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Allylmetallation of 1-Silylalkynes by 2-(Bromozincmethyl)-2-alkenyl Ethers followed by Pd(0)-catalyzed Cyclization: A one-pot Synthesis of 4-Methylenecyclopentenes

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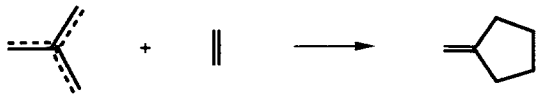
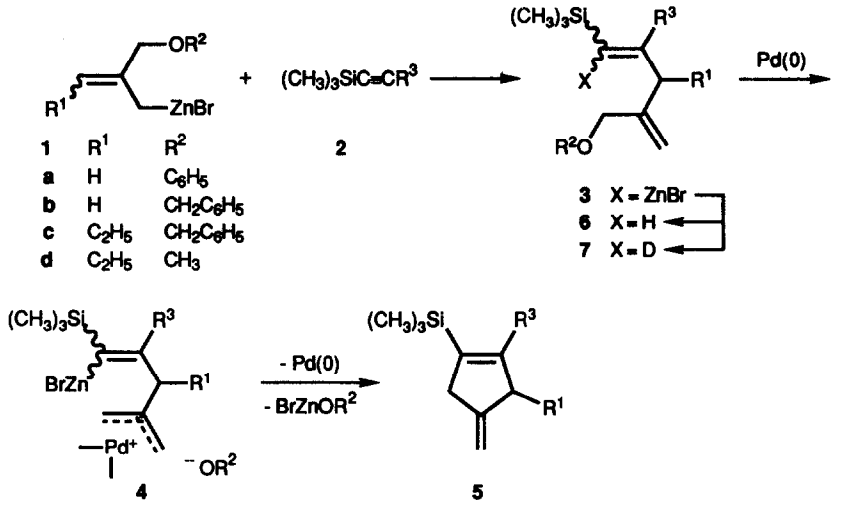
Abstract: *Reaction of 2-(bromozincmethyl)-2-alkenyl ethers* ***1a,b,c,d*** *with 1-(trimethylsilyl)-1-alkynes* ***2*** *afforded carbometallation products* ***3****, which were converted by Pd(0)-catalyzed cyclization to 4-methylenecyclopentenes* ***5****. The rates of both the addition and cyclization step depend on the concentration of the organozinc compound and the preparation of* ***5*** *is best performed using a 1.4-1.8 M solution of* ***1****. At lower concentrations reaction times must be longer and, when* ***1c*** *is reacted, the addition reaction is incomplete and gives rise to a mixture of products (***3*** and* ***14****), which on Pd(0)-treatment leads to a mixture of isomeric methylenecyclopentenes (***5****,* ***15*** *and* ***16****).*

Among the various approaches to five-membered rings,[1] [3+2] cycloaddition methodology involving trimethylenemethane (TMM) building blocks has emerged as a topic of continuous interest (Scheme 1).[2] Three types of trimethylenemethane synthons are in use: (1) 7-alkylidene-2,3-diazanorbornenes;[3] (2) alkylidenecyclopropanes;[2c] (3) 2-[(trimethylsilyl)methyl]allyl esters[2a] and related compounds.[4]



Scheme 1

As part of our program directed towards the exploration of the synthetic potential of carbometallation by functionalized allylmetal compounds,[5] we developed the trimethylenemethane synthon **1**, an allylzinc reagent bearing on C(2) a phenoxymethyl or alkoxymethyl group as a *latent* electrophilic center. To start with, the 1-(trimethylsilyl)-1-alkynes **2** were chosen as substrates. We expected the reaction of **1** with these acetylenes to yield mono-addition products **3**[6] and envisaged that on treatment with Pd(0) the allyl ether moiety in **3** would enable formation of a π-allyl palladium complex (**3** → **4**). The latter would then undergo intramolecular attack by the alkenylzinc part of the molecule, thus permitting cyclization to the 4-methylenecyclopentene derivatives **5** (Scheme 2). In this paper, we describe the results of our investigation.[7]

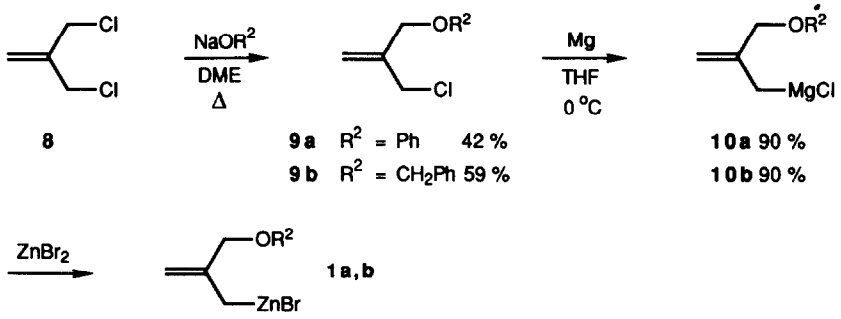


Scheme 2

RESULTS AND DISCUSSION

Preparation of 4-methylenecyclopentenes 5 (R^1 = H) from 1a,b and 1-(trimethylsilyl)-1-alkynes 2.

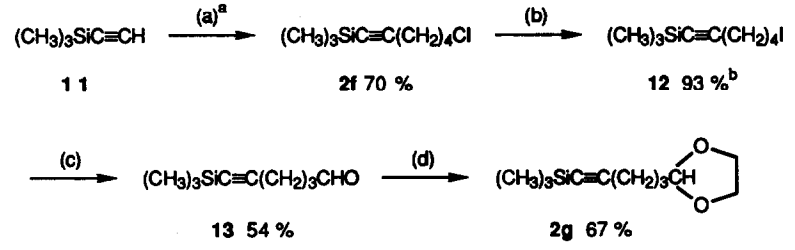
Generation of the trimethylenemethane synthons **1a** and **1b** started by treating the commercially available dichloride **8** with NaOPh and $NaOCH_2Ph$, respectively (Scheme 3). The resulting 2-(chloro- methyl)-2-propenyl ethers **9** were transformed into their Grignard derivatives **10** by addition to magnesium (three times sublimed, 7.25 equiv., activated with 0.25 equiv. 1,2-dibromoethane) in THF (4 ml/mmol, 0 °C) during 6 h . The organozinc compounds **1a** and **1b** were obtained *in situ* by adding the organomagnesium compounds to a solution of anhydrous $ZnBr_2$ (1.5 equiv.) in THF. The salts in the resulting suspension were allowed to settle



Scheme 3

and the supernatant was used directly (**1a,b** = 0.2 M) or after concentration to a 1.8 M solution of the organozinc compounds.

Trimethylsilylacetylenes **2a-e** (Table 1) were prepared by known methods.[8] Alkyne **2f** was obtained by alkylation of trimethylsilylethynyllithium with 1-chloro-4-iodobutane (Scheme 4). Alkyne **2g** was prepared from **2f** by conversion of the latter to the corresponding iodo derivative **12**, Kornblum oxidation to aldehyde **13** and, finally, acetalization with ethylene glycol (Scheme 4).



[a] Conditions. (a) 1. *n*-BuLi, *n*-hexane, THF, -20 °C, 0.5 h; 2. $I(CH_2)_4Cl$, RT, 90 h; (b) NaI, acetone, reflux, 30 h; (c) DMSO, $NaHCO_3$, 150 °C, 5 min.; (d) $HOCH_2CH_2OH$, H^+, benzene, reflux, 7 h. [b] Yield of conversion of **11** into **12**, without purification of **2f**.

Scheme 4

The alkynes **2** (0.5-10 mmol) were heated in a Carius tube with solutions of **1a** or **1b** (1.2 equiv.) for 30 h at 100 °C (0.2 M solution of **1a,b**, method A) or for 3 h at 95 °C (1.8 M solution of **1a**, method B). NH_4Cl or D_2O quench of small portions of the reaction mixture and subsequent GCMS/NMR analysis revealed the presence of **3**, sometimes as two geometric isomers in varying proportions, as indicated by the hydrolysis or deuterolysis products **6** or **7**, respectively. The latter were identified by their ^1H NMR spectra, which readily confirmed the presence of a substituted 1,4-pentadiene moiety [typically (**6a**, single stereoisomer): δ 5.41 (d, ^4J = 1.0 Hz, 1H, =C*H*TMS), 5.25 (m, 1H, $=CH_2$), 5.03 (m, 1H, $=CH_2$), 2.98 (s, 2H, CH_2)]. For conversion into **5**, the carbometallation products **3** were heated in the same vessel in which they had been generated with 5-10 mol% $Pd(PPh_3)_4$ at 65 °C for 24 h (Method A) or 3 h (Method B). Subsequent aqueous work-up afforded the desired 4-methylenecyclopentenes **5**. By-products could not be detected. Results are given in Table 1. The cyclopentenes **5** were identified by their ^1H NMR spectra; characteristic resonances for the 4-methylenecyclopentene system are those of the exocyclic methylene group and those of the ring protons [typically (**5a**): δ 4.90 (m, 2H, $=CH_2$) and δ 3.12 (m, 4H), respectively].

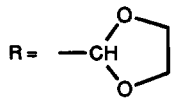
As expected for a bimolecular process, the rate of the addition step was strongly influenced by the concentration of the organometallic compound. Increasing the concentration of **1** from 0.2 M to 1.8 M shortened the reaction time from 30 h to 3 h. It was surprising to find that the addition reaction of **1b** with the 2-hydroxyethyl derivative **2e** (Table 1, entry 6) needed a *longer* time (55 h, employing method A) than the reactions of **1b** with **2f** and **2g** (entries 7 and 9). By contrast, various examples are known of *enhanced* reactivity in carbometallation through anchimeric assistance by metallated hydroxy groups.[9] The cyclization of **3** to **5** with a catalytic amount of $[Pd(PPh_3)_4]$ was accomplished very efficiently, without side reactions and under mild conditions. In this reaction, too, a shorter reaction time (3 vs. 24 h) was sufficient when a higher concentration of **1** had been used. Due to the configurational lability of (1-silyl-1-alkenyl)zinc compounds,[10] both isomers of **3** could be converted to **5**. The rate of stereo-isomerization at the metallated carbon of **3** may

Table 1. Synthesis of 4-Methylenecyclopentenes **5** (R^1 = H).

Entry	RM	Alkyne	Method[a]	Addition		Cyclization	
				Quench	Product[b]	Product	Yields[c] d/e(%)
1	**1a**	**2a**	A	NH_4Cl	**6a**	**5a**	72/-
2	**1a**	**2a**	B	-		**5a**	- /87
3	**1a**	**2b**	A	NH_4Cl	**6b**	**5b**	51/-
4	**1a**	**2c**	A	NH_4Cl	**6c**	**5c**	-
5	**1a**	**2d**	A	NH_4Cl	**6d**	**5d**	78/-
6	**1b**	**2e**[f,g]	A	D_2O	**7e**	**5e**	67/-
7	**1b**	**2f**	A	D_2O	**7f**	**5f**	75/-
8	**1a**	**2f**	B	-		**5f**	-/70
9	**1b**	**2g**	A	D_2O	**7h**	**5g**	91/-

[a] Method A. Addition: **1a** or **1b** (0.2 M, 1.2 equiv.), 100 °C, 30 h; cyclization: 5-10 mol% $Pd(PPh_3)_4$, 65 °C, 24 h. Method B. Addition: **1a** (1.8 M, 1.2 equiv.), 95 °C, 3 h; cyclization: 5-10 mol% $Pd(PPh_3)_4$, 65 °C, 3 h. [b] After hydrolysis or deuterolysis. [c] Yields are based on alkyne **2**. [d] GLC yields. [e] Isolated yields. [f] Depro- tonated by 1 equiv. EtMgBr prior to reaction with **1b**. [g] Addition: 100 °C, 55 h.

2,5	R^3	R^1	**3,6,7**	R^1	R^2	R^3
a	n-C_4H_9	H	**a**	H	C_6H_5	n-C_4H_9
b	CH_2OCH_3	H	**b**	H	C_6H_5	CH_2OCH_3
c	$CH_2OSiBu^tMe_2$	H	**c**	H	C_6H_5	$CH_2OSiBu^tMe_2$
d	$CH_2CH_2OSiMe_3$	H	**d**	H	C_6H_5	$CH_2CH_2OSiMe_3$
e	CH_2CH_2OH	H	**e**	H	$CH_2C_6H_5$	CH_2CH_2OH
f	$CH_2CH_2CH_2CH_2Cl$	H	**f**	H	$CH_2C_6H_5$	$CH_2CH_2CH_2CH_2Cl$
			g	H	C_6H_5	$CH_2CH_2CH_2CH_2Cl$
g	$CH_2CH_2CH_2R$	H	**h**	H	$CH_2C_6H_5$	$CH_2CH_2CH_2R$

R = 

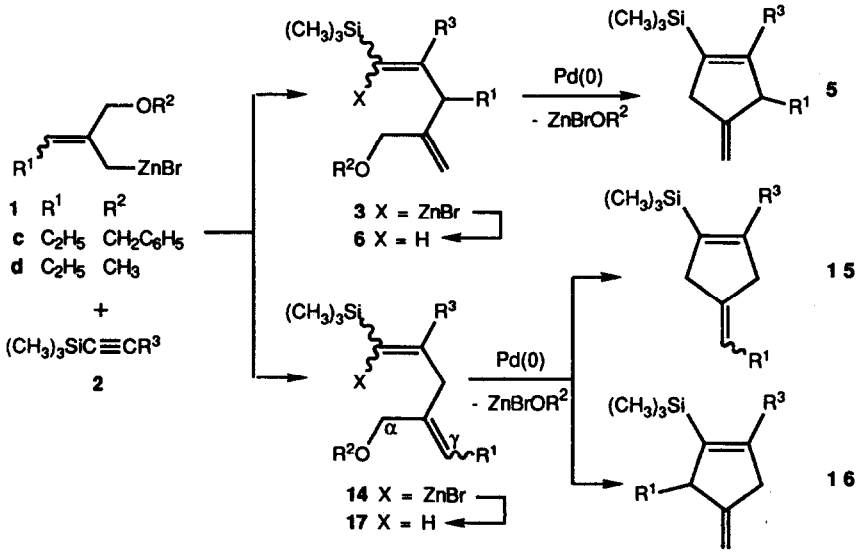
contribute to the reaction time required for complete conversion of **3** into **5**.[10] The fact that not even small amounts of **5** were present after the addition reaction of **1** with **2** proves that uncatalyzed ring closure does not take place. In the case of **2c** (Table 1, entry 4) reaction with **1a** proceeded smoothly; however, Pd-catalyzed ring closure could not be effected. Steric hindrance by the $SiBu^tMe_2$ group may be the reason.

To our knowledge, *intramolecular* reaction of an organozinc halide, a moderately "hard" organometallic nucleophile, with a π-allyl palladium intermediate generated *in situ* from an allyl ether is without precedent.[11,12] Studies on *intermolecular* Pd(0)-catalyzed cross-coupling of phenylzinc chloride with allyl acetate derivatives[13] suggest that the conversion of **3** into **5** might take place via (1) formation of allylpalla-

dium(II) derivatives by the interaction of the allylic ether moiety with [$Pd(PPh_3)_4$], (2) transmetallation, and (3) reductive elimination of Pd(0), yielding the 4-methylenecyclopentenes **5**.

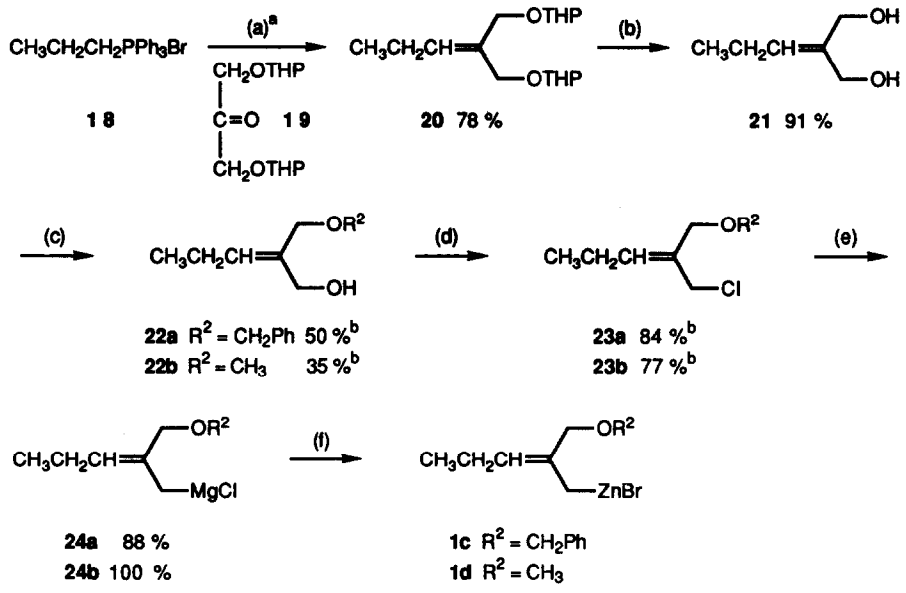
Preparation of substituted 4-methylenecyclopentenes 5 (R^1 = Et) from 1c,d and 1-(trimethylsilyl)- 1-alkynes 2.

Addition of 3-alkylallylzinc halides to alkynes generally results in predominant or exclusive carbon-carbon bond formation at C(3) of the allylmetal reagent.[14] Therefore, it was was expected that addition of the 3-ethylallylzinc derivatives **1c,d** would afford the addition products **3** (R^1 = Et), which on Pd(0)-catalyzed cyclization might result in the formation of the tetrasubstituted cyclopentenes **5** (R^1 = Et) (Scheme 5). It had to be reckoned with, however, that the addition might also lead to **14**, in which case Pd(0)-catalyzed cyclization could give two types of cyclization products, **15** and **16**, arising from **14** by attack at the α- or γ-position, respectively.



Scheme 5

Preparation of the alkyl TMM synthons **1c** and **1d** started with Wittig reaction of the ylide from triphenylpropylphosphonium bromide (**18**) and α,α'-bis(2-tetrahydropyranyloxy)acetone (**19**)[15] (Scheme 6). After hydrolysis of **20**, the diol **21** was transformed into the mono-benzyl and mono-methyl ether **22a** and **22b**, respectively (1:1 mixtures of *E*- and *Z*-isomers). The alcohols **22a**and **22b** were converted to the corresponding chlorides **23a** and **23b** by treatment with methanesulfonyl chloride, LiCl and *s*-collidine in DMF.[16] Then, **23a** and **23b** were transformed into their Grignard derivatives **24a** and **24b** whereafter the organozinc compounds were prepared *in situ* by reaction with $ZnBr_2$. Solutions of the organozinc compounds were used directly (0.2 M) or after concentration to 1.4 M (**1c**) or 1.8 M (**1d**).



[a] Conditions. (a) 1. *n*-BuLi, *n*-hexane, THF, -25 °C → RT, 2 h; 2. RT, 0.5 h; 3. **19**, -25 °C → RT, overnight; 4. Reflux, 3 h; (b) MeOH, PPTS, reflux, 5 h; (c) 1. NaH, DME, reflux, 1 h; 2. $PhCH_2Br$, reflux, 2 h, *or* CH_3I, RT, 2 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 Mixture of *E*- and *Z*-isomers.

Scheme 6

1-(Trimethylsilyl)-1-hexyne **2a** was heated in a Carius tube with **1c** (0.2 M, 1.2 equiv.) at 100 °C for 30 h whereafter a small portion of the reaction mixture was quenched with aqueous NH_4Cl. GLC/NMR analysis revealed that indeed both types of addition products, **3i** (49 %) and **14i** (20 %), had been formed, as indicated by the respective protonation products **6i** and **17i** (Table 2, entry 1). The latter were characterized by their ^1H NMR spectra, which readily confirmed the presence of a 3-ethyl-1,4-pentadiene system or that of a 1,4-heptadiene system [**6i**: δ 5.31 (s, 1H, =C*H*TMS), 5.21 (m, 1H, $=CH_2$), 5.02 (bs, 1H, $=CH_2$), 2.70 (t, ^3J = 7.3 Hz, 1H, CHC_2H_5); **17i** (mixture of diastereomers, component I): δ 5.60 (t, ^3J = 7.2 Hz, 1H, CHC_2H_5), 5.17 (t, ^4J = 0.5 Hz, 1H, =C*H*TMS), 2.89 (s, 2H, CH_2), 2.14-1.99 (m, 2H, CH_2CH_3), 0.92 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3)]. Because a considerable quantity of **2a** was still present (30 %), heating of the reaction mixture was continued at 130 °C for another 30 h (Table 2, entry 2). After this time, analysis of the protonation products showed that the amount of **3i** had decreased substantially (yield: 19 %); on the other hand, the amount of **14i** had only somewhat increased (yield: 27 %). Conversion of **2a**, however, was still incomplete. Nevertheless, the reaction mixture was treated with $[Pd(PPh_3)_4]$ (5 mol%) at 65 °C for 30 h. It was found that indeed all three types of cyclization products were formed (Table 2, entry 2): **5i** (19 %), **15i** (14 %) and **16i** (4 %; yields based on **2a**).[17] The ^1H NMR spectra of **5i** and **16i** show the presence of a 4-methylenecyclopentene system with an ethyl group at C(3) or at C(5), respectively [**5i**: δ 4.98 (m, 1H, $=CH_2$), 4.88 (m, 1H, $=CH_2$), 3.24 (m, 1H, CHC_2H_5), 3.06 (m, 2H, CH_2); **16i**: δ 4.93 (m, 1H, $=CH_2$), 4.84 (m, 1H, $=CH_2$), 3.22-3.13 (m, 1H, CHC_2H_5), 3.04 (AB system, δ(A) = 3.16, dm, 1H, CH_2, δ(B) =

2.92, 1H, CH_2, J(AB) = 20.8 Hz)]. The position of the ethyl group in **5i** (and, by consequence, that in **16i**) was established by 2D NOESY NMR on **5i** (Figure 1).

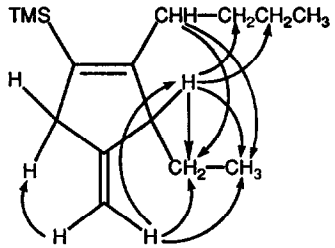


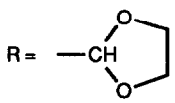
Fig. 1. NOESY data for **5i**.

Table 2. Synthesis of 4-Methylenecyclopentenes **5**, **15** and **16** (R^1 = Et).

Entry	Addition[a]						Cyclization[a]		
	RM	ratio 1:2	conc. (M)	alkyne	T (°C)	t (h)	Products[b] (yield, %) [Ratio 3:14]	T (°C)	t (h)	Products (yield, %)
1	**1c**	1.2	0.2	**2a**	100	30	**3i** (49), **14i** (20)			
2	**1c**	1.2	0.2	**2a**	130	30	**3i** (19), **14i** (27)	65	30	**5i** (19), **15i** (14), **16i** (4)
3	**1c**	3	1.4	**2a**	95	30	**3i** (60), **14i** (11)	65	8	**5i** (68), **15i** (1)
4	**1c**	3	1.4	**2f**	95	8	**3j**, **14j** [85:15][c]			
5	**1c**	3	1.4	**2f**	95	30	**3j**, **14j** [85:15]	65	8	**5j** (76)
6	**1c**	3	1.4	**2g**	95	8	**3k**, **14k** [86:14][c]			
7	**1c**	3	1.4	**2g**	95	30	**3k**, **14k** [86:14]	65	8	**5k** (71)
8	**1d**	3	1.8	**2a**	75	24	**3l**, **14l** [86:14]	75	1.5	**5i** (84[d])

[a] Unless otherwisely stated, yields (based on alkyne **2**) were determined by GLC. [b] Addition products **3** and **14** were identified by their protonation products **6** and **17**, respectively. [c] Reaction not completed. [d] Isolated yield .

2	R^3	**3,6, 14,17**	R^1	R^2	R^3	**5,15, 16**	R^1	R^3
a	n-C_4H_9	**i**	C_2H_5	$CH_2C_6H_5$	n-C_4H_9	**i**	C_2H_5	n-C_4H_9
f	$(CH_2)_4Cl$	**j**	C_2H_5	$CH_2C_6H_5$	$(CH_2)_4Cl$	**j**	C_2H_5	$(CH_2)_4Cl$
g	$(CH_2)_3R$	**k**	C_2H_5	$CH_2C_6H_5$	$(CH_2)_3R$	**k**	C_2H_5	$(CH_2)_3R$
		l	C_2H_5	CH_3	n-C_4H_9			

R = 

The ^{1}H NMR spectrum of **15i** indicates the presence of a 4-propylidenecyclopentene system [δ 5.28 (m, 1H, =C*H*C_2H_5), 3.08 (AB system, δ(A) = 3.17, dm, 2H, H(3,5), δ(B) = 2.99, 2H, H(3,5), J(AB) = 24.3 Hz), 2.07-1.90 (m, 2H, =CHC*H*$_2$CH$_3$), 0.97 (t, ^{3}J = 7.5 Hz, 3H, =CHCH$_2$C*H*$_3$)].

Addition of the 3-ethyl-substituted allylzinc compound **1c** to 1-(trimethylsilyl)-1-alkynes is much slower than that of the parent compounds **1a,b**. Since it was felt that addition products **14** arise under conditions of thermodynamic control from initially formed **3** (compare entries 1 and 2 of Table 2), we reasoned that, in order to achieve complete reaction of the alkyne and to effect preferential formation of addition product **3** (and, ultimately, cyclization product **5**), it would be necessary to raise the concentration of the organozinc compound and to perform the addition reaction at 100 °C or below. Accordingly, **2a** was heated with **1c** (1.4 M, 3 equiv.) at 95 °C for 30 h (Table 2, entry 3). It was found that not only addition was complete now, but that also mainly **3i** (60 %), together with only a minor amount of **14i** (11 %) had been formed. Addition of [Pd(PPh$_3$)$_4$] (5 mol%) and heating the mixture at 65 °C for 8 h gave the desired tetrasubstituted cyclopentene **5i** (68 %), contaminated with only a very small amount of **15i** (1 %). Cyclopentene **16i** could not be detected.

Reactions of acetylenes **2f** and **2g** following the same protocol again resulted in the preferential formation of addition products **3j** and **3k**, respectively (Table 2, entry 5,7). During the course of addition, the ratio of **3** and **14** did not change (compare entries 4,5 (6,7) in Table 2). Pd(0)-catalyzed cyclization gave exclusively the desired 4-methylenecyclopentenes **5j** and **5k**. The addition of **1d** (1.8 M, 3 equiv., 75 °C, 24 h) to **2a** again gave mainly addition product **3l**, together with only a minor amount of **14l** (ratio 86:14, Table 2, entry 8). Pd(0)-catalyzed cyclization led to the exclusive formation of **5l** in 84 % isolated yield.

It is remarkable that in four cases studied (Table 2, entries 3,5,7,8) cyclization products **15** and **16** could not or only in minor amounts be detected, whereas appreciable amounts of the corresponding addition products **14** were produced in the addition step. Possibly, cyclization of **14** is slower than that of **3**, because in **14** the allyl ether is disubstituted, whereas it is monosubstituted in **3**. However, deterioration of the carbometallation products **14** and/or cyclization products **15** and **16** under the reaction conditions used could also account for this.

In conclusion, 1-(trimethylsilyl)-2,3-dialkyl-4-methylenecyclopent-1-enes **5** are easily obtained from 1-(trimethylsilyl)-1-alkynes and 2-(bromozincmethyl)-2-alkenyl ethers in a one-pot procedure involving allylzincation followed by Pd(0)-catalyzed cyclization. Certain functional groups on the 2-alkyl group are tolerated. Together with the vinylsilane moiety and the exocyclic methylene group they offer many possibilities of further synthetic elaboration.

Acknowledgment.
We wish to thank Mr R.F. Schmitz for measuring the HRMS spectra.

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; $CDCl_3$ 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 equiped with a thermal conductivity-detector and using 10% OV-101 as

stationary phase. Analytical gaschromatograms were integrated by 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.

3-Chloro-2-(phenoxymethyl)-1-propene (9a).

To a suspension of NaH (0.750 mol) in DME (600 ml) was added dropwise and with stirring a solution of phenol (70.7 g, 0.750 mol) in DME (300 ml). After refluxing for 1 h, the reaction mixture was cooled to room temperature. 3-Chloro-2-(chloromethyl)-1-propene (**8**) (93.5 g, 0.750 mol) was added in one portion and the reaction mixture was heated under reflux for 45 h. After cooling, the mixture was poured onto saturated $NaHCO_3$ 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*. Distillation gave **9a** (57.7 g, 42 %), bp 110-113 °C (1 Torr). ^{1}H NMR (90 MHz): 7.77-7.47, 7.39-7.11 (m, 5H, C_6H_5), 5.70 (m, 2H, H(1)), 4.94 (bs, 2H, C(2)CH_2O), 4.50 (m, 2H, H(3)). MS: 182 (27, $M^{+\cdot}$), 147 (100), 133 (23), 119 (4), 105 (7), 94 (22), 91 (15), 77 (20), 65 (15), 53 (70). HRMS ($C_{10}H_{11}{}^{35}ClO$): calc. 182. 0498, found 182.0501.

3-Benzyloxy-2-(chloromethyl)-1-propene (9b).

To a mechanically stirred suspension of NaH (60.0 mmol) in DME (120 ml) was added dropwise benzyl alcohol (6.49 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 (**8**) (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*. Distillation provided **9b** (7.00 g, 59 %), bp 120-122 °C (1 Torr). ^{1}H NMR (90 MHz): 7.39 (bs, 5H, C_6H_5), 5.40-5.25 (m, 2H, H(1)), 4.54 (s, 2H, O$CH_2C_6H_5$), 4.15 (bs, 4H, H(3), CH_2Cl). MS: 107 (33), 105 (13), 92 (47), 91 (100), 79 (24), 77 (17), 65 (23), 53 (13), 51 (13). HRMS ($C_{11}H_{12}{}^{35}ClO$ $[M-H]^+$): calc. 195.0577, found 195.063.

3-(Chloromagnesio)-2-(phenoxymethyl)-1-propene (10a).

Magnesium (three times sublimed, turnings, diameter *ca.* 1 mm, 8.81 g, 362 mmol) in THF (150 ml) was activated with 1,2-dibromoethane (2.35 g, 12.5 mmol). The magnetically stirred mixture was cooled to 0 °C and a solution of 3-chloro-2-(phenoxymethyl)-1-propene (**9a**) (9.13 g, 50.0 mmol) in THF (50 ml) was added dropwise in 6 h. Stirring was continued while the reaction mixture was allowed to warm-up to room temperature overnight. The yield amounted to 90 %

3-Benzyloxy-2-(chloromagnesiomethyl)-1-propene (10b).

Following the same procedure as described for the synthesis of **10a**, **10b** was prepared from **9b** in 90 % yield.

3-(Bromozinc)-2-(phenoxymethyl)-1-propene (1a).

To a magnetically stirred solution of $ZnBr_2$ (15.2 g, 67.5 mmol) in THF (25 ml) was added dropwise Grignard reagent **10a** (200 ml, 45 mmol). After the addition was completed, the salts were allowed to settle and the supernatant (concentration *ca.* 0.2 M) was used as such or it was decanted and concentrated at atmospheric pressure to 1.8 M.

3-Benzyloxy-2-(bromozincmethyl)-1-propene (1b).
Prepared from **10b** according to the same procedure as described for the synthesis of **1a**.

6-Chloro-1-(trimethylsilyl)-1-hexyne (2f).
To a magnetically stirred solution of trimethylsilylethyne (**11**) (19.6 g, 0.200 mol) in THF (250 ml), cooled at -20 °C, was added dropwise (0.5 h) *n*-BuLi (1.6 M solution in *n*-hexane, 125 ml, 0.200 mol). 1-Chloro-4-iodobutane (43.7 g, 0.200 mol) was added and the reaction mixture was stirred at room temperature for 90 h. Then, it was poured onto saturated $NaHCO_3$ solution and the water layer was extracted five times with diethyl ether. The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The crude reaction product (40.0 g), containing a considerable amount of the iodide **12**, was used as such when conversion to the latter was intended. Alternatively, it was distilled, giving **2f** (26.4 g, 70 %), bp 104 °C (15 Torr). ^{1}H NMR (90 MHz): 3.59 (t, $^3J(6,5)$ = 5.8 Hz, 2H, H(6)), 2.29 (t, $^3J(3,4)$ = 5.8 Hz, 2H, H(3)), 2.05-1.50 (m, 4H, H(4,5)), 0.17 (s, 9H, TMS). MS: 173 (10), 153 (0.5), 145 (4), 137 (13), 109 (6), 103 (4), 95 (36), 93 (100), 79 (32), 73 (15), 59 (8), 55 (8). HRMS ($C_8H_{14}ClSi$ $[M-CH_3]^+$): calc. 173.0553, found 173.0552.

6-Iodo-1-(trimethylsilyl)-1-hexyne (12).
A solution of crude **2f** (*ca.* 0.15 mol) and NaI (28.2 g, 0.200 mol) in acetone (300 ml) was heated under reflux for 30 h. The reaction mixture was cooled and filtered and the filtrate was concentrated *in vacuo*. The residue was diluted with pentane and poured onto saturated $NaHCO_3$ solution. The water layer was extracted three times with pentane and the combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. Distillation gave **12** (35.1 g; 93 %, based on **11**), bp 134 °C (15 Torr). ^{1}H NMR (90 MHz): 3.23 (t, $^3J(6,5)$ = 6.6 Hz, 2H, H(6)), 2.28 (t, $^3J(3,4)$ = 6.2 Hz, 2H, H(3)), 2.15-1.40 (m, 4H, H(4,5)), 0.17 (s, 9H, TMS). MS: 280 (12, $M^{+\cdot}$), 265 (16), 235 (6), 223 (4), 209 (2), 195 (4), 185 (100), 171 (4), 162 (19), 153 (27), 147 (5), 137 (53), 125 (7), 109 (22), 93 (21), 79 (17), 73 (95), 59 (39), 55 (15). HRMS ($C_9H_{17}ISi$): calc. 280.0143, found 280.0130.

6-(Trimethylsilyl)-5-hexynal (13).
To a magnetically stirred mixture of anhydrous $NaHCO_3$ (25.0 g, 0.30 mol) and DMSO (185 ml), heated at 150 °C, was added, in one portion, **12** (11.8 g, 0.0422 mol). After 5 minutes stirring the flask was cooled rapidly in an ice-water bath. The reaction mixture was poured onto a mixture of ice and water (600 ml) and the aqueous layer was extracted four times with diethyl ether. The combined organic phases were washed with water (3x) and brine, dried ($MgSO_4$) and concentrated at reduced pressure (50 °C, 100 mbar). Distillation of the crude product gave **13** (3.83 g, 54 %), bp 99-104 °C (15 Torr). ^{1}H NMR (90 MHz): 9.82 (t, $^3J(1,2)$ = 1.2 Hz, 1H, H(1)), 2.59 (td, $^3J(2,3)$ = 6.6 Hz, $^3J(2,1)$ = 1.2 Hz, 2H, H(2)), 2.46-2.07 (m, 2H, H(4)), 2.07-1.72 (m, 2H, H(3)), 0.14 (s, 9H, TMS). MS: 168 (0.2, $M^{+\cdot}$), 153 (30), 140 (3), 125 (8), 116 (16), 109 (12), 101 (16), 97 (61), 83 (16), 75 (100), 73 (31), 69 (15), 59 (16), 55 (16).

2-(5-(Trimethylsilyl)-4-pentynyl)-1,3-dioxolane (2g).
To a magnetically stirred solution of aldehyde **13** (3.18 g, 18.9 mmol) in benzene (110 ml) were added 1,2-ethanediol (10 ml) and *p*-toluenesulfonic acid (36 mg, 0.19 mmol). The reaction mixture was refluxed for 7 h using a water separator, filled with molecular sieves (4Å). After cooling, the mixture was poured onto saturated $NaHCO_3$ solution and the water layer was extracted four times with diethyl ether. The combined organic phases were washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. Distillation gave **2g** (2.70 g, 67 %), bp 73-75 °C (1 Torr). ^{1}H NMR (90 MHz): 4.88 (t, $^3J(2,1')$ = 4.0 Hz, 1H, H(2)), 4.04-3.80 (m, 4H, H(4,5)), 2.29 (t, $^3J(3',2')$ = 6.4 Hz, 2H, H(3')), 1.97-1.40 (m, 4H, H(1',2')), 0.17 (s, 9H, TMS). MS: 212 (0.1, $M^{+\cdot}$), 184 (1), 162 (4), 153 (3), 139 (8), 125 (2), 109 (6), 99 (32), 75 (37), 73 (100), 59 (11), 55 (11).

General procedure for the preparation of 4-methylenecyclopentenes 5 (R^1 = H) (Table 1).
Method A. To a solution of **1a** or **1b** in THF (0.2 M, 1.2 equiv.) were added the alkyne **2** (0.5-3 mmol) and, as internal standard, *n*-dodecane (0.5-1 mmol). The magnetically stirred mixture was heated in the Carius tube mentioned in the general experimental section for 30 h at 100 °C. The reaction was monitored by quenching small portions of the reaction mixture with aqueous NH_4Cl or D_2O. $[Pd(PPh_3)_4]$ (5-10 mol%) was added and the heating was continued for 24 h at 65 °C. The reaction

mixture was cooled and poured onto saturated NH_4Cl solution. After extracting the aqueous layer four times with diethyl ether, the combined organic phases were washed with 1 M NaOH (when phenyl ether **1a** was used) or with saturated $NaHCO_3$ solution (when benzyl ether **1b** was used) and with brine, dried (Na_2SO_4) and concentrated at reduced pressure using a 30 cm Vigreux column (50 °C, 200 mbar). The crude reaction product was analyzed by preparative GLC, GCMS and NMR. Yields are based on the alkyne **2**.

Method B. To a solution of **1a** in THF (1.8 M, 1.2 equiv.) was added the alkyne **2** (10 mmol) whereafter the magnetically stirred mixture was heated in standard glass equipment for 3 h at 95 °C (boiling point of the THF solution of the organozinc reagent). After cooling, $[Pd(PPh_3)_4]$ (5 mol%) was added and the heating was continued for 3 h at 65 °C. The reaction mixture was cooled and poured onto saturated NH_4Cl solution. After extracting the aqueous layer four times with diethyl ether, the combined organic phases were washed with 1 M NaOH (2x) and brine, dried (Na_2SO_4), and concentrated at reduced pressure using a 30 cm Vigreux column (50 °C, 200 mbar). The crude product was purified by evaporative distillation (100-150 °C, 16 Torr). Yields are based on the alkyne **2**.

2-Butyl-4-(phenoxymethyl)-1-(trimethylsilyl)-1,4-pentadiene (6a).

Prepared by reaction of **1a** with **2a** (method A) followed by hydrolysis. ^{1}H NMR (250 MHz): 7.33-7.22 (m, 2H, H(3'-Ar,5'-Ar)), 7.00-6.87 (m, 3H, H(2'-Ar,4'-Ar,6'-Ar)), 5.41 (d, ^4J = 1.0 Hz, 1H, H(1)), 5.25 (m, 1H, H(5)), 5.03 (m, 1H, H(5)), 4.43 (s, 2H, C(4)CH_2O), 2.98 (s, 2H, H(3)), 2.06 (m, 2H, H(1'-Bu)), 1.48-1.21 (m, 4H, H(2'-Bu,3'-Bu)), 0.90 (t, ^3J = 7.2 Hz, 3H, H(4'-Bu)), 0.09 (s, 9H, TMS). MS: 302 (3, $M^{+\cdot}$), 287 (0.1), 245 (2), 209 (5), 166 (5), 151 (26), 135 (7), 107 (3), 93 (10), 73 (100), 59 (14), 42 (40). HRMS ($C_{19}H_{30}OSi$): calc. 302.2066, found 302.2046.

1-Butyl-4-methylene-2-(trimethylsilyl)-1-cyclopentene (5a).

Prepared from **1a** and **2a** according to method A (yield: 72 % [GLC]), or according to method B (yield: 87 % [isolated]). ^{1}H NMR (250 MHz): 4.90 (m, 2H, =CH_2), 3.12 (m, 4H, H(3,5)), 2.24-2.13 (m, 2H, H(1'-Bu)), 1.43-1.21 (m, 4H, H(2'-Bu,3'-Bu)), 0.92 (t, ^{3}J(4',3') = 6.9 Hz, 3H, H(4'-Bu)), 0.12 (s, 9H, TMS). ^{13}C NMR (63 MHz): 153.4 (m, C(1*)), 150.8 (quintet, ^{2}J(CH) = 5 Hz, C(4*)), 133.7 (s, C(2)), 105.5 (tquintet, ^{1}J(CH) = 155 Hz, ^{3}J(CH) = 4 Hz, =CH_2), 44.4 (tm, ^{1}J(CH) = 126 Hz, C(3**)), 44.1 (tm, ^{1}J(CH) = 126 Hz, C(5**)), 31.9 (t, ^{1}J(CH) = 125 Hz, C(1'***)), 31.0 (tm, ^{1}J(CH) = 128 Hz, C(2'***)), 22.9 (tm, ^{1}J(CH) = 124 Hz, C(3'***)), 14.1 (qm, ^{1}J(CH) = 123 Hz, C(4')), -0.3 (qquintet, ^{1}J(CH) = 119 Hz, J(CH) = 2 Hz, TMS). MS: 208 (11, $M^{+\cdot}$), 193 (2), 166 (4), 165 (4), 151 (1), 134 (4), 105 (3), 92 (7), 73 (100), 59 (14), 45 (10). HRMS ($C_{13}H_{24}Si$): calc. 208.1647, found 208.1633.

2-(Methoxymethyl)-4-(phenoxymethyl)-1-(trimethylsilyl)-1,4-pentadiene (6b).

Prepared by reaction of **1a** with **2b** (method A) followed by hydrolysis. **6b** Was obtained as a mixture of diastereomers, ratio: 84:16. Major component. ^{1}H NMR (250 MHz): 7.34-7.24 (m, 2H, H(3'-Ar,5'-Ar)), 6.99-6.88 (m, 3H, H(2'-Ar,4'-Ar,6'-Ar)), 5.75 (t, ^4J = 1.5 Hz, 1H, H(1)), 5.26 (m, 1H, H(5)), 5.05 (m, 1H, H(5)), 4.47 (s, 2H, C(4)CH_2O), 3.84 (d, ^4J = 1.5 Hz, 2H, CH_2OCH_3), 3.35 (s, 3H, OCH_3), 2.99 (bs, 2H, H(3)), 0.12 (s, 9H, TMS). Minor component. ^{1}H NMR (250 MHz): 7.34-7.24 (m, 2H, H(3'-Ar,5'-Ar)), 6.99-6.88 (m, 3H, H(2'-Ar,4'-Ar,6'-Ar)), 5.59 (s, 1H, H(1)), 5.26 (m, 1H, H(5)), 5.05 (m, 1H, H(5)), 4.45 (s, 2H, C(4)CH_2O), 3.93 (s, 2H, CH_2OCH_3), 3.31 (s, 3H, OCH_3), 2.99 (bs, 2H, H(3)), 0.11 (s, 9H, TMS). MS (mixture of both components): 290 (12, $M^{+\cdot}$), 275 (2), 258 (3), 243 (6), 197 (3), 186 (12), 171 (8), 165 (10), 151 (12), 133 (12), 107 (16), 93 (27), 89 (53), 73 (100), 59 (39). HRMS ($C_{17}H_{26}O_2Si$, mixture of both components): calc. 290.1702, found 290.1713.

1-(Methoxymethyl)-4-methylene-1-(trimethylsilyl)-1-cyclopentene (5b).

Prepared from **1a** and **2b** according to method A (yield: 51 % [GLC]). ^{1}H NMR (250 MHz): 4.94 (m, 2H, =CH_2), 4.03 (bs, 2H, CH_2OCH_3), 3.31 (s, 3H, OCH_3), 3.21 (t, ^4J = 2.6 Hz, 2H, H(3*)), 3.24 (t, ^4J = 2.6 Hz, 2H, H(5*)), 0.15 (s, 9H, TMS). MS: 196 (3, $M^{+\cdot}$), 181 (16), 164 (15), 149 (4), 92 (43), 89 (72), 73 (100), 59 (38). HRMS ($C_{11}H_{20}OSi$): calc. 196.1283, found 196.1264.

2-((*t*-Butyldimethylsilyl)oxymethyl)-4-(phenoxymethyl)-1-(trimethylsilyl)-1,4-pentadiene (6c). Prepared by reaction of **1a** with **2c** (method A) followed by hydrolysis. **6c** Was obtained as a mixture of diastereomers, ratio: 82:18. Major component. ^{1}H NMR (250 MHz): 7.34-7.24 (m, 2H, H(3'-Ar,5'-Ar)), 7.00-6.89 (m, 3H, H(2'-Ar,4'-Ar,6'-Ar)), 5.81 (t, ^{4}J = 1.5 Hz, 1H, H(1)), 5.24 (m, 1H, H(5)), 5.03 (bs, 1H, H(5)), 4.46 (bs, 2H, C(4)CH_2O), 4.06 (d, ^{4}J = 1.9 Hz, 2H, CH_2OSi), 2.98 (bs, 2H, H(3)), 0.94 (s, 9H, *t*-Bu), 0.12 (s, 9H, TMS), 0.07 (s, 6H, Si$(CH_3)_2$). Minor component. ^{1}H NMR (250 MHz): 7.34-7.24 (m, 2H, H(3'-Ar,5'-Ar)), 7.00-6.89 (m, 3H, H(2'-Ar,4'-Ar,6'-Ar)), 5.77 (t, ^{4}J = 1.5 Hz, 1H, H(1)), 4.93 (m, 1H, H(5)), 4.84 (m, 1H, H(5)), 4.46 (bs, 2H, C(4)CH_2O), 4.04 (d, ^{4}J = 2.2 Hz, 2H, CH_2OSi), 2.88 (s, 2H, H(3)), 0.94 (s, 9H, *t*-Bu), 0.12 (s, 9H, TMS), 0.09 (s, 6H, Si$(CH_3)_2$). MS (mixture of both components): 390 (6, $M^{+\cdot}$), 333 (7), 259 (2), 253 (8), 243 (4), 151 (12), 147 (31), 133 (7), 93 (13), 75 (27), 73 (100), 59 (7), 45 (5). HRMS ($C_{22}H_{38}O_2Si_2$, mixture of both components): calc. 390.2410, found 390.2424.

4-(Phenoxymethyl)-1-(trimethylsilyl)-2-(2-(trimethylsilyloxy)ethyl)-1,4-pentadiene (6d).
Prepared by reaction of **1a** with **2d** (method A) followed by hydrolysis. ^{1}H NMR (90 MHz): 7.40-7.15 (m, 2H, H(3'-Ar,5'-Ar)), 7.05-6.80 (m, 3H, H(2'-Ar,4'-Ar,6'-Ar)), 5.44 (m, 1H, H(1)), 5.26 (m, 1H, H(5)), 5.02 (m, 1H, H(5)), 4.43 (bs, 2H, C(4)CH_2O), 3.67 (t, ^{3}J = 7.0 Hz, 2H, CH_2OTMS), 2.99 (bs, 2H, H(3)), 2.45-2.20 (m, 2H, C$H_2$$CH_2$OTMS), 0.08 (s, 9H, OTMS), 0.10 (s, 9H, TMS). MS: 362 (7, $M^{+\cdot}$), 269 (1), 255 (9), 151 (10), 147 (8), 107 (9), 103 (18), 93 (12), 79 (4), 75 (16), 73 (100), 59 (7), 45 (9). HRMS ($C_{20}H_{34}O_2Si_2$): calc. 362.2097, found 362.2077.

4-Methylene-1-(trimethylsilyl)-2-(2-(trimethylsilyloxy)ethyl)-1-cyclopentene (5d).
Prepared from **1a** and **2d** according to method A (yield: 78 % [GLC]). ^{1}H NMR (250 MHz): 4.91 (m, 2H, =CH_2), 3.63 (t, ^{3}J(2',1') = 7.3 Hz, 2H, H(2')), 3.15 (m, 4H, H(3,5)), 2.47 (t, ^{3}J(1',2') = 7.3 Hz, 2H, H(1')), 0.13 (s, 9H, OTMS), 0.12 (s, 9H, TMS). MS: 268 (8, $M^{+\cdot}$), 253 (1), 179 (2), 165 (13), 152 (4), 147 (14), 133 (3), 119 (1), 105 (4), 103 (10), 91 (14). HRMS ($C_{14}H_{28}OSi_2$): calc. 268.1679, found 268.1662.

5-(Benzyloxymethyl)-3-([1-$^2H_1$]-(trimethylsilyl)methylene)-5-hexen-1-ol (7e).
Prepared by reaction of **1b** with **2e** (method A, 100 °C, 55 h) followed by deuterolysis. **2e** Was deprotonated by EtMgBr (1.2 M solution in THF, 1.0 equiv.) prior to reaction with **1b**. ^{1}H NMR (250 MHz): 7.37-7.27 (m, 5H, C_6H_5), 5.19 (m, 1H, H(6)), 4.97 (m, 1H, H(6)), 4.52 (s, 2H, OC$H_2C_6H_5$), 3.95 (s, 2H, C(5)CH_2O), 3.69 (m, 2H, H(1)), 2.93 (s, 2H, H(4)), 2.34 (t, ^{3}J(2,1) = 6.3 Hz, 2H, H(2)), 1.40 (t, ^{3}J(OH,1) = 5.8 Hz, 1H, OH), 0.11 (s, 9H, TMS). MS: 243 (4), 184 (10), 134 (8), 133 (9), 124 (14), 106 (28), 103 (29), 91 (100), 75 (44), 73 (95), 59 (10), 45 (15).

1-(2-Hydroxyethyl)-4-methylene-2-(trimethylsilyl)-1-cyclopentene (5e).
Prepared from **1b** and **2e** according to method A (conditions of the addition reaction: 100 °C, 55 h). Yield: 67 % (GLC). **2e** Was deprotonated by EtMgBr (1.2 M solution in THF, 1.0 equiv.) prior to reaction with **1b**. ^{1}H NMR (250 MHz): 4.93 (m, 2H, =CH_2), 3.72 (td, ^{3}J = 7.1 Hz, J = 1.1 Hz, 2H, CH_2OH), 3.17 (m, 4H, H(3,5)), 2.52 (t, ^{3}J = 7.1 Hz, 2H, C$H_2$$CH_2$OH), 1.35-1.24 (m, 1H, OH), 0.15 (s, 9H, TMS). MS: 196 (4, $M^{+\cdot}$), 181 (4), 165 (1), 151 (6), 131 (3), 123 (4), 103 (28), 91 (18), 75 (39), 73 (100), 59 (31), 45 (19). HRMS ($C_{11}H_{20}$OSi): calc. 196.1283, found 196.1263.

[1-$^2H_1$]-4-(Benzyloxymethyl)-2-(4-chlorobutyl)-1-(trimethylsilyl)-1,4-pentadiene (7f).
Prepared by reaction of **1b** with **2f** (method A) followed by deuterolysis. **7f** Was obtained as a mixture of diastereomers, ratio: 80:20. Major component. ^{1}H NMR (250 MHz): 7.37-7.27 (m, 5H, C_6H_5), 5.17 (d, ^{4}J = 1.4 Hz, 1H, H(5)), 4.98 (d, ^{4}J = 0.8 Hz, 1H, H(5)), 4.50 (s, 2H, OC$H_2C_6H_5$), 3.92 (s, 2H, C(4)CH_2O), 3.53 (t, ^{3}J(4',3') = 6.5 Hz, 2H, H(4')), 2.88 (s, 2H, H(3)), 2.18-2.10 (m, 2H, H(1')), 1.83-1.67, 1.63-1.47 (m, 4H, H(2',3')), 0.10 (s, 9H, TMS). Minor component. ^{1}H NMR (250 MHz): 7.37-7.27 (m, 5H, C_6H_5), 5.17 (d, ^{4}J = 1.4 Hz, 1H, H(5)), 4.94 (s, 1H, H(5)), 4.52 (s, 2H, OC$H_2C_6H_5$), 3.94 (s, 2H, C(4)CH_2O), 3.53 (t, ^{3}J(4',3') = 6.5 Hz, 2H, H(4')), 2.90 (s, 2H, H(3)), 2.12-2.02 (m, 2H, H(1')), 1.83-1.67, 1.63-1.47 (m, 4H, H(2',3')), 0.09 (s, 9H, TMS). MS (mixture of both components): 351 (0.5, $M^{+\cdot}$), 284 (16), 268 (2), 260 (7), 254 (6), 245 (8), 170 (33), 106 (21), 99 (32), 91 (98), 80 (28), 75 (26), 73 (100), 65 (10), 59 (12), 55 (13).

1-(4-Chlorobutyl)-4-methylene-2-(trimethylsilyl)-1-cyclopentene (5f).
Prepared from **1b** and **2f** according to method A (yield: 75 % [GLC]), or from **1a** and **2f** according to method B (yield: 70 %

[isolated]). ^{1}H NMR (250 MHz): 4.93 (m, 2H, $=CH_2$), 3.55 (t, ^{3}J(4',3') = 6.5 Hz, 2H, H(4'-Bu)), 3.14 (m, 4H, H(3,5)), 2.23 (t, ^{3}J(1',2') = 7.7 Hz, 2H, H(1'-Bu)), 1.85-1.70, 1.64-1.48 (m, 4H, H(2'-Bu,3'-Bu)), 0.13 (s, 9H, TMS). MS: 242 (6, $M^{+\cdot}$), 207 (1), 193 (1), 179 (1), 166 (2), 151 (8), 133 (3), 119 (7), 105 (17), 93 (29), 91 (33), 75 (56), 73 (100). HRMS ($C_{13}H_{23}ClSi$): calc. 242.1257, found 242.1224.

2-(6-(Benzyloxymethyl)-4-([1-$^2H_1$]-(trimethylsilyl)methylene)-6-heptenyl)-1,3-dioxolane (7h). Prepared by reaction of **1b** with **2g** (method A) followed by deuterolysis. **7h** Was obtained as a mixture of diastereomers, ratio: 74:26. Major component. ^{1}H NMR (250 MHz): 7.39-7.27 (m, 5H, C_6H_5), 5.17 (s, 1H, H(7')), 4.98 (d, ^{4}J = 0.8 Hz, 1H, H(7')), 4.84 (t, ^{3}J(2,1') = 4.4 Hz, 1H, H(2)), 4.50 (s, 2H, $OCH_2C_6H_5$), 4.04-3.79 (m, 6H, H(4,5), C(6')CH_2O), 2.89 (s, 2H, H(5')), 2.21-2.11 (m, 2H, H(3')), 1.72-1.48 (m, 4H, H(1',2')), 0.10 (s, 9H, TMS). MS: 375 (0.05, $M^{+\cdot}$), 284 (11), 268 (2), 254 (3), 222 (1), 212 (1), 196 (2), 179 (1), 170 (1), 150 (2), 132 (6), 117 (5), 106 (8), 99 (28), 91 (68), 73 (100), 59 (6), 45 (22). HRMS ($C_{15}H_{26}DO_3Si$ [M-$C_6H_5CH_2$]$^+$, mixture of both components): calc. 284.1784, found 284.1792. Minor component. ^{1}H NMR (250 MHz): 7.39-7.27 (m, 5H, C_6H_5), 5.17 (s, 1H, H(7')), 4.95 (d, ^{4}J = 1.6 Hz, 1H, H(7')), 4.85 (t, ^{3}J(2,1') = 4.4 Hz, 1H, H(2)), 4.52 (s, 2H, $OCH_2C_6H_5$), 4.04-3.79 (m, 6H, H(4,5), C(6')CH_2O), 2.91 (s, 2H, H(5')), 2.15-2.06 (m, 2H, H(3')), 1.72-1.48 (m, 4H, H(1',2')), 0.08 (s, 9H, TMS). MS: 375 (0.05, $M^{+\cdot}$), 374 (0.12), 284 (13), 268 (2), 254 (3), 222 (1), 212 (2), 196 (2), 179 (1), 150 (2), 132 (6), 117 (4), 106 (8), 99 (32), 91 (66), 73 (100), 59 (6), 45 (19). HRMS ($C_{15}H_{26}DO_3Si$ [M-$C_6H_5CH_2$]$^+$, mixture of both components): calc. 284.1784, found 284.1792.

2-(3-(4-Methylene-2-(trimethylsilyl)-1-cyclopentenyl)propyl)-1,3-dioxolane (5g).
Prepared from **1b** and **2g** according to method A (yield: 91 % [GLC]). ^{1}H NMR (250 MHz): 4.92 (m, 2H, $=CH_2$), 4.86 (t, ^{3}J(2,1') = 4.4 Hz, 1H, H(2)), 4.02-3.84 (m, 4H, H(4,5)), 3.14 (m, 4H, H(3",5")), 2.24 (t, ^{3}J(3',2') = 7.7 Hz, 2H, H(3')), 1.72-1.45 (m, 4H, H(1',2')), 0.12 (s, 9H, TMS). MS: 266 (1, $M^{+\cdot}$), 205 (3), 166 (4), 151 (5), 132 (11), 117 (7), 105 (5), 99 (9), 91 (12), 75 (48), 73 (100), 45 (29). HRMS ($C_{15}H_{26}O_2Si$): calc. 266.1702, found 266.1703.

1-(2-Tetrahydropyranyloxy)-2-(2-tetrahydropyranyloxymethyl)-2-pentene (20).
A mechanically stirred suspension of triphenylpropylphosphonium bromide (**18**) (323 g, 0.839 mol) in THF (800 ml) was cooled to -25 °C. Then, *n*-butyllithium (1.6 M solution in *n*-hexane, 525 ml, 0.840 mol) was added dropwise in 1.5 h. The reaction mixture was allowed to warm-up to room temperature in 2 h whereafter stirring was continued for another
0.5 h. After cooling to -25 °C, a solution of α,α'-bis(2-tetrahydropyranyloxy)acetone (**19**)[15] (216.4 g, 0.839 mol) in THF (400 ml) was added dropwise in 0.5 h. The reaction mixture was allowed to warm-up to room temperature overnight
and, subsequently, heated under reflux for 3 h. After cooling, most of the triphenylphosphine oxide and LiBr were removed by filtration. The residue was washed with four portions of diethyl ether. The filtrate and diethyl ether washings were poured onto saturated $NaHCO_3$ solution, and 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*. The crude reaction product (185.6 g), containing almost exclusively Wittig adduct **20** (yield *ca.* 78 %), was used as such in the following step. An analytical sample was obtained by preparative GLC. ^{1}H NMR (90 MHz): 5.70 (t, ^{3}J(3,4) = 7.5 Hz, 1H, H(3)), 4.64 (bs, 1H, H(2'-THP)), 4.62 (bs, 1H, H(2'-THP)), 4.46-3.9 (m, 4H, =C(C)CH_2O), 4.1-3.35 (m, 4H, H(6'-THP)), 2.18 (quintet, ^{3}J = 7.5 Hz, 2H, H(4)), 2.1-1.2 (m, 12H, H(3'-THP,4'-THP,5'-THP)), 1.00 (t, ^{3}J(5,4) = 7.5 Hz, 3H, H(5)).

2-Propylidene-1,3-propanediol (21).
A magnetically stirred solution of crude **20** (*ca.* 0.65 mol) and pyridinium *p*-toluenesulfonate (PPTS, 17.4 g, 65.4 mmol) in methanol (500 ml) was heated under reflux for 5 h. Then, the methanol and the tetrahydropyranyl ether of methanol formed were removed *in vacuo*. In order to achieve complete conversion of **20** into **21**, the sequence: addition of fresh methanol - 5 h reflux - evaporation of methanol and its THP ether, was repeated three times. After the last run, the concentrated reaction mixture was dissolved in dichloromethane and poured onto saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with dichloromethane and the combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. Distillation gave **21** (68.4 g, 91 %), bp 110 °C (4 Torr). ^{1}H NMR (90 MHz): 5.56 (t, ^{3}J(1',2') = 7.4 Hz, 1H, H(1')), 4.31 (s, 2H, CH_2OH), 4.21 (s, 2H, CH_2OH), 2.48 (bs, 2H, OH), 2.12 (quintet, ^{3}J = 7.4 Hz, 2H, H(2')), 1.00 (t, ^{3}J(3',2') = 7.6 Hz, 3H, H(3')).

2-(Benzyloxymethyl)-2-penten-1-ol (22a).

To a mechanically stirred suspension of NaH (0.300 mol) in DME (550 ml) was added dropwise a solution of diol **21** (34.8 g, 0.300 mol) in DME (50 ml). After 1 h reflux, the reaction mixture was cooled to room temperature. Then, with vigorous stirring, benzylbromide (46.3 g, 0.300 mol) was added in one portion. The mixture was heated under reflux for 2 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 ($MgSO_4$) and concentrated *in vacuo*. Distillation gave **22a** as a mixture of diastereomers (30.7 g, 50 %), bp 94 °C ($5 \cdot 10^{-3}$ mbar). Component I. ^{1}H NMR (90 MHz): 7.36 (m, 5H, C_6H_5), 5.67 (t, $^3J(3,4)$ = 6.5 Hz, 1H, H(3)), 4.54 (s, 2H, $OCH_2C_6H_5$), 4.29 (d, $^3J(1,OH)$ = 5.7 Hz, 2H, H(1)), 4.20 (s, 2H, C(2)CH_2O), 2.37-1.86 (m, 2H, H(4)), 1.00 (t, $^3J(5,4)$ = 7.5 Hz, 3H, H(5)). Component II. ^{1}H NMR (90 MHz): 7.36 (m, 5H, C_6H_5), 5.59 (t, $^3J(3,4)$ = 6.5 Hz, 1H, H(3)), 4.54 (s, 2H, $OCH_2C_6H_5$), 4.24-4.09 (m, 2H, H(1)), 4.11 (s, 2H, C(2)CH_2O), 2.37-1.86 (m, 2H, H(4)), 0.99 (t, $^3J(5,4)$ = 7.5 Hz, 3H, H(5)).

2-(Methoxymethyl)-2-penten-1-ol (22b).

After preparing the alkoxide of **21** (0.200 mol, in DME [400 ml]) according to the same procedure as described for the synthesis of **22a**, methyl iodide (28.4 g, 0.200 mol) was added in one portion. Stirring was continued for 2 h at room temperature whereafter aqueous work-up was performed in the same way as described for **22a**. Column chromatography (30 % ethyl acetate/70 % petroleum ether 40-60) provided **22b** as a mixture of diastereomers (8.97 g, 35 %). Component I. ^{1}H NMR (250 MHz): 5.62 (tm, $^3J(3,4)$ = 7.8 Hz, 1H, H(3)), 4.23 (s, 2H), 4.11 (d, ^4J = 0.8 Hz, 2H), 3.34 (s, 3H, OCH_3), 2.30 (bs, 1H, OH), 2.20-2.06 (m, 2H, H(4)), 0.99 (t, $^3J(5,4)$ = 7.5 Hz, 3H, H(5)). Component II. ^{1}H NMR (250 MHz): 5.55 (t, $^3J(3,4)$ = 7.4 Hz, 1H, H(3)), 4.08 (s, 2H), 3.98 (d, ^4J = 0.8 Hz, 2H), 3.33 (s, 3H, OCH_3), 2.30 (bs, 1H, OH), 2.20-2.06 (m, 2H, H(4)), 1.00 (t, $^3J(5,4)$ = 7.5 Hz, 3H, H(5)).

1-Benzyloxy-2-(chloromethyl)-2-pentene (23a).

A solution of **22a** (30.5 g, 0.148 mol), *s*-collidine (20.6 g, 0.170 mol) and LiCl (7.23 g, 0.170 mol) in DMF (250 ml) was cooled to 0 °C. A suspension was formed, which was treated dropwise with methanesulfonyl chloride (19.4 g, 0.170 mol). Stirring was continued for 1 h at 0 °C and, subsequently, for another 2 h at room temperature. The reaction mixture was poured onto ice-water and the aqueous layer was extracted four times with ether-pentane (1:1). The combined organic phases were diluted with an equal volume of pentane and then washed with water (4x), saturated citric acid solution (2x), water (1x), saturated $NaHCO_3$ solution (1x) and brine (1x). Drying (Na_2SO_4), evaporation of solvents and distillation provided **23a** as a mixture of diastereomers (28.1 g, 84 %), bp 112 °C ($3 \cdot 10^{-2}$ mbar). Component I. ^{1}H NMR (90 MHz): 7.36 (m, 5H, C_6H_5), 5.79 (t, $^3J(3,4)$ = 7.5 Hz, 1H, H(3)), 4.51 (s, 2H, $OCH_2C_6H_5$), 4.20 (s, 4H, H(1), CH_2Cl), 2.43-1.90 (m, 2H, H(4)), 1.04 (t, $^3J(5,4)$ = 7.4 Hz, 3H, H(5)). Component II. ^{1}H NMR (90 MHz): 7.36 (m, 5H, C_6H_5), 5.70 (t, $^3J(3,4)$ = 7.5 Hz, 1H, H(3)), 4.51 (s, 2H, $OCH_2C_6H_5$), 4.20 (s, 2H, H(1)), 4.09 (m, 2H, CH_2Cl), 2.43-1.90 (m, 2H, H(4)), 0.99 (t, $^3J(5,4)$ = 7.4 Hz, 3H, H(5)). MS (mixture of both components): 188 (2), 158 (7), 143 (2), 129 (3),
117 (2), 105 (9), 97 (10), 91 (100), 77 (11), 67 (29), 50 (7). HRMS ($C_{13}H_{16}O$ [M-HCl]$^+$, mixture of both compo- nents): calc. 188.1201, found 188.1207.

1-Chloro-2-(methoxymethyl)-2-pentene (23b).

Prepared from **22b** according to the same procedure as described for the synthesis of **23a**. Distillation gave **23b** as a mixture of diastereomers (yield: 77 %), bp 77-79 °C (21 Torr). Component I. ^{1}H NMR (90 MHz): 5.78 (t, $^3J(3,4)$ = 8.0 Hz, 1H, H(3)), 4.14 (s, 2H, C(2)CH_2O), 4.07 (m, 2H, H(1)), 3.31 (s, 3H, OCH_3), 2.20 (quintet, ^3J = 7.6 Hz, 2H, H(4)),
1.05 (t, $^3J(5,4)$ = 7.4 Hz, 3H, H(5)). Component II. ^{1}H NMR (90 MHz): 5.69 (t, $^3J(3,4)$ = 8.0 Hz, 1H, H(3)),
4.13 (m, 2H, C(2)CH_2O), 3.96 (q, ^4J = 0.8 Hz, 2H, H(1)), 3.30 (s, 3H, OCH_3), 2.18 (quintet, ^3J = 7.6 Hz, 2H, H(4)), 1.01 (t, $^3J(5,4)$ = 7.4 Hz, 3H, H(5)). MS (mixture of both components): 148 (3, $M^{+\cdot}$), 119 (89), 116 (95), 113 (93), 107 (8), 99 (42), 91 (26), 86 (61), 81 (100), 79 (81), 71 (87), 67 (72), 55 (47), 53 (64), 45 (94), 40 (94). HRMS ($C_7H_{13}{}^{35}ClO$, mixture of both components): calc. 148.0655, found 148.065.

1-Benzyloxy-2-(chloromagnesiomethyl)-2-pentene (24a).
Following the same procedure for the synthesis of **10a**, **24a** was prepared from **23a** in 88 % yield.

1-(Chloromagnesio)-2-(methoxymethyl)-2-pentene (24b).
Following the same procedure for the synthesis of **10a**, **24b** was prepared from **23b** in 100 % yield.

1-Benzyloxy-2-(bromozincmethyl)-2-pentene (1c).
Prepared from **24a** according to the same procedure as described for the synthesis of **1a**. The THF solution of the organozinc compound was concentrated at atmospheric pressure to 1.4 M.

1-(Bromozinc)-2-(methoxymethyl)-2-pentene (1d).
Prepared from **24b** according to the same procedure as described for the synthesis of **1a**. The THF solution of the organozinc compound was concentrated at atmospheric pressure to 1.8 M.

Attempted preparation of 5i from 1c (0.2 M) and 2a (Table 2, entries 1,2).
The reaction was performed according to method A, starting from **1c** (0.2 M solution in THF, 1.2 equiv.), **2a** (0.154 g, 1.0 mmol) and, as internal standard, *n*-dodecane (0.0850 g, 0.500 mmol).
Addition (100 °C, 30 h; then 130 °C, 30 h). Aqueous work-up gave mixtures of **6i** and **17i** (for yields, see: Table 2, entries 1,2).
Cyclization (65 °C, 30 h). Aqueous work-up gave **5i** (yield: 19 %), **15i** (yield: 14 %) and **16i** (yield: 4 % [GLC yields, based on **2a**]).

2-Butyl-3-ethyl-4-(benzyloxymethyl)-1-(trimethylsilyl)-1,4-pentadiene (6i).
^{1}H NMR (250 MHz): 7.39-7.26 (m, 5H, C_6H_5), 5.31 (s, 1H, H(1)), 5.21 (m, 1H, H(5)), 5.02 (bs, 1H, H(5)), 4.49 (s, 2H, $OCH_2C_6H_5$), 3.89 (s, 2H, C(4)CH_2O), 2.70 (t, ^3J = 7.3 Hz, 1H, H(3)), 2.07 (m, 2H, H(1'-Bu)), 1.58 (quintet, ^3J = 7.4 Hz, 2H, CH_2CH_3), 1.44-1.21 (m, 4H, H(2'-Bu,3'-Bu)), 0.90 (t, ^3J = 6.8 Hz, 3H), 0.88 (t, ^3J = 7.2 Hz, 3H), 0.09 (s, 9H, TMS). MS: 344 (7, $M^{+\cdot}$), 253 (5), 238 (3), 223 (4), 196 (2), 181 (3), 163 (13), 135 (7), 121 (14), 107 (11), 91 (53), 79 (6), 73 (100), 59 (8), 55 (5). HRMS ($C_{22}H_{36}OSi$): calc. 344.2535, found 344.2531.

2-Butyl-4-(benzyloxymethyl)-1-(trimethylsilyl)-1,4-heptadiene (17i).
^{1}H NMR (250 MHz): 7.36-7.27 (m, 5H, C_6H_5), 5.60 (t, ^3J(5,6) = 7.2 Hz, 1H, H(5)), 5.17 (t, ^4J = 0.5 Hz, 1H, H(1)), 4.46 (s, 2H, $OCH_2C_6H_5$), 3.85 (d, ^4J = 0.8 Hz, 2H, C(4)CH_2O), 2.89 (s, 2H, H(3)), 2.14-1.99 (m, 4H, H(6,1'-Bu)), 1.50-1.23 (m, 4H, H(2'-Bu,3'-Bu)), 0.99 (t, ^3J(4',3') = 7.5 Hz, 3H, H(4'-Bu)), 0.92 (t, ^3J(7,6) = 7.0 Hz, 3H, H(7)), 0.08 (s, 9H, TMS). MS: 344 (4, $M^{+\cdot}$), 253 (4), 238 (3), 223 (2), 195 (4), 181 (4), 163 (14), 149 (4), 135 (6), 121 (8), 107 (10), 91 (48), 79 (5), 73 (100), 59 (8), 55 (4). HRMS ($C_{22}H_{36}OSi$): calc. 344.2535, found 344.2534.

2-Butyl-3-ethyl-4-methylene-1-(trimethylsilyl)-1-cyclopentene (5i).
^{1}H NMR (400 MHz): (1) 4.98 (m, 1H, =CH_2), (2) 4.88 (m, 1H, =CH_2), (3) 3.24 (m, 1H, H(3)), (4) 3.06 (m, 2H, H(5)), (5) 2.27 (ddd, J = 13.8 Hz, J = 10.6 Hz, J = 6.3 Hz, 1H, C*Ha*HbC_3H_7), (6) 2.04-1.95 (m, 1H, CHa*Hb*C_3H_7), (7) 1.56 (m, 2H, CH_2CH_3), (8) 1.46 (m, 1H, $CH_2CH_2CHHCH_3$), (9) 1.28 (m, 3H, $CH_2CH_2CHHCH_3$), (10) 0.92 (t, ^3J = 7.0 Hz, 3H, $C_3H_6CH_3$), (11) 0.75 (t, ^3J = 7.4 Hz, 3H, CH_2CH_3), (12) 0.12 (s, 9H, TMS). 2D NOESY NMR (400 MHz, τ_m = 2.0 s): 1(4), 2(3,7,11), 3(7,8,9,11^W), 4(11^W), 5(6,9), 6(7,8,9,11), 7(11), 8(9). ^{13}C NMR (63 MHz): 155.7 (s, C(2*)), 154.3 (s, C(4*)), 133.6 (s, C(1)), 105.3 (tq, ^1J(CH) = 155 Hz, ^3J(CH) = 4 Hz, =CH_2), 53.3 (d, ^1J(CH) = 135 Hz, C(3)), 43.8 (tm, ^1J(CH) = 129 Hz, C(5)), 30.8 (tm, ^1J(CH) = 131 Hz, CH_2), 29.6 (t, ^1J(CH) = 131 Hz, CH_2), 25.1 (t, ^1J(CH) = 127 Hz, CH_2), 23.0 (t, ^1J(CH) = 124 Hz, CH_2), 14.1 (q, ^1J(CH) = 125 Hz, C(4'-Bu)**), 8.9 (q, ^1J(CH) = 126 Hz, CH_2CH_3**), -0.3 (q, ^1J(CH) = 118 Hz, TMS). MS: 236 (8, $M^{+\cdot}$), 221 (2), 207 (9), 194 (9), 179 (1), 162 (3), 149 (1), 133 (2), 120 (3), 105 (3), 91 (4), 73 (100), 59 (9). HRMS ($C_{15}H_{28}Si$): calc. 236.1960, found 236.1962.

1-Butyl-4-propylidene-2-(trimethylsilyl)-1-cyclopentene (15i).
^{1}H NMR (250 MHz): 5.28 (m, 1H, =C*H*CH_2CH_3), 3.08 (AB system, δ(A) = 3.17, dm, J(AB) = 24.3 Hz, 2H, H(3,5), δ(B) = 2.99, J(BA) = 24.3 Hz, 2H, H(3,5)), 2.25-2.13, 2.07-1.90 (m, 4H, H(1'-Bu), =CHC*H*$_2$$CH_3$), 1.49-1.20 (m, 4H, H(2'-Bu,3'-Bu)), 0.97 (t, ^{3}J = 7.5 Hz, 3H, CH_2C*H*$_3$), 0.92 (t, ^{3}J = 6.9 Hz, 3H, H(4'-Bu)), 0.13 (s, 9H, TMS). MS: 236 (18, $M^{+\cdot}$), 221 (4), 207 (1), 194 (3), 179 (1), 162 (26), 147 (1), 133 (6), 120 (25), 91 (5), 73 (100), 59 (14). HRMS ($C_{15}H_{28}Si$): calc. 236.1960, found 236.1955.

1-Butyl-3-ethyl-4-methylene-2-(trimethylsilyl)-1-cyclopentene (16i).
^{1}H NMR (250 MHz): 4.93 (m, 1H, =CH_2), 4.84 (m, 1H, =CH_2), 3.22-3.13 (m, 1H, H(3)), 3.04 (AB system, δ(A) = 3.16, dm, J(AB) = 20.8 Hz, 1H, H(5), δ(B) = 2.92, J(BA) = 20.8 Hz, 1H, H(5)), 2.26-2.16 (m, 2H, H(1'-Bu)), 1.62-1.23 (m, 6H, H(2'-Bu,3'-Bu), C*H*$_2$$CH_3$), 0.92 (t, ^{3}J = 6.9 Hz, 3H), 0.80 (t, ^{3}J = 7.3 Hz, 3H), 0.14 (s, 9H, TMS). MS: 236 (10, $M^{+\cdot}$), 221 (3), 207 (34), 193 (2), 179 (2), 163 (5), 133 (7), 120 (5), 105 (6), 73 (100), 59 (13), 55 (3). HRMS ($C_{15}H_{28}Si$): calc. 236.1960, found 236.1960.

General procedure for the preparation of the 4-methylenecyclopentenes 5i, 5j and 5k starting from 1c (1.4 M) and acetylenes 2a,f,g (Table 2, entries 3-7).

2-Butyl-3-ethyl-4-methylene-1-(trimethylsilyl)-1-cyclopentene (5i) (Table 2, entry 3).
To a solution of **1c** in THF (1.4 M, 5.7 mmol) were added **2a** (0.292 g, 1.90 mmol) and, as internal standard, *n*-dodecane (0.159 g, 0.935 mmol). The magnetically stirred mixture was heated in standard glass equipment for 30 h at 95 °C (boiling point of the THF solution of the organozinc reagent). After cooling, a small portion of the reaction mixture was quenched with aqueous NH_4Cl. Work-up and GLC/NMR analysis indicated the presence of **6i** and **17i** (yields: 60 % and 11 %, respectively [GLC yields, based on **2a**]). To the remainder of the reaction mixture were added THF (6 ml) and [$Pd(PPh_3)_4$] (0.110 g, 0.095 mmol) and the heating was continued at 65 °C for 8 h. The reaction mixture was cooled and poured onto saturated NH_4Cl solution. After extracting the aqueous 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 and consisted of **5i** (yield: 68 %) and **15i** (yield: 1 % [GLC yields, based on **2a**]).

Reaction of 2f (Table 2, entries 4 and 5).
Addition (95 °C, 8/30 h). NH_4Cl quench and work-up gave a mixture of **6j** and **17j** (ratio 85:15/85:15).
Cyclization. Aqueous work-up gave **5j** exclusively (yield: 76 % [GLC, based on **2f**]).

2-(4-Chlorobutyl)-3-ethyl-4-(benzyloxymethyl)-1-(trimethylsilyl)-1,4-pentadiene (6j).
^{1}H NMR (250 MHz): 7.36-7.27 (m, 5H, C_6H_5), 5.30 (s, 1H, H(1)), 5.21 (m, 1H, H(5)), 5.03 (m, 1H, H(5)), 4.49 (s, 2H, OC*H*$_2$$C_6H_5$), 3.89 (bs, 2H, C(4)$CH_2$O), 3.51 (t, ^{3}J = 6.6 Hz, 2H, H(4'-Bu)), 2.71 (t, ^{3}J = 7.2 Hz, 1H, H(3)), 2.09 (t, ^{3}J = 8.2 Hz, 2H, H(1'-Bu)), 1.83-1.66 (m, 2H, C*H*$_2$$CH_3$), 1.66-1.42 (m, 4H, H(2'-Bu,3'-Bu)), 0.89 (t, ^{3}J = 7.2 Hz, 3H, CH_2C*H*$_3$), 0.10 (s, 9H, TMS). MS: 378 (7, $M^{+\cdot}$), 289 (2), 287 (5), 272 (4), 207 (6), 197 (22), 181 (4), 165 (3), 149 (3), 135 (10), 121 (8), 107 (15), 91 (97), 81 (17), 73 (100), 67 (5), 55 (11). HRMS ($C_{22}H_{35}{}^{35}ClOSi$): calc. 378.2146, found 378.2158.

4-(Benzyloxymethyl)-2-(4-chlorobutyl)-1-(trimethylsilyl)-1,4-heptadiene (17j).
Mixture of 2 components, ratio: 79:21. Major component. ^{1}H NMR (250 MHz): 7.39-7.22 (m, 5H, C_6H_5), 5.61 (t, ^{3}J(5,6) = 6.8 Hz, 1H, H(5)), 5.21 (bs, 1H, =C*H*TMS), 4.46 (s, 2H, OC*H*$_2$$C_6H_5$), 3.85 (s, 2H, C(4)$CH_2$O), 3.54 (t, ^{3}J = 6.5 Hz, 2H, H(4'-Bu)), 2.89 (s, 2H, H(3)), 2.22-1.43 (m, 8H, H(6,1'-Bu,2'-Bu,3'-Bu)), 0.99 (t, ^{3}J(7,6) = 7.5 Hz, 3H, H(7)), 0.08 (s, 9H, TMS). Minor component. ^{1}H NMR (250 MHz): 7.39-7.22 (m, 5H, C_6H_5), 5.61 (t, ^{3}J(5,6) = 6.8 Hz, 1H, H(5)), 5.04 (bs, 1H, =C*H*TMS), 4.50 (s, 2H, OC*H*$_2$$C_6H_5$), 3.89 (s, 2H, C(4)$CH_2$O), 3.52 (t, ^{3}J = 6.5 Hz, 2H, H(4'-Bu)), 3.03 (s, 2H, H(3)), 2.22-1.43 (m, 8H, H(6,1'-Bu,2'-Bu,3'-Bu)), 0.89 (t, ^{3}J(7,6) = 7.3 Hz, 3H, H(7)), 0.12 (s, 9H, TMS). MS (mixture of both components): 378 (0.8, $M^{+\cdot}$), 289 (2), 287 (3), 272 (3), 257 (1), 229 (3), 197 (21), 181 (5), 135 (7), 133 (7), 119 (9), 107 (16), 105 (13), 91

(100), 79 (20), 73 (81), 65 (12), 55 (11).

2-(4-Chlorobutyl)-3-ethyl-4-methylene-1-(trimethylsilyl)-1-cyclopentene (5j).
^{1}H NMR (250 MHz): 4.98 (m, 1H, =CH_2), 4.88 (m, 1H, =CH_2), 3.55 (t, ^{3}J = 6.5 Hz, 2H, H(4'-Bu)), 3.24 (m, 1H, H(3)), 3.07 (m, 2H, H(5)), 2.38-2.21 (m, 1H, H(1'-Bu)), 2.13-1.97 (m, 1H, H(1'-Bu)), 1.85-1.33 (m, 6H, H(2'-Bu,3'-Bu), CH_2CH_3), 0.75 (t, ^{3}J = 7.3 Hz, 3H, CH_2CH_3), 0.13 (s, 9H, TMS). MS: 270 (17, $M^{+\cdot}$), 255 (1), 241 (5), 235 (3), 196 (5), 179 (1), 161 (2), 147 (5), 133 (36), 119 (9), 105 (18), 91 (47), 79 (7), 73 (100), 59 (8), 55 (6). HRMS ($C_{15}H_{27}{}^{35}ClSi$): calc. 270.1570, found 270.1568.

Reaction of 2g (Table 2, entries 6 and 7).
Addition (95 °C, 8/30 h). NH_4Cl quench and work-up gave a mixture of **6k** and **17k** (ratio 86:14/86:14 [GLC]).
Cyclization. Aqueous work-up gave **5k** exclusively (yield: 71 % [GLC, based on **2g**]).

2-(3-(5-Ethyl-4-methylene-2-(trimethylsilyl)-1-cyclopentenyl)propyl)-1,3-dioxolane (5k).
^{1}H NMR (250 MHz): 4.96 (m, 1H, =CH_2), 4.86 (m, 1H, =CH_2), 4.84 (t, ^{3}J(2,1') = 4.5 Hz, 1H, H(2)), 4.00-3.75 (m, 4H, H(4,5)), 3.25 (m, 1H, H(5")), 3.06 (m, 2H, H(3")), 2.40-2.00 (m, 2H, H(3')), 1.83-1.34 (m, 6H, H(1',2'), CH_2CH_3), 0.74 (t, ^{3}J = 7.3 Hz, 3H, CH_2CH_3), 0.12 (s, 9H, TMS). MS: 294 (12, $M^{+\cdot}$), 195 (30), 160 (18), 145 (9), 131 (13), 117 (11), 105 (17), 99 (15), 79 (7), 73 (100), 59 (20), 55 (9), 44 (41). HRMS ($C_{17}H_{30}O_2Si$): calc. 294.2015, found 294.201.

Preparation of 5i from 1d and 2a (Table 2, entry 8).
To a solution of **1d** in THF (1.8 M, 18.4 mmol) was added **2a** (0.895 g, 5.81 mmol) whereafter the magnetically stirred mixture was heated in standard glass equipment for 24 h at 75 °C (boiling point of the THF solution of the organozinc reagent). After cooling, a small portion of the reaction mixture was quenched with aqueous NH_4Cl. Work-up and GLC analysis indicated the presence of **6l** and **17l** (ratio: 86:14). [$Pd(PPh_3)_4$] (0.400 g, 0.346 mmol) was added and the heating was continued at 75 °C for 1.5 h. The reaction mixture was worked up as described before. Evaporative distillation (80-160 °C, 4 Torr) gave **5i** (1.15 g, 84 %).

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