Pergamon

Tetrahedron Vol. 51, No. 15, pp. 4421-4438, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01130-3

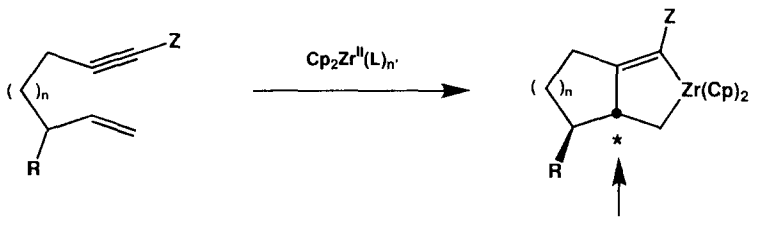
Substrate Control of Diastereoselectivity in Zirconium(II) Mediated Enyne Cyclizations.

Brian L. Pagenkopf, Eric C. Lund and Tom Livinghouse[1*]

Department of Chemistry and Biochemistry
Montana State University
Bozeman, MT 59717

Abstract: The reductive cyclization of an extensive series of chiral enynes by $Cp_2Zr(II)$ complexes has been examined. In most instances excellent substrate control of cyclization stereochemistry was observed.

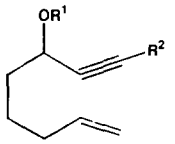
The elucidation of processes that control relative and absolute stereogenesis has become central to the practice of selective organic synthesis. In this context, transformations mediated by transition metals have gained increasing recognition as a powerful means for achieving reaction selectivity. This characteristic is derived, in part, from the ability of transition metals to serve as vehicles for both substrate[2] and reagent[3] based stereocontrol. The intramolecular Pauson-Khand reaction has been utilized quite frequently for the construction of fused 2-cyclopenten-1-ones.[4] Although numerous diastereoselective variations of this cobalt centered annulation exist,[4,5] comparatively little has been reported regarding the corresponding $Cp_2Zr(II)$ mediated cyclizations (Negishi cyclizations).[6] Our interests in the use of Group IV metal templated cyclizations for the synthesis of bioactive [3,4] fused cyclopentenones led us to an early investigation of substrate directed stereocontrol in Zr-enyne cyclizations (**Scheme 1**).[7,8] Herein, we provide the results of a more detailed study of this phenomenon.



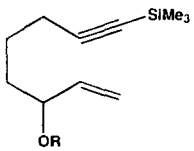
Scheme 1

Synthesis of Chiral Enynes.

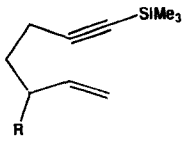
The chiral enynes **1c**, **2b**, and **3b** that were utilized in this investigation were prepared by the union of the appropriate organometallic reagent and aldehyde. Accordingly, treatment of pent-4-en-1-al with lithium (trimethylsilyl)acetylide provided **1c** upon protonation (NH_4Cl_{aq}). Silylation of **1c** (TBDMSCl-imidazole, DMF)[9a] subsequently gave **1a**. Alternatively, C-desilylation of **1c** ($KOH\text{-}H_2O$, CH_3OH) followed by C-sulfenylation (a. LDA, THF; b. CH_3SCN)[10] and final alcohol silylation (vide supra) furnished **1b**. Enynes **2b** and **3b** were prepared in a similar manner from 6-trimethylsilyl-5-hexynal or 5-trimethylsilyl-4-pentynal and vinylmagnesium bromide in 84% and 86% yield respectively. The 3-carboxamido-1-hepten-6-ynes **3c** and **3d** were readily procured in 41% and 64% yield by the *deconjugative* alkylation of *N,N*-diethyl-2-butenamide and (2*S*)-1-(2′-butenoyl)-2-(hydroxymethyl)pyrrolidine respectively with 1-iodo-4-trimethylsilyl-3-butyne followed by O-silylation in the case of **3d**. It is interesting to note that the deconjugative alkylation leading to **3d** afforded a 20:1 ratio of diastereomeric amides. The absolute stereochemical assignment of **3d** is based on analogy with literature precedent.[11] Reduction of **3c** ($LiAlH_4$) provided the 3-(diethylaminomethyl) substituted enyne **3e** in 74% yield. The 4-(hydroxymethyl)-1-hepten-6-yne derivatives **4a** and **4b** were prepared by the decarbomethoxylation of dimethyl 2-(2-propenyl)-2-(2-propynyl)-1,3-propanedioate (NaCl, wet DMF)[12] and subsequent reduction/silylation [1. $LiAlH_4$; 2. (a) *n*-BuLi, (b) Me_3SiCl, (c) HCl_{aq}; 3. TBDMSCl-imidazole, DMF (48% overall)] in the case of **4a**, or *methylation*/SEM ether formation [1. (a) CH_3Li; (b) Me_3SiCl; (c) HCl_{aq}; 2. $SEMCl/(i\text{-}Pr)_2NEt$[9b] (34% overall)] for **4b**. The 4-(silyloxy)-1-hepten-6-yne **4c** was secured in 80% overall yield by the addition of allylmagnesium bromide to 4,4-dichlorobutanal followed by O-silylation[9a] and final bis-elimination/silylation (LDA-Me_3SiCl,[13b] THF, −78 °C). The latter transformation constitutes a new (and synthetically quite useful) variation of the Normant acetylene synthesis.[13a] O-Desilylation of **4c** ($HF_{aq}\text{-}CH_3CN$)[14] provided the free alcohol **4d**.



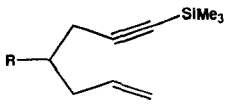
1a: R^1 = TBDMS, R^2 = TMS
1b: R^1 = TBDMS, R^2 = SCH_3
1c: R^1 = H, R^2 = TMS



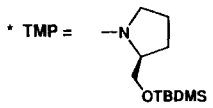
2a: R = TBDMS
2b: R = H



3a: R = TBDMSO
3b: R = OH
3c: R = C(O)NEt$_2$
3d: R = C(O)-1-TMP*
3e: R = CH$_2$N(Et)$_2$



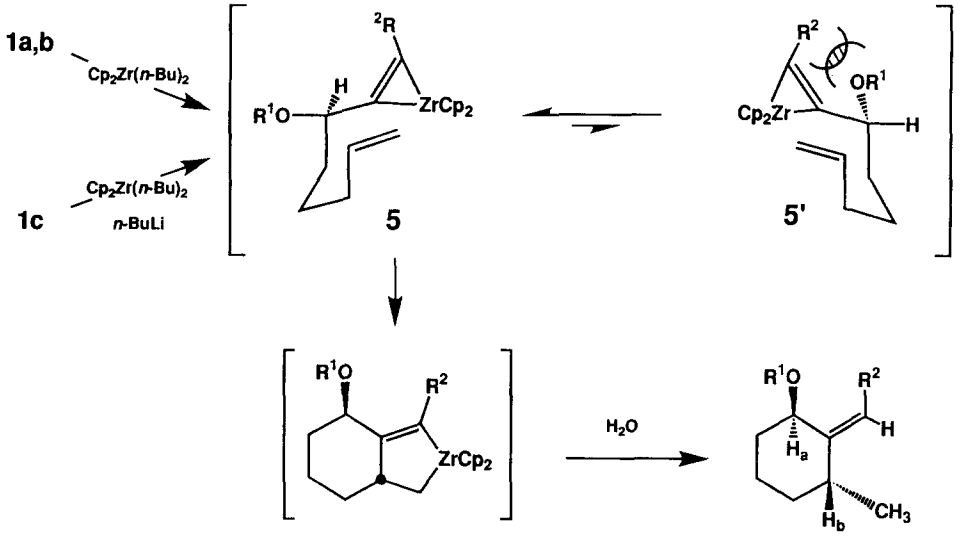
4a: R = TBDMSOCH$_2$
4b: R = SEMOC(CH$_3$)$_2$
4c: R = TBDMSO
4d: R = OH



Cyclization Studies.

The cyclization of 6-(*t*-butyldimethylsilyloxy)-1-octen-7-ynes **1a** and **1b** was conducted in close analogy with literature precedent.[15,16] Accordingly, treatment of Cp_2ZrCl_2 in THF with *n*-BuLi (2 equiv) at −78 °C followed by the addition of the appropriate enyne substrate and subsequent stirring (−78 °C, 0.5 h then 25 °C, 12 h) generated the corresponding zirconacyclopentene **6**. In the case of **1c** the THF solution of Cp_2ZrCl_2 was treated with *3 equiv* of *n*-BuLi prior to the addition of the substrate to effect initial conversion to the corresponding alkoxide derivative. Protonolysis of the reaction mixture [2 equiv of AcOH, 0 °C (3 equiv in the case of **6b**)] gave, in each case, a major cyclized product with > 30:1 diastereoselectivity as determined by capillary G.C. and 300 MHz ^{1}H NMR spectroscopy. The relative stereochemistry of the substituents on alkylidenecyclohexanes **7a-c** prepared in this manner was assigned as trans on the basis of the following spectroscopic data. The coupling constants observed for the silyloxy C-H resonances (H_a) in the cyclohexanes **7a-c** were invariably small in magnitude (ca. 0-3 Hz) as would be expected for equatorially disposed protons. By way of contrast, the allylic hydrogens (H_b) of **7a-c** exhibited both large (ca. 6.0 Hz) and small couplings characteristic of axial protons. Additional evidence for the trans orientation of the silyloxy and methyl substituents as well as for the *Z* geometry of the alkylidene moiety was provided by nuclear Overhauser enhancement difference (NOED) spectroscopy. Significant NOEs were observed between the vinylic hydrogens and the peripheral methyl substituents of the cyclization products **7a-c**. In addition, no observable NOEs were detected between H_a and H_b nor between the vinylic hydrogen and H_b in these products. These data are again consistent with the existence of a trans relationship between H_a and H_b, the equatorial disposition of the C-3 methyl substituent and *Z* alkene geometry.

The foregoing stereochemical results are consistent with the following mechanistic analysis. Reductive elimination of butane from $Cp_2Zr(n\text{-}Bu)_2$ followed by enyne complexation with loss of 1-butene[17] should generate the transient zirconacyclopropenes **5a-c** for which there are two extreme precyclization conformers (e.g., **5** and **5'**). Conformers corresponding to **5'** are expected to be disfavored energetically as a consequence of allylic 1,3-nonbonded interactions between the proequatorial oxygen bearing moiety and the vicinally disposed zirconacyclopropenyl substituent. Accordingly, cyclization via conformers corresponding to **5**, in which allylic 1,3-strain is minimized, should occur preferentially to provide the exo substituted zirconacyclopentenes **6a-c**.

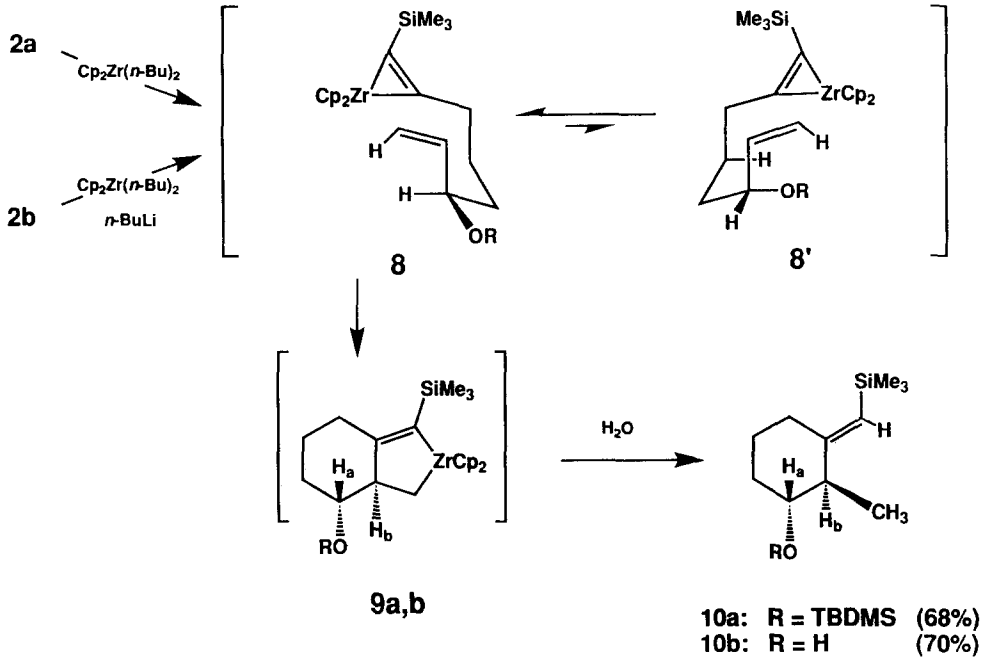


7a: R^1 = TBDMS, R^2 = TMS (79%)
7b: R^1 = TBDMS, R^2 = SCH_3 (53%)
7c: R^1 = H, R^2 = TMS (70%)

Cyclization of the 1-octen-7-yne derivatives **2a** and **2b** (vide supra) followed by protonolysis (vide supra) gave the trans homoallylic ether **10a** and the alcohol **10b** as the predominant stereoisomers (stereoselectivity > 30:1) in 68% and 70% isolated yield respectively. In the case of **10a**, both the silyloxy C-H and allylic hydrogen (H_a and H_b, respectively) exhibited one large [9.0 Hz (H_a), 8.9 Hz (H_b)] and one small [3.0 Hz (H_a), 1.4 Hz (H_b)] coupling constant. Moreover, no observable NOE was detected between H_a and H_b but a relatively strong NOE was observable

between the C-2 methyl substituent and the vinylic hydrogen. These internally consistent data strongly support the designated trans stereochemical and geometrical assignments for **10a**. The homoallylic alcohol **10b** exhibited closely analogous splitting patterns and NOE behavior.

An alternative mechanistic model can be advanced that is consistent with the high selectivity observed for the conversion of **2a** and **b** into **10a** and **b**. As in the case of the zirconacyclopropenes **5a-c**, two extreme precyclization conformers (e.g., **8** and **8'**) can be envisaged. Conformer **8'** is expected to be higher in energy than **8** as a result of an unfavorable quasi 1,3-diaxial interaction between the ether moiety at C-3 and a methylene hydrogen bound to C-5. The energy difference between **8** and **8'** should be further exacerbated by an allylic 1,3-interaction involving the C-3 oxygen substituent and a terminal vinylic hydrogen.[18] Cyclization via **8** leads to the exo-substituted zirconacyclopentenes **9a,b** and ultimately to **10a** and **10b**.



We next directed our attention to the utilization of $Cp_2Zr(II)$ complexes for the annulation of 2,3-disubstituted alkylidenecyclopentane derivatives. In this study five allylic enynes were examined. Cyclization of the allylic enynes **3a** and **3b**, as before, led to the formation of the trans alkylidenecyclopentanes **13a** and **b** in a highly stereocontrolled fashion and in very good yield. In the case of **3a** two diastereomeric cyclization products were formed in a 14:1 ratio. For **3b**, a single stereochemically homogeneous product **13b** was formed as a consequence of $Cp_2Zr(II)$ mediated annulation. In the instances of **13a** and **b**, evidence for relative stereochemistry derived both from NOE spectroscopy and single-crystal X-ray analysis. As in the case of the alkylidenecyclohexanes **10a** and **10b**, the splitting patterns and chemical shift data for the alkylidenecyclopentanes **13a** and **13b** were closely analogous with one another. Similarly, no observable NOE was detected between H_a and H_b. A strong NOE was also observed between the C-2 methyl substituent and the vinylic hydrogen for both **13a** and **13b**. The latter enhancement, however, may not be stereochemically meaningful in view of the expected conformational mobility of the cyclopentane framework. In the instance of **13b**, the *trans* relationship of the pendant methyl and hydroxy substituents as well as the *E* geometry of the alkylidene moiety were ultimately confirmed via single-crystal X-ray analysis of the corresponding 4-phenylbenzoate ester **13f** (Figure 1).

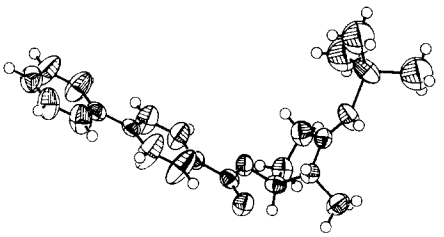
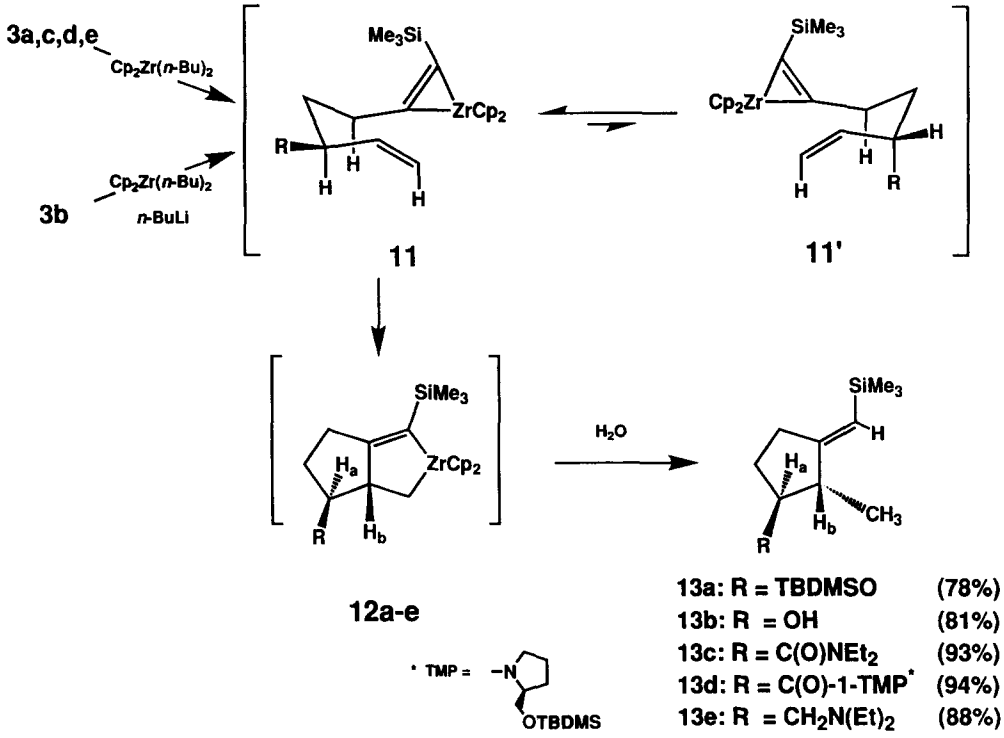


Figure 1. ORTEP diagram of **13f**

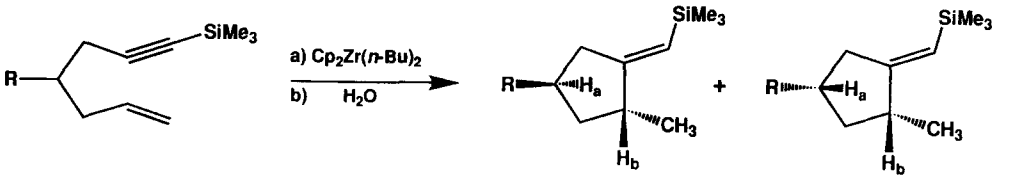
Zirconocene mediated cyclization of enynes bearing carboxamido moieties at the 3-position (e.g., **3c** and **3d**) initially proved problematic. Although cyclization could be achieved to some extent using the standard set of reaction conditions (vide supra), substrate to product conversion was typically below 70% even when an excess of $Cp_2Zr(n\text{-}Bu)_2$ was utilized. In light of the possibility that **3c** and **3d** might be anomalous with respect to their rate of cyclization, we theorized that competitive decomposition of the active Zr(II) species might be responsible for the observed inefficiency of conversion. We have previously shown that complexation with 4-dimethylaminopyridine (DMAP) confers enhanced stability on low valent zirconocene complexes.[19] In accord with the foregoing hypothesis, cyclizations of carboxamides **3c** and **3d** were performed in the presence of 2 equiv each of $Cp_2Zr(n\text{-}Bu)_2$ and DMAP. To our gratification, *the efficiency of cyclization was restored for both of the above substrates under these conditions* to provide the alkylidenecyclopentanes **13c** and

13d in 93% and 94% yield respectively. In each of the above cases a very high level of stereoselectivity was observed as a consequence of substrate controlled cyclization. Specifically, the alkylidenecyclopentanes **13a** and **13b** were formed with > 40:1 diastereoselectivity as determined by capillary G.C.. In the instances of **13c** and **13d**, the indicated products were formed in greater than 99:1 and 50:1 isomeric purity respectively. The assignment of relative stereochemistry for **13c** and **13d** is at present tentative as it rests strictly on the *absence* of NOE's between the vicinal hydrogens H_a and H_b and on analogy with the stereochemical outcome of the cyclizations that led to **13a** and **13b**. In this connection the cyclization of amine **3e** might be seen as stereochemically informative. Exposure of **3e** to $Cp_2Zr(n\text{-}Bu)_2$ under the *standard* set of experimental conditions (*no DMAP*) provided a predominant diastereomeric alkylidenecyclopentane **13e** (stereoselectivity > 40:1) in 88% yield upon protonolysis. As in the previous cases, no detectable NOE was observed between H_a and H_b. However, a strong NOE *was observable* between H_b and the $-CH_2N(Et)_2$ methylene. In light of the corpus of data presented above, it is very likely that the stereochemical outcome of the cyclizations of **3a-e** is analogous.

The excellent diastereoselectivity observed for the preceding five cyclizations can be rationalized as arising from minimization of quasi 1,3-diaxial interactions and 1,3-allylic strain by the adoption of conformers of the type **11** by the Cp_2Zr-alkyne complex prior to cyclization.



The Zr(II) mediated cyclization of several 1-hepten-6-yne substrates bearing a single C-4 substituent was subsequently examined. From the standpoint of substrate derived stereocontrol, substituents of this variety were not expected to be as influential as those proximate to the sites of ring formation. Accordingly, cyclization of **4a** (vide supra) proceeded without incident to furnish the alkylidenecyclopentanes **14a** and **15a** (**14a/15a**=2) in 89% yield. Cyclization of **4b** under analogous conditions provided **14b** and **15b** (**14b/15b**=11) in 99% isolated yield. In the case of **14a** and **15a**, the *minor isomer* **15a** gave a NOE between the C-2 and C-4 hydrogens as would be expected for a molecule possessing *cis* disposed substituents. In addition, the TBDMSOCH_2 ^{1}H resonance of the *minor* isomer **15a** appeared as multi-line pattern (2 dd, δ 3.40) as a consequence of restricted rotation (as might be expected for the *cis* isomer) whereas the TBDMSOCH_2 signal of **14a** appeared as a sharp doublet centered at δ 3.46. For **14b** and **15b**, the absence of a NOE between the C-2 and C-4 methines of the *major isomer* **14b** is consistent with a *trans* stereochemical relationship of these hydrogens. Although quite suggestive, the foregoing data must be viewed as inconclusive and accordingly, the precise stereochemical outcome for the cyclizations of **4a** and **b** is tentative at the time of this writing. The diastereoselectivities observed for the cyclizations of **4a** and **b** can be viewed as arising from nonbonded interactions that are related in origin but *smaller in magnitude* than those of the preceding series (i.e., **3a-e**). Cyclizations of enynes bearing oxygen substituents at the 4-position were next briefly examined. Exposure of **4c** to $Cp_2Zr(n\text{-}Bu)_2$ (1.1 equiv) in the usual manner gave the alkylidenecyclopentanes **14c** and **15c** (**14c/15c**=1) in 80% yield after protonation. Interestingly, the alkoxide derived from *in-situ* deprotonation of **4d** [$Cp_2Zr(n\text{-}Bu)_2$ + *n*-BuLi (1 equiv)] proved *inert* toward Zr(II) mediated cyclization. Presumably, a previously inoperative Zr-ligation effect by the alkoxide moiety was responsible for the observed torpitude of the intended cyclization.[20]



4a-c **14a-c** **15a-c**

a: R = TBDMSOCH$_2$
b: R = SEMOC(CH$_3$)$_2$
c: R = TBDMSO
d: R = OH

14a + 15a (89%)
14b + 15b (99%)
14c + 15c (80%)

4d $\xrightarrow[n\text{-BuLi}]{Cp_2Zr(n\text{-}Bu)_2}$ ***No cyclization***

In summary, several of the factors that appear to influence substrate based control of diastereoselection in $Cp_2Zr(II)$ promoted enyne cyclizations have been illuminated. Although the stereochemical outcome for the preceding annulations has not yet been unequivocally established in all cases, it is evident that a high level of stereocontrol can often be achieved by way of this transition metal-based reaction.

Acknowledgements. Generous support for our research program by grants from the National Science Foundation and the National Institutes of Health is gratefully acknowledged. We are indebted to Mr. Ray Larsen of the MSU X-ray facility for obtaining the crystal structure of **13f** (Figure 1).

EXPERIMENTAL SECTION

General experimental details: Tetrahydrofuran (THF) was distilled from potassium; diethyl ether (Et_2O) was distilled from sodium-benzophenone. Dichloromethane (CH_2Cl_2), *N,N*-dimethylformamide (DMF) and hexamethylphosphoramide (HMPA) were distilled from CaH_2. *N,N*-Diisopropylamine (DIPA), diisopropylethylamine and triethylamine (TEA) were distilled from $LiAlH_4$. Zirconocene dichloride was purchased from Boulder Scientific and was purified by extraction (45 g of zirconocene dichloride) through a pad of dry Celite (4 cm diameter by 10 cm) with CH_2Cl_2 (200 mL) and the resulting crystals were dried in vacuo. 4-Dimethylaminopyridine (DMAP) was purified by sublimation. The molarities for organolithium and alkylmagnesium halide reagents were established by titration with 2-butanol and 1,10-phenanthroline or 2,2'-bipyridyl, respectively, as indicators. Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flamed, oven-dried vessels. ^1H NMR and ^{13}C NMR were measured at 300 and 75 MHz, respectively, with a Bruker AC-300 spectrometer unless otherwise stated. ^1H NMR and ^{13}C NMR chemical shifts are reported as δ values in ppm relative to residual proton signals in $CDCl_3$ (δ = 7.24, 77.0) or C_6D_6 (δ = 7.15, 128.7). ^1H NMR coupling constants are reported in Hz and refer to apparent multiplicities and not true coupling constants. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); p (pentet); sx (sextet); br (broad); m (multiplet); app d (apparent doublet); app t (apparent triplet); dd (doublet of doublets); etc. Infrared spectra were recorded on a Bruker IFS 25 IR. Electron impact mass spectra (70-eV) were recorded with a Hewlet Packard 5970 series mass selective detector. High resolution mass spectra were recorded on a VG Instruments 70E-HF spectrometer. Analytical gas chromatographs were obtained for all products on a Varian Model 3700 gas chromatograph equipped with a flame ionization detector and either an Alltech Econocap SE-54 bonded phase column (15 m length, 0.54 mm id, and 1.2 μm film thickness) or a Heliflex (Alltech) RSL150BP bonded phase column (30 m length, 0.32 mm id, and 0.25 μm film thickness). TLC and column chromatography were performed with Merck silica gel 60 or Aldrich activity 1 basic alumina. Concentrations were performed under reduced pressure with a Büchi rotary evaporator. LDA·THF complex was prepared by dropwise addition of *n*-BuLi (5.1 mL, 9.8 M in heptane, 50 mmol) to a solution of *N,N*-diisopropylamine (7.0 mL, 50 mmol) in THF (4 mL, 50 mmol) and methylcyclohexane (34 mL) maintained at 0 °C. This complex was titrated by the method of Vedejs[21] prior to use.

6-[(1,1-Dimethylethyl)dimethylsilyloxy]-8-(trimethylsilyl)-1-octen-7-yne (1a): ^1H NMR δ 5.78 (m, 1H, C=C*H*), 4.95 (m, 2H, C=CH_2), 4.31 (t, J = 6.3 Hz, 1H, OC*H*), 2.05 (app dd, J = 7.0, 14.0 Hz, 2H, CH_2), 1.63 (m, 2H, CH_2), 1.50 (m, 2H, CH_2), 0.88 (s, 9H, CH_3), 0.13 (s, 9H, CH_3), 0.11 (s, 3H, CH_3), 0.09 (s, 3H, CH_3); IR (CCl_4) 3077, 2167 cm^{-1}; high resolution mass spectrum calcd for $C_{17}H_{34}OSi_2$ (M^+) 310.2139, found 310.2145.

6-[(1,1-Dimethylethyl)dimethylsilyloxy]-8-(methylthio)-1-octen-7-yne (1b): ^{1}H NMR ($CDCl_3$) δ 5.77 (m, 1H, C=C*H*), 4.97 (m, 2H, C=CH_2), 4.41 (app br d, J = 5.53 Hz, 1H, OC*H*), 2.34 (s, 3H, SCH_3), 2.04 (m, 2H, CH_2), 1.66 (m, 2H, CH_2), 1.50 (m, 2H, CH_2), 0.87 (s, 9H, CH_3), 0.03 (s, 3H, CH_3), 0.01 (s, 3H, CH_3); IR (CCl_4) 3077, 2178 cm^{-1}; high resolution mass spectrum calcd for $C_{15}H_{28}OSSi$ (M^+) 284.1623, found 284.1623.

8-(Trimethylsilyl)-1-octen-7-yn-6-ol (1c): ^{1}H NMR ($CDCl_3$) δ 5.79 (m, 1H, C=C*H*), 4.97 (m, 2H, C=CH_2), 4.34 (t, J = 6.3 Hz, 1H, OC*H*), 2.07 (m, 2H, CH_2), 1.92 (br s, 1H, O*H*), 1.73-1.38 (m, 4H, CH_2), 0.15 (s, 9H, CH_3); IR ($CDCl_3$) 3449, 3077, 1642 cm^{-1}; high resolution mass spectrum calcd for $C_{11}H_{20}OSi$ (M^+) 196.1278, found 196.1280.

(1*Z*,2β,6α)-[2-[[(1,1-Dimethylethyl)dimethylsilyloxy]-6-methylcyclohexylidene]methyl]trimethylsilane (7a). A 10 mL round-bottomed flask equipped with a magnetic stirring bar and a septum was charged with Cp_2ZrCl_2 (146 mg, 0.5 mmol) and THF (5 mL). The resulting solution was cooled to −78 °C with stirring and *n*-BuLi (313 μL, 3.20 M in heptane, 1.0 mmol) was added dropwise by syringe. After stirring for a further 10 min at −78 °C a solution of enyne **1a** (98 mg, 0.5 mmol) in THF (1 mL) was added dropwise by syringe. The stirred reaction mixture was allowed to warm to 0 °C over ~5 min whereupon the flask was immersed in a cooling bath containing approximately 75 g ice and 25 mL H_2O. Stirring was continued for 10 h as the reaction mixture attained room temperature. At the end of this time the solution was cooled to 0 °C and degassed H_2O (0.5 mL) was added. Vigorous stirring was continued for a further 15 min at which time the resulting suspension was filtered through a pad of Florisil (3 g). The filter cake was subsequently extracted with benzene (3 x 5 mL), the filtrate was dried with anhydrous $MgSO_4$ and the solvents were removed in vacuo. The residual oil was purified by chromatography on silica gel (2% EtOAc/hexane for elution) to provide 78.2 mg (79%) of **7a** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.19 (br s, 1H, C=C*H*), 4.76 (br s, 1H, OC*H*), 2.85 (m, 1H, C*H*), 2.45 (m, 1H, CH_2), 2.10 (dt, J = 4.1, 13.4 Hz, 1H, CH_2), 1.97 (m, 2H, CH_2), 1.55 (m, 2H, CH_2), 1.10 (d, J = 6.6 Hz, 3H, CH_3), 1.05 (s, 9H, CH_3), 0.28 (s, 9H, CH_3), 0.24 (s, 3H, CH_3), 0.18 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.4, 115.9, 71.2, 38.3, 36.6, 34.0, 25.9, 20.4, 18.3, 18.1, 0.8, −4.3; IR (CCl_4) 3050, 1616 cm^{-1}; high resolution mass spectrum calcd for $C_{17}H_{36}OSi_2$ (M^+) 312.2295, found 312.2304.

(1α,2*Z*,3β)(1,1-Dimethylethyl)dimethyl[[3-methyl-2-[(methylthio)methylene]cyclohexyl]oxy]silane (7b): ^{1}H NMR ($CDCl_3$) δ 5.39 (app d, J = 1.6 Hz, 1H, C=C*H*), 4.81 (app t, J = 3.7 Hz, 1H, OC*H*), 2.52 (m, 1H, C*H*), 2.23 (s, 3H, SCH_3), 1.92 (dt, J = 3.5, 13.3 Hz, 1H, CH_2), 1.74 (m, 2H, CH_2), 1.42 (m, 1H, CH_2), 1.32 (m, 1H, CH_2), 1.22 (m, 1H, CH_2), 0.97 (d, J = 6.7 Hz, 3H, CH_3), 0.86 (s, 9H, CH_3), 0.06 (s, 3H, CH_3), 0.00 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 142.3, 115.7, 67.4, 37.31, 35.2, 32.9, 29.9, 25.8, 20.2, 17.9, 17.5, −4.7, −5.0; IR (CCl_4) 3057 cm^{-1}; high resolution mass spectrum calcd for $C_{15}H_{30}OSSi$ (M^+) 286.1779, found 286.1794.

(1β,2*Z*,3α)-2-(Trimethylsilyl)methylene-3-methylcyclohexanol (7c): ^{1}H NMR ($CDCl_3$) δ 5.42 (s, 1H, C=C*H*), 4.81 (br s, 1H, OC*H*), 2.23 (m, 1H, C*H*), 2.01 (m, 1H, CH_2), 1.60-1.20 (m, 5H, CH_2), 1.11 (d, J = 8.0 Hz, 3H, CH_3), 0.08 (s, 9H, CH_3); IR (thin film) 3371, 2955, 2930, 2857, 1616 cm^{-1}; high resolution mass spectrum calcd for $C_{11}H_{22}OSi$ (M^+) 198.1440, found 198.1436.

3-[(1,1-Dimethylethyl)dimethylsilyloxy]-8-(trimethylsilyl)-1-octen-7-yne (2a): ^{1}H NMR ($CDCl_3$) δ 5.77 (m, 1H, C=C*H*), 5.07 (m, 2H, C=CH_2), 4.11 (m, 1H, OC*H*), 2.20 (t, J = 6.3 Hz, 2H, C≡CCH_2), 1.58 (m, 4H, CH_2), 0.87 (s, 9H, CH_3), 0.12 (s, 9H, CH_3), 0.03 (s, 3H, CH_3), 0.01 (s, 3H, CH_3); IR (CCl_4) 3077, 2174 cm^{-1}; high resolution mass spectrum calcd for $C_{17}H_{34}OSi_2$ (M^+) 310.2139, found 310.2137.

8-(Trimethylsilyl)-1-octen-7-yn-3-ol (2b). A 50 mL round-bottomed flask equipped with a magnetic stirring bar and a septum was charged with THF (5 mL) and vinylmagnesium bromide (1.0 M in

THF, 11 mL, 11 mmol). The resulting solution was cooled to −78 °C and a solution of 6-(trimethylsilyl)-5-hexyn-1-al (1.68 g, 10 mmol) in THF (5 mL) was added dropwise by syringe. The reaction mixture was stirred for 30 min at −78 °C and then allowed to warm to room temperature with stirring. After stirring for an additional 30 min the reaction mixture was transferred to a separatory funnel containing saturated aqueous NH_4Cl (25 mL) and Et_2O (35 mL). The organic layer was separated, sequentially dried with brine (25 mL), anhydrous Na_2SO_4 (5 g) and the solvents were removed in vacuo. The resulting oil was purified by bulb-to-bulb distillation at 70 °C (0.1 torr) to provide the title compound **2b** 1.65 g (84%) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 5.85 (m, 1H, C=C*H*), 5.19 (m, 2H, C=CH_2), 4.12 (m, 1H, OC*H*), 2.23 (m, 2H, C≡CCH_2), 1.60 (m, 5H, CH_2 and O*H*), 0.11 (s, 9H, CH_3); IR (CCl_4) 3542, 3084 cm^{-1}; high resolution mass spectrum calcd for $C_{11}H_{20}OSi$ (M^+) 196.1278, found 196.1274.

(1*E*,2β,3α)-[[(1,1-Dimethylethyl)dimethylsilyloxy]-2-methylcyclohexylidene]methyl]trimethylsilane (10a): ^1H NMR ($CDCl_3$) δ 5.15 (br s, 1H, C=C*H*), 3.13 (m, 1H, OC*H*), 2.45 (app dt, *J* = 3.8, 12.8 Hz, 1H, C=CC*H*), 2.05 (m, 1H, CH_2), 1.87 (m, 2H, CH_2), 1.76 (m, 1H, CH_2), 1.45 (m, 1H, CH_2), 1.23 (m, 1H, CH_2), 1.03 (d, *J* = 6.6 Hz, 3H, CH_3), 0.88 (s, 9H, CH_3), 0.08 (s, 9H, CH_3), 0.03 (s, 3H, CH_3), 0.02 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 160.5, 119.5, 77.4, 49.0, 35.3, 34.4, 26.0, 24.8, 18.1, 14.9, 0.5, −4.1, −4.6; IR (CCl_4) 3050 cm^{-1}; high resolution mass spectrum calcd for $C_{17}H_{36}OSi_2$ (M^+) 312.2295, found 312.2306.

(1α,2β,3*E*)-2-Methyl-3-[(trimethylsilyl)methylene]cyclohexanol (10b): ^1H NMR ($CDCl_3$) δ 5.22 (s, 1H, C=C*H*), 3.25 (m, 1H, OC*H*), 2.41 (app dt, *J* = 5.0, 14.9 Hz, 1H, C=CC*H*), 2.08 (m, 1H, CH_2), 1.96 (m, 2H, CH_2), 1.77 (m, 1H, CH_2), 1.52-1.27 (m, 3H, CH_2 and O*H*), 1.10 (d, *J* = 7.6 Hz, 3H, CH_3), 0.10 (s, 9H, CH_3); ^{13}C NMR (C_6D_6) δ 161.2, 120.9, 76.9, 49.9, 35.1, 34.8, 25.6, 15.4, 1.2; IR (thin film) 3372, 2956, 2933, 2859, 1615 cm^{-1}; high resolution mass spectrum calcd for $C_{11}H_{22}OSi$ (M^+) 198.1440, found 198.1434.

3-[(1,1-Dimethylethyl)dimethylsilyloxy]-7-(trimethylsilyl)-1-hepten-6-yne (3a): ^1H NMR ($CDCl_3$) δ 5.76 (m, 1H, C=C*H*), 5.08 (m, 2H, C=CH_2), 4.22 (app q, *J* = 6.2 Hz, 1H, OC*H*), 2.25 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 0.88 (s, 9H, CH_3), 0.12 (s, 9H, CH_3), 0.05 (s, 3H, CH_3), 0.02 (s, 3H, CH_3); IR (CCl_4) 3084, 2173 cm^{-1}; high resolution mass spectrum calcd for $C_{16}H_{32}OSi_2$ (M^+) 296.1983, found 296.1982.

7-(Trimethylsilyl)-1-hepten-6-yn-3-ol (3b): ^1H NMR ($CDCl_3$) δ 5.85 (m, 1H, C=C*H*), 5.18 (m, 2H, C=CH_2), 4.25 (br d, *J* = 5.9 Hz, 1H, OC*H*), 2.32 (m, 2H, CH_2), 1.83 (br s, 1H, O*H*), 1.72 (app dd, 2H, CH_2), 0.12 (s, 9H, CH_3); IR (CCl_4) 3542, 3084 cm^{-1}; high resolution mass spectrum calcd for $C_{10}H_{18}OSi$ (M^+) 182.1122, found 182.1116.

***N,N*-Diethyl-2-ethenyl-6-(trimethylsilyl)-5-hexynamide (3c).** A solution of *n*-BuLi (2.53 mL, 4.34 M in heptane, 11 mmol) was added dropwise to a magnetically stirred solution of DIPA (1.68 mL, 12 mmol) in THF (300 mL) maintained at −78 °C. After 10 min the mixture was warmed to 0 °C, then recooled to −78 °C. After stirring for an additional 15 min at −78 °C a solution of *N,N*-diethyl-2-buteneamide (1.41 g, 10 mmol) in THF (10 mL) was added dropwise over 5 min and the reaction mixture was then stirred for 1 h at −78 °C. The resulting mixture was subsequently allowed to warm to 23 °C, held at this temperature for 1.5 h and then recooled to −78 °C. A solution of 4-iodo-1-(trimethylsilyl)-1-butyne (3.02 g, 12 mmol) in THF (10 mL) was then introduced dropwise, the −78 °C bath was removed and the reaction mixture allowed to stir 9 h. The resulting solution was quenched with half-saturated aqueous NH_4Cl (200 mL) and the organic phase was separated. The aqueous phase was extracted with 1:1 Et_2O-CH_2Cl_2 (3 x 50 mL). The combined organic phases were washed with 10% aqueous H_2SO_4 (2 x 5 mL), H_2O (5 mL), saturated aqueous $NaHCO_3$ (5 mL), brine (10 mL), dried ($MgSO_4$) and concentrated in vacuo. Chromatography of the residual oil on silica gel (20% EtOAc/hexane for elution) afforded 1.08 g (41%) of **3c** as a light yellow oil:

^{1}H NMR ($CDCl_3$) δ 5.83 (ddd, J = 8.4, 10.4 and 17.6 Hz, 1H, C*H*=CH_2), 5.10 (m, 2H, CH=C*H*$_2$), 3.34 (m, 5H, COC*H* and NC*H*$_2$), 2.2 (m, 2H, C*H*$_2$C≡C), 1.94 (app sx, J = 6.7 Hz, 1H, CO*H*CH$_2$), 1.68 (app sx, J = 6.7 Hz, 1H, CO*H*CH$_2$), 1.19 (t, J = 7.15 Hz, 3H, C*H*$_3$), 1.08 (t, J = 7.2 Hz, 3H, C*H*$_3$), 0.11 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$) δ 172.7, 137.9, 117.3, 107.5, 86.0, 45.9, 42.4, 41.2, 32.0, 18.1, 15.5, 13.3, 0.8; IR (thin film) 2963, 2173, 1647, 1632, 1449, 1250, 1139, 1043, 918, 843, 638 cm^{-1}; m/z 265 (M^+), 192, 165, 100, 73.

(2*S*,2'*S*)-1-[2'-Ethenyl-6'-(trimethylsilyl)-5'-hexynoyl]-2-(hydroxymethyl)pyrrolidine (16). A solution of *n*-BuLi (4.39 mL, 4.78 M in heptane, 21 mmol) was added dropwise to a magnetically stirred solution of DIPA (3.08 mL, 22 mmol) in THF (60 mL) maintained at −78 °C. The resulting mixture was warmed to 0 °C and then recooled to −78 °C. After stirring for an additional 15 min at −78 °C, a solution of (2*S*)-2-(hydroxymethyl)-1-(2'-butenoyl)pyrrolidine (2.52 g, 10 mmol) in THF (20 mL) was added dropwise and the resulting mixture was stirred for 15 min at −78 °C. The reaction mixture was allowed to warm to 22 °C, held at this temperature for 45 min and then recooled to −78 °C. A solution of 4-iodo-1-(trimethylsilyl)-1-butyne (2.52 g, 10 mmol) in THF (10 mL) was then introduced and the reaction mixture was stirred for a further 15 min at −78 °C whereupon stirring was continued for 6 h at 0 °C. After stirring for an additional 3 h at 25 °C the reaction mixture was quenched with half-saturated aqueous NH_4Cl (10 mL) and the solution was concentrated in vacuo to approximately 20 mL. The resulting heterogeneous mixture was extracted with 1:1 CH_2Cl_2-Et_2O (5 x 15 mL), washed with brine (5 mL), dried (Na_2SO_4) and concentrated in vacuo. Chromatography of the residual oil on silica gel (50% EtOAc/hexane for elution) afforded 1.87 g (64%) of **16** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.50 (ddd, J = 8.5, 9.8, 16.0 Hz, 1H, C*H*=CH_2), 5.10 (m, 2H, CH=C*H*$_2$), 4.89 (m, 1H, O*H*) 4.18 (m, 1H, NC*H*CH$_2$OH), 3.65-3.48 (m, 4H, C*H*$_2$NCHC*H*$_2$OH) 3.37 (app q, J = 7.9 Hz, COC*H*), 2.21 (t, J = 6.6 Hz, 2H, C*H*$_2$C≡C), 1.91-1.84 (m, 4H), 1.64-1.55 (m, 2H), 0.09 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$) δ 174.7 (*C*), 136.7 (*C*H), 118.1 (*C*H$_2$), 107.1 (*C*), 86.2 (*C*), 67.8 (*C*H$_2$), 61.8 (*C*H), 48.3 (*C*H$_2$), 48.1 (*C*H), 30.9 (*C*H$_2$), 28.8 (*C*H$_2$), 25.0 (*C*H$_2$), 18.0 (*C*H$_2$), 0.7 (*C*H$_3$); IR (thin film) 3394, 3079, 2957, 2171, 1621, 1615, 1435, 1249, 1047, 842, 760, 668, 637 cm^{-1}.

(2*S*,2'*S*)-1-[2'-Ethenyl-6'-(trimethylsilyl)-5'-hexynoyl]-2-[[(1,1-dimethylethyl)dimethylsilyloxy]-methyl]pyrrolidine (3d). A solution of **16** (4.26 mmol, 1.25 g), imidazole (10.22 mmol, 0.696 g), and *t*-butyldimethylsilyl chloride (4.65 mmol, 0.706 g) in DMF (8 mL) was magnetically stirred at 45 °C for 30 h. The cooled reaction mixture was poured into saturated aqueous $NaHCO_3$ (30 mL) and extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with 10% aqueous H_2SO_4 (5 mL), H_2O (5 mL), brine (10 mL), dried ($MgSO_4$) and concentrated in vacuo. The resulting oil was initially purified by chromatography on silica gel (20% EtOAc/hexane for elution). Final purification by bulb-to-bulb distillation afforded 1.42 g (82%) of **3d** as a viscous clear oil: ^{1}H NMR ($CDCl_3$) δ 5.74 (ddd, J = 8.6, 10.4, 18.5 Hz, 1H, C*H*=CH_2), 5.09 (m, 2H, CH=C*H*$_2$), 4.13 (m, 1H, NC*H*CH$_2$O), 3.68 (d, J = 4.5 Hz, 2H, C*H*$_2$OSi), 3.52 (m, 2H, NC*H*$_2$), 3.32 (m, 1H, COC*H*), 2.21 (t, J = 6.8 Hz, 2H, C*H*$_2$C≡C), 2.10-1.07 (m, 6H, C*H*$_2$), 0.82 (s, 9H, C(C*H*$_3$)$_3$) 0.08 (s, 9H, Si(C*H*$_3$)$_3$), 0.00 (s, 3H, Si(C*H*$_3$)$_2$), 0.03 (s, 3H, Si(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ 172.0, 137.4, 117.5, 107.6, 86.0, 59.1, 58.9, 48.2, 47.9, 31.1, 27.7, 26.5, 24.9, 22.6, 18.1, 0.8, −4.8; IR (thin film) 3082, 2241, 1643, 1490, 1467, 1379, 1260, 1117, 1057, 1002, 912, 733, 687, 645 cm^{-1}; m/z 407 (M^+), 350, 262, 73; high resolution mass spectrum calcd for $C_{22}H_{41}NO_2Si_2$ (M^+) 407.2676, found 407.2667.

3-(Diethylaminomethyl)-7-(trimethylsilyl)-1-hepten-6-yne (3e). To a magnetically stirred solution of $LiAlH_4$ (8.5 mg, 2.2 mmol) in Et_2O (5 mL) at 22 °C was added a solution of **3c** (80 mg, 0.3 mmol) in Et_2O (0.3 mL) in one portion. The reaction mixture was heated at reflux for 36 h, then cooled to 0 °C. To the cooled reaction mixture was added H_2O (2 mL) and aqueous NaOH (1 mL, 2 M). After 15 min of vigorous stirring at room temperature the organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with brine (2 x 2 mL), dried ($MgSO_4$) and concentrated in vacuo. Chromatography of the residual oil on

basic alumina (1% EtOAc/hexane for elution) afforded 56 mg (74%) of **3e** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 5.51 (m, 1H, C*H*=CH_2), 5.02 (m, 2H, CH=C*H*$_2$), 2.48 (dt, J = 1.8 and 6.9 Hz, 4H, N(*CH*$_2$CH$_3$)), 2.29 (m, 2H, NC*H*$_2$), 2.15 (m, 2H, *CH*$_2$C≡C), 1.75 (m, 1H, C*H*), 1.24 (m, 2H, *CH*$_2$CH$_2$C≡C), 0.96 (t, J = 7.1 Hz, 6H, C*H*$_3$), 0.11 (s, 9H, Si(*CH*$_3$)$_3$); ^{13}C NMR ($CDCl_3$) δ 141.1, 115.4, 107.6, 84.4, 57.9, 47.3, 41.5, 31.4, 17.6, 11.5, 0.1; IR (thin film) 3076, 2175, 1639, 1453, 1250, 1041, 914, 841, 760, 637 cm^{-1}; m/z 149 (MH$^+$ − TMS, −Et), 121, 93, 73 (TMS).

(1*E*,2α,3β)-[[(1,1-Dimethylethyl)dimethylsilyloxy]-2-methylcyclopentylidene]methyl]trimethylsilane (13a): ^{1}H NMR ($CDCl_3$) δ 5.23 (d, J = 2.3 Hz, 1H, C=C*H*), 3.52 (dq, J = 8.5, 14.7 Hz, 1H, OC*H*), 2.47 (m, 1H, C*H*), 2.19 (m, 2H, C*H*$_2$), 1.90 (m, 1H, C*H*$_2$), 1.53 (m, 1H, C*H*$_2$), 1.01 (d, J = 6.7 Hz, 3H, C*H*$_3$), 0.88 (s, 9H, C*H*$_3$), 0.06 (s, 9H, C*H*$_3$), 0.04 (s, 3H, C*H*$_3$), 0.03 (s, 3H, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ 163.1, 118.0, 79.3, 49.8, 33.1, 29.2, 25.9, 18.1, 15.6, −0.3, −4.4, −4.7; IR (CCl_4) 3050 cm^{-1}; high resolution mass spectrum calcd for $C_{16}H_{34}OSi_2$ (M$^+$) 298.2139, found 298.2152.

(1β,2α,3*E*)-2-Methyl-3-[(trimethylsilyl)methylene]cyclopentanol (13b): ^{1}H NMR ($CDCl_3$) δ 5.30 (d, J = 2.3 Hz, 1H, C=C*H*), 3.66 (m, 1H, OC*H*), 2.50 (m, 1H, C*H*), 2.31 (m, 1H, C*H*$_2$), 2.22 (m, 2H, C*H*$_2$), 2.01 (m, 1H, C*H*$_2$), 1.06 (d, J = 6.8 Hz, 3H, C*H*$_3$), 0.07 (s, 9H, C*H*$_3$); IR (thin film) 3371, 2957, 2929, 2858, 1625 cm^{-1}; high resolution mass spectrum calcd for $C_{10}H_{20}OSi$ (M$^+$) 184.1283, found 184.1291.

(1α,2β,3E)-*N*,*N*-Diethyl-2-methyl-3-[(trimethylsilyl)methylene]cyclopentane-1-carboxamide (13c). A solution of *n*-BuLi (0.36 mL, 5.9 M in heptane, 2.12 mmol) was added to a magnetically stirred solution of Cp_2ZrCl_2 (307 mg, 1.05 mmol) and DMAP (107 mg, 1.075 mmol) in THF (10 mL) maintained at −78 °C. After 10 min the Dry ice-acetone bath was removed and the vigorously stirred reaction mixture was allowed to warm to −10 °C. As soon as the reaction mixture became homogeneous (usually at −20 °C) the resulting yellow solution was recooled to −78 °C. A solution of **3c** (132 mg, 0.5 mmol) in THF (0.15 mL) was then added dropwise and the resulting mixture was held at −78 °C for 15 min. The Dry ice-acetone bath was subsequently removed, the reaction flask was wrapped in foil and the vigorously stirred solution was allowed to gradually warm to 25 °C. After 10 h at 25 °C, H_2O (1 mL) was added, the reaction mixture was stirred for an additional 5 min and then 10% aqueous H_2SO_4 (1 mL) was added. After 1 h the supernatent solution was decanted and filtered through a pad of silica gel (1 cm diameter by 2 cm) which was subsequently extracted with Et_2O (3 x 10 mL). The filtrate was washed with H_2O (35 mL), and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 x 15 mL) and the combined organic layers were washed with 10% aqueous H_2SO_4 (5 mL), H_2O (5 mL), saturated aqueous $NaHCO_3$ (5 mL), brine (5 mL), dried ($MgSO_4$) and concentrated in vacuo. Chromatography of the residual oil on silica gel (15% EtOAc/hexane for elution) afforded 123 mg (93%) of **11c** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.19 (app d, J = 2.1 Hz, 1H, C=C*H*), 3.34 (app sx, J = 7.1 Hz, 4H, NC*H*$_2$), 2.79-2.67 (m, 1H, C*H*CH$_3$), 2.61-2.48 (m, 1H, C*H*$_2$), 2.36 (m, 1H, C*H*CO), 2.29 (m, 1H, C*H*$_2$), 1.90-1.65 (m, 2H, C*H*$_2$), 1.09 (dt, J = 7.0, 15.8 Hz, 6H, NCH$_2$C*H*$_3$), 0.9 (d, J = 6.6 Hz, 3H, C*H*$_3$), 0.04 (s, 9H, Si(*CH*$_3$)$_3$); ^{13}C NMR ($CDCl_3$) δ 174.5, 165.5, 117.3, 49.5, 46.4, 42.4, 41.2, 32.3, 29.5, 16.9, 15.7, 13.9, 0.4; IR (thin film) 3393, 2960, 1624, 1458, 1381, 1247, 1138, 840 cm^{-1}; m/z 267 (M$^+$), 194, 167, 73; high resolution mass spectrum calcd for $C_{15}H_{29}NOSi$ (M$^+$) 267.2018, found 267.2010.

(1*E*,2α*R*,3β)-2-Methyl-3-[1-oxo-[-1-[2*S*-(1,1-dimethylethyl)dimethylsilyloxymethyl]pyrrolidino]]-methylcyclopentylidenemethyl]trimethylsilane (13d). The enyne **3d** (205 mg, 0.25 mmol) was cyclized according to the procedure described above for **3c** to afford 193 mg (94%) of **11d** as a light yellow oil. ^{1}H NMR ($CDCl_3$) δ 5.18 (app t, J = 2.3 Hz, 1H, C=C*H*), 4.15 (m, 1H, NC*H*CH$_2$), 3.72-3.61 (m, 2H, C*H*$_2$O), 3.59-3.30 (m, 3H, NC*H*$_2$ and COC*H*), 2.62 (m, 1H, C*H*CH$_3$), 2.60-1.68 (m, 8H, C*H*$_2$), 0.99 (d, J = 6.6 Hz, 3H, CHC*H*$_3$), 0.82 (s, 9H, C(*CH*$_3$)$_3$), 0.03 (s, 9H, Si(*CH*$_3$)$_3$), 0.00 (s, 3H, Si(*CH*$_3$)$_2$), −0.02 (s, 3H, Si(*CH*$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ 173.4, 164.8, 116.7, 64.7, 63.1, 58.4, 51.1, 47.7, 46.0, 31.6, 27.6, 25.9, 21.8, 18.1, 16.4, −0.3, −5.4; IR (thin film) 3037, 2955, 2858, 1645, 1422,

1321, 1249, 1103, 841, 967 cm^{-1}; m/z 409 (M^+), 352, 167, 73; high resolution mass spectrum calcd for $C_{22}H_{43}NO_2Si_2$ (M^+) 409.2832, found 409.2850.

(1α,2β,3*E*)-1-(*N,N*-Diethylaminomethyl)-2-methyl-3-[(trimethylsilyl)methylene]cyclopentane (13e). Enyne **3e** (38 mg, 0.15 mmol) was cyclized according to the general procedure utilized for **4a** except after stirring for 10 h the reaction was treated with H_2O (2 mL) and heated at 35 °C for 2 h. The reaction mixture was allowed to cool and then treated with aqueous NaOH (1 mL, 2 M) and Et_2O (2 mL) and the organic layer was separated. The aqueous phase was extracted with Et_2O (4 x 2 mL) and the combined organic layers were washed with brine (2 x 2 mL), dried ($MgSO_4$) and concentrated in vacuo. Chromatography of the residual oil on basic alumina (1% EtOAc/hexane for elution) afforded 31 mg (88%) of **11e** as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 5.48 (app q, J = 2.4 Hz, 1H, C=C*H*), 2.52-2.25 (m, 4H, N*CH*$_2$CH$_3$), 2.23-2.09 (m, 2H, N*CH*$_2$ and 1H, *CH*$_2$C=C), 1.95-1.86 (m, 1H, *CH*$_2$C=C), 1.86-1.78 (m, 1H, *CH*CH$_3$), 1.54-1.40 (m, 1H, *CH*CH$_2$N), 1.26-1.11 (m, 2H, *CH*$_2$), 0.95 (d, J = 6.8 Hz, 3H, CHC*H*$_3$), 0.90 (t, J = 7.0 Hz, 6H, NCH$_2$C*H*$_3$), 0.20 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR (C_6D_6) δ 168.9, 117.6, 59.3, 48.6, 47.5, 46.5, 32.5, 31.3, 19.3, 13.1, 0.7; IR (thin film) 1621, 1459, 1382, 1247, 1203, 1068, 870, 839, 690 cm^{-1}; m/z 253 (M^+), 180, 151, 86; high resolution mass spectrum calcd for $C_{15}H_{31}NSi$ (M^+) 253.2226, found 253.2230.

Methyl-2-(2'-propenyl)-5-pentynoate (17). A magnetically stirred solution of dimethyl 2-(2-propenyl)-2-(2-propynyl)propan-1,3-dioate (1.76 g, 8.82 mmol), NaCl (0.515 g, 8.82 mmol), H_2O (318 μL, 17.6 mmol) in DMF (8 mL) was heated at reflux for 36 h. The cooled reaction mixture was subsequently poured into H_2O (100 ml), and extracted with hexane (4 x 25 mL). The combined organic phases were washed with H_2O (10 mL), brine (20 mL), dried ($MgSO_4$) and concentrated in vacuo. Chromatography of the residual oil on silica gel (10% EtOAc/hexane for elution) afforded 777 mg (62%) of the title compound **17** as a colorless oil: ^1H NMR ($CDCl_3$) δ 5.61 (m, 1H, *CH*=CH$_2$), 5.00 (m, 2H, CH=*CH*$_2$), 3.57 (s, 3H, *CH*$_3$), 2.5 (m, 1H, *CH*CO), 2.3 (m, 4H, *CH*$_2$), 1.90 (t, J = 2.5 Hz, 1H, C≡*CH*); ^{13}C NMR ($CDCl_3$) δ 174.4, 134.9, 118.0, 81.6, 70.5, 52.1, 44.4, 35.5, 20.8; IR (thin film) 3299, 3080, 2122, 1741, 1438, 921.4 cm^{-1}.

4-(Hydroxymethyl)-6-hepten-1-yne (18). A solution of methyl 2-(2-propenyl)-5-pentynoate (**17**) (2.07 g, 13.5 mmol) in Et_2O (5 mL) was added dropwise to a magnetically stirred solution of $LiAlH_4$ (387 mg, 10.2 mmol) in Et_2O (100 mL) at a rate sufficient to maintain a gentle reflux. The reaction mixture was heated at reflux for 3 h, cooled to 0 °C and H_2O (20 mL) was added dropwise, followed by 10% aqueous H_2SO_4 (50 mL). The layers were separated and the aqueous phase was extracted with Et_2O (4 x 20 mL). The combined organic layers were washed with brine (15 mL), dried (Na_2SO_4) and concentrated in vacuo. Chromatography of the residual oil on silica gel (10% EtOAc/hexane for elution) afforded 1.50 g (89%) of the title compound **18** as a colorless oil: ^1H NMR ($CDCl_3$) δ 5.72 (ddt, J = 17.4, 10.0, 2.5 Hz, 1H, *CH*=CH$_2$), 5.01 (m, 2H, CH=*CH*$_2$), 3.58 (m, 2H, HO*CH*$_2$), 2.33 (s, 1H, *HO*), 2.23 (m, 2H, *CH*$_2$CH=CH$_2$), 2.12 (t, J = 7.2 Hz, 2H, *CH*$_2$C≡C), 1.94 (t, J = 2.4 Hz, 1H, C≡*CH*), 1.7 (m, 1H, HOCH$_2$*CH*); ^{13}C NMR ($CDCl_3$) δ 136.6, 117.4, 83.0, 70.4, 65.2, 40.1, 35.4, 20.4; IR (thin film) 3350 (br), 3303, 3078, 2117, 1641, 1438, 1033, 917 cm^{-1}; m/z 124 (M^+), 83.

4-(Hydroxymethyl)-1-(trimethylsilyl)-6-hepten-1-yne (19). A solution of *n*-BuLi (4.86 mL, 4.78 M in heptane, 23.27 mmol) was added to a magnetically stirred solution of 4-(hydroxymethyl)-6-hepten-1-yne (**18**) (1.376 g, 11.1 mmol) in THF (50 ml) maintained at −78 °C. After 1 h chlorotrimethylsilane (2.65 g, 24.4 mmol) was added in one portion and the reaction mixture was allowed to warm to room temperature. After 2 h 10% aqueous HCl (30 mL) was added and the heterogenous mixture was vigorously stirred for 6 h. The organic layer was separated and the aqueous phase was extracted with 1:4 EtOAc-hexane (3 x 20 mL). The combined organic layers were washed with brine (15 mL), dried (Na_2SO_4) and concentrated in vacuo. Chromatography of the residual oil on silica gel (20% EtOAc/hexane for elution) afforded 2.00 g (92%) of the title compound **19** as a colorless

oil: ^{1}H NMR ($CDCl_3$) δ 5.70 (dddd, J = 7.2, 7.2, 10.0, 17.2 Hz, 1H, C*H*=CH_2), 4.99 (m, 2H, CH=C*H*$_2$), 3.54 (m, 2H, C*H*$_2$OH), 2.26 (m, 2H, C*H*$_2$C≡C), 2.12 (ddd, J = 0.9, 6.9, 6.9 Hz, 2H, C*H*$_2$CH=CH$_2$), 2.02 (s, 1H, O*H*), 1.78 (m, 1H, C*H*), 0.06 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$) δ 136.7, 117.42, 105.9, 87.1, 65.6, 40.4, 35.6, 22.1, 0.7; IR (thin film) 3354, 3078, 2174, 1938, 1641, 1250, 1034, 843, 760, 698 cm^{-1}; m/z 196 (M^+), 165, 155, 123, 73.

4-[(1,1-Dimethylethyl)dimethylsiloxymethyl]-1-(trimethylsilyl)-6-hepten-1-yne (4a). A solution of 4-(hydroxymethyl)-1-(trimethylsilyl)-6-hepten-1-yne (**19**) (282 mg, 1.44 mmol), imidazole (235 mg, 3.46 mmol), and *t*-butyldimethylsilyl chloride (238 mg, 1.58 mmol) in DMF (2.8 mL) was magnetically stirred at room temperature for 8 h. The reaction mixture was subsequently poured into saturated aqueous $NaHCO_3$ (50 mL) and the transfer was quantitated with hexane (5 mL). The organic phase was separated and the aqueous phase was extracted with hexane (3 x 10 mL). The organic layers were washed with H_2O (5 mL), brine (10 mL), dried ($MgSO_4$) and concentrated in vacuo to afford 438 mg (98%) of **4a** as a colorless oil which was suitable for use without further purification: ^{1}H NMR ($CDCl_3$) δ 5.78 (m, 1H, C*H*=CH_2), 5.00 (m, 2H, CH=C*H*$_2$), 3.55 (m, 2H, C*H*$_2$O), 2.25 (d, J = 6.2 Hz, 2H, C*H*$_2$C≡C), 2.12 (m, 2H, C*H*$_2$CH=CH$_2$), 1.73 (m, 1H, C*H*), 0.88 (s, 9H, C(C*H*$_3$)$_3$), 0.12 (s, 9H, Si(C*H*$_3$)$_3$), 0.03 (s, 6H, Si(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ 137.2, 117.1, 106.5, 87.0, 64.8, 40.6, 35.3, 26.6, 21.7, 21.4, 0.8, −4.7; IR (thin film) 3079, 2175, 1641, 1250, 1104, 841, 776 cm^{-1}; m/z 310 (M^+), 253, 73.

4-(1,1-Dimethyl-1-hydroxymethyl)-1-(trimethylsilyl)-6-hepten-1-yne (20). To a magnetically stirred solution of methyllithium (11.6 mL, 1.38 M in Et_2O, 16 mmol) maintained at −35 °C was added **17** (761 mg, 5 mmol) dropwise over 45 min. After 1 h the reaction mixture was allowed to warm to 0 °C and then maintained at that temperature for 1h. The solution was subsequently cooled to −78 °C, chlorotrimethylsilane (2.53 mL, 20 mmol) was added and the reaction mixture was allowed to warm to 22 °C. After 4 h, 10% aqueous HCl (20 mL) was added and the heterogeneous mixture was vigorously stirred for 12 h. The organic layer was separated, the aqueous layer was extracted with Et_2O (4 x 10 mL) and the combined organic extracts were washed with H_2O (2 mL), saturated aqueous $NaHCO_3$ (2 x 5 mL), brine (5 mL), dried (Na_2SO_4) and concentrated in vacuo. Chromatography of the residual oil on silica gel (10% EtOAc/hexane for elution) afforded 597 mg (53%) of the title compound **20** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 5.72 (m, 1H, C*H*=CH_2), 5.00 (m, 2H, CH=C*H*$_2$), 2.40-2.03 (m, 4H, C*H*$_2$), 1.55 (m, 1H, C*H*), 1.19 (s, 3H, C*H*$_3$), 1.15 (s, 3H, C*H*$_3$), 0.06 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$) δ 138.2, 116.9, 107.2, 87.8, 73.9, 47.9, 34.2, 28.9, 27.9, 20.1, 0.5; IR (thin film) 3420 (br), 3077, 2963, 2173, 1640, 1426, 1374, 1250, 994, 913, 813, 760, 698, 643 cm^{-1}.

4-[1,1-Dimethyl-1-(2-trimethylsilyl)ethoxymethoxymethyl]-1-trimethylsilyl-6-hepten-1-yne (4b). A magnetically stirred solution of 4-(1,1-dimethyl-1-hydroxymethyl)-1-(trimethylsilyl)-6-hepten-1-yne (**20**) (103 mg, 0.459 mmol) in CH_2Cl_2 (1 mL) was treated with diisopropylethylamine (289 μL, 2.06 mmol) and SEMCl (80 mg, 0.48 mmol). After 1 h the reaction mixture was concentrated in vacuo and the residue was triturated with hexane (4 x 5 mL). The combined organic extracts were washed with H_2O (5 mL), brine (5 mL), dried ($MgSO_4$) and concentrated in vacuo. Chromatography of the residual oil on silica gel (5% EtOAc/hexane for elution) afforded 162 mg (99%) of **4b** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 5.82 (m, 1H, C*H*=CH_2), 5.02 (m, 2H, CH=C*H*$_2$), 4.72 (s, 2H, OC*H*$_2$O), 3.60 (m, 2H, C*H*$_2$CH$_2$TMS), 2.41-2.08 (m, 4H, C*H*$_2$), 1.75 (m, 1H, C*H*), 1.21 (app d, J = 2.5 Hz, 6H, C*H*$_3$), 0.90 (m, 2H, C*H*$_2$TMS), 0.11 (s, 9H, Si(C*H*$_3$)$_3$), 0.00 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$) δ 138.6, 116.5, 107.7, 89.7, 86.5, 79.0, 65.6, 47.6, 34.3, 24.9, 24.7, 20.2, 18.9, 0.7, −0.7; IR (thin film) 3077, 2174, 1640, 1250, 1090, 1071, 916, 840, 760, 650 cm^{-1}; m/z 354 (M^+), 281, 223, 131, 73.

2-(3′,3′-Dichloropropyl)-1,3-dioxolane (21). ^{1}H NMR ($CDCl_3$) δ 5.84 (t, J = 6.0 Hz, 1H, C*H*Cl$_2$), 4.90 (t, J = 2.9 Hz, 1H, O$_2$C*H*), 3.97-3.82 (m, 4H, OC*H*$_2$), 2.31 (m, 2H, C*H*$_2$), 1.90 (m, 2H, C*H*$_2$);

^{13}C NMR ($CDCl_3$) δ 103.8, 74.0, 65.7, 38.4, 30.5; IR (thin film) 2958, 2885, 2762, 1476, 1411, 1236, 1141, 1028, 943, 906, 750, 651 cm^{-1}; m/z 187, 185, 183 ($M^+ - H$), 148, 112, 73.

4,4-Dichlorobutanal (22). A magnetically stirred solution of **21** (9.25 g, 50 mmol) in 1:1 10% aqueous HCl-acetone (200 mL) was heated at reflux for 24 h. The reaction mixture was subsequently concentrated in vacuo and then extracted with Et_2O (3 x 30 mL). The combined organic phases were washed with H_2O (15 mL), brine (15 mL), dried ($MgSO_4$) and concentrated in vacuo. Fractional distillation of the resultant oil (93 °C, 14 mm Hg) afforded 5.57 g (79%) of the title compound **22** as a clear oil: ^1H NMR ($CDCl_3$) δ 9.64 (s, 1H, C*H*O), 5.78 (t, J = 5.8 Hz, 1H, C*H*Cl_2), 2.66 (t, J = 6.9 Hz, 2H, COC*H*$_2$), 2.35 (m, 2H, C*H*$_2$CHCl_2); ^{13}C NMR ($CDCl_3$) δ 200.1, 72.9, 40.1, 36.1; IR (thin film) 2939, 2848, 1726, 1446, 1352, 1255, 1133, 1071, 927, 746, 676 cm^{-1}; m/z 144, 142, 140 (M^+), 105, 76, 75.

7,7-Dichloro-4-hydroxy-1-heptene (23). To a magnetically stirred solution of 4,4-dichlorobutanal (**22**) (1.41 g, 10 mmol) in Et_2O (5 mL) maintained at −10 °C was added a solution of allylmagnesium chloride (17 mL, 0.63 M in THF, 10.7 mmol) dropwise over 20 min. After stirring for 1 h at 0 °C the reaction mixture was poured into ice cold H_2O (10 mL) and acidified with 10% aqueous H_2SO_4. The resultant mixture was then extracted with Et_2O (3 x 10 mL) and the combined organic phases were washed with brine (3 x 5 mL), dried (Na_2SO_4) and concentrated in vacuo. Chromatography of the residual oil on silica gel (20% EtOAc/hexane for elution) afforded 1.78 g (98%) of the title compound **23** as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 5.81 (m, 2H, C*H*Cl_2 and C*H*=CH_2), 5.03 (m, 2H, CH=C*H*$_2$), 3.7 (m, 1H, C*H*OH), 2.45-2.35 (m, 1H, C*H*$_2$), 2.35-2.18 (m, 2H, C*H*$_2$), 2.18-2.10 (m, 1H, C*H*$_2$), 1.85 (s, 1H, O*H*), 1,75-1.65 (m, 1H, C*H*$_2$), 1.65-1.58 (m, 1H, C*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.7, 119.6, 74.3, 70.3, 42.8, 40.7, 33.3; IR (thin film) 3380, 3078, 1640, 1448, 1234, 1071, 998, 924, 865, 784, 747 cm^{-1}.

7,7-Dichloro-4-[(1,1-dimethylethyl)dimethylsiloxy]-1-heptene (24). 7,7-Dichloro-4-hydroxy-1-heptene (**23**) was silylated according to the general procedure utilized for **4a** to afford 1.37 g (94%) of the title compound **24** as a clear oil which was suitable for use without further purification: ^1H NMR ($CDCl_3$) δ 5.74 (m, 2H, C*H*CH_2 and C*H*Cl_2), 5.03 (m, 2H, C*H*CH_2), 3.75 (m, 1H, C*H*OH), 2.22 (m, 4H, C*H*$_2$), 1.68 (m, 2H, C*H*$_2$), 0.87 (s, 9H, C(C*H*$_3$)$_3$), 0.04 (s, 6H, Si(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ 135.2, 117.9, 74.5, 71.6, 42.5, 40.2, 33.2, 26.6, 18.8, −3.6, −3.9; IR (thin film) 3078, 2852, 1642, 1472, 1255, 1091, 9160, 836, 775 cm^{-1}.

4-[(1,1-Dimethylethyl)dimethylsiloxy]-1-(trimethylsilyl)-6-hepten-1-yne (4c). To a magnetically stirred solution of **24** (300 mg, 1.0 mmol) and HMPA (348 μL, 2.0 mmol) in THF (5 mL) maintained at −78 °C was added a solution of LDA·THF (1.17 mL, 0.856 M in methylcyclohexane, 1.0 mmol). After approximately 10 min an additional solution of LDA·THF (1.17 mL, 0.856 M in methylcyclohexane, 1.0 mmol) was added followed by a further portion of LDA·THF (1.76 mL, 0.856 M in methylcyclohexane, 1.5 mmol) 20 min later. The reaction mixture was stirred for 2 h and then warmed to 0 °C. After 45 min the reaction mixture was cooled to −78 °C and chlorotrimethylsilane (0.19 mL, 1.5 mmol) was introduced. After 2 h the reaction was quenched with 10% aqueous H_2SO_4 (5 mL). The mixture was allowed to warm to room temperature, extracted with hexane (3 x 10 mL) and the combined organic layers were washed with H_2O (5 mL), saturated aqueous NH_4Cl (5 mL), brine (3 x 5 mL), dried ($MgSO_4$) and concentrated in vacuo. Chromatography of the residual oil on silica gel (1% EtOAc/hexane for elution) afforded 258 mg (87%) of **4c** as a colorless oil: ^1H NMR ($CDCl_3$) δ 5.80 (dddd, J = 8.3, 8.3, 10.6, 14.4 Hz, 1H, C*H*=CH_2), 5.02 (m, 2H, CH=C*H*$_2$), 3.84 (m, 1H, C*H*O), 2.36 (m, 4H, C*H*$_2$), 0.87 (s, 9H, C(C*H*$_3$)$_3$), 0.12 (s, 9H, Si(C*H*$_3$)$_3$), 0.07 (s, 3H, Si(C*H*$_3$)$_2$), 0.05 (s, 3H, Si(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ 135.3, 118.1, 105.3, 86.9, 71.6, 42.1, 29.1, 27.2, 18.8, 0.7, −3.7, −3.8; IR (thin film) 3078, 2178, 1251, 1098, 916, 841, 808, 668, 642 cm^{-1}; m/z 295 ($M^+ - H$), 255, 239, 223, 147, 73.

4-Hydroxy-1-(trimethylsilyl)-6-hepten-1-yne (4d). Enyne **4d** was prepared by the O-desilylation of **4c** according to a literature[14] procedure: ^{1}H NMR ($CDCl_3$) δ 5.72 (m, 1H, C*H*=CH_2), 5.04 (m, 2H, CH=CH_2), 3.69 (m, 1H, C*H*OH), 2.33 (m, 2H, CH_2C≡C), 2.20 (m, 2H, CH_2), 1.90 (s, 1H, O*H*), 0.04 (s, 9H, Si(CH_3)$_3$); ^{13}C NMR ($CDCl_3$) δ 134.1, 118.2, 103.0, 87.7, 69.1, 40.6, 28.1, 0.0; IR (thin film) 3417 (br), 3076, 2959, 2176, 1642, 1421, 1250, 1020, 917, 842, 760; m/z 182 (M^+) 109, 73.

[[4-[(1,1-Dimethylethyl)dimethylsilyloxymethyl]-2-methylcyclopentylidene]methyl]trimethylsilanes 14a and 15a). To a vigorously stirred mixture of **4a** (77.6, 0.25 mmol) and Cp_2ZrCl_2 (80.4 mg, 0.275 mmol) in THF (3 mL) maintained at −78 °C was added a solution of *n*-BuLi (116 μL, 4.78 M in heptane, 0.552 mmol). After 15 min the Dry ice-acetone bath was removed, the reaction vessel was wrapped in foil, and the reaction mixture was allowed to warm to 25 °C and stirred at this temperature for 10 h. The reaction mixture was quenched with H_2O (1 mL) followed by the addition of 10% aqueous H_2SO_4 (5 mL) 5 min later. After 1 h the resultant mixture was extracted with hexane (3 x 15 mL). The combined organic phases were washed with H_2O (5 mL), saturated aqueous $NaHCO_3$ (5 mL), brine (5 mL), dried ($MgSO_4$) and filtered through a pad of silica gel (1 cm diameter by 1.5 cm) which was subsequently extracted with hexane (3 x 2 mL). The filtrate was concentrated in vacuo to afford 69 mg (89%) of **14a and 15a** as a colorless oil. GLC analysis indicated 99.6% conversion to a 2.1 to 1 mixture of diastereomers: *trans*-**14a**: ^{1}H NMR (C_6D_6) δ 5.42 (m, 1H, C=C*H*), 3.46 (d, J = 6.0 Hz, 2H, OCH_2), 2.62 (m, 1H, CH_2), 2.35 (m, 1H, C*H*CH$_3$), 2.22-2.10 (m, 2H, CH_2 and C*H*), 1.88 (m, 2H, CH_2), 1.09 (d, J = 6.8 Hz, CH_3), 0.97 (s, 9H, −C(CH_3)$_3$), 0.20 (s, 9H, Si(CH_3)$_3$), 0.05 (s, 6H, Si(CH_3)$_2$); *cis*-**15a** 5.40 (m, 1H, C=C*H*), 3.40 (2 dd, J = 4.0, 6.4 Hz, 2H, OCH_2), 2.62 (m, 1H, CH_2), 2.38 (m, 1H, C*H*CH$_3$), 2.22-2.10 (m, 2H, CH_2 and C*H*), 1.78 (m, 1H, CH_2), 1.30 (m, 1H, CH_2), 1.04 (d, J = 7.0 Hz, 3H, CH_3), 0.97 (s, 9H, −C(CH_3)$_3$), 0.19 (s, 9H, Si(CH_3)$_3$), 0.05 (s, 6H, Si(CH_3)$_2$); ^{13}C NMR (C_6D_6) δ 168.0 and 162.4, 118.3 and 117.4, 67.7 and 67.4, 42.6 and 41.9, 41.2 and 40.8, 39.1 and 37.3, 37.4 and 36.6, 26.8, 21.1, 19.2, 0.6, −4.5; IR (thin film) 1632, 1471, 1249, 1099, 838, 774, 685 cm^{-1}; m/z 255 (M^+ − *t*Bu), 180, 73; high resolution mass spectrum calcd for $C_{17}H_{36}OSi_2$ (M^+) 312.2305, found 312.2313 (*cis*) and 312.2321 (*trans*).

[[4-[1,1-Dimethyl-1-[(2-trimethylsilylethoxy)methoxymethyl]]-2-methylcyclopentylidene]methyl]trimethylsilanes 14b and 15b). Enyne **4b** (71 mg, 0.20 mmol) was cyclized according to the general procedure for utilized **4a** to afford 73 mg (99%) of **14b** and **15b** as an 11 to 1 mixture of diastereomers: *trans*-**14b**: ^{1}H NMR (C_6D_6) δ 5.45 (app q, J = 2.3, 1H, C=C*H*), 4.72 (s, 2H, OCH_2O), 3.66 (m, 2H, CH_2CH$_2$TMS), 2.56 (m, 2H, CH_2), 2.35 (m, 1H, C*H*CH$_3$), 1.95-1.71 (m, 2H, CH_2), 1.14 (m, 9H, overlapping C(CH_3)$_2$ and CHCH_3), 0.94 (m, 2H, CH_2TMS), 0.21 (s, 9H, Si(CH_3)$_3$), 0.00 (s, 9H, Si(CH_3)$_3$); ^{13}C NMR (C_6D_6) δ 167.7, 116.8, 90.2, 76.8, 65.6, 50.2, 42.8, 36.9, 34.9, 25.8, 25.1, 19.1, 18.9, 0.7, −0.5; IR (thin film) 1632, 1459, 1379, 1248, 1056, 937, 768 cm^{-1}; m/z 283 (M^+ − TMS), 225, 209, 131, 73; high resolution mass spectrum calcd for $C_{19}H_{40}O_2Si_2$ (M^+) 356.2567, found 356.2563.

[[3-[(1,1-Dimethylethyl)dimethylsilyloxy]-5-methylcyclopentylidene]methyl]trimethylsilanes 14c and 15c). Enyne **4c** (74 mg, 0.25 mmol) was cyclized according to the general procedure for **4a** to afford 60 mg (80%) of **14c** and **15c** as a colorless oil as a 1.1 to 1 mixture of diastereomers: ^{1}H NMR (C_6D_6) δ 5.47 (app q, J = 2.3 Hz, 1H, C=C*H*) and 5.43 (app q, J = 2.4 Hz, 1H, C=C*H*), 4.23-4.18 and 4.15-4.06 (m, 1H, OC*H*), 2.82 and 2.72 (m, 1H, C*H*CH$_3$), 2.55-2.25 (m, 4H, CH_2), 2.00-1.83 (m, 4H, CH_2), 1.13 (d, J = 6.9 Hz, 3H, CH_3) and 1.06 (d, J = 6.9 Hz, 3H, CH_3), 0.96 and 0.94 (s, 9H, CCH_3), 0.17 and 0.16 (s, 9H, Si(CH_3)$_3$), 0.05 (s, 12H, Si(CH_3)$_2$); ^{13}C NMR (C_6D_6) δ 166.1 and 165.3 (*C*), 118.8 and 118.6 (*C*H), 73.3 and 72.9 (*C*H), 44.9 and 44.7 (*C*H$_2$), 44.0 and 43.9 (*C*H$_2$), 40.3 and 39.4 (*C*H), 26.7 (*C*H$_3$), 20.3 and 19.8 (*C*H$_3$), 18.9 (*C*), 0.6 (*C*H$_3$), −3.8 (*C*H$_3$); IR (thin film) 643, 1462, 1248, 1055, 837, 774, 689 cm^{-1}; m/z 297 (M^+ − H), 241, 167, 147, 133, 73; high resolution mass spectrum calcd for $C_{16}H_{34}OSi_2$ (M^+) 298.2148, found 298.2159 and 298.2159.

LITERATURE CITED AND NOTES

1. Fellow of the Alexander von Humboldt Foundation 1993-1995.
2. Hoveyda, A.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307.
3. Noyori, R. *Asymmetric Catalysis in Organic Synthesis*. John Wiley and Sons: New York, 1994.
4. (a) Schore, N. E. in *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp. 1037. (b) Hoye, T. R.; Suriano, J. A. *J. Org. Chem.* **1993**, *58*, 1659 and references therein.
5. For asymmetric variants of the Pauson-Khand reaction using chiral auxiliaries, see: (a) Castro, J.; Sörenson, H.; Riera, A.; Morin, C.; Moyano, A., Pericàs, M. A.; Greene, A. E. *J. Am. Chem. Soc.* **1990**, *112*, 9388. (b) Poch, M.; Valenti, E.; Moyano, A.; Pericàs, M. A.; Castro, J.; DeNicola, A.; Greene, A. E. *Tetrahedron Lett.* **1990**, *31*, 7505.
6. (a) Negishi, E.-i.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) For an extensive review of this chemistry, see: Negishi, E.-i. in *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol 5, pp. 1163-1184. (c) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113. For related references of interest see: Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696; Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435; Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310 and references therein.
7. Lund, E. C.; Livinghouse, T. *J. Org. Chem.* **1989**, *54*, 4487.
8. For additional examples of diastereoselective enyne cyclizations promoted by $Cp_2Zr(II)$ complexes see: (a) Mori, M.; Uesaka, N.; Saitoh, F.; Shibasaki, M. *J. Org. Chem.* **1994**, *59*, 5643. Wender, P. A.; McDonald, F. E. *Tetrahedron Lett.* **1990**, *31*, 3691. Agnel, G.; Negishi, E.-i. *J. Am. Chem. Soc.* **1991**, *113*, 7424. Agnel, G.; Owczarczyk, Z.; Negishi, E.-i. *Tetrahedron Lett.* **1992**, *33*, 1543. RajanBabu, T.V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128. (b) For a recent account that includes several examples of diastereoselective enyne cyclizations mediated by $Cp_2Ti(II)$ complexes see: Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8593.
9. (a) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190. (b) Lipshutz, B.; Pegram, J. J. *Tetrahedron Lett.* **1980**, *21*, 3343.
10. Smith, R.; Livinghouse, T. *Tetrahedron* **1985**, *41*, 3559.
11. (a) Evans, D. A.; Dow, R. L.; Shih, T. L.; Takacs, J. M.; Zahler, R. *J. Am. Chem. Soc.* **1990**, *112*, 5290. (b) Evans, D. A.; Takacs, J. M. *Tetrahedron Lett.* **1980**, *21*, 4233.
12. Stevens, R. V.; Lee, A. W. M. *J. Am. Chem. Soc.* **1979**, *101*, 7032.
13. (a) Villeras, J.; Perriot, P.; Normant, J. F. *Synthesis* **1979**, 502. (b) The use of LDA-Me_3SiCl for the *direct* formation of kinetic silylenol ethers has been reported: Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 495.
14. Newton, R. F.; Reynolds, D. P. *Tetrahedron Lett.* **1979**, *20*, 3981.
15. Negishi, E.-i.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.
16. For a detailed procedure involving a $Cp_2Zr(n\text{-}Bu)_2$ mediated cyclization see: Fagan, P. J. and Nugent, W. A. in *Organic Syntheses*; Meyers, A. I., Ed.; Organic Syntheses, Inc., U.S.A., 1991, Vol. 70, pp. 272-276.
17. (a) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870 and references therein. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544.
18. As a consequence of this type of allylic 1,3-strain the axial conformer of 2-methyl-1-methylene-cyclohexane has been calculated as being only 0.50 kcal/mol higher in energy than the equatorial conformer: Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski, I. J. *J. Am. Chem. Soc.* **1968**, *90*, 5773.
19. Van Wagenen, B. C.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495.
20. Buchwald has noted that certain enynes possessing internal *ether* linkages are comparatively unreactive toward $Cp_2Zr(II)$ mediated cyclization: Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 5803.
21. Vedejs, E.; Engler, D. A.; Telschow, J. E. *J. Org. Chem.* **1978**, *43*, 188.

(*Received* 20 *October* 1994)