Supporting information

Ring-opening metathesis polymerization of a naturally derived macrocyclic glycolipid

Yifeng Peng,[†,‡] John Decatur,[§] Michael A.R. Meier,[*,‡] and Richard A. Gross[*,†]

[†]Center for Biocatalysis and Bioprocessing of Macromolecules, Polytechnic Institute of NYU, Six Metrotech Center, Brooklyn, NY, 11201, USA

[‡]Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, Building 30.42, 76131 Karlsruhe, Germany

[§]Department of Chemistry, NMR center, Columbia University, 3000 Broadway mailcode 3179 New York, NY 10027, USA

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Table-1S. The effect of catalyst loading on the ROMP of **LSL**.

Initiator	Initiator (mol % relative to monomer)	Monomer conversion (%)	M_n (x 10^3)	M_w/M_n
G2	0.5	87	120	1.7
G2	1.1	86	75	1.7
G2	2.2	85	42	1.6
G2	5.5	85	19	1.6
G2	11	83	12	1.5
G2	22	84	6	1.5
G3	1.1	80	187	1.7
G3	2.2	85	117	1.7
G3	5.5	81	57	1.6
G3	11	78	33	1.5
G3	22	80	20	1.5

Figure-2S. G2 catalyzed ROMP of **LSL** at 33 ^{o}C: influence of the reaction media on monomer conversion vs. reaction time.

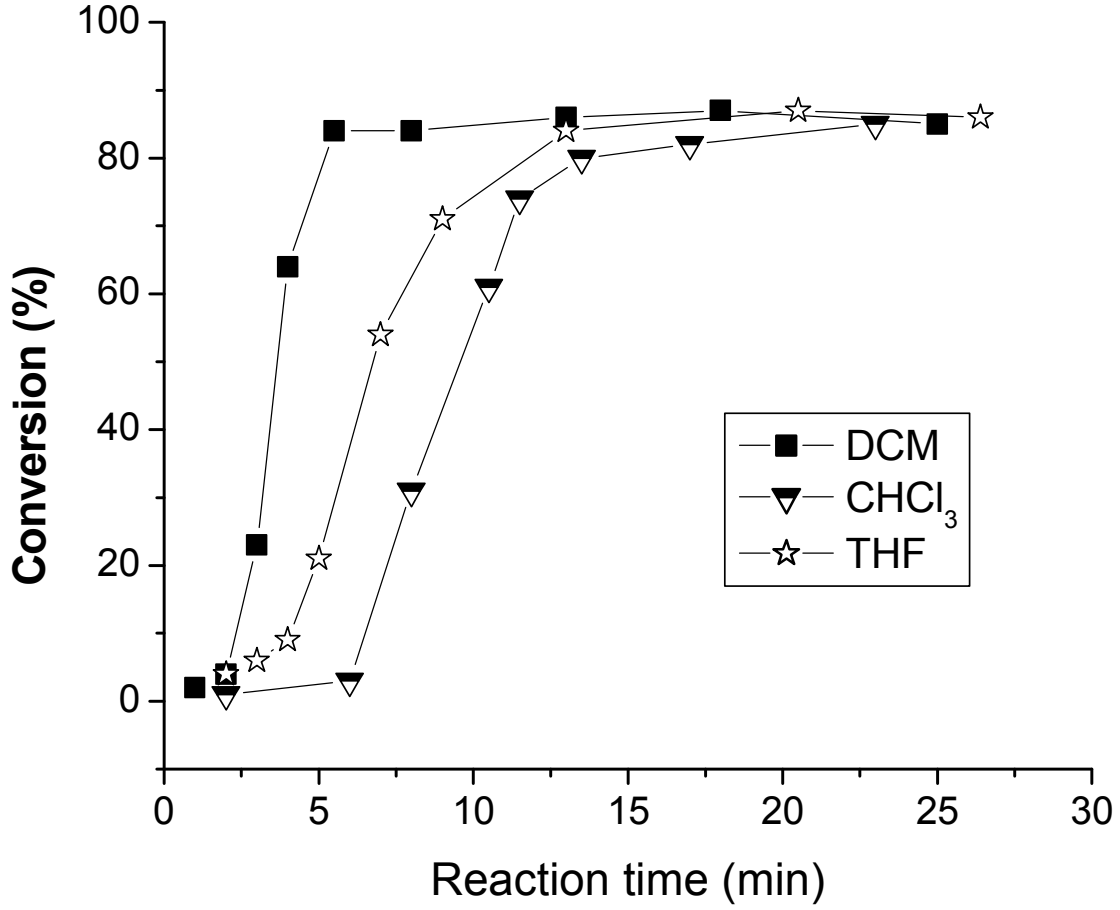
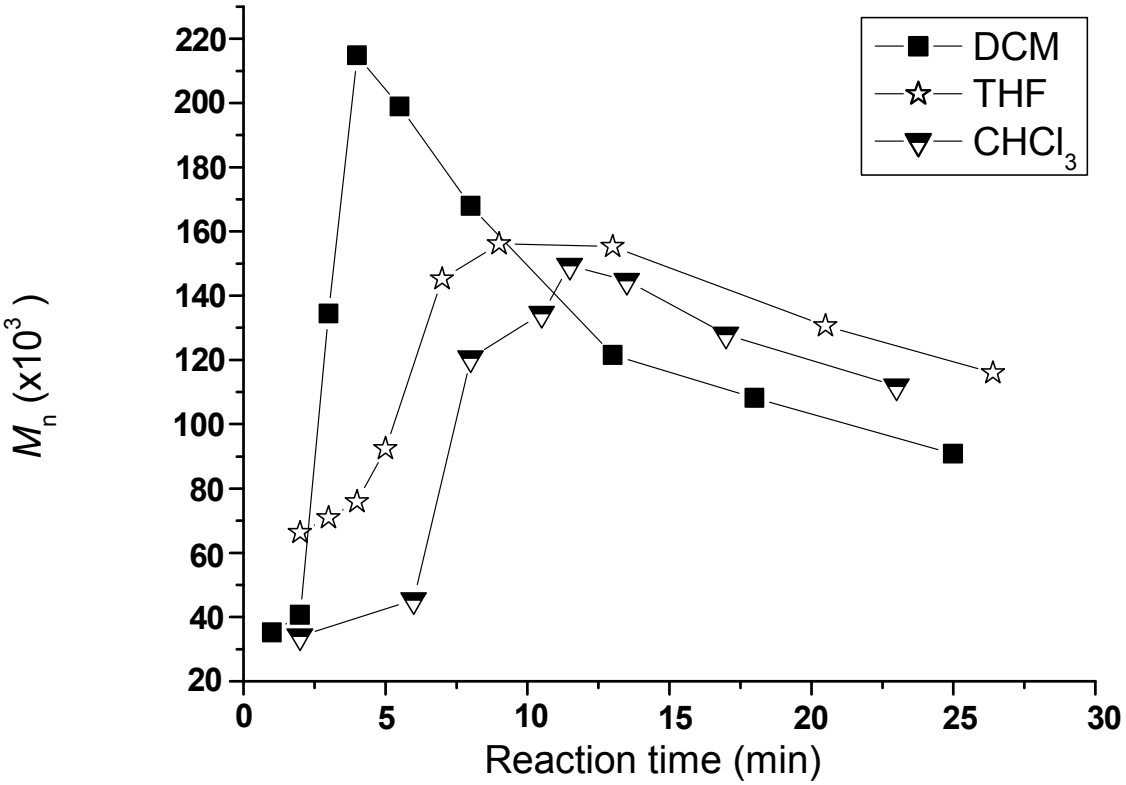


Figure-3S. G2 catalyzed ROMP of **LSL** at 33 ^{o}C: influence of the reaction media on **pLSL** M_n vs. reaction time.



Experimental Methods: NMR. All 2D NMR experiments were performed on a Bruker AVIII 500 with Z axis gradients.

HSQC. The edited HSQC used a standard Bruker pulse program (hsqcedetgpsisp or hsqcedetgpsp.3), which included adiabatic inversion pulses on ^{13}C. Hsqcedetgpsp.3 provided spectra with superior phase behavior. Typical spectral widths were 2500 Hz and 20000 Hz for proton and carbon, respectively, with 2K and 512 points in the respective proton and carbon dimensions. Four scans were taken for each t1 increment.

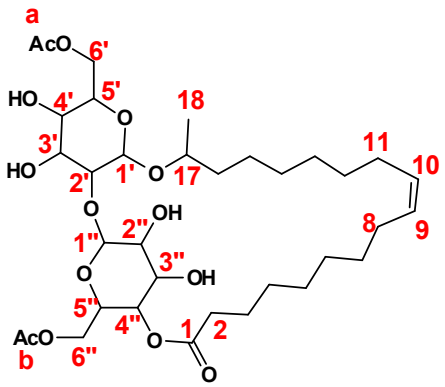
HSQC-TOCSY. The HSQC-TOCSY used the standard Bruker pulse program hsqcdietgpsi. TOCSY mixing times were 80 ms. Typical spectral widths were 2500 Hz and 20000 Hz for proton and carbon, respectively, with 2K and 512 points in the respective proton and carbon dimensions. Twenty four scans were acquired for each t1 increment.

COSY. Magnitude mode COSY spectra used standard Bruker pulse program cosygpppqf. Typical spectral widths were 5000 Hz in both dimensions while 1K and 256 points were taken in the F2 and F1 dimensions, respectively. Typically, 1 scan per t1 increment was acquired.

HMBC. The HMBC used standard Bruker pulse program hmbcgpl2ndqf. Typical spectra widths were 5000 Hz and 28000 Hz for proton and carbon, respectively, with 1600 and 1024 points in the F2 and F1 dimensions, respectively. Typically, 24 scans per t1 increment were acquired.

Discussion of NMR assignments. Assignment of lactonic sophorolipid (**LSL**) monomer carbon and proton NMR spectra was accomplished with the help of two-dimensional COSY, HSQC, HMBC, and HSQC-TOCSY spectra. In Figure-9S, COSY correlates protons that are coupled over 2 or 3 bonds. In Figure-6S, HSQC spectra correlate the chemical shifts of carbons with the chemical shifts of directly attached protons. The phase of the HSQC peak, expressed as the color in the plot, indicates the multiplicity. In an HSQC-TOCSY spectrum as in Figure-7S-1 and Figure-7S-2, the proton signal from an

HSQC carbon-proton pair is then transferred further to protons that are coupled. The result is that signals appear at the proton shift of the neighbors but retain the original carbon shift. The length of the TOCSY mixing time determines the number of transfer steps and was chosen to be 80 ms. Each of the carbon-bound protons from a single sugar ring forms a discrete proton spin system, and for an 80 ms mixing time, the signal is transferred among all protons within the ring. Since proton-proton coupling does not occur across the ester link, there is no transfer to beyond the ring. Use of HSQC and HSQC-TOCSY together with COSY greatly simplifies the task of assignment and allows all the protons on a given ring to be assigned.



In Figure-8S, HMBC cross peaks connect protons with carbons that are 2, 3, or sometimes 4 bonds apart and can provide additional information not present in the HSQC-TOCSY such as connections across glycosidic bonds. For example, C17 (77.68 ppm) can be easily identified in Figure-7S-1, as it shows a HSQC-TOCSY cross peak with the H18 methyl group. In addition, in Figure-8S, C17 (77.68 ppm) shows a HMBC cross peak to H1′ (101.77 ppm), and symmetrically, C1′ shows a HMBC cross peak to H17. Since H17 also shows a connection to the H18 methyl, these HMBC cross peaks establish unambiguous identification of the ring spin systems. Assignment can proceed from either end of the ring. The following is an example: from the HMBC connection above, the H1′ assignment can be made. Then, as shown in Figure-9S, the COSY cross peak between H1′ and H2′ allows assignment of H2′ to 3.217 ppm. The assignment of H3′ is not possible from only COSY due to proton overlap between H3′, H3″, and H5′,

but requires the HSQC-TOCSY. Since the carbon shifts C3′, C3″, and C5′ are distinct, these protons are resolved into the carbon dimension of the HSQC-TOCSY. In Figure-7S-2, at C3′, there are proton-proton connectivity's from H3′ to H1′ (4.341 ppm), H2′ (3.217 ppm), and H4′ (3.084 ppm). At C2′, there are proton-proton connectivity's from H2′ to H1′ (4.341 ppm), H3′ (3.373 ppm), and H4′ (3.084 ppm). Inspection of the intensities indicates the H3′ assignment to be 3.373 ppm since, despite the oscillating character of intensity transfer during TOCSY mixing, experience indicates the single-step transfer is usually stronger than longer range transfers. These proton-proton connectivity's at different carbon shifts provide a self-consistency check. This procedure is repeated until all carbon-proton pairs are assigned, and they are labeled in Figure-4S and 5S.

Figure-4S. ^{1}H NMR of **LSL** (500 MHz, DMSO- d_6).

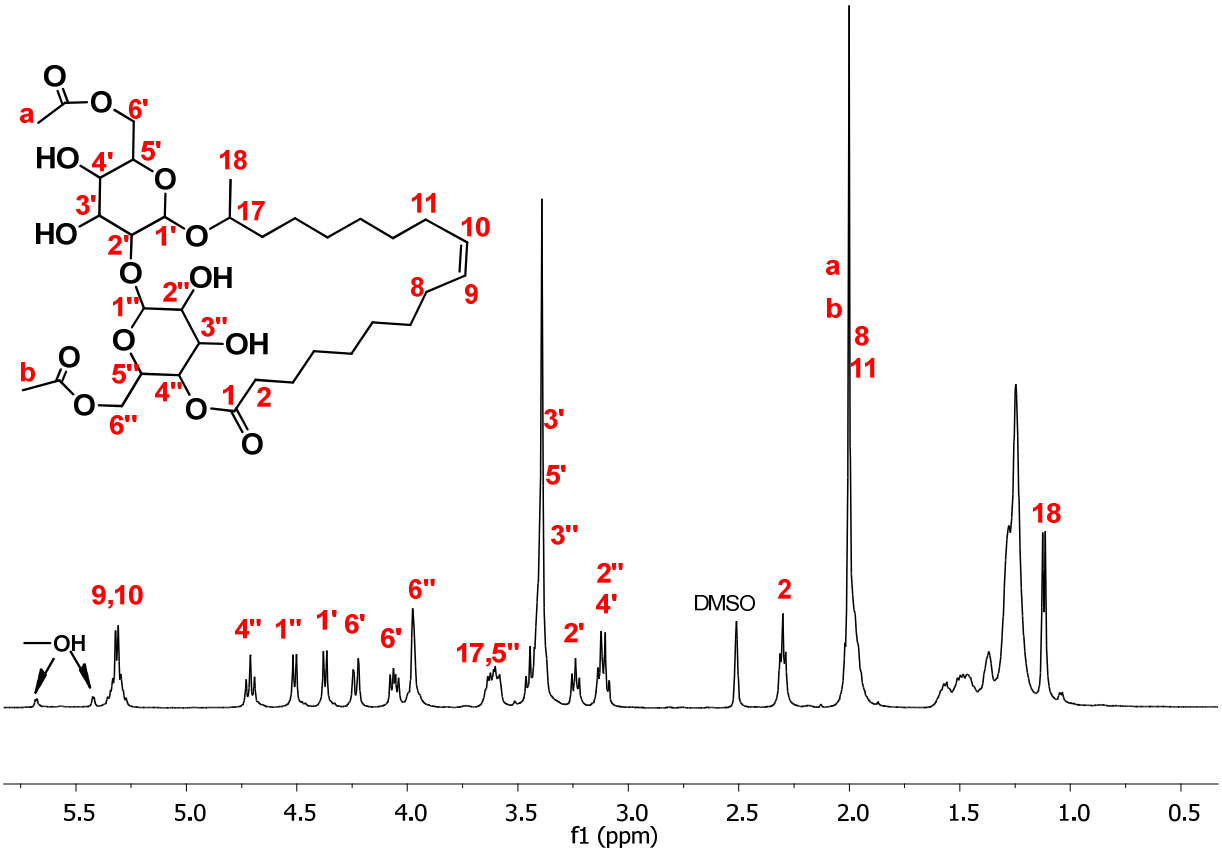


Figure-5S. ^{13}C NMR (inverse-gated decoupling) of **LSL** (300 MHz, DMSO- d_6).

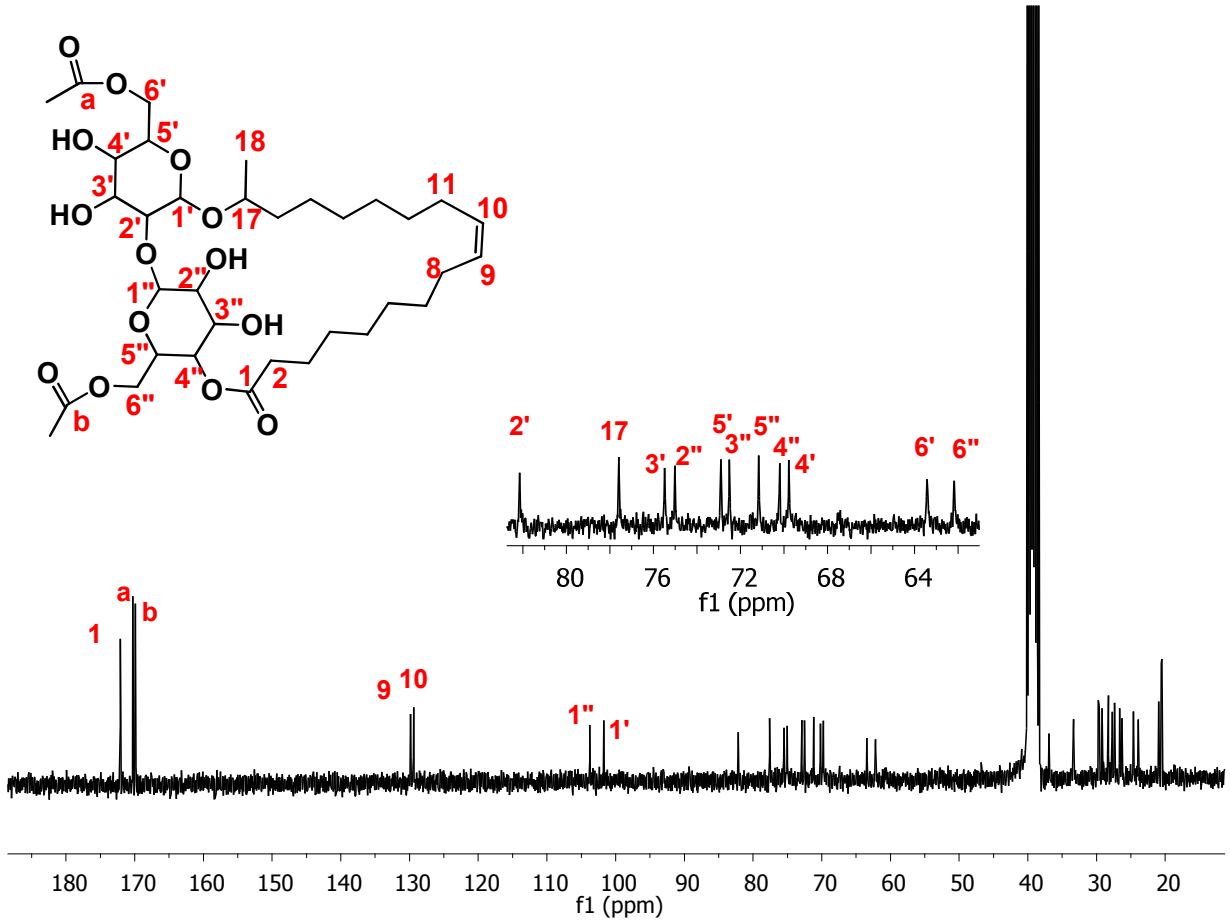


Figure-6S. HSQC spectrum of **LSL** (500 MHz, DMSO-d_6).

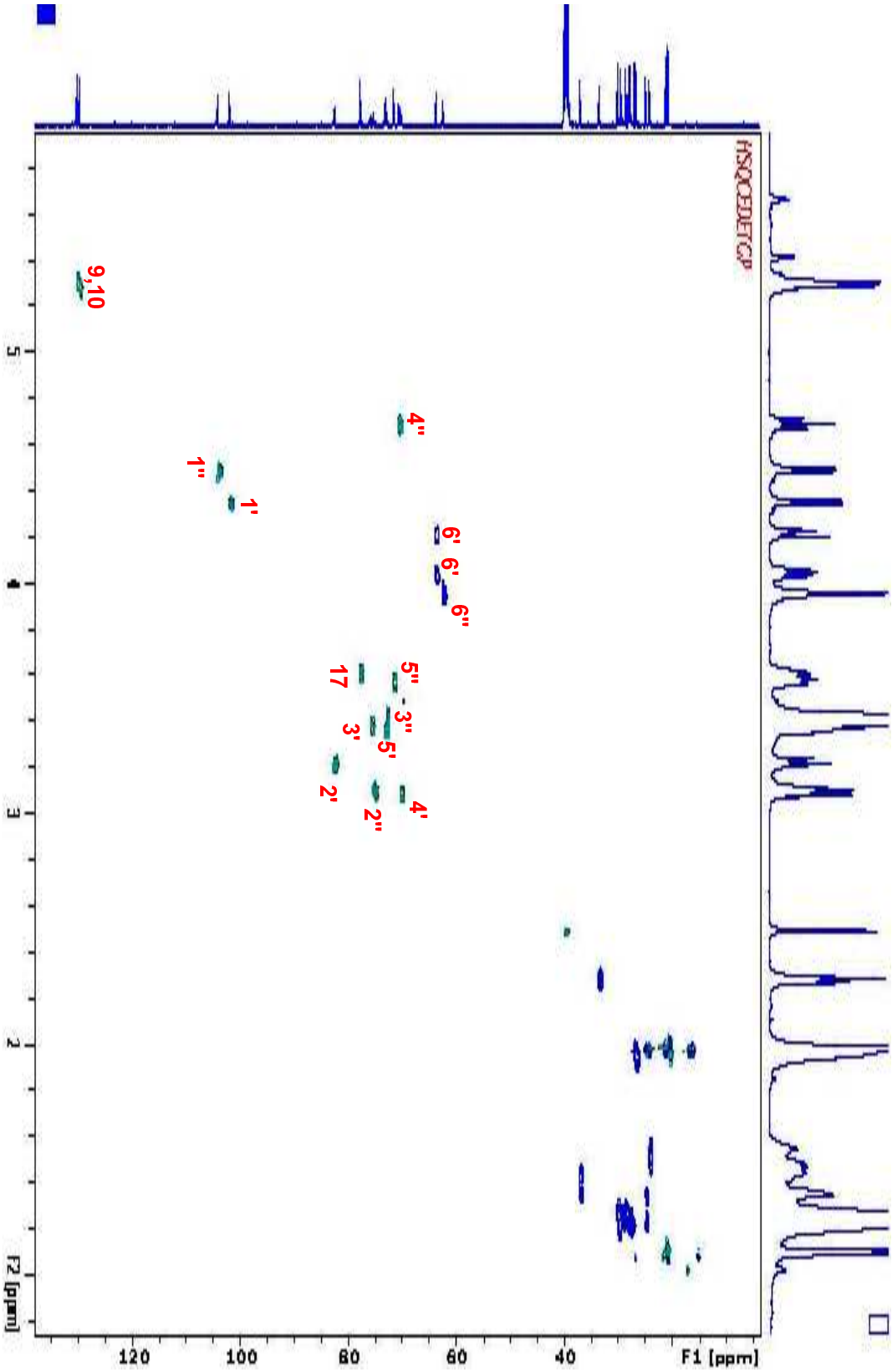


Figure-7S-1. HSQC-TOCSY spectrum of **LSL** (500 MHz, DMSO-d_6).

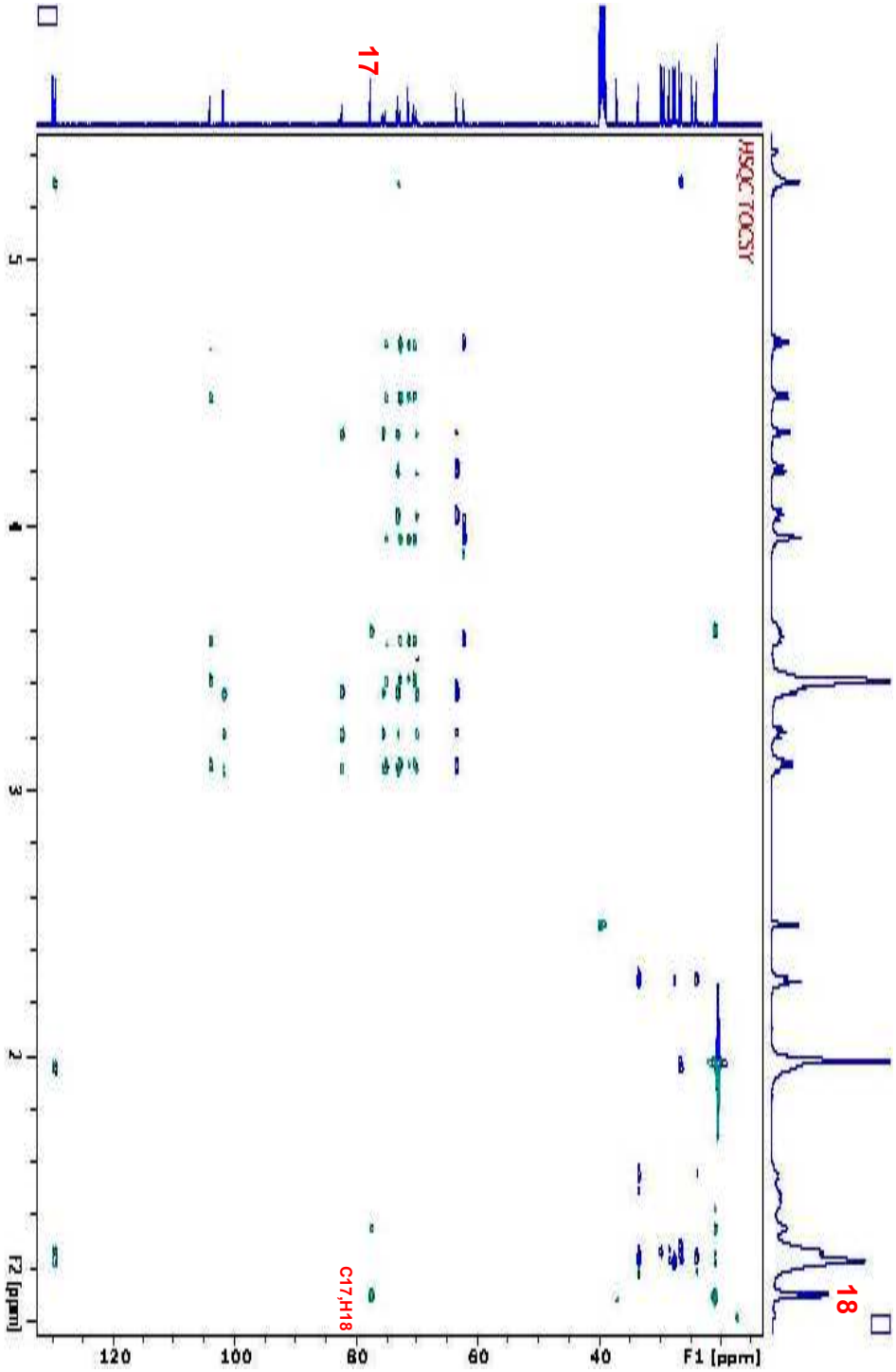


Figure-7S-2. HSQC-TOCSY (expanded) spectrum of **LSL** (500 MHz, DMSO-d_6).

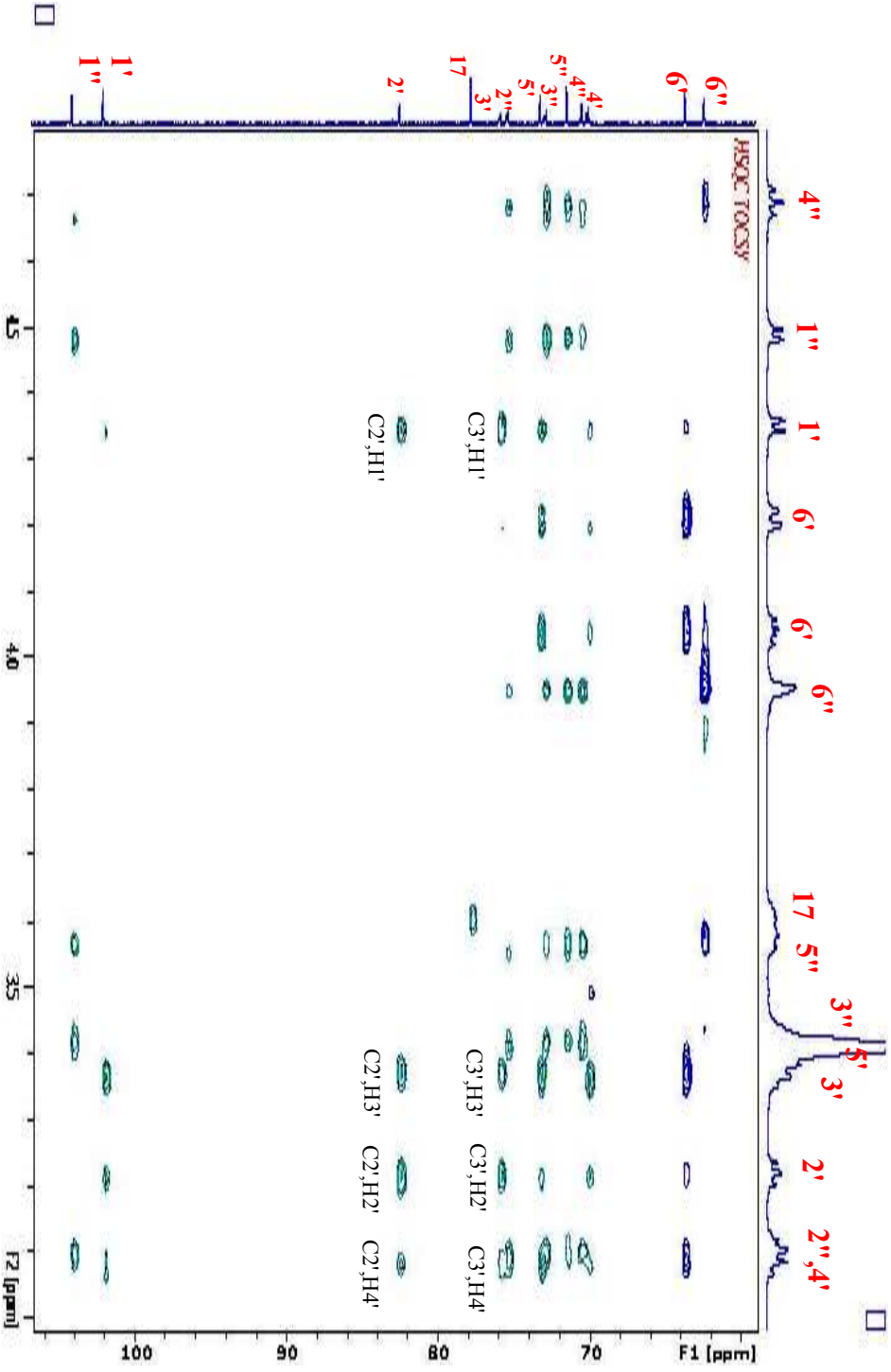


Figure-8S. HMBC spectrum of **LSL** (500 MHz, DMSO-d_6).

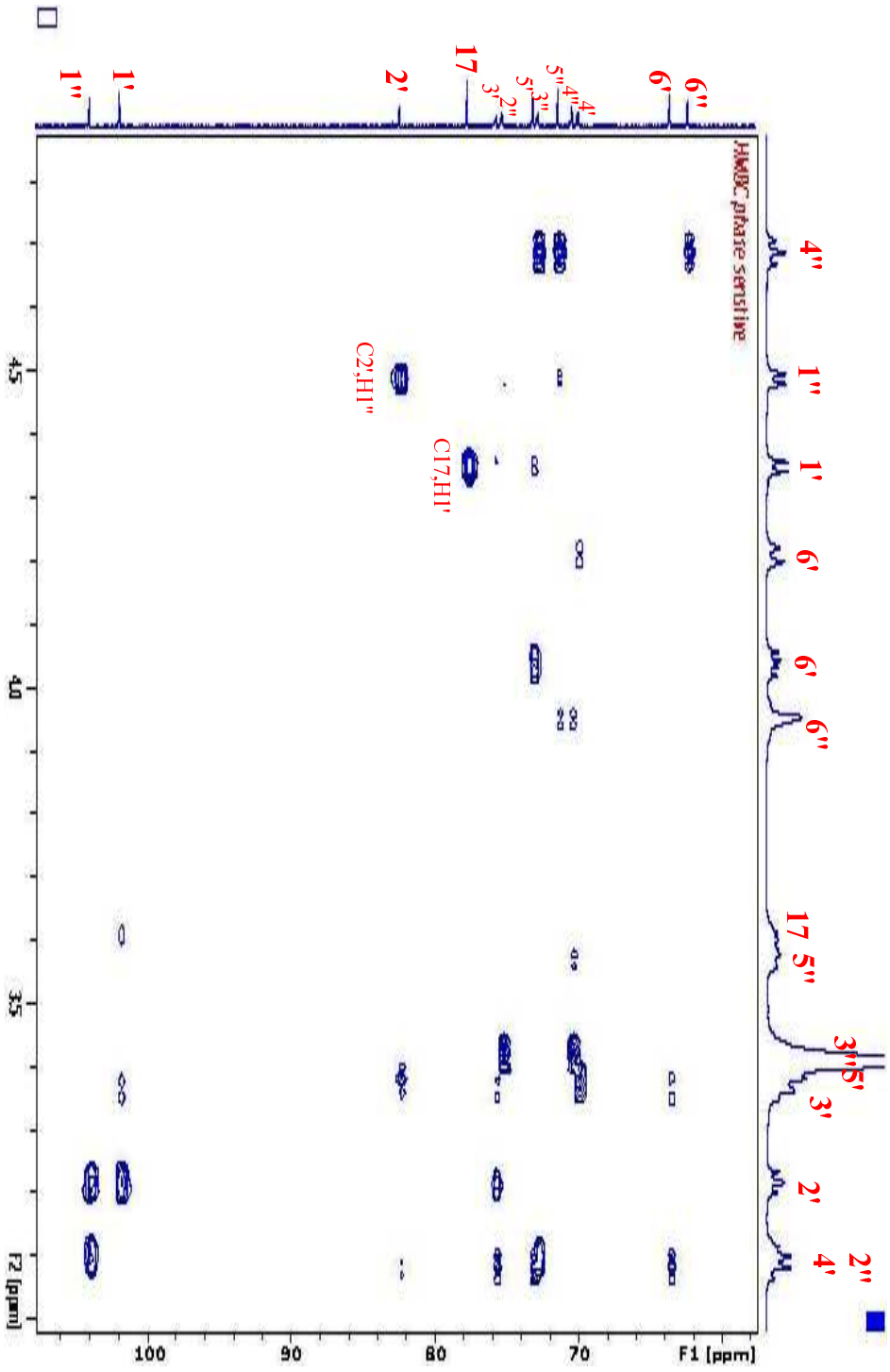


Figure-9S. COSY spectrum of **LSL** (500 MHz, DMSO-d_6).

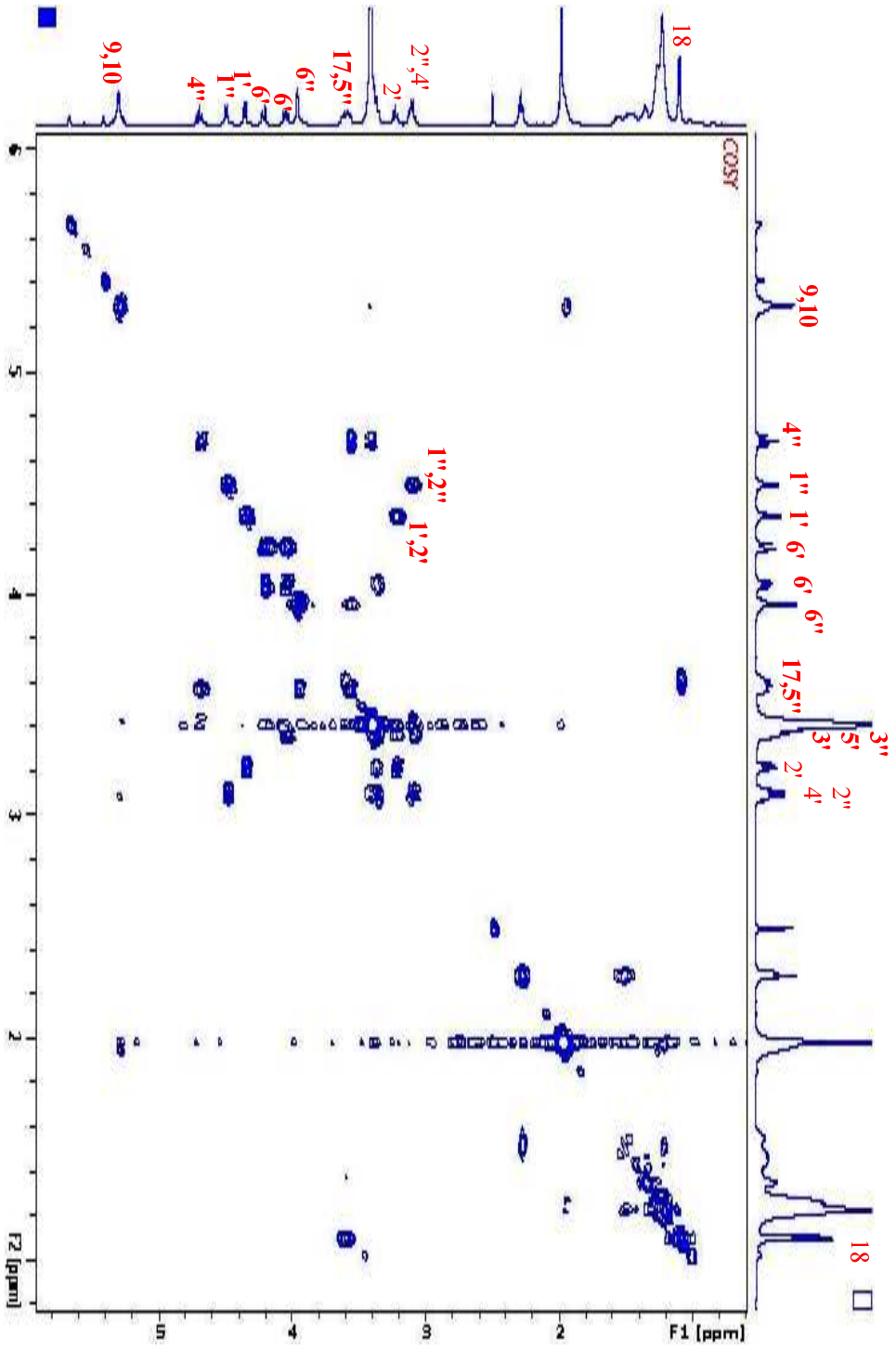


Figure-10S. ^{1}H NMR (500 MHz, DMSO-d_6 with 5% D_2O) of **pLSL** synthesized by: a) G2 and b) G3. In both 10S-a and 10S-b, 75% of the carbon-carbon double bonds are *trans*.