Palladium-Catalyzed Cyclization of Silyl-Substituted Bis(homo)propargylic Alcohols to 2,3-Dihydrofurans

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Ring-opening of oxiranes **1** by the silicon- and sulfur-functionalized propargyl anions **2** yields the corresponding alk-4-yn-1-ols **3**. Cyclization of **3** to 2,3-dihydro-4-phenylthiofurans **5** is achieved by reaction with palladium(II) acetate. The corresponding furans **7** are obtained when copper(II) chloride is added to the reaction mixtures.

Dihydrofuran derivatives are of interest as synthetic intermediates and are also a structural feature in a number of natural products, e.g. aflatoxins.[1] Here, we report an efficient and selective approach to sulfur-substituted 2,3-dihydrofurans **5** by palladium-catalyzed cyclization of 3-thio-5-silyl-substituted alk-4-yn-1-ols **3**. These functionalized bis(homo)propargylic alcohols are synthesized starting from epoxides **1** by reaction with the ω-silyl-substituted sulfur-stabilized alkynyl anions **2**. In this way, products **3** are obtained as diastereomeric mixtures in good yields (Scheme 1, Table 1). Previously, we have used alkynyl anions **2** for the successful preparation of ethynylcyclopropanes from epoxides.[2] However, the anion building block **2** should also be a convenient precursor for the synthesis of five-membered unsaturated oxacycles. In particular, because of their spearhead-type anion structure, the silylalkynes **2** are sterically less hindered than the corresponding allyl anions, and thus react more readily with epoxides, especially with bulky 1,2-disubstituted oxiranes.

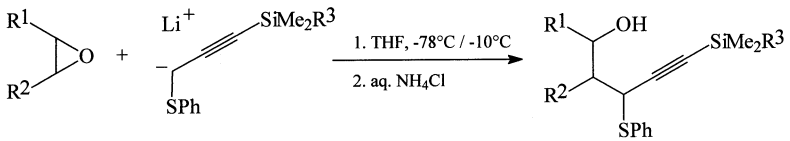
The reaction of **2** with monosubstituted epoxides occurs at −78°C; for the complete conversion of disubstituted oxiranes the temperature is allowed to rise to −10°C. An exception is the ring-opening of the disubstituted epoxide **1e** by **2b** at −10°C. In this case, a migration of the phenyldimethylsilyl group of the starting oxirane to the neighbouring alkoxide oxygen atom results in elimination of the phenylthio group (Scheme 2). The silyl ether is cleaved during chromatographic purification on silica gel to give the corresponding alcohol **4**, which is isolated as a mixture of *E*/*Z* isomers in 47% yield. However, the formation of the desired silyl-substituted bis(homo)propargylic alcohol **3j** can be accomplished in the presence of boron trifluoride−diethyl ether, which allows the reaction of epoxysilane **1e** with alkynyl anion **2b** to be performed at −78°C.

Table 1. Preparation of bis(homo)propargylic alcohols **3**

Products	R^1	R^2	Yield (%)[a] R^3 = Me	R^3 = Ph
3a, **3b**	Me	H	68	78
3c, **3d**	$BnOCH_2$	H	70	71
3e, **3f**	*sec*-C_5H_{11}	Me	51	57
3g, **3h**	$-[CH_2]_4-$		60	70
3i, **3j**	Me	$SiMe_2Ph$	41	64

[a] Isolated yields of pure products.

Scheme 1

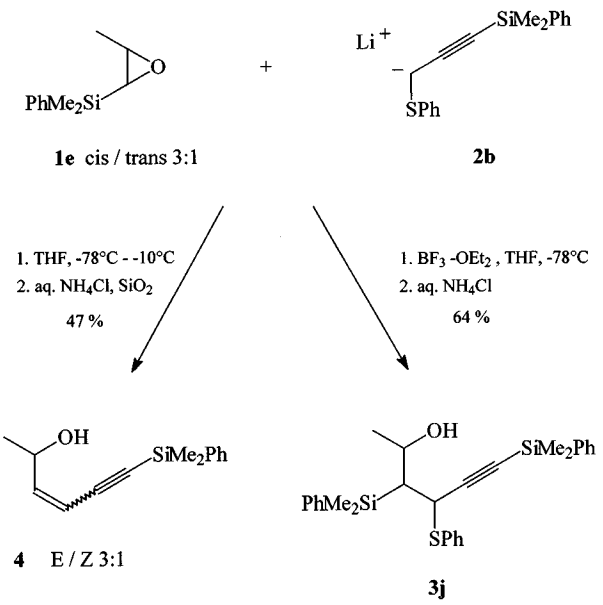


1	R^1	R^2	**2**	R^3
a	Me	H	**a**	Me
b	$BnOCH_2$	H	**b**	Ph
c	s-C_5H_{11}	Me		
d	-$(CH_2)_4$-			
e	Me	$SiMe_2Ph$		

3	R^3	R^1	R^2
	Me	Ph	
a	**b**	Me	H
c	**d**	$BnOCH_2$	H
e	**f**	s-C_5H_{11}	Me
g	**h**	-$(CH_2)_4$-	
i	**j**	Me	$SiMe_2Ph$

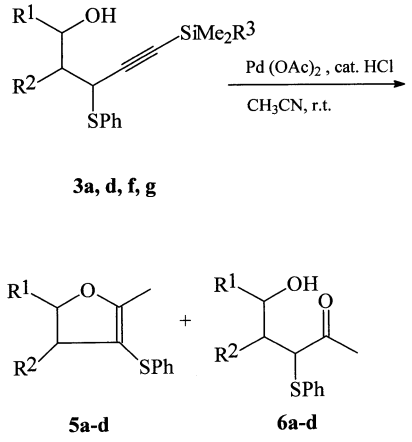
  1434−193X/98/0909−1873 $ 17.50+.50/0

Scheme 2



The cyclization of the ω-silyl-substituted γ-alkynols **3** can be achieved in acetonitrile at room temperature using hydrochloric acid and palladium(II) acetate as catalysts. Under these conditions, the intramolecular addition of the hydroxy group to the C−C triple bond gives exclusively 2,3-dihydrofurans **5** with the sulfur substituent at C-4 in a 5-*exo-dig* ring closure. Moreover, the terminal silyl group is removed in this process. Some γ-hydroxy ketone **6** is obtained as by-product in 15−26% yield, which is the result of hydration of the γ-alkynol **3** (Scheme 3, Table 2).

Scheme 3



When chiral alcohols are used, e.g. those generated by employing optically pure epoxides, the ring closure proceeds with complete retention of configuration. Thus, (−)-(*S*)-propene oxide furnishes chiral (*S*)-2,5-dimethyl-4-phenylthio-2,3-dihydrofuran (**5a**) with excellent optical purity (99% *ee*), as determined by GLC analysis on a chiral cyclodextrin phase.

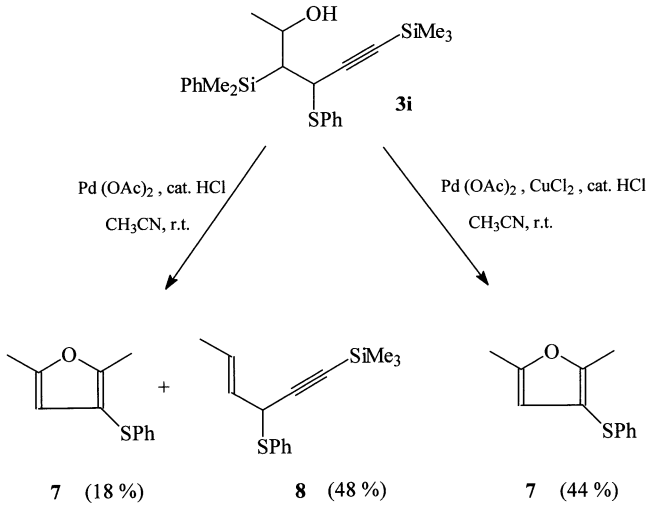
The reaction of the phenyldimethylsilyl-substituted alkynol **3i** with palladium(II) acetate under analogous conditions does not yield the corresponding 3-silyl-substituted 2,3-dihydrofuran, but rather furan **7** in 18% yield, because the additional silyl substituent is eliminated (Scheme 4). However, the major product is the alkenyne **8**, which is formed in 48% yield as a result of Peterson olefination. By the addition of a copper(II) salt, the isolated yield of furan **7** can be increased to 44%.

Table 2. Formation of 2,3-dihydrofurans **5** and ketones **6** from alkynols **3**

Substrate	Products	R^1	R^2	R^3	Yield (%)[a] Dihydrofuran **5**	Ketone **6**
3a	**5a**, **6a**	Me	H	Me	56	18
3d	**5b**, **6b**	$BnOCH_2$	H	Ph	51	21
3f	**5c**, **6c**	*sec*-C_5H_{11}	Me	Ph	54	15
3g	**5d**, **6d**	$-[CH_2]_4-$		Me	1[b]	26[b]

[a] Isolated yields of pure products. − [b] 40% of **3g** recovered.

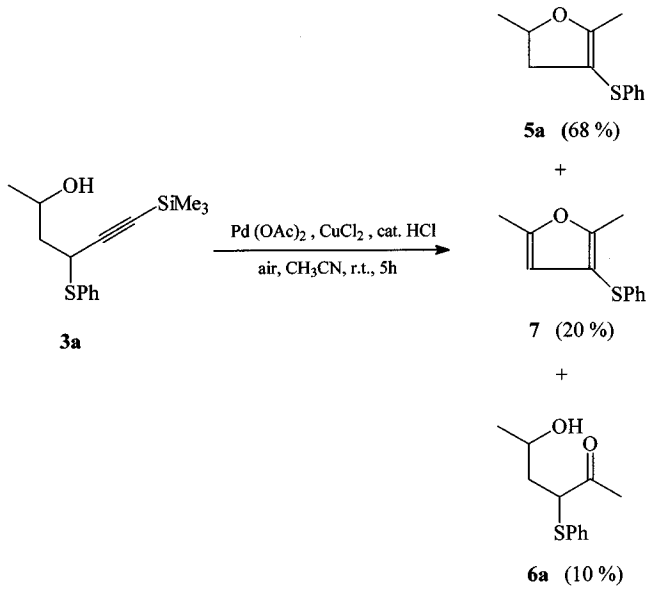
Scheme 4



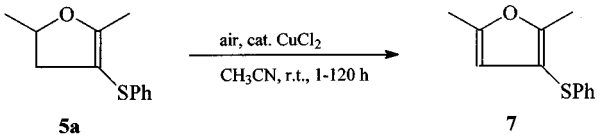
Upon treatment of bis(homo)propargylic alcohol **3a** with palladium(II) acetate and additional copper(II) chloride, the cyclization to 2,3-dihydrofuran **5a** and the in situ oxidation to furan **7** are also observed (Scheme 5). The yield of furan can be increased by extending the reaction time, which is in accord with the dihydrofuran being the precursor of the furan. In fact, the oxidation of dihydrofuran **5a** to the furan **7** can be accomplished merely by the addition of copper(II) chloride (Scheme 6). This method represents a general and simple means of converting substituted 2,3-dihydrofurans into the corresponding furans under mild conditions. Usually, the direct oxidation of dihydrofurans requires high reaction temperatures.[3]

There are a few reports in the literature[4][5][6][7][8][9] on the Pd^{II}-catalyzed cyclization of alkynols. Thus, it is known that dihydrofurans may be formed by palladium-catalyzed cyclization of 4-alkyl-substituted alk-3-yn-1-ols by 5-*endo-dig* ring closure.[4] In contrast, bis(homo)propargylic alcohols with a terminal alkyl substituent on the C−C triple bond cyclize to dihydropyrans in a 6-*endo-dig* manner.[4] In addition, the corresponding hydroxy ketones analogous to

Scheme 5



Scheme 6



6 are obtained, and particularly in acetonitrile they become the major products.

In our case, the silyl group at the acetylenic terminus directs the nucleophilic attack of the hydroxy group to the carbon atom in the β-position to the silicon atom, leading to regioselective formation of the five-membered oxacycle. The application of this method allows the introduction of the sulfur substituent at C-4, in contrast to the situation using alkyl-substituted β-alkynols.

Similarly, γ-lactones have been obtained by the cyclization of 4-(trimethylsilyl)-substituted homopropargylic alcohols with palladium(II) acetate and copper(II) chloride in acetonitrile in a method related to the Wacker process.[10][11] In our case, an analogous process would yield a δ-lactone, but the possibility of the required 6-*endo-dig* ring closure is overruled by the directing effect of silicon.

In summary, the reaction system with palladium(II) acetate described here allows the conversion of silyl-substituted bis(homo)propargylic alcohols into the corresponding substituted 2,3-dihydrofurans in good yields. By the addition of copper(II) chloride to the reaction mixture, the corresponding substituted furans are obtained.

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Experimental Section

General: NMR: Bruker AMX − IR: Pye Unicam SP3-200. − Elemental analyses: Institut für Pharmazeutische Chemie, TU Braunschweig. − Column chromatography: Merck silica gel (70−230 mesh), petroleum ether (PE) of boiling range 60−70°C and ethyl acetate (EA) were used.

Silyl-Substituted Bis(homopropargylic) Alcohols **3a**−**j**. − *General Procedure:* A solution of 1 equiv. of 3-silyl-substituted phenyl propargyl sulfide **2** in dry THF (7 ml/mmol) was cooled to −78°C. Then, 1 equiv. of *n*-BuLi (1.6 M solution in *n*-hexane) was slowly added and the mixture was stirred for 2 h. At −78°C, 1 equiv. of epoxide **1** was added and stirring was continued at this temperature for 2 h to complete the reaction. When starting from disubstituted epoxides, the mixture was warmed to −10°C after the complete addition and then stirred for about 12 h. The cold solution was hydrolyzed by the addition of aqueous NH_4Cl and diethyl ether. After separation of the phases, the organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The resulting crude product was purified by column chromatography on silica gel.

4-Phenylthio-6-(trimethylsilyl)hex-5-yn-2-ol (**3a**): Reaction of propene oxide (**1a**) and **2a** at −78°C. Column chromatography (PE/EA, 10:1) gave 2 diastereomers (1:1*) as a clear oil (68%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.11 (s, each 9 H, $SiMe_3$, $SiMe_3$*), 1.22, 1.23 (each d, *J* = 6.2 Hz, 3 H, CH_3, CH_3*), 1.86 (m, 5 H, 3-H, 3-H*, OH), 2.15 (br. s, 1 H, OH*), 3.93 (t, *J* = 7.4 Hz, 1 H, 4-H), 4.03 (dd, *J* = 9.0 Hz, 5.6 Hz, 1 H, 4-H*), 4.12 (m, each 1 H, 2-H, 2-H*), 7.3 (m, each 3 H, arom. H, arom. H*), 7.5 (m, each 2 H, arom. H, arom. H*). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.2, −0.1 ($SiMe_3$), 23.3, 23.7 (CH_3), 36.6, 36.9 (CHSPh), 43.7, 43.9 (CH_2), 66.0, 66.1 (CHOH), 89.9, 90.0, 104.8, 105.3 (acetylenic C), 128.0, 128.2, 128.7, 128.7, 133.7, 134.0 (arom. CH), 132.8, 133.1 (arom. C). − IR (film): $\tilde{\nu}$ = 3356, 3060, 2963, 2169, 1250, 843, 759, 692 cm^{-1}. − $C_{15}H_{22}OSSi$ (278.5): calcd. C 64.69, H 7.96, S 11.51; found C 64.69, H 7.96, S 11.47.

6-(Dimethylphenylsilyl)-4-phenylthiohex-5-yn-2-ol (**3b**): Reaction of propene oxide (**1a**) and **2b** at −78°C. Column chromatography (PE/EA, 10:1) gave 2 diastereomers (1:1*) as a clear oil (78%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.30 (s, each 6 H, $SiMe_2$, $SiMe_2$*), 1.15, 1.16 (each d, *J* = 6.2 Hz, 3 H, CH_3, CH_3*), 1.82 (m, 4 H, 3-H, 3-H*), 2.00 (br. s, each 1 H, OH, OH*), 3.97−4.16 (m, each 2 H, 2-H, 4-H, 2-H*, 4-H*), 7.2−7.5 (m, each 10 H, arom. H, arom. H*). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −1.02, −0.99, −0.96, −0.03 ($SiMe_2$), 23.3, 23.7 (CH_3), 36.5, 36.7 (CHSPh), 43.5, 43.8 (CH_2), 65.8, 65.9 (CHOH), 87.5, 87.6, 106.7, 107.1 (acetylenic C), 128.7, 128.9, 129.0, 129.6, 130.3, 134.5, 134.8 (arom. CH), 133.6, 133.9, 137.6, 137.7 (arom. C). − IR (film): $\tilde{\nu}$ = 3356, 3069, 2964, 2925, 2169, 1430, 1250, 1116, 816, 733, 701 cm^{-1}. − $C_{20}H_{24}OSSi$ (340.5): calcd. C 70.54, H 7.10, S 9.41; found C 69.96, H 6.95, S 9.30.

1-Benzyloxy-4-phenylthio-6-(trimethylsilyl)hex-5-yn-2-ol (**3c**): Reaction of benzylglycidol (**1b**) and **2a** at −78°C. Column chromatography (PE/EA, 30:1) gave 2 diastereomers (1:1*) as a clear oil (70%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.11 (s, each 9 H, $SiMe_3$, $SiMe_3$*), 1.73 (ddd, *J* = 13.4 Hz, 10.8 Hz, 2.8 Hz, 1 H, CH_2*), 1.84−2.04 (m, 3 H, CH_2, CH_2*), 2.48, 2.54 (each br. s, 1 H, OH, OH*), 3.36 (dd, *J* = 10.0 Hz, 7.2 Hz, 1 H, CH_2O), 3.41 (dd, *J* = 10.0 Hz, 6.8 Hz, 1 H, CH_2O*), 3.50, 3.55 (each t, *J* = 2.8 Hz, each 1 H, CH_2O, CH_2O*), 3.97 (dd, *J* = 8.0 Hz, 6.4 Hz, 1 H, CHSPh), 4.09 (dd, *J* = 10.8 Hz, 4.6 Hz, 1 H, CHSPh*), 4.16 (m, each 1 H, CHOH, CHOH*), 4.56 (s, each 2 H, $PhCH_2$, $PhCH_2$*), 7.1−7.4 (m, each 10 H, arom. H, arom. H*). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.21, −0.15 ($SiMe_3$), 36.0, 36.1 (CHSPh), 38.4, 38.8 (CH_2), 68.0, 68.4 (CHOH), 73.3, 73.3, 73.7, 74.1 ($PhCH_2$, CH_2O), 89.3, 89.7, 104.5, 105.4 (acetylenic C), 127.8, 127.9, 128.1, 128.4, 128.6, 133.6, 134.0 (arom. CH), 132.7, 133.0, 137.7, 137.8

(arom. C). – IR (film): $\tilde{\nu}$ = 3440, 3062, 2957, 2860, 2169, 1583, 1477, 1453, 1250, 1094, 844, 745, 696 cm^{-1}. – $C_{22}H_{28}O_2SSi$ (384.6): calcd. C 68.70, H 7.34, S 8.33; found C 68.70, H 7.36, S 8.24.

1-Benzyloxy-6-(dimethylphenylsilyl)-4-phenylthiohex-5-yn-2-ol (**3d**): Reaction of benzylglycidol (**1b**) and **2b** at −78°C. Column chromatography (PE/EA, 10:1) gave 2 diastereomers (1:1*) as a clear oil (71%). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.36 (s, each 6 H, $SiMe_2$, $SiMe_2$*), 1.70−2.08 (m, each 2 H, CH_2, CH_2*), 2.47 (br. s, each 1 H, OH, OH*), 3.32−3.56 (m, each 2 H, CH_2O, CH_2O*), 4.05 (dd, *J* = 8.5 Hz, 6.2 Hz, 1 H, CHSPh), 4.15 (dd, *J* = 10.7 Hz, 4.5 Hz, 1 H, CHSPh*), 4.16 (m, each 1 H, CHOH, CHOH*), 4.54 (s, each 2 H, $PhCH_2$, $PhCH_2$*), 7.25−7.4 and 7.5−7.55 (m, each 15 H, arom. H, arom. H*). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.97, −0.92 ($SiMe_2$), 36.0, 36.1 (CHSPh), 38.3, 38.8 (CH_2), 67.8, 68.4 (CHOH), 73.3, 73.3, 73.7, 74.1 ($PhCH_2$, CH_2O), 87.1, 87.5, 106.5, 107.3 (acetylenic C), 127.7, 127.8, 127.9, 128.1, 128.4, 128.5, 128.7, 129.3, 133.6, 134.0 (arom. CH), 132.7, 133.0, 136.7, 136.8, 137.7, 137.8 (arom. C). – IR (film): $\tilde{\nu}$ = 3447, 3065, 2956, 2861, 2170, 1250, 1116, 1096, 838, 817, 735, 698 cm^{-1}. – $C_{27}H_{30}O_2SSi$ (446.7): calcd. C 72.60, H 6.77, S 7.18; found C 72.32, H 7.01, S 7.27.

4,6-Dimethyl-3-phenylthio-1-(trimethylsilyl)non-1-yn-5-ol (**3e**): Reaction of 2,3-epoxy-4-methylheptane (**1c**) (2 diastereomers, 3:1) and **2a** at −78°C to −10°C. Column chromatography (PE/EA, 20:1) gave 4 diastereomers (2.9:2.3:1.3:1) as an oil (51%). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.13, 0.14 (each s, 18 H, $SiMe_3$), 0.77−0.95 (m, each 6 H, 9-H, 6-CH_3), 1.01−1.13 (m, each 3 H, 4-CH_3), 1.21−1.48 (m, each 4 H, CH_2), 1.53−1.74 (m, each 2 H, 6-H, OH), 1.85−2.15 (m, each 1 H, 4-H), 3.30, 3.37, 3.50, 3.59 (each m, 1 H, CHOH), 4.31, 4.34, 4.43, 4.48 (each d, *J* = 3.2 Hz, 1 H, CHSPh), 7.25−7.35 (m, each 5 H, arom. H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.24, −0.21, −0.08, −0.06 ($SiMe_3$), 11.8, 11.9, 12.3, 12.3, 14.2, 14.3 (C-9, 6-CH_3, 4-CH_3), 20.3, 20.4 (C-7), 34.1, 34.6 (C-6), 36.6, 36.6 (C-8), 39.9, 40.4 (C-4), 42.1, 42.3 (CHSPh), 76.1, 77.2, 77.9, 78.8 (CHOH), 82.2, 82.8, 83.2, 84.5, 102.4, 102.4, 103.2, 103.4 (acetylenic C), 127.1, 127.2, 127.4, 128.7, 128.8, 128.9, 129.0, 132.0, 132.2, 132.6, 132.7 (arom. CH), 134.7, 134.7, 134.8, 134.8 (arom. C). – IR (film): $\tilde{\nu}$ = 3449, 3060, 2960, 2930, 2170, 1583, 1478, 1439, 1250, 844, 750, 691 cm^{-1}.

4,6-Dimethyl-1-(dimethylphenylsilyl)-3-phenylthionon-1-yn-5-ol (**3f**): Reaction of 2,3-epoxy-4-methylheptane (**1c**) (2 diastereomers, 3:1) and **2b** at −78°C to −10°C. Column chromatography (PE/EA, 20:1) gave 4 diastereomers (3:2.6:1.1:1) as an oil (57%). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.37, 0.38 (each s, each 12 H, $SiMe_2$), 0.78−0.97 (m, each 6 H, 9-H, 6-CH_3), 1.00−1.17 (m, each 3 H, 4-CH_3), 1.20−1.43 (m, each 4 H, CH_2), 1.55−1.79 (m, each 2 H, 6-H, OH), 1.97, 2.02, 2.15, 2.20 (each br. dq, *J* = 6.8 Hz, 3.2 Hz, 1 H, 4-H), 3.42 (dd, *J* = 8.8 Hz, 2.8 Hz, 1 H, CHOH), 3.54 (dd, *J* = 9.6 Hz, 1.6 Hz, 1 H, CHOH), 3.65 (dd, *J* = 9.2 Hz, 2.0 Hz, 1 H, CHOH), 3.76 (dd, *J* = 9.6 Hz, 1.6 Hz, 1 H, CHOH), 4.42, 4.45, 4.52, 4.58 (each d, *J* = 3.2 Hz, 1 H, CHSPh), 7.1−7.6 (m, each 10 H, arom. H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.8 ($SiMe_2$), 11.8, 11.8, 12.0, 12.3, 13.1, 13.3, 13.7, 14.2, 14.2, 14.3, 14.3, 14.4 (C-9, 6-CH_3, 4-CH_3), 20.3, 20.4, 20.5, 20.5 (C-7), 34.0, 34.1, 34.4, 34.5 (C-6), 36.1, 36.6, 36.6, 36.8 (C-8), 40.1, 40.5, 41.2, 41.5 (C-4), 42.1, 42.3, 43.7, 43.8 (CHSPh), 74.7, 75.9, 77.4, 78.7 (CHOH), 87.1, 87.1, 88.6, 88.9, 105.2, 105.4, 107.8, 107.9 (acetylenic C), 127.2, 127.3, 127.4, 127.8, 128.8, 129.2, 129.3, 131.9, 132.1, 132.4, 132.5, 133.5, 133.6 (arom. CH), 134.6, 134.6, 134.7, 134.7, 136.9, 137.0, 137.0, 137.0 (arom. C). – IR (film): $\tilde{\nu}$ = 3483, 3069, 2960, 2931, 2168, 1584, 1480, 1430, 1250, 1115, 838, 816, 733, 701 cm^{-1}. – $C_{25}H_{34}OSSi$ (410.7): calcd. C 73.11, H 8.34, S 7.80; found C 73.13, H 8.35, S 8.30.

2-(1-Phenylthio-3-trimethylsilyl-2-propynyl)cyclohexanol (**3g**): Reaction of cyclohexene oxide (**1d**) and **2a** at −78°C to −10°C. Column chromatography (PE/EA, 30:1) gave 2 diastereomers (2.5:1*) as a yellow oil (60%). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.08*, 0.09 (each s, 9 H, $SiMe_3$, $SiMe_3$*), 1.1−1.3, 1.6−1.75, 1.9−2.05 (m, each 10 H, CH_2, CH_2*, CH, CH*, OH, OH*), 3.54 (td, *J* = 9.6 Hz, 4.8 Hz, 1 H, CHOH), 3.75 (td, *J* = 10.0 Hz, 4.4 Hz, 1 H, CHOH*), 4.17 (d, *J* = 3.6 Hz, 1 H, CHSPh*), 4.46 (d, *J* = 3.2 Hz, 1 H, CHSPh), 7.2−7.5 (m, each 5 H, arom. H, arom. H*). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.06, −0.14* ($SiMe_3$), 24.2*, 24.7, 25.1, 25.5*, 26.0, 28.1*, 35.1*, 35.7 (CH_2), 41.5, 43.0*, 48.7, 49.0* (CH, CHSPh), 71.4*, 72.0 (CHOH), 90.2*, 90.6, 103.2, 104.9* (acetylenic C), 127.2, 127.5*, 128.7, 128.8*, 132.1, 132.7* (arom. CH), 134.5*, 134.7 (arom. C). – IR (film): $\tilde{\nu}$ = 3383, 3059, 2932, 2858, 2167, 1583, 1479, 1449, 1250, 1048, 845, 757, 692 cm^{-1}. – $C_{18}H_{26}OSSi$ (318.5): calcd. C 67.87, H 8.22, S 10.06; found C 67.82, H 8.31, S 10.67.

2-(3-Dimethylphenylsilyl-1-phenylthio-2-propynyl)cyclohexanol (**3h**): Reaction of cyclohexene oxide (**1d**) and **2b** at −78°C to −10°C. Column chromatography (PE/EA, 15:1) gave 2 diastereomers (4.4:1*) as a yellow oil (70%). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.37 (s, each 6 H, $SiMe_2$, $SiMe_2$*), 1.2−1.35, 1.65−1.80, 1.95−2.10 (m, each 10 H, CH_2, CH_2*, CH, CH*, OH, OH*), 3.60, 3.82* (each dt, *J* = 10.0 Hz, 4.8 Hz, 1 H, CHOH, CHOH*), 4.31*, 4.57 (each d, *J* = 3.2 Hz, 1 H, CHSPh, CHSPh*), 7.2−7.5 (m, each 10 H, arom. H, arom. H*). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.77, −0.87* ($SiMe_2$), 24.3*, 24.6*, 24.7, 25.2, 25.5*, 26.2, 35.2*, 35.8 (CH_2), 41.5, 42.9*, 48.8, 49.2* (CH, CHSPh), 72.0*, 72.1 (CHOH), 87.9*, 88.5, 105.2, 106.8* (acetylenic C), 127.3, 127.5*, 127.8, 127.9*, 128.8, 128.9*, 129.3, 129.6*, 132.1, 132.6*, 133.6, 133.8* (arom. CH), 134.6*, 134.7, 137.0*, 137.1 (arom. C). – IR (film): $\tilde{\nu}$ = 3386, 3068, 2932, 2858, 2166, 1481, 1430, 1250, 1115, 1046, 837, 816, 733, 700 cm^{-1}. – $C_{23}H_{28}OSSi$ (380.6): calcd. C 72.58, H 7.41, S 8.42; found C 72.07, H 7.50, S 8.81.

3-(Dimethylphenylsilyl)-4-phenylthio-6-(trimethylsilyl)hex-5-yn-2-ol (**3i**): Reaction of 1-(dimethylphenylsilyl)-1,2-epoxypropane (**1e**) (2 diastereomers, 3:1) and **2a** at −78°C in the presence of $BF_3 \cdot OEt_2$. Column chromatography (PE/EA, 15:1) gave 2 diastereomers (1:1*) as an oil (41%). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.09, 0.16 (each s, 9 H, $SiMe_3$, $SiMe_3$*), 0.43, 0.44, 0.54, 0.57 (each s, 3 H, $SiMe_2$, $SiMe_2$*), 1.21, 1.36 (each d, *J* = 6.4 Hz, 3 H, CH_3, CH_3*), 1.56 (dd, *J* = 7.2 Hz, 1.8 Hz, 1 H, CHSi), 1.70 (dd, *J* = 7.2 Hz, 3.6 Hz, 1 H, CHSi*), 2.6, 2.9 (each br. s, 1 H, OH, OH*), 4.13 (d, *J* = 1.8 Hz, 1 H, CHSPh), 4.26 (d, *J* = 3.6 Hz, 1 H, CHSPh*), 4.22, 4.37 (each m, 1 H, CHOH, CHOH*), 7.1−7.5 (m, each 10 H, arom. H, arom. H*). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −2.9, −2.0, −1.6, −0.9 ($SiMe_2$), −0.4, −0.3 ($SiMe_3$), 23.8, 24.1 (CH_3), 39.2, 39.9, 40.4, 40.9 (CHSi, CHSPh), 68.5, 68.6 (CHOH), 90.8, 91.8, 104.8, 107.1 (acetylenic C), 127.6, 127.7, 127.8, 127.9, 128.7, 128.9, 129.0, 129.2, 132.7, 132.8, 133.8, 134.1 (arom. CH); 134.6, 134.7, 137.8, 138.7 (arom. C). – IR (film): $\tilde{\nu}$ = 3448, 3069, 2961, 2169, 1583, 1479, 1438, 1250, 1113, 843, 737, 701 cm^{-1}. – $C_{23}H_{32}OSSi_2$ (412.7): calcd. C 66.93, H 7.81, S 7.77; found C 66.92, H 7.85, S 7.77.

3,6-Bis(dimethylphenylsilyl)-4-phenylthiohex-5-yn-2-ol (**3j**): Reaction of 1-(dimethylphenylsilyl)-1,2-epoxypropane (**1e**) (2 diastereomers, 3:1) and **2b** at −78°C in the presence of $BF_3 \cdot OEt_2$. Column chromatography (PE/EA, 15:1) gave 2 diastereomers (1:1*) as an oil (64%). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35,

0.41 (each s, 6 H, $SiMe_2$, $SiMe_2$*), 0.44, 0.45, 0.51, 0.54 (each s, 3 H, $SiMe_2$, $SiMe_2$*), 1.22, 1.35 (each d, J = 6.4 Hz, 3 H, CH_3, CH_3*), 1.61 (dd, J = 7.2 Hz, 2.0 Hz, 1 H, CHSi), 1.74* (dd, J = 7.2 Hz, 3.6 Hz, 1 H, CHSi*), 2.50, 2.90 (each br. s, 1 H, OH, OH*), 4.21 (d, J = 2.0 Hz, 1 H, CHSPh), 4.35* (d, J = 3.6 Hz, 1 H, CHSPh*), 4.24, 4.40 (each m, 1 H, CHOH, CHOH*), 7.1−7.4 (m, each 15 H, arom. H, arom. H*). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −2.8, −1.9, −1.7, −1.2, −1.1, −1.09, −1.06, −0.8 ($SiMe_2$), 23.8, 24.1 (CH_3), 39.1, 40.0, 40.5, 40.8 (CHSi, CHSPh), 68.4, 68.5 (CHOH), 88.6, 89.7, 106.7, 108.9 (acetylenic C), 127.6, 127.7, 127.8, 127.8, 127.8, 127.9, 128.7, 128.8, 129.0, 129.2, 129.4, 129.5, 132.5, 132.7, 133.6, 133.7, 134.1 (arom. CH); 134.5, 134.7, 136.3, 136.4, 137.7, 138.5 (arom. C). − IR (film): $\tilde{\nu}$ = 3406, 3069, 2960, 2166, 1583, 1251, 1116, 820, 736, 700 cm^{-1}. − $C_{28}H_{34}OSSi_2$ (474.8): calcd. C 70.83, H 7.22, S 6.75; found C 69.82, H 7.31, S 7.72.

6-(Dimethylphenylsilyl)hex-3-en-5-yn-2-ol (**4**): Reaction of 1-(dimethylphenylsilyl)-1,2-epoxypropane (**1e**) (2 diastereomers, 3:1) and **2b** at −78°C to −10°C. Column chromatography (PE/EA, 9:1) gave 2 diastereomers (*E*/*Z**, 3:1*) as an oil (47%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.31, 0.32* (each s, 6 H, $SiMe_2$, $SiMe_2$*), 1.14, 1.17* (each d, J = 6.4 Hz, 3 H, CH_3, CH_3*), 1.70 (br. s, each 1 H, OH, OH*), 4.20 (dq, J = 6.4 Hz, 1.6 Hz, 1 H, CHOH), 4.73 (m, 1 H, CHOH*), 5.42 (dd, J = 11.0 Hz, 1.0 Hz, 1 H, 4-H*), 5.62 (dd, J = 16.0 Hz, 1.6 Hz, 1 H, 4-H), 5.86 (dd, J = 11.0 Hz, 8.0 Hz, 1 H, 3-H*), 6.14 (dd, J = 16.0 Hz, 6.4 Hz, 1 H, 3-H), 7.2−7.55 (m, each 5 H, arom. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.99*, −0.96 ($SiMe_2$), 22.3*, 22.8 (CH_3), 66.4*, 68.0 (CHOH), 93.0, 98.6*, 102.2*, 104.6 (acetylenic C), 108.9, 133.0*, 148.1*, 148.2 (C=C), 127.8, 127.9*, 129.4, 129.5*, 133.5*, 133.6 (arom. CH), 136.6*, 136.8 (arom. C). − IR (film): $\tilde{\nu}$ = 3356, 3069, 2964, 2145, 1428, 1250, 1116, 1062, 817, 780, 731, 700 cm^{-1}; no elemental analyses of **4** could be obtained because of its tendency to decompose.

Cyclization of γ-Hydroxyalkynes **3**. − *General Procedure:* To a solution of alkynol **3** (1 mmol) in CH_3CN (3 ml/mmol) were added 0.05−0.1 equiv. of $Pd(OAc)_2$ and one drop of conc. HCl. The mixture was stirred at room temperature under air for 2−10 h, depending on the substrate. For the preparation of furans, an additional 0.25 equiv. of $CuCl_2$ was added. When the reaction was complete, the mixture was diluted with $CHCl_3$, washed with water, and dried (Na_2SO_4). Then the solvent was evaporated under reduced pressure. The residue was purified by chromatography on a silica gel column.

2,5-Dimethyl-4-phenylthio-2,3-dihydrofuran (**5a**): Column chromatography (PE) gave a colorless liquid (56%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32 (d, J = 6.2 Hz, 3 H, 2-CH_3), 1.88 (t, J = 2.0 Hz, 3 H, 5-CH_3), 2.25 (ddq, J = 14.0 Hz, 7.6 Hz, 2.0 Hz, 1 H, 3-H), 2.79 (ddq, J = 14.0 Hz, 9.8 Hz, 2.0 Hz, 1 H, 3-H), 4.68 (ddq, J = 9.8 Hz, 7.6 Hz, 6.2 Hz, 1 H, CHO), 7.1−7.3 (m, 5 H, arom. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.3 (5-*C*H_3), 22.0 (2-*C*H_3), 40.7 (CH_2), 77.3 (CHO), 95.3 (=CSPh), 125.0, 126.1, 128.8 (arom. CH), 137.4 (arom. C), 161.5 (=CO). − IR (film): $\tilde{\nu}$ = 3070, 2972, 2922, 2858, 1649, 1583, 1477, 1439, 1377, 1224, 1024, 956, 739, 691 cm^{-1}. − MS; *m*/*z* (%): 206 (100) [M$^+$], 129 (46) [M$^+$ − Ph], 109 (15) [SPh], 77 (20) [Ph]. − $C_{12}H_{14}OS$ (206.3): calcd. C 69.86, H 6.84, S 15.54; found C 69.57, H 6.84, S 15.03. (*S*)-**5a**: $[\alpha]_D^{24}$ = −56.4 (*c* = 0.7 in $CHCl_3$).

2-Benzyloxymethyl-5-methyl-4-phenylthio-2,3-dihydrofuran (**5b**): Column chromatography (PE/EA, 40:1) gave a colorless oil (51%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, CH_3), 2.45 (dd, J = 14.4 Hz, 8.0 Hz, 1 H, 3-H), 2.70 (dd, J = 14.4 Hz, 10.8 Hz, 1 H, 3-H), 3.48 (dd, J = 10.4 Hz, 4.0 Hz, 1 H, CH_2O), 3.55 (dd, J = 10.4 Hz, 6.0 Hz, 1 H, CH_2O), 4.53 (s, 2 H, $PhCH_2$), 4.73 (m, 1 H, CHO), 7.0−7.3 (m, 10 H, arom. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.3 (CH_3), 35.7 (CH_2-ring), 72.2, 73.4 (CH_2O, $PhCH_2$), 79.4 (CHO), 95.7 (=CSPh), 125.0, 126.2, 127.7, 127.7, 128.4, 128.8 (arom. CH), 137.1, 137.9 (arom. C), 161.7 (=CO). − IR (film): $\tilde{\nu}$ = 3061, 3030, 2920, 2859, 1652, 1582, 1477, 1380, 1222, 1119, 740, 695 cm^{-1}. − $C_{19}H_{20}O_2S$ (312.4): calcd. C 73.04, H 6.45, S 10.26; found C 72.47, H 6.49, S 10.02.

3,5-Dimethyl-2-sec-pentyl-4-phenylthio-2,3-dihydrofuran (**5c**): Column chromatography (PE) gave 2 diastereomers (2.4:1*) as a colorless oil (54%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (each t, J = 6.8 Hz, 3 H, CH_3-chain), 0.89 (d, J = 6.8 Hz, each 3 H, CH_3-chain), 1.01 (d, J = 7.0 Hz, each 3 H, 3-CH_3), 1.1−1.5 (m, each 4 H, CH_2), 1.7 (m, each 1 H, CH-chain), 1.91 (d, J = 1.6 Hz, each 3 H, 5-CH_3), 2.68 (br. q, J = 7.0 Hz, 1 H, 3-H), 3.97 (dd, J = 7.0 Hz, 5.2 Hz, each 1 H, CHO), 7.1−7.2 (m, each 5 H, arom. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.5, 12.5* (5-*C*H_3), 14.2, 14.2*, 14.3, 14.3* (CH_3-chain), 20.1, 20.2* (CH_2), 20.2, 20.3* (3-*C*H_3), 34.0*, 34.3 (CH_2), 37.3, 37.3* (CH-chain), 41.5*, 42.1 (C-3), 92.7, 92.8* (CHO), 101.2, 101.2* (=CSPh), 124.9, 124.9*, 126.3, 126.3*, 128.7, 128.7* (arom. CH), 137.8, 137.8* (arom. C), 162.1, 162.1* (=CO). − IR (film): $\tilde{\nu}$ = 3069, 2960, 2925, 2872, 1650, 1582, 1476, 1380, 1226, 999, 739, 692 cm^{-1}. − $C_{17}H_{24}OS$ (276.4): calcd. C 73.86, H 8.75, S 11.59; found C 74.24, H 8.79, S 11.37.

2-Methyl-3-phenylthio-3a,4,5,6,7,7a-hexahydrobenzofuran (**5d**): Column chromatography (PE) gave an oil (1%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.1−1.3, 1.4−1.8 (m, 8 H, CH_2), 2.12 (s, 3 H, CH_3), 2.75 (m, 1 H, CH), 4.01 (m, 1 H, CHO), 7.2 (m, 5 H, arom. H). − IR (film): $\tilde{\nu}$ = 1655 cm^{-1}.

5-Hydroxy-3-phenylthiohexan-2-one (**6a**): Column chromatography (PE/EA, 10:1) gave 2 diastereomers (1:1*) as a colorless oil (18%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.22, 1.26 (each d, J = 6.2 Hz, 3 H, CH_3, CH_3*), 1.80 (m, each 3 H, CH_2, CH_2*, OH, OH*), 2.24, 2.25 (each s, 3 H, 1-H, 1-H*), 3.80 (dd, J = 7.6 Hz, 6.6 Hz, 1 H, CHSPh), 3.87* (dd, J = 9.6 Hz, 4.8 Hz, 1 H, CHSPh*), 4.06 (m, each 1 H, CHOH, CHOH*), 7.2−7.4 (m, each 5 H, arom. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.9, 24.1, 25.8, 26.1 (CH_3), 39.5, 39.6 (CH_2), 53.7, 54.6 (CHSPh), 65.6, 65.9 (CHOH), 128.1, 128.2, 128.9, 129.0, 131.3, 131.4 (arom. CH), 132.8, 132.9 (arom. C), 205.2, 205.3 (C=O). − IR (film): $\tilde{\nu}$ = 3406, 3059, 2970, 2928, 1707, 1584, 1480, 1439, 1377, 1090, 742, 692 cm^{-1}.

6-Benzyloxy-5-hydroxy-3-phenylthiohexan-2-one (**6b**): Column chromatography (PE/EA, 20:1) gave 2 diastereomers (1:1*) as a yellow oil (21%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.95 (m, each 2 H, CH_2, CH_2*), 2.29, 2.30* (each s, 3 H, CH_3, CH_3*), 2.45 (br. s, each 1 H, OH, OH*), 3.3−3.5 (m, each 2 H, CH_2O, CH_2O*), 3.95 (m, each 1 H, CHSPh, CHSPh*), 4.30 (m, each 1 H, CHOH, CHOH*), 4.52, 4.55 (each br. d, J = 12.0 Hz, each 1 H, $PhCH_2$, $PhCH_2$*), 7.2−7.5 (m, each 10 H, arom. H). − IR (film): $\tilde{\nu}$ = 3425, 3061, 3031, 2924, 2861, 1707, 1583, 1478, 1440, 1358, 1100, 742, 697 cm^{-1}.

5-Hydroxy-4,6-dimethyl-3-phenylthiononan-2-one (**6c**): Column chromatography (PE/EA, 10:1) gave 4 diastereomers as an oil (15%). − IR (film): $\tilde{\nu}$ = 3400, 3061, 2961, 2930, 2873, 1719, 1445, 1383, 1085, 747, 695 cm^{-1}.

1-(2-Hydroxycyclohexyl)-1-phenylthiopropan-2-one (**6d**): Column chromatography (PE/EA, 8:1) gave 2 diastereomers (2.5:1*) as an oil (26%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.1−1.3, 1.6−1.8, 1.9−2.1 (m, each 10 H, CH_2, CH_2*, CH, CH*, OH, OH*), 2.24,

2.27* (each s, 3 H, CH_3, CH_3*), 3.55 (m, each 1 H, CHOH, CHOH*), 4.01* (d, J = 4.0 Hz, 1 H, CHSPh*), 4.03 (d, J = 6.4 Hz, 1 H, CHSPh), 7.3 (m, each 5 H, arom. H). − IR (film): $\tilde{\nu}$ = 3422, 3058, 2931, 2858, 1702, 1582, 1442, 1353, 1045, 741, 696 cm^{-1}.

2,5-Dimethyl-3-phenylthiofuran (**7**): Column chromatography (PE) gave a colorless liquid, which was kept in the cold. − ^1H NMR (200 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 5.94 (s, 1 H, 4-H), 7.1−7.3 (m, 5 H, arom. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.7 (CH_3), 13.5 (CH_3), 107.7 (=CSPh), 110.9 (C-4), 124.9, 126.0, 128.8 (arom. CH), 138.3 (arom. C), 150.7, 155.0 (=CO). − IR (film): $\tilde{\nu}$ = 3059, 2920, 1583, 1478, 1439, 1224, 1068, 738, 689 cm^{-1}. − MS; *m/z* (%): 204 (100) [M^+], 109 (6) [SPh], 77 (10) [Ph]. − $C_{12}H_{12}OS$ (204.3): calcd. C 70.55, H 5.92, S 15.69; found C 70.54, H 5.73, S 15.36.

3-Phenylthio-1-(trimethylsilyl)hex-4-en-1-yne (**8**): Column chromatography (PE) gave 1 diastereomer (*trans*) as a colorless oil. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.13 (s, 9 H, $SiMe_3$), 1.67 (dt, J = 6.2 Hz, 1.0 Hz, 3 H, CH_3), 4.36 (dq, J = 6.2 Hz, 1.0 Hz, 1 H, CHSPh), 5.49 (ddq, J = 14.8 Hz, 6.2 Hz, 1.0 Hz, 1 H, 4-H), 5.67 (dq, J = 14.8 Hz, 6.2 Hz, 1 H, 5-H), 7.3−7.5 (m, 5 H, arom. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.8 ($SiMe_3$), 17.5 (CH_3), 41.7 (CHSPh), 90.9, 102.9 (acetylenic C), 128.1, 134.4 (C=C), 127.7, 129.2, 132.9 (arom. CH), 139.8 (arom. C). − IR (film): $\tilde{\nu}$ = 3023, 2959, 2168, 1428, 1252, 1119, 1066, 843, 793, 700 cm^{-1}; no elemental analysis of **8** could be obtained because of its tendency to decompose.

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