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# Quantitative Data on the Effects of Alkyl Substituents and Li–O and Li–N Chelation on the Stability of Secondary α-Oxy-Organolithium Compounds

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**Abstract:** A $\Delta G_{eq}$ stability scale of secondary α-oxy-organolithium compounds was established from measurements of tin–lithium exchange equilibria in THF, and the quantitative effects of substituents at the anionic center on carbanion stability are presented. A new lead–lithium exchange equilibrium reaction was also investigated and shown to be a very useful alternative for the determination of the relative stability of the more sterically hindered organolithium compounds. Alkyl groups adversely affect the stability of organolithium compounds when attached to the carbon bearing the negative charge, but the extent of this effect is highly dependent on the nature of the rest of the substituents attached to the anionic center. Quantitative data on the stabilization imparted to organolithium compounds by Li–O and Li–N chelation have been determined for a variety of systems. The formation of four- and five-membered chelate rings leads to a considerable stabilization of the organolithium compound, while chelation through the formation of six-membered rings affords no extra stabilization to this type of organometallics. Multinuclear NMR experiments carried out on several α-oxy-organolithium compounds to determine their aggregation state are supportive of these species being monomers in THF solution.

**Keywords:** aggregation · chelates · lithium · NMR spectroscopy

## Introduction

Organolithium reagents play a central role in organic synthesis and the factors governing their structure, stability and reactivity have been the object of very active study for decades.[1] A particularly interesting aspect of the chemistry of this type of compounds is how substituents (both proximate and remote to the carbanionic center) influence the stability of these organolithium species. Quantitative data on this fundamental question is still lacking for the most part, due to the difficulty of establishing a general quantitative thermodynamic stability scale of organolithium compounds.[2] Traditionally, the stabilities of organolithium compounds have been determined by measuring the p$K$ of the corresponding carbanions,[3] but the application of this approach to the more basic, highly functionalized, more synthetically useful organolithium reagents is problematic, especially in ethereal solvents, despite of the fact that Streitwieser[4] has provided data for several types of aromatic, heteroaromatic, and benzylic systems, obtained using this method.

We have recently reported the measurement of the relative stabilities of α-heterosubstituted-benzylic organolithium compounds in tetrahydrofuran, thus providing for the first time quantitative data on the effects of the heteroatom adjacent to the carbanionic center, as well as those of the heteroatom's substituents, on the stabilities of these type of highly functionalized organometallics.[2] Our approach is based on the establishment of a Sn–Li exchange between the organolithium under study and a reference compound (as shown in Equation (1) (see below), an equilibrium reaction which favors the pairing of the most stable carbanion with the more electropositive Li atom.[5,6] We report herein the improvement of this Sn–Li exchange equilibrium method, its application to the determination of the stabilities of a more comprehensive set of organolithium compounds, and the determination of the quantitative effects of substituents on the stability of these types of functionalized organometallics. We have chosen THF as the solvent for our studies since most of the synthetic applications of organolithium compounds are carried out in THF solutions.

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## Results and Discussion

The stability scale of organolithium compounds is defined in terms of the Sn–Li exchange equilibrium reaction shown in Equation (1). Measurement of the equilibrium constant of this reaction provides a straightforward method for establishing the difference in thermodynamic stability ($\Delta G_{eq}$) between the involved organolithium compounds $R^1Li$ and $R^2Li$, where $R^2Li$ is used as a reference compound whose stability has been previously established. A list of p$K$ values of aromatic and heteroaromatic carbanions which could be used as reference compounds in THF is available from the work of Fraser and co-workers, who measured the proton transfer equilibrium constants of hydrocarbons **1c**–**6c** with bases of known p$K$ to establish their basicity scale.[7] From Fraser's original p$K$ data in tetrahydrofuran we calculated the $\Delta G_{eq}$ values[8] shown in Figure 1. The reference level of

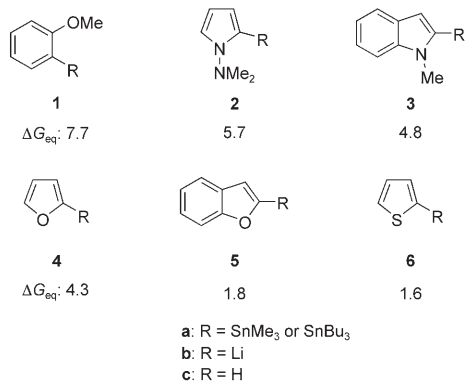



Figure 1. Reference compounds used for tin–lithium exchange reactions. $\Delta G_{eq}$ values in kcal mol$^{-1}$, $T = 223$ K.

0.0 kcal mol$^{-1}$ was assigned to 9-xanthenyllithium, the most stable reference compound used in our previous study.[2] As a first test of our method we chose to measure the relative stabilities of the reference aromatic and heteroaromatic compounds **1**–**6** in order to check if our measurements were congruent with Fraser's basicity scale. The Sn–Li exchange equilibria were achieved by mixing equimolar amounts of stannane ($R^1SnBu_3$ or $R^1SnMe_3$) and organolithium reagents **1b**–**6b** at the appropriate temperature in THF. The concentrations of the relevant stannanes and organolithium species at equilibrium were measured by NMR or GC after low-temperature protonation with deoxygenated methanol (see ref. [2] for details). The reverse reaction was performed in every case to ensure that the equilibrium point had been reached. The $\Delta G_{eq}$ data are reported as a single number when the same $K_{eq}$ was obtained from the forward and reverse reactions, and as an interval when proximate but non-coincident values were obtained.

$$R^1SnR^3{}_3 + R^2Li \rightleftharpoons R^1Li + R^2SnR^3{}_3 \quad (1)$$

It has been established that the Sn–Li exchange reactions proceed through the formation of pentasubstituted stannate species, which are present in the equilibria at undetectably low concentrations (except in very specific cases, such as diaryl- or polyarylated stannanes in THF/HMPA solutions).[9] Since we did not detect in the $^{119}$Sn NMR spectra of the equilibrium mixtures signals at the chemical shift expected for the pentacoordinated stannates (around $\delta$ −280 ppm) we have ruled out the possibility that these species play a significant role in determining the ratios of the products obtained after protonation, and thus that the measured ratios represent the true organolithium and stannane concentrations at equilibrium in each case.

Our data were coincident with those obtained from Fraser's p$K$ values except for the case of 2-lithium-*N*-methylindole (**3b**), which under our experimental conditions was shown to be 0.9 kcal mol$^{-1}$ more stable than 2-lithium-*N*,*N*-dimethylaminopyrrole (**2b**), which suggest an apparent p$K$ of 36.1 for the parent heterocycle, two units lower than the reported value.[7e] A possible explanation of this discrepancy is that the equilibrium point had not been reached under Fraser's conditions as *N*-methylindole possesses no donor substituents which would accelerate the rate of deprotonation by coordination with the base, as anisole and dimethylaminopyrrole do. It must be pointed out that under thermodynamic conditions the rate of α-lithiation in five-membered heterocycles follows the order sulfur > oxygen > N-alkyl.[10]

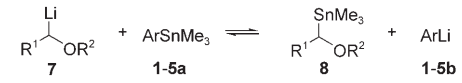
Having established that our Sn–Li exchange method was indeed providing stability data coincident with those derived from p$K$ measurements we undertook a more detailed study of the factors that affect the stability of α-oxy-organolithium compounds. A range of organolithium compounds (**7**, **11**, **13**) and their stannylated precursors (**8**, **12**, **14**) were allowed to equilibrate with the appropriate reference compounds **1**–**6** in THF. The relative stabilities derived from these experiments are shown in Tables 1–3. Table 1 shows the results obtained for α-oxy-*alkyl* organolithium compounds. Perusal of these data allowed us to extract some interesting conclusions on the substituents effects on organolithium stability.

**Effect of the O-substituent**: The same degree of stabilization to the α-carbanion was imparted by an alkyl or an alkoxyalkyl group as the *O*-substituent (compare entries 1 and 2, Table 1), thus the organolithium does not seem to experience an increased stabilization due to the formation of a five-membered chelate with the Li cation through the additional oxygen over the one already present through the three-membered ring chelation with the α-oxygen, thus casting some shadows on the generally accepted notion that a five-membered ring Li–O chelate is present in these organometallics.[5,11] For this particular study tributyltin derivatives **8a** and **8b** were used instead of the less hindered trimethyltin analogues to avoid volatility problems due to their low molecular weight.

As it had already been noticed in our previous study of benzylic organometallics, an α-oxycarbanion is better stabilized when a carbonyl derivative is used as the O-protecting group than when alkyl or alkoxyalkyl groups are employed (compare entries 1–5).[2] The extent of the additional stabili-

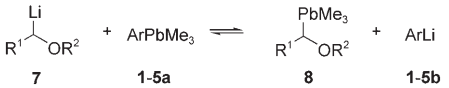
  

Table 1. Relative stability data of α-oxy-alkyllithium compounds **7**.




**7** **1-5a** **8** **1-5b**

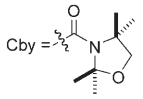
| Entry[a] | Anion | $R^1$ | $R^2$ | ArLi | $\Delta G_{eq}$ |
|---|---|---|---|---|---|
| 1 | **7a** | H | $CH_3$[b] | **1** | 7.9 |
| 2 | **7b** | H | MOM[b] | **1** | 7.9 |
| 3 | **7c** | H | Cby | **2** | 5.5 |
| 4 | **7c** | H | Cby | **3** | 5.4 |
| 5 | **7d** | H | $COR^3$[c] | **2** | 6.0–5.9 |
| 6 | **7e** | $CH_2$= | $(CH_2)_{11}CH_3$ | **5** | 4.7 |
| 7 | **7f** | $CH_2$= | Cby | **2** | 1.6 |
| 8 | **7g** | $CH_3$ | Cby | **1** | 7.5 |
| 9 | **7h** | $CH_3CH_2$ | Cby | **1** | 7.5 |
| 10 | **7i** | $CH_3(CH_2)_3$ | Cby | **1** | 7.5 |
| 11 | **7j** | $(CH_3)_2CH$ | Cby | **1** | 7.5 |
| 12 | **7k** | $(CH_3)_3C$ | Cby | **3** | 5.4 |
| 13 | **7k** | $(CH_3)_3C$ | Cby | **4** | 5.5 |
| 14 | **7l** |  | Cby | **1** | 7.5 |
| 15 | **7m** | $CH_3(CH_2)_8$ | MOM[b] | PhLi | >11.5 |




**7** **1-5a** **8** **1-5b**

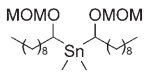
| Entry[a] | Anion | $R^1$ | $R^2$ | ArLi | $\Delta G_{eq}$ |
|---|---|---|---|---|---|
| 16 | **7g** | $CH_3$ | Cby | **1** | 7.5 |
| 17 | **7k** | $(CH_3)_3C$ | Cby | **1** | 7.8 |
| 18 | **7l** |  | Cby | **1** | 7.5 |

[a] Reaction conditions: −50 °C/12 h for entries 1–2; −65 °C/16 h for entries 3–4, 8–10 and 15; −50 °C/16 h for entries 5–6 and 14; −35 °C/24 h for entries 11–13; −78 °C/6 h for entry 7; −25 °C/20 h and 24 h for entries 16 and 17. [b] The $Bu_3Sn$ derivative was used. [c] $R^3$ = triisopropylphenyl.





**9**




**10**

zation imparted by the carbonyl group depends on the nature of the other substituent of the carbanionic center. A difference in stability of approximately $\Delta\Delta G_{eq}$ = 2–2.5 kcal mol$^{-1}$ (a value close to that observed in the benzylic series, 3 kcal mol$^{-1}$) is obtained when no further substitution is present at the carbon bearing the negative charge.[12] A similar stabilization ($\Delta\Delta G_{eq}$ = 3.1 kcal mol$^{-1}$) is observed for the vinyl-lithiums **7e–f** (compare entries 6 and 7). But when the carbanionic center is further substituted by an alkyl group (compare entries 9 and 15) a larger stability difference is observed ($\Delta\Delta G_{eq}$ > 4 kcal mol$^{-1}$).

**Effect of alkyl substituents attached to the carbon bearing the negative charge in α-oxy-organolithium compounds**: When a carbamoyl (Cby) group is used as the O-substituent, the incorporation of an alkyl residue attached to the carbanionic center is destabilizing by about 2 kcal mol$^{-1}$, probably due to the electron-donating properties of the alkyl groups (compare entries 3,4 with 8–11).[13,14] It is remarkable that the presence of up to two alkyl groups at the β-position to the carbon bearing the negative charge has a negligible effect on carbanion stability, as the same $\Delta G_{eq}$ was observed with methyl-, ethyl-, butyl- or isopropyl-substituted organolithiums **7g–j** (compare entries 8–11). An exception to this destabilizing effect of alkyl groups directly attached to the carbanionic center seems to be displayed by the *tert*-butyl group (compare entries 3,4 with 12,13), since the *tert*-butyl substituted carbanion **7k** is apparently as stable as the unsubstituted parent anion **7c** and more stable that the other alkyl substituted anions **7g–j**. We attribute this behavior not to an specific stabilizing effect of the *tert*-butyl group, but to the release of steric strain, present in the starting stannane due to the interaction between the large *tert*-butyl and $Me_3Sn$ groups, upon Sn–Li exchange, which should shift the equilibrium towards the anion **7k**, thus making it *apparently* more stable than the electron-donating properties of the *tert*-butyl group would suggest.[13,14] The stability of a slightly less sterically crowded neopentylic carbanion, such as the cyclohexylmethyl substituted carbamate **7l** (entry 14), is in line ($\Delta\Delta G_{eq}$ = 2.0 kcal mol$^{-1}$) with those of the methyl-, ethyl- and isopropyl-substituted organolithium species, which lends credit to the hypothesis that steric strain in the organostannane lays at the origin of the anomalous behavior of the *tert*-butyl substituted system.

To validate this explanation we decided to explore the use of the equilibrium exchange reactions between lithium and lead to establish the relative stabilities of organolithium compounds.[15] The longer carbon–lead bond lengths should result in diminished steric interactions in the starting organolead compounds, as compared to their tin counterparts, so the measured carbanion stabilities should be less effected by the steric compression of the starting materials. The Li–Pb exchange reaction has been far less studied and utilized than its Li–Sn counterpart, thus we decided to carry out a preliminary study of its characteristics. Firstly, the preparation of the required α-oxy-organolead precursors **8g**,**l** and the reference compound 2-trimethyllead-anisole follows closely that of their tin analogues.[16] The equilibrium exchange reactions between organolithiums **7g**,**l** and 2-trimethyllead-anisole (and their reverse reactions) proceeded under the same conditions, and provided the same relative stability values, as the homologous Sn–Li exchanges (compare entries 8 and 14 with 16 and 18). In this way we showed that the lead–lithium exchange equilibrium reaction is a valid alternative to the tin–lithium method of establishing the relative stabilities of organolithium species. We then determined the stability of the *tert*-butyl substituted carbanion **7k**, using the lead–lithium exchange, and observed a destabilization of about 2.4 kcal mol$^{-1}$ when compared with the unsubstituted parent carbanion **7c** (entry 17 versus entries 3, 4), in line with the effects of all the other alkyl substituents. This result lends credence to our hypothesis of steric crowding in the tin precursor as the origin of the anomalous stability measured for **7k** using the Sn–Li method.

When a MOM group is used as the O-substituent, the incorporation of an alkyl residue attached to the α-carbanion-

ic center is far more destabilizing than when a carbamate group is employed ($>3.6$ kcal mol$^{-1}$, compare entry 2 with 15), which indicates that the amount of destabilization imparted by alkyl groups depends on the type of organolithium to which it is attached. We can only provide a lower range estimation of this effect since the stability of MOMO-decanyllithium **7m** happened to be outside of the range that could be measured using the reference compounds available (up to about $\Delta G_{eq}=9.7$ kcal mol$^{-1}$ by using compound **1**). When we treated the stannylated acetal **8m** with BuLi, clean Sn–Li exchange was observed leading to anion **7m**. But when **7m** was treated with $Me_3Sn$-anisole (**1a**), we observed the formation of small amounts of a new compound to which structure **10** was tentatively assigned. This product can be explained if **7m** and MeLi have similar stabilities.[17] Indeed, when the tributyltin analogue of **8m** was treated with PhLi the [PhLi]/[**7m**] ratio at equilibrium was 87:13, from which a $\Delta G_{eq}=1.7$ kcal mol$^{-1}$ relative to phenyllithium was derived. The main problem with this measurement is that the p$K$ of benzene in THF has not been unambiguously determined.[18] We established a minimum $\Delta G_{eq}$ value for PhLi from the fact that it completely undergoes Sn–Li exchange with $Me_3Sn$-anisole (**1a**) ($\Delta G_{eq}=7.7$ kcal mol$^{-1}$, p$K=$ 39.0), thus providing a $\Delta G_{eq}>9.7$ kcal mol$^{-1}$ (p$K>41$) for PhLi, and $\Delta G_{eq}>11.5$ kcal mol$^{-1}$ for MOM-protected organolithium **7m**.

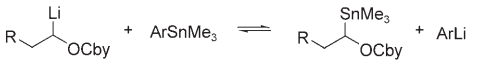
In some selected instances we used two different reference compounds to measure the relative stability of the α-oxycarbanion, and the same, or very close results, were obtained (compare entries 3 and 4, or entries 12 and 13). These duplicate determinations reinforce the reliability of the results and the validity of the method. We also measured selected equilibrium constants (**7h**, **11b** and **11d**) at different temperatures, ranging from $-65$ to $-35$ °C, and concentrations (for **7c**, **7h**, **11b** and **11d**), ranging from 0.02 to 0.2 M, and found that the values for the observed $K_{eq}$ were temperature and concentration independent. These facts point to two important conclusions: 1) the α-oxy-organolithium species and the reference organolithium compounds have definite structures (aggregation states) under the experimental conditions used; 2) the measured stabilities of the organolithium compounds are not dependent on the nature or the aggregation state of the reference compound employed.

The interpretation of the observed substituent effects in structural terms depends on the aggregation states of the organolithiums **7a**–**m**. Boche et al. have provided $^6$Li,$^{13}$C coupling data that strongly suggest that *O*-carbamoyl-alkyllithium compounds are monomeric in THF at low temperatures.[19] Our own measurements (see below) support this assert. In view of this fact, the destabilizing effect of alkyl groups on the stability of *O*-carbamoyl-organolithiums can be attributed exclusively to electron donation to the carbanionic center by the substituent, since the size of the alkyl group appears to have little or no influence. With regard to the aggregation states of α-lithio-ethers and acetals the situation is far less clear, although they appear to be dimers in THF at low temperatures.[19] In any case, from the data shown above it can be clearly deduced that the effects of alkyl groups on the stability of organolithium compounds are highly dependent on the structure of the involved carbanion, even for closely related systems. We propose that the extent of the destabilization imparted by an alkyl group directly attached to a carbon bearing a negative charge is a good measure of the negative charge stabilizing capabilities of the rest of the substituents attached to that carbon (the corollary is that the less stable a carbanion is, the more destabilized it gets by alkyl substitution). Thus it appears that an *O*-carbamoyl group withdraws more negative charge from the carbon directly attached to it than an *O*-alkyl or an *O*-alkoxyalkyl group.

**Effect of remote substituents on alkyllithium stability**: **chelation**: Once it had been established that the Sn–Li exchange equilibria could be used to study the effect of alkyl groups directly attached to the anionic carbon on the stability of organolithium compounds, we set out to apply this method to determine the effects of *remote* substituents on organolithium stability, particularly the effects of Li chelation by heteroatoms.

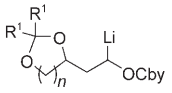
Chelation effects have been implicated in a wide variety of aspects of organolithium chemistry, from structure and aggregation to reactivity and selectivity.[20a] Despite 40 years of research into the origins and applications of these chelation effects, there is still a lack of quantitative data on the strength, or even the occurrence, of these types of interactions in solution.[20b–f] Table 2 shows the stability data measured for a series of organolithium compounds bearing side chains containing potential Li-chelating groups: N, O and S atoms (cation-lone pair interaction). It can be readily seen that the formation of four-membered ($\Delta\Delta G_{eq}=$ 1.7 kcal mol$^{-1}$ for N, compare entry 1 of Table 2 with entries 8 or 9 of Table 1)[21] and five-membered ($\Delta\Delta G_{eq}=2.5$–

Table 2. Effect of chelation on α-oxy-organolithium stability.




**11** **1–2a** **12** **1–2b**

| Entry | Anion | R | $ArSnMe_3$ | $T$ [°C]/$t$ [h] | $\Delta G_{eq}$ |
|---|---|---|---|---|---|
| 1 | **11a** | $Me_2N$ | **2** | −50/24 | 5.8 |
| 2 | **11b** | $Me_2NCH_2$ | **2** | −55/24 | 5.0 |
| 3 | **11c** | $Me_2N(CH_2)_2$ | **1** | −50/24 | 8.0 |
| 4 | **11d** | $MeOCH_2$ | **2** | −50/24 | 5.4–5.5 |
| 5 | **11e** | $MeO(CH_2)_2$ | **1** | −65/24 | 7.5 |
| 6 | **11f** | $MOMOCH_2$ | **2** | −50/24 | 5.7 |
| 7 | **11g** | $TIPSOCH_2$ | **2** | −50/24 | 6.1 |
| 8 | **11h** | $(CH_3)_3COCH_2$ | **1** | −65/24 | 7.1 |
| 9 | **11i** | $MeSCH_2OCH_2$ | **2** | −50/24 | 6.1 |
| 10 | **11j** | $MeSCH_2$ | **2** | −50/24 | 5.4–5.5 |
| 11 | **11k** | – | **2** | −50/16 | 5.5 |
| 12 | **11l** | – | **1** | −50/24 | 7.5 |
| 13 | **11m** | – | **1** | −50/24 | 7.1 |




**11k–m**

**11k**, $n=1$, $R^1=H$
**11l**, $n=1$, $R^1=CH_3$
**11m**, $n=2$, $R^1=CH_3$

2.0 kcal mol$^{-1}$ for N and O, compare entries 2 and 4 of Table 2 with entries 8 or 9 of Table 1) chelate rings leads to stabilization of this kind of organolithium compounds. However, Li–O or Li–N chelation involving the formation of a six-membered ring provides no extra stabilization, as compared with a non-chelating alkyl side chain in this type of systems ($\Delta\Delta G_{eq}=0$ kcal mol$^{-1}$, compare entries 3 and 5 of Table 2 with entries 8 or 9 of Table 1). Additionally, it appears that Li–N chelation affords a greater stabilization than its Li–O counterpart (by about half a kcal mol$^{-1}$, compare entry 2 with 4, Table 2) and this is similar to the stabilization imparted by a sulphur atom ($\Delta\Delta G_{eq}=0$ kcal mol$^{-1}$, compare entry 4 with 10, Table 2), which does not bind to the Li counterion, but exerts a large stabilizing effect due to its high polarizability.[20c]

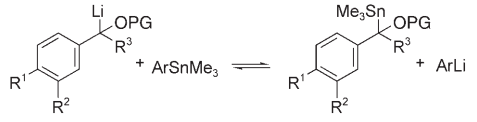
It may be argued that the heteroatom in the side chain of organolithiums **11** could be involved in intramolecular as well as intermolecular coordination, but this last possibility can be disregarded on the account of the lack of influence of the concentration on the stability of organolithiums **11b**,**d**, as mentioned before, as well as our NMR studies described below.

**Influence of O-protecting groups of the side chain**: Once it had been demonstrated that the formation of a five-membered ring chelate gives an important stabilization to this type of α-*O*-carbamoyl organolithiums, we decided to study the influence of the side chain O-protecting group on the stability of the organolithium compounds, in order to derive potentially useful information to be used in synthetic endeavors. For this study we chose methyl (**11d**), methoxymethyl (**11f**), triisopropylsilyl (**11g**), *tert*-butyl (**11h**) and methyl-thiomethyl (**11i**) ethers (Table 2) as representative O-protecting groups. The highest stabilization ($\Delta\Delta G_{eq}\sim$ 2.0 kcal mol$^{-1}$) is observed with the smallest group (Me, compare entries 4, Table 2 with entry 9, Table 1), the amount of stabilization decreases when using more sterically demanding groups ($\Delta\Delta G_{eq}=1.4$ and 0.4 kcal mol$^{-1}$ for TIPS and *tert*-butyl ether respectively, compare entries 7 and 8, Table 2 with entry 9 of Table 1). The negative influence of the steric bulk around the side chain heteroatom on the formation of a five-membered chelate and its effect on the stability of the organolithiums is also observed with the acetals **11k–m**. In this case, the less hindered dioxolane (**11k**) showed a high stabilization ($\Delta\Delta G_{eq}=2.0$ kcal mol$^{-1}$, compare entry 11, Table 2 with entry 9 of Table 1), while its dimethyl counterpart **11l**, or the similarly substituted dioxane **11m**, do not impart additional stabilization, as its $\Delta G_{eq}$ value is similar to the one measured for a plain alkyl chain substituted organolithium ($\Delta\Delta G_{eq}=0.0$–0.4 kcal mol$^{-1}$, compare entries 12 and 13 with entry 5, Table 2 or with entry 9, Table 1).

Since our first foray into the measurement of the relative stabilities of organolithium compounds had been in the realm of benzylic anions,[2] we decided to revisit these systems in order to determine how the stability of such delocalized anions is affected by substitution. The replacement of an α-hydrogen at the carbanionic center by a methyl group has an important destabilizing effect in the aliphatic series of organolithium compounds, and the same trend is observed in the more stable benzylic carbanion **13e** although with a smaller $\Delta\Delta G_{eq}$ (1.2–1.4 kcal mol$^{-1}$) value, a testament of the capability of *both* the *O*-carbamoyl and phenyl substituents to withdraw the extra negative charge from the anionic center.

The presence of an electron-donating or electron-withdrawing substituent at the aromatic ring should clearly influence the stability of the benzylic carbanion. To test if our method could be applied to the assessment of aromatic ring substituent effects on anion stability we investigated compounds **13a–d**. It is well known that a methyl group donates electrons through a mild hyperconjugation effect, and that a methoxy group can exert an electron-donating resonance effect although, due to the difference in electronegativity between oxygen and carbon, it also causes an electron-withdrawing inductive effect. The combination of these two factors results in that a MeO group is electron withdrawing at the *meta* position but in *para* the electron-donating resonance effect is more important.[22] The stability data obtained through Sn–Li exchange of benzyllithium compounds **13a–d** are concordant with the expected theoretical order. The presence of a methoxy group in *meta* is slightly stabilizing while both a *meta*-methyl and a *para*-methoxy substituents exert a destabilizing effect (compare entry 3 with 2 and 4 in Table 3).

Table 3. Relative stability data of benzylic compounds **13**.[a]




**13** **5–6a** **14** **5–6b**

| Entry | Anion | $R^1$ | $R^2$ | $R^3$ | $ArSnMe_3$ | $t$ [h] | $\Delta G_{eq}$ |
|---|---|---|---|---|---|---|---|
| 1 | **13a**[b] | H | H | H | **5** | 12 | 0.8–0.9 |
| 2 | **13b**[b] | H | Me | H | **5** | 24 | 1.3–1.4 |
| 3 | **13c**[b] | H | OMe | H | **5** | 16 | 0.8 |
| 4 | **13d**[b] | OMe | H | H | **5** | 24 | 1.8 |
| 5 | **13e**[c] | H | H | Me | **5** | 1 | 2.2 |
| 6 | **13e**[c] | H | H | Me | **6** | 2 | 2.1 |

[a] All reactions were performed at −78 °C. [b] PG = CON(*i*Pr)$_2$. [c] PG = Cby.

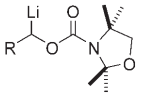
**NMR studies on the aggregation states of α-carbamoyloxy-organolithiums**: Although the Sn–Li or Pb–Li exchange reactions can provide a useful relative scale of thermodynamic stabilities of secondary α-oxy-organolithiums, care must be exercised when deriving structure–stability relationships from these data, since the aggregation states of the involved organolithium species must be known if sound conclusions are to be drawn: all the compounds studied should have the same aggregation state in solution and, preferably, they should be monomers.

To shed some light on the aggregation states of our organolithium species in solution we set up different experi-

ments. As discussed above, when equilibria were run at different concentrations ranging from 0.02 to 0.2 M (for **7c**, **7h**, **11b** and **11d**) there was no noticeable change in the values of the relative stabilities of the organolithium species, which suggests that they are monomeric in THF. We then proceeded to obtain $^{1}H$, $^{6}Li$ and $^{13}C$ NMR spectra[23] of selected α-carbamoyloxy-organolithium compounds (see Table 4) to determine the aggregation states[24] of these compounds in a 0.2 M [$D_8$]THF solution at 163 K. It is known that organolithium compounds tend to be less aggregated in electron donor solvents as THF, which is the solvent used in all of our equilibrium studies, and thus [$D_8$]THF was chosen for the NMR experiments. $^{6}Li$ NMR of all the compounds studied showed only one singlet which indicates the presence of only one species in solution ($\delta = 4.04$ ppm for **7j**, and $\delta =$ 4.56 ppm for **7k** and **11e**). In the $^{13}C$ NMR spectra of **7c**, **7j**, **7k** and **11e** (obtained from Li–Sn exchange of the corresponding stannane and $^{6}LiBu$) the signals originated by the lithiated carbons were split into a triplet (Table 4) which indicates that the carbon is coupled to only one lithium atom, and the magnitude of the $^{13}C,^{6}Li$ coupling constants lie within the range typical of monomeric species. Additionally, these compounds showed remarkable downfield $^{13}C$-chemical shifts of the lithiated carbon atoms which is consistent with a carbenoid nature of α-lithiated carbamates.[19]

Table 4. $^{13}C$ NMR data of selected α-oxy-organolithium compounds in [$D_8$]THF.[a]



| | δ [ppm] | Δδ[b] | $^{1}J(^{13}C,^{6}Li)$ [Hz] |
|---|---|---|---|
| **7c**: R = H | 80 | 29 | broad signal |
| **7e**: R = Me | 102 | 42 | broad signal with $^{7}Li$ |
| **7g**: R = *i*Pr | 112 | 41 | 11.8 (t) |
| **7h**: R = *t*Bu | 117 | 43 | 13.1 (t), 13.3 (t)[c] |
| **11e**: R = $MeO(CH_2)_3$ | 107 | 43 | 10.0 (t) |

[a] $T = 163$ K. [b] Δδ refers to the downfield shift of the O-substituted carbon upon lithiation. [c] Two rotamers.

Additionally we carried out NMR diffusion experiments[25] on compounds **7i** (R = butyl, a non-functionalized side chain unable to provide a coordination site for aggregation), **11b** [R = $Me_2N(CH_2)_2$] and **11d** [R = $MeO(CH_2)_2$] to detect any form of aggregation mediated by the heteroatoms in the side chains; this type of aggregation would not involve Li–C complexation and, therefore, would be undetectable by $^{6}Li,^{13}C$ coupling analysis. All three compounds showed very similar diffusion behaviors (diffusion constants in 0.1 M solutions in [$D_8$]THF at −78 °C: 1.37, 1.34, and 1.38 e−10 $m^2s^{-1}$ for **7i**, **11b**, and **11d**, respectively), a result that indicates they must have very similar sizes and shapes in THF solution, thus ruling out the formation of dimers by intermolecular interaction between the Li cation and the side chain heteroatoms when they are present. We thus conclude that the observed differences in stability among the organolithium compounds that we have studied are due to the electronic and chelating effects of the proximal and distal substituents of the anionic carbon, and not to differences in their aggregation states.

## Conclusions

Sn–Li and Pb–Li exchange equilibria have been established as useful tools for the study of stability-structure relationships of highly functionalized organolithium reagents. This methodology provides valuable quantitative information about the influence of a number of structural factors (electron-donating and -withdrawing capabilities of substituents, steric and chelation effects) on the behavior of these highly synthetically useful compounds.[26]

## Experimental Section

**General**: All reactions were performed under an inert atmosphere of Argon in glassware that had been oven- or flame-dried. Reaction temperatures are reported as the temperature of the bath surrounding the vessel. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled from sodium/benzophenone immediately before use; methylene chloride ($CH_2Cl_2$), pyridine, diisopropylamine, diisopropylethylamine and tetramethylethylenediamine (TMEDA) were distilled from $CaH_2$ and methanol was distilled from $Mg(OMe)_2$. 2,2,4,4-Tetramethyl-1,3-oxazolidine,[27] 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyl chloride,[27] **1a**,[28] **3a**,[29] **4a**,[30] **5a**,[2] **6a**,[31] methyl 2,4,6-triisopropylbenzoate,[32] **8b**,[33] **12b**,[34] and **12l**,[35] were prepared according to the literature.

***N*,*N*-Dimethyl-*N*-(2-trimethylstannanyl-pyrrol-1-yl)-amine (2a)**:[36] BuLi (2.10 mL, 7.08 mmol, 3.29 M in hexane) was added to a solution of 1-(dimethylamino)pyrrole (850 μL, 7.08 mmol) in THF (7.2 mL) at 0 °C. After 2 h, $Me_3SnCl$ (7.40 mL, 7.40 mmol, 1.0 M in THF) was added, the mixture was stirred for 45 min at 0 °C, then quenched by addition of pH 7.0 phosphate buffer and partitioned between $CH_2Cl_2$ (25 mL) and phosphate buffer (20 mL). The aqueous phase was extracted with $CH_2Cl_2$ (20 mL) and the combined organic phase was washed with satd aq $NaHCO_3$ (10 mL) and brine (20 mL), dried with $Na_2SO_4$, filtered and concentrated. The residue was purified by bulb-to-bulb distillation (40 °C at 0.5 mmHg) and **2a** was obtained as a pale yellow oil (1.8 g, 94 %). $^{1}H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.10$ (dd, $J = 1.4$, 2.6 Hz, 1H), 6.27 (m, 1H), 6.05 (dd, $J = 1.4$, 3.6 Hz, 1H), 2.79 (s, 6H), 0.27 ppm (s, $J(^{117}Sn,^{1}H) = 55.1$, $J(^{119}Sn,^{1}H) = 57.4$ Hz, 9H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 133.4$, 114.9 ($J(^{117,119}Sn,^{13}C) = 18.9$ Hz), 112.6 ($J(^{117,119}Sn,^{13}C) = 50.1$ Hz), 108.6 ($J(^{117,119}Sn,^{13}C) = 42.9$ Hz), 48.2, −9.2 ppm ($J(^{117}Sn,^{13}C) = 361.1$, $J(^{119}Sn,^{13}C) = 377.8$ Hz); elemental analysis calcd (%) for $C_9H_{18}N_2Sn$ (272.97): C 39.60, H 6.65, N 10.26; found: C 39.69, H 6.75, N 9.88.

**(2-Methoxyphenyl)-trimethylplumbane (1a-Pb)**: Following the literature procedure[28] but using $Me_3PbCl$ instead of $Me_3SnCl$, 2-bromoanisole (909 mg, 4.86 mmol) afforded **1a-Pb** as a colorless oil (1.4 g, 80 %). $^{1}H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 7.45$ (dd, $J = 1.6$, 6.9 Hz, 1H), 7.29 (m, 1H), 6.97 (q, $J = 7.0$ Hz, 1H), 6.87 (m, 1H), 3.79 (s, 3H), 0.92 ppm (s, $J(^{207}Pb,^{1}H) = 67.0$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 163.3$ ($J(^{207}Pb,^{13}C) = 16.2$ Hz), 137.0 ($J(^{207}Pb,^{13}C) = 300.2$ Hz), 136.8 ($J(^{207}Pb,^{13}C) = 43.8$ Hz), 129.2 ($J(^{207}Pb,^{13}C) = 11.7$ Hz), 121.4 ($J(^{207}Pb,^{13}C) = 62.0$ Hz), 109.3 ($J(^{207}Pb,^{13}C) = 28.2$ Hz), 55.4, −1.80 ppm ($J(^{207}Pb,^{13}C) = 295.0$ Hz); elemental analysis calcd (%) for $C_{10}H_{16}O_3Pb$ (391.44): C, 33.42, H 4.49; found: C 33.45, H 4.76.

**General procedure for alkyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylates 9c, f–k**: A suspension of $Na_2CO_3$ (1.18 g, 11.1 mmol) and 2,2,4,4-tetramethyl-1,3-oxazolidine (955 mg, 7.40 mmol) in $CH_2Cl_2$ (16 mL) was treated with the corresponding alkyl chloroformate (11.1 mmol). The reaction mixture was stirred in a Morton flask at room temperature for 5 h,

quenched by addition of NaOH (0.1 M, 1 mL) and after being stirred for 15 min, dried with $Na_2SO_4$, filtered over Celite and concentrated. The residue was purified by column chromatography (silica gel, EtOAc/hexane 1:3) to give **9c**, **f–k** as colorless oils.

**Methyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (9c)**: 93% yield; $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta = 3.58$ and 3.57 (2s, 2H), 3.53 (brs, 3H), 1.42 and 1.40, 1.36 and 1.35, 1.28 and 1.27, 1.21 and 1.20 ppm (8s, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta = 152.7/152.0$, 95.3/94.4, 76.0/75.7, 60.3/59.3, 51.2, 26.2, 25.1/25.0, 23.9 ppm; IR (CsI): $\tilde{\nu} = 1704\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_9H_{17}NO_3$ (187.24): C 57.73, H 9.15, N 7.48; found: C 57.71, H 9.08, N 7.38.

**Vinyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (9f)**: 97% yield; $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 7.22$ (ddd, $J = 1.7$, 6.3, 14.0 Hz, 1H), 4.75 (m, 1H), 4.42 (dt, $J = 1.7$, 6.3, 1H), 3.74 (s, 2H), 1.55 and 1.41 ppm (2brs, 12H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 149.0/148.2$, 141.2/141.1, 95.4/94.6, 94.2/94.1, 75.7/75.4, 60.3/59.7, 26.2, 25.0, 24.5, 23.3 ppm; IR (CsI): $\tilde{\nu} = 1691\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{10}H_{17}NO_3$ (199.25): C 60.28, H 8.60, N 7.03; found: C 60.30, H 8.67, N 7.41.

**Ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (9g)** see ref. [37], 84% yield.

**Propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (9h)**: 97% yield; $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta = 3.97$ (m, 2H), 3.65 (s, 2H), 1.61 (m, 2H), 1.48, 1.44, 1.34 and 1.29 (4s, 12H), 0.90 ppm (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta = 152.4/151.7$, 95.4/94.4, 76.1/75.8, 65.9, 60.3/59.4, 26.4, 25.2, 24.0, 22.2, 10.7 ppm; IR (CsI): $\tilde{\nu} = 1699\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{11}H_{21}NO_3$ (215.29): C 61.37, H 9.83, N 6.51; found: C 61.01, H 10.05, N 6.65.

**Pentyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (9i)**: 96% yield; $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.07$ (m, 2H), 3.72 (s, 2H), 1.64 (m, 2H), 1.56 and 1.52 (2s, 6H), 1.37 (m, 10H), 0.91 ppm (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta = 152.3/151.6$, 95.2/94.2, 75.8/75.6, 64.0, 60.0/59.0, 28.2/27.9, 26.0, 24.8, 23.6; 21.8, 13.5 ppm; IR (CsI): $\tilde{\nu} = 1701\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{13}H_{25}NO_3$ (243.34): C 64.16, H 10.36, N 5.76; found: C 64.06, H 10.33, N 5.78.

**2-Methylpropyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (9j)**: see ref. [37], 97% yield.

**2,2-Dimethylpropyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (9k)**:[37] The reaction was carried out in a sealed tube at 90 °C for 18 h (96% yield).

**(1-Methylcyclohexyl)methyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (9l)**: A suspension of NaH (60% in mineral oil, 515 mg, 12.9 mmol) in THF (9.0 mL) was treated with (1-methylcyclohexyl)methanol (1.1 g, 8.6 mmol), the mixture was stirred at RT for 30 min and 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyl chloride[27] (1.97 g, 10.3 mmol) in THF (8 mL) was added. The mixture was stirred in a sealed tube at 70 °C overnight, then quenched by addition of pH 7.0 phosphate buffer (5 mL) and partitioned between $CH_2Cl_2$ (20 mL) and phosphate buffer (20 mL). The aqueous phase was extracted with $CH_2Cl_2$ (20 mL) and the combined organic phase was washed with brine (20 mL), dried with $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by column chromatography (silica gel, EtOAc/hexane 1:6) to give **9l** as a white solid (2.0 g, 82%). M.p. 83–84 °C (hexane); $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta = 3.86$ and 3.85 (2s, 2H), 3.73 (s, 2H), 1.56 and 1.54 (2s, 6H), 1.42 and 1.38 (2s, 6H), 1.39 (m, 10H), 0.98 and 0.96 ppm (2s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta = 152.9/152.2$, 95.7/94.5, 76.2/76.0, 73.4, 60.5/59.4, 34.7, 33.8/33.7, 26.6, 26.2, 25.4/25.3, 24.1, 22.9, 21.6 ppm; IR (CsI): $\tilde{\nu} = 1681\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{29}NO_3$ (283.41): C 67.81, H 10.31, N 4.94; found: C 67.43, H 10.45, N 4.97.

**2-(*N*,*N*-Dimethylamino)ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11a-H)**: Following the same procedure as for **9l**, 2-(dimethylamino)ethanol (950 μL) afforded **11a-H** as a colorless oil (1.86 g, 80%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.18$ (m, 2H), 3.72 (s, 2H), 2.58 (m, 2H), 2.28 (s, 6H), 1.56 and 1.52 (2s, 6H), 1.42 and 1.36 ppm (2s, 6H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 152.4/151.7$, 95.5/94.6, 76.1/75.8, 62.1, 60.3/59.5, 57.7, 45.5, 26.2, 25.0, 23.8 ppm; IR (CsI): $\tilde{\nu} = 1700\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{12}H_{24}N_2O_3$ (244.34): C 58.99, H 9.90, N 11.47; found: C 59.01, H 9.98, N 11.54.

**4-(*N*,*N*-Dimethylamino)butyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11c-H)**: Following the same procedure as for **9l**, 4-(dimethylamino)butanol (520 μL, 4.1 mmol) afforded **11c-H** as a colorless oil (1.03 g, 93%). $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta = 4.10$ (m, 2H), 3.72 (s, 2H), 2.31 (t, $J = 7.2$ Hz, 2H), 2.22 (s, 6H), 1.69 (m, 2H), 1.55 (m, 8H), 1.42 and 1.37 ppm (2s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta = 152.1/151.4$, 95.1/94.1, 75.7/75.5, 63.8, 60.0/59.1, 58.8, 44.9, 26.4, 26.1, 24.9, 23.9, 23.7 ppm; IR (CsI): $\tilde{\nu} = 1699\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{14}H_{28}N_2O_3$ (272.39): C 61.73, H 10.36, N 10.28; found: C 61.71, H 9.98, N 10.41.

**3-Methoxypropyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11d-H)**: A suspension of NaH (60% in mineral oil, 123 mg, 3.09 mmol) in THF (15 mL) was treated with (3-hydroxypropyl)-2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (714 mg, 3.09 mmol) and after stirring at RT for 20 min, MeI (290 μL, 4.63 mmol) was added. The resulting mixture was stirred at RT for 6 h, quenched by addition of pH 7.0 phosphate buffer and then partitioned between $CH_2Cl_2$ (20 mL) and phosphate buffer (20 mL). The aqueous phase was extracted with $CH_2Cl_2$ (20 mL) and the combined organic phase was washed with brine (20 mL), dried with $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by column chromatography (silica gel, EtOAc/hexane 1:6) to give **11d-H** as a colorless oil (667 mg, 88%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.17$ (m, 2H), 3.73 (s, 2H), 3.47 (m, 2H), 3.34 (s, 3H), 1.93 (m, 2H), 1.55 and 1.52 (2s, 6H), 1.42 and 1.36 ppm (2s, 6H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 152.5/151.7$, 95.5/94.5, 76.0/75.8, 69.2, 61.4, 60.3/59.4, 58.4, 29.0, 26.2, 25.0, 23.9 ppm; IR (CsI): $\tilde{\nu} = 1699\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{12}H_{23}NO_4$ (245.32): C 58.75, H 9.45, N 5.71; found: C 58.47, H 9.56, N 5.72.

**4-Methoxybutyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11e-H)**: Following the same procedure as for **11d-H**, (4-hydroxybutyl)-2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (790 mg, 3.22 mmol) afforded **11e-H** as a colorless oil (785 mg, 94%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.09$ (m, 2H), 3.72 (s, 2H), 3.41 (t, $J = 5.8$ Hz, 2H), 3.33 (s, 3H), 1.66 (m, 4H), 1.55 and 1.51 (2s, 6H), 1.41 and 1.36 ppm (2s, 6H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 152.2/151.4$, 95.1/94.1, 75.7/75.4, 71.6/71.5, 64.1, 63.7, 57.9, 26.0, 25.9/25.7, 25.3/25.2, 24.7, 23.5 ppm; IR (CsI): $\tilde{\nu} = 1699\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{13}H_{25}NO_4$ (259.35): C 60.21, H 9.72, N 5.40; found: C 60.53, H 10.06, N 5.43.

**3-(Methoxymethoxy)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11f-H)**: Chloromethyl methyl ether was added at 0 °C dropwise to a solution of (3-hydroxypropyl)-2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (640 mg, 2.77 mmol), and diisopropylethylamine (1.7 mL, 9.68 mmol) in $CH_2Cl_2$ (5.5 mL). The resulting mixture was stirred at RT for 1 h, quenched by addition of pH 7.0 phosphate buffer and then partitioned between $CH_2Cl_2$ (15 mL) and phosphate buffer (15 mL). The aqueous phase was extracted with $CH_2Cl_2$ (10 mL) and the combined organic phase was washed with brine (20 mL), dried with $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by column chromatography (silica gel, EtOAc/hexane 1:3) to give **11f-H** as a colorless oil (2.5 g, 94%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.62$, (s, 2H), 4.21 (m, 2H), 3.73 (s, 2H), 3.62 (m, 2H), 3.35 (s, 3H), 1.96 (m, 2H), 1.56 and 1.52 (2s, 6H), 1.42 and 1.36 ppm (2s, 6H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 151.9/151.2$, 95.7, 95.1/94.0, 75.6/75.3, 63.5, 60.9, 59.9/58.9, 54.3, 28.8, 25.9, 24.6, 23.4 ppm; IR (CsI): $\tilde{\nu} = 1699\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{13}H_{25}NO_5$ (275.35): C 56.71, H 9.15, N 5.09, found: C 56.52, H 9.35, N 4.98.

**3-(3-Triisopropylsilyloxy)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11g-H)**: Triisopropylsilylchloride (690 μL, 3.26 mmol) was added to a solution of (3-hydroxypropyl)-2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (629 mg, 2.72 mmol) and imidazole (463 mg, 6.80 mmol) in DMF (1.3 mL). The resulting mixture was stirred at RT for 16 h and then poured over 2 N HCl solution (10 mL) and extracted with EtOAc (3×10 mL), the combined organic phase was washed with satd aq $NaHCO_3$ (15 mL) and brine (15 mL), dried with $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by column chromatogra-

phy (silica gel, EtOAc/hexane 1:10) to give **11g-H** as a colorless oil (957 mg, 91%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$=4.19 (t, $J$=6.2 Hz, 2H), 3.78 (m, 2H), 3.70 (s, 2H), 1.87 (m, 2H), 1.53 and 1.49 (2s, 6H), 1.39 and 1.34 (2s, 6H), 1.04 (m, 3H), 1.03 and 1.02 ppm (2s, 18H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$=152.6/151.9, 95.6/94.6, 76.1/75.9, 61.4, 60.3/59.4, 59.9, 32.2, 26.3, 25.1, 23.9, 17.8/17.6, 12.2/11.7 ppm; IR (CsI): $\tilde{\nu}$=1702 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{20}H_{41}NO_4Si$ (387.64): C 61.97, H 10.66, N 3.61; found: C 62.10, H 10.65, N 3.51.

**3-*tert*-Butoxypropyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11h-H)**: Following the same procedure as for **9l**, 3-*tert*-butoxypropan-1-ol (1.3 mL, 9.73 mmol) afforded **11h-H** as a colorless oil (2.7 g, 97%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$=4.18 (t, $J$=6.1 Hz, 2H), 3.73 (s, 2H), 3.44 (m, 2H), 1.88 (m, 2H), 1.56 and 1.52 (2s, 6H), 1.42 and 1.36 (2s, 6H), 1.18 ppm (s, 9H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$=152.3/151.6, 95.2/94.2, 75.8/75.6, 72.1, 61.5/61.4, 60.0/59.1, 57.7/57.6, 29.7, 27.1, 26.1, 24.8, 23.7 ppm; IR (CsI): $\tilde{\nu}$=1700 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{15}H_{29}NO_4$ (287.40): C 62.69, H 10.17, N 4.87; found: C 62.34, H 10.40, N 4.91.

**3-[(Methylthio)methoxy]propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11i-H)**: (3-Hydroxypropyl)-2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (634 mg, 3.28 mmol) was added to a solution of acetic anhydride (5.2 mL) and acetic acid (1.6 mL) in DMSO (7.7 mL). The resulting mixture was stirred at RT for 48 h and then poured over satd aq $Na_2CO_3$ and extracted with $CH_2Cl_2$ (3×15 mL), the combined organic phase was washed with $H_2O$ (20 mL) and brine (20 mL), dried with $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by column chromatography (silica gel, EtOAc/hexane 1:10) to give **11i-H** as a colorless oil (790 mg, 99%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$=4.63 (s, 2H), 4.18 (m, 2H), 3.73 (s, 2H), 3.62 (m, 2H), 2.22 (s, 3H), 1.97 (m, 2H), 1.56 and 1.53 (2s, 6H), 1.42 and 1.37 ppm (2s, 6H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$=152.1/151.4, 95.2/94.2, 75.7/75.5, 74.7, 64.0, 61.0, 60.0/59.1, 28.6, 26.0, 24.8, 23.6, 13.3 ppm; IR (CsI): $\tilde{\nu}$=1698 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{13}H_{25}NO_4S$ (291.41): C 53.58, H 8.65, N 4.81, S 11.00; found: C 53.35, H 8.90, N 4.71, S 10.76.

**3-(Methylthio)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11j-H)**: Following the same procedure as for **9l**, 3-(methylthio)propan-1-ol (640 μL, 6.22 mmol) gave **11j-H** as a colorless oil (1.61 g, 99%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$=4.18 (t, $J$=6.1 Hz, 2H), 3.72 (s, 2H), 2.57 (m, 2H), 2.10 (s, 3H), 1.95 (m, 2H), 1.55 and 1.51 (2s, 6H), 1.41 and 1.35 ppm (2s, 6H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$=152.0/151.3, 95.2/94.1, 75.7/75.5, 62.5, 60.0/59.0, 30.3, 28.2, 26.0, 24.8/24.7, 23.5, 14.9 ppm; IR (CsI): $\tilde{\nu}$=1698 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{12}H_{23}NO_3S$ (261.38): C 55.14, H 8.87, N 5.36, S 12.27; found: C 54.83, H 9.03, N 5.23, S 11.99.

**2-(1,3-Dioxolan-4-yl)ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11k-H)**: A suspension of NaH (60% in mineral oil, 810 mg, 20.2 mmol) in DMF (6.5 mL) was treated with 3,4-dihydroxybutyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (662 mg, 2.53 mmol), the mixture was stirred at RT for 45 min and dibromomethane (355 μL, 5.1 mmol) was added. The resulting mixture was stirred overnight at RT, then poured over pH 7.0 phosphate buffer and partitioned between $CH_2Cl_2$ (10 mL) and phosphate buffer (10 mL). The aqueous phase was extracted with $CH_2Cl_2$ (3×5 mL) and the combined organic phase was washed with brine (10 mL), dried with $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by column chromatography (silica gel, EtOAc/hexane 1:6) to give **11k-H** as a colorless oil (508 mg, 73%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$=5.03 (s, 1H), 4.88 (s, 1H), 4.23 (br t, $J$=6.6 Hz, 2H), 4.12 (m, 1H), 4.02 (t, $J$=7.0 Hz, 1H), 3.73 (s, 2H), 3.51 (m, 1H), 1.94 (m, 2H), 1.56 and 1.52 (2s, 6H), 1.42 and 1.36 ppm (2s, 6H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$=151.4/150.7, 94.7/93.7, 93.8, 75.2/74.9, 72.2, 68.5, 60.4, 59.6/58.6, 31.9, 25.6, 24.3, 23.1 ppm; IR (CsI): $\tilde{\nu}$=1698 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{13}H_{23}NO_5$ (273.33): C 57.13, H 8.48, N 5.12; found: C 57.11, H 8.72, N 5.04.

**2-(2,2-Dimethyl-1,3-dioxan-4-yl)ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (11m-H)**: Following the same procedure as for **9l**, 2-(2,2-dimethyl-1,3-dioxan-4-yl)ethanol[38] (272 mg, 1.70 mmol) afforded **11m-H** as a white solid (425 mg, 79%). M.p. 58–59°C (hexane); $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$=4.15 (m, 2H), 3.94 (td, $J$=11.9, 2.8 Hz, 2H), 3.80 (ddd, $J$=1.4, 5.4, 11.8 Hz, 1H), 3.70 (s, 2H), 1.77 (m, 2H), 1.56 (m, 2H), 1.52 and 1.48 (2s, 6H), 1.40, 1.39, 1.34 and 1.33 ppm (4s, 12H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$=152.1/151.4, 97.6, 95.2/94.1, 75.7/75.4, 65.4, 60.2/59.2, 60.0/59.0, 35.4, 30.8, 29.4, 26.0, 24.8, 23.6, 18.6 ppm; IR (CsI): $\tilde{\nu}$=1695 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{29}NO_5$ (315.41): C 60.93, H 9.27, N 4.44; found: C 60.74, H 9.37, N 4.48.

**General procedure for the synthesis of organostannanes 8 and 12**: *s*BuLi (1.25 mL, 1.50 mmol, 1.2 M in hexane) was added to a precooled solution (−78°C) of the corresponding carbamate or ester (1.00 mmol) and TMEDA (230 μL, 1.50 mmol) in $Et_2O$ (3.0 mL). After stirring at −78°C for 5 h, $Me_3SnCl$ (1.5 mL, 1.5 mmol, 1.0 M in THF) was added to the reaction mixture. The resulting solution was stirred at the same temperature for 1 h, quenched by addition of pH 7.0 phosphate buffer and then partitioned between $Et_2O$ (10 mL) and phosphate buffer (10 mL). The aqueous phase was extracted with $Et_2O$ (10 mL) and the combined organic phase was washed with brine (10 mL), dried with $Na_2SO_4$, filtered and concentrated. The residue was purified by column chromatography (grade III neutral $Al_2O_3$, hexane to EtOAc/hexane 1:50).

**(Methoxymethyl)tributylstannane (8a)**: Following the literature procedure[39] but using chloromethyl methyl ether previously centrifuged with triethylamine in THF, **8a** was prepared in 98% yield.

**Trimethylstannanylmethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (8c)**: Following the general procedure, **9c** (1.17 g, 6.24 mmol) afforded **8c** as a pale yellow oil (2.09 g, 96%). $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta$=4.07 (m, 2H), 3.71 (s, 2H), 1.54, 1.48, 1.40 and 1.32 (4s, 12H), 0.13 ppm (s, $J(^{117}Sn,^1H)$=53.0, $J(^{119}Sn,^1H)$=54.9 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$=153.2/152.6, 95.1/94.1, 75.8/75.6, 59.9/58.9, 56.2 ($J(^{117}Sn,^{13}C)$=385.3, $J(^{119}Sn,^{13}C)$=404.6 Hz), 26.1, 24.9/24.8, 23.7, −9.4 ppm ($J(^{117}Sn,^{13}C)$=328.1, $J(^{119}Sn,^{13}C)$=345.5 Hz); IR (CsI): $\tilde{\nu}$=1684 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{12}H_{25}NO_3Sn$ (350.05): C 41.18, H 7.20, N 4.00; found: C 41.33, H 7.29, N 4.06.

**Trimethylstannanylmethyl 2,4,6-triisopropylbenzoate (8d)**: Following the general procedure but using *t*BuLi instead of *s*BuLi, **9d** (710 mg, 2.71 mmol) gave **8d** as a colorless oil (530 mg, 46%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=7.02 (s, 2H), 4.36 (s, $J(^{117,119}Sn,^1H)$=16.4 Hz, 2H), 2.85 (m, 3H), 1.26 (d, $J$=7.0 Hz, 18H), 0.24 ppm (s, $J(^{117}Sn,^1H)$=53.6, $J(^{119}Sn,^1H)$=55.4 Hz, 9H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$=171.9 ($J(^{117,119}Sn,^{13}C)$=17.6 Hz), 149.9, 144.8, 130.7, 120.7 ($J(^{117,119}Sn,^{13}C)$=58.7 Hz), 56.5 ($J(^{117}Sn,^{13}C)$=355.5, $J(^{119}Sn,^{13}C)$=371.8 Hz), 34.4, 31.5, 24.2, 23.9, −9.5 ppm ($J(^{117}Sn,^{13}C)$=330.0, $J(^{119}Sn,^{13}C)$=345.3 Hz); IR (CsI): $\tilde{\nu}$=1712 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{20}H_{34}O_2Sn$ (425.20): C 56.50, H 8.06; found: C 56.73, H 8.29.

**(1-(Dodecyloxy)vinyl)trimethylstannane (8e)**: Following the general procedure but using *t*BuLi during 3 h from −78 to 0°C instead of *s*BuLi, 1-(vinyloxy)dodecane (541 mg, 2.55 mmol) afforded **8e** (902 mg, 94%) as a colorless oil. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=4.66 (d, $J$=1.7, $J(^{117,119}Sn,^1H)$=110.2 Hz, 1H), 4.08 (d, $J$=1.7, $J(^{117,119}Sn,^1H)$=35.7 Hz, 1H), 3.64 (t, $J$=6.5 Hz, 2H), 1.64 (m, 2H), 1.26 (m, 18H), 0.88 (m, 3H), 0.18 ppm (s, $J(^{117,119}Sn,^1H)$=55.1 Hz, 9H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$=172.7 ($J(^{117}Sn,^{13}C)$=544.5, $J(^{119}Sn,^{13}C)$=569.8 Hz), 94.9 ($J(^{117,119}Sn,^{13}C)$=82.6 Hz), 66.8 ($J(^{117,119}Sn,^{13}C)$=27.9 Hz), 32.0, 29.7, 29.6, 29.5, 29.4, 29.0, 26.3, 22.7, 14.1, −9.6 ppm ($J(^{117}Sn,^{13}C)$=339.0, $J(^{119}Sn,^{13}C)$=354.8 Hz); elemental analysis calcd (%) for $C_{17}H_{36}OSn$ (375.18): C 54.42, H 9.67; found: C 54.35, H 10.03.

**1-(Trimethylstannyl)vinyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (8f)**: Following the general procedure, **9f** (418 mg, 2.10 mmol) afforded **8f** as a colorless oil (592 mg, 78%). $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$=5.37 and 5.33 (2s, $J(^{117}Sn,^1H)$=91.1, $J(^{119}Sn,^1H)$=94.7 Hz, 1H), 4.62 and 4.61 (2s, $J(^{117,119}Sn,^1H)$=29.4 Hz, 1H), 3.74 (s, 2H), 1.56 and 1.54 (2s, 6H), 1.41 and 1.40 (2s, 6H), 0.17 ppm (s, $J(^{117,119}Sn,^1H)$=55.7 Hz, 9H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$=163.8/163.6, 151.8/151.1, 107.8/107.7 ($J(^{117,119}Sn,^{13}C)$=70.9 Hz), 95.8/95.2, 76.3/76.1, 60.6/60.1, 26.7, 25.5, 25.0, 23.9, −6.5 ppm ($J(^{117}Sn,^{13}C)$=368.3, $J(^{119}Sn,^{13}C)$=385.4 Hz); IR (CsI): $\tilde{\nu}$=1691 cm$^{-1}$ (C=O); elemental analy-

sis calcd (%) for $C_{13}H_{25}NO_3Sn$ (362.06): C 43.13, H 6.96, N 3.87; found: C 43.41, H 7.17, N 4.00.

**1-(Trimethylstannanyl)ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (8g)**: Compound **9g** (342 mg, 1.70 mmol) gave **8g** as a pale yellow oil (537 mg, 87%). $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta$ = 4.52 (q, $J$ = 7.4 Hz, 1H), 3.67 (s, 2H), 1.50 (m, 9H), 1.37 and 1.33 (2s, 6H), 0.06 ppm (s, $J(^{117}Sn,^1H)$ = 51.2, $J(^{119}Sn,^1H)$ = 53.6 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$ = 152.9/152.3, 95.5/94.5, 76.2/76.0, 66.7 ($J(^{117}Sn,^{13}C)$ = 431.7, $J(^{119}Sn,^{13}C)$ = 451.3 Hz), 60.3/59.5, 26.5/26.4, 25.4, 25.3/25.2, 24.3/24.1, 19.3, −9.6 ppm ($J(^{117}Sn,^{13}C)$ = 317.1, $J(^{119}Sn,^{13}C)$ = 330.8 Hz); IR (CsI): $\tilde{\nu}$ = 1679 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{13}H_{27}NO_3Sn$ (364.07): C 42.89, H 7.47, N 3.85; found: C 43.09, H 7.61, N 3.79.

**1-(Trimethylstannanyl)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (8h)**: Compound **9h** (1.05 g, 4.86 mmol) yielded **8h** (1.72 g, 94%) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta$ = 4.48 (td, $J$ = 6.9, 2.5 Hz, 1H), 3.72 (s, 2H), 1.90 (m, 2H), 1.54 (br s, 6H), 1.40 and 1.37 (2s, 6H), 0.99 (td, $J$ = 7.3 Hz, 3.1, 3H), 0.10 ppm (s, $J(^{117}Sn,^1H)$ = 51.2, $J(^{119}Sn,^1H)$ = 53.5 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$ = 153.0/152.3, 95.4/94.4, 76.1/75.9, 73.5 ($J(^{117}Sn,^{13}C)$ = 430.4, $J(^{119}Sn,^{13}C)$ = 451.8 Hz), 60.3/59.3, 26.8, 26.5/26.4, 25.3, 24.2/24.1, 12.5 ($J(^{117,119}Sn,^{13}C)$ = 35.0 Hz), −9.1 ppm ($J(^{117}Sn,^{13}C)$ = 315.4, $J(^{119}Sn,^{13}C)$ = 330.0 Hz); IR (CsI): $\tilde{\nu}$ = 1678 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{14}H_{29}NO_3Sn$ (378.10): C 44.47, H 7.73, N 3.70; found: C 44.86, H 7.99, N 3.76.

**1-(Trimethylstannanyl)pentyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (8i)**: Compound **9i** (800 mg, 3.29 mmol) yielded **8i** (1.10 g, 82%) as a colorless oil. $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$ = 4.53 (m, 1H), 3.72 (s, 2H), 1.84 (m, 2H), 1.53 (m, 6H), 1.35 (m, 10H), 0.91 (t, $J$ = 6.7 Hz, 3H), 0.09 ppm (s, $J(^{117}Sn,^1H)$ = 51.3, $J(^{119}Sn,^1H)$ = 53.3 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$ = 153.1/152.5, 95.4/94.4, 76.1/75.9, 71.7 ($J(^{117}Sn,^{13}C)$ = 434.1, $J(^{119}Sn,^{13}C)$ = 453.9 Hz), 60.2/59.2, 33.2, 29.8 ($J(^{117,119}Sn,^{13}C)$ = 33.5 Hz), 26.3, 25.1, 24.0/23.9, 22.2, 13.8, −9.3 ppm ($J(^{117}Sn,^{13}C)$ = 316.4, $J(^{119}Sn,^{13}C)$ = 331.1 Hz); IR (CsI): $\tilde{\nu}$ = 1678 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{33}NO_3Sn$ (406.15): C 47.32, H 8.19, N 3.45; found: C 47.53, H 8.52, N 3.14.

**2-Methyl-1-(trimethylstannanyl)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (8j)**: Compound **9j** (991 mg, 4.32 mmol) gave **8j** (1.57 g, 93%) as a pale yellow oil. $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta$ = 4.41 and 4.40 (2 d, $J$ = 6.5 Hz, 1H), 3.72 (s, 2H), 2.21 and 2.20 (2 sept, $J$ = 6.7 Hz, 1H), 1.54 (s, 6H), 1.40 and 1.38 (2s, 6H), 0.99 and 0.98 (2 d, $J$ = 6.7 Hz, 6H), 0.11 ppm (s, $J(^{117}Sn,^1H)$ = 50.9, $J(^{119}Sn,^1H)$ = 53.1 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$ = 153.3/152.6, 95.8/94.6, 79.2, 76.3/76.1, 60.5/59.5, 32.0, 26.6/26.5, 25.3, 24.2/24.1, 21.0 ($J(^{117,119}Sn,^{13}C)$ = 27.6 Hz), 20.3/20.2, −8.4 ppm ($J(^{117}Sn,^{13}C)$ = 314.4, $J(^{119}Sn,^{13}C)$ = 328.7 Hz); IR (CsI): $\tilde{\nu}$ = 1679 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{15}H_{31}NO_3Sn$ (392.13): C 45.95, H 7.97, N 3.57; found: C 46.23, H 8.09, N 3.42.

**2,2-Dimethyl-1-(trimethylstannanyl)propyl 2,2,4,4-tetramethyl-oxazolidine-3-carboxylate (8k)**: Following the general procedure with a reaction temperature of −30°C, **9k** (400 mg, 1.64 mmol) gave **8k** (502 mg, 75%) as a colorless oil. $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$ = 4.67 and 4.66 (2s, $J(^{117,119}Sn,^1H)$ = 14.3 Hz, 1H), 3.73 (s, 2H), 1.56 and 1.55 (2s, 6H), 1.42 and 1.40 (2s, 6H), 1.02 and 1.01 (2s, 9H), 0.14 ppm (s, $J(^{117}Sn,^1H)$ = 50.6, $J(^{119}Sn,^1H)$ = 52.8 Hz, 9H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$ = 152.8/152.1, 95.6/94.1, 82.9 ($J(^{117}Sn,^{13}C)$ = 438.4, $J(^{119}Sn,^{13}C)$ = 458.5 Hz), 76.1/75.8, 60.3, 59.0, 35.8, 27.9, 26.5, 25.4/25.3, 25.1/24.8, 24.0/23.8, −7.4 ppm ($J(^{117}Sn,^{13}C)$ = 309.9, $J(^{119}Sn,^{13}C)$ = 324.2 Hz); IR (CsI): $\tilde{\nu}$ = 1679 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{33}NO_3Sn$ (406.16): C 47.32, H 8.19, N 3.45; found: C 47.66, H 8.57, N 3.30.

**(1-Methylcyclohexyl)-1-(trimethylstannanyl)methyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (8l)**: Following the general procedure with a reaction temperature of −30°C, **9l** (705 mg, 2.49 mmol) gave **8l** (610 mg, 75%) as a white solid. M.p. 64–65°C (hexane); $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$ = 4.89 and 4.87 (2s, $J(^{117,119}Sn,^{13}C)$ = 15.6 Hz, 1H), 3.73 (s, 2H), 1.57 and 1.55 (2s, 6H), 1.54–1.28 (m, 10H), 1.41 and 1.39 (2s, 6H), 1.00 (d, $J$ = 4.3 Hz, 3H), 0.14 ppm (s, $J(^{117}Sn,^1H)$ = 50.5, $J(^{119}Sn,^1H)$ = 52.5 Hz, 9H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$ = 153.0/152.2, 95.7/94.3, 82.8 ($J(^{117}Sn,^{13}C)$ = 439.4, $J(^{119}Sn,^{13}C)$ = 457.1 Hz), 76.2/75.9, 60.5/59.2, 38.2, 35.7/35.6, 26.7/26.6, 26.1, 25.6/25.4, 25.3/24.9, 24.1/23.9, 22.8/22.7, 21.8, −7.3 ppm ($J(^{117}Sn,^{13}C)$ = 306.7, $J(^{119}Sn,^{13}C)$ = 320.8 Hz); IR (CsI): $\tilde{\nu}$ = 1673 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{19}H_{37}NO_3Sn$ (446.22): C 51.14, H 8.36, N 3.14; found: C 51.39, H 8.48, N 3.22.

**Tributyl-(1-methoxymethoxy-decyl)stannane (8m)**: A solution of diisopropylamine (440 μL, 3.17 mmol) in THF (10 mL) cooled to 0°C was treated with BuLi (1.8 mL, 2.77 mmol, 1.51 M in hexane) and stirred for 15 min. $Bu_3SnH$ (700 μL, 2.64 mmol) was added, stirred at 0°C for 15 min and then cooled to −78°C. Decanal (400 μL, 2.10 mmol) was added and the resulting mixture was stirred at −78°C for 3.5 h. The reaction was quenched by addition of satd aq $NH_4Cl$ solution (15 mL) and partitioned between EtOAc (20 mL) and $H_2O$ (20 mL). The organic layer was washed with $H_2O$ (20 mL) and brine (20 mL), dried with $Na_2SO_4$, filtered and evaporated to give a residue which was immediately treated with diisopropylethylamine (1.3 mL, 7.39 mmol) in $CH_2Cl_2$ (3.2 mL) and chloromethyl methyl ether (500 μL, 6.60 mmol), which had been previously centrifuged with triethylamine (100 μL) in THF (500 μL). After 12 h stirring at RT, the reaction mixture was partitioned between $CH_2Cl_2$ (15 mL) and pH 7.0 buffer solution (15 mL). The organic layer was washed with brine (15 mL), dried with $Na_2SO_4$, filtered and evaporated. The residue was purified by chromatography through a short column of silica gel (EtOAc/hexane 1:100) to give **8m** (511 mg, 49%) as a colorless oil. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 4.60 (d, $J$ = 6.6 Hz, 1H), 4.54 (d, $J$ = 6.6 Hz, 1H), 4.05 (t, $J$ = 6.6 Hz, 1H), 3.34 (s, 3H), 1.79 (m, 2H), 1.48 (m, 5H), 1.31 (m, 20H), 0.89 ppm (m, 19H); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 96.3 ($J(^{117,119}Sn,^{13}C)$ = 18.8 Hz), 74.0 ($J(^{117}Sn,^{13}C)$ = 385.7, $J(^{119}Sn,^{13}C)$ = 403.7 Hz), 55.4, 35.1, 31.9, 29.6, 29.5, 29.3, 29.2 ($J(^{117,119}Sn,^{13}C)$ = 19.9 Hz), 27.9 ($J(^{117,119}Sn,^{13}C)$ = 29.5 Hz), 27.5 ($J(^{117}Sn,^{13}C)$ = 53.3, $J(^{119}Sn,^{13}C)$ = 55.4 Hz), 22.7, 14.1, 13.7, 9.2 ppm ($J(^{117}Sn,^{13}C)$ = 290.0, $J(^{119}Sn,^{13}C)$ = 303.4 Hz); elemental analysis calcd (%) for $C_{24}H_{52}O_2Sn$ (491.39): C 58.66, H 10.67; found: C 58.55, H 10.69.

**1-(Trimethylplumbyl)ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (8g-Pb)**: Following the general procedure for the synthesis of organostannanes but using $Me_3PbBr$ instead of $Me_3SnCl$, **9g** (303 mg, 1.56 mmol) gave **8g-Pb** (680 mg, 96%) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta$ = 5.20 (q, $J$ = 7.2, $J(^{207}Pb,^1H)$ = 55.0 Hz, 1H), 3.72 (s, 2H), 1.98 and 1.75 (2 d, $J$ = 3.6, $J(^{207}Pb,^1H)$ = 113.8 Hz, 3H), 1.54 and 1.52 (2s, 6H), 1.41, 1.40, 1.37 and 1.36 (4s, 6H), 0.7 ppm (s, $J(^{207}Pb,^1H)$ = 57.2 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$ = 152.4/151.8, 95.5/94.6, 76.2/76.0, 72.0 ($J(^{207}Pb,^{13}C)$ = 428.7 Hz), 60.2/59.4, 26.4/26.3, 25.2/25.1, 24.1/23.9, 21.2 ($J(^{207}Pb,^{13}C)$ = 13.1 Hz), −2.2 ppm ($J(^{207}Pb,^{13}C)$ = 197.4 Hz); IR (CsI): $\tilde{\nu}$ = 1688 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{13}H_{27}NO_3Pb$ (452.56): C 34.50, H 6.01, N 3.10; found: C 34.28, H 6.36, N 3.16.

**2,2-Dimethyl-1-(trimethylplumbyl)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (8k-Pb)**: Following the general procedure for the synthesis of organostannanes but at −30°C and using $Me_3PbBr$ instead of $Me_3SnCl$, **9k** (640 mg, 2.63 mmol) gave **8k-Pb** (915 mg, 70%) as a colorless oil. $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$ = 5.20 and 5.19 (2s, $J(^{207}Pb,^1H)$ = 40.0 Hz, 1H), 3.74 (s, 2H), 1.57, 1.56 and 1.55 (3s, 6H), 1.42, 1.41 and 1.40 (3s, 6H), 1.04 and 1.03 (2 s, 9H), 0.76 ppm (s, $J(^{207}Pb,^1H)$ = 54.8 Hz, 9H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$ = 152.2/151.4, 95.7/94.2, 90.3 ($J(^{207}Pb,^{13}C)$ = 446.0 Hz), 76.1/75.9, 60.4/59.2, 36.8, 28.1 ($J(^{207}Pb,^{13}C)$ = 38.5 Hz), 26.7/26.6, 25.6/25.4, 25.2/24.7, 24.1/23.8, −0.12 ppm ($J(^{207}Pb,^{13}C)$ = 180.9 Hz); IR (CsI): $\tilde{\nu}$ = 1689 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{33}NO_3Pb$ (494.65): C 38.85, H 6.72, N 2.83; found: C 38.99, H 7.08, N 2.93.

**(1-Methylcyclohexyl)(trimethylplumbyl)methyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (8l-Pb)**: Following the general procedure for the synthesis of organostannanes but at −30°C and using $Me_3PbBr$ instead of $Me_3SnCl$, **9l** (635 mg, 2.24 mmol) gave **8l-Pb** (610 mg, 51%) as a white solid. M.p. 83–84°C (hexane); $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$ = 5.41 and 5.40 (2s, $J(^{207}Pb,^1H)$ = 37.1 Hz, 1H), 3.73 (s, 2H), 1.57 and 1.55 (2s, 6H), 1.41 and 1.39 (2s, 6H), 1.38 (m, 10H), 1.03 and 1.01 (2s, 3H), 0.76 ppm (s, $J(^{207}Pb,^1H)$ = 54.2 Hz, 9H); $^{13}$C NMR (62.9 MHz,

$CDCl_3$, rotamers): $\delta = 152.5/151.7$, 95.9/94.5, 90.4 ($J(^{207}Pb,^{13}C) = 451.9$ Hz), 76.3/76.0, 60.6/59.4, 39.2, 36.1 ($J(^{207}Pb,^{13}C) = 33.2$ Hz) and 35.9 ($J(^{207}Pb,^{13}C) = 50.8$ Hz), 26.9/26.7, 26.2, 25.8/25.6, 25.3/24.8, 24.3/23.9, 23.2/23.1 ($J(^{207}Pb,^{13}C) = 34.7$ Hz), 22.0, 0.03 ppm ($J(^{207}Pb,^{13}C) = 175.7$ Hz); IR (CsI): $\tilde{\nu} = 1675\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{19}H_{37}NO_3Pb$ (534.71): C 42.68, H 6.97, N 2.62; found: C 43.00, H 7.29, N 2.69.

**2-(*N*,*N*-Dimethylamino)-1-(trimethylstannanyl)ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12a)**: Compound **11a-H** (715 mg, 2.90 mmol) afforded **13a** (814 mg, 69%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.71$ (m, 1H), 3.60 (s, 2H), 2.57 (m, 2H), 2.10 (s, 6H), 1.42 (s, 6H), 1.29 and 1.24 (2s, 6H), −0.01 ppm (s, $J(^{117,119}Sn\text{-}^1H) = 52.9$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 152.9/152.2$, 95.5/94.5, 76.1/75.9, 70.3 ($J(^{117}Sn,^{13}C) = 433.0$, $J(^{119}Sn,^{13}C) = 452.7$ Hz), 70.2 ($J(^{117}Sn,^{13}C) = 433.0$, $J(^{119}Sn,^{13}C) = 447.8$ Hz), 61.4, 60.2/59.3, 45.8, 26.3/26.2, 25.1, 24.0/23.9, −9.2 ppm ($J(^{117}Sn,^{13}C) = 322.2$, $J(^{119}Sn,^{13}C) = 337.2$ Hz); IR (CsI): $\tilde{\nu} = 1683\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{15}H_{32}N_2O_3Sn$ (407.14): C 44.25, H 7.92, N 6.88; found: C 44.22, H 8.07, N 6.77.

**4-(*N*,*N*-Dimethylamino)-1-(trimethylstannanyl)butyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12c)**: Compound **11c-H** (687 mg, 2.52 mmol) afforded **12c** (852 mg, 78%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.53$ (m, 1H), 3.71 (s, 2H), 2.30 (t, $J = 7.5$ Hz, 2H), 2.22 (s, 6H), 1.85 (m, 2H), 1.58 (m, 2H), 1.53 and 1.51 (2s, 6H), 1.40 and 1.36 (2s, 6H), 0.10 ppm (s, $J(^{117}Sn,^1H) = 51.3$, $J(^{119}Sn,^1H) = 53.4$ Hz, 9H); $^{13}C$ NMR (75 MHz, $CDCl_3$, rotamers): $\delta = 152.8/152.2$, 95.3/94.3, 76.0/75.8, 71.5 ($J(^{117}Sn,^{13}C) = 427.8$, $J(^{119}Sn,^{13}C) = 447.2$ Hz), 60.1/59.2, 59.4, 45.2, 31.4, 26.4/26.3, 25.9, ($J(^{117,119}Sn,^{13}C) = 34.2$ Hz), 25.1, 24.0/23.9, −9.2 ppm ($J(^{117}Sn,^{13}C) = 316.6$, $J(^{119}Sn,^{13}C) = 331.1$ Hz); IR (CsI): $\tilde{\nu} = 1678\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{17}H_{36}N_2O_3Sn$ (435.20): C 46.92, H 8.34, N 6.44; found: C 47.16, H 8.77, N 6.41.

**3-Methoxy-1-(trimethylstannanyl)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12d)**: Compound **11d-H** (886 mg, 3.61 mmol) afforded **12d** (1.15 g, 78%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.61$ (m, 1H), 3.72 (s, 2H), 3.46 (m, 2H), 3.32 (s, 3H), 2.12 (m, 2H), 1.54 and 1.52 (2s, 6H), 1.40 and 1.36 (2s, 6H), 0.09 ppm (s, $J(^{117,119}Sn,^1H) = 52.6$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 153.1/152.4$, 95.5/94.4, 76.1/75.9, 70.5 ($J(^{117,119}Sn,^{13}C) = 38.9$ Hz), 68.4 ($J(^{117}Sn,^{13}C) = 431.9$, $J(^{119}Sn,^{13}C) = 448.8$ Hz), 60.3/59.3, 58.4, 33.5, 26.3/26.2, 25.1, 24.0/23.9, −9.1 ppm ($J(^{117}Sn,^{13}C) = 322.3$, $J(^{119}Sn,^{13}C) = 337.2$ Hz); IR (CsI): $\tilde{\nu} = 1679\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{15}H_{31}NO_4Sn$ (408.13): C 44.14, H 7.66, N 3.43; found: C 44.27, H 7.75, N 3.41.

**4-Methoxy-1-(trimethylstannanyl)butyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12e)**: Compound **11e-H** (600 mg, 2.31 mmol) afforded **12e** (630 mg, 65%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.46$ (m, 1H), 3.67 (s, 2H), 3.36 (t, $J = 6.4$ Hz, 2H), 3.28 (s, 3H), 1.86 (m, 2H), 1.62 (m, 2H), 1.49 and 1.47 (2s, 6H), 1.35 and 1.31 (2s, 6H), 0.05 ppm (s, $J(^{117}Sn,^1H) = 51.3$, $J(^{119}Sn,^1H) = 53.5$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 153.2/152.5$, 95.6/94.6, 76.2/76.0, 72.3, 71.5 ($J(^{117}Sn,^{13}C) = 426.9$, $J(^{119}Sn,^{13}C) = 446.9$ Hz), 60.3/59.4, 58.4, 30.3, 28.0 ($J(^{117,119}Sn,^{13}C) = 36.2$ Hz), 26.5/26.4, 25.3, 24.1/24.0, −9.3 ppm ($J(^{117}Sn,^{13}C) = 317.1$, $J(^{119}Sn,^{13}C) = 331.9$ Hz); IR (CsI): $\tilde{\nu} = 1679\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{33}NO_4Sn$ (422.15): C 45.52, H 7.88, N 3.32.; found: C 45.82, H 8.03, N 3.21.

**3-(Methoxymethoxy)-1-(trimethylstannanyl)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12f)**: Compound **11f-H** (309 mg, 1.12 mmol) afforded **12f** (450 mg, 92%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.62$ (m, 1H), 4.61 (s, 2H), 3.72 (s, 2H), 3.61 (q, $J = 6.1$ Hz, 2H), 3.35 (s, 3H), 2.15 (m, 2H), 1.54 and 1.52 (2s, 6H), 1.40 and 1.36 (2s, 6H), 0.11 ppm (s, $J(^{117}Sn,^1H) = 51.7$, $J(^{119}Sn,^1H) = 53.6$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 153.0/152.3$, 96.2, 95.5/94.4, 76.1/75.9, 68.1 ($J(^{117}Sn,^{13}C) = 427.6$, $J(^{119}Sn,^{13}C) = 445.7$ Hz), 65.3 ($J(^{117,119}Sn,^{13}C) = 41.8$ Hz), 60.3/59.3, 54.9, 33.5, 26.4/26.3, 25.1/25.0, 24.0/23.9, −9.2 ppm ($J(^{117}Sn,^{13}C) = 321.7$, $J(^{119}Sn,^{13}C) = 336.2$ Hz); IR (CsI): $\tilde{\nu} = 1678\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{33}NO_5Sn$ (438.15): C 43.86, H 7.59, N 3.20; found: C 44.24, H 7.68, N 3.37.

**3-(Triisopropylsilyloxy)-1-(trimethylstannanyl)-propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12g)**: Compound **11g-H** (437 mg, 1.13 mmol) afforded **12g** (547 mg, 88%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.58$ (m, 1H), 3.74 (m, 2H), 3.68 (s, 2H), 2.10 (m, 2H), 1.50 and 1.48 (2s, 6H), 1.36 and 1.32 (2s, 6H), 1.03 and 1.01 (2s, 21H), 0.07 ppm (s, $J(^{117,119}Sn,^1H) = 52.5$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 153.2/152.5$, 95.7/94.5, 76.2/76.0, 68.0 ($J(^{117}Sn,^{13}C) = 425.9$, $J(^{119}Sn,^{13}C) = 445.7$ Hz), 61.6 ($J(^{117,119}Sn,^{13}C) = 51.2$ Hz), 60.4/59.4, 37.0, 26.4, 25.3/25.2, 24.1/24.0, 17.9, 11.9 ($J(^{117}Sn,^{13}C) = 59.1$ Hz), −9.3 ppm ($J(^{117}Sn,^{13}C) = 319.2$, $J(^{119}Sn,^{13}C) = 333.7$ Hz); IR (CsI): $\tilde{\nu} = 1679\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{23}H_{49}NO_4SiSn$ (550.45): C 50.19, H 8.97, N 2.54; found: C 50.35, H 9.18, N 2.63.

**3-*tert*-Butoxy-1-(trimethylstannanyl)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12h)**: Compound **11h-H** (1.35 g, 4.70 mmol) afforded **12h** (1.95 g, 92%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.64$ (m, 1H), 3.72 (s, 2H), 3.44 (m, 2H), 2.07 (m, 2H), 1.54 and 1.52 (2s, 6H), 1.40 and 1.36 (2s, 6H), 1.18 (s, 9H), 0.10 ppm (s, $J(^{117}Sn,^1H) = 51.9$, $J(^{119}Sn,^1H) = 53.5$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 153.0/152.4$, 95.5/94.4, 76.1/75.9, 72.5, 68.5 ($J(^{117}Sn,^{13}C) = 429.1$, $J(^{119}Sn,^{13}C) = 450.5$ Hz), 60.3/59.8, 59.5, 59.3, 34.6, 27.3, 26.4/26.3, 25.2/25.1, 24.0/23.9, −9.2 ppm ($J(^{117}Sn,^{13}C) = 319.0$, $J(^{119}Sn,^{13}C) = 333.8$ Hz); IR (CsI): $\tilde{\nu} = 1679\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{18}H_{37}NO_4Sn$ (450.21): C 48.02, H 8.28, N 3.11; found: C 47.65, H 8.54, N 2.84.

**3-[(Methylthio)methoxy]-1-(trimethylstannanyl)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12i)**: Following the general procedure with 100 mol% of *s*BuLi, **11i-H** (335 mg, 1.15 mmol) afforded **12i** (410 mg, 78%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.62$ (m, 1H), 4.61 (s, 2H), 3.71 (s, 2H), 3.60 (m, 2H), 2.14 (m, 2H), 2.13 (s, 3H), 1.53 (br s, 6H), 1.39 and 1.36 (2s, 6H), 0.10 ppm (s, $J(^{117}Sn,^1H) = 51.5$, $J(^{119}Sn,^1H) = 53.8$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 153.2/152.5$, 95.7/94.6, 76.3/76.1, 75.3, 68.2 ($J(^{117}Sn,^{13}C) = 420.0$, $J(^{119}Sn,^{13}C) = 442.4$ Hz), 65.9 ($J(^{117,119}Sn,^{13}C) = 42.1$ Hz), 60.5/59.5, 33.5, 26.5/26.4, 25.3/25.2, 24.2/24.1, 13.9, −9.1 ppm ($J(^{117}Sn,^{13}C) = 320.5$, $J(^{119}Sn,^{13}C) = 335.6$ Hz); IR (CsI): $\tilde{\nu} = 1698\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{33}NO_4SSn$ (454.21): C 42.31, H 7.32, N 3.08, S 7.06; found: C 42.61, H 7.53, N 3.41, S 7.08.

**3-(Methylthio)-1-(trimethylstannanyl)propyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12j)**: Compound **11j-H** (753 mg, 2.88 mmol) afforded **12j** (1.13 g, 92%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 4.56$ (m, 1H), 3.72 (s, 2H), 2.57 (m, 2H), 2.12 (s, 3H), 2.11 (m, 2H), 1.53 and 1.52 (2s, 6H), 1.40 and 1.36 (2s, 6H), 0.12 ppm (s, $J(^{117}Sn,^1H) = 51.5$, $J(^{119}Sn,^1H) = 53.7$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 153.0/152.3$, 95.6/94.4, 76.1/75.9, 70.3 ($J(^{117}Sn,^{13}C) = 414.7$, $J(^{119}Sn,^{13}C) = 433.8$ Hz), 60.3/59.3, 33.4, 32.4 ($J(^{117,119}Sn,^{13}C) = 46.7$ Hz), 26.5/26.4, 25.3, 25.2, 25.1, 24.0/23.9, 15.4, −9.2 ppm ($J(^{117}Sn,^{13}C) = 320.8$, $J(^{119}Sn,^{13}C) = 335.3$ Hz); IR (CsI): $\tilde{\nu} = 1679\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{15}H_{31}NO_3SSn$ (424.19): C 42.47, H 7.37, N 3.30, S 7.56; found: C 42.78, H 7.09, N 3.27, S 7.43.

**2-(1,3-Dioxolan-4-yl)-1-(trimethylstannanyl)ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12k)**: Following the general procedure without TMEDA, **11k-H** (380 mg, 1.39 mmol) afforded **12k** (390 mg, 64%) as a colorless oil. $^1H$ NMR (250 MHz, $CDCl_3$, rotamers): $\delta = 5.03$ (s, 1H), 4.86 (s, 1H), 4.59 (dd, $J = 5.2$, 9.0 Hz, 1H), 4.14 (m, 1H), 4.01 (m, 1H), 3.72 (s, 2H), 3.54 (m, 1H), 2.23 (m, 1H), 2.00 (m, 1H), 1.54 and 1.52 (2s, 6H), 1.40 and 1.36 (2s, 6H), 0.12 ppm (s, $J(^{117}Sn,^1H) = 51.8$, $J(^{119}Sn,^1H) = 54.0$ Hz, 9H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta = 152.9/152.2$, 95.5/94.3, 94.6, 76.0/75.7, 74.1 ($J(^{117,119}Sn,^{13}C) = 38.5$ Hz), 69.1, 68.0 ($J(^{117}Sn,^{13}C) = 427.0$, $J(^{119}Sn,^{13}C) = 436.1$ Hz)/67.9 ($J(^{117}Sn,^{13}C) = 421.5$, $J(^{119}Sn,^{13}C) = 430.2$ Hz), 60.3/59.2, 36.7, 26.3/26.2, 25.0/24.9, 23.9/23.8, −9.1 ppm ($J(^{117}Sn,^{13}C) = 324.5$, $J(^{119}Sn,^{13}C) = 339.4$ Hz); IR (CsI): $\tilde{\nu} = 1679\ cm^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{31}NO_5Sn$ (436.14): C 44.06, H 7.16, N 3.21; found: C 44.10, H 7.11, N 3.12.

**2-(2,2-Dimethyl-1,3-dioxan-4-yl)-1-(trimethylstannanyl)ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (12m)**: Following the general proce-

dure without TMEDA, **11m-H** (403 mg, 1.28 mmol) afforded **12m** (470 mg, 77%) as a colorless oil. $^1$H NMR (250 MHz, $CDCl_3$, rotamers): $\delta$ = 4.52 (m, 1H), 3.98–3.65 (m, 3H), 3.60 (s, 2H), 1.90 (m, 2H), 1.49 (m, 2H), 1.41 (s, 6H), 1.31, 1.29 and 1.25 (3s, 12H), −0.01 and −0.02 ppm (2s, $J(^{117,119}Sn,^1H)$ = 52.7 Hz, 9H); $^{13}$C NMR (62.9 MHz, $CDCl_3$, rotamers): $\delta$ = 152.9/152.2, 98.1/98.0, 95.5/94.3, 76.0/75.8, 67.5 ($J(^{117}Sn,^{13}C)$ = 432.8, $J(^{119}Sn,^{13}C)$ = 449.0 Hz)/67.0 ($J(^{117}Sn,^{13}C)$ = 427.7, $J(^{119}Sn,^{13}C)$ = 444.6 Hz), 66.6/66.4, 60.2/59.2, 59.6, 40.5/40.2, 31.5/30.6, 29.7/29.6, 26.3/26.2, 25.1/25.0, 24.0/23.9, 18.9/18.8, −8.9 ($J(^{117}Sn,^{13}C)$ = 321.5, $J(^{119}Sn,^{13}C)$ = 336.9 Hz), −9.1 ppm ($J(^{117}Sn,^{13}C)$ = 319.4, $J(^{119}Sn,^{13}C)$ = 338.4 Hz); IR (CsI): $\tilde{\nu}$ = 1679 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{19}H_{37}NO_5Sn$ (478.22): C 47.72, H 7.80, N 2.93; found: C 47.36, H 8.02, N 2.91.

**3-Methylbenzyl *N,N*-diisopropylcarbamate (13b-H)**: A solution of diisopropylcarbamyl chloride (600 mg, 3.67 mmol) in pyridine (360 μL, 4.40 mmol) was treated with 3-methylbenzyl alcohol (420 μL, 3.50 mmol) and stirred at 105 °C for 16 h in a sealed tube. The reaction mixture was cooled and then partitioned between 2 M HCl (10 mL) and $Et_2O$ (3× 10 mL), and the combined organic phase was washed with satd aq $NaHCO_3$ (15 mL) and brine (15 mL), dried with $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by column chromatography (silica gel, EtOAc/hexane 1:10) to give **13b-H** (663 mg, 76%) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$, 330 K): $\delta$ = 7.27–7.08 (m, 4H), 5.15 (s, 2H), 3.98 (sept, $J$ = 6.7 Hz, 2H), 2.38 (s, 3H), 1.26 ppm (d, $J$ = 6.7 Hz, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, 330 K, rotamers): $\delta$ = 154.8, 137.3, 136.8, 128.1, 128.0, 127.8, 124.5, 65.9, 45.6, 20.8, 20.6 ppm; IR (CsI): $\tilde{\nu}$ = 1695 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{15}H_{23}NO_2$ (249.36): C 72.25, H 9.30, N 5.62; found: C 71.89, H 9.46, N 5.57.

**3-Methoxybenzyl *N,N*-diisopropylcarbamate (13c-H)**: Same procedure as for **13b-H** but starting with 3-methoxybenzyl alcohol (440 μL, 3.50 mmol) afforded **13c-H** (698 mg, 75%) as a colorless oil after column chromatography (silica gel, EtOAc/hexane 1:8). $^1$H NMR (300 MHz, $CDCl_3$, 330 K): $\delta$ = 7.24 (t, $J$ = 7.6 Hz, 1H), 6.94 (m, 2H), 6.83 (m, 1H), 5.12 (s, 2H), 3.94 (sept, $J$ = 6.7 Hz, 2H), 3.79 (s, 3H), 1.23 ppm (d, $J$ = 6.7 Hz, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, 330 K, rotamers): $\delta$ = 159.5, 155.3, 138.6, 129.3, 119.9, 113.2, 113.0, 66.2, 55.0, 45.9, 20.9 ppm; IR (CsI): $\tilde{\nu}$ = 1693 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{15}H_{23}NO_3$ (265.35): C 67.90, H 8.74, N 5.28; found: C 68.13, H 8.61, N 5.17.

**4-Methoxybenzyl *N,N*-diisopropylcarbamate (13d-H)**: Same procedure as for **13b-H** but starting with 4-methoxybenzyl alcohol (550 mg, 3.98 mmol) afforded **13d-H** (845 mg, 80%) as a colorless oil after column chromatography (silica gel, EtOAc/hexane 1:8). $^1$H NMR (300 MHz, $CDCl_3$, 330 K): $\delta$ = 7.25 (d, $J$ = 8.6 Hz, 2H), 6.84 (d, $J$ = 8.6 Hz, 2H), 5.03 (s, 2H), 3.88 (sept, $J$ = 6.6 Hz, 2H), 3.76 (s, 3H), 1.18 ppm (d, $J$ = 6.6 Hz, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, 330 K, rotamers): $\delta$ = 159.1, 155.1, 129.2, 129.1, 113.6, 65.9, 54.9, 45.8, 20.9 ppm; IR (CsI): $\tilde{\nu}$ = 1691 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{15}H_{23}NO_3$ (265.35): C 67.90, H 8.74, N 5.28; found: C 68.09, H 8.94, N 5.28.

**1-Phenylethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (13e-H)**: A suspension of NaH (60% in mineral oil, 410 mg, 10.3 mmol) in THF (12 mL) was treated with 1-phenyl-ethanol (830 μL, 6.90 mmol), the mixture was stirred at RT for 30 min and 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carbonyl chloride[27] (1.57 g, 8.20 mmol) in THF (2 mL) was added. The mixture was stirred at RT for 5 d and then poured over 2 M HCl solution (15 mL) and extracted with EtOAc (3×20 mL). The combined organic phase was washed with satd aq $NaHCO_3$ (30 mL) and brine (30 mL), dried with $Na_2SO_4$, filtered and concentrated. The resulting residue was purified by column chromatography (silica gel, EtOAc/hexane 1:8) to give **13e-H** as a colorless oil (1.85 g, 97%). $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta$ = 7.25 (m, 5H), 5.80 (q, $J$ = 6.6 Hz, 1H), 3.68 (s, 2H), 1.57, 1.54, 1.53, 1.51, 1.46, 1.41, 1.40, 1.32 ppm (8s, 15H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$ = 152.0/151.2, 142.2/142.1, 128.4, 127.5, 125.9, 95.8/94.7, 76.3/76.0, 72.7, 60.6/59.6, 26.7/26.6, 25.5/25.4, 25.3/25.2, 24.1, 22.5/22.4 ppm; IR (CsI): $\tilde{\nu}$ = 1698 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{16}H_{23}NO_3$ (277.37): C 69.29, H 8.36, N 5.05; Found: C 69.48, H 8.60, N 5.11.

**(3-Methylphenyl)-(trimethylstannanyl)methyl *N,N*-diisopropylcarbamate (14b)**: BuLi (690 μL, 1.10 mmol, 1.6 M in hexane) was added to a pre-cooled (−78 °C) solution of **13b-H** (250 mg, 1.00 mmol) and TMEDA (165 μL, 1.10 mmol) in $Et_2O$ (4.6 mL). After stirring for 30 min, $Me_3SnCl$ (1.1 mL, 1.1 mmol, 1.0 M in THF) was added to the reaction mixture. The resulting solution was stirred at −78 °C for 30 min and then partitioned between $Et_2O$ (10 mL) and pH 7.0 phosphate buffer (10 mL). The aqueous phase was extracted with $Et_2O$ (10 mL) and the combined organic phase was washed with brine (10 mL), dried with $Na_2SO_4$, filtered and concentrated. The residue was purified by column chromatography (grade III neutral $Al_2O_3$, hexane to EtOAc/hexane 1:50). Recrystallization from EtOH gave **14b** as a white solid (392 mg, 95%). M.p. 44–47 °C; $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta$ = 7.17 (t, $J$ = 7.7 Hz, 1H), 6.91 (m, 3H), 5.58 (s, $J(^{117,119}Sn,^1H)$ = 25.0 Hz, 1H), 4.24–3.72 (br m, 2H), 2.32 (s, 3H), 1.24 (d, $J$ = 6.1 Hz, 12H), 0.02 ppm (s, $J(^{117}Sn,^1H)$ = 51.5, $J(^{119}Sn,^1H)$ = 53.6 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$ = 155.9 ($J(^{117,119}Sn,^{13}C)$ = 14.1 Hz), 143.0 ($J(^{117,119}Sn,^{13}C)$ = 14.1 Hz), 137.7 ($J(^{117,119}Sn,^{13}C)$ = 9.9 Hz), 128.2 ($J(^{117,119}Sn,^{13}C)$ = 9.9 Hz), 125.6 ($J(^{117,119}Sn,^{13}C)$ = 12.5 Hz), 124.2 ($J(^{117,119}Sn,^{13}C)$ = 18.8 Hz), 120.7 ($J(^{117,119}Sn,^{13}C)$ = 18.3 Hz), 74.0 ($J(^{117}Sn,^{13}C)$ = 384.6, $J(^{119}Sn,^{13}C)$ = 401.8 Hz), 46.3/45.3, 21.5, 21.4/20.6, −9.0 ppm ($J(^{117}Sn,^{13}C)$ = 320.3, $J(^{119}Sn,^{13}C)$ = 335.5 Hz); IR (CsI): $\tilde{\nu}$ = 1675 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{18}H_{31}NO_2Sn$ (412.16): C 52.45, H 7.58, N 3.40; found: C 52.55, H 7.63, N 3.36.

**(3-Methoxyphenyl)-(trimethylstannanyl)methyl *N,N*-diisopropylcarbamate (14c)**: Same procedure as for **14b** but starting with **13c-H** (265 mg, 1.00 mmol) afforded **14c** (325 mg, 76%) as a white solid after purification by column chromatography (grade III neutral $Al_2O_3$, hexane to EtOAc/hexane 1:20) and recrystallization from EtOH. M.p. 52–53 °C; $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta$ = 7.20 (t, $J$ = 8.2 Hz, 1H), 6.66 (m, 3H), 5.60 (s, $J(^{117,119}Sn,^1H)$ = 25.3 Hz, 1H), 4.21–3.70 (br m, 2H), 3.78 (s, 3H), 1.26 (br s, 12H), 0.03 ppm (s, $J(^{117}Sn,^1H)$ = 51.5, $J(^{119}Sn,^1H)$ = 53.6 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$ = 159.5 ($J(^{117,119}Sn,^{13}C)$ = 10.5 Hz), 155.6 ($J(^{117,119}Sn,^{13}C)$ = 14.6 Hz), 144.8 ($J(^{117,119}Sn,^{13}C)$ = 13.6 Hz), 129.2 ($J(^{117,119}Sn,^{13}C)$ = 9.9 Hz), 115.8 ($J(^{117,119}Sn,^{13}C)$ = 18.3 Hz), 110.0 ($J(^{117,119}Sn,^{13}C)$ = 12.5 Hz), 108.9 ($J(^{117,119}Sn,^{13}C)$ = 18.3 Hz), 73.8 ($J(^{117}Sn,^{13}C)$ = 378.3, $J(^{119}Sn,^{13}C)$ = 396.1 Hz), 54.8, 46.2/45.3, 21.3/20.5, −9.0 ppm ($J(^{117}Sn,^{13}C)$ = 321.9, $J(^{119}Sn,^{13}C)$ = 337.1 Hz); IR (CsI): $\tilde{\nu}$ = 1791 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{18}H_{31}NO_3Sn$ (428.16): C 50.49, H 7.30, N 3.27; found: C 50.70, H 7.20, N 3.06.

**(4-Methoxyphenyl)-(trimethylstannanyl)methyl *N,N*-diisopropylcarbamate (14d)**: Same procedure as for **14b** but starting with **13d-H** (265 mg, 1.00 mmol) afforded **14d** (381 mg, 89%) as a white solid after purification by column chromatography (grade III neutral $Al_2O_3$, hexane to EtOAc/hexane 1:20) and recrystallization from EtOH. M.p. 56–58 °C; $^1$H NMR (300 MHz, $CDCl_3$, 330 K, rotamers): $\delta$ = 7.05 (d, $J$ = 8.8 Hz, 2H), 6.84 (d, $J$ = 8.8 Hz, 2H), 5.55 (s, $J(^{117,119}Sn,^1H)$ = 22.0 Hz, 1H), 3.97 (sept, $J$ = 6.6 Hz, 2H), 3.80 (s, 3H), 1.28 and 1.26 (2 d, $J$ = 6.6 Hz, 12H), 0.06 ppm (s, $J(^{117}Sn,^1H)$ = 51.3, $J(^{119}Sn,^1H)$ = 53.5 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, 330 K, rotamers): $\delta$ = 157.3, 155.9, 135.4/135.3, 125.35 ($J(^{117,119}Sn,^{13}C)$ = 20.4 Hz)/125.32 ($J(^{117,119}Sn,^{13}C)$ = 20.1 Hz), 113.93/113.90 ($J(^{117,119}Sn,^{13}C)$ = 8.9 Hz), 73.9/73.8 ($J(^{117}Sn,^{13}C)$ = 398.9, $J(^{119}Sn,^{13}C)$ = 420.7 Hz), 55.31/55.28, 46.1, 21.2/21.1, −8.7 ppm ($J(^{117}Sn,^{13}C)$ = 318.7, $J(^{119}Sn,^{13}C)$ = 339.6 Hz); IR (CsI): $\tilde{\nu}$ = 1674 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{18}H_{31}NO_3Sn$ (428.16): C 50.49, H 7.30, N 3.27; found: C 50.42, H 7.61, N 3.27.

**1-Phenyl-1-(trimethylstannanyl)ethyl 2,2,4,4-tetramethyl-1,3-oxazolidine-3-carboxylate (14e)**: Following the general procedure of stannylation but stirring only for 1 h after addition of *s*BuLi, **13e-H** (579 mg, 2.09 mmol) gave **14e** (816 mg, 89%) as a white solid after recrystallization from MeOH. M.p. 89–90 °C; $^1$H NMR (300 MHz, $CDCl_3$, rotamers): $\delta$ = 7.31 (t, $J$ = 7.6 Hz, 2H), 7.10 (m, 3H), 3.77 (s, 2H), 1.84 and 1.83 (2s, $J(^{117,119}Sn,^1H)$ = 49.9 Hz, 3H), 1.64, 1.61, 1.58, and 1.56 (4s, 6H), 1.49, 1.47, 1.45, and 1.39 (4s, 6H), −0.02 ppm (s, $J(^{117,119}Sn,^1H)$ = 51.5 Hz, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$, rotamers): $\delta$ = 153.5/152.8, 147.8, 128.1 ($J(^{117,119}Sn,^{13}C)$ = 8.8 Hz), 124.9 ($J(^{117,119}Sn,^{13}C)$ = 9.4 Hz), 123.3/123.2, 95.8/94.9, 79.8, 76.4/76.1, 60.7/59.9, 26.8/26.7, 25.9/25.6, 25.2, 25.1, 24.2, −6.9 ppm ($J(^{117}Sn,^{13}C)$ = 329.2, $J(^{119}Sn,^{13}C)$ = 346.6 Hz); IR (CsI): $\tilde{\nu}$ = 1666 cm$^{-1}$ (C=O); elemental analysis calcd (%) for $C_{19}H_{31}NO_3Sn$ (440.17): C 51.85, H 7.10, N 3.18; found: C 51.63, H 7.13, N 3.16.

**NMR Spectroscopy**

**Preparation of the NMR samples**: [$D_8$]THF was dried from $CaH_2$ by sonication (30 min) and then centrifuged under Ar atmosphere. 100 mol% of a solution of MeLi in $Et_2O$ (1.5 M) or $Bu^6Li$ in pentane was added to a dry NMR tube (with J Young valve) and the solvent was evaporated under vacuum at 0 °C, then dry [$D_8$]THF (250 μL) were added and cooled to −78 °C. A solution of 0.1 mmol of the corresponding organostannane in dry [$D_8$]THF (250 μL) was added and the NMR tube was sealed under a high pressure of Ar.

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