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Ein Gelehrter in einem Laboratorium

ist nicht nur ein Techniker,

er steht auch vor den Naturvorgängen

wie ein Kind vor einer Märchenwelt.

(Marie Curie, 1867-1934)

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Abstract

Peroxides as very reactive oxidative agents are interesting for academic research as well as for industrial applications. Especially peracids are already common substances in bleaching agents (for oxidation of chromophoric colourful substances), epoxidation reactions and consequently for plastic production and other oxidations.

This work contains a feasibility study for determining the possibility of already known catalytic systems in order to gain organic peracids from organic acids *via* oxidation. Thus, different epoxidation catalysts are evaluated as well as complexes with a high peroxo content. The complexes have to be stable against primary oxidizing agents, or need the ability to activate hydrogen peroxide, urea hydrogen peroxide or *tert.*-butyl hydroperoxide. The applied catalysts were methyltrioxorhenium, tungstates as salts or acids, an iron-NHC-complex already established as epoxidation catalyst, a complex by Venturello with high peroxidic content, and peroxymonophosphoric acid as alternative to Caro's acid. For analyzing the oxidation ability of the different complexes, a sequence of organic acids was screened.

Acetic acid with its small size and solubility in polar and apolar solvents showed the highest yields during experimental investigations. Caproic acid was used as model substrate with a longer linear alkyl chain and still spatially accessible. Phthalimido caproic acid was chosen as a model substrate of industrial interest, which comprises a sterically hindered acid containing functional groups. This acid was most challenging due to its solubility, steric demand and reactivity.

Furthermore, iron catalysts and their ligands were synthesized to subsequently investigate their ability to oxidize organic acids. Moreover they are improved complexes to the already known epoxidation catalysts based on iron-NHC-complexes. Based on their ability to epoxidize and with regard to the state of the art research, those complexes could be promising for *in situ* epoxidation and CO_2 activation to gain cyclic carbonates or polycarbonates.

Zusammenfassung

Peroxide sind als sehr reaktive Oxidationsmittel sowohl für die akademische Forschung als auch für industrielle Anwendungen interessant. Besonders Persäuren sind bereits etablierte Stoffe für Bleichmittel (durch die Oxidation chromophorer und damit farbiger Stoffe), Epoxidationsreaktionen und dementsprechend in der Plastikproduktion sowie anderer Oxidationsreaktionen.

Diese Arbeit beinhaltet eine Machbarkeitsstudie, um die Möglichkeit zu überprüfen, bereits bestehende katalytischer Systeme auf die Produktion von Persäuren aus organischen Säuren durch Oxidation anzuwenden. Hierfür wurden verschiedene Epoxidationskatalysatoren sowie Komplexe mit einem hohen Peroxidgehalt geprüft. Die Komplexe müssen gegenüber primären Oxidationsmitteln wie Wasserstoffperoxid, Harnstoffperoxid, oder *tert*-Butylhydroperoxid sowohl stabil sein als auch die Fähigkeit besitzen, sie zu aktivieren. Getestet wurden Methyltrioxorhenium, Wolframate in Form von Salzen und als Säure, ein bereits als Epoxidationskatalysator etablierter Eisen-NHC-Komplex, ein Komplex von Venturello mit einem hohen Peroxidgehalt sowie Peroxomonophosphorsäure als direkte Alternative zur Caro'schen Säure. Um die Oxidationsfähigkeit der verschiedenen Systeme zu testen wurden verschiedene organische Säuren eingesetzt.

Essigsäure zeigte mit seiner kurzen Alkylkette und der hohen Löslichkeit sowohl in polaren als auch apolaren Lösungen die höchsten Ausbeuten während der Experimente. Hexansäure wurde als Modell-Substrat mit längerer Alkylkette verwendet, welches weiterhin sterisch zugänglich ist. Phthalimidohexansäure wurde als Verbindung ausgewählt, welche industriell interessant ist und sowohl räumlich anspruchsvoll ist als auch funktionellen Gruppen beinhaltet. Die Oxidation der letzteren Säure war die größte Herausforderung, da sie wenig löslich, sterisch anspruchsvoll und wenig reaktiv ist.

Des Weiteren wurden Eisenkatalysatoren und deren Liganden synthetisiert, um später ebenfalls die Oxidationsfähigkeit an Säuren zu testen. Neben der Möglichkeit zu epoxidieren, sind sie vielversprechend für die *in situ* Epoxidation mit anschließender CO_2-Aktivierung, um zyklische Carbonate oder Polycarbonate zu generieren.

List of Abbreviations

BADGE ..... *Bisphenol A diglycidyl ether*
BO ..... *bindung order*
CYP ..... *Cytochrome P450*
DCM ..... *dichloromethane*
HMTD ..... *hexamethylene triperoxide diamine*
IDD ..... *isododecane*
^{i}PrOH ..... *isopropanol*
MTO ..... *methyltrioxorhenium*
nwp ..... *non-water-assisted pathway*
PAP ..... *Phthalimidopercaproic acid*
PBA ..... *perbenzoic acid*
PC ..... *phthalimidocaproic acid*
TBHP ..... *tert.-butyl hydroperoxide*
^{t}BuOH ..... *tert.-butanol*
^{t}BuOOH ..... *tert.-butyl hydroperoxide*
THF ..... *tetrahydrofurane*
UHP ..... *urea hydrogen peroxide*
wap ..... *water-assisted pathway*

Content

1 Introduction

1.1 History of Oxygen Discovery and Oxidation Chemistry

Combustion and first oxidations

Oxidation reactions are named after dioxygen, which was the first established oxidizing agent and therefore result in compounds containing oxides. Before scientists could find a coherence between oxygen and oxidations, there were a few other theories. The most important and popular theory was documented the first time by the alchemist Johann Joachim Becher in the 17th century. He examined combustion reactions and named flammable compounds "Phlogistos" (greek: φλογιστός; phlogistós = burned). Based on this research the alchemist Georg Ernst Stahl could postulate the phlogistone theory.[1] Stahl observed the release of gaseous compounds during a combustion, and remaining new substances. The basic idea of his theory was phlogiston being part of every substance, which was released during combustion. Materials containing significant amounts of phlogiston burn completely, while compounds with less phlogiston leave ash or chalk.[2]

This theory was very common and popular during the first half of 18th century, until Antoine Laurent de Lavoisier published his essay *Reflexion sur la phlogistique* in 1785. In his research he discovered the weight increase of a substance (e. g. phosphorous) and the absorption of air during a combustion in a closed vessel, as shown in Figure 1. In his publication he postulated "pure air", which is part of the atmospheric air. He disproved the idea of air as an element due to the separation of the air mixture, and he even succeeded to split water to oxygen ("pure air") and hydrogen ("flammable air"), thus proving that water was no element either and that the phlogiston theory was not right.[2]

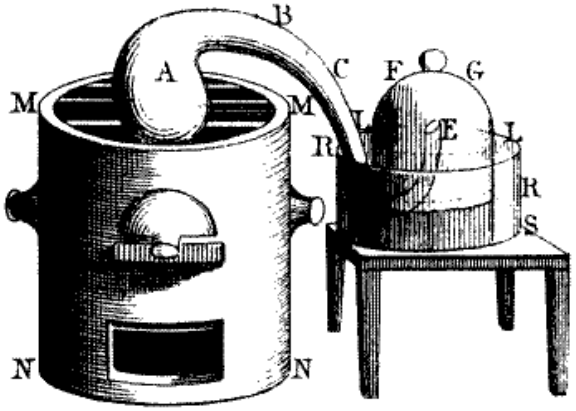
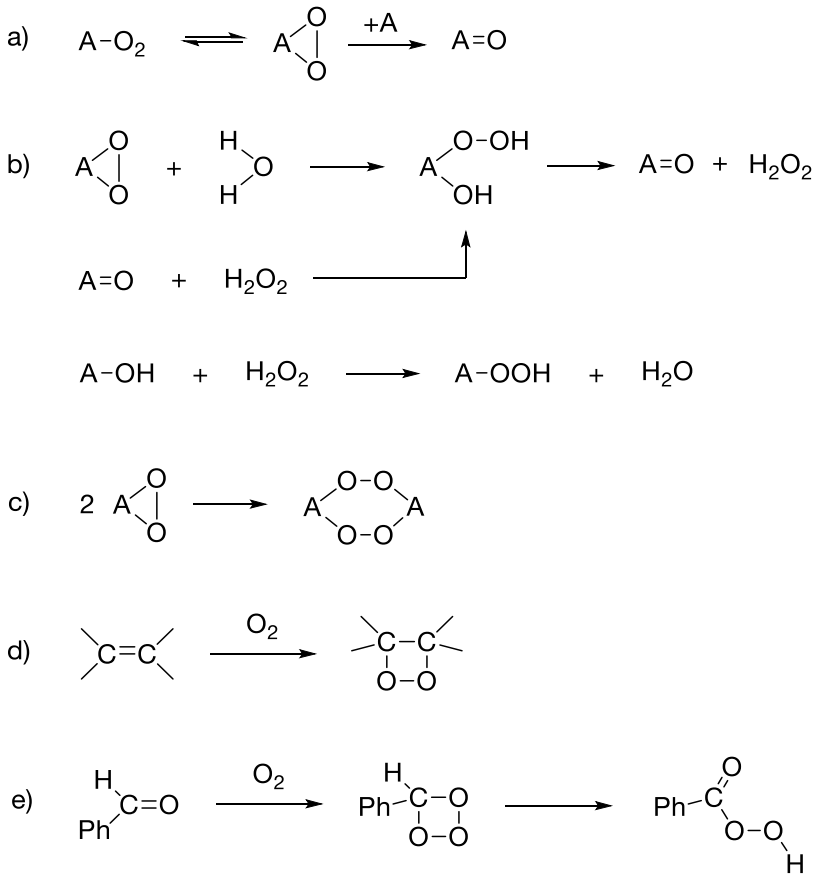


Figure 1: Lavoisier's experiment on the combustion of air.[3]

The ultimate discovery is accredited to Carl Wilhelm Scheele and Joseph Priestley independently. Priestley managed to separate water electrolytically to hydrogen and oxygen, though he could not attribute his experiment to electrochemistry. He and Scheele published their experiences with oxygen in 1774 and 1777, with their essays being the fundament for Lavoisier's work. Due to the false assumption oxygen being the basic component for acids, it was called "oxygenium" (acient greek: ὀξύς; oxys: sharp, sour, acidic. γεννάω; gen-: generate) meaning acid-generator.[4]

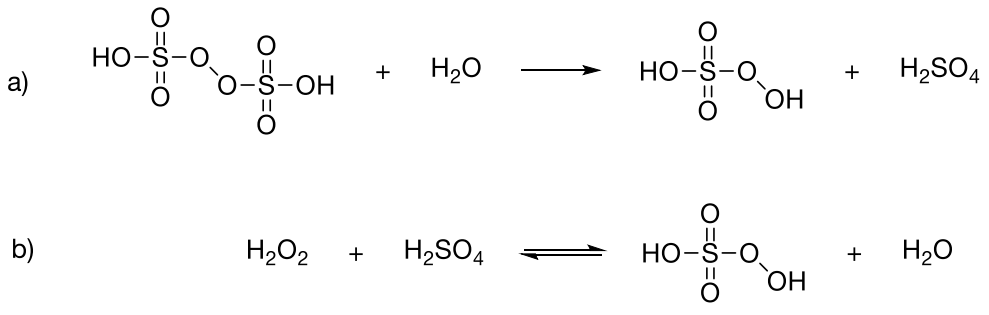
The main reactions of oxygen with organic or inorganic compounds in nature are either combustions or autoxidations (= slow reactions with oxygen without a flame or heat, for the reaction mechanism see Scheme 5). Christian Friedrich Schönbein investigated the first studies to autoxidation in 1840 and defined the active, negatively charged oxygen as ozone, while positively charged oxygen was antozone. The corresponding intermediates he coined as ozonide and antozonide.[5] 39 years later Felix Hoppe-Seyler proposed the mechanism of uncharged oxygen cleavage, where one oxygen react with the substrate while the other one act as the active oxidant, for example in the reaction from water to hydrogen peroxide or dioxygen to ozone.[6]

This theory was dismissed by Moritz Traube 14 years later, who discovered in 1882 that intact oxygen molecules are involved in slow oxidation reactions, and titled the reaction as autoxidation for the first time. His experiments focused mainly on the oxidation of metals. Traube discovered that with moist oxygen the reactions where most promising due to the formation of hydrogen peroxide, which was also responsible for the other observed oxidation effects.[5] Carl Engler not only confirmed Traube's theory but also expanded it. Nevertheless, he did not agree to the thesis that hydrogen peroxide was the primary product of autoxidations but "superoxides". He termed the first labile peroxidic addition product "moloxide" (Scheme 1a), which he published with J. Weissberg in 1904. Reactions with alkenes (Scheme 1d) did not lead to a formation of hydrogen peroxide nor ozone, so he postulated the labile four-membered ring peroxide, which was confirmed later. Schönbein also described previously the oxidation of benzaldehyde and Aleksei Bach also suggested independently the occurrence of the carbonyl by oxygen to gain first the moloxide and later peroxybenzoic acid. Adolf Baeyer and Viktor Villinger later confirmed and isolated both acetone superoxide (example for Scheme 1c) and peroxybenzoic acid (Scheme 1e), but postulated for the peroxybenzoic acid another mechanism.[6, 7]



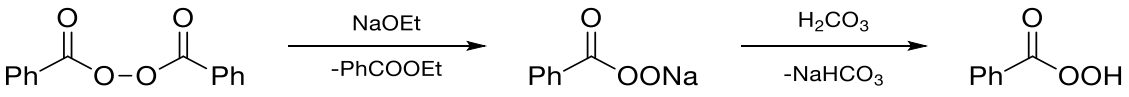
Scheme 1: Moloxide hypothesis (C. Engler, J. Weissberg, 1904). A = acceptor. a) initial addition of molecular oxygen with formation of moloxide and subsequent yield in oxides. b) partial hydrolysis of moloxide with formation of hydrogen peroxide. Secondary peroxides or hydroxides with H_2O_2. c) dimerization of moloxide lead to cyclic diperoxide. d) alkenes with oxygen lead to peroxide products with greater oxidative power. e) oxidation of aldehydes, e.g. bernzaldehyde, lead to a moloxyde which rearranged to peroxybenzoic acid.

In 1899 Baeyer focused his research on Caro's Acid (= peroxymonosulfuric acid), discovered for the first time in 1898 by Heinrich Caro, who detected a nitrobenzene odor during the oxidation of aniline with ammonium persulfate and concentrated sulfuric acid.[8]



Scheme 2: Synthesis of peroxysulfuric acid with a) peroxydisulfuric acid and water b) concentrated sulfuric acid with hydrogen peroxide.

Baeyer and Villiger reported the preparation for the first time using concentrated sulfuric acid, potassium persulfate (equivalents ≈ 3 : 1), and after 10 min adding again ca. 3 parts potassium persulfate. They obtained a white, stable salt with the composition $KHSO_5 \cdot 7\ KHSO_4 \cdot 2\ K_2SO_4$. For the Caro's reagent they proposed the sulphur peroxide species as an active oxidant. To discover the actual formula of monopersulphuric acid, Baeyer and Villiger worked out an analytical method where different titrations with hydrogen peroxide and persulfate with iodide solution were compared. They discovered a 1 : 1 ratio for H_2SO_4 to active O, and proposed H_2SO_5 as compound for Caro's acid. Studies to find more comparable oxidants were achieved, which led them to the first synthesized organic peracids. They gained free perbenzoic acid (PBA) by the reaction of dibenzoyl peroxide with sodium ethoxide, and then protonating the salt with H_2CO_3, a weak proton donor (Scheme 3). PBA showed identical reactivity towards the peroxide test with KI solution and towards the synthesis of nitrosobenzene from aniline.[8]



Scheme 3: Synthesis of the first organic peracid PBA from dibenzoyl peroxide with sodium ethoxide and protonation of the resulting salt.

Those reactions were results of trials and experiences, but the background on how the substances react and behave was still mysterious.

1.2 Peroxides

The first oxidation reactions using peroxides or with peroxo-species as transition states were already mentioned in 1.1. The history of peroxide chemistry started in 1799 when Alexander von Humboldt discovered barium peroxide. 19 years later, Louis Thenard made some experiments with barium peroxide and different acids and received hydrogen peroxide, which he called "oxidized water".[9, 10] With Joseph Gay-Lussac he synthesized sodium peroxide, and started the studies on characteristics of hydrogen peroxide and its salts.

Definition and Occurrence of oxygen ions

Oxygen in his natural appearance is a diatomic molecule O_2, containing two oxygen atoms, where each has 6 electrons surrounding them. In a simple scheme, it seems to have a double bond, but actually dioxygen is a diradical with a single bond. Furthermore is the dioxygen with

one electron with same spin in each π^*-orbital a triplet dioxygen, while there also exist singulett oxygen with either both electrons in one π^*-orbital or with different spins of the electrons in both π^*-orbitals.

Removing one electron from this molecule forms the colourless dioxygenyl-monocation O_2^+. It can be synthesized using platinum hexafluoride or during the reaction of O_2F_2 with Lewis-acidic fluorides. The monocation appears in oxidation state +I, each oxygen atom has an oxidation state of +0.5.

$$O_2 + PtF_6 \rightarrow O_2^+ PtF_6^-$$

Oxygen compounds with metals contain the more stable oxide O^{2-}, which fullfills with 8 electrons the octet rule of noble gases. It is instable in water but appears in melts of metal oxides as well as in salts of oxygenic acids. Furthermore, it is a base in oxide-active media (see H. Lux). The oxidation state of oxygen in the oxide anion is -II.

The yellow hyperoxide O_2^- (earlier: “superoxide”) has one electron more than the neutral O_2 molecule with the single bond but only single radical character left. The molecule appears with a simply negative charge, while each oxygen atom has an oxidation state of -0.5. Hyperoxide is found in alkaline and alkaline-earth metal salts as NaO_2, KO_2, $Mg(O_2)_2$ and $Ba(O_2)_2$. Solvating those salts in water or heating metal hyperoxides, they lead to the release of oxygen and peroxides.

$$2O_2^- + 2H_2O \rightarrow O_2 + H_2O_2 + 2OH^-$$

Peroxide O_2^{2-} has one electron more than the hyperoxide leading to two mono-anionic oxygen atoms in the molecule. It appears in salts as Li_2O_2 or the very popular hydrogen peroxide H_2O_2 and is very reactive.[11] The oxygen atoms are connected *via* a single bond and exist in oxidation state -I. Figure 2 shows an overview of dioxygen with different charges due to their electron content and therefore different binding order (BO).

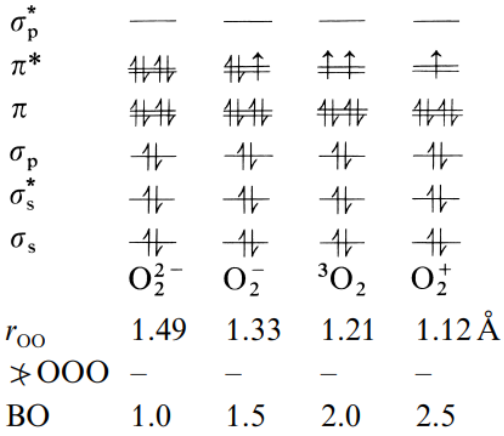
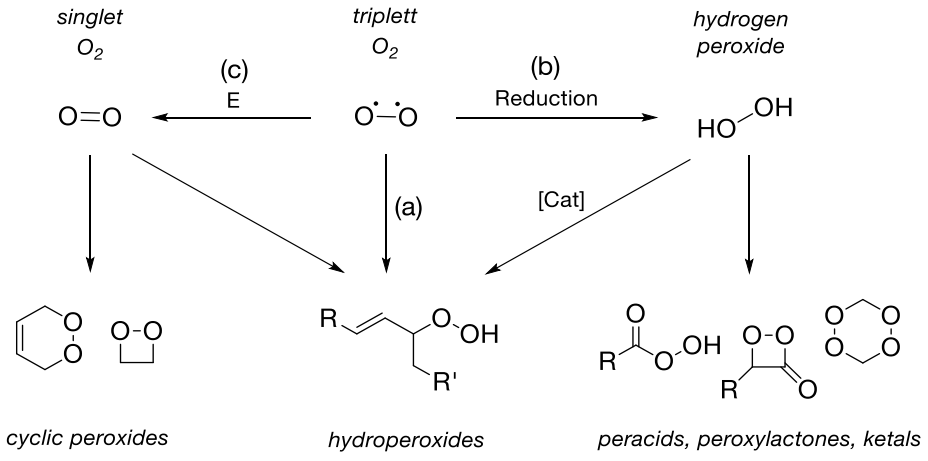


Figure 2: Energy niveau of molecular orbitals: peroxide O_2^{2-}, hyperoxide O_2^-, oxygen O_2, oxygen cation O_2^+.[11] The bond length r gets longer due to more electrons in the antibonding orbitals (π*). The binding order BO is also decreasing with higher electron number.

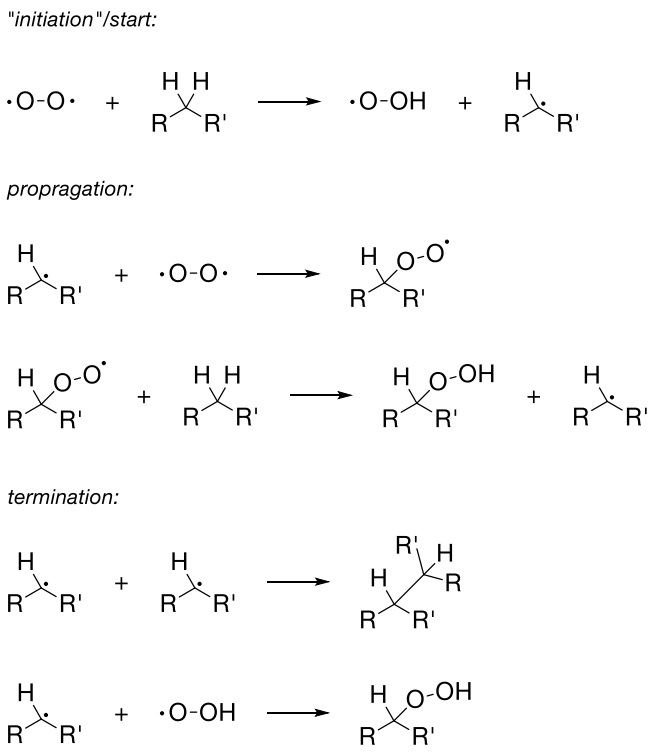
Synthesis and structure

Peroxides can by formed by different methods. As they contain oxygen, they can be derived from oxygen molecules. O_2 is as already mentioned a diradical which also can initiate radical reactions. Consequently, it can react with compounds, which tend to react with radicals and result in hydroperoxides, as seen in Scheme 4(a). The reduction to hydrogen peroxide provides a strong nucleophile, which can be used in many addition or substitution reactions (b). Energy can transform the triplet O_2 into the excited singlet dioxygen, which can react in cycloaddition reactions (c). All three starting compounds show differences in their chemical and physical behaviour as well as their reactivity. For this reason they are excellent molecules in order to gain a broad range of different products. In Scheme 4 are examples for organic peroxides.[12]



Scheme 4: Possible ways to generate peroxides from oxygen.[12]

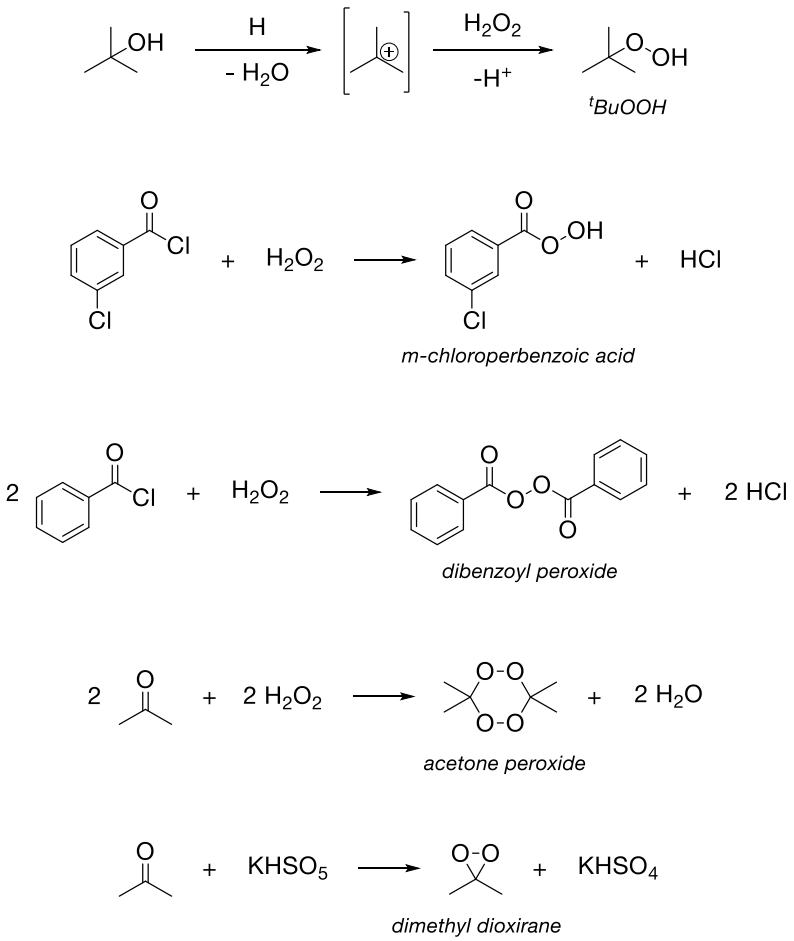
The mechanism for the oxidation reaction to hydroperoxides from dioxygen is assumed to be a radical chain mechanism (as already mentioned in Scheme 4a). In the first step a carbon radical is generated, which reacts further with a new oxygen diradical and continues the chain due to the formation of a new carbon radical. The chain can be terminated due to the reaction of two radicals (see Scheme 5).[12]



Scheme 5: Autoxidation: formation of hydroperoxides du to radical chain mechanism.

This reaction is favoured when there are double bonds next to the formed radical as it is stabilised by mesomerism.

The nucleophilic character of hydrogen peroxide and its anion can also form hydroperoxides, but with alkyl halides as educts. The reaction with derivatives of carboxylic acids lead to peroxidic acids and peroxidic anhydrides, while the reaction with ketones forms peroxidic hemiacetals and peroxidic acetals (see Scheme 6).



Scheme 6: Formation of peroxides using hydrogen peroxide and its derivatives.[12]

An alternative to hydrogen peroxide is peracetic acid, which is formed *in situ* because of isolation difficulties.[12] The salt $KHSO_5$ is a derivative of peroxymonosulfuric acid, which is an important compound in industry regarding oxidation chemistry and is also able to transfer an O-O group to gain peroxides. The discovery of its corresponding acid is already mentioned in “Combustion and first oxidations”. Beside organic peracids, it is also possible to use inorganic peroxy compounds as salts or complexes to transfer the peroxidic group.

Inorganic peroxidic compounds tend to form more superoxides than organic peroxidic compounds. In general the peroxides can be specified in four different groups, all synthesized by direct reaction with O_2, H_2O_2 or other peroxidic species.

- ionic peroxides
- covalent peroxides
- complex peroxides
- peroxo acids

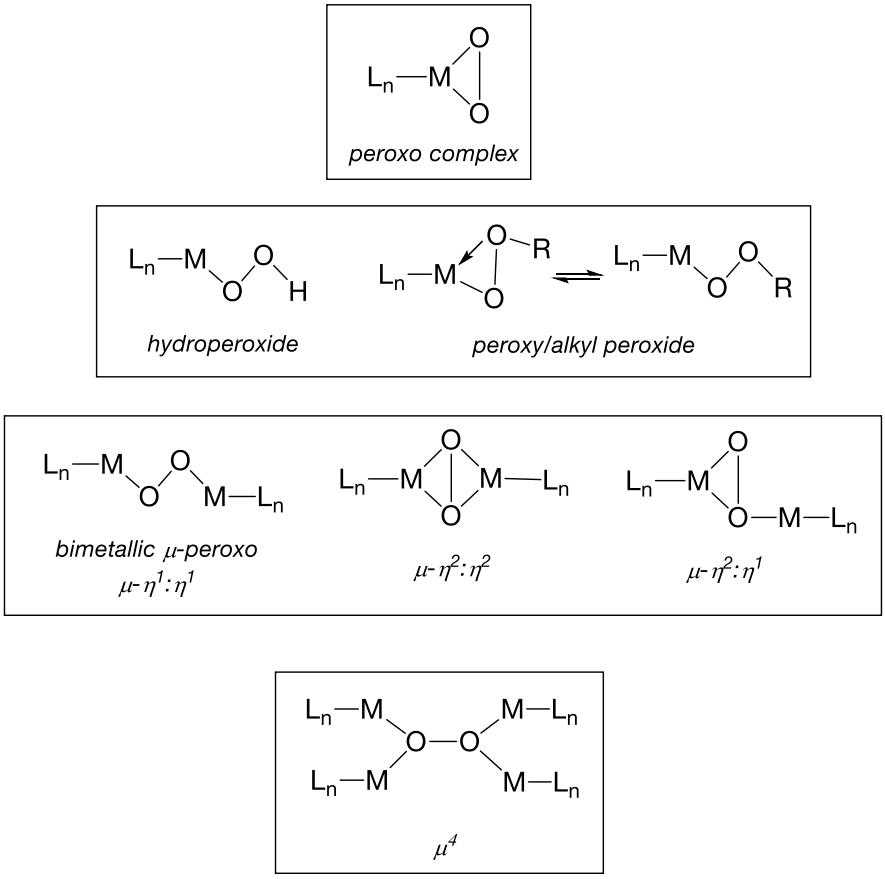
Alkaline (**1**) and alkaline earth elements (**2**) form ionic peroxides, while Elements from the copper (**11**) or zinc family (**12**) generate covalent peroxides with hydrogen. Complex peroxides are built by transition metals (**3-10**) without the copper and zinc family. The last group of peroxo acids are formed by the boron family (**13**), carbon family (**14**), nitrogen family (**15**) as well as the chalcogens (**16**). Those classifications have no clear borders as there are compounds with various properties. Zinc peroxides for example shows a transition between ionic and covalent peroxides. Nevertheless it is a good orientation, and some popular examples are listed in Table 1.[13]

Table 1: Inorganic peroxides classified by their central element. Second line (bold type numbers) = number of group in periodic system.

IONIC PEROXIDES			**COMPLEX PEROXIDES**					**COVALENT PEROXIDES**		**PEROXO ACIDS**				
1	**2**	**3**	**4**	**5**	**6**	**7**	**8-10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Li_2O_2	—									(HBO_3)	$H_2C_2O_6$	HNO_4	—	—
Na_2O_2	MgO_2									H_4AlO_6	—	H_3PO_5	$H_2S_2O_8$	—
K_2O_2	CaO_2	—	TiO_2 · $2H_2O$	K_3VO_8	K_3CrO_8	—	(FeO_2 · xH_2O, CoO_2 · xH_2O, NiO_2 · xH_2O)	CuO_2	ZnO_2	—	$H_2Ge_2O_7$	—	—	—
Rb_2O_2	SrO_2	Y_4O_9 · xH_2O	ZrO_2 · $2H_2O$	K_3NbO_8	Na_2MoO_6	—	—	—	CdO_2	—	$H_2Sn_2O_7$	—	—	—
Cs_2O_2	BaO_2	La_2O_5 · xH_2O	HfO_2 · $2H_2O$	K_3TaO_8	K_2WO_8	Re_2O_8	—	—	HgO_2	Tl_2O_4	Pb_2O_5 · xH_2O	—	—	—
		—	ThO_2 · $2H_2O$		UO_4 · $2H_2O$									

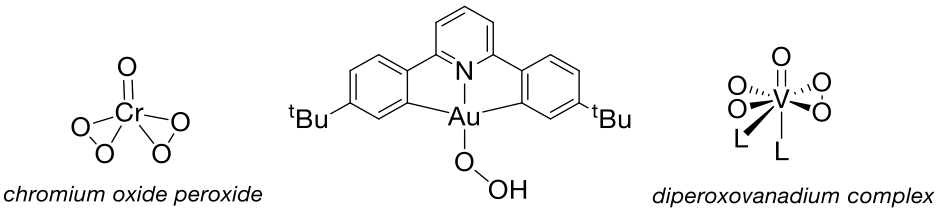
All alkaline metals can form superoxides, as well as Mg, Zn and Cd, but the alkaline earth metals only do this in small concentrations in peroxidic solutions.[9]

Although H_2O_2 is a strong nucleophile, hydrogen peroxide and alkyl peroxides need to be activated to be reactive enough. Besides Brønsted acids and bases, and Lewis acids transition metal catalysts are an interesting implement, especially metals from groups 4-7 as Ti, V, Cr, Mo, W and Re are very active.[14] Milas *et al.* discovered the same activity for oxidation with organic peracids. By the end of the 20th century Katsuki and Sharpless (who won a Nobel Prize in 2001) could gain an enantioselective oxidation of prochiral allylic alcohols with alkyl hydroperoxides catalysed by titanium tetra-alkoxides. The activation of a peroxidic precursor (H_2O_2 or alkyl peroxide) with a metal and therefore the ability to be an oxygen donor is determined by the interaction of the metal centre with the peroxide and its stability. Most intermediates are in fact isolable in solution or even as solid and therefore fully characterized. They mostly share a η^2 triangular arrangement of the peroxo moiety around the metal centre. Vaska defined all μ-peroxo complex structures and they are found with a broad range of different metals, as shown in Scheme 7.[14]



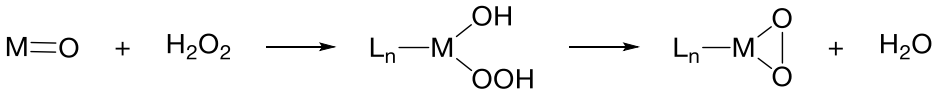
Scheme 7: Peroxidic intermediates. Above: peroxo complex. Down: μ-peroxo complexes.

Some examples show more than one peroxo group. Up to four peroxide anions have been observed surrounding one metal centre. Examples are illustrated in Scheme 8.[15-17]



Scheme 8: Examples for metal complexes containing peroxides.

Peroxidic complexes are easily available by solving the complex in a solution of H_2O_2 or due to the reaction with dioxygen. Stabilisation with a suitable ligand occur before or after the activation. A hydroperoxyl species as in Scheme 9 is already observed with different metals and ligands.[14] Especially by Mimoun *et al.* found a huge range of stable peroxo complexes, which could be isolated and characterized even in solid state.[18-20]



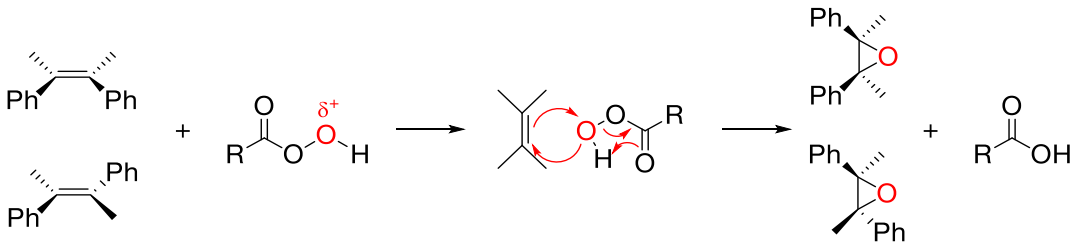
Scheme 9: Activation of hydrogen peroxide with metal complex and suitable, stabilising ligand. Hydroperoxyl intermediate is in some cases stable and detectable. M = Ti(IV), Zr(IV), V(V), Nb(V), Ta(V), Cr(VI), Mo(VI), W(VI), U(VI),… L = aromatic amines, picolinic acids, picolinate N-oxido anions, dicarboxylic acids, O and N containing polydentate ligands,…

Those metastable complexes are good to handle as most of them have not such a high self-combustion as hydrogen peroxide, and are reactive enough to oxidise both electrophilic and nucleophilic compounds with or without heteroatoms, perform radical oxidations and transfer peroxo groups.[14]

Reactivity

Peroxides have become popular for the organic synthesis of epoxides from olefins. While peracids and their salts (like $KHSO_5$ as already mentioned) are strong enough for the oxygen transfer, such peroxides as hydrogen peroxide or *tert.*-butyl hydroperoxide (^{t}BuOOH) need to be activated by a non-metal catalyst as hexafluoroacetone or a suitable metal complex.[21] This chapter only concentrates on epoxidation reactions, as the oxygen transfer is relevant for the assignment to this thesis.

The oxidation of olefins with peracids appears to be a concerted mechanism as the addition proceeds stereospecific in a *syn*-addition (see Scheme 10).



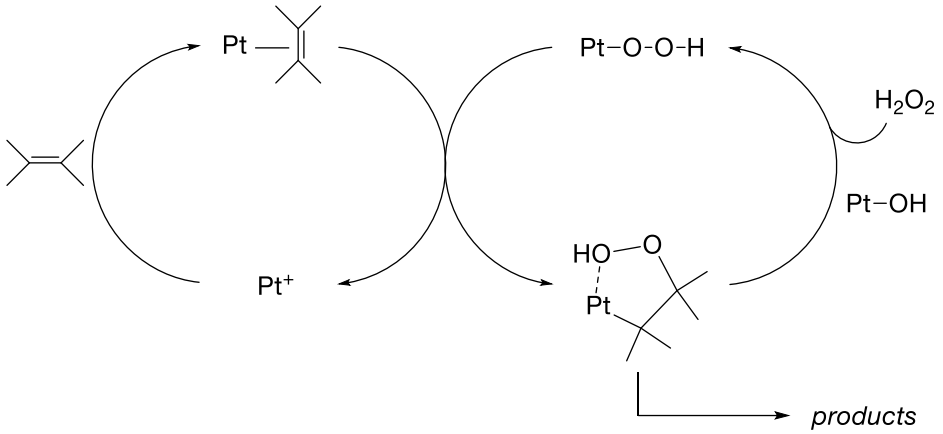
Scheme 10: Epoxidation of an olefin with a peracid. Stereospecific structure remains the same as it proceeds in a *syn*-addition.

The partially positive charged oxygen is attacked by the electron-rich double bond of the alkene, while the carbonyl oxygen attacks the proton and the former bonding electrons link to the alkene, resulting in the epoxide and an acid. Both substituents at the alkene and at the peracid can influence the speed of reaction. While electron-donating groups at the alkene increase the electrophilic attack of the peroxidic oxygen, the peracid needs electron-withdrawing substituents for the same effect.[22]

Another use of peracids is for example the *Baeyer-Villiger*-oxidation, where an ester or lactone is formed from a ketone. Common peracids are peracetic acid or *meta*-chloroperbenzoic acid. In the first step of the mechanism the peracid is deprotonated by the ketone, resulting in a electrophilic carbonyl and an electron-rich peroxide anion. The oxygen attacks the carbonyl C, and in a concerned mechanism migrates one of the ketone substituents to the attacking oxygen, providing to split the O-O bond and separating the acid.[23] Furthermore peracids and peroxides are used for disinfection in medical applications or food chemistry, or to produce initial detonators as acetone peroxide (APEX) or hexamethylene triperoxide diamine (HMTD), but those applications are not further interesting for this thesis.[12]

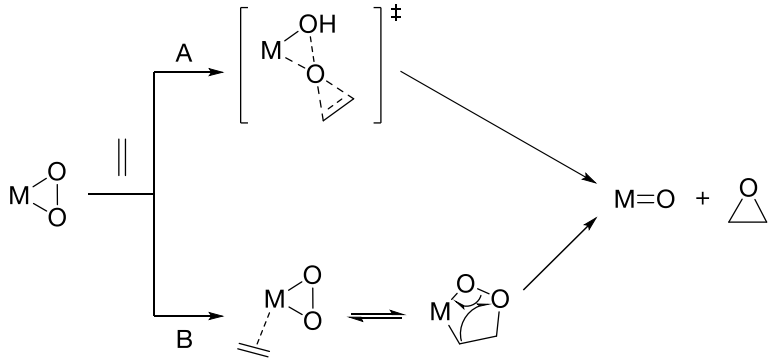
The oxidation mechanisms with metal catalysts are more complex. Depending on the nucleophilic or electrophilic character of the substrate the intermediate between substrate (olefin), catalyst and oxidizing agent varies, but all resulting in compounds with a new oxygen bonding.

The mechanism for electron-poor olefins with metal peroxo complexes is explored by Strukul, who examined the kinetic studies concerning Pt hydroxo derivatives.[24] Platinum activates as already mentioned above the hydrogen peroxide, and activates the substrate towards the nucleophilic attack. This results in a peroxymetallacycle intermediate, which splits into the oxidized product and the Pt-complex with an OH-group, which can be reactivated by a new hydrogen peroxide molecule (see Scheme 11).[14]



Scheme 11: Activation of hydrogen peroxide and an electron-poor olefin with a Pt complex. $Pt^+ = [(dppe)Pt(CF_3)(CH_2Cl_2)]^+$.

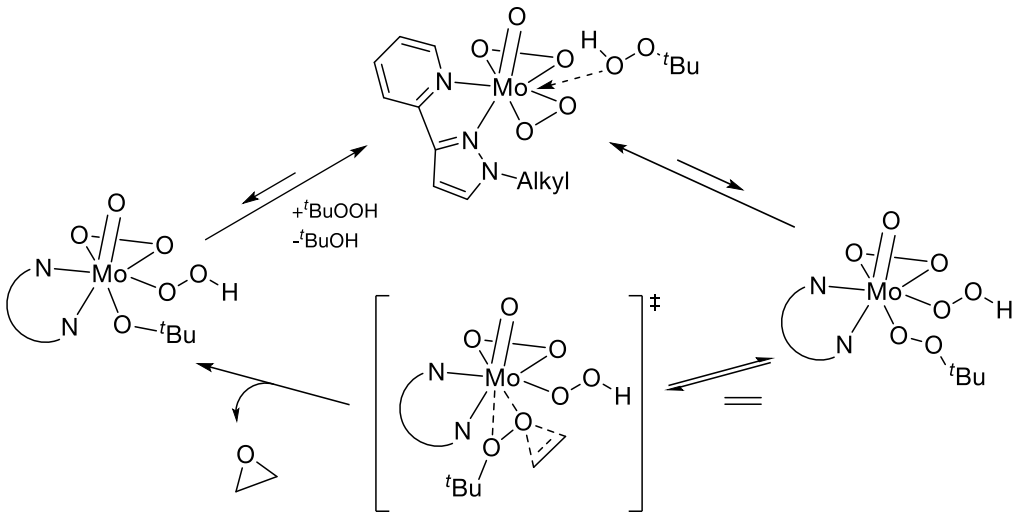
The oxidation of nucleophilic substrates like amines, phosphines, thioethers, etc. takes place with active d^0 metal peroxo complexes as Mo-, W-, Rh-based derivatives and V- and Ti-based complexes. Sharpless and coworkers developed an enantioselective mechanism in agreement with kinetic and spectroscopic data, which is shown in Scheme 12 (path A). A similar mechanism to the electrophilic addition with formation of the peroxymetallacycle was proposed by Mimoun *et al.*, but this coordination requires a preliminary coordination of the substrate to the metal so that the nucleophilic character is reduced (see Scheme 12, path B). Those intermediates were found with Pt and Pd complexes, but there was no isolated species or evidence for d^0 complexes. The mechanism by Sharpless (path A) indicates an η^2-bound alkylperoxo moiety and a coordination of the oxidizing agent through the hydroxylic function to the metal centre.[14]



Scheme 12: Nucleophilic oxidation of olefins to epoxides. Path A by Sharpless with more evidence for d^0 complexes. Path B by Mimoun *via* a peroxymetallacycle intermediate.

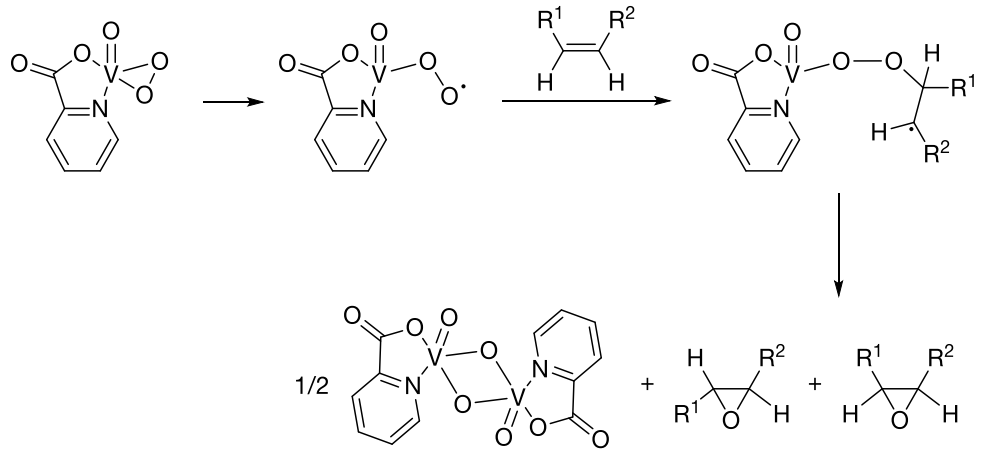
An interesting example is the coordinated complex based on a molybdenum (VI) developed by Thiel *et al.*, shown in Scheme 13. The complex already containing two peroxidic groups (η^2) activates TBHP due to opening one peroxo bond. The olefin can coordinate to the

activated oxygen while the metal centre stabilizes *tert*.-butanol rest. After epoxidation formation *tert*.-butanol can be substituted by a new TBHP molecule. This complex does not react with olefins as long as there is no primary oxidizing agent as TBHP. This shows, that even peroxidic groups in complexes are inevitable as oxygen donors.[14, 21]



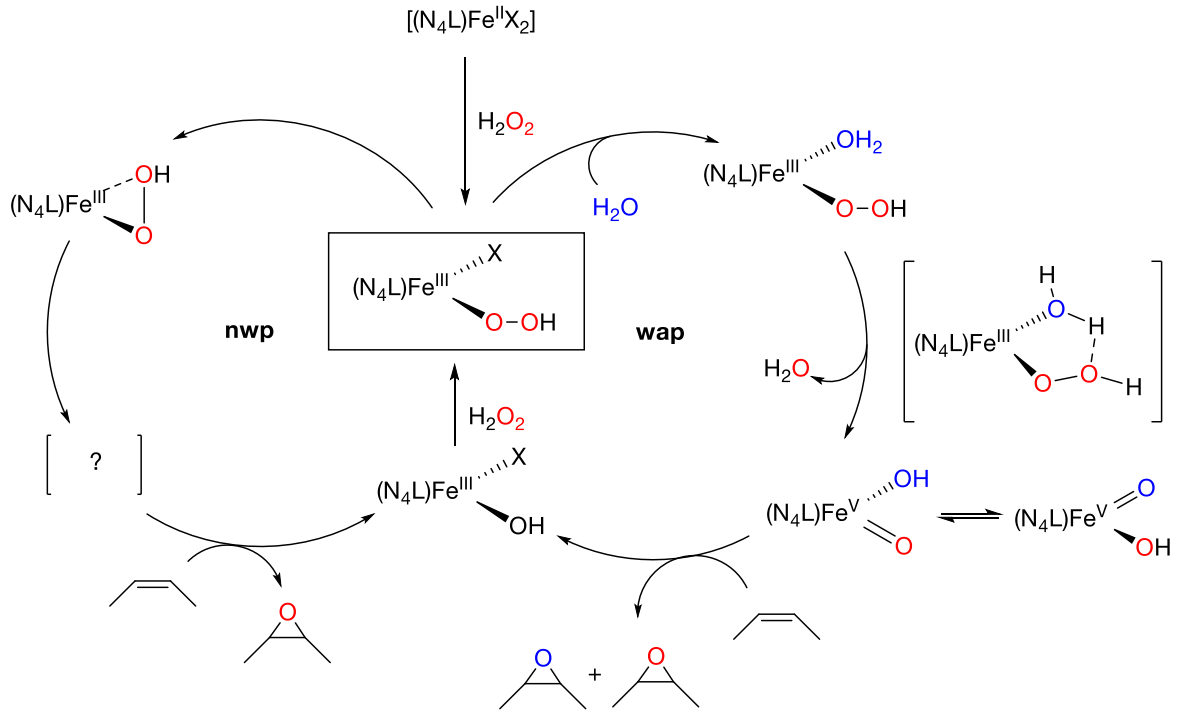
Scheme 13: Nucleophilic epoxidation of an olefin *via* Mo(VI) complex and ^{t}BuOOH. Alkyl = -octadecyl, -prop-2-en-1-yl, -but-3-en-1-yl, -cyclooct-1-en-1-ylmethyl.

A third option for oxidation *via* metal peroxo complexes is the radical oxidation, which has been observed in alkenes, aromatics, alcohols and thioethers.[14] Mimoun and coworkers developed a Vanadium complex $VO(O_2)pic(H_2O)_2$, while Vanadium peroxo derivatives are very characteristic for radical oxidation. The mechanism of the non-selective epoxidation is shown in Scheme 14, but there is to mention that this mechanism is very simplified. In fact, the radical oxidation follows various steps of radical initiation and chain reactions, with $[pic\text{-}VO_3]^{2-}$ or $[pic\text{-}VO]^{2+}$ as intermediates. Furthermore those oxidations are always subsequently decomposing the peroxo compound forming dioxygen.[14]



Scheme 14: Non-selective radical oxidation of an olefin *via* $VO(O_2)pic(H_2O)_2$. Pic = picolinic acid, H_2O ligands were excluded to simplify the scheme.

Though those mechanisms seem clear and well structured, not all catalytic compounds are already categorized and their mechanisms resolved. For example non-heme iron(III)-hydroperoxo complexes with polydentate NHC-ligand systems allow a broad range in epoxidation catalysis. The reaction mechanism is dependent on the labile sites of the ligands. While the mechanism for only one labile site (pentadentate ligands) seems to be radical as the iron(III) hydroperoxo bond is split homolytically. Visser *et al.* also showed, that the iron(III) hydroperoxo intermediate has three orders of magnitude higher than respective iron(IV)-oxo complexes.[25] Complexes with tetradentate ligand systems are divided into trans-labile coordination und cis-labile coordination. While trans-labile coordination systems lead to the formation of Fe^{IV}=O they are comparable with the CYP family (= Cytochrome P450). Those complexes are only able to epoxidize olefins.[25] In contrast *cis*-labile complexes allow the activation of hydrogen peroxide, either water- or non-water-assisted as seen in Scheme 15.



Scheme 15: non-water-assisted (nwp) and water-assisted (wap) pathways of alkene epoxidation from iron(III)-hydroperoxo complex. N_4L = tetradentate ligand.

The Fe^{III}-OOH intermediate is formed in both mechanisms. In the wap mechanism the addition of water leads to a heterolytic cleavage of O-O to a high-valent *cis*-Fe^{V}=O *via* a 5-membered cyclic transition state, which is then able to epoxidate alkenes with an electrophilic attack. Without water-assistance the heterolysis of the O-O is energetically disfavoured. Based on crystallographic studies on Rieske-dependent oxygenase, the Fe^{III}-η^2-OOH seem to be favoured, but the mechanism is still not proven.[25]

Safety issue

Beside its toxicity and health aspects, hydrogen peroxide is a metastable compound in an appropriate concentration, though it can undergo a violent self-decombustion.[26] Under influence of heat or light in combination with catalysts as metals or powder it decomposes to water and dioxygen with a high energy development (ΔH = -98.3 $\frac{kJ}{mol}$). Pure H_2O_2 already decomposes above 80 °C, in concentrations as low as 86% it is detonable. The detonation velocity of 90.7% peroxide in an aqueous solution is 5500-6000 $\frac{m}{s}$.[27] For a safety environment the solutions should be thinned enough and the applied volumes should be low.[28] Campbell and Rutledge made some studies using different vapour concentrations of H_2O_2 and different

pressure [mm Hg] in 9 mm, 15 mm, 25 mm and 35 mm (= diameter) tubes. It shows an inverse square root dependency of the run-up distance to the pressure, and a packing increases the detonation by minimum times two.[29]

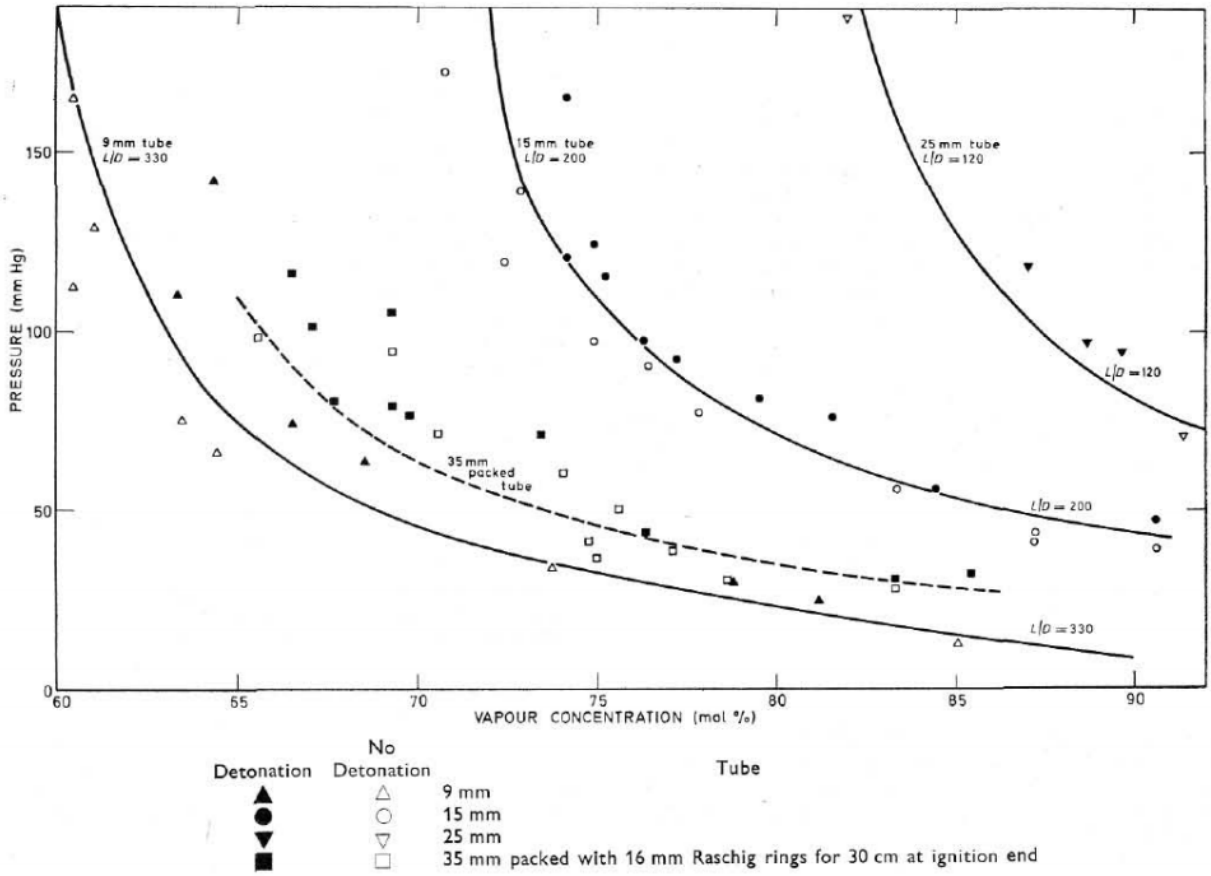


Figure 3: Graph of limiting conditions of concentration and pressure of hydrogen peroxide which will support the transformation to detonation in tubes (5 • 2 m long) and of different diameter.[29]

To stabilise hydrogen peroxide it is possible to dilute it with water or to add stabilizer as sulfuric or phosphoric acid, so potential catalysts for hydrogen peroxide decomposition react with the stabilizer instead.[16] Besides self-decomposition, there are some compounds which react explosively with hydrogen peroxide in concentrations above 70% including ammonia, alkalines, reducing agents and a broad range of organic compounds and metals.[30] Especially Cr(II) or Cu(II) complexes have a high effect on H_2O_2 decomposition (active oxygen loss in 24 h at 100 °C [%]: Cr(II) = 0.1 ppm, Cu(II) = 0.01 ppm).[26]

To have more clearer information about safety handling with hydrogen peroxide, William French developed a detonation triangle containing hydrogen peroxide, water and acetic acid relating to *in situ* formation of peracetic acid for epoxidation catalysis with unsaturated compounds as soybean oil (see Figure 4).[31] The grey area shows the detonable region, so the concentration mixture where the possibility of detonation is very high. It is in evidence that

the area is dependent of the hydrogen peroxide to water ratio, with high hydrogen peroxide and low water concentration being very dangerous.

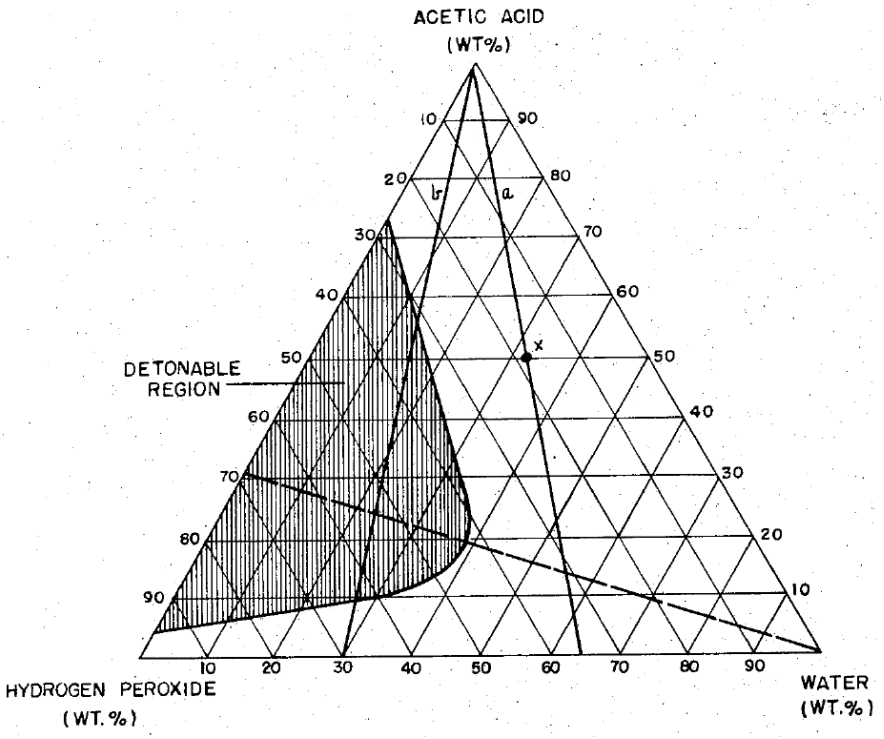


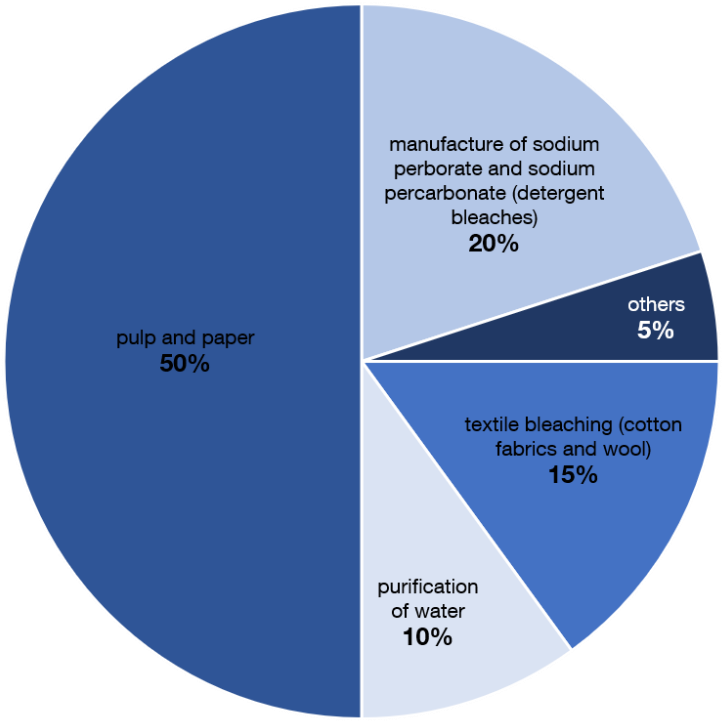
Figure 4: Detonation triangle by W. French, showing the weight% parts of acetic acid, water and hydrogen peroxide to gain a safe environment. The grey area shows the detonable composition.[31]

Different compounds are available to remove residual peroxide, which should be present during the handling. Such compounds are reduced for example Pd on aluminosilicate, $FeSO_4$, active charcoal, MnO_2 or catalase.[26]

Peroxidic compounds, not only hydrogen peroxide but also peracids and other organic compounds containing peroxo groups, are in general very reactive. Therefore transition metal complexes containing peroxide count to the most active oxidants including organic and inorganic compounds.[21]

Application in industry

The biggest industrial use of peroxides is hydrogen peroxide with 4.3 Mio tonnes per year in the world. This compound is used in many sectors as seen in Scheme 16, but primary for bleaching.[32]



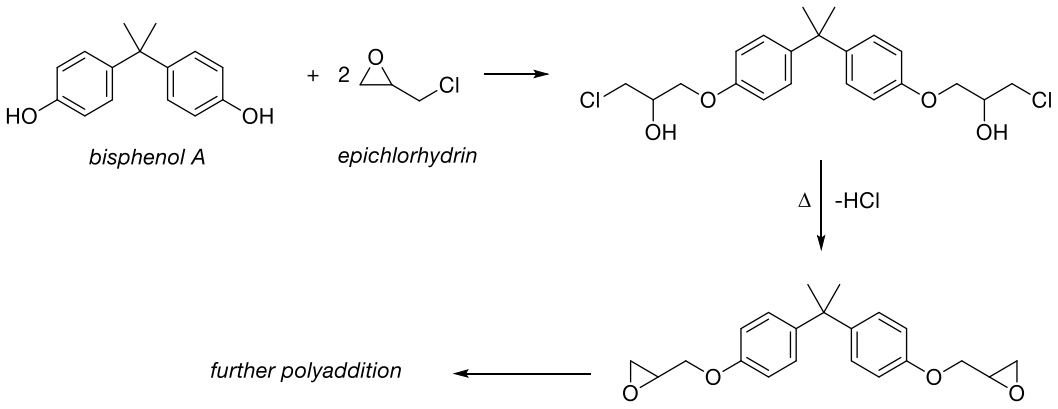
Scheme 16: Uses of hydrogen peroxide in industry.

Especially the oxidative bleaching of pulp and paper requires high amounts of hydrogen peroxide in combination with sodium dithionite ($Na_2S_2O_4$). Furthermore hydrogen peroxide and Caro's acid are used in applications involving metals, which can be separated and extracted from ores or waste, or by simple surface purification.[33]

Other peroxides can also be used for bleaching or textile washing, for example the already mentioned phthalimidoperoxy caproic acid (PAP). Another important and famous peroxide for disinfection is peracetic acid,[34] which is also applied in ε-caprolactam synthesis and therefore relevant for plastics production.[35]

Peroxides are – as already mentioned – a very common substance for epoxide synthesis. Epoxides are widely used compounds in industry for surfactants, paints, resins, diluents and more, therefore their synthesis is one important subject in research. The highest margins are produced with propylene oxide and ethylene oxide, secondly used, inter alia, for PET.[5] A big application of epoxides are epoxy resins or polyepoxides having different characteristics depending on their structure and link to other molecules. They adhere on nearly every surface,

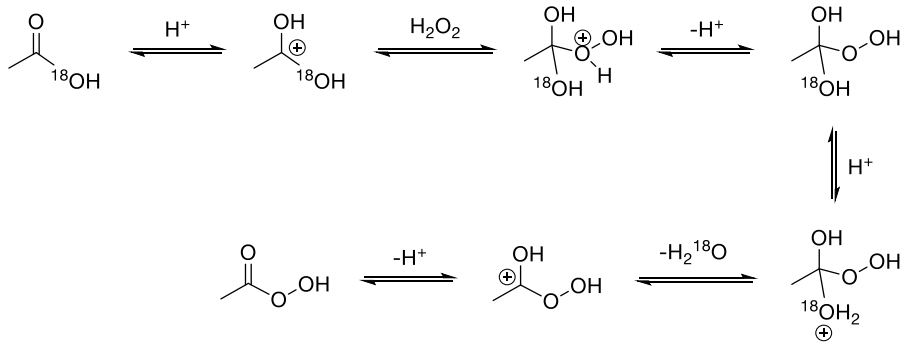
resulting in an excellent coating, adhesive or paint additive, simultaneously being very stable. A famous basic compound is bisphenol A, which can form for example the important epoxy resin BADGE with epichlorhydrin (see Scheme 17).[36]



Scheme 17: Synthesis of epoxy resin with bisphenol A and epichlorhydrin.

1.3 Potential catalysts for peracid synthesis

As Caro's acid is the only known system to generate organic peracids from the oxidation of organic acids, it is important to find an complex or compound, which is chemically active enough to ensure a selective oxidation of the peracid's carboxylic carbon. Llewelyn *et al.* performed isotopic labelling with ^{18}O in the oxidation of acetic acid. They discovered, that during the reaction to peracetic acid with hydrogen peroxide und sulfuric acid as catalyst (already stated as in situ peroxymonosulfuric acid), the ^{18}O of the OH-group gets abstracted as water and the peroxo group originates from hydrogen peroxide (or corresponding to the O-O of Caro's acid) as shown in Scheme 18.[37]



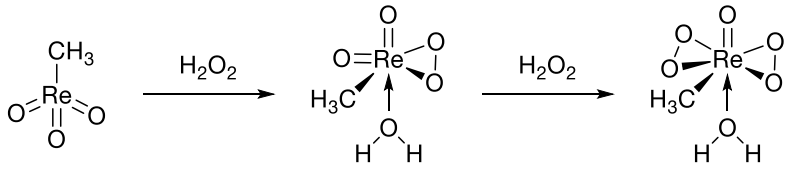
Scheme 18: Proposed mechanism of the oxidation of acetic acid to peracid *via* hydrogen peroxide.

Besides the ability to abstract and transfer oxygen atoms or peroxidic groups selectively to other compounds the potential catalyst needs to be stable against hydrogen peroxide, *tert*.-butyl hydroperoxide or other oxidizing agents, beside its potential activation role. According to this, it needs to be water-stable (as H_2O is a side product from hydrogen peroxide) and air-stable, as some peroxides gain dioxygen during combustion (see radical oxidation in chapter "Reactivity").

As a result, it is obvious to make attempts with epoxidation catalysts, as they are stable against primary oxidizing agents, water and oxygen, and furthermore even activate them. Epoxidation catalysts not only have those properties but also transfer oxygen atoms and peroxo groups. Furthermore, hydrogen peroxide can be activated directly by light, acids or bases or due to its ability to form peracids as Caro's acid, RC(NH)OOH or other organic acids R(CO)OOH.[38]

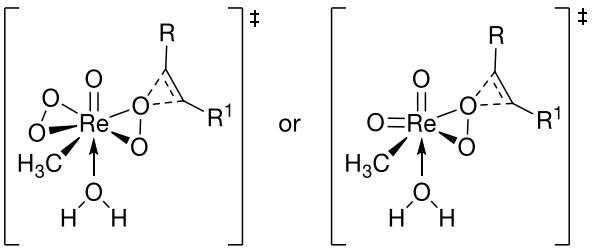
Methyltrioxorhenium

Methyltrioxorhenium (MTO) was found by I. R. Beattie and P. J. Jones and later applied and developed by W. A. Herrmann *et al.* as they developed a rhenium heptoxide/aluminium(III)oxide for olefin metathesis. Subsequently they generated MTO, which was studied intensively by the group.[39] MTO shows the ability to activate hydrogen peroxide, creating a methyl-oxo-bis(η^2-peroxo)rhenium(VII) hydrate, which could be used for the epoxidation of olefins. After activation, it shows a symmetric structure with two η^2-coordinations of the O-O (Scheme 19).



Scheme 19: Activation of hydrogen peroxide with MTO, resulting in symmetric peroxidic catalyst.

The mechanism is not proven, but due to its reactivity an out-of-sphere intermediate is expected by Sharpless (Scheme 20).[20, 39-41]

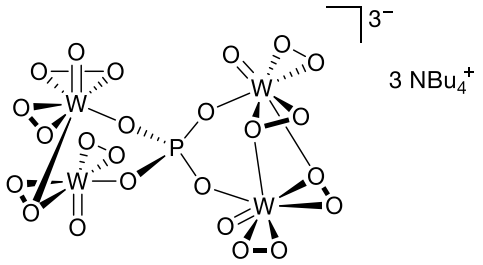


Scheme 20: outer sphere intermediate during olefin epoxidation.

The transfer of oxygen to acids to form peracids is likely, as Fischer detected a not yet identified compound during his studies with MTO and acids, which could involve peracids.[39]

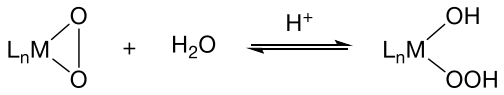
Venturello

The complex by Venturello **W1** (see Scheme 21) shows many η^2-O-O coordinations, which is applied in the epoxidation of sterically demanding substances as soybean oil.[42, 43] Furthermore Jiang *et al.* immobilized the catalyst on modified halloysite nanotubes, as potentially promising basis for heterogeneous catalysis.[44]



Scheme 21: Complex by Venturello **W1**.

In combination with hydrogen peroxide and a phase transfer catalyst as lipophilic tetra-alkylammonium salt the catalyst showed epoxidation ability of terminal, internal, open-chain and cyclic double bond in yields up to 88% for 1-octene and 94% for other alkenes in short reaction times.[14] In water it reversibly forms a hydroxo hydroperoxo species, as shown in Scheme 22.[38]



Scheme 22: Addition of water across a peroxo metal complex.

Furthermore, not only **W1** is an interesting epoxidation catalyst but also tungsten peroxo salts and acids. Reedijk *et al.* used Na_2WO_4 and H_2WO_4 with hydrogen peroxide and different organic acids to epoxidize cyclooctene up to a conversion of 92% with a selectivity of 99%.[45] Figure 5 shows the epoxidation of cyclooctene with different catalytic systems. System **1** had a too low conversion, systems without additional temperature information were applied at 60 °C.

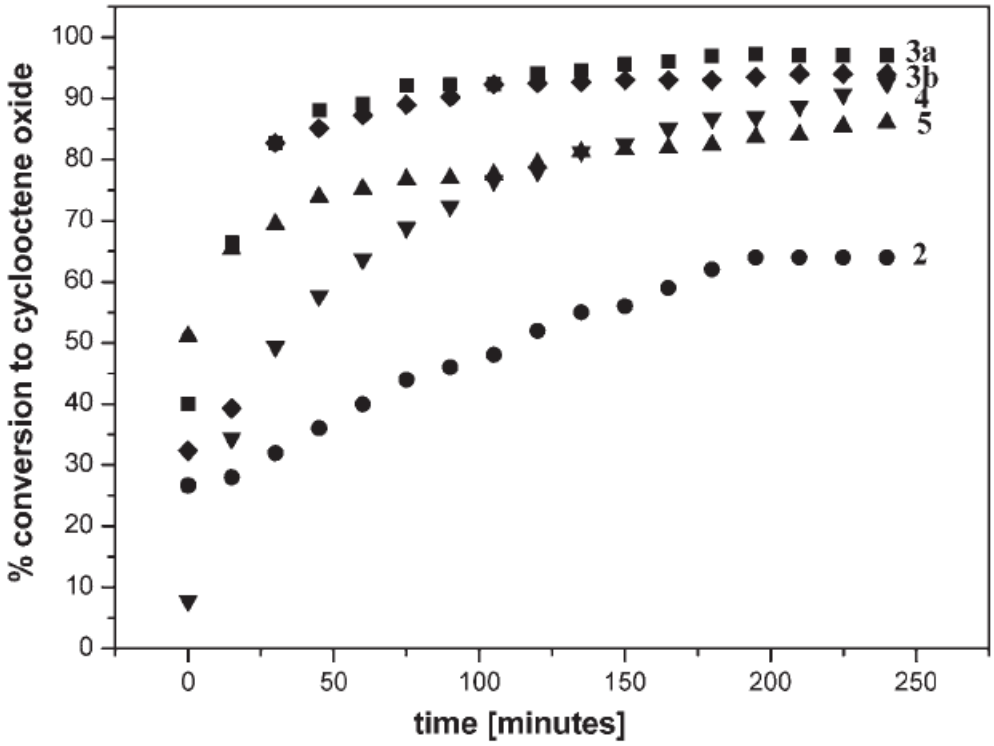
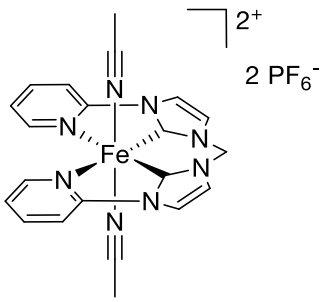


Figure 5: Epoxidation of cyclooctene with different catalytic systems. **2**: Na_2WO_4 (0.4 mol%) + $ClCH_2COOH$ (1.6 mol%), **3a**: Na_2WO_4 (0.2 mol%) + H_2WO_4 (0.2 mol%) + $ClCH_2COOH$ (1.6 mol%), **3b**: **3a** at 20 °C, **4**: H_2WO_4 (0.4 mol%) + $ClCH_2COOH$ (1.6 mol%), **5**: H_2WO_4 (0.4 mol%) at RT.

It is possible that the tungstic acid or its salt form with hydrogen peroxide *in situ* peracetic acid based on chloracetic acid and then epoxidize the alkenes.

Iron-NHC-complex

A common catalyst for olefin epoxidation at the group of Prof. Kühn is [Fe(di(o-imidazol-2-ylidenpyridin)methyl)-$(MeCN)_2$]$(PF_6)_2$ (Scheme 23), in following called **Fe1**.[40, 46, 47]



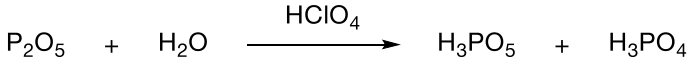
Fe1

Scheme 23: Octahedral structure of Fe [NCCN] with simple CH_2-bridge of the ligand system.

The compound is active with hydrogen peroxide, additionally Kühn *et al.* discovered cyclohexyl peroxide during the catalytic conversion of cyclohexane with **Fe1** and 50% hydrogen peroxide.[47] This result includes that **Fe1** is also able to transfer peroxidic groups. The mechanism involves an activation of hydrogen peroxide at the iron centre and the following transfer to the olefin or other substrates.[48] The mechanism was analysed by different groups and they all ended up with the formation of Fe(III)-hydroperoxo complexes as already shown in Scheme 15.[46]

Peroxymonophosphoric acid

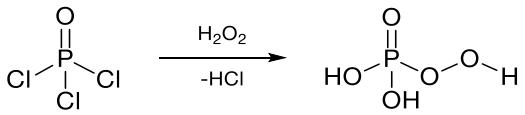
As peroxymonosulfuric acid is a very suitable oxidizing agent for peracids, and phosphorus as similar reactivity and chemical behaviour to sulphur as they are beside each other in the periodic table, it is obvious that peroxymonophosphoric acid should work as alternative to Caro's acid, probably with the same mechanism as shown in Scheme 18. Peroxymonophosphoric acid and phosphoric acid show both hygroscopic behaviour, leading to a higher product stability. But due to the solid state of both compounds the phosphorous alternative can not be adapted as solvent, as it is for Caro's acid.[11] H_3PO_5 was first prepared by Schmidlin and Massini using P_2O_5 and two equivalents of hydrogen peroxide, but this reaction is extremly vigorous and exothermic, resulting in high decomposition of the product H_3PO_5.[49] Another method is the hydrolysis of a peroxodiphosphate in perchloric acid at 45 °C, as shown in Scheme 24.[49, 50]



Scheme 24: Hydrolysis of peroxodiphosphate with perchloric acid to peroxymonophosphoric acid.

Other methods for producing H_3PO_5 with higher stability involve CCl_4 as solvent and 70% hydrogen peroxide or acetonitrile as solvent and 90% hydrogen peroxide. But besides acetonitrile these are all very dangerous and hazardous chemicals.[49, 51]

Another option without using phosphor oxides is the use of $POCl_3$ and 30% hydrogen peroxide, which forms H_3PO_5 in situ. This method even allows to immobilize peroxymonophosphoric acid on an alumina-surface.[52]

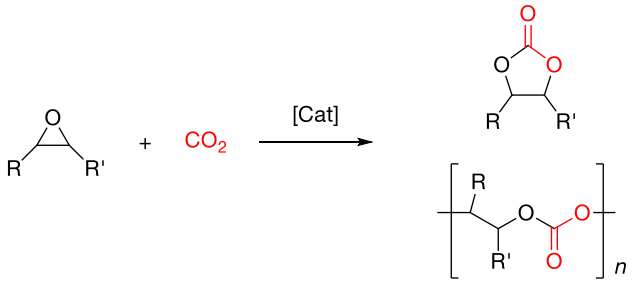


Scheme 25: Synthesis of peroxymonophosphoric acid with $POCl_3$ and 30% hydrogen peroxide.

All publications involving H_3PO_5 deal with epoxidation or oxidation catalysis with transfer of oxygen atoms.[49, 50, 52]

1.4 Improvement of epoxidation catalysts for CO_2 activation

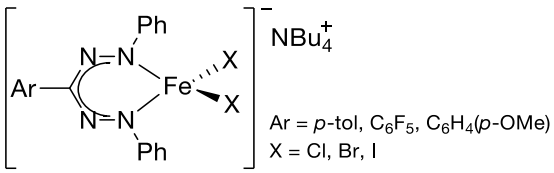
Carbon dioxide utilization is a hot topic in society as researchers and politics discuss about its environmental damage due to its rising content in the atmosphere. Therefore many researchers concentrate on catalytical or non-catalytical activation and conversion of CO_2 to more suitable compounds.[53] One method is to transfer CO_2 in epoxides to gain cyclic carbonates or polycarbonates (Scheme 26).[54]



Scheme 26: Insertion of CO_2 into an epoxide to gain cyclic carbonates or polycarbonates.

Cyclic carbonates for example are used as green solvents or electrolytes for Li-ion batteries.[55] The challenge to find a suitable catalyst is still not achieved. The highest yields and selectivity could be reached using a binary system with a Lewis acid (e. g. metal centre, especially Al, Zn, Co and Cr) and a nucleophile (as halides). The latest focus is based on Fe complexes as it is suitable, cheap and relatively low in toxicity.[56] Furthermore, this metal is able to build bifunctional catalysts, which include both the Lewis acidic metal centre and the nucleophilic multidentate ligands, containing N and/or O donor atoms, but those systems still need a cocatalyst to reach high activity and selectivity.

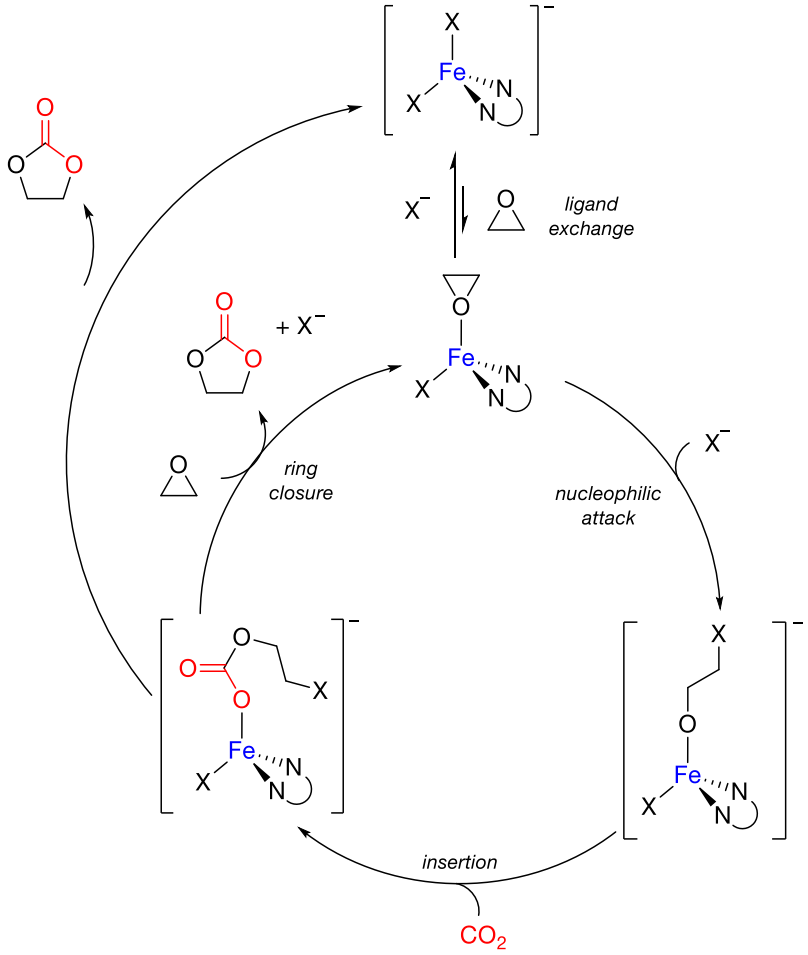
Otten *et al.* discovered an Fe(II) formazanate complex (Scheme 27), which is an active and selective homogenous single-component catalyst for the reaction of epoxides to cyclic carbonates using CO_2.[56]



Scheme 27: Catalytic complex by Otten *et al.* for synthesis of cyclic carbonates *via* epoxides and CO_2.

Using the complex with Ar = *p*-tol and X = Br they reached with the synthesis of propylene carbonate a conversion of > 99%, a selectivity of > 99% and TONs up to 400 (reaction conditions: 30 mmol propylene oxide, 3 mmol mesitylene as internal standard, 0.25 mol% catalyst relative to epoxide, 90 °C and 12 bar CO_2 pressure for 18 h).

Furthermore due to their observations they propose the mechanism seen in Scheme 28.



Scheme 28: Proposed mechanism of cyclic carbonate formation using an Fe(II) complex.

This could be an interesting and new application enlargement to the already known epoxidation complexes based on iron, which are presented by Kühn *et al.*[53, 57, 58] Furthermore those complexes can be modified and improved to be suitable not only for the epoxidation, but also for the in situ epoxidation and additionally insertion of CO_2 to gain cyclic carbonates from olefins.

2 Objectives of this Thesis

Peroxides are not only interesting compounds for academic research but also for industrial applications. As already mentioned, peroxides are used in bleaching systems for diverse fields/areas of application, for example in products for hair, teeth and clothes. However, they have some deficits due to their instability. For this reason, it is important to either stabilize peroxidic compounds (for example with SnO_2 being a stabilizing agent for hydrogen peroxide), or to generate peroxides *in situ*, as it is already applied for peracetic acid using acetic acid and hydrogen peroxide.[35, 59] Another solution are more stable peroxidic compounds as peracids.

Peroxomonosulfuric acid is already a very common oxidation compound in industry to generate bleach activators (= e. g. peracids) originating from acids, for example ε-phthalimidoperoxycapronic acid (PAP). This activator is modified by Solvay to a white milky aqueous suspension with PAP crystals under the patent trademark Eureco™ with improved properties referring to stability, activity and ability for disinfection and safety.[60] Nevertheless the product is produced in Italy, where the diluted sulfuric acid is spread in the sea, an environmentally unfriendly and intolerable behaviour.[61] This method seems less sophisticated and cheaper as the purification of the diluted and contaminated sulfuric acid, which is produced with hundreds of litres during the production of PAP, is quite expensive. Due to the highly environmental danger the release should be avoided.[62, 63] Italy still releases those by-products in the sea, but this is not a sustainable solution for the future.[61]

As there are some systems, which can activate an oxidizing agent as H_2O_2 or ^{t}BuOOH, which means the capture and later release of O-O-groups, an either metallic or non-metallic catalyst as activation agent – which has the same reactivity as peroxomonosulfuric acid – would be of major interest. Obviously, it should be easier and cheaper in purification and recycling. In this case a heterogeneous catalyst presents an ideal solution with regard to an easy separation from the system and simple reactivation by cheap oxidizing agents.

This work is a feasibility study on already known systems in regards to the oxidation of organic acids to peracids and its further improvement. The final organic acid to oxidize is phthalimidocaproic acid. To simplify the research and not to be hindered by functional groups or stereo effects, elementary organic acids were applied. Furthermore, some similar catalytic complexes are formed, which could be interesting for CO_2-activation.

In Table 2 is a brief summary of the systems, the applied acids and the qualitative evaluation.

Table 2: Brief summary of the qualitative evaluation of the tested systems on the acids.

Acid	System	Applicability
Acetic acid	Caro's acid	✓
	$CaWO_4$	✓
Caproic acid	Caro's acid	✓
	MTO/H_2O_2	✓
	MTO/UHP	✗
	$CaWO_4$	✓
	$Na_2WO_4 \cdot H_2O$	✓
	Na_2WO_4	✓
	Na_2WO_4/P_2O_5	✓
	H_2WO_4	✓
	W1	✓
	Fe1	✗
Decanoic acid	Caro's acid	✓
Phthalimidocaproic acid	Caro's acid	✓
	Na_2WO_4	✓
	H_2WO_4	✓
	H_3PO_5	✗

3 Results and Discussion

Due to safety issues and the qualitative character of the feasibility study, the formed peracids were not isolated as well as hydrogen peroxide and other primary oxidizing agents, which were present in stoichiometrically higher equivalents. These components could not be quenched without decreasing the yield, as – for safety reasons – a high concentration of hydrogen peroxide should be avoided. Therefore, given yields are determined with ^{1}H-NMR integral ratios.

3.1 Solubility of phthalimidocaproic acid

To focus more on the oxidation of PC to PAP solubility tests were achieved and recorded in the following Table 3.

Table 3: solubility test of PC in different solvents.

solvent (5 mL)	mass (PC)	comment
acetone	~ 800 mg	
DCM	~ 300 mg	excessive PC floats
benzene	~ 150 mg	
isopropanol	~ 120 mg	^{i}PrOH too fleeting
methanol	~ 500 mg	
^{t}BuOH	~ 1 g	at 40 °C

3.2 Synthesis *via* Caro's acid

The synthesis of peracetic acid *via* Caro's acid was performed according to literature procedure.[37] The permanganometry was proceeded with $KMnO_4$ solution ($0.06\,\frac{\mathrm{mol}}{\mathrm{L}}$) and H_2SO_4, but did not produce suitable results. Iodometry was performed, improved and applied with following products. The procedure is described in the experimental section.

Caproic acid was performed analogue to peracetic acid as well as decanoic acid. Both reactions worked well as long as all reaction steps and compounds were cooled and later stirred at room temperature.

Peracetic acid

Peracetic acid was not isolated as it is still soluble in water and sulfuric acid. The hydrophilic behaviour of the acid and peracid lead to a low yield (24%) as the equilibrium of the reaction is more on the educt side due to its stability. In general, the ^{1}H-NMR spectrum shows a chemical shift of the signal for the methyl protons into lower field about 0.02 ppm. The signal for the acidic proton is not detectable, but this is usual due to deprotonation of the acid and peracid. Therefore, the ^{13}C-NMR spectrum shows signals at 16.6 ppm and 176.3 ppm for the peracid. Both signals are shifted in the higher field, as shown in Figure 6. This effect is described more detailed in chapter "percaproic acid".

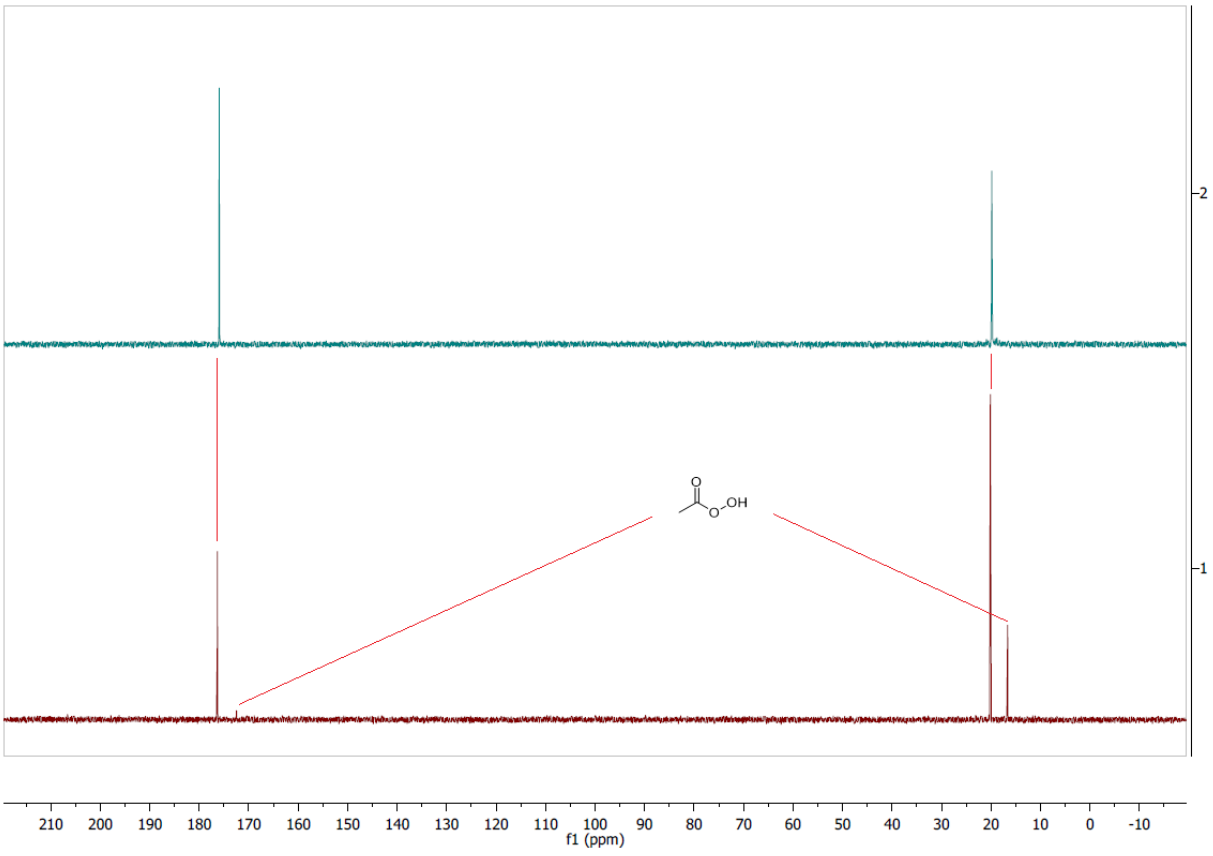


Figure 6: Comparison ^{13}C-NMR spectra of acetic acid (above) and peracetic acid via Caro's acid (below).

A HSQC-NMR spectrum shows the coherence between the shift in ^{13}C-NMR and ^{1}H-NMR spectra shown in Figure 7. This figure only shows the relevant section as there are no signals for acetic protons in ^{1}H-NMR spectrum.

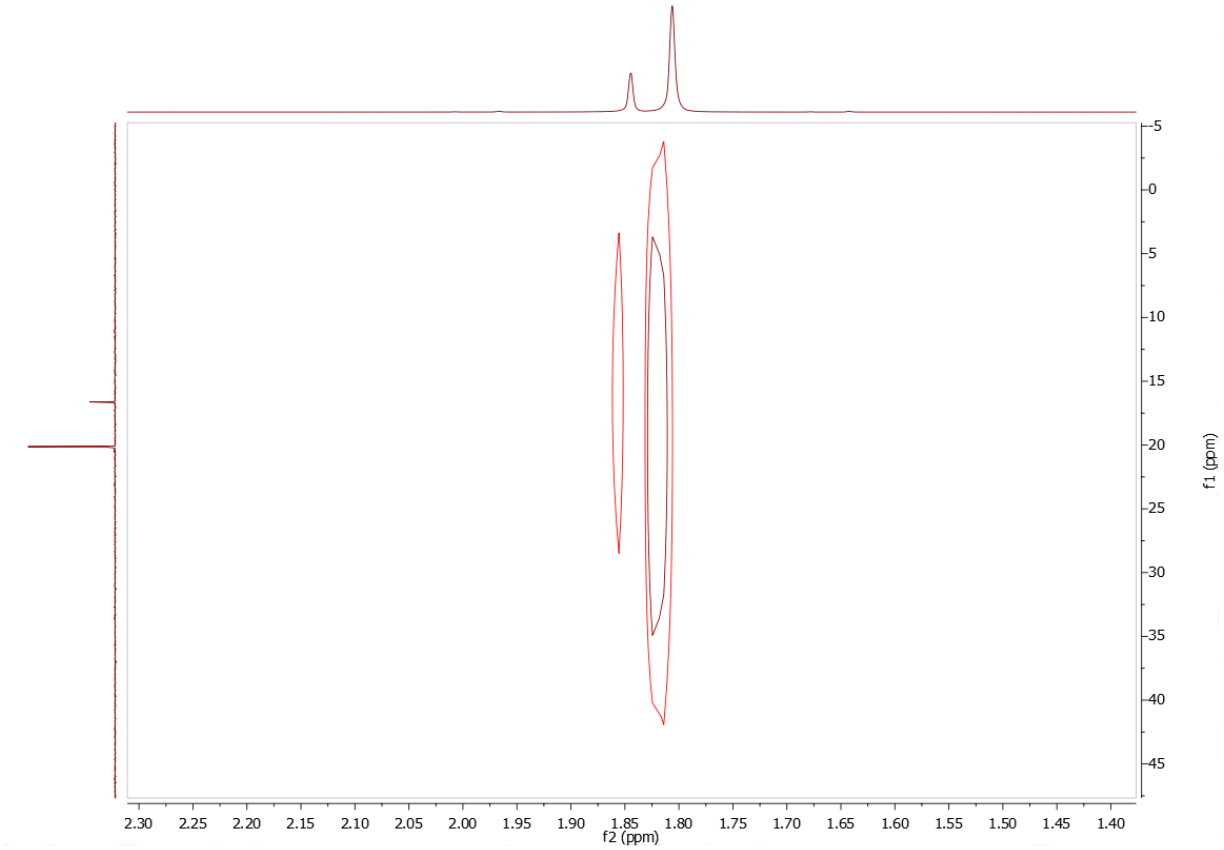


Figure 7: 2D-NMR spectrum of peracetic acid and acetic acid. The smaller signals (downfield shift) of ^{1}H-NMR spectrum cohere with the chemical shift in higher field in ^{13}C-NMR spectrum.

The peracid signals are characteristic and used to identify peracetic acid in other oxidizing systems.

The IR spectrum shows significant reflexions for the peracid. The broader band at 3392 cm^{-1} shows the peroxidic functional group, as shown in Figure 8. The valence vibration of (C-O) and (C=O) are detected at lower wave numbers at 1642 and 1370 cm^{-1}. The nearly identical band at 1227 cm^{-1} for δ(COOH) indicate a change in conformation as the distance between the bands changed.

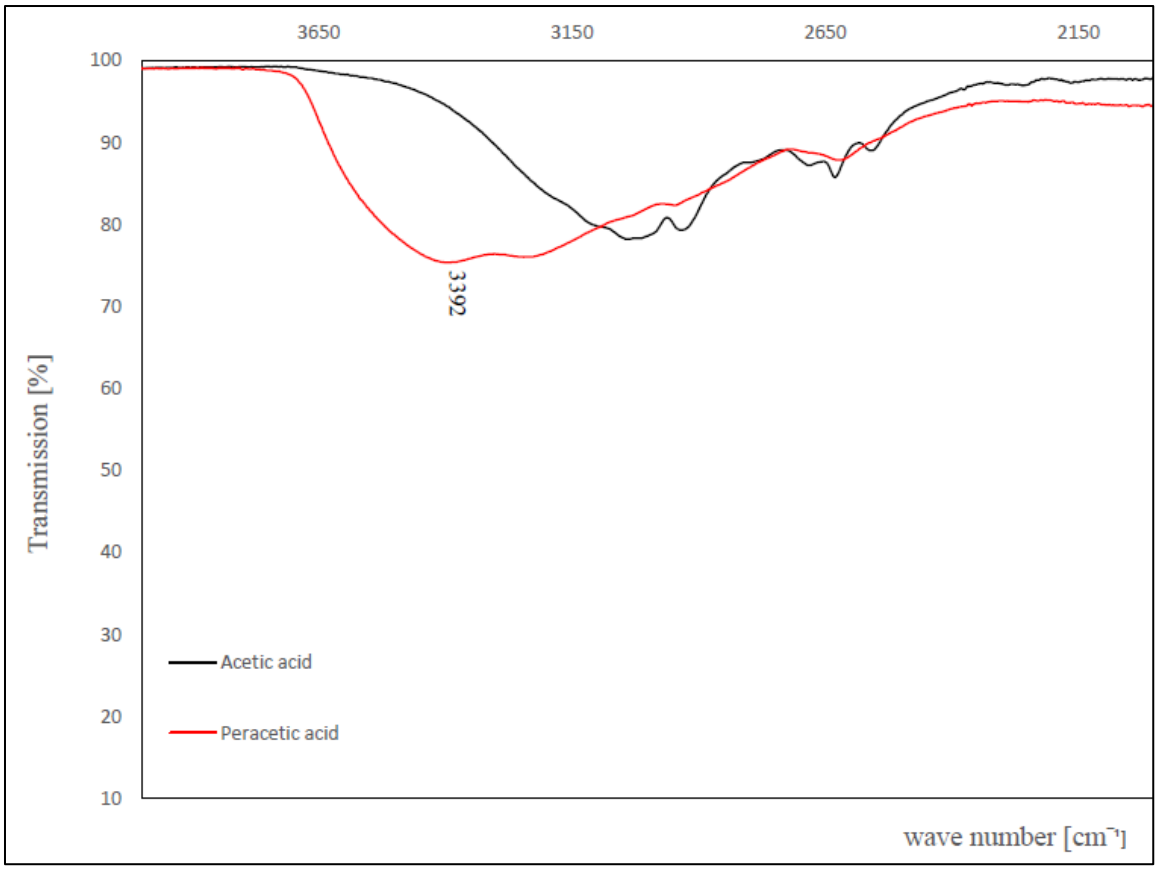


Figure 8: IR spectrum for acetic acid (black) and peracetic acid (red) with the characteristic band at 3392 cm^{-1} for peroxides.

Percaproic acid

The yield for percaproic acid *via* Caro's acid is about 86% and the signals in ^{1}H- and ^{13}C-NMR spectra match with those in literature. Interestingly both spectra do not show downfield shifts but shifts in higher field. The reason could be, that oxygen in carboxylic acids already have the maximum electron-drawing effect in molecules, and the lone pair electrons of the peroxo group have such a high sterical demand, that they push electron density back to the alkyl chain and therefore shield the nuclei again. Comparisons of the alkyl chains are shown in Figure 9 and Figure 10 with caproic acid above and percaproic acid below. The educt is connected with a red line. In the ^{1}H-NMR spectrum a shift and therefore a separation of $C^{4}H_2$ and $C^{5}H_2$ signals at 1.30 ppm and 1.18 ppm is clearly visible, which shows that the electron density effect even affects farer nuclei. The IR spectrum shows again the characteristic broader band at 3269 cm^{-1} for the peracetic ν(O-H) (Figure 11). Furthermore, the band for ν(C=O) at 1752 cm^{-1} of percaproic acid is higher than before at the acid, indicating the formation of the percarboxyl group.

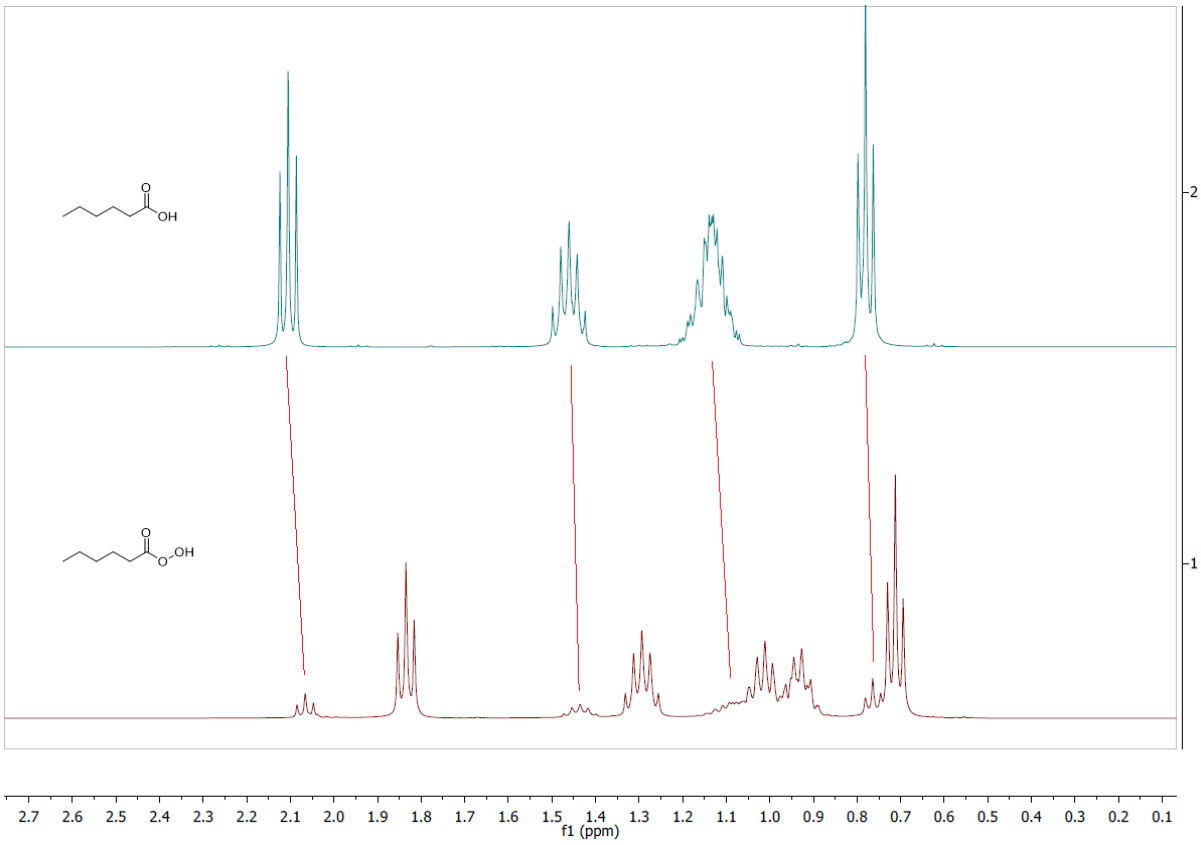


Figure 9: Comparison of alkyl chain caproic acid (above) and percaproic acid (below) with ^{1}H-NMR spectroscopy.

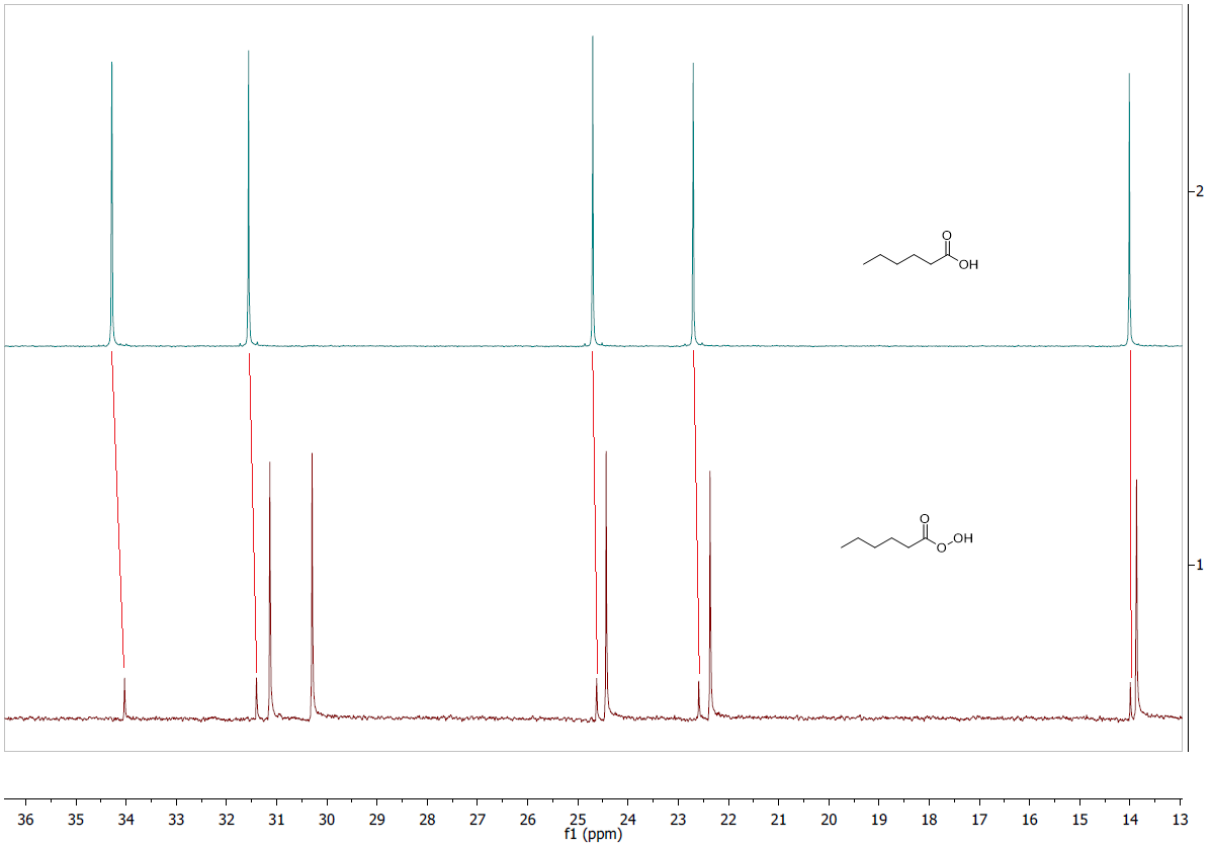


Figure 10: Comparison of alkyl chain caproic acid (above) and percaproic acid (below) with ^{13}C-NMR spectroscopy.

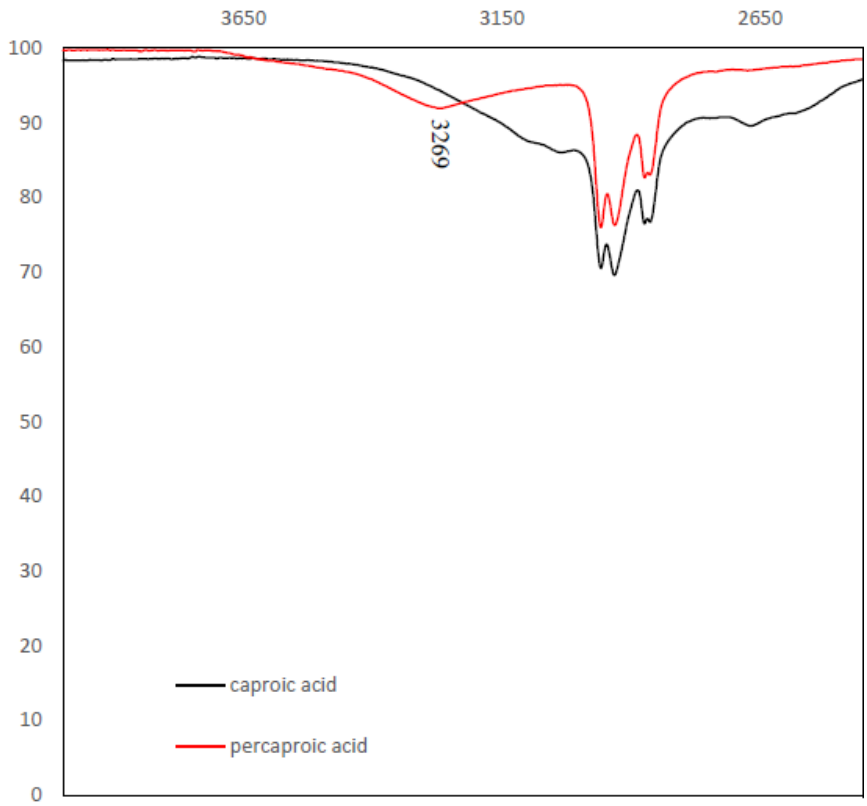


Figure 11: IR spectroscopy: comparison between caproic acid (black) and percaproic acid (red).

Those signals and bands are analogue to peracetic acid and served as comparison for following analytic and for characterization. Beside product, educt and solvent signals are no other signals, indicating could be detected.

Perdecanoic acid

Perdecanoic acid was synthesized with a yield of 90.3%. This result leads to the assumption, that the solubility and hydrophobicity of the product determines the yield. The peracid could be isolated as it precipitates from the reaction mixture.

In the ^{13}C-NMR spectrum, the percarboxyl signal at 174.39 ppm is very characteristic. Again, the affected carbon atoms have a chemical shift in high field, while perdecanoic acid, as first peracid shows no shift for the last methyl group, as it is too far from the peroxo group. The comparison again shows a high field shift from percarboxylate to the CH_3 group.

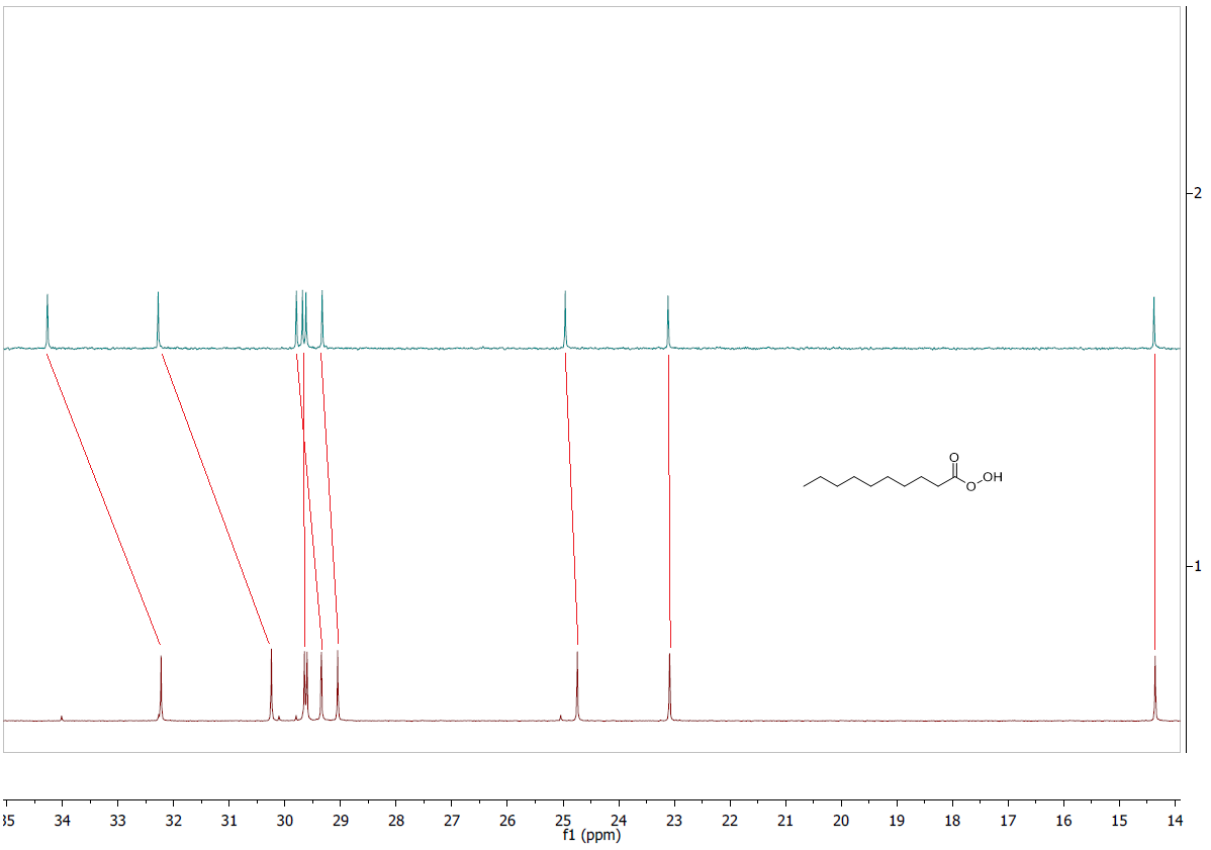


Figure 12: ^{13}C-NMR: Comparison between decanoic acid (above) and perdecanoic acid (below).

The ^{1}H-NMR spectrum does not show these significant signals as there are too many similar alkyl chains. Nevertheless, there is a clear shift from 2.09 ppm to 1.78 ppm for $C^{2}H_2$. The other signals from 1.30 ppm to 0.96 ppm cannot clearly be assigned to certain protons of educt and product.

The IR spectrum has the characteristic broad peracid band at 3260 cm^{-1} for ν (OH), furthermore the shifted band for ν (C=O) at 1750 cm^{-1} and δ (COOH) at 1154 cm^{-1}.

Phthalimidopercaproic acid

PAP was synthesized from PC according to literature.[64] The synthesis was straightforward as the product precipitates out of the reaction mixture and therefore it can be easily isolated with a yield of 94%.

The ^{1}H-NMR spectrum shows no chemical shift for the aromatic protons at 3.37 ppm, 6.90 ppm and 7.47 ppm. The signals for the alkyl protons are again slightly shifted to high field as discussed for previously described peracids. The signals for $C^{5}H_2$ and $C^{3}H_2$ do not overlap anymore and show two distinct quintets.

The ^{13}C-NMR spectrum is more significant as it shows the signal for peroxycarbonyl C at 174.0 ppm. Here analogue the signals for C^3 and C^5 have a light shift in higher field, while the signal for C^2 from the alkyl carbon atoms the highest shift from 33.6 ppm to 29.7 ppm.

The IR spectrum shows similar bands to the other peracids. At 3393 cm^{-1} is a broad signal for the peracidic ν(O-H), additionally shifted band for ν(C=O) at 1759 cm^{-1} for percarboxylic carbon and δ(C-O-OH) at 1150 cm^{-1}.

3.3 Synthesis *via* MTO

Reactions with MTO were proceeded and improved according to literature synthesis for epoxidations.[39] The oxidative solutions were prepared and the amount of “active oxygen” was determined with improved iodometry.

The oxidation of acetic acid with MTO was already discussed in the master’s thesis.[65]

The reaction of caproic acid with MTO was replicated according to literature and the period was endured.[39]

The experiments led to a very small but noticeable amount of peracids with the oxidation of MTO with TBHP or THF peroxide.

Additionally, efforts were made to change the primary oxidation agent from TBHP or THF peroxide to urea hydrogen peroxide (UHP), as it is a cheap and solid peroxidic compound and therefore simple in handling.

A ratio of 1 : 100 (MTO : UHP) was enough to show a light yellow colour, which indicates the formation of the MTO peroxo complex. With a ratio of 1 : 144 (MTO : UHP) the yellow colour appeared faster and brighter. The reaction was stirred between from 30 to 70 min, resulting in a deeper yellow colour and more active species after minimum 45 min. After addition of caproic acid the reaction mixture was stirred up to 12 d with noticeable loss of the yellow colour. Rising the temperature up to 50 °C showed no reaction conversion after 5 d. It seems that the primary oxidizing agent needs to be very active and accessible, especially for such a sterically demanding catalyst as MTO. Even though a yellow colour indicates the activated species, the activation was not enough to oxidize peracetic acid or percaproic acid.

3.4 Synthesis *via* $CaWO_4$

Peracetic acid

The oxidation of acetic acid was performed according to literature synthesis for epoxidations.[66] Heating the mixture up to 95 °C did not result in the oxidation of peracetic acid, so the temperature was varied until a temperature of 65 °C, which was determined as ideal, resulting in a yield of 20% after 4 d.

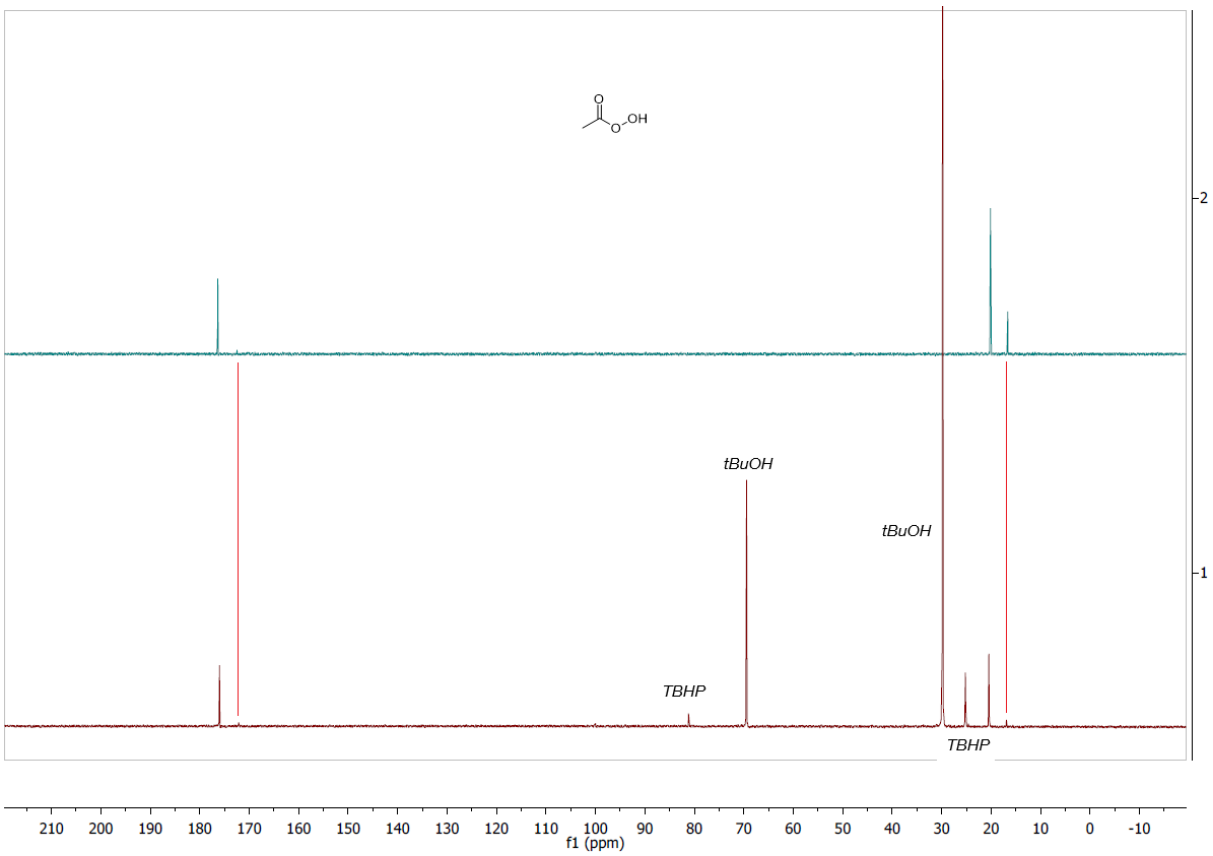


Figure 13: ^{13}C-NMR: Comparison peracetic acid *via* Caro's acid (above) and peracetic acid *via* $CaWO_4$ (below). The signals for peracetic acid are connected with red lines.

The ^{13}C-NMR spectrum shows small but clear signals at 172.13 ppm and 16.19 ppm. The signals by acetic acid at 176.00 ppm and 20.46 ppm are still very high due to its solubility in *tert*.-butanol and the equilibrium on educts side. Other signals are caused by the solvent and oxidizing agent with TBHP at 81.18 ppm (*C*OOH) and 25.19 ppm (*C*H_3) and analogue *tert*.-butanol at 69.43 ppm (*C*OH) and 30.01 ppm (*C*H_3). The ^{1}H-NMR spectrum also shows only the educts signal at 1.83 ppm and solvent signals at 1.00 ppm (additionally D_2O at 4.79 ppm).

Percaproic acid

The ^{13}C-NMR spectrum shows the characteristic signals for *C*OOOH carbon at 173.31 ppm as shown in Figure 14. The light shift of both educts and product signal in the synthesis *via* $CaWO_4$ below compared to the synthesis *via* Caro's acid above could be explained due to the different oxidation system and the involved coordinative effects. The signals at 30.88 ppm and 30.09 ppm for C^2H_2 and C^3H_2 disappear under the signal for *tert*.-butanol at 30.88 ppm. This effect was already noticed in previous experiments with MTO.[65]

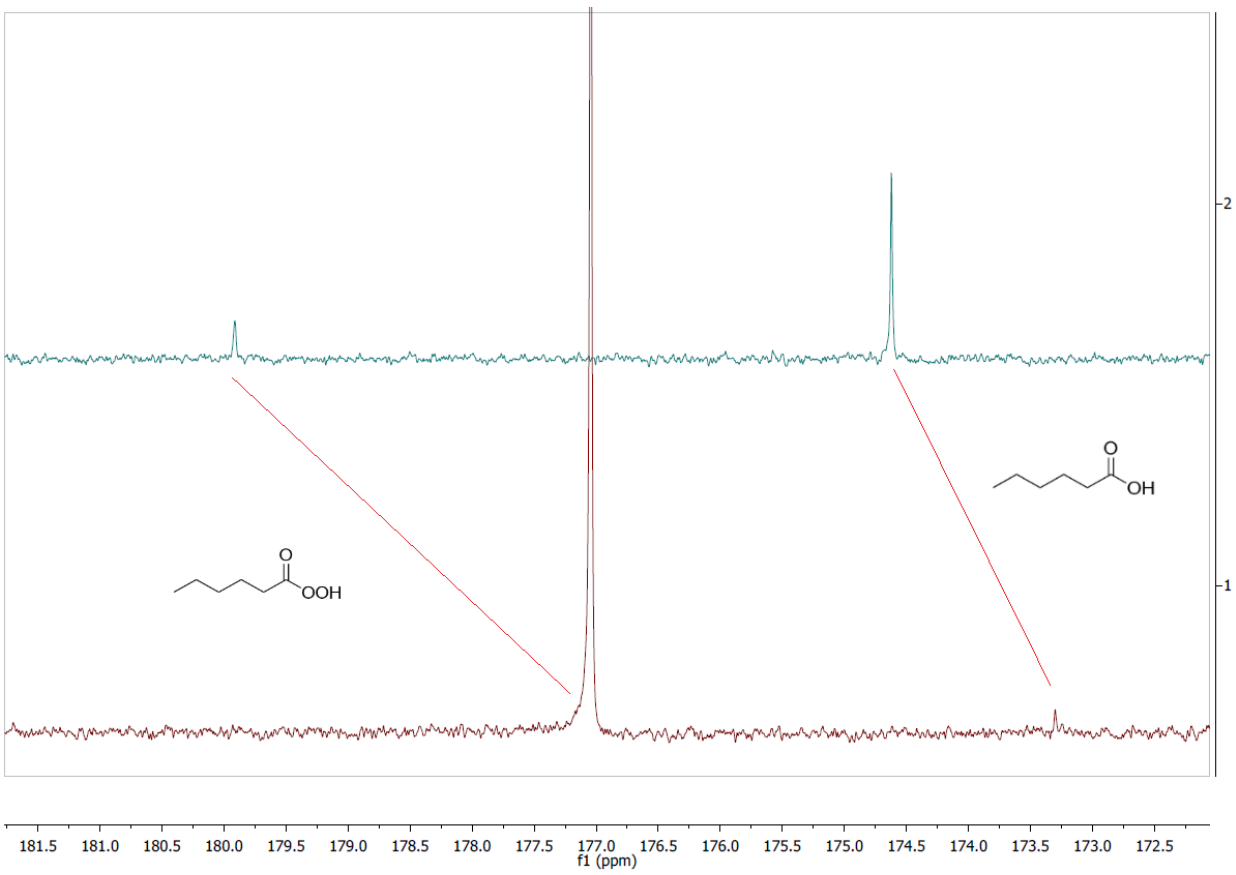


Figure 14: ^{13}C-NMR: Comparison of percaproic acid *via* Caro's acid (above) and percaproic acid *via* $CaWO_4$ (below). The left connected signals show the educt, the right ones the product.

The proton signals for the alkyl chain in ^{1}H-NMR are again too similar to the signals for ^{t}BuOH at 1.22 ppm and therefore not suitable for identification. peracidic and acidic protons are again not detectible as the compounds are deprotonated in equilibrium. Nevertheless, no other signals are present from 16.0 to 7.3 ppm and from 7.0 -2.3 ppm, which indicate no other products.

To decrease the water content of the reaction mixture $MgSO_4$ was added as drying agent. TBHP was prepared as described and cooled down to 0 °C. Different amounts of $MgSO_4$ (1-10 g), the reaction mixture was stirred for 3 h and after filtration $CaWO_4$ was added and the reaction was proceeded as described. No product signals could be detected (up to 12 d reaction period).

3.5 Synthesis *via* Na_2WO_4

Synthesis of percaproic acid and comparison of water-reduction

The oxidation of caproic acid *via* $Na_2WO_4 \cdot 2H_2O$ and phenyl phosphonate was performed according to literature synthesis for epoxidations.[67] The temperature was increased to 55 °C and after 4 d the product decomposed due to reduced NMR-signals. To remove unnecessary water, several efforts were made: The included crystal water in $Na_2WO_4 \cdot 2H_2O$ was removed by drying of Na_2WO_4 under reduced pressure for 3 d. 7.0 %weight could be extracted. Furthermore 50% hydrogen peroxide was applied for the following reactions. The comparison of water-reduced systems from a) full involved water, b) water-reduced Na_2WO_4 with 50% H_2O_2 and c) water-reduced Na_2WO_4 with 50% H_2O_2 and P_2O_5 as drying agent can be seen in Figure 15.

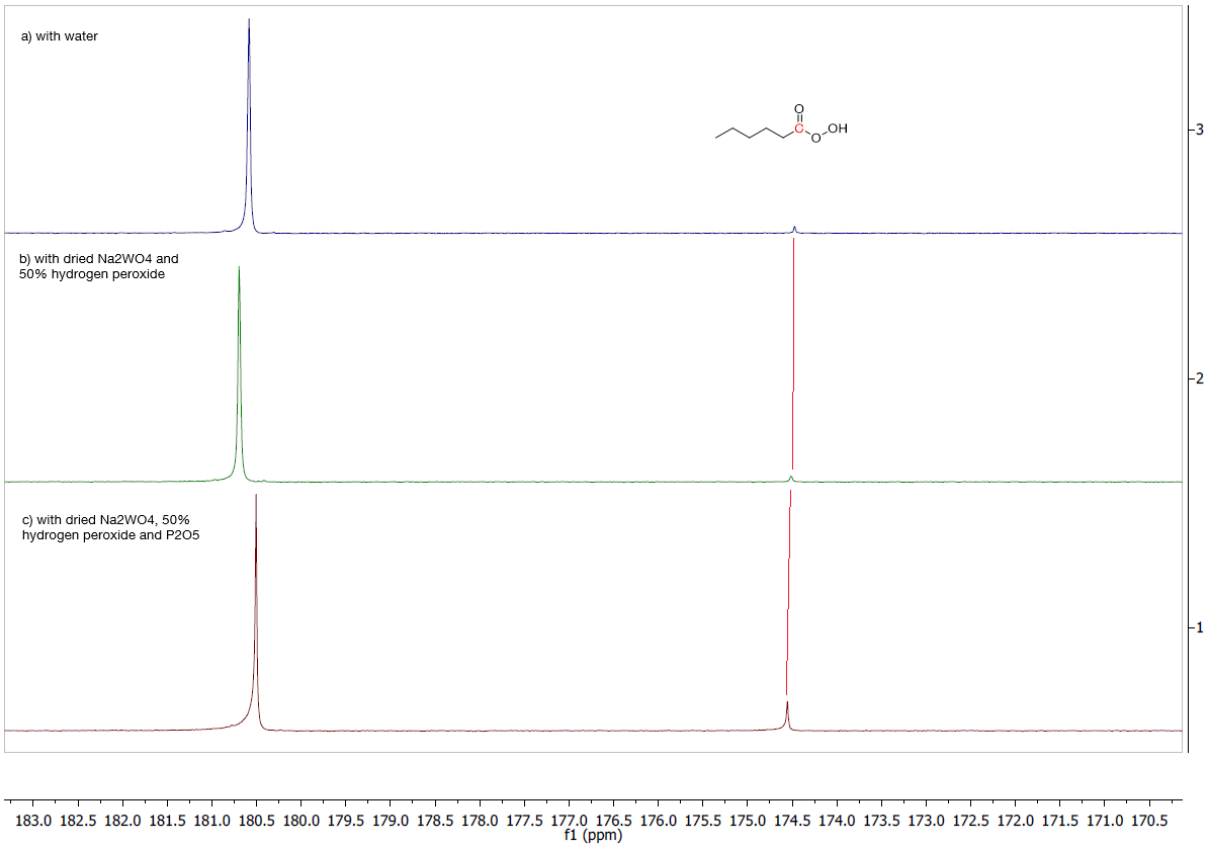


Figure 15: ^{13}C-NMR: Percarboxylate carbon of percaproic acid with a) $Na_2WO_4 \cdot 2H_2O$, b) Na_2WO_4 + 50% H_2O_2, c) Na_2WO_4 + 50% H_2O_2 + P_2O_5. The carbon of the peracid is marked by a red line, whereas other signals are of the acid carbon.

The yield for not dried Na_2WO_4 was only 4.5%. Due to drying and application of 50% H_2O_2 instead of 30% H_2O_2, the contained water was decreased and the yield was increased for 2%. Drying agents and compounds were examined for their suitability, as molecular sieve (3 Å) or Al_2O_3, but both were problematic due to the physical destruction during stirring of the reaction mixture. With P_2O_5 as drying agent the yield could be increased for another 6.5% (to 13%) (Figure 15c). P_2O_5 reacts with water to phosphoric acid H_3PO_4, which has itself a hygroscopic behaviour.[11] Additionally not only phosphorus pentoxide and phosphoric acid are water reducing agents, phosphoric acid also protonates and therefore stabilizes the carboxylic intermediate and forms water as leaving group.

The direct comparison of those experiments shows the high influence of water on the yield and product stability.

Synthesis of PAP

This reaction conditions were applied for the synthesis of PAP resulting in some notable signals for the product. As ^{t}BuOOH seemed to support the reaction and is a suitable solvent for PC, the reaction was reproduced in ^{t}BuOOH, resulting in 21.8% product. In the ^{13}C-NMR

spectrum the ^{t}BuOH signal overlaps with the signal for C^{6} of PAP, but the other signals are detectable. The same effect is seen in ^{1}H-NMR spectrum, where the signals for the solvent overlap with the alkyl proton signals.

Isopropanol was also tried as alternative, but it led together with hydrogen peroxide, to the production of acetone and later acetone peroxide. The ^{13}C-NMR spectrum in Figure 16 shows the signals for acetone peroxide at 109.63 ppm (*O*C*O*) and 20.99 ppm (CH_3).

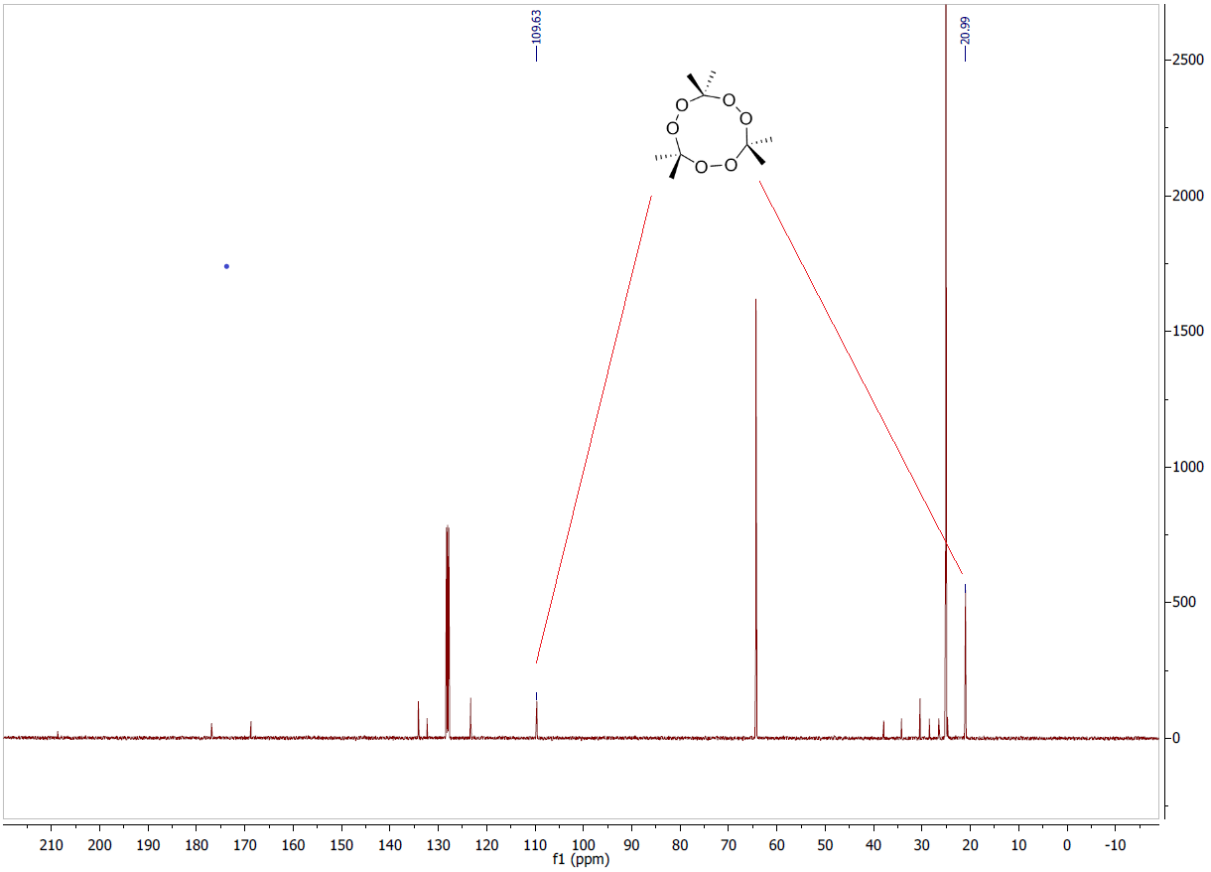


Figure 16: ^{13}C-NMR: evidence for acetone peroxide using isopropanol as solvent.

3.6 Synthesis *via* H_2WO_4

Percaproic acid

The oxidation of caproic acid was performed according to the best performance of oxidation *via* Ca_2WO_4. After 1 d 13.3% peracid were detected at 45 °C. In ^{13}C- and ^{1}H-NMR, the chain signals were again overlapped by the solvent signals of ^{t}BuOH, but the signal for percarboxylic carbon at 173.63 ppm is very significant. In ^{1}H-NMR, the shift trend for alkyl chain protons is still noticeable, as seen in Figure 17. a) shows percaproic acid via Caro's acid, while b) shows the product of the synthesis via H_2WO_4. The red lines indicate the signals for percaproic acid.

At 1.21 ppm is the solvent signal, the remaining signals pertain to caproic acid and illustrate clearly the increasing shift for the peracid.

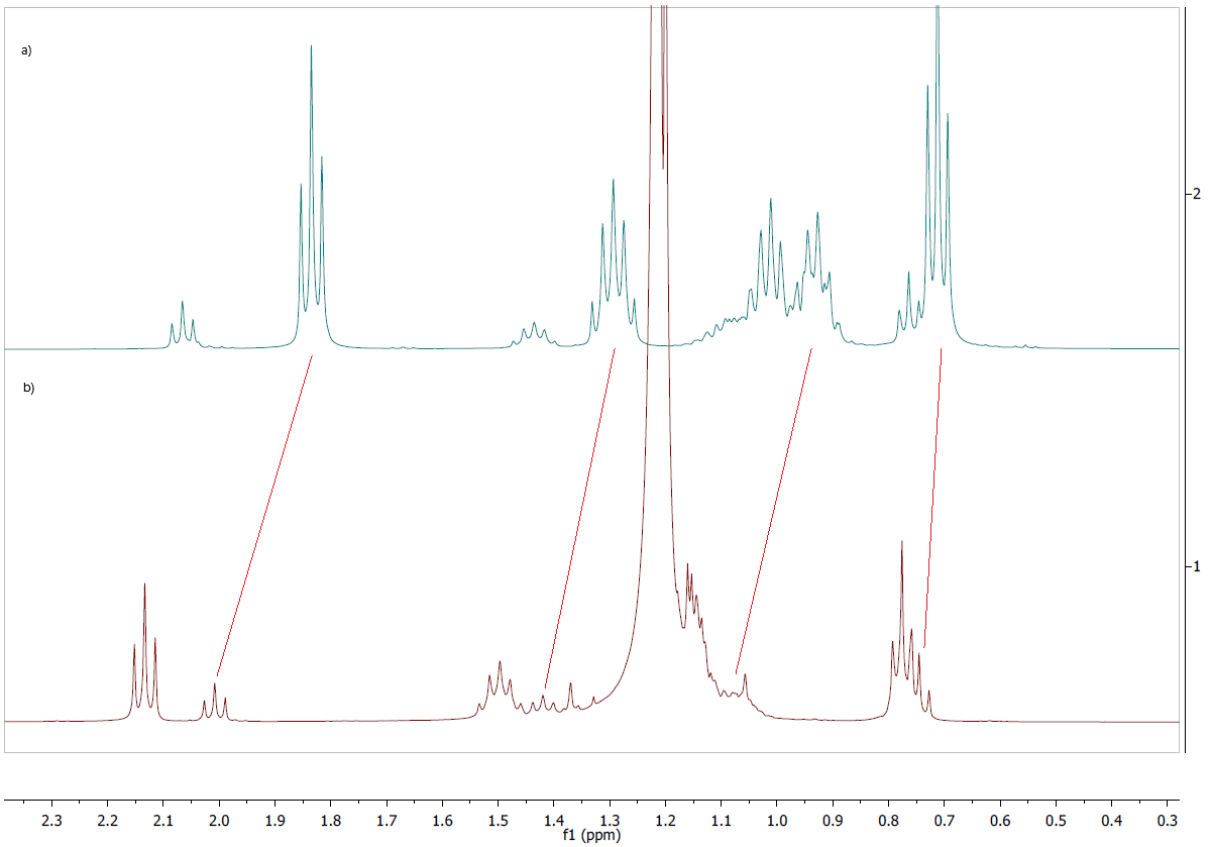


Figure 17: ^{1}H-NMR: Comparison of percaproic acid via a) Caro's acid and b) H_2WO_4. Red lines indicate signals for peracid, signal at 1.21 ppm shows solvent, rest is educt (acid).

After heating to 65 °C, the product decomposes within 1 d. With steady temperature at 45 °C after 7 d 20.6% of the peracid were detected.

Phthalimidopercaproic acid

The reaction was performed with PC resulting in 18% PAP after 7 d. The characterization followed the upper approach. Figure 18 shows the comparison of PAP alkyl chains *via* a)

Caro's acid and b) H_2WO_4. The signal at 25.83 ppm for C^3 has an overlap with TBHP, the signal at 31.10 ppm derives from the solvent ^{t}BuOH.

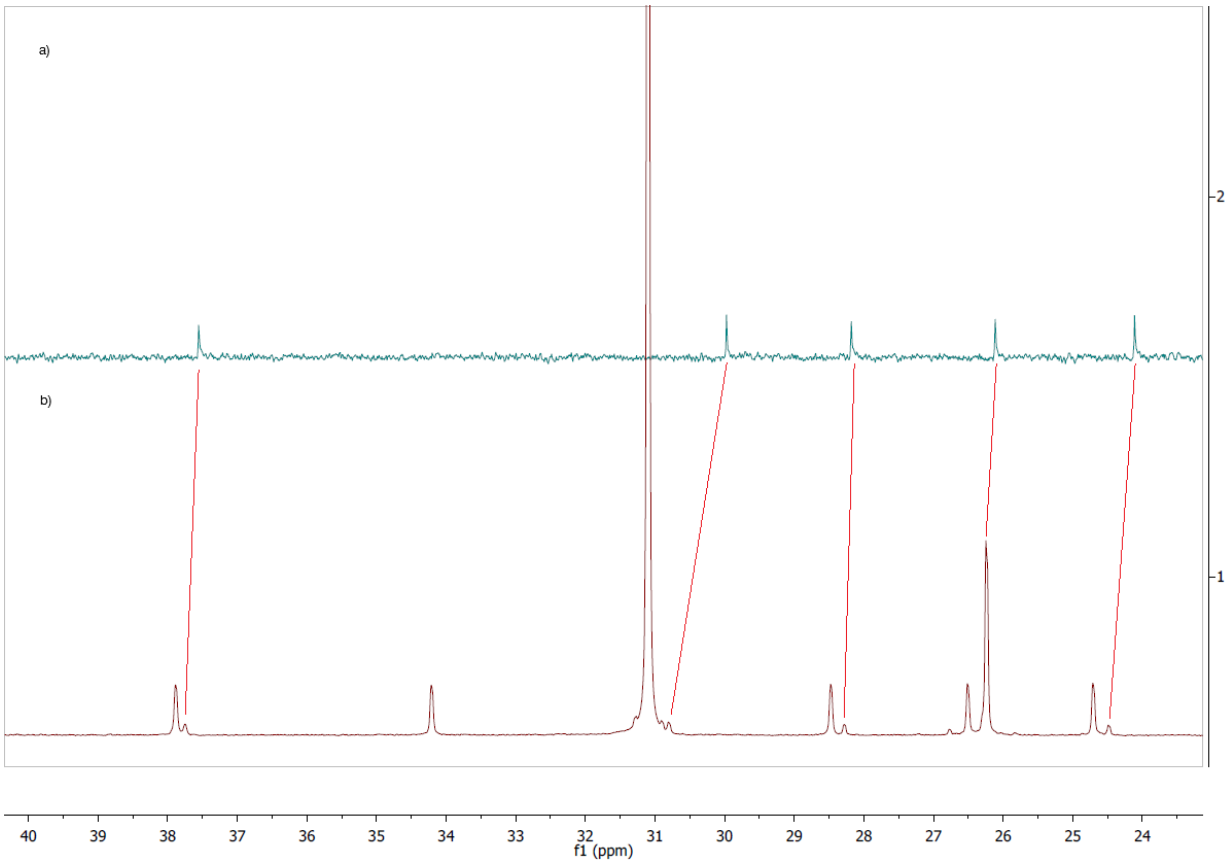


Figure 18: ^{13}C-NMR: Comparison of PAP alkyl chain a) via Caro's acid, b) via H_2WO_4.

3.7 Synthesis *via* Venturello's complex

Synthesis of W1

The synthesis of the complex was performed according to literature.[68] Though the procedure was not problematic, the elemental analysis had a discrepancy of ~7%. An alternative literature demonstrated better results, the synthesis is described in experimental section.[69] Figure 19 the ATR-IR shows the strong ν (W=O) and ν (O-O) stretching frequencies of the product.

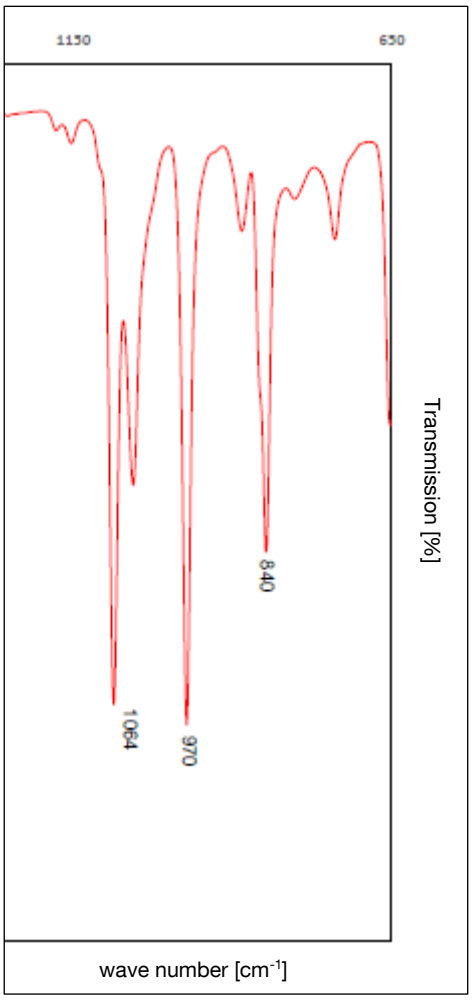


Figure 19: ATR-IR of Venturello's complex W1.

An IR spectrometry using KBr tablets shows transitions in lower waver numbers, as shown in Figure 20. The ν (O-O) at 856.13 cm^{-1} is visible as in the ATR-IR spectrum. Band at 617.77 cm^{-1} and 549.58 cm^{-1} show the asymmetric and symmetric vibrance ν for the peroxidic [$W(O_2)$], while the weak bond at 651.22 cm^{-1} seems to indicate the bridging PO_4^{2-} anion.

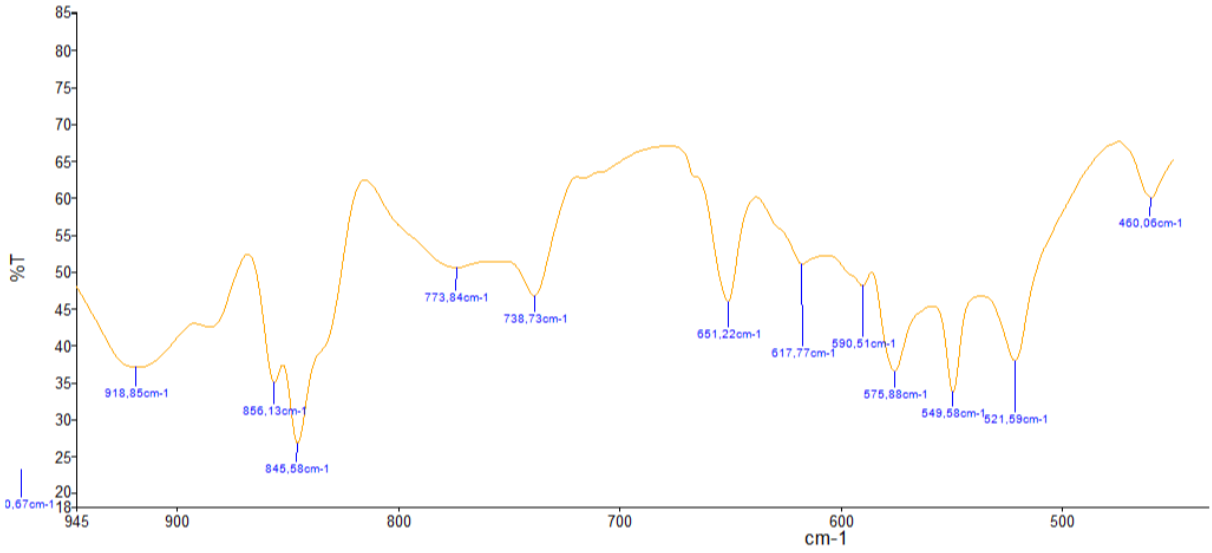


Figure 20: IR with KBr: W1 in lower wave number.

Percaproic acid

The oxidation of caproic acid with Venturello's complex (**W1**) showed acceptable signals in NMR-spectroscopy. The ^{1}H-NMR spectra showed in every measure uncertain multiplets as seen in Figure 22. Nevertheless, the signals can be associated to the product as the position of ^{1}H-NMR signals and ^{13}C-NMR signals are coherent. After 5 d the peracid decomposed as seen in Figure 21.

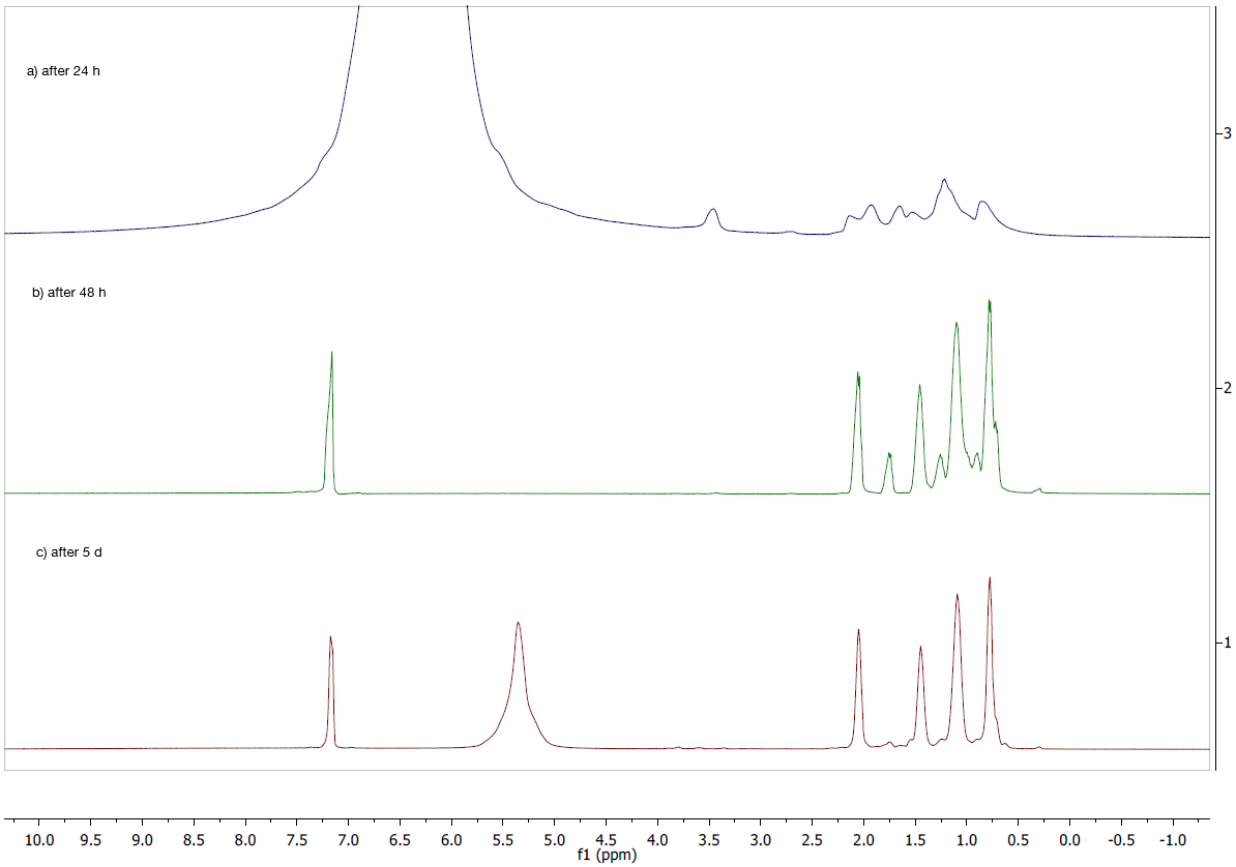


Figure 21: ^{1}H-NMR: Percaproic acid *via* W1 after a) 24 h, b) 48 h, c) 5 d.

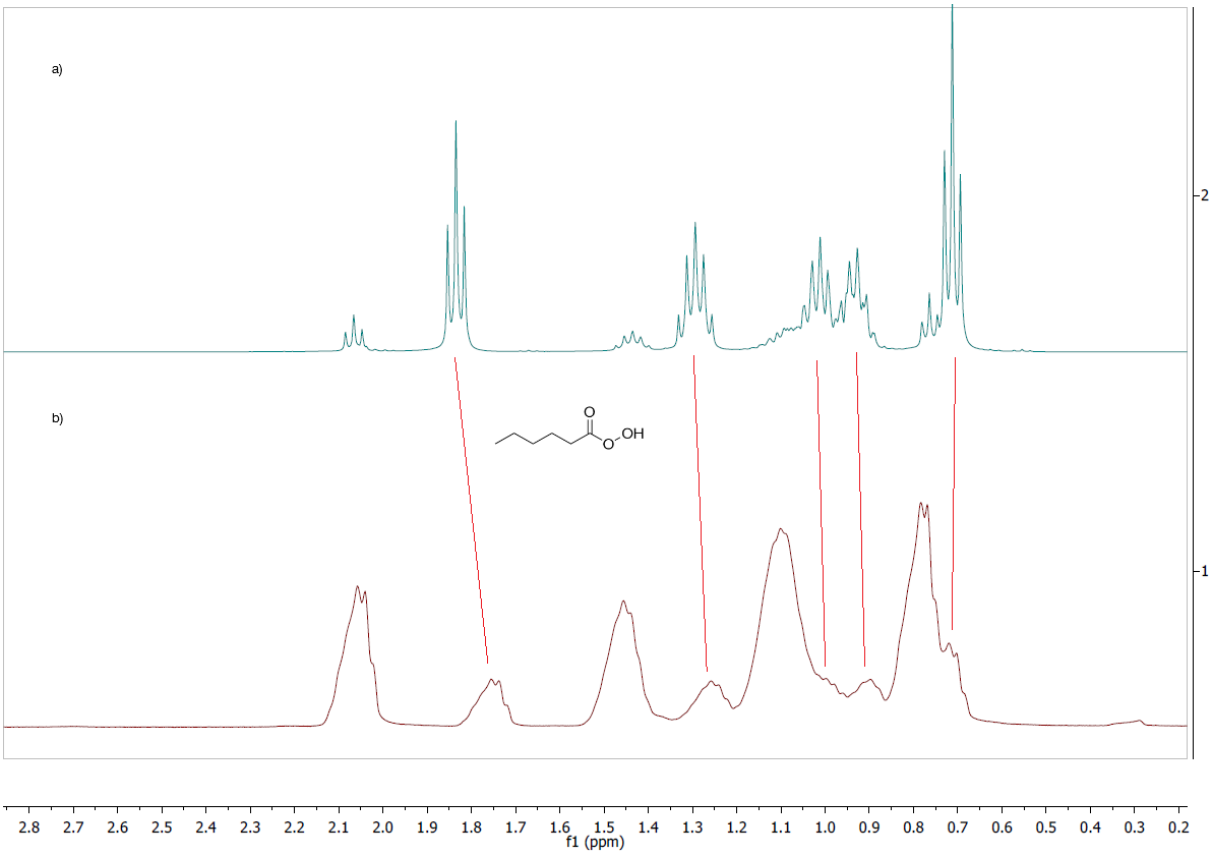
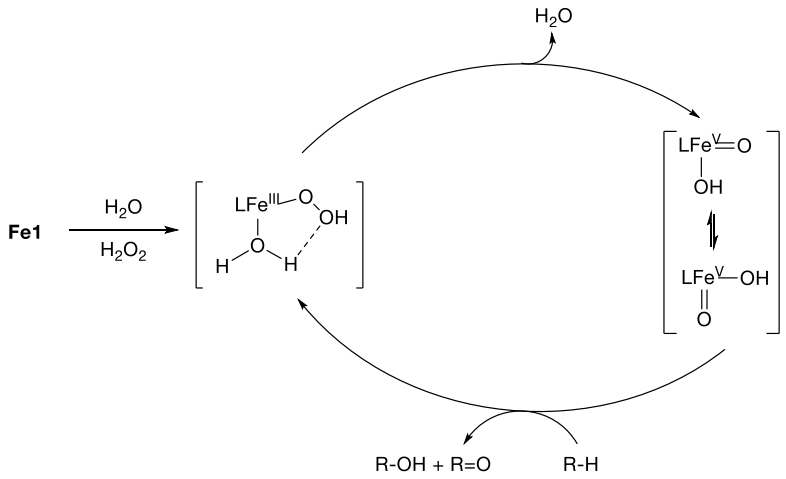


Figure 22: ^{1}H-NMR: Alkyl chain protons of percaproic acid a) *via* Caro's acid, b) *via* W1.

3.8 Synthesis via Fe1

The oxidation of caproic acid *via* Fe(NHC) is discussed in literature and was not successful.[65] The synthesis was performed according to epoxidation reactions and the development examined every 5 to 10 min, later every hour. Furthermore the reaction conditions were adapted to the most successful reaction of MTO in TBHP with no product formation as result.

The activation of **Fe1** with hydrogen peroxide leads to a an iron oxo species with a new oxidation state of +V as shown in Scheme 29 (the mechanism is adaptable for epoxidation of olefins).[70]



Scheme 29: Mechanism for oxidation of alkanes with **Fe1** and similar catalysts and hydrogen peroxide. L = di(o-imidazol-2-ylidenpyridin)methyl.

Fe(V) has a very high electron deficit, leading to a positively charged oxygen in in Fe=O which can react with electron rich compounds as olefins or certain alkanes. In contrast, carboxylic carbons are due to the high oxygen content very electron poor and therefore not suitable for an electrophilic attack of Fe(V). Caro's acid has beside the ability to transfer OOH, the ability to activate organic acids by protonation of the C-OH group, receiving water as good leaving group. This can also be a reason why MTO works in small yields, as the strong Lewis acidic character can activate acids as well.

3.9 Synthesis *via* H_3PO_5

H_3PO_5 was synthesized according to literature with P_2O_5 and 70% hydrogen peroxide.[49] To control the reaction conditions better, the 70% H_2O_2 were dissolved in isododecane (IDD). Due to the segregation of the solutions the reaction temperature could not be controlled under 5 °C and the reaction mixture overheated (2 drops no reaction, 3 drops overheating to 30 °C). Without IDD the reaction overheated as well. The setup was downscaled to $\frac{1}{4}$ and there were breaks included during the addition of hydrogen peroxide, but there was no product. It is possible that the required reaction temperature was not reached, but by now it was not possible to control it without disregarding safety. The reaction mixture was examined for the *in situ* preparation of PAP. With 50% H_2O_2, the ^{13}C-NMR spectrum of the alkyl chain C showed some signals of PAP (Figure 23), but the signal of the percarboxylate carbon was too weak for surely identifying PAP.

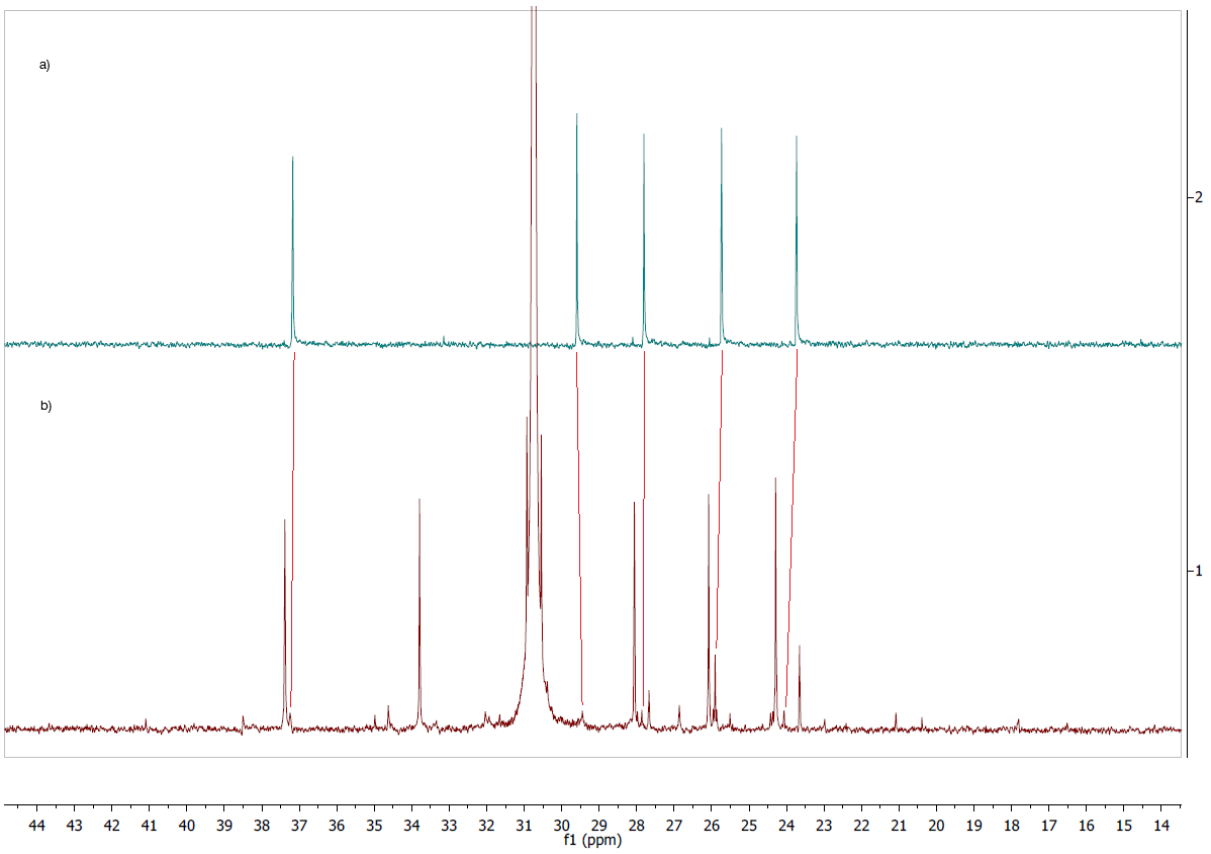


Figure 23: 13C-NMR: alkyl chain of PAP synthesis a) *via* Caro's acid, b) *via* P_2O_5 + 50% H_2O_2 in situ.

The *in situ* oxidation *via* H_3PO_5 was examined equally to Caro's acid. The oxidation of PC was problematic due to solution problems as H_2SO_5 acts as a solvent itself. H_3PO_5 is a solid component already at room temperature, so there is no solvation in the ice bath, which is necessary to control the reaction.

A third literature was examined on PC as well, which indicates the in situ preparation of H_3PO_5 with $POCl_3$ and 30% hydrogen peroxide.[52] The addition of $POCl_3$ to the mixture of hydrogen peroxide, ^{t}BuOH and PC turned the solvent to yellow, indicating the formation of an active species containing peroxidic groups. The active species formed independently of the order in which the compounds were mixed. Furthermore, some solid was formed as the mixture turned slightly turbid. After removal of the ice bath the mixture stayed turbid and yellow, and the colour was quite stable as it was still yellow after up to 10 d stirring with PC. Changing the concentration of H_2O_2 or reaction temperature (up to 65 °C) did not reach any PAP formation.

3.10 Synthesis of L1

Tetrazolo[1,5]pyridine was prepared according to literature.[71] Bis(1-(2-pyridyl)-1,2,3-triazol-4-yl)methane was prepared as well according to the same literature, but the raw product precipitated after stirring with ammonia solution. The solid was separated several times *via* a column and silica gel, but a manual chromatography or HPLC could not reach the same separation as a Flash chromatography used in literature. One problem was the development of heat during the chromatography, leading to a vaporization of the solvents and therefore dehydration of the column. In Figure 24 is shown the mass spectrometry with 305 m/z being the ionized product. Figure 25 shows the UV-Vis spectrum, indicating a too near retention time (13.297 min for the product) to separate the product from the other compounds with HPLC or LC by hand.

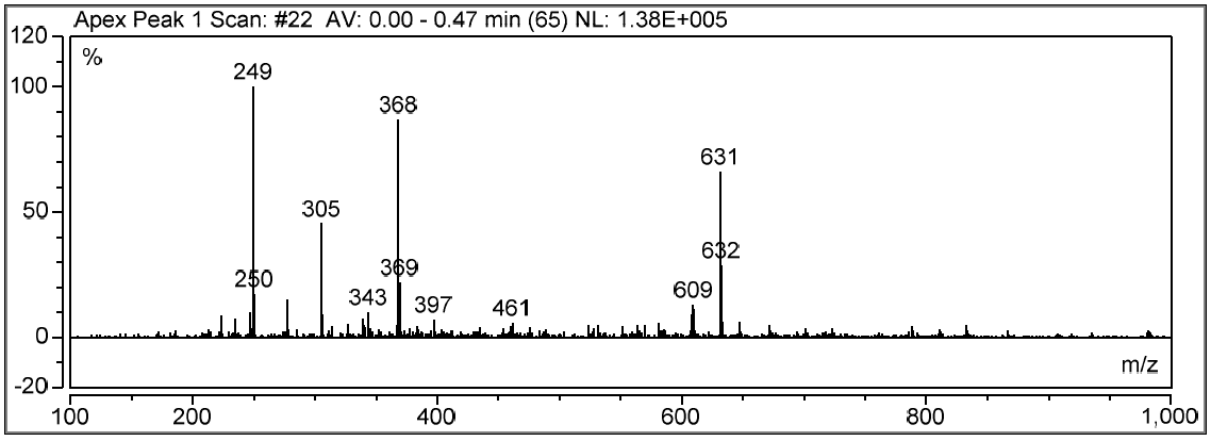


Figure 24: mass spectrometry of the raw product of bis(1-(2-pyridyl)-1,2,3-triazol-4-yl)methane.

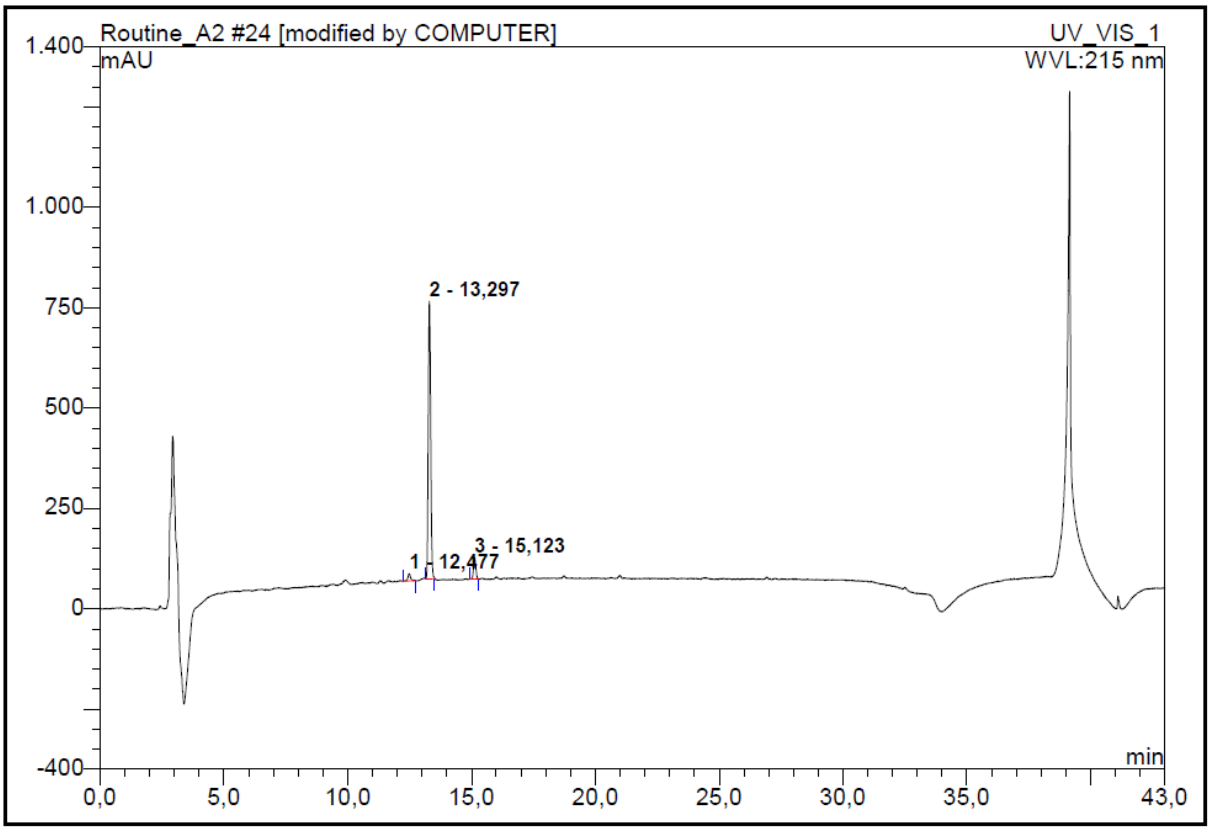


Figure 25: UV-Vis after HPLC chromatography. At 13.29 min is bis(1-(2-pyridyl)-1,2,3-triazol-4-yl)methane, the other

After purification attempts with best results using two times LC, the bis(1-(2-pyridyl)-1,2,3-triazol-4-yl)methane is obtained as described in experimental section and used for methylation.

The methylation was prepared according to literature.[71] As the methylation was not completing (Figure 26), MeOTf addition was added after 2 d and reaction period was prolonged to 3 d, until 41.3% of **L1** was obtained.

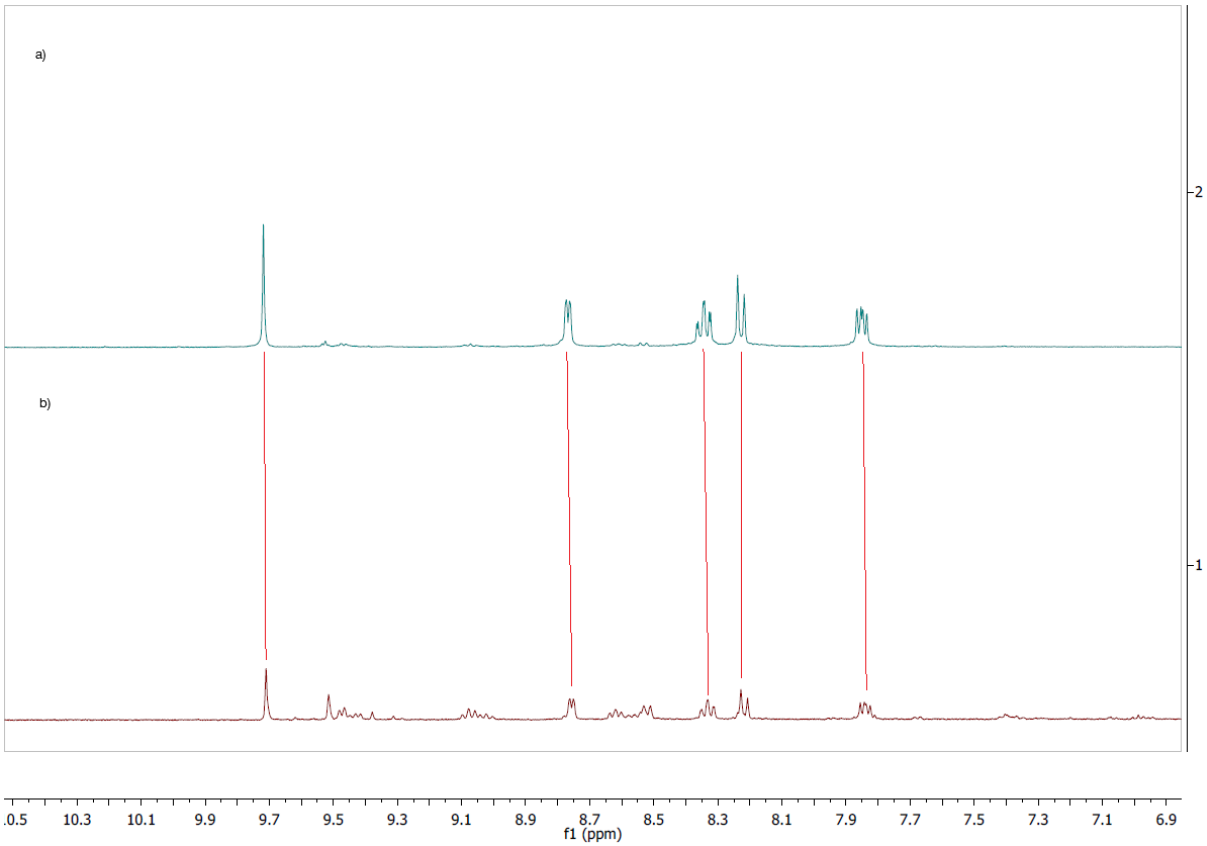


Figure 26: comparison of L1 a) in literature, b) in this work. red lines indicate product, remaining signals are monomethylated species.

3.11 Synthesis of L2

The synthesis was prepared according to literature.[71] During addition of NH_4PF_6 solution a green, sticky product was formed. Due to the colour it seems to be a copper side product. As there is no difference in ^{13}C-NMR spectra (Figure 27), the reason for the different appearance must be inorganic and the suspicion with too much copper is obvious. The raw product was dried under reduced pressure, washed and again prepared with NH_4PF_6 solution. After some attempts with the compound ratio using less copper, the synthesis was improved to the synthesis described in experimental section.

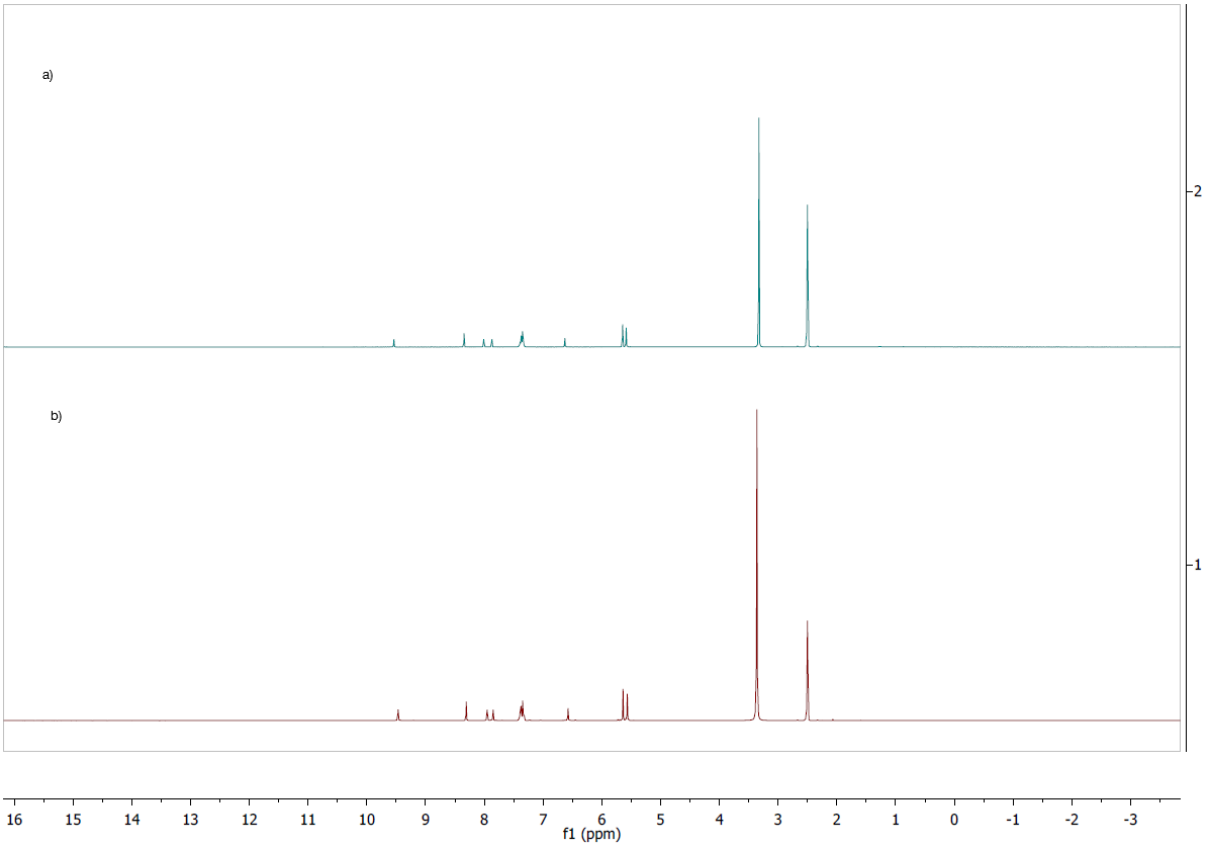


Figure 27: Comparison between a) green and sticky raw product and b) white solid of **L2**.

3.12 Synthesis of L3

The synthesis was performed according to literature.[71] The reaction was stirred for 4 d. After addition of NH_4PF_6 solution the mixture was left for 16 h so the precipitation can be formed slowly. The precipitate showed two different colours: dark orange on bottom and light orange on top. The comparison of those compounds () showed that the darker orange is still impure and require a purification with new precipitation.

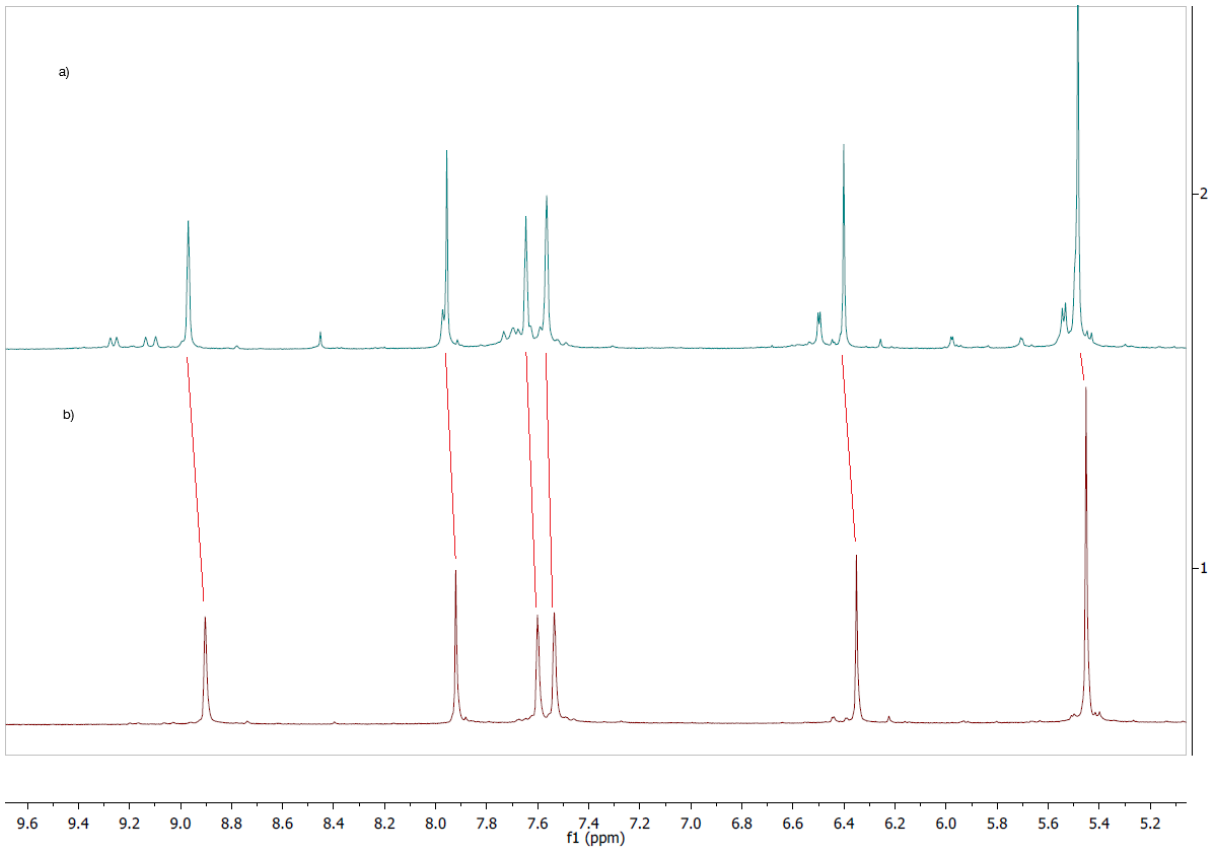


Figure 28: ^{1}H-NMR: comparison of **L3** a) dark orange, b) light orange.

3.13 Synthesis of FeL2(MeCN)$_2$

The synthesis of Fe**L2**(MeCN)$_2$ was performed according to literature.[71] The reaction was stirred for 3 d. After reduction of the solvents, Et_2O was added until an orange solid appeared, then the whatman filtration was performed. This way it was possible to perform the filtration only once or twice instead of three times. The products was pure according to NMR spectra and EA.

4 Conclusion and Outlook

The feasibility study for the oxidation of organic acids to peracids was qualitatively successful. Epoxidation catalysts are an interesting starting material to gain an alternative to Caro's acid. With hydrogen peroxide as primary oxidative material and ^{t}BuOH as solvent the best results could be reached, and with them being low-cost and easily available, they are an interesting combination for industry.

Even though MTO is an electron poor catalyst for oxidation reactions, the transfer from hydrogen peroxide to organic acids to receive peracids was qualitatively successful. The evaluated **Fe1** iron complex which is highly active in olefin epoxidation reaction does not yield any product. It seems that this complex is a poor electron donor and not able to perform an electrophilic attack. Tungstates as salts or acid were applied successfully, and even the complex by Venturello showed noticeable signals for the oxidation of caproic acid. The oxidation of PC was most problematic, starting with solvation problems, the steric demand and functional groups.

Though production formation was confirmed it is still questionable if metal catalysts are the best option for this reaction, as (most) metals also decompose peroxides by their nature. An interesting alternative to Caro's acid could be a phosphor-based system with H_3PO_5. The synthesis of this peracid is difficult due to its high exothermic reactivity. The *in situ* preparation for the oxidation of PC was again not straightforward due to solvation problems and exothermic behaviour. A new approach could be the application of poly phosphoric acid, as it is soluble in water and could form H_3PO_5 *in situ* with hydrogen peroxide as oxidant.

The ligand synthesis for new iron complexes were successful and ligands can be adapted to the iron centre. First approaches for CO_2 activation were already performed but could not be quantified as high pressures are needed which could not be reached in a Fischer-Porter bottle.

5 Experimental Section

5.1 Syntheses

All starting materials were received from commercial sources (*Sigma Aldrich*, *Alfa Aaesar*, *Merck*, *abcr*, *TCI*) and, if not further described, used without any purification. Common organic solvents were dried using an *MBraun* solvent purification system (SPS) and stored under argon and with molecular sieve (3 Å or 4 Å). Solvents were degassed by the *freeze-pump-thaw* method (three times). NMR solvents were purchased from *Eurisotop* and, if necessary, dried and degassed with the mentioned methods. Reactions involving air- or water-sensitive compounds were performed under Argon (99.996%, *Westfalen*) using standard Schlenk techniques or in a glove box (labmaster 130, *MBraun*). Characterization of novel substances was performed by ^{1}H- and ^{13}C-NMR spectroscopy, elemental analysis, mass spectrometry, IR /Raman spectroscopy.

5.2 Analytics

Nuclear Magnetic Resonance Spectroscopy (NMR)

Standard NMR spectra were recorded on a *Bruker* AVIII 400US spectrometer with a broad band probe and a gradient coil (^{1}H: 400.13 MHz, usually 16 scans, ^{13}C: 100.53 MHz, usually 1024 scans, ^{31}P: 400.13 MHz) at 298 k, using standard deuterated solvents. Chemical shifts ([δ]) are referenced to the solvent residual signals with respect to tetramethylsilane (TMS), for ^{31}P with phosphoric acid. If necessary, 2D-experiments were used for a correct assignment of the signals (HH-COSY NMR, HSQC NMR, DOSY NMR). ^{1}H-NMR data are reported as follows: chemical shift in ppm (parts per million), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad, n. r. = not resolved), coupling constant ([Hz]). ^{13}C-NMR spectra signals were referenced to the solvent residual signals with respect to TMS. The evaluation was performed by *MestReNova* software package.

Elemental Analysis

Elemental analyses were carried out by the microanalytical laboratory of the Technical University of Munich on a HEKAtech Euro EA CHNSO-Analyzer and a Varian AA280FS fast sequential AAS spectrometer. Values are given in percent by weight.

Mass Spectrometry

Electron spray ionization mass spectra (ESI-MS) were recorded on *Thermo Scientific* LTQ Fleet Ultra spectrometer in acetonitrile. m/z is reported in an atomic units per elementary charge.

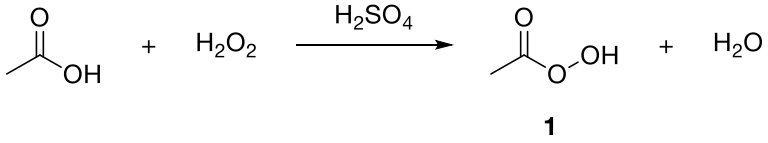
IR/Raman Spectrometry

Infrared spectra were measured on a Alpha FT-IR from Bruker with an ATR device using a platinum diamond. The interferometer range was 450 to 4000 cm^{-1}.

5.3 Synthesis

In general, there were different catalytic systems tested, which are already established as epoxidation catalysts and have the ability to transfer either an oxygen or peroxidic group. To make the systems comparable there were used 4 different acids: acetic acid, caproic acid, decanoic acid and phthalimidocaproic acid. The reactions were performed for qualitative analytics and therefore the reactions were performed until a decomposition of the product took place.

peracetic acid *via* Caro's acid



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Scheme 30: Synthesis of peracetic acid *via* peroxymonosulfuric acid.

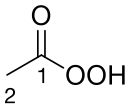
6.73 mL H_2O_2 (30%) (69.30 mmol, 1.0 eq.) are cooled to 0 °C and 0.051 mL concentrated phosphoric (0.97 mmol) are slowly added. After a temperature of 0 °C, 10.00 mL (173.20 mmol, 2.5 eq.) acetic acid are added dropwise without increasing the reaction temperature higher than 5 °C. Then 0.20 mL concentrated sulfuric acid (4.10 mmol, 0.06 eq.) are added and the reaction is stirred for 1 h in the ice bath and thereafter for 24 h at room temperature. The product percentage was 24%.

To decrease the decomposition the product was characterized without further purification.

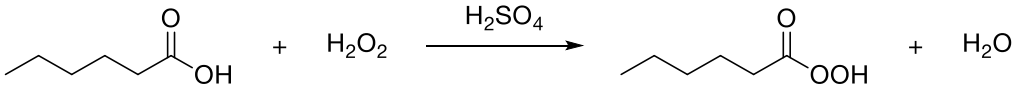
^{1}H-NMR (400 MHz, 298.6 K, D_2O) δ = 1.91 (s, CH_3)

^{13}C-NMR (101 MHz, 298.6 K, D_2O) δ = 172.5 (C^1), 16.6 (C^2)

IR (ATR, $\tilde{\nu}$, in [cm^{-1}]): 3392 (br, ν(OH)), 1642 (s-m, ν(C=O)), 1370 (s, ν(C-O)), 1227 (s-m, δ(COOH))



Percaproic acid *via* Caro's acid



Scheme 31: Synthesis of percaproic acid *via* peroxymonosulphuric acid.

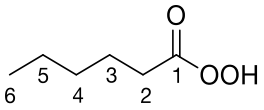
2.50 mL caproic acid (20.00 mmol, 1.0 eq.) are dissolved in 4.64 mL concentrated sulfuric acid (87.10 mmol, 4.4 eq.) and cooled down to -5 °C until the solution turned brown. 2.91 mL H_2O_2 (30%, 30.0 mmol, 1.5 eq.) are added dropwise, the yellow solution is thawed to room temperature and stirred for 3 h. The product percentage was 86%.

To decrease the decomposition the product was characterized without further purification.

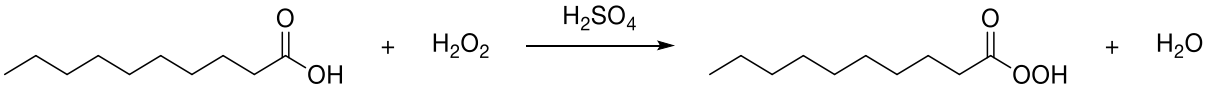
^{1}H-NMR (400 MHz, 298.5 K, C_6D_6) δ = 11.50 (s, 1H, O*H*), 1.83 (t, 2H, C^2*H*$_2$), 1.29 (m, 2H, C^3*H*$_2$), 1.01 (m, 2H, C^4*H*$_2$), 0.93 (m, 2H, zC^5*H*$_2$), 0.71 (t, C^6*H*$_3$).

^{13}C-NMR (101 MHz, 298.5 K, C_6D_6) δ = 174.6 (*C*^{1}), 30.9 (*C*^{2}), 30.1 (*C*^{3}), 24.2 (*C*^{4}), 22.12 (*C*^{5}), 13.6 (*C*^{6}).

IR (ATR, $\tilde{\nu}$, in [cm^{-1}]): 3269 (br, ν(OH)), 1752 (s-m, ν(C=O)), 1154 (s-m, δ(COOH))



Perdecanoic acid *via* Caro's acid



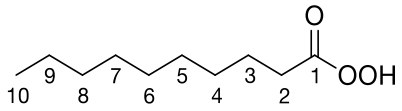
Scheme 32: Synthesis of perdecanoic acid *via* Caro's acid.

8.62 g decanoic acid (50.00 mmol, 0.5 eq.) are dissolved in 25.0 mL concentrated sulphuric acid (469.30 mmol, 9.4 eq.) and cooled down to 0 °C. 10.50 mL H_2O_2 (30%, 0.10 mol, 1.0 eq.) are added dropwise during 15-20 min without increasing the reaction temperature above 5 °C. The solution is stirred for 90 min until the product is precipitated completely. Afterwards the suspension is added to ice water and the white crystals filtered. They are washed with saturated $(NH_4)_2SO_4$ solution (4 x 25.00 mL) and cold water (3 x 25.00 mL). The product is dried under vacuum. 92% yield are reached.

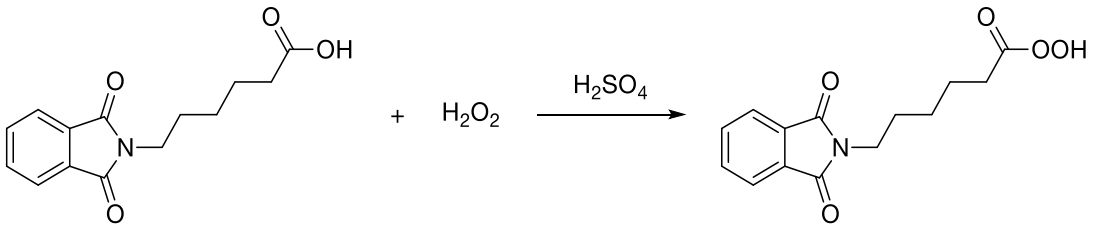
^{1}H-NMR (400 MHz, 298.8 K, C_6D_6) δ = 11.32 (s, 1 H, OH), 1.78 (t, 2 H, C^2H_2), 1.28 (m, 4 H, $C^{3,4}H_2$), 1.19 (m, 4 H, $C^{5,6}H_2$), 1.09 (m, 2 H, C^7H_2), 0.98 (m, 4 H, $C^{8,9}H_2$), 0.91 (t, 3 H, $C^{10}H_3$).

^{13}C-NMR (101 MHz, 298.8 K, C_6D_6) δ = 174.4 (C^1), 32.0 (C^2), 29.9 (C^3), 29.4 (C^4), 29.4 (C^5), 29.1 (C^6), 28.8 (C^7), 24.5 (C^8), 22.8 (C^9), 14.1 (C^{10}).

IR (ATR, $\tilde{\nu}$, in [cm^{-1}]): 3260 (br, ν(OH)), 1750 (s, ν(C=O)), 1154 (s, δ(COOH)), 1104 (s, ν(O-O)), 875 (s, δ(OH-O)).



Phthalimidoperoxocaproic acid *via* Caro's acid



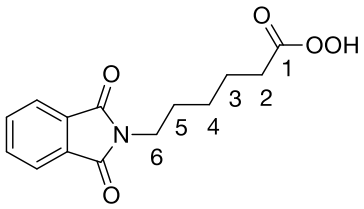
Scheme 33: Synthesis of PAP *via* Caro's acid.

6.53 g PC (25.00 mmol, 1.0 eq.) are dissolved in 12.50 mL concentrated sulphuric acid (0.23 mmol, 9.4 eq.) and cooled down to 0 °C. 10.50 mL H_2O_2 (30%, 0.10 mol, 4.0 eq.) are added dropwise for 10-15 min without increasing the temperature over 5 °C. The solution is stirred for 10 min until the product precipitates completely. The suspension is added to 50.00 mL ice water and the product is filtered. Then, the product is washed with saturated $(NH_4)_2SO_4$ solution (4 x 25.00 mL) and cold water (3 x 25.00 mL). The product is dried under vacuum. 6.51 g of PAP (94%) are obtained.

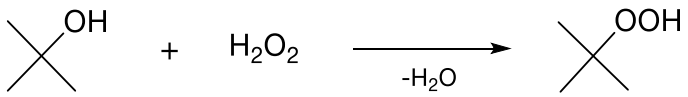
^{1}H-NMR (400 MHz, 298.8 K, C_6D_6) δ = 11.40 (s, 1 H, OH), 7.47 (m, 2 H, $CH_{arom.}$), 6.90 (m, 2 H, $CH_{arom.}$), 3.37 (m, 2 H, C^6H_2), 1.68 (m, 2 H, C^2H_2), 1.30 (m, 2 H, C^5H_2), 1.18 (m, 2 H, C^3H_2), 0.85 (t, 2 H, C^4H_2).

^{13}C-NMR (101 MHz, 298.8 K, C_6D_6) δ = 174.0 (C^1), 167.8 (C=O), 133.4 ($C_{arom.}$), 132.4 ($C_{arom.}$), 122.75 ($C_{arom.}$), 37.3 (C^6), 29.7 (C^2), 27.9 (C^5), 25.9 (C^3), 23.9 (C^4).

IR (ATR, $\tilde{\nu}$, in [cm^{-1}]): 3393 (br, ν(OH)), 1759 (s, ν(C=O)), 1150 (s, δ(COOH)), 935 (s, ν(O-O$^-$)), 741 (s, δ(OH-O)).



Oxidative solution I (with *tert.*-butanol)



Scheme 34: Synthesis of ^{t}BuOOH.

78.60 g ^{t}BuOH (1.10 mol, 1.0 eq.) are melted and 30.00 mL H_2O_2 (30%. 1.20 mmol, 1.2 eq.) are added. The solution is cooled down to 0 °C and after addition of 30.00 g $MgSO_4$, the mixture is stirred for 3 h at cooled temperature. The solid is filtrated and the content of the peroxidic species in the mother liquor (= oxidative solution I) is determined by iodometric titration.

Therefore 3.00 mL oxidative solution I are diluted in 97.00 mL water. 20.00 mL of diluted solution are combined with 20.00 mL diluted sulphuric acid (1 M). 1.00 g KI are added and the solution is again diluted with water to total volume of 100 ml. After 1 h the solution is then titrated with 0.10 M $Na_2S_2O_3$ solution until the solution becomes yellow. Shortly before the colour vanishes, a few drops of fresh starch solution are added for better identification of the turnover point. The titration is completed after discolouration.

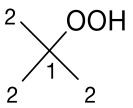
The oxidative solution I is stored in the fridge.

Titration: Peroxide content = 5.2 molL^{-1}

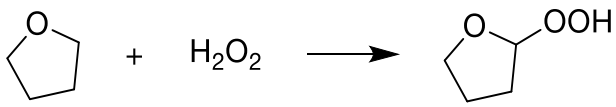
^{1}H-NMR (400 MHz, 298.8 K, D_2O) δ = 1.27 (s, 9 H, 3 CH_3).

^{13}C-NMR (101 MHz, 298.8 K, D_2O) δ = 69.4 (C^1), 30.3 (3 C^2).

IR (ATR, $\tilde{\nu}$, in [cm^{-1}]): 3326 (br, ν(OH)), 2974 (s, ν(C-H)), 1367 (s, ν(C-O)), 1192 (s, δ(COOH)), 902 (s, δ(OH-O)).



Oxidative solution II (with THF)



Scheme 35: Synthesis of THF peroxide.

100.00 mL freshly distilled THF are cooled down to 0 °C and combined with 30.00 mL H_2O_2 (30%). The solution is stirred for 30 min under cooling and 30.00 g of $MgSO_4$ are added, and afterwards stirred for another 3 h. The suspension is filtrated and the mother liquor (= oxidative solution II) is then iodometrically titrated.

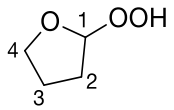
Therefore 3.00 mL oxidative solution I are diluted in 97.00 mL water. 20.00 mL of diluted solution are combined with 20.00 mL diluted sulphuric acid (1 M). 1.00 g KI are added and the solution again diluted with water to a total volume of 100 ml. After 1 h the solution is titrated with 0.10 M $Na_2S_2O_3$ solution until a yellow colour appears. Shortly before the colour vanishes a few drops of fresh starch solution are added for better identification of the turnover point. The titration is completed after discolouration.

The oxidative solution I is stored in the fridge.

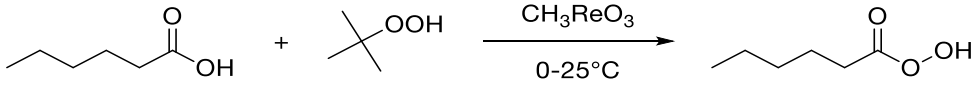
Titration: Peroxide content = 6.0 $molL^{-1}$

^{1}H-NMR (400 MHz, 298.0 K, C_6H_6) δ = 3.27 (q, 3 H, C^1H, C^4H_2), 1.1 (t, 4 H, 2 $C^{2,3}H_2$).

^{13}C-NMR (101 MHz, 298.0 K, C_6H_6) δ = 65.8 (2 $C^{1,4}$), 15.0 (2 $C^{2,3}$)



Percaproic acid *via* MTO and oxidative solution I

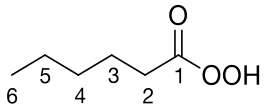


Scheme 36: oxidation of caproic acid *via* MTO and ^{t}BuOOH.

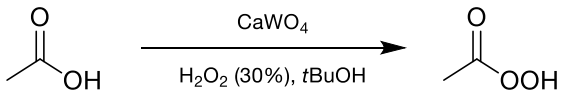
19.20 mL oxidative solution I (0.10 mol, 4.0 eq.) are cooled down to 0 °C. 50.00 mg MTO (0.20 mmol, 0.008 eq.) are added and the solution is stirred for 20 min, until the solution turns yellow and the active species is formed. 3.12 mL caproic acid (25.00 mmol, 1.0 eq.) are added and the solution is stirred for 2 h under cooling. After thawing to room temperature the reaction solution is stirred for 11 d. The product percentage is 13%.

^{1}H-NMR (400 MHz, 298.5 K, C_6D_6) δ = 2.02 (t, 2H, C^2H_2), 1.43 (m, 2H, C^3H_2), 1.10 (m, 4H, $C^{4,5}H_2$), 0.75 (t, 3H, C^6H_3).

^{13}C-NMR (101 MHz, 298.5 K, C_6D_6) δ = 173.3 (C^1), 31.1 (C^2), 31.0 (C^3), 24.5 (C^4), 22.2 (C^5), 13.7 (C^6).



Peracetic acid *via* $CaWO_4$

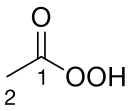


Scheme 37: Synthesis of peracetic acid *via* $CaWO_4$.

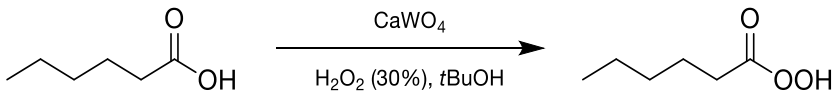
To a solution of 9.00 mL H_2O_2 (30%, 2.72 g, 80.0 mmol, 4 eq.), 9.00 mL (7.11 g, 95.9 mmol, 4.8 eq.) ^{t}BuOH and 57.00 mg $CaWO_4$ (0.198 mmol, 0.01 eq.) are added. The solution is stirred and warmed up to 45 °C until a yellow colour appears. 1.14 mL acetic acid (1.20 g, 20.0 mmol, 1.0 eq.) are added slowly and warmed up to 65 °C. After 4 d product signals (14%) can be identified.

^{1}H-NMR (D_2O, 298.8 K, 400.13 MHz): δ [ppm] = 1.87 (s, 3 H, CH_3) (acidic protons are desolved)

^{13}C-NMR (D_2O, 298.8 K, 100.53 MHz): δ [ppm] = 172.13 (COOOH), 16.19 (CH_3).



Percaproic acid *via* $CaWO_4$

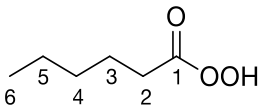


Scheme 38: Synthesis of Percaproic acid *via* $CaWO_4$.

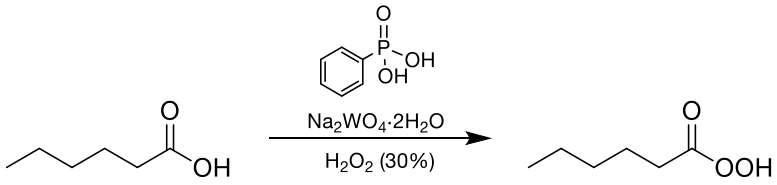
To a solution of 9.00 mL H_2O_2 (30%, 2.72 g, 80.00 mmol, 4.0 eq.) 9.00 mL ^{t}BuOH (7.11 g, 95.90 mmol, 4.8 eq.) and 57.00 mg $CaWO_4$ (0.198 mmol, 0.01 eq.) are added. The solution is stirred and warmed up to 45 °C until a yellow colour appeared. 2.50 mL caproic acid (2.32 g, 20.00 mmol, 1.0 eq.) are added slowly and the solution is warmed up to 65 °C. After 14 h some product signals (6.1%) can be identified.

^{1}H-NMR (C_6D_6, 298.8 K, 400.13 MHz): δ [ppm] = 1.97 (t,C^2H_2), 1.11 (t, C^5H_2), 0.74 (t, 3 H, C^6H_3), (acidic protons desolved, missing CH_2-groups under ^{t}BuOH signal).

^{13}C-NMR (C_6D_6, 298.8 K, 100.53 MHz): δ [ppm] = 173.30 (C^1OOOH), 28.28 (C^2H_2), 26.98 (C^3H_2), 24.48 (C^4H_2), 22.21 (C^5H_2), 13.71 (C^6H_3).



Percaproic acid *via* Phenylphosphoric acid and $Na_2WO_4 \cdot 2\ H_2O$

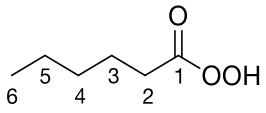


Scheme 39: Percaproic acid *via* Na_2WO_4 and phenylphosphoric acid.

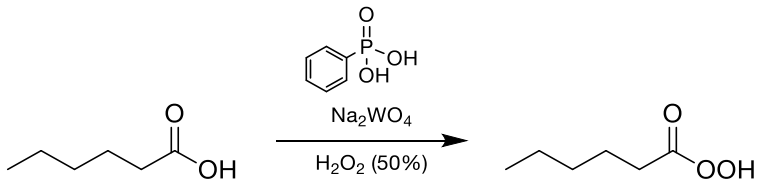
3.30 mg $Na_2WO_4 \cdot 2\ H_2O$ (0.01 mmol, 0.001 eq.), 4.04 mg methyltrioctylammonium chloride (0.01 mmol, 0.001 eq.) and 1.60 mg phenylphosphoric acid (0.01 mmol, 0.001 eq.) are solved in 2.55 mL H_2O_2 (30%, 0.85 g, 25.00 mmol, 2.5 eq.). The reaction mixture is stirred for 10 min at room temperature. Afterwards, 1.25 mL caproic acid (1.16 g, 10.00 mmol, 1.0 eq.) are added. Product signals can be identified after 3 d (4.5%).

^{1}H-NMR (C_6D_6, 298.8 K, 400.13 MHz): δ [ppm] = 1.98 (t, 2 H, C^2H_2), 1.39 (t, 2H, C^3H_2), 1.03 (t, 4H, $C^{4,5}H_2$), 0.62 (t, 3 H, C^6H_3), (signal for OOH too weak).

^{13}C-NMR (C_6D_6, 298.8 K, 100.53 MHz): δ [ppm] = 174.23 (C^1OOOH), 31.12 (C^2H_2), 30.40 (C^3H_2), 24.42 (C^4H_2), 22.27 (C^5H_2), 13.71 (C^6H_3).



Percaproic acid *via* Phenylphosphoric acid and Na_2WO_4 (water reduced)

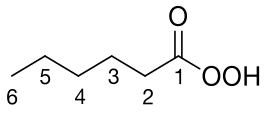


Scheme 40: Percaproic acid *via* dried Na_2WO_4 and phenylphosphoric acid.

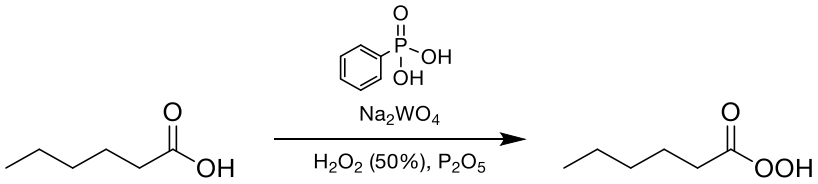
$Na_2WO_4 \cdot 2\ H_2O$ is dried over 16 h under vacuum *via* Schlenk technique. 3.12 mg dried Na_2WO_4 (0.01 mmol, 0.001 eq.), 4.04 mg methyltrioctylammonium chloride (0.01 mmol, 0.001 eq.) and 1.6 mg phenylphosphoric acid (0.01 mmol, 0.001 eq.) are solved in 1.40 mL H_2O_2 (50%, 0.84 g, 25.00 mmol, 2.5 eq.). The reaction mixture is stirred for 2 h at room temperature. 1.25 mL caproic acid (1.16 g, 10.0 mmol, 1.0 eq.) are added. After 1 h the temperature is set on 55 °C. The highest product signals are achieved after 1 d (6.5%).

^{1}H-NMR (C_6D_6, 298.8 K, 400.13 MHz): δ [ppm] = 1.91 (t, 2 H, C^2H_2), 1.34 (t, 2H, C^3H_2), 1.00 (t, 4H, $C^{4,5}H_2$), 0.62 (t, 3 H, C^6H_3), (signal for OOH too weak).

^{13}C-NMR (C_6D_6, 298.8 K, 100.53 MHz): δ [ppm] = 174.27 (C^1OOOH), 31.10 (C^2H_2), 30.36 (C^3H_2), 24.40 (C^4H_2), 22.26 (C^5H_2), 13.67 (C^6H_3).



Percaproic acid *via* Phenylphosphoric acid and Na_2WO_4 (water reduced, with P_2O_5 as drying agent)

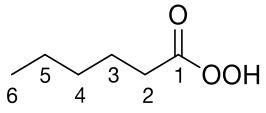


Scheme 41: Percaproic acid *via* dried Na_2WO_4, phenylphosphoric acid and P_2O_5 as drying agent.

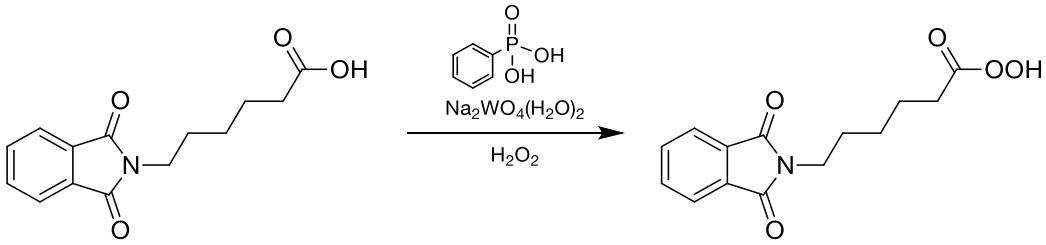
$Na_2WO_4 \cdot 2\ H_2O$ is dried over 16 h under vacuum *via* Schlenk technique. 3.12 mg dried Na_2WO_4 (0.01 mmol, 0.001 eq.), 4.04 mg methyltrioctylammonium chloride (0.01 mmol, 0.001 eq.) and 1.58 mg phenylphosphoric acid (0.01 mmol, 0.001 eq.) are solved in 1.40 mL H_2O_2 (50%, 0.84 g, 25.00 mmol, 2.5 eq.) and the reaction mixture is stirred for 2 h at room temperature. Then 1.25 mL caproic acid (1.16 g, 10.00 mmol, 1.0 eq.) are added. After 2 h the temperature is set on 55 °C. The highest product signals are achieved after 1 d (12.5%).

^{1}H-NMR (C_6D_6, 298.8 K, 400.13 MHz): δ [ppm] = 1.98 (t, 2 H, C^3H_2), 1.39 (t, 2H, C^4H_2), 1.03 (t, 4H, $C^{4,5}H_2$), 0.72 (t, 3H, C^6H_3), (signal for OOH too weak).

^{13}C-NMR (C_6D_6, 298.8 K, 100.53 MHz): δ [ppm] = 174.55 (C^1OOOH), 31.35 (C^2H_2), 30.64 (C^3H_2), 24.64 (C^4H_2), 22.50 (C^5H_2), 13.90 (C^6H_3).



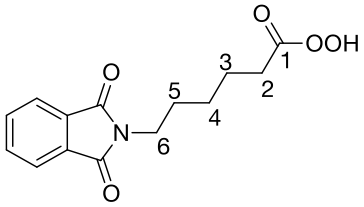
Phthalimidopercaproic acid *via* Phenylphosphoric acid and Na_2WO_4



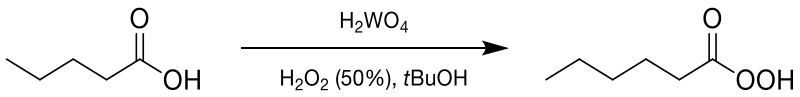
Scheme 42: Phthalimidopercaproic acid *via* Phenylphosphoric acid and Na_2WO_4.

3.12 mg dried Na_2WO_4 (0.01 mmol, 0.01 eq.), 4.04 mg methyltrioctylammonium chloride (0.01 mmol, 0.01 eq.) and 1.58 mg phenylphosphoric acid (0.01 mmol, 0.01 eq.) are solved in 1.40 mL H_2O_2 (50%, 0.84 g, 25.00 mmol, 25 eq.) and 3.70 mL ^{t}BuOH. The reaction mixture is stirred for 1 h at room temperature. 261 mg PC (1.00 mmol, 1.0 eq.) are added. After 1 h the temperature is set on 55 °C. The highest product signals are achieved after 6 d (21.8%).

^{13}C-NMR (C_6D_6, 298.8 K, 100.53 MHz): δ [ppm] = 173.44 (C^1), 169.18 (C=O), 134.46 (C_{arom}), 133.26 (C_{arom}), 123.57 (C_{arom}), 38.79 (C^6), 30.08 (C^2), 28.25 (C^5), 26.21 (C^3), 24.46 (C^4).



Percaproic acid *via* H_2WO_4

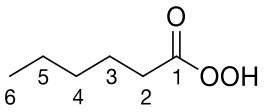


Scheme 43: Synthesis of Percaproic acid *via* H_2WO_4.

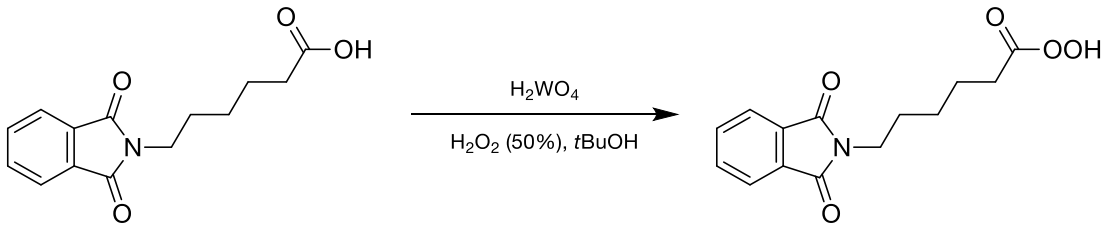
To a solution of 4.95 mL H_2O_2 (50%, 2.97 g, 80.00 mmol, 4.0 eq.) and 9.00 mL ^{t}BuOH (7.11 g, 95.90 mmol, 4.8 eq.) are added 49.47 mg H_2WO_4 (0.198 mmol, 0.01 eq.). The solution is stirred and warmed up to 45 °C. 2.50 mL caproic acid (2.32 g, 20.00 mmol, 1.0 eq.) are added slowly. After 5 d the highest product signals are achieved (23.1%).

^{1}H-NMR (C_6D_6, 298.8 K, 400.13 MHz): δ [ppm] = 2.01 (t,C^2H_2), 1.42 (t, C^3H_2), 1.14 (t, C^4H_2) 1.06 (t, C^5H_2), 0.74 (t, 3 H, C^6H_3), (acidic protons desolved, missing CH_2-groups under ^{t}BuOH signal).

^{13}C-NMR (C_6D_6, 298.8 K, 100.53 MHz): δ [ppm] = 173.63 (C^1OOOH), 28.13 (C^2H_2), 28.13 (C^3H_2), 24.72 (C^4H_2), 22.45 (C^5H_2), 13.94 (C^6H_3).



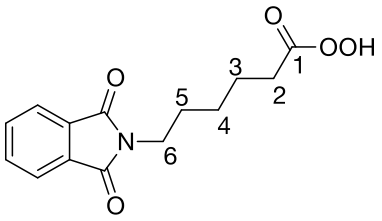
Phthalimidopercaproic acid *via* H_2WO_4



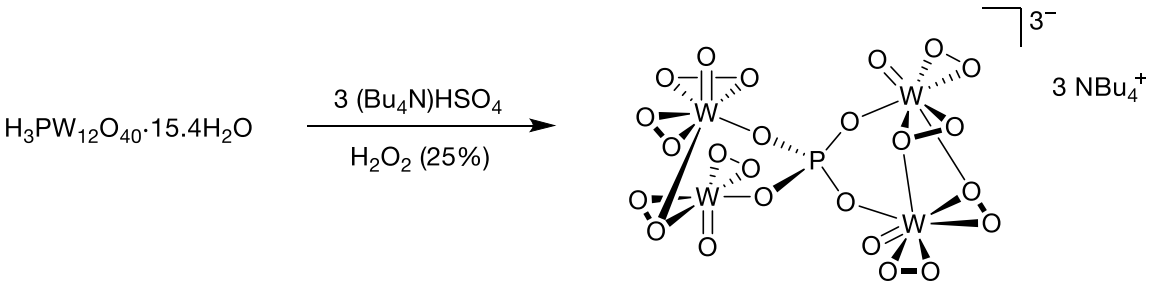
Scheme 44: Synthesis of Phthalimidocaproic acid *via* H_2WO_4.

To a solution of 4.95 mL H_2O_2 (50%, 2.97 g, 80.0 mmol, 4 eq.) and 9.0 mL ^{t}BuOH (7.11 g, 95.9 mmol, 4.8 eq.) are added 49.47 mg H_2WO_4 (0.198 mmol, 0.01 eq.). The solution is stirred and warmed up to 45 °C. Then, 5.23 g PC (20.0 mmol, 1.0 eq.) are added. After 7 d the highest product signals are achieved (18.7%).

^{13}C-NMR (C_6D_6, 298.8 K, 100.53 MHz): δ [ppm] = 173.22 (C^1OOOH), 168.67 (C=O), 134.19 (C_{arom}), 132.24 (C_{arom}), 123.36 (C_{arom}), 37.75 (C^6), 30.81 (C^2), 28.28 (C^5), 25.83(C^3), 24.49 (C^4).



Synthesis of W1



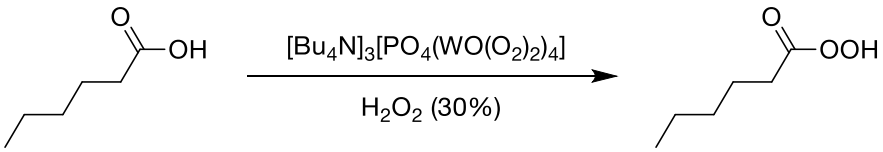
Scheme 45: Synthesis of $(Bu_4N)_3\{PO_4[WO(O_2)_2]_4\}$.

4.01 g $H_3PW_{12}O_{40}\cdot 15.4\ H_2O$ (1.27 mmol, 1.0 eq.) are solved in 5 mL H_2O. 34.00 mL H_2O_2 (25%, 0.25 mol, 200.0 eq.) are slowly added and the reaction mixture is stirred for 30 min at room temperature. A solution of 1.29 g Bu_4NHSO_4 (3.81 mmol, 3.0 eq.) in 2.00 mL H_2O is added and stirred for 1 h. The suspension is filtered and the solid washed with water (3 x 5 mL) and dried in vacuum at the *Schlenk*-line.

IR (ATR, $\tilde{\nu}$, in [cm^{-1}]): 1064 (vs, ν_s (W=O_t)), 970 (s, double, ν_{as}(W=O_t)), 840 (m, ν (O-O)).

EA: [%] calc.: C (30.7), H (5.8), N (2.24), P (1.65), W (39.16). found: C (29.04), H (5.79), N (2.15), P (1.57), W (38.82).

Percaproic acid *via* $(Bu_4N)_3\{PO_4[WO(O_2)_2]_4\}$

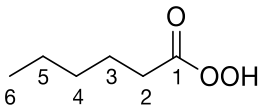


Scheme 46: Oxidation of caproic acid *via* $(Bu_4N)_3\{PO_4[WO(O_2)_2]_4\}$ and 30% H_2O_2.

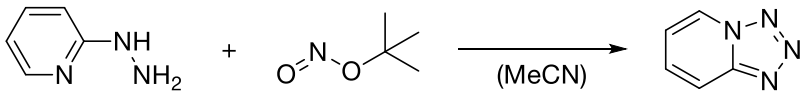
50 mg $(Bu_4N)_3\{PO_4[WO(O_2)_2]_4\}$ (0.198 mmol, 0.15 eq.) are solved in 4.00 mL H_2O_2 (30%). 0.16 mL caproic acid (151 mg, 1.30 mmol, 1 eq.) are added slowly and the reaction mixture is stirred at 90 °C for 16 h. The highest product signals are achieved after 48 h (25.7%)

^{1}H-NMR (C_6D_6, 298.8 K, 400.13 MHz): δ [ppm] = 1.76 (t,C^2H_2), 1.26 (t, C^3H_2), 1.00 (t, C^4H_2), 0.90 (t, C^5H_2), 0.72 (t, 3 H, C^6H_3), (acidic protons desolved).

^{13}C-NMR (C_6D_6, 298.8 K, 100.53 MHz): δ [ppm] = 174.62(C^1OOOH), 31.06 (C^2H_2), 30.18 (C^3H_2), 24.36 (C^4H_2), 22.32 (C^5H_2), 13.87 (C^6H_3).



Tetrazolo[1,5-α]pyridin



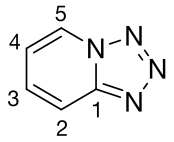
Scheme 47: Synthesis of tetrazolo[1,5-α]pyridine

25.00 g 2-hydrazinopyridine (0.23 mol, 1.0 eq.) are solved in 200 mL acetonitrile and cooled to 0 °C. During a period of 20 min a solution of 118.10 g *tert.*-butylnitrite (1.15 mol, 5.0 eq.) in 200 mL acetonitrile are added. The occurred orange solution is thawed to room temperature and stirred for 18 h. Afterwards 500 mL ethylacetate are added and the solution washed with saturated Na_2CO_3 solution (2 x 100 mL), water (1 x 100 mL) and saturated NaCl solution (2 x 100 mL). After drying over Na_2SO_4 and under vacuum 19.50 g (70.8%) of an orange solid is received.

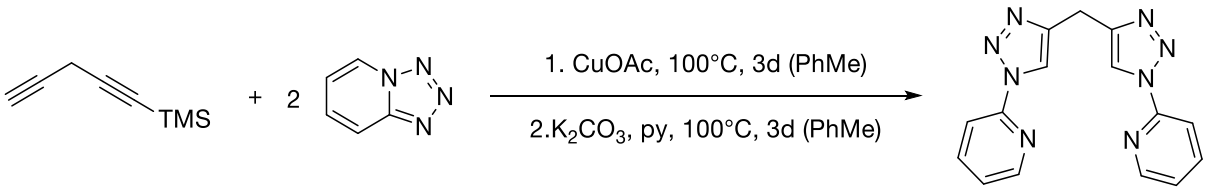
^{1}H-NMR ($CDCl_3$, 298.8 K, 400.13 MHz): δ [ppm] = 8.73 (d, 1H, H_{ar}), 7.93 (d, 1H, H_{ar}), 7.57 (d, 1H, H_{ar}), 7.14 (d, 1H, H_{ar}).

^{13}C-NMR ($CDCl_3$, 298.8 K, 100.53 MHz): δ [ppm] = 148.74 (C^1), 131.94 (C_{ar}), 125.60 (C_{ar}), 116.67 (C_{ar}), 116.21 (C_{ar}).

EA [%]: calc.(in %): C (50.0), H (3.4), N (46.6). found: C (49.89), H (3.24), N (46.12).



Bis(1-(2-pyridyl)-1,2,3-triazol-4-yl)methane



Scheme 48: Synthesis of bis(1-(2-pyridyl)-1,2,3-triazol-4-yl)methane.

1.37 g tetrazolo[1,5-α]pyridine (11.41 mmol, 2.0 eq.) are prepared with 139.75 mg CuOAc (1.14 mmol, 0.2 eq.), solved in 30.00 mL $toluol_{dd}$ and 777.0 mg 1-trimethylsilyl-1,4-pentadiin (5.70 mmol, 1.0 eq.) are added. The reaction mixture is boiled at 100 °C for 3 d and then cooled to room temperature. 6 mL H_2O_d are added, as well as 1.5 g K_2CO_3 (10.84 mmol, 1.9 eq.) and 0.5 mL pyridine (495.00 mg, 6.27 mmol, 1.0 eq.). The mixture is again boiled at 100 °C and for 3 d. After cooling to room temperature to the suspension are added 100 mL $CDCl_3$, 30 mL isopropanol and 100 mL NH_3 solution (2 M) and stirred vigorously for 12 h. After filtration 350 mg (19.5%) of the product is purified through 2 columns.

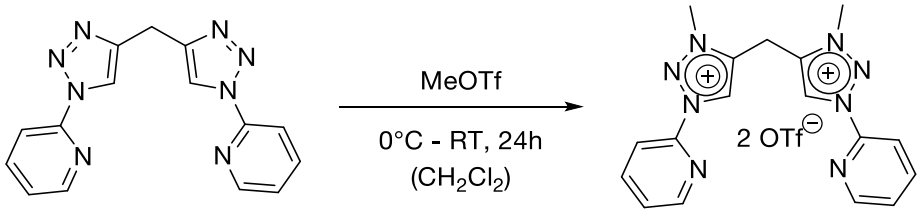
^{1}H-NMR (DMSO-d^6, 298.8 K, 400.13 MHz): δ [ppm] = 8.72 (s, 2H, H_{trz}), 8.59 (m, 2H, H_{py}), 8.12 (m, 4H, H_{py}), 7.54 (m, 2H, H_{py}), 4.31 (s, 2H, CH_2).

^{13}C-NMR (DMSO-d^6, 298.8 K, 100.53 MHz): δ [ppm] = 148.90 (C_{py}), 145.45 (C_{trz}), 140.08 (C_{py}), 124.18 (C_{py}), 119.94 (CH_{trz}), 113.56 (C_{py}), 21.99 (CH_2).

ESI-MS (m/z): product calc: 304.32. found: 305.

Rf(CH_2Cl_2 : MeOH = 95 : 5) ≈ 0.5.

4,4'-methylene bis(3-methyl-1-(2-pyridinyl)-1,2,3-triazolium) triflate



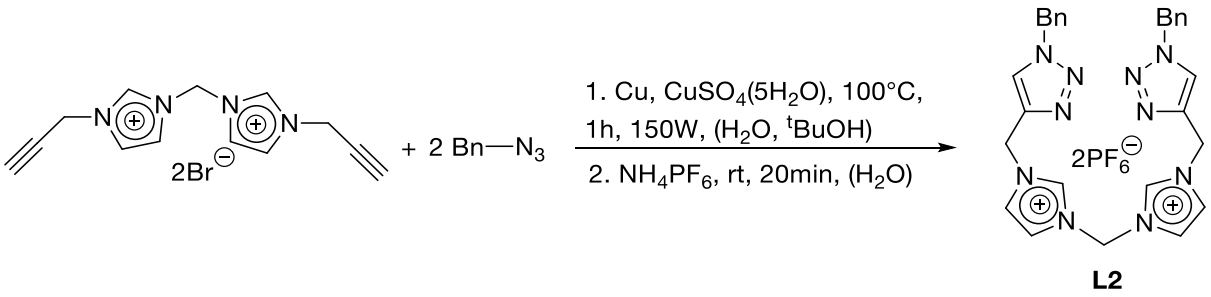
L1

Scheme 49: Synthesis of 4,4'-methylene bis(3-methyl-1-(2-pyridinyl)-1,2,3-triazolium) triflate **L1**

0.14 g bis(1-(2-pyridyl)-1,2,3-triazol-4-yl) methane (0.46 mmol, 1.0 eq.) are dissolved in 4.20 mL DCM_d and cooled to 0 °C. 0.12 mL (1.06 mmol, 2.3 eq.) MeOTf are added dropwise and after 30 min is the mixture thawed to room temperature. The solution is stirred vigorously for 2 d and 0.12 mL MeOTf (1.06 mmol, 2.3 eq.) are added again. The mixture is stirred for another 3 d. Afterwards the solution and excessive MeOTf are removed under reduced pressure. The brown solid is dissolved in 3 mL MeCN and 15 mL of Et_2O until the product precipitates. After repeating the precipitation 121 mg (41.3%) of a bright solid is received.

^{1}H-NMR (DMSO-d^6, 298.8 K, 400.13 MHz): δ [ppm] = 9.71 (s, 2H, CH_{trz}), 8.77 (dd, 2H, CH_{py}), 8.33 (dd, 2H, CH_{py}), 8.23 (d, 2H, CH_{py}), 7.84 (dd, 2H, CH_{py}), 4.96 (s, 2H, CH_2), 4.48 (s, 6H, CH_3).

Methylenbis(1-(1-benzyl-1,2,3-triazol-4-yl)methylimidazolium)hexafluorophosphate.



L2

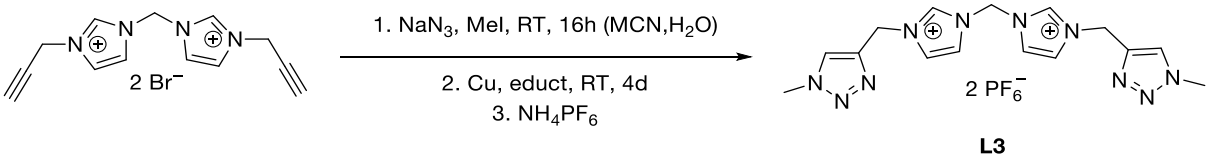
Scheme 50: Synthesis of Methylenbis(1-(1-benzyl-1,2,3-triazol-4-yl)methylimidazolium)hexafluorophosphate **L2**

161.00 mg 1,1'-methylene bis(3-propargylimidazolium)bromide (0.50 mmol, 1.0 eq.), 0.144 mL benzyl azid (153.00 mg, 1.15 mmol, 2.3 eq.), 1.06 mg Cu powder (0.03 mmol, 0.06 eq.) and 11.2 mg $CuSO_4$ (0.07 mmol, 0.14 eq.) are solved in 2 mL H_2O and 2 mL ^tBuOH in a microwave vessel. The mixture is boiled at 100 °C and 150 W for 1 h. After removing the solvents under reduced pressure at 60 °C the raw product is dissolved in 20 mL hot water and filtrated. The mother liquor is slowly added to a solution of 339.00 mg NH_4PF_6 (2.50 mmol, 5.0 eq.) in 5 mL H_2O. 259.75 mg (80%) of a white powder is received, which is filtrated and washed with water (3 x 15 mL), MeOH (1 x 15 mL) and Et_2O (3 x 15 mL) and dried in an oven.

^{1}H-NMR (DMSO-d^6, 298.8 K, 400.13 MHz): 9.53 (t, 2H, NCHN), 8.34 (s, 2H, CH_{trz}), 8.00 (t, 2H, CH_{Im}), 7.86 (t, 2H, CH_{Im}), 7.35 (m, 10H, CH_{Bn}), 6.62 (s, 2H, NCH_2N), 5.64 (s, 4H, $N_{trz}CH_2C_{ar}$), 5.57 (s, 4H, $N_{Im}CH_2C_{trz}$).

ESI-MS (m/z): product-PF_6^- calc.: 637.21, found: 636.96; product-$2PF_6^-$ calc.: 492.25. found: 491.20; 2 x product + 3 x PF_6^- calc.: 1419.38, found: 1418.76.

Methylenbis(1-(1-methyl-1,2,3-triazol-4-yl)methylimidazolium)hexafluorophosphate



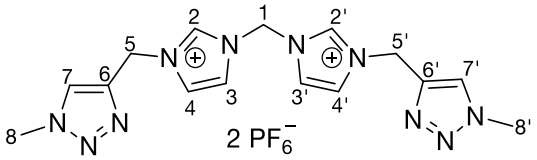
L3

Scheme 51: Synthesis of Methylenbis(1-(1-methyl-1,2,3-triazol-4-yl)methylimidazolium)hexafluorophosphate **L3**

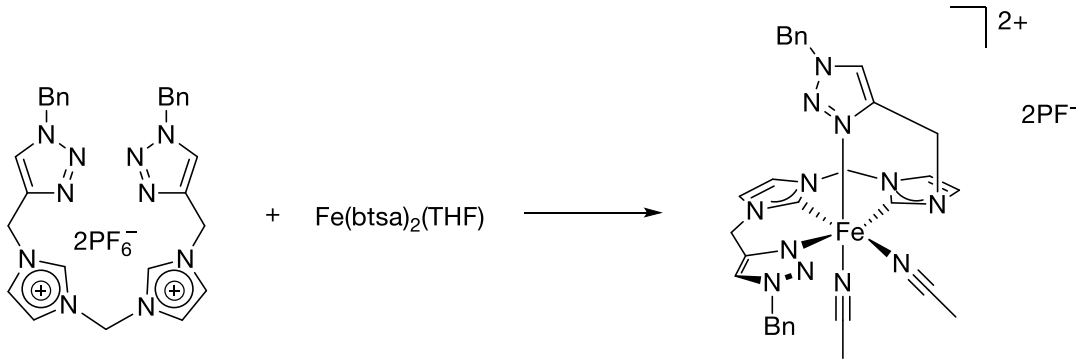
683.63 mg NaN_3 (10.52 mmol, 3.5 eq.) are solved in 3 mL H_2O and 3 mL MeCN with 0.40 mL MeI (6.61 mmol, 2.2 eq.) and stirred at room temperature for 16 h. 1.16 g 1,1′-methylene-bis(propargylimidazolium) bromide (3.00 mmol, 1.0 eq.) and 668.23 mg copper chips (10.52 mmol, 3.5 eq.) are added with 5.00 mL ^{t}BuOH and 5.0 mL (H_2O), and the mixture is stirred at room temperature for 4 d. The suspension is filtrated over celite and the solvents are removed under reduced pressure. The intermediate compound is dissolved in H_2O and filtrated over Al_2O_3 (neutral). Solvents are reduced until only water is left, and the intermediate is dissolved in water again and an aqueous film of 17.00 mL NH_4PF_6 solution (7.51 mmol, 2.5 eq.) is covered in top. During 1-2 h the product precipitates completely. The solution is poured away and the product is washed with H_2O and Et_2O, afterwards dried at 60 °C. 1.62 g (86%) of orange product is obtained.

^{1}H-NMR (CD_3CN, 298.8 K, 400.13 MHz): 8.90 (s, 2H, C^2H), 7.92 (s, 2H, C^7H, $C^{7'}H$), 7.60 (t, 2H, C^3H, $C^{3'}H$), 7.54 (t, 2H, C^4H, $C^{4'}H$), 6.35 (s, 2H, C^1H_2), 5.45 (s, 4H, C^5H_2, $C^{5'}H_2$), 4.07 (s, 6H, C^8H_3, $C^{8'}H_3$).

EA [%]: calc.: C (28.58), H (3.20), N (22.22), F (36.17), P (9.83). found: C (28.14), H (3.13), N (21.32).



Synthesis of FeL2(MeCN)$_2$



Scheme 52: Synthesis of Fe**L2**(MeCN)$_2$

0.50 g **L1** (1.02 mmol, 1.0 eq.) are dissolved in 4.5 mL MeCN. 329.70 mg Fe(btsa)$_2$ (0.73 mmol, 1.15 eq.) are dissolved in another Schlenk tube and freezed in liquid nitrogen. The solution with the ligand is layered on top of the frozen Fe(btsa)$_2$ solution and the mixture is slowly thawed to room temperature while stirring. After 14 h solvents are reduced under reduced pressure, until 2 mL remain. 2 mL of Et_2O_{dry} are added and the first raw product precipitates. After a Whatman filtration 10 mL Et_2O are added until the product precipitates completely. An orange powder as product is gained.

^{1}H-NMR (CD_3CN, 298.8 K, 400.13 MHz): 8.18 (s, 2H, 2 CH_{trz}), 7.69 (s, 1H, CH_{Im}), 7.55 (s, 1H, CH_{Im}), 7.48 (m, 3H, 2 CH_{Im}, CH_{ar}), 7.38 (m, 6H, CH_{ar}), 7.31 (m, 2H, CH_{ar}), 7.09 (m, 1H, CH_{ar}), 6.25 (d, 1H, CH_2), 6.10 (s, 1H, CH_2), 5.79 (d, 1H, CH_2), 5.75 (s, 2H, CH_2), 5.72 (d, 1H, CH_2), 5.57 (m, 1H, CH_2), 5.50 (d, 1H, CH_2), 5.35 (s, 2H, CH_2), 1.94 (s, 6H, CH_3CN).

^{13}C-NMR *(lit.)* (101 MHz, CD_3CN, 298 K, 101 MHz): δ [ppm] = 202.44 (C_{Carben}), 197.27 (C_{Carben}), 146.35 (C_{trz}), 145.87 (C_{trz}), 144.92 (C_{ar}), 136.17 (C_{ar}), 136.08 (C_{ar}), 130.06 (C_{ar}), 129.96 (C_{ar}), 129.81 (C_{ar}), 129.61 (C_{ar}), 129.48 (C_{ar}), 129.27 (C_{ar}), 125.10 (C_{ar}), 124.92 (C_{trz}), 124.83 (C_{trz}), 124.76 (C_{Im}), 124,66 (C_{Im}), 123.97 (C_{Im}), 123.83 (C_{Im}) 62.97 (NCH_2N), 55.99 ($N_{trz}CH_2C_{ar}$), 55.87 ($N_{trz}CH_2C_{ar}$), 45.35 ($N_{Im}CH_2C_{trz}$), 44.66 ($N_{Im}CH_2C_{trz}$).

EA [%]: calc.: C (40.45), H (3.72), N (18.26), Fe (6.07), F (24.77), P (6.73). found: C (39.83), H (3.67), N (17.03).

6 Literature

1. Geiß, R., *Die Verwandlung der Stoffe*. 2017, Berlin, Heidelberg: Springer Spektrum.
2. Weyer, J., *Geschichte der Chemie - Altertum, Mittelalter, 16. bis 18. Jahrhundert*. Vol. 1. 2018, Berlin, Heidelberg: Springer Spektrum. 576.
3. Cdang. *File:Lavoisier decomposition air.png*. 2008; Available from: https://commons.wikimedia.org/wiki/File:Lavoisier_decomposition_air.png?uselang=de.
4. Sidiropoulos, S.S., *POCKET Wörterbuch: Altgriechisch - Deutsch*. 2016: Books on Demand.
5. Scheurer, A., et al., *Peroxide Chemistry: Mechanistic and Preparative Aspects of Oxygen Transfer*. 2000.
6. Schulz, M., *Landmarks in the Development of Organic Peroxide Chemistry*, in *Peroxide Chemistry*, W. Adam, Editor. 2005. p. 1-38.
7. Baeyer, A. and V. Villiger, *Ueber die Einwirkung des Caro'schen Reagens auf Ketone.* Berichte der deutschen chemischen Gesellschaft, 1900. **33**(1): p. 858-864.
8. Renz, M. and B. Meunier, *100 Years of Baeyer–Villiger Oxidations.* European Journal of Organic Chemistry, 1999. **1999**(4): p. 737-750.
9. Volnov, I.I., *Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals*. 2012: Springer US.
10. Ostwald, W. and K.D. Sedlacek, *Der Stein der Weisen: Wie die Alchemie zur Chemie wurde*. 2016: Books on Demand.
11. Wiberg, N., *Lehrbuch der Anorganischen Chemie*. 2008.
12. Brandl, H., E. Täuscher, and D. Weiß, *Keine Angst vor Peroxiden.* Chemie in unserer Zeit, 2016. **50**(2): p. 130-139.
13. Cotton, F.A., *Progress in Inorganic Chemistry*. 2009: Wiley.
14. Valeria Conte, O.B., *Transition Metal Peroxides. Synthesis and Role in Oxidation Reactions*, in *PATAI'S Chemistry of Functional Groups*. 2009.
15. Roşca, D.-A., et al., *Gold peroxide complexes and the conversion of hydroperoxides into gold hydrides by successive oxygen-transfer reactions.* Nature Communications, 2013. **4**(1): p. 2167.
16. Riedel, E. and C. Janiak, *Anorganische Chemie*. 2011: De Gruyter.
17. Butler, A., M.J. Clague, and G.E. Meister, *Vanadium Peroxide Complexes.* Chemical Reviews, 1994. **94**(3): p. 625-638.
18. Dickman, M.H. and M.T. Pope, *Peroxo and Superoxo Complexes of Chromium, Molybdenum, and Tungsten.* Chemical Reviews, 1994. **94**(3): p. 569-584.
19. Mimoun, H., *Oxygen Transfer from Inorganic and Organic Peroxides to Organic Substrates: A Common Mechanism?* Angewandte Chemie International Edition in English, 1982. **21**(10): p. 734-750.
20. Kühn, F.E., R.W. Fischer, and W.A. Herrmann, *Methyltrioxorhenium.* Chemie in unserer Zeit, 1999. **33**(4): p. 192-198.
21. Bolm, C., *Peroxide Chemistry: Mechanistic and Preparative Aspects of Oxygen Transfer*. 2005. p. 494-510.
22. Brückner, R. and W. Zettlmeier, *Reaktionsmechanismen: Organische Reaktionen, Stereochemie, Moderne Synthesemethoden*. 2014: Springer Berlin Heidelberg.
23. Vollhardt, K.P.C., H. Butenschön, and N.E. Schore, *Organische Chemie*. 2011: VCH [Imprint].
24. Strukul, G., *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*. 2013: Springer Netherlands.
25. Hölzl, S.M., et al., *Speciation in iron epoxidation catalysis: A perspective on the discovery and role of non-heme iron(III)-hydroperoxo species in iron-catalyzed oxidation reactions.* Coordination Chemistry Reviews, 2017. **352**: p. 517-536.

26. Jones, C.W. and J.H. Clark, *Introduction to the preparation and properties of hydrogen peroxide*, in *Applications of Hydrogen Peroxide and Derivatives*, C.W. Jones and J.H. Clark, Editors. 1999, The Royal Society of Chemistry. p. 1-36.
27. Zukas, J.A., W. Walters, and W.P. Walters, *Explosive Effects and Applications*. 2002: Springer New York.
28. Müller, P., et al., *Houben-Weyl Methods of Organic Chemistry Vol. VIII, 4th Edition: Peroxides, Carbonic Acid Derivatives, Carboxylic Acids, Carboxylic Acid Derivatives*. 2014: Thieme.
29. G. A. Campbell, P.V.R., *Detonation of hydrogen peroxide vapour.* Institution of Chemical Engineers Symposium Series, 1972. **33**.
30. Gestis, *Wasserstoffperoxid >=70 %*. Gestis.
31. French, W.H., *In Situ Epoxidation Process*, U.S.P. Office, Editor. 1967, Ashland Oil & Redining Company: Kentucky.
32. online, T.E.C.I.-. *Hydrogen peroxide*. 2016.
33. Jones, C.W. and J.H. Clark, *Miscellaneous uses for hydrogen peroxide technology*, in *Applications of Hydrogen Peroxide and Derivatives*, C.W. Jones and J.H. Clark, Editors. 1999, The Royal Society of Chemistry. p. 231-256.
34. Block, S.S., *Disinfection, Sterilization, and Preservation.* Soil Science, 1977. **124**(6): p. 378.
35. Speight, J.G., *Ullmann's Encyclopedia of Industrial Chemistry.* Petroleum Science and Technology, 1999. **17**(3-4): p. 445-445.
36. Ha Q. Pham, M.J.M., *Epoxy Resins*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2005.
37. Dul'neva, L.V. and A.V. Moskvin, *Kinetics of Formation of Peroxyacetic Acid.* Russian Journal of General Chemistry, 2005. **75**(7): p. 1125-1130.
38. Jones, C.W. and J.H. Clark, *Activation of hydrogen peroxide using inorganic and organic species*, in *Applications of Hydrogen Peroxide and Derivatives*, C.W. Jones and J.H. Clark, Editors. 1999, The Royal Society of Chemistry. p. 37-78.
39. Fischer, R.W., *Methyltrioxorhenium*, in *Chemistry*. 1994, Technical University of Munich: Munich.
40. Kück, J.W., R.M. Reich, and F.E. Kühn, *Molecular Epoxidation Reactions Catalyzed by Rhenium, Molybdenum, and Iron Complexes.* The Chemical Record, 2016. **16**(1): p. 349-364.
41. Herrmann, W.A., et al., *Methylrhenium Oxides: Synthesis from R2O7 and Catalytic Activity in Olefin Metathesis.* Angewandte Chemie International Edition in English, 1988. **27**(3): p. 394-396.
42. Kamata, K., et al., *Highly Selective Epoxidation of Cycloaliphatic Alkenes with Aqueous Hydrogen Peroxide Catalyzed by [PO4{WO(O2)2}4]3−/Imidazole.* ChemCatChem, 2014. **6**(8): p. 2327-2332.
43. Barrio, L., J.M. Campos-Martín, and J.L.G. Fierro, *Spectroscopic and DFT Study of Tungstic Acid Peroxocomplexes.* The Journal of Physical Chemistry A, 2007. **111**(11): p. 2166-2171.
44. Jiang, J., et al., *Epoxidation of soybean oil catalyzed by peroxo phosphotungstic acid supported on modified halloysite nanotubes.* Applied Surface Science, 2012. **258**(17): p. 6637-6642.
45. Maheswari, P.U., et al., *A Na2WO4/H2WO4-Based Highly Efficient Biphasic Catalyst towards Alkene Epoxidation, using Dihydrogen Peroxide as Oxidant.* Advanced Synthesis & Catalysis, 2005. **347**(14): p. 1759-1764.
46. Kück, J.W., et al., *Epoxidation of Olefins Catalyzed by a Molecular Iron N-Heterocyclic Carbene Complex: Influence of Reaction Parameters on the Catalytic Activity.* ChemCatChem, 2014. **6**(7): p. 1882-1886.
47. Haslinger, S., et al., *Iron-catalyzed oxidation of unreactive CH bonds: Utilizing bio-inspired axial ligand modification to increase catalyst stability.* Journal of Catalysis, 2015. **331**: p. 147-153.

48. Traylor, T.G. and F. Xu, *Mechanisms of reactions of iron(III) porphyrins with hydrogen peroxide and hydroperoxides: solvent and solvent isotope effects.* Journal of the American Chemical Society, 1990. **112**(1): p. 178-186.
49. Zhu, T., H.-m. Chang, and J.F. Kadla, *A new method for the preparation of peroxymonophosphoric acid.* Canadian Journal of Chemistry, 2003. **81**(2): p. 156-160.
50. Soni, N.K., et al., *Kinetics and mechanism of oxidation of l-ascorbic acid by peroxomonophosphate in aqueous acid medium.* International Journal of Chemical Kinetics, 2013. **45**(1): p. 41-46.
51. Ogata, Y., Y. Sawaki, and T. Ohno, *Mechanism for oxidation of phenylacetylenes with peroxymonophosphoric acid. Oxirene as an intermediate inconvertible to ketocarbene.* Journal of the American Chemical Society, 1982. **104**(1): p. 216-219.
52. Lakouraj, M.M. and V. Hasantabar, *Alumina-supported monoperphosphoric acid for selective oxidation of sulfides to sulfoxides.* Journal of Sulfur Chemistry, 2011. **32**(1): p. 93-98.
53. Tappe, N.A., et al., *Current advances in the catalytic conversion of carbon dioxide by molecular catalysts: an update.* Dalton Transactions, 2018. **47**(38): p. 13281-13313.
54. Pescarmona, P.P. and M. Taherimehr, *Challenges in the catalytic synthesis of cyclic and polymeric carbonates from epoxides and CO2.* Catalysis Science & Technology, 2012. **2**(11): p. 2169-2187.
55. Sakakura, T. and K. Kohno, *The synthesis of organic carbonates from carbon dioxide.* Chemical Communications, 2009(11): p. 1312-1330.
56. Kamphuis, A.J., et al., *Highly Selective Single-Component Formazanate Ferrate(II) Catalysts for the Conversion of CO2 into Cyclic Carbonates.* ChemSusChem, 2019. **12**(15): p. 3635-3641.
57. Schmidt, A., et al., *Synthesis and characterization of novel cyclopentadienyl molybdenum imidazo[1,5-a]pyridine-3-ylidene complexes and their application in olefin epoxidation catalysis.* Journal of Catalysis, 2014. **319**: p. 119-126.
58. Schlagintweit, J.F., et al., *Exploring different coordination modes of the first tetradentate NHC/1,2,3-triazole hybrid ligand for group 10 complexes.* Dalton Transactions, 2019. **48**(39): p. 14820-14828.
59. Schumb, W., *Stabilization of Concentrated Solutions of Hydrogen Peroxide.* Industrial & Engineering Chemistry, 1957. **49**(10): p. 1759-1762.
60. Harke, *Eureco™*. 2013.
61. Paolini, F., "*Salting fresh waters*" *Industries, Tourism and the Environment on Tuscany's Central-Southern Coast.* Storia e Futuro, 2012. **29**.
62. Amdur, M.O., *Health effects of air pollutants: sulfuric acid, the old and the new.* Environmental health perspectives, 1989. **81**: p. 109-122.
63. Claudio Cavallotti, m.M., Alessandro Zaro, Attillo Lagostina, Ugo Piero Bianchi, *Process for producing aryl imido-peralkanoic acid*, E.P. Office, Editor. 1991: Europe.
64. Hans-Peter Gethöffer, G.R., *Phthalimidoperoxihexansäure, Verfahren zu deren Herstellung und deren Verwendung*, E.P. Office, Editor. 1988, Clariant: Germany.
65. Tappe, N.A., *Oxidation von organischen Carbonsäuren mittels geeigneter katalytischer Systeme*, in *Chemistry*. 2016, Technical University of Munich: Garching.
66. Tressler, C.M., P. Stonehouse, and K.S. Kyler, *Calcium tungstate: a convenient recoverable catalyst for hydrogen peroxide oxidation.* Green Chemistry, 2016. **18**(18): p. 4875-4878.
67. Sato, K., M. Aoki, and R. Noyori, *A "Green" Route to Adipic Acid: Direct Oxidation of Cyclohexenes with 30 Percent Hydrogen Peroxide.* Science, 1998. **281**(5383): p. 1646-1647.
68. Aubry, C., et al., *Reinvestigation of epoxidation using tungsten-based precursors and hydrogen peroxide in a biphase medium.* Inorganic Chemistry, 1991. **30**(23): p. 4409-4415.

69. Pai, Z.P., et al., *Catalytic oxidation of olefins and alcohols with hydrogen peroxide in a two-phase system giving mono- and dicarboxylic acids.* Russian Chemical Bulletin, 2005. **54**(8): p. 1847-1854.
70. Lindhorst, A.C., S. Haslinger, and F.E. Kühn, *Molecular iron complexes as catalysts for selective C–H bond oxygenation reactions.* Chemical Communications, 2015. **51**(97): p. 17193-17212.
71. Schlagintweit, J.F., *Synthese und Charakterisierung Tetradentater Liganden für Übergangsmetallkomplexe mit 1,2,3-Triazol- und 1,2,3-Triazol-5-ylidendonoren*, in *Chemistry*. 2017, TUM: Garching bei München.

7 Attachment

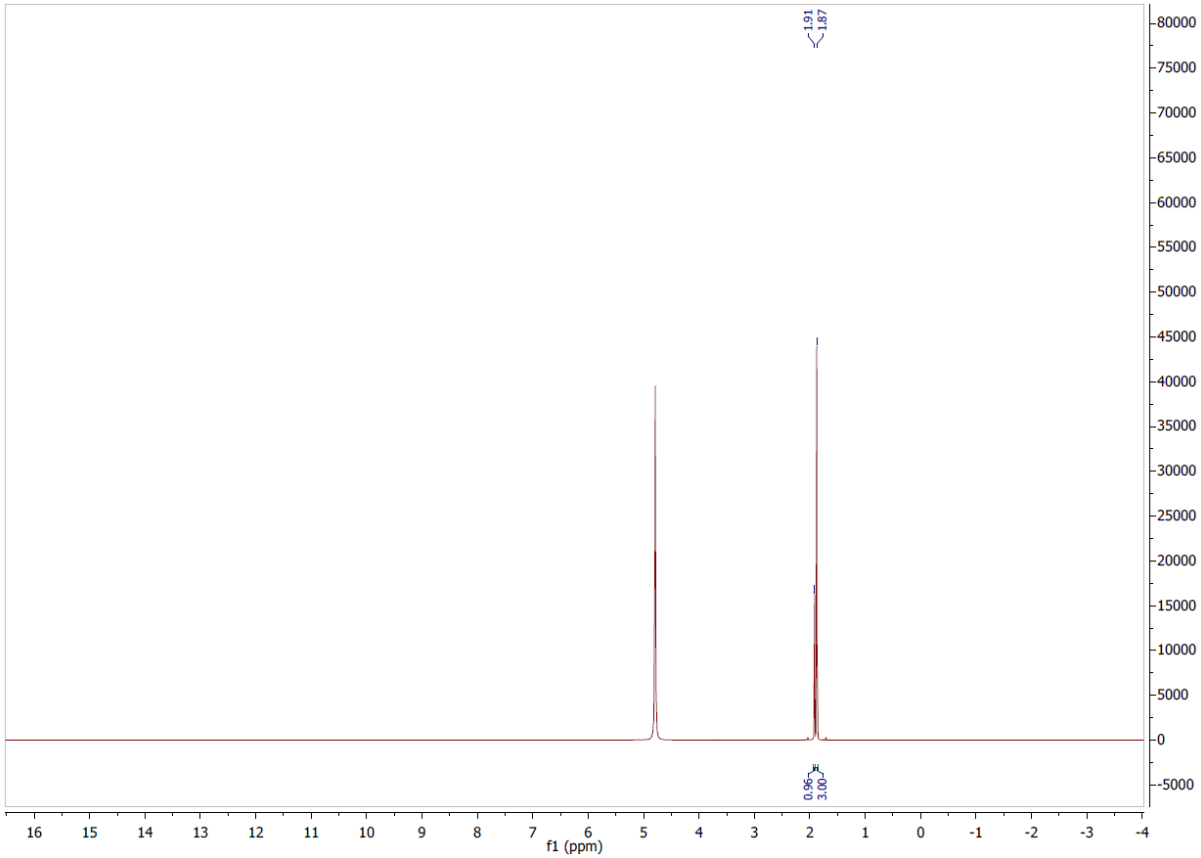


Figure 29: ^{1}H-NMR: peracetic acid *via* Caro's acid.

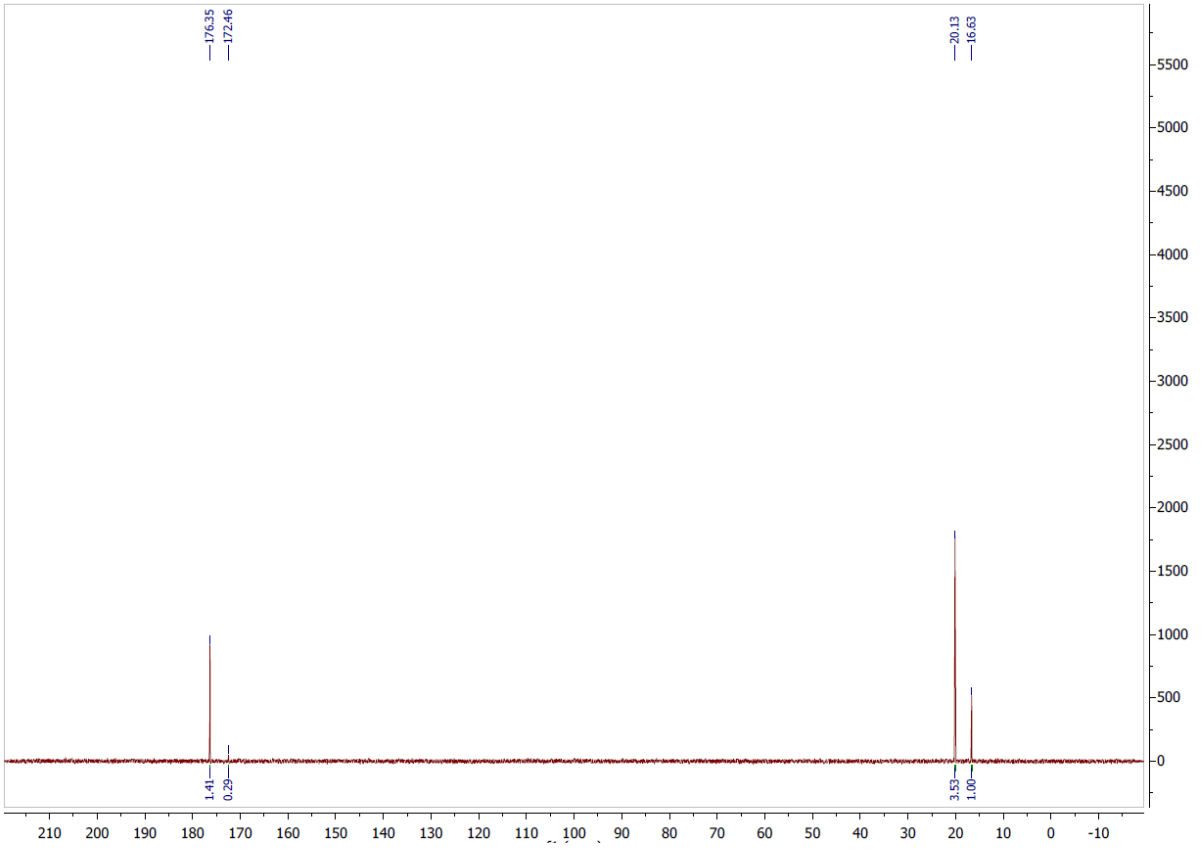


Figure 30: ^{13}C-NMR: peracetic acid *via* Caro's acid.

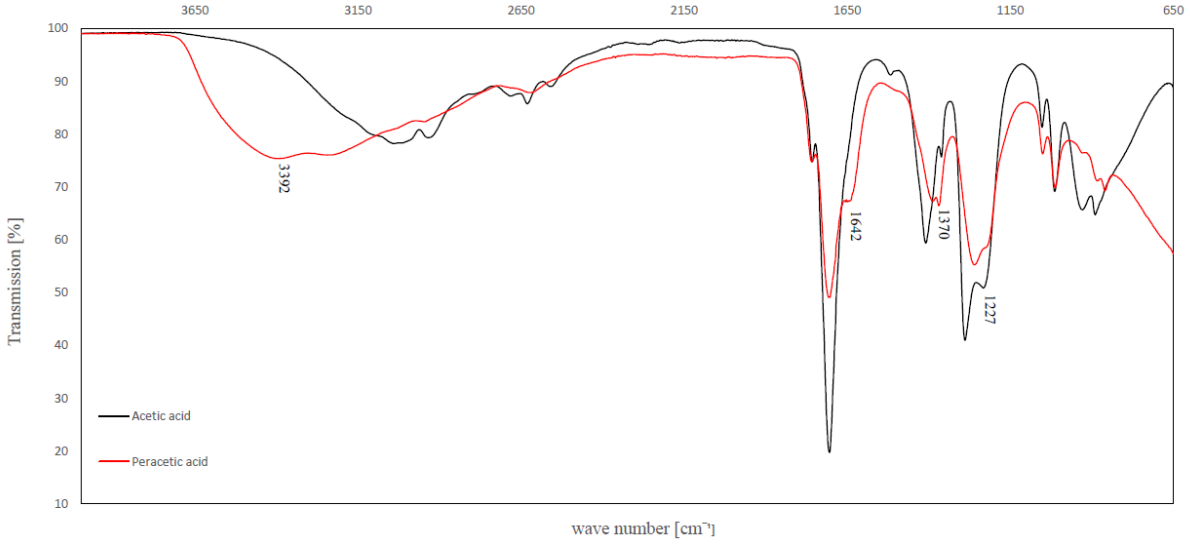


Figure 31: IR: peracetic acid *via* Caro's acid.

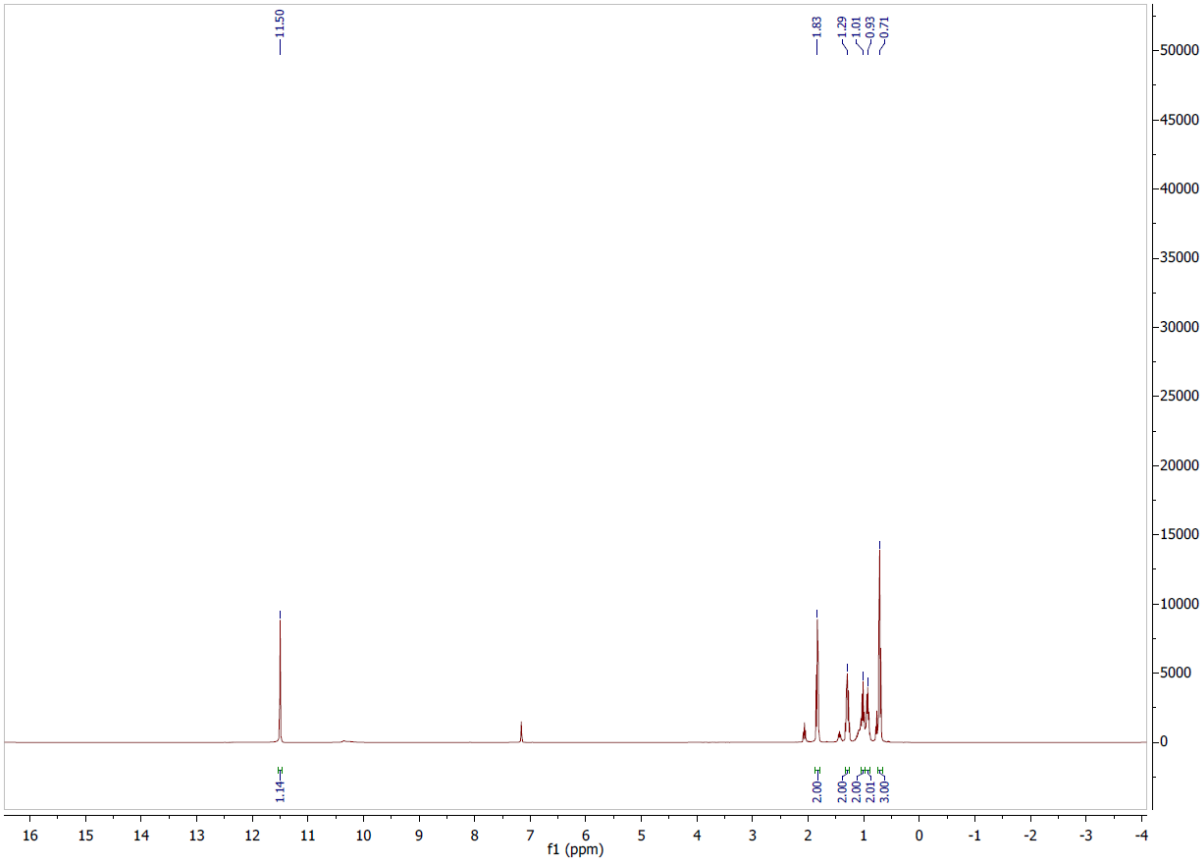


Figure 32: ^{1}H-NMR: percaproic acid *via* Caro's acid.

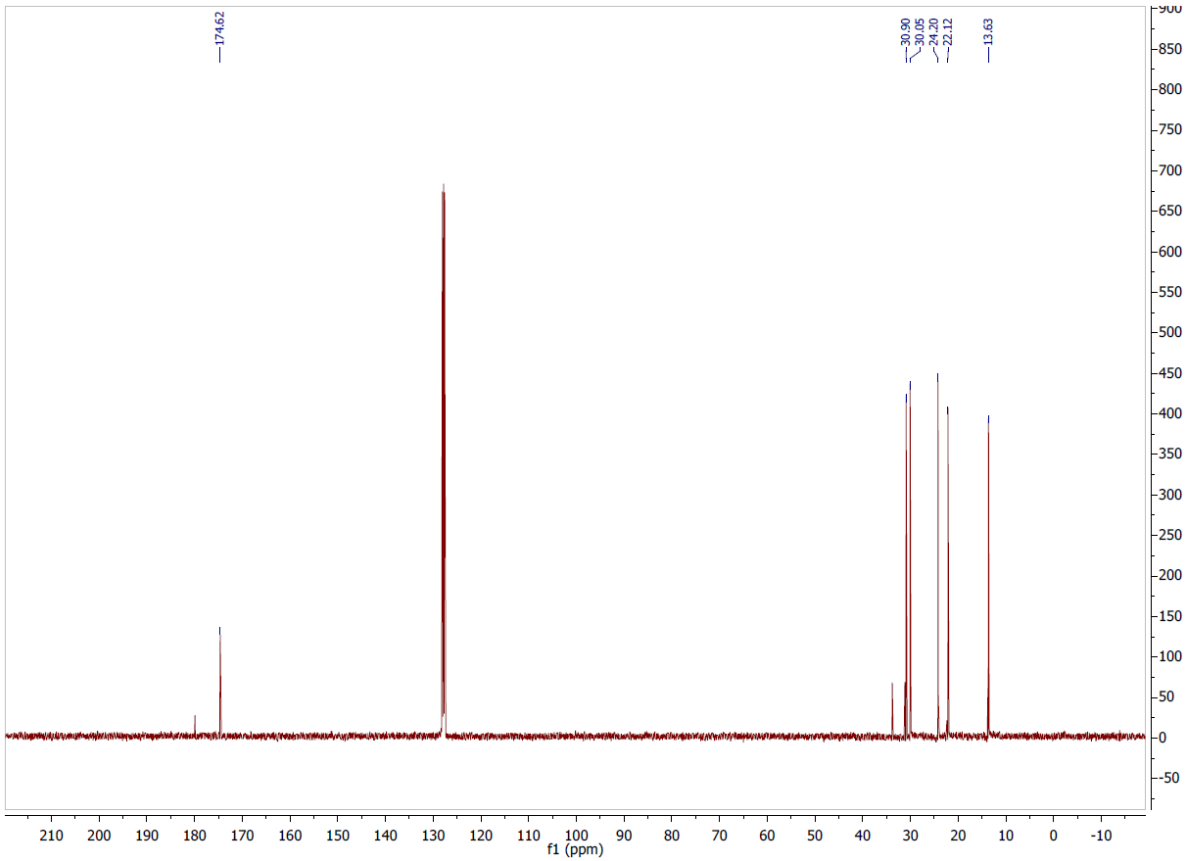


Figure 33: ^{13}C-NMR: percaproic acid *via* Caro's acid.

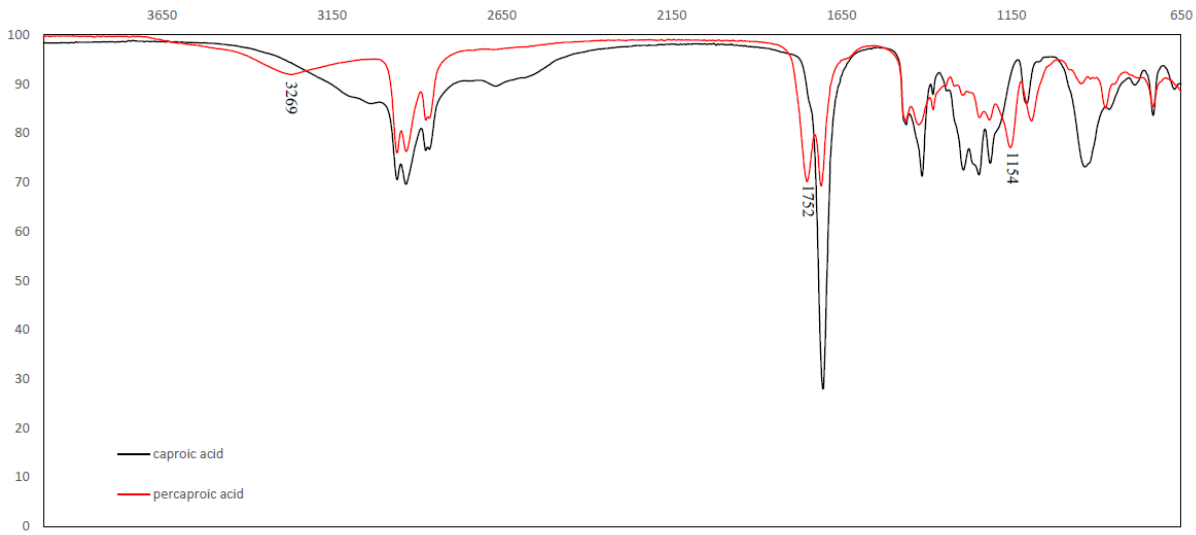


Figure 34: IR spectroscopy: Comparison caproic acid (black) with percaproic acid (red).

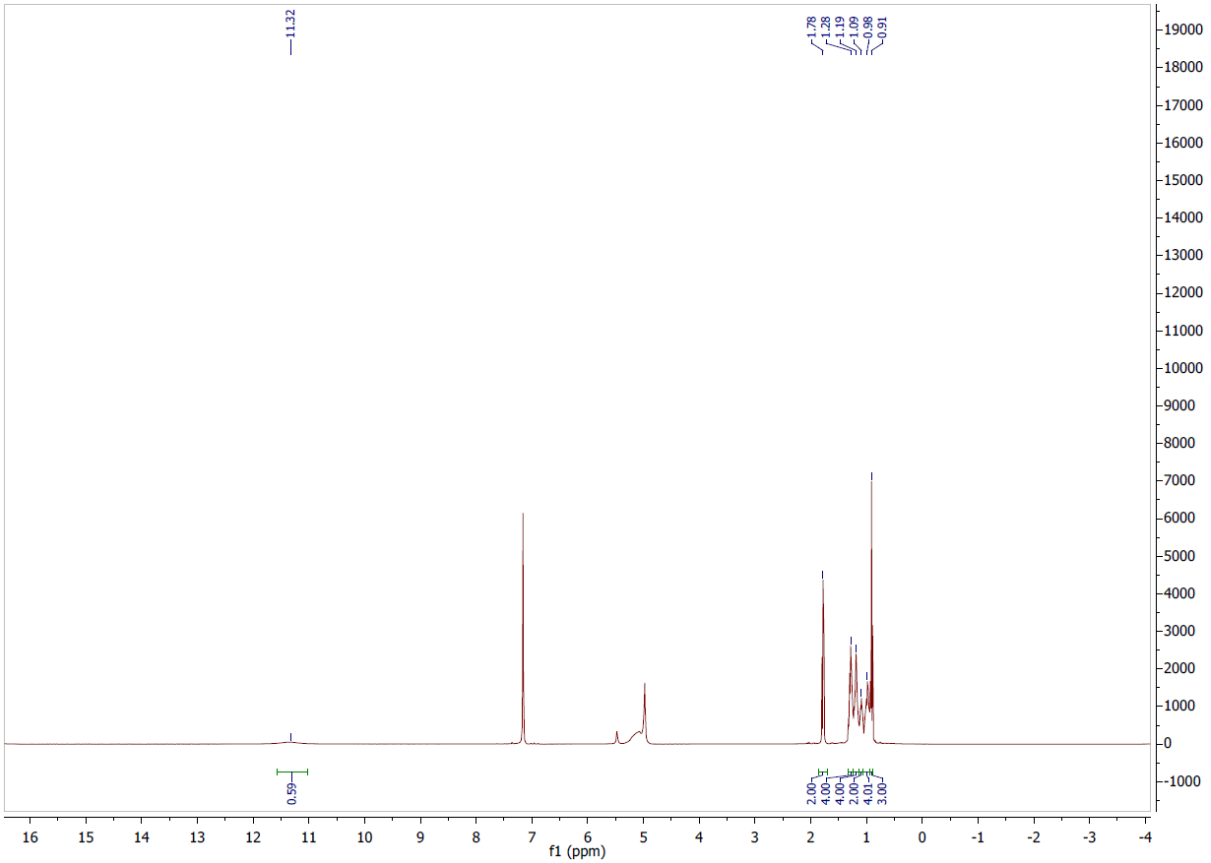


Figure 35: ^{1}H-NMR: perdecanoic acid *via* Caro's acid.

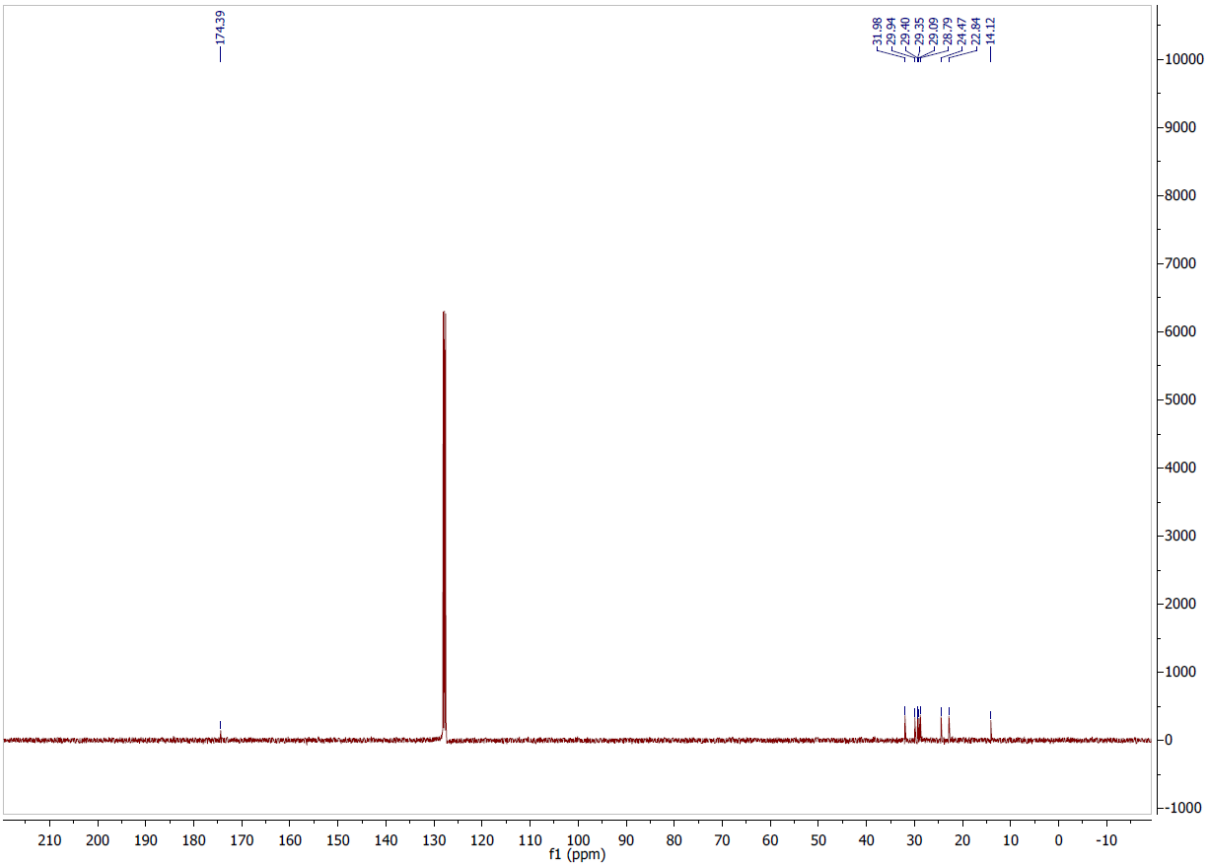


Figure 36: ^{13}C-NMR: perdecanoic acid *via* Caro's acid.

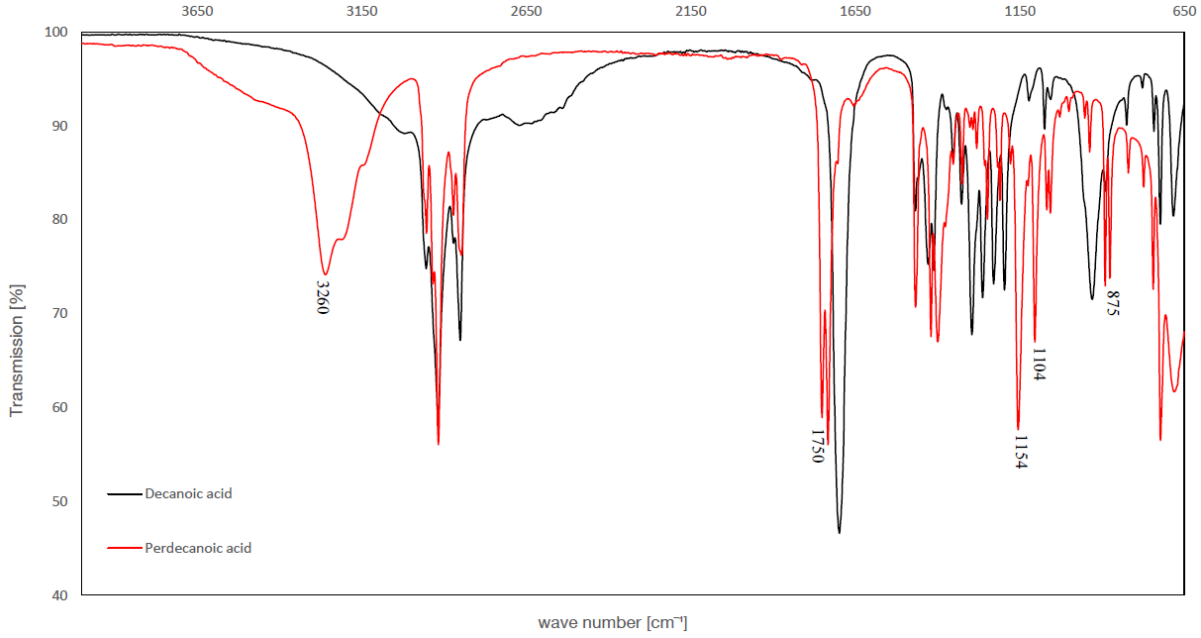


Figure 37: IR: perdecanoic acid *via* Caro's acid.

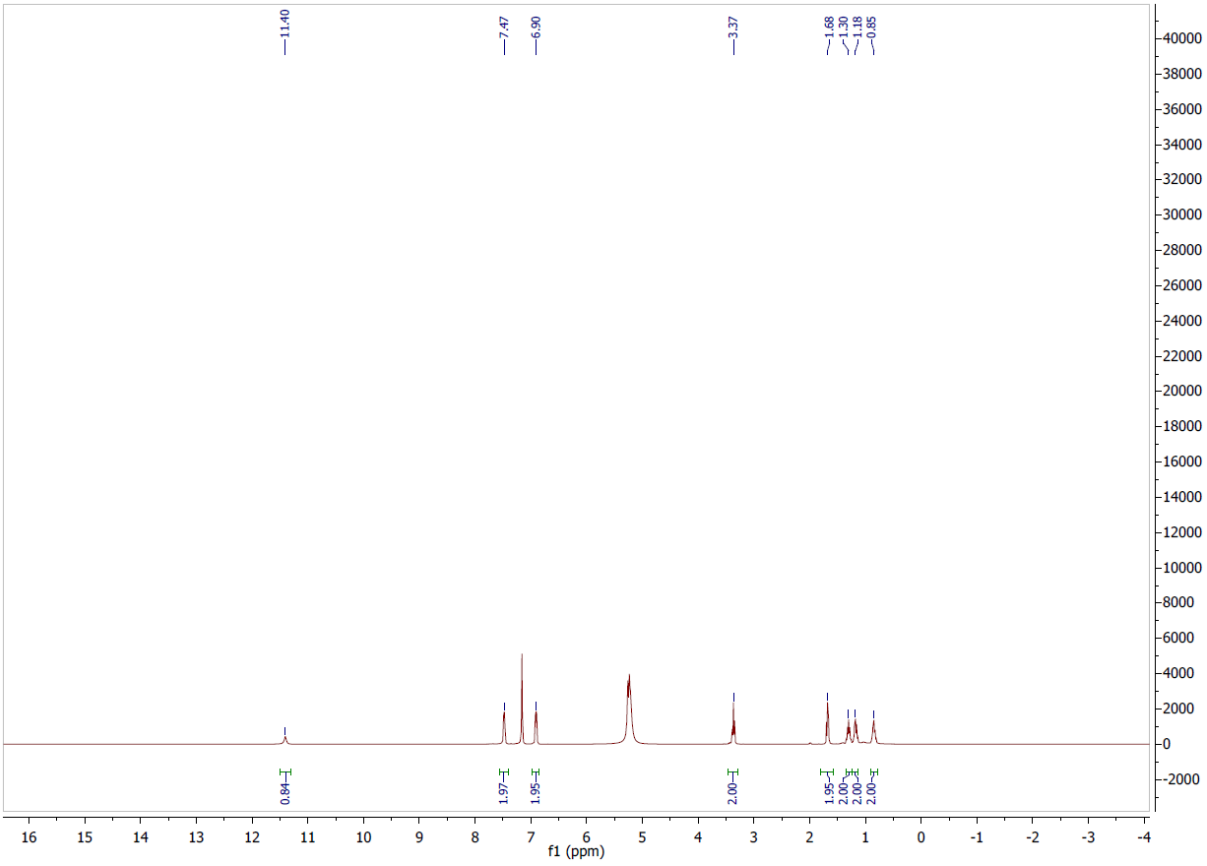


Figure 38: ^{1}H-NMR: PAP *via* Caro's acid.

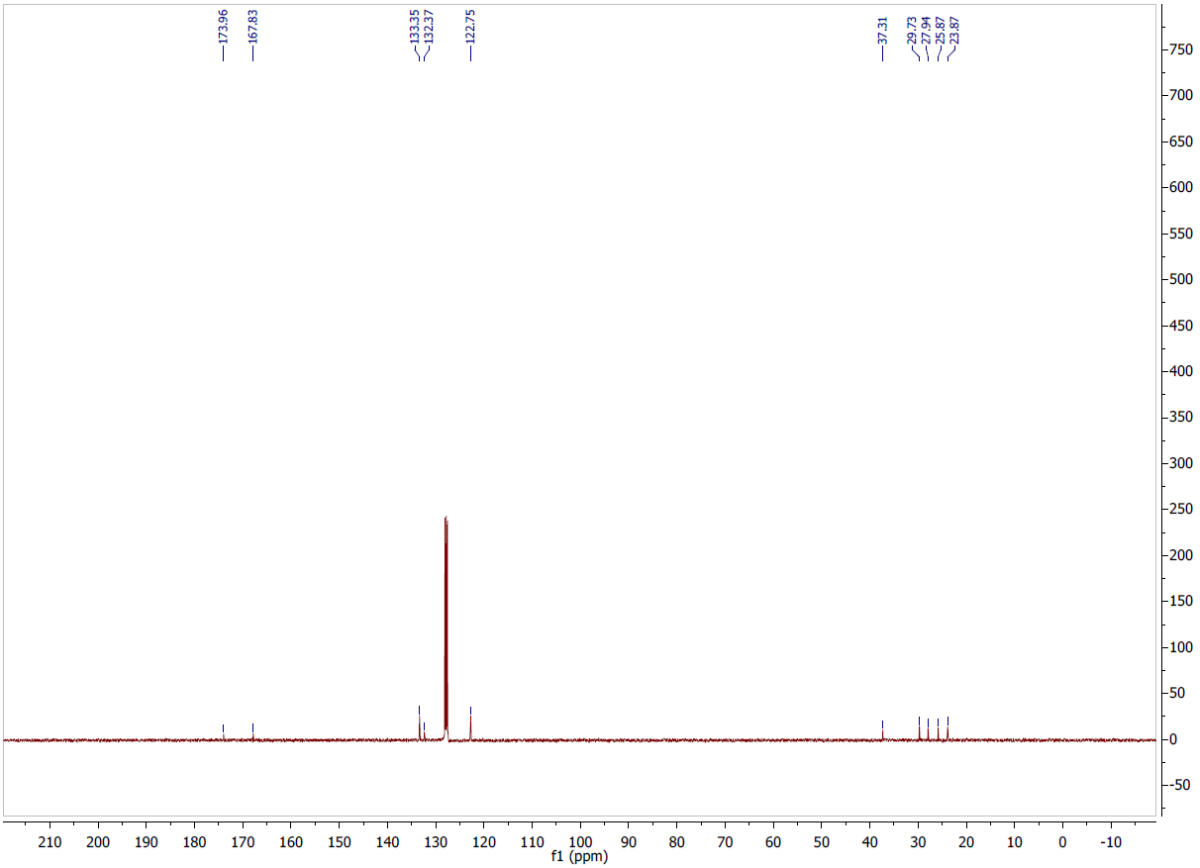


Figure 39: ^{13}C-NMR: PAP *via* Caro's acid.

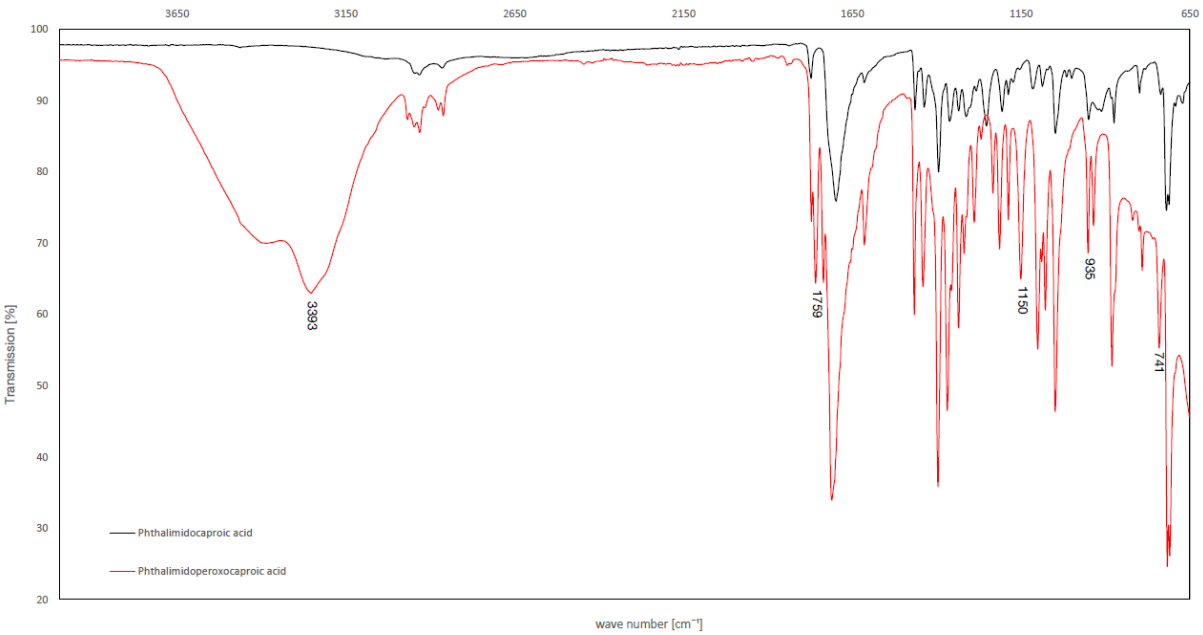


Figure 40: IR: PAP *via* Caro's acid.

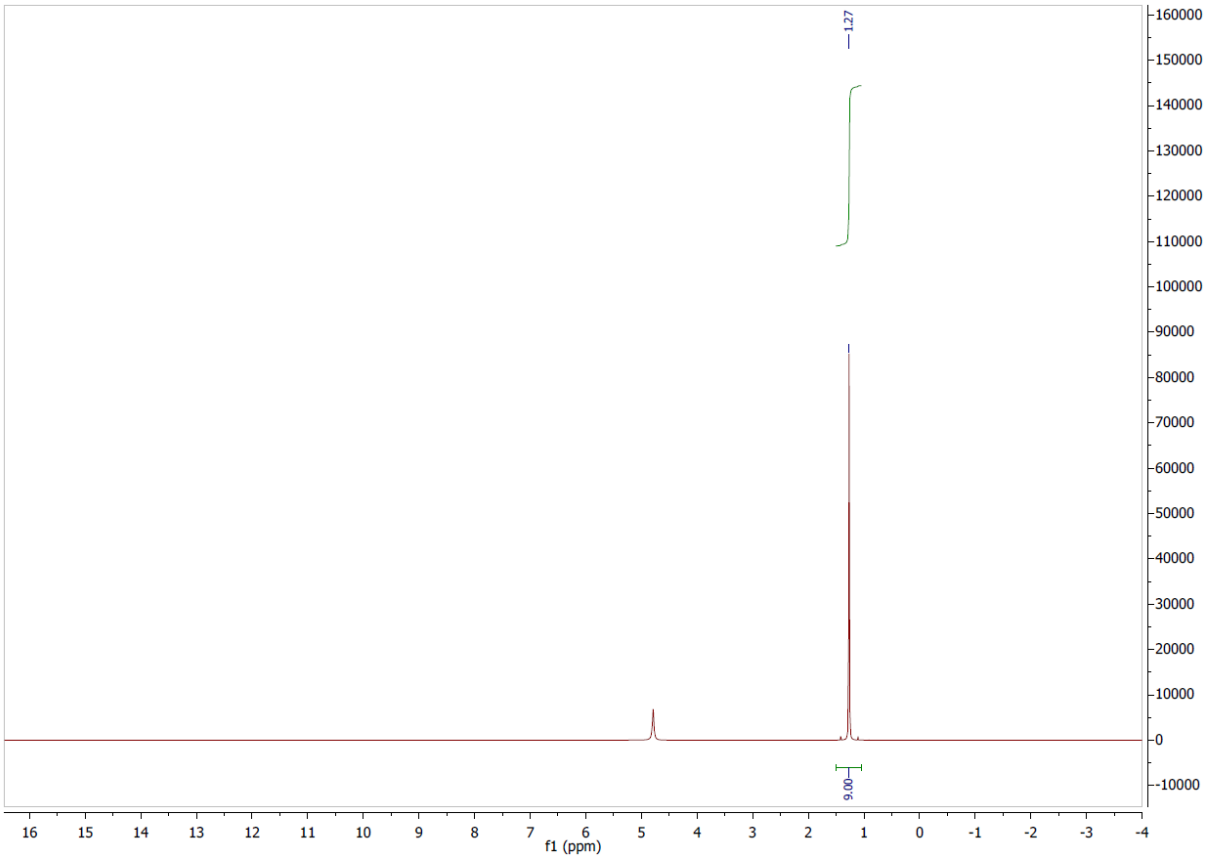


Figure 41: ^{1}H-NMR: oxidative solution I.

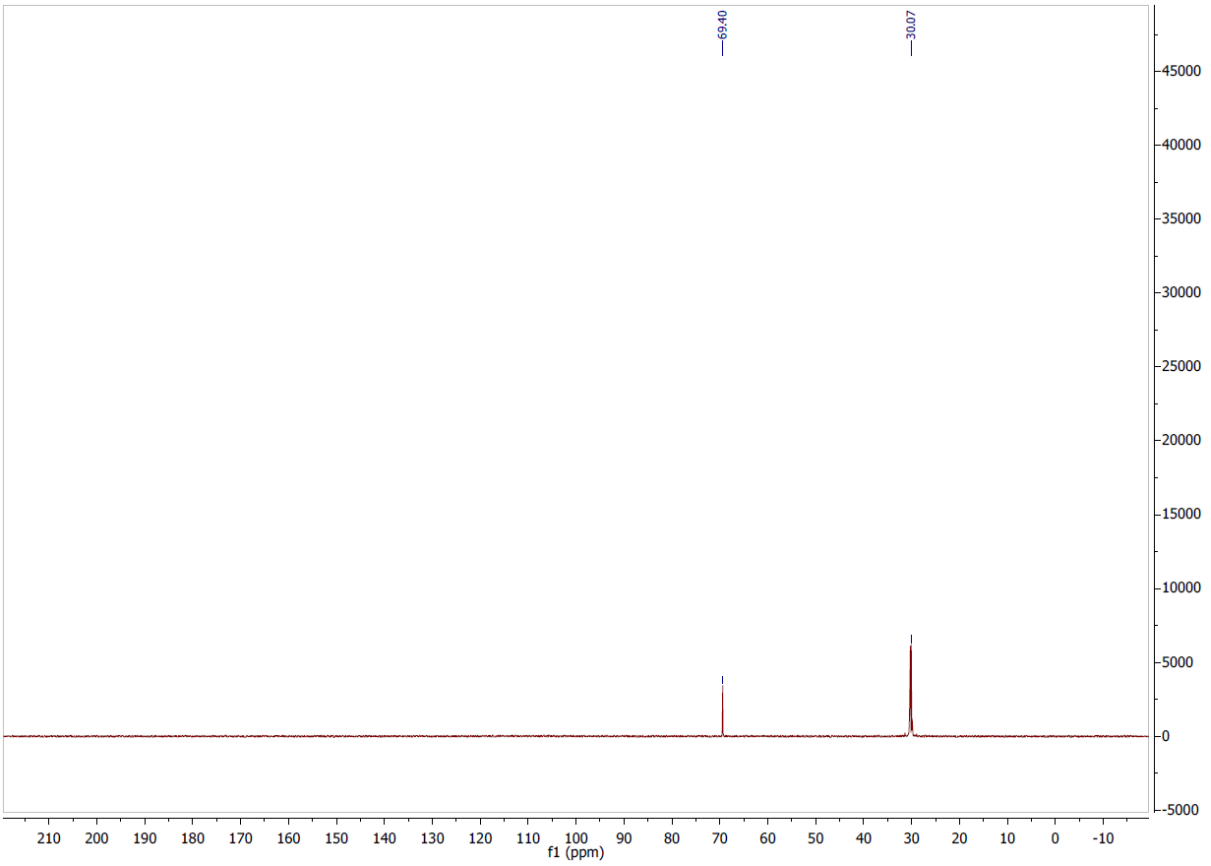


Figure 42: ^{13}C-NMR: oxidative solution I.

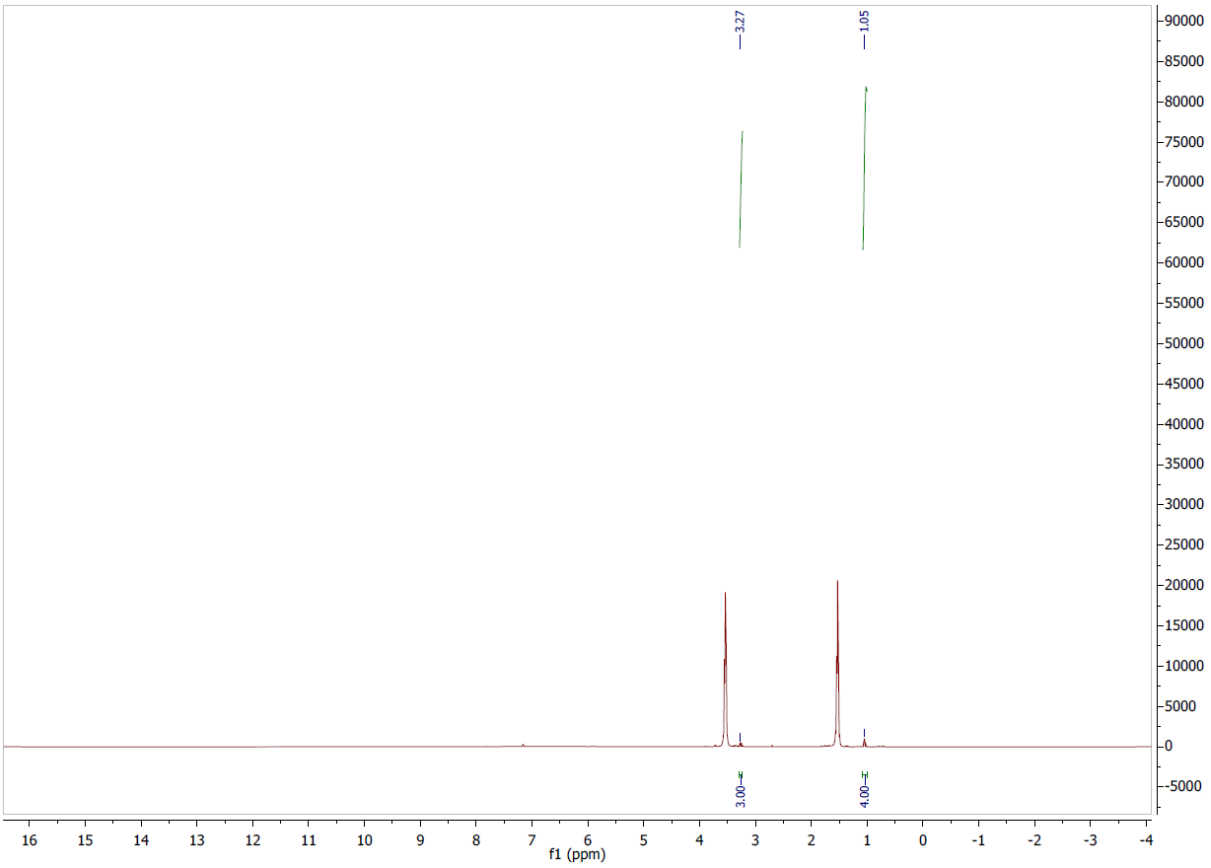


Figure 43: ^{1}H-NMR: oxidative solution II.

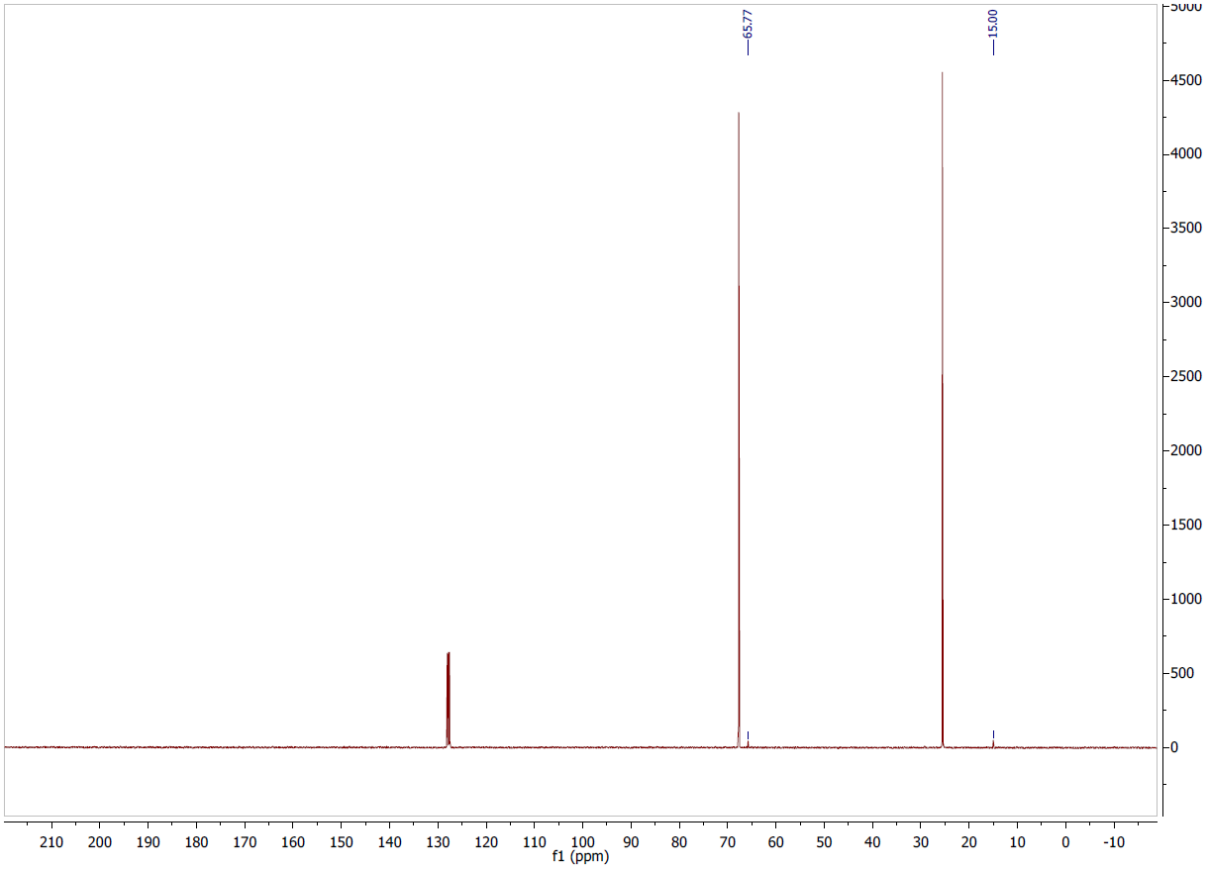


Figure 44: ^{13}C-NMR: oxidative solution II.

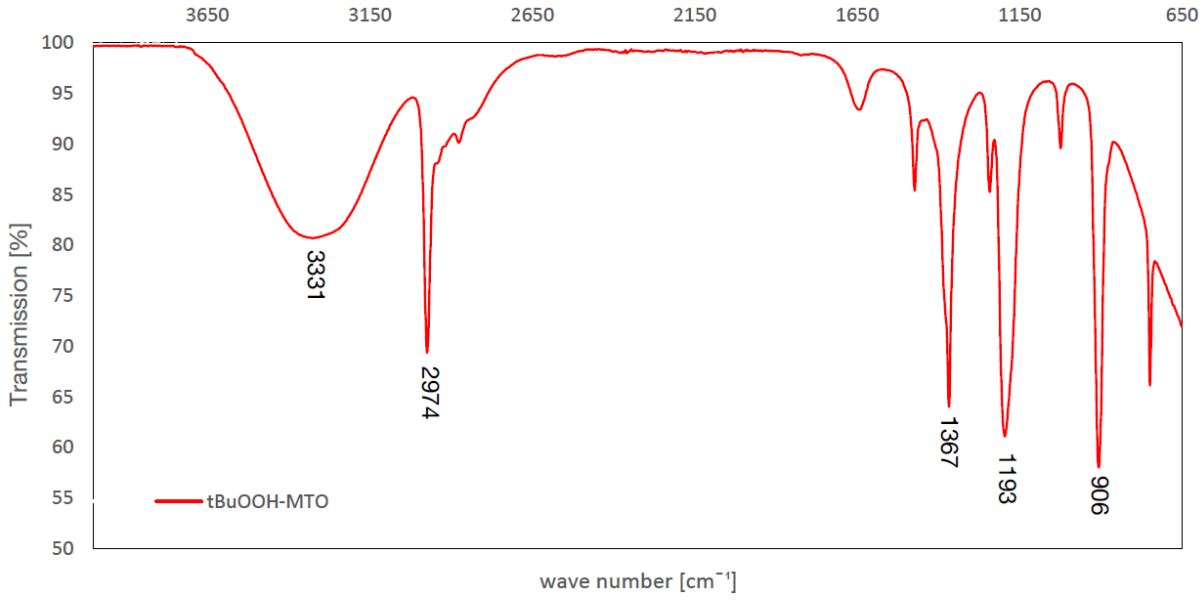


Figure 45: IR: oxidative solution I with MTO.

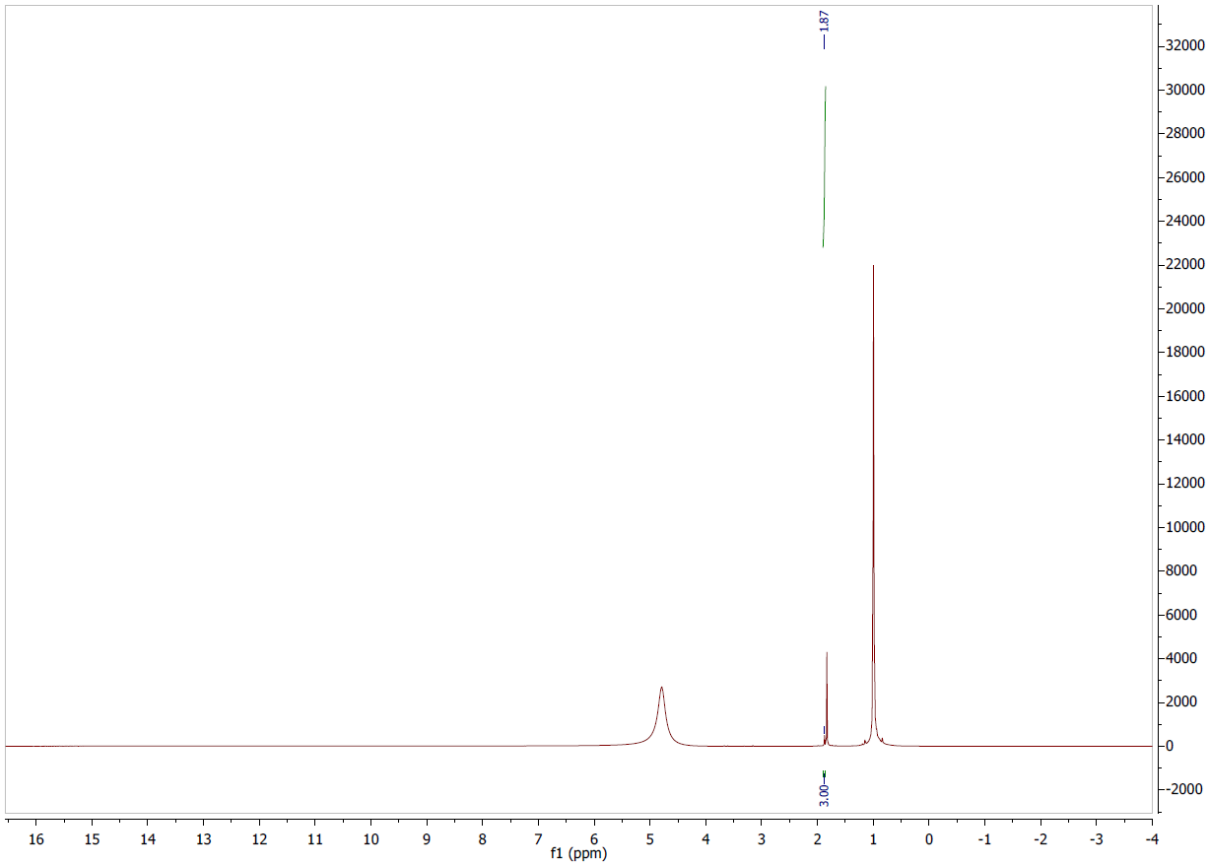


Figure 46: ^{1}H-NMR: peracetic acid *via* $CaWO_4$.

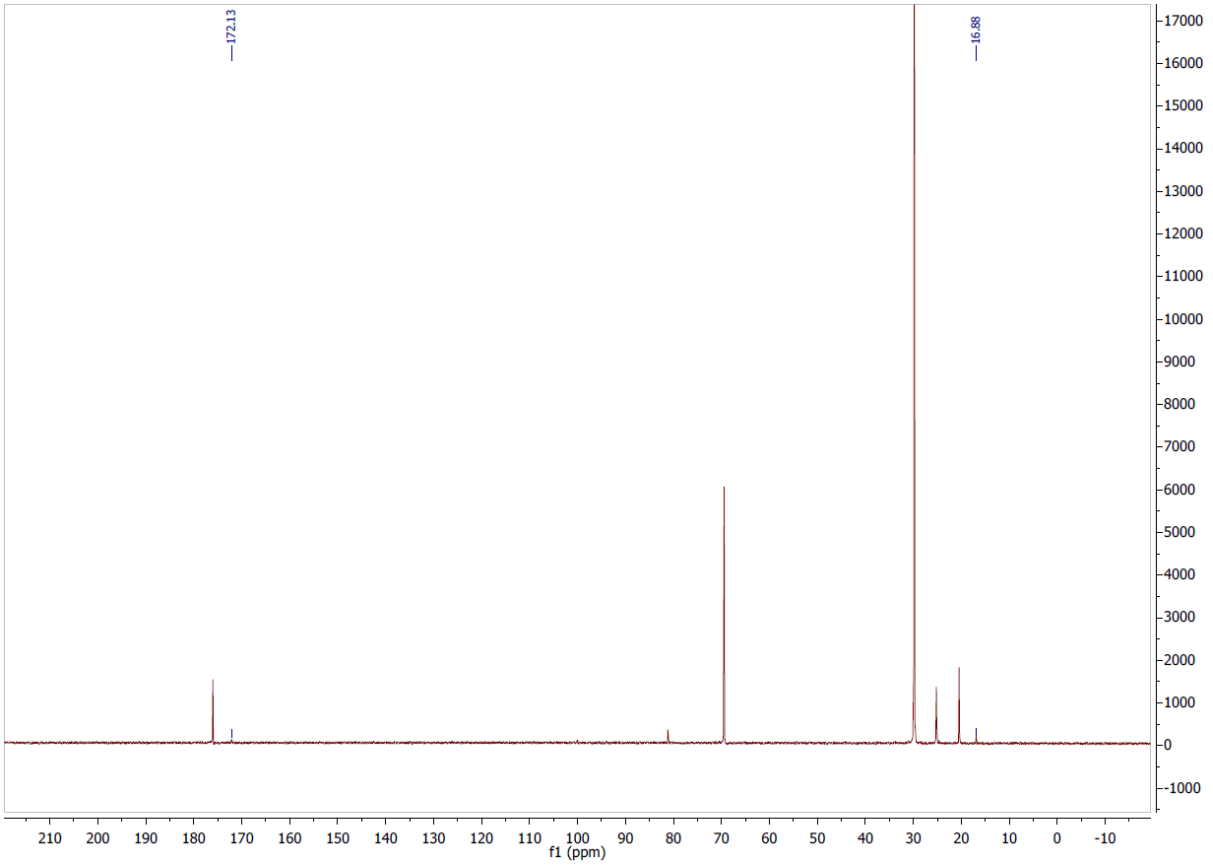


Figure 47: ^{13}C-NMR: peracetic acid *via* $CaWO_4$.

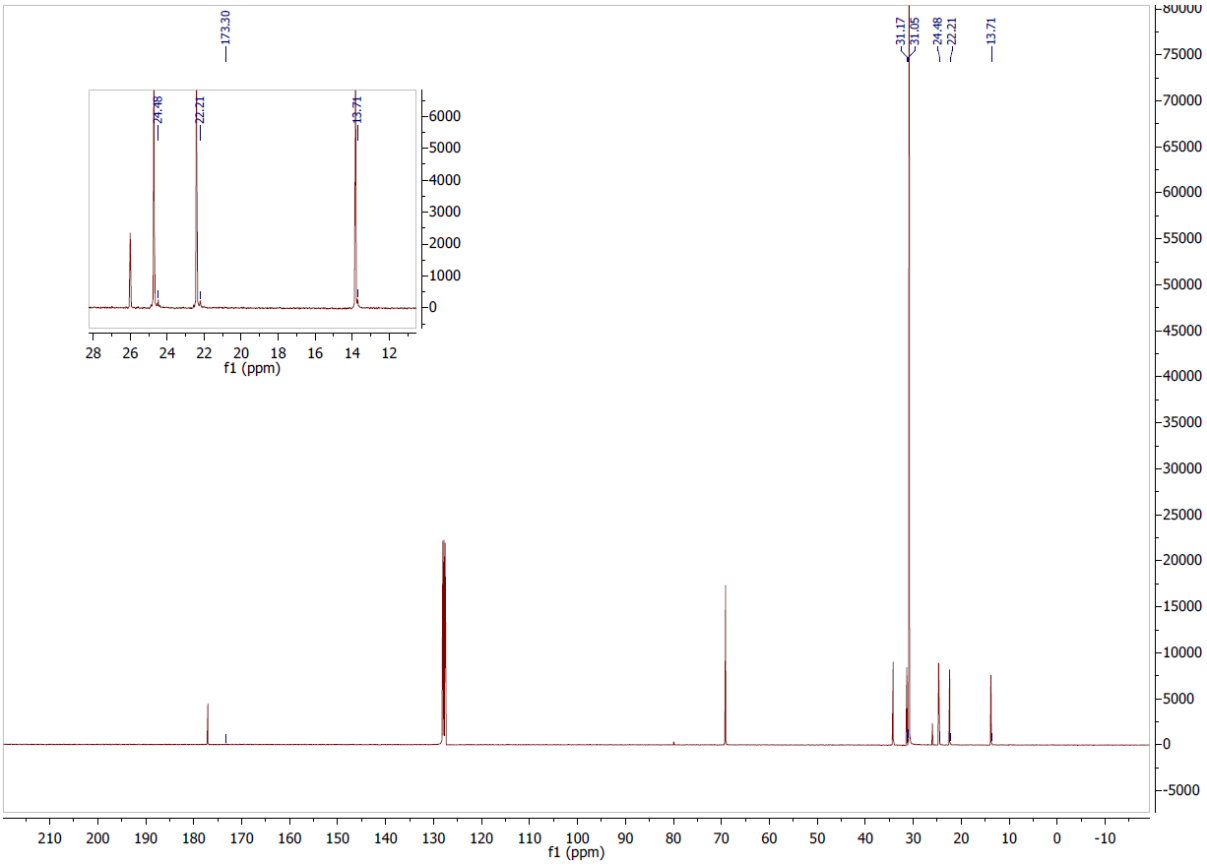


Figure 48: ^{13}C-NMR: percaproic acid *via* $CaWO_4$.

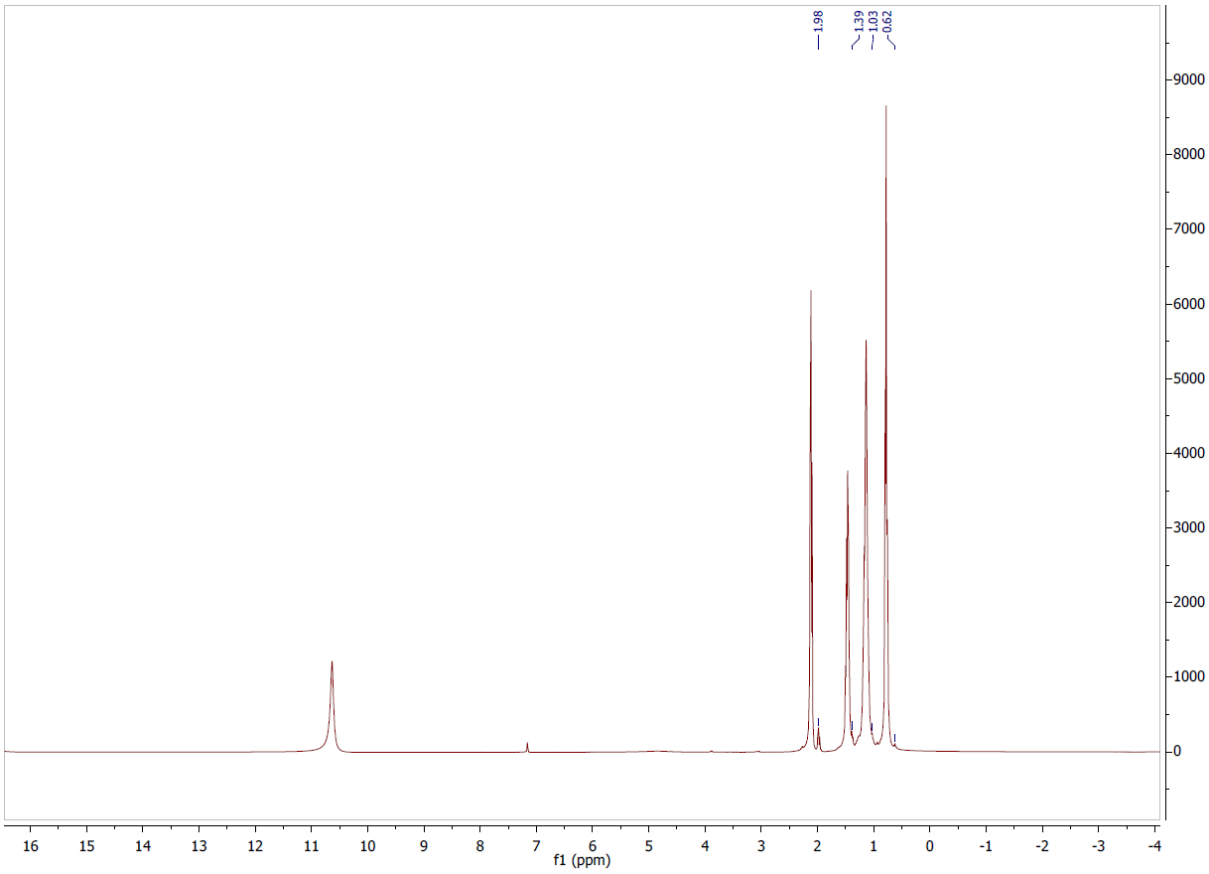


Figure 49: ^{1}H-NMR: percaproic acid *via* $Na_2WO_4 \cdot 2H_2O$.

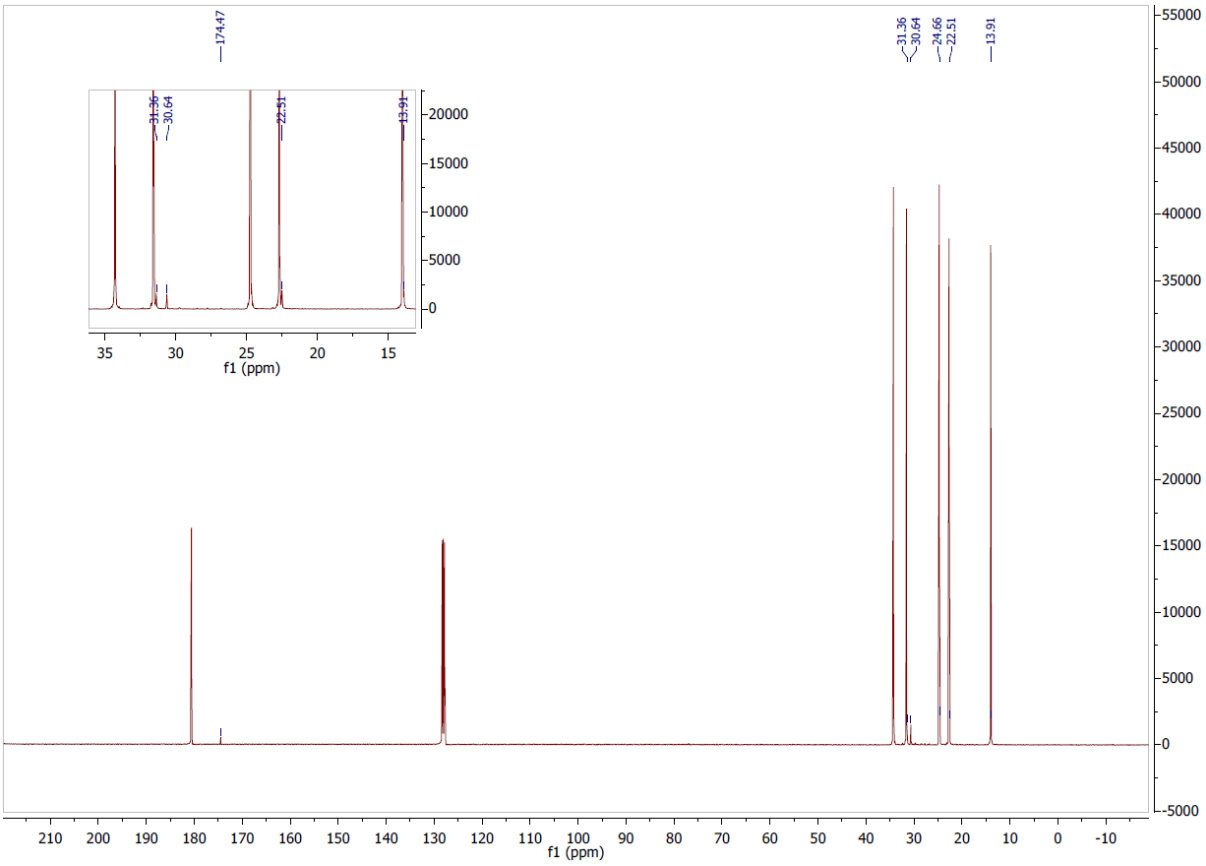


Figure 50: ^{13}C-NMR: percaproic acid *via* $Na_2WO_4 \cdot 2H_2O$.

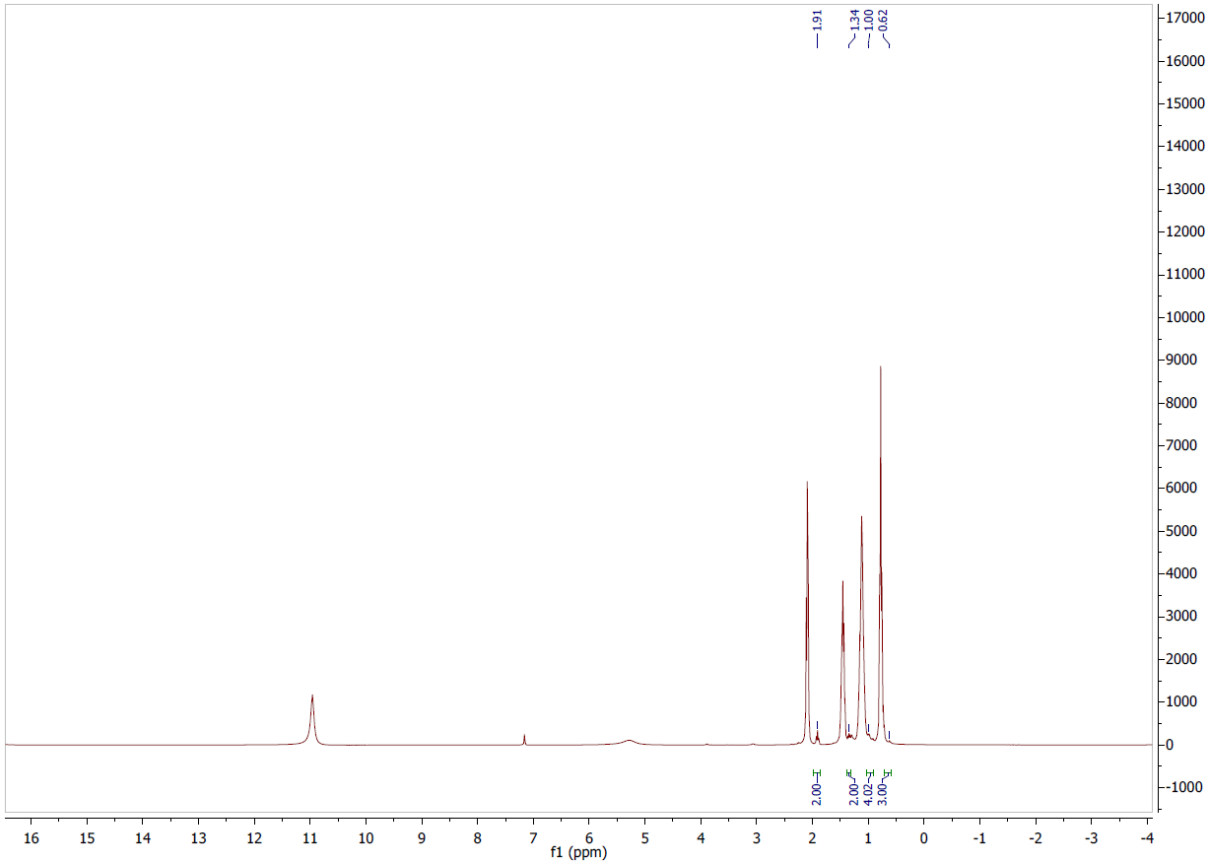


Figure 51: ^{1}H-NMR: percaproic acid *via* Na_2WO_4 and 50% H_2O_2.

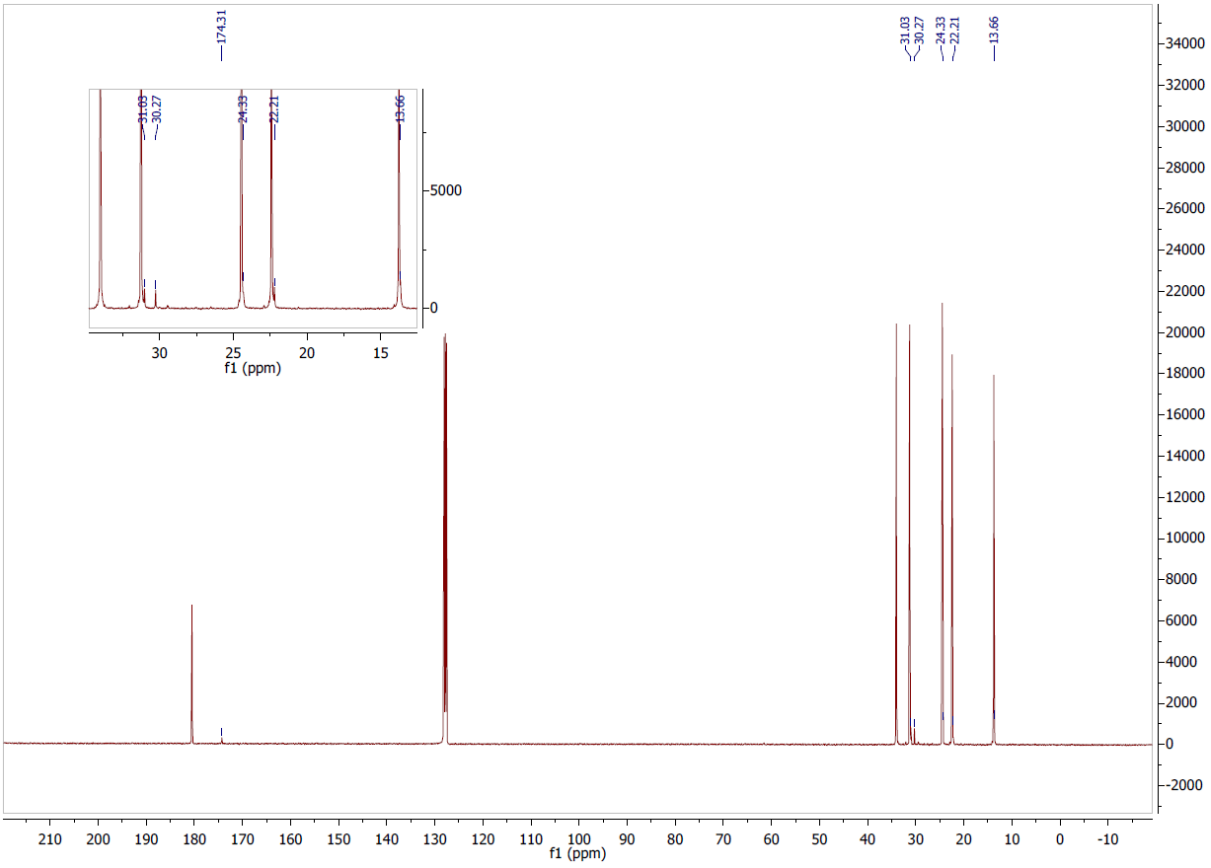


Figure 52: ^{13}C-NMR: percaproic acid *via* Na_2WO_4 and 50% H_2O_2.

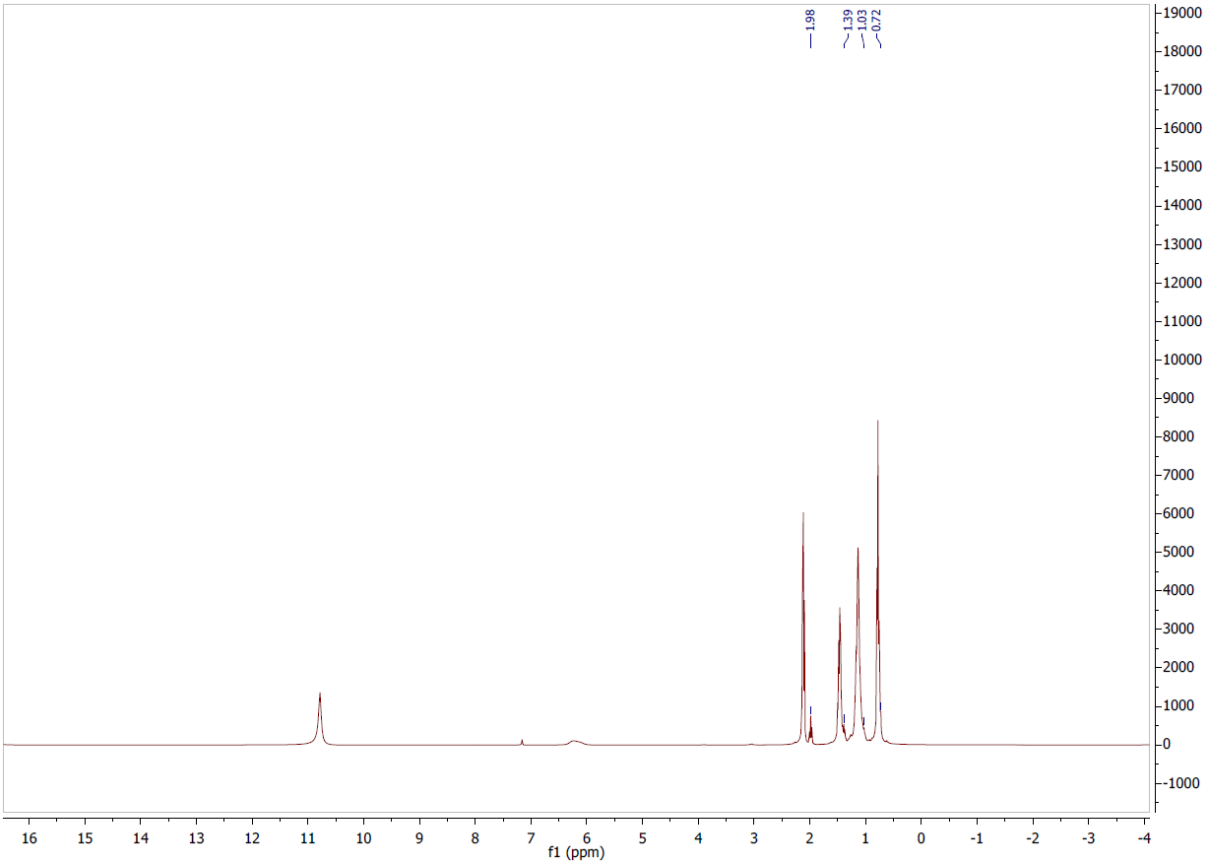


Figure 53: ^{1}H-NMR: percaproic acid *via* Na_2WO_4, 50% H_2O_2 and P_2O_5.

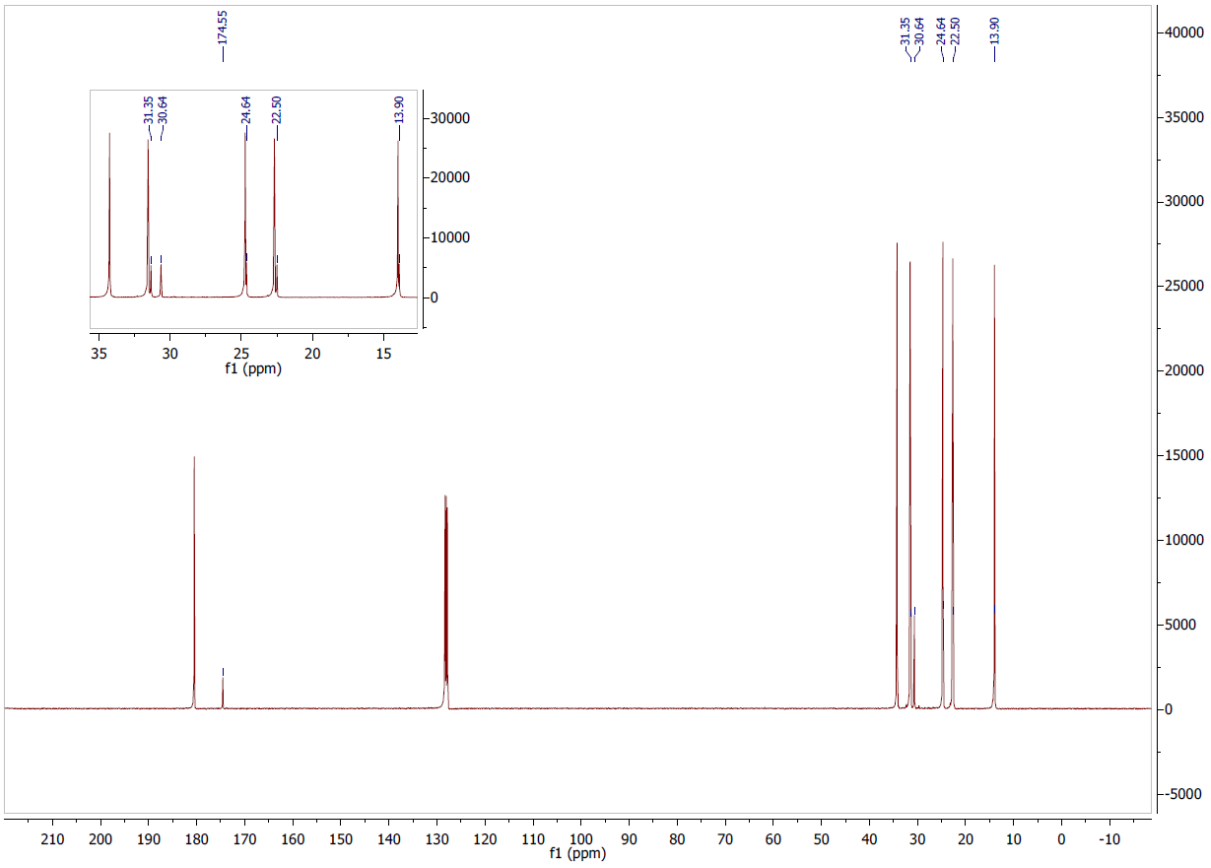


Figure 54: ^{13}C-NMR: percaproic acid *via* Na_2WO_4, 50% H_2O_2 and P_2O_5.

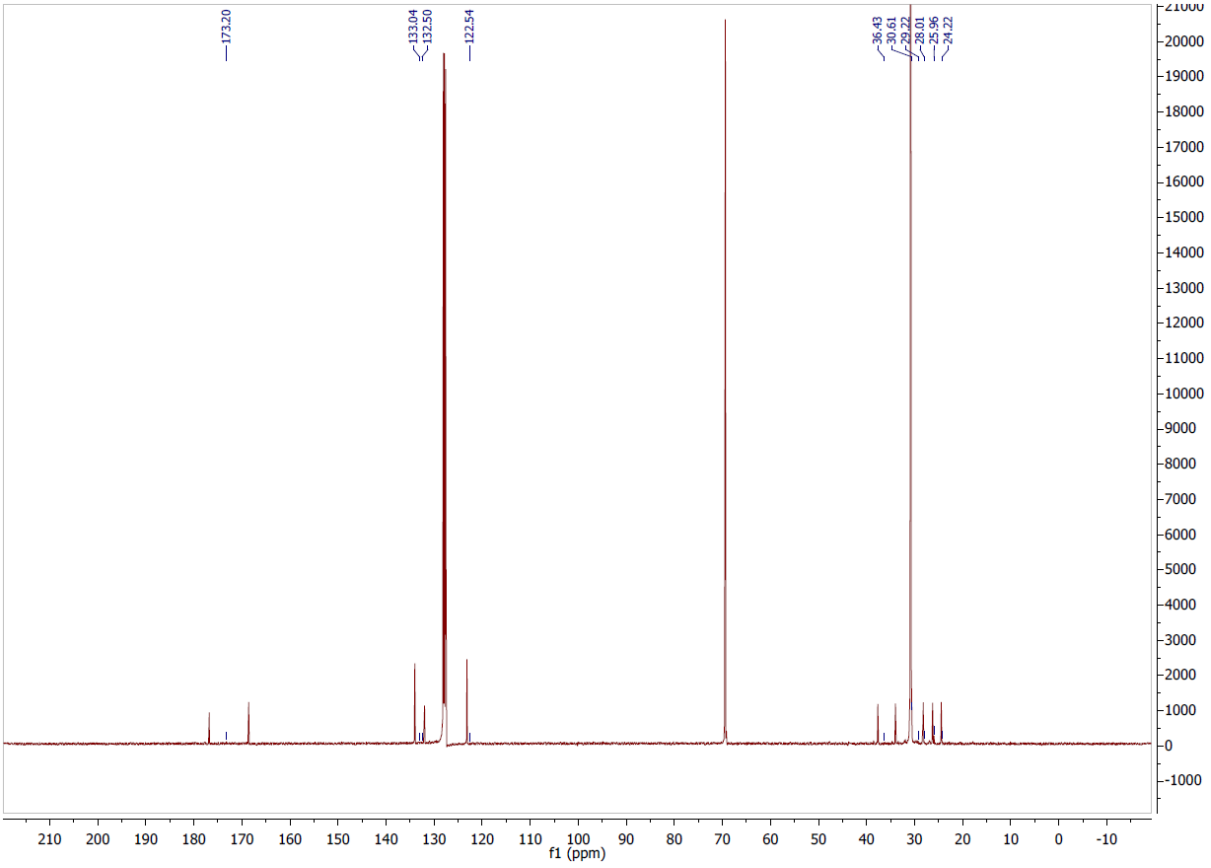


Figure 55: ^{13}C-NMR: PAP *via* Na_2WO_4, 50% H_2O_2 and P_2O_5.

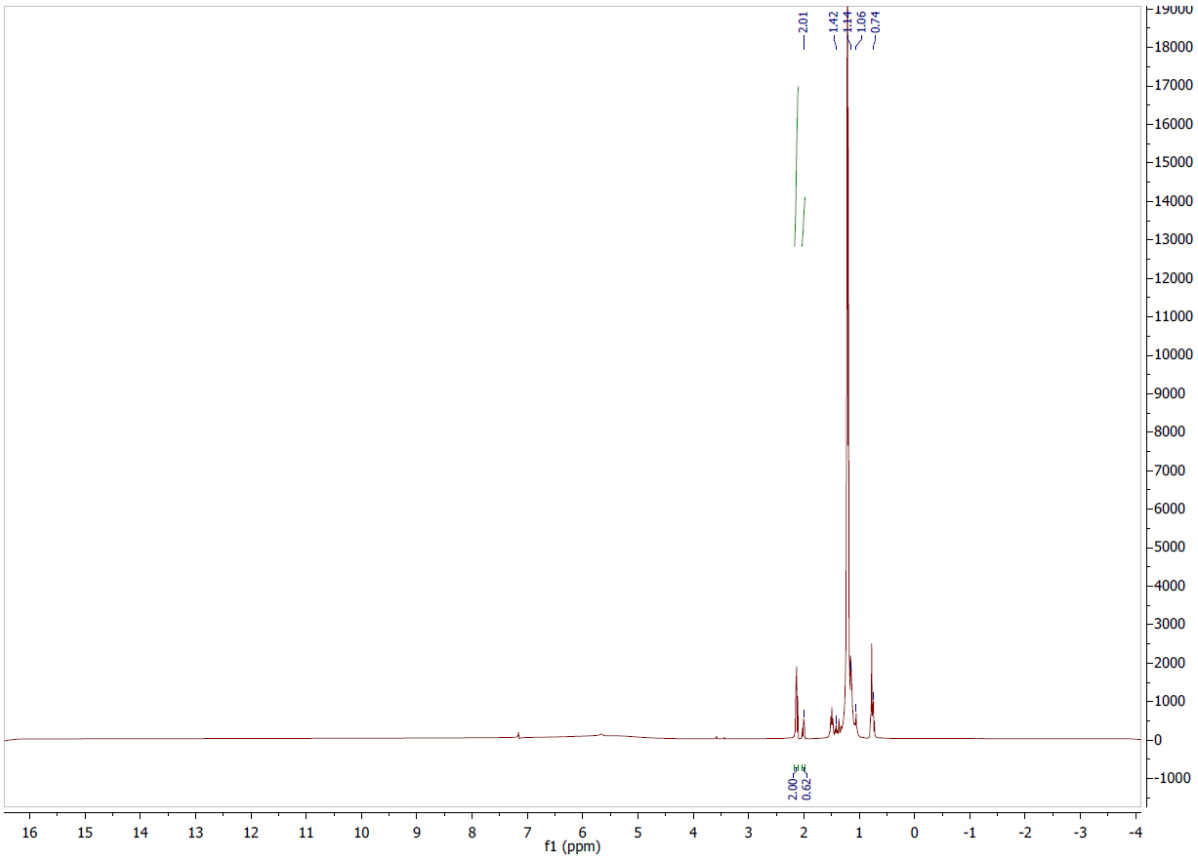


Figure 56: ^{1}H-NMR: percaproic acid *via* H_2WO_4.

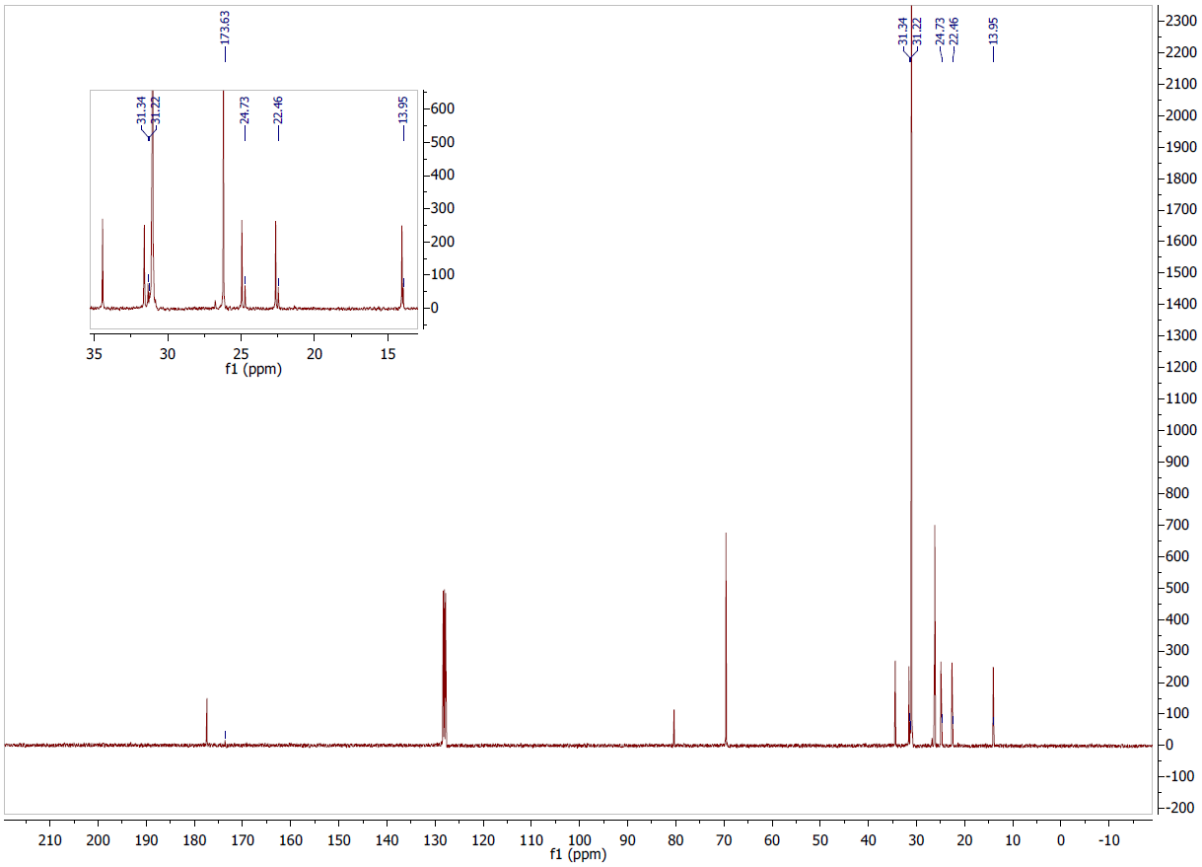


Figure 57: ^{13}C-NMR: percaproic acid *via* H_2WO_4.

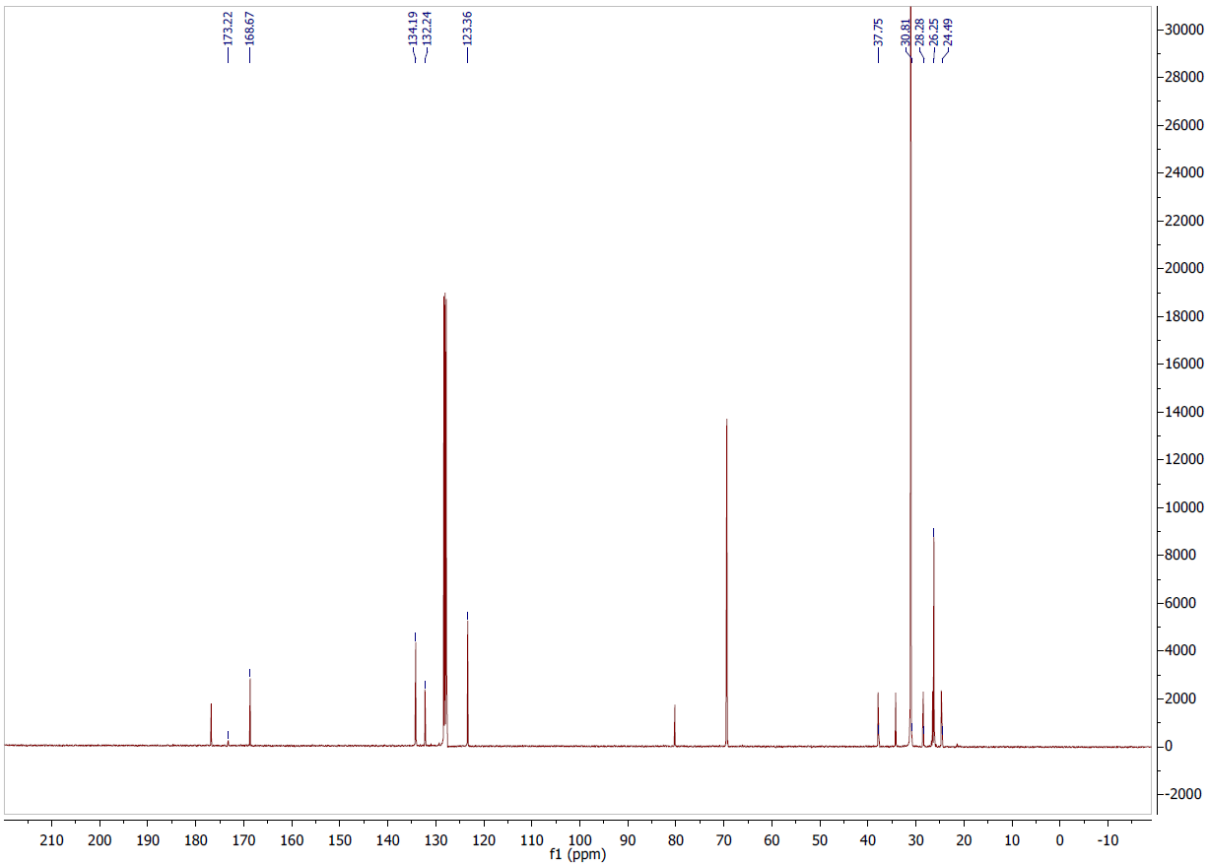


Figure 58: ^{13}C-NMR: PAP *via* H_2WO_4.

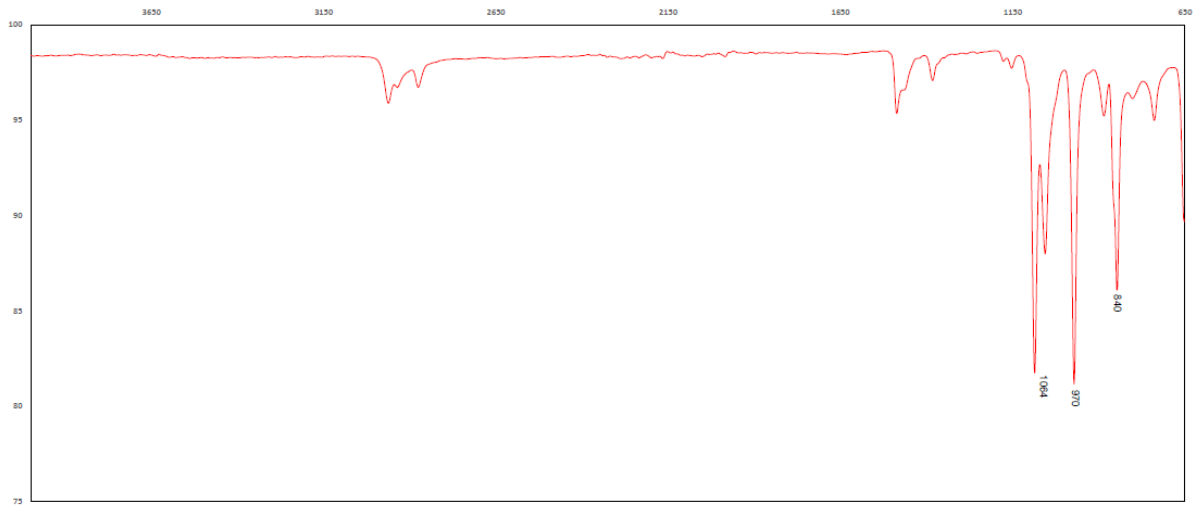


Figure 59: ATR-IR: Venturello Complex (**W1**).

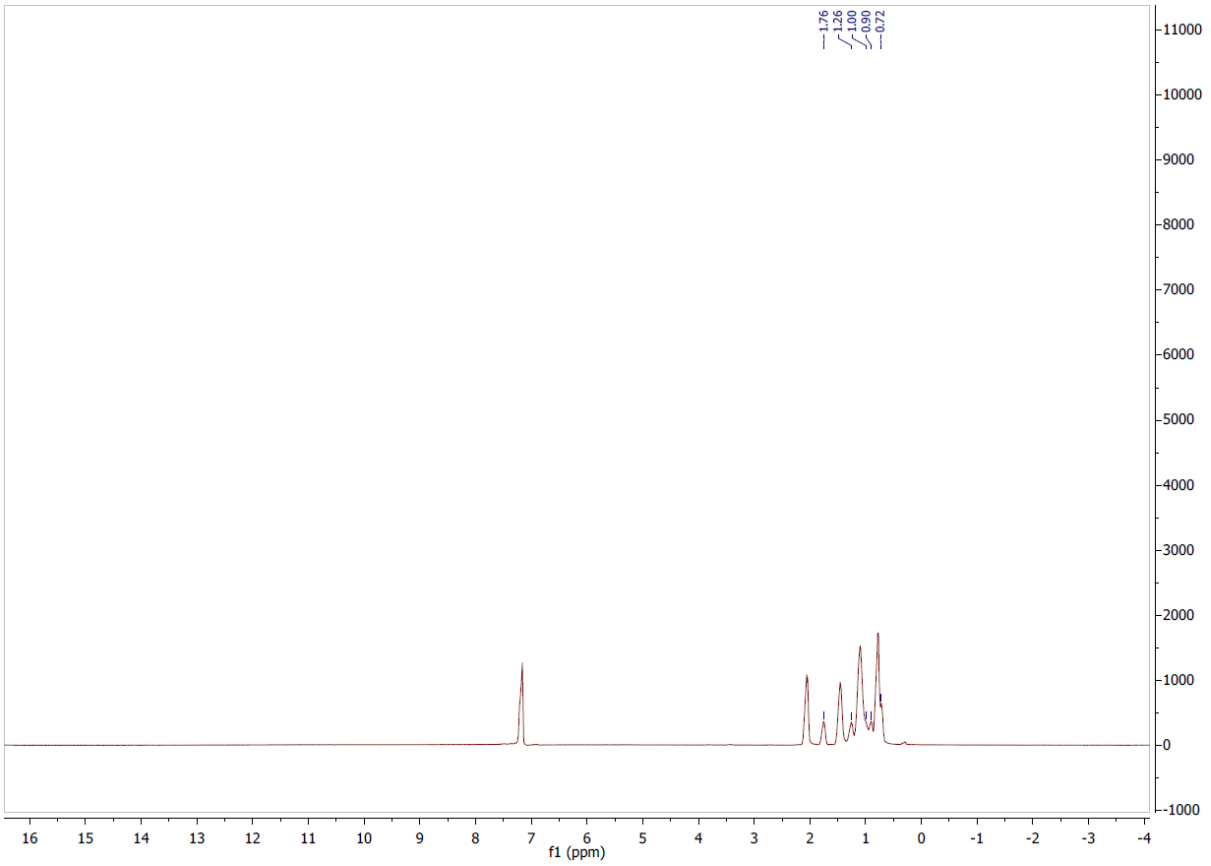


Figure 60: ^{1}H-NMR: percaproic acid *via* W1.

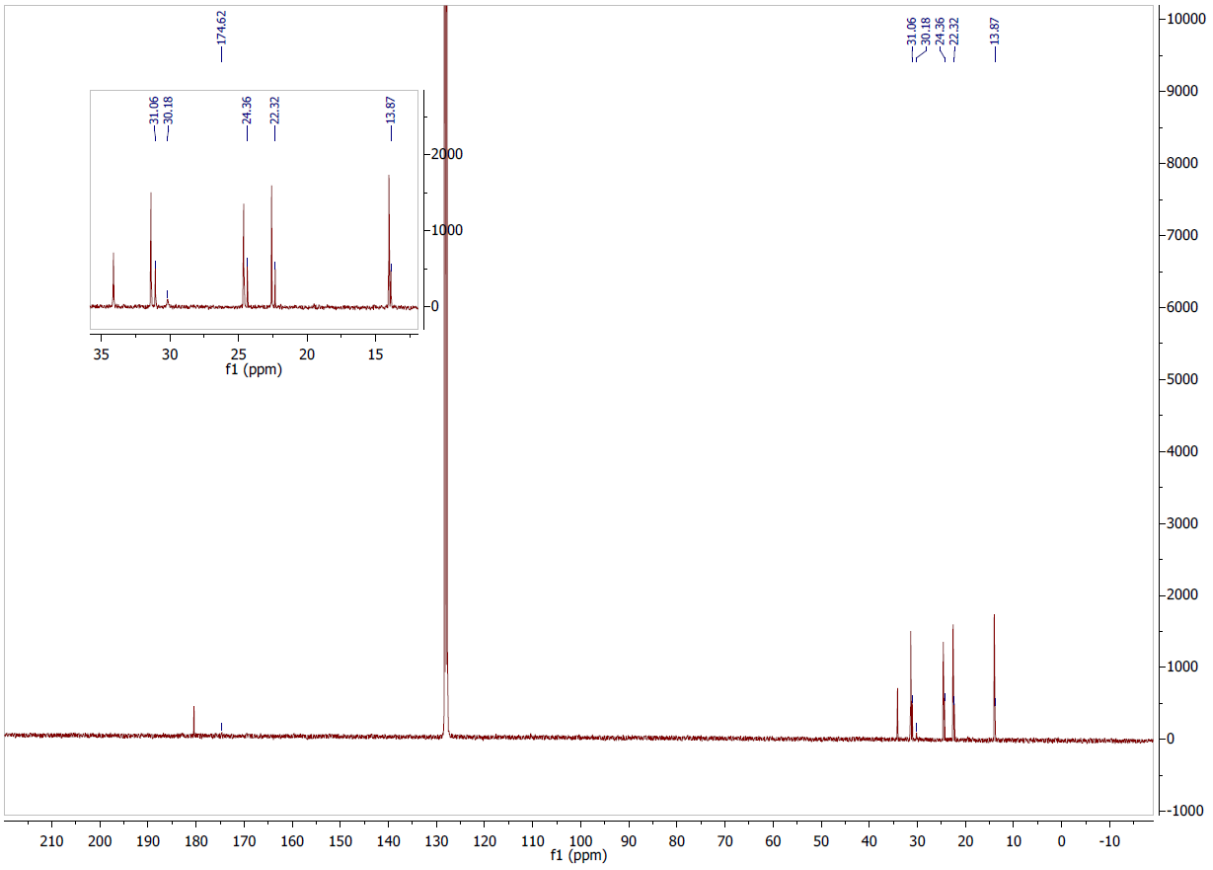


Figure 61: ^{13}C-NMR: percaproic acid *via* W1.

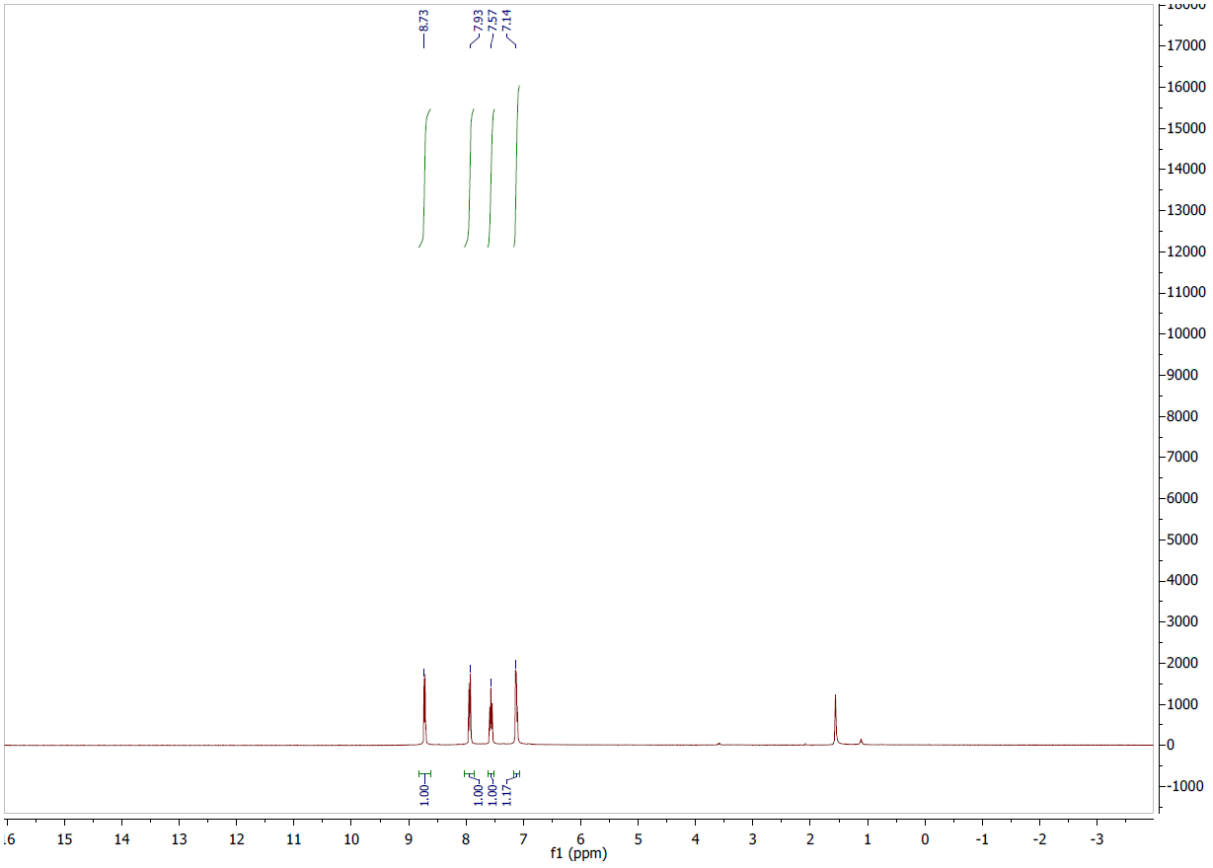


Figure 62: ^{1}H-NMR: tetrazolo[1,5]pyridine

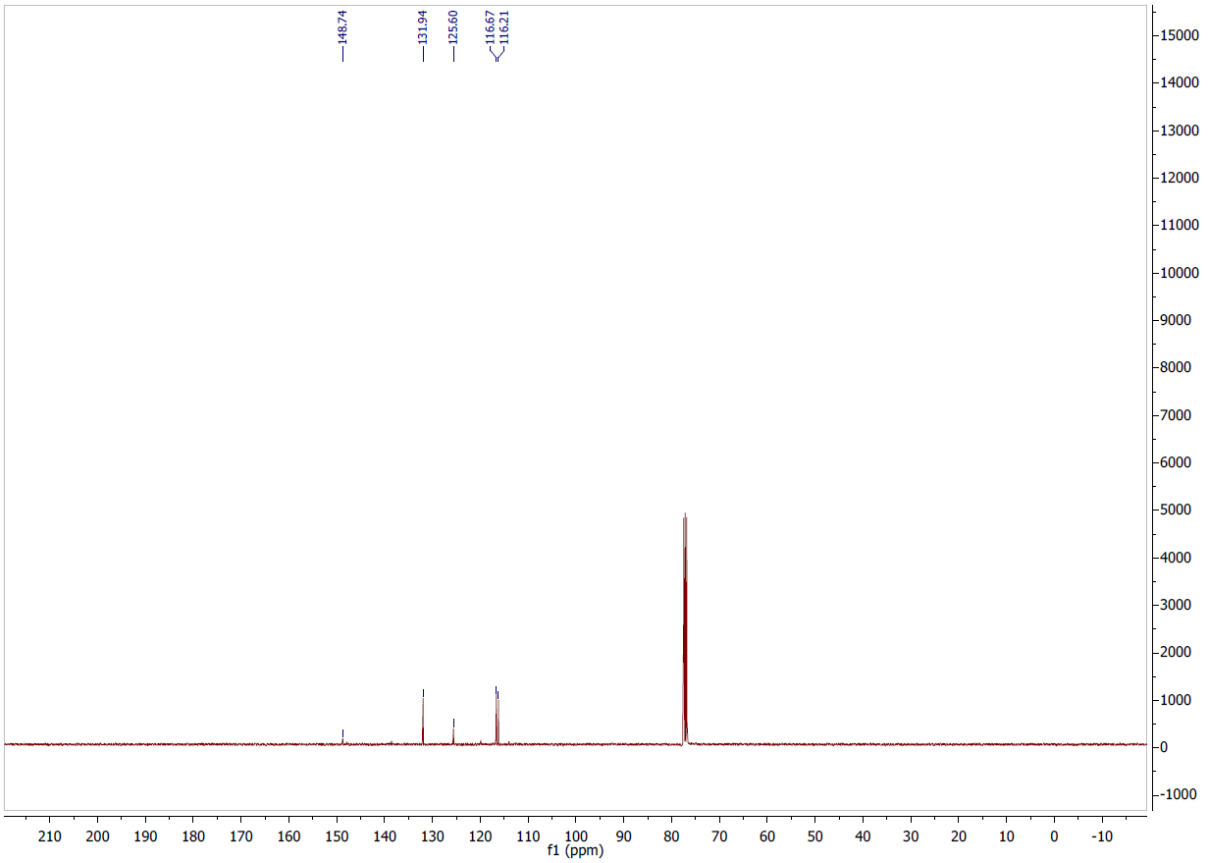


Figure 63: ^{13}C-NMR: tetrazolo[1,5]pyridine.

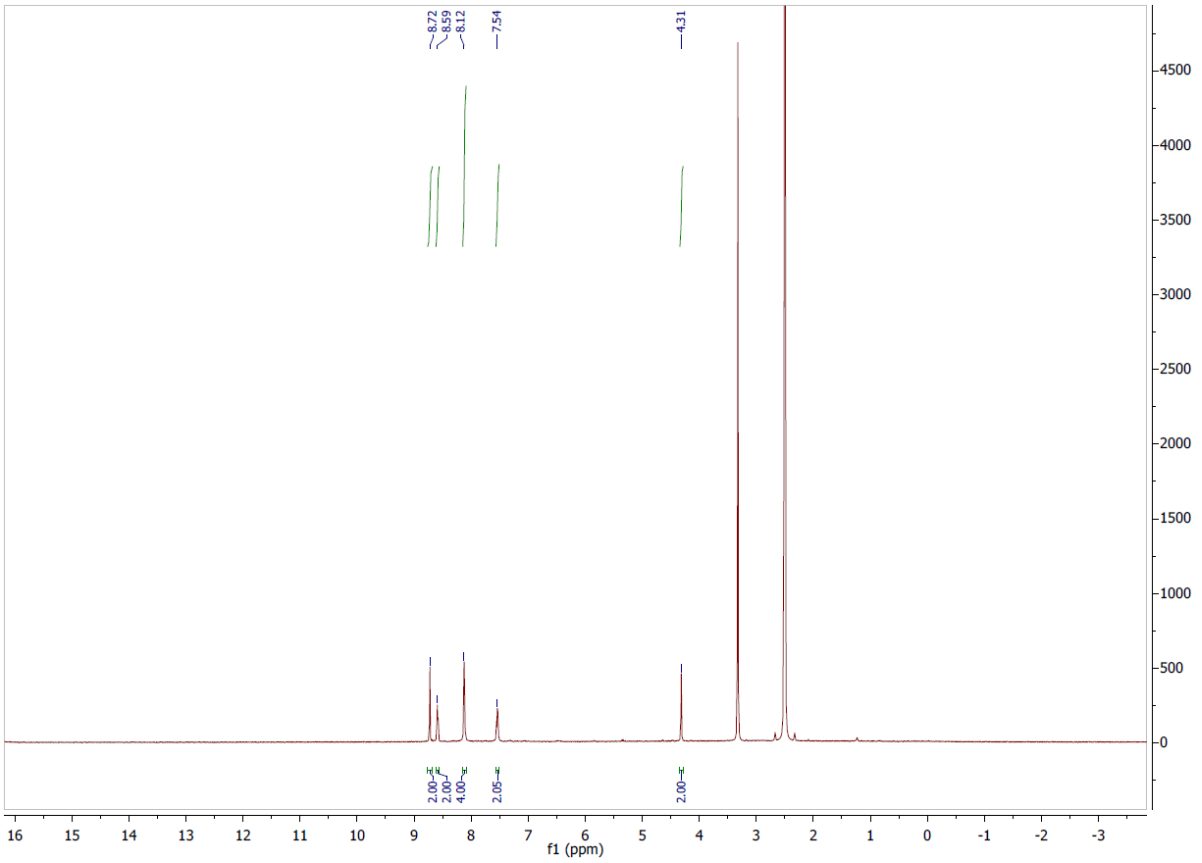


Figure 64: ^{1}H-NMR: bis(1-(2-pyridyl)-1,2,3-triazol-4-yl)methane.

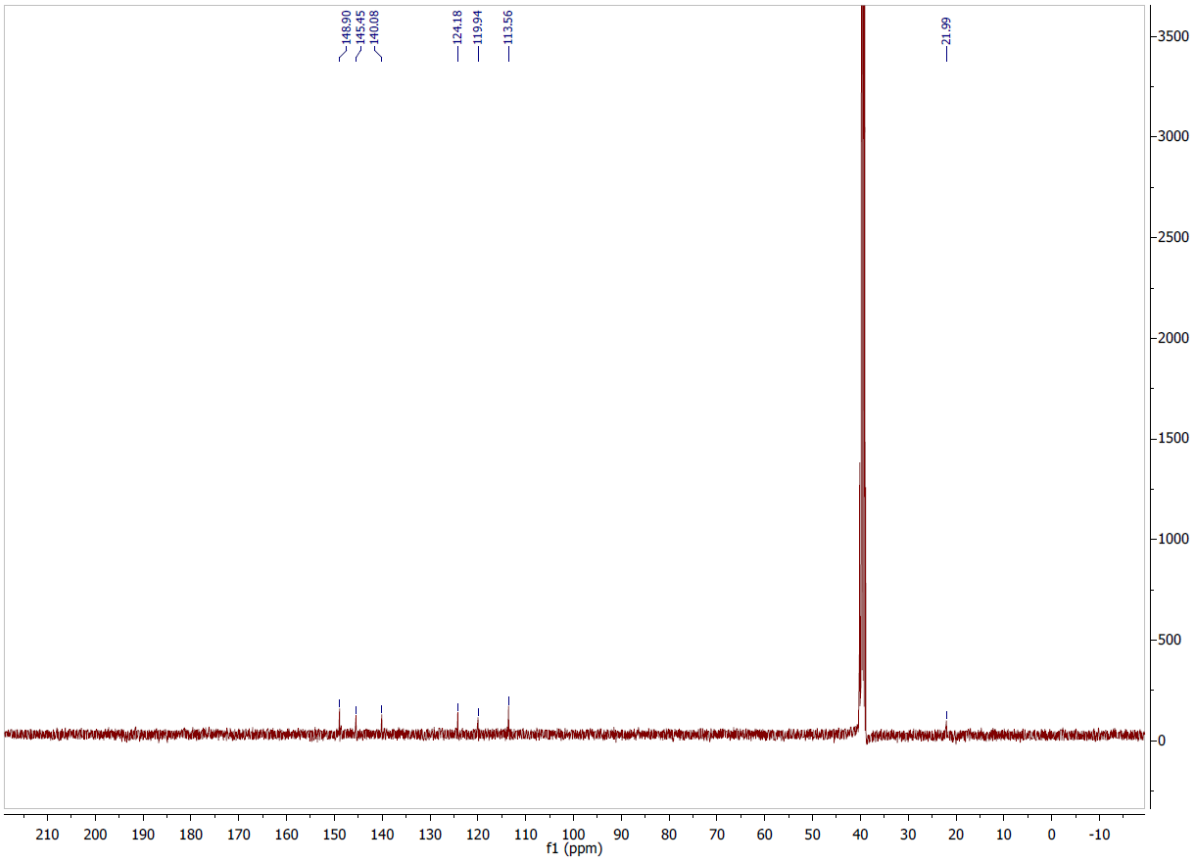


Figure 65: ^{13}C-NMR: bis(1-(2-pyridyl)-1,2,3-triazol-4-yl)methane.

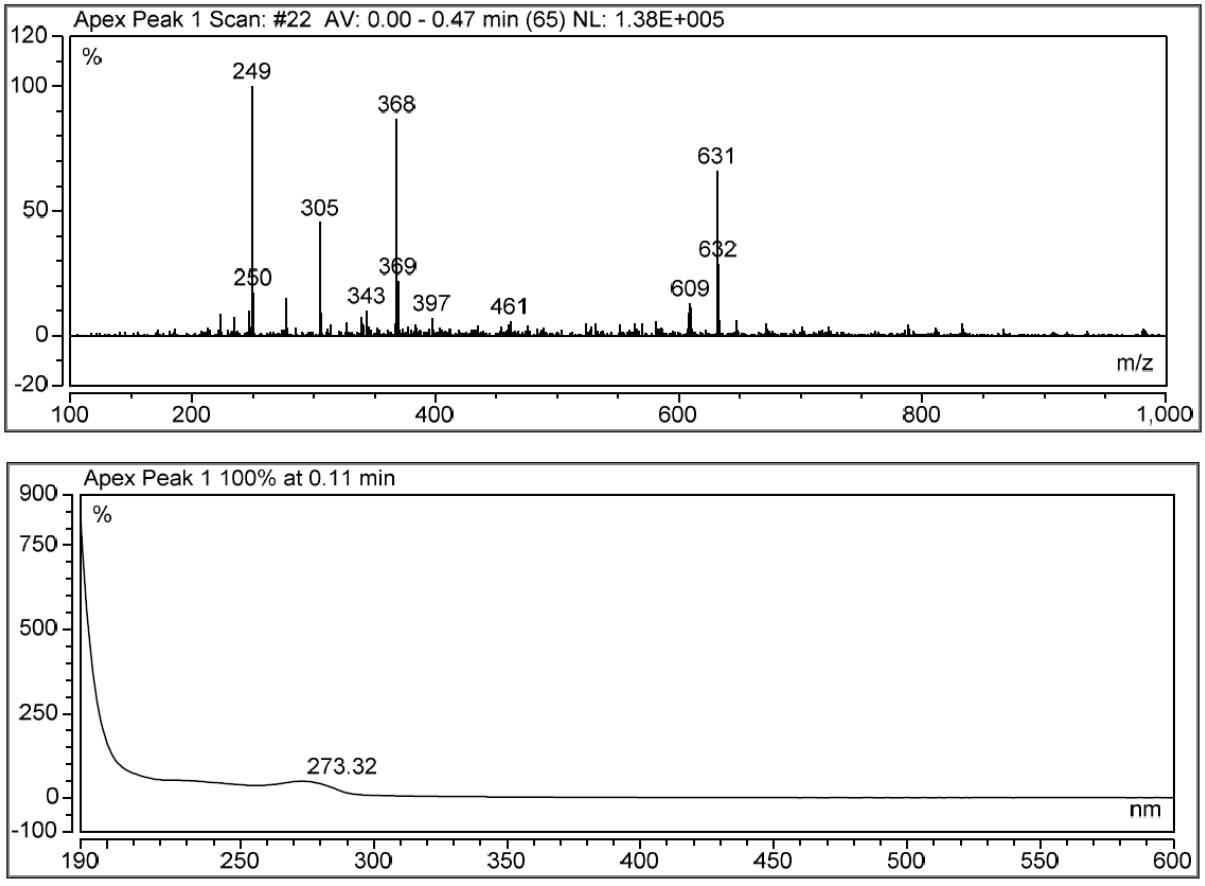


Figure 66: HPLC: bis(1-(2-pyridyl)-1,2,3-triazol-4-yl)methane.

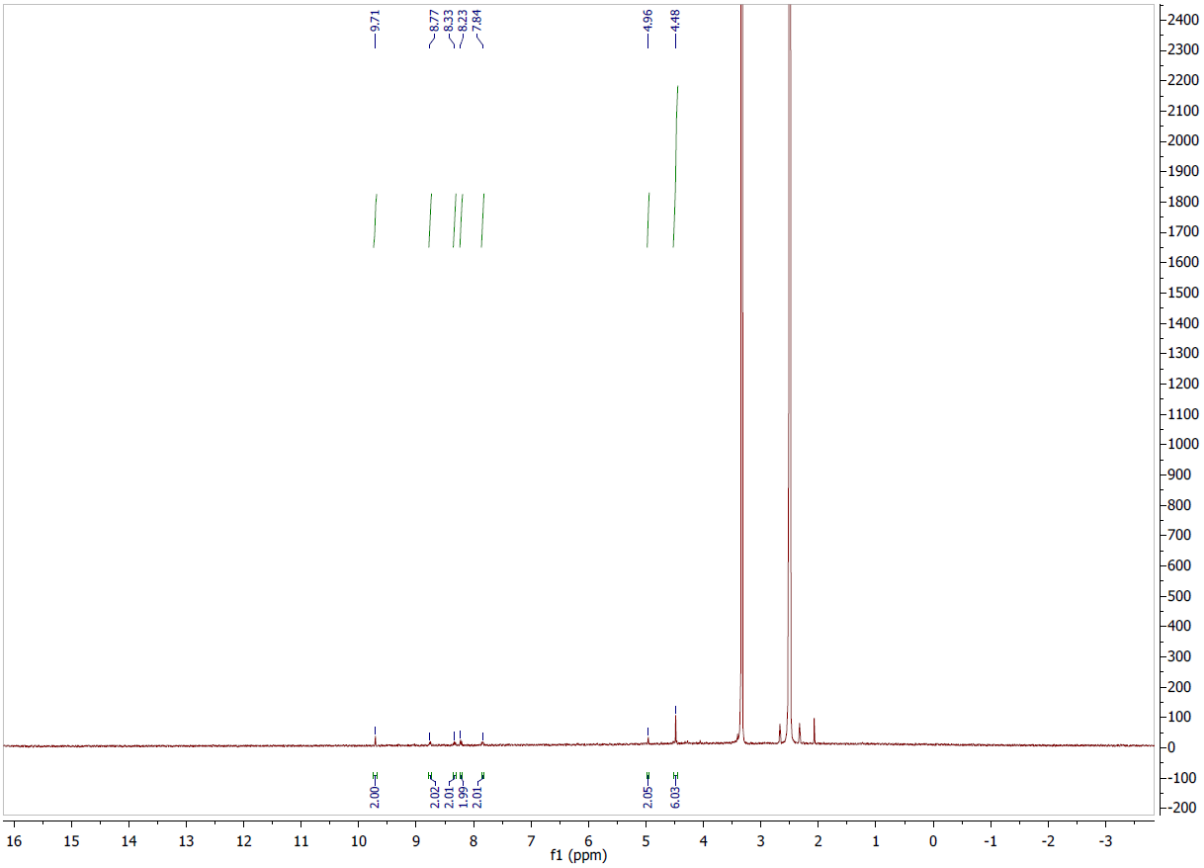


Figure 67: ^{1}H-NMR: **L1**.

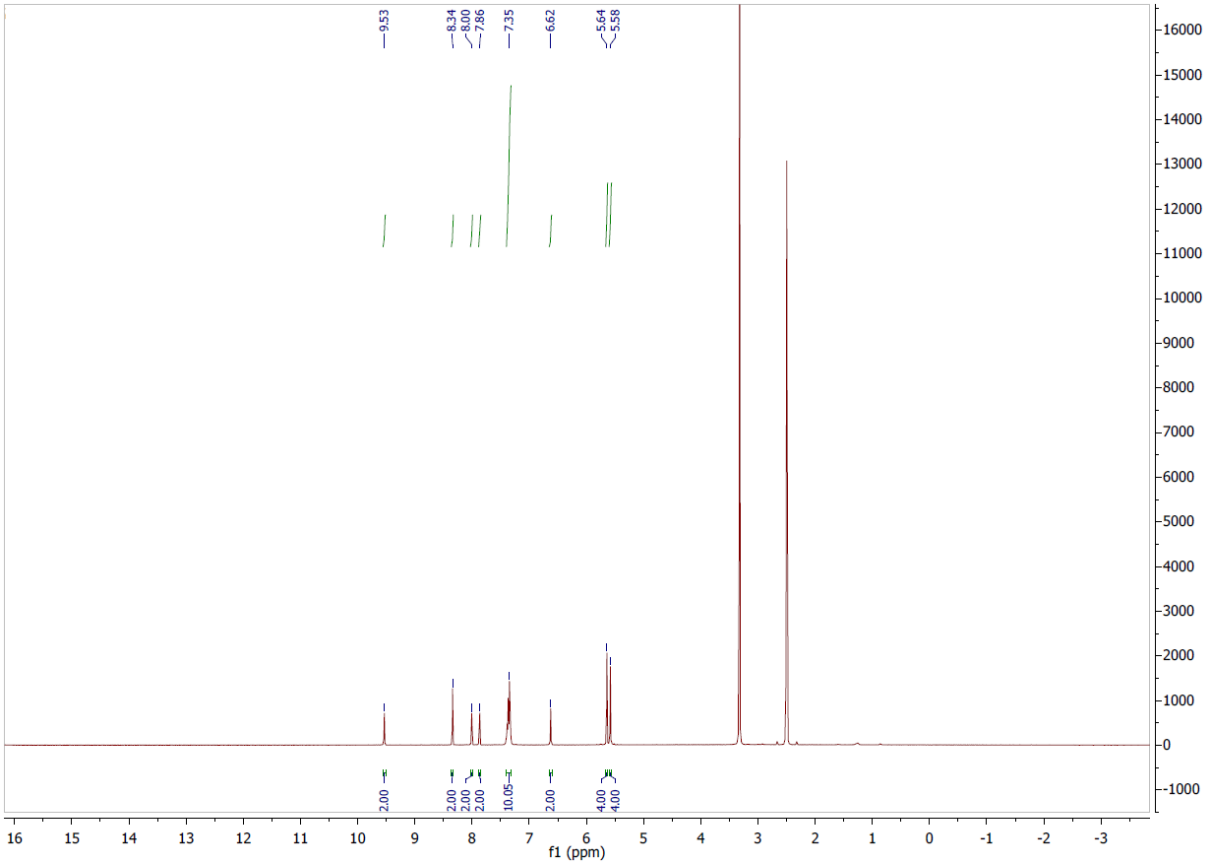


Figure 68: ^{1}H-NMR: **L2**.

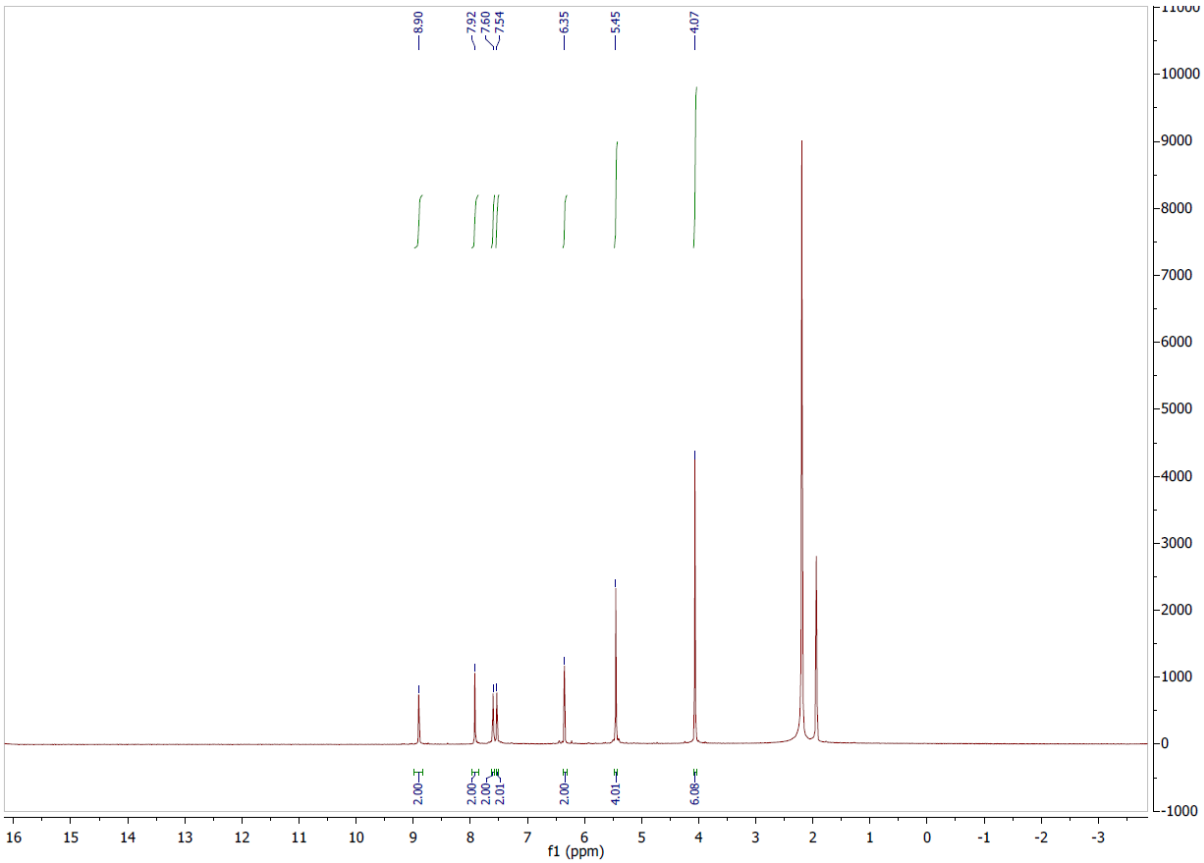


Figure 69: ^{1}H-NMR: **L3**.

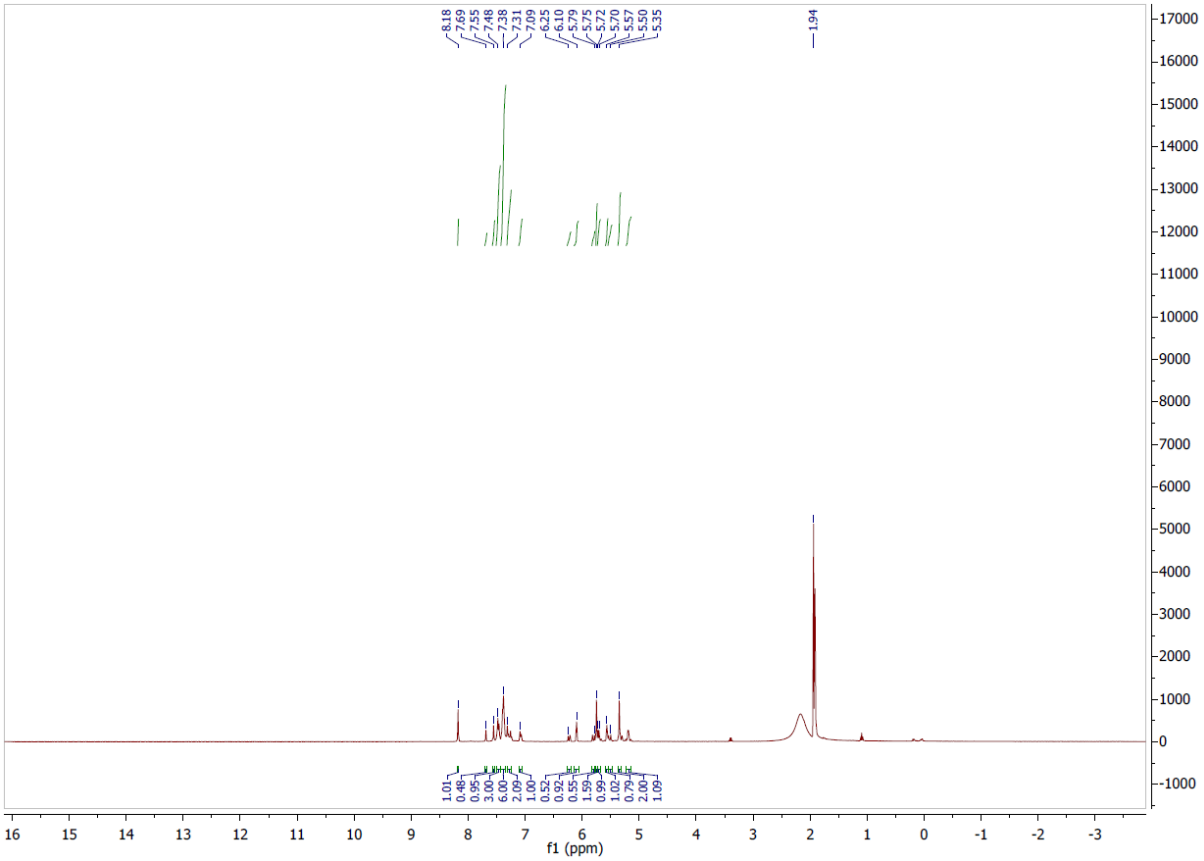


Figure 70: ^{1}H-NMR: **FeL2**.