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Facile Cu-free Sonogashira cross-coupling of nucleoside C-6 arylsulfonates with terminal alkynes

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ABSTRACT

The combination of $PdCl_2[CH_3CN]_2$ with XPhos is an efficient catalytic system for the Sonogashira-type cross-coupling of 2′-deoxyguanosine O^6-arylsulfonates with terminal alkynes. The reactions generally proceed under mild conditions requiring no Cu co-catalyst to give the corresponding C-6-alkynylated deoxynucleosides in moderate to good yields.

1. Introduction

The acetylenic moiety is commonly found in a number of natural products and biologically active molecules.[1] Once incorporated in organic molecules, the acetylenic core can serve as important synthetic intermediates because alkynes can undergo a wide variety of reactions. As a result, this has prompted interest in the design of efficient synthetic methods for the incorporation of the acetylenic unit in organic molecules. One such method for the incorporation of the acetylenic unit in organic molecules is the Sonogashira cross-coupling method.[2] In recent years, the Sonogashira reaction has undoubtedly become one of the most widely used reactions in organic synthesis for the formation of a C(sp)–C(sp^2) bond. In the original Sonogashira cross-coupling reaction, a terminal alkyne is coupled with an aryl or vinyl halide or triflate, using a palladium catalyst and a Cu(I) salt as co-catalyst.[3] Various modifications of the original Sonogashira cross-coupling reaction have been reported in the past decade.[4–15]

The modification of nucleosides continues to be an important area in organic research due to the wide variety of applications that modified nucleosides possess and the biological importance of nucleosides in general. For example, modified nucleosides have been shown to act as enzyme inhibitors and antagonists, and have the potential to be lowly toxic, yet effective as antiviral and anticancer agents.[16,17] Modified nucleoside analogs, substituted at the C-6 position, have been reported to possess a wide range of biological activities.[18–22] The alkynylation of nucleosides by the Sonogashira cross-coupling reaction is well documented in the literature.[15,21,23–26] However, most of the successful Sonogashira cross-coupling alkynylation of nucleosides, reported thus far, have involved the use of halopurine nucleosides as electrophiles reacting with terminal alkynes.

An important modification of the Sonogashira cross-coupling reaction we have been exploring in our lab, for the synthesis of modified nucleosides, is the Cu-free method.[15] The use of copper is sometimes limited by the formation of insoluble copper acetylides, which are potentially explosive. In addition, Buchwald and co-workers reported the potential oligomerization of the alkyne starting material when using a copper co-catalyst in the conventional Sonogashira cross-coupling method.[4] Historically, the identity of the group being displaced in a Sonogashira-type cross-coupling has been a halide. However, examples have been cited in the literature in which the halogen has been replaced with a sulfonate as the leaving group in the synthesis of modified nucleosides. For example, the facile displacement of a sulfonate on the C-6 position of nucleosides by oxygen and nitrogen nucleophiles has been reported.[27] An analogous Suzuki-type cross-coupling has been developed in which nucleoside arylsulfonates were reacted with arylboronic acids to create a new C–C bond at the C-6 position of 2′-deoxyguanosine.[28]

The use of tosylates as the leaving group in a Sonogashira-type cross-coupling, especially in the coupling of non-nucleosidic aromatic compounds with terminal acetylenes, has been reported.[4,29] A Cu-free Pd-catalyzed cross-coupling of vinyl tosylates with terminal acetylenes has been reported by Fu and co-workers.[29] Similarly, Gelman and co-workers reported the first Sonogashira-type cross-coupling of aryl tosylates with terminal alkynes under Cu-free conditions.[4] However, to the best of our knowledge, there has been no literature precedence on the displacement of sulfonates in general, and tosylates in particular, on nucleosides using terminal alkynes through a Sonogashira-type cross-coupling.

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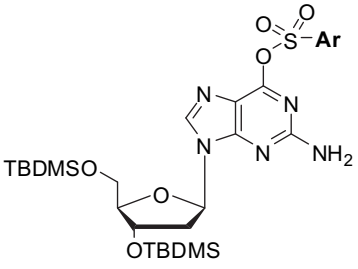
To add to the current state of knowledge in the field, our group has been particularly interested in investigating the development of efficient methods to synthesize C-6-alkynyl-substituted nucleosides. As a part of our ongoing interest in transition metal-mediated syntheses of modified nucleosides,[30] we recently reported a modified Sonogashira-type cross-coupling in the C-6-alkynylation of protected 2′-deoxyadenosine.[15] Therefore, in this work, we set out to evaluate both the conventional Sonogashira cross-coupling method and the modified versions, in the coupling of protected 2′-deoxyguanosine sulfonates with terminal acetylenes, toward the synthesis of C-6-alkynylated deoxynucleosides. Herein, we report our initial results that show a convenient Sonogashira-type cross-coupling of protected 2′-deoxyguanosine sulfonates with terminal acetylenes to afford C-6-alkynyl-substituted nucleosides.

2. Results and discussion

Our synthetic strategy toward the C-6-alkynylated deoxyribonucleoside derivatives involved a Sonogashira-type cross-coupling of protected 2′-deoxyguanosine sulfonates with terminal acetylenes. Initial attempts to sulfonate the unprotected 2′-deoxyguanosine resulted in a complex mixture of products probably due to the reactivity of the polar hydroxyl groups with the sulfonyl chloride. We then decided to protect the hydroxyl groups prior to sulfonation. In order to obtain the deoxyribonucleoside starting material for cross-coupling, the hydroxyl groups of commercially available 2′-deoxyguanosine (dG) were protected as the silyl ether using *tert*-butyldimethylsilyl chloride (TBDMS-Cl), imidazole, and DMF. The O^6 position of the protected dG was then sulfonated using either 2-mesitylenesulfonyl chloride or *p*-toluenesulfonyl chloride (Fig. 1).



1a: Ar = 2,4,6-trimethylphenyl
1b: Ar = 4-methylphenyl

Figure 1. Structures of nucleoside arylsulfonates synthesized from 2′-deoxyguanosine and evaluated.

Following sulfonation, the dG sulfonates were coupled with phenylacetylene for initial optimization using a Cu-free Sonogashira-type cross-coupling reaction. The reactivities of protected 2′-deoxyguanosine *p*-toluenesulfonate and protected 2′-deoxyguanosine mesitylenesulfonate were compared and results showed a greater reactivity of 2′-deoxyguanosine *p*-toluenesulfonate, perhaps due to the steric hindrance of the mesitylenesulfonate. We then used 2′-deoxyguanosine *p*-toluenesulfonate as the nucleoside starting material for the optimization experiments.

In the optimization experiments, several different combinations of palladium species, ligands, bases, and solvents were investigated. Three different Pd species, $PdPCl_2[CH_3CN]_2$, $Pd(PPh_3)_4$, and $PdCl_2(PPh_3)_2$, and three ligands, **L-1**, **L-2**, and **L-3** were investigated (Fig. 2). Two bases Cs_2CO_3 and Et_3N were used while CH_3CN, DMF, dioxane, DME, toluene, and THF were investigated as possible solvents. The use of Cs_2CO_3 was discontinued after poor solubility and very low percent yields were recorded each time the base was used during the optimization experiments. The use of Et_3N as the organic base gave better results with all the solvents tested. Among the solvents examined, THF, based on solubility and percentage recovery of product, turned out to be the best and was used throughout the optimization. The ligands and Pd species were selected for this experiment because they had been used effectively in experiments similar to this one in previously published work.[4,15]

For preliminary studies, we used 5 mol % Pd species, 15 mol % ligand, and 4.5 equiv Et_3N as base for the coupling of 2′-deoxyguanosine sulfonates with phenylacetylene in THF at 90 °C. In the course of the optimization experiments, it was noticed that the combination of any of the Pd species with any of the ligands and Et_3N in THF resulted in product formation (Table 1). When Pd $(Ph_3P)_4$ was used as the Pd species, a better yield was obtained using **L-3** (Table 1, entry 3), which is consistent with results from our previous work, albeit, Et_3N was used in this case and not Cs_2CO_3 due to solubility problems. The yields for the same Pd species were rather low using **L-1** and **L-2** (Table 1, entries 1 and 2). When the Pd species was switched to $PdCl_2(PPh_3)_2$, a much better yield was obtained with **L-1**, albeit, the yields were comparable between **L-1** and **L-2** (Table 1, entries 4 and 5). However, the yield with **L-3** dropped from 85% (Table 1, entry 3) to 57% (Table 1, entry 6) when the Pd species $Pd(Ph_3P)_4$ was replaced with $PdCl_2(PPh_3)_2$. The use of $PdCl_2(CH_3CN)_2$ as the Pd species resulted in a much better yield of 86% using **L-1** in just 8 h (Table 1, entry 7). When the same reaction was run, under the same set of conditions as in entry 7, for 24 h, a slightly lower yield of 79% was obtained. Comparatively, the yields were much lower with **L-2** and **L-3** when $PdCl_2(CH_3CN)_2$ was used as the Pd species (Table 1, entries 8 and 9). Although the effect of the ligands on the different Pd species has not been investigated at this time, it can be deduced from the optimization experiments that **L-1** works best with $PdCl_2(CH_3CN)_2$, **L-2** works best with

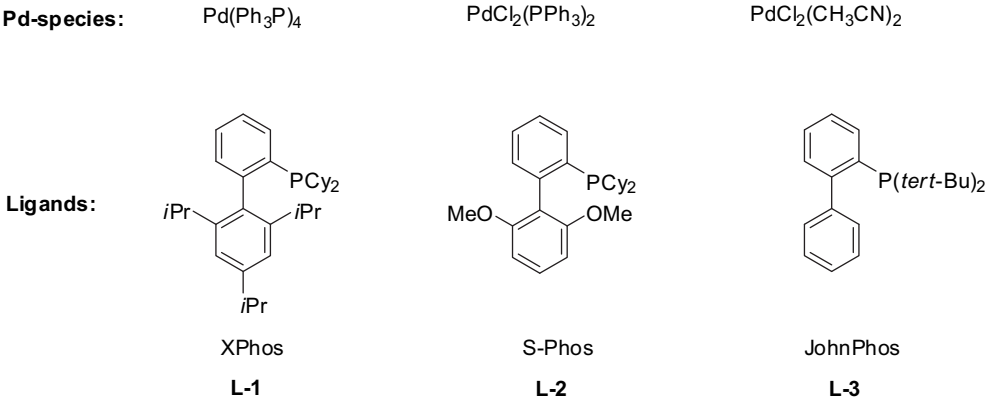
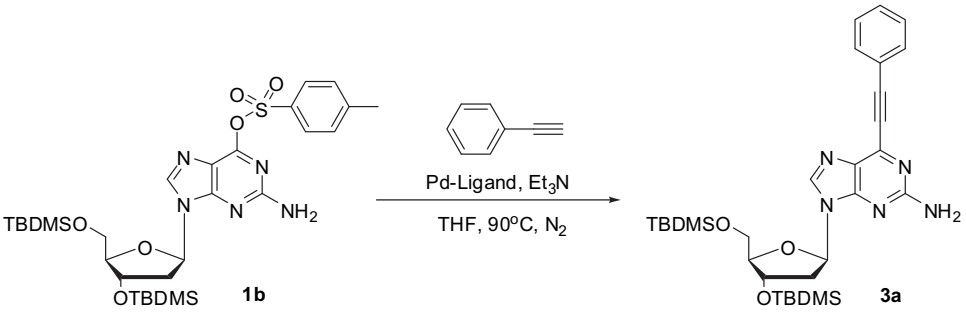


Figure 2. Pd-species and ligands investigated. The symbol Cy_2 stands for dicyclohexyl.

$PdCl_2(PPh_3)_2$, and **L-3** works best with $Pd(Ph_3P)_4$ (Table 1, entries 3, 5, and 7). It should be noted that although the yields of entry 3 and 7, 85% and 86%, respectively, are comparable, we chose the system in entry 7 because of less time required for reaction completion and because the Pd species and ligand were more readily available to us.

We also decided to investigate the optimum Pd-species/ligand ratio. Thus, using the optimized reaction conditions, we carried out reactions with different ratios of $PdCl_2(CH_3CN)_2$ and **L-1** with or without CuI (Table 2).

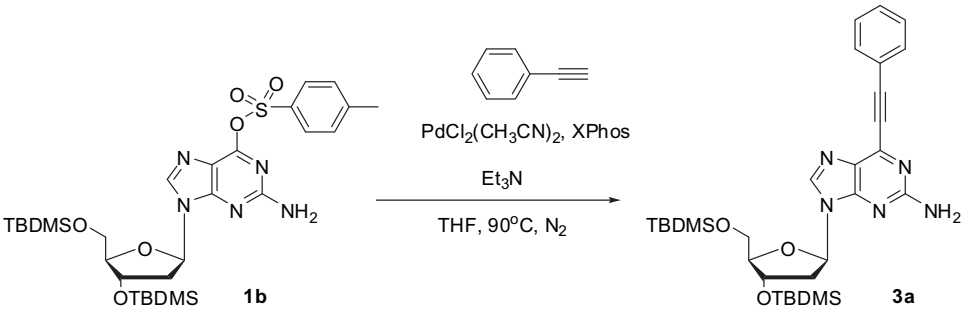
Table 1
Optimization study for the Sonogashira cross-coupling of phenylacetylene with 2′-deoxyguanosine *p*-toluenesulfonate



Entry	Pd-species	Ligand	Time (h)	Yield (%)[a,b]
1	$Pd(Ph_3P)_4$	**L-1**	24	49
2	$Pd(Ph_3P)_4$	**L-2**	24	34
3	$Pd(Ph_3P)_4$	**L-3**	24	85
4	$PdCl_2(PPh_3)_2$	**L-1**	24	76
5	$PdCl_2(PPh_3)_2$	**L-2**	24	73
6	$PdCl_2(PPh_3)_2$	**L-3**	24	57
7	$PdCl_2(CH_3CN)_2$	**L-1**	8	86
8	$PdCl_2(CH_3CN)_2$	**L-2**	24	53
9	$PdCl_2(CH_3CN)_2$	**L-3**	24	48

[a] The percentage yield is the calculated yield of the recovered product from an average of two runs.
[b] Reactions were carried out in THF at 90 °C, with 1.0 equiv of protected 2′-deoxyguanosine *p*-toluenesulfonate, 1.5 equiv of phenylacetylene, 0.05 equiv of Pd-species, 0.15 equiv of ligand, and 4.5 equiv of Et_3N. **L-1**: XPhos; **L-2**: S-Phos; **L-3**: JohnPhos.

Table 2
Optimization of catalyst-ligand ratio in the coupling of 2′-deoxyguanosine sulfonates with phenylacetylene



Entry	CuI (mol %)	Pd-species (mol %)	Ligand (mol %)	Yield (%)[a,b]
1	0	5	15	86
2	5	5	15	83
3	10	10	30	63
4	15	15	45	58
5	0	10	30	75
6	0	2.5	7.5	72

[a] The percentage yield is the calculated yield of the recovered product after two runs. The Pd-species is $PdCl_2(CH_3CN)_2$. Ligand (**L-1**) is 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos). All reactions were run for 24 h except in entry 6 where it took 36 h for reaction completion.
[b] Reactions were carried out with 1.0 equiv of protected 2′-deoxyguanosine *p*-toluenesulfonate, 1.5 equiv of phenylacetylene, 4.5 equiv of Et_3N, and **L-1** as XPhos.

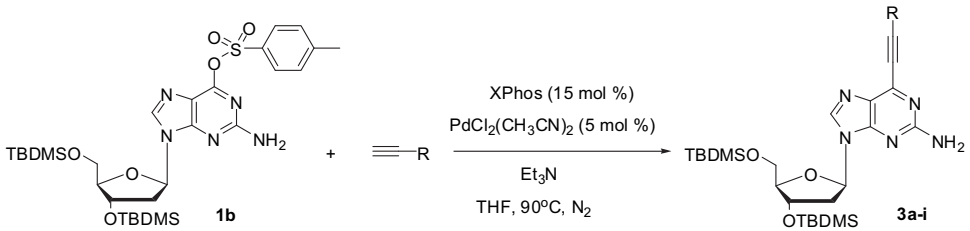
Our preliminary experiments established the combination of $PdCl_2(CH_3CN)_2$/**L-1** and Et_3N in THF at 90 °C as the optimal conditions for the Sonogashira-type cross-coupling of 2′-deoxyguanosine sulfonates with phenylacetylene. Since CuI is commonly used in the conventional Sonogashira cross-coupling reactions, and since we are using sulfonates for the first time as the leaving group in a Sonogashira-type cross-coupling, we decided to investigate if the use of CuI would be more efficient.

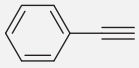
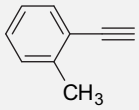
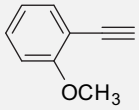
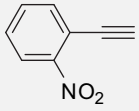
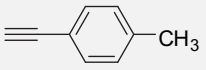
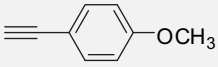
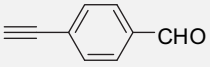
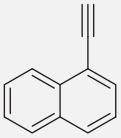
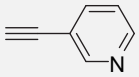
The most effective catalytic system was the use of 5 mol % $PdCl_2(CH_3CN)_2$, 15 mol % **L-1** under Cu-free conditions (Table 2, entry 1). When 5 mol % CuI was used in the presence of 5 mol % $PdCl_2(CH_3CN)_2$and 15 mol % **L-1**, there was no significant change in the yield from 86% to 83% (Table 2, entry 2). Increasing the catalyst loading did not result in improvement in the yield but rather the yield decreased. At 10 mol % CuI, 10 mol % $PdCl_2(CH_3CN)_2$, and 30 mol % **L-1**, the yield of product decreased to 63% (Table 2,

entry 3). With a catalyst loading of 15 mol % CuI, 15 mol % $PdCl_2(CH_3CN)_2$, and 45 mol % **L-1**, only a modest yield of 58% was obtained (Table 2, entry 4). This proved to us that the reaction should be carried out effectively under Cu-free conditions. Therefore, as a logical next step, we decided to investigate the optimum ratio for the Pd-species and **L-1**. Increasing the catalyst loading to 10 mol % $PdCl_2(CH_3CN)_2$, 30 mol % **L-1** under Cu-free conditions resulted in a decrease in the yield from 86% to 75% (Table 2, entry 5). Also, decreasing the catalyst loading to 2.5 mol % $PdCl_2(CH_3CN)_2$, 7.5 mol % **L-1** under Cu-free conditions resulted in 72% yield of product with reaction only complete after 36 h (Table 2, entry 6). Therefore, we established that the most effective catalytic system is the use of 5 mol % $PdCl_2(CH_3CN)_2$ and 15 mol % **L-1** under Cu-free conditions.

Our optimized reaction conditions were used to study the scope of the Sonogashira-type cross-coupling of 2′-deoxyguanosine *p*-toluenesulfonate with various terminal acetylenes incorporating a wide array of functional groups (Tables 3 and 4). All the aromatic acetylenes investigated, with the exception of 2-nitrophenylacetylene, reacted to give products in good to excellent yields (Table 3). We found that aromatic acetylenes containing electron-releasing groups were more reactive with 2′-deoxyguanosine *p*-toluenesulfonate (Table 3, entries 2, 3, 5, and 6). Among the aromatic acetylenes containing electron-releasing groups, the *ortho*-substituted derivatives (Table 3, entries 2 and 3) gave better yields than the *para*-substituted derivatives (Table 3, entries 5 and 6). Two aromatic acetylenes containing electron-withdrawing groups, an *ortho*-substituted nitro group (Table 3,

Table 3
Sonogashira-type cross-coupling of aromatic acetylenes with 2′-deoxyguanosine *p*-toluenesulfonate



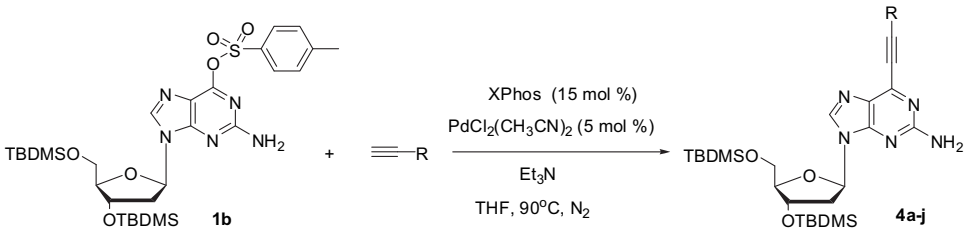
Entry	R	Product	Time (h)	Yield (%)[a]
1		**3a**	8	86
2		**3b**	10	91
3		**3c**	10	95
4		**3d**	24	0
5		**3e**	12	74
6		**3f**	12	82
7		**3g**	24	51
8		**3h**	10	85
9		**3i**	12	59

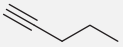
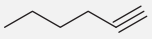
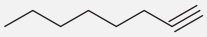
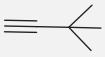
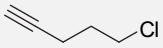
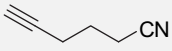
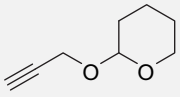
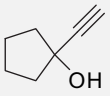
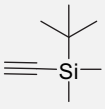
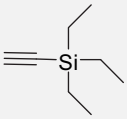
[a] Reactions were carried out in THF at 90 °C, nucleoside concentration was 0.148 mmol in 2 mL THF. Reactions were carried out with 1.0 equiv of protected 2′-deoxyguanosine *p*-toluenesulfonate, 1.5 equiv of terminal alkyne, 0.05 equiv of $PdCl_2(CH_3CN)_2$, 0.15 equiv of XPhos, and 4.5 equiv of Et_3N.

entry 4) and a *para*-substituted formyl group (Table 3, entry 7), were investigated. The *ortho*-substituted aromatic acetylene did not result in any product formation; instead a substantial amount of starting material was isolated (Table 3, entry 4). However, the *para*-substituted aromatic acetylene gave a modest 51% yield of product formation (Table 3, entry 7). To explore the versatility of our optimized cross-coupling conditions, we decided to investigate the reactivity of terminal acetylenes containing an extended aromatic system or heterocycle. The extended aromatic terminal acetylene, 1-ethynylnaphthalene, gave the cross-coupling product **3h** in 85% yield (Table 3, entry 8). The reactivity of *N*-heteroaryl acetylene was also investigated. For example, 3-pyridinyl acetylene reacted with 2′-deoxyguanosine *p*-toluenesulfonate to give the cross-coupling product **3i** in 59% yield (Table 3, entry 9).

(Table 4, entries 1–3). The use of a more substituted aliphatic acetylene, 3,3-dimethyl-1-butyne, resulted in no product formation after 24 h (Table 4, entry 4). However, the use of a substrate, 1-pentyne, substituted at the fifth carbon with a chloro- or cyano-group resulted in a slight increase in the yield of the cross-coupled products **4e** and **4f** (Table 4, entries 5 and 6). The optimized reaction condition also tolerated acid sensitive functional groups, such as OTHP ether containing terminal acetylene (Table 4, entry 7). For example, the reaction of the terminal acetylene 2-(prop-2-ynyloxy)tetrahydro-2*H*-pyran with 2′-deoxyguanosine *p*-toluenesulfonate resulted in the cross-coupled product **4g** obtained in a modest 55% yield (Table 4, entry 7). The terminal acetylene, 1-ethynylcyclopentanol also reacted with 2′-deoxyguanosine *p*-toluenesulfonate to give 75% of the cross-coupled product **4h**

Table 4
Sonogashira-type cross-coupling of aliphatic acetylenes with 2′-deoxyguanosine *p*-toluenesulfonate



Entry	R	Product	Time (h)	Yield (%)[a]
1		**4a**	12	66
2		**4b**	12	63
3		**4c**	12	58
4		**4d**	24	0
5		**4e**	10	70
6		**4f**	10	69
7		**4g**	12	55
8		**4h**	12	75
9		**4i**	12	72
10		**4j**	12	79

[a] Reactions were carried out in THF at 90 °C, nucleoside concentration was 0.148 mmol in 2 mL THF. Reactions were carried out with 1.0 equiv of protected 2′-deoxyguanosine *p*-toluenesulfonate, 1.5 equiv of terminal alkyne, 0.05 equiv of $PdCl_2(CH_3CN)_2$, 0.15 equiv of XPhos, and 4.5 equiv of Et_3N.

After successfully applying our optimized reaction conditions to the cross-coupling of aromatic acetylenes, we then investigated the cross-coupling of aliphatic acetylenes (Table 4). With simple unsubstituted aliphatic acetylenes, moderate to good yields were obtained in the cross-coupling with 2′-deoxyguanosine *p*-toluenesulfonate

(Table 4, entry 8). Terminal alkynes having the silyl moiety, *tert*-butyl(ethynyl)dimethylsilane and triethyl(ethynyl)silane, also reacted with 2′-deoxyguanosine *p*-toluenesulfonate to afford moderate to good yields of the cross-coupling products **4i** and **4j**, respectively (Table 4, entries 9 and 10).

3. Conclusion

In summary, we have developed a Cu-free Sonogashira-type cross-coupling of terminal acetylenes of varying functionality with the O^6-arylsulfonyl derivative of 2′-deoxyguanosine. The reactions generally proceed to completion within 24 h, afford moderate to good yields, and are tolerant to different functional groups. Efforts are underway to optimize the reaction conditions further and expand the scope to incorporate other nucleosides and terminal acetylenes.

4. Experimental section

4.1. General methods

All reactions were carried out in oven-dried glassware under a nitrogen atmosphere. All the reagents were obtained from commercial sources and were used without further purification. Thin-layer chromatography was performed on silica gel plates containing fluorescent indicator. Column chromatographic separation was performed using 230–400 mesh silica gel. ^{1}H NMR spectra (300 MHz) and ^{13}C data (75 MHz) were obtained in $CDCl_3$ or DMSO-d_6. Coupling constants (J) are reported in Hertz (Hz). The sugar protons are numbered 1′–5′ starting at the anomeric carbon and moving along the carbon chain to the primary carbinol carbon.

4.2. Typical procedure for the cross-coupling of 2′-deoxyguanosine sulfonates with terminal alkynes

The Pd species (0.0074 mmol), ligand (0.0222 mmol), 2′-deoxyguanosine sulfonate (0.1484 mmol), Et_3N (0.666 mmol), and THF (2 mL) were placed in the reaction vial. The vial was flushed with N_2 gas and stirred at room temperature for 30 min. Half of the terminal alkyne was added to the vial (0.111 mmol). The vial was flushed with N_2 gas and stirred in an oil bath at 90 °C for 30 min. The second half of the terminal alkyne was added to the vial (0.111 mmol). The vial was flushed with N_2 gas and stirred in an oil bath at 90 °C until completion of reaction. The reaction mixture was then cooled to room temperature, diluted with EtOAc, and washed with water. The combined organic layers were dried with anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel, packed with CH_2Cl_2, and eluting sequentially with 2% EtOAc/CH_2Cl_2, 5% EtOAc/CH_2Cl_2, and 8% EtOAc/CH_2Cl_2 to give the desired product.

4.3. Experimental data

*4.3.1. 2-Amino-6-[phenylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**3a**).* Brown oil (86%), R_f (5% EtOAc in CH_2Cl_2)=0.33. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.10 (s, 1H, Ar–H), 7.71–7.69 (m, 2H, Ar–H,), 7.38–7.35 (m, 3H, Ar–H), 6.34 (t, 1H, 1′, J=6.3 Hz), 5.27 (br s, 2H, NH_2), 4.59–4.56 (m, 1H, 3′), 3.99 (app q, 1H, 4′, $J\approx$3.3 Hz), 3.81 (dd, 1H, 5′, J=4.1, 11.3 Hz), 3.75 (dd, 1H, 5′, J=3.3, 11.3 Hz), 2.62–2.54 (m, 1H, 2′), 2.40–2.33 (m, 1H, 2′), 0.92, 0.89 (2s, 18H, $SiC(CH_3)_3$), 0.11, 0.07 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.9, 153.7, 141.8, 140.2, 132.9, 130.1, 129.1, 128.5, 128.4, 121.3, 88.0, 83.9, 72.1, 62.9, 41.1, 26.1, 25.9, 18.5, 18.1, −4.6, −5.3. HRMS exact mass calculated for $C_{30}H_{45}N_5O_3Si_2$ (M^++H) 580.3061, found 580.3128.

*4.3.2. 2-Amino-6-[2-(methyl)phenylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**3b**).* Yellow oil (91%), R_f (5% EtOAc in CH_2Cl_2)=0.25. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07 (s, 1H, Ar–H), 7.64 (d, 1H, Ar–H, J=7.7 Hz), 7.30–7.14 (m, 3H, Ar–H), 6.34 (t, 1H, 1′, J=6.3 Hz), 5.29 (br s, 2H, NH_2), 4.60–4.57 (m, 1H, 3′), 3.98 (app q, 1H, 4′, $J\approx$3.3 Hz), 3.80 (dd, 1H, 5′, J=4.4, 11.3 Hz), 3.74 (dd, 1H, 5′, J=3.3, 11.3 Hz), 2.63–2.55 (m, 1H, 2′), 2.60 (s, 3H, CH_3), 2.40–2.33 (m, 1H, 2′), 0.90, 0.89 (2s, 18H, $SiC(CH_3)_3$), 0.09, 0.06 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.3, 153.5, 141.7, 141.3, 133.1, 131.2, 130.1, 129.5, 125.7, 122.4, 121.4, 87.9, 87.0, 83.8, 72.1, 62.9, 40.9, 26.1, 25.9, 21.0, 18.5, 18.1, −4.6, −5.4. HRMS exact mass calculated for $C_{31}H_{47}N_5O_3Si_2$ (M^++H) 594.3217, found 594.3275.

*4.3.3. 2-Amino-6-[2-(methoxy)phenylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**3c**).* Yellow oil (95%), R_f (8% EtOAc in CH_2Cl_2)=0.11. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07 (s, 1H, Ar–H), 7.65 (d, 1H, Ar–H, J=9.1 Hz), 7.36–7.33 (m, 1H, Ar–H), 6.93–6.91 (m, 2H, Ar–H), 6.34 (t, 1H, 1′, J=6.1 Hz), 5.41 (br s, 2H, NH_2), 4.60–4.56 (m, 1H, 3′), 3.98 (app q, 1H, 4′, $J\approx$3.6 Hz), 3.94 (s, 3H, OCH_3), 3.81 (dd, 1H, 5′, J=4.1, 11.3 Hz), 3.75 (dd, 1H, 5′, J=3.3, 11.3 Hz), 2.61–2.53 (m, 1H, 2′), 2.40–2.32 (m, 1H, 2′), 0.91, 0.90 (2s, 18H, $SiC(CH_3)_3$), 0.10, 0.07 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.1, 159.3, 153.5, 141.3, 134.7, 131.6, 129.2, 128.5, 120.5, 111.1, 110.7, 94.5, 87.9, 83.8, 72.1, 62.9, 56.0, 41.1, 29.8, 25.9, 18.5, 18.1, −4.7, −5.3. HRMS exact mass calculated for $C_{31}H_{47}N_5O_4Si_2$ (M^++H) 610.3167, found 610.3233.

*4.3.4. 2-Amino-6-[4-(methyl)phenylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**3e**).* Brown oil (74%), R_f (5% EtOAc in CH_2Cl_2)=0.25. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07 (s, 1H, Ar–H), 7.57 (d, 2H, Ar–H, J=8.3 Hz), 7.14 (d, 2H, Ar–H, J=7.4 Hz), 6.32 (t, 1H, 1′, J=6.1 Hz), 5.16 (br s, 2H, NH_2), 4.58–4.57 (m, 1H, 3′), 3.98 (app q, 1H, 4′, $J\approx$3.3 Hz), 3.81–3.74 (m, 2H, 5′), 2.60–2.52 (m, 1H, 2′), 2.37 (s, 3H, CH_3), 2.27–2.00 (m, 1H, 2′), 0.89, 0.88 (2s, 18H, $SiC(CH_3)_3$), 0.08, 0.05 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.0, 153.6, 141.6, 140.5, 138.1, 132.8, 129.3, 128.5, 118.3, 98.5, 88.0, 83.9, 82.4, 72.1, 62.9, 41.0, 25.9, 21.8, 18.5, 18.1, −4.7, −5.4. HRMS exact mass calculated for $C_{31}H_{47}N_5O_3Si_2$ (M^++H) 594.3217, found 594.3271.

*4.3.5. 2-Amino-6-[4-(methoxy)phenylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**3f**).* Brown oil (82%), R_f (5% EtOAc in CH_2Cl_2)=0.12. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07 (s, 1H, Ar–H), 7.65 (d, 2H, Ar–H, J=8.5 Hz), 6.88 (d, 2H, Ar–H, J=8.8 Hz), 6.34 (t, 1H, 1′, J=6.6 Hz), 5.14 (br s, 2H, NH_2), 4.60–4.56 (m, 1H, 3′), 3.99 (app q, 1H, 4′, $J\approx$3.5 Hz), 3.83 (s, 3H, OCH_3), 3.81 (dd, 1H, 5′, J=4.1, 11.3 Hz), 3.75 (dd, 1H, 5′, J=3.3, 11.3 Hz), 2.64–2.55 (m, 1H, 2′), 2.40–2.33 (m, 1H, 2′), 0.91, 0.90 (2s, 18H, $SiC(CH_3)_3$), 0.10, 0.07 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.1, 158.8, 153.6, 141.6, 134.7, 133.2, 129.0, 115.0, 114.2, 113.5, 88.0, 84.0, 82.0, 72.1, 62.9, 55.4, 41.0, 25.9, 18.5, 18.1, −4.7, −5.3. HRMS exact mass calculated for $C_{31}H_{47}N_5O_4Si_2$ (M^++H) 610.3167, found 610.3225.

*4.3.6. 2-Amino-6-[4-(formyl)phenylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**3g**).* Brown oil (51%), R_f (5% EtOAc in CH_2Cl_2)=0.22. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.03 (s, 1H, CHO), 8.14 (s, 1H, Ar–H), 7.87 (2d, 4H, Ar–H, J=8.3 Hz), 6.35 (t, 1H, 1′, J=6.6 Hz), 5.21 (br s, 2H, NH_2), 4.61–4.57 (m, 1H, 3′), 4.00 (app q, 1H, 4′, $J\approx$3.3 Hz), 3.83 (dd, 1H, 5′, J=4.1, 11.3 Hz), 3.76 (dd, 1H, 5′, J=3.3, 11.3 Hz), 2.63–2.54 (m, 1H, 2′), 2.42–2.35 (m, 1H, 2′), 0.91, 0.90 (2s, 18H, $SiC(CH_3)_3$), 0.10, 0.08 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.3, 164.5, 159.2, 154.3, 136.5, 134.2, 133.4, 133.3, 129.5, 129.2, 128.5, 88.1, 84.1, 72.1, 62.8, 41.3, 26.1, 25.7, 18.5, 18.1, −4.7, −5.4. HRMS exact mass calculated for $C_{31}H_{45}N_5O_4Si_2$ (M^++H) 608.3010, found 608.3080.

*4.3.7. 2-Amino-6-[naphthalene-1-ylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**3h**).* Brown oil (85%), R_f (5% EtOAc in CH_2Cl_2)=0.13. ^{1}H NMR

(300 MHz, $CDCl_3$) δ: 8.63 (d, 1H, Ar–H, J=8.5 Hz), 8.15 (s, 1H, Ar–H), 7.96–7.85 (m, 3H, Ar–H), 7.66–7.61 (m, 1H, Ar–H), 7.56–7.44 (m, 2H, Ar–H), 6.37 (t, 1H, 1′, J=6.5 Hz), 5.26 (br s, 2H, NH_2), 4.63–4.59 (m, 1H, 3′), 4.01 (app q, 1H, 4′, $J\approx$3.4 Hz), 3.83 (dd, 1H, 5′, J=4.1, 11.3 Hz), 3.77 (dd, 1H, 5′, J=3.3, 11.3 Hz), 2.66–2.57 (m, 1H, 2′), 2.43–2.34 (m, 1H, 2′), 0.92, 0.90 (2s, 18H, $SiC(CH_3)_3$), 0.11, 0.09 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.5, 152.3, 150.6, 149.8, 146.1, 135.6, 134.6, 133.8, 124.7, 120.4, 108.6, 88.3, 86.8, 84.4, 71.8, 62.7, 41.9, 38.0, 29.7, 25.8, 24.1, 18.5, 18.1, −4.7, −5.3. HRMS exact mass calculated for $C_{34}H_{47}N_5O_3Si_2$ (M^++H) 630.3217, found 630.3290.

*4.3.8. 2-Amino-6-[pyridin-3-ylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**3i**).* Brown oil (59%), R_f (5% EtOAc in CH_2Cl_2)=0.20. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.95 (s, 1H, Ar–H), 8.65 (br s, 1H, Ar–H), 8.28 (s, 1H, Ar–H), 8.08 (d, 1H, Ar–H, J=7.7 Hz), 7.39–7.35 (m, 1H, Ar–H), 6.34 (t, 1H, 1′ J=6.6 Hz), 5.92 (br s, 2H, NH_2), 4.60–4.56 (m, 1H, 3′), 4.02 (app q, 1H, 4′, $J\approx$3.0 Hz), 3.85 (dd, 1H, 5′, J=3.6, 11.3 Hz), 3.77 (dd, 1H, 5′, J=3.0, 11.3 Hz), 2.57–2.49 (m, 1H, 2′), 2.45–2.37 (m, 1H, 2′), 0.91, 0.90 (2s, 18H, $SiC(CH_3)_3$), 0.10, 0.09 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.3, 150.7, 149.9, 149.3, 144.7, 140.5, 139.8, 129.3, 123.6, 116.5, 84.5, 83.8, 83.7, 74.6, 71.9, 62.8, 41.3, 25.9, 18.5, 18.2, −5.8, −5.4. HRMS exact mass calculated for $C_{29}H_{44}N_6O_3Si_2$ (M^++H) 581.3013, found 581.3086.

*4.3.9. 2-Amino-6-[pent-1-ynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**4a**).* Yellow oil (66%), R_f (5% EtOAc in CH_2Cl_2)=0.12. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07 (s, 1H, Ar–H), 6.31 (t, 1H, 1′, J=6.6 Hz), 5.33 (br s, 2H, NH_2), 4.58–4.54 (m, 1H, 3′), 3.98 (app q, 1H, 4′, $J\approx$3.3 Hz), 3.81 (dd, 1H, 5′, J=4.1, 11.3 Hz), 3.74 (dd, 1H, 5′, J=3.0, 11.3 Hz), 2.59–2.51 (m, 1H, 2′), 2.54 (t, 2H, J=7.1 Hz), 2.39–2.31 (m, 1H, 2′), 1.77–1.65 (m, 2H), 1.05 (t, 3H, J=7.3 Hz), 0.90, 0.89 (2s, 18H, $SiC(CH_3)_3$), 0.09, 0.07 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.7, 155.9, 154.5, 146.6, 140.4, 134.0, 129.7, 129.0, 117.1, 87.9, 84.0, 72.0, 62.9, 41.0, 26.0, 21.8, 18.5, 18.1, −4.7, −5.3. HRMS exact mass calculated for $C_{27}H_{47}N_5O_3Si_2$ (M^++H) 546.3217, found 546.3290.

*4.3.10. 2-Amino-6-[hex-1-ynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**4b**).* Brown oil (63%), R_f (5% EtOAc in CH_2Cl_2)=0.25. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.03, (s, 1H, Ar–H), 6.31 (t, 1H, 1′, J=6.6 Hz), 5.07 (br s, 2H, NH_2), 4.59–4.55 (m 1H, 3′), 3.98 (app q, 1H, 4′, $J\approx$3.4 Hz), 3.80 (dd, 1H, 5′, J=4.1, 11.2 Hz), 3.74 (dd, 1H, 5′, J=3.6, 11.2 Hz), 2.57–2.53 (m, 3H, 2′, and CH_2), 2.37–2.35 (m, 1H, 2′), 1.72–1.62 (m, 2H), 1.54–1.42 (m, 2H), 1.24 (t, 3H, J=7.1 Hz), 0.92, 0.89 (2s, 18H, $SiC(CH_3)_3$), 0.09, 0.06 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.4, 153.7, 141.2, 140.6, 132.4, 129.7, 129.2, 128.7, 88.0, 83.9, 71.9, 62.9, 41.0, 29.8, 26.0, 25.7, 22.3, 19.2, 18.2, −4.7, −5.7. HRMS exact mass calculated for $C_{28}H_{49}N_5O_3Si_2$ (M^++H) 560.3374, found 560.3444.

*4.3.11. 2-Amino-6-[oct-1-ynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**4c**).* Brown oil (58%), R_f (5% EtOAc in CH_2Cl_2)=0.29. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.04 (s, 1H, Ar–H), 6.31 (t, 1H, 1′, J=6.6 Hz), 5.12 (br s, 2H, NH_2), 4.59–4.55 (m, 1H, 3′), 3.98 (app q, 1H, 4′, $J\approx$3.3 Hz), 3.81 (dd, 1H, 5′, J=4.1, 11.3 Hz), 3.74 (dd, 1H, 5′, J=3.3, 11.3 Hz), 2.61–2.52 (m, 3H, 2′, and CH_2), 2.38–2.31 (m, 1H, 2′), 1.73–1.63 (m, 2H), 1.49–1.40 (m, 2H), 1.31–1.24 (m, 7H), 0.90, 0.87 (2s, 18H, $SiC(CH_3)_3$), 0.09, 0.07 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.8, 142.0, 132.4, 129.7, 128.8, 128.6, 87.7, 84.0, 72.1, 62.9, 41.2, 31.7, 29.8, 28.1, 26.0, 25.6, 22.4, 20.0, 18.5, 18.1, 13.8, −4.5, −5.7. HRMS exact mass calculated for $C_{30}H_{53}N_5O_3Si_2$ (M^++H) 588.3687, found 588.3758.

*4.3.12. 2-Amino-6-[5-chloropent-1-ynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**4e**).* Yellow oil (70%), R_f (5% EtOAc in CH_2Cl_2)=0.13. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06 (s, 1H, Ar–H), 6.31 (t, 1H, 1′, J=6.5 Hz), 5.18 (br s, 2H, NH_2), 4.56–4.55 (m, 1H, 3′), 3.98–3.94 (m, 1H, 4′), 3.83–3.75 (m, 2H, 5′), 3.70 (t, 2H, J=7.4 Hz), 2.75 (t, 2H, J=7.0 Hz), 2.59–2.51 (m, 1H, 2′), 2.38–2.31 (m, 1H, 2′), 2.18–2.09 (m, 2H), 0.89, 0.88 (2s, 18H, $SiC(CH_3)_3$), 0.08, 0.06 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.6, 155.9, 154.6, 145.6, 140.4, 134.0, 129.7, 129.0, 117.1, 87.9, 84.0, 72.0, 62.9, 41.0, 25.8, 21.8, 18.5, 18.1, −4.7, −5.4. HRMS exact mass calculated for $C_{27}H_{46}ClN_5O_3Si_2$ (M^++H) 580.2828, found 580.2880.

*4.3.13. 2-Amino-6-[hex-5-ynenitrile]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**4f**).* Brown oil (69%), R_f (5% EtOAc in CH_2Cl_2)=0.16. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.12 (s, 1H, Ar–H), 6.32 (t, 1H, 1′, J=6.6 Hz), 5.37 (br s, 2H, NH_2), 4.57–4.55 (m, 1H, 3′), 3.99 (app q, 1H, 4′, $J\approx$3.0 Hz), 3.82 (dd, 1H, 5′, J=3.8, 11.3 Hz), 3.74 (dd, 1H, 5′, J=2.5, 11.3 Hz), 2.76 (t, 2H, J=6.6 Hz), 2.62 (t, 2H, J=6.6 Hz), 2.56–2.50 (m, 1H, 2′), 2.40–2.33 (m, 1H, 2′), 2.10–2.01 (m, 2H), 0.90, 0.89 (2s, 18H, $SiC(CH_3)_3$), 0.09, 0.07 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.4, 153.9, 142.3, 141.1, 129.3, 119.0, 88.1, 84.2, 84.0, 72.1, 62.0, 41.2, 26.1, 25.8, 24.1, 19.1, 18.2, 18.1, 16.5, −4.7, −5.4. HRMS exact mass calculated for $C_{28}H_{46}N_6O_3Si_2$ (M^++H) 571.3170, found 571.3227.

*4.3.14. 2-Amino-6-[3-(tetrahydro-2H-pyran-2-yloxy)prop-1-ynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**4g**).* Brown oil (55%), R_f (5% EtOAc in CH_2Cl_2)= 0.17. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.08 (s, 1H, Ar–H), 6.32 (t, 1H, 1′, J=6.6 Hz), 5.15 (br s, 2H, NH_2), 4.92 (s, 1H,), 4.58 (s, 2H), 4.01–3.97 (m, 1H, 3′), 3.89–3.72 (m, 4H, 4′, 5′, and 2H), 3.58–3.53 (m, 1H, 5′), 2.60–2.52 (m, 1H, 2′), 2.39–2.27 (m, 1H, 2′), 1.84–1.42 (m, 6H), 0.90, 0.89 (s, 18H, $SiC(CH_3)_3$), 0.09, 0.07 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.4, 149.7, 145.2, 142.3, 130.2, 88.0, 84.1, 83.8, 75.3, 72.1, 62.9, 62.1, 54.7, 41.0, 30.2, 26.1, 25.8, 25.4, 19.01, 18.5, 18.1, −4.6, −5.4. HRMS exact mass calculated for $C_{30}H_{51}N_5O_5Si_2$ (M^++H) 618.3429, found 618.3484.

*4.3.15. 2-Amino-6-[1-(ethynyl)cyclopentanol]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**4h**).* Brown oil (75%), R_f (5% EtOAc in CH_2Cl_2)=0.19. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.16 (s, 1H, Ar–H), 6.30 (t, 1H, 1′, J=6.6 Hz), 5.25 (br s, 2H, NH_2), 4.59–4.56 (m, 1H, 3′), 4.20 (br s, 1H, OH), 3.97 (app q, 1H, 4′, $J\approx$3.3 Hz), 3.78 (dd, 1H, 5′, J=4.4, 11.3 Hz), 3.72 (dd, 1H, 5′, J=3.6, 11.3 Hz), 2.68–2.59 (m, 1H, 2′), 2.37–2.31 (m, 1H, 2′), 2.17–2.06 (m, 4H) 1.92–1.85 (m, 2H), 1.81–1.74 (m, 2H), 0.90, 0.87 (2s, 18H, $SiC(CH_3)_3$), 0.09, 0.05 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.5, 153.2, 142.1, 141.4, 129.3, 102.2, 87.9, 84.0, 74.4, 72.2, 63.0, 60.5, 53.5, 42.4, 25.8, 23.8, 18.1, 14.3, −4.6, −5.4. HRMS exact mass calculated for $C_{29}H_{49}N_5O_4Si_2$ (M^++H) 588.3323, found 588.3377.

*4.3.16. 2-Amino-6-[tert-butyldimethylsilylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**4i**).* Yellow oil (72%), R_f (5% EtOAc in CH_2Cl_2)=0.24. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.09 (s, 1H, Ar–H), 6.30 (t, 1H, 1′, J=6.6 Hz), 5.35 (br s, 2H, NH_2), 4.59–4.54 (m, 1H, 3′), 3.98 (app q, 1H, 4′, $J\approx$3.3 Hz), 3.81–3.70 (m, 2H, 5′), 2.59–2.50 (m, 1H, 2′), 2.39–2.31 (m, 1H, 2′), 1.03 (s, 9H), 0.90, 0.89 (2s, 18H, $SiC(CH_3)_3$), 0.25 (s, 6H), 0.09, 0.06 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.6, 150.2, 146.7, 142.3, 132.1, 129.2, 88.0, 83.9, 72.1, 62.9, 40.9, 26.3, 26.0, 25.8, 18.5, 18.1, 16.8, −4.7, −4.8, −5.4. HRMS exact mass calculated for $C_{30}H_{55}N_5O_3Si_3$ (M^++H) 618.3613, found 618.3669.

*4.3.17. 2-Amino-6-[triethylsilylethynyl]-9-[2′-deoxy-3′,5′-bis-O-(tert-butyldimethylsilyl)-β-D-erythro-pentafuranosyl]purine (**4j**).* Orange oil (79%), R_f (5% EtOAc in CH_2Cl_2)=0.23. ^{1}H NMR

(300 MHz, $CDCl_3$) δ: 8.05 (s, 1H, Ar–H), 6.29 (t, 1H, 1′, J=6.6 Hz), 5.25 (br s, 2H, NH_2), 4.57–4.55 (m, 1H, 3′), 3.96 (app q, 1H, 4′, $J \approx 3.3$ Hz), 3.80–3.69 (m, 2H, 5′), 2.59–2.50 (m, 1H, 2′), 2.37–2.30 (m, 1H, 2′), 1.05 (t, 9H, CH_3, J=7.8 Hz), 0.88, 0.86 (2s, 18H, $SiC(CH_3)_3$), 0.74 (q, 6H, CH_2, J=7.8 Hz), 0.08, 0.05 (2s, 12H, $Si((CH_3)_2)$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.6, 149.7, 145.2, 141.4, 129.7, 110.5, 98.6, 87.9, 83.7, 71.9, 62.9, 40.8, 26.1, 18.5, 18.1, 7.6, 4.2, −4.7, −5.4. HRMS exact mass calculated for $C_{30}H_{55}N_5O_3Si_3$ (M^++H) 618.3613, found 618.3669.

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Supplementary data

General experimental procedures and characterization data for all new products (^1H and ^{13}C NMR, and HRMS). In addition, ^1H NMR spectra of compounds **3a**, **3b**, **3c**, **3e**, **3f**, **3g**, **3h**, **3i**, **4a**, **4b**, **4c**, **4e**, **4f**, **4g**, **4h**, **4i**, **4j** and nucleoside arylsulfonates. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.08.032.

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