SYNTHESIS OF (*E*)-6-ALKENYLPURINES *via* Pd-CATALYZED STANNATION/PROTODESTANNATION TANDEM PROCESS OF ALKYNYLPURINES

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A methodology for the synthesis of (*E*)-6-alkenylpurines, starting from 6-iodopurines, based on a Pd-catalyzed stannation/protodestannation protocol, is described. The alkynylation reactions were catalyzed by $Pd(OAc)_2/PPh_3$ in acetonitrile. The Pd-catalyzed stannation itself provided a mixture of *Z* regioisomers but following protodestannation using TFA induces *Z* to *E* isomerization giving (*E*)-6-alkenylpurines. The reactivity of other 2- and 8-alkynyl purines has also been studied.

Keywords: Alkynes; Hydrostannation; Isomerization; Purine; Protodestannation.

Biological activities of 2-, 6- and 8-C–C-substituted purines have been previously well described. Among the other, purines bearing alkenyl and alkynyl moieties are associated with a wide variety of applications. For instance, 6-alkynylpurines posses cytokinin[1], cytotoxic[2] and inhibitory activity against mycobacterium tuberculosis[3]. Compared to 6-alkynylpurine, 2-alkynylpurines constitute a large group of adenosine A-receptor agonists[4], antagonist[5] and P2Y1 receptor antagonist[6] together with CDK inhibitor activity[7]. In sharp contrast, alkynyl species introduced to the 8-position of purines are mainly used as luminescent labels in biomolecules[8]. Moreover, some of them have been evaluated as antagonist of A3 adenosine receptor[9], agonists of A2A adenosine receptor[4d] and compounds with cytotoxicity[10]. Also various alkenylpurines were reported as compounds with significant biological activity, e.g. antimycobacterial[3], cytotoxic[2a], and cytokinin activity[1a,11] and inhibition of 15-lipoxygenase[12], and inhibitors of adenosine receptors[13]. Recently, 6-(2-dialkylamino)vinylpurine ribonucleosides were evaluated as strong cytostatic and HCV antiviral agents[14a]. In addition,

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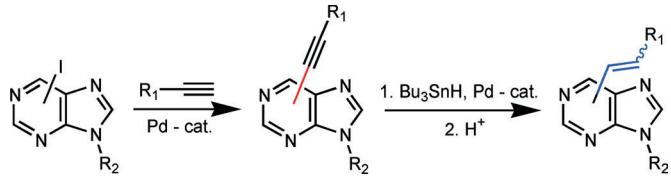
some alkenylpurines have been proposed as DNA base-pairs[2b,15] and novel cross-linking agents[16].

Although the biological importance of C–C-substituted purines has been established, the number of efficient methodologies available for introduction of various C substituents including the alkenyl moiety are limited and very often lack general applicability. Nowadays, alkynylpurines were exclusively prepared by Sonogashira cross-coupling of halopurines and alkynes in the presence of Pd^0/Cu(I) catalyst[8a,15,17]. On contrary, diverse procedures are available for introduction of alkenes. Thus, alkenylpurines are mostly prepared by transition metals-catalyzed cross-coupling reactions of *O*-tosylpurines or halopurines with alkenylstannanes[18], alkenylzinc[19] or alkenylboron reagents[20]. Different approaches, e.g. partial hydrogenation of 2-, 6- or 8-alkynylpurines[1a,4e,21], Heck reaction of iodopurines[22], Heck reaction of vinylpurines[1a,23], conjugated addition of O-, N-, S-nucleophiles to 6-ethynylpurines[14b] and other[24] were published. Despite of well established methodologies for introduction of various substituents into the 6-position of the purine ring a number of these methods have some drawbacks such as difficult preparations of polyfunctional alkenylboronates or organostannanes reagents and occurrence of side reactions[25]. Therefore we were looking for an alternative approach mainly to 6-alkenylpurine derivatives. Since alkynylpurines are easily accessible *via* the Sonogashira reaction, which is in addition very tolerant to functional groups, the approach using partial hydrogenation of alkynylpurines seems to be especially useful. However, while partial hydrogenation of 2- and 8-alkynylpurines to the corresponding (*Z*)-alkenes has been documented[4e,21], the reduction of 6-alkynylpurines has been accomplished only on 9-unsubstituted (9*H*) purine derivatives. On the other hand, 9-substituted 6-alkynylpurines have been reported to be always overhydrogenated to 6-alkylpurines using the Lindlar catalyst[1a]. Therefore we decided to explore a novel approach relying on Pd-catalyzed Sonogashira reaction and one-pot Pd-catalyzed hydrostannation/Sn–C bond protodestannation (Scheme 1). Our intended approach to the synthesis of alkenylpurines benefits from a wide functional group tolerance and it has not been reported to our knowledge, yet.

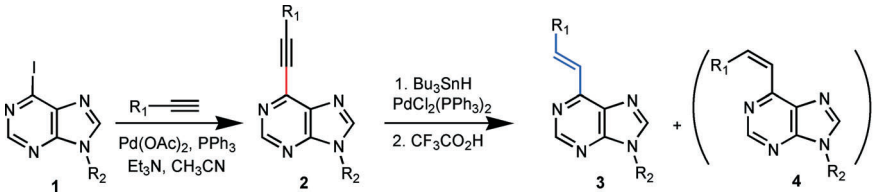


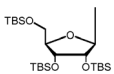
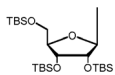
SCHEME 1

The transformation of 9-substituted 6-iodo-9*H*-purine in the reaction sequence above was attempted first. The results of the Pd-catalyzed alkynylation–Pd-catalyzed stannation/protodestannation tandem process of 9-benzyl-6-iodo-9*H*-purine (**1**) are summarized in Table I. The first step, Pd-catalyzed alkynylation, was accomplished in dry MeCN [26] using $Pd(OAc)_2$ (2 mole %)/PPh_3 (4 mole %) at 80 °C. Phenylacetylene, 5-cyanopentyne and propargyl alcohol reacted smoothly with **1a** under these conditions even in the absence of Cu_2I_2 giving after 1 h the desired product in high yield. The presence of Cu_2I_2 led in these cases to subsequent decompo-

TABLE I

The synthesis of (*E*)-6-alkenyl-9-substituted purines via Pd-catalyzed alkynylation[a] and subsequent Pd-catalyzed stannation/protodestannation[b] tandem process of 9-substituted 6-iodo-9*H*-purines



Entry	R_1	R_2	Yield, % of **2**[a]	Yield, % of **3**[b]	Yield, % of **4**[b]
1	Ph	**1a**, $PhCH_2$	**2a**, 92	**3a**, 82	**4a**, 0
2	$CH_3(CH_2)_4$	**1a**, $PhCH_2$	**2b**, 88[c]	**3b**, 85	**4b**, 0
3	CH_2OH	**1a**, $PhCH_2$	**2c**, 88	**3c**, 60	**4c**, 0
4	$(CH_2)_3CN$	**1a**, $PhCH_2$	**2d**, 94	**3d**, 71 (30[d])	**4d**, 0 (41[d])
5	Ph	**1b**, 	**2e**, 60	**3e**, 50 (55[d,e])	**4e**, 0 (20[d,e])
6	CH_2OH	**1b**, 	**2f**, 62	**3f**, 57	**4f**, 0

[a] Reaction conditions: iodopurines **1** (1.0 equiv.), Et_3N (3.0 equiv.), alkynes (2.0 equiv.), $Pd(OAc)_2$ (2 mole %), PPh_3 (4 mole %), MeCN were stirred at 80 °C for 1 h. [b] Reaction conditions: alkynes **2** (1.0 equiv.), Bu_3SnH (1.5 equiv.), $PdCl_2(PPh_3)_2$ (5 mole %), THF were stirred at 23 °C for 2 h, followed by addition of TFA (8.0 equiv.) and stirred at 23 °C for 1 h. [c] Addition of mole % of Cu_2I_2 is required. [d] AcOH–MeOH 2:5 was used instead of TFA. [e] Inseparable mixture of isomers, the yield was obtained by ^1H NMR.

sition of the initially formed alkynylpurines, which lowered the yield and made the isolation of the products more difficult. Also coupling of nucleoside **1b** with phenylethyne and propargyl alcohol proceeded smoothly without Cu_2I_2, however, the product was accompanied by a complex mixture of chomatographically immobile by-products. On contrary, the completion of the reaction of hept-1-yne with **1a** required a prolonged reaction time (3 h) along with 4 mole % of Cu_2I_2. The prepared alkynylpurines **2a–2c** were submitted to the Pd-catalyzed hydrostannation/protodestannation procedure. The preliminary experiments with $PdCl_2(PPh_3)_2$, cheap, readily available and most widely being used catalyst in Pd-catalyzed hydrostannation, turned out to be a good choice and no further exploration had to be taken. Thus, hydrostannation of **2** using 1.5 equivalents of Bu_3SnH and 5 mole % of $PdCl_2(PPh_3)_2$ was accomplished within 2 h at room temperature. The following protodestannation with trifluoroacetic acid (TFA) at room temperature afforded exclusively (*E*)-alkenes **3** in isolated yields ranging from 50 to 85% (Table I). From other commonly available acids also a solution of acetic acid in methanol (2:5) has been tested but a mixture of (*E*)- and (*Z*)-alkenes was obtained in the case of alkynes **2d**, **2e** (Table I, entries 4, 5). In the case of hydrostannation of **2c** isolation of the intermediate stannane was accomplished. The results clearly indicate that hydrostannation of **2c** using Bu_3SnH (1.5 equiv.) and $PdCl_2(PPh_3)_2$ (5 mole %) followed by flash chromatography (silica gel) proceeded in *cis* manner giving stananes **5** and **6** [27] along with an inseparable mixture of (*E*)- and (*Z*)-alkenes **3c**, **4c** in 22% isolated yield (50:50 *E*/*Z*) (Chart 1). The *E* stereochemistry of isolated stannylalkenes **5** and **6** was determined by examination of ^{117}Sn-H coupling constants (58.00 and 59.00 Hz). The reported values for *cis* $J^{117}_{\text{Sn-H}}$ are 50–80 Hz, while for *trans* $J^{117}_{\text{Sn-H}}$ are 95–155 Hz [28]. On contrary, hydrostannation of **2b** led to a mixture of (*Z*)- and (*E*)-stannanes **7**, **8** ($J^{117}_{\text{Sn-H}}$ = 61.8 and 101.7 Hz) accompanied by alkenes **3b** and **4b** in overall 24% isolated yield. Isolation of alkenes **3b**, **4b**, **3c**, **4c** after Pd-catalyzed stannation was somewhat surprising. However, ^{1}H NMR (using acid-free $CDCl_3$) examination of the crude hydrostannation reaction mixture of **2d** using 1.5 equivalents Bu_3SnH and 5 mole % $PdCl_2(Ph_3)_2$ showed quantitative consumption of the starting alkyne **2d** (2 h, 23 °C) and no presence of alkenes **3d** and **4d**. Also further addition of Bu_3SnH to the reaction mixture did not evoke the formation of alkenes **3d** and **4d**. In principle, besides acid catalysis the *cis–trans* isomerization of alkenes can be caused by variety of factors, including free radicals or presence of transition metal complexes. However, based on previous experiments, we believe that the acidity of silica gel is responsible for

C–Sn protodestannation, and in some cases for *cis*- to *trans*-alkene isomerization. Similar *trans–cis* isomerization of 8-alkenylpurines in contact with silica gel has been reported[23]. Moreover, this has been supported by isomerization of **4d**, which gives **3d** quantitatively upon heating to 50 °C with TFA in THF for 24 h. Despite a complexity of the reaction mixture after Pd-catalyzed stannation, the following protodestannation step allowed the preparation of pure (≥98% *E*) (*E*)-6-alkenylpurines **3a–3f** in good yields (Table I). Therefore we extended the Pd-catalyzed stannation/protodestannation methodology to other alkynylpurines.

Similarly to 6-alkynylpurines **2**, 2-alkynyl-6-methoxypurines **10**, as example of 2,6-disubstituted purines, were prepared *via* Pd-catalyzed alkynylation in high yields (Table II). Under the previous conditions in the absence of Cu_2I_2 the 2-iodo-9-isopropyl-6-methoxy-9*H*-purine (**9**) was smoothly alkynylated only by phenylethyne. In case of propargyl alcohol and hept-1-yne addition of 4 mole % of Cu_2I_2 was necessary to achieve quantitative conversion of **9** to **10b**, **10c** (Table II, entries 2, 3). Alkynes **10a–10c** were then subjected to stannation/protodestannation protocol. While 2-(2-phenylethenyl)-9-isopropyl-6-methoxy-9*H*-purine (**10a**) formed a 20:80 mixture of *E*/*Z* alkenes in 86% overall isolated yield (Table II, entry 1),

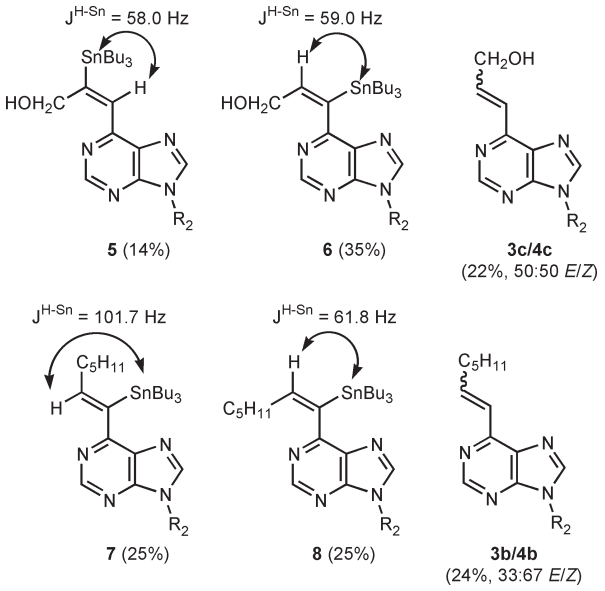
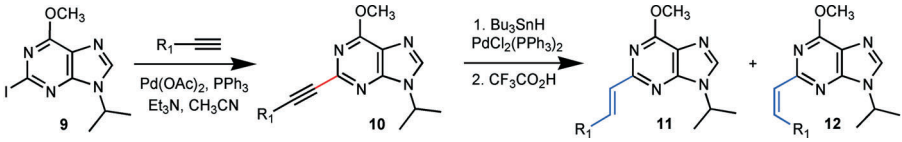


CHART 1
The structure of products isolated after the Pd-catalyzed stannation of **2b** and **2c**

alkynes **10b**, **10c** afforded *cis*-alkenes **12b** and **12c** exclusively (Table II, entries 2, 3). In the case of *cis*-alkenes **12a–12c** no isomerization was observed even after prolonged heating with TFA (24 h, 50 °C). Only in the case of **12c** extensive decomposition was observed. Evidently, the ability of the double bond to isomerize under acidic conditions is suppressed in 2-alkenylpurines.

In order to fully explore the chemo-diversity of the purine moiety 8-alkynylpurines have been prepared and tested under the stannation/protodestannation protocol (Table III). Compared to 2- and 6-iodopurines **1a**, **1b**, **9** the first step, alkynylation, gave barely acceptable yield of the corresponding 8-alkynylpurines from a synthetic point of view. Only phenylethyne (1.1 equiv.) reacted smoothly with 6-chloro-8-iodo-9-isopropyl-9*H*-purine (**13**) in the presence of $Pd(OAc)_2/PPh_3$ and Et_3N without Cu_2I_2 giving 8-alkynylpurine **14a** in 73% isolated yield. However, the isolated yields of **14b**, **14c** were lowered due to reductive deiodination, which led to the formation of 6-chloro-9-isopropyl-9*H*-purine in 30 and 15% yield, respectively (Table III, entries 2, 3). With **14a–14c** in our hands the Pd-catalyzed stannation/protodestannation process has been tested. The results are summarized in Table III. Phenylethyne **14a** afforded a mix-

TABLE II
Pd-catalyzed alkynylation[a] and subsequent stannation/protodestannation[b] of 2-iodo-9-isopropyl-6-methoxy-9*H*-purine **9**

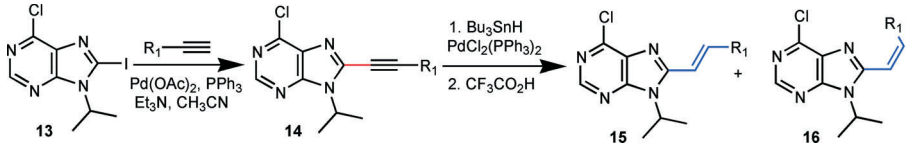


Entry	R_1	Yield, % of **10**[a]	Yield, % of **11**[b]	Yield, % of **12**[b]
1	Ph	**10a**, 96	**11a** + **12a** (20:80), 86	
2	$CH_3(CH_2)_4$	**10b**, 90[c]	0	**12b**, 80
3	CH_2OH	**10c**, 82[c]	0	**12c**, 84

[a] Reaction conditions: **9** (1.0 equiv.), Et_3N (3.0 equiv.), alkynes (2.0 equiv.), $Pd(OAc)_2$ (2 mole %), PPh_3 (4 mole %), MeCN were stirred at 80 °C for 1 h. [b] Reaction conditions: alkynes **10** (1.0 equiv.), Bu_3SnH (1.5 equiv.), $PdCl_2(PPh_3)_2$ (5 mole %), THF were stirred at 23 °C for 2 h, followed by addition of TFA (8.0 equiv.) and stirred at 23 °C for 1 h. [c] Addition of 4 mole % of Cu_2I_2 is required.

ture of (*E*)- and (*Z*)-alkenes **15a**, **16a** that was subsequently isomerized with TFA after heating in THF at 50 °C giving pure *E* isomer **15a**. Also alkyne **14b** formed the mixture of geometrical isomers **15b** and **16b** inseparable by column chromatography (Table III, entry 2). However, in this case additional heating of the isolated mixture of **15b** and **16b** in the presence of TFA in THF at 50 °C for 24 h did not affect the ratio of *E*/*Z* stereoisomers. Selective (≥98% *E*) formation of *trans*-alkenes was observed only for **14c** (Table III, entry 3). In conclusion we have developed a new procedure for the selective preparation of (*E*)-6-alkenylpurines relying on Pd-catalyzed alkynylation followed by a Pd-catalyzed stannation/protodestannation tandem process. First step, Pd-catalyzed alkynylation, proceeded smoothly with 2 mole % Pd(OAc)/4 mole % PPh_3 in MeCN at 80 °C, however, in some cases 4 mole % addition of Cu_2I_2 was required. Using the Pd-catalyzed stannation/protodestannation protocol 6-alkynylpurines were converted to *trans*-9-benzyl or 9-β-D-ribofuranosyl-6-alkenylpurine derivatives bearing both simple alkyl/aryl and nitrile and hydroxyl groups. Apparently, the Pd-catalyzed stannation proceeds in *cis* manner but the following protodestannation is accompanied by acid-catalyzed *Z* to *E* isomerization. Similar tendency to

TABLE III
Pd-catalyzed alkynylation[a] and Pd-catalyzed stannation/protodestannation[b] of 6-chloro-8-iodo-9-isopropyl-9*H*-purine **13**



Entry	R_1	Yield, % of **14**[a]	Yield, % of **15**[b]	Yield, % of **16**[b]
1	Ph	**14a**, 73	**15a** + **16a** (26:74), 73 **15a**, 71[c]	
2	$CH_3(CH_2)_4$	**14b**, 37 (30[d])	**15b** + **16b** (33:67), 75	
3	CH_2OH	**14c**, 58 (15[d])	**15c**, 58	**16c**, 0

[a] Reaction conditions: iodopurines **1** (1.0 equiv.), Et_3N (3.0 equiv.), alkynes (2.0 equiv.), $Pd(OAc)_2$ (2 mole %), PPh_3 (4 mole %), MeCN were stirred at 80 °C for 1 h. [b] Reaction conditions: alkynes **14** (1.0 equiv.), Bu_3SnH (1.5 equiv.), $PdCl_2(PPh_3)_2$ (5 mole %), THF were stirred at 23 °C for 2 h followed by addition of TFA (8.0 equiv.) and stirred at 23 °C for 1 h. [c] ≥98% *E* **15a** was obtained by heating of a mixture of **15a** + **16a** with TFA in THF at 50 °C for 24 h. [d] Formation of 6-chloro-9-isopropyl-9*H*-purine was observed as by-product.

form (*E*)-alkenes was observed with 8-alkynylpurines **14**. On contrary, Pd-catalyzed stannation/protodestannation of 2-alkynylpurines **10** led to *cis*-alkenes. Although the study of the scope and limitations of our procedure are ongoing it is clear that the stannation/protodestannation route is able to accommodate a wide variety of functional groups. Further studies are underway in our laboratory to extend this method.

EXPERIMENTAL

All reactions were performed under an argon atmosphere. NMR spectra (δ, ppm; *J*, Hz) were measured on a Varian Gemini 300 (^{1}H, 300.07 MHz; ^{13}C, 75.46 MHz), a Bruker AMX3 400 (^{1}H, 400.13 MHz; ^{13}C, 100.62 MHz) or a Bruker DRX 500 Avance (^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz) spectrometer at 298 K. Unambiguous assignment of the NMR signals is based on ^{13}C{^{1}H}, ^{13}C APT, COSY, HMQC and ^{13}C HMBC spectra. IR spectra (ν, cm^{-1}) were recorded on a Nicolet 750 FT-IR. Mass spectra were measured on a ZAB-SEQ (VG Analytical). The solvents were dried and degassed by standard procedures; silica gel (Merck, Silica Gel 60, 40–63 μm) was used for column chromatography. 9-Benzyl-6-iodo-9*H*-purine[29] (**1a**), 6-iodo-9-(*O*,*O*,*O*-tris(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl)-9*H*-purine[30] (**1b**), 6-methoxy-2-iodo-9-isopropyl-9*H*-purine[31] (**9**), and 6-chloro-9-isopropyl-9*H*-purine[32] were prepared by the reported procedures, other compounds were purchased. The isomerical purity of isolated alkenes was determined by ^{1}H and ^{13}C NMR spectroscopy.

6-Chloro-8-iodo-9-isopropyl-9*H*-purine (**13**)

To a solution of diisopropylamine (0.84 ml, 6 mmol) in dry THF (5 ml) cooled to –78 °C was added *n*-BuLi (2.73 ml, 6 mmol, 2.5 M solution in hexanes). The resulting mixture was stirred at –78 °C for 15 min. Formed solution of LDA was then dropwise added to a solution of 6-chloro-9-isopropyl-9*H*-purine (0.786 g, 4 mmol) and cooled to –78 °C. The resulting yellow solution was stirred at –78 °C for 5 min followed by addition of a solution of I_2 (1.52 g, 6 mmol) in dry THF (6 ml). The resulting mixture was stirred at –78 °C for 10 min, quenched with saturated aqueous solution of $Na_2S_2O_3$ (20 ml), extracted with CH_2Cl_2, concentrated in vacuo and flash chromatography (hexane–EtOAc 1:2) afforded the title compound (1.0 g, 78%). The crude product was purified by crystallization from CH_2Cl_2–heptane. Light brown solid; m.p. 187–189 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 1.75 d, 6 H, ^3J = 6.9 (CH_3); 4.84 m, 1 H (CH); 8.64 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$): 20.7, 54.2, 107.9, 134.7, 149.3, 150.9, 152.3. IR ($CHCl_3$): 3002, 1586, 1558, 1444, 1431, 1373, 1327, 1280, 1249, 1148. For $C_8H_8ClIN_4$ calculated: 29.79% C, 2.50% H, 17.37% N; found: 29.70% C, 2.33% H, 17.19% N.

9-Benzyl-6-(phenylethynyl)-9*H*-purine (**2a**)

Acetonitrile (10 ml) and triethylamine (1.35 ml, 9.8 mmol) were added to a mixture of 9-benzyl-6-iodo-9*H*-purine (1.09 g, 3.25 mmol), phenylacetylene (0.71 ml, 6.5 mmol), $Pd(OAc)_2$ (0.015 g, 0.065 mmol) and PPh_3 (0.034 g, 0.13 mmol). The resulting mixture was stirred at 80 °C for 1 h, evaporated to dryness in vacuo and column chromatography (hexane– EtOAc, 1:2) afforded the title compound (0.922 g, 92%) as white solid; m.p. (tolu-

ene) 116–118 °C (ref.[33] 114–117 °C). ^{1}H NMR (300 MHz, $CDCl_3$): 5.45 s, 2 H (CH_2); 7.28–7.41 m, 8 H (Ar-H); 7.72 m, 2 H (Ar-H); 8.10 s, 1 H (H-8); 8.98 s, 1 H (H-2).

9-Benzyl-6-(hept-1-ynyl)-9*H*-purine (**2b**)

Acetonitrile (10 ml) and triethylamine (1.35 ml, 9.8 mmol) were added to a mixture of 9-benzyl-6-iodo-9*H*-purine (1.09 g, 3.25 mmol), hept-1-yne (0.86 ml, 6.5 mmol), Cu_2I_2 (0.025 g, 0.13 mmol), $Pd(OAc)_2$ (0.015 g, 0.065 mmol) and PPh_3 (0.034 g, 0.13 mmol). The resulting mixture was stirred at 80 °C for 3 h, evaporated to dryness in vacuo and column chromatography (hexane–EtOAc, 1:1) afforded the title compound (0.865 g, 88%) as brownish solid; m.p. (toluene) 41–45 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 0.90 t, 3 H, ^3J = 7.3 (CH_3); 1.32–1.36 m, 2 H (CH_2); 1.42–1.48 m, 2 H (CH_2); 1.67–1.73 m, 2 H (CH_2); 2.58 t, 2 H, ^3J = 7.2 (CH_2); 5.42 s, 2 H (CH_2); 7.26–7.35 m, 5 H (Ar-H); 8.05 s, 1 H (H-8); 8.91 s, 1 H (H-2). ^{13}C NMR (125 MHz, $CDCl_3$): 13.9, 19.9, 22.2, 27.8, 31.2, 47.3, 76.0, 101.7, 127.8, 128.6, 129.1, 134.2, 134.9, 142.4, 144.7, 151.4, 152.7. IR ($CHCl_3$): 2861, 1583, 1497, 1456, 1443, 1404, 1329. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{19}H_{20}N_4$: 304.1688; found: 304.1699.

3-(9-Benzyl-9*H*-purin-6-yl)prop-2-yn-1-ol (**2c**)

Acetonitrile (10 ml) and triethylamine (1.35 ml, 9.8 mmol) were added to a mixture of 9-benzyl-6-iodo-9*H*-purine (1.09 g, 3.25 mmol), propargyl alcohol (0.38 ml, 6.5 mmol), $Pd(OAc)_2$ (0.015 g, 0.065 mmol) and PPh_3 (0.034 g, 0.13 mmol). The resulting mixture was stirred at 80 °C for 1 h, evaporated to dryness in vacuo and column chromatography (EtOAc–MeOH, 20:1) afforded the title compound (0.750 g, 88%) as light brown solid; m.p. (toluene–heptane) 124–127 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 4.65 s, 2 H (CH_2); 5.46 s, 2 H (CH_2); 7.33 m, 5 H (Ar-H); 8.25 s, 1 H (H-8); 8.95 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$): 47.7, 51.2, 80.0, 99.0, 128.0, 128.9, 129.4, 134.3, 135.0, 141.4, 146.0, 151.6, 152.9. IR ($CHCl_3$): 3339, 3009, 2236, 1585, 1499, 1456, 1445, 1405, 1331, 1195, 1149, 1059, 1023. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{15}H_{12}N_4O$: 264.1011; found: 264.1010.

6-(9-Benzyl-9*H*-purin-6-yl)hex-5-ynenitrile (**2d**)

Acetonitrile (3 ml) and triethylamine (0.42 ml, 3.0 mmol) were added to a mixture of 9-benzyl-6-iodo-9*H*-purine (0.336 g, 1.0 mmol), hex-5-ynenitrile (0.186 g, 2.0 mmol), $Pd(OAc)_2$ (0.004 g, 0.02 mmol) and PPh_3 (0.010 g, 0.04 mmol). The resulting mixture was stirred at 80 °C for 2 h, evaporated to dryness in vacuo and column chromatography (EtOAc–MeOH, 20:1) afforded the title compound (0.282 g, 94%) as yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): 2.02–2.12 m, 2 H (CH_2); 2.62 t, 2 H, ^3J = 7.3 (CH_2); 2.78 t, 2 H, ^3J = 6.7 (CH_2); 5.44 s, 2 H (CH_2); 7.26–7.38 m, 5 H (Ar-H); 8.07 s, 1 H (H-8); 8.93 s, 1 H (H-2). ^{13}C NMR (125 MHz, $CDCl_3$,): 16.6, 19.2, 24.4, 47.6, 77.9, 97.7, 119.2, 128.1, 128.9, 129.4, 134.6, 135.0, 141.8, 145.4, 151.8, 152.9. IR (KBr): 3090, 3061, 3037, 2942, 2236, 1582, 1498, 1455, 1442, 1404, 1327, 1243, 1213, 1197, 1147, 1120, 1079, 1055, 1029, 989, 977, 946, 913, 853, 823, 806, 773, 729, 699, 666, 645, 611, 543. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{18}H_{15}N_5$: 301.1327; found: 301.1318.

6-(Phenylethynyl)-9-(*O*,*O*,*O*-tris(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl)-9*H*-purine (**2e**)

Acetonitrile (2 ml) and triethylamine (0.10 ml, 0.75 mmol) were added to a mixture of 6-iodo-9-(*O*,*O*,*O*-tris(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl)-9*H*-purine (0.180 g, 0.25 mmol), phenylacetylene (0.055 ml, 0.50 mmol), $Pd(OAc)_2$ (0.001 g, 0.005 mmol) and PPh_3 (0.0026 g, 0.01 mmol). The resulting mixture was stirred at 80 °C for 2 h, evaporated to dryness in vacuo and column chromatography (hexane–Et_2O, 2:1) afforded the title compound (0.104 g, 60%) as yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): –0.26 (s, 3 H); 0.05 (s, 3 H); 0.10 (s, 6 H); 0.14 (s, 3 H); 0.15 (s, 3 H); 0.78 (s, 9 H); 0.93 (s, 9 H); 0.95 (s, 9 H); 3.77–3.84 (m, 1 H); 3.98–4.06 (m, 1 H); 4.12–4.18 (m, 1 H); 4.30–4.34 (m, 1 H); 4.64–4.70 (m, 1 H); 6.13 (d, 1 H, *J* = 5.3); 7.34–7.42 (m, 3 H); 7.71–7.76 (m, 2 H); 8.49 (s, 1 H); 8.94 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): –5.3, –5.0, –4.7, 17.8, 18.0; 18.5, 25.6, 25.8, 26.1, 62.5, 72.0, 75.9, 84.3, 85.7, 88.3, 98.3, 121.5, 128.4, 129.8, 132.7, 134.8, 141.8, 144.2, 151.4, 152.5. IR (KBr): 3058, 2954, 2929, 2897, 2857, 2216, 1632, 1599, 1578, 1487, 1472, 1463, 1442, 1405, 1389, 1362, 1331, 1255, 1216, 1194, 1166, 1143, 1112, 1072, 1004, 993, 968, 939, 838, 813, 778, 757, 689, 672, 642, 537, 529. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{36}H_{58}N_4O_4Si_3 - C_4H_9$: 637.3062; found: 637.3058.

3-(9-(*O*,*O*,*O*-Tris(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl)-9*H*-purin-6-yl)prop-2-yn-1-ol (**2f**)

Acetonitrile (2 ml) and triethylamine (0.10 ml, 0.75 mmol) were added to a mixture of 6-iodo-9-(*O*,*O*,*O*-tris(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl)-9*H*-purine (0.180 g, 0.25 mmol), propargyl alcohol (0.029 ml, 0.50 mmol), $Pd(OAc)_2$ (0.001 g, 0.005 mmol) and PPh_3 (0.0026 g, 0.01 mmol). The resulting mixture was stirred at 80 °C for 2 h, evaporated to dryness in vacuo and column chromatography (hexane–EtOAc, 1:1) afforded the title compound (0.101 g, 62%) as yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$): –0.29 (s, 3 H); –0.06 (s, 3 H); 0.10 (s, 3 H); 0.11 (s, 3 H); 0.13 (s, 3 H); 0.14 (s, 3 H); 0.77 (s, 9 H); 0.93 (s, 9 H); 0.95 (s, 9 H); 3.7 (dd, 1 H, *J* = 11.4, *J* = 2.6); 4.02 (dd, 1 H, *J* = 11.4, *J* = 4.1); 4.15 (m, 1 H); 4.31 (t, 1 H, *J* = 3.8); 4.60–4.70 (m, 3 H); 6.12 (d, *J* = 5.2); 8.58 (s, 1 H); 8.90 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$,): –5.4, –5.1, –4.7, 17.8, 18.1, 18.5, 25.6, 25.8, 26.1, 51.3, 62.5, 72.0, 75.9, 80.1, 85.8, 97.7, 134.8, 141.2, 144.6, 151.2, 152.5. IR (KBr): 2955, 2929, 2858, 2236, 1636, 1583, 1495, 1472, 1464, 1444, 1405, 1385, 1362, 1333, 1255, 1213, 1164, 1128, 1073, 1045, 1003, 970, 940, 868, 838, 813, 779, 672, 643. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{31}H_{56}N_4O_5Si_3 - C_4H_9$: 591.2854; found: 591.2847.

9-Isopropyl-6-methoxy-2-(phenylethynyl)-9*H*-purine (**10a**)

Acetonitrile (6 ml) and triethylamine (0.76 ml, 5.7 mmol) were added to a mixture of 2-iodo-9-isopropyl-6-methoxy-9*H*-purine (0.60 g, 1.9 mmol), phenylacetylene (0.42 ml, 3.8 mmol), $Pd(OAc)_2$ (0.009 g, 0.038 mmol) and PPh_3 (0.020 g, 0.076 mmol). The resulting mixture was stirred at 80 °C for 1 h, evaporated to dryness in vacuo and column chromatography (hexaneE–tOAc, 1:2) afforded the title compound (0.522 g, 96%) as yellow solid; m.p. (toluene) 118–121 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 1.62 d, 6 H, ^3J = 6.5 (CH_3); 4.24 s, 3 H (OCH_3); 4.99 m, 1 H (NCH); 7.28–7.39 m, 3 H (Ar-H); 7.69 d, ^3J = 7.5 (Ar-H); 8.04 s, 1 H (H-8). ^{13}C NMR (125 MHz, $CDCl_3$): 22.8, 47.0, 54.5, 85.7, 88.6, 121.2, 121.8, 128.3, 129.2, 132.4, 140.4, 145.3, 151.7, 160.6. IR ($CHCl_3$): 2213, 1592, 1569, 1491, 1462, 1390, 1376. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{17}H_{16}N_4O$: 292.1324; found: 292.1327.

2-(Hept-1-ynyl)-9-isopropyl-6-methoxy-9*H*-purine (**10b**)

Acetonitrile (6 ml) and triethylamine (0.76 ml, 5.7 mmol) were added to a mixture of 2-iodo-9-isopropyl-6-methoxy-9*H*-purine (0.60 g, 1.9 mmol), hept-1-yne (0.50 ml, 3.8 mmol), Cu_2I_2 (0.014 g, 0.076 mmol), $Pd(OAc)_2$ (0.009 g, 0.038 mmol) and PPh_3 (0.020 g, 0.076 mmol). The resulting mixture was stirred at 80 °C for 1 h, evaporated to dryness in vacuo and column chromatography (hexane–EtOAc, 1:2) afforded the title compound (0.485 g, 90%) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$,): 0.94 t, 3 H, ^3J = 7.3 (CH_3); 1.33–1.41 m, 2 H (CH_2); 1.43–1.49 m, 2 H (CH_2); 1.59 d, 6 H, ^3J = 6.7 (CH_3); 1.67–1.73 m, 2 H (CH_2); 2.49 t, 2 H, ^3J = 7.4 (CH_2); 4.21 s, 3 H (OCH_3); 4.99 m, 1 H (NCH); 8.03 s, 1 H (H-8). ^{13}C NMR (75 MHz, $CDCl_3$): 13.5, 19.0, 21.8, 22.4, 27.5, 30.8, 46.5, 53.9, 80.0, 88.8, 120.6, 139.9, 145.1, 151.2, 160.1. IR ($CHCl_3$): 2872, 1594, 1571, 1463, 1391, 1374. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{16}H_{22}N_4O$: 286.1794; found: 286.1789.

3-(9-Isopropyl-6-methoxy-9*H*-purin-2-yl)prop-2-yn-1-ol (**10c**)

Acetonitrile (6 ml) and triethylamine (0.76 ml, 5.7 mmol) were added to a mixture of 2-iodo-9-isopropyl-6-methoxy-9*H*-purine (0.60 g, 1.9 mmol), propargyl alcohol (0.22 ml, 3.8 mmol), Cu_2I_2 (0.014 g, 0.076 mmol), $Pd(OAc)_2$ (0.009 g, 0.038 mmol) and PPh_3 (0.020 g, 0.076 mmol). The resulting mixture was stirred at 80 °C for 1 h, evaporated to dryness in vacuo and column chromatography (EtOAc–MeOH, 20:1) afforded the title compound (0.380 g, 82%) as brownish solid; m.p. (toluene) 183–185 °C. ^{1}H NMR (500 MHz, DMSO): 1.53 d, 6 H, ^3J = 6.7 (CH_3); 4.06 s, 3 H (OCH_3); 4.35 s, 2 H (CH_2O); 4.80 m, 1 H (CH); 8.55 s, 1 H (H-8). ^{13}C NMR (75 MHz, $CDCl_3$): 22.0, 47.2, 49.2, 54.1, 83.5, 86.1, 120.6, 142.9, 143.6, 151.5, 159.9. IR ($CHCl_3$): 1595, 1571, 1464, 1391, 1373. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{12}H_{14}N_4O_2$: 246.1117; found: 246.1114.

6-Chloro-9-isopropyl-8-(phenylethynyl)-9*H*-purine (**14a**)

Acetonitrile (14 ml) and triethylamine (1.94 ml, 14.0 mmol) were added to a mixture of 6-chloro-8-iodo-9-isopropyl-9*H*-purine (1.50 g, 4.6 mmol), phenylacetylene (0.56 ml, 5.1 mmol), $Pd(OAc)_2$ (0.021 g, 0.093 mmol) and PPh_3 (0.049 g, 0.186 mmol). The resulting mixture was stirred at 80 °C for 1 h, evaporated to dryness in vacuo and column chromatography (hexane–EtOAc, 4:1) afforded the title compound (0.933 g, 72%) as yellow solid; m.p. (toluene) 171–179 °C. ^{1}H NMR (300 MHz, $CDCl_3$,): 1.76 d, 6 H, ^3J = 6.9 (CH_3); 5.14 m, 1 H (CH); 7.40–7.45 m, 3 H (Ar-H); 7.62 d, 2 H, ^3J = 7.5 (Ar-H); 8.69 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$,): 21.2, 49.3, 78.3, 97.6, 120.2, 128.7, 130.5, 131.9, 132.2, 138.9, 150.4, 151.3, 151.7. IR ($CHCl_3$): 2941, 2874, 2222, 1587, 1558, 1503, 1470, 1442, 1428, 1391, 1375, 1340, 1252. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{16}H_{13}N_4Cl$: 296.0829; found: 296.0834.

6-Chloro-8-(hept-1-ynyl)-9-isopropyl-9*H*-purine (**14b**)

Acetonitrile (14 ml) and triethylamine (1.94 ml, 14.0 mmol) were added to a mixture of 6-chloro-8-iodo-9-isopropyl-9*H*-purine (1.50 g, 4.6 mmol), hept-1-yne (1.22 ml, 9.3 mmol), $Pd(OAc)_2$ (0.021 g, 0.093 mmol) and PPh_3 (0.049 g, 0.186 mmol). The resulting mixture was stirred at 80 °C for 1 h, evaporated to dryness in vacuo and column chromatography (hexane–EtOAc, 3:1) afforded the title compound (0.50 g, 37%) as yellow solid; m.p. 58–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$,): 0.82 t, 3 H, *J* = 7.2 (CH_3); 1.23–1.41 m, 4 H (2 × CH_2);

1.55–1.60 m, 2 H (CH_2); 1.63 d, 6 H, ^3J = 7.2 (CH_3); 2.47 t, 2 H, ^3J = 7.2 (CH_2); 4.97 m, 1 H (CH); 8.59 s, 1 H (H-2). ^{13}C NMR ($CDCl_3$, 125 MHz): 13.9, 19.5, 21.1, 22.1, 27.4, 31.1, 49.8, 70.4, 100.9, 131.5, 139.3, 150.2, 151.3, 151.6. IR ($CHCl_3$): 2959, 2936, 2870, 2240, 1733, 1586, 1558, 1483, 1443, 1427, 1357, 1340. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{15}H_{19}N_4Cl$: 290.1298; found: 290.1298.

3-(6-Chloro-9-isopropyl-9*H*-purin-8-yl)prop-2-yn-1-ol (**14c**)

Acetonitrile (14 ml) and triethylamine (1.94 ml, 14.0 mmol) were added to a mixture of 6-chloro-8-iodo-9-isopropyl-9*H*-purine (1.50 g, 4.6 mmol), propargyl alcohol (0.54 ml, 9.3 mmol), $Pd(OAc)_2$ (0.021 g, 0.093 mmol) and PPh_3 (0.049 g, 0.186 mmol). The resulting mixture was stirred at 80 °C for 1 h, evaporated to dryness in vacuo and column chromatography (hexane–EtOAc, 1:2) afforded the title compound (0.714 g, 62%) as white amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$): 1.73 d, 6 H, ^3J = 6.9 (CH_3); 4.64 s, 2 H (CH_2); 5.07 m, 1 H (CH); 8.73 s, 1 H (H-2). ^{13}C NMR ($CDCl_3$, 75 MHz): 21.1, 50.4, 50.7, 73.4, 98.1, 131.1, 138.5, 150.4, 151.5, 151.9. IR ($CHCl_3$): 3604, 3302, 2939, 2243, 1588, 1559, 1482, 1443, 1393, 1377, 1341. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{11}H_{11}N_4OCl$: 250.0621; found: 250.0632.

(*E*)-9-Benzyl-6-(phenylethenyl)-9*H*-purine (**3a**)

To a solution of **2a** (0.102 g, 0.33 mmol) and $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) in dry THF (4 ml) was added Bu_3SnH (0.13 ml, 0.50 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (6 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–hexane, 2:1) afforded the title compound (0.084 g, 82%) as colorless amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$): 5.46 s, 2 H (CH_2); 7.26–7.44 m, 8 H (Ar-H); 7.73 m, 3 H (2 Ar-H + 1 =CH); 8.05 s, 1 H (H-8); 8.42 d, 1 H, ^3J = 16.4 (=CH); 8.96 s, 1 H (H-2). In accordance with ref.[19] ^{13}C NMR (125 MHz, $CDCl_3$): 47.2, 122.3, 127.8, 127.9, 128.5, 128.8, 129.1, 129.4, 130.9, 135.1, 136.1, 139.8, 143.9, 151.9, 152.6, 153.8. In accordance with ref.[19]

(*E*)-9-Benzyl-6-(hept-1-enyl)-9*H*-purine (**3b**)

To a solution of **2b** (0.10 g, 0.33 mmol) and $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) in dry THF (4 ml) was added Bu_3SnH (0.13 ml, 0.50 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (6 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–hexane, 1:1) afforded the title compound (0.086 g, 85%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$,): 0.86–0.94 m, 3 H (CH_3); 1.25–1.36 m, 2 H (CH_2); 1.53–1.64 m, 2 H (CH_2); 2.58 dt, 2 H, ^3J = 7.0, ^3J = 1.4 (CH_2); 5.44 s, 2 H (CH_2); 7.02 d, 1 H, ^3J = 15.7 (=CH); 7.25–7.38 m, 5 H (Ar-H); 7.66 dt, 1 H, ^3J = 15.7, ^3J = 7.0 (=CH); 8.02 s, 1 H (H-8); 8.90 s, 1 H (H-2). In accordance with ref.[20b] ^{13}C NMR (75 MHz, $CDCl_3$): 13.8, 22.3, 28.0, 31.2, 33.3, 46.9, 124.8, 127.5, 128.2, 128.8, 130.2, 135.1, 143.6, 145.0, 151.5, 152.4, 154.0.

In accordance with ref.[20b] IR ($CHCl_3$): 2960, 2930, 2857, 1649, 1585, 1497, 1454, 1404, 1328. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{19}H_{22}N_4$: 306.1844; found: 306.1850.

(*E*)-3-(9-Benzyl-9*H*-purin-6-yl)prop-2-en-1-ol (**3c**)

To a solution of **2c** (0.087 g, 0.33 mmol) and $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) in dry THF (4 ml) was added Bu_3SnH (0.13 ml, 0.50 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (6 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–MeOH, 20:1) afforded the title compound (0.053 g, 60%) as greenish solid; m.p. 78–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$,): 4.51 dd, 2 H, ^3J = 4.4, ^3J = 1.9 (CH_2); 5.41 s, 2 H (CH_2); 7.26–7.36 m, 6 H (5 Ar-H + 1 =CH); 7.70 dt, 1 H, ^3J = 15.9, ^3J = 4.4 (=CH); 8.02 s, 1 H (H-8); 8.87 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$,): 47.2, 62.6, 123.5, 127.8, 128.6, 129.1, 130.4, 134.9, 143.5, 144.1, 151.8, 152.4, 153.5. IR ($CHCl_3$): 3297, 1710, 1656, 1587, 1498, 1455, 1404, 1329. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{15}H_{14}N_4O$: 266.1168; found: 266.1176.

(*E*)-(9-Benzyl-9*H*-purin-6-yl)hex-5-ennitrile (**3d**)

To a solution of **2d** (0.090 g, 0.30 mmol) and $PdCl_2(PPh_3)_2$ (11 mg, 0.015 mmol) in dry THF (3 ml) was added Bu_3SnH (0.12 ml, 0.45 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (6 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–MeOH, 20:1) afforded the title compound (0.065 g, 71%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): 2.02–2.12 m, 2 H (CH_2); 2.62 t, 2 H, ^3J = 7.3 (CH_2); 2.78 t, 2 H, ^3J = 6.7 (CH_2); 5.44 s, 2 H (CH_2); 7.26–7.38 m, 5 H (Ar-H); 8.07 s, 1 H (H-8); 8.93 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$): 16.6, 19.2, 24.3, 47.6, 97.7, 119.2, 128.1, 128.9, 129.4, 132.2, 134.6, 135.0, 141.8, 145.4, 151.8, 152.9. IR (KBr): 3090, 3061, 3037, 2942, 2236, 1582, 1498, 1455, 1442, 1404, 1327, 1243, 1213, 1197, 1147, 1120, 1079, 1055, 1029, 989, 977, 946, 913, 853, 823, 806, 773, 729, 699, 666, 645, 611, 543. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{18}H_{17}N_5$: 303.1484; found: 303.1481.

(*Z*)-(9-Benzyl-9*H*-purin-6-yl)hex-5-ennitrile (**4d**)

To a solution of **2d** (0.090 g, 0.30 mmol) and $PdCl_2(PPh_3)_2$ (11 mg, 0.015 mmol) in dry THF (3 ml) was added Bu_3SnH (0.12 ml, 0.45 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then AcOH (1 ml, 1 M solution in methanol) was added at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–MeOH, 20:1) afforded **3d** (0.027 g, 30%), and **4d** (0.038 g, 41%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): 1.89–1.99 m, 2 H (CH_2); 2.44 t, 2 H, ^3J = 7.3 (CH_2); 3.04–3.12 m, 2 H (CH_2); 5.44 s, 2 H (CH_2); 6.22 dt, 1 H, ^3J = 7.9, ^3J = 11.7 (=CH); 7.17 d, 1 H, ^3J = 11.7 (=CH); 7.27–7.36 m, 5 H (Ar-H); 8.00 s, 1 H (H-8); 8.95 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$): 17.0, 25.5, 28.8,

47.5, 120.00, 123.5, 128.1, 128.8, 129.4, 131.9, 135.4, 141.2, 144.0, 151.9, 152.5, 154.8. IR (KBr): 3103, 2924, 2852, 2243, 1639, 1581, 1495, 1456, 1437, 1421, 1392, 1369, 1346, 1325, 1288, 1275, 1238, 1206, 1190, 1143, 1129, 1076, 1025, 1000, 982, 961, 942, 894, 858, 825, 788, 729, 701, 679, 648, 595, 546, 522, 462. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{18}H_{17}N_5$: 303.1484; found: 303.1482.

(*E*)-6-(Phenylethenyl)-9-(*O*,*O*,O-tris(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl)-9*H*-purine (**3e**)

To a solution of **2e** (0.080 g, 0.115 mmol) and $PdCl_2(PPh_3)_2$ (4 mg, 0.006 mmol) in dry THF (2 ml) was added Bu_3SnH (0.046 ml, 0.17 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (2 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (Et_2O–hexane, 1:3) afforded the title compound (0.040 g, 50%) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): –0.25 s, 3 H (CH_3); –0.04 s, 3 H (CH_3); 0.11 2 × s, 6 H (2 × CH_3); 0.15 s, 3 H (CH_3); 0.16 s, 3 H (3 × CH_3); 0.79 s, 9 H ($C(CH_3)_3$); 0.94 s, 9 H ($C(CH_3)_3$); 0.97 s, 9 H ($C(CH_3)_3$); 3.76–3.85 m, 1 H (CH); 4.01–4.09 m, 1 H (CH); 4.12–4.19 m, 1 H (CH); 4.30–4.37 m, 1 H (CH); 4.68–4.74 m, 1 H (CH); 6.14 d, 1 H, ^3J = 5.3 (CH); 7.35–7.46 m, 3 H (Ar-H); 7.70–7.78 m, 3 H (2 Ar-H + 1 =CH); 8.39 d, 1 H, ^3J = 16.1 (=CH); 8.44 s, 1 H (H-8); 8.91 s, 1 H (H-2). In accordance with ref.[2a] IR (KBr): 3059, 3022, 2954, 2929, 2897, 2858, 1636, 1585, 1491, 1472, 1463, 1450, 1406, 1389, 1362, 1327, 1255, 1215, 1166, 1149, 1136, 1073, 1046, 997, 969, 939, 838, 813, 778, 752, 691, 673, 646, 535, 485. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{36}H_{60}N_4O_4Si_3 - C_4H_9$: 639.3218; found: 639.3204.

(*Z*)-6-(Phenylethenyl)-9-(*O*,*O*,*O*-tris(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl)-9*H*-purine (**4e**)

To a solution of **2e** (0.080 g, 0.115 mmol) and $PdCl_2(PPh_3)_2$ (4 mg, 0.006 mmol) in dry THF (2 ml) was added Bu_3SnH (0.046 ml, 0.17 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then AcOH (1 ml, 1 M solution in methanol) was added at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (Et_2O–hexane, 1:3) afforded an inseparable mixture of **3e** + **4e** 75%; ratio 73:27 (^{1}H NMR) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) from mixture with **3e**: –0.30 s, 3 H (CH_3); –0.05 s, 3 H (CH_3); 0.11 2 × s, 6 H (2 × CH_3); 0.15 s, 3 H (CH_3); 0.16 s, 3 H (CH_3); 0.78 s, 9 H ($C(CH_3)_3$); 0.94 s, 9 H ($C(CH_3)_3$); 0.97 s, 9 H $C(CH_3)_3$); 3.76–3.83 m, 1 H (CH); 3.99–4.06 m, 1 H (CH); 4.12–4.16 m, 1 H (CH); 4.30–4.35 m, 1 H (CH); 4.68–4.72 m, 1 H (CH); 6.11 d, 1 H, ^3J = 5.3 (CH); 7.08 d, 1 H, ^3J = 12.6 (=CH); 7.14 d, 1 H, ^3J = 12.6 (=CH); 7.2–7.24 m, 3 H (Ar-H); 7.43–7.47 m, 2 H (Ar-H); 8.34 s, 1 H (H-8); 8.84 s, 1 H (H-2).

(*E*)-3-(9-(*O*,*O*,*O*-Tris(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl)-9*H*-purin-6-yl)prop-2-en-1-ol (**3f**)

To a solution of **2f** (0.118 g, 0.182 mmol) and $PdCl_2(PPh_3)_2$ (6 mg, 0.009 mmol) in dry THF (3 ml) was added Bu_3SnH (0.073 ml, 0.27 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (2 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated

aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–MeOH, 20:1) afforded the title compound (0.068 g, 57%) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): –0.29 s, 3 H (CH_3); –0.07 s, 3 H (CH_3); 0.09 2 × s, 6 H (2 × CH_3); 0.12 s, 3 H (CH_3); 0.13 s, 3 H (CH_3); 0.76 s, 9 H ($C(CH_3)_3$); 0.92 s, 9 H ($C(CH_3)_3$); 0.94 s, 9 H ($C(CH_3)_3$); 3.75–3.82 m, 1 H (CH); 3.98–4.05 m, 1 H (CH); 4.11–4.16 m, 1 H (CH); 4.28–4.33 m, 1 H (CH); 4.48–4.54 m, 2 H (CH_2); 4.64–4.68 m, 1 H (CH); 6.10 d, 1 H, ^3J = 5.3 (CH); 7.25–7.34 m, 1 H (=CH); 7.69 dt, ^3J = 15.8, ^3J = 4.7 (=CH); 8.40 s, 1 H (H-8); 8.84 s, 1 H (H-2). ^{13}C NMR(75 MHz, $CDCl_3$): –5.4, –5.1, –4.7, 17.8, 18.1, 18.5, 25.6, 25.8, 26.1, 62.5, 63.0, 72.0, 75.9, 85.6, 88.2, 124.1, 131.4, 142.2, 143.2, 151.7, 152.3, 153.4. IR (KBr): 2955, 2929, 2898, 2858, 1654, 1587, 1495, 1472, 1463, 1406, 1390, 1362, 1330, 1255, 1215, 1166, 1150, 1126, 1073, 1046, 1000, 969, 940, 869, 838, 813, 778, 673, 646. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{31}H_{58}N_4O_5Si_3 - C_4H_9$: 593.3011; found: 593.3027.

(*E*)-9-Isopropyl-6-methoxy-2-(phenylethenyl)-9*H*-purine (**11a**) and
(*Z*)-9-Isopropyl-6-methoxy-2-(phenylethenyl)-9*H*-purine (**12a**)

To a solution of **10a** (0.134 g, 0.46 mmol) and $PdCl_2(PPh_3)_2$ (16 mg, 0.023 mmol) in dry THF (3 ml) was added Bu_3SnH (0.19 ml, 0.69 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (2 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–hexane, 1:2) afforded an inseparable mixture of **11a** + **12a** (0.121 g, 89%; 20:80 *E*/*Z*). Heating of this mixture with TFA in THF to 50 °C for 24 h did not affect the *E*/*Z* ratio. ^{1}H NMR (500 MHz, $CDCl_3$), **11a** + **12a**: 1.53 d, 6 H, ^3J = 6.8 (CH_3); 1.64 d, 6 H, ^3J = 6.8 (CH_3); 3.80 s, 3 H (OCH_3); 4.76 m, 1 H (CH); 4.94 m, 1 H (CH); 6.73 d, 1 H, ^3J = 12.4 (=CH); 6.97 d, 1 H, ^3J = 12.4 (=CH); 7.22–7.28 m, 3 H (Ar-H); 7.41 d, 2 H, ^3J = 7.5 (Ar-H); 7.64 d, 2 H, ^3J = 7.5 (Ar-H); 7.93 s, 1 H (H-8); 7.97 s, 1 H (H-8); 8.00 d, 2 H, ^3J = 16.0 (Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$), **11a** + **12a**: 22.6, 22.7, 47.0, 47.1, 53.9, 56.7, 120.2, 127.2, 127.4, 127.6, 128.0, 128.6, 128.7, 129.2, 129.3, 136.4, 135.5, 136.8, 137.4, 139.6, 139.9, 157.9, 160.0. IR ($CHCl_3$), **11a** + **12a**: 2983, 1594, 1572, 1465, 1392, 1353. HRMS (EI), **11a** + **12a**: *m/z* $[M]^+$ calculated for $C_{17}H_{18}N_4O$: 294.1481; found: 292.1474.

(*Z*)-2-(Hept-1-enyl)-9-isopropyl-6-methoxy-9*H*-purine (**12b**)

To a solution of **10b** (0.095 g, 0.33 mmol) and $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) in dry THF (4 ml) was added Bu_3SnH (0.13 ml, 0.50 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (6 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–hexane, 2:1) afforded the title compound (0.076 g, 80%) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): 0.90 t, 3 H, ^3J = 6.9 (CH_3); 1.34–1.38 m, 4 H (2 × CH_2); 1.53–1.59 m, 2 H (CH_2); 1.62 d, 6 H, ^3J = 6.8 (2 × CH_3); 2.92 m, 2 H (CH_2); 4.17 s, 3 H (OCH_3); 4.86 m, 1 H (CH); 6.09 dt, 1 H, ^3J = 11.9, ^3J = 5.5 (=CH); 6.49 d, 1 H, ^3J = 11.9 (=CH); 7.94 s, 1 H (H-8). ^{13}C NMR (75 MHz, $CDCl_3$): 14.0, 22.5, 22.6, 29.2, 29.3, 31.8, 47.1, 53.9, 119.6, 128.1, 139.7, 141.7, 152.0, 159.1, 160.1. IR ($CHCl_3$): 2958, 2927, 2872, 2857,

1595, 1572, 1464, 1391, 1382, 1355. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{16}H_{24}N_4O$: 288.1950; found: 288.1941.

(*Z*)-3-(9-Isopropyl-6-methoxy-9*H*-purin-2-yl)prop-2-en-1-ol (**12c**)

To a solution of **10c** (0.081 g, 0.33 mmol) and $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) in dry THF (4 ml) was added Bu_3SnH (0.13 ml, 0.50 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (6 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–hexane, 1:1, then EtOAc–MeOH, 20:1) afforded the title compound (0.068 g, 84%) as yellowish solid; m.p. 75–79 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 1.63 d, 6 H, ^3J = 6.8 (2 × CH_3); 4.20 s, 3 H (OCH_3); 4.60 d, 2 H, ^3J = 5.5 (CH_2); 4.86 m, 1 H (CH); 6.39–6.42 m, 1 H (=CH); 6.67 d, 1 H, ^3J = 12.1 (=CH); 8.04 s, 1 H (H-8). ^{13}C NMR (125 MHz, $CDCl_3$): 22.5, 47.4, 54.3, 59.6, 119.9, 130.1, 139.3, 140.4, 151.7, 157.7, 160.6. IR ($CHCl_3$): 1594, 1572, 1466, 1392, 1382, 1351, 1234. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{12}H_{16}N_4O_2$: 248.1273; found: 248.1270.

(*E*)-6-Chloro-9-isopropyl-8-(2-phenylethenyl)-9*H*-purine (**15a**)

To a solution of **14a** (0.098 g, 0.33 mmol) and $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) in dry THF (4 ml) was added Bu_3SnH (0.13 ml, 0.50 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (6 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–hexane, 1:4) afforded 26:74 mixture of **15a** + **16a** in 73% yield. The mixture was dissolved in dry THF (4 ml), CF_3CO_2H (0.2 ml, 2.64 mmol) was added, the resulting mixture was stirred at 50 °C for 24 h, concentrated in vacuo and column chromatography (EtOAc–hexane, 1:4) gave the title compound (0.069 g, 71%) as white solid; m.p. 158–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 1.77 d, 6 H, ^3J = 6.9 (2 × CH_3); 5.03 m, 1 H (CH); 7.14 d, 1 H, ^3J = 15.7 (=CH); 7.40–7.46 m, 3 H (Ar-H); 7.65 d, 2 H, ^3J = 7.5 (Ar-H); 8.17 d, 1 H, ^3J = 15.7 (=CH); 8.65 s, 1 H (H-2). ^{13}C NMR (125 MHz, $CDCl_3$): 21.4, 48.6, 112.1, 127.6, 128.9, 129.9, 131.8, 135.1, 141.0, 148.9, 150.3, 152.9, 153.1. IR ($CHCl_3$): 3063, 2938, 2360, 2335, 1633, 1587, 1558, 1480, 1458, 1431, 1394, 1352. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{16}H_{15}N_4Cl$: 298.0985; found: 298.0983.

(*Z*)-6-Chloro-9-isopropyl-8-(2-phenylethenyl)-9*H*-purine (**16a**)

This compound can be isolated from the above 26:74 mixture of isomers **15a** and **16a** before isomerization by chromatography (EtOAc–hexane, 1:4) in 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 1.38 d, 6 H, ^3J = 6.9 (2 × CH_3); 4.57 m, 1 H (CH); 6.56 d, 1 H, ^3J = 12.4 (=CH); 7.19–7.27 m, 6 H (5 Ar-H + 1 =CH); 8.67 s, 1 H (H-2). ^{13}C NMR (125 MHz, $CDCl_3$): 20.4, 49.8, 116.2, 128.5, 128.9, 129.0, 131.7, 134.8, 140.4, 149.7, 150.6, 152.3, 152.6. IR ($CHCl_3$): 2942, 1642, 1587, 1558, 1447, 1431, 1373, 1342. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{16}H_{15}N_4Cl$: 298.0985; found: 298.0967.

(*E*)-6-Chloro-8(hept-1-en-1-yl)-9-isopropyl-9*H*-purine (**15b**) and
(*Z*)-6-Chloro-8-(hept-1-en-1-yl)-9-isopropyl-9*H*-purine (**16b**)

To a solution of **14b** (0.096 g, 0.33 mmol) and $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) in dry THF (4 ml) was added Bu_3SnH (0.13 ml, 0.50 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (6 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–hexane, 1:3) afforded 33:67 mixture of **15b** + **16b** (0.072 g, 75%) as a colorless oil inseparable by column chromatography. Heating of this mixture with TFA in THF to 50 °C for 24 h did not affect the *E*/*Z* ratio. ^{1}H NMR (500 MHz, $CDCl_3$), **15b** + **16b**: 0.88–0.93 (m, 6 H, **15b** + **16b**); 1.33–1.37 (m, 8 H, **15b** + **16b**); 1.51–1.57 (m, 4 H, **15b** + **16b**); 1.70 (d, *J* = 7.0, 6 H, **16b**); 1.72 (d, *J* = 7.0, 6 H, **15b**); 2.35–2.39 (m, 2 H, **15b**); 2.72–2.77 (m, 2 H, **16b**); 4.88 (m, 1 H, **16b**); 4.93 (m, 1 H, **15b**); 6.35–6.38 (m, 1 H, **16b**); 6.43 (d, *J* = 11.8, 1 H, **16b**); 6.53 (d, *J* = 15.3, 1 H, **15b**); 7.35 (dt, *J* = 15.3, *J* = 7.1, 1 H, **15b**); 8.63 (s, 1 H, **15b**); 8.65 (s, 1 H, **16b**). ^{13}C NMR (125 MHz, $CDCl_3$), **15b** + **16b**: 13.9, 21.2, 21.3, 22.4, 28.0, 28.6, 29.6, 31.4, 31.4, 33.4, 48.4, 48.7, 114.5, 115.2, 131.6, 146.2, 146.6, 148.7, 149.5, 150.2, 150.5, 152.31, 152.33, 152.8, 153.3. IR ($CHCl_3$), **15b** + **16b**: 2959, 2930, 2858, 1731, 1647, 1590, 1559, 1457, 1440, 1371, 1336, 1251, 1152. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{15}H_{21}N_4Cl$: 292.1455; found: 292.1469.

(*E*)-3-(6-Chloro-9-isopropyl-9*H*-purin-8-yl)prop-2-en-1-ol (**15c**)

To a solution of **14c** (0.083 g, 0.33 mmol) and $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) in dry THF (4 ml) was added Bu_3SnH (0.13 ml, 0.50 mmol). The resulting mixture was stirred at ambient temperature for 2 h, then THF was removed in vacuo followed by addition of TFA (0.2 ml, 2.7 mmol) in THF (6 ml) at ambient temperature after 1 h, THF was evaporated in vacuo and the resulting oil residue was dissolved in ethyl acetate (10 ml), washed with saturated aqueous $NaHCO_3$ (2 × 10 ml), dried with Na_2SO_4, concentrated in vacuo and column chromatography (EtOAc–hexane, 2:1) afforded the title compound (0.048 g, 58%) as white solid; m.p. 153–156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 1.70 d, 6 H, ^3J = 6.9 (2 × CH_3); 4.51 dd, 2 H, ^3J = 3.8, ^3J = 1.9 (CH_2); 4.92 m, 1 H (CH); 6.88 dt, 1 H, ^3J = 15.4, ^3J = 1.9 (=CH); 7.39 dt, 1 H, ^3J = 15.4, ^3J = 3.8 (=CH); 8.62 s, 1 H (H-2). ^{13}C NMR (125 MHz, $CDCl_3$): 21.3, 48.8, 62.1, 113.7, 131.5, 143.9, 149.0, 150.4, 152.8, 153.1. IR ($CHCl_3$): 3354, 2997, 2938, 1656, 1589, 1559, 1486, 1439, 1394, 1349. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{11}H_{13}N_4OCl$: 252.0778; found: 252.0781.

(*E*)-3-(9-Benzyl-9*H*-purin-6-yl)-2-(tributylstannyl)prop-2-en-1-ol (**5**) and
(*E*)-3-(9-Benzyl-9*H*-purin-6-yl)-3-(tributylstannyl)prop-2-en-1-ol (**6**)

To a solution of **2c** (0.174 g, 0.66 mmol) and $PdCl_2(PPh_3)_2$ (0.023 g, 5 mole %) in dry THF (8 ml) was added Bu_3SnH (0.30 ml, 0.99 mmol). The resulting mixture was stirred at ambient temperature for 2 h, concentrated in vacuo and column chromatography on silica gel afforded **5** (0.051 g, 14%; EtOAc–hexane, 1:3), **6** (0.130 g, 35%; EtOAc–hexane, 1:1), and the 50:50 mixture of **3c** + **4c** (0.039 g, 22%; EtOAc–MeOH, 20:1).

*Compound **5**, yellow oil*. ^{1}H NMR (300 MHz, $CDCl_3$): 0.88 t, 9 H, ^3J = 7.3 (3 × CH_3); 1.05–1.10 m, 6 H (3 × CH_2); 1.27–1.39 m, 6 H (3 × CH_2); 1.50–1.61 m, 6 H (3 × CH_2); 4.68 s,

2 H (CH_2); 5.43 s, 2 H (CH_2); 7.26–7.35 m, 5 H (Ar-H); 7.44 s, 1 H, $^3J^{H\text{-}Sn}$ = 58 (=CH); 8.04 s, 1 H (H-8); 8.92 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$): 10.2, 13.7, 27.3, 29.0, 47.3, 65.2, 127.8, 128.6, 129.1, 130.1, 131.3, 135.0, 143.9, 151.7, 151.9, 152.1, 168.6. IR ($CHCl_3$): 2958, 2926, 2871, 2852, 1600, 1583, 1561, 1494, 1454, 1402, 1328. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{23}H_{31}N_4OSn$ – C_4H_{10}: 499.1520; found: 499.1539.

Compound ***6****, yellow oil*. ^{1}H NMR (300 MHz, $CDCl_3$): 0.78 t, 9 H, ^3J = 7.3 (3 × CH_3); 0.85–0.98 m, 6 H (3 × CH_2); 1.16–1.28 m, 6 H (3 × CH_2); 1.35–1.47 m, 6 H (3 × CH_2); 3.91 dd, 2 H, ^3J = 7.7, ^3J = 7.1 (CH_2); 5.25 t, 1 H, ^3J = 7.1 (CH); 5.42 s, 2 H (CH_2); 6.60 t, 1 H, ^3J = 7.7, $^3J^{H\text{-}Sn}$ = 59 (=CH); 7.26–7.35 m, 5 H (Ar-H); 7.96 s, 1 H (H-8); 8.89 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$,): 10.9, 13.5, 27.1, 28.7, 47.3, 59.9, 127.9, 128.6, 129.1, 130.0, 134.9, 143.3, 144.8, 145.0, 150.7, 152.6, 161.4. IR ($CHCl_3$): 3340, 2957, 2926, 2871, 2852, 1567, 1497, 1458, 1442, 1402, 1327. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{23}H_{31}N_4OSn$ – C_4H_{10}: 499.1520; found: 499.1500.

(*Z*)-9-Benzyl-6-(2-(tributylstannyl)hept-1-enyl)-9*H*-purine (**7**) and
(*E*)-9-Benzyl-6-(2-(tributylstannyl)hept-1-enyl)-9*H*-purine (**8**)

To a solution of **2b** (0.20 g, 0.66 mmol) and $PdCl_2(PPh_3)_2$ (0.023 g, 5 mole %) in dry THF (8 ml) was added Bu_3SnH (0.30 ml, 0.99 mmol). The resulting mixture was stirred at ambient temperature for 2 h, concentrated in vacuo and column chromatography on silica gel afforded **7** (0.090 g, 25%; EtOAc–hexane, 1:9), **8** (0.090 g, 25%; EtOAc–hexane, 1:9), and the 33:66 mixture of **3b** + **4b** (0.046 g, 24%; EtOAc–hexane, 1:1).

Compound ***7****, yellowish oil*. ^{1}H NMR (300 MHz, $CDCl_3$): 0.81–0.89 m, 12 H (4 × CH_3); 0.94–1.02 m, 8 H (4 × CH_2); 1.19–1.34 m, 8 H (4 × CH_2); 1.41–1.51 m, 8 H (4 × CH_2); 2.37 m, 2 H (CH_2); 5.43 s, 2 H (CH_2); 7.25–7.36 m, 5 H (Ar-H); 7.80 t, 1 H, ^3J = 7.4, $J^{H\text{-}Sn}$ = 101.7 (=CH); 7.96 s, 1 H (H-8); 8.80 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$): 12.3, 13.9, 14.0, 22.6, 27.2, 29.1, 29.4, 31.8, 35.5, 47.0, 127.6, 128.4, 129.0, 130.3, 135.4, 142.6, 143.1, 151.4, 151.9, 156.0, 161.4. IR ($CHCl_3$): 2870, 2854, 1577, 1566, 1497, 1456, 1442, 1403, 1376, 1325. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{27}H_{39}N_4Sn$ – C_4H_{10}: 539.2197; found: 539.2224.

Compound ***8****, yellowish oil*. ^{1}H NMR (300 MHz, $CDCl_3$): 0.76–0.81 m, 12 H (4 × CH_3); 0.85–0.93 m, 8 H (4 × CH_2); 1.14–1.31 m, 8 H (4 × CH_2); 1.35–1.40 m, 8 H (4 × CH_2); 2.12 m, 2 H (CH_2); 5.42 s, 2 H (CH_2); 6.16 t, 1 H, ^3J = 6.9, $^3J^{H\text{-}Sn}$ = 61.8 (=CH); 7.25–7.36 m, 5 H (Ar-H); 7.94 s, 1 H (H-8); 8.87 s, 1 H (H-2). ^{13}C NMR (75 MHz, $CDCl_3$): 10.9, 13.55, 13.6, 22.3, 27.3, 28.8, 29.0, 31.3, 32.1, 47.0, 127.7, 128.4, 129.0, 130.3, 135.3, 139.9, 142.9, 147.1, 150.8, 152.4, 163.5. IR ($CHCl_3$): 2870, 2854, 1577, 1566, 1497, 1456, 1442, 1403, 1376, 1325. HRMS (EI): *m/z* $[M]^+$ calculated for $C_{27}H_{39}N_4Sn$ – C_4H_{10}: 539.2197; found: 539.2224.

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