

Supporting Information

An *In Situ* Generated Polymer Electrolyte via Anionic Ring-Opening Polymerization for Lithium-Sulfue Batteries

Quinton J. Meisner,^a Sisi Jiang,^a Pengfei Cao,^b Tobias Glossmann,^c Andreas Hintennach,^d
and Zhengcheng Zhang,^{a*}

^a*Chemical Sciences and Engineering Division,
Argonne National Laboratory,
Lemont, Illinois 60439, United States of America*

^b*Chemical Sciences Division,
Oakridge National Laboratory, Oak Ridge, Tennessee 37830, United States of America*

^c*Mercedes-Benz Research & Development North America, Inc.,
Redford, Michigan 48239, United States of America*

^d*Daimler AG (Mercedes-Benz Cars),
Group Research, HPC G012-BB, 71034 Boeblingen, Germany*

1. Materials and Methods

1,3-dioxolane (DOL, 99% ~75 ppm BHT), 1,2-dimethoxyethane (DME, 99.9% HPLC grade), lithium bis(trifluoromethyl sulfonyl) imide (LiTFSI, 99.98%), sodium hydride (NaH, 90%, dry powder), tetrahydrofuran (THF, 99.9%, anhydrous), ethylene glycol diglycidyl ether mixture (TCI), methanol (99.9%), thiourea (99.0%), sulfur (99.99%), and lithium sulfide (99.98%) were acquired from Sigma-Aldrich; Silica gel (230-400 mesh, grade 60) and diethyl ether (ACS grade) were acquired from Thermo-Fischer Scientific; Epichlorohydrin (99%, anhydrous) and 2-methoxyethanol (99%) were acquired from Acros Organics; Sodium sulfate (Na_2SO_4 , anhydrous, ACS grade) was purchased from VWR (BDH).

All electrolyte solvents were distilled by short-path distillation. Episulfides G_1S , SG_xS , and DOL were dried over CaH_2 for >48 h and then passed through a 0.2 μm filter before use. DME was dried over 4 Å molecular sieves. LiTFSI was dried at 125 °C under a high vacuum for 24 h. G_1S and SG_xS were stored in the freezer at -10°C in an argon-filled glovebox to ensure stability over extended periods with no signs of premature polymerization after several months. DOL showed no signs of degradation or polymerization while stored in the glovebox before or after this study.

Water content was determined by Karl-Fischer titration using a Mettler-Toledo C30 Coulometric Titrator using Reagent E. G_1S and SG_xS were not tested for water content due to their instability to Karl-Fischer reagents.

All electrolytes were prepared in the glovebox by weighing the appropriate LiTFSI mass and then dissolving it in 0.5 mL of electrolyte solvent. This was then diluted to 1.0 mL to provide exact molar concentrations. From this solution, 0.25 mL was removed and weighed and then cross-linker (SG_xS) was added as a function of wt%. All electrolytes containing episulfides were either used immediately or stored in the glovebox freezer at -10°C after formulation to reduce the chance of premature polymerization.

Lithium polysulfide (Li_2S_6) solutions for *ex situ* polymerization of G_1S and SG_xS was prepared as described in our previous publication.^[1]

Ex situ polymerizations were performed in vacuum dried glass sample vials by preparing 0.5 mL of electrolyte as described above. 2 μL of 0.2 M Li_2S_6 in DME was added to the electrolyte solution with stirring. This solution was allowed to rest at ambient temperature in the glovebox without stirring for 5 h to ensure full polymerization.

2. Electrode Preparation

Sulfurized-polyacrylonitrile (SPAN) cathodes were generously provided by Daimler Corporation and were cut into discs with a diameter of 15 mm. Sulfur loading was 1.5 mg/cm^2 .

Elemental sulfur electrodes used for EIS time dependent measurements were prepared as described in our previous publication.^[1]

3. Electrochemical Testing

2032-coin cells were assembled in an argon filled glovebox with lithium foil as the anode and SPAN as the cathode. Solupor 7PO3A (diameter = 16 mm) was used as the separator and the liquid monomer electrolyte was kept at a constant volume of 40 μL per cell ($\text{E}/\text{S} = 15 \mu\text{L}/\text{mg}$). Cell cycling was conducted using a Maccor series 4000 battery cycler at constant current

determined by active material loading in the cathode. Charge steps for Li-S cells were set to terminate either through voltage cutoff mode (3.0 V) or capacity cutoff at x1.5 the previous discharge step.

Electrochemical impedance spectroscopy (EIS) was performed using a Solartron Analytical 1400 Cell Test System from 1.0 MHz to 0.1 Hz at OCV. Bulk ionic conductivity of monomer electrolytes and polymer electrolytes were evaluated using a stainless-steel coin cell assembly with a PTFE washer filled with electrolyte. Polymer electrolytes were prepared by the addition of 1 μL of 0.25 M Li_2S_x in DME ($x \sim 6$, final $[\text{S}_x^{2-}] = 2 \text{ mM}$) before assembly, this was allowed to rest at ambient conditions for 1 week prior to EIS testing. The PTFE washer dimensions were set at 0.177 cm thickness (l) and 0.502 cm^2 internal area (πr^2). EIS was used to determine the Ohm resistance (R_Ω) from the highest frequency Z' intercept which was used with Equation 1 to determine the bulk ionic conductivity (σ) of the electrolyte.

$$\sigma = \frac{l}{\pi r^2 \cdot R_\Omega} \cdot 1000 \quad [1]$$

Conductivity was determined for temperatures within the range of 0 – 60°C at every 10°C for polymerized electrolytes, allowing the samples the temperature acclimate for at least 10 min after reaching the set value. Monomer electrolyte conductivity was determined only at ambient temperature. For each sample and temperature, the EIS measurement was conducted in triplicate and the conductivity determined for each measurement prior to statistical analysis.

Cyclic voltammetry (CV) was conducted using a Gamry Potentiostat Reference 600+ inside an argon filled glovebox. Lithium electrodes were prepared by attaching fresh lithium foil to a glass electrode with an internal copper wire. The platinum (working) and lithium (counter and reference) electrodes were immersed in a vial containing 1.0 mL of electrolyte solution. The voltage was swept from -0.5 V to either 3.0 V or 5.0 V vs Li^+/Li starting at OCV three times with a scan rate of 10 mV/s.

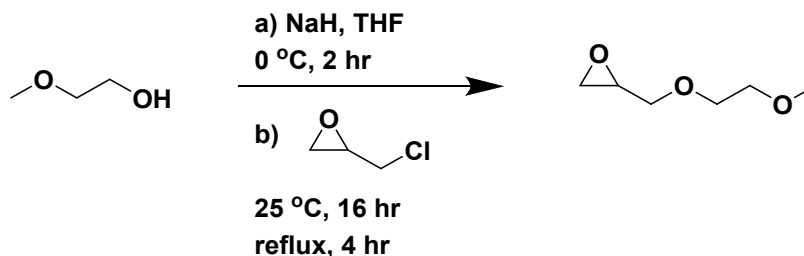
4. Post-test Analysis

Li-S cells were prepared analogous to previously described and cycled for 5 cycles before being stopped and cell parts harvested for analysis. After de-crimping the cell stacks were separated (in the case of cells containing polymerized electrolyte, forcibly so). Samples bound for SEM were each washed twice with 300 μL of fresh DOL and allowed to dry for several minutes under an argon atmosphere before being transferred in an air-tight container to the instrument for mounting. Samples were mounted quickly on SEM mounts in open air and then immediately transferred into the instrument's vacuum chamber.

Cell parts used for NMR analysis were not pre-washed but were rather transferred out of the glovebox neat after removal of the lithium chip. These cell parts were set stirring in a sealed vial containing 3 mL of DCM with 3 drops of H_2O over 1 week to dissolve the polymer electrolyte (linear polymer). After 1 week, the supernatant was removed and passed through a small pad of Na_2SO_4 to dry and solvent removed under reduced pressure. This sample was then subjected to NMR analysis by redissolving in CDCl_3 (NMR).

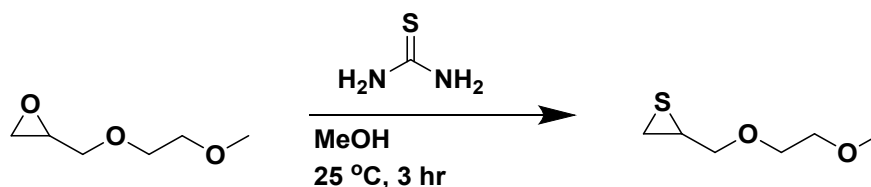
5. Synthesis of Monomers

5.1 Synthesis of 2-[(2-methoxyethoxy)methyl]oxirane^[2]



To an oven dried 250 mL RBF, sodium hydride (60% in mineral oil, 4.202 g, 105.05 mmol) was added and flushed with dry nitrogen. This was rinsed three times with pentane and the supernatant removed via cannula each time and remaining solid powder dried under vacuum. This was re-suspended in anhydrous THF (80 mL) and cooled to 0°C, at which point 2-methoxyethanol (7.90 mL, 100.2 mmol) was added dropwise while stirring. The resulting mixture was allowed to come to ambient temperature over 2 hr. Finally, epichlorohydrin (7.80 mL, 99.7 mmol) was added portion wise and the mixture was then allowed to stir at ambient temperature under nitrogen for 16 hr. The reaction mixture was then refluxed for 4 h, cooled to ambient temperature and then filtered through a pad of Celite 545 (15 cm). Following this the filtrate was concentrated under reduced pressure to give the crude reaction mixture as a clear-orange liquid. This was purified by fractional short-path vacuum distillation at 12 kPa from 92.0 – 94.0°C to give the target compound as a clear-colorless liquid in 25.7% yield (3.3919 g, 25.67 mmol). ¹H NMR (300 MHz, CDCl₃): δ/ppm 3.80 (dd, J= 11.7, 3.0 Hz, 1H), 3.74 – 3.41 (m, 5H), 3.38 (s, 3H), 3.20 – 3.15 (m, 1H), 2.80 (d, J= 4.2 Hz, 0.5H) 2.79 (d, J= 4.1 Hz, 0.5H), 2.61 (d, J= 2.7 Hz, 0.5H), 2.60 (d, J= 2.7 Hz, 0.5H); ¹³C NMR (70 MHz, CDCl₃): δ/ppm 72.22, 72.02, 70.76, 59.23, 50.96, 44.41; GC-MS *m/z* (% relative intensity, ion): 131.0 (M⁺, 0.3), 87.0 (CH₂OCHCH₂OCH₂⁺, 16), 73.0 (CH₂OCHCH₂O⁺, 21), 59.0 (CH₃OCH₂CH₂⁺, 100), 57.0 (CH₂OCHCH₂⁺, 73).

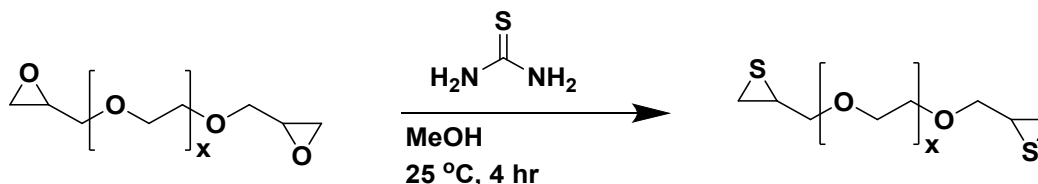
5.2 Synthesis of 2-[(2-methoxyethoxy)methyl]thiirane (“G₁S”)^[3]



2-[(2-Methoxyethoxy)methyl]oxirane (5.2842 g, 40.0 mmol) was added to a 250 mL RBF and dissolved in MeOH (100 mL). To this, thiourea (30.5247 g, 401.0 mmol) was added while stirring at ambient temperature and atmosphere. After 3 h the milky white dispersion was filtered through a medium glass frit, diluted with Et₂O (100 mL) and washed 4 with H₂O (20 mL, x6). The organic phase was dried via Na₂SO₄, passed through a short plug of silica, and solvent removed under reduced pressure. The pure product was received as a clear-colorless liquid in

71.0% yield (4.2067 g, 28.4 mmol) which was dried via CaH_2 under an argon atmosphere over 48 h in a -10°C freezer and then passed through a $0.2\ \mu\text{m}$ filter and stored at -10°C until use. ^1H NMR (300 MHz, CDCl_3): δ/ppm 3.73 – 3.45 (m, 6H), 3.40 (s, 3H), 3.10 (m, 1H), 2.53 (dt, $J=6.2, 1.1\ \text{Hz}$, 1H), 2.22 (dd, $J=5.4, 1.3\ \text{Hz}$, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ/ppm 76.01, 71.90, 70.35, 59.14, 31.99, 23.94.

5.2 Synthesis of 1,2-bis(2,3-epithiopropoxy)ethane mixture (“SG_xS”)



Ethylene glycol diglycidyl ether mixture ($x = 1 - 3$, 3.4532 g, 19.846 mmol) was added to a 250 mL RBF and dissolved in MeOH (50 mL). To this thiourea (38.5424 g, 506.337 mmol) was added and the resulting white mixture was allowed to stir at ambient temperature and pressure for 4 h. Following this the milky white dispersion was filtered through a medium glass frit, diluted with Et_2O (100 mL), and washed with H_2O (x10, 25 mL). The organic layer was dried via Na_2SO_4 , passed through a plug of silica, and solvent removed under reduced pressure. The pure product was received as a viscous clear-colorless liquid in 29.6% yield (1.2113 g, 5.872 mmol) which was dried via CaH_2 under an argon atmosphere over 1 week in a -10°C freezer and then passed through a $0.2\ \mu\text{m}$ filter and stored at -10°C until use. ^1H NMR (300 MHz, CDCl_3): δ/ppm 3.79 – 3.49 (m, 8H), 3.14 – 3.06 (m, 1H), 2.55 – 2.51 (m, 1H), 2.25 – 2.20 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ/ppm 78.76, 78.69, 75.96, 75.88, 75.26, 75.15, 70.98, 70.86, 70.78, 70.41, 70.37, 43.85, 32.28, 32.09, 32.05, 23.83, 23.74.

6. Supplemental Figures

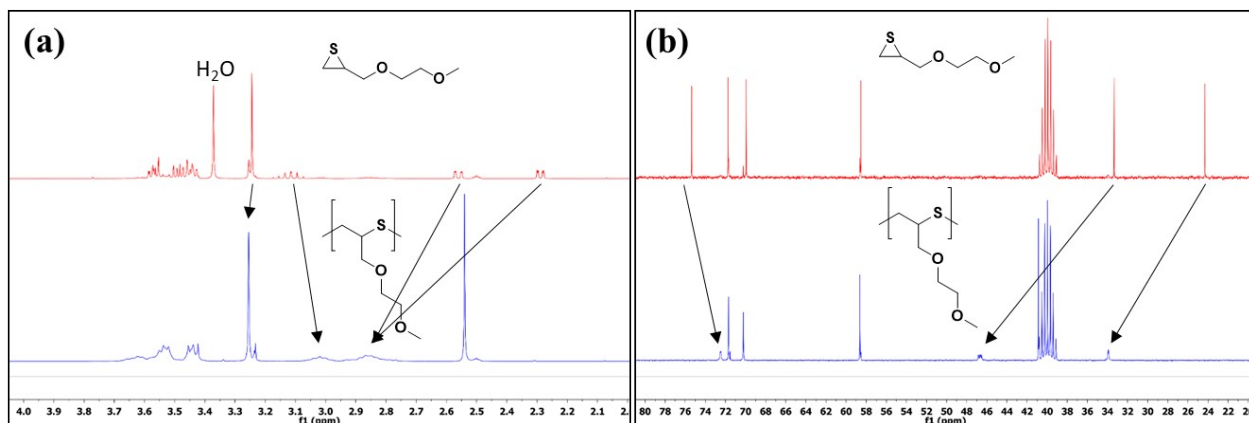


Figure S1. (a) ^1H NMR and (b) ^{13}C NMR of G_1S monomer (*top*) and *ex situ* prepared PG_1S (*bottom*) extracted with DMSO, in DMSO-D_6 ; DMSO-H_6 2.54 ppm (^1H) and 40.87 ppm (^{13}C), $\text{DMSO-H}_1\text{D}_5$ 2.50 ppm (^1H), DMSO-D_6 39.96 ppm (^{13}C).

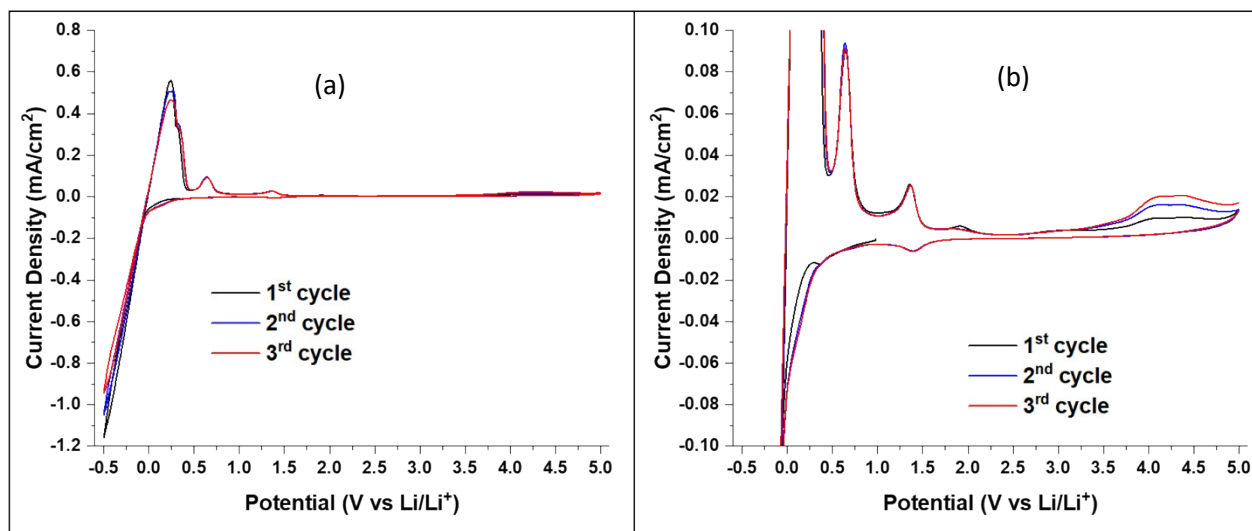


Figure S2. (a) Cyclic voltammetry traces of 1.0 M LiTFSI $\text{DOL:DME:G}_1\text{S}$ (35:35:30)+2wt% SG_xS from OCV to -0.5 V and to 5.0 V vs Li^+/Li with a scan rate of 10 mV/s; (b) expanded figure (working, counter, and reference electrodes were Pt, Li and Li, respectively).

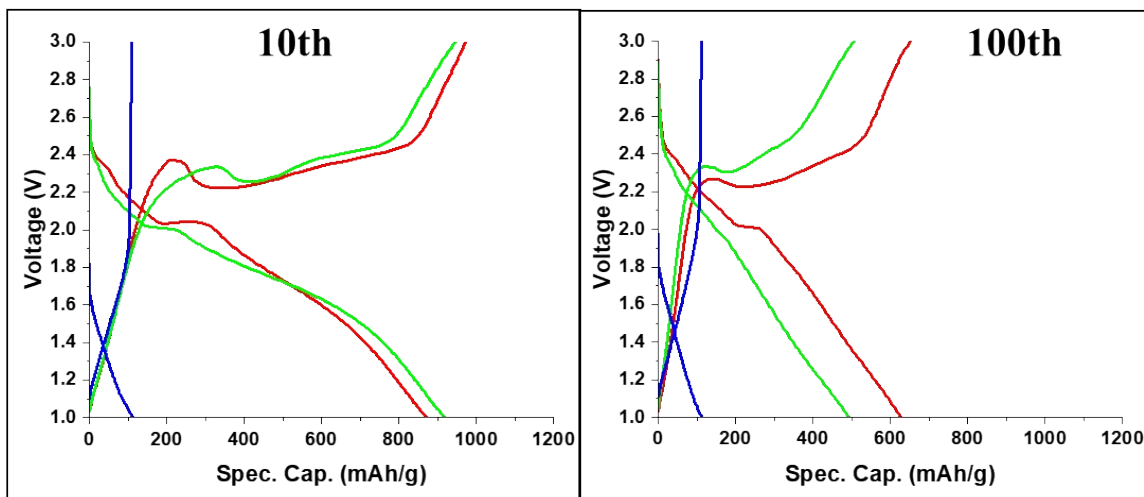


Figure S3. 10th and 100th charge-discharge voltage profiles for Li-S cells using 1.0 M LiTFSI DOL:DME:G₁S+2wt% SG_xS with G₁S at 20% (*red*), 40% (*green*), and 60% (*blue*) v/v with the remaining volume DOL:DME (1:1) to equal 100%.

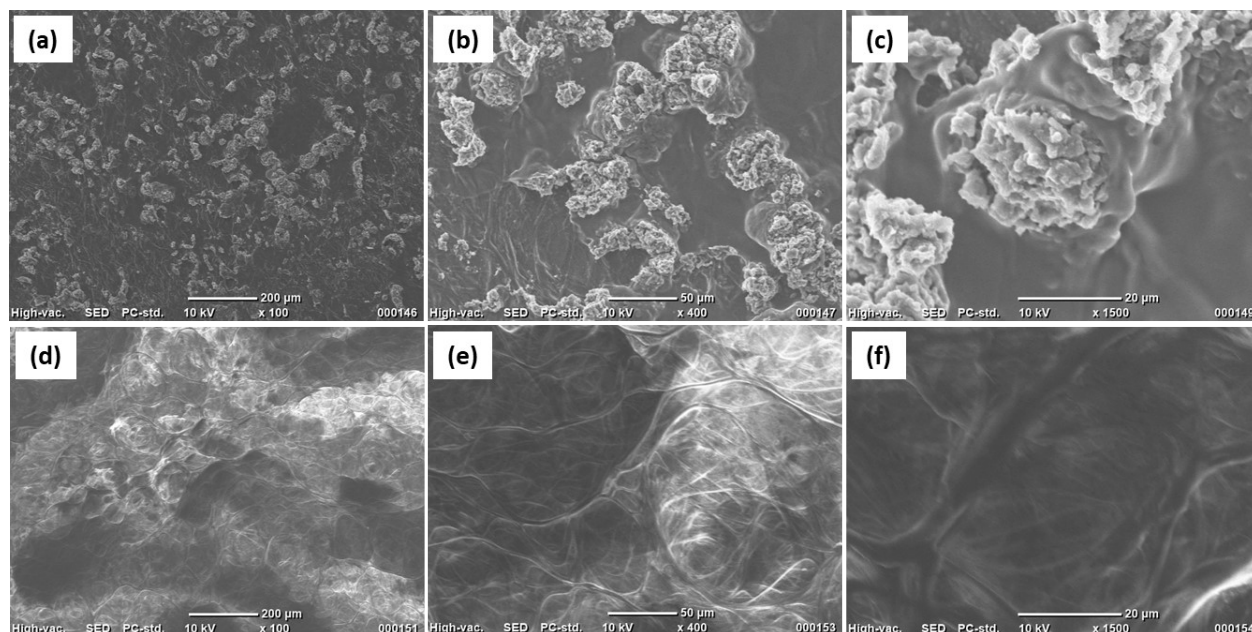


Figure S4. (a-c) SEM images of Solupor 7PO3A separator after 5 cycles with 1.0 M LiTFSI DOL:DME:G₁S (30:30:40)+2wt% SG_xS and (d-f) with 1.0 M LiTFSI DOL:DME (50:50) after washing with DOL; scale bars shown.

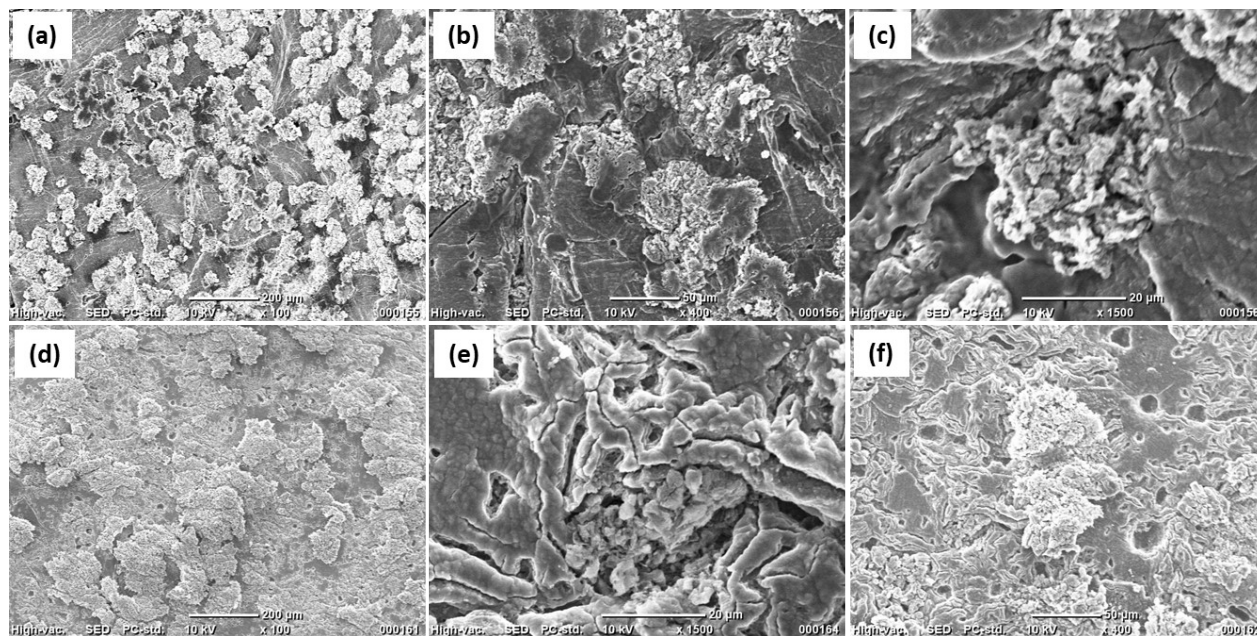


Figure S5. (a-c) SEM images of lithium anode after 5 cycles with 1.0 M LiTFSI DOL:DME:G₁S (30:30:40)+2wt% SG_xS and (d-f) with 1.0 M LiTFSI DOL:DME (50:50) after washing with DOL; scale bars shown.

7. Spectroscopic Data

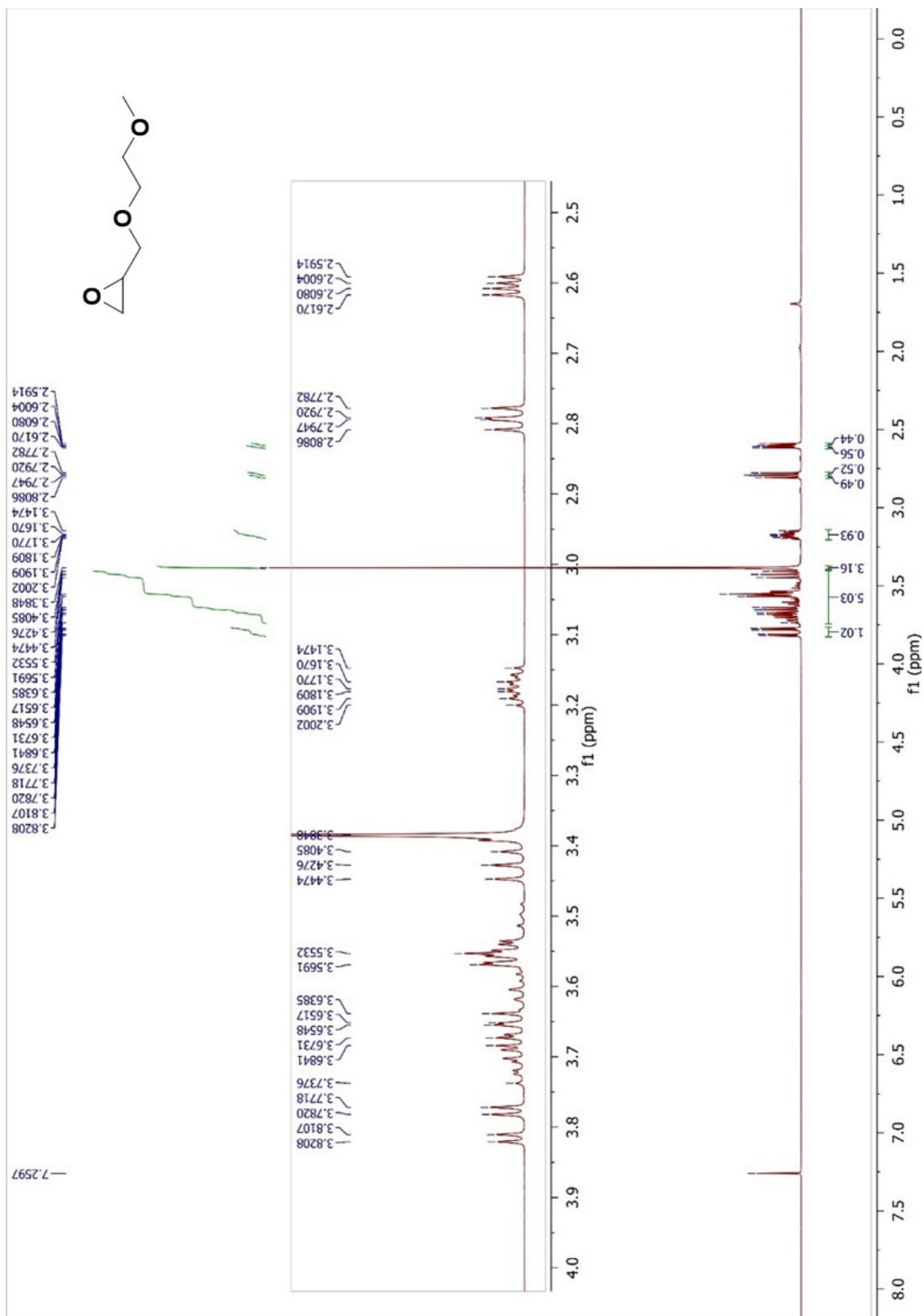


Figure S6. ^1H (300 MHz) spectra of 2-[(2-methoxyethoxy)methyl]oxirane in CDCl_3 .

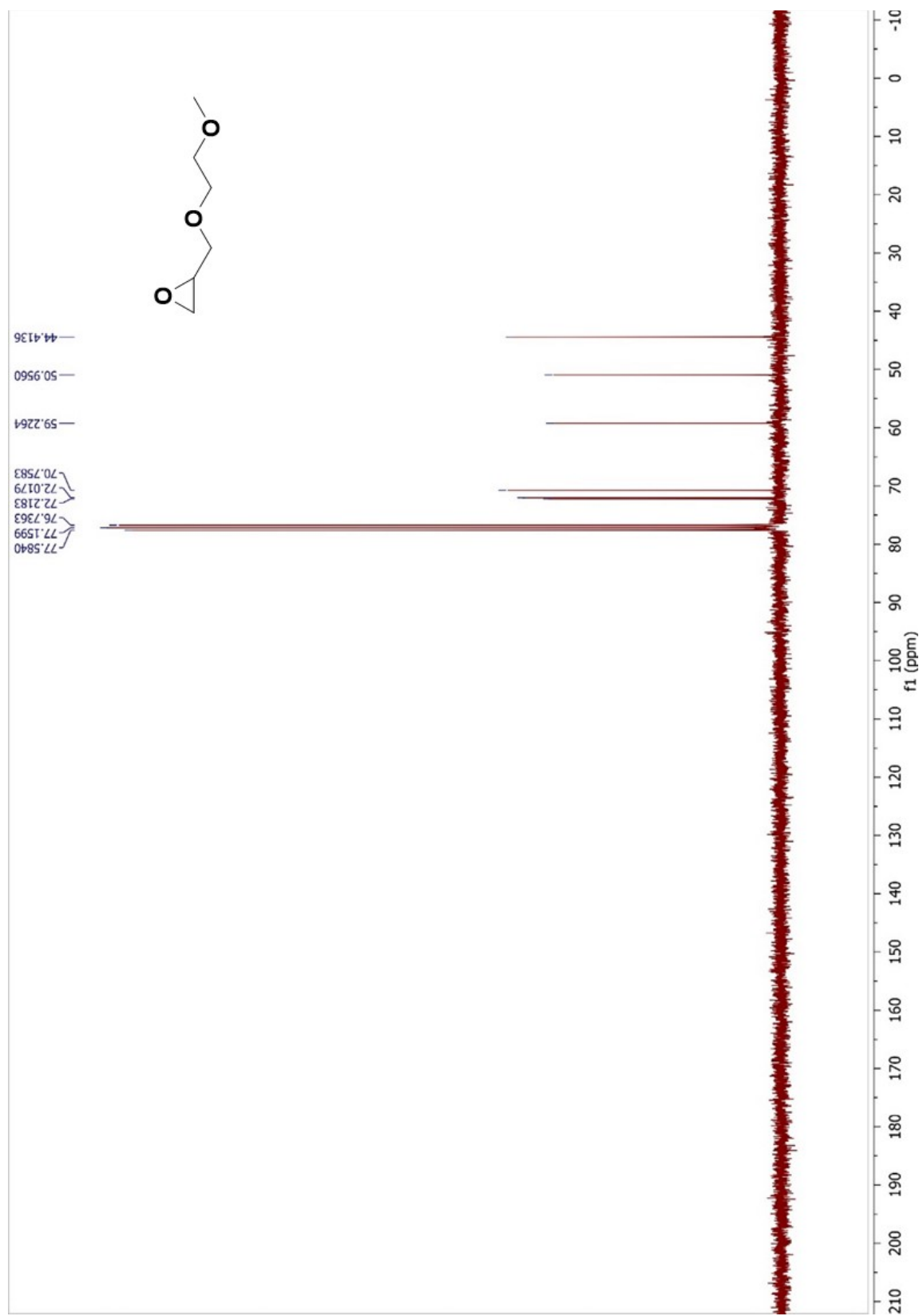


Figure S7. ^{13}C (75 MHz) spectra of 2-[(2-methoxyethoxy)methyl]oxirane in CDCl_3 .

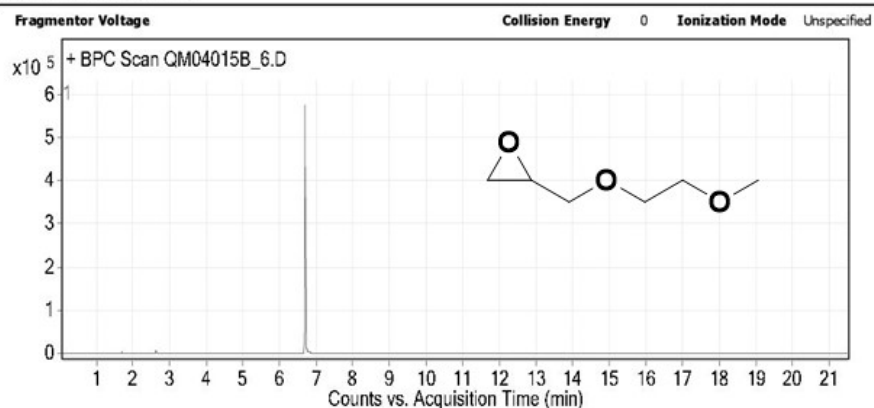
Qualitative Analysis Report

Data Filename QM04015B_6.D **Sample Name** QM04015B
Sample Type **Position** 6
Instrument Name GCMS **User Name** 5977-GCMS\GCMS
Acq Method QM_lowVP_Diethyl Ether Diluent.M **Acquired Time** 9/10/2019 5:05:33 PM
IRM Calibration Status Not Applicable **DA Method** default.m
Comment

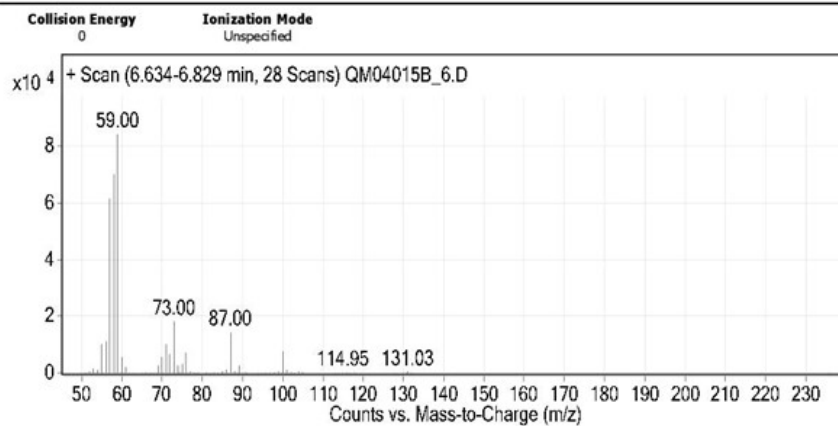
Expected Barcode **Sample Amount**

Dual Inj Vol 1 **TuneName** ATUNE.U
TunePath D:\MassHunter\GCMS\1\5977 **MSFirmwareVersion** 6.00.16
OperatorName 5977-GCMS\GCMS **RunCompletedFlag** TRUE

User Chromatograms



User Spectra



Peak List

m/z	z	Abund
55		9959.68

Figure S8. GC-MS of 2-[(2-methoxyethoxy)methyl]oxirane.

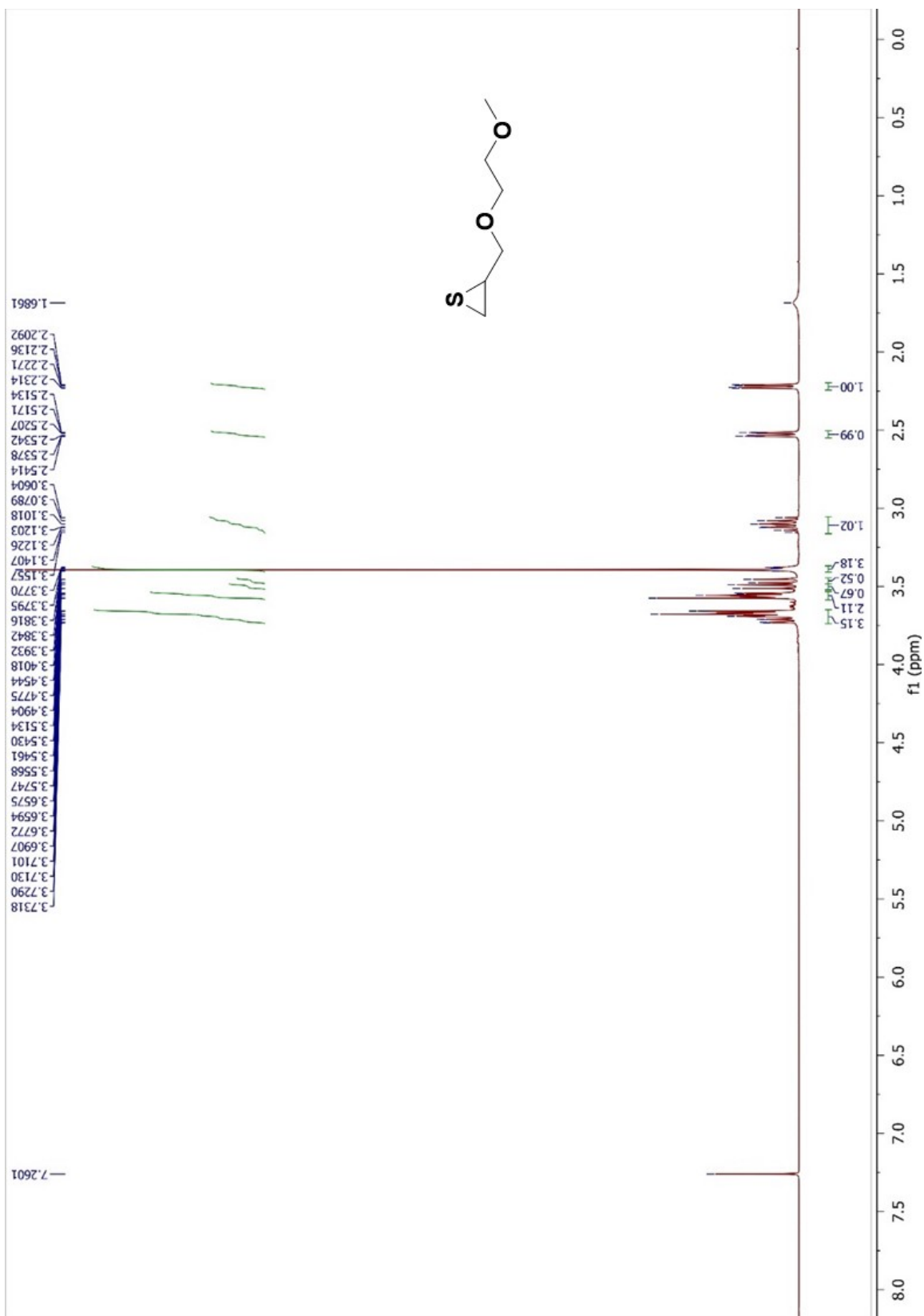


Figure S9. ¹H (300 MHz) spectra of 2-[(2-methoxyethoxy)methyl]thiirane (G₁S) in CDCl₃.

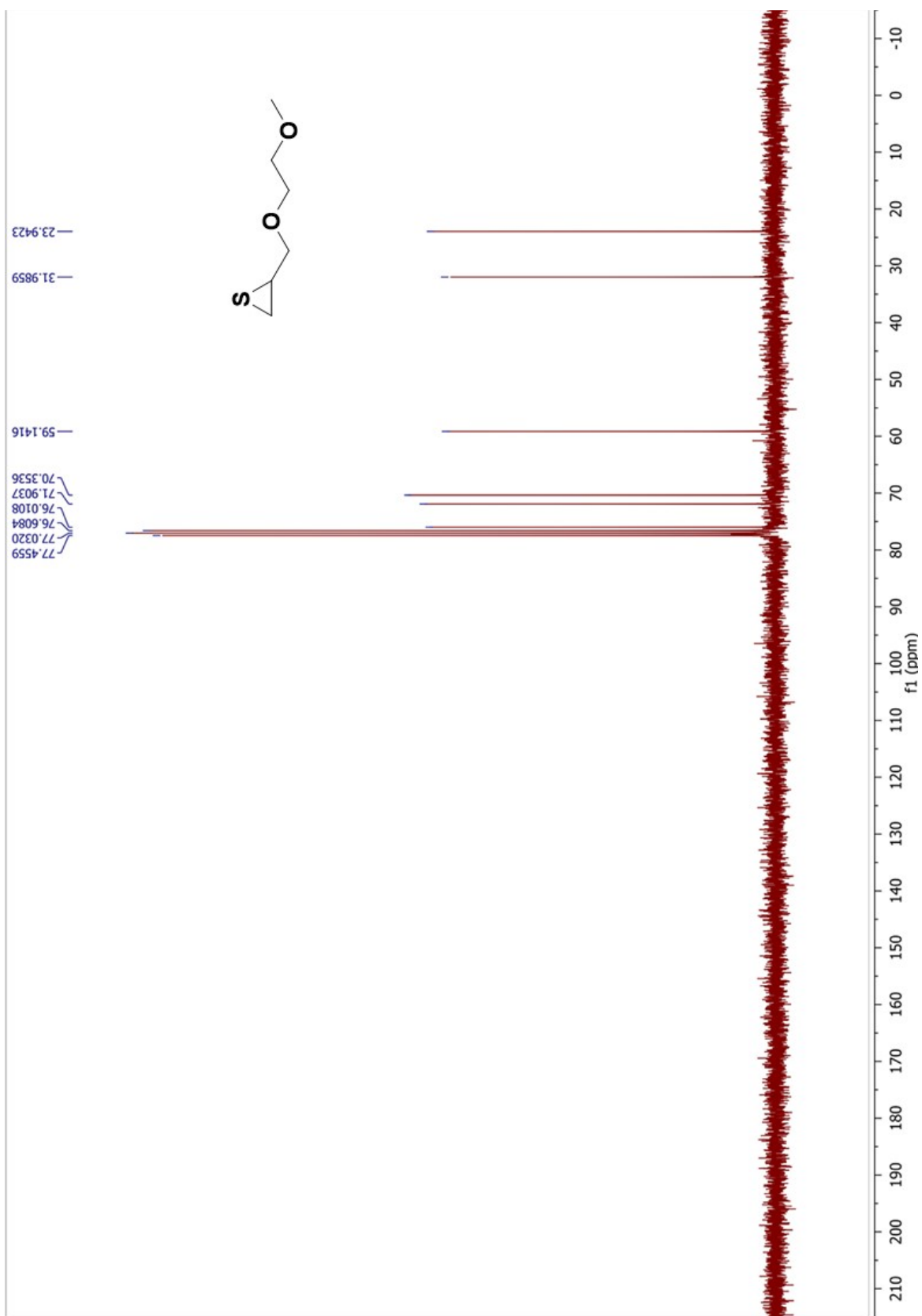


Figure S10. ^{13}C (75 MHz) spectra of 2-[(2-methoxyethoxy)methyl]thiirane (G₁S) in CDCl₃.

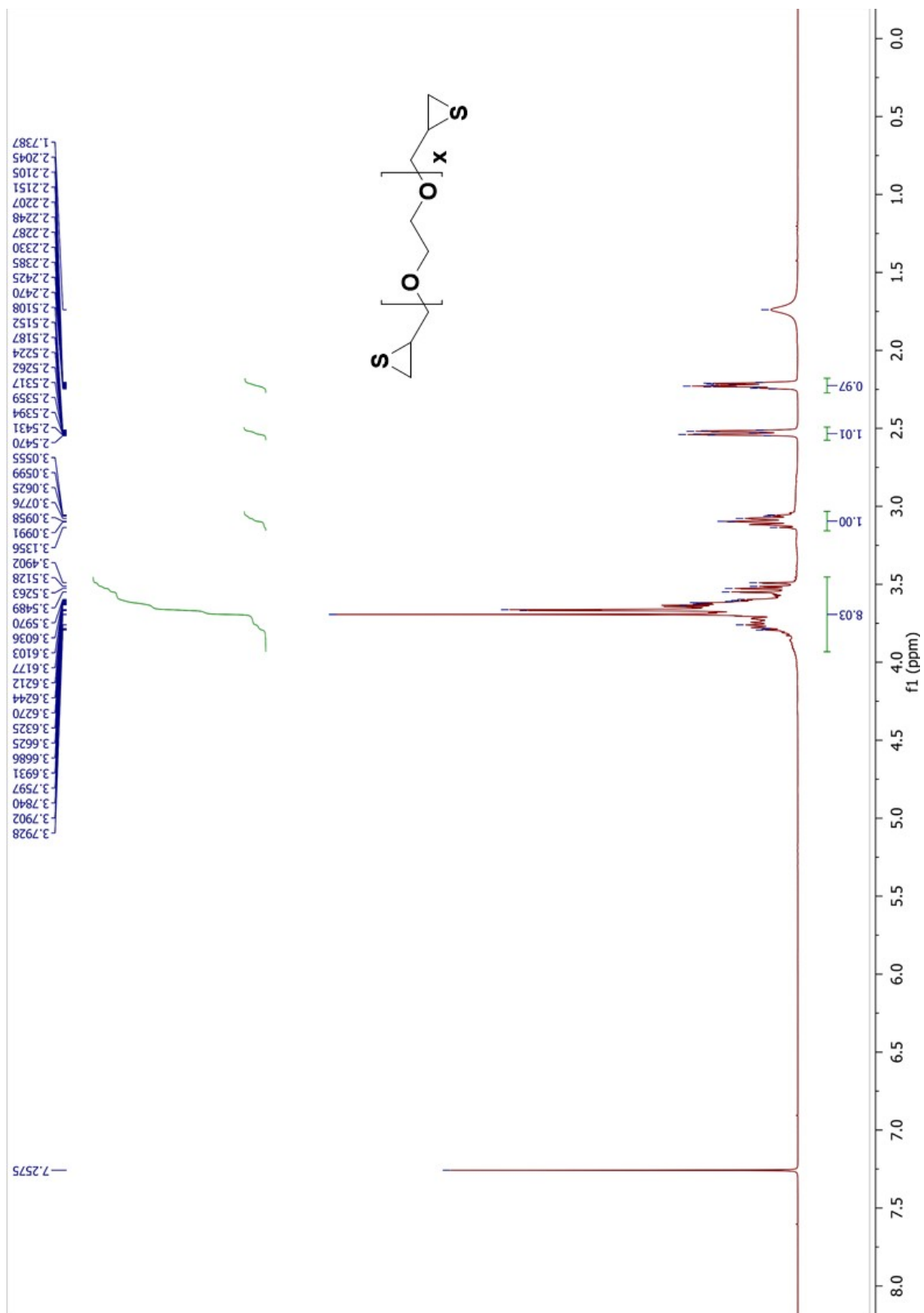


Figure S11. ^1H (300 MHz) spectra of 1,2-bis(2,3-epithiopropoxy)ethane mixture (SG_xS) in CDCl_3 .

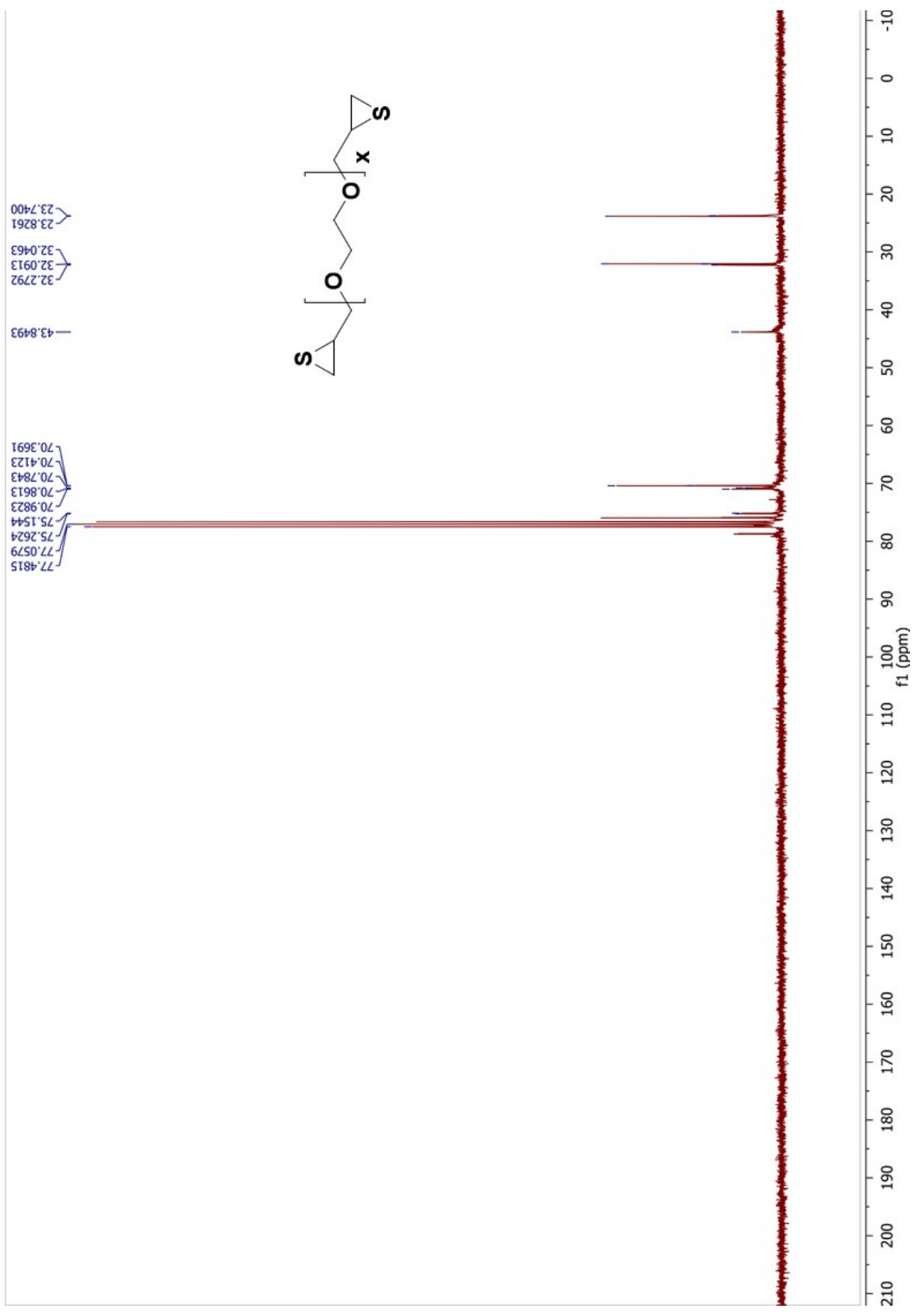


Figure S12. ^{13}C (75 MHz) spectra of 1,2-bis(2,3-epithiopropoxy)ethane mixture (SG_xS) in CDCl_3 .

Concentration: 0.10 mg/ml
 Injection Volume: 200.0 ul

Workbook Details

Eluent: DMF with LiBr

Flow Rate: 1.00 ml/min

Column Set:

Column Set Length: 0 mm

Detector: RI

Temperature: 55

Analysis Using Method: PEO Cal

Comments: in DMF with LiBr

Results File: C:\Cirrus Workbooks\DMF with LiBr\sheng-0005.rst

Detector Constants

Mass Constant:

Low LS Const:

High LS Const:

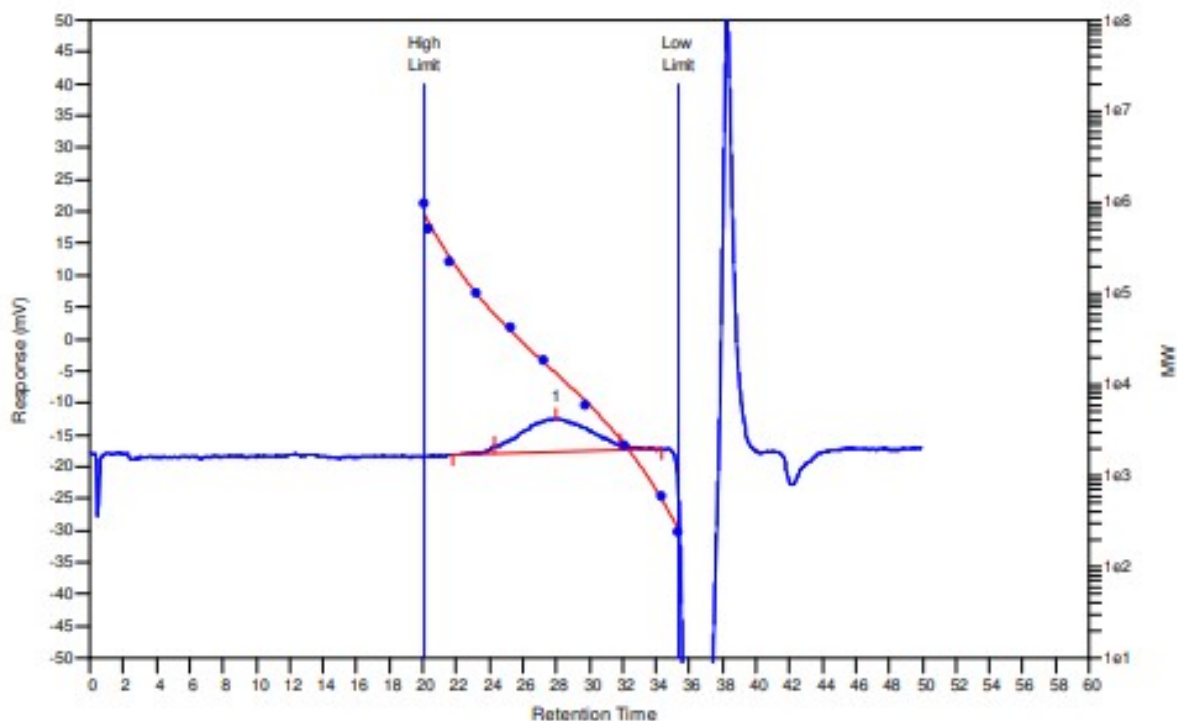
Mass Calculation Method: mins

Calculated Concentration:

Calculated dn/dc:

MW Calculation Method:

Use high angle below: logM



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13375	10620	16496	23865	31141	15508	1.5533

Figure S13. GPC of PG1S in DMF with LiBr.

References

- [1] Q. J. Meisner, T. Rojas, T. Glossmann, A. Hintennach, Q. Liu, J. Cao, P. C. Redfern, A. T. Ngo, L. A. Curtiss, Z. Zhang, *J. Electrochem. Soc.* **2020**, *167*, 070528.
- [2] X. Sun, J.-P. Lindner, B. Bruchmann, A. D. Schlüter, *Macromolecules* **2014**, *47*, 7337-7346.
- [3] R. L. Pederson, K. K. C. Liu, J. F. Rutan, L. Chen, C. H. Wong, *The Journal of Organic Chemistry* **1990**, *55*, 4897-4901.