Combinatorial and automated synthesis of phosphodiester galactosyl-cluster on solid support by click chemistry assisted by microwaves

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Table S1. Calculated masses of each galactosyl-cluster for negative mode

Compounds	Formula for $[M-H]^-$	Calculated mass (Negative mode)
9aL11	$C_{44}H_{74}N_8O_{27}P_2^-$	**1208.06**
9aL12	$C_{49}H_{82}N_8O_{27}P_2^-$	**1276.18**
9aL22	$C_{54}H_{90}N_8O_{27}P_2^-$	**1344.29**
9bL111	$C_{61}H_{104}N_{11}O_{38}P_3^-$	**1691.47**
9bL112	$C_{66}H_{112}N_{11}O_{38}P_3^-$	**1759.59**
9bL122	$C_{71}H_{120}N_{11}O_{38}P_3^-$	**1827.71**
9bL222	$C_{76}H_{128}N_{11}O_{38}P_3^-$	**1895.83**
9cL1111	$C_{78}H_{134}N_{14}O_{49}P_4^-$	**2174.88**
9cL1112	$C_{83}H_{142}N_{14}O_{49}P_4^-$	**2243.00**
9cL1122	$C_{88}H_{150}N_{14}O_{49}P_4^-$	**2311.12**
9cL1222	$C_{93}H_{158}N_{14}O_{49}P_4^-$	**2379.24**
9cL2222	$C_{98}H_{166}N_{14}O_{49}P_4^-$	**2447.36**

HPLC Analysis and MS Characterization:

High performance liquid chromatography (HPLC) analyses were performed on a Waters-Millipore instrument equipped with, a reodyn injector a 600S controller and a Model 996 photodiode array detector. A reverse phase C18 Nucleosil (5 μm) column (150 × 4.6 mm; Macherey-Nagel, Germany) was used at a flow rate of 1 mL min^{-1} using a linear gradient of acetonitrile 5% to 40% in 0.05 M aqueous triethylammonium acetate (pH 7) for 25 min. MALDI-TOF mass spectra were recorded on a Voyager mass spectrometer (Perseptive Biosystems, Framingham, MA) equipped with a nitrogen laser. MALDI conditions were: accelerating voltage 24000V; guide wire 0.05% of accelerating voltage; grid voltage 94% of the accelerating voltage delay extraction time 150 ns. One microliter of crude glycocluster sample was mixed with 5 μL of a saturated solution of 2,4,6–trihydroxyacetophenone (THAP) in acetonitrile:water (1:1 v/v) containing 10% of ammonium citrate and few beads of DOWEX 50W-X8 ammonium sulfonic acid resin were added. Then 1 μL of the mixture was placed on a plate and dried at ambient temperature and pressure.

Figure S1 HPLC and MALDI-TOF MS of 9a from 8a and 4:3 in a 1:2 or 2:1 ratio and MS of each HPLC peak

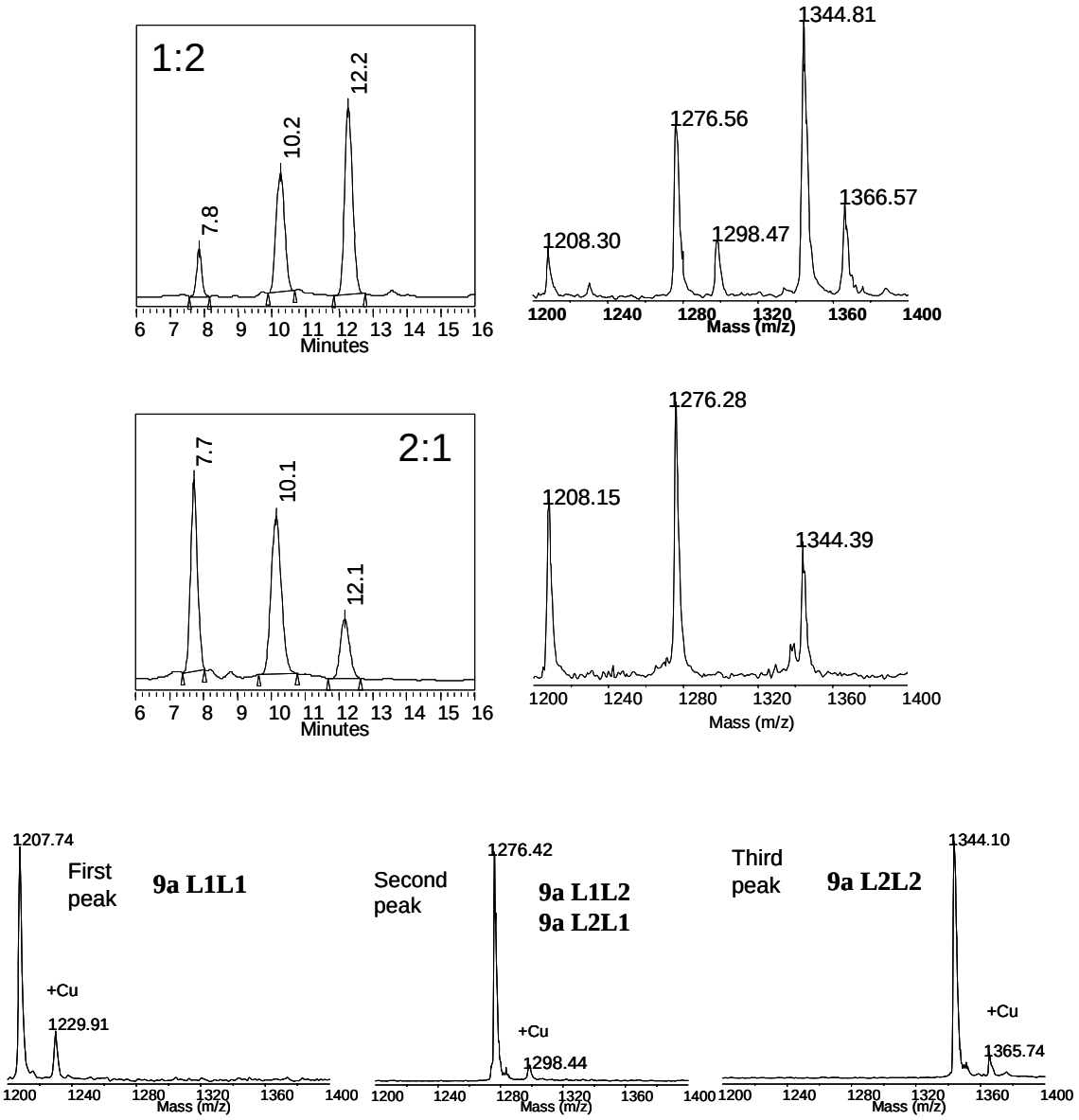

Figure S2 HPLC and MALDI-TOF MS of 9b from 8b and 4:3 in a 1:2 or 2:1 ratio and MS of each HPLC peak

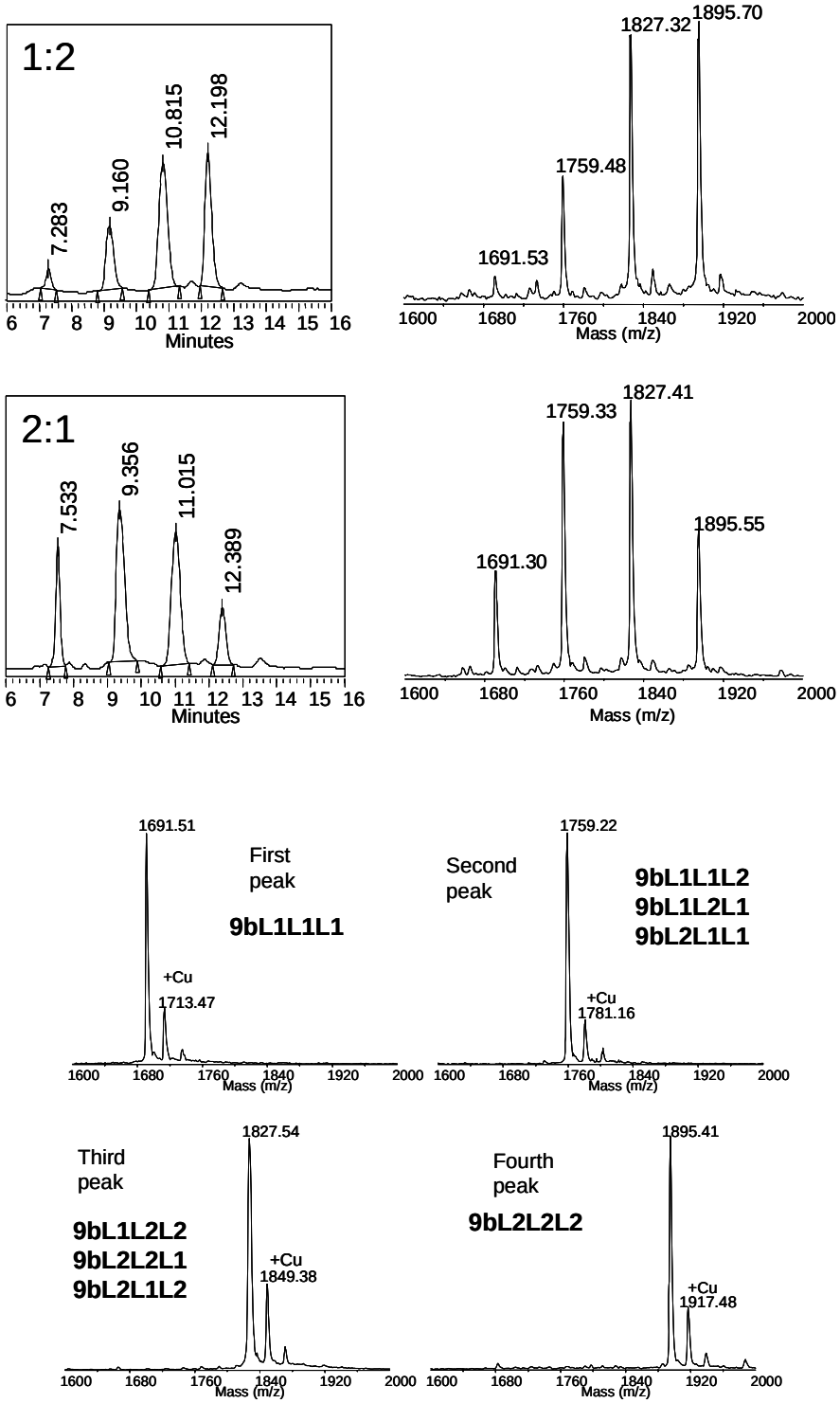

Figure S3 HPLC and MALDI-TOF MS of 9c from 8c and 4:3 in a 1:2 or 2:1 ratio and MS of each HPLC peak

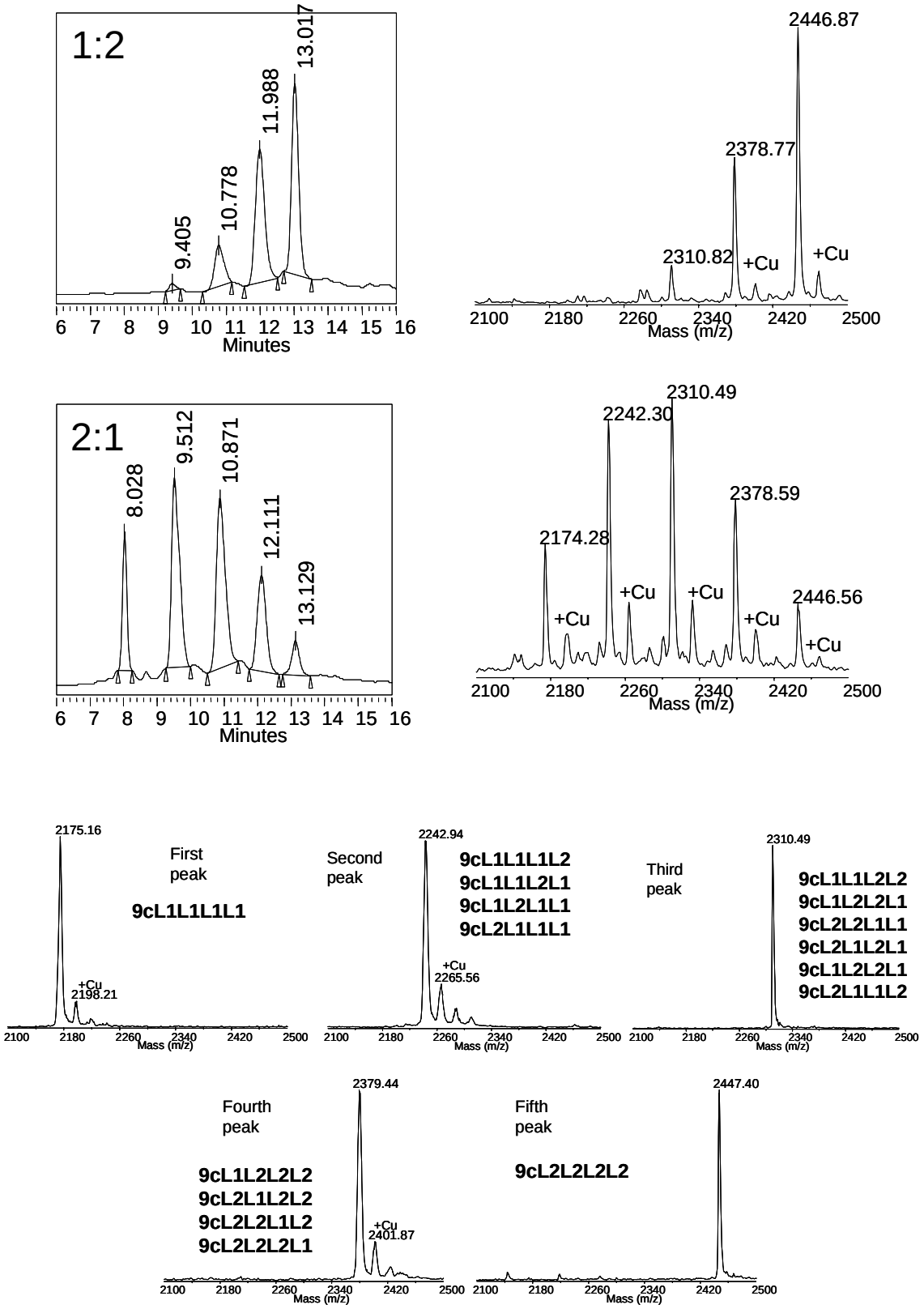

Figure S4 ^{1}H NMR spectrum of 1

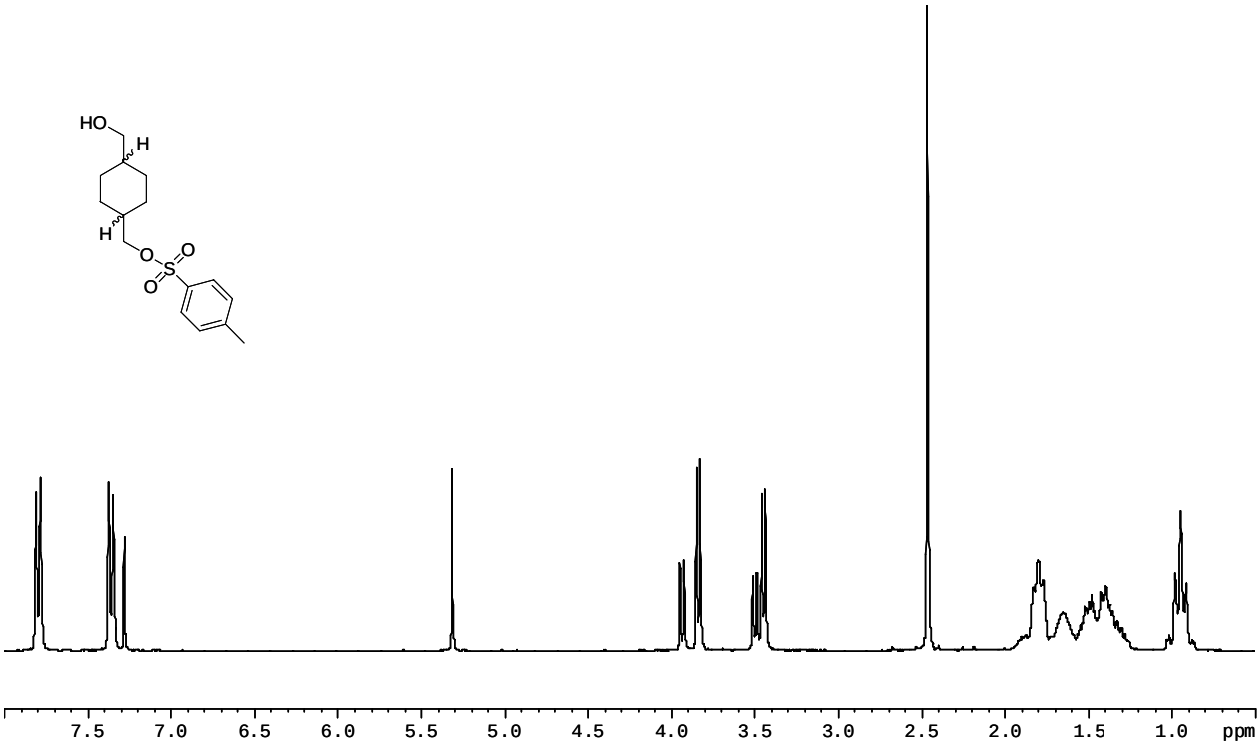

Figure S5 ^{13}C NMR spectrum of 1

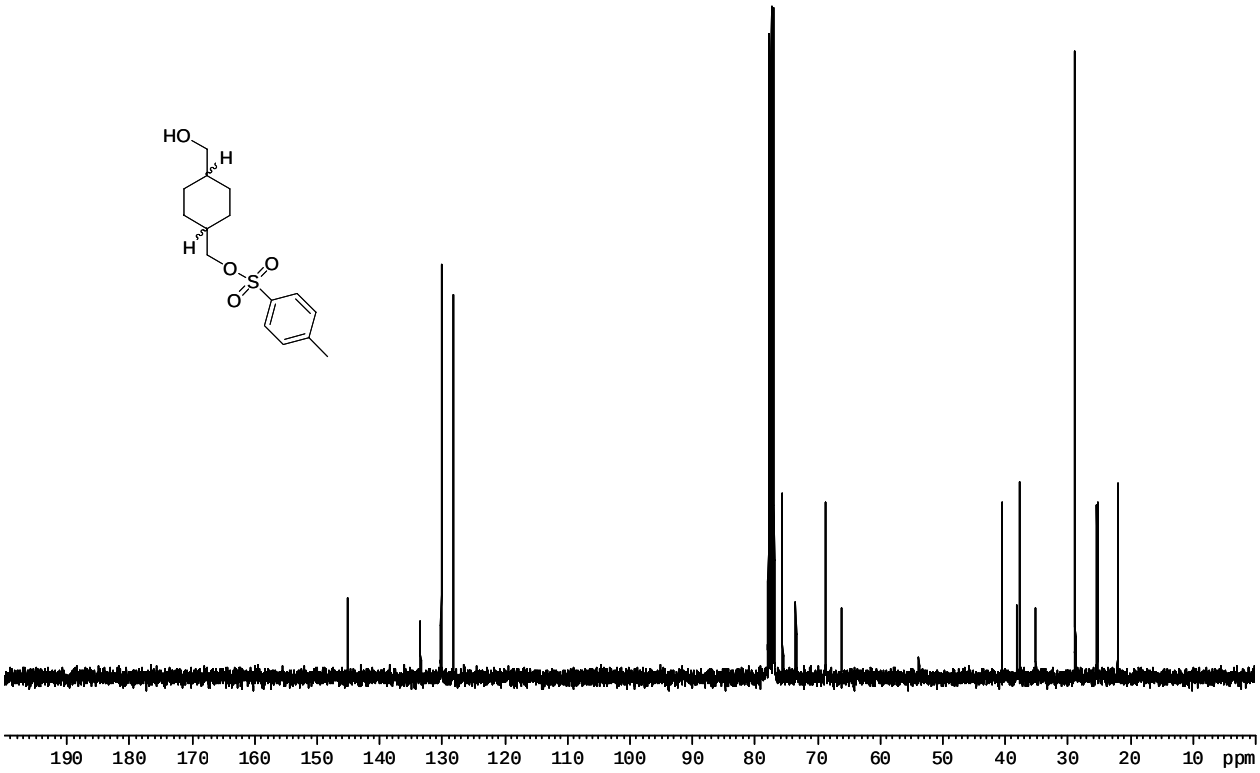

Figure S6 ^{1}H NMR spectrum of 2

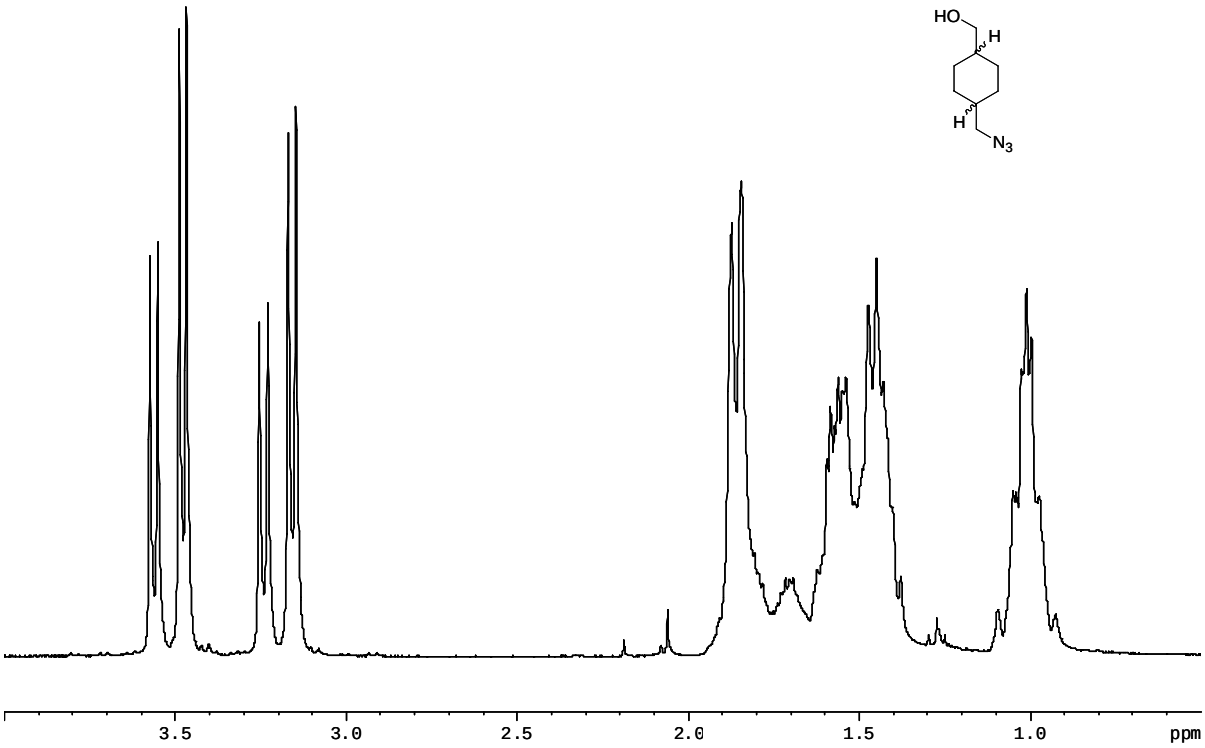

Figure S7 ^{13}C NMR spectrum of 2

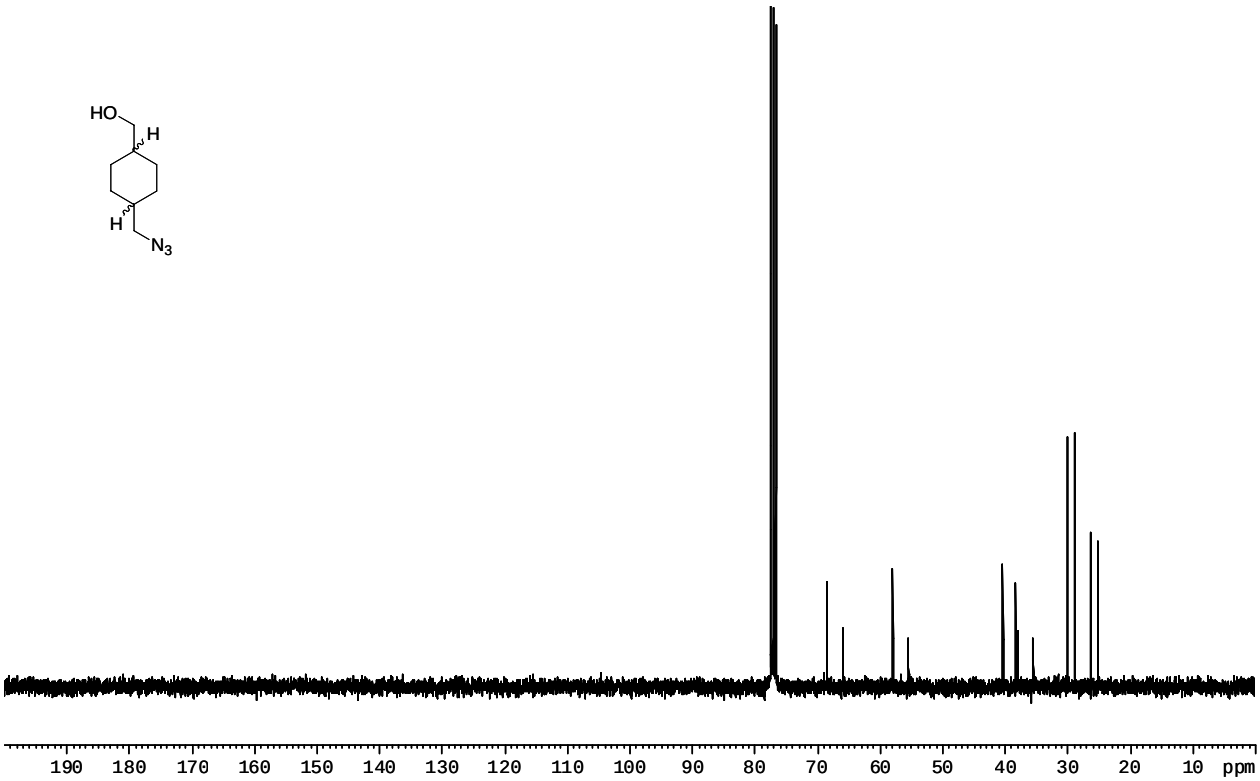

Figure S8 ^{1}H NMR spectrum of 3

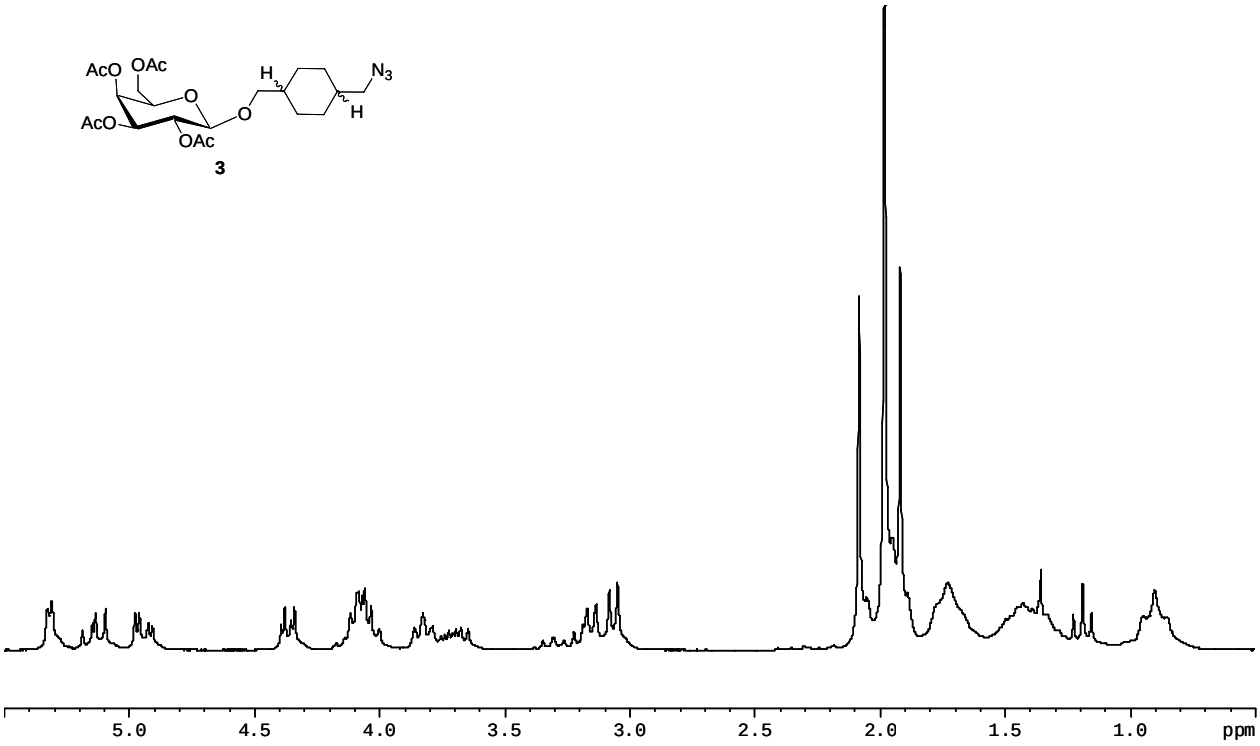

Figure S9 ^{13}C NMR spectrum of 3

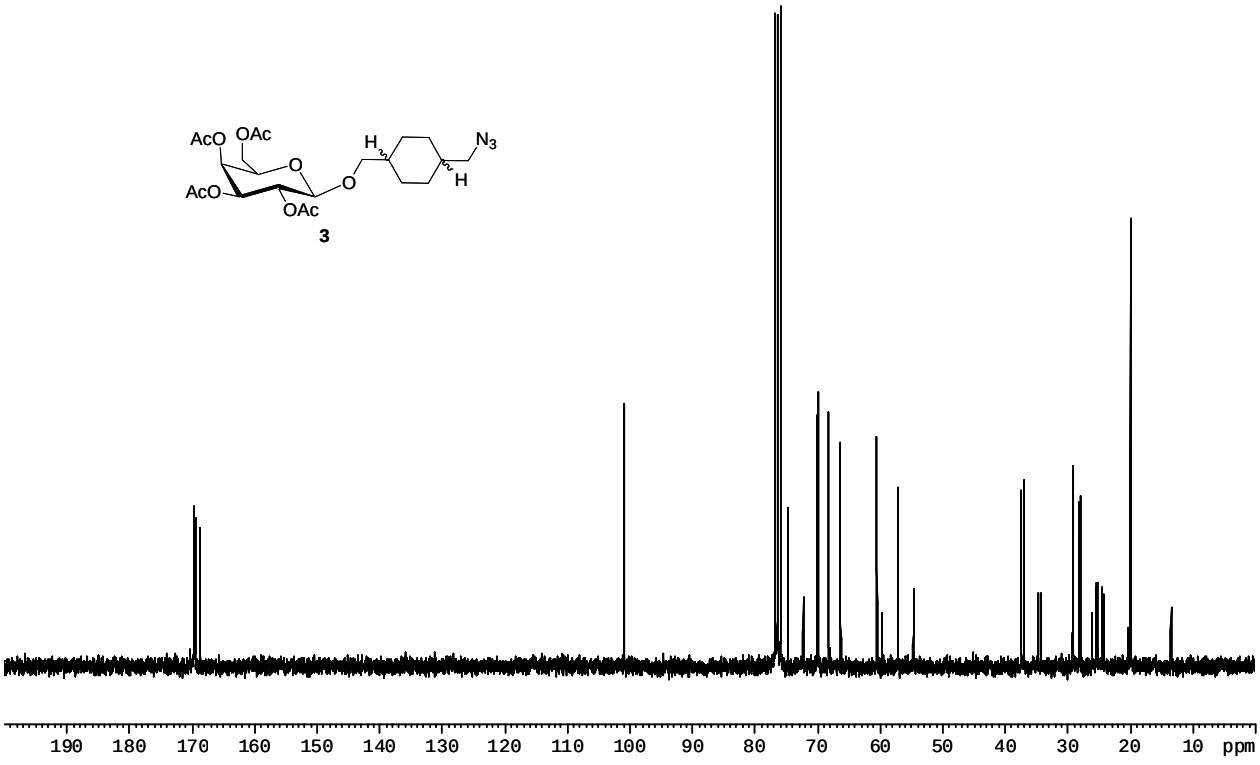

Figure S10 ^{1}H NMR spectrum of 6

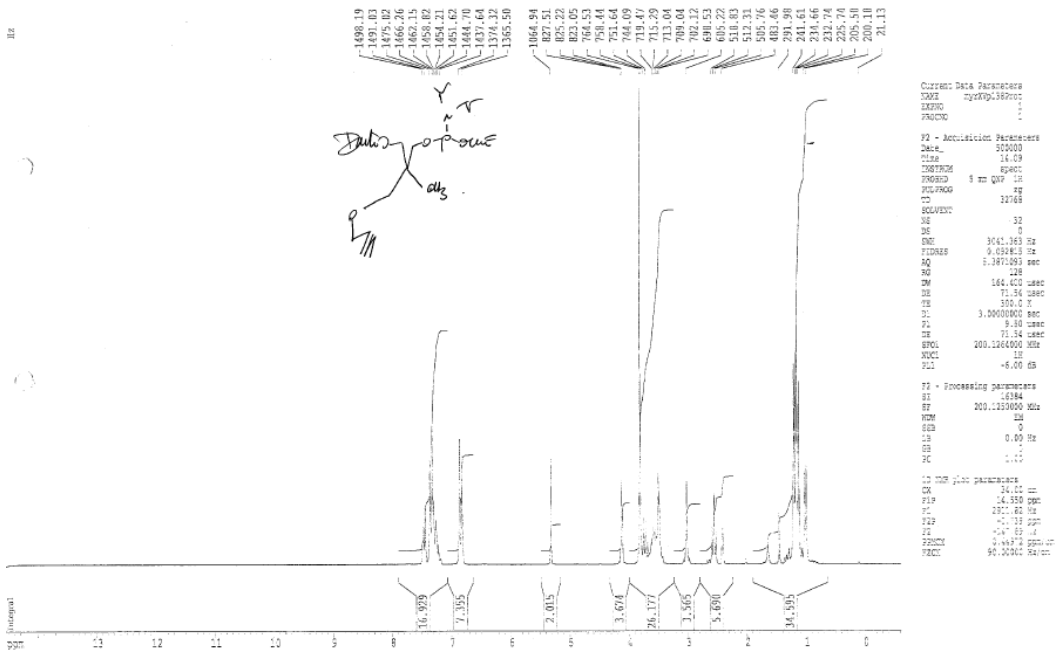

Figure S11 ^{13}C NMR spectrum of 6

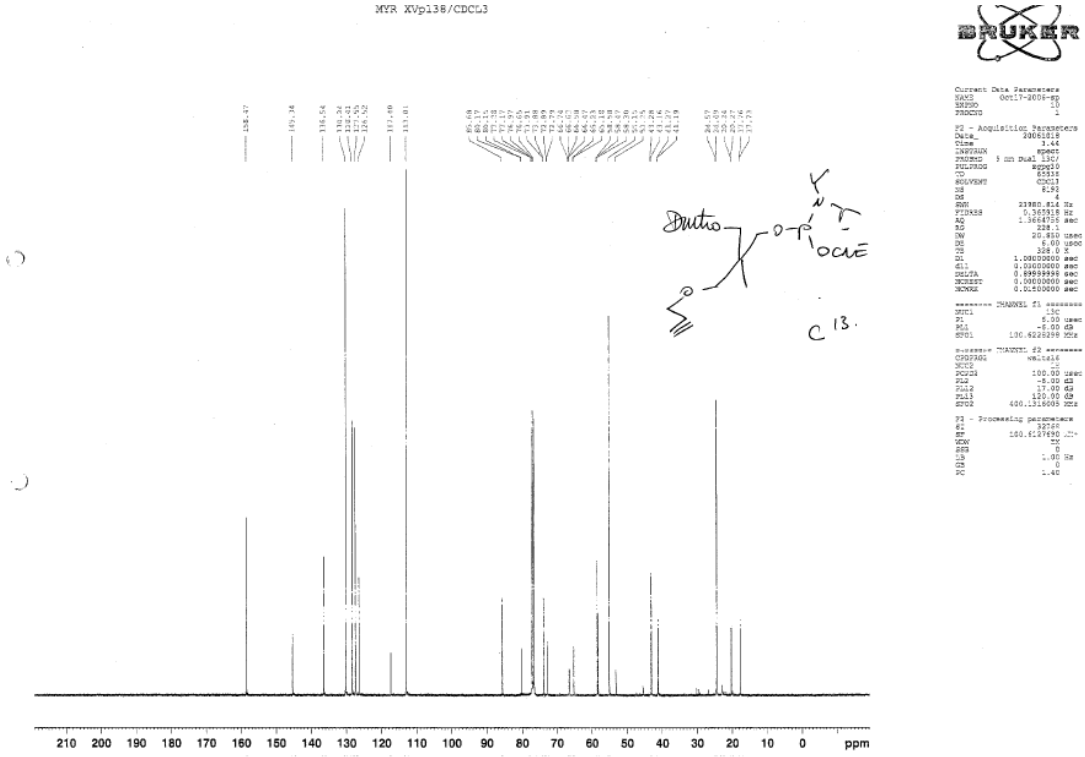

Figure S12 ^{31}P NMR spectrum of 6