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Preparation of 1-Fluoroglycosides from 1-Arylthio and 1-Arylselenoglycosides Using 4-Methyl(difluoroiodo)benzene

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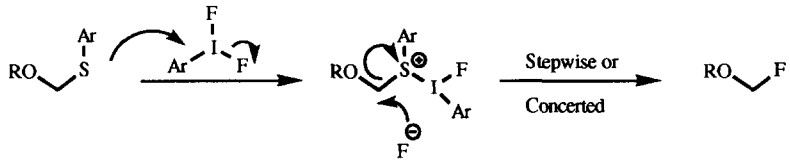
Abstract: Treatment of readily available thio- and selenoglycosides with the reagent 4-methyl(difluoroiodo)benzene leads to the formation of the corresponding fluoroglycosides in moderate to good yield.

Introduction

Fluoroglycosides are attractive materials[1] as they can be readily utilised for stereoselective glycosylation reactions[2] and as probes for biological mechanisms of action[3]. It is their versatility that provides a major impetus for the development of methods for their preparation and a number of useful procedures have been developed[4]. As part of our studies on development of hypervalent iodoarene difluorides as selective reagents for the introduction of fluorine into organic molecules[5], we had noted that the electrophilic iodine centre had a particular affinity for divalent sulphur in cephalosporin[6] and dithioketal derivatives[7] and this, as in the case of the Stork dethioacetalisation method[8], served to create an activated leaving group. We therefore reasoned, as shown in scheme 1, that this feature could also be used to prepare a sulphonium species at the anomeric centre of carbohydrates and hence to achieve site specific fluorination.

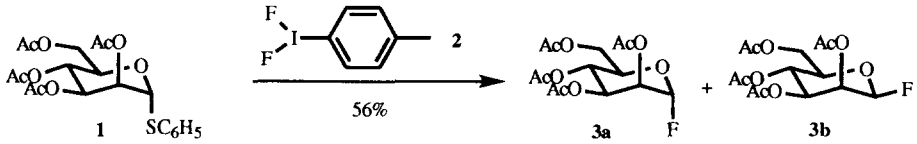


Scheme 1

We have recently reported the results of our preliminary study which confirmed the viability of such a process[9] and now provide herein full details of this transformation. The ready availability of the thioglycoside precursors[4,10] and the iodoarene difluoride reagent make this method convenient for the preparation of fluoroglycosides. We also describe some new investigations into the action of iodoarene difluoride reagents on phenylselenoglycosides[11] and show that, while fluoroglycosides can also be prepared from this alternative precursor class under similar reaction conditions, the stereochemical outcome may differ.

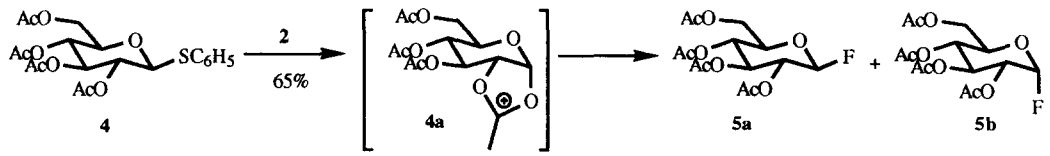
Results and Discussion

Thioglycosides. Our initial work utilised the mannose derived thioglycoside **1** (Scheme 2) which on treatment with *p*-methyliodobenzenedifluoride **2** leads to the formation of the expected axial fluoroglycoside **3a** as the major product (**3a**:**3b** ratio, 10:1); thereby illustrating the feasibility of the overall displacement process.



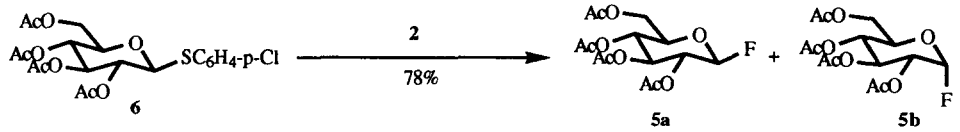
Scheme 2

In a similar fashion and in agreement with our initial expectation that such reactions would proceed by an S_N1-type mechanism, treatment of the glucose derivative **4**, led to the formation of fluoroglycosides **5a** and **5b** (Scheme 3). In this case the formation of the α-acetoxonium ion **4a** presumably shields the stereoelectronically favoured axial attack of fluoride and explains the formation of both isomers (**3a**:**3b** ratio, 3:2).



Scheme 3

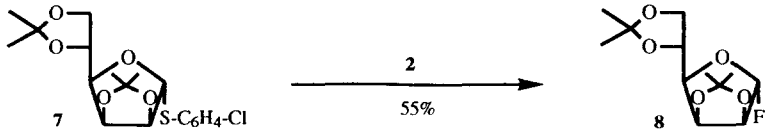
It is worthy of note that modification of the aromatic portion of the thioglycoside can be a useful tactic in improving the process (Scheme 4). Thus by using a *p*-chloro-phenylthioglycoside **6** in the reaction, the yields of product fluoroglycosides **5a** and **5b** are significantly improved (**5a**:**5b** ratio, 3:2).



Scheme 4

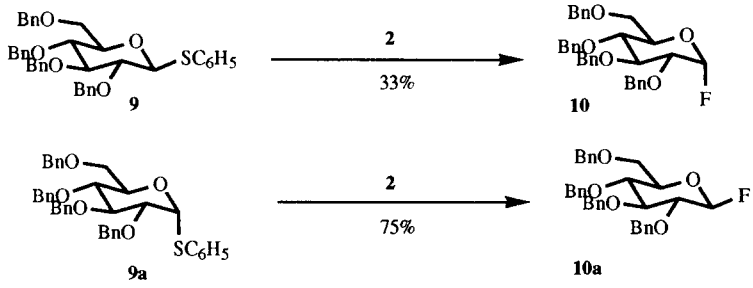
We assume that this result reflects the improved leaving group ability of the *p*-chloro-phenylthio moiety as opposed to a difference in its affinity for the hypervalent iodine reagent.

The procedure can also be extended to the preparation of furanose derivatives, as shown by treatment of phenylthiofuranose **7** with reagent **2** which leads to the fluoroglycoside **8** in moderate yield (55%); the geometry of this substrate demands, of course, that the reaction proceed with retention of configuration, possibly *via* an S_N1-like pathway followed by delivery of fluoride anion from the convex face (Scheme 5).



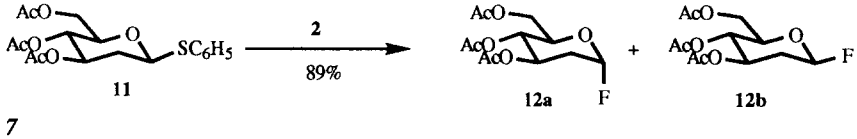
Scheme 5

We then decided to examine substrates in which neighbouring group participation would be negligible in order to determine whether the fluorination could proceed *via* an S_N2-like mechanism. Thus treatment of phenylthioglycoside **9** with reagent **2** led to the fluoroglycoside **10** with inversion, albeit in rather modest yield (33%). By way of contrast phenylthioglycoside **9a** gave the inverted fluoroglycoside product **10a** in good yield (75%) (Scheme 6). It may be that the lack of anomeric assistance in cleavage of the carbon-sulphur bond of the intermediate sulphonium species derived from **9** slows the displacement process to such a degree that competing debenzylation becomes an important alternative reaction pathway[12] and hence reduces the yield.



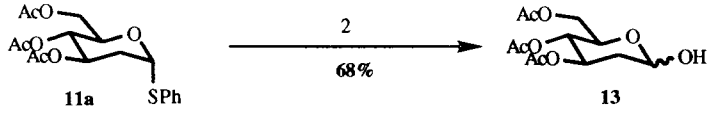
Scheme 6

Further studies then utilised the 2-deoxy-glucopyranoses (Scheme 7). As expected the displacement of the β-phenylthioglycoside **11** led largely to the formation of the α-fluoroglycoside **12a** *via* inversion (**12a:12b** ratio, 3:1) although it was interesting to note that trace quantities of pyranoses **13**[13] were also formed.



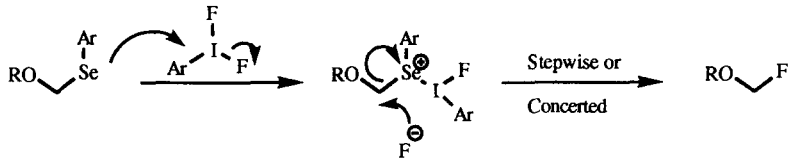
Scheme 7

To our great surprise however, treatment of the axial phenylthioglycoside **11a** with the reagent **2** led only to the formation of a mixture of pyranoses **13** (Scheme 8). We were aware that nucleophilic displacements, both in terms of substrate and of product, can be expected to be much more facile in the 2-deoxy series, and numerous attempts were made to carry out the reaction using several batches of reagent **2**. In every case however, we were unable to isolate any fluoroglycoside from the anomalous substrate **11a**, in spite of our success in isolating such products both in the case of the equatorial precursor **11** (Scheme 7) and in related selenium congeners (*vide infra*, Schemes 11 and 12)



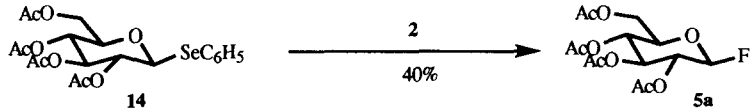
Scheme 8

Selenoglycosides. It was of considerable interest to examine the feasibility and stereochemical outcome of the related process utilising selenoglycosides as shown below in Scheme 9.



Scheme 9

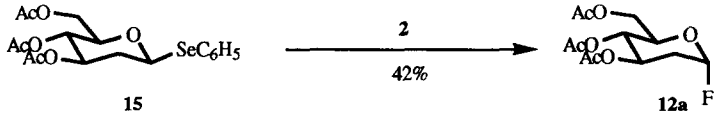
In order to illustrate the viability of this concept the phenylselenoglycoside **14**[14] was transformed to the fluoroglycoside **5a** with retention of configuration in moderate yield (Scheme 10).



Scheme 10

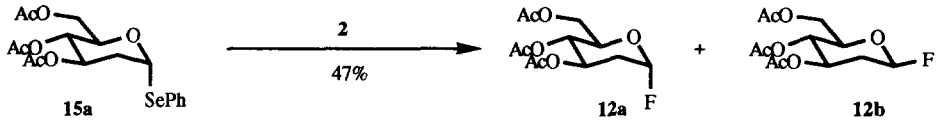
It is possible that the improved leaving group ability of the intermediate selenonium species ensures rapid formation of an acetoxonium ion from which the β-fluoride is formed. Our ability to isolate the axial fluoroglycoside **5b** in other closely related reactions encourages us to suggest however that the reaction does not produce any of this material.

The 2-deoxy-phenylselenoglycosides could also be transformed into the fluoroglycosides (Scheme 11); thus the β-phenylselenoglycoside **15**[11] provided fluoroglycoside **12a** (42%) on treatment with reagent **2**, indicative of clean inversion.



Scheme 11

However in marked contrast to the thioglycoside series the axial selenoglycoside **15a** reacted with fluorinating agent **2** to give a mixture of fluoroglycosides **12a** and **12b** in 47% yield (**12a**:**12b** ratio, 2:1).



Scheme 12

From a mechanistic standpoint, it is clear that the present reaction exhibits many of the classical characteristics relating to neighbouring group participation by substituents at C-2, which encourages a predictable stereochemical outcome. In the absence of such effects however, it is of even greater interest to note the significant difference which appears to exist between analogous thio- and selenoglycoside derivatives; with the former showing a preference for reactions involving an S_N2 like inversion of configuration, and the latter exhibiting a tendency for S_Ni like retention. This is particularly clear in the 2-deoxy series, but is also mirrored

in the relative ratios obtained with the tetra-O-acetyl glucose examples. In practical terms, we have shown that the use of readily available crystalline and organic soluble hypervalent iodoarene difluorides in equimolar amount with thio- and selenoglycosides provides a simple and effective method for the small scale preparation of fluoroglycosides. The reaction is compatible with the range of standard protecting groups used in carbohydrate chemistry.

Experimental

General. All reagents were used as supplied or purified using standard techniques, all thioglycosides and selenoglycoside precursors were prepared by literature methods[4,10,11,14] unless otherwise stated. All reactions were carried out using oven-dried glassware and under nitrogen unless otherwise stated. Analytical thin layer chromatography (tlc) was carried out using pre-coated glass backed plates (Merck Kieselgel 60 F254). Petrol refers to light petroleum ether (40 °C-60 °C) and ether to diethyl ether; all solvents were purified by distillation. ^{19}F NMR were recorded at 84.3 MHz on a Jeol FX90Q instrument using fluorotrichloromethane as a standard; ^{1}H NMR were recorded at 270MHz on a Jeol GSX 270 MHz instrument unless otherwise stated, or at 500 MZ on a Bruker AM-500 in $CDCl_3$; all coupling constants are given in Hertz.

(4-Chlorophenylthio) 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (6). α-D-glucose pentaacetate (10.0 g, 25.6 mmoles) in dichloromethane (60 ml) was treated with 4-chlorothiophenol (7.4 g, 51.2 mmoles) and the mixture cooled to 0 °C. Boron trifluoride etherate (14.2 g, 100.0 mmoles) was added dropwise and the solution was allowed to warm to room temperature overnight. The reaction was stirred for a further 6 days and then poured into ice cold sodium hydroxide solution (150 ml). The organic layer was separated and washed with NaOH solution (150 ml), water (100 ml) and dried over magnesium sulphate. Filtration and removal of the solvent *in vacuo* gave a colourless oil which solidified on standing. Further purification by recrystallisation (petrol:ether, 1:5, 250 ml, then EtOH, 200 ml) gave the product **6** as white solid (4.9 g, 40.3%), m.p. 111-111.5 °C.

δ_H; 7.45 (2H, d, J = 8.5 Hz), 7.3 (2H, d, J = 8.8 Hz), 5.22 (1H, t, J = 9.3 Hz), 5.02 (1H, t, J = 9.8 Hz), 4.9 (1H, t, J = 10 Hz), 4.65 (1H, d, J = 10 Hz), 4.2 (2H, m), 3.7 (1H, m), 2.09 (3H, s), 2.08 (3H, s), 2.02 (3H, s), 1.99 (3H, s); δ_C (67.9, $CDCl_3$); 170.4, 170.1, 169.3, 169.2, 135.0, 129.5, 129.0, 73.9, 69.8, 68.1, 62.0, 20.7, 20.6, 20.5, 20.2; m/z 332 $(M\text{-}SPhCl)^+$, 169, 109, 43. Anal. Calcd. for $C_{20}H_{23}ClO_9S$: C 50.58, H 4.88. Found C 50.77, H 4.72.

(4-Chlorophenylthio) 2,3,5,6-di-O-isopropylidene-α-D-mannofuranose (7). Diacetone mannose (820 mg, 3.14 mmoles) was dissolved in dry dichloromethane (6.0 ml) and treated with bis(4-chlorophenylsulphide) (900 mg, 3.14 mmoles). The mixture was stirred at room temperature overnight and the solution concentrated *in vacuo* to 50% of its original volume and subjected to purification using silica-gel chromatography ($CHCl_3$) to give product **7** as a white solid (0.8 g, 72%) m.p. 115-117 °C. $[\alpha]_D^{20}$ -108.7 (c=1, $CHCl_3$); δ_H; 7.41 (2H, d, J = 8.6 Hz), 7.26 (2H, d, J = 8.6 Hz), 4.91 (1H, dd, J = 11.9, 3.8 Hz), 4.9 (1H, m), 4.8 (1H, dd, J = 5.6, 3.5 Hz), 4.53 (1H, dt, J = 8, 4.9 Hz), 4.15 (2H, d, J = 5 Hz), 3.6 (1H, dd, J = 8, 3.5 Hz), 1.56 (3H, s), 1.46 (3H, s), 1.39 (3H, s), 1.38 (3H, s); m/z 387 $(M+H)^+$, 371, 329, 289, 271, 243, 185, 154, 127, 101, 85. HRMS for $C_{18}H_{23}ClO_5S$ requires 387.1033 found 387.1033.

General procedure for the preparation of fluoroglycosides from thioglycosides. *p*-Methyliodobenzenedifluoride[15] in dichloromethane was added dropwise to a stirred solution of the thioglycoside at -78 °C in a polypropylene flask. The reaction was allowed to warm to room temperature over a period of 30 minutes to overnight and water and sodium bicarbonate was added. Magnesium sulphate was then added and the reaction mixture filtered and the solvent evaporated *in vacuo* to give the crude product. Purification was carried out using silica-gel chromatography to give the products.

2,3,4,6-Tetra-O-acetyl-α–D-mannopyranosyl fluoride (3a).[16] Compound **3a** was prepared from thioglycoside **1** (0.91 mmoles) and 4-methyl(difluoroiodo)benzene (0.91 mmoles) in dichloromethane (2.0 ml) using the standard fluorination procedure (-78 °C to r.t. overnight, silica-gel chromatography, petrol:acetone, 7:3). Yield = 177 mg, 56%. The isomer ratio (>10:1, α:β) was initially estimated from examination of the ^{19}F NMR spectrum of the crude reaction mixture and supported by the isolated fractions as described. Further purification by silica-gel chromatography (petrol:ether, 8:2) furnished the pure α-anomer **3a** (160 mg) and a mixture of α/β anomers **3a** and **3b** respectively (13 mg). **3a:** δ_F ; 138.8 (d, J = 48.8 Hz); δ_H; 5.58 (1H, dd, J = 49, 1.95 Hz), 5.4 (1H, dd, J = 3, 1.5 Hz), 5.36-5.33 (2H, m), 4.33-4.27 (1H, m), 4.19-4.13 (2H, m), 2.18 (3H, s), 2.11 (3H, s), 2.06 (3H, s), 2.01 (3H, s). **3b**: δ_F; 142.7 (dd, J = 48.8, 9.8 Hz). The proton NMR spectrum of the minor fraction (13 mg) enriched in the β-isomer was consistent with that reported in the literature.[16]

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl fluoride (5a) and 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl fluoride (5b).[16,17] Compounds **5a** and **5b** were prepared from thioglycoside **4** (1.51 mmoles) and 4-methyl(difluoroiodo)benzene (1.51 mmoles) in dichloromethane (2.0 ml) using the standard fluorination procedure (-78 °C to r.t. overnight, silica-gel chromatography, petrol:ethyl acetate, 3:1). Yield = 344 mg, 65% (**5a**:**5b** ratio, 3:2).

Compound **5a** was also prepared from selenoglycoside **14** (0.154 mmoles) and 4-methyl(difluoroiodo)benzene (0.125 mmoles) in dichloromethane (5 ml) (-78 °C to r.t., 90 minutes). The reaction mixture was evaporated *in vacuo* and purification using silica-gel chromatography (ether:petrol, gradient 20-30%) gave the fluoride **5a**. Yield = 21.6 mg, 40%; **5a:** δ_F ; 137.8 (dd, J = 48.8, 9.8 Hz); δ_H ; 5.3 (1H, dd, J = 52.1, 6.1 Hz), 5.13 (2H, m), 5.1-4.95 (1H, m), 4.25-4.05 (2H, m), 3.85 (1H, m), 2.1 (3H, s), 2.0 (3H), 2.0 (3H, s), 1.95 (3H, s); **5b:** δ_F ; 150.6 (dd, J = 53.7, 24.4 Hz); δ_H ; 5.69 (1H, dd, J = 52.9, 2.68 Hz), 5.43 (1H, t, J = 10.0 Hz), 5.09 (1H, t, J = 10.0 Hz), 4.89 (1H, m, J = 24.2, 10.1, 2.7 Hz), 4.25-4.05 (3H, m), 2.07 (3H, s), 2.07 (3H, s), 2.01 (3H, s), 2.0 (3H, s).

2,3,5,6-Di-O-isopropylidene-α-D-mannofuranosyl fluoride (8)[4,18]. Compound **8** was prepared from thioglycoside **7** (0.78 mmoles) and 4-methyl(difluoroiodo)benzene (0.78 mmoles) in dichloromethane (1.0 ml) using the standard fluorination procedure (-78 °C to r.t. overnight, silica-gel chromatography, chloroform). Yield = 110 mg, 55%; δ_F; 129.2 (d, J = 58.6 Hz); δ_H ; 5.69 (1H, d, J = 59.3 Hz), 4.9-4.7 (2H, m), 4.5-4.1 (4H, m), 1.46 (6H, s), 1.39 (3H, s), 1.35 (3H, s).

2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl fluoride (10)[19]. Compound **10** was prepared from thioglycoside **9** (0.50 mmoles) and 4-methyl(difluoroiodo)benzene (0.50 mmoles) in dichloromethane (2.0 ml) using the standard fluorination procedure (-78 °C to r.t. overnight, silica-gel chromatography, petrol:acetone, 9:1). Yield = 89 mg, 33%; δ_F ; 150 (dd, J = 53.7, 24.4 Hz); δ_H ; 7.35-7.08 (20H, m), 5.55 (1H, dd, J = 53.4, 2.4 Hz), 4.98-4.44 (7H, m), 4.0-3.49 (7H, m).

2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl fluoride (10a)[19]. Compound **10a** was prepared from thioglycoside **9a** (0.10 mmoles) and 4-methyl(difluoroiodo)benzene (0.10 mmoles) in dichloromethane (2.0 ml) using the standard fluorination procedure (-78 °C to r.t. overnight, silica-gel chromatography, petrol:acetone, 8:2). Yield = 41 mg, 75% ; δ_F ; 138.4 (d, J = 48.8 Hz); δ_H ; 7.41-7.12 (20H, m), 5.24-4.40 (10H, m), 4.0-3.5 (5H, m).

3,4,6-Tri-O-acetyl-2-deoxy-α-D-glucopyranosyl fluoride (12a)[4,16,17]**3,4,6 tri-O-acetyl-2-deoxy-β-D-glucopyranosyl fluoride (12b)**[4,16,17] **and 3,4,6 tri-O-acetyl-2-deoxy-β-D-glucopyranoside (13)**[13]. Compounds **12a** and **12b** were prepared from thioglycoside **11** (1.03 mmoles) and 4-methyl(difluoroiodo)benzene (1.2 mmoles) in dichloromethane (5 ml) using the standard fluorination procedure (-78 °C to r.t., 30 minutes, silica-gel chromatography, gradient: petrol:ether 3:1, 2:1, 1;1). Yield (269 mg, 89%) (**12a**:**12b** ratio, 3:1). Trace quantities of **13** were also usually observed from these reactions.

Compounds **12a** and **12b** were prepared from selenoglycoside **15a** (40.1 μmole) and 4-methyl(difluoroiodo)benzene (32.6 μmoles) in dichloromethane (4.0 ml) (-78 °C to r.t., 1.5 hours). The reaction mixture was evaporated *in vacuo* and purification using silica-gel chromatography (ether:petrol, 2:1) gave the fluorides **12a** and **12b**. Yield (5.54 mg, 47%) Ratio (**12a**:**12b** ratio, 2:1).

Compound **12a** was prepared from selenoglycoside **15** (34.5 μmole) and 4-methyl(difluoroiodo)benzene (28.1 μmoles) in dichloromethane (4.0 ml) (-78 °C to r.t., 1.5 hours). The reaction mixture was evaporated *in vacuo* and purification using silica-gel chromatography (ether:petrol, 2:1) gave the fluoride **12a** (4.21 mg, 42%).

Compound **13** was prepared as a mixture of anomers from thioglycoside **11a** (8 μmoles) and 4-methyl(difluoroiodo)benzene (9.6 μmoles) in dichloromethane (2 ml) using the standard fluorination procedure (-78 °C to r.t. overnight, silica-gel chromatography, gradient : petrol:ether 1:1, 1:2, 1:3). This was identical to material independently prepared by the recently disclosed literature procedure[13].

Yield (10.0 mg, 43%) **12a**; δ_F ; 131 (dd, J = 49, 39 Hz); δ_H (500MHz; $CDCl_3$) 5.75 (1H, d, J = 51 Hz), 5.3 (1H, m, J = 9.6, 5.4 Hz), 5.1 (1H, t, J = 9.9 Hz), 4.3 (1H, dd, J = 12.4, 4.2 Hz), 4.15 (1H, m, J = 10.2, 4.2, 2.1 Hz), 4.10 (1H, dd, J = 12.4, 2.15 Hz), 2.5 (1H, m, J = 1.38 Hz), 2.1 (3H, s), 2.09 (3H, s), 2.03 (3H, s), 1.85 (1H, m); **12b**: δ_F ; 125 (dt, J = 52, 14.6, 9.7 Hz); δ_H (500MHz; $CDCl_3$) 5.5 (1H, m, J = 52, 6.5, 2.6 Hz), 5.08 (1H, t), 5.0 (1H, m, J = 8, 5 Hz), 4.3 (1H, dd, J = 12, 5.4 Hz), 4.33 (1H, dd, J = 12, 5.4 Hz), 4.3 (1H, m, J = 12, 3.8 Hz), 3.9 (1H, m, J = 5.3, 4 Hz), 2.45 (1H, m, J = 5, 2.6 Hz), 2.1 (3H, s), 2.07 (3H, s), 2.06 (3H,s), 2.0 (1H, m).

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