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Transformation of β-chalcogeno alkenylboranes into tetrasubstituted olefins

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Abstract—In view of generating trisubstituted vinylic chalcogen derivatives, β-chalcogeno alkenylboranes generated through the chalcogen electrophile induced rearrangements of 1-alkynyltrialkyl borates have been subjected to Suzuki–Miyaura coupling and to boron to copper transmetalation followed by alkylation. Some of the trisubstituted vinyl sulfides obtained by this latter strategy have been converted efficiently into the title olefins through the $NiCl_2$(dmpe) catalyzed coupling with various Grignard reagents.

1. Introduction

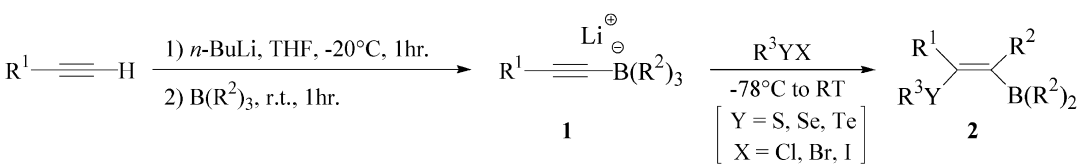
Recently we have reported on the efficient and highly stereoselective rearrangement of 1-alkynyltrialkyl borates triggered by chalcogen (S, Se, Te) electrophiles.[1] We have also shown that the β-chalcogeno alkenylboranes produced via this rearrangement can be protodeborylated with essentially complete retention of stereochemistry to produce the corresponding vinyl sulfides, -selenides or -tellurides in excellent yields. Finally, the latter have been converted into trisubstituted olefins either by nickel catalyzed coupling with Grignard reagents, or through Te/Li exchange (in the case of alkylvinyl tellurides) followed by reaction of the so obtained vinyllithiums with carbonyl compounds.

We now wish to report a detailed account of our efforts aimed at the conversion of the β-chalcogeno alkenylboranes into the title olefins. As previously,[1] these key intermediates **2** are formed in high yield on reaction of various chalcogenyl halides with the in situ prepared lithium 1-alkynyltrialkyl borates **1** (Scheme 1).

Some of these compounds are stable crystalline solids on which X-ray structure determination have been carried out. In all the cases examined, the boron and chalcogen moieties have shown a *cis* relationship, attesting thereby the high stereoselectivity of the rearrangement. Our goal will be to preserve this stereochemistry throughout the two successive steps leading to the target olefins: (i) electrophilic substitution of the boron moiety by a carbon fragment and (ii) replacement of the chalcogenyl group.

2. Results and discussion

Considering the much greater sensitivity of the C–B bond as compared to the C–S(Se,Te) bonds, we decided to transform first the β-chalcogeno alkenylboranes into fully substituted vinyl chalcogenides **3** (Scheme 2). For this purpose, we have investigated two different strategies: (i) the Suzuki–Miyaura coupling and (ii) the boron to copper exchange followed by alkylation.



Scheme 1.

Keywords: Rearrangement of 1-alkynyltrialkyl borates; Trisubstituted vinyl chalcogenides; Tetrasubstituted olefins; Alkenylboranes; Suzuki–Miyaura coupling; Transmetalation; Nickel catalyzed coupling with Grignard reagents.
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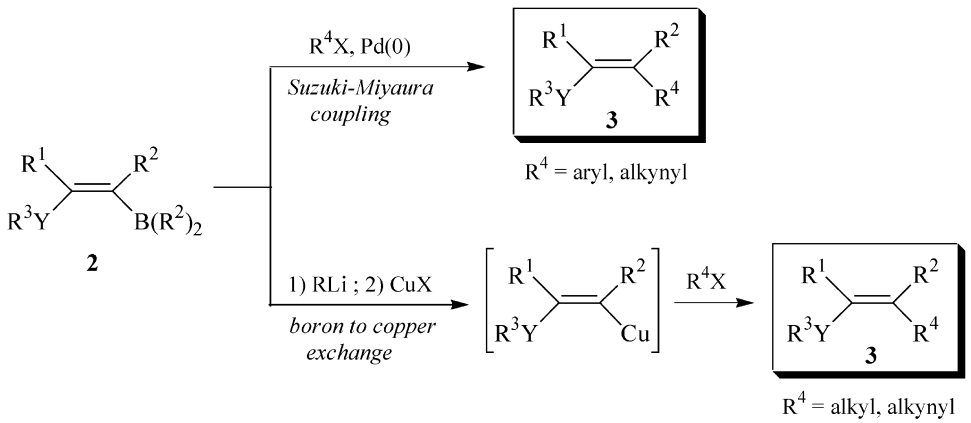


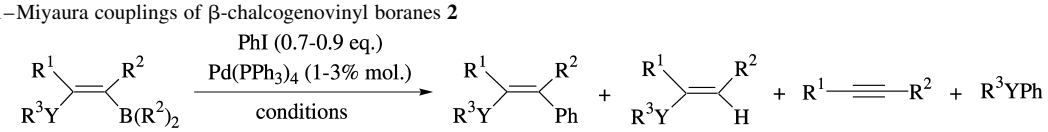
Scheme 2.

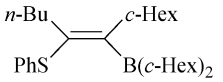
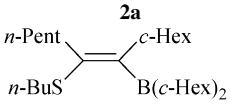
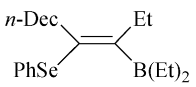
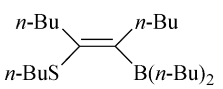
2.1. Suzuki–Miyaura coupling of β-chalcogeno alkenylboranes

The palladium catalyzed reaction between organoboron compounds and alkynyl, alkenyl and aryl halides has appeared to be a powerful and useful methodology for the formation of carbon–carbon bonds.[2] Since the reagents and conditions of the so-called Suzuki–Miyaura coupling should not alter the vinylchalcogen moiety, we have tested it on four different β-chalcogeno alkenylboranes under various conditions. The quite limited success of the method is illustrated by the results shown in Table 1.

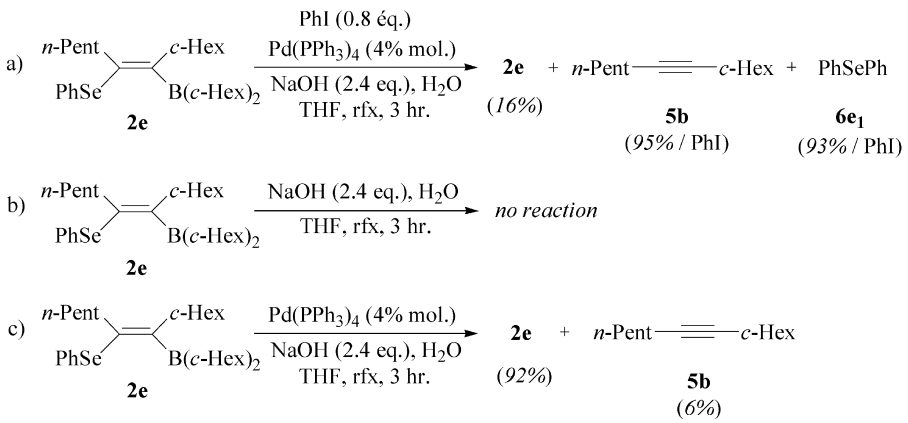
It turns out that the two major side reactions competing with the desired coupling are the elimination of both heteroatomic moieties leading to an internal alkyne and the protodeborylation producing vinyl chalcogenides. These reactions can occur separately or concomitantly. In order to gain some insight into the details of these side reactions, we have carried out a few additional experiments. Thus, (*E*)-1-cyclohexyl-1-(dicyclohexylboryl)-2-(phenylseleno)-1-heptene **2e** has been subjected to a typical Suzuki–Miyaura coupling reaction using iodobenzene as electrophile (Scheme 3a). As can be seen, none of the desired vinyl selenide was observed. Instead, *n*-pentylcyclohexylacetylene **5b** and diphenylselenide **6e$_1$** were formed in almost quantitative yields (with respect to the amount of iodobenzene used). In this case, elimination of the boron and selenium moieties, accompanied by the consumption of iodobenzene by the insipient selenolate anion producing

Table 1. Suzuki–Miyaura couplings of β-chalcogenovinyl boranes **2**



Entry	Reagent	Base (equiv./PhI)	Conditions	Yield (%)			
				3	**4**	**5**	**6**
1	 **2a**	NaOH aq. (3.0)	THF, rfx 3 h	33 (**3a$_1$**)	—	62 (**5a**)	59 (**6a$_1$**)
2	**2a**	K_3PO_4 (3.0)	DMF/THF rfx, 18 h	33 (**3a$_1$**)	—	58 (**5a**)	58 (**6a$_1$**)
3	**2a**	Na_2HPO_4 (3.0)	DMF/THF rfx, 16 h	0[a] (**3a$_1$**)	—	—	—
4	**2a**	Na_2CO_3 (2.4)	DMF/THF rfx, 16 h	0[a] (**3a$_1$**)	—	—	—
5	**2a**	Bu_4NF (2.0)	THF, rfx 13 h	37 (**3a$_1$**)	27 (**4a**)	35 (**5a**)	37 (**6a$_1$**)
6	 **2b**	Bu_4NF (2.0)	THF, rfx 13 h	70 (**3b$_1$**)	Traces (**4b**)	9 (**5b**)	—
7[b]	 **2c**	NaOH aq. (3.0)	THF, rfx 16 h	0 (**3c$_1$**)	61 (**4c**)	—	—
8[b]	 **2d**	Bu_4NF (2.0)	THF, rfx 20 h	37 (**3d$_1$**)	[c]	—	—
9[b]	**2d**	K_3PO_4 (2.0)	DMF/THF rfx, 28 h	34 (**3d$_1$**)	[c]	—	—

[a] **2a** was recovered quantitatively.
[b] These experiments were carried out in situ, without isolation of the alkenylborane.
[c] The formation of these compounds has not been quantified.



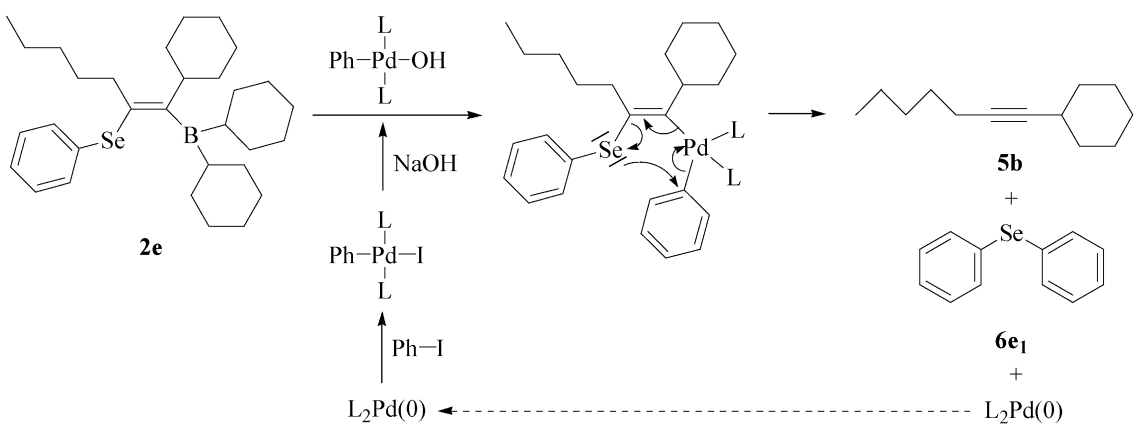
Scheme 3.

diphenylselenide,[3] completely predominated. However, when **2e** was refluxed in THF with aqueous sodium hydroxide, no elimination occurred and the starting material was recovered entirely (Scheme 3b). Similarly, refluxing **2e** under the same conditions but in the presence of the palladium catalyst produced only trace amounts of the internal alkyne **5b**, leaving 92% of **2e** unchanged (Scheme 3c). These results indicate that coordination of hydroxide ion onto the boron atom of the starting β-chalcogeno alkenylboranes is not responsible for the elimination. Therefore, this side reaction must occur at the level of a β-chalcogeno alkenylpalladium intermediate. Moreover, the latter species should contain the phenyl group already attached to palladium, since withdrawing iodobenzene from the reaction mixture brings about a remarkable decrease of the alkyne's yield. Scheme 4 shows the series of events which seems the most probable.

In the light of the above, it is much easier to understand the results of Table 1. Indeed, entry 1 shows that the behaviour of β-phenylthio alkenylborane **2a** towards the Suzuki–Miyaura coupling is fairly comparable to that of **2e**; the difference lies in the ratio of coupling to elimination, that is roughly 1:2 for **2a** instead of 0:100 for **2e**. Clearly, the phenylthio group (a weaker leaving group than the phenylseleno group) allows the coupling reaction to compete to some extent with *syn*-elimination. In agreement with this view, β-butylthio alkenylborane **2b** led to a good yield of vinyl sulfide $\mathbf{3b_1}$ and only to a small amount of *n*-pentylcyclohexylacetylene **5b** (Table 1, entry 6).

The nature of the 'base' required for the Suzuki–Miyaura couplings does not seem to be decisive here since the amounts of coupling product formed from **2a** were almost identical, regardless of whether NaOH, K_3PO_4 or Bu_4NF were used (Table 1, entries 1, 2, and 5). Surprisingly, in the presence of sodium hydrogenphosphate or sodium carbonate, no reaction took place at all (Table 1, entries 3 and 4).

As mentioned above, the second major side reaction observed was protodeborylation of β-chalcogeno alkenylboranes **2** producing the corresponding vinyl chalcogenides **4**. According to earlier findings,[4] secondary alkyl and cycloalkyl substituted alkenylboranes are usually very reluctant to this reaction, whereas primary alkyl derivatives undergo protodeborylation efficiently. While this trend is reasonably well confirmed by entries 6 and 7 of Table 1, we cannot rationalize the presence of (*E*)-1-cyclohexyl-2-(phenythio)-1-hexene **4a** (27%) among the products in entry 5. In view of the nearly quantitative yield in *n*-pentylcyclohexylacetylene **5b** in the experiment with **2e** (Scheme 3a), formation of only traces of 3-tetradecyne **5c** from **2c** is also rather puzzling (Table 1, entry 7). In this case, the main product appeared to be (*E*)-4-(phenylseleno)-3-tetradecene **4c** (61%) arising from protodeborylation. It is interesting to note that this latter process does not appear to take place exclusively by coordination of hydroxide ion



Scheme 4.

onto **2e** to form a vinylic borate complex followed by reaction with water. Indeed, refluxing **2e** for 16 h with aqueous sodium hydroxide in THF gave only a 35% yield of vinyl selenide **4c**. This suggests that protodeborylation may also be subject to palladium catalysis,[5] in an analogous way to the *syn*-elimination outlined in Scheme 4. Finally, the experiments carried out on **2d** (Table 1, entries 8 and 9) confirm the difficulty to get good yields of coupling product when the boron atom is substituted with primary alkyl groups.

Over the years, several alternative protocols appeared in the literature aiming to improve the performance of the less efficient Suzuki–Miyaura couplings. We tried two of these: the first one, introduced by Soderquist and co-workers,[6] consists in transforming the starting alkenylborane into vinylborinate by anhydrous Me_3NO mediated oxidation before applying the coupling conditions; the second alternative involves boron to copper transmetalation prior to coupling.[7] In our case, neither procedure allowed us to improve the yield of vinyl sulphide **3d$_1$**, starting from **2d**.

Additionally, we also carried out Suzuki–Miyaura coupling experiments on β-butylthio alkenylborane **2b** (the best performing one in Table 1) using benzyl bromide and 1-bromo-1-heptyne as electrophiles. The first one (Scheme 5a) gave deceptively bad results; the *syn*-elimination side reaction largely predominated, in spite of the *n*-butylthio substituant on the starting compound, and only trace amounts of the desired vinyl sulphide **3b$_2$** were formed. In contrast, coupling of **2b** with 1-bromo-1-heptyne produced the butylthioenyne **3b$_3$** in excellent yield (Scheme 5b). The high propensity of 1-halogeno-1-alkynes for Suzuki–Miyaura coupling had been noted earlier.[8]

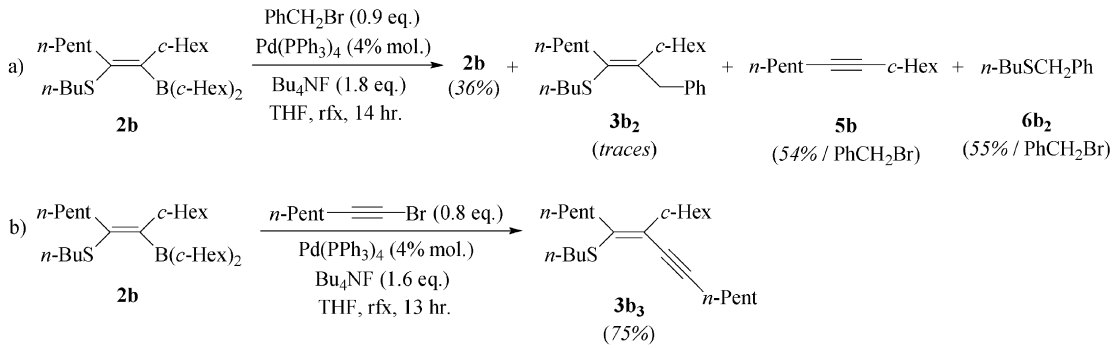
In all cases, the *Z*/*E* ratio of isolated vinyl sulphides (determined by GC) was greater than 98:2. While the absolute stereochemistry of all compounds was not rigorously established, a reasonable assumption is made that the coupling reaction proceeds as usual, with retention of configuration.[2] Finally, in spite of this satisfactory stereochemical outcome and due to the two side reactions occuring competitively with the desired cross-coupling, the whole methodology turns out to be mainly unsuitable for the electrophilic substitution of our intermediates. Nevertheless, in some specific cases, this procedure allows an efficient and straightforward synthesis of trisubstituted vinylsulfides with almost complete control of the stereochemistry.

2.2. Boron to copper transmetalation followed by alkylation

This is a well documented method for carrying out carbodeborylation of various boron derivatives, particularly alkenylboranes leading to olefinic products.[9] Starting from our β-chalcogeno alkenylboranes **2**, we should synthesize fully substituted vinyl chalcogenides which in turn should lead to a variety of olefins with high degrees of regio- and stereoselectivities.

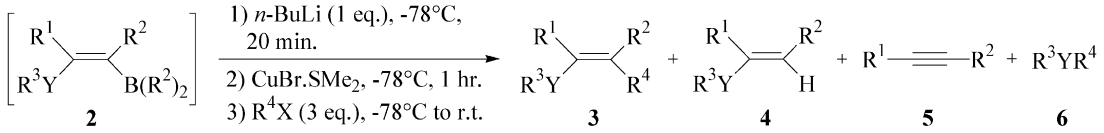
Two types of experimental procedures have been explored. In the first one, both the activation of β-chalcogeno alkenylboranes **2** and the transmetalation have been carried out at low temperature (−78 °C) and in the absence of additives. The results of this procedure using various substrates and electrophiles are displayed in Table 2. Clearly, several situations can be distinguished. Whatever the electrophile used, methyl iodide or allyl bromide, carbodeborylations of β-phenylseleno- and β-phenyltelluro alkenylboranes failed almost completely (Table 2, entries 16–19). As in the coupling experiments, *syn* elimination leading to the appropriate internal alkyne and to phenylmethyl (or allyl) chalcogenides was largely predominating.[10] Somewhat unexpectedly, B–Cu transmetalation followed by allylation of **2k** gave the product **3k$_4$** in excellent yield (Table 2, entry 15). Conjunction of factors such as a sterically less congested vinylcopper intermediate, the weakest leaving group, and the more reactive electrophile may be responsible for this observation.

In all the remaining experiments of Table 2, β-phenylthio- or β-butylthio alkenylboranes have been used as substrates in the presence of various electrophiles. Although *syn* elimination did occur on β-phenylthio derivatives in a few poorly performing reactions, this side reaction was no longer a serious competitor in most of the cases. Thus, high yields of vinyl sulphide could be obtained with methyl iodide (Table 2, entries 7 and 12), allyl bromide (Table 2, entries 1, 2, and 13) and 1-iodo-1-heptyne (Table 2, entries 3 and 14) as electrophiles. Surprisingly, ethylation and benzylation gave poor results (Table 2, entries 4, 8, and 9); once again, significant *syn* elimination and protodeborylation were observed, as illustrated by the formation

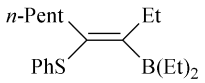
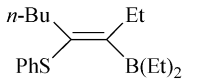
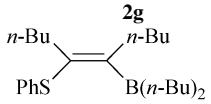
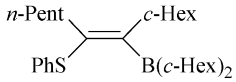
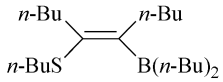
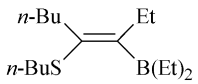
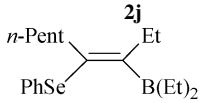
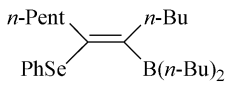
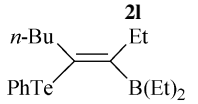


Scheme 5.

Table 2. Carbodeborylation of β-chalcogenovinyl boranes **2**



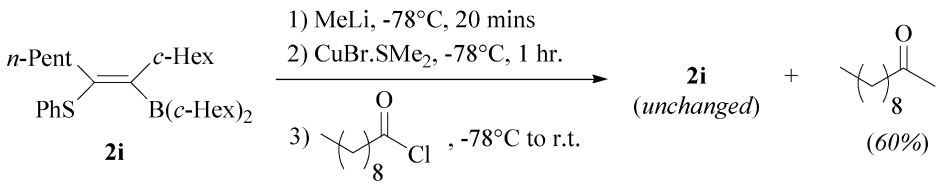
2 **3** **4** **5** **6**

Entry	Reagent	R^4X (equiv.)	Yield (%)			
			3	**4**	**5**	**6**
1	 **2f**	CH_2=CH–CH_2Br	81 (**3f$_4$**)	—	—	—
2[a]	 **2g**	CH_2=CH–CH_2Br	74 (**3g$_4$**)	—	—	—
3	**2g**	*n*-Pent-C≡C–I[b]	63 (**3g$_3$**)	—	—	—
4	**2g**	$PhCH_2Br$	13 (**3g$_2$**)	[c]	[c]	[c]
5	**2g**	MeCOCl	29 (**3g$_5$**)	[c]	[c]	[c]
6	**2g**	PhCOCl	32 (**3g$_6$**)	[c]	[c]	[c]
7	 **2h**	MeI	72 (**3h$_7$**)	[c]	—	—
8	**2h**	EtI	3 (**3h$_8$**)	11 (**4h**)	41 (**5h**)	5 (**6h$_8$**)
9	**2h**	$PhCH_2Br$	11 (**3h$_2$**)	[c]	[c]	[c]
10[d]	 **2i**	MeI	0[e] (**3i$_7$**)	—	—	—
11[d,f]	**2i**	MeI	6[g] (**3i$_7$**)	—	—	—
12	 **2d**	MeI	68 (**3d$_7$**)	[c]	—	—
13	 **2j**	CH_2=CH–CH_2Br	74 (**3j$_4$**)	—	—	—
14	**2j**	*n*-Pent-C≡C–I[b]	59 (**3j$_3$**)	—	—	—
15	 **2k**	CH_2=CH–CH_2Br	71 (**3k$_4$**)	—	—	—
16	 **2l**	MeI	0 (**3l$_7$**)	—	67 (**5l**)	56 (**6l$_7$**)
17[a]	**2l**	MeI	0 (**3l$_7$**)	—	70 (**5l**)	54 (**6l$_7$**)
18	 **2m**	CH_2=CH–CH_2Br	0 (**3m$_4$**)	[c]	—	—
19[a]	**2m**	CH_2=CH–CH_2Br	0 (**3m$_4$**)	[c]	[c]	61 (**3m$_4$**)

[a] MeOLi was used instead of *n*-BuLi.
[b] 1.25 equiv. were introduced.
[c] The formation of these compounds has not been quantified.
[d] These experiments were carried out with isolated starting material.
[e] **2i** was recovered quantitatively.
[f] MeLi was used instead of *n*-BuLi.
[g] 88% of **2i** were recovered.

of the side products **4h** and **5h** during the carbodemetalation of **2h** with ethyl iodide (Table 2, entry 8). This latter process seemed to occur in the acylation reactions as well, although it does not explain alone the modest yields in β-phenylthio enones (Table 2, entries 5 and 6). Nevertheless, it has been reported that simple vinylcopper species display only limited reactivity towards acid chlorides.[11] Finally, it should be noted that the activation step can be carried out with lithium methoxide instead of *n*-butyllithium without a significant decrease in the vinyl sulfide's yield (Table 1, compare entries 1 and 2).

On the other hand, transmetalation of sterically hindered alkenylboranes was unsuccessful using *n*-butyllithium and only slightly better using methyllithium (Table 2, entries 10 and 11). That steric inhibition prevents the complexation of



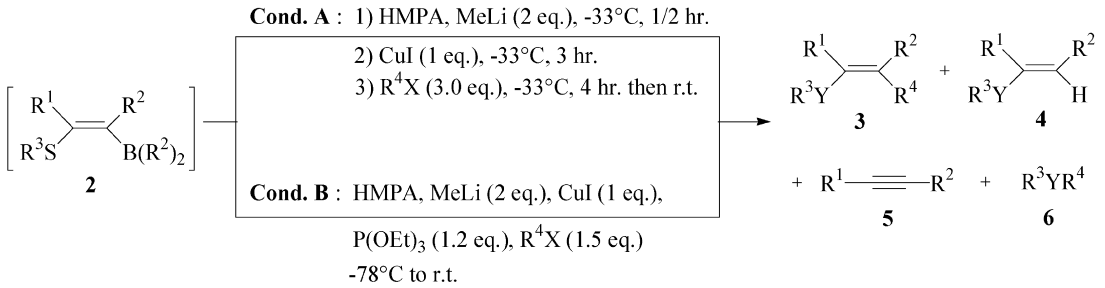
Scheme 6.

the base on the borane in these cases is attested by two observations: (i) the starting β-phenylthio alkenylborane **2i** was recovered unchanged and (ii) when methyl iodide was replaced by decanoyl chloride in the experiment of Table 2, entry 11, 2-undecanone was formed in good yield (Scheme 6), supporting the intermediary formation of methylcopper instead of the desired vinylcopper.

On the basis of the above observations regarding the synthesis of fully substituted vinyl selenides and -tellurides, we decided to limit our further investigations to the improvement of the carbodemetalation efficiency of the sulfur derivatives. This was achieved for most of the unsatisfactory results shown in Table 2 by means of the second type of experimental procedure for boron to copper transmetalation, consisting in carrying out the process in the presence of additives (such as HMPA or $P(OEt)_3$) and/or at somewhat higher temperature.[12,13] Quite spectacular improvements have been observed (Table 3).

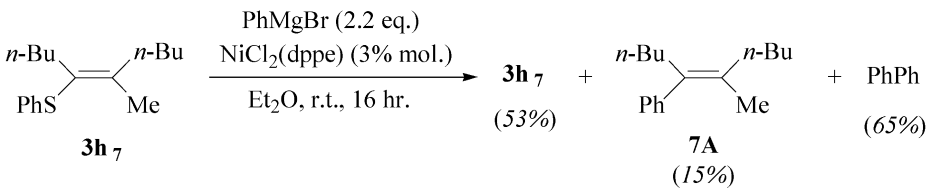
Remarkably, even the sterically hindered alkenylboranes appeared to undergo efficient transmetalation (Table 3,

Table 3. Carbodeborylation of β-chalcogenovinyl boranes **2**



Entry	Reagent		R^4X	Condition	Yield (%)			
					3	**4**	**5**	**6**
1[a]	*n*-Pent, *c*-Hex, PhS, B(*c*-Hex)$_2$	**2i**	MeI	A	69 (**3i$_7$**)	—	[b]	—
2[a]	*n*-Bu, *sec*-Bu, *n*-BuS, B(*sec*-Bu)$_2$	**2n**	CH_2=CH–CH_2Br	A	71 (**3n$_4$**)	—	—	—
3[a]	*n*-Pent, *c*-Hex, PhS, B(*c*-Hex)$_2$	**2i**	EtI	A	28 (**3i$_8$**)	—	24 (**5b**)	—
4	*n*-Bu, *n*-Bu, PhS, B(*n*-Bu)$_2$	**2h**	EtI	A	29 (**3h$_8$**)	—	33 (**5h**)	24 (**6h$_8$**)
5	*n*-Bu, *n*-Bu, PhS, B(*n*-Bu)$_2$	**2h**	EtI	B	45 (**3h$_8$**)	—	21 (**5h**)	19 (**6h$_8$**)
6	*n*-Bu, *n*-Bu, *n*-BuS, B(*n*-Bu)$_2$	**2d**	EtI	B	66 (**3d$_8$**)	—	[b]	[b]
7	*n*-Bu, *n*-Bu, PhS, B(*n*-Bu)$_2$	**2h**	$PhCH_2Br$	B	62 (**3h$_2$**)	—	[b]	[b]
8	*n*-Bu, *n*-Bu, *n*-BuS, B(*n*-Bu)$_2$	**2d**	$PhCH_2Br$	B	64 (**3d$_2$**)	—	[b]	[b]

[a] These experiments were carried out with isolated starting material.
[b] The formation of these compounds has not been quantified.



Scheme 7.

entries 1–3) under conditions A (MeLi, HMPA, −33 °C). Consequently, methylation and allylation of the vinyl copper intermediates gave the desired products in high yield. However, ethyl iodide gave only a modest yield in vinyl sulfide **3i$_8$** because, in this case, the less reactive electrophile allowed *syn* elimination to compete to a larger extent. This interpretation is supported by the next three runs (Table 3, entries 4–6). Indeed, the considerably less hindered alkenylborane **2h** gave essentially the same results (Table 3, compare entries 3 and 4), whereas at lower temperature (conditions B: MeLi, HMPA, $P(OEt)_3$, −78 °C), the ethylation yield increased to 45% (Table 3, entry 5). Applying conditions B to vinylborane **2d** carrying the poorer butylthio leaving group in β position led to ethylation product **3d$_8$** in good yield (Table 3, compare entries 5 and 6). These latter conditions also allowed to carry out benzylation reactions in a satisfactory manner (Table 3, entries 7 and 8).

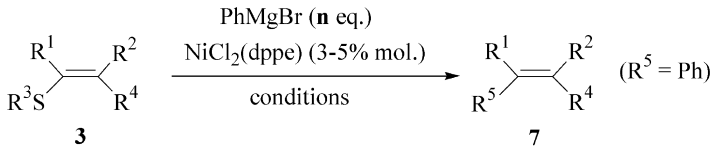
The boron to copper transmetalation of alkenylboranes is known to occur with almost complete retention of the configuration.[9] For all the experiments described here, the ratio of stereoisomers in the crude product was greater than 98:2, in favour of the structures drawn in Tables 2 and 3 (vide infra for ascertainment of stereochemistry). Furthermore, in most of the cases, no trace of the other stereoisomer could be detected after purification, neither by ^{1}H NMR nor GC. At this point, we can therefore conclude that the present strategy gives access to a fairly large variety of fully substituted vinyl sulfides with excellent stereochemical control. In itself, this is an appreciable achievement taking into account the usefulness of this class of compounds, and especially that of the corresponding vinyl sulfoxides and -sulfones.[14]

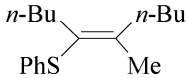
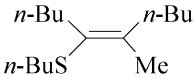
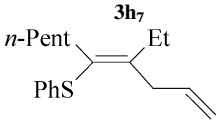
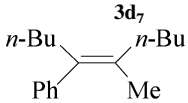
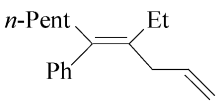
2.3. Synthesis of tetrasubstituted olefins from vinylsulfides

We have reported on the efficient conversion of various vinyl chalcogenides into trisubstituted olefins using the well known nickel catalyzed coupling with Grignard reagents.[1] Starting from vinyl sulfides, this transformation appeared to occur with excellent yield and stereoselectivity by the use of 1,2-bis-(diphenylphosphinoethane) nickel chloride ($NiCl_2$-(dppe)). However, applying the conditions used earlier to the coupling of fully substituted vinyl sulfide **3h$_7$** with phenylmagnesium bromide gave disappointing results: the desired olefin was formed in low yield and about half of the starting material was recovered unchanged (Scheme 7). Prolonging the reaction time did not bring about higher conversion.

In addition, GC and GC–MS monitoring of the coupling reaction revealed the presence in the reaction mixture of a substantial amount of 5-methyldecen-6-thiol. Formation of this thioenol (or of its magnesium salt) could be due to the

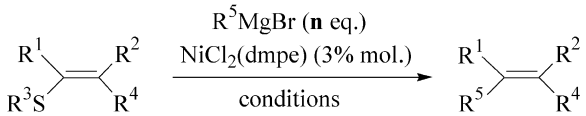
Table 4. Synthesis of tetrasubstituted olefins



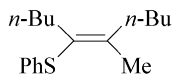
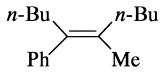
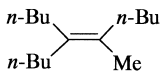
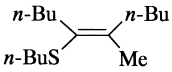
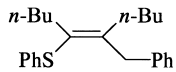
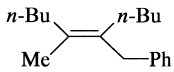
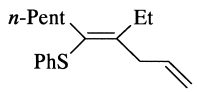
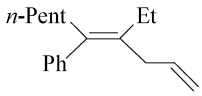
Entry	Reagent		*n*	Conditions	Product		Yield (%)
1		**3h$_7$**	2.4	Et_2O, rfx, 48 h		**7A**	28
2	**3h$_7$**		10	Et_2O, rt, 16 h	**7A**		13
3		**3d$_7$**	1.5	Et_2O, rt, 15 h	**7A**		0[a]
4	**3d$_7$**		2	Benzene, rfx, 15 h	**7A**		0[a]
5		**3f$_4$**	2.4	Et_2O, rt, 18 h		**7B**	26[b]
6	**3f$_4$**		2.4	Et_2O, rfx, 38 h	**7B**		27

[a] **3d$_7$** was recovered quantitatively.
[b] 43% of **3f$_4$** were recovered, and 59% of biphenyl were also formed.

Table 5. Synthesis of tetrasubstituted olefins



3 **7**

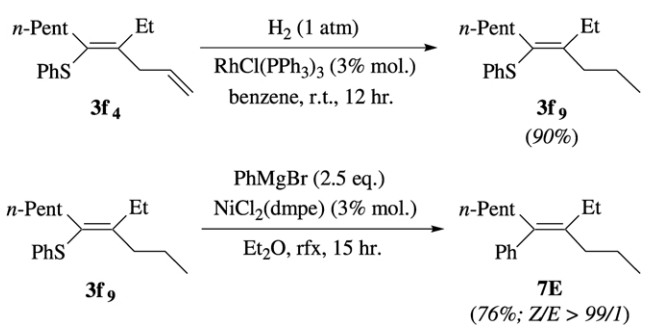
Entry	Reagent	R^5	*n*	Conditions	Product	*E*/*Z*	Yield (%)
1	 **3h₇**	Ph	5	Et_2O, rfx, 16 h	 **7A**	>98:2	66
2	**3h₇**	Ph	5	Et_2O, rfx, 24 h	**7A**	>96:4	75
3	**3h₇**	Ph	5	Et_2O, rt, 24 h	**7A**	>96:4	36[a]
4	**3h₇**	Ph	2.5	Et_2O, rfx, 14.5 h	**7A**	>99:1	82
5	**3h₇**	*n*-Bu	2.5	Et_2O, rfx, 22.5 h	 **7C**	—	70
6	 **3d₇**	Ph	5	Et_2O, rfx, 16 h	**7A**	—	0[b]
7	**3d₇**	Ph	3	Bu_2O, 90 °C, 15 h	**7A**	—	0[b]
8	 **3h₂**	Me	2.5	Et_2O, rfx, 10 days	 **7D**	>99:1	24[c]
9	 **3f₄**	Ph	2.5	Et_2O, rfx, 23 h	 **7B**	<1:99	38
10	**3f₄**	Ph	5	Et_2O, rfx, 22.5 h	**7B**	<1:99	38

[a] 43% of **3h₇** were recovered.
[b] **3d₇** was recovered quantitatively.
[c] 60% of **3h₂** were recovered.

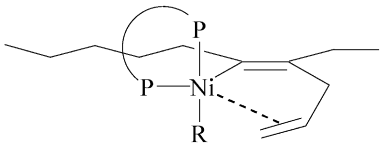
preferential insertion of Ni(0) during the catalytic cycle into the S–phenyl bond instead of the S–vinyl bond, itself arising from the notably higher steric congestion of the vinylic moiety in **3h₇**. The resulting thioenolate may have led to blocking of the reaction, leaving a large part of starting **3h₇** unchanged. Furthermore, the limited performance of $NiCl_2$(dppe) is not restricted to the case displayed in Scheme 7; it is a poor catalyst for the coupling under different conditions of other fully substituted vinyl sulfides too (Table 4).

In connection with the coupling of unsaturated halogen compounds with vinylic and allylic Grignard reagents, Kumada and co-workers found that 1,2-bis-(dimethylphosphinoethane) nickel chloride ($NiCl_2$(dmpe)[15]) exhibited superior activity as compared to the corresponding dppe and dppp catalysts.[16] We anticipated that the more electron donating and less bulky dmpe ligand would confer higher activity to this catalyst in the coupling reactions of our sterically congested vinyl sulfides too. As witnessed in Table 5, this expectation was confirmed, at least in part. Indeed, the reaction of **3h₇** with phenylmagnesium bromide has now produced the desired olefin **7A** in excellent yield (Table 5, entry 4; compare to Scheme 7), and it also works well with butylmagnesium bromide (Table 5, entry 5). Nevertheless, it can be seen (Table 5, entries 1–4) that the reaction conditions, especially the ratio of reactants and reaction time, play an important role in the efficiency as well as the stereoselectivity of these couplings. Unfortunately, even this catalyst was found unable to couple butylvinyl sulfide **3d₇** which was recovered quantitatively from two different runs (Table 5, entries 6 and 7). Phenylvinyl sulfides bearing benzyl (**3h₂**) or allyl (**3f₄**) moieties next to the phenylthio group represent intermediary cases in which the conversion was not higher than 20–40% (Table 5, entries 8–10). The reason for this limited conversion is unclear, but it is interesting to note that vinylsulfide **3f₉**, produced by catalytic hydrogenation of compound **3f₄**, gave the olefin **7E** in high yield on coupling with PhMgBr (Scheme 8).

Therefore, the ability of nickel to coordinate C,C double bonds appears responsible for the above limitations, possibly through intramolecular coordination of the terminal double bond in the vinylnickel intermediate (Scheme 9).



Scheme 8.



R = SPh, SMgBr, Ph

Scheme 9.

Finally, DiffNOE experiment carried out on olefin **7D** gave the anticipated result: irradiation of the benzylic hydrogens (s, 3.40 ppm) brought about disappearance of almost all the signals in the difference spectrum with the exception of a large singlet persisting at 1.72 ppm due to the methyl group *cis* to benzyl group. This shows thereby that both steps of the transformation of β-phenylthio alkenylboranes into tetrasubstituted olefins have taken place with retention of configuration of the C,C double bond.

3. Conclusion

In conclusion, we had shown that chalcogen electrophile induced rearrangements of 1-alkynyltrialkyborates give access with good to excellent efficiencies and in well defined regio- and stereochemical ways to a large variety of disubstituted vinyl sulfides, -selenides and -tellurides (see Ref. 1). Due to the weaker vinylic C–Se and C–Te bonds leading to higher leaving propensity of the selenium and tellurium moieties, only trisubstituted vinyl sulfides can be obtained in satisfactory yields through the carbodeborylation protocol (boron to copper transmetalation followed by alkylation). With the exception of a few cases, all the accessible vinyl sulfides can be transformed into the corresponding tri- or tetrasubstituted olefins by means of the nickel catalyzed coupling with aliphatic or aromatic Grignard reagents.

4. Experimental

4.1. General

All glassware, syringes and needles were oven dried at 120 °C for several hours prior to use. The glassware were assembled while hot and cooled under a stream of argon. ^{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) were used for column chromatography. THF and Et_2O were distilled from sodium/benzophenone. HMPA was distilled from CaH_2. Methyl iodide, ethyl iodide, iodobenzene, allyl bromide, benzyl bromide, acetyl chloride, benzoyl chloride, decanoyl chloride, and triethyl phosphite were purchased from Aldrich and distilled prior to use. The other reagents were purchased from Aldrich and used without further purification, except tetrakis(triphenylphosphine)palladium,[17] 1-halo-1-heptynes,[18] and 1,2-bis-(dimethylphosphinoethane) nickel chloride,[15] which were synthesized according to the reported procedures. The synthesis and characterization of the starting β-chalcogeno alkenylboranes has been described previously.[1]

4.2. Suzuki–Miyaura couplings

4.2.1. Representative procedure (RP-1) for the Suzuki–Miyaura coupling of isolated alkenylboranes. Synthesis of (*Z*)-1-cyclohexyl-1-phenyl-2-(phenylthio)-1-hexene ($\mathbf{3a_1}$). In a 25 mL two-necked flask, equipped with an argon inlet and a magnetic stirring bar, were successively introduced a THF solution (3 mL) of **2a** (0.450 g; 1 mmol), tetrakis(triphenylphosphine)palladium (0.045 g; 4 mol%), and a THF solution (2 mL) of iodobenzene (0.163 g; 0.8 mmol; 0.8 equiv.). Tetrabutylammonium fluoride (1.6 mL of a 1 M solution in THF; 1.6 mmol; 1.6 equiv.) was added, and the reaction mixture was heated to reflux for 13 h. After cooling to room temperature, the solution was diluted with 15 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 0.046 g of *n*-butylcyclohexylacetylene **5a** (35% yield), 0.055 g of diphenylsulphide $\mathbf{6a_1}$ (37% yield), 0.073 g of (*E*)-1-cyclohexyl-2-(phenylthio)-1-hexene **4a** (27% yield),[1] and 0.103 g of $\mathbf{3a_1}$ (37% yield) as a colorless liquid. IR (neat): 3074, 3058, 3020, 2930, 2855, 1584, 1476, 1441, 1072, 1025, 909, 739, 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, J=7.3 Hz), 0.94–1.04 (1H, m), 1.07–1.18 (2H, m), 1.28–1.37 (4H, m), 1.51–1.61 (3H, m), 1.74 (4H, m), 2.33 (2H, t, J=7.3 Hz), 2.77 (1H, tt, J=12.0, 2.9 Hz), 7.00–7.30 (10H, m); ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 14.0, 22.4, 25.7, 26.6, 31.5, 31.7, 32.0, 42.4, 125.5, 126.4, 127.5, 128.6, 129.0, 129.4, 130.6, 136.9, 141.0; MS (EI): 350 (M^+, 100), 273 (54), 226 (8), 217 (9), 183 (14), 171 (8), 155 (13), 141 (19), 129 (20), 117 (23), 91 (33), 55 (11); HRMS: *m/z* for $C_{24}H_{30}S$, calcd: 350.2068. Found: 350.2060.

4.2.2. (*Z*)-2-(*n*-Butythio)-1-cyclohexyl-1-phenyl-1-heptene ($\mathbf{3b_1}$). Synthesized according to RP-1 and starting from **2b**. Column chromatography (silica gel; pentane) afforded *n*-pentylcyclohexylacetylene **5b** (9% yield) and $\mathbf{3b_1}$ (70% yield), as a colorless liquid. IR (neat): 3078, 3055, 3025, 2956, 2929, 2854, 1595, 1489, 1450, 1378, 1271, 1140, 1072, 891, 769, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, J=7.2 Hz), 0.96 (3H, t, J=6.8 Hz), 0.97–1.10 (3H, m), 1.22–1.44 (10H, m), 1.60–1.73 (7H, m), 2.38–2.45 (4H, m), 2.69 (1H, tt, J=11.7, 3.2 Hz), 6.95–6.98 (2H, m), 7.24–7.34 (3H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.6, 14.1, 21.9, 22.6, 25.8, 26.6, 29.1, 30.5, 31.4, 31.7, 31.8, 32.1, 42.2, 126.1, 127.3, 130.0, 130.8, 141.3, 147.7; MS (EI): 344 (M^+, 65), 287 (100), 253 (7), 231 (5), 217 (6), 205 (6), 183 (13), 171 (8), 155 (6), 141 (12), 129 (14), 115 (16), 91 (18), 55 (12). Anal. Calcd for $C_{23}H_{36}S$: C, 80.17; H, 10.53. Found: C, 79.93; H, 10.55.

4.2.3. (*E*)-3-(*n*-Butylthio)-2-cyclohexyl-1-phenyl-2-octene ($\mathbf{3b_2}$). The attempted synthesis of $\mathbf{3b_2}$ was performed according to RP-1 and starting from **2b**. Traces of $\mathbf{3b_2}$ were

detected by GC–MS in the crude product. Column chromatography (silica gel; pentane) afforded **2b** (36% yield), *n*-pentylcyclohexylacetylene **5b** (54% yield) and benzyl-*n*-butylthioether **6b$_2$** (55% yield; ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.88 (3H, t, J=7.0 Hz), 1.26–1.63 (4H, m), 2.41 (2H, t, J=6.9 Hz), 3.70 (2H, s), 7.25–7.32 (5H, m); MS (EI): 180 (M^+, 29), 91 (100), 65 (8)).

4.2.4. (*Z*)-6-(*n*-Butylthio)-7-cyclohexyl-6-tetradecene-8-yne (3b$_3$). Synthesized according to RP-1 and starting from **2b**. Column chromatography (silica gel; pentane/Et_2O, 99:1) afforded **3b$_3$** (75% yield), as a yellow liquid. IR (neat): 2958, 2930, 2856, 2212, 1570, 1463, 1452, 1380, 1262, 1101, 890 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (9H, m), 1.10–1.67 (24H, m), 1.74–1.78 (2H, m), 2.30 (2H, t, J=7.8 Hz), 2.35 (1H, m), 2.41 (2H, t, J=6.8 Hz), 2.73 (2H, t, J=7.4 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.7, 14.0, 14.0, 19.8, 22.1, 22.2, 22.5, 25.9, 26.4, 28.7, 29.1, 31.2, 31.6, 31.8, 31.9, 41.0, 79.0, 97.6, 127.5, 139.1; MS (EI): 362 (M^+, 23), 305 (100), 249 (55), 223 (33), 181 (36), 167 (14), 115 (7), 91 (13), 81 (26), 55 (21); HRMS: *m*/*z* for $C_{24}H_{42}S$, calcd: 362.3007. Found: 362.3013.

4.2.5. Representative procedure (RP-2) for the in situ Suzuki–Miyaura coupling of air-sensitive alkenylboranes. Synthesis of (*Z*)-6-(*n*-butylthio)-5-phenyl-5-decene (3d$_1$). A 50 mL two-necked flask, equipped with a reflux condenser, an argon inlet and a magnetic stirring bar, was charged with a THF solution (4 mL) of 1-hexyne (0.164 g; 2 mmol). At −20 °C were added 1.25 mL of *n*-butyllithium (1.6 M in hexane; 2 mmol). After 1 h of stirring at −20 °C, 2 mL of tributylborane (1 M solution in THF; 2 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 (4 mL) of *n*-butylsulfenyl chloride (0.249 g; 2 mmol) was added dropwise. The cooling bath was then removed and the mixture was stirred for 30 min at room temperature. To this solution was successively added tetrakis(triphenylphosphine)palladium (0.092 g; 4 mol%), a THF solution (1 mL) of iodobenzene (0.367 g; 1.8 mmol; 0.9 equiv.) and 3.6 mL of tetrabutylammonium fluoride (1 M in THF; 3.6 mmol; 1.8 equiv.). The reaction mixture was heated to reflux for 20 h. After cooling to room temperature, the solution was diluted with 15 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 0.204 g of **3d$_1$** (37% yield) as a colorless liquid. IR (neat): 3055, 3020, 2958, 2930, 2871, 1597, 1490, 1463, 1441, 1379, 1135, 1101, 1070, 769, 700 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.77–1.05 (9H, m), 1.14–1.71 (12H, m), 2.38 (6H, m), 7.04–7.33 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.6, 13.9, 14.1, 21.9, 22.6, 22.7, 30.5, 31.3, 31.4, 31.6, 31.8, 35.2, 126.2, 127.7, 128.8, 130.8, 142.9, 143.5; MS (EI): 304 (M^+, 100), 261 (35), 247 (94), 205 (10), 191 (20), 171 (9), 157 (10), 143 (15), 129 (42), 115 (21), 91 (27), 57 (13). Anal. Calcd for $C_{20}H_{32}S$: C, 78.88; H, 10.59. Found: C, 79.05; H, 10.20.

4.2.6. (*Z*)-3-Phenyl-4-(phenylseleno)-3-tetradecene (3c$_1$). The attempted synthesis of **3c$_1$** was performed according to RP-2, through the preparation of **2c**. Sodium hydroxide (3.0 equiv.) was used instead of tetrabutylammonium fluoride, and the mixture was heated to reflux for 16 h. Column chromatography (silica gel; pentane) afforded (*E*)-4-(phenylseleno)-3-tetradecene **4c** (61% yield), as a yellowish liquid. IR (neat): 3071, 2961, 2927, 2854, 1580, 1475, 1462, 1439, 1377, 1144, 1068, 1023, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, J=6.8 Hz), 1.01 (3H, t, J=7.3 Hz), 1.21–1.37 (14H, m), 1.47 (2H, m), 2.14 (2H, quint., J=7.6 Hz), 2.24 (2H, t, J=7.6 Hz), 5.93 (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 14.1, 22.7, 22.8, 29.0, 29.1, 29.3, 29.5, 29.6, 31.9, 32.8, 126.7, 129.0, 131.1, 131.6, 132.5, 139.7; MS (EI): 352 (M^+, 76), 226 (99), 198 (32), 183 (15), 158 (67), 145 (13), 111 (17), 97 (38), 83 (51), 69 (100), 55 (99); HRMS: *m*/*z* for $C_{20}H_{32}Se$, calcd: 352.1669. Found: 352.1674.

4.3. Boron to copper transmetalation

4.3.1. Representative procedure (RP-3) for the boron to copper transmetalation (Scheme 6). Synthesis of (*Z*)-4-ethyl-5-(phenylthio)-1,4-decadiene (3f$_4$). A 100 mL two-necked flask, equipped with a reflux condenser, an argon inlet and a magnetic stirring bar, was charged with a THF solution (26 mL) of 1-heptyne (1.538 g; 16 mmol). At −20 °C were added 10 mL of *n*-butyllithium (1.6 M in hexane; 16 mmol). After 1 h of stirring at −20 °C, 16 mL of triethylborane (1 M solution in THF; 16 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 (18 mL) of benzenesulfenyl chloride (2.312 g; 16 mmol) was added dropwise. The cooling bath was then removed and the mixture was stirred for 30 min at room temperature. The reaction flask was cooled to −78 °C and 10 mL of *n*-butyllithium (1.6 M in hexane; 16 mmol) were introduced. After 20 min, the mixture was transferred via cannula to a separate reaction flask containing 3.290 g of $CuBr{\cdot}SMe_2$ (16 mmol) in 16 mL of THF maintained at −78 °C. After an additional hour of stirring at −78 °C, 4.15 mL of allyl bromide (48 mmol; 3 equiv.) were added, and the reaction flask was gradually warmed to room temperature. The mixture was then diluted with 80 mL of Et_2O, and washed three times with 30 mL of a mixture of saturated aqueous NH_4Cl and NH_4OH (4:1, v/v), and two times with 20 mL of water. The organic phase was dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (silica gel; pentane) to afford 3.568 g of **3f$_4$** (81% yield) as a colorless liquid. IR (neat): 3075, 2960, 2873, 1639, 1584, 1477, 1439, 1376, 1086, 1025, 994, 912, 739, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (3H, t, J=7.1 Hz), 1.09 (3H, t, J=7.6 Hz), 1.18–1.29 (4H, m), 1.50 (2H, m), 2.21 (2H, t, J=7.8 Hz), 2.24 (2H, q, J=7.6 Hz), 3.20 (2H, d, J=6.4 Hz), 4.99–5.05 (2H, m), 5.77 (1H, ddt, J=16.9, 10.0, 6.3 Hz), 7.10–7.15 (1H, m), 7.17–7.26 (4H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ13.3, 14.0, 22.5, 25.4, 29.0, 31.6, 32.9, 38.6, 115.5, 125.2, 128.2, 128.4, 128.7, 136.3, 137.1, 147.1; MS (EI): 274 (M^+, 39), 197 (100), 183 (6), 127 (16), 109 (11), 91 (17), 79 (21), 67 (12), 55 (10). Anal. Calcd for $C_{18}H_{26}S$: C, 78.77; H, 9.55. Found: C, 78.22; H, 9.66.

4.3.2. (*Z*)-4-Ethyl-5-(phenylthio)-1,4-nonadiene (3g$_4$). Synthesized according to RP-3, through the preparation of **2g**. The activation step was performed by transfer (through

cannula) of the alkenylborane mixture on a suspension of lithium methoxide in THF, previously cooled to −78 °C (prepared by addition of 1 equiv. of *n*-butyllithium over a THF solution of methanol at −78 °C, followed by stirring at room temperature for 1 h). Column chromatography (silica gel; pentane) afforded **3g$_4$** (74% yield), as a colorless liquid. IR (neat): 3075, 2961, 2932, 2873, 1638, 1614, 1584, 1477, 1459, 1439, 1376, 1215, 1086, 1025, 942, 912, 739, 692 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.85 (3H, t, J=6.8 Hz), 1.09 (3H, t, J=7.5 Hz), 1.13–1.59 (4H, m), 2.15–2.29 (4H, m), 3.21 (2H, d, J=6.4 Hz), 4.91–5.12 (2H, m), 5.78 (1H, ddt, J=17.4, 9.4, 6.2 Hz), 7.15–7.28 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ13.3, 14.0, 22.5, 25.4, 31.5, 32.7, 38.6, 115.5, 125.2, 128.2, 128.3, 128.7, 136.3, 137.1, 147.1; MS (EI): 260 (M$^+$, 42), 183 (100), 127 (17), 109 (13), 91 (18), 79 (23), 67 (13), 55 (9). Anal. Calcd for $C_{17}H_{24}S$: C, 78.40; H, 9.29. Found: C, 77.91; H, 9.32.

4.3.3. (*Z*)-5-(*n*-Butylthio)-4-ethyl-1,4-nonadiene (3j$_4$). Synthesized according to RP-3, through the preparation of **2j**. Column chromatography (silica gel; pentane) afforded **3j$_4$** (74% yield), as a colorless liquid. IR (neat): 3078, 2961, 2932, 2873, 1638, 1609, 1461, 1434, 1377, 1216, 994, 909 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.88–1.06 (9H, m), 1.14–1.67 (8H, m), 2.13 (2H, q, J=7.4 Hz), 2.26 (2H, t, J=7.7 Hz), 2.55 (2H, t, J=7.2 Hz), 3.16 (2H, d, J=6.2 Hz), 4.88–5.09 (2H, m), 5.77 (1H, ddt, J=17.6, 9.3, 6.2 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ13.3, 13.7, 14.1, 22.0, 22.6, 25.3, 31.1, 31.5, 31.8, 31.9, 38.3, 114.9, 129.5, 136.7, 142.1; MS (EI): 240 (M$^+$, 9), 183 (100), 169 (8), 149 (8), 127 (31), 107 (19), 93 (20), 79 (19), 67 (13), 55 (12); HRMS: *m*/*z* for $C_{15}H_{28}S$, calcd: 240.1912. Found: 240.1919.

4.3.4. (*Z*)-4-Ethyl-5-(phenylseleno)-1,4-decadiene (3k$_4$). Synthesized according to RP-3, through the preparation of **2k**. Column chromatography (silica gel; pentane) afforded **3k$_4$** (71% yield), as a yellowish liquid. IR (neat): 3072, 2960, 2931, 2868, 1638, 1580, 1438, 1376, 1069, 1023, 994, 912, 735, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (3H, t, J=7.1 Hz), 1.07 (3H, t, J=7.6 Hz), 1.19–1.31 (4H, m), 1.49 (2H, m), 2.23 (2H, q, J=7.3 Hz), 2.26 (2H, t, J=7.8 Hz), 3.20 (2H, d, J=6.4 Hz), 4.99–5.05 (2H, m), 5.77 (1H, ddt, J=16.8, 10.0, 6.8 Hz), 7.18–7.26 (3H, m), 7.36 (2H, m); ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 13.4, 14.0, 22.5, 25.2, 29.4, 31.5, 34.7, 41.0, 115.5, 126.1, 128.7, 128.9, 131.4, 131.9, 136.4, 145.3; MS (EI): 322 (M$^+$, 50), 245 (100), 175 (7), 157 (11), 123 (8), 109 (25), 95 (54), 91 (32), 79 (40), 67 (51), 55 (41); HRMS: *m*/*z* for $C_{18}H_{26}Se$, calcd: 322.1200. Found: 322.1202.

4.3.5. (*E*)-6-(*n*-Butylthio)-5-methyl-5-decene (3d$_7$). Synthesized according to RP-3, through the preparation of **2d** and the use of methyl iodide as electrophile. Column chromatography (silica gel; pentane) afforded **3d$_7$** (68% yield), as a colorless liquid. IR (neat): 2959, 2931, 2861, 1619, 1464, 1377, 1273, 1222, 1103, 993, 744 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.83–0.98 (9H, m), 1.13–1.65 (12H, m), 1.92 (3H, s), 2.04–2.33 (4H, m), 2.55 (2H, t, J=7.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.7, 14.0, 20.8, 22.0, 22.6, 22.8, 30.7, 31.4, 31.9, 31.9, 32.1, 34.6, 127.9, 139.3; MS (EI): 242 (M$^+$, 75), 199 (50), 185 (100), 143 (26), 129 (10), 109 (19), 101 (23), 95 (16), 87 (17), 81 (12), 69 (21), 67 (21), 55 (24); HRMS: *m*/*z* for $C_{15}H_{30}S$, calcd: 242.2068. Found: 242.2063.

4.3.6. (*E*)-5-Methyl-6-(phenylthio)-5-decene (3h$_7$). Synthesized according to RP-3, through the preparation of **2h** and the use of methyl iodide as electrophile. Column chromatography (silica gel; pentane) afforded **3h$_7$** (72% yield), as a colorless liquid. IR (neat): 3072, 2958, 2930, 2861, 1620, 1584, 1477, 1466, 1440, 1377, 1086, 1025, 738, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, J=7.4 Hz), 0.96 (3H, t, J=7.0 Hz), 1.26 (2H, m), 1.39 (2H, m), 1.43–1.50 (4H, m), 1.98 (3H, s), 2.24 (2H, t, J=7.6 Hz), 2.25 (2H, t, J=7.6 Hz), 7.09–7.13 (1H, m), 7.17 (2H, m), 7.22–7.26 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ14.0, 14.0, 21.2, 22.5, 22.9, 30.7, 31.4, 33.4, 34.6, 124.9, 126.5, 127.5, 128.7, 137.6, 144.8; MS (EI): 262 (M$^+$, 100), 219 (32), 164 (39), 149 (32), 135 (19), 123 (16), 109 (19), 95 (13), 81 (12), 67 (21), 55 (28). Anal. Calcd for $C_{17}H_{26}S$: C, 77.80; H, 9.98. Found: C, 77.41; H, 10.44.

4.3.7. (*Z*)-6-Ethyl-5-(phenylthio)-5-tridecene-7-yne (3g$_3$). Synthesized according to RP-3, through the preparation of **2g** and the use of 1-iodo-1-heptyne (1.25 equiv.) as electrophile. Column chromatography (silica gel; pentane) afforded **3g$_3$** (63% yield), as a yellowish liquid. IR (neat): 3072, 3060, 2959, 2932, 2861, 2218, 1731, 1583, 1475, 1465, 1440, 1377, 1329, 1068, 1086, 1025, 743, 692 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.78–0.94 (6H, m), 1.15 (3H, t, J=7.5 Hz), 1.20–1.57 (10H, m), 2.11–2.41 (6H, m), 7.16–7.38 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ13.5, 13.7, 13.9, 19.6, 22.2, 22.3, 26.8, 28.5, 31.0, 31.1, 31.5, 80.4, 96.3, 126.5, 127.3, 128.6, 131.2, 135.3, 138.5; MS (EI): 314 (M$^+$, 25), 258 (7), 237 (37), 205 (12), 181 (100), 149 (7), 119 (7), 105 (10), 91 (21), 77 (12), 55 (9); HRMS: *m*/*z* for $C_{21}H_{30}S$, calcd: 314.2068. Found: 314.2072.

4.3.8. (*Z*)-5-(*n*-Butylthio)-6-ethyl-5-tridecene-7-yne (3j$_3$). Synthesized according to RP-3, through the preparation of **2j** and the use of 1-iodo-1-heptyne (1.25 equiv.) as electrophile. Column chromatography (silica gel; pentane/Et_2O, 99.5:0.5) afforded **3j$_3$** (59% yield), as a colorless liquid. IR (neat): 2959, 2931, 2861, 2218, 1580, 1462, 1378, 1329, 1271, 1133, 1101, 1061, 746 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 0.84–0.99 (9H, m), 1.08 (3H, t, J=7.6 Hz), 1.19–1.62 (14H, m), 2.08–2.48 (6H, m), 2.74 (3H, t, J=7.6 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.5, 13.7, 13.9, 14.0, 19.7, 22.0, 22.2, 22.6, 26.7, 28.6, 31.1, 31.3, 31.6, 31.8, 80.4, 96.5, 123.3, 139.7; MS (EI): 294 (M$^+$, 23), 237 (35), 205 (8), 181 (100), 125 (11), 107 (7), 91 (9), 55 (5); HRMS: *m*/*z* for $C_{19}H_{34}S$, calcd: 294.2381. Found: 294.2387.

4.3.9. (*Z*)-3-Benzyl-4-(phenylthio)-3-octene (3g$_2$). Synthesized according to RP-3, through the preparation of **2g** and the use of benzyl bromide as electrophile. Kugelrohr distillation followed by column chromatography (silica gel; pentane) afforded **3g$_2$** (13% yield), as a yellowish liquid. IR (neat): 3062, 3027, 2960, 2931, 2872, 1601, 1584, 1494, 1477, 1454, 1441, 1117, 1089, 1027, 739, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, J=7.2 Hz), 1.06 (3H, t, J=7.6 Hz), 1.26 (2H, m), 1.53 (2H, m), 2.17 (2H, q, J=7.5 Hz), 2.27 (2H, t, J=7.8 Hz), 3.86 (2H, s), 7.10–7.28 (10H, m); ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 13.4, 14.0,

22.5, 25.0, 31.6, 32.6, 39.6, 125.3, 125.9, 128.3, 128.3, 128.7, 128.8, 137.1, 140.2, 148.0; MS (EI): 310 (M^+, 100), 281 (9), 219 (10), 177 (8), 167 (8), 157 (11), 145 (23), 129 (44), 117 (21), 105 (8), 91 (65), 65 (8). Anal. Calcd for $C_{21}H_{26}S$: C, 81.23; H, 8.44. Found: C, 81.10; H, 8.73.

4.3.10. (*Z*)-3-Ethyl-4-(phenylthio)-3-octen-2-one ($3g_5$). Synthesized according to RP-3, through the preparation of **2g** and the use of acetyl chloride as electrophile. Column chromatography (silica gel; pentane/Et_2O, 95:5) afforded $\mathbf{3g_5}$ (29% yield), as a yellow liquid. IR (neat): 3060, 2960, 2933, 2873, 1692, 1583, 1478, 1440, 1377, 1350, 1241, 1140, 1096, 1025, 744, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.80 (3H, t, J=7.3 Hz), 1.10 (3H, t, J=7.6 Hz), 1.21 (2H, m), 1.45 (2H, m), 2.18 (2H, t, J=7.8 Hz), 2.40 (3H, s), 2.41 (2H, q, J=7.5 Hz), 7.22–7.32 (5H, m); ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 13.4, 13.8, 22.3, 24.2, 30.5, 31.1, 31.2, 126.9, 129.0, 130.4, 134.6, 134.8, 147.7, 204.7; MS (EI): 262 (M^+, 60), 247 (7), 185 (6), 153 (100), 135 (6), 110 (19); HRMS: m/z for $C_{16}H_{22}OS$, calcd: 262.1391. Found: 262.1395.

4.3.11. (*Z*)-2-Ethyl-1-phenyl-3-(phenylthio)-hept-2-ene-1-one ($3g_6$). Synthesized according to RP-3, through the preparation of **2g** and the use of benzoyl chloride as electrophile. Column chromatography (silica gel; pentane/Et_2O, 95:5) afforded $\mathbf{3g_5}$ (32% yield), as a yellowish liquid. IR (neat): 3060, 2959, 2932, 2873, 1665, 1597, 1581, 1478, 1449, 1315, 1279, 1245, 1026, 1168, 1024, 897, 743, 711, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, J=7.3 Hz), 1.10 (3H, t, J=7.6 Hz), 1.33 (2H, m), 1.59 (2H, m), 2.29 (2H, t, J=7.8 Hz), 2.51 (2H, q, J=7.6 Hz), 7.15–7.25 (5H, m), 7.46 (2H, m), 7.54 (1H, m), 7.95 (2H, m); ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 13.1, 13.9, 22.5, 25.1, 30.7, 30.8, 31.1, 126.7, 128.6, 128.8, 129.1, 130.5, 132.9, 133.0, 134.5, 137.0, 146.6, 198.1; MS (EI): 324 (M^+, 35), 281 (11), 247 (8), 215 (79), 173 (31), 159 (12), 145 (14), 105 (100), 77 (57); HRMS: m/z for $C_{21}H_{24}OS$, calcd: 324.1548. Found: 324.1552.

4.3.12. Representative procedure (RP-4) for the boron to copper transmetalation (Scheme 7, conditions A). Synthesis of (*E*)-2-cyclohexyl-3-(phenylthio)-2-octene ($3i_7$). A three-necked 25 mL flask equipped with a septum and a flexible side-arm containing 0.191 g (1 mmol) of copper(I) iodide was placed under argon, and charged with a THF solution (3 mL) of **2i** and 0.5 mL of HMPA. At −33 °C, 1.42 mL of methyllithium were introduced (1.4 M in ether; 2 mmol; 2 equiv.) and the flask was keeped at this temperature for 30 min before the addition of the copper iodide. The mixture was maintained at −33 °C for 3 h under vigorous stirring before the introduction of methyl iodide (0.19 mL; 3 mmol; 3 equiv.). The stirring was continued for 4 h at −33 °C and then the cooling bath was removed. The reaction mixture was diluted with 20 mL of Et_2O and washed with a mixture (4:1, v/v) of saturated aqueous ammonium chloride and aqueous ammonium hydroxide (28%), and with water; the organic phase was dried over $MgSO_4$ and made free of solvent under reduced pressure. The purification by column chromatography (silica gel; pentane) gave a mixture of $\mathbf{3i_7}$ and *n*-pentylcyclohexylacetylene **5b**. The latter was removed by Kugelrohr distillation under reduced pressure to give essentially pure $\mathbf{3i_7}$ (69% yield). IR (neat): 3071, 3061, 2930, 2854, 1611, 1584, 1476, 1448, 1376, 1143, 1086, 1025, 738, 691 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.86 (3H, t, J=6.2 Hz), 1.15–1.85 (16H, m), 1.89 (3H, s), 2.27 (2H, t, J=7.4 Hz), 2.60 (1H, m), 7.09–7.24 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 16.6, 22.5, 26.1, 26.6, 29.1, 31.2, 31.5, 33.6, 42.5, 124.8, 125.7, 127.3, 128.7, 137.7, 149.3; MS (EI): 302 (M^+, 100), 287 (7), 225 (65), 164 (46), 149 (12), 135 (18), 123 (13), 109 (22), 91 (18), 81 (28), 67 (18), 55 (29). Anal. Calcd for $C_{20}H_{30}S$: C, 79.41; H, 9.99. Found: C, 79.36; H, 10.01.

4.3.13. (*E*)-4-*sec*-Butyl-5-(*n*-butylthio)-1,4-nonadiene ($3n_4$). Synthesized according to RP-4, starting from **2n** and using allyl bromide as electrophile. Column chromatography (silica gel; pentane) afforded $\mathbf{3n_4}$ (71% yield), as a colorless liquid. IR (neat): 3079, 2961, 2931, 2874, 1637, 1601, 1461, 1425, 1378, 1215, 993, 907 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.82 (3H, t, J=7.4 Hz), 0.89–0.99 (9H, m), 1.34–1.52 (10H, m), 2.21 (1H, m), 2.39 (1H, m), 2.49–2.73 (3H, m), 2.97 (1H, dd, J=15.2, 6.4 Hz), 3.15 (1H, dd, J=15.2, 6.4 Hz), 4.94–5.02 (2H, m), 5.11 (1H, ddt, J=16.9, 10.5, 6.2 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 12.4, 13.7, 14.1, 19.6, 22.0, 22.6, 28.2, 30.6, 31.4, 31.9, 32.0, 33.9, 38.6, 114.5, 130.6, 138.2, 143.4; MS (EI): 268 (M^+, 10), 239 (23), 211 (75), 183 (66), 169 (9), 155 (100), 141 (7), 121 (13), 107 (18), 93 (23), 79 (23), 67 (16), 57 (22). Anal. Calcd for $C_{17}H_{32}S$: C, 76.05; H, 12.01. Found: C, 76.07; H, 11.98.

4.3.14. (*E*)-3-Cyclohexyl-4-(phenylthio)-3-nonene ($3i_8$). Synthesized according to RP-4, starting from **2i** and using ethyl iodide as electrophile. The purification by column chromatography (silica gel; pentane) gave a mixture of $\mathbf{3i_8}$ and *n*-pentylcyclohexylacetylene **5b**. The latter was removed by Kugelrohr distillation under reduced pressure (24% yield of **5b**) to give essentially pure $\mathbf{3i_8}$ (28% yield), as a colorless liquid. IR (neat): 3071, 2930, 2854, 1584, 1476, 1450, 1376, 1085, 1025, 892, 738, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, J=7.1 Hz), 1.02 (3H, t, J=7.3 Hz), 1.15–1.48 (11H, m), 1.59–1.83 (5H, m), 2.19 (2H, t, J=7.8 Hz), 2.32 (2H, q, J=7.5 Hz), 2.60 (1H, tt, J=11.6, 3.4 Hz), 7.08–7.25 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 15.5, 22.5, 24.0, 26.1, 26.7, 29.4, 31.4, 31.7, 32.8, 42.9, 124.9, 126.6, 127.8, 128.7, 137.7, 154.7; MS (EI): 316 (M^+, 100), 287 (86), 239 (46), 178 (27), 163 (9), 149 (8), 135 (13), 123 (16), 109 (17), 95 (24), 81 (25), 67 (21), 55 (29); HRMS: m/z for $C_{21}H_{32}S$, calcd: 316.2225. Found: 316.2218.

4.3.15. Representative procedure (RP-5) for the boron to copper transmetalation (Scheme 7, conditions B). Synthesis of (*E*)-5-ethyl-6-(phenylthio)-5-decene ($3h_8$). A three-necked 50 mL flask equipped with a septum and a flexible side-arm containing 0.382 g (2 mmol) of copper(I) iodide was placed under argon. A THF solution (3 mL) of 1-hexyne (0.164 g; 2 mmol) was introduced and cooled to −20 °C; *n*-butyllithium (1.6 M in hexane; 1.25 mL; 2 mmol) was added and the mixture was stirred for 1 h. 2 mL of tri-*n*-butylborane (1 M in THF; 2 mmol) were then introduced, the cooling bath was removed and the mixture was stirred for 1 h at room temperature. After cooling to −78 °C, a solution of benzenesulfenyl chloride (0.289 g; 2 mmol) in 3 mL THF was added dropwise; the flask was

warmed to room temperature for 15 min, and cooled again to −78 °C. Methyllithium (1.4 M in ether; 2.9 mL; 4 mmol; 2 equiv.) was introduced and the mixture was stirred for 15 min before successive addition of copper iodide, HMPA (2 mL), triethylphosphite (0.41 mL; 2.4 mmol; 1.2 equiv.) and ethyl iodide (0.24 mL; 3 mmol; 1.5 equiv.). The cooling bath was allowed to warm-up to room temperature and stirring was continued overnight. The reaction mixture was diluted with 20 mL of Et_2O and washed with a mixture (4:1, v/v) of saturated aqueous ammonium chloride and aqueous ammonium hydroxide (28%), and with water; the organic phase was dried over $MgSO_4$ and made free of solvent under reduced pressure. GC analysis via calibration using tridecane as internal standard revealed the presence of 5-decyne **5h** (21% yield) and ethylthiobenzene **6h$_8$** (19% yield). Kugelrohr distillation followed by column chromatography (silica gel; pentane) afforded **3h$_8$** (45% yield), as a colorless liquid. IR (neat): 3069, 2959, 2931, 2872, 1583, 1477, 1459, 1439, 1377, 1085, 1025, 738, 691 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.85–1.08 (9H, m), 1.19–1.50 (8H, m), 2.08–2.36 (4H, m), 2.41 (2H, q, J=7.6 Hz), 7.07–7.25 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.7, 14.0, 22.4, 23.1, 27.7, 31.2, 31.5, 32.0, 32.8, 124.9, 126.2, 127.7, 128.7, 137.6, 150.7; MS (EI): 276 (M^+, 100), 233 (34), 178 (37), 163 (22), 149 (8), 135 (19), 123 (23), 109 (14), 95 (15), 81 (24), 69 (23), 55 (24); HRMS: m/z for $C_{18}H_{28}S$, calcd: 276.1912. Found: 276.1910.

4.3.16. (*E*)-6-(*n*-Butylthio)-5-ethyl-5-decene (3d$_8$). Synthesized according to RP-5, through the preparation of **2d**. Column chromatography (silica gel; pentane) afforded **3d$_8$** (66% yield), as a colorless liquid. IR (neat): 2960, 2931, 2862, 1611, 1461, 1378, 1272, 1222, 1102, 745 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.87–1.03 (12H, m), 1.13–1.64 (12H, m), 2.01–2.33 (4H, m), 2.37 (2H, q, J=7.6 Hz), 2.54 (2H, t, J=7.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.4, 13.7, 14.0, 14.1, 22.0, 22.6, 22.9, 27.2, 31.1, 31.4, 31.7, 31.9, 31.9, 127.5, 145.4; MS (EI): 256 (M^+, 61), 213 (37), 199 (100), 157 (16), 143 (7), 123 (7), 109 (7), 101 (15), 95 (12), 81 (21), 69 (17), 67 (15), 55 (20). Anal. Calcd for $C_{16}H_{32}S$: C, 74.92; H, 12.57. Found: C, 74.71; H, 12.48.

4.3.17. (*Z*)-5-Benzyl-6-(phenylthio)-5-decene (3h$_2$). Synthesized according to RP-5, through the preparation of **2h** and the use of benzyl bromide as electrophile. Kugelrohr distillation followed by column chromatography (silica gel; pentane) afforded **3h$_2$** (62% yield). IR (neat): 3062, 3027, 2958, 2931, 2862, 1601, 1584, 1494, 1477, 1451, 1440, 1379, 1088, 1026, 739, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, J=7.3 Hz), 0.91 (3H, t, J=7.3 Hz), 1.27 (2H, m), 1.33 (2H, m), 1.45 (2H, m), 1.54 (2H, m), 2.13 (2H, t, J=7.8 Hz), 2.27 (2H, t, J=7.8 Hz), 3.86 (2H, s), 7.11–7.28 (10H, m); ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 14.0, 22.5, 22.9, 31.0, 31.5, 31.7, 32.6, 40.0, 125.3, 125.9, 128.2, 128.3, 128.6, 128.8, 129.1, 137.1, 140.2, 146.7; MS (EI): 338 (M^+, 100), 281 (9), 247 (13), 185 (14), 143 (17), 129 (38), 117 (22), 91 (73). Anal. Calcd for $C_{23}H_{30}S$: C, 81.60; H, 8.93. Found: C, 81.64; H, 9.05.

4.3.18. (*Z*)-5-Benzyl-6-(*n*-butylthio)-5-decene (3d$_2$). Synthesized according to RP-5, through the preparation of **2d** and the use of benzyl bromide as electrophile. Kugelrohr distillation followed by column chromatography (silica gel; pentane) afforded **3d$_2$** (64% yield), as a yellowish liquid. IR (neat): 3083, 3062, 3027, 2958, 2930, 2862, 1602, 1494, 1456, 1379, 1273, 1221, 1100, 1030, 957, 729, 700 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.93–1.00 (9H, m), 1.14–1.66 (12H, m), 2.02 (2H, t, J=7.3 Hz), 2.33 (2H, t, J=7.4 Hz), 2.54 (2H, t, J=6.9 Hz), 3.82 (2H, s), 7.03–7.24 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.7, 13.9, 14.1, 21.9, 22.7, 22.8, 30.9, 31.2, 31.4, 31.7, 31.9, 39.7, 125.7, 128.2, 128.6, 130.4, 140.7, 141.9; MS (EI): 318 (M^+, 100), 275 (16), 261 (32), 227 (39), 185 (31), 171 (22), 143 (24), 129 (63), 91 (68); HRMS: m/z for $C_{21}H_{34}S$, calcd: 318.2381. Found: 318.2377.

4.4.. Nickel catalyzed coupling of vinylsulfides

4.4.1. Representative procedure (RP-6) for the cross-coupling of vinylsulfides with Grignard reagents. Synthesis of (*E*)-5-methyl-6-phenyl-5-decene (7A). In a 25 mL two-necked flask, equipped with an argon inlet and a magnetic stirring bar, were introduced a solution of **3h$_7$** (0.210 g; 0.8 mmol) in Et_2O (7 mL) and $NiCl_2$(dmpe) (0.007 g; 0.025 mmol; 3% mol.). Phenylmagnesium bromide (0.67 mL of a 3 M solution in Et_2O; 2 mmol; 2.5 equiv.) was added and the reaction mixture was stirred at room temperature for 14.5 h before the addition of 1 mL of saturated aqueous NH_4Cl. 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) providing 0.152 g of biphenyl and 0.151 g of **7A** (82% yield) as a colorless liquid. IR (neat): 3078, 3058, 3022, 2958, 2929, 2860, 1600, 1574, 1492, 1465, 1442, 1378, 1133, 1105, 1071, 771, 744, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.85 (3H, t, J=7.2 Hz), 0.97 (3H, t, J=7.1 Hz), 1.19–1.28 (4H, m), 1.36–1.49 (4H, m), 1.50 (3H, s), 2.18 (2H, t, J=7.7 Hz), 2.34 (2H, t, J=7.3 Hz), 7.07–7.10 (2H, m), 7.19–7.23 (1H, m), 7.27–7.33 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.2, 19.9, 22.7, 22.9, 30.8, 33.7, 33.7, 125.6, 127.8, 129.0, 131.3, 135.8, 144.4; MS (EI): 230 (M^+, 65), 187 (16), 173 (27), 145 (35), 131 (100), 117 (40), 105 (13), 91 (43). Anal. Calcd for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 88.59; H, 11.13.

4.4.2. (*Z*)-4-Ethyl-5-phenyl-1,4-decadiene (7B). Synthesized according to RP-6, starting from **3f$_4$**. The reaction mixture was heated to reflux for 23 h. Column chromatography (silica gel; pentane) afforded **7B** (38% yield), as a colorless liquid. IR (neat): 3078, 3058, 3021, 2962, 2931, 2873, 2861, 1636, 1600, 1491, 1460, 1440, 1376, 1071, 994, 910, 766, 702 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.83 (3H, t, J=6.4 Hz), 1.04 (3H, t, J=7.4 Hz), 1.15–1.30 (6H, m), 2.18 (2H, q, J=7.4 Hz), 2.31 (2H, t, J=7.6 Hz), 2.58 (2H, d, J=6.4 Hz), 4.78–5.02 (2H, m), 5.77 (1H, ddt, J=18.2, 8.6, 6.1 Hz), 7.02–7.31 (5H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.4, 14.0, 22.6, 23.7, 28.1, 31.8, 34.0, 37.2, 114.9, 125.9, 127.8, 128.7, 134.7, 137.3, 137.7, 143.7; MS (EI): 242 (M^+, 100), 213 (27), 185 (10), 171 (99), 157 (20), 143 (64), 129 (67), 115 (20), 105 (12), 91 (55); HRMS: m/z for $C_{18}H_{26}$, calcd: 242.2035. Found: 242.2033.

4.4.3. 5-*n*-Butyl-6-methyl-5-decene (7C). Synthesized according to RP-6, using *n*-butylmagnesium bromide

(0.5 M in Et_2O) as the Grignard reagent. The reaction mixture was heated to reflux for 22.5 h. Column chromatography (silica gel; pentane) afforded **7C** (70% yield), as a colorless liquid. IR (neat): 2958, 2929, 2861, 1656, 1465, 1341, 1289, 1222, 1151, 1106, 896, 727 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.90 (9H, m), 1.11–1.41 (12H, m), 1.61 (3H, s), 1.98 (6H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.1, 17.9, 22.8, 23.0, 23.1, 31.0, 31.1, 31.5, 31.8, 32.1, 33.9, 128.4, 133.3; MS (EI): 210 (M^+, 38), 153 (13), 125 (12), 112 (45), 97 (58), 83 (50), 69 (100), 55 (69); HRMS: *m/z* for $C_{15}H_{30}$, calcd: 210.2348. Found: 210.2354.

4.4.4. (*E*)-5-Benzyl-6-methyl-5-decene (7D). Synthesized according to RP-6, starting from **3h$_2$**, and using methylmagnesium bromide (3 M in Et_2O) as the Grignard reagent. The reaction mixture was heated to reflux for 10 days. Column chromatography (silica gel; pentane) afforded **3h$_2$** (60% yield), and a mixture of (*E*)-5-benzyl-5-decene (2% yield) and **7D** (24% yield) in a 8:92 ratio (determined by ^1H NMR), as a colorless liquid. IR (neat): 3084, 3063, 3028, 2958, 2929, 2861, 1603, 1494, 1455, 1378, 1103, 1074, 1030, 727, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, *J*=7.1 Hz), 0.93 (3H, t, *J*=7.3 Hz), 1.23–1.44 (8H, m), 1.72 (3H, s), 1.95 (2H, t, *J*=7.8 Hz), 2.09 (2H, t, *J*=7.8 Hz), 3.40 (2H, s), 7.13–7.18 (3H, m), 7.24–7.28 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 14.0, 14.1, 18.6, 23.0, 31.0, 31.2, 31.6, 34.0, 37.6, 125.5, 128.2, 128.4, 131.0, 131.3, 141.2; MS (EI): 244 (M^+, 80), 187 (97), 145 (38), 131 (72), 117 (50), 105 (21), 97 (32), 91 (10%), 83 (20), 69 (23), 55 (72); HRMS: *m/z* for $C_{18}H_{28}$, calcd: 244.2191. Found: 244.2198.

4.4.5. (*Z*)-4-Ethyl-5-phenyl-4-decene (7E). Synthesized according to RP-6, starting from **3f$_9$**. The reaction mixture was heated to reflux for 15 h. Column chromatography (silica gel; pentane) afforded **7E** (76% yield), as a colorless liquid. IR (neat): 3078, 3057, 3021, 2961, 2930, 2871, 1600, 1575, 1491, 1465, 1442, 1377, 1133, 1071, 770, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.72 (3H, t, *J*=7.3 Hz), 0.83 (3H, t, *J*=6.8 Hz), 1.05 (3H, t, *J*=7.3 Hz), 1.21–1.26 (6H, m), 1.28 (2H, m), 1.78 (2H, t, *J*=7.8 Hz), 2.17 (2H, q, *J*=7.5 Hz), 2.28 (2H, t, *J*=6.8 Hz), 7.05 (2H, m), 7.17–7.21 (1H, m), 7.26–7.30 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.7, 14.1, 14.2, 22.0, 22.6, 23.7, 28.1, 31.9, 34.1, 34.5, 125.6, 127.7, 129.0, 136.0, 137.2, 144.3; MS (EI): 244 (M^+, 100), 215 (23), 201 (10), 187 (6), 173 (45), 159 (18), 145 (84), 131 (98), 117 (84), 105 (21), 91 (69), 77 (10), 69 (9), 55 (13). Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.87; H, 11.72.

4.4.6. Catalytic hydrogenation of 3f$_4$. Synthesis of (*Z*)-4-ethyl-5-(phenylthio)-4-decene (3f$_9$). A two-necked 25 mL flask equipped with a septum was placed under hydrogen atmosphere. A solution of **3f$_4$** (1.067 g; 3.89 mmol) in hydrogen flushed benzene and chlorotris(triphenylphosphine)rhodium(I) (0.111 g; 0.12 mmol; 3 mol%) were successively introduced, and the resulting brown solution was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was extracted with Et_2O (3×15 mL). The combined organic layers were filtered over celite, and then concentrated under reduced pressure. Column chromatography (silica gel; pentane) afforded 0.962 g of **3f$_9$** (90% yield), as a colorless liquid. IR (neat): 3072, 2961, 2932, 2872, 1584, 1477, 1463, 1440, 1377, 1133, 1087, 1067, 1025, 739, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.84 (3H, t, *J*=7.1 Hz), 0.90 (3H, t, *J*=7.6 Hz), 1.09 (3H, t, *J*=7.3 Hz), 1.17–1.29 (4H, m), 1.39–1.52 (4H, m), 2.19 (2H, t, *J*=7.8 Hz), 2.23 (2H, q, *J*=7.3 Hz), 2.38 (2H, t, *J*=7.8 Hz), 7.09–7.13 (1H, m), 7.17 (2H, m), 7.21–7.25 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.5, 14.0, 14.2, 22.3, 22.6, 22.6, 29.1, 31.6, 32.9, 36.1, 125.0, 126.8, 127.8, 128.7, 137.6, 150.3; MS (EI): 276 (M^+, 100), 247 (34), 178 (50), 163 (19), 149 (7), 135 (17), 123 (21), 109 (12), 95 (22), 81 (22), 69 (23), 55 (30). Anal. Calcd for $C_{18}H_{28}S$: C, 78.20; H, 10.21. Found: C, 77.83; H, 10.21.

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