An efficient synthesis of novel sucrose-containing dilactams

Mykhaylo A. Potopnyk · Sławomir Jarosz

Received: 27 September 2012 / Accepted: 29 November 2012 / Published online: 17 January 2013
© The Author(s) 2013. This article is published with open access at Springerlink.com

Abstract An efficient and convenient approach to sucrose-containing dilactams has been developed. The method, based on reaction of regioisomeric 6,6'-di-O-[(aminomethyl)phenyl]-1',2,3,3',4,4'-hexa-O-methylsucrose with isophthaloyl or 2,6-pyridinedicarbonyl dichlorides, provided the 1:1-macrocycles in good yields.

Keywords Carbohydrates · Macrocycles · Alkylation · Reductions · Cyclization

Introduction

Macrocyclic compounds are important in supramolecular chemistry [1]. Especially interesting are chiral receptors capable of enantioselective complexation of a variety of important chiral guests. Carbohydrates, inexpensive, renewable raw materials available optically pure, are particularly useful in planning and executing the synthesis of such chiral hosts. The different configurations and conformations of carbohydrates can be incorporated in the target macrocycle, which makes these compounds convenient chiral synthetic analogs of poly(ethylene glycol) (PEG) reagents [2].

Chiral crown and aza-crown ethers with carbohydrate scaffolds have been extensively used as chiral catalysts in asymmetric synthesis [3–5]. Michael addition [3, 4, 6, 7], and Darzens reactions [3–5, 7, 8]). Carbohydrate-containing macrocycles have also been investigated as fluorescent molecular sensors for cations [9, 10] and anions [11].

Sucrose, the most common disaccharide occurring in nature, is a promising building block for synthesis of such chiral macrocyclic receptors [12–14]. Its aza-crown derivatives enabled highly enantioselective complexation of the (S)-1-phenylethylammonium cation [15].

Isophthalic and pyridine-2,6-diamides, because of their proton-donor properties, are convenient scaffolds used as building blocks in the synthesis of macrocyclic receptors designed for complexation of anions [16], ion pairs [17], zwitterions [18], and amino acid derivatives [19]. The anion-complexing properties of such diamides have been exploited in templated syntheses of catenane [20] and rotaxane [21] systems. Macrocycles incorporating the pyridine-2,6-diamide functionality are known as molecular turnstiles [22]. Combination of the sucrose scaffold with isophthalic or pyridine-2,6-diamide units may be useful means of synthesis of a new type of chiral receptor with interesting properties.

Very recently, we reported an effective procedure for synthesis of 1',2,3,3',4,4'-hexa-O-methyl-6,6'-di-O-(methylsulfonyl)sucrose (1; four steps, 48 % overall yield) which was used for preparation of macrocyclic bis-amides 3a–3c and 4a–4c (Scheme 1). Condensation of dimesylate 1 with 2 equiv. of the appropriate nitrophenol (ortho, meta, or para) followed by reduction of the nitro groups provided the expected 6,6'-di-O-(aminophenyl)-1',2,3,3',4,4'-hexa-O-methylsucroses (2a–2c). Reaction of dianilines 2a and 2b (o or m) with isophthaloyl or 2,6-pyridinedicarbonyl dichlorides (5 and 6) afforded the monomeric macrocycles in excellent yields, whereas reaction of the p-diamines furnished dimers as the major products (Scheme 1), with smaller amounts of the expected monomers 3c, 4c [23].
A crucial aspect of the synthesis of this type of receptor is the relative orientation of the two amino groups in the energetically accessible conformations of the substrates. The amino groups in the \( p \)-substituted derivative 2c are rather distant from each other (compared with the \( o \) and \( m \) analogs 2a and 2b). Thus, the intermediate formed in reaction of the acid dichloride (5 or 6) with the first amino group will react preferentially with a second molecule of 2c (to form the dimer) rather than undergo the intramolecular reaction of the acid dichloride (which furnishes both the monomers and the dimers in the reaction with dichlorides 5 or 6; Scheme 1) only in the length of the chain, we were able to suppress formation of the dimer and obtain monomeric macrocycles in good yield. This strategy was applicable to the synthesis of sucrose-derived macrocycles containing isophthalic and pyridine-2,6-diamide groups.

**Experimental**

All reported NMR spectra were recorded with a Varian Vnmrs-600 MHz spectrometer (at 600 and 150 MHz for \(^1\)H and \(^13\)C NMR spectra, respectively); solutions were prepared in CDCl\(_3\) with TMS as the internal standard. Most of the resonances were assigned by COSY (\(^1\)H–\(^1\)H) and gradient selected HSQC and HMBC correlations. IR spectra (CHCl\(_3\), film) were recorded on a Perkin Elmer FT-IR Spectrum 2000. Mass spectra were recorded with an ESI/MS Mariner (PerSeptive Biosystem) mass spectrometer. Elemental analysis was performed with a Perkin-Elmer 2400 CHN analyzer; results agreed satisfactorily with calculated values. Optical rotation was measured with a Jasco DIP-360 digital polarimeter; solutions were prepared in CH\(_2\)Cl\(_2\) (\( c = 1 \)). Flash chromatography was performed on silica gel (Merck, 230–400 mesh). The organic phases were dried over anhydrous magnesium sulfate.

**General procedure for preparation of 6,6'-di-O-(cyanophenyl)-1',2,3,3',4',4'-hexa-O-methylsuccroses (8a–8c)**

To a solution of 291 mg compound 1 (0.5 mmol) in 25 cm\(^3\) dry DMF, 345 mg K\(_2\)CO\(_3\) (2.5 mmol) was added than 179 mg of the corresponding cyanophenol 7a–7c (1.5 mmol). The mixture was stirred for 24 h at 100 °C then cooled to room temperature. Water (50 cm\(^3\)) and 50 cm\(^3\) AcOEt were added, the organic phase was separated, and the aqueous
phase was extracted with ethyl acetate (4 × 50 cm³). Combined organic solutions were washed with water (2 × 30 cm³). 30 cm³ brine, dried, concentrated, and the product was isolated by flash chromatography (hexane–ethyl acetate, 9:1 to 7:3) to afford 8a–8c.

(a) K₂CO₃, DMF, 100 °C, 24 h; (b) LiAlH₄, THF, 60 °C, 1 h; (c) 5 or 6, Et₃N, CH₂Cl₂, rt, 1 h

Fig. 1 Macrocyclic diamides 10a–10c and 11a–11c

6,6’-Di-O-(2-cyanophenyl)-1’,2,3,3’,4,4’-hexa-O-methylsucrose (8a, C₃₂H₄₀N₂O₁₁)
Colorless oil; yield: 255 mg (81%); TLC: Rₚ = 0.47 (hexane/AcOEt 1:2); [α]D sup34 = +55.9° cm⁻¹ g⁻¹; IR: ν = 2,983, 2,934, 2,832, 2,228, 1,741, 1,599, 1,581, 1,494, 1,449, 1,374,
1.292, 1.261, 1.185, 1.164, 1.102, 1.045, 1.018, 0.983, 0.879, 0.835, 0.757, 0.667, 0.566, 0.497 cm⁻¹; ¹H NMR: δ = 7.55 (dd, J = 7.7 Hz, 1.7 Hz, 1H, Ar), 7.53 (dd, J = 7.5 Hz, 1.7 Hz, 1H, Ar), 7.51 (dd, J = 8.4 Hz, 7.6 Hz, 1.6 Hz, 1H, Ar), 7.37 (dd, J = 8.5 Hz, 7.6 Hz, 1.7 Hz, 1H, Ar), 6.99–7.07 (m, 3H, Ar), 6.95 (dd, J = 7.6 Hz, 7.6 Hz, 1H, Ar), 5.59 (d, J₁₂ = 3.7 Hz, 1H, H-1'), 4.32–4.34 (m, 2H, 2H-6'), 4.23–4.27 (m, 3H, H-5', 2H-6'), 4.18–4.21 (m, 1H, H-5'), 4.09 (d, J₃₄', = 6.7 Hz, 1H, H-3'), 3.90 (dd, J₃₄', = 6.7 Hz, J₄₅', = 6.1 Hz, 1H, H-4'), 3.66 (d, J₁₁', = 11.1 Hz, 1H, H-1'), 3.60 (s, 3H, CH₃), 3.54 (s, 3H, CH₃), 3.51 (dd, J₃₂ = 9.7 Hz, J₃₄ = 9.1 Hz, 1H, H-3), 3.49 (s, 3H, CH₃), 3.47 (s, 3H, CH₃), 3.46 (s, 3H, CH₃), 3.43 (d, J₁₁', = 11.1 Hz, 1H, H-1'), 3.42 (s, 3H, CH₃), 3.34 (dd, J₃₄ = 9.1 Hz, J₄₅ = 10.0 Hz, 1H, H-4), 3.16 (dd, J₁₂ = 3.7 Hz, J₂₃ = 9.7 Hz, 1H, H-2') ppm; ¹³C NMR: δ = 160.49, 160.33, 134.33, 134.15, 133.82, 133.82, 121.13, 121.01, 116.40, 116.30, 112.79, 112.79 (12 C-Ar, Ar-C), 104.98 (C-2'), 102.33 (CN), 102.25 (CN), 90.02 (C-1), 85.88 (C-3'), 84.92 (C-4'), 83.12 (C-3), 81.46 (C-2), 79.16 (C-4), 78.83 (C-5'), 73.30 (C-1'), 70.42 (C-6'), 69.71 (C-5), 68.52 (C-6), 60.63, 60.47, 59.51, 58.75, 58.55, 58.46 (6 × OCH₃) ppm; HRMS (ESI): calculated for C₃₃H₄₀N₂O₁₁Na [M + Na]⁺ 651.2524, found 651.2525.

6,6'-Di-O-(3-cyanophenyl)-1',2,3,3',4,4'-hexa-O-methylsuccrose (8b, C₂₂H₄₀N₂O₁₁) Colorless oil; yield: 265 mg (84 %); TLC: Rf = 0.51 (hexane/AcOEt 1:2); [α]D⁰ = +56.3⁰ cm² g⁻¹; IR: ν = 3,075, 2,982, 2,933, 2,831, 2,231, 1,741, 1,597, 1,579, 1,483, 1,432, 1,328, 1,291, 1,265, 1,185, 1,148, 1,101, 1,017, 983, 873, 790, 756, 682, 616, 517, 475 cm⁻¹; ¹H NMR: δ = 7.36 (dd, J = 7.8 Hz, 8.0 Hz, 1H, Ar), 7.28 (dd, J = 7.8 Hz, 8.2 Hz, 1H, Ar), 7.24 (d, J = 7.6 Hz, 1H, Ar), 7.20 (d, J = 7.4 Hz, 1H, Ar), 7.12–7.17 (m, 3H, Ar), 7.11 (dd, J = 8.2 Hz, 2.3 Hz, 1H, Ar), 5.60 (d, J₁₂ = 3.7 Hz, 1H, H-1'), 4.29 (m, 1H, H-6'), 4.12–4.23 (m, 5H, H-5, H-5'), 2H-6', 4.11 (d, J₃₄', = 7.6 Hz, 1H, H-3'), 3.97 (dd, J₃₄', = 7.6 Hz, J₄₅', = 7.3 Hz, 1H, H-4'), 3.64 (s, 3H, CH₃), 3.61 (d, J₁₁', = 11.0 Hz, 1H, H-1'), 3.53 (s, 3H, CH₃), 3.51 (s, 3H, CH₃), 3.49 (m, 1H, H-3), 3.47 (s, 3H, CH₃), 3.44 (s, 3H, CH₃), 3.43 (d, J₁₁', = 11.0 Hz, 1H, H-1'), 3.22 (dd, J = 10.2 Hz, 8.9 Hz, 1H, H-4), 3.16 (dd, J₁₂ = 3.7 Hz, J₂₃ = 9.7 Hz, 1H, H-2') ppm; ¹³C NMR: δ = 158.74, 158.65, 130.47, 130.26, 124.83, 124.76, 119.90, 119.84, 118.51, 118.51, 117.48, 117.39 (12 × C- Ar), 113.30 (CN), 113.16 (CN), 104.39 (C-2'), 89.39 (C-1), 85.34 (C-3'), 83.79 (C-4'), 83.21 (C-3), 81.64 (C-2), 79.47 (C-4), 78.53 (C-5'), 73.70 (C-1'), 69.66 (C-5), 69.30 (C-6'), 67.80 (C-6), 60.76, 60.58, 59.42, 58.65, 58.47, 58.43 (6 × OCH₃) ppm; HRMS (ESI): calculated for C₃₃H₄₀N₂O₁₁Na [M + Na]⁺ 651.2524, found 651.2522.

General procedure for synthesis of 6,6'-di-O-[-4-(aminomethyl)phenyl]-1',2,3,3',4,4'-hexa-O-methylsuccroses (9a–9c) To a cooled (0 °C) solution of 215 mg compound 8a–8c (0.34 mmol) in 30 cm³ dry THF, 93 mg LiAlH₄ (2.45 mmol) was added slowly within 5 min. The mixture was stirred for 1 h at 60 °C and cooled to room temperature. Excess hydride was carefully decomposed with 10 cm³ water and 40 cm³ aqueous potassium bisulfate (KH₂SO₄). Ethyl acetate (50 cm³) was added, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 40 cm³). The combined organic solutions were dried, concentrated, and the crude product was used in the next step without purification.

General procedure for syntheses of macrocyclic diamides 10a–10c and 11a–11c This reaction was conducted under an argon atmosphere: 35 mg isophthaloyl or 2,6-pyridinedicarbonyl dichloride (5 or 6, 0.17 mmol) was dissolved in 20 cm³ dry CH₂Cl₂ and added dropwise to a stirred solution of 108 mg diamine 9a–9c (0.17 mmol) in 40 cm³ dry CH₂Cl₂ containing 71 mm³ Et₃N (0.51 mmol), and the mixture was stirred for
1 h at room temperature. The resulting solution was concentrated in vacuum and the residue was dissolved in 40 cm$^3$ ethyl acetate and 20 cm$^3$ water. Saturated K$_2$CO$_3$ solution (10 cm$^3$) was added, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 $\times$ 30 cm$^3$). The combined organic extracts were washed with 20 cm$^3$ water and 10 cm$^3$ brine, dried, concentrated, and the products were isolated by flash chromatography (hexane–ethyl acetate, 50:50 to 25:75).

6,6'-Di-O-[[benzene-1,3-diybis(carboxylaminomethyl)]-2,2'-diphenyl]-1',2,3',3',4',4'-hexa-O-methylsuccrose (10a, C$_{44}$H$_{50}$N$_2$O$_{13}$)

White solid; yield: 84 mg (64%); m.p.: 134°C; TLC: $R_f$ = 0.35 (AcOEt); [$\alpha$]$_{D}^{22}$ = +78.8° cm$^2$ g$^{-1}$; IR: $\tilde{\nu}$ = 3,347, 3,064, 2,982, 2,933, 2,830, 1,658, 1,603, 1,590, 1,526, 1,495, 1,451, 1,359, 1,318, 1,293, 1,250, 1,186, 1,161, 1,100, 1,049, 1,017, 1,004, 982, 941, 882, 825, 753, 710, 593, 527 cm$^{-1}$; $^1$H NMR: $\delta$ = 8.01–8.05 (m, 2H, isophthalic), 7.57 (s, 1H, isophthalic), 7.52 (t, $J = 7.7$ Hz, 1H, isophthalic), 7.32 (d, $J = 7.3$ Hz, 1H, Ar), 7.26–7.31 (m, 3H, Ar), 6.92–6.96 (m, 2H, Ar), 6.90 (d, $J = 8.5$ Hz, 1H, Ar), 6.85 (br s, 1H, NH), 6.74 (d, $J = 8.0$ Hz, 1H, Ar), 6.66 (br s, 1H, NH), 4.72–4.77 (m, 2H, CH$_2$N), 4.59 (d, $J_{1,2}$ = 3.3 Hz, 1H, H-1), 4.51 (dd, $J = 13.8$ Hz, 6.2 Hz, 1H, CH$_2$N), 4.45 (dd, $J = 13.6$ Hz, 6.5 Hz, 1H, CH$_2$N), 4.27 (dd, $J_{6,\tilde{6}}$ = 9.9 Hz, $J_{6,\tilde{6}}$ = 2.3 Hz, 1H, H-6'), 4.14–4.20 (m, 2H, H-5', H-6'), 4.08 (d, $J_{5,4}$ = 7.4 Hz, 1H, H-3'), 3.93–3.97 (m, 2H, H-5', H-6'), 3.76 (dd, $J_{6,\tilde{6}}$ = 10.0 Hz, $J_{6,\tilde{6}}$ = 1.5 Hz, 1H, H-6), 3.70 (dd, $J_{4,\tilde{4}}$ = 7.5 Hz, $J_{4,\tilde{4}}$ = 7.4 Hz, 1H, H-4'), 3.56 (s, 3H, CH$_3$), 3.47 (s, 3H, CH$_3$), 3.46 (m, 1H, H-3), 3.440 (s, 3H, CH$_3$), 3.435 (s, 3H, CH$_3$), 3.40–3.43 (m, 2H, H-1', H-4), 3.39 (s, 3H, CH$_3$), 3.23 (s, 3H, CH$_3$), 3.14 (d, $J_{1,1}$ = 11.2 Hz, 1H, H-1), 2.75 (dd, $J_{2,1}$ = 3.3 Hz, $J_{2,3}$ = 9.5 Hz, 1H, H-2) ppm; $^1$C NMR: $\delta$ = 166.68 (C=O), 166.75 (C=O), 156.65, 156.81, 156.81 (2 x C=Ar), 135.53, 135.42, 131.21, 130.87 (4 x C-isophthalic), 131.09, 130.84, 129.43, 129.31 (4 x C=Ar), 129.16 (C-isophthalic), 127.05, 125.73 (2 x C=Ar), 123.80 (C-isophthalic), 121.72, 121.10, 112.51, 110.99 (4 x C=Ar), 104.37 (C-2'), 90.41 (C-1'), 84.70 (C-3'), 84.09 (C-4'), 82.72 (C-3), 81.31 (C-2), 78.59 (C-4'), 77.87 (C-5'), 75.35 (C-1'), 70.95 (C-6'), 70.25 (C-5), 66.07 (C-6), 60.67, 60.33, 59.67, 58.87, 58.04, 57.99 (6 x OCH$_3$), 41.53, 40.94 (2 x CH$_3$N) ppm; HRMS (ESI): calecd for C$_{44}$H$_{50}$N$_2$O$_{13}$Na [M + Na]$^+$ 789.3205, found 789.3228.

6,6'-Di-O-[[pyridine-1,3-diybis(carboxylaminomethyl)]-2,2'-diphenyl]-1',2,3',3',4',4'-hexa-O-methylsuccrose (10b, C$_{44}$H$_{50}$N$_2$O$_{13}$)

White solid; yield: 82 mg (63%); m.p.: 111°C; TLC: $R_f$ = 0.36 (AcOEt); [$\alpha$]$_{D}^{22}$ = +59.8° cm$^2$ g$^{-1}$; IR: $\tilde{\nu}$ = 3,333, 2,981, 2,931, 2,830, 1,654, 1,599, 1,586, 1,535, 1,487, 1,448, 1,358, 1,290, 1,267, 1,237, 1,183, 1,151, 1,100, 1,056, 1,017, 997, 983, 956, 876, 755, 691, 622 cm$^{-1}$; $^1$H NMR: $\delta$ = 7.97–8.01 (m, 2H, isophthalic), 7.91 (s, 1H, isophthalic), 7.52 (dd, $J = 7.8$ Hz, 7.8 Hz, 1H, isophthalic), 7.24 (dd, $J = 7.8$ Hz, 7.9 Hz, 1H, Ar), 7.19 (dd, $J = 7.8$ Hz, 8.0 Hz, 1H, Ar), 6.97 (s, 1H, Ar), 6.91 (d, $J = 7.8$ Hz, 1H, Ar), 6.87–6.89 (m, 2H, Ar), 6.82–6.86 (m, 2H, Ar), 6.69 (dd, $J = 5.6$ Hz, 5.6 Hz, 1H, NH), 6.64 (dd, $J = 5.6$ Hz, 5.6 Hz, 1H, NH), 5.70 (d, $J_{1,2}$ = 3.8 Hz, 1H,
H-1), 4.65 (m, 2H, CH2N), 4.50 (dd, J = 14.7 Hz, 5.6 Hz, 1H, CH2N), 4.42 (dd, J = 14.5 Hz, 5.6 Hz, 1H, CH2N), 4.12–4.23 (m, 4H, H-5, H-6, 2 × H-6′), 4.06–4.12 (m, 1H, H-5′), 4.09 (d, Jd,4 = 8.0 Hz, 1H, H-3′), 4.03 (br d, Jd,6 = 9.1 Hz, 1H, H-6), 3.97 (dd, Jd,7 = 8.0 Hz, Jf,5′ = 8.0 Hz, 1H, H-4′), 3.61 (s, 3H, CH3), 3.58 (d, Jf,1′ = 10.9 Hz, 1H, H-1′), 3.49 (s, 3H, CH3), 3.48 (dd, Jd,3 = 9.6 Hz, Jd,4 = 9.3 Hz, 1H, H-3′), 3.45 (s, 3H, CH3), 3.42 (d, Jf,1′ = 10.9 Hz, 1H, H-1′), 3.41 (s, 6H, 2CH3), 3.40 (s, 3H, CH3), 3.36 (ddd, Jd,4 = 9.3 Hz, Jd,5 = 9.6 Hz, 1H, H-4), 3.21 (dd, Jd,1 = 3.8 Hz, Jf,3 = 9.6 Hz, 1H, H-2) ppm; 13C NMR: δ = 166.71 (C-O), 166.34 (C-O), 159.20, 159.01, 139.63, 139.28 (4 × C–Ar), 134.69, 134.56 (2 × C-isophthalic), 130.78 (2C-isophthalic), 129.79, 129.77 (2H, C–Ar, 129.39, 124.05 (2 × C-isophthalic), 121.64, 121.80, 115.13, 114.48, 113.75, 112.49 (6 × C–Ar), 104.15 (C-2′), 88.69 (C-1′), 85.02 (C-3′), 83.17 (C-3), 83.03 (C-4′), 81.29 (C-2), 79.14 (C-4), 78.08 (C-5′), 74.83 (C-1′), 69.66 (C-5), 68.95 (C-6′), 66.30 (C-6), 60.65, 60.46, 59.41, 58.95, 58.39, 58.03 (6 × CH3), 44.25, 43.95 (2 × CH2N) ppm; HRMS (ESI): calcd for C40H50N2O13Na [M + Na]+ 789.3202, found 789.3214.

6.6'-Di-O-[[benzene-1,3-diy-bis(carboxylaminomethyl)]-3,3'-diphenyl]-1',2,3,3',4,4'-hexa-O-methylsucrose (11b, C39H49N3O13

White solid; yield: 86 mg (66%); m.p.: 125 °C; TLC: Rf = 0.39 (AcOEt); [α]D22 = +58.2° cm2 g−1; IR: ν = 3,317, 2,980, 2,930, 2,831, 1,649, 1,613, 1,586, 1,452, 1,415, 1,452, 1,359, 1,319, 1,300, 1,248, 1,160, 1,101, 1,024, 983, 951, 824, 754, 700, 603, 580 cm−1; 1H NMR: δ = 8.34–8.38 (m, 2H, pyridine), 8.04 (t, J = 7.8 Hz, 1H, pyridine), 7.90 (dd, J = 5.1 Hz, 6.6 Hz, 1H, NH), 7.85 (dd, J = 5.6 Hz, 5.6 Hz, 1H, NH), 7.25 (dd, J = 7.5 Hz, 7.9 Hz, 1H, Ar), 7.10 (dd, J = 7.9 Hz, 7.9 Hz, 1H, Ar), 6.92 (d, J = 7.5 Hz, 1H, Ar), 6.91 (d, J = 7.9 Hz, 1H, Ar), 6.81–6.89 (m, 4H, Ar), 5.59 (d, Jd,1 = 3.7 Hz, 1H, H-1), 4.70 (dd, J = 14.7 Hz, 6.6 Hz, 1H, CH2N), 4.61 (dd, J = 14.7 Hz, 5.6 Hz, 1H, CH2N), 4.58 (dd, J = 14.7 Hz, 5.6 Hz, 1H, CH2N), 4.44 (dd, J = 14.7 Hz, 5.1 Hz, 1H, CH2N), 4.31 (m, 1H, H-6′), 4.21 (dd, Jd,4 = 10.1 Hz, Jf,5′ = 3.9 Hz, Jf,6 = 1.6 Hz, 1H, H-4′), 4.10–4.17 (m, 3H, H-5′, H-6′, H-6′), 4.08 (d, Jd,4 = 7.7 Hz, 1H, H-3′), 4.05 (dd, Jd,6 = 10.2 Hz, Jd,5 = 3.9 Hz, 1H, H-6), 3.90 (dd, Jd,4 = 7.7 Hz, Jf,5′ = 7.7 Hz, 1H, H-4′), 3.64 (s, 3H, CH3), 3.58 (d, Jd,1′ = 11.0 Hz, 1H, H-1′), 3.52 (dd, Jd,3 = 9.4 Hz, Jd,4 = 9.2 Hz, 1H, H-3), 3.50 (s, 3H, CH3), 3.48 (s, 3H, CH3), 3.45 (s, 3H, CH3), 3.41 (d, Jd,1′ = 11.0 Hz, 1H, H-1′), 3.34 (s, 3H, CH3), 3.29 (dd, Jd,4 = 9.2 Hz, Jd,5 = 10.1 Hz, 1H, H-4), 3.19 (dd, Jd,1 = 3.7 Hz, Jf,3 = 9.4 Hz, 1H, H-2) ppm; 13C NMR: δ = 163.14 (C=O), 163.08 (C=O), 159.16, 158.93 (2 × C–Ar), 148.63, 148.54 (2 × C-pyridine), 139.25, 139.13 (2 × C–Ar), 139.13 (C-pyridine), 129.96, 129.92 (2 × C–Ar), 125.17, 125.14 (2 × C-pyridine), 121.11, 120.84, 114.41, 114.17, 113.74, 112.95 (6 × C–Ar), 104.07 (C-2′), 89.93 (C-1), 84.93 (C-3′), 83.61 (C-4′), 83.23 (C-3), 81.51 (C-2), 79.45 (C-4′), 78.37 (C-5′), 74.19 (C-1′), 69.70 (C-5), 69.23 (C-6′), 66.77 (C-6), 60.69, 60.47, 59.34, 58.53, 58.41, 58.22 (6 × CH3O), 43.66, 43.63 (2 × CH2N) ppm; HRMS (ESI): calcd for C39H49N3O13Na [M + Na]+ 790.3158, found 790.3125.
6,6′-Di-O-[[pyridine-1,3-diyl-bis(carbonylaminomethyl)]-4,4′-diphenyl]-1′,2,3′,4,4′-hexa-O-methylsucrose (11c, C_{30}H_{39}N_{3}O_{13}S)

White solid; yield: 97 mg (74 %); m.p.: 115 °C; TLC: R_{f} = 0.37 (AcOEt); \[
[\delta]_{D}^{22} = +28.4^\circ \text{cm}^{2} \text{g}^{-1}; \\
\text{IR: } \nu = 3,330, 2,982, 2,932, 2,831, 1,671, 1,613, 1,585, 1,535, 1,449, 1,363, 1,301, 1,287, 1,248, 1,151, 1,100, 1,023, 1,003, 984, 949, 897, 827, 753, 677, 646, 603, 582 \text{ cm}^{-1}; \\
\text{H NMR: } \delta = 8.35 \text{ (dd, J = 7.8 Hz, 1H, pyridine), 8.32 \text{ (dd, J = 7.8 Hz, 1H, pyridine), 8.05 \text{ (t, J = 7.8 Hz, 1H, pyridine), 7.69 \text{ (dd, J = 4.6 Hz, 5.4 Hz, 1H, NH), 7.63 \text{ (dd, J = 4.6 Hz, 4.8 Hz, 1H, NH), 7.26 \text{ (d, J = 8.7 Hz, 2H, Ar), 7.02 \text{ (d, J = 8.7 Hz, 2H, Ar), 6.93 \text{ (d, J = 8.7 Hz, 2H, Ar), 6.73 \text{ (d, J = 8.7 Hz, 2H, Ar), 5.52 \text{ (d, J_{1,2} = 3.7 Hz, 1H, H-1), 4.67 \text{ (dd, J = 5.5 Hz, 14.2 Hz, 1H, CH2N), 4.57 \text{ (dd, J = 5.9 Hz, 14.9 Hz, 1H, CH2N), 4.53 \text{ (dd, J_{6,5}, J_{6,6} = 6.8 Hz, J_{6,5} = 10.0 Hz, 1H, H-6'), 4.46 \text{ (dd, J = 4.2 Hz, 14.9 Hz, 1H, CH2N), 4.42 \text{ (dd, J = 4.1 Hz, 14.2 Hz, 1H, CH2N), 4.34 \text{ (dd, J_{5,6} = 1.3 Hz, J_{5,6} = 6.6 Hz, J_{5,5} = 10.3 Hz, 1H, H-5), 4.24 \text{ (dd, J_{5,6}, J_{5,5} = 3.2 Hz, J_{5,5} = 6.8 Hz, J_{5,5} = 7.6 Hz, 1H, H-5'), 4.22 \text{ (dd, J_{6,5} = 1.3 Hz, J_{6,6} = 9.6 Hz, 1H, H-6), 4.15 \text{ (dd, J_{6,5} = 7.9 Hz, J_{6,5} = 7.6 Hz, 1H, H-4'), 4.12 \text{ (d, J_{Y,Y} = 7.9 Hz, 1H, H-3'), 4.10 \text{ (dd, J_{6,5} = 6.6 Hz, J_{6,6} = 9.6 Hz, 1H, H-6), 4.08 \text{ (dd, J_{6,6}, J_{6,6} = 10.0 Hz, J_{6,6}, J_{6,5} = 3.2 Hz, 1H, H-6'), 3.65 \text{ (s, 3H, CH3), 3.58 \text{ (s, 6H, CH3), 3.57 \text{ (d, J_{1,1} = 11.0 Hz, 1H, H-1'), 3.55 \text{ (m, 4H, H-3, CH3), 3.47 \text{ (s, 3H, CH3), 3.45 \text{ (s, 3H, CH3), 3.40 \text{ (d, J_{1,1} = 11.0 Hz, 1H, H-1'), 3.15 \text{ (dd, J_{2,1} = 3.7 Hz, J_{2,2} = 9.6 Hz, 1H, H-2), 3.13 \text{ (dd, J_{3,3} = 8.7 Hz, J_{4,5} = 10.3 Hz, 1H, H-4) ppm; } ^{13}C \text{ NMR: } \delta = 162.90 \text{ (C=O), 162.77 \text{ (C=O), 158.49, 158.42 (2 \times C=Ar), 148.59, 148.43, 139.23 (3 \times C=pyridine), 129.70 (2C-Ar), 129.61, 129.11 (2 \times C=Ar), 128.17 (2C-Ar), 124.81, 124.76 (2 \times C=pyridine), 114.92 (2C-Ar), 114.70 (2C-Ar), 103.71 (C-2'), 88.70 (C-1), 84.51 (C-4'), 83.70 (C-3'), 83.34 (C-3), 81.73 (C-2), 80.20 (C-4), 79.01 (C-5'), 73.99 (C-1'), 69.93 (C-5), 69.42 (C-6'), 68.06 (C-6), 60.68, 60.47, 59.34, 58.91, 58.75, 58.42 (6 \times OCH3), 43.66, 43.06 (2 \times CH2N) ppm; } \text{HRMS (ESI): calcld for C}_{30}H_{39}N_{3}O_{13}Na [M + Na]^+ 790.3158, found 790.3196.}

Acknowledgments The support from grant POIG.01.02.01-14-102/09 (part-financed by the European Union within the European Regional Development Fund) is acknowledged.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

1. Steed JW, Atwood JL (2009) Supramolecular chemistry, 2nd edn. Wiley, Chichester
2. Bakó P, Keglevich G, Rapi Z, Tóke L (2012) Curr Org Chem 16:297
3. Bakó P, Makó A, Keglevich G, Kubinyi M, Pál K (2005) Tetrahedron Asymmetry 16:1861
4. Makó A, Szöllösy Á, Keglevich G, Menyhárd DK, Bakó P, Tóke L (2008) Monatsch Chem 139:525
5. Rapi Z, Szabó T, Keglevich G, Szöllösy Á, Drahos L, Bakó P (2011) Tetrahedron Asymmetry 22:1189
6. Bakó T, Bakó P, Keglevich G, Báthori N, Czegler M, Tata P, Novák T, Parlagh G, Tóke L (2003) Tetrahedron Asymmetry 14:1917
7. Bakó P, Rapi Z, Keglevich G, Szabó T, Sóti PL, Vigh T, Grün A, Holczbauer T (2011) Tetrahedron Lett 52:1473
8. Rapi Z, Bakó P, Keglevich G, Szöllösy Á, Drahos L, Botyánszki A, Holczbauer T (2012) Tetrahedron Asymmetry 23:489
9. Xie J, Ménard M, Maisonneuve S, Metivier R (2007) J Org Chem 72:5980
10. Hsieh YC, Chir JL, Wu HH, Guo CQ, Wu AT (2010) Tetrahedron Lett 51:109
11. Yang ST, Liao DJ, Chen SJ, Hu CH, Wu AT (2012) Analyst 137:1553
12. Jarosz S, Listkowski A (2003) J Carbohydr Chem 22:753
13. Jarosz S, Listkowski A (2006) Can J Chem 84:492
14. Lewandowski B, Jarosz S (2010) Org Lett 12:2532
15. Lewandowski B, Jarosz S (2008) Chem Commun 47:6399
16. Sansone F, Baldini L, Casnati A, Lazzarotto M, Ugazzoli F, Ungaro R (2002) Proc Natl Acad Sci USA 99:4842
17. Kima SK, Sessler JL (2010) Chem Soc Rev 39:3784
18. Santos SM, Costa PJ, Lankshear MD, Beer PD, Félix V (2010) J Phys Chem B 114:11173
19. Gasparini F, Mistici D, Pierini M, Villani C (2002) Org Lett 4:3993
20. Evans NH, Rahman H, Leontiev AV, Greenham ND, Orłowski GA, Zeng Q, Jacobs RMJ, Serpell CJ, Kilah NL, Davis JJ, Beer PD (2012) Chem Sci 3:1080
21. Evans NH, Serpell CJ, Beer PD (2011) Chem Commun 47:8775
22. Tóke L, Graf E, Kyritsakas N, Hosseini MW (2012) Chem Eur J 18:10419
23. Potopnyk MA, Cnoch P, Jarosz S (2012) Org Lett 14:4258