## **Supporting Information**

- Figure S1. HPLC Chromatogram (silica, CHCl<sub>3</sub>:MeOH = 98:2, 1 ml/min) of aglycone
  UV = 254 nm, t<sub>R</sub> = 4.453 min.
- 2. Figure S2. HPLC Chromatogram (silica, CHCl<sub>3</sub>: MeOH = 95:5, 1 ml/min) of aglycone **6**, UV = 254 nm,  $t_R$  = 3.592 min.
- 3. Figure S3. HPLC Chromatogram (silica, CHCl<sub>3</sub>, 1 ml/min) of aglycone 7, UV = 270 nm,  $t_R = 8.223 \ \text{min}$
- 4. Figure S4. Calibration curve of **5** based on the HPLC analysis.
- 5. Figure S5. Calibration curve of **6** based on the HPLC analysis.
- 6. Figure S6. Calibration curve of **7** based on the HPLC analysis.
- 7. Figure S7. Time-dependent reduction profile of TEMPO *O*-galactoside **3** with 60  $\mu$ L of  $\beta$ -galactosidase in 0.1 M PBS (pH 7.4) at 323 K. Each data represents mean  $\pm$  S.D., n = 3.
- 8. Table S1. Pseudo-first-order rate constants k (min<sup>-1</sup>) for the initial rate of reduction of TEMPO O-galactosides with 60  $\mu$ L of  $\beta$ -galactosides at 323 K, based on the Figure S7. (mean  $\pm$  S.D., n = 3)
- 9. Figure S8. ESR spectrum of 2.
- 10. Figure S9. ESR spectrum of 3.
- 11. Figure S10. ESR spectrum of **4**.

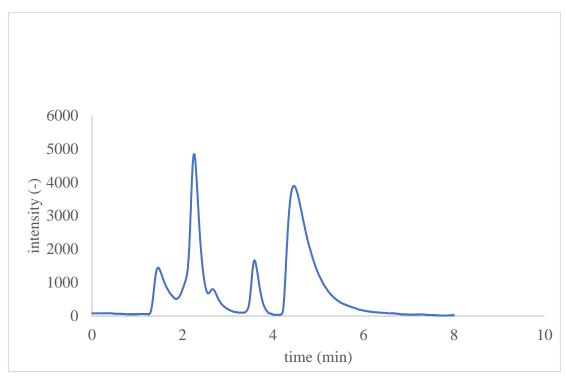


Figure S1. HPLC Chromatogram (silica, CHCl $_3$ :MeOH = 98:2, 1 ml/min) of aglycone 5, UV = 254 nm,  $t_R$  = 4.453 min.

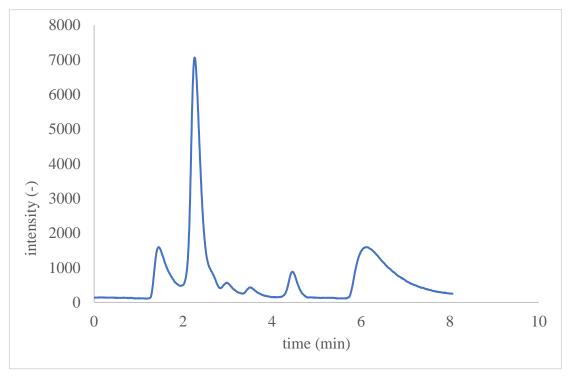


Figure S2. HPLC Chromatogram (CHCl $_3$ :MeOH = 95:5, 1 ml/min) of aglycone **6**, UV = 254 nm,  $t_R$  = 3.59 min.

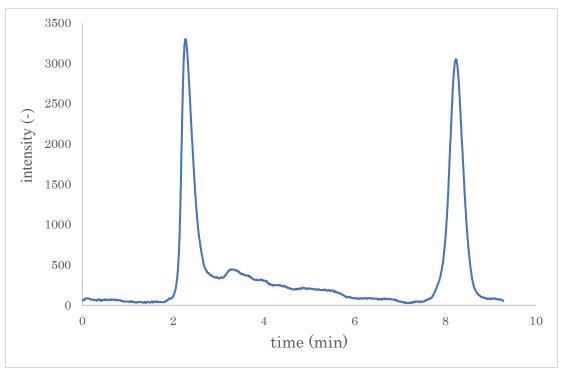


Figure S3. HPLC Chromatogram (CHCl<sub>3</sub>, 1 ml/min) of aglycone **7**, UV = 270 nm,  $t_R$  = 8.22 min.

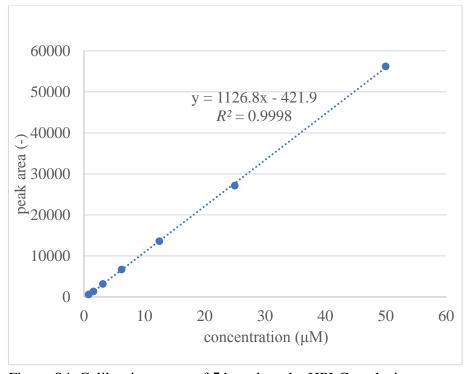


Figure S4. Calibration curve of **5** based on the HPLC analysis.

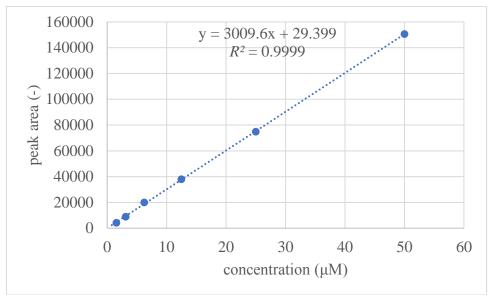


Figure S5. Calibration curve of **6** based on the HPLC analysis.

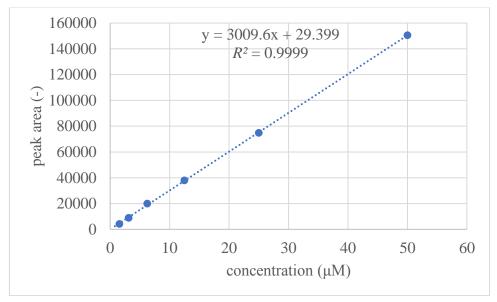


Figure S6. Calibration curve of **7** based on the HPLC analysis.

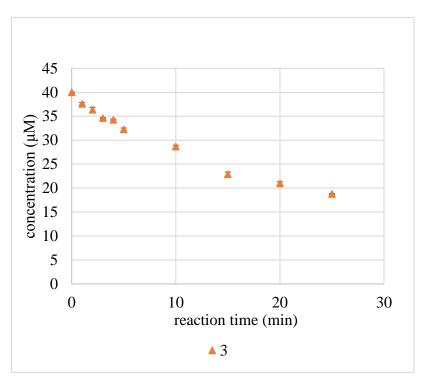


Figure S7. Time-dependent reduction profile of TEMPO *O*-galactoside **3** with 60  $\mu$ L of  $\beta$ -galactosidase in 0.1 M PBS (pH 7.4) at 323 K. Each data represents mean  $\pm$  S.D., n = 3.

Table S1. Pseudo-first-order rate constants k (min<sup>-1</sup>) for the initial rate of reduction of TEMPO O-galactoside **3** with 60 μL of  $\beta$ -galactosidase at 323 K, based on the Figure S7. (mean  $\pm$  S.D., n = 3)

Compound	k (min <sup>-1</sup> )	$R^2$
3	$4.2 \times 10^{-2} \pm 1.9 \times 10^{-3}$	0.99

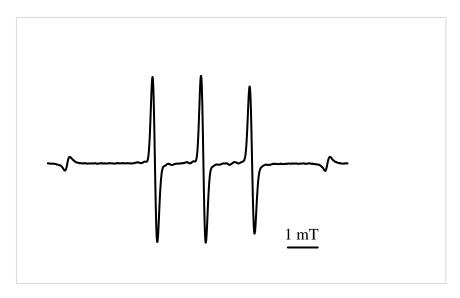


Figure S8. ESR spectrum of 2.

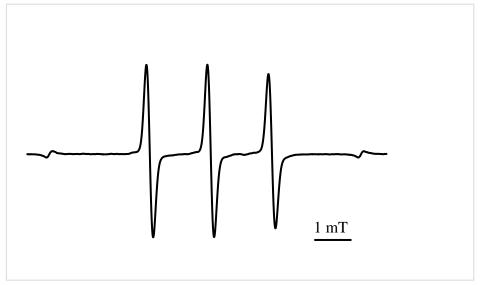


Figure 9. ESR spectrum of 3.

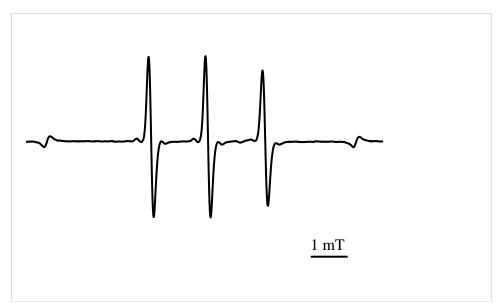


Figure 10. ESR spectrum of 4.