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Chalcogen electrophile induced rearrangement of 1-alkynyltrialkyl borates: controlled syntheses of trisubstituted olefins from 1-alkynes

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Abstract—The reaction of 1-alkynyltrialkyl borates with sulfenyl, selenenyl and tellurenyl halides produces β-chalcogeno alkenylboranes in good yields, with a *cis* relationship between the boron and the chalcogen moities. Protodeborylation of these compounds by acetic acid, or by a transmetalation–protonolysis sequence, leads to vinyl chalcogenides, which can be converted to alkenes by means of a nickel catalyzed coupling with Grignard reagents. Since the last two steps occur with retention of the stereochemistry, the overall sequence represents a highly regio- and stereoselective olefin synthesis.

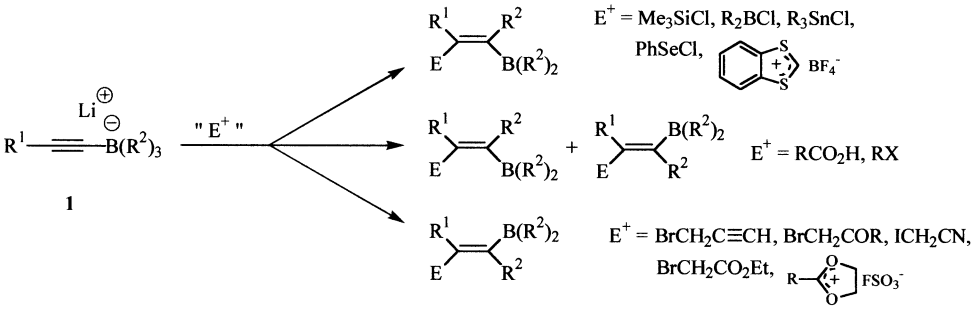
1. Introduction

A fair number of methods have become available for the generation of variously substituted vinylmetallic intermediates.[1] One of these methods, i.e. the electrophile induced rearrangement of 1-alkynyltrialkyl borates **1**,[2] leads to vinylboranes that have proved to be quite versatile intermediates in organic synthesis[3] (Scheme 1). However, it has appeared that, depending on the electrophile used to trigger the rearrangement, the alkenylboranes formed can be stereochemically homogeneous or mixtures of stereoisomers. This in turn is most relevant to the stereochemistry of the final olefinic product and to the synthetic usefulness of the whole process.

It has been shown that electrophiles like trimethylchlorosilane,[4] dialkylchloroboranes,[2a] trialkyltin chlorides,[5] benzeneselenenyl chloride,[5a,6] benzodithiolium tetrafluoroborate[7] induce the rearrangement in such a way that the migrating group of the starting 1-alkynyltrialkyl borates and the entering electrophile end up on opposite (*trans*) sides of the emerging vinylboranes.

On the other hand, rearrangements mediated by some so called 'complex' alkylating agents[8] like propargyl bromide, iodoacetonitrile, α-bromo ketones and esters, as well as 2-alkyl-1,3-dioxolanium salts[9] lead to the reverse double bond configuration. Still other electrophiles, such as the proton of carboxylic acids[10] and common alkylating agents[11] produce mixtures of olefins after protodeborylation of the intermediate alkenylboranes, the reactions of thexyldialkylalkynyl borates being considerably more stereoselective.[12]

Even though chalcogen electrophiles are known to react with olefinic and acetylenic systems, they have not



Scheme 1.

Keywords: olefin synthesis; alkynyltrialkyl borate; rearrangement; vinyl boranes; vinyl sulphides; vinyl selenides; vinyl tellurides.
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attracted much attention in relation with the rearrangement of 1-alkynyltrialkyl borate salts. Hooz and Mortimer have reported that the reaction of lithium 1-hexynyltriethyl borate with benzenesulfenyl chloride led to a stereoisomeric mixture of vinyl sulfides after hydrolysis,[5a] whereas the reaction of lithium 1-hexynyltricyclopentyl borate with benzeneselenenyl chloride was suggested to place the migrating cyclopentyl and the entering selenenyl groups *trans* to each other.[6]

Therefore, we have decided to reinvestigate more thoroughly the title reaction in the presence of chalcogen electrophiles with the primary aim of ascertaining its stereochemistry. Additionally, we felt that the now well documented transition metal catalyzed reactions of the vinylic intermediates flanked by two different heteroatomic moieties should allow to construct highly substituted alkenes in a fully controlled fashion.

In this paper we wish to report details of our results on the highly regio- and stereoselective synthesis of trisubstituted olefins[13] using this methodology.

2. Results and discussion

In view of establishing their efficiency and stereochemical outcome, the rearrangements of various 1-alkynyltrialkyl borates have been carried out in the presence of different chalcogenyl halides (S, Se, Te). As shown in Scheme 2, the reactions proceeded smoothly under mild conditions.

The yields stated are those in purified products (by column chromatography or by distillation). Vinylic boron-chalcogene derivatives **2a**–**e** are stable crystalline solids; **2f** is a stable liquid, and **2g** is an unstable, air-sensitive liquid. It is also noteworthy that in all cases the rearrangement occurred cleanly; side reactions such as (i) α-attack of the electrophiles on the triple bond, (ii) attack on the R^2 groups or (iii) *syn* elimination leading to internal alkynes R^1–CC–R^2 have not been observed or have taken place to negligible extents. Thus, only trace amounts of 1-(phenylseleno)- and 1-(phenyltelluro)-1-heptyne, as well as *n*-pentylcyclohexylacetylene could be detected in the corresponding crude products (Scheme 2, entries 4 and 5).

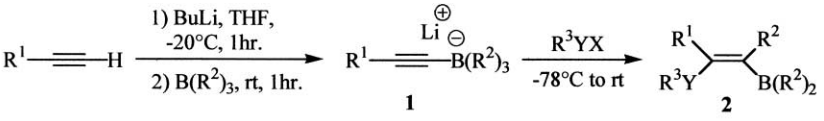
Furthermore, it has appeared for the first time that tellurenyl halides[14] can induce the reaction with comparable efficiency (Scheme 2, entry 5) to that of their sulfenyl and selenenyl analogs. The interesting chemistry of vinyl tellurides described in recent years[15] confers particular significance to this finding.

Good quality monocrystals of compounds **2b**–**e** could be grown from chloroform solutions, which allowed us to determine their structure by X-ray crystallography.[16] Most gratifyingly, in all four cases the migrating alkyl group and entering chalcogen moiety exhibit *trans* stereochemical relationships (as depicted in Scheme 2). This is an important starting point for our inquiry of the synthetic usefulness of the rearrangement.

In subsequent work we have not attempted to isolate the intermediate vinylic boron-chalcogen compounds **2**; instead, we have subjected them to protodeborylation in a one pot sequence leading to the 1,2-disubstituted vinyl chalcogenides (sulfides, selenides, tellurides) **3**.

It can be seen in Scheme 3 that as long as R^2 is a primary alkyl group, all the alkenylboranes readily underwent protonolysis of the carbon–boron bond by means of acetic acid, whereas those bearing secondary alkyl or cycloalkyl groups on boron appeared very resistant to protonolysis. Thus, refluxing alkenylborane **2b** overnight in THF in the presence of 3 equiv. of acetic acid left it essentially unchanged. This observation, as well as similar ones made by others[17] contrast with the reportedly easy and efficient protonolysis of analogous α-halogeno alkenylboranes.[18]

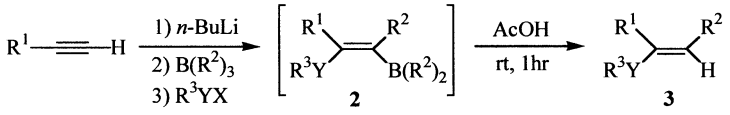
In spite of its efficiency, protodeborylation of β-(phenylthio)- and β-(butylthio) alkenylboranes **2** (R^2= primary alkyl) was found extremely sensitive to the way the work-up was conducted, in the sense that aqueous work-up (i.e. quenching the reaction mixture with aqueous



Entry	R^1	R^2	R^3YX	Yield (%)	
1	Bu	*c*-Hex	PhSCl	**2a**	71
2	Pent	*c*-Hex	PhSCl	**2b**	84
3	Pent	*c*-Hex	BuSCl	**2c**	72
4	Pent	*c*-Hex	PhSeCl	**2d**	72[a]
5	Pent	*c*-Hex	PhTeI	**2e**	69[a]
6	Bu	*s*-Bu	BuSCl	**2f**	80
7	Bu	Et	PhSCl	**2g**	79

a) Small amounts of R^1-CC-YR^3 and R^1-CC-R^2 were also formed.

Scheme 2.



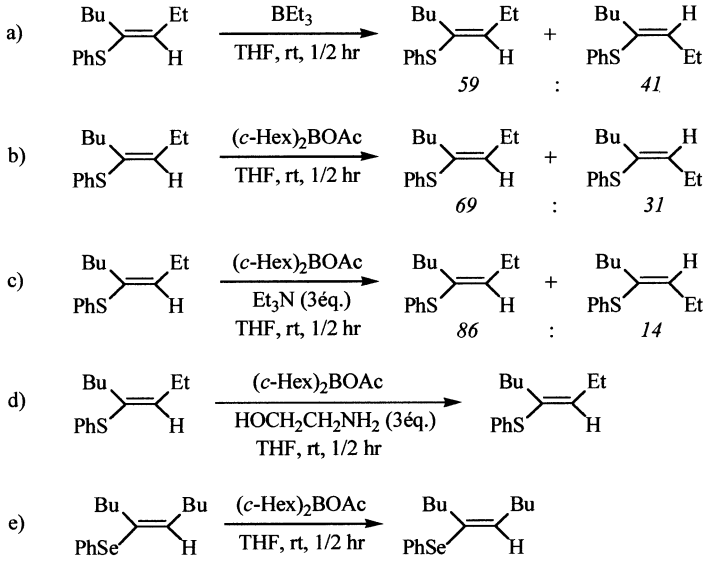
Entry	R^1	R^2	R^3YX	Method[a]		Yield (%)
1	Bu	Et	PhSCl	A	**3g**	74[b]
2	Bu	Bu	PhSCl	A	**3h**	73[c]
3	Ph	Et	PhSCl	A	**3i**	70
4	THPO-CH_2-CH_2	Et	PhSCl	A	**3j**	69
5	Pent	*c*-Hex	PhSCl	-	**3b**	-
6	Pent	Et	BuSCl	A	**3k**	83
7	Pent	Hex	PhSeCl	B	**3l**	65
8	Bu	Bu	PhSeCl	B	**3m**	81
9	Pent	Et	PhTeI	B	**3n**	62
10	Bu	Et	BuTeBr	B	**3o**	70

a) A: Non-aqueous work-up; ethanolamine was added after the protodeborylation was achieved ; B: aqueous work-up (see experimental part). b) Protodeborylation was carried out at 60°C. c) This vinyl sulfide appeared very sensitive towards isomerisation on standing.

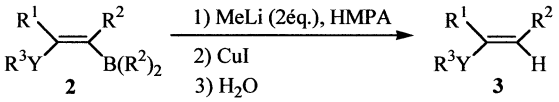
Scheme 3.

sodium bicarbonate) invariably led to more or less extensively isomerized vinyl sulfides **3**. On the contrary, when triethylamine, or better ethanolamine[19] was used to quench the reaction mixture (see Section 3), the stereochemical integrity of the products was completely preserved (*E*/*Z*>98:2 in all cases). In fact, occasionally the triethylamine-based procedure gave more capricious results than that using ethanolamine. In this regard we have noticed that in the former case the crude products still contained large amounts of borane by-products, whereas the ethanolamine treatment led to crude products essentially free of borane. This observation suggested that the borane by-products of the acetic acid mediated protodeborylations, namely acetoxydialkyl boranes, might have caused the isomerization of vinyl sulfides **3**. The experiments shown in Scheme 4 lend strong support to this hypothesis; however, we have not further investigated the mechanism of the isomerizations. Interestingly, this problem of isomerization during aqueous work-up was not encountered in the protodeborylation of β-seleno- and β-telluro vinyl derivatives **2**; indeed, (*E*)-5-(phenylseleno)-5-decene appeared insensitive to the presence of acetoxydicyclohexylborane (Scheme 4e).

In as much as it can be inferred from the X-ray structures that the rearrangements follow the same stereochemical course in all the cases, and if the protodeborylation of compounds **2** occurs as usual[3a,17,18] with retention of



Scheme 4.



Entry	R^1	R^2	R^3Y	conditions		Yield (%)
1	Bu	*c*-Hex	PhS	1) MeLi, 0°C, 30min 2) CuI, -30°C, 30min, 0°C, 1hr 3) H_2O	**3a**	55[a]
2	Bu	*c*-Hex	PhS	1) MeLi, -23°C, 30min 2) CuI, -23°C, 3hr 3) H_2O	**3a**	74[b]
3	Bu	*c*-Hex	PhS	1) MeLi, -33°C, 30min 2) CuI, -33°C, 3hr 3) H_2O	**3a**	81[c]
4	Pent	*c*-Hex	BuS	1) MeLi, -23°C, 30min 2) CuI, -23°C, 3hr 3) H_2O	**3c**	86
5	Bu	*s*-Bu	BuS	"	**3f**	80
6	Bu	*c*-Hex	PhSe	"	**3d**	0[d]

a) 23% (NMR yield) of BuCC*c*Hex recovered; b) 9% (isolated yield) of BuCC*c*Hex recovered; c) Traces of BuCC*c*Hex detected in the crude product; d) Quantitative yield of PentCC*c*Hex.

Scheme 5.

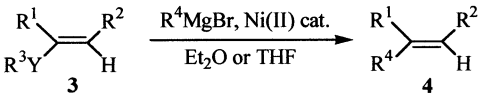
stereochemistry, vinyl chalcogenides **3** should have the structures shown in Scheme 3. These assumptions have been comfirmed by NOE measurements carried out on (*E*)- and (*Z*)-5-phenyl-5-decene prepared from (*E*)- and (*Z*)-5-(phenylthio)-5-decene, respectively (vide infra).

As mentioned above, the sterically hindered vinyl boranes **2** (R^2=secondary alkyl or cycloalkyl) were found reluctant towards protonolysis of the C–B bond without prior activation of the boron moiety. This latter can be achieved in several ways among which the most efficient one is the boron to copper transmetallation sequence.[17,20,21] A few examples of this procedure applied to β-(phenylthio)- or β-(butylthio) alkenylboranes are shown in Scheme 5.

Two factors have appeared to play an important role in the efficiency of this process; both of them are related to the *syn* elimination of the boron and chalcogen moieties producing the undesired internal alkynes R^1–CC–R^2. This elimination can take place either at the stage of the first formed β-chalcogeno alkenylborate intermediates (eventually in equilibrium with the corresponding vinyllithiums), or at the next formed β-chalcogeno alkenylcopper (or cuprate) derivatives. In any event, it proceeds faster at higher temperatures and with better chalcogen leaving groups. Thus, in the case of β-(phenylthio) alkenylborane **2a** decreasing the reaction temperature to −33°C leads to substantial increase in the yields of vinyl sulfide **3a** and to a concomitant decrease in the yields of the elimination product, that is butylcyclohexylacetylene (Scheme 5, entries 1–3). Due to the lower propensity of the β-(butylthio) derivatives **2c** and **2f** to undergo the *syn* elimination reactions, their protodeborylations took place in high yields at −23°C without formation of the corresponding internal alkynes (Scheme 5, entries 4 and 5). By contrast, the β-(phenylseleno) compound **2d** led to quantitative production of pentylcyclohexylacetylene even at −33°C (Scheme 5, entry 6). At lower temperatures the boron to copper transmetallation did not occur.

The last step in the synthesis of the targetted trisubstituted alkenes was the conversion of the vinyl chalcogenides (S, Se, Te) **3** into olefins **4**.

As shown in Scheme 6, a straightforward way of doing this conversion is the now well documented[22] nickel catalyzed coupling of **3** with Grignard reagents. Even though the overall results are quite satisfactory, these transformations, like other transition metal catalyzed coupling reactions, have appeared very sensitive to the structure of the phosphine ligand. It was found initially[22a,b] that bis(triphenylphosphino)nickel chloride was an appropriate catalyst precursor; however, later work has revealed that ligands such as bis-(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)propane (dppp) gave higher yields and better stereoselectivities.[22c–e] Our observation is also that dppe is a good ligand for all the couplings involving vinyl sulfides (Scheme 6, entries 1–7). One can notice, however, that different relative amounts of Grignard reagents may be necessary to obtain satisfactory yields. Thus, while the couplings of phenylvinyl sulfides with phenylmagnesium bromide required at least 2 equiv. of the latter reagent[22a] (Scheme 6, entries 1–4), the reaction of butylvinyl sulfide with 1.5 equiv. of phenylmagnesium bromide took place with excellent yield (Scheme 6, entry 5). Nevertheless, coupling of the same butylvinyl sulfide occurred efficiently only in the presence of a large excess of butylmagnesium bromide (Scheme 6, entries 6 and 7).



Ent.	R^1	R^2	R^3Y	R^4MgBr (éq.)	Conditions		Yield(%)
1	Bu	Bu	PhS	PhMgBr (2,2)	$NiCl_2$(dppe) (4%), Et_2O, rt, 15hr	**4a**	78[a]
2	Bu	Et	PhS	PhMgBr (2,2)	$NiCl_2$(dppe) (3%), Et_2O, rt, 16hr	**4b**	87[a]
3	Bu	Et	PhS	CH_2=CH-$(CH_2)_3$MgBr (2,2)	$NiCl_2$(dppe) (3%), Et_2O, rt, 15hr	**4c**	76[a]
4	Bu	Et	PhS	BuMgBr (2,4)	$NiCl_2$(dppe) (3%), Et_2O, rt, 15hr	**4d**	88
5	Pent	Et	BuS	PhMgBr (1,5)	$NiCl_2$(dppe) (3%), Et_2O, rt, 14hr	**4e**	82[a]
6	Pent	Et	BuS	BuMgBr (1,5)	$NiCl_2$(dppe) (3%), Et_2O, rt, 15hr	**4f**	46[b,c]
7	Pent	Et	BuS	BuMgBr (5)	$NiCl_2$(dppe) (3%), Et_2O, rt, 15hr	**4f**	73[b]
8	Pent	Hex	PhSe	PhMgBr (2,5)	$NiCl_2(PPh_3)_2$ (4%), Et_2O, rfx, 14hr	**4g**	68[a]
9	Bu	Bu	PhSe	MeMgBr (2,5)	$NiCl_2$(dppe) (3%) Et_2O, rt, 15hr	**4h**	0
10	Pent	Hex	PhSe	MeMgBr (2,5)	$NiCl_2$(dppp) (5%) Et_2O, rfx, 8hr	**4i**	61[b]
11	Bu	Bu	PhSe	BuMgBr (2,5)	$NiCl_2$(dppp) (3%) Et_2O, rfx, 14hr	**4j**	30
12	Pent	Et	PhTe	PhMgBr (2,5)	$NiCl_2(PPh_3)_2$ (5%), THF, rfx, 3hr	**4e**	77[d]

a) $E/Z > 97/3$; b) $E/Z < 3/97$; c) 33% starting material recovered; d) E/Z : 9/1.

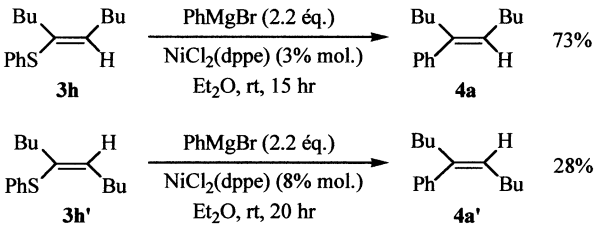
Scheme 6.

Regarding the nickel catalyzed coupling process, vinyl selenides and tellurides display much similarity to vinyl sulfides.[22j–p] In agreement with earlier findings[22j] by Takei et al. we have observed for the coupling of phenylvinyl selenides: (i) efficient reaction with PhMgBr in the presence of $NiCl_2(PPh_3)_2$ (Scheme 6, entry 8). This catalyst has also been found to perform satisfactorily in the couplings of methylvinyl selenides with trimethylsilylmethylmagnesium chloride[22k] (but in those cases use of dimethoxyethane as solvent was necessary). (ii) while $NiCl_2$(dppe) was totally ineffective for the reaction with methylmagnesium bromide, the coupling took place in the presence of $NiCl_2$(dppp) (Scheme 6, entries 9,10). (iii) The reaction with butylmagnesium bromide gave low yields (Scheme 6, entry 11) even in the presence of $NiCl_2$(dppp), in spite of the reportedly good performance[22j] of this catalyst under comparable circumstances. Presumably, in this case the undesired β-hydride elimination at the Ni-butyl moiety is an efficient competitor of the coupling reaction.

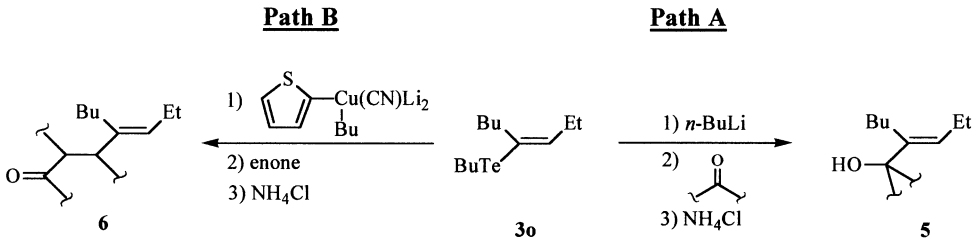
At this stage it was appropriate to check the structure of olefins **4**, especially their stereochemistry. This has been done by NMR spectroscopy (DiffNOE technique) in the case of 5-phenyl-5-decene. The (*E*) and (*Z*) stereoisomers of this olefin have been prepared from (*E*)- and (*Z*)-5-(phenylthio)-5-decene **3h** and **3h′** (themselves obtained through protodeborylation of the intermediate with acetic acid followed by aqueous work-up (Method B; see Section 3), and chromatographic separation), respectively, according to Scheme 7.

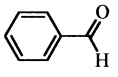
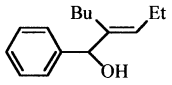
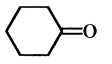
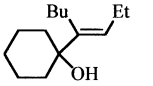
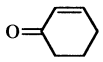
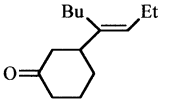
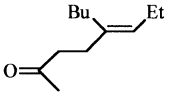
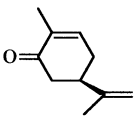
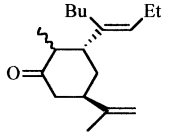
The characteristic ^1H NMR resonances of these olefins (see also Section 3) are (i) for (*E*)-5-phenyl-5-decene **4a**: 5.63 ppm (t, J=7.3 Hz, olefinic proton), 2.48 ppm (t, J=7.1 Hz, allylic CH_2 *trans* to the olefinic proton), 2.19 ppm (q, J=7.3 Hz, allylic CH_2 *trans* to the phenyl group) and (ii) for (*Z*)-5-phenyl-5-decene **4a′**: 5.42 ppm (t, J=7.3 Hz, olefinic proton), 2.31 ppm (t, J=7.0 Hz, allylic CH_2 *cis* to the olefinic proton), 1.91 ppm (q, J=7.3 Hz, allylic CH_2 *cis* to the phenyl group). In the DiffNOE spectrum (resulting from irradiation of the olefinic proton) of the former compound all signals vanish except those of the phenyl multiplet and of the allylic quartet, witnessing for the (*E*) stereochemistry of the double bond, whereas the same kind of difference spectrum of the latter olefin shows only the two allylic multiplets, indicating (*Z*) stereochemistry.

Finally, vinyl tellurides have been converted into the target olefins in two ways: (i) phenylvinyl tellurides such as **3n** (Scheme 3) smoothly underwent the nickel catalyzed coupling with Grignard reagents[22m,n] (Scheme 6, entry 12), and (ii) based on extensive studies of tellurium–metal



Scheme 7.



Path	Carbonyl compound	Product	Yield (%)
A		 (**5a**)	73
A		 (**5b**)	70
B		 (**6a**)	63
B		 (**6b**)	59
B		 (**6c**)	65

Scheme 8.

exchange reactions,[15] butylvinyl telluride **3o** have been transformed into functionalized olefins **5** and **6** according to Scheme 8.

It has been shown by Comasseto and coworkers that, on treatment with butyllithium, arylvinyl tellurides gave mixtures of aryl- and vinyllithiums, whereas under similar conditions alkylvinyl tellurides produce the corresponding vinyllithiums in good yields and with retention of stereochemistry.[15a,d] In our case, the vinyllithium formed from **3o** gave the allylic alcohols **5a** and **5b** in good yields on reaction with benzaldehyde and cyclohexanone, respectively (Scheme 8, Path A). On the other hand, cleavage of the C_{vinyl}–Te bond of **3o** by means of a higher order cyanocuprate[15c,d,f–i,23] gave the corresponding vinylcuprate which underwent clean Michael additions to α,β-unsaturated ketones to produce γ,δ-unsaturated ketones **6a–c** (Scheme 8, Path B).

In conclusion, the great stereoselectivity of the title process combined with an appropriate choice of reagent at each step leads to a flexible trisubstituted olefin synthesis.

3. Experimental

3.1. General

All glassware, syringes and needles were oven dried at 120°C for several hours prior to use. The glasswares were assembled while hot and cooled under a stream of argon. Melting points were recorded on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H (400 and 90 MHz) and ^{13}C (100.4 and 22.5 MHz) NMR spectra were recorded on either a JEOL JNM EX-400 or a JEOL JNM EX-90 with $CDCl_3$ as solvent and Me_4Si as internal standard. IR spectra were recorded on a BIORAD FTS-165 spectrometer. Elemental analysis were carried out using a Carlo-Erba NA 1500 C, H, N analyser. Low resolution mass measurements were carried out using a Hewlett–Packard HP6890 GC-MS instrument (ionization potential: 70 eV); relative intensities of the ions are given in parentheses. High resolution mass spectra were recorded on a Micromass AutoSpec 6F mass spectrometer. Merck silica gel 9385 (0.040–0.063 mm) and 5111 (0.015–0.040 mm) and Aldrich basic aluminum oxide (~150 mesh) were used for column chromatography. THF and Et_2O were distilled from sodium/benzophenone. HMPA was distilled from CaH_2. 1-Hexyne, 1-heptyne, phenylacetylene, 3-butyn-1-ol, 5-bromo-1-pentene, benzaldehyde, cyclohexanone, cyclohexenone, methyl vinyl ketone, (*R*)-(−)-carvone and thiophene were purchased from Aldrich and distilled prior to use. The other reagents were purchased from Aldrich and used without further purification, except trihexylborane, tricyclohexylborane, benzenesulfenyl chloride, butylsulfenyl chloride, phenyltellurenyl iodide, butyltellurenyl iodide and 4-((tetrahydropyranyl)oxy)-1-butyne, which were synthesized according to the reported procedures.

3.1.1. Representative procedure for the synthesis of secondary dialkyl alkenyl boranes. Preparation of (*E*)-1-cyclohexyl-1-(dicyclohexylboryl)-2-(phenylthio)-1-hexene (2a). A 100 ml two-necked flask, equipped with an argon inlet and a magnetic stirring bar, was charged with a THF solution (15 ml) of 1-hexyne (0.822 g; 10 mmol). *n*-Butyllithium (6.25 ml of a 1.6 M solution in hexane; 10 mmol) was added at −20°C. After 1 h of stirring at −20°C, freshly prepared tricyclohexylborane (20 ml of a 0.5 M solution in THF; 10 mmol) was introduced and the reaction mixture was allowed to warm to room temperature for 1 h. After cooling to −78°C, a THF solution (20 ml) of benzenesulfenyl chloride (1.445 g; 10 mmol) was added dropwise. The cooling bath was then removed and the mixture was stirred for 30 min at room temperature. The solution was diluted with 50 ml of Et_2O, washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (silica gel; pentane) to afford 3.205 g (71% yield) of **2a** as a viscous colorless liquid, which crystallized on standing. Mp 70–72°C; IR (KBr): 3061, 2926, 2851, 1584, 1478, 1446, 738, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=6.8 Hz), 1.05–1.35 (19H, m), 1.45–1.86 (17H, m), 2.25 (2H, t, J=7.8 Hz), 2.36 (1H, m), 7.11–7.26 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.4, 26.2, 26.8, 27.1, 28.3, 28.5, 29.7, 29.9, 30.4, 31.1, 32.6, 36.0, 42.3, 123.3, 125.4, 127.5, 128.5, 136.9; MS (EI): 450 (M^+, 3), 367 (100), 361 (22), 285 (48), 279 (11), 257 (6), 203 (16), 175 (13), 135 (12), 55 (8).

3.1.2. (*E*)-1-Cyclohexyl-1-(dicyclohexylboryl)-2-(phenylthio)-1-heptene (2b). The same procedure as for the preparation of **2a** was duplicated, using 1-heptyne. Column chromatography (silica gel; pentane) afforded **2b** as a white solid (84% yield) which could be recrystallized from $CHCl_3$. Mp 85–86°C; IR (KBr): 3060, 2924, 2846, 2776, 1584, 1478, 1444, 735, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, J=6.8 Hz), 1.09–1.29 (21H, m), 1.46–1.86 (17H, m), 2.24 (2H, t, J=7.8 Hz), 2.36 (1H, m), 7.10–7.26 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.5, 26.2, 26.8, 27.1, 28.3, 28.5, 28.5, 29.7, 29.9, 30.5, 31.5, 32.6, 36.0, 42.3, 123.3, 125.4, 127.6, 128.5, 136.9, 168.6; MS (EI): 464 (M^+, 4), 381 (100), 299 (96), 271 (23), 217 (34), 189 (51), 135 (59), 121 (31), 55 (34); Anal. Calcd for $C_{31}H_{49}BS$: C, 80.14; H, 10.63. Found: C, 80.00; H, 10.81.

3.1.3. (*E*)-2-(Butylthio)-1-cyclohexyl-1-(dicyclohexylboryl)-1-heptene (2c). The same procedure as for the preparation of **2a** was duplicated, using 1-heptyne and butylsulfenyl chloride. Column chromatography (silica gel; pentane) afforded **2c** as a white solid (72% yield) which could be recrystallized from $CHCl_3$. Mp 56–57°C; IR (KBr): 2919, 2846, 2769, 1600, 1444 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.90 (6H, m), 1.15–1.69 (42H, m), 2.10–2.27 (3H, m), 2.53 (2H, t, J=7.1 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$):δ 13.7, 14.1, 22.2, 22.6, 26.3, 26.9, 27.4, 28.1, 28.5, 28.8, 29.8, 30.0, 30.5, 31.5, 31.6, 32.7, 33.6, 34.9, 41.6, 126.0, 162.8; MS (EI): 444 (M^+, 3), 361 (100), 279 (47), 271 (8), 189 (15), 149 (8), 83 (6), 57 (7); Anal. Calcd for $C_{29}H_{53}BS$: C, 78.34; H, 12.01. Found: C, 78.08; H, 12.67.

3.1.4. (*E*)-1-Cyclohexyl-1-(dicyclohexylboryl)-2-(phenylseleno)-1-heptene (2d). The same procedure as for the preparation of **2a** was duplicated, using 1-heptyne and phenylselenenyl chloride. Column chromatography (silica gel; pentane) afforded **2d** as a white solid (72% yield) which could be recrystallized from $CHCl_3$. Mp 100–101°C; IR (KBr): 3059, 2926, 2847, 2776, 1580, 1477, 1445, 732, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=6.8 Hz), 1.07–1.31 (21H, m), 1.50–1.86 (17H, m), 2.33 (2H, t, J=7.6 Hz), 2.37 (1H, m), 7.14–7.31 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 26.2, 26.9, 27.1, 28.3, 28.6, 29.1, 30.2, 30.3, 31.4, 32.3, 32.7, 36.1, 43.2, 122.5, 126.0, 128.8, 130.0, 132.8, 167.8; MS (EI): 512 (M^+, 2), 429 (63), 347 (21), 240 (39), 189 (38), 158 (88), 55 (100); Anal. Calcd for $C_{31}H_{49}BSe$: C, 72.79; H, 9.66. Found: C, 73.53; H, 9.53.

3.1.5. (*E*)-1-Cyclohexyl-1-(dicyclohexylboryl)-2-(phenyltelluro)-1-heptene (2e). The same procedure as for the preparation of **2a** was duplicated, using 1-heptyne and phenyltellurenyl iodide. Column chromatography (silica gel; pentane) afforded **2e** as a pale yellow solid (69% yield) which could be recrystallized from $CHCl_3$. Mp 98–99°C; IR (KBr): 3055, 2926, 2846, 2774, 1575, 1474, 1443, 725, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, J=6.8 Hz), 1.08–1.33 (21H, m), 1.50–1.89 (17H, m), 2.39–2.43 (3H, m), 7.17 (3H, m), 7.47 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$):δ 14.1, 22.6, 26.3, 27.0, 27.2, 28.3, 28.7, 30.2, 30.9, 31.1, 31.2, 32.8, 34.6, 35.8, 45.3, 111.1, 116.9, 126.9, 129.0, 135.2; MS (EI): 562 (M^+, 16), 479 (100), 395 (17), 273 (34), 265 (22), 189 (10), 179 (29), 195 (10), 83 (10); Anal. Calcd for $C_{31}H_{49}BTe$: C, 66.47; H, 8.82. Found: C, 67.18; H, 9.02.

3.1.6. (*E*)-4-(Di-*sec*-butylboryl)-5-(butylthio)-3-methyl-4-nonene (2f). The same procedure as for the preparation of **2a** was duplicated, using tri-*sec*-butylborane and butylsulfenyl chloride. Column chromatography (silica gel; pentane) afforded **2f** as a viscous colorless liquid in 80% yield. IR (neat): 2960, 2931, 2870, 1563, 1461, 1376, 994 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88–1.25 (30H, m), 1.38 (4H, m), 1.52 (4H, m), 1.58–1.76 (2H, m), 2.14–2.32 (3H, m), 2.55 (2H, t, J=7.4 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 12.7, 13.7, 14.0, 14.2, 15.5, 15.7, 16.0, 18.7, 18.8, 22.3, 22.5, 26.7, 26.8, 29.5, 29.6, 29.9, 30.6, 31.5, 33.3, 38.0, 126.6; MS (EI): 352 (M^+, 1), 295 (100), 239 (84), 205 (10), 183 (18), 149 (15), 115 (15), 57 (20); HRMS (CI): m/z for $C_{22}H_{46}BS$, Calcd: 353.3413. Found: 353.3411.

3.1.7. (*E*)-3-(Diethylboryl)-4-(phenylthio)-3-octene (2g). A 50 ml two-necked flask, equipped with an argon inlet and a magnetic stirring bar, was charged with a THF solution (10 ml) of 1-hexyne (0.657 g; 8 mmol). At −20°C were added 5 ml of *n*-butyllithium (1.6 M in hexane; 8 mmol). After 1 h of stirring at −20°C, 8 ml of triethylborane (1 M solution in THF; 8 mmol) were introduced and the reaction mixture was allowed to warm to room temperature for 1 h. After cooling to −78°C, a THF solution (10 ml) of benzenesulfenyl chloride (1.156 g; 8 mmol) was added dropwise. The cooling bath was then removed and the mixture was stirred for 30 min at room temperature. After removal of the solvents under reduced pressure, the residue was extracted

with pentane (ca. 2×5 ml) via a syringe, the extracts being collected in a 25 ml, argon flushed flask, equipped with an argon inlet. The pentane was then removed under vacuum, and the residue was directly distilled in a Kugelrohr apparatus under reduced pressure (bp 120–130°C at 0.2 mm Hg), giving 1.808 g of **2g** (79% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=7.3 Hz), 0.91 (6H, t, J=7.8 Hz), 1.00 (3H, t, J=7.5 Hz), 1.15 (4H, q, J=7.8 Hz), 1.29 (2H, m), 1.48 (2H, m), 2.21 (2H, t, J=7.5 Hz), 2.25 (2H, q, J=7.5 Hz), 7.11–7.15 (1H, m), 7.19–7.30 (4H, m).

3.1.8. Representative procedure for the protodeborylation of alkenyl boranes with acetic acid (Method A). Preparation of (*E*)-4-(phenylthio)-3-octene (3g). A 50 ml two-necked flask under an argon atmosphere, containing a stirred solution of 1-hexyne (0.197 g; 2.4 mmol) in THF (4 ml), was cooled to −20°C. *n*-Butyllithium (1.5 ml of a 1.6 M solution in hexane; 2.4 mmol) was added, and the reaction mixture was stirred for 1 h at −20°C. Triethylborane (2.4 ml of a 1 M solution in THF; 2.4 mmol) was introduced and the reaction mixture was allowed to warm to room temperature. After 1 h of stirring, the flask was cooled to −78°C and a solution of benzenesulfenyl chloride (0.347 g; 2.4 mmol) in THF (3 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature, charged with 20 ml of Et_2O, and a solution of acetic acid (0.317 g; 4.8 mmol; 2.2 equiv.) in Et_2O (2 ml) was introduced. After 1 h of stirring, 1 ml of ethanolamine (16.6 mmol; 7 equiv.) was added, giving rise to a biphasic system, and the mixture was vigourously stirred for 15 min. The two layers were then separated, the ethereal one was concentrated, and the pale yellow liquid residue was extracted with pentane (3×15 ml). The combined pentane layers were dried over sodium carbonate, and concentrated. The crude product was purified by column chromatography (basic alumina; pentane) to give 0.390 g of **3g** (74% yield) as a colorless liquid. IR (neat): 3072, 2962, 2932, 2873, 1584, 1477, 1440, 1378, 1151, 1088, 1025, 741, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, J=7.0 Hz), 1.02 (3H, t, J=7.3 Hz), 1.27 (2H, m), 1.47 (2H, m), 2.15 (2H, quint., J=7.3 Hz), 2.18 (2H, t, J=7.3 Hz), 5.84 (1H, t, J=7.3 Hz), 7.15–7.20 (1H, m), 7.25–7.32 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 14.1, 22.3, 22.5, 30.8, 126.1, 128.8, 129.9, 133.2, 135.9, 138.5; MS (EI): 220 (M^+, 78), 178 (69), 150 (100), 135 (78), 110 (48), 69 (34), 55 (30); HRMS: *m*/*z* for $C_{14}H_{20}S$, Calcd: 220.1286. Found: 220.1287.

3.1.9. (*E*)-5-(Phenylthio)-5-decene (3h). The same procedure as for the preparation of **3g** was repeated, using tributylborane, except that the mixture was heated at 60°C for 1 h after the introduction of acetic acid. **3h** was obtained as a colorless liquid in 73% yield. IR (neat): 3068, 2958, 2930, 2864, 1584, 1477, 1440, 1379, 1150, 1090, 1025, 740, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, J=7.3 Hz), 0.92 (3H, t, J=7.0 Hz), 1.27 (2H, m), 1.31–1.41 (4H, m), 1.47 (2H, m), 2.15 (4H, m), 5.85 (1H, t, J=7.5 Hz), 7.16–7.20 (1H, m), 7.25–7.31 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.3, 22.4, 28.8, 30.8, 30.9, 31.6, 126.1, 128.8, 129.9, 133.6, 136.1, 137.1; MS (EI): 248 (M^+, 83), 205 (39), 150 (100), 135 (57), 123 (25), 110 (35), 97 (25), 83 (27), 67 (25), 55 (30); Anal. Calcd for $C_{16}H_{24}S$: C, 77.36; H, 9.74. Found: C, 77.60; H, 10.16.

3.1.10. (*E*)-1-Phenyl-1-(phenylthio)-1-butene (3i). The same procedure as for the preparation of **3g** was duplicated, using phenylacetylene. **3i** was obtained as a colorless liquid in 70% yield. This compound spontaneously isomerized on standing at room temperature. IR (neat): 3076, 3058, 3020, 2967, 2931, 2873, 1583, 1478, 1440, 1071, 1025, 762, 741, 699 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.99 (3H, t, J=7.3 Hz), 2.15 (2H, quint., J=7.5 Hz), 6.13 (1H, t, J=7.5 Hz), 7.04–7.39 (10H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.2, 23.7, 126.3, 127.4, 127.9, 128.6, 129.3, 130.3, 133.3, 135.2, 138.1, 138.3; MS (EI): 240 (M^+, 100), 211 (33), 131 (73), 121 (27), 115 (42), 91 (59), 77 (16); HRMS: *m*/*z* for $C_{16}H_{16}S$, Calcd: 240.0973. Found: 240.0970.

3.1.11. (*E*)-1-[(Tetrahydropyran-2-yl)oxy]-3-phenylthio-3-hexene (3j). The same procedure as for the preparation of **3g** was duplicated, using 4-[(tetrahydropyran-2-yl)oxy]-1-butyne. **3j** was obtained as a colorless liquid in 69% yield. IR (neat): 3059, 2943, 2873, 1584, 1477, 1440, 1351, 1202, 1136, 1121, 1068, 1034, 990, 870, 742, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (3H, t, J=7.3 Hz), 1.47–1.80 (6H, m), 2.21 (2H, quint., J=7.3 Hz), 2.50 (2H, m), 3.50 (2H, m), 3.83 (2H, m), 4.55 (1H, br s), 5.99 (1H, t, J=7.3 Hz), 7.16–7.20 (1H, m), 7.25–7.32 (4H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 19.4, 22.6, 25.4, 30.6, 31.7, 62.1, 65.6, 98.7, 126.2, 128.8, 129.3, 129.7, 135.8, 141.1; MS (EI): 292 (M^+, 6), 208 (10), 183 (14), 159 (18), 135 (7), 110 (13), 85 (100), 67 (15); HRMS: *m*/*z* for $C_{17}H_{24}O_2S$, Calcd: 292.1497. Found: 292.1504.

3.1.12. (*E*)-4-(Butylthio)-3-nonene (3k). The same procedure as for the preparation of **3g** was duplicated, using 1-heptyne and butylsulfenyl chloride. **3k** was obtained as a colorless liquid in 83% yield. IR (neat): 2961, 2931, 2873, 2861, 1624, 1462, 1379, 1152, 886, 732 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.82–1.06 (9H, m), 1.15–1.66 (10H, m), 2.10 (4H, m), 2.63 (2H, t, J=7.0 Hz), 5.31 (1H, t, J=7.2 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.7, 14.0, 14.5, 22.0, 22.1, 22.5, 28.6, 30.8, 31.1, 31.6, 31.7, 127.8, 134.2; MS (EI): 214 (M^+, 49), 171 (9), 157 (100), 115 (49), 102 (63), 81 (31), 69 (35), 55 (31); HRMS: *m*/*z* for $C_{13}H_{26}S$, Calcd: 214.1755. Found: 220.1750.

3.1.13. Representative procedure for the protodeborylation of alkenyl boranes with acetic acid (Method B). Preparation of (*E*)-6-(phenylseleno)-6-tridecene (3l). A 50 ml two-necked flask under an argon atmosphere, containing a stirred solution of 1-heptyne (0.577 g; 6 mmol) in THF (9 ml), was cooled to −20°C. *n*-Butyllithium (3.75 ml of a 1.6 M solution in hexane; 6 mmol) was added, and the reaction mixture was stirred for 1 h at −20°C. Trihexylborane (10 ml of a 0.6 M solution in THF; 6 mmol) was introduced and the reaction mixture was allowed to warm to room temperature. After 1 h of stirring, the flask was cooled to −78°C and a solution of phenylselenenyl chloride (1.149 g; 6 mmol) in THF (8 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature and acetic acid (1.03 ml; 18 mmol; 3 equiv.) was introduced. After 1 h of stirring, the mixture was diluted with Et_2O

(30 ml), washed with saturated aqueous $NaHCO_3$ and with water, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (silica gel; pentane) to give 1.323 g of **3l** (65% yield) as a pale yellow liquid. IR (neat): 3071, 2958, 2928, 2857, 1580, 1465, 1439, 1378, 1068, 1023, 735, 691, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (6H, m), 1.20–1.51 (14H, m), 2.11 (2H, q, J=7.3 Hz), 2.24 (2H, t, J=7.5 Hz), 5.94 (1H, t, J=7.3 Hz), 7.21–7.27 (3H, m), 7.45 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.1, 22.5, 22.6, 28.6, 28.9, 29.4, 31.3, 31.7, 32.9, 126.6, 128.9, 131.2, 131.9, 132.4, 138.5; MS (EI): 338 (M^+, 75), 307 (44), 275 (15), 243 (11), 198 (45), 158 (43), 111 (27), 97 (49), 83 (57), 69 (100), 55 (91); HRMS: *m/z* for $C_{19}H_{30}Se$, Calcd: 338.1513. Found: 338.1509.

3.1.14. (*E*)-5-(Phenylseleno)-5-decene (3m). The same procedure as for the preparation of **3l** was duplicated, using 1-hexyne and tributylborane. **3m** was obtained as a pale yellow liquid in 81% yield. IR (neat): 3071, 2958, 2929, 2871, 1580, 1475, 1438, 1379, 1023, 735, 691 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.80–0.98 (6H, m), 1.15–1.56 (8H, m), 2.17 (4H, m), 5.94 (1H, t, J=7.3 Hz), 7.19–7.52 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.9, 22.2, 22.3, 29.2, 31.1, 31.6, 32.6, 126.6, 129.0, 131.1, 131.8, 132.4, 138.4; MS (EI): 296 (M^+, 98), 253 (8), 198 (53), 183 (20), 158 (53), 129 (17), 117 (13), 97 (47), 83 (58), 69 (40), 55 (100); HRMS: *m/z* for $C_{16}H_{24}Se$, Calcd: 296.1043. Found: 296.1042; Anal. Calcd for $C_{16}H_{24}Se$: C, 65.07; H, 8.19. Found: C, 64.72; H, 8.34.

3.1.15. (*E*)-4-(Phenyltelluro)-3-nonene (3n). The same procedure as for the preparation of **3l** was duplicated, using triethylborane and phenyltellurenyl iodide. Purification was carried out by column chromatography (silica gel pretreated with triethylamine/pentane (5:95, v/v); eluting with pentane). **3n** was obtained as a yellow liquid in 62% yield. IR (neat): 3066, 2961, 2928, 2856, 1574, 1473, 1434, 1377, 1140, 1064, 1018, 731, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.85 (3H, t, J=7.3 Hz), 1.00 (3H, t, J=7.5 Hz), 1.19–1.28 (4H, m), 1.45 (2H, m), 2.16 (2H, quint., J=7.3 Hz), 2.33 (2H, t, J=7.5 Hz), 6.20 (1H, t, J=7.3 Hz), 7.18–7.26 (3H, m), 7.70 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.1, 22.5, 23.6, 29.3, 31.1, 35.8, 114.3, 119.4, 127.3, 129.1, 137.7, 146.5; MS (EI): 332 (M^+, 73), 276 (6), 208 (37), 130 (6), 83 (34), 77 (48), 69 (100), 55 (76); HRMS: *m/z* for $C_{15}H_{22}Te$, Calcd: 332.0784. Found: 332.0792.

3.1.16. (*E*)-4-(Butyltelluro)-3-octene (3o). The same procedure as for the preparation of **3l** was duplicated, using triethylborane and butyltellurenyl iodide, except that purification was carried out by distillation under reduced pressure (bp 73–77°C at 0.26 mm Hg). **3o** was obtained as a yellow liquid in 70% yield. IR (neat): 2960, 2927, 2871, 1637, 1459, 1377, 1247, 1161, 1140, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (6H, t, J=7.3 Hz), 0.97 (3H, t, J=7.5 Hz), 1.29–1.48 (6H, m), 1.75 (2H, m), 2.13 (2H, quint., J=7.3 Hz), 2.32 (2H, t, J=7.5 Hz), 2.70 (2H, t, J=7.3 Hz), 5.98 (1H, t, J=7.3 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 6.3, 13.4, 14.0, 14.2, 22.1, 23.3, 25.1, 31.9, 33.8, 36.0, 115.8, 143.6; MS (EI): 298 (M^+, 47), 241 (6), 186 (9), 110 (9), 81 (11), 69 (100), 55 (54); HRMS: *m/z* for $C_{12}H_{24}Te$, Calcd: 298.0940. Found: 298.0945.

3.1.17. (*Z*)-5-(Phenylthio)-5-decene (3h′). The same procedure as for the preparation of **3l** was duplicated, using 1-hexyne, tributylborane and benzenesulfenyl chloride. Analysis of the crude product revealed the presence of two stereoisomers that could be separated by column chromatography (silica gel; pentane). (*E*)- and (*Z*)-5-(phenylthio)-5-decene (**3h** and **3h′**) were obtained as colorless liquids in 42 and 27%, respectively. **3h′**: IR (neat): 3073, 2958, 2928, 2858, 1584, 1477, 1465, 1439, 1379, 1094, 1025, 739, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.84 (3H, t, J=7.3 Hz), 0.90 (3H, t, J=7.1 Hz), 1.22 (2H, m), 1.32–1.41 (4H, m), 1.45 (2H, m), 2.15 (2H, t, J=7.8 Hz), 2.33 (2H, t, J=7.2 Hz), 5.89 (1H, t, J=7.1 Hz), 7.14–7.18 (1H, m), 7.23–7.30 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 14.0, 21.9, 22.3, 29.6, 30.7, 31.6, 37.2, 125.6, 128.7, 129.2, 133.1, 135.8, 136.7; MS (EI): 248 (M^+, 77), 205 (36), 150 (100), 135 (52), 123 (24), 110 (36), 97 (26), 83 (29), 67 (25), 55 (34).

3.1.18. Representative procedure for the protodeborylation of thio-alkenyl boranes by means of the activation–transmetallation–protonolysis sequence. Preparation of (*E*)-1-cyclohexyl-2-(phenylthio)-1-hexene (3a). In a 25 ml two-necked flask, equipped with an argon inlet and a magnetic stirring bar, were introduced a THF solution (3 ml) of **2a** (0.410 g; 0.91 mmol) and 0.45 ml of HMPA. Methyllithium was added at −33°C (1.3 ml of a 1.4 M solution in Et_2O; 1.82 mmol) and the reaction mixture was stirred for 30 min at −33°C. Copper iodide (0.173 g; 0.91 mmol) was then introduced and the reaction mixture was vigorously stirred for 3 h at −33°C. The reaction was quenched with water (2 ml), and the cooling bath was removed. After dilution of the solution with 20 ml of Et_2O, the organic layer was washed with saturated aqueous NH_4Cl and then with water, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (silica gel; pentane) to afford 0.203 g of **3a** (81% yield) as a colorless liquid. IR (neat): 3072, 2926, 2852, 1584, 1476, 1446, 1025, 960, 898, 740, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, J=7.3 Hz), 1.11–1.34 (7H, m), 1.47 (2H, m), 1.65–1.76 (5H, m), 2.18 (2H, t, J=7.5 Hz), 2.29 (1H, m), 5.73 (1H, d, J=9.8 Hz), 7.14–7.18 (1H, m), 7.24–7.30 (4H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 22.3, 25.8, 25.9, 31.1, 33.0, 38.4, 125.9, 128.7, 129.5, 131.8, 136.3, 143.6; MS (EI): 274 (M^+, 50), 197 (37), 150 (100), 135 (18), 123 (17), 109 (27), 95 (18), 79 (23), 67 (24), 55 (21); HRMS: *m/z* for $C_{18}H_{26}S$, Calcd: 274.1755. Found: 274.1751.

3.1.19. (*E*)-1-Cyclohexyl-2-(butylthio)-1-heptene (3c). The same procedure as for the preparation of **3a** was duplicated, using 1-heptyne and butylsulfenyl chloride, except that activation and transmetallation were performed at −23°C. **3c** was obtained as a colorless liquid in 86% yield. IR (neat): 2958, 2927, 2854, 1623, 1449, 893, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.91 (6H, m), 1.04–1.74 (20H, m), 2.19 (2H, t, J=7.8 Hz), 2.24 (1H, m) 2.61 (2H, t, J=7.4 Hz), 5.16 (1H, d, J=8.9 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.7, 14.0, 22.1, 22.5, 26.0, 28.9, 30.8, 31.2, 31.6, 31.9, 33.5, 37.9, 132.5, 133.0; MS (EI):

268 (M^+, 23), 211 (100), 155 (12), 143 (9), 130 (12), 115 (12), 95 (9), 81 (12), 67 (10), 55 (12); Anal. Calcd for $C_{17}H_{32}S$: C, 76.05; H, 12.01. Found: C, 76.06; H, 11.97.

3.1.20. (*E*)-5-(Butylthio)-3-methyl-4-nonene (3f). The same procedure as for the preparation of **3a** was repeated, using tri-*sec*-butylborane and butylsulfenyl chloride, except that activation and transmetallation were performed at −23°C. **3f** was obtained as a colorless liquid in 80% yield. IR (neat): 2960, 2930, 2872, 1653, 1460, 1378, 1164, 777, 745 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.76–0.98 (12H, m), 1.13–1.66 (10H, m), 2.11–2.43 (3H, m), 2.62 (2H, t, J=6.9 Hz), 5.11 (1H, d, J=9.7 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 11.9, 13.7, 14.0, 21.1, 22.1, 22.5, 30.4, 30.9, 31.2, 31.3, 31.7, 35.0, 133.2, 133.3; MS (EI): 228 (M^+, 30), 213 (8), 199 (100), 171 (54), 143 (6), 130 (7), 115 (8), 101 (13), 81 (11), 67 (16), 55 (14); Anal. Calcd for $C_{14}H_{28}S$: C, 73.61; H, 12.35. Found: C, 72.96; H, 12.06.

3.1.21. Representative procedure for the cross-coupling reaction of vinylchalcogenides with Grignard reagents. Preparation of (*E*)-5-phenyl-5-decene (4a). In a 25 ml two-necked flask, equipped with an argon inlet and a magnetic stirring bar, were introduced a solution of **3h** (0.248 g; 1 mmol) in Et_2O (7 ml) and $NiCl_2$(dppe) (0.016 g; 0.03 mmol). Phenylmagnesium bromide (4.4 ml of a 0.5 M solution in Et_2O; 2.2 mmol) was added and the reaction mixture was stirred at room temperature for 15 h. One milliliter of saturated aqueous NH_4Cl was then introduced and, after dilution with Et_2O, the organic layer was separated, washed with 10 ml of aqueous NaOH (1 M) and with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (silica gel; pentane) to give 0.169 g of **4a** (78% yield) as a colorless liquid. IR (neat): 3057, 3024, 2958, 2930, 2870, 2861, 1600, 1494, 1463, 1379, 1105, 762, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J=7.1 Hz), 0.93 (3H, t, J=7.1 Hz), 1.30–1.43 (8H, m), 2.19 (2H, q, J=7.3 Hz), 2.48 (2H, t, J=7.1 Hz), 5.63 (1H, t, J=7.3 Hz), 7.18–7.35 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.9, 14.0, 22.5, 22.7, 28.3, 29.5, 29.7, 30.9, 32.1, 126.3, 128.1, 129.1, 140.1, 143.6; MS (EI): 216 (M^+, 24), 174 (10), 159 (34), 145 (8), 131 (22), 118 (100), 105 (7), 91 (43), 77 (6); HRMS: m/z for $C_{16}H_{24}$, Calcd: 216.1878. Found: 216.1880.

3.1.22. (*Z*)-5-Phenyl-5-decene (4a′). The same procedure as for the preparation of **4a** was duplicated, starting from (*Z*)-5-(phenylthio)-5-decene **3h′** and using 8 mol% of $NiCl_2$(dppe). After 20 h at room temperature, the conversion was incomplete (50% GC; no evolution was observed after a prolonged time of stirring). The purification by column chromatography (silica gel; pentane) gave **4a′** (28% yield) as a colorless liquid. IR (neat): 3058, 3023, 2958, 2929, 2859, 1601, 1493, 1464, 1442, 1379, 1105, 1071, 770, 702; ^1H NMR (400 MHz, $CDCl_3$): δ 0.80–0.87 (6H, m), 1.21–1.33 (8H, m), 1.91 (2H, q, J=7.2 Hz), 2.31 (2H, t, J=6.8 Hz), 5.42 (1H, t, J=7.3 Hz), 7.11–7.33 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.9, 14.0, 22.3, 28.6, 30.4, 32.4, 39.0, 126.2, 127.2, 127.9, 128.4, 140.9, 141.7; MS (EI): 216 (M^+, 21), 174 (11), 159 (34), 145 (8), 131 (22), 118 (99), 117 (100), 105 (7), 91 (43), 77 (6).

3.1.23. (*E*)-4-Phenyl-3-octene (4b). The same procedure as for the preparation of **4a** was used, starting from **3g**. **4b** was obtained as a colorless liquid in 87% yield. IR (neat): 3059, 3024, 2962, 2932, 2873, 1600, 1493, 1460, 1378, 1073, 1032, 863, 763, 697 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.79–1.13 (6H, m), 1.22–1.48 (4H, m), 2.20 (2H, quint., J=7.3 Hz), 2.48 (2H, t, J=7.4 Hz), 5.63 (1H, t, J=7.3 Hz), 7.19–7.36 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.4, 21.8, 22.7, 29.4, 31.0, 126.3, 128.1, 130.6, 139.6, 143.5; MS (EI): 188 (M^+, 21), 146 (26), 131 (100), 118 (69), 103 (10), 91 (31), 77 (8); HRMS: m/z for $C_{14}H_{20}$, Calcd: 188.1565. Found: 188.1569.

3.1.24. (*E*)-6-Butyl-1,6-nonadiene (4c). The same procedure as for the preparation of **4a** was duplicated, starting from **3g** and using 4-pentenylmagnesium bromide (0.5 M in Et_2O). The purification by column chromatography (silica gel; pentane) gave a mixture of **4c** (85%) and 1,9-decadiene (15%). The latter was removed by Kugelrohr distillation under reduced pressure to give essentially pure **4c** (76% yield) as a colorless liquid. IR (neat): 3079, 2961, 2931, 2859, 1662, 1642, 1460, 1378, 991, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (3H, t, J=7.1 Hz), 0.95 (3H, t, J=7.4 Hz), 1.30–1.36 (4H, m), 1.49 (2H, quint., J=7.7 Hz), 1.97–2.07 (8H, m), 2.48 (2H, t, J=7.1 Hz), 4.96 (1H, d, J=9.9 Hz), 5.02 (1H, dm, J=17.8 Hz), 5.12 (1H, t, J=6.9 Hz), 5.84 (1H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.7, 21.0, 22.9, 27.6, 29.7, 30.8, 33.6, 36.3, 114.3, 126.8, 138.6, 139.1; MS (EI): 180 (M^+, 2), 151 (7), 137 (10), 124 (73), 109 (21), 95 (56), 84 (99), 67 (72), 55 (100); HRMS: m/z for $C_{13}H_{24}$, Calcd: 180.1878. Found: 180.1875.

3.1.25. 4-Butyl-3-octene (4d). The same procedure as for the preparation of **4a** was duplicated, starting from **3g** and using 2.4 equiv. of butylmagnesium bromide (0.5 M in Et_2O). **4d** was obtained as a colorless liquid in 88% yield. IR (neat): 2961, 2931, 2874, 2861, 1661, 1462, 1379, 850 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.85–1.01 (9H, m), 1.21–1.48 (8H, m), 1.84–2.07 (6H, m), 5.09 (1H, t, J=7.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.7, 21.0, 22.6, 22.9, 29.7, 30.5, 30.8, 36.6, 126.3, 139.1; MS (EI): 168 (M^+, 37), 126 (11), 111 (9), 97 (9), 84 (100), 69 (87), 55 (75); HRMS: m/z for $C_{12}H_{24}$, Calcd: 168.1878. Found: 168.1874.

3.1.26. (*E*)-4-Phenyl-3-nonene (4e). The same procedure as for the preparation of **4a** was duplicated, starting from **3k** and using 1.5 equiv. of phenylmagnesium bromide (0.5 M in Et_2O). **4e** was obtained as a colorless liquid in 82% yield. IR (neat): 3059, 3025, 2961, 2931, 2872, 2861, 1600, 1493, 1462, 1377, 863, 759, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.85 (3H, t, J=7.1 Hz), 1.05 (3H, t, J=7.5 Hz), 1.23–1.35 (6H, m), 2.20 (2H, quint., J=7.5 Hz), 2.47 (2H, t, J=7.3 Hz), 5.63 (1H, t, J=7.3 Hz), 7.18–7.35 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.4, 21.9, 22.5, 28.5, 29.7, 31.8, 126.3, 128.1, 130.6, 139.7, 143.5; MS (EI): 202 (M^+, 21), 159 (6), 146 (30), 131 (100), 118 (84), 103 (10), 91 (34), 77 (8); HRMS: m/z for $C_{15}H_{22}$, Calcd: 202.1722. Found: 202.1717.

The same compound could be obtained starting from **3n**. In this case, $NiCl_2(PPh_3)_2$ (5 mol%) was used as the catalyst

with THF as the solvent, and the reaction mixture was heated to reflux for 3 h (77% yield).

3.1.27. (*Z*)-4-Butyl-3-nonene (4f). The same procedure as for the preparation of **4a** was duplicated, starting from **3k** and using 5.0 equiv. of BuMgBr (0.5 M in Et_2O). **4f** was obtained as a colorless liquid in 73% yield. IR (neat): 2961, 2931, 2873, 2860, 1662, 1464, 1379, 851, 732 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.85–1.01 (9H, m), 1.26–1.50 (10H, m), 1.92–2.08 (6H, m), 5.09 (1H, t, J=7.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.7, 21.0, 22.5, 22.6, 28.3, 30.0, 30.5, 32.0, 36.6, 126.3, 139.1; MS (EI): 182 (M^+, 35), 140 (4), 126 (8), 111 (7), 97 (27), 84 (100), 69 (77), 55 (74); HRMS: *m/z* for $C_{13}H_{26}$, Calcd: 182.2035. Found: 182.2038.

3.1.28. (*E*)-6-Phenyl-6-tridecene (4g). The same procedure as for the preparation of **4a** was duplicated, starting from **3l** and using 2.5 equiv. of phenylmagnesium bromide (0.5 M in Et_2O), except that $NiCl_2(PPh_3)_2$ (4 mol%) was used as the catalyst and the reaction mixture was heated to reflux for 14 h. **4g** was obtained as a colorless liquid in 68% yield. IR (neat): 3058, 3024, 2957, 2927, 2858, 1599, 1494, 1463, 1379, 1074, 1032, 759, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.83–0.91 (6H, m), 1.26–1.43 (14H, m), 2.18 (2H, q, J=7.3 Hz), 2.47 (2H, t, J=7.3 Hz), 5.63 (1H, t, J=7.1 Hz), 7.18–7.35 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.1, 22.5, 22.7, 28.4, 28.6, 29.1, 29.7, 29.9, 31.8, 126.3, 128.1, 129.1, 140.1, 143.5; MS (EI): 258 (M^+, 14), 202 (6), 187 (17), 159 (6), 145 (5), 131 (21), 118 (100), 105 (10), 91 (41), 77 (3), 55 (6); HRMS: *m/z* for $C_{19}H_{30}$, Calcd: 258.2348. Found: 258.2342.

3.1.29. (*Z*)-6-Methyl-6-tridecene (4i). The same procedure as for the preparation of **4a** was duplicated, starting from **3l** and using 2.5 equiv. of methylmagnesium bromide (3 M in Et_2O), except that $NiCl_2$(dppp) (5 mol%) was used as the catalyst and the reaction mixture was heated to reflux for 8 h. **4i** was obtained as a colorless liquid in 61% yield. IR (neat): 2959, 2927, 2858, 1667, 1465, 1378, 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.87–0.92 (6H, m), 1.22–1.38 (14H, m), 1.67 (3H, br s), 1.87–2.01 (4H, m), 5.11 (1H, t, J=7.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.1, 22.7, 23.4, 27.7, 27.8, 29.1, 30.1, 31.7, 31.8, 125.3, 135.4; MS (EI): 196 (M^+, 28), 140 (5), 125 (18), 112 (15), 97 (24), 83 (49), 69 (100), 55 (67); HRMS: *m/z* for $C_{14}H_{28}$, Calcd: 196.2191. Found: 196.2194.

3.1.30. 5-Butyl-5-decene (4j). The same procedure as for the preparation of **4a** was duplicated, starting from **3m** and using 2.5 equiv. of butylmagnesium bromide (0.5 M in Et_2O), except that $NiCl_2$(dppp) (3 mol%) was used as the catalyst and the reaction mixture was heated to reflux for 14 h. The purification by column chromatography (silica gel; pentane) gave a mixture of **4j** (83%) and (*Z*)-5-decene (17%). The latter was removed by Kugelrohr distillation under reduced pressure to give essentially pure **4j** (30% yield) as a colorless liquid. IR (neat): 2958, 2928, 2872, 2859, 1661, 1464, 1379, 1106, 847, 730 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.85–0.97 (9H, m), 1.27–1.38 (12H, m), 1.89–2.08 (6H, m), 5.10 (1H, t, J=7.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 22.4, 22.5, 22.9, 27.4, 29.8, 30.6, 30.8, 32.4, 36.7, 124.6, 139.5; MS (EI): 196 (M^+, 38), 154 (8), 139 (6), 126 (3), 112 (23), 97 (69), 83 (79), 69 (74), 55 (100); HRMS: *m/z* for $C_{14}H_{28}$, Calcd: 196.2191. Found: 196.2189.

3.1.31. Representative procedure for the C–Te cleavage of vinyltellurides with butyllithium (Path A). Preparation of (*E*)-2-butyl-1-phenyl-2-penten-1-ol (5a). In a 25 ml two-necked flask, equipped with an argon inlet and a magnetic stirring bar, was introduced a THF solution (3 ml) of **3o** (0.244 g; 0.825 mmol). At −78°C was added 0.57 ml of *n*-butyllithium (1.6 M in hexane; 0.91 mmol), and the reaction mixture was stirred for 30 min at −78°C prior to the introduction of a THF solution (2 ml) of benzaldehyde (0.097 g; 0.91 mmol). The reaction mixture was stirred for 30 min at −78°C, then the cooling bath was removed, followed by 30 min of stirring at room temperature. Two milliliter of saturated aqueous NH_4Cl were then added for quenching. After dilution of the solution with 20 ml of Et_2O, the organic layer was washed with saturated aqueous NH_4Cl and with water, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (silica gel; pentane/Et_2O: 8:2) to afford 0.132 g of **5a** (73% yield) as a yellow liquid. IR (neat): 3371, 3063, 3030, 2961, 2932, 2871, 1604, 1493, 1454, 1378, 1187, 1071, 1015, 744, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.82 (3H, t, J=7.1 Hz), 1.01 (3H, t, J=7.5 Hz), 1.13–1.27 (4H, m), 1.80–1.87 (2H, m), 1.95–2.01 (1H, m), 2.09 (2H, quint., J=7.3 Hz), 5.16 (1H, s), 5.60 (1H, t, J=7.1 Hz), 7.24–7.37 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.8, 14.3, 20.9, 23.0, 27.4, 31.7, 78.1, 126.5, 127.3, 128.1, 128.8, 140.7, 142.8; MS (EI): 218 (M^+, 78), 189 (60), 175 (22), 161 (100), 143 (27), 133 (53), 115 (17), 105 (76), 91 (21), 79 (50), 55 (20); HRMS: *m/z* for $C_{15}H_{22}O$, Calcd: 218.1671. Found: 218.1666.

3.1.32. 1-[(*E*)-1-Butyl-1-butenyl]cyclohexan-1-ol (5b). The same procedure as for the preparation of **5a** was duplicated, using cyclohexanone. The purification was carried out by column chromatography (silica gel; pentane/Et_2O: 9:1) to afford **5b** as a yellow liquid in 70% yield. IR (neat): 3413, 3043, 2935, 2870, 1453, 1377, 1257, 1150, 1133, 1035, 959, 857 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.85–1.06 (6H, m), 1.20–1.68 (15H, m), 1.88–2.21 (4H, m), 5.45 (1H, t, J=7.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.9, 14.5, 21.2, 22.2, 23.5, 25.7, 27.5, 33.1, 36.5, 74.2, 125.7, 145.5; MS (EI): 210 (M^+, 29), 181 (91), 167 (42), 153 (15), 139 (100), 125 (20), 111 (24), 81 (30), 69 (42), 55 (44); HRMS: *m/z* for $C_{14}H_{26}O$, Calcd: 210.1984. Found: 210.1984.

3.1.33. Representative procedure for the C–Te cleavage of vinyltellurides with dilithium butyl 2-thienyl cyanocuprate (Path B). Preparation of 3-[(*E*)-1-butyl-1-butenyl]cyclohexanone (6a). In a 25 ml two-necked flask, equipped with an argon inlet and a magnetic stirring bar, was introduced a THF solution (2 ml) of thiophene (0.210 g; 2.5 mmol). *n*-Butyllithium (1.56 ml of a 1.6 M solution in hexane; 2.5 mmol) was added at −78°C, the temperature was raised to −10°C, and the mixture was stirred for 30 min. This solution was transferred via cannula to another flask containing a suspension of CuCN (0.180 g; 2.0 mmol) in THF (3 ml) previously cooled to −78°C. Removing the

cooling bath gave an homogeneous pale yellow solution, which was cooled again to −78°C prior to the introduction of *n*-butyllithium (1.25 ml of a 1.6 M solution in hexane; 2.0 mmol). The reaction mixture was stirred for 15 min at −78°C, and then the cooling bath was removed before the introduction of a THF solution (3 ml) of **3o** (0.592 g; 2.0 mmol). After 1 h of stirring at room temperature, the solution was cooled to −78°C and cyclohexenone (0.195 ml; 2.0 mmol) was added. The cooling bath was removed, and the reaction mixture was stirred for 20 min at room temperature. A mixture of saturated aqueous solution of NH_4Cl and NH_4OH (4:1, v/v; 10 ml) and 30 ml of ethyl acetate were then added. The organic layer was separated, washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (silica gel; pentane/ethyl acetate: 96:4) to give 0.262 g of **6a** (63% yield) as a pale yellow liquid. IR (neat): 2959, 2933, 2871, 1714, 1459, 1422, 1346, 1317, 1260, 1222, 1104, 1030, 930, 873, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (3H, t, J=6.9 Hz), 0.97 (3H, t, J=7.3 Hz), 1.29–1.35 (4H, m), 1.54–1.67 (2H, m), 1.91 (1H, m), 1.94–2.12 (5H, m), 2.25–2.42 (5H, m), 5.15 (1H, t, J=6.8 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.9, 14.5, 20.9, 22.9, 23.0, 25.4, 29.4, 31.0, 31.6, 41.3, 45.1, 47.7, 126.4, 141.3, 212.0; MS (EI): 208 (M^+, 82), 179 (48), 165 (100), 151 (72), 137 (30), 123 (49), 109 (34), 95 (70), 81 (59), 69 (70), 65 (78); Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.54; H, 11.92.

3.1.34. (*E*)-5-Butyl-5-octen-2-one (6b). The same procedure as for the preparation of **6a** was duplicated, using methyl vinyl ketone. **6b** was obtained as a pale yellow liquid in 59% yield. IR (neat): 2960, 2932, 2873, 2861, 1719, 1665, 1460, 1360, 1284, 1160, 1070, 940, 837, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (3H, t, J=7.3 Hz), 0.96 (3H, t, J=7.7 Hz), 1.31–1.37 (4H, m), 1.98–2.06 (4H, m), 2.18 (3H, s), 2.27 (2H, t, J=7.5 Hz), 2.55 (2H, t, J=7.8 Hz), 5.12 (1H, t, J=7.1 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.5, 20.9, 22.7, 29.9, 30.7, 42.6, 127.0, 137.3, 208.9; MS (EI): 182 (M^+, 2), 164 (17), 153 (4), 139 (6), 124 (17), 109 (12), 95 (40), 82 (100), 67 (29), 55 (37); HRMS: *m/z* for $C_{12}H_{22}O$, Calcd: 182.1671. Found: 182.1676.

3.1.35. (3*R*,5*R*)-5-[(*E*)-1-Butyl-1-butenyl]-1-methyl-4-(1-methyl-ethenyl)-cyclohexanone (6c). The same procedure as for the preparation of **6a** was duplicated, using (*R*)-(−)-carvone. The purification was carried out by column chromatography (silica gel; pentane/ethyl acetate: 98:2) to afford **6c** as a colorless liquid in 65% yield. While ^1H and ^{13}C NMR spectra show essentially one stereoisomer, we observe close signals in GC, which seem to indicate the formation of two diastereoisomers (epimers in C-2). IR (neat): 3084, 2961, 2932, 2872, 1710, 1645, 1453, 1376, 1231, 1210, 1176, 891, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, J=6.8 Hz), 0.93 (3H, t, J=7.3 Hz), 1.04 (3H, d, J=6.8 Hz), 1.24–1.36 (4H, m), 1.72 (3H, s), 1.74–1.80 (2H, m), 1.93 (1H, dm, J=13.7 Hz), 2.01 (2H, quint., J=7.3 Hz), 2.06–2.12 (1H, m), 2.27 (1H, ddd, J=14.7, 11.2 and 1.5 Hz), 2.49–2.57 (2H, m), 2.65 (1H, m), 2.76 (1H, m), 4.72 (1H, s), 4.78 (1H, s), 4.81 (1H, t, J=7.1 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 12.0, 14.0, 14.6, 21.0, 21.2, 22.8, 30.9, 31.1, 32.9, 39.8, 45.3, 45.4, 47.2, 110.1, 128.9, 137.0, 147.6, 213.9; MS (EI): 262 (M^+, 30), 247 (4), 233 (9), 219 (12), 204 (22), 191 (15), 177 (8), 165 (28), 153 (100), 135 (24), 123 (26), 109 (50), 97 (90), 81 (61), 69 (64), 55 (68); HRMS: *m/z* for $C_{18}H_{30}O$, Calcd: 262.2297. Found: 262.2297.

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