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Stereoselective synthesis of vinylic (Z)-*vic*-bis(arylchalcogenides)

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Abstract

Alkyne-titanium complexes **3**, readily prepared *in situ* by the reaction of alkynes with Ti(O-*i*-Pr)$_4$/2 *i*-PrMgCl, react with electrophilic chalcogen species under mild conditions to provide the corresponding addition products in fair to good yields. The obtained vinylic *vic*-bis(arylchalcogenides) **4** are useful synthetic intermediates for introducing vinyl functions into organic molecules.
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1. Introduction

Alkenyl chalcogenides have a considerable synthetic importance since they are valuable precursors for the preparation of several organic compounds [1]. The synthesis of vinylic chalcogenides has therefore attracted the attention of several research groups, and many novel methods for their preparation have been proposed in the last years [1]. We have prepared several functionalized vinylic compounds [2]; however, the synthesis of vinylic *vic*-bis(chalcogenides) has not been much studied. The most important methods are based on the free-radical addition of dichalcogenides to alkynes and the palladium-catalyzed coupling reaction of dichalcogenides with alkynes [3]. For the free-radical addition of dichalcogenides, the reaction seems to be effective only for terminal and activated alkynes. This reaction was also effective for terminal and internal alkynes when a binary system of (PhS)$_2$-(PhSe)$_2$ was employed. The products are formed exclusively or preferentially with the *E*-configuration [4]. The thiotelluration and selenotelluration of acetylenes was also described for terminal alkynes, although less efficiently [5].

Furthermore, the addition of dichalcogenides via a palladium-catalyzed coupling reaction afforded good results

and the *Z*-isomer was formed preferentially or exclusively; however, internal alkynes did not react or the yields were very low [6]. A new procedure was recently described for the polymer-supported Pd stereoselective S–S bond addition to terminal alkynes; however, the methodology was not useful for Ph$_2$Se$_2$ addition [7]. A sequence of hydroboration–iodination of 1,2-bis-alkylselenoacetylenes furnished *vic*-bis(selenides) of *Z*-preferential stereochemistry [8]. Methods were also developed for the synthesis of less substituted *vic*-bis(chalcogenides) [9].

Recently, Sato and coworkers have developed a method for synthesizing a variety of organotitanium complexes starting from a divalent titanium complex **1**, generated from Ti(O-*i*-Pr)$_4$/2 *i*-PrMgCl and unsaturated hydrocarbons [10]. Thus, the reaction of **1** with alkynes afforded the (η^2-alkyne)Ti(O-*i*-Pr)$_2$ derivatives **3** which are vicinal vinylic dianion equivalents (Scheme 1) [11].

2. Results and discussion

In connection with our research interest on the synthesis of vinylic *vic*-bis(arylchalcogenides) we would like to report herein a new access to *Z*-vinyl tetrasubstituted *vic*-bis(selenides) **4**, by the reaction of organotitanium complex **3** with electrophilic arylseleno species (Scheme 2). Noteworthy, to the best of our knowledge, the only example of titanium–

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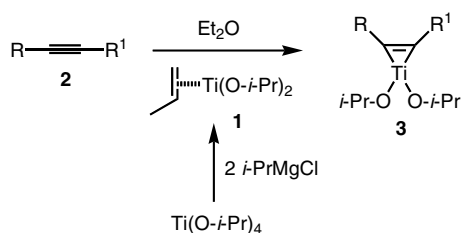
Scheme 1.

selenium transmetalation is the reaction of titanacyclopent-adienes with selenocyanogen [12].

It may be seen in Table 1 that the intermediate 3 reacted with arylselenenyl bromide to afford the corresponding vinylic Z-*vic*-bis(arylselenides) 4 in fair to good yields.

Low yields were obtained by the use of PhSeCl or phenylselenophtalimide as eletrophilic chalcogen. In these cases the monoselenation derivative was formed as a by-product in low yields.

All reactions demonstrated to be highly stereoselective, affording exclusively the Z-isomer of the vinylic *vic*-bis(arylselenides), the only exception observed being with the methyl propiolate and the phenylselenium group as electrophile (entry 2, Table 1), where a small amount of the E-isomer was isolated. By comparative experiments with other examples, we found that the compound 4b

Scheme 2.

was the only one sensitive to isomerization during the course of extraction/purification and after prolonged exposure to light a 1:1 (E + Z) mixture of isomers was observed. Interestingly, however, when the 4-chlorophenylseleno group was used this isomerization was not observed (entry 3, Table 1). The stereochemistry of the products 4 was determined by comparison with known compounds. It is described that, on the reaction of titanium intermediates 3 with two electrophiles, both groups are attached to the same side of the double bond [10,11]. As expected, both arylselenium groups were located in a cis junction, as confirmed by comparison with previously described compounds. For example, for 4a, the ^{13}C data for the allylic CH_2 in the E- and Z-isomers are very different, at 40.3 and 37.0 ppm, respectively [3b]. We observed the signal for 4a at 36.6 ppm, in very good agreement with a Z-stereochemistry.

The reaction demonstrated to be general since functionalized internal alkynes, such as conjugated acetylenic esters (propiolates), thioalkynes and protected propargyl alcohols afforded the corresponding acetylene complexes. The amount of organotitanium complex 1 necessary was dependent on the structure of the alkyne. For 4-octyne 1.1 equivalents were enough, while for methyl propiolate 3 equivalents of the reagent 1 were necessary to get good yields. For the other alkynes, 2 equivalents of 1 furnished good yields. The use of higher amounts of the reagent 1 had no further influence on the yields. For the compounds 4i and 4j (entries 9 and 10) the THP derivative of propargyl alcohol was employed as starting material; however, the corresponding free alcohol was isolated after work-up with 1 N HCl.

In connection with the present findings, we observed that the alkyne-titanium complex 3 also affords Z-*vic*-bis(phenylthio)alkenes by the reaction with electrophilic

Table 1
Synthesis of vinylic Z-*vic*-bis(arylselenides) according to Scheme 2

Entry	R	R^1	Ar	Product	Yield (%)[a]
1	n-C$_3$H$_7$	n-C$_3$H$_7$	C$_6$H$_5$	4a	63
2[b]	n-C$_5$H$_{11}$	CO$_2$Me	C$_6$H$_5$	4b	70
3	n-C$_5$H$_{11}$	CO$_2$Me	4-Cl-C$_6$H$_4$	4c	58
4	n-C$_5$H$_{11}$	CO$_2$$i$-Pr	C$_6$H$_5$	4d	73
5	n-C$_5$H$_{11}$	CO$_2$$i$-Pr	4-Cl-C$_6$H$_4$	4e	54
6	n-C$_4$H$_9$	SC$_6$H$_5$	C$_6$H$_5$	4f	60
7	n-C$_4$H$_9$	SC$_6$H$_5$	4-Cl-C$_6$H$_4$	4g	54
8	n-C$_5$H$_{11}$	SCH$_3$	C$_6$H$_5$	4h	63
9	C$_6$H$_5$	CH$_2$OH	C$_6$H$_5$	4i	58
10	C$_6$H$_5$	CH$_2$OH	4-Cl-C$_6$H$_4$	4j	62

[a] Isolated yields of the pure products after column chromatography.
[b] In this case it was observed a Z/E isomeric ratio of 10:1 established by ^{1}H NMR (400 MHz).
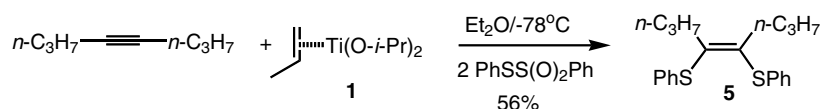
Scheme 3.
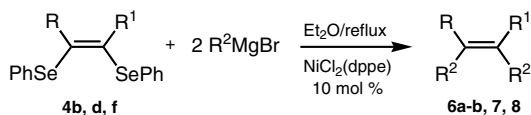
Scheme 4.

sulfur species. Thus, as shown in Scheme 3, the complex derived from 4-octyne reacted with 2 equivalents of $PhSSO_2Ph$ to afford the corresponding vinylic bis(sulfide) **5** in 56% yield.

The obtained *vic*-bis(arylseleno) olefins **4** are of synthetic interest, because vinylic selenides are useful intermediates for introducing of vinyl functions into various organic molecules [13]. Thus, in the next step the cross-coupling reactions of *vic*-bis(arylseleno) olefins with Grignard reagents under nickel catalysis were performed (Scheme 4). Initially, the reaction of vinylic bis(phenylselenide) **4f** was carried out with 4 equivalents of n-C_4H_9MgBr under $NiCl_2(dppe)$ catalysis, in Et_2O as solvent [14].

When 5 mol% of catalyst or less were used, no reaction was observed; however, using 10 mol% of catalyst gave total consumption of starting material and the desired product **6a** was isolated in 75% yield (entry 1, Table 2). The same result was observed in the reaction of **4f** with n-$C_8H_{17}MgBr$, and the product **6b** was obtained in 65% yield (entry 2, Table 2). Complete chemoselectivity was observed in these reactions since only the phenylseleno groups were removed, leaving the phenylthio group intact, despite the fact that Ni(II) complexes such as $NiCl_2(PPh_3)_2$ and $NiCl_2(dppe)$ also catalyzes the cross-coupling reaction of vinylic sulfides with Grignard reagents [15]. An interesting result was observed in this transformation with the α,β-unsaturated esters **4b** and **4d**. Here, both selenium groups were removed but the products presented only one alkyl group in their structure, at the β-position, the α-carbon being substituted by hydrogen in place of the phenylselenium group, as in tri-substituted vinylics **7** and **8** (entries 3 and 4, Table 2) [2b]. Presumably, the presence of the ester group at the α-position would be the responsible for the coupling reaction with Grignard reagent do not take part. The ester function was also not affected by the Grignard reagent.

In summary, the results obtained show that this method represents a very convenient and highly stereoselective synthesis of *Z*-vinylic *vic*-bis(arylchalcogenides) under mild condition, properly complementing the described methods

to access this class of compounds. The obtained vinylic *vic*-bis(arylselenides) exhibit interesting synthetic properties and are useful intermediates for introducing vinyl functions into organic molecules.

3. Experimental

3.1. General

All ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker DPX 400 instrument, using $CDCl_3$ as solvent. Chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane or $CHCl_3$, and J values are given in hertz. Infrared spectra were recorded on a Nicollet-Magna spectrometer. Elemental analyses were carried out on a Perkin–Elmer 2400. All reactions were performed in flame-dried glassware under a positive pressure of argon. Air- and moisture sensitive reagents and solvents were transferred via syringe, and were introduced into reaction vessels through a rubber septum. Et_2O was distilled over sodium before use, i-PrCl was distilled from calcium hydride under argon. 4-Octyne and $Ti(O$-i-$Pr)_4$ were purchased from commercial sources and were distilled before use. All the reactions were monitored by thin layer chromatography (TLC) carried out using Merck 60 F_{254} plates with a 0.25 mm thickness. Column chromatography was carried out using Merck silica gel 60 (230–400 mesh).

3.2. General procedure for the synthesis of vinylic vic-bis(arylselenides) 4a–j

To a stirred solution of $Ti(O$-i-$Pr)_4$ (0.284 g, 1.0 mmol) and 4-octyne (0.110 g, 1.0 mmol) in ether (7 mL) was added a 1.45 M ethereal solution of i-PrMgCl (1.38 mL, 2.0 mmol) at $-78\,°C$ to give a yellow homogeneous mixture. The solution was warmed to $-50\,°C$ over 0.5 h, during this period its color turned brown. After stirring at the same temperature for 3 h, the solution was cooled to $-78\,°C$, and a solution of the arylselenenyl bromide (2.2 mmol) in ether (5 mL) was added and the stirring was continued for 2 h at the same temperature. The reaction was stopped by the dropwise addition of 1 N HCl (5 mL) at $-78\,°C$. The organic layer was separated and the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to give an oil, which

Table 2
Cross-coupling reaction of the *vic*-bis(phenylseleno) compounds **4b**, **4d** and **4f** with Grignard reagents according to Scheme 4

Entry	Vinylic bis(selenide)	R	R^1	R^2	$R^{2'}$	Product	Yield (%)[a]
1	**4f**	n-C_4H_9	SC_6H_5	n-C_4H_9	n-C_4H_9	**6a**	75
2	**4f**	n-C_4H_9	SC_6H_5	n-C_8H_{17}	n-C_8H_{17}	**6b**	65
3	**4d**	n-C_5H_{11}	CO_2i-Pr	n-C_4H_9	H	**7**	82
4	**4b**	n-C_5H_{11}	CO_2Me	n-C_4H_9	H	**8**	85

[a] Isolated yields of the pure products after column chromatography.

was chromatographed on silica gel to afford **4a** (0.266 g, 63%).

(*Z*)-4,5-Bis(phenylseleno)-4-octene (**4a**) [3a]: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.56–7.51 (m, 4H); 7.27–7.24 (m, 6H); 2.27 (t, 4H, *J* = 7.2 Hz); 1.47 (sext, 4H, *J* = 7.2 Hz); 0.75 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.3; 133.6; 131.0; 128.9; 127.3; 36.6; 22.8; 13.5.

(*Z*) and (*E*)-2,3-bis(phenylseleno)-oct-2-enoic acid methyl ester (**4b**): ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61–7.23 (m, 10H); 3.59 (*E*) and 3.49 (*Z*) (s, 3H); 2.65 (*E*) and 2.48 (*Z*) (t, 2H, *J* = 7.5 Hz); 1.43–0.94 (m, 6H); 0.76 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.1; 165.4; 136.4; 136.1; 132.0; 131.9; 131.6; 130.4; 130.2; 129.3; 129.0 (2C); 128.9; 128.8 (2C); 128.7; 127.0; 126.5; 118.6; 114.3; 52.2; 51.8; 38.4; 35.3; 30.1; 29.3; 29.1; 21.9 (2C); 13.6 (2C). IR (film): *v* = 3060; 2956; 1698; 1574 cm^{-1}. MS: *m/z* (%) = 466 (9); 464 (6); 154 (29); 77 (100). Anal. Calc. for C$_{21}$H$_{24}$O$_2$Se$_2$: C, 54.09; H, 5.19. Found: C, 55.01; H, 5.53.

(*Z*)-2,3-Bis(4-chlorophenylseleno)-oct-2-enoic acid methyl ester (**4c**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55–7.25 (m, 8H); 3.57 (s, 3H); 2.46 (t, 2H, *J* = 7.6 Hz); 1.38 (quint, 2H, *J* = 7.6 Hz); 1.12–0.98 (m, 4H); 0.78 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.5; 161.2; 137.5; 135.6; 133.6; 133.2; 129.5; 129.3; 128.5; 127.3; 119.0; 52.2; 35.6; 31.1; 29.3; 22.0; 13.8. IR (film): *v* = 2949; 1684; 1563; 1218 cm^{-1}. MS: *m/z* (%) = 536 (13); 535 (6); 191 (100); 95 (24). Anal. Calc. for C$_{21}$H$_{22}$Cl$_2$O$_2$Se$_2$: C, 47.13; H, 4.14. Found: C, 47.08; H, 3.93.

(*Z*)-2,3-Bis(phenylseleno)-oct-2-enoic acid isopropyl ester (**4d**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64–7.51 (m, 4H); 7.35–7.24 (m, 6H); 4.82 (sept, 1H, *J* = 6.4 Hz); 2.45 (t, 2H, *J* = 7.6 Hz); 1.42–0.96 (m, 12H); 0.77 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.9; 157.5; 136.3; 132.2; 130.5; 129.3; 129.1; 129.0; 128.7; 127.2; 120.3; 68.8; 35.5; 31.2; 29.3; 22.1; 21.4; 13.8. IR (film): *v* = 3056; 2956; 1712; 1574; 1221 cm^{-1}. MS: *m/z* (%) = 496 (4); 494 (13); 279 (24); 77 (100). Anal. Calc. for C$_{23}$H$_{28}$O$_2$Se$_2$: C, 55.88; H, 5.71. Found: C, 55.48; H, 5.49.

(*Z*)-2,3-Bis(4-chlorophenylseleno)-oct-2-enoic acid isopropyl ester (**4e**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55–7.23 (m, 8H); 4.86 (sept, 1H, *J* = 6.4 Hz); 2.43 (t, 2H, *J* = 7.6 Hz); 1.42–0.98 (m, 12H); 0.78 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.7; 157.8; 137.4; 135.4; 133.6; 133.5; 129.5; 129.2; 128.6; 127.4; 120.5; 69.1; 35.5; 31.2; 29.3; 22.1; 21.5; 13.8. IR (film): *v* = 3072; 2985; 1710; 1561; 1254 cm^{-1}. MS: *m/z* (%) = 564 (2); 563 (6); 191 (24); 139 (24); 43 (100). Anal. Calc. for C$_{23}$H$_{26}$Cl$_2$O$_2$Se$_2$: C, 49.04; H, 4.65. Found: C, 49.18; H, 4.51.

(*Z*)-1,2-Bis(phenylseleno)-1-phenylthio-1-hexene (**4f**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68–7.66 (m, 2H); 7.38–7.09 (m, 13H); 2.58 (t, 2H, *J* = 7.6 Hz); 1.39 (quint, 2H, *J* = 7.6 Hz); 1.05 (sext, 2H, *J* = 7.6 Hz); 0.67 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.5; 136.8;

136.0; 133.4; 131.5; 130.9; 129.1; 128.7; 128.6; 127.4; 126.0; 119.1; 36.2; 31.8; 22.1; 13.5. IR (film): *v* = 3063; 2954; 1579; 1470 cm^{-1}. MS: *m/z* (%) = 500 (5); 190 (35); 109 (9); 81 (75); 77 (100). Anal. Calc. for C$_{24}$H$_{24}$SSe$_2$: C, 57.37; H, 4.81. Found: C, 57.26; H, 4.87.

(*Z*)-1,2-Bis(4-chlorophenylseleno)-1-phenylthio-1-hexene (**4g**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58–7.56 (m, 2H); 7.32–7.05 (m, 11H); 2.58 (t, 2H, *J* = 7.6 Hz); 1.39 (quint, 2H, *J* = 7.6 Hz); 1.10 (sext, 2H, *J* = 7.6 Hz); 0.72 (t, 3H, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.6; 136.9; 135.9; 135.1; 133.9; 129.4; 128.8 (2C); 128.7 (2C); 128.7; 128.2; 126.3; 120.8; 36.3; 31.7; 22.1; 13.6. IR (film): *v* = 3053; 2959; 1579; 1475; 1091 cm^{-1}. MS: *m/z* (%) = 572 (4); 571 (2); 190 (77); 81 (100). Anal. Calc. for C$_{24}$H$_{22}$Cl$_2$SSe$_2$: C, 50.46; H, 3.88. Found: C, 50.51; H, 4.15.

(*Z*)-1,2-Bis(phenylseleno)-1-methylthio-1-hexene (**4h**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59–7.2 (m, 10H); 2.53 (t, 2H, *J* = 7.2 Hz); 2.20 (s, 3H); 1.38 (quint, 2H, *J* = 7.2 Hz); 1.15–1.00 (m, 4H); 0.77 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.3; 136.0; 131.4; 130.9; 130.1; 128.9; 128.3; 126.7; 121.6; 35.5; 31.2; 28.8; 22.1; 19.4; 13.8. IR (film): *v* = 3070; 2913; 1574; 1474; 730 cm^{-1}. MS: *m/z* (%) = 456 (13); 454 (12); 142 (27); 95 (45); 77 (100). Anal. Calc. for C$_{20}$H$_{24}$SSe$_2$: C, 52.87; H, 5.32. Found: C, 52.98; H, 5.30.

(*Z*)-3-Phenyl-2,3-bis(phenylseleno)-prop-2-en-1-ol (**4i**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66–7.64 (m, 2H); 7.34–6.96 (m, 13H); 3.96 (s, 2H); 1.88 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.9; 137.8; 135.5; 132.6; 132.2; 129.6; 129.5; 129.3; 128.8; 128.2; 127.5 (2C); 127.4; 127.2; 63.3. IR (film): *v* = 3390; 3052; 2929; 1575; 1474 cm^{-1}. MS: *m/z* (%) = 446 (8); 444 (7); 132 (4); 115 (100); 77 (79). Anal. Calc. for C$_{21}$H$_{18}$OSe$_2$: C, 56.77; H, 4.08. Found: C, 56.56; H, 4.33.

(*Z*)-3-Phenyl-2,3-bis(4-chlorophenylseleno)-prop-2-en-1-ol (**4j**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58–7.56 (m, 2H); 7.31–7.28 (m, 2H); 7.12–6.95 (m, 9H); 3.96 (s, 2H); 1.84 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.7; 137.5; 136.9; 134.3; 133.9; 131.9; 129.5 (2C); 128.8; 128.6 (2C); 127.8 (2C); 127.7; 63.5. IR (film): *v* = 3431; 3062; 2944; 1592; 1428 cm^{-1}. Anal. Calc. for C$_{21}$H$_{16}$Cl$_2$OSe$_2$: C, 49.15; H, 3.14. Found: C, 49.49; H, 3.20.

3.3. Preparation of vinylic vic-bis(phenylsulfide) (5)

To a stirred solution of Ti(O-*i*-Pr)$_4$ (0.284 g, 1.0 mmol) and 4-octyne (0.110 g, 1.0 mmol) in Et$_2$O (7 mL) was added a 1.45 M ethereal solution of *i*-PrMgCl (1.38 mL, 2.0 mmol) at −78 °C to give a yellow homogeneous mixture. The solution was warmed to −50 °C over 0.5 h, during this period its color turned brown. After stirring at the same temperature for 3 h, the solution was cooled to −78 °C, and a solution of PhSS(O)$_2$Ph (0,55 g, 2.2 mmol) in Et$_2$O (5 mL) was added and the stirring was continued for 2 h at the same temperature. The reaction was terminated by dropwise addition of 1 N HCl (5 mL) at

−78 °C. The organic layer was separated and the aqueous layer was extracted with ether (3×10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to leave an oil, which was chromatographed on silica gel to afford the vinylic *vic*-bis(phenylsulfide) **5** (0.183 g, 56%).

(*Z*)-4,5-Bis(phenylthio)-4-octene (**5**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35–7.18 (m, 10H); 2.28 (t, 4H, $J = 7.2$ Hz); 1.53 (sext, 4H, $J = 7.2$ Hz); 0.82 (t, 6H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.1; 135.1; 130.4; 128.9; 126.5; 35.1; 22.6; 13.7. Anal. Calc. for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36. Found: C, 72.86; H, 7.76.

3.4. General procedure for the NiCl$_2$(dppe)-catalyzed cross-coupling reaction of vinylic bis(chalcogenides) (4) with Grignard reagents

To a solution of the (*Z*)-1,2-bis(phenylseleno)-1-phenyl-thio-1-hexene (**4f**) (0.502 g, 1 mmol) and NiCl$_2$(dppe) (0.054 g, 0.1 mmol) in diethyl ether (5 mL) was added 1 M ether solution of *n*-butyl magnesium bromide (4 mL, 4 mmol) under argon atmosphere and the mixture was stirred for 14 h at reflux temperature until finishing of the reaction (judged by TLC). The mixture was treated with 1 N HCl solution, extracted with ethyl acetate and the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo and the residue was chromatographed on silica gel to afford the vinylic (**6a**) (0.228 g, 75%).

(1,2-Dibutyl-hex-1-enyl sulfanyl)-benzene (**6a**): ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.27–7.09 (m, 5H); 2.39 (t, 2H, $J = 7.6$ Hz); 2.19 (t, 4H, $J = 7.6$ Hz); 1.53–1.18 (m, 12H); 0.99–0.81 (m, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 149.1; 137.6; 128.6; 127.8; 126.8; 124.9; 34.2; 32.6; 32.3; 31.5; 31.4; 31.1; 23.0; 22.8; 22.4; 13.9. MS: *m/z* (%) = 305 (14); 304 (59); 261 (32); 227 (3); 191 (23); 81 (33); 77 (17); 55 (100). Anal. Calc. for $C_{20}H_{32}S$: C, 78.88; H, 10.59. Found: C, 78.53; H, 10.55.

(2-Butyl-1-octyl-dec-1-enyl sulfanyl)-benzene (**6b**): ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.23–7.09 (m, 5H); 2.38 (t, 2H, $J = 7.2$ Hz); 2.18 (t, 4H, $J = 7.2$ Hz); 1.55–1.22 (m, 28H); 0.92–0.86 (m, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 149.1; 137.6; 128.6; 127.9; 126.9; 124.9; 34.2; 32.9; 32.5; 31.9; 31.8; 31.4; 29.9; 29.5; 29.4; 29.3; 29.28; 29.24; 28.9; 22.8; 22.68; 22.65; 14.09; 14.07; 14.02. MS: *m/z* (%) = 416 (23); 123 (28); 81 (46); 77 (8); 57 (63); 55 (100). Anal. Calc. for $C_{28}H_{48}S$: C, 80.70; H, 11.61. Found: C, 80.25; H, 11.59.

3-Butyl-oct-2-enoic acid methyl ester (**7**): ^{1}H NMR (200 MHz, CDCl$_3$) δ 5.62 (s, 1H); 3.67 (s, 3H); 2.59 (t, 2H, $J = 7.2$ Hz); 2.14 (t, 2H, $J = 7.2$ Hz); 1.49–1.31 (m, 10H); 0.94–0.89 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.8; 165.1; 114.5; 50.5; 37.9; 32.0; 31.9; 29.7; 28.2; 22.4; 22.3; 13.8; 13.7. MS: *m/z* (%) = 212 (19); 181 (25); 114 (100); 96 (58); 82 (70). Anal. Calc. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.92; H, 11.33.

3-Butyl-oct-2-enoic acid isopropyl ester (**8**): ^{1}H NMR (200 MHz, CDCl$_3$) δ 5.58 (s, 1H); 5.02 (sept, 1H, $J = 7.4$ Hz); 2.58 (t, 2H, $J = 7.4$ Hz); 2.12 (t, 2H,

$J = 7.4$ Hz); 1.49–1.23 (m, 16H); 0.94–0.88 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.1; 121.1; 115.6; 66.4; 38.0; 32.1; 32.0; 29.8; 28.3; 22.5; 22.4; 21.9; 13.9; 12.8. MS: *m/z* (%) = 240 (11); 198 (24); 181 (34); 100 (100); 96 (40); 82 (58); 55 (70). Anal. Calc. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.93; H, 11.45.

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