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New chiral oligopyridines—4,4′-bis(disaccharide)-functionalised 2,2′-bipyridines and 4′-(disaccharide)-functionalised 2,2′:6′,2″-terpyridines

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ABSTRACT

A new class of oligopyridine ligands bearing disaccharides linked to the 4- and 4′-positions of a 2,2′-bipyridine or the 4′-position of a 2,2′:6′,2″-terpyridine metal-binding domain are described. Representative ligands with furanosylfuranose and pyranosylpyranose (cellobiose) substituents have been prepared.

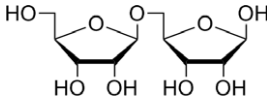
1. Introduction

Enantiopure chiral ligands are widely used in organometallic and coordination chemistry,[1] and have applications ranging from the preparation of diastereoisomerically pure complexes, enantioselective catalysis and enantioselective recognition.[2,3] In general, the ligands are prepared using enantiopure species from the chiral pool.[4] Of all the classes of compounds in the chiral pool, sugars are probably the cheapest and most widely available and, at the same time, less frequently encountered as components of chiral ligands.[5] The latter observation reflects the large number of functional groups in sugars, which can compete for metal-binding, the hydrophilicity and the tendency for unprotected sugars to have low solubilities in solvents other than water, and the possibility of equilibria between open chain and various ring forms. A number of examples of oligopyridine and related ligands with sugar substituents have been described.[6–9] To the best of our knowledge, only one example of an oligopyridine ligand bearing disaccharide substituents has been described,[10a] although an adduct between cobalt complexes of 2,2′-bipyridine-4,4′-diboronic acid and cellobiose has been described.[10b] We are interested in the use of chiral ligands containing 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) 2,2′:6′,2″-terpyridine (tpy) metal-binding domains for the modular preparation of new hybrid organic–inorganic materials,[11] and in this paper we describe the synthesis of 2,2′-bipyridines and 2,2′:6′,2″-terpyridines bearing disaccharide substituents.

2. Results and discussion

2.1. Target disaccharides

To establish the use of disaccharides as chiral auxillaries, we selected representative furanosylfuranose and pyranosylpyranose examples for comparison with ribofuranose and glucopyranosyl compounds that we have previously described. We wanted as general a synthetic route as possible that would allow us to prepare both hydrophobic protected and hydrophilic deprotected ligands and complexes. The target sugars that we selected were β-D-ribofuranosyl-(1→5)-D-ribofuranose **1** (β form shown) and β-D-glucopyranosyl-(1→4)-D-glucose (cellobiose) **2** (β form shown).



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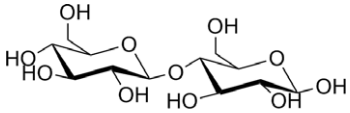

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The disaccharides were functionalised at the anomeric position with an electrophilic substituent (target compounds **3** and **4** with 2-haloethyloxy substituents) and subsequently reacted with a nucleophilic oligopyridine derivative. Preliminary studies with

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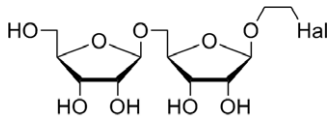
model monosaccharides indicated that a spacer was necessary to give hydrolytically stable derivatives. For the initial studies, the nucleophilic oligopyridine of choice was 4,4′-bis(hydroxy)-2,2′-bipyridine **5** (conveniently depicted as the hydroxypyridine tautomer).



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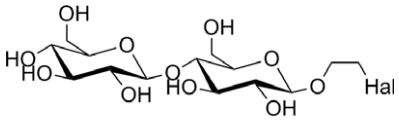

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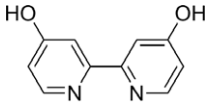

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2.2. Synthesis of β-D-ribofuranosyl-(1→5)-D-ribofuranosides

The preparation of the pentaacetate of **3** (**12**, Hal = Cl, **14** Hal = I) is presented in Scheme 1, and starts with the commercially available compound 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose **6**, which was converted to the 2-chloroethyl 2,3,5-tri-*O*-acetyl-β-D-ribofuranoside **7** in 64% yield by sequential reaction with $SnCl_4$ in acetonitrile followed by treatment with 2-chloroethanol in acetonitrile, analogous to the known conversion of tetra-*O*-acetyl-β-D-arabinofuranose to 2-chloroethyl 2,3,5-tri-*O*-acetyl-β-D-arabinofuranoside.[12] It is critical that the 2-chloroethanol is added very slowly to prevent the concurrent formation of significant amounts of the α-anomer. The diastereotopic protons of the C-5 methylene group are well separated and appear at δ 4.16 and 4.31 ppm. Assignment of the sugar protons was made by a combination of COSY and NOESY spectroscopy, and the stereochemistry was confirmed by a solid state structural determination[13] which established that the β-anomer had been formed. Compound **7** was deprotected by treatment with either hydroxide-form Amberlyst A-26 in methanol or methanolic sodium methoxide[14] to give 2-chloroethyl β-D-ribofuranoside **8** in essentially quantitative yield. Figure 1 shows the generic numbering scheme used for the ligands and their precursors.

The primary alcohol at the 5-position in **8** was then selectively protected by reaction with trityl chloride in pyridine, following the method of Isobe[15] to give 2-chloroethyl 5-*O*-trityl-β-D-ribofuranoside **9** as a pale yellow oil in 76% yield. The secondary alcohols at the 2,3-positions were then protected by reaction with acetic anhydride in pyridine[16] to give 2-chloroethyl 2,3-di-*O*-acetyl-5-*O*-trityl-β-D-ribofuranoside **10** in 94% yield as a yellow oil. The trityl protection was removed by reaction with 5% TFA in $CHCl_3$ under conditions optimised for arabinofuranosides[17] to give 2-chloroethyl 2,3-di-*O*-acetyl-β-D-ribofuranoside **11** as a colourless oil. The ^1H NMR spectrum of a solution of **11** in $CDCl_3$ exhibited a single hydroxy proton at δ 2.25 ppm, which exchanged upon the addition of a few drops of D_2O.

The critical reaction step is the formation of the disaccharide, and we adopted the methodology developed for analogous reactions of 2,3-di-*O*-acetyl-β-D-arabinofuranosides.[12] An acetonitrile solution of **11** was coupled with 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose **6** using $SnCl_4$ as Lewis acid to give 2-chloroethyl 2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl-(1→5)-2,3-di-*O*-acetyl-α-D-ribofuranoside **12** as a colourless oil in 41% yield (10% overall from **6**). The ^1H NMR spectrum of disaccharide **12** in $CDCl_3$ showed two sharp singlets at δ 5.09 and 5.04 ppm for the anomeric protons on each furanose ring, and is strong evidence for the formation of a single major diastereoisomer. The appearance of these signals as singlets is evidence for the expected β,β configuration. A 10% impurity exhibits a doublet (J 1.1 Hz) at δ 5.07 ppm, and is tentatively assigned to the α,β-diastereoisomer 2-chloroethyl 2,3,5-tri-*O*-acetyl-α-D-ribofuranosyl-(1→5)-2,3-di-*O*-acetyl-β-D-ribofuranoside **13**. The assignment of the ^1H and ^{13}C NMR spectra was made using the usual range of 2D techniques. The NOESY spectra establish the configuration of the disaccharide. The assignment of H-1^I and H-1^{II} follows from the NOESY cross-peak between the H-1 at δ 3.71 ppm and the singlet at δ 5.04, allowing the latter to be unambiguously assigned to H-1^I. Further evidence for the proposed structure is the observation of cross-peaks between H-1^{II} at δ 5.09 ppm and the diastereotopic protons of H-5^I at δ 3.90 and 3.57 ppm.

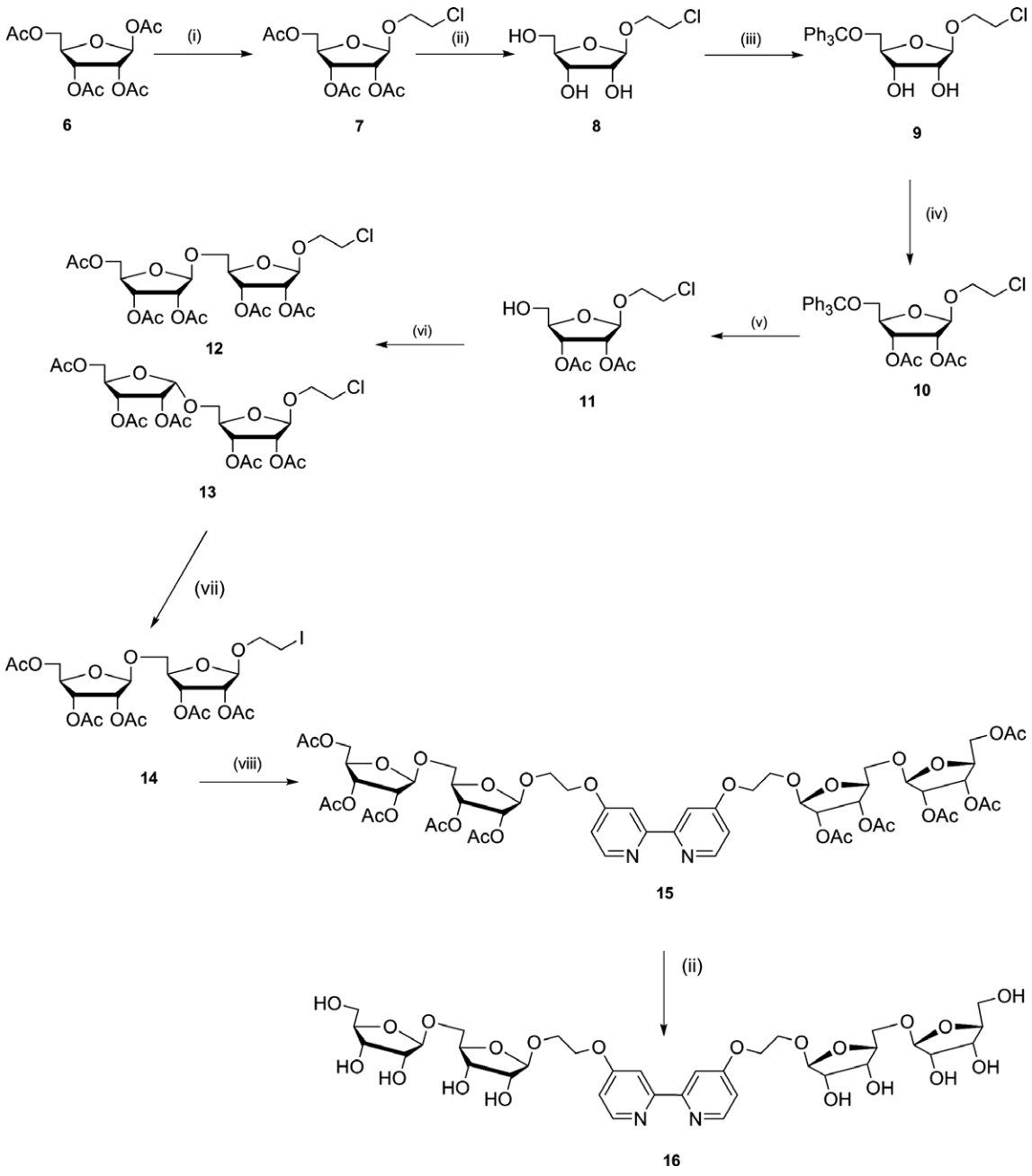
A second confirmation of the 1→5 coupling is found in the ^1H–^{13}C correlation spectra. The HMQC spectra establish C-1^{II} at δ 105.2 ppm through a cross-peak with the proton signal at δ 5.09 ppm, and C-5^I is assigned to the peak at δ 68.9 ppm which shows cross-peaks to both the diastereotopic H-5^I signals at δ 3.90 and 3.57 ppm. The 1→5 linkage of the rings is confirmed by the observation in the HMBC spectrum of a cross-peak between the ^{13}C NMR signal at δ 68.9 ppm and the ^1H signal at δ 5.09 ppm corresponding to the three-bond coupling between H-1^{II} and C-5^I.

The 2-chloroethyl compound **12** was converted to the more electrophilic 2-iodoethyl compound **14** in 97% yield by heating with NaI in acetone in a sealed tube. This compound was fully characterised by the usual spectroscopic and spectrometric methods. The NMR spectra of **12** and **14** were essentially identical, with the only significant differences being the upfield shifting of both the ^1H ($\Delta\delta = \delta$ **12** $- \delta$ **14**, 0.37 ppm) and ^{13}C signals ($\Delta\delta$ = 40.2 ppm) for H-2 between **12** and **14**. The 2D spectra show the same correlations between the A and the B rings as in **12**.

2.3. Synthesis of 4,4′-bis(β-D-ribofuranosyl-(1→5)-β-D-ribofuranosyloxy-2-ethoxy)-2,2′-bipyridines

The protected bpy ligand **15** was prepared in 18% yield as a white solid by the reaction of 2 equiv of the protected, electrophilic disaccharide **14** with 1 equiv of 4,4′-dihydroxy-2,2′-bipyridine[18] **5** in dry DMF in the presence of K_2CO_3 (Scheme 2). The new ligand was fully characterised by conventional methods and combustion analysis indicated that it had been obtained as a hemihydrate. The stereochemistry at the sugar is retained, with the two protons at the anomeric centers H-1^I and H-1^{II} appearing as singlets confirming the β,β stereochemistry at these positions, and all five methyl groups of the acetate protection are resolved. The H-5^{Ar} and H-3^{Ar} protons show cross-peaks in the NOESY spectrum confirming the attachment of the bpy metal-binding domain to the linker. The compound is optically active with a rotation $[\alpha]_D^{293}$ of −27.2.

Deprotection of **15** proceeded smoothly upon reaction with methanolic NaOMe for 4.5 h after which removal of solvent gave the deprotected bpy conjugate **16** in quantitative yield. The ^1H NMR spectrum of ligand **16** in CD_3OD showed that the acetyl groups had been quantitatively removed, and the compound was fully characterised by conventional methods. The NOESY spectrum shows the expected cross-peaks between H-3^{Ar} and H-5^{Ar} and the linker H-2 protons and a combination of NOESY and 1D ^1H NMR



Scheme 1. Synthesis of the disaccharide **14** and conversion to the bpy derivatives **15** and **16**. Reagents and conditions: (i) $SnCl_4$, MeCN, $ClCH_2CH_2OH$, 65%; (ii) NaOMe, MeOH, 100%; (iii) Ph_3CCl, pyridine, 76%; (iv) Ac_2O, pyridine, 94%; (v) TFA, $CHCl_3$, 54%; (vi) $SnCl_4$, MeCN, **6**, 41%; (vii) NaI, Me_2CO, 97%; (viii) **5**, K_2CO_3, DMF.

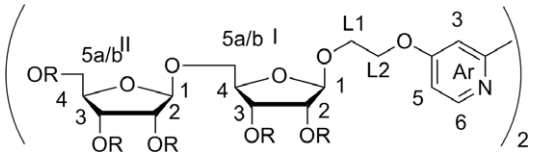


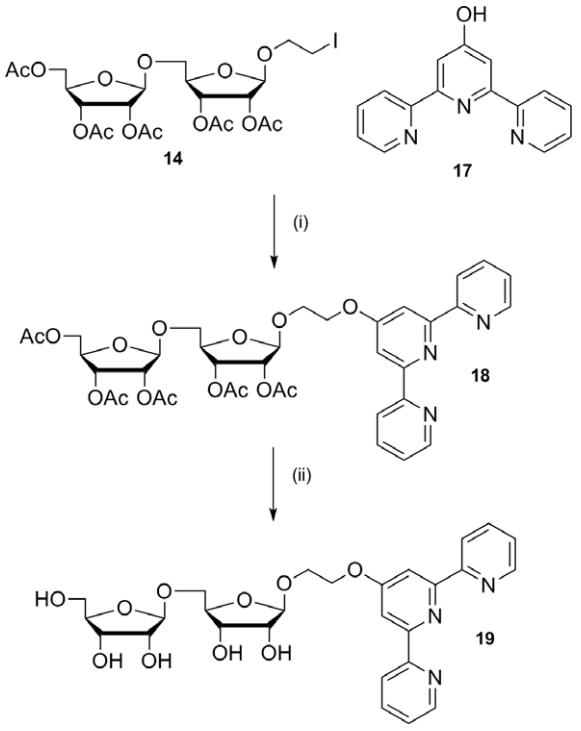
Figure 1. Generic numbering scheme adopted for describing the NMR spectra of the new ligands.

spectra establish that the β,β configuration is maintained. The high resolution mass spectrum confirms the complete removal of the acetate protection and the constitution of the compound (parent ion + sodium observed). The synthetic transformations are summarised in Scheme 1.

2.4. Synthesis of a 4′-(β-D-ribofuranosyl-(1→5)-β-D-ribofuranosyloxy-2-ethoxy)-2,2′:6′,2″-terpyridine

In addition to didentate ligands in which it is hoped that the disaccharide functionality will control the configuration at the metal center in tris-chelate complexes, we are also interested in 4′-substituted tpy ligands in which the topological linearity across the metal in a $\{M(tpy)_2\}$ complex is a powerful motif for the synthesis of novel materials. As prototype structures for such metallooligosaccharides we have prepared the analogous 4′-(β-D-ribofuranosyl-(1→5)-β-D-ribofuranosyloxy-2-ethoxy)-2,2′:6′,2″-terpyridine (Scheme 2).

The reaction of **14** with the nucleophile 4′-hydroxy-2,2′:6′,2″-terpyridine[19] **17** in DMF in the presence of K_2CO_3 proceeded smoothly to give the new protected tpy-disaccharide conjugate



Scheme 2. Synthesis of protected (**18**) and deprotected (**19**) 4′-(β-D-ribofuranosyl-(1→5)-β-D-ribofuranosyloxy-2-ethoxy)-2,2′:6′,2″-terpyridines. Reagents and conditions: (i) K_2CO_3, DMF 12%; (ii) NaOMe, MeOH 96%.

18 as a white solid. Microanalysis and high resolution MS confirmed the formation of the desired ligand, and NMR methods were used to establish the configurational purity **18**. Deprotection under the standard conditions using sodium methoxide in methanol gave the disaccharide **19** in 96% yield. Once again, the standard NMR techniques were used to fully characterise the compound and establish the stereochemistry at the sugars.

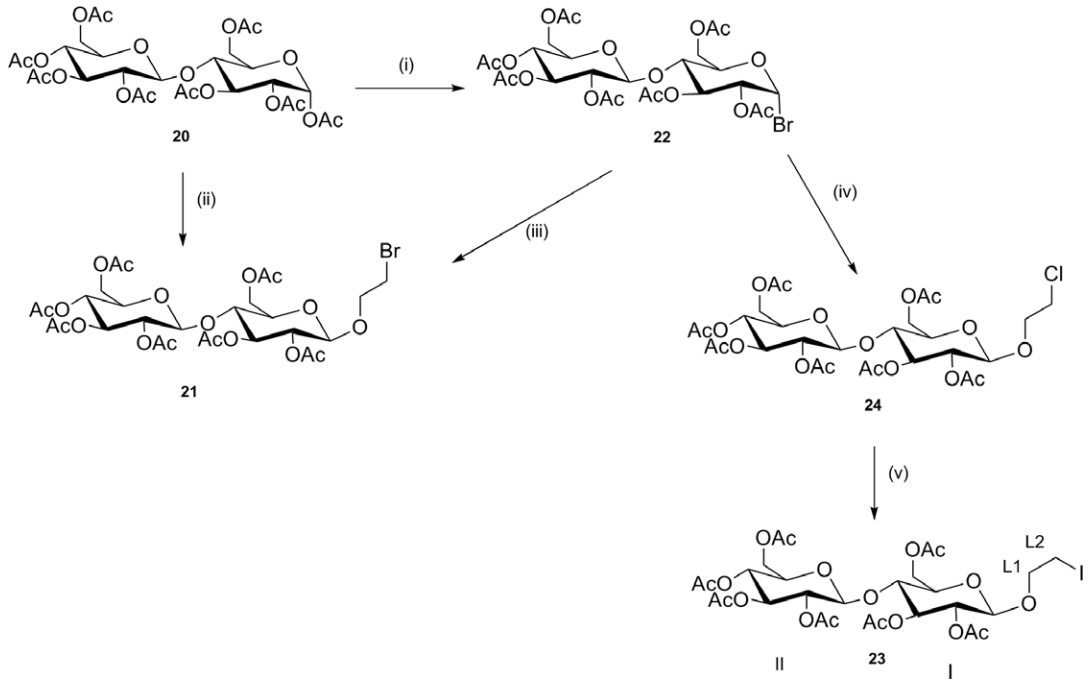
2.5. Synthesis of β-D-glucopyranosyl-(1→4)-D-glucose (cellobiose) derivatives

We decided, once again, to introduce an ethoxy spacer between the disaccharide and the metal-binding domain. The synthetic approach was, in this case, a little easier as cellobiose derivatives are commercially available. Our starting point was the fully protected octaacetate **20**. We initially considered the 1-(2-bromoethoxy)heptaacetyl derivative **21** as a target and investigated the direct preparation of **21** from **20** by reaction with 2-bromoethanol and BF_3 in a one-step reaction,[20] but only obtained **21** in 5% yield. We suspect the low yield is due to the slow formation of the 1,2-acyloxonium cation intermediate from the 1,2-*cis*-diacetate.

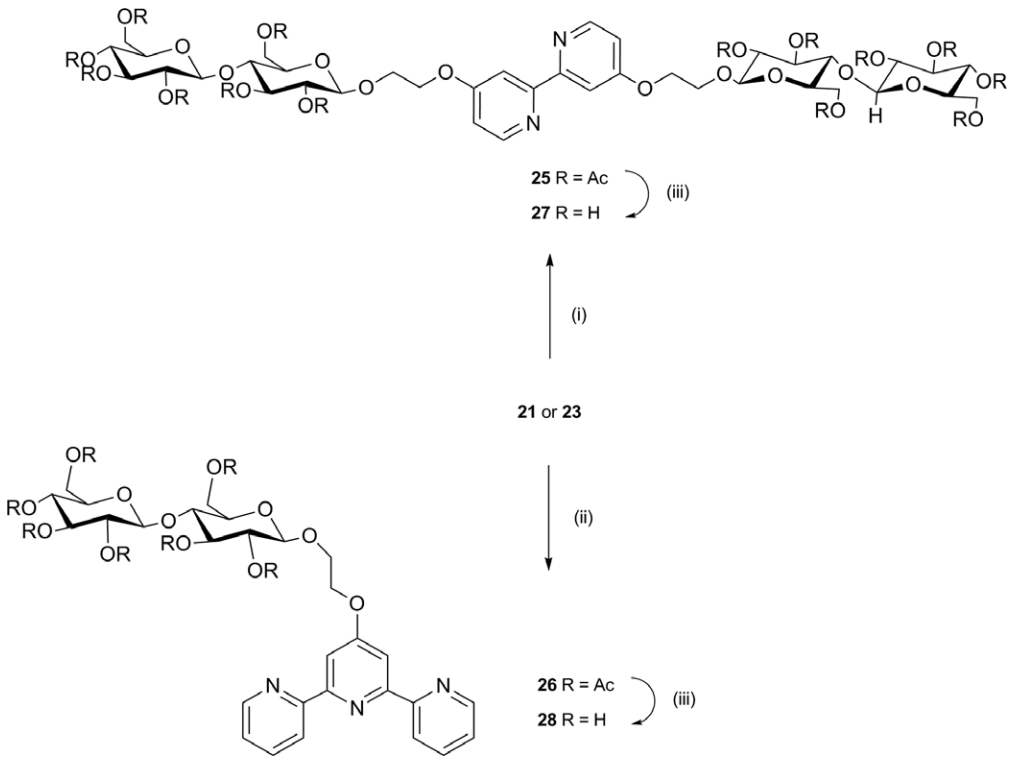
Accordingly, we followed a slightly modified literature route in which **20** was converted to the bromo-compound **22** by reaction with HBr in acetic acid.[21,22] Reaction of **22** with 2-bromoethanol in the presence of silver(I) triflate (instead of the literature silver(I) carbonate)[22] gave compound **21** as a very hygroscopic solid. We settled upon the non-hygroscopic iodo compound **23** as our intermediate of choice, which was prepared in 39% overall yield from **22** by reaction with 2-chloroethanol in the presence of silver(I) carbonate to give the 2-chloroethyl derivative **24** followed by halogen exchange with sodium iodide in acetone.[21] These transformations are summarised in Scheme 3.

2.6. Synthesis of β-D-glucopyranosyl-(1→4)-D-glucose (cellobiose) derivatives of 2,2′-bipyridine and 2,2′:6′,2″-terpyridine

The preparation of cellobiose derivatives of bpy and tpy was achieved using strictly analogous methods to those described for the β-D-ribofuranosyl-(1→5)-β-D-ribofuranosyloxy-2-ethoxy derivatives in the preceding sections. The key step was, in each case, the reaction of the nucleophilic oligopyridine **5** or **17** with the fully protected heptaacetyl 2-bromoethoxy- (**21**) or 2-iodoethoxy- (**23**) cellobiose derivatives in the presence of potassium carbonate gave the desired protected disaccharide-functionalised



Scheme 3. Synthetic transformations within the cellobiose series. The nomenclature system adopted for the assignment of the NMR spectra is illustrated for **23**. Reagents and conditions: (i) HBr, AcOH, 92%; (ii) $HOCH_2CH_2Br$, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 5%; (iii) $HOCH_2CH_2Br$, *sym*-collidine, AgO_3SCF_3, CH_2Cl_2, 23%; (iv) Ag_2CO_3, $HOCH_2CH_2Cl$, 53%; (v) NaI, Me_2CO, 80%.



Scheme 4. Reagents and conditions: (i) K_2CO_3, DMF, ~10–20%; (ii) K_2CO_3, DMF or MeCN, 18–23%; (iii) NaOMe, MeOH, 85–95%.

compounds **25** and **26** in modest yield after chromatographic work-up. Deprotection using sodium methoxide in methanol, as described in the previous sections, yielded the desired deprotected ligands **27** and **28** in quantitative or near quantitative yields as hygroscopic solids or gums. Marginally better yields were obtained using **23**. The synthetic routes are summarised in Scheme 4.

The protected and deprotected bpy and tpy conjugates were fully characterised as discussed in detail for the β-D-ribofuranosyl-(1→5)-D-ribofuranosides above. The key observations relate to the stereochemistry at the anomeric positions and at the ring linkage. In each case, NOESY spectra exhibited cross-peaks between H-1^{I} and H-1 L^{1}, and between H-1^{II} and H-4^{I} establishing the linkages unambiguously. The ^{3}J coupling constants of ~8 Hz observed for H-1^{I} and H-2^{I} establish the β-configuration at these positions.

3. Conclusions

We have described synthetic routes to protected and deprotected disaccharide-functionalised oligopyridines. Specifically, compounds in which two disaccharides are supported on a bpy scaffold or one on a tpy scaffold have been reported. These compounds are likely to be useful for the preparation of metalloglycodendrimers and metallated analogues of linear polysaccharides and studies relating to the coordination behaviour of these ligands will be reported in a future publication.

4. Experimental

4.1. General

Infrared spectra were recorded on a Shimadzu FTIR-8400 S spectrophotometer with samples as solids using a Golden Gate ATR accessory. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 500 or 400 spectrometers, and chemical shifts are referenced with respect to residual solvent peaks and quoted with respect to TMS = δ 0 ppm. Mass spectra were recorded using Kratos MS-50, Kratos MS-890, VG-70-250, Kratos MS-902, Micromass LCT or LCQ or PerSeptive Biosystems Voyager-RPBiospectrometry Workstation spectrometers. Electronic absorption spectra were recorded on Shimadzu UV 3101PC, Perkin–Elmer Lambda 9 or Varian-Cary 5000 spectrophotometers. Optical rotation measurements were recorded on a Perkin–Elmer 341 polarimeter in 10 cm quartz cuvettes at the sodium D line (589 nm) and at 293 K. The compounds 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose and octaacetyl-α-D-cellobiose were used as supplied; the chloroethoxy derivative **24**[22] and compounds **5**[18] and **17**[19] were prepared by the literature methods.

4.2. 2-Chloroethyl 2,3,5-tri-*O*-acetyl-β-D-ribofuranoside (7)

1,2,3,5-tetra-*O*-Acetyl-β-D-ribofuranose (1.00 g, 3.14 mmol) was dissolved in MeCN (5 mL) and $SnCl_4$ (1 M solution in CH_2Cl_2, 0.58 mL, 3.1 mmol) was added dropwise under N_2. The mixture was stirred at room temperature for 15 min after which 2-chloroethanol (0.21 mL, 3.1 mmol) in dry MeCN (5 mL) was added dropwise over 60 min, and stirring was continued for a further 30 min. Saturated aqueous $NaHCO_3$ solution was then added dropwise to the cooled (0 °C) solution, which was then filtered through Celite to remove tin oxides and hydroxides. The Celite was washed with hot $CHCl_3$ and the combined filtrates were washed with water and brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (silica, CH_2Cl_2–MeOH (2%)) to give **7** as a colourless oil (0.68 g, 64%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 5.33 (H-3, m, 1H), 5.28 (H-2, br d, 1H, J 4.83 Hz), 5.05 (H-1, s, 1H), 4.31 (H-5a/5b, dd, 1H), 4.31 (H-4, m, 1H), 4.16 (H-5b/5a, m, 1H), 3.95 (H-OC$H_{2\alpha}$, m, 1H), 3.70 (H-OC$H_{2\alpha}$, m, 1H), 3.61 (H-CH_2Cl, m, 2H), 2.11 (H-OAc, s, 3H), 2.09 (H-OAc, s, 3H), 2.05 (H-OAc, s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) δ/ppm 170.6 (CO), 169.7 (CO), 169.6 (CO), 105.4 (C-1), 78.8 (C-4), 74.7 (C-2), 71.4 (C-3), 68.2 (C-OCH_2), 64.5 (C-5), 42.4 (C-CH_2Cl), 20.8 (C-OAc), 20.6 (C-OAc), 20.5 (C-OAc); HRMS (ESMS): m/z

361.0671, 363.0626, calcd for $[M+Na]^+$, 361.0666, 363.0637; IR: $\tilde{\nu}$/cm^{-1} 1751s, 1443w, 1373m, 1234s, 1088w 1049w, 964w, 540s, 525s, 447s; $[\alpha]_D^{293}$ −25.8 ($CHCl_3$, 1.2 g in 100 mL). Anal. Calcd for $C_{13}H_{19}ClO_8$: C, 46.10; H, 5.65. Found: C, 46.37; H, 5.59.

4.3. 2-Chloroethyl β-D-ribofuranoside (8)

Route 1. Compound **7** (22 mg, 65 μmol) and hydroxide-form Amberlyst A-26 (100 mg) were stirred in MeOH (10 mL) for 2 h after which the solvent was removed in vacuo to yield **8** as a colourless oil (14 mg, 100%).

Route 2. Compound **7** (1.23 g, 3.64 mmol) was dissolved in MeOH (35 mL) and a solution of NaOMe (0.27 g, 5.0 mmol) in MeOH (2 mL) was added, and the reaction mixture was stirred vigorously at room temperature under a $CaCl_2$ tube for 2 h. The solvent was then removed in vacuo to yield **8** as a colourless oil (0.75 g, 97%). ^{1}H NMR (CD_3OD, 500 MHz) δ/ppm 4.89 (H-1, s, 1H), 4.05 (H-3, dd, 1H, *J* 4.73, 7.10 Hz), 3.93 (H-1^L, m, 1H), 3.93 (H-4, m, 1H), 3.90 (H-2, br d, 1H, *J* 4.29 Hz), 3.72 (H-5a/5b, dd, 1H, *J* 3.40, 11.79 Hz), 3.65 (H-1^L, m, 1H), 3.64 (H-2^L, m, 2H), 3.57 (H-5b/5a, dd, 1H, *J* 6.62, 11.80 Hz); ^{13}C{^{1}H} NMR (CD_3OD, 125 MHz) δ/ppm 107.4 (C-1), 83.5 (C-4), 74.9 (C-2), 71.2 (C-3), 67.7 (C-1^L), 63.5 (C-5), 42.6 (C-2^L); HRMS (ESMS): *m/z* 235.0355, 237.0327, calcd for $[M+Na]^+$, 235.0349, 237.0320.

4.4. 2-Chloroethyl 5-trityl-β-D-ribofuranoside (9)

Trityl chloride (1.48 g, 5.31 mmol) was added to solution of **8** in dry pyridine (9 mL), and the mixture was stirred at 50 °C overnight. The reaction mixture was then coevaporated with toluene (2 × 20 mL), redissolved in $CHCl_3$ (50 mL), washed with water (2 × 10 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude residue was purified by column chromatography (silica, hexane–ethyl acetate (7:9)) to yield compound **9** as a pale yellow oil (1.23 g, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 7.46 (H-2^{Ar}, m, 6H), 7.31 (H-3^{Ar}, m, 6H), 7.24 (H-4^{Ar}, m, 3H), 5.00 (H-1, s, 1H), 4.29 (H-3, m, 1H), 4.11 (H-2, H-4, m, 2H), 3.87 (H-1^L, m, 1H), 3.64 (H-1^L, m, 1H), 3.48 (H-2^L, m, 2H), 3.30 (H-5, d, 2H, *J* 5.36 Hz), 2.53 (H-2-OH, d, 1H, *J* 3.15 Hz), 2.25 (H-3-OH, d, 1H, *J* 5.99 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ/ppm 143.8 (C-1^{Ar}), 128.7 (C-2^{Ar}), 127.9 (C-3^{Ar}), 127.1 (C-4^{Ar}), 107.2 (C-1), 86.8 (C-*C*Ph3), 82.2 (C-4), 75.2 (C-2), 72.8 (C-3), 67.9 (C-1^L), 65.0 (C-5), 42.7 (C-2^L); ESMS: *m/z* 477.5, 479.4 $[M+Na]^+$.

4.5. 2-Chloroethyl 2,3-di-*O*-acetyl-5-*O*-trityl-β-D-ribofuranoside (10)

Ac_2O (2.8 mL) was added dropwise to a solution of **9** (1.18 g, 2.60 mmol) in dry pyridine (3 mL) at 0 °C, and the reaction mixture was stirred at room temperature overnight. After 20 h, the remaining Ac_2O was hydrolysed with water while cooling in an ice-bath. The aqueous solution was then extracted with $CHCl_3$ (3 × 20 mL), and the combined organic phases were washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was coevaporated with toluene (2 × 15 mL) to remove any pyridine to give **10** as a pale yellow viscous oil (1.31 g, 94%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 7.45 (H-2^{Ar}, m, 6H), 7.30 (H-3^{Ar}, m, 6H), 7.24 (H-4^{Ar}, m, 3H), 5.37 (H-3, m, 1H), 5.31 (H-2, d, 1H, *J* 4.73 Hz), 5.06 (H-1, s, 1H), 4.31 (H-4, m, 1H), 3.85 (H-1^L, m, 1H), 3.64 (H-1^L, m, 1H), 3.47 (H-2^L, m, 2H), 3.26 (H-5a/b, H-5b/a, m, 2H), 2.11 (H-OAc, s, 3H), 2.02 (H-OAc, s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ/ppm 169.65 (CO), 169.64 (CO), 143.7 (C-1^{Ar}), 128.7 (C-2^{Ar}), 127.9 (C-3^{Ar}), 127.1 (C-4^{Ar}), 105.3 (C-1), 86.7 (C-CPh$_3$), 79.9 (C-4), 74.7 (C-2), 72.1 (C-3), 68.0 (C-1^L), 64.5 (C-5), 42.2 (C-2^L), 20.65 (C-OAc), 20.57 (C-OAc); $[\alpha]_D^{293}$ −11.8 ($CHCl_3$, 0.55 g in 100 mL); ESMS: *m/z* 561.5, 563.4 $[M+Na]^+$, 1098.8, 1100.8 $[2M+Na]^+$. Anal. Calcd for $C_{30}H_{31}ClO_7 \cdot 1/4PhMe$: C, 67.79; H, 5.87. Found: C, 67.41; H, 5.91.

4.6. 2-Chloroethyl 2,3-di-*O*-acetyl-β-D-ribofuranoside (11)

A solution of **10** (1.27 g, 2.36 mmol) in $CHCl_3$ (10 mL) was cooled to 0 °C and a 5% solution of TFA in $CHCl_3$ (5 mL) was added dropwise. After 45 min, the reaction mixture was coevaporated with EtOH (2 × 10 mL) and concentrated in vacuo. The crude residue was purified by column chromatography (silica, initially hexane–ethyl acetate (5:1) than hexane–ethyl acetate (9:7)) to give **11** as a colourless oil (0.376 g, 54%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 5.41 (H-3, t, 1H, *J* 5.20 Hz), 5.30 (H-2, dd, 1H, *J* 1.10, 5.20 Hz), 5.07 (H-1, s, 1H), 4.24 (H-4, ddd, 1H, *J* 3.78, 6.47, 7.10 Hz), 3.96 (H-1^L, m, 1H), 3.85 (H-5a/5b, dd, 1H, *J* 3.15, 4.41 Hz), 3.82 (H-1^L, m, 1H), 3.69 (H-5b/5a, dd, 1H, *J* 4.10, 8.51 Hz), 3.66 (H-2^L, m, 2H), 2.24 (H-OH, m, 1H), 2.12 (H-OAc, s, 3H), 2.07 (H-OAc, s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ/ppm 170.0 (CO), 169.6 (CO), 105.7 (C-1), 82.7 (C-4), 75.5 (C-2), 71.1 (C-3), 68.8 (C-1^L), 62.7 (C-5), 42.8 (C-2^L), 20.6 (C-OAc); $[\alpha]_D^{293}$ −22.1 (CH_3OH, 0.55 g in 100 mL); ESMS: *m/z* 319.4, 321.3 $[M+Na]$, 615.0, 617.0 $[2M+Na]$.

4.7. 2-Chloroethyl 2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl-(1→5)-2,3-di-*O*-acetyl-α-D-ribofuranoside (12)

$SnCl_4$ (1 M in CH_2Cl_2, 0.720 mL, 3.92 mmol) was added dropwise to a solution of 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose (1.25 g, 3.92 mmol) in MeCN (5 mL) under nitrogen. The mixture was stirred at room temperature for 15 min after which **11** (1.16 g, 3.92 mmol) dissolved in dry CH_3CN (5 mL) was added dropwise very slowly, and the mixture was stirred for a further 30 min. After dropwise addition of saturated aqueous $NaHCO_3$ to the cooled solution, the reaction mixture was filtered through Celite, the Celite was washed well with hot $CHCl_3$ and the combined filtrates were washed with water and brine, dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography (silica gel: hexane–ethyl acetate (3:8)) to yield compound **12** (and 10% of α,β-diastereoisomer **13**) as a colourless oil (0.888 g, 41%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 5.32 (H-3^{II}, m, 1H), 5.30 (H-3^I, m, 1H), 5.28 (H-2^{II}, d, 1H, *J* 5.04 Hz), 5.25 (H-2^I, d, 1H, *J* 4.73 Hz), 5.09 (H-1^{II}, s, 1H), 5.04 (H-1^I, s, 1H), 4.33 (H-5^{II}, dd, 1H, *J* 3.78, 10.40 Hz), 4.31 (H-4^{II}, m, 1 H), 4.26 (H-4^I, td, 1H, *J* 3.78, 6.94, 10.72 Hz), 4.16 (H-5^{II}, dd, 1H, *J* 5.20, 10.88 Hz), 3.97 (H-1^L, m, 1H), 3.90 (H-5^I, dd, 1H, *J* 3.78, 10.72 Hz), 3.71 (H-1^L, m, 1H), 3.65 (H-2^L, m, 2H), 3.57 (H-5^I, dd, 1H, *J* 6.94, 10.72 Hz), 2.11 (H-OAc, s, 9H), 2.07 (H-OAc, s, 3H), 2.05 (H-OAc, s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ/ppm 170.7 (CO), 169.8 (CO), 169.65 (CO × 2), 169.58 (CO), 105.3 (C-1^I), 105.2 (C-1^{II}), 79.7 (C-4^I), 78.5 (C-4^{II}), 74.6 (C-2^I, C-2^{II}), 71.6 (C-3^I), 71.3 (C-3^{II}), 68.9 (C-5^I), 68.1 (C-1^L), 64.5 (C-5^{II}), 42.6 (C-2^L), 20.8 (C-OAc), 20.62 (C-OAc × 2), 20.56 (C-OAc), 20.5 (C-OAc); ESMS: *m/z* 577.6, 579.4 $[M+Na]^+$, 1130.7, 1132.7 $[2M+Na]^+$.

4.8. 2-Iodoethyl 2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl-(1→5)-2,3-di-*O*-acetyl-α-D-ribofuranoside (14)

A solution of **12** (0.210 g, 0.379 mmol) and sodium iodide (0.289 g, 1.93 mmol) in acetone (2 mL) was heated at 85 °C in a sealed tube for 30 h. The solvent was removed in vacuo, and the residue was suspended in water, extracted with $CHCl_3$ (2 × 25 mL), dried over Na_2SO_4, filtered and concentrated in vacuo to yield compound **14** as a colourless oil (0.237 g, 97%). 1H NMR ($CDCl_3$, 500 MHz) δ/ppm 5.31 (H-3^{II}, m, 1H), 5.29 (H-3^I, m, 1H), 5.28 (H-2^{II}, d, 1H, *J* 2.84 Hz), 5.24 (H-2^I, d, 1H, *J* 4.89 Hz), 5.09

(H-1^{II}, s, 1H), 5.04 (H-1^{I}, s, 1H), 4.33 (H-5^{II}, dd, 1H, *J* 3.47, 10.40 Hz), 4.31 (H-4^{II}, m, 1H), 4.25 (H-4^{I}, td, 1H, *J* 4.10, 6.94, 11.03 Hz), 4.16 (H-5^{II}, dd, 1H, *J* 5.52, 11.19 Hz), 3.97 (H-1^{L}, m, 1H), 3.90 (H-5^{I}, dd, 1H, *J* 4.10, 10.72 Hz), 3.73 (H-1^{L}, m, 1H), 3.60 (H-5^{I}, dd, 1H, *J* 6.62, 10.72), 3.27 (H-2^{L}, td, 2H, *J* 1.26, 6.94, 8.04 Hz), 2.12 (H-OAc, s, 3H), 2.11 (H-OAc, s, 6H), 2.07 (H-OAc, s, 3H), 2.05 (H-OAc, s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) δ/ppm 170.7 (CO), 169.8 (CO), 169.7 (CO), 169.6 (CO × 2), 105.1 (C-1^{II}), 105.1 (C-1^{I}), 79.6 (C-4^{I}), 78.5 (C-4^{II}), 74.7 (C-2^{I}/C-2^{II}), 74.6 (C-2^{II}/C-2^{I}, 71.6 (C-3^{I}), 71.3 (C-3^{II}), 69.0 (C-5^{I}), 68.8 (C-1^{L}), 64.5 (C-5^{II}), 20.9 (C-OAc), 20.6 (C-OAc × 3), 20.5 (C-OAc), 2.4 (C-2^{L}); ESMS: *m/z* 669.4 $[M+Na]^+$, 1315.4 $[2M+Na]^+$.

4.9. Protected bpy ligand (15)

4,4′-Dihydroxy-2,2′-bipyridine **5** (30 mg, 160 μmol) and dry K_2CO_3 (130 mg, 942 μmol) were stirred in dry DMF (10 mL) at 75 °C under N_2 for 1 h after which a solution of **14** (203 mg, 314 μmol) in dry DMF (5 mL) was added to the suspension, and the reaction mixture was stirred at 75 °C under N_2 overnight. The solvent was removed in vacuo, and the residue was suspended in water followed by extraction with $CHCl_3$ (2 × 25 mL). The organic extracts were combined, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude residue was purified by column chromatography (silica, CH_2Cl_2–MeOH (4%)) to yield **15** as a white solid (35 mg, 18%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 8.45 (H-6^{Ar}, d, 2H, *J* 5.68 Hz), 7.97 (H-3^{Ar}, d, 2H, *J* 2.84 Hz), 6.87 (H-5^{Ar}, dd, 2H, *J* 2.84, 5.68 Hz), 5.32 (H-3^{II}, m, 2H), 5.30 (H-3^{I}, m, 2H), 5.27 (H-2^{II}, d, 2H, *J* 5.04 Hz), 5.26 (H-2^{I}, d, 2H, *J* 5.36 Hz), 5.11 (H-1^{I}, s, 2H), 5.09 (H-1^{II}, s, 2H), 4.32 (H-5^{II}, dd, 2H, *J* 3.47, 10.72 Hz), 4.30 (H-4^{II}, H-2^{L}, m, 6H), 4.26 (H-4^{I}, td, 2H, *J* 3.78, 6.94, 10.72 Hz), 4.16 (H-5^{II}, dd, 2H, *J* 5.68, 11.35 Hz), 4.12 (H-1^{L}, m, 2H), 3.91 (H-5^{I}, dd, 2H, *J* 3.78, 10.72 Hz), 3.86 (H-1^{L}, m, 2H), 3.57 (H-5^{I}, dd, 2H, *J* 6.94, 10.40), 2.10 (H-OAc, s, 6H), 2.08 (H-OAc, s, 12H), 2.05 (H-OAc, s, 6H), 2.02 (H-OAc, s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) δ/ppm 170.6 (CO), 169.8 (CO), 169.6 (CO × 3), 165.7 (C-4^{Ar}), 157.8 (C-2^{Ar}), 150.2 (C-6^{Ar}), 111.4 (C-5^{Ar}), 106.6 (C-3^{Ar}), 105.3 (C-1^{II}), 105.2 (C-1^{I}), 79.8 (C-4^{I}), 78.5 (C-4^{II}), 74.7 (C-2^{I}, C-2^{II}), 74.6 (C-2^{I}, C-2^{II}, 71.8 (C-3^{I}), 71.3 (C-3^{S3B}), 69.1 (C-5^{I}), 67.0 (C-2^{L}), 65.9 (C-1^{L}), 64.4 (C-5^{II}), 20.8 (C-OAc), 20.6 (C-OAc × 3), 20.5 (C-OAc); $[\alpha]_D^{293}$ −27.2 ($CHCl_3$, 0.60 g in 100 mL). ESMS: *m/z* 1247.4 $[M+Na]^+$. Anal. Calcd for $C_{54}H_{68}N2O_{30}{\cdot}0.5H_2O$: C, 52.51; H, 5.59; N, 2.27. Found: C, 52.56; H, 5.50; N, 2.20.

4.10. Deprotected bpy ligand (16)

A solution of **15** (12 mg, 9.80 μmol) in absolute MeOH (10 mL) was treated with 0.2 mL of a solution of sodium methoxide prepared by dissolving sodium (0.25 g) in MeOH (50 mL). The reaction mixture was stirred vigorously at room temperature for 4.5 h, followed by removal of solvent in vacuo to yield **16** as a white solid (8 mg, 100%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 8.43 (H-6^{Ar}, d, 2H, *J* 5.99 Hz), 7.82 (H-3^{Ar}, d, 2H, *J* 2.52 Hz), 7.04 (H-5^{Ar}, dd, 2H, *J* 2.52, 5.99 Hz), 4.94 (H-1^{I}, s, 2H), 4.92 (H-1^{II}, s, 2H), 4.31 (H-2^{L}, t, 4H, *J* 4.57 Hz), 4.11 (H-3^{II}, dd, 2H, *J* 4.73, 7.25 Hz), 4.07 (H-1^{L}, m, 2H), 4.06 (H-4^{I}, m, 2H), 4.02 (H-3^{I}, dd, 2H, *J* 4.10, 8.51 Hz), 3.93 (H-4^{II}, m, 2H), 3.91 (H-2^{I}, H-2^{II}, d, 4H, *J* 4.41 Hz), 3.87 (H-5^{I}, dd, 2H, *J* 3.15, 11.03 Hz), 3.80 (H-1^{L}, m, 2H), 3.72 (H-5^{II}, dd, 2H, *J* 3.15, 11.67 Hz), 3.56 (H-5^{II}, dd, 2H, *J* 5.99, 11.67 Hz), 3.51 (H-5^{I}, dd, 2H, *J* 7.25, 11.03 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) δ/ppm 166.4 (C-4^{Ar}), 157.3 (C-2^{Ar}), 150.1 (C-6^{Ar}), 110.8 (C-5^{Ar}), 107.84 (C-3^{Ar}), 107.78 (C-1^{II}), 107.6 (C-1^{I}), 83.5 (C-4^{II}), 82.0 (C-4^{I}), 74.9 (C-2^{II}), 74.7 (C-2^{I}, 71.8 (C-3^{I}), 71.0 (C-3^{II}), 69.9 (C-5^{I}), 67.4 (C-2^{L}), 65.5 (C-1^{L}), 63.2 (C-5^{II}). $[\alpha]_D^{293}$ −23.4 (CH3OH, 0.50 g in 100 mL). HRMS (ESMS): *m/z* 811.2738, calcd for [M+Na], 811.2749.

4.11. Protected tpy ligand (18)

A mixture of 4′-hydroxy-2,2′:6′,2″-terpyridine **17** (76 mg, 300 μmol) and K_2CO_3 (126 mg, 915 μmol) (10 mL) at 75 °C under N_2 for 1 h after which **14** (197 mg, 305 μmol) in dry DMF (5 mL) was added, and the reaction mixture was stirred at 75 °C under N_2 overnight. Work-up as for **15** followed by the crude residue was purified by column chromatography (silica, ethyl acetate) gave **18** as a white solid (28 mg, 12%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 8.67 (H-6^{Ar}, d, 2H, *J* 4.73 Hz), 8.60 (H-3^{Ar}, d, 2H, *J* 7.88 Hz), 8.03 (H-3′^{Ar}, s, 2H), 7.83 (H-4^{Ar}, td, 2H, *J* 1.89, 7.57 Hz), 7.31 (H-5^{Ar}, td, 2H), 5.33 (H-3^{I}, m, 1H), 5.31 (H-3^{II}, m, 1H), 5.28 (H-2^{II}, d, 1H, *J* 4.73 Hz), 5.26 (H-2^{I}, d, 1H, *J* 4.89 Hz), 5.16 (H-1^{I}, s, 1H), 5.13 (H-1^{II}, s, 1H), 4.40 (H-2^{L}, m, 2H), 4.33 (H-5^{II}, dd, 1H, *J* 3.78, 11.67 Hz), 4.31 (H-4^{II}, m, 1H), 4.27 (H-4^{I}, td, 1H, *J* 3.78, 6.94, 10.72 Hz), 4.16 (H-5^{II}, dd, 1H, *J* 5.05, 11.04 Hz), 4.13 (H-1^{L}, m, 1H), 3.93 (H-5^{I}, dd, 1H, *J* 4.10, 11.03 Hz), 3.90 (H-1^{L}, m, 1H), 3.62 (H-5^{I}, dd, 1H, *J* 7.25, 10.72 Hz), 2.10 (H-OAc, s, 3H), 2.08 (H-OAc, s, 3H), 2.06 (H-OAc, s, 3H), 2.05 (H-OAc, s, 3H), 2.01 (H-OAc, s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) δ/ppm 170.7 (CO), 169.7 (CO), 169.6 (CO × 2), 169.5 (CO), 166.8 (C-4′^{Ar}), 157.2 (C-2′^{Ar}), 156.0 (C-2^{Ar}), 149.0 (C-6^{Ar}), 136.8 (C-4^{Ar}), 123.8 (C-5^{Ar}), 121.3 (C-3^{Ar}), 107.4 (C-3′^{Ar}), 105.4 (C-1^{II}), 105.1 (C-1^{I}), 79.9 (C-4^{I}), 78.5 (C-4^{II}), 74.71 (C-2^{I}), 74.69 (C-2^{II}), 71.9 (C-3^{I}), 71.4 (C-3^{II}), 69.2 (C-5^{I}), 67.3 (C-2^{L}), 66.0 (C-1^{L}), 64.4 (C-5^{II}), 20.8 (C-OAc), 20.6 (C-OAc × 3), 20.5 (C-OAc); $[\alpha]_D^{293}$ −17.8 ($CHCl_3$, 0.50 g in 100 mL); Anal. Calcd for $C_{37}H_{41}N_3O_{15}{\cdot}0.25H_2O$: C, 57.55; H, 5.38; N, 5.44. Found: C, 57.43; H, 5.38; N, 5.31.

4.12. Deprotected tpy ligand (19)

Compound **18** (13 mg, 16.9 μmol) was stirred vigorously for 4.5 h in MeOH (10 mL) containing NaOMe (60 μmol, prepared by dissolving 0.25 g of sodium in 50 mL MeOH). The solvent was removed in vacuo to yield compound **19** as a gummy white solid (9.0 mg, 96%). ^{1}H NMR (CD_3OD, 500 MHz) δ/ppm 8.63 (H-6^{Ar}, m, 2H), 8.56 (H-3^{Ar}, d, 2H, *J* 7.88 Hz), 7.95 (H-4^{Ar}, td, 2H, *J* 1.58, 7.88 Hz), 7.94 (H-3^{Ar}, s, 2H), 7.43 (H-5^{Ar}, td, 2H), 4.97 (H-1^{I}, s, 1H), 4.95 (H-1^{II}, s, 1H), 4.38 (H-2^{L}, t, 2H, *J* 4.57 Hz), 4.13 (H-3^{II}, dd, 1H, *J* 4.89, 7.10 Hz), 4.09 (H-1^{L}, m, 1H), 4.07 (H-3^{I}, S-4^{II}, m, 2 H), 3.93 (H-2^{I}, S-2^{II}, S-4^{I}, m, 3H), 3.90 (H-5^{I}, dd, 1H, *J* 3.15, 11.35 Hz), 3.84 (H-1^{L}, m, 1H), 3.73 (H-5^{II}, dd, 1H, *J* 3.47, 11.98 Hz), 3.57 (H-5^{II}, dd, 1H, *J* 5.99, 11.67 Hz), 3.55 (H-5^{I}, dd, 1H, *J* 6.94, 11.03 Hz)); $^{13}C\{^{1}H\}$ NMR (CD_3OD, 126 MHz) δ/ppm 167.2 (C-4′^{Ar}), 157.0 (C-2′^{Ar}), 155.7 (C-2^{Ar}), 148.6 (C-6^{Ar}), 137.3 (C-4^{Ar}), 124.1 (C-5^{Ar}), 121.6 (C-3^{Ar}), 107.8 (C-1^{II}), 107.6 (C-1^{I}), 107.2 (C-3′^{Ar}), 83.5 (C-4^{II}), 82.0 (C-4^{I}), 75.0 (C-2^{II}), 74.7 (C-2^{I}), 71.8 (C-3^{I}), 71.0 (C-3^{II}), 69.9 (C-5^{I}), 67.5 (C-2^{L}), 65.6 (C-1^{L}), 63.2 (C-5^{II}); $[\alpha]_D^{293}$ −12.8 (CD_3OD, 0.60 g in 100 mL); HRMS (ESMS): *m/z* 580.1918, calcd for $[M+Na]^+$, 580.1907.

4.13. 1-Bromoethyl-β-D-cellobiose heptaacetate (21)

Route 1. A solution of bromo compound **22** (0.950 g, 1.36 mmol) in dry CH_2Cl_2 (7 mL) was added dropwise (20 min) to a cold (−78 °C) solution of silver triflate (0.479 g, 1.86 mmol), *sym*-collidine (0.18 mL, 1.38 mmol) and 2-bromoethanol (0.45 mL, 6.48 mmol) in CH_2Cl_2 (12 mL) under N_2. The mixture was stirred in the dark for 23 h, during which time it had warmed to room temperature. The yellowish precipitate was filtered, and the colourless filtrate was washed consecutively with hydrochloric acid (1 M), water, saturated aqueous $NaHCO_3$, water, dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by column chromatography (silica gel: CH_2Cl_2–MeOH (2%)). Removal of the solvent in vacuo yielded **21** as an off-white solid (0.237 g, 23%).

Route 2. Octaacetyl-α-D-cellobiose **20** (2.00 g, 2.95 mmol) and 2-bromoethanol (0.43 mL, 6.20 mmol) were stirred in dry CH_2Cl_2 (30 cm^3) for 10 min at 0 °C. $BF_3{\cdot}Et_2O$ (1 M in CH_2Cl_2, 1.87 mL, 15 mmol) was then added to the solution dropwise over a period of 15 min. The reaction mixture was stirred for a further 1 h at 0 °C, before stirring at room temperature for 5 h. The reaction mixture was quenched by pouring in ice-water, extracted with CH_2Cl_2, washed with water, saturated $NaHCO_3$, water, dried over Na_2SO_4 and filtered. The solvent was removed in vacuo, and the crude residue was purified by column chromatography using the same solvent system as above, to yield **21** as an off-white solid (0.106 g, 5%).

4.14. Protected bpy ligand (25)

Route 1. A mixture of **5** (36.0 mg, 191 μmol) and K_2CO_3 (159 mg, 1.15 mmol) was stirred in dry DMF (10 mL) under N_2 for 1 h at 75 °C after which bromo-compound **21** (283 mg, 382 μmol) in DMF (2 mL) was added, and the reaction mixture was stirred overnight. The solvent was removed in vacuo and the residue was suspended in water, extracted with $CHCl_3$ (3 × 20 mL), the extract dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by column chromatography using a (silica gel: CH_2Cl_2–MeOH (4%)) to yield **25** as an off-white solid (26 mg, 9%).

Route 2. As above using **23** (302 mg, 382 μmol), **5** (36 mg, 191 μmol) and K_2CO_3 (159 mg, 1150 μmol), the crude residue was purified by column chromatography to give **25** as an off-white solid (47 mg, 16%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 8.44 (H-6^{Ar}, d, 2H, *J* 5.68 Hz), 7.93 (H-3^{Ar}, d, 2H, *J* 2.52 Hz), 6.83 (H-5^{Ar}, dd, 2H, *J* 2.52, 5.68 Hz), 5.18 (H-3^{I}, t, 2H, *J* 9.30 Hz), 5.13 (H-3^{II}, t, 2H, *J* 9.46 Hz), 5.05 (H-4^{II}, t, 2H, *J* 9.46 Hz), 4.92 (H-2^{I}, d, 2H, *J* 7.88 Hz), 4.90 (H-2^{II}, d, 2H, *J* 7.88 Hz), 4.61 (H-1^{I}, d, 2H, *J* 7.88 Hz), 4.51 (H-6^{II}, dd, 2H, *J* 2.21, 11.67 Hz), 4.51 (H-1^{II}, d, 2H, *J* 7.88 Hz), 4.35 (H-6^{I}, dd, 2H, *J* 4.41, 12.61 Hz), 4.26 (H-2^{L}, m, 4H), 4.13 (H-1^{L}, m, 2H), 4.08 (H-6^{II}, dd, 2H, *J* 5.04, 11.98 Hz), 4.02 (H-6^{I}, dd, 2H, *J* 2.21, 12.30 Hz), 3.93 (H-1^{L}, m, 2H), 3.77 (H-4^{I}, t, 2H, *J* 9.46 Hz), 3.65 (H-5^{II}, m, 2H), 3.62 (H-5^{I}, m, 2H), 2.09 (H-OAc, s, 6H), 2.07 (H-OAc, s, 6H), 2.01 (H-OAc, s, 6H), 1.99 (H-OAc, s, 12H), 1.97 (H-OAc, s, 6H), 1.93 (H-OAc, s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) δ/ppm 170.5 (CO), 170.3 (CO), 170.2 (CO), 169.8 (CO), 169.6 (CO), 169.3 (CO), 169.1 (CO), 165.7 (C-4^{Ar}), 157.7 (C-2^{Ar}), 150.2 (C-6^{Ar}), 111.4 (C-5^{Ar}), 106.5 (C-3^{Ar}), 100.9 (C-1^{I}), 100.8 (C-1^{II}), 76.4 (C-4^{I}), 72.9 (C-3^{II}), 72.8 (C-5^{II}), 72.4 (C-3^{I}), 72.0 (C-5^{I}), 71.6 (C-2^{II}), 71.4 (C-2^{I}), 67.8 (C-1^{L}), 67.7 (C-4^{II}), 67.0 (C-2^{L}), 61.7 (C-6^{I}), 61.5 (C-6^{II}), 20.9 (C-OAc), 20.7 (C-OAc), 20.6 (C-OAc), 20.5 (C-OAc × 4): ESMS: *m/z* 1514 [M+H]$^+$, 1535.5 [M+Na]$^+$; $[\alpha]_D^{293}$ −14.8 ($CHCl_3$, 0.35 g in 100 mL) Anal. Calcd for $C_{66}H_{84}N_2O_{38}{\cdot}3H_2O$: C, 50.54; H, 5.74; N, 1.79. Found: C, 50.34; H, 5.46; N, 1.91.

4.15. Deprotected bpy ligand (27)

A solution of **25** (33 mg, 22 μmol) in MeOH (10 mL) was treated with a NaOMe solution (40 μL) prepared by dissolving 0.25 g of sodium in MeOH (50 mL). The reaction mixture was stirred vigorously for 3.5 h in a round-bottomed flask equipped with a $CaCl_2$ guard. The solvent was removed in vacuo to yield **27** as a white solid (20 mg, 100%). ^{1}H NMR (CD_3OD, 500 MHz) δ/ppm 8.43 (H-6^{Ar}, d, 2H, *J* 5.99 Hz), 7.84 (H-3^{Ar}, d, 2H, *J* 2.52 Hz), 7.02 (H-5^{Ar}, dd, 2H, *J* 2.52, 5.67 Hz), 4.41 (H-1^{I}, d, 2H, *J* 8.20 Hz), 4.39 (H-1^{II}, d, 2H, *J* 8.51 Hz), 4.38 (H-2^{L}, m, 4H), 4.23 (H-1^{L}, m, 2H), 4.00 (H-1^{L}, m, 2H), 3.86 (H-6^{I}, H-6^{II}, m, 6H), 3.64 (H-6^{II}, dd, 2H, *J* 5.52, 11.82 Hz), 3.57 (H-4^{I}, t, 2H, *J* 9.14 Hz), 3.52 (H-3^{I}, t, 2H, *J* 8.83 Hz), 3.42 (H-5^{I}, m, 2H), 3.35 (H-3^{II}, t, 2H, *J* 8.83 Hz), 3.32-3.25 (H-5^{II}, H-2^{I}, H-4^{II}, m, 6H), 3.21 (H-2^{II}, t, 2H, *J* 8.83 Hz); 13C NMR (126 MHz, CD_3OD): δ/ppm 166.4 (C-4^{Ar}), 157.3 (C-2^{Ar}), 150.0 (C-6^{Ar}), 111.0 (C-5^{Ar}), 107.8 (C-3^{Ar}), 103.2 (C-1^{II}), 103.1 (C-1^{I}), 79.1 (C-4^{I}), 76.7 (C-5^{II}), 76.4 (C-3^{II}), 75.1 (C-5^{I}), 74.9 (C-3^{I}), 73.5 (C-2^{II}), 73.6 (C-2^{I}), 70.0 (C-4^{II}), 67.64 (C-2^{L}), 67.58 (C-1^{L}), 61.0 (C-6^{II}), 60.3 (C-6^{I}); ESMS *m/z* 947.8 [M+Na]$^+$.

4.16. Protected tpy ligand (26)

Route 1. A mixture of 4′-hydroxy-2,2′:6′,2″-terpyridine **17** (36 mg, 143 μmol) and K_2CO_3 (59 mg, 43 μmol) was stirred in dry CH_3CN (10 mL) under N_2 for 1 h at 80 °C after which **21** (106 mg, 143 μmol) in CH_3CN (4 mL), was added, and the reaction mixture was stirred. After 2 h, KI (24 mg, 143 μmol) was added and the solution was stirred overnight, the solvent was removed in vacuo and the residue was suspended in water, extracted with $CHCl_3$ (3 × 20 mL), dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by column chromatography using a short column (silica gel: CH_2Cl_2–MeOH (2%)) to yield **26** as an off-white solid (24 mg, 19%).

Route 2. As above using **17** (79 mg, 320 μmol), K_2CO_3 (132 mg, 957 μmol), dry DMF (10 mL), **21** (237 mg, 319 μmol) dissolved in DMF (5 mL), KI (53 mg, 319 μmol) gave **26** (52 mg, 18%).

Route 3. As above using compound **23** (113 mg, 143 μmol), **17** (36 mg, 140 μmol), K_2CO_3 (59 mg, 429 μmol) and DMF (10 cm^3) gave **26** as an off-white solid (30 mg, 23%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm 8.68 (H-6^{Ar}, d, 2H, *J* 4.73 Hz), 8.61 (H-3^{Ar}, d, 2H, *J* 7.88 Hz), 8.01 (H-3′^{Ar}, s, 2H), 7.84 (H-4^{Ar}, td, 2H, *J* 1.89, 7.73 Hz), 7.32 (H-5^{Ar}, td, 2H), 5.20 (H-3^{I}, t, 1H, *J* 9.30 Hz), 5.13 (H-3^{II}, t, 1H, *J* 9.46 Hz), 5.05 (H-4^{II}, t, 1H, *J* 9.61 Hz), 4.94 (H-2^{I}, m, 1H), 4.92 (H-2^{II}, m, 1H), 4.66 (H-1^{I}, d, 1H, *J* 7.88 Hz), 4.52 (H-6^{II}, dd, 1H, *J* 1.89, 11.98 Hz), 4.51 (H-1^{II}, d, 1H, *J* 7.57 Hz), 4.37 (H-2^{L}, m, 2H), 4.35 (H-6^{I}, dd, 1H, *J* 4.10, 12.30 Hz), 4.17 (H-1^{L}, m, 1H), 4.10 (H-6^{II}, dd, 1H, *J* 5.04, 11.98 Hz), 4.02 (H-6^{I}, dd, 1H, *J* 2.05, 12.45 Hz), 3.98 (H-1^{L}, m, 1H), 3.80 (H-4^{I}, t, 1H, *J* 9.61 Hz), 3.66 (H-5^{II}, m, 1H), 3.64 (H-5^{I}, m, 1H), 2.10 (H-OAc, s, 3H), 2.07 (H-OAc, s, 3H), 2.01 (H-OAc, s, 3H), 1.99 (H-OAc, s, 6H), 1.97 (H-OAc, s, 3H), 1.96 (H-OAc, s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ppm 170.5 (CO), 170.4 (CO), 170.2 (CO), 169.8 (CO), 169.7 (CO), 169.3 (CO), 169.1 (CO), 166.8 (C-4′^{Ar}), 157.2 (C-2′^{Ar}), 155.9 (C-2^{Ar}), 149.1 (C-6^{Ar}), 136.8 (C-4^{Ar}), 123.9 (C-5^{Ar}), 121.3 (C-3^{Ar}), 107.2 (C-3′^{Ar}), 100.85 (C-1^{I}), 100.79 (C-1^{II}), 76.4 (C-4^{I}), 73.0 (C-3^{II}), 72.8 (C-5^{II}), 72.5 (C-3^{I}), 71.9 (C-5^{I}), 71.6 (C-2^{II}), 71.5 (C-2^{I}), 67.8 (C-1^{L}, C-4^{II}), 67.2 (C-2^{L}), 61.9 (C-6^{I}), 61.5 (C-6^{II}), 20.9 (C-OAc), 20.66 (C-OAc), 20.55 (C-OAc × 5); HRMS (ESMS): *m/z* 934.2825 ([M+Na]$^+$, calcd 934.2858); ESMS: *m/z* 934.6 [M+Na]$^+$; $[\alpha]_D^{293}$ −23.0 ($CHCl_3$, 0.35 g in 100 mL). Anal. Calcd for $C_{43}H_{49}N_3O_{19}{\cdot}0.5CHCl_3$: C, 53.77; H, 5.10; N, 4.33. Found: C, 53.90; H, 5.08; N, 4.29.

4.17. Deprotected tpy ligand (28)

Route 1. **26** (19 mg, 20.9 μmol) and Amberlyst A-26 hydroxide form (100 mg) were added to MeOH (10 mL), and the mixture was stirred at room temperature for 5.5 h. The mixture was filtered and evaporated to dryness to give **28** as a white solid (12 mg, 92%).

Route 2. A solution of **26** (11 mg, 12.1 μmol) in MeOH (10 mL) was treated with a NaOMe solution (60 μL) prepared by dissolving 0.25 g of sodium in MeOH (50 cm^3). The reaction mixture was stirred vigorously for 6 h in a round-bottomed flask equipped with a $CaCl_2$ guard tube. The solvent was then removed in vacuo to yield **28** as a white solid (7.5 mg, 100%).

^{1}H NMR (CD_3OD, 500 MHz): δ/ppm 8.63 (H-6^{Ar}, d, 2H, *J* 4.73 Hz), 8.56 (H-3^{Ar}, d, 2H, *J* 8.20 Hz), 7.96 (H-3′^{Ar}, s, 2H), 7.94 (H-4^{Ar}, td, 2H, *J* 1.58, 7.88 Hz), 7.42 (H-5^{Ar}, td, 2H), 4.47 (H-2^{L}, m, 2H), 4.44 (H-1^{I}, d, 1H, *J* 7.88 Hz), 4.40 (H-1^{II}, d, 1H, *J* 7.57 Hz), 4.26 (H-1^{L}, m, 1H), 4.05 (H-1^{L}, m, 1H), 3.87 (H-6^{I}, m, 2H), 3.85 (H-6^{II}, dd, 1H, *J* 2.21, 7.88 Hz), 3.65 (H-6^{II}, dd, 1H, *J* 5.52, 11.83 Hz), 3.55 (H-4^{I}, t, 1H, *J* 9.61 Hz), 3.53 (H-3^{I}, t, 1H, *J* 8.49 Hz), 3.44 (H-5^{I}, m, 1H), 3.29

(H-2^{I}, H-3^{II}, H-4^{II}, H-5^{II}, m, 4H), 3.21 (H-2^{II}, t, 1H, *J* 4.41 Hz); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD): δ/ppm 167.2 (C-$4'^{Ar}$), 157.1 (C-$2'^{Ar}$), 155.9 (C-2^{Ar}), 148.6 (C-6^{Ar}), 137.2 (C-4^{Ar}), 124.0 (C-5^{Ar}), 121.5 (C-3^{Ar}), 107.4 (C-$3'^{Ar}$), 103.3 (C-$1^{I/II}$), 103.2 (C-$1^{II/I}$), 79.4 (C-4^{I}), 76.7 (C-5^{II}), 76.6 (C-3^{II}), 75.2 (C-5^{I}), 75.0 (C-3^{I}), 73.6 (C-2^{II}), 73.5 (C-2^{I}), 70.1 (C-4^{II}), 67.8 (C-2^{L}), 67.7 (C-1^{L}), 61.1 (C-6^{II}), 60.6 (C-6^{I}); HRMS (ESMS): *m/z* 640.2115 ($[M+Na]^+$, calcd 640.2118); ESMS: *m/z* 640.1 $[M+Na]^+$.

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