

## Introduction

Green chemistry is the design of chemical syntheses and processes with the aim of reducing the generated amount of dangerous and environmentally unfriendly substances.<sup>1</sup> Nowadays, the current environmental issues lead to an increase in importance of green chemistry. Alcohols are normally oxidized with chromium (VI) compounds, which are very toxic. The goal of this research project is replacing the latter with less toxic oxidators. The influence of reaction time on the yield of a green oxidation of 1-naphthalenemethanol is studied. Further, various green oxidations of benzhydrol will be explored. The general oxidation reactions are shown in figure 1.

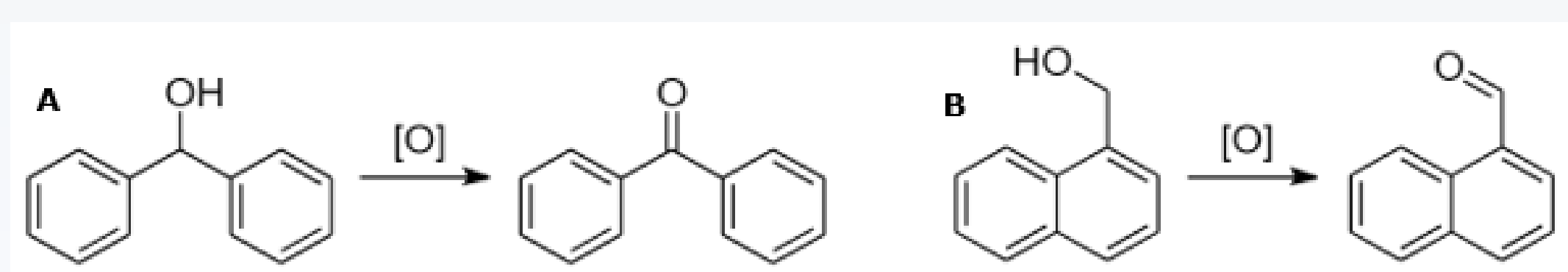


Figure 1: General reaction for (A) the oxidation of benzhydrol to benzophenone and (B) the oxidation of 1-naphthalenemethanol to 1-naphthalenemethanal.

## Materials and methods

- $\pm 1$  gram 1-naphthalenemethanol was oxidized by 5% NaOCl using TEMPO (2,2,6,6-tetramethylpiperidinyloxy) as a catalyst.<sup>2</sup> A series of experiments are performed with a variable reaction time, under normal atmospheric conditions at a temperature between 7°C-15°C.
- Benzhydrol was oxidized, respectively by 5% NaOCl and tetrabutylammoniumhydrogensulfate (TBAHSO<sub>4</sub>) as a phase transfer catalyst<sup>3</sup>, by 5% NaOCl and acetic acid<sup>4</sup> and by potassiumpermanganate (KMnO<sub>4</sub>) and TBAHSO<sub>4</sub> as phase transfer catalyst in dichloromethane<sup>5</sup>. A solvent free oxidation of benzhydrol was performed by using KMnO<sub>4</sub> and copper sulfate pentahydrate.<sup>6</sup>
- Column chromatography is performed to purify the end products. Silica and a mixture of heptane/ethyl acetate in a 4/1 ratio is used as stationary and mobile phase, respectively. The separation was checked by thin layer chromatography.
- Verification of the oxidation reactions was done by IR and <sup>1</sup>H-NMR. A PerkinElmer FT-IR-spectrometer and a Spinsolve Education 43 MHz NMR-spectrometer were used.

## Results and discussion

Figure 2 summarizes the results for the oxidation of 1-naphthalenemethanol. The curve shows an exponential increase in yield of 1-naphthalenemethanal as a function of reaction time.

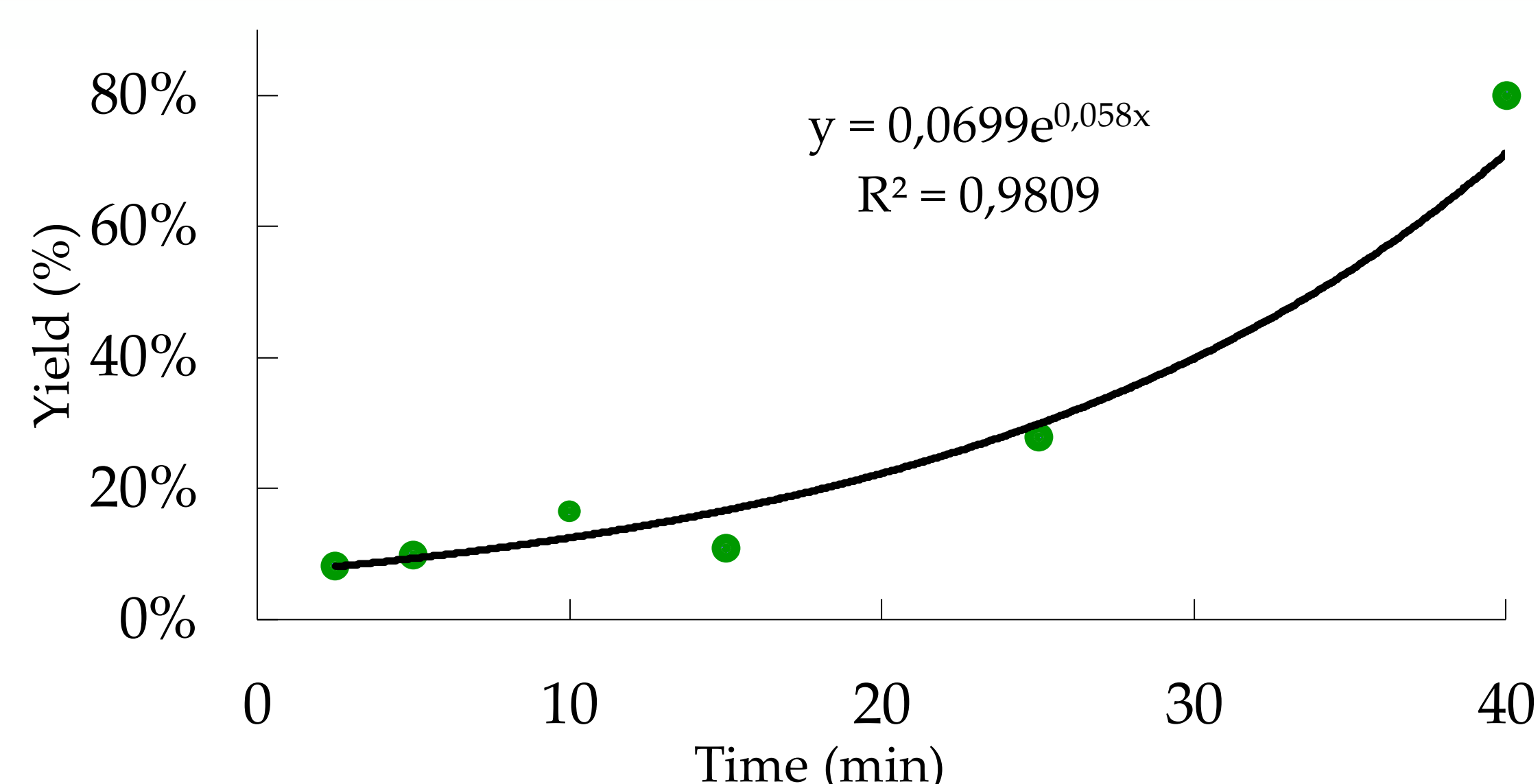


Figure 2: Yield of 1-naphthalenemethanal in function of reaction time.

## References

1. EPA. Basics of Green Chemistry. [Updated 2020 december 18. Available from <https://www.epa.gov/greenchemistry/basics-greenchemistry#twelve>].
2. Gabriel Tojo, Marcos Fernández. Oxidation of Alcohols to Aldehydes and Ketones. Springer Science Business Media, Inc. Santiago De Compostela, Spain. 2006
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5. Basheer K, Joseph J, Nair T. Kinetics of the Oxidation of Benzhydrols with Permanganate under Phase Transfer Catalysis in Organic Solvents. Modern Research in Catalysis. 2013;2(2):35-38.
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Figure 3 features the infrared spectrum of 1-naphthalenemethanal. It confirms the partial oxidation due to the use of TEMPO as a catalyst (no further oxidation to the acid). The vibration at 1683 cm<sup>-1</sup> indicates the carbonyl of the aldehyde. The peak of 2724 cm<sup>-1</sup> shows the Fermi-resonance of the overtone of the aldehyde CH stretch vibration. Note that the broad band, centered around 3300 cm<sup>-1</sup> and typically observed in the spectrum of the alcohol (and acid), has disappeared here.

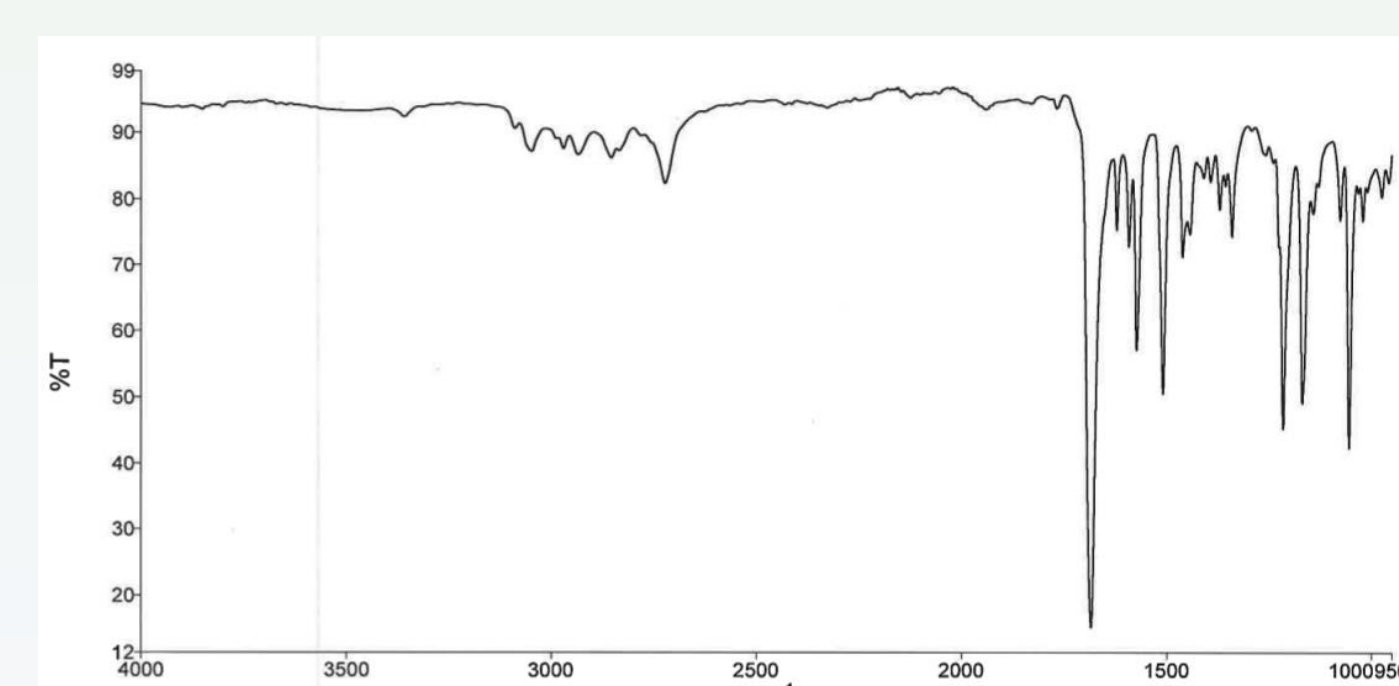


Figure 3: Infrared spectrum of 1-naphthalenemethanal.

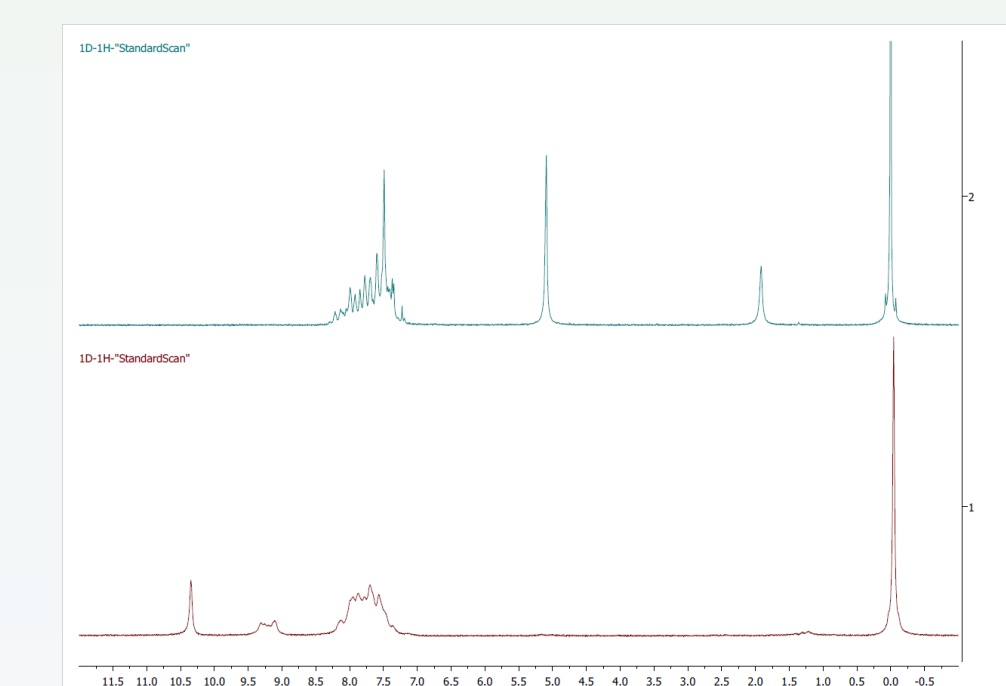


Figure 4: <sup>1</sup>H NMR spectrum of 1-naphthalenemethanal.

Further confirmation of the partial oxidation and purification is done by <sup>1</sup>H NMR spectroscopy. The Figure 4 shows the <sup>1</sup>H NMR-spectra of 1-naphthalenemethanal (below) and 1-naphthalenemethanol (on top). The hydroxyl group associated to the peak at 2,0 ppm disappears in the <sup>1</sup>H NMR spectra of the end product, same as the methylene group corresponding to the peak at 5,1 ppm. The peak appearing at 10,4 ppm in the <sup>1</sup>H NMR spectra of the end product originates from the proton of the aldehyde function.

Table 1: A summary of the various oxidations of benzhydrol.

Summary of the oxidations of benzhydrol				
Reaction	Reagents	Reaction time and temperature	End product (IR)	Yield
1	Benzhydrol, 5% NaOCl and TBAHSO <sub>4</sub>	30 minutes at room temperature	Benzophenone as well as benzhydrol in the end product	/-
2	Benzhydrol, 5% NaOCl and TBAHSO <sub>4</sub>	30 minutes at room temperature	Benzophenone	7,8%
3	Benzhydrol, 5% NaOCl and TBAHSO <sub>4</sub>	1 hour at room temperature	Benzophenone	3,8%
4	Benzhydrol, 5% NaOCl and acetic acid	25 minutes at room temperature	Benzophenone as well as heptane in the end product	17,5%
5	Benzhydrol, KMnO <sub>4</sub> and CuSO <sub>4</sub> · 5H <sub>2</sub> O	30 minutes at 100 °C	Benzophenone as well as benzhydrol in the end product	14,0%
6	Benzhydrol, KMnO <sub>4</sub> , TBAHSO <sub>4</sub> , H <sub>2</sub> O-demi and DClM	30 minutes at room temperature	/-	/-

<sup>\*</sup>Mass of the end product was indeterminate.  
<sup>\*\*</sup>End product did not contain benzophenone.

A summary of the results of the oxidations of benzhydrol is presented in table 1. Notice the rather low yields for the reactions, which were mainly caused by the poor separation of unreacted benzhydrol and benzophenone during column chromatography. Even though the sixth reaction had the interesting green prospect of not needing column chromatography to purify the end product, the reaction failed. Figure 5 shows, as an example, the IR-spectrum of the end product of the third reaction (see table 1). The sharp intense carbonyl peak of benzophenone is clearly visible around 1650 cm<sup>-1</sup>.

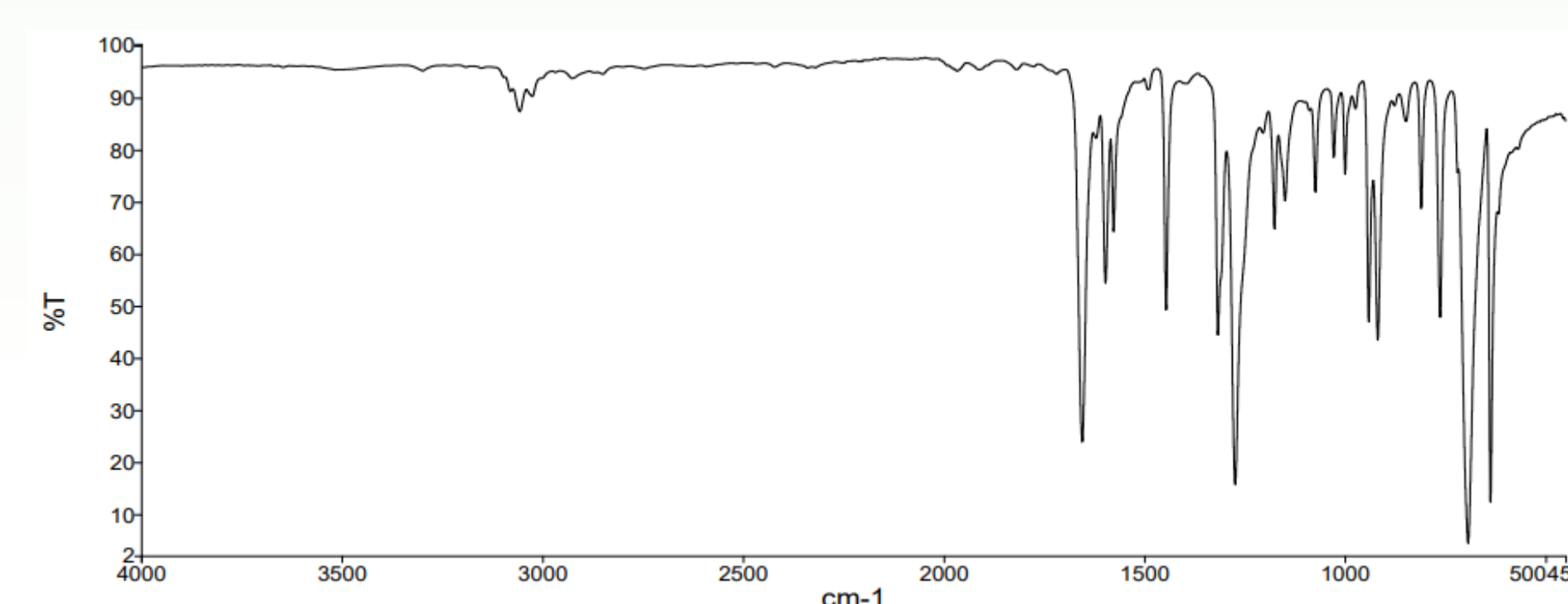


Figure 5: IR-spectrum of benzophenone, synthesized using the 3<sup>rd</sup> reaction (see table 1).

## Conclusion

The IR and <sup>1</sup>H NMR spectra confirm that the partial reduction of 1-naphthalenemethanol was successful. Under the used conditions, an exponential increase in yield in function of time was observed, up to 80% after 40 minutes.

Various oxidation methods of benzhydrol resulted in benzophenone. However, the yields of the reactions are low. This was mainly caused by the poor separation by column chromatography, which needs improvement in future work.