Intramolecular Ene and Related Reactions, 5[3g]

Stereoselective Formation of *trans*-1,2-Disubstituted Cyclopentanes by Intramolecular Cyclisation of Allylsilane Alkylidene 1,3-Dioxo Compounds

Lutz F. Tietze* and Michael Ruther

Institut für Organische Chemie der Universität Göttingen,
Tammannstraße 2, D-3400 Göttingen, F.R.G.

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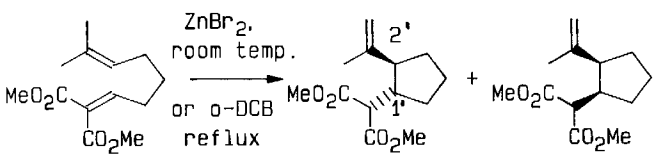
The alkylidene 1,3-dioxo compounds **4a–d** with an allylsilane moiety undergo a fluoride-, Lewis acid- and TMSOTf-induced intramolecular cyclisation to give almost exclusively the *trans*-1,2-disubstituted cyclopentanes **5a–d** in good to excellent yields. The diastereoselectivity of the reaction was determined as a function of the 1,3-dioxo moiety and the inductor. The best results were obtained with $FeCl_3/Al_2O_3$ followed by TMSOTf and Me_2AlCl; the highest selectivity was found in the cyclisation of **4b** with TMSOTf leading to **5b** and **6b** in a ratio of 99.8:0.2. $FeCl_3/Al_2O_3$ and TMSOTf have not previously been used for this type of reaction. The alkylidene 1,3-dioxo compounds **4a–d** were synthesised by Knoevenagel condensation of the aldehyde **11** with the malonic acid derivatives **14a–d**.

Many natural compounds like the iridoids, the prostaglandines, and brefeldine contain a cyclopentane ring system. Therefore, an increased interest in the stereoselective synthesis of this skeleton has emerged[1]. We have recently shown that *trans*-1,2-disubstituted cyclopentanes **2** can easily be prepared by an intramolecular ene reaction of alkylidenemalonates like **1**[2]. The main advantage of this reaction is its high stereoselectivity (**2**:**3** > 99:1) and the simple accessibility of the starting material by a Knoevenagel condensation of a malonate and an appropriate aldehyde. In addition, also *trans*-1,2-disubstituted cyclohexanes can be synthesized applying this method[3]. However, good results are obtained only by using alkylidene 1,3-dicarbonyl compounds like **1** with a trisubstituted double bond as the ene moiety. Decrease of the substitution level at the alkene group would lower its HOMO energy and thus decrease the reaction rate in this HOMOene-LUMOenophile-controlled transformation. In order to broaden the scope of the reaction we investigated the use of an allylsilane as the terminating group in the cyclisation.



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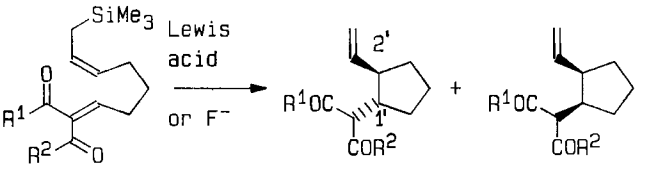
C–C bond formation by Lewis acid- and fluoride-catalysed reaction of α,β-unsaturated ketones and allylsilanes is a well-known and widely used method[4,5]. Also, the intermolecular transformation of α,β-unsaturated dicarboxylates with allylsilanes proceeds with good yield, though less often applied[6]. However, the intramolecular reaction of the latter type was not observed so far, but only desilylation of the substrate[7].

In contrast, transformation of the alkylidenemalonates **4a–d** by means of Lewis acids-, trimethylsilyl trifluoromethanesulfonate-(TMSOTf-), and fluoride-initiation gives the corresponding *trans*-1,2-disubstituted cyclopentanes **5a–d** with good to excellent yields and high selectivities as shown in this paper. The best results have been obtained with $FeCl_3$ on Al_2O_3, Me_2AlCl, and TMSOTf. It should be pointed out that the diastereoselectivity of the cyclisation strongly depends on the structure of the dioxo moiety and the initiator used (Table 1). The necessary alkylidene 1,3-dicarbonyl compounds **4a–d** have been obtained by Knoevenagel condensation of aldehyde **11** with various 1,3-dioxo compounds **14**.



4a–d 5a–d 6a–d

4–6	R1	R2
a	OMe	OMe
b	OBzl	OBzl
c	-NMeCONMe-	
d	-OCMe2O-	

An unselective synthesis of a mixture of the (*Z*)- and (*E*)-aldehyde **11** (4:1) has already been described by Proctor[8a,b]. To obtain pure (*Z*)-**11** we have developed two different pathways (Scheme 1): 1. Pure (*Z*)-**11** was obtained with 33% overall yield in six steps starting with 2-(hydroxymethyl)-tetrahydropyran (**7**), which was transformed into **8** accord-

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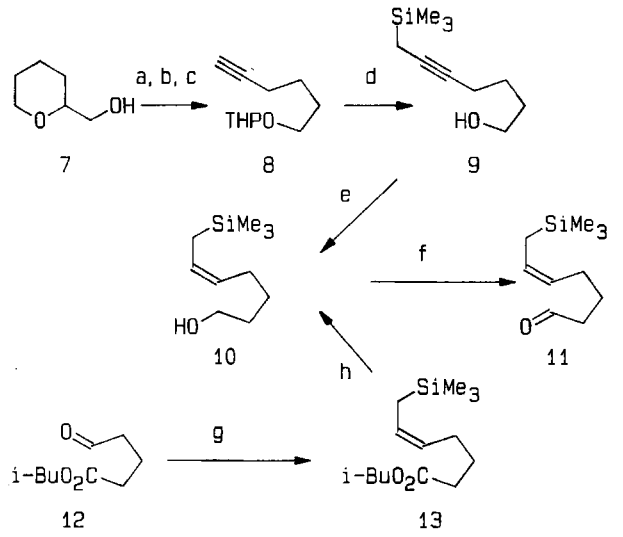
ing to Tufariello[9] in 56% overall yield. Silylation, deprotection, and reduction according to Hiemstra and Speckamp[10] yielded allylsilane **10** via **9** in 69% yield (based on **8**). The hydrogenation of **9** to give the (*Z*)-allylsilane **10** occurs with remarkable high selectivity (GLC: >99:1). Swern oxidation[11] allowed to smoothly transform **10** to the acid-sensitive aldehyde **11**. 2. The aldehyde **11** could also be synthesized in a much shorter sequence with only three steps from isobutyl 4-oxopentanoate (**12**)[12] as starting material with 36% overall yield; however, a 93:7 mixture of (*Z*)- and (*E*)-**11** is obtained in this case, due to the not completely selective Wittig reaction of **12** to give **13**, according to Seyfert and Fleming[8]. For the following reactions the pure aldehyde (*Z*)-**11** was used.

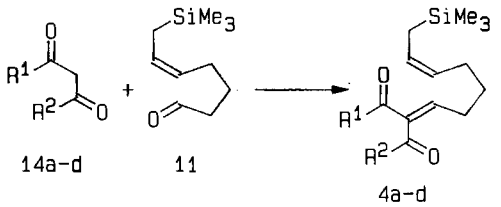
Scheme 1. Syntheses of the aldehyde (*Z*)-**11**



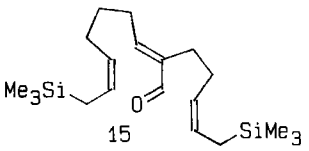
a) $SOCl_2$/pyridine, b) $NaNH_2/NH_3$, c) DHP/HCl, d) n-butyllithium/THF/ICH_2TMS, H_2SO_4, e) P-2 Ni/H_2, f) $(COCl)_2$/DMSO, g) $PPh_3{=}CHCH_2TMS$/THF, h) $LiAlH_4$

The synthesis of the Knoevenagel products **4a–d** was achieved by condensation of the malonic acid derivatives **14a–d** and the aldehyde **11** with piperidinium acetate or ethylenediammonium diacetate as catalysts in dichloromethane at 0°C in 48–72% yield. In addition, the corresponding aldol product **15** and Michael adducts were formed, which however could be separated by column chromatography. **4a–d** are highly sensitive compounds which may already undergo cyclisation or decomposition by a longer contact with silica gel. They usually were not isolated, but directly cyclised after rapid chromatography. Thus, **4c** and **4d** could not be characterized[13], however for **4a** and **4b** full spectroscopic data were obtained with the characteristic low-field absorption for 3-H at δ = 7.06 and 7.09, respectively, as a triplet with J = 8 Hz.

A main aim in our investigations was to determine the selectivity in the transformation depending on the inductor used and the structure of the substrate. Thus, the Lewis acids $TiCl_4$, Et_2O-BF_3, $ZnBr_2$, Me_2AlCl, and $FeCl_3/Al_2O_3$ as well as TMSOTf and NBu_4F/SiO_2 were applied for the cyclisation of **4a–d** to give the *trans*- and *cis*-cyclopentane derivatives **5a–d** and **6a–d**.The ratio of **5a**/**6a** and **5b**/**6b** was examined by capillary GLC of the crude mixtures after aqueous workup. The meldrumates **5d**/**6d** were transformed into the dimethyl malonates **5a**/**6a** by acid-catalysed methanolysis before detection. The ratio of the barbiturates **5c**/**6c** was determined by NMR spectroscopy since they are not volatile. It is of interest that enolization of **5c** occurs in chloroform after longer standing even at 5°C.



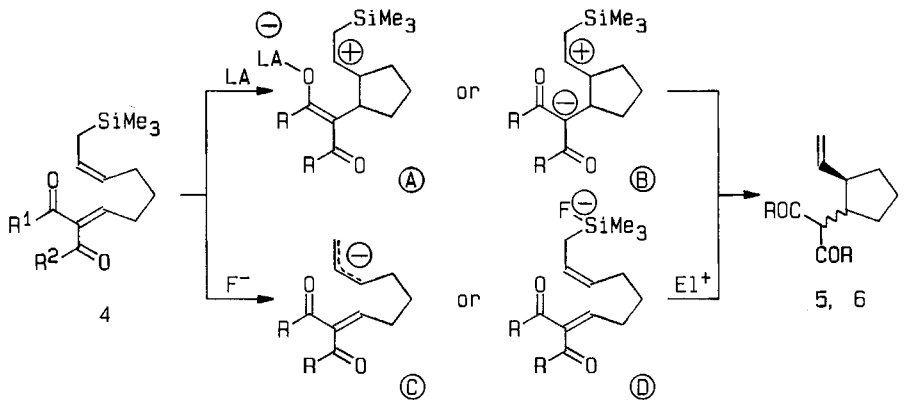
14	R1	R2
a	OMe	OMe
b	OBzl	OBzl
c	-NMeCONMe-	
d	$-OCMe_2O-$	



It has been discussed that the fluoride-initiated reaction of allylsilanes proceeds by an allylic C–Si bond cleavage to give formally an allylic anion, which adds to carbonyl compounds in good yields; however, it seems more likely that a hypervalent silyl anion is formed as intermediate (Scheme 2, C and D, respectively)[5]. For the cyclisation of **4** to give the cyclopentane derivatives **5** and **6** tetra-*n*-butylammonium fluoride (TBAF) was the least effective inductor. Thus, with **4a** and **4b** the cyclisation could not be achieved even in the presence of *N,N'*-dimethylpropyleneurea (DMPU) as cosolvent and with **4c** and **4d** the yields and selectivities were the lowest compared to the other inductors (Table 1).

The classical Lewis acids[4,14] $TiCl_4$ and Et_2O-BF_3 gave good selectivities and mediocre to good yields (Table 1). Notable is the decomposition of the barbiturate **4c** in the presence of $TiCl_4$. Variation of the reaction conditions in a wide range did not lead to cyclisation products in this case. $ZnBr_2$ could also be used with the advantage of performing the reaction at room temperature, however, the selectivities were slightly lower. On an average the best results were obtained with $FeCl_3/Al_2O_3$ which was successfully introducted by us for the ene reaction[3] and which gives **5a–d**/**6a–d** in a ratio of 98.8:1.2 to >95:5 in 67 to 90% yields. Also Me_2AlCl, introduced by Schinzer[15] in the Sakurai reaction[5c], and TMSOTf[16], which has not been applied so far in this type of transformation, showed good results. The ratio of the cyclopentanes **5a**/**6a** and **5b**/**6b** exceeded 99.3:0.7, whereby in the cyclisation of **4b** with TMSOTf as inductor the highest selectivity was found with **5b**:**6b** = 99.8:0.2. The cyclic compounds **4c** and **4d**, however, were converted in the presence of TMSOTf into **5c**/**6c** and **5d**/**6d** with lower selectivity and lower yield.

Scheme 2. Fluoride- and Lewis acid-initiated cyclisation of **4**



The Lewis acid-induced cyclisations were usually carried out at −78 °C under N_2 with the exception of the reaction with $ZnBr_2$ (23 °C) and the cyclisation of the barbiturate **4c**.

Table 1. Effect of Lewis acid, fluoride, and dicarbonyl moiety in the cyclisation of **4** to **5** and **6**

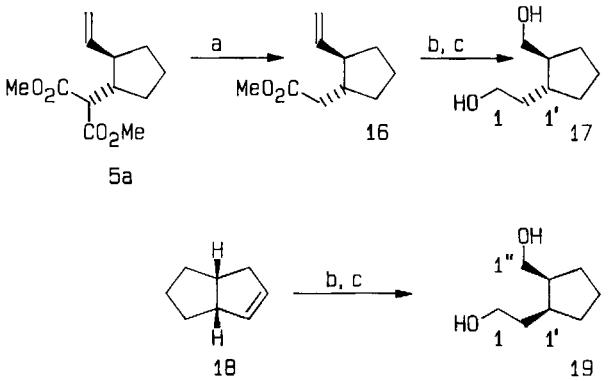
Catalyst	Starting material	Time [h]	Yield [%]	Product ratio[a] [5:6]	ni-de [5-6]/[5+6]
NBu_4F/SiO_2 23°C	4a			decomposition	
	4b			decomposition	
	4c	6	62	85 :15[c]	70
	4d	5	41	89.0:11.0 ±0.3[b]	78.1
$TiCl_4$ −78°C	4a	3	81	96.6: 3.4 ±0.2	93.2
	4b	3	66	97.2: 2.8 ±0.2	94.4
	4c[f]			decomposition	
	4d	6	75	90.6: 9.4 ±0.1[b]	81.1
$BF_3 \cdot OEt_2$ −78°C	4a	5	47	96.8: 3.2 ±0.7	93.6
	4b	5	60	96.6: 3.4 ±0.2	93.3
	4c[f]	5	61	>95: 5[c]	>90
	4d	6	77	91.9: 8.1 ±0.2[b]	83.8
$ZnBr_2$ 23°C	4a	4	54	95.8: 4.2 ±0.3	91.6
	4b	12	70	93.5: 6.5 ±0.1	87.0
	4c[f]	24	74	>95: 5[c]	>90
	4d	24	40	89.3:10.7 ±0.6[b]	78.6
Me_2AlCl −78°C	4a	3	86	99.7: 0.3 ±0.1[e]	99.3
	4b	3	62	99.3: 0.7 ±0.1[e]	98.5
	4c[f]	48	67	>90:10[c]	>80
	4d	6	69	92.0: 8.0 ±0.2[b,e]	84.1
$FeCl_3/Al_2O_3$ −78°C	4a	4	73	98.8: 1.2 ±0.1[e]	97.6
	4b	4	90	97.3: 2.7 ±1.8[e]	94.6
	4c[g]	24	67	>95: 5[c]	>90
	4d	4	73	96.8: 3.2 ±1.1[b,e]	93.6
TMSOTf −78°C	4a	4	97	99.6: 0.4 ±0.2[e]	99.2
	4b	3	66	99.8: 0.2 ±0.7[e]	99.6
	4c[f]	24	47	>95: 5[d]	>90
	4d	4	45	94.8: 5.2 ±0.3[b,e]	89.5

[a] The ratio was determined by capillary GLC. — [b] Ratio of dimethyl malonate after transformation. — [c] Determined by ^{13}C-NMR spectroscopy. — [d] Determined by ^1H-NMR spectroscopy. — [e] Average of three experiments. — [f] Performed at room temp. — [g] Performed at −15 °C.

In general, the cyclisation of **4c** was most difficult, and the results depended on the reaction conditions. In some cases no cyclisation was observed initially and only decomposed material was obtained. In all cases, the Lewis acid had to be used in more than one equivalent, otherwise an incomplete transformation was found.

The determination of the configuration of the cyclopentane derivatives **5a–d** was difficult, since cyclopentanes do not exist in a rigid conformation. However, an X-ray analysis of **20** has been performed, and the NMR data of **5a–d** were compared with those of **20**. In addition, **5a** was transformed by demethoxycarbonylation[17], ozonolysis, and reduction into the *trans*-1,2-disubstituted cyclopentane **17**. On the other hand, the commercially available bicycloocten **18**[18] gave the *cis*-1,2-disubstituted cyclopentane **19** on ozonolysis and reduction (Scheme 3). Although the NMR spectra of the *trans*- and *cis*-1,2-disubstituted cyclopentanes **17** and **19** are quite similar, it could clearly be demonstrated that they are not identical.

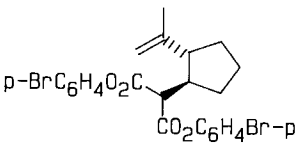
Scheme 3. Determination of the configuration of **5a**. Transformation of **5a** into **17** and **18** into **19**



a) DMSO/H_2O/NaCl/160°C, b) O_3/CH_2Cl_2, c) $LiAlH_4$/THF

In the ^1H-NMR spectrum of **17** signals for the diastereotopic protons 1-H_2 and 1″-H_2 are found at δ = 3.19, 3.45, 3.51, and 3.66 and in the spectrum of **19** at δ = 3.23, 3.37,

3.41 and 3.48. C-1 and C-1″ in **17** absorb at δ = 61.3 and 66.6 and in **19** at 61.9 and 62.7. Finally, in the GLC analysis **17** and **19** exhibited a different retention time. Since **19** is obtained from a *cis*-1,2-disubstituted cyclopentane derivative, the *trans*-1,2-disubstitution is therefore proved for **17**. An isomerisation during the transformation of **18** to **19** at C-2′ can be excluded although it is possible in principle since a formyl group at C-2′ is formed intermediately; however, this would also apply for the transformation of **5a** into **17**, and therefore a mixture of **17** and **19** should be found in both cases.



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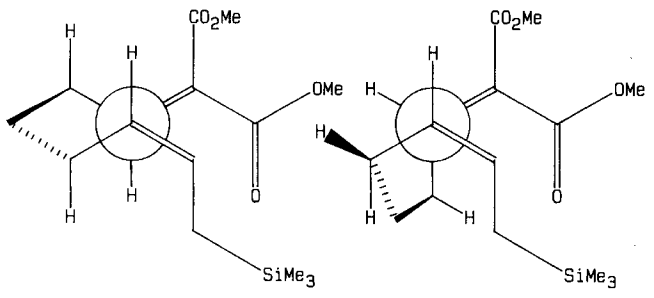
In the ^{1}H-NMR spectra of **5a–d** the signals of the vinyl protons are found at δ = 4.86–5.14 (2″-H) and 5.51–5.62 (1″-H) and of 1′-H and 2′-H around δ = 2.3 and 2.5, respectively. It is of interest that the chemical shift values are the same for 1′-H ad 2′-H in **5a** at δ = 2.30 with $CDCl_3$ as solvent, whereas separate signals are found in C_6D_6 at δ = 2.45 and 2.29. C-1′ and C-2′ of **5a** absorb in C_6D_6 at δ = 45.1 and 49.0, respectively. In contrast, the signals of 1′-H and 2′-H as well as C-1′ and C-2′ of the barbiturate **5c** are reversed. Thus, 1′-H with δ = 2.28 and C-2′ with δ = 47.2 absorb at higher field than 2′-H with δ = 2.52 and C-1′ with δ = 50.0. This can be explained by assuming a different conformation of the dioxo moiety in **5a** and **5c**. This explanation is supported by the vicinal coupling constants with $J_{1',2}$ = 7.6 Hz for **5a** and $J_{1',5}$ = 3.3 Hz for **5c**[19]. The cyclisation of **4a–d** in the presence of different inductors always yields the *trans*-1,2-disubstituted cyclopentanes **5a–d** as the main products. We have proved that the reaction is kinetically controlled since an isomerisation of the products under reaction conditions does not occur. Thus, treatment of mixtures of **5a**/**6a** with Me_2AlCl as well as TMSOTf does not alter their ratios.



In the formation of the *trans*- and *cis*-substituted cyclopentanes **5a–d** and **6c–d**, respectively, the transition structures **K-1** and **K-2** can be discussed. Both structures should be conformationally relatively rigid because of allylic 1,3-strain[20] due to the disubstituted sp^2 center of the acceptor moiety (sp^2-geminal effect[3]) and the *Z* configuration of the allylsilane. Though calculations have not been performed so far, from models it can be deduced that there is a severe steric interaction between one methoxycarbonyl group and the allylsilane moiety in **K-2**, rendering **K-2** less favourable as transition structure. Thus, the geminal substitution at the acceptor moiety in **4a–d** is the main reason for the observed *trans*-selectivity, since the fluoride-initiated cyclisation of the corresponding allylsilane with one alkoxycarbonyl group (*E*) at the acceptor moiety gives a 1,2-disubstituted cyclopentane with a *trans*-*cis*-ratio of 1.67:1[21]. This shows again that our concept of using alkylidene or benzylidene 1,3-dicarbonyls as acceptor moieties in intramolecular hetero Diels-Alder reactions[13b] ene reactions[3] and allylsilane cyclisations has three main advantages:

1. Simple preparation of the acceptor moiety by a Knoevenagel condensation[22] of an appropriate aldehyde and a 1,3-dicarbonyl compound.

2. High reactivity of the acceptor moiety due to a low-lying LUMO. This allows it to perform the transformations in a sequential fashion in many cases.

3. High induced and non-induced diastereoselectivity because of a conformational rigidity of the possible transition structure due to the geminal substitution at the acceptor moiety (sp^2-geminal effect[3]).

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for their generous support.

Experimental

^{1}H and ^{13}C NMR: Varian XL-200, VXR-200, XL-500, and FT-80 A; multiplicities were determined with the APT pulse sequence. – MS: Varian MAT 311A; high resolution: Varian MAT 731. – IR: Bruker IFS 25. – UV: Varian Cary 219. – GLC: Varian 3700 with Merck-Hitachi D-2000; Macherey-Nagel & Co, 0.25 µm, chemically bound SE 30, 0.32 mm × 50 m fused silica. – Melting points: Kofler melting point apparatus (corrected values). – Elemental analyses were carried out in the analytical laboratory of the university. – Ozonisations: Fischer (Model 502). – All solvents were destilled prior to use. All reactions were carried out under nitrogen and monitored by TLC (Macherey-Nagel Alugram Sil G/UV_{254}). Products were isolated by column or flash chromatography (CC or FC) on SiO_2 (CC: ICN Silica 63–200, 60 A, ICN Biochemicals, Eschwege, FC: Baker 30–60 active). – Solvents used for TLC and column chromatography for **5a–d**/**6a–d**: A: petroleum ether/diethyl ether (5:1), B: petroleum ether/diethyl ether (2:1). – All chiral compounds are obtained as racemic mixtures.

Preparation of (Z)-7-(Trimethylsilyl)-5-hepten-1-ol (**10**). – *Route 1*

(Z)-7-(Trimethylsilyl)-5-heptyn-1-ol (**9**) was prepared following a method used by Hiemstra and Speckamp[10] to synthesize 6-(trimethylsilyl)-4-hexyn-1-ol. To a magnetically stirred solution of 47.4 g (260 mmol) of THP-protected 5-hexyn-1-ol (**8**)[9] in 250 ml of dry THF at –30°C under nitrogen was added dropwise 26.5 ml (265 mmol) of a 10 M solution of *n*-butyllithium in hexane. After stirring for 15 min at –30°C and further 15 min at 0°C, 41.2 ml (277 mmol) of (iodomethyl)trimethylsilane[23] was added. Then the reaction flask was covered with aluminium foil, and the mixture

(light-sensitive) was heated for 20 h at 58–60°C. After cooling to room temp., 500 ml of ether/petroleum ether (1:1) was added. The mixture was washed with water (4 × 250 ml), brine (100 ml), dried ($MgSO_4$), and concentrated in vacuo. The yellow oil obtained (79.0 g) was dissolved in 450 ml of methanol containing (0.2 ml of concd. H_2SO_4, and the solution was stirred at room temp. for ca. 12 h. Then the mixture was diluted with 500 ml of diethyl ether/petroleum ether (1:1) and successively washed with satd. $NaHCO_3$ solution (500 ml), water (400 ml), and brine (400 ml), dried ($MgSO_4$) and concentrated in vacuo. the residue was destilled to furnish 34.5 g (72%) of **9** as a colorless liquid. B.p. 86–87.5°C/0.8 Torr, R_f = 0.72 [petroleum ether/ethyl acetate (2:1)]. GLC (50–5°C/min): t_R = 18.50 min. – IR (film): $\tilde{\nu}$ = 3358 cm^{-1} (OH), 2952, 2880 (CH), 2200 (C≡C), 1250, 1070, 1062, 1032, 850 ($SiMe_3$). – ^1H NMR ($CDCl_3$): δ = 0.06 (s, 9H, $SiMe_3$), 1.39 (t, J = 2.6 Hz, 2H, 7-H), 1.44–1.75 (m, 5H, 2-, 3-H, OH), 2.05–2.25 (m, 2H, 4-H), 3.65 (t, J = 7 Hz, 2H, 1-H). – ^{13}C NMR ($CDCl_3$): δ = –2.33 ($SiMe_3$), 6.64 (C-7), 18.44 (C-4), 25.47 (C-3), 31.53 (C-2), 61.81 (C-1), 77.43, 78.29 (C-5, -6). – MS (70 eV): m/z (%) = 184 (2) [M^+], 169 (4) [$M^+ - CH_3$], 111 (2) [$M^+ - SiMe_3$], 93 (9) [111 – H_2O], 73 (100) [$SiMe_3^+$], 43 (13) [$C_3H_5^+$].

$C_{10}H_{20}OSi$ (184.4) Calcd. 184.1283 Found 184.1283 (MS)

Heptenol **10**: To a stirred solution of 417 mg (1.68 mmol) of $Ni(OAc)_2 \cdot 4\ H_2O$ in 9 ml of 95% ethanol at room temp., kept under hydrogen atmosphere, was added 1.63 ml (1.65 mmol) of an 1 M $NaBH_4$ solution in 95% ethanol. The mixture turned black immediately. After 1 min 9 drops of 1,2-diaminoethane was added and 10 min later 6.00 g (32.6 mmol) of propargylsilane **9**. The mixture was stirred for 2 d at room temp. under hydrogen (1 atm). For workup a small amount of active charcoal was added and the mixture filtrated over Celite. The reaction flask and the Celite were washed several times with dichloromethane (total 450 ml). The combined blue-colored organic solutions were washed with water (2 × 100 ml), dried (K_2CO_3), and concentrated in vacuo. The residue was destilled to furnish 5.81 g (96%) of **10** as a colorless liquid. B.p. 93–96°C/1.5 Torr, R_f = 0.39 [petroleum ether/diethyl ether (2:1)]. GLC (50–5°C/min): t_R = 17.83 min. – IR (film): $\tilde{\nu}$ = 3344 cm^{-1} (OH), 3006, 2952, 2936, 2864 (CH), 1646 (C=C), 1456, 1418, 1392, 1248 ($SiMe_3$), 1152, 1064 (CO), 856 ($SiMe_3$). – ^1H NMR ($CDCl_3$): δ = –0.03 (s, 9H, $SiMe_3$), 1.44 (d, J = 8 Hz, 2H, 7-H), 1.26–1.66 (m, 5H, 2-, 3-H, OH), 2.01 (q, J = 7 Hz, 2H, 4-H), 3.64 (t, J = 7 Hz, 2H, 1-H), 5.26 (dtt, J = 11; 7.1; 1.2 Hz, 1H, 5-H), 5.42 (dtt, J = 11; 8.5; 1.2 Hz, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = –1.99 ($SiMe_3$), 18.27 (C-7), 25.77, 26.58 (C-3, -4), 32.16 (C-2), 62.15 (C-1), 125.4, 127.1 (C-5, -6). – MS (70 eV): m/z (%) = 186 (2) [M^+], 171 (1) [$M^+ - CH_3$], 73 (100) [$SiMe_3^+$], 67 (43) [$C_5H_7^+$], 54 (36) [$C_4H_6^+$]. $C_{10}H_{22}OSi$ (186.4) Calcd. C 64.45 H 11.90 Found C 64.55 H 11.89

Preparation of Heptenol **10**. – *Route 2*

(Z)-Isobutyl 7-(Trimethylsilyl)-5-heptenoate (**13**) was prepared by a procedure developed by Seyferth and Fleming[8c]. To a stirred suspension of methyltriphenylphosphonium iodide (6.82 g, 16.9 mmol) in dry THF (40 ml) at 0°C under nitrogen was added dropwise 11.7 ml (18.7 mmol) of 1.6 M *n*-butyllithium in hexane over 30 min. The deeply red colorled mixture was warmed to room temp., stirred for 1 h, and recooled to 0°C. Then 3.62 g (16.9 mmol) of (iodomethyl)trimethylsilane[21] was added over 10 min and the mixture slowly warmed to room temp. to precipitate the newly formed phosphonium salt. After 1.5 h the suspension was cooled to –78°C and treated with a second equivalent of 1.6 M *n*-butyllithium (11.7 ml, 18.7 mmol) in hexane to give a dark red solution. The mixture was allowed to warm to room temp. and was stirred for further 1.5 h to complete the formation of [(2-trimethylsilyl)-ethylidene]triphenylphosphorane. The mixture was cooled to –78°C and 2.58 g (15.0 mmol) of aldehyde **12** in 10 ml of dry THF was added quickly in one portion. After 30 min the suspension was allowed to warm slowly to room temp. and stirred for a further 16 h. Then it was quenched by pouring into satd. aqueous NH_4Cl solution (100 ml) and extracted with petroleum ether (3 × 200 ml). The combined organic extracts were dried with $MgSO_4$, evaporated and the residue destilled under reduced pressure to furnish 2.17 g (57%) of allylsilane **13**. An analytical pure sample was obtained by flash chromatography [petroleum ether/diethyl ether (30:1)]. B.p. 74–76°C/0.05 Torr, R_f = 0.60 [petroleum ether/diethyl ether (10:1)]. GLC (50–5°C/min): t_R = 20.84 min. – IR (film): $\tilde{\nu}$ = 2958 cm^{-1}, 2898, 2876 (CH), 1740 (C=O), 1646 (C=C), 1468, 1420, 1380 (CH), 1248, 1208, 1164, 1066 (C–O), 1018, 1008, 854 ($SiMe_3$). – ^1H NMR ($CDCl_3$): δ = 0.00 (s, 9H, $SiMe_3$), 0.96 (d, J = 6.7 Hz, 6H, CH_3), 1.50 (dd, J = 8.5; 1 Hz, 2H, 7-H), 1.73 (quint m, J = 7.5 Hz, 2H, 3-H), 1.98 [nonett, J = 6.7 Hz, $CH(CH_3)_2$], 2.09 (q br, J = 7.5 Hz, 2H, 4-H), 2.36 (t, J = 7.5 Hz, 2H, 2-H), 3.94 (d, J = 6.7 Hz, 2H, OCH_2), 5.35 (m_c, 1H, 5-H), 5.54 (m_c, 2H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = –1.83 ($SiMe_3$), 18.45 (C-7), 19.09 (C-3′, -4′), 25.03, 26.38, 33.88 (C-2, -3, -4), 27.70 (C-2′), 70.37 (C-1′), 126.2, 126.5 (C-5, -6), 173.8 (C-1). – MS (70 eV): m/z (%) = 256 (5) [M^+], 201 (12), 185 (9) [$M^+ - C_5H_{11}$], 183 (14) [$M^+ - SiMe_3$], 145 (14), 129 (15), 117 (49), 110 (10) [$C_7H_{10}O^+$], 82 (12) [$C_6H_{10}^+$], 75 (26), 73 (100) [$SiMe_3^+$], 57 (21) [$C_4H_9^+$], 45 (16), 41 (22) [$C_3H_7^+$].

$C_{14}H_{28}O_2Si$ (256.2) Calcd. C 65.57 H 11.00 Found C 65.42 H 10.98

Heptenol **10**: To a stirred suspension of 750 mg (19.8 mmol) of $LiAlH_4$ in 90 ml of dry THF at 0°C was gradually added 6.77 g (26.5 mmol) of allylsilane **13** in 20 ml of THF. The mixture was allowed to warm to room temp., stirred for ca. 12 h, and quenched by addition of ice. The precipitated white aluminium salts were dissolved in satd. aqueous NH_4Cl solution and the organic phase separated. The aqueous layer was extracted with diethyl ether (3 × 100 ml), the organic phases were combined and washed with satd. aqueous $NaHCO_3$ (50 ml), water (50 ml), and brine (50 ml) and dried ($MgSO_4$). After evaporation the residue was destilled under reduced pressure to furnish 3.73 g (76%) of **10** as a *cis/trans* = 93:7 mixture. Spectroscopic data as above.

(Z)-7-(Trimethylsilyl)-5-heptenal (**11**): To a magnetically stirred solution of 3.00 ml (34.4 mmol) of oxalyl chloride in 90 ml of dry dichloromethane, kept under nitrogen at –78°C, was added slowly (1 h) a cooled solution of 4.90 ml (68.7 mmol) of DMSO dissolved in 15 ml of dichloromethane; the temp. in the flask should not rise above –70°C. During the addition of the first 10 ml heavy gas evolution occurred. After the addition was complete the mixture was stirred for 10 min at –78°C, and then 4.00 g (21.5 mmol) of alcohol **10**, dissolved in 35 ml of dichloromethane, was added over a periode of 6 min. After 30 min the solution was treated with 19.1 ml (137 mmol) of dry triethylamine under rising of the temp. to –65°C. The mixture was recooled to –78°C, stirred 5 min at that temp., and then allowed to warm to room temp. Water (150 ml) was added, the organic phase separated and the aqueous phase extracted with dichloromethane (3 × 70 ml). The combined organic phases were successively washed with aqueous HCl (1%, 70 ml), $NaHCO_3$ solution (5%, 70 ml), water (50 ml), and brine (50 ml) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue destilled to furnish 3.36 g (85%) of **11** as a slight yellow oil. B.p. 80–83°C/4.5 Torr, R_f = 0.46 [petroleum ether/diethyl ether (10:1)]. GLC (50–5°C/min): t_R = 15.67 min. – IR (film): $\tilde{\nu}$ = 3008 cm^{-1} (C=C), 2954, 2894, 2820 (CH), 2716, 1728 (C=O), 1648 (C=C), 1454, 1414, 1392, 1362 (CH), 1318, 1250 ($SiMe_3$), 854

($SiMe_3$). – ^1H NMR ($CDCl_3$): δ = 0.00 (s, 9H, $SiMe_3$), 1.47 (dm, J = 8.5 Hz, 2H, 7-H), 1.70 (quint, J = 7.1 Hz, 2H, 3-H), 2.06 (qm, J = 7.1 Hz, 2H, 4-H), 2.46 (td, J = 7.1; 2 Hz, 2H, 2-H), 5.25 (dtt, J = 11; 7.1; 1.2 Hz, 1H, 5-H), 5.48 (dtt, J = 11; 8.5; 1.2 Hz, 1H, 6-H), 9.82 (t, J = 2 Hz, 1H, 1-H). – ^{13}C NMR ($CDCl_3$): δ = −1.96 ($SiMe_3$), 18.35 (C-7), 21.98, 26.13 (C-3, -4), 43.22 (C-2), 125.9, 126.6 (C-5, -6), 202.2 (C-1). – MS (70 eV): *m/z* (%) = 184 (1) [M^+], 169 (4) [$M^+ - CH_3$], 155 (2) [$M^+ - CHO$], 141 (7) [$M^+ - C_2H_3O$], 73 (100) [$SiMe_3^+$], 59 (8) [$C_3H_7O^+$].

$C_{10}H_{20}OSi$ (184.4) Calcd. C 65.15 H 10.94
Found C 65.15 H 10.94

Preparation of the Double Activated Alkylidene Compounds **4** *by Knoevenagel Condensation*

General Procedure 1: In a flame-dried flask with 5 g of molecular sieve (4 Å) were mixed 3.00 mmol (1.1 eq.) of the dioxo compound **14a** or **14b** in 7 ml of anhydrous dichloromethane and 65 mg (0.1 eq.) of piperidinium acetate at 0°C under nitrogen. To the stirred suspension 500 mg (2.71 mmol) of **11**, dissolved in 5 ml of dichloromethane, was added over 3 min. The reaction was monitored by TLC and every 2 h a further portion of catalyst (0.1 eq.) was added until completion (4–7 h). The mixture was warmed to room temp., and molecular sieve removed by filtration, the solvent evaporated, and the residue purified by chromatography on silica gel (200–250 g, 60–200 mesh, solvent as indicated).

General Procedure 2: In a flame-dried flask with 5 g of molecular sieve (4 Å) were mixed 3.00 mmol (1.1 eq.) of dioxo compound **14c** or **14d** in 7 ml of anhydrous chloroform and 21 mg (5 mol %) of ethylenediammonium diacetate (EDDA) unter nitrogen. The stirred suspension was cooled to 0°C, and a solution of 500 mg (2.71 mmol) of **11** in chloroform was added over 3 min. The mixture was stirred at this temp. until completation (5 h, TLC, solvent as indicated). Workup as in general procedure 1.

Methyl (Z)-2-(Methoxycarbonyl)-9-(trimethylsilyl)-2,7-nonadienoate (**4a**): Reaction of **14a** with **11** according to general procedure 1 followed by chromatography [petroleum ether/ethyl acetate (25:1)] gave 102 mg (22%) of **15** and 510 mg (63%) of **4a**.

Fraction 1: *(2E,7Z)-9-(Trimethylsilyl)-2-[(Z)-5-(trimethylsilyl)-3-pentenyl]-2,7-nonadienal* **15**: R_f = 0.62 [petroleum ether/ethyl acetate (25:1)]. – IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (CH), 1738, 1728 (C=O), 1646 (C=C), 1438, 1364 (CH), 1248 ($SiMe_3$), 1198, 1156, 1094, 1062, 1028, 858, 844 ($SiMe_3$). – ^1H NMR ($CDCl_3$): δ = −0.05 (s, 9H, $SiMe_3$), −0.03 (s, 9H, $SiMe_3$), 1.42 (d, J = 8 Hz, 2H, 5′- or 9-H), 1.44 (d, J = 8 Hz, 5′- or 9-H), 1.54 (quint, J = 7.5 Hz, 2H, 5-H), 2.04 (q, J = 7.5 Hz, 4H, 2′-, 6-H), 2.25 (q, J = 7.5 Hz, 2H, 1′- or 4-H), 2.37 (q, J = 7.5 Hz, 2H, 1′- or 4-H), 5.16–5.54 (m, 4H, 3′-, 4′-, 7-, 8-H), 6.47 (t, J = 7.5 Hz, 1H, 3-H), 9.39 (s, 1H, 1-H). – ^{13}C NMR ($CDCl_3$): δ = −1.85 ($SiMe_3$), 18.37, 18.51 (C-5′, -9), 24.09, 25.98, 26.63, 28.65, 28.75 (C-1′, -2′, -4, -5, -6), 126.2, 126.5 (C-3′, -4′, -7, -8), 143.3 (C-2), 155.1 (C-3), 195.0 (C-1).

Fraction 2: **4a**: R_f = 0.30 [etyl acetate/petroleum ether (1:5)]. GLC (50–5°C/min) t_R = 31.27 min. – IR (film): $\tilde{\nu}$ = 3006 cm^{-1} (C=C), 2954, 2898, 2862 (CH), 1730 (C=O), 1646 (C=C), 1438, 1370 (CH), 1252, 1228 ($SiMe_3$), 1152, 1096, 1064 (C–O), 856 ($SiMe_3$). – ^1H NMR ($CDCl_3$): δ = −0.03 (s, 9H, $SiMe_3$), 1.43 (dd, J = 8.5; 1.2 Hz, 2H, 9-H), 1.51 (quint, J = 7.5 Hz, 2H, 5-H), 2.01 (q, J = 7.5 Hz, 2H, 6-H), 2.31 (q, J = 7.5 Hz, 2H, 4-H), 3.77 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 5.21 (dtt, J = 11; 7.5; 1.2 Hz, 1H, 7-H), 5.44 (dtt, J = 11; 8.5; 1.2 Hz, 1H, 8-H), 7.06 (t, J = 8 Hz, 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = −2.02 ($SiMe_3$), 18.29 (C-9), 26.35, 28.18 (C-5, -6), 29.30 (C-4), 51.86, 51.97 (OCH_3), 126.0, 126.3 (C-7, 8), 127.9 (C-2), 150.0 (C-3), 164.1, 165.6 (C-1, -1′). – MS (70 eV): *m/z* (%) = 298 (0.5) [M^+], 283 (1) [$M^+ - CH_3$], 158 (28), 139 (34), 126 (24), 108 (12), 89 (14), 73 (100) [$SiMe_3^+$], 59 (18) [CO_2Me^+].

$C_{15}H_{26}O_4Si$ (298.5) Calcd. C 60.37 H 8.78
Found C 60.43 H 8.73

Benzyl (Z)-2-(Benzyloxycarbonyl)-9-(trimethylsilyl)-2,7-nonadienoate (**4b**): Reaction of **14b** with **11** according to general procedure 1 followed by chromatography [petroleum ether/ethyl acetate (25:1)] gave 882 mg (72%) of **4b**. Byproducts were not characterized. R_f = 0.57 [petroleum ether/diethyl ether (5:1)]. – IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (CH), 1728 (C=O), 1646 (C=C), 1456, 1386 (CH), 1248 ($SiMe_3$), 1216 (C–O), 856 ($SiMe_3$). – ^1H NMR ($CDCl_3$): δ = 0.00 (s, 9H, $SiMe_3$), 1.43 (dd, J = 8.5; 1.2 Hz, 2H, 9-H), 1.46 (quint, J = 7.5 Hz, 2H, 5-H), 1.98 (qm, J = 7.5 Hz, 2H, 6-H), 2.30 (q, J = 7.5 Hz, 2H, 4-H), 5.18 (dtt, J = 11; 7.5; 1.2 Hz, 1H, 7-H), 5.22 (s, 2H, OCH_2), 5.27 (s, 2H, OCH_2), 5.41 (dtt, J = 11; 8.5; 1.2 Hz, 1H, 8-H), 7.09 (t, J = 8 Hz, 1H, 3-H), 7.33 (s, 10H, Ph). – ^{13}C NMR ($CDCl_3$): δ = −1.84 ($SiMe_3$), 18.44 (C-9), 26.50, 28.27, 29.46 (C-4, -5, -6), 66.79, 66.97 (OCH_2), 126.1, 126.4 (C-7, -8), 128.0, 128.1, 128.25, 128.30, 128.5 (*m,o,p*-Ph, C-2), 135.3, 135.5 (*i*-Ph), 150.8 (C-3), 163.7, 165.1 (C-1, -1′). – MS (70 eV): *m/z* (%) = 450 (1) [M^+], 342 (3) [$M^+ - C_7H_8O$], 310 (7), 251 (4), 181 (6), 161 (2), 117 (1), 91 (100) [$C_7H_7^+$], 73 (24) [$SiMe_3^+$].

$C_{27}H_{34}O_4Si$ (450.6) Calcd. C 71.96 H 7.60
Found C 71.91 H 7.65

Synthesis of **4c**: Reaction of **14c** with **11** according to general procedure 2 followed by chromatography [petroleum ether/ethyl acetate (4:1)] gave 525 mg (60%) of **4c** as an oil, which crystallised on standing. The compound could not be characterised due to its instability and was used for the cyclisation as obtained after chromatography.

Synthesis of **4d**: Reaction of **14d** with **11** according to general procedure 2 followed by chromatography [petroleum ether/diethyl ether (6:1)] gave 403 mg (48%) of **4d** as an oil, which crystallised on standing. The compound could not be characterised due to its instability and was used for the cyclisation as obtained after chromatography.

Cyclisation Experiments. – General Procedures

1) *Cyclisation of* **4a,b** *and* **d** *with* Me_2AlCl, *TMSOTf*, Et_2O-BF_3, $TiCl_4$: To a cooled and stirred solution (−78°C) of dienoate **4** (1.00 mmol) in dichloromethane (5 ml) was added 1.2 equiv. of the inductor. Stirring was continued at this temp. until completion of the cyclisation (3–6 h, TLC).

2) *Cyclisation of* **4c** *with* Me_2AlCl, *TMSOTf*, Et_2O-BF_3: To a cooled and stirred solution (−78°C) of dienoate **4c** (1.00 mmol) in dichloromethane (5 ml) was added 1.2 equiv. of the inductor. Stirring was continued, and the mixture was allowed to warm to room temp. After 6 h the solution was recooled to −78°C and again 1.2 equiv. of inductor added. The mixture was warmed to room temp. and stirred until completion of the cyclisation (TLC).

3) *Cyclisation of* **4a,b** *and* **d** *with* $FeCl_3/Al_2O_3$: To a cooled suspension (−78°C) of the Lewis acid (1.20 mmol, adsorbed on 1.20 g of basic aluminia) in dichloromethane (5 ml) was added slowly with stirring a solution of dienoate **4** (1.00 mmol) in dichloromethane (2 ml). Stirring was continued and the mixture kept at this temp. until completion of the cyclisation (TLC).

4) *Cyclisation of* **4c** *with* $FeCl_3/Al_2O_3$: To a cooled suspension (−78°C) of the Lewis acid (1.20 mmol, adsorbed on 1.20 g basic aluminia) in dichloromethane (5 ml) was added slowly with stirring a solution of dienoate **4c** (1.00 mmol) in dichloromethane (2 ml).

The mixture was warmed to −15°C in 10 min with stirring and kept at this temp. until completion of the cyclisation (TLC).

5) *Cyclisation with $ZnBr_2$:* To a suspension of the Lewis acid (1.20 mmol) in dichloromethane (5 ml) at room temp. was added slowly with stirring a solution of dienoate **4a–d** (1.00 mmol) in dichloromethane (2 ml). Stirring was continued until completion of the cyclisation (TLC).

6) *Cyclisation with NBu_4F/SiO_2:* To a cooled (0°C) suspension of NBu_4F/SiO_2 (2.20 mmol) in dry THF (2 ml) was added slowly a solution of dienoate **4** (1.00 mmol) in THF (1 ml). The mixture turned yellow immediately and was allowed to warm to room temp. and stirred until completion of the cyclisation (TLC).

Workup Procedures for the Cyclisations

1) *Normal Workup:* The mixture was hydrolyzed by adding of 1–2 ml of satd. $NaHCO_3$ solution and warming to room temp. within 15 min. The solvent was evaporated and the residue distributed between diethyl ether (10 ml) and water (10 ml). The organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 15 ml). The combined organic phases were washed (brine, 10 ml) and dried ($MgSO_4$). Evaporation of the solvent and FC of the residue yielded the cyclopentanes as a mixture of two diastereomeres.

2) *Workup After Cyclisations to* **5d**, *Followed by Methanolysis:* After addition of triethylamine (2 ml) the mixture was warmed to room temp. within 15 min and filtered over 15 g SiO_2 (CH_2Cl_2) to remove polar impurities. The filtrate was evaporated, the residue solved in dry methanol (2 ml), and the solution acidified with 2 drops of concd. HCl. After refluxation for 2–5 h (TLC, formation of **5a/6a**) the mixture was diluted with water (2 ml) and extracted with petroleum ether (3 × 10 ml). The combined organic phases were washed (brine, 10 ml), dried ($MgSO_4$), and evaporated to give **5a** and **6a**. The ratio of **5a/6a** was determined and equated with the ratio of **5d/6d**.

Cyclisation to Dimethyl (1'RS,2'RS)-2-(2-Vinylcyclopentyl)propanedioate (**5a**)

$TiCl_4$: 135 mg (0.45 mmol) of **4a** was cyclised with 59 µl of $TiCl_4$ at −78°C within 3 h (TLC, solvent A) according to general procedure 1. Normal workup (1) gave 82.9 mg (81%) of **5a/6a**.

$Et_2O–BF_3$: 84.4 mg (0.28 mmol) of **4a** was cyclised with 42 µl of $Et_2O–BF_3$ at −78°C within 5 h (TLC, solvent A) according to general procedure 1. Normal workup (1) gave 30.0 mg (47%) of **5a/6a**.

$ZnBr_2$: 150 mg (0.50 mmol) of **4a** was cyclised with 136 mg of $ZnBr_2$ at 23°C within 4 h (TLC, solvent A) according to general procedure 5. Normal workup (1) gave 61.0 mg (54%) of **5a/6a**.

$FeCl_3/Al_2O_3$: 220 mg (0.74 mmol) of **4a** was cyclised with 884 mg of $FeCl_3/Al_2O_3$ at −78°C within 4 h (TLC, solvent A) according to general procedure 3. Normal workup (1) gave 122 mg (73%) of **5a/6a**.

Me_2AlCl: 45.7 mg (0.15 mmol) of **4a** was cyclised with 180 µl of 1 M Me_2AlCl in hexane at −78°C within 3 h (TLC, solvent A) according to general procedure 1. Normal workup (1) gave 29.9 mg (86%) of **5a/6a**.

TMSOTf: 45.9 mg (0.15 mmol) of **4a** was cyclised with 34 µl of TMSOTf at −78°C within 4 h (TLC, solvent A) according to general procedure 1. Normal workup (1) gave 33.7 mg (97%) of **5a/6a**.

5a: R_f = 0.43 (solvent A). GLC (50–5°C/min): $t_{R,5a}$ = 21.67 min, $t_{R,6a}$ = 22.07 min. – IR (film): $\tilde{\nu}$ = 2954 cm^{-1}, 2872 (CH), 1738 (C=O), 1640 (C=C), 1436, 1320 (CH), 1244, 1200, 1154, 1082, 1024 (CO). – ^1H NMR (C_6D_6): δ = 1.31 (m_c, 1H, 3'-H), 1.49 (m_c, 2H, 4'-H), 1.52 (m_c, 1H, 5'-H), 1.74 (m_c, 1H, 3'-H), 2.06 (dddd, *J* = 13; 8; 6; 5.7 Hz, 1H, 5'-H), 2.29 (quint, *J* = 8.7 Hz, 1H, 2'-H), 2.45 (dddd, *J* = 9.5; 8.7; 8.0; 7.6 Hz, 1H, 1'-H), 3.39 (s, 6H, OCH_3), 3.54 (d, *J* = 7.6 Hz, 1H, 2-H), 4.94 (dd, *J* = 10; 2 Hz, 1H, 2''-H_{cis}), 5.03 (dd, *J* = 17; 2 Hz, 1H, 2''-H_{trans}), 5.62 (ddd, *J* = 17; 10; 8.7 Hz, 1H, 1''-H). – ^{13}C NMR ($CDCl_3$): δ_{5a} = 23.49 (C-4'), 30.06 (C-5'), 33.30 (C-3'), 44.92 (C-1'), 48.89 (C-2'), 52.02, 52.22 (OCH_3), 55.04 (C-2), 114.4 (C-2''), 141.6 (C-1''), 169.2 (C-1, -3); δ_{6a} = 22.78 (C-4'), 28.23 (C-5'), 31.48 (C-3'), 43.25 (C-1')*, 45.43 (C-2')*, 52.45 (OCH_3), 53.89 (C-2), 115.6 (C-2''), 138.3 (C-1''); (C_6D_6) δ_{5a} = 23.71 (C-4'), 30.20 (C-5'), 33.45 (C-3'), 45.06 (C-1'), 48.99 (C-2'), 51.53 (OCH_3), 51.64 (OCH_3), 55.10 (C-2), 114.3 (C-2''), 142.0 (C-1''), 169.0 (C-1, -3). – MS (70 eV): *m/z* (%) = 226 (1) [M^+], 163 (16), 145 (27), 135 (12), 133 (87), 132 (49), 101 (26), 100 (23), 94 (100), 79 (67), 59 (12) [CO_2Me^+].

$C_{12}H_{18}O_4$ (226.3) Calcd. C 63.70 H 8.02
Found C 63.88 H 8.16

Cyclisations to Dibenzyl 2-(2-Vinylcyclopentyl)-1,3-propanedioate (**5b/6b**)

$TiCl_4$: 94.3 mg (0.21 mmol) of **4b** was cyclised with 28 µl of $TiCl_4$ at −78°C within 3 h (TLC, solvent A) according to general procedure 1. Normal workup (1) gave 52.0 mg (66%) of **5b/6b**.

$Et_2O–BF_3$: 144 mg (0.32 mmol) of **4b** was cyclised with 47 µl of $Et_2O–BF_3$ at −78°C within 5 h (TLC, solvent A) according to general procedure 1. Normal workup (1) gave 72.6 mg (60%) of **5b/6b**.

$ZnBr_2$: 357 mg (0.79 mmol) of **4b** was cyclised with 214 mg of $ZnBr_2$ at 23°C within 12 h (TLC, solvent A) according to general procedure 5. Normal workup (1) gave 208 mg (70%) of **5b/6b**.

$FeCl_3/Al_2O_3$: 91.5 mg (0.20 mmol) of **4b** was cyclised with 244 mg of $FeCl_3/Al_2O_3$ at −78°C within 4 h (TLC, solvent A) according to general procedure 3. Normal workup (1) gave 68.9 mg (90%) of **5b/6b**.

Me_2AlCl: 98.7 mg (0.22 mmol) of **4b** was cyclised with 260 µl of 1 M Me_2AlCl in hexane at −78°C within 3 h (TLC, solvent A) according to general procedure 1. Normal workup (1) gave 51.7 mg (62%) of **5b/6b**.

TMSOTf: 81.4 mg (0.18 mmol) of **4b** was cyclised with 39 µl of TMSOTf at −78°C within 3 h (TLC, solvent A) according to general procedure 1. Normal workup (1) gave 45.0 mg (66%) of **5b/6b**.

Dibenzyl (1'RS,2'RS)-2-(2-Vinylcyclopentyl)-1,3-propanedioate (**5b**): R_f = 0.59 (solvent A). GLC (50–10°C/min) = $t_{R,5b}$ = 28.74 min, $t_{R,6b}$ = 29.16 min. – IR (film): $\tilde{\nu}$ = 3034 cm^{-1} (C=C), 2954, 2872 (CH), 1732 (C=O), 1640 (C=C), 1498, 1454, 1378, 1314 (CH), 1248, 1220, 1150 (C–O), 1080, 1056, 1026 (C–O), 1000. – ^1H NMR (C_6D_6): δ = 1.08–1.73 (m, 5H, 3'-, 4'-, 5'-H), 1.99 (m_c, 1H, 5'-H), 2.26 (m_c, 1H, 2'-H), 2.43 (m_c, 1H, 1'-H), 3.56 (d, *J* = 7.5 Hz, 1H, 2-H), 4.86 (dd, *J* = 10; 2 Hz, 1H, 2''-H_{cis}), 4.97 (s, 4H, CH_2O), 4.97 (ddd, *J* = 17; 2; 0.8 Hz, 1H, 2''-H_{trans}), 5.54 (ddd, *J* = 17; 10; 8.5 Hz, 1H, 1''-H), 6.98–7.10 (m, 5H, Ph), 7.08–7.20 (m, 5H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 23.46 (C-4'), 29.70 (C-5'), 33.11 (C-3'), 44.78 (C-1'), 48.74 (C-2'), 55.01 (C-2), 66.76, 66.82 (CH_2O), 114.5 (C-2''), 128.13, 128.17, 128.23, 128.46 (*o,m,p*-Ph), 135.35, 135.40 (*i*-Ph), 141.5 (C-1''), 168.4, 168.5 (C-1, -3). – MS (70 eV): *m/z* (%) = 378 (0.2) [M^+], 297 (2), 287 (5), 269 (2), 251 (2), 183 (21), 153 (1), 135 (2), 117 (2), 107 (6), 94 (3), 92 (11), 91 (100), 79 (4), 65 (4).

$C_{24}H_{26}O_4$ (378.5) Calcd. C 76.17 H 6.92
Found C 76.14 H 7.09

Cyclisations to 1,3-Dimethyl-5-(2-vinylcyclopentyl)-2,4,6(1H,3H,5H)-pyrimidinetrione (**5c/6c**)

Et_2O-BF_3: 115 mg (0.36 mmol) of **4c** was cyclised with 53 µl of Et_2O-BF_3 at 23°C within 5 h (TLC, solvent B) according to general procedure 2. Normal workup (1) gave 54.3 mg (61%) of **5c/6c**.

$ZnBr_2$: 99.5 mg (0.31 mmol) of **4c** was cyclised with 83.5 mg of $ZnBr_2$ at 23°C within 24 h (TLC, solvent B) according to general procedure 5. Normal workup (1) gave 56.8 mg (74%) of **5c/6c**.

$FeCl_3/Al_2O_3$: 333 mg (1.03 mmol) of **4c** was cyclised with 1.24 g of $FeCl_3/Al_2O_3$ at −15°C within 24 h (TLC, solvent B) according to general procedure 4. Normal workup (1) gave 173 mg (67%) of **5c/6c**.

Me_2AlCl: 40.0 mg (0.12 mmol) of **4c** was cyclised with 150 µl of 1 M Me_2AlCl in hexane at 23°C within 48 h (TLC, solvent B) according to general procedure 2. Normal workup (1) gave 20.9 mg (67%) of **5c/6c**.

TMSOTf: 32.6 mg (0.10 mmol) of **4c** was cyclised with 22 µl of TMSOTf at 23°C within 24 h (TLC, solvent B) according to general procedure 1. Normal workup (1) gave 11.8 mg (47%) of **5c/6c**.

NBu_4F/SiO_2: 87.3 mg (0.27 mmol) of **4c** was cyclised with 540 mg of NBu_4F/SiO_2 at 23°C within 6 h (TLC, solvent B) according to general procedure 6. Normal workup (1) gave 41.8 mg (62%) of **5c/6c**.

(1'RS,2'RS)-1,3-Dimethyl-5-(2-vinylcycopentyl)-2,4,6(1H,3H,5H)-pyrimidinetrione (**5c**): R_f = 0.36 (solvent B). − IR (film): $\tilde{\nu}$ = 3426 cm^{-1} ($CONR_2$), 3078, 2962, 2872, 2808 (CH), 1746, 1680 ($CONR_2$), 1512, 1450, 1422, 1380 (CH), 1288, 1278, 1150, 1118, 1075, 758. − UV (acetonitrile): λ_{max} (lg ε) = 226 nm (3.792), 265 (2.987). − ^1H NMR (C_6D_6): δ = 1.03−1.73 (m, 6H, 3'-, 4'-, 5'-H), 2.28 (dtd, *J* = 11; 9; 3.3 Hz, 1'-H), 2.52 (dtd, *J* = 11; 9; 7.7 Hz, 1H, 2'-H), 3.01 (s, 3H, NCH_3), 3.04 (s, 3H, NCH_3), 3.22 (d, *J* = 3.3 Hz, 1H, 5-H), 4.98 (dd, *J* = 10; 2.2 Hz, 1H, 2''-H_{cis}), 5.13 (ddd, *J* = 17.2; 2.2; 0.7 Hz, 1H, 2''-H_{trans}), 5.51 (ddd, *J* = 17.2; 10; 7.7 Hz, 1H, 1''-H). − ^{13}C NMR ($CDCl_3$): δ = 22.71 (C-4'), 28.18, 28.35 (NCH_3), 28.64 (C-5'), 32.33 (C-3'), 47.19 (C-2'), 49.88 (C-5), 50.24 (C-1'), 115.7 (C-2''), 140.7 (C-1''), 151.8 (C-2), 168.3, 168.8 (C-4, -6). (C_6D_6): δ = 22.93 (C-4'), 27.87, 28.02 (NCH_3), 28.58 (C-5'), 32.48 (C-3'), 47.37 (C-2'), 49.81 (C-5), 49.96 (C-1'), 115.5 (C-2''), 141.2 (C-1''), 151.6 (C-2), 168.6 (C-6), 170.8 (C-4). Tautomer of **5c**: ^{13}C NMR: δ = 25.51 (C-4'), 27.58 (NCH_3), 28.70 (C-5'), 34.99 (C-3'), 43.85 (C-2'), 55.33 (C-1'), 77.73 (C-5), 114.3 (C-2''), 142.0 (C-1''), 151.1 (C-2), 170.3, 170.8 (C-4, -6). − MS (70 eV): *m/z* (%) = 250 (6) [M^+], 235 (2), 221 (3), 207 (2), 182 (4), 158 (21), 157 (100), 156 (21), 99 (20), 94 (55), 82 (12), 79 (81), 77 (21), 67 (20), 58 (19), 53 (20), 42 (15), 41 (37).

$C_{13}H_{18}N_2O_3$ (250.3) Calcd. C 62.38 H 7.25 N 11.19
Found C 62.41 H 7.35 N 11.14

Cyclisations to Isopropylidene 2-(2-Vinylcyclopentyl)-1,3-propanedioate (**5d/6d**) *Followed by Methanolysis to* **5a/6a**

$TiCl_4$: 69.7 mg (0.28 mmol) of **4d** was cyclised with 30 µl of $TiCl_4$ at −78°C within 6 h (TLC, solvent B) according to general procedure 1. Workup (2) gave 38.1 mg (75%) of **5a/6a**.

Et_2O-BF_3: 67.2 mg (0.22 mmol) of **4d** was cyclised with 32 µl of Et_2O-BF_3 at −78°C within 6 h (TLC, solvent B) according to general procedure 1. Workup (2) gave 37.7 mg (77%) of **5a/6a**.

$ZnBr_2$: 65.9 mg (0.21 mmol) of **4d** was cyclised with 57.3 mg of $ZnBr_2$ at 23°C within 24 h (TLC, solvent B) according to general procedure 5. Workup (2) gave 19.0 mg (40%) of **5a/6a**.

$FeCl_3/Al_2O_3$: 144 mg (0.46 mmol) of **4d** was cyclised with 556 mg of $FeCl_3/Al_2O_3$ at −78°C within 4 h (TLC, solvent B) according to general procedure 3. Normal workup (2) gave 76.8 mg (73%) of **5a/6a**.

Me_2AlCl: 72.5 mg (0.23 mmol) of **4d** was cyclised with 280 µl of 1 M Me_2AlCl in hexane at −78°C within 6 h (TLC, solvent B) according to general procedure 1. Workup (2) gave 36.6 mg (69%) of **5a/6a**.

TMSOTf: 71.9 mg (0.23 mmol) of **4d** was cyclised with 51 µl of TMSOTf at −78°C within 4 h (TLC, solvent B) according to general procedure 1. Workup (2) gave 23.7 mg (45%) of **5a/6a**.

NBu_4F/SiO_2: 41.4 mg (0.13 mmol) of **4d** was cyclised with 265 mg of NBu_4F/SiO_2 at 23°C within 5 h (TLC, solvent B) according to general procedure 6. Workup (2) gave 12.3 mg (41%) of **5a/6a**.

The spectroscopic data for compound **5a** are given above. Isolation of the primarily formed cyclisation product **5d** was possible using the workup 2 without methanolysis.

Isopropylidene (1'RS,2'RS)-2-(2-Vinylcyclopentyl)-1,3-propanedioate (**5d**): M.p. 75−78°C (diethyl ether/petroleum ether). R_f = 0.41 (solvent B). − IR (KBr): $\tilde{\nu}$ = 2998 cm^{-1}, 2956, 2938, 2872 (CH), 1776, 1744 (C=O), 1638 (C=C), 1456, 1390, 1368, 1340 (CH), 1326, 1300, 1266, 1248, 1206, 1170, 1140, 1060 (C−O), 1006. − ^1H NMR (C_6D_6): δ = 0.88 (d, *J* = 0.7 Hz, 3H, CH_3), 1.15 (d, *J* = 0.7 Hz, 3H, CH_3), 1.10−1.92 (m, 6H, 3'-, 4'-, 5'-H), 2.65 (m_c, 1H, 1'-H*), 3.15 (m_c, 1H, 2'-H*), 3.44 (d, *J* = 2 Hz, 1H, 2-H), 5.01 (ddd, *J* = 10; 2.3; 0.5 Hz, 1H, 2''-H_{cis}), 5.14 (ddd, *J* = 17.2; 2.3; 0.7 Hz, 1H, 2''-H_{trans}), 5.61 (ddd, *J* = 17.2; 10; 9 Hz, 1H, 1''-H). − ^{13}C NMR ($CDCl_3$): δ = 23.41 (C-4'), 27.17 (C-5'), 27.17, 28.37 (CH_3), 32.60 (C-3'), 44.69, 45.95, 47.54 (C-2, -1', -2'), 104.7 (C-5), 116.0 (C-2''), 141.4 (C-1''), 164.5, 166.1 (C-1, -3). − MS (70 eV): *m/z* (%) = 180 (5) [$M^+ - CH_3COCH_3$], 162 (6), 145 (6), 135 (6), 107 (5), 95 (10), 94 (100) [$C_7H_{10}^+$], 80 (10), 79 (54), 67 (10), 59 (11), 53 (8), 43 (29) [CH_3CO^+].

$C_{13}H_{18}O_4$ (238.4) Calcd. C 65.71 H 7.61
Found C 65.53 H 7.77

Transformation of **5a** *into* **17**

1. *Methyl (1'RS,2'RS)-2-(2-Vinylcyclopentyl)acetate* (**16**): A solution of 256 mg (1.13 mmol) of **5a** in 2 ml of DMSO was treated with 85.0 mg (1.47 mmol) of sodium chloride in 0.1 ml of water and heated at 160°C for 36 h. After cooling to room temp. 40 ml water was added and the mixture extracted with petroleum ether (6 × 15 ml). The combined extracts were washed (brine, 10 ml) and dried ($MgSO_4$). The solvent was evaporated and the residue purified by flash chromatography on silica gel to furnish 75.4 mg (40%) of **16** as a sweet smelling colourless liquid. The low yield of **16** is probably a result of its low boiling point. R_f = 0.24 [petroleum ether/diethyl ether (30:1)]. − IR (film): $\tilde{\nu}$ = 2952 cm^{-1}, 2870 (CH), 1740 (C=O), 1640 (C=C), 1436, 1372, 1326 (CH), 1292, 1250, 1198, 1176, 1144, 1078, 1020 (C−O). − ^1H NMR ($CDCl_3$): δ = 0.97−1.54 (m, 4H), 1.54−2.09 (m, 5H), 2.41 (m_c, 1H), 3.34 (s, 3H, OCH_3), 4.94 (m_c, 2H, 2''-H), 5.54 (m_c, 1H, 1''-H). − ^{13}C NMR (C_6D_6): δ = 23.54 (C-4'), 32.20, 32.77 (C-3', -5'), 38.35 (C-2), 42.60 (C-1'), 50.84, 51.23 (OCH_3, C-2'), 114.5 (C-2''), 142.1 (C-1''), 172.9 (C-1). − MS (70 eV): *m/z* (%) = 168 (11) [M^+], 153 (2) [$M^+ - CH_3$], 139 (19), 137 (19), 136 (34), 109 (17), 108 (82), 107 (15), 95 (79), 94 (100), 93 (17), 81 (11), 80 (19), 79 (59), 75 (11), 74 (36), 67 (39), 59 (16), 55 (24), 54 (32), 53 (13), 43 (56), 41 (39).

$C_{10}H_{16}O_2$ (168.1) Calcd. C 71.39 H 9.59
Found C 71.50 H 9.41

2. *trans-2-[2-(Hydroxymethyl)cyclopentyl]ethanol* (**17**): Through a cooled solution (−78°C) of 75.4 mg (0.45 mmol) of **16** in 10 ml of dichloromethane were bubbled ozone until the mixture turned

deep blue. Stirring was continued for 30 min at −78°C, excess of ozone was removed with a nitrogen stream. The colorless solution obtained was allowed to warm to room temp. The solvent was evaporated at <20°C and the residue dissolved in 2 ml of dry THF. The solution was added dropwise to a cooled suspension (−10°C) of 13.3 mg (0.35 mmol) of $LiAlH_4$ in 5 ml of dry THF and the mixture heated for 12 h at 60°C. Water was added to destroy excess $LiAlH_4$, then 10% H_2SO_4 was added to solve the precipitated salts. The organic layer was separated, the aqueous layer extracted with diethyl ether (3 × 10 ml), and the combined organic layers were washed with satd. aqueous $NaHCO_3$ (10 ml), water (10 ml), and brine (10 ml) and dried ($MgSO_4$). After evaporation of the solvent the residue was purified by flash chromatography on silica gel [diethyl ether/petroleum ether (8:1)] to furnish 61.8 mg (96%) of **17** as a colorless liquid. R_f = 0.19 [diethyl ether/petroleum ether (5:1)]. GLC (50−5°C/min): t_R = 18.55 min. − IR (film): $\tilde{\nu}$ = 3332 cm^{-1} (OH), 2940, 2868 (CH), 1450, 1430, 1376 (CH), 1052, 1022 (C−O). − ^1H NMR (C_6D_6): δ = 0.96−1.30 (m, 2H), 1.30−1.60 (m, 4H), 1.50−1.90 (m, 4H), 2.93 (m, 2H), 3.19 (dd, *J* = 10.2; 7.5 Hz, 1H), 3.45 (dd, *J* = 10.2; 5.2 Hz, 1H), 3.51 (dd, *J* = 11; 5.7 Hz, 1H), 3.66 (dd, *J* = 11; 6 Hz, 1H). − ^{13}C NMR ($CDCl_3$): δ = 24.64 (C-4′), 29.48, 33.62, 38.36 (C-2, -3′, -5′), 38.78 (C-1′), 46.62 (C-2′), 61.33, 66.57 (C-1, -1″). − MS (70 eV): *m/z* (%) = 145 (1) [M^+ + H], 144 (0.2) [M^+], 126 (5), 108 (40), 97 (38), 96 (57), 95 (100), 93 (54), 82 (49), 81 (57), 79 (49), 68 (57), 67 (95), 55 (33), 54 (17), 41 (57).

$C_8H_{16}O_2$ (144.1) Calcd. C 66.63 H 11.18
Found C 66.54 H 11.26

cis-2-[2-(Hydroxymethyl)cyclopentyl]ethanol (**19**): Through a cooled solution (−78°C) of 2.00 g (18.5 mmol) of **18** in 50 ml of dichloromethane ozone was bubbled until the solution turned deep blue. Stirring was continued for further 30 min, and excess of ozone was removed with a nitrogen stream. The colorless solution obtained was allowed to warm to room temp. The solvent was removed at <20°C and the residue dissolved in 20 ml of dry THF. The solution was added dropwise to a cooled suspension (−10°C) of 0.38 g (10.0 mmol) of $LiAlH_4$ in 30 ml of dry THF, and the mixture was heated for 12 h at 60°C. Workup as for **17** afforded 2.01 g (75%) of **19** as a colorless liquid. R_f = 0.19 [diethyl ether/petroleum ether (5:1)]. GLC (50−5°C/min): t_R = 19.14 min. − IR (film): $\tilde{\nu}$ = 3332 cm^{-1} (OH), 2946, 2872 (CH), 1474, 1450, 1434, 1378 (CH), 1052, 1032 (C−O). − ^1H NMR (C_6D_6): δ = 1.02−1.73 (m, 10H), 1.84 (m_c, 1H), 1.99 (m_c, 1H), 3.23 (dd, *J* = 10.7; 6.3 Hz, 1H), 3.37 (ddd, *J* = 10.5; 8; 6 Hz, 1H), 3.41 (dd, *J* = 10.7; 7.7 Hz, 1H), 3.48 (ddd, *J* = 10.5; 6.7; 5 Hz, 1H). − ^{13}C NMR ($CDCl_3$): δ = 22.59 (C-4′), 27.98, 31.12, 32.06 (C-2, -3′, -5′), 38.20 (C-1′), 44.48 (C-2′), 61.89, 62.69 (C-1, -1″). − MS (70 eV): *m/z* (%) = 145 (0.3) [M^+ + H], 126 (1), 114 (8), 108 (20), 96 (40), 95 (100), 93 (37), 82 (43), 81 (41), 79 (35), 68 (73), 67 (100), 57 (23), 55 (49), 54 (22), 53 (17), 41 (73).

$C_8H_{16}O_2$ (144.1) Calcd. C 66.63 H 11.18
Found C 66.70 H 11.14

CAS Registry Numbers

4a: 126134-80-3 / **4b**: 126134-79-0 / **4c**: 126134-83-6 / **4d**: 126134-82-5 / **5a**: 126134-81-4 / **5b**: 126134-88-1 / **5c**: 126134-89-2 / **5d**: 126134-90-5 / **8**: 1720-37-2 / **9**: 86486-03-5 / (*Z*)-**10**: 92121-08-9 / (*E*)-**10**: 92121-11-4 / **11**: 92121-09-0 / **12**: 126134-84-7 / **13**: 126134-85-8 / **14a**: 108-59-8 / **14b**: 15014-25-2 / **14c**: 769-42-6 / **14d**: 2033-24-1 / **15**: 126134-86-9 / **16**: 126134-87-0 / **17**: 24137-83-5 / **18**: 930-99-4 / **19**: 15773-82-7 / ICH_2TMS: 4206-67-1 / Me_2AlCl: 1184-58-3 / TMSOTf: 27607-77-8 / Et_2O-BF_3: 109-63-7 / $TiCl_4$: 7550-45-0 / $FeCl_3$: 7705-08-0 / Al_2O_3: 1344-28-1 / $ZnBr_2$: 7699-45-8 / NBu_4F: 429-41-4 / SiO_2: 7631-86-9

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