Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

for

Oligosaccharide sensing with chromophore-modified curdlan in aqueous media

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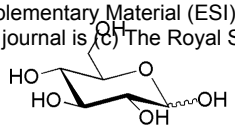
Experimental

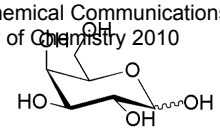
Instruments

^{1}H NMR spectra at 600 MHz, ^{13}C NMR spectra at 150 MHz, and 2D-COSY, HSQC, and HMBC spectra at 600 MHz were recorded in DMSO-d_6 on a Varian INOVA-600 instrument. IR spectrum was recorded on a JASCO FT/IR-460 plus spectrometer. UV/vis and CD spectra were measured in a quartz cell (with light path of 1 cm) by using JASCO V-560 and J-720WI spectrometers equipped with an ETC-505T temperature controller.

Materials

Curdlan, purchased from Wako, was dried under high vacuum at 80 °C prior to use. D-Glucose (**1**), L-glucose (**2**), D-galactose (**3**), D-mannose (**4**), D-allose (**5**), D-fructose (**6**), D-sorbose (**7**), D-tagatose (**8**), D-fucose (**9**), D-ribose (**10**), 2-deoxy-D-ribose (**11**), D-arabinose (**12**), L-arabinose (**13**), sucrose (**14**), lactose (**15**), D-maltose (**16**), D-trehalose (**17**), D-turanose (**18**), D-cellobiose (**19**), D-raffinose (**20**), D-melezitose (**21**), D-maltotriose (**22**), stachyose (**23**), and acarbose (**24**) were purchased from Wako, SIGMA, Across Organics or Alfa Aesar and used without further purification.


glucose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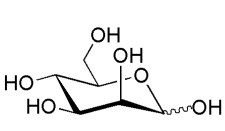
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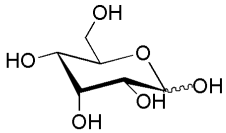
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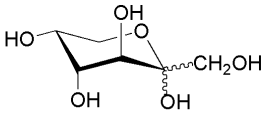
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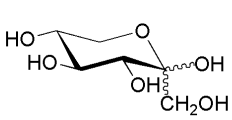
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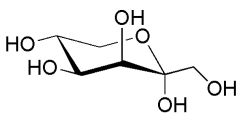
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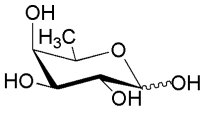
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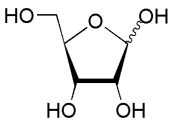
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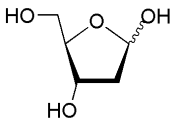
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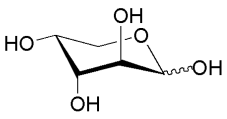
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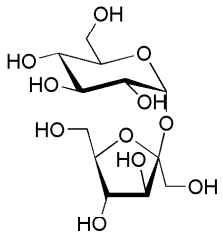
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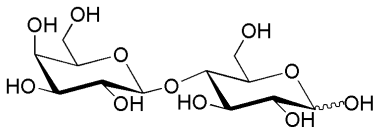
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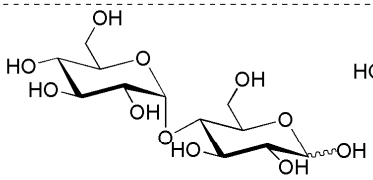
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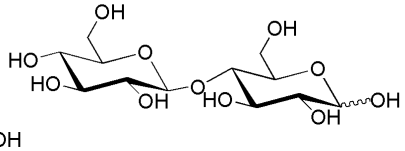
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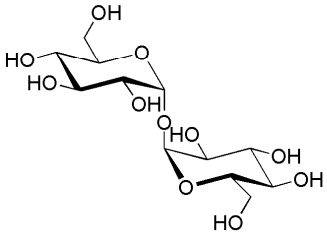
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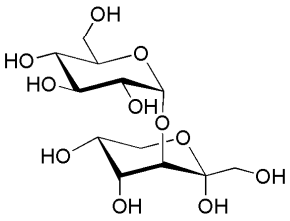
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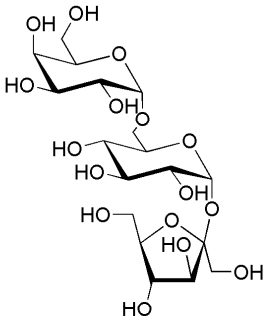
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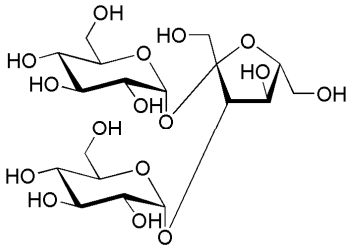
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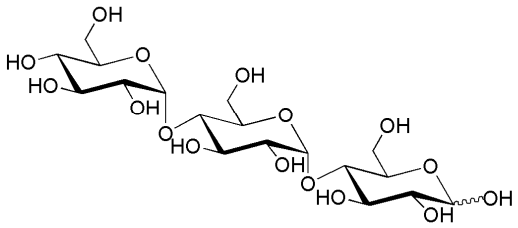
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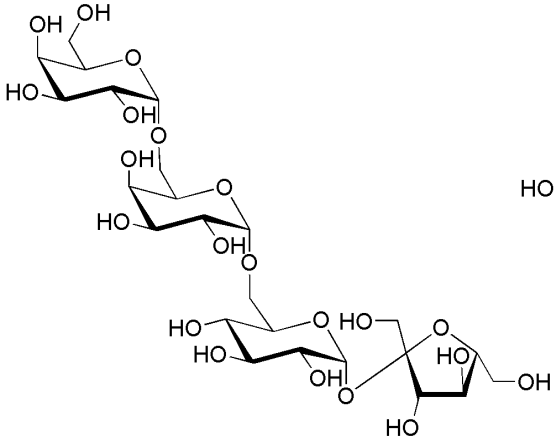
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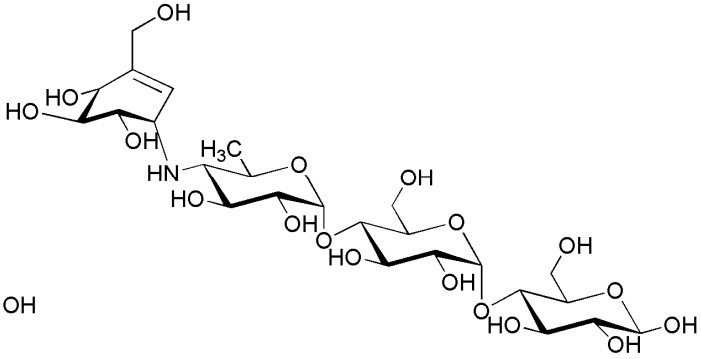
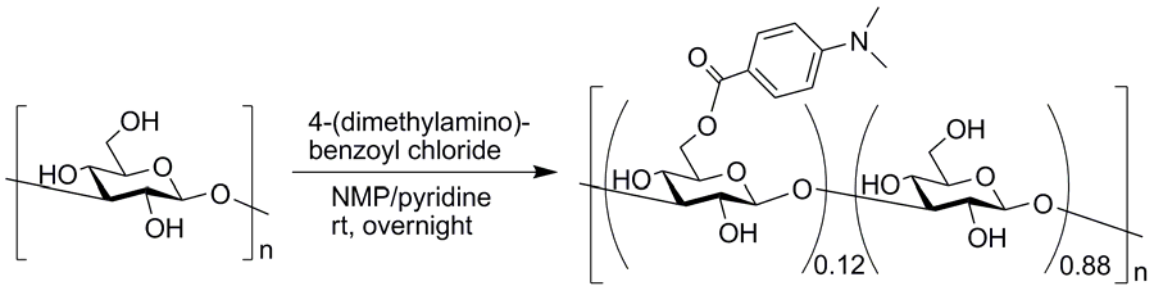

acarbose

Synthesis and Characterization of Modified Curdlan



DABz-Cur
92% yield

6-*O*-(4-(Dimethylamino)benzoyl)curdlan (DABz-Cur). Curdlan (344 mg, 2.12 mmol based on the glucose unit) was added to dry *N*-methyl-2-pyrrolidinone (NMP) (20 mL) placed in a 50 mL three-necked flask. The resulting highly viscous solution was heated to 100 °C and stirred overnight at that temperature, to which 4-(dimethylamino)benzoyl chloride (195 mg, 1.06 mmol) dissolved in dry NMP (10 mL) and pyridine (2 mL) were added. The reaction mixture was stirred for 16 h at room temperature and then slowly poured onto methanol (400 mL) to give a white precipitate, which was collected, washed with methanol (2 × 20 mL, centrifuged at 3000 rpm for 15 min), and then dried under high vacuum to afford 6-*O*-(4-(dimethylamino)benzoyl)curdlan (**DABz-Cur**) as white solid (352 mg, 1.96 mmol in monomer unit) in 92% yield. ^{1}H NMR (DMSO-d_6, 600 MHz, 15 ºC) δ_H 7.82 (H_a), 6.70 (H_b), 5.29 (-OH), 5.19 (-OH), 4.90 (-OH), 4.64 (-OH, $H_{6b'}$), 4.51 (H1,1'), 4.12 ($H_{6a'}$), 3.69 (H_{6b}), 3.52-3.39 (H_{6a}, $H_{3/3'}$), 3.30-3.17 ($H_{5/5'}$, $H_{2/2'}$, $H_{4/4'}$), 3.00 (Me-N); ^{13}C NMR (DMSO-d_6, 150 MHz, 15 ºC) δ_C 165.8 (C=O), 153.4 (C_c), 131.2 (C_a), 115.6 (C_d), 110.7 (C_b), 103.1 ($C_{1/1'}$), 86.2 ($C_{3/3'}$), 76.4 ($C_{5/5'}$), 72.9 ($C_{2/2'}$), 68.5 ($C_{4/4'}$), 63.2 ($C_{6a'/b'}$), 60.9 ($C_{6a/b}$), Me-N (overlapped with DMSO peak by HSQC spectrum); Anal. Calcd for $(C_{59}H_{92}NO_{43}\cdot 2H_2O)_n$: C, 46.03; H, 6.29; N, 0.91%; Found: C, 45.99; H, 6.28; N, 1.09%; IR (KBr) ν 3412, 2904, 1684, 1605, 1532, 1437, 1373, 1316, 1284, 1188, 1160, 1081, 1043, 991, 891, 767 cm^{-1}.

^{1}H and ^{13}C NMR spectra and HSQC spectrum of 6-*O*-(4-(dimethylamino)benzoyl)curdlan (DABz-Cur)

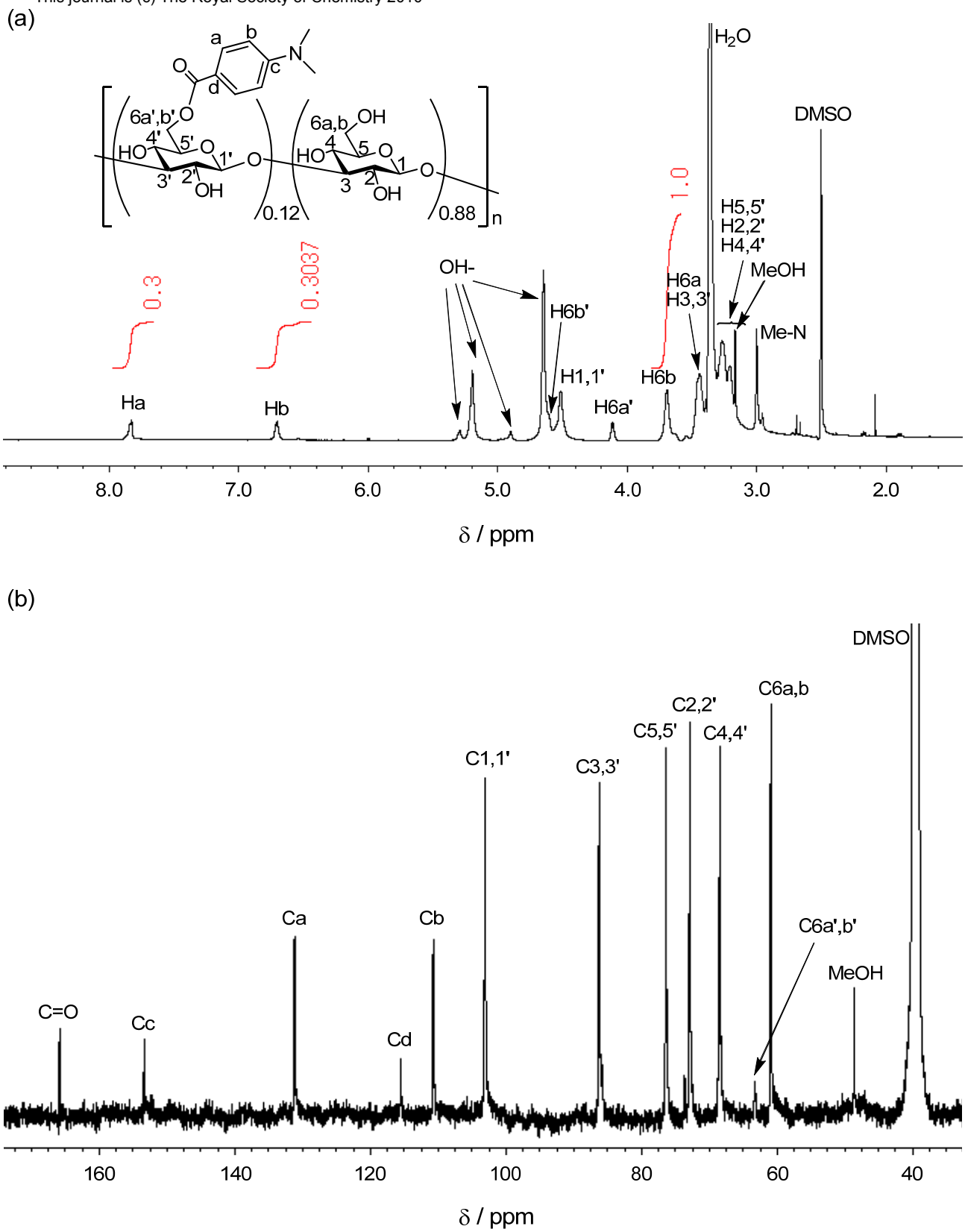


Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra of 6-*O*-(4-(dimethylamino)-benzoyl)curdlan (**DABz-Cur**) in DMSO-d_6 at room temperature.

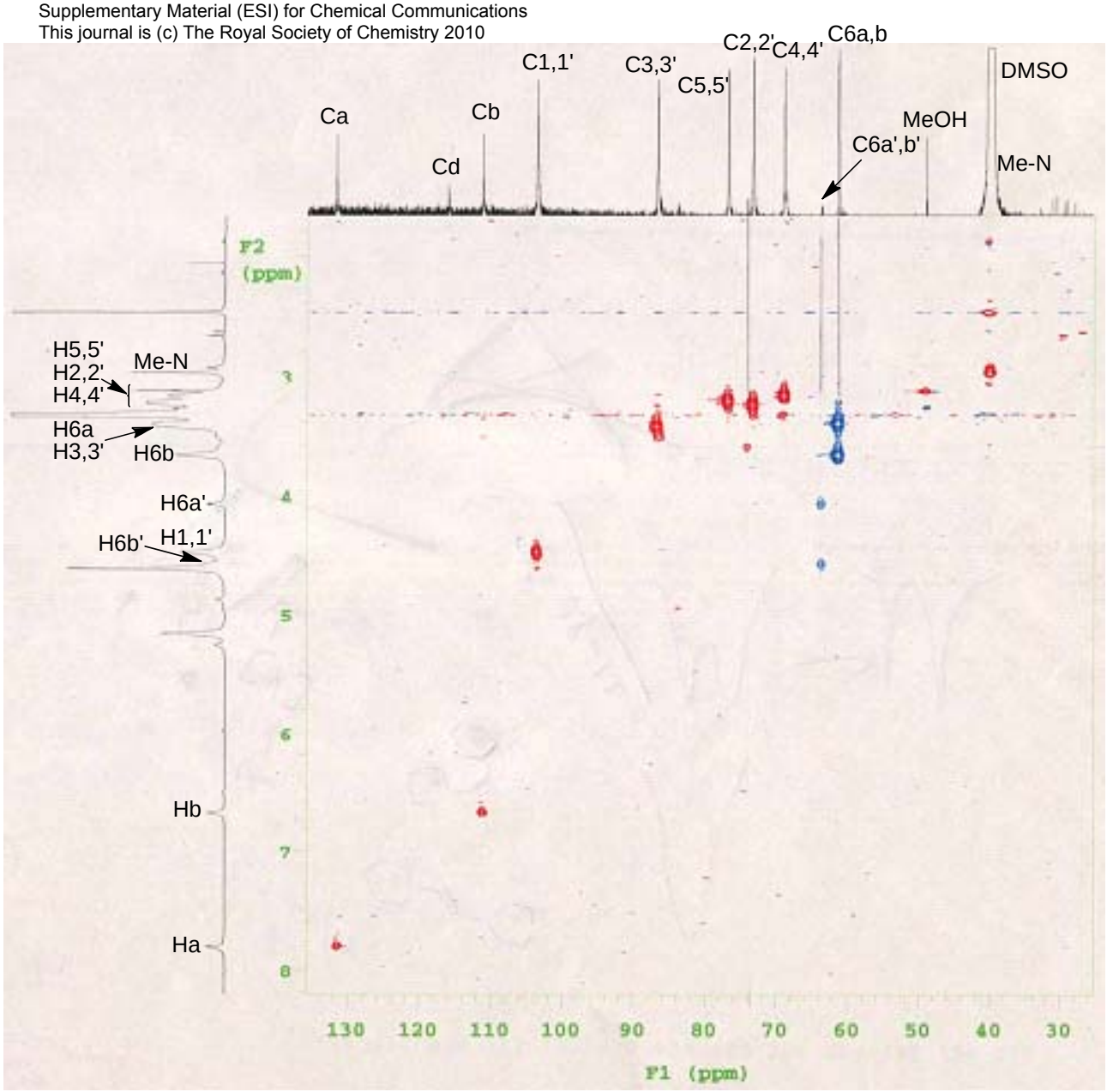


Figure S2. HSQC spectrum of **DABz-Cur** in DMSO-d_6 at room temperature.

CD spectral changes upon addition of acarbose, stachyose, D-maltose, D-fructose, sucrose, and lactose

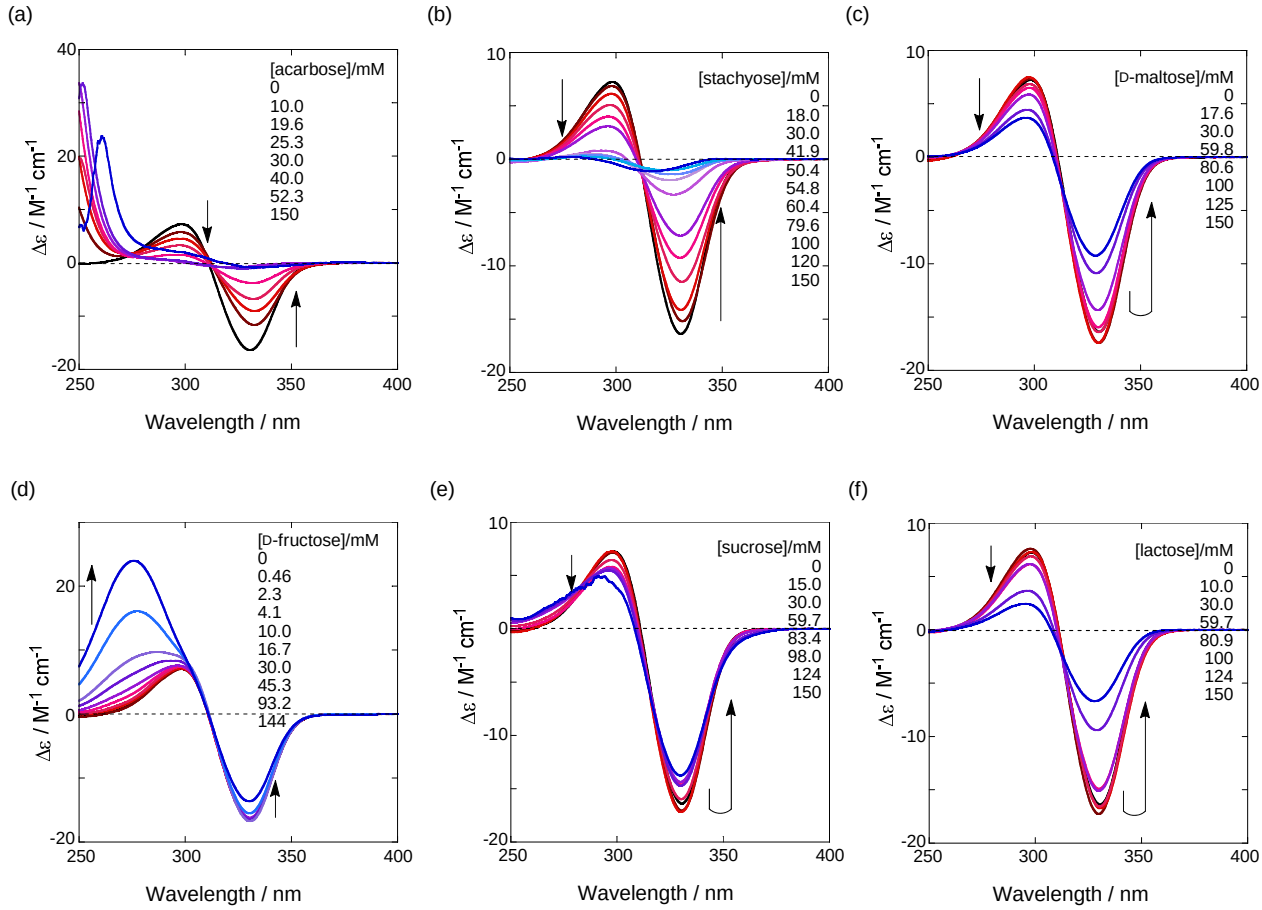


Figure S3. CD spectral changes of **DABz-Cur** (0.462 mM in monomer unit) in 1:9 DMSO-H_2O upon addition of (a) acarbose (0-150 mM), (b) stachyose (0-150 mM), (c) D-maltose (0-150 mM), (d) D-fructose (0-144 mM), (e) sucrose (0-150 mM), and (f) lactose (0-150 mM) at 25 °C.

The new band emerging at 250-280 nm in Figure S3a is assignable to the CD of added acarbose, while the increasing CD intensity at 250-300 nm for fructose (Figure S3d) is due to the equilibrium to the keto form.

CD intensity change as a function of the concentration of D-fructose, sucrose, and lactose

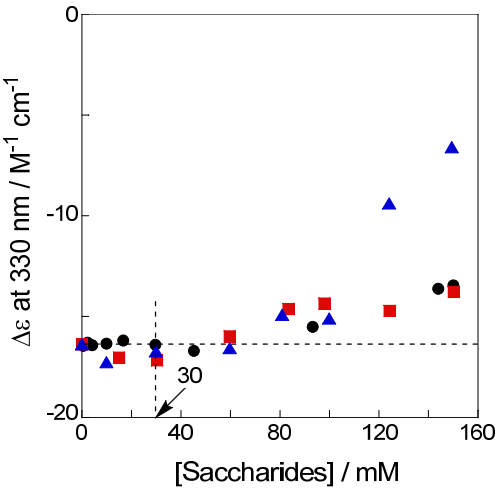


Figure S4. Plots of molar ellipticity at 330 nm of **DABz-Cur** (0.462 mM in monomer unit) in 1:9 DMSO-H_2O as a function of disaccharide concentration; D-fructose (circle), sucrose (square), and lactose (triangle).