

Electronic supplementary information

High yield synthesis of HMF from glucose and fructose by selective catalysis with water-tolerant rare earth metal triflates assisted by choline chloride

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1. Reagents

α -D-(+)-glucose : Sigma Aldrich 96%

D-(-)-fructose : Sigma Aldrich 99%

Choline chloride : Alfa Aesar 98%

2. Solvents

Methyl ethyl ketone : Alfa Aesar 98.5%

Methyl propyl ketone : Sigma Aldrich 99%

3. Catalysts

Aluminium chloride hexahydrate: Sigma Aldrich 99.9%

Iron(III) chloride hexahydrate: 99% Fluka

Zinc chloride anhydrous: Alfa Aesar 98%

Erbium chloride hexahydrate: Alfa Aesar 99.9%

Ytterbium chloride anhydrous: 99.9 Alfa Aesar

Scandium(III) trifluoromethanesulfonate : Sigma Aldrich 99%

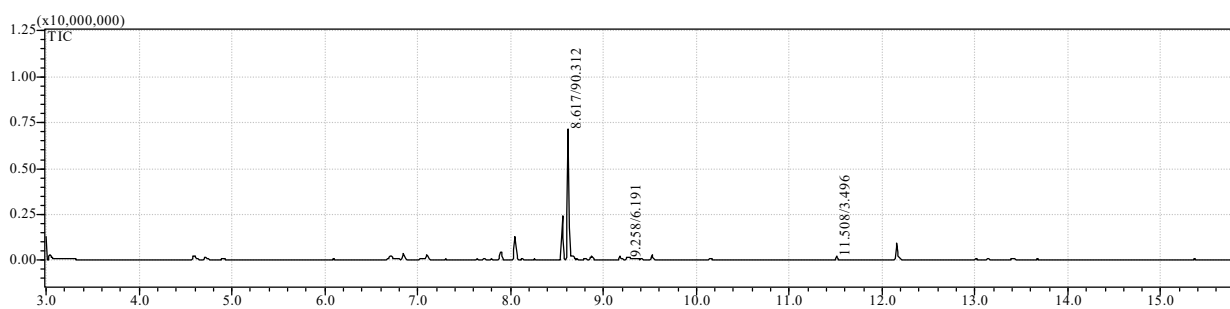
Cerium chloride heptahydrate: Sigma Aldrich 99.9%

Holmium(III) trifluoromethanesulfonate : Sigma Aldrich 98%

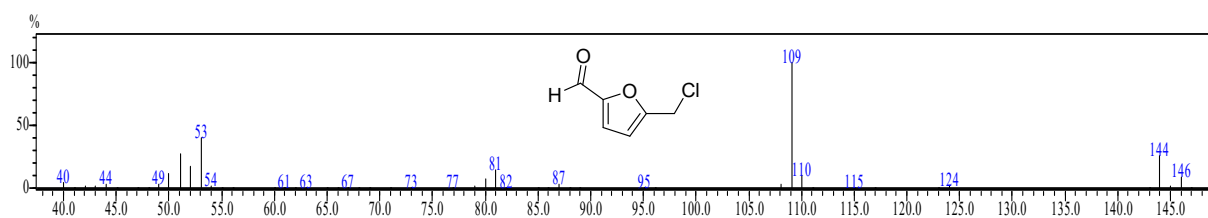
Erbium(III) trifluoromethanesulfonate : Sigma Aldrich 98%

4. Mass spectra of the optimized reaction using different catalysts

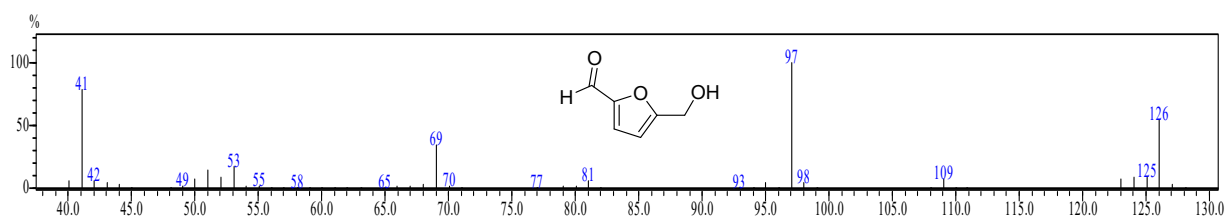
4.1 Optimized reaction starting from glucose using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, (HMF yield = 35%)



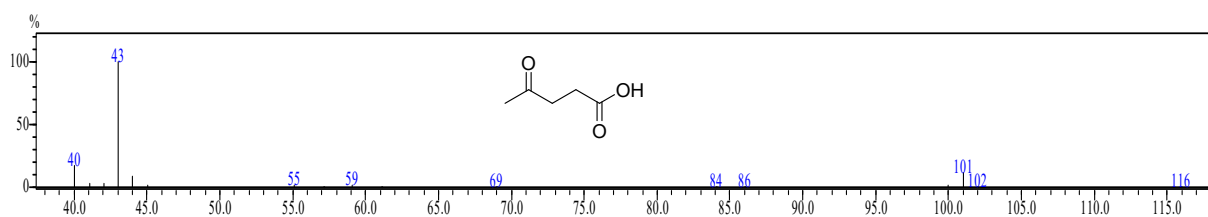
Retention time: 8.558



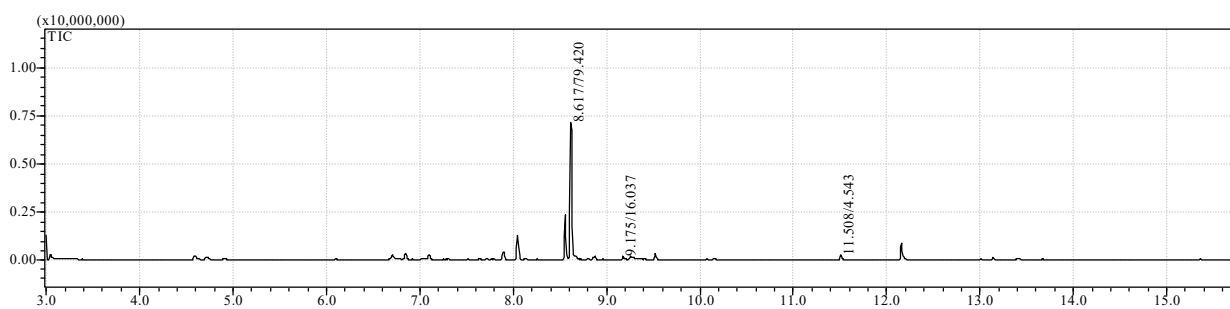
Retention time: 9.250



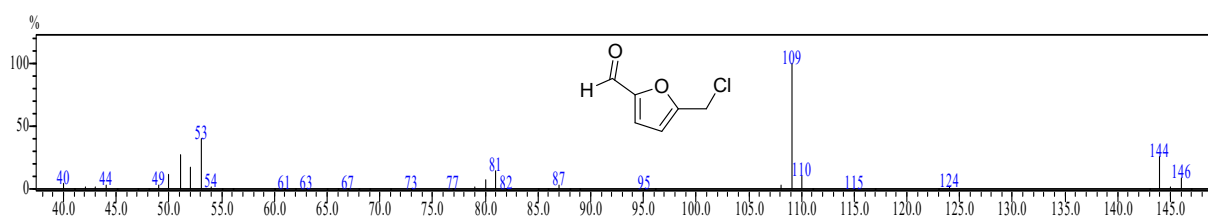
Retention time: 11.508



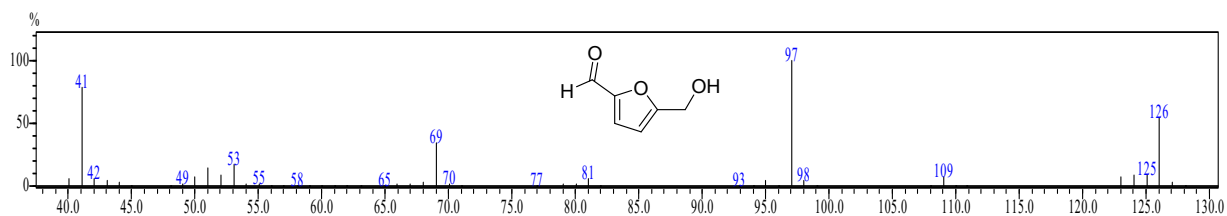
4.2 Optimized reaction starting from glucose using $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (HMF yield = 55%)



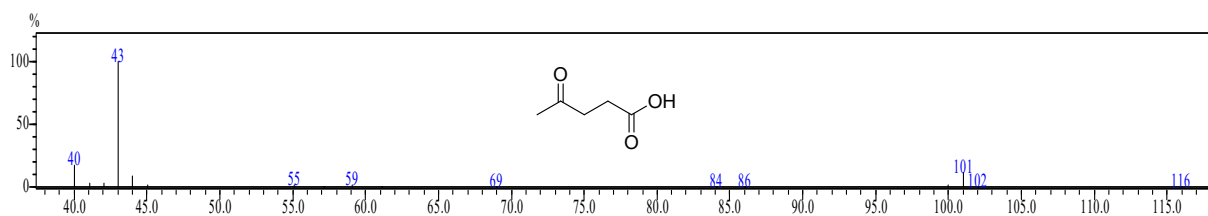
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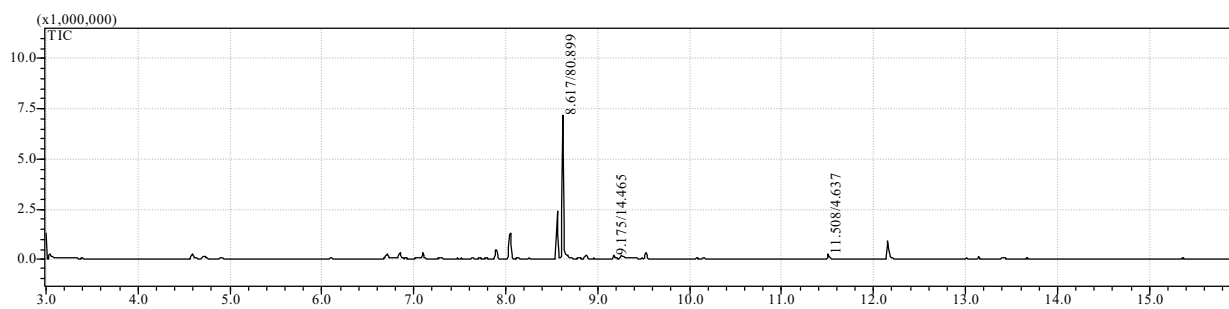
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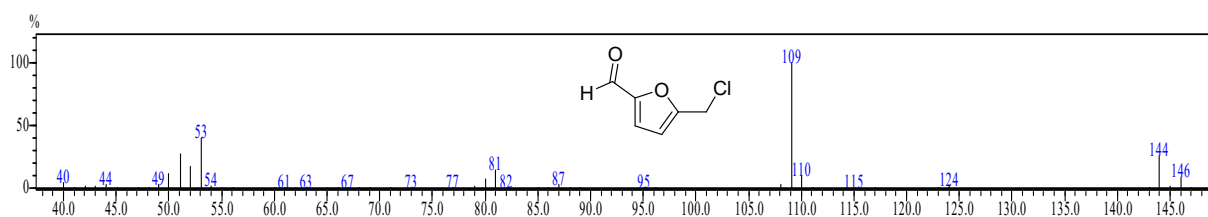
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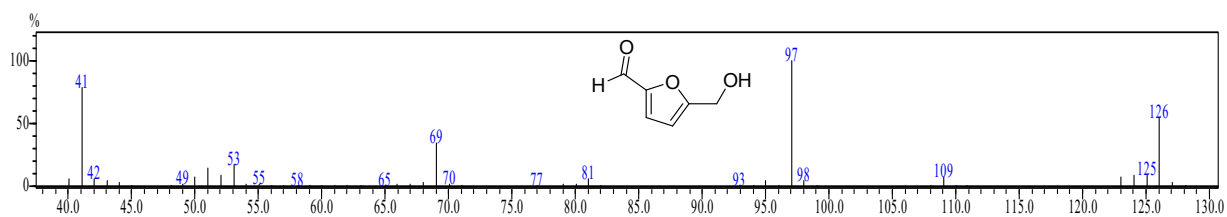
4.3 Optimized reaction starting from glucose using $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, (HMF yield = 65%)



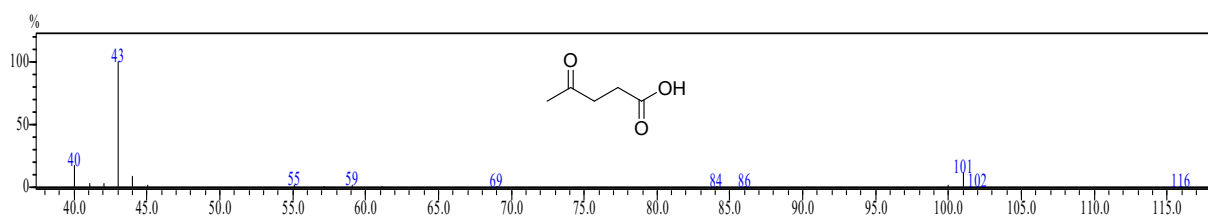
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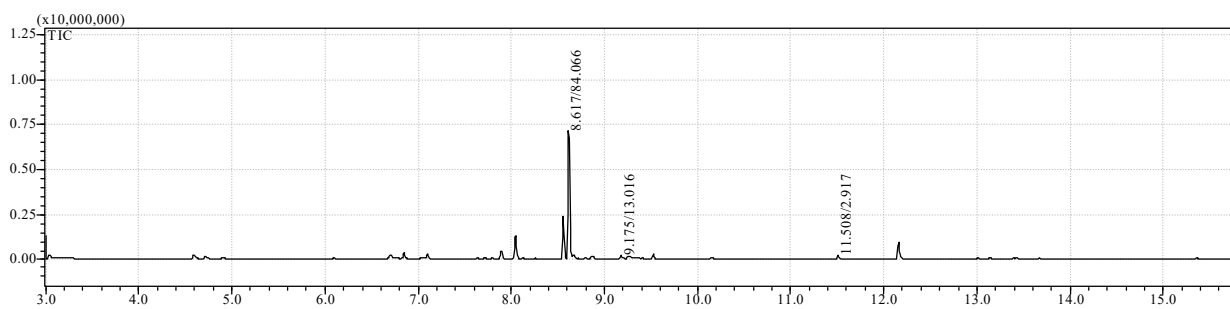
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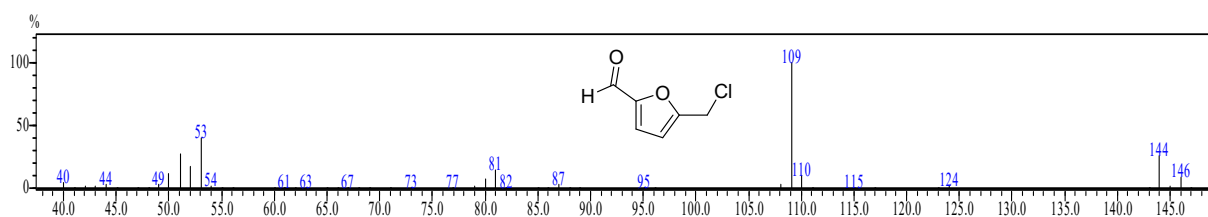
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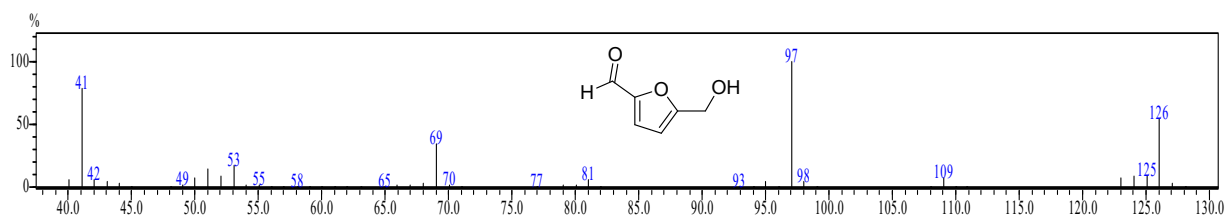
4.4 Optimized reaction starting from glucose using $\text{Fe(III)Cl}_3 \cdot 6\text{H}_2\text{O}$, (HMF yield = 45%)



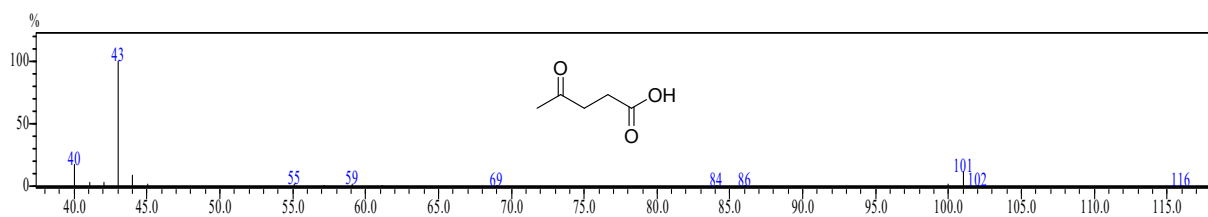
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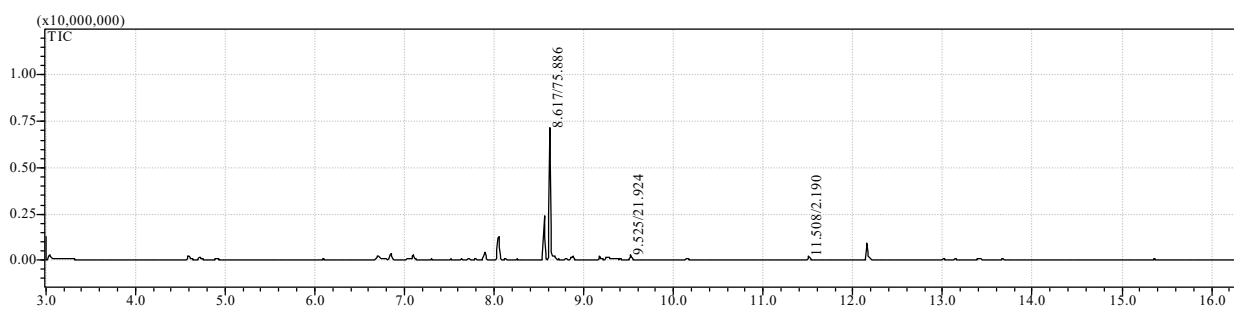
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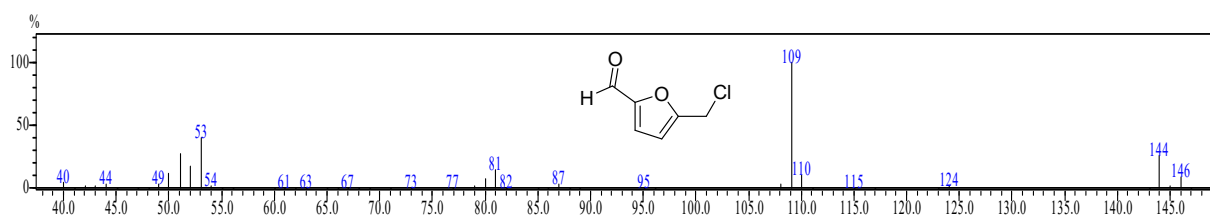
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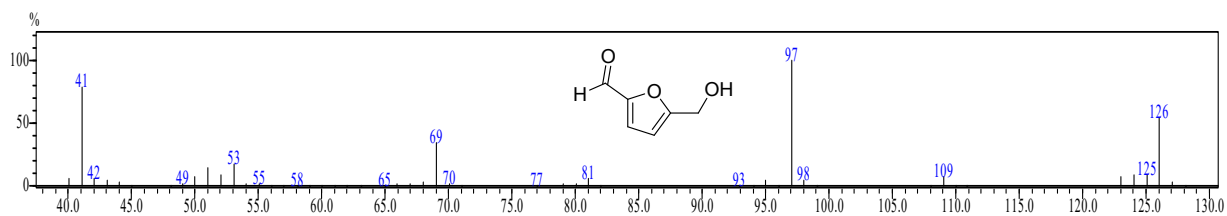
4.5 Optimized reaction starting from glucose using ZnCl₂ anhydrous, (HMF yield = 22%)



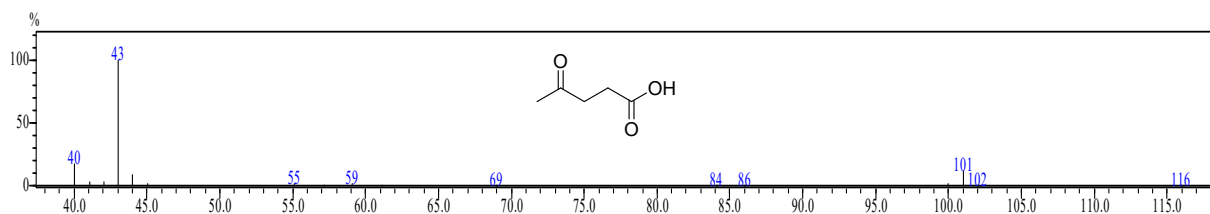
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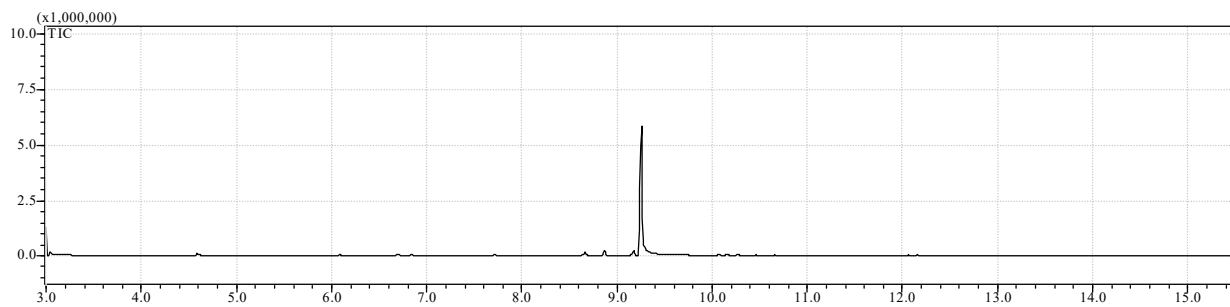
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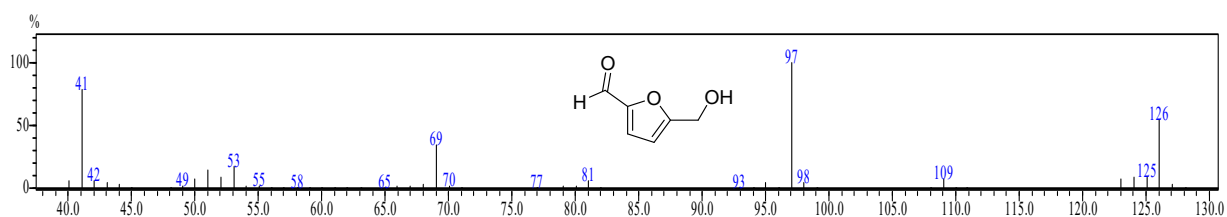
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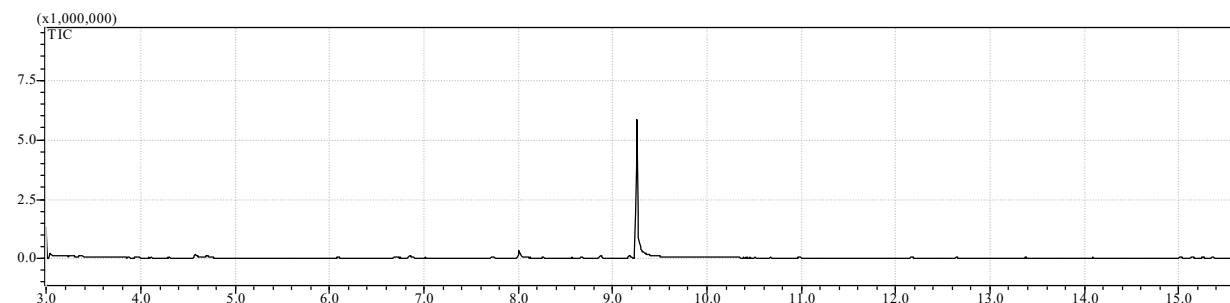
4.6 Optimized reaction starting from glucose using La(III)(OTf)_3



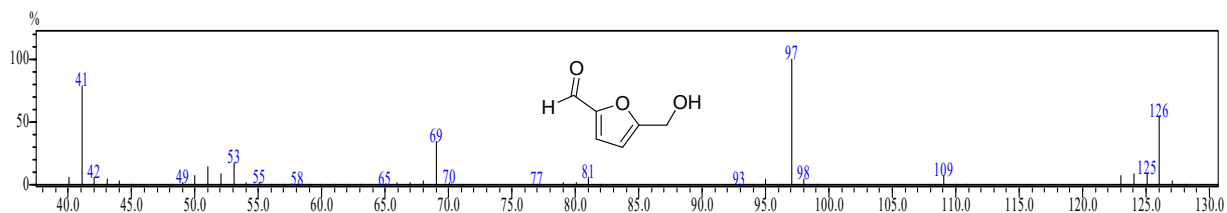
Retention time = 9.259



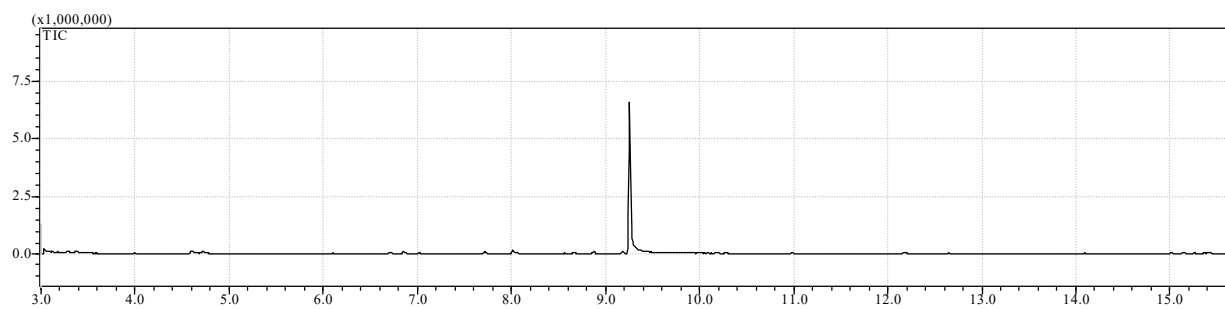
4.7 Optimized reaction starting from glucose using Ce(III)(OTf)_3



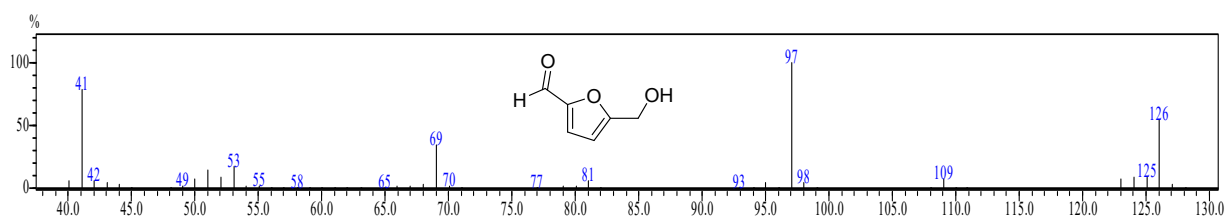
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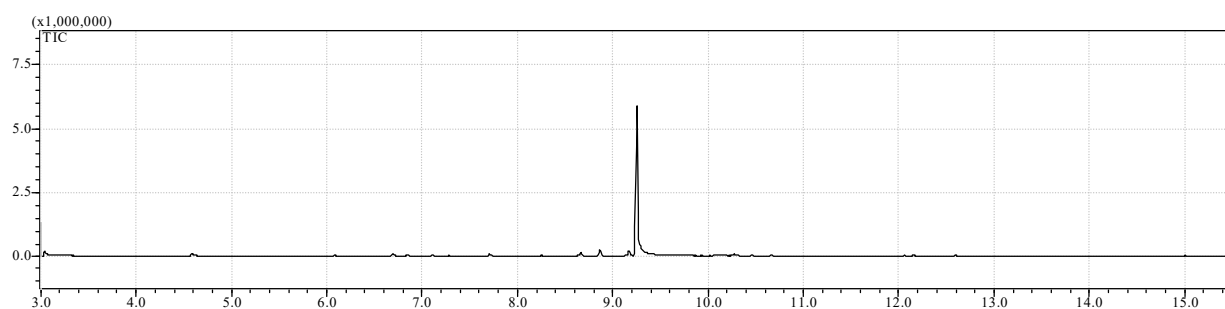
4.8 Optimized reaction starting from glucose using Ho(III)(OTf)_3



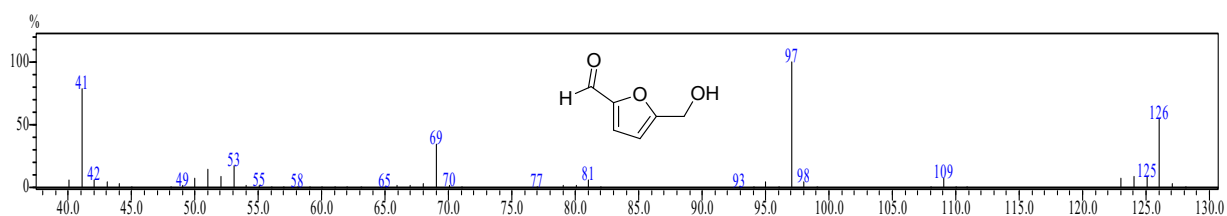
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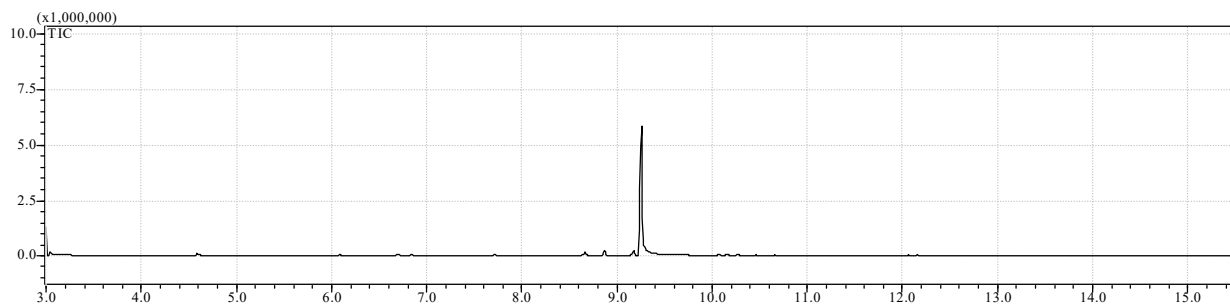
4.9 Optimized reaction starting from glucose using Er(III)(OTf)₃



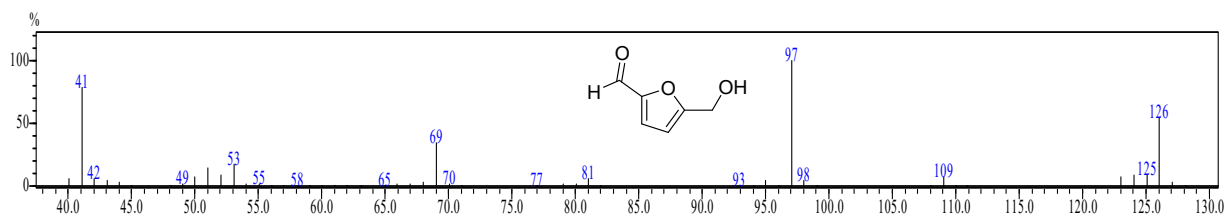
Retention time = 9.257



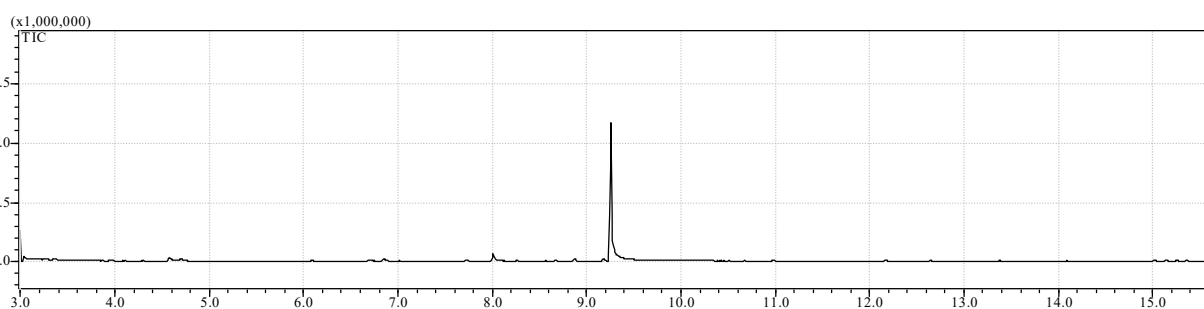
4.10 Optimized reaction starting from glucose using Yb(III)(OTf)₃



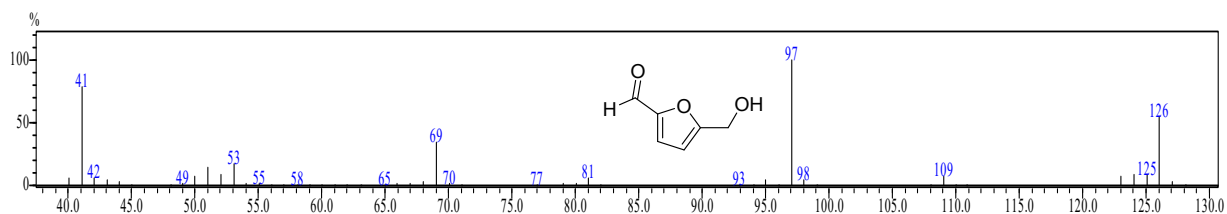
Retention time = 9.253



4.11 Optimized reaction starting from glucose using Sc(III)(OTf)_3

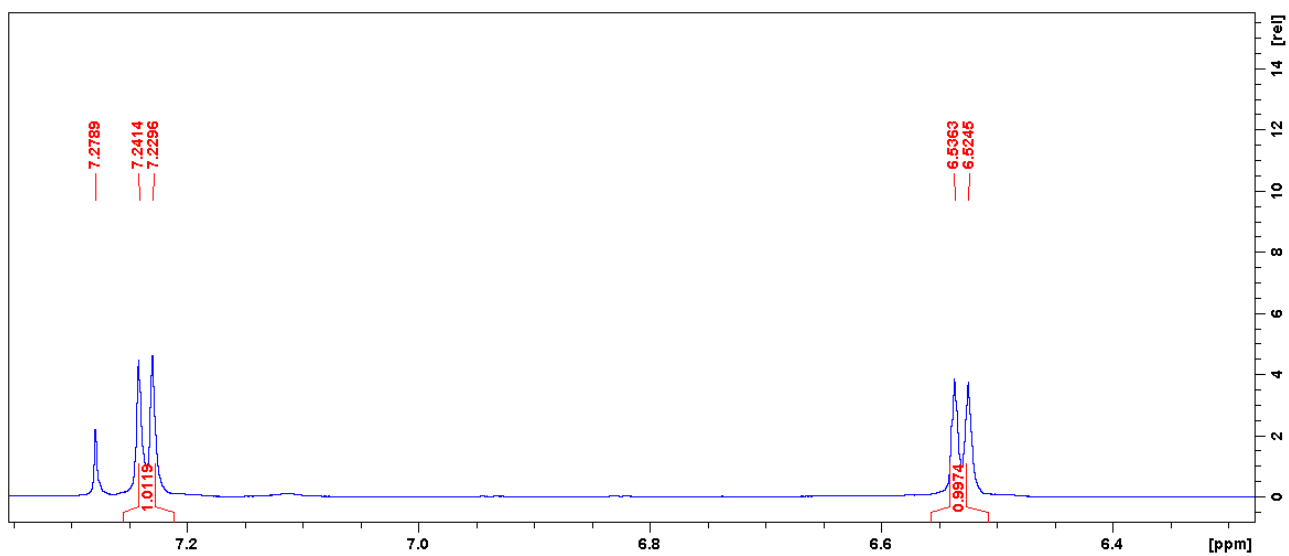
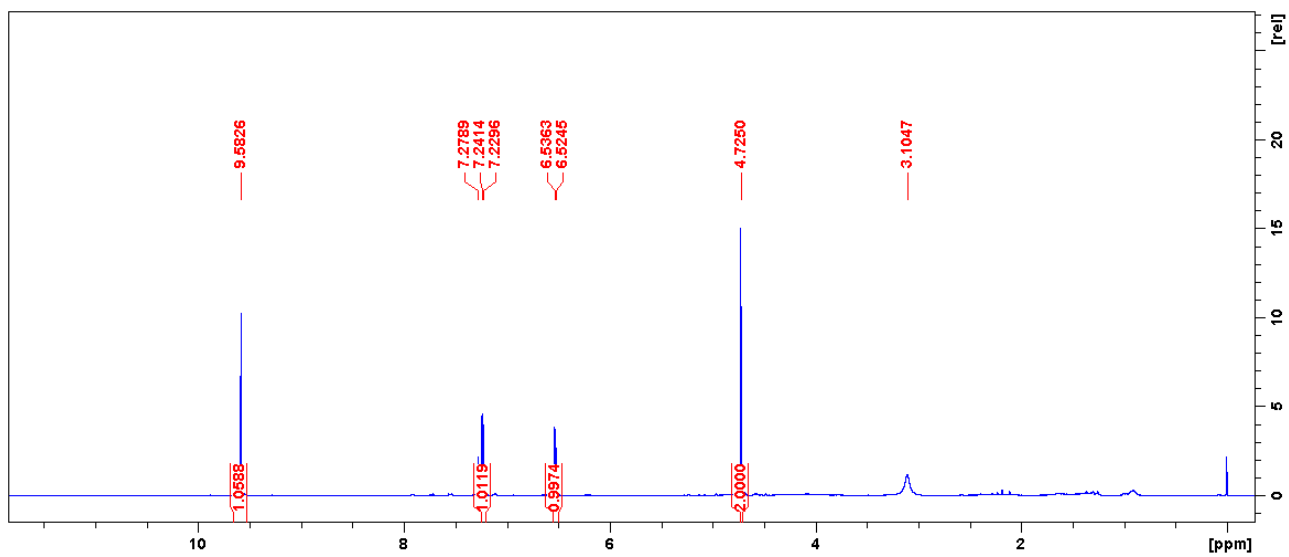


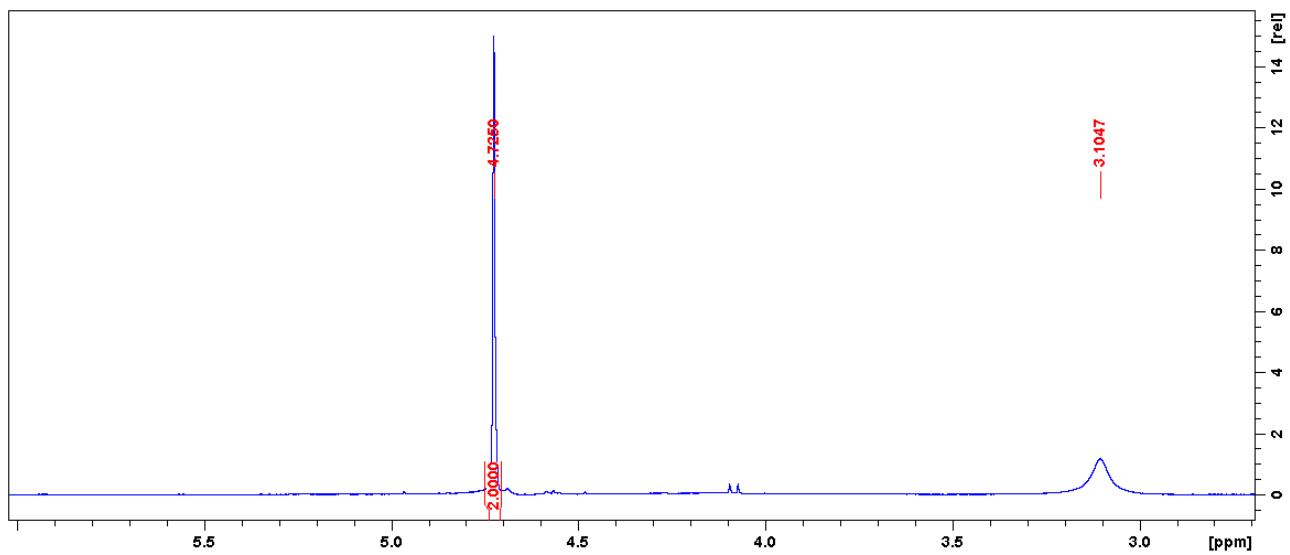
Retention time = 9.251



5. ^1H NMR spectra of the HMF obtained without any purification

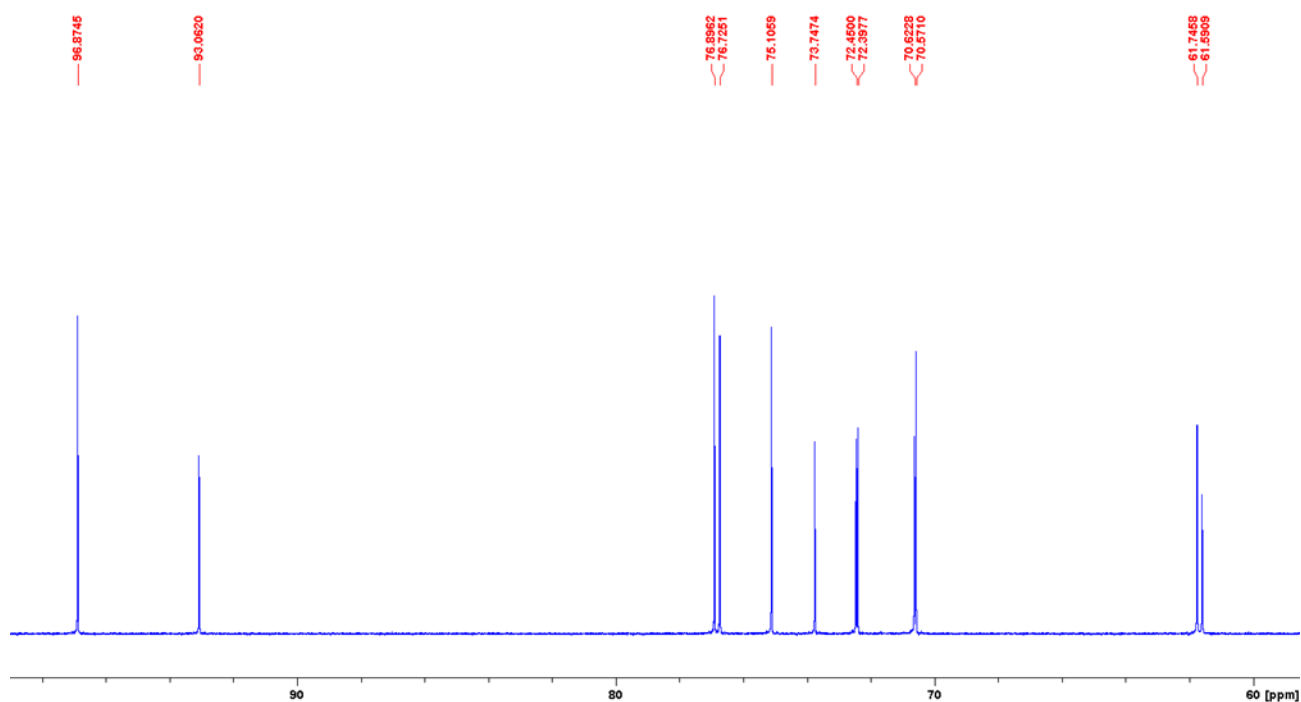
(in CDCl₃ and TMS as reference)



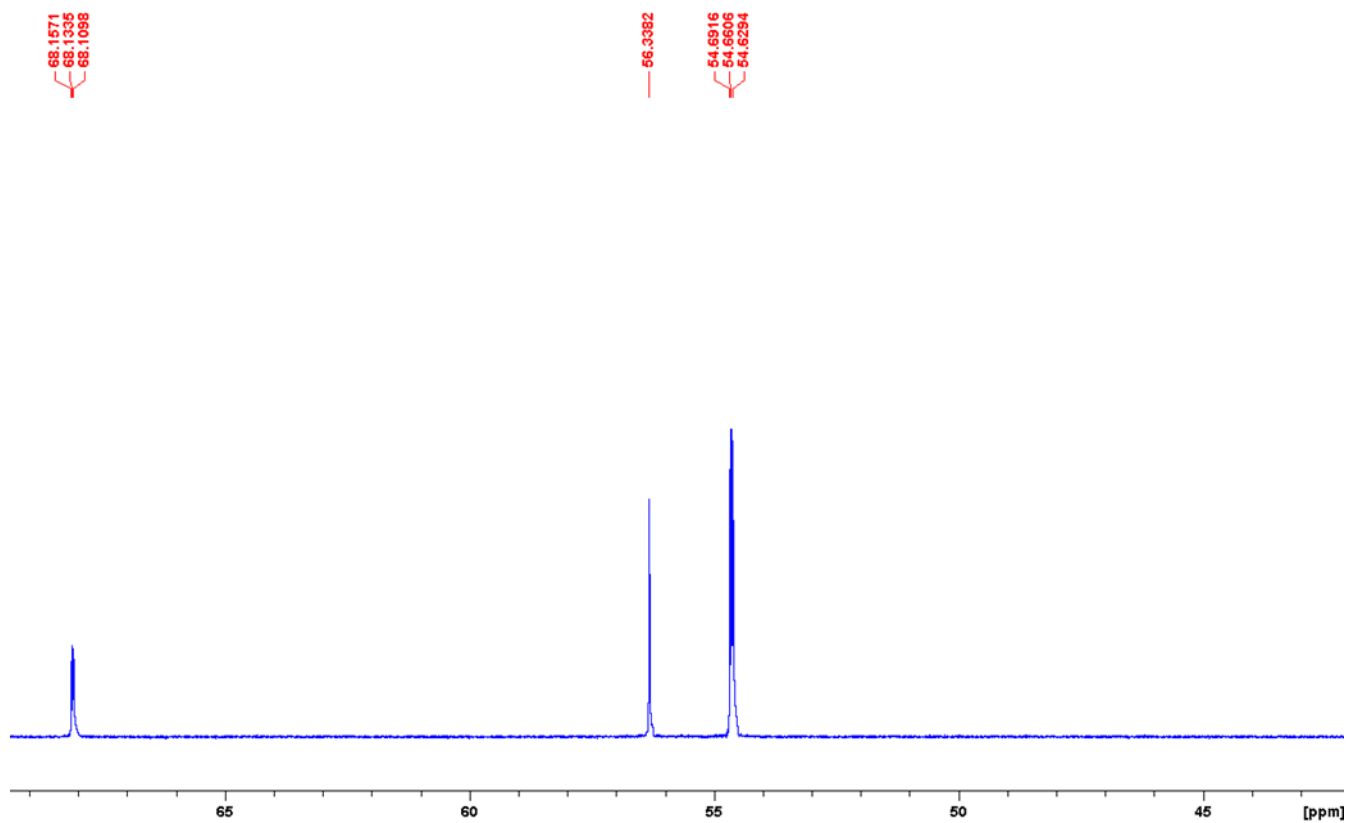


6. ^{13}C NMR spectra of glucose, choline chloride and mixture Glucose/ $\text{Sc}(\text{OTf})_3$ /Choline Chloride in D_2O

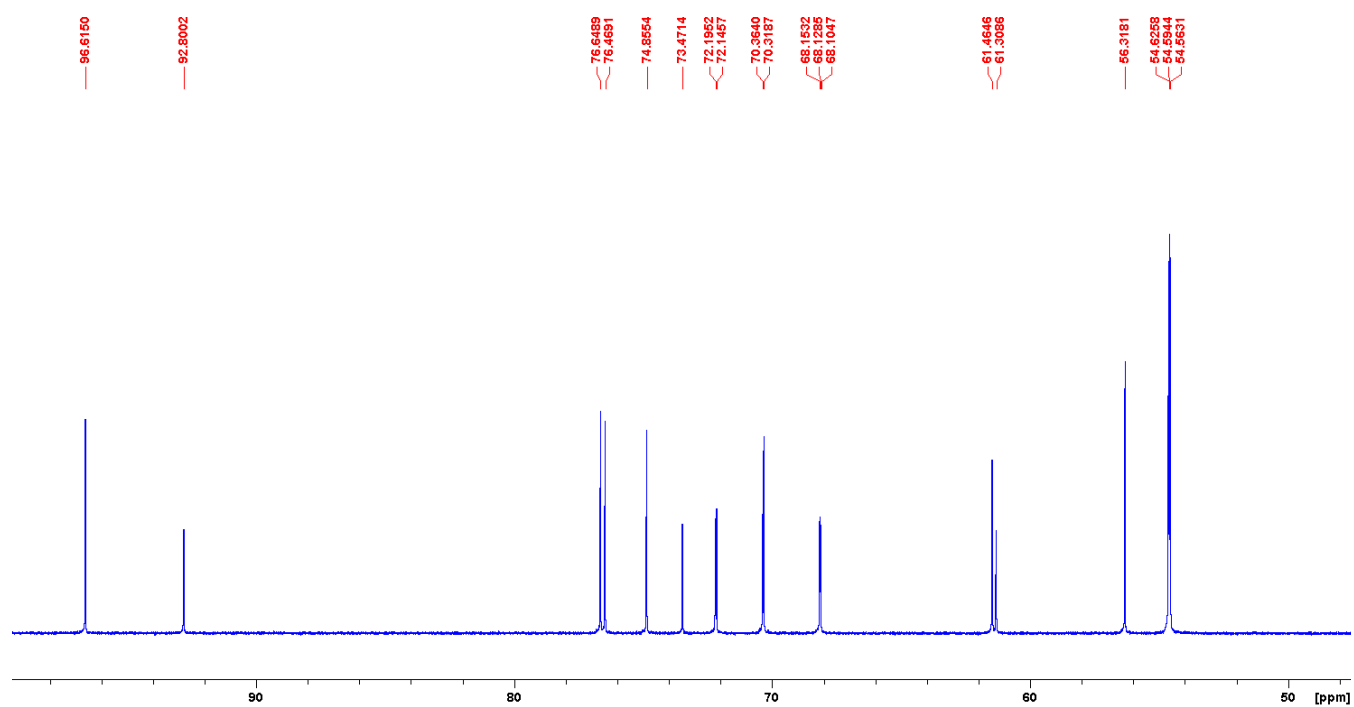
^{13}C NMR Glucose



^{13}C NMR of Choline Chloride



¹³C NMR of mixture Glucose/Sc(OTf)₃/Choline Chloride^a



^a The mixture was prepared by using same molar ratio described in the manuscript.

Dual display of ^{13}C NMR of Glucose (red) and ^{13}C NMR of mixture Glucose/ $\text{Sc}(\text{OTf})_3$ /Choline Chloride (blu) with magnification of region of anomeric carbon

