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Electronic Supplementary Information

for

Phase-selective gelators based on closed-chain glucose derivatives: their applications in the removal of dissolved aniline/nitrobenzene, and toxic dyes from contaminated water

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Table S1: Gelation abilities of compounds 1a-e and 2a-e in organic liquids[a]

Solvent	State									
	1a	1b	1c	1d	1e	2a	2b	2c	2d	2e
Aniline	G	G	Gs	S	S	Gs	Gs	S	S	S
N,N-Dimethylaniline	Gs	Gs	S	S	S	Gs	G	S	S	S
Nitrobenzene	Gs	G	Gs	S	S	Gs	G	S	Gs	Gs
p-Anisaldehyde	G	G	G	S	S	G	G	S	Gs	S
Methanol	Is	P	P	G	Is	G	S	G	G	Is
Ethanol	G	G	G	G	Is	G	G	G	G	Is
Benzyl alcohol	G	G	G	Gs	G	Gs	G	S	Gs	S
n-Hexane	G	P	G	Gs	Is	G	G	G	G	Is
Cyclohexane	G	Gs	S	S	Is	G	G	G	Gs	Is
Acrylic acid	G	G	G	G	P	G	G	G	G	S
Ethyl acetate	Gs	Gs	S	S	S	S	G	S	S	S
Ethyl acetoacetate	G	G	G	Gs	S	G	G	G	G	S
Methyl benzoate	S	Gs	S	Gs	S	Gs	G	S	S	S
DMSO	Gs	Gs	G	G	Gs	Gs	Gs	S	S	Gs

[a] The mixture of 30 mg of each gelator and 0.3 mL of a known liquid was heated until the gelator was dissolved completely, and then cooled to room temperature to form gel. G = gel state; S = solution state; P = precipitate; Is = insoluble state; Gs = unstable gel state. All gels formed at room temperature are stable at least for one month.

Table S2: Minimum gelation concentration (MGC) and gel-to-sol transition temperature (*T*g) of the resulting gels of gelators 1a-e and 2a-e in organic liquids

Solvents	MGC (wt%)[a]/*T*g (°C)									
	1a	1b	1c	1d	1e	2a	2b	2c	2d	2e
Aniline	2.4/38	3.6/39	—	—	—	—	—	—	—	—
N,N-Dimethylaniline	—	—	—	—	—	—	4.2/29	—	—	—
Nitrobenzene	—	3.2/35	—	—	—	—	4.0/31	—	—	—
p-Anisaldehyde	2.8/41	1.6/42	3.6/45	—	—	5.1/37	3.0/36	—	—	—
Methanol	—	—	—	5.1/65	—	1.5/62	—	1.2/58	1.9/56	—
Ethanol	2.3/65	1.9/64	2.8/64	5.1/63	—	1.5/51	2.1/51	2.0/48	2.1/47	—
Benzyl alcohol	2.0/48	2.1/48	2.8/46	—	3.7/31	—	2.4/38	—	—	—
n-Hexane	2.3/42	—	4.3/40	—	—	2.2/47	2.8/45	1.9/43	3.9/41	—
Cyclohexane	3.4/29	—	—	—	—	1.9/58	3.2/56	1.8/53	—	—
Acrylic acid	1.6/61	1.5/63	1.2/60	1.7/57	—	2.4/49	1.7/48	3.8/45	2.0/44	—
Ethyl acetate	—	—	—	—	—	—	4.9/30	—	—	—
Ethyl acetoacetate	3.2/52	1.8/50	2.8/47	—	—	3.9/44	3.9/42	4.9/44	4.1/40	—
Methyl benzoate	—	—	—	—	—	—	4.6/31	—	—	—
DMSO	—	—	1.1/45	1.7/40	—	—	—	—	—	—

[a] wt % represents the mass percentage concentration.

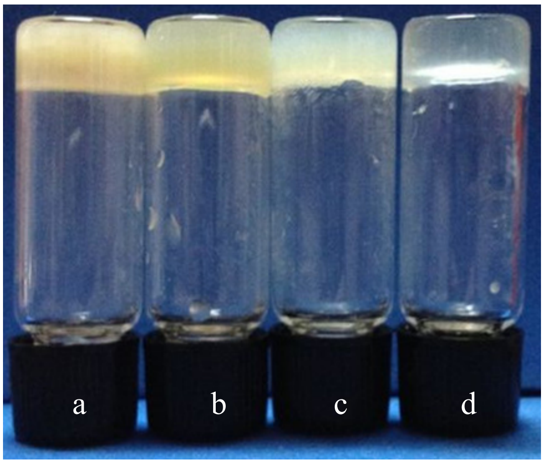


Figure S1: Photo of the gels formed in aniline by using **1a** (a) and **1b** (b) as the gelators, as well as in nitrobenzene with **1b** (c) and **2b** (d) as the gelators at their MGCs.

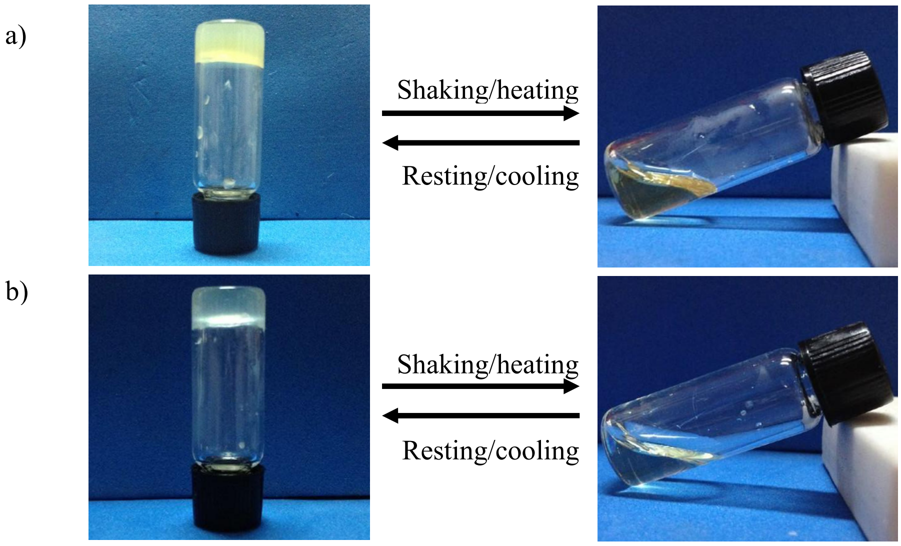


Figure S2: Reversible sol-to-gel transitions of gel **1b** (a) in aniline and gel **2b** (b) in nitrobenzene at their MGCs, stimulated by shaking or heating.

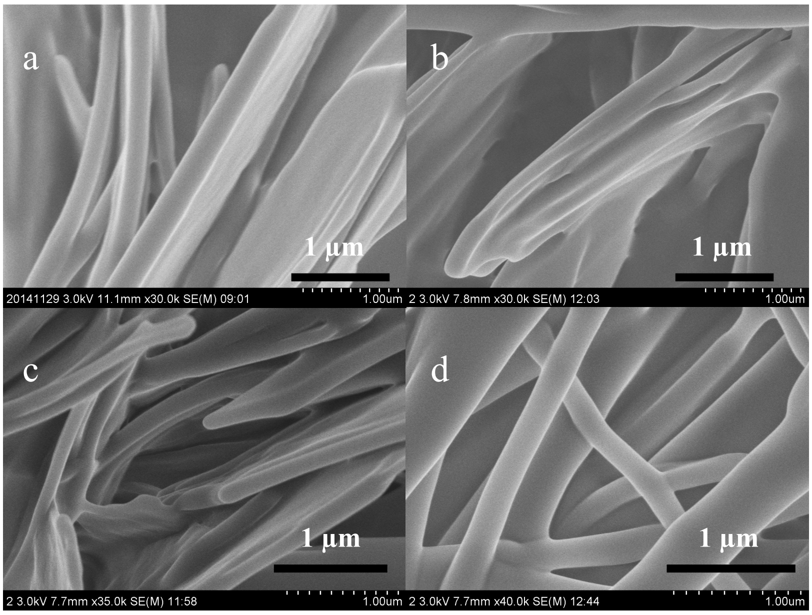


Figure S3: SEM images of xerogels prepared by **1a**-aniline gel (a), **1b**-aniline gel (b), **1b**-nitrobenzene gel (c), and **2b**-nitrobenzene gel (d) at their MGCs.

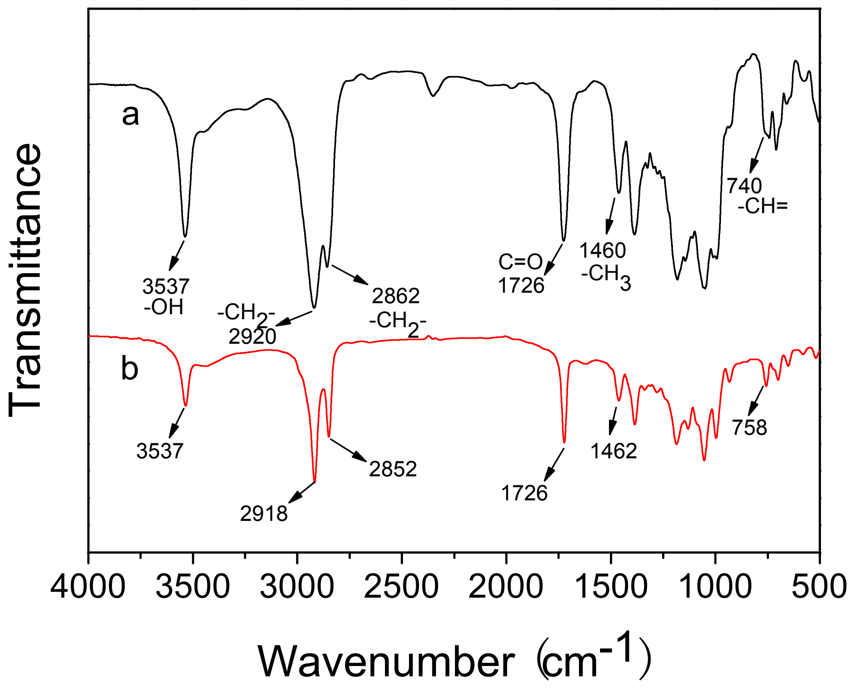


Figure S4: FT-IR spectra of **2b**: (a) neat solid, (b) xerogel from nitrobenzene at its MGC.

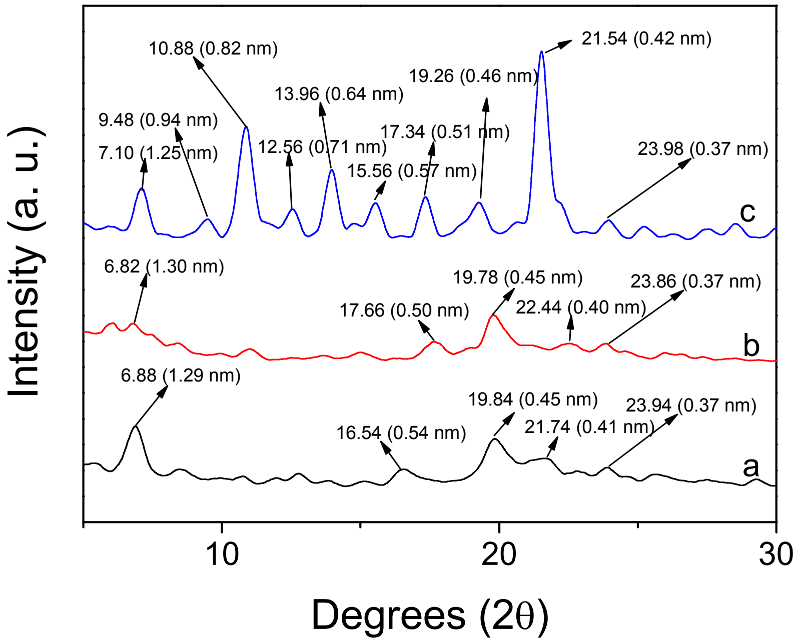


Figure S5: X-ray diffraction patterns at room temperature of (a) **1b** xerogel from aniline, (b) **1b** xerogel from nitrobenzene, and (c) **2b** xerogel from nitrobenzene.

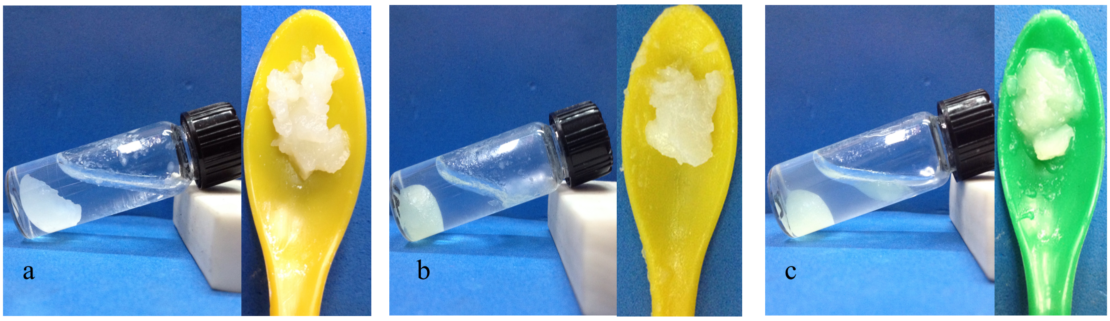


Figure S6: Phase-selective gelation of the organic phase in a two-phase mixture of aniline or nitrobenzene and water (0.5 mL/2.0 mL) by mechanical shaking, and photographs of the separated gels obtained by simple filtration: (a) **1b**-aniline gel (60 mg/ml in aniline phase), (b) **1b**-nitrobenzene gel (60 mg/ml in nitrobenzene phase), (c) **2b**-nitrobenzene gel (70 mg/ml in nitrobenzene phase).

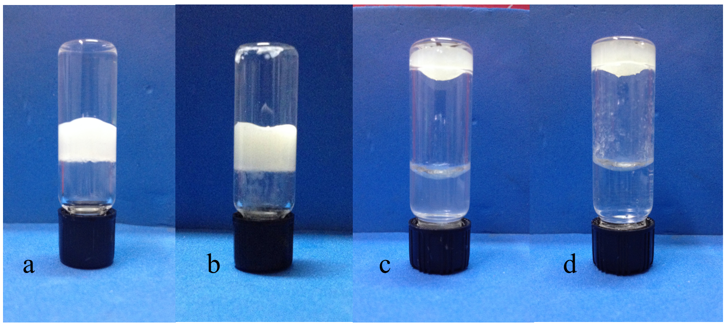


Figure S7: Inverted vials of aniline (1.0 mL) or nitrobenzene (0.5 mL) gels formed phase-selectively in 2.0 mL of water: (a) **1a**-aniline gel (45 mg/ml in aniline phase), (b) **1b**-aniline gel (60 mg/ml in aniline phase), (c) **1b**-nitrobenzene gel (60 mg/ml in nitrobenzene phase), (d) **2b**-nitrobenzene gel (70 mg/ml in nitrobenzene phase).

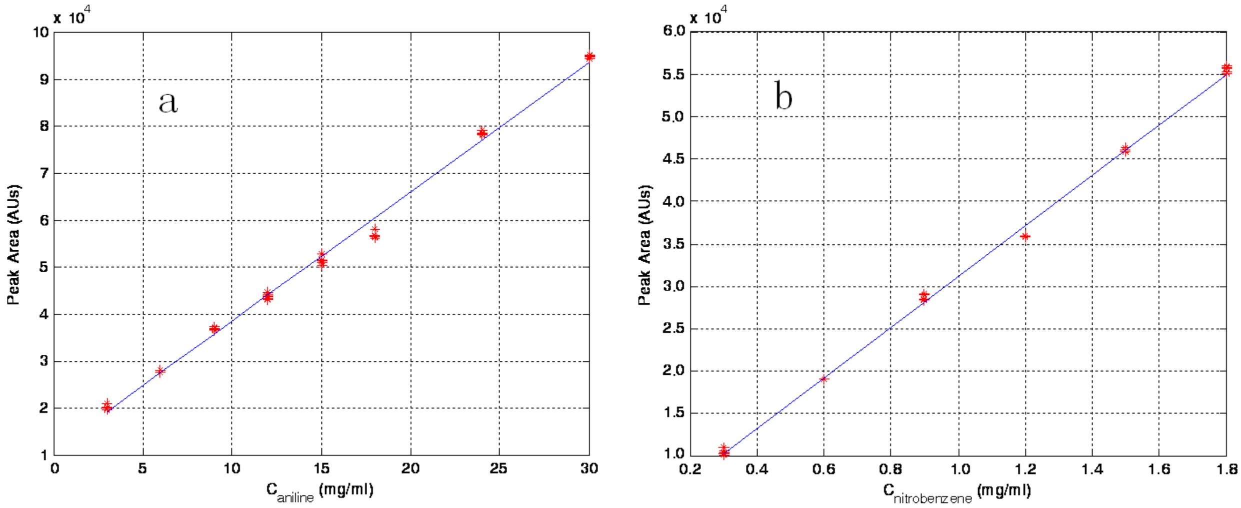


Figure S8 The concentrations of aniline (a) and nitrobenzene (b) in water plotted versus the peak area recorded by HPLC at 25 °C, pH = 7.0. The markers for each concentration mean the parallel measurements of the peak area for six times (the different shapes of the markers have no special meanings). The solid lines are the linear regression results based on a least squares analysis.

Prior to determination of the removal efficiency using a PSG, the relationship between the concentration of aniline or nitrobenzene in water and the peak areas recorded by HPLC was ascertained by diluting an aqueous stock solution of aniline (30 mg/mL) or nitrobenzene (3 mg/mL). The resulting linear regression equations for aniline and nitrobenzene are $y = 10^4 \times (0.28x + 1.1)$ ($R^2 = 0.995$) and $y = 10^4 \times (3.0x + 0.12)$ ($R^2 = 0.999$), respectively.[1]

Table S3: The performance parameters of 1a and 1b for the removal of aniline from water[a]

Gelator	Weight of gelator (mg)[b]	Concentration of aniline (mg/mL)[c]	Removal efficiency (%)[d]
1a	0	33 (0.001)[e]	0
	12.5	5.7 (0.004)	82
	15	5.2 (0.002)	83
	17.5	3.7 (0.002)	88
	20	1.8 (0.004)	94
	22.5	0.5 (0.005)	98
1b	0	33 (0.001)	0
	18.8	6.5 (0.003)	79
	21.3	6.4 (0.003)	80
	23.8	5.8 (0.004)	81
	26.3	4.4 (0.004)	86
	28.8	1.9 (0.005)	94

[a] The volume ratio of aniline/water is 0.5 mL/2.0 mL. [b] The concentration of the gelator was determined in 0.5 mL of aniline. [c] The concentration of aniline in water was determined according to the corresponding absorption peak area of aniline by the calculation in the equation of linear regression. [d] The removal efficiency was calculated according to the equation: $(C_I-C_R)/C_I$, in which C_I represents the initial concentration of aniline in water without the addition of the gelator; C_R is the residual concentration of aniline in the presence of the gelator. [e] The relative standard deviation for six measurements of each sample was calculated for the peak area detection, and the average value was given for the estimation of the concentration of aniline.

Table S4: The performance parameters of 1b and 2b for the removal of nitrobenzene from water[a]

Gelator	Weight of gelator (mg)[b]	Concentration of nitrobenzene (mg/mL)[c]	Removal efficiency (%)[d]
1b	0	1.6 (0.001)[e]	0
	20.0	0.9 (0.001)	44
	22.5	0.5 (0.003)	66
	25.0	0.4 (0.006)	71
	27.5	0.3 (0.005)	80
	30.0	0.2 (0.006)	88
2b	0	1.6 (0.001)	0
	25.0	1.1 (0.002)	31
	27.5	0.5 (0.003)	71
	30.0	0.3 (0.004)	78
	32.5	0.3 (0.004)	79
	35.0	0.2 (0.006)	85

[a] The volume ratio of nitrobenzene/water is 0.5 mL/2.0mL. [b] The concentration of the gelator was determined in 0.5 mL of nitrobenzene. [c] The concentration of nitrobenzene in water was determined according to the corresponding absorption peak area of nitrobenzene by the calculation in the equation of linear regression. [d] The removal efficiency was calculated according to the equation: $(C_I-C_R)/C_I$, in which C_I represents the initial concentration of nitrobenzene in water without the addition of the gelator; C_R is the residual concentration of nitrobenzene in the presence of the gelator. [e] The relative standard deviation for six measurements of each sample was calculated for the peak area detection, and the average value was given for the estimation of the concentration of nitrobenzene.

Table S5: The performance parameters of 1a and 1b for the removal of aniline and nitrobenzene in 2 mL of water with different volume of organic liquids

PSG	1a/aniline[a]			1b/nitrobenzene[b]		
Volume of organic phase (mL)	0.25	0.1	0.05	0.25	0.1	0.05
Initial concentration (mg/mL)	31 (0.001)[c]	33 (0.0009)	32 (0.0007)	0.9 (0.0007)	0.88 (0.003)	0.88 (0.003)
Residual concentration (mg/mL)	1.7 (0.006)	0.35 (0.01)	0.1 (0.009)	0.19 (0.01)	0.17 (0.008)	0.17 (0.007)
Removal efficiency (%)	94	98	99	78	80	80

[a] The concentration of **1a** in aniline phase is 4.2 wt%. [b] The concentration of **1b** in nitrobenzene phase is 4.7 wt%. [c] The relative standard deviation for six measurements of each sample was calculated for the peak area detection, and the average value was given.

Table S6: The removal effect of both aniline and nitrobenzene in their water mixture with 1b as the PSG[a]

Solvent	Aniline	Nitrobenzene
Volume of organic phase (mL)	0.25	0.25
Initial concentration (mg/mL)	9.6 (0.003)[b]	0.84 (0.005)
Residual concentration (mg/mL)	0.6 (0.009)	0.11 (0.004)
Removal efficiency (%)	94	87

[a] The volume of water is 2.0 mL, and the concentration of **1b** in the organic phase is 5.1 wt%. [b] The relative standard deviation for six measurements of each sample was calculated for the peak area detection, and the average value was given.

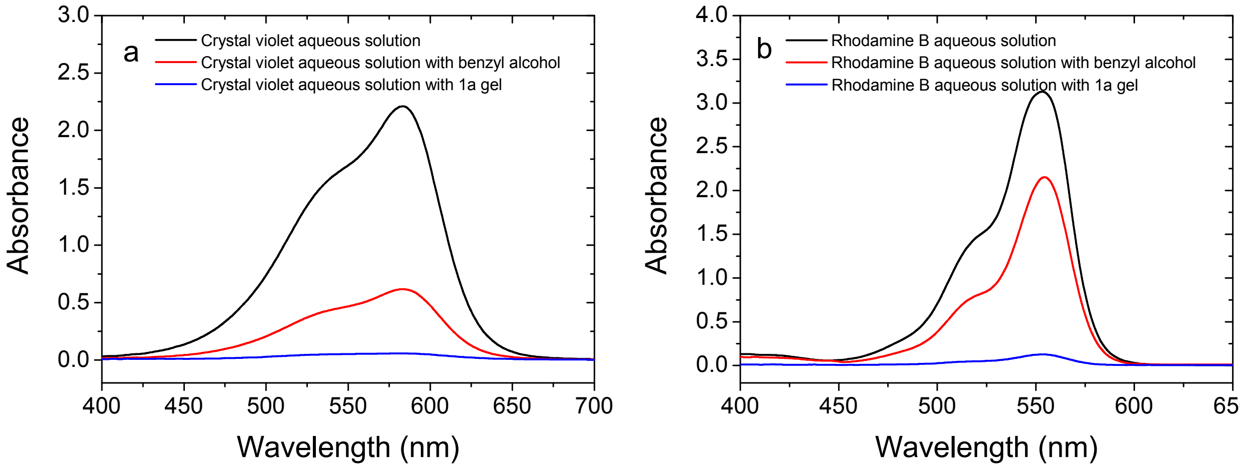


Figure S9: UV/vis spectra of the aqueous solutions (2.0 mL) of (a) CV (0.098 mmol·L^{-1}), and (b) rhodamine B (0.17 mmol·L^{-1}) without and with the extraction/adsorption of the dyes by benzyl alcohol or **1a**-benzyl alcohol gel (2.3 wt% of **1a** in 0.2 mL of benzyl alcohol) after ~24 h at 25 °C.

The rate of the dye adsorption can be estimated by the following equations:[2]

$$q_e = (Co - Ce)\,V/m \qquad (1)$$

q_e is the amount of the dye adsorption (mg/g), m is the weight of the adsorbing agent (g), Ce is the equilibrium concentration of the dye in solution (mg/L), Co is the initial concentration of the dye in solution (mg/L), and V is the volume (L) of the dye solution.

$$dq_t/dt = k_2\,(q_e - q_t)^2 \qquad (2)$$

q_e and q_t are the amounts (mg/g, dye mass per mass of the gelator) of the dye adsorption at equilibrium and time t, respectively, and k_2 is the pseudo second-order adsorption constant (g/mg h).

The maximum dye adsorption can be determined by equation (1). The pseudo second-order kinetics can be obtained by equation (2).

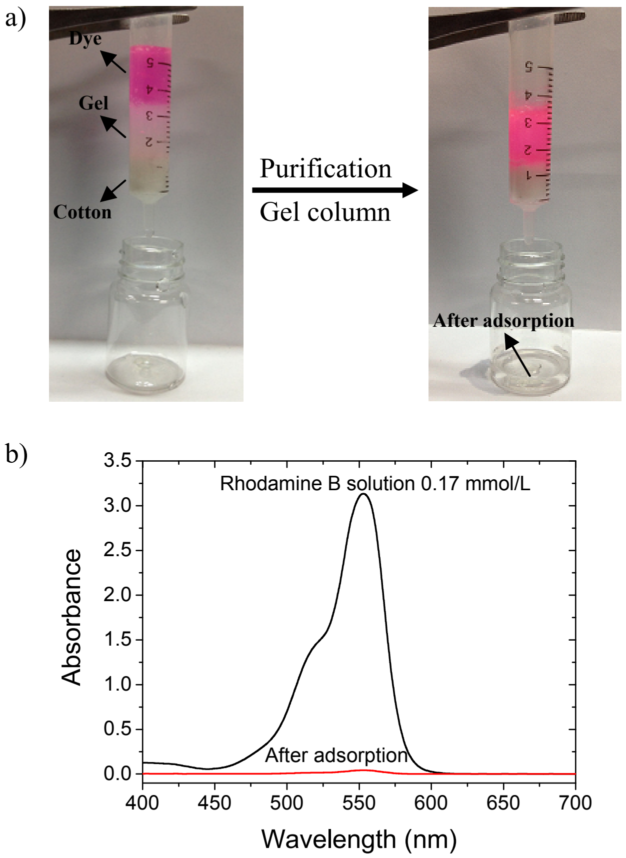


Figure S10: (a) Removal of rhodamine B from its aqueous solution by **1a**-benzyl alcohol gel (2.3 wt% of **1a** in 2.0 mL of benzyl alcohol) column. (b) UV/vis spectral changes of the aqueous solution of rhodamine B (0.17 mmol·L^{-1}) before and after purification by gel column.

Table S7: The Removal efficiencies of CV and Rhodamine B with 1a as the adsorbent in different realization means

Dye	**Crystal violet**			**Rhodamine B**		
Adsorbing agent	**Gel**[a]	**Xerogel**[b]	**Gel column**[c]	**Gel**	**Xerogel**	**Gel column**
Initial concentration (mmol·L^{-1})	0.098	0.098	0.098	0.17	0.17	0.17
Final concentration (mmol·L^{-1})[d]	0.0024	0.0085	0.00087	0.0040	0.030	0.0024
Removal efficiency (%)	97	91	99	97	82	98

[a] The concentration of the gelator **1a** in benzyl alcohol is 2.3 wt%, and the adsorbing result was recorded after ~24 h. [b] The xerogel was prepared by drying **1a**-benzyl alcohol gel (2.3 wt% in 0.2 mL of benzyl alcohol) in vacuum simultaneously frozen in liquid nitrogen. [c] The gel column was created by a plastic syringe filled with 2 mL of 1a-benzyl alcohol gel (2.3 wt%). [d] The relative standard deviations for each sample of the final CV concentrations are 0.02, 0.06, and 0.005, respectively for gel, xerogel, and gel column method, and 0.01, 0.009, and 0.01 are for the final concentrations of Rhodamine B with the method of gel, xerogel, and gel column, respectively.

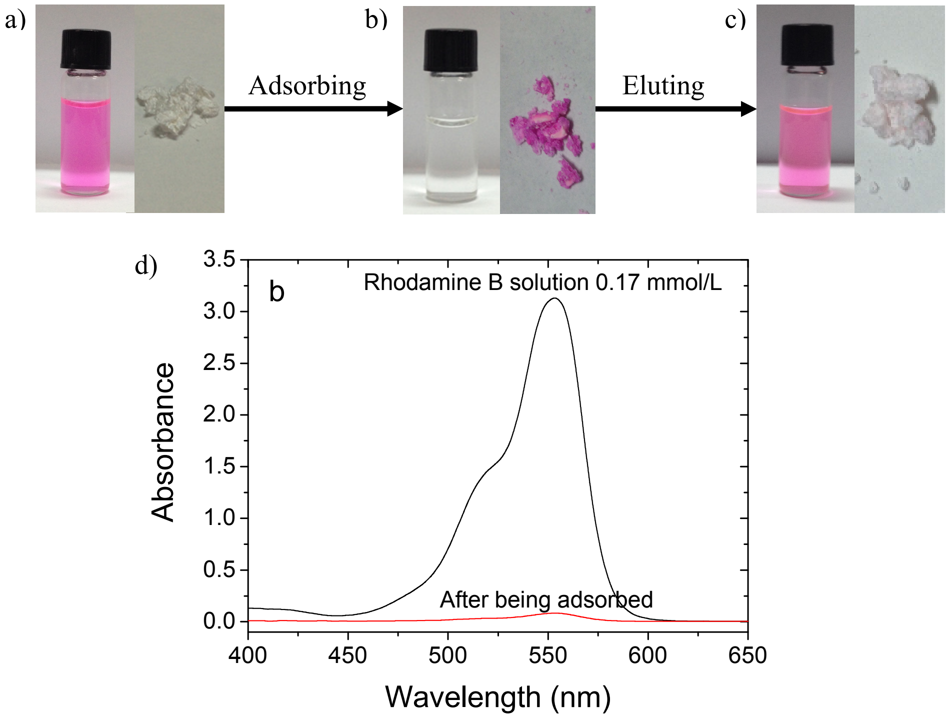


Figure S11: Photographs of (a) an aqueous solution of rhodamine B (0.17 mmol·L^{-1}) and the xerogel obtained from **1a**-benzyl alcohol gel (4.6 wt% of **1a** in 0.2 mL of benzyl alcohol), (b) rhodamine B-adsorbed xerogel and the clear water, (c) the xerogel after being eluted by methanol and the CV solution in methanol. (d) UV/vis spectral changes of an aqueous solution of rhodamine B before and after adsorption (~24 h) of the dye by the xerogel obtained from **1a**-benzyl alcohol gel (4.6 wt% of **1a** in 0.2 mL of benzyl alcohol) at 25 °C. The removal efficiency under this condition was determined to be 97 %.

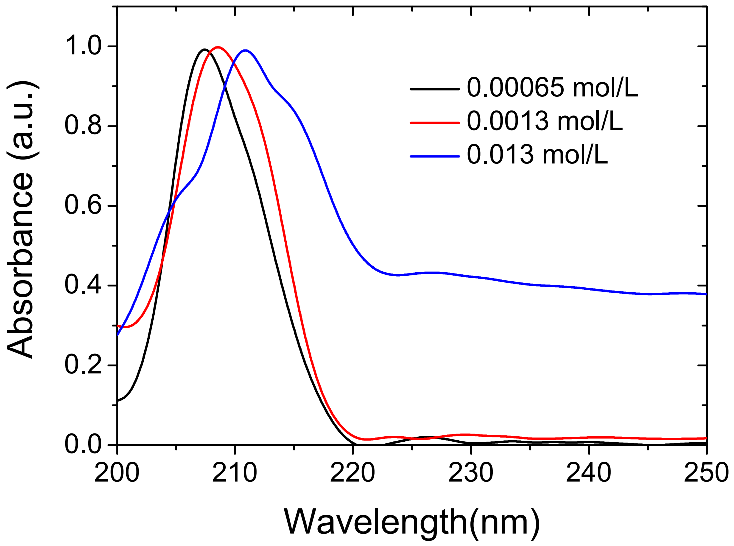


Figure S12: Normalized UV spectra of **1b** in ethanol as the concentration was increased from 0.00065 mol·L^{-1} to 0.013 mol·L^{-1}.

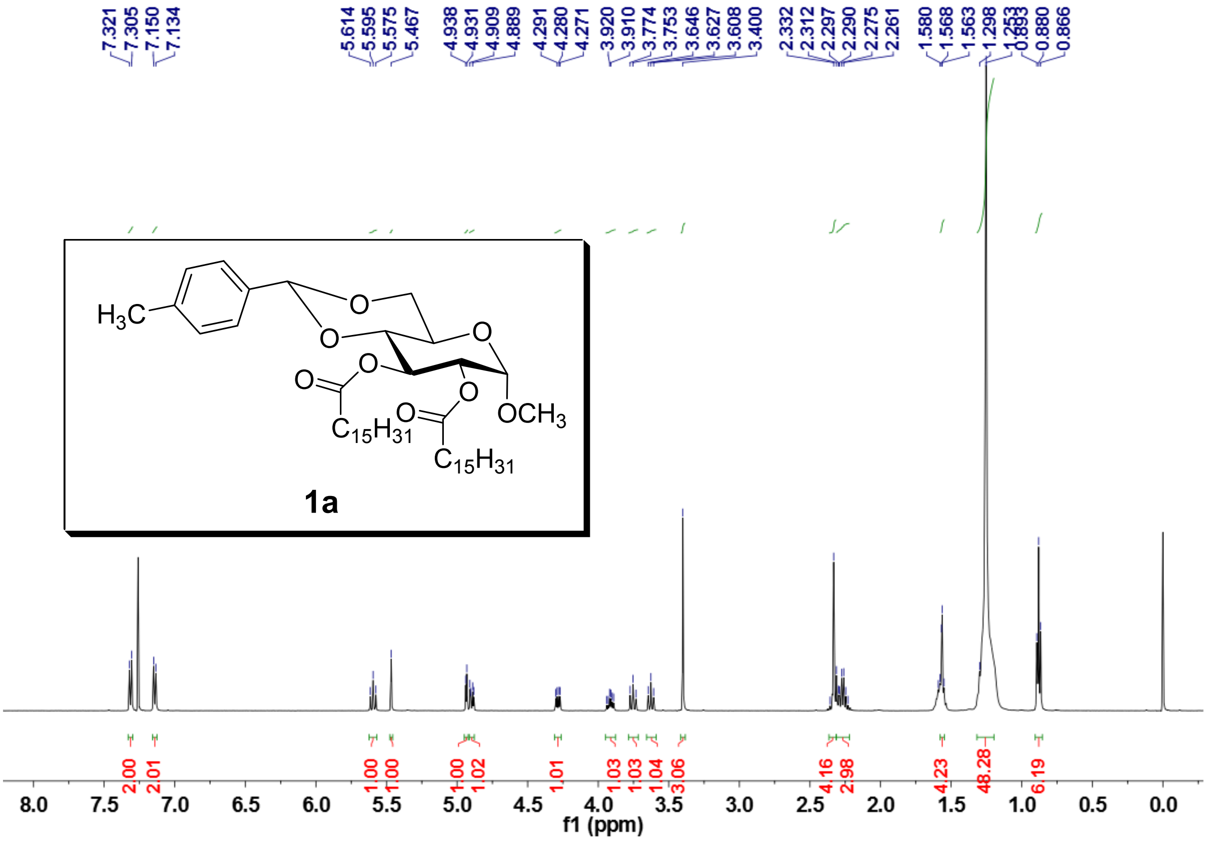
Reference:

1. Environmental Protection Bureau of China. *Standard Methods for Examination of Water and Wastewater*, China Environmental Science Press, Beijing, 4th edn., 2002, pp. 548- 555.

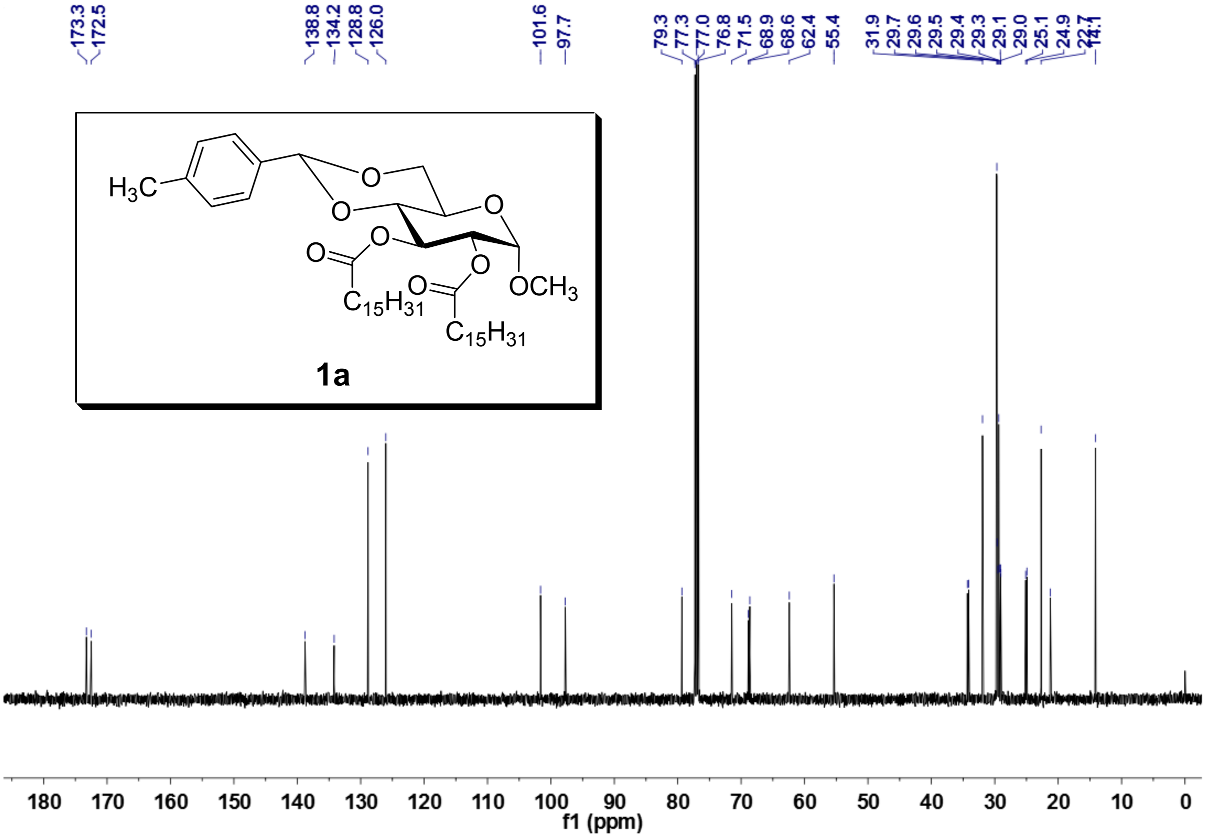
2. B. O. Okesola, D. K. Smith, *Chem. Commun.*, 2013, **49**, 11164–11166.

NMR

Compound **1a** ^{1}H NMR



Compound **1a** ^{13}C NMR



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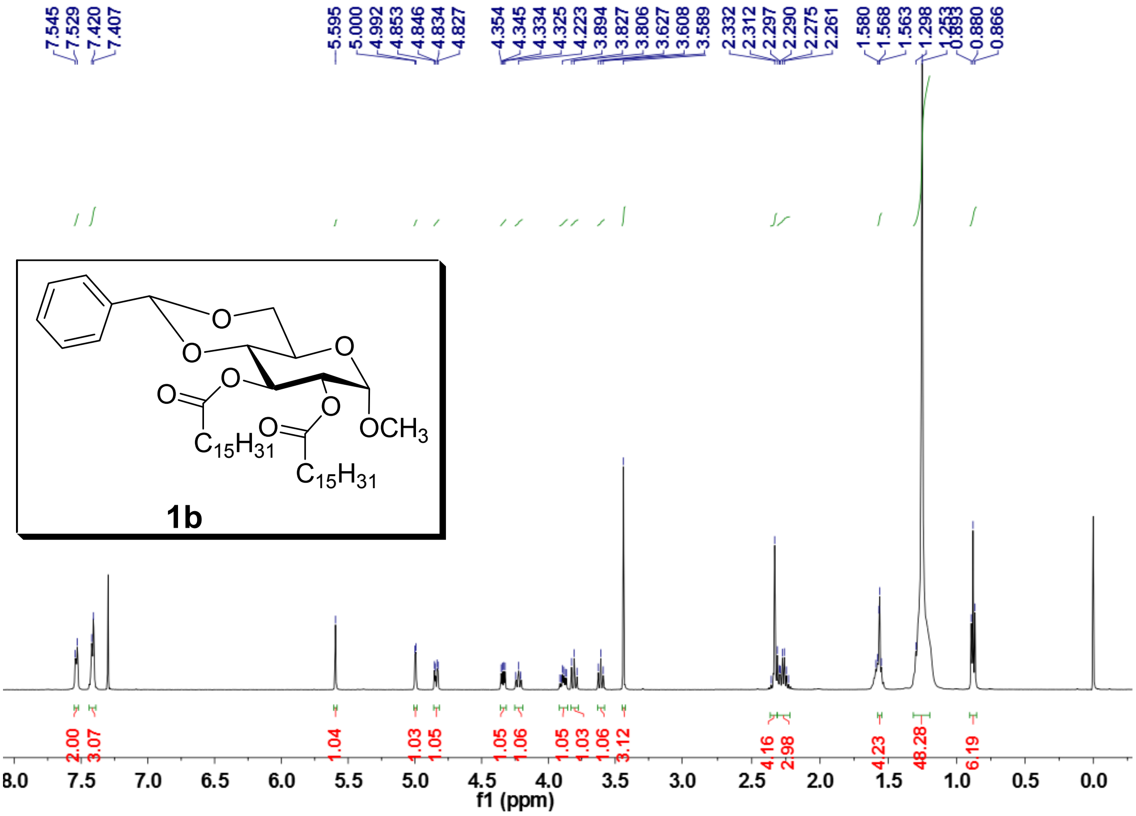

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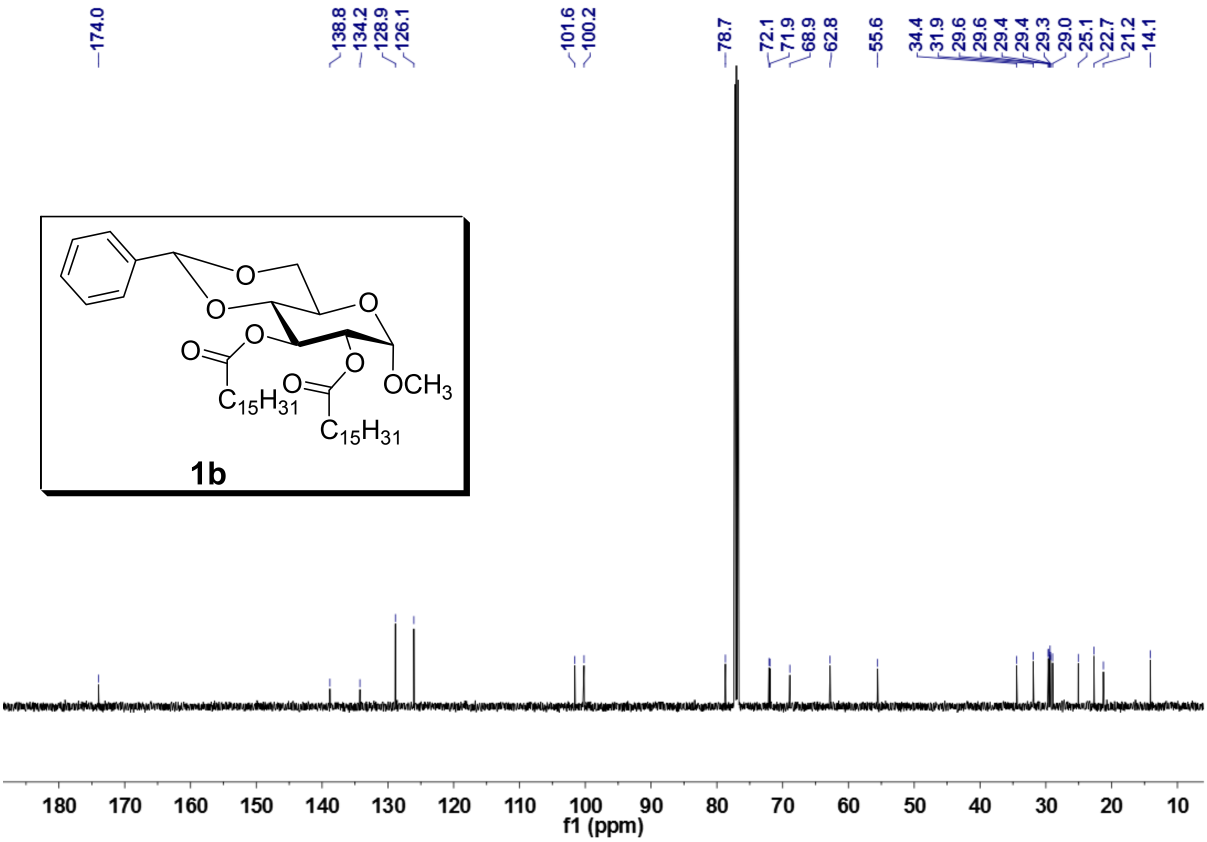

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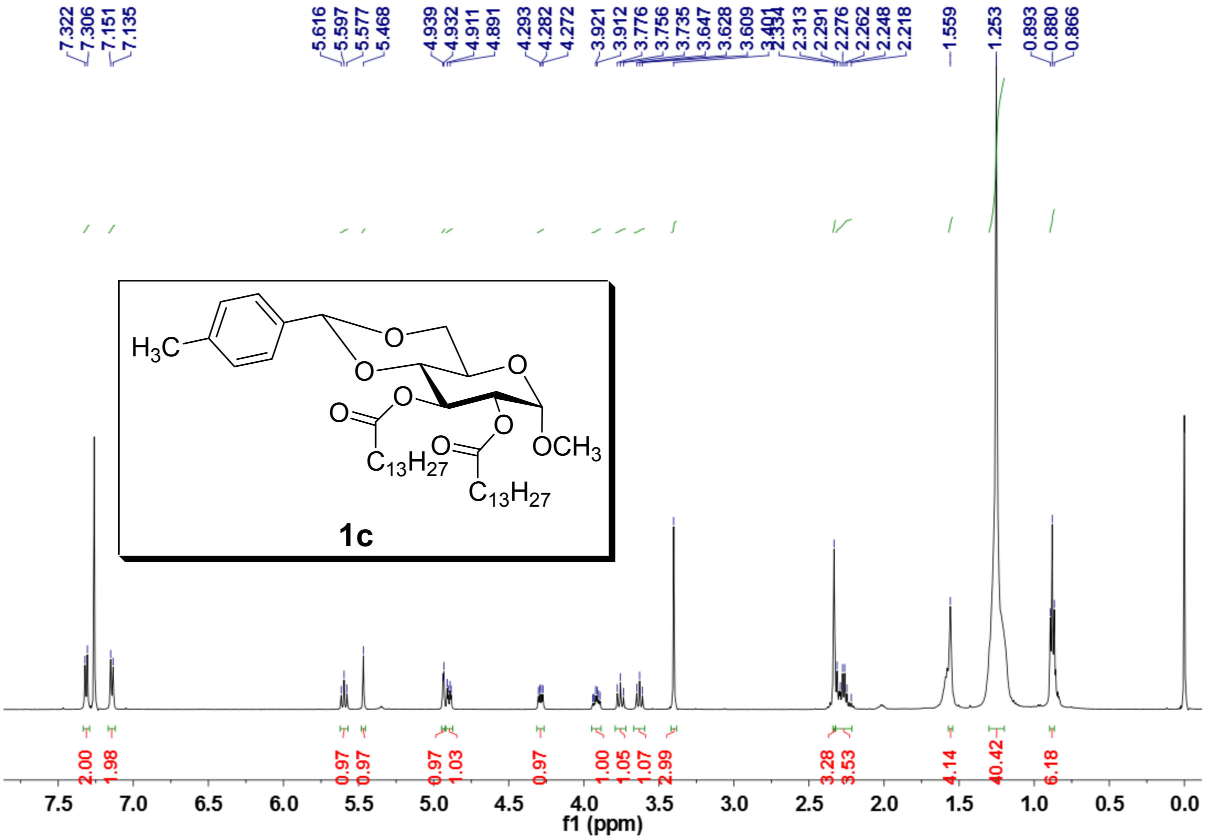

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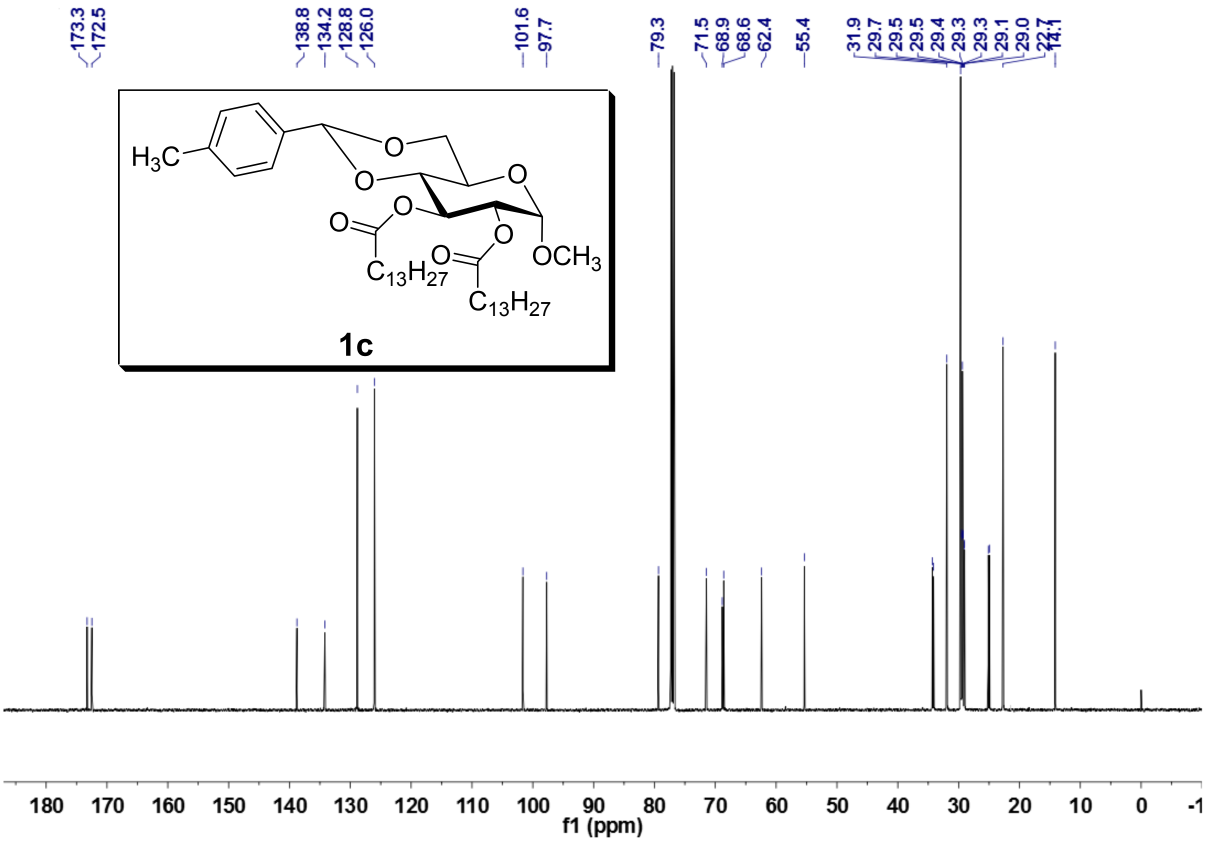

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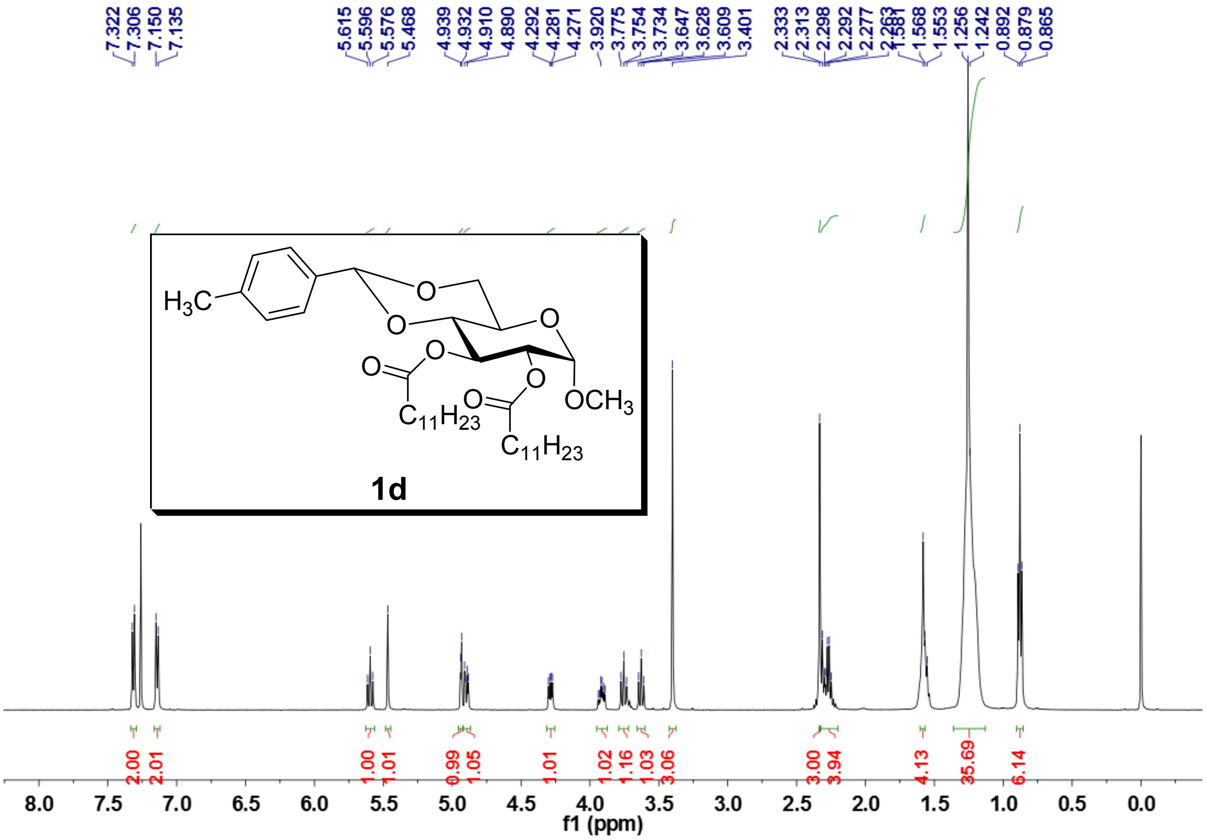

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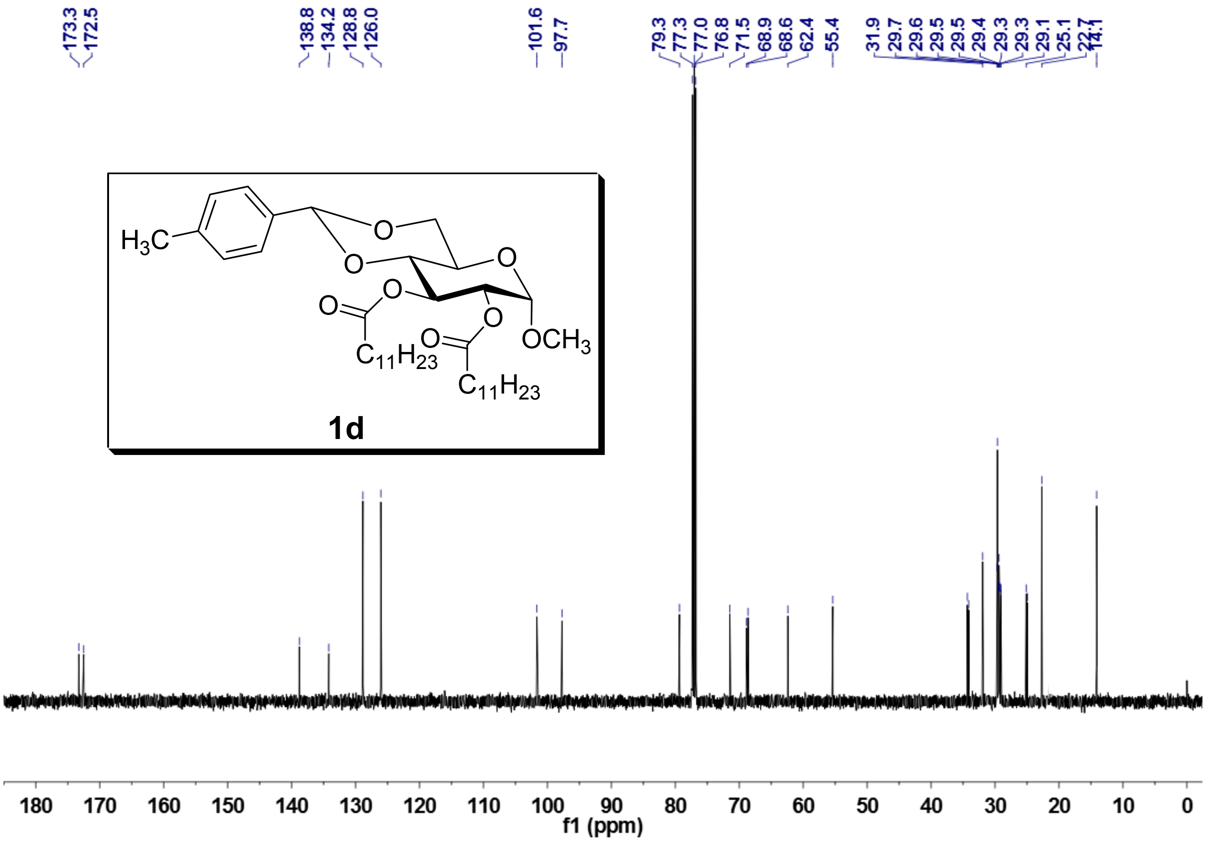

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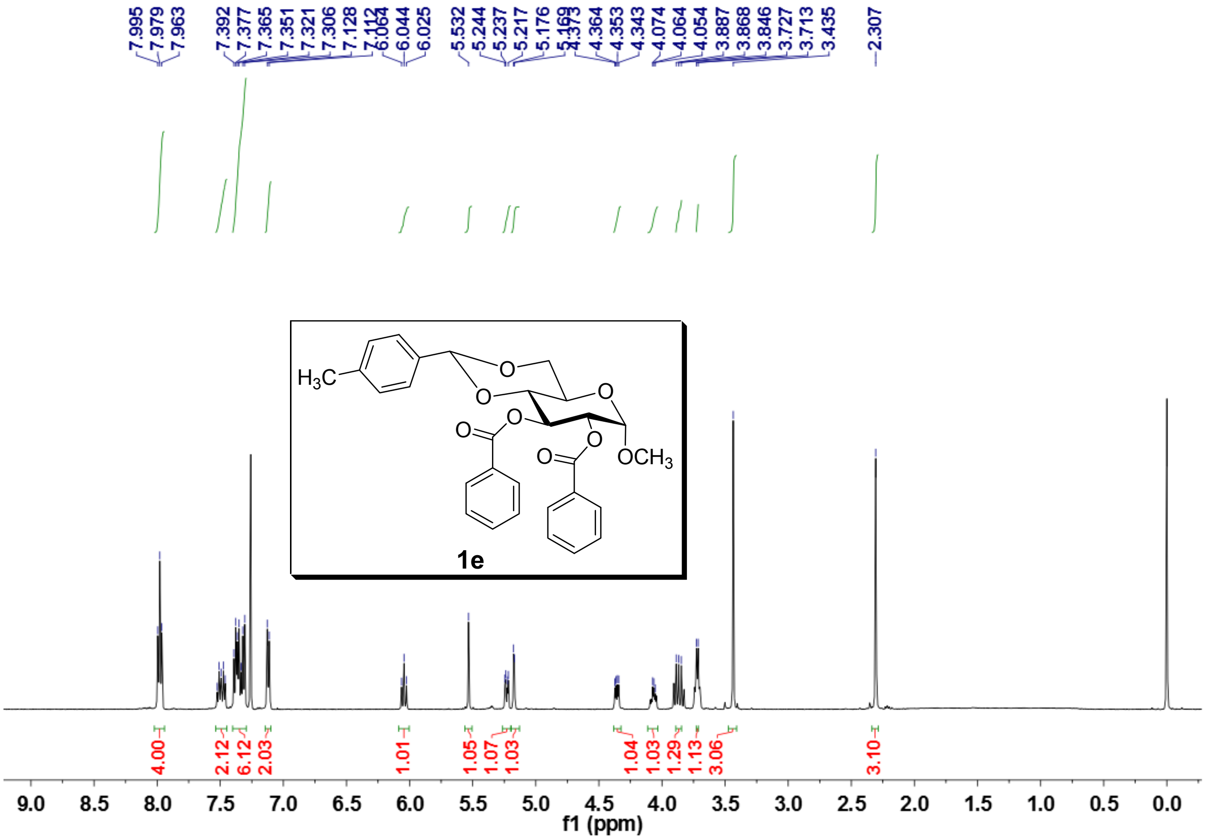

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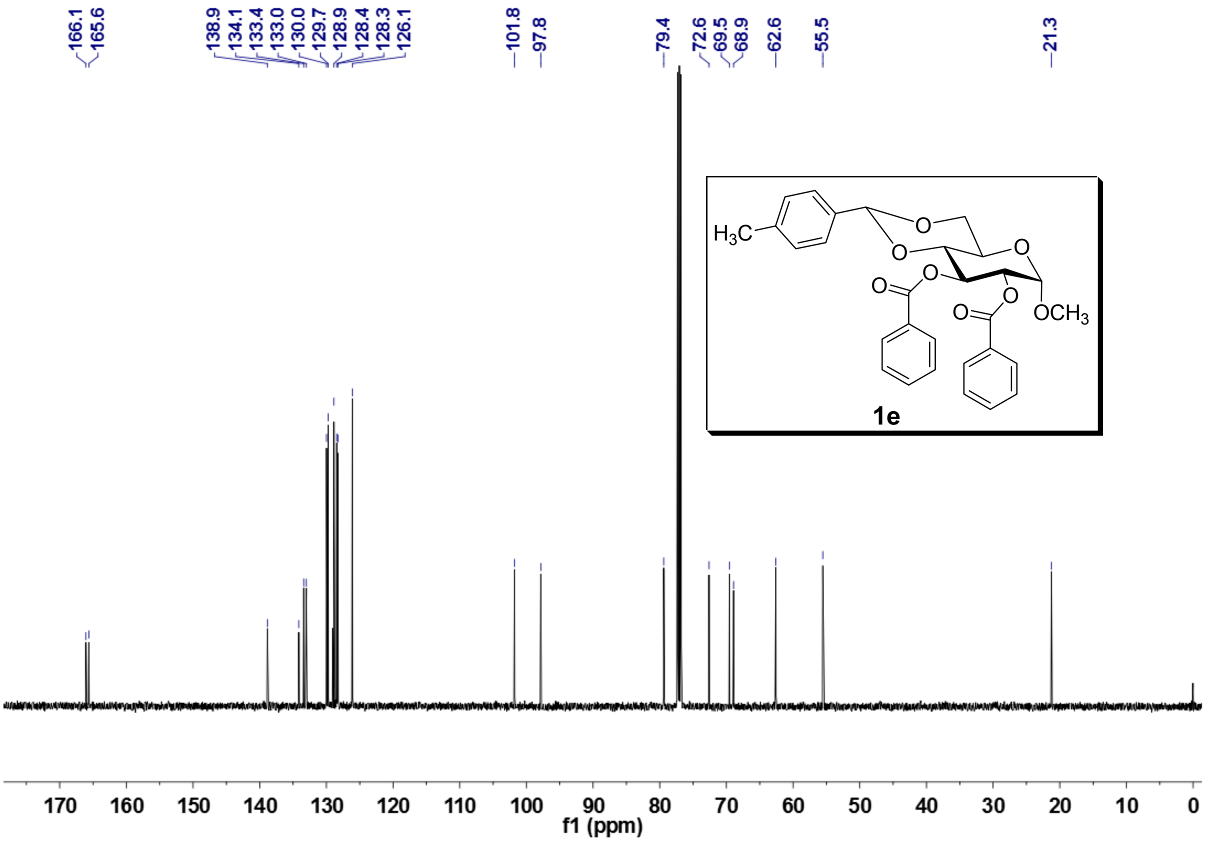

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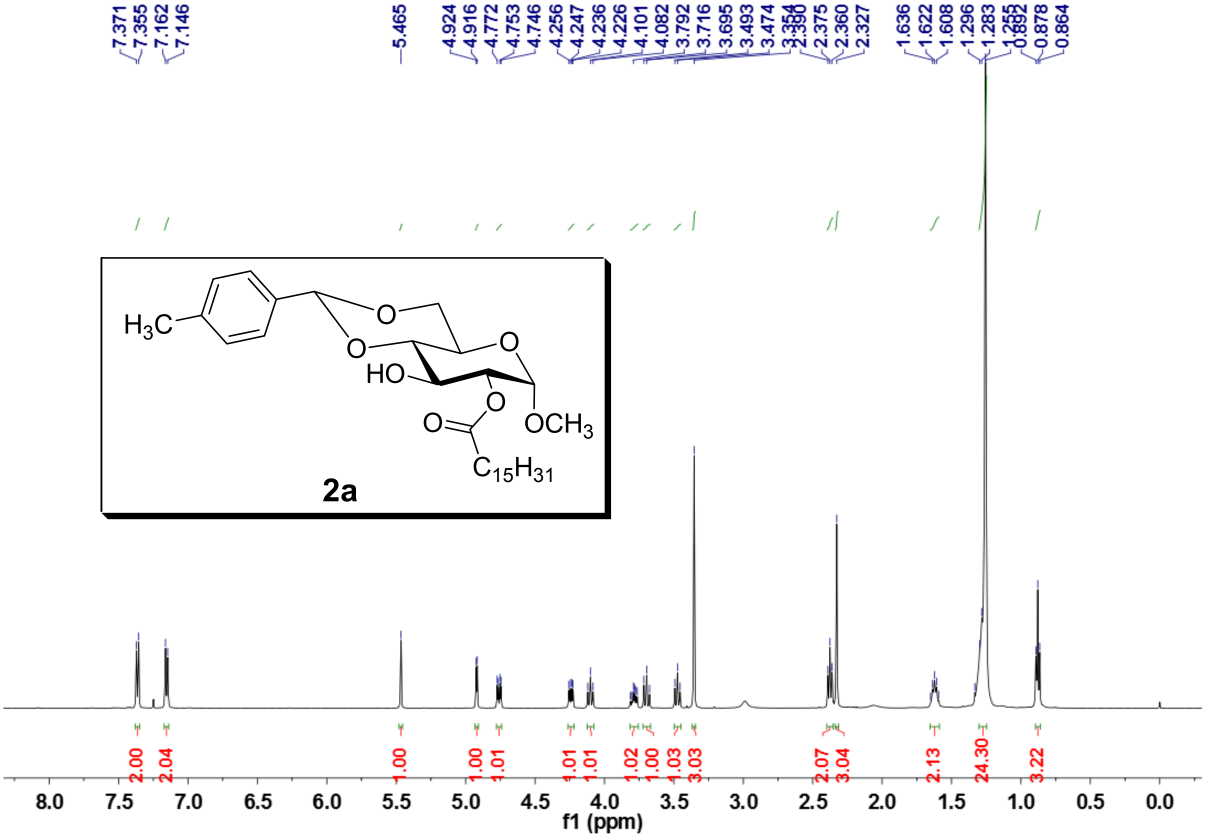

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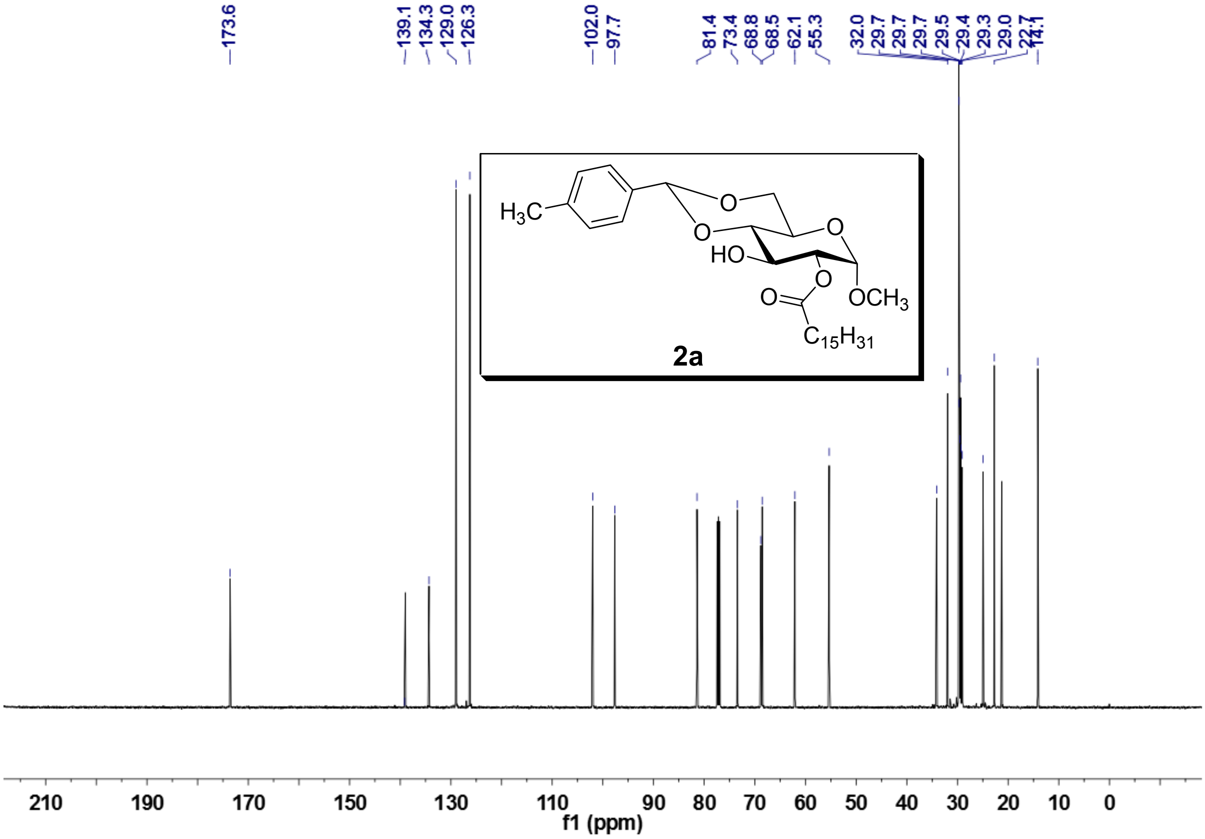

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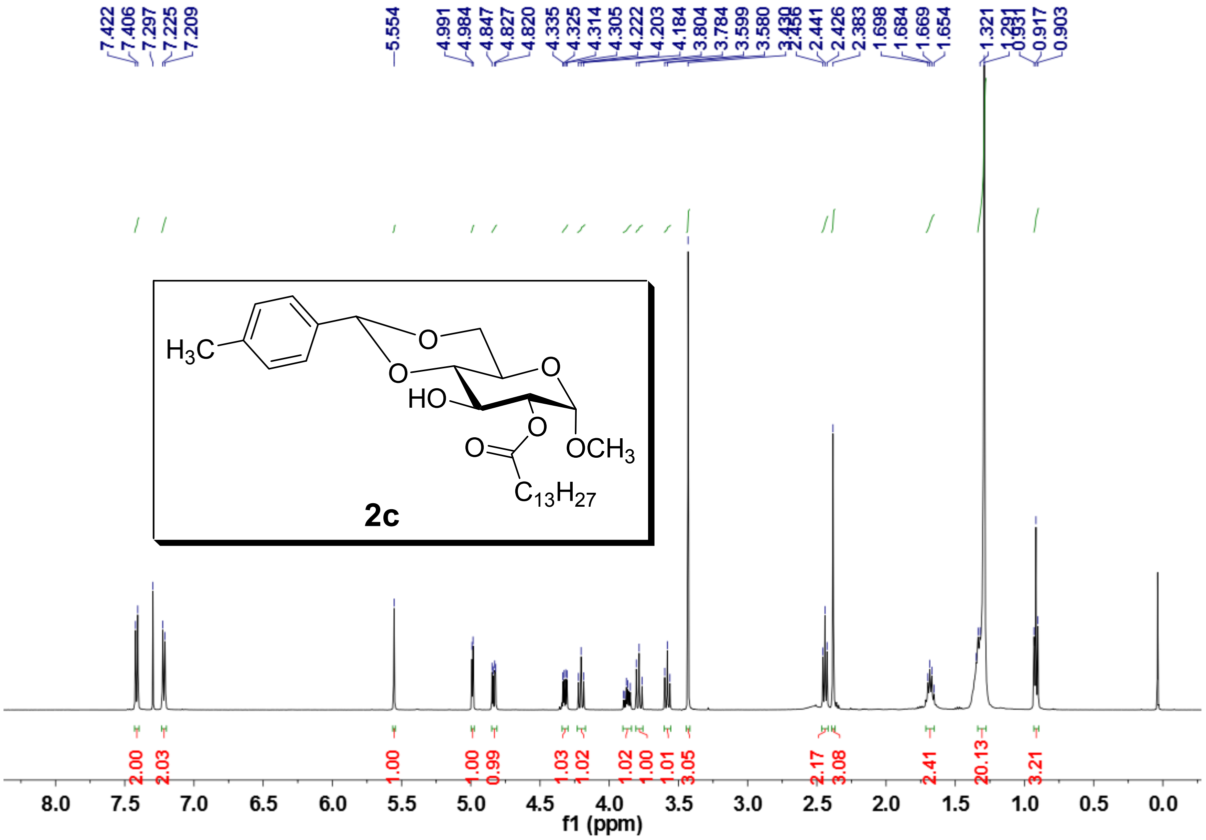
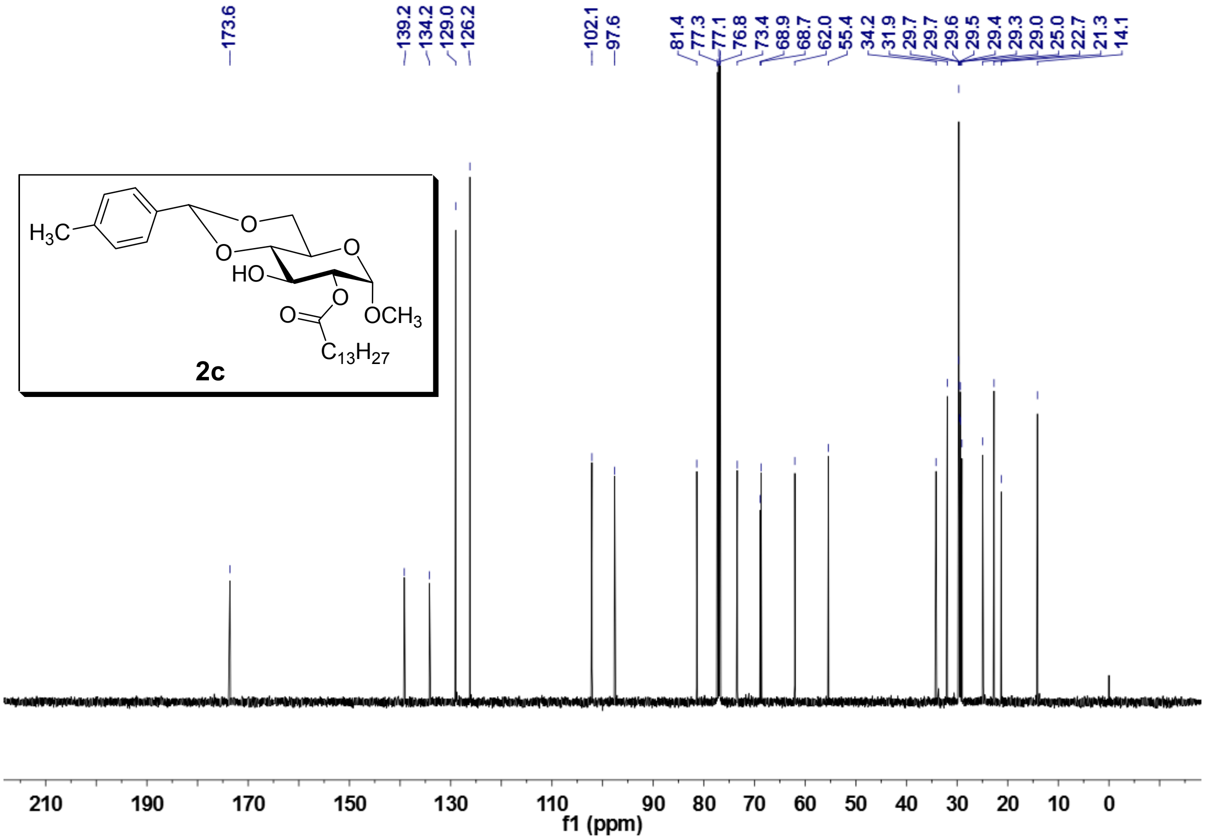


Compound **2c** ^{13}C NMR



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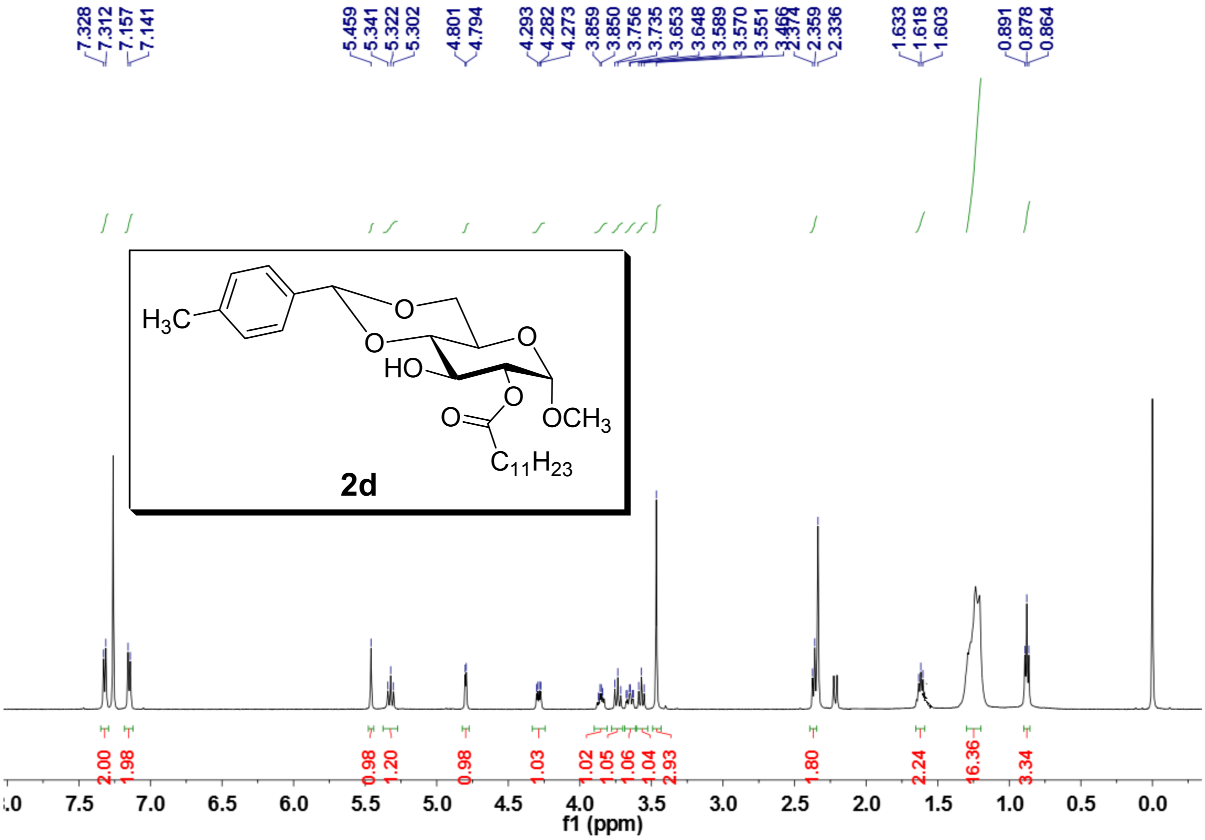
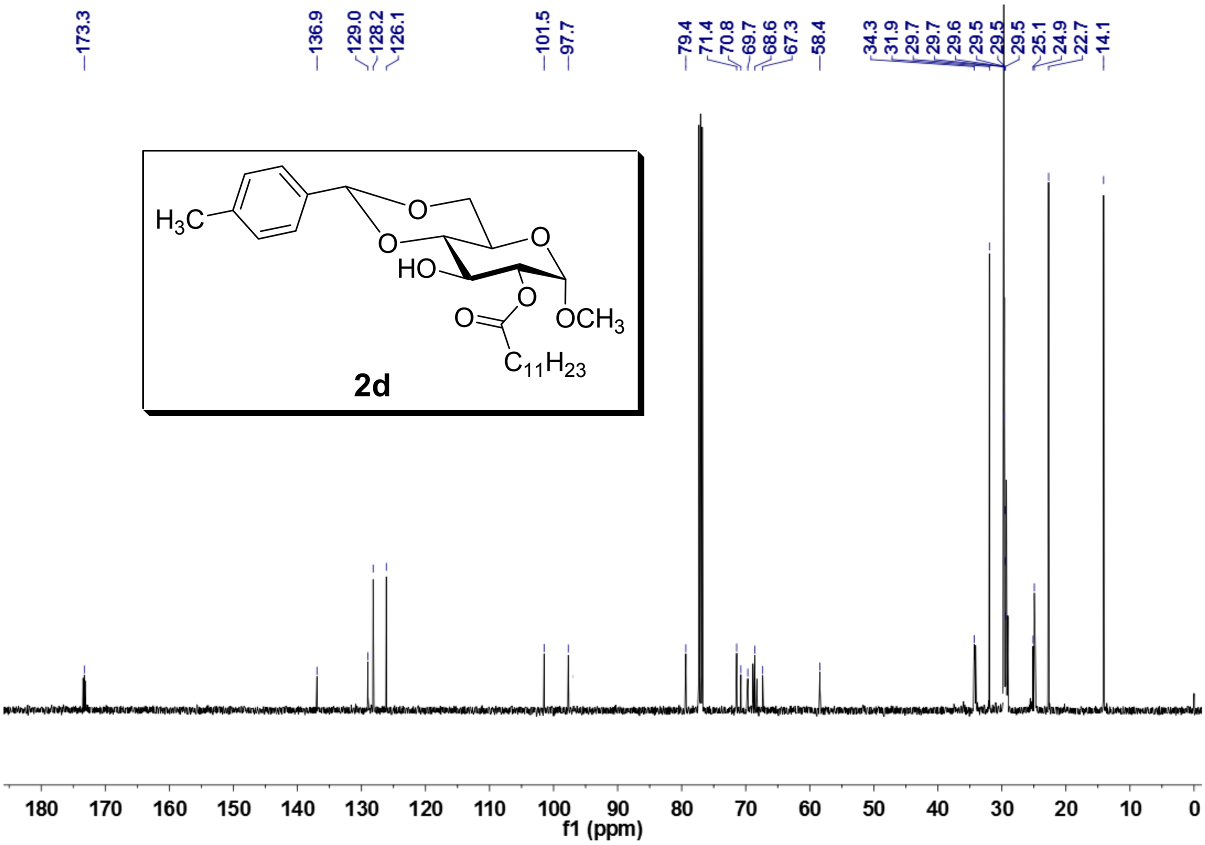
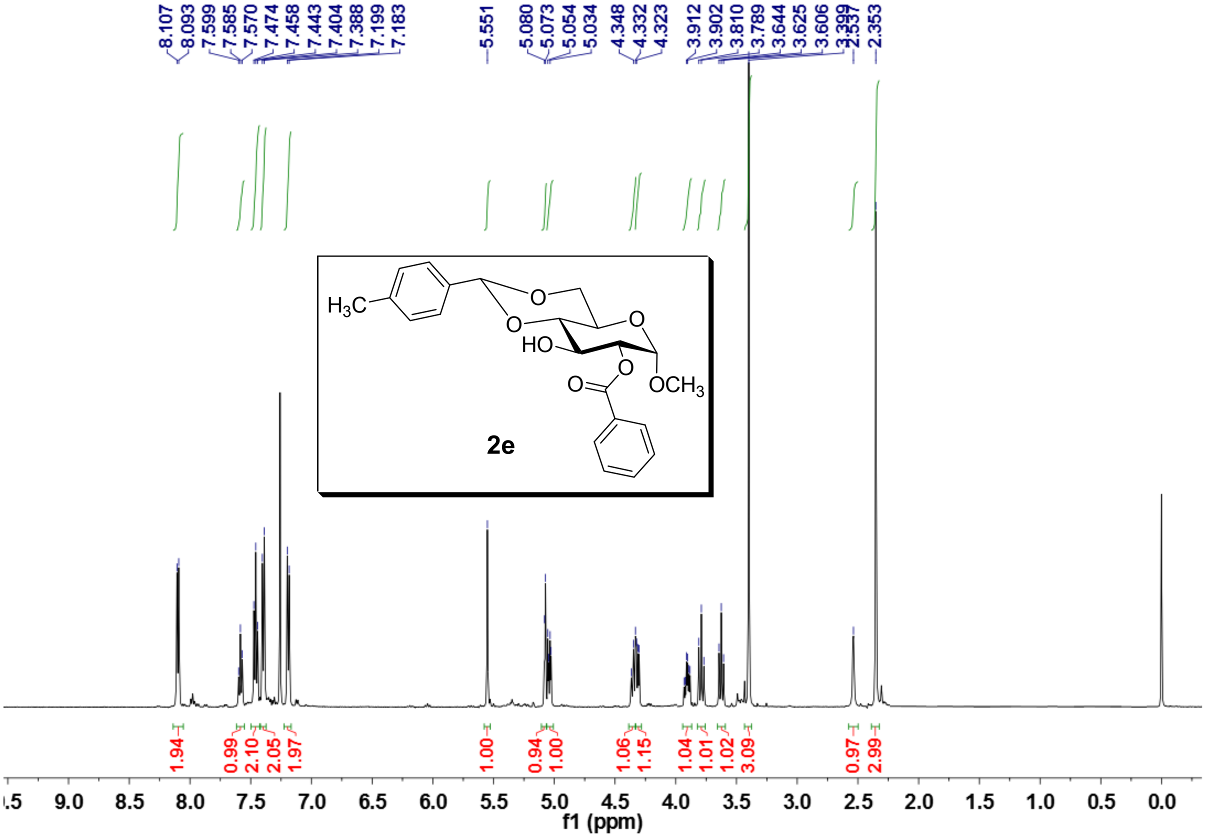


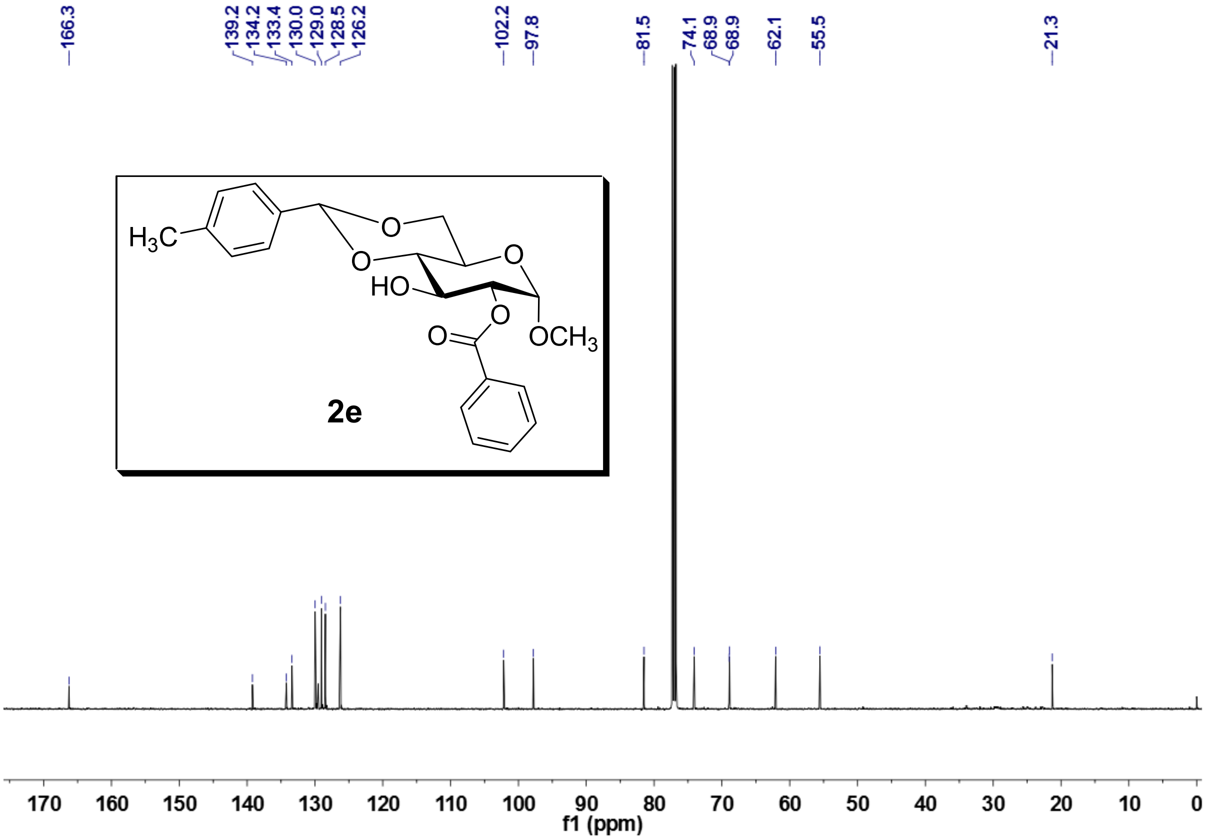
Compound **2d** ^{13}C NMR



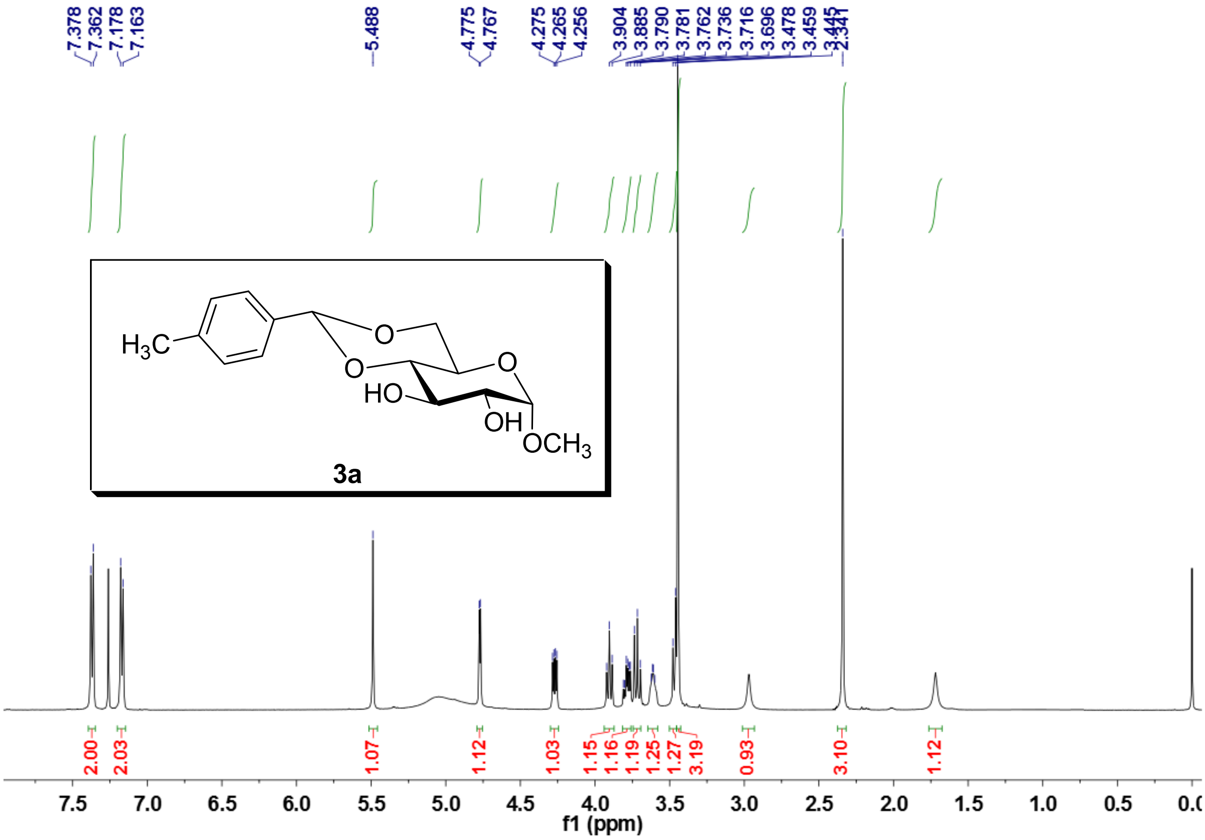
Compound **2e** ^{1}H NMR



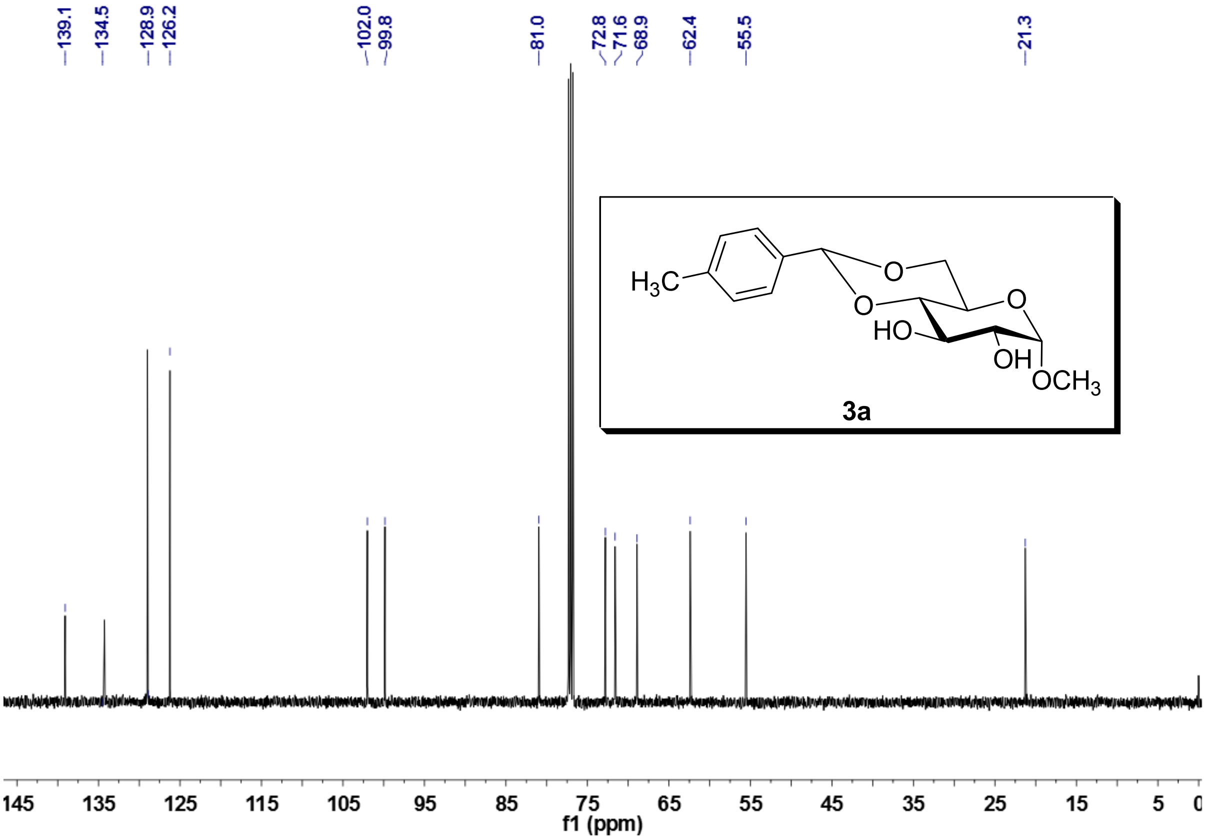
Compound **2e** ^{13}C NMR



Compound **3a** ^{1}H NMR

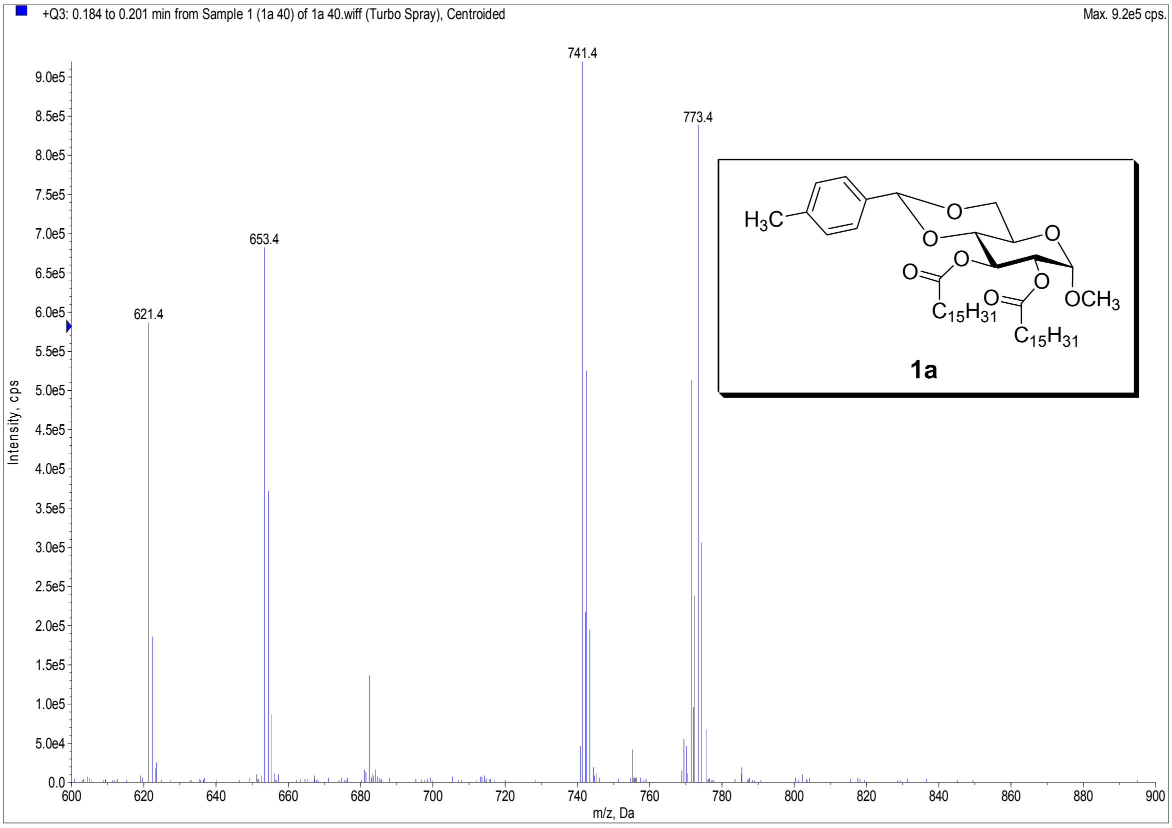


Compound **3a** ^{13}C NMR

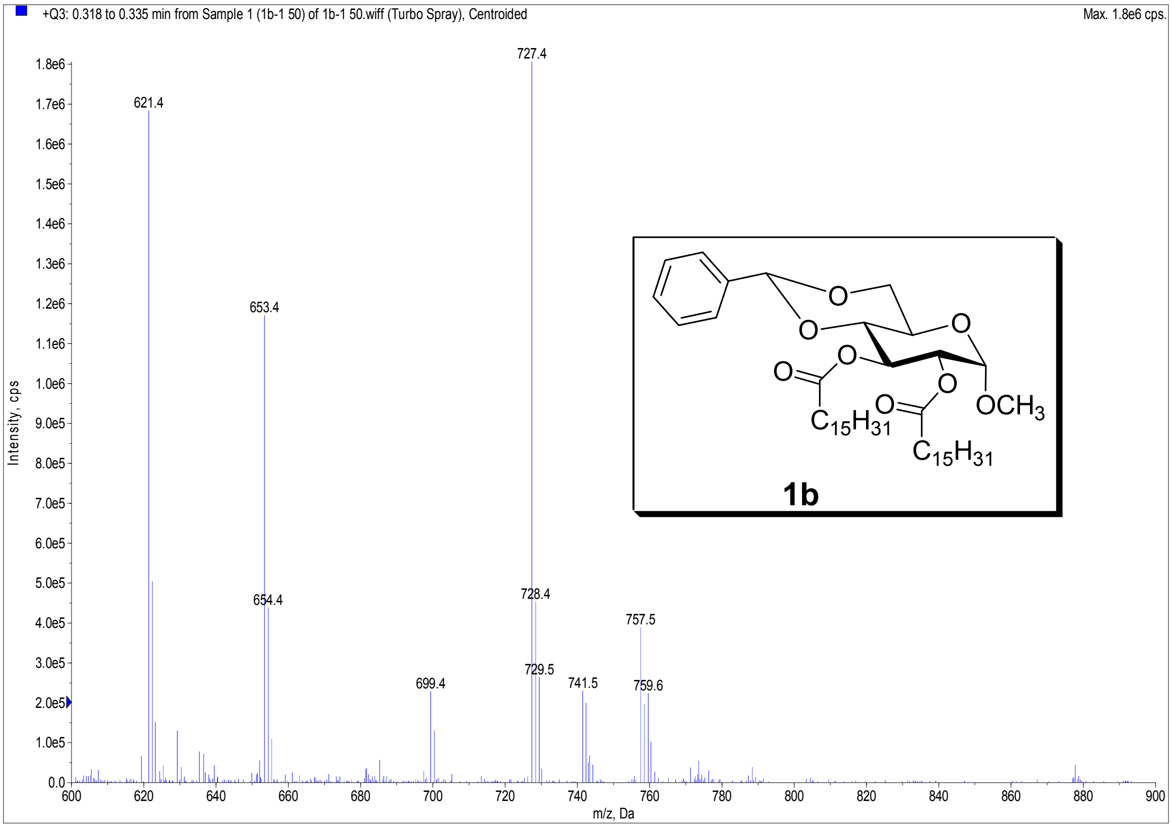


MS

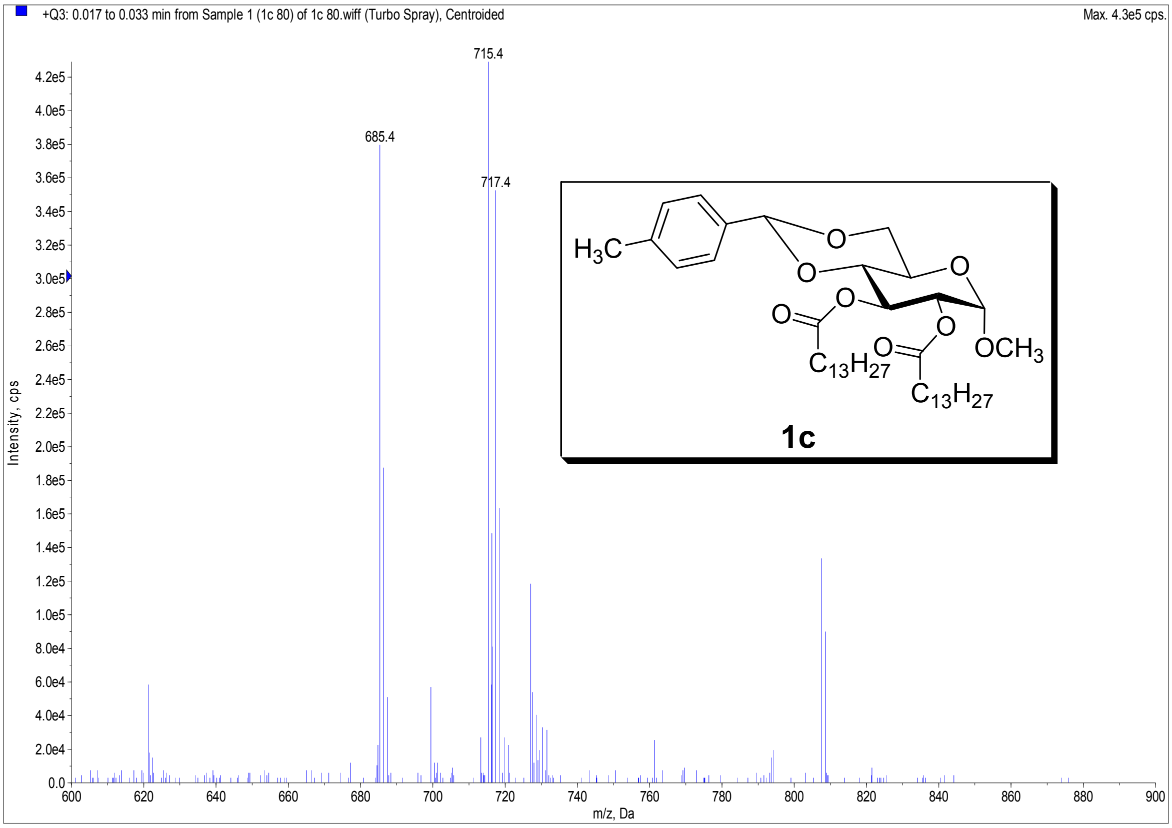
Compound **1a**



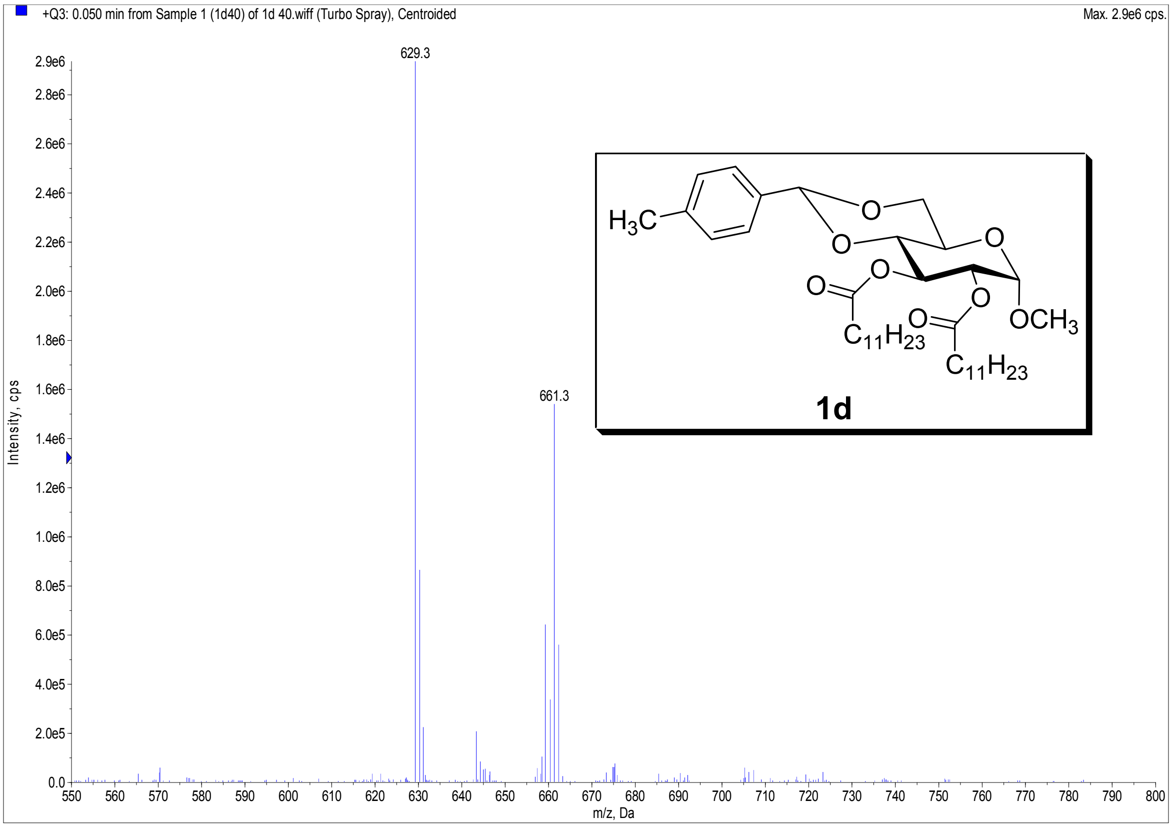
Compound **1b**



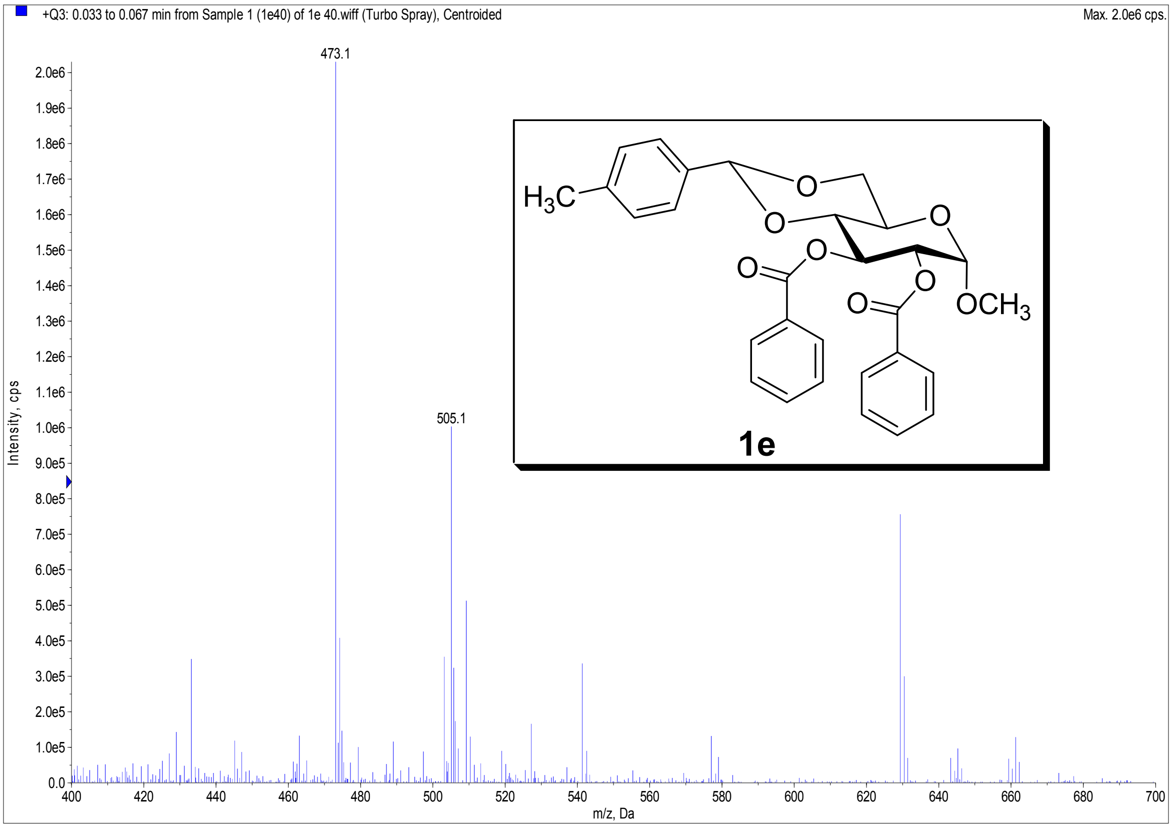
Compound **1c**



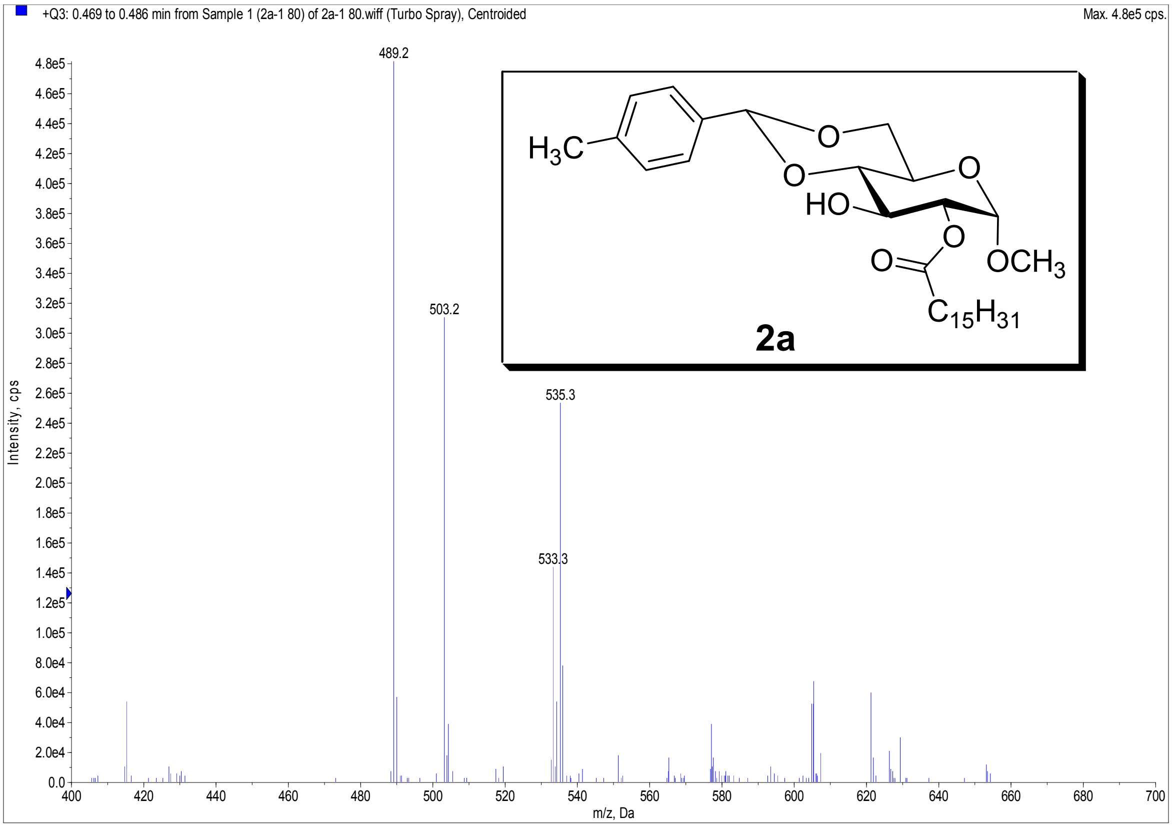
Compound **1d**



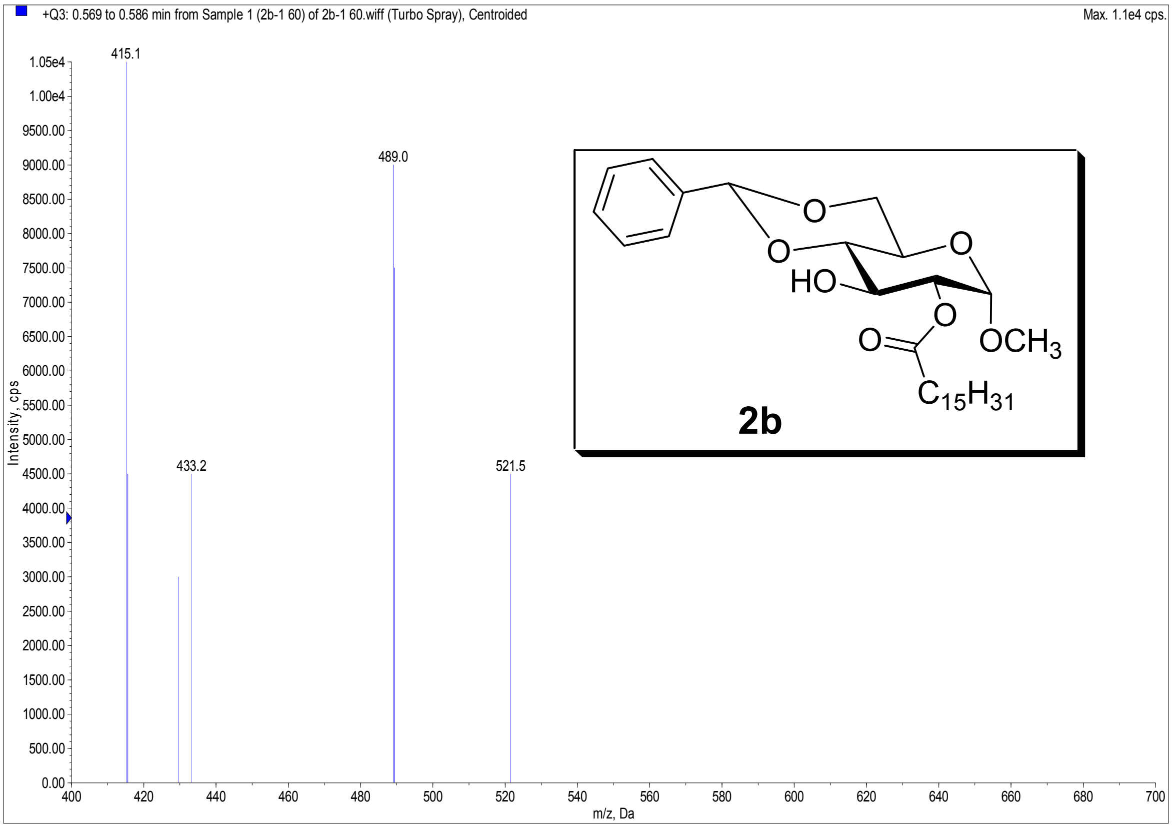
Compound **1e**



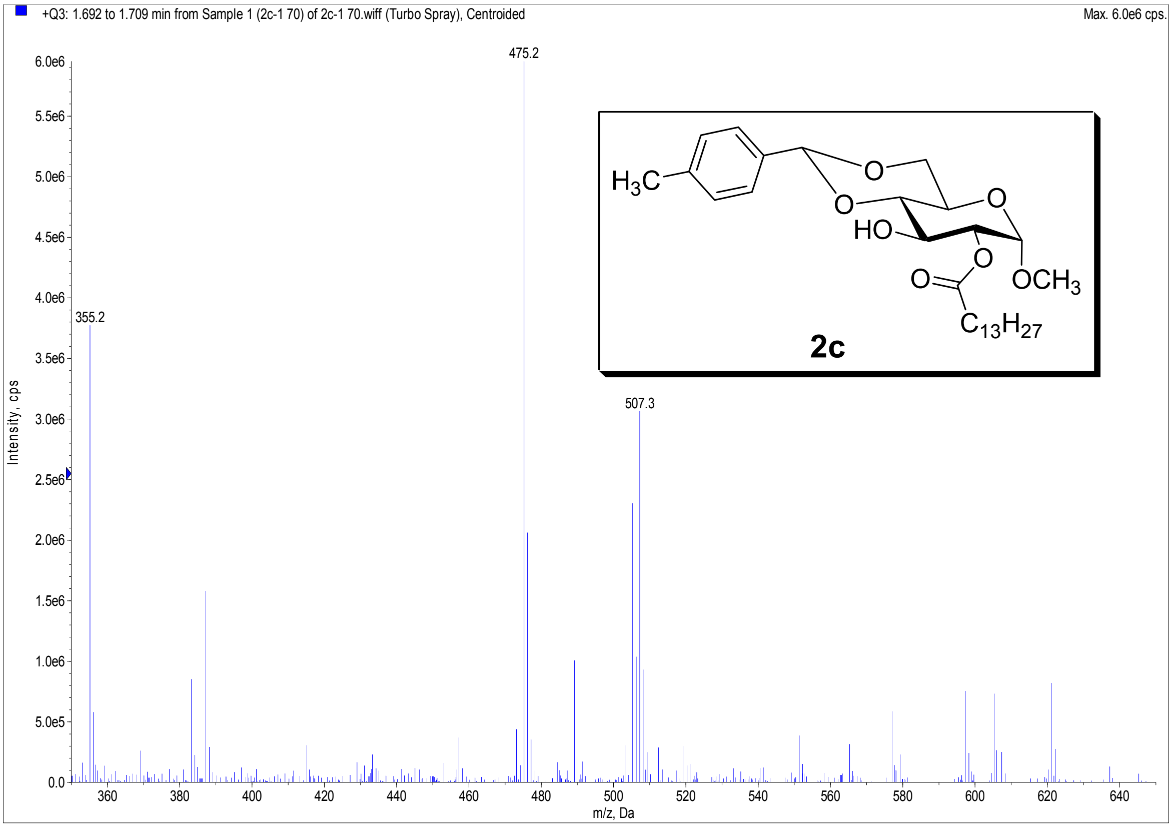
Compound **2a**



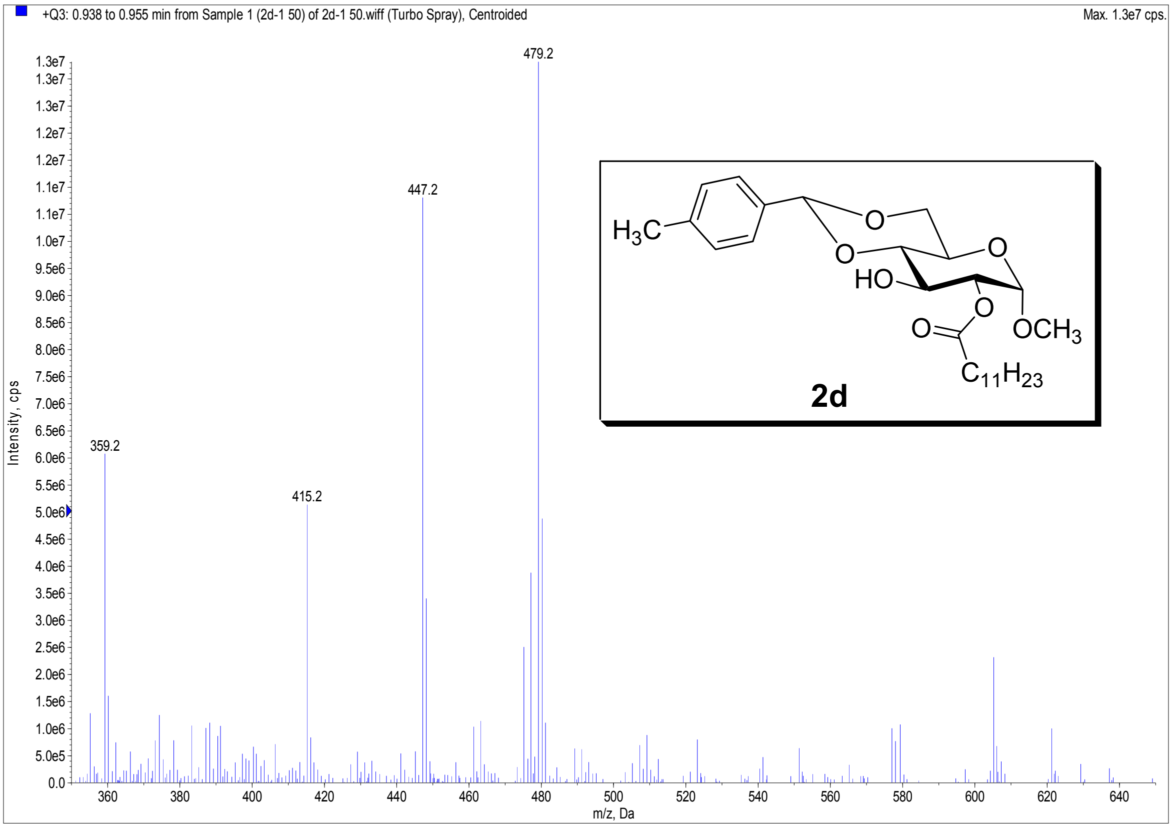
Compound **2b**



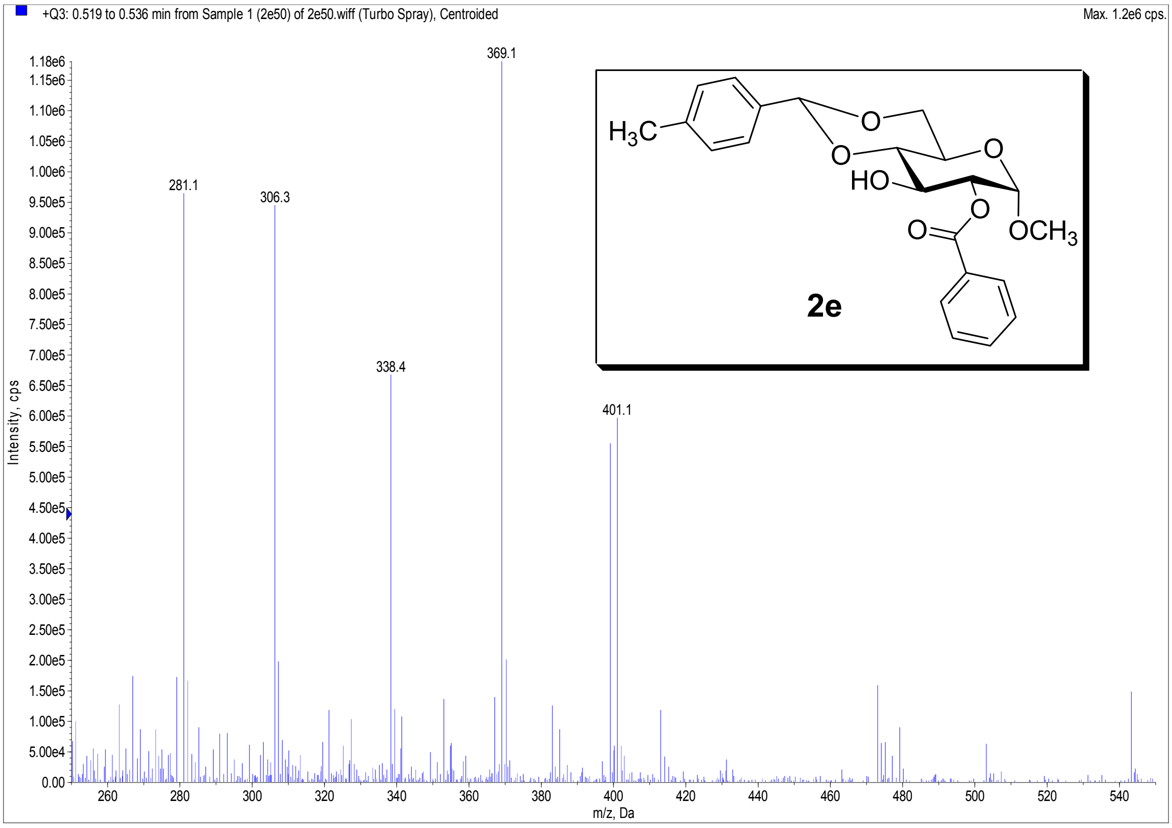
Compound **2c**



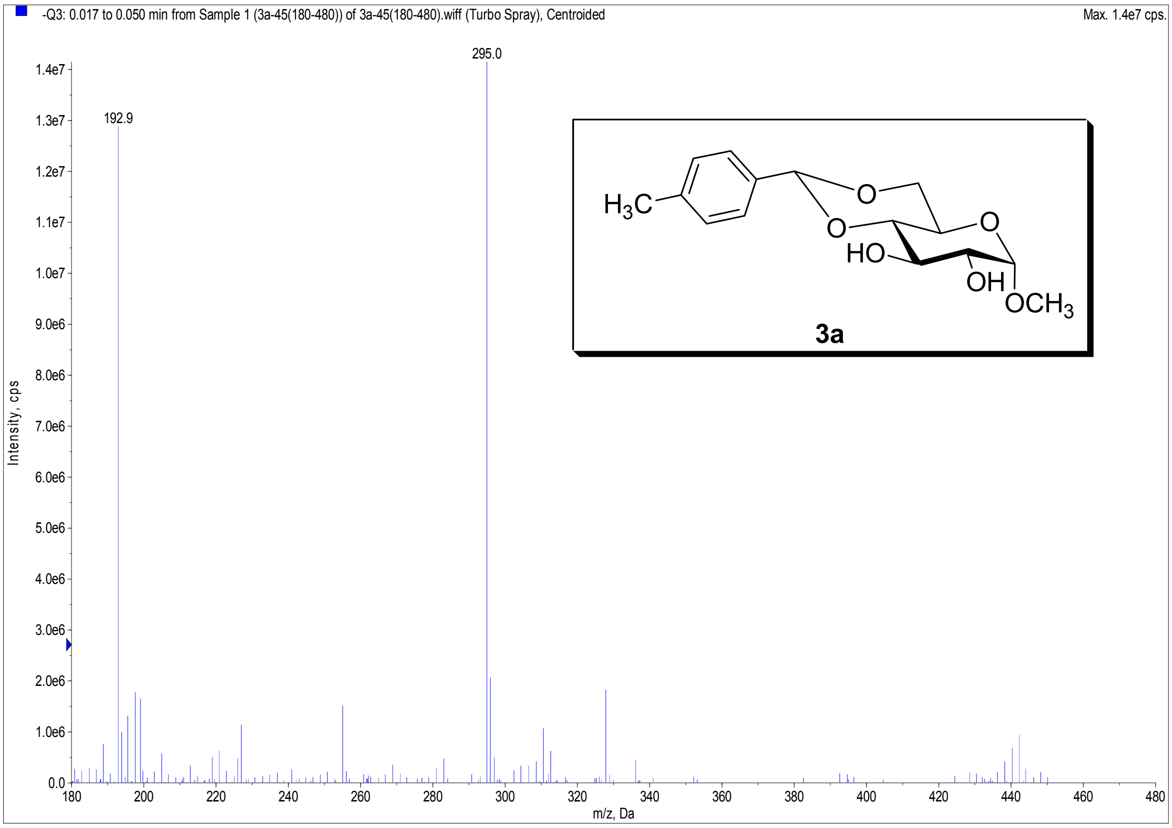
Compound **2d**



Compound **2e**



Compound **3a**


-Q3: 0.017 to 0.050 min from Sample 1 (3a-45(180-480)) of 3a-45(180-480).wiff (Turbo Spray), Centroided
Max. 1.4e7 cps.
295.0
192.9
Intensity, cps
1.4e7
1.3e7
1.2e7
1.1e7
1.0e7
9.0e6
8.0e6
7.0e6
6.0e6
5.0e6
4.0e6
3.0e6
2.0e6
1.0e6
0.0
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
m/z, Da
H3C
O
O
O
HO
OH
OCH3
3a