-MS and found insignificant tin contamination (between $\delta = 3.8$ and 1.7 ppm). These results are in agreement with the constant tin loading in polymer, showing that the loss of tin from the supported reagent **1a**, as well as the metal leaching, was negligible after five runs.

Table 6. Functional group capacity values and yields of homoallylic alcohols.

Run	Yield[a] [%]	% Sn[b]	Tin loading[c] [mmol g^{-1}]	Tin content in **9a**[d] [ppm]
1	95	18.1	1.53	3.8±0.2
2	95	17.4	1.47	3.6±0.3
3	94	17.5	1.47	2.9±0.2
4	92	17.2	1.45	3.3±0.2
5	90	18.1	1.53	1.7±0.2

[a] Isolated yield of 1-phenyl-but-3-en-1-ol (**9a**). [b] Percentage of tin in the regenerated polymer **1a** determined by elemental analysis [c] Tin loading on the regenerated polymer **1a**. [d] Tin content in the final products **9a** determined by ICP-MS analysis.

Conclusion

We have developed an efficient method for the synthesis of polymer-bounded functionalized tin reagents **1a–d**. This method offers several advantages, including mild reaction conditions, in situ formation of allylzincs, and good loadings in allyltins (1.1 to 1.4 mmol g^{-1}). We have also shown the usefulness of these new polymer-supported organotin reagents **1a–d** for the allylstannation of aldehydes. The mechanism aspects of the allylation of aldehydes with polymer-supported allyltins **1a–d** in the presence of cerium or indium salts were briefly explored through an extrapolation of the reaction involving crotyltri-*n*-butyltin. The experimental allylation procedure with use of polymer-supported allyltins in the presence of either $CeCl_3{\cdot}7H_2O/NaI$ (10%) or InX_3 (X = Br, Cl) is reasonably convenient and environmentally friendly, since only a negligible amount of tin remains in the final products (<5 ppm). Moreover, the recovered resins can be regenerated and reused several times without notable loss of activity. Accordingly, these new immobilized reagents are particularly adaptable to automated parallel synthesis without significant tin contamination, allowing access to libraries of homoallylic alcohols, a strategy potentially extendable to other fine chemicals.

Experimental Section

General

With the exception of di- or tributyltin derivatives, which were obtained from Crompton, the other starting materials were purchased from Aldrich or Acros and were used without further purification. Amberlite XE-305 was a Rohm and Haas product and was purchased from Interchim. Dibutylphenyltin hydride was prepared by a described procedure.[41] Diethyl ether and THF were distilled over sodium/benzophenone ketyl and cyclohexane was distilled over calcium hydride.

Melting points (uncorrected) were determined on a C. Reichert microscope apparatus.

^{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 at 25°C. Chemical shifts (δ) are expressed in ppm downfield of tetramethylsilane (TMS), used as internal standard, and coupling constants (*J*) are expressed in Hertz.

Solid-state MAS-NMR experiments were performed at room temperature with a Bruker Avance 500 spectrometer operating at 186.5 MHz for ^{119}Sn with a 4 mm double-bearing Bruker probehead. ^{119}Sn MAS spectra were acquired with ^{1}H TPPM decoupling[42] during acquisition and a MAS frequency of 10 kHz. The repetition time was set to 20 s for quantitative purposes since $^{119\mathrm{Sn}}T_1$ were measured to be of the order of 3 s for all kind of Sn cores. In a control experiment performed on a mixture of two different Sn species (Sn–X, Sn–C), with a repetition time of 300 s no modification of the integrations was observed relative to spectra obtained with a repetition time of 20 s. Spectra were referenced to Me_4Sn with use of Ph_4Sn as a secondary reference ($\delta = -121.15$ ppm).[30]

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}):[29a] aromatic C–H stretchings, 3082, 3059, 3025; aliphatic C–H stretchings, 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 analyses were carried out by the CNRS Analysis Central Laboratory, Vernaison, France, on a Perkin–Elmer 2400 analyzer.

X-ray energy-dispersive spectrometry (EDS) measurements were carried out on a PGT spectrometer (Prism model) with use of appropriate standards in view of quantitative measurements.

ICP-MS analyses were performed on 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 every five samples, and memory effect was also checked between each sample.

Synthesis

Synthesis of poly(4-chlorobutyl)styrene:[9a] TMEDA (8.7 mL, 57.7 mmol) and a solution of *n*-butyllithium (2.5 M in hexanes, 27.7 mL, 69.2 mmol) were added successively, under argon, to a suspension of Amberlite XE 305 (6.0 g) in dry cyclohexane (15 mL). The reaction mixture was heated at 65°C for 4 h. The resin was then washed under argon with dry cyclohexane (8×20 mL), and this procedure (TMEDA, *n*-butyllithium) was repeated once. The resulting orange lithiated polymer was then washed under argon with dry THF (12×20 mL). 1-Bromo-4-chlorobutane (7.9 mL, 68.6 mmol) was added, at 0°C under argon, to the lithiated polymer suspension in dry THF (50 mL). The mixture was stirred at room temperature for 18 h and the resulting polymer was then successively washed with a THF/H_2O mixture (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 **1** was obtained as a white resin (7.8 g) and was found to contain 2.21 mmol of C–Cl g^{-1}: IR (KBr): $\tilde{\nu}$ = 3082, 3059, 3025, 2921, 2850, 1942, 1870, 1802, 1719, 1601, 1586, 1493, 1452, 1028, 759, 698, 650, 539 cm^{-1}; elemental analysis (%) found: C 82.59, H 7.72, Cl 7.86, Br 0.43.

Synthesis of poly[4-(dibutylphenylstannyl)butyl]styrene:[9a] Dibutylphenyltin hydride (8.62 g, 27.7 mmol) was slowly added, at 0°C under argon, to a solution of lithium diisopropylamide (30.5 mmol) in dry THF. The resulting mixture was stirred for 1 h at 0°C and subsequently added at 0°C under argon to the dry poly(4-chlorobutyl)styrene (6.0 g). The mixture was allowed to warm up to room temperature and stirred for 18 h. The resulting polymer was successively washed with a mixture of THF/H_2O (1:1 *v*/*v*, 60 mL), THF (6×60 mL), and absolute ethanol (4×60 mL) and dried under vacuum (0.5 mbar) at 60°C for 5 h. Poly[4-(dibutylphenylstannyl)butyl]styrene was obtained as a white resin (10.4 g) and was found to contain 1.33 mmol of Sn g^{-1}: ^{119}Sn MAS-NMR: $\delta = -43.4$ ppm; IR (KBr): $\tilde{\nu}$ = 3082, 3059, 3025, 2921, 2850, 1942, 1870, 1802, 1719, 1601, 1586, 1493, 1452, 1073, 1028, 759, 726, 698 cm^{-1}; elemental analysis (%) found: C 74.87, H 7.12, Sn 15.76, Cl <0.20.

Synthesis of poly[4-(dibutyliodostannyl)butyl]styrene 5a:[9a] A solution of iodine (3.81 g, 15.0 mmol) in absolute ethanol (50 mL) was added to the poly[4-(dibutylphenylstannyl)butyl]styrene (10.0 g) and the resulting mixture was stirred at 60°C for 18 h in the dark. The polymer was successively washed with a mixture of THF/aqueous $Na_2S_2O_3$ (1:1 v/v, 60 mL), THF (6×60 mL), and absolute ethanol (4×60 mL) and dried under vacuum (0.5 mbar) at 60°C for 5 h. Polymer **5a** was obtained as a pale yellow resin (10.7 g) and was found to contain 1.16 mmol of Sn–I g^{-1}: ^{119}Sn MAS-NMR: $\delta = +80.5$ ppm; IR (KBr): $\tilde{\nu}$ = 3082, 3059, 3025, 2921, 2850, 1942, 1870, 1802, 1719, 1601, 1586, 1493, 1452, 1073, 1028, 759, 698 cm^{-1}; elemental analysis (%) found: C 63.22, H 7.00, Sn 14.30, I 14.78.

General procedure for the synthesis of polymer-supported allyltin reagents 1a–d with isolated allylzinc bromide reagents: A solution of allylzinc bromide[43] (7.0 mmol) was added to a suspension of polymer **5a** (3.0 g, 3.48 mmol) in dry THF (10 mL) and the resulting mixture was stirred at 45°C for 18 h. The polymer **1a** was successively washed with a mixture of THF/aqueous NH_4Cl (1:1 v/v, 30 mL), THF (6×30 mL), and absolute ethanol (4×30 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h. The same procedure was used for **1b**, **1c**, and **1d**, in the two last cases with preparation of the functional allylzinc bromide, which must be done at 19 °C.[28]

General procedure for the synthesis of polymer-supported allyltin reagents 1a–d in a Barbier mode: Allyl bromide (17.4 mmol) was added to a suspension of polymer **5a** (3.0 g, 3.48 mmol) and zinc powder (30 mesh, 17.4 mmol) in dry THF (10 mL), and the resulting mixture was stirred at 45 °C for 18 h. The polymer was successively washed with a mixture of THF/aqueous NH_4Cl (1:1 v/v, 30 mL), THF (6×30 mL), and absolute ethanol (4×30 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h.

Polymer 1a: Polymer **1a** was obtained as a white resin and was found to contain 1.41 mmol of $Sn\,g^{-1}$: ^{119}Sn MAS-NMR: $\delta = -18.5$ ppm; IR (KBr): $\tilde{\nu} = 1622\ cm^{-1}$; elemental analysis (%) found: C 70.06, H 8.41, Sn 16.68, I <0.20.

Polymer 1b: Polymer **1b** was obtained as a white resin and was found to contain 1.11 mmol of $Sn\,g^{-1}$: ^{119}Sn MAS-NMR: $\delta = -17.1$ ppm; IR (KBr): $\tilde{\nu} = 1629\ cm^{-1}$; elemental analysis (%) found: C 71.82, H 8.50, Sn 13.22, I <0.20.

Polymer 1c: Polymer **1c** was obtained as a white resin and was found to contain 1.23 mmol of $Sn\,g^{-1}$: ^{119}Sn MAS-NMR: $\delta = -12.1$ ppm; IR (KBr): $\tilde{\nu} = 1710, 1612\ cm^{-1}$; elemental analysis (%) found: C 72.41, H 7.70, Sn 14.56, I 0.62.

Polymer 1d: Polymer **1d** was obtained as a yellow resin and was found to contain 1.19 mmol of $Sn\,g^{-1}$: ^{119}Sn MAS-NMR: $\delta = -9.5$ ppm; IR (KBr): $\tilde{\nu} = 2200\ cm^{-1}$; elemental analysis (%) found: C 72.05, H 7.71, Sn 14.09, N 1.66, I 0.56.

It is worth noting that the sums of the mass percentages turn out to be around 95 % for the four polymers. This problem does not appear to be due to bad evaluation of tin since the N/Sn ratio is good in **1d**. Another possibility might be the presence of oxygenated solvents or of zinc salts remaining in the matrix. In order to make a broad evaluation of these hypotheses, EDS measurements were performed on **1a** and **1c**. The given results are each the average of three measurements. In the case of **1a** (obtained from **5a** with allylmagnesium chloride), an evaluation of tin, halogens, magnesium, zinc, carbon, and oxygen afforded the following values (normalized to 100 % in weight, italic numbers are under the limits of the precision of the measurement): Sn (12.55), Br (*0.13*), I (*0.06*), Cl (3.02), Mg (1.10), Zn (*0.17*), C (76.94), O (6.02). Similar measurements carried out on **1c** (obtained from recycled **5b** upon treatment with **8c** and Zn) afforded the following set of values: Sn (9.99), Br (0.19), I (0.11), Cl (0.30), Mg (*0.03*), Zn (0.25), C (82.0), 0 (7.12). In spite of the unavoidable uncertainty in the low mass fractions of zinc, magnesium, and the halogens, they are in satisfactory agreement with the presence of residual magnesium or zinc dihalides, since the molar ratio of zinc or magnesium to halogen is roughly 1 to 2.

The excess of oxygen (about 6 % in **1a** and 4.4 % in **1c** with allowance for the presence of the ester function) can reasonably be assigned to retained oxygenated solvents in the matrix. Although needing to be checked in a more efficient way, it is worth noting that the presence of magnesium or zinc salts, as well as that of oxygenated solvents in the matrix, is not prohibitive either for the regeneration of the grafted allyltins or for their subsequent treatment with aldehydes, due to the fact that allylation is usually performed in the presence of Lewis acids.

General procedure for the $BF_3{\cdot}OEt_2$-promoted allylstannation of aldehydes: Benzaldehyde (1.7 mmol) and a solution of $BF_3{\cdot}OEt_2$ (6.8 mmol) were added dropwise at −78 °C, under argon to a suspension of polymer **1a–c** (1.3 g, 1.8 mmol) in dry CH_2Cl_2. The reaction mixture was stirred at −78 °C for 2 h and was then quenched with a THF/H_2O mixture (1:1 *v/v*). The polymer was filtered and was washed first with diethyl ether (6×40 mL) and then with THF (6×40 mL). The filtrate was extracted with diethyl ether, washed with brine (50 mL), dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by chromatography on silica gel. The resulting polymer, on the other hand, was washed with absolute ethanol (4×40 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h before being reused in reaction with allylzinc reagents.

General procedure for the allylstannation of aldehydes promoted by $CeCl_3{\cdot}7H_2O$/NaI (10 %): Aldehyde (1.0 mmol), $CeCl_3{\cdot}7H_2O$ (1.0 mmol), and NaI (0.1 mmol) were successively added to a suspension of polymer **1a,b** (1.0 g, 1.4 mmol) in CH_3CN. The reaction mixture was stirred at 60 °C for 24 h and was then quenched with HCl (0.1 M, 10 mL). The polymer was filtered and was washed first with diethyl ether (6×30 mL) and then with THF (6×30 mL). The filtrate was extracted with diethyl ether and washed with brine (50 mL), dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by chromatography on silica gel. Otherwise, the resulting polymer was washed with absolute ethanol (4×40 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h before being reused. Polymer **5b** was obtained as a white resin and was found to contain 1.36 mmol of $Sn{-}Cl\,g^{-1}$. ^{119}Sn MAS-NMR: $\delta = +147$ ppm; elemental analysis (%) found: C 67.64, H 7.44, Sn 16.12, Cl 6.01.

Characterization of homoallylic alcohols: All compounds were obtained by the above general procedure for the allylstannation of aldehydes promoted by $CeCl_3{\cdot}7H_2O$/NaI (10 %). In the EI-MS spectra, the fragmentation scheme is mainly governed by benzylic scission, followed by minor subsequent fragmentations including extrusion of carbon monoxide from the hydroxytropylium ion,[44] while CI-MS spectra mainly exhibit quasi molecular ions for $[M{+}NH_4]^+$ and for $[M{-}H_2O{+}NH_4]^+$.

1-Phenylbut-3-en-1-ol (9a):[45] Compound **9a** was obtained from benzaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (141 mg, 95 %) after purification by flash chromatography (petroleum ether/ethyl acetate 88:12, $R_f = 0.16$); ^1H NMR: $\delta = 2.02$ (d, $J = 3.3$ Hz, 1H), 2.44–2.58 (m, 2H), 4.72–4.75 (ddd, $J = 3.3, 5.4, 8.1$ Hz, 1H), 5.14–5.21 (m, 2H), 5.82 (ddt, $J = 7.1, 10.2, 17.2$ Hz, 1H), 7.24–7.37 (m, 5H) ppm; ^{13}C NMR: $\delta = 43.8, 73.3, 118.3, 125.8\ (2\times C), 127.5, 128.4\ (2\times C), 134.6, 143.9$ ppm; IR (KBr): $\tilde{\nu} = 3390, 3076, 3065, 3030, 2925, 2856, 1641, 1600, 1493, 1464, 1048, 915, 756, 699\ cm^{-1}$; MS (EI, 70 eV): *m/z* (relative intensity): 107 (100), 79 (68), 77 (31), 51 (9).

1-(4-Bromophenyl)but-3-en-1-ol (10a):[46] Compound **10a** was obtained from 4-bromobenzaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (225 mg, 99 %) after purification by flash chromatography (petroleum ether/ethyl acetate 88:12, $R_f = 0.26$); ^1H NMR: $\delta = 2.27$ (brs, 1H), 2.38–2.53 (m, 2H), 4.67 (dd, $J = 5.7, 7.5$ Hz, 1H), 5.12–5.18 (m, 2H), 5.69–5.83 (m, 1H), 7.21 and 7.46 (AA′BB′ system, $J = 8.1$ Hz, 4H) ppm; ^{13}C NMR: $\delta = 43.8, 72.6, 118.9, 121.3, 127.6\ (2\times C), 131.5\ (2\times C), 134.0, 142.9$ ppm; MS (EI, 70 eV): *m/z* (relative intensity): 228/226 (1), 211/209 (1), 187/185 (92), 159/157 (25), 105 (8), 78 (54), 77 (100), 51 (21), 41 (11), 39 (18); MS (CI, NH_3): *m/z* (relative intensity): 246/244 (3), 228/226 (100), 211/209 (13).

1-(4-Nitrophenyl)but-3-en-1-ol (11a):[45] Compound **11a** was obtained from 4-nitro-benzaldehyde (1.0 mmol) and polymer **1a** as a brown oil (188 mg, 97 %) after purification by flash chromatography (petroleum ether/ethyl acetate 85:15, $R_f = 0.15$); ^1H NMR: $\delta = 2.46$–2.59 (m, 3H), 4.85 (dd, $J = 4.8, 8.1$ Hz, 1H), 5.13–5.19 (m, 2H), 5.70–5.84 (m, 1H), 7.51 and 8.17 (AA′BB′ system, $J = 9.0$ Hz, 4H) ppm; ^{13}C NMR $\delta = 43.9, 72.1, 119.6, 123.6\ (2\times C), 126.6\ (2\times C), 133.2, 147.2, 151.2$ ppm; MS (EI, 70 eV): *m/z* (relative intensity): 152 (100), 124 (3), 122 (12), 106 (16), 105 (16), 94 (20), 78 (20), 77 (20), 51 (14), 41 (8), 39 (12); MS (CI, NH_3): *m/z* (relative intensity): 228 (5), 211 (100), 146 (24).

1-(4-Methoxyphenyl)but-3-en-1-ol (12a):[46] Compound **12a** was obtained from 4-methoxybenzaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (146 mg, 88 %) after purification by flash chromatography (petroleum ether/ethyl acetate 85:15, $R_f = 0.40$); ^1H NMR: $\delta = 2.32$ (brs, 1H), 2.47 (t, $J = 6.9$ Hz, 2H), 3.77 (s, 3H), 4.64 (t, $J = 6.9$ Hz, 1H), 5.08–5.15 (m, 2H), 5.77 (ddt, $J = 17.4, 10.2, 6.9$ Hz, 1H), 6.86 and 7.25 (AA′BB′ system, 4H) ppm; ^{13}C NMR: $\delta = 43.6, 55.1, 72.9, 113.7\ (2\times C), 118.0, 127.0\ (2\times C), 134.6, 136.0, 158.9$ ppm; MS (CI, NH_3): *m/z* (relative intensity): 178 (2), 161 (100).

1-(2-Tosylaminophenyl)but-3-en-1-ol (13a):[47] Compound **13a** was obtained from 2-tosylaminobenzaldehyde (1.0 mmol) and polymer **1a** as a white solid (264 mg, 83 %) after purification by flash chromatography (petroleum ether/ethyl acetate 85:15, $R_f = 0.21$); ^1H NMR: $\delta = 2.28$–2.34 (m, 2H), 2.37 (s, 3H), 4.64 (dd, $J = 6.0, 8.1$ Hz, 1H), 5.03–5.14 (m, 2H), 5.57–5.71 (m, 1H), 7.04 (d, $J = 8.1$ Hz, 2H), 7.17–7.25 (m, 3H), 7.47 (d, J = 8.4 Hz, 1 H), 7.70 (d, J = 8.1 Hz, 2 H) ppm; ^{13}C NMR: δ = 21.5, 41.3, 73.4, 119.3, 121.8, 124.5, 127.1 (2 × C), 127.8, 128.6, 129.6 (2 × C), 132.0, 133.7, 135.8, 137.0, 143.8 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 317 (5), 300, (5), 276 (27), 248 (14), 156 (20), 155 (56), 145 (29), 144 (31), 121 (17), 120 (17), 93 (37), 92 (20), 91 (100), 65 (33), 41 (10), 39 (13).

1-(3-Bromophenyl)but-3-en-1-ol (14a):[48] Compound **14a** was obtained from 3-bromobenzaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (194 mg, 85 %) after purification by flash chromatography (petroleum ether/ethyl acetate 9:1, R_f = 0.26); ^{1}H NMR: δ = 2.18 (brs, 1 H), 2.39–2.56 (m, 2 H), 4.69 (dd, J = 4.8, 7.8 Hz, 1 H), 5.15–5.20 (m, 2 H), 5.71–5.85 (m, 1 H), 7.18–7.28 (m, 2 H), 7.38–7.42 (m, 1 H), 7.52 (s, 1 H) ppm; ^{13}C NMR: δ = 43.8, 72.5, 119.0, 122.6, 124.4, 128.9, 130.0, 130.6, 133.9, 146.2 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 187/185 (83), 159/157 (38), 78 (46), 77 (100), 51 (26), 41 (10), 39 (17); MS (CI, NH_3): *m/z* (relative intensity): 246/244 (24), 228/226 (100).

1-(2,6-Dichlorophenyl)-but-3-en-1-ol (15a):[49] Compound **15a** was obtained from 2,6-dichloro-benzaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (201 mg, 93 %) after purification by flash chromatography (petroleum ether/ethyl acetate 9:1, R_f = 0.40); ^{1}H NMR: δ = 2.68 (q, J = 6.6 Hz, 1 H), 2.84 (q, J = 6.6 Hz, 1 H), 2.92 (d, J = 9.3 Hz, 1 H), 5.07–5.16 (m, 2 H), 5.49 (dt, J = 6.6, 9.3 Hz, 1 H), 5.77–5.91 (m, 1 H), 7.13 (t, J = 8.1 Hz, 1 H), 7.29 (d, J = 8.1 Hz, 2 H) ppm; ^{13}C NMR: δ = 40.0, 71.4, 118.1, 128.9, 129.4 (2 × C), 133.8, 134.3 (2 × C), 137.2 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 179/177/175 (10/60/100), 151/149/147 (1/4/6), 141/139 (3/10), 113/111 (12/41), 75 (32), 41 (6), 39 (10); MS (CI, NH_3): *m/z* (relative intensity): 238/236/234 (10/63/100), 220/218/216 (2/12/19).

1-(3,4,5-Trimethoxyphenyl)but-3-en-1-ol (16a):[50] Compound **16a** was obtained from 3,4,5-trimethoxy-benzaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (177 mg, 74 %) after purification by flash chromatography (CH_2Cl_2/ethanol 98:2, R_f = 0.13); ^{1}H NMR: δ = 2.11 (d, J = 2.7 Hz, 1 H), 2.45–2.52 (m, 2 H), 3.83 (s, 3 H), 3.87 (6 H, s), 4.64–4.69 (m, 1 H), 5.14–5.23 (m, 2 H), 5.75–5.87 (m, 1 H), 6.59 (s, 2 H) ppm; ^{13}C NMR: δ = 43.9, 56.1, 60.8, 73.4, 102.6 (2 × C), 118.5, 134.5, 137.1, 139.7, 153.2 (2C) ppm; MS (EI, 70 eV): *m/z* (relative intensity): 238 (10), 220 (4), 197 (100), 169 (72), 154 (32), 139 (15), 138 (52).

1-(4-Dimethylaminophenyl)-but-3-en-1-ol (17a):[51] Compound **17a** was obtained from 4-dimethylamino-benzaldehyde (1.0 mmol) and polymer **1a** as a yellow oil (147 mg, 77 %) after purification by flash chromatography (petroleum ether/ethyl acetate 8:2, R_f = 0.24); ^{1}H NMR: δ = 2.49–2.60 (m, 2 H), 2.76 (s, 1 H), 2.97 (6 H, s), 4.63 (t, J = 6.3 Hz, 1 H), 5.12–5.21 (m, 2 H), 5.78–5.92 (m, 1 H), 6.77 and 7.25 (AA′BB′ system, J = 8.7 Hz, 4 H) ppm; ^{13}C NMR: δ = 40.5 (2 × C), 43.2, 73.0, 112.4 (2 × C), 117.1, 126.6 (2 × C), 132.0, 134.9, 149.8 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 173 (85), 172 (100), 157 (55), 156 (20), 129 (40), 128 (34) ppm; MS (CI, NH_3): *m/z* (relative intensity): 192 (72), 174 (100), 150 (8).

1-(Pyridin-3-yl)but-3-en-1-ol (18a):[52] Compound **18a** was obtained from pyridine-3-carboxaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (129 mg, 86 %) after purification by flash chromatography (CH_2Cl_2/ethanol 95:5, R_f = 0.31); ^{1}H NMR: δ = 2.38–2.51 (m, 2 H), 4.67 (t, J = 6.3 Hz, 1 H), 4.98–5.04 (m, 2 H), 5.13 (brs, 1 H), 5.64–5.77 (m, 1 H), 7.17 (dd, J = 7.8, 4.8 Hz, 1 H), 7.65 (ddd, J = 7.8, 1.8, 1.8 Hz, 1 H), 8.24 (dd, J = 4.8, 1.8 Hz, 1 H), 8.31 (d, J = 1.8 Hz, 1 H) ppm; ^{13}C NMR: δ = 43.4, 70.7, 118.1, 123.3, 133.8, 133.9, 140.0, 147.2, 147.8 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 108 (100), 80 (20), 78 (10), 53 (15); MS (CI, NH_3): *m/z* (relative intensity): 150 (100), 108 (12).

1-(6-Methoxypyridin-3-yl)but-3-en-1-ol 19a:[52] Compound **19a** was obtained from 6-methoxypyridine-3-carboxaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (158 mg, 88 %) after purification by flash chromatography (CH_2Cl_2/ethanol 98:2, R_f = 0.12); ^{1}H NMR: δ = 2.34 (brs, 1 H), 2.48 (t, J = 6.9 Hz, 2 H), 3.91 (s, 3 H), 4.67–4.71 (m, 1 H), 5.12–5.18 (m, 2 H), 5.70–5.82 (m, 1 H), 6.72 (d, J = 8.7 Hz, 1 H), 7.59 (dd, J = 8.7, 2.4 Hz, 1 H), 8.06 (d, J = 2.4 Hz, 1 H) ppm; ^{13}C NMR: δ = 43.5, 53.5, 70.8, 110.8, 118.8, 131.9, 133.9, 136.7, 144.6, 163.8 ppm; IR (KBr): $\tilde{\nu}$ = 3373, 3078, 2945, 1639, 1609, 1574, 1452 cm^{-1}; MS (EI, 70 eV): *m/z* (relative intensity): 180 $[M+H]^+$ (8), 138 (100), 110 (4), 95 (11); MS (CI, NH_3): *m/z* (relative intensity): 180 (100), 138 (7) ppm.

1-(6-Bromopyridin-2-yl)but-3-en-1-ol (20a): Compound **20a** was obtained from 6-bromopyridine-2-carboxaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (194 mg, 85 %) after purification by flash chromatography (CH_2Cl_2, R_f = 0.20); ^{1}H NMR: δ = 2.41–2.69 (m, 2 H), 3.31 (d, J = 5.4 Hz, 1 H), 4.74–4.80 (m, 1 H), 5.09–5.16 (m, 2 H), 5.73–5.87 (m, 1 H), 7.30 (d, J = 7.8 Hz, 1 H), 7.37 (d, J = 7.8 Hz, 1 H), 7.54 (t, J = 7.8 Hz, 1 H) ppm; ^{13}C NMR: δ = 42.6, 72.3, 118.7, 119.2, 126.7, 133.7, 139.0, 141.2, 163.6 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 229/227 (3), 188/186 (100), 158/156 (11), 106 (35), 79 (11), 78 (47), 51 (23), 41 (7), 39 (11); elemental analysis calcd (%) for $C_9H_{10}BrNO$ (228.09): C 47.39, H 4.42, Br 35.03, N 6.14, O 7.01; found: C 47.03, H 4.21, Br 35.09, N 6.33.

1-(Quinolin-3-yl)but-3-en-1-ol (21a):[52] Compound **21a** was obtained from quinoline-3-carboxaldehyde (1.0 mmol) and polymer **1a** as a yellow oil (136 mg, 68 %) after purification by flash chromatography (petroleum ether/ethyl acetate 6:4, R_f = 0.20); ^{1}H NMR: δ = 2.47 (brs, 1 H), 2.58–2.72 (m, 2 H), 4.99 (dd, J = 7.5, 5.4 Hz, 1 H), 5.18–5.24 (m, 2 H), 5.77–5.91 (m, 1 H), 7.55 (dt, J = 8.1, 0.9 Hz, 1 H), 7.70 (dt, J = 8.1, 1.5 Hz, 1 H), 7.82 (d, J = 8.1 Hz, 1 H), 8.12 (d, J = 8.1 Hz, 1 H), 8.15 (d, J = 2.1 Hz, 1 H), 8.89 (d, J = 2.1 Hz, 1 H) ppm; ^{13}C NMR: δ = 43.8, 71.2, 119.3, 126.8, 127.8 (2 × C), 129.1, 129.3, 132.7, 133.6, 136.5, 147.6, 149.3 ppm; IR (KBr): $\tilde{\nu}$ = 3138, 2943, 1636 cm^{-1}; MS (EI, 70 eV): *m/z* (relative intensity): 199 (1), 158 (100), 130 (36), 103 (11), 77 (13); MS (CI, NH_3): *m/z* (relative intensity): 200 (100), 182 (5), 158 (71) ppm.

1-(Furan-2-yl)but-3-en-1-ol (22a):[53] Compound **22a** was obtained from furan-2-carboxaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (120 mg, 87 %) after purification by flash chromatography (petroleum ether/ethyl acetate 9:1, R_f = 0.20); ^{1}H NMR: δ = 2.20 (brs, 1 H), 2.57–2.64 (m, 2 H), 4.74 (t, J = 6.3 Hz, 1 H), 5.12–5.21 (m, 2 H), 5.73–5.87 (m, 1 H), 6.25 (d, J = 3.3 Hz, 1 H), 6.33 (dd, J = 3.3, 1.8 Hz, 1 H), 7.37 (d, J = 1.8 Hz, 1 H) ppm; ^{13}C NMR: δ = 40.1, 66.9, 106.1, 110.1, 118.6, 133.7, 142.0, 156.0 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 138 (2), 97 (100), 69 (14), 41 (32), 39 (18).

1-(Thiophen-2-yl)but-3-en-1-ol (23a):[53] Compound **23a** was obtained from thiophene-2-carboxaldehyde (1.0 mmol) and polymer **1a** as a yellow oil (137 mg, 89 %) after purification by flash chromatography (petroleum ether/ethyl acetate 92:8, R_f = 0.20); ^{1}H NMR: δ = 2.56 (brs, 1 H), 2.59–2.65 (m, 2 H), 4.95–5.00 (m, 1 H), 5.16–5.23 (m, 2 H), 5.77–5.91 (m, 1 H), 6.98 (d, J = 3.0 Hz, 2 H), 7.26 (t, J = 3.0 Hz, 1 H) ppm; ^{13}C NMR: δ = 43.5, 69.2, 118.4, 123.6, 124.4, 126.4, 133.8, 147.7 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 154 (2), 113 (100), 85 (38), 45 (16), 41 (8), 39 (12).

Dec-1-en-4-ol (24a):[54] Compound **24a** was obtained from heptaldehyde (1.0 mmol) and polymer **1a** as a colorless oil (128 mg, 82 %) after purification by flash chromatography (petroleum ether/ethyl acetate 9:1, R_f = 0.35); ^{1}H NMR: δ = 0.88 (t, J = 6.6 Hz, 3 H), 1.22–1.45 (10 H, m), 1.63 (brs, 1 H), 2.08–2.34 (m, 2 H), 3.63 (brs, 1 H), 5.10–5.16 (m, 2 H), 5.76–5.86 (m, 1 H) ppm; ^{13}C NMR: δ = 14.1, 22.6, 25.6, 29.3, 31.8, 36.8, 41.9, 70.7, 118.0, 134.9 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 115 (13), 97 (37), 69 (13), 55 (100), 43 (25), 41 (21); MS (CI, NH_3): *m/z* (relative intensity): 174 (100), 156 (4), 97 (18).

3-Methyl-1-phenylbut-3-en-1-ol (9b):[55] Compound **9b** was obtained from benzaldehyde (1.0 mmol) and polymer **1b** as a colorless oil (146 mg, 90 %) after purification by flash chromatography (petroleum ether/ethyl acetate 88:12, R_f = 0.20); ^{1}H NMR: δ = 1.79 (brs, 3 H), 2.18 (d, J = 2.4 Hz, 1 H), 2.42 (d, J = 6.6 Hz, 2 H), 4.82 (dt, J = 2.4, 6.6 Hz, 1 H), 4.87 (brs, 1 H), 4.93 (brs, 1 H), 7.25–7.33 (m, 5 H) ppm; ^{13}C NMR: δ = 22.3, 48.4, 71.4, 114.1, 125.8 (2 × C), 127.5, 128.4 (2 × C), 142.4, 144.1 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 107 (100), 105 (8), 79 (56), 77 (23), 56 (6), 51 (7); MS (CI, NH_3): *m/z* (relative intensity): 180 (26), 162 (100), 145 (37) ppm; IR (KBr): $\tilde{\nu}$ = 3074, 3066, 3030, 2857, 2932, 2872, 2856, 1645, 1600, 1494, 1464, 1559, 1055, 891, 756, 700 cm^{-1}.

1-(4-Bromophenyl)-3-methylbut-3-en-1-ol (10b):[56] Compound **10b** was obtained from 4-bromo-benzaldehyde (1.0 mmol) and polymer **1b** as a white solid (220 mg, 91 %) after purification by flash chromatography (petroleum ether/ethyl acetate 9:1, R_f = 0.24); ^{1}H NMR: δ = 1.80 (s, 3 H), 2.16 (d, J = 2.4 Hz, 1 H), 2.37–2.39 (m, 2 H), 4.75–4.80 (m, 1 H), 4.85 (s, 1 H), 4.94 (s, 1 H), 7.26 and 7.47 (AA′BB′ system, J = 8.4 Hz, 4 H) ppm; ^{13}C NMR: δ = 22.3, 48.4, 70.7, 114.5, 121.2, 127.5 (2 × C), 131.5 (2×C), 142.0, 143.0 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 242/240 (0.5), 225/223 (4), 187/185 (75), 185/183 (23), 159/157 (26), 128 (12), 105 (9), 78 (59), 77 (100), 56 (19), 51 (20); MS (CI, NH_3): *m/z* (relative intensity): 260/258 (4), 242/240 (100), 225/223 (31), 186/184 (10).

3-Methyl-1-(4-nitrophenyl)but-3-en-1-ol 11b:[57] Compound **11b** was obtained from 4-nitro-benzaldehyde (0.6 mmol) and polymer **1b** as a yellow solid (114 mg, 92%) after purification by flash chromatography (petroleum ether/ethyl acetate 85:15, $R_f = 0.24$); ^{1}H NMR: $\delta = 1.82$ (s, 3H), 2.32 (brs, 1H), 2.35–2.48 (m, 2H), 4.88–4.94 (m, 2H), 4.99 (s, 1H), 7.56 and 8.21 (AA′BB′ system, $J = 8.7$ Hz, 4H) ppm; ^{13}C NMR: $\delta = 22.2$, 48.5, 70.4, 115.1, 123.7 (2×C), 126.5 (2×C), 141.4, 147.3, 151.4 ppm; MS (CI, NH_3): *m/z* (relative intensity): 225 (100), 160 (26).

1-(4-Methoxyphenyl)-3-methylbut-3-en-1-ol 12b:[55] Compound **12b** was obtained from 4-methoxy-benzaldehyde (0.6 mmol) and polymer **1b** as a colorless oil (89 mg, 78%) after purification by flash chromatography (petroleum ether/ethyl acetate 85:15, $R_f = 0.34$); ^{1}H NMR: $\delta = 1.79$ (s, 3H), 2.08 (d, $J = 1.5$ Hz, 1H), 2.40–2.44 (m, 2H), 3.81 (s, 3H), 4.77 (dd, $J = 8.1$, 5.7 Hz, 1H), 4.85 (d, $J = 0.9$ Hz, 1H), 4.91 (d, $J = 0.9$ Hz, 1H), 6.86–6.91 (m, 2H), 7.28–7.32 (m, 2H) ppm; ^{13}C NMR: $\delta = 22.4$, 48.2, 55.3, 71.1, 113.8 (2×C), 113.9, 127.0, 136.2, 142.5, 159.0 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 192 (1), 174 (2), 159 (4), 137 (100), 135 (11), 109 (28), 94 (17), 77 (17); MS (CI, NH_3): *m/z* (relative intensity): 210 (2), 192 (6), 175 (100), 154 (9), 137 (9).

3-Methyl-1-(2-tosylaminophenyl)-but-3-en-1-ol 13b:[58] Compound **13b** was obtained from 2-tosylamino-benzaldehyde (1.0 mmol) and polymer **1b** as a white solid (295 mg, 89%) after purification by flash chromatography (petroleum ether/ethyl acetate 8:2, $R_f = 0.45$); ^{1}H NMR: $\delta = 1.69$ (s, 3H), 2.19 (dd, $J = 4.2$, 13.8 Hz, 1H), 2.28 (dd, $J = 9.9$, 13.8 Hz, 1H), 2.37 (s, 3H), 2.56 (brs, 1H), 4.68 (dd, $J = 9.9$, 4.2 Hz, 1H), 4.75 (s, 1H), 4.92 (s, 1H), 7.04 (m, 2H), 7.18–7.24 (m, 3H), 7.49 (d, $J = 8.1$ Hz, 1H), 7.70 (d, $J = 8.1$ Hz, 2H), 8.57 (s, 1H) ppm; ^{13}C NMR: $\delta = 21.4$, 22.0, 45.1, 71.3, 114.6, 121.7, 124.4, 127.0, 127.5, 128.4, 129.5, 132.0, 135.8, 136.9, 141.3, 143.6 ppm; MS (EI 70 eV): *m/z* (relative intensity): 331 (4), 275 (5), 158 (100), 143 (30), 120 (41), 91 (36), 65 (18) ppm; IR (KBr): $\tilde{\nu} = 3491$, 3239, 2922, 1159 cm^{-1}.

General procedure for the InX_3-promoted allylstannation of aldehydes: Aldehyde (1.0 mmol) and $InBr_3$ or $InCl_3$ (1.0 mmol) were added to a suspension of polymer (1.0 g, 1.4 mmol) in CH_2Cl_2. The reaction mixture was stirred at 25 °C for 3 h and was then quenched with HCl (0.1 M, 10 mL). The polymer was filtered and was washed first with diethyl ether (6×30 mL) and then 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 crude product was purified by chromatography on silica gel. The resulting polymer **5c** (obtained with use of $InBr_3$ as a promoter), on the other hand, was washed with absolute ethanol (4×40 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h to be reused. Polymer **5c** was obtained as a white resin and was found to be a Sn–Br-type polymer containing 1.22 mmol of Sn–Br g^{-1}. ^{119}Sn MAS-NMR: $\delta = +133$ ppm; elemental analysis (%) found: C 66.72, H 6.85, Sn 14.43, Br 11.82.

Ethyl 4-hydroxy-2-methylene-4-phenylbutanoate (9c):[59] Compound **9c** was obtained from benzaldehyde (0.5 mmol) and polymer **1c** as a colorless oil (100 mg, 91%) after purification by flash chromatography (petroleum ether/ethyl acetate 88:12, $R_f = 0.10$); ^{1}H NMR: $\delta = 1.32$ (t, $J = 7.2$ Hz, 3H), 2.66 (dd, $J = 14.1$, 8.4 Hz, 1H), 2.78 (dd, $J = 14.1$, 4.2 Hz, 1H), 2.92 (d, $J = 3.6$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 4.87 (ddd, $J = 8.4$, 4.2, 3.6 Hz, 1H), 5.58 (d, $J = 1.2$ Hz, 1H), 6.22 (d, $J = 1.2$ Hz, 1H), 7.23–7.37 (m, 5H) ppm; ^{13}C NMR: $\delta = 14.2$, 42.6, 61.1, 73.2, 125.7 (2×C), 127.5, 128.2, 128.4 (2×C), 137.2, 144.0, 167.8 ppm; IR (KBr): $\tilde{\nu} = 3460$, 3074, 3030, 2981, 2960, 2929, 2872, 1715, 1630, 1500, 1455, 1193, 756, 700 cm^{-1}; MS (EI, 70 eV): *m/z* (relative intensity): 220 (2), 175 (5), 174 (18), 157 (7), 129 (15), 114 (88), 107 (100), 105 (18), 86 (73), 79 (71), 77 (46), 69 (21), 68 (48), 40 (20), 29 (14).

Ethyl 4-(4-bromophenyl)-4-hydroxy-2-methylenebutanoate (10c): Compound **10c** was obtained from 4-bromo-benzaldehyde (0.5 mmol) and polymer **1c** as a colorless oil (144 mg, 96%) after purification by flash chromatography (petroleum ether/ethyl acetate 8:2, $R_f = 0.31$); ^{1}H NMR: $\delta = 1.30$ (t, $J = 7.2$ Hz, 3H), 2.60 (dd, $J = 14.1$, 8 Hz, 1H), 2.76 (ddd, $J = 14.1$, 4.2, 0.9 Hz, 1H), 3.45 (d, $J = 3.3$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 4.87 (ddd, $J = 8$, 4.2, 3.3 Hz, 1H), 5.55 (dd, $J = 1.5$, 0.9 Hz, 1H), 6.22 (d, $J = 1.5$ Hz, 1H), 7.22 and 7.44 (AA′BB′ system, 4H) ppm; ^{13}C NMR: $\delta = 14.1$, 42.4, 61.1, 72.4, 121.0, 127.4 (2×C), 128.4, 131.3 (2×C), 136.7, 142.9, 167.7 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 254/252 (11), 185/183 (4), 173 (14), 128 (10), 68 (100), 40 (30); MS (CI, NH_3): *m/z* (relative intensity): 318/316 (13), 301/299 (25), 283/281 (49), 272/270 (100); elemental analysis calcd (%) for $C_{13}H_{15}BrO_3$ (299.16): C 52.19, H 5.05, Br 26.71, O 16.04; found: C 52.24, H 5.17, Br 26.65.

Ethyl 4-hydroxy-2-methylene-4-(4-nitrophenyl)butanoate (11c): Compound **11c** was obtained from 4-nitrobenzaldehyde (0.5 mmol) and polymer **1c** as a colorless oil (122 mg, 92%) after purification by flash chromatography (petroleum ether/ethyl acetate 8:2, $R_f = 0.21$); ^{1}H NMR: $\delta = 1.30$ (t, $J = 7.2$ Hz, 3H), 2.60 (dd, $J = 14.1$, 8.1 Hz, 1H), 2.80 (ddd, $J = 14.1$, 4.2, 0.9 Hz, 1H), 3.48 (d, $J = 3.6$ Hz, 1H), 4.21 (q, $J = 7.2$ Hz, 2H), 4.98 (ddd, $J = 8.1$, 4.2, 3.6 Hz, 1H), 5.56 (dd, $J = 1.2$, 0.9 Hz, 1H), 6.22 (d, $J = 1.2$ Hz, 1H), 7.61 and 8.16 (AA′BB′ system, 4H) ppm; ^{13}C NMR: $\delta = 14.1$, 42.6, 61.4, 72.3, 123.6 (2×C), 126.5 (2×C), 129.0, 136.3, 147.1, 151.4, 167.9 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 248 (3), 220 (6), 152 (8), 128 (10), 114 (66), 86 (52), 77 (19), 69 (22), 68 (100), 51 (13), 40 (46); elemental analysis calcd (%) for $C_{13}H_{15}NO_5$ (265.26): C 58.86, H 5.70, N 5.28, O 30.16; found: C 58.26, H 5.82, N 5.26.

Ethyl 4-hydroxy-4-(4-methoxyphenyl)-2-methylenebutanoate (12c): Compound **12c** was obtained from 4-methoxy-benzaldehyde (0.5 mmol) and polymer **1c** as a colorless oil (90 mg, 72%) after purification by flash chromatography (petroleum ether/ethyl acetate 8:2, $R_f = 0.22$); ^{1}H NMR: $\delta = 1.31$ (t, $J = 7.2$ Hz, 3H), 2.66 (ddd, $J = 14.1$, 7.8, 0.6 Hz, 1H), 2.67 (d, $J = 3.9$ Hz, 1H), 2.76 (ddd, $J = 14.1$, 4.5, 0.9 Hz, 1H), 3.80 (s, 3H), 4.22 (q, $J = 7.2$ Hz, 2H), 4.84 (ddd, $J = 7.8$, 4.5, 3.9 Hz, 1H), 5.58 (ddd, $J = 1.2$, 0.9, 0.6 Hz, 1H), 6.23 (d, $J = 1.2$ Hz, 1H), 6.87 and 7.28 (AA′BB′ system, 4H) ppm; ^{13}C NMR: $\delta = 14.1$, 42.4, 55.2, 61.0, 72.7, 113.7 (2×C), 126.9 (2×C), 128.0, 136.1, 137.2, 158.9, 167.7 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 250 (2), 204 (5), 137 (100), 109 (20), 94 (11), 77 (12), 57 (31), 31 (33); elemental analysis calcd (%) for $C_{14}H_{18}O_5$ (250.29): C 67.18, H 7.25, O 25.57; found: C 66.97, H 7.35.

4-Hydroxy-2-methylene-4-(4-nitrophenyl)butanenitrile (11d): Compound **11d** was obtained from 4-nitrobenzaldehyde (0.5 mmol) and polymer **1d** as a yellow solid (80 mg, 73%) after purification by flash chromatography (petroleum ether/ethyl acetate 8:2, $R_f = 0.10$); ^{1}H NMR: $\delta = 2.40$ (d, $J = 3.0$ Hz, 1H), 2.65–2.67 (m, 2H), 5.09–5.14 (m, 1H), 5.80 (s, 1H), 6.00 (s, 1H), 7.56 and 8.23 (AA′BB′ system, 4H) ppm; ^{13}C NMR: $\delta = 44.2$, 71.1, 118.2, 118.8, 124.0 (2×C), 126.6 (2×C), 134.1, 147.7, 149.6 ppm; MS (EI, 70 eV): *m/z* (relative intensity): 170 (70), 169 (100), 152 (18), 142 (11); MS (CI, NH_3): *m/z* (relative intensity): 236 (100), 219 (45), 171 (8); elemental analysis calcd (%) for $C_{11}H_{10}N_2O_3$ (218.21): C 60.55, H 4.62, N 12.84, O 22.00; found: C 60.30, H 4.95, N 12.48.

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