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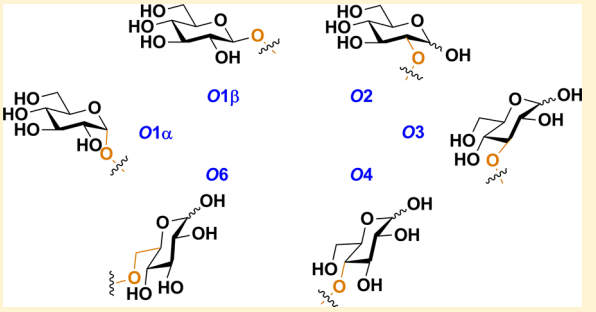
Synthesis of *O*-1−*O*-6 Substituted Positional Isomers of D-Glucose−Thioether Ligands and Their Ruthenium Polypyridyl Conjugates

Lucien N. Lameijer,* Julien le Roy, Stefan van der Vorm, and Sylvestre Bonnet*

Leiden Institute of Chemistry, Leiden University, Gorlaeus Laboratories, P.O. Box 9502, Leiden 2300 RA, The Netherlands

Supporting Information

ABSTRACT: A library of positional isomers of D-glucose (*O*-1−*O*-6) as ligands and their 11 light-active ruthenium conjugates has been synthesized. A protecting group strategy without the necessity of using palladium on carbon for the modification for the 2-*O* and 4-*O* position allows for the incorporation of sulfur donor atoms as ligands for transition metal complexes.



INTRODUCTION

Carbohydrates are a class of biomolecules ubiquitously present in nature, comprising monosaccharides, oligosaccharides, and polysaccharides, of which monosaccharides cannot be hydrolyzed further into smaller units. These molecules are recognized as important building blocks in the cell wall of bacteria,[1,2] in plants,[3] in the exoskeleton of insects,[4] in cell recognition processes,[5] and in the backbone of RNA and DNA[6] and are associated with many different physiological and disease-related processes.[7,8] Among them, D-glucose is the most well-known monosaccharide as it serves as the primary source of chemical energy in eukaryotic cells for the production of ATP.[9] Otto Warburg found that cancer cells have an increased glycolysis rate for the production of ATP compared to normal cells.[10] As a consequence, glucose transporters (GLUTs) 1 and 3 are overexpressed in cancer cells.[11] In recent years, there has been a growing interest in using this effect to selectively deliver molecules of interest to cancer cells. In the field of diagnostic imaging, the well-known radiotracer 2-deoxy-2-[^{18}F]-fluoroglucose (2-FDG) selectively accumulates in cancer cells since its metabolic breakdown is hampered by the replacement of a hydroxyl group on the 2-position of D-glucose by fluoride.[12] This clinically approved agent allows PET imaging of tumors anywhere in the whole body. In the field of medicinal chemistry, glufosfamide has shown some success as a safer alternative for ifosfamide, an alkylating agent used in cancer treatment. The therapeutic efficiency of glufosfamide is thought to be higher due to its increased water solubility and preferred uptake in malignant cells versus normal cells.[13] Recently, Palay et al. have demonstrated that a series of glucose conjugates of platinum-based medicines are taken up via GLUT1.[14,15] This result is in contrast to the observation of Schubiger, who found that none of their radiodiagnostic glycoconjugates based on ^{99m}Tc were taken up via glucose transporters.[16]

For ruthenium(II) polypyridyl-based drugs, this effect has not been thoroughly investigated. Our group has been involved in a research program aimed at targeting ruthenium-based light-activated anticancer prodrugs to GLUT transporters by glucose conjugation.[17,18] These photoactivated chemotherapeutic prodrugs are typically protected from binding to biomolecules in the dark by thioether ligands, which under visible light irradiation are photosubstituted by water, thereby activating the prodrug.[19−21] En route to functionalizing such complexes with glucose, it came out that all available synthetic routes toward a series of positional isomers of glucose were incompatible with the presence of thioether groups, which deactivate Pd/C catalysts used to deprotect benzyl protecting groups. For that reason, we developed and report here on a series of new synthetic routes toward all positional isomers of glucose that are compatible with the presence of sulfur-based ligands.[22] As traces of palladium also often interfere with the biological activity of pharmaceuticals,[23] these new routes do not make use of palladium catalysts. PEGylation of all positional isomers was also realized to vary the spacer between the thioether ligands and the glucose moiety. The coordination of the thioether−glucose ligands to known photoactive ruthenium(II) polypyridyl precursors afford 11 ruthenium−glucose conjugates (Figure 1) as a demonstration that such molecules can be obtained on a synthetical useful scale. Recent publications describe the more photophysical and/or biological properties of these type of complexes.[17,18]

RESULTS AND DISCUSSION

Five hydroxyl groups are available for modification in D-glucose, of which the 1-*O* position is modified via chemical glycosylation.[24] Recently, Patra et al. have demonstrated that

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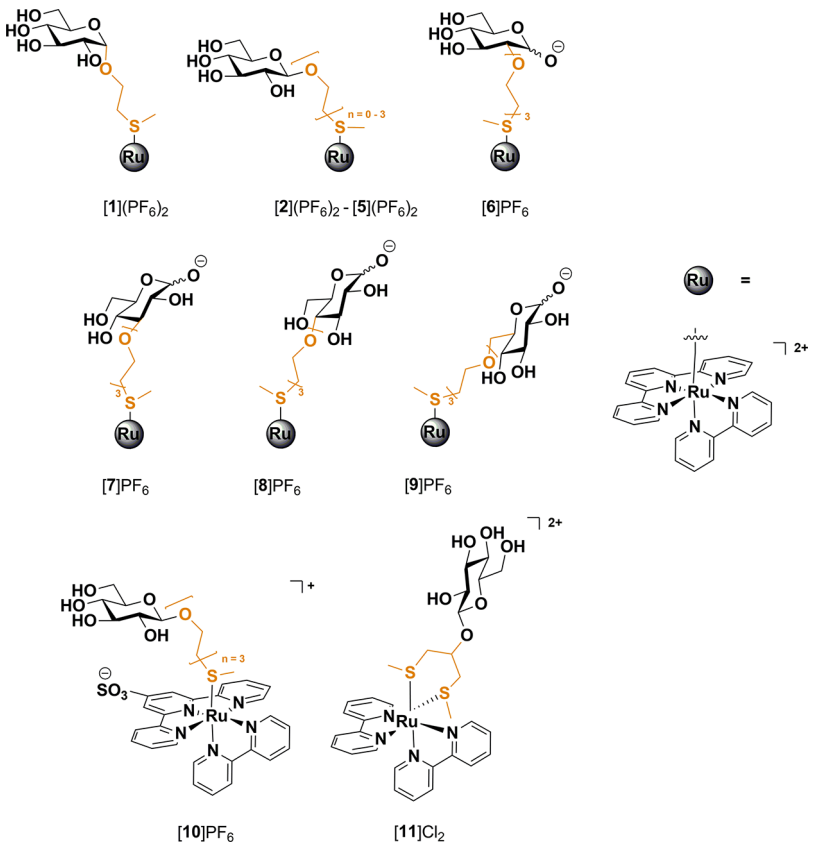
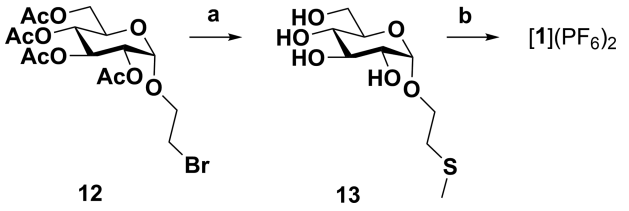


Figure 1. Overview of *O*-1 to *O*-6 positional D-glucose ruthenium(II) polypyridyl conjugates presented in this study.

the spacer length exerts influence over the GLUT-mediated uptake of platinum complexes in cells;[14] however, there is currently no established understanding of this effect in cationic ruthenium(II) polypyridyl compounds. Therefore, oligoethylene glycol spacers $[OCH_2CH_2]_n$ with varying lengths ($n = 0-3$) were introduced in glycoconjugates $[\mathbf{1}](PF_6)_2$–$[\mathbf{5}](PF_6)_2$ (Figure 1). The first complex in this series ($[\mathbf{1}](PF_6)_2$) was synthesized starting from precursor **12** (Scheme 1).[25] This

Scheme 1[a]

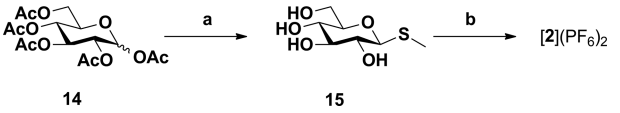


[a]Reaction conditions: (a) (i) NaSMe in DMF, rt, 16 h, (ii) NaOMe in MeOH, 66% over two steps; (b) [Ru(tpy)(bpy)Cl]Cl in H_2O, 80 °C, 16 h, 39%.

building block and NaSMe were used in a S_N2 reaction, ensuring the installment of the thioether group, affording **13**. This ligand was then reacted with [Ru(tpy)(bpy)Cl]Cl, affording the orange (λ_{max} = 450 nm) glycoconjugate $[\mathbf{1}](PF_6)_2$.

For complex $[\mathbf{2}](PF_6)_2$, a three-step one-pot synthesis starting from peracetylated glucose **14** (Scheme 2) was adapted from Valerio et al.,[26] which afforded the *trans*-glucopyranoside as the only diastereoisomer. Treatment of this compound with sodium methoxide in methanol afforded fully deprotected **15** in

Scheme 2[a]



[a]Reaction conditions: (a) (i) I_2, Et_3SiH in DCM, rt, 10 min, (ii) thiourea in MeCN, 80 °C, 30 min, (iii) MeI, Et_3N, rt, 10 min, (iv) cat. NaOMe in MeOH, rt, overnight, 57% over four steps; (b) [Ru(tpy)(bpy)Cl]Cl in H_2O, 80 °C, 48 h, 28%.

a 55% overall yield. Subsequent reaction of this ligand with [Ru(tpy)(bpy)Cl]Cl then gave the orange complex $[\mathbf{2}](PF_6)$.

A different approach was employed for the installment of the ethylene glycol-based linkers (n = 1–3) for complexes $[\mathbf{3}](PF_6)_2$–$[\mathbf{5}](PF_6)_2$ and $[\mathbf{11}]Cl_2$ (Figure 1). The disarmed Schmidt donor **20** (Scheme 3) was chosen due to its straightforward synthesis and robustness. The benzoyl protecting group in this building block was favored over the more common acetyl group, due to its lower reactivity.[27] Furthermore, this donor was chosen to reduce the possible formation of orthoesters, a common side reaction when using acetyl-bearing donors.[28] Commercially available 2-(methylthio)ethanol was used as an acceptor and condensed with donor **20** (Scheme 3), affording **21**, which after de-*O*-benzoylation acquired deprotected **24**. Compounds **25**, **26**, and **28** were acquired in a similar fashion using acceptors **18**, **19**, and 1,3-bis(methylthio)propan-2-ol, respectively. The synthesis of the corresponding ruthenium complexes was found to be straightforward, by reacting excess ligand with the ruthenium species [Ru(tpy)(bpy)Cl]Cl or $[Ru(bpy)_2Cl_2]$. Their purification, however, was found arduous due to the increased water solubility of these compounds.

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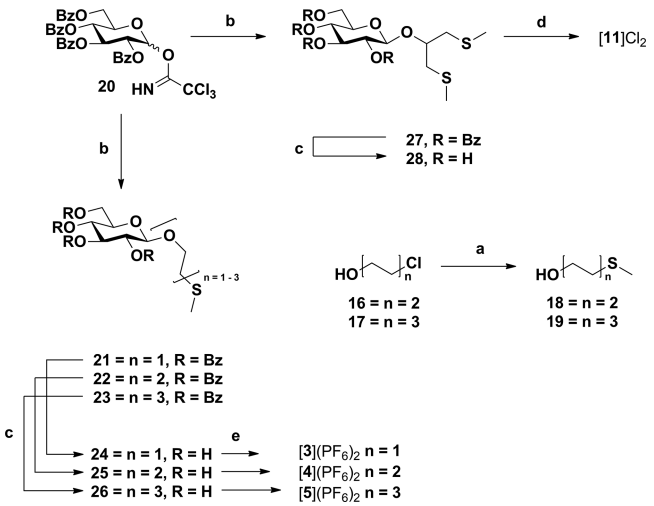
Scheme 3[a]



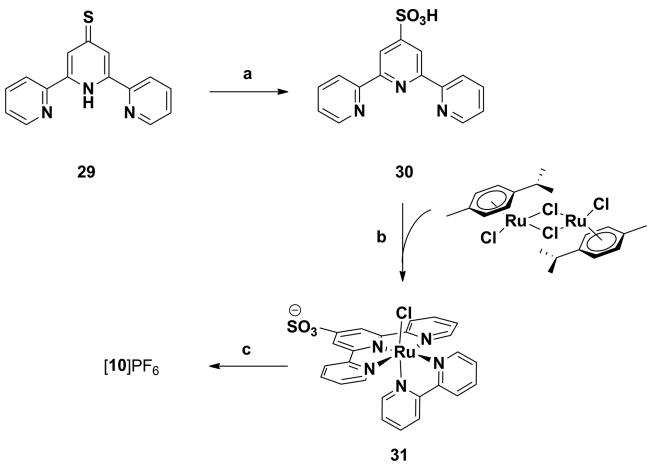
[a]Reaction conditions: (a) 2-(2-chloroethoxy)ethanol or 2-[2-(2-chloroethoxy)ethoxy]ethanol, NaSMe in THF, reflux, 6 h, 89% for **18**, 85% for **19**; (b) 2-(methylthio)ethanol, 1,3-bis(methylthio)propanol, **18** or **19**, cat. TMSOTf in DCM, 4 Å molecular sieves, rt, 4 h, 81% for **21**, 66% for **22**, 85% for **23**, 90% for **27**; (c) NaOMe in MeOH, rt, 88% for **24**, 86% for **25**, 91% for **26**, 70% for **28**; (d) $[Ru(bpy)_2Cl_2]$ in H_2O, 80 °C, 59% for $[\mathbf{11}]Cl_2$; (e) [Ru(tpy)(bpy)Cl]Cl in H_2O, 80 °C, 39% for $[\mathbf{3}](PF_6)_2$, 66% for $[\mathbf{4}](PF_6)_2$, 65% for $[\mathbf{5}](PF_6)_2$.

Common workup methods were not applicable, and the lability of these compounds on C-18 columns prevented reverse-phase chromatographic purification. The most reproducible approach was by purification over silica using a mixture of acetone, water, and aqueous KPF_6, followed by Sephadex LH-20 size exclusion purification to remove excess salt and minor impurities. This method afforded the orange (λ_{max} = 450 nm) ruthenium polypyridyl derivatives $[\mathbf{3}](PF_6)_2$–$[\mathbf{5}](PF_6)_2$ and $[\mathbf{11}]Cl_2$ in moderate to good yields (28–66%).

Park and co-workers have demonstrated that glucose bioprobes with a formal charge of +1 are taken up preferentially over neutral and negatively charged probes.[29] To allow future study of the effect on the overall charge for ruthenium(II) polypyridyl drugs on uptake and toxicity, a derivative of [Ru(tpy)(bpy)Cl]Cl bearing a negative charge on the spectator terpyridine ligand was also synthesized. Compound **31** (Scheme 4) was prepared starting from thione **29**,[30] which was oxidized using in situ generated peracetic acid followed by hydrogenation using 10% palladium on carbon to reverse partial overoxidation to its *N*-oxide, affording ligand **30**. A one-pot synthesis using (*p*-cymene)ruthenium(II) chloride dimer **30** and bpy provided complex **31**. Reaction of ligand **26** (Scheme 3) with this complex then gave the ruthenium complex $[\mathbf{10}](PF_6)_2$.

Demonstrations of the covalent modification of the 2-*O* position of D-glucose with an alkyl-based linker have been given by Dumas et al. and Patray and co-workers.[14,31] Both groups chose a similar approach starting from methyl 3,5,6-*tri*-*O*-benzyl-α/β-D-glucofuranoside followed by installment of the linker and subsequent deprotection of the protection groups using dihydrogen and palladium on carbon. Sulfur-based linkers, however, poisoned the palladium catalysts, which made removal of the benzyl protecting groups impossible following this approach.[22,32] Other methods to remove benzyl groups, such as Birch reductions, have been reported to cleave thioethers.[33] Therefore, all described approaches for the functionalization of

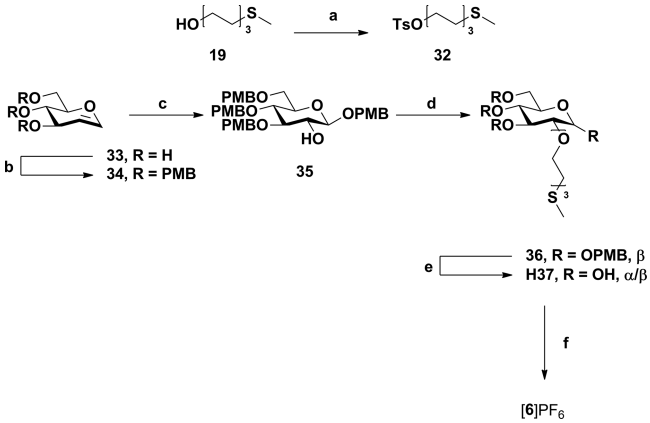
Scheme 4[a]



[a]Reaction conditions: (a) (i) H_2O_2 in AcOH, 70 °C, 6 h, (ii) H_2, Pd/C, 40 °C, overnight, 24% over two steps; (b) bpy in MeOH, 60 °C, 72%; (c) **25**, in H_2O, 80 °C, 16 h, 38%.

the *O*-2 position in D-glucose with a metal-binding moiety, including the glucofuranoside approach described by Schubiger or Lippard, or the approach via a benzylorthoacetate intermediate described by Miao et al.[34] were found unsuitable for thioether-containing compounds. We therefore devised a new protecting group strategy improving the 10-step, 5% yield procedure published by Lippard et al.[14] and employing the α-oxirane method developed by the group of Danishefsky[35,36] and attempted by Dumas et al. (Scheme 5).[31] Using this method, D-

Scheme 5[a]



[a]Reaction conditions: (a) **19**, TsCl, Et_3N in DCM, 0 °C to rt, 16 h, 92%; (b) PMB–Cl, NaH in DMF, 0 °C to rt, 16 h, 84%; (c) (i) DMDO (0.088 M in acetone) in DCM, 0 °C to rt, 3 h, (ii) PMB–OH, $ZnCl_2$ in THF, −78 °C to rt, 16 h, 39% over two steps; (d) **32**, NaH in DMF, 0 °C to rt, 6 h, 80%; (e) (i) cat. HCl in HFIP/DCM, 5 min, (ii) $MeNH_2$ in MeOH/H_2O, 60 °C, 30 min, 67%; (f) $[Ru(tpy)(bpy)(H_2O)](PF_6)_2$ in acetone/H_2O, 80 °C, 24 h, 36%.

glucal was protected using the *p*-methoxy benzyl (PMB) group, affording **34**. Treatment of this compound with freshly prepared dimethyldioxirane (DMDO) afforded its corresponding 1,2-anhydrosugar, which was then condensed with *p*-methoxy benzyl alcohol (PMB–OH) in the presence of anhydrous $ZnCl_2$ in THF, affording β-substituted **35**, while simultaneously liberating the 2-*O* position. This compound was then treated

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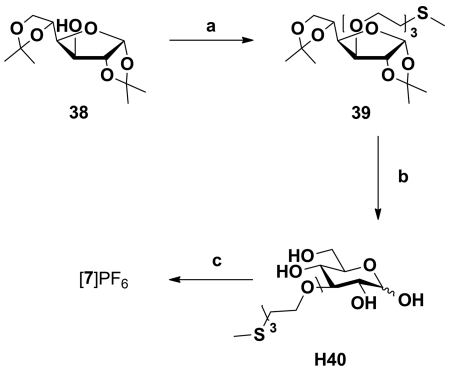
with tosylate **32** (Scheme 5) for the installment of the thioether moiety. This conversion proceeded smoothly, which is in contrast to the observation of Schubiger et al., who had to divert to the furanoside approach due to difficulties encountered during the installment of their iminodiacetic acid-based spacer.[31] With compound **36** in hand, a recently described method[37] using 37% hydrochloric acid in hexafluoroisopropanol (HFIP) was used to remove all four PMB groups simultaneously. After the reaction was quenched using Et_3N ,an intermediate species was observed (m/z = 463.4 found, 463.2 calcd) corresponding to the desired product **H37** and a PMB group. This same intermediate was also observed in the presence of a mild reducing agent such as Et_3SiH. However, when this intermediate was treated with $MeNH_2$ in MeOH,[38] the methyl thioether could be liberated, acquiring hemiacetal **H37** in five steps (18% overall yield). After reaction of this compound with $[Ru(tpy)(bpy)(H_2O)](PF_6)_2$ glycoconjugate $[Ru(tpy)(bpy)(\mathbf{37})]PF_6$, ($[\mathbf{6}]PF_6$) was acquired instead of $[Ru(tpy)(bpy)(\mathbf{H37})](PF_6)_2$. This is most likely due to the relatively protic nature of the anomeric proton, resulting in deprotonation during purification on Sephadex and replacement of one of the PF_6 counterions by the "charged" deprotonated glucose species as interpreted by elemental analysis. On mass, however, only the 2+ species is observed, indicating that reprotonation occurs in solution. This behavior was observed for all hemiacetal glucose derivatives.

The most straightforward thioether functionalization in these series of ligands was the modification of the 3-*O* position of D-glucose. Starting from diacetone glucose **38** (Scheme 6),[39−41]

Scheme 6[a]

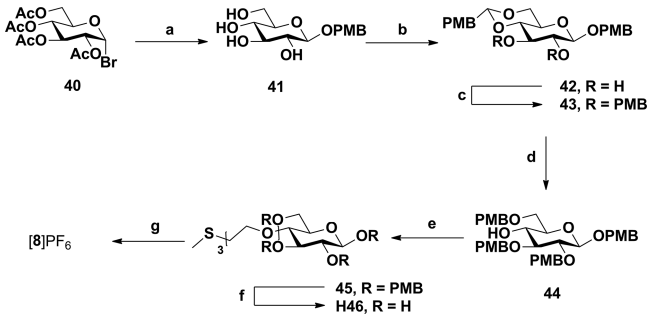


[a]Reaction conditions: (a) **32**, NaH in DMF, 0 °C to rt, 16 h, 91%; (b) Amberlite IR-120 H^+ in H_2O, 60 °C, 24 h, 46%; (c) [Ru(tpy)(bpy)Cl]Cl in H_2O, 80 °C, 16 h, 37%.

the thioether moiety was installed using **32** (Scheme 5), affording compound **39**, which was subsequently hydrolyzed using Amberlite IR-120 H^+, affording **H40** in 42% overall yield. Glycoconjugation of **H40** with [Ru(tpy)(bpy)Cl]Cl gave the orange (λ_{max} = 450 nm) complex $[Ru(tpy)(bpy)(\mathbf{40})]PF_6$ ($[\mathbf{7}]PF_6$).

The 4-*O* position of D-glucose was modified starting from acetobromo-α-D-glucose **40** (Scheme 7). Using a procedure first described by Kaji et al., this building block was converted in situ to its anomeric iodide, followed by a Koenigs−Knorr-type glycosylation with *p*-methoxy benzyl alcohol as an acceptor and Ag_2CO_3 as a base.[42] De-*O*-acetylation furnished intermediate **41**, followed by 4,6-*O*-benzylidenation and installment of PMB groups, affording fully protected **43**. With this building block in

Scheme 7[a]

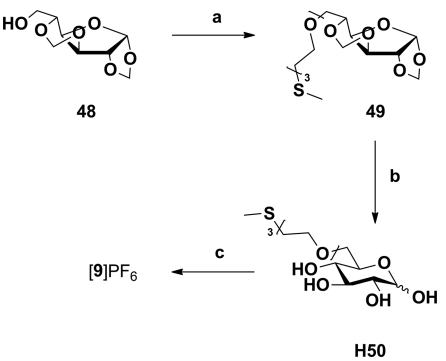


[a]Reaction conditions: (a) (i) PMB−OH, I_2, Ag_2CO_3 in Et_2O, rt, 24 h, (ii) NaOMe in MeOH, rt, 4 h, 72% over two steps; (b) α,α,4-trimethoxytoluene, cat. *p*-TsOH·H_2O in DMF, 60 °C, 16 h, 89%; (c) PMB−Cl, NaH in DMF, 0 °C to rt, 78%; (d) $NaCNBH_3$, TFA in DMF, 0 °C to rt, 48 h, 95%; (e) **32**, NaH in DMF, 0 °C to rt, 6 h, 78%; (f) cat. HCl in HFIP/DCM, 30 min, 29%; (g) [Ru(tpy)(bpy)Cl]Cl in H_2O, 80 °C, 64%.

hand, a reductive opening using $NaCNBH_3$ and TFA liberated the 4-*O* position, which could then be alkylated via a Williamson etherification using **32** described in the previous sections, affording **45**. Global deprotection was achieved by treatment with HFIP/HCl, which gave thioether ligand **H46** in an 11% overall yield. The subsequent reaction of **H46** with $[Ru(tpy)(bpy)(H_2O)](PF_6)_2$ afforded glycoconjugate $[Ru(tpy)(bpy)(\mathbf{46})]PF_6$ ($[\mathbf{8}]PF_6$). The synthesis of **H46** was also attempted via an alternative approach using α-methyl glucose following a similar protecting group strategy. However, this proved to be unsuccessful due to the inertness of the anomeric methyl acetal toward acid.

Finally, the 6-*O* position of D-glucose was easily modified starting from dimethyl glucose **48** (Scheme 8),[43] which could be

Scheme 8[a]



[a](a) **32**, NaH in DMF, 0 °C to rt, 3 h, 78%; (b) 2 M HCl in H_2O, 60 °C, 1 h, 70%; (c) [Ru(tpy)(bpy)Cl]Cl in H_2O, 80 °C, 16 h, 17%.

converted to **49** using a Williamson etherification with tosylate **32**, followed by acid hydrolysis using dilute hydrochloric acid, affording methyl thioether **H50** in 55% over two steps. Glycoconjugation with [Ru(tpy)(bpy)Cl]Cl afforded $[Ru(tpy)(bpy)(\mathbf{50})]PF_6$ ($[\mathbf{9}]PF_6$).

CONCLUSION

In this work, we have presented efficient and robust routes to all positional isomers of D-glucose bearing a thioether ligand bound to a light-cleavable ruthenium(II) polypyridyl complex. The

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general protecting−deprotecting group strategy presented in this work is compatible with compounds bearing donor atoms such as sulfur, without the need of palladium catalysts until final coordination to the functional ruthenium compound. These routes might possibly be extended to application with other functionalized ligands, such as carboxylates, amines, or pyridines. The study of this library of ruthenium(II) glycoconjugates might shed light on the influence of the stereochemistry of glucose functionalization on GLUT-mediated uptake and the metabolism of the ruthenium−glucose conjugates by enzymes such as hexokinase II.

EXPERIMENTAL SECTION

General. Reagents were purchased from Sigma-Aldrich and used without further purification. 2,2′:6′,2″-Terpyridine (tpy) was ordered from ABCR GmbH & Co. Dry solvents were collected from a Pure Solve MD5 solvent dispenser from Demaco. For all inorganic reactions, solvents were deoxygenated by bubbling dinitrogen through the solution for 30 min. All organic reactions were carried out under a diniotrogen atmosphere at rt. Flash chromatography was performed on silica gel (Screening devices B.V.) with a particle size of 40−64 μM and a pore size of 60 Å. TLC analysis was conducted on TLC aluminum foils with a silica gel matrix (Supelco, silica gel 60, 56524) with detection by UV absorption (254 nm), by spraying with 10% H_2SO_4 in ethanol or with a solution of $NH_4Mo_7O_{24}{\cdot}4H_2O$ (25 g/L), $NH_4CeSO_4{\cdot}H_2O$ (10 g/L), 10% H_2SO_4 in H_2O, followed by charring at ∼250 °C on a heating plate. Optical rotation measurements were performed on a Propol automated polarimeter (sodium D line, λ = 589 nm) with a concentration of 10 mg/mL (c = 1) unless stated otherwise. Infrared spectra were recorded on a PerkinElmer UATR (Single Reflection Diamond) Spectrum Two device (4000−700 cm^{-1}; resolution 4 cm^{-1}). ^1H NMR and ^{13}C NMR were recorded in CD_3OD and $CDCl_3$ with a chemical shift (δ) relative to the solvent peak on a Bruker AV 400 or AV 500 unit. High-resolution mass spectra were recorded by direct injection (2 μL of 2 μM solution in water/acetoneitrile; 50/50; v/v and 0.1% formic acid) in a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electrospray (250 °C) with a resolution (R) = 60 000 at m/z 400 (mass range m/z = 150−2000) and dioctylphtalate (m/z = 391.28428) as a lock mass. The high-resolution mass spectrometer was calibrated prior to measurements with a calibration mixture (Thermo Finnigan). Melting point ranges were determined on a Stuart SMP30 unit. Elemental analysis for glycoconjugates [**1**]$(PF_6)_2$−[**5**]$(PF_6)_2$, [**6**]PF_6−[**10**]PF_6, and [**11**]Cl_2 was performed at Mikrolab Kolbe, Germany.

Synthesis. *(2-Methylthio)ethyl-α-D-glucopyranoside (**13**).* 2,3,4,6-Tetra-*O*-acetyl-(2-bromo)ethyl-α-D-glucopyranoside[25] (135 mg, 0.297 mmol) was dissolved in dry DMF (3 mL), and to this solution was added fresh NaSMe (23 mg, 0.33 mmol). The reaction was stirred overnight, after which it was diluted with EtOAc (25 mL), washed with water (2×) and aq $NaHCO_3$ (2×), and dried (Na_2SO_4). Concentration in vacuo was followed by purification of the residue by silica column chromatography (10% MeOH in DCM), affording the title compound (50.0 mg, 0.197 mmol, 66% over two steps) as a colorless oil: R_f = 0.84 (20% MeOH in DCM); IR (neat) 3350, 2918, 1639, 1426, 1018; ^1H NMR (400 MHz, CD_3OD) δ 4.80 (d, J = 3.8 Hz, 1H, H-1), 3.91−3.75 (m, 2H, C*H*H H-6, C*H*H OCH_2), 3.69−3.58 (m, 4H, H-4, H-5, C*H*H H-6, C*H*H OCH_2), 3.37 (dd, J = 9.7, 3.8 Hz, 1H, H-2), 3.25 (d, J = 9.3 Hz, 1H, H-3), 2.73 (td, J = 6.9, 1.8 Hz, 2H, OCH_2SMe), 2.12 (s, 3H, OCH_2SMe); ^{13}C NMR (101 MHz, CD_3OD) δ 100.3 (C-1), 75.1 (C-4), 73.9 (C-5), 73.5 (C-2), 71.8 (C-3), 68.4 (OCH_2), 62.7 (C-6), 34.3 (OCH_2SMe), 15.8 (OCH_2SMe); HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_9H_{18}O_6SNa$ 277.0716, found 277.0711.

*Methylthio-β-D-glucopyranoside (**15**).* α/β-D-Glucose pentaacetate (4.99 g, 12.4 mmol) was dissolved in anhydrous DCM (20 mL), and to this solution were added I_2 (4.84 g, 19.0 mmol) and Et_3SiH (2.90 mL, 18.2 mmol). This mixture was allowed to stir for 10 min, after which it was diluted with DCM (100 mL) and washed with aqueous saturated $Na_2S_2O_3$ (1×) and Na_2CO_3 (1×). Layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated in vacuo. The crude was coevaporated with toluene (3×) and redissolved in dry MeCN (20 mL), followed by the addition of thiourea (1.46 g, 19.2 mmol). The mixture was then heated for 30 min at 80 °C, after which it was allowed to cool down to rt, followed by the addition of MeI (1.60 mL, 25.7 mmol) and Et_3N (7.10 mL, 50.9 mmol). After an additional stirring for 10 min, the mixture was concentrated in vacuo, followed by purification of the residue over silica (0 to 50% Et_2O in PE), yielding methyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside as a yellow foam (2.71 g, 7.24 mmol). This compound was then dissolved in dry MeOH (70 mL) followed by the addition of a catalytic amount of NaOMe, which after stirring overnight was quenched upon the addition of Amberlite IR-120 H^+. Filtration was followed by concentration in vacuo, yielding the title compound as a colorless oil (1.48 g, 7.04 mmol, 57% over four steps): R_f = 0.63 (20% MeOH in DCM); IR (neat) 3336, 2923, 2881, 1425, 1017; ^1H NMR (400 MHz, CD_3OD) δ 4.35 (d, J = 9.6 Hz, 1H, H-1), 3.93 (d, J = 11.8 Hz, 1H, C*H*H H-6), 3.77−3.68 (m, 1H, C*H*H H-6), 3.48−3.35 (m, 3H, H-3, H-4, H-5), 3.31 (t, J = 9.1 Hz, 1H, H-2), 2.26 (s, 3H, S*Me*); ^{13}C NMR (101 MHz, CD_3OD) δ 87.1 (C-1), 81.8 (C-3), 79.3 (C-4), 73.5 (C-2), 71.3 (C-5), 62.7 (C-6), 12.0 (S*Me*); HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_7H_{14}O_5SNa$ 233.0454, found 233.0444.

*2-(Methylthio)ethoxy)ethanol (**18**).* To a flame-dried round-bottom flask was added freshly prepared NaSMe[44] (1.21 g, 15.5 mmol) under argon. Deoxygenated THF (50 mL) was added, followed by the addition of 2-chloroethoxy)ethanol (1.50 mL, 14.2 mmol). This solution was heated at 60 °C for 6 h, after which it was allowed to cool to room temperature. The mixture was diluted with EtOAc (100 mL) and washed with aqueous $NaHCO_3$ (2×) and water (1×). The layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated in vacuo, affording a slightly yellowish oil (1.89 g, 13.9 mmol, 89%): IR (neat) 3480, 2907, 2866, 1611, 1512; ^1H NMR (400 MHz, $CDCl_3$) δ 3.68 (m, 2H, CH_2), 3.62 (t, J = 6.7 Hz, 2H, CH_2), 3.54 (d, J = 5.1 Hz, 2H, CH_2), 2.94−2.81 (s, 1H, OH), 2.66 (t, J = 6.6 Hz, 2H, SCH_2), 2.10 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.1 (CH_2), 69.9 (CH_2), 61.5 (CH_2), 33.6 (SCH_2), 15.8 (SCH_3); HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_5H_{12}O_2SNa$ 159.0450, found 159.0457.

*2-[2-(2-(Methylthio)ethoxy)ethoxy]ethanol (**19**).* The procedure was followed as described for **18** using NaSMe[44] (4.23 g, 60.4 mmol) and 2-[2-(2-chloroethoxy)ethoxy]ethanol (10.0 g, 59.3 mmol). **19** was afforded as a colorless oil (9.25 g, 51.0 mmol, 85%): IR (neat) 3427, 2915, 2869, 1105, 1063; ^1H NMR (400 MHz, $CDCl_3$) δ 3.61−3.42 (m, 10H, 5 × CH_2), 3.09 (s, 1H, OH), 2.60−2.50 (m, 2H, 1 × CH_2), 2.03−1.94 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.4 (CH_2), 70.2 (CH_2), 70.1 (CH_2), 70.0 (CH_2), 61.3 (CH_2) 33.13 (SCH_2), 15.7 (SCH_3); HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_7H_{16}O_3SNa$ 203.0712, found 203.0713.

*(2-Methylthio)ethyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranoside (**21**).* 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate[45] (370 mg, 0.364 mmol) and 2-(methylthio)ethanol (100 μL, 1.15 mmol) were coevaporated three times with anhydrous toluene, after which they were dissolved in anhydrous DCM (36 mL). Freshly activated 4 Å molecular sieves were added, and the mixture was allowed to stir for 15 min, after which a catalytic amount of TMSOTf (20.0 μL, 111 μmol) was added. After stirring for 4 h at room temperature, the reaction was quenched upon the addition of Et_3N (100 μL, 0.714 mmol) and concentrated in vacuo followed by purification of the residue over silica (10% to 50% EtOAc in PE), affording the title compound as a clear oil (270 mg, 0.410 mmol, 81%): R_f = 0.74 (30% EtOAc in PE); IR (neat) 3064, 2922, 2853, 1720, 1258; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07−8.02 (m, 2H, H_{arom}), 8.00−7.96 (m, 2H, H_{arom}), 7.94−7.90 (m, 2H, H_{arom}), 7.87−7.81 (m, 2H, H_{arom}), 7.60−7.25 (m, 12H, H_{arom}), 5.93 (t, J = 9.7 Hz, 1H, H-3), 5.70 (t, J = 9.7 Hz, 1H, H-4), 5.56 (dd, J = 9.8, 7.8 Hz, 1H, H-2), 4.93 (d, J = 7.8 Hz, 1H, H-1), 4.67 (dd, J = 12.2, 3.2 Hz, 1H, C*H*H H-6), 4.52 (dd, J = 12.1, 5.4 Hz, 1H, C*H*H H-6), 4.19 (ddd, J = 8.6, 5.4, 3.2 Hz, 1H, H-5), 4.09 (dt, J = 10.2, 6.7 Hz, 1H, C*H*H OCH_2), 3.78 (dt, J = 10.3, 7.3 Hz, 1H, C*H*H OCH_2), 2.67 (t, J = 6.9 Hz, 2H, CH_2SMe), 2.01 (s, 3H, CH_2SMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C═O Bz), 165.9 (C═O Bz), 165.3 (C═O Bz), 165.2 (C═O Bz), 133.6 ($C_{H\ arom}$), 133.4 ($C_{H\ arom}$), 133.3

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($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.8 ($C_{H\ arom}$), 129.7 ($C_{q\ arom}$), 129.4 ($C_{q\ arom}$), 128.9 ($C_{q\ arom}$), 128.8 ($C_{q\ arom}$), 128.5 ($C_{H\ arom}$), 128.5 ($C_{H\ arom}$), 128.5 ($C_{H\ arom}$), 128.4 ($C_{H\ arom}$), 101.4 (C-1), 73.0 (C-3), 72.4 (C-5), 71.9 (C-2), 69.8 (C-4), 69.8 (OCH_2), 63.2 (C-6), 33.4 (CH_2SMe), 16.1 (CH_2SMe); HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{37}H_{38}O_{10}SN$ 688.2211, found 688.2222.

*[2-(2-(Methylthio)ethoxy)]ethyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranoside (**22**).* The general procedure described for **21** was followed, with 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate (6.00 g, 8.14 mmol) and 2-(2-(methylthio)ethoxy)ethanol (1.24 g, 9.10 mmol). Purification of the residue by silica column purification (0−25% EtOAc in PE) afforded the title compound as a clear oil (3.86 g, 5.40 mmol, 66%): R_f = 0.34 (33% EtOAc in PE); IR (neat) 3064, 2919, 1722, 1602, 1249; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−8.01 (m, 2H, H_{arom}), 8.00−7.96 (m, 2H, H_{arom}), 7.93−7.88 (m, 2H, H_{arom}), 7.86−7.81 (m, 2H, H_{arom}), 7.58−7.24 (m, 12H, H_{arom}), 5.92 (t, J = 9.7 Hz, 1H, H-3), 5.69 (t, J = 9.7 Hz, 1H, H-4), 5.54 (dd, J = 9.9, 7.7 Hz, 1H, H-2), 4.99 (d, J = 7.8 Hz, 1H, H-1), 4.65 (dd, J = 12.1, 3.2 Hz, 1H, C*H*H H-6), 4.51 (dd, J = 12.1, 5.1 Hz, 1H, C*H*H H-6), 4.18 (ddd, J = 10.1, 5.2, 3.1 Hz, 1H, H-5), 4.00 (dt, J = 11.4, 4.1 Hz, 1H, C*H*H OCH_2), 3.81 (ddd, J = 11.1, 6.9, 3.8 Hz, 1H, C*H*H OCH_2), 3.58 (dt, J = 6.7, 3.7 Hz, 2H, OCH_2), 3.48 (t, J = 6.7 Hz, 2H, OCH_2), 2.44 (t, J = 6.7 Hz, 2H, CH_2SMe), 2.03 (s, 3H, CH_2SMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (C═O Bz), 165.9 (C═O Bz), 165.3 (C═O Bz), 165.2 (C═O Bz), 133.6 ($C_{H\ arom}$), 133.4 ($C_{H\ arom}$), 133.3 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.7 ($C_{q\ arom}$), 129.4 ($C_{q\ arom}$), 128.9 ($C_{q\ arom}$), 128.9 ($C_{q\ arom}$), 128.5 ($C_{H\ arom}$), 128.5 ($C_{H\ arom}$), 128.4 ($C_{H\ arom}$), 101.4 (C-1), 73.0 (C-3), 72.3 (C-5), 72.0 (C-2), 70.6 (OCH_2), 70.2 (OCH_2), 69.8 (C-4), 69.4 (OCH_2), 63.2 (C-6), 33.5 (CH_2SMe), 16.1 (CH_2SMe); HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{39}H_{42}O_{11}SN$ 732.2473, found 732.2484.

*2-[2-(2-(Methylthio)ethoxy)ethoxy]ethyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranoside (**23**).* The general procedure described for **21** was followed, with 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate[45] (2.65 g, 3.58 mmol) and **19** (792 mg, 4.39 mmol). Purification of the residue over silica (10% to 50% EtOAc in PE) afforded the title compound as a clear oil (2.32 g, 3.06 mmol, 85%): R_f = 0.16 (20% EtOAc in PE); $[\alpha]_D^{20}$ ($CHCl_3$) +18.0; IR (neat) 3063, 2918, 2869, 1722, 1451; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.6 Hz, 2H, H_{arom}), 7.97 (d, J = 8.6 Hz, 2H, H_{arom}), 7.90 (d, J = 8.7 Hz, 2H, 2H, H_{arom}), 7.83 (d, J = 8.6 Hz, 2H, H_{arom}), 7.58−7.43 (m, 3H, H_{arom}), 7.43−7.29 (m, 7H, H_{arom}), 7.29−7.21 (m, 2H, H_{arom}), 5.93 (t, J = 9.7 Hz, 1H, H-3), 5.70 (t, J = 9.7 Hz, 1H, H-4), 5.55 (dd, J = 9.7, 7.8 Hz, 1H, H-2), 5.01 (d, J = 7.8 Hz, 1H, H-1), 4.66 (dd, J = 12.1, 3.1 Hz, 1H, CH*H* H-6), 4.51 (dd, J = 12.1, 5.1 Hz, 1H, CH*H* H-6), 4.20 (ddd, J = 9.9, 5.1, 3.1 Hz, 1H, H-5), 4.03−3.95 (m, 1H, CH*H*—OCH_2), 3.83 (m, 1H, CH*H*—OCH_2), 3.69−3.56 (m, 2H, OCH_2), 3.55 (t, J = 6.9 Hz, 2H, OCH_2), 3.50−3.42 (m, 2H, OCH_2), 3.37 (t, J = 4.6 Hz, 2H, OCH_2), 2.64 (t, J = 6.9 Hz, 2H, CH_2SMe), 2.11 (s, 3H, SCH_3); ^{13}C NMR (101 MHz, CD_3OD) δ 166.1 (C═O Bz), 165.8 (C═O Bz), 165.2 (C═O Bz), 165.1 (C═O Bz), 133.5 (CH_{arom}), 133.3 (CH_{arom}), 133.2 (CH_{arom}), 129.8 (CH_{arom}), 129.8 (CH_{arom}), 129.6 ($C_{q\ arom}$), 129.4 ($C_{q\ arom}$), 128.8 ($C_{q\ arom}$), 128.4 (CH_{arom}), 128.4 (CH_{arom}), 101.3 (C-1), 73.0 (C-3), 72.2 (C-5) 72.0 (C-2), 70.7 (OCH_2), 70.5 (OCH_2), 70.2 (OCH_2), 69.8 (C-4), 69.4 (OCH_2), 63.2 (OCH_2), 33.4 (CH_2SMe), 16.0 (CH_2SMe); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{41}H_{42}O_{12}SNa$ 781.2289, found 781.2280.

*(2-Methylthio)ethyl-β-D-glucopyranoside (**24**).* The protected glucoside **23** (240 mg, 0.410 mmol) was dissolved in MeOH (6 mL), after which a catalytic amount of NaOMe was added. The solution was allowed to stir for 16 h, after which Amberlite IR-120 H^+ was added, until a neutral pH. The resin was filtered off, and the mixture was concentrated in vacuo. Purification of the residue over silica (0 to 10% MeOH in DCM) afforded the title compound as a colorless oil (80.0 mg, 0.315 mmol, 88%): R_f = 0.15 (5% MeOH in DCM); IR (neat) 3351, 2919, 2881, 1072, 1016; ^{1}H NMR (400 MHz, CD_3OD) δ 4.30 (d, J = 7.8 Hz, 1H, H-1), 4.03 (dt, J = 10.1, 7.1 Hz, 1H, C*H*H OCH_2), 3.87 (dd, J = 11.9, 1.8 Hz, 1H, C*H*H H-6), 3.74 (dt, J = 10.1, 7.1 Hz, 1H, C*H*H OCH_2), 3.69−3.64 (m, 1H, C*H*H H-6), 3.39−3.33 (m, 1H, H-4), 3.29−3.26 (m, 2H, H-3, H-5), 3.21−3.15 (m, 1H, H-2), 2.73 (t, J = 7.1 Hz, 2H, CH_2SMe), 2.13 (s, 3H, CH_2SMe); ^{13}C NMR (101 MHz, CD_3OD) δ 104.4 (C-1), 77.9 (C-3), 77.9 (C-4), 75.0 (C-2), 71.6 (C-5), 70.0 (OCH_2), 62.7 (C-6), 34.3 (CH_2SMe), 15.7 (CH_2SMe); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_9H_{18}O_6SNa$ 277.0714, found 277.0716.

*[2-(2-(Methylthio)ethoxy)]-ethyl-β-D-glucopyranoside (**25**).* The procedure as described for **24** was followed, using protected glycoside **22** (560 mg, 0.780 mmol) and THF/MeOH (10 mL, 1:1). Purification of the crude over silica (0 to 20% acetone in DCM) afforded the title compound as a white solid (200 mg, 0.670 mmol, 86%): R_f = 0.19 (10% acetone in DCM); IR (neat) 3304, 2919, 1075, 1354, 1028; ^{1}H NMR (400 MHz, CD_3OD) δ 4.31 (d, J = 7.8 Hz, 1H, H-1), 4.05−3.96 (m, 1H, C*H*H OCH_2), 3.87 (dd, J = 11.9, 1.8 Hz, 1H, C*H*H H-6), 3.78−3.62 (m, 6H, C*H*H H-6, C*H*H OCH_2, 2 × OCH_2), 3.40−3.25 (m, 3H, H-3, H-4, H-5), 3.19 (dd, J = 9.3, 7.5 Hz, 1H, H-2), 2.68 (t, J = 6.8 Hz, 2H, CH_2SMe), 2.13 (s, 3H, CH_2SMe); ^{13}C NMR (101 MHz, CD_3OD) δ 104.4 (C-1), 78.0 (C-3), 78.0 (C-4), 75.1 (C-2), 71.6 (C-5), 71.5 (OCH_2), 71.2 (OCH_2), 69.7 (OCH_2), 62.8 (C-6), 34.2 (CH_2SMe), 15.8 (CH_2SMe); mp 89.9−90.8 °C; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{11}H_{22}O_7SNa$ 321.0978, found 321.0976.

*2-[2-(2-(Methylthio)ethoxy)ethoxy]ethyl β-D-glucopyranoside (**26**).* The protected glucoside **23** (973 mg, 1.28 mmol) was dissolved in MeOH (10 mL), after which a catalytic amount of NaOMe was added. The solution was allowed to stir for 16 h, after which Amberlite IR-120 H^+ was added, until reaching a neutral pH. The resin was filtered off, and the mixture was concentrated in vacuo. Purification of the residue over silica (0−10% MeOH in DCM) afforded the title compound as a colorless oil (400 mg, 1.17 mmol, 91%): R_f = 0.29 (10% MeOH in DCM); $[\alpha]_D^{20}$ (MeOH) −10.0; IR (neat) 3371, 2915, 2874, 1073, 1031; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (d, J = 7.8 Hz, 1H, H-1), 4.06 (ddd, J = 10.2, 5.0, 3.0 Hz, 1H, C*H*H OCH_2), 3.90 (dd, J = 11.9, 1.7 Hz, 1H, C*H*H OCH_2), 3.82−3.65 (m, 10H, C*H*H OCH_2, H-5, H-6, 3 × CH_2 OCH_2), 3.45−3.37 (m, 1H, H-3), 3.37−3.28 (m, 1H, H-4), 3.24 (dd, J = 9.1, 7.8 Hz, 1H, H-2), 2.72 (t, J = 6.8 Hz, 2H, OCH_2), 2.17 (s, 3H, SCH_3); ^{13}C NMR (101 MHz, CD_3OD) δ 104.4 (C-1), 77.9 (C-3), 75.0 (C-4), 71.6 (OCH_2), 71.5 (C-5), 71.5 (2 × OCH_2), 71.1 (OCH_2), 69.6 (OCH_2), 62.7 (C-6), 34.2 (CH_2SMe), 15.9 (CH_2SMe); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{13}H_{26}O_8SNa$ 365.1241, found 365.1238

*[1,3-Bis(methylthio)]-propyl-2,3,4,6-tetra-O-benzoyl-β-D-glucopyranoside (**27**).* The general procedure described for **21** was followed, with 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate (5.00 g, 6.75 mmol) and 1,3-bis(methylthio)propanol (830 μL, 6.09 mmol). Purification of the residue by silica column purification (0−20% EtOAc in PE) afforded the title compound as a clear oil (3.95 g, 5.40 mmol, 90%): R_f = 0.55 (20% EtOAc in PE); IR (neat) 2919, 2853, 1722, 1601, 1259; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.00 (m, 2H, H_{arom}), 7.99−7.94 (m, 2H, H_{arom}), 7.91 (d, J = 7.8 Hz, 2H, H_{arom}), 7.85−7.79 (m, 2H, H_{arom}), 7.60−7.24 (m, 12H, H_{arom}), 5.91 (t, J = 9.7 Hz, 1H, H-3), 5.65 (t, J = 9.7 Hz, 1H, H-4), 5.52 (dd, J = 10.1, 7.7 Hz, 1H, H-2), 5.09 (d, J = 7.9 Hz, 1H, H-1), 4.67 (dd, J = 12.1, 3.1 Hz, 1H, C*H*H H-6), 4.48 (dd, J = 12.2, 5.6 Hz, 1H, C*H*H H-6), 4.18 (ddd, J = 9.3, 5.7, 3.0 Hz, 1H, H-5), 4.04−3.91 (m, 1H, C*H*(CH_2SMe)$_2$), 2.86 (dd, J = 13.8, 4.4 Hz, 1H, C*H*H CH(CH_2SMe)$_2$), 2.81−2.71 (m, 2H, CH_2 CH(CH_2SMe)$_2$), 2.61 (td, J = 13.5, 7.4 Hz, 1H, C*H*H CH(CH_2SMe)$_2$), 2.06 (s, 3H, SMe), 1.90 (s, 3H, SMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C═O Bz), 165.9 (C═O Bz), 165.4 (C═O Bz), 165.3 (C═O Bz), 133.6 ($C_{H\ arom}$), 133.4 ($C_{H\ arom}$), 133.4 ($C_{H\ arom}$), 133.3 ($C_{H\ arom}$), 130.0 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.6 ($C_{q\ arom}$), 129.5 ($C_{q\ arom}$), 128.9 ($C_{q\ arom}$), 128.8 ($C_{q\ arom}$), 128.6 ($C_{H\ arom}$), 128.4 ($C_{H\ arom}$), 101.7 (C-1), 80.2 (CH(CH_2SMe)$_2$), 73.0 (C-3), 72.4 (C-5), 72.1 (C-2), 69.9 (C-4), 63.2 (C-6), 38.4 (CH_2 CH(CH_2SMe)$_2$), 37.8 (CH_2 CH-(CH_2SMe)$_2$), 16.7 (2 × SMe); HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{39}H_{42}O_{10}S_2N$ 748.2245, found 748.2254.

*[1,3-Bis(methylthio)]-propyl-β-D-glucopyranoside (**28**).* The procedure as described for **22** was followed, using protected glycoside **27** (3.20 g, 4.38 mmol) and DCM/MeOH (50 mL, 1:50). Purification of the residue over silica (0 to 10% MeOH in DCM) afforded **28** as a white

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foam (960 mg, 3.05 mmol, 70%): R_f = 0.24 (100% EtOAc); IR (neat) 3368, 2916, 1424, 1071, 1016; ^{1}H NMR (400 MHz, CD_3OD) δ 4.45 (d, J = 7.8 Hz, 1H, H-1), 4.06 (p, J = 5.8 Hz, 1H, C*H*($CH_2SMe)_2$), 3.90−3.83 (m, 1H, C*H*H H-6), 3.70−3.63 (m, 1H, C*H*H H-6), 3.41−3.33 (m, 1H, H-3), 3.33−3.26 (m, 2H, H-4, H-5), 3.24−3.14 (m, 1H, H-2), 2.94−2.83 (m, 3H, C*H*H, CH_2 $CH(CH_2SMe)_2$), 2.79 (dd, J = 13.8, 5.6 Hz, 1H, C*H*H $CH(CH_2SMe)_2$), 2.15 (s, 6H, 2 × *SMe*); ^{13}C NMR (101 MHz, CD_3OD) δ 104.1 (C-1), 79.4 ($CH(CH_2SMe)_2$), 77.9 (C-3), 77.9 (C-4), 75.2 (C-2), 71.5 (C-5), 62.7 (C-6), 39.0 (CH_2 $CH(CH_2SMe)_2$) 37.9 (CH_2 $CH(CH_2SMe)_2$), 16.6 (*SMe*), 16.4 (*SMe*); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{11}H_{22}O_6S_2Na$ 337.0750, found 337.0752

*[2,2′:6′,2″-Terpyridine]-4′-sulfonic acid (**30** (HS-tpy))*. [2,2′:6′,2″-Terpyridine]-4′(1′*H*)-thione[46] (534 mg, 2.01 mmol) was suspended in acetic acid (6 mL). and to this mixture was added 30% H_2O_2 (1 mL). The resulting purple mixture was heated at 70 °C for 12 h and concentrated in vacuo. The crude was then redissolved in H_2O, followed by the addition of 10% Pd/C (32 mg) and purged with H_2 (5 min). After stirring overnight at 40 °C under a H_2 atmosphere, the reaction was filtered over Celite, concentrated, and purified over silica (0 to 10% MeOH in DCM), affording the title compound as a bright yellow powder (151 mg, 0.428 mmol, 24%): R_f = 0.37 (20% MeOH in DCM); IR (neat) 3391, 3064, 1622, 1398, 1189; ^{1}H NMR (400 MHz, D_2O) δ 8.09 (dd, J = 4.9, 1.9 Hz, 2H, T_3, T_3''), 7.84 (s, 2H, T_3', T_5'), 7.61 (d, J = 7.4 Hz, 2H, T_6, T_6''), 7.54 (td, J = 7.7, 1.9 Hz, 2H, T_4, T_4''), 7.15 (ddd, J = 7.4, 5.0, 1.4 Hz, 2H, T_5, T_5''); ^{13}C NMR (101 MHz, D_2O) δ 154.9 ($C_{q\ arom}$), 152.7 ($C_{q\ arom}$), 152.7 ($C_{q\ arom}$), 148.1 (T_3, T_3''), 138.1 (T_4, T_4''), 124.9 (T_5, T_5''), 121.8 (T_6, T_6''), 116.5 (T_3, T_3''); HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{12}N_3O_3S$ 314.0594, found 314.0600.

*[Ru(S-tpy)(bpy)(Cl)] (**31**)*. Compound **30** (134 mg, 0.428 mmol) was dissolved in MeOH (10 mL), and to this solution was added 100 mg of washed Amberlite Na^+. After the mixture stirred for 5 min at rt, the ion-exchange resin was filtered off and the filtrate was concentrated in vacuo, affording a pinkish solid. This compound was then together with dichloro(*p*-cymene)ruthenium(II) dimer (130 mg, 0.213 mmol) redissolved in deoxygenated MeOH (5 mL) and heated to 60 °C. A solution of bpy (69.0 mg, 0.440 mmol) in MeOH (2.3 mL) was then added dropwise over 10 min from which the color of the solution changed from purple to red. After stirring for 2 h under nitrogen, the solution was allowed to cool to rt, after which Et_2O (20 mL) was added. The resulting precipitate was filtered and washed with Et_2O (3×), affording a brown powder (185 mg, 0.306 mmol, 72%): R_f = 0.29 (10% MeOH in DCM); mp > 350 °C; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{19}ClN_5O_3RuS$ 605.9935, found 605.9946.

*2-(2-(2-(Methylthio)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (**32**)*. Compound **19** (715 mg, 3.97 mmol) was dissolved in dry DCM (40 mL), and the mixture was cooled to 0 °C. To this solution were added Et_3N (850 ul, 6.09 mmol) and Ts-Cl (1.12 g, 5.87 mmol). The reaction was allowed to stir overnight, after which it was diluted with DCM (100 mL) and transferred to a separatory funnel. After washing with water (1×) and brine (1×), the layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by silica column chromatography (0 to 50% EtOAc in PE) afforded the title compound as a colorless oil (1.22 g, 3.64 mmol, 92%): R_f = 0.78 (50% EtOAc in PE); IR (neat) 2917, 2868, 1598, 1353, 1174; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H, H_{arom}), 7.30 (d, J = 8.1 Hz, 2H, H_{arom}), 4.18−4.02 (m, 2H, CH_2), 3.65−3.61 (m, 2H, CH_2), 3.57 (t, J = 6.8 Hz, 2H, CH_2), 3.51 (m, 4H, 2 × CH_2), 2.60 (t, J = 6.8 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3 tosyl), 2.07 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7 ($C_{q\ arom}$), 132.7 ($C_{q\ arom}$), 129.7 ($C_{H\ arom}$), 127.7 ($C_{H\ arom}$), 70.5 (CH_2), 70.4 (CH_2), 70.0 (CH_2), 69.2 (CH_2), 68.5 (CH_2), 33.2 (SCH_2), 21.5 (CH_3 tosyl), 15.8 (SCH_3); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{14}H_{22}O_5S_2Na$ 357.0801, found 357.0800.

*3,4,6-Tri-O-(4-methoxybenzyl)-D-glucal (**34**)*. To a cooled solution (0 °C) of D-glucal in dry DMF (230 mL) was slowly added NaH (60% dispersion in mineral oil, 3.10 g, 77.5 mmol) followed by the addition of 4-methoxybenzyl chloride (10.1 mL, 74.5 mmol). After the mixture stirred overnight under a dinitrogen atmosphere, H_2O (10 mL) was added and the mixture was allowed to stir for another 10 min. The mixture was further diluted with EtOAc (200 mL), transferred to a separatory funnel, and washed with water (3×) and brine (3×). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification by silica column chromatography (0 to 15% EtOAc in PE) afforded **34** (9.82 g, 19.4 mmol, 84%) as a clear oil that solidified upon standing over a longer time: R_f = 0.66 (10% EtOAc in PE); IR (neat) 2999, 2863, 2907, 1647, 1512; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.3 Hz, 4H, H_{arom}), 7.04 (d, J = 8.5 Hz, 2H, H_{arom}), 6.75 (dd, J = 11.9, 8.1 Hz, 6H, H_{arom}), 6.31 (d, J = 6.2 Hz, 1H, H-1), 4.74 (dd, J = 6.2, 3.2 Hz, 1H, H-2), 4.64 (d, J = 10.9 Hz, 1H, C*H*H PMB), 4.52−4.35 (m, 5H, C*H*H PMB, 2 × CH_2 PMB), 4.07 (dd, J = 6.5, 2.2 Hz, 1H, H-3), 3.92 (dt, J = 8.6, 4.1 Hz, 1H, H-5), 3.70 (s, 3H, CH_3 PMB), 3.69 (s, 4H, CH_3 PMB, H-4), 3.69 (s, 3H, CH_3 PMB), 3.66−3.58 (m, 2H, CH_2 H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3 ($C_{H\ arom}$), 159.3 ($C_{H\ arom}$), 159.3 ($C_{H\ arom}$), 144.7 (C-1), 130.6 ($C_{q\ arom}$), 130.4 ($C_{q\ arom}$), 130.1 ($C_{q\ arom}$), 129.7 ($C_{H\ arom}$), 129.6 ($C_{H\ arom}$), 129.5 ($C_{H\ arom}$), 113.9 ($C_{H\ arom}$), 113.9 ($C_{H\ arom}$), 100.2 (C-2), 76.9 (C-5), 75.6 (C-2), 74.2 (C-4), 73.5 (CH_2 PMB), 73.2 (CH_2 PMB), 70.3 (CH_2 PMB), 68.3 (C-6), 55.4 (3 × CH_3 PMB); HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{30}H_{38}O_7N$ 524.2643, found 524.2655.

*(4-Methoxybenzyl)-3,4,6-Tri-O-(4-methoxybenzyl)-β-D-glucopyranoside (**35**)*. To a solution of protected glycoside **35** (821 mg, 1.62 mmol) in dry DCM (8 mL) under a dinitrogen atmosphere were added freshly activated 4 Å molecular sieves. After stirring for 15 min, the mixture was allowed to cool to 0 °C and freshly prepared dimethyldioxirane in acetone (20 mL, 88 mM) was slowly added. The mixture was stirred for 3 h and allowed to reach rt, after which it was filtered over Celite and concentrated in vacuo. The crude was then, together with 4-methoxyl benzyl alcohol (335 mg, 2.42 mmol), redissolved in dry THF under a dinitrogen atmosphere, followed by the addition of freshly activated 4 Å molecular sieves. After stirring for 15 min, the mixture was cooled down to −78 °C and a cooled solution (10 °C) of $ZnCl_2$ in dry THF (2.43 mL, 1 M) was added dropwise over 10 min. The mixture was allowed to stir overnight at rt, after which it was filtered over Celite, concentrated in vacuo, and purified by silica column chromatography (0 to 20% EtOAc in PE) to afford **35** (413 mg, 0.625 mmol, 39% over two steps) as a colorless oil: R_f = 0.48 (40% EtOAc in PE); IR (neat) 3480, 3000, 2907, 1611, 1511; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 8.5, 4.8 Hz, 6H, H_{arom}), 7.08 (d, J = 8.6 Hz, 2H, H_{arom}), 6.98−6.77 (m, 8H, H_{arom}), 4.87 (dd, J = 15.4, 11.2 Hz, 2H, CH_2 PMB), 4.76 (dd, J = 10.7, 6.4 Hz, 2H, CH_2 PMB), 4.63−4.42 (m, 4H, 2 × CH_2 PMB), 4.32 (d, J = 7.3 Hz, 1H, H-1), 3.80 (s, 6H, 2 × CH_3 PMB), 3.79 (s, 3H, CH_3 PMB), 3.79 (s, 3H, CH_3 PMB), 3.70 (m, 2H, H-6), 3.62−3.50 (m, 3H, H-2, H-3, H-4), 3.45 (dd, J = 9.9, 4.1 Hz, 1H, H-5), 2.41 (s, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 ($C_{q\ arom}$), 159.3 ($C_{q\ arom}$), 159.3 ($C_{q\ arom}$), 130.9 ($C_{q\ arom}$), 130.4 ($C_{q\ arom}$), 130.3 ($C_{q\ arom}$), 130.0 ($C_{H\ arom}$), 129.7 ($C_{H\ arom}$), 129.7 ($C_{H\ arom}$), 129.6 ($C_{H\ arom}$), 129.3 ($C_{q\ arom}$), 114.0 ($C_{H\ arom}$), 113.9 ($C_{H\ arom}$), 113.9 ($C_{H\ arom}$), 101.5 (C-1), 84.3 (C-2), 77.4 (C-3), 75.3 (C-4), 74.9 (CH_2 PMB), 74.7 (C-5), 73.2 (CH_2 PMB), 70.8 (CH_2 PMB), 68.5 (C-6), 55.4 (4 × CH_3 PMB); HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{38}H_{48}O_{10}N$ 678.3273, found 678.3302.

*(4-Methoxybenzyl)-2-O-(2-[2-(2-(methylthio)ethoxy)ethoxy]-ethyl)-3,4,6-tetra-O-(4-methoxybenzyl)-β-D-glucopyranoside (**36**)*. Glycoside **35** (333 mg, 0.504 mmol) was dissolved in dry DMF (5 mL) and cooled to 0 °C. To this solution was added NaH (60% dispersion in mineral oil, 26 mg, 0.65 mmol) portionwise followed by the addition of tosylate **32** (185 mg, 0.554 mmol). After the mixture stirred for 6 h at rt under a dry atmosphere, MeOH was added (1 mL). The mixture was then diluted with EtOAc (50 mL), transferred to a separatory funnel, and washed with water (3×) and brine (3×). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by column chromatography (0 to 30% EtOAc in PE) afforded the title compound **36** as a milky oil (334 mg, 0.405 mmol, 80%): R_f = 0.39 (40% EtOAc in PE); IR (neat) 2999, 2864, 2835, 1612, 1512; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.18 (m, 6H, H_{arom}), 7.07 (dd, J = 8.7, 4.8 Hz, 2H, H_{arom}), 6.92−6.75 (m, 8H, H_{arom}), 4.96−4.80 (m, 2H, CH_2 PMB), 4.78−4.66 (m, 2H, CH_2 PMB), 4.62−4.37 (m, 5H, CH_2 PMB, H-1), 4.06 (dt, J = 9.9, 4.6 Hz, 1H, C*H*H

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OCH_2), 3.85 (q, J = 5.2 Hz, 1H, C*H*H OCH_2), 3.81 (s, 3H, CH_3 PMB), 3.80 (s, 3H, CH_3 PMB), 3.79 (s, 3H, CH_3 PMB), 3.79 (s, 3H, CH_3 PMB), 3.74−3.66 (m, 2H, H-6), 3.66−3.53 (m, 9H, H-3, 4 × OCH_2), 3.49 (t, J = 9.2 Hz, 1H, H-4), 3.40 (ddd, J = 9.7, 5.1, 2.2 Hz, 1H, H-5), 3.29 (t, J = 8.3 Hz, 1H, H-2), 2.62 (t, J = 7.0 Hz, 2H, CH_2SMe), 2.10 (s, 3H, CH_2SMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3 (C_q arom), 159.3 (C_q arom), 159.3 (C_q arom), 159.3 (C_q arom), 131.1 (C_q arom), 130.5 (C_q arom), 130.4 (C_q arom), 129.8 (C_H arom), 129.7 (C_H arom), 129.7 (C_H arom), 129.6 (C_H arom), 113.8 (C_H arom), 102.1 (C-1), 84.4 (C-4), 83.3 (C-2), 77.6 (C-4), 75.3 (CH_2 PMB), 74.9 (C-5), 74.7 (CH_2 PMB), 73.2 (CH_2 PMB), 72.1 (OCH_2), 70.9 (OCH_2), 70.9 (CH_2 PMB), 70.6 (OCH2), 70.5 (OCH2), 70.4 (OCH2), 68.7 (C-6), 55.4 (4 × CH_3 PMB), 33.4 (CH_2SMe), 16.1 (CH_2SMe); HRMS (ESI) m/z [M + NH_4]$^+$ calcd for $C_{45}H_{62}O_{12}SN$ 840.3987, found 840.4002.

*2-O-(2-[2-(2-(Methylthio)ethoxy)ethoxy]ethyl)-α/β-D-glucopyranoside (**H37**).* Compound **36** (241 mg, 0.293 mmol) was dissolved in a mixture of DCM/HFIP (1:1, 3 mL), and to this solution were added 5 drops of 37% HCl in H_2O. The color immediately changed to dark red, and after stirring for 5 min, the mixture was quenched upon the addition of Et_3N (500 μL, 3.59 mmol). The mixture was then concentrated in vacuo and redissolved in H_2O (5.8 mL), followed by the addition of a solution of $MeNH_2$ in MeOH (145 μL, 2M, 0.29 mmol). After the reaction mixture was heated for 30 min at 60 °C, the solvents were removed under reduced pressure and the resulting residue was purified by silica column chromatography (0 to 20% MeOH in DCM) to afford the fully deprotected hemiacetal **H37** (67 mg, 0.196 mmol, 67%) as a clear oil: R_f = 0.54 (25% MeOH in DCM); IR (neat) 3411, 2917, 2865, 1115, 1042; ^{1}H NMR (400 MHz, CD_3OD) δ 5.29 (d, J = 3.5 Hz, 1H, H-1α), 4.53 (d, J = 7.8 Hz, 1H, H-1β), 4.04 (dt, J = 11.3, 4.4 Hz, 1H, C*H*H H-6), 3.89−3.70 (m, 8H), 3.70−3.59 (m, 19H), 3.42−3.32 (m, 1H, H-3β), 3.30−3.20 (m, 2H), 3.03−2.86 (m, 1H, H-2β), 2.68 (t, J = 6.8 Hz, 4H, 2 × CH_2SMe), 2.13 (s, 6H, 2 × CH_2SMe); ^{13}C NMR (101 MHz, CD_3OD) δ 98.1 (C-1β), 91.8 (C-1α), 85.1 (C-1β), 82.4, 77.9, 77.5, 73.9, 72.8, 72.6, 71.9, 71.9, 71.6, 71.6, 71.5, 71.5, 71.4, 71.2, 71.1, 71.0, 62.8 (C-6α), 62.7 (C-6β), 34.2 (2 × CH_2SMe), 15.9 (2 × CH_2SMe); HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{13}H_{26}O_8SNa$ 365.1241, found 365.1251.

*1,2:5,6-Di-O-isopropylidene-3-O-(2-[2-(2-(methylthio)ethoxy)-ethoxy]ethyl)-α-D-glucofuranose (**38**).* To a cooled solution of diacetone glucose (200 mg, 0.768 mmol) in dry DMF (8 mL) was added 60% NaH in mineral oil (80.0 mg, 2.00 mmol). After the mixture stirred for 5 min, tosylate **32** was added and the mixture was left overnight. After the reaction was quenched with MeOH (1 mL), Et_2O (50 mL) was added and the reaction was transferred to a separatory funnel. After the mixture was washed with water (1×), aq $NaHCO_3$ (1×), and brine (1×), the layers were separated and the organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue over silica (0−50% EtOAc in PE) gave **38** as a clear oil. (294 mg, 0.700 mmol, 91%): R_f = 0.73 (50% EtOAc in PE); IR (neat) 2985, 2871, 1456, 1371, 1058; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (d, J = 3.8 Hz, 1H, H-1), 4.57 (d, J = 3.6 Hz, 1H, H-2), 4.31 (dt, J = 7.8, 5.9 Hz, 1H, H-5), 4.14−4.10 (m, 1H, H-3), 4.09−4.05 (m, 1H, C*H*H H-6), 3.99 (dd, J = 8.6, 5.8 Hz, 1H, C*H*H H-6), 3.92 (d, J = 3.1 Hz, 1H, H-4), 3.79−3.71 (m, 2H, OCH_2), 3.68−3.60 (m, 8H, 4 × OCH_2), 2.69 (t, J = 6.9 Hz, 2H, CH_2SMe), 2.14 (s, 3H, CH_2SMe), 1.49 (d, J = 2.7 Hz, 3H, CH_3 isopropylidene), 1.42 (s, 3H, CH_3 isopropylidene), 1.34 (s, 3H, CH_3 isopropylidene), 1.31 (d, J = 3.6 Hz, 3H, CH_3 isopropylidene); ^{13}C NMR (101 MHz, $CDCl_3$) δ 111.9 (C_q isopropylidene), 109.0 (C_q isopropylidene), 105.4 (C-1), 82.8 (C-2), 82.7 (C-4), 81.2 (C-3), 72.7 (C-5), 70.8 (OCH_2), 70.7 (OCH_2), 70.6 (OCH_2), 70.5 (OCH_2), 70.28, 67.3 (C-6), 33.5 (CH_2SMe), 27.0 (CH_3 isopropylidene), 27.0 (CH_3 isopropylidene), 26.4 (CH_3 isopropylidene), 25.6 (CH_3 isopropylidene), 16.2 (CH_2SMe); HRMS (ESI) m/z [M + NH_4]$^+$ calcd for $C_{19}H_{38}O_8SN$ 440.2313, found 440.2320.

*3-O-(2-[2-(2-(Methylthio)ethoxy)ethoxy]ethyl)-α/β-D-glucopyranoside (**H40**).* To a suspension of compound **38** in H_2O was added Amberlite IR-120 H^+, and this mixture was stirred for 24 h at 60 °C, after which it was filtered and concentrated in vacuo. Purification of the residue over silica (0 to 10% MeOH in DCM) afforded the title compound **H40** as a clear oil (α/β = 1:1, 81 mg, 0.24 mmol, 46%): R_f = 0.32 (10% MeOH in DCM); IR (neat) 3369, 2918, 2873, 1104, 1077; ^{1}H NMR (400 MHz, CD_3OD) δ 5.08 (d, J = 3.6 Hz, 1H, H-1α), 4.47 (d, J = 7.7 Hz, 1H, H-1β), 4.24−3.13 (m, 40H), 2.67 (t, J = 6.9 Hz, 4H, 2 × CH_2SMe), 2.11 (s, 6H, 2 × CH_2SMe); ^{13}C NMR (101 MHz, CD_3OD) δ 98.1 (C-1β), 94.0 (C-1α), 87.6, 84.5, 77.8, 76.1, 73.7, 73.1, 73.0, 72.2, 72.1, 71.6, 71.4, 71.4, 71.3, 71.1, 62.8 (C-6β), 62.6 (C-6α), 34.2 (2 × OCH_2SMe), 15.9 (2 × OCH_2SMe); HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{13}H_{26}O_8SNa$ 365.1241, found 365.1243.

*(4-Methoxybenzyl)-β-D-glucopyranoside (**41**).* To a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (3.00 g, 7.30 mmol) and 4-methoxybenzyl alcohol (5.04 g, 36.5 mmol) in dry Et_2O (75 mL) were added freshly activated 4 Å molecular sieves. The resulting mixture was allowed to stir for 10 min, after which Ag_2CO_3 (6.00 g, 21.8 mmol) and I_2 (1.85 g, 7.30 mmol) were added. After the mixture stirred an additional 24 h under a dinitrogen atmosphere at rt in the dark, the reaction mixture was filtered over Celite, diluted with EtOAc (200 mL), and washed with 1 M $Na_2S_2O_3$ (3×), aq $NaHCO_3$ (3×), and brine (3×). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by silica column chromatography (20% EtOAc in DCM) afforded (4-methoxybenzyl)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (2.39 g), which was then redissolved in dry MeOH (70 mL) followed by the addition of a catalytic amount of NaOMe. The resulting mixture was allowed to stir for 4 h, after which Amberlite IR-120 H^+ was added until a neutral pH, filtered, and concentrated in vacuo, affording the title compound **41** as a clear oil (1.57 g, 5.23 mmol, 72% over two steps): R_f = 0.57 (20% MeOH in DCM); IR (neat) 3335, 2924, 1612, 1027, 819; ^{1}H NMR (400 MHz, CD_3OD) δ 7.32 (d, J = 8.6 Hz, 2H, H_{arom}), 6.95−6.71 (m, 2H, H_{arom}), 4.85 (d, J = 18.0 Hz, 1H, C*H*H PMB), 4.58 (d, J = 11.3 Hz, 1H, C*H*H PMB), 4.31 (d, J = 7.8 Hz, 1H, H-1), 3.89 (dd, J = 12.0, 2.2 Hz, 1H, C*H*H H-6), 3.68 (dd, J = 12.0, 5.5 Hz, 1H, C*H*H H-6), 3.42−3.14 (m, 4H, H-2, H-3, H-4, H-5); ^{13}C NMR (101 MHz, CD_3OD) δ 160.8 ($C_{q\ arom}$), 130.9 ($C_{H\ arom}$), 130.9 ($C_{q\ arom}$), 114.6 ($C_{H\ arom}$), 102.9 (C-1), 78.0 (C-3), 78.0 (C-4), 75.1 (C-2), 71.7 (C-5), 71.4 (CH_2 PMB), 62.8 (C-6), 55.7 (CH_3 PMB); HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{14}H_{20}O_7Na$ 323.1107, found 323.1088.

*(4-Methoxybenzyl)-4,6-O-(4-methoxybenzylidene)-β-D-glucopyranoside (**42**).* To a solution of **41** (309 mg, 1.03 mmol) in dry DMF (5 mL) were added 4-methoxybenzaldehyde dimethyl acetal (135 μL, 0.793 mmol) and *p*-TsOH·H_2O (10 mg, 0.05 mmol). The resulting reaction mixture was heated at 60 °C for 16 h, after which it was concentrated in vacuo. Saturated aqueous $NaHCO_3$ (50 mL) was added, and the mixture was further diluted with EtOAc (200 mL) and transferred to a separatory funnel. After the mixture was washed with aq $NaHCO_3$ (3×), water (3×) and brine (3×), the layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated in vacuo. Compound **43** (382 mg, 0.910 mmol, 89%) was obtained after silica column chromatography (0 to 10% MeOH in DCM) as a white powder: R_f = 0.48 (10% MeOH in DCM); IR (neat) 3480, 2869, 1612, 1516, 1244; ^{1}H NMR (400 MHz, CD_3CN) δ 7.39 (d, J = 8.8 Hz, 2H, H_{arom}), 7.31 (d, J = 8.7 Hz, 2H, H_{arom}), 7.00−6.86 (m, 4H, H_{arom}), 5.50 (s, 1H, CH PMB acetal), 4.76 (d, J = 11.5 Hz, 1H, C*H*H PMB), 4.55 (d, J = 11.5 Hz, 1H, C*H*H PMB), 4.43 (d, J = 7.8 Hz, 1H, H-1), 4.24 (dd, J = 10.3, 4.6 Hz, 1H, C*H*H H-6), 3.78 (s, 6H, 2 × CH_3 OMe), 3.72 (t, J = 9.9 Hz, 1H, C*H*H H-6), 3.62−3.50 (m, 1H, H-3), 3.49−3.33 (m, 2H, H-4, H-5), 3.26 (td, J = 8.1, 3.7 Hz, 1H, H-2); ^{13}C NMR (101 MHz, CD_3CN) δ 161.1 ($C_{q\ arom}$), 160.4 ($C_{q\ arom}$), 131.3 ($C_{q\ arom}$), 130.7 ($C_{H\ arom}$), 128.6 ($C_{H\ arom}$), 114.6 ($C_{H\ arom}$), 114.4 ($C_{H\ arom}$), 103.4 (C-1), 102.1 (CH PMB acetal), 81.6 (C-4), 75.6 (C-2), 74.3 (C-3), 71.4 (CH_2 PMB), 69.3 (C-6), 67.2 (C-5), 55.9 (2 × CH_3 PMB); HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{22}H_{27}O_8$ 419.1700, found 419.1710.

*(4-Methoxybenzyl)-2,3-di-O-(4-methoxybenzyl)-4,6-O-(4-methoxybenzylidene)-β-D-glucopyranoside (**43**).* To a cooled solution (0 °C) of *p*-methoxy benzylidene protected **42** (377 mg, 0.900 mmol) in dry DMF (9 mL) was slowly added NaH (60% dispersion in mineral oil, 80.0 mg, 2.00 mmol) followed by the addition of 4-methoxybenzyl chloride (255 μL, 1.89 mmol). After stirring for 5 h under a dinitrogen atmosphere, the reaction was quenched upon the addition of MeOH (3 mL). The mixture was further diluted with Et_2O (200 mL), transferred to a separatory funnel, and washed with water (1×), aq $NaHCO_3$ (1×),

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and brine (1×). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification by silica column chromatography (0 to 20% EtOAc in PE) yielded the title compound **43** as a clear oil (447 mg, 0.680 mmol, 76%): R_f = 0.74 (40% EtOAc in PE); IR (neat) 3480, 2869, 1612, 1516, 1244; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.9 Hz, 2H, H_{arom}), 7.36−7.18 (m, 5H, H_{arom}), 7.00−6.78 (m, 6H, H_{arom}), 5.54 (s, 1H, CH benzylidene), 4.89 (d, J = 11.4 Hz, 1H, C*H*H PMB), 4.82 (dd, J = 10.8, 5.6 Hz, 2H, CH_2 PMB), 4.71 (dd, J = 16.0, 10.7 Hz, 2H, CH_2 PMB), 4.65−4.57 (m, 2H, C*H*H PMB, H-1), 4.37 (dd, J = 10.5, 5.0 Hz, 1H, C*H*H H-6), 3.82 (s, 6H, 2 × CH_3 PMB), 3.82 (s, 3H, CH_3 PMB), 3.80 (s, 3H, CH_3 PMB), 3.69 (p, J = 9.1 Hz, 2H, H-3, H-4), 3.49 (t, J = 7.9 Hz, 1H, H-2), 3.40 (td, J = 9.5, 5.0 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1 ($C_{q\ arom}$), 159.5 ($C_{q\ arom}$), 159.3 ($C_{q\ arom}$), 159.3 ($C_{q\ arom}$), 130.8 ($C_{q\ arom}$), 130.6 ($C_{q\ arom}$), 129.9 ($C_{H\ arom}$), 129.8 ($C_{H\ arom}$), 129.8 ($C_{H\ arom}$), 129.3 ($C_{q\ arom}$), 127.4 ($C_{H\ arom}$), 113.9 ($C_{H\ arom}$), 113.8 ($C_{H\ arom}$), 113.7 ($C_{H\ arom}$), 103.0 (C-1), 101.2 (CH PMB acetal), 81.9 (C-2), 81.5 (C-3), 80.7 (C-4), 75.1 (CH_2 PMB), 74.9 (CH_2 PMB), 71.4 (CH_2 PMB), 68.9 (C-6), 66.2 (C-5), 55.4 (3 × CH_3 PMB), 55.3 (CH_3 PMB acetal); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{38}H_{42}O_{10}Na$ 681.2670, found 681.2671.

*(4-Methoxybenzyl)-2,3,6-tri-O-(4-methoxybenzyl)-β-D-glucopyranoside (**44**).* Fully protected glycoside **43** (400 mg, 0.610 mmol) was dissolved in DMF (12 mL), and to this solution were added freshly activated 4 Å molecular sieves and fresh $NaCNBH_3$ (385 mg, 6.13 mmol). After the mixture stirred for 15 min, the solution was cooled to 0 °C, and a precooled solution (0 °C) of trifluoroacetic acid (1.2 mL) in dry DMF (3 mL) on 4 Å molecular sieves was then added dropwise over 15 min. The reaction mixture was maintained at rt for 48 h and filtered over Celite, diluted with EtOAc (100 mL), and transferred to a separatory funnel. After washing with water (1×), aq $NaHCO_3$ (1×), and brine (1×), the organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by column chromatography over silica (0 to 30% EtOAc in PE) afforded **44** (385 mg, 0.580 mmol, 95%) as a clear oil: R_f = 0.48 (40% EtOAc in PE); IR (neat) 3480, 3000, 2907, 1612, 1512; ^{1}H NMR (400 MHz, CD_3Cl_3) δ 7.42−7.16 (m, 8H, H_{arom}), 6.87 (tdd, J = 8.9, 4.7, 2.6 Hz, 8H, H_{arom}), 4.92−4.82 (m, 3H, C*H*H PMB, CH_2 PMB), 4.67−4.53 (m, 5H, C*H*H PMB, 2 × CH_2 PMB), 4.49 (d, J = 7.2 Hz, 1H, H-1), 3.82 (s, 3H, CH_3 PMB), 3.81 (s, 3H, CH_3 PMB), 3.81 (s, 3H, CH_3 PMB), 3.80 (s, 3H, CH_3 PMB), 3.79−3.66 (m, 2H, H-6), 3.59−3.51 (m, 1H, H-5), 3.48−3.36 (m, 3H, H-2, H-3, H-4); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 ($C_{q\ arom}$), 152.7 ($C_{q\ arom}$), 152.5 ($C_{q\ arom}$), 130.7 ($C_{H\ arom}$), 130.0 ($C_{H\ arom}$), 129.9 ($C_{H\ arom}$), 129.8 ($C_{H\ arom}$), 129.5 ($C_{H\ arom}$), 114.1 ($C_{H\ arom}$), 113.9 ($C_{H\ arom}$), 102.5 (C-1), 83.8 (C-4), 81.6 (C-2), 75.0 (CH_2 PMB), 74.5 (CH_2 PMB), 74.2 (C-3), 73.4 (CH_2 PMB), 71.7 (C-5), 71.1 (CH_2 PMB), 70.2 (C-6), 55.4 (4 × CH_3 PMB); HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{38}H_{48}O_{10}N$ 678.3273, found 678.3321.

*(4-Methoxybenzyl)-2-O-(2-[2-(2-(methylthio)ethoxy)ethoxy]-ethyl)-3,6-tri-O-(4-methoxybenzyl)-β-D-glucopyranoside (**45**).* Compound **44** (300 mg, 0.454 mmol) was dissolved in dry DMF (5 mL), and the mixture was cooled to 0 °C, after which 60% NaH in mineral oil (31 mg, 0.77 mmol) was added. This mixture was allowed to stir for 5 min, after which tosylate **32** (177 mg, 0.530 mmol) was added dropwise. The reaction was allowed to stir for 6 h, after which it was quenched upon the addition of MeOH (2 mL), diluted with Et_2O (20 mL), and transferred to a separatory funnel. After washing with aq $NaHCO_3$ (1×), water (1×), and brine (1×), the layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by column chromatography (0 to 40% EtOAc in PE) afforded the title compound **45** as a clear oil (291 mg, 0.354 mmol, 78%): R_f = 0.38 (40% EtOAc in PE); IR (neat) 2998, 2907, 2836, 1612, 1513; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.18 (m, 8H, H_{arom}), 6.94−6.79 (m, 8H, H_{arom}), 4.97−4.50 (m, 8H, 4 × CH_2 PMB), 4.46 (d, J = 7.8 Hz, 1H, H-1), 3.95 (dt, J = 9.8, 4.5 Hz, 1H, C*H*H OCH_2), 3.81−3.74 (m, 1H, C*H*H H-6), 3.76−3.63 (m, 3H, C*H*H H-6, 2 × C*H*H OCH_2), 3.65−3.50 (m, 8H, H-5, C*H*H OCH_2, 3 × OCH_2), 3.46−3.38 (m, 3H, H-2, H-3, H-4), 2.66 (t, J = 6.9 Hz, 2H, C*H*$_2$SMe), 2.12 (s, 3H, CH_2SMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 ($C_{q\ arom}$), 159.4 ($C_{q\ arom}$), 131.1 ($C_{q\ arom}$), 130.8 ($C_{q\ arom}$), 130.6 ($C_{q\ arom}$), 130.0 ($C_{H\ arom}$), 129.8 ($C_{H\ arom}$), 129.5 ($C_{H\ arom}$), 113.9 ($C_{H\ arom}$), 113.8 ($C_{H\ arom}$), 102.5 (C-1), 84.3 (C-5), 82.0 (C-2), 78.7 (C-3), 75.4 (CH_2 PMB), 75.0 (C-4), 74.6 (CH_2 PMB), 73.2 (CH_2 PMB), 72.2 (OCH_2), 71.0 (CH_2 PMB), 70.9 (OCH_2), 70.7 (OCH_2), 70.6 (OCH_2), 70.4 (CH_2SMe), 68.8 (C-6), 33.5 (4 × CH_3 PMB), 16.2 (CH_2SMe); HRMS (ESI) m/z $[M + NH_4]^+$ calcd for $C_{45}H_{62}O_{12}SN$ 840.3987, found 840.4028.

*4-O-(2-[2-(2-(Methylthio)ethoxy)ethoxy]ethyl)-α/β-D-glucopyranoside (**H46**).* Compound **45** (108 mg, 0.131 mmol) was dissolved in a mixture of DCM/HFIP (1:1, 2 mL), and to this solution were added 4 drops of 37% HCl. The mixture slowly turned red to deep purple in 30 min, after which it was quenched with Et_3N (0.5 mL) and concentrated in vacuo. The crude was redissolved in MeOH (5 mL); Amberlite IR-120 H^+ was added, and the mixture was stirred for 5 min, filtered, and concentrated. Purification of the resulting residue over silica (0 to 15% MeOH in DCM) afforded the title compound **H46** as a clear oil (13 mg, 0.038 mmol, 29%): R_f = 0.57 (20% MeOH in DCM); IR (neat) 3370, 2918, 2873, 1104, 1077; ^{1}H NMR (400 MHz, CD_3OD) δ 5.09 (d, J = 3.7 Hz, 1H, H-1α), 4.45 (d, J = 7.7 Hz, 1H, H-1β), 4.02−3.58 (m, 28H), 3.47 (t, J = 8.9 Hz, 1H, H-3β), 3.29−3.19 (m, 2H), 3.13 (dd, J = 9.2, 7.9 Hz, 1H, H-2β), 2.68 (t, J = 6.8 Hz, 4H, 2 × OC*H*$_2$SMe), 2.13 (s, 6H, 2 × OCH_2SMe); ^{13}C NMR (100 MHz, CD_3OD) δ 98.2 (C-1β), 93.9 (C-1α), 80.5, 80.3, 78.2, 77.0, 76.3, 75.0, 73.9, 72.9, 72.0, 71.7, 71.5, 71.2, 62.5 (C-1β), 62.4 (C-1α), 34.3 (2 × OCH_2SMe), 15.9 (OCH_2SMe); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{13}H_{26}O_8SNa$ 365.1241, found 365.1251.

*1,2:3,5-Bis(O-methylidene)-6-O-(2-[2-(2-(methylthio)ethoxy)-ethoxy]ethyl)α-D-glucofuranose (**49**).* To a cooled (0 °C) solution of 1,2:3,5-bis(*O*-methylidene)-α-D-glucofuranose (206 mg, 1.00 mmol) in dry DMF (10 mL) was added 60% NaH in mineral oil (57 mg, 1.42 mmol). After 10 min, **19** (385 mg, 1.15 mmol) was added dropwise, and the resulting mixture was stirred for 3 h at rt, after which it was quenched upon the addition of MeOH (2 mL). The reaction mixture was extracted with Et_2O (50 mL) and washed with aq $NaHCO_3$ (2×), water (2×), and brine (2×). The layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated in vacuo. The resulting residue was then purified by silica column chromatography (0 to 60% EtOAc in PE) affording **49** as a colorless oil (286 mg, 0.78 mmol, 78%): R_f = 0.57 (50% EtOAc in PE); IR (neat) 2867, 1455, 1082, 1184, 1058; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (d, J = 3.8 Hz, 1H, H-1), 5.12 (d, J = 5.9 Hz, 1H, C*H*H methylene), 5.08 (s, 1H, CH_2 methylene), 5.03 (s, 1H, CH_2 methylene), 4.78 (d, J = 6.0 Hz, 1H, C*H*H methylene), 4.46 (d, J = 3.9 Hz, 1H, H-2), 4.37 (d, J = 3.0 Hz, 1H, H-3), 4.14 (t, J = 4.4 Hz, 1H, H-5), 4.03 (d, J = 2.7 Hz, 1H, H-4), 3.85 (dd, J = 10.5, 3.9 Hz, 1H, C*H*H H-6), 3.75 (dd, J = 10.5, 4.8 Hz, 1H, C*H*H H-6), 3.64 (dd, J = 11.8, 5.6 Hz, 10H, 4 × OCH_2), 2.69 (t, J = 6.9 Hz, 2H, CH_2SMe), 2.14 (s, 3H, CH_2SMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.4 (C-1), 96.6 (CH_2 methylene), 88.2 (CH_2 methylene), 83.9 (C-2), 76.8 (C-3), 76.1 (C-4), 72.5 (C-6), 71.6 (C-5), 71.0 (OCH_2), 70.7 (OCH_2), 70.7 (OCH_2), 70.7 (OCH_2), 70.4 (OCH_2), 33.5 (OCH_2SMe), 16.2 (OCH_2SMe); HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{27}O_8S$ 367.1421, found 367.1430.

*6-O-(2-[2-(2-(Methylthio)ethoxy)ethoxy]ethyl)-α/β-D-glucopyranoside (**H50**).* Compound **49** was dissolved in 2 M HCl (5 mL), and this mixture was heated at 100 °C for 1 h, after which the reaction was neutralized with 1 M NaOH (10 mL) and concentrated in vacuo. Purification of the residue by silica column chromatography (0 to 20% MeOH in DCM) afforded **H50** as a colorless oil (101 mg, 0.295 mmol, 70%): R_f = 0.50 (20% MeOH in DCM); IR (neat) 3368, 2917, 2874, 1427, 1078; ^{1}H NMR (500 MHz, CD_3OD) δ 5.13 (d, J = 3.7 Hz, 1H, H-1α), 4.52 (d, J = 7.7 Hz, 1H, H-1β), 4.06−3.94 (m, 4H), 3.91−3.87 (m, 1H, CHH H-6α/β), 3.86−3.77 (m, 2H), 3.75−3.64 (m, 20H, 10 × OCH_2), 3.49−3.38 (m, 3H), 3.41 (ddd, J = 9.8, 8.8, 6.0 Hz, 2H), 3.34−3.30 (m, 1H), 3.25−3.22 (m, 2H), 2.72 (t, J = 6.8 Hz, 4H, 2 × CH_2SMe), 2.16 (s, 6H, 2 × CH_2SMe); ^{13}C NMR (126 MHz, CD_3OD) δ 98.1 (C-1β), 94.0 (C-1α), 87.6, 84.4, 77.8, 76.1, 73.6, 73.0 (OCH_2), 73.0 (OCH_2), 73.0, 72.1 (OCH_2), 72.1 (OCH_2), 71.6 (OCH_2), 71.6 (OCH_2), 71.4 (OCH_2), 71.4 (OCH_2), 71.3, 71.1 (OCH_2), 71.1 (OCH_2), 62.8 (C-6α/β), 62.7 (C-6α/β), 34.2 (2 × CH_2SMe), 15.9 (2 × CH_2SMe); HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{13}H_{26}O_8SNa$ 365.1241, found 365.1252.

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*[Ru(tpy)(bpy)(**13**)](PF$_6$)$_2$ ([**1**](PF$_6$)$_2$).* [Ru(tpy)(bpy)Cl]Cl (63 mg, 0.112 mmol) and **13** (93 mg, 0.366 mmol) were dissolved in deoxygenated H_2O (18 mL), and this mixture was heated at 80 °C for 16 h, after which it was concentrated in vacuo. Purification of the residue by silica column chromatography (100/0/0 to 100/80/20 acetone/water/aq KPF_6), followed by purification over Sephadex LH-20 (MeOH), afforded the title compound as a red solid (44 mg, 42.4 μmol, 39%): R_f = 0.69 (100/80/20 acetone/water/aq KPF_6); ^{1}H NMR (400 MHz, CD_3OD) δ 9.85 (d, *J* = 5.7 Hz, 1H, 1), 8.81 (d, *J* = 8.0 Hz, 1H, 4), 8.77 (d, *J* = 8.2 Hz, 2H, T$_3$′, T$_5$′), 8.62 (d, *J* = 8.1 Hz, 2H, T$_6$, T$_6$″), 8.58 (d, *J* = 7.8 Hz, 1H, 10), 8.44−8.34 (m, 2H, T$_4$′, 3), 8.18−8.04 (m, 3H, T$_5$, T$_5$″, 2), 7.92 (td, *J* = 7.8, 1.6 Hz, 1H, 9), 7.79 (d, *J* = 5.6 Hz, 2H, T$_3$, T$_3$″), 7.45 (ddd, *J* = 7.3, 5.6, 1.4 Hz, 2H, T$_4$, T$_4$″), 7.34−7.26 (m, 1H, 7), 7.23 (ddd, *J* = 7.3, 5.7, 1.3 Hz, 1H, 8), 4.69 (d, *J* = 3.7 Hz, 1H, H-1), 3.79−3.68 (m, 2H, C*H*H H-6, C*H*H OCH$_2$), 3.64−3.34 (m, 5H, C*H*H H-6, C*H*H OCH$_2$, H-2, H-3, H-5), 3.29−3.20 (m, 1H, H-4), 2.12−1.91 (m, 2H, *CH*$_2$SMe), 1.39 (s, 3H, CH$_2$*SMe*); ^{13}C NMR (101 MHz, CD_3OD) δ 159.3 (C$_{q\ arom}$), 158.7 (C$_{q\ arom}$), 158.1 (C$_{q\ arom}$), 157.9 (C$_{q\ arom}$), 154.3 (C$_H$ T$_3$, T$_3$″), 153.5 (C$_H$ 1), 150.8 (C$_H$ 7), 140.1 (C$_H$ T$_5$, T$_5$″), 139.4 (C$_H$ T$_4$′), 139.3 (C$_H$ 9), 138.3 (C$_H$ 3), 129.8 (C$_H$ T$_4$, T$_4$″), 129.4 (C$_H$ 2), 128.4 (C$_H$ 8), 126.2 (C$_H$ T$_6$), 126.2 (C$_H$ T$_6$″), 125.9 (C$_H$ 4), 125.5 (C$_H$ T$_3$′, T$_5$′), 125.1 (C$_H$ 10), 100.2 (C-1), 75.1 (C-5), 74.3 (C-3), 73.1 (C-2), 71.7 (C-4), 64.8 (OCH$_2$), 62.8 (C-6), 35.9 (*CH*$_2$SMe), 14.8 (CH$_2$*SMe*); HRMS (ESI) *m*/*z* [M]$^{2+}$ calcd for $C_{34}H_{37}N_5O_6RuS$ 372.5749, found 372.5756. Elemental analysis calcd (%) for [**1**](PF$_6$)$_2$·2MeOH: C, 39.35; H, 4.13; N, 6.37. Found: 41.45; H, 4.18; N, 6.35.

*[Ru(tpy)(bpy)(**15**)](PF$_6$)$_2$ ([**2**](PF$_6$)$_2$).* The title compound was synthesized analogous according to the procedure described for [**1**](PF$_6$)$_2$ using [Ru(tpy)(bpy)Cl)]Cl (200 mg, 0.357 mmol) and **15** (100 mg, 0.476 mmol) in H_2O (60 mL), affording [**2**](PF$_6$)$_2$ as an orange powder (98.4 mg, 99.3 μmol, 28%): R_f = 0.15 (100/80/20 acetone/water/aq KPF_6); ^{1}H NMR (400 MHz, CD_3OD) δ 10.01 (d, *J* = 4.1 Hz, 1H, 1), 8.82 (dt, *J* = 8.2, 1.1 Hz, 1H, 4), 8.76 (ddd, *J* = 8.2, 4.3, 0.9 Hz, 2H, T$_3$′, T$_5$′), 8.66−8.56 (m, 3H, T$_6$, T$_6$″, 10), 8.43−8.36 (m, 2H, T$_4$′, 3), 8.13−8.02 (m, 3H, T$_5$, T$_5$″, 2), 7.93 (ddd, *J* = 8.2, 7.0, 2.1 Hz, 1H, 9), 7.86 (ddd, *J* = 5.5, 1.5, 0.7 Hz, 1H, T$_3$), 7.80 (ddd, *J* = 5.5, 1.5, 0.7 Hz, 1H, T$_3$″), 7.44 (ddt, *J* = 7.8, 5.5, 1.3 Hz, 2H, T$_4$, T$_4$″), 7.27−7.18 (m, 2H, 7, 8), 3.52 (d, *J* = 9.1 Hz, 1H, H-1), 3.43 (t, *J* = 3.6 Hz, 2H, H-6), 3.02−2.90 (m, 3H, H-2, H-3, H-4), 2.48 (d, *J* = 8.7 Hz, 1H, H-5), 1.39 (s, 3H, *SMe*); ^{13}C NMR (101 MHz, CD_3OD) δ 163.4 (C$_{q\ arom}$), 160.7 (C$_{q\ arom}$), 160.0 (C$_{q\ arom}$), 159.8 (C$_{q\ arom}$), 158.9 (C$_{q\ arom}$), 158.2 (C$_{q\ arom}$), 158.0 (C$_{q\ arom}$), 154.5 (C$_H$ T$_3$), 154.3 (C$_H$ T$_3$″), 153.8 (C$_H$ 1), 150.4 (C$_H$ 7), 140.2 (C$_H$ T$_5$), 140.1 (C$_H$ T$_5$″), 139.6 (C$_H$ T$_4$′), 139.5 (C$_H$ 9), 138.2 (C$_H$ 3), 129.7 (C$_H$ T$_4$), 129.6 (C$_H$ T$_4$″), 129.0 (C$_H$ 2), 128.5 (C$_H$ 8), 126.1 (C$_H$ 4), 126.0 (C$_H$ T$_6$), 125.9 (C$_H$ T$_6$″) 125.3 (C$_H$ T$_3$′, T$_5$′), 125.1 (C$_H$ 10), 85.7 (C-1), 82.7 (C-5), 78.6 (C-2), 71.3 (C-3), 70.0 (C-4), 61.8 (C-6), 9.0 (*SMe*); HRMS (ESI) *m*/*z* [M]$^{2+}$ calcd for $C_{32}H_{33}N_5O_5RuS$ 350.5618, found 350.5629. Elemental analysis calcd (%) for [**2**](PF$_6$)$_2$: C, 38.18; H, 3.30; N, 6.96. Found: 38.93; H, 3.39; N, 7.19.

*[Ru(tpy)(bpy)(**24**)](PF$_6$)$_2$ ([**3**](PF$_6$)$_2$).* The title compound was synthesized analogous according to the procedure described for [**1**](PF$_6$)$_2$ using [Ru(tpy)(bpy)Cl)]Cl (101 mg, 0.180 mmol) and **24** (75.7 mg, 0.298 mmol) in H_2O (30 mL), affording the title compound as a hygroscopic orange powder (73.3 mg, 70.7 μmol, 39%): R_f = 0.36 (100/10/20 acetone/water/aq KPF_6); ^{1}H NMR (500 MHz, CD_3OD) δ 9.85 (dd, *J* = 5.6, 0.7 Hz, 1H, 1), 8.81 (dd, *J* = 17.9, 8.2 Hz, 3H, 4, T$_3$′, T$_5$′), 8.63 (d, *J* = 8.1 Hz, 2H, T$_6$, T$_6$″), 8.59 (d, *J* = 8.2 Hz, 1H, 10), 8.45−8.36 (m, 2H, T$_4$′, 3), 8.14−8.04 (m, 3H, T$_5$, T$_5$″, 2), 7.93 (td, *J* = 7.8, 1.5 Hz, 1H, 9), 7.80 (td, *J* = 5.4, 0.8 Hz, 2H, T$_3$, T$_3$″), 7.45 (ddd, *J* = 7.6, 5.5, 1.3 Hz, 2H, T$_4$, T$_4$″), 7.30 (ddd, *J* = 5.7, 1.5, 0.7 Hz, 1H, 7), 7.23 (ddd, *J* = 7.2, 5.7, 1.3 Hz, 1H, 8), 4.15 (d, *J* = 7.8 Hz, 1H, H-1), 3.88−3.76 (m, 2H, C*H*H H-6, C*H*H OCH$_2$), 3.57 (ddd, *J* = 12.7, 11.5, 5.6 Hz, 2H, C*H*H H-6, C*H*H OCH$_2$), 3.26 (m, 1H, H-3), 3.23−3.17 (m, 2H, H-2, H-4), 3.09 (dd, *J* = 9.2, 7.8 Hz, 1H, H-5), 1.98 (t, *J* = 5.6 Hz, 2H, C*H*$_2$SMe), 1.39 (s, 3H, CH$_2$*SMe*); ^{13}C NMR (126 MHz, CD_3OD) δ 159.3 (C$_{q\ arom}$), 159.3 (C$_{q\ arom}$), 158.8 (C$_{q\ arom}$), 158.2 (C$_{q\ arom}$), 158.0 (C$_{q\ arom}$), 154.4 (C$_H$ T$_3$), 154.4 (C$_H$ T$_3$″), 153.6 (C$_H$ 1), 150.8 (C$_H$ 7), 140.1 (C$_H$ T$_5$, T$_5$″), 139.5 (T$_4$′), 139.4 (C$_H$ 9), 138.3 (C$_H$ 3), 129.8 (C$_H$ T$_4$, T$_4$″), 129.2 (C$_H$ 2), 128.4 (C$_H$ 8), 126.2 (T$_6$, T$_6$″), 125.9 (C$_H$ 4), 125.5 (T$_3$′, T$_5$′), 125.1 (C$_H$ 10), 104.2 (C-1), 78.2 (C-3), 78.1 (C-4), 74.9 (C-2), 71.5 (C-5), 66.6 (OCH$_2$), 62.6 (C-6), 35.8 (*CH*$_2$SMe), 14.8 (CH$_2$*SMe*); HRMS (ESI) *m*/*z* [M]$^{2+}$ calcd for $C_{34}H_{37}N_5O_6RuS$ 372.5749, found 372.5758. Elemental analysis calcd (%) for [**3**](PF$_6$)$_2$: C, 39.47; H, 3.60; N, 6.77. Found: 40.57; H, 3.53; N, 7.00.

*[Ru(tpy)(bpy)(**25**)](PF$_6$)$_2$ ([**4**](PF$_6$)$_2$).* The title compound was synthesized analogous according to the procedure described for [**1**](PF$_6$)$_2$ using [Ru(tpy)(bpy)Cl)]Cl (94.2 mg, 0.168 mmol) and **25** (71.0 mg, 0.238 mmol) in H_2O (28 mL), affording the title compound as a hygroscopic orange powder (120 mg, 111 μmol, 66%): R_f = 0.56 (50/30/20 acetone/water/aq KPF_6); ^{1}H NMR (400 MHz, CD_3OD) δ 9.83 (d, *J* = 5.7 Hz, 1H, 1), 8.79 (dd, *J* = 14.9, 8.1 Hz, 3H, 4, T$_3$′, T$_5$′), 8.60 (dd, *J* = 16.6, 8.1 Hz, 2H, T$_6$, T$_6$″), 8.43−8.34 (m, 2H, T$_4$′, 3), 8.10 (m, 3H, T$_5$, T$_5$″, 2), 7.91 (td, *J* = 7.8, 1.5 Hz, 1H, 9), 7.80 (d, *J* = 4.7 Hz, 1H, T$_3$, T$_3$″), 7.51−7.41 (m, 2H, T$_4$, T$_4$″), 7.32−7.27 (m, 1H, 7), 7.23 (ddd, *J* = 7.2, 5.7, 1.3 Hz, 1H, 8), 4.27 (d, *J* = 7.8 Hz, 1H, H-1), 3.97−3.89 (m, 1H, C*H*H OCH$_2$), 3.85 (dd, *J* = 11.8, 1.7 Hz, 1H, C*H*H H-6), 3.71−3.58 (m, 2H, C*H*H H-6, C*H*H OCH$_2$), 3.54 (dd, *J* = 5.4, 3.8 Hz, 2H, OCH$_2$), 3.46 (t, *J* = 5.5 Hz, 2H, OCH$_2$), 3.35 (m, *J* = 2.4 Hz, 1H, H-3), 3.28−3.22 (m, 3H, H-4, H-5), 3.12 (dd, *J* = 9.0, 7.8 Hz, 1H,), 1.96−1.88 (m, 2H, *CH*$_2$SMe), 1.40 (s, 3H, CH$_2$*SMe*); ^{13}C NMR (101 MHz, CD_3OD) δ 159.3 (C$_{q\ arom}$), 158.7 (C$_{q\ arom}$), 158.1 (C$_{q\ arom}$), 157.9 (C$_{q\ arom}$), 154.4 (C$_H$ T$_3$, T$_3$″), 153.4 (C$_H$ 1), 150.8 (C$_H$ 7), 140.1 (T$_5$, T$_5$″), 139.5 (C$_H$ T$_4$′), 139.3 (C$_H$ 9), 138.3 (C$_H$ 3), 129.8 (C$_H$ T$_4$, T$_4$″), 129.3 (C$_H$ 2), 128.4 (C$_H$ 8), 126.2 (C$_H$ T$_6$), 125.9 (C$_H$ T$_6$″), 125.5 (C$_H$ 4), 125.1 (C$_H$ T$_3$′, T$_5$′), 104.4 (C-1), 78.1 (C-3), 78.0 (C-4), 75.1 (C-2), 71.6 (C-5), 71.4 (OCH$_2$), 69.7 (OCH$_2$), 68.2 (OCH$_2$), 62.7 (C-6), 35.6 (*CH*$_2$SMe), 15.2 (CH$_2$*SMe*); HRMS (ESI) *m*/*z* [M]$^{2+}$ calcd for $C_{36}H_{41}N_5O_7RuS$ 394.5880, found 394.5887. Elemental analysis calcd (%) for [**4**](PF$_6$)$_2$: C, 40.08; H, 3.83; N, 6.49. Found: 40.78; H, 3.97; N, 6.34.

*[Ru(tpy)(bpy)(**26**)](PF$_6$)$_2$ ([**5**](PF$_6$)$_2$).* The title compound was synthesized analogous according to the procedure described for [**1**](PF$_6$)$_2$ using [Ru(tpy)(bpy)Cl)]Cl (102 mg, 0.182 mmol) and **26** (100 mg, 0.292 mmol) in H_2O (30 mL), affording the title compound as a red solid (130 mg, 116 μmol, 65%): R_f = 0.35 (100/80/20 acetone/water/aq KPF_6); ^{1}H NMR (400 MHz, CD_3OD) δ 9.83 (d, *J* = 5.8 Hz, 1H, 1), 8.81 (dd, *J* = 12.6, 7.9 Hz, 3H, 4, T$_3$′, T$_5$′), 8.62 (dd, *J* = 17.9, 8.1 Hz, 3H, T$_6$, T$_6$″, 10), 8.46−8.35 (m, 2H, T$_4$′, 3), 8.10 (t, *J* = 8.3 Hz, 3H, T$_5$, T$_5$″, 2), 7.93 (t, *J* = 7.9 Hz, 1H, 9), 7.80 (d, *J* = 5.8 Hz, 2H, T$_3$, T$_3$″), 7.47 (t, *J* = 6.6 Hz, 2H, T$_4$, T$_4$″), 7.30 (d, *J* = 5.8 Hz, 1H, 7), 7.23 (t, *J* = 6.6 Hz, 1H, 8), 4.26 (d, *J* = 7.8 Hz, 1H, H-1), 4.06−3.91 (m, 1H, C*H*H OCH$_2$), 3.86 (d, *J* = 11.8 Hz, 1H, C*H*H H-6), 3.73−3.39 (m, 10H, C*H*H H-6, C*H*H OCH$_2$, 4 × OC*H*$_2$), 3.35 (m, 1H, H-5), 3.26 (d, *J* = 6.3 Hz, 2H, H-3, H4), 3.10 (t, *J* = 8.5 Hz, 1H, H-2), 1.90 (d, *J* = 5.6 Hz, 2H, OC*H*$_2$SMe), 1.41 (s, 3H, OCH$_2$*SMe*); ^{13}C NMR (101 MHz, CD_3OD) δ 157.9 (C$_{q\ arom}$), 157.4 (C$_{q\ arom}$), 156.8 (C$_{q\ arom}$), 156.6 (C$_{q\ arom}$), 153.1 (C$_H$ T$_3$, T$_3$″), 152.1 (C$_H$ 1), 149.5 (C$_H$ 7), 138.8 (C$_H$ T$_5$,T$_5$″), 138.2 (C$_H$ 9), 138.0 (C$_H$ T$_4$′), 136.9 (C$_H$ 3), 128.5 (C$_H$ T$_4$, T$_4$″), 127.9 (C$_H$ 8), 127.1 (C$_H$ 2), 124.9 (C$_H$ T$_6$, T$_6$″), 124.6 (C$_H$ 4), 124.1 (C$_H$ T$_3$, T$_5$′), 123.8 (C$_H$ 10), 103.1 (C-1), 76.6 (C-3, C-5), 73.7 (C-2), 70.3 (C-4), 70.0 (OCH$_2$), 69.9 (OCH$_2$), 69.8 (OCH$_2$), 68.3 (OCH$_2$), 67.0 (OCH$_2$), 61.3 (C-6), 34.1 (OCH$_2$SMe), 14.00 (OCH$_2$*SMe*); HRMS (ESI) *m*/*z* [M]$^{2+}$ calcd for $C_{38}H_{45}N_5O_8RuS$ 416.6011, found 416.6025. Elemental analysis calcd (%) for [**5**](PF$_6$)$_2$·3H$_2$O: C, 38.78; H, 4.37; N, 5.95. Found: 39.27; H, 4.68; N, 5.95.

*[Ru(tpy)(bpy)(**37**)]PF$_6$ ([**6**]PF$_6$).* [Ru(tpy)(bpy)(H$_2$O)](PF$_6$)$_2$ (35.9 mg, 45.0 μmol) and **H37** (30.3 mg, 44.7 μmol) were dissolved in a deoxygenated mixture of acetone/H_2O (4:1, 8 mL) and heated at 50 °C for 16 h, after which the reaction mixture was concentrated in vacuo and purified over Sephadex LH-20 (MeOH), affording the title compound as a red solid (18 mg, 18.4 μmol, 41%): R_f = 0.52 (acetone/water/aq KPF_6 100/80/20); ^{1}H NMR (500 MHz, CD_3OD) δ 9.84 (d, *J* = 5.6 Hz, 1H, 1), 8.88−8.80 (m, 3H, 4, T$_3$′, T$_5$′), 8.67 (d, *J* = 7.1 Hz, 2H, T$_6$, T$_6$″), 8.62 (d, *J* = 7.5 Hz, 1H, 10), 8.43 (q, *J* = 7.9 Hz, 2H, T$_4$′, 3), 8.17−8.08 (m, 3H, T$_5$, T$_5$″, 2), 7.95 (td, *J* = 7.8, 1.5 Hz, 1H, 9), 7.81 (d, *J* = 5.5 Hz, 2H, T$_3$, T$_3$″), 7.48 (ddd, *J* = 7.2, 5.5, 1.3 Hz, 2H, T$_4$, T$_4$″), 7.36−7.28 (m, 1H, 7), 7.24 (ddd, *J* = 7.2, 5.7, 1.3 Hz, 1H, 8), 5.23 (d, *J* = 3.5 Hz, 0.5H, H-1α), 4.45 (d, *J* = 7.8 Hz, 0.5H, H-1β), 3.99 (dt, *J* = 11.1, 4.6 Hz,

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0.5H C*H*H OCH_2 α/β), 3.86 (dd, J = 11.8, 2.3 Hz, 0.5H, C*H*H H-6α), 3.81−3.55 (m, 7.5H, C*H*H H-6α, CH_2 H-6β, H-3α, H-5α, H-5β, C*H*H OCH_2 α/β, 1 × OCH_2 α/β, 2 × OCH_2 α+β), 3.51−3.47 (m, 2H, OCH_2), 3.45 (ddd, J = 6.4, 5.2, 1.6 Hz, 2H, OCH_2), 3.30−3.20 (m, 1.5H, H-3β, H-4β, H-4α), 3.16 (dd, J = 9.6, 3.5 Hz, 0.5H, H-2α), 2.91 (dd, J = 8.9, 7.8 Hz, 0.5H, H-2β), 1.97−1.89 (m, 2H, CH_2SMe), 1.43 (s, 1.5H, CH_2SMe α), 1.42 (s, 1.5H, CH_2SMe β); ^{13}C NMR (126 MHz, CD_3OD) δ 159.3 ($C_{q\ arom}$), 158.8 ($C_{q\ arom}$), 158.2 ($C_{q\ arom}$), 158.0 ($C_{q\ arom}$), 154.4 (C_H T_3, T_3''), 153.4 (C_H 1), 150.8 (C_H 7), 140.2 (C_H T_5, T_5''), 139.6 (C_H T_5, T_5''), 139.4 (C_H T_4', 9), 138.4 (C_H 3), 129.9 (C_H T_4, T_4''), 129.3 (C_H 2), 128.4 (C_H 8), 126.3 (C_H T_6, T_6''), 126.0 (C_H 4), 125.5 (C_H T_3', T_5'), 125.2 (C_H 10), 98.1 (C-1β), 91.8 (C-1α), 85.2 (C-2β), 82.5 (C-2α), 78.0, 77.6, 73.9, 72.9, 72.6, 71.8, 71.8, 71.6, 71.3, 71.3, 71.2, 70.9, 68.4, 68.3, 62.8 (C-6α/β), 62.7 (C-6α/β), 35.7 (CH_2SMe), 35.6 (CH_2SMe), 15.4 (CH_2SMe), 15.4 (CH_2SMe); HRMS (ESI) m/z $[M + H]^{2+}$ calcd for $C_{38}H_{45}N_5O_8RuS$ 416.6011, found 416.6028. Elemental analysis calcd (%) for [**6**]PF_6·3H_2O: C, 44.27; H, 4.89; N, 6.79. Found: 44.70; H, 4.73; N, 6.49.

*[Ru(tpy)(bpy)(**40**)]PF_6 ([**7**]PF_6).* The title compound was synthesized analogous according to the procedure described for [**1**]$(PF_6)_2$ using [Ru(tpy)(bpy)Cl)]Cl (59.1 mg, 0.105 mmol) and **H40** (40.0 mg, 0.117 mmol) in H_2O (18 mL), affording the title compound as a red solid (44.2 mg, 39.3 μmol, 37%): R_f = 0.55 (100/80/20 acetone/water/aq KPF_6); ^{1}H NMR (500 MHz, CD_3OD) δ 9.86 (d, J = 5.9 Hz, 1H, 1), 8.96−8.80 (m, 3H, 4, T_3', T_5'), 8.74−8.69 (m, 2H, T_6, T_6''), 8.67−8.62 (m, 1H, 10), 8.51−8.40 (m, 2H, T_4', 3), 8.15 (dtd, J = 9.6, 4.4, 2.4 Hz, 3H, T_5, T_5'', 2), 8.01−7.93 (m, 1H, 9), 7.87−7.79 (m, 2H, T_3, T_3''), 7.55−7.46 (m, 2H, T_4, T_4''), 7.36−7.32 (m, 1H, 7), 7.27 (ddt, J = 7.3, 5.7, 1.5 Hz, 1H, 8), 5.10 (d, J = 3.6 Hz, 0.5H, H-1α), 4.51 (d, J = 7.6 Hz, 0.5H, H-1β), 4.29−3.08 (m, 15H), 1.96 (t, J = 5.4 Hz, 2H, 2 × CH_2SMe), 1.45 (s, 3H, 2 × CH_2SMe); ^{13}C NMR (126 MHz, CD_3OD) δ 159.3 ($C_{q\ arom}$), 158.8 ($C_{q\ arom}$), 158.2 ($C_{q\ arom}$), 158.0 ($C_{q\ arom}$), 154.4 (C_H T_3, T_3''), 153.4 (C_H 1), 150.8 (C_H 7), 140.2 (C_H T_5, T_5''), 139.6 (C_H T_4'), 139.4 (C_H 9), 138.3 (C_H 3), 129.9 (C_H T_4, T_4''), 129.3 (C_H 2), 128.4 (C_H 8), 126.3 (C_H T_6, T_6''), 126.0 (C_H 4), 125.5 (C_H T_3', T_5'), 125.2 (C_H 10), 98.2 (C-1β), 94.0 (C-1α), 87.6, 84.4, 77.8, 76.1, 73.7, 73.0, 73.0, 72.0, 72.0, 71.6, 71.4, 71.3, 71.2, 71.2, 71.1, 71.1, 68.4, 68.3, 62.6 (C-6α/β), 62.5 (C-6α/β), 35.7 (2 × CH_2SMe), 15.4 (2 × CH_2SMe); HRMS (ESI) m/z $[M + H]^{2+}$ calcd for $C_{38}H_{45}N_5O_8RuS$ 416.6011, found 416.6024. Elemental analysis calcd (%) for [**7**]PF_6·2H_2O: C, 45.02; H, 4.87; N, 6.91. Found: C, 44.82; H, 4.61; N, 6.79.

*[Ru(tpy)(bpy)(**46**)]PF_6 ([**8**]PF_6).* [Ru(tpy)(bpy)(H_2O)]$(PF_6)_2$ (25.8 mg, 32.0 μmol) and **H46** (11.0 mg, 32.1 μmol) were dissolved in a deoxygenated mixture of acetone/H_2O (4:1, 6 mL) and heated at 50 °C for 48 h, after which the reaction mixture was concentrated in vacuo and purified over Sephadex LH-20 (MeOH), affording the title compound as a red solid (23 mg, 23.5 μmol, 73%): R_f = 0.61 (100/80/20 acetone/water/aq KPF_6); ^{1}H NMR (500 MHz, CD_3OD) δ 9.85 (dd, J = 5.5, 1.1 Hz, 1H, 1), 8.86 (d, J = 8.3 Hz, 1H, 4), 8.83 (d, J = 8.1 Hz, 2H, T_3', T_5'), 8.69−8.66 (m, 2H, T_6, T_6''), 8.63 (dt, J = 8.2, 1.1 Hz, 1H, 10), 8.47−8.41 (m, 2H, T_4', 3), 8.13 (td, J = 7.8, 1.5 Hz, 3H, T_5, T_5'', 2), 7.96 (td, J = 7.9, 1.5 Hz, 1H, 9), 7.82 (dd, J = 5.7, 1.6 Hz, 2H, T_3, T_3''), 7.49 (ddt, J = 7.3, 5.4, 1.8 Hz, 2H, T_4, T_4''), 7.31 (ddd, J = 5.7, 1.6, 0.8 Hz, 1H, 7), 7.25 (ddd, J = 7.2, 5.7, 1.3 Hz, 1H, 8), 5.11 (d, J = 3.7 Hz, 0.5H, H-1α), 4.44 (d, J = 7.8 Hz, 0.5H, H-1β), 3.98−3.05 (m, 15H), 1.95 (t, J = 5.5 Hz, 2H, 2 × CH_2SMe), 1.43 (s, 1.5H, CH_2SMe), 1.43 (s, 1.5H, CH_2SMe); ^{13}C NMR (126 MHz, CD_3OD) δ 159.3 ($C_{q\ arom}$), 158.8 ($C_{q\ arom}$), 158.2 ($C_{q\ arom}$), 158.0 ($C_{q\ arom}$), 154.4 (C_H T_3), 154.4 (C_H T_3'), 153.4 (C_H 1), 150.8 (C_H 7), 140.2 (C_H T_5, T_5''), 139.6 (C_H T_4'), 139.4 (C_H 9), 138.3 (C_H 3), 129.9 (C_H T_4, T_4''), 129.3 (C_H 2), 128.4 (C_H 8), 126.3 (C_H T_6, T_6''), 125.9 (C_H 4), 125.5 (C_H T_3', T_5'), 125.2 (C_H 10), 98.3 (C-1β), 93.9 (C-1α), 80.6, 80.4, 78.1, 77.0, 76.3, 74.9, 73.8, 72.8, 72.0, 71.9, 71.3, 71.2, 71.2, 68.4, 68.4, 62.5 (C-6 α/β), 62.4 (C-6α/β), 35.7 (CH_2SMe), 35.6 (CH_2SMe), 15.3 (2 × CH_2SMe); HRMS (ESI) m/z $[M + H]^{2+}$ calcd for $C_{38}H_{45}N_5O_8RuS$ 416.6011, found 416.6026. Elemental analysis calcd (%) for [**8**]PF_6·2.5H_2O: C, 44.62; H, 4.93; N, 6.85. Found: 45.17; H, 5.16; N, 6.55.

*[Ru(tpy)(bpy)(**50**)]PF_6 ([**9**]PF_6).* The title compound was synthesized analogous according to the procedure described for [**1**]$(PF_6)_2$ using [Ru(tpy)(bpy)Cl)]Cl (58.8 mg, 0.105 mmol) and **H50** (42.0 mg, 123 μmol) in H_2O (18 mL), affording the title compound as a red solid (23.5 mg, 24.1 μmol, 23%): R_f = 0.36 (16/4/1 acetone/water/1 M HCl); ^{1}H NMR (500 MHz, CD_3OD) δ 9.86 (ddd, J = 5.6, 1.5, 0.7 Hz, 1H, 1), 8.89−8.87 (m, 1H, 4), 8.85 (d, J = 8.2 Hz, 2H, T_3', T_5'), 8.69 (dd, J = 8.2, 1.2 Hz, 2H, T_6, T_6''), 8.67−8.62 (m, 1H, 10), 8.50−8.41 (m, 2H, T_4', 3), 8.16−8.10 (m, 3H, T_5, T_5'', 2), 7.97 (td, J = 7.8, 1.5 Hz, 1H, 9), 7.84 (ddd, J = 5.6, 1.5, 0.7 Hz, 2H, T_3, T_3''), 7.50 (ddd, J = 7.2, 5.6, 1.4 Hz, 2H, T_4, T_4''), 7.33 (dq, J = 5.9, 0.9 Hz, 1H, 7), 7.26 (ddd, J = 7.2, 5.7, 1.3 Hz, 1H, 8), 5.10 (d, J = 3.6 Hz, 0.5H, H-1α), 4.50 (d, J = 7.6 Hz, 0.5H, H-1β), 3.99−3.08 (m, 15H), 1.96 (t, J = 5.5 Hz, 2H, 2 × CH_2SMe), 1.44 (s, 3H, 2 × CH_2SMe); ^{13}C NMR (126 MHz, CD_3OD) δ 159.3 ($C_{q\ arom}$), 158.8 ($C_{q\ arom}$), 158.2 ($C_{q\ arom}$), 158.0 ($C_{q\ arom}$), 154.4 (C_H T_3'), 153.4 (C_H 1), 150.8 (C_H 7), 140.2 (C_H T_5, T_5''), 139.6 (C_H T_4'), 139.4 (C_H 9), 138.3 (C_H 3), 129.9 (C_H T_4, T_4''), 129.3 (C_H 2), 128.4 (C_H 8), 126.3 (C_H T_6, T_6''), 126.0 (C_H 4), 125.6 (C_H T_3'), 125.5 (C_H T_5'), 125.1 (C_H 10), 98.2 (C-1β), 94.0 (C-1α), 87.6, 84.4, 77.8, 76.1, 73.7, 73.0, 73.0, 73.0, 72.0, 72.0, 71.3, 71.3, 71.2, 71.2, 71.1, 68.4, 68.3, 62.6 (C-6α/β), 62.5 (C-6α/β), 35.7 (2 × CH_2SMe), 15.4 (2 × CH_2SMe); HRMS (ESI) m/z $[M + H]^{2+}$ calcd for $C_{38}H_{45}N_5O_8RuS$ 416.6011, found 416.6026. Elemental analysis calcd (%) for [**9**]PF_6·2H_2O: C, 45.02; H, 4.87; N, 6.91. Found: C, 44.88; H, 4.59; N, 6.78.

*[Ru(S-tpy)(bpy)(**26**)]PF_6 ([**10**]PF_6).* A deoxygenated solution of **31** (40.0 mg, 0.0661 mmol) and **26** (48.0 mg, 0.140 mmol) in H_2O (11 mL) was heated at 80 °C for 16 h, after which it was concentrated in vacuo. The resulting residue was then purified over silica (100/0/0 to 100/95/5 in acetone/water/aq KPF_6), followed by purification over Sephadex LH-20 (MeOH) to afford the title compound as a red microcrystalline solid (18 mg, 24.4 μmol, 37%): R_f = 0.46 (100/80/20 acetone/water/aq KPF_6); ^{1}H NMR (500 MHz, CD_3OD) δ = 9.84 (d, J = 5.9 Hz, 1H, 1), 9.03 (s, 2H, T_3', T_5'), 8.81 (d, J = 8.2 Hz, 1H, 4), 8.73 (d, J = 8.1 Hz, 2H, T_6, T_6''), 8.58 (d, J = 8.2 Hz, 1H, 10), 8.43 (t, J = 7.9 Hz, 1H, 3), 8.13 (dt, J = 13.2, 7.4 Hz, 3H, 2, T_4, T_4''), 7.95 (t, J = 7.7 Hz, 1H, 9), 7.81 (d, J = 5.9 Hz, 2H, T_3, T_3''), 7.60−7.43 (m, 2H, T_5, T_5''), 7.25 (dt, J = 12.7, 6.0 Hz, 2H, 8, 7), 4.30 (d, J = 7.8 Hz, 1H, H-1), 4.00 (dd, J = 10.6, 5.3 Hz, 1H, C*H*H OCH_2), 3.86 (d, J = 12.0 Hz, 1H, C*H*H H-6), 3.67 (m, 4H, C*H*H H-6, C*H*H OCH_2, 2 × OCH_2), 3.57 (dd, J = 5.7, 3.4 Hz, 2H, OCH_2), 3.48 (dd, J = 5.8, 3.4 Hz, 2H, OCH_2), 3.44 (t, J = 5.5 Hz, 2H, OCH_2), 3.41−3.36 (m, 1H, H-3), 3.29 (m, 2H, H-4, H-5), 3.14 (t, J = 8.5 Hz, 1H, H-2), 1.91 (t, J = 5.5 Hz, 2H, CH_2SMe), 1.41 (s, 3H, CH_2SMe); ^{13}C NMR (126 MHz, CD_3OD) δ 159.2 ($C_{q\ arom}$), 158.7 ($C_{q\ arom}$), 157.9 ($C_{q\ arom}$), 157.7 ($C_{q\ arom}$), 154.8 ($C_{q\ arom}$), 154.2 (C_H T_3, T_3''), 153.2 (C_H 1), 150.6 (C_H 7), 140.4 (C_H T_4, T_4''), 139.8 (C_H 3), 139.6 (C_H 9), 130.2 (C_H T_5, T_5''), 129.3 (C_H 8) 128.5 (C_H 2), 126.7 (C_H T_6, T_6''), 125.9 (C_H 4), 125.1 (C_H 10), 121.7 (CH T_3', T_5'), 104.2 (C-1), 77.8 (C-3, C-5), 74.9 (C-2), 71.4 (C-5), 71.1 (OCH_2), 71.0 (OCH_2), 69.7 (OCH_2), 68.0 (OCH_2), 62.5 (C-6), 35.2 (CH_2SMe), 15.2 (CH_2SMe); HRMS (ESI) m/z $[M]^+$ calcd for $C_{38}H_{44}N_5O_{11}RuS_2$ 912.1517, found 912.1543. Elemental analysis calcd (%) for [**10**]PF_6·0.5KPF_6·5H_2O: C, 36.84; H, 4.39; N, 5.65. Found: 36.83; H, 4.40; N, 5.36.

*Δ/Λ-[Ru(tpy)(bpy)(**28**)]$(PF_6)_2$ ([**11**]Cl_2).* [Ru$(bpy_2)Cl_2$] (73.0 mg, 0.151 mmol) and **28** (46.0 mg, 0.146 mmol) were dissolved in deoxygenated H_2O (10 mL), and this mixture was heated at 80 °C for 16 h, after which the mixture was concentrated in vacuo. Purification by Sephadex LH-20 (MeOH) afforded the title compound as an inseparable mixture of diastereomers (69.0 mg, 0.0864 mmol, 59%): R_f = 0.28 (16/4/1 acetone/water/1 M HCl); ^{1}H NMR (500 MHz, CD_3OD) δ 10.02 (dd, J = 5.7, 1.4 Hz, 1H), 9.86 (dd, J = 5.7, 1.4 Hz, 1H), 9.50 (dd, J = 5.7, 1.4 Hz, 1H), 9.42 (dd, J = 5.7, 1.3 Hz, 1H), 8.81 (d, J = 8.2 Hz, 2H), 8.79−8.76 (m, 2H), 8.69−8.62 (m, 4H), 8.45−8.36 (m, 4H), 8.12 (tt, J = 8.0, 1.8 Hz, 4H), 8.06 (dddd, J = 13.5, 7.3, 5.6, 1.4 Hz, 5H), 7.63 (td, J = 5.7, 1.4 Hz, 2H), 7.57 (ddd, J = 7.5, 5.7, 1.4 Hz, 2H), 7.49−7.42 (m, 4H), 4.65 (d, J = 7.8 Hz, 1H), 4.58 (d, J = 7.8 Hz, 1H), 3.92 (ddd, J = 19.8, 11.8, 1.9 Hz, 2H), 3.78−3.70 (m, 1H), 3.62 (dd, J = 11.9, 6.4 Hz, 1H), 3.50−3.35 (m, 10H), 3.30 (t, J = 8.2 Hz, 1H), 3.27−3.20 (m, 2H), 3.13 (dd, J = 14.0, 6.4 Hz, 1H), 3.02 (dd, J = 13.9, 7.1 Hz, 1H), 2.92 (dd, J = 13.1, 2.1 Hz, 1H), 2.80 (dd, J = 13.1, 1.7 Hz, 1H), 1.53 (s, 3H), 1.50 (s, 3H), 1.25 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ 159.1, 159.1, 159.0, 158.9, 158.1, 158.0, 157.9, 155.4, 155.0, 154.9, 154.8, 152.0, 152.0, 151.9, 151.9, 140.3, 140.2,

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130.8, 130.0, 129.9, 129.5, 129.3, 129.0, 129.0, 128.9, 126.2, 126.1, 126.0, 125.6, 125.6, 125.5, 125.4, 104.2, 103.6, 78.4, 78.3, 78.3, 78.2, 75.3, 75.3, 75.2, 71.6, 71.6, 62.7, 40.5, 38.6, 38.4, 37.4, 18.5, 18. 1, 16.1, 16.0; HRMS (ESI) m/z $[M]^{2+}$ calcd for $C_{31}H_{38}N_4O_6RuS_2$ 364.0633, found 364.0646. Elemental analysis calcd (%) for $[\mathbf{11}]Cl_2 \cdot 3H_2O$: C, 43.66; H, 5.20; N, 6.57. Found: 43.34; H, 5.35; N, 6.29.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b01342.

^1H and ^{13}C spectra for **13**, **15**, **18**, **19**, **21**−**28**, **30**−**32**, **34**−**36**, **H37**, **38**, **H40**, **41**−**45**, **H46**, **49**, **H50**, $[\mathbf{1}](PF_6)_2$−$[\mathbf{5}](PF_6)_2$, $[\mathbf{6}]PF_6$−$[\mathbf{10}]PF_6$, and $[\mathbf{11}]Cl_2$ (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*(S.B.) E-mail: bonnet@chem.leidenuniv.nl.

*(L.N.L.) E-mail: l.n.lameijer@rug.nl.

ORCID

Lucien N. Lameijer: 0000-0003-2841-4742

Stefan van der Vorm: 0000-0002-4047-9373

Sylvestre Bonnet: 0000-0002-5810-3657

Notes

The authors declare no competing financial interest.

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Due to a production error, the corresponding author details for the first author were inadvertently omitted in the version that published on November 2, 2018. The authorship has been corrected and reposted on November 5, 2018.

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