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Synthesis of glycosyl fluorides from thio-, seleno-, and telluroglycosides and glycosyl sulfoxides using aminodifluorosulfinium tetrafluoroborates

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ABSTRACT

Glycosyl fluorides can be synthesized from thio-, seleno-, and telluroglycosides and glycosyl sulfoxides using the aminodifluorosulfinium tetrafluoroborate reagents Xtalfluor-E and -M, with or without added N-bromosuccinimide. Mechanistic studies provide evidence that fluoride is delivered from the tetrafluoroborate counterion.

1. Introduction

Glycosyl fluorides are useful substrates for glycoside hydrolases and glycosyltransferases.[1] They have been used for rate measurement of enzyme-catalyzed reactions through the ability to monitor the release of fluoride ion with fluoride-ion-selective electrodes[2] or fluoride-specific colorimetric reagents.[3–5] Glycosyl fluorides are also useful intermediates in the synthesis of glycoconjugates using either enzymes (e.g., glycoside hydrolase-catalyzed transglycosylation,[6] or using glycosynthases,[7,8] or glycosyltransferases[9]) or chemical approaches with a range of fluorophilic promoters such as $SnCl_2$–AgOTf, $BF_3{\cdot}Et_2O$, Cp_2ZrCl_2 and $Yb(OTf)_3$.[10]

The synthesis of glycosyl fluorides can be achieved by various approaches,[11] including direct displacement reactions of glycosyl halides (typically bromides and chlorides) with for example, AgF,[12] $AgBF_4$[13] or ZnF_2.[14] Alternatively, glycosyl acetates can be converted to glycosyl fluorides using anhydrous HF[15] or HF·pyridine[16] complex. Deoxofluorination reagents such as diethylaminosulfur trifluoride (DAST),[17,18] and more recently the newly introduced Xtalfluor reagents (vide infra),[19–21] and fluolead[22] may be used to convert otherwise protected sugar hemiacetals to glycosyl fluorides (Fig. 1). Limitations apply to anhydrous HF, which can cleave interglycosidic bonds,[23] and many glycosyl bromides and chlorides cannot be easily obtained. Moreover, HF·pyridine, DAST and fluolead are moisture-sensitive reagents that require plastic reaction flasks owing to the release of highly reactive HF.

Nicolaou reported that thioglycosides can be converted to glycosyl fluorides upon treatment with DAST, with the process being accelerated by the inclusion of stoichiometric N-bromosuccinimide.[24] Selenoglycosides and telluroglycosides are also effective substrates.[25,26] DAST is a moisture-sensitive liquid that is thermally unstable and corrosive, requiring the use of non-glass reaction vessels.[27] Couturier and co-workers have introduced the thermally-stable aminodifluorosulfinium tetrafluoroborates Xtalfluor-E and Xtalfluor-M, which are crystalline solids with good moisture stability and low hygrophilicity, and can be used for deoxofluorination of alcohols and hemiacetals in borosilicate glassware (Fig. 1).[19,20] Aminodifluorosulfinium salts are stronger electrophiles than DAST and consequently react rapidly with nucleophiles. However, unlike DAST they do not release fluoride ion and so require the addition of either exogenous fluoride sources such as $Et_3N{\cdot}3HF$ or $Et_3N{\cdot}2HF$, or strong, non-nucleophilic

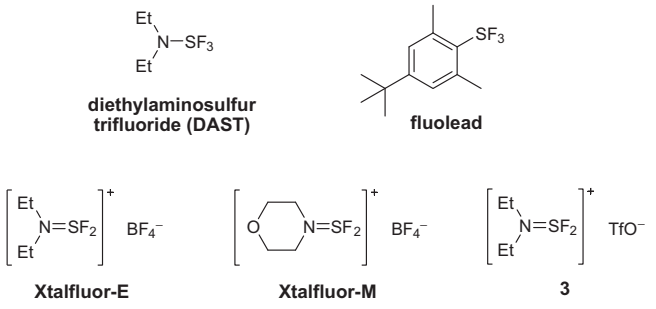

Figure 1. Fluorinating reagents.

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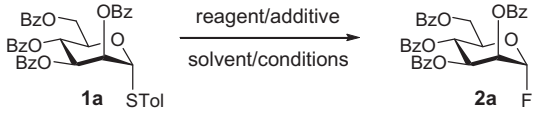
Table 1
Investigation of the reaction of aryl thiomannoside **1a** with diethylaminodifluorosulfinium reagents



Entry	Reagent	Additive	Solvent/conditions	Yield (%)
1	DAST	NBS	CH_2Cl_2, 0 °C to rt 18 h	62
2	XtalF-E		CH_2Cl_2, 0 °C to rt 18 h	nr
3	XtalF-E	NBS	CH_2Cl_2, 0 °C to rt 18 h	80
4	XtalF-E		CH_2Cl_2, reflux, 18 h	81
5	XtalF-E		DCE, reflux, 15 min	90
6	XtalF-M		DCE, reflux, 15 min	84
7	$Et_2N = SF_2OTf$ (**3**)	—	DCE, reflux, 18 h	nr
8	$Et_2N = SF_2OTf$ (**3**)	Bu_4NBF_4	DCE, reflux, 15 min	83

bases such as DBU, to prevent unwanted side-reactions.[20] Given the drawbacks in the use of DAST for fluorination reactions of thioglycosides, we sought to examine the use of aminodifluorosulfinium reagents for this purpose.

2. Results and discussion

Initially, we investigated the fluorination of the aryl thiomannoside **1a** (Table 1). To set a benchmark for comparison, we investigated the transformation of **1a**–**2a** using DAST in the presence of 1.5 equiv NBS (entry 1, 62%). Xtalfluor-E was unreactive at room temperature (entry 2), but in the presence of NBS gave a smooth conversion to **2a** in good yield (entry 3, 80%). In the absence of NBS, 18 h of reflux was required when using CH_2Cl_2 (bp 40 °C) but upon switching to the higher boiling solvent 1,2-dichloroethane (DCE, bp 84 °C), the reaction was complete within 15 min (entries 4 and 5). A similar yield was obtained using Xtalfluor-M (entry 6).

Reactions of alcohols with Xtalfluor-reagents have been described as 'fluoride-starved',[20] as addition of a nucleophile to the dialkylaminodifluorosulfinium ion does not result in the release of fluoride ion, in contrast to nucleophilic substitution reactions of DAST. Consequently, addition of exogenous fluoride sources can improve yields in deoxofluorinations with Xtalfluor-reagents. In the case of Table 1, entries 5 and 6, excellent yields are achieved without the need for additional fluoride. Conceivably, the reactive fluoride that is ultimately found in the product might arise from addition products of dialkylaminodifluorosulfinium ion, or might arise from the tetrafluoroborate anion, which can act as a fluoride ion source.[13] We probed the source of fluorine in the product through the preparation of diethylaminodifluorosulfinium triflate (**3**),[20] which does not possess a counterion that can release fluoride. Treatment of **1a** with **3** for prolonged periods did not result in the formation of product (entry 7); however, addition of Bu_4NBF_4 resulted in an excellent yield of **2a**, providing evidence that the tetrafluoroborate counterion is the source of fluoride. This result is reminiscent of the Xtalfluor-E activation of *N*-alkylprolinols, which in the presence of tetrabutylammonium azide undergo ring expansion to 3-azidopiperidines.[28]

We next explored the scope of the transformation. As shown in Table 2, a range of thioglycosides could be converted to glycosyl fluorides. In every case the α-anomer was the sole isomer isolated. Entries 1–4 show that acetylated or benzoylated aryl thioglycosides of various configurations are cleanly converted to the corresponding α-glycosyl fluoride. Entry 5 shows that an alkyl thioglycoside is also converted to the corresponding α-glycosyl fluoride. Entries 6 and 7 show the conditions are compatible with benzyl ethers affording **2g** (75%) and benzylidene acetals to afford **2h** (45%), although yields are somewhat compromised. In both of these cases, the reactions were very rapid even in refluxing dichloromethane, and close monitoring of the reaction was necessary to prevent decomposition of the product upon extended heating. An attempt to fluorinate **1g** using Xtalfluor-E and NBS at 0 °C led to a reduced yield of **2g** (40%) and also resulted in the isolation of the corresponding bromide (see footnote b). This result implies that the corresponding bromide may be an intermediate in the NBS-promoted reaction, and under the mild reaction conditions the 'fluoride-starved' nature of the Xtalfluor reagent does not provide sufficient free fluoride ion to complete the reaction. Entry 8 shows that the isopropylidene-protected thioglycoside **1i** can be converted to the corresponding glycosyl fluoride **2i** in good yield. The β-cellobiosyl disaccharide **1j** was converted to the cellobiosyl fluoride **2j** in excellent yield (entry 9). Finally, the glucosyl-mannoside **1k** (entry 10) was converted to the corresponding fluoride **2k** in 45% yield, somewhat lower than optimized conditions recently reported using DAST/NBS (63%).[29]

Caddick et al. reported that selenoglycosides can be converted to glycosyl fluorides in moderate yields using 4-methyl(difluoroiodo)benzene.[30] DAST in combination with NBS or NIS is more effective and converts both seleno- and tellurogycosides to α-linked glycosyl fluorides in good yields.[25] Xtalfluor-E in dichloroethane also proved an effective reagent and converted selenoglycoside **1l** and telluroglycoside **1m** smoothly to the corresponding glycosyl fluorides under the conditions established for thioglycosides (Table 3, entries 1 and 2).

Mechanistic investigations have suggested that alcohols add rapidly to aminodifluorosulfinium ions, and thus that these represent potent electrophiles.[20] Accordingly, we wondered whether it might be possible to convert glycosyl sulfoxides to glycosyl fluorides. Treatment of aryl and alkyl glycosyl sulfoxides **1n** and **1o** with Xtalfluor-E afforded the corresponding glycosyl fluorides in excellent yields (Table 3, entries 3 and 4). This reaction presumably proceeds by addition of the sulfoxide oxygen to the aminodifluorosulfinium ion and thus bears some similarity to the activation of glycosyl sulfoxides with triflic anhydride as in the Kahne glycosylation.[31]

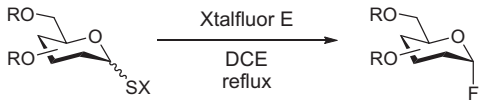
In conclusion, Xtalfluor-E and M represent convenient alternatives to DAST and DAST/NBS for the conversion of acylated thio-, seleno- and telluroglycosides to α-glycosyl fluorides. The reaction occurs rapidly at ambient conditions in the presence of NBS, but conveniently can be performed in its absence at reflux in dichloroethane. Somewhat lower yields were obtained for benzyl- and benzylidene-protected substrates, which may relate to the lower stability of the resulting 'armed'[32] glycosyl fluorides under the reaction conditions. Interestingly, glycosyl sulfoxides could be converted to glycosyl fluorides, a transformation that has received only scant attention using DAST.[33] Mechanistic studies reveal that the fluorine found in the product derives from the tetrafluoroborate counterion, revealing additional complexity in the reactivity of these promising new nucleophilic fluorination reagents.[34–36]

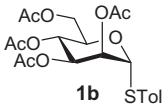
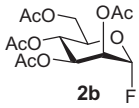
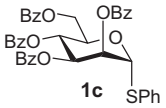
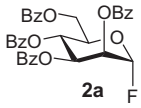
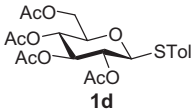
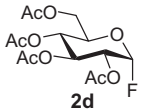
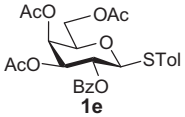
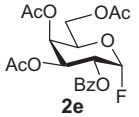
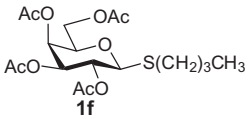
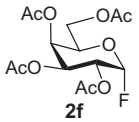
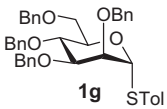
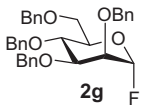
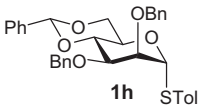
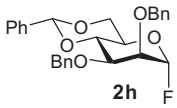
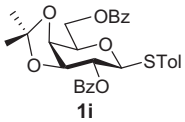
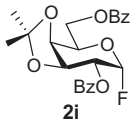
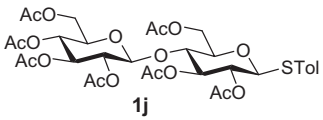
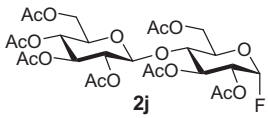
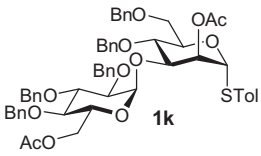
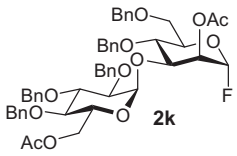
3. Experimental section

3.1. General methods

All reactions were performed under a nitrogen atmosphere. Dichloromethane was dried over alumina according to the method of Pangborn and co-workers.[37] 1,2-Dichloroethane (DCE) was used as received. Petroleum spirits refer to the fraction boiling at 40–60 °C. Reactions were monitored by TLC analysis (pre-coated Silica Gel 60 F_{254} plates, 250 μm layer thickness on aluminum) and

Table 2
Conversion of thioglycosides to glycosyl fluorides with Xtalfluor-E

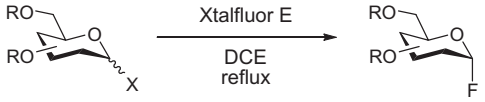


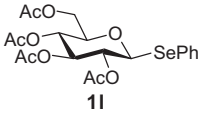
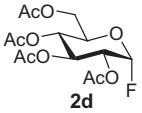
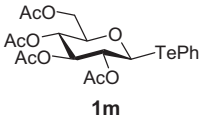
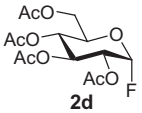
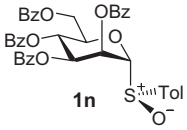
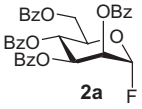
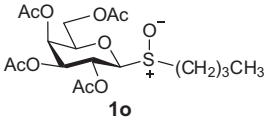
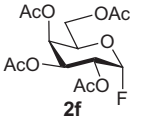
Entry	Substrate	Product	Time	Yield (%)
1	 **1b**	 **2b**	30 min	94
2	 **1c**	 **2a**	15 min	84
3	 **1d**	 **2d**	15 min	95
4	 **1e**	 **2e**	15 min	84
5	 **1f**	 **2f**	15 min	86
6	 **1g**	 **2g**	30 min[a]	75 (40)[b]
7	 **1h**	 **2h**	15 min[a]	45
8	 **1i**	 **2i**	15 min	85
9	 **1j**	 **2j**	30 min	87
10	 **1k**	 **2k**	2 h[a]	45 (63%)[c]

[a] The reaction was performed in refluxing CH_2Cl_2.
[b] Yield obtained using Xtalfluor-E (1.5 equiv), NBS (1.5 equiv), CH_2Cl_2 at 0 °C. 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl bromide was also isolated in 18% yield.
[c] Yield obtained using DAST (1.5 equiv), NBS (1.5 equiv), CH_2Cl_2, rt, 16 h.[29]

visualized with a 254 nm UV light and/or by staining with CAM solution (5 g of cerium sulfate, 25 g of ammonium molybdate, 50 mL of concd H_2SO_4, and 450 mL of H_2O). Flash chromatography was performed according to the method of Still et al.[38] ^1H NMR spectra were obtained on Varian instruments at 400 MHz or 500 MHz in $CDCl_3$. Chemical shifts are reported in parts per million with the residual solvent peak used as an internal standard. NMR spectra are tabulated as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br s = broad singlet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, tt = triplet of triplet), number of protons, and coupling constant(s). ^{13}C NMR spectra were measured at 100 or 125 MHz. IR spectra were obtained on a Perkin–Elmer Spectrum One FTIR spectrometer with a zinc selenide/diamond Universal ATR sampling accessory as a thin film. Xtalfluor-E and M were purchased from Sigma Aldrich.

Table 3
Conversion of seleno- and telluroglycosides, and glycosyl sulfoxides to glycosyl fluorides with Xtalfluor-E



Entry	Substrate	Product	Time	Yield (%)
1	 **1l**	 **2d**	30 min	83
2	 **1m**	 **2d**	15 min	79
3	 **1n**	 **2a**	1 h	85
4	 **1o**	 **2f**	15 min	93

3.2. Investigation of fluorination reactions of 1a to afford 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl fluoride (2a)

3.2.1. Xtalfluor-E and NBS

A solution of 4-methylphenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside **1a**[39] (182 mg, 0.259 mmol) in CH_2Cl_2 (2.5 mL) at 0 °C was treated with Xtalfluor-E (84 mg, 0.37 mmol) and NBS (69 mg, 0.39 mmol). The resulting mixture was allowed to warm to rt for 18 h, then was quenched with satd $NaHCO_3$ (1 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and the organic phase was washed with brine (5 mL), dried ($MgSO_4$), and concentrated. The crude residue was purified by flash chromatography to give fluoride **2a** (124 mg, 80%) as a fluffy white material: $[\alpha]_D^{24}$ −86.2 (*c* 1.5, $CHCl_3$; lit.[40] −86.2°); ^{1}H NMR (500 MHz): δ 8.12–8.10 (m, 2H, Ph), 8.03–8.01 (m, 2H, Ph), 7.95–7.93 (m, 2H, Ph), 7.84–7.82 (m, 2H, Ph), 7.61–7.56 (m, 2H, Ph), 7.52–7.49 (m, 2H, Ph), 7.44–7.34 (m, 2H, Ph), 7.28–7.24 (m, 2H, Ph), 6.20 (t, $J_{3,4} = J_{4,5}$ 10.0 Hz, 1H, H4), 5.93–5.90 (m, 1H, H3), 5.87 (dd, $J_{1,2}$ 1.5, $J_{1,F}$ 48.8 Hz, 1H, H1), 5.86 (dd, $J_{1,2}$ 2.0, $J_{2,3}$ 3.2 Hz, 1H, H2), 4.76 (dd, $J_{5,6}$ 2.4, $J_{6,6}$ 12.4 Hz, 1H, H6a), 4.60 (ddd, $J_{4,5}$ 2.4, $J_{5,6}$ 2.4, 3.6 Hz, 1H, H5), 4.48 (dd, $J_{5,6}$ 3.6, $J_{6,6}$ 12.5 Hz, 1H, H6b); ^{13}C (125 MHz): δ 166.2, 165.5, 165.4, 165.2 (4C, C=O), 133.9, 133.7, 133.5, 133.3, 130.0, 129.9, 128.9, 128.8, 128.6, 128.5, 128.4, 105.1 (d, $J_{C,F}$ 212 Hz, 1C, C1), 71.3, 69.3, 68.9, 68.5, 65.9, 62.0. The spectral data were in agreement with those reported.[41]

3.2.2. DAST and NBS

According to Section 3.2.1, 4-methylphenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside **1a**[39] (182 mg, 0.259 mmol) in CH_2Cl_2 (2.5 mL) at 0 °C was treated with DAST (40 μL, 0.406 mmol) and NBS (69 mg, 0.39 mmol). The resulting mixture was allowed to react at rt for 18 h. Workup and flash chromatography gave fluoride **2a** (125 mg, 62%) as a fluffy white material.

3.2.3. Xtalfluor-M

According to Section 3.2.1, 4-methylphenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside **1a**[39] (175 mg, 0.249 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-M (95 mg, 0.39 mmol) at reflux for 15 min. Workup and flash chromatography gave fluoride **2a** (125 mg, 84%) as a fluffy white material.

3.2.4. DAST-OTf salt + Bu_4NBF_4

According to Section 3.2.1, 4-methylphenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside **1a**[39] (176 mg, 0.249 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with $Et_2NSF_2{\cdot}OTf$ **3**[20] (118 mg, 0.405 mmol) followed by Bu_4NBF_4 (124 mg, 0.377) at reflux for 15 min. Workup and flash chromatography gave fluoride **2a** (124 mg, 83%) as a fluffy white material.

3.3. General procedure for Xtalfluor-E fluorination

Xtalfluor-E or M (1.5 equiv) were added to a solution of thio-, seleno-, telluroglycoside or glycosyl sulfoxide (0.1 mmol) in CH_2Cl_2 or $(ClCH_2)_2$ (1 mL). The mixture was heated at reflux, then cooled to rt and quenched with satd $NaHCO_3$ (1 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and the organic phase was washed with brine (5 mL), dried ($MgSO_4$), and concentrated. The crude residue was purified by flash chromatography to give glycosyl fluoride.

3.3.1. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl fluoride (2a)

(i) According to Section 3.3, 4-methylphenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside **1a**[39] (181 mg, 0.258 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (84 mg, 0.367 mmol) at reflux for 15 min to give fluoride **2a** (138 mg, 90%) as a fluffy white material.

(ii) According to Section 3.3, phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside **1c**[42] (173 mg, 0.251 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (89 mg, 0.389 mmol) at reflux for 15 min to give fluoride **2a** (126 mg, 84%) as a fluffy white material.

(iii) According to the general procedure, tolyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside $(R)_S$-S-oxide **1n** (see Section 3.3.11) (150 mg, 0.209 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (83 mg, 0.362 mmol) at reflux for 1 h to give fluoride **2a** (106 mg, 85%) as a fluffy white material.

3.3.2. 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl fluoride (2b)

According to Section 3.3, 4-methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside **1b**[43] (103 mg, 0.227 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (82 mg, 0.36 mmol) at reflux for 30 min to give fluoride **2b** (76 mg, 96%) as colorless oil: $[\alpha]_D^{22}$ +17.1 (*c* 1.5, $CHCl_3$; lit.[44] +22°); ^{1}H NMR (500 MHz): δ 5.56 (dd, $J_{1,2}$ 2.0, $J_{1,F}$ 48.5 Hz, 1H, H1), 5.39–5.33 (m, 3H, H2,3,4), 4.28 (dd, $J_{6,6}$ 16.0, $J_{5,6}$ 5.5 Hz, 1H, H6a), 4.18 (dd, $J_{5,6}$ 3.0, $J_{6,6}$ 16.0, 1H, H6b), 4.19–4.13 (m, 1H, H5), 2.17 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H); ^{13}C (125 MHz): δ 170.7, 169.8, 169.8, 169.7 (4C, C=O), 104.9 (d, $J_{C,F}$ 222 Hz, 1C, C1), 71.0, 68.3, 68.0, 67.7, 65.2, 62.0, 20.8, 20.8, 20.7. The spectral data were in agreement with those reported.[30]

3.3.3. 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl fluoride (2d)

(i) According to Section 3.3, 4-methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside **1d** (103 mg, 0.227 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (84 mg, 0.367 mmol) at reflux for 15 min to give fluoride **2d** (75 mg, 95%) as a pale yellow oil.

(ii) According to the general procedure, phenyl 2,3,4,6-tetra-*O*-acetyl-1-seleno-β-D-glucopyranoside **1l**[45] (126 mg, 0.259 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (84 mg, 0.367 mmol) at reflux for 30 min to give fluoride **2d** (75 mg, 83%).

(iii) According to the general procedure, phenyl 2,3,4,6-tetra-*O*-acetyl-1-telluro-β-D-glucopyranoside **1m**[45] (45 mg, 0.084 mmol) in $(ClCH_2)_2$ (1.2 mL) was treated with Xtalfluor-E (32 mg, 0.139 mmol) at reflux for 15 min to give fluoride **2d** (25 mg, 86%): $[\alpha]_D^{24}$ +82.9 (*c* 1.5, $CHCl_3$; lit.[44] +80°); ^{1}H NMR (500 MHz): δ 5.73 (dd, $J_{1,2}$ 2.0, $J_{1,F}$ 53.0 Hz, 1H, H1), 5.48 (dd, $J_{2,3}$ 10.0, $J_{3,4}$ 9.5 Hz, 1H, H3), 5.14 (dd, $J_{4,5}$ 10.0, $J_{3,4}$ 9.5 Hz, 1H, H4), 4.93 (dddd, $J_{1,2}$ 2.5, $J_{2,3}$ 10.0, $J_{2,F}$ 24.0 Hz, 1H, H2), 4.27 (dd, $J_{6,6}$ 12.5, $J_{5,6}$ 5.0 Hz, 1H, H6a), 4.18 (ddd, $J_{4,5}$ 10, $J_{5,6}$ 4.0, 2.5 Hz, 1H, H5), 4.14 (dd, $J_{5,6}$ 2.5, $J_{6,6}$ 12.5 Hz, 1H, H6b), 2.09, 2.09, 2.03, 2.01 (4s, 12H, Ac); ^{13}C (125 MHz): δ 170.6, 170.1, 170.0, 169.5 (4C, C=O), 103.9 (d, $J_{C,F}$ 225 Hz, 1C, C1), 77.4, 77.1, 76.9, 70.4, 70.2, 69.9, 69.9, 69.5, 67.5, 61.3, 20.8, 20.7, 20.6. The spectral data were in agreement with those reported.[30]

3.3.4. 3,4,6-Tri-*O*-acetyl-2-*O*-benzoyl-α-D-galactopyranosyl fluoride (2e)

According to Section 3.3, 4-methylphenyl 3,4,6-tri-*O*-acetyl-2-*O*-benzoyl-1-thio-β-D-galactopyranoside **1e**[46] (129 mg, 0.250 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (83 mg, 0.362 mmol) at reflux for 15 min to give fluoride **2e** (86 mg, 84%) as a white solid: $[\alpha]_D^{25}$ +128.7 (*c* 1.15, $CHCl_3$); IR ν 1750, 1370, 1230, 1162, 1112, 1073, 1049 cm^{-1}; ^{1}H NMR (500 MHz): δ 8.03–8.01 (m, 2H, Ph), 7.61–7.58 (m, 1H, Ph), 7.45 (t, *J* 8.0 Hz, 2H, Ph), 5.92 (dd, $J_{1,2}$ 2.5, $J_{1,F}$ 53.5 Hz, 1H, H1), 5.60–5.57 (m, 2H, H3,4), 5.46–5.39 (m, 1H, H2), 4.47 (t, $J_{5,6}$ = $J_{5,6}$ 6.5 Hz, 1H, H5), 4.21–4.13 (m, 2H, H6a,6b), 2.17, 2.07, 1.95 (3s, 9H, Ac); ^{13}C (125 MHz): δ 170.4, 170.1, 170.0 (3C, CH_3CO), 165.9 (1C, PhCO), 133.9, 130.0, 128.9, 104.6 (d, $J_{C,F}$ 225 Hz, 1C, C1), 69.2, 69.1, 68.2, 68.0, 67.6, 67.1, 61.4, 20.8, 20.7, 20.7; HRMS (ESI) *m/z* calcd for $C_{19}H_{21}FO_9Na$ $[M+Na]^+$ 435.1067, found 435.1064.

3.3.5. 2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl fluoride (2f)

(i) According to Section 3.3, butyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside **1f**[47] (104 mg, 0.247 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (89 mg, 0.389 mmol) at reflux for 30 min to give fluoride **2f** (79 mg, 86%) as a clear oil.

(ii) According to the general procedure, butyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-galactopyranoside S-oxide **1o** (109 mg, 0.250 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (86 mg, 0.38 mmol) at reflux for 15 min to give fluoride **2f** (83 mg, 93%): $[\alpha]_D^{23}$ +94.6 (*c* 1.5, $CHCl_3$; lit.[44] +96°); ^{1}H NMR (500 MHz): δ 5.78 (dd, $J_{1,2}$ 3.0, $J_{1,F}$ 53.5 Hz, 1H, H1), 5.51 (dd, $J_{3,4}$ 3.5, $J_{4,5}$ 1.5 Hz, 1H, H4), 5.34 (dd, $J_{2,3}$ 11.0, $J_{3,4}$ 3.5 Hz, 1H, H3), 5.16 (ddd, $J_{2,3}$ 11.0, $J_{1,2}$ 2.5, $J_{2,F}$ 23.5 Hz, 1H, H2), 4.40 (dt, $J_{5,6}$ 7.0, 7.0, $J_{4,5}$ 1.5 Hz, 1H, H5), 4.17–4.09 (m, 2H, H6a,6b), 2.15, 2.11, 2.03, 2.00 (4s, 12H, Ac); ^{13}C (125 MHz): δ 170.4, 170.3, 170.1, 170.0 (4C, C=O), 104.4 (d, $J_{C,F}$ 225 Hz, 1C, C1), 69.0, 69.0, 67.6, 67.5, 67.1, 61.4, 20.8, 20.7. The spectral data were in agreement with those reported.[44]

3.3.6. 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl fluoride (2g)

According to Section 3.3, 4-methylphenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyranoside **1g**[48] (153 mg, 0.237 mmol) in CH_2Cl_2 (2.5 mL) was treated with Xtalfluor-E (84 mg, 0.37 mmol) at reflux for 60 min to give fluoride **2g** (97 mg, 75%) as a clear oil: $[\alpha]_D^{26}$ +29.1 (*c* 1.1, $CHCl_3$; lit.[49] +25.9°); ^{1}H NMR (500 MHz): δ 7.37–7.27 (m, 17H, Ph), 7.18–7.16 (m, 2H, Ph), 5.59 (dd, $J_{1,2}$ 1.6, $J_{1,F}$ 50.8 Hz, 1H, H1), 4.86 (d, *J* 10.8 Hz, 1H, benzyl-CH), 4.79 (d, *J* 12.0 Hz, 1H, benzyl-CH), 4.71–4.62 (m, 4H, benzyl-CH), 4.51–4.57 (m, 2H, benzyl-CH), 4.08 (t, *J* 9.5 Hz, 1H, H4), 3.93–3.86 (m, 3H, H2,3,5), 3.77 (dd, $J_{6,6}$ 10.8, $J_{5,6}$ 5.5 Hz, 1H, H6a), 3.71 (dd, $J_{6,6}$ 10.8, $J_{5,6}$ 2.4 Hz, 1H, H6b); ^{13}C (125 MHz): δ 138.3, 138.3, 138.0, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 106.6 (d, $J_{C,F}$ 275 Hz, 1C, C1), 79.3, 75.3, 74.3, 74.2, 73.8, 73.6, 73.5, 73.4, 72.7, 68.8. The spectral data were in agreement with those reported.[41]

3.3.7. 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl fluoride (2h)

According to Section 3.3, 4-methylphenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside **1h**[50] (150 mg, 0.270 mmol) in CH_2Cl_2 (2.5 mL) was treated with Xtalfluor-E (89 mg, 0.39 mmol) at reflux for 60 min to give fluoride **2h** (55 mg, 46%) as a clear oil: $[\alpha]_D^{26}$ +10.8 (*c* 0.5, $CHCl_3$; lit.[51] +13°); ^{1}H NMR (500 MHz): δ 7.52–7.50 (m, 2H, Ph), 7.41–7.28 (m, 12H, Ph), 5.66 (s, 1H, benzylidene-CH), 5.50 (dd, $J_{1,2}$ 1.5, $J_{1,F}$ 49.5 Hz, 1H, H1), 4.88 (d, *J* 12.0 Hz, 2H, benzyl-CH), 4.73 (d, *J* 12.0 Hz, 1H, benzyl-CH), 4.71 (d, *J* 11.5 Hz, 1H, benzyl-CH), 4.31 (dd, $J_{5,6}$ 4.5, $J_{6,6}$ 10.0 Hz, 1H, H6), 4.40 (dd, $J_{3,4}$ = $J_{4,5}$ 9.5 Hz, 1H, H4), 3.99–3.92 (m, 3H, H2,3,5), 3.87 (dd, $J_{5,6}$ 10.5, $J_{6,6}$ 10.0 Hz, 1H); ^{13}C (125 MHz): δ 138.5, 137.7, 137.5, 129.1, 128.7, 128.5, 128.4, 128.3, 128.2, 127.8, 127.7, 126.2, 107.2 (d, $J_{C,F}$ 225 Hz, 1C, C1), 101.8, 78.5, 75.7, 75.2, 74.9, 74.4, 73.6, 68.5, 66.3, 66.3. The spectral data were in agreement with those reported.[51]

3.3.8. 2,6-Di-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-galactopyranosyl fluoride (2i)

According to Section 3.3, 4-methylphenyl 2,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside **1i**[52] (125 mg, 0.234 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (89 mg, 0.39 mmol) at reflux for 15 min to give fluoride **2i** (86 mg, 85%) as a white solid: $[\alpha]_D^{23}$ +75.6 (*c* 1.15, $CHCl_3$); IR (CH_2Cl_2) *ν* 1723, 1452, 1267, 1170, 1110, 1072, 709 cm^{-1}; ^1H NMR (500 MHz): *δ* 8.10–8.08 (m, 4H, Ph), 7.61–7.56 (m, 2H, Ph), 7.47–7.44 (m, 2H, Ph), 5.83 (dd, $J_{1,2}$ 3.0, $J_{1,F}$ 53.5 Hz, 1H, H1), 5.20 (ddd, $J_{2,F}$ 23.6, $J_{1,2}$ 3.0, $J_{2,3}$ 7.2 Hz, 1H, H2), 4.71–4.60 (m, 4H, H3,5,6a,6b), 4.45 (d, *J* 5.2 Hz, 1H, H4), 1.58, 1.39 (2s, 6H, CMe_2); ^{13}C (125 MHz): *δ* 166.5, 165.9, 133.7, 133.4, 130.1, 129.9, 129.3, 128.6, 128.6, 110.8, 104.6 (d, $J_{C,F}$ 225 Hz, 1C, C1), 73.0, 70.9, 70.7, 68.6, 68.6, 63.8, 27.8, 26.3 (2C, CMe_2); HRMS (ESI) *m/z* calcd for $C_{23}H_{24}FO_7$ $[M+H]^+$ 431.1506, found 431.1495.

3.3.9. Hepta-*O*-acetyl-α-cellobiosyl fluoride (2j)

According to Section 3.3, 4-methylphenyl hepta-*O*-acetyl-1-thio-β-cellobioside **1j**[53] (165 mg, 0.222 mmol) in $(ClCH_2)_2$ (2.5 mL) was treated with Xtalfluor-E (81 mg, 0.35 mmol) at reflux for 30 min to give fluoride **2j** (123 mg, 87%) as a white solid: $[\alpha]_D^{23}$ +34.2 (*c* 0.42, $CHCl_3$; lit.[54] +30.6°); ^1H NMR (500 MHz): *δ* 5.65 (dd, $J_{1,2}$ 3.0, $J_{1,F}$ 53.5 Hz, 1H, H1), 5.45 (dd, $J_{2,3}$ = $J_{3,4}$ 10.0 Hz, 1H, H3), 5.14 (dd, *J* 9.0, 9.5 Hz, 1H, H3′/4′), 5.05 (dd, *J* 9.5, 10.0 Hz, 1H, H3′/4′), 4.92 (dd, $J_{1,2}$ 8.0, $J_{2,3}$ 9.5 Hz, 1H, H2′), 4.86 (ddd, $J_{2,F}$ 24.0, $J_{1,2}$ 3.0, $J_{2,3}$ 10.0 Hz, 1H, H2), 4.55–4.52 (m, 1H, H6a), 5.53 (d, $J_{1,2}$ 8.0 Hz, 1H, H1′), 4.34 (dd, $J_{6,6}$ 12.5, $J_{5,6}$ 4.5 Hz, 1H, H6′a), 4.13 (dd, $J_{6,6}$ 12.5, $J_{5,6}$ 4.5 Hz, 1H, H6b), 4.09 (dd, $J_{4,5}$ 10.0, $J_{5,6}$ 1.5, 4.0 Hz, 1H, H5), 4.04 (dd, $J_{6,6}$ 12.5, $J_{5,6}$ 2.0 Hz, 1H, H6′b), 3.82 (dd, $J_{3,4}$ = $J_{4,5}$ 10.0 Hz, 1H, H4), 3.66 (ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 2.0, 4.5 Hz, 1H, H5′), 2.13, 2.08, 2.07, 2.03, 2.02, 2.00, 1.97 (7s, 21H, Ac); ^{13}C (125 MHz): *δ* 170.6, 170.3, 170.3, 170.3, 169.6, 169.4, 169.0, 103.8 (d, $J_{C,F}$ 225 Hz, 1C, C1), 100.6, 75.5, 73.0, 72.2, 71.7, 70.8, 70.8, 70.6, 70.4, 68.9, 68.0, 61.8, 61.3, 20.9, 20.7, 20.7, 20.6, 20.6. The spectral data were in agreement with those reported.[54]

3.3.10. 2-*O*-Acetyl-3-*O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-di-*O*-benzyl-α-D-mannopyranosyl fluoride (2k)

According to Section 3.3, 4-methylphenyl 2-*O*-acetyl-3-*O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-4,6-di-*O*-benzyl-1-thio-α-D-mannopyranoside **1k**[29] (41 mg, 0.042 mmol) in CH_2Cl_2 (2 mL) was treated with Xtalfluor-E (17 mg, 0.074 mmol) at reflux for 2 h to give fluoride **2k** (17 mg, 45%) as a clear oil: $[\alpha]_D^{22}$ +28.5 (*c* 1.25, $CHCl_3$; lit.[29] +30.6°); ^1H NMR (500 MHz): *δ* 7.34–7.13 (m, 25H, Ph), 5.72–5.61 (dd, $J_{1,2}$ 2.0, $J_{1,F}$ 49.5 Hz, 1H, H1), 5.25 (dd, $J_{1,2}$ 2.0, $J_{2,3}$ 2.0 Hz, 1H, H2′), 5.13 (d, *J* 12.0 Hz, 1H, benzyl-CH), 5.00 (d, $J_{1,2}$ 3.5 Hz, 1H, H1′), 4.86 (d, *J* 12.0 Hz, 1H, benzyl-CH), 4.82 (d, *J* 10.5 Hz, 1H, benzyl-CH), 4.63 (d, *J* 12.5 Hz, 1H, benzyl-CH), 4.62 (d, *J* 12.0 Hz, 1H, benzyl-CH), 4.55 (d, *J* 12.5 Hz, 1H, benzyl-CH), 4.55 (d, *J* 10.0 Hz, 1H, benzyl-CH), 4.52 (d, *J* 11.5 Hz, 1H, benzyl-CH), 4.47 (d, *J* 11.5 Hz, 1H, benzyl-CH), 4.27 (dd, $J_{5,6}$ 5.0, $J_{6,6}$ 12.0 Hz, 1H, H6a), 4.09 (dd, $J_{5,6}$ 2.0, $J_{6,6}$ 12.0 Hz, 1H, H6b), 4.05 (dd, $J_{2,3}$ 10.0, $J_{3,4}$ 9.0 Hz, 1H, H3′), 4.03 (dd, $J_{2,3}$ 2.0, $J_{3,4}$ 2.0 Hz, 1H, H3), 4.03 (dd, $J_{3,4}$ 9.5, $J_{4,5}$ 9.5 Hz, 1H, H4), 3.94–3.97 (m, 1H, H5), 3.87–3.91 (m, 1H, H5′), 3.77 (dd, $J_{5,6}$ 4.0, $J_{6,6}$ 11.0 Hz, 1H, H6′a), 3.68 (dd, $J_{5,6}$ 2.0, $J_{6,6}$ 11.0 Hz, 1H, H6′b), 3.50 (dd, $J_{1,2}$ 3.5, $J_{2,3}$ 10.0 Hz, 1H, H2′), 3.44 (dd, $J_{3,4}$ 9.0, $J_{4,5}$ 9.0 Hz, 1H, H4′), 2.14, 2.03 (2 × s, 2 × 3H, Ac); ^{13}C NMR (125 MHz): *δ* 170.9, 170.2, 138.6, 138.5, 138.1, 138.0, 137.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 104.7 (d, $J_{C,F}$ 212 Hz, 1C, C1), 99.8, 81.7, 79.6, 78.4, 75.8, 75.2, 75.1, 74.0, 73.6, 73.3, 73.2, 70.7, 70.4, 70.1, 68.4, 63.1, 21.2, 20.9. The spectral data were previously reported in error;[29] this report corrects the previous data.

3.3.11. Tolyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside (R)$_S$-S-oxide (1n)

*m*CPBA (17 mg, 85%, 0.0837 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of 4-methylphenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside **1a**[39] (53 mg, 0.075 mmol) in CH_2Cl_2 (2 mL) at −78 °C. After 15 min the reaction was quenched with satd $NaHCO_3$ then extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were washed with brine, dried and concentrated. The crude was then purified by flash chromatography (30% ethyl acetate/pet. spirit) to give the (*R*)-sulfoxide **1n** (52 mg, 96%) as a white solid: $[\alpha]_D^{24}$ −131.7 (*c* 1.1, $CHCl_3$); IR *ν* 1729, 1452, 1315, 1264, 1178, 1107, 1094, 1070, 1027, 709 cm^{-1}; ^1H NMR (500 MHz): *δ* 8.11–8.10 (m, 2H, Ar), 8.02–8.00 (m, 2H, Ar), 7.92–7.90 (m, 2H, Ar), 7.86–7.84 (m, 2H, Ar), 7.70–7.68 (m, 2H, Ar), 7.60–7.52 (m, 3H, Ar), 7.44–7.33 (m, 9H, Ar), 7.30–7.25 (m, 2H, Ar), 6.50 (dd, $J_{1,2}$ 2.0, $J_{2,3}$ 3.0 Hz, 1H, H2), 6.33 (dd, $J_{2,3}$ 3.0, $J_{3,4}$ 10,0 Hz, 1H, H3), 6.14 (dd, $J_{3,4}$ = $J_{4,5}$ 10.0 Hz, 1H, H4), 5.32 (ddd, $J_{4,5}$ 10.0, $J_{5,6}$ 2.0, 5.0 Hz, 1H, H5), 5.09 (d, $J_{1,2}$ 2.0 Hz, 1H, H1), 4.61 (dd, $J_{5,6}$ 2.0, $J_{6,6}$ 12.5 Hz, 1H, H6a), 4.53 (dd, $J_{5,6}$ 5.0, $J_{6,6}$ 12.5 Hz, 1H, H6b), 2.34 (s, 3H, CH_3); ^{13}C (125 MHz): *δ* 166.2, 165.6, 165.3, 165.0, 142.7, 136.7, 133.7, 133.6, 133.3, 130.5, 130.1, 129.9, 129.9, 129.1, 128.9, 128.6, 128.4, 124.6, 94.8 (1C, C1), 94.7, 74.9, 70.6, 67.3, 67.2, 66.5, 63.0, 21.7 (1C, CH_3); HRMS (ESI) *m/z* calcd for $C_{41}H_{34}O_{10}SNa$ $[M+Na]^+$ 741.1765, found 741.1763. The configuration at sulfur was assigned as (*R*) based on analyzes of related compounds.[55]

3.3.12. Butyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside S-oxide (1o)

*m*CPBA (382 mg, 75%, 1.66 mmol) was added in one portion to a solution of butyl 2,3,4,6-tetra-*O*-acetyl-thio-β-D-galactopyranoside **1f**[47] (500 mg, 1.19 mmol) in CH_2Cl_2 (20 mL) at −78 °C. After 15 min at −78 °C the reaction was warmed to −55 °C for 30 min, quenched with satd $NaHCO_3$ then extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with brine, dried, and concentrated. The crude was then purified by flash chromatography (60% ethyl acetate/pet. spirits) to give the sulfoxide **1o** (3:1 mixture of stereoisomers, 335 mg, 65%) as a white fluffy material: HRMS (ESI) *m/z* calcd for $C_{18}H_{28}O_{10}SNa$ $[M+Na]^+$ 459.1295, found 459.1294. Partial ^1H NMR (400 MHz): *δ* 5.65 (dd, $J_{1,2}$ = $J_{2,3}$ 10.0, 1H, minor H2), 5.38 (dd, $J_{1,2}$ = $J_{2,3}$ 10.2, 1H, major H2); 5.17 (dd, $J_{3,4}$ 3.2, $J_{2,3}$ 10.0 Hz, 1H, minor H3); 5.12 (dd, $J_{2,3}$ 10.0, $J_{3,4}$ 3.2 Hz, 1H, major H3); 4.31 (d, $J_{1,2}$ 10.0, 1H, major H1), 2.16, 2.07, 2.04, 1.99 (4s, 4 × 3H, major Ac), 2.16, 2.07, 2.04, 2.00 (4s, 4 × 3H, minor Ac), 0.971 (t, *J* 7.2, 3H, major CH_3), 0.966 (t, *J* 7.2, 3H, minor CH_3); ^{13}C NMR (100 MHz): *δ* 170.36, 170.34, 170.2, 170.0, 169.97, 168.8, 90.7 (1C, major C1), 87.48 (1C, minor C1), 75.7, 75.6, 72.0, 71.3, 67.00, 66.95, 65.8, 64.1, 61.5, 61.1, 47.2, 47.0, 24.9, 24.1, 22.2, 22.1, 20.80, 20.76, 20.73, 20.67, 20.66, 20.63, 20.59, 13.74, 13.71.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2012.04.016.

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