Title	Bioinspired aryldiazonium carbohydrate coatings: reduced adhesion of foulants at polymer and stainless steel surfaces in a marine environment
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Publication date	2017-12-04
Original Citation	Myles, A., Haberlin, D., Esteban-Tejeda, L., Angione, M. D., Browne, M. P., Hoque, M. K., Doyle, T. K., Scanlan, E. M. and Colavita, P. E. (2017) 'Bioinspired aryldiazonium carbohydrate coatings: reduced adhesion of foulants at polymer and stainless steel surfaces in a marine environment', ACS Sustainable Chemistry and Engineering, 6(1), pp. 1141-1151. doi:10.1021/acssuschemeng.7b03443
Type of publication	Article (peer-reviewed)
Link to publisher's version	10.1021/acssuschemeng.7b03443
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Download date	2024-05-07 19:19:04
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Supplementary Information

Bioinspired Aryldiazonium Carbohydrate Coatings: Reduced Adhesion of Foulants at Polymer and Stainless Steel Surfaces in a Marine Environment

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Total number of Pages: 13
Total number of Figures: 6
Total number of Reaction Schemes: 2

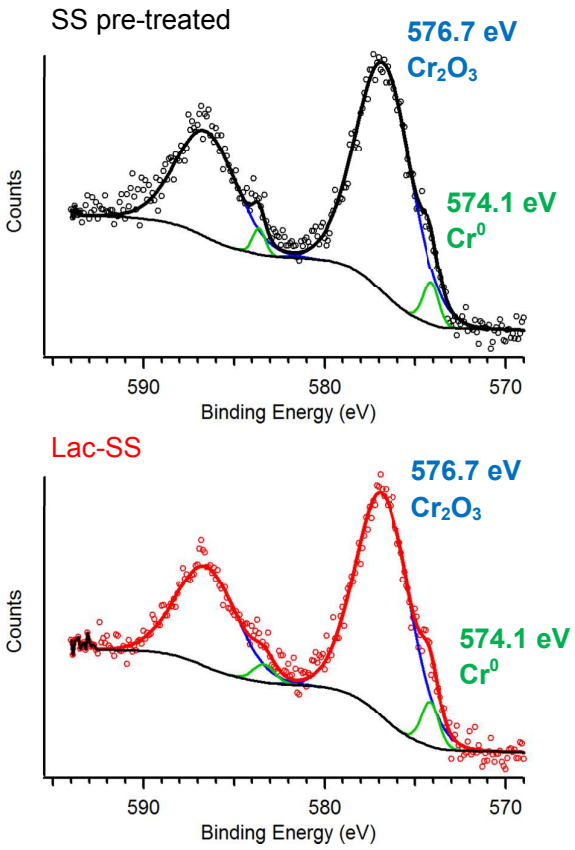


Figure S1. Cr 2p region showing fits to Cr_2O_3 and Cr^0 contributions; doublet peaks were fixed in a 2:1 ratio. The energy split was found to be 9.8 eV in good agreement with reference values.[1]

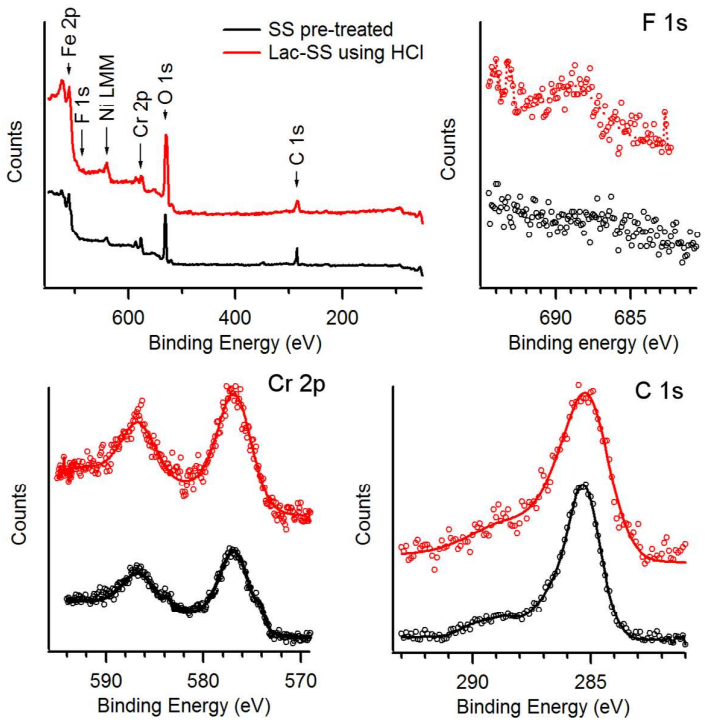
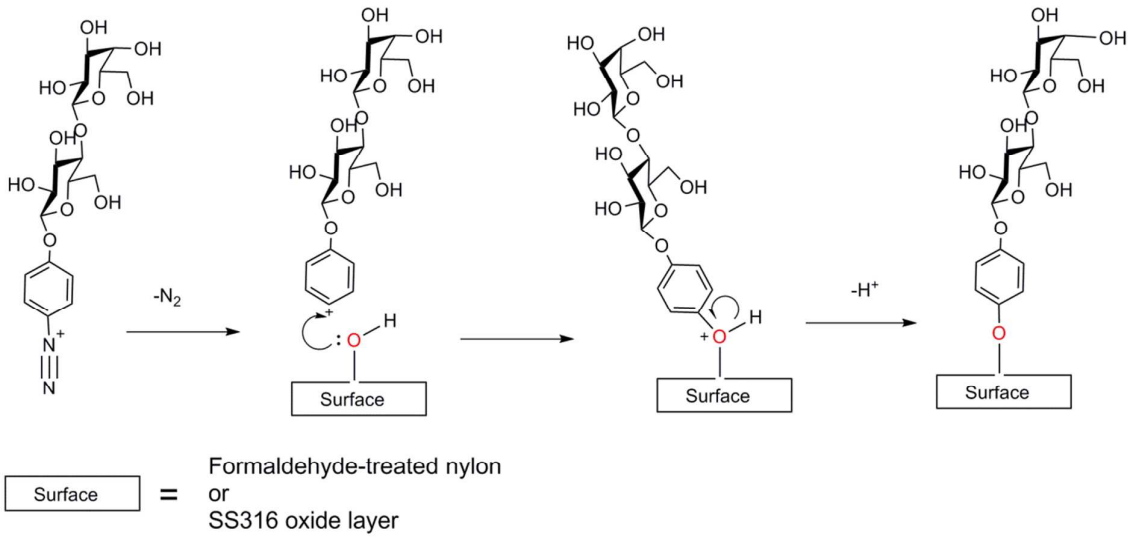


Figure S2. Survey spectrum, C 1s, F 1s and Cr 2p regions (50 eV pass energy) of a SS316 sample modified with 2-fluoro-4-aminophenol-β-D-lactopyranose using HCl in place of HBF_4 under identical functionalization conditions. Spectra are compared to that of a pre-treated SS316 surface. The presence of a F 1s peak confirms that functionalization takes place with chloride counterions in the aryldiazonium salt, and that the F 1s signal in Figure 5 of the main text does not arise from contamination with tetrafluoroborate.



Scheme S1. Proposed S_N1 mechanism for the reaction of aryldiazonium salts with –OH groups at surfaces, based on the well understood hydrolysis reaction in solution.[2] Both nylon 6 and SS316 display –OH groups after the pre-treatment process described in the Experimental Section in the main text.

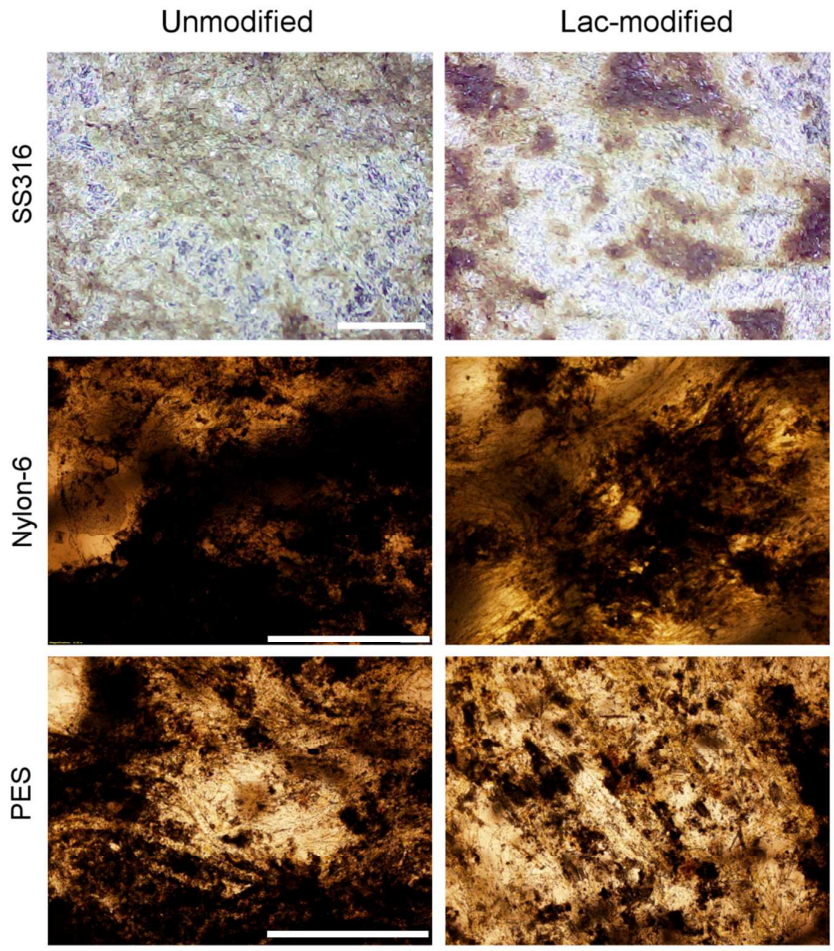


Figure S3. Optical microscope images of SS316, nylon-6 and PES coupons extracted after 20 day immersion in coastal waters prior to rinsing; scalebar = 1 mm. Left column: typical images for coupons that had not undergone coating with lactosides prior to immersion. Right column: typical images for coupons that had undergone coating with lactosides prior to immersion. All samples displayed biomass accumulation and the density of foulants appears to be similar independently of surface coating.

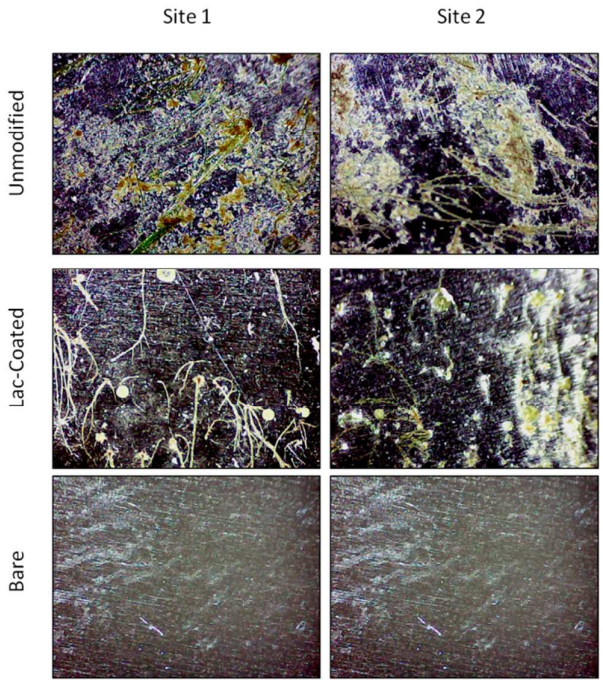


Figure S4. Optical microscope images of SS316 coupons extracted after 20 day immersion in coastal waters at sites 1 and 2 (see Figure 1); samples were rinsed under the same conditions prior to imaging. Top row: coupons not coated with an aryldiazonium layer of glycosides. Middle row: coupons coated with a layer of lactosides prior to immersion. Bottom row: a coupon sample as supplied by the vendor, without undergoing any immersion tests. All samples displayed biomass accumulation but the density of foulants is higher on unmodified than on lactoside-modified samples. Similar conclusions can be drawn based on images of samples from either site. All images have a width of 6.2 mm.

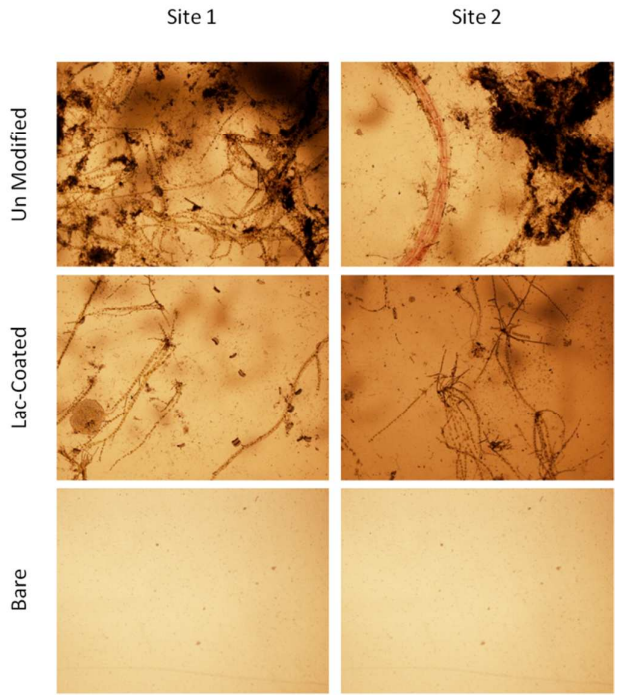


Figure S5. Optical microscope images of Nylon-6 coupons extracted after 20 day immersion in coastal waters at sites 1 and 2 (see Figure 1); samples were rinsed under the same conditions prior to imaging. Top row: coupons not coated with an aryldiazonium layer of glycosides. Middle row: coupons coated with a layer of lactosides prior to immersion. Bottom row: a coupon sample as supplied by the vendor, without undergoing any immersion tests. All samples displayed biomass accumulation but the density of foulants is higher on unmodified than on lactoside-modified samples. Similar conclusions can be drawn based on images of samples from either site. All images have a width of 2.6 mm.

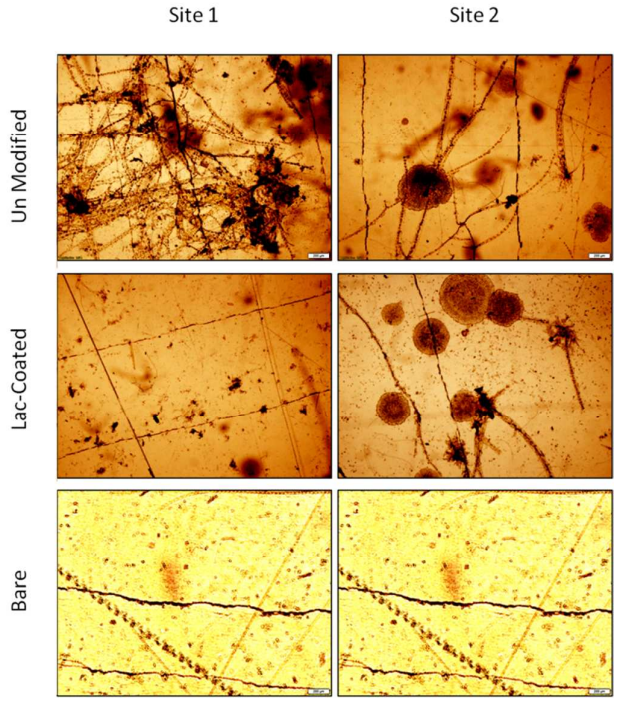
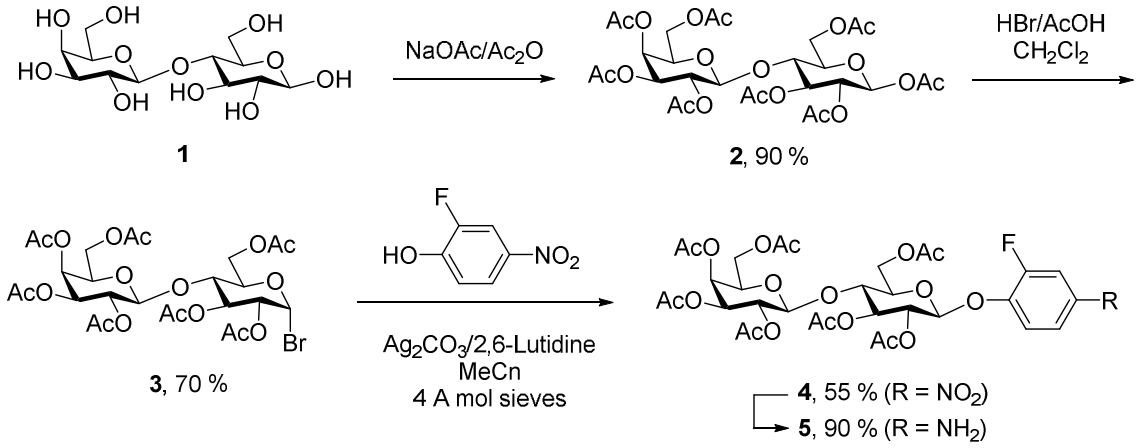


Figure S6. Optical microscope images of PES coupons extracted after 20 day immersion in coastal waters at sites 1 and 2 (see Figure 1); samples were rinsed under the same conditions prior to imaging. Top row: coupons not coated with an aryldiazonium layer of glycosides. Middle row: coupons coated with a layer of lactosides prior to immersion. Bottom row: a coupon sample as supplied by the vendor, without undergoing any immersion tests. All samples displayed biomass accumulation but the density of foulants is higher on unmodified than on lactoside-modified samples. Similar conclusions can be drawn based on images of samples from either site. All images have a width of 2.6 mm.

Text S1. Preparation of fluorinated precursor compound

Commercially available D-Lactose **1** was peracetylated on treatment with sodium acetate and acetic anhydride to give **2**. The product was converted to the corresponding lactosyl bromide **3** upon treatment with hydrogen bromide in acetic acid.[3] Glycosylation of the bromide with 2-fluro-4-nitrophenol furnished **4** exclusively as the β-anomer which was reduced through catalytic hydrogenation to give **5**. The synthesis of the deprotected sugar required for XPS analysis was prepared as previously reported.[3]



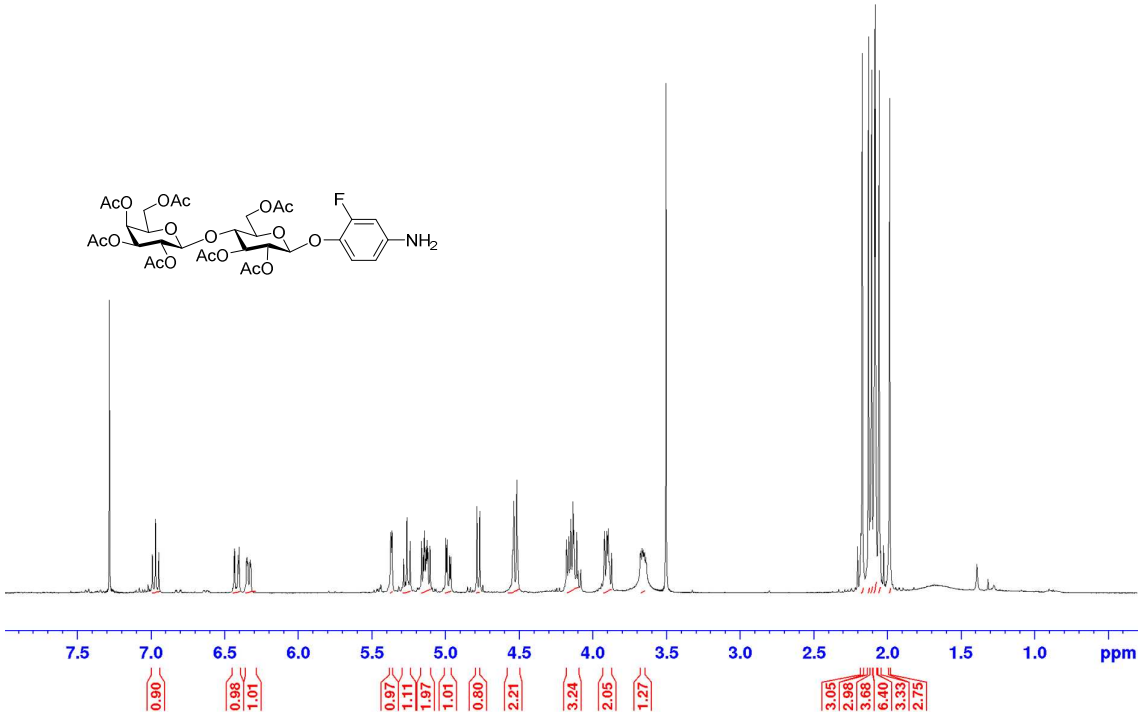
Scheme S2. Synthetic strategy for the preparation of fluorinated lactose grafting agent **5** from lactose.

2-Fluoro-4-aminophenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside 5

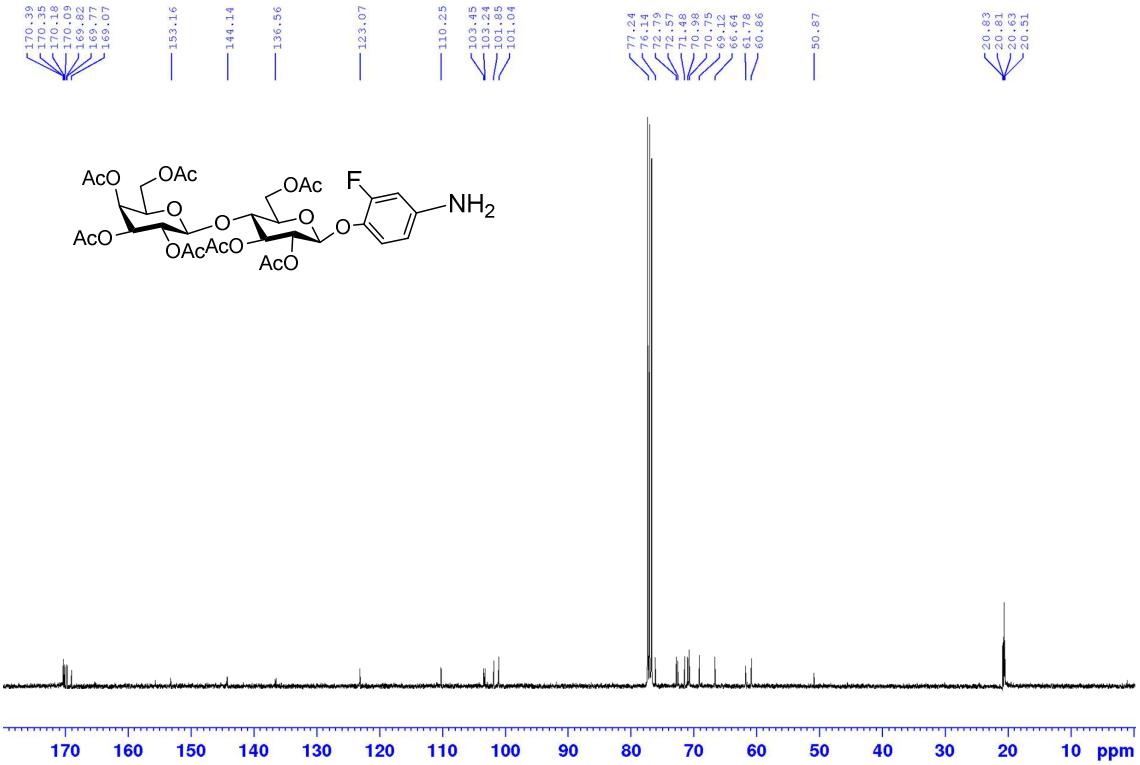
Lactosyl derivative **4** (2.0 g, 2.58 mmol) was dissolved in MeOH (50 ml) and the solution was degassed under N_2 for 10 min. Pd(OH) on carbon (50 mg) as added and the mixture was further degassed for an additional 10 min. The flask was evacuated and subsequently saturated with H_2 over a period of 2 h and monitored via TLC until complete consumption of the starting material was observed. The reaction mixture was filtered through a 0.4 micron filter and the solvent removed to give a solid product (1.7 g; 90%). ^{1}H-NMR (400 MHz, $CDCl_3$), δ ppm. 6.97 (1H, t, *J* = 8.6 Hz, H5-ar), 6.42 (1H, dd, *J* = 12.1 Hz, *J*= 2.89 Hz, H6-ar), 6.33 (1H, m, H3-ar), 5.38 (1H, d, *J* = 2.7 Hz, H4-Gal), 5.27 (1H, d, *J* = 8.67 Hz, H3-Glc), 5.13-5.16 (2H, m, H2-glc,H2-gal), 4.49 (1H, m, H3-gal), 4.74 (1H, d, *J* = 7.7 Hz, H1-glc), 4.49 (2H, m, H1-gal, H6-glc), 4.16-4.03 (3H, m, H6'-glc, H6-gal, H6'-gal), 3.90-3.83 (2H, m, H5-gal, H4-glc), 3.65 (1H, m, H5-glc), 2.17, 2.13, 2.11, 2.09, 2.08, 2.06, 1.93 (21H, m, 7 x CH_3, OAc) ; ^{13}C-NMR (100 MHz, $CDCl_3$), δ ppm. 170.4, 170.3, 170.2, 170.1, 169.8, 169.8, 169.1 (7 x C=O, OAc), 153.2 (C2 aromatic), 144.1 (C4 aromatic), 136.5 (C1 aromatic), 123.0 (C3 aromatic), 110.3 (C6 aromatic), 103.3 (C5 aromatic), 101.8 (C1-glc), 101.0 (C1-gal), 76.4 (C4-glc), 72.8 (C5-glc), 72.6 (C3-glc), 71.5 (C2-glc), 71.0 (C3-gal), 70.8 (C5-gal), 69.1 (C2-gal), 66.6 (C4-gal), 61.8 (C6-glc), 60.9 (C6-gal) 20.8, 20.8, 20.6, 20.6, 20.6, 20.6, 2.05 (7 x CH_3, OAc). ^{19}F-NMR (376.4 MHz, $CDCl_3$), δ ppm. -139.10 (1F, s, F1-ar); [M+Na]+ calculated for $C_{32}H_{40}FNNaO_{18}$ = 768.2122, Found 768.2117.

NMR ^{1}H, ^{13}C, ^{19}F of compound 5:

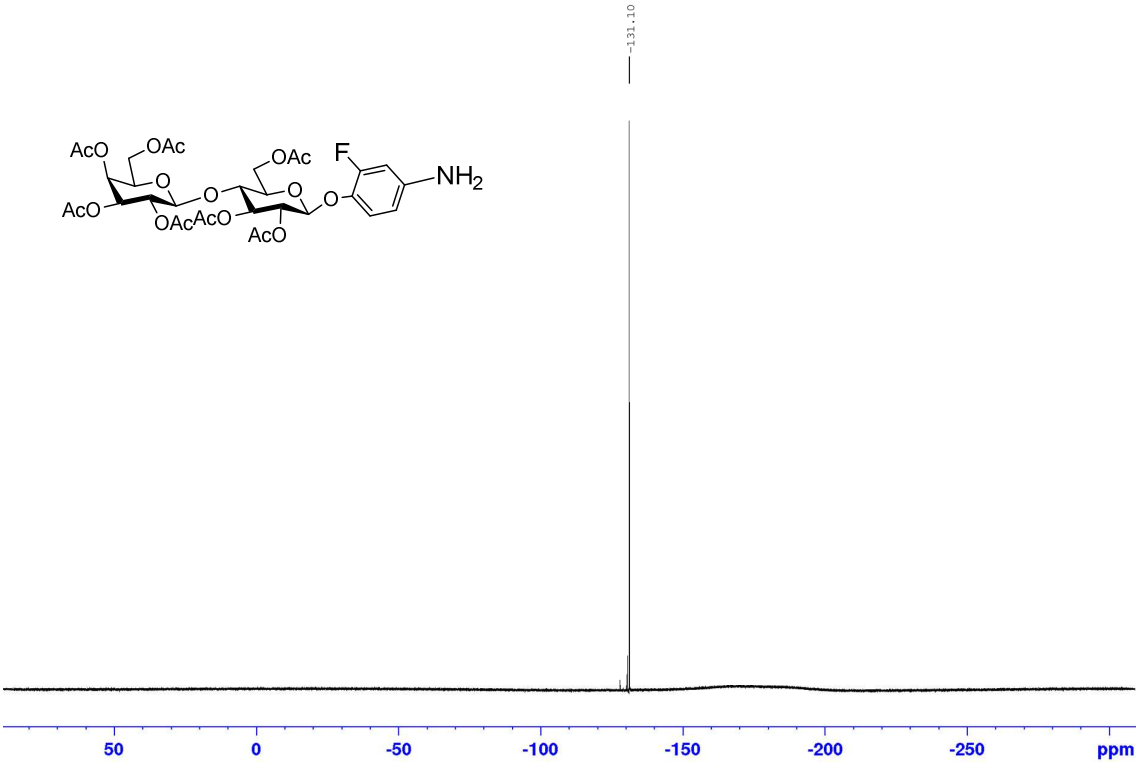
(Compound 5) ^{1}H NMR spectrum, 400 MHz, ($CDCl_3$)



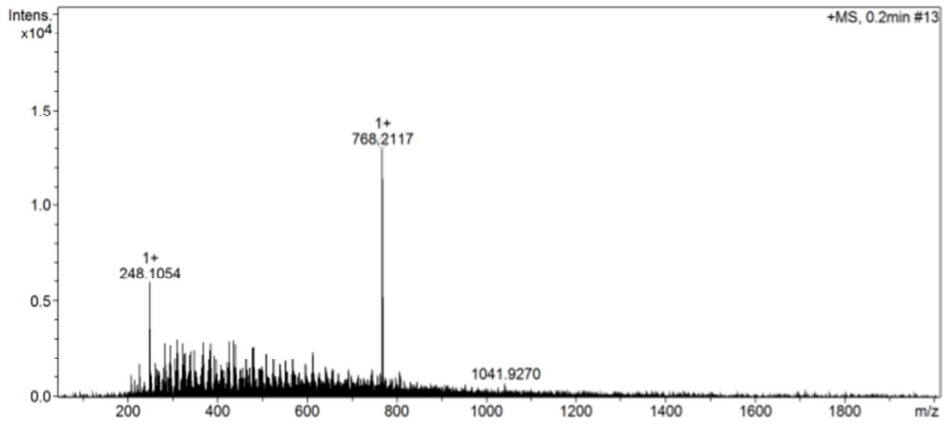
(Compound 5) ^{13}C NMR spectrum, 100 MHz, ($CDCl_3$)



(Compound 5) ^{19}F NMR spectrum, 376.4 MHz, ($CDCl_3$)



(Compound 5) ESI+ Mass Spectrum



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
768.211656	1	C32H40FNNaO18	768.212162	0.5	0.7	12.5	ok	even	36.0

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