

## Reactive Organometallics from Organotellurides: Application in Organic Synthesis

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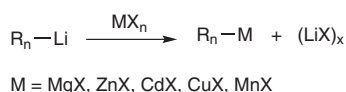
Neste artigo é revisada a preparação de organometálicos reativos a partir de teluretos orgânicos. É comentado o uso dos organometálicos preparados dessa maneira na síntese de substâncias bioativas.

In this paper the preparation of reactive organometallics starting from organotellurides is reviewed. The application of the reactive organometallics prepared in this way in the synthesis of bioactive compounds is commented.

**Keywords:** organotellurides, tellurides, organometallics, natural products

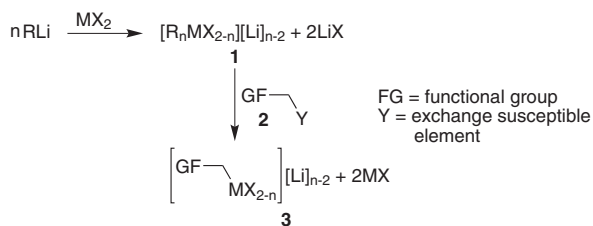
### 1. Introduction

Organometallic reagents occupy a central position in organic synthetic procedures and undoubtedly they are the most extensively used carbon-carbon and carbon-heteroatom bond forming promoters. Among them, organolithiums are the most versatile because of their unique reactivity as bases or nucleophiles, and also because almost all other organometallics can be accessed from them by transmetalation reactions (Scheme 1).



**Scheme 1.** Transmetalation of organolithium compounds to other reactive organometallics.

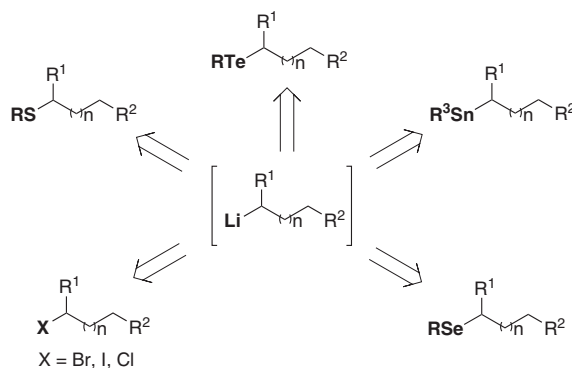
However, the high reactivity of organolithiums is frequently a disadvantage, leading to the use of time and money costing protection-deprotection chemistry when they are used as reactants or source of other organometallics. As an alternative to the use of organolithiums, milder non functionalized organometallics **1** can be generated from a commercially available organolithium and an inorganic salt, and then reacted with **2**, a precursor of the structurally more complex organometallic **3**, which is more selective than the corresponding organolithium (Scheme 2).



**Scheme 2.** Functionalized organometallics by element / metal exchange.

Only a few classes of organoelemental compounds (Figure 1) fulfill the necessary requirements to be replaced by a metal. Among these classes of compounds are the organotellurides, which have been efficiently transformed into a number of organometallics by tellurium / metal exchange.

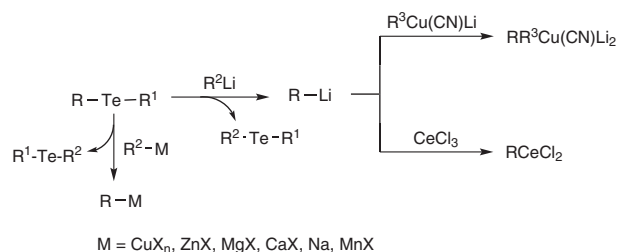
This methodology focused mainly the Te / Li exchange, because it is fast and clean, leading to useful



**Figure 1.** Sources of organolithium compounds.

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organolithiums and other organometallics derived from them by transmetalation or even to other organoelemental compounds not easily obtained by other methods, as for example *Z*-vinyl stannanes. However, the direct Te / metal exchange is also well documented for Te/Zn, Te/Cu, Te/Mg and Te/Ca exchanges. This easy access to a range of organometallics from organotellurides allowed the use of these organochalcogenides in the synthesis of biologically active compounds. The above comments are summarized in Scheme 3.



**Scheme 3.** Reactive organometallics by Te / metal exchange.

Considering Scheme 3, we can conclude that an organometallic ( $R^2Li$  or  $R^2M$ ) attacks the tellurium atom of a diorganotelluride ( $R-Te-R^1$ ) generating another organometallic ( $R-M$ ) if the latter is more stable than the former one.

Having in mind the many stereoselective methods to prepare organotellurides<sup>1-4</sup> and the transformations shown in Scheme 3, we can conclude that organotellurides constitute one of the best options to access structurally complex reactive organometallics by element/metal exchange reactions using easily available organometallics such as commercially available *n*-butyllithium.

Notwithstanding the intensive activity in this area in the last two decades, the use of organotellurides as a

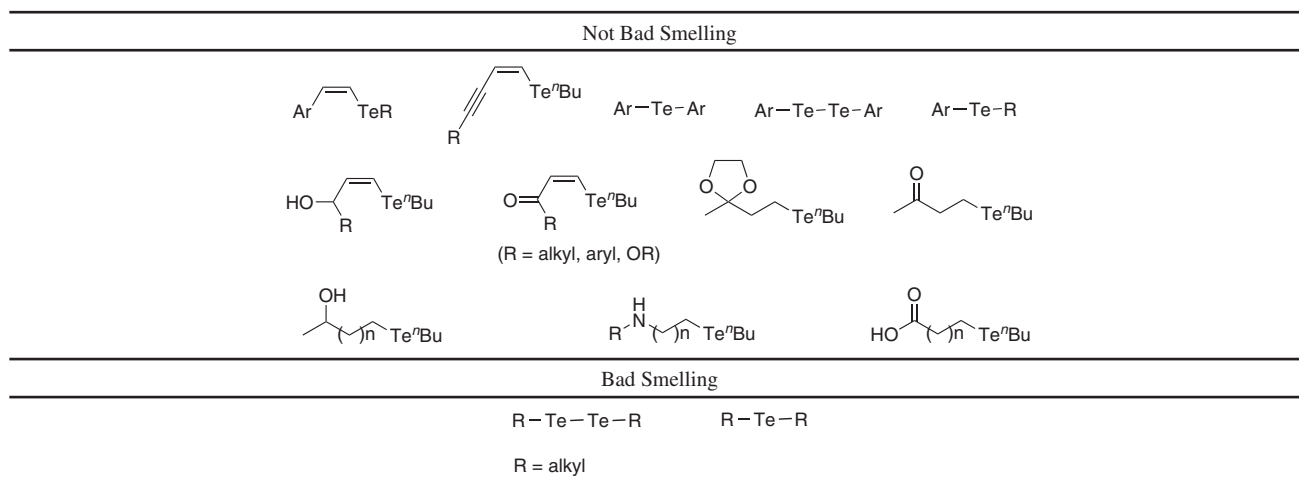
source of reactive organometallics has been considered with suspicion by the synthetic organic chemists. We can attribute this attitude to negative comments made in the early literature, when the organic chemistry of tellurium compounds was still in its infancy and little was known about it. More recently, the organic chemists dedicated to the tellurium chemistry did not contribute to destroy the myths about the tellurium compounds. Some colleagues use to simply repeat what is found in the older literature about the instability, bad smell and toxicity of the organotellurides, with no comments on their own experience and on the recent findings by other colleagues on these subjects.

The experience of our group gained in the course of the last thirty years show that these negative comments can not be considered a rule. Most organic compounds of tellurium are not bad smelling at all and some of them even present pleasant smell. In Figure 2, are shown some classes of organotellurides with comments about their smell.

By “*not bad smelling*” we mean that the compound presents a smell not more unpleasant than the common reagents used in a synthetic organic chemistry laboratory, like benzophenone or any other reagent that need not to be handled in a hood due to its smell. By “*bad smelling*” we mean compounds which present a smell that can be compared, for example, to ethanethiol or dimethylsulfide.

In some cases, after some time a “*not bad smelling*” compound can begin to present a very unpleasant smell. This fact probably is due to the decomposition of the parent compound, leading to bad smelling dialkyltellurides or dialkylditellurides.

To our present knowledge, only the low molecular weight dialkyltellurides or dialkylditellurides correspond to the comments made in the old literature about the bad smell of organotellurides. Another concern about organotellurides refers to their stability to the air or light.



**Figure 2.** The relationship between the structure of organotellurides and their smell.

Many papers comment on the instability of organotellurides when in presence of air or light. Our experience show that organotellurides when in solution and in the presence of air slowly deposit a white amorphous solid. However, by evaporating the solvent, no perceptible decomposition occurs and the organotellurides can be safely handled in the presence of air or light. A recent paper<sup>5</sup> reports that an organotelluride dissolved in hexane was refluxed for 3 h in the presence of air in the dark with no perceptible decomposition. On the other hand, organotellurides in hexane under an oxygen atmosphere at room temperature under sunlight irradiation were rapidly transformed into the corresponding aldehydes. These experiments suggest that organotellurides are not oxygen sensitive provided that light irradiation is absent. These results are highly interesting and merit to be more intensely explored to determine the optimal working conditions when organotellurides are handled.

The last controversial concern involving the organic derivatives of tellurium is their toxicity. Some toxicological studies were published<sup>6</sup> and some biological activities of organic and inorganic compounds of tellurium were reported.<sup>7</sup> However, the data are still very scarce and their biological role is not clearly established. As far as we know, no report on the poisoning by organotellurides do exist in the literature.

The aim of this manuscript is to briefly review the most important methods to introduce tellurium into organic substrates and to show the transformation of the resulting organotellurides into reactive organometallics. The application of the reactive organometallics derived from organotellurides in the synthesis of bioactive molecules will be commented in the final section.

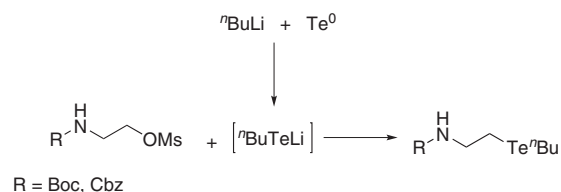
## 2. Introduction of Tellurium into Organic Substrates

There are many synthetic transformations mediated by tellurium reagents. These methodologies have been exhaustively reviewed several times in the last three decades.<sup>1-4,8</sup> In this paper, only those with a great synthetic potential will be briefly commented. Most of them use elemental tellurium as the starting material, generating the reactive tellurium species *in situ*, avoiding in this way the manipulation of bad smelling low molecular weight dialkylditellurides.

### 2.1. Nucleophilic substitution with metal organotellurolates

This is a long known and well established transformation leading to organotellurides.<sup>3,8</sup> The most

practical and synthetically useful method to generate a metal organotellurolate is the reaction of a commercially available organolithium with elemental tellurium. The *in situ* generated lithium organotellurolates react with electrophiles to give the corresponding organotellurides. This process corresponds to an inversion of polarity of the electrophile, since, as we will discuss later, the organotellurides are precursors of organolithiums. In Scheme 4 is given a recent example of this transformation.<sup>9</sup>

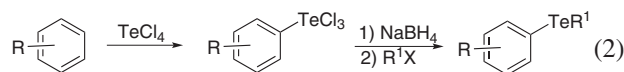
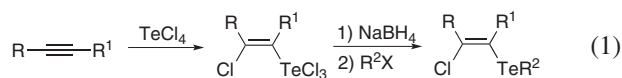


Scheme 4.

Alkali tellurides and alkali ditellurides can be generated by a number of methods,<sup>1-3</sup> and react *in situ* with alkylating agents to give the corresponding dialkyltellurides and dialkylditellurides.<sup>1-3</sup>

### 2.2. Interaction of tellurium tetrachloride with alkynes and aromatics

Tellurium tetrachloride reacts with alkynes and aromatics to give respectively precursors of (*Z*)-vinyl tellurides<sup>10</sup> and alkyl-aryl-tellurides as shown in equations 1 and 2.

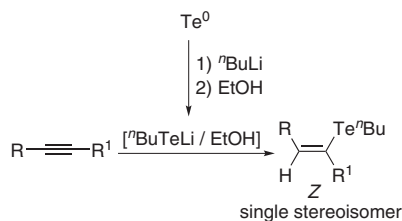


This last transformation (equation 2) was subject of two recent improvements. In one study the electrophilic substitution was performed in a solventless process<sup>11</sup> and in another one the hygroscopic tellurium tetrachloride was prepared and reacted *in situ* with the aromatic compound.<sup>12</sup>

### 2.3. Hydrotelluration of alkynes and alkenes

The hydrotelluration of alkynes is one of the most studied reactions in the context of the organotellurium chemistry and has been constantly reviewed.<sup>1-4,13</sup> The method of choice to perform this transformation involves the *in situ* generation of a hydrotellurating system from elemental tellurium and *n*-butyllithium followed by a proton source, and its reaction with alkynes.<sup>14</sup> This method replaces

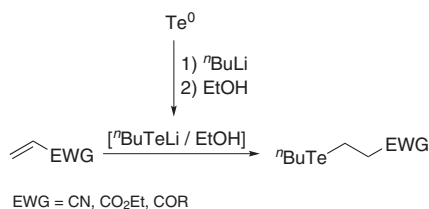
the more traditional method, which uses the bad smelling dibutylditelluride as the starting material. In Scheme 5 is shown the general procedure for this transformation.



**Scheme 5.** Hydrotelluration of alkynes.

The most important feature of this methodology is that it occurs in an *anti* fashion, leading to the *Z* olefin exclusively. All other hydrometallation reactions known to date occur in a *syn* fashion to give the *E* olefine.<sup>15</sup> One of the most synthetically useful hydrometallation reaction is the hydrostannylation, which usually gives the *E* stanane, but very often present stereo- and regiochemical problems, giving mixture of the possible regio- and stereoisomers.<sup>16</sup> The hydrotelluration, on the contrary is 100% *Z* stereoselective and normally is 100% also regioselective.<sup>13</sup>

The hydrotelluration methodology has been successfully applied to activated olefins, constituting a useful method to prepare functionalized alkyltellurides, as illustrated in Scheme 6.



**Scheme 6.** Hydrotelluration of alkenes.

In summary, the hydrotelluration of alkenes and alkynes is a well established and general method to introduce tellurium into organic substrates. The products of these

transformation present interesting synthetic applications as will be commented later.

#### 2.4. Vinylic substitution using metal organotellurolates

Vinylic acetates, tosylates, triflates and phosphonates react with metal tellurolates to give the corresponding vinylic tellurides of the *Z* configuration irrespective of the configuration of the starting material (Scheme 7).<sup>17</sup>

An addition-elimination mechanism was proposed for this transformation. The strong oxygen-tellurium through space interaction should be responsible for the high stereoselectivity observed.<sup>17</sup>

The methods to introduce tellurium into organic substrates commented above are the most general and synthetically useful, although many others are described in the literature.<sup>1-4,8</sup>

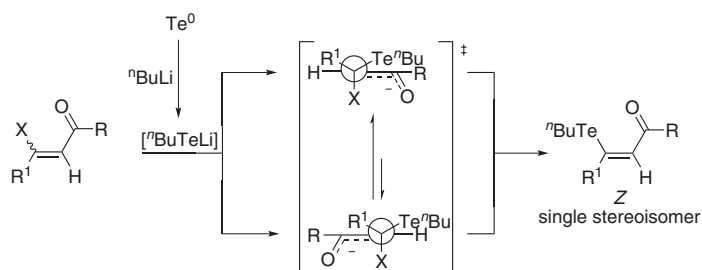
### 3. The Tellurium / Metal Exchange Reaction

#### 3.1. The tellurium / lithium exchange reaction

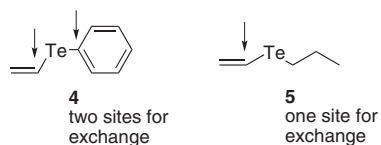
As commented in the introduction, to date the most explored synthetic application of organotellurides is the Te / metal exchange. By far the most employed is the Te / Li exchange. In the following we will briefly comment on this and others Te / metal exchange reactions. The demonstration that the Te / Li exchange is possible was performed in the 1970s and early 1980s.<sup>18-21</sup> Later on the reaction has been intensely studied and improved.

A general requirement for a successful and selective exchange is the existence of differentiated carbon atoms linked to the tellurium atom. One of the carbon atoms linked to the tellurium atom must give rise to a more stable carbanionic center than the other one. This principle is illustrated in Scheme 8.

In the phenyl-vinyl telluride (**4**) there are two sites for exchange, since two sp<sup>2</sup>-hybridized carbanions can be formed on reaction of **4** with *n*-butyllithium. In the case of phenyl-butyl telluride (**5**) there is just one site for exchange,



**Scheme 7.** Vinylic tellurides by an addition-elimination process.



Scheme 8.

since the exchange with the alkyl group linked to tellurium should lead to a  $sp^3$ -hybridized carbanion, which presents stability similar to *n*-butyllithium.

The generalized use of vinylic tellurides as source of vinylolithiums and other vinyl organometallics was only possible with the advent of the aliphatic derivatives of tellurium, which before the 1980s were considered by the chemists as too unstable to be handled. The aryl derivatives were preferred for being more easily handled. Since we developed methods to prepare alkyl derivatives of tellurium, and showed that they are stable enough to be handled without need for special experimental conditions,<sup>22,23</sup> this branch of chemistry experienced a considerable evolution. A large number of compounds was submitted to the Te / Li exchange

reaction and the transformation proved to be of general application.<sup>1-4,24</sup> When vinylic tellurides were used, the retention of geometry was observed in all cases. When dialkyltellurides were submitted to the exchange reaction, depending on the nature of the alkyl groups linked to tellurium, *s*-butyllithium or *t*-butyllithium were required to successfully perform the exchange reaction. In Figure 3 are shown representative tellurides which were transformed into organolithiums on reaction with the appropriate commercial alkylolithiums.

As commented in the introduction, organolithiums can be transformed by transmetalation into several other organometallics of synthetic value. In Figure 4 are shown representative examples of such transformations performed starting from an organotelluride.

*Z*-Vinylic tellurides were transformed in a straightforward way into *Z*-vinylstannanes and *Z*-vinylpinacolboronates by Te / Li exchange reaction, followed by capture of the *Z*-vinylolithium with the appropriate tin<sup>39,40</sup> or boron<sup>40</sup> electrophile. In Figure 5 are given representative examples of the tin and boron compounds prepared in this way.

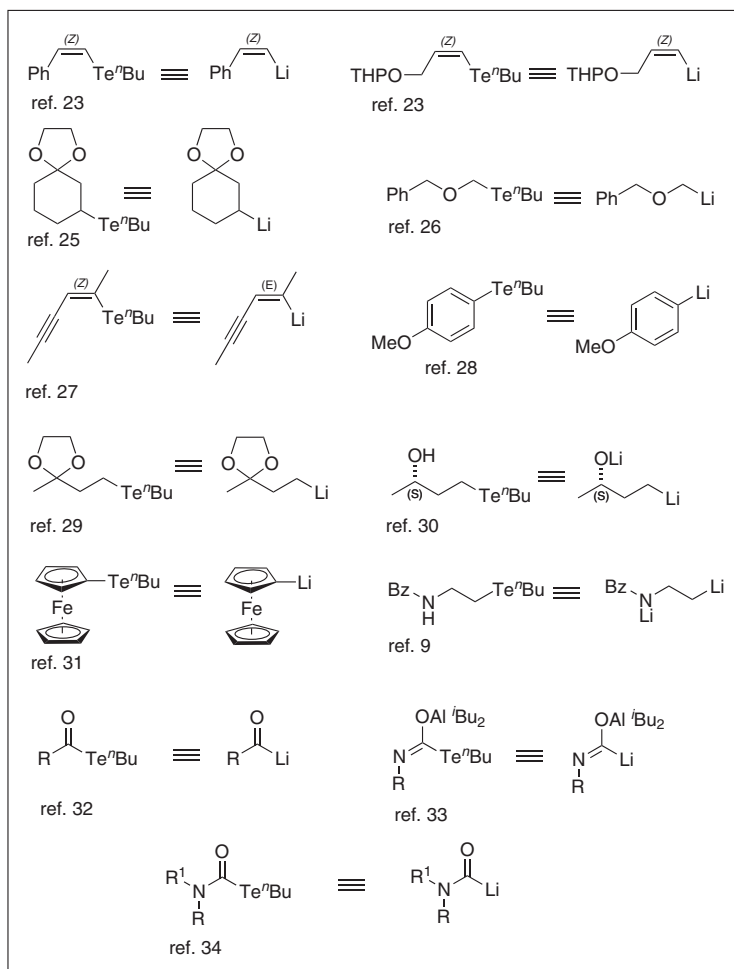
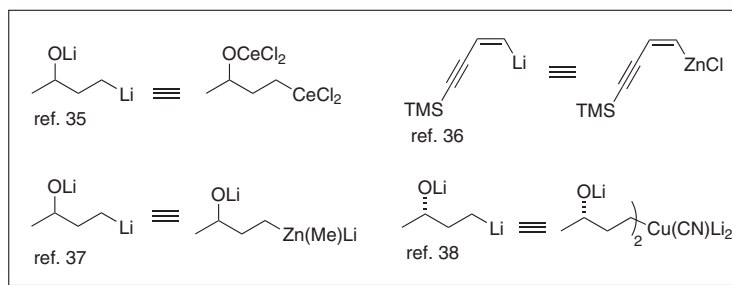
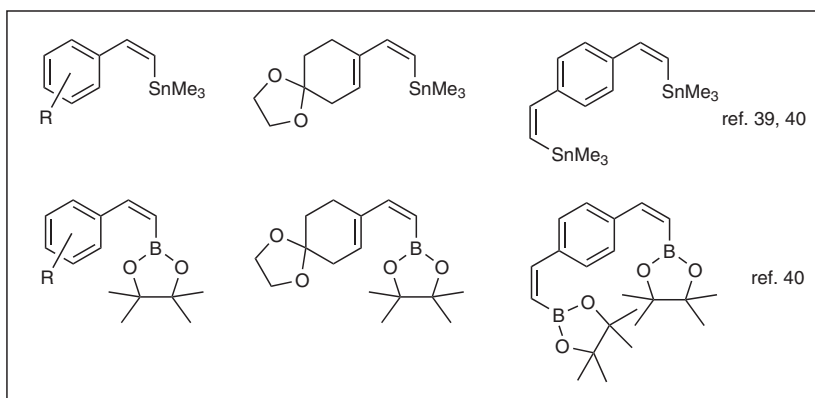


Figure 3. Organolithium compounds by Te / Li exchange reactions.



**Figure 4.** Organometallics by Te / Li exchange followed by transmetalation

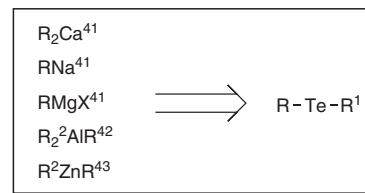


**Figure 5.** Z-Vinylstannanes and Z-vinylpinacolboronates from Z-vinyl tellurides.

### 3.2. Direct transformation of organotellurides into organosodium, calcium, magnesium, aluminum, zinc, copper and manganese compounds

Organotellurides can be transformed into the title organometallics by direct reaction of the telluride with a commercially available or easily prepared organo-derivative of the mentioned metals. The first five transformations were little investigated, the Te/Cu exchange was extensively studied and the Te/Mn exchange was recently investigated in details. In Figure 6 are schematically shown the five first title exchanges with the respective original references.

The Te/Cu exchange, discovered in our group, has been investigated in more detail, leading to very useful cuprates, which react with organic substrates in the usual way and has been applied in the synthesis of biologically active compounds. In Scheme 9 is shown the general transformation, with capture of the resulting cuprate by an

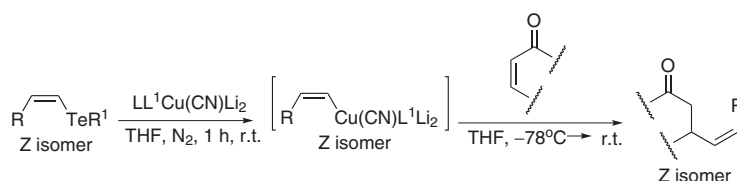


**Figure 6.** Direct transformation of tellurides into reactive organometallics.

enone. More details about this important transformation can be found in recent reviews.<sup>1-4</sup>

In Figure 7, are shown representative cuprates which were prepared by the method shown in Scheme 10. An important feature of the transformation of vinylic tellurides into vinylic cuprates is that the transformation occurs with retention of the *Z* double bond geometry.

Recently it was discovered in our laboratory that the easily prepared di-*n*-butylmanganese promotes the Te/Mn exchange leading to more complex organomanganese compounds, as shown in Scheme 10.<sup>48</sup>



**Scheme 9.** Tellurium / copper exchange reaction.

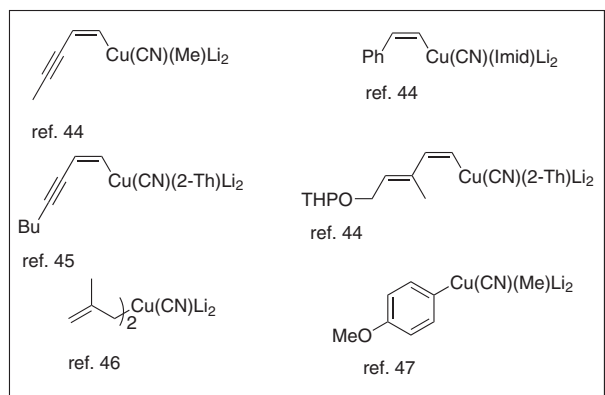
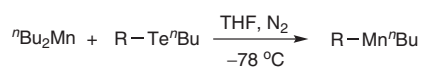


Figure 7. Lithium organocyanocuprates from tellurides.



Scheme 10. Te / Mn exchange reaction.

The resulting mixed organomanganese compounds react with organic substrates in the usual way.<sup>49</sup> In Figure 8 are shown representative examples of organomanganese compounds prepared by Te / Mn exchange reaction.

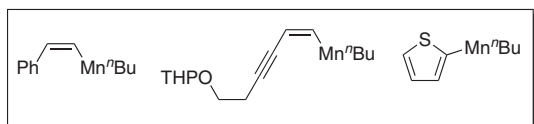


Figure 8. Organomanganese compounds from organotellurides.

#### 4. Application of the Te / Metal Exchange Reaction in the Synthesis of Bioactive Compounds

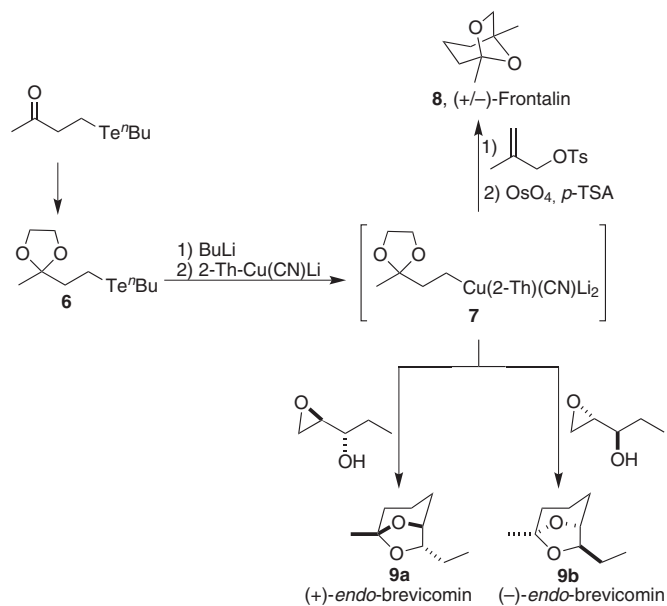
The use of a synthetic methodology for the preparation of compounds with a practical appeal is the final proof of its usefulness. The Te / metal exchange reaction offers a wide range of possibilities for this end. However, the bad reputation (in part unjust!) of the tellurium compounds has hampered their application in organic synthesis. In the following we will comment on the synthesis of some biologically active molecules which make use of the Te / metal exchange methodology. Some of these synthesis are enantioselective thanks to the recent efforts of our group to prepare enantiomerically pure tellurium compounds by means of biocatalytic methods.<sup>50</sup> As can be observed, the tellurium based methodologies present superior results, especially when the *Z* stereoselectivity of the hydrotelluration is considered. The preparation of *Z*-organometallics by the classical methods is not a trivial process,<sup>15</sup> contrary to the straightforward way to access such species employing tellurium methodologies.

As commented in Section 3.1, treatment of telluride **6** with *n*-butyllithium at  $-78\text{ }^\circ\text{C}$ , results in the formation of a lithium masked homoenolate which reacts as expected with various electrophiles.<sup>25,29</sup> By adding 2-ThCu(CN)Li to the resulting solution, the corresponding functionalized higher order cyanocuprate **7** is produced.<sup>25</sup> (+/-)-Frontalin<sup>51</sup> (**8**) and both enantiomers of *endo*-brevicomine<sup>52</sup> (**9a** and **9b**) were prepared in 79 and 70% overall yield respectively by using **7** as a key intermediate (Scheme 11).

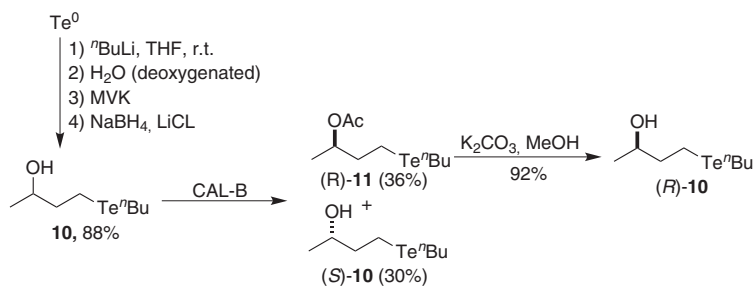
Hydroxy telluride **10** can be prepared in a large scale process in one pot operation by reacting elemental tellurium with butyllithium, followed by addition of a proton source, resulting in the formation of a hydrotellurating reagent ( ${}^n\text{BuTeLi} / \text{H}_2\text{O}$ ) which adds to methyl vinyl ketone (MVK) in a Michael addition processes as discussed in section 2.3. The resulting ketotelluride can be reduced *in situ* to the hydroxy telluride **10** in good yield.<sup>22</sup> Both enantiomers of telluride **10** were obtained in 99% *e.e.* by enzymatic kinetic resolution using CAL-B in organic solvents (Scheme 12).<sup>53</sup>

Valerolactone (**12**) composes the fragrance blend of the most representative Italian white wine varieties of Campania. In addition, it exhibits a potential antifungal property against *Monilinia laxa* and *Rhizopus stolonifer* and is also a potent inhibitor of mouse coumarin 7-hydroxylases (CYP2A5). This lactone was prepared from the enantioenriched hydroxy telluride (*R*)-**10** by reaction with 2 equiv. of *n*-butyllithium followed by carbon dioxide. Its enantiomer, lactone (*S*)-**12**, was prepared from telluride (*S*)-**10**, by the same protocol and used as starting material in the synthesis of the *E/Z* isomeric mixture of spiroketals **13a** and **13b**.<sup>35</sup> This synthetic step required the preparation of the di-cerium salt **14**, generated by the addition of 2 equiv. of butyllithium to a mixture of the optically active hydroxy telluride (*R*)-**10** and cerium chloride in THF at  $-78\text{ }^\circ\text{C}$ . The acid / base and tellurium / lithium exchange reactions were so fast, that even traces of the butyl addition byproduct were not detected. The resulting organocerium dianion was reacted with lactone (*S*)-**12** allowing the isolation of (*2R,5S,7S*)-**13a** and (*2R,5R,7S*)-**13b** as a 1:1 isomeric mixture. These compounds are constituents of the flavor of Jamaican rum (Scheme 13).<sup>35</sup>

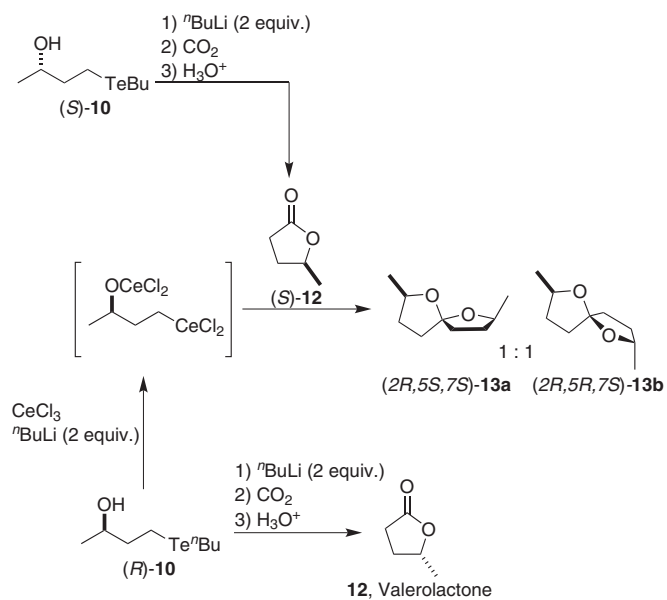
Hydroxy telluride (*S*)-**10** and its racemic mixture were employed as starting materials in the synthesis of the components of the pheromone blend of *Mayetiola destructor*, *Drosophila mulleri* and *Contarinia pisi*. Acetate **15**, component of the pheromone blend of *C. pisi*, was prepared in 80% overall yield from racemic **10** in two steps. (*S*)-**10** was converted into the corresponding di-lithium salt which was treated with copper cyanide (see



Scheme 11.

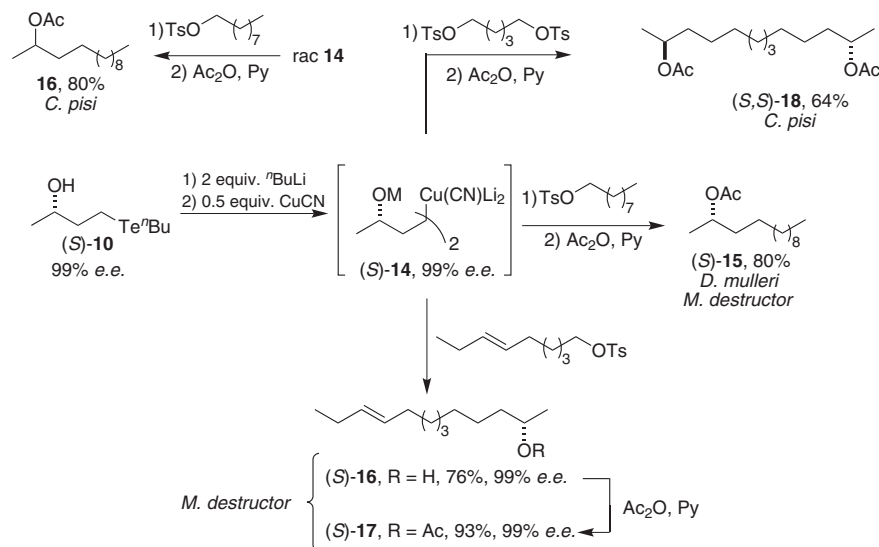


Scheme 12.



Scheme 13.





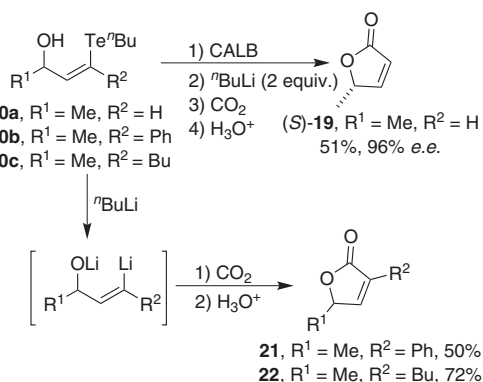
Scheme 14.

section 2.5) resulting in the optically active higher order cyanocuprate (*S*)-**14**. This organometallic was reacted with the appropriate tosylates allowing the preparation of compounds (*S*)-**15** in 80%, (*S*)-**16** in 76%, (*S*)-**17** in 70% and also di-acetate (*S,S*)-**18** in 64% overall yields (Scheme 14).<sup>38</sup>

Similarly, hydroxy vinyl tellurides were used as dianionic entities in the synthesis of some racemic and optically active natural bioactive butenolides.  $\alpha$ -Angelica lactone [(*S*)-**19**] was synthesized by treating hydroxy telluride (*S*)-**20** (96% *e.e.*) with two equiv. of *n*-butyllithium and then capturing the optically active dianion with carbon dioxide. Quenching the reaction mixture with an acidic solution leads to the lactone in 51% isolated yield and 96% *e.e.* after column chromatography purification.<sup>54</sup> It was reported that this lactone acts in the glutathione *S*-transferase (GST) detoxification system when dietary administrated to Wistar rats. Racemic **21** and **22** were also obtained in 50 and 72% yield, respectively, by the same procedure from the corresponding tellurides. Butenolide **21** have moderate activity against filamentous fungi and antifungal activity against human pathogens whereas **22** is a metabolite of *Streptomyces griseus* (Scheme 15).<sup>54</sup>

This strategy was applied as a key step for the construction of the lactone ring in the total synthesis of (+)-blastmycinone (**30**), (–)-blastmycinolactol (**28**), (+)-antimycinone (**31**) and (–)-NFX-2 (**29**).<sup>55</sup> These compounds are degradation products of macrocyclic dilactone (+)-antimycin A (**32**) (Scheme 16) and exhibit a number of biological activities.

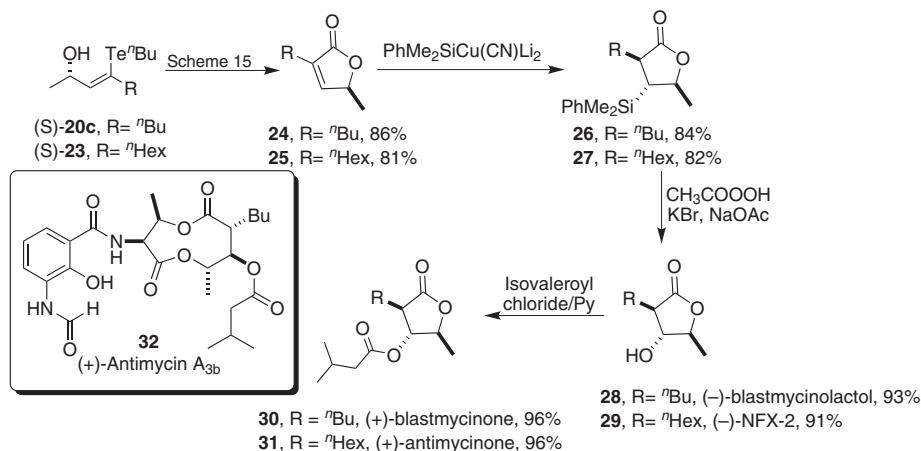
Hydroxy telluride **20c** (94% *e.e.*) and its analogue **23** (96% *e.e.*) were obtained in their enantioenriched



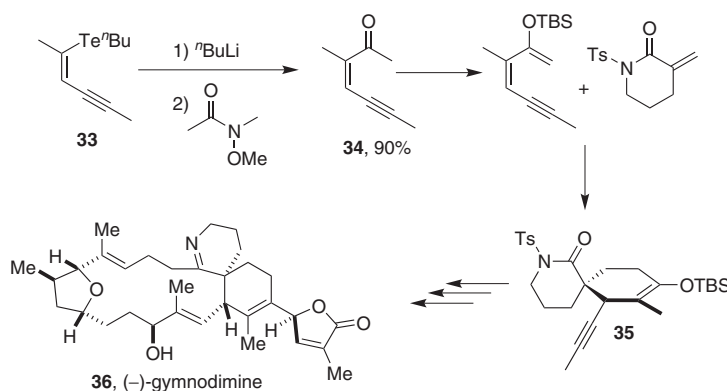
Scheme 15.

form by enzymatic kinetic resolution (CAL-B in organic solvent). Both were submitted to analogous transformations (Scheme 16), resulting in the corresponding lactones **24** and **25** in 86 and 81% isolated yield respectively. Michael addition of a silyl-cyanocuprate to **24** and **25** occur *anti* to the methyl group and the resulting enolate in the workup captures a proton *syn* to the silyl group, affording the desired lactones **26** and **27** exclusively as the *trans,trans*-isomers. The silyl groups were converted into the OH group by oxidation with peracetic acid and potassium bromide yielding (–)-blastmycinolactol (**28**) in 93% and (–)-NFX-2 (**29**) in 91%. Einhorn esterification of lactones **28** and **29** yielded two other natural products, (–)-blastmycinone (**30**) and (+)-antimycinone (**31**), both in 96% isolated yield (Scheme 16).<sup>55</sup>

The tellurium / lithium exchange reaction was used in the preparation of the pure *Z* enone **34** (90%), which was converted into a silyl-enol-ether, used as a diene in a Diels-Alder cycloaddition, generating a spiro lactame **35**.<sup>27</sup> This compound was employed in the attempted total synthesis of



Scheme 16.

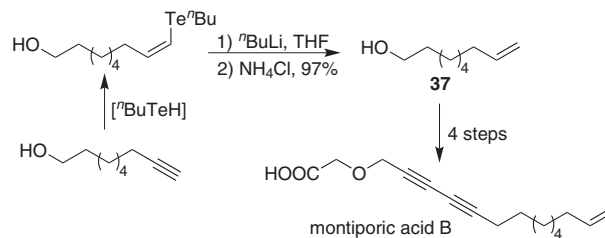


Scheme 17.

(-)-gymnodimine **36** (Scheme 17), a marine toxin produced by the dinoflagellate *Gymnodinium cf. mikimotoi*, found in New Zealand oysters. This toxin is responsible for seafood intoxications, paralytic shellfish poisoning and diarrhetic shellfish poisoning, also called gastroenteritis.<sup>27</sup>

A mild alternative to the conventional triple bond reduction was performed by hydrotelluration of a terminal alkyne. The resulting *Z*-vinyl telluride was treated with two equiv. of *n*-butyllithium followed by acidic workup yielding the terminal olefin **37**. This compound was converted into montiporic acid B after four additional steps (Scheme 18).<sup>56</sup> Montiporic acid B was isolated from eggs of the scleractinian coral *Montipora digitata* and exhibits antimicrobial activity against *Escherichia coli* and cytotoxicity against P-388 murine leukemia cells.<sup>56</sup>

The polyene sex pheromones **38**, **39** and **40** and the flavor principle **41** were synthesized from the common vinyl telluride **42** which was submitted to a tellurium / lithium exchange reaction resulting in the formation of the geometrically pure *Z*-vinyl lithium **43**. Reaction of this lithium reagent with appropriate aldehydes afforded the corresponding alcohols **44-47**. Compounds **46** and **47** were spontaneous and quantitatively transformed



Scheme 18.

into the corresponding aldehydes which were used in the preparation of **38** and **39** (Scheme 19).<sup>57</sup>

Triene **38** is a sex pheromone component of the marine brown algae *Fucus serratus*, *Dictyopteris plagiogramma* and *Dictyopteris australis*. In addition, this compound is also present in the essential oil of galbanum (*Ferula gabaniflua*). Compound **39** and **40** are sex pheromone components of the marine brown alga *Sargassum horneri* and *Fucus serratus*, respectively. Diene methyl ester **41** is a component of the flavor principles of ripe Bartlett pears.<sup>57</sup>

The C-7-C24 fragment (**49**) of Macrolactin F (**50**) was recently synthesized<sup>58</sup> by an epoxide opening reaction, performed by a cyanocuprate prepared from the *Z*-vinyl telluride **48** (R = THP).<sup>44</sup> Fragment **51** was prepared by a



## Acknowledgments

The authors thank FAPESP, CAPES and CNPq for financial support.



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## References

- Petragnani, N.; Stefani, H. A.; *Tellurium in Organic Synthesis*, Second Edition: Second, Updated and Enlarged Edition (Best Synthetic Methods), Academic Press: London 2007.
- Comasseto, J. V.; Clososki, G. C.; Cunha, R. L. O. R. In *Tellurium in: Comprehensive Organometallic Chemistry III*; Mingos, D. M. P.; Crabtree, R. H.; eds.; Elsevier: Amsterdam; vol. 9, pp. 587-648, 2007.
- Comasseto, J. V.; Barrientos-Astigarraga, R. E.; *Aldrichim. Acta* **2000**, 33, 66.
- Zeni, G.; Lüdtke, D. S.; Panatieri, R. B.; Braga, A. L.; *Chem. Rev.* **2006**, 106, 1032.
- Ouchi, A.; Hyugano, T.; Liu, C.; *Org. Lett.* **2009**, 11, 4870.
- Nogueira, C. W.; Zeni, G.; *Chem. Rev.* **2004**, 104, 6255.
- Cunha, R. L. O. R.; Gouvea, I. E.; Juliano, L.; *An. Acad. Bras. Cienc.* **2009**, 81, 393.
- Irgolic, K. C. In *Organotellurium Compounds* (Houben-Weyl), *Methods of Organic Chemistry*, Klamann, D., ed., vol. E12b, Georg Thieme Verlag: Stuttgart, 1990.
- Vargas, F.; Toledo, F. T.; Comasseto, J. V.; *J. Braz. Chem. Soc.* **2010**, 11, 2072.
- Cunha, R. L. O. R.; Zukerman-Schpector, J.; Caracelli, I.; Comasseto, J. V.; *J. Organomet. Chem.* **2006**, 691, 4807.
- Cunha, R. L. O. R.; Omori, A. T.; Castelani, P.; Toledo, F. T.; Comasseto, J. V.; *J. Organomet. Chem.* **2004**, 689, 3631.
- Petragnani, N.; Mendes, S. R.; Silveira, C. C.; *Tetrahedron Lett.* **2008**, 49, 2371.
- Comasseto, J. V.; Vieira, M. L.; Zinn, F. K.; *J. Braz. Chem. Soc.* **2001**, 12, 586.
- Zeni, G.; Formiga, H. B.; Comasseto, J. V.; *Tetrahedron Lett.* **2000**, 41, 1311.
- Bateson, J. H.; Mitchell, M. B.; *Organometallic Reagents in Organic Synthesis*, Academic Press: London, 1994.
- Baba, A.; Shibata, I.; Yasuda, M. In *Tin in: Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., eds.; Elsevier: Oxford, vol. 9, pp. 341-379, 2007.
- Barrientos-Astigarraga, R. E.; Castelani, P.; Sumida, C.; Comasseto, J. V.; *Tetrahedron Lett.* **1999**, 40, 7717; Comasseto, J. V.; Barrientos-Astigarraga, R. E.; Sumida, C. Y.; Santos, P. S.; Almeida, L. C. J.; *Phosphorus, Sulfur, Silicon Relat. Elem.* **2001**, 171, 465; Barrientos-Astigarraga, R. E.; Castelani, P.; Sumida, C.; Comasseto, J. V.; *Tetrahedron* **2002**, 58, 1051.

18. Seebach, D.; Beck, A. K.; *Chem. Ber.* **1975**, *108*, 314.
19. Luppold, E.; Mueller, E.; Winter, W.; *Zeits. Naturf. Teil B: Anorg. Chem.* **1976**, *31B*, 1654.
20. Kauffman, T.; *Angew. Chem., Int. Ed.* **1982**, *21*, 410.
21. Brandt, C. A.; Comasseto, J. V.; Nakamura, W.; Petraghani, N.; *J. Chem. Res. (S)* **1983**, 156.
22. Comasseto, J. V.; Dabdoub, M. J.; Dabdoub, V. B.; Petraghani, N.; *J. Organomet. Chem.* **1986**, *308*, 211.
23. Comasseto, J. V.; Barros, S. M.; Berriel, J. N.; *Tetrahedron Lett.* **1989**, *30*, 7353.
24. Comasseto, J. V.; Dos Santos, A. A.; *Phosphorus, Sulfur Silicon Relat. Elem.* **2008**, *183*, 939.
25. Comasseto, J. V.; Dos Santos, A. A.; *J. Braz. Chem. Soc.* **2005**, *16*, 511.
26. Hiirio, T.; Atarashi, Y.; Kambe, N.; Fujiwara, S.; Ogawa, A.; Ryu, Y.; Sonoda, N.; *Organometallics* **1990**, *9*, 1355.
27. Yang, Y.; Cohn, S. T.; Romo, D.; *Org. Lett.* **2000**, *2*, 763.
28. Cunha, R. L. O. R.; Omori, A. T.; Castelani, P.; Toledo, F. T.; Comasseto, J. V.; *J. Organomet. Chem.* **2004**, *689*, 3631.
29. Inoue, T.; Atarashi, Y.; Kambe, N.; Ogawa, A.; Sonoda, N.; *Synlett* **1995**, 209.
30. Princival, J. L.; Barros, S. M. G.; Comasseto, J. V.; Dos Santos, A. A.; *Tetrahedron Lett.* **2005**, *46*, 4423.
31. Chieffi, A.; Comasseto, J. V.; Snieckus, V.; *Synlett* **2000**, *2*, 269.
32. Hiirio, T.; Morita, Y.; Inoue, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N.; *J. Am. Chem. Soc.* **1990**, *112*, 455.
33. Kambe, N.; Inoue, T.; Takeda, T.; Fujiwara, S.-I.; Sonoda, N.; *J. Am. Chem. Soc.* **2006**, *128*, 12650.
34. Hiirio, T.; Mogami, T.; Kambe, N.; Fujiwara, S.-I.; Sonoda, N.; *Synth. Commun.* **1990**, *20*, 703.
35. Dos Santos, A. A.; Princival, J. L.; Comasseto, J. V.; Barros, S. M.; Brainer Neto, J. E.; *Tetrahedron* **2007**, *63*, 5167.
36. Barrientos-Astigarraga, R. E.; Moraes, D. N.; Comasseto, J. V.; *Tetrahedron Lett.* **1999**, *40*, 265.
37. Princival, J. L.; Dos Santos, A. A.; Comasseto, J. V.; *Tetrahedron Lett.* **2009**, *50*, 6368.
38. Ferrarini, R. S.; Dos Santos, A. A.; Comasseto, J. V.; *Tetrahedron: Asymmetry* **2009**, *20*, 2043.
39. Mirzayans, P. M.; Pouwer, R. H.; Williams, C. M.; *Org. Lett.* **2008**, *10*, 3861.
40. Mirzayans, P. M.; Pouwer, R. H.; Williams, C. M.; Bernhardt, P. V.; *Tetrahedron* **2009**, *65*, 8297.
41. Kanda, T.; Sugino, T.; Kambe, N.; Sonoda, N.; *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 103.
42. Terao, J.; Kambe, N.; Sonoda, N.; *Synlett* **1996**, 779.
43. Terao, J.; Kambe, N.; Sonoda, N.; *Tetrahedron Lett.* **1996**, *37*, 4741.
44. Tucci, F. C.; Chieffi, A.; Comasseto, J. V.; Marino, J. P.; *J. Org. Chem.* **1996**, *61*, 4975.
45. Araujo M. A.; Barrientos-Astigarraga, R. E.; Ellensohn, R. M.; Comasseto, J. V.; *Tetrahedron Lett.* **1999**, *40*, 5115.
46. Castelani, P.; Comasseto, J. V.; *Organometallics* **2003**, *22*, 2108.
47. Castelani, P.; Luque, S.; Comasseto, J. V.; *Tetrahedron Lett.* **2004**, *45*, 4473.
48. Silva, M. S.; Comasseto, J. V.; Dos Santos, A. A.; *Tetrahedron Lett.* **2010**, *51*, 5426.
49. Cahiez, G.; Duplais, C.; Buendia, J.; *Chem. Rev.* **2009**, *109*, 1434.
50. Comasseto, J. V.; Gariani, R. A.; *Tetrahedron* **2009**, *65*, 8447.
51. Dos Santos, A. A.; Ferrarini, R. S.; Princival, J. L.; Comasseto, J. V.; *Tetrahedron Lett.* **2006**, *47*, 8933.
52. Dos Santos, A. A.; Ferrarini, R. S.; Princival, J. L.; Comasseto, J. V.; *J. Braz. Chem. Soc.* **2008**, *19*, 811.
53. Dos Santos, A. A.; Da Costa, C. E.; Princival, J. L.; Comasseto, J. V.; *Tetrahedron: Asymmetry* **2006**, *17*, 2252.
54. Bassora, B. K.; Da Costa, C. E.; Gariani, R. A.; Comasseto, J. V.; Dos Santos, A. A.; *Tetrahedron Lett.* **2007**, *48*, 1485.
55. Ferrarini, R. S.; Comasseto, J. V.; Dos Santos, A. A.; unpublished results.
56. Stefani, H. A.; Costa, I. M.; Zeni, G.; *Tetrahedron Lett.* **1999**, *40*, 9215.
57. Dabdoub, M. J.; Dabdoub, V. B.; Baroni, A. C. M.; Hurtado, G. R.; Barbosa, S. L.; *Tetrahedron Lett.* **2010**, *51*, 1666.
58. Oliveira, R. A.; Oliveira, J. M.; Rahmeier, L. H. S.; Comasseto, J. V.; Marino, J. P.; Menezes, P. H.; *Tetrahedron Lett.* **2008**, *49*, 5759.
59. Marino, J. P.; McClure, M. S.; Holub, D. P.; Comasseto, J. V.; Tucci, F. C.; *J. Am. Chem. Soc.* **2002**, *124*, 1664.

Submitted: April 14, 2010

Published online: August 5, 2010

FAPESP has sponsored the publication of this article.