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1,3-Dipolar cycloaddition of sugar azides with benzyne: a novel synthesis of 1,2,3-benzotriazolyl glycoconjugates

Basi V. Subba Reddy [a,*], Karanam Praneeth [a,b], Jhillu S. Yadav [a]

[a] Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad 500 007, India
[b] IICT an Associate Institution of University of Hyderabad, Hyderabad 500 046, India

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ABSTRACT

Glycosyl azides undergo smooth 1,3-dipolar cycloaddition with benzyne generated in situ from 2-(trimethylsilyl)phenyltrifluoromethanesulfonate and cesium fluoride under mild conditions to furnish 1,2,3-benzotriazole-linked glycoconjugates in excellent yields and with high stereoselectivity. This method provides a novel class of benzotriazole linked glycoconjugates in a single-step reaction. This is the first example of a fluoride-triggered 1,3-dipolar cycloaddition of benzyne with glycosyl azides.

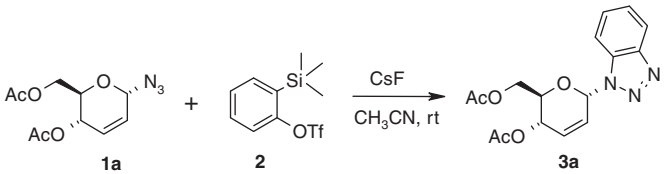
1. Introduction

1,2,3-Benzotriazoles are important structural scaffolds in various biologically active molecules.[1,2] They exhibit a wide spectrum of pharmacological properties and clinical applications such as antiinflammatory, antinociceptive, antitumor, and antitubercular activities.[3–5] In addition to this, they are important intermediates, protecting groups, and end products in organic synthesis.[6] Furthermore, glycosyl amines are of great importance in nucleoside chemistry.[7–9] Recently, the synthesis of *N*-triazolyl-bridged glycoconjugates have been reported via 'Click' chemistry.[10] However, the synthesis of 1,2,3-benzotriazolyl glycosides involves the Ferrier rearrangement of glycals with benzotriazole using trifluoroacetic acid.[11,12] This approach often requires high temperature, prolonged reaction time (two days), and a sealed tube to achieve satisfactory results. The alternative method for the synthesis of benzotriazole is the cycloaddition of azides with arynes.[13–15] In recent years, benzyne was generated in situ from 2-(trimethylsilyl)phenyl trifluoromethanesulfonate using cesium fluoride under mild conditions and used in various cycloaddition reactions.[16–21] Since benzotriazole-linked glycoconjugates have become increasingly useful and important in glycobiology,[22–25] the development of a simple, convenient, and efficient method for their synthesis in a single-step operation is desirable.

2. Results and discussion

Following our interest on azide–alkyne cycloadditions,[26,27] we herein report a novel method for the synthesis of benzotriazolyl glycosides via the 1,3-dipolar cycloaddition of glycosyl azides with benzyne under mild conditions. Initially, we have prepared glycosyl azides from glycals and trimethylsilyl azide via the Ferrier rearrangement.[28] The azides thus formed were then subjected to 1,3-dipolar cycloaddition. [29]Accordingly, treatment of 2,3-dideoxyglycosyl azide (**1a**) with 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (**2**) and cesium fluoride in acetonitrile at room temperature gave the corresponding benzotriazolyl-2,3-dideoxy glycoside (**3a**) in 86% yield (Scheme 1).

This result provided the incentive for further study with various sugar azides such as 4,6-di-*O*-benzyl- (**1b**) and 4,6-di-*O*-allyl-2,3-dideoxy-α-D-glycosyl azides (**1c**). These glycosyl azides reacted readily with benzyne under similar conditions to produce 1,2,3-benzotriazole-linked 2,3-dideoxypyranosides in excellent yields (Table 1, entries b and c). Next, we have attempted the cycloaddi-



Scheme 1. Synthesis of the benzotriazolyl-2,3-dideoxy glycoside (**3a**).

* Corresponding author. Tel.: +91 40 27193535; fax: +91 40 27160512.
E-mail address: basireddy@iict.res.in (B.V. Subba Reddy).

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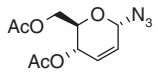
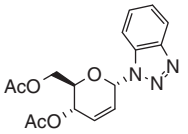
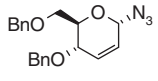
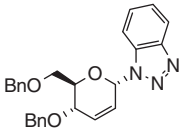
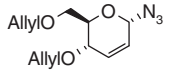
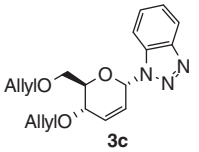
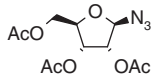
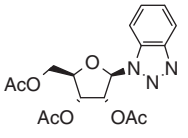
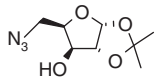
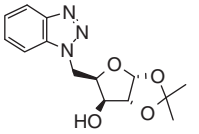
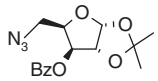
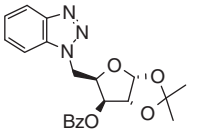
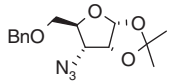
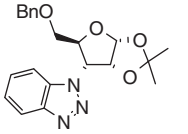
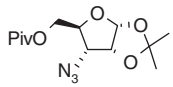
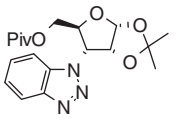
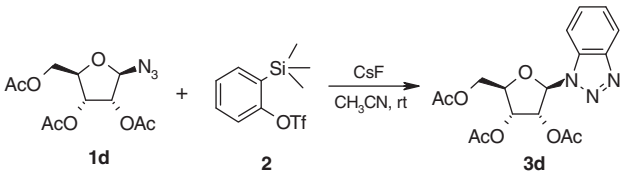
Table 1
1,3-Dipolar cycloaddition of various azides with benzyne in the presence of cesium fluoride

Entry	Sugar azide	Product[a]	Time (h)	Yield[b] (%)
a	 **1a**	 **3a**	12.0	86
b	 **1b**	 **3b**	13.0	88
c	 **1c**	 **3c**	12.0	92
d	 **1d**	 **3d**	16.0	94
e	 **1e**	 **3e**	8.0	88
f	 **1f**	 **3f**	9.0	90
g	 **1g**	 **3g**	12.0	80
h	 **1h**	 **3h**	14.0	80

[a] All products were characterized by NMR, IR, and mass spectrometry.
[b] Yield refers to pure products after chromatography.

tion of benzyne with an azide derived from D-ribose. Interestingly, 2,3,5-tri-*O*-acetyl-β-D-ribfuranosyl azide (**1d**) participated well in benzyne–azide cycloaddition to afford the 1,2,3-benzotriazolyl-D-ribonucleoside (**3d**) in 94% yield (entry d, Scheme 2).

Encouraged by the above results, we turned our attention to extend this method for primary azides. Interestingly, primary azides such as 5-azido-5-deoxy-D-xylose (**1e**, **1f**) also underwent smooth cycloaddition with benzyne to furnish the corresponding benzotriazole-linked D-xylose derivatives (Table 1, entries e and f). Similarly, 3-azido-3-deoxy-D-ribose derivatives **1g** and **1h** also participated effectively in this cycloaddition (Table 1, entries g and h). Thus



1d **2** **3d**

Scheme 2. Synthesis of a 1,2,3-benzotriazolyl-D-ribonucleoside.

various azido sugars such as D-ribosfuranosyl azide, 3-azido-3-deoxy-D-ribose, and 5-azido-5-deoxy-D-xylose were successfully converted into their 1,2,3-benzotriazolyl derivatives by using this procedure. Notably, a variety of protecting groups such as benzyl and allyl ethers and ester derivatives like acetyl and pivolyl esters were well tolerated under the reaction conditions. As solvent, acetonitrile gave the best results. The cycloaddition was successfully carried out with the azides derived from both hexose and pentose sugars. The scope and generality of this reaction is illustrated with respect to various primary and secondary azides, and the results are presented in Table 1.

Mechanistically, the reaction proceeds via the formation of a benzyne intermediate from 2-(trimethylsilyl)phenyltrifluoromethanesulfonate and CsF. The benzyne thus formed may undergo simultaneously 1,3-dipolar cycloaddition with glycosyl azide to furnish 1,2,3-benzotriazole linked glycoside as depicted in Scheme 3.

Although other fluoride ion sources such as KF and tetrabutylammonium fluoride (TBAF) have effectively been used to generate benzyne, CsF is found to be the best fluoride ion source under the given conditions in terms of yields.

3. Conclusions

In conclusion, we have successfully developed a novel and efficient method for the synthesis of 1,2,3-benzotriazole-linked glycoconjugates via azide–aryne cycloaddition. The method is mild and convenient and provides easy access to a variety of benzotriazole-linked glycoconjugates that may find application in nucleoside synthesis.

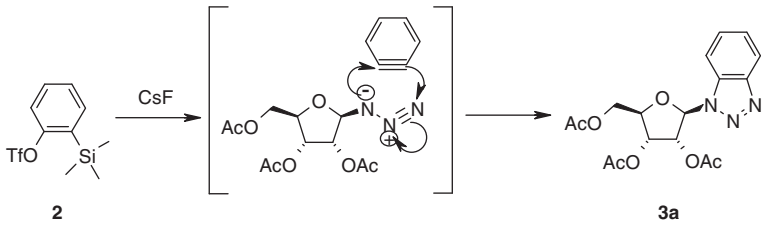
4. Experimental

4.1. General methods and materials

All the products were characterized by ^{1}H and ^{13}C NMR, IR spectroscopy and by high-resolution mass spectrometry (HRMS). Melting points recorded are uncorrected. Analytical TLC was performed using 2.5 × 5-cm plates coated with a 0.25 mm thickness of silica gel (60F-254), and visualization was accomplished with *p*-anisaldehyde solution and subsequent charring over a hot plate. ^{1}H NMR spectra were recorded at 300 MHz with TMS as the internal reference. ^{13}C NMR spectra are recorded at 75 MHz with $CDCl_3$ as the internal reference. Chemical shifts are given in parts per million downfield from internal standard Me_4Si and coupling constants are given in Hertz. IR spectra were recorded on Perkin–Elmer 881 and FTIR-8210 PC Shimadzu spectrophotometers. Mass spectra were recorded on a JEOL JMS-600H high-resolution spectrometer using the ESI mode at 70 eV. Optical rotations were measured at ambient temperature (25 °C) in $CHCl_3$ solutions with a polarimeter using a 1-mL capacity cell with 100-mm path length, and concentrations are in g/100 mL.

4.2. General experimental procedure for the preparation of triazole-linked glycoconjugates

To a stirred solution of aryne precursor (1.2 mmol) and azide (1 mmol) in dry CH_3CN (3 mL) was added CsF (2 mmol), and the



Scheme 3. A plausible reaction mechanism.

resulting mixture was stirred for an appropriate time (Table 1). After complete conversion, as indicated by TLC, the mixture was quenched with satd aq $NaHCO_3$ and extracted with EtOAc (3×5 mL). The combined organic layers were dried over anhyd Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by column chromatography on silica gel using EtOAc–hexane as eluent to afford the pure benzotriazole derivative.

4.2.1. [(2*R*,3*S*,6*R*)-3-(Acetyloxy)-6-(1*H*-1,2,3-benzotriazol-1-yl)-3,6-dihydro-2*H*-2-pyranyl]methyl acetate (3a)

Light-yellow solid, mp 132–134 °C; $[\alpha]_D^{25}$ 198 (*c* 1.15, $CHCl_3$); IR (KBr): *v* 2925, 2854, 1735, 1647, 1453, 1227, 1161, 1068, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.03 (d, 1H, *J* = 8.3 Hz), 7.51–7.38 (m, 2H), 7.31 (t, 1H, *J* = 6.7 Hz), 6.79 (d, 1H, *J* = 5.2 Hz), 5.70 (td, 1H, *J* = 1.5, 5.2 Hz), 5.32 (dd, 1H, *J* = 5.2, 10.5 Hz), 5.06 (t, 1H, *J* = 5.2 Hz), 4.60–4.54 (m, 1H), 4.26–4.22 (m, 2H), 2.03 (s, 3H), 1.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.4, 169.8, 148.1, 134.1, 127.4, 123.9, 120.1, 112.9, 109.7, 95.4, 70.5, 67.5, 61.5, 51.1, 20.6, 20.2. ESIMS: *m/z*: 332 $(M+H)^+$. HRESIMS: Calcd for $C_{16}H_{18}N_3O_5$ *m/z* 332.1246; Found, *m/z* 332.1232.

4.2.2. 1-5-(Benzyloxy)-6-[(benzyloxy)methyl]-5,6-dihydro-2*H*-2-pyranyl-1*H*-1,2,3-benzotriazole (3b)

White solid, mp 162–164 °C; $[\alpha]_D^{25}$ +99.7 (*c* 0.7, $CHCl_3$); IR (neat): *v* 3448, 3036, 2922, 2856, 1723, 1651, 1492, 1451, 1362, 1239, 1094, 745, 669 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.95 (d, 1H, *J* = 7.3 Hz), 7.54–7.41 (m, 1H), 7.33–7.05 (m, 10H), 6.98–6.84 (m, 2H), 6.64–6.59 (m, 1H), 5.67–5.57 (m, 1H), 4.92 (t, 1H, *J* = 5.6 Hz), 4.75 (dd, 1H, *J* = 2.0, 6.1 Hz), 4.67–4.16 (m, 4H), 4.11–4.01 (m, 1H), 3.81–3.76 (m, 1H), 3.65–3.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.0, 146.3, 136.7, 132.1, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 126.9, 123.3, 119.6, 110.9, 110.2, 79.8, 78.0, 73.9, 72.2, 72.4, 68.0; ESIMS: *m/z*: 428 $(M+H)^+$. HRESIMS: Calcd for $C_{26}H_{26}N_3O_3$ *m/z* 428.1974; Found, *m/z* 428.1987.

4.2.3. 1-5-(Allyloxy)-6-[(allyloxy)methyl]-5,6-dihydro-2*H*-2-pyranyl-1*H*-1,2,3-benzotriazole (3c)

Yellow solid, mp 146–148 °C; $[\alpha]_D^{25}$ −26.8 (*c* 1.50, $CHCl_3$); IR (neat): *v* 3448, 2924, 2854, 1651, 1459, 1086, 748, 569 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.04 (t, 1H, *J* = 8.3 Hz), 7.67–7.58 (m, 1H), 7.47–7.27 (m, 2H), 6.81–6.61 (m, 1H), 5.96–5.81 (m, 1H), 5.73–5.59 (m, 1H), 5.33–4.85 (m, 5H), 4.74–4.62 (m, 1H), 4.30–3.93 (m, 5H), 3.85–3.60 (m, 2H), 3.40–3.31 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.0, 146.5, 134.1, 133.5, 127.1, 123.9, 120.0, 118.0, 117.5, 110.9, 110.4, 94.9, 78.1, 73.0, 72.7, 71.6, 67.9, 60.2; ESIMS: *m/z*: 328 $(M+H)^+$. HRESIMS: Calcd for $C_{18}H_{22}N_3O_3$ *m/z* 328.1661; Found, *m/z* 428.1654.

4.2.4. (2*R*,3*R*,4*R*,5*R*)-4-(Acetyloxy)-2-[(acetyloxy)methyl]-5-(1*H*-1,2,3-benzotriazol-1-yl)tetrahydro-3-furanyl acetate (3d)

Light-yellow solid, mp 132–134 °C; $[\alpha]_D^{25}$ −28.1 (*c* 1.80, $CHCl_3$); IR (KBr): *v* 2926, 2853, 1746, 1516, 1454, 1240, 1045, 750, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.05 (d,1H, *J* = 8.7 Hz), 7.67 (d, 1H, *J* = 7.7 Hz), 7.50 (t, 1H, *J* = 7.7 Hz), 7.38 (t, 1H, *J* = 6.7 Hz), 6.29 (d, 1H, *J* = 8.7 Hz), 5.86 (t, 1H, *J* = 2.9 Hz), 5.72 (dd, 1H, *J* = 2.9, 8.7 Hz), 5.30–5.26 (m, 2H), 5.08 (t, 1H, *J* = 6.7 Hz), 2.24 (s, 3H), 2.08 (s, 3H), 1.8 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.2, 169.0, 168.2, 146.5, 127.9, 124.4, 120.5, 120.4, 110.5, 83.5, 68.2, 67.0, 66.0, 63.6, 20.7, 20.5, 20.1. ESIMS: *m/z*: 378 $(M+H)^+$. HRESIMS: Calcd for $C_{17}H_{20}N_3O_7$ *m/z* 378.1301; Found, *m/z* 378.1295.

4.2.5. (3a*R*,5*R*,6*S*,6a*R*)-5-(1*H*-1,2,3-Benzotriazol-1-ylmethyl)-2,2-dimethylperhydrofuro[2,3-*d*][1,3]dioxol-6-ol (3e)

Light-yellow solid, mp 146–148 °C; $[\alpha]_D^{25}$ −52.7 (*c* 2.10, $CHCl_3$); IR (KBr): *v* 3467, 2983, 2941, 1706, 1498, 1440, 1381, 1221, 1074, 1012, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.94 (d, 1H, *J* = 9.0 Hz), 7.60 (d, 1H, *J* = 8.3 Hz), 7.42 (t, 1H, *J* = 7.5 Hz), 7.30 (t, 1H, *J* = 7.5 Hz), 5.96 (d, 1H, *J* = 3.7 Hz), 5.01 (dd, 1H, *J* = 7.5, 14.3 Hz), 4.79 (dd, 1H, *J* = 6.0, 14.3 Hz), 4.59–4.50 (m, 2H), 4.28–4.18 (m, 2H), 1.34 (s, 3H), 1.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.3, 133.4, 127.7, 124.2, 119.5, 111.8, 109.5, 105.0, 85.2, 79.2, 74.4, 46.1, 26.6, 26.0. ESIMS: *m/z*: 292 $(M+H)^+$. HRESIMS: Calcd for $C_{14}H_{18}N_3O_4$ *m/z* 292.1297; Found, *m/z* 292.1290.

4.2.6. (3a*R*,5*R*,6*S*,6a*R*)-5-(1*H*-1,2,3-Benzotriazol-1-ylmethyl)-2,2 dimethylperhydrofuro[2,3-*d*][1,3]dioxol-6-yl benzoate (3f)

White solid, mp 100–102 °C; $[\alpha]_D^{25}$ −1.9 (*c* 2.30, $CHCl_3$); IR (KBr): *v* 2987, 2932, 1725, 1452, 1264, 1102, 1027, 750, 712, 675 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.01–7.90 (m, 3H), 7.56–7.19 (m, 6H), 5.98 (d, 1H, *J* = 3.3 Hz), 5.46 (d, 1H, *J* = 1.8 Hz), 4.98 (dd, 1H, *J* = 2.8, 13.4 Hz), 4.86–4.70 (m, 2H), 4.64 (d, 1H, *J* = 3.3 Hz), 1.36 (s, 3H), 1.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.9, 145.7, 133.7, 133.2, 129.6, 128.5, 127.3, 123.7, 119.7, 112.3, 109.6, 104.8, 83.2, 77.9, 76.7, 76.5, 46.8, 26.4, 25.9. ESIMS: *m/z*: 396 $(M+H)^+$. HRESIMS: Calcd for $C_{21}H_{22}N_3O_5$ *m/z* 396.1559; Found, *m/z* 396.1550.

4.2.7. [(3a*R*,5*S*,6*R*,6a*R*)-6-(1*H*-1,2,3-Benzotriazol-1-yl)-2,2-dimethylperhydrofuro[2,3-*d*][1,3]dioxol-5-yl]methyl benzyl ether (3g)

Colorless oil; $[\alpha]_D^{25}$ −55.7 (*c* 0.35, $CHCl_3$); IR (neat): *v* 3447, 2956, 1646, 1497, 1454, 1377, 1218, 1162, 1076, 1027, 888, 746, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.99 (d, 1H, *J* = 8.3 Hz), 7.54 (d, 1H, *J* = 8.3 Hz), 7.42–7.23 (m, 7H), 5.94 (d, 1H, *J* = 3.7 Hz), 4.95–4.88 (m, 1H), 4.78–4.60 (m, 4H), 4.43 (d, 1H, *J* = 11.1 Hz), 3.95 (d, 1H, *J* = 3.7 Hz), 1.34 (s, 3H), 1.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.9, 136.4, 132.7, 128.5, 128.1, 127.8, 127.2, 123.8, 119.5, 112.0, 110.1, 105.1, 81.9, 87.6, 79.1, 71.9, 46.7, 26.6, 26.0; ESIMS: *m/z*: 382 $(M+H)^+$. HRESIMS: Calcd for $C_{21}H_{24}N_3O_4$ *m/z* 382.1766; Found, *m/z* 382.1772.

4.2.8. [(3a*R*,5*S*,6*R*,6a*R*)-6-(1*H*-1,2,3-Benzotriazol-1-yl)-2,2-dimethylperhydrofuro[2,3-*d*][1,3]dioxol-5-yl]methyl pivalate (3h)

White solid, mp 116–118 °C; $[\alpha]_D^{25}$ −26.8 (*c* 1.50, $CHCl_3$); IR (neat): *v* 3449, 2974, 2931, 1737, 1455, 1377, 1276, 1143, 1067, 888, 747, 630 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.04 (d, 1H, *J* = 803 Hz), 7.61 (d, 1H, *J* = 8.3 Hz), 7.46 (t, 1H, *J* = 7.5 Hz), 7.34 (t,

1H, J = 7.5 Hz), 5.92 (d, 1H, J = 3.5 Hz), 5.26 (d, 1H, J = 3.5 Hz), 4.98 (dd, 1H, J = 4.1, 14.1 Hz), 4.78–4.57 (m, 2H), 4.47 (d, 1H, J = 3.5 Hz), 1.41 (s, 3H), 1.33–1.23 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.6, 145.5, 132.8, 127.7, 123.5, 119.4, 112.0, 109.3, 104.3, 82.8, 76.1, 75.5, 46.5, 38.6, 26.6, 26.1; ESIMS: m/z: 376 $(M+H)^+$. HRESIMS: Calcd for $C_{19}H_{26}N_3O_5$ m/z 376.1872; Found, m/z 376.1870.

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