

Preparation of Biomass-Derived Furfuryl Acetals by Transacetalization Reactions Catalyzed by Nanoporous Aluminosilicates

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1) Catalyst Preparation

a) Nanoporous Aluminosilicate Al-13-(2.42)¹

Cetyltrimethylammonium bromide (CTAB) (4.0 g, 11 mmol) was dissolved in a solution of hydrochloric acid (2.5 ml, 0.1 M) and ethanol (17.5 mL). TEOS (25 mL, 112 mmol) was then added and the mixture stirred for 10 minutes at 40 °C. The solution was cooled to room temperature and aluminium nitrate nonahydrate (3.35 g, 8.95 mmol) was added in one portion. The mixture was stirred for 20 minutes and then left to age at room temperature for 24 hours. The resultant orange solid was crushed into a fine powder and then calcined in air at 650 °C for 5 hours to remove the organic template to give a fine white powder. The plain silicate material was made in a similar manner except that no aluminium nitrate nonahydrate was added. All catalysts were stored at 140 °C for 12 hours prior to use.

b) Nanoporous Aluminosilicate Al-13-(3.18)²

Cetyltrimethylammonium bromide (CTAB) (4.0 g, 11 mmol) was dissolved in a solution of hydrochloric acid (2.5 mL, 0.1 M), ethanol (17.5 mL) and water (22.5 mL). Tetraethyl orthosilicate (25 ml, 112 mmol) was then added and the mixture stirred for 10 minutes at 40 °C. The solution was cooled to room temperature and aluminium nitrate nonahydrate (3.35 g, 8.95 mmol) was added in one portion. The mixture was stirred for 20 minutes and then left to age at room temperature for 24 hours. The resultant orange solid was crushed into a fine powder and calcined in air at 650 °C for 5 hours to remove the organic template to give a fine white powder. All materials were stored at 140 °C for at least 12 hours prior to use.

c) Nanoporous Borosilicate B-13-(3.54)³

Cetyltrimethylammonium bromide (4.0 g, 11 mmol) was dissolved in a solution of hydrochloric acid (2.5 mL, 0.1 M), ethanol (17.5 mL) and water (22.5 mL). Tetraethyl orthosilicate (25 ml, 112 mmol) was then added and the mixture stirred for 10 minutes at 40 °C. The solution was cooled to room temperature and boric acid (553 mg, 8.95 mmol) was added in one portion. The mixture was stirred for 20 minutes and then left to age at room temperature for 24 hours. The resultant white solid was crushed into a fine powder and calcined in air at 650 °C for 6 hours to remove the organic template to give a fine white powder. All materials were stored at 140 °C for at least 24 hours prior to use.

d) Nanoporous Borosilicate B-13-(2.34)

Cetyltrimethylammonium bromide (4.0 g, 11 mmol) was dissolved in a solution of hydrochloric acid (2.5 mL, 0.1 M), ethanol (17.5 mL). Tetraethyl orthosilicate (25 ml, 112 mmol) was then added and the mixture stirred for 10 minutes at 40 °C. The solution was cooled to room temperature and boric acid (553 mg, 8.95 mmol) was added in one portion. The mixture was stirred for 20 minutes and then left to age at room temperature for 24 hours. The resultant white solid was crushed into a fine powder and calcined in air at 650 °C for 6 hours to

remove the organic template to give a fine white powder. All materials were stored at 140 °C for at least 24 hours prior to use.

e) Mixed Metal Silicates: Typical procedure for the Preparation of B-Al-13-(2.20)

Cetyltrimethylammonium bromide (4.0 g, 11 mmol) was dissolved in a solution of hydrochloric acid (2.5 mL, 0.1 M), ethanol (17.5 mL). Tetraethyl orthosilicate (25 ml, 112 mmol) was then added and the mixture stirred for 10 minutes at 40 °C. The solution was cooled to room temperature and aluminium nitrate nonahydrate (3.35 g, 8.95 mmol) was added in one portion followed by boric acid (553 mg, 8.95 mmol). The mixture was stirred for 20 minutes and then left to age at room temperature for 24 hours. The resultant white solid was crushed into a fine powder and calcined in air at 650 °C for 6 hours to remove the organic template to give a fine white powder. All materials were stored at 140 °C for at least 24 hours prior to use. The corresponding Ce-Al-(2.60) and Ze-Al-(2.13) materials were prepared in a similar fashion employing cerium nitrate hexahydrate and zirconium (iv) acetylacetonate respectively.

2) Catalyst Characterization

Specific surface areas were obtained by the BET method at liquid nitrogen temperatures using a Micromeritics Gemini or a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at 120 °C under a flow of helium for 2 hours prior to analysis. Pore sizes were obtained using a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at 120 °C under vacuum for 3 hours prior to analysis. Pore sizes were calculated by applying the non-local density functional theory (NLDFT) method to the N₂ sorption isotherm at -196 °C employing Quantachrome AS-1 software data reduction parameters. Low angle XRD patterns were obtained using a Panalytical X'Pert Pro diffractometer. Measurements were performed in transmission mode at room temperature using monochromatic CuK α 1 radiation. TEM analysis was performed on a Jeol 2100 instrument operated at 200 kV. Samples were prepared by dispersion in methanol by sonication and deposited onto lacey carbon coated 300 mesh copper grids. ATR FT-IR spectra were obtained using a Perkin Elmer Spectrum Two spectrometer. NH₃-TPD experiments were carried out using a Quantachrome ChemBet TPR/TPD Chemisorption Analyser. Prior to the measurements, approximately 30 mg of sample was activated by heating at 100 °C for 1 h. The sample was then cooled to room temperature before treating with ammonia for 30 minutes. Physically adsorbed ammonia was removed by purging with helium at 90 °C for 1 hour before the NH₃-TPD analysis. The NH₃-TPD of the samples was carried out by increasing the cell temperature linearly from 90 °C to 900 °C, with a heating rate of 20 °C min⁻¹ and a helium flow rate of 80 cm³ min⁻¹. Elemental compositions were obtained with a JOEL scanning electron microscope fitted with an EDX detector using a 20 KeV accelerating voltage. MAS-NMR spectra were obtained courtesy of the EPSRC National Solid State NMR Service, Durham University. Aluminium spectra were obtained using a Varian VNMRs system, with direct excitation (DE) and the results

are reported relative to an external 1M aqueous $\text{Al}(\text{NO}_3)_3$ solution. Silicon spectra were obtained using a Varian Unity Inova spectrometer with a DE or cross polarisation (CP) from protons and the results are reported in ppm with respect to neat tetramethylsilane.

3) Catalyst Testing and Product Analysis

All reactions were carried out in a stirred batch reactor. Product mixtures were analyzed by ^1H NMR recorded at 400 MHz in CDCl_3 and by GC–MS techniques. Percentage yields and selectivity were determined from quantitative ^1H NMR experiments using *para*-xylene as the internal standard by integration of the relevant signals⁴ from crude spectra and confirmed by GC–MS analysis. GC–MS analysis was performed using a Thermo Scientific Trace 1300 GC and Thermo Scientific TSQ 8000 Evo MS employing a VF-5ms capillary column ($30\text{m} \times 0.25\text{mm}$ i.d. and $0.25\mu\text{m}$) and a gradient temperature profile with an initial temperature of 50°C for 3 minutes rising to 280°C at a rate of $20^\circ\text{C min}^{-1}$.

4) Crude Furaldehyde

A $10\ \mu\text{g/mL}$ methanol solution of the crude furaldehyde used in this study gave a UV absorption of 0.160 at 272 nm.



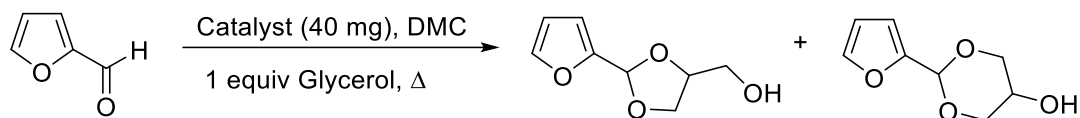
Figure S1: Representative sample of crude furaldehyde used in this study

5) Catalyst Isolation and Recycling

Al-13-(3.18) catalyst was isolated from reactions by filtration and washed with methanol ($2 \times 1\ \text{mL}$) and dried under vacuum. Once dry, the yellow catalyst was reactivated by calcination at 650°C for 3 hours to provide the catalyst as a fine white powder that was stored at 140°C prior to use.

Catalyst Optimisation Studies

Table S1: Optimisation of Telescoped Acetalisation/Transacetalisation Reaction



Entry	Catalyst	ROH (5 equiv)	Conversion (%)	Ratio 2a:2b (%)	Yield 2a:2b (%) ^b
1	B-13-(3.54)	-	<5	-	<5
2	B-13-(3.54)	PrOH	<5	-	<5
3	B-13-(2.43)	-	<5	-	<5
4	B-13-(2.43)	PrOH	<5	-	<5
5	B-Al-13-(2.20)	-	<5	-	<5
6	B-Al-13-(2.20)	PrOH	<5	-	<5
7	Ce-Al-13-(2.60)	-	<5	-	<5
8	Ce-Al-13-(2.60)	PrOH	<5	-	<5
9	Zr-Al-13-(2.13)	-	12	67:33	12
10	Zr-Al-13-(2.13)	PrOH	29	67:33	27

^a Experimental: The catalyst (40 mg) was added to a solution of crude furaldehyde (96mg, 1 mmol) and glycerol (1 mmol) in DMC (2 mL) and the reaction heated to 80 °C for 1 hour.

^b Determined by ¹H NMR analysis of the crude reaction mixture.

Figure S2: ^1H NMR of Pure Furaldehyde Dimethyl Acetal⁵

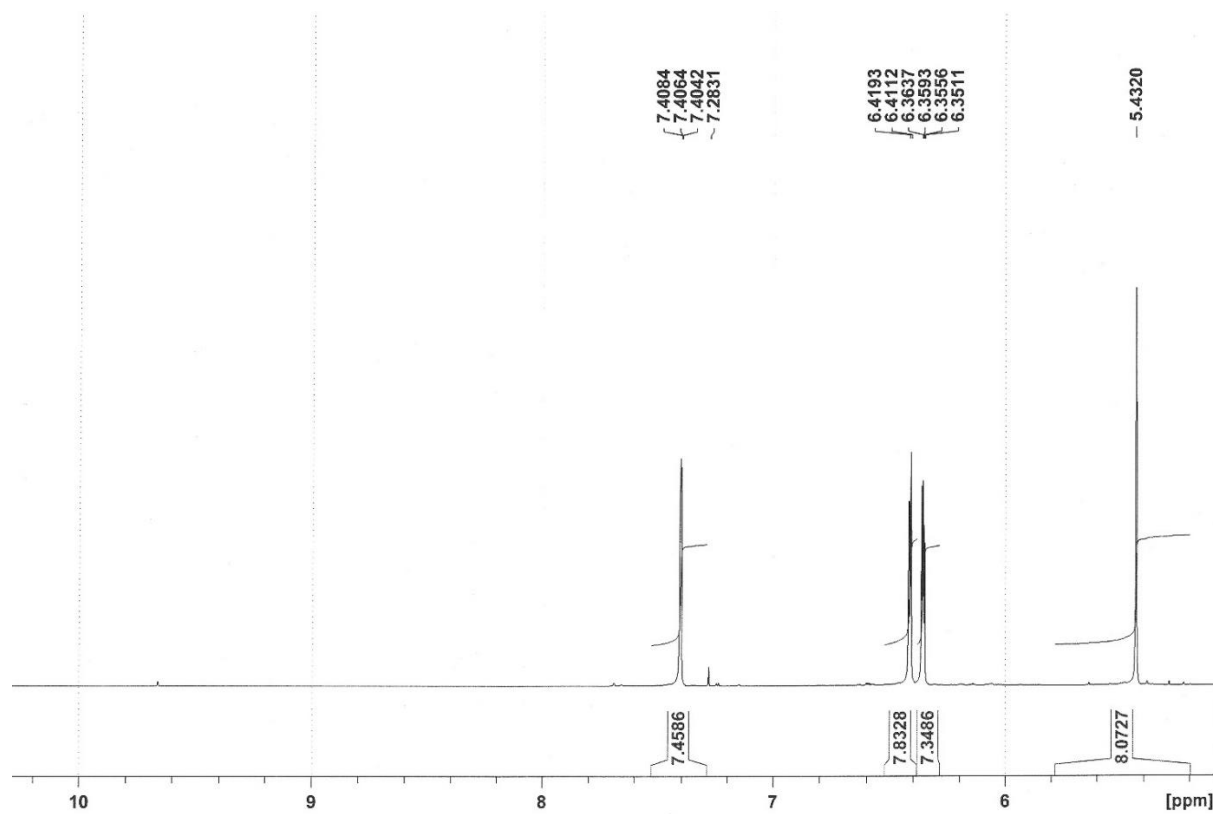


Figure S3: ^1H NMR Crude Furaldehyde Dimethyl Acetal Al-13-(3.18) 60 °C 1hr

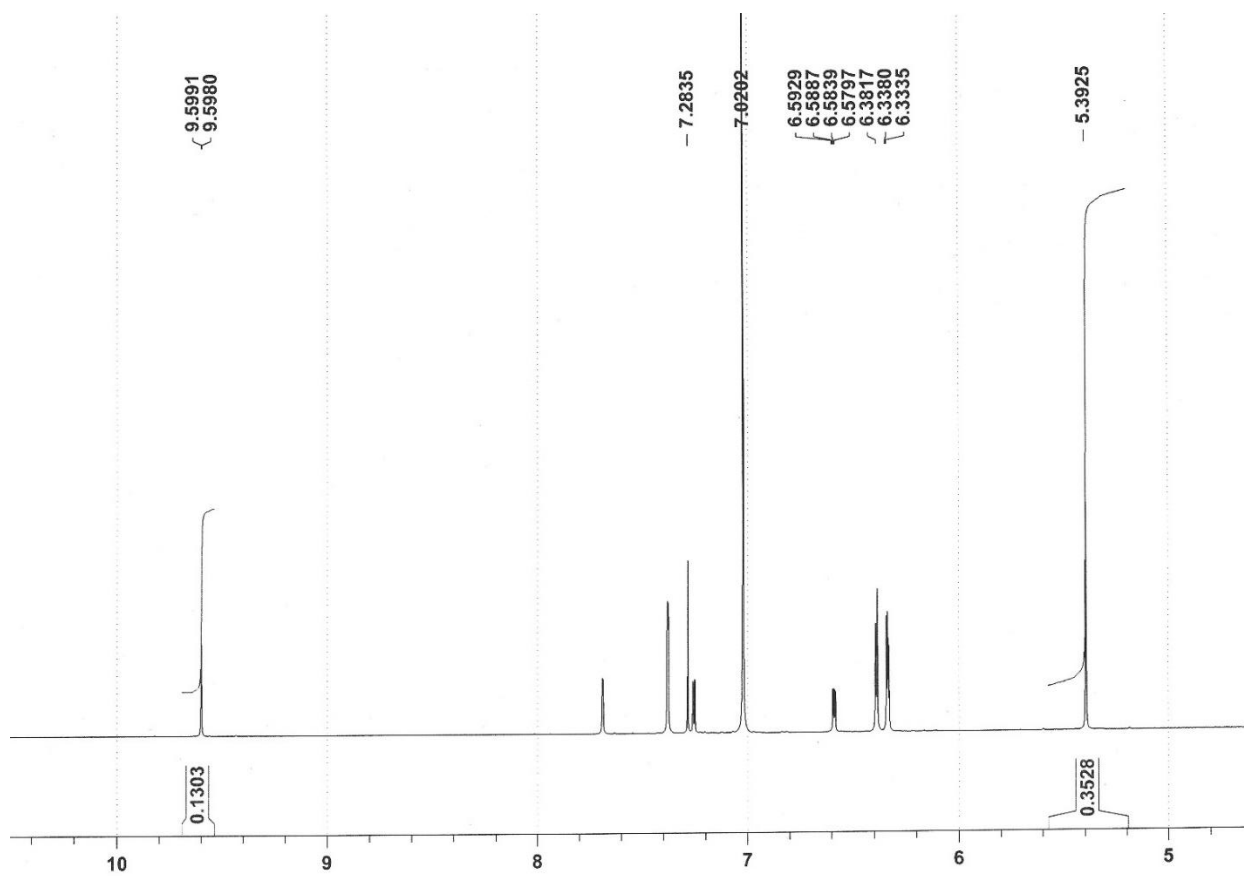


Figure S4: GC-MS Crude Furaldehyde Dimethyl Acetal Al-13-(3.18) 60 °C 1hr

RT = 5.23 mins is internal standard

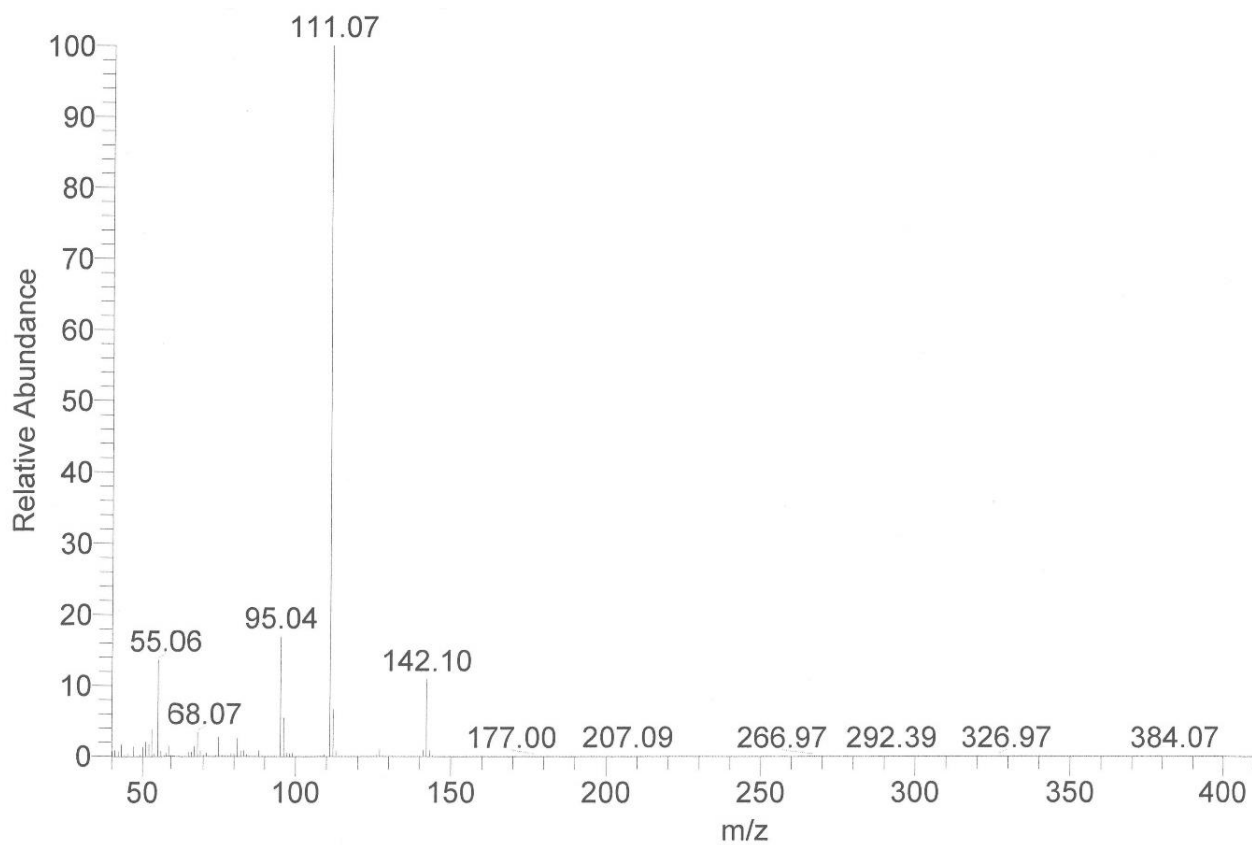
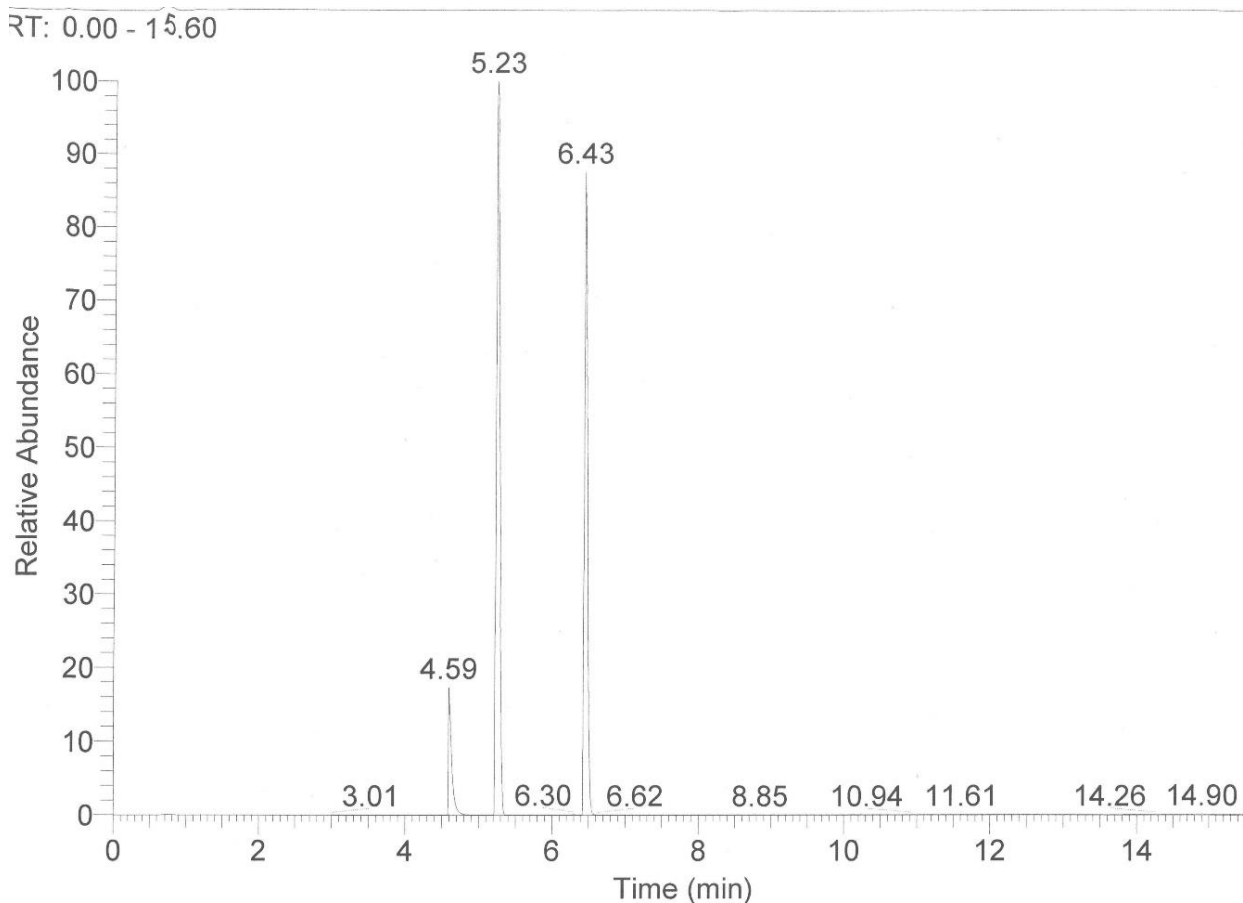


Figure S5: GC-MS Crude Telescoped Reaction Al-13-(3.18) 80 °C 1hr DMC 5 equiv MeOH

RT = 5.20 mins is internal standard

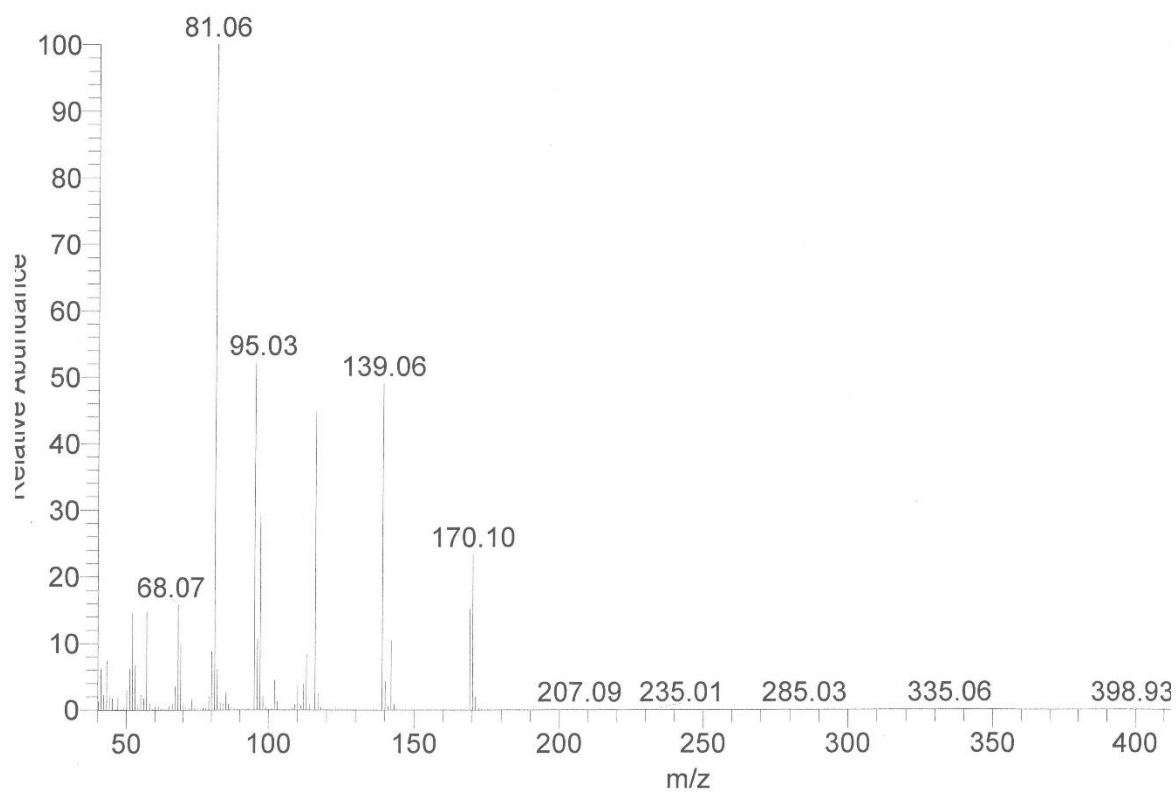
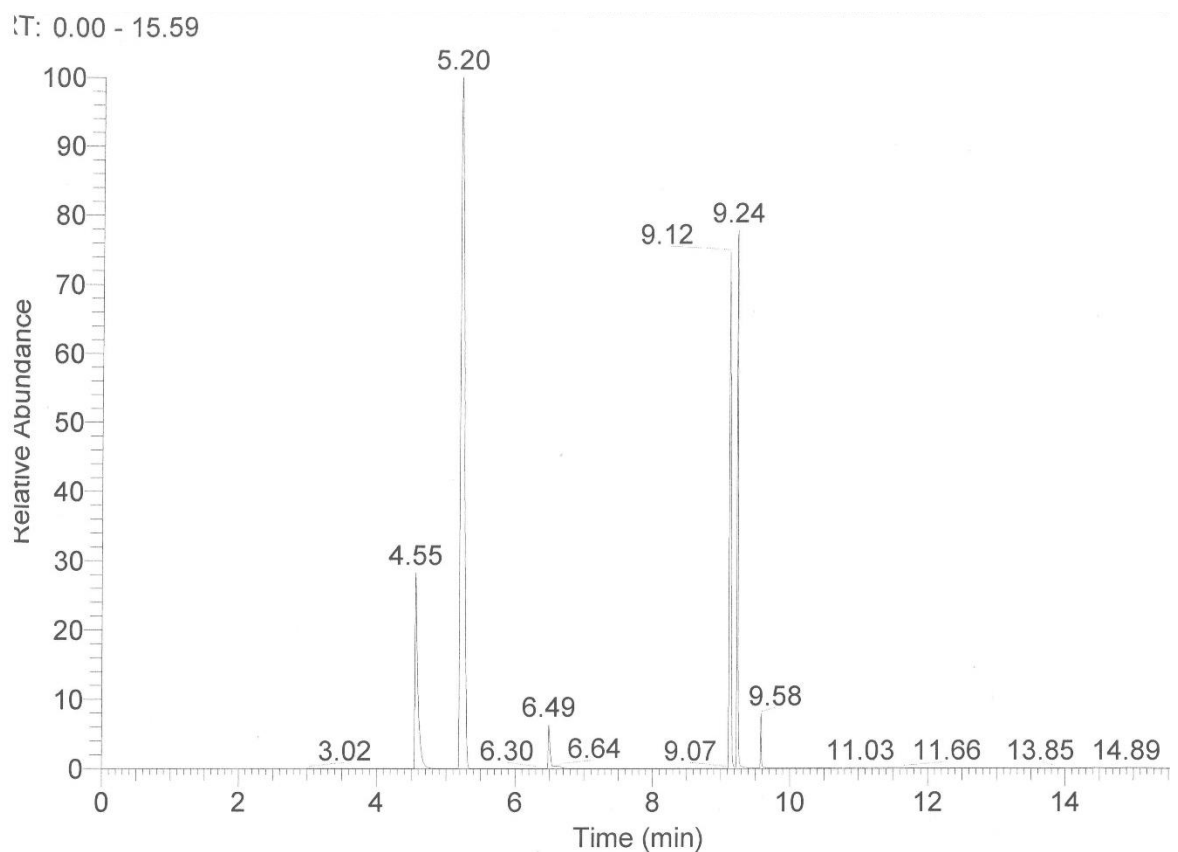


Figure S6: ^1H NMR Crude Telescoped Reaction Al-13-(3.18) 80 °C 1hr DMC with 5 equiv MeOH

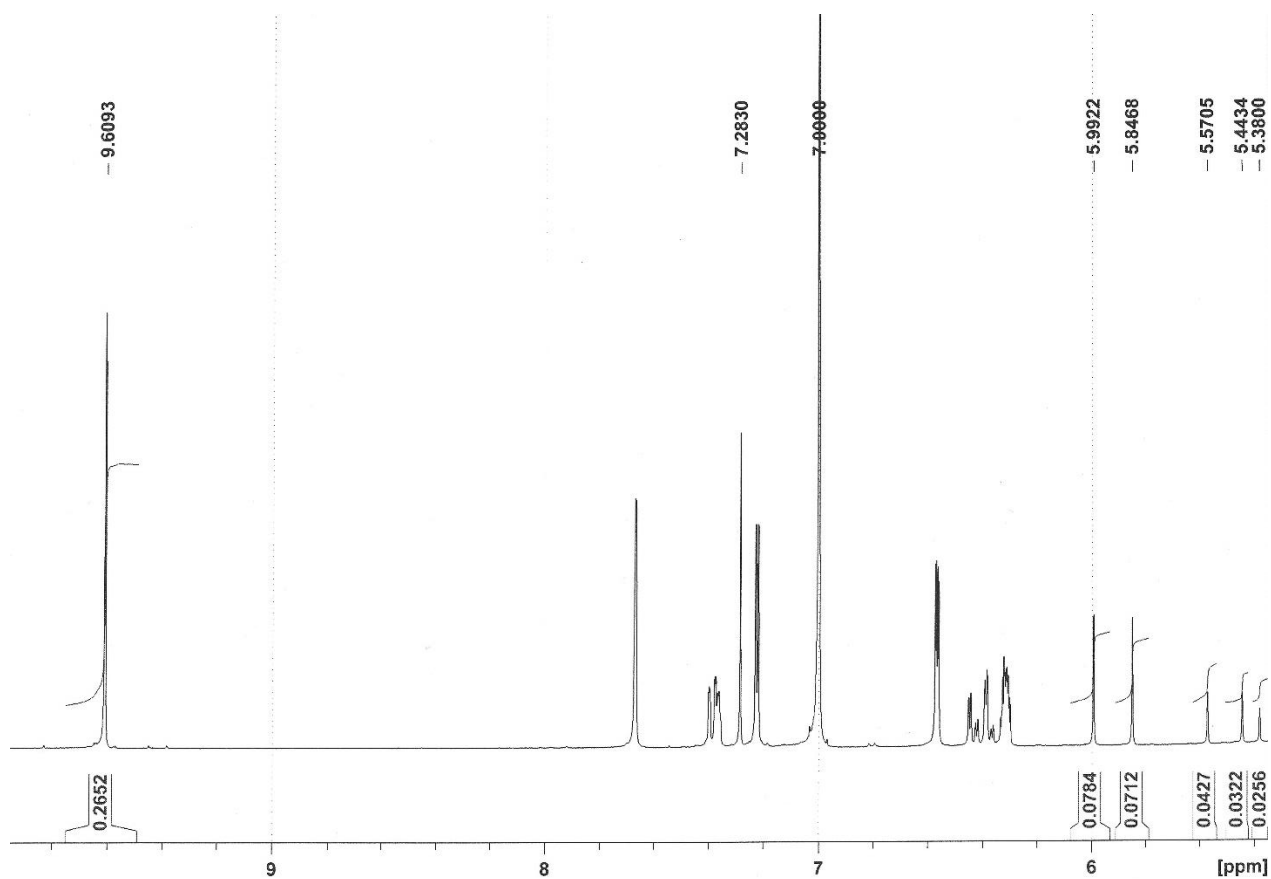


Figure S7: GC-MS Crude Telescoped Reaction Al-13-(3.18) 80 °C 1hr DMC with 5 equiv PrOH

RT = 5.21 mins is internal standard

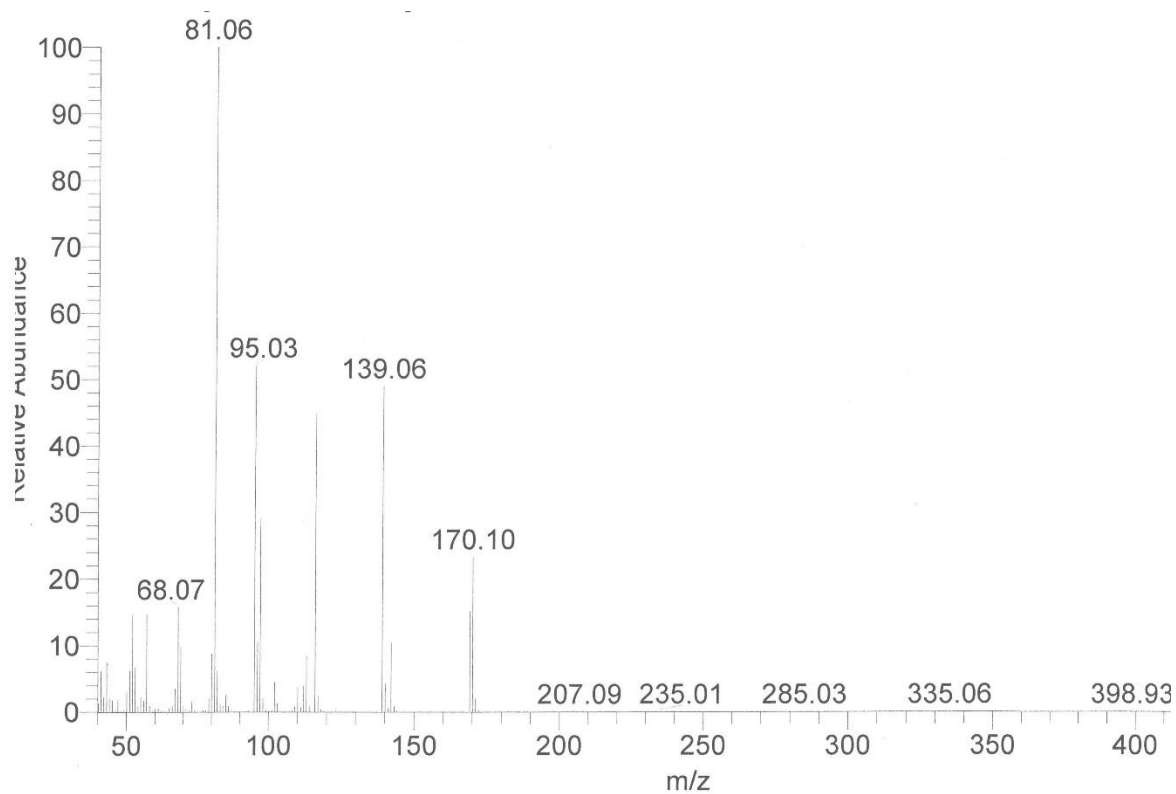
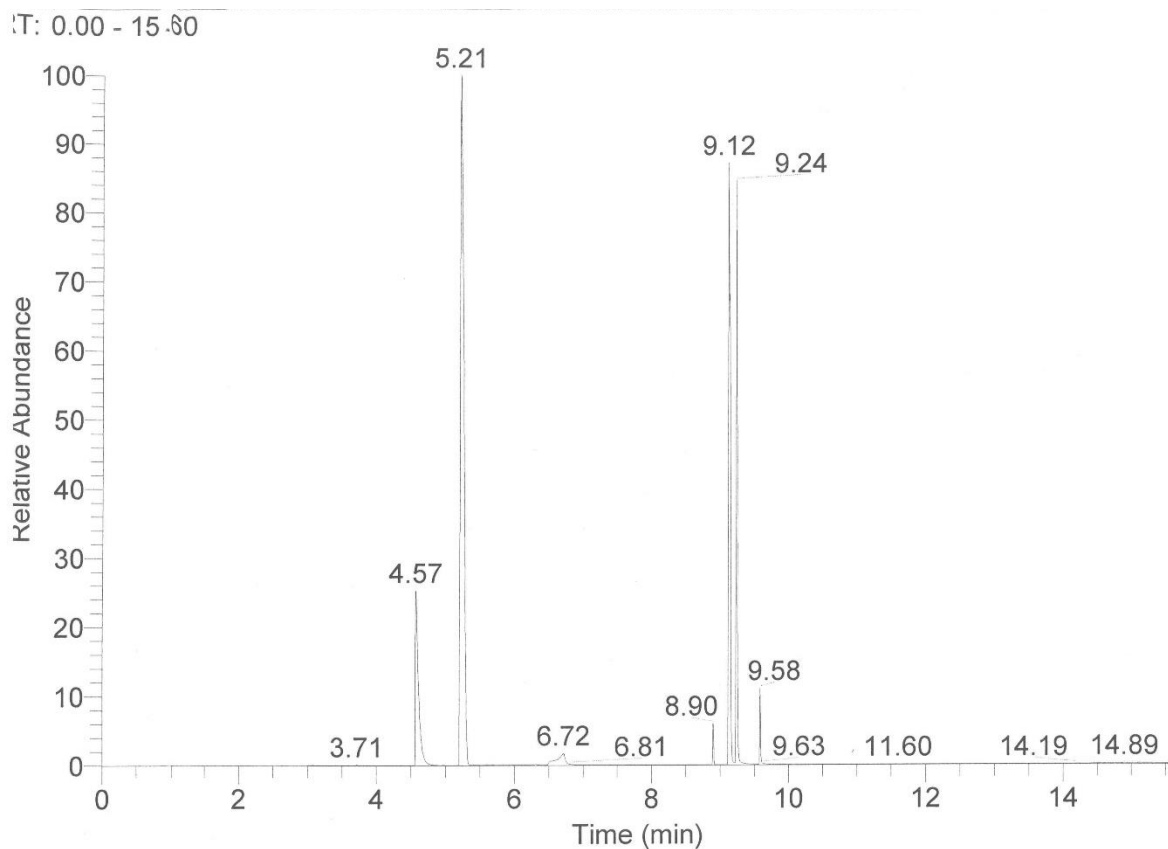


Figure S8: ¹H NMR Crude Telescoped Reaction Al-13-(3.18) 80 °C 1hr DMC with 5 equiv PrOH

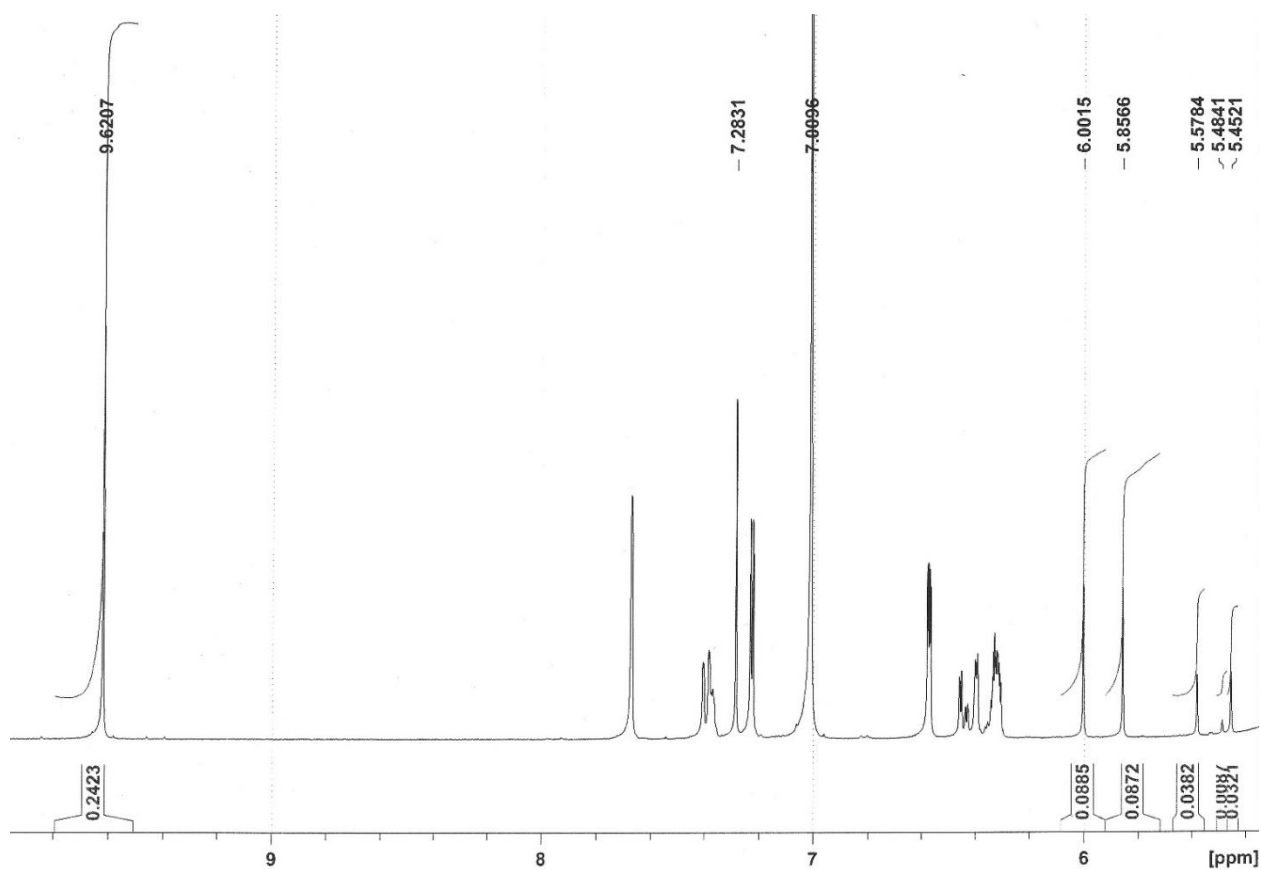
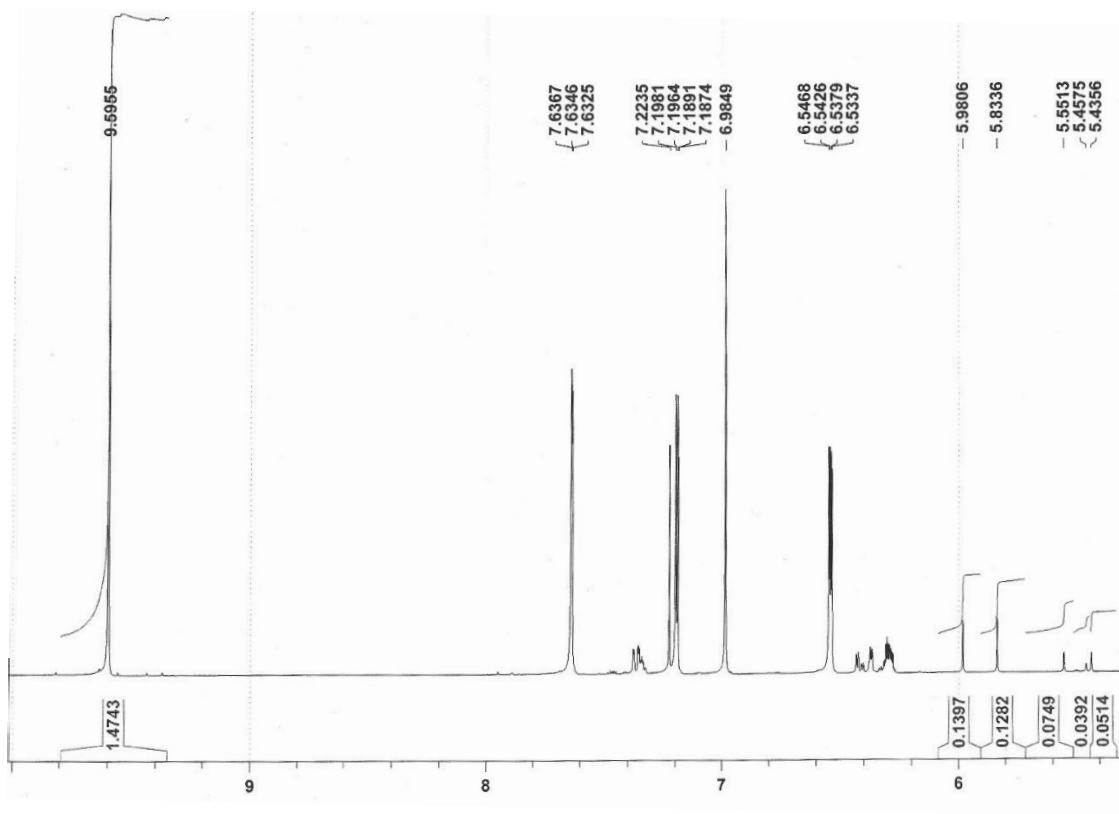


Figure S9: ¹H NMR Crude Telescoped Reaction Al-13-(3.18) 80 °C 1hr DMC 4 equiv Furaldehyde with 5 equiv PrOH



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