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On the Chemoselectivity of Formation of 2-(α-Hydroxyalkyl)-2,5-Dihydrofurans from Allenic Diols

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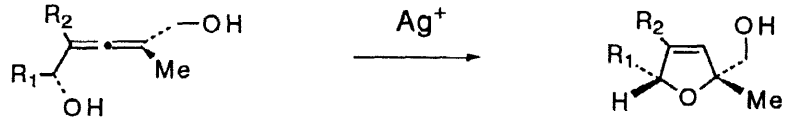
Abstract: The Ag(I)-promoted cyclization of 2,5-pentadiene-1,5-diols containing both a tertiary and a secondary or primary hydroxyl group, has been examined. In general, the reaction displays a preference for cyclization through the more hindered tertiary hydroxyl group, sometimes to the exclusion of alternative pathways involving secondary or primary carbinol centers.

INTRODUCTION

The 5-*endo* cyclization of α-allenic alcohols affords 2,5-dihydrofurans which are themselves useful synthetic intermediates[1] and structural elements in natural products.[2] This transformation can be effected under basic conditions[3] or, more generally, with transition metal salts acting as Lewis acid promoters.[1a,b,4] Among the latter, the Ag(I)-promoted[1a,b,4a-d] cycloisomerization of α-allenols has proven particularly useful. This reaction utilizes mild reaction conditions and provides high yields of dihydrofurans in a stereospecific manner. The synthesis of 2-(α-hydroxyalkyl)-2,5-dihydrofurans has been possible using this method by cyclization of α,α'-allenic diols where one of the two hydroxyl groups was conveniently protected.[1a] In two isolated cases the cyclization was effected directly from the fully unprotected diols resulting in the observation of a remarkable preference for cyclization of secondary over primary hydroxyl groups, in spite of the former being more hindered (Scheme 1).



R_1, R_2 = $(CH_2)_4$

R_1 = R_2 = Me

Scheme 1

The allenic diols used for these transformations had been synthesized by organocuprate S_N2' displacements on alkynyloxiranes bearing a propargylic hydroxyl group.[1a] More recently, these type of compounds has been prepared by SmI_2-mediated coupling between alkynyloxiranes and ketones.[5] Since a number of diols with different combinations of primary, secondary and tertiary hydroxyl groups was available, it was considered interesting to check the generality of the aforementioned preference and to try to rationalize the factors leading to the observed chemoselectivity. Additionally, the overall conversion depicted in Scheme 2 would allow the two-step synthesis of 2-(α-hydroxyalkyl)-2,5-dihydrofurans **2, 3** from readily available alkynyloxiranes and ketones without any need for additional protection-deprotection steps.

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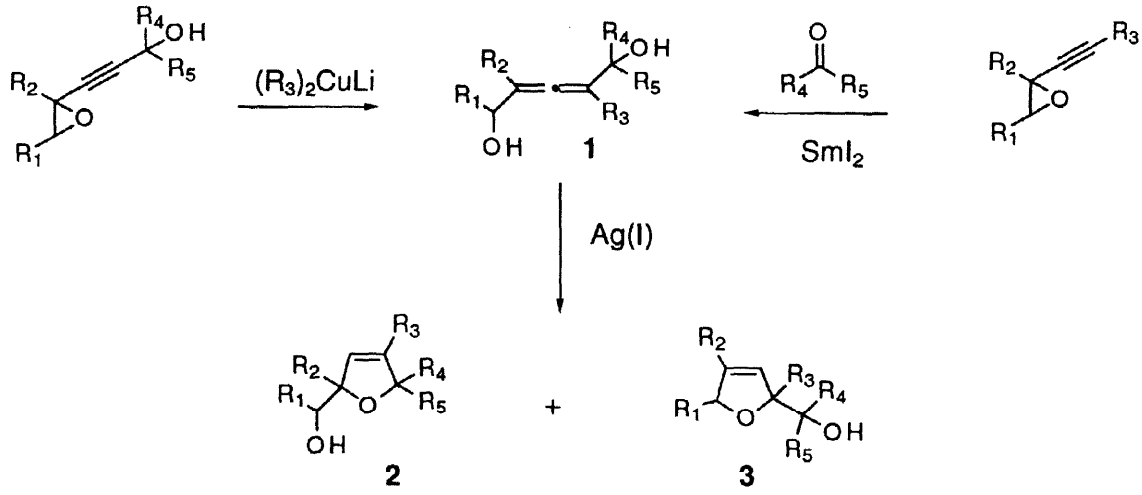
RESULTS AND DISCUSSION

Allenic diols **1** (prepared from alkynyloxiranes and ketones by SmI_2-mediated coupling[5]) were treated with $AgNO_3$ and $CaCO_3$ in acetone/H_2O[1a] or simply with $AgNO_3$/acetone[4d] to provide in all cases high yields of dihydrofurans products **2, 3** (Table). As previously noted,[4d] reactions run in the absence of $CaCO_3$ and H_2O afforded in general better yields. The diastereomeric ratios of the starting diols **1** were maintained in the dihydrofuran products, evidencing the stereospecifity of the reaction.[1a,b,4b-d] For dihydrofurans **2a-d** the stereochemical assignments were confirmed by NOE experiments performed on the separated isomers. Thus, a NOE between the carbinol proton and the heterocyclic C_3-H was found for the minor (*syn*) isomer of **2a-c**, whereas the corresponding major isomers (*anti*) and the single isomer **2d** showed none.



Scheme 2

For all the cyclic substrates **1a-d** cyclization took place preferentially through the more hindered tertiary hydroxyl group of **1**. This is in line with the preference for cyclization of secondary over primary hydroxyl groups previously reported.[1a] Furthermore, our results suggest that the origin of these preferences probably lies in the selective formation of the Ag(I)-allene complex that better accommodates both a positive charge and the steric requirements of the allene terminus. Thus, for substrates **1a-c** the greater steric bulk of the tertiary carbinol moiety is reinforced by the better stabilization of positive charge provided by a more substituted allene terminus leading in these cases to the exclusive formation of dihydrofurans **2a-c**. Diol **1d**, on the other hand, affords a mixture of **2d** and **3d** where the former still predominates, indicating that when both allene termini are equally substituted, complexation at the less congested site is the dominant factor controlling selectivity.[1a]

With the acyclic diols **1e** and **1f** the same trends were observed. The cyclization of **1e** afforded exclusively the dihydrofuran **2e**, the result of a remarkable preference for cyclization of a tertiary hydroxyl group over a primary one. On the other hand, diol **1f** gave a mixture of **2f** and **3f** with the former greatly predominating. Dihydrofuran **3f** proved to be unstable, undergoing oxidation to the corresponding furan **4**, that was also unstable.[6]

The silyl-protected allenes **1g** were unusual in that they displayed a divergent behaviour in their cyclizations. Both diastereomers cyclized quantitatively but with little selectivity (see Table). Diol ***anti*-1g** produced a 1.85:1 mixture of the corresponding **2g** and **3g** whereas ***syn*-1g** approximately reversed this ratio

(1:2.3). It is likely that the steric bulk of the silyl protecting group tends to equalize the steric requirements around the allene termini in **1g**. As a result, reactions are rather unselective and increasing amounts of dihydrofurans **3** are observed.

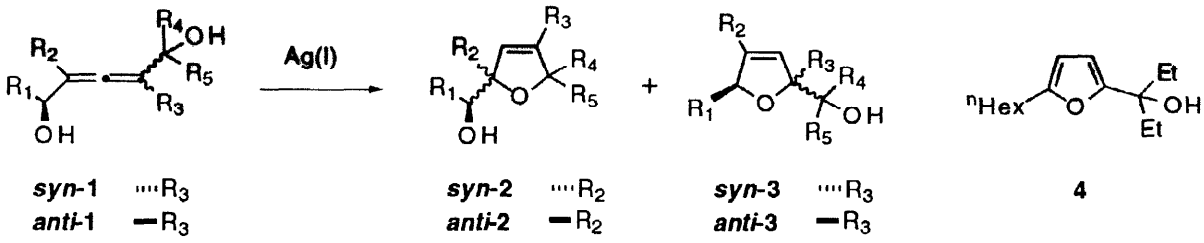


Table. Ag(I)-Promoted Cyclization of Allenic Diols.

Diol	R_1	R_2	R_3	R_4	R_5	*anti*-1/ *syn*-1	*anti*-2/ *syn*-2	2/3	Yield (%)
1a	$(CH_2)_4$		H	$(CH_2)_5$		4.8/1	4.6/1	1/0	73[a]
1b	$(CH_2)_4$		H	Me	Me	2.2/1	2.4/1	1/0	70[a]
1c	$(CH_2)_4$		H	Et	Et	6.7/1	7.3/1	1/0	93[b]
1d	$(CH_2)_4$		Me	$(CH_2)_5$		1/0	1/0	3.7/1	70[a]
1e	H	^{n}Hex	$(CH_2)_2OY$[c]	$(CH_2)_5$		-	-	1/0	83[b]
1f	^{n}Hex	H	H	Et	Et	1/1	1/1.1	6.7/1[d]	97[b]
***anti*-1g**	CH_2OY[c]	Me	Me	$(CH_2)_5$		1/0	1/0	1.85/1	100[b]
***syn*-1g**	CH_2OY[c]	Me	Me	$(CH_2)_5$		0/1	0/1	1/2.3	100[b]

[a] Reaction run with $AgNO_3/CaCO_3/Me_2CO/H_2O$. Reaction run with $AgNO_3/Me_2CO$. [c] Y = $SiPh_2{}^tBu$. [d] Ratio **2f/3h + 4**.

In summary, the silver(I)-promoted cyclization of α,α'-allenic diols **1** containing tertiary and secondary or primary hydroxyl groups shows a preference for formation of products through the more hindered tertiary hydroxyl group. This selectivity appears to be born out of both steric and electronic effects with the former being the dominant factor.

Experimental.

General. Flash column chromatography[7] was performed on silica gel (230-400 mesh). HPLC purifications were carried out with either LiChrosorb Si60 (7μm, 25 x 2.5 cm) (column 1) or μPorasil (10μm, 19 x 1.5 cm) (column 2) columns. ^1H and ^{13}C RMN spectra were obtained in $CDCl_3$ at 250 MHz and 62.9 MHz, respectively. IR data include only characteristic absorptions. Mass spectra were obtained at 70 eV.

All the allenic diol substrates **1** were prepared by SmI_2-promoted coupling between appropriate alkynyloxiranes and ketones.[5] Experimental procedures for Ag(I)-promoted cyclizations of allenic alcohols have been previously reported.[1a,4d]

1-Hydroxy-7-oxadispiro[5.1.5.2]pentadec-14-ene (2a). The crude product was purified by flash chromatography (10% EtOAc in hexanes) to afford in order of elution the *syn* - and *anti* -isomers of **2a**. Data for the *syn*-isomer: ^1H NMR δ 1.2-1.8 (m, 18H), 2.01 (d, *J* = 7.0 Hz, 1H, O*H*), 3.3-3.4 (m, 1H, C*H*-OH), 5.68 (d, *J* = 6.1 Hz, 1H, H-15), 5.91 (d, *J* = 6.0 Hz, 1H, H-14); ^{13}C NMR δ 22.2, 22.8, 23.3, 23.3, 25.4,

31.0, 36.6, 38.6, 39.4, 72.5, 89.0, 90.9, 130.4, 134.2; IR (neat) υ 3580, 3450, 1450 cm^{-1}; HRMS calcd for $C_{14}H_{22}O_2$ 222.16198, found 222.15930. Data for the *anti*-isomer: m.p. 70-71°C; ^1H NMR δ 1.3-1.7 (m, 17H), 2.0 (m, 1H), 2.09 (d, J = 2.2 Hz, 1H, O*H*), 3.5 (m, 1H, C*H*-OH), 5.93 (d, J = 6.22 Hz, 1H, H-15), 6.06 (d, J = 6.22 Hz, 1H, H-14); ^{13}C NMR δ 23.4, 23.8, 23.9, 25.3, 31.3, 38.5, 38.9, 39.5, 74.4, 88.4, 93.3, 126.8, 135.4; IR ($CHCl_3$) υ 3450, 1455 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.62; H, 9.98. Found: C, 75.46; H, 9.91.

6-Hydroxy-2,2-dimethyl-1-oxaspiro[4.5]dec-3-ene (2b). Flash chromatography (10% EtOAc in hexanes) yielded in order of elution the *syn*- and *anti*-isomers of **2b**. Data for the *syn*-isomer: mp 44-45°C; ^1H NMR δ 1.2-1.8 (m, 14H), 1.34 (s, CH_3, overlapped with mult at 1.2-1.8), 2.0 (d, J = 6.7 Hz, 1H, O*H*), 3.4-3.5 (m, 1H, C*H*-OH), 5.65 (d, J = 6.0 Hz, 1H, H-4), 5.76 (d, J = 6.0 Hz, 1H, H-3); ^{13}C NMR δ 22.2, 22.5, 29.2, 29.8, 30.9, 36.0, 72.6, 87.2, 91.8, 129.7, 135.7; IR ($CHCl_3$) υ 3580, 3470, 1460 cm^{-1}; HRMS calcd for $C_{11}H_{18}O_2$ 182.13068, found 182.13047. Data for the *anti*-isomer: mp 57-59°C; ^1H NMR δ 1.2-1.5 (m, 8H), 1.34 (s, CH_3, overlapped with mult at 1.2-1.5), 1.36 (s, CH_3, overlapped with mult at 1.2-1.5), 1.5-1.8 (m, 5H), 2.0 (m, 1H), 2.03 (d, J = 1.6 Hz, 1H, O*H*), 3.5 (m, 1H, C*H*-OH), 5.89 (s, 2H, H-4 and H-3); ^{13}C NMR δ 23.9, 24.0, 28.9, 29.8, 31.5, 38.8, 74.6, 86.5, 94.2, 126.1, 137.3; IR (KBr) υ 3440, 1455 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.47; H, 9.96. Found: C, 72.03; H, 9.90.

2,2-Diethyl-6-hydroxy-1-oxaspiro[4.5]dec-3-ene (2c). The crude product was purified by flash chromatography (20% EtOAc in hexanes) to yield the diastereomeric dihydrofurans as oils. Data for the *syn*-isomer: ^1H NMR δ 0.86 (t, J = 7.8 Hz, 3H, CH_3), 0.89 (t, J = 7.8 Hz, 3H, CH_3), 1.0-1.9 (m, 12H), 2.22 (d, J = 4.1 Hz, 1H, O*H*), 3.5 (m, 1H, H-6), 5.75 (d, J = 6.1 Hz, 1H, H-4), 5.81 (d, J = 6.1 Hz, 1H, H-3); ^{13}C NMR δ 8.8, 21.2, 22.9, 30.5, 31.5, 32.5, 34.5, 73.1, 91.3, 92.8, 130.1, 133.5; HRMS calcd for $C_{13}H_{21}O_2$ (M-1) 209.154155, found 209.153945. Data for the *anti*-isomer: ^1H NMR δ 0.86 (t, J = 7.5 Hz, 3H, CH_3), 0.90 (t, J = 7.5 Hz, 3H, CH_3), 1.3-1.4 (m, 3H), 1.5-1.8 (m, 8H), 1.9-2.0 (m, 1H), 2.03 (d, J = 2.9 Hz, 1H, O*H*), 3.5 (m, 1H, H-6), 5.89 (d, J = 6.2 Hz, 1H, H-4), 5.91 (d, J = 6.2 Hz, 1H, H-3); ^{13}C NMR δ 8.8, 23.5, 23.7, 31.5, 31.8, 37.8, 74.7, 92.1, 93.3, 127.5, 135.0; IR (neat) υ 3400; 1450, 1000 cm^{-1}; HRMS calcd for $C_{13}H_{22}O_2$ 210.161980, found 210.161495.

1-Hydroxy-14-methyl-7-oxadispiro[5.1.5.2]pentadec-14-ene (2d) and 2-(1-hydroxycyclohexyl)-2-methyl-2H-4,5,6,7-tetrahydrobenzofuran (3d). The crude product was purified by by flash chromatography (10% EtOAc in hexanes) to yield **2d** and **3d** as an inseparable mixture: ^1H NMR δ 1.1-1.7 (m), 1.30 (s, overlapped with m at 1.1-1.7, CH_3-, **3d**), 1.70 (d, overlapped with m at 1.1-1.7, J = 1.5 Hz, CH_3, **2d**), 1.9-2.0 (m, 1H), 2.02 (d, J = 2.4 Hz, 1H, O*H*), 2.3 (m, 1H, H-4, **3d**), 2.50 (d, J = 13.0 Hz, H-4, **3d**), 3.4-3.5 (m, 1H, H-1, **2d**), 4.4 (m, 1H, C*H*-OH, **3d**), 5.25 (t, J = 1.9 Hz, 1H, H-3, **3d**), 5.53 (c, J = 1.4 Hz, 1H, H-15, **2d**); ^{13}C NMR δ 12.5, 21.6, 21.9, 22.1, 23.2, 23.4, 24.0, 24.0, 25.3, 25.9, 26.8, 27.2, 31.4, 31.7, 32.1, 36.1, 36.4, 37.0, 39.0, 74.7, 75.9, 85.5, 88.1, 91.4, 95.1, 120.5, 121.0, 145.3; IR (neat) υ 3450, 1670, 1450 cm^{-1}; HRMS calcd for $C_{15}H_{24}O_2$ 236.17763, found 236.17820.

4-[2-(tert-Butyldiphenylsilyloxy)ethyl]-2-hexyl-2-hydroxymethyl-1-oxaspiro[4.5]dec-3-ene (2e). The crude product was purified by by flash chromatography (10% EtOAc in hexanes) to yield **2e** as an oil: ^1H NMR δ 0.87 (distorted t, 3H, CH_3), 1.05 (s, 9H, (CH_3)$_3$-C), 1.1-1.3 (m, 9H), 1.4-1.7 (m, 11H), 1.82 (t, J = 6.3

Hz, 1H, O*H*), 2.20 (t, *J* = 6.9 Hz, 2H, C_4-CH_2), 3.37 (dd, *J* = 10.9, 6.2 Hz, 1H, C*H*-OH), 3.44 (dd, *J* = 10.9, 6.6 Hz, 1H, C*H*-OH), 3.82 (t, *J* = 6.9 Hz, 2H, CH_2-O-Si), 5.19 (s, 1H, H-3), 7.3-7.4 (m, 6H), 7.6-7.7 (m, 4H); ^{13}C NMR δ 14.1, 19.1, 21.8, 22.1, 22.6, 24.4, 25.2, 26.8, 29.5, 29.8, 31.7, 35.9, 36.4, 37.4, 62.5, 68.2, 89.4, 90.6, 122.7, 127.6, 129.6, 133.7, 135.5, 145.2; IR (neat) υ 3450, 1115 cm^{-1}. Anal. calcd for $C_{34}H_{50}O_3Si$: C, 76.35; H, 9.43. Found: C, 76.25; H, 9.30.

Cyclization of ***1f***. Purification of the crude by flash chromatography (5% EtOAc in hexanes) afforded a mixture of **2f**, **3f** and **4**, that were separated by HPLC (Column 1, 8% EtOAc in hexanes, 12 mL/min). Data for **5,5-diethyl-2-(1-hydroxyheptyl)-2,5-dihydrofuran (2f)** (less polar isomer): t_R = 21 min; ^{1}H NMR δ 0.8-0.9 (m, 9H, CH_3), 1.3-1.7 (m, 14H), 2.37 (d, *J* = 3.2 Hz, 1H, O*H*), 3.4 (m, 1H, C*H*-OH), 4.50 (br d, *J* = 6.9 Hz, 1H, H-2), 5.69 (dd, *J* = 6.3, 1.7 Hz, 1H, H-3), 5.73 (d, *J* = 6.6 Hz, 1H, H-4); ^{13}C NMR δ 8.2, 8.8, 14.1, 22.6, 25.6, 29.4, 31.6, 31.8, 32.5, 33.1, 74.8, 89.7, 93.7, 126.6, 134.0; IR ($CHCl_3$) υ 3400, 1460 cm^{-1}. Data for the more polar isomer of **2f**: t_R = 38 min; ^{1}H NMR δ 0.8-1.0 (m, 9H, CH_3), 1.3-1.4 (m, 8H), 1.5-1.7 (m, 6H), 1.94 (d, *J* = 3.5 Hz, 1H, O*H*), 3.6 (m, 1H, C_2-C*H*OH), 4.7 (m, 1H, H-2), 5.78 (dd, *J* = 6.3, 2.0 Hz, 1H, H-3), 5.82 (d, *J* = 6.7 Hz, 1H, H-4); ^{13}C NMR δ 8.2, 8.8, 14.1, 22.6, 25.9, 29.3, 31.0, 31.8, 32.4, 32.8, 72.9, 89.3, 93.3, 125.7, 134.6; IR υ ($CHCl_3$) υ 3400, 1460 cm^{-1}; HRMS calcd for $C_{15}H_{28}O_2$ (M-OH) 223.20619, found 223.20618. Data for **2-(1-ethyl-1-hydroxypropyl)-5-heptyl-2,5-dihydrofuran (3f)** (unstable oil): t_R = 23 min; ^{1}H NMR δ 0.8-1.0 (m, 9H, CH_3), 1.2-1.6 (m, 14H), 4.77 (br s, 2 H, H-2 and H-5), 5.78 (d, *J* = 6.0, 1H), 5.91 (d, *J* = 6.0 Hz, 1H). Data for **2-(1-ethyl-1-hydroxypropyl)-5-heptylfuran (4)** (unstable oil): t_R = 20 min; ^{1}H NMR δ 0.8-1.0 (m, 9H, CH_3), 1.2-1.3 (m, 6H), 1.6 (m, 2H), 1.7-1.8 (m, 4H), 2.51 (t, *J* = 8.9 Hz, 2H), 5.89 (d, *J* = 4.7 Hz, 1H), 6.07 (d, *J* = 4.7 Hz, 1H).

Cyclization of ***anti-1g***. Flash chromatography (10% EtOAc in hexanes) of the crude product afforded in order of elution ***anti*-2g** and ***anti*-3g**. Data for **(2*R**, 1'*R**)-2-[(2-*tert*-butyldiphenylsilyloxy-1-hydroxy)ethyl]-2,4-dimethyl-1-oxaspiro[4.5]dec-3-ene (*anti*-2g)**: ^{1}H NMR δ 1.07 (s, 9H, $(CH_3)_3$-C), 1.23 (s, 3H, C_2-CH_3), 1.3-1.7 (m, 13H), 1.63 (d, overlapped with m at 1.3-1.7, *J* = 1.4 Hz, C_4-CH_3), 2.66 (d, *J* = 3.3 Hz, 1H, O*H*), 3.6 (m, 1H, C*H*-OH), 3.70 (dd, *J* = 10.2, 6.8 Hz, 1H, C*H*-OSi), 3.79 (dd, *J* = 10.2, 4.1 Hz, 1H, C*H*-OSi), 5.3 (m, 1H, H-3), 7.3-7.4 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 12.1, 19.2, 21.9, 21.9, 24.6, 25.3, 26.8, 35.5, 36.3, 65.0, 77.4, 87.7, 88.9, 124.3, 127.7, 129.6, 133.3, 135.5, 142.8; IR ($CHCl_3$) υ 3500, 1450, 1110 cm^{-1}; HRMS calcd for $C_{25}H_{31}O_3Si$ (M-^{t}Bu) 407.204249, found 407.204033. Data for **(2*R**, 5*R**)-2-[(*tert*-butyldiphenylsilyloxymethyl)-5-(1-hydroxycyclohexyl)-3,5-dimethyl-2,5-dihydrofuran (*anti*-3g)**: ^{1}H NMR δ 1.05 (s, 9H, $(CH_3)_3$-C), 1.0-1.1 (m, 1H), 1.2-1.3 (m, 4H), 1.27 (s, overlapped with m at 1.2-1.3, C_5-CH_3), 1.3-1.4 (m, 1H), 1.6-1.7 (m, 7H), 1.73 (s, 3H, C_3-CH_3), 1.78 (d, *J* = 0.9 Hz, 1H, O*H*), 3.66 (dd, *J* = 10.8, 4.0 Hz, 1H, C*H*-OSi), 3.78 (dd, *J* = 10.8, 4.0 Hz, 1H, C*H*-OSi), 4.61 (m, 1H, H-2), 5.43 (m, 1H, H-4), 7.3-7.4 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 12.9, 19.3, 21.6, 22.1, 25.9, 26.9, 31.8, 32.1, 66.0, 75.8, 89.1, 94.7, 127.1, 127.6, 129.5, 129.6, 133.5, 133.6, 135.7, 135.7, 136.6; IR ($CHCl_3$) υ 3480, 1450, 1140, 1115, 1070 cm^{-1}; HRMS calcd for $C_{29}H_{39}O_2Si$ 447.271934, found 447.271292.

Cyclization of ***syn-1g***. Flash chromatography (10% EtOAc in hexanes) of the crude product afforded in order of elution ***syn*-2g** and ***syn*-3g**. Data for **(2*S**, 1'*R**)-2-[(2-*tert*-butyldiphenylsilyloxy-1-**

hydroxy)ethyl]-2,4-dimethyl-1-oxaspiro[4.5]dec-3-ene (*syn*-**2g**): ^{1}H NMR δ 1.06 (s, 9H, $(CH_3)_3$-C), 1.20 (s, 3H, C_2-CH_3), 1.2-1.7 (m, 13H), 1.60 (d, overlapped with m at 1.2-1.7, J = 1.4 Hz, C_4-CH_3), 2.67 (s, 1H, O*H*), 3.6-3.7 (m, 2H, C*H*-OH and C*H*-OSi), 3.7 (m, 1H, C*H*-OSi), 5.3 (m, 1H, H-3), 7.3-7.4 (m, 6H), 7.6-7.7 (m, 4H); ^{13}C NMR δ 12.1, 19.2, 21.9, 22.0, 24.0, 25.3, 26.8, 35.4, 36.3, 65.0, 77.4, 87.6, 88.8, 124.4, 127.7, 129.6, 133.4, 135.6, 142.6; IR ($CHCl_3$) υ 3480, 1590 cm^{-1}; HRMS calcd for $C_{28}H_{37}O_3Si$ (M-CH_3) 449.251199, found 449.252657. Data for (**2*R**,5*S****)-**2**-[(*tert*-**butyldiphenylsilyloxymethyl)-5-(1-hydroxycyclohexyl)-3,5-dimethyl-2,5-dihydrofuran** (*syn*-**3g**): ^{1}H NMR δ 1.05 (s, 9H, $(CH_3)_3$-C), 1.25 (s, 3H, C_5-CH_3), 1.3-1.7 (m, 9H), 1.71 (s, 3H, C_3-CH_3), 1.8 (m, 1H), 2.94 (s, 1H, O*H*), 3.61 (dd, J = 11.2, 2.4 Hz, 1H, C*H*-OSi), 3.84 (dd, J = 11.2, 3.4 Hz, 1H, C*H*-OSi), 4.6 (m, 1H, C_2-H), 5.58 (br s, $W_{1/2}$ = 5.1 Hz, 1H, H-4), 7.3-7.4 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 12.5, 19.1, 21.2, 21.6, 26.2, 26.8, 31.5, 33.2, 64.6, 74.3, 86.3, 94.5, 127.7, 128.1, 129.7, 129.8, 132.8, 132.9, 135.2, 135.6, 135.7; IR ($CHCl_3$) υ 3500, 1450, 1110 cm^{-1}. Anal. calcd for $C_{29}H_{40}O_3Si$: C, 74.96; H, 8.68. Found: C, 74.48; H, 8.75.

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REFERENCES AND NOTES

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