

# **Towards Understanding of Electrolyte Degradation in Lithium-Mediated Non-Aqueous Electrochemical Ammonia Synthesis with Gas Chromatography-Mass Spectrometry**

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## **Supporting information**

### **General findings and reminders about the GCMS technique**

Gas chromatography coupled with analyzers is being widely developed to investigate Li-ion batteries in organic electrolytes on or after operation.<sup>1</sup> Their ageing and electrochemical reactions are of interest in order to commercialize the method towards sustainable and efficient applications. Gas chromatography/mass spectrometry (GCMS) is one of the viable techniques used, as it is promising towards measuring the side reaction and/or decomposition products formed during reaction.<sup>1-3</sup> However, this technique has some intrinsic limitations. First, according to the molecule volatility, the thorough selection and change of the chromatographic column is required to analyze the overall degradation compounds.<sup>1</sup> The database from which the compounds can be identified is not exhaustive and offer only approximations in the field. Secondly, the chromatographic column has to be maintained often because it gets contaminated after several experiments. The contamination usually accumulates on the tip of the column in the inlet and comes from non-volatile compounds, such as salts e.g. LiClO<sub>4</sub> or other and high boiling point polymers and tars. The maintaining of the column usually is performed once a month by removing a piece of the column and changing all the ferrules. Then the column is washed with organic solvents e.g. THF and EtOH by injecting some amounts of these solvents at 100-150 °C. Regarding the chromatograms, the peak intensity on the chromatogram depends on both the compound concentration and on its ionization capability, limiting the detection of a compound that is difficult to ionize. The MS detector however is very sensitive to the experimental parameters, and allows thorough identification of components by providing fragmentation patterns of the molecules constructed into one entity with different databases. However, if one is careful with approximations, the GCMS system can be employed efficiently for characterization of the soluble materials in various liquids, with the aim of gaining insight into reaction mechanisms involved in the Li-mediated electrochemical ammonia synthesis (LiMEAS). It is important to mention that due to limitations in GCMS with respect to temperature, it is not possible to analyze polymeric substances in order to avoid contamination of the system.

The so called total ion current (TIC) chromatogram in chromatography represents the sum of the intensities across the entire mass range being detected at every point in the analysis or time point.<sup>4</sup> The range is typically more than several hundred m/z. In mixtures of the compounds or complicated samples, the TIC chromatogram often provides quite limited information and usually hides the peaks in the chromatogram as multiple analytes elute simultaneously, obscuring the identification of individual eluting species.

On the other hand, the extracted-ion chromatogram (XIC or EIC), which can be named a reconstructed-ion chromatogram (RIC) as well, one separate or more  $m/z$  values representing one or more eluting compounds of interest are recovered ('extracted') from the entire data set for a GCMS experiment.<sup>4</sup> The example of such an extraction of masses from the entire range is shown in Figure 3 in the main text. The total intensity, or base peak intensity, within a mass tolerance range around a particular analyte's mass-to-charge ratio is plotted at every time point in the performed GCMS analysis experiment. The size of the mass tolerance range typically depends on the instrument which is acquiring the data with its mass accuracy and mass resolution. This is of great importance and useful for revisiting data to detect previously-unsuspected compounds, also to possibly detect and highlight potential isomers if applicable, resolve suspected co-eluting substances, or the most important to provide clean chromatograms of compounds of interest what is given as an example in Figure 3 in the main text. XIC is generated by separating the ions of interest from a heavy and complicated data file which is heavily loaded containing with the full mass spectrum over time after the fact and different scan steps. XIC is different from selected-ion chromatograms, discussed below, in which data is acquired for only one specific  $m/z$  values.

### **Instrumentation and analysis procedure development**

The GCMS system and analysis were optimized to prevent any possible contamination from surrounding air. The schematic of the instrumentation is shown in Figure S1. This enables us to characterize the volatile soluble degradation compounds stemming from the electrolyte sample. The system had three temperature sectors: the injection inlet operated at 200 °C, the GC oven with temperature program for separation of different materials by their boiling points, and the source sector in MS kept constant at 200 °C. The chromatographic columns were connected in series for separation of different molecules by their polarity and chemical interaction with the column, as shown in Figure S1. The injected sample amount is thoroughly optimized to record the sufficient chromatograms without overloading the detector, and the flow rate of the carrier He gas is tuned. The temperature program used in the GC system is shown in Figure S3. This procedure was optimized and applied for all the experiments of this study. After injection and separation in the GC separation columns, the sample is directly introduced to the MS sector. After decomposition by electron ionization with 30 eV, the sample is directed to the MS analysis sector and the fragmentation patterns were recorded in time with the Waters Corp. working station with MassLynx v4.0 software. After that, fragment particles by masses were combined and the molecules constructed. The possible molecules formed after the data analysis were confirmed by standard solutions made in-house. Finally, the mechanisms of the chemical reactions driven by chemical potential were constructed as visualized in Figures 4a-g.

### **Quantification of ammonia by GCMS**

The ammonia signal in GCMS is mostly overlaying with H<sub>2</sub>O signal. However, it depends on the GC program used. The current program (Figure S2) was optimized not for separating ammonia from H<sub>2</sub>O, but for analyzing organic volatile species in three different systems. If the GC program is modified in the way that the dwelling at 50 °C is kept for 6 min and the ramping towards 100 °C is done with 5 °C/min steps, ammonia can be separated from H<sub>2</sub>O. An example of such a chromatogram is shown in Figure S5. However, the GC program had to be optimized and used for analyzing the decomposition products in order to save time. With this in mind, the ammonia was quantified by the well-established indophenol method described in the experimental part and literature.<sup>5,6</sup>

## Figures

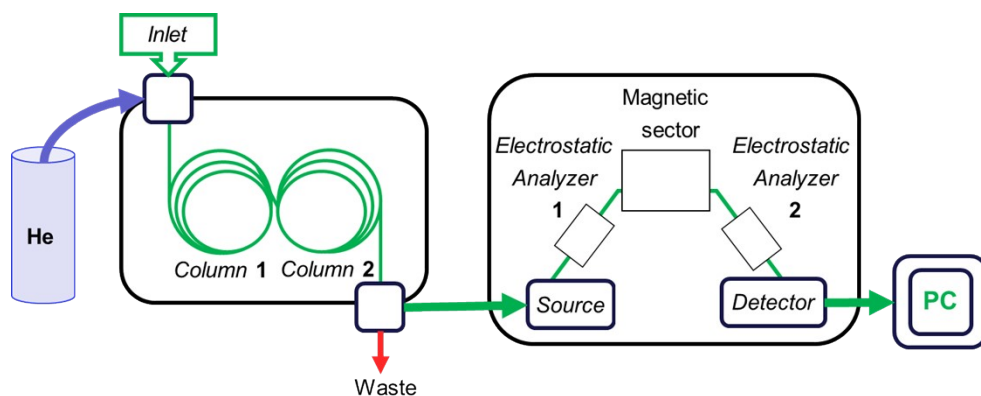


Figure S1. A schematic of GCMS instrumental setup used in this study. Green color represents the full path of the liquid sample from injection to the analysis and characterization.

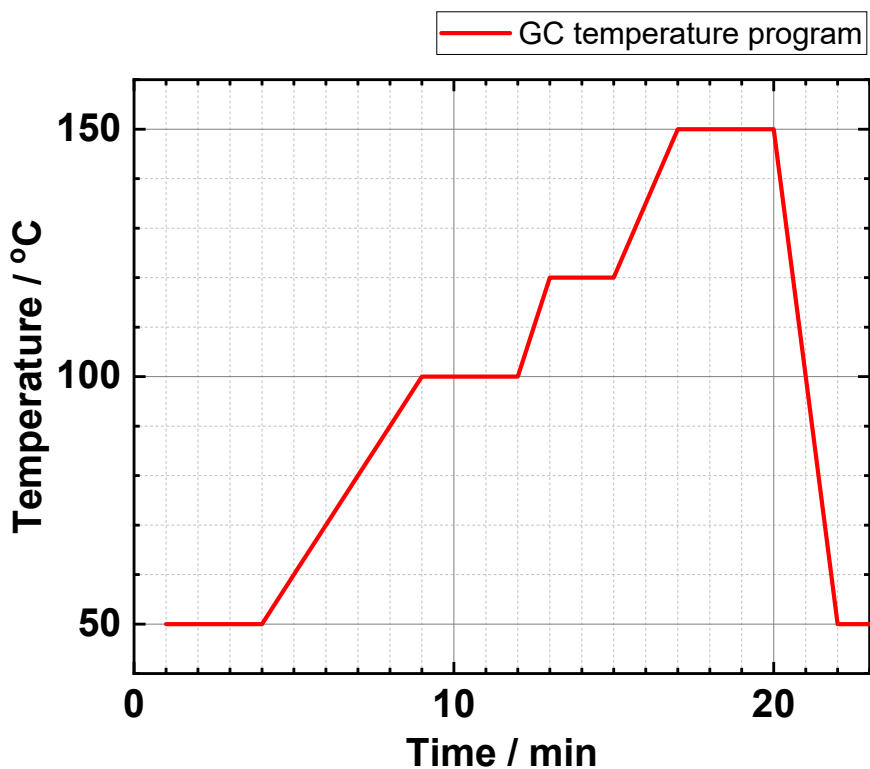
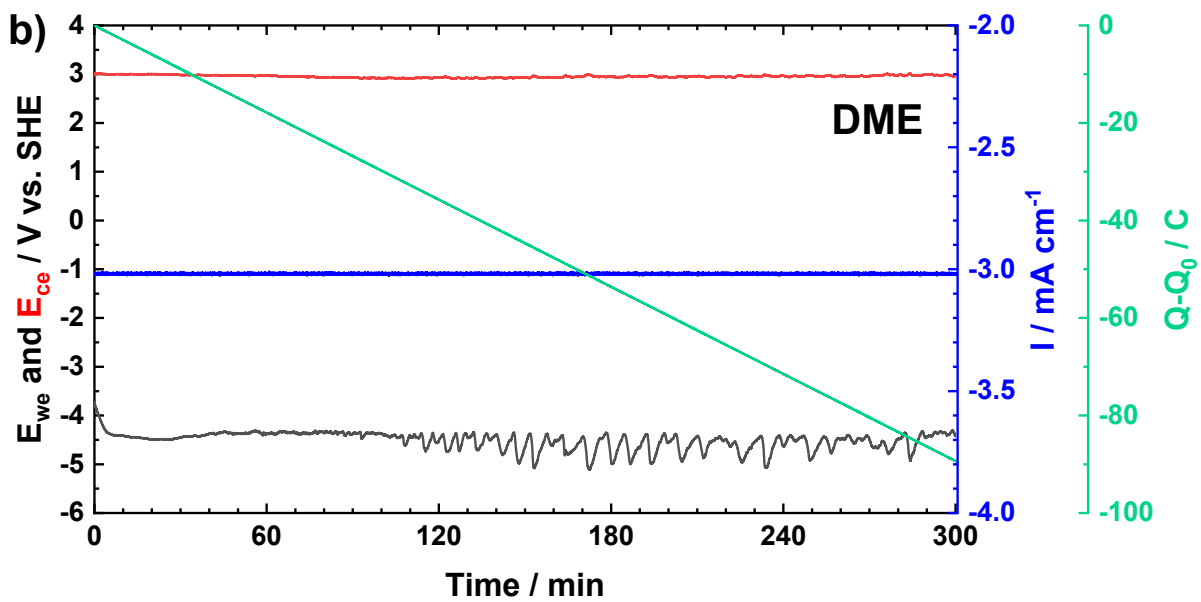
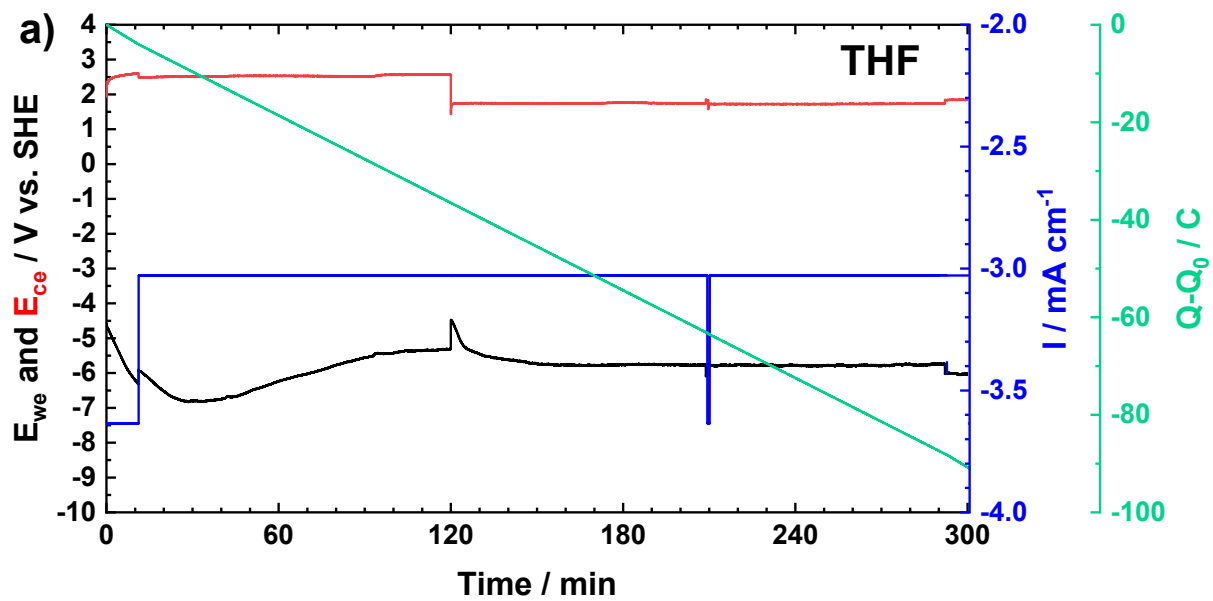


Figure S2. A schematic of the heating profile in the GC part used in this study. Both, the sample inlet in the GC part and the inlet from GC to MS were kept at 200 °C



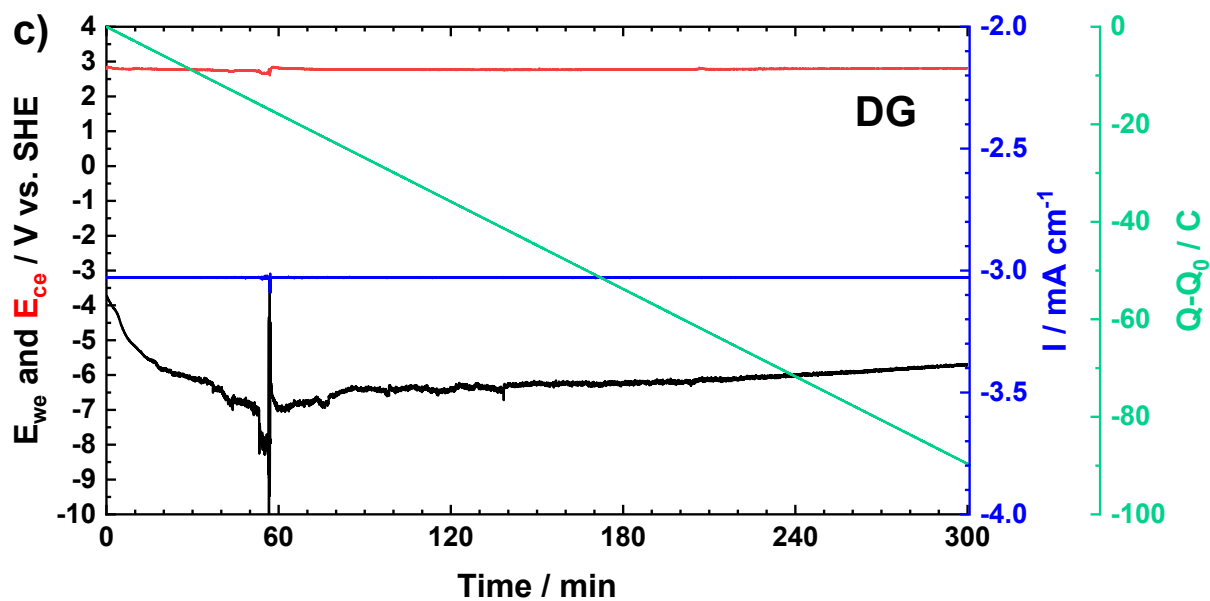


Figure S3. Experimental conditions of LiMEAS in three different electrolytes: (a) THF; (b) DME and (c) DG.

### Chemical reaction mechanisms towards decomposition products of Figure 4 in THF-based electrolyte after LiMEAS

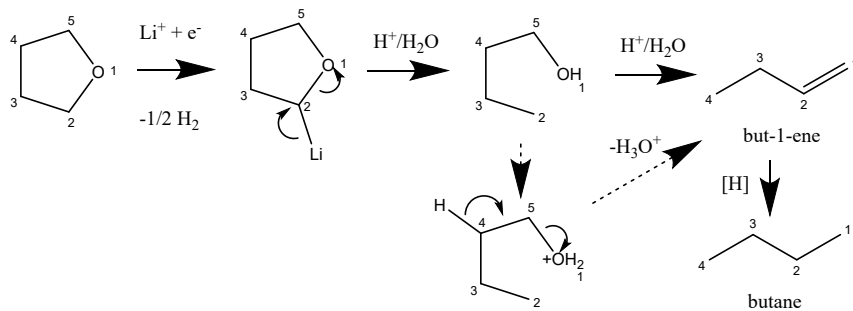
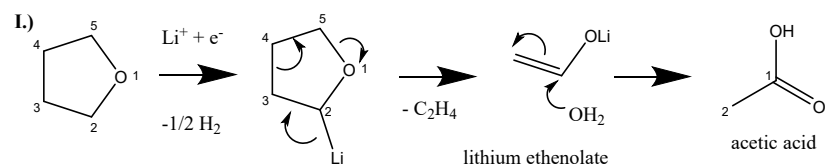


Figure S4a. Compound (1).



II.) Anodic oxidation of acetaldehyde or ethanol in the electrolyte :

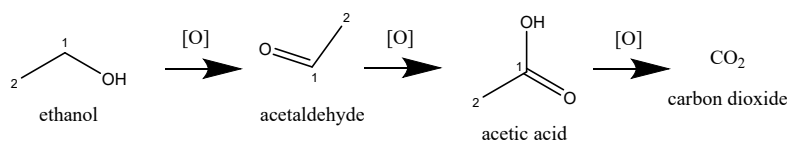
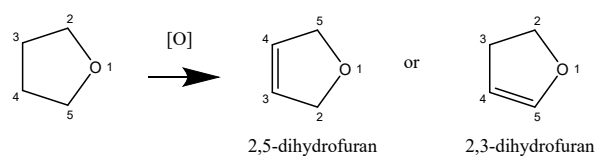


Figure S4b. Compound (2) and (10). Compound (10) forms after acid-base reaction between acetic acid and ammonia ( $\text{NH}_3$ ).



If the later one, then the following can happen:

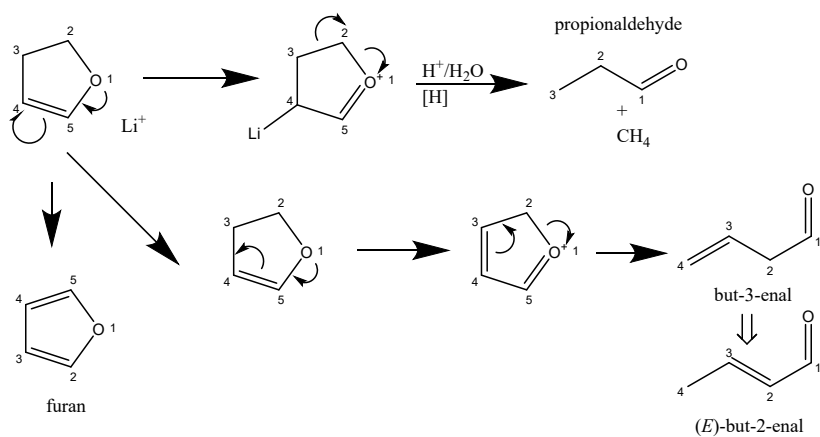


Figure S4c. Compounds (4) and (8).

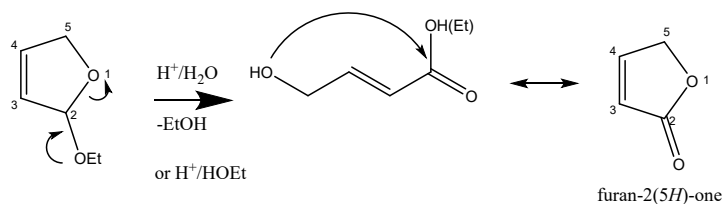
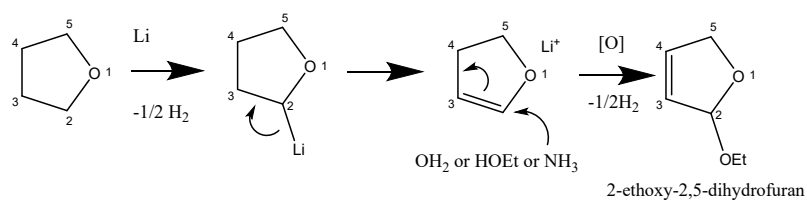
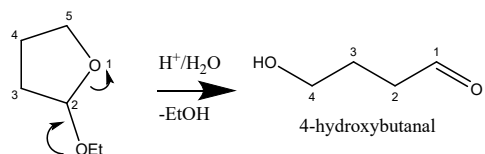
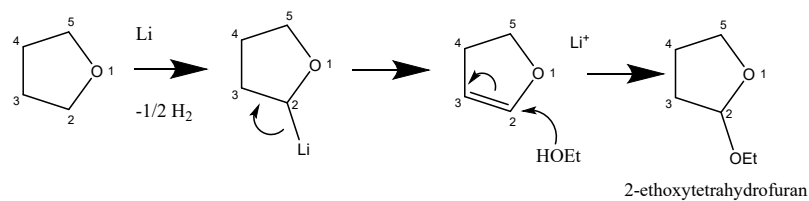


Figure S4d. Compound (5)



Important! Regarding the later butanal it can be catalyzed by protons:

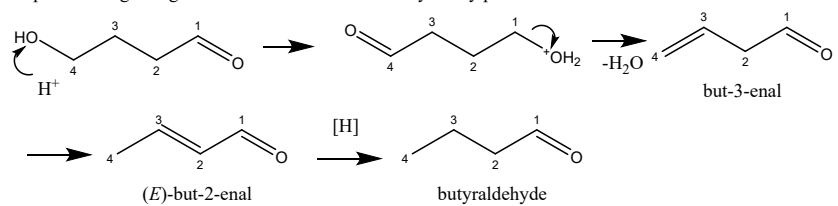
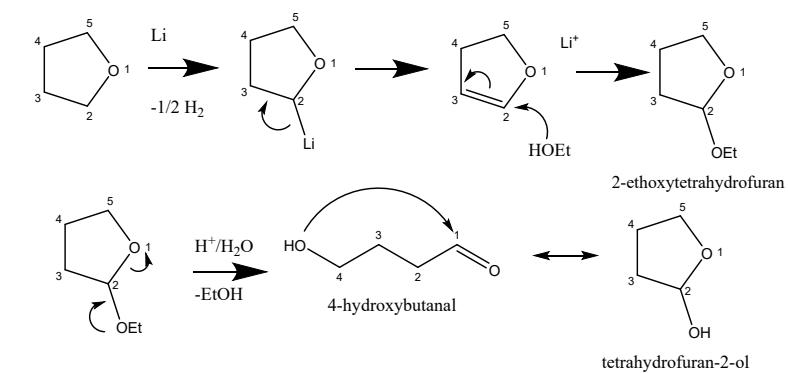


Figure S4e Compound (6) can be formed by reduction of Compound (4) or by the mechanism above.



Important! Regarding the later butanal it can be catalyzed by protons:

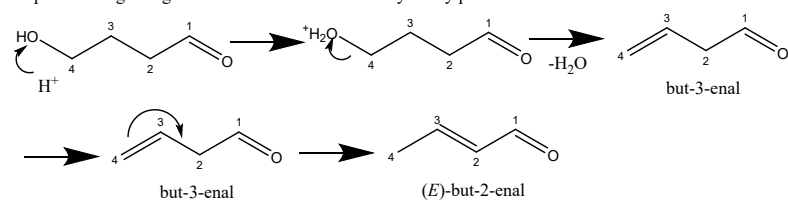


Figure S4f. Compound (7).

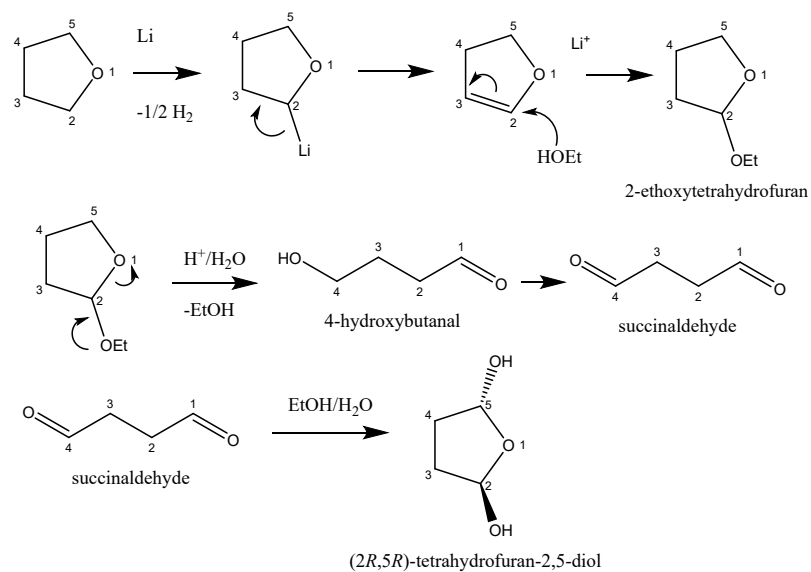


Figure S4g. Compound (9)



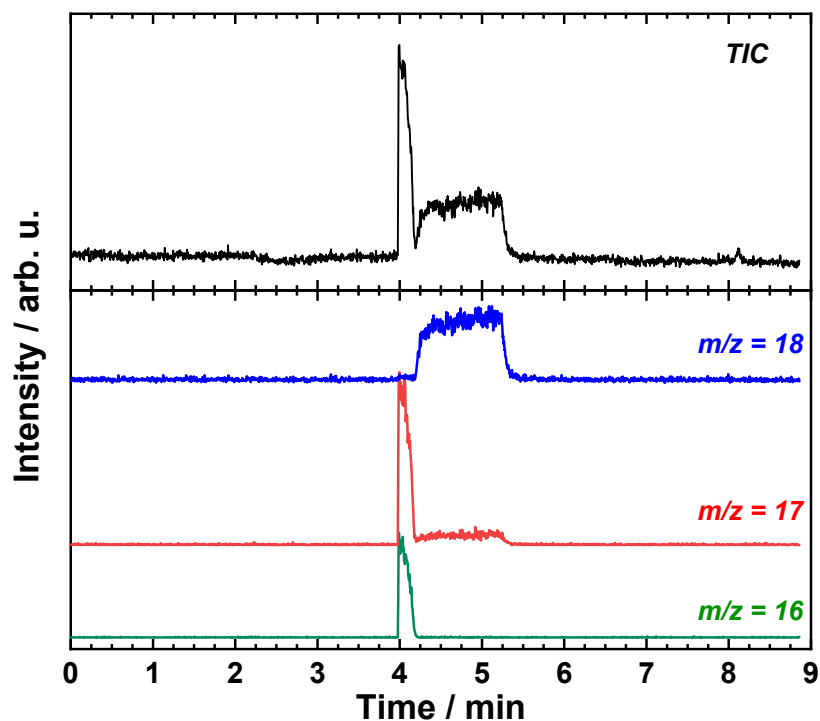


Figure S5. The chromatogram of ammonia solution (28 % in H<sub>2</sub>O) in THF. The elution of THF occurs at ~12 min, so it was skipped for convenient to read the figure.

## References

1. Y. P. Stenzel, F. Horsthemke, M. Winter and S. Nowak, *Separations*, 2019, **6**, 26.
2. G. Gachot, S. Grugeon, I. Jimenez-Gordon, G. G. Eshetu, S. Boyanov, A. Lecocq, G. Marlair, S. Pilard and S. Laruelle, *Anal. Methods*, 2014, **6**, 6120-6124.
3. G. Gachot, P. Ribiere, D. Mathiron, S. Grugeon, M. Armand, J. B. Leriche, S. Pilard and S. Laruelle, *Anal Chem*, 2011, **83**, 478-485.
4. K. K. Murray, R. K. Boyd, M. N. Eberlin, G. J. Langley, L. Li and Y. Naito, *Pure and Applied Chemistry*, 2013, **85**, 1515-1609.
5. P. L. Searle, *The Analyst*, 1984, **109**, 549.
6. S. Z. Andersen, V. Colic, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Norskov and I. Chorkendorff, *Nature*, 2019, **570**, 504-508.