

Electronic Supporting Information

Solubility of Hydrocarbon Oils in Alcohols ($\leq C_6$) and Synthesis of Difusel Carbonate for Degreasing.

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General Experimental Methods

Thin-layered chromatography (TLC) was made on aluminum backed silica gel (60 Å) plates containing fluorescent indicator ($\lambda = 254$ nm) and visualized with 10% phosphomolybdic acid stain. In further support for the chemical identity and purity of the molecules made in this report, elemental microanalysis of difusel carbonate was made by Atlantic Microlab, Inc. (Norcross, GA). Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was performed on solutions of acid digested difusel carbonate using a Thermo Scientific iCAP 6000 Series ICP Spectrometer.

Gas Chromatography-Mass Spectrometry

All GC-MS spectra were collected on a Thermo Scientific Trace 1310 Gas Chromatograph Exactive GC orbitrap mass spectrometer (San Jose, CA). The GC oven method began at 40 °C for 3 min, then ramped to 300 °C at a rate of 10 °C/min, and was held at 300 °C for 5 min. The gas-phase separation was achieved using a Thermo Scientific TG-5SILSMS column, 30 m x 0.25 mm x 0.25 μ m (San Jose, CA). A split flow mode of injection was used at 10 mL/min with a split ratio of 10.0. The inlet temperature was held at 275 °C. Eluted compounds passed through a heated auxiliary line (300 °C) and were directed toward the ion source region of the mass spectrometer, held at 305 °C, where they were subjected to positive mode chemical ionization (CI). Ultra high purity methane (Specialty Air Technologies, Long Beach, CA) was used as the CI gas at a flow rate of 1.50 mL/min. The mass range of the mass spectrometer was set from 50 to 550 atomic mass units.

Nuclear Magnetic Resonance Spectroscopy

All data were collected on a Bruker Ascend 500 MHz nuclear magnetic resonance spectrometer (1H at 500; ^{13}C at 125 MHz). Nuclear magnetic resonance data (free-induction decay's) were processed using ACD/NMR Processor software (Advanced Chemistry Development Inc., Toronto). All spectra were referenced to solvent or tetramethylsilane.

Melting Point and Freezing Point

The experiments to determine the melting point and freezing point of difusel carbonate was measured by using a TA Instruments Q200 differential scanning calorimeter (DSC). Analyte (2–4 mg) in a hermetically sealed aluminum pan was cooled to –80 °C under a nitrogen atmosphere (50 mL/min) followed by slow heating to 30 °C at a rate of 5 °C/min.

Bomb Calorimetry

The gross heats of combustion (H_c), or calorific values, of difusel carbonate was obtained using a Parr 6725 Semi-micro Calorimeter outfitted with a Parr Calorimeter Thermometer according to the standard method.¹ Benzoic acid was used as the internal standard (e.g., spike) for the tests and to calculate the energy equivalent of the instrument. Between each combustion measurement, the oxygen bomb was disassembled and cleaned with distilled water. The gross heat of combustion (H_c) was calculated from the average of three separate measurements of each analyte (70–90 mg). There was only 1.3% maximum standard deviation in the measurements of each analyte. From the H_c (kJ/g), the net heat of combustion (H_n) in kJ/g was calculated,^{2,3} Eq. 1:

$$H_n = H_c - [21.96 \times (\text{weight fraction hydrogen of the analyte})] \quad (1)$$

Ignition Quality Test (IQT) and Derived Cetane Number (DCN)

The derived cetane number for difusel carbonate (sample volume 100 mL) was collected by the Southwest Research Institute[®] (San Antonio, TX) using an Ignition Quality Test apparatus according to the published method.⁴

Flash Point

The flash point data for difusel carbonate (sample volume 2 mL) was collected with a Grabner Instruments MiniFlash FLP by the closed cup method.⁵

Density and Kinematic Viscosity

Density and kinematic viscosity of difusel carbonate was obtained simultaneously using an Anton-Paar SVM 3001 Stabinger viscometer by the published method.⁶ The instrument was injected with analyte (~3 mL) and set to run from 30 to 40 °C in 5 °C increments. The data was collected at 40 °C as this is the temperature specified in ASTM 975 for diesel fuels.⁷

References

1. ASTM D240-17 (2017) *Standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter*. ASTM International, West Conshohocken, Pennsylvania, USA.
2. Babrauskas, V. (1992) Related quantities (a) heat of combustion and potential heat. In: Babrauskas, V., & Grayson, S. J. (eds) *Heat release in fires*, Elsevier Applied Science, London.
3. Jessup, R. S. (1960) Precise measurement of heat of combustion with a bomb calorimeter. U.S. Department of Commerce, National Bureau of Standards, Washington. <http://www.dtic.mil/dtic/tr/fulltext/u2/a286701.pdf>. [accessed 28 Aug 2018]

4. ASTM D6890-16e2 (2018) *Standard test method for determination of ignition delay and derived cetane number (DCN) of diesel fuel oils by combustion in a constant chamber*. ASTM International, West Conshohocken, Pennsylvania, USA.
5. ASTM D7094-17a (2017) *Standard test method for flash point by modified continuous closed cup (MCCCFP) tester*. ASTM International, West Conshohocken, Pennsylvania, USA.
6. ASTM D4052-18 (2018) *Standard test method for density, relative density, and API gravity of liquids by digital density meter*. ASTM International, West Conshohocken, Pennsylvania, USA.
7. ASTM D975-18 (2018) *Standard specifications for diesel fuel oils*. ASTM International, West Conshohocken, Pennsylvania, USA.

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Table S1. Heat of combustion data for difusel carbonate

Trial	MW of Sample (g/mol)	Density of Sample (g/mL)	Mass of Sample (g)	Gross HOC of Sample (KJ/g)	Gross HOC of Sample (KJ/mol)	HOV of water (KJ/mol)	NHOC (KJ/mol)	Volumetric NHOC (MJ/L)	Average	SD	RSD <1%	Gravimetric NHOC (MJ/kg)
1	202.29	0.90937	0.4300	32.6057	6595.807	447.26	6148.547	27.640				
2	202.29	0.90937	0.4864	32.7604	6627.101	447.26	6179.841	27.781	27.698	0.061	0.220	30.459
3	202.29	0.90937	0.3504	32.6769	6610.210	447.26	6162.950	27.705				

Table S2. Density of DFC at various temperatures.

Temperature (°C)	Density (g/cm ³)
39.999	0.88725
35.000	0.89179
30.000	0.89623
25.000	0.90062
19.999	0.90499
14.999	0.90937
9.999	0.91375
4.999	0.91813
-0.001	0.92251
-5.001	0.92676
-10.001	0.93110
-15.002	0.93545
-20.000	0.93982

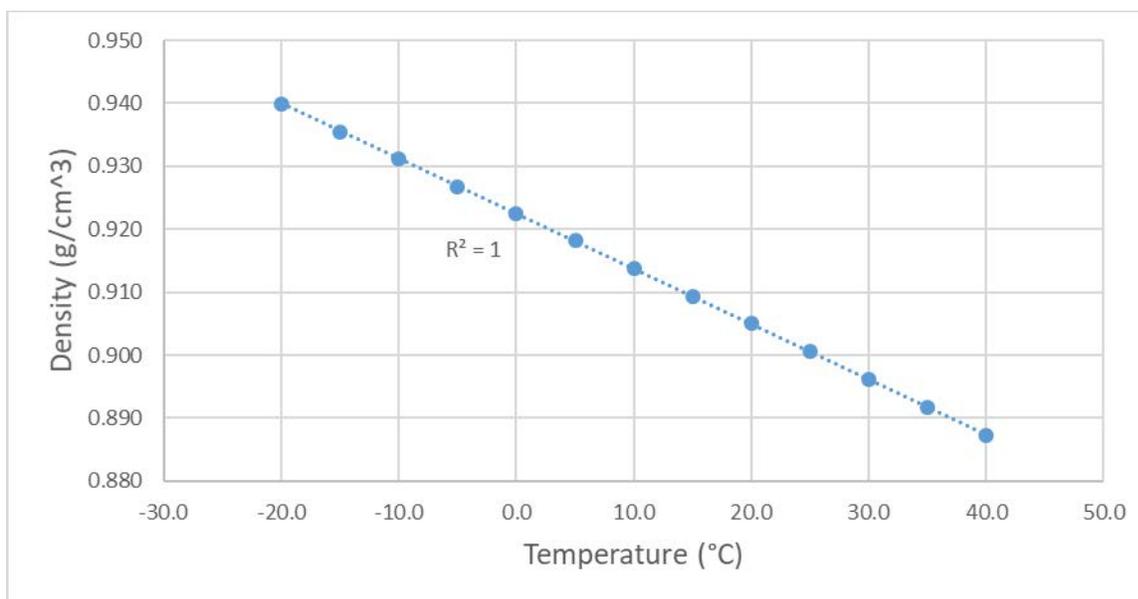


Figure S1. Plot of density versus temperature for DFC.

Table S3. Kinematic viscosity versus temperature for DFC.

Temperature (°C)	Kin. Visc. (mm ² /s)
39.999	2.0166
35.000	2.2102
30.000	2.4376
25.000	2.7056
19.999	3.0236
14.999	3.4026
9.999	3.8596
4.999	4.4164
-0.001	5.1039
-5.001	5.9998
-10.001	7.1092
-15.002	8.5476
-20.000	10.4640

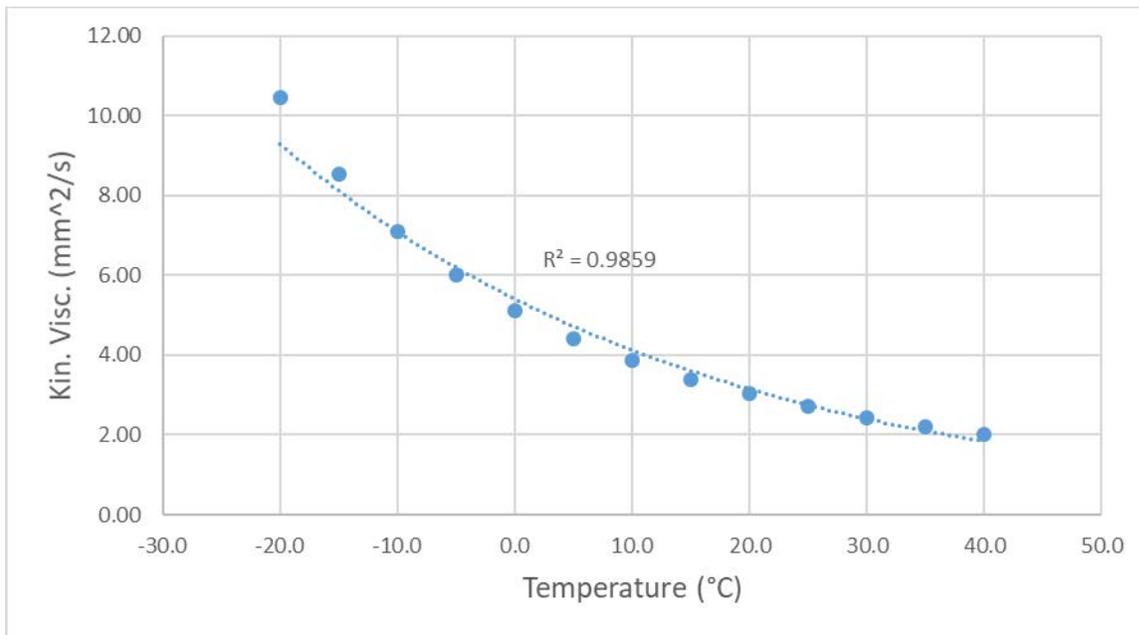


Figure S2. Plot of kinematic viscosity versus temperature for DFC.

Figure S3 ^1H NMR of dried fusel oil (CDCl_3)

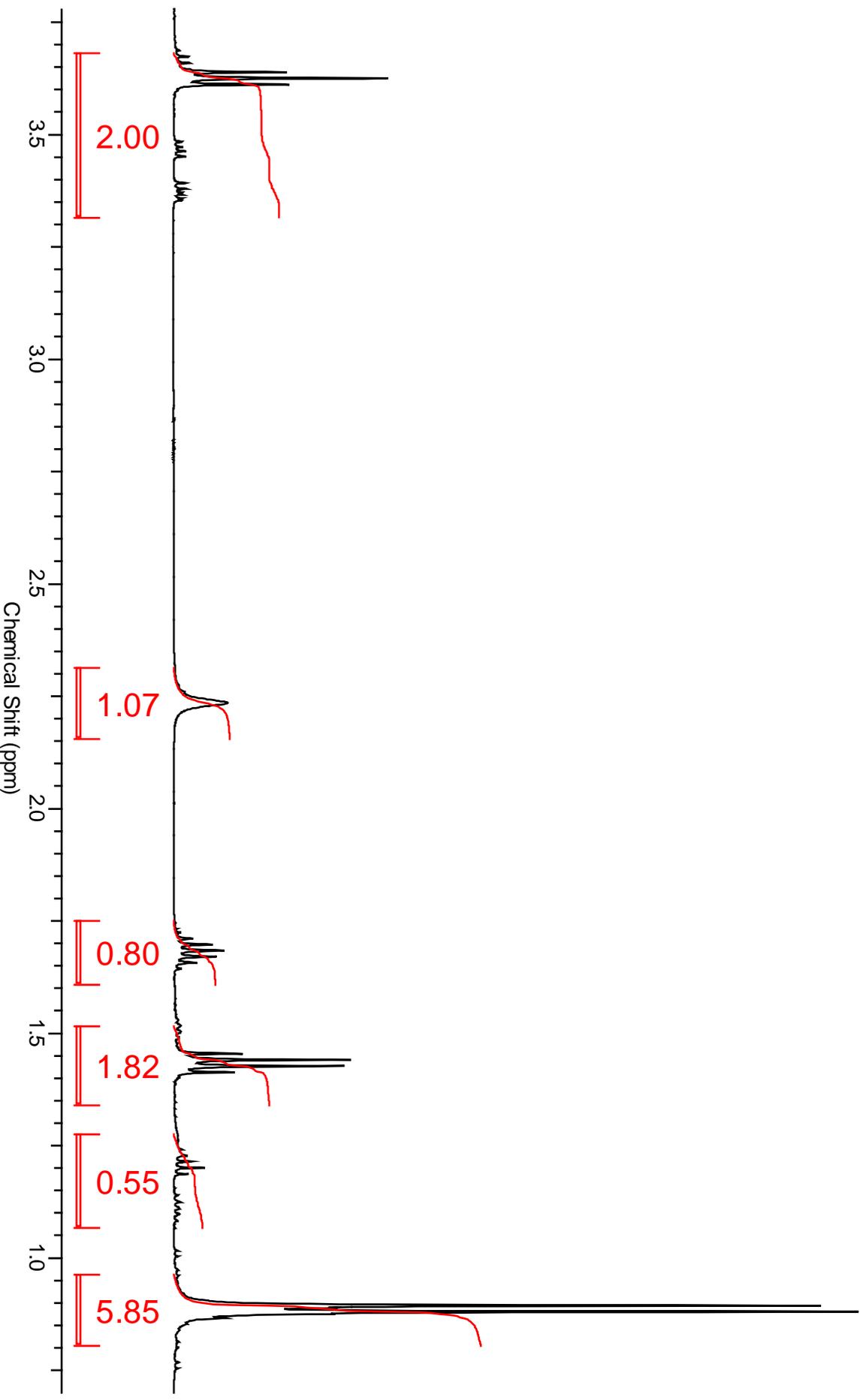


Figure S4 ^{13}C NMR of dried fusel oil (CDCl_3)

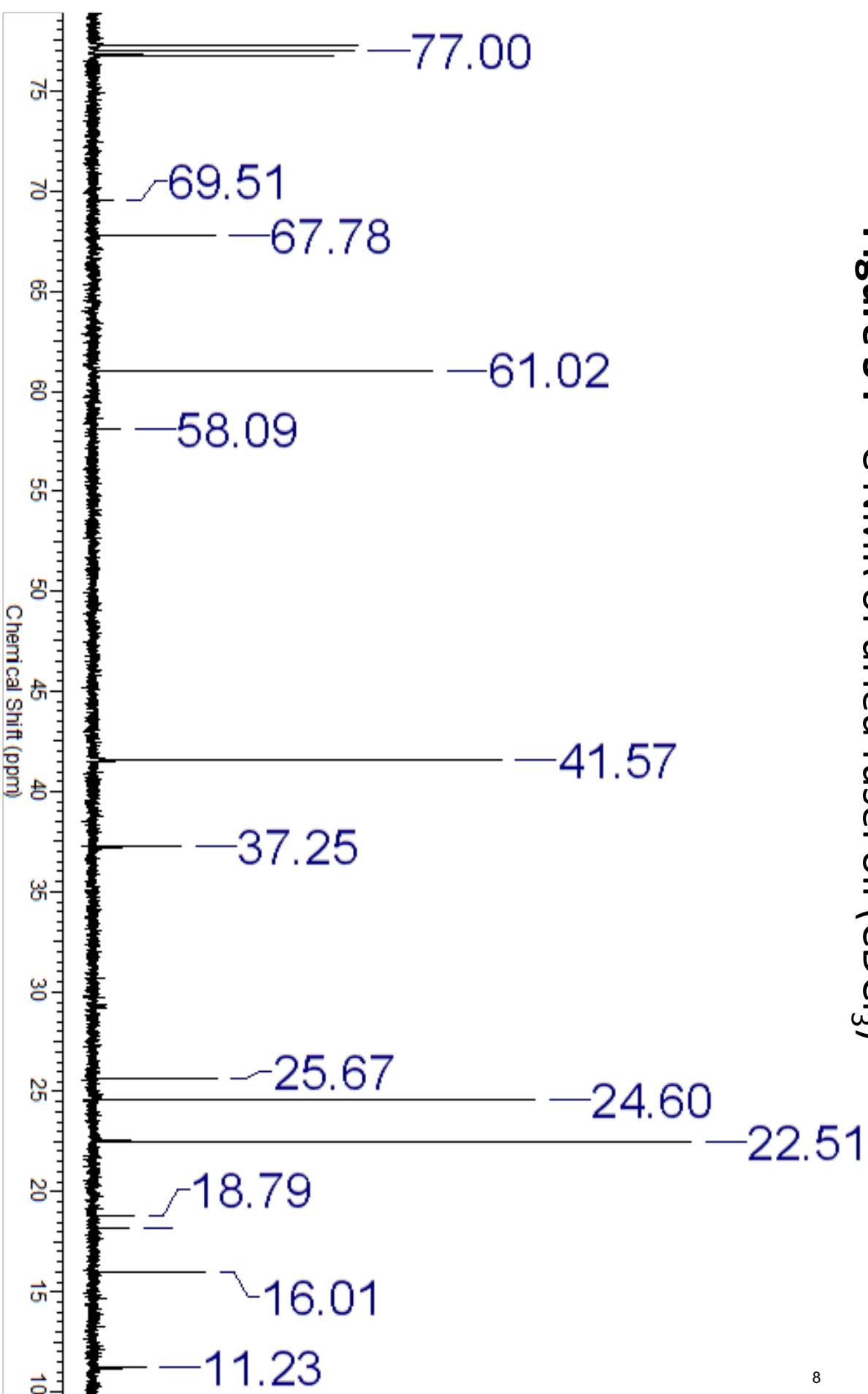


Figure S5 ^1H NMR of difusel carbonate (DFC) (CDCl_3)

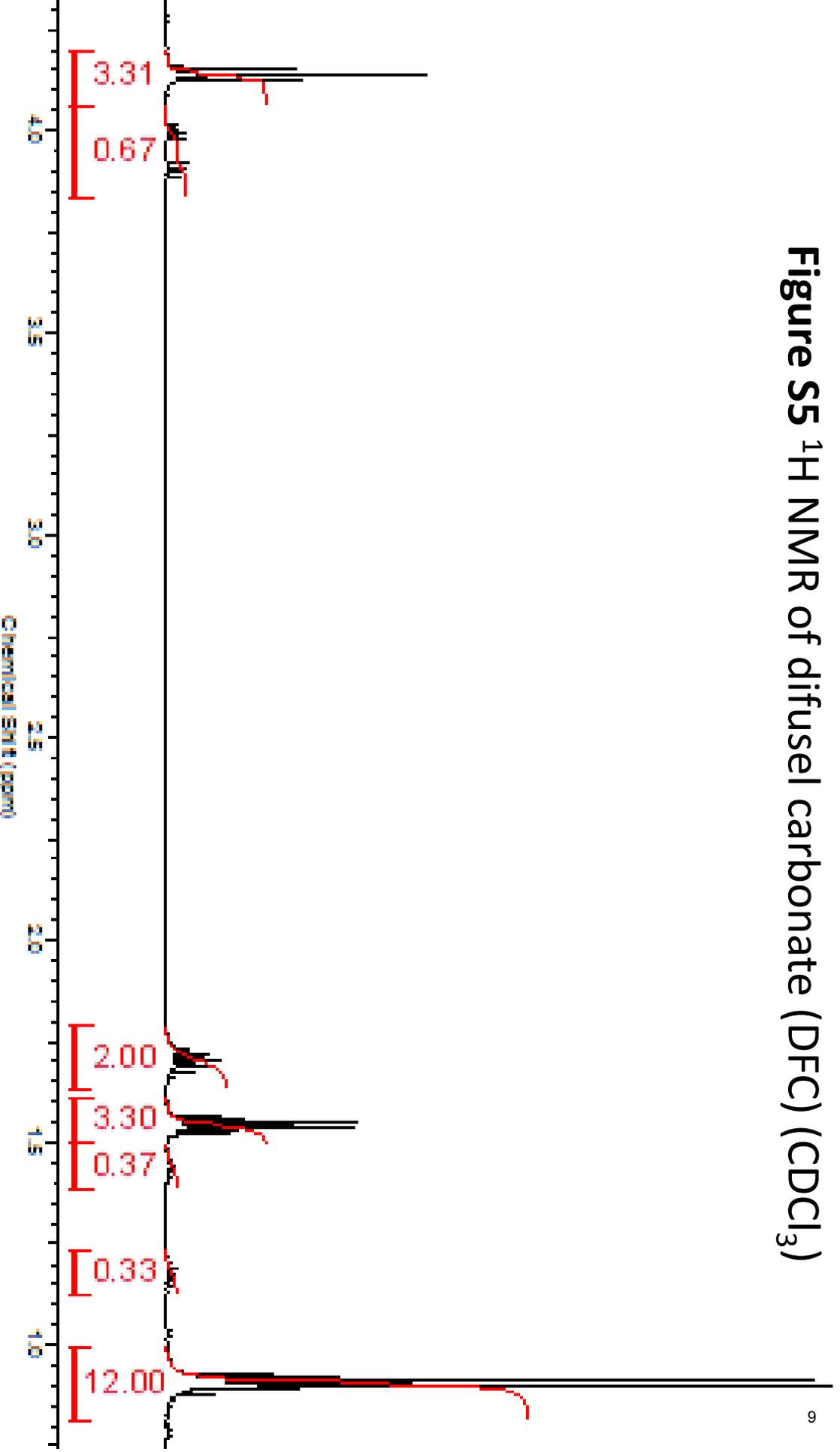


Figure S6 ^{13}C NMR of difusel carbonate (DFC) (CDCl_3)

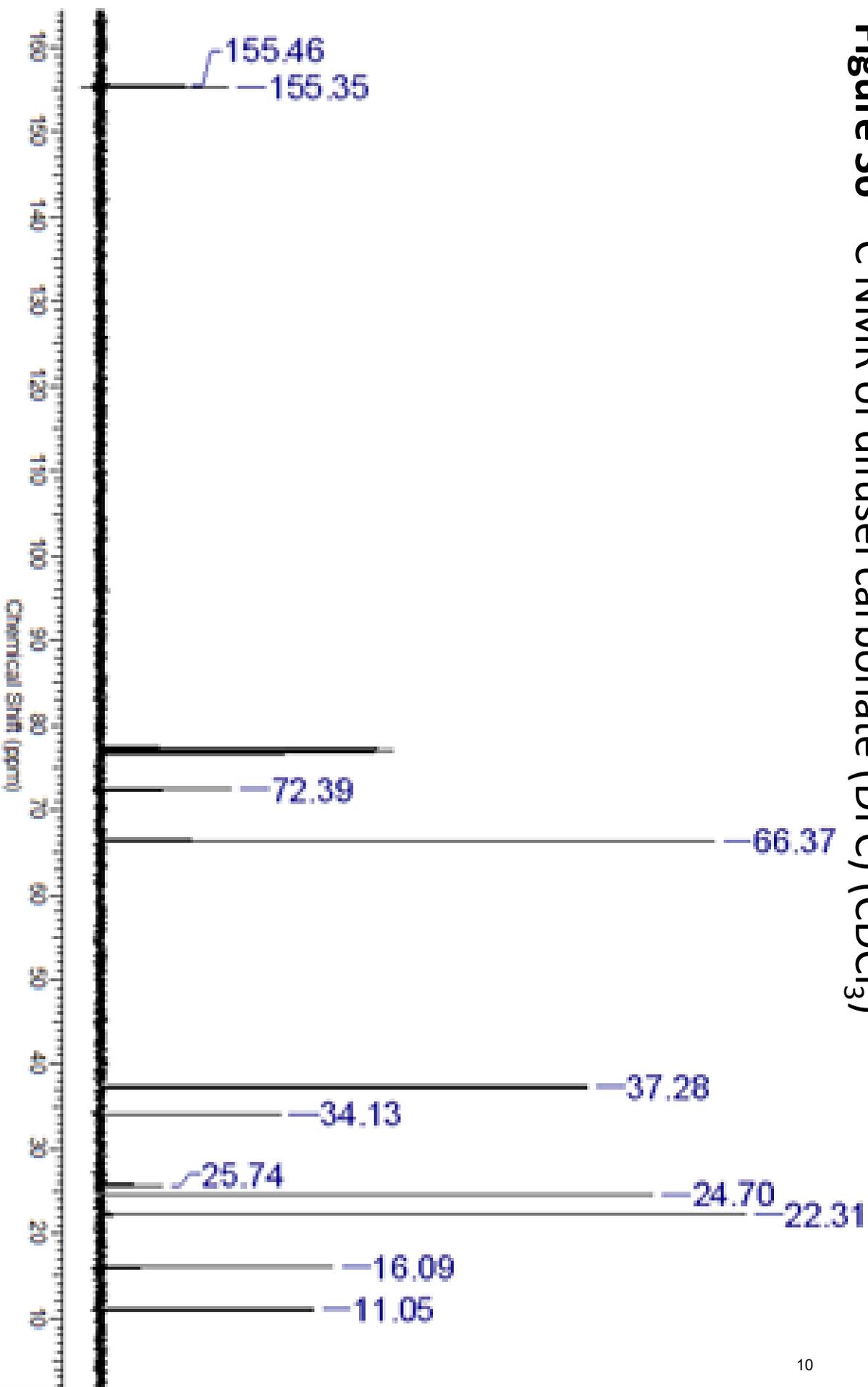
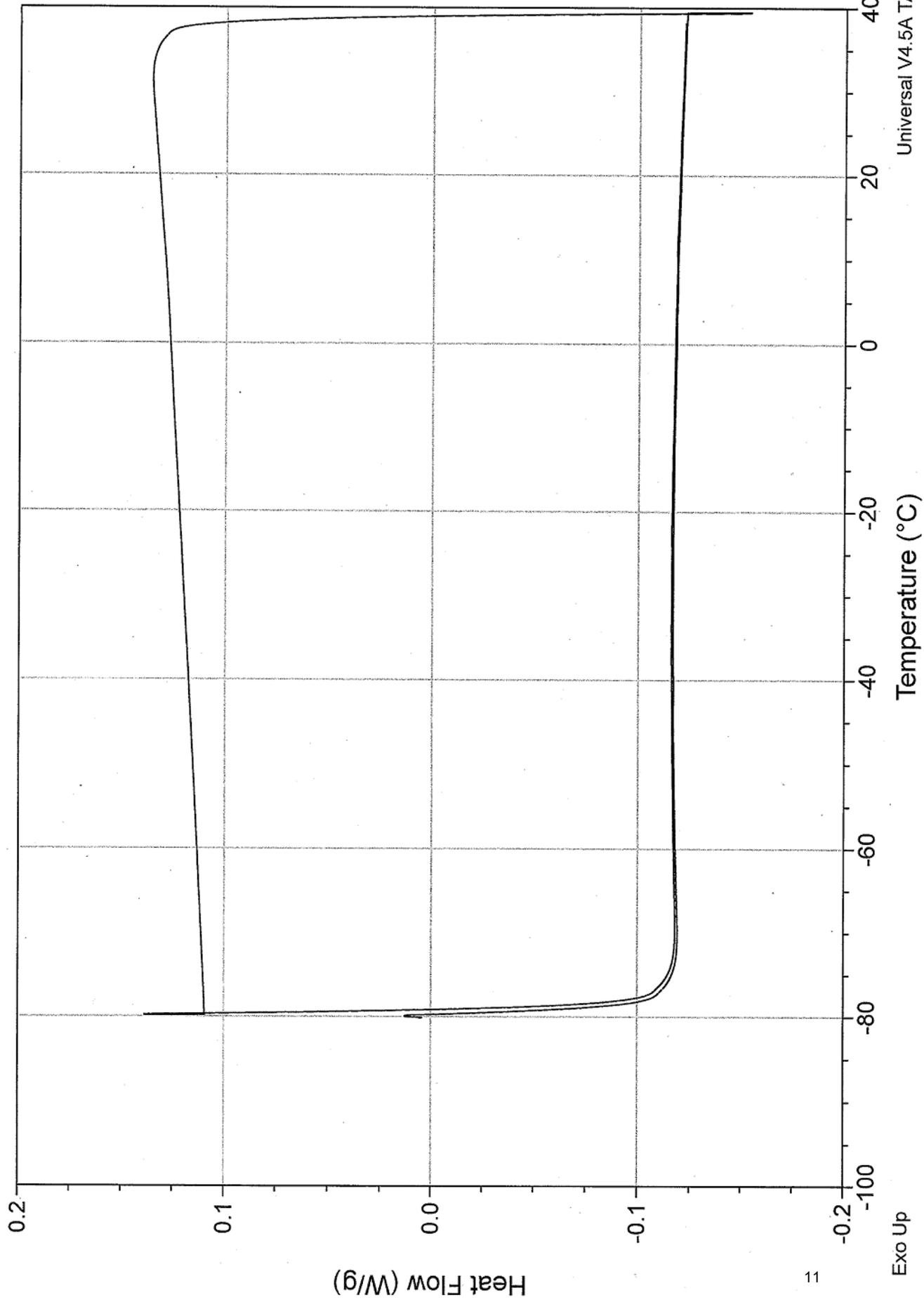


Figure S7 DSC thermogram DFC (10 °C/min)



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Exo Up

Figure S8 ^1H NMR (CDCl_3) difusel carbonate made using KOH catalyst

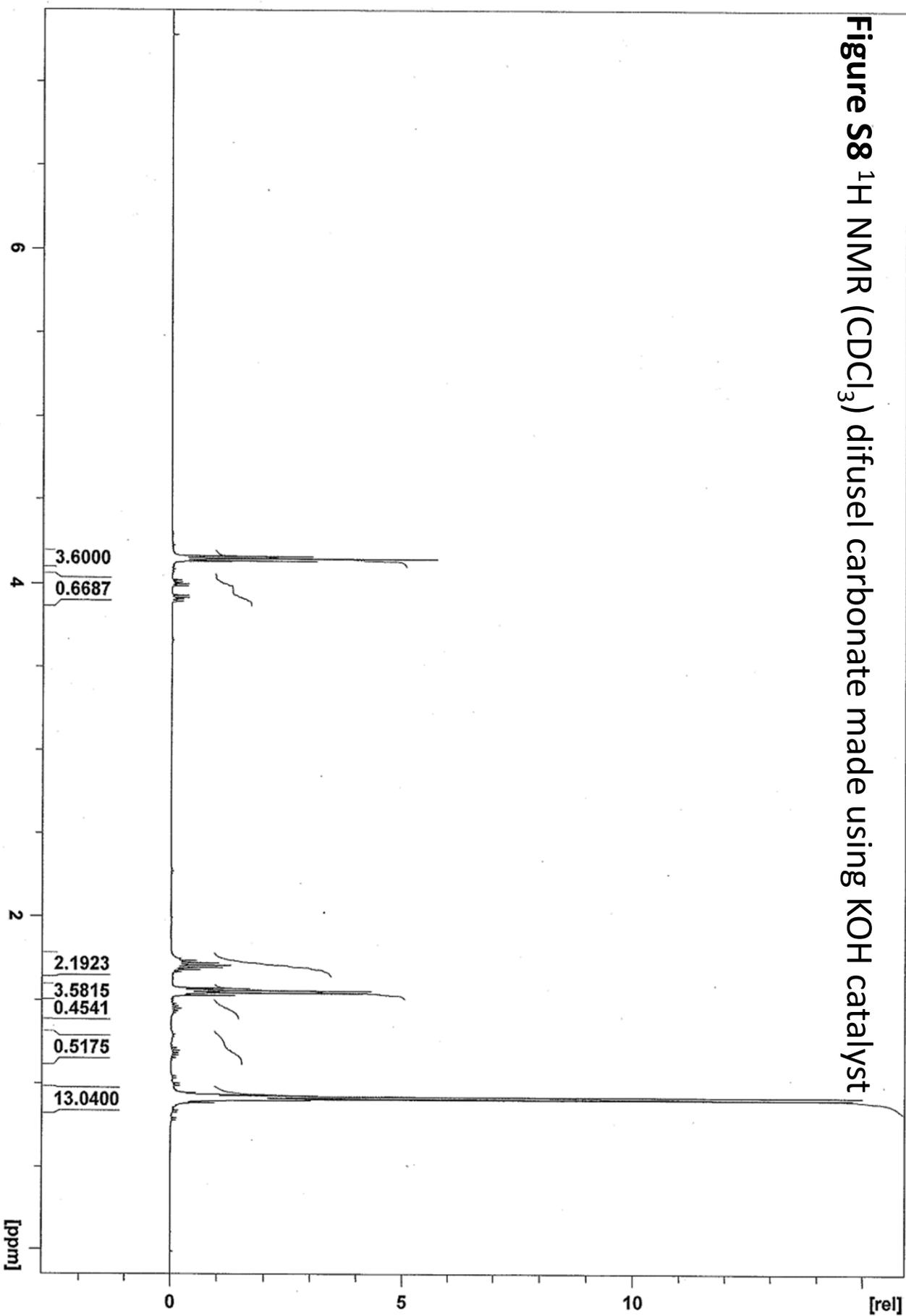


Figure S9 GC trace for DFC

RT: 0.00 - 31.00

NL:
1.71E9
TIC MS
FY19_179

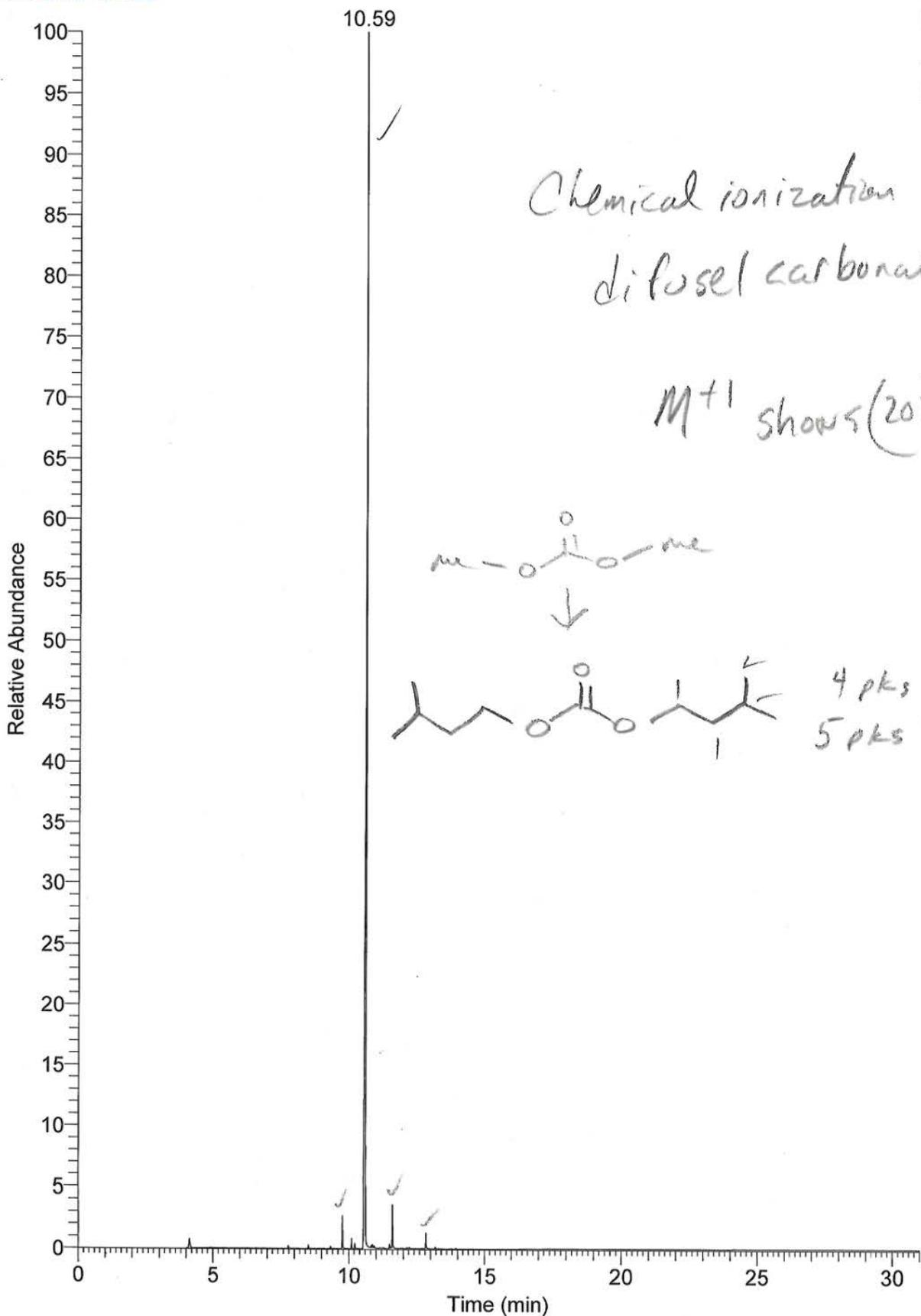


Figure S10 Mass Spectrum DFC

C:\TraceFinderData\...NF
CI 20deg/min hold 15

FY19_179 #2564 RT: 10.56 AV: 1 NL: 2.50E8

T: FTMS + p CI Full ms [50.0000-550.0000]

