Biomimetic Crystallization of Calcium Carbonate Spherules Controlled by Hyperbranched Polyglycerols

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Supporting Information

Contents

I. Table S1. Characterization of Polyglycerols 1-5

Polyglycerol	M_n [g/mol][a,b]	PDI (M_w/M_n)[c]	DB (Degree of branching)[d]	Degree of functionalization [%][e]	Hydroxyl number[f]
1	4350[a]	1.26	0.56		68
2	2960[a]	1.29	0.57		40
Carboxylate **3-Na**	5950[b]			29	
Carboxylate **4-Na**	4100[b]			35	
Sulfate **5-H**	7600[b]			59	
Sulfate **5-Na**	8480[b]			59	

[a] Determined from GPC (DMF). [b] Calculated using the M_n of the polyglycerol core and the experimental degree of functionalization. [c] Determined from GPC (DMF). [d] Determined from ^{13}C NMR spectra. [e] **5-H** and **5-Na**: Degree of sulfation (ds) obtained from ICP-AES analysis; **3-Na** and **4-Na**: degree of carboxylation (dc) obtained from titration. [f] The hydroxy number calculated from titration.

II. Table S2. pH values of solutions ($CaCl_2$/polymer/H_2O)[a]

Polymer	**3-Na**	**4-Na**	**5-H**	**5-Na**	**5-Im**	**6-H**
pH	7.10	7.13	1.67	7.02	6.17	1.72

[a] 10 mM of Ca^{2+}; 5 $g.L^{-1}$ of polymer.

III. Copies of GPC, ^{1}H NMR, ^{13}C NMR and IR spectra of polyglycerols 1-5

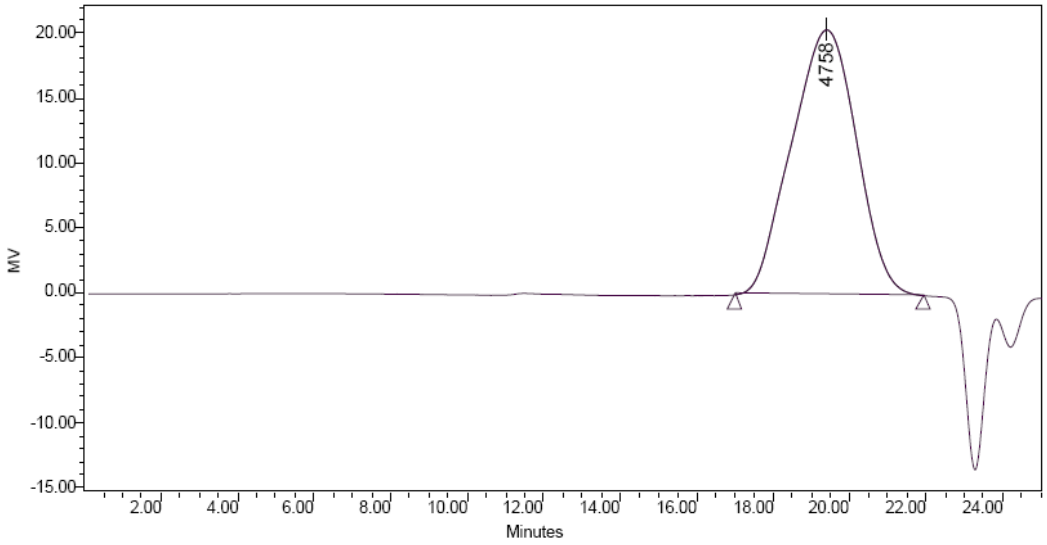


Fig. S1 Gel permeation chromatography (GPC) trace of polyglycerol **1** in DMF.

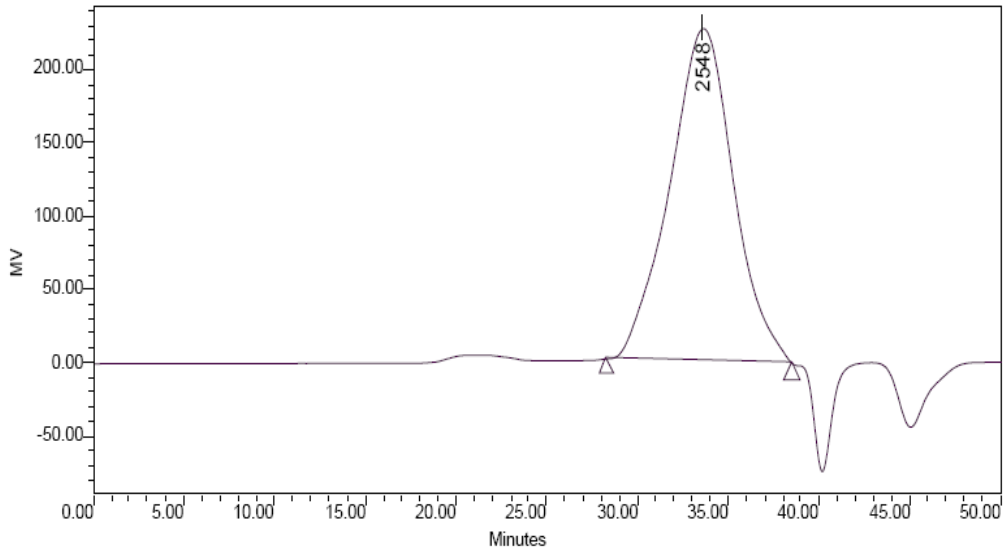
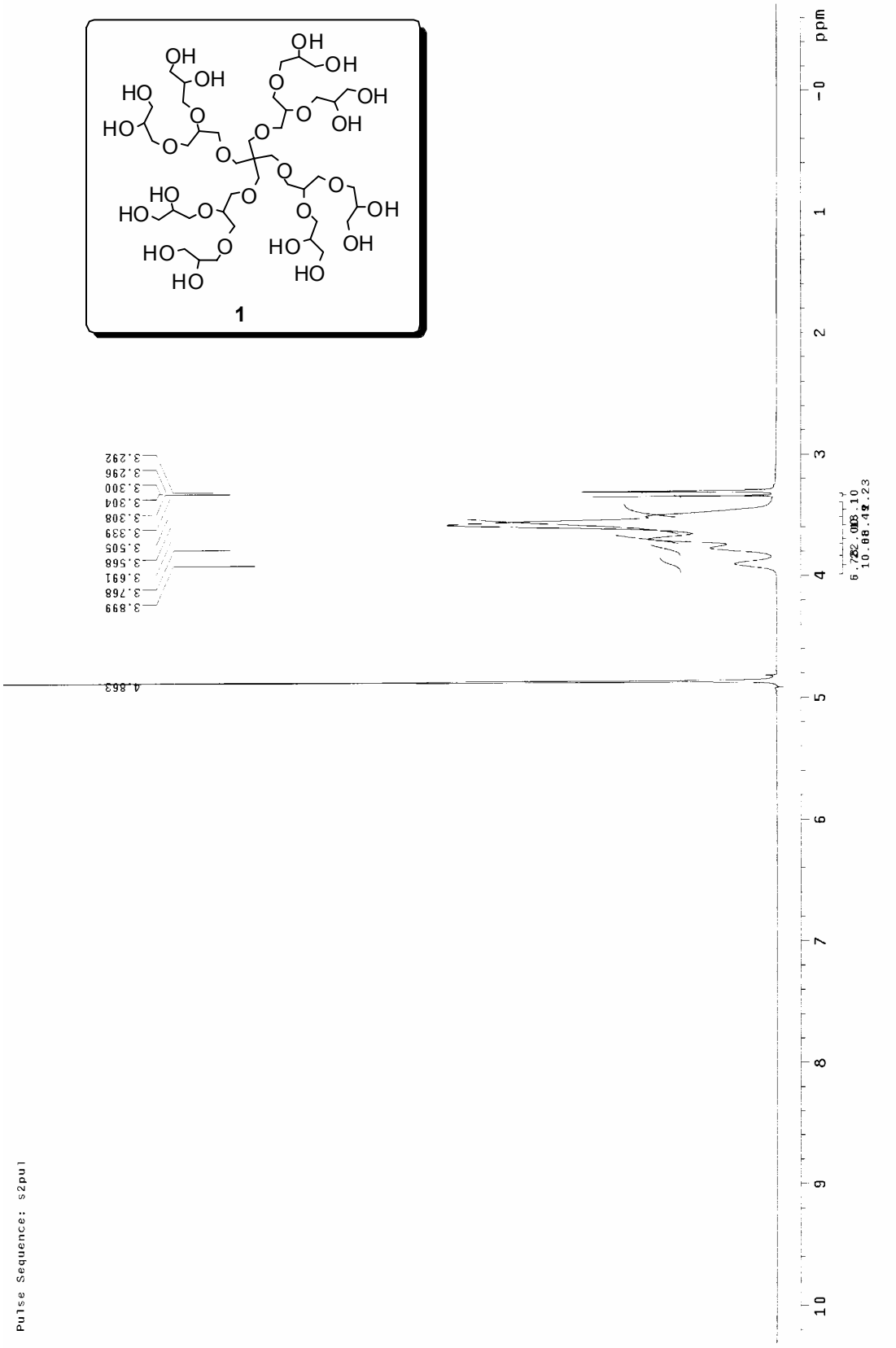


Fig. S2 Gel permeation chromatography (GPC) trace of polyglycerol **2** in DMF.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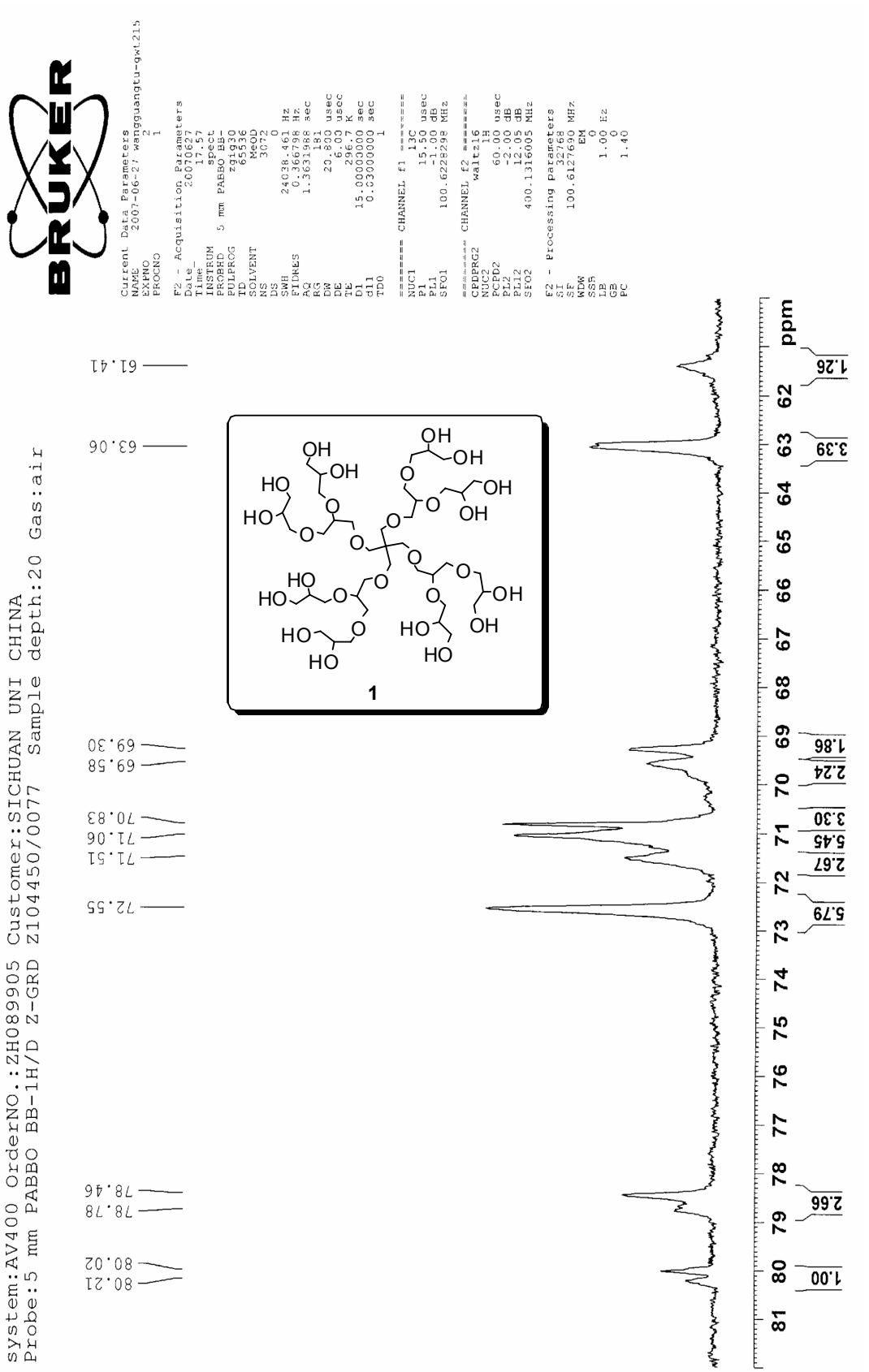
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SFO1 100.6228298 MHz
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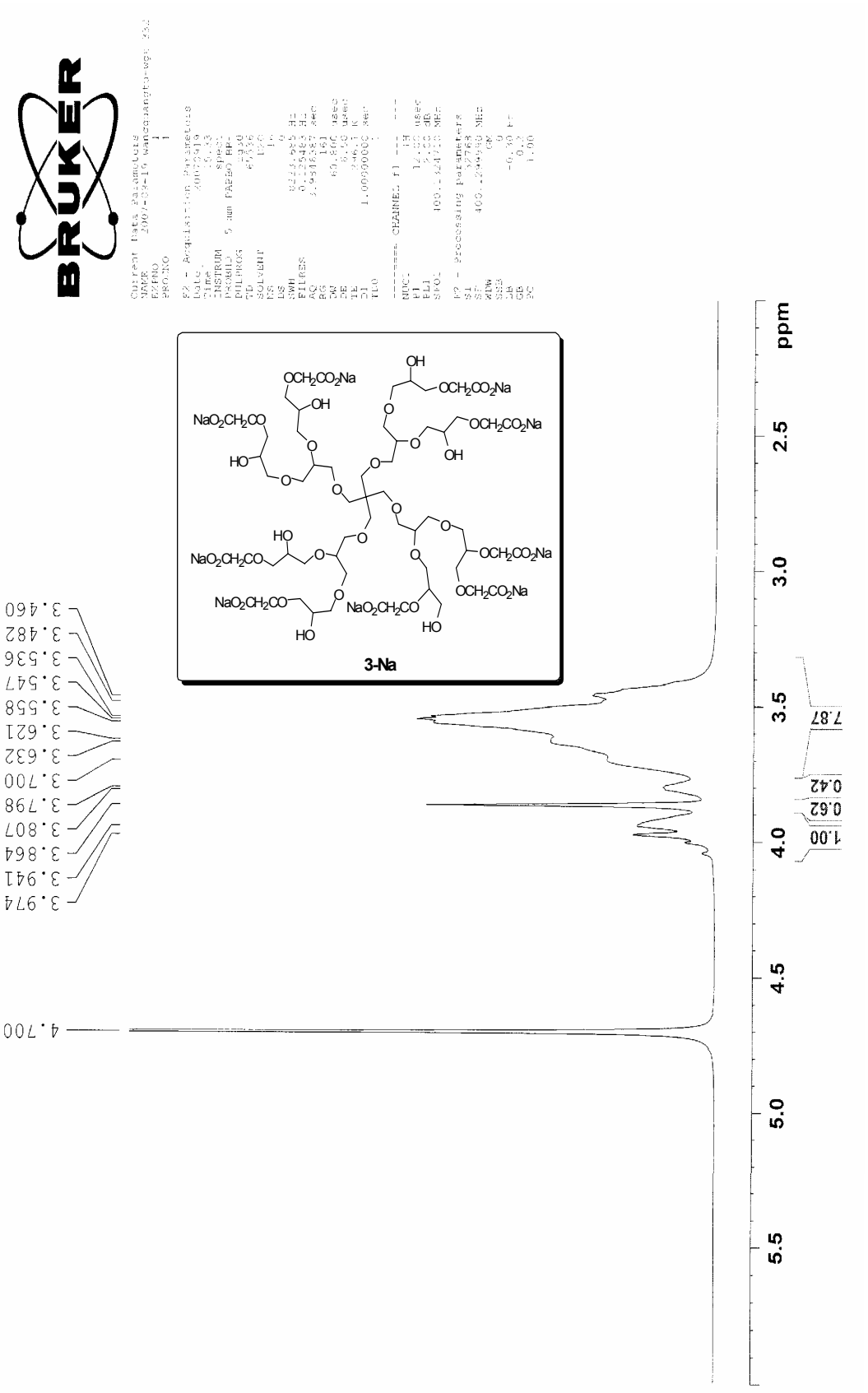
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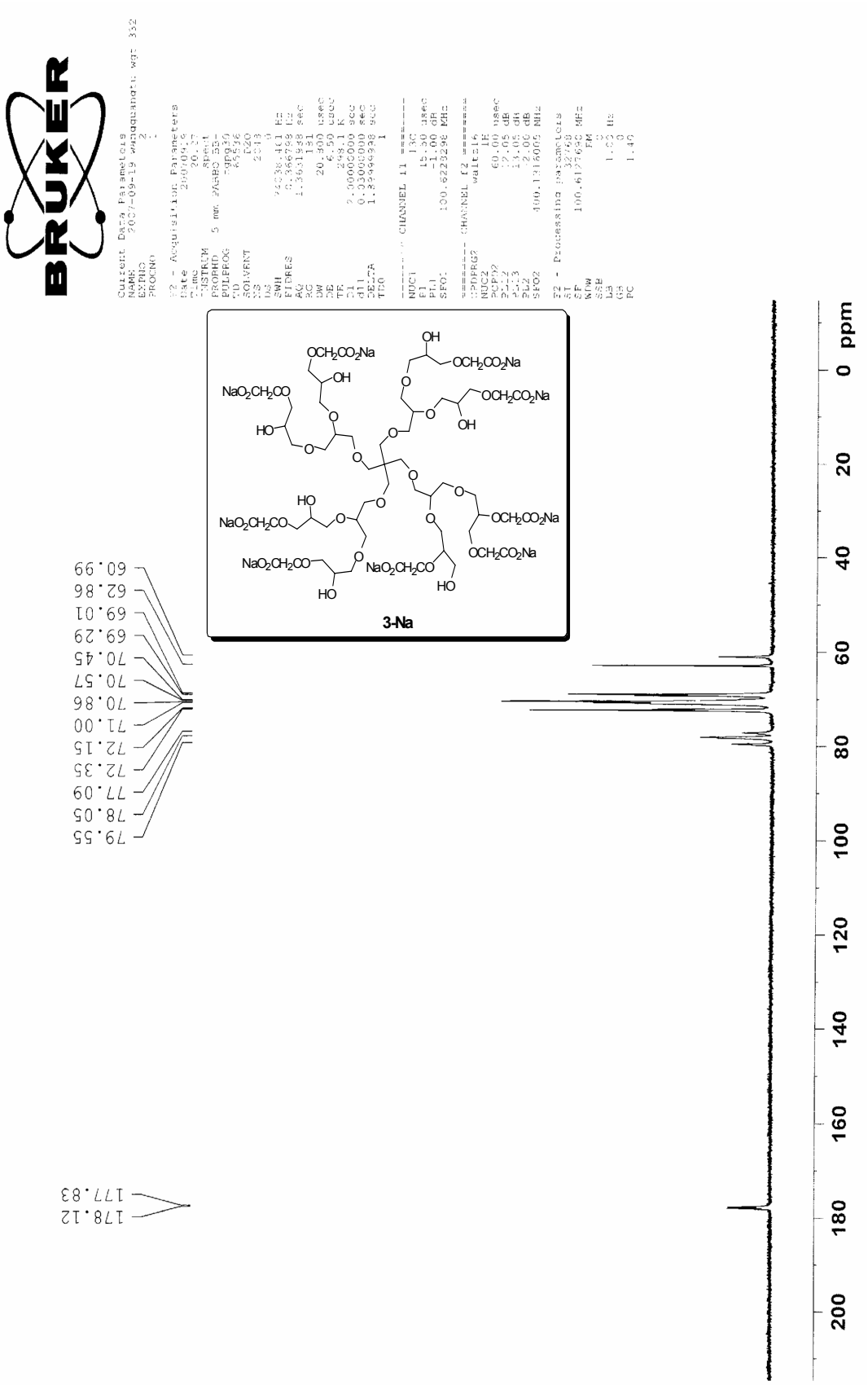
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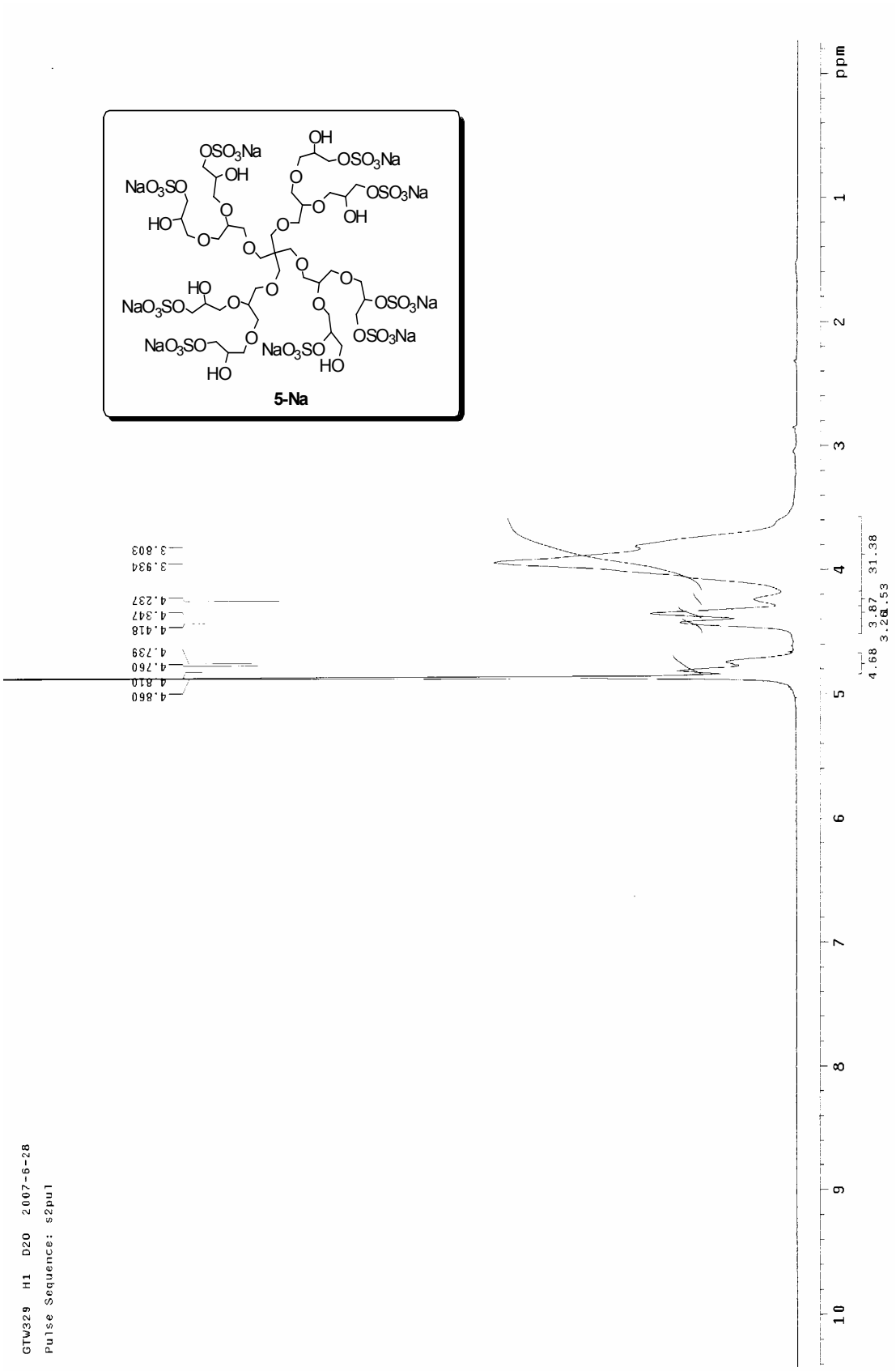
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2
3
4
5
6
7
8
9
10
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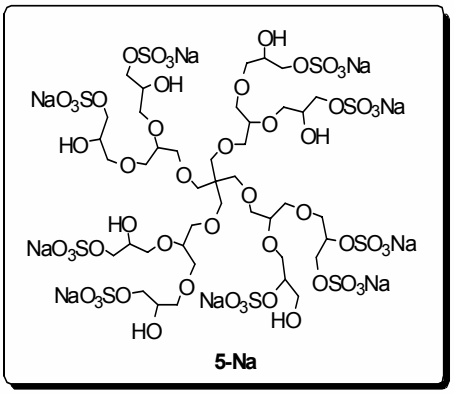

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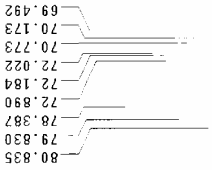

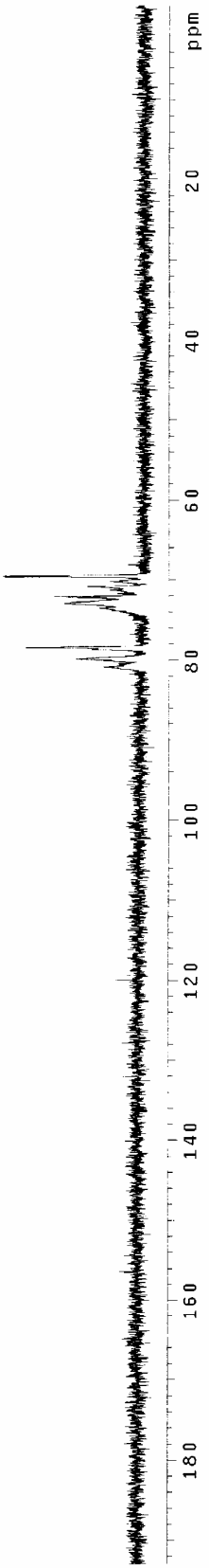

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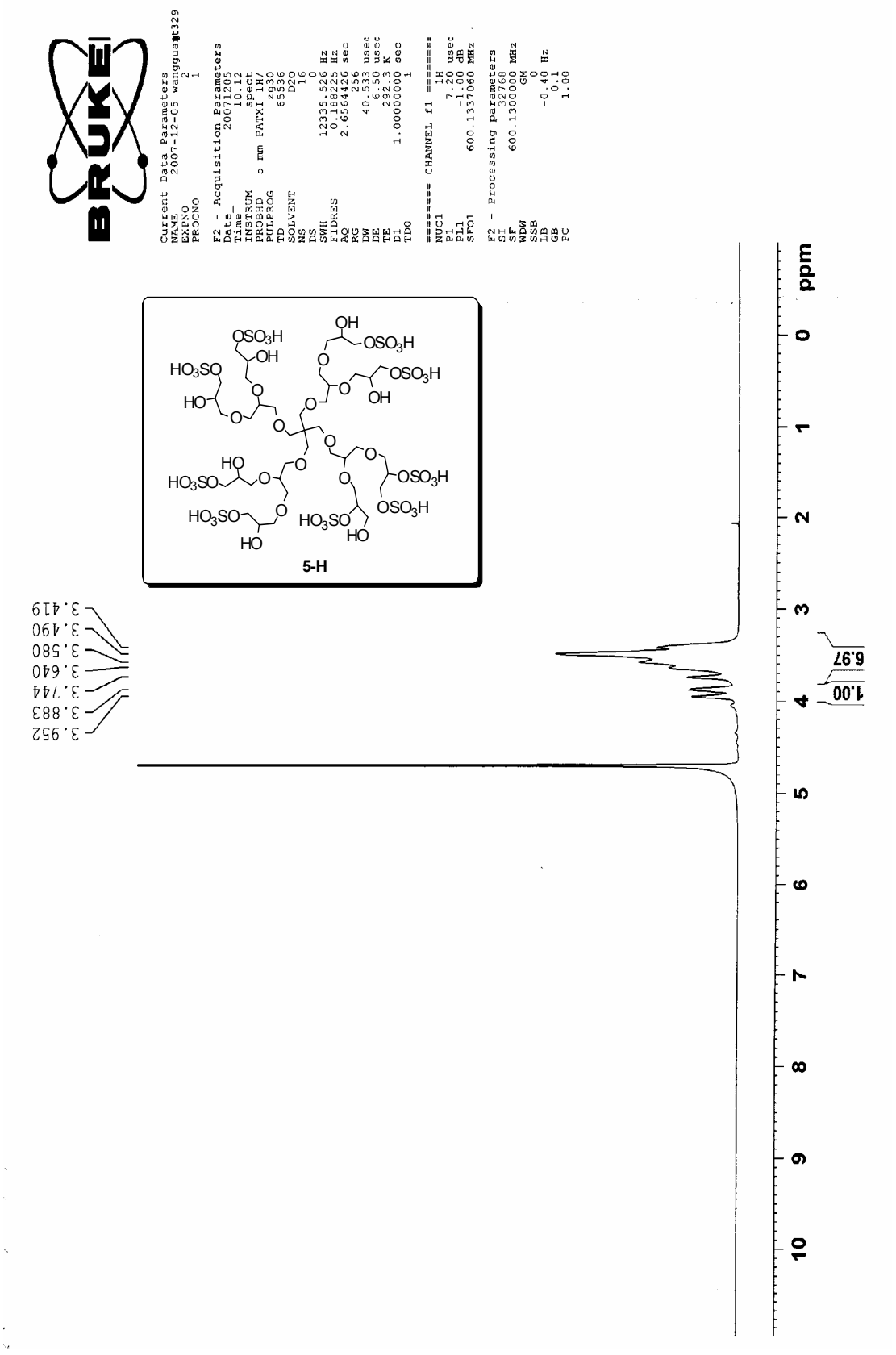
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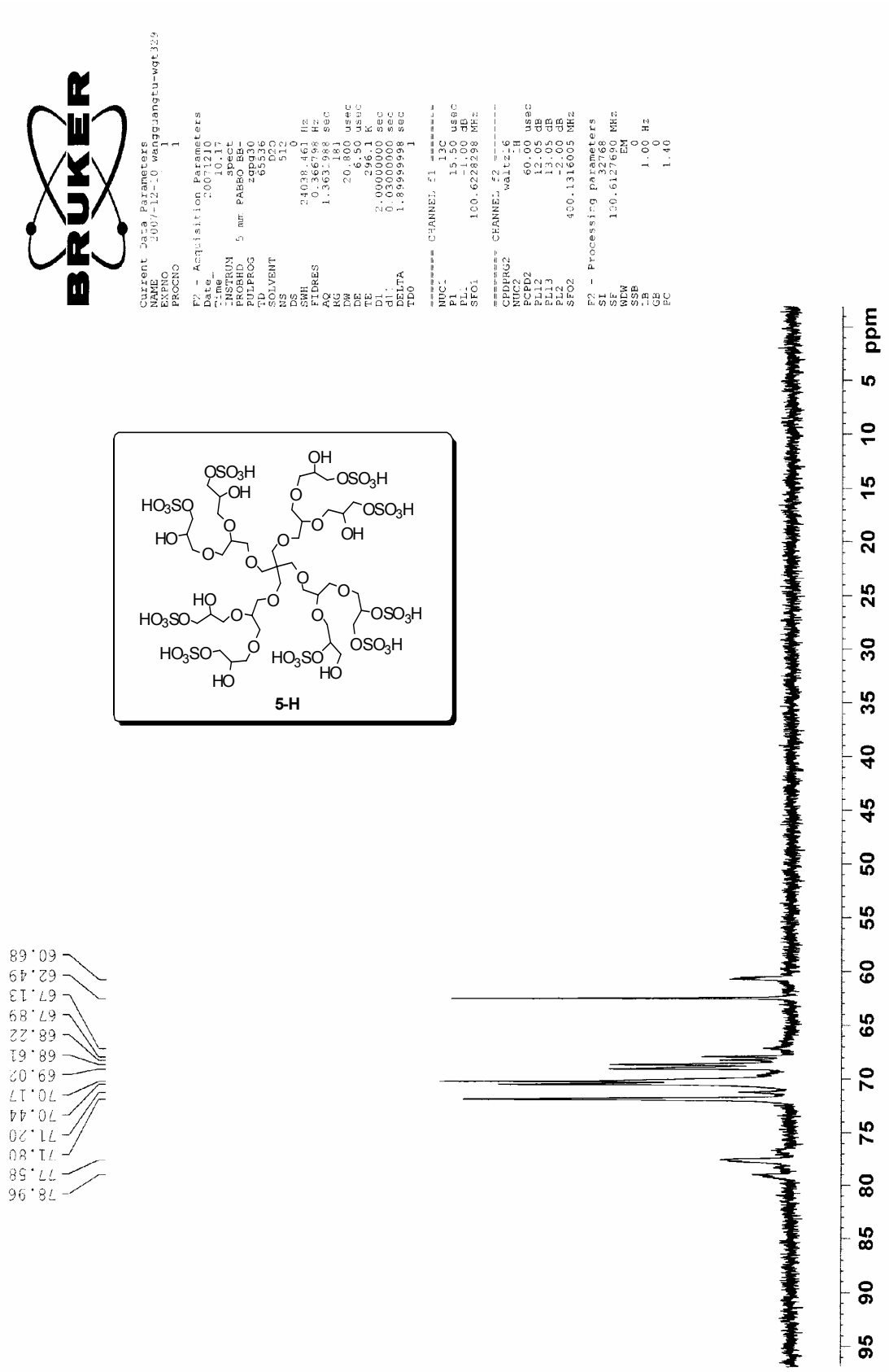
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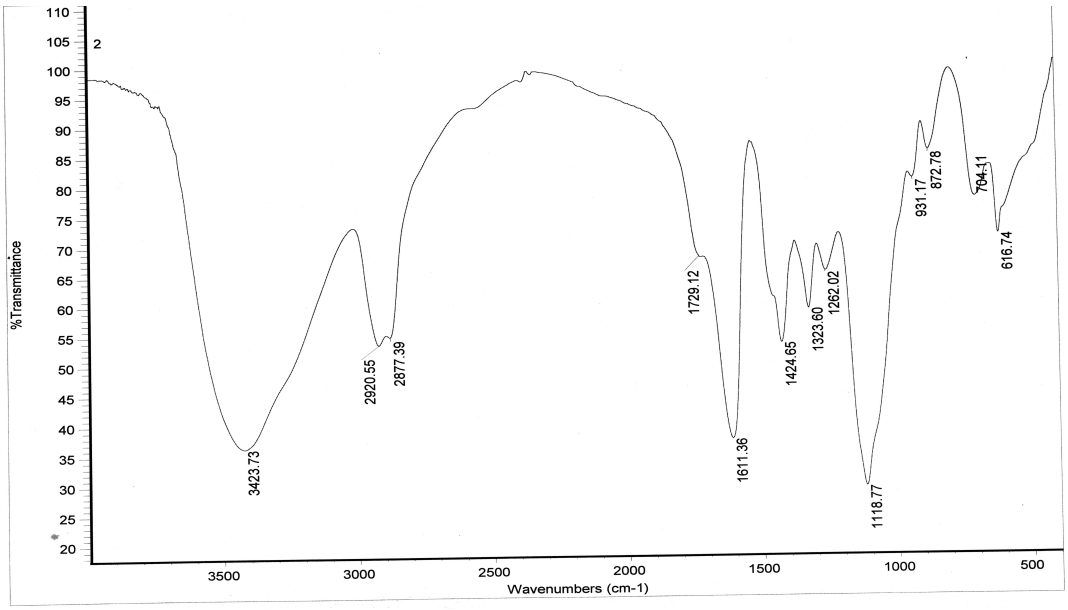

Fig. S3 IR spectrum of polyglycerol carboxylate **3-Na**.

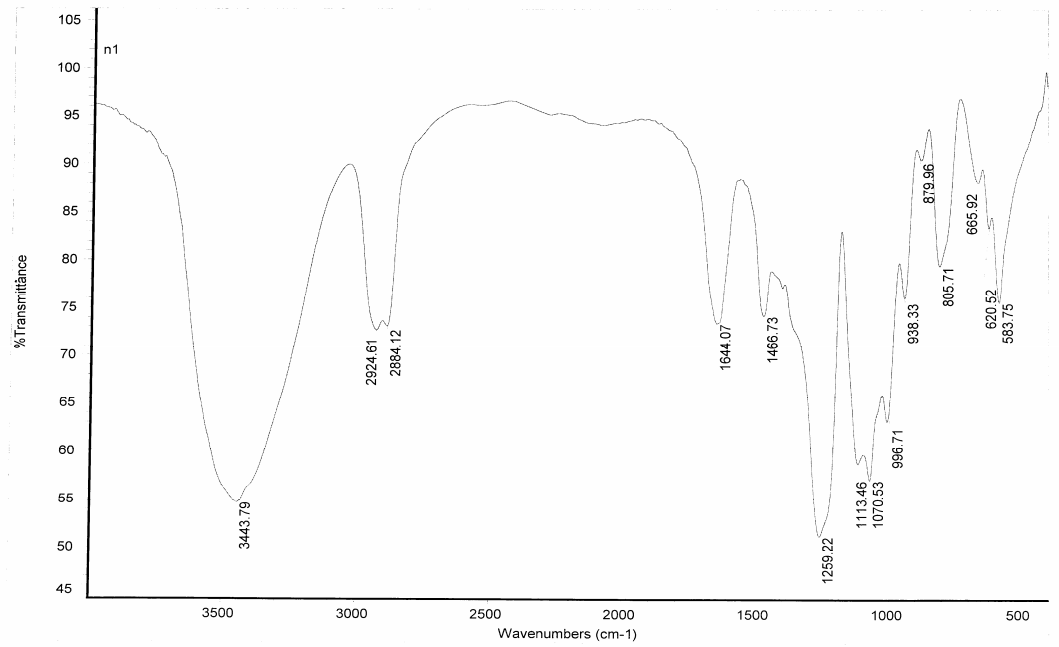

Fig. S4 IR spectrum of polyglycerol sulfate **5-Na**.

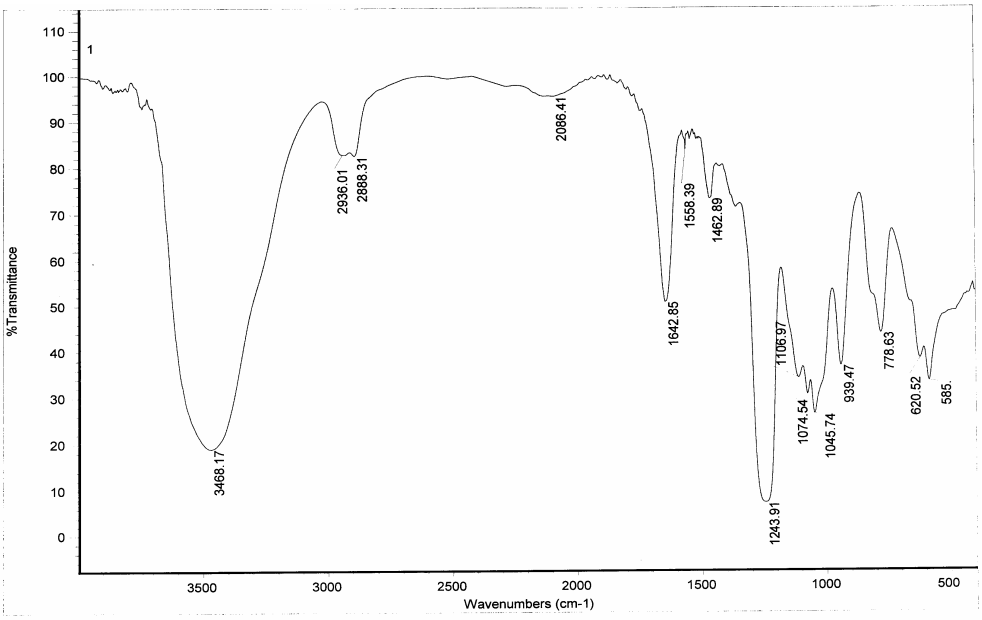

Fig. S5 IR spectrum of polyglycerol hydrogen sulfate **5-H**.

IV. Copies of IR and TGA of the $CaCO_3$ crystals

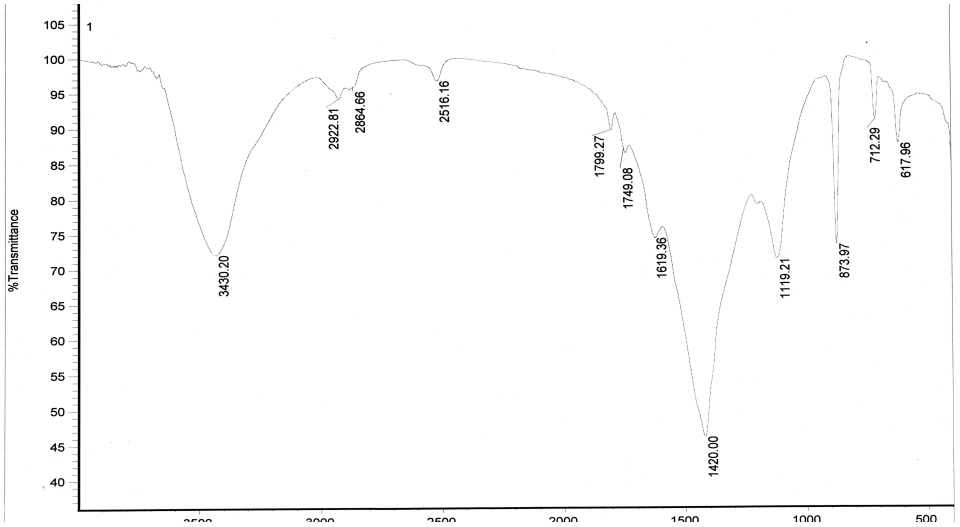

Fig. S6 IR spectrum of the crystals of $CaCO_3$ particles obtained after 2 days in the prsence of polyglycerol carboxylate **3-Na** (5 gL^{-1}) and Ca^{2+} (10 mM).

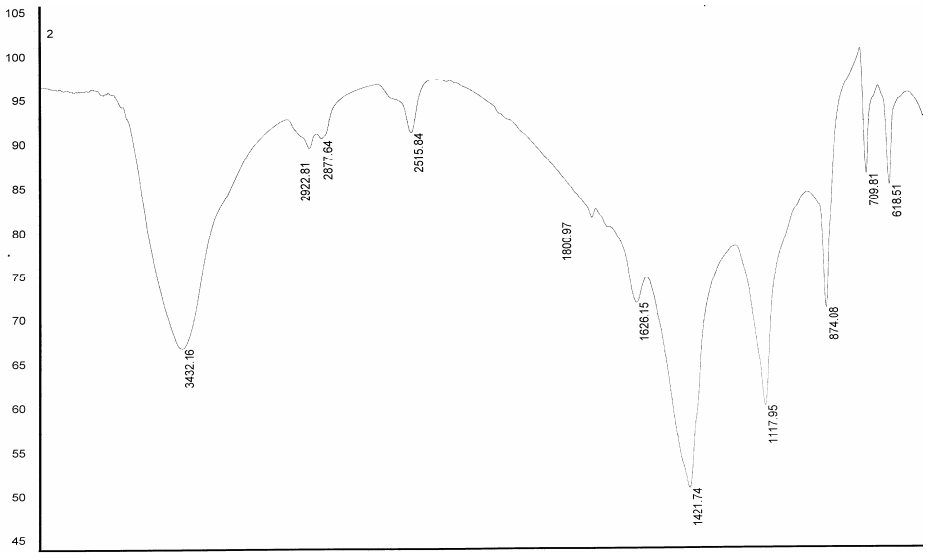

Fig. S7 IR spectrum of the crystals of $CaCO_3$ particles obtained after 2 days in the prsence of polyglycerol sulfate **5-H** (5 gL^{-1}) and Ca^{2+} (10 mM).

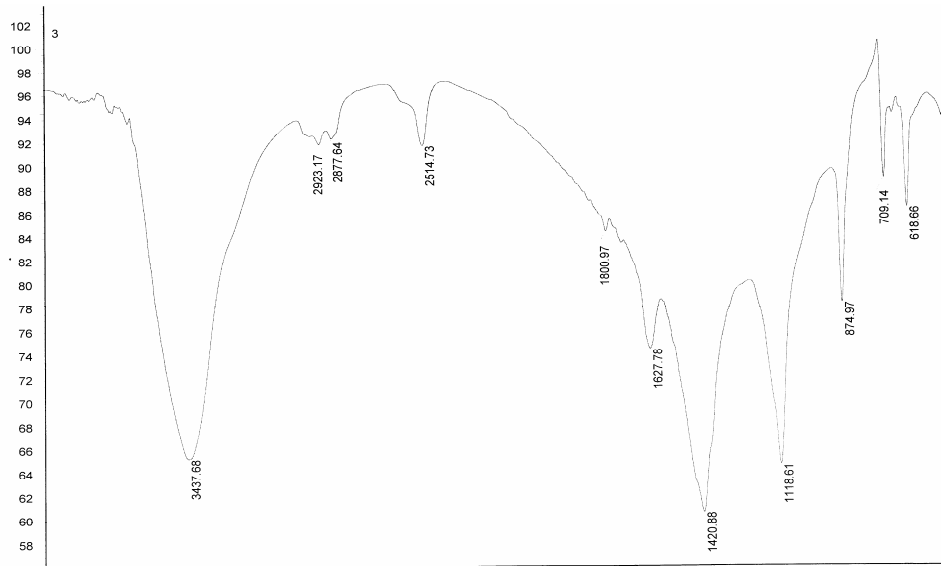

Fig. S8 IR spectrum of the crystals of $CaCO_3$ particles obtained after 2 days in the prsence of polyglycerol sulfate **5-Na** (5 gL^{-1}) and Ca^{2+} (10 mM).

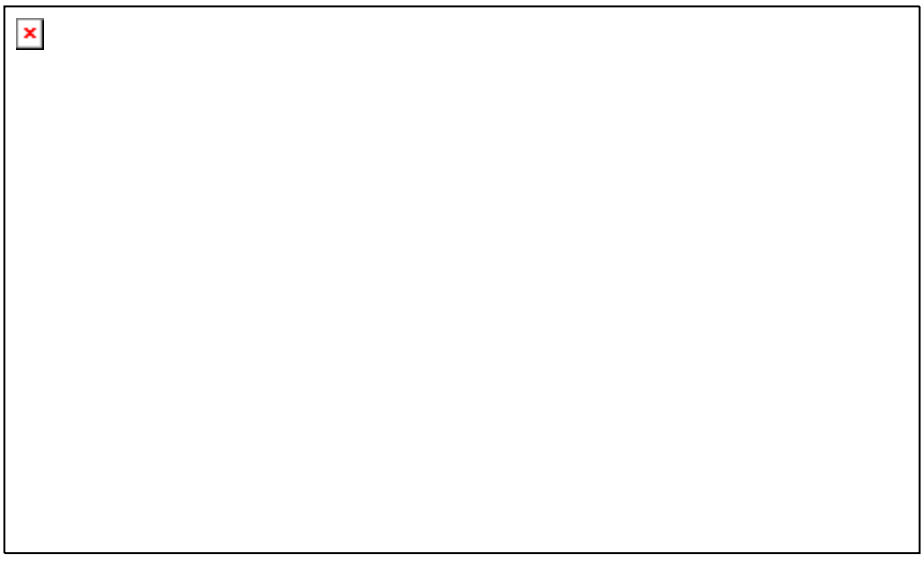

Fig. S9 IR spectrum of the crystals of $CaCO_3$ particles obtained after 2 days in the prsence of polyglycerol sulfate **5-Im** (5 gL^{-1}) and Ca^{2+} (10 mM).

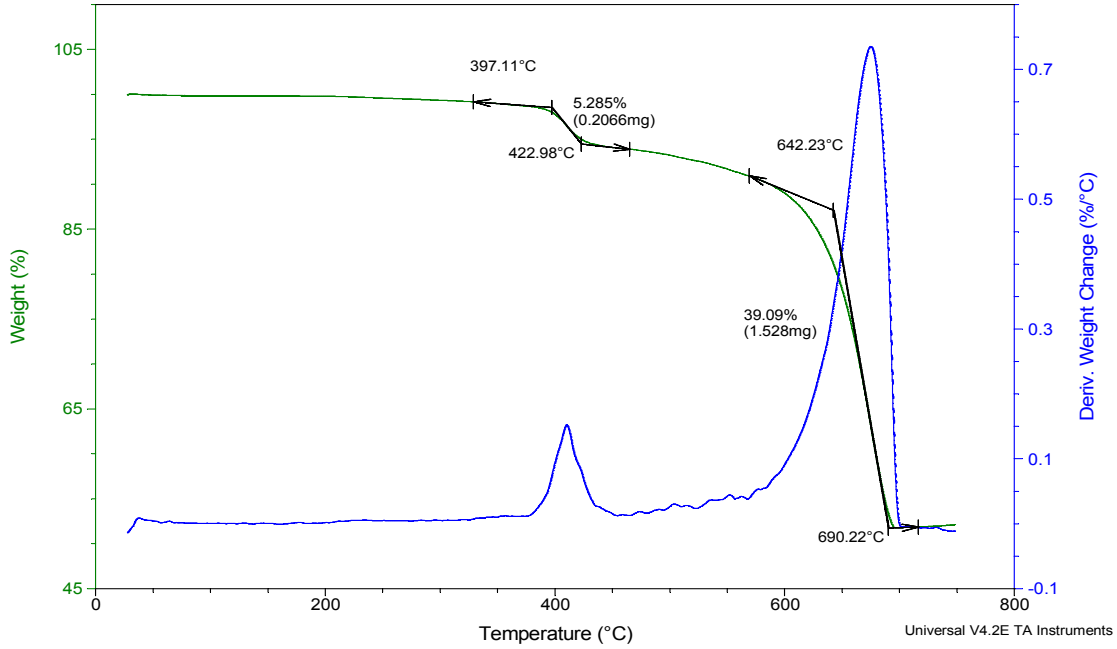

Fig. S10 Thermogravimetric (TG) curve of $CaCO_3$ formed after two days in the presence of **5-Na** (5 gL^{-1}) and Ca^{2+} (10 mM).