

# Hydrolytic Polycondensation of Diethoxydimethylsilane in Carbonic Acid

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## Supplementary information

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**General information:** All the reagents were purified in accordance with well-known techniques<sup>1,2</sup>. Hexane, toluene were dried by refluxing with Na, THF – with CaH<sub>2</sub>, and further distillation under argon.

**Methods:** <sup>1</sup>H NMR spectra were recorded on a Bruker AC-250 spectrometer (Germany) operating at 250 MHz; <sup>13</sup>C, <sup>29</sup>Si NMR spectra were recorded on a Bruker Avance II-300 spectrometer (Germany) operating at 75.5 MHz for <sup>13</sup>C nuclei and 59.6 MHz for <sup>29</sup>Si nuclei. Chemical shifts are reported in ppm and referenced to the residual nondeuterated solvent frequencies ( $\delta = 7.25$  ppm) for <sup>1</sup>H NMR; deuterated chloroform ( $\delta = 77.00$  ppm) for <sup>13</sup>C NMR; tetramethylsilane ( $\delta = 0.00$  ppm) for <sup>29</sup>Si NMR.

Gel-permeation chromatography analysis was performed on a device consisting of: a high-pressure pump STAYER 2 (Aquilon, Russia), a Smartline RI 2300 refractive index detector (KNAUER, Germany), a JETSTREAM 2 PLUS thermostat (KNAUER, Germany). Conditions: 40 °C ( $\pm 0.1$  °C), eluent – THF or toluene (1.0 mL/min), Phenogel columns (Phenomenex, USA) 300  $\times$  7.8 mm with 5  $\mu$ m particles (pore size 10 Å). Data were detected and processed using the Mul'tiKhrom 1.6 GPKh program packages (Ampesand, Russia).

Infrared spectra were measured on Bruker Equinox 55/S. Conditions: resolution 4 cm<sup>-1</sup>, number of scanings – 100, thin films on silicon support.

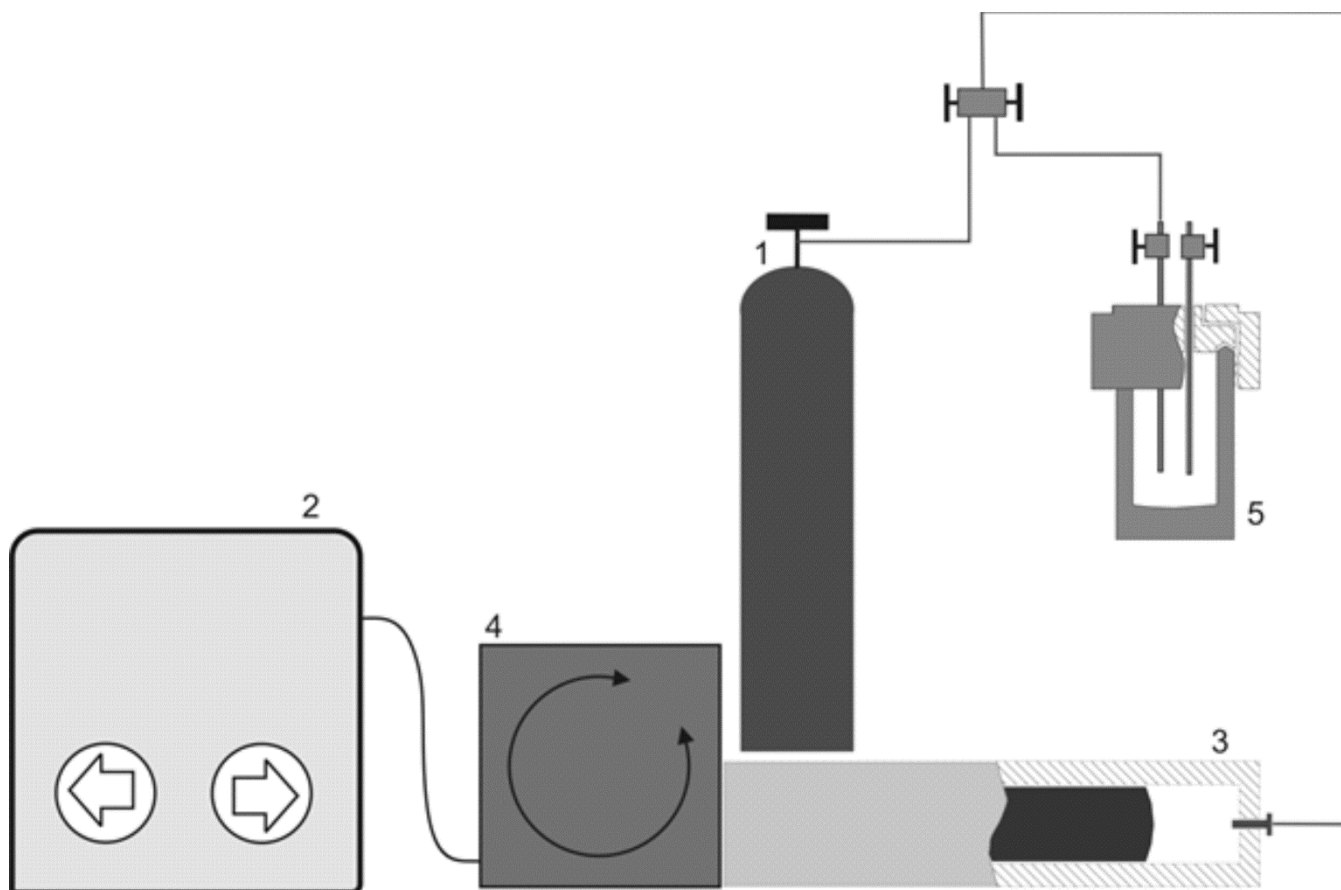
GLC analysis was performed on a chromatograph (chromatec 500.2, Russia) at 50—280 °C, 20°/min; detector – katharometer, columns (2 mm  $\times$  2 m) with 5 % SE-30 stationary phase deposited onto Chromaton-N-AW-HMDS, helium as a carrier gas (60mL/min). Data were detected and processed using the Chromatec Analytic 2.6 program packages (Chromatec, Russia).

Water bidistillate was deionized on Milli-Q System (Millipore, France).

#### **References:**

- (1) Gordon, A; Ford, R. Satellite of chemist. MIR: Moscow, 1976.
- (2) Armarego, W. L. F.; Perrin, D. D. Purification of laboratory chemicals. Elsevier Science: Oxford, 2002.

## General Procedure



**Figure S1.** CO<sub>2</sub> pressure generating system

The system consists of CO<sub>2</sub> tank (1), an electromotor operating module (2), automatic high-pressure generator (3) driven by electromotor (4) (the operating module and motor-driven generator are SITEC system type 750-1101-1-S, SITEC, Switzerland) and a high-pressure vessel (5).

At first, 5ml of deionized water and 10 ml of DMDES are placed in the high-pressure vessel, the vessel is then sealed and connected to the CO<sub>2</sub> pressure generating system via the high-pressure valve. Liquid CO<sub>2</sub> is passed from the tank through the system of high-pressure capillary tubes and valves to the generator and the vessel. The tank is then closed and motor-driving pressure generator creates the necessary pressure (150 or 350 bar) in the high-pressure vessel at ambient temperature (22–24°C). Then the high-pressure valve of the vessel is sealed, the vessel is disconnected from the system and placed in the thermostat (Binder, FD 115, Germany) that is pre-set to a reaction temperature (60 or 120 °C).

The heating results in corresponding increase of the pressure in the isolated vessel containing CO<sub>2</sub>. The resulted pressure in the vessel after heating is calculated using the NIST Chemistry WebBook program available online (National Institute of Standards and Technology, USA).

After the exposure (for 10, 60 or 180 min) the vessel is removed from the thermostat, decompressed slowly and opened. The products of reaction are then taken out.

The yield of siloxane products was estimated in accordance with the mass balance data for the reagents and the products. In all cases the mass loss did not exceed 3–5 %.

Since the stationary phase was not effective for the separation of hydroxyl-containing compounds, in order to determine the ratio between cyclic and linear siloxanes by means of GLC, hydroxyl groups were blocked with chlorodimethylvinylsilane as follows.

### **Blocking technique**

A 10 wt. % solution of dimethylsiloxane oligomer (1.5 g, 0.02 mol) in hexane was dropwise added to a solution of chlorodimethylvinylsilane (4.9 g, 0.04 mol) and pyridine (3.2 g, 0.04 mol) in hexane (20 mL). The reaction mixture was stirred for 4 h. The product was washed with water till neutral medium was observed. Afterwards, it was dried with sodium sulfate, filtered and fractionally distilled.

As a result of distillation there were obtained a distillate fraction and a residue fraction. The former contained hexane, tetramethyldivinylsiloxane and a little amount of D<sub>3</sub> and D<sub>4</sub>; the latter was a mixture of cyclic and linear oligodimethylsiloxanes. The volatile components were analyzed by means of GLC; whereas the residue fraction was analyzed by GLC, GPC, IR, and <sup>1</sup>H NMR spectroscopies. Identification of the products (GLC) was conducted with the use of pure standards. The ratio between cyclic and linear siloxanes was estimated in accordance with the mass balance data for the products in consideration of their concentration in both distillate and residue.

After blocking, 1.0–1.2 g of the products were obtained (yield, 70—80 %).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ ppm, 0–0.14 (m, Si(CH<sub>3</sub>)<sub>2</sub>); 0.15 (m, (CH<sub>2</sub>=CH)Si(CH<sub>3</sub>)<sub>2</sub>); 5.65–6.25 (m, SiCH=CH<sub>2</sub>).

IR (cm<sup>-1</sup>): 3010, 1700, 1400, 1250, 1080, 1050, 990, 810.

# <sup>1</sup>H NMR Spectral Data for reaction mixtures

Table 1, entry 1

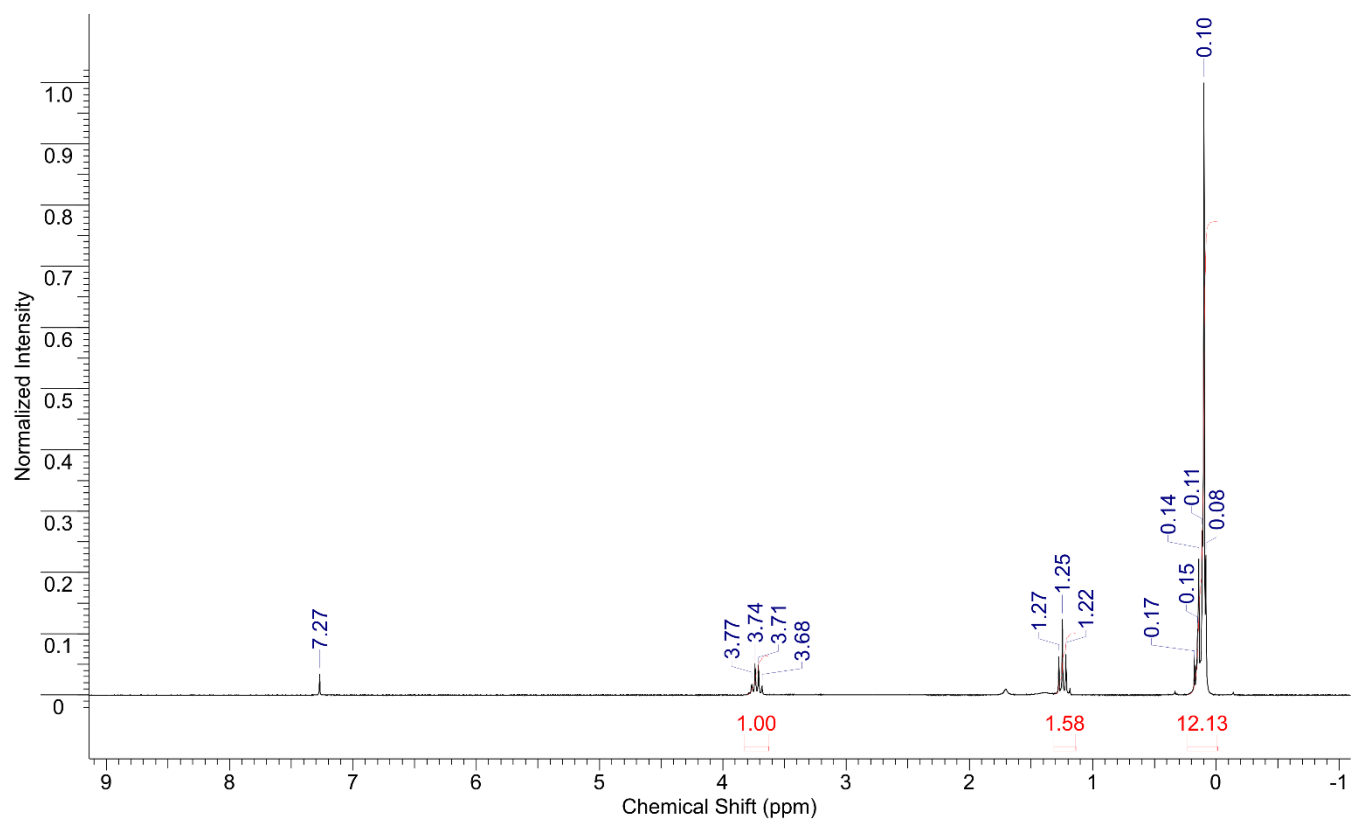
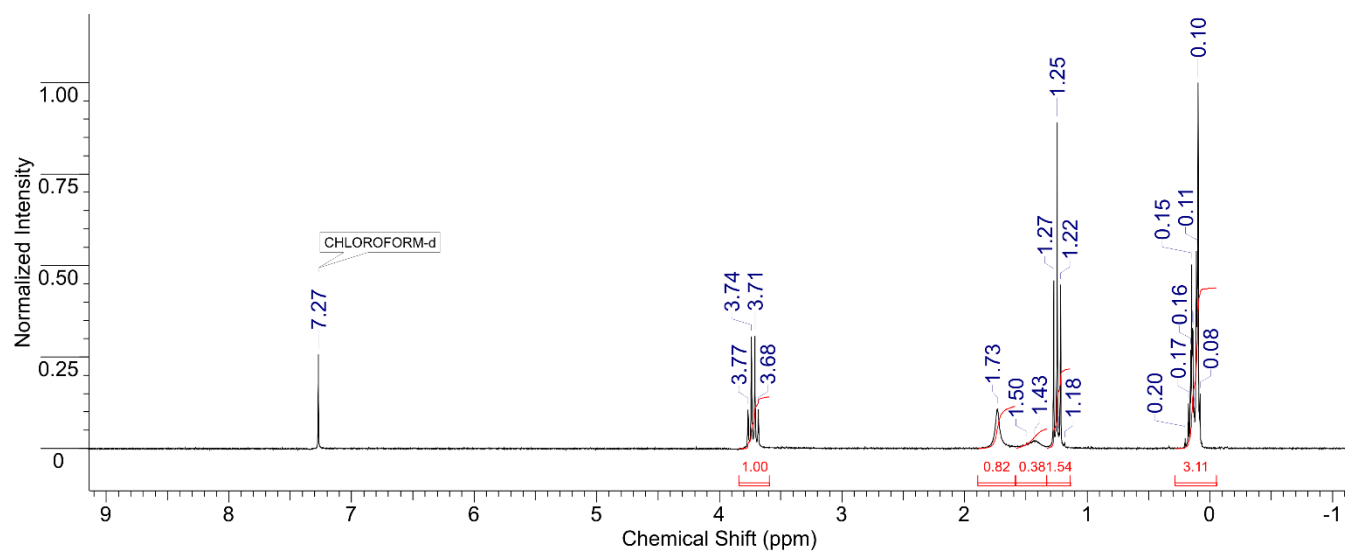
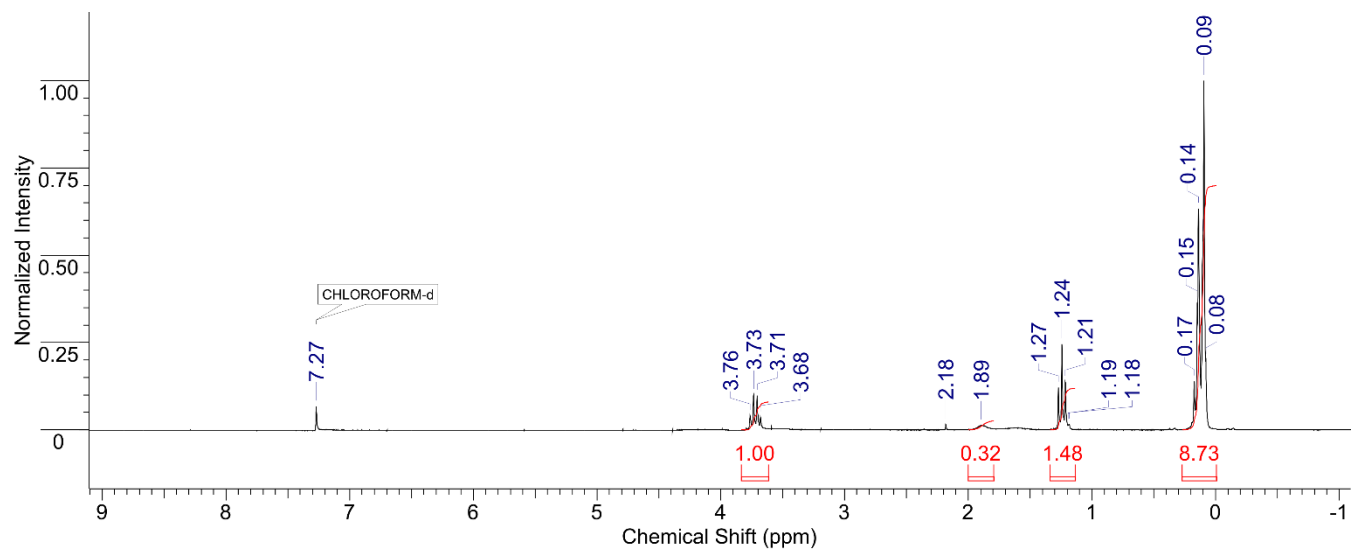


Table 1, entry 2



**Table 1, entry 3**





**Table 1, entry 4**

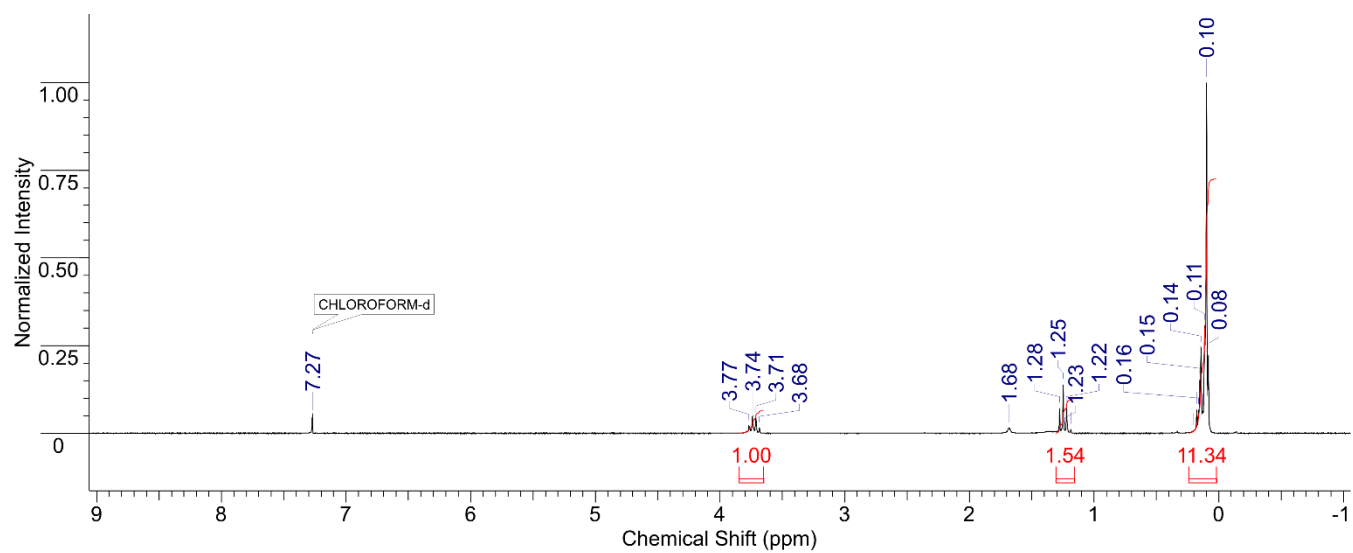


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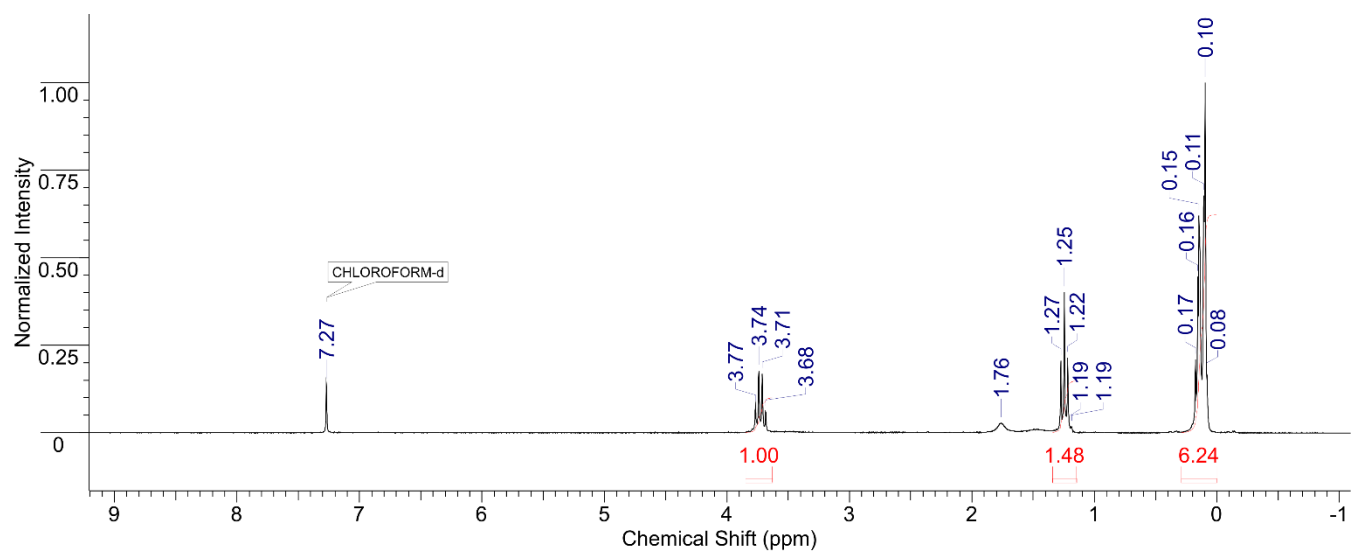
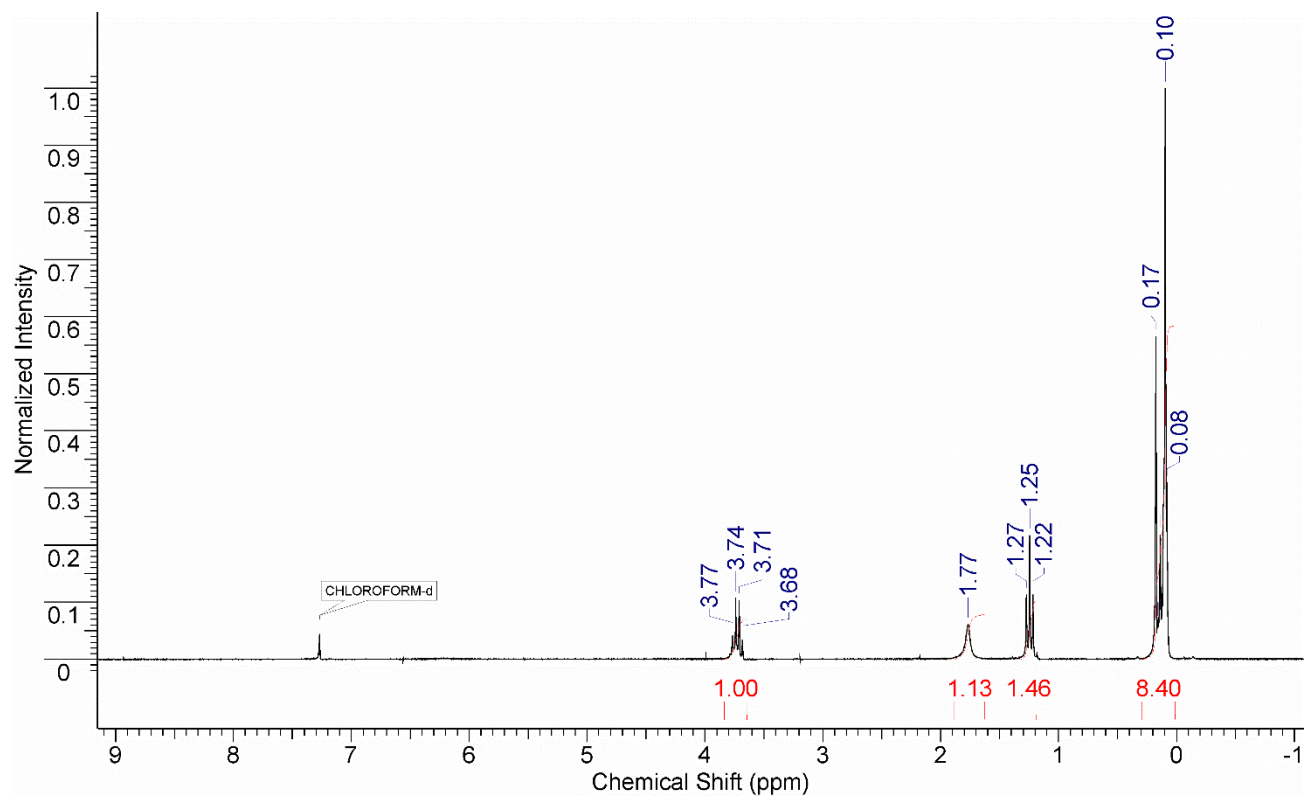


Table 1, entry 6



# <sup>1</sup>H NMR Spectral Data for blocked products

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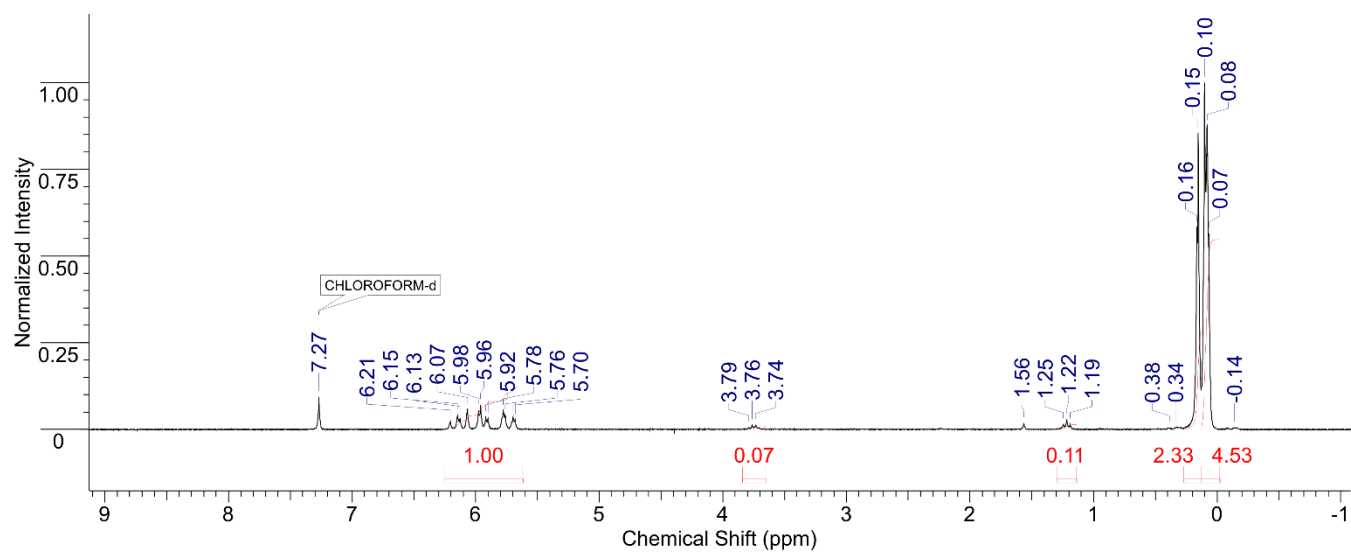


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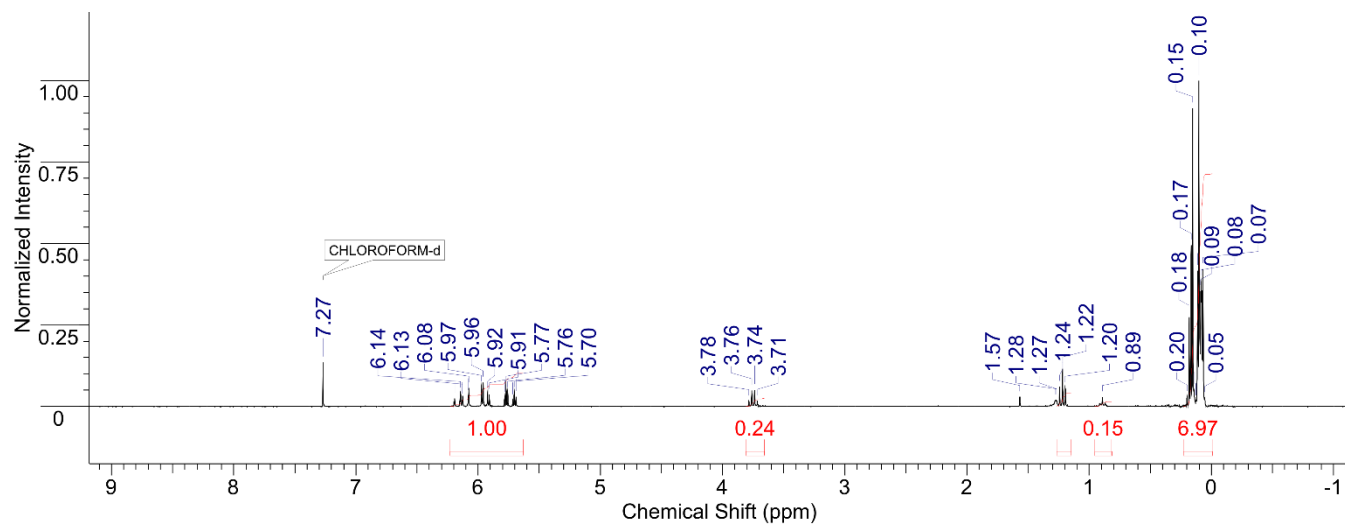


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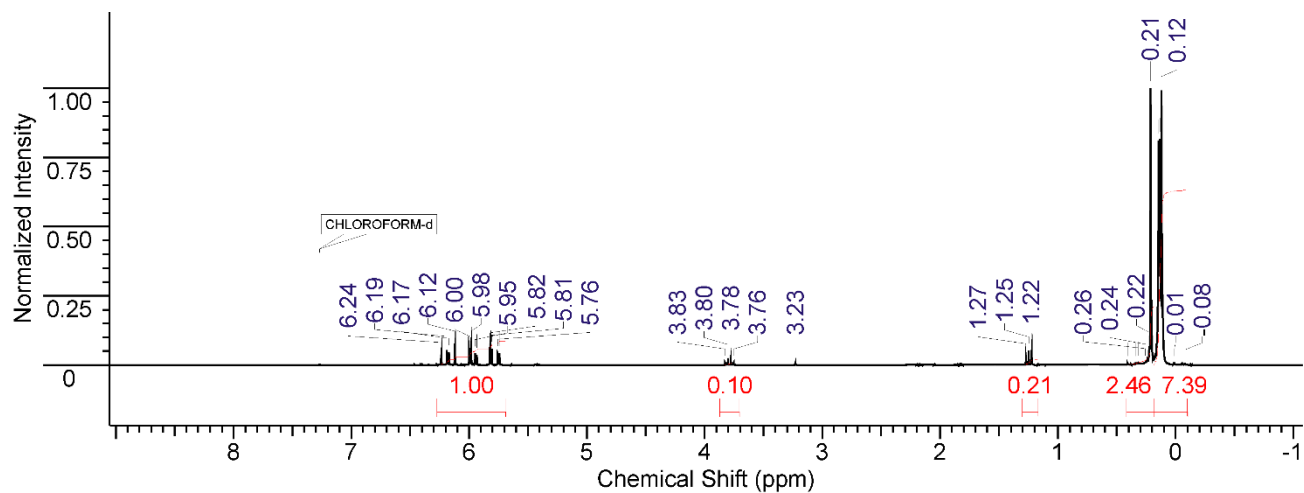


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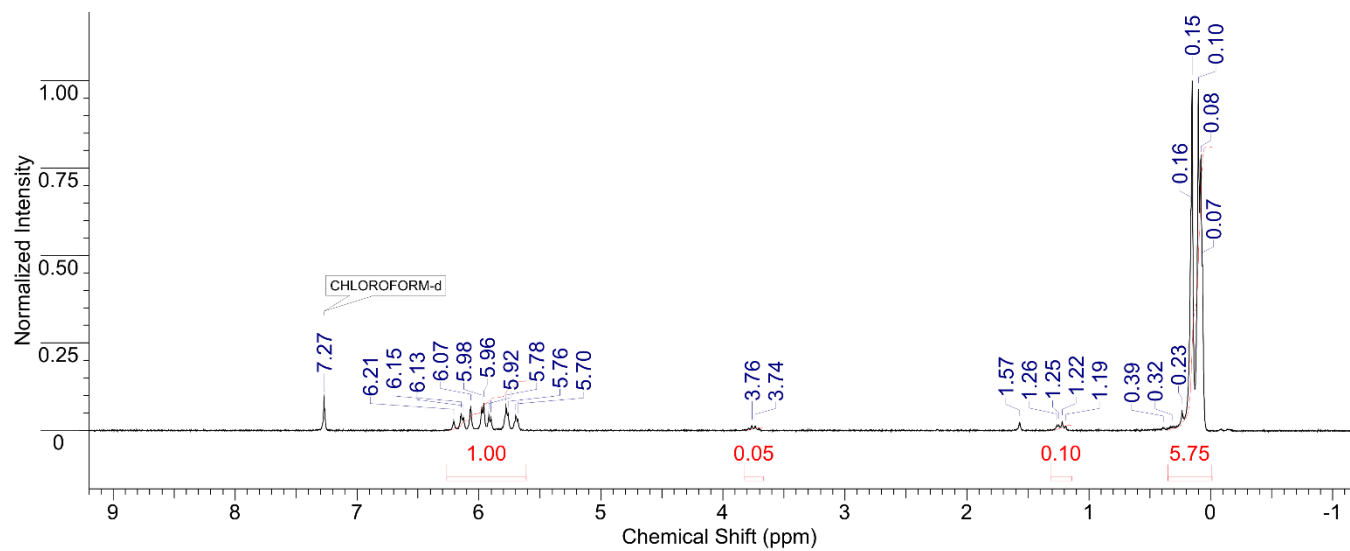


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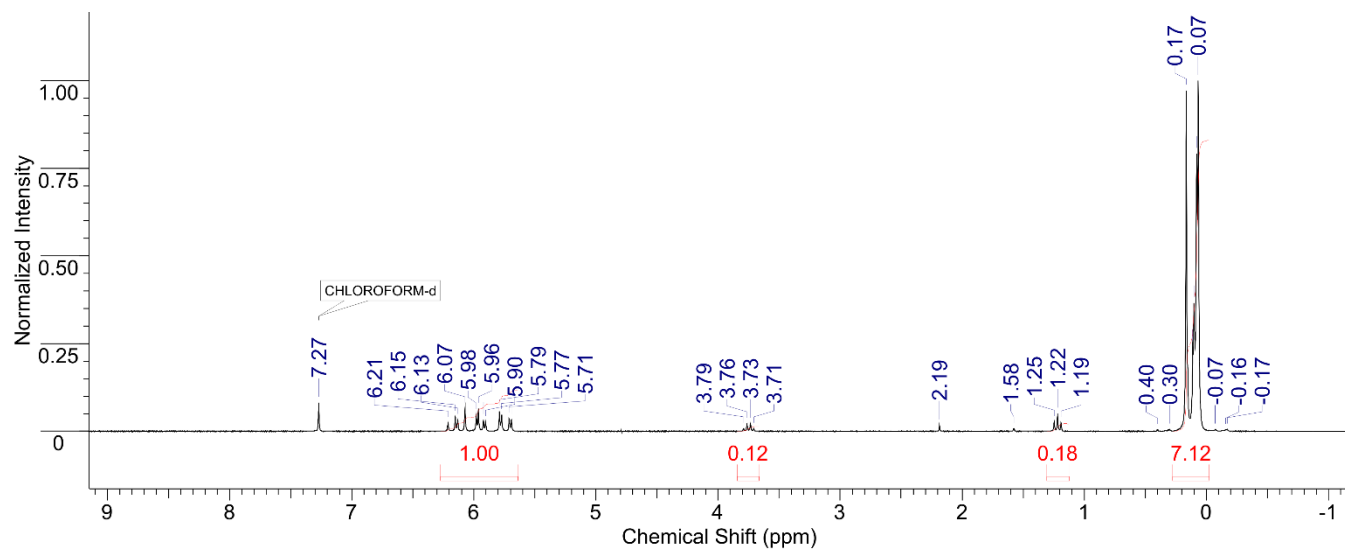
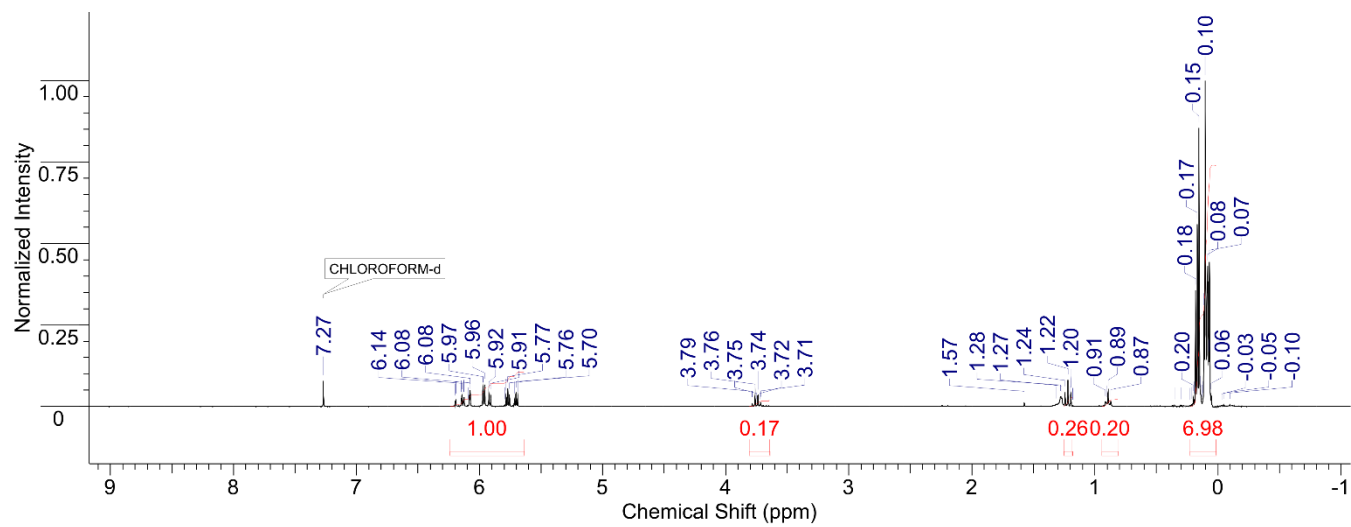




Table 1, entry 6



# IR spectral data for reaction mixtures

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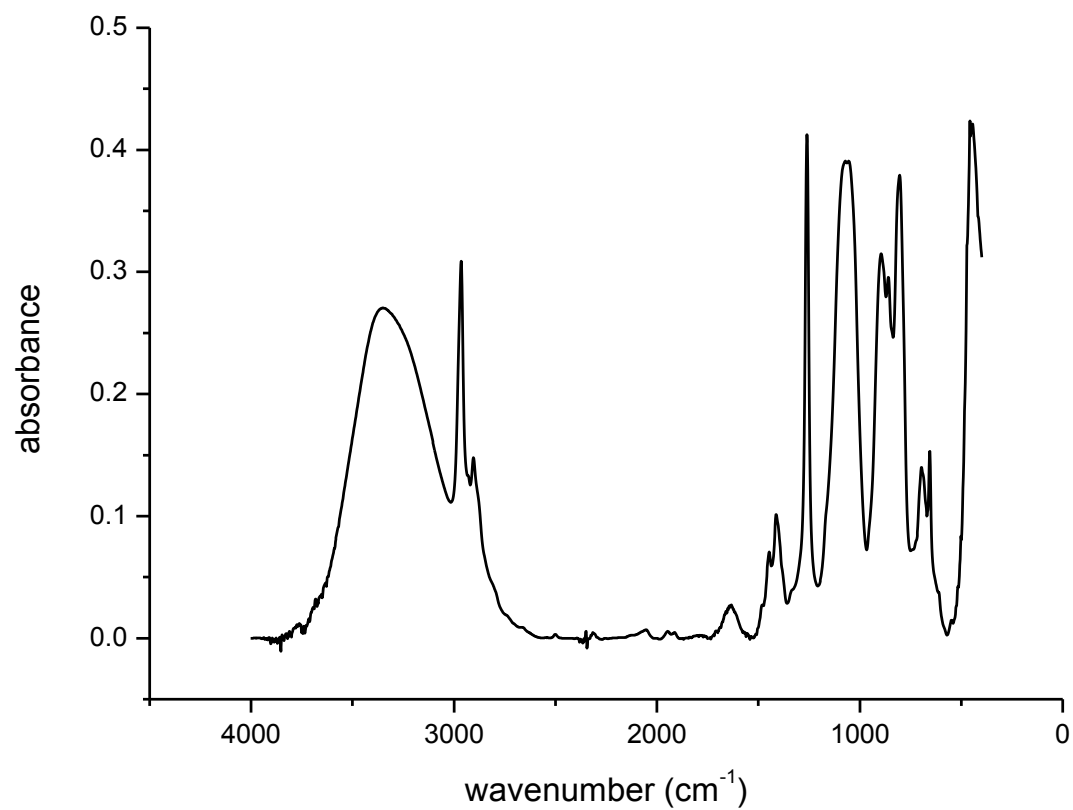


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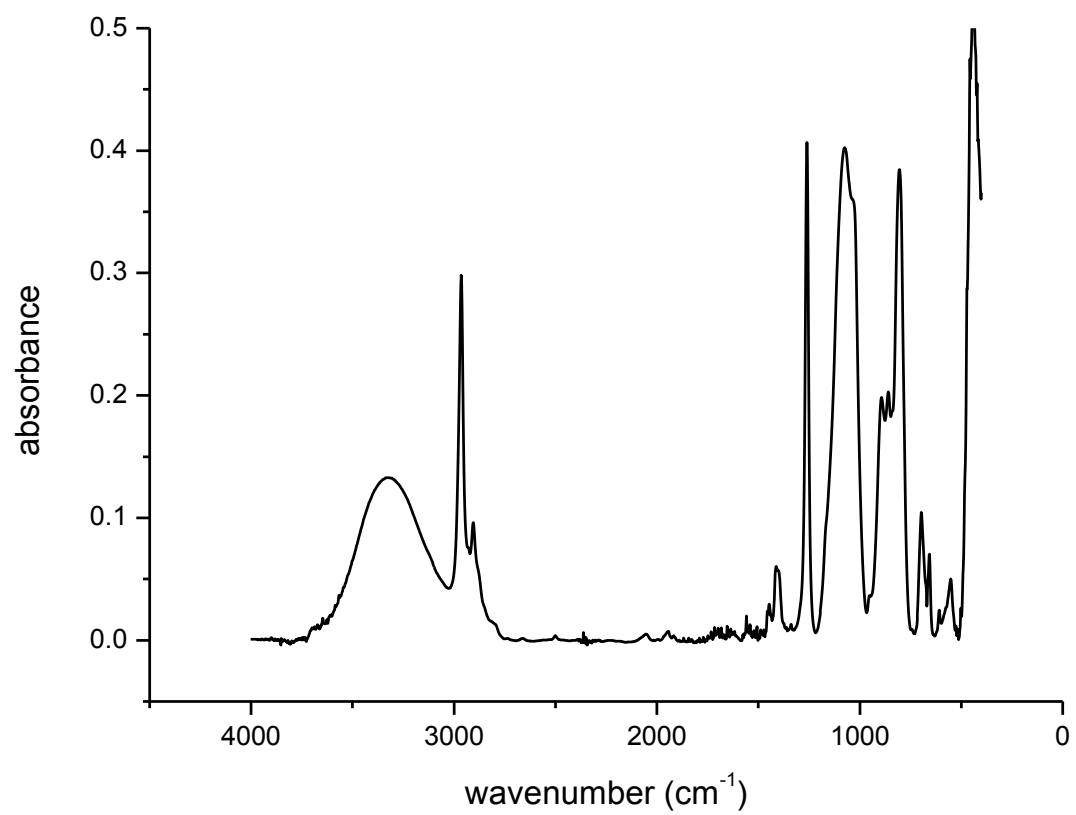
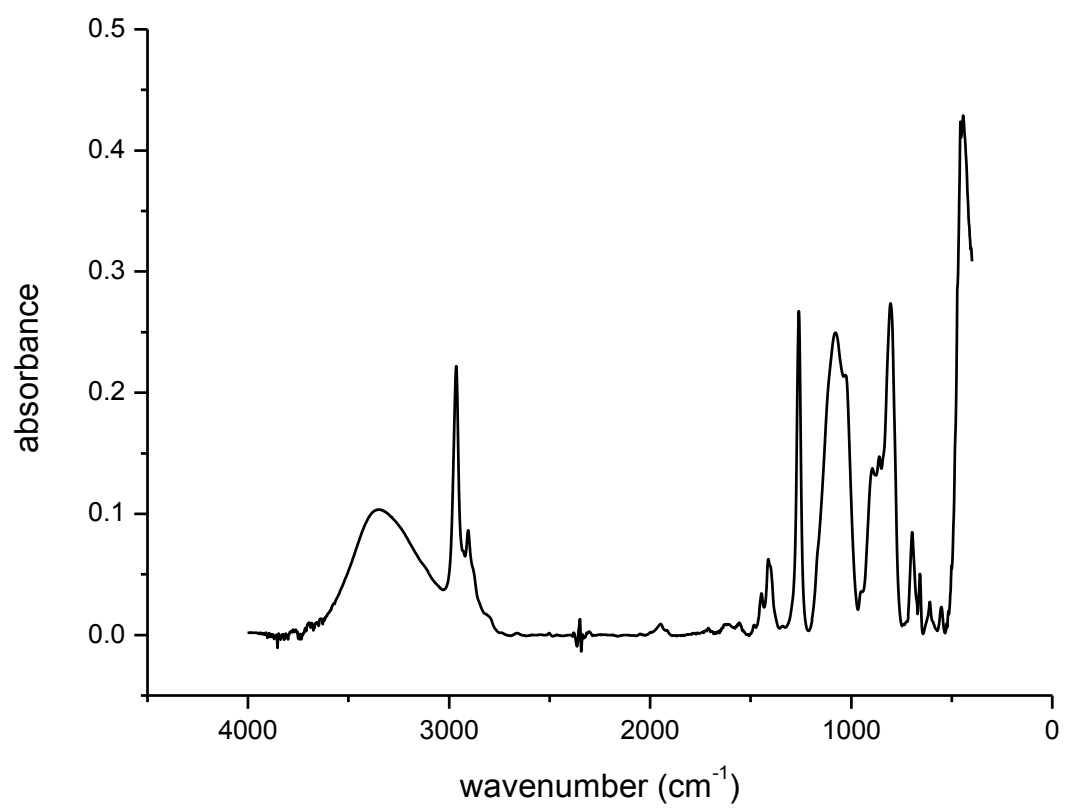


Table 1, entry 5



# IR spectral data for locked products

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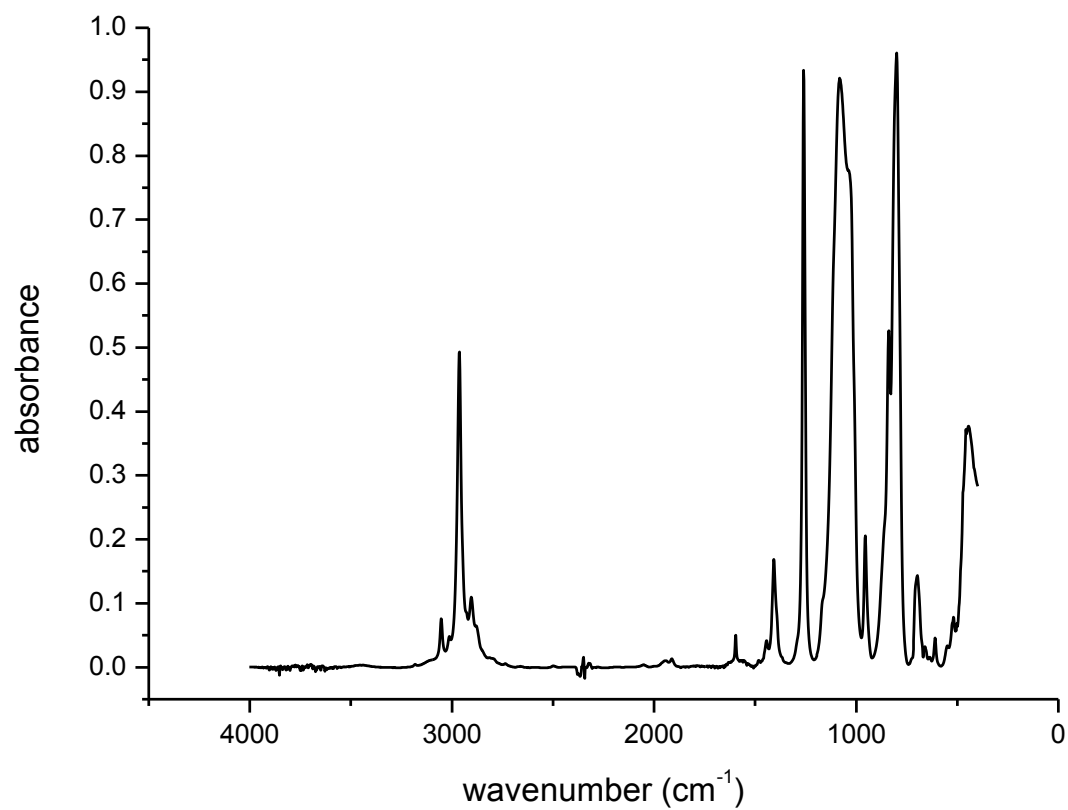


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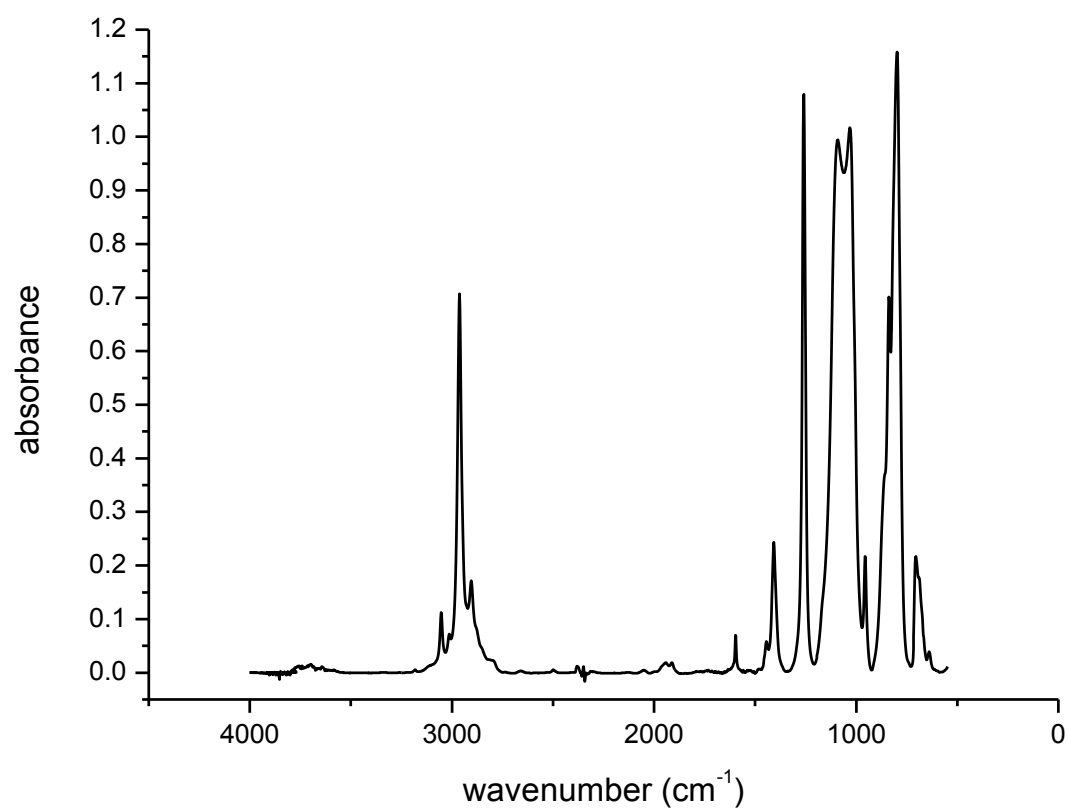
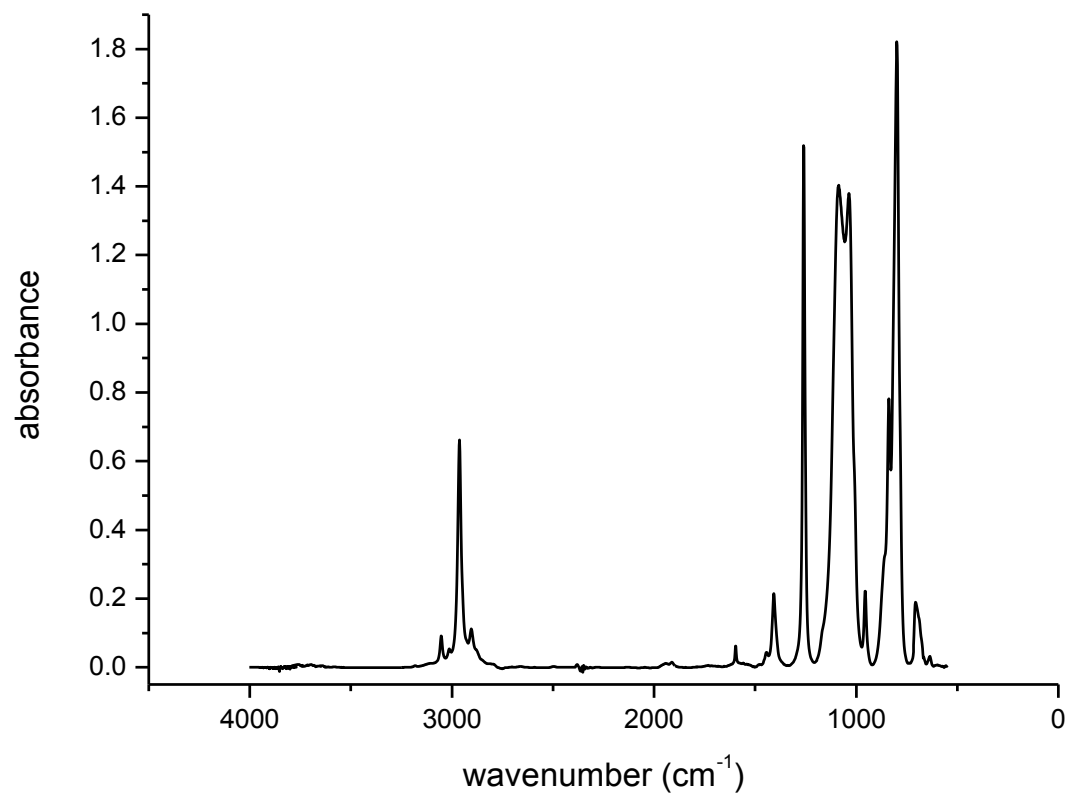
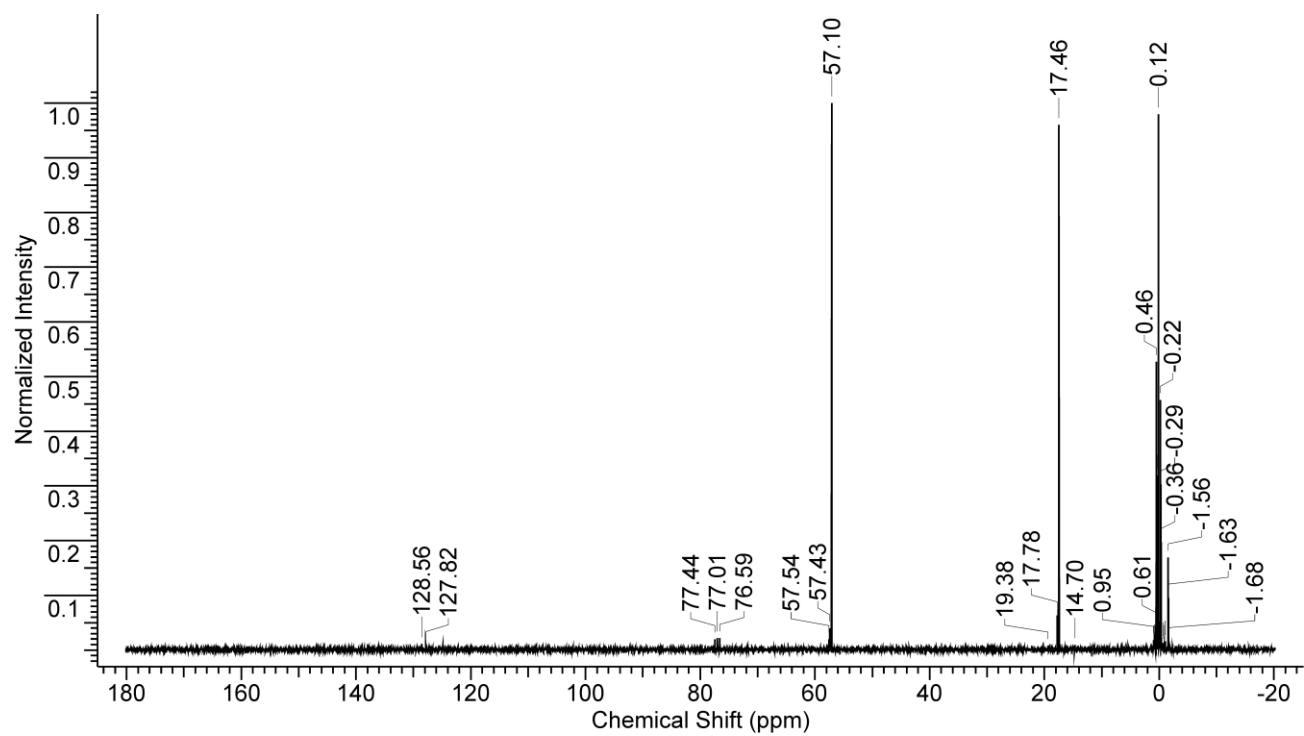


Table 1, entry 5



# <sup>13</sup>C NMR spectral data for reaction mixtures

Table 1, entry 2





**Table 1, entry 3**

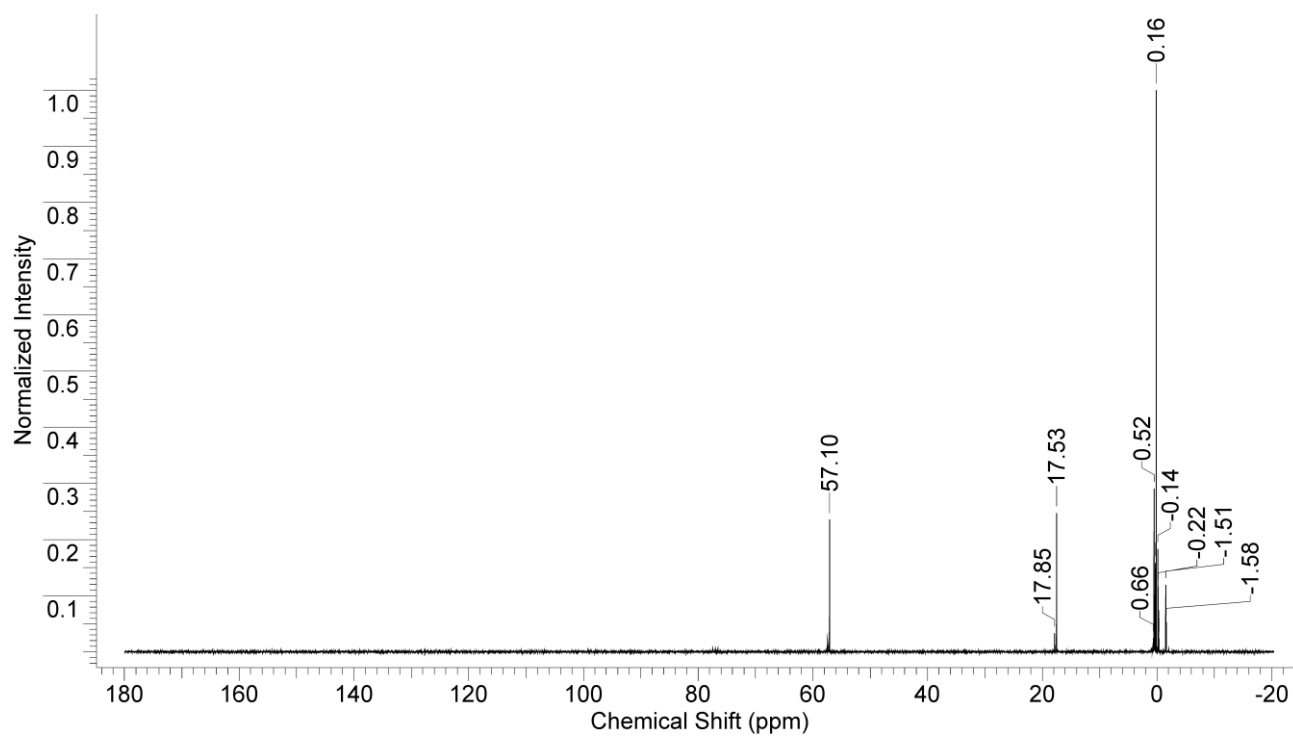
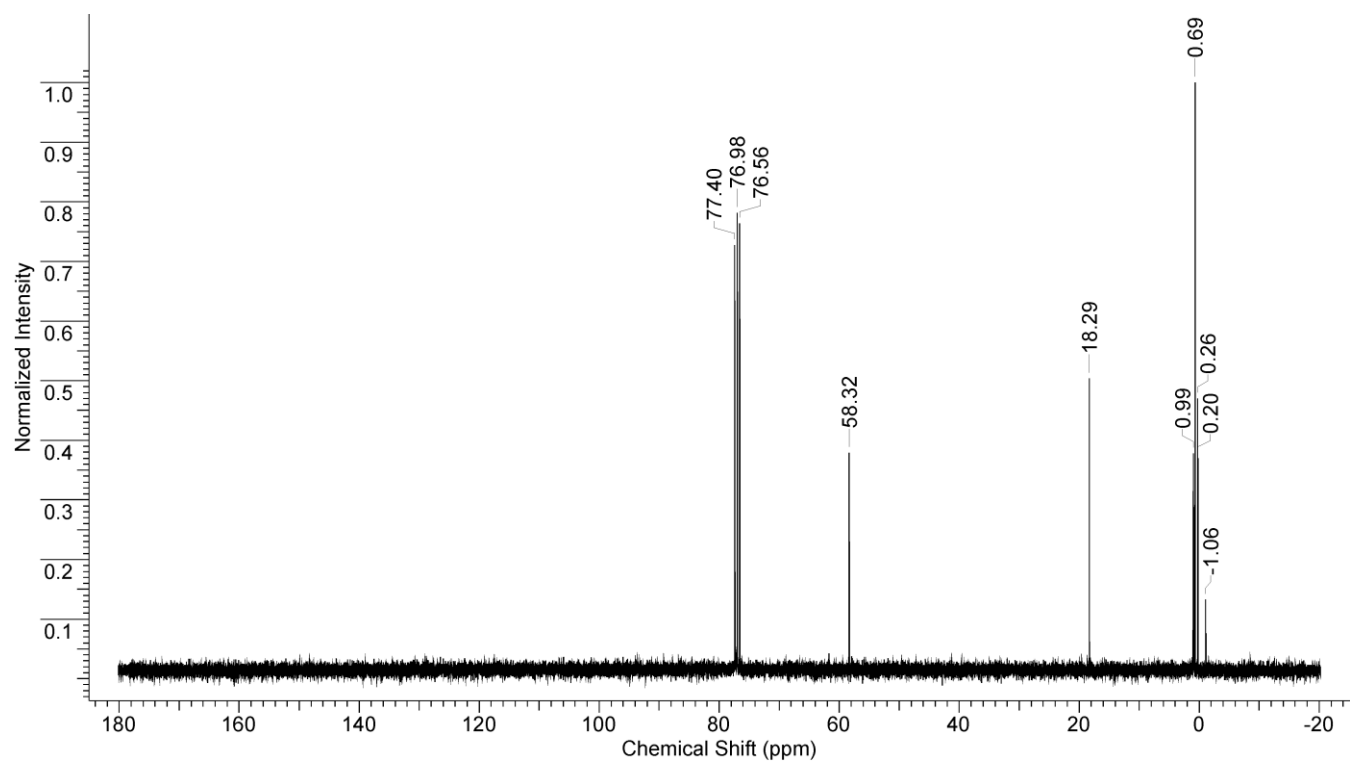


Table 1, entry 5



# <sup>13</sup>C NMR spectral data for blocked products

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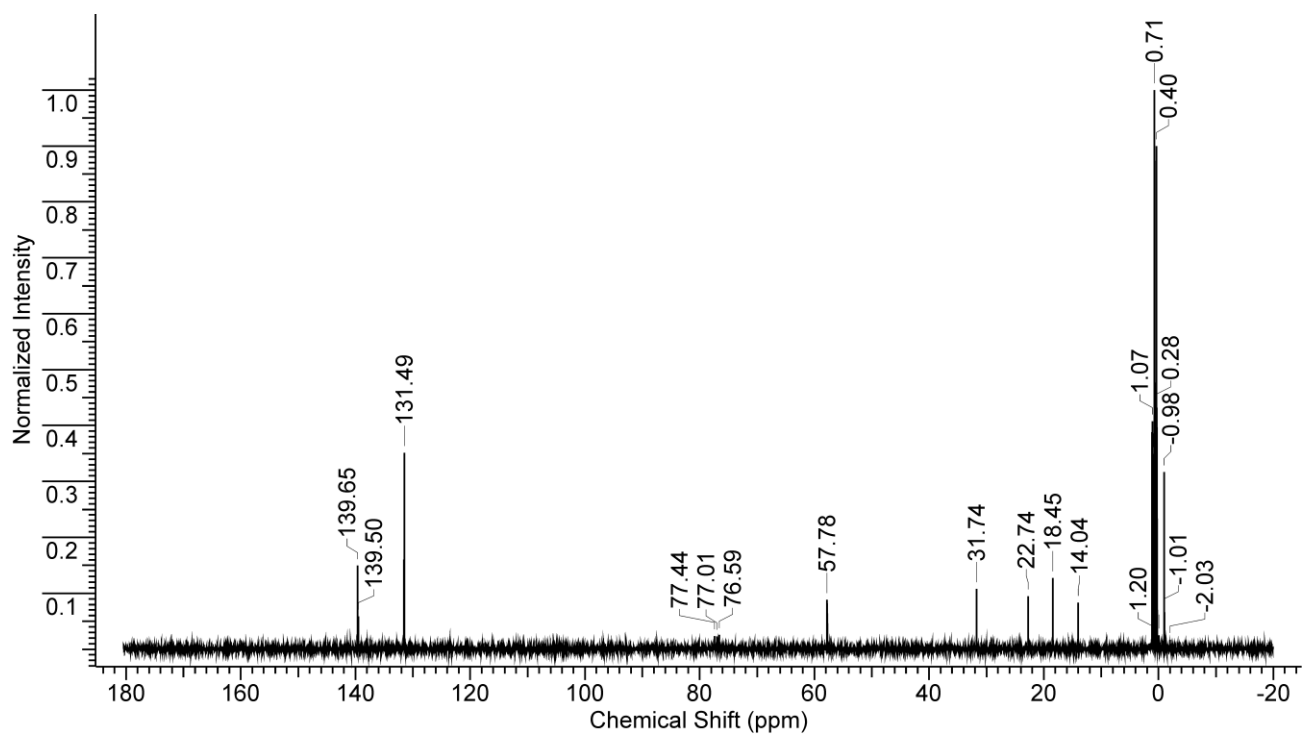


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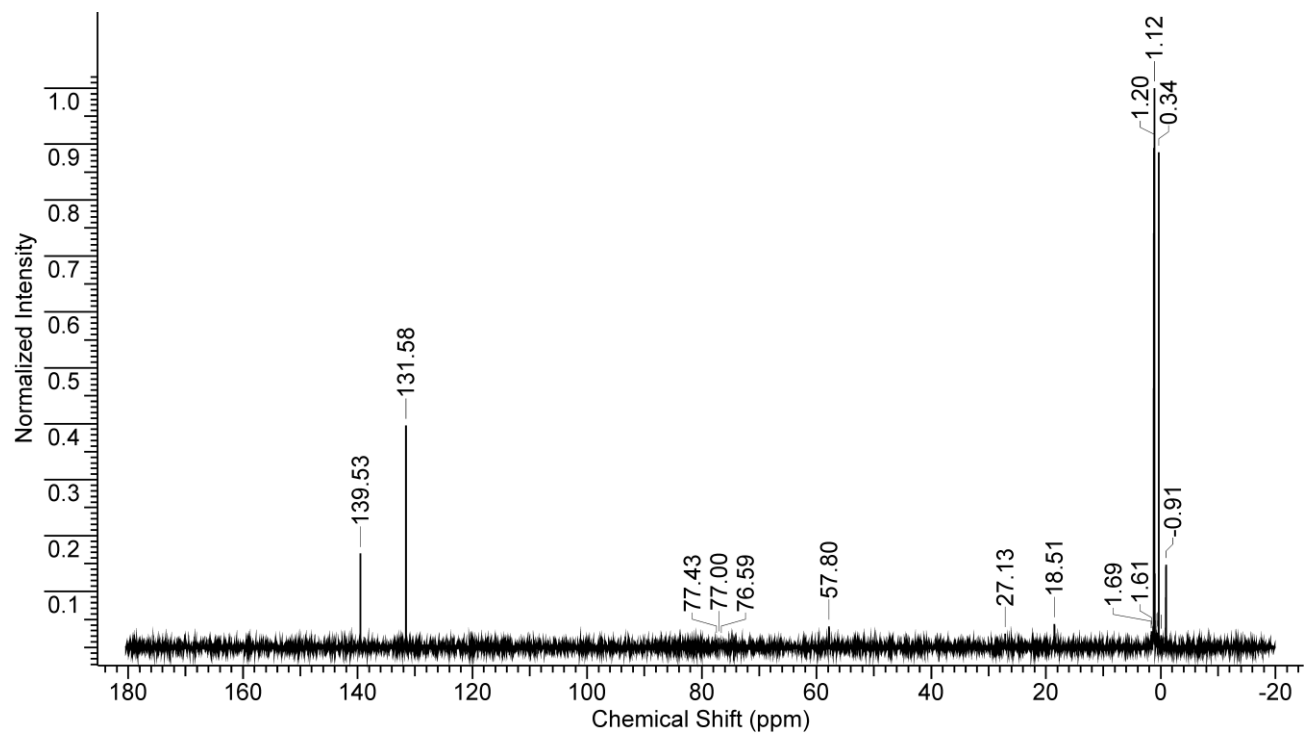
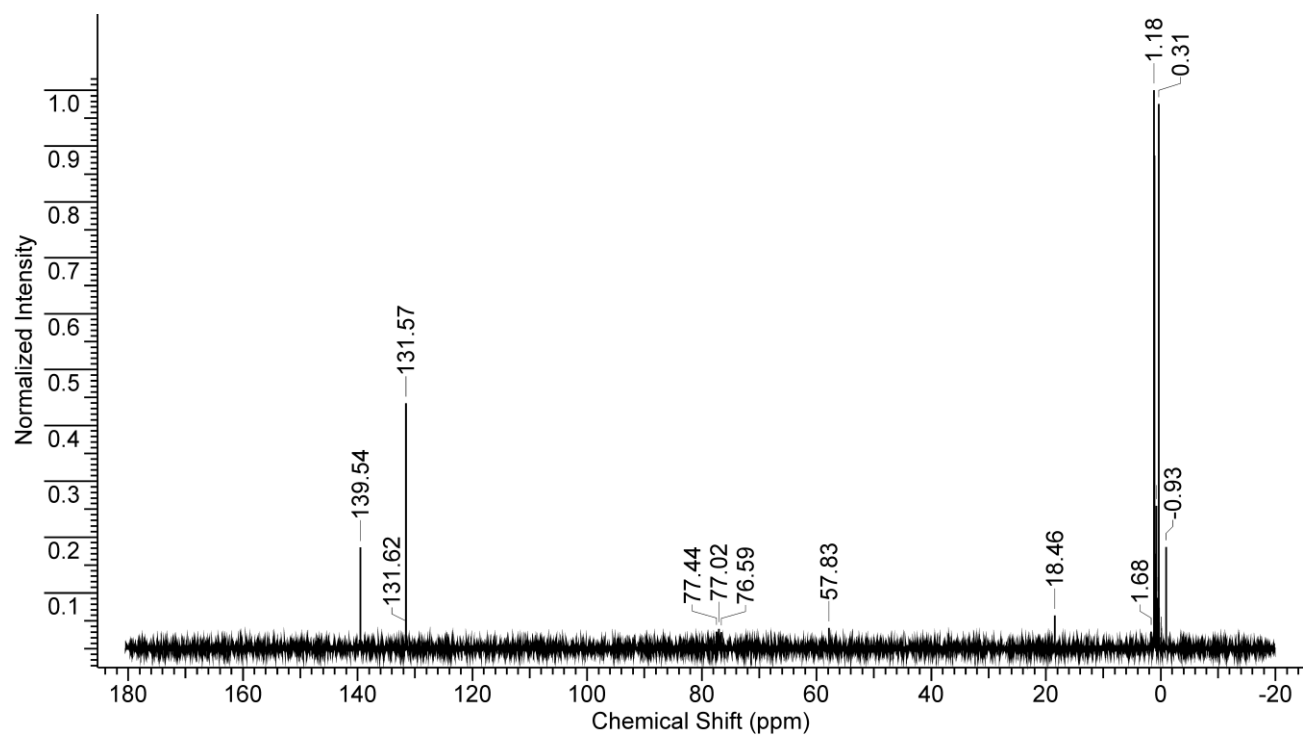


Table 1, entry 5



<sup>29</sup>Si NMR spectral data for reaction mixtures

Table 1, entry 2

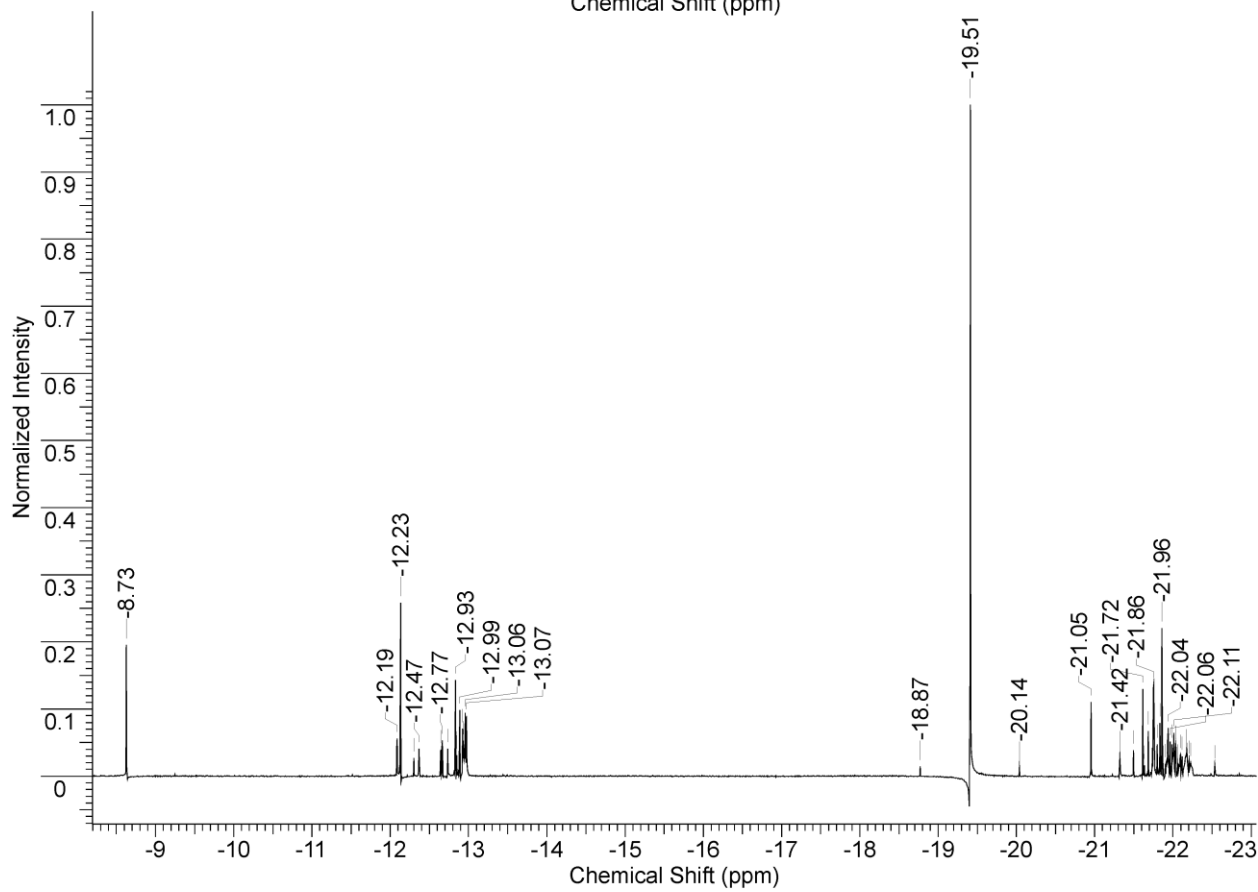
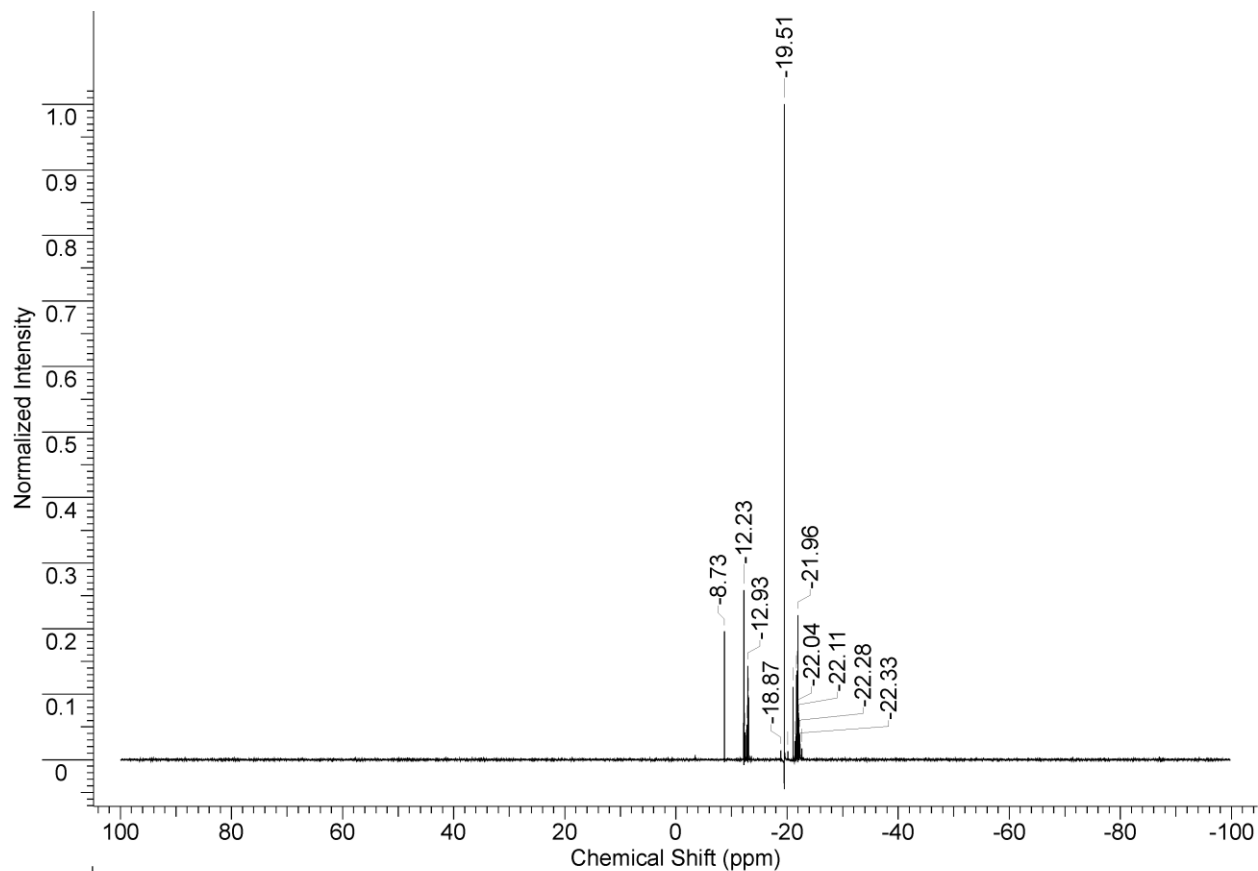


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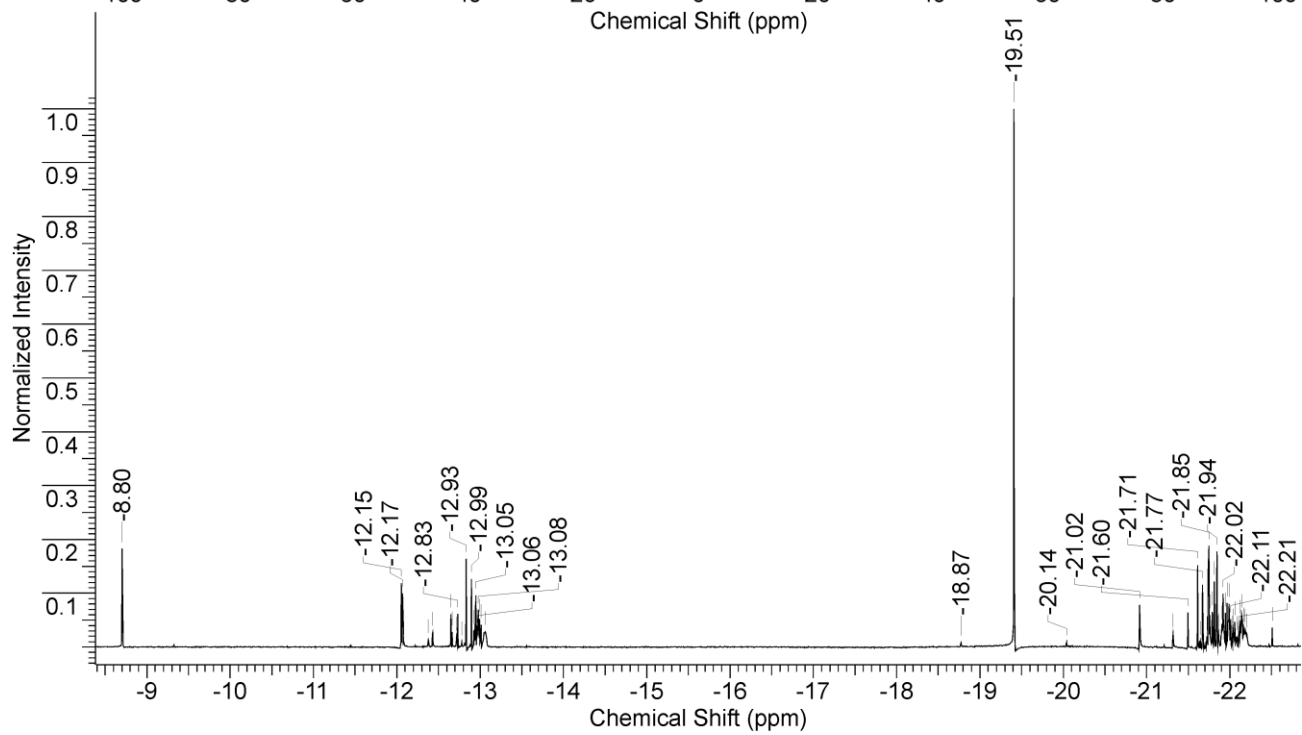
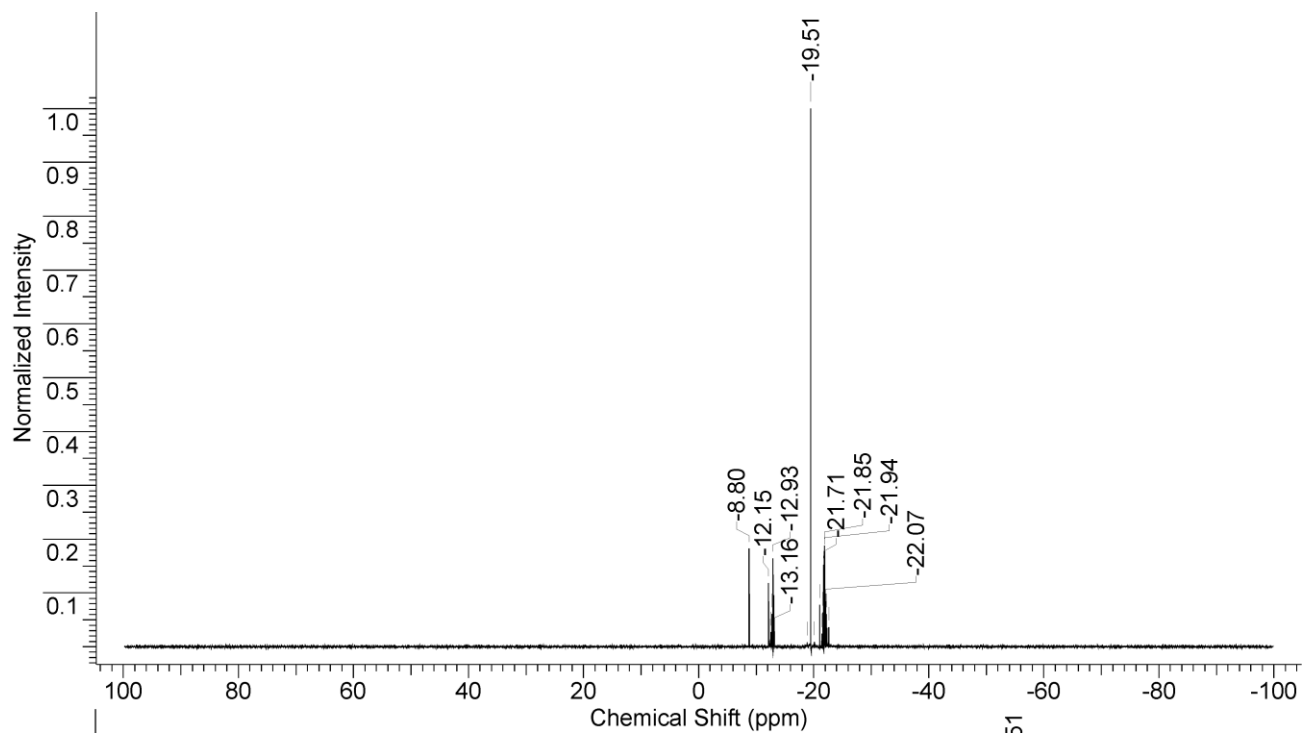
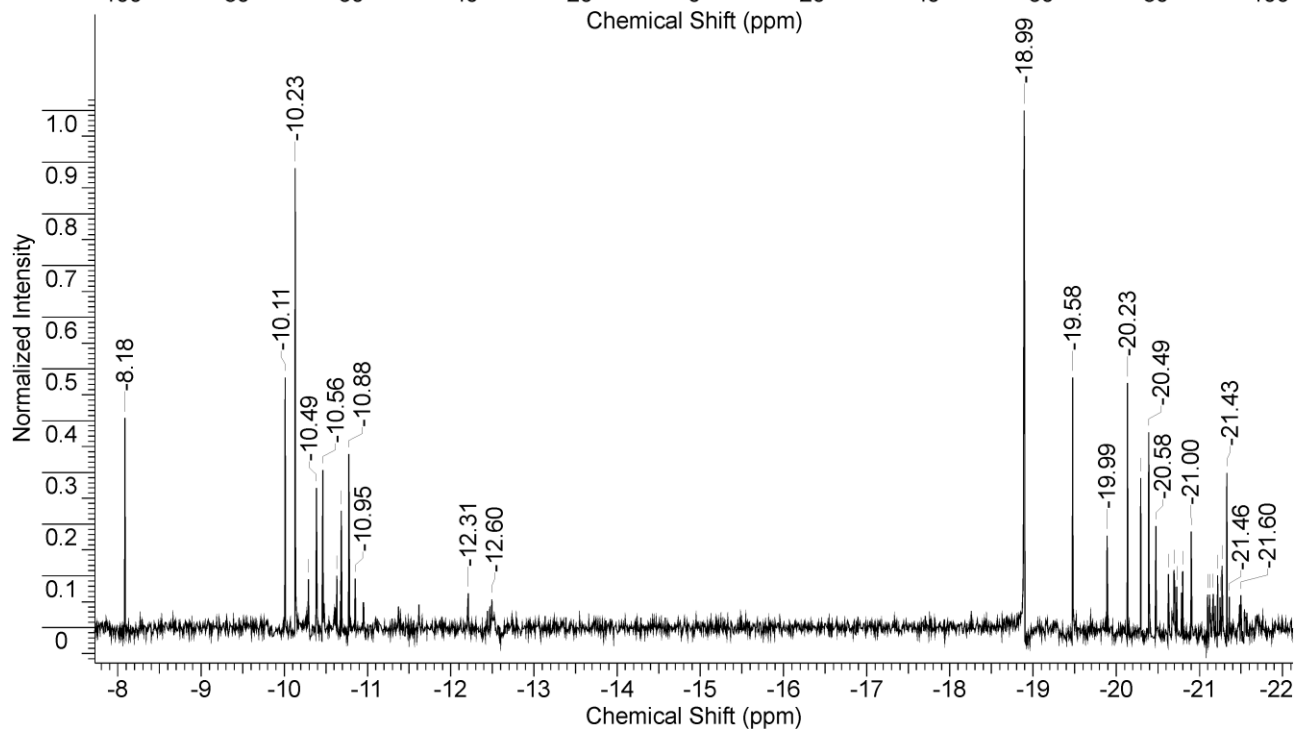
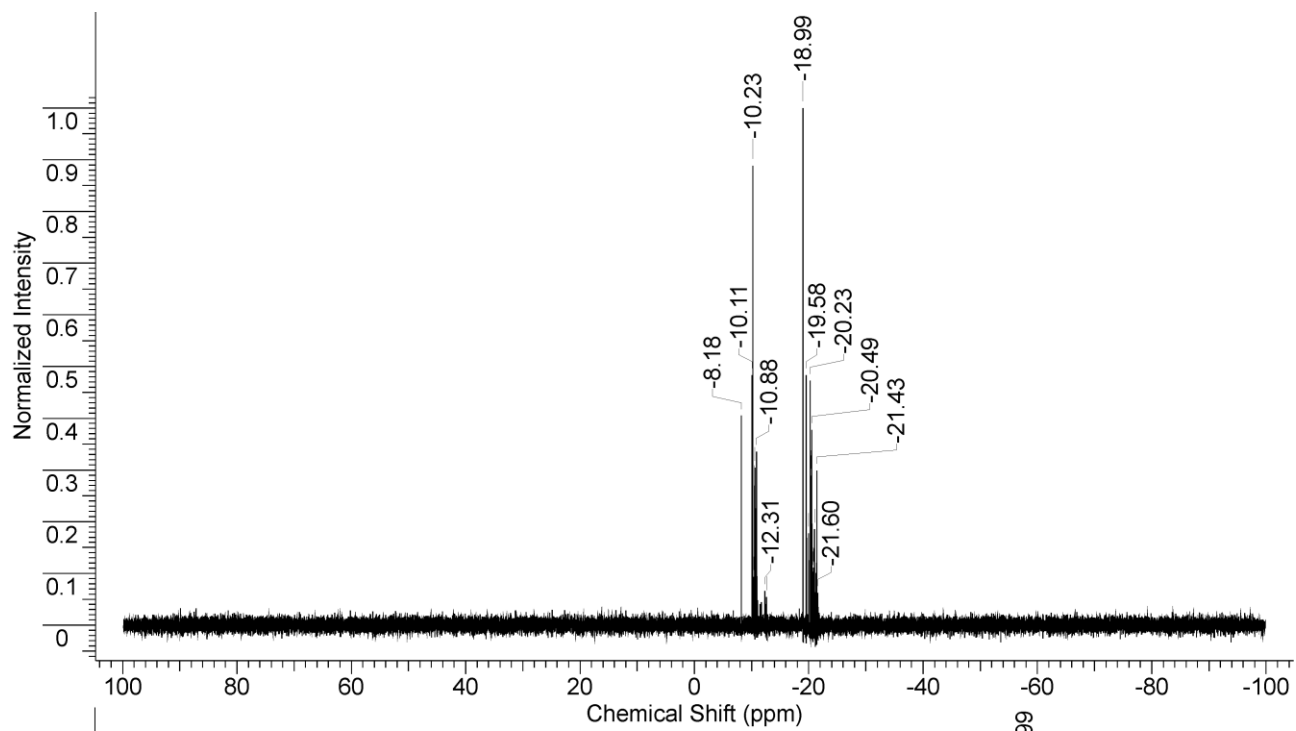


Table 1, entry 5





# <sup>29</sup>Si NMR spectral data for blocked products

Table 1, entry 2

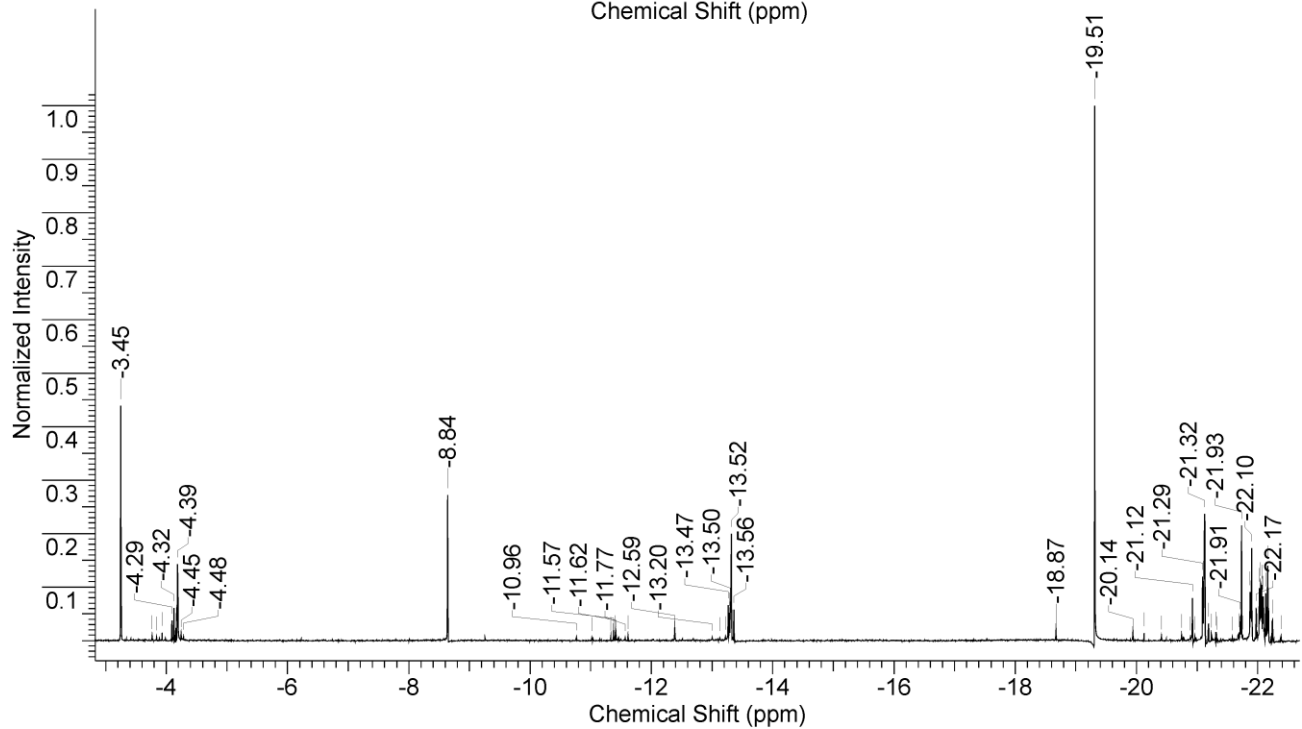
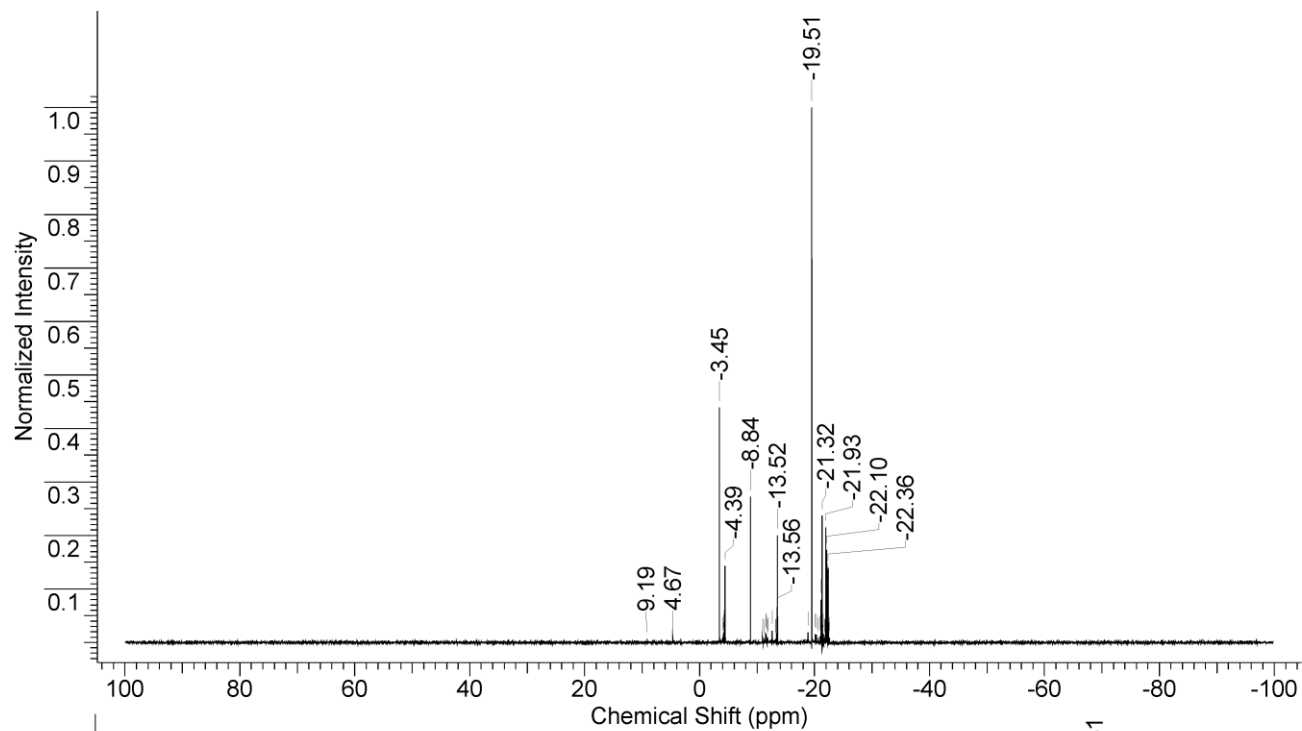


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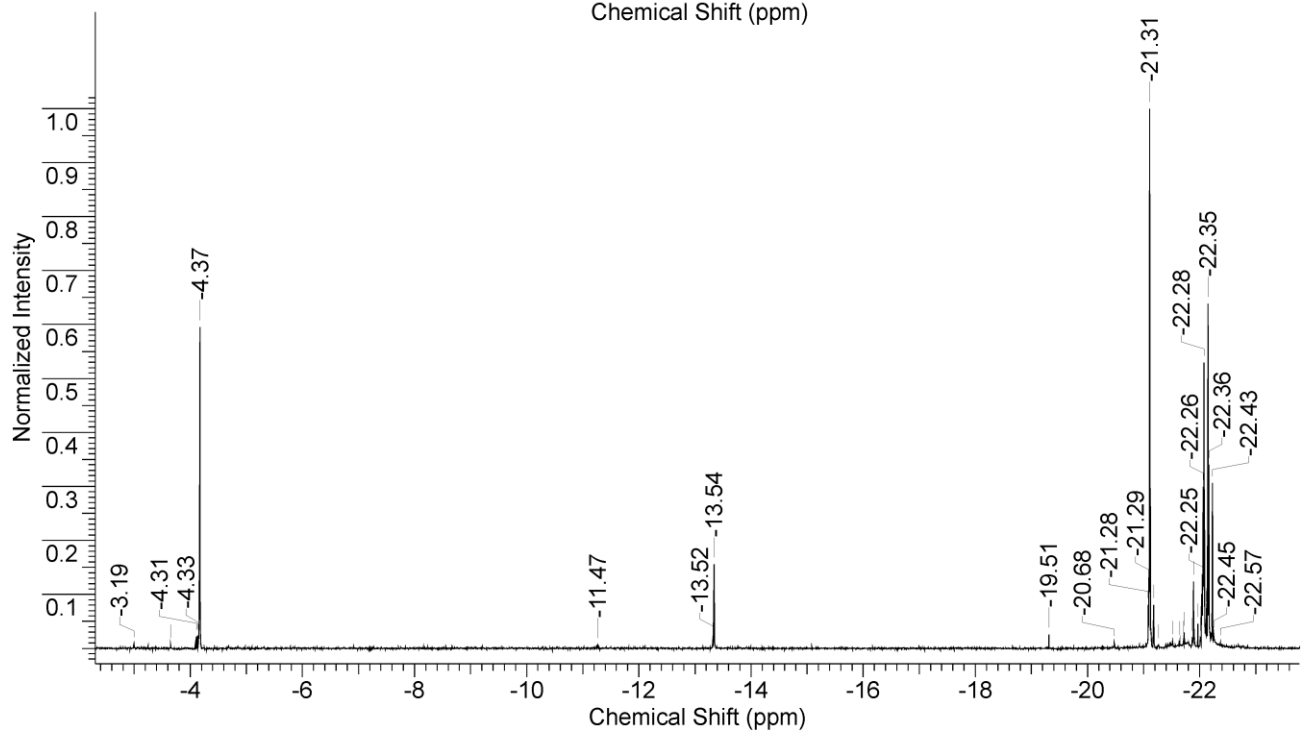
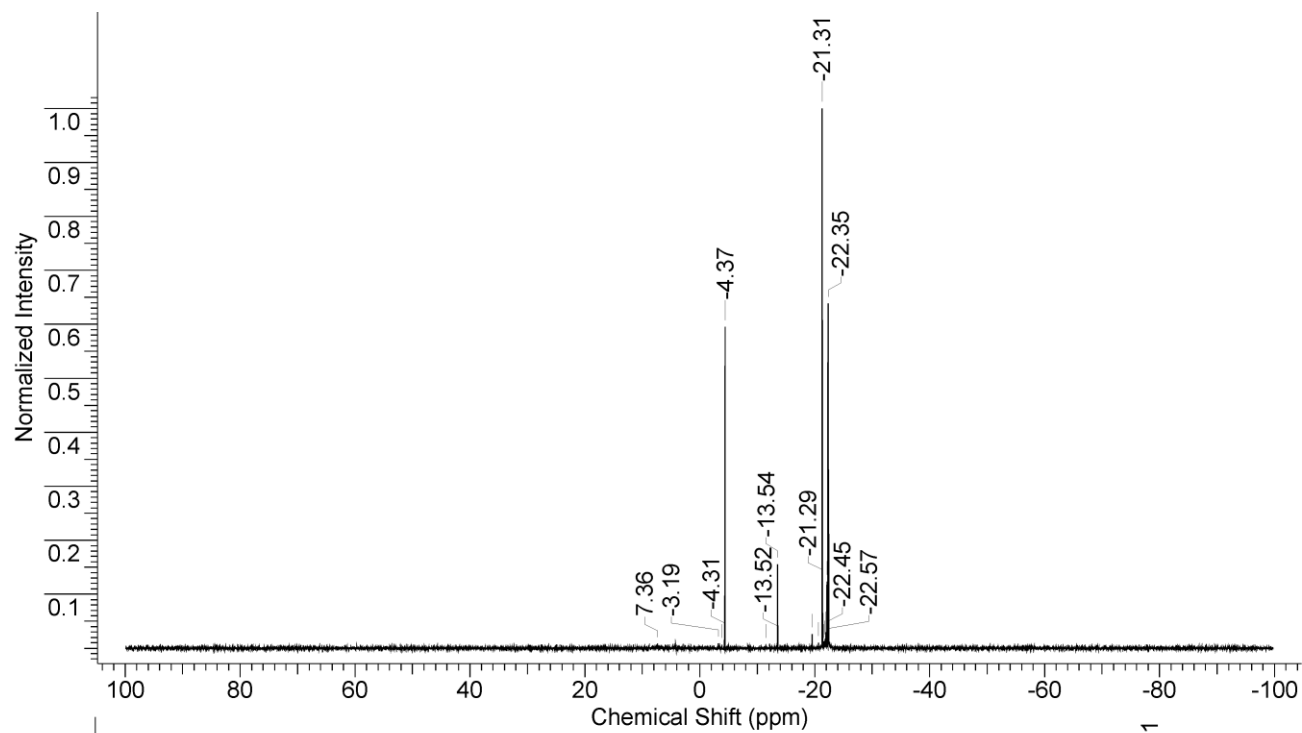
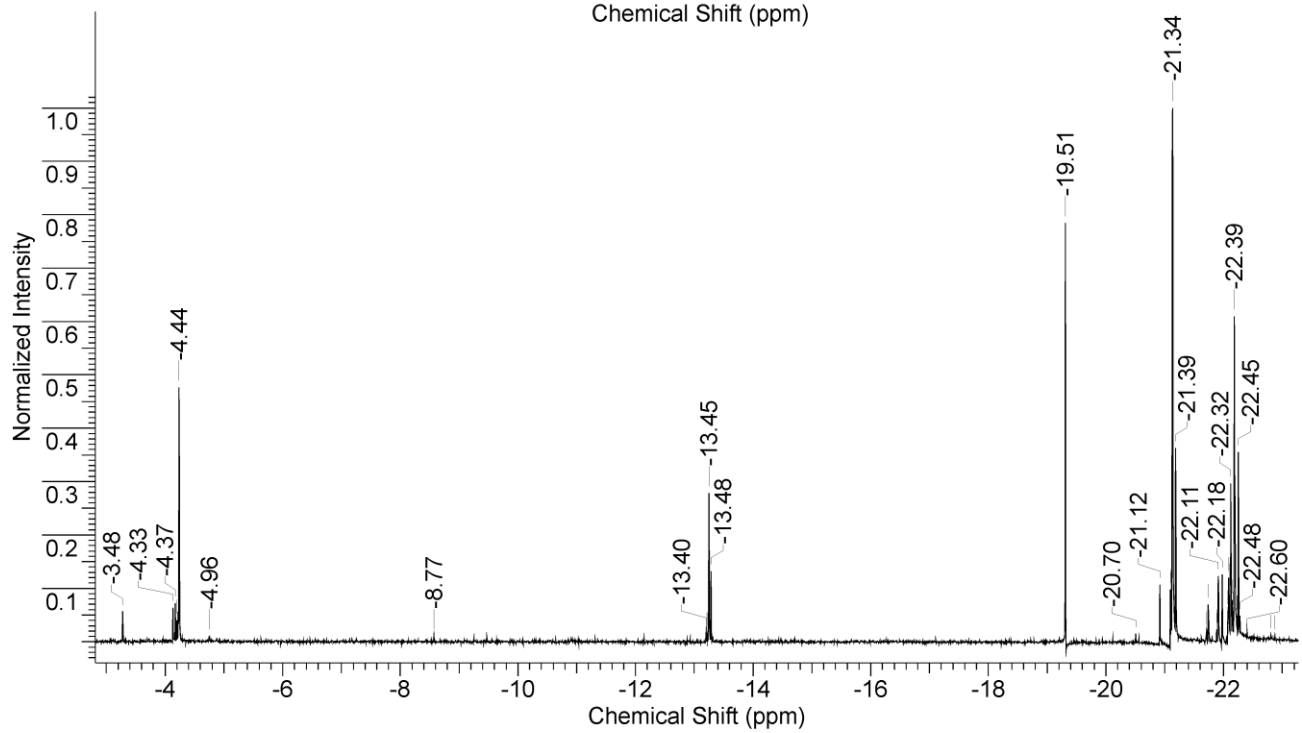
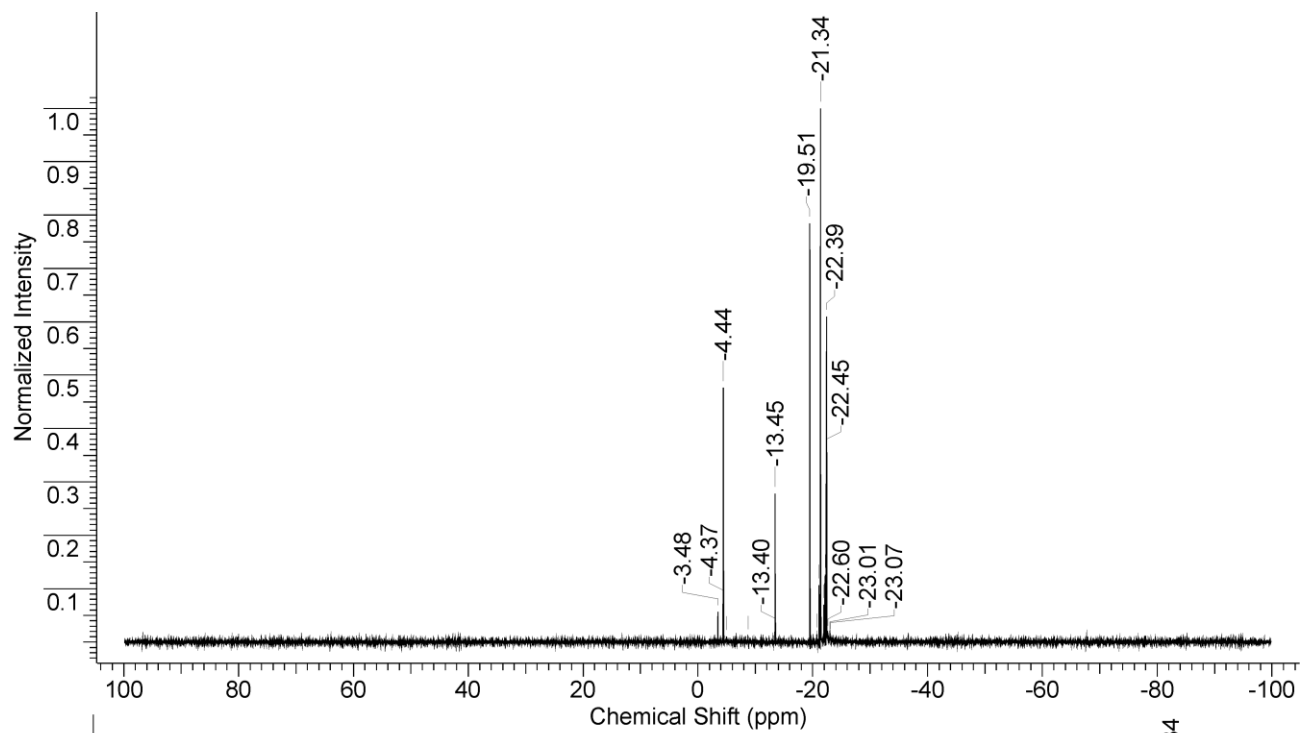
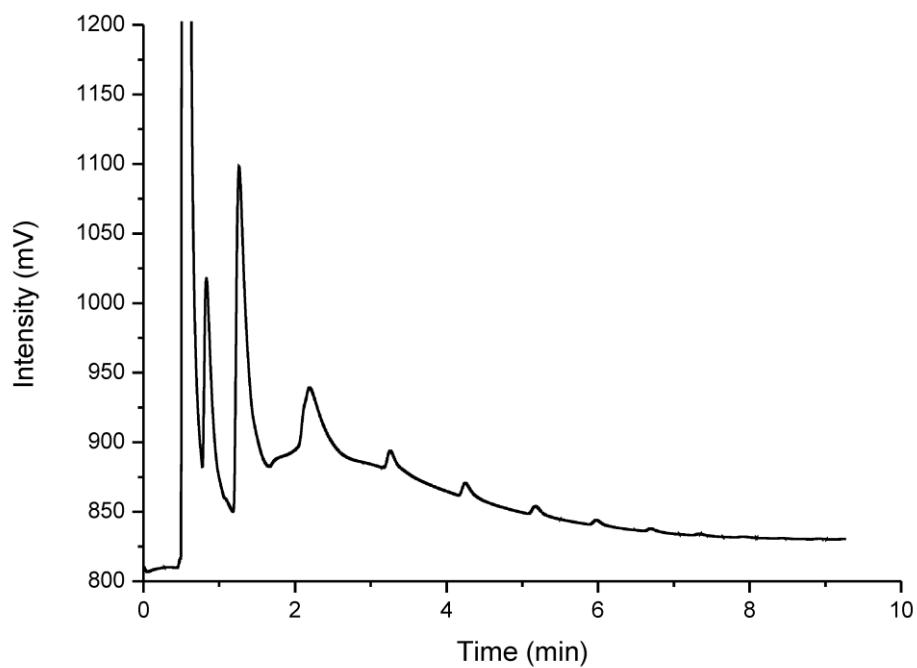
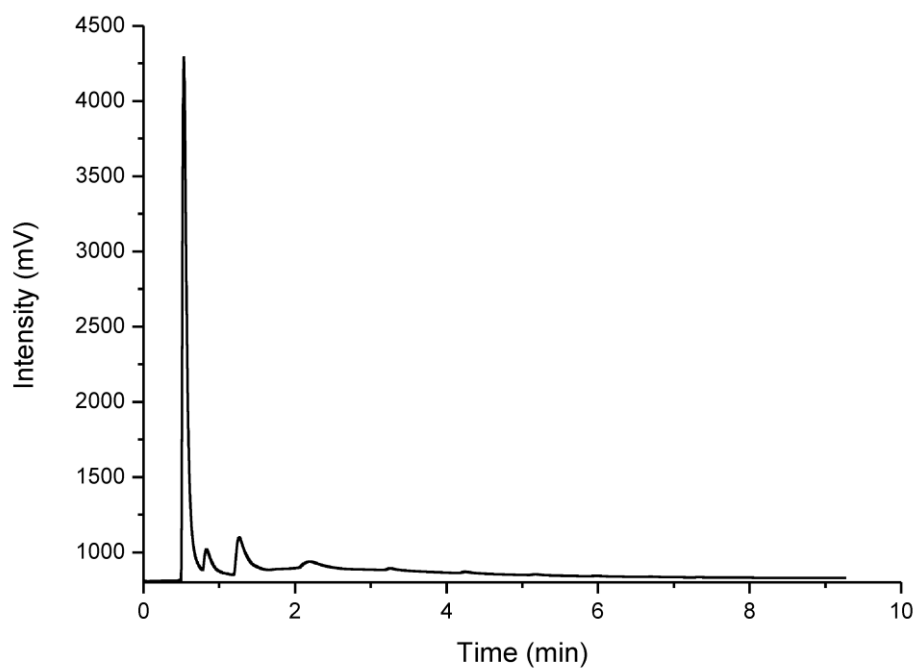


Table 1, entry 5



# GLC-curves of reaction mixtures

Table 1, entry 2



**Table 1, entry 3**

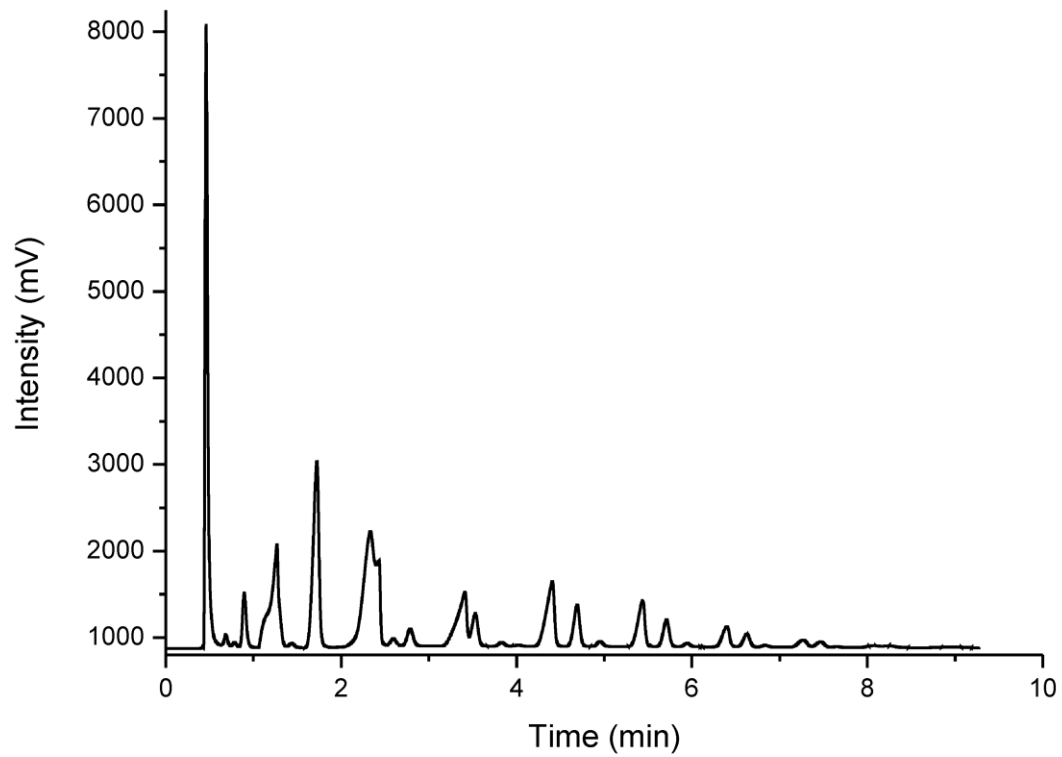
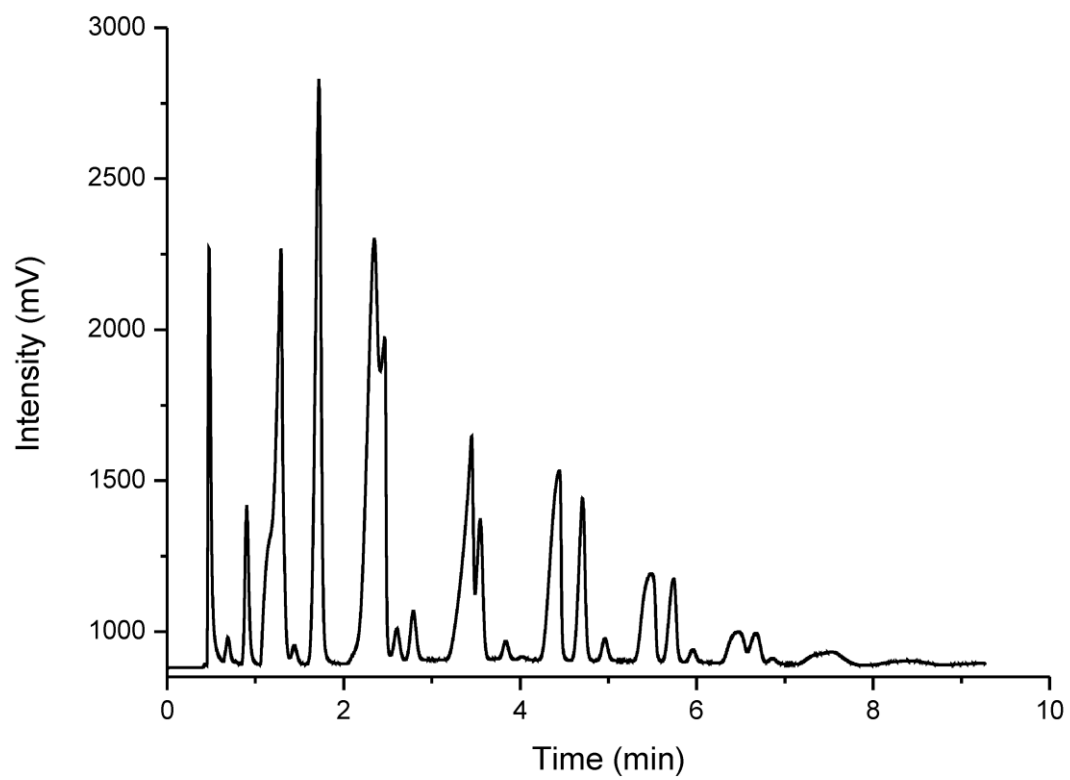
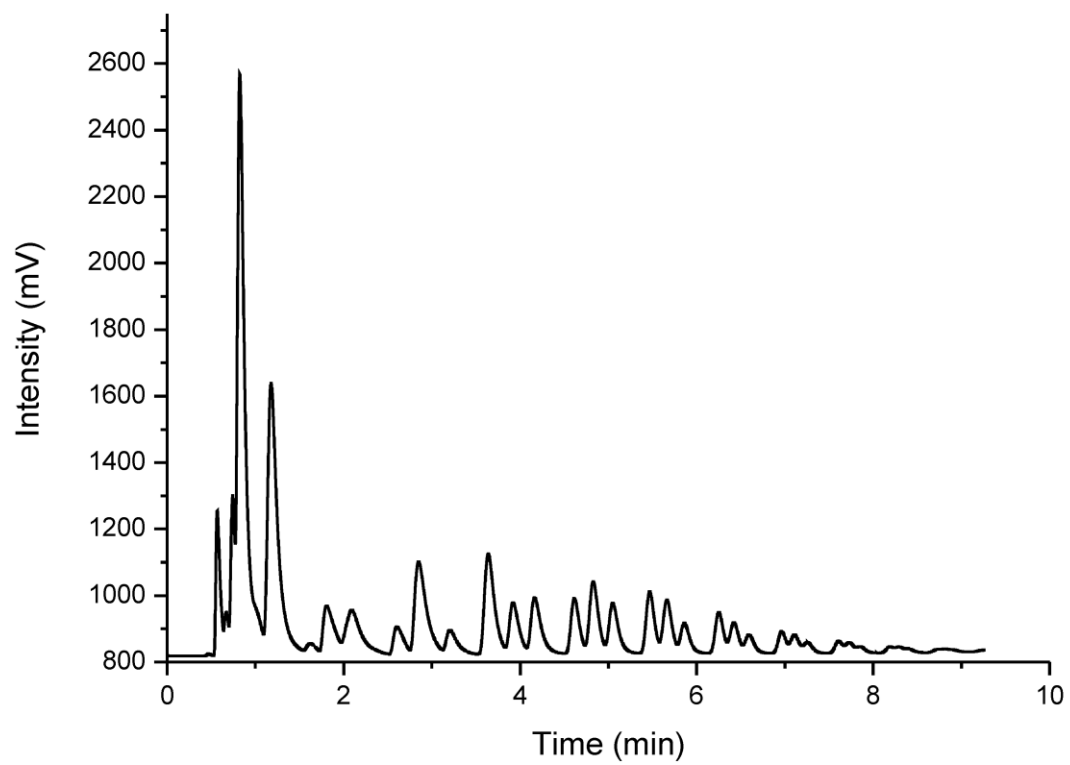


Table 1, entry 5



## GLC-curves of blocked products

Table 1, entry 2



**Table 1, entry 3**

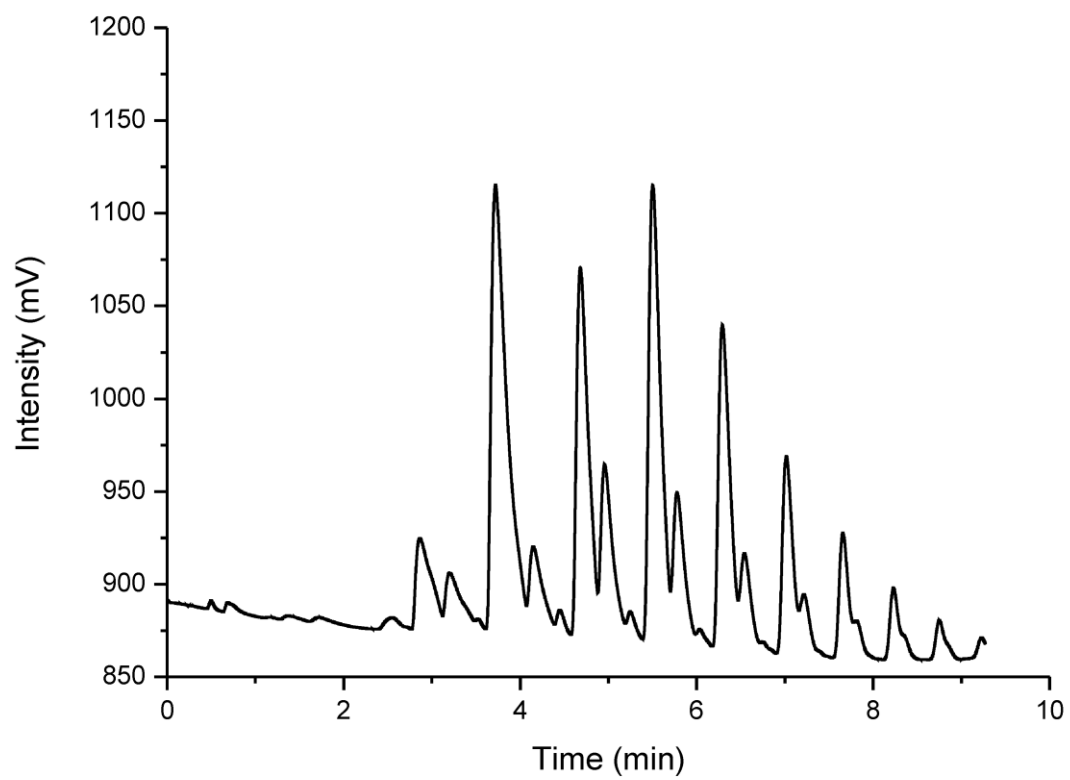
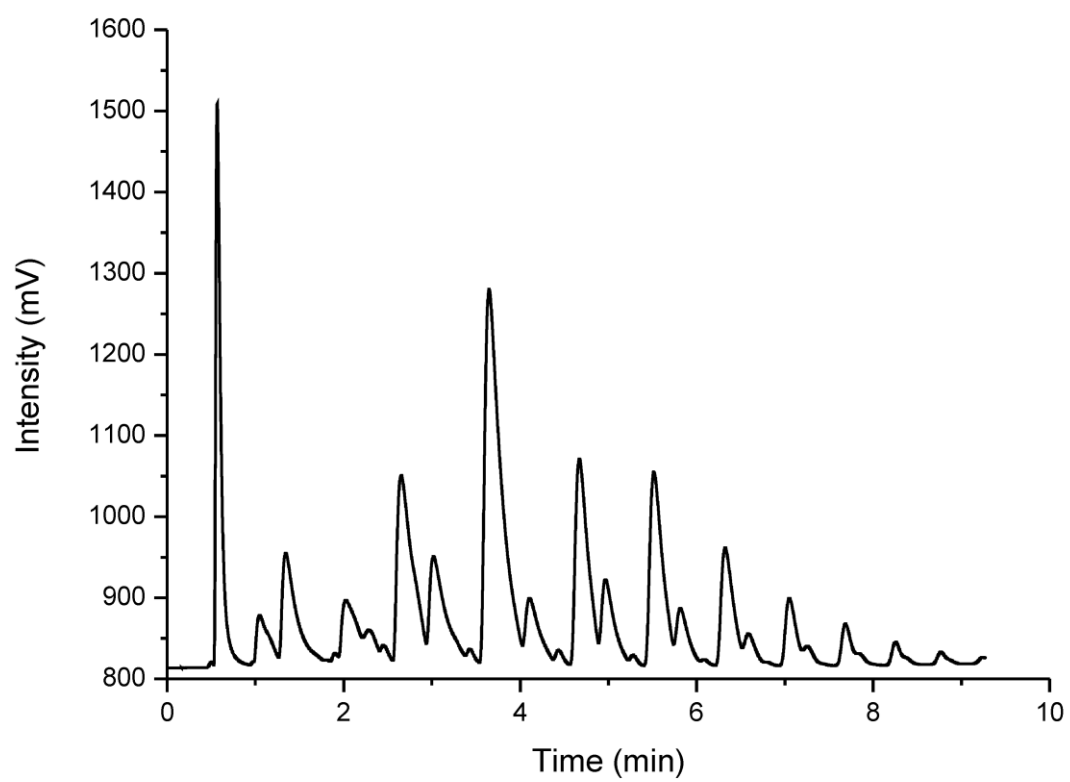


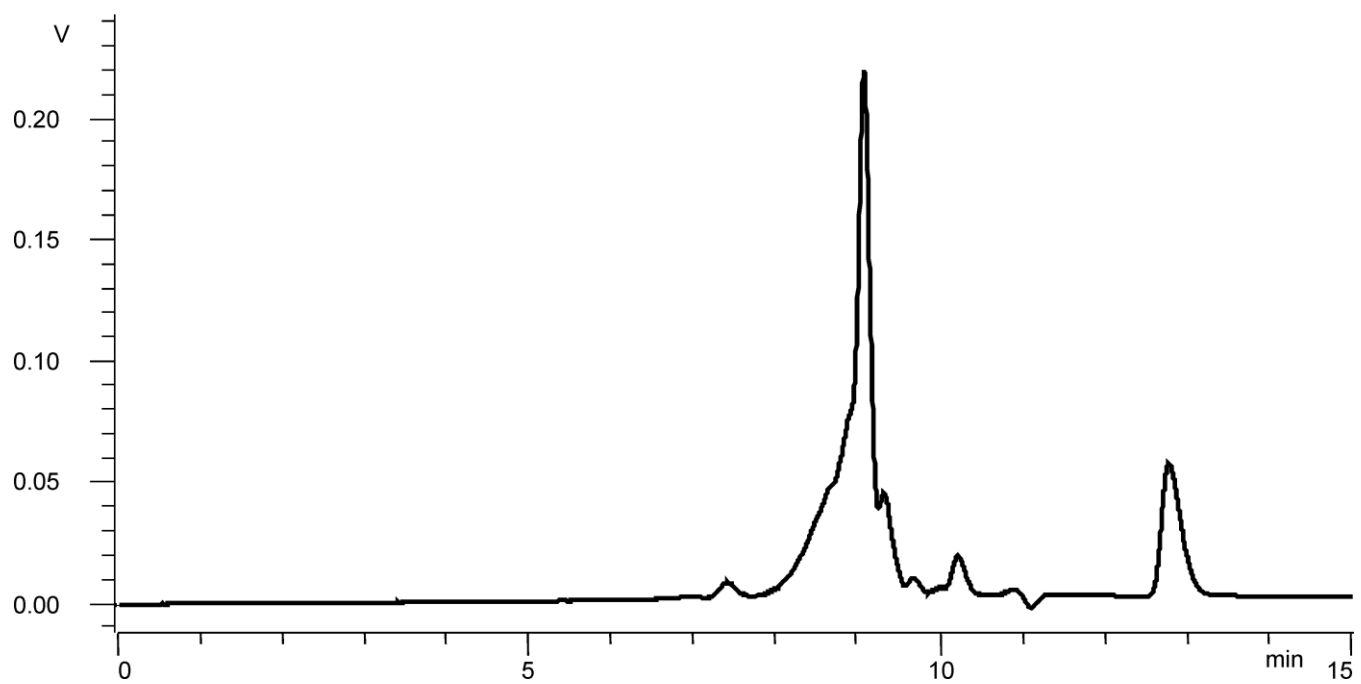


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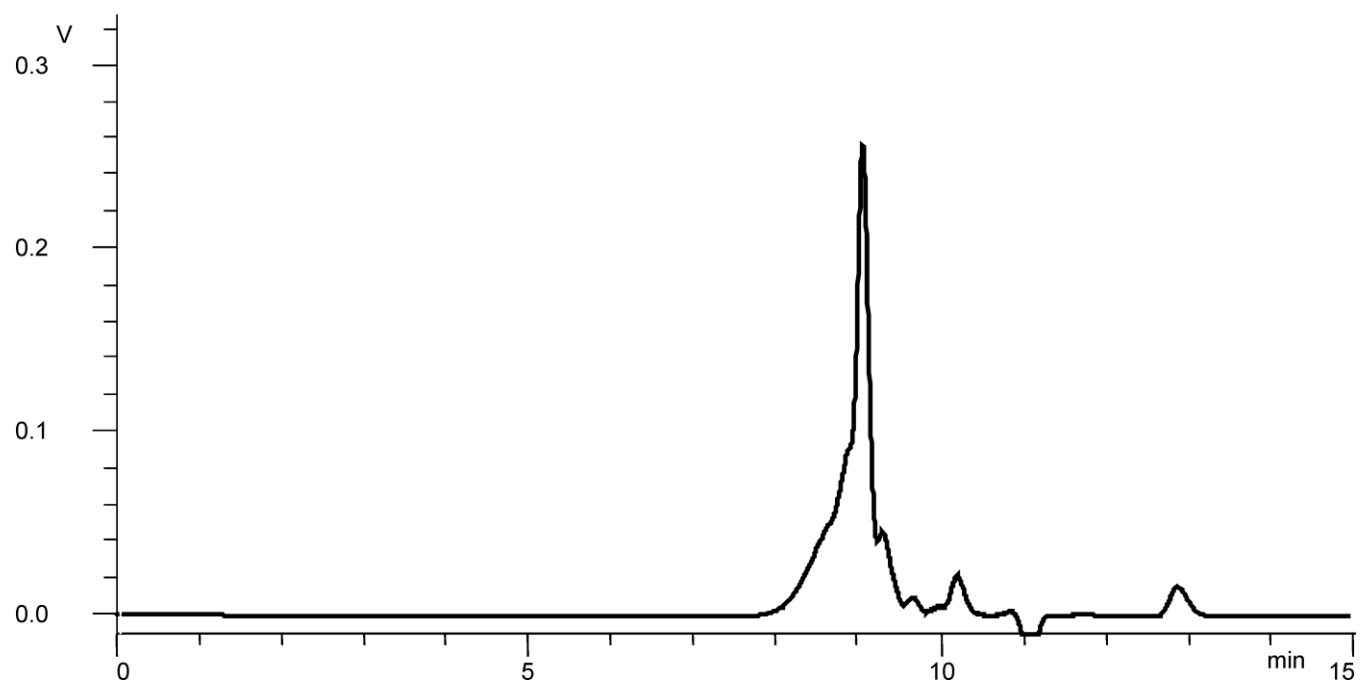


# GPC-curves of reaction mixtures

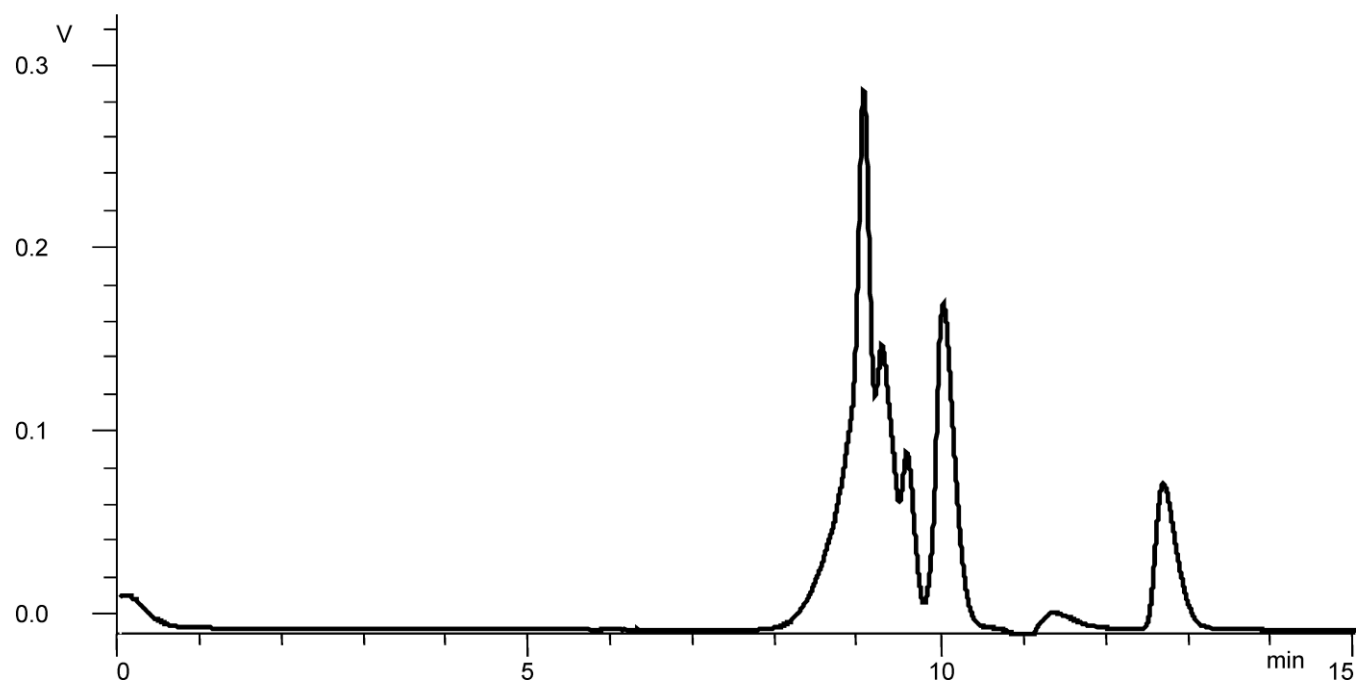
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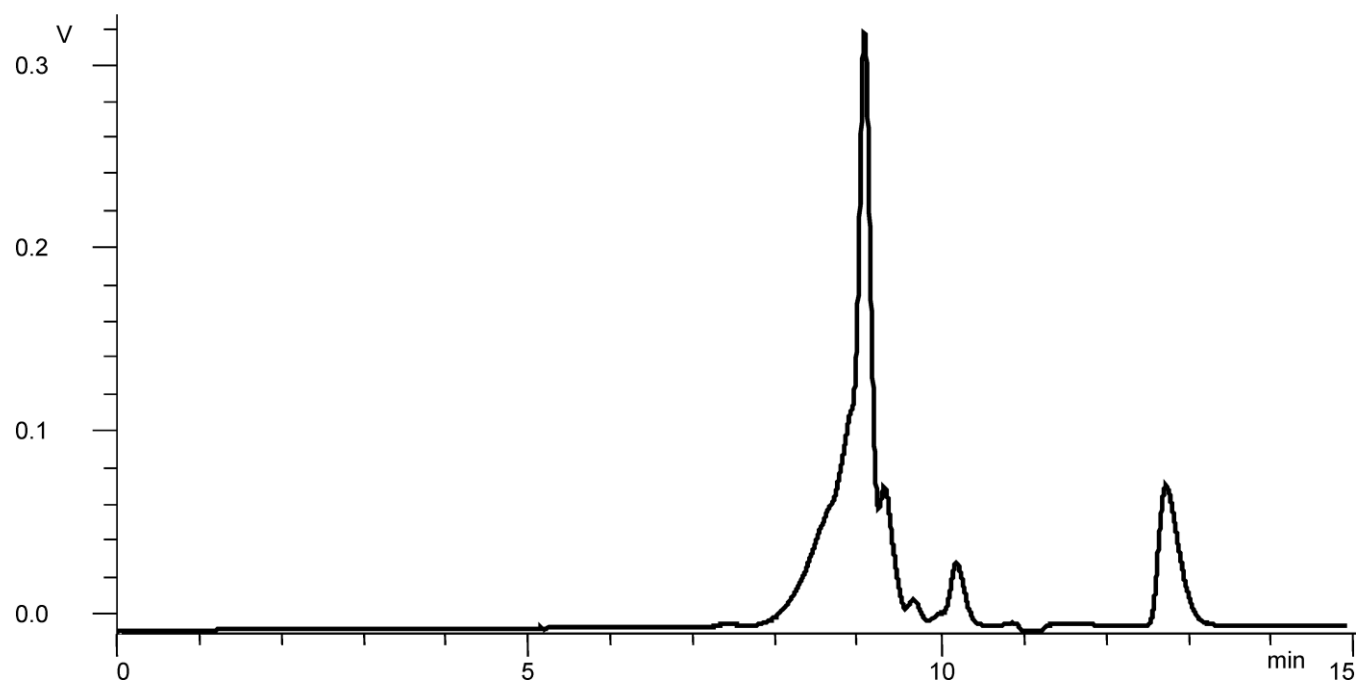
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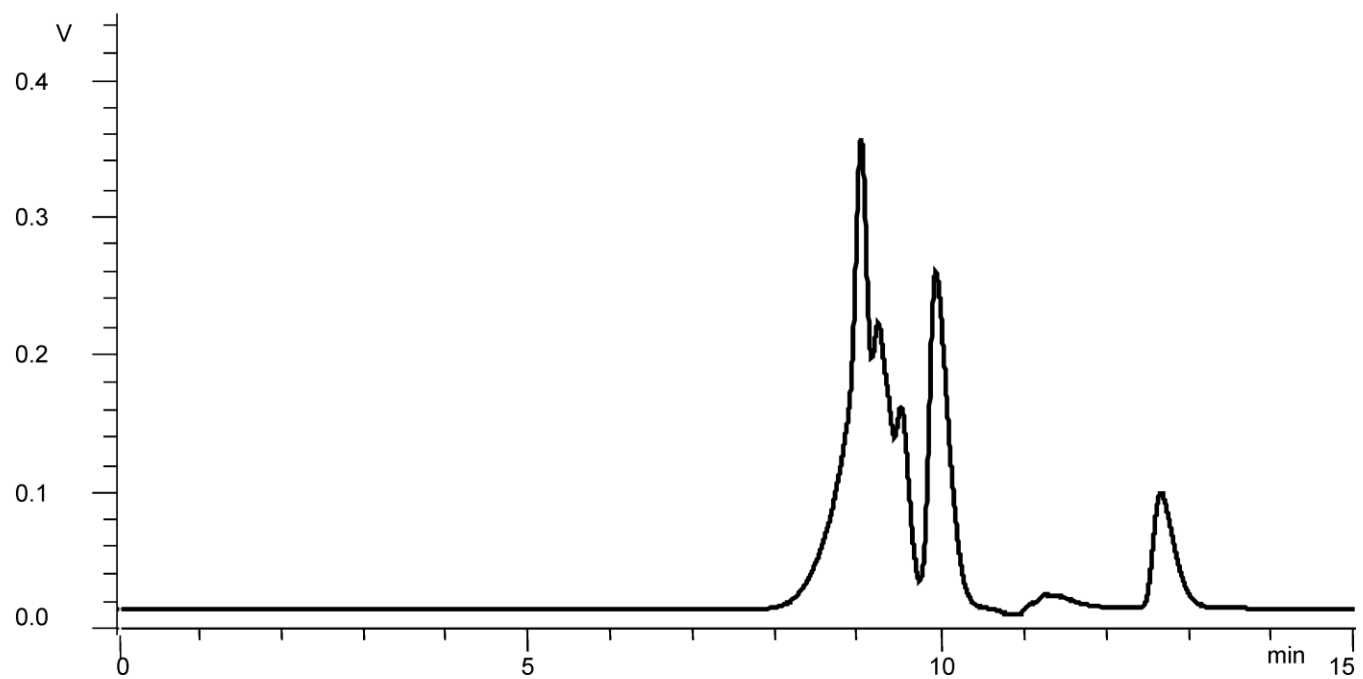
**Table 1, entry 3**



**Table 1, entry 4**



**Table 1, entry 5**



**Table 1, entry 6**

