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Towards the synthesis of a 2-deoxy-2-fluoro-D-mannose building block and characterisation of an unusual 2-*S*-phenyl anomeric pyridinium triflate salt *via* 1 → 2 *S*-migration

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A B S T R A C T

Regio- and stereo-selective synthetic routes to 2-deoxy-2-fluoro-D-mannose building blocks are often experimentally challenging when using Selectfluor with the corresponding glycal. We targeted a late-stage method to introduce fluorine in a stereospecific manner using inversion *via* a triflate. Accordingly, synthesis of a conventionally protected 2-deoxy-2-fluoro-D-mannose β-thioglycoside donor, directly applicable to oligosaccharide synthesis, was attempted using C2-triflate inversion of the corresponding D-glucoside with TBAF. Unexpectedly, an anomeric pyridinium salt was isolated when attempting to form the C2-triflate using Tf_2O in pyridine. Indicatively, this proceeds *via* a 1 → 2 *S*-migration delivering a 1,2-*trans* product with α-D-manno configuration and the anomeric pyridinium in a pseudo-equatorial position. The structure of this unexpected intermediate was confirmed in the solid-state using X-ray crystallography. Omission of the pyridine solvent led to dimer formation. Switching the aglycone to an *O-para*-methoxyphenyl enabled smooth C2 inversion to the desired 2-deoxy-2-fluoro D-mannose system, suitably equipped for further anomeric manipulation.

1. Introduction

Fluorinated carbohydrates have proven highly valuable tools for the study of carbohydrate processing enzymes [1]. The large stereo-electronic changes induced in such molecules through the electronegativity of fluorine and the utility of ^{19}F as an NMR reporter have facilitated their widespread development as probes and inhibitors [2–8], and for manipulating glycopolymer properties [9–13]. Fluorinated carbohydrates are not naturally occurring and various approaches to introduce the halogen into requisite building blocks have therefore been developed [14–16]. As part of a wider program targeting the synthesis of mimetic D-mannose and D-mannuronate containing systems [17–22], including fluorinated derivatives, we required synthetic access to an appropriately protected 2-deoxy-2-fluoro-D-manno glycosyl donor. Methods for the synthesis of 2-deoxy-2-fluoro-D-mannose have been developed using a variety of approaches [23,24], including early methods using F_2 and XeF_2 as fluorine sources [25,26]. The most widespread method involves the reaction of an appropriately protected D-glucal with an electrophilic fluorinating agent (commonly Selectfluor®), to afford separable hemi-acetal mixtures of 2-deoxy-2-fluoro-D-mannose and the C2-epimer 2-deoxy-2-fluoro-D-glucose [27–30] (Scheme 1a). The efficiency of this approach, even at the early stage of a target synthesis, is not ideal, with the procedure often taking several days and being further complicated by practical difficulties encountered when separating C2 epimeric hemiacetal mixtures by chromatography, frequently necessitating bringing such compound mixtures through further transformations until separation becomes feasible.

The use of a nucleophilic fluoride source displacing a triflate in an S_N2 reaction has been adapted for the synthesis of many fluorinated carbohydrates, however the use of this approach for the synthesis of 2-deoxy-2-fluoro-D-mannose has been limited to anomeric methyl glycosides [31]. This restricts the immediate tractability of such compounds for the synthesis of glycan targets as it often requires harsh conditions to hydrolyse the *O*-glycoside and access malleable donors. In this work we aimed to develop the synthesis of a tractable 2-deoxy-2-fluoro-D-mannose building block using the triflate inversion approach (Scheme 1b), with the wider aim of providing glycosyl donors for oligosaccharide synthesis. We have developed a similar approach for the synthesis of a 4-SAc modified D-glucose [32].

2. Results and discussion

We initiated our synthesis to install fluorine at C2 of D-mannose as outlined in Scheme 2. Upon consulting the literature, we were unable to

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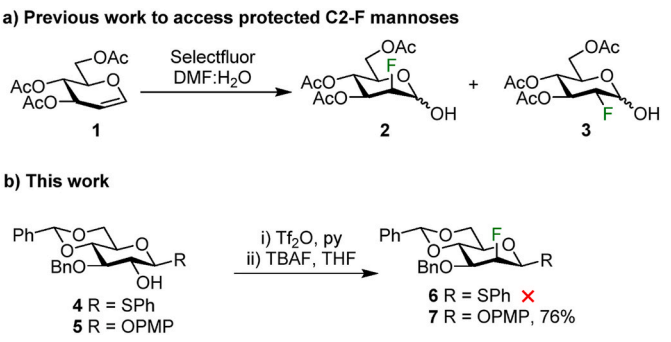


Scheme 1. a) Common glycal functionalisation approach to access D-gluco and D-manno configured C2-fluoro sugars b) This work, targeting C2–F D-mannose using S_N2 inversion from the corresponding C2-D-glucose triflate.

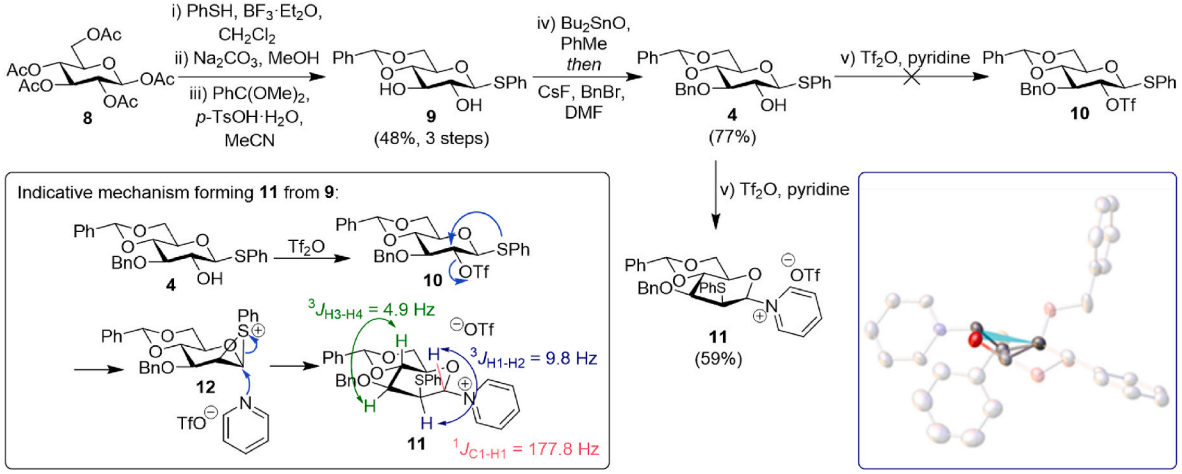
find examples of a direct D-glucose to D-mannose inversion using DAST, although examples for D-mannose to D-glucose are known, alongside other pyranoses [33–35]. Indeed, Crich and colleagues noted that for the synthesis of the α-thioglycoside form of target compound **6**, DAST treatment of the corresponding glucoside failed, producing mixtures of furanoses and elimination compounds [36]. Their material was ultimately accessed *via* the aforementioned glycal chemistry, as compound **6** has been [23]. We envisaged using a two-step inversion of the corresponding glucose thioglycoside *via* a C2 triflate, completing nucleophilic displacement with appropriate fluoride source (e.g., TBAF) to effect a stereocontrolled inversion (see Scheme 1b).

Beginning with commercial glucose penta-*O*-acetate **8**, we installed an anomeric β-thioglycoside and 4,6-*O*-benzylidine acetal using standard transformations, affording C2,C3-diol **9** in 48 % yield over three steps (Scheme 2). A C3 regioselective *O*-benzylation was completed next using tin acetal chemistry [37], affording the desired C2-alcohol **4** in 77 % yield. Overall, the conversion of **8** to **4** required no chromatography and was completed on multigram scale. With alcohol **4** to hand, we treated this material with 2.1 equivalents of Tf_2O using pyridine as solvent. TLC showed complete consumption of **4** after 1 hour and formation of a new spot which remained on the baseline in a 100 % EtOAc TLC solvent system. Following aqueous workup, the resulting off-white solid was recrystallised from EtOH to afford a white crystalline solid in 59 % yield (no other products were isolated). Upon NMR characterisation and inspection of the appropriate scalar coupling constants it became apparent that the desired C2-trilfate **10** had not formed: H1 was observed at δ = 6.18 ppm, significantly downfield of what would be expected for an anomeric thioglycoside. The ^{13}C NMR chemical shift of C2, δ = 51.1 ppm, was different to that expected of carbon bonded to triflate. Whilst the ^3J coupling constant for H1–H2 was indicative of a 1, 2-trans relationship ($^3J_{H1\text{-}H2}$ = 9.8 Hz), the comparative H3–H4 coupling was smaller than expected ($^3J_{H3\text{-}H4}$ = 4.9 Hz), indicating a $^4C_1$ D-mannose conformation was not present. Finally, the $^1J_{C\text{-}H}$ coupling constant (176 Hz) was significantly larger than observed for related β-thioglycosides (~155 Hz).

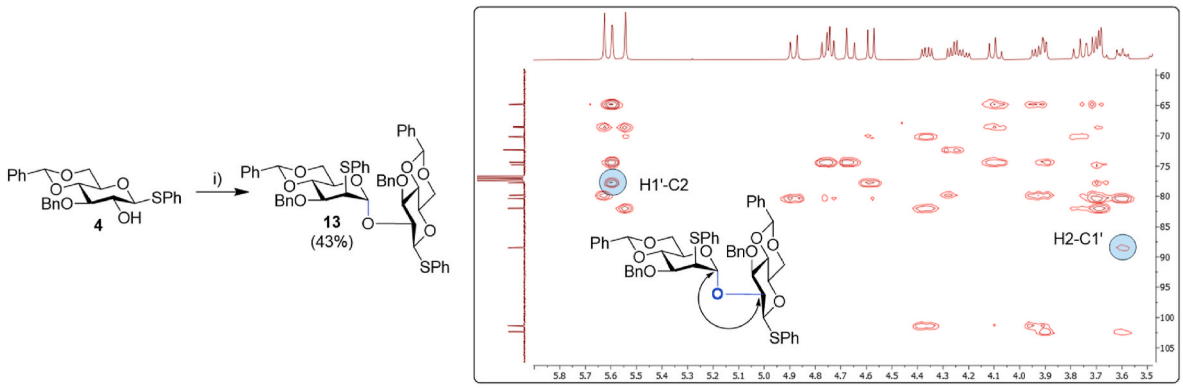
Fortunately, the as yet unidentified product of this reaction was crystalline, and we completed X-Ray diffraction, confirming the structure to be an unusual anomeric pyridinium salt **11**, where the thiophenyl group had migrated to C2 and the D-manno configuration was formed. An indicative mechanism of formation for triflate salt **11** is shown in Scheme 2, alongside the X-Ray crystal structure. Similar 1 → 2 *S*-migrations have been observed in pyranose and furanose systems [36, 38–43], and during C2–OH DAST fluorination of protected D-mannose methyl glycosides [34]. The conformation of **11** in the solid state is unusual, not corresponding to conventional pyranose systems (e.g., $^4C_1$, $^1C_4$). The 4,6-*O*-benzylidene ring retains its expected chair conformation whilst within the pyranose ring C1–O5–C3–C4 appear coplanar in a $B_{2,5}$ conformation. The RMSD (root mean squared deviation) provides a measure of how much each of the component atoms (O5, C1, C3 and C4) in **11** used to generate the plane of the solid-state structure deviate from the best fit plane. The RMSD of the four atoms of the plane is 0.114 Å, whereas the C2-plane distance is 0.642(7) Å and C5-plane distance is 0.617(6) Å.

Despite the anomeric pyridinium group being α-linked and *trans* to the *S*-phenyl group, the ring distortion meant it adopted a pseudo-equatorial orientation. The preference for anomeric cationic nitrogen substituents to adopt an equatorial orientation in pyranoses is well reported and results in $^1C_4$ or $^4C_1$ chair conformations [44–46]. There has been significant debate about the origin of this effect with the existence of a stereoelectronic "reverse anomeric effect" being proposed and disputed [44,47–51]. This effect is now usually rationalised as resulting from steric hindrance to solvation of the positive charge when the cationic substituent is axial [52]. In the case of **11,** ring flip to afford an equatorial pyridinium is prevented by the 4,6-*O*-benzylidene and a pseudo equatorial orientation is instead achieved through the observed $B_{2,5}$ conformation. To the best of our knowledge this is the first disclosure characterising bicyclic system **11** in both solution and solid state.

In order to try to prevent the formation of salt **11**, we changed solvent from pyridine to dichloromethane and repeated the reaction using the same equivalents of Tf_2O, alongside four equivalents of DIPEA as a non-nucleophilic base to neutralise the TfOH formed (Scheme 3). Upon



Scheme 2. Synthesis of C2–OH glucose thioglycoside **4**, attempted triflate formation to form **10** and isolation of pyridinium salt **11** as the reaction product. An indicative mechanism to form **11** from **4** is shown inside the black box. The blue bordered box shows the $B_{2,5}$ solid state structure of **11** with the ring atoms coloured, the remainder paled out for clarity and the O1–C1–C3–C4 plane in blue. The C1–N^+ bond length is 1.483(6) Å and the O5–C1 is 1.406(6) Å.

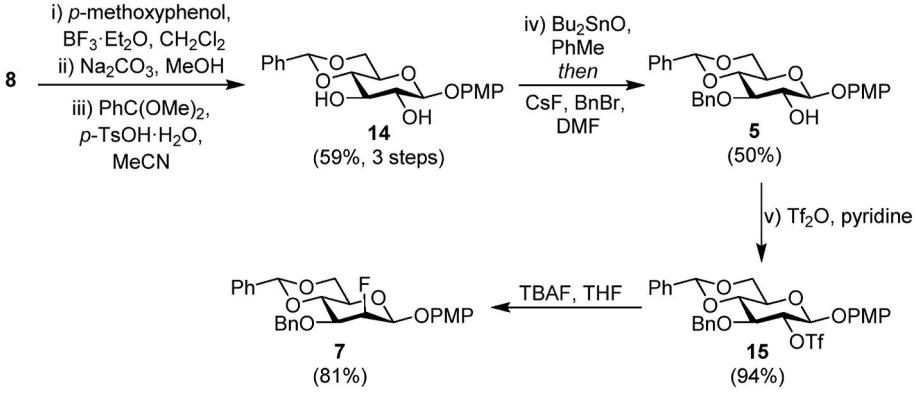


Scheme 3. a) Formation of D-manno-D-gluco dimer **13**. Reaction conditions: i) Tf_2O, DIPEA, CH_2Cl_2 b) HMBC NMR (400 × 100 MHz) highlighting through bond correlations to support assignment of structure.

Table 1
NMR assignment of D-*manno*-D-*gluco* dimer **13**. The β-thioglycoside is denoted as the reducing end sugar.

Ring No.		1	2	3	4	5	6	
δ (ppm)	^{13}C	88.5	77.8	80.3	82.0	70.2	68.5/68.6	
δ (ppm)	^{1}H	4.58	3.65–3.55	3.82–3.64	3.82–3.64	3.46	4.36	3.82–3.64
	Multiplicity	d	m	m	m	dddd	dd	m
	J (Hz)	9.6				9.2, 4.7, 4.7, 4.6	10.5, 5.0	

Ring No.		1′	2′	3′	4′	5′	6′	
δ (ppm)	^{13}C	102.4	55.4	74.4	79.8	64.8	68.5/68.6	
δ (ppm)	^{1}H	5.59	3.90	4.30–4.19	4.09	4.30–4.19	3.93	3.82–3.64
	Multiplicity	d	dd	m	dd	m	dd	m
	J (Hz)	1.3	4.9, 1.6		9.7, 9.7		10.1, 4.8	



Scheme 4. Successful synthesis of C2–F D-mannose glycoside **7**.

workup and isolation of the material we again observed an unexpected product. Using a combination of 1D and 2D NMR alongside HRMS, we assigned the product structure as dimer **13**, indicating that in the absence of pyridine the only available nucleophile to intercept an intermediate of type **12** (Scheme 2) was alcohol **4**. The low yield (43 %) was attributed to formation of several other degradation products which were observable by TLC. Table 1 records a full NMR assignment of dimer **13**, including ^{1}H and ^{13}C NMR chemical shifts and coupling constants. A similar dimerisation reaction with formation of a 1→2-linked disaccharide was previously reported by Roy [53].

Given the migration issue encountered using thioglycoside **4** and an observed competing nucleophilicity towards dimer formation, we switched the aglycone to *para*-methoxyphenyl, thus introducing less nucleophilic oxygen and advocating that this group could later be removed selectively under oxidative conditions (e.g., CAN [37,54]) and then manipulated to an appropriate donor. Accordingly, we returned to compound **8** and completed a similar series of reactions through diol **14** to alcohol **5** (Scheme 4). Upon treatment with Tf_2O compound **5** was smoothly converted to the desired triflate **15** in 94 % yield. The chemical shift of C2 increased significantly to $\delta = 84.1$ ppm (compared to $\delta = 73.6$ ppm in **5**) and a ^{19}F NMR chemical shift was observed at $\delta = -74.1$ ppm, indicative of triflate formation. From here the material was inverted at C2 using TBAF, affording the desired C2–F D-mannose configured glycoside **7** in 81 % yield. ^{19}F NMR showed the presence of a new chemical shift at $\delta = -218.3$ ppm and loss of triflate. C2 was a doublet with a large coupling constant of 191.4 Hz, typical of geminal C–F coupling, whilst C3 was also a doublet with a smaller coupling constant (16.9 Hz). This route to fluorinated D-mannoside **7** proved scalable, with 10 g quantities prepared routinely.

3. Conclusion

During the development of a synthesis towards a 2-deoxy-2-fluoro-D-mannose donor using nucleophilic substitution of an appropriate triflate

with fluoride we observed and characterised an unexpected 1,2-SPh migration product, in the form of an anomeric pyridinium triflate salt. X-Ray crystallographic analysis of this material confirmed an unusual pyranose conformation where the endocyclic oxygen and anomeric carbon are above a plane constituted by the remaining pyranose ring carbons. The distortion from the expected chair conformation enables the anomeric pyridinium to adopt a pseudo equatorial position on the lower face of the ring, *trans* to the migrated SPh group at C2. Modifying the anomeric substituent to an *O*-*para*-methoxyphenyl group enables efficient synthesis of the desired 2-deoxy-2-fluoro-D-mannose-*O*-glycoside in six steps and 22 % overall yield from commercial material.

CRediT authorship contribution statement

Sean T. Evans: Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Graham J. Tizzard:** Formal analysis, Data curation. **Robert A. Field:** Writing – review & editing, Supervision, Funding acquisition. **Gavin J. Miller:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Attached SI file

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carres.2024.109275.

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