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Intramolecular Zinc-ene Reactions of Alkynes; Preparation of 1,5-Annulated 4-Methylenecyclopentenes

Jaap van der Louw, Juul L. van der Baan, Corine M.D. Komen, Adri Knol, Franciscus J.J. de Kanter, Friedrich Bickelhaupt, and Gerhard W. Klumpp*

Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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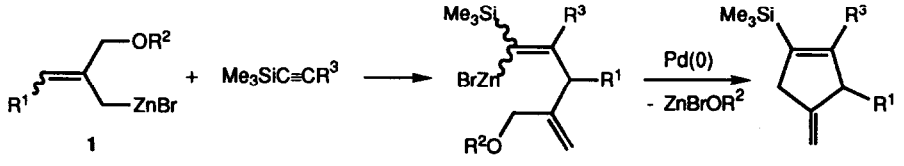
Key Words: carbometallation; allylzincation; 2-alkenylzinc compounds; Pd(0)-catalysis; cyclopentenes.

Abstract: *Intramolecular Type I zinc-ene reaction of 3-(alk-m-ynyl)-2-(methoxymethyl)-2-propenylzinc bromides 2 (m = 4,5,6) gave five-, six- and seven-membered carbometallation products 3, which on Pd(0)-catalyzed cyclization were converted to 1,5-annulated 4-methylenecyclopentenes 4. Preparation of 4-methylenecyclopentenes by intramolecular Type II zinc-ene reactions of 2-(alk-m-ynyloxymethyl)-2- alkenylzinc bromides 6 (m = 2,3) followed by Pd(0)-catalyzed rearrangement of the carbometallation products 7 is not possible. Addition as well as rearrangement are slow or do not take place.*

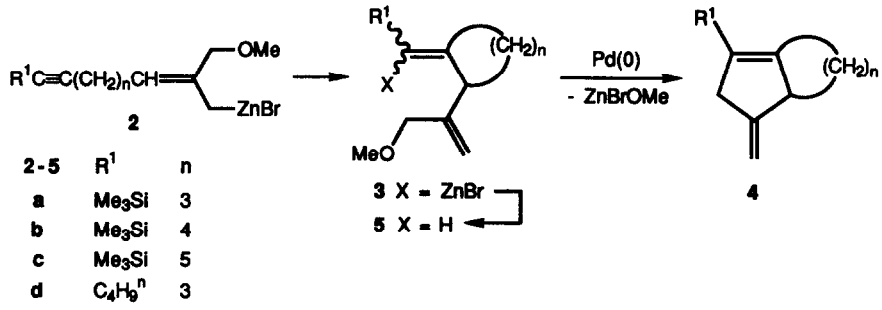
2-Alkenylmetal compounds, in particular those of zinc, boron, magnesium and aluminium, are well-known agents for allylmetallation of alkynes.[1] Recently, we developed an efficient one-pot synthesis of 4-methylenecyclopentenes[2] which consists of the regiospecific allylzincation of 1-(trimethylsilyl)-1-alkynes by 2-(bromozincmethyl)-2-alkenyl ethers **1** followed by Pd(0)-catalyzed cyclization of the carbometallation products (Scheme 1). As a sequel we explored the feasibility of performing the first reaction step, the allylzincation, intramolecularly. Type I[3] zinc-ene reaction of 3-(alk-m-ynyl)-2-(methoxymethyl)-2-propenylzinc bromides **2a-c** (R^1 = TMS, m = 4,5,6) was envisioned to yield five-, six- and seven-membered carbometallation products



Scheme 1

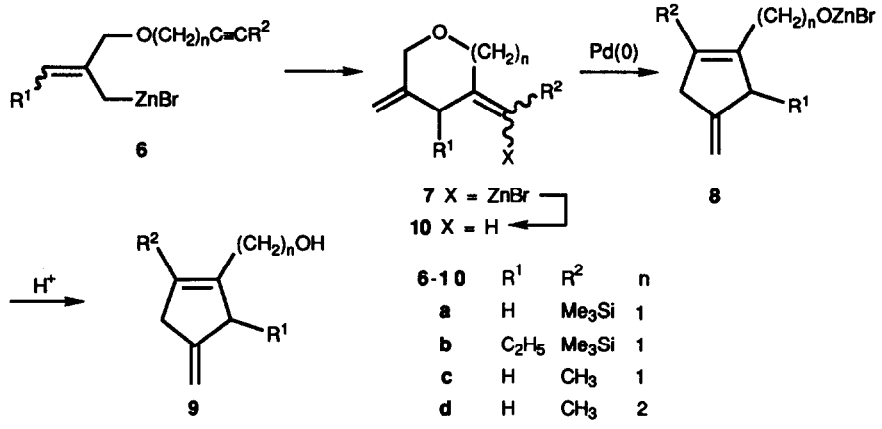
3a-c, which on Pd(0)-catalyzed cyclization might be converted to the 1,5-annulated 4-methylene-2-(trimethyl)-cyclopentanes **4a-c** (Scheme 2). Because *intramolecular* allylzincation permits addition to internal

alkynes,[4] in contrast to *intermolecular* allylzincation which only proceeds with 1-alkynes, this sequence was



Scheme 2

also studied with **2d**, in which the activating trimethylsilyl group is replaced by a deactivating alkyl group and which would lead to a 1,5-annulated 2-alkyl-4-methylenecyclopentene derivative. In similar vein, the feasibility was studied of constructing 4-methylenecyclopentenes **9** by Type II zinc-ene reaction of the 2-(alk-m-ynyloxymethyl)-2-alkenylzinc bromides **6** (m = 2,3) followed by Pd(0)-catalyzed rearrangement of the addition products **7** (Scheme 3). In this paper, we describe the results of our investigation.[5]



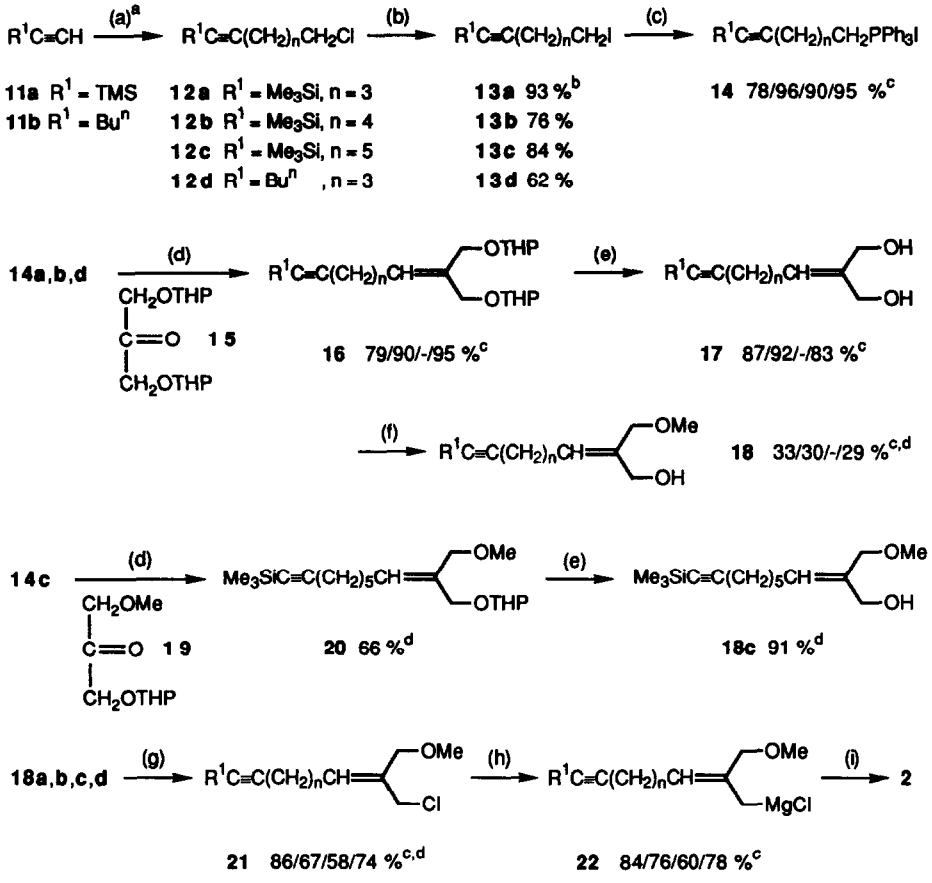
Scheme 3

RESULTS AND DISCUSSION

Preparation of 1,5-annulated 4-methylenecyclopentenes 4.

For the synthesis of the organozinc compounds **2** two different routes were followed (Scheme 4). First, iodides **13b,c,d** were prepared as described previously for **13a**.[2b] They were then transformed into the phosphonium salts **14** by reaction with triphenylphosphine in boiling benzene.With the silylated iodides **13a,b,c** this reaction was best carried out using 0.6 ml of benzene per mmol of **13**. With concentrations larger or smaller than 0.6 ml/mmol, phosphonium salt formation was accompanied by desilylation. Phosphonium

salts **14a,b,d** were subjected to a Wittig reaction with α,α'-bis-(2-tetrahydropyranyloxy)acetone (**15**)[6] giving **16a,b,d**. After hydrolysis of **16a,b,d** (Dowex 50W/ methanol), the diols **17a,b,d** were transformed into the mono-methyl ethers **18a,b,d** (1:1 mixtures of *E*- and Z-isomers). In order to prevent desilylation of diols **17a,b**, etherification had to be performed by treatment with NaH (1 mmol per mmol diol) in the presence of a large excess of methyl iodide.

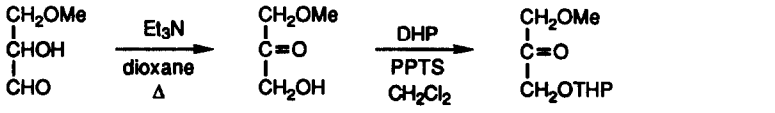


[a] Conditions. (a) 1. *n*-BuLi, *n*-hexane, THF, -20 °C, 0.5 h; 2. $I(CH_2)_nCH_2Cl$, RT, 90 h; (b) NaI, acetone, reflux, 30 h; (c) PPh_3, benzene (0.6 ml/mmol), reflux, 6 h; (d) 1. *n*-BuLi, *n*-hexane, THF, -20 °C → RT, 3.5 h; 2. RT, 0.5 h; 3. **15** or **19**, -30 °C → RT, 64 h; (e) Dowex 50W, MeOH, RT, 2 h; (f) **17a,b**: 1. MeI (4 equiv.), THF; 2. NaH (1 equiv.), THF, 0 °C; 3. RT, 2 h; **17d**: 1. NaH (1 equiv.), THF, reflux, 1 h; 2. MeI (1 equiv.), RT, 18 h; (g) 1. MesCl, LiCl, *s*-collidine, DMF, 0 °C, 1 h; 2. RT, 2 h; (h) Mg, THF, 0 °C; (i) $ZnBr_2$. [b] Yields of conversion **11** → **13**. [c] Yields of **a/b/c/d**. [d] 1:1 Mixture of *E*- and Z-isomers.

Scheme 4

Because the conversion of the symmetrical diols **17a,b,d** into mono-methyl ethers **18a,b,d** could only be accomplished in low yield, **18c** (1:1 mixture of *E*- and Z-isomers) was prepared in an alternative way by Wittig reaction of phosphonium salt **14c** with ketone **19** followed by hydrolysis of product **20** (Dowex 50W/methanol). Chlorination[7] of **18a-d**, Grignard reagent formation and, finally, conversion to the

organozinc compounds **2a-d** were carried out as described before.[2b] Grignard reagent formation was accompanied by formation of protonation and/or Wurtz coupling product(s) (10-20 %). Ketone **19** was obtained by triethylamine catalyzed isomerization[8] of 3-O-methylglyceraldehyde (**23**)[9] to 1-hydroxy-3-methoxyacetone (**24**) followed by conversion to the THP ether (Scheme 5).



23 **24** **19** 24 % (based on 23)

Scheme 5

Intramolecular reaction of the organozinc compounds **2** afforded addition products **3**, resulting from carbon-carbon bond formation at C(3) of the allylzinc moiety, exclusively. The reaction was found to take place with remarkable ease (Table 1). Indeed, it was possible not only to react **2a,b,c**, bearing a trimethylsilyl group, but also **2d**, in which the trimethylsilyl group is replaced by a (deactivating) alkyl group. Corresponding *intermolecular* allylzincations of internal alkynes do not occur.[10] The dynamic structure of allylmagnesium[11] and allylzinc compounds[12] allowed both geometric isomers of the chlorides **21** to be transformed, *via* **22** and **2**, into the monocyclic products **3**.

Table 1. Reaction conditions and yields of the reaction sequence **2** → **3** → **4**.

	Reaction conditions		Yields[a] of **4** (%)
	Ene reaction	Pd(0)-catalyzed cyclization[b]	
2a	RT, 2 h	RT, 3.5 h	84[c]
2b	65 °C, 2 h	65 °C, 2 h[d]	67[e]
2c	65 °C, 24 h	65 °C, 4 h[d]	44[e]
2d	65 °C, 8 h	RT, 4 h	75[e]

[a] Yields are based on the Grignard reagent **22**. [b] Carried out *in situ* by adding 5 mol% [$Pd(PPh_3)_4$]. [c] GLC yield. [d] No cyclization at RT. [e] Isolated yield.

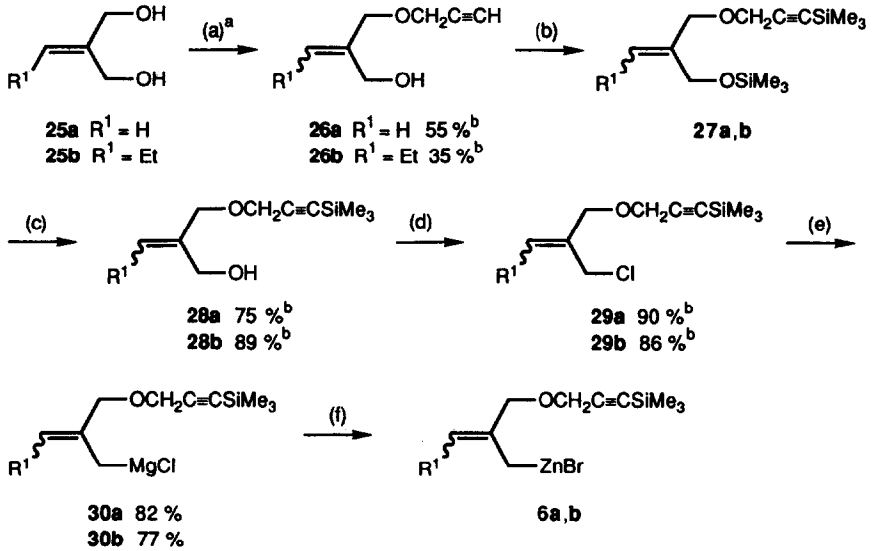
As expected, reaction temperature and reaction time of the addition were dependent on the size of the ring to be formed. The reaction of **2a** (formation of a 5-membered ring) was complete after 2 h stirring at room temperature; on the other hand, ring closure of **2b** and **2c** (formation of a 6-membered and a 7-membered ring, respectively) required 2 h and 24 h heating at 65 °C, respectively.Unknown by-products were formed together with the seven-membered ring compound **3c**. Addition products **3** were characterized by the corresponding protonation products **5**, whose ^{1}H NMR spectra showed the presence of a substituted 1,4-pentadiene system [typically (**5a**, major component): δ 5.31 (q, ^4J = 2.3 Hz, 1H, =C*H*TMS), 5.15 (m, 1H, $=CH_2$), 4.98 (m, 1H, $=CH_2$), 3.22-3.08 (m, 1H, CH)]. GCMS/NMR analysis indicated the presence of two geometric isomers in the case of **5a,b,c** (ratio *ca.* 9:1) and one in case of **5d**, which is in agreement with the fact that intramolecular allylzincation of internal alkynes results in the exclusive formation of only one stereoisomer,

i.e. the *syn*-carbometallation product.[4]

The cyclization of **3** to **4** by a catalytic amount of $[Pd(PPh_3)_4]$ was accomplished quantitatively, without side reactions and under mild conditions (Table 1). Due to the configurational lability of (1-silyl-1-alkenyl)zinc compounds,[13] both isomers of **3a,b,c** could be converted to **4**. The structure of cyclization products **4** was confirmed by ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR spectrum of **4a** is typical [δ 4.81 (septet, J = 1.3 Hz, 1H, $=CH_2$), 4.77 (septet, J = 1.3 Hz, 1H, $=CH_2$), 3.54-3.39 (m, 2H, H(3,5)), 3.17 (dquintet, ^{2}J = 18.8 Hz, J = 1.5 Hz, 1H, H(3)), 2.29-2.19 (m, 2H), 2.08-1.90 (m, 3H), 1.29-1.06 (m, 1H), 0.09 (s, 9H, TMS)]. The low overall yield in which cyclization product **4c** was obtained can largely be attributed to the addition step in which, as mentioned, by-products were formed. In contrast to (1-*silyl*-1-alkenyl)zinc compounds, (1-*alkyl*-1-alkenyl)zinc compounds like **3d** are configurationally stable.[14] Therefore, the quantitative ring closure of **3d** demonstrates that indeed, the zinc-ene reaction had occurred stereospecifically *syn*.[4] This agrees with the assumption that allylzincation of alkynes proceeds by a concerted process through a six-center transition state.[1]

*Attempted preparation of 4-methylenecyclopentenes **9** from organozinc compounds **6**.*

The results described above clearly show the reaction temperature required for *intramolecular* allylzincation of 1-(trimethylsilyl)alkynes to be much lower than the temperature required for the *intermolecular* version of this reaction.[2] Furthermore, the successful preparation of **4d** demonstrates that intramolecular allylzincation of internal alkynes followed by Pd(0)-catalyzed cyclization permits the synthesis of 4-methylenecyclopentenes carrying an alkyl group instead of a trimethylsilyl group at C(2). We therefore reasoned that the reaction sequence depicted in Scheme 3 might be a route to both 2-trimethylsilyl- and 2-alkyl-1-(ω-hydroxyalkyl)-4-methylenecyclopentenes.

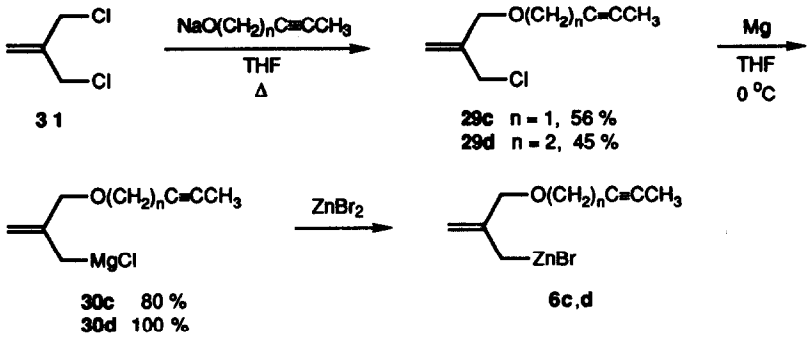


[a] Conditions. (a) 1. NaH, THF, reflux, 1 h; 2. $BrCH_2C{\equiv}CH$, reflux, 18 h; (b) 1. *n*-BuLi (2 equiv.), *n*-hexane, diethyl ether, -40 °C; 2. $ClSiMe_3$ (2 equiv.), -40 °C → RT, 1 h; 3. RT, 18 h; (c) 5 % citric acid in MeOH, reflux, 5 h; (d) 1. MesCl, LiCl, *s*-collidine, DMF, 0 °C, 1 h; 2. RT, 2 h; (e) Mg, THF, 0 °C; (f) $ZnBr_2$. [b] 1:1 Mixtures of *E*- and *Z*-isomers.

Scheme 6

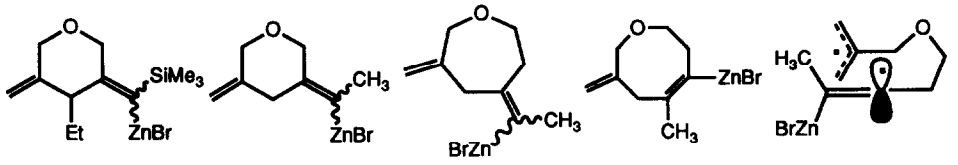
Preparation of zinc compounds **6a,b** started (Scheme 6) by conversion of the diols **25a**[15] and **25b**[2b] to the

propargyl ethers **26a** and **26b**, respectively, **26b** being a 1:1 mixture of *E*- and *Z*-isomers. **26a** And **26b** were transformed into the bis-trimethylsilyl compounds **27a** and **27b** from which the mono-trimethylsilyl derivatives **28a** and **28b** were obtained by treatment with citric acid in methanol. Then, chlorination, Grignard reagent formation and, finally, conversion to the organozinc compounds were performed according to the same procedures as described for the preparation of the organozinc derivatives **2**. Grignard reagent formation was accompanied by formation of protonation and/or Wurtz coupling product(s) (10-20%). Preparations of **6c** and **6d** followed our synthesis of **1** (R^1=H, R^2=Ph, CH_2Ph: Scheme 7).[2b]



Scheme 7

Organozinc compounds **6** were heated in a Carius tube at 75-130 °C whereafter the reaction mixtures were quenched, either with aqueous NH_4Cl or with D_2O. GLC/NMR analysis of the crude reaction products led to the results presented in Table 2. Appreciable amounts of the desired addition products were formed only in two cases, *i.e.* **6b** and **6d**. Zinc-ene reaction of **6b** gave only the addition product **7b**, which corresponds to carbon-carbon bond formation at C(3) of the allylmetal moiety. Assignment of **7b** was based on the ^{1}H NMR spectrum of its protonation product **10b** [δ 5.30 (bs, 1H, =C*H*TMS), 4.87 (bs, 1H, $=CH_2$), 4.78 (bs, 1H, $=CH_2$), 4.11 (AB system, δ(A) = 4.27, J(AB) = 12.6 Hz, 1H, H(6), δ(B) = 3.95, 1H, H(6)), 4.13 (AB system, δ(A) = 4.19, J(AB) = 13.2 Hz, 1H, H(2), δ(B) = 4.07, 1H, H(2)), 3.05 (dd, ^{3}J(4,1') = 10.4 Hz and 4.9 Hz, 1H, H(4)), 1.89-1.42 (m, 2H, H(1')), 0.89 (t, ^{3}J(2',1') = 7.4 Hz, 3H, H(2')), 0.14 (s, 9H, TMS)]. The intramolecular nature of the reaction notwithstanding, relatively forcing conditions had to be applied (100 °C, 24 h). Even more severe reaction conditions were required to effect cyclization of organozinc compound **6d** (130 °C, 24 h). As indicated by the protonation products (**10d**, **34d**) formed by NH_4Cl quench, the reaction gave three types of carbometallation products: the two geometric isomers of the seven-membered ring system **7d** and a small amount of the eight-membered ring compound **35d**. Surprisingly, **6a** failed to undergo

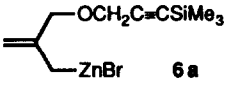
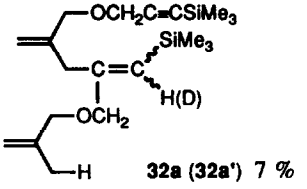
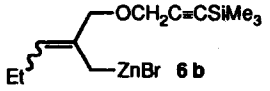
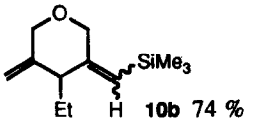
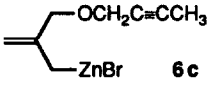
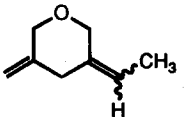
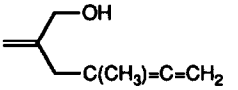
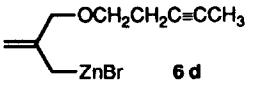
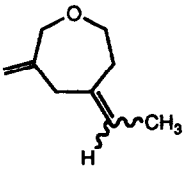
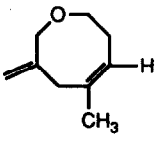


7b **7c** **7d** **35d** **39**

cyclization, even at 130 °C. Under these conditions, the organozinc compound slowly decomposed. After hydrolysis (deuterolysis) a small amount of compound **32a** (**32a'**) was obtained. This compound could arise

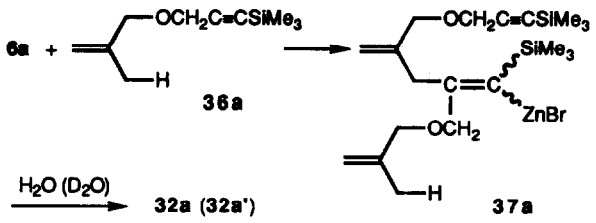
(Scheme 8) by *intermolecular* addition of **6a** to the triple bond of **36a**, formed in small amounts during preparation of the Grignard reagent **30a**. Reaction of **6c** (75 °C, 24 h) gave zinc-ene adduct **7c** in only 4 % yield. The main product was the allene **38c** (Scheme 9), as revealed by its protonation product **33c** [^{1}H NMR δ 5.14 (m, 1H, =CH_2), 4.97 (m, 1H, =CH_2), 4.63 (sextet, $^5J(6,3) = {}^5J(6,CH_3) = 3.0$ Hz, 2H, H(6)), 4.12 (bs, 2H, H(1)), 2.79 (bs, 2H, H(3)), 1.70 (t, $^5J(CH_3,6) = 3.0$ Hz, 3H, CH_3), 1.58 (bs, 1H, OH)].

Table 2. Products obtained from THF solutions of **6** by heating followed by hydrolysis (deuterolysis).

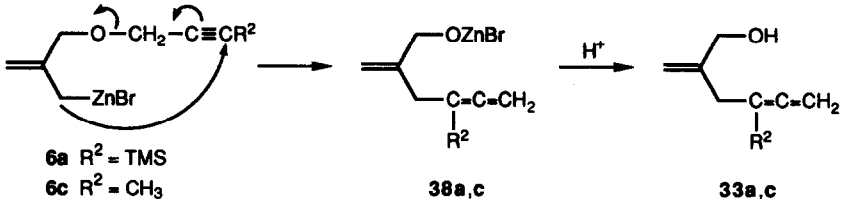
Entry	Starting material	T(°C)	t(h)	Products/Yield[a]
1	 **6a**	130	24	 **32a (32a')** 7 %
2	 **6b**	100	24	 **10b** 74 %
3	 **6c**	75	24	 **10c** 4 %  **33c** 83 %
4	 **6d**	130	24	 **10d** 40 % (56:44)  **34d** 4 %

[a] GLC yields, based on Grignard reagents **30**.

Comparing the reactions of **2a** and **6a** one concludes that Type I zinc-ene reactions of alkynes take place much easier than Type II reactions. Similar observations were reported for Type I and II magnesium-ene reactions of alkenes.[3] Transition states of Type II reactions are conformationally more demanding and the



Scheme 8



Scheme 9

difficulties seem aggravated if the enophile is sp-hybridized. The difference in behaviour between **6b** and the related compounds **6a,c,d** remains enigmatic. Intramolecular S_N 2' reaction of **6c** (Scheme 9), might be the source of **38c** and therefrom **33c**. The corresponding allene **38a** expected from **6a** might easily undergo (intramolecular ?) desilylation and subsequent decomposition. In the case of the homopropargyl ether **6d** S_N 2' reaction is impossible. The lack of stereoselectivity in the formation of **7d** (→**10d**), which contrasts strongly with the high stereoselectivity observed in the formation of **3d**, seems a consequence of the severe reaction conditions used and may indicate non-concerted reaction, for example, through **39**.

Pd(0)-catalyzed rearrangement was attempted only in case of **7b** (5 mol% $[Pd(PPh_3)_4]$, 75 °C, 24 h). Unfortunately, only deterioration of the organozinc compound was observed.

CONCLUSION

Tandem addition - Pd(0)-catalyzed cyclization starting from 2-(bromozincmethyl)-2-alkenyl ethers and 1-(trimethylsilyl)-1-alkynes constitutes a valuable one-pot synthesis of 4-methylenecyclopentenes. Type I zinc-ene reactions starting from 3-(alk-m-ynyl)-2-(methoxymethyl)-2-propenylzinc bromides lead to five-, six- and seven-membered carbometallation products which on Pd(0)-catalyzed cyclization can be converted to 1,5-annulated 4-methylenecyclopentene derivatives. The intramolecular nature of the addition step permits the synthesis of 4-methylenecyclopentenes bearing an alkyl group instead of a trimethylsilyl group at C(2). Overall, bicyclic molecules apt for further elaboration are obtained from open-chain starting materials in a one-pot procedure. Construction of 4-methylenecyclopentenes by Type II zinc-ene reactions followed by Pd(0)-catalyzed rearrangement is not possible. Both the addition and the rearrangement step are slow or do not take place.

Acknowledgment.

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EXPERIMENTAL

General information

All boiling points are uncorrected. NMR spectra were recorded on a Bruker WH-90 (^{1}H, 90 MHz), a Bruker WM-250 (^{1}H, 250.13 MHz; ^{13}C, 62.89 MHz) or on a Bruker MSL 400 (^{1}H, 400.13 MHz) spectrometer; CDCl3 was used as solvent. Chemical shifts (δ) are reported in ppm using $CHCl_3$ (^{1}H) or $CDCl_3$ (^{13}C) as internal standard. Assignments marked with *, **, *** and **** may have to be mutually reversed. 2D COSY NMR and 2D NOESY NMR data are listed as follows: number of signal(number of signal for which an interaction is observed); weak interactions are marked with ^{w} (weak). Routine GCMS spectra were recorded on a Hewlett Packard 5890 MSD spectrometer (70 eV) in combination with a Hewlett Packard HPGC 5890 gaschromatograph. HRMS spectra were measured on a Finnigan MAT 90 spectrometer (70 eV). Analytical and preparative gaschromatography (GLC) were performed on an Intersmat IGC 121 gaschromatograph equipped with a thermal conductivity-detector and using 10% OV-101 as stationary phase. Analytical gaschromatograms were integrated with a Hewlett Packard 3390 A integrator. Solvents used: THF distilled from NaH and, subsequently, from sodium benzophenone ketyl; DME distilled from NaH; diethyl ether distilled from $LiAlH_4$; DMSO distilled from CaH_2; acetone, benzene, CH_2Cl_2 and DMF dried over molecular sieves (4Å); methanol dried over molecular sieves (3Å). $ZnBr_2$ was dried *in vacuo* in the reaction vessel to be used by heating with a burner; afterwards the flask was flushed three times with nitrogen. LiCl and NaI were dried at 80 °C *in vacuo*.

All reactions were carried out in a nitrogen atmosphere. Reactions involving organometallics were carried out using glassware which was oven-dried at 150 °C for 18 h, assembled hot, evacuated, heated with a burner and, finally, flushed five times with nitrogen. For pressure reactions a Carius tube with valve and N_2-inlet[18] was used, previously oven-dried at 180 °C for 18 h. Transfer of solvents, reagents and solutions was accomplished by using syringes, or by using teflon or stainless steel tubing. The determination of the concentration of the organomagnesium compounds and organozinc compounds was carried out by titration of a known volume of the solution with acid-base using methyl red as indicator.[19] In many cases, yields were determined by GLC using an internal standard (*n*-decane, *n*-dodecane or *n*-tridecane). Calibration of the thermal-conductivity detector was achieved using solutions of known concentrations of internal standard and products.

7-Chloro-1-(trimethylsilyl)-1-heptyne (12b).

Prepared from trimethylsilylethyne (**11a**) and 1-chloro-5-iodopentane according to a procedure described before.[2b] The crude reaction product was used as such in the following step. An analytical sample was obtained by preparative GLC. ^{1}H NMR (90 MHz): 3.58 (t, ^{3}J(7,6) = 6.4 Hz, 2H, H(7)), 2.45-2.10 (m, 2H, H(3)), 2.10-1.40 (m, 6H, H(4,5,6)), 0.22 (s, 9H, TMS). MS: 187 (7), 151 (6), 109 (5), 93 (100), 83 (4), 73 (13), 55 (8), 43 (5). HRMS ($C_9H_{16}ClSi$ [M-CH_3]$^+$): calc. 187.070, found 187.0710.

8-Chloro-1-(trimethylsilyl)-1-octyne (12c).

Prepared from **11a** and 1-chloro-6-iodohexane according to a procedure described before.[2b] The crude reaction product was used as such in the following step. An analytical sample was obtained by preparative GLC. ^{1}H NMR (90 MHz): 3.59 (t, ^{3}J(8,7) = 6.6 Hz, 2H, H(8)), 2.42-2.18 (m, 2H, H(3)), 2.04-1.37 (m, 8H, H(4,5,6,7)), 0.21 (s, 9H, TMS). MS: 201 (5), 165 (2), 154 (1), 137 (1), 123 (1), 107 (56), 95 (36), 93 (100), 83 (6), 79 (14), 73 (25), 69 (7), 59 (6), 55 (7).

1-Chloro-5-decyne (12d).

Prepared from 1-hexyne (**11b**) and 1-chloro-4-iodobutane according to a procedure described before.[2b] The crude reaction product was used as such in the following step. An analytical sample was obtained by preparative GLC. ^{1}H NMR (90 MHz): 3.60 (t, ^{3}J(1,2) = 6.0 Hz, 2H, H(1)), 2.40-1.20 (m, 12H, H(2,3,4,7,8,9)), 1.20-0.85 (m, 3H, H(10)). MS: 137 (1), 130 (2), 121 (1), 109 (2), 95 (30), 81 (61), 67 (100), 54 (94).

7-Iodo-1-(trimethylsilyl)-1-heptyne (13b).

Prepared from (crude) **12b** according to a procedure described before.[2b] Distillation gave **13b** (76 %, based on **11a**), bp 108-110 °C (5 Torr). ^{1}H NMR (90 MHz): 3.24 (t, ^{3}J(7,6) = 6.4 Hz, 2H, H(7)), 2.45-2.10 (m, 2H, H(3)), 2.10-1.40 (m, 6H, H(4,5,6)), 0.22 (s, 9H, TMS). MS: 294 (2, $M^{+\cdot}$), 279 (29), 185 (100), 151 (9), 123 (10), 109 (10), 93 (20), 73 (67), 59 (9), 45 (3). HRMS ($C_{10}H_{19}ISi$): calc. 294.0300, found 294.030.

8-Iodo-1-(trimethylsilyl)-1-octyne (13c).

Prepared from (crude) **12c** according to a procedure described before.[2b] Distillation gave **13c** (84 %, based on **11a**), bp 85 °C

($2 \cdot 10^{-2}$ mbar). ^{1}H NMR (90 MHz): 3.23 (t, ^{3}J(8,7) = 6.8 Hz, 2H, H(8)), 2.43-2.10 (m, 2H, H(3)), 2.10-1.25 (m, 8H, H(4,5,6,7)), 0.20 (s, 9H, TMS). MS: 308 (1, $M^{+\cdot}$), 293 (32), 211 (4), 185 (100), 165 (7), 155 (7), 137 (9), 123 (8), 107 (30), 96 (10), 83 (15), 73 (55), 59 (15), 41 (11). HRMS ($C_{11}H_{21}ISi$): calc. 308.048, found 308.044.

1-Iodo-5-decyne (13d)
Prepared from (crude) **12d** according to a procedure described before.[2b] Distillation gave **13d** (62 %, based on **11b**), bp 100-105 °C (5 Torr). ^{1}H NMR (90 MHz): 3.23 (t, ^{3}J(1,2) = 6.6 Hz, 2H, H(1)), 2.45-1.20 (m, 12H, H(2,3,4,7,8,9)), 1.20-0.80 (m, 3H, H(10)). MS: 264 (5, $M^{+\cdot}$), 183 (12), 155 (9), 127 (6), 109 (4), 95 (100), 81 (85), 67 (63), 55 (43), 41 (50). HRMS ($C_{10}H_{17}I$): calc. 264.0374, found 264.034.

Triphenyl(6-(trimethylsilyl)-5-hexynyl)phosphonium iodide (14a).
A magnetically stirred solution of iodide **13a** (49.6 g, 0.177 mol) and triphenylphosphine (46.4 g, 0.177 mol) in benzene (106 ml) was heated at reflux temperature for 6 h. The precipitate was filtered, washed with benzene and dried *in vacuo* at 50 °C, giving **14a** (74.4 g, 78 %).

Triphenyl(7-(trimethylsilyl)-6-heptynyl)phosphonium iodide (14b).
Prepared from **13b** according to the same procedure as described for the synthesis of **14a**. Evaporation of benzene gave **14b** as a colourless viscous oil (yield: 96 %). ^{1}H NMR (90 MHz): 8.00-7.60 (m, 15H, C_6H_5), 3.85-3.35 (m, 2H, H(1')), 2.30-2.00 (m, 2H, H(5')), 2.00-1.35 (m, 6H, H(2',3',4')), 0.10 (s, 9H, TMS).

Triphenyl(8-(trimethylsilyl)-7-octynyl)phosphonium iodide (14c).
Prepared from **13c** according to the same procedure as described for the synthesis of **14a**. Evaporation of benzene gave **14c** as a colourless viscous oil (yield: 90 %). ^{1}H NMR (90 MHz): 8.00-7.60 (s, 15H, C_6H_5), 3.80-3.40 (m, 2H, H(1')), 2.25-2.00 (m, 2H, H(6')), 1.95-1.10 (m, 8H, H(2',3',4',5')), 0.10 (s, 9H, TMS).

5-Decynyltriphenylphosphonium iodide (14d).
Prepared from **13d** according to the same procedure as described for the synthesis of **14a**. Evaporation of benzene gave **14d** as a colourless viscous oil (yield: 95 %). ^{1}H NMR (90 MHz): 8.00-7.60 (m, 15H, C_6H_5), 3.90-3.45 (m, 2H, H(1')), 2.40-1.60 (m, 8H), 1.50-1.15 (m, 4H), 1.00-0.70 (m, 3H, H(10')).

1-Hydroxy-3-methoxypropanone (24).
To a magnetically stirred solution of 3-O-methylglyceraldehyde (**23**)[9] (65.4 g, 0.628 mol) in dioxane (260 ml) was added triethylamine (2.32 g, 0.0229 mol). The mixture was heated under reflux for 4 h and then concentrated *in vacuo*. The crude reaction product (62.5 g) was used as such in the following step. ^{1}H NMR (90 MHz): 4.50 (s, 2H), 4.18 (s, 2H), 3.50 (s, 3H).

1-Methoxy-3-(2-tetrahydropyranyloxy)propanone (19).
A solution of crude **24**, obtained from the experiment described above, 2,3-dihydro-4*H*-pyran (DHP, 60.4 g, 0.718 mol) and pyridinium *p*-toluenesulfonate (PPTS, 14.5 g, 57.4 mmol) in CH_2Cl_2 (75 ml) was stirred at room temperature for 92 h. The reaction mixture was poured onto saturated $NaHCO_3$ solution and the aqueous layer was extracted four times with CH_2Cl_2. The combined organic phases were washed with water, dried (Na_2SO_4) and concentrated *in vacuo*.
Column chromatography (40 % ethyl acetate/60 % petroleum ether 40-60) gave **19** (25.5 g, 24 %, based on **23**). ^{1}H NMR (90 MHz): 4.65 (m, 1H, H(2'-THP)), 4.36 (AB system, δ(A) = 4.49, J(AB) = 18.4 Hz, 1H, δ(B) = 4.23, J(BA) =18.4 Hz, 1H), 4.27 (s, 2H), 4.05-3.38 (m, 2H, H(6'-THP)), 3.43 (s, 3H, OCH_3), 2.00-1.45 (m, 6H, H(3'-THP,4'-THP,5'-THP)). MS: 188 (0.2, $M^{+\cdot}$), 187 (2), 158 (8), 115 (3), 101 (9), 85 (100), 67 (11), 57 (14), 45 (37). HRMS($C_9H_{16}O_4$): calc. 188.1044, found 188.1122.

1-(2-Tetrahydropyranyloxy)-2-(2-tetrahydropyranyloxymethyl)-8-(trimethylsilyl)-2-octen-7-yne (16a).
To a magnetically stirred suspension of **14a** (68.8 g, 0.127 mol) in THF (190 ml), cooled at -20 °C, was added dropwise *n*-BuLi (1.6 M solution in *n*-hexane, 79.4 ml, 0.127 mol). The reaction mixture was allowed to warm-up to room temperature in 3.5 h after which stirring was continued for another 0.5 h. Then, at -30 °C, α,α'-bis(2- tetrahydropyranyloxy)acetone (**15**)[6] (32.8 g, 0.127 mol) was added in 5 minutes. The reaction mixture was allowed to warm-up to room temperature overnight (12 h), whereafter stirring was continued for another 52 h. Then, it was filtered and the filtrate was poured onto saturated $NaHCO_3$ solution. The water layer was extracted four times with diethyl ether and the combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. In order to remove by-products and the last amounts of triphenylphosphine oxide, the crude reaction product was shaken with four portions of pentane. The combined pentane washings were dried (Na_2SO_4) and concentrated *in vacuo*, giving **16a** (39.4 g, 79 %). ^{1}H NMR (90 MHz): 5.69 (t, ^{3}J(3,4) = 7.6 Hz, 1H, H(3)), 4.65 (bs, 2H, H(2'-THP)), 4.40-3.95 (m, 4H, H(1), C(2)CH_2O), 3.95-3.40 (m, 4H, H(6'-THP)), 2.26 (m, 4H, H(4,6)), 2.0-1.4 (m, 14H, H(5,3'-THP,4'-THP,5'-

THP)), 0.18 (s, 9H, TMS).

1-(2-Tetrahydropyranyloxy)-2-(2-tetrahydropyranyloxymethyl)-9-(trimethylsilyl)-2-nonen-8-yne (16b).
Following the same procedure as described for the synthesis of **16a**, **16b** was prepared from **14b** and **15** in 90 % yield. ^{1}H NMR (90 MHz): 5.64 (t, ^{3}J(3,4) = 7.6 Hz, 1H, H(3)), 4.58 (bs, 2H, H(2'-THP)), 4.33-3.8 (m, 4H, H(1), C(2)CH_2O), 4.0-3.28 (m, 4H, H(6'-THP)), 2.30-1.97, 1.97-1.1 (m, 20H, H(4,5,6,7,3'-THP,4'-THP,5'-THP)), 0.09 (s, 9H, TMS).

1-Methoxy-2-(2-tetrahydropyranyloxymethyl)-10-(trimethylsilyl)-2-decen-9-yne (20).
Following the same procedure as described for the synthesis of **16a**, **20** was prepared from **14c** and **19** in 66 % yield. ^{1}H NMR (90 MHz): 5.62 (t, ^{3}J(3,4) = 7.0 Hz, 1H, H(3)), 4.56 (bs, 1H, H(2'-THP)), 4.30-3.20 (m, 6H, H(1,6'-THP), C(2)CH_2O), 3.24 (s, 3H, OCH_3), 2.3-1.9 (m, 4H, H(4,8)), 1.9-1.1 (m, 12H, H(5,6,7,3'-THP,4'-THP,5'-THP)), 0.09 (s, 9H, TMS).

1-(2-Tetrahydropyranyloxy)-2-(2-tetrahydropyranyloxymethyl)-2-dodecen-7-yne (16d).
Following the same procedure as described for the synthesis of **16a**, **16d** was prepared from **14d** and **15** in 95 % yield. ^{1}H NMR (90 MHz): 5.63 (t, ^{3}J(3,4) = 6.8 Hz, 1H, H(3)), 4.58 (bs, 2H, H(2'-THP)), 4.4-3.8 (m, 4H, H(1), C(2)CH_2O), 4.0-3.3 (m, 4H, H(6'-THP)), 2.4-1.9 (m, 6H, H(4,6,9)), 2.0-1.1 (m, 18H, H(5,10,11,3'-THP,4'-THP,5'-THP)), 1.05-0.70 (m, 3H, H(12)).

2-(6-(Trimethylsilyl)hex-5-ynylidene)-1,3-propanediol (17a).
To a solution of **16a** (42.6 g, 0.108 mol) in methanol (120 ml) was added Dowex 50W (X8, 200-400 mesh, 21.6 g) after which the mixture was stirred at room temperature for 2 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. In order to achieve complete conversion of **16a** to **17a**, the procedure was repeated two times. After the last run, the concentrated reaction product was dissolved in ethyl acetate and poured onto saturated $NaHCO_3$ solution. After extracting the water layer three times with ethyl acetate, the combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*, giving **17a** (21.3 g, 87 %). ^{1}H NMR (90 MHz): 5.56 (t, ^{3}J(1',2') = 7.8 Hz, 1H, H(1')), 4.36 (s, 2H, CH_2OH), 4.26 (s, 2H, CH_2OH), 2.45-1.90 (m, 4H, H(2',4')), 1.8-1.4 (m, 4H, H(3'), OH), 0.2 (s, 9H, TMS). MS: 209 (18), 193 (5), 183 (3), 169 (6), 147 (29), 133 (11), 129 (10), 119 (13), 117 (15), 91 (19), 78 (31), 75 (63), 73 (100), 59 (14), 55 (16).

2-(7-(Trimethylsilyl)hept-6-ynylidene)-1,3-propanediol (17b).
Prepared from **16b** in 92 % yield according to the same procedure as described for the synthesis of **17a**. ^{1}H NMR (90 MHz): 5.55 (t, ^{3}J(1',2') = 6.6 Hz, 1H, H(1')), 4.29 (bs, 2H, CH_2OH), 4.18 (bs, 2H, CH_2OH), 2.37-1.98 (m, 4H, H(2',5')), 1.80-1.25 (m, 6H, H(3',4'), OH), 0.13 (s, 9H, TMS).

2-(Methoxymethyl)-10-(trimethylsilyl)-2-decen-9-yn-1-ol (18c).
Following the same procedure as described for the synthesis of **17a**, **18c** was prepared from **20** in 91 % yield. **18c** Was obtained as a mixture of diastereomers. Major Component. ^{1}H NMR (90 MHz): 5.59 (t, ^{3}J(3,4) = 6.8 Hz, 1H, H(3)), 4.24 (s, 2H, CH_2OCH_3), 4.11 (d, ^{3}J(1,OH) = 3.6 Hz, 2H, H(1)), 3.32 (s, 3H, OCH_3), 2.36-1.9 (m, 4H, H(4,8)), 1.8-1.1 (m, 7H, H(5,6,7), OH), 0.15 (s, 9H, TMS). Minor Component. ^{1}H NMR (90 MHz): 5.66 (t, ^{3}J(3,4) = 6.8 Hz, 1H, H(3)), 4.00 (d, ^{4}J = 0.6 Hz, 2H, CH_2OCH_3), 4.11 (d, ^{3}J(1,OH) = 3.6 Hz, 2H, H(1)), 3.36 (s, 3H, OCH_3), 2.36-1.9 (m, 4H, H(4,8)), 1.8-1.1 (m, 7H, H(5,6,7), OH), 0.15 (s, 9H, TMS). MS (mixture of both components): 253 (3), 235 (3), 221 (3), 205 (6), 201 (5), 190 (17), 175 (9), 163 (8), 145 (17), 131 (41), 118 (30), 105 (35), 91 (51), 73 (100), 59 (37), 45 (41). HRMS ($C_{14}H_{25}O_2Si$ [M-CH_3]$^+$): calc. 253.1627, found 253.167.

2-(Dec-5-ynylidene)-1,3-propanediol (17d).
Prepared from **16d** in 83 % yield according to the same procedure as described for the synthesis of **17a**. ^{1}H NMR (90 MHz): 5.65 (t, ^{3}J(1',2') = 7.0 Hz, 1H, H(1')), 4.32 (bs, 2H, CH_2OH), 4.20 (bs, 2H, CH_2OH), 2.9-2.4 (m, 2H, OH), 2.4-1.8 (m, 6H, H(2',4',7')), 1.8-1.1 (m, 6H, H(3',8',9')), 1.1-0.6 (m, 3H, H(10')).

2-(Methoxymethyl)-8-(trimethylsilyl)-2-octen-7-yn-1-ol (18a).
To a magnetically stirred solution of **17a** (9.45 g, 41.8 mmol) and methyl iodide (23.7 g, 167 mmol) in THF (30 ml), cooled at 0 ^{o}C, was added dropwise in 1.5 h a suspension of NaH (41.8 mmol) in THF (20 ml). After the addition was completed, stirring was continued at room temperature for 2 h. The reaction mixture was poured onto saturated NH_4Cl solution and the aqueous layer was extracted four times with diethyl ether. The combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Column chromatography (25 % ethyl acetate/75 % petroleum ether 40-60) gave **18a** (3.32 g, 33 %). ^{1}H NMR (90 MHz): 5.65 (t, ^{3}J(3,4) = 7.6 Hz, 1H, H(3)), 4.15 (d, ^{3}J = 5 Hz, 2H, H(1)), 4.11 (bs, 2H, CH_2OCH_3), 3.38 (s, 3H, OCH_3), 2.4-2.0 (m, 4H, H(4,6)), 1.8-1.4 (m, 3H, H(5), OH), 0.18 (s, 9H, TMS).

2-(Methoxymethyl)-9-(trimethylsilyl)-2-nonen-8-yn-1-ol (18b).
Following the same procedure as described for the synthesis of **18a**, **18b** was prepared from **17b** in 30 % yield. **18b** Was obtained as a mixture of diastereomers. Component I. ^{1}H NMR (90 MHz): 5.64* (t, ^{3}J(3,4) = 6.8 Hz, 1H, H(3)), 4.23** (s, 2H, C*H*$_2$OCH$_3$), 4.18-4.03 (m, 2H, H(1)), 3.34 (s, 3H, OCH$_3$), 2.45-1.95 (m, 4H, H(4,7)), 1.85-1.30 (m, 4H, H(5,6)), 1.28 (t, ^{3}J(OH,1) = 6.8 Hz, 1H, OH), 0.14 (s, 9H, TMS). Component II. ^{1}H NMR (90 MHz): 5.57* (t, ^{3}J(3,4) = 6.8 Hz, 1H, H(3)), 3.98** (s, 2H, C*H*$_2$OCH$_3$), 4.18-4.03 (m, 2H, H(1)), 3.34 (s, 3H, OCH$_3$), 2.45-1.95 (m, 4H, H(4,7)), 1.85-1.30 (m, 4H, H(5,6)), 1.28 (t, ^{3}J(OH,1) = 6.8 Hz, 1H, OH), 0.14 (s, 9H, TMS).

2-(Methoxymethyl)-2-dodecen-7-yn-1-ol (18d).
To a mechanically stirred suspension of NaH (0.120 mol) in THF (200 ml) was added dropwise a solution of diol **17d** (25.1 g, 0.120 mol) in THF (50 ml). After 1 h reflux, the reaction mixture was cooled to room temperature. Methyl iodide (16.8 g, 0.118 mol) was added with vigorous stirring and in one portion. Stirring was continued for 18 h at room temperature whereafter aqueous work-up was performed as described above. Column chromatography (25 % ethyl acetate/75 % petroleum ether 40-60) gave **18d** as a mixture of diastereomers (7.71 g, 29 %). Component I. ^{1}H NMR (90 MHz): 5.64 (t, ^{3}J(3,4) = 8.0 Hz, 1H, H(3)), 4.26 (d, ^{3}J(1,OH) = 5.6 Hz, 2H, H(1)), 4.11 (bs, 2H, C*H*$_2$OCH$_3$), 3.36 (s, 3H, OCH$_3$), 2.45-2.00 (m, 6H, H(4,6,9)), 1.8-1.1 (m, 7H, H(5,10,11), OH), 1.1-0.8 (m, 3H, H(12)). Component II. ^{1}H NMR (90 MHz): 5.56 (t, ^{3}J(3,4) = 8.0 Hz, 1H, H(3)), 4.14 (d, ^{3}J(1,OH) = 5.6 Hz, 2H, H(1)), 4.00 (bs, 2H, C*H*$_2$OCH$_3$), 3.34 (s, 3H, OCH$_3$), 2.45-2.00 (m, 6H, H(4,6,9)), 1.8-1.1 (m, 7H, H(5,10,11), OH), 1.1-0.8 (m, 3H, H(12)).

1-Chloro-2-(methoxymethyl)-8-(trimethylsilyl)-2-octen-7-yne (21a).
Prepared from **18a** according to a procedure described before.[2b] Evaporative distillation (90-140 °C, 3 Torr) provided **21a** as a mixture of diastereomers (3.07 g, 86 %). Component I. ^{1}H NMR (90 MHz): 5.77* (t, ^{3}J(3,4) = 8.6 Hz, 1H, H(3)), 4.18** (s, 2H), 4.15** (s, 2H), 3.36*** (s, 3H, OCH$_3$), 2.48-2.10 (m, 4H, H(4,6)), 1.86-1.45 (m, 2H, H(5)), 0.20 (s, 9H, TMS). Component II. ^{1}H NMR (90 MHz): 5.68* (t, ^{3}J(3,4) = 8.6 Hz, 1H, H(3)), 4.11** (s, 2H), 3.99** (d, J = 1 Hz, 2H), 3.34*** (s, 3H, OCH$_3$), 2.48-2.10 (m, 4H, H(4,6)), 1.86-1.45 (m, 2H, H(5)), 0.20 (s, 9H, TMS). MS (mixture of both components): 243 (3), 177 (3), 149 (7), 135 (11), 119 (27), 117 (34), 109 (9), 105 (9), 97 (14), 93 (31), 91 (30), 89 (30), 79 (36), 73 (100), 67 (10), 59 (27), 55 (12). HRMS ($C_{12}H_{20}{}^{35}ClOSi$ [M-CH$_3$]$^+$, mixture of both components): calc. 243.0972, found 243.0964.

1-Chloro-2-(methoxymethyl)-9-(trimethylsilyl)-2-nonen-8-yne (21b).
Prepared from **18b** according to a procedure described before.[2b] Evaporative distillation (90-140 °C, 3 Torr) gave **21b** as a mixture of diastereomers (yield: 67 %). Major component. ^{1}H NMR (90 MHz): 5.79 (t, ^{3}J(3,4) = 8.4 Hz, 1H, H(3)), 4.11 (s, 2H, C*H*$_2$OCH$_3$), 4.04 (d, ^{4}J = 0.7 Hz, 2H, H(1)), 3.29 (s, 3H, OCH$_3$), 2.45-1.90 (m, 4H, H(4,7)), 1.80-1.35 (m, 4H, H(5,6)), 0.13 (s, 9H, TMS). Minor component. ^{1}H NMR (90 MHz): 5.69 (t, ^{3}J(3,4) = 8.4 Hz, 1H, H(3)), 4.11 (s, 2H, C*H*$_2$OCH$_3$), 3.95 (bs, 2H, H(1)), 3.28 (s, 3H, OCH$_3$), 2.45-1.90 (m, 4H, H(4,7)), 1.80-1.35 (m, 4H, H(5,6)), 0.13 (s, 9H, TMS). MS (mixture of both components): 257 (1), 189 (2), 163 (4), 149 (5), 133 (46), 117 (30), 105 (16), 93 (41), 79 (15), 73 (100), 59 (23), 45 (41). HRMS ($C_{13}H_{22}{}^{35}ClOSi$ [M-CH$_3$]$^+$, mixture of both components): calc. 257.1129, found 257.111.

1-Chloro-2-(methoxymethyl)-10-(trimethylsilyl)-2-decen-9-yne (21c).
Prepared from **18c** according to a procedure described before.[2b] Evaporative distillation (90-140 °C, 3 Torr) gave **21c** as a mixture of diastereomers (yield: 58 %). Component I. ^{1}H NMR (90 MHz): 5.78 (t, ^{3}J(3,4) = 8.6 Hz, 1H, H(3)), 4.13 (s, 2H, C*H*$_2$OCH$_3$), 4.07 (d, ^{4}J = 1.0 Hz, 2H, H(1)), 3.33 (s, 3H, OCH$_3$), 2.45-1.87 (m, 4H, H(4,8)), 1.80-1.15 (m, 6H, H(5,6,7)), 0.17 (s, 9H, TMS). Component II. ^{1}H NMR (90 MHz): 5.19 (t, ^{3}J(3,4) = 8.6 Hz, 1H, H(3)), 4.13 (s, 2H, C*H*$_2$OCH$_3$), 3.96 (s, 2H, H(1)), 3.31 (s, 3H, OCH$_3$), 2.45-1.87 (m, 4H, H(4,8)), 1.80-1.15 (m, 6H, H(5,6,7)), 0.17 (s, 9H, TMS).

1-Chloro-2-(methoxymethyl)-2-dodecen-7-yne (21d).
Prepared from **18d** according to a procedure described before.[2b] Evaporative distillation (90-140 °C, 3 Torr) gave **21d** as a mixture of diastereomers (yield: 74 %). Component I. ^{1}H NMR (90 MHz): 5.78 (t, ^{3}J(3,4) = 8.8 Hz, 1H, H(3)), 4.16 (s, 2H, C*H*$_2$OCH$_3$), 4.09 (s, 2H, H(1)), 3.33 (s, 3H, OCH$_3$), 2.47-1.88 (m, 6H, H(4,6,9)), 1.88-1.19 (m, 6H, H(5,10,11)), 1.09-0.79 (m, 3H, H(12)). Component II. ^{1}H NMR (90 MHz): 5.68 (t, ^{3}J(3,4) = 8.8 Hz, 1H, H(3)), 4.13 (s, 2H, C*H*$_2$OCH$_3$), 3.97 (d, ^{4}J = 0.6 Hz, 2H, H(1)), 3.32 (s, 3H, OCH$_3$), 2.47-1.88 (m, 6H, H(4,6,9)), 1.88-1.19 (m, 6H, H(5,10,11)), 1.09-0.79 (m, 3H, H(12)).

1-(Chloromagnesio)-2-(methoxymethyl)-8-(trimethylsilyl)-2-octen-7-yne (22a).
Magnesium (three times sublimed, turnings, diameter *ca.* 1 mm, 1.76 g, 72.4 mmol) in THF (30 ml) was activated with 1,2-dibromoethane (0.47 g, 2.5 mmol). The magnetically stirred mixture was cooled to 0 °C and a solution of chloride **21a** (2.59 g, 10.0 mmol) and *n*-decane (internal standard, 0.500 g) in THF (10 ml) was added dropwise in 10 h. Stirring was continued while

the reaction mixture was allowed to warm-up to room temperature overnight. The yield amounted to 84 %.

1-(Chloromagnesio)-2-(methoxymethyl)-9-(trimethylsilyl)-2-nonen-8-yne (22b).
Following the same procedure as described for the synthesis of **22a**, **22b** was prepared from **21b** in 76 % yield. In a second experiment, *n*-decane was used as internal standard.

1-(Chloromagnesio)-2-(methoxymethyl)-10-(trimethylsilyl)-2-decen-9-yne (22c).
Following the same procedure as described for the synthesis of **22a**, **22c** was prepared from **21c** in 60 % yield.

1-(Chloromagnesio)-2-(methoxymethyl)-2-dodecen-7-yne (22d).
Following the same procedure as described for the synthesis of **22a**, **22d** was prepared from **21d** in 78 % yield. In a second experiment, *n*-decane was used as internal standard.

General procedure for the preparation of the 1,5-annulated 4-methylenecyclopentenes 4.
Grignard reagents **22** were added in 5 minutes to a magnetically stirred solution of $ZnBr_2$ (1.5 equiv.) in THF (0.5 ml/mmol $ZnBr_2$). After the addition was completed, the reaction mixture was stirred for 0.5 h at room temperature. Stirring was continued at room temperature for another 1.5 h (**2a**) or the reaction mixture was heated under reflux for 2-24 h (**2b,c,d**). The reaction was monitored by quenching small portions of the reaction mixture with aqueous NH_4Cl. $[Pd(PPh_3)_4]$ (5-10 mol%) was added and the reaction mixture was stirred again, at room temperature (**3a,d**; 3.5 and 4 h, respectively) or at reflux temperature (**3b,c**; 2 and 4 h,respectively). The mixture was worked-up by pouring it onto saturated NH_4Cl solution and extracting the water layer four times with diethyl ether. The combined organic phases were washed with saturated $NaHCO_3$ solution and brine, dried (Na_2SO_4) and concentrated at reduced pressure using a 30 cm Vigreux column. The crude reaction product was analyzed by GLC, GCMS and NMR or, alternatively, purified by evaporative distillation. Yields are based on Grignard reagents **22**.

Reaction of 2a.
Zinc-ene reaction (RT, 2 h). NH_4Cl quench and work-up gave **5a** as a mixture of diastereomers (ratio: 82:18).
Pd(0)-catalyzed cyclization (RT, 3.5 h). Aqueous work-up gave **4a** (yield: 84 % [GLC]).

1-(1-(Methoxymethyl)ethenyl)-2-((trimethylsilyl)methylene)cyclopentane (5a).
Major component. ^1H NMR (250 MHz): 5.31 (q, ^4J = 2.3 Hz, 1H, =C*H*TMS), 5.15 (m, 1H, H(2')), 4.98 (m, 1H, H(2')), 3.96-3.76 (m, 2H, CH_2OCH_3), 3.33 (s, 3H, OCH_3), 3.22-3.08 (m, 1H, H(1)), 2.55-1.47 (m, 6H, H(3,4,5)), 0.09 (s, 9H, TMS). Minor component. ^1H NMR (250 MHz): 5.31 (q, ^4J = 2.3 Hz, 1H, =C*H*TMS), 5.02 (m, 1H, H(2')), 4.94 (m, 1H, H(2')), 3.96-3.76 (m, 2H, CH_2OCH_3), 3.29 (s, 3H, OCH_3), 3.22-3.08 (m, 1H, H(1)), 2.55-1.47 (m, 6H, H(3,4,5)), 0.16 (s, 9H, TMS). MS (mixture of both components): 224 (4, $M^{+\cdot}$), 209 (11), 192 (2), 179 (1), 151 (2), 135 (2), 119 (23), 105 (15), 91 (30), 89 (51), 79 (8), 73 (100), 59 (35).

4-Methylene-2-(trimethylsilyl)bicyclo[3.3.0]oct-1-ene (4a).
^1H NMR (250 MHz): 4.81 (septet, ^4J = 1.3 Hz, 1H, =CH_2), 4.77 (septet, ^4J = 1.3 Hz, 1H, =CH_2), 3.54-3.39 (m, 2H, H(3,5)), 3.17 (dquintet, ^2J = 18.8 Hz, ^4J = 1.5 Hz, 1H, H(3)), 2.29-2.19 (m, 2H), 2.08-1.90 (m, 3H), 1.29-1.06 (m, 1H), 0.09 (s, 9H, TMS). ^{13}C NMR (63 MHz): 163.3 (s, C(1^*)), 155.3 (s, C(4^*)), 128.1 (s, C(2)), 104.3 (tq, ^1J(CH) = 155 Hz, ^3J(CH) = 4 Hz, =CH_2), 57.9 (d, ^1J(CH) = 128 Hz, C(5)), 48.1 (tm, ^1J(CH) = 129 Hz, C(3)), 28.7 (t, ^1J(CH) = 130 Hz, C(6^{**})), 28.5 (t, ^1J(CH) = 130 Hz, C(7^{**})), 25.3 (t, ^1J(CH) = 128 Hz, C(8^{**})), -1.1 (q, ^1J(CH) = 118 Hz, TMS). MS: 192 (12, $M^{+\cdot}$), 177 (4), 161 (1), 149 (2), 134 (3), 118 (39), 105 (4), 91 (11), 75 (40), 73 (100), 59 (15). HRMS ($C_{12}H_{20}Si$): calc. 192.1334, found 192.1310.

Reaction of 2b.
Zinc-ene reaction (65 °C, 2 h). NH_4Cl quench and work-up gave **5b** as a mixture of diastereomers (ratio: 94:6).
Pd(0)-catalyzed cyclization (65 °C, 2 h). Aqueous work-up and evaporative distillation (100-140 °C, 1 Torr) gave **4b** (yield: 67 %). In another experiment, the yield was determined by GLC (52 %).

1-(1-(Methoxymethyl)ethenyl)-2-((trimethylsilyl)methylene)cyclohexane (5b).
Major component. ^1H NMR (250 MHz): 5.26 (m, 1H, =C*H*TMS), 5.08 (bs, 1H, =CH_2), 4.98 (bs, 1H, =CH_2), 3.83 (AB system, δ(A) = 3.88, J(AB) = 12.6 Hz, 1H, CH_2OCH_3, δ(B) = 3.78, J(BA) = 12.6 Hz, 1H, CH_2OCH_3), 3.33 (s, 3H, OCH_3), 2.75 (dd, ^3J(1,6) = 9.7 Hz and 3.8 Hz, 1H, H(1)), 2.46 (dm, J = 12.0 Hz, 1H, H(3)), 2.23 (t, J = 6.9 Hz, 1H), 2.15-1.97 (m, 2H), 1.87-1.36 (m, 4H), 0.09 (s, 9H, TMS). MS: 238 (1, $M^{+\cdot}$), 223 (3), 166 (2), 133 (13), 119 (13), 105 (12), 91 (29), 89 (47), 79

(8), 73 (100), 59 (40), 45 (33). Minor component. ^{1}H NMR (250 MHz): 5.32 (d, ^{4}J = 1.5 Hz, 1H, =C*H*TMS), 5.08 (bs, 1H, =CH_2), 4.98 (bs, 1H, =CH_2), 3.83 (AB system, δ(A) = 3.88, J(AB) = 12.6 Hz, 1H, CH_2OCH_3, δ(B) = 3.78, J(BA) = 12.6 Hz, 1H, CH_2OCH_3), 3.36 (s, 3H, OCH_3), 2.75 (dd, ^{3}J(1,6) = 9.7 Hz and 3.8 Hz, 1H, H(1)), 2.46 (dm, J = 12.0 Hz, 1H, H(3)), 2.23 (t, J = 6.9 Hz, 1H), 2.15-1.97 (m, 2H), 1.87-1.36 (m, 4H), 0.06 (s, 9H, TMS). MS: 238 (0.4, $M^{+\cdot}$), 223 (2), 166 (2), 133 (12), 119 (15), 105 (15), 89 (50), 73 (100), 59 (47), 45 (30).

7-Methylene-9-(trimethylsilyl)bicyclo[4.3.0]non-9-ene (4b).
^{1}H NMR (400 MHz): (1) 4.92 (m, 1H, =CH_2), (2) 4.86 (m, 1H, =CH_2), (3) 3.13 (m, 2H, H(8)), (4) 2.94 (m, 1H, H(6)), (5) 2.60 (dm, ^{2}J = 13.5 Hz, 1H, H(2)), (6) 2.07 (m, 1H, H(5)), (7) 1.96 (m, 1H, H(2)), (8) 1.82 (m, 1H, H(3)), (9) 1.79 (m, 1H, H(4)), (10) 1.43 (m, 1H, H(4)), (11) 1.18 (m, 1H, H(3)), (12) 1.11 (m, 1H, H(5)), (13) 0.12 (s, 9H, TMS). 2D COSY NMR (400 MHz): 1(2,3,4), 2(3,4), 3(7), 4(6,12), 5(7,8,9,11), 6(8^W,9,10,12), 7(8,9,11), 8(9,10,11,12), 9(10,11,12), 10(11,12), 11(12). 2D NOESY NMR (400 MHz, τ_m = 0.75 s): 1(2,3,4^W), 2(3,4^W), 3(13), 5(7,8^W,9,13), 6(12), 9(10,11), 10(11), 11(12). ^{13}C NMR (63 MHz): 155.55 (s, C(1*)), 155.51 (s, C(7*)), 129.0 (s, C(9)), 104.5 (tq, ^{1}J(CH) = 155 Hz, ^{3}J(CH) = 4 Hz, =CH_2), 52.4 (d, ^{1}J(CH) = 127 Hz, C(6)), 43.4 (tm, ^{1}J(CH) = 129 Hz, C(8)), 34.2 (t, ^{1}J(CH) = 129 Hz, C(2**)), 29.9 (t, ^{1}J(CH) = 130 Hz, C(3**)), 27.3 (t, ^{1}J(CH) = 125 Hz, C(4**)), 25.7 (t, ^{1}J(CH) = 122 Hz, C(5**)), -0.4 (q, ^{1}J(CH) = 119 Hz, TMS). MS: 206 (44, $M^{+\cdot}$), 191 (14), 149 (4), 132 (48), 117 (17), 104 (12), 91 (16), 73 (100), 59 (12), 45 (9). HRMS ($C_{13}H_{22}Si$): calc. 206.1491, found 206.136.

Reaction of 2c.
Zinc-ene reaction (65 °C, 24 h). NH_4Cl quench and work-up gave **5c** as a mixture of diastereomers (ratio: 94:6).
Pd(0)-catalyzed cyclization (65 °C, 4 h). Aqueous work-up and evaporative distillation (100-140 °C, 1 Torr) gave **4c** (yield: 44 %).

1-(1-(Methoxymethyl)ethenyl)-2-((trimethylsilyl)methylene)cycloheptane (5c).
Major component. ^{1}H NMR (250 MHz): 5.28 (s, 1H, =C*H*TMS), 5.05 (m, 1H, =CH_2), 4.96 (bs, 1H, =CH_2), 3.93-3.77 (m, 2H, CH_2OCH_3), 3.30 (s, 3H, OCH_3), 2.97 (dd, ^{3}J(1,7) = 10.9 Hz and 4.0 Hz, 1H, H(1)), 2.43-2.31 (m, 1H, H(3)), 2.23 (t, J = 6.8 Hz, 1H), 2.18-1.98 (m, 1H), 1.98-1.67 (m, 2H), 1.57-1.19 (m, 5H), 0.10 (s, 9H, TMS). MS: 252 (1, $M^{+\cdot}$), 237 (5), 147 (11), 133 (12), 119 (11), 105 (22), 91 (23), 89 (47), 79 (12), 73 (100), 59 (30), 45 (29). Minor component. ^{1}H NMR (250 MHz): 5.46 (d, ^{4}J = 0.8 Hz, 1H, =C*H*TMS), 5.05 (m, 1H, =CH_2), 4.96 (bs, 1H, =CH_2), 3.93-3.77 (m, 2H, CH_2OCH_3), 3.35 (s, 3H, OCH_3), 2.97 (dd, ^{3}J(1,7) = 10.9 Hz and 4.0 Hz, 1H, H(1)), 2.43-2.31 (m, 1H, H(3)), 2.23 (t, J = 6.8 Hz, 1H), 2.18-1.98 (m, 1H), 1.98-1.67 (m, 2H), 1.57-1.19 (m, 5H), 0.10 (s, 9H, TMS). MS: 252 (1, $M^{+\cdot}$), 237 (6), 165 (3), 147 (13), 133 (13), 119 (12), 105 (24), 91 (25), 89 (50), 79 (13), 73 (100), 59 (43), 45 (38).

8-Methylene-10-(trimethylsilyl)bicyclo[5.3.0]dec-10-ene (4c).
^{1}H NMR (250 MHz): 4.89 (m, 1H, =CH_2), 4.84 (m, 1H, =CH_2), 3.28-3.18 (m, 1H, H(7)), 3.11 (quintet, ^{4}J = 2.1 Hz, 2H, H(9)), 2.53-2.26 (m, 2H, H(2)), 1.90-1.36 (m, 8H, H(3,4,5,6)), 0.12 (s, 9H, TMS). ^{13}C NMR (63 MHz): 158.3 (s, C(1*)), 156.3 (s, C(8*)), 131.8 (s, C(10)), 104.0 (t, ^{1}J(CH) = 154 Hz, =CH_2), 55.3 (d, ^{1}J(CH) = 126 Hz, C(7)), 43.5 (tm, ^{1}J(CH) = 130 Hz, C(9)), 34.7 (t, ^{1}J(CH) = 128 Hz, C(2**)), 31.1 (t, ^{1}J(CH) = 114 Hz, C(3**)), 30.8 (t, ^{1}J(CH) = 114 Hz, C(4**)), 28.3 (t, ^{1}J(CH) = 123 Hz, C(5**)), 28.0 (t, ^{1}J(CH) = 123 Hz, C(6**)), -0.5 (q, ^{1}J(CH) = 116 Hz, TMS). MS: 220 (34, $M^{+\cdot}$), 205 (6), 146 (37), 131 (12), 118 (7), 105 (6), 91 (9), 73 (100), 59 (12), 45 (7). HRMS ($C_{14}H_{24}Si$): calc. 220.1647, found 220.160.

Reaction of 2d.
Zinc-ene reaction (65 °C, 8 h). NH_4Cl quench and work-up gave (*E*)-**5d** exclusively.
Pd(0)-catalyzed cyclization (RT, 4 h). Aqueous work-up and evaporative distillation (100-140 °C, 1 Torr) gave **4d** (yield: 75 %). In another experiment, the yield was determined by GLC (73 %).

(*E*)-1-(1-(Methoxymethyl)ethenyl)-2-pentylidenecyclopentane [(*E*)-5d].
^{1}H NMR (250 MHz): 5.16 (tq → 10 lines, ^{3}J(1',2') = 7.2 Hz, ^{4}J(1',1) = ^{4}J(1',3) = 2.5 Hz, 1H, H(1')), 5.11 (q, ^{4}J = 2.1 Hz, 1H, =CH_2), 4.97 (m, 1H, =CH_2), 3.88 (AB system, δ(A) = 3.92, dm, J(AB) = 13.0 Hz, 1H, CH_2OCH_3, δ(B) = 3.83, dt, J(BA) = 13.0 Hz, ^{4}J = 1.1 Hz, 1H, CH_2OCH_3), 3.34 (s, 3H, OCH_3), 3.17-3.06 (m, 1H, H(1)), 2.42-2.10 (m, 2H, H(3)), 2.06-1.94 (m, 2H, H(2')), 1.94-1.68 (m, 2H, H(4*)), 1.65-1.47 (m, 2H, H(5*)), 1.39-1.22 (m, 4H, H(3',4')), 0.95-0.83 (m, 3H, H(5')).

2-Butyl-4-methylenebicyclo[3.3.0]oct-1-ene (4d).
^{1}H NMR (250 MHz): 4.85-4.77 (m, 2H, =CH_2), 3.51-3.32 (m, 2H, H(3,5)), 2.98 (B part of AB system, ^{2}J = 18.0 Hz, 1H, H(3)), 2.26-1.84 (m, 7H, H(6,7,8,1')), 1.48-1.09 (m, 5H, H(7,2',3')), 0.90 (t, ^{3}J(4',3') = 6.9 Hz, 3H, H(4')). ^{13}C NMR (63 MHz): 154.5

(s, C(1*)), 144.5 (s, C(2*)), 129.7 (s, C(4)), 104.9 (tq, ^{1}J(CH) = 155 Hz, ^{3}J(CH) = 4 Hz, =CH_2), 55.6 (d, ^{1}J(CH) = 127 Hz, C(5)), 46.2 (tm, ^{1}J(CH) = 133 Hz, C(3)), 30.1 (tm, ^{1}J(CH) = 133 Hz, CH_2), 29.5 (t, ^{1}J(CH) = 131 Hz, CH_2), 28.9 (t, ^{1}J(CH) = 128 Hz, CH_2), 27.9 (td, ^{1}J(CH) = 131 Hz, J(CH) = 4 Hz, CH_2), 22.7 (tm, ^{1}J(CH) = 133 Hz, CH_2), 22.6 (t, ^{1}J(CH) = 124 Hz, CH_2), 13.9 (q, ^{1}J(CH) = 124 Hz, CH_3). MS: 176 (27, $M^{+\cdot}$), 147 (13), 133 (22), 119 (100), 105 (22), 91 (53), 77 (11), 65 (6), 53 (3), 41 (12). HRMS ($C_{13}H_{20}O$): calc. 176.1565, found 176.149.

2-(2-Propynyloxymethyl)-2-propen-1-ol (26a).
After preparing the alkoxide from diol **25a**[15] (13.2 g, 0.150 mol) and NaH (0.150 mol) in THF (150 ml) according to the procedure described for the synthesis of **18d**, propargyl bromide (17.9 g, 0.150 mol) was added with vigorous stirring and in one portion. The reaction mixture was heated under reflux for 18 h, cooled, and worked-up as described before. Column chromatography (20 % ethyl acetate/80 % petroleum ether 40-60) gave **26a** (10.4 g, 55 %). ^{1}H NMR (90 MHz): 5.20 (m, 2H, H(3)), 4.17 (s, 2H, H(1)), 4.14 (s, 2H, C(2)CH_2O), 4.16 (d, ^{4}J = 2.2 Hz, 2H, OCH_2C≡C), 2.47 (t, ^{4}J = 2.2 Hz, 1H, C≡CH), 2.15 (s, 1H, OH).

2-(2-Propynyloxymethyl)-2-penten-1-ol (26b).
Prepared from diol **25b**[2b] according to the procedure described for the synthesis of **26a**. Column chromatography (25 % ethyl acetate/75 % petroleum ether 40-60) gave **26b** as a mixture of diastereomers (5.00 g, 35 %). Component I. ^{1}H NMR (90 MHz): 5.70* (t, ^{3}J(3,4) = 5.6 Hz, 1H, H(3)), 4.24 (s, 2H, C(2)CH_2O), 4.16 (d, ^{4}J = 2.0 Hz, 2H, OCH_2C≡CH), 4.40-4.00 (m, 2H, H(1)), 2.49 (t, ^{4}J = 2.0 Hz, 1H, C≡CH), 2.37-1.90 (m, 2H, H(4)), 1.78 (bs, 1H, OH), 1.29** (t, ^{3}J(5,4) = 7.6 Hz, 3H, H(5)). Component II. ^{1}H NMR (90 MHz): 5.64* (t, ^{3}J(3,4) = 5.6 Hz, 1H, H(3)), 4.24 (s, 2H, C(2)CH_2O), 4.16 (d, ^{4}J = 2.0 Hz, 2H, OCH_2C≡CH), 4.40-4.00 (m, 2H, H(1)), 2.49 (t, ^{4}J = 2.0 Hz, 1H, C≡CH), 2.37-1.90 (m, 2H, H(4)), 1.78 (bs, 1H, OH), 1.05** (t, ^{3}J(5,4) = 7.6 Hz, 3H, H(5)).

2-(3-(Trimethylsilyl)-2-propynyloxymethyl)-2-propen-1-ol (28a).
To a mechanically stirred solution of **26a** (6.30 g, 50.0 mmol) in diethyl ether (150 ml), cooled at -40 °C, was added in 1 h *n*-BuLi (1.6 M solution in *n*-hexane, 62.5 ml, 100 mmol). The temperature of the resulting suspension was maintained at -40 °C while chlorotrimethylsilane (12.0 g, 110.0 mmol) was introduced over a period of 30 minutes. The mixture was allowed to warm-up to room temperature in 1 h whereafter stirring was continued for another 18 h. After pouring the reaction mixture onto saturated $NaHCO_3$ solution, the water layer was extracted four times with diethyl ether. The combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. In order to effect cleavage of the trimethylsilyl ether, the crude reaction product was boiled for 5 h with citric acid in methanol (5 %, 250 ml). The reaction mixture was concentrated *in vacuo*, diluted with ethyl acetate and poured onto saturated $NaHCO_3$ solution. Work-up was completed as described above. Evaporative distillation of the crude product gave **28a** (7.31 g, 75 %).
^{1}H NMR (90 MHz): 5.20 (m, 2H, H(3)), 4.18 (bs, 2H, H(1)), 4.15 (s, 2H, OCH_2C≡C), 4.14 (bs, 2H, C(2)CH_2O), 2.05 (bs, 1H, OH), 0.2 (s, 9H, TMS).

2-(3-(Trimethylsilyl)-2-propynyloxymethyl)-2-penten-1-ol (28b).
Prepared from **26b** in 89 % yield according to the same procedure as described for the synthesis of **28a**. **28b** Was obtained as a mixture of diastereomers. Component I. ^{1}H NMR (90 MHz): 5.68* (t, ^{3}J(3,4) = 7.6 Hz, 1H, H(3)), 4.24 (bs, 2H), 4.15 (s, 2H, OCH_2C≡C), 4.13 (bs, 2H), 2.18 (quintet, ^{3}J(4,5) = ^{3}J(4,3) = 7.6 Hz, 2H, H(4)), 2.2-1.9 (m, 1H, OH), 1.04 (t, ^{3}(5,4) = 7.6 Hz, 3H, H(5)), 0.22 (s, 9H, TMS). Component II. ^{1}H NMR (90 MHz): 5.61* (t, ^{3}J(3,4) = 7.6 Hz, 1H, H(3)), 4.24 (bs, 2H), 4.15 (s, 2H, OCH_2C≡C), 4.13 (bs, 2H), 2.18 (quintet, ^{3}J(4,5) = ^{3}J(4,3) = 7.6 Hz, 2H, H(4)), 2.2-1.9 (m, 1H, OH), 1.04 (t, ^{3}(5,4) = 7.6 Hz, 3H, H(5)), 0.22 (s, 9H, TMS).

3-Chloro-2-(3-(trimethylsilyl)-2-propynyloxymethyl)-1-propene (29a).
Prepared from **28a** according to the same procedure as described for the synthesis of **21a**. Evaporative distillation (90-140 °C, 3 Torr) gave **29a** in 90 % yield. ^{1}H NMR (90 MHz): 5.31 (m, 2H, H(1)), 4.16 (s, 4H, CH_2OCH_2), 4.10 (s, 2H, H(3)), 0.20 (s, 9H, TMS).

1-Chloro-2-(3-(trimethylsilyl)-2-propynyloxymethyl)-2-pentene (29b).
Prepared from **28b** according to the same procedure as described for the synthesis of **21a**. Evaporative distillation (90-140 °C, 3 Torr) gave **29b** as a mixture of diastereomers (yield: 86 %). Component I. ^{1}H NMR (90 MHz): 5.82* (t, ^{3}J(3,4) = 7.4 Hz, 1H, H(3)), 4.24** (s, 2H, C(2)CH_2O), 4.14 (s, 2H, OCH_2C≡C), 4.11*** (s, 2H, H(1)), 2.21 (quintet, ^{3}J(4,3) = ^{3}J(4,5) = 7.4 Hz, 2H, H(4)), 1.07**** (t, ^{3}J(5,4) = 7.4 Hz, 3H, H(5)), 0.22 (s, 9H, TMS). Component II. ^{1}H NMR (90 MHz): 5.74* (t, ^{3}J(3,4) = 7.4 Hz, 1H, H(3)), 4.17** (s, 2H, C(2)CH_2O), 4.14 (s, 2H, OCH_2C≡C), 4.10*** (s, 2H, H(1)), 2.21 (quintet, ^{3}J(4,3) = ^{3}J(4,5) = 7.4 Hz, 2H, H(4)), 1.04**** (t, ^{3}J(5,4) = 7.4 Hz, 3H, H(5)), 0.22 (s, 9H, TMS).

1-(2-(Chloromethyl)-2-propenyloxy)-2-butyne (29c).
To a mechanically stirred suspension of NaH (60.0 mmol) in THF (120 ml) was added dropwise 2-butyn-1-ol (4.20 g, 60.0 mmol). After refluxing for 1 h, the reaction mixture was cooled to room temperature. Then, with vigorous stirring, 3-chloro-2-(chloromethyl)-1-propene (**31**) (7.50 g, 60.0 mol) was added in one portion. The mixture was heated under reflux for 18 h, cooled, and then poured onto saturated $NaHCO_3$ solution. After extracting the aqueous layer four times with diethyl ether, the combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. Column chromatography (3 % ethyl acetate/97 % petroleum ether 40-60) of the crude reaction product gave **29c** (5.33 g, 56 %). The chloride was purified further by evaporative distillation (150 °C, 50 Torr). ^{1}H NMR (90 MHz): 5.40-5.24 (m, 2H, $=CH_2$), 4.14 (m, 6H, CH_2OCH_2, CH_2Cl), 1.79 (t, $^5J(4,1) = 2.4$ Hz, 3H, H(4)). MS: 130 (4), 128 (13), 123 (7), 113 (3), 109 (8), 105 (5), 95 (9), 93 (36), 79 (13), 77 (13), 69 (15), 53 (100), 50 (14). HRMS ($C_8H_{11}O$ [M-^{35}Cl]$^+$): calc. 123.0810, found 123.0808.

5-(2-(Chloromethyl)-2-propenyloxy)-2-pentyne (29d).
Prepared from **31** and 3-pentyn-1-ol according to the same procedure as described for the synthesis of **29c**. Distillation gave **29d** in 45 % yield, bp 59-62 °C (1 Torr). ^{1}H NMR (90 MHz): 5.37-5.23 (m, 2H, $=CH_2$), 4.13 (s, 2H, $=C(C)CH_2O$), 4.12 (s, 2H, CH_2Cl), 3.51 (t, $^3J(5,4) = 6.6$ Hz, 2H, H(5)), 2.44 (tq → 10 lines, $^3J(4,5) = 6.6$ Hz, $^5J(4,1) = 2.4$ Hz, 2H, H(4)), 1.80 (t, $^5J(1,4) = 2.4$ Hz, 3H, H(1)). MS: 171 (0.2), 157 (9), 137 (30), 119 (8), 109 (9), 97 (12), 89 (43), 77 (11), 67 (35), 53 (100). HRMS ($C_9H_{13}O$ [M-^{35}Cl]$^+$): calc. 137.0966, found 137.0964.

3-(Chloromagnesio)-2-(3-(trimethylsilyl)-2-propynyloxymethyl)-1-propene (30a).
Following the same procedure as described for the synthesis of **22a**, **30a** was prepared from **29a** in 82 % yield. *n*-Decane was added as internal standard.

1-(Chloromagnesio)-2-(3-(trimethylsilyl)-2-propynyloxymethyl)-2-pentene (30b).
Following the same procedure as described for the synthesis of **22a**, **30b** was prepared from **29b** in 77 % yield. *n*-Decane was added as internal standard.

1-(2-(Chloromagnesiomethyl)-2-propenyloxy)-2-butyne (30c).
Following the same procedure as described for the synthesis of **22a**, **30c** was prepared from **29c** in 80 % yield. *n*-Dodecane was added as internal standard.

5-(2-(Chloromagnesiomethyl)-2-propenyloxy)-2-pentyne (30d).
Following the same procedure as described for the synthesis of **22a**, **30d** was prepared from **29d** in 100 % yield. *n*-Tridecane was added as internal standard.

Attempted preparation of 4-methylenecyclopentenes 9 from 6.
Grignard reagents **30** (10-15 mmol) were added in 5 minutes to a magnetically stirred solution of $ZnBr_2$ (1.5 equiv.) in THF (0.5 ml/mmol $ZnBr_2$). After 0.5 h stirring, the reaction mixture was heated in a Carius tube at 75-130 °C for 24 h (Table 2). After cooling, a small portion of the mixture was subjected to a NH_4Cl and/or to a D_2O quench, worked-up as described before and analyzed by GLC, GCMS and NMR. The (unsuccessful) attempt to achieve Pd(0)-catalyzed rearrangement of **7b** was performed according to the same procedure as described for the conversion of **3** to **4** (conditions: 75 °C, 24 h). Yields (determined by GLC) are based on Grignard reagents **30**.

Rearrangement of 6a (130 °C, 24 h).
NH_4Cl (D_2O) quench and work-up gave **32a** (**32a'**) (yield: 7 %).

2-(2-Methyl-2-propenyloxymethyl)-1-(trimethylsilyl)-4-(3-(trimethylsilyl)-2-propynyloxymethyl)-1,4-pentadiene (32a).
^{1}H NMR (250 MHz): 5.76 (bs, 1H, H(1)), 5.14 (m, 1H, $=CH_2$), 4.97 (bs, 2H, $=CH_2$), 4.90 (bs, 1H, $=CH_2$), 4.15 (s, 2H, OCH_2), 3.99 (bs, 2H, OCH_2), 3.87 (bs, 2H, OCH_2), 3.85 (d, $^4J = 1.2$ Hz, 2H, OCH_2), 2.91 (bs, 2H, H(3)), 1.75 (bs, 3H, CH_3), 0.19 (s, 9H, TMS), 0.13 (s, 9H, TMS).

[1-$^2H_1$]-2-(2-Methyl-2-propenyloxymethyl)-1-(trimethylsilyl)-4-(3-(trimethylsilyl)-2-propynyloxymethyl)-1,4-pentadiene (32a').
^1H NMR (250 MHz): 5.14 (m, 1H, $=CH_2$), 4.97 (bs, 2H, $=CH_2$), 4.90 (bs, 1H, $=CH_2$), 4.15 (s, 2H, OCH_2), 3.99 (bs, 2H, OCH_2), 3.87 (bs, 2H, OCH_2), 3.85 (s, 2H, OCH_2), 2.91 (bs, 2H, H(3)), 1.75 (bs, 3H, CH_3), 0.19 (s, 9H, TMS), 0.13 (s, 9H, TMS).

Rearrangement of 6b (100 °C, 24 h).
NH_4Cl quench and work-up gave **10b** (yield: 74 %).

4-Ethyl-3-methylene-5-((trimethylsilyl)methylene)oxane (10b).
^1H NMR (250 MHz): 5.30 (bs, 1H, $=CHTMS$), 4.87 (bs, 1H, $=CH_2$), 4.78 (bs, 1H, $=CH_2$), 4.11 (AB system, δ(A) = 4.27, J(AB) = 12.6 Hz, 1H, H(6), δ(B) = 3.95, J(BA) = 12.6 Hz, 1H, H(6)), 4.13 (AB system, δ(A) = 4.19, J(AB) = 13.2 Hz, 1H, H(2), δ(B) = 4.07, J(BA) = 13.2 Hz, 1H, H(2)), 3.05 (dd, $^3J(4,1')$ = 10.4 Hz and 4.9 Hz, 1H, H(4)), 1.89-1.42 (m, 2H, H(1')), 0.89 (t, $^3J(2',1')$ = 7.4 Hz, 3H, H(2')), 0.14 (s, 9H, TMS). MS: 210 (1, $M^{+\cdot}$), 209 (3), 195 (13), 181 (33), 167 (4), 142 (3), 105 (12), 91 (22), 79 (10), 77 (10), 75 (77), 73 (100), 67 (12), 59 (25). HRMS ($C_{12}H_{21}OSi$ $[M-H]^+$): calc. 209.1362, found 209.13.

Rearrangement of 6c (75 °C, 24 h).
NH_4Cl quench and work-up gave **10c** (yield: 4 %) and **33c** (yield: 83 %).

3-Ethylidene-5-methyleneoxane (10c).
^1H NMR (250 MHz): 5.38 (qm, ^3J = 6.5 Hz, 1H, $=CHCH_3$), 4.83 (m, 2H, $=CH_2$), 4.15 (bs, 2H, H(2)), 4.07 (bs, 2H, H(6)), 3.05 (bs, 2H, H(4)), 1.65 (dm, ^3J = 6.5 Hz, 3H, $=CHCH_3$). MS: 124 (0.3, $M^{+\cdot}$), 123 (2), 109 (21), 94 (27), 79 (35), 69 (19), 53 (100).

4-Methyl-2-methylene-4,5-hexadien-1-ol (33c).
^1H NMR (250 MHz): 5.14 (m, 1H, $=CH_2$), 4.97 (m, 1H, $=CH_2$), 4.63 (sextet, $^5J(6,3) = {}^5J(6,CH_3)$ = 3.0 Hz, 2H, H(6)), 4.12 (bs, 2H, H(1)), 2.79 (bs, 2H, H(3)), 1.70 (t, $^5J(CH_3,6)$ = 3.0 Hz, 3H, CH_3), 1.58 (bs, 1H, OH). MS: 124 (7, $M^{+\cdot}$), 109 (34), 95 (25), 93 (100), 91 (54), 81 (14), 79 (31), 77 (40), 67 (22), 55 (31), 53 (38). HRMS ($C_8H_{12}O$): calc. 124.0888, found 124.0877.

Rearrangement of 6d (130 °C, 24 h).
NH_4Cl quench and work-up gave **10d** (yield: 40 %; mixture of 2 diastereomers, ratio 56:44) and **34d** (yield: 4 %).

5-Ethylidene-3-methyleneoxepane (10d).
Major component. ^1H NMR (250 MHz): 5.44-5.27 (m, 1H, $=CHCH_3$), 4.96-4.83 (m, 2H, $=CH_2$), 4.19 (bs, 2H, H(2)), 3.70 (t, $^3J(7,6)$ = 4.8 Hz, 2H, H(7)), 3.08 (bs, 2H, H(4)), 2.33 (m, 2H, H(6)), 1.65 (dm, ^3J = 6.8 Hz, 3H, $=CHCH_3$). Minor component. ^1H NMR (250 MHz): 5.44-5.27 (m, 1H, $=CHCH_3$), 4.96-4.83 (m, 2H, $=CH_2$), 4.16 (bs, 2H, H(2)), 3.71 (t, $^3J(7,6)$ = 5.2 Hz, 2H, H(7)), 3.02 (bs, 2H, H(4)), 2.41 (t, $^3J(6,7)$ = 5.2 Hz, 2H, H(6)), 1.60 (dm, ^3J = 6.5 Hz, 3H, $=CHCH_3$).

2*H*-3,4,7,8-Tetrahydro-5-methyl-3-methyleneoxocin (34d).
^1H NMR (250 MHz): 5.50 (tm, $^3J(6,7)$ = 7.7 Hz, 1H, H(6)), 4.96-4.83 (m, 2H, $=CH_2$), 4.09 (bs, 2H, H(2)), 3.76-3.64 (m, 2H, H(8)), 2.98 (bs, 2H, H(4)), 2.33 (m, 2H, H(7)), 1.72 (m, 3H, CH_3).

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