Synthesis of 6-substituted purin-2-ones with potential cytokinin activity

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6-Substituted purin-2-ones have been prepared by completely regioselective addition of Grignard reagents to an *N*-protected purin-2-one followed by rearomatisation and deprotection. The target compounds may be regarded as analogues of the potent cytokinins *trans*-zeatin and benzylaminopurine (BAP), and most of the BAP analogues did induce increased weight growth in radish cotyledons. *N*-Protected (*E*)-6-styrylpurin-2-one underwent head to tail [2+2] dimerisation to the 1α,2α,3β,4β-substituted cyclobutane **15**, when exposed to ordinary daylight. When irradiated with UV-light, the *trans*-compound isomerised to the corresponding *cis*-isomer. The structure of compound **15** was determined by single crystal X-ray diffraction methods at 150 K.

Introduction

Cytokinins are plant hormones with a wide range of biological effects.[1] They promote cell division and cell growth and they are involved in the retardation of senescence. All known naturally occurring cytokinins are 6-alkylaminopurines. In most instances, these compounds are unsubstituted in the purine 2- and 8-positions, but 6-alkylaminopurin-2-ones have recently been isolated from both higher plants and micro-organisms,[2] and identified as plant growth stimulators. This kind of biological activity is also found among synthetic 6-alkylaminopurin-2-ones.[3] The NH group in the purine 6-position in natural cytokinins is not essential for all hormonal activities. Several purine derivatives bearing alkynyl, alkenyl or alkyl substituents in the 6-position do exhibit stimulating effects on plant growth.[4] We have previously demonstrated that C–C bond formation in the 6-position of *N*,*N*-dialkylated purin-2-ones[5] as well as *N*,*N*,*N*-trialkylated 2-oxopurinium salts,[6] easily can be achieved by regioselective addition of Grignard reagents, and we report herein that this strategy can be utilised in syntheses of 6-substituted purin-2-ones with potential cytokinin activity.

Both 6-benzylaminopurine (BAP) and *trans*-zeatin are highly active naturally occurring cytokinins,[1] and in this study we chose BAP analogues and zeatin analogues with the general structure outlined in Fig. 1 as our target molecules.

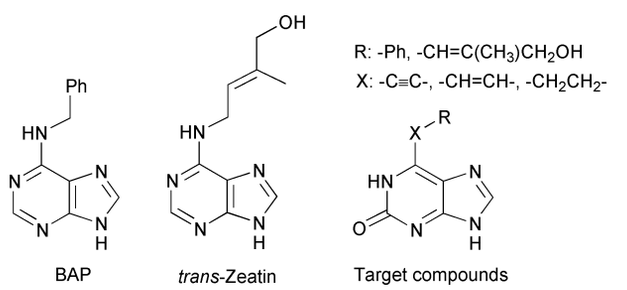
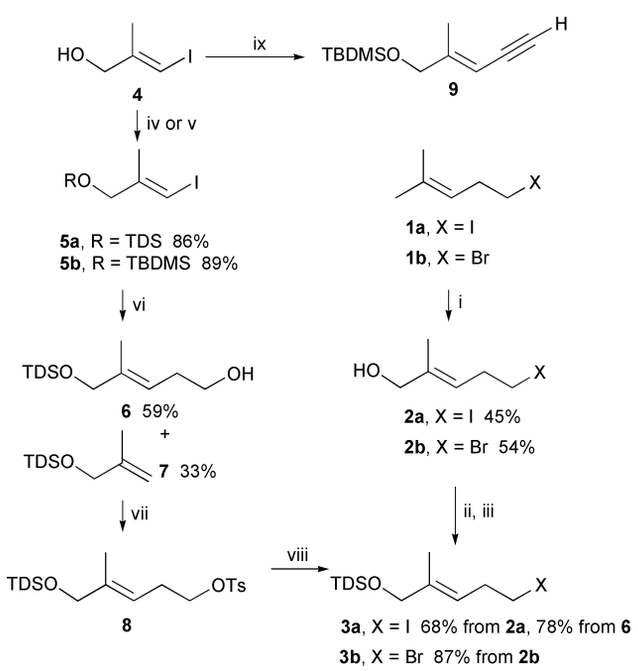


Fig. 1 Structures of the cytokinines 6-benzylaminopurine (BAP) and *trans*-zeatin and general structure of the target analogues.

Results and discussion

The Grignard reagents required for the introduction of the C-6 substituents in the BAP analogues were generated from 1-chloro-2-phenylethane, (*E*)-styryl bromide and phenylacetylene respectively, and the syntheses of the reagents required for the *trans*-zeatin analogue side chains are outlined in Scheme 1. It is claimed that both halides **2** are available from cyclopropyloxiranes,[7] but the experimental details reported for the synthesis of the oxirane as well as for the ring-openings are sparse. Instead the halides **1** were prepared from cyclopropyl methyl ketone by addition of methylmagnesium halide and subsequent Julia rearrangement on the resulting carbinol as previously described.[8] The hydroxy function in compounds **2** was introduced by allylic oxidation of the alkenes **1** with selenium dioxide and *tert*-butyl hydroperoxide, essentially as reported for **2b** before,[9] and, finally, the allylic alcohols were *O*-silylated with



Scheme 1 *Reagents and conditions*: i, SeO_2, *t*-BuO_2H, CH_2Cl_2; ii, TDS-Cl, base, DMF; iii, for **3a**, NaI, acetone, Δ; iv, TDS-Cl, DMAP, Et_3N, CH_2Cl_2 for **5a**; v, TBS-Cl, imidazole, DMF for **5b**; vi, *t*-BuLi, oxirane, THF, −78 °C; vii, Ts-Cl, pyridine; viii, NaI, acetone; ix, see refs. 11 and 4.

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Table 1 Synthesis of compounds **13** and **14**

R in **13**	R′ in **13** and **14**	Yield (%) **13**[a]	**14**[b]
$-CH_2CH_2Si(CH_3)_2$	$-CH_2CH_2Ph$	47, **13a**[c]	—[d]
$-Si(CH_3)_2Bu^t$	$-CH_2CH_2Ph$	66, **13b**	81, **14a**
$-Si(CH_3)_2Bu^t$	(*E*)-CH=CHPh	67, **13c**	90, **14b**
$-Si(CH_3)_2Bu^t$	(*Z*)-CH=CHPh	71, **13d**[e]	—[f]
$-Si(CH_3)_2Bu^t$	–C≡C–Ph	76, **13e**	69, **14d**[g]
$-Si(CH_3)_2Bu^t$	(E)-$CH_2CH_2CH{=}C(CH_3)CH_2OH$[h]	61, **13f**	80, **14e**
$-Si(CH_3)_2Bu^t$	$-CH_2CH_2CH{=}C(CH_3)_2$	78, **13g**	79, **14f**
$-Si(CH_3)_2Bu^t$	$-CH{=}CH_2$	63, **13h**	—
$-Si(CH_3)_2Bu^t$	(E,E)-$CH{=}CH{-}CH{=}C(CH_3)CH_2OH$[ij]	49, **13i**	68, **14g**
$-Si(CH_3)_2Bu^t$	(E)-$C{\equiv}C{-}CH{=}C(CH_3)CH_2OH$[j]	82, **13j**	76, **14h**

[a] Yield of isolated compounds prepared by addition of Grignard reagent to the oxopurines **11** followed by DDQ oxidation unless otherwise noted. [b] Yield of isolated compounds. [c] The oxidation was achieved with MnO_2 in CH_2Cl_2. [d] Complex mixture. [e] Formed by isomerisation of compound **13c**. [f] A *ca*. 2 : 1 mixture of *E* and *Z*-isomers was formed. [g] The cleavage was performed with Me_4NF in EtOH followed by AcOH. [h] In compound **13**, the hydroxy group is protected as a TDS ether. [i] Formed by Heck coupling on compound **13h**. [j] In compound **13**, the hydroxy group is protected as a TBS ether.

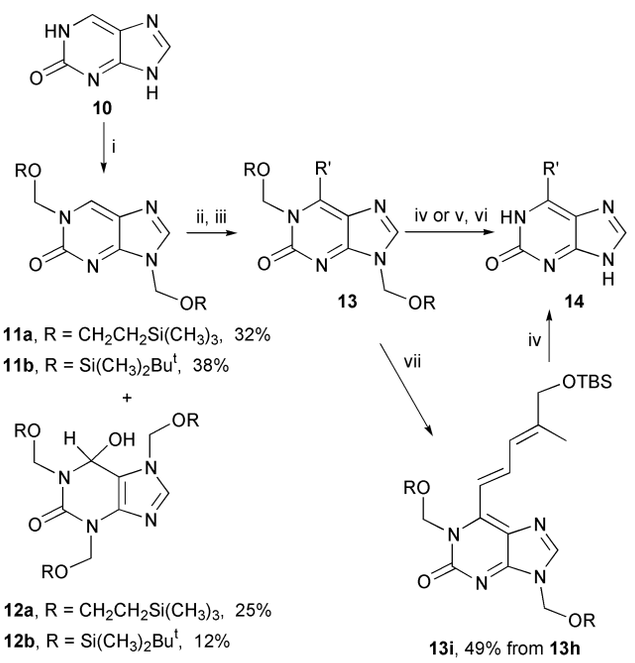
thexyldimethylsilyl† chloride (TDS-Cl) to give the desired halides **3**. In the synthesis of the iodide **3a**, some of the corresponding chloride was formed during silylation and the crude product was therefore treated with sodium iodide.

Compound **3a** was also synthesised by an alternative route. Geometrically pure vinyl iodide **4** is readily available in large quantities by literature methods,[10] and we chose this compound as starting material for the preparation of alkyne **9**, and alkyl halide **3a**. Compound **4** was *O*-silylated with thexyldimethylsilyl chloride (TDS-Cl), treated with *tert*-butyllithium (*t*-BuLi) and the lithiated alkene thus formed was trapped with oxirane to give the alcohol **6** together with the terminal alkene **7** from the unreacted alkenyllithium. Compound **6** could readily be converted to iodide **3a** *via* the toluene-*p*-sulfonate **8**. For the synthesis of the reagents required for the enyne side chain in the target compound (X = –C≡C–; Fig. 1), vinyl iodide **4** was converted to the alkyne **9** as described before.[4,11]

Previously we have introduced substituents at the 6-position of *N*,*N*-dibenzylpurin-2-ones[5] by addition of Grignard reagents, but for the synthesis of the cytokinin analogues shown in Fig. 1, easily removable *N*-substituents were required. We chose silicon-based protecting groups, and when purin-2-one **10**[6] was reacted with 2-(trimethylsilyl)ethoxymethyl chloride (SEM-Cl)[12,13] or (*tert*-butyldimethylsilyloxy)methyl chloride,[14,15] 1,9-dialkylated purines **11** were formed together with various amounts of trialkylated water adducts **12** as well as minor amounts of other unidentified dialkylated isomers (Scheme 2). These results are consistent with our earlier results from *N*-benzylation of purin-2-one **10**.[5,6,16] As before, the position of the *N*-substituents was confirmed by long-range HETCOR NMR techniques.[5,6]

The 6-substituents were introduced by completely regioselective addition of the desired Grignard reagent followed by rearomatisation of the crude adducts with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Scheme 2, Table 1). Again long-range HETCOR NMR techniques were employed in the structure elucidation of the products **13**. For the synthesis of the diene **13i** we chose to introduce the side chain in two steps: first, addition of the ethenyl Grignard reagent followed by DDQ oxidation to give compound **13h**; and secondly, subjection of compound **13h** to Heck coupling with the iodide **5b**. When unprotected iodo alcohol **4** was used in the Heck reaction, some aldehyde was also formed in addition to the desired allylic alcohol.

Attempts to remove the SEM-protecting groups from compound **13a** with tetrabutylammonium fluoride (TBAF) or tetramethylammonium fluoride resulted in a complex mixture, but when the (*tert*-butyldimethylsilyloxy)methyl-protected compounds **13** were reacted with tetramethylammonium fluoride, the target compounds **14** were formed cleanly.

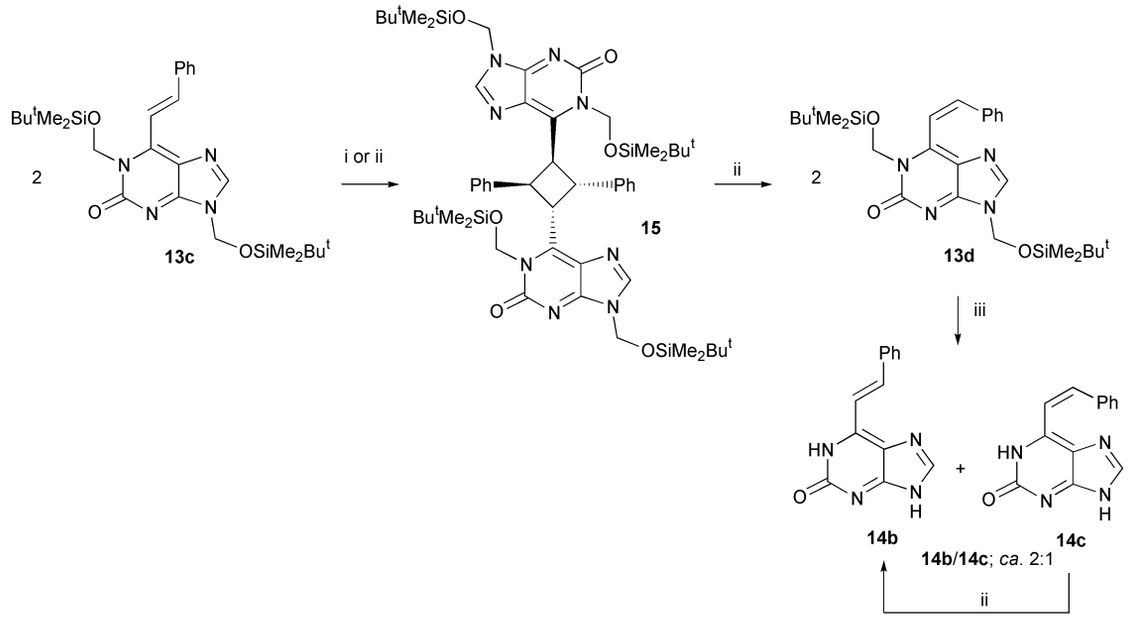


Scheme 2 *Reagents and conditions*: i, $ROCH_2Cl$, $EtN(i\text{-}Pr)_2$, CH_2Cl_2; ii, R′MgX, THF, −78 °C; iii, DDQ, PhH; iv, Me_4NF, MeCN; v, Me_4NF, EtOH; vi, AcOH; vii, compound **5b**, $Pd(OAc)_2$, $EtN(i\text{-}Pr)_2$, DMF, 55 °C.

When exposed to ordinary daylight, the (*E*)-6-styrylpurine **13c** underwent head to tail [2+2] dimerisation to the substituted cyclobutane **15** (Scheme 3). The regiochemistry was confirmed by X-ray crystallography (Fig. 2, Table 2), which also revealed that the relative stereochemistry of the cyclobutane was 1α,2α,3β,4β. Extensive decomposition took place when tetramethylammonium fluoride-mediated deprotection of compound **15** was attempted.

When irradiated with UV-light, the (*Z*)-styryl isomer **13d** was formed in more than 80% yield from both the (*E*)-isomer **13c** and the cyclobutane **15** (Scheme 3, Table 3). Irradiating the (*Z*)-compound **13d** under the same conditions resulted in only minor isomerisation to the (*E*)-isomer **13c**. Tetramethylammonium fluoride-mediated removal of the *N*-protecting groups in the (*Z*)-compound **13d** gave a *ca*. 2 : 1 mixture of (*E*)-isomer **14b** and (*Z*)-isomer **14c**. UV-Irradiation of the mixture only resulted in additional (*Z*) to (*E*) isomerisation, and pure (*E*)-compound **14b** was completely inert under these conditions. It appears that the unprotected 6-styryl-2-oxopurines **14b** and **14c** and the *N*-protected analogues **13c** and

† The IUPAC name for thexyl is 1,1,2-trimethylpropyl.



Scheme 3 *Reagents and conditions*: i, daylight; ii, *hν*, EtOH; iii, Me_4NF, MeCN.

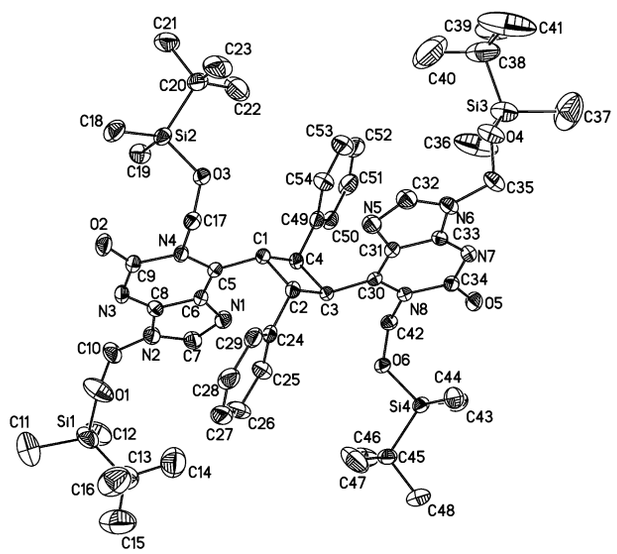


Fig. 2 Molecular structure of **15** with partial atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. H-atoms are left out for clarity.

Table 2 Crystal data and intensity collection and refinement data for **15**

Formula	$C_{54}H_{84}N_8O_6Si_4$
Formula weight/g mol^{-1}	1053.65
Crystal size/mm	0.8 × 0.5 × 0.3
Color, shape	Pale yellow, block
Crystal system	Orthorhombic
Space group	$Pca2_1$ (No. 29)
Cell dimensions/Å	a = 11.7867(3)
	b = 15.9615(4)
	c = 33.1308(9)
Volume/Å^3	6233.0(3)
Z	4
ρ_{calc}/g cm^{-3}	1.123
F(000)	2272
Diffractometer	Siemens SMART[21]
Radiation	Mo-Kα (λ = 0.71073 Å)
Monochromator	Graphite crystal
T/K	150
Scan mode	ω-scans
No. of sets of exposures	5
Exposure time per frame/s	45
Crystal to detector distance/cm	5.0
2θ range/°	2.56–60.00
Index ranges	$-16 \le h \le 12$
	$-22 \le k \le 22$
	$-46 \le l \le 44$
Absorption correction	Multi-scan[21]
No. of reflections measured	71281
No. of reflections used in refinement	17916
No. of reflections with $I > 2\sigma(I)$, n	14539
Refinement	On F^2
No. of refined parameters, p	709
$R = \Sigma\|\Delta F\|/\|F_o\|$[a] $[I > 2\sigma(I)]$	0.0581
$R_w = \{\Sigma[w(\Delta F)^2/w(F_o)^2]\}^{\frac{1}{2}}$[b] $[I > 2\sigma(I)]$	0.1477
$S = \{\Sigma[w(\Delta F)^2/(n-p)]\}^{\frac{1}{2}}$ $[I > 2\sigma(I)]$	1.038
Residual electron density/e Å^{-3}	+1.137, −0.444

[a] $\Delta F = |F_o| - |F_c|$. [b] $w = (\sigma^2(F_o^2) + (0.083P)^2 + 3.500P)^{-1}$, where $P=(F_o^2 + 2F_c)/3$.

13d exhibit exactly opposite behaviour under photochemical conditions. Furthermore, the photochemical properties of (*E*)-6-styryl-2-oxopurine **14b** also differ from those reported for (*E*)-6-styrylpurine. The latter compound is isomerised to the (*Z*)-isomer under photochemical conditions.[17]

The evaluation of the cytokinin activity of the 6-substituted 2-oxopurines **14** was based on their ability to stimulate radish cotyledon growth and the results are given in Table 4. The seeds were treated with 10 μM solutions of the purines and the growth effects were measured as the increase in cotyledon weight after 72 h compared to a control sample. For comparison, the potent cytokinin BAP was also included and the difference in weight between the cotyledons grown in the presence of BAP and the control sample was defined as 100% weight increase. The results for compounds **14** are given as a percentage of the increase obtained with BAP.

In contrast to the zeatin analogues we have studied before,[4] the purin-2-ones **14e**–**h** (Table 4, entries 6–9) were essentially inactive. In many instances some weight retardation was actually seen. The BAP analogues **14a**–**c**, on the other hand, did induce increased growth at 10 μM concentration (Table 4, entries 2–4). The effects were *ca.* 30–60% of that obtained using BAP. The ineffectiveness of the alkyne **14d** as a cytokinin (Table 4, entry 5) was not totally unexpected. In connection with our study on antimycobacterial purines,[18] we have previously found high cytotoxicity for 6-alkynylpurin-2-ones.[19] In addition to stimulation of growth, naturally occurring cytokinins also

Table 3 Photochemical isomerisation of 6-styrylpurines

Starting material	Conditions	Product distribution (%) from ^{1}H NMR		
		(*E*)-Isomer **13c** or **14b**	Cyclobutane	(*Z*)-Isomer **13d** or **14c**
13c	*hv*, EtOH, 20 h	50 (**13c**)	—[a]	50 (**13d**)
13c	*hv*, EtOH, 72 h[b]	15 (**13c**)	—[a]	85 (**13d**)
15	*hv*, EtOH, 24 h	6 (**13c**)	4 (**16**)	90 (**13d**)
13d	*hv*, EtOH, 72 h[b]	18 (**13c**)	—[a]	82 (**13d**)
14b	*hv*, EtOH, 72 h	100 (**14b**)	—[a]	—[a]

[a] Not detectable in the ^{1}H NMR spectrum. [b] No further significant changes after 140–190 h.

Table 4 Cytokinin activity of benzylaminopurine (BAP) and 6-substituted 2-oxopurines

Entry	Compound	Substituent in the 2-oxopurine 6-position[a]	% Weight increase relative to BAP (10 μM conc.)[a]
1	BAP	$-NHCH_2Ph$[b]	100
2	**14a**	$-CH_2CH_2Ph$	27
3	**14b**	(*E*)-CH=CHPh	30
4	**14b**–**14c** (*ca.* 2 : 1)	(*Z*)-CH=CHPh in **14c**	56
5	**14d**	–C≡C–Ph	4
6	**14e**	(E)-$CH_2CH_2CH{=}C(CH_3)CH_2OH$	—[c]
7	**14f**	$-CH_2CH_2CH{=}C(CH_3)_2$	2
8	**14g**	(E,E)-CH=CH–CH=$C(CH_3)CH_2OH$	2
9	**14h**	(E)-C≡C–CH=$C(CH_3)CH_2OH$	—[d]

[a] Comparison of weight gain between radish cotyledon grown in 0 μM and 1, 10 or 100 μM purine solution, the results are given as % of the weight increase obtained with BAP. [b] The structure of BAP is shown in Fig. 1. [c] No change compared to control. [d] Weight retardation relative to control (0 μM) was observed.

delay senescence most probably by acting as antioxidants.[1] Studies of the antioxidant/radical scavenging properties of the cytokinin analogues **14** are in progress in our laboratories and preliminary results indicate that substantially increased antioxidant activity is found among compounds **14** compared with the plant hormones BAP and *trans*-zeatin.

Experimental

The ^{1}H NMR spectra were recorded at 500 MHz with a Bruker Avance DRX 500 instrument, at 300 MHz with a Bruker Avance DPX 300 instrument or at 200 MHz with a Bruker Avance DPX 200 instrument. The ^{1}H decoupled ^{13}C NMR spectra were recorded at 125, 75 or 50 MHz using the above-mentioned spectrometers. *J* values are given in Hz. Mass spectra under electron impact conditions (EI) were recorded at 70 eV ionising voltage with a VG Prospec instrument, and are presented as *m*/*z* (% rel. int.). CH_4 was employed as the ionisation gas for chemical ionisation (CI). Electrospray MS spectra were recorded with a Bruker Apex 47e FT-ICR mass spectrometer. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany. Melting points are uncorrected. Silica gel for flash chromatography was purchased from Merck, Darmstadt, Germany (Merck No. 9385). Analytical thin layer chromatography was performed with E. Merck silica gel $60F_{254}$ 0.25 mm plates (Merck No. 1.05554). THF and Et_2O were distilled from sodium–benzophenone. PhH was dried over sodium wire. CH_2Cl_2 was predried with $CaCl_2$, distilled from CaH_2 and stored over 4 Å molecular sieves. Acetone was dried with boric anhydride prior to distillation. MeCN, DMF, triethylamine, *N*-ethyldiisopropylamine and pyridine were distilled from CaH_2 and stored over 4 Å molecular sieves. Tetramethylammonium fluoride tetrahydrate was dried by azeotropic distillation with absolute EtOH and the residue was dissolved in dry MeCN. 5-Iodo-2-methylpent-2-ene **1a**,[8] 5-bromo-2-methylpent-2-ene **1b**,[8] (*E*)-3-iodo-2-methylprop-2-en-1-ol **4**,[10] (*E*)-1-(*tert*-butyldimethylsilyloxy)-2-methylpent-2-en-4-yne **9**,[4,11] 1,9-dihydro-2*H*-purin-2-one **10**,[6] (*tert*-butyldimethylsilyloxy)methyl chloride,[14] and (*E*)-1-bromo-2-phenylethene[20] were prepared according to literature procedures. All other reagents were commercially available and used as received. Single crystals of **15** were obtained by slow crystallisation from EtOAc–hexane.

Crystal structure determination of compound 15‡

Crystal data. $C_{54}H_{84}N_8O_6Si_4$, $M = 1053.65$, orthorhombic, $a = 11.7867(3)$, $b = 15.9615(4)$, $c = 33.1308(9)$ Å, $U = 6233.0(3)$ Å^3, $T = 150$ K, space group $Pca2_1$ (No. 29), $Z = 4$, μ(Mo-Kα) = 0.145 mm^{-1}, 71281 reflections measured, 17916 unique ($R_{int} = 0.0432$) which were used in the refinement. Final $R(F^2) = 0.0581$ and $wR(F^2) = 0.1477$.

Data collection and structure solution. Single-crystal X-ray data was collected with a Siemens SMART CCD diffractometer.[21] Sadabs[22] was used to correct for absorption. The Bravais lattice is primitive orthorhombic with systematic absences corresponding to either $Pca2_1$ (non-centrosymmetric) or *Pcam* (centrosymmetric). Statistics for the normalised structure factors ($|E^2 - 1| = 0.804$ compared to the theoretical values 0.968 and 0.736 for centrosymmetric and non-centrosymmetric space groups, respectively) indicate that the structure is non-centrosymmetric. The structure was readily solved by direct methods in the space group $Pca2_1$

Refinement. Refinement performed with SHELXTL.[23] Positional parameters for all heavy atoms were refined. Hydrogen atoms were kept in idealised positions, refining a single C–H distance for all H atoms connected to the same C atom. Heavy atoms were refined anisotropically, whereas U_{iso} for the hydrogen atoms were fixed at $1.2U_{eq}$ (–CH– and $-CH_2-$) and $1.5U_{eq}$ ($-CH_3$) of the parent C atom. Experimental data, crystal data and refinement results are summarised in Table 2. Atomic scattering factors are taken from ref. 24.

‡ CCDC reference number 163628. See http://www.rsc.org/suppdata/p1/b1/b101327k/ for crystallographic files in .cif or other electronic format.

(*E*)-5-Iodo-2-methylpent-2-en-1-ol 2a[7]

To a mixture of selenium dioxide (262 mg, 2.36 mmol) in dry CH_2Cl_2 (5 cm^3) at ambient temperature was added *tert*-butyl hydroperoxide (5.5 M solution in decane, 1.7 cm^3, 9.35 mmol). The mixture was stirred for 30 minutes under N_2 before 5-iodo-2-methylpent-2-ene **1a** (990 mg, 4.7 mmol) in dry CH_2Cl_2 (5 cm^3) was added. After an additional 2.5 h, benzene (5 cm^3) was added and the mixture evaporated *in vacuo*. The residue was dissolved in diethyl ether (20 cm^3) and washed with 10% aqueous potassium hydroxide (6 × 5 cm^3) followed by brine (5 cm^3) prior to drying ($MgSO_4$) and evaporation *in vacuo*. The product was purified by flash chromatography eluting with EtOAc–hexane (1 : 6) followed by EtOAc–hexane (1 : 4) to give the *iodo alcohol* **2a** (480 mg, 45%) as a colourless oil; R_f 0.16 (1 : 3, EtOAc–hexane); δ_H(200 MHz; $CDCl_3$; Me_4Si) 1.61 (3 H, s, Me), 2.10 (1 H, s, OH), 2.59 (2 H, q, *J* 7.2, CH_2), 3.10 (2 H, t, *J* 7.2, ICH_2), 3.95 (2 H, s, OCH_2) and 5.34 (1 H, br t, *J* 7.2, CH); δ_C(50 MHz; $CDCl_3$; Me_4Si) 5.4 (ICH_2), 13.8 (Me), 31.7 (CH_2), 68.1 (OCH_2), 123.7 (=CH) and 137.4 (=C); *m*/*z* (EI) 225.9848 (M^+. $C_6H_{11}IO$ requires 225.9855), 99 (23%), 81 (32), 49 (30), 43 (100) and 41 (61).

(*E*)-5-Bromo-2-methylpent-2-en-1-ol 2b

The compound was prepared from 5-bromo-2-methylpent-2-ene **1b** (4.89 g, 30 mmol), selenium dioxide (1.65 g, 15 mmol) and *tert*-butyl hydroperoxide (5.5 M solution in decane, 12 cm^3, 60 mmol) in dry CH_2Cl_2 (25 cm^3) as described for **1a** above. The product was purified by flash chromatography eluting with EtOAc–hexane 1 : 9, 1 : 6 and finally 1 : 3 to give the *bromo alcohol* **2b** (2.88 g, 54%) as a colourless oil; R_f 0.15 (1 : 3, EtOAc–hexane); δ_H(200 MHz; $CDCl_3$; Me_4Si) 1.63 (3 H, s, Me), 1.92 (1 H, s, OH), 2.58 (2 H, q, *J* 7.2, CH_2), 3.33 (2 H, t, *J* 7.2, $BrCH_2$), 3.97 (2 H, s, OCH_2) and 5.38 (1 H, br t, *J* 7.2, CH); δ_C(50 MHz; $CDCl_3$; Me_4Si) 13.8 (Me), 31.1 (CH_2), 32.4 ($BrCH_2$), 68.1 (OCH_2), 121.7 (=CH) and 137.9 (=C); *m*/*z* (EI) 179.9971/177.9993 (M^+. $C_6H_{11}BrO$ requires 179.9973/177.9993), 85 (25%), 81 (20), 71 (100), 57 (11), 55 (11), 43 (43) and 41 (31). Spectroscopic data are in good agreement with those reported before.[9]

(*E*)-1-Thexyldimethylsilyloxy-5-iodo-2-methylpent-2-ene 3a

Method A. Imidazole (569 mg, 8.36 mmol) was added to a solution of (*E*)-5-iodo-2-methylpent-2-en-1-ol **2a** (630 mg, 2.79 mmol) in dry DMF (10 cm^3) under N_2 at 0 °C. Thexyldimethylsilyl chloride (600 mg, 3.36 mmol) was added dropwise and the resulting mixture was left in the refrigerator for 62 h and poured into brine and diethyl ether (1 : 1, 40 cm^3). The aqueous phase was extracted with diethyl ether (4 × 20 cm^3), and the combined organic solutions were washed with brine (2 × 30 cm^3) prior to drying ($MgSO_4$) and evaporation *in vacuo*. The crude product was dissolved in dry acetone (25 cm^3), sodium iodide (1.67 g, 11.1 mmol) was added and the solution was heated at reflux for 70 h under N_2 before the solvent was evaporated *in vacuo*. The residue was partitioned between water and diethyl ether (1 : 1, 40 cm^3) and the layers were separated. The aqueous phase was extracted with diethyl ether (2 × 20 cm^3) and the combined organic solutions were washed with brine (20 cm^3) prior to drying ($MgSO_4$) and evaporation *in vacuo*. The residue was purified by flash chromatography eluting with EtOAc–hexane (1 : 50) to give the *iodide* **3a** (700 mg, 68%) as a colourless oil (Found: C, 45.3; H, 8.2. $C_{14}H_{29}IOSi$ requires C, 45.6; H, 7.9%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.09 (6 H, s, $SiMe_2$), 0.85 (6 H, s, Me in thexyl), 0.87 (6 H, d, *J* 6.9, Me in thexyl), 1.57 (3 H, s, Me), 1.62 (1 H, m, CH in thexyl), 2.61 (2 H, m, CH_2), 3.11 (2 H, t, *J* 7.4, CH_2I), 3.96 (2 H, s, CH_2O) and 5.36 (1 H, m, =CH); δ_C(50 MHz; $CDCl_3$; Me_4Si) −3.3 ($SiMe_2$), 5.5 (CH_2I), 13.7 (Me), 18.5 (Me in thexyl), 20.4 (Me in thexyl), 25.3 (C in thexyl), 31.9 (CH_2), 34.2 (CH in thexyl), 67.8 (CH_2O), 122.3 (=CH) and 137.2 (=C); *m*/*z* (CI) 368 (M^+, 1%), 283 (54), 241 (23), 209 (21), 157 (100), 155 (22), 83 (53), 81 (46), 75 (32) and 73 (19).

Method B. Sodium iodide (833 mg, 5.56 mmol) was added to a stirred solution of crude (*E*)-5-thexyldimethylsilyloxy-4-methylpent-3-en-1-yl toluene-*p*-sulfonate **8** in dry acetone (40 cm^3). The solution was heated at reflux for 44 h under N_2 before the solvent was evaporated *in vacuo*. The residue was partitioned between water and diethyl ether (1 : 1, 40 cm^3). The separated aqueous phase was extracted with diethyl ether (2 × 20 cm^3) and the combined organic solutions were washed with brine (20 cm^3) prior to drying ($MgSO_4$) and evaporation *in vacuo*. The residue was purified by flash chromatography eluting with EtOAc–hexane (1 : 50) to give the *iodide* **3a** (401 mg, 78% from **6**) as a colourless oil.

(*E*)-5-Bromo-1-thexyldimethylsilyloxy-2-methylpent-2-ene 3b

N-Ethyldiisopropylamine (0.5 cm^3, 2.92 mmol) was added to a solution of (*E*)-5-bromo-2-methylpent-2-en-1-ol **2b** (435 mg, 2.43 mmol) in dry CH_2Cl_2 (10 cm^3) and dry DMF (10 cm^3) under N_2 at 0 °C. Thexyldimethylsilyl chloride (480 mg, 2.67 mmol) was added dropwise and the resulting mixture was left in the refrigerator for 72 h and diluted with water (10 cm^3) and saturated NH_4Cl solution (10 cm^3). The aqueous phase was extracted with diethyl ether (2 × 25 cm^3). The combined organic solutions were washed with 1 M HCl (2 × 20 cm^3), water (20 cm^3), and brine (20 cm^3) prior to drying ($MgSO_4$) and evaporation *in vacuo*. The residue was purified by flash chromatography eluting with EtOAc–hexane (1 : 100) to give the *bromide* **3b** (680 mg, 87%) as a colourless oil (Found: C, 52.7; H, 9.3. $C_{14}H_{29}BrOSi$ requires C, 52.3; H, 9.1%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.08 (6 H, s, $SiMe_2$), 0.84 (6 H, s, Me in thexyl), 0.87 (6 H, d, *J* 6.9, Me in thexyl), 1.59 (3 H, s, Me), 1.64 (1 H, m, CH in thexyl), 2.59 (2 H, m, CH_2), 3.34 (2 H, t, *J* 7.3, CH_2Br), 3.98 (2 H, s, CH_2O) and 5.39 (1 H, m, =CH); δ_C(75 MHz; $CDCl_3$; Me_4Si) −3.4 ($SiMe_2$), 13.6 (Me), 18.5 (Me in thexyl), 20.3 (Me in thexyl), 25.2 (C in thexyl), 31.2 (CH_2Br), 32.5 (CH_2), 34.1 (CH in thexyl), 67.8 (CH_2O), 120.3 (=CH) and 137.7 (=C); *m*/*z* (CI) 321/319 (M + 1, 1/1%), 251 (22), 237 (60), 235 (59), 157 (67), 85 (21), 81 (100), 75 (65), 73 (40) and 67 (23).

(*E*)-1-Thexyldimethylsilyloxy-3-iodo-2-methylprop-2-ene 5a

To a solution of (*E*)-3-iodo-2-methylprop-2-en-1-ol **4** (3.0 g, 15.2 mmol) in dry CH_2Cl_2 (20 cm^3) under N_2 at 0 °C were added triethylamine (4.7 cm^3, 30.4 mmol), DMAP (41 mg, 0.33 mmol) and thexyldimethylsilyl chloride (3.5 cm^3, 16.0 mmol). After stirring for 2 h at 0 °C and 16 h at ambient temperature under N_2 the solvent was removed *in vacuo* and the residue dissolved in diethyl ether (35 cm^3). The solution was washed with saturated aqueous ammonium chloride (80 cm^3) and 5% aqueous sodium hydrogen carbonate (35 cm^3) prior to drying ($MgSO_4$) and evaporation *in vacuo*. The product was purified by Kugelrohr distillation (0.4 mm Hg, 100 °C) to give the *vinyl iodide* **5a** (4.95 g, 86%) as a colourless oil (Found: C, 42.4; H, 7.6. $C_{12}H_{25}IOSi$ requires C, 42.35; H, 7.4%); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.08 (6 H, s, $SiMe_2$), 0.83 (6 H, s, Me in thexyl), 0.86 (6 H, d, *J* 7.1, Me in thexyl), 1.5–1.7 (1 H, m, CH in thexyl), 1.75 (3 H, s, Me), 4.06 (2 H, s, CH_2) and 6.17 (1 H, br s, =CH); δ_C(50 MHz; $CDCl_3$; Me_4Si) −3.5 ($SiMe_2$), 18.5 (Me in thexyl), 20.2 (Me in thexyl), 21.1 (Me), 25.1 (C in thexyl), 34.1 (CH in thexyl), 66.9 (CH_2), 75.8 (=CH) and 146.7 (=C); *m*/*z* (CI) 340 (M^+, 4%), 256 (13), 255 (100), 215 (7), 185 (54), 129 (6), 128 (7), 127 (10) and 113 (7).

(*E*)-1-*tert*-Butyldimethylsilyloxy-3-iodo-2-methylprop-2-ene 5b

To a solution of (*E*)-3-iodo-2-methylprop-2-en-1-ol **4** (1.12 g, 5.7 mmol) in dry DMF (5 cm^3) under N_2 were added imidazole (0.77 g, 11.4 mmol) and *tert*-butyldimethylsilyl chloride (0.9 g,

5.97 mmol). After stirring for 19 h at ambient temperature under N_2, the solution was diluted with water (5 cm^3) and Et_2O (25 cm^3). The phases were separated and the organic phase washed with aqueous 1 M HCl (5 cm^3), saturated aqueous sodium hydrogen carbonate (5 cm^3) and brine (5 cm^3) prior to drying ($MgSO_4$) and evaporation *in vacuo*. This gave the protected *alcohol* **5b** (1.58 g, 89%) as a colourless oil which was used without further purification. Spectroscopic data were in good agreement with those reported before.[25]

(*E*)-5-Thexyldimethylsilyloxy-4-methylpent-3-en-1-ol 6 and 1-thexyldimethylsilyloxy-2-methylprop-2-ene 7

To a stirred solution of (*E*)-1-thexyldimethylsilyloxy-3-iodo-2-methylprop-2-ene **5a** (1.02 g, 3.0 mmol) in dry THF (10 cm^3) under N_2 at −78 °C was added *tert*-butyllithium (1.5 M in pentane, 4 cm^3, 6 mmol) dropwise during 25 min before oxirane (1 g, 23 mmol) in dry THF (2 cm^3) was added. The resulting mixture was stirred for 1 h at −78 °C and 1.5 h at ambient temperature under N_2, cooled to 0 °C and diluted with saturated aqueous ammonium chloride (15 cm^3). The phases were separated and the aqueous phase extracted with CH_2Cl_2 (3 × 15 cm^3). The combined organic phases were dried ($MgSO_4$) and evaporated *in vacuo*. The products were isolated by flash chromatography eluting with EtOAc–hexane (1 : 12) followed by EtOAc–hexane (1 : 6).

The more polar fraction yielded the *alcohol* **6** (457 mg, 59%) as a colourless oil (Found: C, 65.1; H, 11.65. $C_{14}H_{30}O_2Si$ requires C, 65.05; H, 11.7%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.07 (6 H, s, $SiMe_2$), 0.84 (6 H, s, Me in thexyl), 0.86 (6 H, d, *J* 6.8, Me in thexyl), 1.49 (1 H, m, OH), 1.61 (4 H, m, CH in thexyl and Me), 2.30 (2 H, m, CH_2), 3.62 (2 H, m, CH_2), 3.98 (2 H, s, CH_2OSi) and 5.38 (1 H, m, =CH); δ_C(50 MHz; $CDCl_3$; Me_4Si) −3.4 ($SiMe_2$), 13.6 (Me), 18.5 (Me in thexyl), 20.3 (Me in thexyl), 25.2 (C in thexyl), 31.1 (CH_2), 34.1 (CH in thexyl), 62.3 (CH_2), 68.1 (CH_2), 119.6 (=CH) and 137.9 (=C); *m*/*z* (CI) 259 (M+1, 1%), 258 (1), 173 (78), 159 (20), 157 (20), 155 (21), 143 (27), 105 (31), 81 (69) and 75 (100).

The less polar fraction yielded the *alkene* **7** (213 mg, 33%) as a colourless oil (Found: C, 67.6; H, 12.0. $C_{12}H_{26}OSi$ requires C, 67.2; H, 12.2%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.09 (6 H, s, $SiMe_2$), 0.86 (6 H, s, Me in thexyl), 0.88 (6 H, d, *J* 6.9, Me in thexyl), 1.64 (1 H, m, *J* 6.9, CH in thexyl), 1.68 (3 H, s, Me), 4.00 (2 H, s, CH_2), 4.78 (1 H, m, =CH) and 4.96 (1 H, m, =CH); δ_C(50 MHz; $CDCl_3$; Me_4Si) −3.5 ($SiMe_2$), 18.5 (Me in thexyl), 19.0 (Me), 20.3 (Me in thexyl), 25.2 (C in thexyl), 34.2 (CH in thexyl), 66.6 (CH_2), 109.1 (=CH_2) and 144.7 (=C); *m*/*z* (CI) 215 (M+1, 3%), 131 (14), 130 (13), 129 (100), 115 (13), 85 (6), 84 (14), 76 (3), 75 (40) and 73 (13).

(*E*)-5-Thexyldimethylsilyloxy-4-methylpent-3-en-1-yl toluene-*p*-sulfonate 8

A solution of tosyl chloride (531 mg, 2.78 mmol) in dry pyridine (8 cm^3) was stirred under N_2 at 0 °C for 30 min and added to (*E*)-5-thexyldimethylsilyloxy-4-methylpent-3-en-1-ol **6** (360 mg, 1.39 mmol). The resulting solution was stirred under N_2 at 0 °C for 3 h and left in the refrigerator for 40 h. The solution was then poured into ice–water (40 cm^3) and extracted with diethyl ether (80 cm^3). The organic phase was washed with aqueous 1 M HCl (40 cm^3), saturated aqueous sodium hydrogen carbonate (40 cm^3) and brine (40 cm^3) prior to drying ($MgSO_4$) and evaporation *in vacuo*. This gave the *toluene-p-sulfonate* **8** as a colourless oil which was used without further purification; δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.05 (6 H, s, $SiMe_2$), 0.82 (6 H, s, Me in thexyl), 0.86 (6 H, d, *J* 6.9, Me in thexyl), 1.52 (3 H, s, Me), 1.60 (1 H, m, CH in thexyl), 2.33 (2 H, m, CH_2), 2.43 (3 H, s, ArMe), 3.91 (2 H, s, CH_2OSi), 3.99 (2 H, t, *J* 7.1, CH_2OAr), 5.25 (1 H, m, =CH), 7.32 (2 H, d, *J* 8.0, Ar) and 7.76 (2 H, d, *J* 8.0, Ar); δ_C(50 MHz; $CDCl_3$; Me_4Si) −3.4 ($SiMe_2$), 13.5 (Me), 18.5 (Me in thexyl), 20.3 (Me in thexyl), 21.6 (ArMe), 25.2 (C in thexyl), 27.4 (CH_2), 34.1 (CH in thexyl), 67.8 (CH_2OSi), 69.7 (CH_2OAr), 117.1 (=CH), 127.9 (CH in Ar), 129.8 (CH in Ar), 133.3 (C in Ar), 138.5 (=C) and 144.6 (C in Ar); *m*/*z* (CI) 413 (M+1, 1%), 229 (69), 157 (43), 93 (21), 83 (20), 81 (100), 75 (35), 69 (22) and 55 (18).

1,9-Dihydro-1,9-bis{[2-(trimethylsilyl)ethoxy]methyl}-2*H*-purin-2-one 11a and 6-hydroxy-1,3,6,7-tetrahydro-1,3,7-tris{[2-(trimethylsilyl)ethoxy]methyl}-2*H*-purin-2-one 12a

[2-(Trimethylsilyl)ethoxy]methyl chloride (1.020 g, 6.12 mmol) in dry CH_2Cl_2 (10 cm^3) was added slowly to a mixture of 1,9-dihydro-2*H*-purin-2-one **10** (178 mg, 1.31 mmol) and *N*-ethyldiisopropylamine (0.57 cm^3, 3.25 mmol) in dry CH_2Cl_2 (10 cm^3) under N_2 at 0 °C. After stirring for 1 h at 0 °C and an additional 17 h at ambient temperature, the mixture was evaporated *in vacuo*, and the products were separated by flash chromatography eluting with EtOAc–hexane (1 : 1) followed by EtOAc–hexane (2 : 1), EtOAc, EtOAc–EtOH (25 : 1) and EtOAc–EtOH (10 : 1).

The more polar fraction yielded the *dialkyl purine* **11a** (164 mg, 32%) as a yellow oil. Recrystallisation from EtOAc–hexane gave colourless crystals, mp 103–105 °C (Found: C, 51.8; H, 8.1. $C_{17}H_{32}N_4O_3Si_2$ requires C, 51.5; H, 8.1%); δ_H(500 MHz; $CDCl_3$; Me_4Si) −0.06 (9 H, s, $SiMe_3$), −0.03 (9 H, s, $SiMe_3$), 0.89 (2 H, t, *J* 8.2, $SiCH_2$), 0.96 (2 H, t, *J* 8.5, $SiCH_2$), 3.60 (2 H, t, *J* 8.2, OCH_2), 3.67 (2 H, t, *J* 8.5, OCH_2), 5.39 [2 H, s, N(9)CH_2], 5.43 [2 H, s, N(1)CH_2], 7.92 (1 H, s, H-8) and 8.30 (1 H, s, H-6); δ_C(50 MHz; $CDCl_3$; Me_4Si) −1.5 (2 × $SiMe_3$), 17.8 ($SiCH_2$), 18.1 ($SiCH_2$), 67.5 (OCH_2), 68.2 (OCH_2), 71.5 [N(9)CH_2], 79.3 [N(1)CH_2], 123.9 (C-5), 137.7 (C-6), 147.3 (C-8), 155.6 (C-2) and 159.9 (C-4); *m*/*z* (CI) 396 (M^+, 3%), 295 (11), 281 (14), 280 (55), 265 (19), 222 (32), 193 (12) and 73 (100).

The less polar fraction yielded the *adduct* **12a** (177 mg, 25%) as a yellow oil (Found: C, 50.7; H, 8.5. $C_{23}H_{48}N_4O_5Si_3$ requires C, 50.7; H, 8.9%); δ_H(500 MHz; $CDCl_3$; Me_4Si) −0.02 (9 H, s, $SiMe_3$), 0.007 (9 H, s, $SiMe_3$), 0.009 (9 H, s, $SiMe_3$), 0.8–1.0 (6 H, m, 3 × $SiCH_2$), 2.75 (1 H, br s, OH), 3.5–3.7 (6 H, m, 3 × OCH_2), 5.06 [1 H, d, *J* 10.4, H_A in N(1)CH_2], 5.15 [1 H, d, *J* 10.7, H_A in N(7)CH_2], 5.27 [1 H, d, *J* 10.7, H_B in N(7)CH_2], 5.34 [2 H, s, N(3)CH_2], 5.40 [1 H, d, *J* 10.4, H_B in N(1)CH_2], 6.26 (1 H, d, *J* 5.9, H-6) and 7.36 (1 H, s, H-8); δ_C(125 MHz; $CDCl_3$; Me_4Si) −1.6 (3 × $SiMe_3$), 17.5 ($SiCH_2$), 17.8 ($SiCH_2$), 17.9 ($SiCH_2$), 65.8 (OCH_2), 66.1 (OCH_2), 66.3 (OCH_2), 71.0 [N(3)CH_2], 73.9 (C-6), 74.8 [N(1)CH_2 and N(7)CH_2], 106.3 (C-5), 135.6 (C-8), 138.8 (C-4) and 152.0 (C-2); *m*/*z* (CI) 544 (M^+, 1%), 528 (19), 527 (39), 441 (29), 280 (12), 268 (17), 75 (30) and 73 (100).

1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-2*H*-purin-2-one 11b and 6-hydroxy-1,3,6,7-tetrahydro-1,3,7-tris-[(*tert*-butyldimethylsilyloxy)methyl]-2*H*-purin-2-one 12b

(*tert*-Butyldimethylsilyloxy)methyl chloride (1.106 g, 6.12 mmol) in dry CH_2Cl_2 (10 cm^3) was added slowly to a mixture of 1,9-dihydro-2*H*-purin-2-one **10** (278 mg, 2.04 mmol) and *N*-ethyldiisopropylamine (1.04 cm^3, 6.12 mmol) in dry CH_2Cl_2 (10 cm^3) under N_2 at 0 °C. After stirring for 1 h at 0 °C and an additional 21 h at ambient temperature, the mixture was evaporated *in vacuo*, and the products were separated by flash chromatography eluting with EtOAc–hexane (2 : 3) followed by EtOAc–hexane (1 : 1) and EtOAc–hexane–EtOH–NH_3(conc.) (40 : 20 : 1 : 1).

The more polar fraction yielded the *dialkyl purine* **11b** (325 mg, 38%) as colourless crystals mp 164–166 °C (from EtOAc–hexane) (Found: C, 54.15; H, 8.5. $C_{19}H_{36}N_4O_3Si_2$ requires C, 53.7; H, 8.5%); δ_H(500 MHz; $CDCl_3$; Me_4Si) 0.10 (6 H, s, $SiMe_2$), 0.16 (6 H, s, $SiMe_2$), 0.86 (9 H, s, *t*-Bu), 0.93 (9 H, s, *t*-Bu), 5.51 [2 H, s, N(1)CH_2], 5.59 [2 H, s, N(9)CH_2], 7.97 (1 H, s, H-8) and 8.45 (1 H, s, H-6); δ_C(75 MHz; $CDCl_3$; Me_4Si) −5.3 (2 × $SiMe_2$), 17.9 (C in *t*-Bu), 18.1 (C in *t*-Bu), 25.5 (Me in

t-Bu), 25.6 (Me in *t*-Bu), 66.8 [N(9)CH_2], 73.9 [N(1)CH_2], 123.7 (C-5), 136.4 (C-6), 146.3 (C-8), 154.7 (C-2) and 158.3 (C-4); *m*/*z* (EI) 424 (M^+, 0.3%), 368 (23), 367 (78), 338 (27), 337 (100), 307 (22), 75 (19) and 73 (91).

The less polar fraction yielded the *adduct* **12b** which was purified further by flash chromatography eluting with EtOAc–hexane–Et_3N (30 : 20 : 1) to give the *adduct* **12b** (145 mg, 12%) as a colourless oil (Found: C, 53.5; H, 9.0. $C_{26}H_{54}N_4O_5Si_3$ requires C, 53.2; H, 9.3%); δ_H(500 MHz; $CDCl_3$; Me_4Si) −0.04 (3 H, s, SiMe), −0.01 (3 H, s, SiMe), 0.00 (3 H, s, SiMe), 0.002 (3 H, s, SiMe), 0.04 (3 H, s, SiMe), 0.05 (3 H, s, SiMe), 0.76 (9 H, s, Me in *t*-Bu), 0.79 (18 H, s, 2 × Me in *t*-Bu), 3.65 (1 H, d, *J* 8.5, OH), 5.15 [1 H, d, *J* 9.2, H_A in N(1)CH_2], 5.30 [1 H, d, *J* 9.6, H_A in N(7)CH_2], 5.30 [1 H, d, *J* 9.2, H_B in N(1)CH_2], 5.31 [1 H, d, *J* 9.3, H_A in N(3)CH_2], 5.35 [1 H, d, *J* 9.3, H_B in N(3)CH_2], 5.45 [1 H, d, *J* 9.6, H_B in N(7)CH_2], 6.18 (1 H, d, *J* 8.5, H-6) and 7.18 (1 H, s, H-8); δ_C(75 MHz; $CDCl_3$; Me_4Si) −5.3 (SiMe), −5.2 (2 × SiMe), −5.1 (SiMe), −5.0 (2 × SiMe), 18.3 (C in *t*-Bu), 18.4 (C in *t*-Bu), 18.5 (C in *t*-Bu), 25.7 (Me in *t*-Bu), 25.9 (Me in *t*-Bu), 26.0 (Me in *t*-Bu), 66.4 [N(3)CH_2], 70.2 [N(1)CH_2 and N(7)CH_2], 74.0 (C-6), 106.9 (C-5), 135.4 (C-8), 139.0 (C-4) and 151.4 (C-2); *m*/*z* (EI) 530 (18%), 529 (53), 367 (21), 337 (16), 115 (21), 89 (56), 75 (48), 73 (100), 57 (43) and 56 (15).

1,9-Dihydro-1,9-bis{[2-(trimethylsilyl)ethoxy]methyl}-6-[2-(phenyl)ethyl]-2*H*-purin-2-one 13a

To a solution of 1,9-dihydro-1,9-bis{[2-(trimethylsilyl)ethoxy]-methyl}-2*H*-purin-2-one **11a** (200 mg, 0.47 mmol) in dry THF (5 cm^3) under N_2 at −78 °C was added dropwise a 1 M solution of Grignard reagent (0.94 cm^3, 0.94 mmol, generated from 1-chloro-2-phenylethane and magnesium in dry THF under N_2). The mixture was stirred for 19 h while slowly being allowed to reach ambient temperature. The solution was diluted with saturated aqueous ammonium chloride (5 cm^3), the phases were separated and the aqueous phase extracted with EtOAc (3 × 6 cm^3). The combined organic phases were dried ($MgSO_4$) and evaporated *in vacuo*. The crude product was dissolved in CH_2Cl_2 (15 cm^3) and MnO_2 (2.2 g) was added. The resulting mixture was stirred at ambient temperature for 3 h under N_2 and filtered through a plug of silica gel before the solvent was evaporated *in vacuo*. The product was isolated by flash chromatography eluting with EtOAc–hexane (2 : 1) followed by EtOAc–hexane (3 : 1) and EtOAc to give the *phenylethylpurine* **13a** (90 mg, 47%) as a yellow oil; R_f 0.18 (1 : 3, EtOAc–hexane); δ_H(500 MHz; $CDCl_3$; Me_4Si) −0.04 (18 H, s, 2 × $SiMe_3$), 0.85–0.90 (4 H, m, 2 × $SiCH_2$), 3.12 (2 H, t, *J* 7.8, $PhCH_2$), 3.46 [2 H, t, *J* 7.8, C(6)CH_2], 3.61 (2 H, t, *J* 8.2, OCH_2), 3.72 (2 H, t, *J* 8.2, OCH_2), 5.37 [2 H, s, N(9)CH_2], 5.56 [2 H, s, N(1)CH_2], 7.2–7.3 (5 H, m, Ph) and 7.84 (1 H, s, H-8); δ_C(125 MHz; $CDCl_3$; Me_4Si) −1.4 (2 × $SiMe_3$), 17.8 ($SiCH_2$), 18.3 ($SiCH_2$), 30.9 [C(6)CH_2], 35.2 ($PhCH_2$), 67.4 (OCH_2), 67.5 (OCH_2), 71.5 [N(9)CH_2], 74.5 [N(1)CH_2], 123.1 (C-5), 126.8 (CH in Ph), 128.3 (CH in Ph), 128.7 (CH in Ph), 139.6 (C in Ph), 145.3 (C-8), 155.5 (C-6), 156.6 (C-2) and 158.0 (C-4); *m*/*z* (CI) 501 (M + 1, 1%), 442 (29), 385 (17), 384 (48), 311 (24), 91 (17), 75 (38) and 73 (100); *m*/*z* (electrospray) 501.2712 (M + 1. $C_{25}H_{41}N_4O_3Si_2$ requires 501.2712).

1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-[2-(phenyl)ethyl]-2*H*-purin-2-one 13b

To a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyl-oxy)methyl]-2*H*-purin-2-one **11b** (288 mg, 0.68 mmol) in dry THF (10 cm^3) under N_2 at −78 °C was added dropwise a 1 M solution of Grignard reagent (1.0 cm^3, 1.0 mmol, generated from 1-chloro-2-phenylethane and magnesium in dry THF under N_2). The mixture was stirred for 2 h at −78 °C and 1 h at ambient temperature and diluted with CH_2Cl_2 (10 cm^3). The solution was washed with saturated aqueous ammonium chloride (2 × 10 cm^3) and saturated aqueous sodium hydrogen carbonate (2 × 10 cm^3), dried ($MgSO_4$) and evaporated *in vacuo*. The crude product was dissolved in dry benzene (30 cm^3), DDQ (150 mg, 0.68 mmol) was added and the resulting mixture was stirred at ambient temperature for 4 h under N_2 before the mixture was filtered and the solvent evaporated *in vacuo*. The product was isolated by flash chromatography eluting with EtOAc–hexane (1 : 1) to give the *phenylethylpurine* **13b** (239 mg, 66%) as yellow crystals. Recrystallisation from EtOAc–hexane gave colourless crystals, mp 112–113 °C (Found: C, 61.65; H, 8.4. $C_{27}H_{44}N_4O_3Si_2$ requires C, 61.3; H, 8.4%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.09 (6 H, s, $SiMe_2$), 0.13 (6 H, s, $SiMe_2$), 0.84 (9 H, s, *t*-Bu), 0.85 (9 H, s, *t*-Bu), 3.15 (2 H, m, $PhCH_2$), 3.47 [2 H, m, C(6)CH_2], 5.52 [2 H, s, N(9)CH_2], 5.64 [2 H, s, N(1)CH_2], 7.1–7.3 (5 H, m, Ph) and 7.83 (1 H, s, H-8); δ_C(75 MHz; $CDCl_3$; Me_4Si) −5.3 (SiMe), −5.2 (SiMe), 17.9 (C in *t*-Bu), 18.0 (C in *t*-Bu), 25.5 (Me in *t*-Bu), 25.7 (Me in *t*-Bu), 30.6 [C(6)CH_2], 35.1 ($PhCH_2$), 66.6 [N(9)CH_2], 69.5 [N(1)CH_2], 123.1 (C-5), 126.7 (CH in Ph), 128.3 (CH in Ph), 128.7 (CH in Ph), 139.7 (C in Ph), 144.7 (C-8), 154.8 (C-6), 155.8 (C-2) and 157.2 (C-4); *m*/*z* (EI) 528 (M^+, 1%), 472 (18), 471 (50), 443 (13), 442 (36), 441 (100) and 73 (34).

(*E*)-1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-[2-(phenyl)ethenyl]-2*H*-purin-2-one 13c

To a solution of (*E*)-1-bromo-2-phenylethene (490 mg, 2.13 mmol) in dry Et_2O (4 cm^3) under N_2 at −78 °C was added *t*-BuLi (1.4 M in pentane, 3.1 cm^3, 4.26 mmol). After stirring for 1 h at −78 °C and 1.5 h at −35 °C, $MgBr_2$ [generated from 1,2-dibromoethane (480 mg, 2.56 mmol) and Mg (62 mg, 2.56 mmol)] in dry Et_2O (2 cm^3) was added. The resulting mixture was kept for 30 min at −35 °C and 30 min at ambient temperature before it was dropwise added to 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-2*H*-purin-2-one **11b** (600 mg, 1.41 mmol) in dry THF (10 cm^3) under N_2 at −78 °C. The mixture was allowed to slowly reach ambient temperature. After 20 h the mixture was worked up and oxidised with DDQ (320 mg, 1.41 mmol) as described for compound **13b** above. The product was isolated by flash chromatography eluting with EtOAc–hexane (1 : 1) to give the *phenylethenylpurine* **13c** (500 mg, 67%) as a yellow oil; R_f 0.18 (2 : 3, EtOAc–hexane); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.09 (6 H, s, $SiMe_2$), 0.14 (6 H, s, $SiMe_2$), 0.84 (9 H, s, *t*-Bu), 0.87 (9 H, s, *t*-Bu), 5.55 [2 H, s, N(9)CH_2], 5.86 [2 H, s, N(1)CH_2], 7.35–7.4 (3 H, m, Ph), 7.44 [1 H, d, *J* 16.2, C(6)CH], 7.60 (2 H, m, Ph), 7.93 (1 H, s, H-8) and 8.50 (1 H, *J* 16.2, CH); δ_C(75 MHz; $CDCl_3$; Me_4Si) −4.9 (SiMe), −4.8 (SiMe), 18.3 (2 × C in *t*-Bu), 25.9 (Me in *t*-Bu), 26.0 (Me in *t*-Bu), 67.2 [N(9)CH_2], 70.7 [N(1)CH_2], 116.5 [C(6)CH], 122.1 (C-5), 128.3 (CH in Ph), 129.2 (CH in Ph), 130.8 (CH in Ph), 136.0 (C in Ph), 145.8 (C-8), 147.6 (=CH), 148.7 (C-6), 156.1 (C-2) and 157.9 (C-4); *m*/*z* (EI) 469 (M^+ − *t*-Bu, 41%), 439 (58), 182 (94), 145 (84), 85 (64), 75 (52), 71 (85), 57 (100), 55 (42) and 43 (87); *m*/*z* (electrospray) 527.2890 (M + 1. $C_{27}H_{44}N_4O_3Si_2$ requires 527.2868).

(*Z*)-1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-[2-(phenyl)ethenyl]-2*H*-purin-2-one 13d

A solution of (*E*)-1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyl-oxy)methyl]-6-[2-(phenyl)ethenyl]-2*H*-purin-2-one **13c** (80 mg) in ethanol (10 cm^3) was irradiated with a Hg-lamp for 8 days. Flash chromatography on silica gel eluting with hexane–EtOAc (1 : 1) followed by hexane–EtOAc (1 : 4) gave the *phenylethen-ylpurine* **13d** as a yellow oil (57 mg, 71%) (Found: C, 61.6; H, 6.7. $C_{27}H_{42}N_4O_3Si_2$ requires C, 61.6; H, 6.9%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.02 (6 H, s, $SiMe_2$), 0.10 (6 H, s, $SiMe_2$), 0.79 (9 H, s, *t*-Bu), 0.81 (9 H, s, *t*-Bu), 5.44 [2 H, s, N(9)CH_2], 5.74 [2 H, s, N(1)CH_2], 6.59 [1 H, d, *J* 12.4, C(6)CH], 7.1–7.2 (3 H, m, Ph), 7.14 (1 H, *J* 12.4, CH) and 7.63 (1 H, s, H-8); δ_C(75 MHz; $CDCl_3$; Me_4Si) −5.3 ($SiMe_2$), 17.8 (C in *t*-Bu), 18.0 (C in

t-Bu), 25.4 (Me in *t*-Bu), 25.6 (Me in *t*-Bu), 66.5 [N(9)CH_2], 70.6 [N(1)CH_2], 115.7 [C(6)CH], 121.8 (C-5), 128.4 (CH in Ph), 128.7 (CH in Ph), 135.0 (C in Ph), 139.7 (=CH), 145.5 (C-8), 149.7 (C-6), 155.7 (C-2) and 157.9 (C-4); *m*/*z* (EI) 526 (M^+, 1%), 471 (20), 470 (28), 469 (69), 441 (27), 440 (40), 439 (100), 73 (50) and 57 (16).

1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-[2-(phenyl)ethynyl]-2*H*-purin-2-one 13e

To a solution of EtMgBr (1 M in THF, 1 cm^3, 1 mmol) in dry THF (1 cm^3) was added phenylethyne (122 mg, 1.2 mmol) in dry THF (1 cm^3) under N_2 at −78 °C. The resulting white suspension was allowed to reach ambient temperature and heated to reflux for 2 h before it was cooled to ambient temperature, and added dropwise to a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-2*H*-purin-2-one **11b** (200 mg, 0.47 mmol) in dry THF (4 cm^3) under N_2 at −78 °C. The solution was allowed to slowly reach ambient temperature. After 13 h the reaction mixture was worked up and oxidised with DDQ as described for compound **13b** above. The product was isolated by flash chromatography eluting with EtOAc–hexane (1 : 1) to give the *phenylethynylpurine* **13e** (187 mg, 76%) as pale yellow crystals, mp 158–160 °C (from EtOAc–hexane) (Found: C, 61.4; H, 7.7. $C_{27}H_{40}N_4O_3Si_2$ requires C, 61.8; H, 7.7%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.06 (6 H, s, $SiMe_2$), 0.10 (6 H, s, $SiMe_2$), 0.83 (18 H, s, 2 × *t*-Bu), 5.52 [2 H, s, N(9)CH_2], 5.87 [2 H, s, N(1)CH_2], 7.3–7.6 (5 H, m, Ph) and 7.94 (1 H, s, H-8); δ_C(75 MHz; $CDCl_3$; Me_4Si) −5.3 (2 × SiMe), 17.9 (C in *t*-Bu), 18.0 (C in *t*-Bu), 25.5 (Me in *t*-Bu), 25.6 (Me in *t*-Bu), 66.7 [N(9)CH_2], 71.8 [N(1)CH_2], 78.0 (Pur-*C*≡), 107.0 (≡*C*-Ph), 120.2 (C in Ph), 126.1 (C-5), 128.6 (CH in Ph), 130.8 (CH in Ph), 132.5 (CH in Ph), 133.2 (C-6), 146.7 (C-8), 155.1 (C-2) and 158.2 (C-4); *m*/*z* (EI) 524 (M^+, 1%), 469 (15), 468 (25), 467 (59), 440 (11), 439 (31), 437 (100), 190 (14), 159 (11) and 73 (42).

(*E*)-1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-(4-methyl-5-thexyldimethylsilyloxypent-3-en-1-yl)-2*H*-purin-2-one 13f

To a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-2*H*-purin-2-one **11b** (287 mg, 0.68 mmol) in dry THF (9 cm^3) under N_2 at −78 °C was added dropwise a 0.3 M solution of Grignard reagent [4.0 cm^3, 1.2 mmol, generated from (*E*)-5-bromo-1-thexyldimethylsilyloxy-2-methylpent-2-ene **3b** and magnesium in dry Et_2O under N_2]. The mixture was stirred for 24 h while being allowed to reach ambient temperature and worked up and oxidised with DDQ as described for compound **13b** above. The product was isolated by flash chromatography on silica gel eluting with EtOAc–hexane (1 : 1) to give the *silylated allyl alcohol* **13f** (275 mg, 61%) as a yellow oil (Found: C, 59.3; H, 9.7. $C_{33}H_{64}N_4O_4Si_3$ requires C, 59.6; H, 9.7%); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.01 (6 H, s, $SiMe_2$), 0.02 (6 H, s, $SiMe_2$), 0.06 (6 H, s, $SiMe_2$), 0.76–0.80 (30 H, m, 2 × *t*-Bu and 4 × Me in thexyl), 1.47 (3 H, s, Me), 1.53 (1 H, m, CH in thexyl), 2.49 (2 H, m, CH_2), 3.17 [2 H, t, *J* 7.6, C(6)CH_2], 3.87 (2 H, s, OCH_2), 5.41 (1 H, m, =CH), 5.45 [2 H, s, N(9)CH_2], 5.69 [2 H, s, N(1)CH_2] and 7.78 (1 H, s, H-8); δ_C(75 MHz; $CDCl_3$; Me_4Si) −5.4 (SiMe), −3.6 (SiMe), 13.3 (Me), 17.8 (C in *t*-Bu), 18.3 (C in *t*-Bu), 20.2 (Me in thexyl), 25.0 (C in thexyl), 25.4 (Me in *t*-Bu), 25.5 (Me in *t*-Bu), 27.1 (CH_2), 28.2 [C(6)CH_2], 34.0 (CH in thexyl), 66.5 [N(9)CH_2], 67.5 (OCH_2), 69.4 [N(1)CH_2], 120.7 (=CH), 123.0 (C-5), 137.0 (=C), 144.5 (C-8), 155.3 (C-2), 155.8 (C-6) and 157.0 (C-4); *m*/*z* (EI) 664 (M^+, 1%), 609 (22), 608 (49), 607 (100), 580 (15), 579 (33), 578 (20), 577 (41), 549 (19) and 73 (46).

1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-(4-methylpent-3-en-1-yl)-2*H*-purin-2-one 13g

To a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-2*H*-purin-2-one **11b** (200 mg, 0.47 mmol) in dry THF (5 cm^3) under N_2 at −78 °C was added dropwise a 0.53 M solution of Grignard reagent (2 cm^3, 0.8 mmol, generated from 5-bromo-2-methylpent-2-ene **1b** and magnesium in dry THF under N_2). The mixture was stirred for 18 h while slowly being allowed to reach ambient temperature and worked up and oxidised with DDQ as described for compound **13b** above. The product was isolated by flash chromatography eluting with EtOAc–hexane (1 : 1) to give the *alkene* **13g** (186 mg, 78%) as a yellow oil (Found: C, 59.2; H, 9.0. $C_{25}H_{46}N_4O_3Si_2$ requires C, 59.2; H, 9.15%); δ_H(500 MHz; $CDCl_3$; Me_4Si) 0.06 (6 H, s, $SiMe_2$), 0.11 (6 H, s, $SiMe_2$), 0.83 (18 H, s, 2 × *t*-Bu), 1.52 (3 H, s, Me), 1.62 (3 H, s, Me), 2.49 (2 H, m, CH_2), 3.19 (2 H, t, *J* 7.6, CH_2), 5.15 (1 H, m, =CH), 5.50 [2 H, s, N(9)CH_2], 5.74 [2 H, s, N(1)CH_2] and 7.83 (1 H, s, H-8); δ_C(75 MHz; $CDCl_3$; Me_4Si) −5.4 (2 × $SiMe_2$), 17.5 (Me), 17.8 (C in *t*-Bu), 17.9 (C in *t*-Bu), 25.4 (Me in *t*-Bu), 25.5 (Me in *t*-Bu), 27.6 (CH_2), 28.4 [C(6)CH_2], 66.6 [N(9)CH_2], 69.4 [N(1)CH_2], 121.4 (=CH), 123.1 (C-5), 134.2 (=C), 144.6 (C-8), 155.5 (C-2), 155.9 (C-6) and 156.9 (C-4); *m*/*z* (CI) 503 (M + 1, 28%), 449 (24), 115 (25), 89 (21), 75 (65), 73 (34), 69 (33), 58 (20), 57 (100), 56 (32) and 55 (51).

1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-ethenyl-2*H*-purin-2-one 13h

To a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-2*H*-purin-2-one **11b** (212 mg, 0.5 mmol) in dry THF (5 cm^3) under N_2 at −78 °C was added dropwise a solution of ethenylmagnesium bromide (1 M in THF, 0.75 cm^3, 0.75 mmol). The resulting solution was allowed to slowly reach ambient temperature. After 17 h the reaction mixture was worked up and oxidised with DDQ (113 mg, 0.5 mmol) as described for compound **13b** above. The product was isolated by flash chromatography eluting with EtOAc–hexane (1 : 1) followed by EtOAc–hexane (3 : 2) to give the *ethenylpurine* **13h** (142 mg, 63%) as a yellow oil; R_f 0.13 (1 : 1, EtOAc–hexane); δ_H(300 MHz; $CDCl_3$; Me_4Si) 0.08 (6 H, s, $SiMe_2$), 0.11 (6 H, s, $SiMe_2$), 0.83 (9 H, s, 2 × *t*-Bu), 0.84 (9 H, s, 2 × *t*-Bu), 5.52 [2 H, s, N(9)CH_2], 5.75 [2 H, s, N(1)CH_2], 6.1–6.2 (1 H, m, =CH_2), 6.9–7.1 (2 H, m, CH= and =CH_2) and 7.89 (1 H, s, H-8); δ_C(75 MHz; $CDCl_3$; Me_4Si) −5.3 (2 × $SiMe_2$), 17.9 (2 × C in *t*-Bu), 25.5 (Me in *t*-Bu), 25.6 (Me in *t*-Bu), 66.7 [N(9)CH_2], 70.1 [N(1)CH_2], 121.9 (C-5), 125.4 (=CH_2), 132.8 (CH=), 145.9 (C-8), 148.1 (C-6), 155.4 (C-2) and 158.1 (C-4); *m*/*z* (EI) 450 (M^+, 0.3%), 394 (18), 393 (52), 365 (17), 364 (29), 363 (100), 89 (11), 73 (47) and 28 (49). HRMS: found 450.2458, calc. for $C_{21}H_{38}N_4O_3Si_2$ 450.2482.

(*E*,*E*)-1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-(5-*tert*-butyldimethylsilyloxy-4-methylpenta-1,3-dien-1-yl)-2*H*-purin-2-one 13i

To a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-ethenyl-2*H*-purin-2-one **13h** (148 mg, 0.33 mmol) in dry DMF (1 cm^3) under N_2 were added *N*-ethyldiisopropylamine (0.17 cm^3, 0.99 mmol), palladium(II) acetate (7 mg, 0.033 mmol) and (*E*)-1-*tert*-butyldimethylsilyloxy-3-iodo-2-methylprop-2-ene **5b** (123 mg, 0.39 mmol) in dry DMF (1 cm^3). The resulting mixture was heated at 40 °C for 17 h before saturated aqueous ammonium chloride (15 cm^3) was added and the mixture was extracted with EtOAc (3 × 25 cm^3), dried (Na_2SO_4) and evaporated *in vacuo*. The product was isolated by flash chromatography eluting with EtOAc–hexane (1 : 3), followed by EtOAc–hexane (1 : 2) and finally 2 : 3 to give the *diene* **13i** (102 mg, 49%) as a yellow oil; R_f 0.30 (1 : 1, EtOAc–hexane); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.07 (6 H, s, $SiMe_2$), 0.08 (6 H, s, $SiMe_2$), 0.11 (6 H, s, $SiMe_2$), 0.84 (18 H, s, *t*-Bu), 0.91 (9 H, s, *t*-Bu), 1.90 (3 H, s, Me), 4.17 (2 H, m, CH_2OSi), 5.53 [2 H, s, N(9)CH_2], 5.80 [2 H, s, N(1)CH_2], 6.44 (1 H, d, *J* 11.7, CH=), 6.82 (1 H, d, *J* 15.2, CH=), 7.85 (1 H, s,

H-8) and 8.58 (1 H, dd, J_1 11.7, J_2 15.2, =CH); δ_C(50 MHz; $CDCl_3$; Me_4Si) −5.4 (SiMe), −5.2 (SiMe), 14.8 (Me), 17.9 (C in *t*-Bu), 18.3 (C in *t*-Bu), 25.5 (Me in *t*-Bu), 25.6 (Me in *t*-Bu), 25.8 (Me in *t*-Bu), 66.7 [N(9)CH_2], 67.1 (OCH_2), 70.0 [N(1)CH_2], 118.5 (CH=), 121.3 (C-5), 123.3 (CH=), 144.0 (=CH), 144.6 (C-8), 148.6 (=C), 148.9 (C-6), 155.5 (C-2) and 157.2 (C-4); *m*/*z* (EI) 635 (M^+, 0.4%), 578 (31), 577 (62), 548 (37), 547 (70) and 89 (36); *m*/*z* (electrospray) 635.3809 (M + 1. $C_{31}H_{58}N_4O_4Si_3$ requires 635.3839).

(*E*)-1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-(5-*tert*-butyldimethylsilyloxy-4-methylpent-3-en-1-yn-1-yl)-2*H*-purin-2-one 13j

To a solution of EtMgBr (1 M in THF, 1 cm^3, 1 mmol) in dry THF (1 cm^3) was added (*E*)-1-(*tert*-butyldimethylsilyloxy)-2-methylpent-2-en-4-yne **9** (252 mg, 1.2 mmol) in dry THF (1 cm^3) under N_2 at −78 °C. The resulting white suspension was allowed to reach ambient temperature, heated to reflux for 2 h and cooled to ambient temperature before the Grignard reagent was added dropwise to a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-2*H*-purin-2-one **11b** (200 mg, 0.47 mmol) in dry THF (4 cm^3) under N_2 at −78 °C. The solution was allowed to slowly reach ambient temperature and after 13 h it was worked up and oxidised with DDQ as described for compound **13b** above. The product was isolated by flash chromatography eluting with EtOAc–hexane (3 : 2) followed by EtOAc–hexane (1 : 1) to give the *enyne* **13j** (245 mg, 82%) as pale yellow crystals, mp 114–117 °C (Found: C, 59.2; H, 8.8. $C_{31}H_{56}N_4O_4Si_3$ requires C, 58.8; H, 8.9%); δ_H(300 MHz; $CDCl_3$; Me_4Si) −0.01 (6 H, s, $SiMe_2$), 0.01 (6 H, s, $SiMe_2$), 0.05 (6 H, s, $SiMe_2$), 0.76 (9 H, s, *t*-Bu), 0.77 (9 H, s, *t*-Bu), 0.83 (9 H, s, *t*-Bu), 1.94 (3 H, s, Me), 4.12 (2 H, s, CH_2OSi), 5.46 [2 H, s, N(9)CH_2], 5.76 [2 H, s, N(1)CH_2], 5.97 (1 H, s, =CH) and 7.84 (1 H, s, H-8); δ_C(50 MHz; $CDCl_3$; Me_4Si) −5.7 (SiMe), −5.43 (SiMe), −5.41 (SiMe), 16.9 (Me), 17.7 (C in *t*-Bu), 17.9 (C in *t*-Bu), 18.1 (C in *t*-Bu), 25.4 (Me in *t*-Bu), 25.5 (Me in *t*-Bu), 25.6 (Me in *t*-Bu), 66.1 (CH_2OSi), 66.5 [N(9)CH_2], 71.6 [N(1)CH_2], 81.7 (C≡), 101.6 (=CH), 106.2 (C≡), 125.7 (C-5), 133.8 (C-6), 146.1 (C-8), 155.1 (C-2), 157.9 (C-4) and 159.0 (=C); *m*/*z* (EI) 632 (M^+, 0.4%), 577 (25), 576 (48), 575 (100), 547 (11), 546 (19), 545 (39), 228 (19), 75 (16) and 73 (46).

1,9-Dihydro-6-[2-(phenyl)ethyl]-2*H*-purin-2-one 14a

To a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-[2-(phenyl)ethyl]-2*H*-purin-2-one **13b** (59 mg, 0.11 mmol) in dry acetonitrile (4 cm^3) was added a 1 M solution of tetramethylammonium fluoride in dry acetonitrile (0.45 cm^3). The solution was stirred under N_2 for 24 h at ambient temperature before the solution was evaporated *in vacuo*. The product was isolated by flash chromatography on silica gel eluting with $CHCl_3$–MeOH–NH_3 (20 : 6 : 1) to give the *phenylethylpurine* **14a** (81%, 22 mg) as yellow crystals, mp >300 °C (decomp.) (Found: C, 64.5; H, 5.1. $C_{13}H_{12}N_4O$ requires C, 65.0; H, 5.0%); δ_H(500 MHz; DMSO-d_6; Me_4Si) 3.09 (4 H, m, 2 × CH_2), 7.1–7.3 (5 H, m, Ph), 8.06 (1 H, s, H-8) and 12.1 (2 H, br s, 2 × NH); δ_C(125 MHz; DMSO-d_6; Me_4Si) 30.6 (CH_2), 32.8 (CH_2), 122.1 (C-5), 125.8 (CH in Ph), 127.9 (CH in Ph), 128.0 (CH in Ph), 140.1 (C in Ph), 144.3 (C-8), 152.8 (C-6), 156.5 (C-2) and 159.1 (C-4); *m*/*z* (EI) 240 (M^+, 100%), 239 (57), 163 (34), 150 (11), 91 (47) and 65 (9).

(*E*)-1,9-Dihydro-6-[2-(phenyl)ethenyl]-2*H*-purin-2-one 14b

To a solution of (*E*)-1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-[2-(phenyl)ethenyl]-2*H*-purin-2-one **13c** (126 mg, 0.26 mmol) in dry acetonitrile (4 cm^3) was added a 1 M solution of tetramethylammonium fluoride in dry acetonitrile (1.0 cm^3). The solution was stirred under N_2 for 15 h at ambient temperature before the solution was evaporated *in vacuo*. The product was isolated by flash chromatography on silica gel eluting with $CHCl_3$–MeOH–NH_3 (50 : 10 : 1) followed by $CHCl_3$–MeOH–NH_3 (20 : 6 : 1), $CHCl_3$–MeOH–NH_3 (10 : 4 : 1) and $CHCl_3$–MeOH–NH_3 (5 : 3 : 1) to give the *ethenylpurine* **14b** (55 mg, 90%) as yellow crystals, mp >300 °C (darkened above 150 °C.); R_f 0.19 (10 : 4 : 1, $CHCl_3$–MeOH–NH_3); δ_H(200 MHz; DMSO-d_6; Me_4Si) 7.29 (1 H, d, *J* 16.4, CH=), 7.4–7.5 (3 H, m, CH in Ph), 7.6–7.7 (2 H, m, CH in Ph), 8.20 (1 H, s, H-8), 8.37 (1 H, d, *J* 16.4, =CH) and 9.4 (2 H, br s, 2 × NH); δ_C(125 MHz; DMSO-d_6; Me_4Si) 118.6 [C(6)CH], 120.8 (C-5), 127.1 (CH in Ph), 128.6 (CH in Ph), 129.4 (CH in Ph), 135.2 (C in Ph), 140.8 (=CH), 144.9 (C-8), 146.3 (C-6), 156.7 (C-2) and 159.1 (C-4); *m*/*z* (electrospray) 239.0936 (M + 1. $C_{13}H_{10}N_4O$ requires 239.0927).

(*Z*)-1,9-Dihydro-6-[2-(phenyl)ethenyl]-2*H*-purin-2-one 14c

To a solution of (*Z*)-1,9-dihydro-1,9-di[(*tert*-butyldimethylsilyloxy)methyl]-6-[2-(phenyl)ethenyl]-2*H*-purin-2-one **13d** (57 mg, 0.11 mmol) in dry acetonitrile (3 cm^3) under N_2 was added a 1 M solution of tetramethylammonium fluoride in dry acetonitrile (0.43 cm^3). The solution was stirred for 19 h at ambient temperature before the solution was evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel eluting with $CHCl_3$–MeOH–NH_3 (50 : 10 : 1) followed by $CHCl_3$–MeOH–NH_3 (20 : 6 : 1) to give a 2 : 1 mixture of the *styrylpurines* **14b** and **14c** (20 mg, 78% total yield) as yellow crystals. The ^{1}H NMR resonances belonging to the *Z*-isomer **14c** are given; δ_H(300 MHz; DMSO-d_6; Me_4Si) 6.60 (1 H, br d, CH=), 7.05 (1 H, d, *J* 12.1, =CH), 7.2–7.3 (m, 5 H, CH in Ph) and 7.99 (1 H, s, H-8).

1,9-Dihydro-6-[2-(phenyl)ethynyl]-2*H*-purin-2-one 14d

To a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-[2-(phenyl)ethynyl]-2*H*-purin-2-one **13e** (81 mg, 0.154 mmol) in dry ethanol (5 cm^3) under N_2 was added a 1 M solution of tetramethylammonium fluoride in dry ethanol (0.62 cm^3). The solution was stirred for 23 h at ambient temperature before AcOH (conc.) was added. After an additional 5 h the solution was evaporated *in vacuo*. The product was isolated by flash chromatography on silica gel eluting with $CHCl_3$–MeOH–NH_3 (20 : 6 : 1) followed by $CHCl_3$–MeOH–NH_3 (10 : 4 : 1) to give the *alkyne* **14d** (25 mg, 69%) as yellow crystals, mp >300 °C (darkened above *ca*. 200 °C); R_f 0.14 (10 : 4 : 1, $CHCl_3$–MeOH–NH_3) (Found: C, 65.55; H, 3.5. $C_{13}H_8N_4O$ requires C, 66.1; H, 3.4%); δ_H(300 MHz; DMSO-d_6; Me_4Si) 7.4–7.7 (5 H, m, CH in Ph), 8.31 (1 H, s, H-8) and 12.5 (2 H, br s, 2 × NH); δ_C(75 MHz; DMSO-d_6; 60 °C; Me_4Si) 82.2 (C≡), 97.5 (C≡), 120.2 (C in Ph), 125.8 (C-5), 128.7 (CH in Ph), 130.1 (CH in Ph), 131.8 (CH in Ph), 135.0 (C-6), 145.4 (C-8), 158.2 (C-2) and 158.7 (C-4); *m*/*z* (electrospray) 237.0775 (M + 1. $C_{13}H_8N_4O$ requires 237.0776).

(*E*)-1,9-Dihydro-6-(5-hydroxy-4-methylpent-3-en-1-yl)-2*H*-purin-2-one 14e

To a solution of (*E*)-1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-(4-methyl-5-thexyldimethylsilyloxypent-3-en-1-yl)-2*H*-purin-2-one **13f** (100 mg, 0.15 mmol) was added tetramethylammonium fluoride (1.2 mmol) in dry acetonitrile (4 cm^3). The solution was stirred under N_2 for 40 h at ambient temperature before the solution was evaporated *in vacuo*. The product was isolated by flash chromatography on silica gel eluting with $CHCl_3$–MeOH–NH_3 (10 : 4 : 1) to give the *allylic alcohol* **14e** (28, mg, 80%) as yellow crystals, mp >200 °C (decomp.); R_f 0.18 (10 : 4 : 1, $CHCl_3$–MeOH–NH_3); δ_H(300 MHz; DMSO-d_6; Me_4Si) 1.49 (3 H, s, Me), 2.47 (2 H, q, *J* 7.3, CH_2), 2.84 [2 H, t, *J* 7.3, C(6)CH_2], 3.72 [2 H, s, CH_2OH], 4.68 (1 H, br s, OH), 5.32 (1 H, m, =CH), 8.05 (1 H, s, H-8); δ_C(75 MHz; DMSO-d_6; Me_4Si) 13.5 (Me), 25.8 (CH_2), 29.0 [C(6)CH_2], 66.1 (CH_2OH), 121.1 (=CH), 121.9 (C-5), 137.2

(=C), 144.6 (C-8), 153.1 (C-6), 156.6 (C-2) and 159.7 (C-4); *m*/*z* (EI) 234 (M^+, 1%), 121 (76), 107 (29), 95 (26), 93 (66), 80 (32), 79 (79), 67 (64) and 66 (63). *m*/*z* (electrospray) 235.1190 (M + 1. $C_{11}H_{15}N_4O_2$ requires 235.1190).

1,9-Dihydro-6-(4-methylpent-3-en-1-yl)-2*H*-purin-2-one 14f

To a solution of 1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-(4-methylpent-3-en-1-yl)-2*H*-purin-2-one **13g** (80 mg, 0.16 mmol) in dry acetonitrile (4 cm^3) was added a 1 M solution of tetramethylammonium fluoride in dry acetonitrile (0.63 cm^3). The solution was stirred under N_2 for 24 h at ambient temperature before the solution was evaporated *in vacuo*. The product was isolated by flash chromatography on silica gel eluting with $CHCl_3$–MeOH–NH_3 (50 : 10 : 1) to give the *alkene* **14f** (27 mg, 79%) as yellow crystals, mp >250 °C (decomp.); R_f 0.17 (50 : 10 : 1, $CHCl_3$–MeOH–NH_3) (Found: C, 60.3; H, 6.3. $C_{11}H_{14}N_4O$ requires C, 60.5; H, 6.5%); δ_H(500 MHz; DMSO-d_6; Me_4Si) 1.50 (3 H, s, Me), 1.60 (3 H, s, Me), 2.43 (2 H, m, CH_2), 2.81 [2 H, t, *J* 7.5, C(6)CH_2], 5.10 (1 H, m, =CH), 8.03 (1 H, s, H-8) and 12.1 (2 H, br s, 2 × NH); δ_C(75 MHz; DMSO-d_6; Me_4Si) 17.5 (Me), 25.4 (Me), 26.3 (CH_2), 29.1 [C(6)CH_2], 121.9 (C-5), 122.3 (=CH), 132.6 (=C), 144.5 (C-8), 153.1 (C-6), 156.6 (C-2) and 159.6 (C-4); *m*/*z* (EI) 218 (M^+, 34%), 203 (31), 175 (14), 163 (8), 151 (9), 150 (100), 135 (6), 122 (10) and 69 (11).

(*E*,*E*)-1,9-Dihydro-6-(5-hydroxy-4-methylpenta-1,3-dien-1-yl)-2*H*-purin-2-one 14g

To a solution of (*E*,*E*)-1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-(5-*tert*-butyldimethylsilyloxy-4-methylpenta-1,3-dien-1-yl)-2*H*-purin-2-one **13i** in dry acetonitrile (3 cm^3) was added a 1 M solution of tetramethylammonium fluoride in dry acetonitrile (0.96 cm^3). The solution was stirred under N_2 for 22 h at ambient temperature before the solution was evaporated *in vacuo*. The product was isolated by flash chromatography on silica gel eluting with $CHCl_3$–MeOH–NH_3 (50 : 10 : 1) followed by $CHCl_3$–MeOH–NH_3 (20 : 6 : 1) and $CHCl_3$–MeOH–NH_3 (10 : 4 : 1) to give the *diene* **14g** (25 mg, 68%) as yellow crystals, mp >300 °C (darkened above *ca.* 140 °C); R_f 0.28 (10 : 4 : 1, $CHCl_3$–MeOH–NH_3); δ_H(300 MHz; DMSO-d_6; Me_4Si) 1.86 (3 H, s, Me), 4.00 (2 H, s, CH_2OH), 5.09 (1 H, br s, OH), 6.35 (1 H, d, *J* 11.2, CH=), 6.58 (1 H, d, *J* 15.5, CH=), 8.11 (1 H, s, H-8), 8.35 (1 H, dd, *J* 15.5, *J* 11.2, =CH) and 10.0 (2 H, br s, 2 × NH); δ_C(75 MHz; DMSO-d_6; Me_4Si) 14.6 (Me), 65.4 (CH_2OH), 118.5 (HC=), 120.4 (C-5), 122.0 (=CH), 125.6 (=C), 139.0 (=CH), 145.3 (C-8), 149.8 (HC=), 156.5 (C-2) and 160.0 (C-4); *m*/*z* (electrospray) 233.1049 (M + 1. $C_{11}H_{12}N_4O_2$ requires 233.1033).

(*E*)-1,9-Dihydro-6-(5-hydroxy-4-methylpent-3-en-1-yn-1-yl)-2*H*-purin-2-one 14h

To a solution of (*E*)-1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-(5-*tert*-butyldimethylsilyloxy-4-methylpent-3-en-1-yn-1-yl)-2*H*-purin-2-one **13j** (126 mg, 0.20 mmol) in dry acetonitrile (4 cm^3) was added a 1 M solution of tetramethylammonium fluoride in dry acetonitrile (1.2 cm^3). The solution was stirred under N_2 for 24 h at ambient temperature before the solution was evaporated *in vacuo*. The product was subjected to flash chromatography twice on silica gel eluting with $CHCl_3$–MeOH–NH_3 (6 : 3 : 1) the first time and $CHCl_3$–MeOH–NH_3 (10 : 4 : 1) the second time to give the *enyne* **14h** (35 mg, 76%) as yellow crystals, mp >300 °C (darkened above 150 °C.); R_f 0.16 (10 : 4 : 1, $CHCl_3$–MeOH–NH_3); δ_H(300 MHz; DMSO-d_6; Me_4Si) 1.97 (3 H, s, Me), 4.03 (2 H, d, *J* 5.4, CH_2), 5.24 (1 H, t, *J* 5.4, OH), 5.89 (1 H, s, =CH), 8.20 (1 H, s, H-8) and 12.3 (2 H, br s, 2 × NH); δ_C(75 MHz; DMSO-d_6; Me_4Si) 16.9 (Me), 64.6 (CH_2), 84.6 (C≡), 98.5 (C≡), 100.6 (=CH), 125.9 (C-5), 134.1 (C-6), 145.8 (C-8), 158.1 (C-2), 159.0 (C-4) and 160.1 (=C); *m*/*z* (electrospray) 231.0877 (M + 1. $C_{11}H_{10}N_4O_2$ requires 231.0882).

(1α,2α,3β,4β)-1,3-Bis{1,9-dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-2-oxo-2*H*-purin-6-yl}-2,4-diphenylcyclobutane 15

(*E*)-1,9-Dihydro-1,9-bis[(*tert*-butyldimethylsilyloxy)methyl]-6-[2-(phenyl)ethenyl]-2*H*-purin-2-one **13c** (95 mg, 0.18 mmol) was stored in a round-bottomed flask without protection from daylight for 14 days. Flash chromatography on silica gel, eluting with hexane–EtOAc (3 : 2) followed by hexane–EtOAc (1 : 1), gave the *cyclobutane* **15** as a yellow oil (46 mg, 48%). Recrystallisation from EtOAc–hexane gave colourless crystals, mp 241–244 °C (Found: C, 61.8; H, 7.9. $C_{54}H_{84}N_8O_6Si_4$ requires C, 61.55; H, 8.0%); δ_H(200 MHz; $CDCl_3$; Me_4Si) −0.05 (6 H, s, $SiMe_2$), −0.01 (6 H, s, $SiMe_2$), 0.07 (6 H, s, $SiMe_2$), 0.23 (6 H, s, $SiMe_2$), 0.79 (18 H, s, Me in *t*-Bu), 0.86 (18 H, s, Me in *t*-Bu), 5.29 [1 H, d, *J* 9.5, H_A in N(1)CH_2], 5.39 [1 H, d, *J* 9.7, H_A in N(9)CH_2], 5.52 [1 H, d, *J* 9.7, H_B in N(9)CH_2], 5.56 [1 H, dd, J_1 17.0, J_2 7.7, C(6)CH in cyclobutane], 6.12 [1 H, dd, J_1 17.0, J_2 7.7, PhCH in cyclobutane], 5.52 [1 H, d, *J* 9.7, H_B in N(1)CH_2], 7.0–7.1 (6 H, m, CH in Ph), 7.2–7.3 (4 H, m, CH in Ph), 7.87 (H-8) and 12.5 (1 H, br s, NH); δ_C(75 MHz; $CDCl_3$; Me_4Si) −5.6 (SiMe), −5.3 (SiMe), −5.1 (SiMe), −4.9 (SiMe), 17.9 (C in *t*-Bu), 25.6 (Me in *t*-Bu), 44.2 [C(6)CH in cyclobutane], 44.7 (PhCH in cyclobutane), 66.6 [N(9)CH_2], 69.8 [N(1)CH_2], 124.3 (C-5), 127.6 (CH in Ph), 128.5 (CH in Ph), 138.0 (C in Ph), 144.7 (C-8), 152.5 (C-6), 155.6 (C-2) and 157.8 (C-4); *m*/*z* (electrospray) 1053.5688 (M + 1. $C_{54}H_{84}N_8O_6Si_4$ requires 1053.5664).

Procedure for determination of cytokinin activity

The cytokinin activities of the compounds were determined using the bioassay described by Letham,[26] and in ref. 4.

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