Palladium Catalysis in Allylic Alkylations and Rearrangements in Pyrimidines

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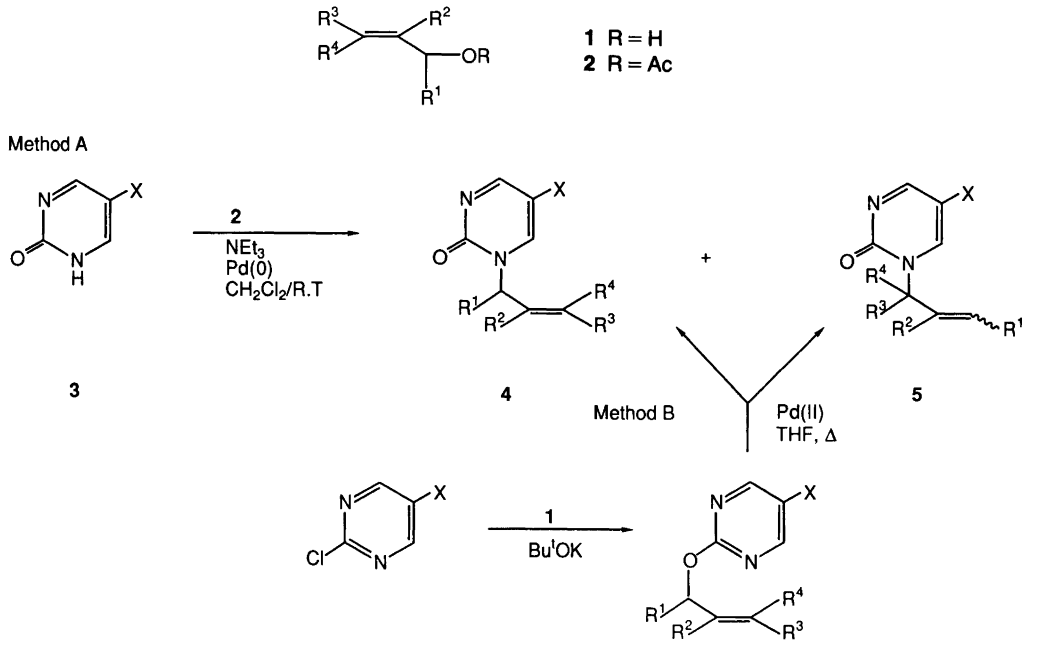
The regiochemistry of the alkylation of 2-pyrimidinones with π-allylpalladium complexes from allylic acetates and Pd(0) depends on the substitution pattern in the allylic system. In Pd(II)-catalysed rearrangements of 2-propenyloxypyrimidines the preference for a 1,3-rearrangement or the Claisen 3,3-rearrangement is influenced by the substitution pattern in the allylic system. Pd(0) forms π-allylpalladium complexes with 2-propenyloxypyrimidines which give rise to rearrangement products. The product ratios in the Pd(II) and Pd(0) rearrangements in unsymmetrically substituted allylic systems are different. The rearrangement reactions, especially the Pd(II) rearrangement, give access to products which are difficult to prepare by direct alkylation.

Substitution reactions of allylic compounds in the form of π-allylpalladium complexes with nucleophiles constitute a widely used synthetic method for alkylations.[1] The palladium-catalysed rearrangement of allylic derivatives is an alternative and useful alkylation reaction.[1,2] As part of our investigations of metaphase-arresting pyrimidinones,[3] we report herein on allylic alkylation reactions. We have found in preliminary work that 2-stannyloxypyrimidines can be alkylated with allyl acetate in the presence of a Pd(0) catalyst.[4] The relatively high acidity of 5-halo-2-pyrimidinones, e.g. pK_a 7.3 for the 5-bromo compound,[5] makes the anion well suited for substitution reactions with π-allylpalladium complexes. The initial experiments in this work showed that the triethylammonium salts of the 2-pyrimidinones were more reactive than the corresponding 2-tributylstannyloxypyrimidines in nucleophilic substitutions on π-allylpalladium complexes, and these salts were used in the further study. The reactions were run in dichloromethane at ambient temperature using Pd(0) generated *in situ* from palladium(II) acetate and triisopropyl phosphite.



3 4 5 6 7

Scheme 1.

Table 1. Pd-catalysed alkylation of 2-pyrimidinones with allylic acetates **2** (Method A), and Pd-catalysed rearrangements of 2-allyloxypyrimidines **7** (Method B and C).

2/7	R^1	R^2	R^3	R^4	X	Method A[a]			Method B[b]			Method C[c]		
						Yield[d]/%		Ratio[e] **4**:**5**	Yield[d]/%		Ratio[e] **4**:**5**	Yield[d]/%		Ratio[e] **4**:**5**
						4	**5**		**4**	**5**		**4**	**5**	
a	H	H	H	H	Cl	60	–[f]	–[f]	–	–	–	–	–	–
						94[f]	–[f]	–[f]	–	–	–	–	–	–
b	H	H	H	H	Br	–	–	–	94	–[f]	–[f]	75	–[f]	–[f]
c	H	Me	H	H	Br	73	–[f]	–[f]	0	0	–	83	–[f]	–[f]
d	H	H	Me	H	Br	0	46	33:67	0	93	0:100	60	0	67:33
e	H	H	Ph	H	Br	50	0	–	0	40[h]	–:>90	80	0	100:0
f	Pentyl	H	H	H	Cl	0	57	–	–	–	–	–	–	–
g	Pentyl	H	H	H	Br	0	65	–:>95	0	79	–:>90	0	75	11:89
h	H	H	Me	Me	Br	46	0	–	0	36[i]	–:>95	75	0	100:0
i	Pentyl	H	Me_3Si	H	Cl	17	0	–	–	–	–	–	–	–
j	Pentyl	H	Me_3Si	H	Br	–	–	–	0	0	–	88	0	100:0
k	H	OMe	Ph	H	Br	–	–	–	0	0	–	60	0	100:0
l	Me	SPh	H	H	Br	–	–	–	0	0	–	60	0	73:27
m	Me	H	H	H	Br	–	–	31:69	–	–	0:100[j]	–	–	10:90

The yields and product compositions are given after 16 h.
[a]*Method A:* 5 % $Pd[(OiPr)_3P]_4$ + allylic acetates and 5-halo-2-pyrimidinones. Method B: 5 % $(PhCN)_2PdCl_2$ and compounds **7**. [c]*Method C:* 7 % $Pd[(OiPr)_3P]_4$ and compound **7**. [d]Yield of purified product. [e]From ^1H NMR spectrum of the crude product. [f]**4** and **5** are identical. [g]7 % $Pd(Ph_3P)_4$. [h]25 % **7e** in the crude product. [i]43 % **7h** in the crude product. [j]4 % **7m** in the crude product.

The regioselectivity in the reaction with substituted allylic complexes seems to depend on the type of substituent, the type of nucleophile and the ligand used.[6] In the reactions between the pyrimidinones **3** and allylic acetates, mixtures of the isomeric products **4** and **5** were obtained (Table 1, Method A). The reactions were stopped after 16 h when the starting material was no longer present. Substitution at the more substituted carbon in the allylic palladium complex is favoured initially, but the reaction is reversible and with time the less substituted isomer becomes the major product. Thus in a separate study it was shown that in the reaction between 5-bromo-2(1*H*)-pyrimidinone and 2-butenyl acetate the isomer ratio **4d**:**5d** was ca. 2:3 after 11 h. The ratio was gradually changed to ca. 3:2 after 37 h when the experiment was stopped (Table 2, Method A). In the reaction with 1-methylpropenyl acetate the ratio **4m**:**5m** was ca. 4:1 after 3.5 h, 1:1 after 11 h, and had reached a constant value of 1:9 when the experiment was stopped after 37 h. In the corresponding rearrangement of the allylic ether **7m** using Pd(0) catalysis (Scheme 2), as discussed below, the ratio **4m**:**5m** was ca. 3:2 after 3.5 h and had reached the constant value of 1:9 when the experiment was stopped after 30 h (Table 2, Method C).

In order to gain access to highly substituted allylic derivatives, work on the rearrangement of 2-allyloxypyrimidines was initiated. Palladium-catalysed rearrangements in allylic systems have been reported to be useful in organic synthesis,[1c,2b,7] and related rearrangements have also been reported in heterocyclic series.[8]

2-Allyloxypyrimidines are available from 2-chloropyrimidines and allylic alcohols under basic conditions;[9] we have used potassium *tert*-butoxide in THF at 0 °C. 2-Allyloxypyrimidine does not undergo the Claisen rearrangement to any extent by being heated alone up to 200 °C;[10] metal catalysts, however, can accelerate the reaction by a factor of up to 10^{12} over the thermal reaction rate.[2b] We find that 2-allyloxy-5-bromopyrimidine, when treated with a 5 % mol equivalent of Pd(II) in THF at 70 °C for 16 h, gives the rearranged product, 1-allyl-5-bromo-2(1*H*)pyrimidinone (**4b**) in 94 % yield (Table 1, Method B). The rearrangement is also catalysed by Pd(0) (see below) and does not take place in the absence of a catalyst.

Table 2. Pd-catalysed alkylation of 2-pyrimidinones with allylic acetates **2** (Method A), and Pd(0)-catalysed rearrangement of 2-allyloxypyrimidines **7** (Method C). Product composition (**4**:**5**) at different time intervals.

2/7	R^1	R^2	R^3	R^4	X	Time/h	Method A Ratio **4**:**5**	Method C Ratio **4**:**5**
d	H	H	Me	H	Br	3	Little product	–
						11	39:61	–
						16	34:66	63:37
						30	57:43	–
						37	62:38	–
m	Me	H	H	H	Br	3.5	77:23	59:41
						11	50:50	37:64
						16	31:69	35:65
						30	10:90	10:90
						37	10:90	–

The Claisen rearrangement proceeds well for 5-bromo-2-(2-butenyloxy)pyrimidine **7d** using Pd(II)-catalysis. For its methyl isomer 5-bromo-2-(2-methylpropenyloxy)pyrimidine (**7c**), however, no 3,3-sigmatropic rearrangement was observed. In the former a methyl group is in the γ-allylic position, in the latter the methyl group is in the β-position. It is known that alkyl substituents in the β-position reduce the rate of reaction in Claisen rearrangements,[11] as well as in the Pd(II)-catalysed rearrangements.[8d] The rate reduction has been attributed to difficulties in formation of a tertiary C–Pd bond.[2b] A π-donor substituent in the β-position also strongly influences the reaction rate,[12,13] which is clearly seen in the case of the β-methoxy derivative **7k** and the β-phenylthio derivative **7l**. Both failed to undergo the Claisen rearrangement. Compound **7j**, which has an α,γ-disubstituted allylic system, also failed to react. Changes in the solvent (dichloromethane, DMF) or temperature had no effect.

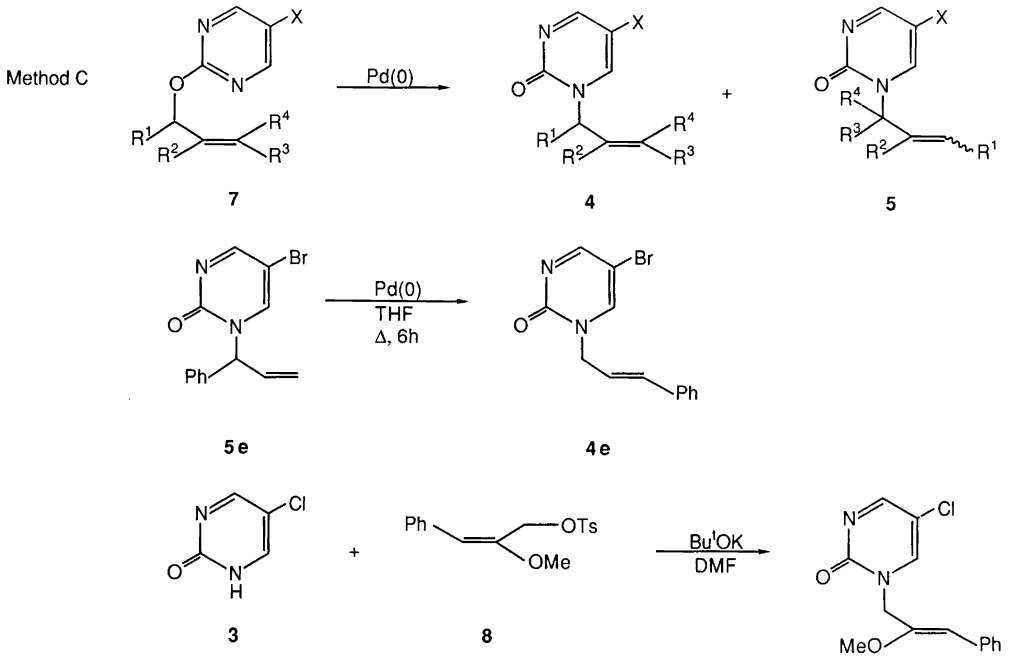
In the rearrangement reactions of the γ-phenylallyl derivative **7e** and the γ,γ-dimethylallyl derivative **7h**, equilibria were formed between the substrate **7e** (**7h**), and the *N*-alkylated isomers **4e** (**4h**) and **5e** (**5h**). For the dimethyl derivative the ratio **7h**:**5h** was 3:2 (^{1}H NMR). The equilibrium was verified by using the *N*-alkylated isomer **5h** as the substrate which led to the formation of the same ratio of products in the reaction mixture.

Several allylic-type derivatives, including allylic ethers, have been used with Pd(0)-catalysis for allylation reactions.[1e] Hence it was anticipated that the allylic ethers **7** could be rearranged by Pd(0)-catalysis. A π-allylpalladium complex similar to that formed in the reaction with allylic acetates (Scheme 1) would be expected. The rearrangements proceed well under Pd(0)-catalysis. The relative yields of the products **4** and **5** in the substituted allylic derivatives were different from those in the Pd(II)-catalysed reaction which show that the reactions proceed by different mechanisms. However, the relative yields of the products **4** and **5** are also different to some extent from the relative yields in the allylic acetate reactions. This may, in part, be due to different reaction conditions. The rearrangement takes place under essentially neutral conditions, whereas one mole equivalent of base is used in the reaction of the 5-halo-2-pyrimidinones with the allylic acetates, and a modified reaction mechanism may be operative.

For the rearrangement of the simple allylic ether **7a** tris(triphenylphosphine)rhodium(I) chloride was a good catalyst (yield 93 %). When the substrates **7** were substituted in the allylic system, Rh(I) failed to induce rearrangements. With molybdenum hexacarbonyl there was no reaction.

From the literature it is known that 3-methylallyl systems, with Pd(0) catalysis, give a mixture of 1,3- and 3,3-rearranged products, whereas the 3-phenyl analogue gives only the 1,3-isomer.[2b] In the reaction of the 3-methylallyl derivative **7d**, a mixture of both rearrangement products is formed, whereas the 3-phenyl analogue **7e** gives only the 1,3-rearrangement product. This reaction was studied further. Heating isomer **5e** with Pd(0) in THF, which corresponds to the conditions used in the rearrangement reactions, gave the 1,3-product **4e**. (Scheme 2). Hence compound **5e** serves as an allylic substrate, in a reversible reaction which is thermodynamically controlled.

The yields in the Pd(0)-catalysed 1,3-rearrangement reactions are generally better than in the Pd(0)-catalysed



Scheme 2.

allylic acetate alkylations (Table 1; Method A/Method C). In alkylation reactions with functionalized allylic systems the 1,3-allylic rearrangement of the ether may be superior to the direct alkylation reactions. Thus the allylic ether **7k** is readily available from the corresponding olate and the 2-chloropyrimidine and undergoes the 1,3-rearrangement to form **7k** (60 %) on Pd(0)-catalysis. Direct alkylation of 5-chloro-2(1*H*)-pyrimidinone with the unstable *p*-toluenesulphonate **8**, however, gave the analogous product **9** in low yield (13 %). Similarly the rearrangement of the allylic ether **7l** took place readily with formation of **4l** (60 %) but this product was not available by the direct alkylation using the corresponding *p*-toluenesulphonate. By suitable choices of substrate, the Pd(II)-catalysed reaction can be used for attaching secondary or tertiary carbons to the nitrogen, which is of importance since direct alkylation becomes more difficult as the number of substituents on the alkylating carbon increases.

Experimental

The ^{1}H NMR spectra were recorded at 300 MHz and the ^{13}C NMR spectra at 75 MHz. The mass spectra under electron-impact conditions were recorded at 70 eV ionizing energy. Ammonia was used for chemical ionization (CI); the spectra are presented as *m/z* (% rel. int.).

3-Phenylthio-3-buten-2-ol (**1l**).[14,15] Phenyl vinyl sulfide (12.0 mmol) was added, with stirring, to a solution of lithium diisopropylamide (12.0 mmol) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (18.3 mmol) in dry THF (50 ml) under N_2 at −78 °C. The solution was stirred for 10 min before acetaldehyde (12.0 mmol) was added. The mixture was stirred for 30 min at −78 °C and 30 min at ambient temperature, water was added and the solution was extracted with diethyl ether (×2). The ether solution was washed with water (×5), and the solution was evaporated. The product was purified by distillation; yield 46 %, b.p. 92–94 °C (0.1 mm Hg). ^{1}H NMR ($CDCl_3$): δ 1.40 (CH_3, d, *J* 6.5 Hz), 3.40 (OH), 4.34 (CH, q, *J* 6.5 Hz), 4.94 and 5.50 (=CH_2, 2×s), 7.2–7.5 (Ph). MS: 280 (0.2, *M*), 136 (99), 135 (100), 109 (10), 91 (70), 77 (18), 66 (12), 65 (17).

(E)-*1-Trimethylsilyl-1-octen-3-ol* (**1i**). Diisobutylaluminium hydride (5.30 ml, 5.30 mmol) was added to a solution of (*E*)-1-trimethylsilyl-1-octen-3-one[16] (0.70 g, 3.54 mmol) in dry THF (10 ml) under N_2 at −78 °C. The mixture was stirred for 1 h, warmed slowly to 0 °C and stirred at this temperature for 30 min before methanol and water were added. The solid was removed by filtration, the filtrate evaporated and the residue subjected to flash chromatography on silica gel using hexane–EtOAc 10:1 (v/v) as the eluent; yield 75 %, oily substance. Found: C, 66.39; H, 11.95. Calc. for $C_{11}H_{24}OSi$: C, 65.92; H, 12.07. ^{1}H NMR ($CDCl_3$): δ 0.02 (Me_3Si), 0.84 and 1.3–1.5 (C_5H_{11}), 3.95–4.05 (C*H*OH, m), 5.79 (Me_3SiCH=, dd, *J* 18.5, 1 Hz), 5.99 (C*H*=, dd, *J* 18.5, 5.5 Hz). ^{13}C NMR ($CDCl_3$): δ 0.4 (Me_3Si), 13.8/ 22.4/ 24.9/ 31.6/ 36.7 (C_5H_{11}), 74.5 (CHO), 128.8 (CH=), 148.6 (CH=). MS: 200 (0.2, *M*), 144 (17), 129 (20), 111 (11), 101 (10), 99 (5), 75 (100), 73 (64).

(E)-*1-Pentyl-3-trimethylsilyl-2-propenyl acetate* (**2i**). Acetic anhydride (0.238 g, 2.77 mmol) in dry dichloromethane (10 ml) was added dropwise to a solution of 1-trimethylsilyl-1-octen-3-ol (0.462 g, 2.31 mmol) and 4-(*N,N*-dimethylamino)pyridine (0.353 g, 2.88 mmol) in dry dichloromethane (10 ml) under N_2 at 0 °C. The mixture was stirred for 1 h at 0 °C, diluted with dichloromethane and shaken with aqueous $CuSO_4$ (×4), $NaHCO_3$ (×2) and with saturated aqueous sodium chloride solution (×1). The dried ($MgSO_4$) solution was evaporated and the residual material was subjected to flash chromatography on silica gel eluting with hexane–EtOAc 15:1 (v/v); yield 85 %, oily substance. Anal. $C_{13}H_{26}O_2Si$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.04 (Me_3Si), 0.85/1.2–1.3/1.5–1.6 (C_5H_{11}), 2.15 (Ac), 5.2 (CHO), 5.79 (Me_3SiCH=, dd, *J* 19, 1 Hz), 5.90 (C*H*=, dd, *J* 19,5 Hz). ^{13}C NMR ($CDCl_3$): δ 0.5 (Me_3Si), 13.8/ 22.5/ 24.6/ 31.4/ 33.9 (C_5H_{11}), 21.1 (*Me*CO), 76.0 (CHO), 131.0 (CH=), 143,6 (CH=), 170.2 (Me*C*O). MS: 242 (4, *M*), 213 (69), 200 (66), 167 (42), 129 (44), 117 (62), 75 (48), 73 (100).

*Preparation of substituted 1-(2-alkenyl)-5-halo-2(1*H*-pyrimidinones using allylic acetates and Pd(0).* Triethylamine (0.29 g, 2.87 mmol) in dry dichloromethane (10 ml) was added to a suspension of the 5-halo-2(1*H*)-pyrimidinone (2.87 mmol) in dry dichloromethane (10 ml) and the mixture was stirred under N_2 at ambient temperature for 15 min before the allylic acetate (2.87 mmol), palladium(II) acetate (0.032 g, 0.144 mmol) and triisopropyl phosphite (0.24 g, 1.15 mmol) were added. The mixture was stirred overnight, diluted with dichloromethane and washed with saturated, aqueous sodium chloride. The dried ($MgSO_4$) solution was evaporated and the product was purified by flash chromatography on silica gel, eluting with EtOAc.

*5-Chloro-1-(2-propenyl)-2-(1*H*)-pyrimidinone (***4a***).*[9]

*5-Bromo-1-(2-methyl-2-propenyl)-2(1*H*)-pyrimidinone*(**4c**), (**5c**). Compound **4c** was obtained from 2-methyl-2-propenyl acetate,[17] m.p. 122 °C. Anal. $C_8H_9BrN_2O$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.77 (Me, s), 4.48 (NCH_2, s), 4.90 and 5.10 (CH=, 2×s), 7.49 (H-4, d, *J* 3 Hz), 8.60 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 20.0 (Me), 55.8 (NCH_2), 96.8 (C-5), 116.0 (CH_2=), 138.9 (CH=), 146.4 (C-6), 154.5 (C-2), 166.6 (C-4). MS: 230/228 (41/42, *M*), 229 (90), 227 (91), 160 (27), 158 (21), 149 (34), 80 (50), 55 (100).

(E)-*5-Bromo-1-(3-phenyl-2-propenyl)-2(1*H*)-pyrimidinone* (**4e**). Compound **4e** was obtained from (*E*)-3-phenyl-2-propenyl acetate.[18] m.p. 196 °C. Found: C, 54.19; H, 3.98. Calc. for $C_{13}H_{11}BrN_2O$: C, 53.73; H, 3.81. ^{1}H NMR [$(CD_3)_2SO$]: δ 4.73 (NCH_2, dd, *J* 7, 1 Hz), 6.5–6.6

(CH_2CH=, m), 6.76 (PhC*H*=, d, *J* 16 Hz), 7.4–7.6 (Ph), 8.68 (H-4,d, *J* 3 Hz), 8.74 (H-6, d). ^{13}C NMR [$(CD_3)_2SO$]: δ 52.3 (CH_2N), 95.9 (C-5), 123.2 (CH=), 126.5/ 128.6/ 128.7/ 135.9 (Ph), 133.9 (CH=), 149.1 (C-6), 153.8 (C-2), 166.3 (C-4). MS: 292/290 (9/10, *M*), 177 (13), 175 (14), 118 (10), 117 (100), 116 (97), 115 (62), 91 (31).

*5-Bromo-1-(3-methyl-2-butenyl)-2-(1*H*)-pyrimidinone* (**4h**). Compound **4h** was obtained from 3-methyl-2-butenyl acetate,[17] m.p. 120 °C. Anal. $C_9H_{11}BrN_2O$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.79 and 1.84 (2×Me, 2×s), 4.50 (CH_2N, d, *J* 7.5 Hz), 5.3–5.35 (CH=, m), 7.76 (H-4, d, *J* 3 Hz), 8.54 (H-6, d). ^{13}C NMR ($CDCl_3$) δ 17.9, 25.6 (2×Me), 48,0 (CH_2N), 96.2 (C-5), 116.0 (CH=), 141.8 (C=), 145.9 (C-6), 154.3 (C-2), 165.6 (C-4). MS: 244/242 (14/16, *M*), 177 (14), 175 (16), 95 (6), 80 (6), 69 (78), 68 (100), 67 (30).

(E)-*5-Chloro-1-(1-pentyl-3-trimethylsilyl-2-propenyl)-2(1*H*)-pyrimidinone* (**4i**). Compound **4i** was obtained from (*E*)-1-pentyl-3-trimethylsilyl-2-propenyl acetate. ^{1}H NMR ($CDCl_3$): δ 0.05 (Me_3Si), 0.79/1.1–1.3/1.6–1.8 (C_5H_{11}), 5.2–5.3 (NCH), 5.82 (Me_3SiCH=, dd, *J* 19, 1 Hz), 5.94 (CHC*H*=, dd, *J* 19, 5 Hz), 7.49 (H-4, d, *J* 3 Hz), 8.42 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 0.8 (Me_3Si), 13.7/ 22.1/ 25.2/ 31.1/ 33.0 (C_5H_{11}), 61,0 (CHN), 110.9 (C-5), 135.2 (CH=), 141.5 (CH=), 142.0 (C-6), 154.4 (C-2), 163.9 (C-4).

*5-Bromo-1-(1-methyl-2-propenyl)-2(1*H*)-pyrimidinone* (**5d**). Compound **5d** was made from (*E*)-2-butenyl acetate,[17] m.p. 64 °C. Found: C, 42.43; H, 4.06. Calc. for $C_8H_9BrN_2O$: C, 41.94; H, 3.96. ^{1}H NMR ($CDCl_3$): δ 1.50 (Me, d, *J* 7 Hz), 5.3–5.5 ($CH=CH_2$), 5.9–6.0 (NCH), 7.73 (H-4, d, *J* 3 Hz), 8.54 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 18.1 (Me), 55.0 (CHN), 97.0 (C-5), 119.7 (CH_2=), 135.7 (CH=), 144.3 (C-6), 154.1 (C-2), 165.9 (C-4). MS: 230/228 (15/15, *M*), 201 (9), 175 (12), 149 (8), 106 (8), 80 (22), 55 (100), 54 (66).

(E)-*5-Chloro-1-(2-octenyl)-2-(1*H*)-pyrimidinone* (**5f**). Compound **5f** was obtained from 1-pentyl-2-propenyl acetate,[18] m.p. 103 °C. Anal. $C_{12}H_{17}ClN_2O$. ^{1}H NMR ($CDCl_3$): δ 0.89/1.2–1.4/2.0–2.1 (C_5H_{11}), 4.47 (NCH_2, d, *J* 7 Hz), 5.5–5.6/ 5.8–5.9 (CH=CH), 7.74 (H-4, d, *J* 3 Hz), 8.51 (H-6, d). ^{13}C NMR ($CDCl_3$):δ 14.0/ 22.4/ 28.4/ 31.4/ 32.3 (C_5H_{11}), 58.2 (NCH_2), 111.0 (C-5), 122.0 (CH=), 139.5 (CH=), 144.2 (C-6), 154.6 (C-2), 164.7 (C-4). MS: 242/240 (4/12, *M*), 184 (42), 131 (33), 81 (39), 69 (62), 68 (35), 55 (60), 54 (100).

(E)-*5-Bromo-1-(2-octenyl)-2(1*H*)-pyrimidinone* (**5g**). Compound **5g** was made from 1-pentyl-2-propenyl acetate,[18] m.p. 110 °C. Found: C 50.11; H 5.81. Calc. for $C_{12}H_{17}BrN_2O$: C, 50.53; H, 6.00. ^{1}H NMR ($CDCl_3$): δ 0.9/1.2–1.5/205–2.1 (C_5H_{11}), 4.47 (NCH_2, d, *J* 7 Hz), 5.5–5.6/5.8–5.9 (CH=CH), 7.80 (H-4, d, *J* 3 Hz), 8.56 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 13.8/ 22.2/ 28.2/ 31.1/ 32.0 (C_5H_{11}), 52.6 (NCH_2), 96.3 (C-5), 121.8 (CH=), 139.3 (CH=), 146.2 (C-6), 154.3 (C-2), 166.0 (C-4). MS: 286/284 (8/8, *M*), 229 (26), 227 (25), 110 (16), 81 (39), 69 (60), 55 (59), 54 (100).

Pd(II)-Catalysed rearrangement of 2-(2-alkenyloxy)-5-halopyrimidines (**7**). The 2-(2-alkenyloxy)-5-halopyrimidine (0.8 mmol) and bis(benzonitrile)palladium(II) chloride (0.04 mmol) in dry THF (7 ml) under N_2 was heated under reflux for 16 h. The solution was evaporated and the residue subjected to flash chromatography on silica gel eluting with EtOAc. Compounds **5d** and **5g** are characterized above. The yields are given in Table 1.

*5-Bromo-1-(2-propenyl)-2(1*H*)-pyrimidinone* (**4b**), (**5b**). Compound **4b** was obtained from 2-allyloxy-5-bromopyrimidine, m.p. 144 °C. Anal. $C_7H_7BrN_2O$: C, H. ^{1}H NMR ($CDCl_3$): δ 4.5–4.6 (NCH_2), 5.3–5.4 (CH_2=), 5.9–6.0 (CH=), 7.80 (H-4, d, *J* 3 Hz), 8.57 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 53.0 (CH_2N), 96.4 (C-5), 120.9 (CH_2=), 130.3 (CH), 146.3 (C-6), 154.0 (C-2), 166.2 (C-4). MS: 216/214 (26/27, *M*), 215 (48), 213 (48), 160 (17), 158 (13), 80 (37), 52 (20), 41 (100).

*5-Bromo-1-(1-phenyl-2-propenyl)-2(1*H*)-pyrimidinone* (**5e**). Compound **5e** was made from 5-bromo-2-(3-phenyl-2-propenyloxy)pyrimidine, m.p. 125 °C. ^{1}H NMR ($CDCl_3$): δ 5.17 (CH_2=, dd, *J* 17,1 Hz), 5.55 (CH_2=, dd, *J* 10, 1 Hz), 6.1–6.3 (CH=, m), 6.57 (NCH, d, *J* 5 Hz), 7.3–7.5 (Ph), 7.67 (H-4, d, *J* 3 Hz), 8.53 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 62.4 (CHN), 96.5 (C-5), 120.6 (CH_2=), 127.6/ 128.5/ 128.7/ 133.2 (Ph), 135.5 (CH=), 144.7 (C-6), 153.6 (C-2), 165.6 (C-4). MS: 292/290 (2/2, *M*), 118 (9), 117 (100), 116 (28), 115 (37), 91 (17), 80 (6), 77 (5).

*5-Bromo-1-(1,1-dimethyl-2-propenyl)-2(1*H*)-pyrimidinone* (**5h**). Compound **5h** was made from 5-bromo-2-(3-methyl-2-butenyloxy)pyrimidine, m.p. 80 °C. Anal. $C_9H_{11}BrN_2O$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.77 (2×Me, s), 5.3–5.4 (CH_2=), 6.1–6.2 (CH=), 7.99 (H-4, d, *J* 3 Hz), 8.50 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 24.9 (2×Me), 65.5 (NC), 95.8 (C-5), 115.5 (CH_2=), 140.9 (CH=), 144.5 (C-6), 153.6 (C-2), 164.7 (C-4). MS: 244/242 (2/2, *M*), 175 (7), 95 (9), 69 (60), 68 (59), 67 (35), 53 (18), 41 (100).

Pd(0)-Catalysed rearrangement of 2-(2-alkenyloxy)-5-halopyrimidines (**7**). A mixture of the 2-(2-alkenyloxy)-5-halopyrimidine (0.8 mmol), palladium(II) acetate (0.013 g, 0.056 mmol) and triisopropyl phosphite (0.083 g, 0.4 mmol) in dry THF (7 ml) under N_2 was heated under reflux for 16 h. The solution was evaporated and the residual material was subjected to flash chromatography on silica gel eluting with EtOAc. Compounds **4b** (**5b**), **4c** (**5c**), **4e**, **4h** and **5g** have all been characterized above. The yields are given in Table 1.

(E)-*5-Bromo-1-(2-butenyl-2(1H)-pyrimidinone* (**4d**). Compound **4d** was obtained from (*E*)-5-bromo-2-(2-butenyloxy)-pyrimidine, m.p. 142 °C. Anal. $C_8H_9BrN_2O$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.78 (Me, d, *J* 6.5 Hz), 4.47 (CH_2O, d, *J* 6.5 Hz), 5.5–6.0 (CH=CH, m), 7.86 (H-4, d, *J* 3 Hz), 8.55 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 17.6 (Me), 52.5 (CH_2N), 96.7 (C-5), 123.1 (CH=), 133.6 (CH=), 146.4 (C-6), 154.2 (C-2), 165.9 (C-4). MS: 230/228 (18/17, *M*), 229 (15), 227 (15), 149 (9), 95 (10), 80 (12), 55 (100), 54 (68).

(E)-*5-Bromo-1-(1-pentyl-3-trimethylsilyl-2-propenyl)-2(1H)-pyrimidinone* (**4j**). Compound **4j** was obtained from (*E*)-5-bromo-2-(1-pentyl-3-trimethylsilyl-2-propenyloxy)-pyrimidine, m.p. 66 °C. Anal. $C_{15}H_{25}BrN_2OSi$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.11 (Me_3Si), 0.78/1.1–1.4/1.6–1.8 (C_5H_{11}), 5.2 (NCH), 5.82 (Me_3SiCH=, dd, *J* 19.1 Hz), 5.95 (CH=CH, dd, *J* 19.5 Hz), 7.58 (H-4, d, *J* 3 Hz), 8.45 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 0.8 (Me_3Si), 13.6/ 22.1/ 25.1/ 31.0/ 32.9 (C_5H_{11}), 61.1 (CHN), 95.8 (C-5), 135.2 (CH=), 141.5 (CH=), 144.3 (C-6), 154.2 (C-2), 165.3 (C-4). MS: 358/356 (3/3, *M*), 301 (7), 233 (15), 231 (16), 167 (7), 111 (11), 99 (9), 73 (100).

5-Bromo-1-(2-methoxy-3-phenyl-2-propenyl)-2(1H)-pyrimidinone (**4k**). Compound **4k** was obtained from (*Z*)-5-bromo-2-(2-methoxy-3-phenyl-2-propenyloxy)pyrimidine, m.p. 112 °C. Anal. $C_{14}H_{13}BrN_2O_2$. ^{1}H NMR ($CDCl_3$): δ 3.64 (OMe), 4.74 (CH_2, s), 5.88 (CH=, s), 7.4–7.6 (Ph), 7.88 (H-4, d, *J* 3 Hz), 8.58 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 51.0 (CH_2N), 57.1 (OMe), 97.1 (C-5), 116.8 (CH=), 127.6/ 128.4/ 128.8/ 134.0 (Ph), 145.8 (C-6), 148.4 (C=), 154.3 (C-2), 166.7 (C-4). MS: 322/320 (4/4, *M*), 147 (19), 146 (100), 131 (26), 117 (16), 115 (25), 103 (25), 91 (14).

5-Bromo-1-(1-methyl-2-phenylthio-2-propenyl)-2(1H)-pyrimidinone (**4l**). Compound **4l** was obtained from 5-bromo-2-(1-methyl-2-phenylthio-2-propenyloxy)pyrimidine, oily substance. ^{1}H NMR ($CDCl_3$): δ 1.55 (Me, d, *J* 7 Hz), 5.45–5.55 (NCH), 5.73 / 5.48 (CH_2=, 2×s), 7.32 (Ph), 7.72 (H-4, d, *J* 3 Hz), 8.46 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 18.5 (Me), 57.1 (NCH), 96.9 (C-5), 120.4 (CH_2=), 129.3/ 129.5/ 130.8/ 133.0 (Ph), 143.2 (C=), 144.0 (C-6), 153.9 (C-2), 166.0 (C-4). MS(CI): 338/336 (21/27, *M*+1), 261 (13), 259 (17), 225 (100), 165 (51), 131 (72), 99 (9), 97 (26).

5-Chloro-1-(2-methoxy-3-phenyl-2-propenyl)-2(1H)-pyrimidinone (**9**). A solution of (*Z*)-2-methoxy-3-phenyl-2-propen-1-ol (1.00 g, 6.10 mmol) in dry diethyl ether (10 ml) was added dropwise, with stirring, to sodium hydride (0.2 g, 6.71 mmol; 80 % in oil) in dry diethyl ether (10 ml) under N_2 at ambient temperature. The mixture was heated under reflux for 2 h, stirred at ambient temperature for 18 h, and cooled to −60 °C, and a solution of tosyl chloride (1.16 g, 6.10 mmol) in dry diethyl ether (20 ml) was added dropwise with stirring. The mixture was stirred for 2 h at −60 °C, allowed to reach ambient temperature. Dry DMF (50 ml) was added and the diethyl ether was removed from the solution of the sulphonate **8** under reduced pressure. This solution was added dropwise with stirring to the potassium salt of 5-chloro-2(1*H*)-pyrimidinone in dry DMF (50 ml) under N_2 at ambient temperature. The salt of the pyrimidinone was prepared from potassium *tert*-butoxide (0.74 g, 6.10 mmol) and 5-chloro-2-pyrimidinone (0.79 g, 6.10 mmol) in DMF (50 ml). The reaction mixture, after the addition of the *p*-toluenesulphonate solution, was stirred at ambient temperature for 4 h, after which time the DMF was distilled off under reduced pressure (0.01 mmHg), water was added, and the mixture was extracted with chloroform. The chloroform solution was washed with water (×3) and dried ($MgSO_4$) and the solvent was removed under reduced pressure. The product was purified by trituration with diethyl ether; yield: 13 %, m.p. 133 °C. Anal. $C_{14}H_{13}ClN_2O_2$. ^{1}H NMR ($CDCl_3$): δ 3.62 (OMe), 4.78 (NCH_2, s), 5.90 (CH=, s), 7.2–7.3 (Ph), 7.84 (H-4, d, *J* 3 Hz), 8.57 (H-6, d). ^{13}C NMR ($CDCl_3$): δ 51.1 (NCH_2), 57.2 (OMe), 111.5 (C-5), 116.9 (CH=), 127.7/ 128.5/ 128.9/ 134.0 (Ph), 143.6 (C-6), 148.4 (C=), 154.5 (C-2), 165.2 (C-4). MS: 278/276 (1/5, *M*), 147 (20), 146 (100), 131 (36), 117 (19), 115 (30), 103 (31), 91 (13).

Preparation of substituted 2-(2-alkenyloxy)-5-halopyrimidines (**7**). A solution of the allylic alcohol **1** (2.84 mmol) in dry THF (5 ml) was added dropwise with stirring to potassium *tert*-butoxide (0.35 g, 3.1 mmol) in dry THF (5 ml) under N_2 at 0 °C. The mixture was stirred at 0 °C for 15 min whereupon a solution of 5-bromo-2-chloropyrimidine[9] (0.50 g, 2.58 mmol) in dry THF (5 ml) added dropwise at 0 °C. The resulting solution was stirred at ambient temperature for 8 h, diluted with diethyl ether and washed with water (×3). The dried ($MgSO_4$) solution was evaporated, and the residue was subjected to flash chromatography on silica gel eluting with hexane–EtOAc 6:1 (v/v).

2-Allyloxy-5-chloropyrimidine (**7a**).[9]

2-Allyloxy-5-bromopyrimidine (**7b**). Compound **7b** was obtained from allyl alcohol; 82 % yield, m.p. 28–30 °C. ^{1}H NMR ($CDCl_3$): δ 4.85–4.9 (OCH_2, m), 5.3/5.45 (CH=CH_2, 2×m), 6.1 (C*H*=CH_2, m), 8.55 (H-4, 6, s). ^{13}C NMR ($CDCl_3$): δ 68.7 (CH_2O), 111.9 (C-5), 118.3 (CH_2=), 132.2 (CH=), 159.6 (C-4,6), 163.6 (C-2). MS: 216/214 (25/28, *M*), 215 (60), 213 (59), 187 (20), 185 (19), 160 (50), 158 (47), 41 (100).

5-Bromo-2-(2-methyl-2-propenyloxy)pyrimidine (**7c**). Compound **7c** was obtained from 2-methyl-2-propenol, yield 81 %, m.p. 67 °C. Anal. $C_8H_9BrN_2O$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.85 (Me, s), 4.78 (OCH_2, s), 4.97 and 5.09 (CH_2=, 2×s), 8.53 (H-4, 6, s). ^{13}C NMR ($CDCl_3$): δ 19.5 (Me), 71.3 (CH_2O), 111.9 (C-5), 113.0 (CH_2=), 139.9 (C=), 159.6 (C-4,6), 163.7 (C-2). MS: 230/228 (6/6, *M*), 160 (16), 158 (17), 120 (16), 118 (17), 106 (11), 55 (87), 39 (100).

(E)-*5-Bromo-2-(2-butenyloxy)pyrimidine* (**7d**). Compound **7d** was obtained from (*E*)-2-butenol in 85 % yield, m.p. 33 °C. Found: C, 42.39; H, 3.95. Calc. for $C_8H_9BrN_2O$: C, 41.94; H, 3.96. ^{1}H NMR ($CDCl_3$): δ 1.74 (Me, dd, *J* 6.5, 1 Hz), 4.79 (CH_2, d, *J* 6.5 Hz), 5.7–5.95 (CH=CH), 8.53 (H-4, 6, s). ^{13}C NMR ($CDCl_3$): δ 17.5 (Me), 68.5 (CH_2O), 111.4 (C-5), 124.8 (CH=), 131.1 (CH=), 159.2 (C-4, 6), 163.4 (C-2). MS: 230/228 (2/2, *M*), 201 (6), 160 (6), 120 (9), 118 (10), 95 (18), 55 (100), 54 (83).

(E)-*5-Bromo-2-(3-phenyl-2-propenyloxy)pyrimidine* (**7e**). Compound **7e** was obtained from (*E*)-3-phenyl-2-propenol in 87 % yield, m.p. 91 °C. Anal. $C_{13}H_{11}BrN_2O$; C, H. ^{1}H NMR ($CDCl_3$): δ 5.04 (CH_2, dd, *J* 6, 1 Hz), 6.4–6.5 (CH_2CH=, m), 6.76 (PhC*H*=, d, *J* 16 Hz), 7.3–7.4 (Ph), 8.55 (H-4, 6, s). ^{13}C NMR ($CDCl_3$): δ 68.3 (CH_2), 111.7 (C-5), 123.0 (CH=), 126.4/ 127.8/ 128.4/ 136.1 (Ph), 133.7 (CH=), 159.5 (C-4, 6), 163.5 (C-2). MS: 292/290 (2/2, *M*), 263 (9), 262 (10), 118 (9), 117 (100), 116 (20), 115 (28), 91 (11).

5-Bromo-2-(1-pentyl-2-propenyloxy)pyrimidine (**7g**). Compound **7g** was obtained from 1-octen-3-ol in 79 % yield, oily substance. Anal. $C_{12}H_{17}BrN_2O$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.88/1.3–1.5/1.7–1.9 (C_5H_{11}), 5.15–5.2/5.3–5.4 (=CH_2, 2×m), 5.4–5.5 (OCH), 5.9–5.95 (C*H*=), 8.52 (H-4, 6, s). ^{13}C NMR ($CDCl_3$): δ 13.7/ 22.3/ 24.5/ 31.4/ 34.1 (C_5H_{11}), 78.1 (CHO), 111.2 (C-5), 116.4 (CH_2=). 136.4 (CH=), 159.2 (C-4, 6), 163.3 (C-2). MS: 286/284 (4/5, *M*), 215 (22), 213 (19), 82 (16), 81 (45), 69 (71), 55 (56), 54 (100).

5-Bromo-2-(3-methyl-2-butenyloxy)pyrimidine (**7h**). Compound **7h** was obtained from 3-methyl-2-butenol in 60 % yield, oily substance. Anal. $C_9H_{11}BrN_2O$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.77 (2×Me), 4.86 (OCH_2, d, *J* 7 Hz), 5.5 (CH=, m), 8.52 (H-4, 6, s). ^{13}C NMR ($CDCl_3$): δ 18.2/25.8 (2×Me), 65.0 (CH_2O), 111.5 (C-5), 118.7 (CH=), 139.1 (C=), 159.5 (C-4, 6), 163.8 (C-2). MS: 244/242 (2/2, *M*), 177 (7), 175 (9), 120 (6), 69 (64), 67 (34), 41 (100).

(E)-*5-Bromo-2-(1-pentyl-3-trimethylsilyl-2-propenyloxy)-pyrimidine* (**7j**). Compound **7j** was obtained from 1-trimethylsilyl-1-octen-3-ol in 67 % yield, oily substance. Anal. $C_{15}H_{25}BrN_2OSi$: C, H, ^{1}H NMR ($CDCl_3$): δ 0.01 (Me_3Si), 0.84/1.2–1.4/1.6–1.8 (C_5H_{11}), 5.4 (OCH, m), 5.58 (Me_3SiCH=, dd, *J* 19, 1 Hz), 6.02 (C*H*=, dd, *J* 19, 5.5 Hz), 8.47 (H-4, 6, s). ^{13}C NMR ($CDCl_3$): δ 1.5 (Me_3Si), 15.4/ 23.9/ 26.2/ 33.0/ 35.6 (C_5H_{11}), 81.2 (OCH), 112.7 (C-5), 133.0 (CH=), 145.0 (CH=), 160.9 (C-4, 6), 165.0 (C-2). MS: 358/356 (1/1, *M*), 299 (19), 233 (20), 231 (21), 113 (9), 99 (10), 85 (7), 73 (100).

(Z)-*5-Bromo-2-(2-methoxy-3-phenyl-2-propenyloxy)pyrimidine* (**7k**). Compound **7k** was obtained from 2-methoxy-3-phenyl-2-propenol[19] in 59 % yield, m.p. 47 °C. Anal. $C_{14}H_{13}BrN_2O_2$. ^{1}H NMR ($CDCl_3$): δ 3.82 (OMe), 5.05 (CH_2, s), 5.81 (CH=, s), 7.2–7.6 (Ph), 8.54 (H-4, 6, s). ^{13}C NMR ($CDCl_3$): δ 56.5 (MeO), 67.2 (CH_2), 112.2 (C-5), 112.7 (C=), 126.6/128.2/ 128.7/ 135.2 (Ph), 150.3 (C=), 159.6 (C-4, 6), 163.3 (C-2). MS: 322/320 (18/18, *M*), 147 (100), 146 (53), 117 (50), 115 (60), 104 (29), 103 (44), 91 (34).

5-Bromo-2-(1-methyl-2-phenylthio-2-propenyloxy)pyrimidine (**7l**). Compound **7l** was obtained from 3-phenylthio-3-buten-2-ol in 65 % yield, m.p. 84 °C. Anal. $C_{14}H_{13}BrN_2OS$. ^{1}H NMR ($CDCl_3$): δ 1.62 (Me, d, *J* 6.5 Hz), 5.07 / 5.58 (CH_2=, 2×s), 5.57 (CHO, q, *J* 6. 7 Hz), 7.3–7.5 (Ph), 8.48 (H-4, 6, s). ^{13}C NMR ($CDCl_3$): δ 20.5 (Me), 75.3 (CHO), 111.9 (C-5), 114.5 (CH_2=), 127.9/ 129.1/ 132.5/ 133.0 (Ph), 145.8 (C=), 159.5 (C-4, 6), 162.9 (C-2). MS: 338/336 (0.2/0.2, *M*), 229 (99), 227 (100), 177 (22), 175 (25), 162 (18), 109 (19), 91 (20).

5-Bromo-2-(1-methyl-2-propenyloxy)pyrimidine (**7m**). Compound **7m** was obtained from 1-methyl-2-propenol in 70 % yield, oily substance. ^{1}H NMR ($CDCl_3$): δ 1.47 (Me, d, *J* 6.5 Hz), 5.15–5.2/5.3–5.35 (=CH_2, 2×m), 5.5–5.6 (OCH), 5.9–6.0 (CH=), 8.52 (H-4,6, s). ^{13}C NMR ($CDCl_3$): δ 19.9 (Me), 74.2 (CHO), 111.3 (C-5), 115.7 (CH_2=), 137.5 (CH=), 159.3 (C-4,6), 163.1 (C-2). MS: 320/228 (2/2, *M*), 176 (6), 174 (7), 120 (5), 118 (4), 95 (98), 55 (98), 54 (100).

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