SuFEx-Based Synthesis of Polysulfates

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General Methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX-400 and Varian Inova-400 instruments at 295 K unless otherwise noted. Chemical shifts (δ) are expressed in parts per million relative to residual $CHCl_3$, acetone, or DMSO as internal standards. Proton magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz. Carbon magnetic resonance (^{13}C NMR) spectra were recorded at 100 MHz. Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; sex, sextet; sept, septet; app, apparent. Infrared spectra were recorded on a ThermoNicolet Avatar 370 Fourier transform infrared spectrometer and are expressed in wavenumbers (cm^{-1}). Melting points (mp) were determined using a Thomas-Hoover melting point apparatus and are uncorrected. GCMS data were recorded on an Agilent 7890A GC system with an Agilent 5975C Inert MSD system operating in electron impact (EI+) mode [T_o = 50^{o}C for 2.25 min; ramp to 300^{o}C at 60^{o}C/min; hold at 300^{o}C for 4 min]. HPLC analysis was performed on an Agilent 1100 LC/MSD with an Agilent 1100 SL mass spectrometer (electrospray ionization, ES) eluting with 0.1% trifluoroacetic acid in H_2O and 0.05% trifluoroacetic acid in CH_3CN. Precoated Merck F-254 silica gel plates were used for thin layer analytical chromatography (TLC) and visualized with short wave UV light or by potassium permanganate stain. Column chromatography was carried out employing EMD (Merck) Silica Gel 60 (40-63 am). GPC analysis was carried out on a Shimadzu LC20 HPLC system equipped with a diode-array and a refractive index detector, and Waters Styragel HR-3 and HR-4 (5 μm particle size, 7.2 mm diameter) connected in series and placed in a column oven. The system was calibrated with ReadyCal polystyrene standards, M_n range 500 g/mol to 600,000 g/mol), eluting with HPLC grade DMF with 0.1% (wt.) of LiBr as a modifier. The accuracy of calibration was verified at regular intervals. A Wyatt MiniDawn TREOS detector was used for multi-angle light scattering (MALS) analysis. Unless otherwise noted, all starting materials and solvents were purchased from Aldrich, Acros Organics, Fisher, TCI, Alfa Aesar or Strem Chemicals and used as received. Dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) were obtained as '99.5% Extra Dry over Molecular Sieves' from Acros Organics. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was obtained from Alfa Aesar and used as received. 2-tert-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diaza-phosphorine (BEMP) was obtained from Sigma Aldrich as a 1M solution in hexanes. Sulfuryl fluoride gas (SO_2F_2, commercially produced under the trade name Vikane®) was a gift from Dow Agro.

General Polymerization Procedures

Small Scale Bulk Polymerization – (Table 1)

A-A (**2a;** 1-5 mmol) and B-B (**2b-e;** 1-5 mmol) monomers were combined in a 16 mL thick glass-walled, screw capped vessel containing a Teflon-coated magnetic stir bar and sealed with a PTFE/Sil septum. This reactor was then placed into a 150 ^{o}C oil bath with stirring, and once the monomers melted, catalyst was introduced to initiate polymerization. Heating was continued for 2 hours, at which point the solidified mixture was cooled and diluted with ~1-2 mL DMF per 1 g of polymer. Dissolution was assisted by vigorous heating with a heat gun or by re-introduction to the 150 ^{o}C oil bath. Once fully dissolved, the DMF solution was poured into ~100 mL of methanol per 1g of polymer to precipitate white BPA-polysulfate as a either a fiber or powder depending on molecular weight. The obtained polymers were then dried at 65 ^{o}C in a vacuum oven and subjected to GPC analysis.

Large Scale Bulk Polymerization – (0.5 mol scale)

A 1L 3-necked round-bottomed flask equipped with a reflux condenser, two rubber septums (one of which contained a thermometer for internal measurements) and a Teflon-coated magnetic stir bar was charged with **2a** (98.1 g, 0.25 mol) and **2c** (114.5 g, 0.25 mol). The reaction vessel was placed into an oil bath and brought to 135 ^{o}C (ca. 120 ^{o}C internal temperature). Once the monomers melted, 1 mol% of

BEMP as a 1M solution in hexanes (5 mL; 5 mmol) was added. Within 5 min, *tert*-butyldimethylfluorosilane (TBSF) was observed refluxing, and the temperature stabilized at ca. 120 °C after briefly increasing to 122 °C. After approximately 45 min, the reaction mixture solidified and stirring ceased. Heating was continued for an additional 45 min at which point the reflux condenser was replaced by a distillation head, and TBSF was distilled off (at 140-150 °C; 56 g was isolated). DMF (300 mL) was then added to the solid crude BPA-polysulfate product, and heating was continued at 130-135 °C until stirring was restored and all the polymer had dissolved. The resulting clear, colorless DMF solution was allowed to cool to *ca.* 60 °C and then slowly poured at a continuous and consistent rate into a jar containing 3L of vigorously stirred (overhead stirrer) methanol at ambient temperature, resulting in the formation of long, fibrous BPA-polysulfate strands. This material (144 g) was dried overnight at 65°C in a vacuum, analyzed by GPC. PDI = 1.7; M_n = 120,000 Da referenced to polystyrene standards; M_n = 58,000 determined by MALS; $T_{g\,=}$ 98 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31 (app s, 8H), 1.61 (2, 6H); Clad. For $(C_{15}H_{14}O_4S)_n$: C, 62.05; H, 4.86; S, 11.04. Found: C, 61.98; H, 4.80; S, 10.84; F, 0.33.

Substrate scope Polymerization/Solution Polymerization – (Table 3)

Bis(fluorosulfate) (**4-11a** and **14**; 1-3 mmol) and bis(silyl ether) monomers (TMS **2b**, **4b-5b** and TBS **2c**, **6-13c**; 1-3 mmol) were combined in a 16 mL thick glass-walled screw-capped vessel equipped with a Teflon-coated magnetic stir bar and sealed with a PTFE/Sil septum. This mixture was dissolved in 1 mL of NMP per 1 mmol substrate (~1 M solution with respect to each monomer) and treated with 20 mol% of DBU. Stirring was continued for 24 hour at room temperature. The reaction mixtures were then heated with a heat gun to dissolve any precipitated polymer and the resulting homogenous solution (in some cases additional DMF was necessary to achieve complete dissolution) was added directly to ~100 mL of methanol per 1g polymer at ambient temperature to precipitate the polysulfate copolymers.

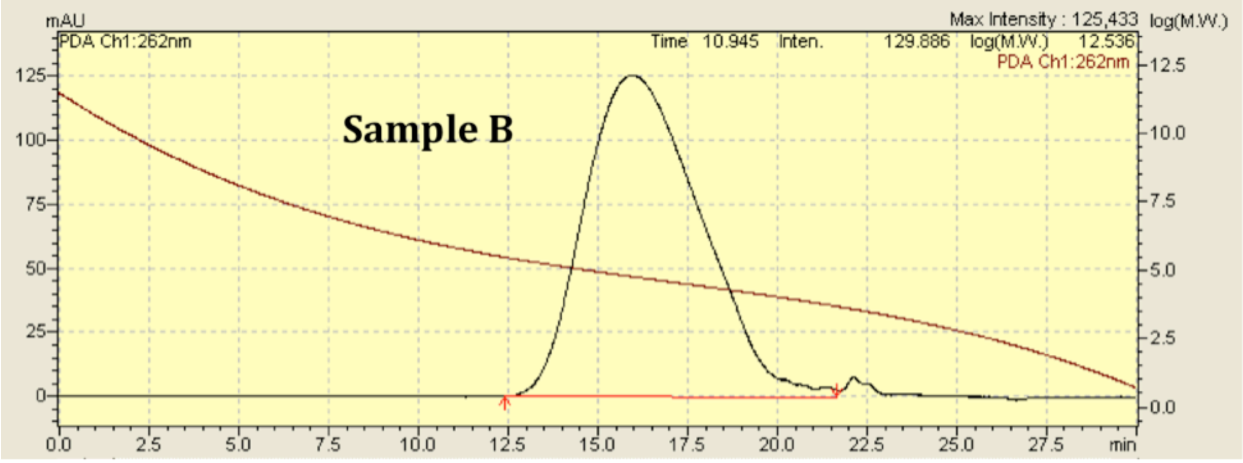
GPC Analysis

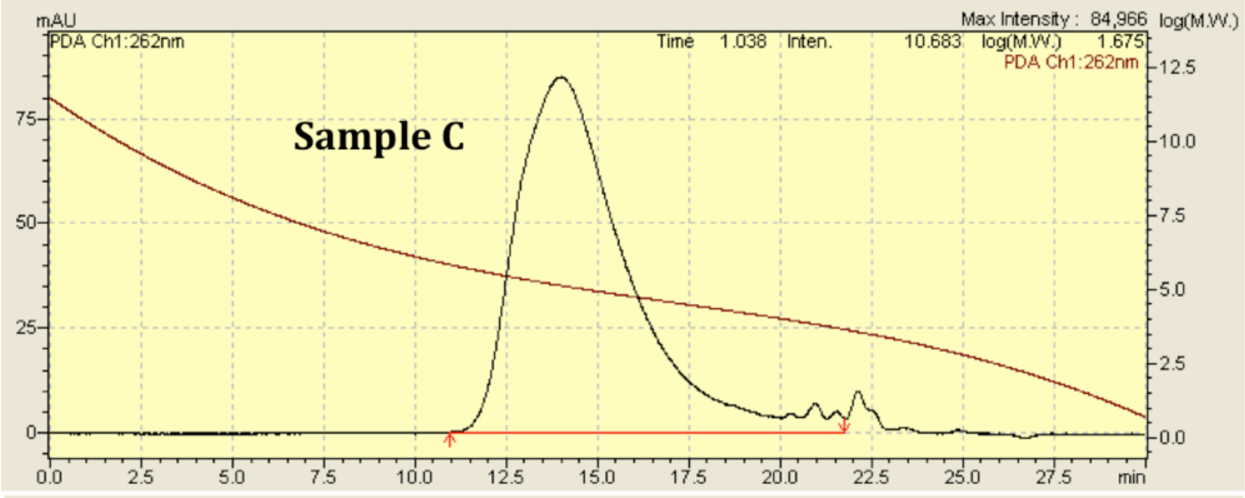
GPC was used to determine number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity (PDI). The system was calibrated using narrow molecular weight polystyrene standards. For several samples, multi-angle light scattering (Wyatt MiniDawn TREOS) detector was also used. Mobile phase was HPLC grade DMF with 0.1% (wt.) LiBr modifier. Representative GPC traces and MALS analysis reports are provided for the key polymer samples. Experimental GPC curves, shown throughout this document, are presented as normalized curves with arbitrary Y-axis units for either RI or UV (262 nm, 8 nm window from PDA) signals.

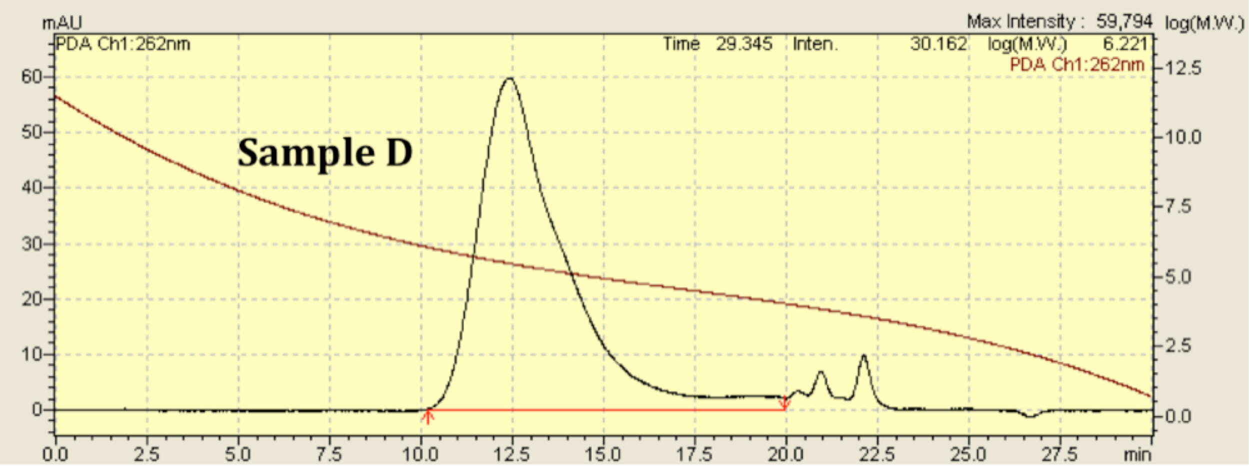
		PS Standards	**MALS**	
Conditions:		**M_n (g/mol)**	**M_n (g/mol)**	**Dispersity**
Bulk (TMS, 1% BEMP)	**(A)**	17000	2500	1.3
Bulk (TMS, 20% DBU)	**(B)**	38000	10600	1.4
Bulk (TBS, 20% DBU)	**(C)**	66000	19600	1.4
Bulk (TBS, 1% BEMP)	**(D)**	120000	58000	1.7

(Letter designations from Table 1, main text)


mAU
PDA Ch1:262nm
Time 15.663 Inten. 176.707 log(M.W.) 13.155
Max Intensity : 163,087
log(M.W.)
PDA Ch1:262nm
Sample A
175
150
125
100
75
50
25
0
12.5
10.0
7.5
5.0
2.5
0.0
0.0 2.5 5.0 7.5 10.0 12.5 15.0 17.5 20.0 22.5 25.0 27.5 min


mAU
PDA Ch1:262nm
Time 10.945 Inten. 129.886 log(M.W.) 12.536
Max Intensity : 125,433
log(M.W.)
PDA Ch1:262nm
Sample B
125
100
75
50
25
0
12.5
10.0
7.5
5.0
2.5
0.0
0.0 2.5 5.0 7.5 10.0 12.5 15.0 17.5 20.0 22.5 25.0 27.5 min


mAU
PDA Ch1:262nm
Time 1.038 Inten. 10.683 log(M.W.) 1.675
Max Intensity : 84,966
log(M.W.)
PDA Ch1:262nm
Sample C
75
50
25
0
12.5
10.0
7.5
5.0
2.5
0.0
0.0 2.5 5.0 7.5 10.0 12.5 15.0 17.5 20.0 22.5 25.0 27.5 min

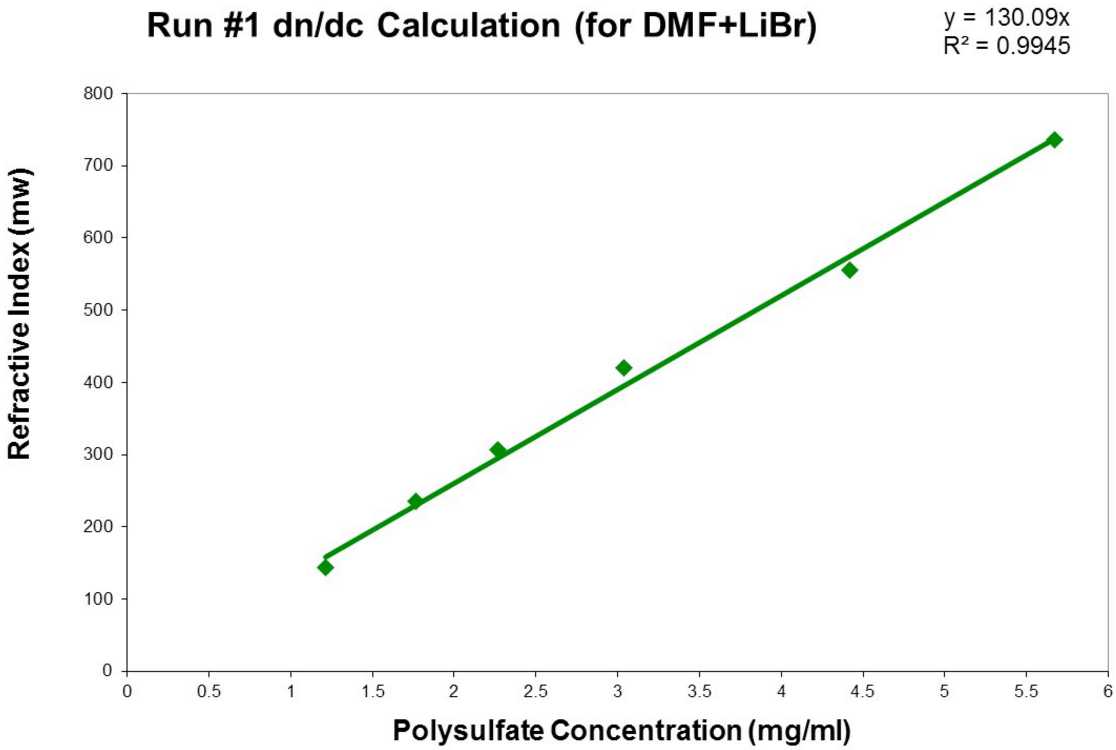


Multi-angle Light Scattering (MALS) Data

The differential index of refraction (dn/dc) was determined using batch method by plotting the refractive index of the polymer solution versus varying solution concentrations. The mobile phased used to dissolve BPA-polysulfate ("sample D", Mn =120,000 Da based on polystyrene standards) for dn/dc determination and subsequent MALS analysis was HPLC grade DMF with 0.1% LiBr (wt.). The dn/dc was obtained in duplicate.

Run #1 dn/dc = 0.13009
Run #2 dn/dc = 0.12623

Entry	Run #1		Run #2	
	Polysulfate Conc. (mg/mL)	Refractive Index (mv)	Polysulfate Conc. (mg/mL)	Refractive Index (mv)
1	1.22	144	0.74	84
2	1.77	236	1.38	203
3	2.27	306	1.84	248
4	3.04	420	2.77	381
5	4.42	556	3.68	475
6	5.67	736	4.50	593
7			6.14	755
8			6.92	848


Run #1 dn/dc Calculation (for DMF+LiBr)
y = 130.09x
R² = 0.9945
Refractive Index (mw)
800
700
600
500
400
300
200
100
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
Polysulfate Concentration (mg/ml)

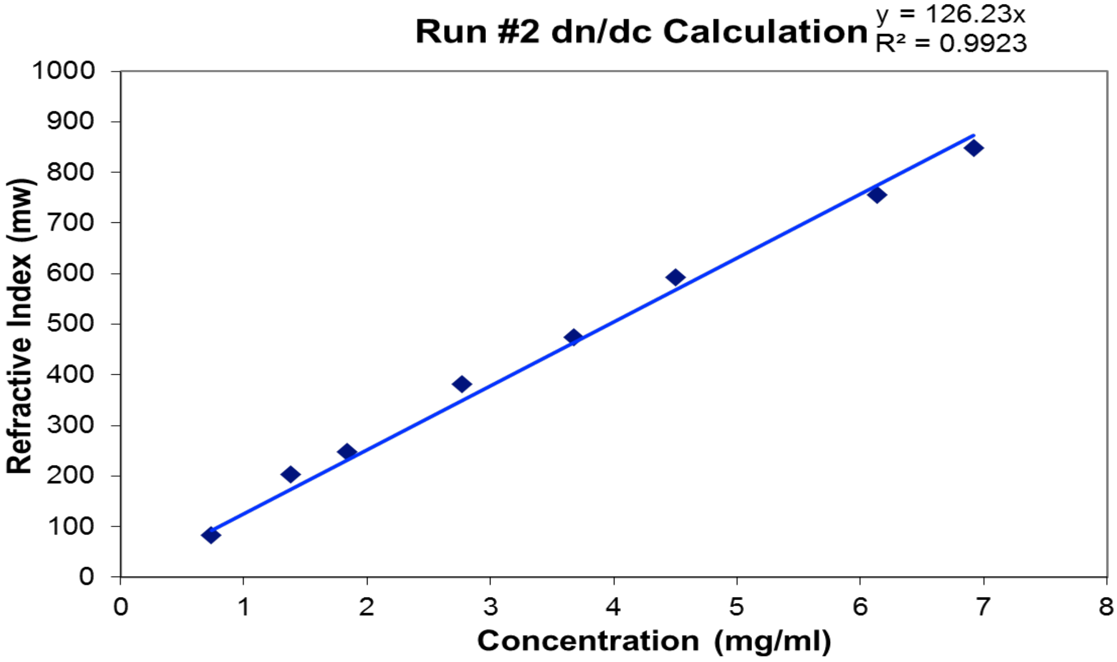
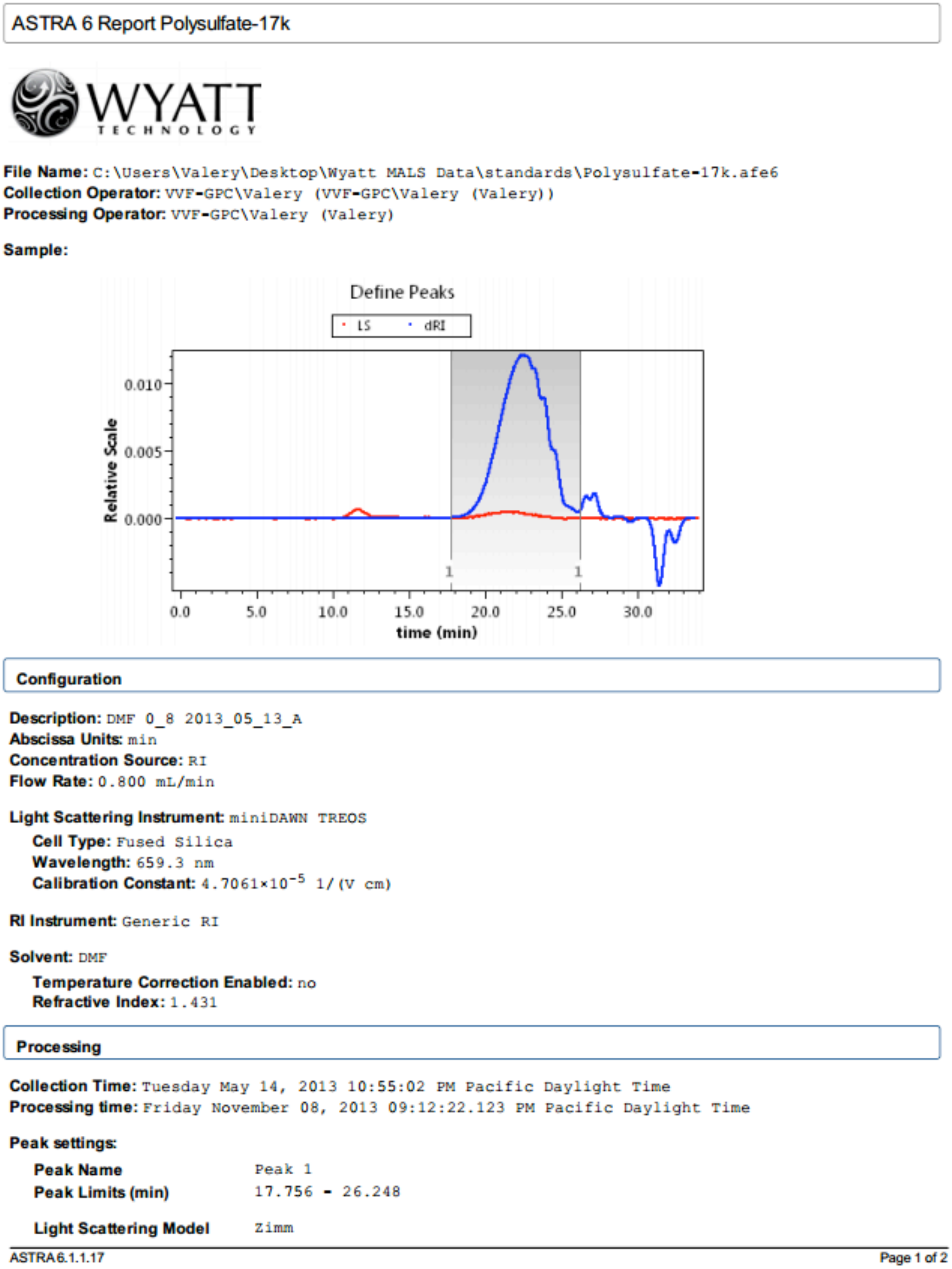

Run #2 dn/dc Calculation
y = 126.23x
R² = 0.9923
Refractive Index (mw)
1000
900
800
700
600
500
400
300
200
100
0
0
1
2
3
4
5
6
7
8
Concentration (mg/ml)

Table 1, Entry 1 ***SAMPLE A***



ASTRA 6 Report Polysulfate-17k

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Collection Operator: `VVF-GPC\Valery (VVF-GPC\Valery (Valery))`
Processing Operator: `VVF-GPC\Valery (Valery)`

Sample:

Configuration

Description: DMF 0_8 2013_05_13_A
Abscissa Units: min
Concentration Source: RI
Flow Rate: 0.800 mL/min

Light Scattering Instrument: miniDAWN TREOS
  Cell Type: Fused Silica
  Wavelength: 659.3 nm
  Calibration Constant: 4.7061×10^{-5} 1/(V cm)

RI Instrument: Generic RI

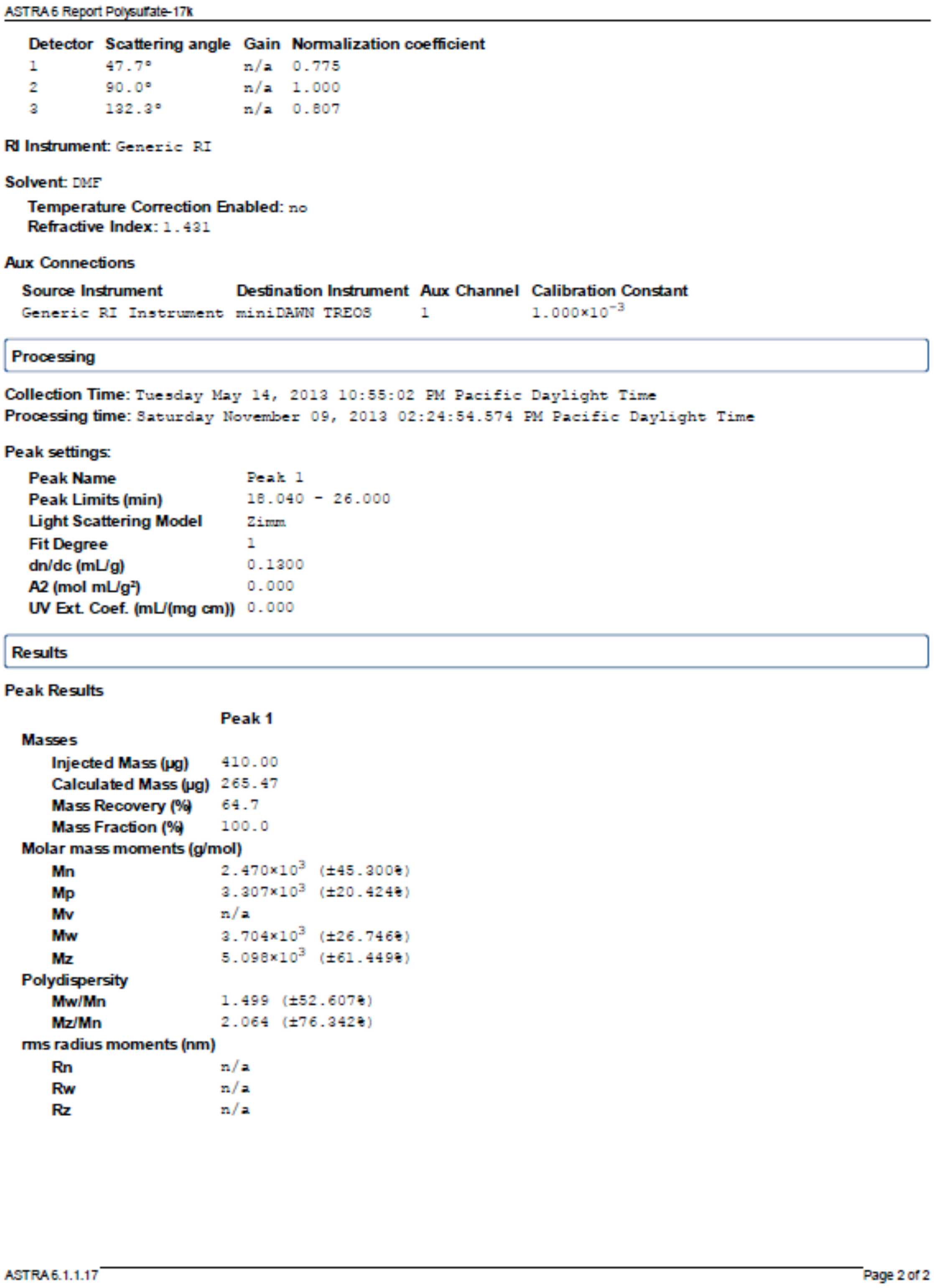
Solvent: DMF
  Temperature Correction Enabled: no
  Refractive Index: 1.431

Processing

Collection Time: Tuesday May 14, 2013 10:55:02 PM Pacific Daylight Time
Processing time: Friday November 08, 2013 09:12:22.123 PM Pacific Daylight Time

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	17.756 - 26.248
Light Scattering Model	Zimm



ASTRA 6 Report Polysulfate-17k

Detector	Scattering angle	Gain	Normalization coefficient
1	47.7°	n/a	0.775
2	90.0°	n/a	1.000
3	132.3°	n/a	0.807

RI Instrument: Generic RI

Solvent: DMF

Temperature Correction Enabled: no
Refractive Index: 1.431

Aux Connections

Source Instrument	Destination Instrument	Aux Channel	Calibration Constant
Generic RI Instrument	miniDAWN TREOS	1	1.000×10^{-3}

Processing

Collection Time: Tuesday May 14, 2013 10:55:02 PM Pacific Daylight Time
Processing time: Saturday November 09, 2013 02:24:54.574 PM Pacific Daylight Time

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	18.040 - 26.000
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1300
A2 (mol mL/g²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

Results

Peak Results

	Peak 1
Masses	
Injected Mass (µg)	410.00
Calculated Mass (µg)	265.47
Mass Recovery (%)	64.7
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	2.470×10^{3} (±45.300%)
Mp	3.307×10^{3} (±20.424%)
Mv	n/a
Mw	3.704×10^{3} (±26.746%)
Mz	5.098×10^{3} (±61.449%)
Polydispersity	
Mw/Mn	1.499 (±52.607%)
Mz/Mn	2.064 (±76.342%)
rms radius moments (nm)	
Rn	n/a
Rw	n/a
Rz	n/a

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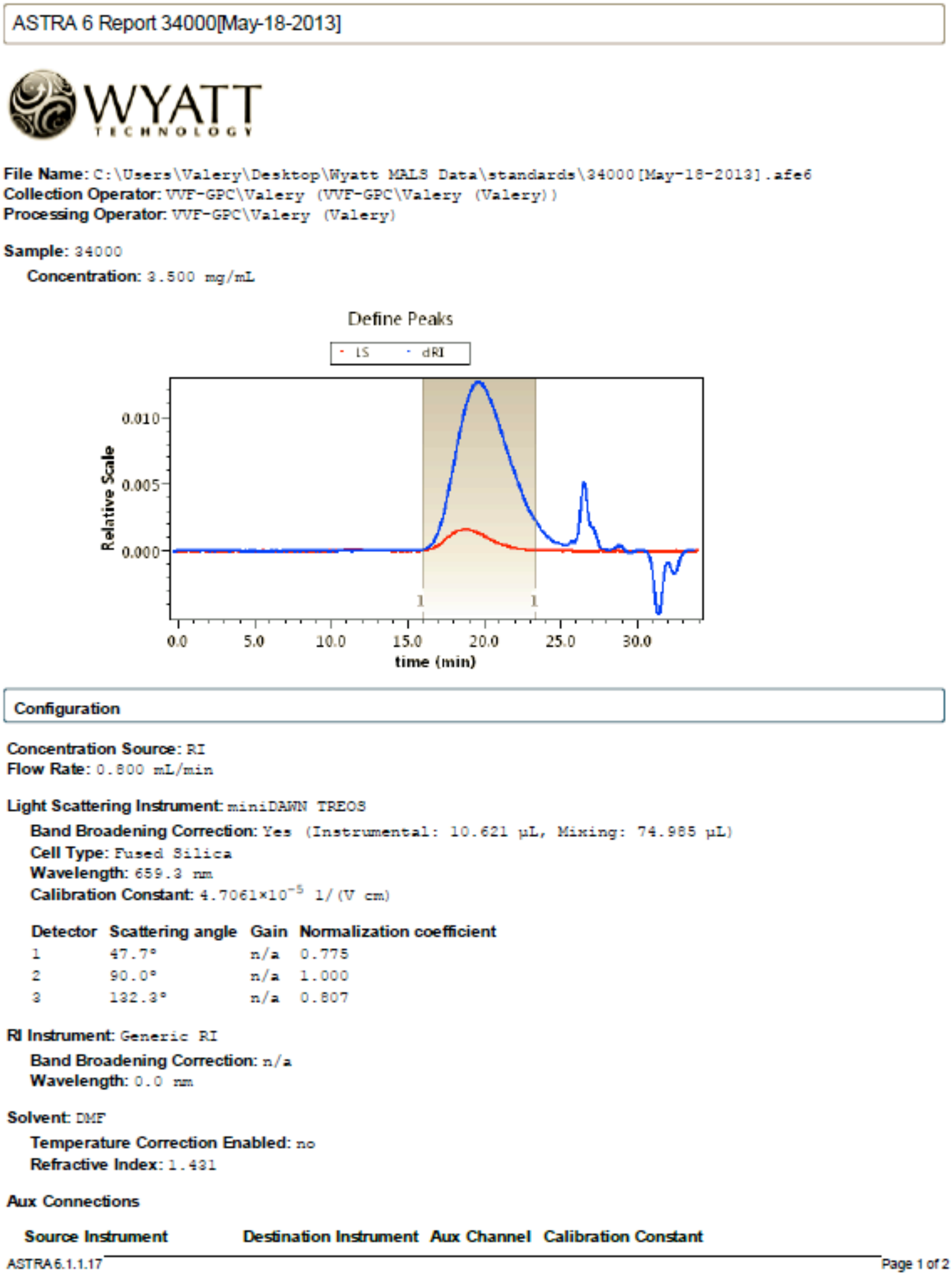
Table 1, Entry 2



ASTRA 6 Report 34000[May-18-2013]

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Collection Operator: VVF-GPC\Valery (VVF-GPC\Valery (Valery))
Processing Operator: VVF-GPC\Valery (Valery)

Sample: 34000
Concentration: 3.500 mg/mL

Configuration

Concentration Source: RI
Flow Rate: 0.800 mL/min

Light Scattering Instrument: miniDAWN TREOS
Band Broadening Correction: Yes (Instrumental: 10.621 µL, Mixing: 74.985 µL)
Cell Type: Fused Silica
Wavelength: 659.3 nm
Calibration Constant: 4.7061×10^{-5} 1/(V cm)

Detector	Scattering angle	Gain	Normalization coefficient
1	47.7°	n/a	0.775
2	90.0°	n/a	1.000
3	132.3°	n/a	0.807

RI Instrument: Generic RI
Band Broadening Correction: n/a
Wavelength: 0.0 nm

Solvent: DMF
Temperature Correction Enabled: no
Refractive Index: 1.431

Aux Connections

Source Instrument	Destination Instrument	Aux Channel	Calibration Constant

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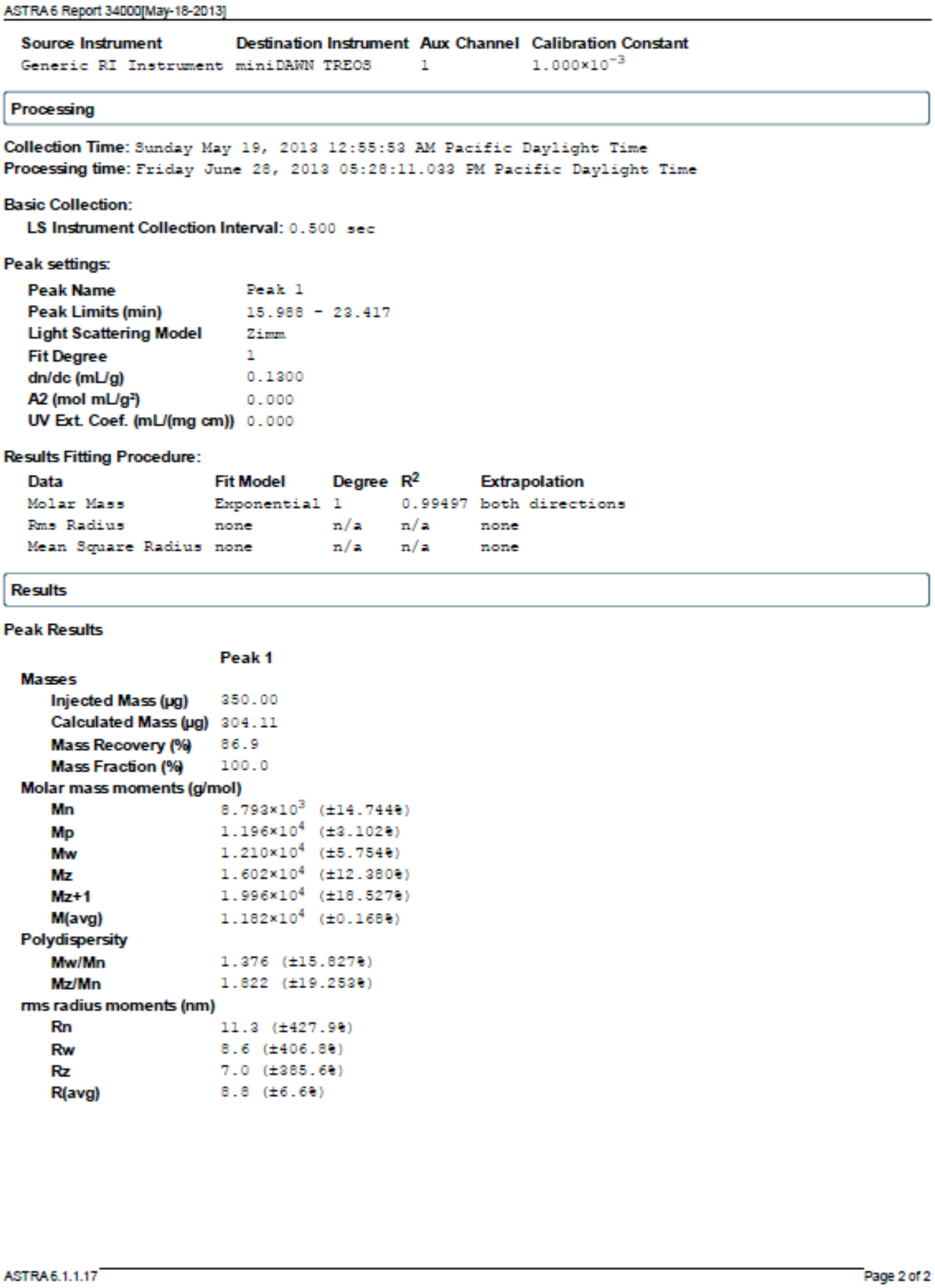


Source Instrument	Destination Instrument	Aux Channel	Calibration Constant
Generic RI Instrument	miniDAWN TREOS	1	1.000×10^{-3}

Processing

Collection Time: Sunday May 19, 2013 12:55:53 AM Pacific Daylight Time
Processing time: Friday June 28, 2013 05:28:11.033 PM Pacific Daylight Time

Basic Collection:

LS Instrument Collection Interval: 0.500 sec

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	15.988 - 23.417
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1300
A2 (mol mL/g²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

Results Fitting Procedure:

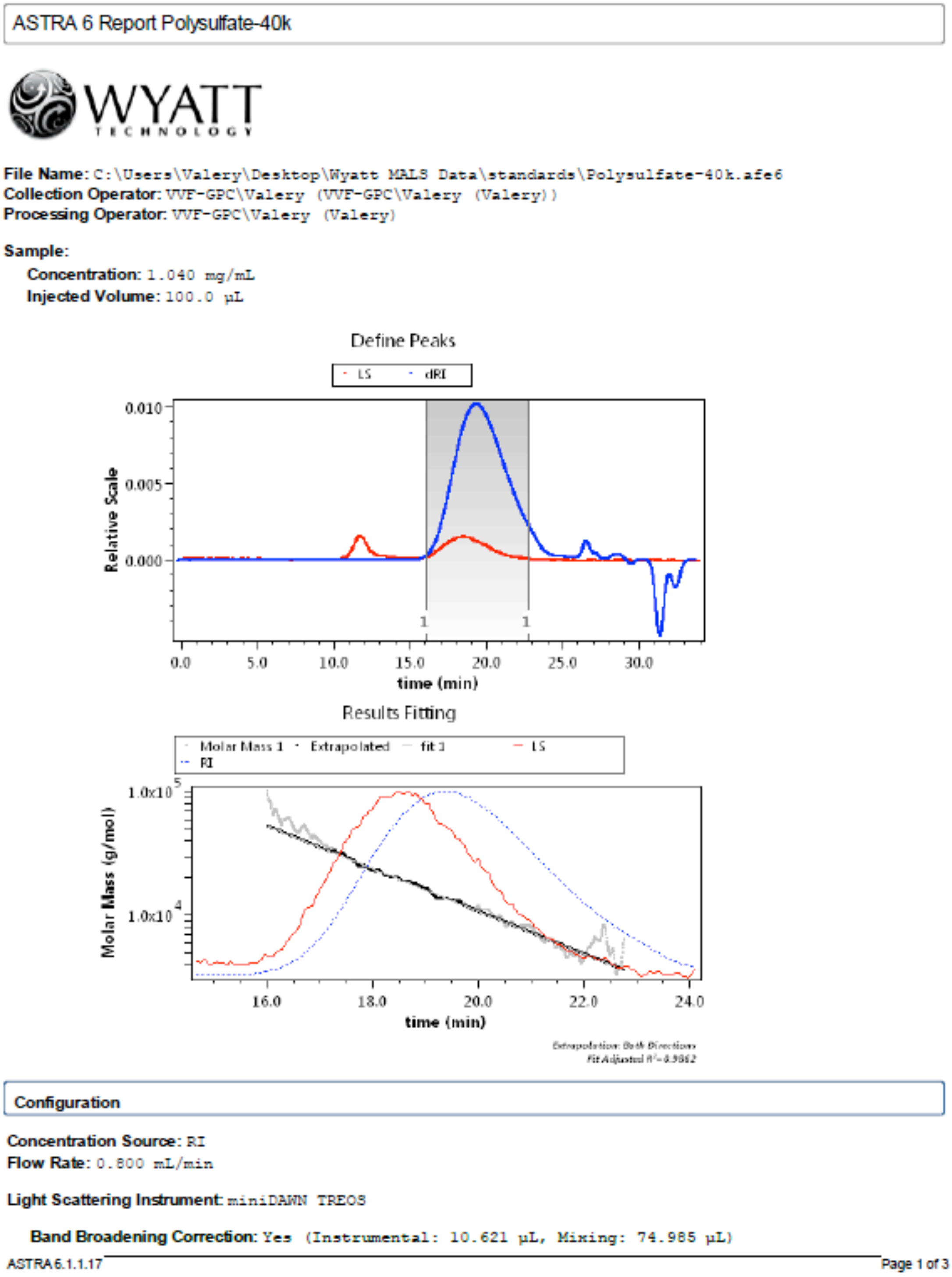
Data	Fit Model	Degree	R^2	Extrapolation
Molar Mass	Exponential	1	0.99497	both directions
Rms Radius	none	n/a	n/a	none
Mean Square Radius	none	n/a	n/a	none

Results

Peak Results

	Peak 1
Masses	
Injected Mass (µg)	350.00
Calculated Mass (µg)	304.11
Mass Recovery (%)	86.9
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	8.793×10^{3} (±14.744%)
Mp	1.196×10^{4} (±3.102%)
Mw	1.210×10^{4} (±5.754%)
Mz	1.602×10^{4} (±12.380%)
Mz+1	1.996×10^{4} (±18.527%)
M(avg)	1.182×10^{4} (±0.168%)
Polydispersity	
Mw/Mn	1.376 (±15.827%)
Mz/Mn	1.822 (±19.253%)
rms radius moments (nm)	
Rn	11.3 (±427.9%)
Rw	8.6 (±406.8%)
Rz	7.0 (±385.6%)
R(avg)	8.8 (±6.6%)

Table 1, Entry 3 ***SAMPLE B***



ASTRA 6 Report Polysulfate-40k

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Collection Operator: `VVF-GPC\Valery (VVF-GPC\Valery (Valery))`
Processing Operator: `VVF-GPC\Valery (Valery)`

Sample:
Concentration: `1.040 mg/mL`
Injected Volume: `100.0 µL`

Define Peaks

Results Fitting

Extrapolation: Both Directions
Fit Adjusted R^2 = 0.9862

Configuration

Concentration Source: `RI`
Flow Rate: `0.800 mL/min`

Light Scattering Instrument: `miniDAWN TREOS`

Band Broadening Correction: `Yes (Instrumental: 10.621 µL, Mixing: 74.985 µL)`

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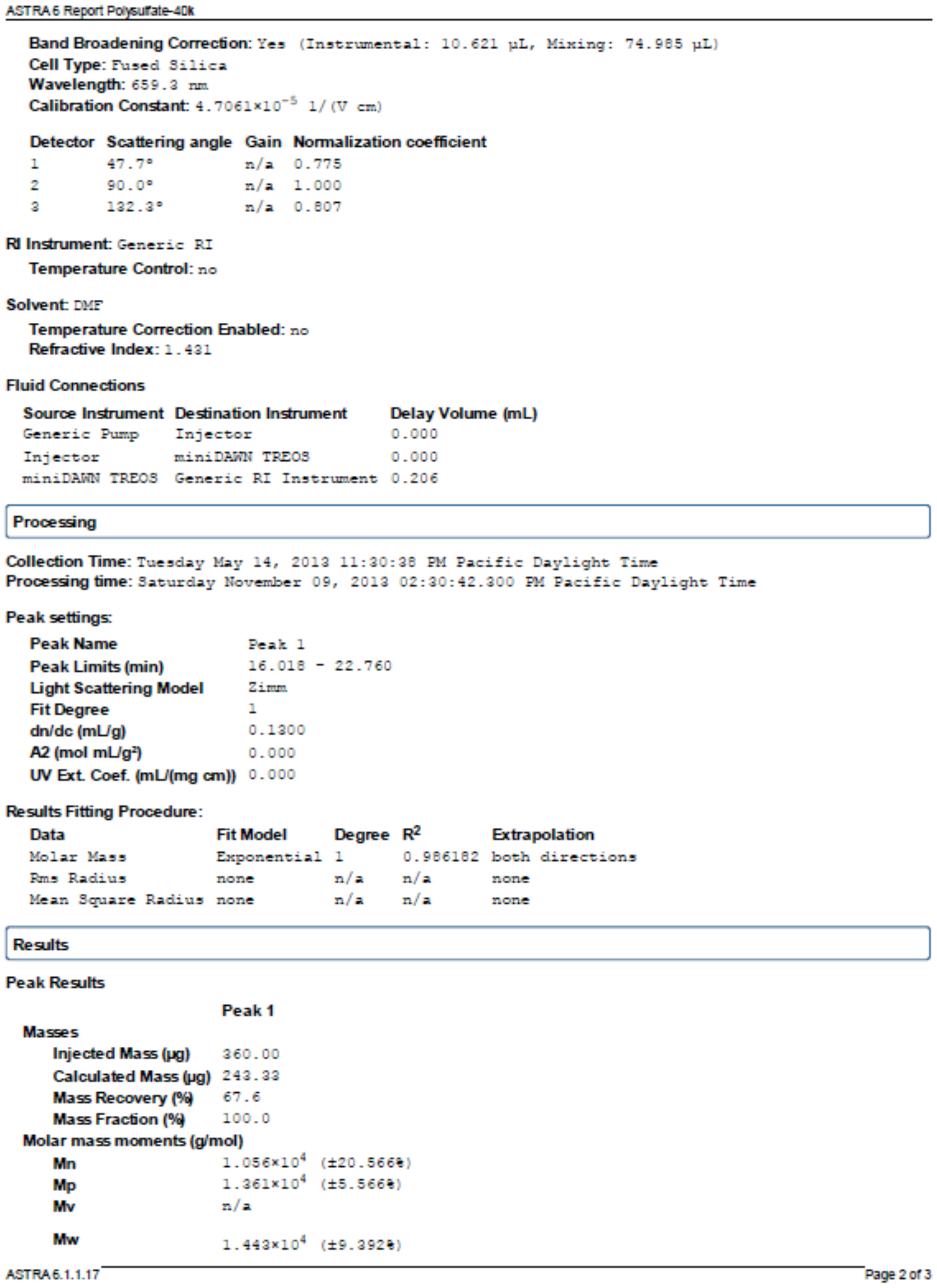

ASTRA 6 Report Polysulfate-40k

Band Broadening Correction: Yes (Instrumental: 10.621 µL, Mixing: 74.985 µL)
Cell Type: Fused Silica
Wavelength: 659.3 nm
Calibration Constant: 4.7061×10^{-5} 1/(V cm)

Detector	Scattering angle	Gain	Normalization coefficient
1	47.7°	n/a	0.775
2	90.0°	n/a	1.000
3	132.3°	n/a	0.807

RI Instrument: Generic RI
Temperature Control: no

Solvent: DMF
Temperature Correction Enabled: no
Refractive Index: 1.431

Fluid Connections

Source Instrument	Destination Instrument	Delay Volume (mL)
Generic Pump	Injector	0.000
Injector	miniDAWN TREOS	0.000
miniDAWN TREOS	Generic RI Instrument	0.206

Processing

Collection Time: Tuesday May 14, 2013 11:30:38 PM Pacific Daylight Time
Processing time: Saturday November 09, 2013 02:30:42.300 PM Pacific Daylight Time

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	16.018 - 22.760
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1300
A2 (mol mL/g²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

Results Fitting Procedure:

Data	Fit Model	Degree	R^2	Extrapolation
Molar Mass	Exponential	1	0.986182	both directions
Rms Radius	none	n/a	n/a	none
Mean Square Radius	none	n/a	n/a	none

Results

Peak Results

	Peak 1
Masses	
Injected Mass (µg)	360.00
Calculated Mass (µg)	243.33
Mass Recovery (%)	67.6
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	1.056×10^{4} (±20.566%)
Mp	1.361×10^{4} (±5.566%)
Mv	n/a
Mw	1.443×10^{4} (±9.392%)

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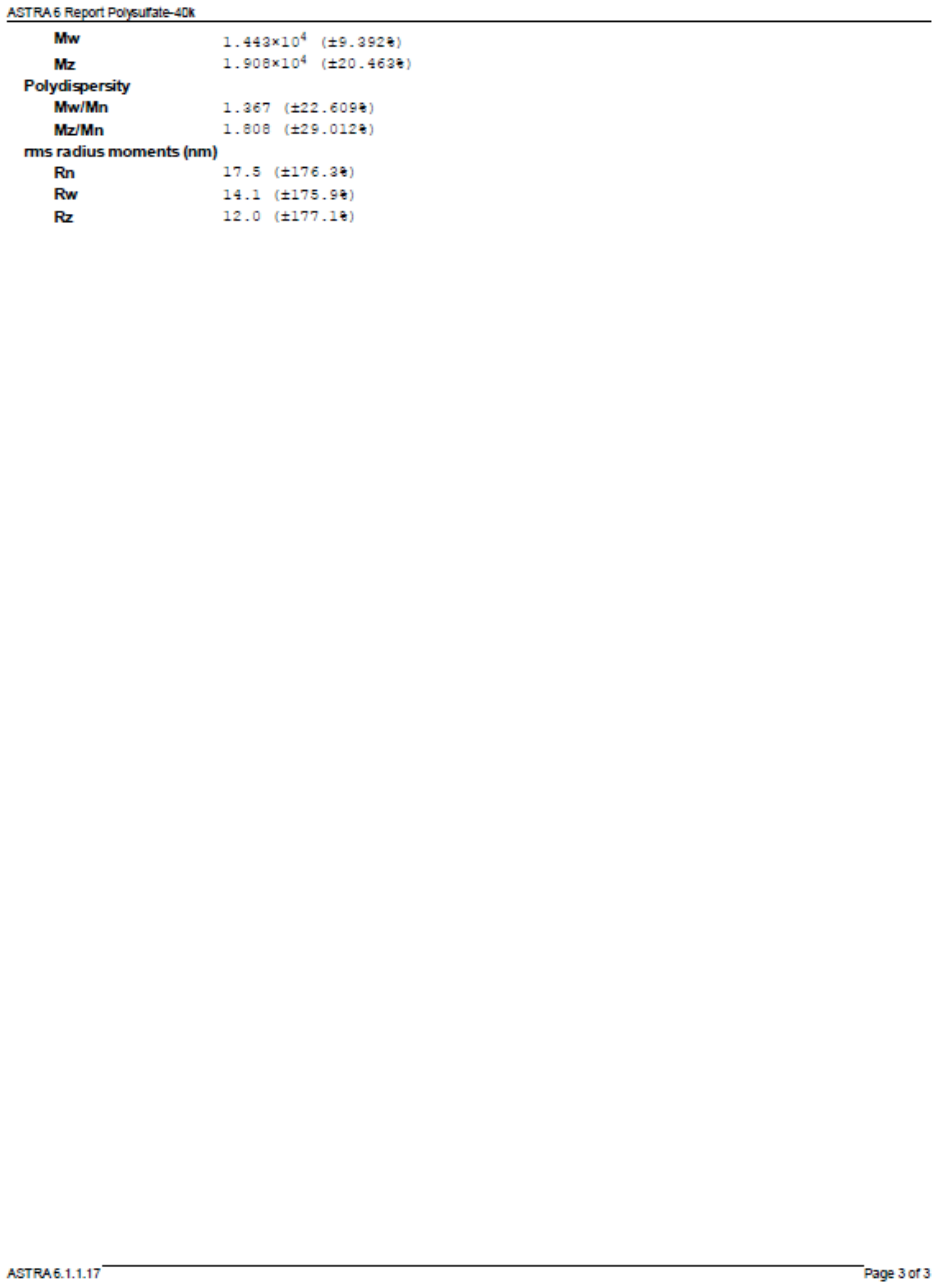
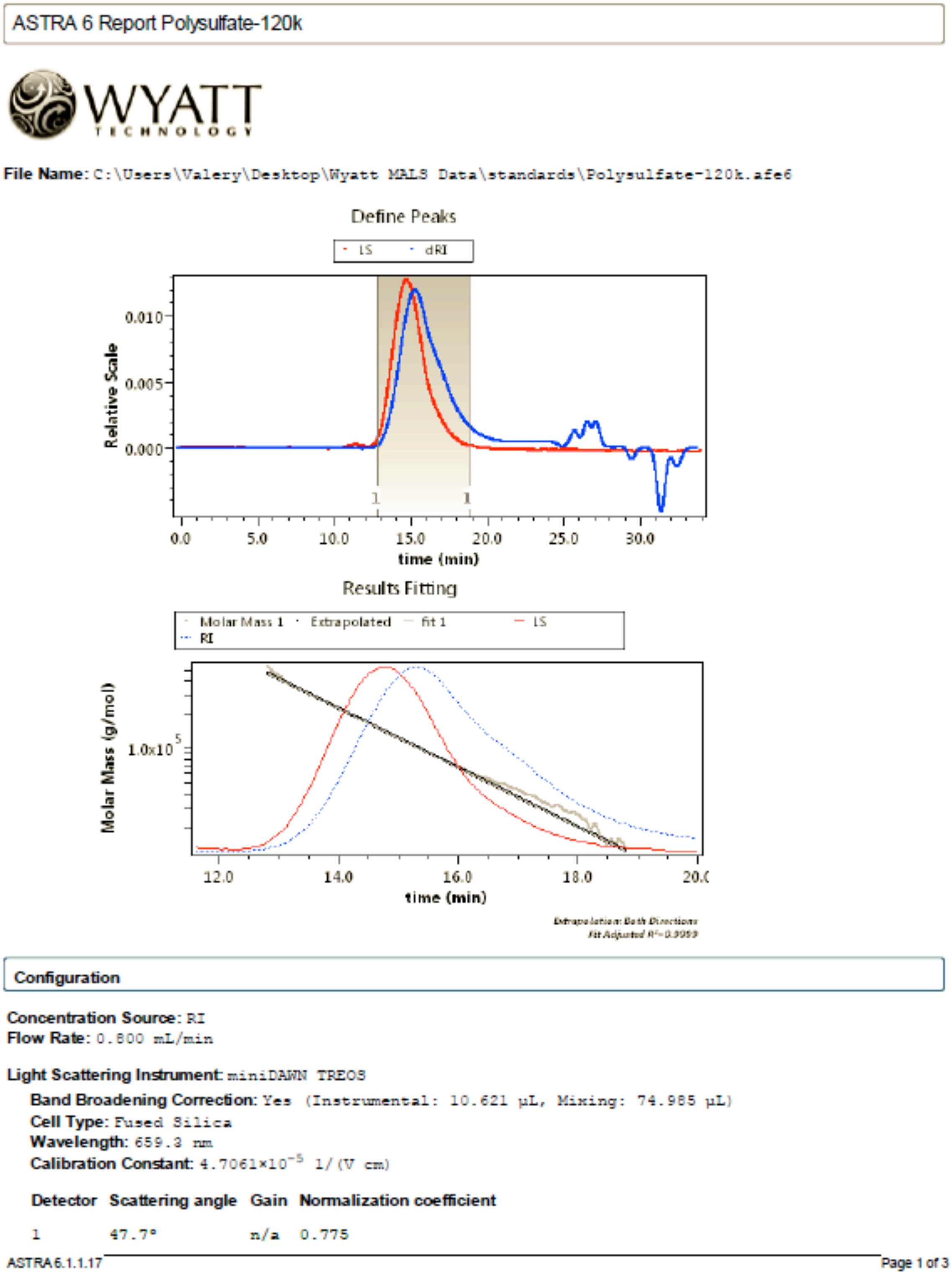


Mw	1.443×10^4 (±9.392%)
Mz	1.908×10^4 (±20.463%)
Polydispersity	
Mw/Mn	1.367 (±22.609%)
Mz/Mn	1.808 (±29.012%)
rms radius moments (nm)	
Rn	17.5 (±176.3%)
Rw	14.1 (±175.9%)
Rz	12.0 (±177.1%)

Table 1, Entry 4 ***SAMPLE D***



ASTRA 6 Report Polysulfate-120k

File Name: `C:\Users\Valery\Desktop\Wyatt MALS Data\standards\Polysulfate-120k.afe6`

Define Peaks

Results Fitting

Extrapolation: Both Directions
Fit Adjusted R^2=0.9959

Configuration

Concentration Source: RI
Flow Rate: 0.800 mL/min

Light Scattering Instrument: miniDAWN TREOS
Band Broadening Correction: Yes (Instrumental: 10.621 µL, Mixing: 74.985 µL)
Cell Type: Fused Silica
Wavelength: 659.3 nm
Calibration Constant: 4.7061×10^{-5} 1/(V cm)

Detector	Scattering angle	Gain	Normalization coefficient
1	47.7°	n/a	0.775

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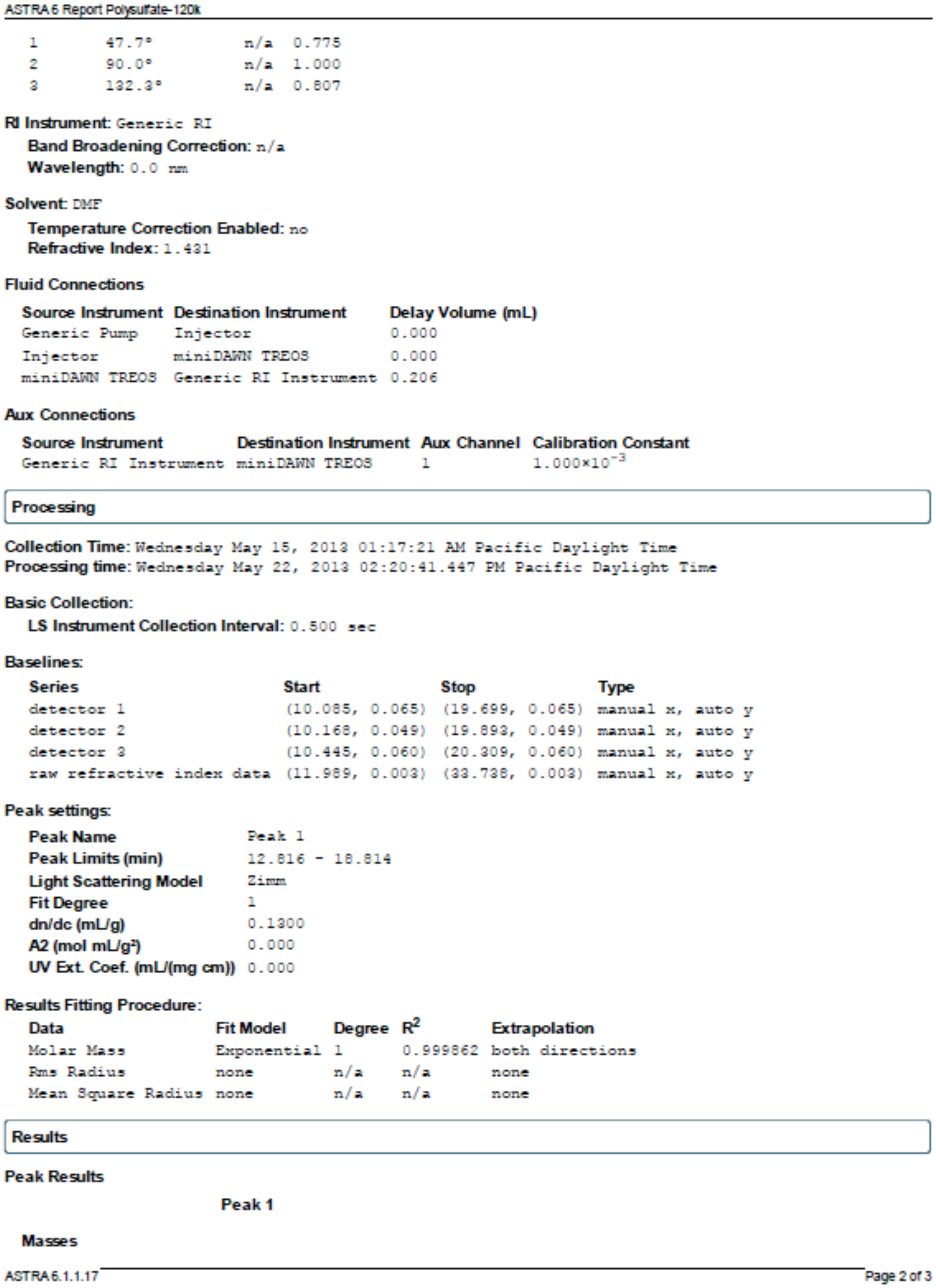


1	47.7°	n/a	0.775
2	90.0°	n/a	1.000
3	132.3°	n/a	0.807

RI Instrument: Generic RI

Band Broadening Correction: n/a
Wavelength: 0.0 nm

Solvent: DMF

Temperature Correction Enabled: no
Refractive Index: 1.431

Fluid Connections

Source Instrument	Destination Instrument	Delay Volume (mL)
Generic Pump	Injector	0.000
Injector	miniDAWN TREOS	0.000
miniDAWN TREOS	Generic RI Instrument	0.206

Aux Connections

Source Instrument	Destination Instrument	Aux Channel	Calibration Constant
Generic RI Instrument	miniDAWN TREOS	1	1.000×10^{-3}

Processing

Collection Time: Wednesday May 15, 2013 01:17:21 AM Pacific Daylight Time
Processing time: Wednesday May 22, 2013 02:20:41.447 PM Pacific Daylight Time

Basic Collection:

LS Instrument Collection Interval: 0.500 sec

Baselines:

Series	Start	Stop	Type
detector 1	(10.085, 0.065)	(19.699, 0.065)	manual x, auto y
detector 2	(10.168, 0.049)	(19.893, 0.049)	manual x, auto y
detector 3	(10.445, 0.060)	(20.309, 0.060)	manual x, auto y
raw refractive index data	(11.989, 0.003)	(33.738, 0.003)	manual x, auto y

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	12.816 - 18.814
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1300
A2 (mol mL/g²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

Results Fitting Procedure:

Data	Fit Model	Degree	R^2	Extrapolation
Molar Mass	Exponential	1	0.999862	both directions
Rms Radius	none	n/a	n/a	none
Mean Square Radius	none	n/a	n/a	none

Results

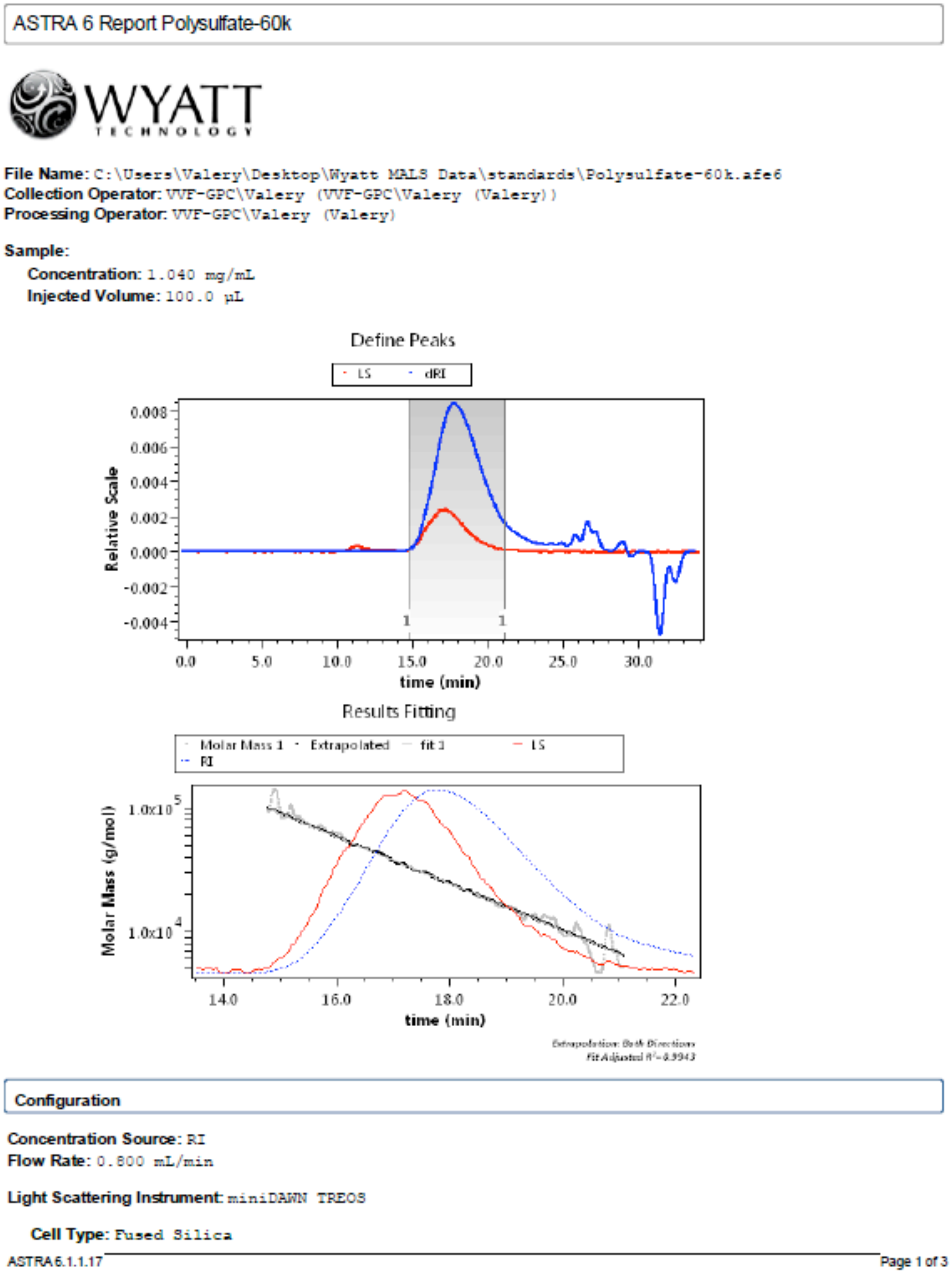
Peak Results

Peak 1

Masses

Masses	
Injected Mass (µg)	227.00
Calculated Mass (µg)	218.23
Mass Recovery (%)	96.1
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	5.800×10^{4} (±6.125%)
Mp	1.047×10^{5} (±0.626%)
Mv	n/a
Mw	9.947×10^{4} (±1.312%)
Mz	1.474×10^{5} (±2.707%)
Polydispersity	
Mw/Mn	1.715 (±6.264%)
Mz/Mn	2.542 (±6.697%)
rms radius moments (nm)	
Rn	n/a
Rw	12.0 (±45.5%)
Rz	16.9 (±12.3%)
R(avg)	16.7 (±0.4%)

Table 1, Entry 8 ***SAMPLE C***



ASTRA 6 Report Polysulfate-60k

File Name: `C:\Users\Valery\Desktop\Wyatt MALS Data\standards\Polysulfate-60k.afe6`
Collection Operator: `VVF-GPC\Valery (VVF-GPC\Valery (Valery))`
Processing Operator: `VVF-GPC\Valery (Valery)`

Sample:
Concentration: `1.040 mg/mL`
Injected Volume: `100.0 µL`

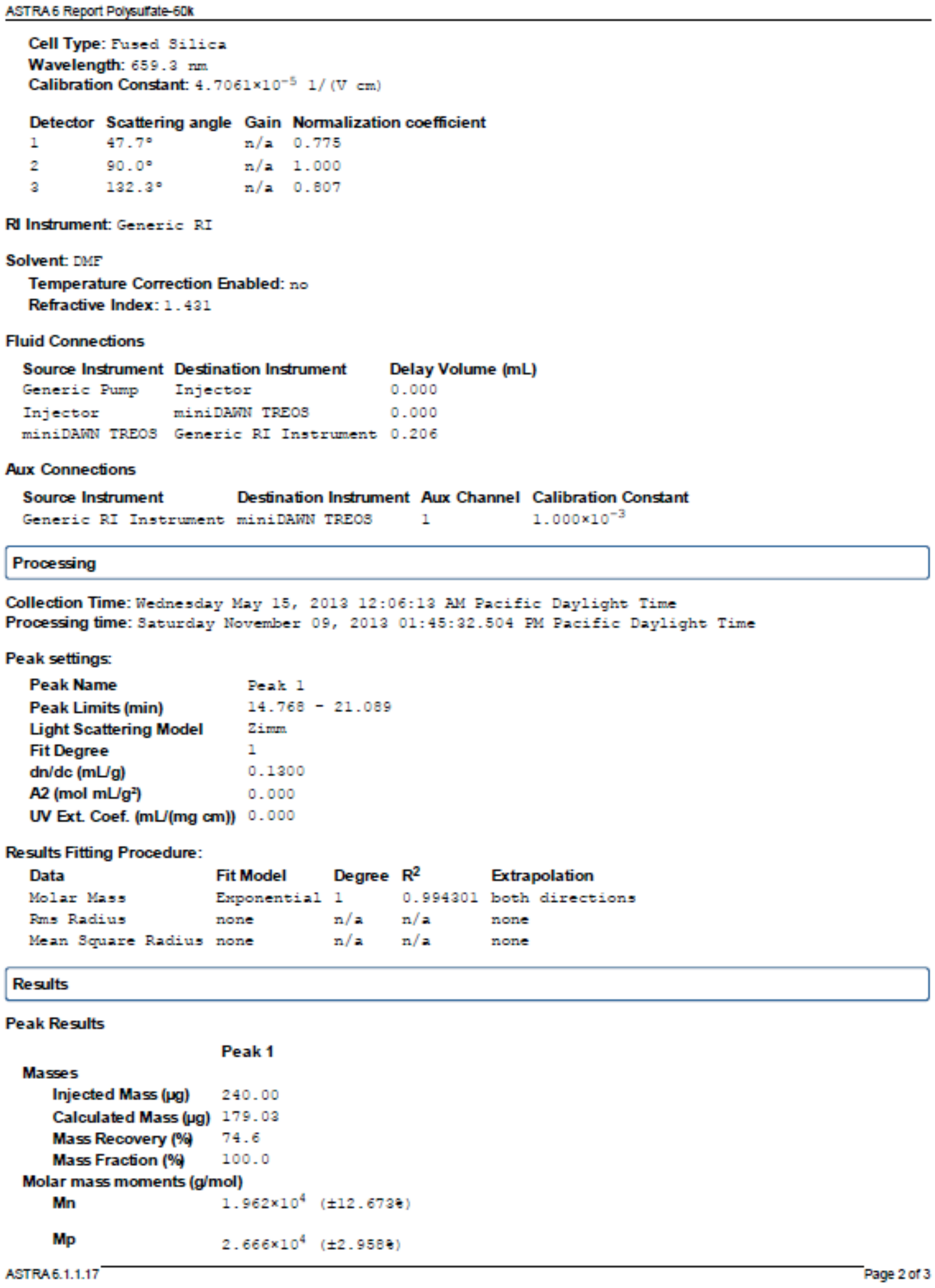
Configuration

Concentration Source: `RI`
Flow Rate: `0.800 mL/min`

Light Scattering Instrument: `miniDAWN TREOS`

Cell Type: `Fused Silica`

ASTRA 6.1.1.17 Page 1 of 3



Cell Type: Fused Silica
Wavelength: 659.3 nm
Calibration Constant: 4.7061×10^{-5} 1/(V cm)

Detector	Scattering angle	Gain	Normalization coefficient
1	47.7°	n/a	0.775
2	90.0°	n/a	1.000
3	132.3°	n/a	0.807

RI Instrument: Generic RI

Solvent: DMF
Temperature Correction Enabled: no
Refractive Index: 1.431

Fluid Connections

Source Instrument	Destination Instrument	Delay Volume (mL)
Generic Pump	Injector	0.000
Injector	miniDAWN TREOS	0.000
miniDAWN TREOS	Generic RI Instrument	0.206

Aux Connections

Source Instrument	Destination Instrument	Aux Channel	Calibration Constant
Generic RI Instrument	miniDAWN TREOS	1	1.000×10^{-3}

Processing

Collection Time: Wednesday May 15, 2013 12:06:13 AM Pacific Daylight Time
Processing time: Saturday November 09, 2013 01:45:32.504 PM Pacific Daylight Time

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	14.768 - 21.089
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1300
A2 (mol mL/g²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

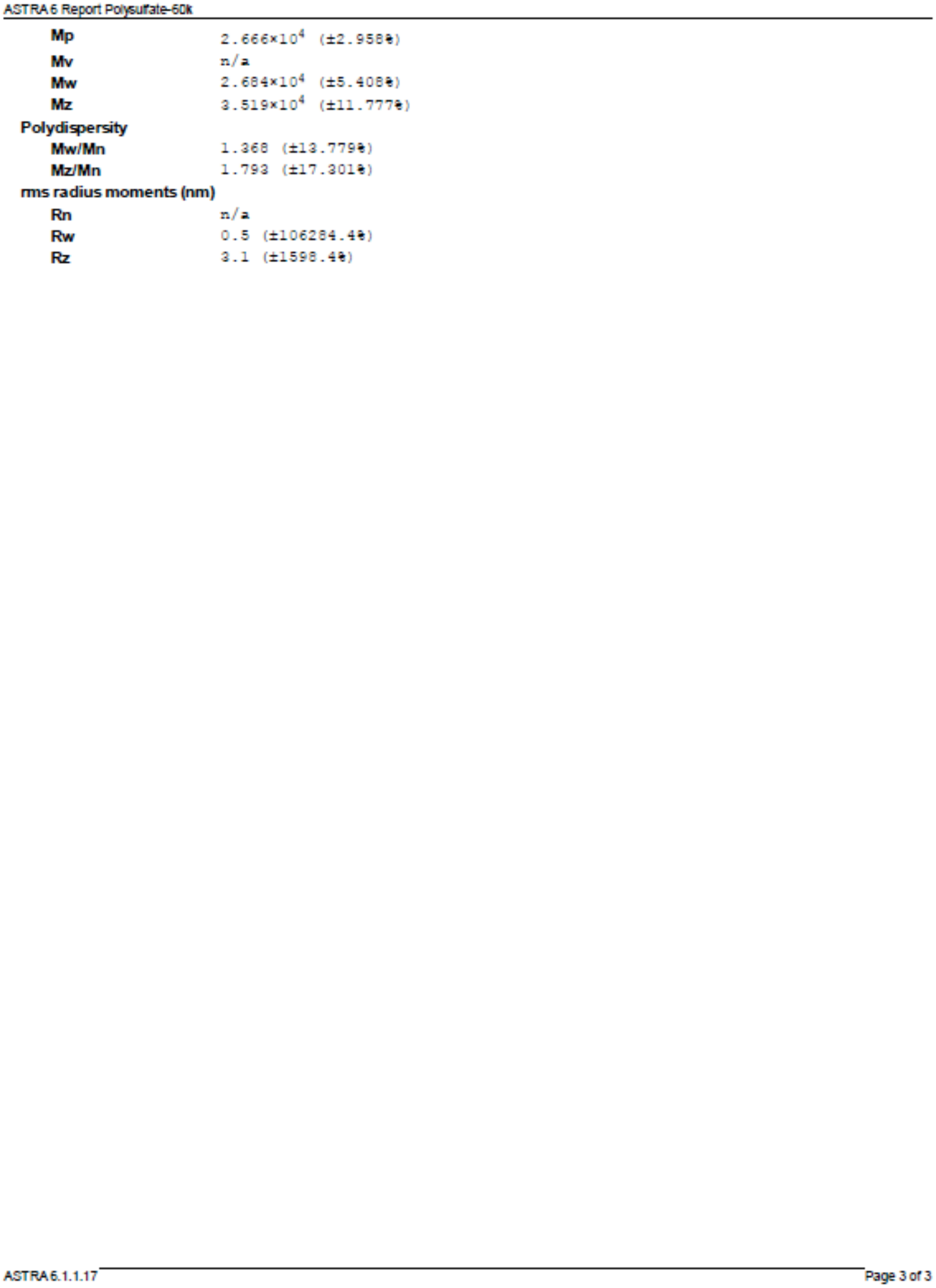
Results Fitting Procedure:

Data	Fit Model	Degree	R²	Extrapolation
Molar Mass	Exponential	1	0.994301	both directions
Rms Radius	none	n/a	n/a	none
Mean Square Radius	none	n/a	n/a	none

Results

Peak Results

	Peak 1
Masses	
Injected Mass (µg)	240.00
Calculated Mass (µg)	179.03
Mass Recovery (%)	74.6
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	1.962×10^{4} (±12.673%)
Mp	2.666×10^{4} (±2.958%)

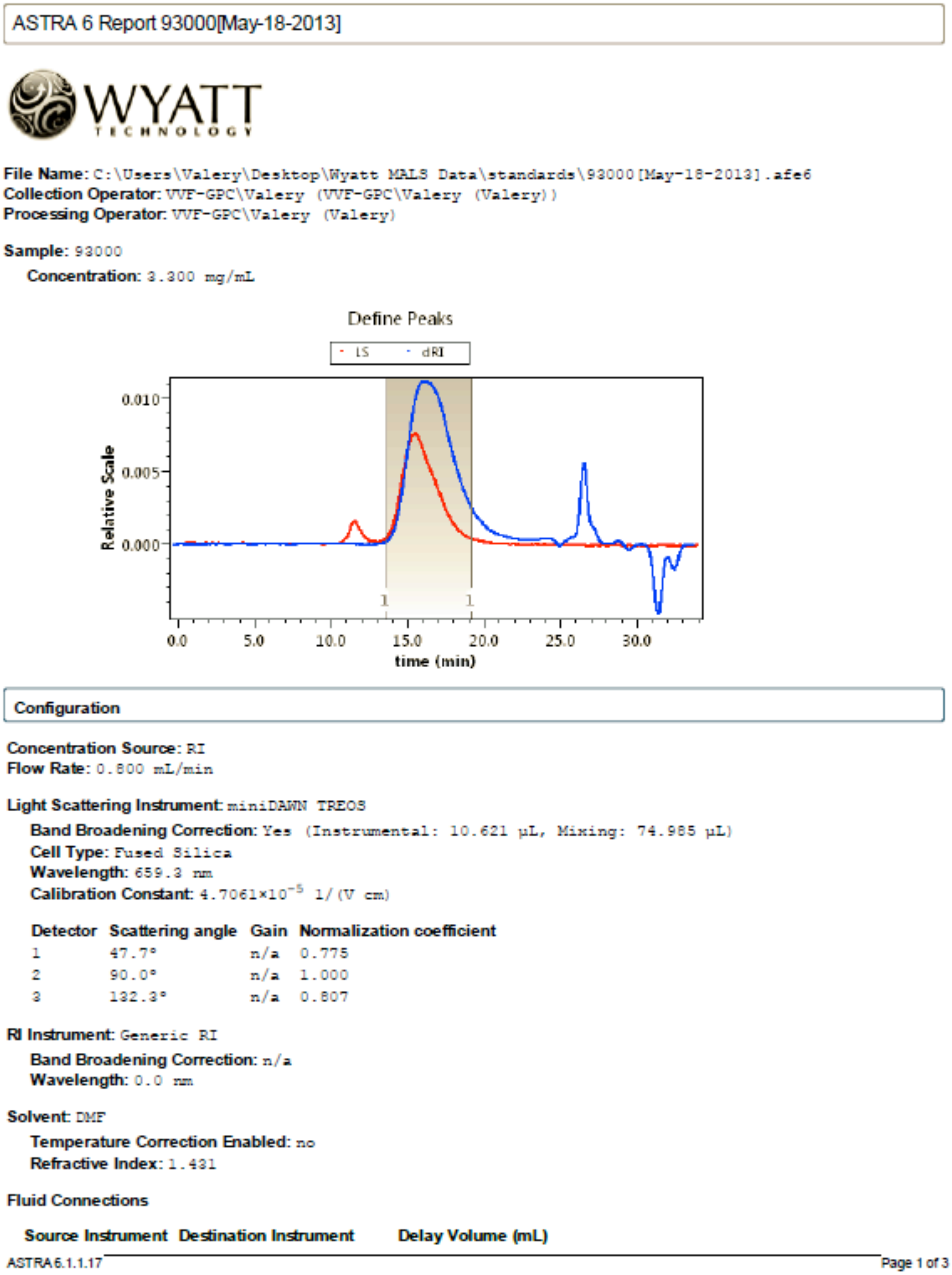


ASTRA 6 Report Polysulfate-60k

Mp	2.666×10^{4} (±2.958%)
Mv	n/a
Mw	2.684×10^{4} (±5.408%)
Mz	3.519×10^{4} (±11.777%)
Polydispersity	
Mw/Mn	1.368 (±13.779%)
Mz/Mn	1.793 (±17.301%)
rms radius moments (nm)	
Rn	n/a
Rw	0.5 (±106284.4%)
Rz	3.1 (±1598.4%)

ASTRA 6.1.1.17 Page 3 of 3

Table 1, Entry 9



ASTRA 6 Report 93000[May-18-2013]

File Name: C:\Users\Valery\Desktop\Wyatt MALS Data\standards\93000[May-18-2013].afe6
Collection Operator: VVF-GPC\Valery (VVF-GPC\Valery (Valery))
Processing Operator: VVF-GPC\Valery (Valery)

Sample: 93000
Concentration: 3.300 mg/mL

Define Peaks

Configuration

Concentration Source: RI
Flow Rate: 0.800 mL/min

Light Scattering Instrument: miniDAWN TREOS
Band Broadening Correction: Yes (Instrumental: 10.621 µL, Mixing: 74.985 µL)
Cell Type: Fused Silica
Wavelength: 659.3 nm
Calibration Constant: 4.7061×10^{-5} 1/(V cm)

Detector	Scattering angle	Gain	Normalization coefficient
1	47.7°	n/a	0.775
2	90.0°	n/a	1.000
3	132.3°	n/a	0.807

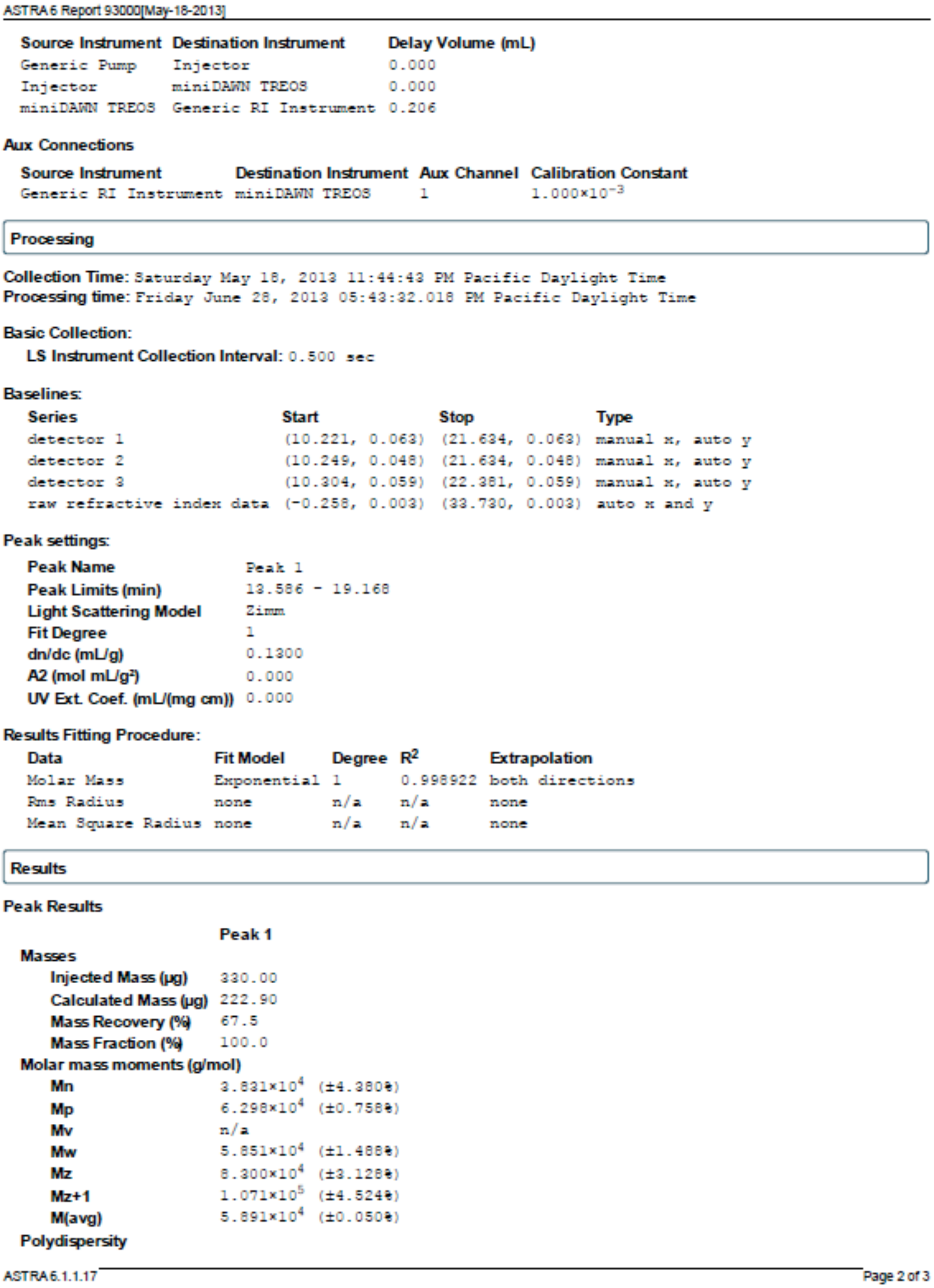
RI Instrument: Generic RI
Band Broadening Correction: n/a
Wavelength: 0.0 nm

Solvent: DMF
Temperature Correction Enabled: no
Refractive Index: 1.431

Fluid Connections

Source Instrument	Destination Instrument	Delay Volume (mL)

ASTRA 6.1.1.17 Page 1 of 3



Source Instrument	Destination Instrument	Delay Volume (mL)
Generic Pump	Injector	0.000
Injector	miniDAWN TREOS	0.000
miniDAWN TREOS	Generic RI Instrument	0.206

Aux Connections

Source Instrument	Destination Instrument	Aux Channel	Calibration Constant
Generic RI Instrument	miniDAWN TREOS	1	1.000×10^{-3}

Processing

Collection Time: Saturday May 18, 2013 11:44:43 PM Pacific Daylight Time
Processing time: Friday June 28, 2013 05:43:32.018 PM Pacific Daylight Time

Basic Collection:

LS Instrument Collection Interval: 0.500 sec

Baselines:

Series	Start	Stop	Type
detector 1	(10.221, 0.063)	(21.634, 0.063)	manual x, auto y
detector 2	(10.249, 0.048)	(21.634, 0.048)	manual x, auto y
detector 3	(10.304, 0.059)	(22.381, 0.059)	manual x, auto y
raw refractive index data	(-0.258, 0.003)	(33.730, 0.003)	auto x and y

Peak settings:

Peak Name	Peak 1
Peak Limits (min)	13.586 - 19.168
Light Scattering Model	Zimm
Fit Degree	1
dn/dc (mL/g)	0.1300
A2 (mol mL/g²)	0.000
UV Ext. Coef. (mL/(mg cm))	0.000

Results Fitting Procedure:

Data	Fit Model	Degree	R^2	Extrapolation
Molar Mass	Exponential	1	0.998922	both directions
Rms Radius	none	n/a	n/a	none
Mean Square Radius	none	n/a	n/a	none

Results

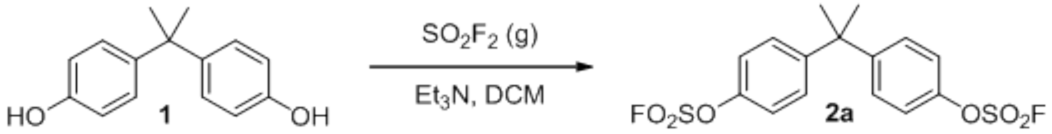
Peak Results

	Peak 1
Masses	
Injected Mass (µg)	330.00
Calculated Mass (µg)	222.90
Mass Recovery (%)	67.5
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	3.831×10^{4} (±4.380%)
Mp	6.298×10^{4} (±0.758%)
Mv	n/a
Mw	5.851×10^{4} (±1.488%)
Mz	8.300×10^{4} (±3.128%)
Mz+1	1.071×10^{5} (±4.524%)
M(avg)	5.891×10^{4} (±0.050%)
Polydispersity	

Polydispersity	
Mw/Mn	1.527 (±4.626%)
Mz/Mn	2.167 (±5.382%)
rms radius moments (nm)	
Rn	10.2 (±90.6%)
Rw	11.7 (±40.9%)
Rz	13.6 (±20.5%)
R(avg)	13.3 (±0.7%)

Preparation of AA and BB Monomers

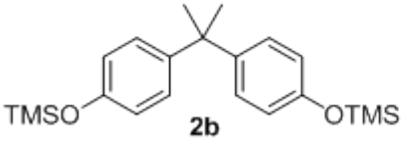
General procedure for the preparation of bis-fluorosulfate 'AA' monomer:



4,4'-(Propane-2,2-diyl)bis(4,1-phenylene) disulfofluoridate (2a). Bisphenol-A (**1**; 20 g, 0.088 mol) and triethylamine (30 mL, 21.8 g, 0.216 mol) were dissolved in CH_2Cl_2 (200 mL) in a 500 mL round-bottomed flask equipped with a stirring bar. The headspace of the reaction vessel was evacuated and filled with sulfuryl fluoride gas introduced via a needle attached to a balloon. The reaction was allowed to stir at room temperature for 12h, at which time GC-MS analysis indicated complete conversion. The reaction mixture was then concentrated *in vacuo*, re-dissolved in 300 mL of EtOAc and washed sequentially with 300 mL of 0.6M HCl (1x), 200 mL sat. $NaHCO_3$ (1x), 200 mL sat. NaCl (1x), and dried over Na_2SO_4. Removal of the volatiles produced **2a** as a yellow oil that crystallized as a white solid that was subsequently dried under vacuum (33.3 g, 84.9 mmol, 98%): mp 49-52 ^{o}C; IR (neat) m_{ix} 1499, 1441, 1409, 1368, 1229, 1186, 1137, 1083, 1015, 949, 911, 840, 812, 793, 772, 599, 564, 538, 502, 472 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 8H), 1.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 148.4, 128.9, 120.7, 43.1, 30.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ 37.2; GC-MS (EI) m/z = 392.1 [M]$^{+}$.

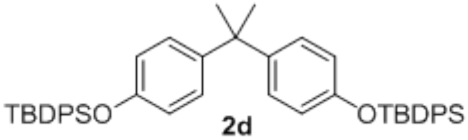
General procedure for the preparation of bis-silyl 'BB' monomer:

(4,4'-(Propane-2,2-diyl)bis(4,1-phenylene))bis(oxy)bis(tert-butyldimethylsilane) (2c). Bisphenol-A (**1**; 50 g, 0.219 mol), imidazole (45 g, 0.662 mol) and 4-dimethylaminopyridine (1.3 g, 0.11 mol) were dissolved in a mixture of 500 mL of CH_2Cl_2 and 40 mL of DMF in a 3L round-bottomed flask equipped with a stirring bar. *tert*-Butyldimethylsilyl chloride (69 g, 0.46 mol) was added portion-wise to the reaction, which quickly resulted in the generation of a white precipitate. The reaction mixture was stirred for 3h, filtered to remove all solids (imidazole-HCl) and concentrated *in vacuo*. The resulting oil was dissolved in 750 mL of EtOAc and briefly washed with 700 mL of 1M HCl (1x), 400 mL sat. $NaHCO_3$ (1x), 500 mL sat. NaCl (1x) and then dried over Na_2SO_4. Removal of the volatiles gave **2c** as a colorless oil that crystallized as a colorless solid and was subsequently dried under vacuum (96.3 g, 0.211 mmol, 96%): mp 84-87 ^{o}C; IR (neat) λ_{max} 2953, 1501, 1441, 1230, 1184, 1137, 1015, 911, 828, 810, 773, 592, 563, 539 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 8.8 Hz, 4H), 6.72 (d, J = 8.8 Hz, 4H), 1.62 (s, 6H), 0.98 (s, 18H), 0.19 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 143.8, 127.8, 119.3, 41.9, 31.2, 25.8, 18.3, -4.3; GC-MS (EI) m/z = 456.4 [M]$^{+}$.



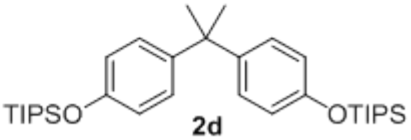
2b

(4,4'-(Propane-2,2-diyl)bis(4,1-phenylene))bis(oxy)bis(trimethylsilane) (2b) was purchased from GELEST, INC., and used as received.



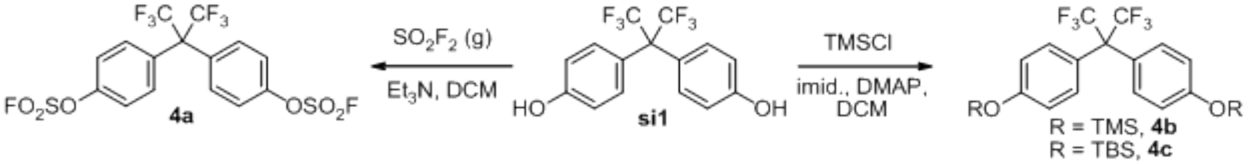
2d

(4,4'-(Propane-2,2-diyl)bis(4,1-phenylene))bis(oxy)bis(tert-butyldiphenylsilane) (2d) was prepared following the general procedure for the preparation of bis-silyl 'BB' monomers, with substitution of *tert*-butyldimethylsilyl chloride with *tert*-butyldiphenylsilyl chloride. Purification via flash chromatography (SiO_2, 0→5% EtOAc-hexanes; $R_f = 0.5$ at 10% EtOAc-hexanes) yielded **2d** as a white crystalline solid (~27.8 g, 39.4 mmol, 90%): mp 94-98 °C; IR (neat) λ_{max} 1501, 1442, 1230, 1164, 1138, 913, 822, 797, 773, 742, 700, 594, 563, 541, 502 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 1.6, 8.0 Hz, 8H), 7.57-7.38 (m, 12H), 7.01 (d, J = 8.9 Hz, 4H), 6.79 (d, J = 8.8 Hz, 4H), 1.63 (s, 6H), 1.25 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 143.6, 135.7, 133.3, 129.9, 127.8, 127.6, 119.0, 41.7, 31.1, 26.7, 19.6;



2d

(4,4'-(Propane-2,2-diyl)bis(4,1-phenylene))bis(oxy)bis(triisopropylsilane) (2e) was prepared following the general procedure for the preparation of bis-silyl 'BB' monomers, with substitution of *tert*-butyldimethylsilyl chloride with triisopropylsilyl chloride. **2e** was isolated as a colorless, viscous oil (23.1 g, 42.5 mmol, 97%): IR (neat) λ_{max} 2943, 2864, 1604, 1504, 1462, 1257, 1176, 1106, 1012, 912, 882, 833, 743, 680, 609, 559, 482 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 8.7 Hz, 4H), 6.79 (d, J = 8.7 Hz, 4H), 1.64 (s, 6H), 1.36-1.18 (m, 6H), 1.13 (d, J = 7.2 Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 143.7, 127.8, 119.3, 41.9, 31.3, 18.1, 12.8; LRMS (EI) m/z = 497.4 $[M - CH(CH_3)_2]^+$.



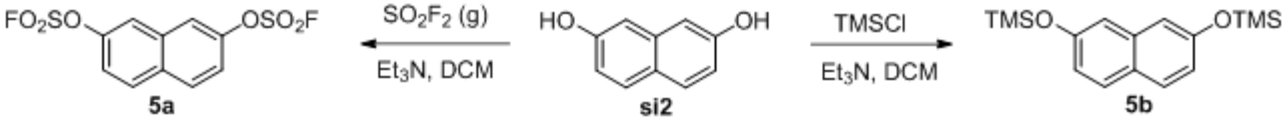
Bisphenol AF (2,2-bis(4-hydroxyphenol)hexafluoropropane; **si1**) was obtained from Oakwood Chemicals and used as received.

4,4'-(Perfluoropropane-2,2-diyl)bis(4,1-phenylene) disulfofluoridate (4a) was prepared following the general procedure for the preparation of bis-fluorosulfonate 'AA' monomers. **4a** was isolated as white crystalline solid: mp 128-130 °C; IR (neat) λ_{max} 1506, 1450, 1261, 1240, 1208, 1163, 1144, 1019, 968, 911, 840, 805, 768, 737, 697, 645, 575, 536 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (app d, J = 9.0 Hz, 4H), 7.42 (dd, J = 0.6, 9.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 133.6, 132.6, 123.7 (q, J =

E287.5 Hz), 121.3, 64.2 (app t, $J = 25.8$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ 38.2, -64.1; LRMS (EI) m/z = 500.0 $[M]^+$.

(4,4'-(Perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy)bis(trimethylsilane) (4b) was prepared following the general procedure for the preparation of bis-silyl 'BB' monomers, with substitution of *tert*-butyldimethylsilyl chloride with trimethylsilyl chloride. **4b** was isolated as a beige solid: mp 46-50 °C; IR (neat) λ_{max} 2959, 1611, 1513, 1450, 1242, 1204, 1168, 1135, 967, 912, 828, 753, 737, 700, 545, 505 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, $J = 9.2$ Hz, 4H), 6.81 (d, $J = 9.1$ Hz, 4H), 0.29 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 131.7, 126.4, 124.6 (q, J = 287.8 Hz), 119.6, 63.9 (t, J = 25.5 Hz), -0.32; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.4; LRMS (EI) m/z = 480.2 $[M]^+$.

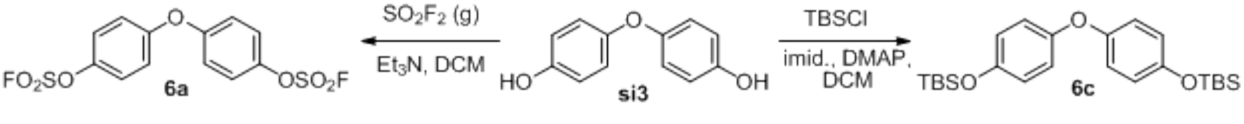
(4,4'-(Perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(oxy)bis(tert-butyldimethylsilane) 4c was prepared following the general procedure for the preparation of bis-silyl 'BB' monomers. **4c** was isolated as a white crystalline solid: mp 167-170 °C; IR (neat) λ_{max} 2952, 2932, 2859, 1611, 1513, 1468, 1275, 1244, 1202, 1168, 1134, 968, 911, 830, 804, 777, 727, 701, 667, 556 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, $J = 8.7$, 4H), 6.80 (d, $J = 9.0$ Hz, 4H), 0.99 (s, 18H), 0.23 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 131.7, 126.3, 124.6 (app d, $J = 285.1$ Hz), 119.6, 63.8 (t, $J = 25.2$ Hz), 25.8, 18.3, -4.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.4; LRMS (EI) m/z = 451.0 $[M – Si(Me)_2t\text{-}Bu]^+$.



Naphthalene-2,7-diol (**si2**) was purchased from Acros Organics and used as received.

Naphthalene-2,7-diyl disulfofluoridate 5a was prepared following the general procedure for the preparation of bis-fluorosulfonate 'AA' monomers. **5a** was isolated as white powder (12.3 g, 38 mmol, 87%): mp 122-124 °C; IR (neat) λ_{max} 1439, 1365, 1219, 1187, 1137, 1115, 960, 922, 896, 839, 801, 637, 582, 530, 470 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (d, $J = 2.2$ Hz, 2H), 8.28 (d, $J = 9.1$ Hz, 2H), 7.82 (dd, $J = 2.4$, 9.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.3, 133.3, 131.6, 120.9, 119.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ 38.1; LRMS (EI) m/z = 324.0 $[M]^+$.

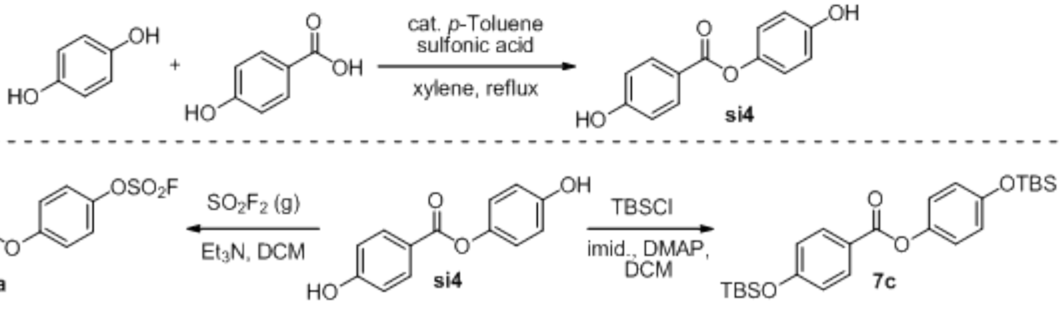
2,7-Bis(trimethylsilyloxy)naphthalene 5b was prepared by dissolving 7 g of the diol and 20.3 mL of triethylamine (2.2 equiv.) in dichloromethane, followed by dropwise addition of 12.2 mL of TMSCl (2.2 equiv.). After stirring at room temperature for 4 h, the mixture was concentrated, taken up in hexanes, and passed through a Celite path eluting with hexanes. After concentration and thorough drying under vacuum, **5b** was isolated as a yellow oil (13.1 g, 43.5 mmol, 99%): IR (neat) λ_{max} 2958, 2856, 1630, 1604, 1507, 1460, 1427, 1365, 1250, 1211, 1151, 1110, 909, 833, 743, 697, 612, 489 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, $J = 8.9$ Hz, 2H), 7.12 (d, $J = 2.3$ Hz, 2H), 6.99 (dd, $J = 2.3$, 8.8 Hz, 2H), 0.37 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 136.2, 129.3, 125.4, 120.0, 114.0, -0.42; LRMS (EI) m/z = 304.1 $[M]^+$.



4,4'-Oxydiphenol (**si3**) was purchased from AK Scientific and used as received.

4,4'-Oxybis(4,1-phenylene) disulfofluoridate 6a was prepared following the general procedure for the preparation of bis-fluorosulfonate ‘AA’ monomers. **6a** was isolated as white crystalline solid (8.2 g, 22.5 mmol, 75%): mp 53-55 ^{o}C; IR (neat) λ_{max} 1499, 1443, 1230, 1162, 1132, 1100, 909, 839, 818, 768, 754, 602, 540, 501 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dtd, J = 0.9, 3.7, 10.6 Hz, 4H), 7.11 (dt, J = 3.7, 9.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 145.8, 122.9, 120.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ 36.9; LRMS (EI) m/z = 366.0 $[M]^+$.

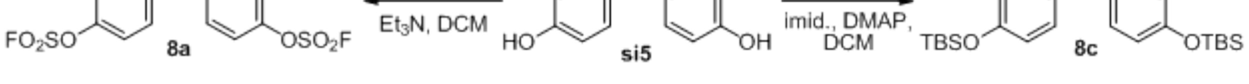
(4,4'-Oxybis(4,1-phenylene)bis(oxy))bis(tert-butyldimethylsilane) (6c) was prepared following the general procedure for the preparation of bis-silyl ‘BB’ monomers. **6c** was isolated as a clear, colorless, viscous oil (11.9 g, 27.8 mmol, 93%): IR (neat) λ_{max} 2930, 2857, 1491, 1451, 1251, 1213, 1144, 1096, 908, 871, 835, 778, 691, 504 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89-6.82 (m, 4H), 6.80-6.77 (m, 4H), 0.99 (s, 18H), 0.19 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 151.3, 120.9, 119.6, 25.8, 18.3, -4.3; LRMS (EI) m/z = 430.3 $[M]^+$.



4-Hydroxyphenyl 4-hydroxybenzoate (**si4**) was prepared through the condensation of hydroquinone with 4-hydroxybenzoic acid.[1]

4-(Fluorosulfonyloxy)phenyl 4-(fluorosulfonyloxy)benzoate (7a) was prepared following the general procedure for the preparation of bis-fluorosulfonate ‘AA’ monomers. Purification via flash chromatography (SiO_2, 5→15% EtOAc-hexanes; R_f = 0.52 at 20% EtOAc-hexanes) yielded **7a** as a white powder (1.77 g, 4.5 mmol, 45%): mp 103-105 ^{o}C; IR (neat) λ_{max} 1740, 1497, 1443, 1260, 1230, 1135, 1068, 1015, 909, 801, 757, 689, 612, 540, 491 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 9.0 Hz, 1H), 7.52 (dd, J = 0.7, 9.0, 1H), 7.47-7.40 (m, 1H), 7.36 (d, J = 9.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 153.6, 150.3, 147.5, 132.9, 129.5, 123.7, 122.5, 121.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ 38.8, 37.24; LRMS (EI) m/z = 393.8 $[M]^+$.

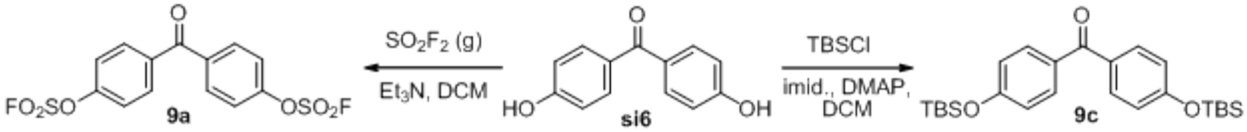
4-(tert-butyldimethylsilyloxy)phenyl 4-(tert-butyldimethylsilyloxy)benzoate (7c) was prepared following the general procedure for the preparation of bis-silyl ‘BB’ monomers. Purification via flash chromatography (SiO_2, 2% EtOAc-hexanes; R_f = 0.56 at 5% EtOAc-hexanes) yielded **7c** as a white powder (2.05 g, 4.4 mmol, 45%): mp 69-73 ^{o}C; IR (neat) λ_{max} 2956, 2928, 2857, 1737, 1601, 1501, 1442, 1252, 1232, 1187, 1160, 1067, 1010, 904, 822, 782, 692, 540, 501 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.9 Hz, 2H), 7.06 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 1.01 (s, 9H), 1.00 (s, 9H), 0.26 (s, 6H), 0.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 160.7, 153.3, 145.2, 132.3, 122.8, 122.6, 120.7, 120.2, 25.8, 25.8, 18.4, 18.3, -4.2, -4.3; LRMS (EI) m/z = 458.2 $[M]^+$.



4,4'-Thiodiphenol (**si5**) was purchased from Alfa Aesar and used as received.

4,4'-Thiobis(4,1-phenylene) disulfofluoridate (8a) was prepared following the general procedure for the preparation of bis-fluorosulfonate ‘AA’ monomers. **8a** was isolated as off-white crystalline solid (17.1 g, 44.7 mmol, 98%): mp 54-56 ^{o}C; IR (neat) λ_{max} 1485, 1442, 1230, 1177, 1139, 1101, 1014, 909, 835, 803, 769, 581, 540, 496 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 9.0 Hz, 4H), 7.32 (dd, J = 0.9, 9.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 136.2, 133.0, 122.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ 37.7; LRMS (EI) m/z = 382.0 [M]$^{+}$.

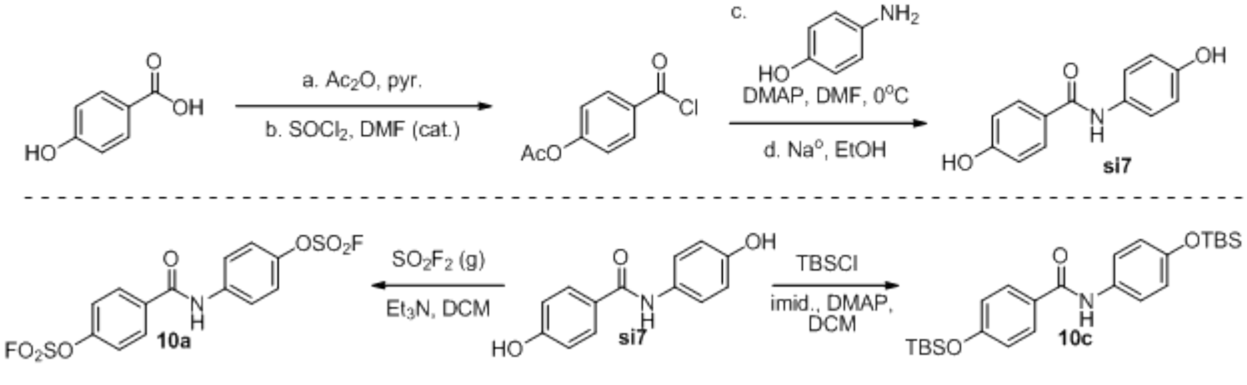
(4,4'-Thiobis(4,1-phenylene)bis(oxy))bis(tert-butyldimethylsilane) (9c) was prepared following the general procedure for the preparation of bis-silyl ‘BB’ monomers. **9c** was isolated as a clear, colorless, viscous oil (20.3 g, 46 mmol, 99%): IR (neat) λ_{max} 2929, 2856, 1586, 1485, 1444, 1254, 1231, 1140, 1072, 1013, 907, 821, 804, 772, 739, 673, 585, 521, 498 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 0.98 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 132.7, 128.1, 121.0, 25.8, 18.3, -4.3; LRMS (EI) m/z = 446.3 [M]$^{+}$.



Bis(4-hydroxyphenyl)methanone (**si6**) was purchased from AK Scientific and used as received.

4,4'-Carbonylbis(4,1-phenylene) disulfofluoridate (9a) was prepared following the general procedure for the preparation of bis-fluorosulfonate ‘AA’ monomers. **9a** was isolated as white crystalline solid (11.1 g, 29.3 mmol, 98%): mp 91-94 ^{o}C; IR (neat) λ_{max} 1672, 1591, 1440, 1409, 1268, 1231, 1138, 1015, 907, 808, 761, 667, 632, 540, 494, 466 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.87 (m, 4H), 7.60-7.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 152.7, 137.0, 132.3, 121.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ 38.6; LRMS (EI) m/z = 378.0 [M]$^{+}$.

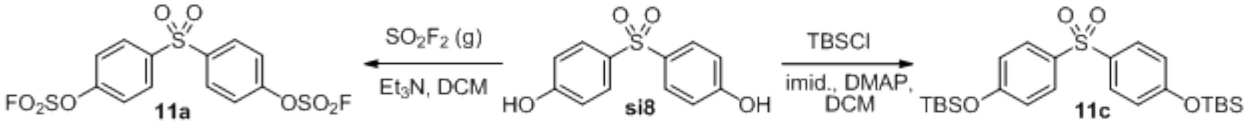
Bis(4-(tert-butyldimethylsilyloxy)phenyl)methanone (9c) was prepared following the general procedure for the preparation of bis-silyl ‘BB’ monomers. **9c** was isolated as a colorless low melting solid (13.3 g, 30 mmol, 99%): IR (neat) λ_{max} 2960, 2930, 2857, 1651, 1596, 1505, 1466, 1254, 1160, 1105, 904, 836, 803, 773, 713, 682, 494 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (app d, J = 8.8 Hz, 4H), 6.90 (app d), J = 8.8 Hz, 4H), 1.00 (s, 18H), 0.25 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 159.7, 132.3, 131.4, 119.8, 25.7, 18.4, -4.2; LRMS (EI) m/z = 442.3 [M]$^{+}$.



4-Hydroxy-(4-hydroxyphenyl)benzamide (**si7**) was prepared in four steps from with 4-hydroxybenzoic acid and 4-aminophenol.[2]

4-(Fluorosulfonyloxy)-*N*-(4-(fluorosulfonyloxy)phenyl)benzamide (10a) was prepared following the general procedure for the preparation of bis-fluorosulfonate 'AA' monomers. Purification via flash chromatography yielded **10a** as a white powder (1.86 g, 4.7 mmol, 50%): mp 160-167 ^{o}C; IR (neat) λ_{max} 3417, 1677, 1600, 1524, 1503, 1437, 1405, 1309, 1258, 1225, 1176, 1138, 1104, 1018, 910, 864, 849, 833, 804, 775, 694, 616, 542, 510, 469 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.15 (d, J = 8.9 Hz, 2H), 7.96 (d, J = 9.3 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 151.5, 145.2, 139.5, 135.4, 130.6, 121.9, 121.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ 39.6, 38.27; LRMS (EI) m/z =393.0 [M]$^{+}$.

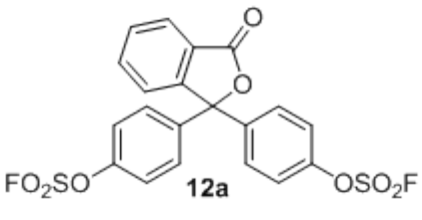
4-(*tert*-Butyldimethylsilyloxy)-*N*-(4-(tert-butyldimethylsilyloxy)phenyl)benzamide (10c) was prepared following the general procedure for the preparation of bis-silyl 'BB' monomers. Purification via flash chromatography yielded **10c** as a white powder (2.26 g, 4.9 mmol, 61%): mp 209-210 ^{o}C; IR (neat) λ_{max} 3298, 2952, 2929, 2889, 2856, 1640, 1603, 1505, 1469, 1406, 1254, 1168, 1101, 1009, 909, 833, 777, 733, 690, 505 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.75 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 0.99 (s, 9H), 0.98 (s, 9H), 0.22 (s, 6H), 0.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 159.0, 152.5, 131.9, 128.9, 128.0, 122.0, 120.5, 120.3, 25.7, 25.7, 18.4, 18.3, 4.3, 4.3; LRMS (EI) m/z = 457.3 [M]$^{+}$.



4,4'-Sulfonyldiphenol (**si8**) was purchased from Alfa Aesar and used as received.

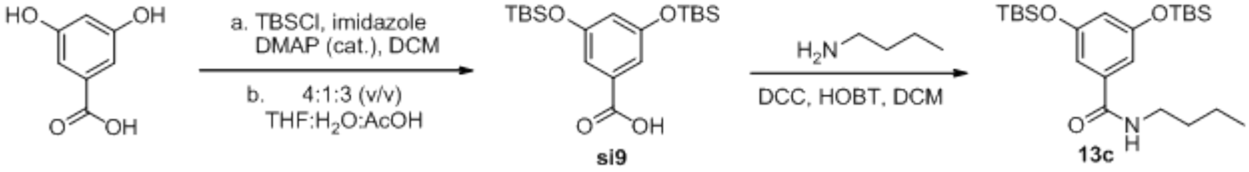
4,4'-Sulfonylbis(4,1-phenylene) disulfofluoridate (11a) was prepared following the general procedure for the preparation of bis-fluorosulfonate 'AA' monomers. **11a** was isolated as white powder (7.5 g, 91%): mp 118-122 ^{o}C; IR (neat) λ_{max} 1586, 1486, 1451, 1405, 1324, 1291, 1231, 1178, 1139, 1103, 1015, 907, 850, 810, 783, 688, 589, 574, 538, 509, 466 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 9.1 Hz, 4H), 7.53 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 141.3, 130.7, 122.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ 39.2; LRMS (EI) m/z = 413.9 [M]$^{+}$.

(4,4'-Sulfonylbis(4,1-phenylene)bis(oxy))bis(tert-butyldimethylsilane) (11c) was prepared following the general procedure for the preparation of bis-silyl 'BB' monomers, with substitution of *tert*-butyldimethylsilyl chloride with trimethylsilyl chloride. **11c** was isolated as a white powder (8.8 g, 92%): mp 135-137 ^{o}C; IR (neat) λ_{max} 2930, 2857, 1587, 1492, 1469, 1314, 1273, 1151, 1105, 902, 838, 781, 757, 679, 645, 616, 574, 542 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.8 Hz, 4H), 6.88 (d, J = 8.8 Hz, 4H), 0.96 (s, 18H), 0.2 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 134.5, 129.6, 120.1, 25.6, 18.3, -4.3; LRMS (EI) m/z = 478.2 [M]$^{+}$.



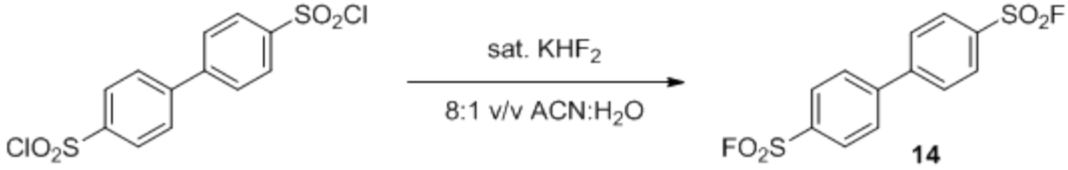
12a

4,4'-(3-Oxo-1,3-dihydroisobenzofuran-1,1-diyl)bis(4,1-phenylene) disulfofluoridate (12a) was prepared from phenolphthalein following the general procedure for the preparation of bis-silyl 'BB' monomers, with substitution of *tert*-butyldimethylsilyl chloride with trimethylsilyl chloride. **12a** was isolated as a white solid: mp 93-98 °C; IR (neat) λ_{max} 1761, 1500, 1443, 1410, 1288, 1229, 1139, 1081, 1016, 974, 938, 906, 846, 802, 753, 691, 638, 571, 534, 503, 476 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (ddd, J = 0.8, 1.1, 7.7 Hz, 1H), 7.79 (td, J = 1.2, 7.5 Hz, 1H), 7.65 (td, J = 0.9, 7.5 Hz, 1H), 7.57 (dt, J = 0.8, 7.8 Hz, 1H), 7.47 (d, J = 9.1 Hz, 4H), 7.35 (dd, J = 0.8, 9.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 150.4, 150.2, 141.1, 135.0, 130.4, 129.4, 126.8, 125.4, 124.0, 121.5, 89.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ 37.9; LRMS (EI) m/z = 489.1 [M]$^+$.



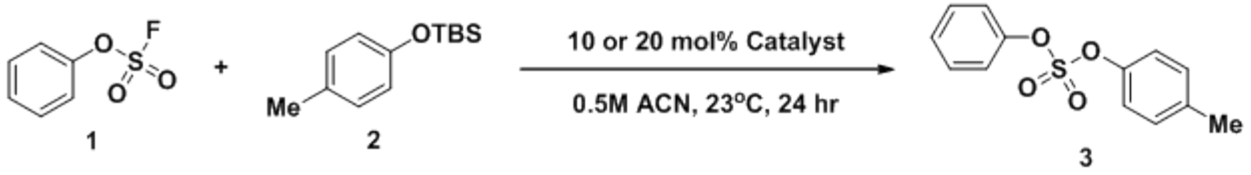
3,5-Bis(tert-butyldimethylsilyloxy)benzoic acid (**si9**) was prepared by global TBS protection of 3,5-dihydroxybenzoic acid, followed by selective liberation of the acid moiety.[3]

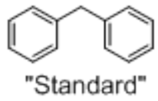
Butyl-3,5-bis(tert-butyldimethylsilyloxy)benzamide (13c). A 50 mL round-bottomed flask equipped with a stirring bar and rubber septum was charged with **si9** (0.76 g, 2.0 mmol) and placed under argon. 15 mL dry DCM was added followed by the addition of hydroxybenzotriazole (HOBT; 0.3 g, 2.2 mmol) and *N,N'*-dicyclohexylcarbodiimide (DCC; 0.45 g, 2.2 mmol) in that order by partial removal of the septum. The resulting slurry was stirred at room temperature for 10 min. Butan-1-amine (0.3 mL, 0.22 g, 3.0 mmol) was then added drop wise and the reaction mixture was stirred overnight. The resulting heterogeneous solution was then filtered over a Buchner funnel and the filtrate was further diluted with DCM and briefly washed with 0.5 M HCl. The aqueous layer was extracted once more with DCM and the combined organics were dried over Na_2SO_4. The crude reaction mixture was then concentrated on to silica gel via rotary evaporation and subjected to flash chromatography (SiO_2, 10% EtOAc-hexanes; R_f = 0.3 at 10% EtOAc-hexanes) to afford **13c** as a white crystalline solid (0.76 g, 1.8 mmol): mp 114-117 °C; IR (neat) λ_{max} 3294, 2929, 2857, 1632, 1583, 1543, 1438, 1334, 1253, 1163, 1027, 1004, 935, 829, 778, 692, 667, 486 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, J = 2.1 Hz, 2H), 6.43 (t, J = 2.1 Hz, 1H), 6.02 (app s, 1H), 3.41 (q, J = 7.1 Hz, 2H), 1.58 (p, J = 7.7 Hz, 2H), 1.39 (sex, J = 7.2 Hz, 2H), 0.97 (s, 18H), 0.95 (t, J = 7.3 Hz, 3H), 0.19 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 156.8, 137.1, 114.9, 112.1, 39.9, 31.8, 25.8, 20.3, 18.3, 13.9, -4.3; LRMS (EI) m/z = 437.3 [M]$^+$.



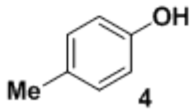
Biphenyl-4,4'-disulfonyl difluoride (14). Biphenyl-4,4'-disulfonylchloride (purchased from TCI chemicals; 5.0 g, 0.014 mol) was dissolved in 40 mL acetonitrile and 5 mL water with stirring. To this mixture was added 4 equiv. of saturated aqueous KHF_2 (1.2 g). The reaction was allowed to proceed 3 h. The mixture was extracted twice with 30 mL ethyl acetate. The organic fractions were combined, washed with water, brine, and then dried over $MgSO_4$. Solvent was removed under vacuum to provide **14** as a yellow solid (4.1 g, 90%): mp 194-197 °C; IR (neat) λ_{max} 1589, 1405, 1205, 1095, 816, 771, 750, 709, 569, 535, 493 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.16 (d, J = 8.5 Hz, 4H), 7.88 (dd, J = 0.7, 8.7 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.9, 133.4 (d, J = 15.2 Hz), 129.4, 128.9; ^{19}F NMR (376 MHz, CDCl$_3$) δ 66.1; LRMS (EI) m/z = 318.0 [M]$^+$.

Table S1; Catalyst Screen



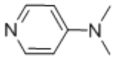
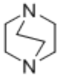
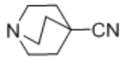
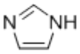
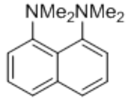
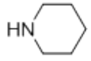

"Standard"

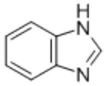
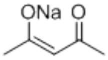
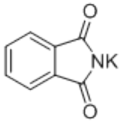
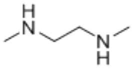
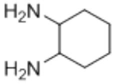
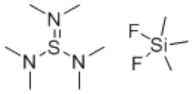
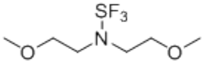
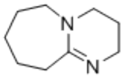
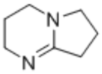
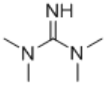
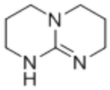
Standard added for GC/MS endpoint analysis. Concentration; 0.1M.

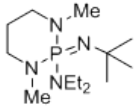
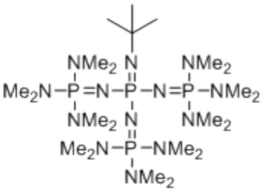
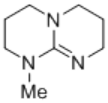
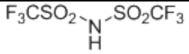
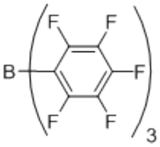
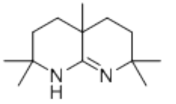
Byproduct: 

Experimental Setup: A 0.5 M acetonitrile stock solution of the starting reagents was prepared in the following manner: phenyl fluorosulfate (**1**) (2.667 g, 12.0 mmol), *tert*-butyldimethyl(*p*-tolyloxy)silane (**2**) (2.112 g, 12.0 mmol) and diphenylmethane (standard, 0.403 g, 2.4 mmol) were dissolved in enough dry acetonitrile to obtain 24 mL (combined mL) of stock solution, which was subsequently placed under the atmosphere of argon. 0.4 mL aliquots were parceled out into 1 mL scintillation vials, thereby providing sixty individual 0.2 mmol reactions. Approximately 10 or 20 mol% catalyst, as shown in the table below, was then added to the reaction vials. The headspace was flushed with argon and the reaction mixtures were shaken for 24 hrs at room temperature. Finally, 15 µL aliquots of each reaction mixture were diluted with 1 mL EtOAc and subjected to GC/MS endpoint analysis. Calculated endpoints shown below in Catalyst Table 1 were not confirmed by isolation and are considered 'crude.' The percentages shown below may vary by ±5% and are meant to serve as a general overview of the effective catalysts for this reaction.

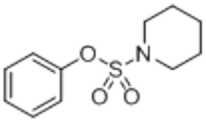
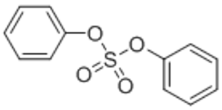
Catalyst Screening **Table S1:**

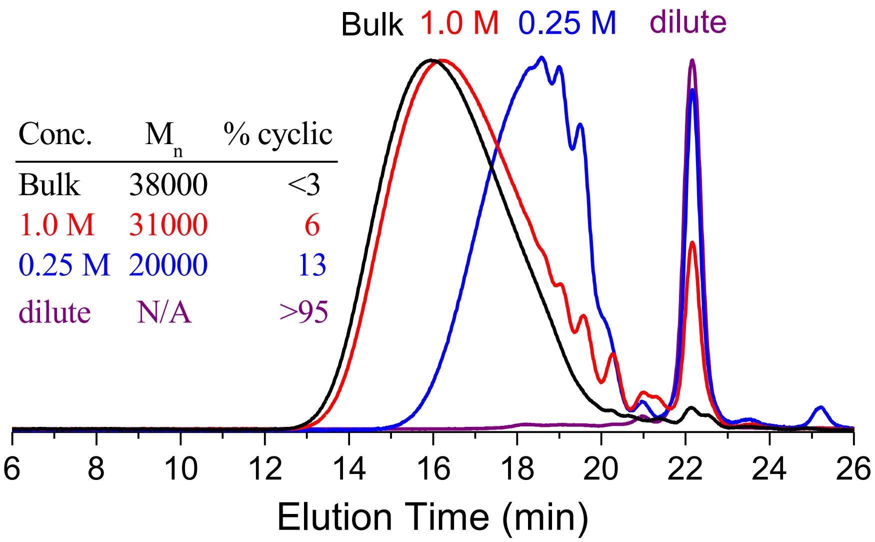
Catalyst (mol %)[a]	Product , %[b]	Remaining Starting Materials[c]	Additional Information
0. No Catalyst	0%	100% **1** 100% **2**	
1. 10% Triethylamine	0%	100% **1** 100% **2**	
2. 10% DMAP 	0%	100% **1** 100% **2**	
3. 10% Pyridine	0%	100% **1** 100% **2**	
4. 10% DABCO 	0%	100% **1** 100% **2**	
5. 10% 4-Cyanoquinuclidine 	0%	100% **1** 100% **2**	
6. 10% Imidazole 	0%	100% **1** 100% **2**	
7. 10% Proton Sponge 	0%	100% **1** 100% **2**	
8. 10% *n*-Butyl amine	<1%	<95% **1** >100% **2**	
9. 10% Piperidine 	~5%	<85% **1** >85% **2**	Contains **4** (5%)[d] and **5**[e]
10. 10% Benzimidazole	0%	100% **1** 100% **2**	

			
11. 10% K^+OAc^-	0%	100% **1** 100% **2**	
12. 10% $PhO^-Na^+ \cdot 3H_20$	<1%	<90% **1** 100% **2**	Contains **6**[f]
13. 20% NaOMe	0%	100% **1** 100% **2**	
14. 10% 	0%	100% **1** 100% **2**	
15. 10% 	>1%	>95% **1** >95% **2**	
16. 20% KOH	>1%	>95% **1** >95% **2**	
17. 10% NaCN	0%	100% **1** 100% **2**	
18. 10% NaN_3	0%	100% **1** 100% **2**	
19. 20% NaOH	0%	100% **1** 100% **2**	
20. 10% BaOH $\cdot 8H_20$	0%	100% **1** 100% **2**	
21. 10% KO*t*Bu	<20%	~80% **1** ~80% **2**	
22. 10% 	>1%	>95% **1** >95% **2**	
23. 10% 	0%	100% **1** 100% **2**	
24. 20% $NaN(CN)_2$	0%	100% **1** 100% **2**	
25. 10% Na_2CO_3	0%	100% **1** 100% **2**	
26. 10% K_3PO_4	<5%	>90% **1** >95% **2**	
27. 10% CsF	>90%	<5% **1** <5% **2**	
28. 20% KF	~60%	>30% **1** <20% **2**	Contains **4** (5%)
29. 10% TASF 	>90%	<5% **1** <5% **2**	
30. 10% $Bu_4N^+F^-$	>90%	<5% **1** <5% **2**	
31. 10% $Bu_4N^+Cl^-$	0%	100% **1** 100% **2**	
32. 10% 	~40%	>50% **1** <5% **2**	Contains **4** (25%)
33. 20% NaI	0%	100% **1** 100% **2**	
34. 10% PPh_3	0%	100% **1** 100% **2**	
35. 20% PMe_2Ph	0%	100% **1** 100% **2**	
36. 10% DBU 	>95%	0% **1** 0% **2**	
37. 10% DBN 	>95%	<5% **1** <5% **2**	
38. 10% TMG 	>95%	0% **1** 0% **2**	
39. 10% TBD 	>70%	>25% **1** 10% **2**	Contains **4** (20%)
40. 10% BEMP	>95%	0% **1** 0% **2**	

			
41. 10% *t*-Bu-P_4 	>95%	0% **1** 0% **2**	
42. 10% MeTBD 	>95%	0% **1** 0% **2**	
43. 10% 	0%	>95% **1** <15% **2**	Contains **4** (80%)
44. 10% 	0%	100% **1** <5% **2**	Contains **4** (95%)
45. 10% 	~80%	<20% **1** <5% **2**	Contains **4** (10%)
46. 20% $Et_4N^+OH^-$	~20%	>55% **1** <20% **2**	Contains **4** (45%)
47. 20% $NaBF_4$	0%	100% **1** 100% **2**	
48. 10% $TiCl_4\cdot 2THF$	0%	100% **1** >70% **2**	Contains **4** (25%)
49. 10% $SnCl_2\cdot 2H_20$	0%	100% **1** <5% **2**	Contains **4** (95%)
50. 10% $BF_3\cdot OEt_2$	0%	100% **1** <5% **2**	Contains **4** (90%)
51. 10% $ZnCl_2$	0%	100% **1** 100% **2**	
52. 10% $ZnBr_2$	0%	100% **1** 100% **2**	
53. 10% $AlEt_3$	0%	100% **1** 100% **2**	
54. 10% Et_2AlCl	0%	100% **1** 100% **2**	

[a] Catalyst amount was measured as close as practically possible to 10 or 20 mol%. [b] Percentage of product in the crude reaction mixture is calculated from a molarity-based calibration curve derived from compound **3**. Yield may vary by ±5%. [c] Remaining starting material percentage was derived from the initial reaction mixture concentration in reference to diphenylmethane (internal standard). Actual yield of **1** and **2** may vary by ±5%. [d] Percentage of phenol **4** is in reference to starting material **2**, i.e. actual yield of **4** may vary by ±5%.

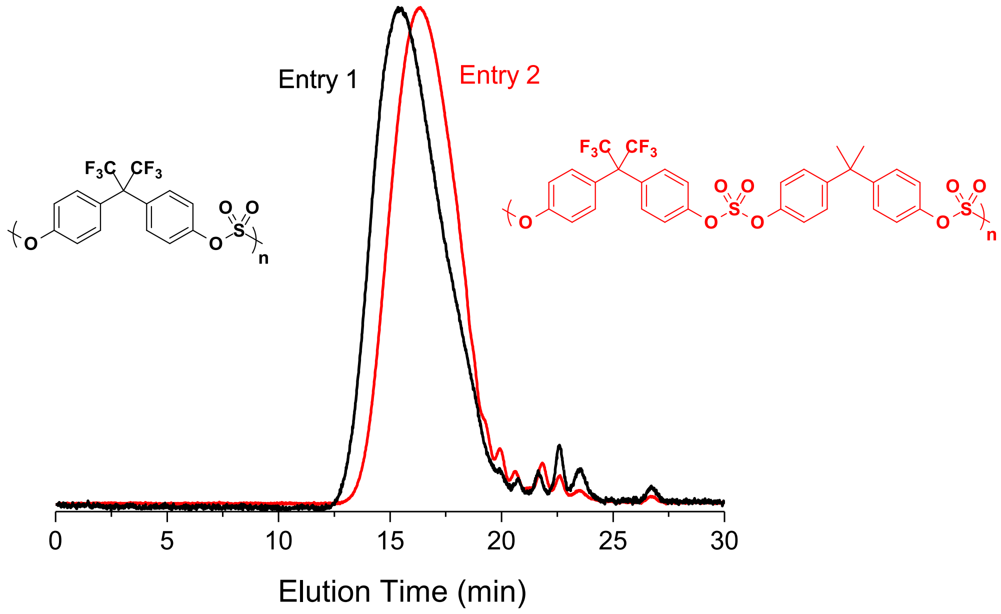
[e] Observed Product  [f] Observed Product 

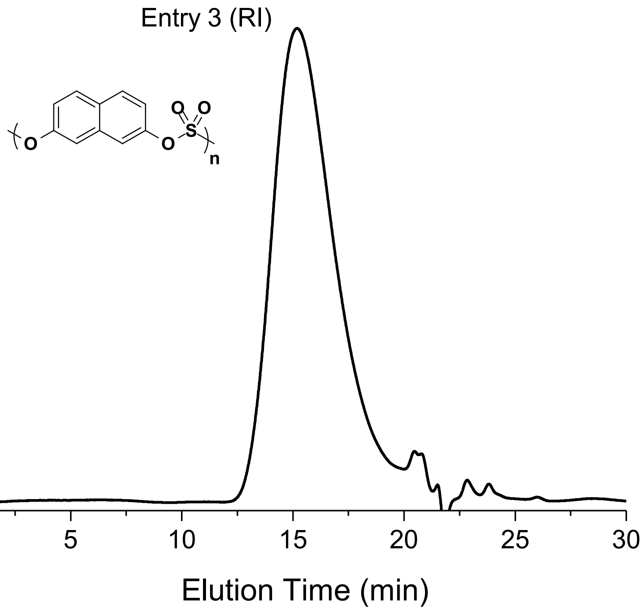


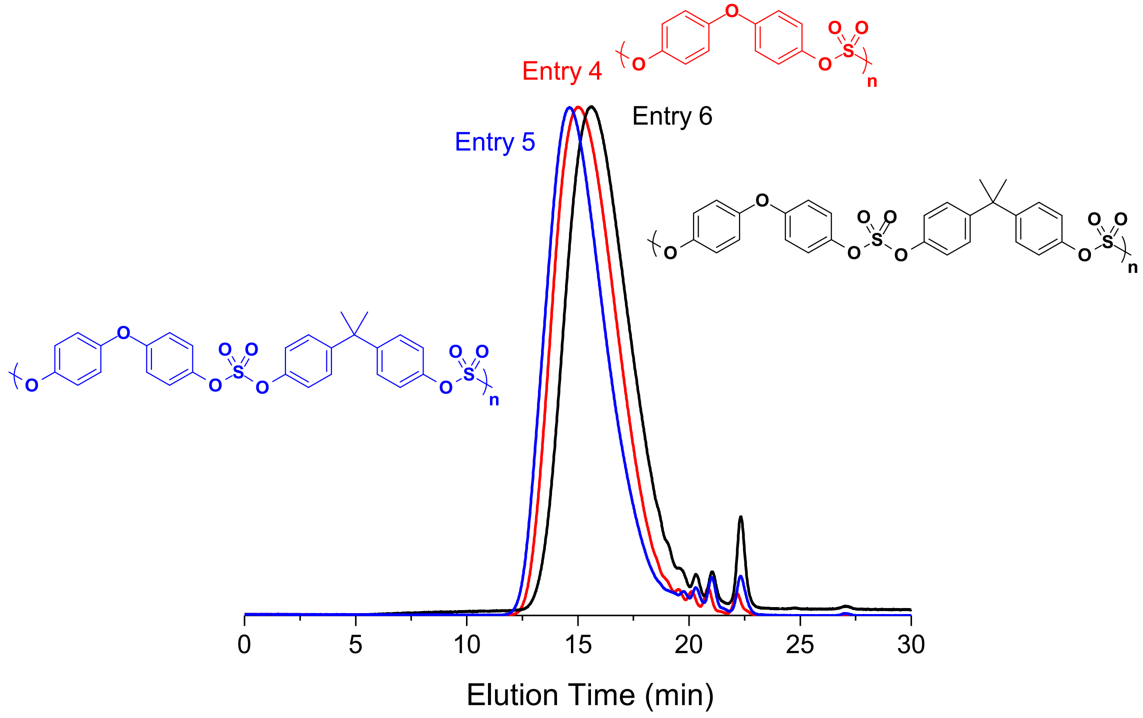
Conc.	M_n	% cyclic
Bulk	38000	<3
1.0 M	31000	6
0.25 M	20000	13
dilute	N/A	>95

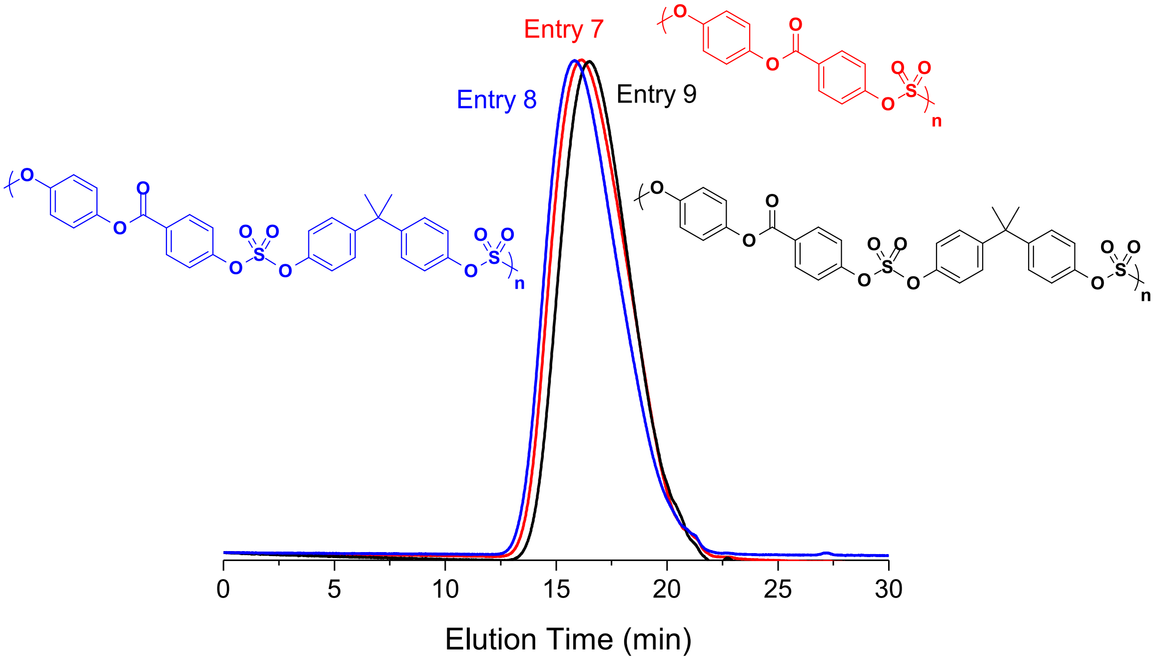
Figure S1. *Effect of concentration on co-polymerization of 2a and 2b. Normalized GPC traces are shown.* M_n *via polystyrene standards.*

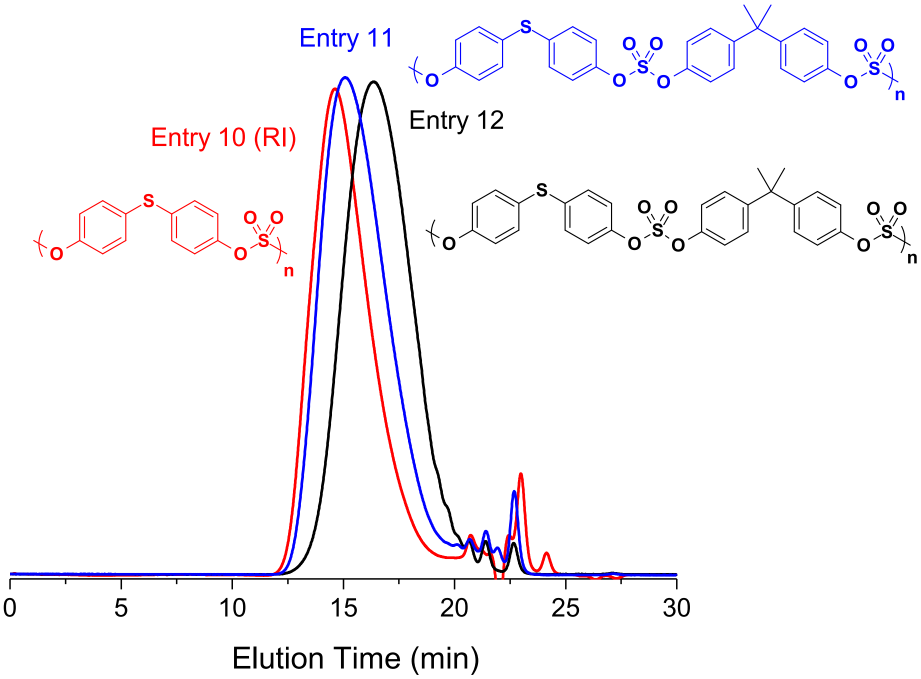
Accompanying GPC Traces for main text Table 3

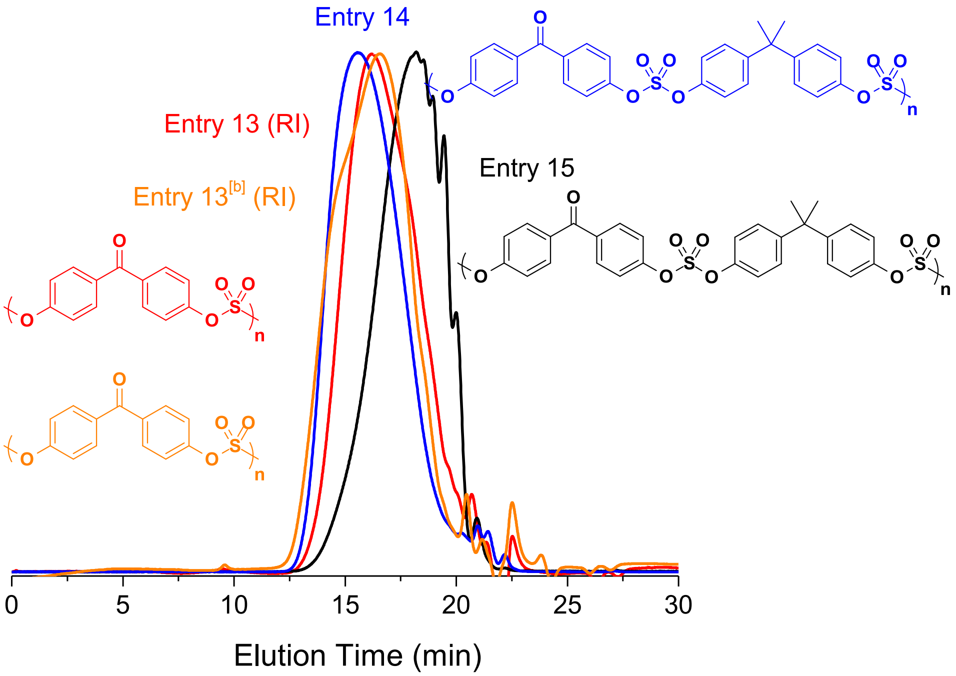


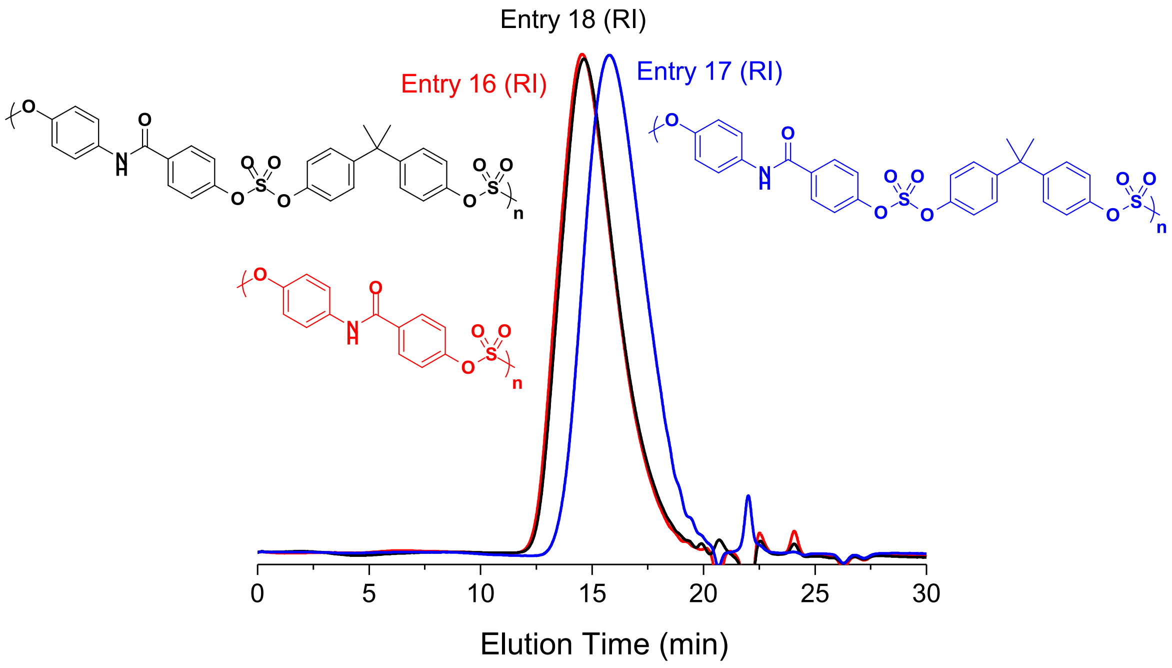


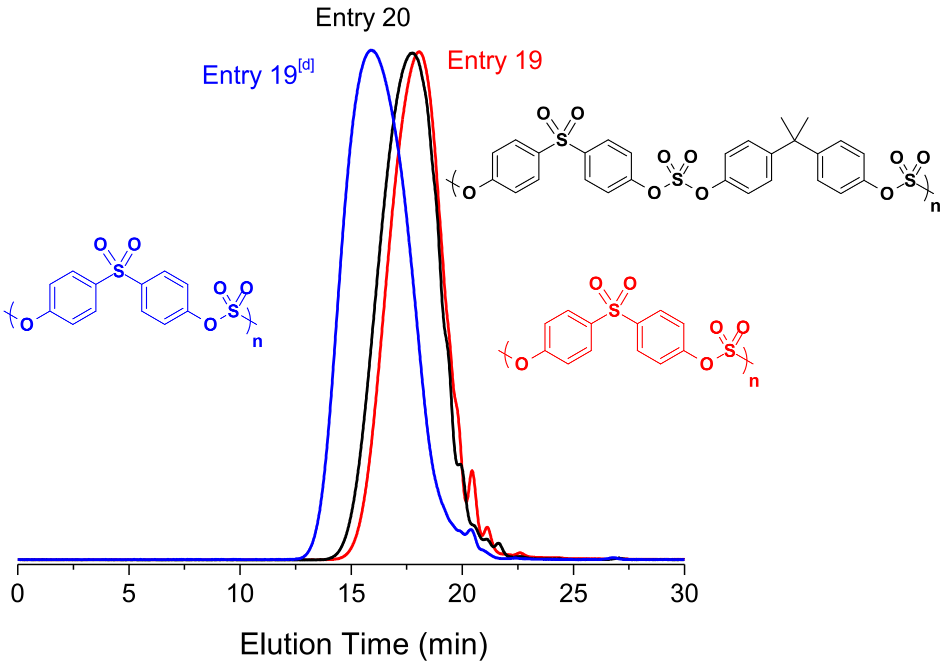

Entry 4
Entry 6
Entry 5
0
5
10
15
20
25
30
Elution Time (min)

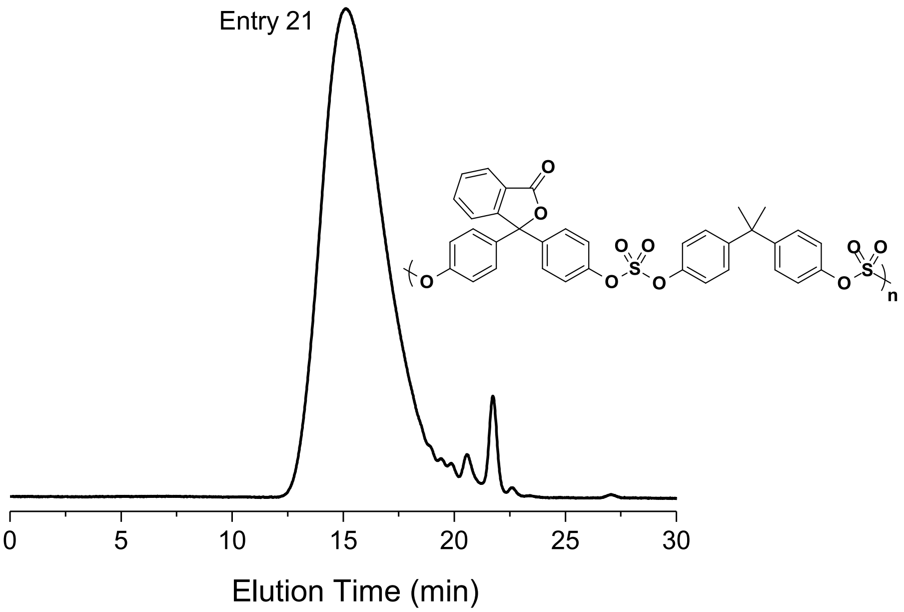

Entry 7
Entry 8
Entry 9
0
5
10
15
20
25
30
Elution Time (min)

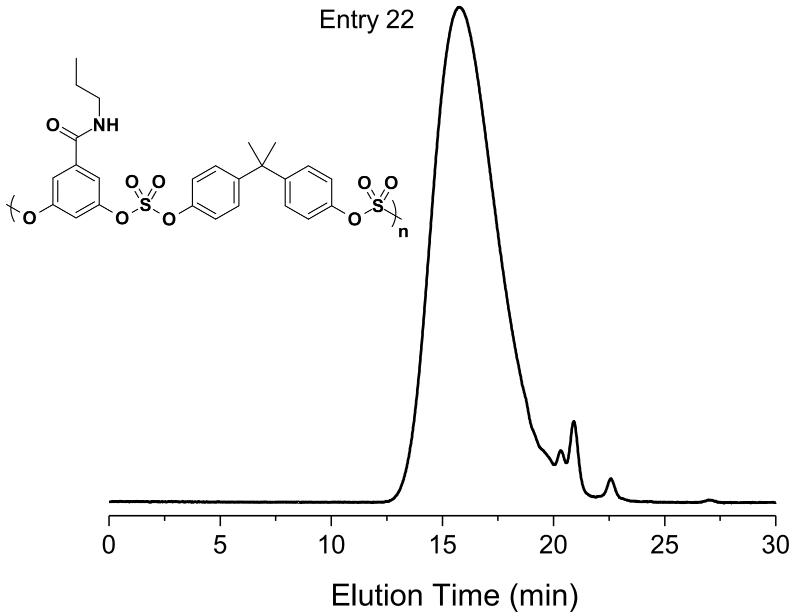

Entry 11
Entry 12
Entry 10 (RI)
0
5
10
15
20
25
30
Elution Time (min)

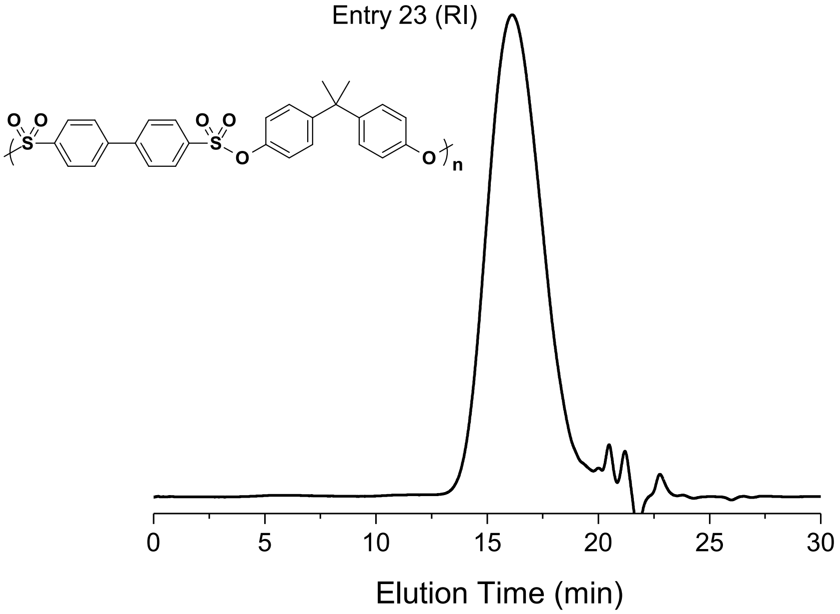

Entry 14
Entry 13 (RI)
Entry 13[b] (RI)
Entry 15
0
5
10
15
20
25
30
Elution Time (min)


Entry 18 (RI)
Entry 16 (RI)
Entry 17 (RI)
0
5
10
15
20
25
30
Elution Time (min)


Entry 20
Entry 19[d]
Entry 19
0
5
10
15
20
25
30
Elution Time (min)


Entry 21
0
5
10
15
20
25
30
Elution Time (min)
n


Entry 22
NH
n
0
5
10
15
20
25
30
Elution Time (min)


Entry 23 (RI)
O
O
S
O
O
S
O
O
n
0
5
10
15
20
25
30
Elution Time (min)

Processing/Molding Information

Polysulfate fiber/powder was extruded through a melt flow indexer at 200 °C. The thin extrudate was cooled to RT and pelletized by hand with scissors. Polysulfate pellets were compression molded into thin films and other sample molds using a Carver press set at 230 °C for 20 minutes total (10 minutes with no pressure, followed by 10 minutes at 25,000 psi). Samples were removed from the press and quenched in water. Tensile dog bones were punched from polysulfate plaques using a sharpened steel "cookie cutter" mold in the Carver press at room temperature. BPA-polycarbonate (Lexan®) samples of unknown grade were prepared under the same compression molding conditions for comparison.

Thermal, Physical, and Mechanical Properties

Glass transition

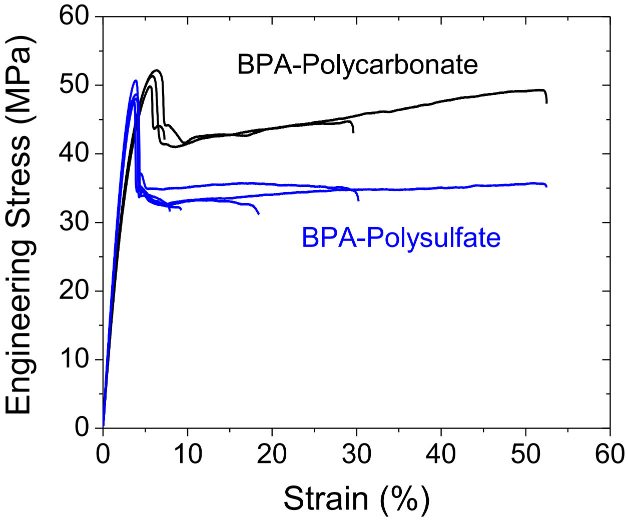
Glass transition temperature (T_g) of BPA-polysulfate was determined using a TA Q2000 DSC. A heat/cool/heat program ranging from 0 °C to 220 °C at 10 °C/min was used. T_g was taken from the 2nd heating scan.

Density

Density of BPA-polysulfate was measured using the Archimedes method at room temperature with an analytical balance. Mass was averaged over 4 measurements and recorded to 4 decimal places. Density was calculated and reported to 3 decimal places as 1.310 g/cc.

Tensile properties

Tensile measurements were made with an MTS Insight 10 electromechanical test frame equipped with a 2.5kN load cell. Tests were conducted at ambient temperature in triplicate at a strain rate of 10%/min. Engineering stress-strain behavior of both polysulfate and polycarbonate is depicted in the figure below. Similar to polycarbonate, polysulfate exhibited yielding followed by neck formation, stabilization and propagation. Preliminarily, it appears that BPA-polysulfate has a higher modulus and slightly lower yield stress compared with BPA-polycarbonate at least under the specific conditions used. Strain at break reached over 50% but was limited by sample defects in both cases. True elongation may be significantly higher.

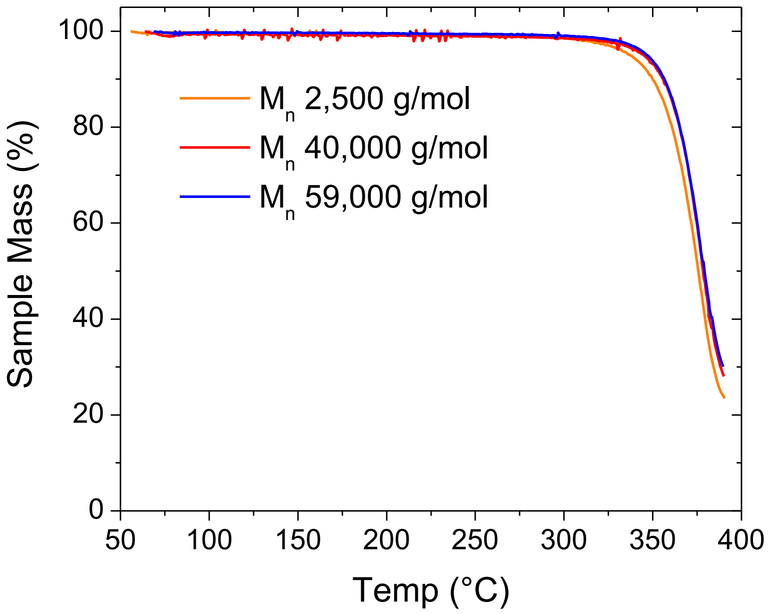


Oxygen permeability

Oxygen permeation tests were conducted on a Mocon OX-TRAN® 2/21 instrument using a continuous-flow testing cell method approved by the ASTM (D3985). Measurements were made on two separate BPA-polysulfate film samples both at 23 °C and 0% RH. Further details on this method can be found elsewhere.[4]

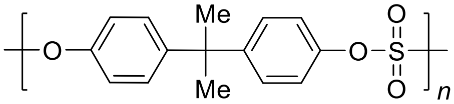
Thermal decomposition

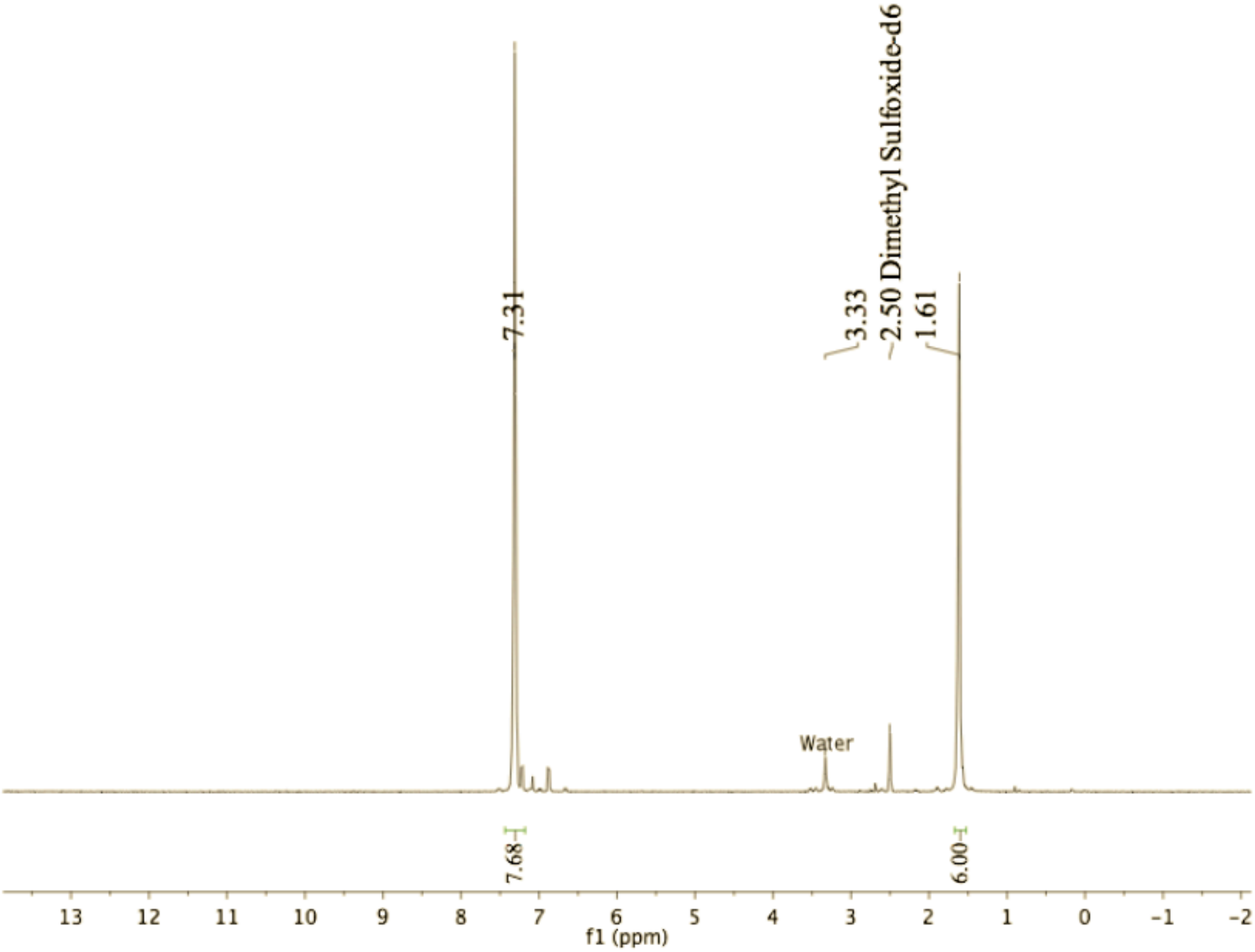
Thermal decomposition of BPA-polysulfate was measured using a TA Q5000IR TGA with a heating rate of 10 °C/min. Representative results indicating good thermal stability are shown in the following figure.



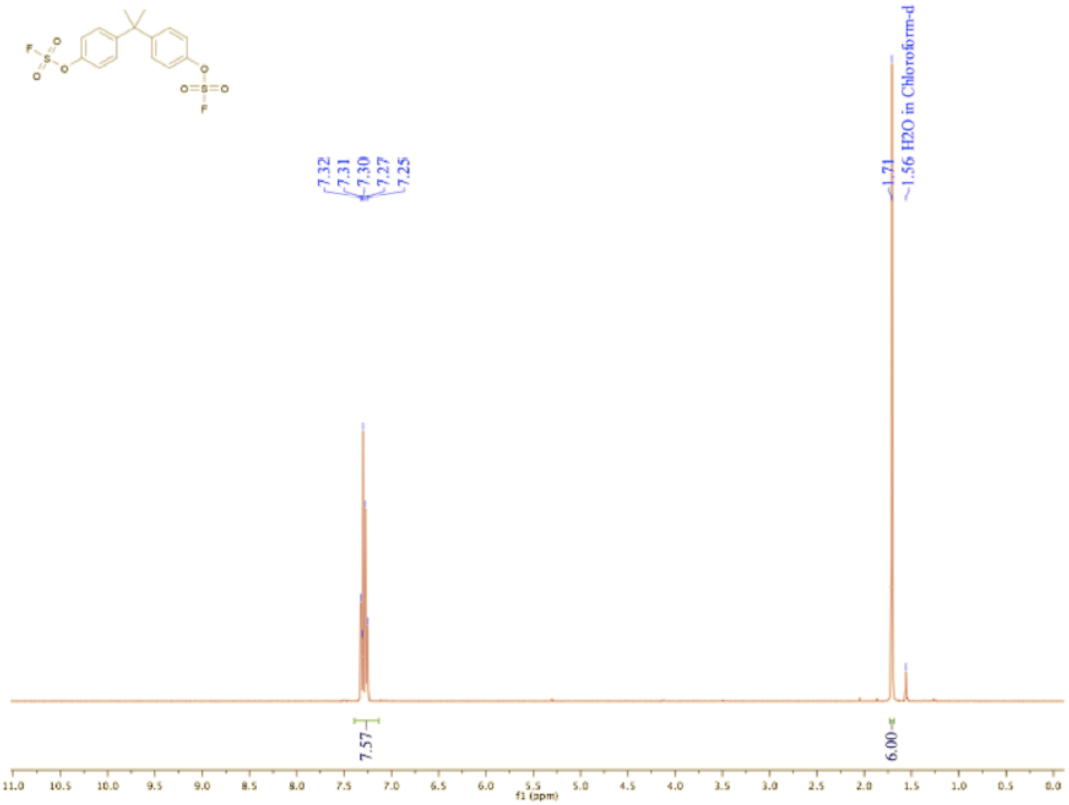
^{1}H and ^{13}C NMR Spectra

Polysulfate

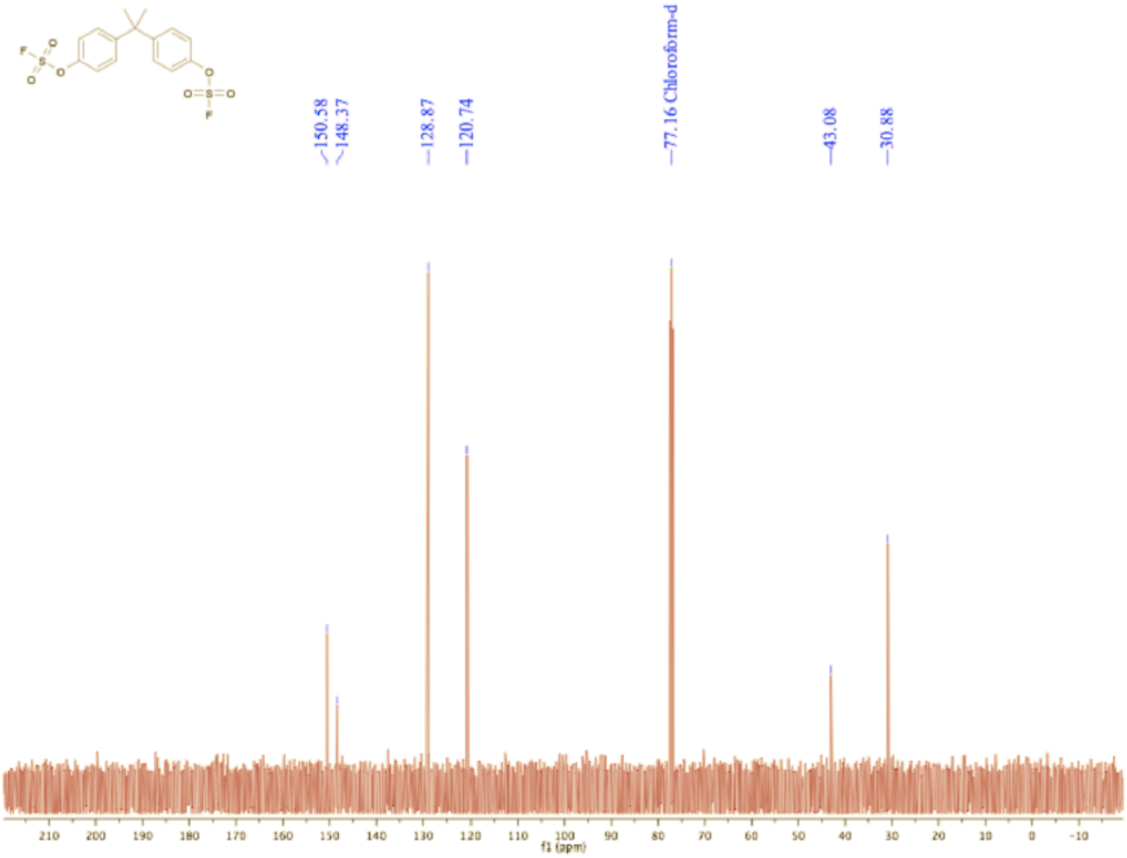




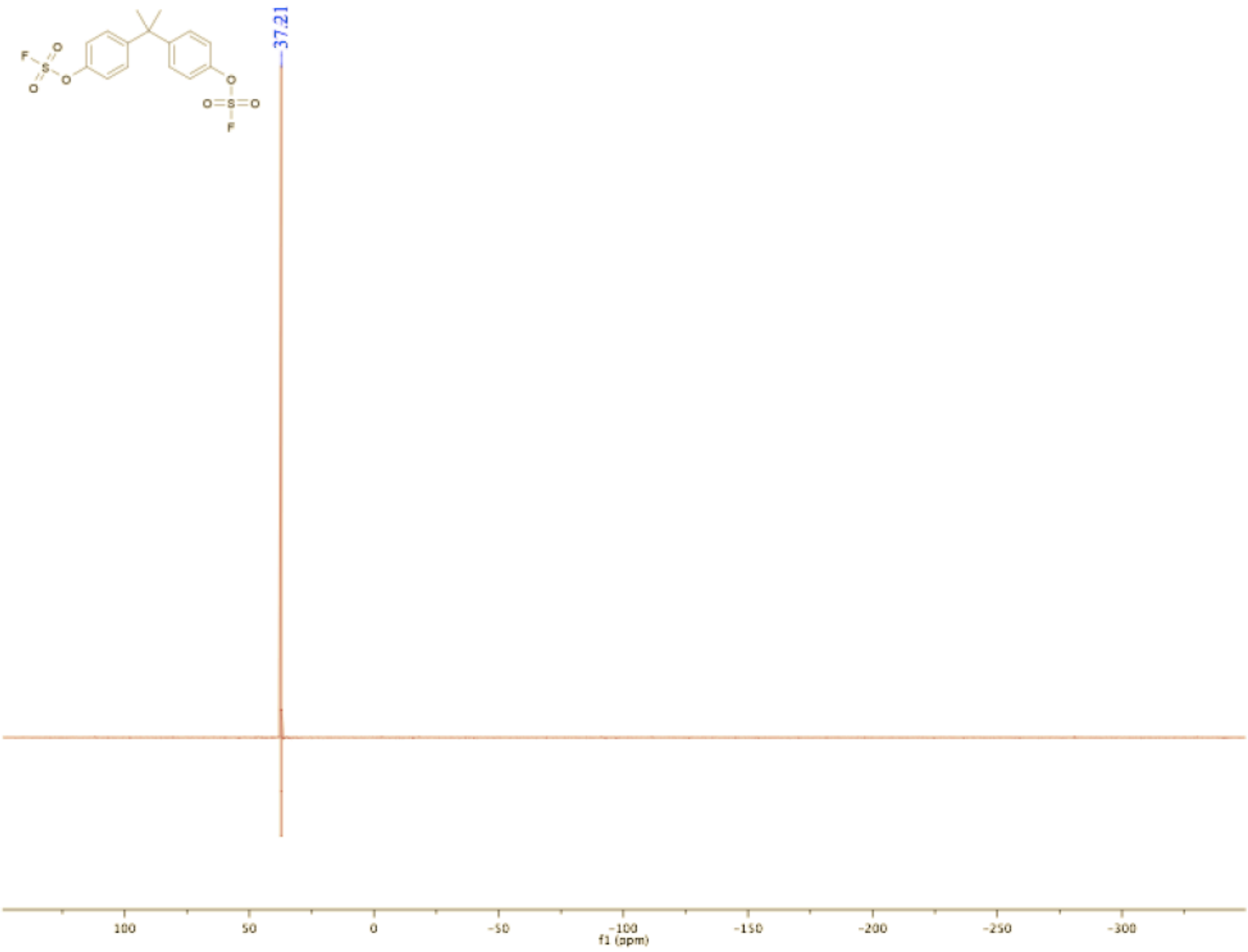
Monomers

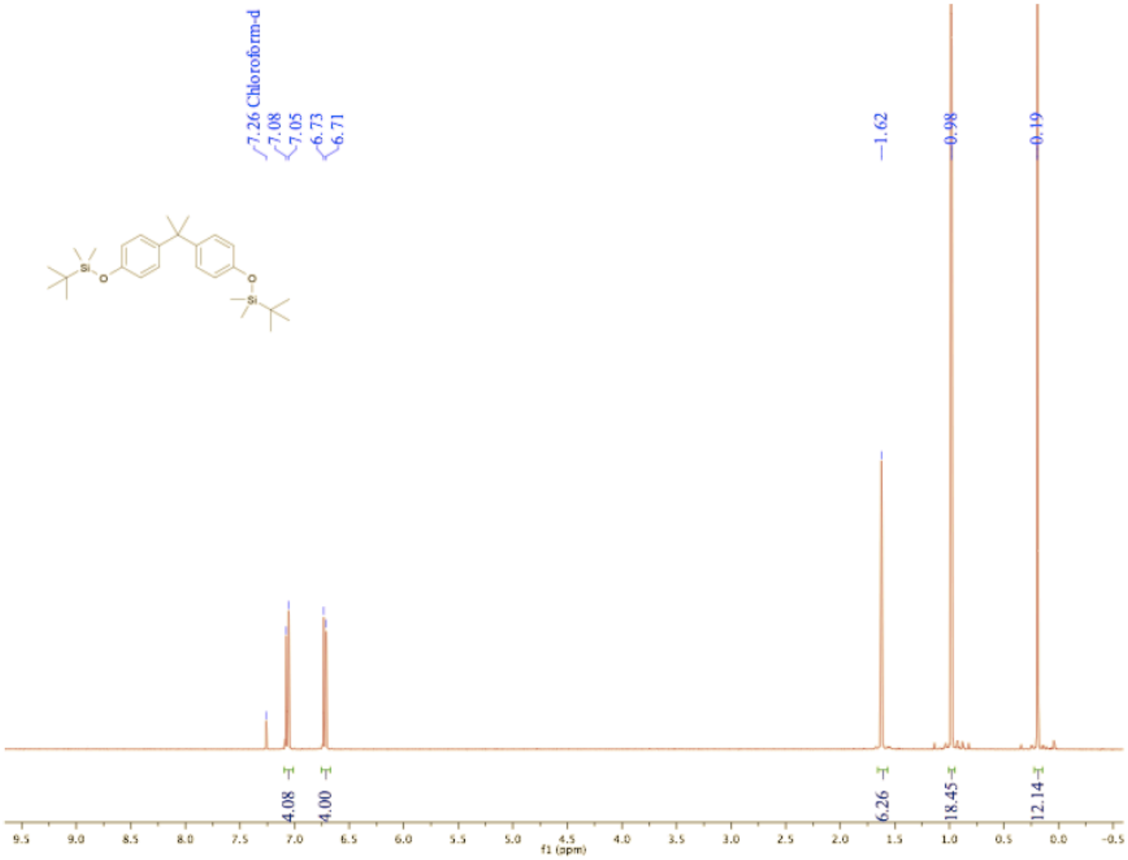


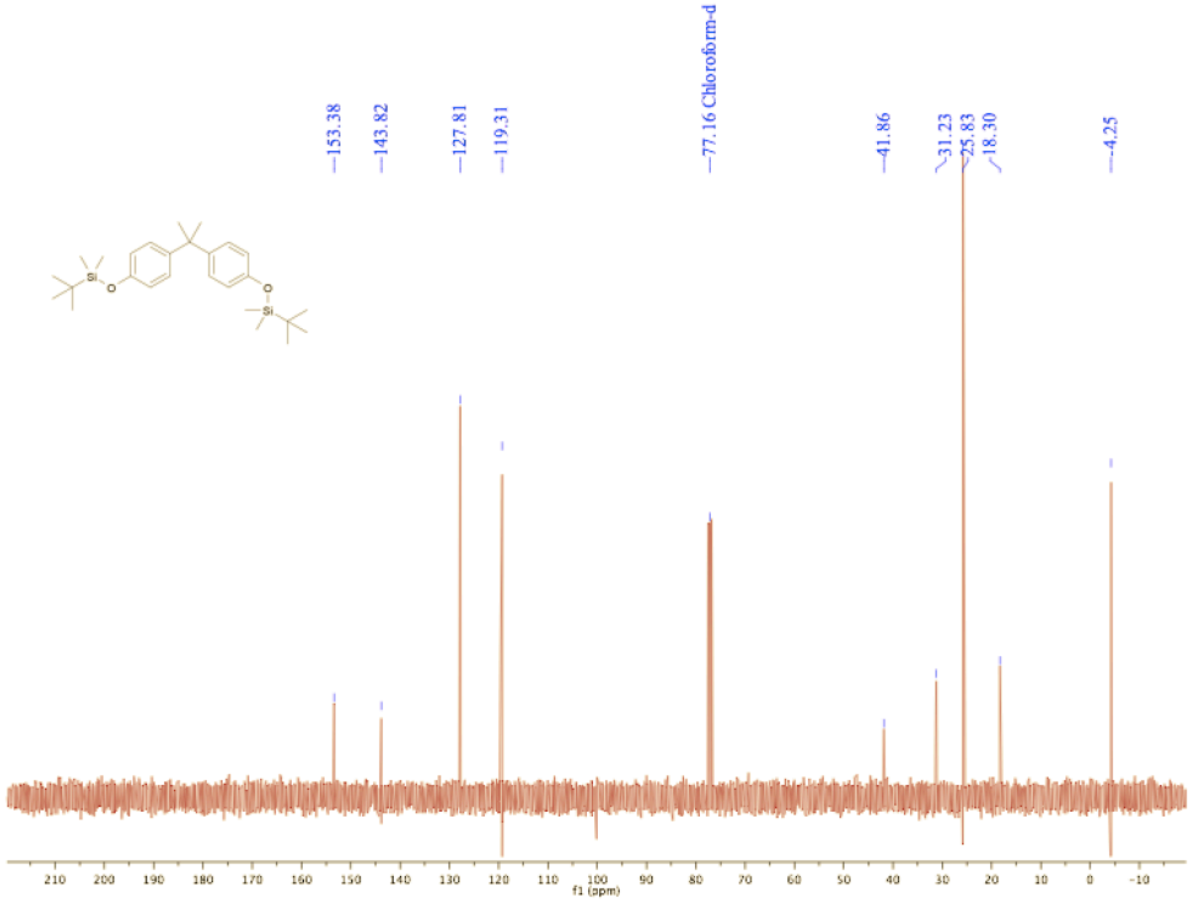
7.32
7.31
7.30
7.27
7.25
1.71
1.56 H2O in Chloroform-d
7.57
6.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

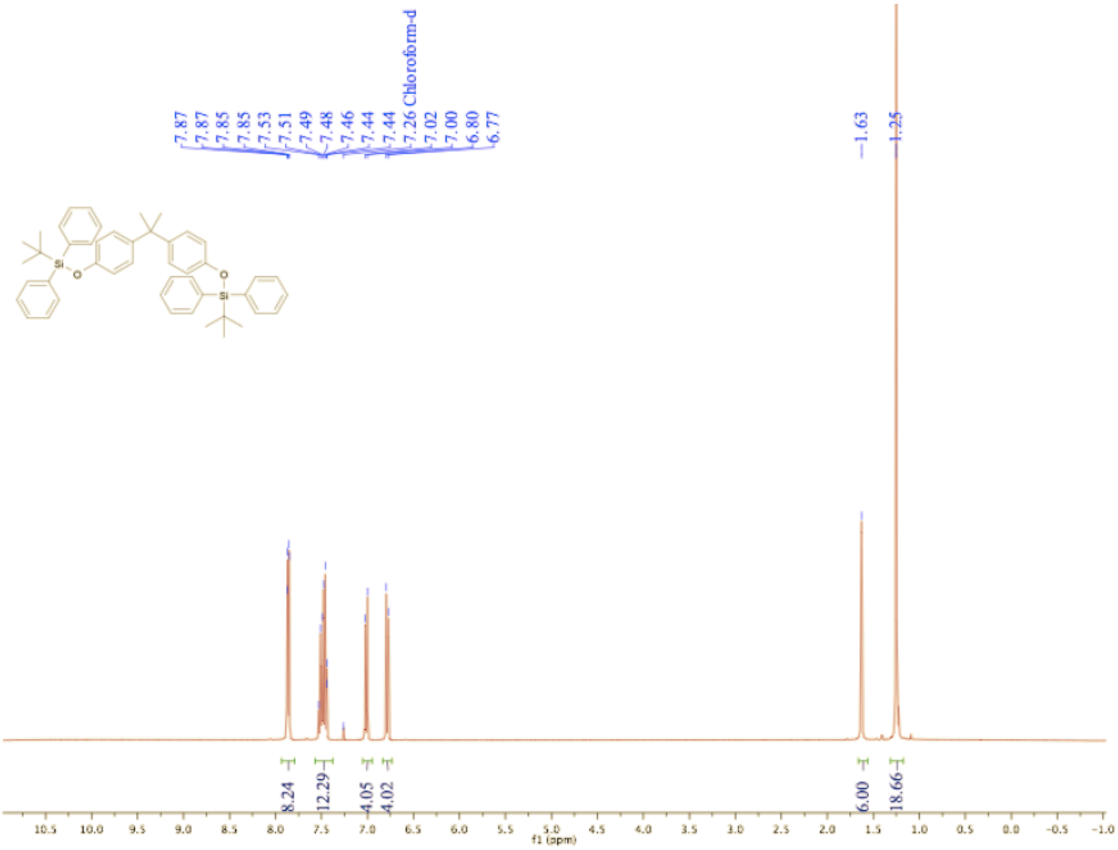


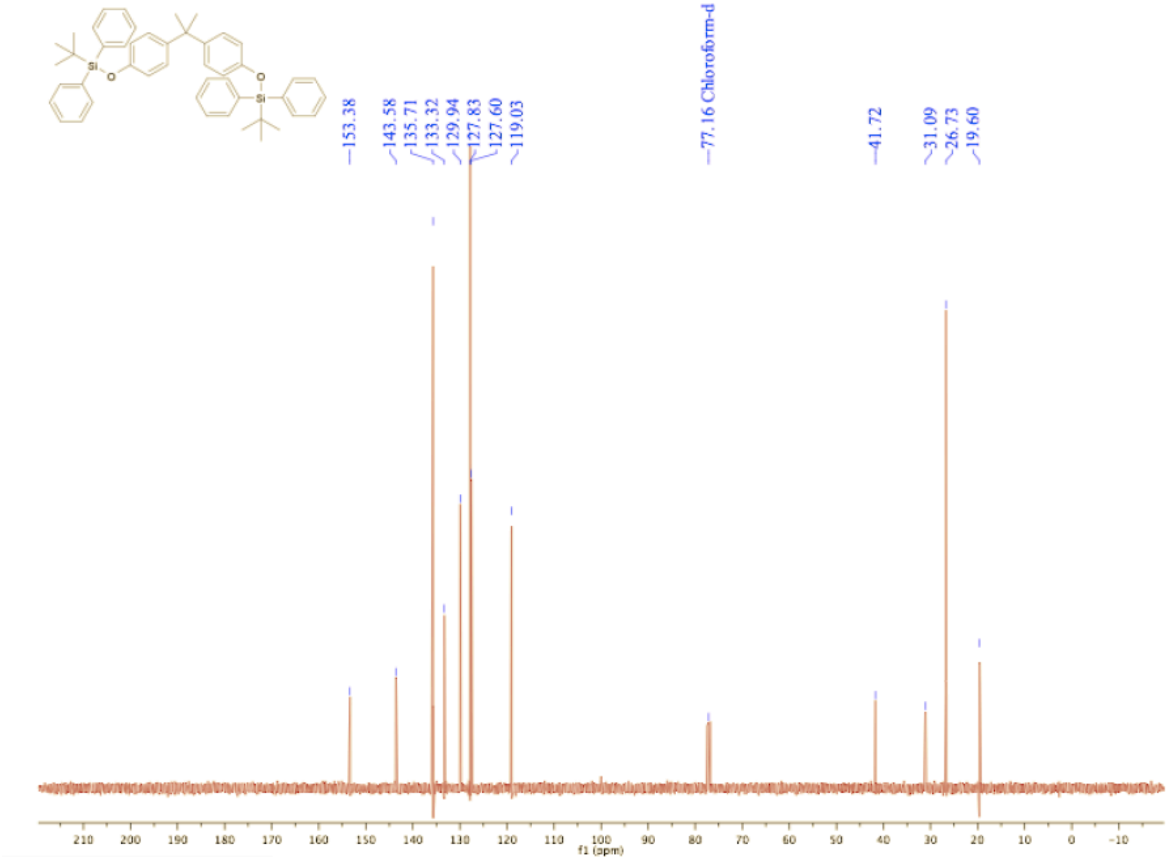
150.58
148.37
128.87
120.74
77.16 Chloroform-d
43.08
30.88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

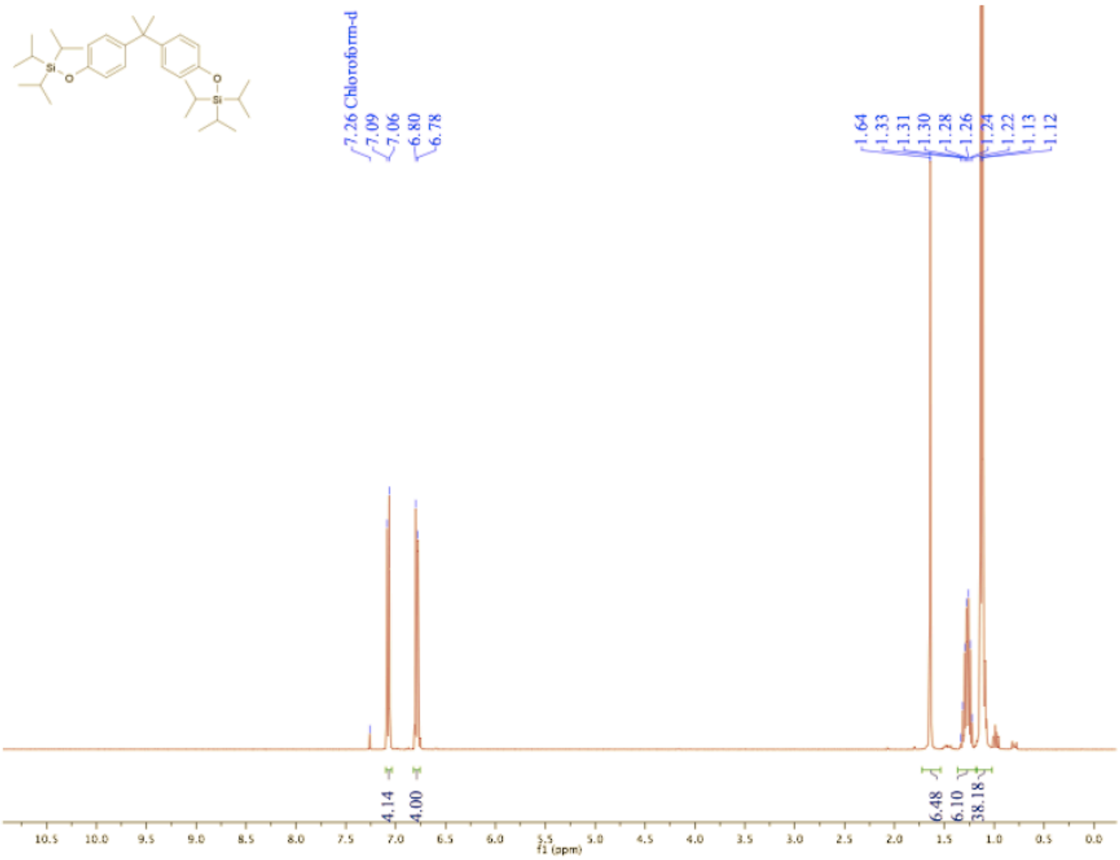

37.21
F
S
O
O
O
O
O
S
O
F
100
50
0
-50
-100
f1 (ppm)
-150
-200
-250
-300

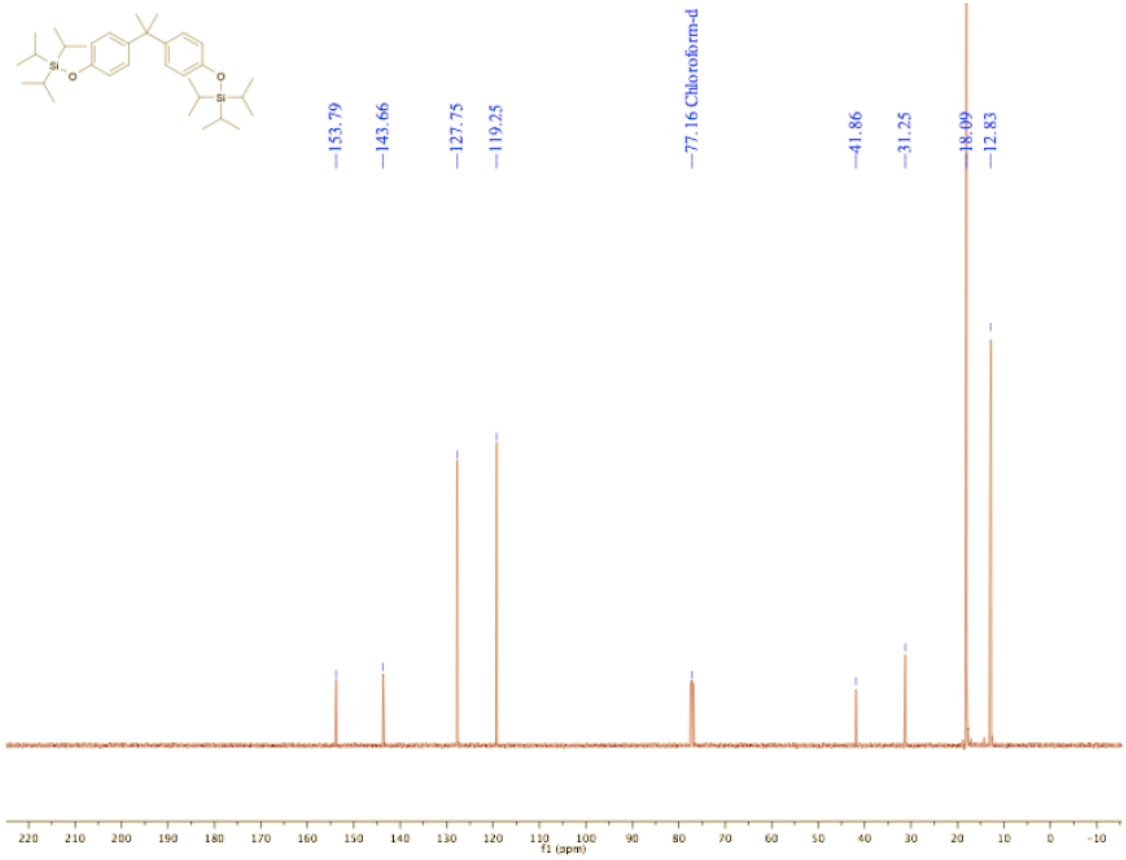

7.26 Chloroform-d
7.08
7.05
6.73
6.71
1.62
0.98
0.19
4.08
4.00
6.26
18.45
12.14
Si
O
O
Si
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

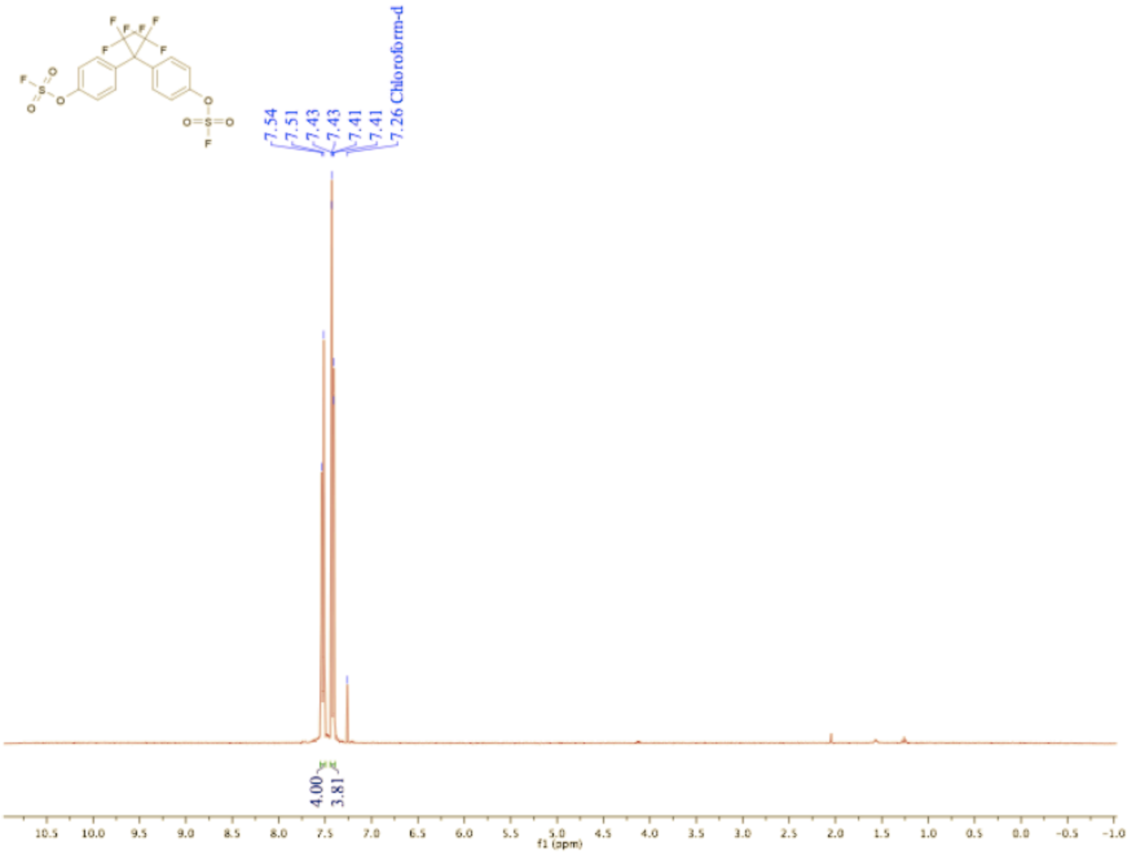

153.38
143.82
127.81
119.31
77.16 Chloroform-d
41.86
31.23
25.83
18.30
-4.25
Si
O
O
Si
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

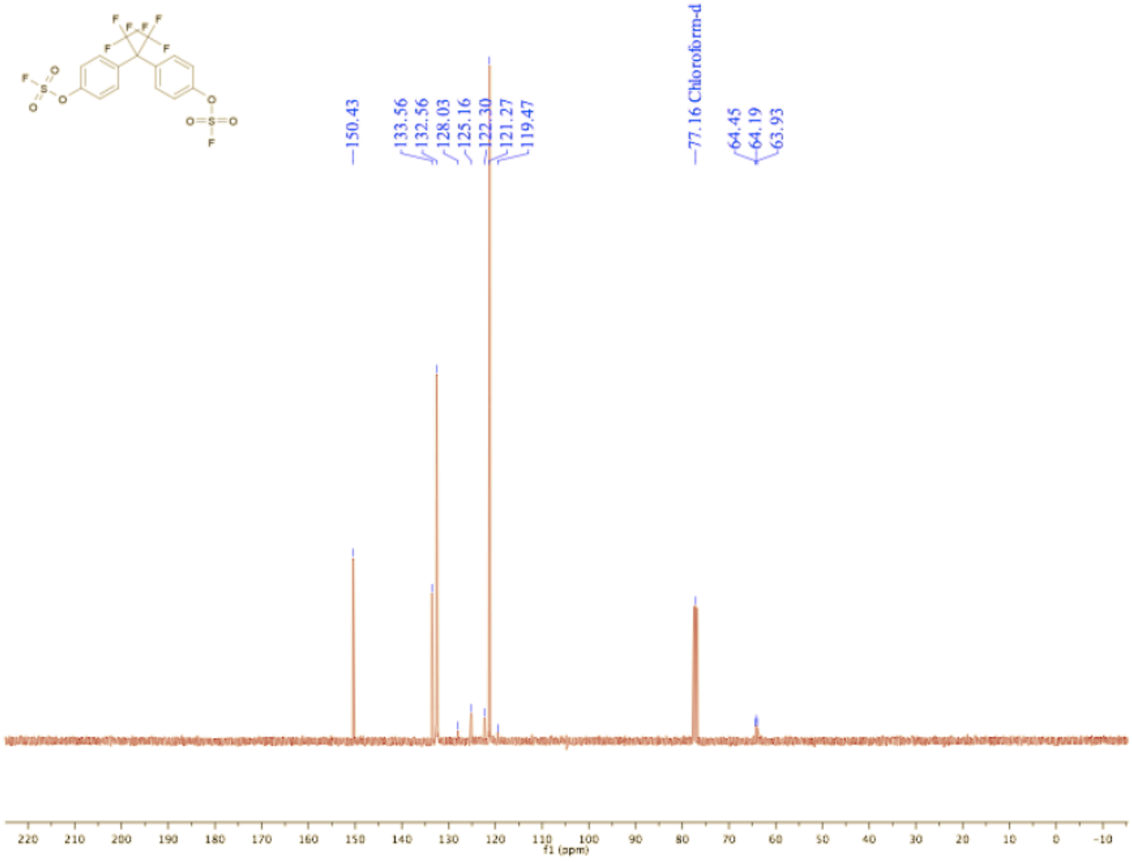

7.87
7.87
7.85
7.85
7.53
7.51
7.49
7.48
7.46
7.44
7.44
7.26 Chloroform-d
7.02
7.00
6.80
6.77
1.63
1.25
8.24
12.29
4.05
4.02
6.00
18.66
Si
O
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

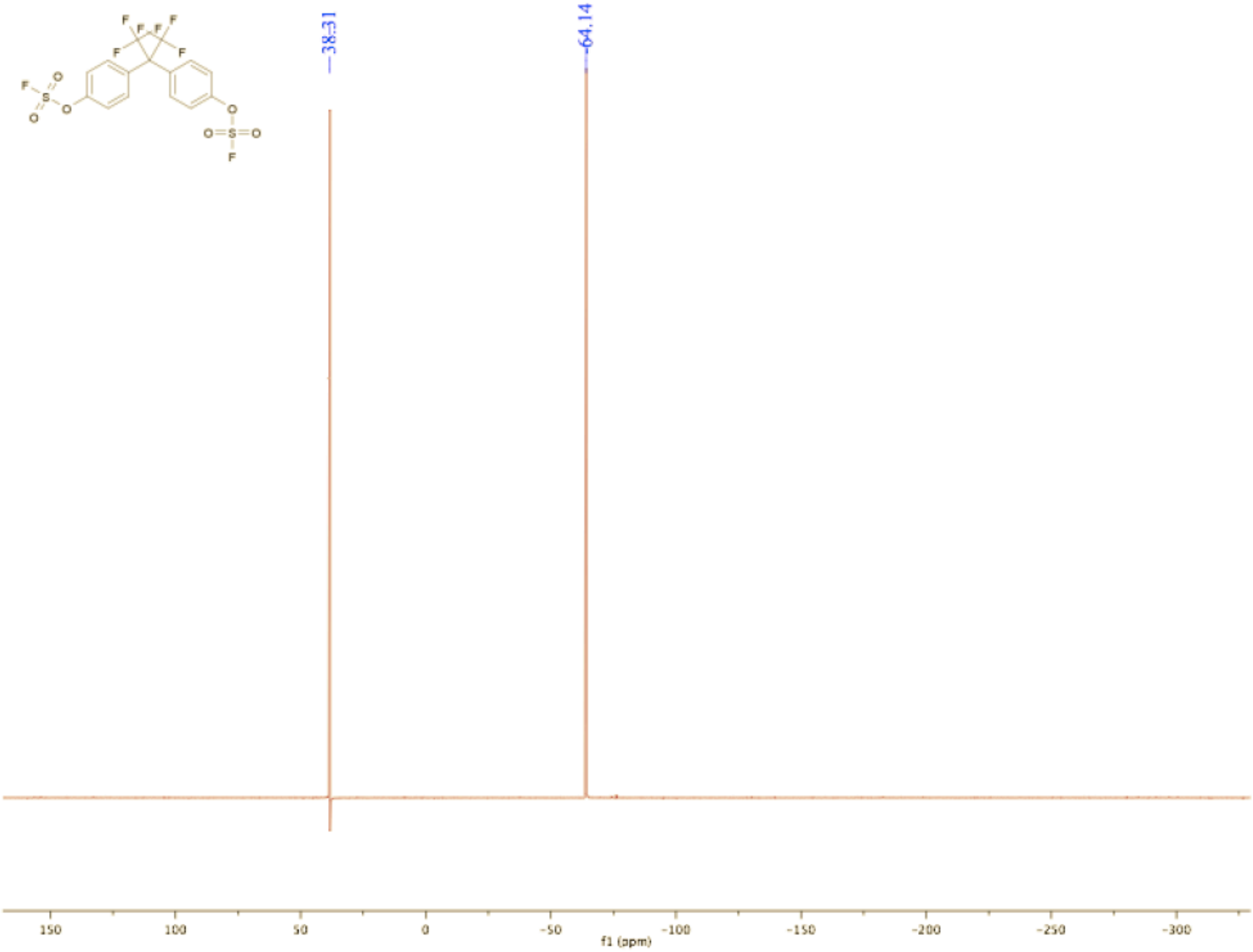

153.38
143.58
135.71
133.32
129.94
127.83
127.60
119.03
77.16 Chloroform-d
41.72
31.09
26.73
19.60
Si
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

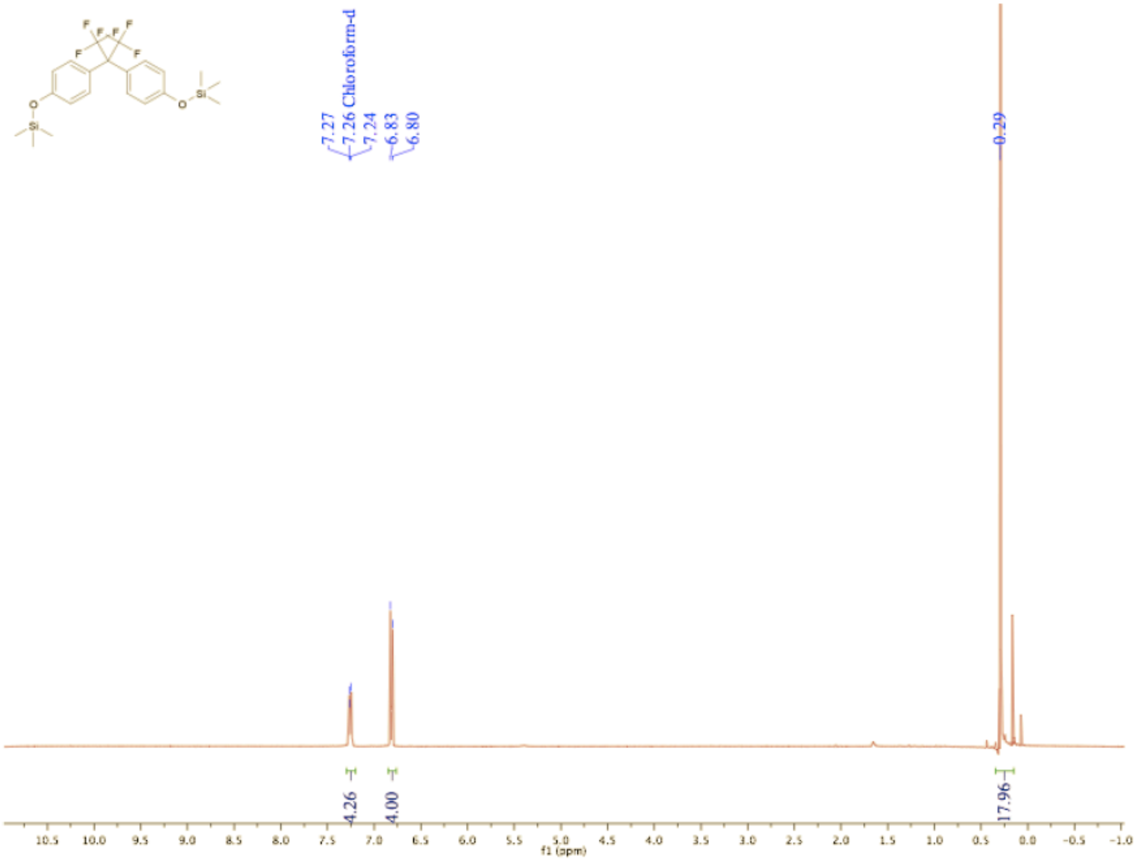

Si
O
O
Si
7.26 Chloroform-d
7.09
7.06
6.80
6.78
1.64
1.33
1.31
1.30
1.28
1.26
1.24
1.22
1.13
1.12
4.14
4.00
6.48
6.10
38.18
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Si
O
O
Si
153.79
143.66
127.75
119.25
77.16 Chloroform-d
41.86
31.25
18.09
12.83
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

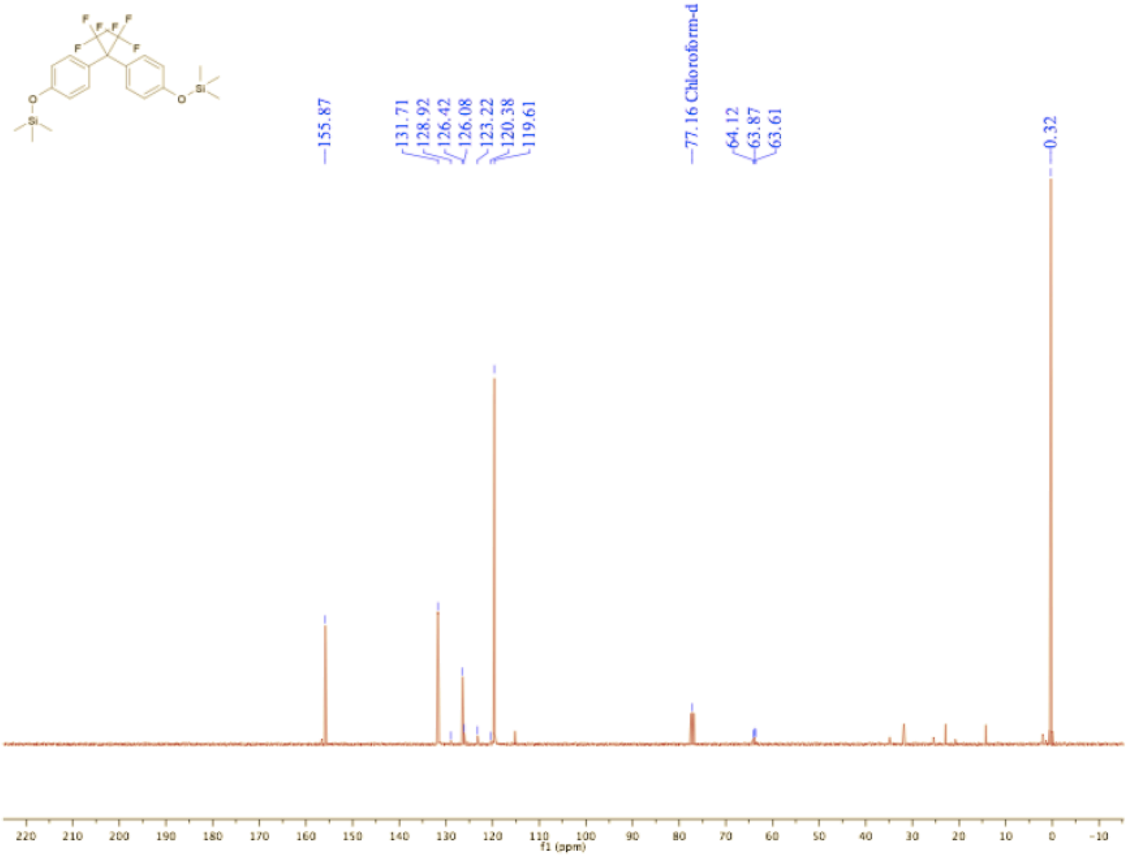

7.54
7.51
7.43
7.43
7.41
7.41
7.26 Chloroform-d
4.00
3.81
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


150.43
133.56
132.56
128.03
125.16
122.30
121.27
119.47
77.16 Chloroform-d
64.45
64.19
63.93
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

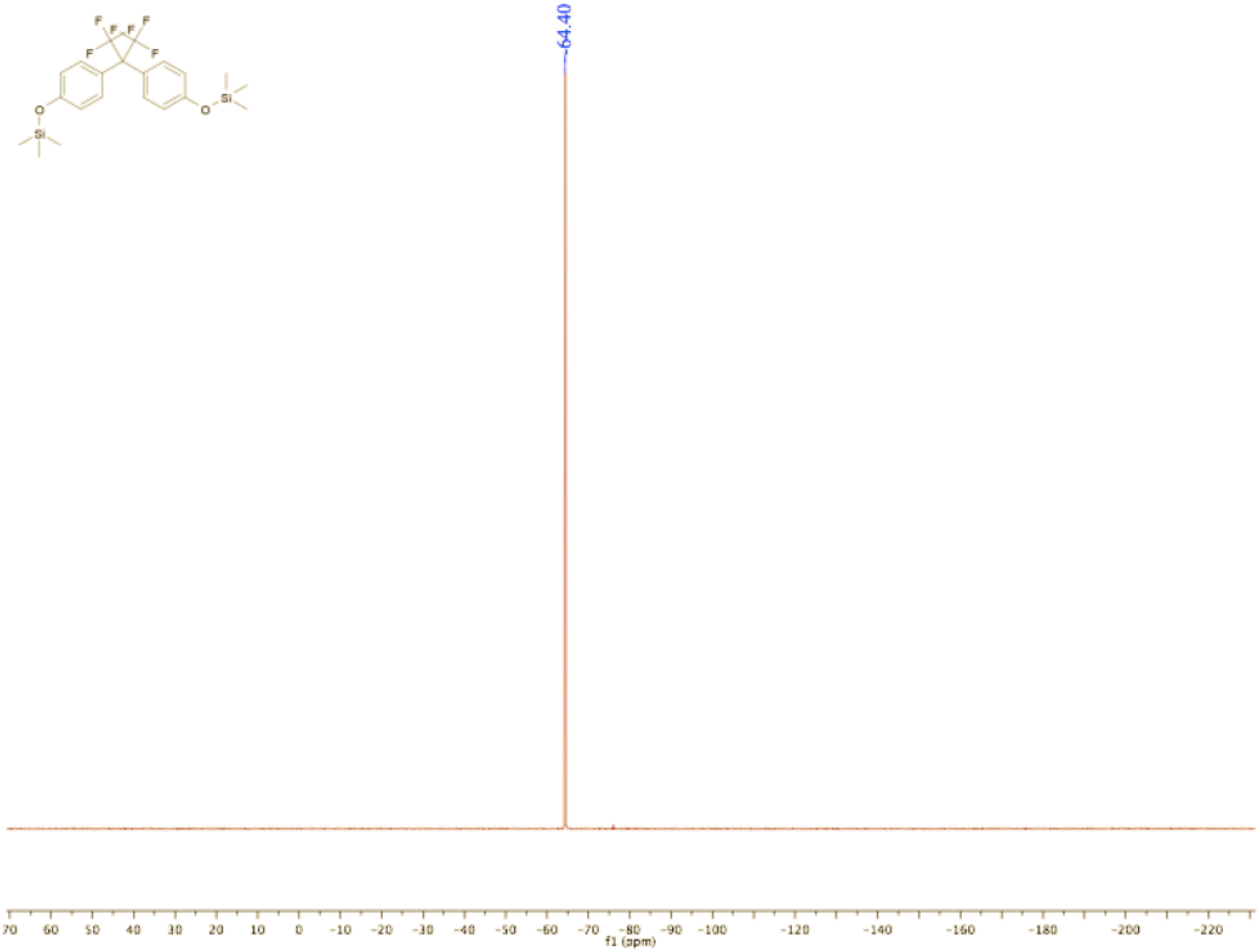

38.31
-64.14
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

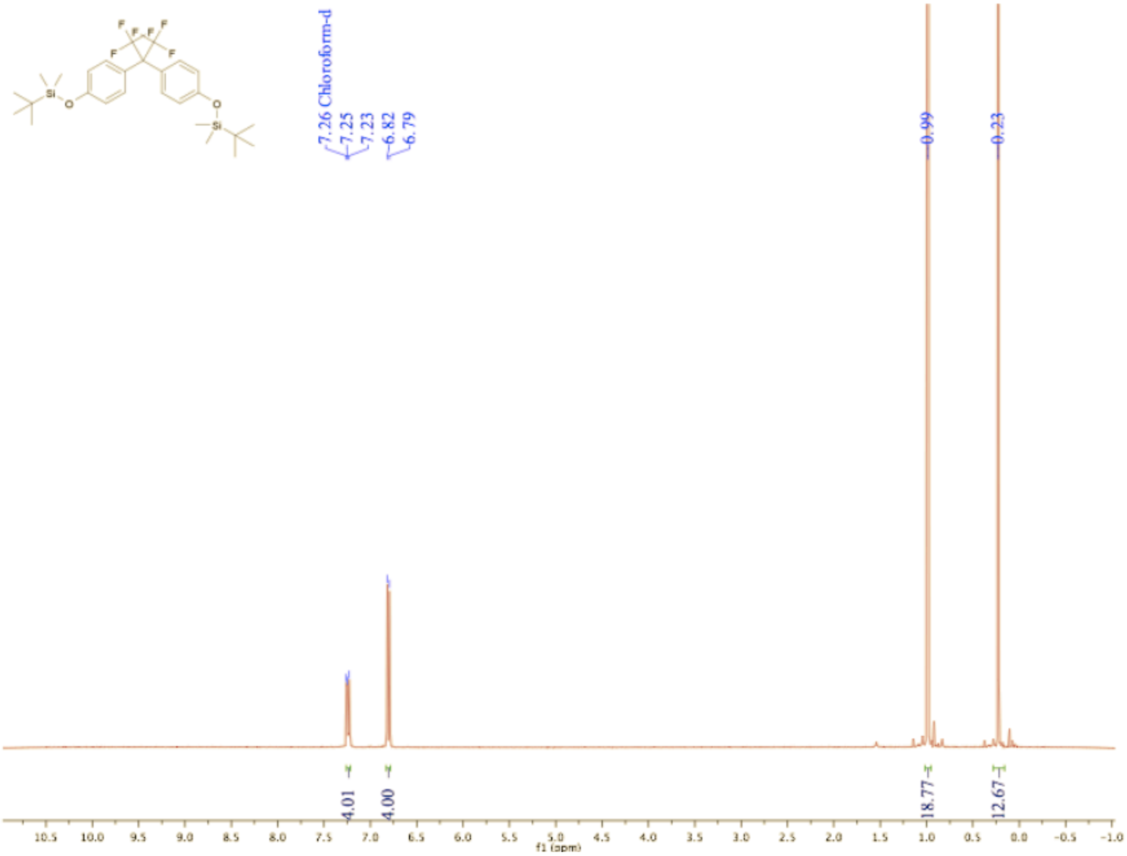


F
F
F
F
F
F
O
Si
O
Si
7.27
7.26 Chloroform-d
7.24
6.83
6.80
0.29
4.26
4.00
17.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

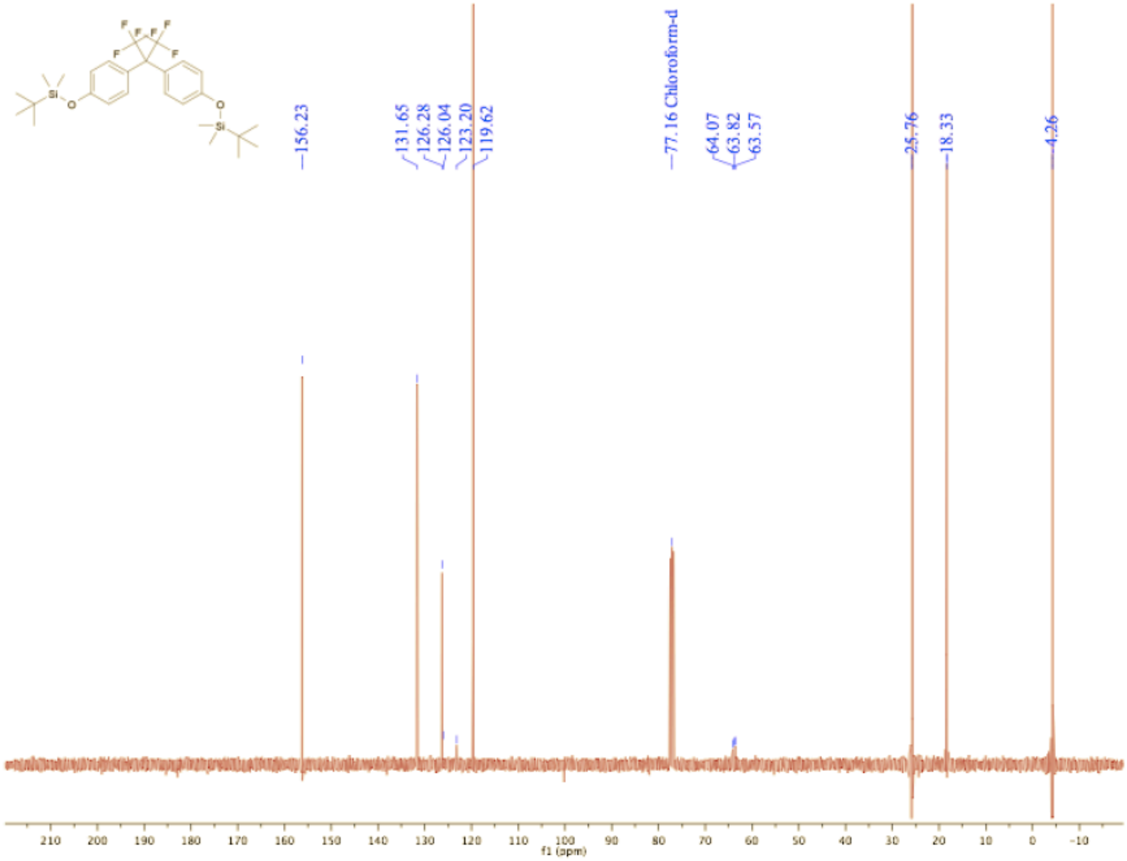


F
F
F
F
F
F
O
Si
O
Si
155.87
131.71
128.92
126.42
126.08
123.22
120.38
119.61
77.16 Chloroform-d
64.12
63.87
63.61
0.32
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

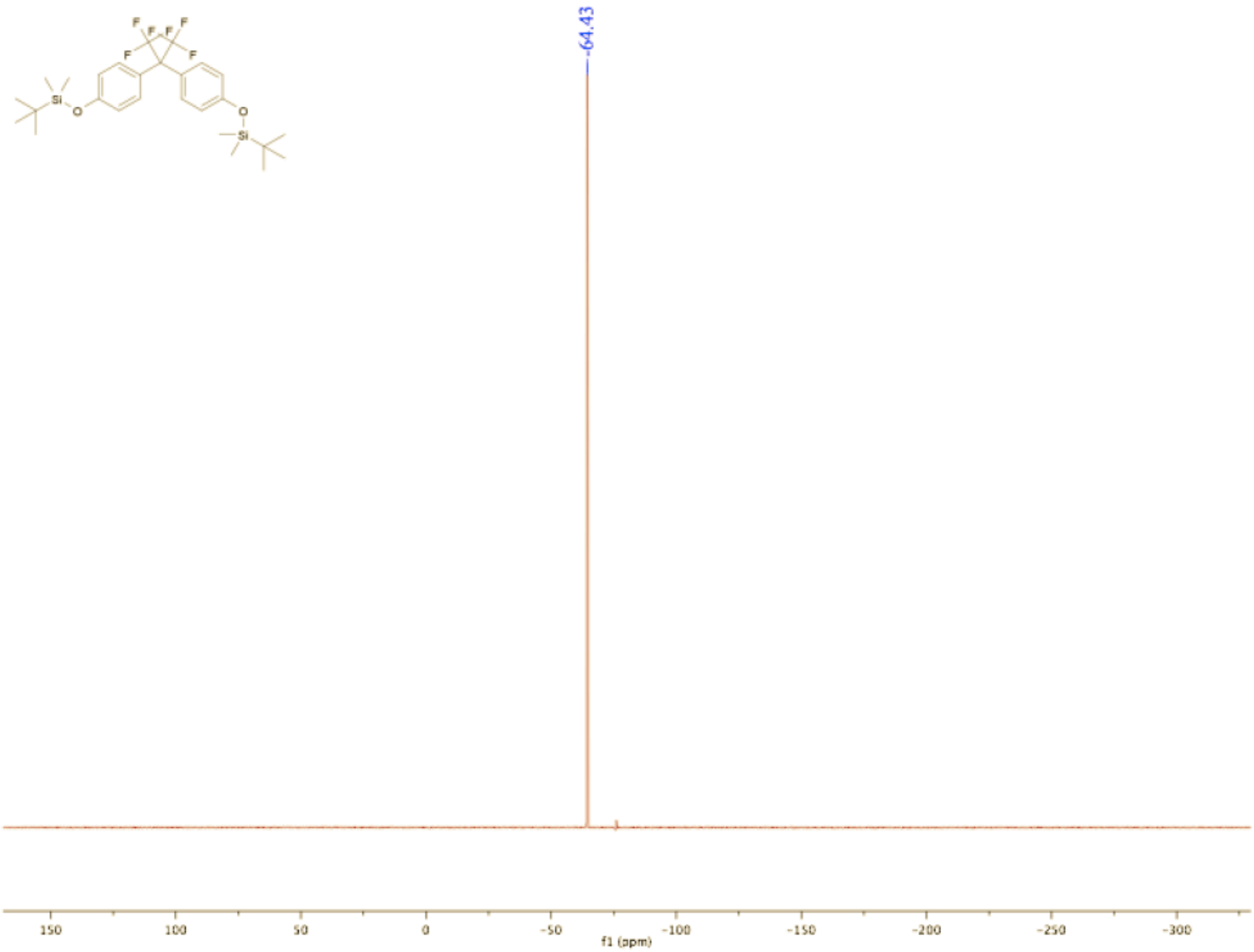

F
F
F
F
F
F
O
Si
O
Si
-64.40
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

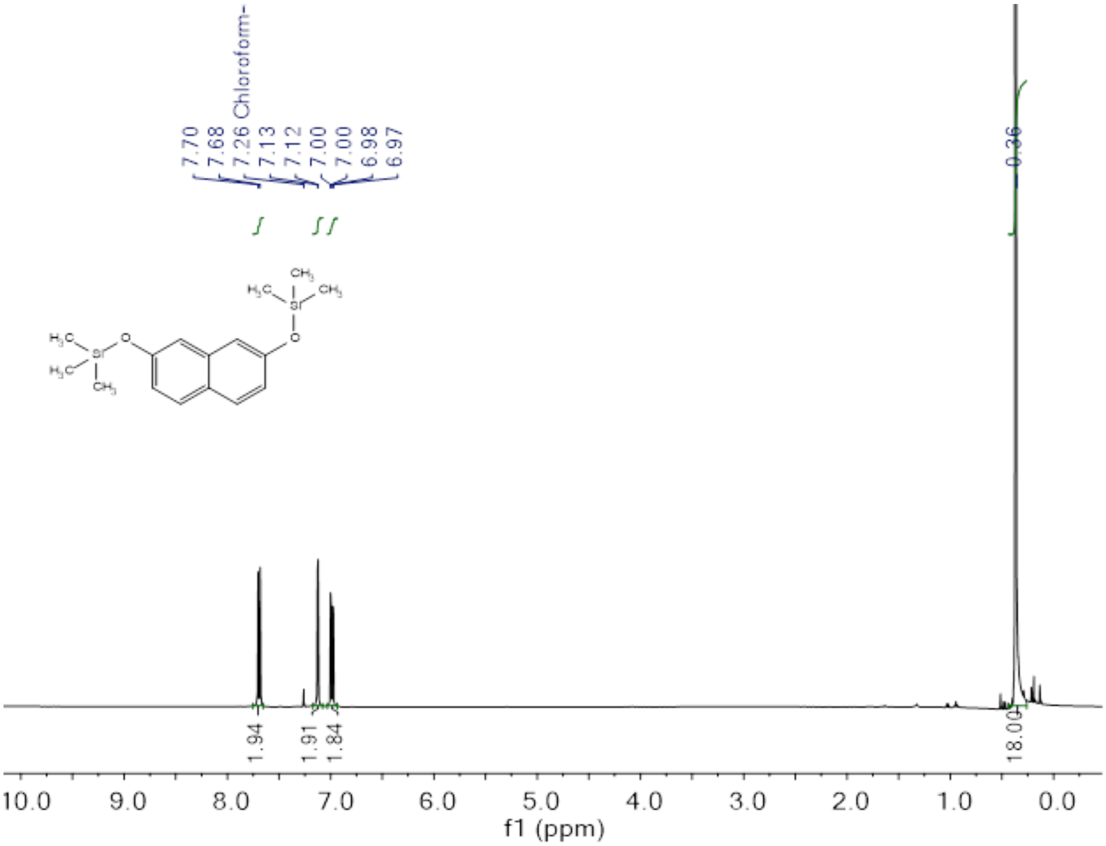


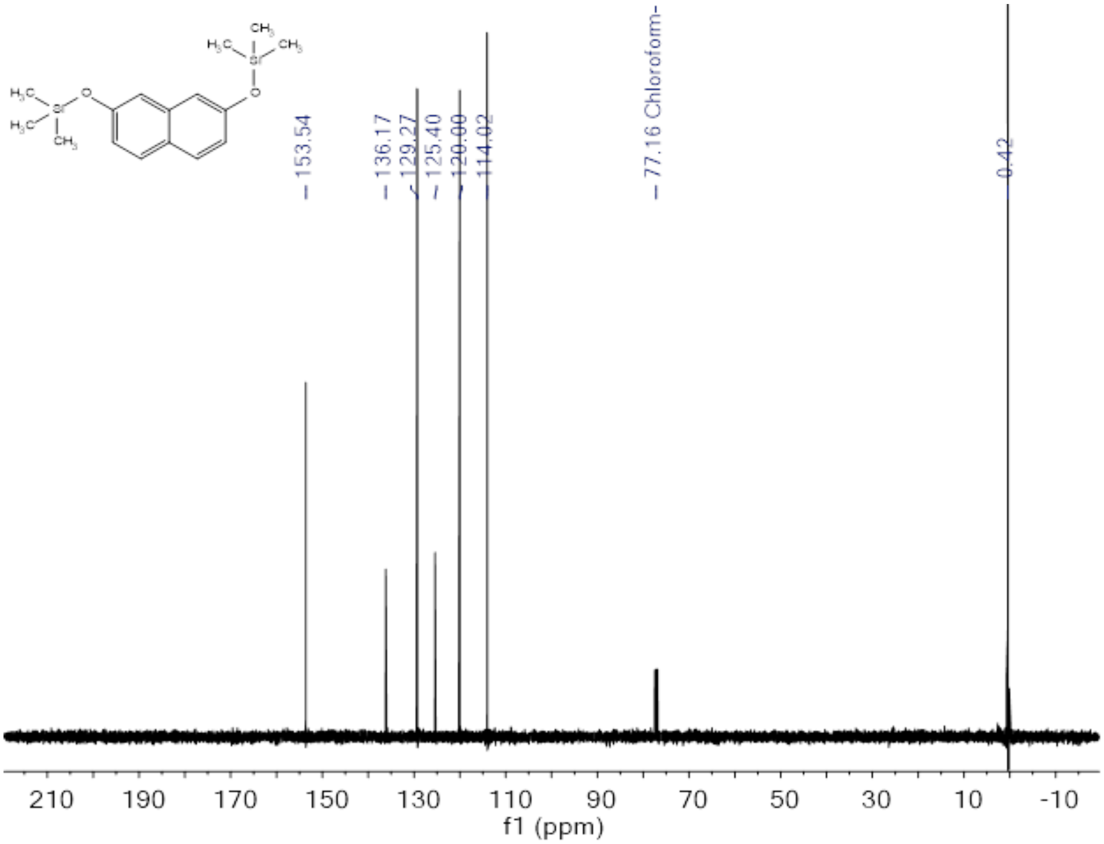
F F F F
F F
Si
O
O
Si
7.26 Chloroform-d
7.25
7.23
6.82
6.79
0.99
0.23
4.01
4.00
18.77
12.67
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

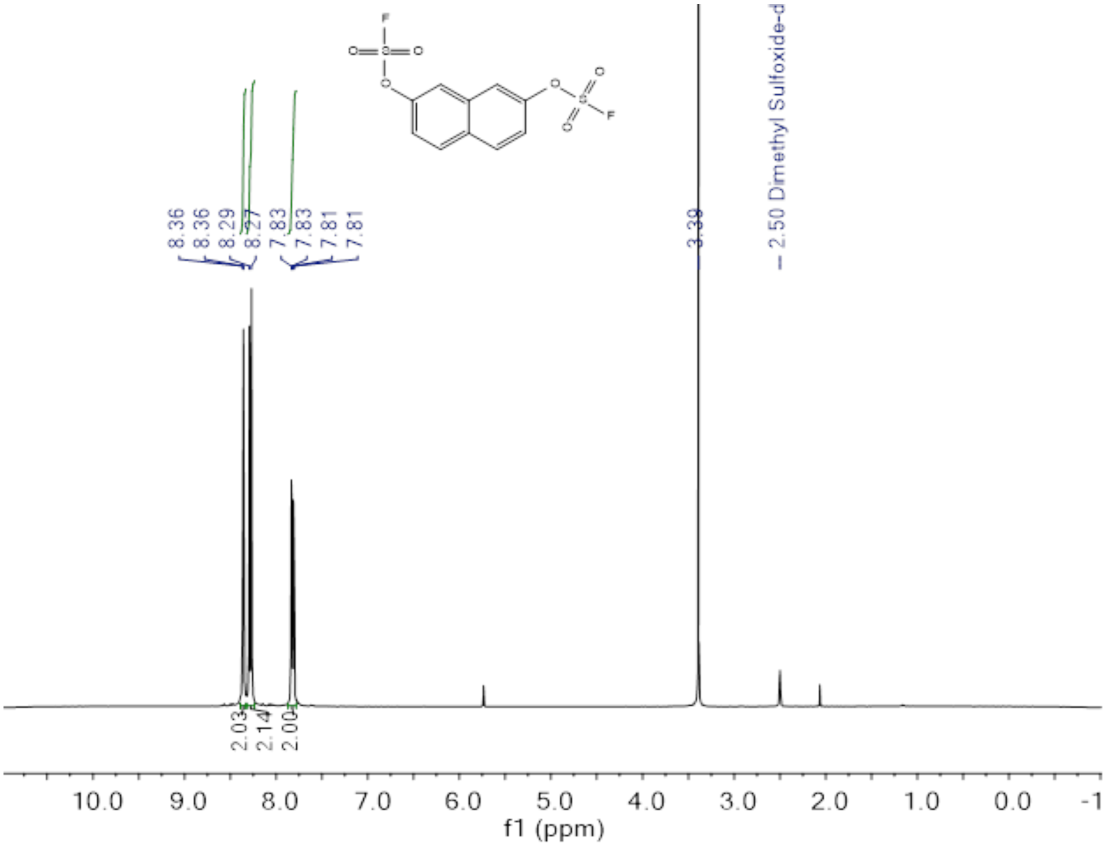


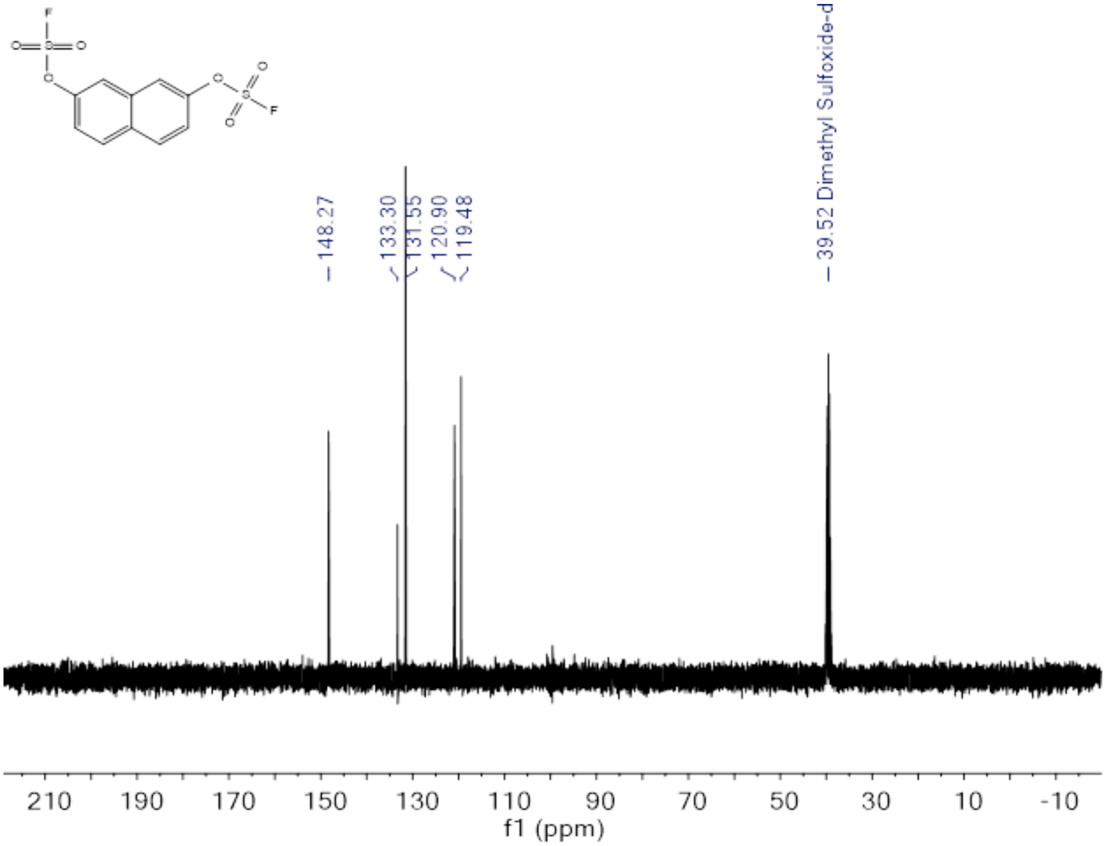
F F F F
F F
Si
O
O
Si
156.23
131.65
126.28
126.04
123.20
119.62
77.16 Chloroform-d
64.07
63.82
63.57
25.76
18.33
-4.26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

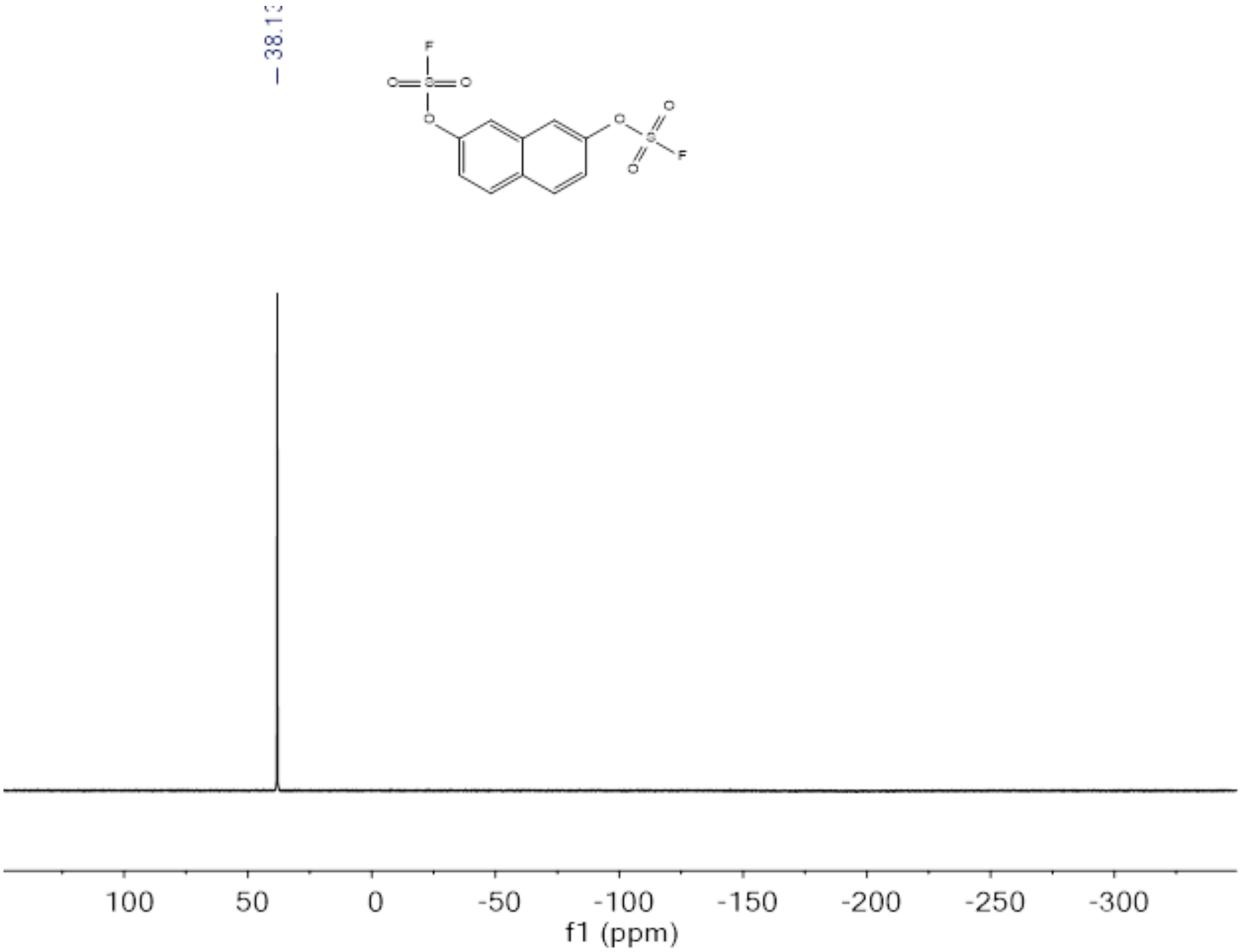

-64.43
F
F
F
F
F
F
Si
O
O
Si
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

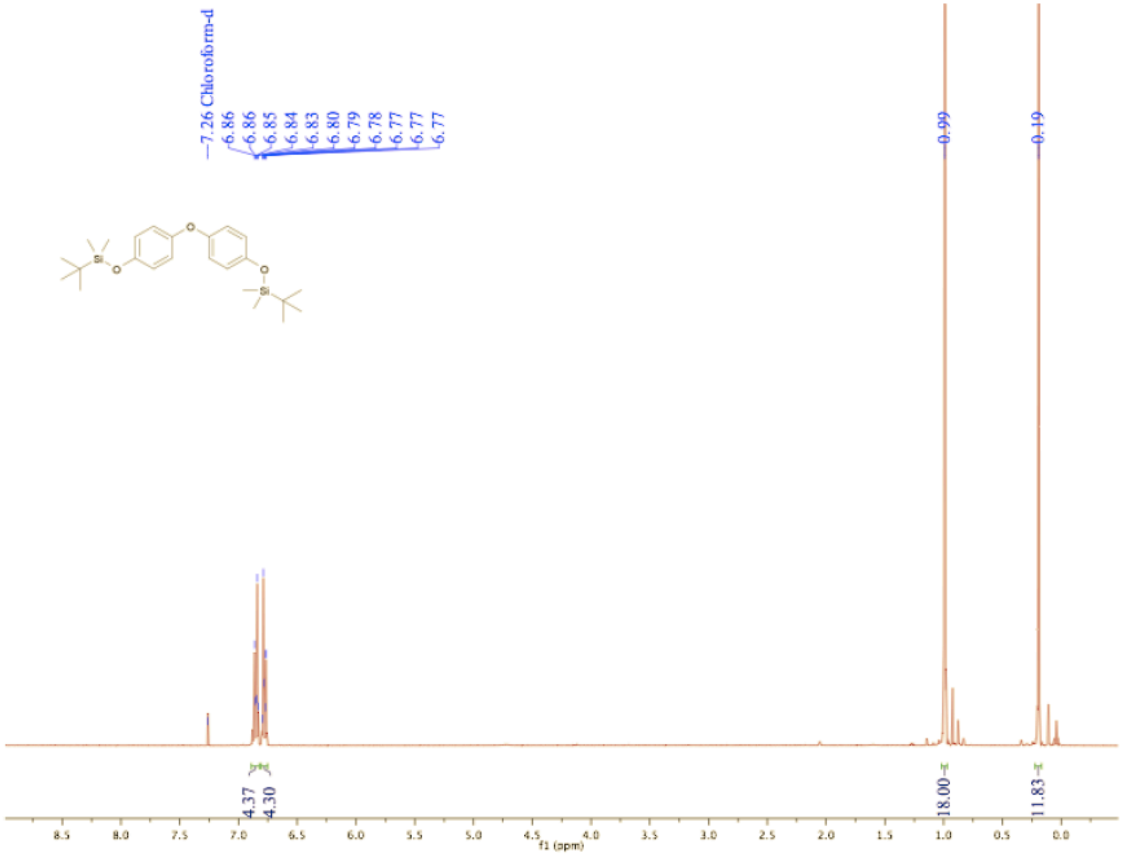

7.70
7.68
7.26 Chloroform-
7.13
7.12
7.00
7.00
6.98
6.97
0.36
1.94
1.91
1.84
18.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
H3C
H3C
CH3
Si
O
CH3
H3C
CH3
Si
O


153.54
136.17
129.27
125.40
120.00
114.02
77.16 Chloroform-
0.42
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)
H3C
H3C
CH3
Si
O
CH3
H3C
CH3
Si
O

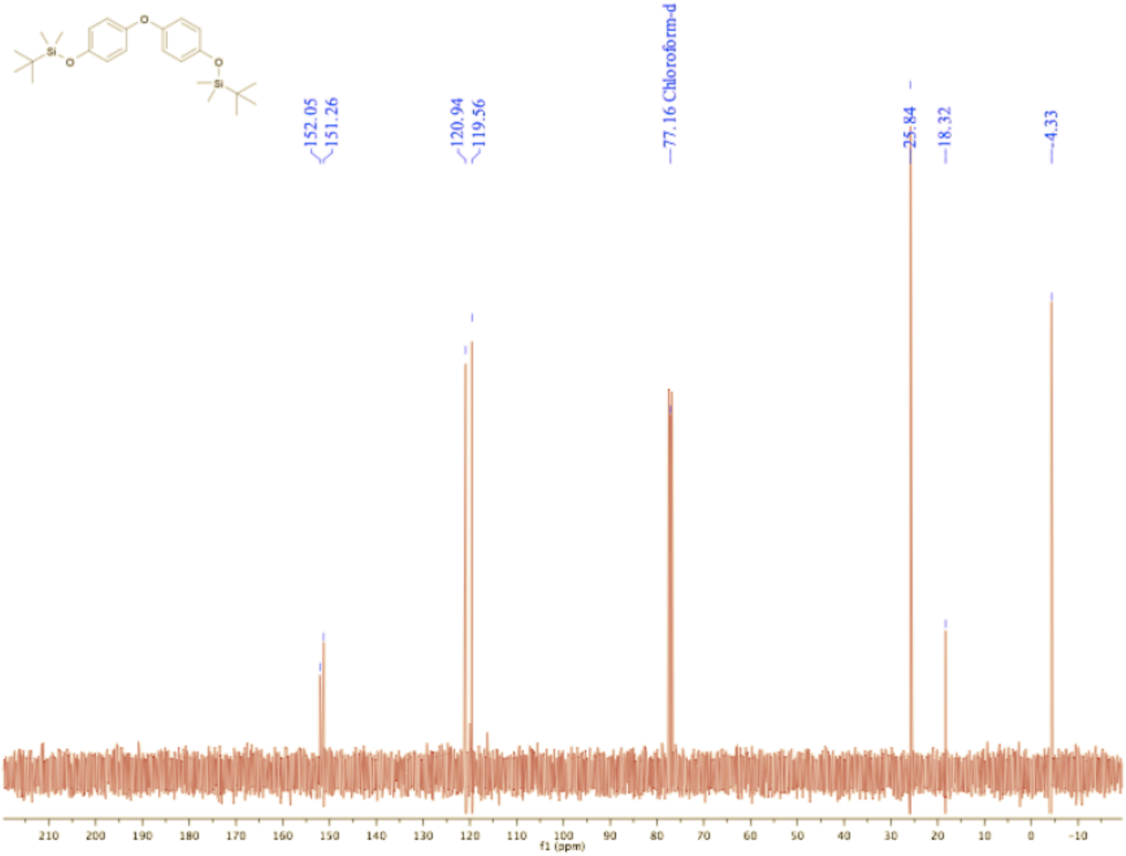

8.36
8.36
8.29
8.27
7.83
7.83
7.81
7.81
3.39
2.50 Dimethyl Sulfoxide-d
2.03
2.14
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)
F
O
S
O
O
O
S
O
F


148.27
133.30
131.55
120.90
119.48
39.52 Dimethyl Sulfoxide-d
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)
F
O
S
O
O
O
S
O
F

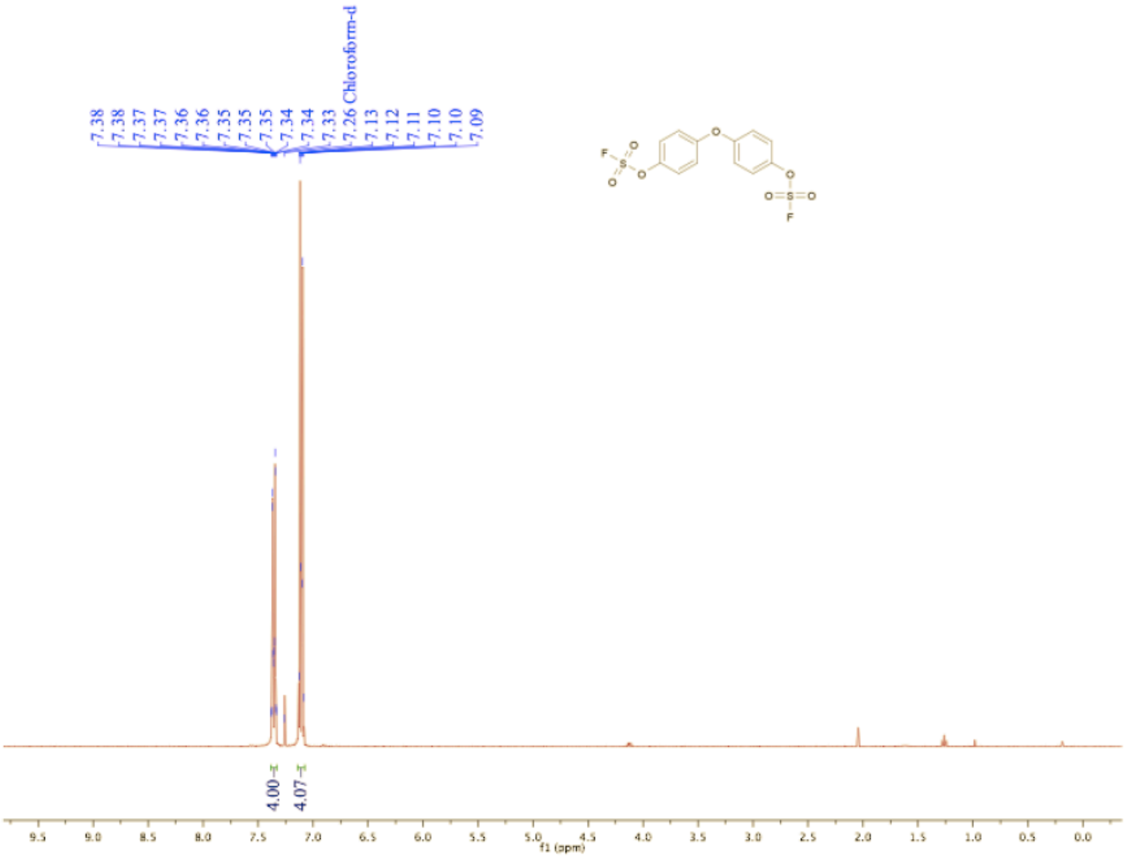

38.1
F
O
S
O
O
O
S
O
F
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

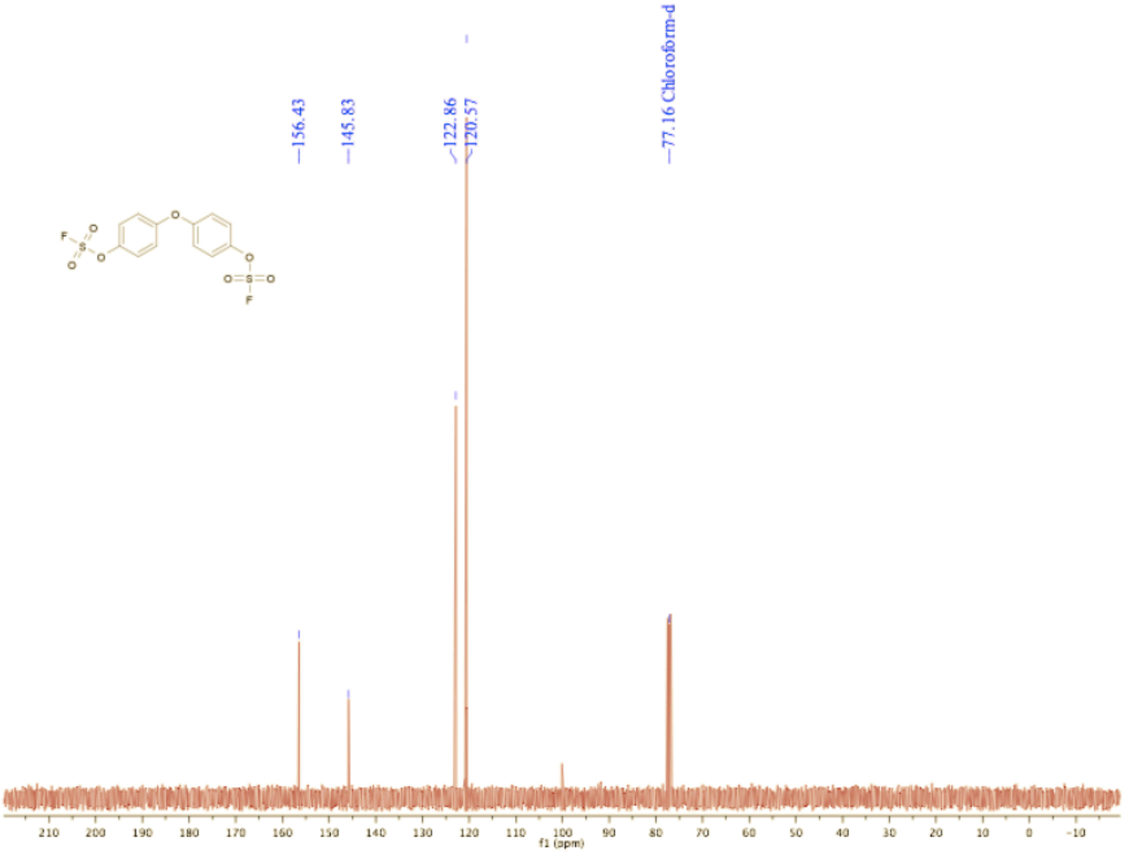


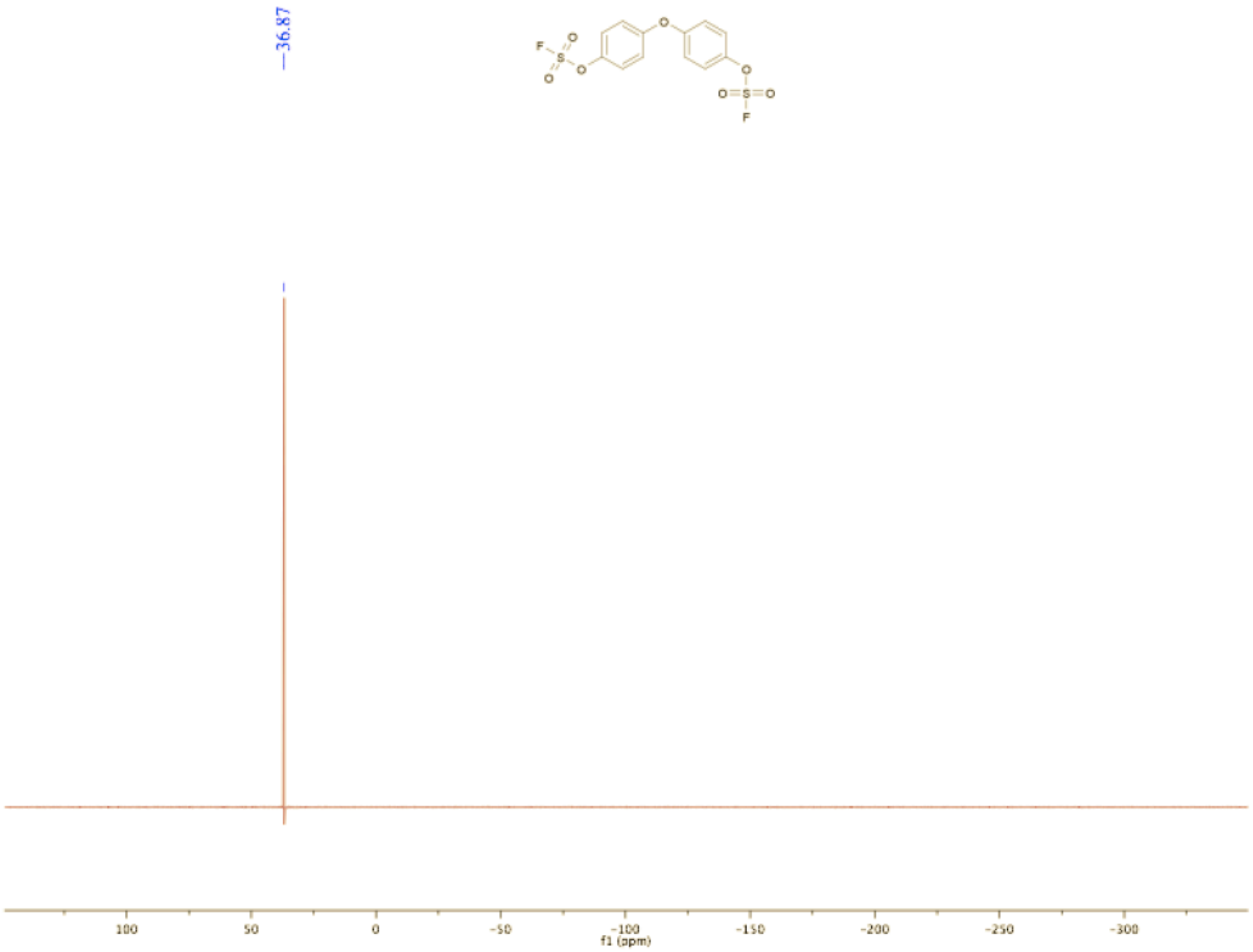
Si
O
O
O
Si
7.26 Chloroform-d
6.86
6.86
6.85
6.84
6.83
6.80
6.79
6.78
6.77
6.77
6.77
0.99
0.19
4.37
4.30
18.00
11.83
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



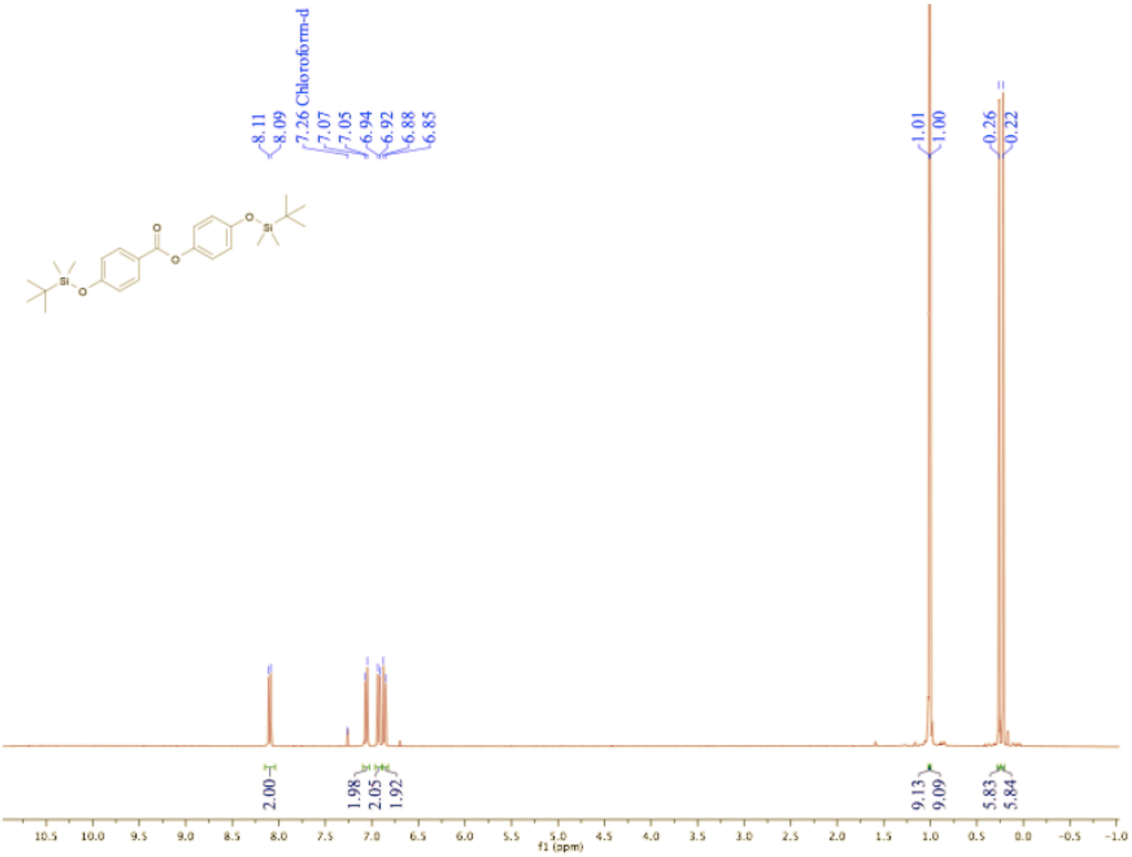
Si
O
O
O
Si
152.05
151.26
120.94
119.56
77.16 Chloroform-d
25.84
18.32
-4.33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

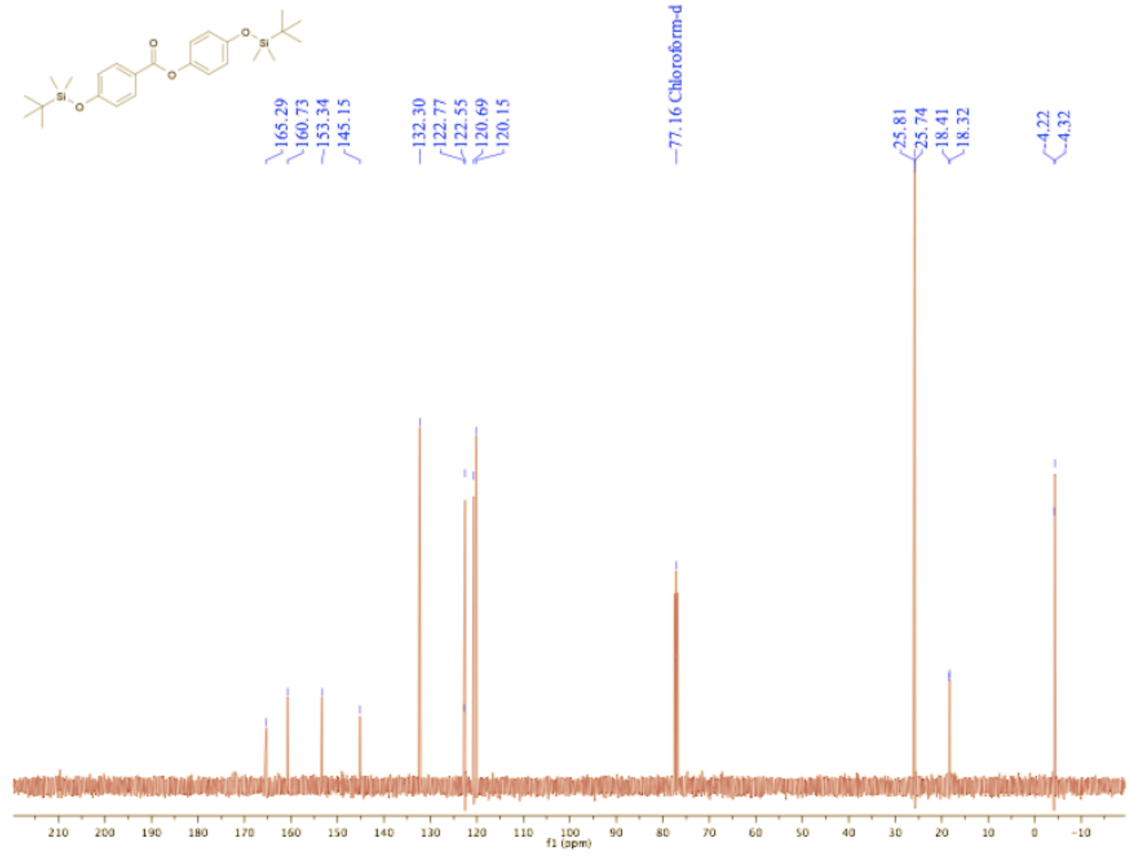

7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.26 Chloroform-d
7.13
7.12
7.11
7.10
7.10
7.09
4.00
4.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
F
S
O
O
O
O
O
O
S
O
F

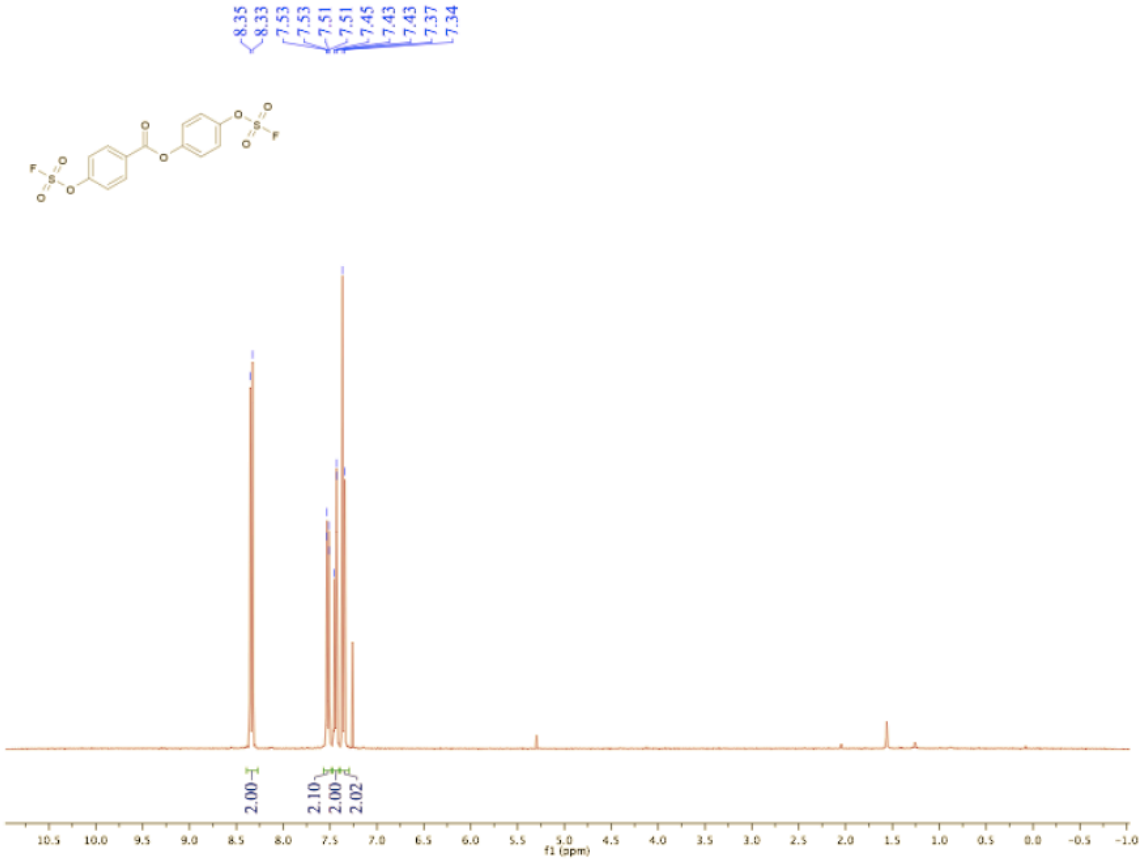

156.43
145.83
122.86
120.57
77.16 Chloroform-d
F
S
O
O
O
O
O
O
S
O
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

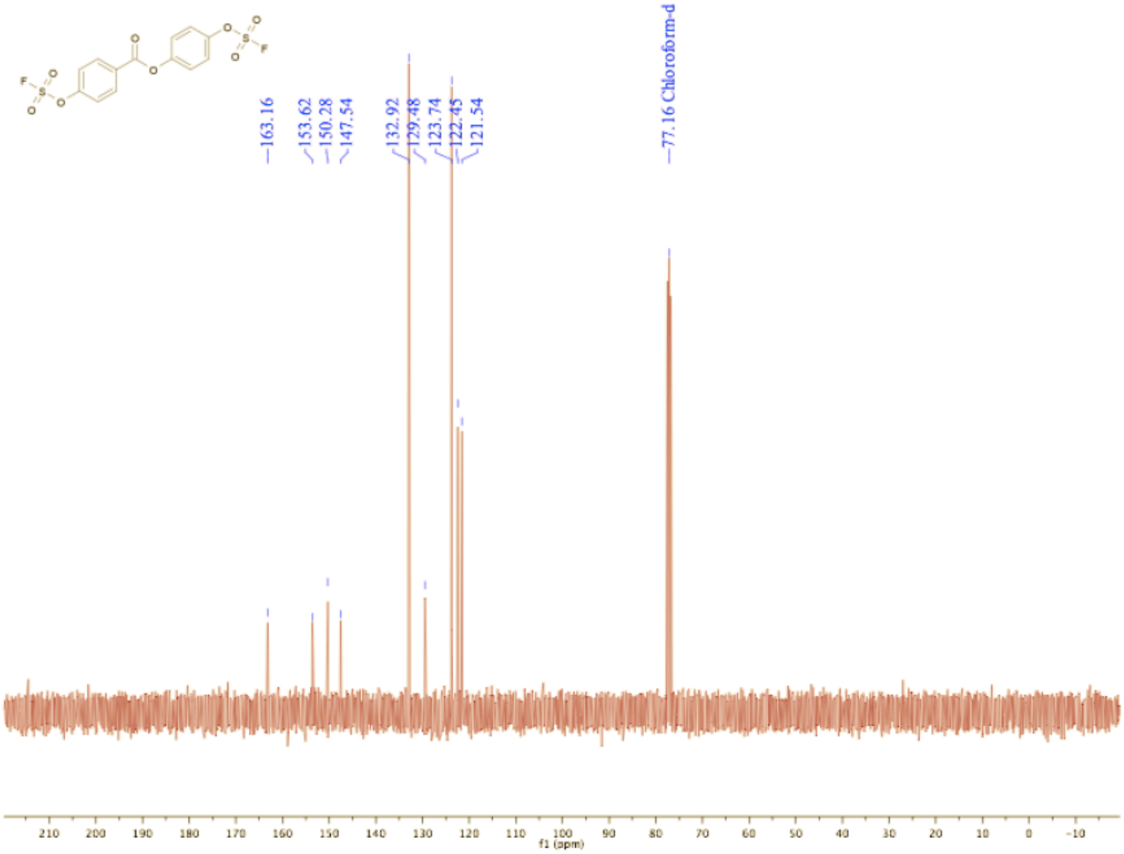


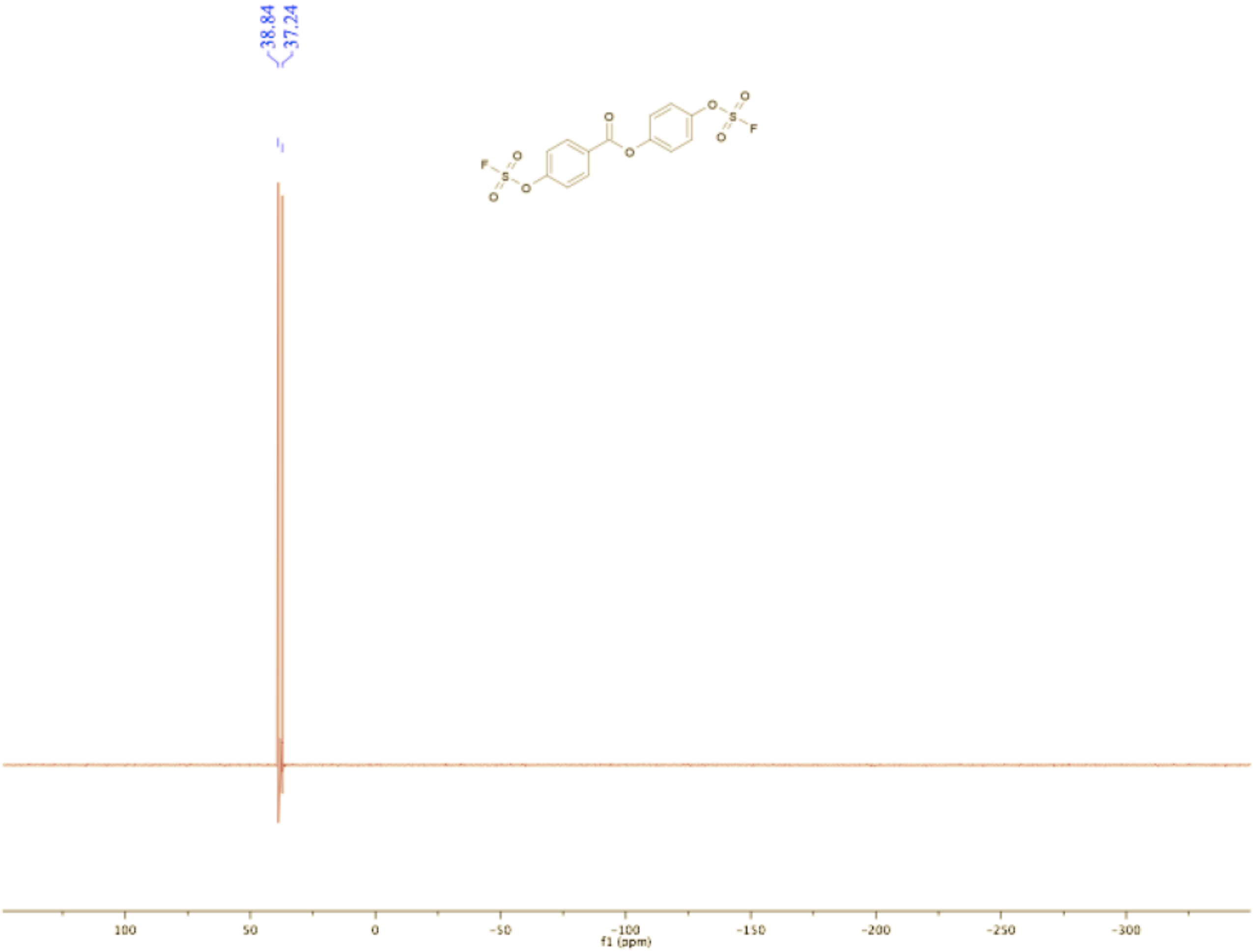
36.87
F
S
O
O
O
O
O
O
S
O
F
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

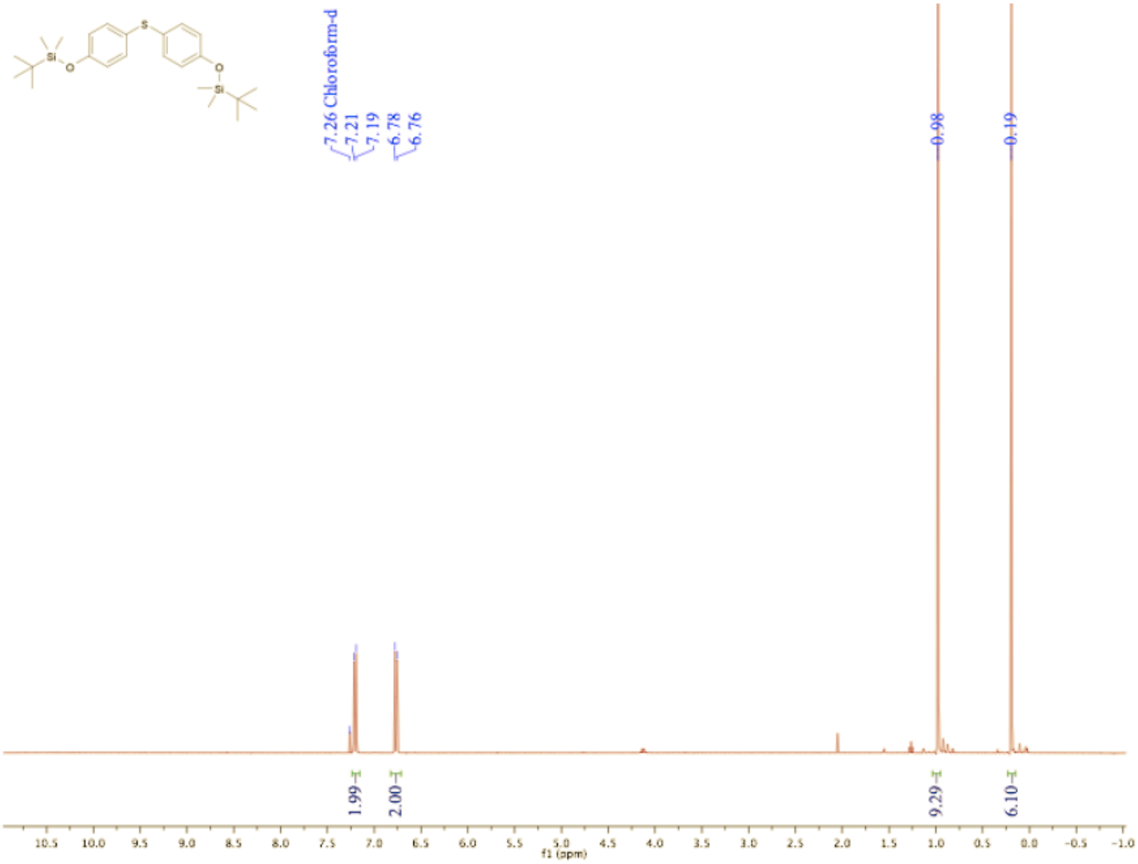

8.11
8.09
7.26 Chloroform-d
7.07
7.05
6.94
6.92
6.88
6.85
1.01
1.00
0.26
0.22
Si
O
O
O
O
Si
2.00
1.98
2.05
1.92
9.13
9.09
5.83
5.84
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


Si
O
O
O
O
Si
165.29
160.73
153.34
145.15
132.30
122.77
122.55
120.69
120.15
77.16 Chloroform-d
25.81
25.74
18.41
18.32
-4.22
-4.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

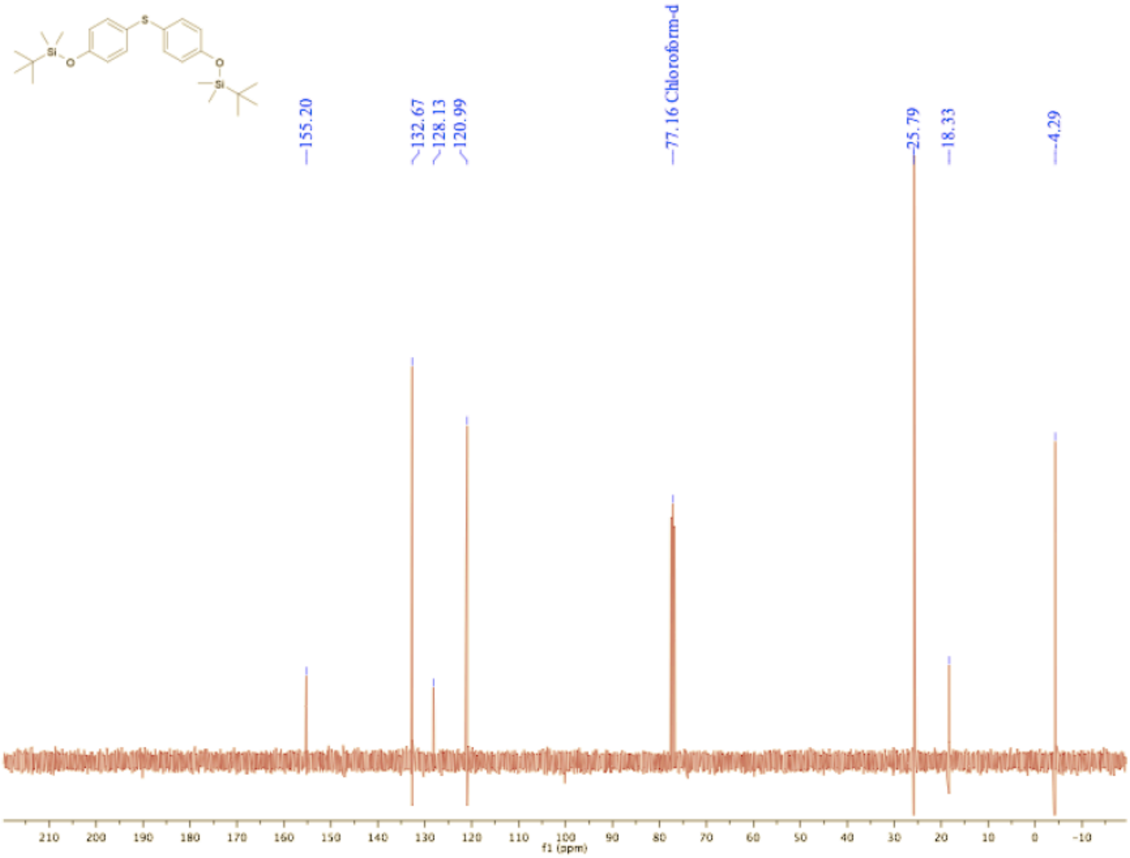

8.35
8.33
7.53
7.53
7.51
7.51
7.45
7.43
7.43
7.37
7.34
F
O
S
O
O
O
O
O
S
O
O
F
2.00
2.10
2.00
2.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


163.16
153.62
150.28
147.54
132.92
129.48
123.74
122.45
121.54
77.16 Chloroform-d
F
O
S
O
O
O
O
O
S
O
O
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

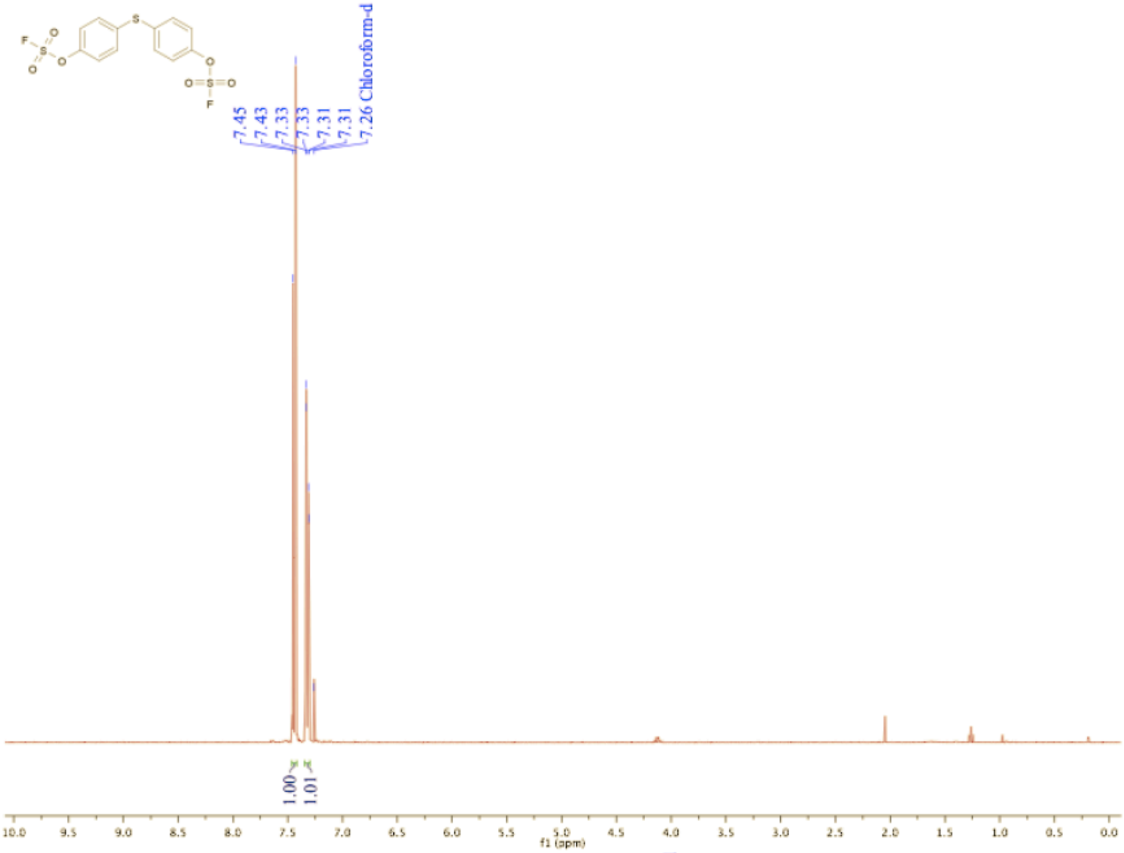

38.84
37.24
F
O
S
O
O
O
O
O
S
O
O
F
100
50
0
-50
-100
f1 (ppm)
-150
-200
-250
-300

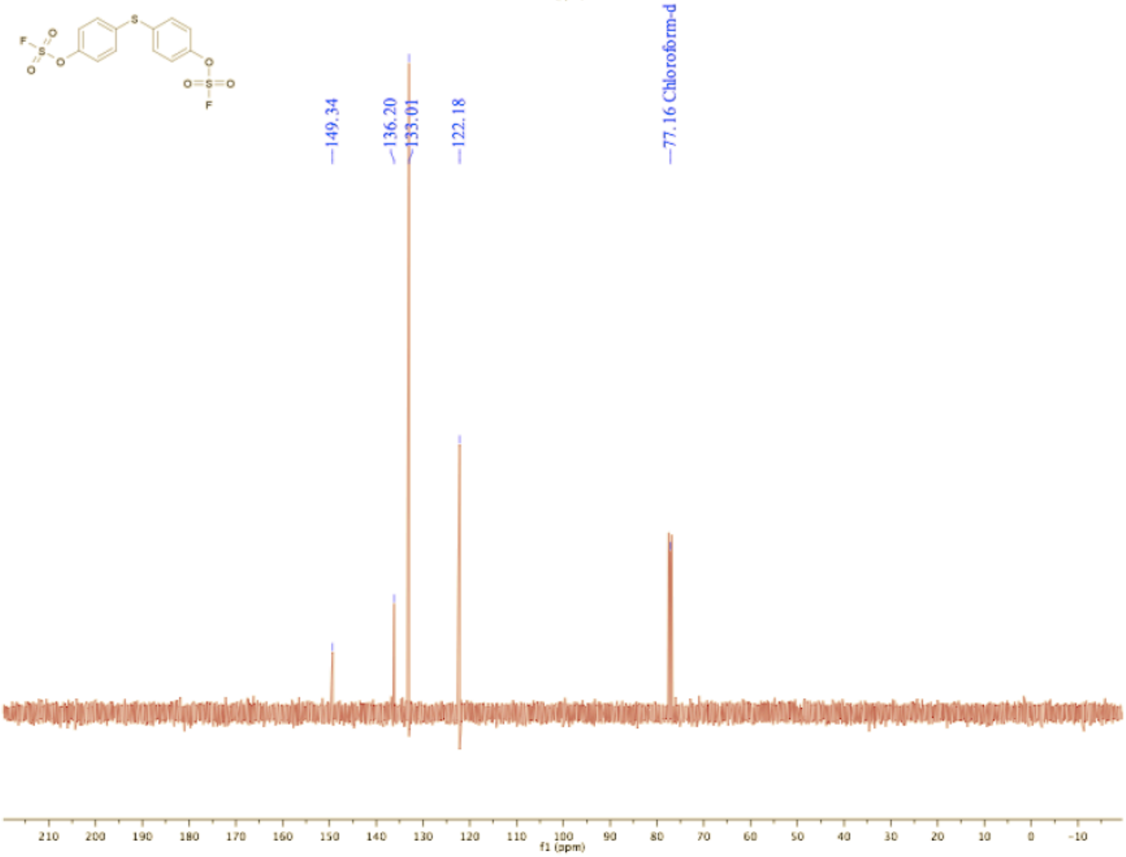


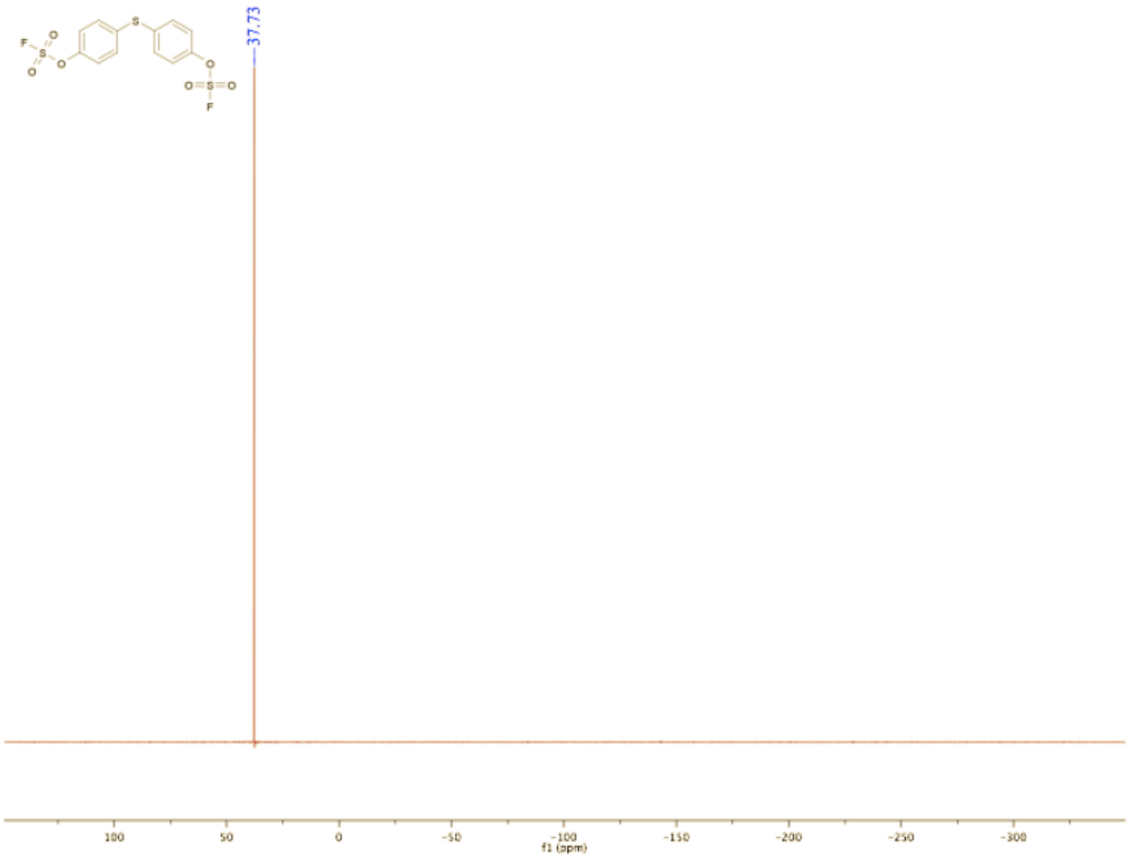
7.26 Chloroform-d
7.21
7.19
6.78
6.76
0.98
0.19
1.99
2.00
9.29
6.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

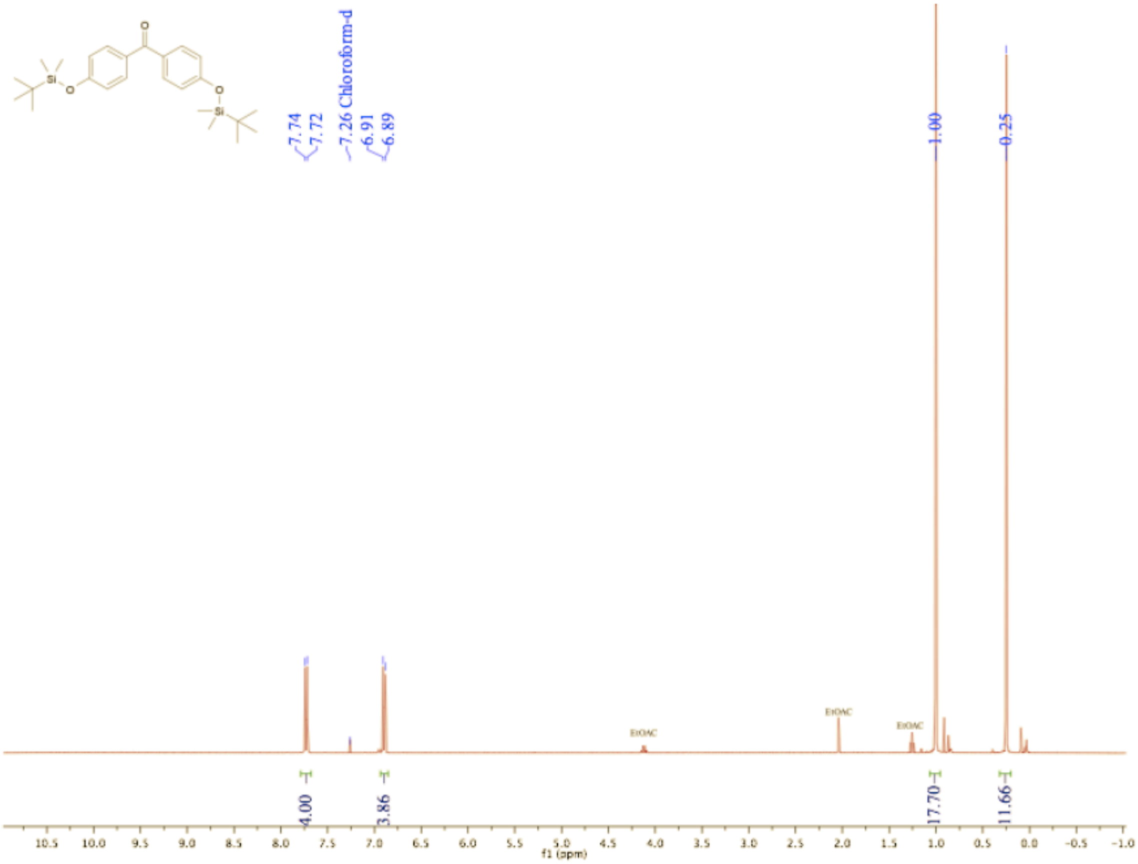


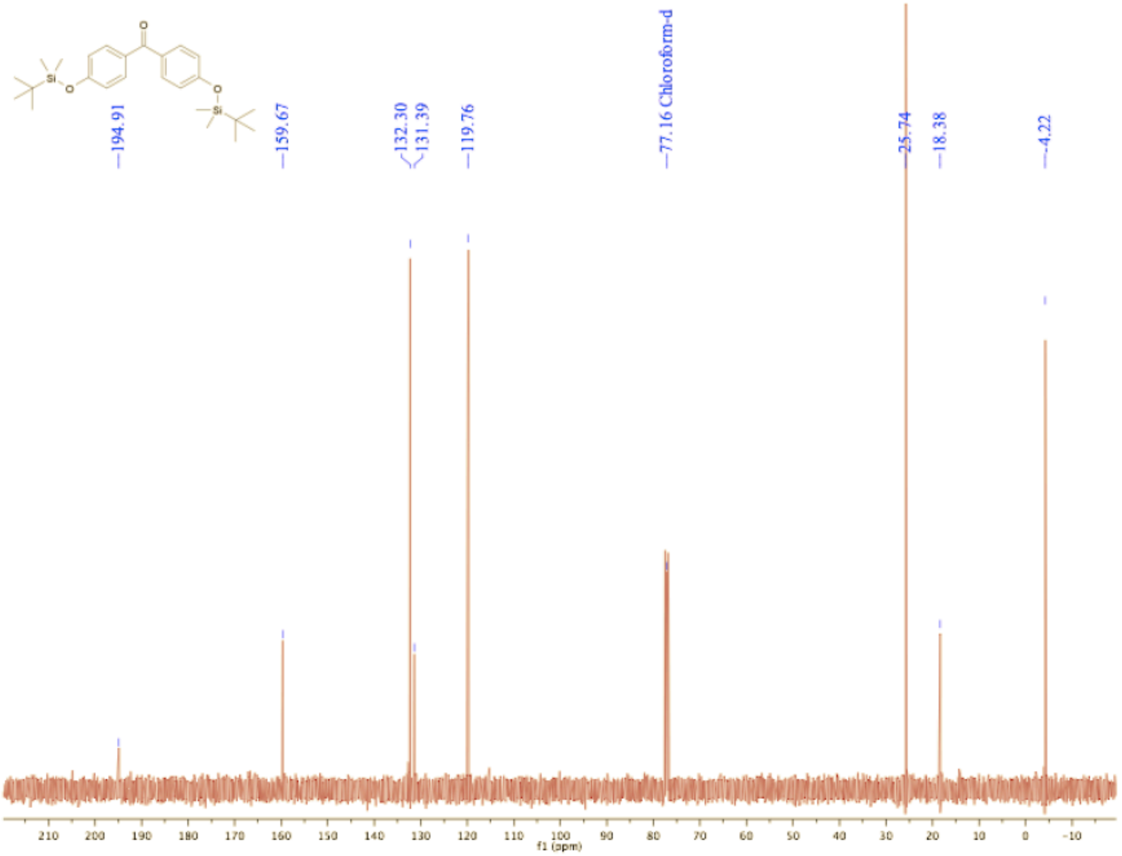
155.20
132.67
128.13
120.99
77.16 Chloroform-d
25.79
18.33
-4.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

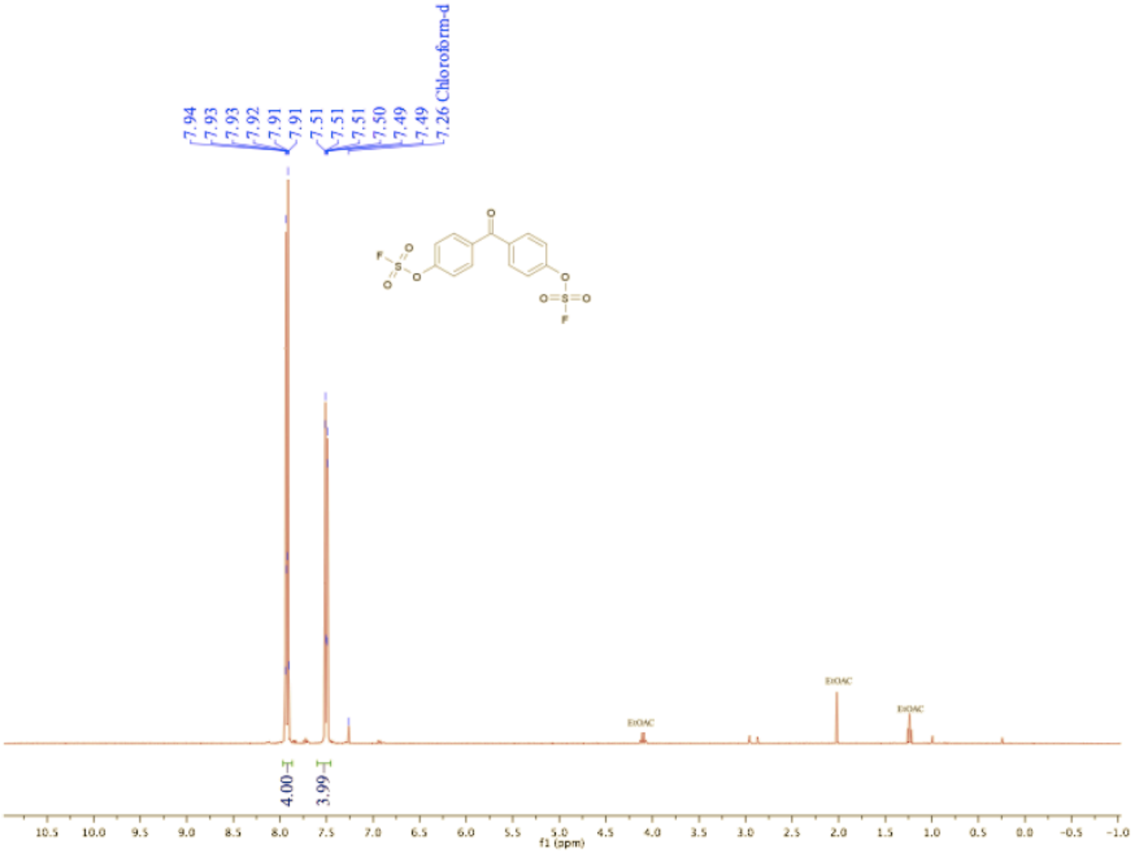

7.45
7.43
7.33
7.33
7.31
7.31
7.26 Chloroform-d
1.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
F S O O O S O S O F

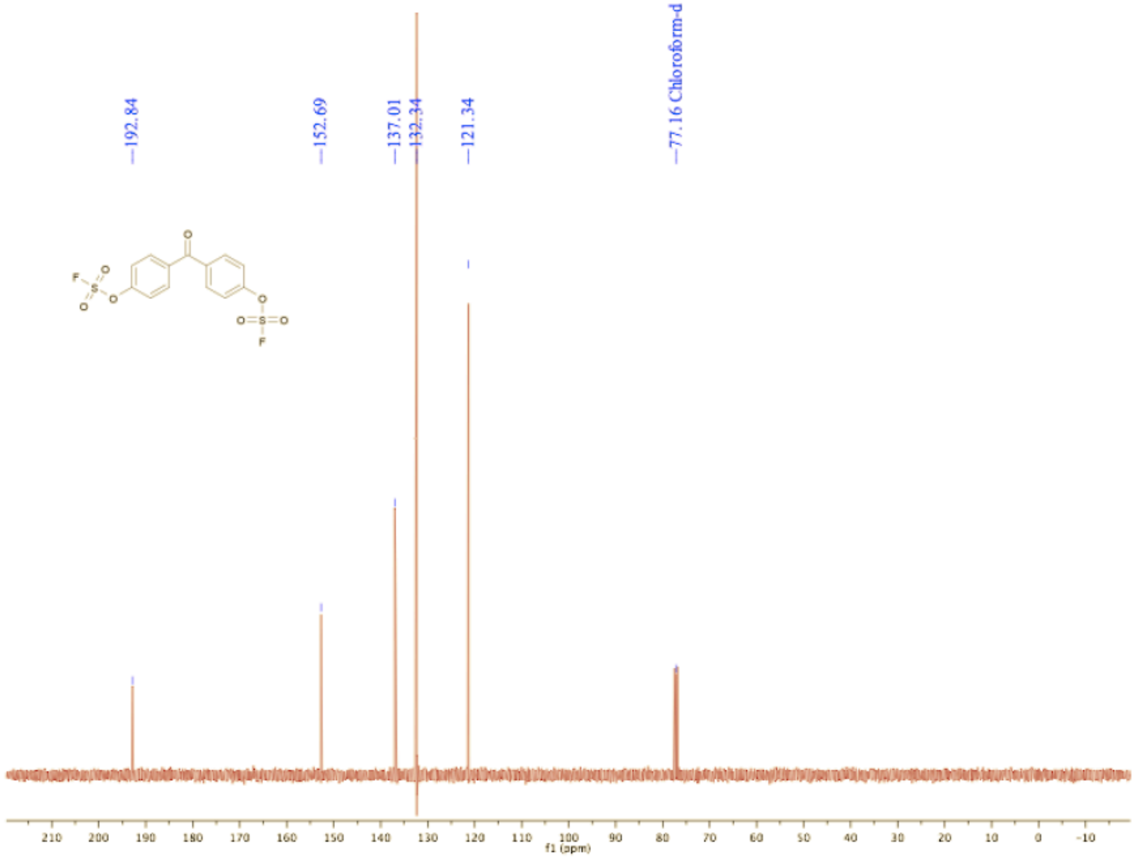

149.34
136.20
133.01
122.18
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
F S O O O S O S O F

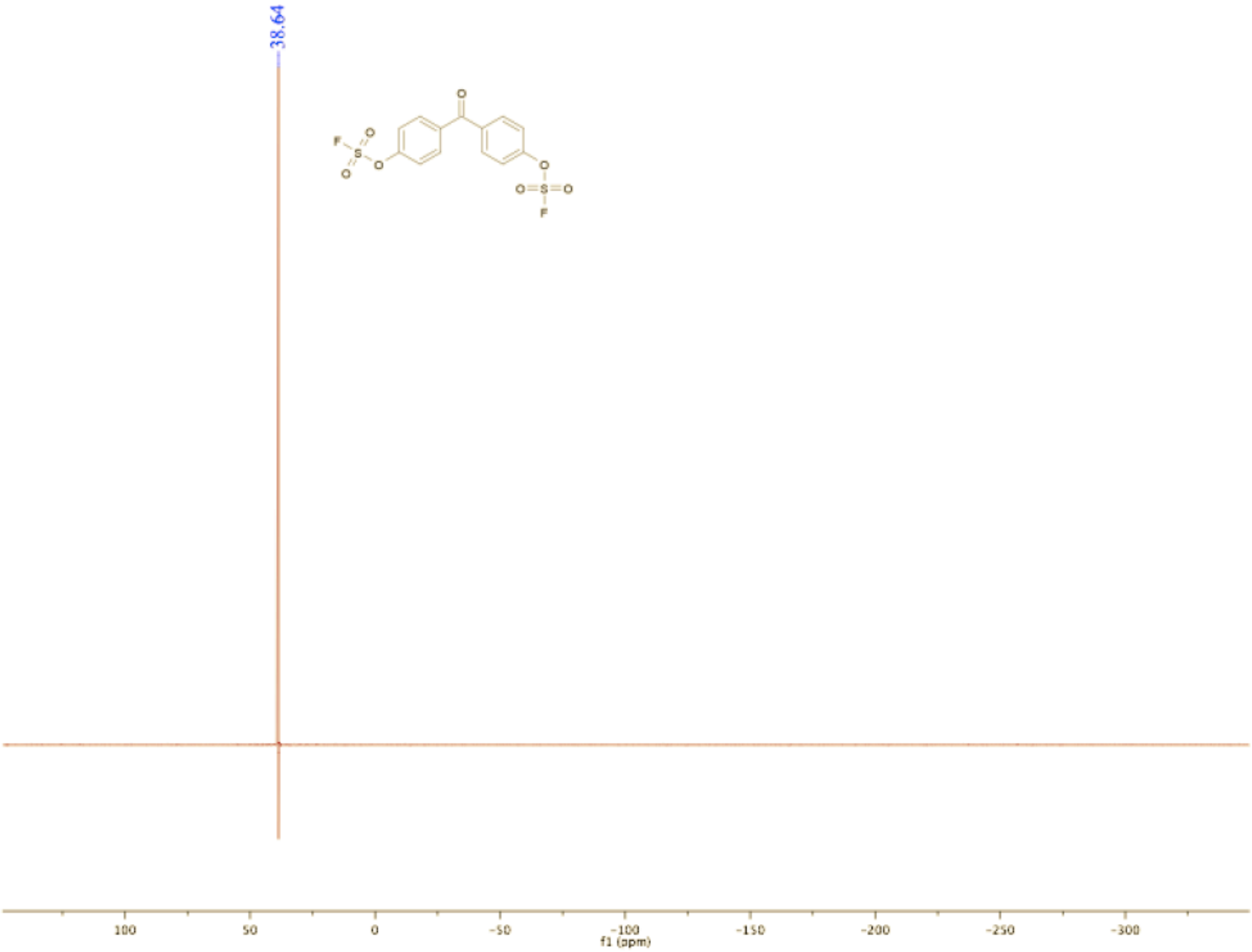

37.73
F
O
S
O
O
S
O
O
S
O
F
100
50
0
-50
-100
f1 (ppm)
-150
-200
-250
-300

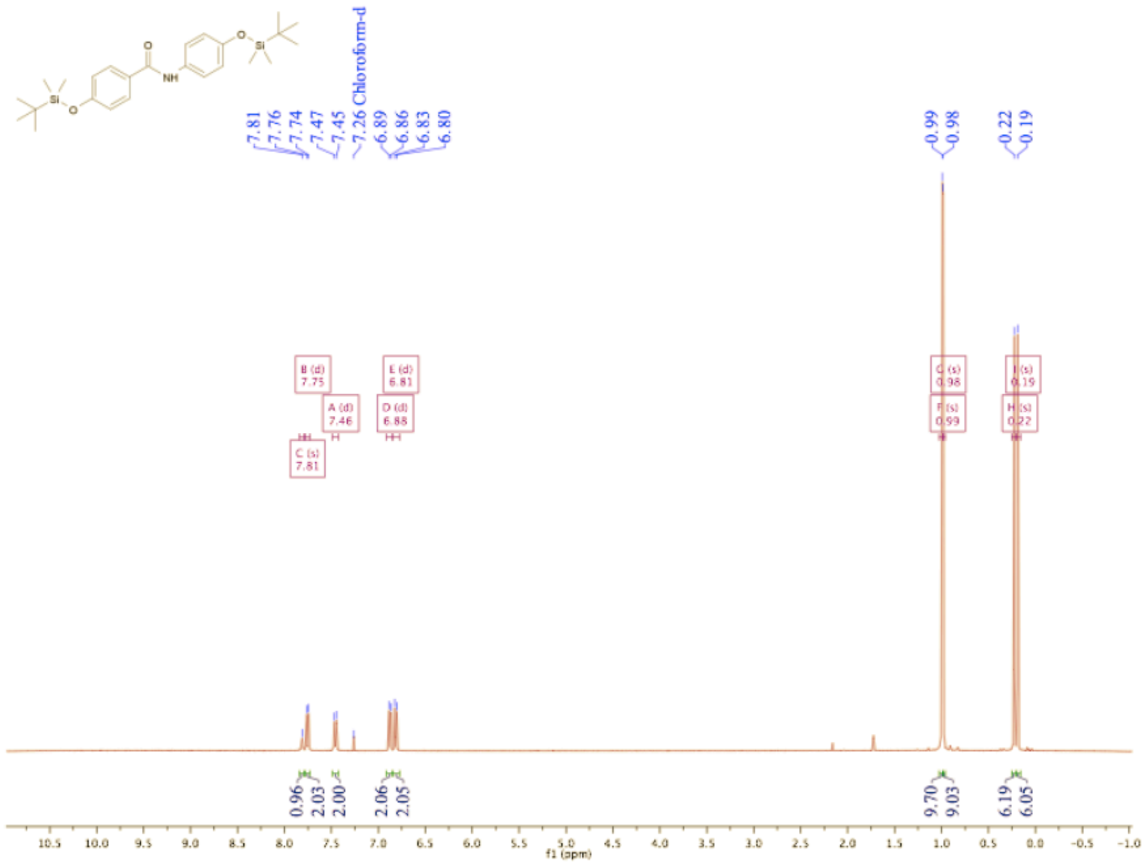

7.74
7.72
7.26 Chloroform-d
6.91
6.89
1.00
0.25
EtOAC
EtOAC
EtOAC
4.00
3.86
17.70
11.66
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

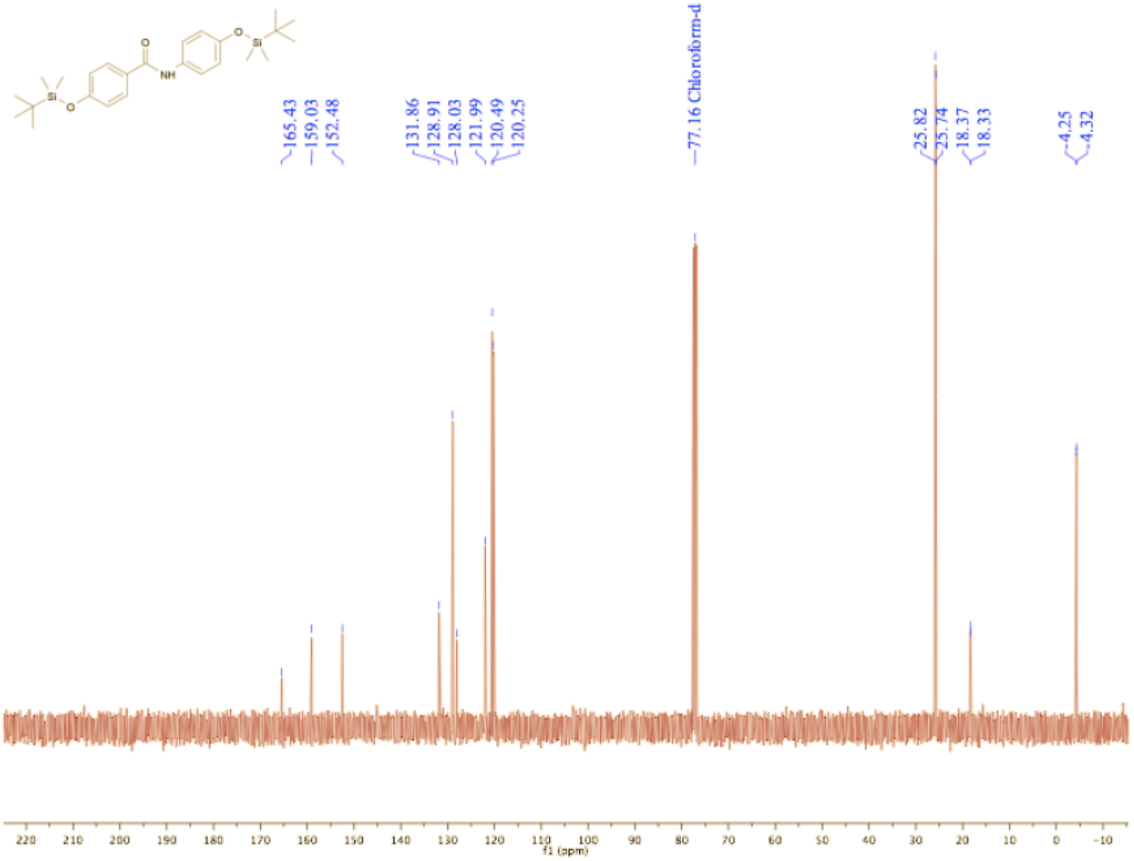

194.91
159.67
132.30
131.39
119.76
77.16 Chloroform-d
25.74
18.38
-4.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

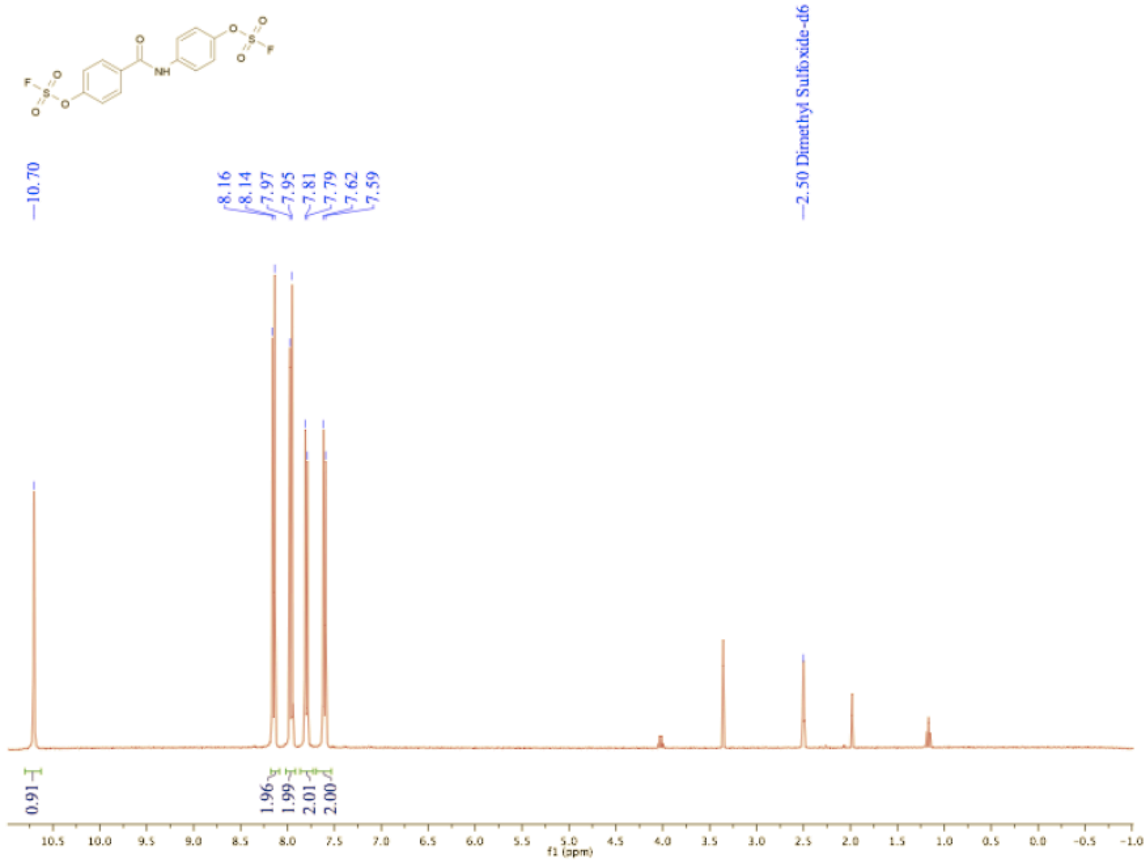

7.94
7.93
7.93
7.92
7.91
7.91
7.51
7.51
7.51
7.50
7.49
7.49
7.26 Chloroform-d
EtOAC
EtOAC
EtOAC
4.00
3.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
O
F
S
O
O
O
S
O
O
F


192.84
152.69
137.01
132.34
121.34
77.16 Chloroform-d
O
F
S
O
O
O
S
O
O
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

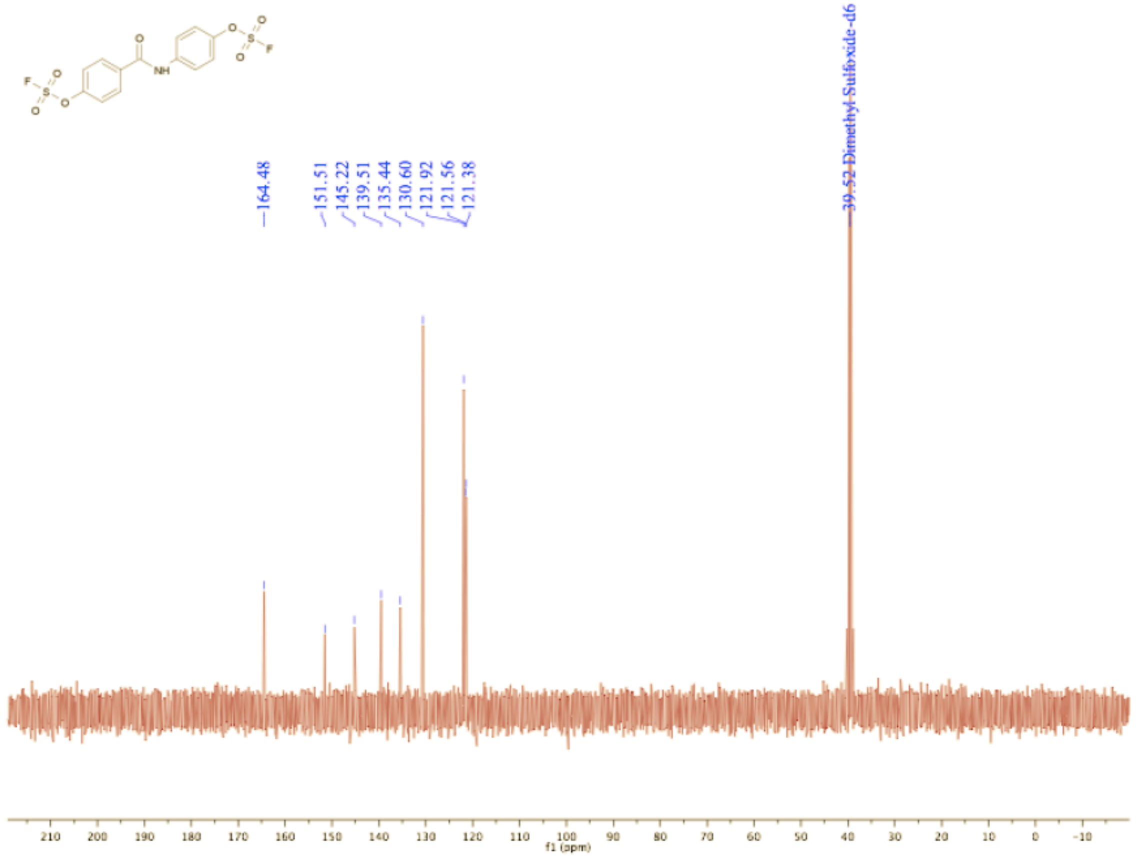

38.64
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)


NH
O
Si
7.81
7.76
7.74
7.47
7.45
7.26 Chloroform-d
6.89
6.86
6.83
6.80
0.99
0.98
0.22
0.19
B (d) 7.75
A (d) 7.46
C (s) 7.81
E (d) 6.81
D (d) 6.88
G (s) 0.98
F (s) 0.99
I (s) 0.19
H (s) 0.22
0.96
2.03
2.00
2.06
2.05
9.70
9.03
6.19
6.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

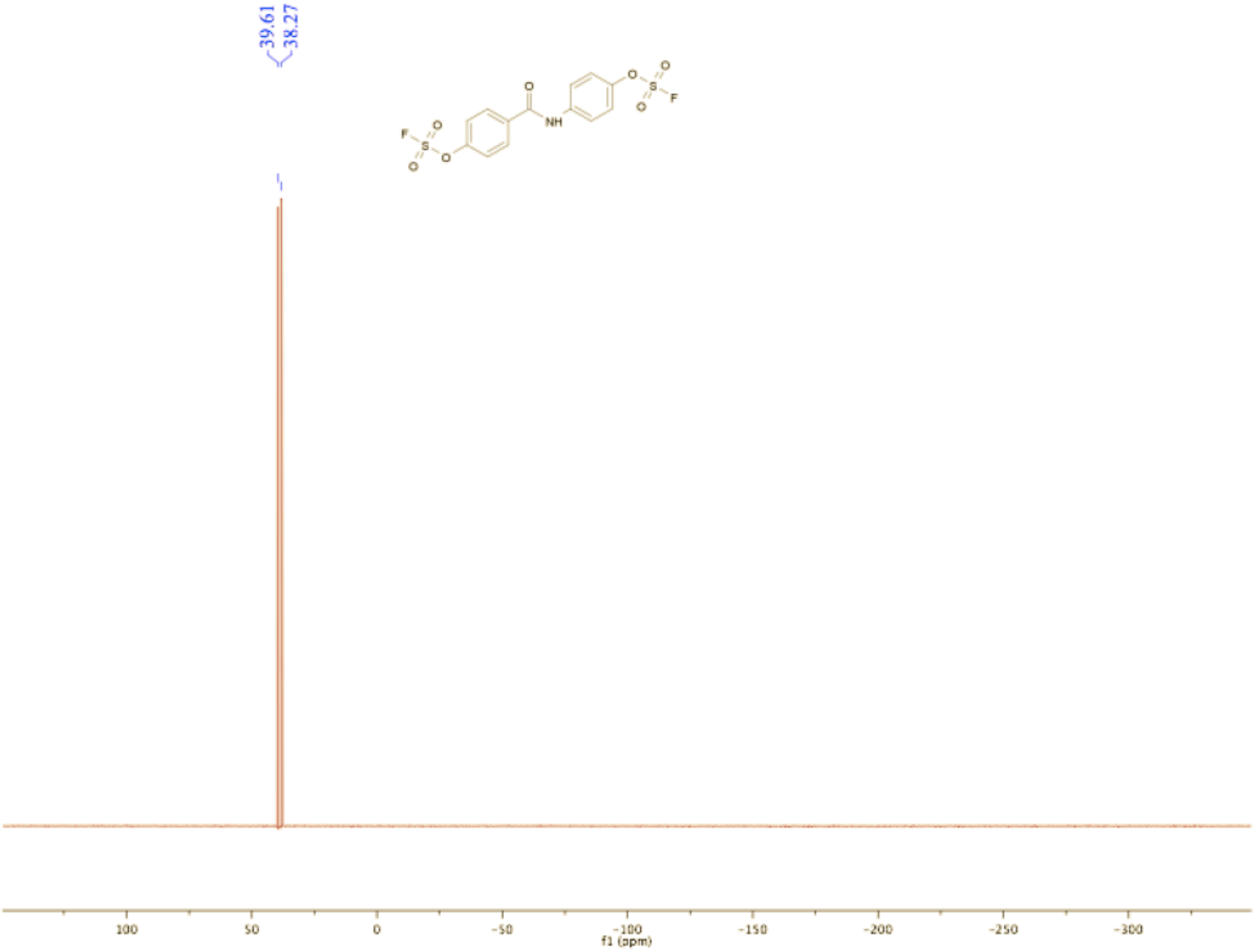

NH
O
Si
165.43
159.03
152.48
131.86
128.91
128.03
121.99
120.49
120.25
77.16 Chloroform-d
25.82
25.74
18.37
18.33
-4.25
-4.32
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

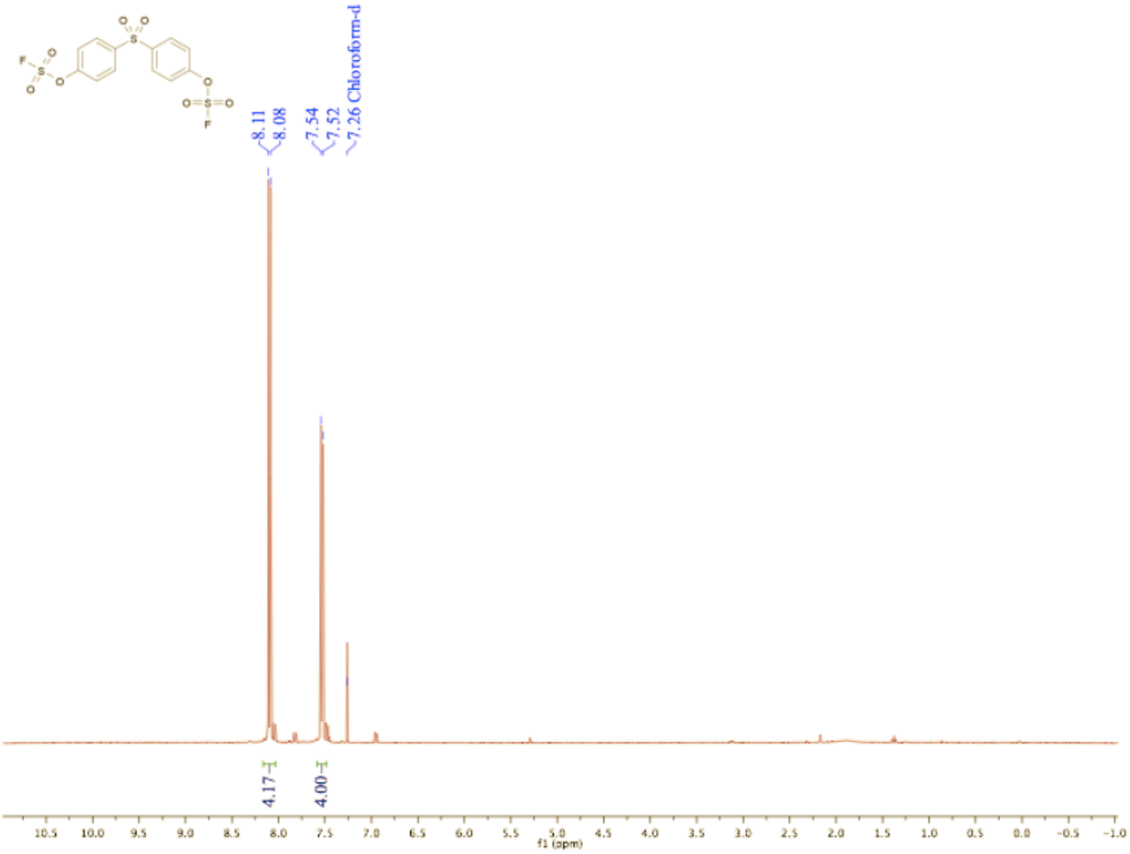


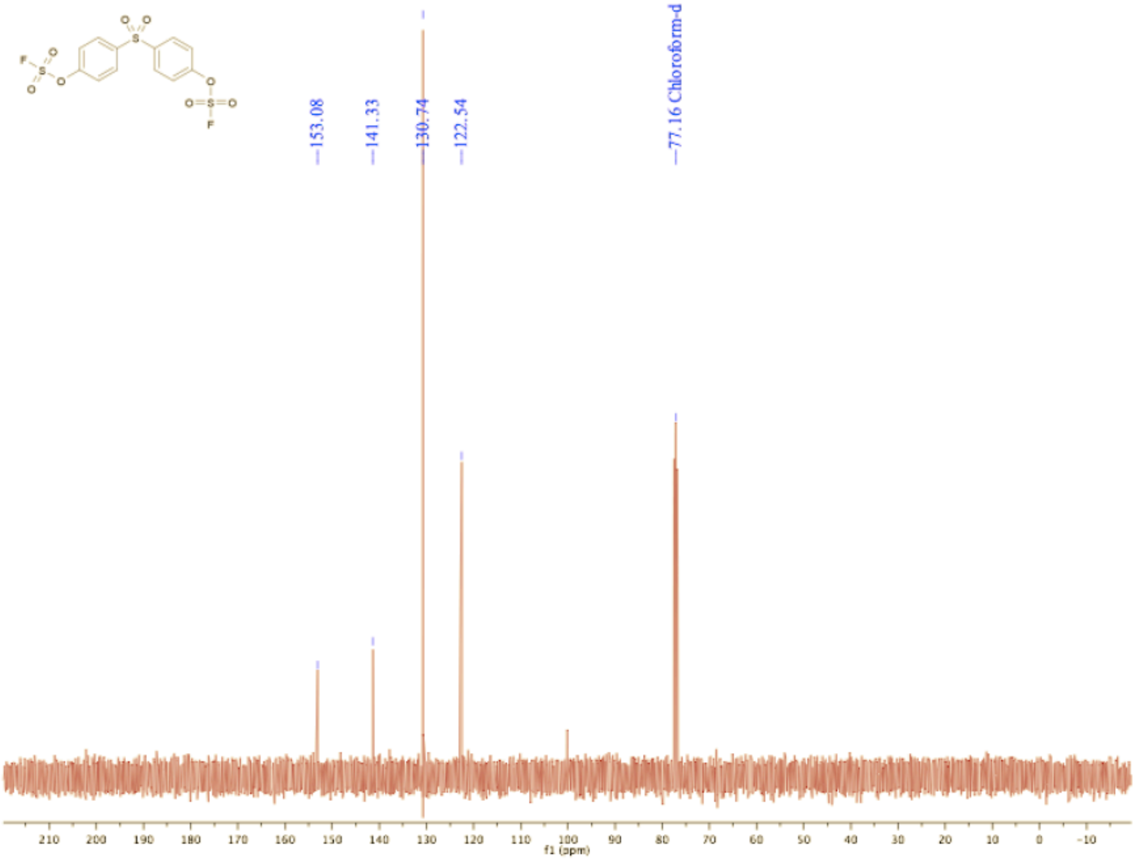
F
O
S
O
O
O
NH
O
S
O
F
O
10.70
8.16
8.14
7.97
7.95
7.81
7.79
7.62
7.59
2.50 Dimethyl Sulfoxide-d6
0.91
1.96
1.99
2.01
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

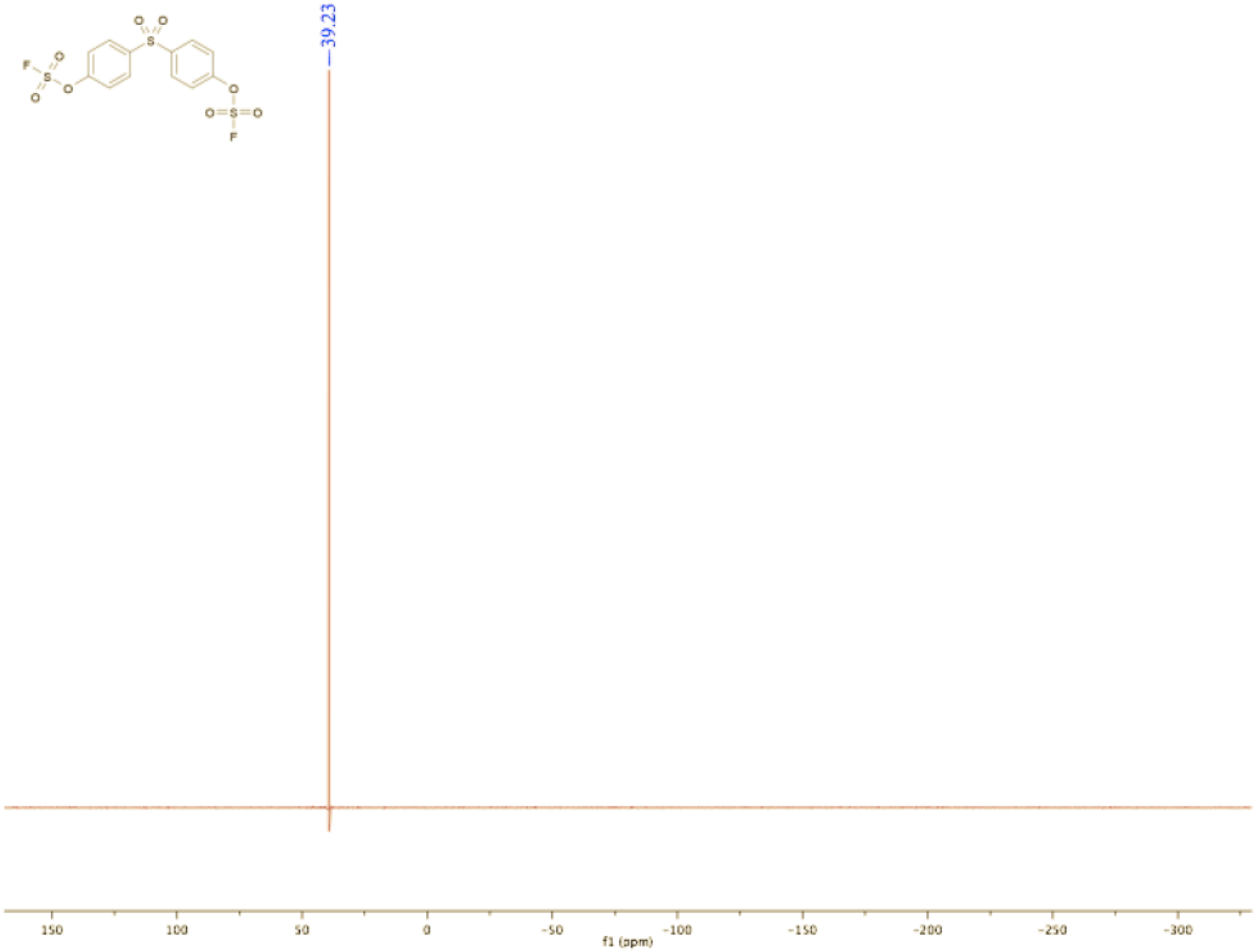


F
O
S
O
O
O
NH
O
S
O
F
O
164.48
151.51
145.22
139.51
135.44
130.60
121.92
121.56
121.38
39.52 Dimethyl Sulfoxide-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

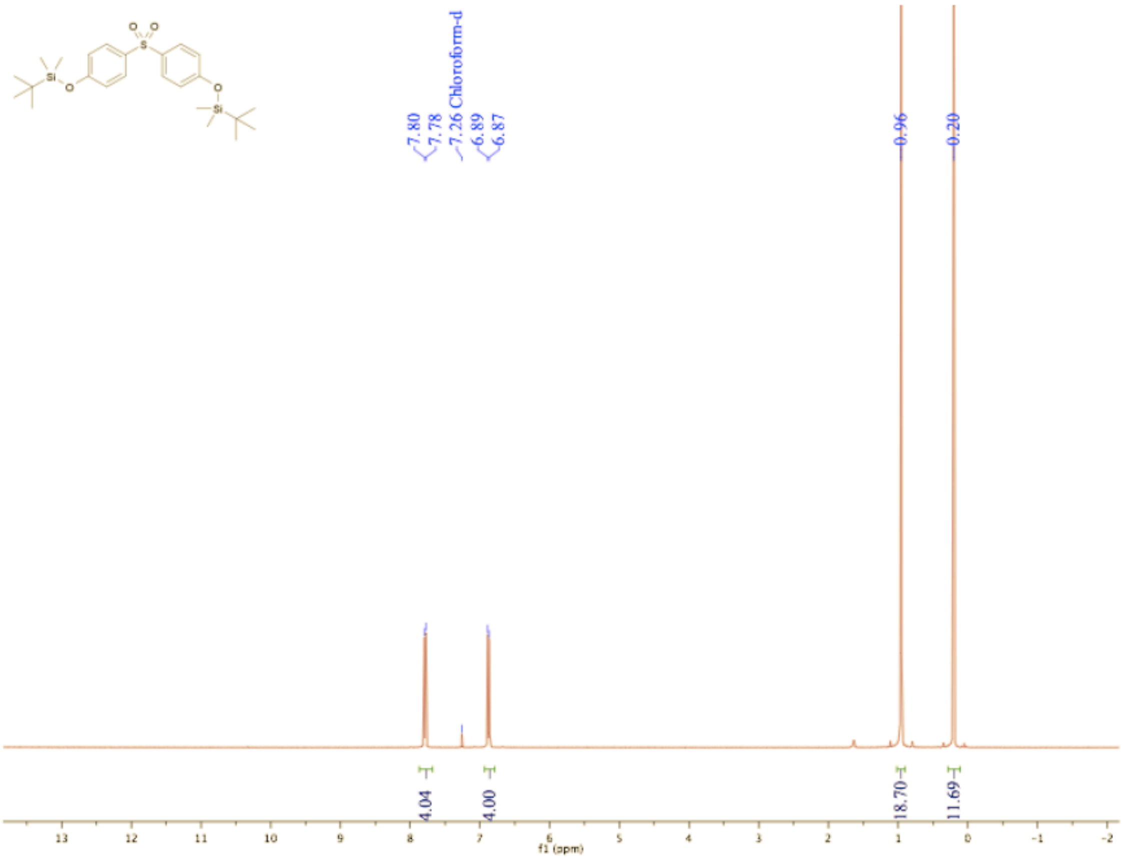

39.61
38.27
F
S
O
O
O
NH
O
O
S
O
F
100
50
0
-50
-100
f1 (ppm)
-150
-200
-250
-300

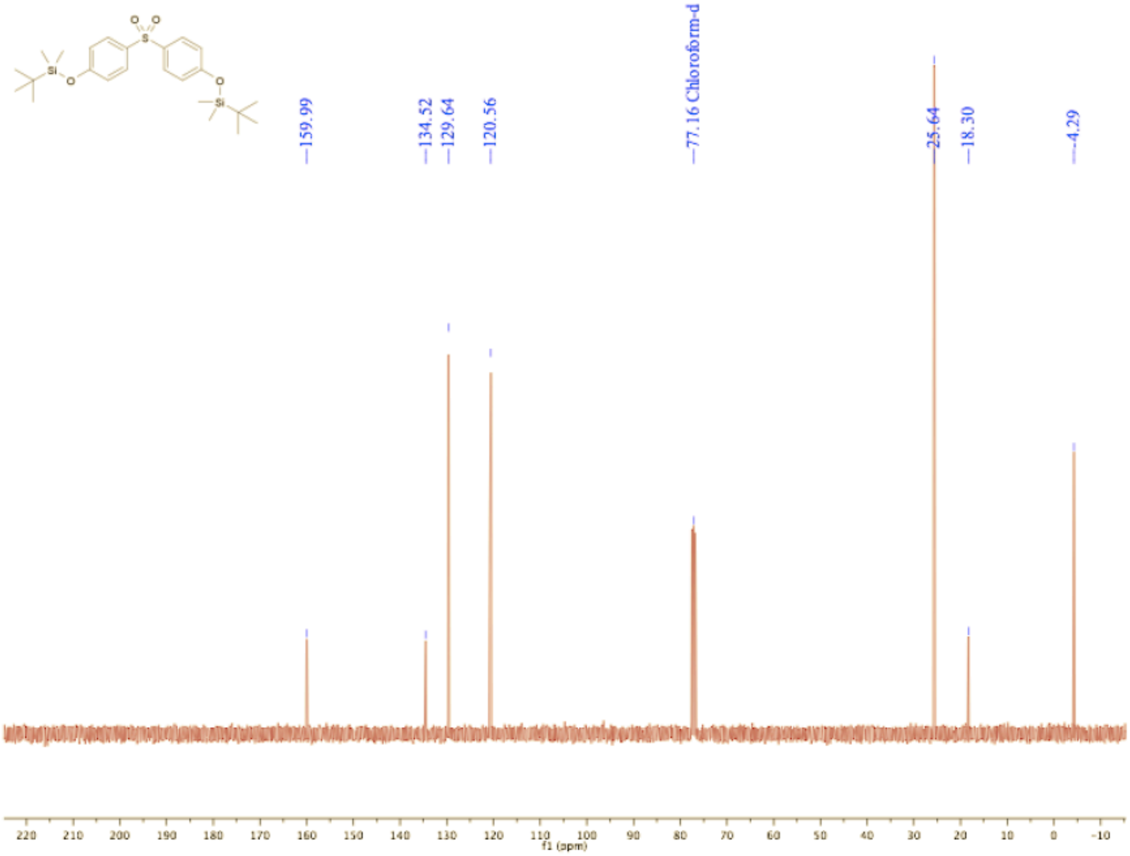

8.11
8.08
7.54
7.52
7.26 Chloroform-d
4.17
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

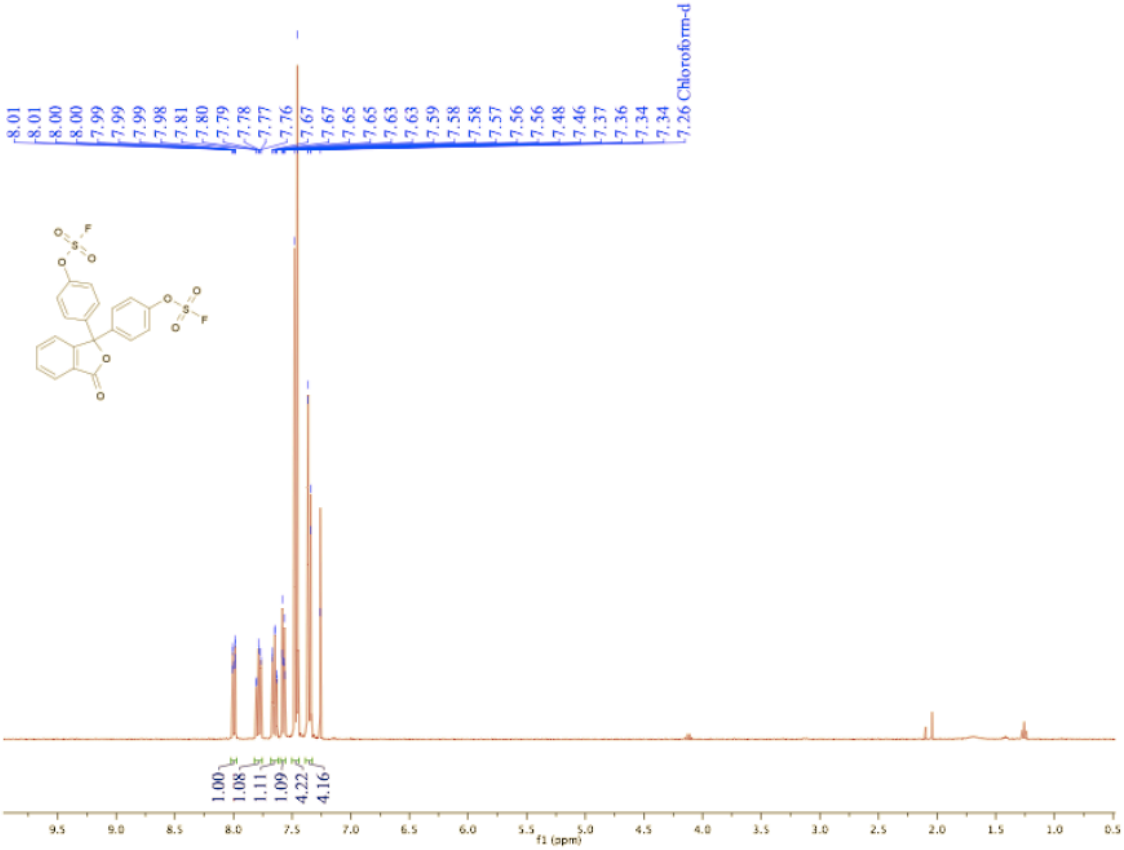

153.08
141.33
130.74
122.54
77.16 Chloroform-d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

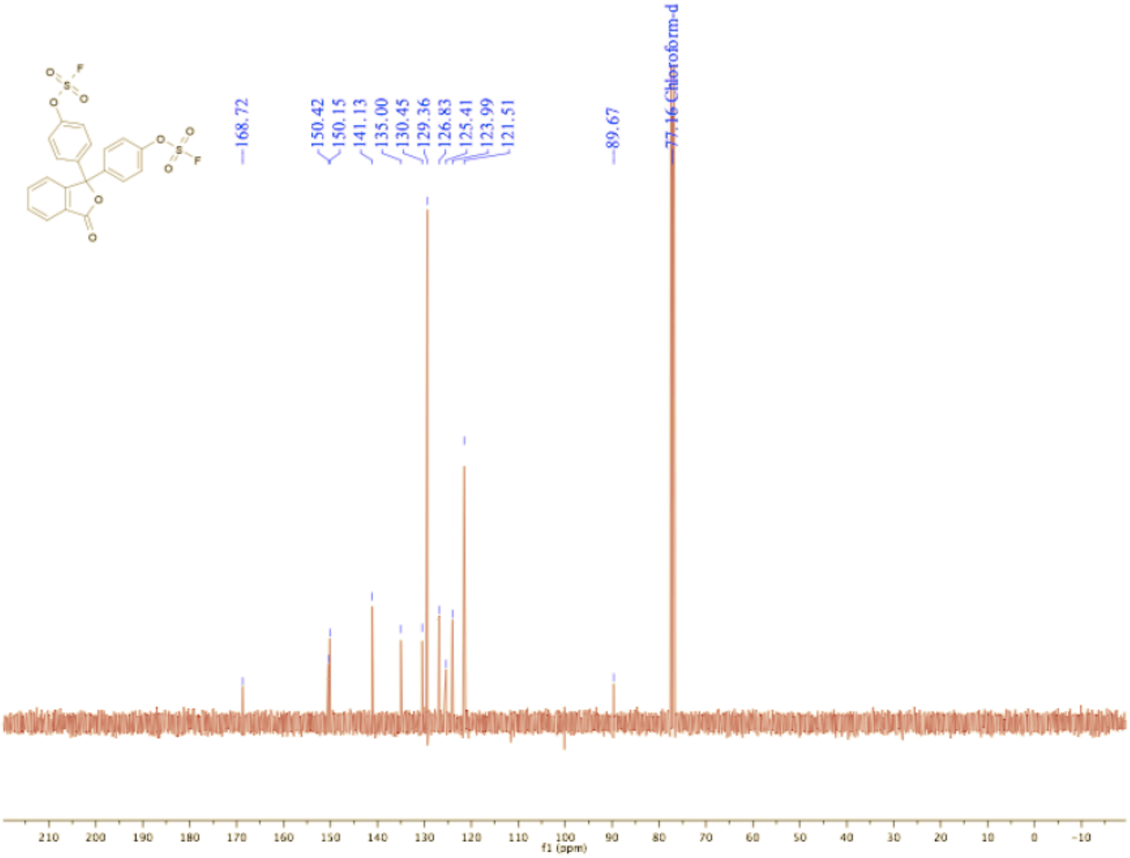


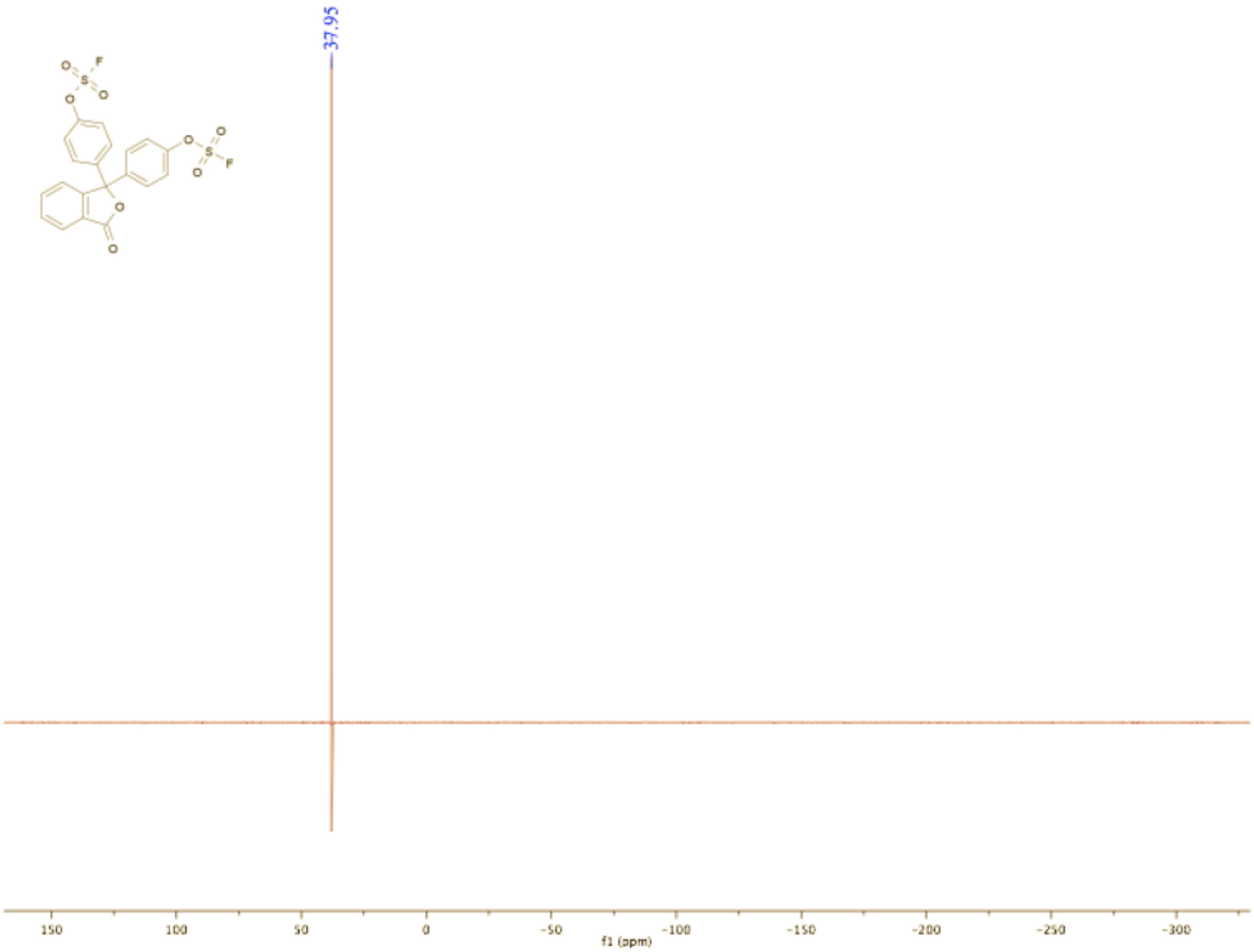
39.23
F
O
S
O
O
O
S
O
O
O
S
O
F
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)


O O
S
Si
O
O
Si
7.80
7.78
7.26 Chloroform-d
6.89
6.87
0.96
0.20
4.04
4.00
18.70
11.69
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

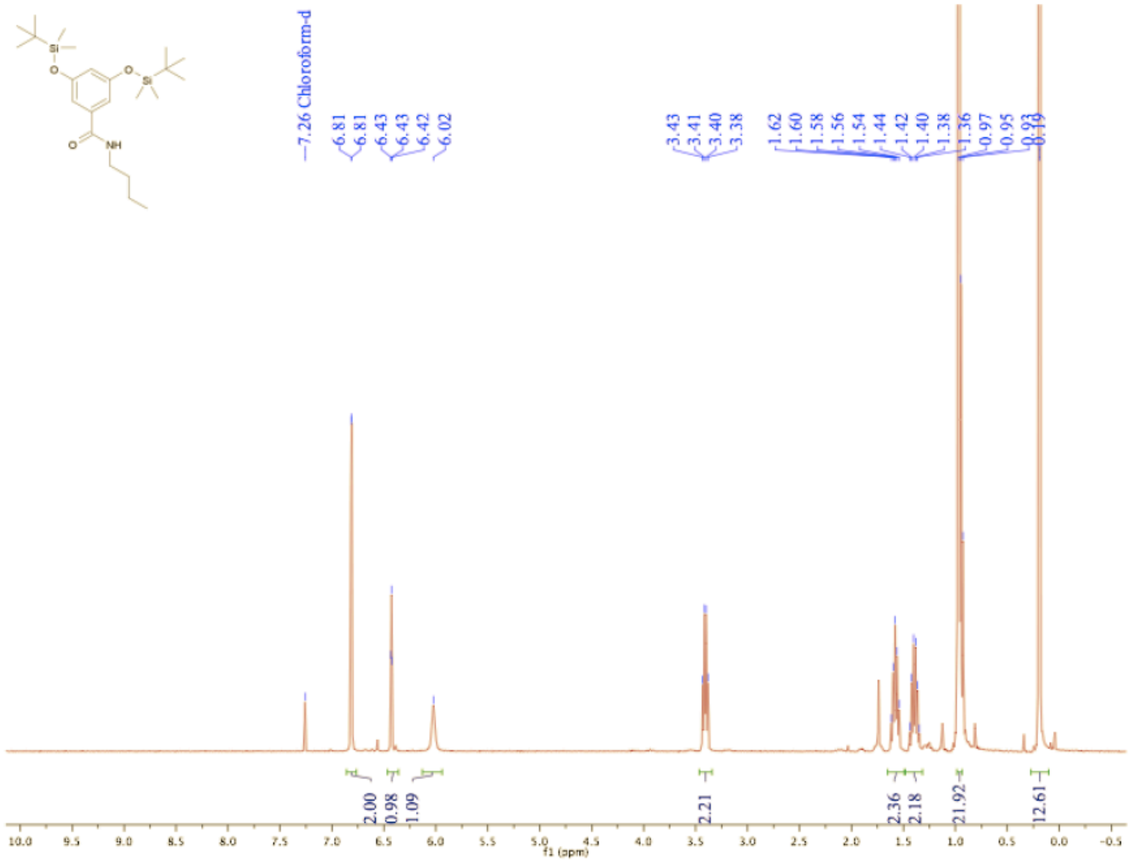

O O
S
Si
O
O
Si
159.99
134.52
129.64
120.56
77.16 Chloroform-d
25.64
18.30
-4.29
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.01
8.01
8.00
8.00
7.99
7.99
7.99
7.98
7.81
7.80
7.79
7.78
7.77
7.76
7.67
7.67
7.65
7.65
7.63
7.63
7.59
7.58
7.58
7.57
7.56
7.56
7.48
7.46
7.37
7.36
7.34
7.34
7.26 Chloroform-d
1.00
1.08
1.11
1.09
4.22
4.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

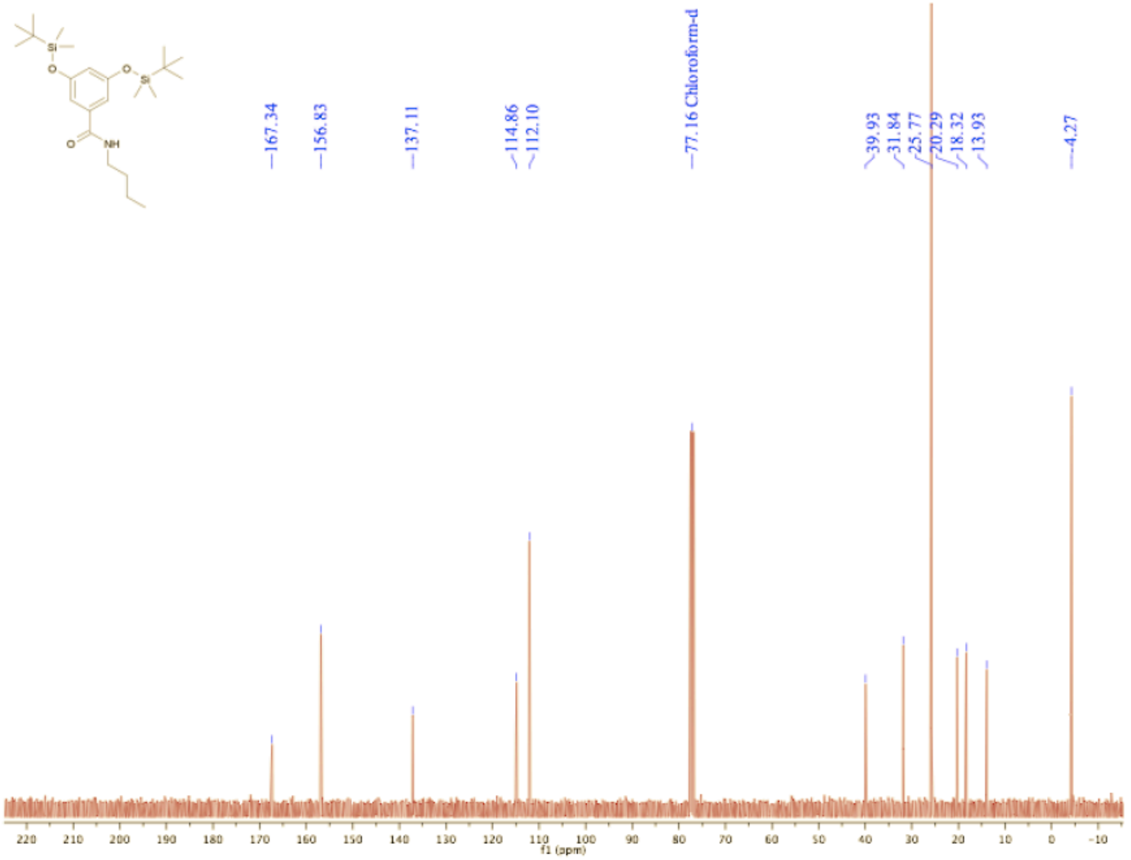

168.72
150.42
150.15
141.13
135.00
130.45
129.36
126.83
125.41
123.99
121.51
89.67
77.16 Chloroform-d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



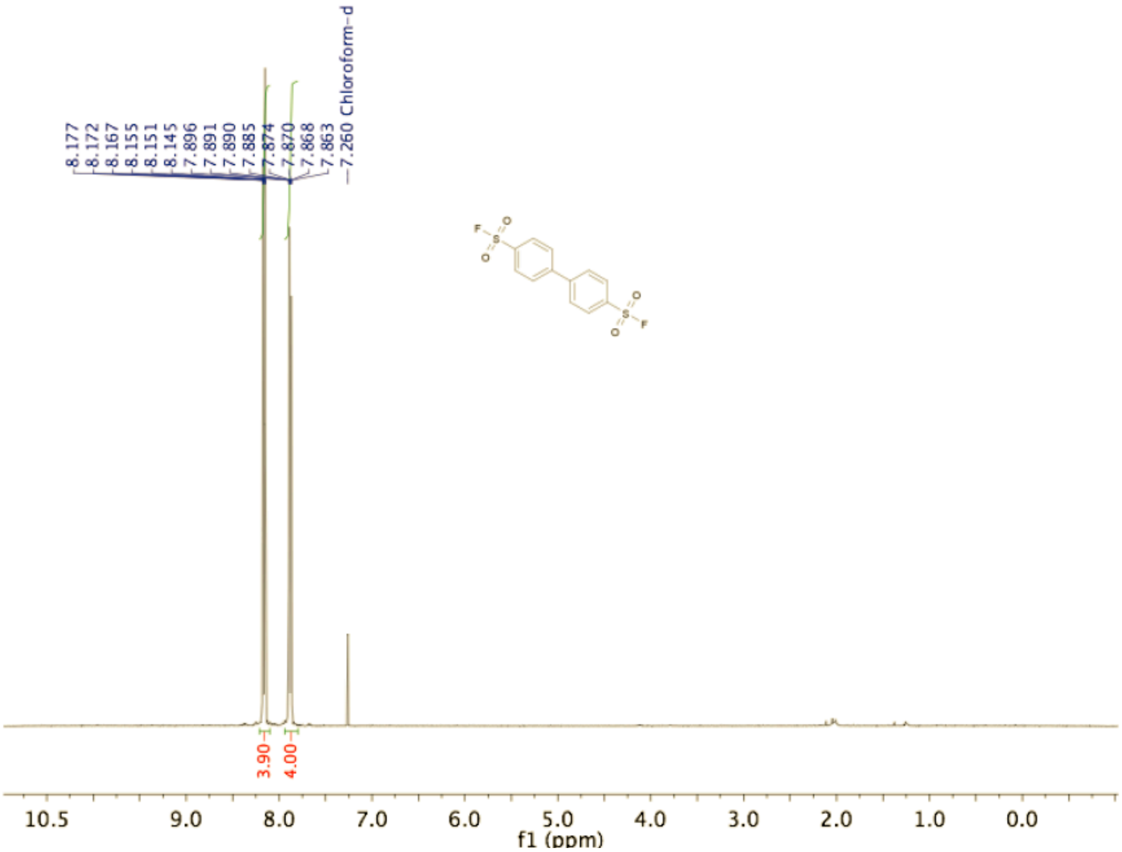
37.95
O
S
F
O
O
O
S
O
F
O
O
O
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

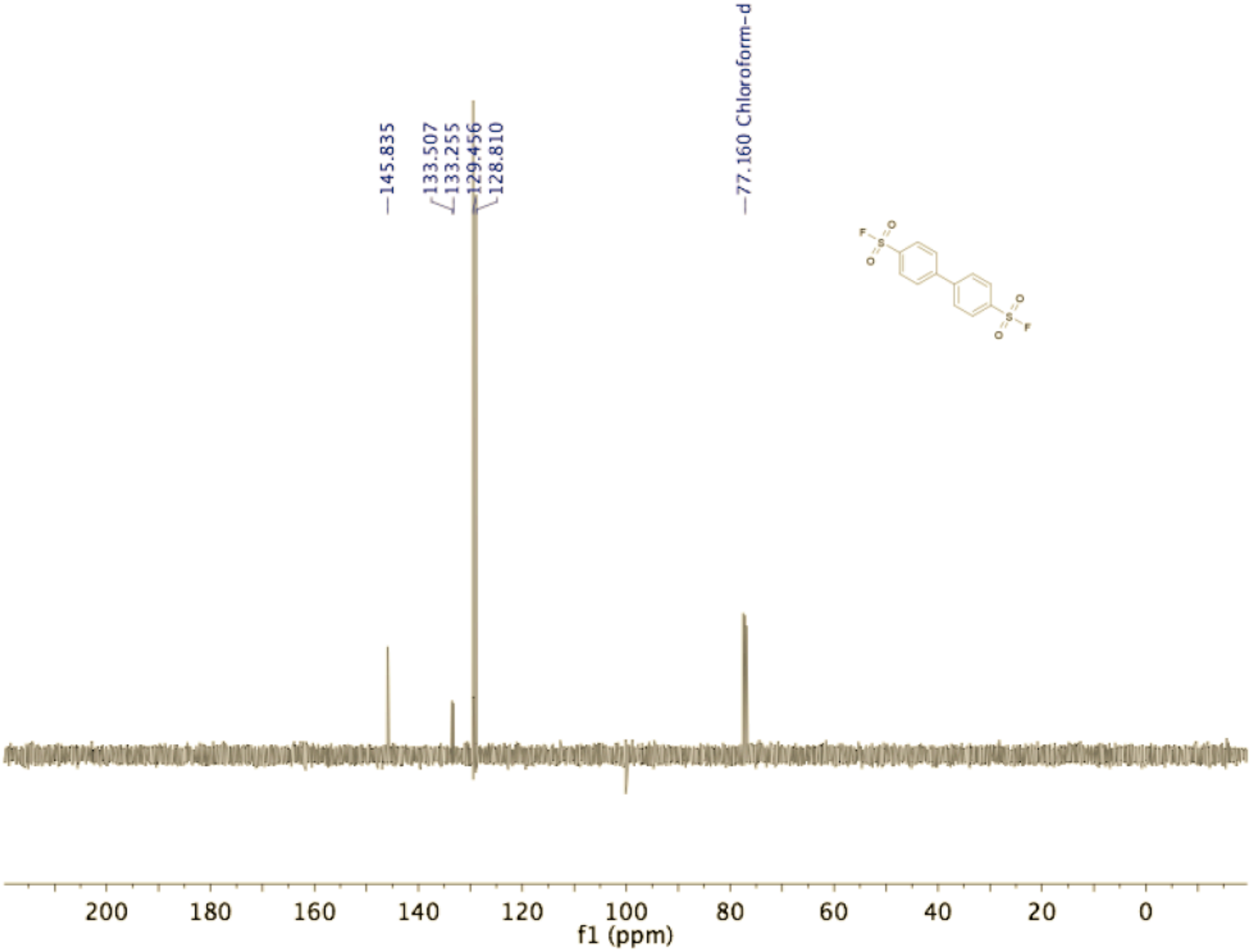


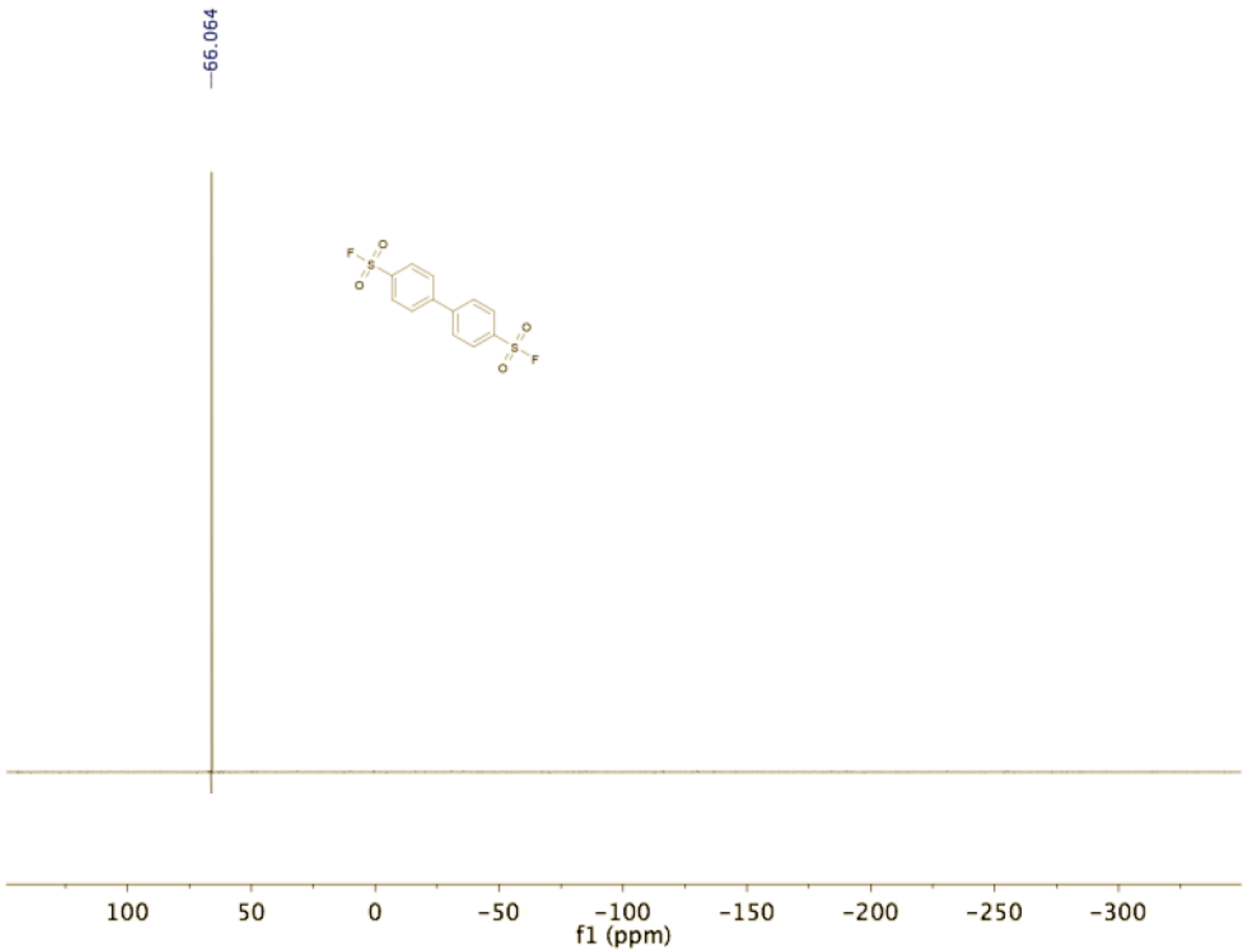
7.26 Chloroform-d
6.81
6.81
6.43
6.43
6.42
6.02
3.43
3.41
3.40
3.38
1.62
1.60
1.58
1.56
1.54
1.44
1.42
1.40
1.38
1.36
0.97
0.95
0.93
0.19
2.00
0.98
1.09
2.21
2.36
2.18
21.92
12.61
f1 (ppm)



167.34
156.83
137.11
114.86
112.10
77.16 Chloroform-d
39.93
31.84
25.77
20.29
18.32
13.93
-4.27
f1 (ppm)


8.177
8.172
8.167
8.155
8.151
8.145
7.896
7.891
7.890
7.885
7.874
7.870
7.868
7.863
7.260 Chloroform-d
F
S
O
O
O
O
S
F
3.90
4.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


145.835
133.507
133.255
129.456
128.810
77.160 Chloroform-d
F
S
O
O
O
O
S
F
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



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[2] a) C. H. Röhrig, C. Loch, J.-Y. Guan, G. Siegal, M. Overhand, ChemMedChem 2007, 2, 1054-1070; b) P. W. Elsinghorst, J. S. Cieslik, K. Mohr, C. Tränkle, M. Gütschow, Journal of Medicinal Chemistry 2007, 50, 5685-5695.

[3] M. E. El-Khouly, E. S. Kang, K.-Y. Kay, C. S. Choi, Y. Aaraki, O. Ito, Chem.--Eur. J. 2007, 13, 2854-2863.

[4] a) D. J. Sekelik, E. V. Stepanov, S. Nazarenko, D. Schiraldi, A. Hiltner, E. Baer, Journal of Polymer Science Part B: Polymer Physics 1999, 37, 847-857; b) L. Kwisnek, S. Nazarenko, C. E. Hoyle, Macromolecules 2009, 42, 7031-7041.