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## ENVIRONMENTALLY-BENIGN GLYCOSYLATION REACTION USING ODORLESS *THIO*-GLYCOSIDES AND HYPERVALENT IODINE(III) REAGENT

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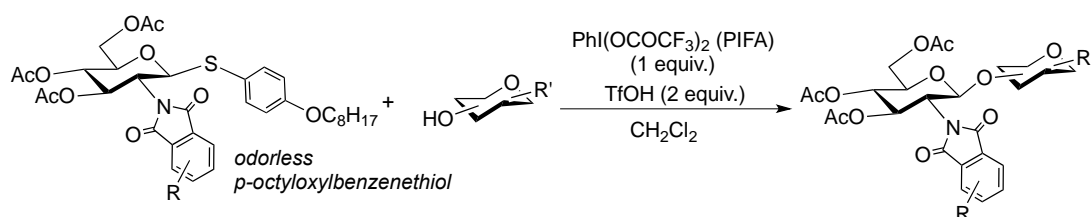
**Abstract** – We discovered that the hypervalent iodine(III) reagent could mediate the glycosylation reaction by activating the *thio*-glycoside donors which were prepared from glycosyl 1-*O*-acetate and odorless *p*-octyloxybenzenethiol. By using this method, trisaccharides as well as disaccharides could be easily synthesized under mild reaction conditions. All the chemicals employed in this method are environmentally-benign.

In celebration of Professor Tohru Fukuyama on his 70th Birthday

The glycosylation reaction is essential for the synthesis of biologically-potent oligosaccharides, of which the activities are related with, e.g., the inflammation reaction, fertilization, bacterial and viral infection and immune responses.<sup>1</sup> A number of glycosylation methods has been developed using different donors for the construction of the glycoside linkages in the past few decades.<sup>2-5</sup> Among the various glycosyl donors, *thio*-glycosides have attracted carbohydrate chemists due to their stability, accessibility, compatibility and orthogonality compared to other donors.<sup>6-8</sup> While the *thio*-glycosides are rather stable under diverse conditions of protection and deprotection of the hydroxyl and amino groups, they can be easily and selectively activated under moderate conditions by electrophilic/thiophilic promoters. Various promoters have been attempted to be developed in order to activate the *thio*-glycosides, such as metal salts,<sup>9-13</sup> halonium reagents<sup>14-22</sup> and organic sulfonium reagents.<sup>23-28</sup> The iodonium species are currently

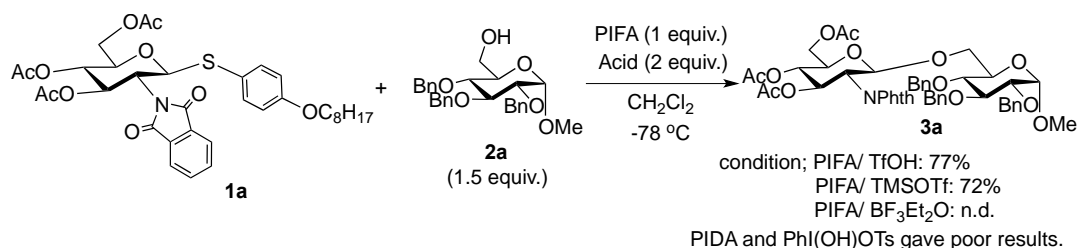
recognized as the most efficient promoters, like *N*-iodosuccinimide, in combination with a catalytic amount of a Brønsted or Lewis acid.<sup>29-36</sup> Although the methods were effective in performing a variety of glycosylations, there still remains an unsolved limitation.

We recently reported a novel glycosylation reaction of a *thio*-glycoside using the hypervalent iodine(III) as an activator.<sup>37-54</sup> However, this method was developed as an alternative method of a conventional one, which requires an excess amount of odorous methanethiol or benzenethiol for preparation of the *thio*-glycoside and generates the thiols as a waste product during the reaction. We now report the glycosylation using a *thio*-glycoside donor, which was prepared with odorless *p*-octyloxybenzenethiol to overcome these concerns, followed by the activation with the hypervalent iodine(III) reagent. Furthermore, the method was used to synthesize a trisaccharide to show the utility as a new glycosylation reaction.<sup>53,54</sup> Needless to say, the syntheses of disaccharides and monosaccharides were also performed in advance of the trisaccharides.



Scheme 1. The hypervalent iodine(III)-induced metal-free glycosylation using *thio*-glycosides prepared with an odorless thiol

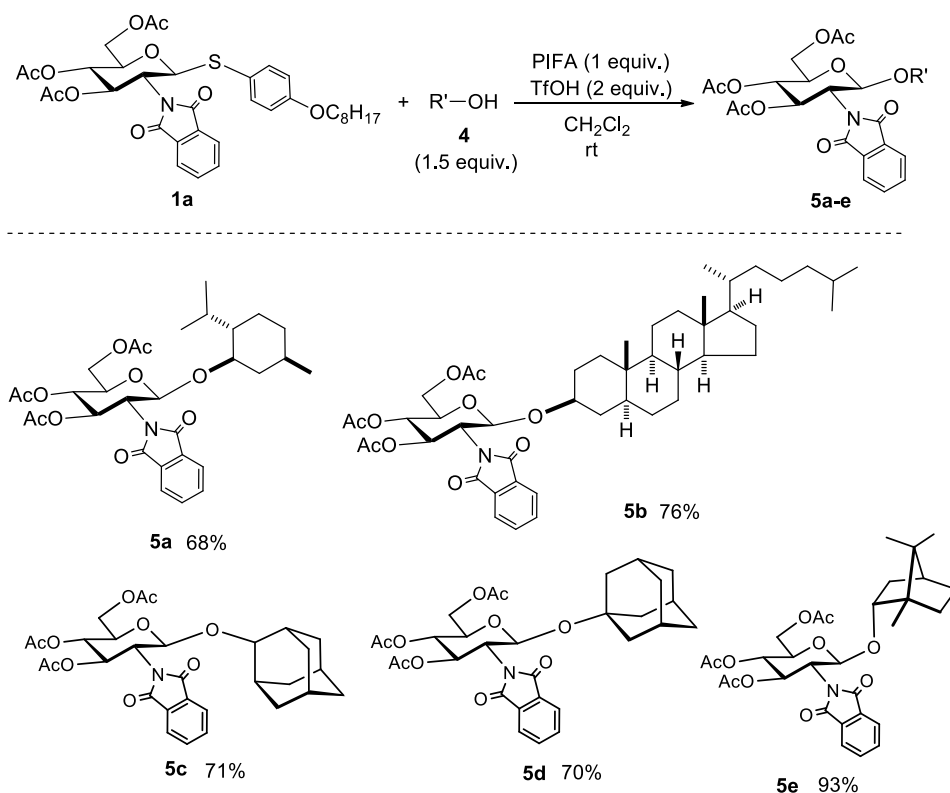
The donor glycoside *p*-octyloxyphenyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-1-*thio*- $\beta$ -D-glucopyranoside **1a** was initially prepared by the method reported by our group.<sup>53,54</sup> Based on our previous research of the glycosylation,<sup>51,52</sup> we examined the glycosylation reaction, in which the *thio*-glycoside donor **1a** was activated by the combination of phenyliodine(III) bis(trifluoroacetate) (PIFA) and various acids. As a result, the reaction of the combination of PIFA and TfOH afforded the best result. Unfortunately, other iodine(III) reagents, such as phenyliodine(III) diacetate (PIDA) and PhI(OH)OTs, showed a decreased yield. The use of TMSOTf or methanesulfonic acid instead of TfOH afforded no significant results.



Scheme 2. Influence of iodine(III) reagents and acids

Thus, the combination of PIFA and TfOH was then employed as the activator of the *thio*-glycoside donor prepared with the odorless *p*-octyloxybenzenethiol. Under the well-optimized conditions, the reaction between the *thio*-glycoside **1a** and various alkanols **4a-e** smoothly proceeded as shown in Table 1, and the glycosylation products **5a-e** were obtained in good yields at room temperature. When (*l*)-menthol **4a** and a secondary alcohol **4b** having fusion rings and an alcohol **4c** having an adamantane skeleton were employed as the acceptor substrates, the corresponding glycosylation products **5a**, **5b**, and **5c** were obtained in good yields. Despite the steric hindrance caused by the adamantane skeleton, the tertiary alcohol **5d** was glycosylated in 70% yield under the same reaction conditions. Moreover, even the substrates carrying a much more hindered alcohol, such as the (-)-borneols **4e**, could be glycosylated to produce the product **5e**. It is noted that the glycosylation yields to afford **5a-e** improved more than the reactions in which methyl *thio*-*N*-phthaloyl-D-glucosaminide was employed as a glycosyl donor. This result encouraged us to apply the method to the synthesis of an oligisaccharide.

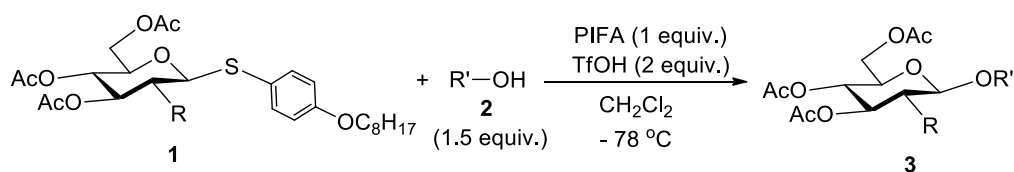
Table 1. The glycosylation reaction between *thio*-glycoside **1a** prepared with an odorless thiol and various alkanols **4**



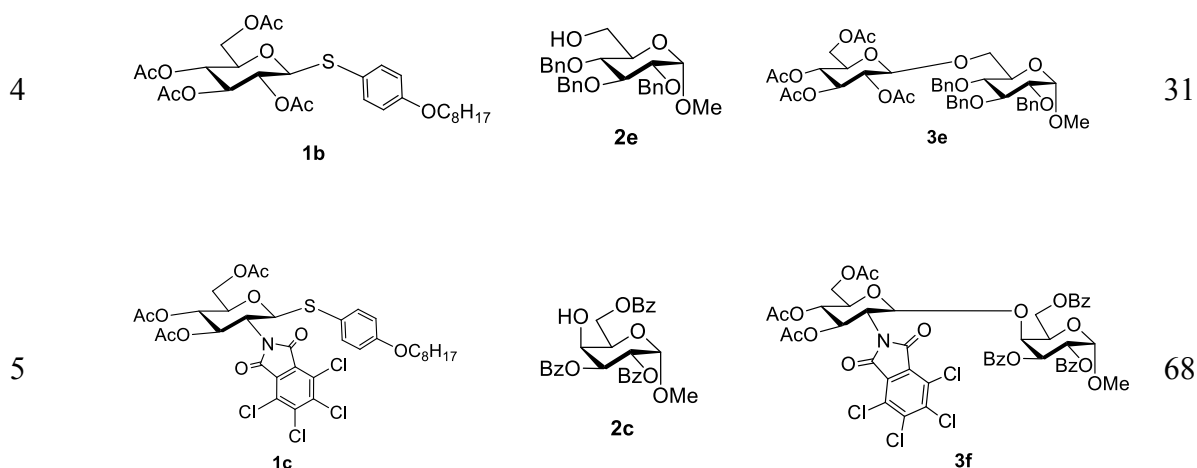
[a] Reactions were carried out by adding PIFA (0.20 mmol) to a stirred solution of the starting glycosyl donor **1a** (0.20 mmol) and glycosyl acceptors **4** (0.30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) in the presence of TfOH (0.40 mmol) at room temperature. [b] Yield of isolated product.

Next, the disaccharide syntheses under our glycosylation conditions were carried out using *p*-octyloxyphenyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-1-*thio*- $\beta$ -D-glucopyranoside **1a** and the benzoylated glucosyl acceptor **2b** as the donor and acceptor substrates, respectively. As a result, the glycosylations of the glycosyl donor **1a** with the benzoylated glucosyl acceptor **2b** having a free hydroxyl group at the C-6 position proceeded in good yield (entry 1). Glycosylation using the galactosyl acceptor **2c** having a free hydroxyl group at the C-4 position also proceeded with a good yield under similar conditions (entry 2). When the acetonide-protected acceptor **2d** was used, the glycosylation reaction gave the corresponding disaccharide **3d** in good yield without being affected by any steric hindrance (entry 3). The oxonium intermediates bearing phthalimide is more stable than that of acetoxy group, owing to the stronger effect of neighboring group participation of phthalimide. When the donor **1c** of which the amino protecting group was substituted with tetrachlorophthalimide was used, the reaction occurred in good yield in spite of not optimizing the reaction conditions (entry 5).

Table 2. Disaccharide syntheses using *thio*-glycoside **1** prepared with an odorless thiol

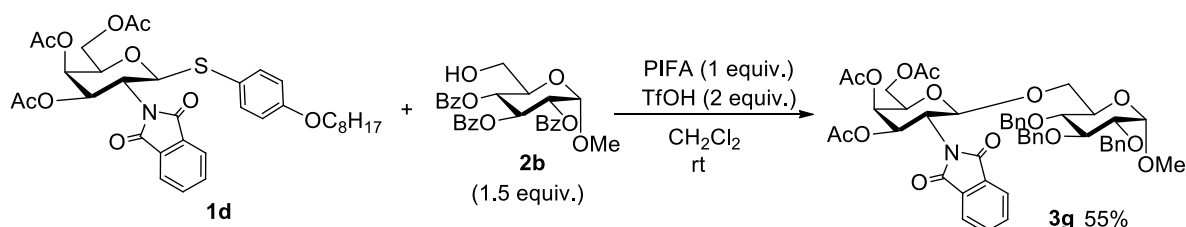


Entry	Donor	Acceptor	Product	Yield (%) <sup>a,b</sup>
1				63
2	//			59
3	//			53



[a] Reactions were carried out by adding PIFA (0.20 mmol) to a stirred solution of the starting glycosyl donor **1** (0.20 mmol) and glycosyl acceptors **2** (0.30 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL) in the presence of TfOH (0.40 mmol) at  $-78^\circ\text{C}$ . [b] Yield of the isolated product.

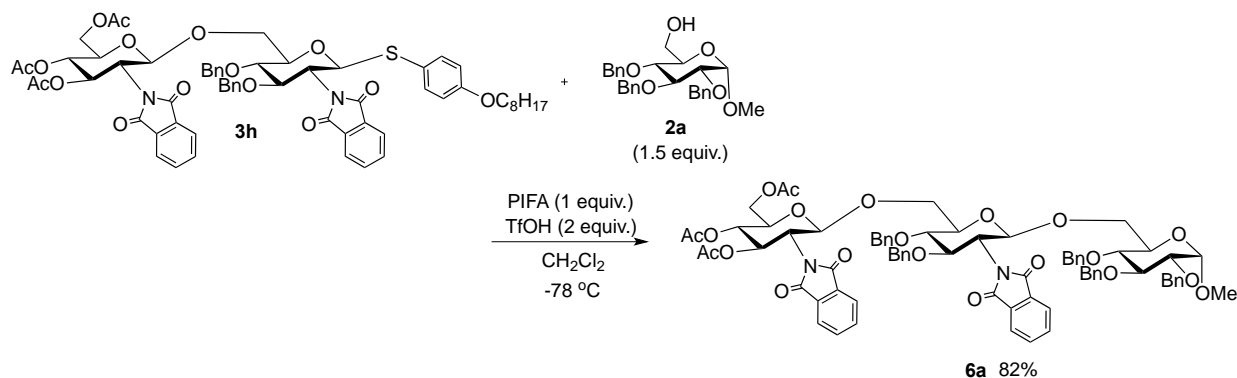
The glycosylation reactions using a galactosamine derivative as the donor substrate were subsequently performed. The *p*-octyloxyphenyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-1-*thio*- $\beta$ -D-galactopyranoside **1d** was synthesized from 2-deoxy-2-phthalimido-D-galactose tetraacetate by the literature method.<sup>53</sup> For the glycosylation reaction using the *p*-octyloxyphenyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-1-*thio*- $\beta$ -D-galactopyranoside **1d** and **2b** as a donor and an acceptor, respectively, the corresponding disaccharide **3g** was produced in a low yield. Meanwhile, when the reaction time was prolonged and the reaction was performed at room temperature, the yield was improved and the corresponding glycosylated product was obtained in good yield.



Scheme 3. The glycosylation reaction between galactosamine derivative **1d** prepared with an odorless thiol

The synthesis of the trisaccharides by the above glycosylation was also performed using the disaccharide **3h** as the donor substrate and the benzylated glucosyl acceptor **2a** as the acceptor substrate. As a result,

the reaction successfully progressed and the desired trisaccharide **6a** was obtained in high or satisfactory yields.



Scheme 4. The synthesis of trisaccharide **6a** using the hypervalent iodine(III) induced metal-free glycosylation

In conclusion, we found that the hypervalent iodine, PIFA, is an excellent promoter of the *p*-octyloxyphenyl *thio*-glycosides in the presence of TfOH for the glycosylation reaction affording satisfactory results and the method was very effective for synthesizing not only the mono- and disaccharides, but also a trisaccharide. Therefore, the combination of the *thio*-glycoside and PIFA in the presence of TfOH would provide an alternative method for the synthesis of biologically-active oligosaccharides. Future research involving mechanistic studies to expand the synthesis of the oligosaccharides will be published elsewhere.

## EXPERIMENTAL

**General Remarks:** The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded by a JEOL JMN-400 spectrometer operating at 400 MHz in  $\text{CDCl}_3$  at 25 °C with tetramethylsilane as the internal standard. Data are reported as follows: chemical shift in ppm ( $\delta$ ), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constant (Hz). The infrared spectra (IR) were obtained using a Hitachi 270-50 spectrometer, absorptions are reported in reciprocal centimeters. The mass spectra were obtained using a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. The high resolution mass spectra were performed by the Elemental Analysis Section of Osaka University. Column chromatography and TLC were carried out on Merck Silica gel 60 (230-400 mesh) and Merck Silica gel F254 plates (0.25 mm), respectively. The spots and bands were detected by UV irradiation (254, 365 nm).

**Materials:**  $\text{PhI}(\text{OCOCF}_3)_2$  (PIFA), 1-*O*-methyl 2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside **2**, (*l*)-menthol, cholestanol, 2- and 1-adamantanols, (-)- and (+)-borneol are commercially available and used as received. All other starting materials are commercially available. They were used without further purification.

*p*-Octyloxyphenyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-1-thio- $\beta$ -D-glucopyranoside **1a** was synthesized by the method in the literature,<sup>53</sup> *i.e.*,  $\text{BF}_3\text{Et}_2\text{O}$  (268 mL, 2.12 mmol) was added to a solution of 2-deoxy-2-phthalimido-1,3,4,6-tetra-*O*-acetyl-D-glucopyranose (676 mg, 1.41 mmol), and *p*-octyloxybenzenethiol (506 mg, 2.12 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) at 0 °C and the mixture was stirred for 20 h at rt. After the reaction, the reaction mixture was poured into ice water and extracted with EtOAc. The organic layer was washed with a saturated aqueous solution of NaCl, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 2:1) to afford *p*-octyloxyphenyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-1-thio- $\beta$ -D-glucopyranoside **1a** (829 mg, 89%) as a colorless syrup.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.89 (3H, t,  $J = 7.0$  Hz), 1.78 (2H, quint,  $J = 7.0$  Hz), 1.83, 2.01, 2.10 (3H, each s), 3.86 (1H, dq,  $J = 10.0, 2.4$  Hz), 3.93 (2H, t,  $J = 6.6$  Hz), 4.20 (1H, dd,  $J = 12.3, 2.4$  Hz), 4.26 (1H, dd,  $J = 12.3, 5.0$  Hz), 4.28 (1H, t,  $J = 10.0$  Hz), 5.09 (1H, t,  $J = 10.0$  Hz), 5.56 (1H, d,  $J = 10.0$  Hz), 5.76 (1H, t,  $J = 10.0$  Hz), 6.78, 7.33 (2H, each d,  $J = 8.8$  Hz), 7.76 (2H, dd,  $J = 5.3, 3.0$  Hz), 7.88 (2H, dd,  $J = 5.3, 3.0$  Hz) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_5\text{D}_5\text{N}$ ):  $\delta$  13.6, 19.5, 19.7, 20.0, 22.2, 25.8, 28.7, 28.76, 28.85, 31.3, 53.8, 61.9, 67.6, 68.6, 71.6, 75.9, 83.2, 114.9 (2C), 120.5, 122.3 (2C), 130.9, 131.3, 134.2, 134.3, 135.8 (2C), 159.7, 166.9, 167.8, 169.0, 169.7, 169.8 ppm; IR: 2930, 2856, 1778, 1747, 1719, 1593, 1495, 1470  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{34}\text{H}_{50}\text{O}_{10}\text{NSNa}$   $[\text{M}+\text{Na}]^+$ : 678.2349, found: 678.2343.

*p*-Octyloxyphenyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-1-thio- $\beta$ -D-galactopyranoside **1d** was also prepared from 2-deoxy-2-phthalimino-D-galactose tetraacetate and *p*-octyloxybenzenethiol with good yield (83%) in the same way as the synthesis of **1d**, *i.e.*, **1d** was obtained by the reaction of 2-deoxy-2-phthalimino-D-galactose tetraacetate with *p*-octyloxybenzenethiol in the presence of  $\text{BF}_3\text{Et}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.

***p*-Octyloxyphenyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-1-thio- $\beta$ -D-galactopyranoside (1d)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.85-0.86 (3H, m), 1.26-1.29 (8H, m), 1.41 (2H, m), 1.74 (2H, q,  $J = 6.8$  Hz), 1.81 (3H, s), 2.02 (3H, s), 2.14 (3H, s), 3.89 (2H, t,  $J = 6.4$  Hz), 4.03-4.05 (1H, m), 4.09-4.14 (1H, m), 4.18-4.20 (1H, m), 4.56 (1H, t,  $J = 10.8$  Hz), 5.45 (1H, s), 5.54 (1H, d,  $J = 9.3$  Hz), 5.77 (1H, d,  $J = 10.8$  Hz), 6.75-6.77 (2H, m), 7.31-7.34 (2H, m), 7.75-7.76 (2H, m), 7.86 (2H, brs) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 20.5, 20.7, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 50.1, 61.6, 66.8, 68.0, 68.9, 74.4, 77.2, 84.6, 114.8 (2C), 121.3, 123.6, 123.7, 132.6, 132.8, 134.3, 134.4, 135.8 (2C), 159.8, 166.1, 167.2, 169.8, 170.3, 170.4 ppm; IR (KBr): 3052, 2930, 2857, 2253, 1748, 1716, 1594, 1569, 1494, 1470, 1384, 1245, 1174,

1118, 1088, 1045, 912, 831, 741, 672  $\text{cm}^{-1}$ ; HRFABMS calcd for  $\text{C}_{34}\text{H}_{41}\text{NNaO}_{10}\text{S}$   $[\text{M}+\text{Na}]^+$  678.2349, found 678.2343.

### General procedure

To a stirred solution of *p*-octyloxyphenyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-1-thio- $\beta$ -D-glucopyranoside **1a** and 1-*O*-methyl 2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside **2** (0.2 mmol, 1 equiv) in the presence of MS 4A in  $\text{CH}_2\text{Cl}_2$  (1 ml, 0.2 M), TfOH (0.4 mmol, 2 equiv) was added at  $-78^\circ\text{C}$ . PIFA (0.2 mmol, 1 equiv) was subsequently added to the reaction mixture with stirring, and then stirred for an additional 3 h under the same conditions, while the reaction was monitored by TLC. A saturated aqueous solution of  $\text{NaHCO}_3$  was added to the mixture when the reaction was completed. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , then evaporated to dryness. The crude residue was purified by column chromatography on silica gel (eluent: *n*-hexane/  $\text{CH}_2\text{Cl}_2$ ) to give the pure glycosylation product **3a** in 77% yield. The PhSSPh was produced as a by product.

### Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-D-glucopyranosyl- $\beta$ (1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside (3a)

mp  $150\text{--}151^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.78 (3H, s), 1.96 (3H, s), 2.02 (3H, s), 3.10 (3H, s), 3.16 (1H, t,  $J = 9.2$  Hz), 3.31 (1H, dd,  $J = 10.0, 3.6$  Hz), 3.57-3.60 (2H, m), 3.75-3.82 (2H, m), 4.01-4.12 (3H, m), 4.23-4.35 (4H, m), 4.50 (1H, d,  $J = 12.0$  Hz), 4.58 (1H, d,  $J = 11.2$  Hz), 4.65 (1H, d,  $J = 11.6$  Hz), 4.78 (1H, d,  $J = 11.8$  Hz), 5.11 (1H, t,  $J = 11.2$  Hz), 5.36 (1H, d,  $J = 8.4$  Hz), 5.72 (1H, dd,  $J = 11.4, 8.8$  Hz), 6.94-6.96 (2H, m), 7.14-7.24 (15H, m), 7.48 (2H, brs) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.4, 20.6, 20.8, 54.4, 55.0, 62.0, 68.7, 68.9, 69.1, 70.7, 71.9, 73.4, 74.7, 75.7, 77.5, 79.6, 81.8, 97.8, 98.3, 123.5, 127.5, 127.6, 127.7, 127.9, 127.93, 128.1, 128.3 (2C), 128.4, 131.1, 134.1, 137.7, 138.1, 138.6, 169.4, 170.2, 170.8 ppm; IR (KBr): 2930, 1752, 1719, 1455, 1386, 1366, 1234, 1071, 1043, 913, 745, 700, 647  $\text{cm}^{-1}$ ; HRFABMS calcd for  $\text{C}_{48}\text{H}_{51}\text{NNaO}_{15}$   $[\text{M}+\text{Na}]^+$  904.3156, found 904.3151.

### (-)-Menthyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido- $\beta$ -D-glucopyranoside (5a)

mp  $130\text{--}131^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.68 (6H, d,  $J = 3.4$  Hz), 0.78 (3H, d,  $J = 7.3$  Hz), 0.85-1.22 (4H, m), 1.50-1.70 (5H, m), 1.84 (3H, s), 2.01 (3H, s), 2.06 (3H, s), 3.37 (1H, td,  $J = 10.8, 4.0$  Hz), 3.80-3.85 (1H, m), 4.12-4.29 (3H, m), 5.11 (1H, t,  $J = 9.2$  Hz), 5.37 (1H, d,  $J = 8.4$  Hz), 5.79 (dd, 1H,  $J = 10.7, 8.8$  Hz), 7.70-7.74 (2H, m), 7.83-7.85 (2H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  15.4, 20.5, 20.66, 20.7, 20.8, 22.0, 22.9, 25.0, 31.2, 34.0, 40.3, 47.3, 54.9, 62.5, 69.5, 70.9, 71.4, 78.4, 95.7, 123.5 (2C), 134.2 (2C), 169.6, 170.2, 170.7 ppm; IR (KBr): 2954, 2923, 2870, 1751, 1719, 1387, 1260, 1231, 1102, 1079, 1035, 806, 748, 721  $\text{cm}^{-1}$ ; HRFABMS: calcd for  $\text{C}_{30}\text{H}_{39}\text{NNaO}_{10}$   $[\text{M}+\text{Na}]^+$  596.2472, found 596.2466.

### Cholestan-3 $\beta$ -yl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido- $\beta$ -D-glucopyranoside (5b)

mp 167-170 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.57 (3H, s), 0.62 (3H, s), 0.81-1.83 (40H, m), 1.88 (3H, s), 2.00 (3H, s), 2.08 (3H, s), 3.47-3.52 (1H, m), 3.80-3.86 (1H, m), 3.99-4.14 (1H, m), 4.24-4.32 (2H, m), 5.13 (1H, t,  $J = 9.2$  Hz), 5.43 (1H, d,  $J = 8.8$  Hz), 5.75 (1H, t,  $J = 9.2$  Hz), 7.71-7.73 (2H, m), 7.83-7.85 (2H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.9, 12.2, 18.6, 20.5, 20.6, 20.8, 21.1, 22.5, 22.8, 23.8, 24.1, 28.0, 28.2, 28.6, 29.1, 32.0, 34.3, 35.36, 35.4, 35.7, 36.1, 36.9, 39.5, 39.9, 42.5, 44.5, 54.2, 54.9, 56.2, 56.4, 62.2, 69.1, 70.9, 71.6, 79.5, 96.9, 123.6 (2C), 131.4 (2C), 134.2 (2C), 169.5, 170.2, 170.8 ppm; IR (KBr): 2927, 2867, 1748, 1716, 1387, 1229, 1074, 1040, 833, 803, 749, 721, 678  $\text{cm}^{-1}$ ; HRFABMS calcd for  $\text{C}_{47}\text{H}_{67}\text{NNaO}_{10}$   $[\text{M}+\text{Na}]^+$  828.4663, found 828.4568.

#### **2-Adamantyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido- $\beta$ -D-glucopyranoside (5c)**

mp 187-190 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22-1.35 (4H, m), 1.46-1.76 (10H, m), 1.81 (3H, s), 2.00 (3H, s), 2.09 (3H, s), 3.74 (1H, brs), 3.84 (1H, dq,  $J = 7.8, 2.4$  Hz), 4.12 (1H, dd,  $J = 12.0, 2.4$  Hz), 4.31-4.39 (2H, m), 5.16 (1H, t,  $J = 9.3$  Hz), 5.40 (1H, d,  $J = 8.2$  Hz), 5.82 (1H, dd,  $J = 10.7, 9.2$  Hz), 7.70-7.72 (2H, m), 7.82-7.84 (2H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.5, 20.7, 20.8, 26.9, 27.0, 30.9, 31.2, 31.3, 33.2, 36.1, 36.5, 37.2, 54.8, 62.1, 69.2, 70.7, 71.6, 81.4, 96.3, 123.5 (2C), 131.3 (2C), 134.3 (2C), 169.5, 170.3, 170.8 ppm; IR (KBr): 2911, 2852, 1761, 1716, 1387, 1226, 1043, 903, 817, 791, 746, 722, 684  $\text{cm}^{-1}$ ; HRFABMS calcd for  $\text{C}_{30}\text{H}_{35}\text{NNaO}_{10}$   $[\text{M}+\text{Na}]^+$  592.2159, found 592.2153.

#### **1-Adamantyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido- $\beta$ -D-glucopyranoside (5d)**

mp 185-189 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22-1.25 (4H, m), 1.45-1.57 (7H, m), 1.67-1.70 (4H, m), 1.83 (3H, s), 2.00 (3H, s), 2.06 (3H, s), 3.83-3.88 (1H, m), 4.08-4.12 (1H, m), 4.25-4.31 (2H, m), 5.09 (1H, t,  $J = 9.6$  Hz), 5.54 (1H, d,  $J = 8.0$  Hz), 5.82 (1H, dd,  $J = 10.7, 9.2$  Hz), 7.71-7.74 (2H, m), 7.83-7.85 (2H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.5, 20.7, 20.8, 29.7, 30.5 (2C), 35.9 (2C), 42.1 (2C), 55.0, 62.5, 69.4, 70.8, 71.3, 75.8, 91.6, 123.6 (2C), 131.4 (2C), 134.2 (2C), 169.6, 170.2, 170.7 ppm; IR (KBr): 2911, 2854, 1749, 1718, 1386, 1275, 1262, 1226, 1068, 1031, 971, 789, 750, 724  $\text{cm}^{-1}$ ; HRFABMS calcd for  $\text{C}_{30}\text{H}_{35}\text{NNaO}_{10}$   $[\text{M}+\text{Na}]^+$  592.2159, found 592.2153.

#### **(-)-Bornyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido- $\beta$ -D-glucopyranoside (5e)**

mp 130-134 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.45-0.58 (2H, m), 0.72 (3H, s), 0.74 (3H, s), 0.79 (3H, s), 0.96-1.02 (1H, m), 1.22-1.41 (3H, m), 1.58-1.64 (1H, m), 2.82 (3H, s), 2.00 (3H, s), 2.08 (3H, s), 3.79-3.83 (1H, m), 3.89-3.93 (1H, m), 4.13 (1H, dd,  $J = 12.0, 2.4$  Hz), 4.28-4.33 (2H, m), 5.15 (1H, t,  $J = 9.6$  Hz), 5.25 (1H, d,  $J = 8.0$  Hz), 5.82 (1H, dd,  $J = 10.8, 8.8$  Hz), 7.70-7.73 (2H, m), 7.83-7.85 (2H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.2, 18.8, 19.6, 20.5, 20.7, 20.8, 26.3, 27.9, 35.8, 44.6, 47.7, 49.1, 54.9, 62.2, 69.4, 70.6, 71.6, 83.6, 96.9, 123.5 (2C), 131.3 (2C), 134.3 (2C), 169.5, 170.2, 170.8 ppm; IR (KBr): 2955, 2874, 1749, 1718, 1386, 1368, 1226, 1076, 1033, 752, 722, 675  $\text{cm}^{-1}$ ; HRFABMS calcd for  $\text{C}_{30}\text{H}_{37}\text{NNaO}_{10}$   $[\text{M}+\text{Na}]^+$  594.2315, found 594.2310.

**Methyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-*D*-glucopyranosyl)- $\beta$ -(1  $\rightarrow$  6)-2,3,4-tri-*O*-benzoyl- $\alpha$ -*D*-glucopyranoside (3b)<sup>55</sup>**

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>):  $\delta$  1.84 (3H, s), 2.00 (3H, s), 2.03 (3H, s), 3.05 (3H, s), 3.59 (1H, dd,  $J = 7.3, 3.4$  Hz), 3.86 (1H, d,  $J = 7.5$  Hz), 4.05 (1H, d,  $J = 10.5$  Hz), 4.10–4.13 (m, 2H), 4.31 (dd, 1H,  $J = 12.5, 4.5$  Hz), 4.36 (t, 1H,  $J = 10.0, 9.0$ , Hz), 4.70 (1H, d,  $J = 3.4$  Hz), 5.05 (1H, dd,  $J = 3.9, 2.4$  Hz), 5.14 (1H, t,  $J = 9.3$  Hz), 5.25 (1H, t,  $J = 9.8$  Hz), 5.40 (1H, d,  $J = 8.8$  Hz), 5.80 (1H, t,  $J = 9.8$  Hz), 5.99 (1H, t,  $J = 9.8$  Hz), 7.19–7.49 (7H, m), 7.71–7.90 (12H, m) ppm.

**Methyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-*D*-glucopyranosyl)- $\beta$ -(1  $\rightarrow$  4)-2,3,6-tri-*O*-benzoyl- $\alpha$ -*D*-galactopyranoside (3c)**

mp 87–89 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.81 (3H, s), 1.94 (3H, s), 2.04 (3H, s), 3.33 (3H, s), 3.61–3.65 (1H, m), 3.95–3.99 (1H, m), 4.07–4.12 (1H, m), 4.30 (1H, t,  $J = 6.4$  Hz), 4.37–4.49 (2H, m), 4.58–4.62 (1H, m), 4.70–4.71 (1H, m), 4.96 (1H, d,  $J = 3.4$  Hz), 5.10 (1H, t,  $J = 9.3$  Hz), 5.21–5.25 (1H, m), 5.46–5.50 (2H, m), 5.77 (1H, dd,  $J = 8.8, 2.0$  Hz) 7.34–7.33 (6H, m), 7.42 (3H, t,  $J = 7.3$  Hz), 7.50–7.56 (2H, m), 7.70–7.74 (6H, m), 8.03 (2H, d,  $J = 6.8$  Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 20.3, 20.4, 20.5, 54.7, 55.2, 61.4, 63.9, 67.9, 68.0, 68.7, 70.1, 71.5, 73.3, 77.4, 97.4 (2C), 123.7 (2C), 128.1 (2C), 128.2, 128.3, 129.0 (2C), 129.5 (6C), 129.9 (3C), 131.3 (2C), 133.0 (2C), 133.2, 133.8 (2C), 165.0, 165.9, 166.7, 169.3, 169.9, 170.7 ppm; IR (KBr): 3055, 2987, 2685, 2358, 2306, 1718, 1387, 1259, 1044, 896, 765 cm<sup>-1</sup>; MS (MALDI-TOF):  $m/z$  (%): calcd for C<sub>48</sub>H<sub>45</sub>NNaO<sub>18</sub>: 946.25; [M+Na]<sup>+</sup>; found: 946.17 (100), 947.15 (50), 948.15 (26).

**2-Deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-*D*-glucopyranosyl- $\beta$ -(1  $\rightarrow$  6)-1,2:3,4-di-*O*-isopropylidene- $\alpha$ -*D*-galactopyranoside (3d)<sup>56</sup>**

mp 207–210 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.98 (6H, s), 1.19 (3H, s), 1.35 (3H, s), 1.82 (3H, s), 1.98 (3H, s), 2.07 (3H, s), 3.64–3.66 (2H, m), 3.83–3.96 (3H, m), 4.04–4.14 (2H, m), 4.25–4.37 (3H, m), 5.06 (1H, d,  $J = 5.4$  Hz), 5.14 (1H, dd,  $J = 10.0, 9.5$  Hz), 5.40 (1H, d,  $J = 8.3$  Hz), 5.80 (1H, dd,  $J = 10.7, 9.1$  Hz), 7.66–7.68 (2H, m), 7.78–7.79 (2H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  20.4, 20.6, 20.7, 24.1, 24.6, 25.3, 25.8, 54.5, 62.0, 67.4, 69.0, 70.1, 70.5, 70.6, 70.8, 71.5, 76.7, 77.0, 77.3, 95.9, 99.3, 107.9, 109.3, 123.4, 133.7, 169.5, 170.1, 170.7 ppm.

**Methyl (2,3,4,6-tetra-*O*-acetyl-*D*-glucopyranosyl)- $\beta$ -(1  $\rightarrow$  6)-2,3,4-tri-*O*-benzoyl- $\alpha$ -*D*-glucopyranoside (3e)<sup>57</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.99 (9H, s), 2.07 (3H, s), 3.43 (3H, s), 3.66–3.70 (2H, m), 4.01–4.06 (2H, m), 4.19–4.25 (2H, m), 4.56 (1H, d,  $J = 8.3$  Hz), 5.00–5.07 (2H, m), 5.17–5.22 (3H, m), 5.39 (1H, t,  $J = 9.8$  Hz), 6.10 (1H, t,  $J = 9.8$  Hz), 7.24–7.52 (9H, m), 7.81–7.83 (2H, m), 7.90–7.95 (4H, m) ppm.

**Methyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-tetrachlorophthalimido-*D*-glucopyranosyl)- $\beta$ -(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzoyl- $\alpha$ -*D*-galactopyranoside (3f)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.88 (3H, s), 1.95 (3H, s), 2.03 (3H, s), 3.37 (3H, s), 3.60-3.62 (1H, m), 3.96-3.99 (1H, m), 4.09-4.11 (1H, m), 4.32 (1H, bs), 4.40 (1H, dd,  $J = 8.8, 8.0$  Hz), 4.45-4.50 (1H, m), 4.56-4.63 (1H, m), 4.71 (1H, bs), 4.91 (1H, bs), 5.14 (1H, t,  $J = 9.2$  Hz), 5.28-5.35 (1H, m), 5.45-5.52 (2H, m), 5.72 (1H, t,  $J = 9.8$  Hz), 7.24-7.31 (5H, m), 7.43-7.55 (4H, m), 7.72-7.77 (4H, m), 8.03 (2H, d,  $J = 9.8$  Hz) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.5, 20.6, 55.4, 55.6, 61.3, 63.6, 67.6, 68.1, 68.5, 70.2, 71.7, 73.4, 97.1, 97.7, 127.7, 128.3, 128.4, 128.9, 129.5, 129.8, 129.9, 133.1, 133.3, 133.6, 140.1, 165.6, 166.0, 166.7, 169.3, 170.4, 170.7 ppm.

**Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-*D*-galactopyranosyl- $\beta$ -(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- $\alpha$ -*D*-glucopyranoside (3g)**

mp 58-67 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.77 (3H, s), 1.98 (3H, s), 2.10 (3H, s), 3.10 (3H, s), 3.16 (1H, t,  $J = 9.2$  Hz), 3.31 (1H, dd,  $J = 9.6, 3.6$  Hz), 3.55-3.60 (2H, m), 3.77 (1H, t,  $J = 9.2$  Hz), 4.00-4.15 (5H, m), 4.30-4.33 (2H, m), 4.50-4.66 (4H, m), 4.78 (1H, d,  $J = 11.8$  Hz), 5.28 (1H, d,  $J = 8.4$  Hz), 5.40 (1H, d,  $J = 3.4$  Hz), 5.73 (1H, dd,  $J = 11.2, 3.2$  Hz), 6.96-6.98 (2H, m), 7.14-7.24 (15H, m), 7.45 (2H, brs) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.5, 20.7, 20.72, 51.2, 54.9, 61.3, 66.6, 68.0, 68.7, 69.1, 70.8, 73.3, 74.7, 75.6, 77.6, 79.7, 81.8, 97.8, 98.7, 123.4 (2C), 127.6, 127.7, 127.86, 127.9 (3C), 128.0 (3C), 128.2 (3C), 128.4 (3C), 134.1 (2C), 137.7, 138.1, 138.6, 169.8, 170.3, 170.4 ppm; IR (KBr): 3029, 2926, 1752, 1717, 1454, 1389, 1368, 1235, 1131, 1070, 1052, 950, 798, 750, 724  $\text{cm}^{-1}$ ; HRFABMS calcd for  $\text{C}_{48}\text{H}_{51}\text{NNaO}_{15}$  [ $\text{M}+\text{Na}$ ] $^+$  904.3156, found 904.3151.

**Methyl 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-*D*-glucopyranosyl- $\beta$ -(1 $\rightarrow$ 6)-[2-deoxy-2-phthalimido-3,4-di-*O*-benzyl-*D*-glucopyranosyl]- $\beta$ -(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- $\alpha$ -*D*-glucopyranoside (6a)<sup>58</sup>**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.83 (3H, s), 1.98 (3H, s), 2.07 (3H, s), 3.18 (3H, s), 3.14-3.20 (1H, m), 3.35 (1H, dd,  $J = 9.6, 3.2$  Hz), 3.42 (1H, t,  $J = 8.4$  Hz), 3.51-3.62 (3H, m), 3.78-3.86 (3H, m), 3.95-4.43 (12H, m), 4.55 (1H, d,  $J = 12.0$  Hz), 4.59 (1H, dd,  $J = 10.2, 3.2$  Hz), 4.68 (1H, t,  $J = 8.4$  Hz), 4.80 (1H, d,  $J = 10.8$  Hz), 5.08 (1H, d,  $J = 8.4$  Hz), 5.16 (1H, t,  $J = 9.2$  Hz), 5.58 (1H, d,  $J = 8.0$  Hz), 5.73 (1H, dd,  $J = 10.8, 8.8$  Hz), 6.74-6.91 (8H, m), 7.12-7.82 (22H, m), 7.81-7.94 (3H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.5, 20.6, 20.7, 54.6, 54.9, 55.6, 61.8, 67.4, 67.9, 68.9, 69.1, 70.7, 71.9, 73.4, 74.6, 74.7, 75.0, 75.4, 75.5, 79.0, 79.5, 79.7, 81.8, 97.4, 98.0, 123.0, 123.6, 127.3, 127.4, 127.5, 127.7, 127.8, 128.0, 128.1, 128.2, 128.4, 128.5, 131.3, 133.5, 134.2, 137.4, 137.8, 138.2, 138.8, 169.4, 170.2, 170.8 ppm.

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