Carbohydrate Research 357 (2012) 139–142

Contents lists available at SciVerse ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Note

A facile one-pot synthesis of biphenyl methyl-C-β-D-glycosides

Ramanathan Rajaganesh, Thangamuthu Mohan Das *

Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India

ARTICLE INFO

Article history:
Received 24 February 2012
Received in revised form 30 April 2012
Accepted 3 May 2012
Available online 11 May 2012

Keywords:
Protected sugars
C-Glycosides
Biphenyl derivatives
One-pot reaction

ABSTRACT

Facile one-pot synthesis of biphenyl methyl-C-β-D-glycosides was carried out using 4,6-*O*-protected-C-glycoside, aromatic aldehydes and malononitrile in pyrrolidine as an organocatalyst. Studies reveal that the use of pyrrolidine resulted in a better yield.

The chemistry of C-glycosides has been extensively developed due to the diversity of biological and pharmaceutical applications.[1–4] C-Glycosides as subunits occur in a variety of biologically important natural products and also in synthetic compounds.[5] More recently, aryl-C-β-glycosides[6,7] have been reported to possess potent SGLT2 inhibitor activity (Fig. 1). Multicomponent reactions emerged as a powerful tool for the construction of several novel and complex molecular structures with diversities of biological activities and pharmaceutical applications.[8] Several biologically important polysubstituted biphenyl derivatives have been developed via multicomponent reactions.[9–12] Thus a new synthetic route to C-glycosides could have a major impact on the potential applications of these useful compounds.

4,6-*O*-Butylidene-D-glucopyranose and 1-(4,6-*O*-butylidene-β-D-glycopyranosyl)propan-2-one (**3**) were synthesized by adopting procedures reported in the literature.[13] Biphenyl methyl-C-β-D-glucopyranosides (**6a**–**g**) were synthesized in one-step from the reaction of 1-(4,6-*O*-butylidene-D-glucopyranosyl)propane-2-one (**3**), aromatic aldehydes (**4a**–**g**) and malononitrile (**5**) in the presence of pyrrolidine as an organocatalyst (Scheme 1). Optimization of reaction condition shows, use of 1 equiv of methyl ketone (**3**), 1 equiv of aromatic aldehydes (**4a**–**g**) and 2 equiv of malononitrile (**5**) gives the desired biphenyl derivatives (**6a**–**g**) in moderate yield. Details about the use of different solvents and bases for the optimization of reaction conditions are given in ESI. The structures of the resulting biphenyl C-glycoside derivatives (**6a**–**g**) were determined by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The multiplets appearing in the range of 6.80–7.52 ppm correspond to the aromatic protons of the resultant products. The appearance of a broad peak around 7.00 ppm in the ^{1}H NMR spectrum corresponds to exchange protons (–NH_2) which is absent in the substrates. Disappearance of an aldehyde peak in the product and also a peak at 2.13 ppm, which corresponds to the methyl group of –CH_2COCH_3 of sugar derivative confirms the product formation. In addition, disappearance of carbonyl and methyl carbons of –*C*O–*C*H_3 which appear at 200 and 30 ppm, respectively in the substrates further confirms the structure of the expected product. Moreover, appearance of a peak at δ 115.0 ppm in the ^{13}C NMR spectrum which is characteristic for two –CN groups ensures the product formation. Structure of aromatic aldehydes, biphenyl-C-glycosides, reaction time and product yields is given in Table 1.

Thus, we have designed and synthesized biphenyl methyl-C-glycosides having a methylene group that favours flexibilities of the molecule as is observed with sugar-β-lactam derivatives.[14,15] An efficient one-pot synthetic methodology reported in this paper has the advantages of using wide scope of substrates, under mild reaction conditions, simple work-up and high yield and it is expected to provide a way for potential application in the synthesis of several C-glycosyl natural product derivatives.

1. Experimental section

1.1. General methods

D-Glucose, acetylacetone and all substituted aldehydes were obtained from Sigma–Aldrich Chemicals Pvt. Ltd USA and were of high purity. Butyraldehyde, organic catalyst (pyrrolidine) and other bases were obtained from SRL India. Other reagents such as sodium hydrogen carbonate and solvents (AR Grade) were obtained from

* Corresponding author. Tel.: +91 44 22202814; fax: +91 44 22352494.
E-mail address: tmdas_72@yahoo.com (T. Mohan Das).

0008-6215/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carres.2012.05.001

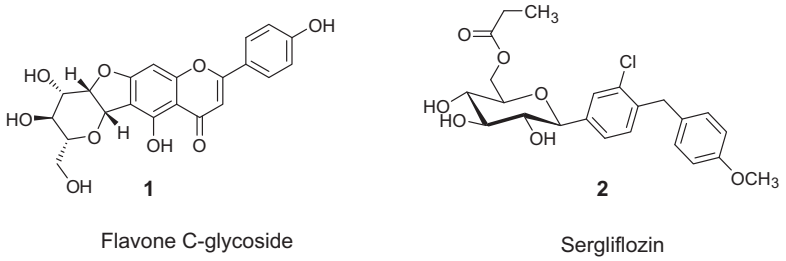
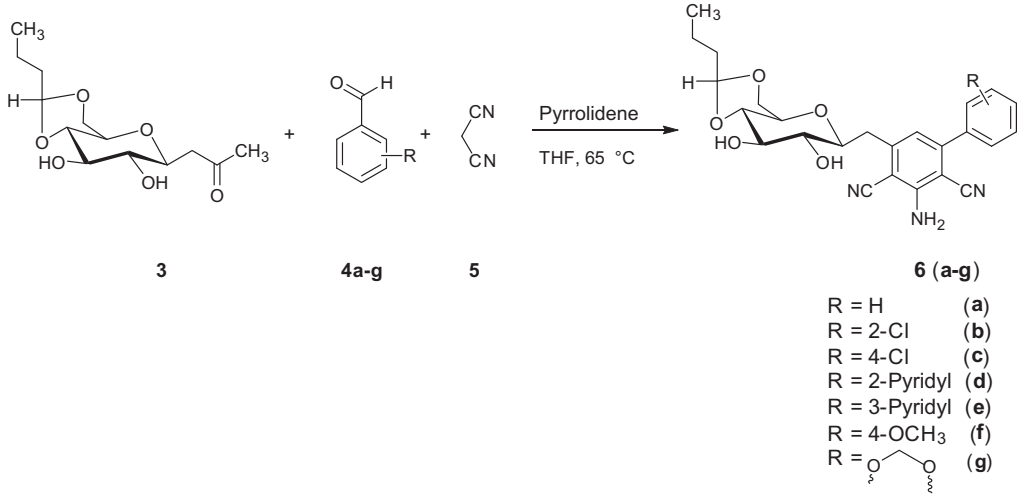


Figure 1. Representative examples of C-glycosides (**1**) and (**2**).



Scheme 1. Synthesis of biphenyl methyl-C-β-D-glycosides (**6a**–**g**).

Sd-fine, India of high purity and were used without any further purification. Column chromatography was performed on silica gel (100–200 mesh). NMR spectra were recorded on a Brucker DRX 300 MHZ instrument in either $CDCl_3$ or DMSO-d_6 (with a few drops of $CDCl_3$). Chemical shifts are referenced to internal TMS. Elemental analyses were performed using a Perkin–Elmer 2400 series CHNS/O analyser. While assigning the spectral data several abbreviations were used and these include 'Ar' for aromatic, 'Ace' for acetal, 'Ano' for anomeric, 'Sac' and H-1′–H-6′ for saccharide and 'H_a' for methylene protons that connect between the sugar and biphenyl moieties.

1.2. General procedure for the synthesis of biphenyl-methyl-C-β-D-4,6-*O*-butylidene-D-glucopyranose derivatives (6a–g)

To a solution of C-β-glycosidic ketone (**3**, 1.0 mmol) in 10 mL of anhydr THF were added pyrrolidine (2.5 mmol) and aromatic aldehyde (**4a**, 1.0 mmol). Reaction mixture was refluxed until completion of reaction. To the reflux solution malononitrile (**5**, 2.0 mmol) was added and the reaction mixture was evaporated under reduced pressure. The crude product was slurried with silica gel and purified by flash chromatography.

1.2.1. Physicochemical and spectral data for 2-amino-4-(phenyl-1-yl)-6-[(4,6-*O*-butylidene-β-D-glucopyranosyl)-methyl] isophthalonitrile (6a)

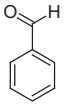
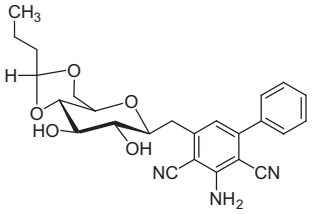
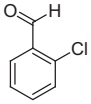
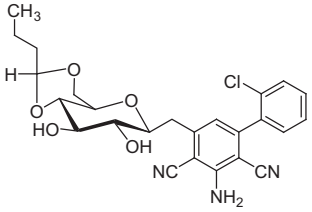
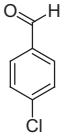
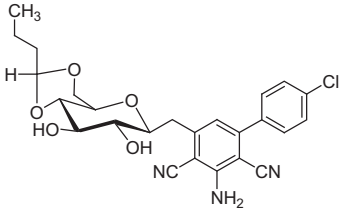
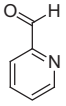
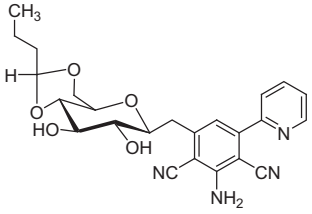
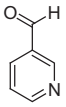
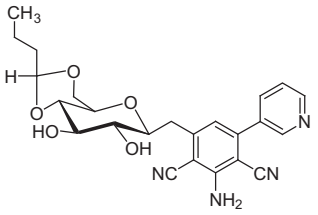
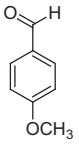
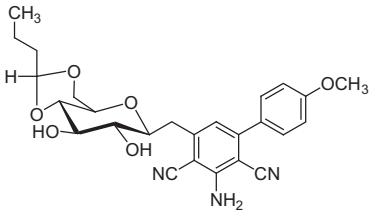
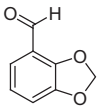
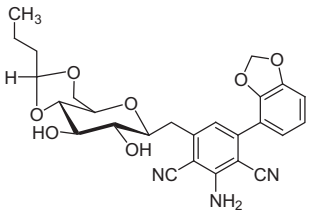
From 1-(4,6-*O*-butylidene-β-D-glucopyranosyl)propane-2-one (**3**) (0.274 g, 1.0 mmol), 1-phenylcarboxaldehyde (**4a**) (0.106 g, 1.0 mmol), malononitrile (**5**) (0.132 g, 2.0 mmol).

Brown solid (0.301 g, 67%); mp 102–104 °C; ^{1}H NMR ($CDCl_3$): δ_H 7.51–7.52 (m, 4H, Ar-H), 6.80 (s, 1H, Ar-H), 5.23 (s, 2H, –NH_2), 4.54 (t, *J* 4.5 Hz, 2H, Ace-H), 4.09 (t, *J* 3.3 Hz, 1H, H-4′), 3.68–3.76 (m, 2H, H-1, H-3′), 3.58–3.64 (m, 2H, H-5′, H-6′), 3.40–3.48 (m, 3H, H-2′, Sac-OH), 3.23–3.25 (m, 3H, H_a & Sac-OH), 1.61–1.63 (br, 2H, –CH_2), 1.59 (m, 2H, –CH_2), 0.90 (t, *J* 7.5 Hz, 3H, –CH_3). ^{13}C NMR ($CDCl_3$): δ_C 152.7 (Ar-C), 149.7 (Ar-C), 148.0 (Ar-C), 137.5 (Ar-C), 129.6 (Ar-C), 128.8 (Ar-C), 128.4 (Ar-2C), 120.8 (Ar-2C), 116.1 (Ar-*C*N), 115.6 (Ar-*C*N), 102.5 (Ace-C), 97.07 (Ar-C), 94.4 (Ar-C), 80.3 (C-5), 79.4 (C-3), 75.2 (C-1), 74.2 (C-2), 70.4 (C-4), 68.2 (C-6), 37.5 (–CH_2–Ar), 36.2 (–CH_2), 17.5 (–CH_2), 13.9 (–CH_3). Anal. Calcd for $C_{25}H_{27}N_3O_5$: C, 66.80; H, 6.05; N, 9.35. Found: C, 66.32; H, 6.28; N, 9.10.

1.2.2. Physicochemical and spectral data for 2-amino-4-(chlorophenyl-2-yl)-6-[(4,6-*O*-butylidene-β-D-glucopyranosyl)-methyl] isophthalonitrile (6b)

From 1-(4,6-*O*-butylidene-β-D-glucopyranosyl)propane-2-one (**3**) (0.270 g, 1.0 mmol), 2-chlorophenylcarboxaldehyde (**4b**) (0.140 g, 1.0 mmol), malononitrile (**5**) (0.132 g, 2.0 mmol). Yellow solid (0.241 g, 50%); mp 110–112 °C; ^{1}H NMR ($CDCl_3$): δ_H 7.51–7.63 (m, 1H, Ar-H), 7.39–7.44 (m, 2H, Ar-H), 7.30–7.36 (m, 2H, Ar-H), 6.75 (s, 1H, Ano-H), 5.33 (s, 2H, –NH_2), 4.53 (t, *J* 4.8 Hz, 1H, Ace-H), 4.05–4.08 (broad, 1H, H-4′), 3.60–3.80 (m, 2H, H-1′, H-3′), 3.39–3.43 (m, 3H, H-2′, H-5′, H-6′), 3.22 (d, *J* 4.8 Hz, 2H, Sac-OH), 2.29–2.35 (m, 2H, H_a), 1.59–1.63 (m, 2H, –CH_2), 1.44 (m, 2H, –CH_2), 0.92 (t, *J* 7.5 Hz, 3H, –CH_3). ^{13}C NMR ($CDCl_3$): δ_C 152.4 (Ar-C), 148.2 (Ar-C), 147.4 (Ar-C), 136.3 (Ar-C), 136.0 (Ar-C), 132.3 (Ar-C), 130.5 (Ar-2C), 130.1 (Ar-2C), 127.1 (Ar-2C), 115.0 (Ar-2×*C*N), 102.5 (Ace-C), 96.0 (C-5), 80.3 (C-3), 79.0 (C-1), 74.9 (C-2), 70.4 (C-4), 68.2 (C-6), 36.2 (–CH_2–Ar), 32.0 (–CH_2), 17.5 (–CH_2), 14.0 (–CH_3). Anal. Calcd for $C_{25}H_{26}ClN_3O_5$: C, 62.05; H, 5.42; N, 8.68. Found: C, 62.32; H, 5.28; N, 8.40.

Table 1
One-pot synthesis of biphenyl methyl-C-β-D-glycosides (**6a**–**g**)

Entry	Aromatic aldehydes (**4a**–**g**)	Biphenyl-methyl-C-β-D-glycosides (**6a**–**g**)	Time (h)	Yield (%)
1	 (**a**)		30	67
2	 (**b**)		37	50
3	 (**c**)		33	72
4	 (**d**)		42	57
5	 (**e**)		40	42
6	 (**f**)		32	68
7	 (**g**)		45	47

1.2.3. Physicochemical and spectral data for 2-amino-4-(chlorophenyl-4-yl)-6-[(4,6-*O*-butylidene-β-D-glucopyranosyl)-methyl] isophthalonitrile (6c)

From 1-(4,6-*O*-butylidene-β-D-glucopyranosyl)propane-2-one (**3**) (0.274 g, 1.0 mmol), 4-chlorophenylcarboxaldehyde (**4c**) (0.140 g, 1.0 mmol), malononitrile (**5**) (0.122 g, 2.0 mmol). White solid (0.348 g, 72%); mp 152–154 °C; ^{1}H NMR ($CDCl_3$): δ_H 7.40 (s, 2H, Ar-H), 7.20 (s, 2H, Ar-H), 6.67 (s, 1H, Ano-H), 5.27 (s, 2H, $-NH_2$), 4.45 (t, *J* 5.1 Hz, 1H, Ace-H), 3.96–4.01 (m, 1H, Ace-H), 3.59–3.64 (m, 1H, H-4′), 3.49–3.54 (m, 1H, H-3′), 3.28–3.40 (m, 2H, H-1′, H-2′), 3.11–3.20 (m, 3H, H-5′, H-6′, Sac-OH), 2.80–2.88 (m, 1H, Sac-OH), 2.70 (s, 2H, H_a), 1.50–1.56 (m, 2H, $-CH_2$),

1.18–1.32 (m, 2H, –CH_2), 0.86 (t, *J* 7.2 Hz, 3H, –CH_3). ^{13}C NMR ($CDCl_3$): δ_C 152.8 (Ar-C), 148.3 (Ar-C), 135.9 (Ar-C), 135.8 (Ar-C), 129.7 (Ar-C), 129.1 (Ar-C), 127.4 (Ar-C), 120.5 (Ar-2C), 115.8 (Ar-*C*N), 115.5 (Ar-*C*N), 102.5 (Ace-C), 97.2 (Ar-C), 94.1 (Ar-C), 80.3 (Ar-C), 79.4 (C-5), 77.3 (C-3), 75.1 (C-1), 74.3 (C-2), 70.4 (C-4), 68.2 (C-6), 37.6 (–*C*H_2–Ar), 36.2 (–*C*H_2), 17.4 (–*C*H_2), 13.9 (–*C*H_3). Anal. Calcd for $C_{25}H_{26}ClN_3O_5$: C, 62.05; H, 5.42; N, 8.68. Found: C, 62.12; H, 5.20; N, 8.20.

1.2.4. Physicochemical and spectral data for 2-amino-4-(pyridin-2-yl)-6-[(4,6-*O*-butylidene-β-D-glucopyranosyl)-methyl] isophthalonitrile (6d)

From 1-(4,6-*O*-butylidene-β-D-glucopyranosyl)propane-2-one (**3**) (0.274 g, 1.0 mmol), 2-pyridinecarboxaldehyde (**4d**) (0.107 g, 1.0 mmol), malononitrile (**5**) (0.122 g, 2.0 mmol). Brown solid (0.189 g, 42%); mp 122–124 °C; ^{1}H NMR ($CDCl_3$): δ_H 8.29–8.34 (m, 2H, Ar-H), 7.53 (d, *J* 7.8 Hz, 1H, Ar-H), 7.08 (t, *J* 4.8 Hz, 1H, Ar-H), 6.36 (s, 1H, Ano-H), 5.74 (s, 1H, –NH_2), 4.98 (broad 1H, –NH_2), 4.92 (broad 1H, Ace-H), 4.68 (s, 1H, Ace-H), 3.88–3.95 (m, 1H, H-4′), 3.60–3.64 (m, 1H, H-3′), 3.12–3.18 (m, 4H, H-1′, H-2′, H-5′, H-6′), 2.80–2.89 (m, 3H, H_a & Sac-OH), 2.45–2.52 (m, 1H, Sac-OH), 1.17–1.18 (m, 2H, –CH_2), 0.86–1.01 (m, 2H, –CH_2), 0.51 (t, *J* 7.2 Hz, 3H, –CH_3). ^{13}C NMR ($CDCl_3$): δ_C 158.3 (Ar-C), 154.9 (Ar-C), 153.8 (Ar-C), 153.5 (Ar-C), 150.3 (Ar-C), 140.8 (Ar-C), 138.6 (Ar-C), 128.6 (Ar-C), 128.3 (Ar-C), 124.5 (Ar-C), 120.8 (Ar-*C*N), 120.2 (Ar-*C*N), 106.9 (Ace-C), 102.9 (Ar-C), 98.4 (C-5), 85.3 (C-3), 84.6 (C-1), 79.4 (C-2), 75.3 (C-4), 72.9 (C-6), 42.3 (–*C*H_2–Ar), 41.0 (–*C*H_2), 22.1 (–*C*H_2), 18.7 (–*C*H_3). Anal. Calcd for $C_{24}H_{26}N_4O_5$: C, 63.99; H, 5.82; N, 12.44. Found: C, 63.50; H, 5.39; N, 12.32.

1.2.5. Physicochemical and spectral data for 2-amino-4-(pyridin-3-yl)-6-[(4,6-*O*-butylidene-β-D-glucopyranosyl)-methyl] isophthalonitrile (6e)

From 1-(4,6-*O*-butylidene-β-D-glucopyranosyl)propane-2-one (**3**) (0.274 g, 1.0 mmol), 3-pyridinecarboxaldehyde (**4e**) (0.107 g, 1.0 mmol), malononitrile (**5**) (0.132 g, 2.0 mmol). Brown solid (0.256 g, 57%); mp 142–144 °C; ^{1}H NMR ($CDCl_3$): δ_H 8.60–8.65 (m, 2H, Ar-H), 7.81–7.84 (m, 1H, Ar-H), 7.37–7.40 (m, 1H, Ar-H), 6.66 (s, 2H, –NH_2), 5.96 (s, 1H, Ano-H), 5.06 (broad, 1H, Ace-H), 4.77 (broad 1H, Ace-H), 4.44 (t, *J* 4.8 Hz, 1H, H-4), 3.92–3.96 (m, 1H, H-3′), 3.43–3.52 (m, 2H, H-1′, H-2′), 3.30–3.35 (m, 2H, H-5′, H-6′), 3.09–3.19 (m, 3H, H_a & Sac-OH), 2.81–2.84 (m, 1H, Sac-OH), 1.47–1.52 (m, 2H, –CH_2), 1.28–1.35 (m, 2H, –CH_2), 0.80 (t, *J* 7.2 Hz, 3H, –CH_3). ^{13}C NMR ($CDCl_3$): δ_C 158.2 (Ar-C), 154.9 (Ar-C), 153.8 (Ar-C), 153.6 (Ar-C), 150.3 (Ar-C), 140.7 (Ar-C), 138.5 (Ar-C), 128.2 (Ar-C), 124.5 (Ar-C), 120.7 (Ar-*C*N), 120.1 (Ar-*C*N), 106.9 (Ace-C), 102.9 (Ar-C), 98.5 (Ar-C), 85.3 (C-5), 84.6 (C-3), 79.5 (C-1), 79.3 (C-2), 75.3 (C-4), 72.9 (C-6), 42.3 (–*C*H_2–Ar), 41.0 (–*C*H_2), 22.1 (–*C*H_2), 18.7 (–*C*H_3). Anal. Calcd for $C_{24}H_{26}N_4O_5$: C, 63.99; H, 5.82; N, 12.44. Found: C, 63.32; H, 5.40; N, 12.20.

1.2.6. Physicochemical and spectral data for 2-amino-4-(methoxyphenyl-4-yl)-6-[(4,6-*O*-butylidene-β-D-glucopyranosyl)-methyl] isophthalonitrile (6f)

From 1-(4,6-*O*-butylidene-β-D-glucopyranosyl)propane-2-one (**3**) (0.274 g, 1.0 mmol), 4-methoxyphenylcarboxaldehyde (**4f**) (0.136 g, 1.0 mmol), malononitrile (**5**) (0.132 g, 2.0 mmol). Pale yellow solid (0.306 g, 68%); mp 143–145 °C; ^{1}H NMR ($CDCl_3$): δ_H 7.50–7.57 (m, 1H, Ar-H), 7.34 (s, 1H, Ar-H), 7.02 (d, *J* 8.4 Hz, 1H, Ar-H), 6.78–6.89 (m, 2H, –NH_2), 5.30 (s, 2H, Ace-H), 4.53 (d, *J* 4.5 Hz, 1H, Ano-H), 4.06–4.09 (d, *J* 8.7 Hz, 1H, H-4′), 3.81 (s, 2H, H-3′, H-1′), 3.74 (s, 5H, H-2′, H-5′, H-6′, Sac-OH), 3.40 (t, *J* 6.6 Hz, 2H, H_a), 3.23–3.25 (m, 3H, –OCH_3), 2.82–2.93 (m, 1H, Sac-OH), 1.70 (m, 2H, –CH_2), 1.45 (m, 2H, –CH_2), 0.74 (t, *J* 7.5 Hz, 3H, –CH_3). ^{13}C NMR ($CDCl_3$): δ_C 160.7 (Ar-C), 152.9 (Ar-C), 149.4 (Ar-2C), 147.9 (Ar-C), 129.8 (Ar-2C), 129.7 (Ar-C), 120.1 (Ar-2C), 114.3 (Ar-2×*C*N), 102.5 (Ace-C), 96.2 (Ar-C), 94.0 (Ar-C), 80.3 (C-5) 79.5 (C-3), 77.3 (C-1), 75.0 (C-2), 74.3 (C-4), 70.4 (C-6), 55.3 (-OCH_3), 36.2 (–*C*H_2–Ar), 27.0 (–*C*H_2), 17.5 (–*C*H_2), 14.0 (–*C*H_3). Anal. Calcd for $C_{26}H_{29}N_3O_6$: C, 65.12; H, 6.10; N, 8.76. Found: C, 65.50; H, 6.29; N, 8.46.

1.2.7. Physicochemical and spectral data for 2-amino-4-(benzo[1,3]-dioxol-4-yl)-6-[(4,6-*O*-butylidene-β-D-glucopyranosyl)-methyl] isophthalonitrile (6g)

From 1-(4,6-*O*-butylidene-β-D-glucopyranosyl)propane-2-one (**3**) (0.274 g, 1.0 mmol), piperanal (**4g**) (0.150 g, 1.0 mmol), malononitrile (**5**) (0.122 g, 2.0 mmol). White solid (0.231 g, 47%); mp 161–163 °C; ^{1}H NMR ($CDCl_3$): δ_H 7.27 (s, 2H, Ar-H), 6.99–7.04 (m, 1H, Ar-H), 6.90–6.93 (m, 1H, Ar-H), 6.74 (s, 1H, Ar-H), 5.96–6.05 (m, 1H, Ar-H), 5.25 (broad, 1H, –NH_2), 4.52 (t, *J* 4.8 Hz, 1H, Ano-H), 4.06–4.10 (m, 1H, Ace-H), 3.68–3.71 (m, 1H, H-4′), 3.56–3.66 (m, 1H, H-3′), 3.44–3.47 (m, 2H, H-1′, H-2′), 3.36–3.43 (m, 3H, H-5′, H-6′, Sac-OH), 3.21–3.23 (m, 2H, Sac-OH), 2.88–2.96 (m, 2H, H_a), 1.35–1.40 (m, 2H, –CH_2), 1.25 (m, 2H, –CH_2), 0.94 (t, *J* 7.2 Hz, 3H, –CH_3). ^{13}C NMR ($CDCl_3$): δ_C 152.7 (Ar-C), 149.4 (Ar-2C), 148.1 (Ar-C), 147.8 (Ar-C), 131.4 (Ar-C), 122.7 (Ar-2C), 120.6 (Ar-C), 118.3 (Ar-*C*N), 118.7 (Ar-*C*N), 108.7 (Ace-C), 108.6 (Ar-C), 102.5 (Ar-C), 101.6 (Ar-C), 97.0 (C-5), 80.3 (C-3), 79.4 (C-1), 75.2 (C-2), 74.2 (C-4), 70.4 (C-6), 68.2 (Ar-CH_2), 37.4 (–*C*H_2–Ar), 36.2 (–*C*H_2), 17.4 (–*C*H_2), 13.9 (–*C*H_3). Anal. Calcd for $C_{26}H_{27}N_3O_7$: C, 63.28; H, 5.51; N, 8.51. Found: C, 63.50; H, 5.29; N, 8.16.

Acknowledgements

T.M. acknowledges financial support from the SERC-DST, New Delhi. We also thank DST, New Delhi for 300 MHz NMR spectrometer under FIST scheme to the Department of Organic Chemistry, University of Madras, Chennai.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2012.05.001.

References

1. Komiotisa, D.; Balzarinib, J.; Parmenopouloua, V.; Mantaa, S.; Kiritsisa, C. *Eur. J. Med. Chem.* **2011**, *46*, 5668–5674.
2. Shao, H.; Wang, Z.; Lacroix, E.; Wu, S.-H.; Jennings, H. J.; Zou, W. *J. Am. Chem. Soc.* **2002**, *124*, 2130–2131.
3. Barluenga, S.; Simonsen, K. B.; Littlefield, E. S.; Ayida, B. K.; Vourloumis, D.; Winters, G. C.; Takahashi, M.; Shandrick, S.; Zhao, Q.; Han, Q.; Hermann, T. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 713–718.
4. Flachsmann, F.; Schellhaas, K.; Moya, C. E.; Jacobs, R. S.; Fenical, W. *Bioorg. Med. Chem.* **2010**, *18*, 8324–8333.
5. Yin, J.; Linker, T. *Org. Biomol. Chem.* **2012**, *10*, 2351–2362.
6. Dwek, R. A. *Chem. Rev.* **1996**, *96*, 683–720.
7. Varki, A. *Glycobiology* **1993**, *3*, 97–130.
8. Kim, M. J.; Lee, J.; Kang, S. Y.; Lee, S.-H.; Son, E.-J.; Jung, M. E.; Lee, S. H.; Song, K.-S.; Lee, M. W.; Han, H.-K.; Kim, J.; Lee, J. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 3420–3425.
9. Misra, M.; Sharma, R.; Kant, R.; Maulik, P. R.; Tripathi, R. P. *Tetrahedron* **2011**, *67*, 740–748.
10. Raghukumar, V.; Thirumalai, D.; Ramakrishnan, V. T.; Karunakaran, V.; Ramamurthy, P. *Tetrahedron* **2003**, *59*, 3761–3768.
11. Yi, C.; Blum, C.; Liu, S. X.; Frei, G.; Neels, A.; Renaud, L. S.; Decurtins, S. *J. Org. Chem.* **2008**, *73*, 3596–3599.
12. Nagarajan, S.; Mohan Das, T. *Carbohydr. Res.* **2009**, *344*, 1028–1031.
13. Nagarajan, S.; Mohan Das, T.; Arjun, P.; Raaman, N. *J. Mater. Chem.* **2009**, *19*, 4587–4596.
14. Palomo, C.; Aizpurua, J. M.; Balentova, E.; Azcune, I.; Santos, J. I.; Jimenez-Barbero, J.; Canada, J.; Miranda, J. I. *Org. Lett.* **2008**, *10*, 2227–2230.
15. Nagarajan, S.; Arjun, P.; Raaman, N.; Shah, A.; Sobhia, M. E.; Mohan Das, T. *Tetrahedron* **2012**, *68*, 3037–3045.