Supplementary Materials

Chemoenzymatic Synthesis of New Aromatic Esters of Mono- and Oligosaccharides

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Figure S1. Chemical structures of aromatic compounds tested as substrates for lipases.
Table S1. Transesterification reaction conversions of α-D-glucose, sucrose, lactose, inulin with methyl 3-(4-hydroxyphenyl) propionate (HPPME) catalyzed by native lipases after 72 hours of reaction.

| Carbohydrate | Biocatalyst               | Conversion(%) |
|--------------|---------------------------|---------------|
| α-D-glucose  | *Pseudomonas fluorescens* | 2             |
|              | *Candida antarctica B*    | 1             |
|              | *Thermomyces lanuginosus* | 6             |
|              | *Pseudomonas fluorescens* | 1             |
| sucrose      | *Candida antarctica B*    | < 1           |
|              | *Thermomyces lanuginosus* | 4             |
|              | *Pseudomonas fluorescens* | 1             |
| lactose      | *Candida antarctica B*    | < 1           |
|              | *Thermomyces lanuginosus* | 3             |
|              | *Pseudomonas fluorescens* | 1             |
| inulin       | *Candida antarctica B*    | < 1           |
|              | *Thermomyces lanuginosus* | 4             |

Figure S2. MALDI-TOF MS spectrum of the reaction mixture from α-methyl-glucose acylation with HPPA catalyzed by Novozyme 435, after 72 h, containing the 6-O-[3-(4-hydroxyphenyl)propionyl] methyl-α-D-glucoside product.
Figure S3. MALDI-TOF MS spectrum of the reaction mixture from α-methyl-glucose acylation with HPPA catalyzed by Novozyme 435, after 72 h, containing 6-O-[3-(4-hydroxyphenyl) propionyl] octyl-β-D-glucoside (2), after 72 h.

Figure S4. FT-IR spectra of α-methyl-glucose (a); HPPA (b) and 6-O-[3-(4-hydroxyphenyl) propionyl] methyl-α-D-glucoside (c). Insert is zoom in of the spectrum at wavenumber 2000–600 cm⁻¹.
Figure S5. FT-IR spectra of β-octyl-glucose (a); HPPA (b) and 6-O-[3-(4-hydroxyphenyl)propionyl] octyl-β-D-glucoside (c). Insert is zoom in of the spectrum at wavenumber 2000–600 cm⁻¹.

Figure S6. ¹H-NMR spectrum of 6-O-[3-(4-hydroxyphenyl)propionyl] methyl-α-D-glucoside (collected in DMSO-d₆).
Figure S7. $^{13}$C-NMR spectrum of 6-O-[3-(4-hydroxyphenyl) propionyl] methyl-α-D-glucoside (collected in DMSO-d$_6$).

Figure S8. 135DEPT-NMR spectrum of 6-O-[3-(4-hydroxyphenyl)propionyl] methyl-α-D-glucoside (collected in DMSO-d$_6$).
Figure S9. $^1$H-NMR spectrum of 6-O-[3-(4-hydroxyphenyl)propionyl] octyl-β-D-glucoside (2).

Figure S10. $^{13}$C-NMR spectrum of 6-O-[3-(4-hydroxyphenyl)propionyl] octyl-β-D-glucoside (2).
Figure S11. 13CDEPT-NMR spectrum of 6-O-[3-(4-hydroxyphenyl)propionyl] octyl-β-D-glucoside (2).

Figure S12. 1H-NMR spectrum of 1,2-O-isopropylidene-glucofuranose.
Figure S13. $^{13}$C-NMR spectrum of 1,2-O-isopropylidene-glucofuranose.

Figure S14. 135DEPT-NMR spectrum of 1,2-O-isopropylidene-glucofuranose.
**Figure S15.** FT-IR spectra of glucose (a) 1,2-O-isopropylidenglucose (b) 1,2:5,6-di-O-isopropylidenglucose (c) Insert is zoom in of the spectrum at wavenumber 2000–600 cm$^{-1}$.

**Figure S16.** FT-IR spectra of D-glucose (a) isopropylidene-D-glucose (b) 6-O-[3-(4-hydroxyphenyl)propionyl]-1,2-O-isopropylidene-D-glucofuranose (3). Insert is zoom in of the spectrum at wavenumber 2000–600 cm$^{-1}$.
Figure S17. MALDI TOF MS spectrum of the reaction mixture after acylation of 1,2-O-isopropylidene sucrose with HPPA, catalyzed by Novozyme 435 after 72 h.

Figure S18. $^{13}$C-NMR spectrum of 6-O-[3-(4-hydroxyphenyl)propionyl]-1,2-O-isopropylidene-D-glucofuranose.
Figure S19. $^1$H-NMR spectrum of 6-O-[3-(4-hydroxyphenyl)propionyl]-1,2-O-isopropylidene-D-glucofuranose.

Figure S20. 135DEPT NMR spectrum of 6-O-[3-(4-hydroxyphenyl)propionyl]-1,2-O-isopropylidene-D-glucofuranose.
Figure S21. FT-IR spectra of (a) sucrose; (b) 2,1′,4,6-di-O-isopropylidene sucrose (4).

Figure S22. $^{13}$C-NMR spectrum of 2,1′,4,6-di-O-isopropylidene sucrose (4).
Figure S23. $^1$H-NMR spectrum of 2,1′:4,6-di-O-isopropylidene sucrose (4).

Figure S24. 135 DEPT NMR spectrum of 2,1′:4,6-di-O-isopropylidene sucrose (4).

\[ \beta\text{-D-lactose} \xrightarrow{i} 2,3,5,6,4′,6′\text{-tri-O-isopropylidene lactose dimethyl acetal} + 2,3,5,6,3′,4′\text{-tri-O-isopropylidene lactose dimethyl acetal}(5) \]
Scheme S1. Reaction scheme of 2,3;5,6:4′,6′-tri-O-isopropylidene dimethyl lactose and 2,3;5,6:3′,4′-tri-O-isopropylidene dimethyl lactose (5) synthesis by acetalization of lactose with 2,2-dimethoxypropane, in the presence of p-toluenesulfonic acid, at reflux, 24 h.

Figure S25. $^{13}$C-NMR spectrum of 2,3;5,6:3′,4′-tri-O-isopropylidene dimethyl lactose (5).

Figure S26. $^1$H-NMR spectrum of 2,3;5,6:3′,4′-tri-O-isopropylidene dimethyl lactose (5).
Figure S27. 135DEPT NMR spectrum of 2,3:5,6:3′,4′-tri-O-isopropylidene dimethyl lactose (5).

Figure S28. MALDI-TOF MS spectrum of the reaction mixture after esterification of 2,3:5,6:3′, 4′-tri-O-isopropylidene dimethyl lactose with HPPA, in tert-butanol at 60 °C in the presence of Novozyme 435.