Tellurium in Organic Synthesis. Preparation of *Z*-Vinylic Cuprates from *Z*-Vinylic Tellurides and Their Reaction with Enones and Epoxides

Fábio C. Tucci, André Chieffi, and João V. Comasseto*

Instituto de Química, Universidade de São Paulo, Caixa Postal 26077, São Paulo, Brazil

Joseph P. Marino*

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

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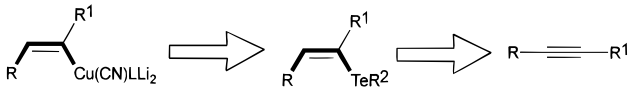
Z-Vinylic tellurides, obtained with 100% stereoselectivity by the hydrotelluration of acetylenes, are easily transformed into *Z*-vinylic higher order cyanocuprates by reaction with preformed Me_2-$Cu(CN)Li_2$, *n*-$Bu_2Cu(CN)Li_2$, or *n*-Bu(2-Th)$Cu(CN)Li_2$, with total retention of the double-bond configuration. The resulting vinylic higher order cyanocuprates react with unhindered enones to give the corresponding 1,4-addition products in good yields. Reaction of the vinylic higher order cyanocuprates with monosubstituted epoxides at 0 °C gives the homoallylic alcohols resulting from the attack to the less-substituted carbon atom, while the disubstituted epoxides failed to react. Allylic epoxides react at −78 °C with the vinylic higher order cyanocuprates to give mixtures of 1,2- and 1,4-opening products, the 1,4-product predominating. In all cases the double-bond configuration of the original vinylic telluride was preserved. The vinylic cuprates derived from simple vinylic tellurides and conjugated 1-telluroenynes react with epoxides at 0 °C, while vinylic cuprates derived from conjugated 1-tellurodienes required the addition of 1 equiv of $BF_3{\cdot}Et_2O$ to give the homoallylic alcohols on reaction with epoxides. The opening of optically pure epoxides through tellurium/copper transmetalation is stereospecific, giving one single stereoisomer of the corresponding homoallylic alcohol.

Introduction

The growth of the organic chemistry of tellurium is well documented in several review articles and books.[1] A significant number of transformations promoted by inorganic and organic tellurium reagents has been reported in the last years, justifying the recent publication of a monograph devoted to the uses of tellurium in organic synthesis.[2] Some of the transformations are unique and present advantages over more traditional methods. The hydrotelluration of acetylenes/transmetalation sequence described in this paper is an example of a unique transformation offered by organic tellurium compounds (Scheme 1).

Scheme 1



Background

A transmetalation reaction involving a vinylic telluride was first mentioned by Kauffman in 1982.[3] At that time very few methods existed in the literature to prepare vinylic tellurides and none of them was stereoselective. Presently vinylic tellurides can be obtained by reaction of vinylic Grignard reagents with organotellurenyl halides,[3,4] reaction of vinylic tellurolate anions with alkyl halides,[4b,5] vinylic substitution of vinyl halides with organotellurolate anions,[4b,6] Wittig reaction of α-telluro phosphoranes with aldehydes,[7] Horner reaction of α-telluro phosphonates with aldehydes,[8] addition of tellurium tetrachloride,[4a,9] aryltellurium trichloride,[10] and aryltellurenamides[11] to acetylenes, radical-initiated carbotelluration of alkynes with diorganotellurides,[12] photoinduced addition of diphenyl ditelluride to acetylenes,[13]

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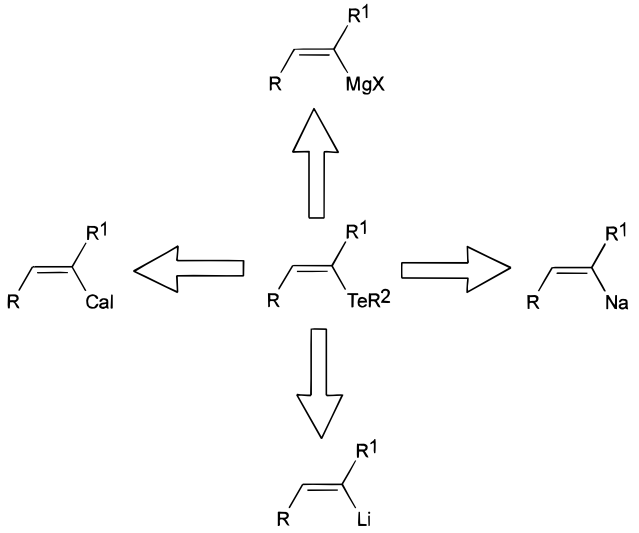
photolysis of acyl tellurides containing an internal acetylenic group,[14] hydrotelluration of acetylenes with aryl or alkyl tellurolate anions in ethanol,[4b,15] or a mixture of elemental tellurium and alkaline solution of sodium borohydride in ethanol,[15m] reaction of acetylenes with elemental tellurium under superbasic conditions,[16] and reaction of acetylenic tellurides with sodium borohydride in ethanol.[17]

The hydrotelluration reactions[4b,15−17] are highly stereoselective leading to the exclusive formation of the *Z*-vinylic tellurides, in contrast with other hydrometalation reactions of acetylenes, which give the *E* isomer preferentially.[18] The easy access to vinylic tellurides of defined *Z* stereochemistry led us[15a,19] and others[20] to use them as precursors of *Z*-vinylic organometallics, especially of *Z*-vinyllithiums.[15a] The transmetalation reactions occur rapidly at low temperature and with retention of the *Z* stereochemistry of the carbon−carbon double bond (Scheme 2).

These easy and stereoselective transmetalations induced us to explore the use of vinylic tellurides as

Scheme 2



precursors of the widely used vinylcopper reagents.[21] Vinylcopper intermediates are classically prepared by reacting the corresponding lithium or Grignard reagent with an appropriate copper salt.[21] In some cases, however, it is advisable to overcome the previous formation of the lithium or Grignard reagent.[21c−f] In such cases a transmetalation between a preformed higher order cuprate and another vinylic organometallic has been successfully applied.[21c−f,22] Vinylstananes,[23] vinylalanes,[24] and vinylzirconocenes[25] have been used as sources of *E*-vinylic higher order cuprates by this method (Scheme 3).

The driving force for these transformations is mainly the change of an sp^3-hybridized ligand in the coordination sphere of copper for an sp^2-hybridized ligand.[26] The most synthetically important methods to prepare vinylic higher order cuprates through transmetalation reactions, shown in Scheme 3, lead to the *E*-vinylic higher order cuprate. The access to the *Z*-vinylic higher order cuprates by transmetalation using described methodologies involves multistep procedures as reported recently.[27] In contrast, the vinylic telluride route shown in Scheme 4 is an easy and straightforward way to these important intermediates of *Z* stereochemistry.

Results and Discussion

There is a generalized misconception concerning the stability of organotelluriums. These compounds are

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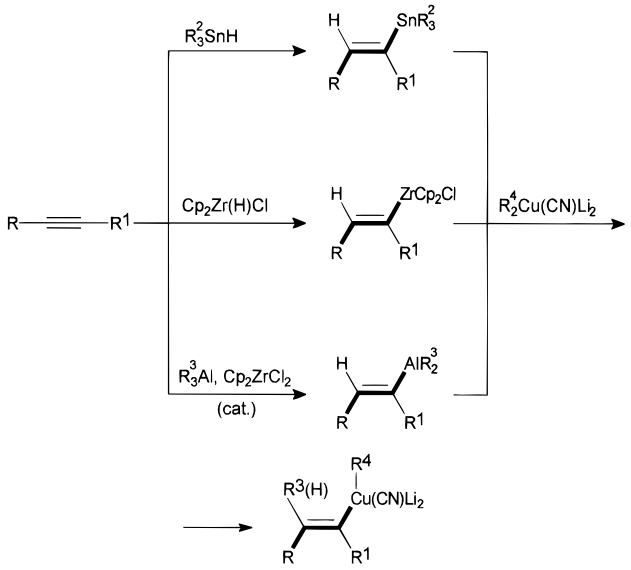
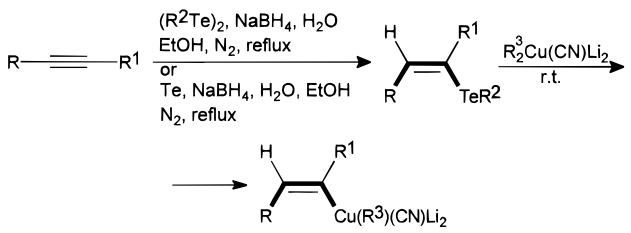
Scheme 3



Scheme 4



thought to be malodorous and sensitive to the air and ambient light. However, the majority of the tellurium compounds described in this paper are thermally and photochemically stable, and except for the low-weight aliphatic derivatives, they are almost odorless compounds. Nevertheless, the aliphatic derivatives (and to a lesser extent also the aromatic ones) when exposed to the air in solution are slowly transformed into an amorphous white powder. Of course, proper care such as use of gloves and well-ventilated hoods must be taken in handling such compounds. Any contact with skin or breathing of the vapors of the volatile derivatives must be avoided, since tellurium is metabolized as dimethyl telluride, which causes an intense garlic breath which persists for several days.

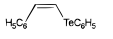
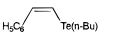
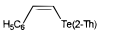
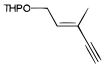
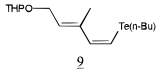
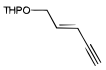
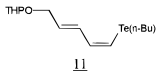
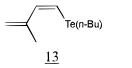
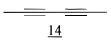
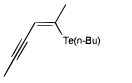
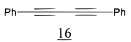
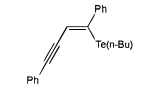
The starting diorganoditellurides used in the hydrotelluration of acetylenes were obtained by reacting elemental tellurium with the appropriate organolithium compound in tetrahydrofuran at room temperature followed by air oxidation of the intermediate organotellurolate[2] (eq 1).

$$\mathrm{RLi} + \mathrm{Te} \xrightarrow[\text{r.t.}]{\mathrm{THF}} [\mathrm{RTeLi}] \xrightarrow{\text{air}} \mathrm{RTeTeR} \qquad (1)$$

R = C_6H_5 (2), n-Bu (4), 2-Th (6)

Dibutyl ditelluride is a dark-red oil of penetrating odor, which must be stored at low temperature in an inert atmosphere. Long exposure of this compound to the air must be avoided. The preparation, purification, and handling of dibutyl ditelluride must be conducted in a well-ventilated hood. Contact with the skin and breathing of the vapors must be avoided. Diphenyl ditelluride and dithienyl ditelluride are almost odorless dark-red solids stable to the air and ambient light.

Table 1. Vinylic Tellurides Prepared

Entry	Acetylene	Ditelluride	Vinylic Telluride	Reaction Time (h)	Yield (%)
1.	1	$(C_6H_5Te)_2$ 2	 3	20	93
2.	1	$(n\text{-BuTe})_2$ 4	 5	2	81
3.	1	$(2\text{-ThTe})_2$ 6	 7	24	60
4.	 8	4	 9	4	83
5.	 10	4	 11	5	89
6.	 12	4	 13	5	75
7.	 14	4	 15	3	65
8.	 16	4	 17	3	74

The vinylic tellurides used in this work were prepared by two methods: by hydrotelluration of acetylenes and by reaction of vinylic Grignard reagents with organotellurenyl halides. The former method consists of the reduction of diorganoditellurides with sodium borohydride in ethanol followed by the addition reaction of the formed organotellurolate with the apropriate acetylene[2,4b,15a,m,o] (eq 2).

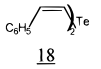
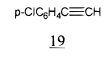
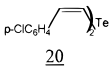
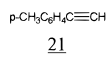
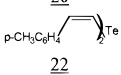
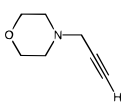
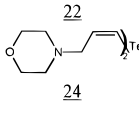
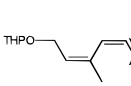
$$\mathrm{RTeTeR} \xrightarrow[\text{EtOH, } N_2\text{, r.t.}]{\mathrm{NaBH_4}} 2\,[\mathrm{RTe^-}] \xrightarrow[\text{reflux}]{\mathrm{R^1{-}{\equiv}{-}R^2}} \mathrm{H(R^1)C{=}C(R^2)TeR} \qquad (2)$$

Experimentally, the diorganoditelluride and the acetylene were mixed in ethanol at room temperature under nitrogen. To this mixture was added sodium borohydride portionwise until the red color of the diorganoditelluride faded. The mixture was then maintained with heat under reflux for the time indicated in Table 1. Care must be taken to avoid the presence of oxygen in the reaction mixture. The nitrogen must be carefully deoxygenated,[28] to avoid reoxidation of the tellurolate to the starting diorganoditelluride. During the reduction step, solid sodium borohydride was added in small portions; otherwise a copious gas evolution was observed and the reaction became uncontrollable. After the workup, the vinylic tellurides were obtained as yellow oils or solids, which were purified by flash chromatography on silica gel. As mentioned before, long exposures of the solutions containing the vinylic tellurides to the air must be avoided to prevent oxidation.

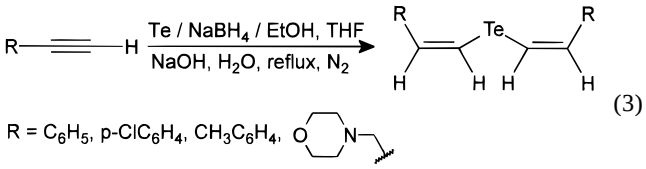
A similar procedure was applied to prepare bis-vinylic tellurides, by reacting elemental tellurium with sodium borohydride in a mixture of sodium hydroxide, water, ethanol, and THF. Heating the mixture under reflux gave a violet solution, which was reacted with excess (30%) of the appropriate acetylene to give the bis-vinylic

(28) Gordon, A. J.; Richard, A. F. *The Chemist's Companion*; John Wiley & Sons: New York, 1972.

Table 2. Bis-Vinylic Tellurides Prepared

	Acetylene	Bis-Vinylic Telluride	Reaction Time (h)	Yield (%)
1.	1	 18	36	78
2.	 19	 20	24	87
3.	 21	 22	36	70
4.	 23	 24	40	72
5.	 8	 25	48	60

telluride (eq. 3). As the reaction occurred in a biphasic system, the reaction time is greatly dependent on the stirring rate and reaction scale, and the progress of the reaction must be monitored by sampling the reaction mixture and exposing it to oxygen. If the sample turns violet, more time is needed to consume the starting acetylene.



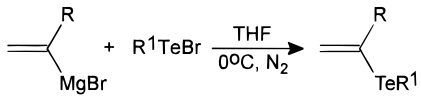
(3)

In both cases the products had the *Z* stereochemistry, as demonstrated by their ^{1}H NMR spectra. The nonconjugated acetylenes gave a small amount of the isomer substituted at C_2 as a byproduct, which could be separated from the main product by column chromatography on silica gel. All of the vinylic tellurides prepared by hydrotelluration of acetylenes are configurationally stable, and even after long standing at room temperature no isomerization was observed. It is worth mentioning that the hydrotelluration reaction works only with terminal aryl- and alkylacetylenes conjugated to a double bond leading to disubstituted olefins. Exceptions are the diyne systems, which are more reactive; even the disubstituted alkylacetylenes gave the vinylic tellurides on reaction with organotellurolates. These acetylenes did not give vinylic tellurides on reaction with the Te/$NaBH_4$/NaOH system. The corresponding tellurophenes were formed instead[29] (see Table 2 for yields and reaction conditions).

Concerning the reactivity of the tellurium species in the hydrotelluration of acetylenes, the alkyl tellurolates react faster than the aromatic analogs, as evidenced by the longer reaction time in the last case (entries 1 and 3, Table 1).

The second method used to prepare the vinylic tellurides used in this work consisted of the reaction of vinyl Grignard reagents with aryltellurenyl halides[3,4] (eq. 4).

Reaction of Vinylic Telluride/$R_RR_TCu(CN)Li_2$ Systems with Enones. With efficient methods to prepare stereoselectively the starting vinylic tellurides in hand, we initiated the study of their transmetalation with higher order dilithium cyanocuprates.[30] Addition of a



(4)

R=H;	R^1=C_6H_5 (26)	82%
H;	2-Th (27)	70%

yellow solution of preformed dilithium dimethylcyanocuprate (**29**)[21e,23b] in THF to a solution of *n*-butyl(*Z*)-styryl telluride (**5**) in THF at room temperature led to a red solution presumably containing Me((*Z*)-C_6H_5CH=CH)Cu(CN)Li_2. To this solution, cooled to −78 °C, was added cyclohexenone. The solution turned immediately yellow, and then it was allowed to reach room temperature. At this temperature, after 20 min of stirring, the reaction was quenched with a 4:1 mixture of ammonium chloride/ammonium hydroxide and worked up in the usual way. After chromatographic purification, the 1,4-addition product (*Z*)-6-phenyl-5-hexen-2-one (entry 1, Scheme 5) was obtained in 90% yield. Having demonstrated that the transmetalation of vinylic tellurides with higher order dilithium cyanocuprates is feasible and highly stereoselective, we turned our attention to the influence of the vinylic telluride structure and the higher order cyanocuprate composition on the reaction course. Schemes 5 and 6 summarize our results.

Concerning the telluride structure, it can be observed in Scheme 5 that phenyl vinyl tellurides (*26*) are not suitable as a source of vinylcopper reagents, since both the vinyl and the phenyl groups are transmetalated and add 1,4 to the enone, as could be anticipated, since both carbanions are sp^2 hybridized. Butyl vinyl tellurides, on the contrary, suffer exclusive tellurium/vinyl transmetalation leading to the desired vinyl transfer products. The more appropriate vinylic tellurides are, however, the bisvinylic tellurides, since 1 equiv of these reagents constitutes a source of 2 equiv of the corresponding higher order vinylic cyanocuprate.

From the results reported in Scheme 6, we can see that the butyl group (cuprate **30**) is not a convenient residual ligand on the preformed cuprate (R_R) since it adds 1,4 to the enone, leading to a mixture of products. Methyl (cuprate **29**), 2-thienyl (2-Th) (cuprate **31**), and imidazoyl (Imid) (cuprate **32**) groups are all efficient residual ligands, leading to the exclusive 1,4-transfer of the vinyl group. The 2-thienyl ligand (cuprate **31**) was used in most cases both because of its commercial availability as (2-Th)Cu(CN)Li[21e] and its higher reactivity compared to that of the imidazoyl ligand.[31]

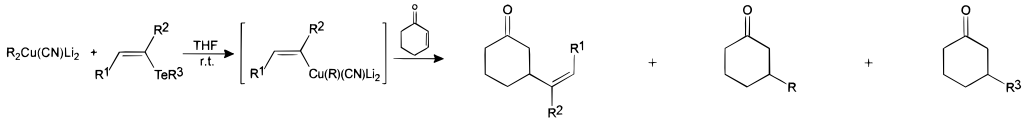
In all instances a volatile and apolar byproduct containing tellurium was formed and was removed from the reaction mixture by evaporation or by flash chromatography on silica gel eluting with hexane. The 1,4-addition product was eluted with hexane/ethyl acetate mixtures, the solvent ratios depending on the structure of the products. All operations should be conducted in a well-ventilated hood, avoiding skin contact and breathing of the vapors. A useful procedure to avoid the inconvenience of manipulating the volatile tellurium byproducts consists of treating the reaction mixture with a diluted

(29) Mack, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 896.

(30) For preliminary communications, see: (a) Comasseto, J. V.; Berriel, J. N. *Synth. Commun.* **1990**, *20*, 1681 and corrigenda, Comasseto, J. V. *Synth. Commun.* **1992**, *22*, 2431. (b) Tucci, F. C.; Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 5721. (c) Tucci, F. C.; Marino, J. P.; Comasseto, J. V. *Synlett* **1993**, 721.

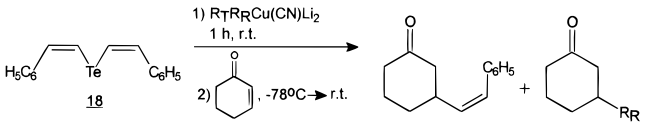
(31) Lipshutz, B. H.; Fatheree, P.; Hagen, W.; Stevens, K. L. *Tetrahedron Lett.* **1992**, *33*, 1041.

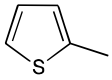
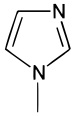
Scheme 5



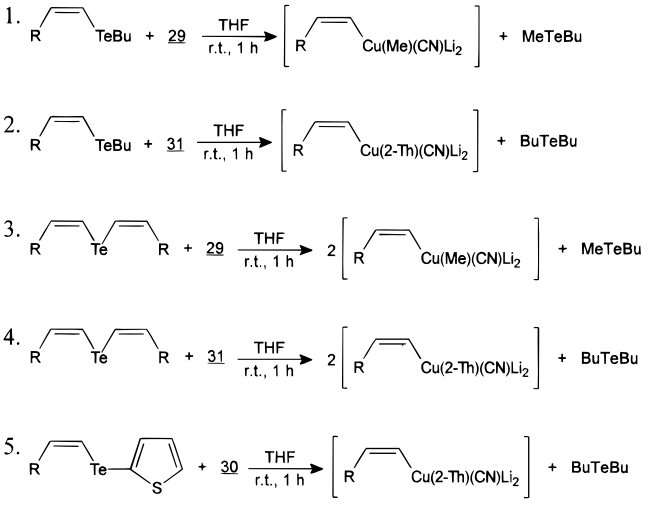
1. R=Me (29); R^1=C_6H_5; R^2=H; R^3=n-Bu (5)	90%	trace	—
2. R=Me (29); R^1=H; R^2=C_6H_5; R^3=n-Bu (28)	88%	trace	—
3. R=n-Bu (30); R^1=H; R^2=H; $R^3C_6H_5$ (26)	55%	—	45%
4. R=n-Bu (30); R^1=C_6H_5; R^2=H; R^3=n-Bu (5)	75%	23%	—

Scheme 6



R_T	R_R			
1. n-Bu	n-Bu	(30)	75%	23%
2. Me	Me	(29)	90%	trace
3. n-Bu		(31)	82%	—
4. n-Bu		(32)	88%	—

Scheme 7



solution of sodium hypochlorite, which transforms the volatile tellurides into the corresponding nonvolatile oxidation products. In Scheme 7 are shown the general transmetalation pathways leading to the *Z*-vinylic cyanocuprates. The last reaction pathway is worth mentioning since it involves the reaction of the easily prepared dilithium dibutylcyanocuprate with a vinyl 2-thienyl telluride, which generates the higher order vinyl 2-thienyl cyanocuprate (entry 5, Scheme 7) in a single step, and the R_R ligand (2-Th) arising from the starting vinyl 2-thienyl telluride (**27**), which avoids the previous formation of the mixed cuprate n-BuCu(2-Th)-(CN)Li_2 (**31**).

The 1,4-addition reaction is sensitive to the structure of the enone (Table 3). β-disubstituted enones such as mesityl oxide gave very low yield (1−5%) of the 1,4-addition product on reaction with **29**.[30a] Three representative enones were used with success, methyl vinyl ketone (**33**), cyclohexenone (**37**), and 4,4-dimethyl-2,3-cyclohexenone (**42**). In all cases the yields of the 1,4-addition product were good.[30b] No significant change in yield was observed on changing the R_R from 2-Th to Me. The purification of the reaction product is very simple and consists of removal of the Cu^{II} species by washing the organic phase with a 4/1 mixture of saturated solutions of NH_4Cl and NH_4OH, followed by evaporation of the solvent and the tellurium byproduct at reduced pressure. Pure samples of the 1,4-addition products were obtained by column chromatography on silica gel.

In some cases, besides the 1,4-addition product, tellurium-free byproducts were observed which were identified as the coupling products of the vinylic moiety of the vinylic telluride with the R_T of the starting higher order dilithium cyanocuprate. By refluxing the reaction mixture of the dilithium cyanocuprate with several vinylic tellurides in the absence of the enone, the coupling product was obtained in reasonable yields with retention of the *Z* stereochemistry of the double bond (Table 4).

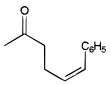
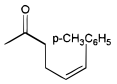
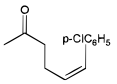
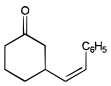
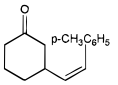
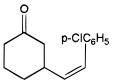
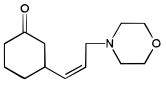
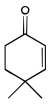
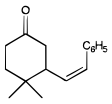
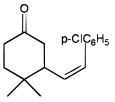
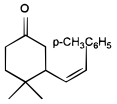
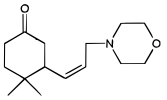
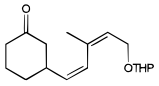
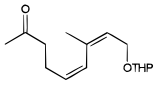
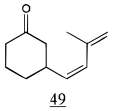
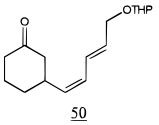
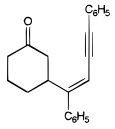
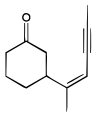
Recently Sonoda and co-workers obtained similar results using the lower order Me_2CuLi.[32] A more detailed study of this reaction is in progress in our laboratory, where it has been shown that the counterion of the original cuprate plays an important role in this cross-coupling reaction, which gives the coupling product in good yields at room temperature when one or both counterions are $MgBr^+$.[33]

For the purpose of generating the vinylic cyanocuprate in good yield, care must be taken to use a good quality alkyllithium to generate the starting dilithium cyanocuprate, since precipitated impurities in the alkyllithium solution lead to the formation of considerable amounts of the cross-coupling product.

Reaction of Vinylic Telluride/$R_RR_TCu(CN)Li_2$ Systems with Epoxides. Homoallylic alcohols are important synthetic intermediates and appear as intermediates in several important total syntheses.[34] The tellurium chemistry described in this paper should be an attractive way of stereoselectively generating such systems through an epoxide opening reaction with a *Z*-vinylic higher order cyanocuprate generated by transmetalation of a *Z*-vinylic telluride with an appropriate higher order cyanocuprate $R_RR_TCu(CN)Li_2$. Initially we tested the epoxide opening

(32) Ogawa, A.; Tsuboi, Y.; Obayashi, R.; Yokoyama, K.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 1600.
(33) Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1994**, *35*, 4063.
(34) See for example: Corey, E. J.; Cheng, X. M. *The Logic of Chemical Synthesis*; John Wiley & Sons: New York, 1989.
(35) Korach, M.; Nielsen, D. R.; Rideout, W. H. *Organic Syntheses*; Wiley: New York, 1973; Collect.Vol. V, p 414.
(36) Schaefer, J. P.; Endres, L. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 285.
(37) Lipshutz, B. H.; Moretti, R.; Crow, R. *Organic Synthesis* **1990**, *69*, 80.
(38) (a) Frick, J. A.; Klassen, J. B.; Bathe, A.; Abramson, J. M.; Rapoport, H. *Synthesis* **1992**, 621. (b) Mosher, H. S.; Dale, J. A.; Dull, D. L. *J. Org. Chem.* **1969**, *34*, 2543.

Table 3. Vinylic Telluride $\xrightarrow[\text{THF, rt, 1 h}]{R_T R_R Cu(CN)Li_2}$ $\xrightarrow[-78\ °C \rightarrow rt]{\text{enone}}$ **Product + Dialkyl Telluride**

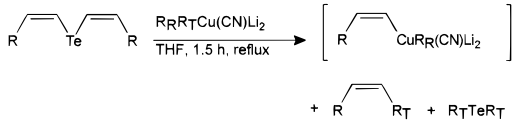
Entry	Vinylic Telluride	Dilithium Cyanocuprate	Enone	Product	Yield (%)
1.	18	31	 33	 34	77
2.	22	31	33	 35	69
3.	20	31	33	 36	65
4.	18	31	 37	 38	82
5.	5	29	37	38	90
6.	5	32	37	38	88
7.	18	29	37	38	90
8.	22	31	37	 39	70
9.	20	31	37	 40	66
10.	24	31	37	 41	76
11.	24	29	37	41	82
12.	18	31	 42	 43	65
13.	18	29	42	43	70
14.	20	31	42	 44	71
15.	22	31	42	 45	71
16.	24	31	42	 46	54
17.	24	29	42	46	60
18.	25	31	37	 47	78
19.	9	29	37	47	?
20.	25	31	33	 48	60
21.	13	29	37	 49	77
22.	11	29	37	 50	61
23.	17	29	37	 51	65
24.	15	29	37	 52	63

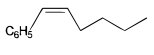
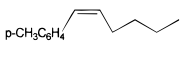
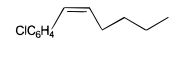
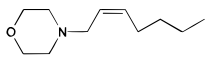
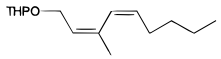
reaction with three representative higher order cyanocuprates and found that the 2-thienyl cyanocuprate (**31**) is the cuprate of choice for this transformation as shown in Scheme 8.

Three representative vinylic tellurides were used (**18**, **9**, **15**). The transmetalation reaction of these tellurides with the higher order cyanocuprate **31** was performed as described for the 1,4-addition to enones. After 1 h of stirring at room temperature, the mixed cuprate was cooled to 0 °C and the epoxide was added. It must be noted that the epoxides did not react at temperatures lower than −10 °C. Exceptions were the allylic epoxides, which reacted with the vinylic telluride/**31** system at −78 °C. The same care taken during the workup in the reaction with enones must be taken in the reaction with epoxides, since dibutyl telluride is formed as a byproduct. Table 5 summarizes the results obtained in the epoxide opening reaction. From this table several conclusions arise. Reaction with monosubstituted epoxides (entries 1, 2, 10−17, Table 5) gave the product of the attack to the less-substituted carbon atom in good yields. Disubstituted epoxides **76** and **77** failed to react with the vinylic telluride **18**/cuprate **31** even in the presence of $BF_3 \cdot Et_2O$[21] (entries 8 and 9, Table 5). Reaction of the telluride **18**/cuprate **31** with styrene oxide led to a mixture of the homoallylic alcohols **63** and **64** in a 1:1.2 ratio (entry 3, Table 5). The allylic epoxides **65** and **68** merit special attention (entries 4, 5, 13, 14, 18, and 19, Table 5). It is known that lower order cyanocuprates react with such epoxides in an SN_2 mechanism, leading to the homoallylic alcohols with the hydroxyl group at C_4.[39] On the other hand, higher order cyanocuprates give mixtures of 1,2- and 1,4-epoxide opening products.[40] As shown in Table 5 the vinylic telluride/cuprate **31** behaves as a typical

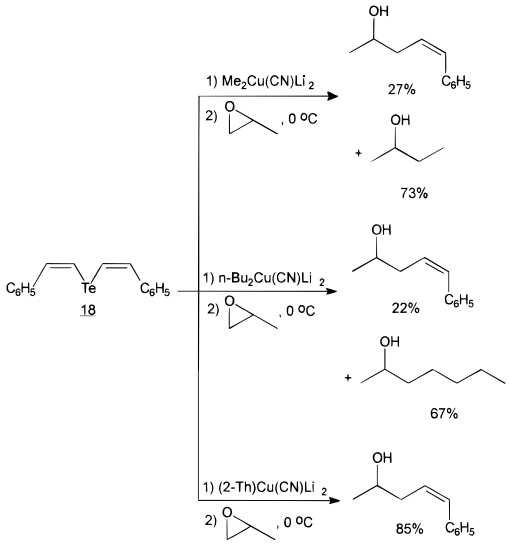
(39) Marino, J. P.; De la Pradilla, R. F.; Laborde, E. *J. Org. Chem.* **1987**, *52*, 4898.
(40) Marino, J. P. unpublished.

Table 4



Telluride	$R_RR_TCu(CN)Li_2$	Product	Yield[a] (%)
18	30	 53	69
22	30	 54	50
19	30	 55	67
23	30	 56	46
25	30	 57	50

Scheme 8



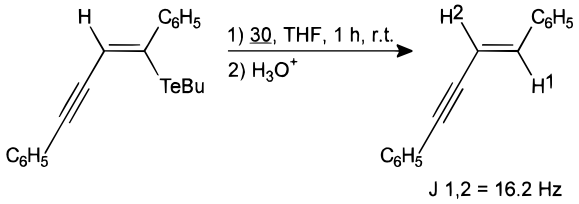
higher order cyanocuprate leading to a predominant 1,4-opening product (entries 4, 5, 13, 14, 18, and 19, Table 5) but with low regioselectivity. The vinylic cyanocuprate derived from telluride **9** required the addition of $BF_3 \cdot Et_2O$ to promote the epoxide opening, indicating the lower reactivity of this system when compared with the ones derived from the vinylic tellurides **15** and **18** (entries 10−12, Table 5).

A surprising result was the isolation of the tellurated products **73** and **75** in the reaction of the bis-vinylic telluride **18**/cuprate **31** system with epoxides **71** and **74** (entries 6 and 7, Table 5). In entry 6 a mixture of the epoxide opening product by the vinylic cuprate **72** and the epoxide opening product by the vinyltelluro group **73** was detected in ~2:1 ratio; in entry 7 only the tellurated product **75** was detected. This fact is difficult to rationalize, since a vinyl tellurolate should be the active species in the epoxide opening and an organotellurolate behaves as the nontransferable group (R_R) toward higher order cyanocuprates.[41] On the other hand, when the same epoxides **71** and **74** were reacted with the vinylic tellurides **9** and **15**/cuprate **31** system, no tellurated products were detected (entries 11, 12, 16, and 17, Table 5). In addition, in all other cases the vinylic telluride **18**/cuprate **31** system reacted with epoxides leading to the nontellurated epoxide opening products (entries 1−5, Table 5). With all these facts in mind we can conclude that the anomalous behavior observed for entries 6 and 7 can be attributed to the particular nature of the epoxides **71** and **74** and the telluride **18**, which in the transition state should interact in such a way as to favor the attack of the tellurium atom to the epoxide, although at present we do not have enough experimental evidences to propose a plausible mechanism for this transformation.

Another feature that must be pointed out in the epoxide opening through tellurium/copper transmetalation is their stereospecificity (entries 12 and 17, Table 5). Optically pure epoxide **74**[38a] reacted through the usual SN_2 mode with the cyanocuprates generated from the tellurides **9** and **15** to give one single stereoisomer of the corresponding homoallylic alcohols. The stereospecificity of the transformation was demonstrated by derivatizing the alcohols with Mosher's acid chloride.[38b] The ^{19}F NMR spectrum of the resulting ester showed a single peak. This observation opens a new perspective for the use of tellurium/copper transmetalation in the synthesis of natural products.

Spectroscopic Data

Hydrotelluration of Alkynes. The *Z* double bond of the telluride starting materials was assigned on the basis of the corresponding coupling constant values (*J*) for the vinyl protons (^1H NMR), as described earlier.[4b,15m,o] For tellurides **15** and **17**, which do not possess two vicinal protons, the double-bond stereochemistry was assigned by transmetalating them with the higher order cyanocuprate **30** and quenching the vinylcopper intermediates with a proton source. By assuming that the transmetalation step would occur with total retention of the double-bond geometry, it was possible to determine the initial telluride configuration[15o] (eq. 5).



(5)

1,4-Additions to Enones. All the products obtained through the transmetalation/1,4-addition to enones sequence were subjected to ^1H NMR, ^{13}C NMR, IR, LRMS, and HRMS analyses (see Experimental Section). Our major concerns regarding these products were (a) verifying the *Z* stereochemical integrity of the double bond in the 1,4-addition products and (b) attesting the regioselective mode of 1,4-addition rather than the 1,2-addition. These concerns were readily alleviated by analyzing, respectively, the *J* between the two vinyl protons (^1H NMR) and the carbonyl absorption peaks in both the IR and the ^{13}C NMR spectra (Table 6).

As seen in Table 6, both the *Z*-olefinic geometry and the carbonyl moiety were readily identified by analyzing the spectroscopic data. ^1H NMR coupling constants for

(41) Comasseto, J. V.; Chieffi, A. unpublished.

Table 5. Telluride $\xrightarrow[\text{2. epoxide}]{\text{1. 31, THF, 1 h, rt}}$ **Product + $(n\text{-Bu})_2$Te**

Entry	Telluride[a]	Epoxide	Product[b]	Yield (%)	Entry	Telluride[a]	Epoxide	Product[b]	Yield (%)
1.	18	58	59	85	12.	9	74	80	64g
2	18	60	61	82	13.	9	65	81 + 82 (3.6 : 1)	78
3.	18	62	63 + 64 (1 : 1.2)	91	14.	9	68	83 + 84 (5.2 : 1)	89
4.	18	65[c]	66 + 67 (3.4 : 1)	74	15.	15	60	85	67
5.	18	68[d]	69 + 70 (3 : 1)	94	16.	15	71	86	74
6.	18	71[e]	72 + 73 (1.9 : 1)	73	17.	15	74	87	55
7.	18	74[f]	75	45	18.	15	65	88 + 89 (1.9 : 1)	86
8.	18	76	no reaction		19.	15	68	90 + 91 (1.2 : 1)	72
9.	18	77	no reaction						
10.	9	60	78	61g					
11.	9	71	79	60g					

[a] One equivalent of the telluride **18** was reacted with 2 equiv of the cuprate **31**; 1 equiv of the tellurides **9** and **15** was reacted with 1 equiv of the cuprate **31**. [b] When a mixture of products was obtained, the ratio was determined after the separation of the products by column chromatography on silica gel. [c] The epoxide was prepared according to ref 35. [d] Prepared by monoepoxidation of cyclohexadiene.[36] [e] Prepared according to ref 37. [f] Prepared according to ref 38. [g] One equivalent of $BF_3{\cdot}Et_2O$ was added at −78 °C immediately before the addition of the epoxide, and the resulting solution was maintained at this temperature for 2 h.

the vicinal *Z*-hydrogens ranged from 11.2 to 11.7 Hz, indicating the presence of *Z*-olefins. The exceptions to these observations are the products derived from the tellurides **14** and **16**, which do not have vicinal hydrogens on the transmetalated double bond and, therefore, had their stereochemistry assigned by analogy to the experiments described in eq 5. Evidence for the carbonyl carbon presence, and thus for the exclusive 1,4-addition, is clearly verified by the ^{13}C NMR carbonyl chemical shifts (ranging from 207.71 to 211.17 ppm) and by the IR absorption frequencies (from 1697 to 1717 cm^{-1}).

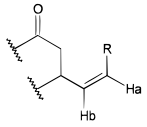
Epoxide Openings. As with the Michael addition products, the homoallylic alcohols obtained from the epoxide openings with the *Z*-vinyl cuprates were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies and LRMS and HRMS. Due to the simplicity of the structures obtained, our major concern was to determine whether or not stereochemical retention had been achieved around the *Z* double bond. Analysis of the *J* values between the two vinyl hydrogens provided strong evidence of the total *Z* double-bond geometry retention in the process. The *J* values ranged from 11.3 to 11.8 Hz, typical of *Z*-olefins. The chemical shifts, the *J* values, and the IR absorptions for the OH moiety of the homoallylic alcohols obtained are listed in Table 7.

The relative stereochemistry, as well as the regiochemistry of the products derived from the opening of the allylic epoxides, was determined through comparison with data from the literature and through some decoupling ^{1}H NMR experiments.

In order to determine the regiochemistry of the two isomers obtained from the reaction of cyclohexadiene monoepoxide and the cuprate generated from telluride **18**, separate decoupling experiments were performed (Figures 1 and 2).

By observing the ^{1}H NMR in Figure 1, we noticed that H^1 is shifted downfield (4.24 ppm) when compared to the corresponding proton in Figure 2 (3.65 ppm). This is evidence that H^1 in Figure 1 is allylic and, therefore, belongs to a 1,4-adduct. The saturation of the H^1 signal (4.24 ppm) in Figure 1 caused an observable simplification of the signals relative to H^2 (5.64 ppm), H^3 (5.77

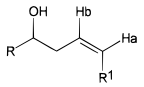
Table 6. Spectroscopic Data Relative to the 1,4-Addition Products



	^{1}H NMR		^{13}C NMR[a]	IR[c]
compd	Ha[a,b]	Hb[a,b]	δ(C=O)	ν(C=O)
34	6.45 (d; $J = 11.5$)	5.66−5.53 (m)	207.95	1716
35	6.39 (d; $J = 11.7$)	5.59−5.46 (m)	207.75	1716
36	6.38 (d; $J = 11.7$)	5.67−5.55 (m)	207.71	1716
48	5.88 (d; $J = 11.3$)	5.52−5.36 (m)	207.82	1717
38	6.41 (d; $J = 11.5$)	5.50 (dd; $J_1 = 10.3$, $J_2 = 11.5$)	209.75	1711
39	6.37 (d; $J = 11.5$)	5.44 (dd; $J_1 = 10.0$, $J_2 = 11.5$)	210.21	1712
40	6.27 (d; $J = 11.5$)	5.44 (dd; $J_1 = 10.1$, $J_2 = 11.5$)	210.08	1713
41	5.37−5.19 (m)		210.53	1713
47	5.82 (d; $J = 11.6$)	5.23 (dd; $J_1 = 10.0$, $J_2 = 10.6$)	210.60	1712
49	5.82 (d; $J = 11.6$)	5.26 (dd; $J_1 = J_2 = 11.6$)	210.61	1713
50	5.91 (dd; $J_1 = J_2 = 10.9$)	5.23 (dd; $J_1 = J_2 = 10.9$)	210.47	1713
51	5.80 (s)		210.60	1712
52	5.24 (s)		211.17	1697
43	6.53 (d; $J = 11.7$)	5.53 (dd; $J_1 = J_2 = 11.7$)	210.90	1713
45	6.49 (d; $J = 11.6$)	5.49 (dd; $J_1 = J_2 = 11.6$)	210.88	1715
46	5.62−5.38 (m)	5.62−5.38 (m)	210.61	1706

[a] Chemical shift in δ (ppm) coupling constants (J) in Hz. [b] Splitting patterns are assigned as s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. [c] Infrared frequencies in cm^{-1}.

Table 7. Spectroscopic Data Relative to Epoxide Opening Products



	^{1}H NMR[a,b]		IR[c]
compd	HA	Hb	ν(OH)
59	6.56 (d; $J = 11.7$)	5.71 (dt; $J_1 = 7.3$; $J_2 = 11.7$)	3368
61	6.58 (d; $J = 11.5$)	5.74 (dt; $J_1 = 7.4$, $J_2 = 11.5$)	3360
63	6.70 (d; $J = 11.6$)	5.92 (dd; $J_1 = 10.5$, $J_2 = 11.6$)	3378
64	6.55 (d; $J = 11.7$)	5.70 (dt; $J_1 = 7.0$, $J_2 = 11.7$)	3374
65	6.45 (d; $J = 11.3$)	5.36 (dd; $J_1 = 10.3$, $J_2 = 11.3$)	3319
67	6.51 (d; $J = 11.5$)	5.37 (dd; $J_1 = 10.4$, $J_2 = 11.5$)	3342
69	6.45 (d; $J = 11.5$)	5.42 (dt; $J_1 = J_2 = 11.5$)	3365
70	6.65 (d; $J = 11.5$)	5.45−5,42 (m)	3384
72	6.54 (d; $J = 11.7$)	5.73 (dt; $J_1 = 7.4$, $J_2 = 11.7$)	3441
78	5.99 (d; $J = 11.8$)	5.44 (dt; $J_1 = 7.5$, $J_2 = 11.8$)	3408
79	5.93 (d; $J = 11.8$)	5.43 (dt; $J_1 = 7.3$, $J_2 = 11.8$)	3441
80	5.95 (d; $J = 11.8$)	5.44 (dt; $J_1 = 7.3$, $J_2 = 11.8$)	3455
81	5.88−5.83 (m)	5.08 (dd; $J_1 = J_2 = 11.4$)	3395
82	5.91 (d; $J = 11.5$)	5.10 (dd; $J_1 = J_2 = 11.5$)	
83	5.84 (d; $J = 11.6$)	5.13 (dd; $J_1 = J_2 = 11.6$)	3411
85	5.32 (s)		3377
86	5.34 (s)		3448
87	5.34 (s)		3412
88	5.23 (dd; $J_1 = 1.5$, $J_2 = 2.3$)		3394
89	5.35 (dd; $J_1 = 1.5$, $J_2 = 2.1$)		3404
90	5.27 (dd; $J_1 = 1.5$, $J_2 = 2.3$)		3373
91	5.30 (s)		3383

[a] Chemical shift in δ (ppm) coupling constants (J) in Hz. [b] Splitting patterns are assigned as s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. [c] Infrared frequencies in cm^{-1}.

ppm), and H^6 (1.50−1.42 ppm). The irradiation of H^4 (3.39 ppm) caused simplifications of H^2 (5.64 ppm), H^3 (5.77 ppm), H^5 (2.11−1.89 ppm), and of the vinyl proton of the *Z*-styrene group. There was no observable influence of H^1 on H^4 signals and vice versa, indicating that neither are vicinal and, thus, the structure drawn in Figure 1 is the correct one for this substance (1,4-adduct).

On the other hand, experimental results shown in Figure 2 led us to conclude that the 1,2-adduct was the one in question. When H^1 (3.65 ppm) was irradiated, H^2 (3.41−3.36 ppm) and H^6 (2.01−1.57 ppm) had their signals simplified. Saturation of H^2 (3.41−3.36 ppm) caused changes in the signals of H^1 (3.65 ppm), H^3 (5.44 ppm), and the vinyl protons of the styrene group. All of these observations led us to conclude that H^1 and H^2 are vicinals in the structure presented in Figure 2 and, therefore, allowed us to unequivocally identify it as the 1,2-adduct.

Similar decoupling experiments were performed with the cyclopentadiene monoxide derivatives and led to similar conclusions.

The relative stereochemical outcomes of the reactions between the allylic epoxides and the cuprates generated from *Z*-vinyl tellurides were assigned through comparison with the literature data.

For the cyclopentadiene monoxide derivatives, it is known[42] that *cis*-1,4-disubstituted cyclopentenes demonstrate large chemical shifts differences for their H^5

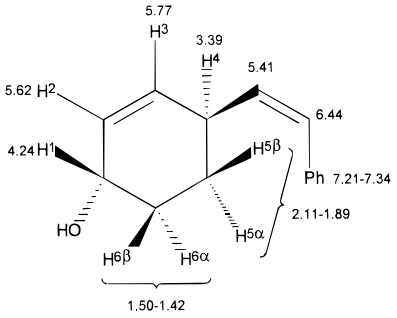


Figure 1. Decoupling experiment (^{1}H NMR) on **69**.

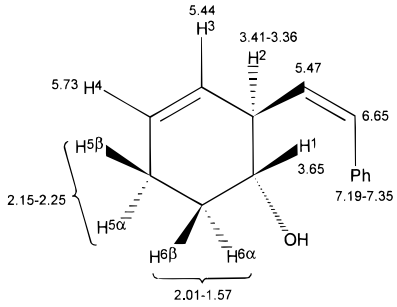
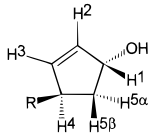


Figure 2. Decoupling experiment (^{1}H NMR) on **70**.

Table 8. Chemical Shifts (^{1}H NMR) of the H^5 Protons of the 1,4-Adducts of Cyclopentadiene Monoxide Derivatives



compd	$H^{5\alpha}$ and $H^{5\beta}$ (ppm)
66	2.09−1.93 (m, 2H)
81	1.92−1.69 (m, 2H)
88	1.92−1.69 (m, 2H)

protons in the ^{1}H NMR spectra. Such differences can be as large as 1 ppm in some cases.[42] On the other hand, for *trans*-1,4-disubstituted cyclopentenes, the chemical shift difference does not exceed 0.3 ppm.[42] By analyzing the H^5 chemical shift differences on the 1,4-adducts of cyclopentadiene monoxide derivatives, we concluded that all of them are *trans* (Table 8).

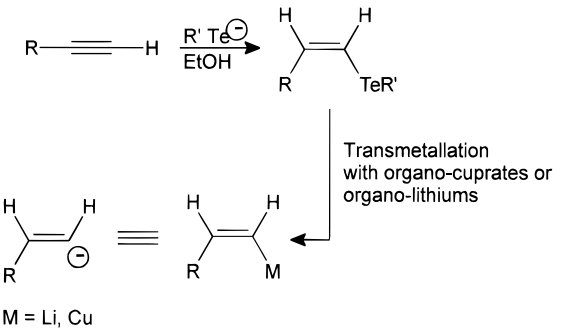
The 1,2-adducts of cyclopentadiene monoepoxide were assumed to be *trans* due to the normal SN_2 mode of reaction (*trans*-diaxial).

The stereochemical assignment of the cyclohexadiene monoepoxide derivatives was based on the results previously reported by one of us,[43] in a work that describes the reaction between cyclohexadiene monoxide and a series of lower order cyanocuprates.

Conclusion

In summary, we have shown that the hydrotelluration of terminal acetylenes is highly stereoselective in the sense that only *Z*-vinyl tellurides are obtained. These *Z*-vinyl tellurides, in turn, have proven to be excellent precursors of *Z*-vinyl higher order cyanocuprates, establishing, therefore, a new and unique method of accessing *Z*-vinylcuprates through transmetalation chemistry. Trapping the incipient vinyl-cuprates species with α,β-unsaturated ketones and with epoxides has provided an efficient way to obtain, respectively, Z-4-vinyl-substituted ketones and *Z*-homoallylic alcohols.

Scheme 9



The vinyl tellurides presented in this work are easily prepared, stereochemically stable compounds. The possibility of hydrotellurating conjugated enynes and diynes enables one to access more elaborated *Z*-vinyl cuprates, and can consequently transform the synthetic sequence into a more convergent one.

The overall hydrotelluration of a terminal acetylene/transmetalation with an organometallic reagent can be viewed as a way of transforming a terminal acetylene into a *Z*-vinylic anion (Scheme 9).

Applications of the methodology described in this paper on the synthesis of natural products are currently under investigation and will be reported in due course.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on either a 200 MHz or a 360 MHz spectrometer in $CDCl_3$. Elemental analyses were performed at the Microanalytical Laboratory of the Institute of Chemistry, Universidade de São Paulo. Column chromatographic separations were carried out with Merck silica gel (230−400 mesh) according to the procedure by Still and co-workers.[44] Thin layer chromatography (TLC) was performed on silica gel 60 F-254 on aluminum. All solvents used were previously dried and distilled according to the usual methods.[45] THF, diethyl ether, and 1,4-dioxane were distilled from sodium/benzophenone under N_2 immediately before use. Tellurium metal (320 mesh) was purchased from Aldrich and dried overnight in an oven at 100 °C, and CuCN was obtained from Aldrich and dried under vacuum in an Abderhalden apparatus over P_2O_5, under refluxing methanol. *n*-BuLi (in hexane solution) was purchased from Aldrich and titrated[46] prior to use. MeLi was prepared from MeI and Li metal in diethyl ether, according to the literature procedure.[47] The following reagents were prepared according to the literature procedures: (4-methylphenyl)acetylene,[48] (4-chlorophenyl)acetylene.[48] (*E*)-2-penten-4-yn-1-ol,[49] diphenyldiacetylene,[50] *N*-propargylmorpholine,[49] dithienyl ditelluride,[51] dibutyl ditelluride,[52] diphenyl ditelluride,[53] cyclohexadiene monoxide,[36]

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cyclopentadiene monoxide,[35] 2-[(benzyloxy)methyl]oxirane,[37] (*R*)-[2-(benzyloxy)ethyl]oxirane.[38] The remaining chemicals were obtained from commercial sources. The tetrahydropyranylation of alcohols was performed according to the literature procedure.[54] All operations were carried out in flame-dried glassware, under an inert atmosphere of dry and deoxygenated N_2.

Dithienyl Ditelluride (6).[51] Thiophene (4.0 g, 47.6 mmol) was added to a three-necked flask containing THF (100 mL) under nitrogen and magnetic stirring. The solution was cooled to −78 °C, and *n*-BuLi (24.2 mL of a 2 M solution in hexane, 48.4 mmol) was slowly added. The mixture was stirred for 1 h at 0 °C, and then elemental tellurium (5.8 g 45.4 g atom) was added all at once. The mixture was stirred at room temperature for 30 min and then cautiously poured into an Erlenmeyer flask containing water (600 mL). The mixture was diluted with methylene chloride (400 mL), and oxygen was bubbled through the mixture for 1 h. The solution was then stirred overnight in the presence of air. The organic phase was then separated, washed with saturated solution of NaCl (200 mL), and dried with $MgSO_4$. After filtration and removal of the solvent, the residue was recrystallized from absolute ethanol. Yield 5.51 g (58%); mp: 88−91 °C (lit.[51] mp 89−90 °C).

Dibutyl Ditelluride (4).[52] To a suspension of Te (Aldrich 200 mesh, 40 mmol, 5.10 g) in THF (50 mL) under nitrogen at 0 °C was added *n*-BuLi (44 mmol, 22 mL of a solution 2.0 M in hexane). The mixture was stirred for 35 min at 0 °C and for aditional 15 min at rt. The mixture was cautiously poured into an Erlenmeyer flask containing water (100 mL) and stirred in presence of atmospheric oxygen for 15 min. The organic phase was then separated, diluted with ethyl acetate (100 mL), washed with saturated solution of NH_4Cl (200 mL) and brine (200 mL), and dried with $MgSO_4$. Dibutyl ditelluride was obtained after filtration and removal of the solvent. Yield 6.79 g (92%).

General Procedure for the Preparation of the Bis-Vinylic Tellurides.[15m] Sodium borohydride (3.40 g, 90 mmol) was added in small portions to a suspension of elemental tellurium (3.83 g, 30 g atom) in absolute ethanol (150 mL) under magnetic stirring and nitrogen atmosphere deoxygenated. To this mixture were added sodium hydroxide (3.20 g, 80 mmol) in water (150 mL) and THF (50 mL). The mixture was then heated at reflux until all the tellurium was consumed and a violet solution was formed. The heating was then removed, and the appropriate acetylene (78 mmol) was added. After ca. 30 min the mixture turned yellow, and then it was refluxed for the time indicated in Table 2. The progress of the reaction was monitored by sampling the reaction mixture and exposing it to oxygen. If the sample turned violet, more time was necessary to consume the acetylene. After the end of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (500 mL). The organic phase was separated, washed with saturated solution of sodium chloride (2 × 200 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure, and the residue was purified by recrystallization from absolute ethanol when solid or by flash chromatography on silica gel when liquid.

Bis[(*Z*)-2-phenyl-1-ethenyl] telluride (18):[15m] yield 7.81 g (78%); mp 48−49 °C (lit.[15m] mp 52−54 °C); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.44 (d, J = 10.6 Hz, 1H), 7.39−7.21 (m, 5H), 6.99 (d, J = 10.6 Hz, 1H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 138.84, 137.41, 128.44, 127.56, 127.35, 108.88.

Bis[(*Z*)-2-(4-methylphenyl)-1-ethenyl] telluride (22):[15m] yield 7.60 g (70%); mp 70−72 °C (lit.[15m] mp 77−78 °C); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.39 (d, J = 10.6 Hz, 1H), 7.13 (s, 4H), 6.90 (d, J = 10.6 Hz, 1H), 2.31 (s, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 137.37, 137.16, 136.00, 129.09, 127.55, 107.78, 21.21.

Bis[(*Z*)-2-(4-chlorophenyl)-1-ethenyl] telluride (20):[15m] yield 10.52 g (87%); mp 80−82 °C (lit.[15m] mp 84−86 °C); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.38 (d, J = 10.5 Hz, 1H), 7.24(AB system, J_{AB} = 8.2 Hz, 2H, Dn = 36), 7.00 (d, J = 10.5 Hz, 1H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 137.14, 136.45, 133.35, 128.67, 128.77, 109.36.

Bis[(*Z*)-3-(*N*-morpholino)-1-propenyl telluride (24):[15m] yield 8.21 g (72%); mp 76−77 (lit.[15m] mp 72−74 °C); 200 MHz ^{1}H NMR ($CDCl_3$) δ 6.98 (d, J = 9.9 Hz, 1H), 6.42 (dd, J = 4.7, 9.9 Hz, 1H), 3.77(t, J = 4.6 Hz, 4H), 2.92 (dd, J = 4.7, 1.2 Hz, 2H), 2.48(t, J = 4.6 Hz, 4H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 131.18, 115.40, 66.95, 60.08, 53.15.

Bis[(*Z*,*Z*)-5-((tetrahydropyranyl)oxy)-3-methyl-1,3-pentadienyl] telluride (25).[15m] yield 8.82 g (60%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.06 (d, J = 10.6 Hz, 1H), 6.79 (d, J = 10.6 Hz, 1H), 5.52(t, J = 6.8 Hz, 1H), 4.60(t, J = 3.3 Hz, 1H), 4.21 (dd, J = 12.1, 6.5 Hz, 1H), 4.05−3.82 (m, 2H), 3.53−3.47 (m, 1H), 1.87 (s, 3H), 1.82−1.42 (m, 6H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 137.68, 135.30, 125.99, 108.84, 97.68, 63.51, 61.80, 30.30, 25.15, 21.37, 19.13.

General Procedure for the Preparation of the Butyl Vinyl Tellurides. To a solution of the dibutyl ditelluride (0.93 g, 2.5 mmol) and the appropriate acetylene (5.5 mmol) in absolute ethanol (15 mL) under nitrogen (deoxygenated by bubbling through a solution of VCl_3 (pH = 1) with Zn/Hg amalgam) and magnetic stirring was added $NaBH_4$ (0.24 g, 6.3 mmol) in small portions until the color of the solution turned from dark red to pale yellow. The mixture was then refluxed for the time indicated in Table 1. The mixture was cooled to room temperature and treated with water (2 mL), 10% aqueous sodium hydroxide solution (2 mL), and ethyl acetate (100 mL). The organic phase was separated and washed with water (2 × 50 mL) and with saturated NaCl solution (2 × 50 mL). After drying ($MgSO_4$) and filtration, the solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate.

(*Z*)-2-Phenylethenyl-1′-butyl telluride (5):[4b] yield 1.17 g (81%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.38 (d, J = 10.7 Hz, 1H), 7.31−7.19 (m, 5H), 6.98 (d, J = 10.7 Hz, 1H), 2.71(t, J = 7.4 Hz, 2H), 1.80 (m, 2H), 1.40 (m, 2H), 0.91(t, J = 7.4 Hz, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 138.92, 136.72, 128.24, 127.49, 127.15, 105.28, 33.88, 24.86, 13.35, 8.93.

(*Z*)-3-Methyl-1,3-butadienyl 1-butyl telluride (13): yield 0.94 g (75%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 6.84 (d, J = 10.6 Hz, 1H), 6.72 (d, J = 10.6 Hz, 1H), 5.06 (s, 1H), 4.83 (s, 1H), 2.66(t, J = 7.6 Hz, 2H), 1.90 (s, 3H), 1.79 (m, 2H), 1.40 (m, 2H), 0.93(t, J = 7.6 Hz, 3H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 143.63, 138.61, 114.90, 104.40, 33.85, 24.86, 21.87, 13.33, 8.63; exact mass calcd for $C_9H_{16}Te$ 254.0314, found 254.0302.

(*Z*,*E*)-5-((Tetrahydropyranyl)oxy)-3-methyl-1,3-pentadienyl 1-butyl telluride (9): yield 1.52 g (83%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 6.83 (d, J = 10.6 Hz, 1H), 6.65 (d, J = 10.6 Hz, 1H), 5.51(t, J = 6.9 Hz, 1H), 4.68(t, J = 2.8 Hz, 1H), 4.31 (dd, J = 12.2, 5.7 Hz, 1H), 4.17 (dd, J = 12.2, 6.6 Hz, 1H), 3.92−3.85 (m, 1H), 3.55−3.45 (m, 1H), 2.65 (t, J = 7.6 Hz, 2H), 1.84 (s, 3H), 1.83−1.72 (m, 3H), 1.60−1.52 (m, 5H), 1.39 (m, 2H), 0.92(t, J = 7.6 Hz, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 139.95, 138.66, 134.92, 126.29, 103.38, 97.56, 75.03, 63.13, 62.17, 33.87, 30.60, 25.43, 24.69, 19.43, 15.84, 13.36, 8.67; exact mass calcd for $C_{15}H_{26}O_2Te$ 368.0995, found 368.0987.

(*Z*,*E*)-5-((Tetrahydropyranyl)oxy)-1,3-pentadienyl 1-butyl telluride (11): yield 1.57 g (89%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 6.81−6.77 (m, 2H), 6.25(ddt, J = 15.1, 9.3, 1.4 Hz, 1H), 5.88(dt, J = 15.1, 6.3 Hz, 1H), 4.66(t, J = 3.5 Hz, 1H), 4.29 (ddd, J = 13.2, 5.6, 1.5 Hz, 1H), 4.05 (ddd, J = 13.2, 6.6, 1.3 Hz, 1H), 3.90−3.81 (m, 1H), 3.55−3.49 (m, 1H), 2.71(t, J = 7.5 Hz, 2H), 1.89−1.69 (m, 4H), 1.66−1.46 (m, 4H), 1.39 (m, J = 7.5 Hz, 2H), 0.92(t, J = 7.5 Hz, 3H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 136.84, 132.93, 131.32, 106.03, 97.75, 67.09, 61.99, 33.98, 30.47, 25.32, 24.78, 19.27, 13.28, 6.82; exact mass calcd for $C_{14}H_{24}O_2Te$ 354.0839, found 354.0853.

(*Z*)-1-Methyl-1-penten-3-ynyl 1-butyltelluride (15):[15o] yield 0.86 g (65%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.94 (m, 1H), 2.78(t, J = 7.6 Hz, 2H), 2.22 (s, 3H), 2.00 (s, 3H), 1.78 (m, 2H), 1.41 (m, 2H), 0.93(t, J = 7.6 Hz, 3H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 128.59, 114.24, 91.50, 79.57, 34.36, 26.84, 25.07, 13.33, 4.73, 4.39.

(*Z*)-1,4-Diphenyl-1-buten-3-ynyl 1-butyl telluride (17):[15o] yield 1.44 g (74%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.66−

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7.32 (m, 10H), 6.46 (s, 1H), 2.60(t, J = 7.5 Hz, 2H), 1.68 (m, J = 7.5 Hz, 2H), 1.30 (m, J = 7.5 Hz, 2H), 0.85(t, J = 7.5 Hz, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 142.12, 137.13, 131.34, 128.29, 128.03, 123.34, 116.20, 90.36, 33.83, 24.93, 13.24, 8.86.

(*Z*)-Styryl 2-thienyl Telluride (7). Sodium borohydride (0.42 g, 11.2 mmol) was added in small portions to a flask containing dithienyl ditelluride (1.69 g, 0.4 mmol), phenyl acetylene (1.02 g, 10.0 mmol), and absolute ethanol (25 mL), under nitrogen and magnetic stirring. The color of the solution changed from dark red to pale yellow. The mixture was refluxed for 24 h, turning dark brown, and then was treated with water (3 mL) and 10% aqueous NaOH (3 mL). The mixture was diluted with ethyl acetate (100 mL) and transferred to a separatory funnel containing water (50 mL). The organic phase was separated, washed with water (50 mL), and dried with $MgSO_4$. After filtration the solvent was evaporated, and the residue was chromatographed in silica gel, eluting with hexane. For **7**: yield 1.50 g (60%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.41−7.13 (m, 7H), 7.37 (d, J = 10.4 Hz, 1H), 6.95 (d, J = 10.4 Hz, 1H), 6.91 (dd, J = 5.0, 3.6 Hz, 1H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 140.93, 136.29, 134.32, 128.89, 128.44, 127.40, 126.86, 126.01, 116.04, 111.00. Anal. Calcd for $C_{12}H_{10}$-STe C, 45.93; H, 3.21. Found: C, 46.27; H, 3.25.

Preparation of Phenylvinyl Butyl Telluride (28). To a three-necked flask equiped with a reflux condenser, dropping funnel, and nitrogen inlet were placed Mg (0.51 g, 21.0 g atom) and one crystal of I_2. The flask was flamed with a heat gun. After the flask was cooled to room temperature, a solution of the corresponding vinylic halide (4 mmol) in THF (25 mL) was added all at once. The violet color of the mixture vanished. Then a solution of the corresponding vinylic halide (16.0 mmol) in THF (25 mL) was slowly added at a rate which maintains gentle reflux. After the end of the addition the dark solution was refluxed for 30 min. The mixture was cooled to room temperature, and elemental tellurium (2.30 g, 18.0 g atom) was added. The resulting green suspension was refluxed for 30 min and then cooled to room temperature. *n*-Butyl bromide (2.50 g, 18.0 mmol) was added, and the mixture was stirred for 20 min. After this time, the reaction mixture turned yellow. The flask was immersed in an ice bath until cooled to 0 °C, and then a saturated solution of NH_4Cl (10 mL) was cautiously added. The mixture was transferred to a separatory funnel with the aid of 100 mL of ethyl acetate. After the addition of water (50 mL), the organic phase was separated, washed with saturated solution of sodium chloride (2 × 50 mL), and dried with $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel eluting with hexane. For **28**: yield 2.00 g (43%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.50−744 (m, 2H), 7.34−7.21 (m, 3H), 6.15 (s, 1H), 5.71 (s, 1H), 2.65(t, J = 7.4 Hz, 2H), 1.72 (m, J = 7.4 Hz, 2H), 1.32 (m, J = 7.4 Hz, 2H), 0.85(t, J = 7.4 Hz, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 143.31, 128.24, 127.76, 127.66, 126.38, 124.24, 33.45, 25.03, 13.32, 8.17. Anal. Calcd for $C_{12}H_{16}Te$ C, 50.06; H, 5.61. Found: C, 49.99; H, 5.78.

General Procedure for the Preparation of Vinyl Aryl Tellurides. A solution of bromine (1.60 g, 10 mmol) in benzene (10 mL) was added to a flask containing the corresponding ditelluride (10 mmol) in THF (20 mL) under N_2 at 0 °C. The dark mixture was stirred for 15 min at this temperature and then slowly transferred via cannula to a solution of vinylmagnesium bromide (22 mmol) in THF (50 mL), prepared as described above, at 0 °C. The color of the solution changed from black to yellow. After the end of the addition, the resulting solution was warmed to room temperature, stirred for 30 min, and then treated with saturated solution of ammonium chloride (150 mL). The mixture was diluted with ethyl acetate (150 mL) and transferred to a separatory funel. The organic phase was separated, washed with water (100 mL) and brine (2 × 150 mL), and dried with $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel eluting with hexane to give the corresponding telluride.

Vinyl 2-thienyl telluride (27): yield 3.33 g (70%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.49 (dd, J = 1.1, 5.2 Hz, 1H), 7.42 (dd, J = 1.1, 3.5 Hz, 1H), 7.05 (dd, J = 10.1, 17.6 Hz, 1H), 6.99 (dd, J = 3.5, 5.2 Hz, 1H), 6.25 (d, J = 10.1 Hz, 1H), 5.69 (d, J = 17.6 Hz, 1H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 141.54, 134.74, 129.00, 126.53, 111.95, 98.27.

Vinyl phenyl telluride (26): yield 1.81 g (78%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 5.81 (d, J = 10.1 Hz, 1H), 7.18 (dd, J = 17.6, 10.1 Hz, 1H), 7.15−7.27 (m, 3H); 7.34−7.49 (m, 2H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 137.88, 129.30, 128.27, 127.76, 112.66, 110.34.

A. General Procedure for the Transmetalation of Vinylic and Bis-Vinylic Tellurides with (2-Th)Cu(Bu)-(CN)Li$_2$. *n*-Butyllithium (1.35 mL of a 1.84M solution in hexane, 2.5 mmol) was added to a solution of thiophene (0.21 g, 2.5 mmol) in THF (2 mL) previously cooled to −78 °C under nitrogen. The temperature was raised to −10 °C, and the solution was stirred for 30 min. The yellow solution was transferred via cannula to another flask containing a suspension of CuCN (0.18 g, 2.0 mmol) in THF (3 mL) previously cooled to −78 °C. Heating the mixture to room temperature produced a homogeneous solution which was then cooled to −78 °C and treated dropwise with *n*-butyllithium (1.1 mL of a 1.84M solution in hexane, 2.0 mmol). The stirring was maintained for 15 min at −78 °C, and then the mixture was heated to room temperature. A solution of the bis-vinylic telluride (1.1 mmol) or the vinylic telluride (2.1 mmol) in THF (2 mL) was added. After being stirred for 1 h at room temperature, the solution containing the vinylic cuprate was ready to be reacted with the electrophile.

B. General Procedure for the Transmetalation of Vinylic and Bis-Vinylic Tellurides with Me$_2$Cu(CN)Li$_2$. Methyllithium (3.6 mL of a 1.1M solution in diethyl ether, 4 mmol) was added to a suspension of CuCN (0.18 g; 2.2 mmol) in THF (5 mL) under nitrogen at −78 °C. The colorless solution was stirred for 30 min at −78 °C and then heated to room temperature. A solution of the vinylic telluride (2.0 mmol) or of the bis-vinylic telluride (1.0 mmol) in THF (3 mL) was added, and the mixture was stirred at room temperature for 1 h. The solution containing the vinylic cuprate was then ready to be treated with the electrophile.

C. Transmetalation of Vinyl 2-Thienyl Tellurides with *n*-Bu$_2$Cu(CN)Li$_2$. To a suspension of CuCN (0.18 g, 2.0 mmol) in THF (mL) under at −78 °C was added *n*-butyllithium (2.2 mL of a 1.8 M solution in hexane, 4.0 mmol). The resulting solution was stirred for 30 min at this temperature, heated to room temperature, and then treated with the appropriate vinyl thienyl telluride (2.0 mmol) dissolved in THF (3 mL). The mixture was stirred at room temperature for 1 h and then cooled to −78 °C. The solution containing the vinylic cuprate was then ready to be used.

D. General Procedure for the Transmetalation of Bis-Vinylic Tellurides with *n*-Bu$_2$Cu(CN)Li$_2$. To a suspension of CuCN (0.18 g, 2.0 mmol) in THF (5 mL) under nitrogen at −78 °C was added *n*-butyllithium (2.2 mL of a 1.8 M solution in hexane, 4.0 mmol). The homogeneous solution was stirred for 30 min at −78 °C and then heated to room temperature. A solution of the bis-vinylic telluride (1.0 mmol) in THF (3 mL) was added, and the mixture was stirred for 15 min at room temperature. The solution was then ready to be treated with the appropriate electrophile.

Reaction of Enones with the Vinylic Telluride/R$_R$R$_T$-Cu(CN)Li$_2$ Systems. To a solution of the vinylic telluride/$R_RR_TCu(CN)Li_2$ system prepared as in A, B, C, or D cooled to −78 °C was added the appropriate enone (2.0 mmol) via syringe. The cooling bath was removed, and the mixture was stirred for 20 min at room temperature, then treated with a mixture of saturated solutions of NH_4Cl and NH_4OH (4:1), and extracted with ethyl acetate (30 mL). The organic phase was separated, washed with a saturated solution of NaCl (2 × 50 mL), and dried with $MgSO_4$. The solvent was evaporated, and the residue was chromatographed on a silica gel column eluting first with hexane to remove the diorganotelluride and then with a mixture of hexane/ethyl acetate (5:1). The R_RR_T-$Cu(CN)Li_2$ system used in each case is indicated in Table 3.

(*Z*)-6-Phenyl-5-hexen-2-one (34): yield 0.268 g (77%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.38−7.18 (m, 5H), 6.45 (d, J = 11.5 Hz, 1H), 5.66−5.53 (m, 1H), 2.68−2.53 (m, 4H), 2.13 (s, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 207.95, 137.15, 130.63, 129.94,

128.68, 128.19, 126.70, 43.59, 29.82, 22.85. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.85; H, 8.05.

(*Z*)-6-(4-Methyl phenyl)-5-hexen-2-one (35): yield 0.259 g (69%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.23−7.09 (m, 4H), 6.39 (d, J = 11.7 Hz, 1H), 5.59−5.46 (m, 1H), 2.66−2.49 (m, 4H), 2.32 (s, 3H), 2.09 (s, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 207.75, 136.25, 134.22, 129.82, 129.64, 128.76, 128.49, 43.47, 29.64, 22.79, 20.99. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.69; H, 8.52.

(*Z*)-6-(4-Chlorophenyl)-5-hexen-2-one (36): yield 0.270 g (65%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.33−7.16 (m, 4H), 6.38 (d, J = 11.7 Hz, 1H), 5.67−5.55 (m, 1H), 2.57 (d, J = 3.2 Hz, 4H), 2.14 (s, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 207.71, 135.56, 132.35, 131.31, 129.92, 128.64, 128.28, 43.31, 29.79, 22.68. Anal. Calcd for $C_{12}H_{13}ClO$: C, 69.07; H, 6.28. Found: C, 68.92; H, 6.39.

3-[(*Z*)-2-Phenyl-1-ethenyl]cyclohexanone (38): yield 0.328 g (82%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.36−7.18 (m, 5H), 6.41 (d, J = 11.5 Hz, 1H), 5.50 (dd, J = 10.3, 11.5 Hz, 1H), 3.14−2.98 (m, 1H), 2.43−1.46 (m, 8H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 209.85, 136.54, 134.63, 128.24, 128.01, 127.93, 126.52, 47.24, 40.63, 37.40, 31.19, 24.61. Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.58; H, 8.11.

3-[(*Z*)-2-(4-Methylphenyl-1-ethenyl]cyclohexanone (39): yield 0.300 g (70%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.23−7.06 (m, 4H), 6.37 (d, J = 11.5 Hz, 1H), 5.44 (dd, J = 10.0, 11.5 Hz, 1H), 3.16−2.98 (m, 1H), 2.32 (s, 3H), 2.49−1.44 (m, 8H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 210.21, 136.46, 134.22, 133.91, 128.85, 128.46, 129.16, 47.56, 40.92, 37.67, 31.52, 24.88, 20.94. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83,-92; H, 8.34.

3-**[(*Z*)-2-(4-Chlorophenyl-1-ethenyl]cyclohexanone (40):** yield 0.309 g (66%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.20 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.27 (d, J = 11.5 Hz, 1H), 5.44 (dd, J = 10.1, 11.5 Hz, 1H), 2.95−2.86 (m, 1H), 2.39−1.44 (m, 8H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 210.08, 135.55, 132.63, 129.61, 128.42, 127.52, 47.48, 40.98, 37.71, 31.49, 24.92. Anal. Calcd for $C_{14}H_{15}ClO$: C, 71.64; H, 6.44. Found: C, 71.55; H, 6.52.

3-[(*Z*)-3-(*N*-Morpholino)-1-propenyl]cyclohexanone (41): yield 0.340 g (76%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 5.37−5.19 (m, 2H), 3.25(t, J = 4.6 Hz, 4H), 2.91−2.85 (m, 2H), 2.83−2.78 (m, 1H), 2.44(t, J = 4.6 Hz, 4H), 2.20−1.89 (m, 4H), 1.72−1.47 (m, 4H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 210.53, 135.84, 125.64, 66.83, 55.44, 53.51, 47.55, 41.01, 27.49, 31.41, 25.14 exact mass for $C_{13}H_{21}NO_2$ 223.1572, found 223.1547.

4,4-Dimethyl-3-[(*Z*)-2-phenyl-1-ethenyl]cyclohexanone (43): yield 0.265 g (65%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.35−7.16 (m, 5H), 6.53 (d, J = 11.7 Hz, 1H), 5.53(t, J = 11.7 Hz, 1H), 2.97−2.83 (m, 1H), 2.51−2.22 (m, 4H), 1.85−1.46 (m, 2H), 1.09 (s, 3H), 0.90 (s, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 210.90, 137.10, 131.79, 130.58, 128.30, 128.22, 126.70, 44.83, 43.65, 39.55, 38.04, 33.04, 28.79, 19.78. Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.91; H, 9.12.

4,4-Dimethyl-3-[(*Z*)-(4-methyl phenyl)-1-ethenyl]cyclohexanone (45): yield 0.344 g (71%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.25−7.00 (m, 4H), 6.49 (d, J = 11.6 Hz, 1H), 5.49-(t, J = 11.6 Hz, 1H), 2.98−2.84 (m, 1H), 2.50−2.22 (m, 4H), 2.33 (s, 3H), 1.81−1.47 (m, 2H), 1.09 (s, 3H), 0.91 (s, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 210.88, 136.37, 134.20, 131.26, 130.47, 128.91, 128.25, 44.88, 43.68, 39.59, 38.07, 33.05, 28.80, 21.06, 19.82. Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.15; H, 9.15.

4,4-Dimethyl-3-[(*Z*)-3-(*N*-morpholino)-1-propenyl]cyclohexanone (46): yield 0.301 g (60%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 5.62−5.38 (m, 2H), 3.71(t, J = 4.7 Hz, 4H), 3.00 (d, J = 6.1 Hz, 2H), 2.70−2.57 (m, 1H), 2.42(t, J = 4.7 Hz, 4H), 2.35−2.13 (m, 3H), 1.88−1.56 (m, 3H), 1.06 (s, 3H), 0.97 (s, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 210.61, 132.43, 127.56, 66.72, 55.49, 53.47, 45.02, 43.57, 39.58, 37.91, 32.99, 28.72, 19.60. Anal. Calcd for $C_{15}H_{25}NO_2$: C, 71.67; H, 10.02; N, 5.57. Found: C, 71.61; H, 10.02; N, 5.77.

3-[(*Z*)-3-Methyl-1,3-butadienyl]cyclohexanone (49): yield 0.253 g (77%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.82 (d, J = 11.6 Hz, 1H), 5.26(t, J = 11.6 Hz, 1H), 4.94 (s, 1H), 4.82 (s, 1H), 3.11−3.04 (m, 1H), 2.40−2.04 (m, 5H), 1.85 (s, 3H), 1.78−1.65 (m, 2H), 1.57−1.46 (m, 1H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 210.61, 141.21, 133.60, 115.39, 48.09, 41.05, 37.96, 32.00, 25.07, 23.09; exact mass calcd for $C_{11}H_{16}O$ 164.1201, found 164.1196.

3-[(*Z*,*E*)-5-((Tetrahydropyranyl)oxy)-1,3-pentadienyl]-cyclohexanone (50): yield 0.324 g (61%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 6.41 (dd, J = 11.2, 16.3 Hz, 1H), 5.91(t, J = 10.9 Hz, 1H), 5.75(dt, J = 6.6, 16.3 Hz, 1H), 5.23(t, J = 10.9 Hz, 1H), 4.58 (dd, J = 3.2, 7.0 Hz, 1H), 4.23 (dd, J = 5.8, 12.9 Hz, 1H), 3.96 (dd, J = 6.6, 12.9 Hz, 1H), 3.84−3.78 (m, 1H), 3.48−3.43 (m, 1H), 2.90−2.87 (m, 1H), 2.34-1.98 (m, 6H), 1.81−1.39 (m, 8H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 210.47, 134.22, 130.67, 127.43, 126.98, 97.83, 61.18, 62.10, 47.55, 40.97, 37.59, 31.48, 30.42, 25.24, 25.06, 19.33; exact mass calcd for $C_{16}H_{24}O_3$ 265.1804, found 265.1808.

3-[(*Z*)-1,4-Diphenyl-1-buten-3-ynyl]cyclohexanone (51): yield 0.390 g (65%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.52−7.22 (m, 10H), 5.80 (s, 1H), 3.46−3.39 (m, 1H), 2.81(t, J = 13.7 Hz, 1H), 2.57−1.70 (m, 7H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 210.60, 155.51, 140.82, 131.15, 128.37, 128.30, 128.20, 127.80, 127.26, 123.18, 109.00, 96.48, 86.37, 45.82, 43.83, 41.18, 29.73, 25.75. Anal. Calcd for $C_{12}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.84; H, 6.84.

3-[(*Z*)-1-Methyl-1-penten-3-ynyl]cyclohexanone (52): yield 0.222 g (63%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.24 (s, 1H), 3.30−3.21 (m, 1H), 2.44−2.23 (m, 4H), 2.15−2.09 (m, 1H), 1.95 (s, 3H), 1.74 (s, 3H), 1.81−1.65 (m, 3H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 211.17, 150.09, 106.30, 89.30, 76.27, 45.35, 42.64, 41.18, 29.10, 25.52, 18.22, 4.41; exact mass calcd for $C_{12}H_{16}O$ 176.1201, found 176.1216.

General Procedure for the Epoxide Opening with Vinylic Telluride/(2-Th)Cu(Bu)(CN)Li$_2$ Systems. To a solution of the vinylic telluride/(2-Th)Cu(Bu)(CN)Li$_2$ system prepared as described in A, cooled to −78 °C, was added the appropriate epoxide (2.0 mmol) via syringe. In the case of the allylic epoxides, the mixture was stirred for 1 h at −78 °C and then worked up. In the other cases the cooling bath was removed and the mixture was stirred for 2 h at room temperature. In both cases the workup was performed by adding a mixture of saturated solutions of NH_4Cl and NH_4OH (4:1) and extracting with ethyl acetate (30 mL). The organic phase was separated, washed with saturated solution of NaCl (2 × 50 mL), and dried with $MgSO_4$. The solvent was evaporated, and the residue was chromatographed on silica gel eluting first with petroleum ether to remove the tellurium containing byproduct and then with petroleum ether/ethyl acetate (4:1). For entries 10−12 (Table 5) $BF_3{\cdot}Et_2O$ (0.25 mL, 2.0 mmol) was added at −78 °C prior to the addition of the epoxide, and the mixture was stirred at −78 °C for 2 h before performing the workup described above.

(*Z*)-1-Phenyl-1-octen-4-ol (61): yield 0.335 g (82%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.40−7.20 (m, 5H), 6.58 (d, J = 11.5 Hz, 1H), 5.74(dt, J = 7.4,11.5 Hz, 1H), 3.74−3.71 (m, 1H), 2.52−2.48 (m, 2H), 1.66−1.32 (m, 7H), 0.89(t, J = 5.8 Hz, 1H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 137.29, 131.45, 128.74, 128.42, 128.17, 126.72, 71.84, 36.78, 36.42, 27.81, 22.68, 14.01; exact mass calcd for $C_{14}H_{20}O$ 204.1514, found 204.1518.

(*Z*)-2,4-Diphenyl-3-buten-1-ol (63): yield 0.185 g (41%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.34−7.20 (m, 10H) 6.54 (d, J = 11.7 Hz, 1H), 5.70(dt, J = 7.0, 11.7 Hz, 1H), 4.76 (dd, J = 5.4, 7.9 Hz, 1H), 2.84−2.72 (m, 2H), 2.12 (br, 1H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 143.89, 137.12, 131.56, 128.69, 128.43, 128.15, 127.81, 127.61, 126.24, 125.86, 74.13, 38.13; exact mass calcd for $C_{16}H_{16}ONH_4$ 242.1545, found 242.1552.

(*Z*)-1,4-Diphenyl-3-buten-1-ol (64): yield 0.223 g (50%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.36−7.22 (m, 10H) 6.70 (d, J = 11.8 Hz, 1H), 5.91 (dd, J = 10.5, 11.8 Hz, 1H), 4.11−4.02 (m, 1H), 3.79−3.75 (m, 2H), 1.56 (br, 1H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 141.36, 136.79, 131.81, 131.29, 128.86, 128.63, 128.22, 127.75, 127.04, 126.85, 67.44, 46.72; exact mass calcd for $C_{16}H_{16}O$ 224.1201, found 224.1198.

(*Z*)-(1-Benzyloxy)-5-phenylpent-4-en-2-ol (72): yield 0.257 g (48%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.35−7.18 (m, 10H), 6.54 (d, J = 11.7 Hz, 1H), 5.73(dt, J = 7.4, 11.7 Hz, 1H), 4.50 (s, 2H), 3.92 (m, 1H), 3.49 (dd, J = 3.3, 9.5 Hz, 1H), 3.35 (dd, J = 7.4, 9.5 Hz, 1H), 2.53(dt, J = 1.8, 6.7 Hz, 2H), 2.54 (br, 1H);

90 MHz ^{13}C NMR ($CDCl_3$) δ 137.82, 137.14, 131.05, 128.68, 128.37, 128.12, 127.70, 127.66, 127.62, 126.66, 73.90, 73.28, 70.35, 32.38; exact mass calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1477.

(*Z*)-2-Phenyl-1-ethenyl 1-(3-benzyloxy)-2-hydroxypropyl telluride (73): yield 0.198 g (25%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.39−7.22 (m, 11H), 7.00 (d, J = 10.7 Hz, 1H), 4.55 (s, 2H), 4.05−4.00 (m, 1H), 3.59 (dd, J = 4.1, 9.4 Hz, 1H), 3.51 (dd, J = 6.3, 9.4 Hz, 1H), 2.90 (d, J = 6.3 Hz, 1H), 2.63 (br, 1H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 137.19, 128.46, 128.38, 128.16, 127.85, 127.79, 127.70, 127.48, 127.39, 105.42, 73.98, 73.39, 70.54, 13.99; exact mass calcd for $C_{18}H_{20}O_2Te$ 398.0525, found 398.0531.

(*Z*)-2-Phenyl-1-ethenyl 1-(4-benzyloxy)-2-hydroxybutyl telluride (75): yield 0.367 g (45%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.39−7.21 (m, 11H), 7.00 (d, J = 12.0 Hz, 1H), 4.53 (s, 2H), 4.20 (m, 1H), 3.76−3.53 (m, 2H), 2.92 (m, 2H), 1.96−1.70 (m, 2H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 138.70, 137.64, 136.73, 128.24, 128.18, 127.55, 127.48, 127.32, 127.13, 105.36, 73.03, 70.72, 68.21, 37.06, 19.03; exact mass calcd for $C_{19}H_{22}O_2Te$ 412.0682, found 412.0673.

Compounds **66** and **67** were separated by column chromatography on silica gel eluting with hexane/ethyl acetate (4:1).

4-[(*Z*)-2-Phenyl-1-ethenyl]cyclopent-2-en-1-ol (66): yield 0.212 g (57%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.35−7.21 (m, 5H), 6.45 (d, J = 11.3, 1H), 5.91(dt, J = 2.1, 5.5 Hz, 1H), 5.88 (ddd, J = 0.4, 1.8, 5.5 Hz, 1H), 5.36 (dd, J = 10.3, 11.3 Hz, 1H), 4.95−4.91 (m, 1H), 4.08−4.04 (m, 1H), 2.06 (ddd, J = 2.9, 7.5, 14.1 Hz, 1H), 1.97 (ddd, J = 6.9, 5.4, 14.1 Hz, 1H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 138.60, 137.12, 135.12, 133.74, 129.08, 128.64, 128.19, 126.76, 77.16, 42.86, 41.72; exact mass calcd for $C_{13}H_{14}O$ 186.1045, found 186.1041.

2-[(*Z*)-2-Phenyl-1-ethenyl]cyclopent-3-en-1-ol (67): yield 0.064 g (17%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.36−7.22 (m, 5H), 6.51 (d, J = 11.5 Hz, 1H), 5.77 (ddd, J = 5.9, 2.0, 4.1 Hz, 1H), 5.64 (ddd, J = 5.9, 2.0, 4.1 Hz, 1H), 5.37 (dd, J = 11.5, 10.4 Hz, 1H), 4.25 (m, 1H), 3.78−3.74 (m, 1H), 2.78(ddt, J = 4.0, 3.6, 17.1 Hz, 1H), 2.32(ddt, J = 1.6, 3.6, 17.1 Hz, 1H), 1.75 (br, 1H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 137.06, 132.33, 132.12, 130.08, 128.98, 128.81, 128.27, 126.89, 78.89, 53.73, 41.42; exact mass calcd for $C_{13}H_{14}O$ 186.1045, found 186.1039.

Compounds **69** and **70** were separated by column chromatography on silica gel eluting with hexane/ethyl acetate (4:1).

4-[(*Z*)-2-Phenyl-1-ethenyl]cyclohex-2-en-1-ol (69): yield 0.282 g (70%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.34−7.21 (m, 5H), 6.45 (d, J = 11.5 Hz, 1H), 5.77 (d, J = 10.0 Hz, 1H), 5.65 (d, J = 10.0 Hz, 1H), 5.42 (dd, J = 10.4, 11.5 Hz, 1H), 4.26−4.23 (m, 1H), 3.39−3.38 (m, 1H), 2.31 (br, 1H), 2.11−2.05 (m, 1H), 1.92−1.89 (m, 1H), 1.50−1.42 (m, 2H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 137.13, 135.25, 132.13, 131.26, 128.96, 128.49, 128.16, 126.70, 66.15, 34.55, 31.06, 27.32; exact mass calcd for $C_{14}H_{16}O$ 200.1201, found 200.1186.

2[(*Z*)-2-Phenyl-1-ethenyl]cyclohex-3-en-1-ol (70): yield 0.094 g (24%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.35−7.19 (m, 5H), 6.65 (d, J = 11.5 Hz, 1H), 5.75−5.70 (m, 1H), 5.50−5.42 (m, 2H), 3.65 (dd, J = 7.6, 3.1, 10.4 Hz, 1H), 3.41−3.36 (m, 1H), 2.25−2.15 (m, 2H), 2.01−1.94 (m, 1H), 1.79 (br, 1H), 1.67−1.57 (m, 1H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 136.84, 133.48, 132.01, 128.71, 128.28, 127.69, 127.36, 126.97, 72.11, 43.87, 29.27, 24.53; exact mass calcd for $C_{14}H_{16}O$ 200.1201, found 200.1191.

(*E,Z*)-1-((Tetrahydropyranyl)oxy)-3-methylundeca-2,4-dien-7-ol (78): yield 0.366 g (61%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.99 (d, J = 11.8 Hz, 1H), 5.52(t, J = 6.7 Hz, 1H), 5.44(dt, J = 7.5, 11.8 Hz, 1H), 4.65 (s, 1H), 4.31 (dd, J = 6.3, 12.5, 1H), 4.13 (dd, J = 7.3, 12.5 Hz, 1H), 3.92−3.86 (m, 1H), 3.68−3.64 (m, 1H), 3.53−3.50 (m, 1H), 2.45−2.41 (m, 2H), 1.82 (s, 3H), 1.85−1.73 (m, 3H), 1.65−1.30 (m, 10H), 0.91(t, J = 6.6 Hz, 3H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 135.96, 134.76, 126.51, 126.42, 97.89, 71.83, 63.51, 62.25, 36.65, 36.58, 30.65, 27.81, 25.44, 22.68, 19.51, 17.11, 14.00; exact mass calcd for $C_{17}H_{30}O_3$-NH_4 300.2539, found 300.2545.

(*E,Z*)-8-((Tetrahydropyranyl)oxy)-6-methyl-(1-benzyloxy)octa-4,6-dien-2-ol (79): yield 0.437 g (60%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.38−7.22 (m, 5H), 5.93 (d, J = 11.8 Hz, 1H), 5.52(t, J = 6.8 Hz, 1H), 4.09 (dd, J = 7.2, 12.6 Hz, 1H), 3.91−3.83 (m, 2H), 3.54−3.50 (m, 1H), 3.48 (dd, J = 3.4, 9.4 Hz, 1H), 3.35 (dd, J = 7.4, 9.4 Hz, 1H), 2.78 (br, 1H), 2.07(dt, J = 1.6, 5.6 Hz, 2H), 1.79 (s, 3H), 1.81−1.48 (m, 6H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 137.73, 135.68, 134.04, 128.16, 127.47, 126.19, 125.69, 97.60, 73.82, 73.08, 70.26, 63.28, 61.94, 32.45, 30.41, 25.22, 19.25, 16.85; exact mass calcd for $C_{21}H_{30}O_4NH_4$ 364.2488, found 364.2485.

(7−5)-(*E,Z*)-(9-Benzyloxy)-1-((tetrahydropyranyl)oxy)-3-methylnona-2,4-dien-7-ol (80): yield 0.484 g (64%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.36−7.26 (m, 5H), 5.95 (d, J = 11.8 Hz, 1H), 5.53(t, J = 6.5 Hz, 1H), 5.44(dt, J = 7.3, 11.8 Hz, 1H), 4.64(t, J = 3.6 Hz, 1H), 4.52 (s, 2H), 4.31 (dd, J = 6.2, 12.4 Hz, 1H), 4.11 (dd, J = 7.2, 12.4 Hz, 1H), 3.91−3.83 (m, 2H), 3.73−3.61 (m, 2H), 3.54−3.48 (m, 1H), 2.97 (br, 1H), 2.49−2.40 (m, 2H), 1.80 (s, 3H), 1.84−1.68 (m, 3H), 1.62−1.52 (m, 4H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 137.88, 135.99, 134.28, 128.39, 127.67, 127.60, 126.41, 126.31, 97.89, 73.27, 71.29, 69.01, 63.51, 62.23, 36.50, 35.92, 30.64, 25.42, 19.50, 17.08; exact mass calcd for $C_{12}H_{32}O_4NH_4$ 378.2644, found 378.2648; $[\alpha]_D$ −2.27(*c* 5.43, $CHCl_3$).

4-[(*Z,E*)-5-((Tetrahydropyranyl)oxy)-3-methyl-1,3-pentadienyl]cyclopent-2-en-1-ol (81): yield 0.322 g (61%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.88−5.79 (m, 2H), 5.53(t, J = 6.6 Hz, 1H), 5.08(t, J = 11.4, 1H), 4.91−4.89 (m, 1H), 4.65-4.63 (m, 1H), 4.36−4.30 (m, 1H), 4.18−4.04 (m, 2H), 3.92−3.86 (m, 1H), 3.55−3.49 (m, 1H), 2.52 (br, 1H), 2.04−1.97 (m, 1H), 1.82 (s, 3H), 1.92−1.69 (m, 2H), 1.61−1.51 (m, 6H); 90 M Hz ^{13}C NMR ($CDCl_3$) δ 138.52, 135.67, 133.39, 131.95, 125.83, 97.79, 76.68, 63.43, 62.03, 42.99, 41.71, 30.44, 25.24, 19.28, 16.98; exact mass calcd for $C_{16}H_{24}O_3NH_4$ 282.2069, found 282.2063.

4-[(*Z,E*)-5-((Tetrahydropyranyl)oxy)-3-methyl-1,3-pentadienyl]cyclohex-3-en-1-ol (82): yield 0.089 g (17%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.84 (d, J = 11.6 Hz, 1H), 5.72 (d, J = 10.0 Hz, 1H), 5.55 (d, J = 11.6 Hz, 1H), 5.51(t, J = 6.6 Hz, 1H), 5.13(t, J = 10.9 Hz, 1H), 4.65(t, J = 3.3 Hz, 1H), 4.33−4.28 (m, 1H), 4.23−4.20 (m, 1H), 4.15−4.08 (m, 1H), 3.91−3.86 (m, 1H), 3.53−3.50 (m, 1H), 3.36−3.34 (m, 1H), 2.82 (br, 1H), 2.08−2.03 (m, 1H), 1.89−1.69 (m, 3H), 1.80 (s, 3H), 1.60−1.32 (m, 6H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 135.82, 133.39, 132.40, 132.01, 130.82, 125.58, 97.73, 65.93, 63.35, 62.06, 34.68, 30.98, 30.44, 27.56, 25.23, 19.29, 16.94; exact mass calcd for $C_{17}H_{26}O_3NH_4$ 296.2226, found 296.2000.

(*Z*)-5-Methylundec-4-en-2-yn-7-ol (85): yield 0.241 g (67%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.32 (d, J = 1.6 Hz, 1H), 3.79−3.72 (m, 1H), 2.48 (dd, J = 8.7, 13.3 Hz, 1H), 2.31 (dd, J = 4.3, 13.3 Hz, 1H), 1.90 (s, 3H), 1.77 (s, 3H), 1.48−1.26 (m, 6H), 0.87(t, J = 6.9, 3H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 147.06, 107.88, 87.96, 77.16, 70.30, 42.39, 37.12, 27.75, 23.02, 22.59, 13.93, 4.14; exact mass calcd for $C_{12}H_{20}O$ 180.1514, found 180.1518.

(*Z*)-(1-Benzyloxy)-4-methylocta-4-en-6-yn-2-ol (86): yield 0.361 g (74%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.35−7.25 (m, 5H), 5.34 (s, 1H), 4.56 (s, 2H), 4.09−3.97 (m, 1H), 3.53 (dd, J = 3.4, 9.6 Hz, 1H), 3.42 (dd, J = 7.4, 9.6 Hz, 1H), 2.55−2.42 (m, 3H), 1.91 (d, J = 1.6 Hz, 3H), 1.81 (s, 3H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 146.29, 137.97, 128.31, 127.61, 108.05, 88.23, 77.07, 74.17, 73.25, 69.09, 38.26, 23.03, 4.22; exact mass calcd for $C_{16}H_{22}O_2$ 244.1463, found 244.1466.

(7*S*)-(*Z*)-(9-Benzyloxy)-5-methylnon-4-en-2-yn-7-ol (87): yield 0.285 g (55%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 7.36−7.25 (m, 5H), 4.52 (s, 2H), 4.05−4.02 (m, 1H), 3.76−3.72 (m, 1H), 3.68−3.63 (m, 1H), 2.94 (d, J = 3.2 Hz, 1H), 2.56−2.45 (m, 2H), 1.93 (d, J = 2.2 Hz, 3H), 1.80 (s, 3H), 1.82−1.76 (m, 4H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 146.87, 137.90, 128.32, 127.59, 127.54, 107.85, 87.89, 77.23, 73.19, 69.54, 68.84, 42.15, 36.04, 23.01, 4.25; exact mass calcd for $C_{17}H_{22}O_2$ 259.1698, found 259.1687; $[\alpha]_D$ −2.68(*c* = 4.08, $CHCl_3$).

Compounds **88** and **89** were separated by column chromatography on silica gel eluting with hexane/ethyl acetate (4:1).

4-[(*Z*)-1-Methylpent-1-en-3-ynyl]cyclopent-2-en-1-ol (88): yield 0.183 g (56%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.90(dt, J = 2.2, 5.5 Hz, 1H), 5.74 (ddd, J = 0.8, 2.2, 5.5 Hz, 1H), 5.23 (dd, J = 1.5, 2.3 Hz, 1H), 4.92−4.89 (m, 1H), 4.39−4.35 (m, 1H), 2.31 (br, 1H), 1.95−1.91 (m, 2H), 1.92 (s, 3H), 1.50 (d, J = 0.8 Hz, 3H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 150.65, 137.82, 134.49,

106.44, 88.63, 77.52, 77.00, 48.13, 38.47, 18.09, 4.45; exact mass calcd for $C_{11}H_{14}O$ 162.1045, found 162.1039; mp 63−66 °C.

2-[(*Z*)-1-Methylpent-1-en-3-ynyl]cyclopent-3-en-1-ol (89): yield 0.096 g (30%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.80 (ddd, J = 2.3, 4.5, 6.0 Hz, 1H), 5.53 (ddd, J = 2.0, 4.1, 6.0 Hz, 1H), 5.35 (dd, J = 1.6, 2.1 Hz, 1H), 4.31 (m, 1H), 4.07 (m, 1H), 2.76 [(ddd, J = 2.1, 4.1, 7.2 Hz), 2.71 (ddd, J = 2.1, 4.1, 7.2 Hz), 1H], 2.39 (m, 1H), 2.09 (d, J = 3.6 Hz, 1H), 1.97 (m, 3H), 1.61 (dd, J = 0.7, 1.4, 3H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 149.77, 130.82, 129.80, 106.69, 88.43, 77.60, 77.27, 59.05, 41.63, 19.29, 4.38; exact mass calcd for $C_{11}H_{15}O$ 163.1123, found 163.1120; mp 68−69 °C.

Compounds **90** and **91** were separated by column chromatography on silica gel eluting with hexane/ethyl acetate (4:1).

4-[(*Z*)-1-Methylpent-1-en-3-ynyl]cyclohex-2-en-1-ol (90): yield 0.139 g (39%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.79 (d, J = 10.2 Hz, 1H), 5.39(dq, J = 1.6, 10.2 Hz, 1H), 5.27 (dd, J = 1.5, 2.3 Hz, 1H), 4.28 (br, 1H), 3.70−3.65 (m, 1H), 2.20−2.14 (m, 1H), 1.97 (dd, J = 0.6, 2.3 Hz, 3H), 1.94 (br, 1H), 1.82−1.78 (m, 1H), 1.63 (dd, J = 0.6, 1.3 Hz, 3H), 1.55−1.49 (m, 2H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 151.96, 132.27, 131.82, 106.23, 88.40, 76.73, 67.01, 40.20, 32.47, 25.23, 18.76, 4.37; exact mass calcd for $C_{12}H_{16}O$ 176.1201, found 176.1206; mp 82−83 °C.

2-[(*Z*)-1-Methylpent-1-en-3-ynyl]cyclohex-3-en-1-ol (91): yield 0.115 g (33%); 360 MHz ^{1}H NMR ($CDCl_3$) δ 5.77−5.73 (m, 1H), 5.49(t, J = 1.0 Hz, 1H), 5.30 (d, J = 9.9 Hz, 1H), 3.72−3.61 (m, 2H), 2.20−2.17 (m, 2H), 2.08−2.03 (m, 2H), 1.96 (s, 3H), 1.70 (s, 3H), 1.73−1.64 (m, 1H); 90 MHz ^{13}C NMR ($CDCl_3$) δ 149.24, 127.93, 127.27, 109.00, 88.86, 76.64, 69.40, 49.32, 30.46, 24.95, 18.61, 4.33; exact mass calcd for $C_{12}H_{16}O$ 176.1201, found 176.1207.

General Procedure for the Coupling Reaction between Vinylic Tellurides and 30. To a suspension of CuCN (0.18 g, 2.0 mmol) in THF (5 mL), under nitrogen and cooled to −78 °C, was added *n*-BuLi (2.2 mL of a 1.8 M solution in hexane, 4.0 mmol). The formed homogeneous solution was stirred for 30 min at −78 °C. Then the cooling bath was removed, and the mixture was allowed to reach room temperature. A solution of the bis-vinylic telluride (1.00 mmol) in THF (3 mL) was then added, and the mixture was stirred for 15 min at room temperature and then refluxed for additional 1.5 h. The heating source was removed, and the mixture was cooled to room temperature, treated with saturated solution of NH_4Cl (10 mL), and diluted with ethyl acetate (30 mL). The organic phase was separated and washed with a 2% solution of sodium hypochlorite (2 × 30 mL) and then with a saturated solution of NaCl (50 mL). The organic phase was dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel eluting with hexane.

(*Z*)-1-Phenyl-1-hexene (53): yield 0.220 g (69%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.34−7.17 (m, 5H), 6.39 (d, J = 11.6 Hz, 1H), 5.65(dt, J = 11.6, 6.9 Hz, 1H), 2.32 (dd, J = 6.9, 13.4 Hz, 2H), 1.50−1.28 (m, 4H), 0.88(t, J = 6.8 Hz, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) δ 137.83, 133.16, 128.74, 128.44, 128.08, 126.38, 32.18, 29.75, 22.44, 13.97; HRMS calcd 160.1252, found 160.1250.

(*Z*)-1-(4-Methyl phenyl)-1-hexene (54): yield 0.174 g (50%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.14(AA′BB′ system, J_{AB} = 8.2 Hz, Du = 12.9, 4H), 2.32 (s, 3H), 2.37−2.27 (m, 2H), 1.54−1.25 (m, 4H), 0.89(t, J = 6.9 Hz, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) 136.00, 134.98, 132.46, 128.78, 128.66, 128.55, 32.21, 28.39, 22.43, 21.11, 13.96; HRMS calcd 174.1408, found 174.1415.

(*Z*)-1-(4-Chlorophenyl)-1-hexene (55): yield 0.260 g (67%); 200 MHz ^{1}H NMR ($CDCl_3$) δ 7.10(AA′BB′ system, J_{AB} = 8.5 Hz, Du = 19.7, 4H), 6.21 (d, J = 11.6 Hz, 1H), 5.54(dt, J = 11.6, 7.3 Hz, 1H), 2.16 (dd, J = 7.3, 13.8 Hz, 2H), 1.37−1.15 (m, 4H), 0.77(t, J = 6.9 Hz, 3H); 50 MHz ^{13}C NMR ($CDCl_3$) 136.15, 133.75, 132.05, 129.99, 127.50, 127.33, 31.98, 28.24, 22.33, 13.87; HRMS calcd 194.0862, found 194.0875.

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Supporting Information Available: ^{1}H NMR spectra (58 pages) This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; see any current masthead page for ordering information.

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