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Regio- and stereoselective synthesis of *Z*-vinylic tellurides from propargylic alcohols: a route to chiral *Z*-enynes

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Abstract—*tert*-Butyldimethylsilyl ethers of propargylic alcohols are hydrotellurated regioselectively to give 1,2-*Z*-vinylic tellurides. Enantiomerically pure propargylic alcohols give enantiomerically pure vinylic tellurides, which are coupled with alkynes under Pd catalysis to give enantiomerically pure allylic enynols.

1. Introduction

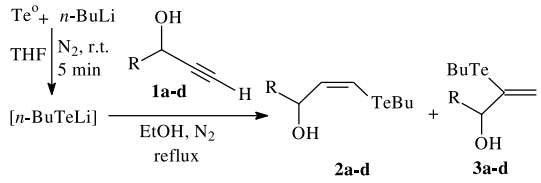
Hydrotelluration of alkynes gives *Z*-vinylic tellurides exclusively,[1] whereas other hydrometallation reactions give the *E*-vinyl organometallics preferentially.[2] The transformation of *Z*-vinylic tellurides into *Z*-organometallics is well established[1] and recently it was used in the first step of the synthesis of Macrolactin A, an antiviral macrolactone.[3] Although the hydrotelluration of conjugated alkynes gives only the 1,2-regioisomer, the hydrotelluration of propargylic alcohols **1** leads to the formation of 1,2- and 2,2-substituted allylic alcohols **2** and **3**, respectively[4] (Scheme 1). Another limitation of the hydrotelluration reaction consists in the traditional use of dibutylditelluride as starting material, which is a bad smelling compound and is not commercially available. Recently, we solved this problem by substituting the classically used methodology[1] by a different one, consisting in the reaction of commercially available elemental tellurium and *n*-butyllithium, which generates lithium butyltellurolate.[1] In the presence of water or ethanol, this intermediate reacts with alkynes[5] leading to *Z*-vinylic tellurides in yields similar to the ones obtained by the dibutylditelluride/sodium borohydride method (Scheme 1).[1,5] In view of the occurrence of allylic alcohols in the structure of many natural products[6] or synthetic intermediates,[7] we decided to investigate the hydrotelluration of propargylic alcohols in order to control its regiochemistry. In this work the lithium *n*-butyltellurolate/EtOH methodology was employed throughout.

2. Results and discussion

Initially, the propargylic alcohols **1a–d** were hydrotellurated by reacting them with the system *n*-BuTeLi/EtOH in order to verify the influence of their structures in the isomeric ratios of the formed vinylic tellurides. The results are presented in Table 1.

As can be observed, isomeric mixtures of **2** and **3** were obtained. The isomeric ratios suggest that the nature of the R group has a deep influence in the regioselectivity of the hydrotelluration reaction. As the steric demand of the R group increases, the amount of the desired 1,2-regioisomer increases. In view of these results, we decided to increase the steric demand at C_3 by protecting the OH function with bulky protecting groups. Three commonly used protecting groups were chosen for this purpose (Scheme 2, Table 2). Initially alcohol **1b** was protected with the three bulky protecting groups, leading to the propargylic ethers **4a–c**, which were submitted to hydrotelluration (Scheme 2, Table 2).

As can be observed the hydrotelluration of **4a**,**b** occurred in good yields and with high regioselectivity. The *tert*-butyldimethylsilyl (TBDMS) protected product presented



Scheme 1.

Keywords: *Z*-Vinylic tellurides; Propargylic alcohols; Chiral *Z*-enynes.
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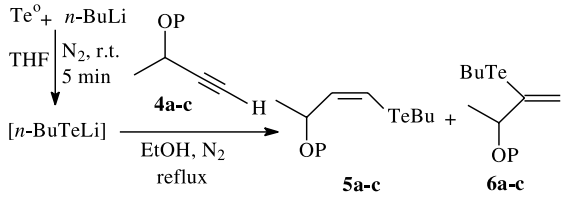
Table 1. Hydrotelluration of propargylic alcohols **1a–d** produced according to Scheme 1

Entry	R	Time (h)	Yield (%)[a]	Isomeric ratio (2:3)[b]
1	H (**a**)	4	80	1:3
2	CH_3 (**b**)	6	74	2:3
3	$(CH_3)_2CH$ (**c**)	6	60	2:1
4	Ph (**d**)	6	60	2:1

[a] Isolated yields after column chromatography on silica gel.
[b] The isomeric ratio was determined by ^1H NMR data and confirmed by GC analysis.



Scheme 2.

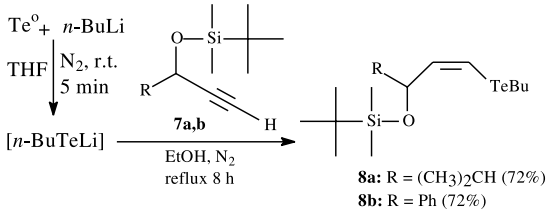
a 10:1 regioisomeric ratio in favor of the 1,2-isomer **5a**, confirming the steric control of the reaction. The tetrahydropyranyl group conferred a moderate selectivity leading to a 6:1 ratio (entry 2, Table 2). The propargylic alcohol protected by the trityl group did not react with the hydrotellurating agent (entry 3, Table 3). In view of the good results obtained by using the TBDMS group, the propargylic ethers **7a**,**b** were prepared and submitted to the hydrotelluration conditions. In this case, it was observed the exclusive formation of the 1,2-substituted vinylic tellurides **8a**,**b** in 72% isolated yield (Scheme 3).

Recently, we obtained chiral propargylic alcohols by a kinetic resolution of the racemic mixture using Novozyme 435.[8] In order to prepare enantiomerically enriched vinylic tellurides, we prepared (*S*)-(+)-**11a** and (*R*)-(−)-**11a** (Scheme 4) using our kinetic resolution conditions and submitted them to the hydrotelluration conditions, obtaining the chiral vinylic tellurides (*S*)-(+)-**8b** and (*R*)-(−)-**8b** (Scheme 4). Vinylic tellurides are precursors of enynes and enediynes by Te-Sonogashira reactions with alkynes[9,10] or alkynoates[9] promoted by Pd. In order to obtain chiral allylic enynols, we submitted compound **8b** to the coupling reaction with 1-heptyne promoted by $PdCl_2$/CuI[9,10] and then deprotected the TBDMS-ether **13** with tetrabutylammonium fluoride (TBAF). Initially racemic **14** was prepared and then the whole sequence was repeated to obtain (*S*)-(+)-**14** and (*R*)-(−)-**14** (Scheme 5).

Table 3. Coupling of chiral *Z*-vinylic tellurides with zincates using palladium and copper as catalysts produced according to Scheme 6

Entry	R	Compound	Yield (%)[a]
1	n-C_5H_{11}	(*S*)-(+)-**13a**	77
2	n-C_5H_{11}	(*R*)-(−)-**13a**	71
3	Ph	(*S*)-(+)-**13b**	87
4	Ph	(*R*)-(−)-**13b**	87

[a] Isolated yields after column chromatography on silica gel.



Scheme 3. Regioselective synthesis of *Z*-vinylic tellurides **8a**,**b** from propargylic ethers **7a**,**b**.

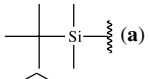
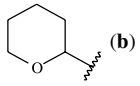
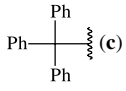
In order to use catalytic amounts of Pd, we then performed the coupling reaction of (*S*)-(+)-**8b** and (*R*)-(−)-**8b** with the zinc alkynoate as described recently.[9b] In this case 10 mol% of $Pd(PPh_3)_4$ was used as catalyst, leading to the coupled products **13a**,**b** in good yields (Scheme 6, Table 3).

To demonstrate that the enantiomeric excesses of the starting materials (*S*)-(+)-**11a** and (*R*)-(+)-**12** are kept unchanged throughout the transformations described in Schemes 4–6, compound (*R*)-(−)-**13a** was deprotected with TBAF to give alcohol (*R*)-(−)-**14** with an enantiomeric excess similar to the one of (*R*)-(+)-**12** (Fig. 1).

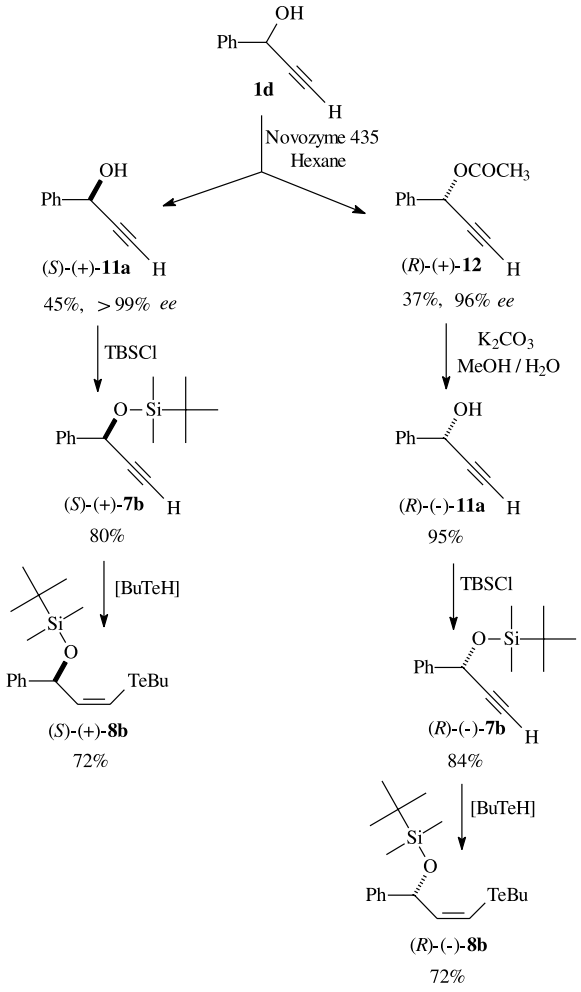
3. Conclusions

In conclusion, the hydrotelluration of propargylic alcohols

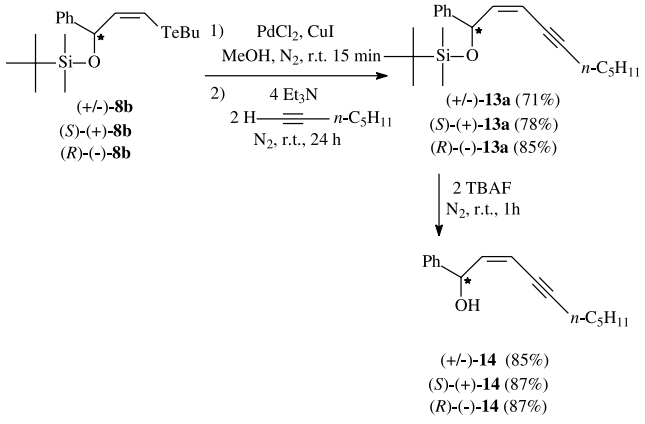
Table 2. Hydrotelluration of propargylic ethers **4a–c** produced according to Scheme 2

Entry	P	Time (h)	Yield (%)[a]	Isomeric ratio (5:6)[b]
1	 (**a**)	8	74	10:1
2	 (**b**)	8	73	6:1
3	 (**c**)	24	N.R.[c]	—

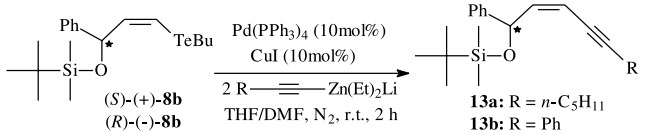
[a] Isolated yields after column chromatography on silica gel.
[b] The isomeric ratio was determined by ^1H NMR data and confirmed by GC analysis.
[c] The product was not formed.



Scheme 4. Regioselective synthesis of chiral *Z*-vinylic tellurides (*S*)-(+)-**8b** and (*R*)-(−)-**8b**.



Scheme 5. Synthesis of racemic and chiral *Z*-enynes **13a** and **14**.



Scheme 6.

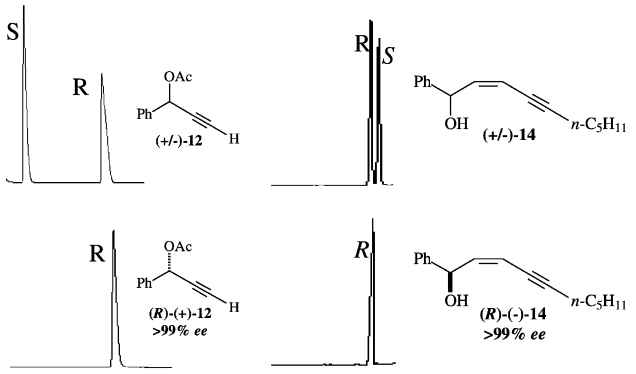


Figure 1. Chiral chromatography of (+/−)-**12**, (+/−)-**14**, (*R*)-(+)-**12** and (*R*)-(−)-**14**.

can be controlled to give the 1,2-regioisomer by transforming them into the bulky *tert*-butyldimethylsilyl ether. By using an enantiomerically enriched starting propargylic alcohol, enantiomerically enriched vinylic tellurides are obtained, which are chiral building blocks to the synthesis of chiral allylic enynols.

4. Experimental

4.1. Materials

All reagents and solvents used were previously purified and dried in agreement with the literature.[11] THF was distilled from sodium/benzophenone under N_2 immediately before use.[11] *n*-BuLi was titrated using 1,10-phenanthroline as indicator prior to use.[12] N_2 gas used in the reactions was deoxygenated and dried as described in the literature.[11,13] All operations were carried out in flame-dried glassware. Column chromatography separations were carried out with Vetec silicagel 60 (0.063–0.200 mm, 70–230 mesh) or Acros Organics silicagel (0.035–0.075 mm, pore diameter ca 6 nm). Tellurium metal (−200 mesh) was obtained from Aldrich Chemical Co. and dried overnight in an oven at 100 °C. Palladium dichloride and copper (I) iodide were purchased from Aldrich Chemical Co. and dried in a desiccator containing $CaCl_2$ and P_2O_5 under vacuum. *Tetrakis*(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) was prepared as described in the literature[14] and maintained in amber flask under nitrogen atmosphere. The following reagents were prepared according to literature procedures: 4-methyl-pent-1-yn-3-ol (**1c**);[15] 1-phenyl-2-propyn-1-ol (**1d**);[15] *tert*-butyl (but-3-yn-2-yloxy) dimethylsilane (**4a**);[16] 2-(but-3-yn-2-yloxy)-tetrahydro-2*H*-pyran (**4b**);[17] (but-3-yn-2-yloxy) triphenylmethane (**4c**);[18] (4-methyl-pent-1-yn-3-yloxy) (*tert*-butyl) dimethylsilane (**7a**)[16] and (1-phenyl-prop-2-ynyloxy) (*tert*-butyl) dimethylsilane (**7b**).[16] These last compounds presented analytical data which agree with the proposed structures. Novozyme 435 (immobilized lipase from *Candida antartica*) was obtained as a gift from Novozymes Brasil (Paraná-Brazil). The remaining chemicals were obtained from commercial sources.

4.2. Instrumentation

^1H and ^{13}C NMR spectra were obtained on a Bruker AC-200 (200 MHz, ^1H; 50 MHz, ^{13}C) or DRX-500 (500 MHz, ^1H;

125 MHz, ^{13}C) or on a Varian INOVA 300 (300 MHz, ^{1}H; 75 MHz, ^{13}C) spectrometers. All spectra were taken in $CDCl_3$ and the chemical shifts are given in ppm with respect to tetramethylsilane (TMS) used as internal standard. ^{125}Te NMR spectra were obtained on a Bruker DRX-500 (157 MHz, ^{125}Te) spectrometer using $CDCl_3$ as solvent. The chemical shifts refer to diphenyl ditelluride $(PhTe)_2$ in $CDCl_3$ (1 mol L^{-1}) ($\delta=420$ ppm at 25 °C) as external standard. Enantiomeric excesses of the enzyme-catalyzed reactions were determined using a Shimadzu GC-17A gas chromatograph equipped with a chiral capillary column Chirasil-Dex CB β-cyclodextrin (25 m×0.25 mm) or with a chiral capillary column Gamma Dex 120 Supelco (30 m×0.25 mm×0.25 μm film thickness). Optical rotation values were measured in a Jasco DIP-378 polarimeter and the reported data refer to the Na-line value using a 0.1 dm cuvette. Low resolution mass spectra were obtained on a Shimadzu CG-17A/CGMS-QP5050A instrument. Near IR spectra were obtained on a Bomem MB-100 spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of the Institute of Chemistry, Universidade de São Paulo. The IUPAC names were obtained using the software ChemDraw Ultra, version 8.0.

4.3. Typical procedures

4.3.1. Preparation of *Z*-vinylic tellurides.[5b] To a 50 mL two-necked round-bottomed flask equipped with magnetic stirring, heating and reflux condenser under nitrogen atmosphere were added elemental tellurium (0.254 g, 2 mmol) and THF (10 mL). To the suspension obtained, *n*-BuLi (1.3 mL, 2 mmol of a 1.5 mol L^{-1} solution in hexane) was added dropwise at room temperature. A clear solution was formed after 5 min of stirring. After that, the appropriate alkyne (2.4 mmol) in deoxygenated ethanol (20 mL) was added and the resulting mixture was refluxed by the time indicated in the Tables 1 and 2 and Scheme 3. The reaction was quenched with brine (50 mL) followed by extraction with ethyl acetate (3×50 mL). The extracts were dried over $MgSO_4$ and then filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using appropriate eluent.

4.3.2. (*Z*)-3-(Butyltellanyl)prop-2-en-1-ol (2a)/2-(butyltellanyl) prop-2-en-1-ol (3a).[4a] Eluent: hexane/ethyl acetate (9:1); yield: 0.386 g (80%); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.77 (ddd, $J=9.6$, 1.2, 1.5 Hz, 0.4H), 6.40 (ddd, $J=9.6$, 5.2, 5.4 Hz, 0.4H), 6.16 (dd, $J=1.6$, 1.5 Hz, 1H), 5.52 (dd, $J=1.3$, 1.2 Hz, 1H), 4.19 (s, 1H), 4.11 (dd, $J=3.6$, 3.3 Hz, 0.4H), 2.72 (t, $J=7.5$ Hz, 2H), 2.60 (t, $J=4.8$ Hz, 0.8H), 1.74 (m, 2.8H), 1.36 (m, 2.8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 137.4, 127.1, 122.7, 104.6, 70.1, 64.9, 34.0, 33.7, 25.0, 24.8, 13.3, 7.1, 6.1.

4.3.3. (+/−)-(*Z*)-4-(Butyltellanyl)but-3-en-2-ol (2b)/(+/−)-3-(butyltellanyl) but-3-en-2-ol (3b). Eluent: hexane/ethyl acetate (9:1); yield: 0.379 g (74%); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.69 (dd, $J=9.6$, 0.9 Hz, 1H), 6.28 (dd, $J=9.6$, 6.9 Hz, 1H), 6.12 (d, $J=0.9$ Hz, 1.5H), 5.40 (s, 1.5H), 4.33 (quint, $J=6.3$ Hz, 1H), 4.22 (q, $J=5.7$ Hz, 1.5H), 2.73 (t, $J=7.9$ Hz, 3H), 2.65 (t, $J=7.5$ Hz, 2H), 1.77 (m, 5H), 1.39 (m, 5H), 1.33 (d, $J=6.3$ Hz, 4.5H), 1.27 (d, $J=6.6$ Hz, 3H), 0.92 (t, $J=7.2$ Hz, 7.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 142.0, 135.6, 120.7, 103.2, 74.1, 70.5, 34.0, 33.4, 25.1, 24.9, 23.8, 22.4, 13.3, 7.1, 6.4; Near IR (film) ν (cm^{-1}) 3387, 2959, 2926, 2866, 1597, 1455, 1370, 1177; LRMS *m/z* (relative intensity) 258 (13%, M^+), 184 (21%), 71 (30%), 57 (100%)/258 (13%, M^+), 184 (7%), 71 (100%), 57 (60%). Anal. Calcd for $C_8H_{16}OTe$ C 37.56, H 6.30. Found C 37.75, H 6.12.

4.3.4. (+/−)-(*Z*)-1-(Butyltellanyl)-4-methyl-pent-1-en-3-ol (2c)/(+/−)-2-(butyltellanyl)-4-methyl-pent-1-en-3-ol (3c). Eluent: hexane/ethyl acetate (9:1); yield: 0.341 g (60%); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.82 (dd, $J=9.8$, 0.8 Hz, 1H), 6.28 (dd, $J=9.8$, 7.1 Hz, 1H), 6.11 (d, $J=0.9$ Hz, 1H), 5.48 (s, 1H), 3.90 (dd, $J=6.5$, 6.48 Hz, 1H), 3.53 (d, $J=7.1$ Hz, 1H), 2.75 (dt, $J=7.5$, 3.0 Hz, 2H), 2.65 (dt, $J=7.5$, 1.9 Hz, 2H), 1.78 (m, 6H), 1.40 (m, 4H), 1.00 (d, $J=6.6$ Hz; 3H), 0.96 (d, $J=6.7$ Hz, 6H), 0.92 (m, 9H), 0.86 (d, $J=6.7$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 139.3, 133.9, 122.2, 105.7, 84.1, 79.2, 34.1, 33.8, 33.5, 33.4, 25.2, 24.5, 19.5, 18.1, 17.8, 17.7, 13.3, 7.1, 6.4; Near IR (film) ν (cm^{-1}) 3429, 3060, 2958, 2927, 2870, 1598, 1463, 1380, 1030, 1009; LRMS *m/z* (relative intensity) 284 (11%, M^+), 282 (7%), 185 (13%), 183 (9%), 99 (10%), 81 (87%), 57 (100%), 284 (7%, M^+), 282 (4%), 185 (11%), 183 (7%), 99 (6%), 81 (16%), 57 (100%). Anal. Calcd for $C_{10}H_{20}OTe$ C 42.31, H 7.10. Found C 42.59, H 6.61.

4.3.5. (+/−)-(*Z*)-3-(Butyltellanyl)-1-phenyl-prop-2-en-1-ol (2d)/(+/−)-2-(butyltellanyl)-1-phenyl-prop-2-en-1-ol (3d). Eluent: hexane/ethyl acetate (9:1); yield: 0.382 g (60%); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.34 (m, 7.5H), 6.86 (dd, $J=9.9$, 1.5 Hz, 1H), 6.48 (dd, $J=9.9$, 6.6 Hz, 1H), 6.29 (d, $J=1.2$ Hz, 0.5H), 5.62 (d, $J=1.2$ Hz, 0.5H), 5.26 (d, $J=6.3$ Hz, 1H), 5.20 (d, $J=3.6$ Hz, 0.5H), 2.67 (t, $J=7.2$ Hz; 3H), 2.57 (t, $J=7.5$ Hz, 1.5H), 2.46 (d, $J=5.1$ Hz, 0.5H), 2.16 (d, $J=2.7$ Hz, 1H), 1.79 (m, 4H), 1.66 (m, 2H), 1.40 (m, 5H), 0.93 (t, $J=7.5$ Hz, 4H), 0.87 (t, $J=7.2$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 142.5, 140.1, 132.7, 128.6, 128.3, 127.8, 127.7, 126.4, 126.2, 123.6, 105.0, 79.8, 76.4, 34.3, 33.6, 25.3, 25.2, 13.5, 7.7, 7.3; Near IR (film) ν (cm^{-1}) 3397, 3084, 3061, 3025, 2957, 2925, 2870, 2857, 1596, 1491, 1454, 1377, 1035, 761, 699; LRMS *m/z* (relative intensity) 320 (18%, M^+), 318 (17%), 204 (28%), 115 (100%), 89 (8%), 77 (47%), 57 (62%), 320 (13%, M^+), 318 (13%), 261 (25%), 149 (20%), 131 (88%), 115 (100%), 91 (7%), 77 (88%), 57 (72%). Anal. Calcd for $C_{13}H_{18}OTe$ C 49.12, H 5.71. Found C 49.36, H 5.46.

4.3.6. (+/−)-((*Z*)-4-(Butyltellanyl) but-3-en-2-yloxy) (*tert*-butyl) dimethylsilane (5a)/(+/−)-(3-(butyltellanyl) but-3-en-2-yloxy) (*tert*-butyl)dimethylsilane (6a). Eluent: hexane; yield: 0.548 g (74%); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.54 (dd, $J=9.9$, 0.6 Hz, 1H), 6.23 (dd, $J=9.9$, 7.2 Hz, 1H), 4.28 (dt, $J=6.7$, 0.9 Hz, 1H), 2.63 (dt, $J=7.8$, 3.6 Hz, 2H), 1.75 (quint, $J=7.2$ Hz, 2H), 1.38 (sext, $J=7.5$ Hz, 2H), 1.18 (d, $J=6.6$ Hz, 3H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 143.9, 100.2, 72.0, 34.1, 26.0, 24.9, 23.4, 18.2, 13.3, 6.8, −4.3, −4.6; ^{125}Te NMR (157 MHz, $CDCl_3$) δ (ppm) 265; Near IR (film) ν (cm^{-1}) 2958, 2929, 2886, 2857, 1640, 1463, 1200, 1117, 1092; LRMS *m/z* (relative intensity) 372 (6%, M^+), 370 (5%), 315 (13%), 241 (12%), 185 (22%),

183 (15%), 181 (11%), 127 (100%), 75 (47%), 73 (59%), 57 (18%), 55 (20%). Anal. Calcd for $C_{14}H_{30}OSiTe$ C 45.44, H 8.17. Found C 45.38, H 8.05.

4.3.7. (+/−)-2-((*Z*)-4-(Butyltellanyl) but-3-en-2-yloxy)-tetrahydro-2*H*-pyran (5b)/(+/−)-2-(3-(butyltellanyl) but-3-en-2-yloxy)-tetrahydro-2*H*-pyran (6b). Eluent: hexane; yield: 0.496 g (73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.79 (dd, J=9.7, 0.6 Hz, 1H), 6.67 (dd, J=9.8, 0.9 Hz, 0.2H), 6.31 (dd, J=9.8, 7.1 Hz, 0.2H), 6.13 (dd, J=9.7, 7.9 Hz, 1H), 6.09 (d, J=1.0 Hz, 0.2H), 6.08 (d, J=1.0 Hz, 0.2H), 4.71 (dd, J=4.4, 3.1 Hz, 0.2H), 4.61 (dd, J=4.5, 3.0 Hz, 0.2H), 4.59 (dd, J=6.5, 0.6 Hz, 1H), 4.34 (ddt, J=7.8, 6.5, 0.6 Hz, 1H), 4.30–4.26 (m, 0.4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 145.0, 140.1, 134.3, 120.2, 105.5, 102.4, 96.7, 96.5, 96.1, 74.5, 73.7, 63.1, 62.6, 62.6, 34.1, 33.4, 30.9, 30.9, 30.6, 26.0, 25.5, 25.4, 25.3, 22.9, 20.5, 20.0, 19.7, 19.6, 19.4, 13.4, 6.9, 6.8, 5.2; Near IR (film) ν (cm^{-1}) 2954, 2929, 2870, 1598, 1462, 1454, 1368, 1201, 1121, 1077, 1034, 1021, 986; LRMS *m/z* (relative intensity) 340 (6%, M^+), 256 (3%), 242 (10%), 184 (17%), 85 (70%), 67 (25%), 57 (100%), 340 (5%), 256 (8%), 201 (10%), 182 (6%), 85 (87%). Anal. Calcd for $C_{13}H_{24}O_2Te$ C 45.93, H 7.12. Found C 45.91, H 6.83.

4.3.8. (+/−)-((*Z*)-1-(Butyltellanyl)-4-methyl-pent-1-en-3-yloxy) (*tert*-butyl)dimethylsilane (8a). Eluent: hexane; yield: 0.573 g (72%); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.67 (dd, J=9.6, 0.6 Hz, 1H), 6.17 (dd, J=9.6, 8.1 Hz, 1H), 3.78 (dd, J=7.9, 5.7 Hz, 1H), 2.65 (m, 2H), 1.76 (quint, J=7.5 Hz, 2H), 1.70 (m, 1H), 1.39 (dq, J=7.2, 7.5 Hz, 2H), 0.92 (t, J=7.2 Hz, 3H), 0.86 (d, J=6.9 Hz, 6H), 0.89 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 142.0, 103.0, 80.6, 34.9, 34.1, 25.9, 24.9, 18.4, 18.1, 17.9, 13.3, 6.9, −4.0, −4.8; ^{125}Te NMR (157 MHz, $CDCl_3$) δ (ppm) 267; Near IR (film) ν (cm^{-1}) 2957, 2929, 2886, 2857, 1598, 1465, 1125, 1069; LRMS *m/z* (relative intensity) 398 (2%, M^+), 357 (28%), 355 (24%), 155 (23%), 115 (5%), 81 (15%), 75 (36%), 73 (100%), 57 (19%), 55 (11%). Anal. Calcd for $C_{16}H_{34}OSiTe$ C 48.27, H 8.61. Found C 48.45, H 8.21.

4.3.9. (+/−)-((*Z*)-3-(Butyltellanyl)-1-phenyl-allyloxy) (*tert*-butyl)dimethylsilane (8b). Eluent: hexane; yield: 0.622 g (72%); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.38–7.37 (m, 2H), 7.33–7.29 (m, 2H), 7.21–7.24 (m, 1H), 6.68 (dd, J=9.6, 0.6 Hz, 1H), 6.33 (dd, J=9.6, 7.6 Hz, 1H), 5.21 (d, J=7.6 Hz, 1H), 2.64–2.74 (m, 2H), 1.79 (dt, J=7.5, 7.4 Hz, 2H), 1.40 (dq, J=7.5, 7.4 Hz, 2H), 0.92 (t, J=4.1 Hz, 3H), 0.92 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 143.5, 142.5, 128.3, 127.1, 125.8, 102.2, 34.1, 26.0, 24.9, 18.3, 13.4, 7.4, −4.2, −4.6; ^{125}Te NMR (157 MHz, $CDCl_3$) δ (ppm) 278; Near IR (film) ν (cm^{-1}) 3062, 3025, 2956, 2929, 2888, 2857, 1597, 1463, 1254, 1089, 1066, 868, 838; LRMS *m/z* (relative intensity) 432 (3%, M^+), 377 (7%), 303 (3%), 247 (20%), 189 (23%), 115 (100%), 73 (82%), 57 (17%). Anal. Calcd for $C_{19}H_{32}OSiTe$ C 52.81, H 7.46. Found C 53.15, H 7.27.

4.3.10. Kinetic resolution of compound 1d using Novozyme 435.[8] To a 125 mL Erlenmeyer flask were added hexane (HPLC grade) (20 mL), vinyl acetate (1 mL), Novozyme 435 (0.300 g) and 1-phenyl-prop-2-yn-1-ol (**1d**) (0.560 g, 4 mmol). The reaction mixture was stirred on a rotary shaker (32 °C, 170 rpm) for 40 min. After that, the mixture was filtered and the solvent evaporated. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (9:1) as eluent. The enatiomeric rate (*E*) for the kinetic resolution of 1-phenyl-prop-2-yn-1-ol (**1d**) was > 200 and the convertion (*c*) was 50%.

4.3.11. (*S*)-(+)-1-Phenyl-prop-2-yn-1-ol (11a). Yield: 0.218 g (39%); enantiomeric excess (*ee*): >99%; $[\alpha]_D^{25}$ = +16.3 (*c* 4.34, $CHCl_3$), 99% *ee* {Lit. $[\alpha]_D^{25}$ = +20.0 (*c* 1.13, $CHCl_3$), 72% *ee*}[19] ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.56–7.51 (m, 2H), 7.50–7.28 (m, 3H), 5.43 (d, J=2.2 Hz, 1H), 2.65 (d, J=2.0 Hz, 1H), 2.49 (s_{broad}, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 140.0, 128.6, 128.4, 126.5, 83.5, 74.7, 64.3; Near IR (film) ν (cm^{-1}) 3371, 3293, 3088, 3065, 3033, 2880, 2118, 1454, 1276, 1022, 739, 699, 651; LRMS *m/z* (relative intensity) 132 (86%, M^+), 131 (100%), 115 (26%), 103 (42%), 89 (12%), 77 (75%), 63 (20%), 53 (84%).

4.3.12. (*R*)-(+)-1-Phenyl-prop-2-ynyl acetate (12). Yield: 0.339 g (46%); enantiomeric excesses (*ee*): 96–99%; $[\alpha]_D^{25}$ = +4.4 (*c* 4.33, $CHCl_3$), 98% *ee*; {Lit. $[\alpha]_D^{25}$ = +3.4 (*c* 1.07, $CHCl_3$), 85% *ee*}[19] ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.59–7.52 (m, 2H), 7.47–7.39 (m, 3H), 6.48 (d, J=2.2 Hz, 1H), 2.68 (d, J=2.0 Hz, 1H), 2.13 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 169.6, 136.5, 129.0, 128.6, 127.6, 80.2, 75.3, 65.2, 20.9; Near IR (film) ν (cm^{-1}) 3289, 3066, 3036, 2940, 2126, 1742, 1456, 1371, 1228, 760, 698, 653; LRMS *m/z* (relative intensity) 174 (M^+, 9.6%), 132 (37.2%), 114 (100.0%), 103 (8.0%), 89 (11.8%), 77 (11.2%), 63 (13.5%), 43 (44.6%).

4.3.13. Preparation of compound (*R*)-(−)-11a.[20] To a 25 mL two-necked round-bottomed flask equipped with magnetic stirring were added (*R*)-(+)-**12** (0.330 g, 1.9 mmol), methanol (3 mL), water (3 mL) and K_2CO_3 (0.262 g, 1.9 mmol). The mixture was stirred at room temperature for 12 h. After that, the reaction was quenched with brine (15 mL) followed by extraction with ethyl acetate (4 x 15 mL). The extracts were dried over $MgSO_4$ and then filtered. The solvent was evaporated under reduced pressure.

(R)-(−)-1-Phenyl-prop-2-yn-1-ol (**11a**). Yield: 0.238 g (95%); $[\alpha]_D^{25}$ = −24.7 (*c* 2.20, $CHCl_3$). (The spectral data agreed with those obtained for compound (*S*)-(+)-**11a**.)

4.3.14. Preparation of (*S*)-(+)-7b and (*R*)-(−)-7b.[16] To a 25 mL two-necked round-bottomed flask equipped with magnetic stirring under nitrogen atmosphere were added (*S*)-(+)-**11a** or (*R*)-(−)-**11a** (0.210 g, 1.6 mmol), $CHCl_3$ (2.5 mL), *tert*-butyldimethylsilyl chloride (0.271 g, 1.8 mmol) and imidazole (0.238 g, 3.5 mmol). The mixture was stirred at room temperature for 12 h. After that, the reaction was diluted with CH_2Cl_2 (20 mL) and washed with water (3×100 mL). The organic phase was dried over $MgSO_4$ and then filtered. The solvent was evaporated under reduced pressure.

*(R)-(−)-1-Phenyl-prop-2-ynyloxy) (*tert*-butyl) dimethyl silane* (**7b**).[16b] Yield: 0.331 g (84%); $[\alpha]_D^{25}$ = −16.62 (*c* 2.10, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.51–

7.47 (m, 2H), 7.38–7.28 (m, 3H), 5.48 (d, $J=2.2$ Hz, 1H), 2.53 (d, $J=2.2$ Hz, 1H), 0.94 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H); LRMS *m/z* (relative intensity) 231 (1%), 189 (100%), 179 (46%), 159 (1%), 145 (2%), 135 (18%), 115 (78%), 105 (28%), 89 (9%), 83 (45%), 75 (21%), 57 (8%).

*(S)-(+)-1-Phenyl-prop-2-ynyloxy) (*tert*-butyl) dimethyl silane* (**7b**). Yield: 0.315 g (80%); $[\alpha]_D^{25}=+9.35$ (*c* 2.00, $CHCl_3$). (The spectral data agreed with those obtained for compound (*R*)-(−)-**7b**).

4.3.15. Preparation of compounds (*S*)-(+)-8b and (*R*)-(−)-8b. The reactions were performed as described in Section 4.3.1. in a 1.2 mmol scale.

*((S,Z)-(+)-3-(Butyltellanyl)-1-phenylallyloxy) (*tert*-butyl)-dimethylsilane* (**8b**). Yield: 0.373 g (72%); $[\alpha]_D^{25}=+137.39$ (*c* 2.30, $CHCl_3$). (The spectral data agreed with those obtained for compound (+/−)-**8b**).

*((R,Z)-(−)-3-(Butyltellanyl)-1-phenylallyloxy) (*tert*-butyl)-dimethylsilane* (**8b**). Yield: 0.373 g (72%); $[\alpha]_D^{25}=-144.50$ (*c* 2.00, $CHCl_3$). (The spectral data agreed with those obtained for compound (+/−)-**8b**).

4.3.16. Preparation of compounds (+/−)-13, (*S*)-(+)-13a and (*R*)-(−)-13a: cross-coupling reaction using $PdCl_2$/CuI.[9a,10] To a 25 mL two-necked round-bottomed flask equipped with magnetic stirring under nitrogen atmosphere were added $PdCl_2$ (0.124 g, 0.7 mmol), CuI (0.133 g, 0.7 mmol), methanol (7 mL) and the telluride **8b** (0.300 g, 0.7 mmol). The mixture was stirred at room temperature for 15 min under nitrogen atmosphere. After that, 1-heptyne (0.135 g, 1.4 mmol) and triethylamine (0.4 mL, 0.283 g, 2.8 mmol) were added to the reaction mixture which was stirred under nitrogen atmosphere at room temperature for 24 h. Then, the solids were filtered off over celite®, washing several times with methanol. The solvent was evaporated under reduced pressure. To the residue was added brine (30 mL), and the mixture was extracted with ethyl acetate (3×30 mL). The combined organic phases were dried over $MgSO_4$ and then filtered. The organic solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using hexane as eluent. The analytical data of products were obtained after purification by preparative thin layer chromatography using hexane as eluent.

4.3.17. (+/−)-(*Z*)-*tert*-Butyl-dimethyl-(1-phenyl-dec-2-en-4-ynyloxy)-silane (13). Yield: 0.170 g (71%). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.46–7.41 (m, 2H), 7.35–7.18 (m, 3H), 5.90–5.78 (m, 2H), 5.55–5.42 (m, 1H), 2.39 (td, $J=6.8$, 2.2 Hz, 2H), 1.59 (quint, $J=7.0$ Hz, 2H), 1.47–1.24 (m, 4H), 0.93 (s, 9H), 0.90 (t, $J=7.0$ Hz, 3H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 144.6, 143.9, 128.2, 127.0, 125.4, 108.7, 95.6, 77.1, 72.2, 31.2, 28.5, 25.9, 22.2, 19.5, 18.3, 13.4, −4.4, −4.9; Near IR (film) ν (cm^{-1}) 3063, 3029, 2956, 2931, 2859, 2216, 1603, 1492, 1464, 1390, 1254, 1091, 1068, 874, 837, 744, 698; LRMS *m/z* (relative intensity) 342 (1%, M^+), 327 (1%), 285 (91%), 267 (1%), 229 (4%), 211 (26%), 203 (7%), 189 (8%), 169 (4%), 153 (18%), 141 (18%), 129 (9%), 115 (17%), 105 (5%), 91 (25%), 75 (100%), 55 (2%). Anal. Calcd for $C_{22}H_{34}OSi$ C 77.13, H 10.00. Found C 77.39, H 10.05.

*((S,Z)-(+)-1-Phenyl-dec-2-en-4-ynyloxy) (*tert*-butyl) dimethyl-silane* (**13a**). Yield: 0.187 g (78%); $[\alpha]_D^{25}=+192.50$ (*c* 2.30, $CHCl_3$). (The spectral data agreed with those obtained for compound (+/−)-**13**).

*((R,Z)-(−)-1-Phenyl-dec-2-en-4-ynyloxy) (*tert*-butyl) dimethylsilane* (**13a**). Yield: 0.204 g (85%); $[\alpha]_D^{25}=-254.35$ (*c* 2.30, $CHCl_3$). (The spectral data agreed with those obtained for compound (+/−)-**13**).

4.3.18. Preparation of compounds (+/−)-14, (*S*)-(+)-14 and (*R*)-(−)-14.[21] To a 15 mL two-necked round-bottomed flask equipped with magnetic stirring under nitrogen atmosphere were added the appropriate *Z* enyne (+/−)-**13** (0.150 g, 0.4 mmol) and tetrabutylammonium fluoride (1.0 mol L^{-1} solution in THF) (0.8 mL, 0.8 mmol). The reaction mixture was stirred under nitrogen atmosphere at room temperature for 1 h. The reaction was quenched with brine (50 mL) followed by extraction with ethyl acetate (3×50 mL). The extracts were dried over $MgSO_4$ and then filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (9:1) as eluent. The analytical data of the products were obtained after purification by preparative thin layer chromatography using hexane/ethyl acetate (9:1) as eluent.

4.3.19. (+/−)-(*Z*)-1-Phenyl-dec-2-en-4-yn-1-ol 14. Yield: 0.077 g (85%). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.47–7.23 (m, 5H), 5.99 (dd, $J=10.5$, 8.3 Hz, 1H), 5.79 (d, $J=8.3$ Hz, 1H), 5.60 (dt, $J=10.5$, 2.0 Hz, 1H), 2.37 (td, $J=7.0$, 2.2 Hz, 2H), 2.22 (s_{broad}, 1H), 1.58 (quint, $J=6.9$ Hz, 2H), 1.48–1.25 (m, 4H), 0.91 (t, $J=6.8$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 142.8, 142.8, 128.5, 127.6, 125.8, 110.7, 96.8, 76.6, 72.0, 31.1, 28.41, 22.2, 19.6, 14.0; Near IR (film) ν (cm^{-1}) 3386, 3085, 3062, 3029, 2957, 2931, 2860, 2214, 1602, 1493, 1453, 1378, 1046, 746, 699; LRMS *m/z* (relative intensity) 228 (3%, M^+), 213 (0.5%), 199 (2%), 185 (6%), 171 (34%), 157 (44%), 143 (14%), 128 (29%), 115 (20%), 105 (100%), 91 (36%), 77 (65%), 65 (16%), 55 (31%); Anal. Calcd for $C_{16}H_{20}O$ C 84.16, H 8.83. Found C 83.98, H 8.66.

(S,Z)-(+)-1-Phenyl-dec-2-en-4-yn-1-ol (**14**). Yield: 0.079 g (87%); $[\alpha]_D^{25}=+350.50$ (*c* 2.00, $CHCl_3$). (The spectral data agreed with those obtained for compound (+/−)-**14**).

(R,Z)-(−)-1-Phenyl-dec-2-en-4-yn-1-ol (**14**). Yield: 0.079 g (87%); $[\alpha]_D^{25}=-308.33$ (*c* 1.20, $CHCl_3$). (The spectral data agreed with those obtained for compound (+/−)-**14**).

4.3.20. Cross-coupling reaction using $Pd(PPh_3)_4$ and CuI as catalysts.[9b] *Preparation of the zinc reagent*. To a 15 mL two-necked round-bottomed flask equipped with magnetic stirring under nitrogen atmosphere were added the appropriate alkyne (1 mmol) and THF (4 mL). Then, *n*-BuLi (0.77 mL, 1 mmol of a 1.3 mol L^{-1} solution in hexane) was added dropwise at −70 °C, and the mixture was stirred for 10 min. After that, Et_2Zn (1 mL, 1 mmol of a 1.0 mol L^{-1} solution in THF) was added to the reaction mixture which was

then warmed to room temperature. The zinc reagent became ready for use.

Cross-coupling reaction. To a 25 mL two-necked round-bottomed flask equipped with magnetic stirring under nitrogen atmosphere were added the telluride **8b** (0.216 g, 0.5 mmol), THF (4 mL), $Pd(PPh_3)_4$ (0.027 g, 0.05 mmol), CuI (0.095 g, 0.05 mmol), DMF (4 mL) and the appropriate zinc reagent (1 mmol of the solution prepared above) via syringe. The reaction mixture was stirred under inert atmosphere at room temperature for 2 h. The reaction was quenched with brine (50 mL) followed by extraction with ethyl acetate (3× 50 mL). The extracts were dried over $MgSO_4$ and then filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using hexane as eluent. The analytical data of the products were obtained after purification by preparative thin layer chromatography using hexane as eluente.

*((*S,Z*)-(+)-1-Phenyl-dec-2-en-4-ynyloxy) (*tert*-butyl) dimethylsilane* (**13a**). Yield: 0.133 g (78%). (For spectral data see Section 4.3.16.)

*((*R,Z*)-(−)-1-Phenyl-dec-2-en-4-ynyloxy) (*tert*-butyl) dimethylsilane* (**13a**). Yield: 0.145 g (85%). (For spectral data see Section 4.3.16.)

*((*S,Z*)-(+)-1,5-Diphenyl-pent-2-en-4-ynyloxy) (*tert*-butyl) dimethylsilane* (**13b**). Yield: 0.151 g (87%); $[\alpha]_D^{25} = +266.67$ (*c* 0.37, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.50–7.23 (m, 10H), 6.01 (d, $J=10.5$ Hz, 1H), 5.97 (dd, $J=9.9$, 9.0 Hz, 1H), 5.72 (d, $J=9.9$ Hz, 1H), 0.94 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); 50 MHz RMN ^{13}C ($CDCl_3$) (ppm) 145.9, 143.5, 131.5, 128.4, 128.3, 128.3, 127.1, 125.5, 108.1, 94.2, 85.9, 72.3, 25.8, 25.8, 18.3, −4.4, −4.9; Near IR (film) ν (cm^{-1}) 2955, 2930, 2857, 1948, 1877, 1805, 1740, 1597, 1490, 1467, 1254, 1092, 1064, 1027, 1005, 954, 939; LRMS *m/z* (relative intensity) 348 (3%, M^+), 293 (7%), 292 (28%), 291 (100%), 218 (16%), 217 (78%), 216 (17%), 215 (51%), 213 (31%), 202 (39%), 115 (40%), 91 (18%), 75 (47%), 73 (34%), 57 (14%); Anal. Calcd for $C_{23}H_{28}OSi$ C 79.26, H 8.10. Found C 79.38, H 8.10.

*((*R,Z*)-(−)-1,5-Diphenyl-pent-2-en-4-ynyloxy) (*tert*-butyl) dimethylsilane* (**13b**). Yield: 0.151 g (87%); $[\alpha]_D^{25} = -308.33$ (*c* 0.37, $CHCl_3$). (The spectral data agreed with those obtained for compound (*S*)-(+)-**13b**).

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