

**Direct synthesis of cyclic carbonate from olefin and CO₂
catalyzed by MoO₂(acac)₂–quaternary ammonium salt
system**

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Supplementary Information

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1. Preparation of catalysts and oxidant

1.1 Preparation of $\text{MoO}_2(\text{acac})_2$

The complex was prepared by the literature methods [1]. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (30.0 g) was dissolved in H_2O (100 ml) and acetylacetone (40 ml) was added. The pH of the solution was adjusted to 3.5 using 10% HNO_3 and a solid began to precipitate. Yellow $\text{MoO}_2(\text{acac})_2$ was isolated by filtration, washed with H_2O , ethanol, and ether, and dried in vacuo.

1.2 Preparation of ionic liquids

$[\text{bmim}]\text{Cl}$ was obtained according to literatures[2-3]. To a vigorously stirred solution of 1-methylimidazole (1.25mol) in toluene (125mL) at 0 °C, 1- chlorobutane (144 mL, 1.38 mol) was added. The solutions were heated to reflux at ca. 110 °C for 24 h, after which they were placed in a freezer at ca. -20 °C for 12 h. The toluene was decanted from the remaining viscous oils/semi-solids and recrystallized from acetonitrile and then repeatedly recrystallized from ethyl acetate to yield white crystalline solids, which were dried in vacuo to give $[\text{bmim}]\text{Cl}$.

$[\text{bmim}]\text{Br}$ was obtained according to literatures[2-3]. Equal mol of 1-methylimidazole and 1-bromobutane was stirred for 24 h at 70 °C. Ethyl acetoacetate was used as extractant to remove the reactants. The ionic liquid obtained was dried at ca. 70 °C in vacuo for ca. 24 h.

$[\text{bmim}]\text{BF}_4$ was obtained according to literatures[2-3]. Equal mol of NaBF_4 and $[\text{bmim}]\text{Cl}$ were added in acetone and stirred for 24 h. The suspension was filtered to remove the precipitated chloride salt. The solvent was removed in rotatory evaporator. Dichloromethane was then added and the obtained white solid was filtered. Dichloromethane was then removed in rotatory evaporator and the organic phase was repeatedly washed with small dichloromethane until no precipitation of AgCl occurred on addition of a concentrated AgNO_3 solution. The solvent was removed in in rotatory evaporator and the resulting ionic liquid was dried at ca. 100 °C in vacuo for ca. 24 h.

1.3 Preparation of polyoxometalates

$[(n\text{-C}_7\text{H}_{15})_4\text{N}]_6\text{SiW}_{11}\text{CoO}_{39}$ was prepared by removing the solvent under reduced pressure after cation exchange with an aqueous solution of the corresponding potassium salts in excessive amount with toluene solution of $(n\text{-C}_7\text{H}_{15})_4\text{NBr}$ by the method of literature [4-6]. $\text{K}_6\text{SiW}_{11}\text{CoO}_{39}$ was obtained according to the reference method [7]. 7.2 mmol $(n\text{-C}_7\text{H}_{15})_4\text{NBr}$ was dissolved in 40 mL toluene and 2 mmol $\text{K}_6\text{SiW}_{11}\text{CoO}_{39}$ was dissolved in 10 mL water. The mixture was shaken violently and the organic solution was separated. $[(n\text{-C}_7\text{H}_{15})_4\text{N}]_6\text{SiW}_{11}\text{CoO}_{39}$ was obtained by removing the solvent under reduced pressure [4-6].

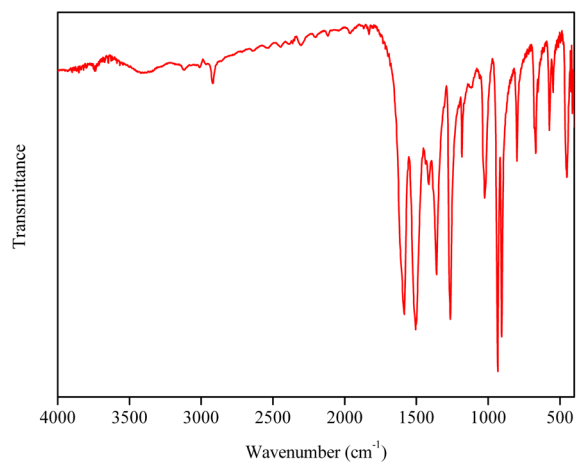
$[(n\text{-C}_7\text{H}_{15})_4\text{N}]_6\text{GeW}_{11}\text{MnO}_{39}$ was prepared using similar method [4-8].

1.4 Preparation of anhydrous *t*-butyl hydroperoxide

Anhydrous *t*-butyl hydroperoxide in toluene was synthesized from refluxing 70% *t*-butyl hydroperoxide aqueous solution and toluene following the literature procedure [9]. TBHP concentration was determined by iodometric titration [9-10] and was found to be 3.25 M.

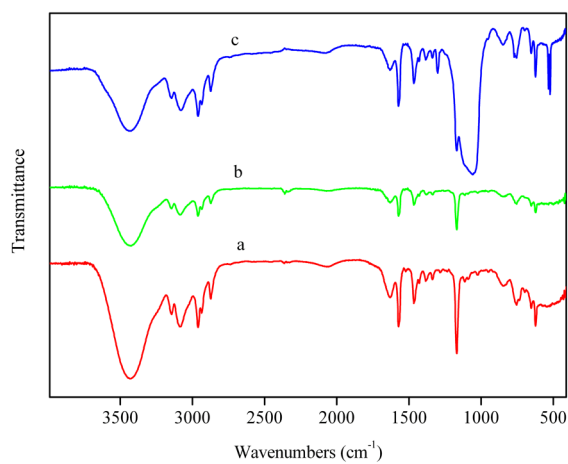
2. IR spectra for catalysts

2.1 IR spectrum for $\text{MoO}_2(\text{acac})_2$



sFig. 1 IR spectrum for $\text{MoO}_2(\text{acac})_2$

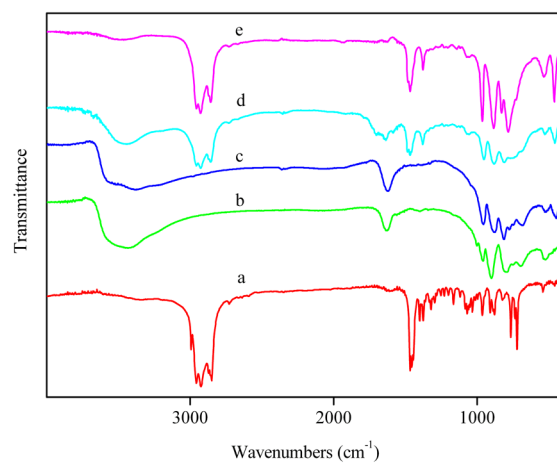
2.2 IR spectra ionic liquids



sFig. 2 IR spectra for ionic liquids

- (a) [bmim]Cl
- (b) [bmim]Br
- (c) [bmim]BF₄

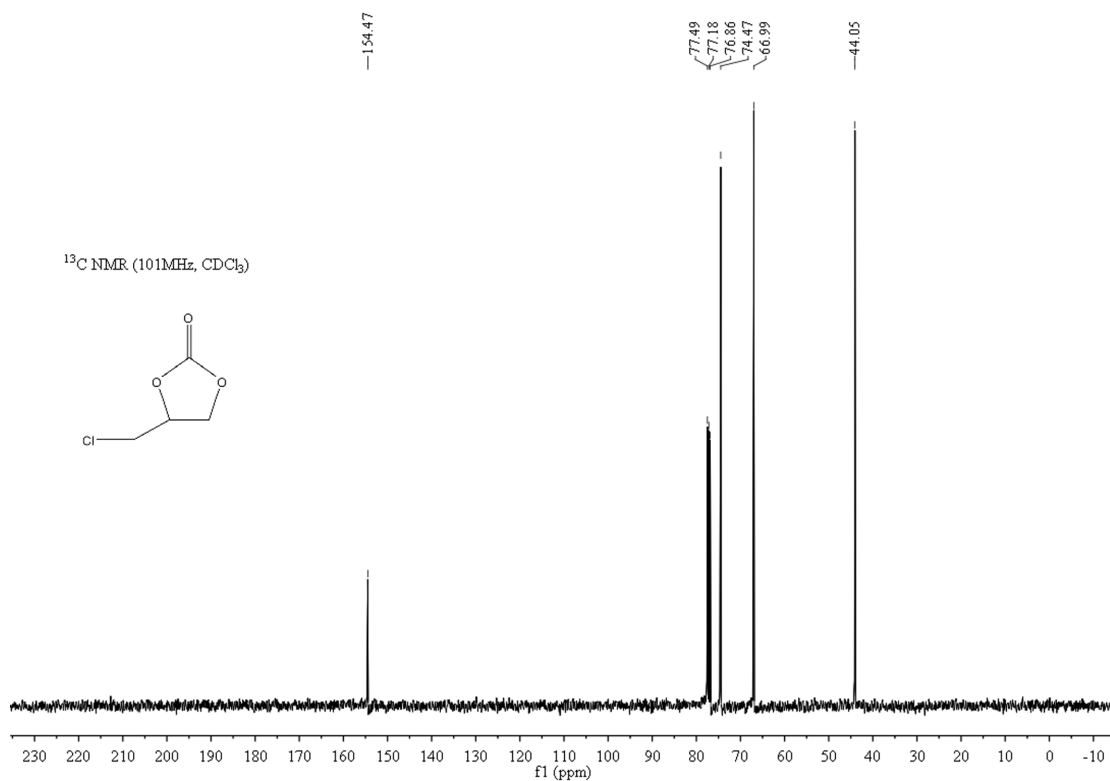
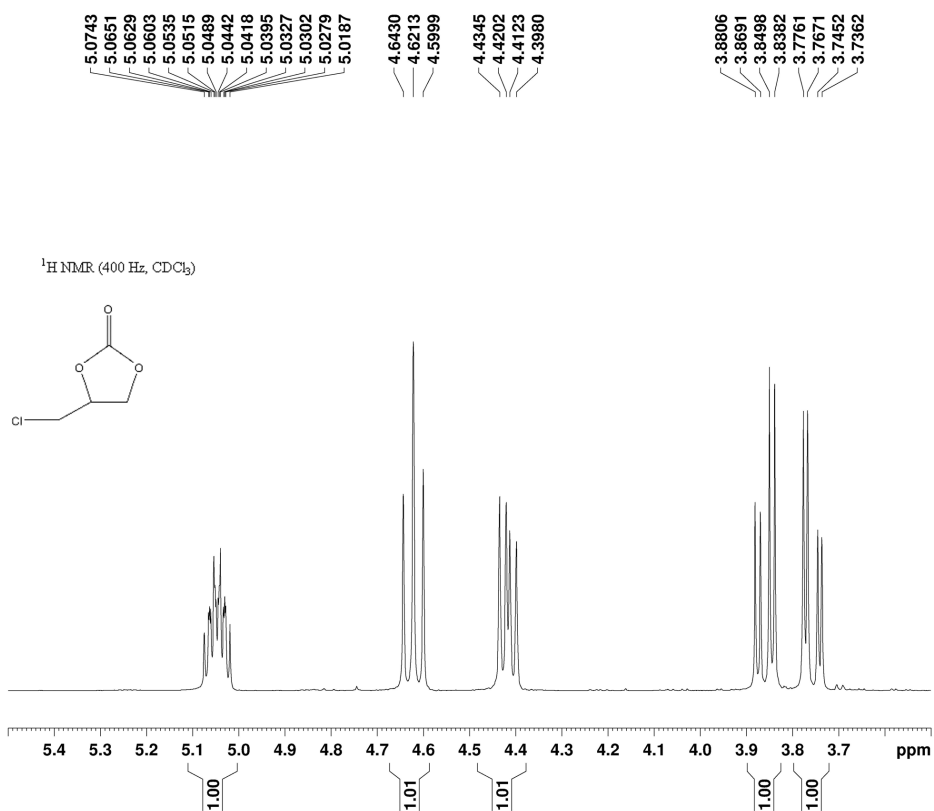
2.3 IR spectra for polyoxometalates

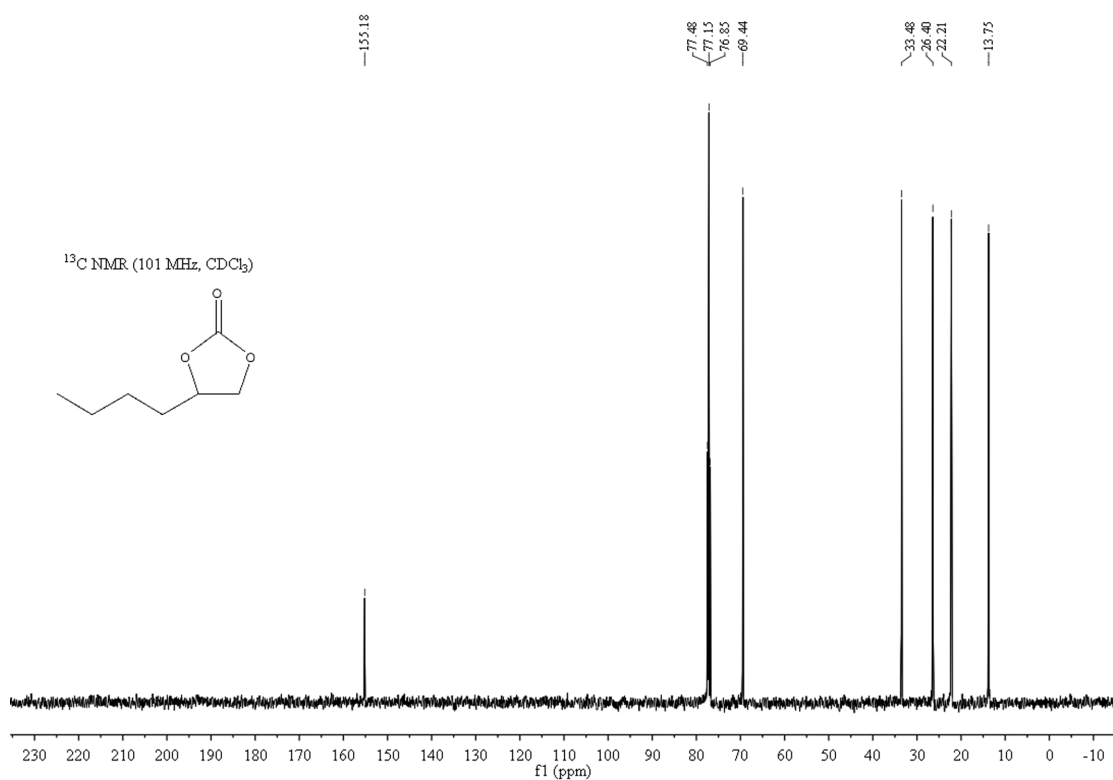
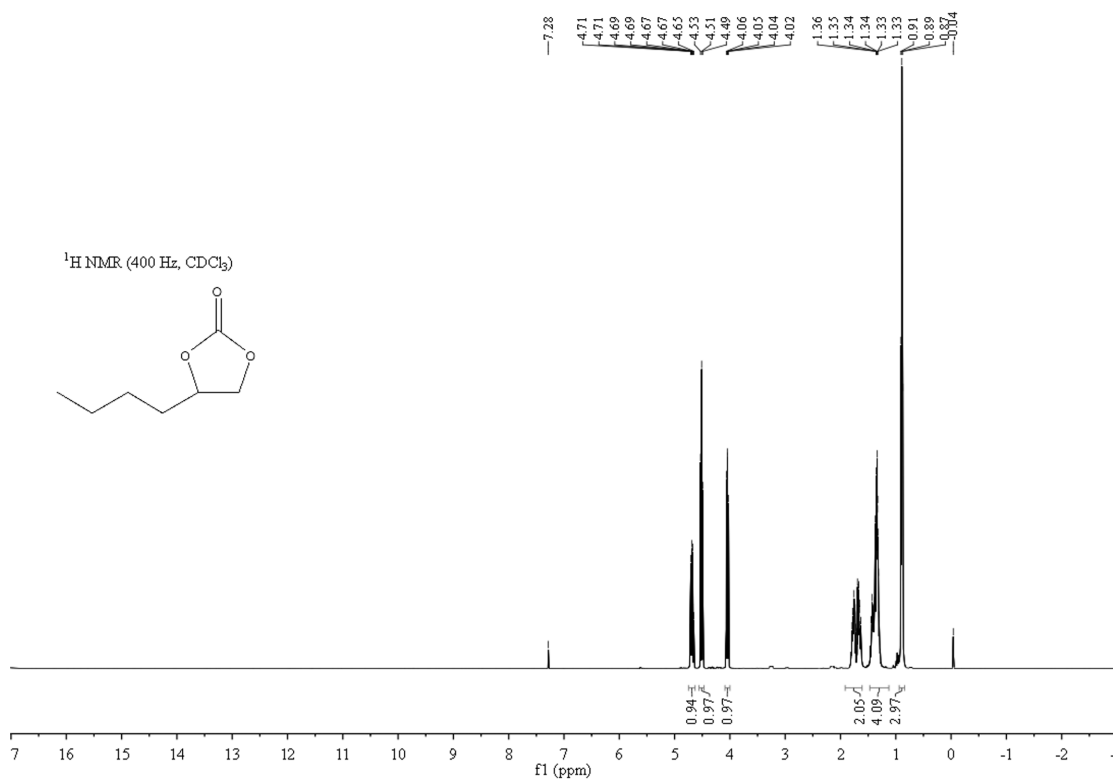


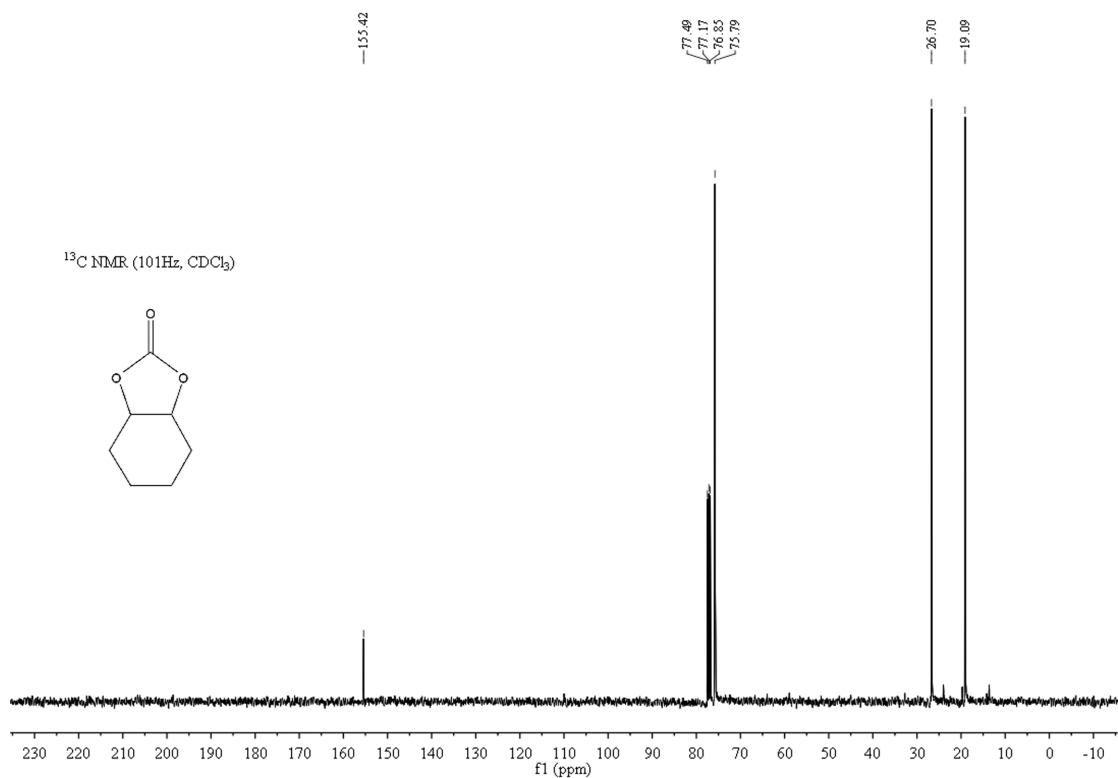
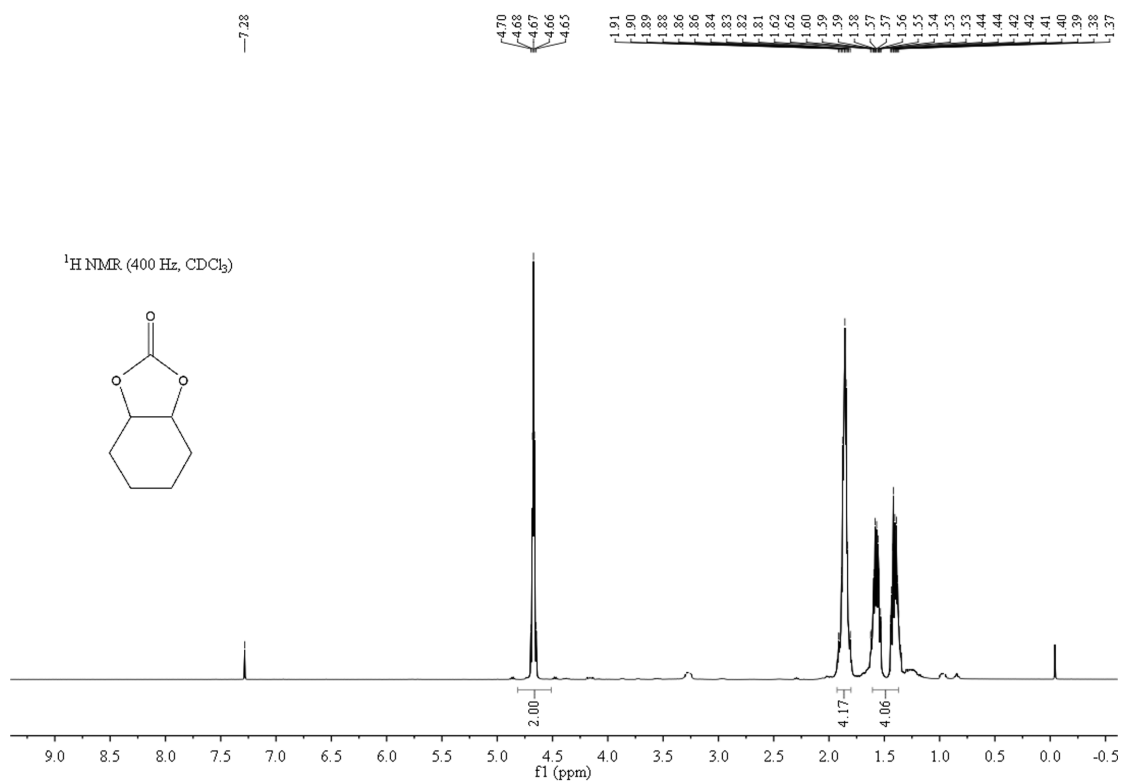
sFig. 3 IR spectra for polyoxometalates

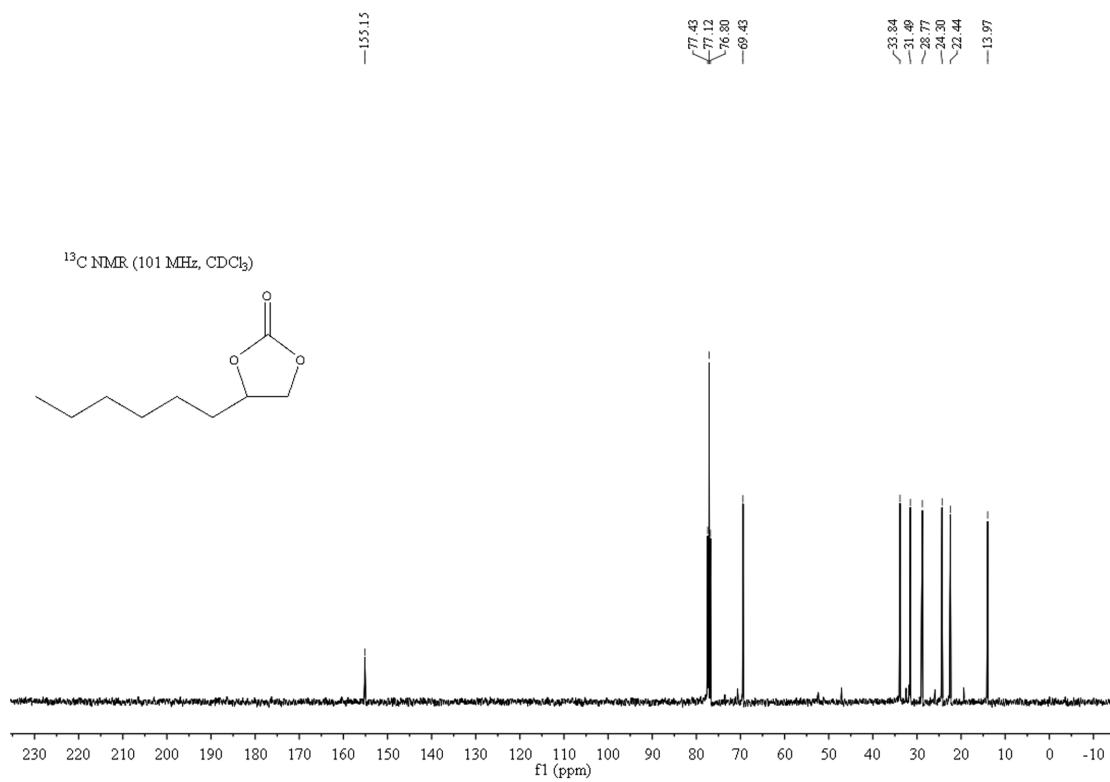
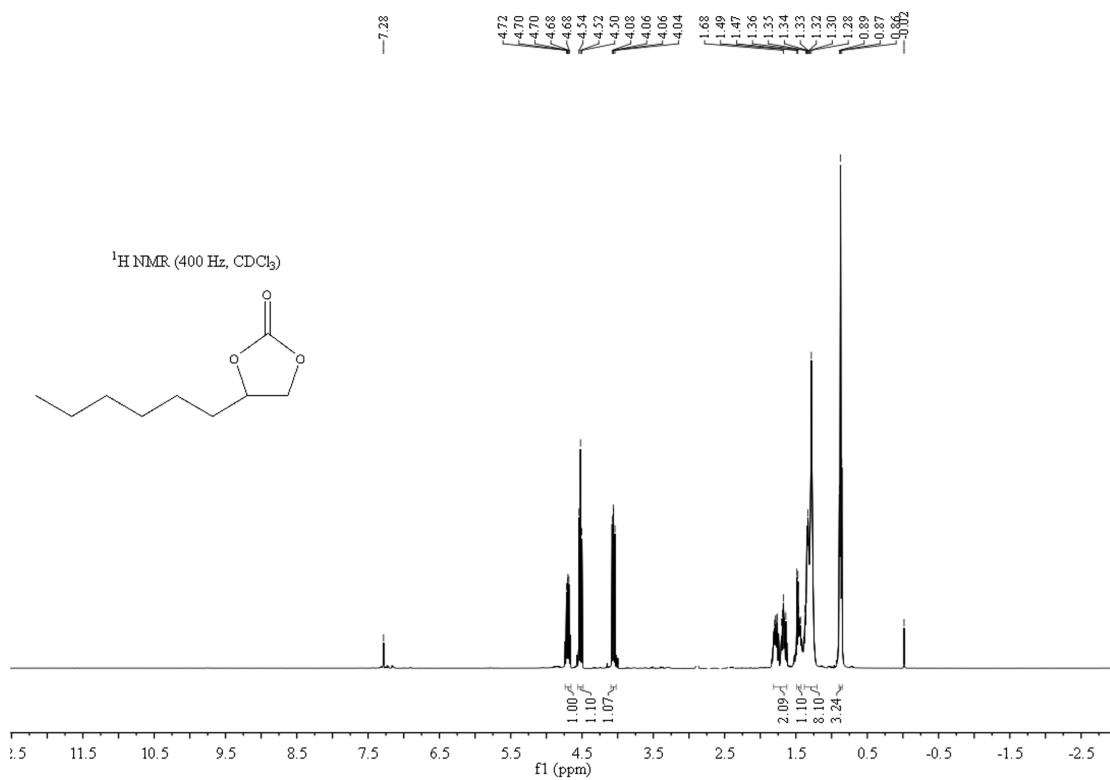
- (a) $n\text{-(C}_7\text{H}_{15})_4\text{NBr}$
- (b) $\text{K}_6\text{SiW}_{11}\text{CoO}_{39}$
- (c) $\text{K}_6\text{GeW}_{11}\text{MnO}_{39}$
- (d) $[\text{n-(C}_7\text{H}_{15})_4\text{N}]_6\text{SiW}_{11}\text{CoO}_{39}$
- (e) $[\text{n-(C}_7\text{H}_{15})_4\text{N}]_6\text{GeW}_{11}\text{MnO}_{39}$

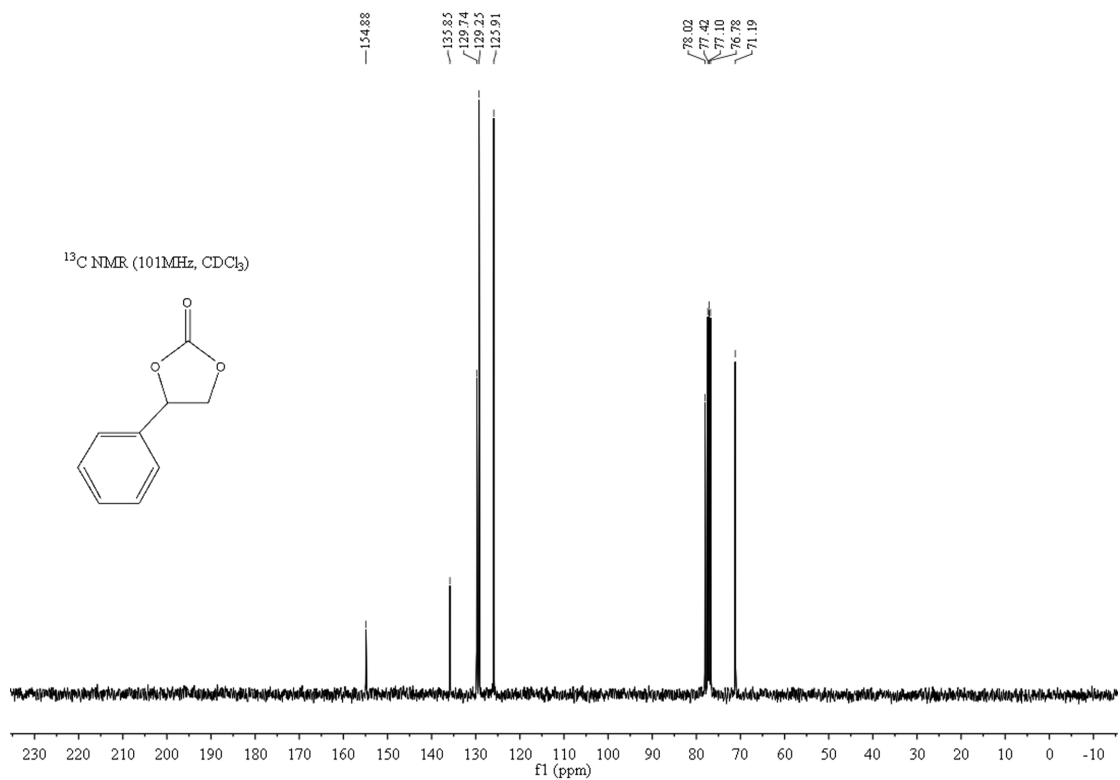
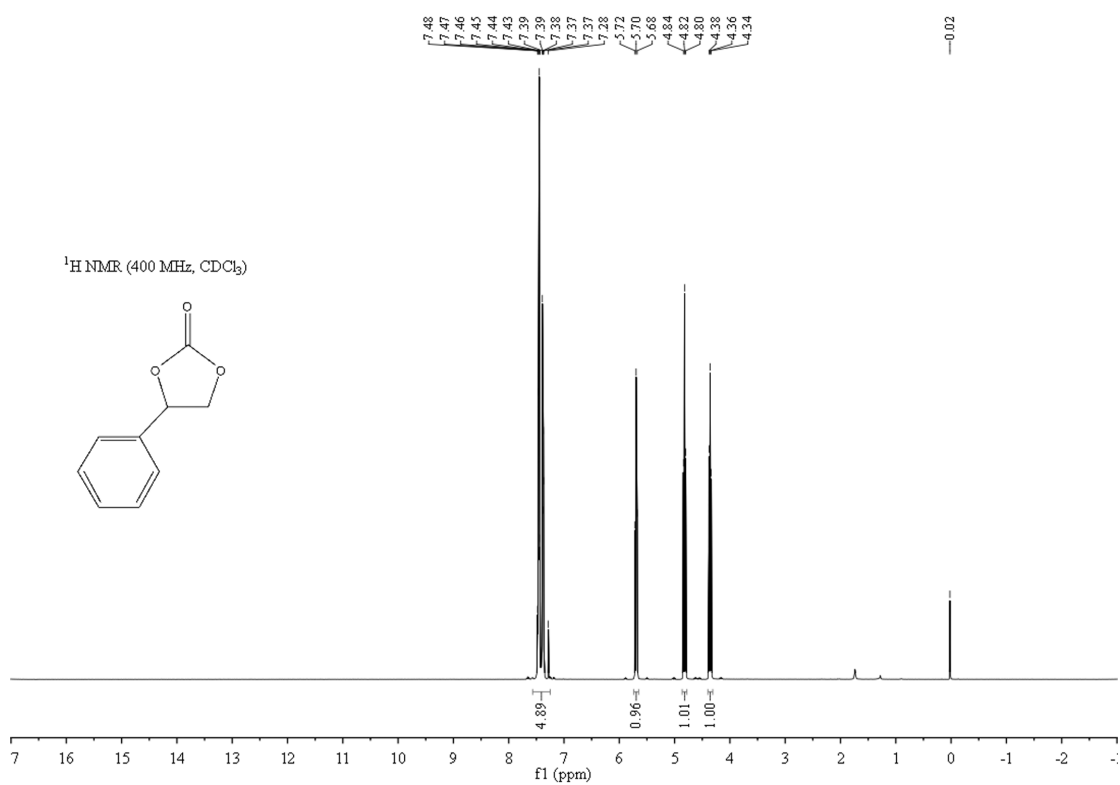
3 NMR spectra for cyclic carbonates



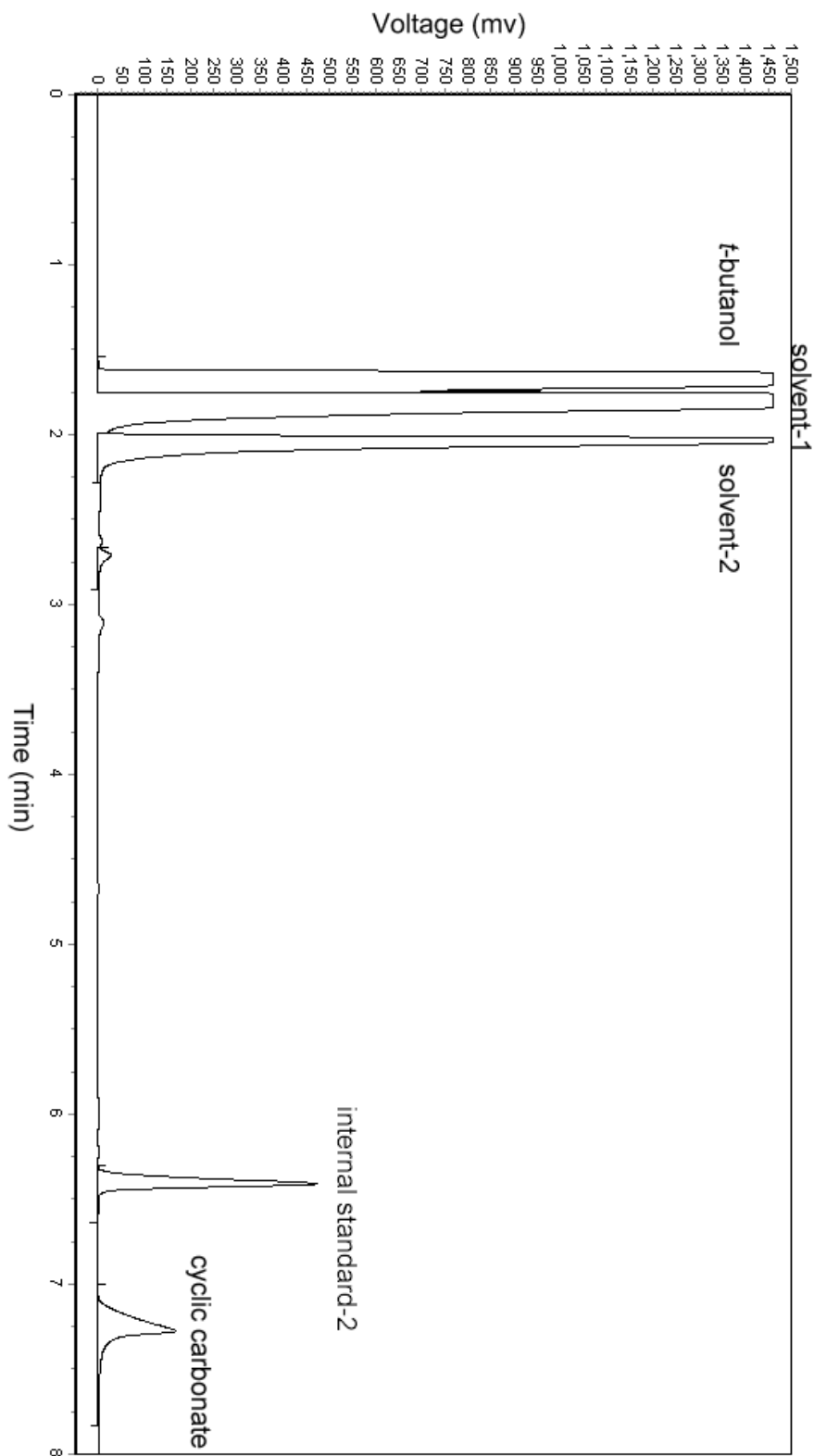
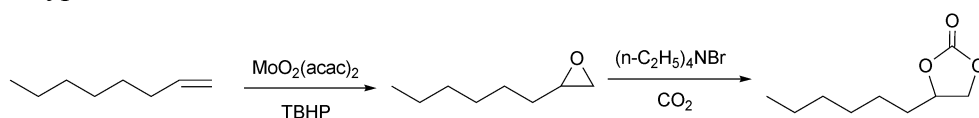


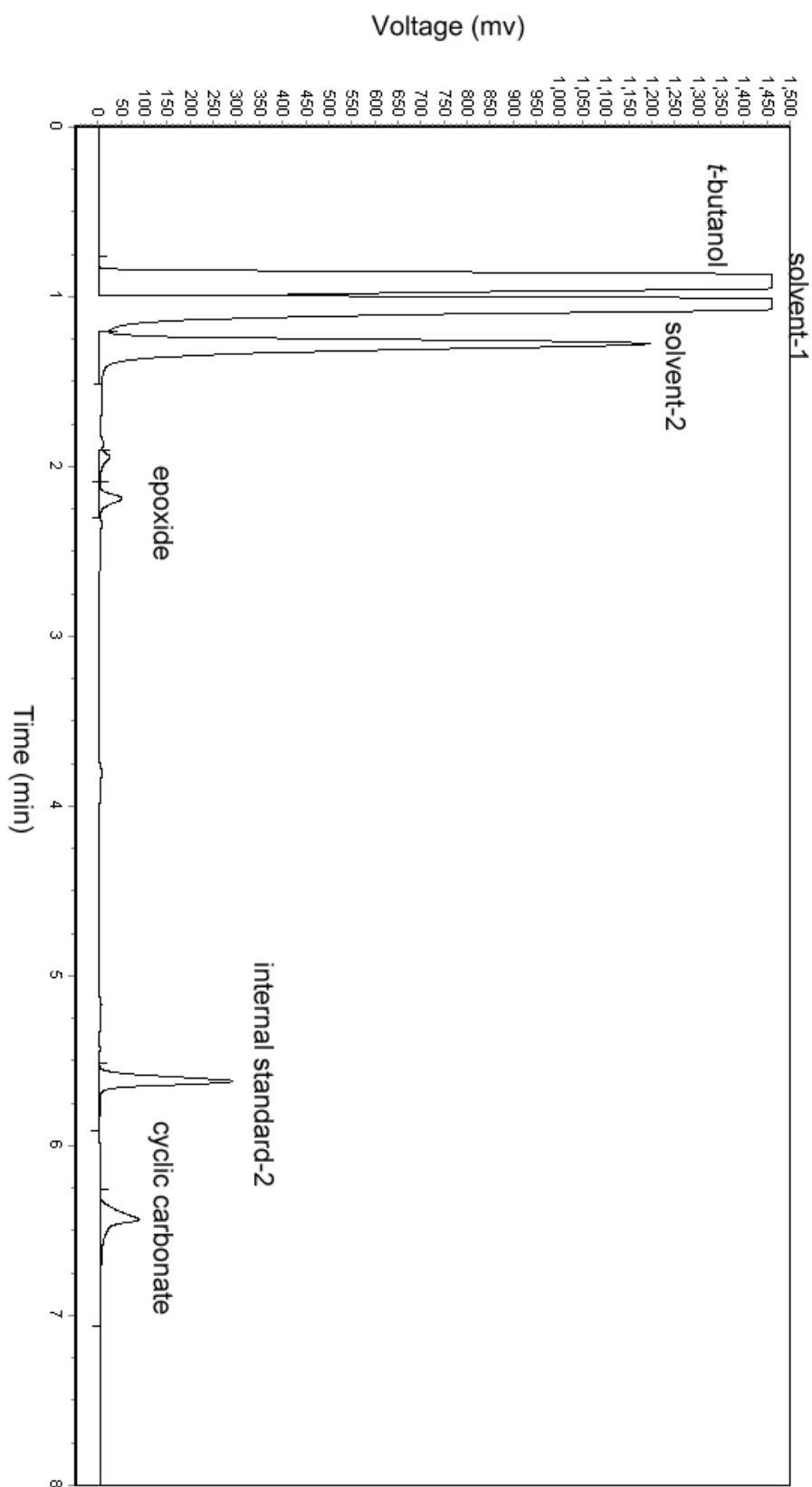
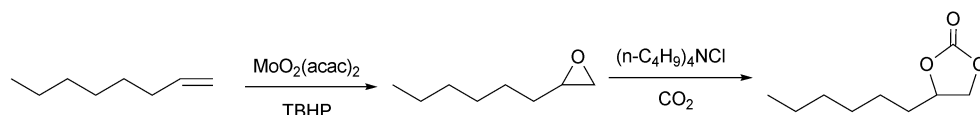


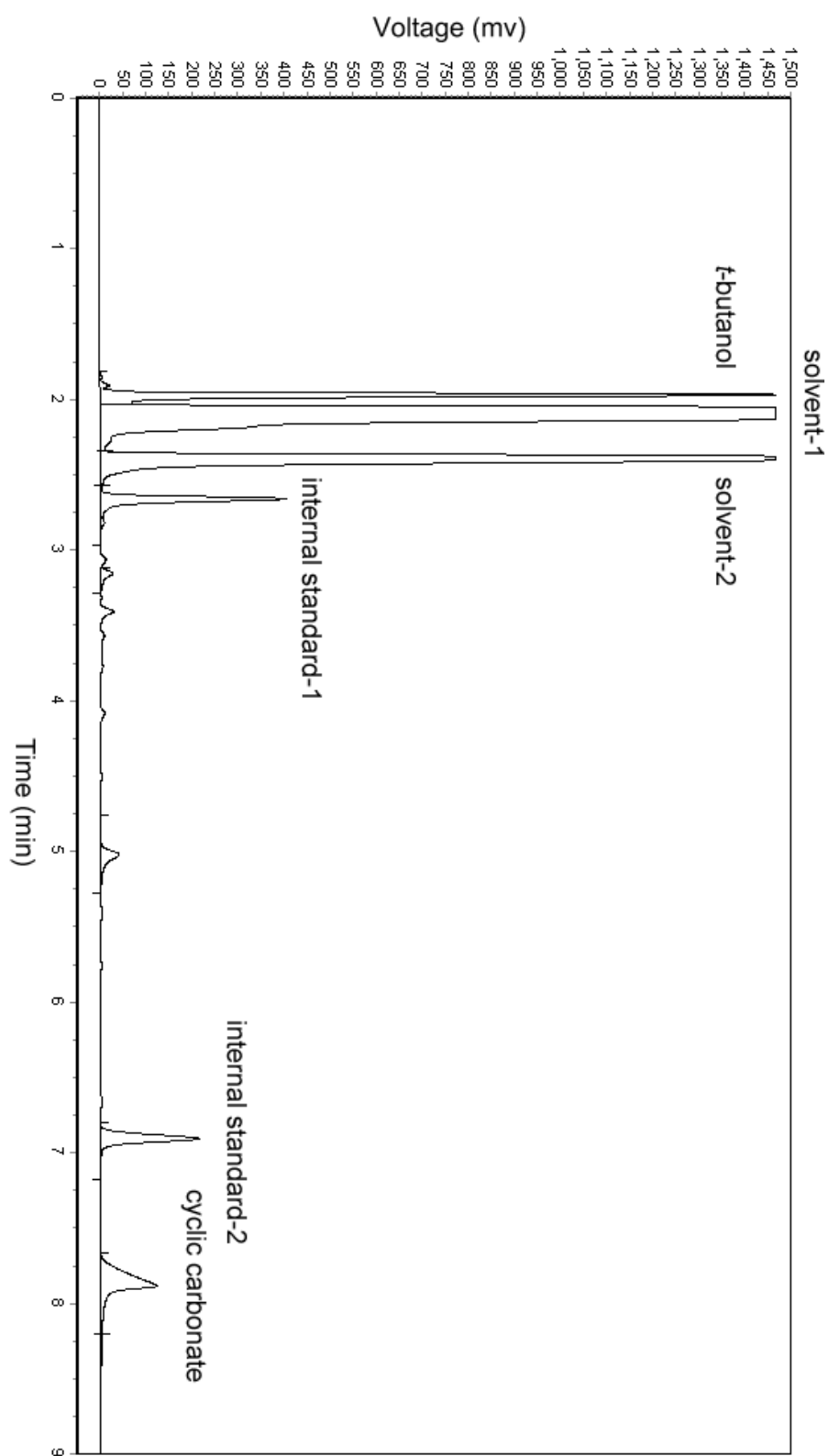
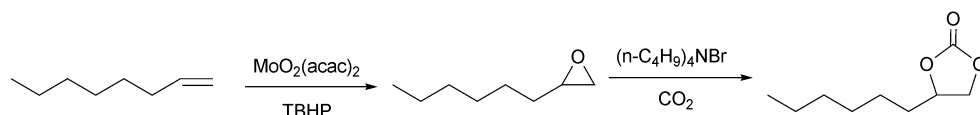


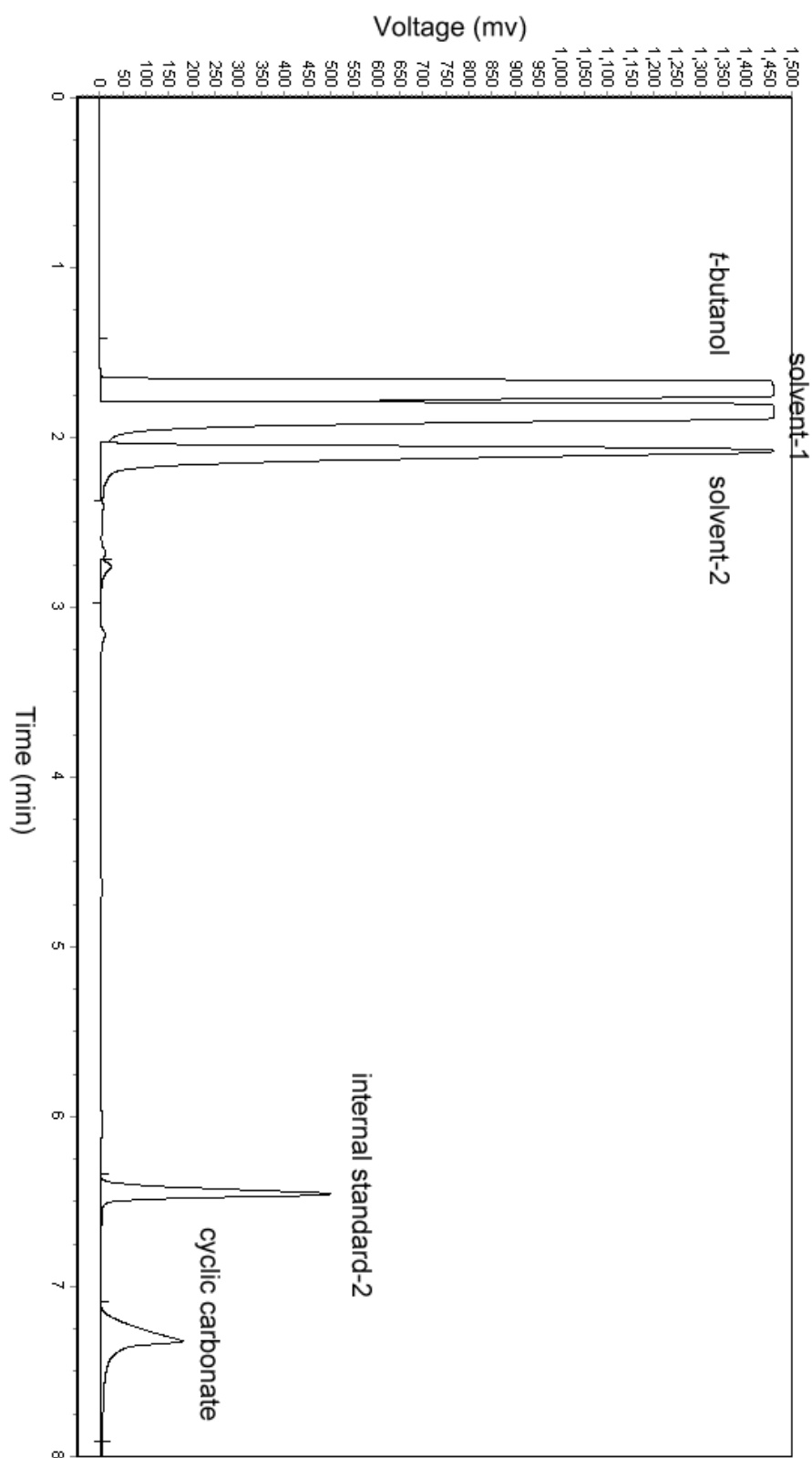
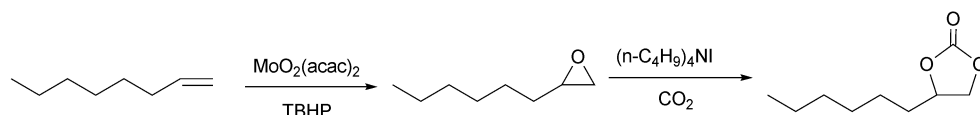


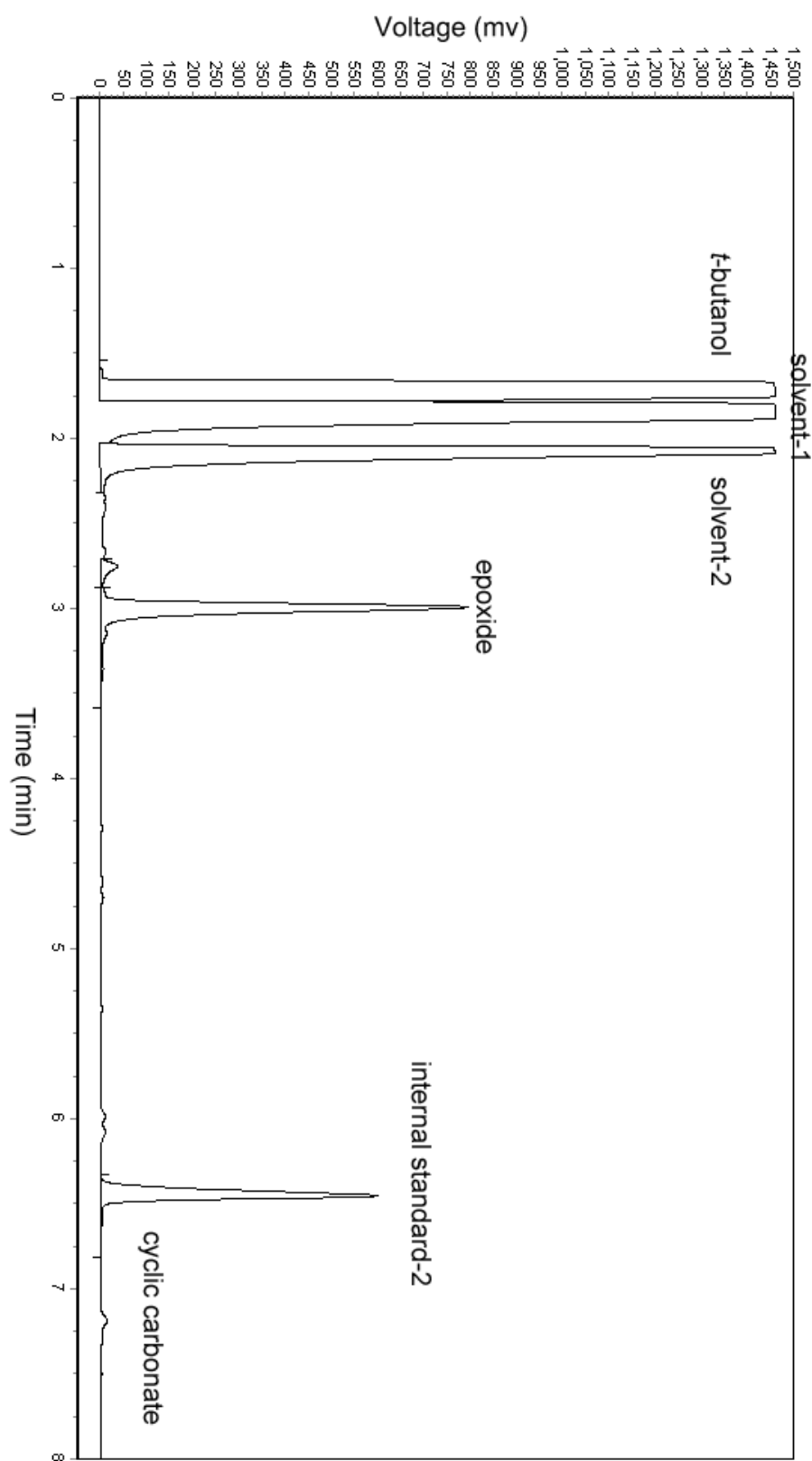
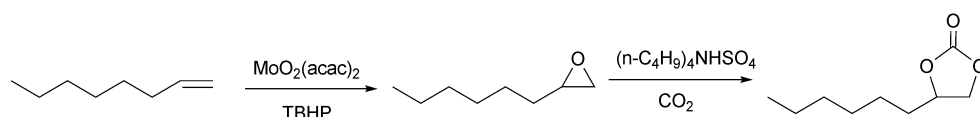
4 Typical GC chart of the reaction mixture

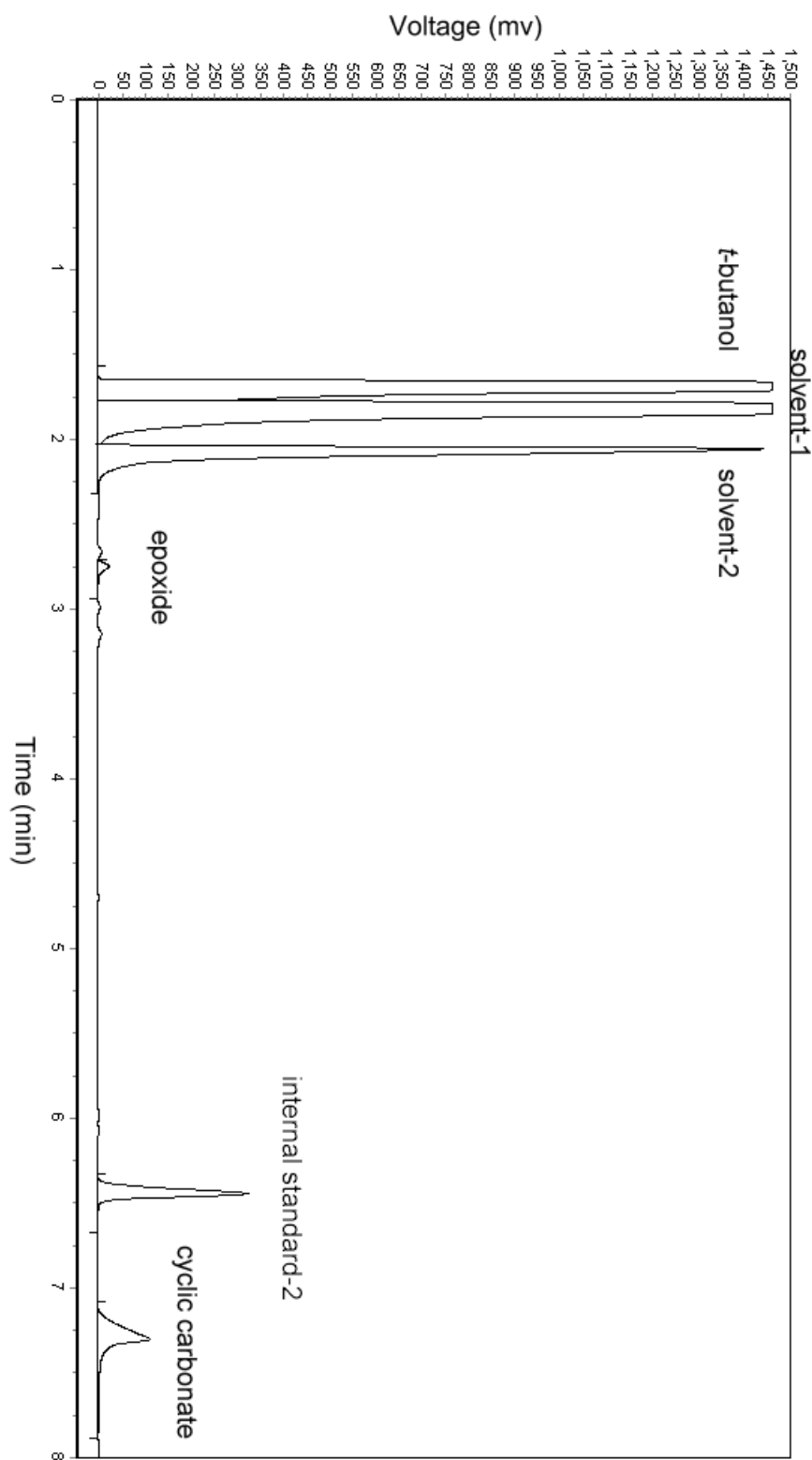
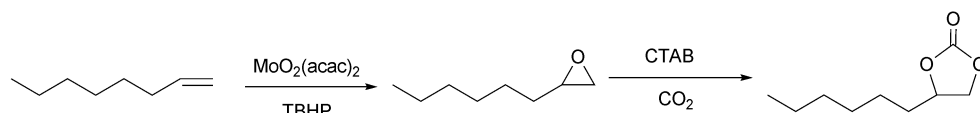


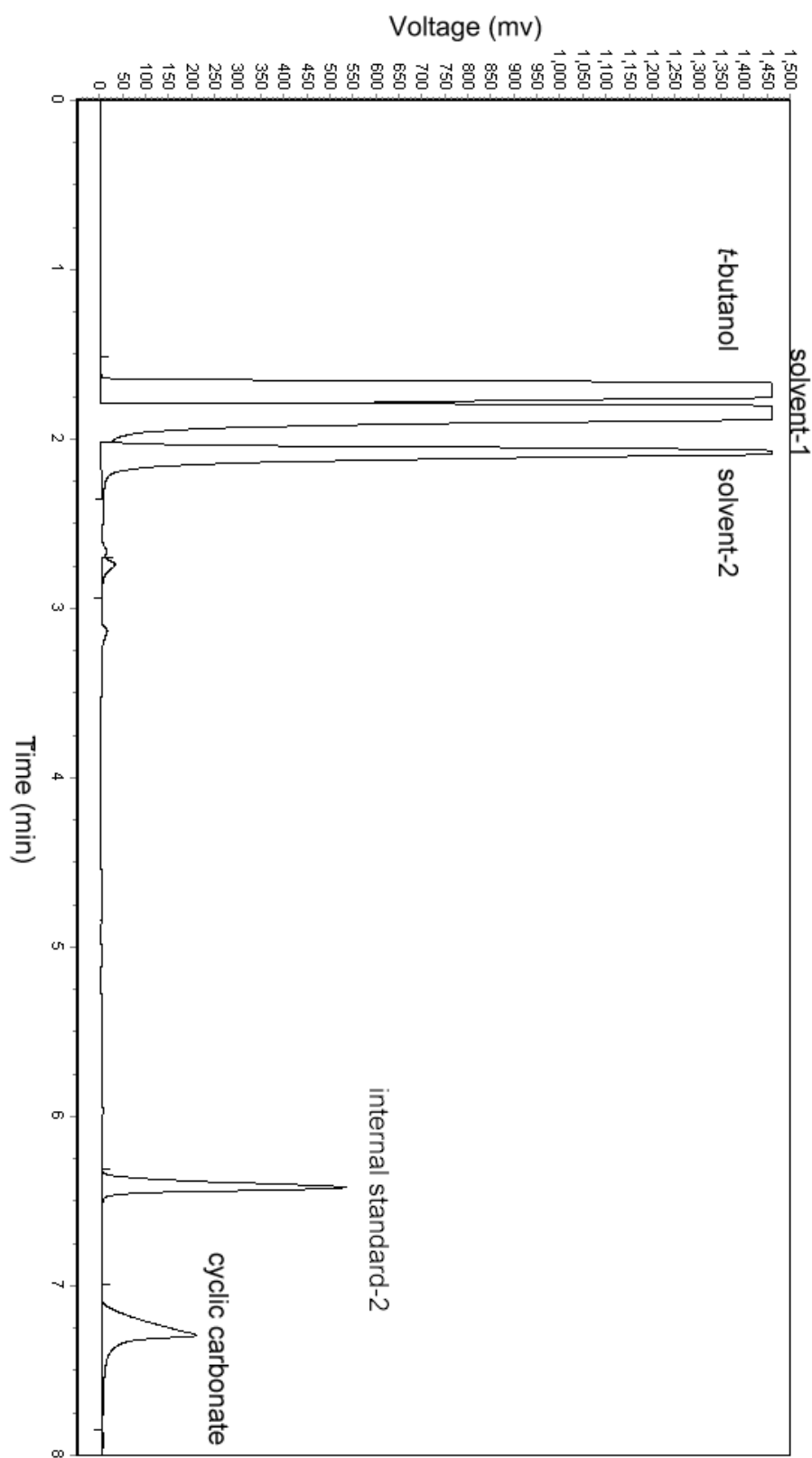
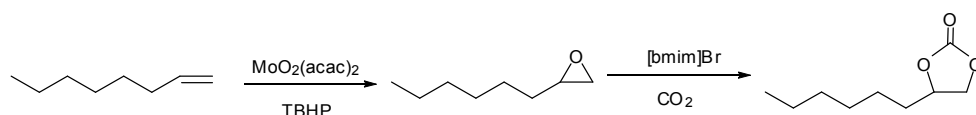


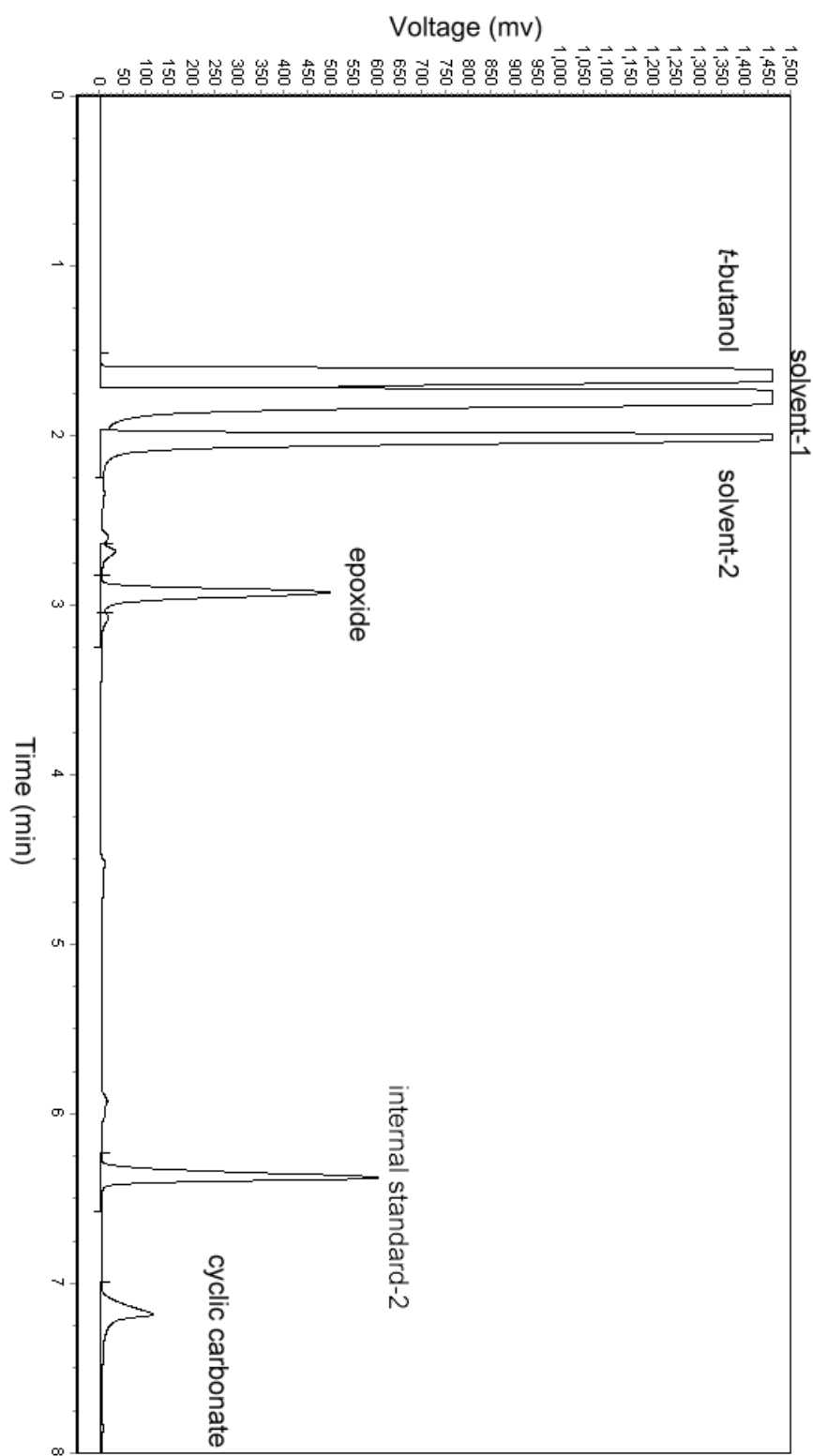
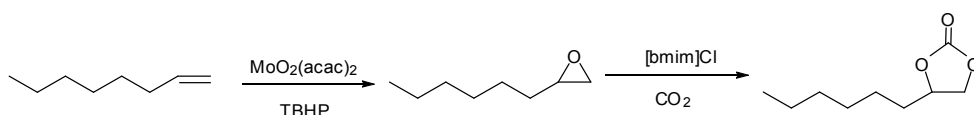


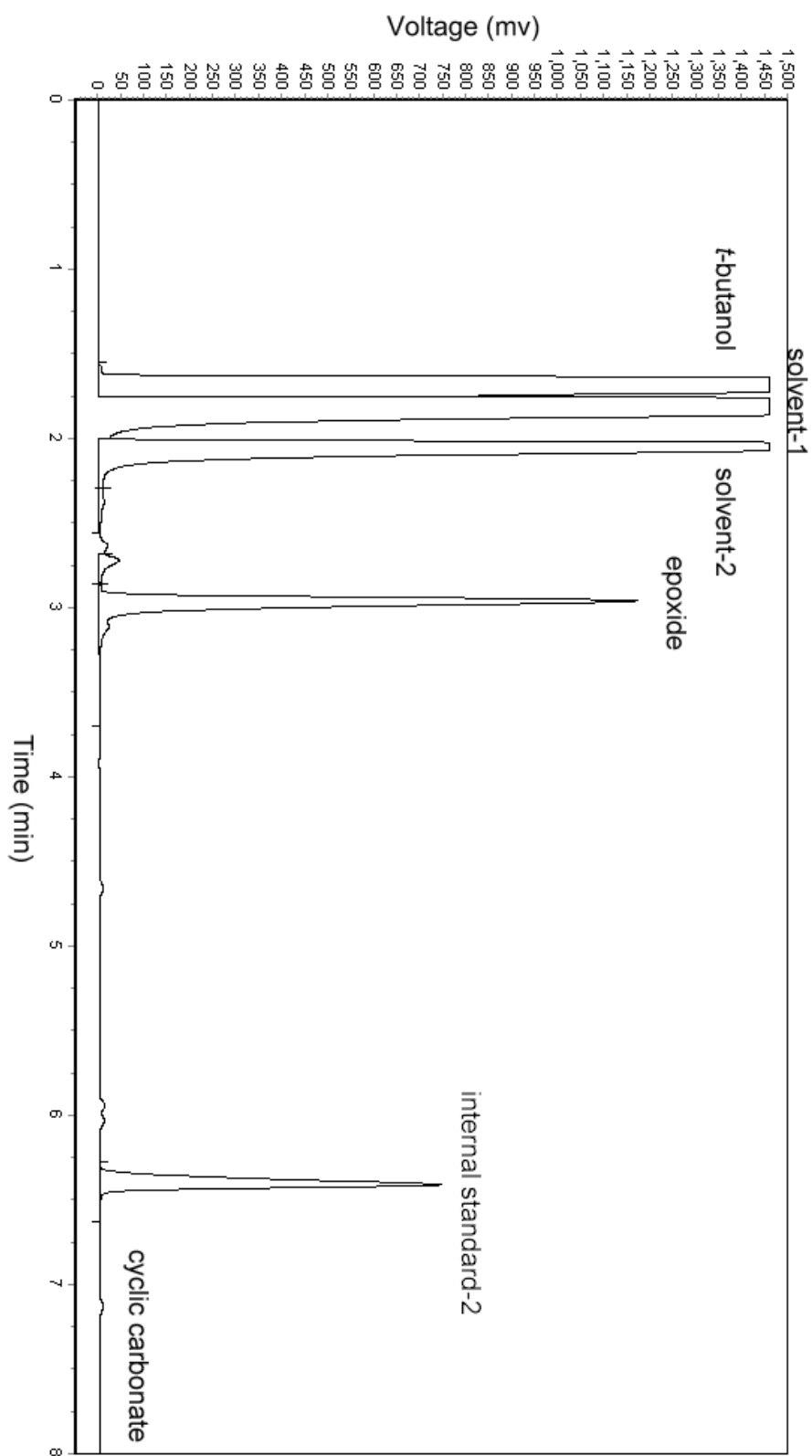
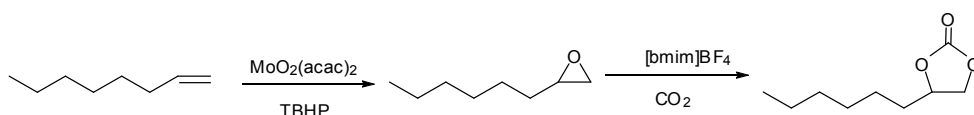


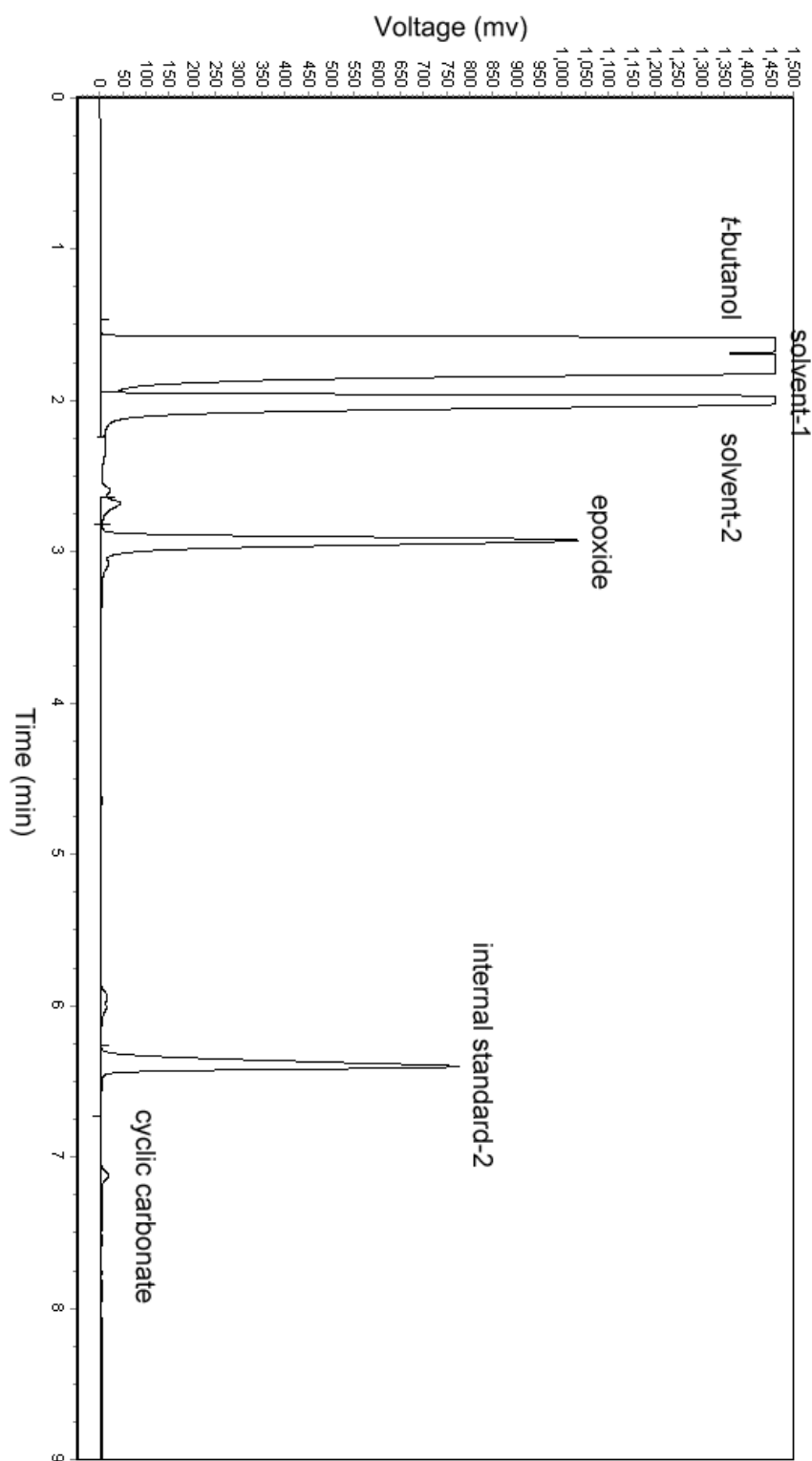
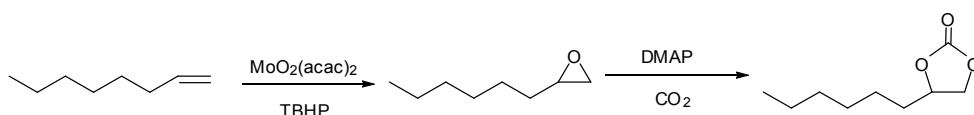


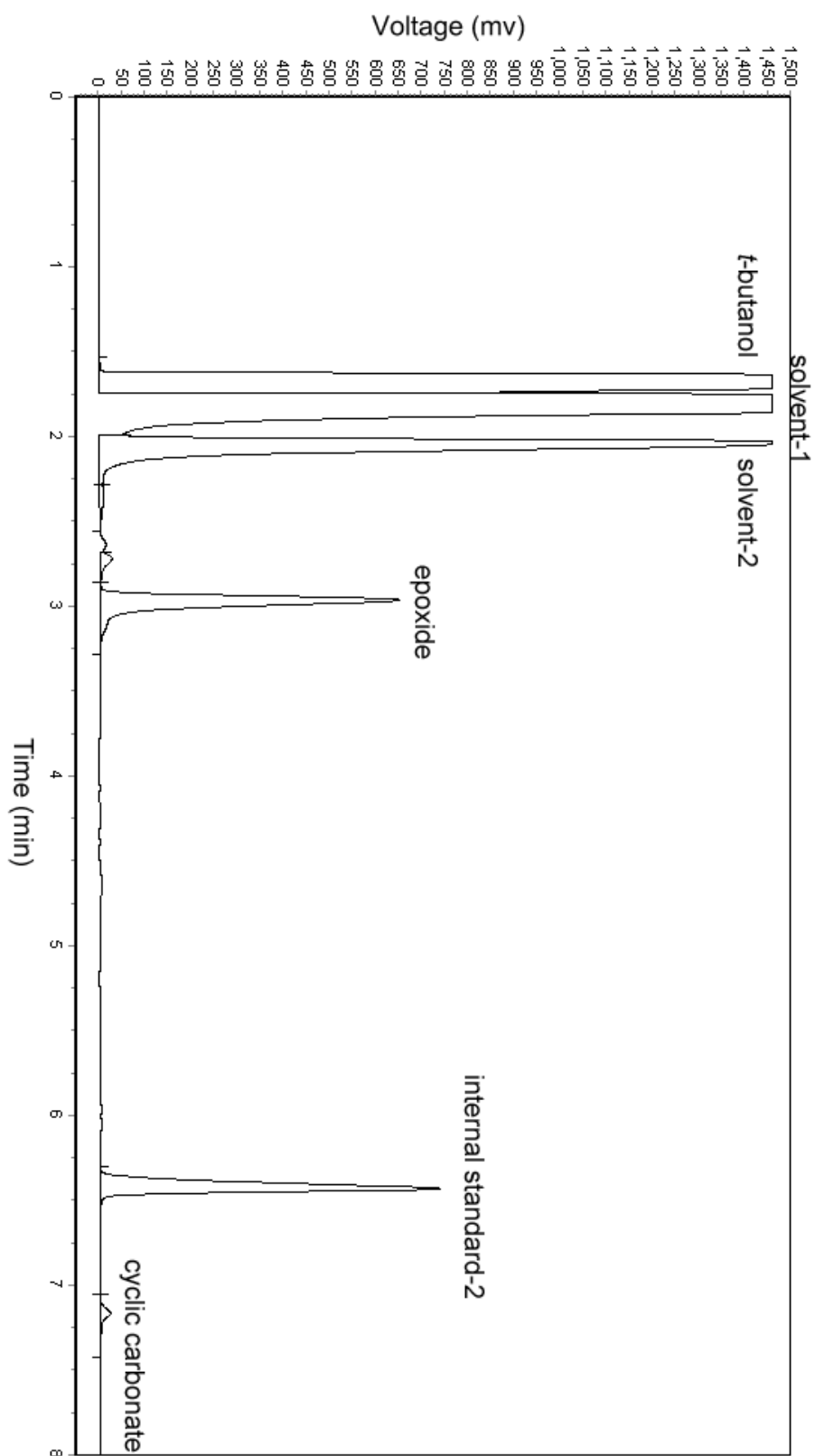
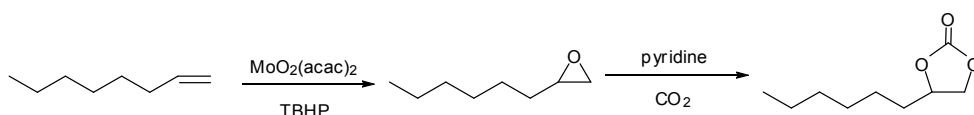


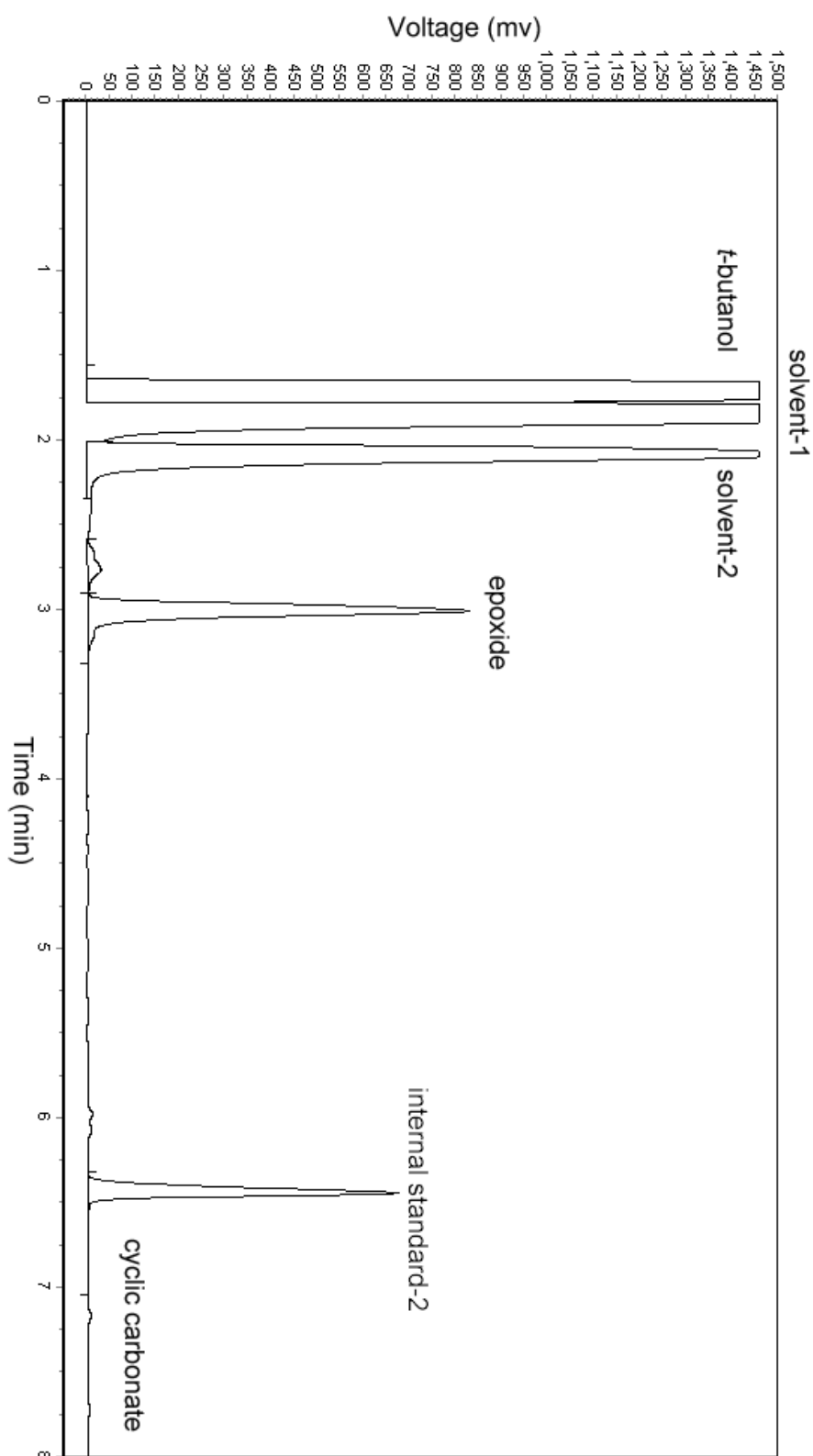
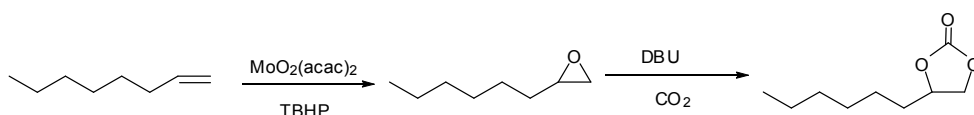


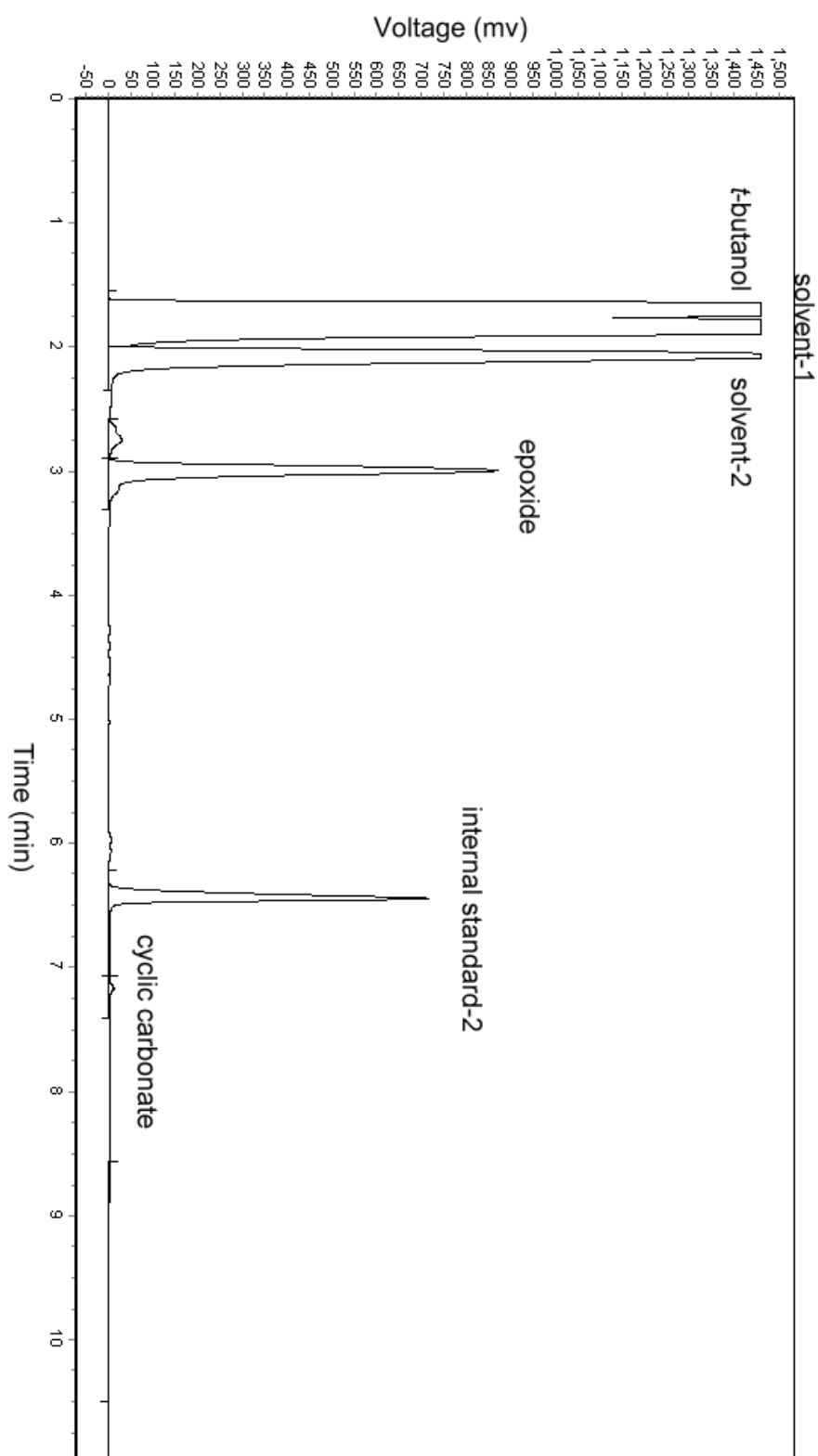
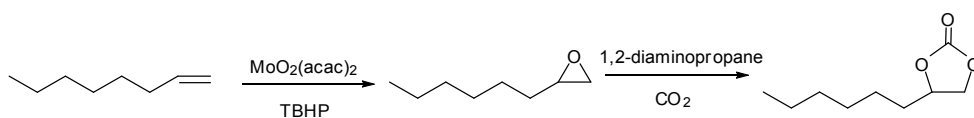


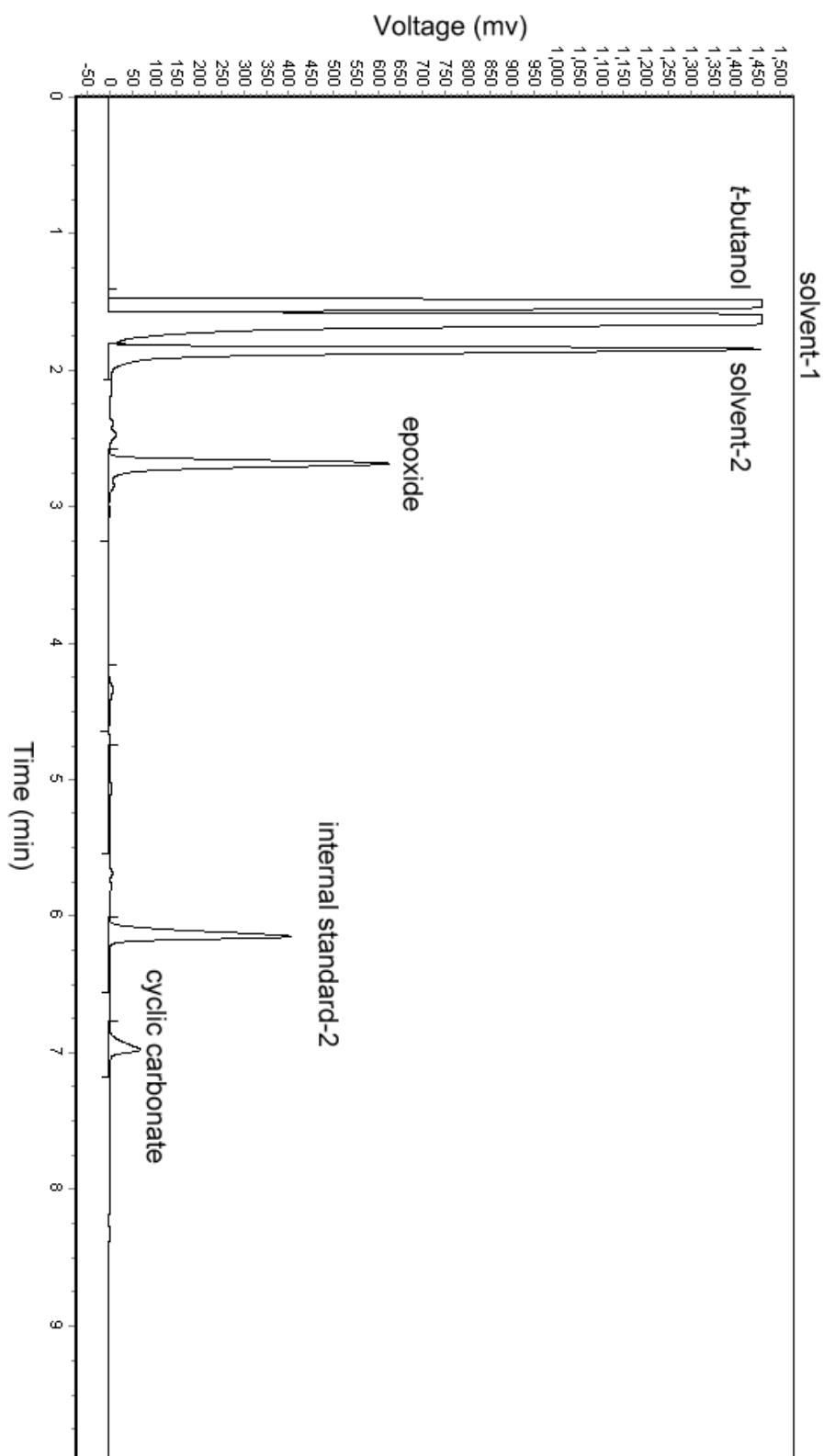
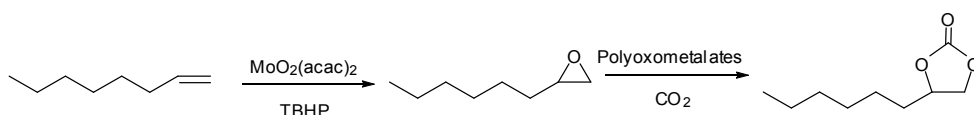


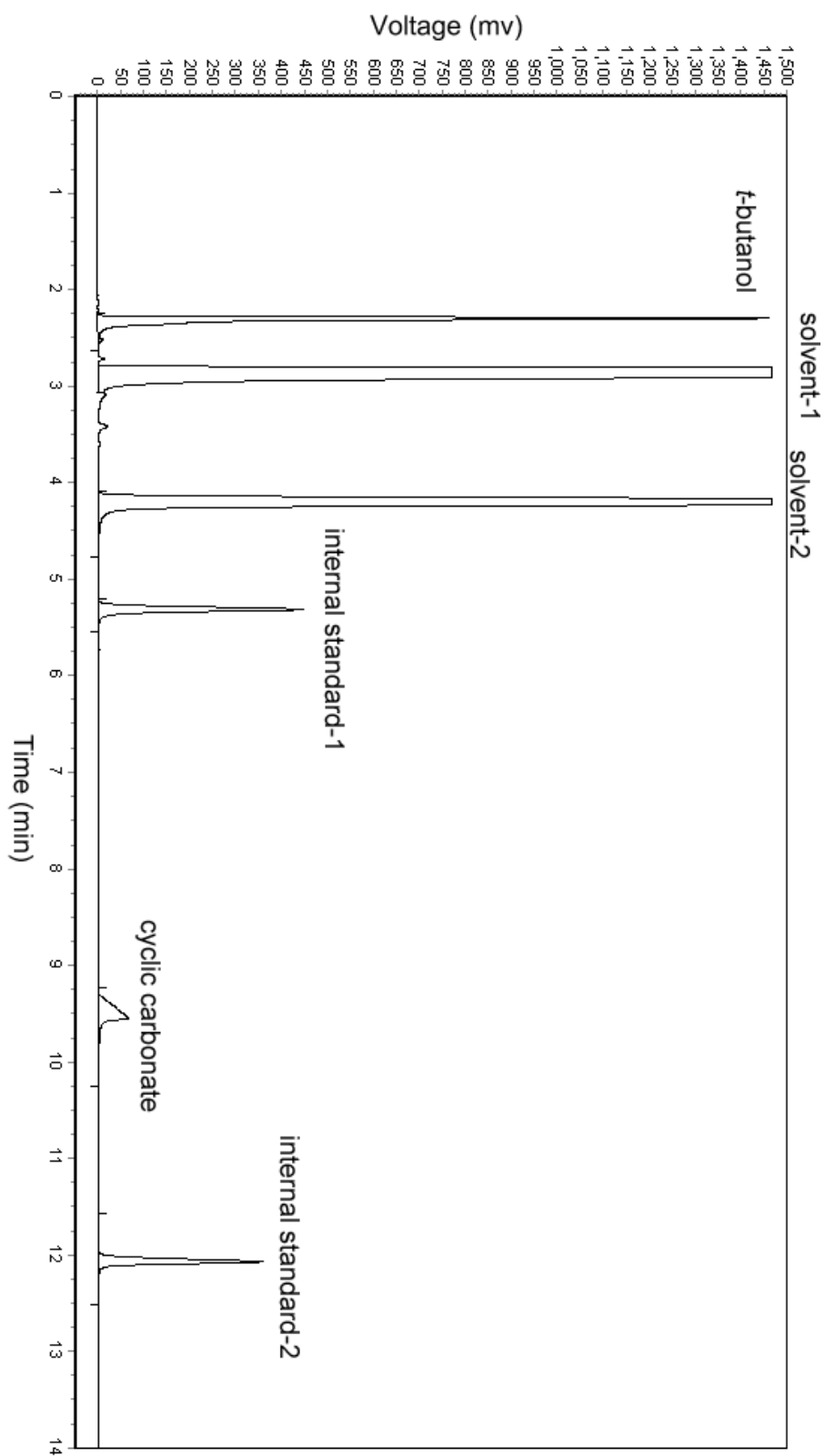
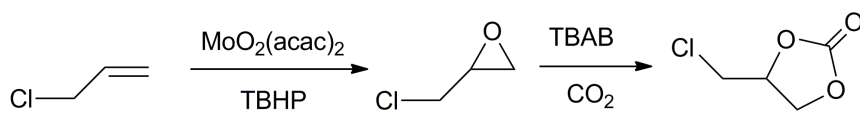


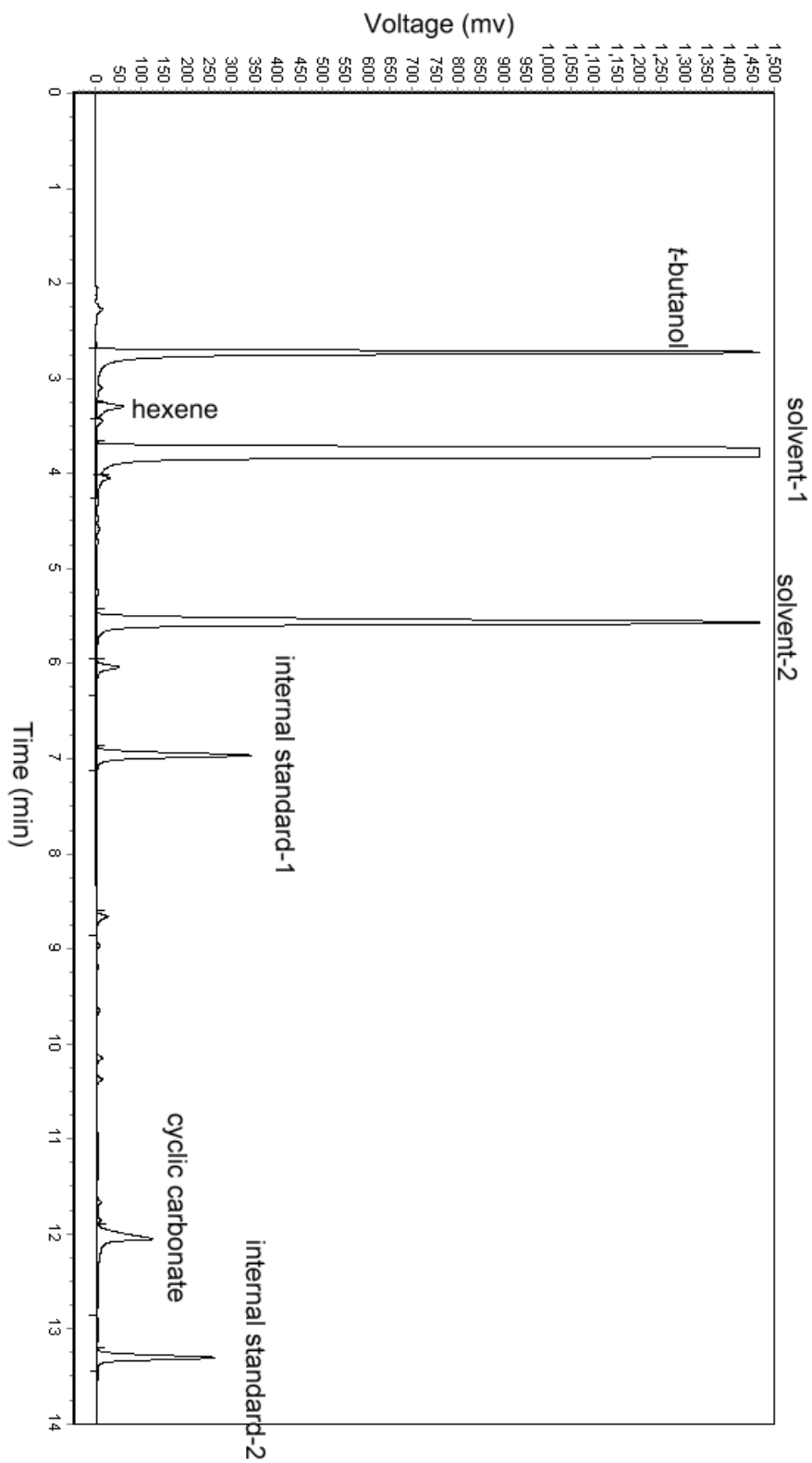
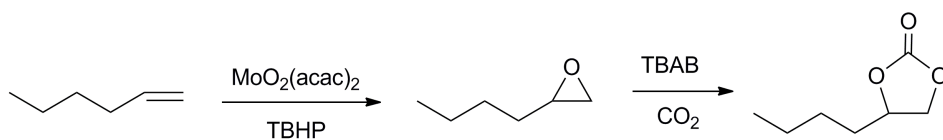


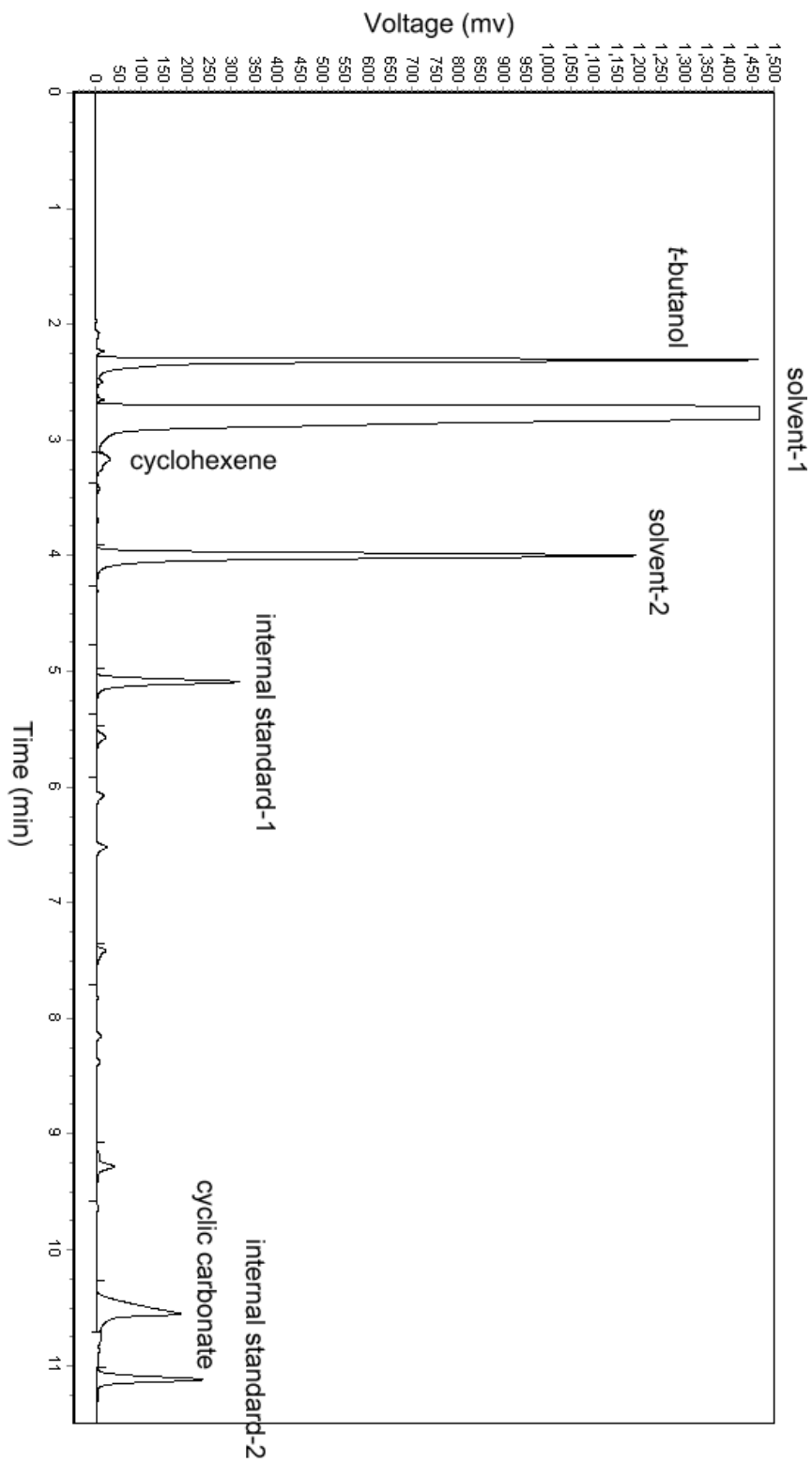
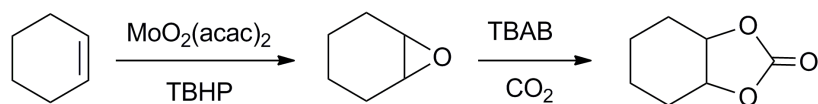


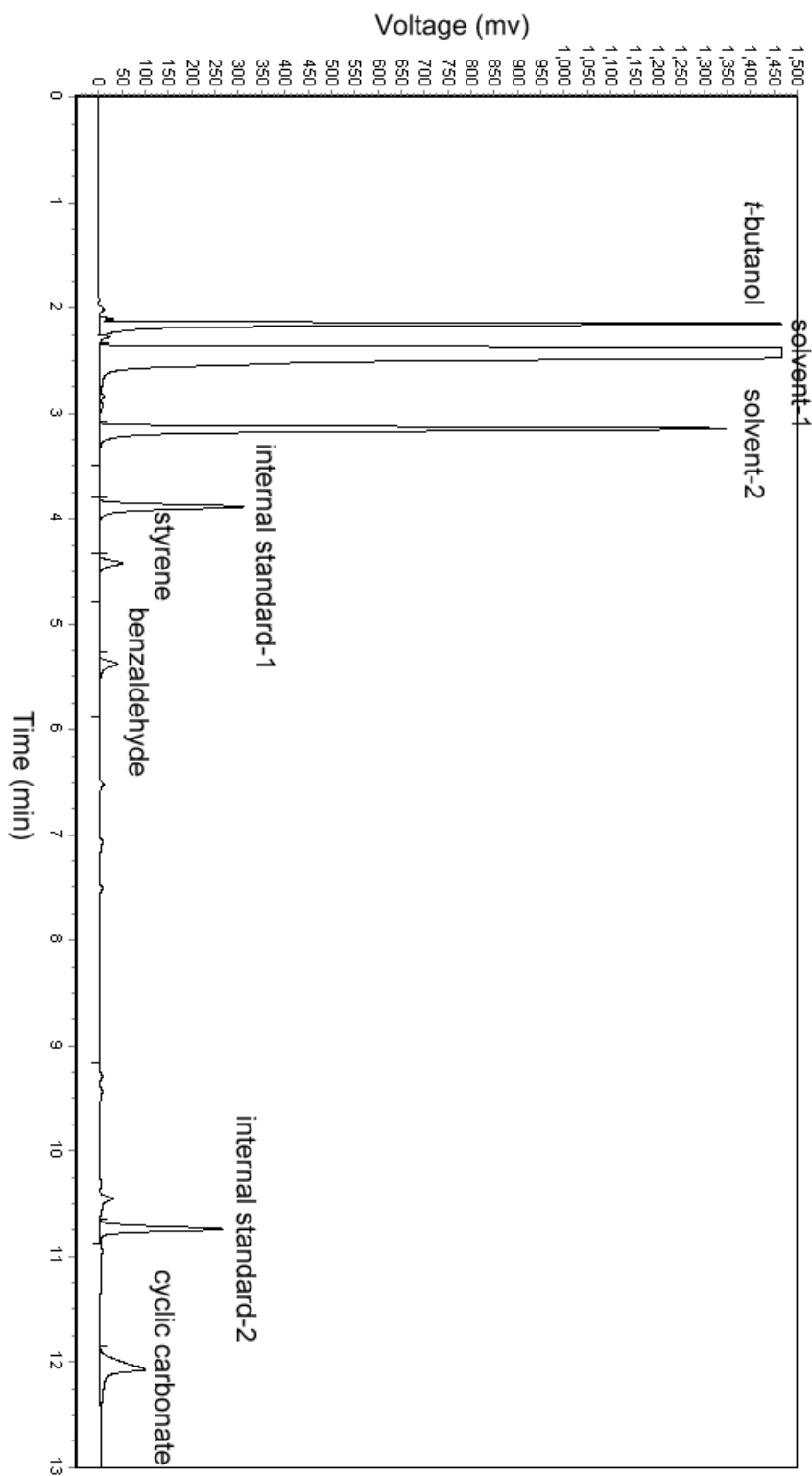
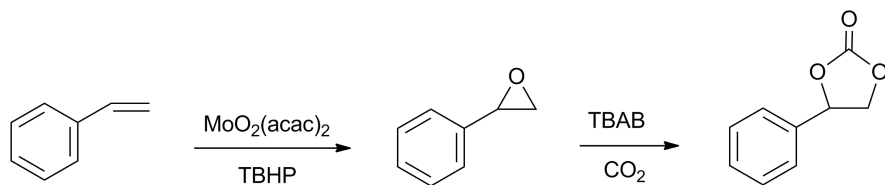












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