

# Institut de Chimie de Clermont-Ferrand



**Demi-Journée de l'ICCF**

**Vendredi 12 Juillet 2024**

**9h00 - 12h30**

**Amphi Recherche**

*Merci aux participants et à Stéphanie Bonnefoy, Carole Turpin et Aurélie Violette pour leur aide précieuse !*



# Programme

Heure	Intervenants	Titre de l'intervention	Equipe
9h	Camille <b>Gadona</b>	Synthesis of valuable unsymmetrical $\alpha$ -hydroxyketones through two enzymatic carboligation pathways.	<b>BIOMETA</b>
9h20	Batiste <b>Clavier</b>	Oxydes de manganese fluorés comme matériau d'anode pour les batteries Lithium-Ion.	<b>MI</b>
9h40	Régis <b>Porhiel</b>	Lab-scale Operando measurements for lithium-ion batteries investigation.	<b>MI</b>
10h	Zacharie <b>Bordas</b>	Development of solid-phase synthesis to access peptide oligomers containing crowded tert-butyl side chains.	<b>COM</b>
10h20	Julien <b>Devemy</b>	Point sur la QVT/QVCT à l'ICCF	
<b>Pause Café</b>			
11h	Marina <b>Anastasiou</b>	Exploring the potential of sewage sludge derived biochar: A sustainable approach on wastewater treatment.	<b>PHOTOCHIMIE</b>
11h20	Hugo <b>Clermont</b>	Toward a new analytical approach for monitoring ROS during homogeneous and heterogeneous AOPs.	<b>PHOTOCHIMIE</b>
11h40	Yongrong <b>Zou</b>	Homogenous advanced oxidation processes for the removal of nano-plastics in water.	<b>PHOTOCHIMIE</b>
12h	Vincent <b>Théry</b>	Comparaison des déplacements chimiques calculés en Ab initio versus l'expérience : Application au Bore.	<b>COM</b>
12h20	Fabrice <b>Leroux</b>	Clôture de la 1/2 journée	



## Synthesis of valuable unsymmetrical $\alpha$ -hydroxyketones through two enzymatic carbonylation pathways

Camille Gadona<sup>1</sup>, Giuseppe Arbia<sup>1</sup>, Nicolas Duguet<sup>2</sup>, Franck Charmantra<sup>1</sup>, Laurence Hecquet<sup>1</sup>

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A chemoenzymatic strategy is investigated to obtain highly valuable unsymmetrical  $\alpha$ -hydroxyketones (acyloins), precursors of vinylene carbonate, useful building blocks for prodrugs synthesis such as medoxomil.<sup>1</sup> Two enzymatic pathways were investigated to obtain  $\alpha$ -hydroxyketones (Fig 1). According pathway A, TK catalyses the irreversible transfer of a ketol or acyl group from an  $\alpha$ -ketoacid donor to an aldehyde acceptor with concomitant decarboxylation of the donor and release of carbon dioxide. The  $\alpha$ -ketoacid could be generated *in situ* from the corresponding D-aminoacid with a D-aminoacid oxidase (D-AAO), as initiated by our group.<sup>2,3</sup> The more challenging pathway B was based a TK promiscuous activity which consists in a condensation between two aldehydes, allowing atom economy and the use of cheap substrates.<sup>4</sup> To improve TK activity toward the targeted substrates, variants will be designed by rational mutagenesis based on the analysis of TK active site.

Finally, the unsymmetrical  $\alpha$ -hydroxyketones will be used with organocatalysts such as *N*-heterocyclic carbenes (NHC) and a carbonyl source for the synthesis of vinylene carbonates<sup>5</sup> never investigated before due to the difficulty to control the regioselectivity by chemical ways (collaboration with ICBMS, Lyon).

This chemo-enzymatic strategy combining enzymes and organocatalysts in a one-pot could be performed sequentially or simultaneously avoiding the purification of intermediates and will considerably expand the scope of vinylene carbonates.

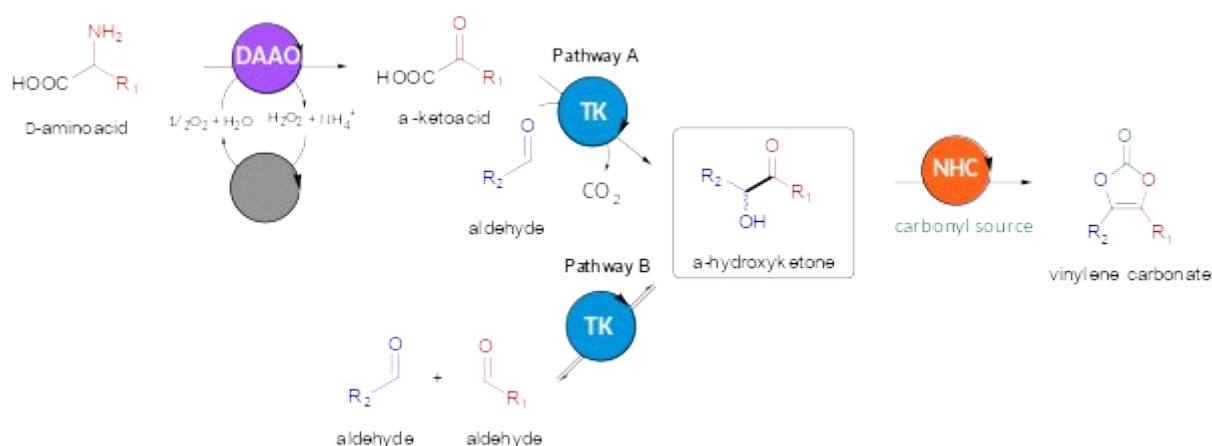


Fig. 1: Chemoenzymatic strategy investigate to obtain highly valuable unsymmetrical  $\alpha$ -hydroxyketones

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- [2] L'enfant et al, *Adv. Synth. Catal.* **2019**, 361, 2550-2558
- [3] N. Ocal et al, *Adv. Synth. Catal.* **2023**, 365, 78-87
- [4] G. Arbia et al, *Green Chem.* **2024**, 26, 7320-7330
- [5] K. Onida et al, *Adv. Synth. Catal.* **2021**, 363, 5129-5137



## OXYDES DE MANGANESE FLUORÉS COMME MATERIAU D'ANODE POUR LES BATTERIES LITHIUM-ION

Batiste CLAVIER<sup>1</sup>, Régis PORHIEL<sup>1</sup>, Taylan KARAKOC<sup>2</sup>, Dominique BEGIN<sup>2</sup>, Sergey PRONKIN<sup>2</sup>, Sylvie BEGIN<sup>3</sup>, Asma FATNASSI<sup>4</sup>, Sandrine BERTHON-FABRY, Katia GUERIN<sup>1,4</sup>, Elodie PETIT<sup>1</sup>, Malika EL-GHOZZI<sup>1</sup>

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La batterie lithium-ion connaît un essor considérable depuis ces quinze dernières années. Les performances électrochimiques de tels dispositifs dépendent tout particulièrement des propriétés des matériaux d'électrode que ce soit en termes de capacité spécifique, de conductivité ionique et électronique, de leur surface spécifique et de leur compatibilité avec l'électrolyte<sup>[1]</sup>. Les oxydes de métaux de transition occupent actuellement une part importante dans la recherche et le développement des dispositifs de stockage de l'énergie en tant que matériaux de cathode ou d'anode dans les batteries Li-ion<sup>[2,3]</sup>. Les problèmes de réversibilité inhérents à ces matériaux peuvent être résolus par un dopage au fluor<sup>[4]</sup>.

Ce travail, fruit d'une collaboration nationale entre 3 laboratoires (ANR Infine), présentera l'apport de la fluoration sur les performances électrochimiques de nanoparticules de  $Mn_3O_4$  en tant que matériau d'anode pour les batteries Li-ion. Deux procédés de fluoration seront présentés et comparés : la fluoration moléculaire par  $F_{2(g)}$  et la fluoration radicalaire par  $XeF_{2(s)}$ .

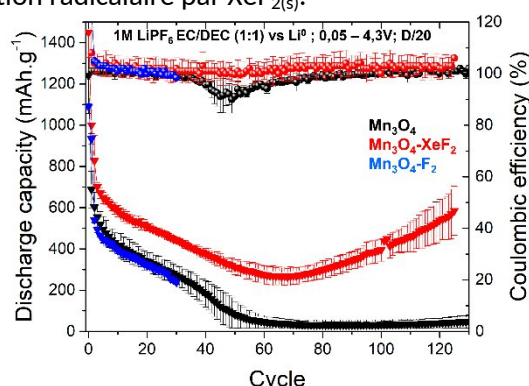


Figure 1 : Performances électrochimiques de  $Mn_3O_4$  en tant que matériau d'anode

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[3] Roy, P., Srivastava, S. K. *J. Mater. Chem. A*, **2015**, 3(6), 2454-2484.

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## Lab-scale *Operando* measurements for lithium-ion batteries investigation

Régis PORHIEL<sup>1</sup>, Batiste CLAVIER<sup>1</sup>, Elodie PETIT<sup>1</sup>, Malika EL GHOZZI<sup>1</sup>, Katia GUÉRIN<sup>1</sup>

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Lithium-ion batteries have become the dominant energy storage technology, finding applications across a wide range of fields, from portable electronics to electric vehicles. Several challenges still face the wider development of lithium-ion batteries, such as the limited abundance of raw materials required for the electrodes, the lifetime of the batteries, or the safety concerns arising from a wide scale implementation. Extensive research is thus needed in order to tackle these issues, including the physicochemical characterization of the battery components at different stages of their life.

Among characterization methods, *Operando* measurements are the most advanced techniques, as they allow monitoring the real time evolution of the battery in working condition, in specifically designed cells (Figure 1.b).<sup>1</sup> These techniques were however limited to synchrotron or neutron-source experiments, as highly energetic and definite beams are required for a real-time monitoring. In recent years, lab-scale instruments improvement allows *operando* techniques to be developed in the laboratory, without requiring the uncertain and time-consuming beam time proposal process.<sup>2</sup>

This presentation aims at introducing *Operando* techniques recently developed at the ICCF and their potential applications in lithium-ion batteries investigation. The complex electrochemical mechanism of FeF<sub>3</sub> active material will be introduced through *operando* Raman spectroscopy characterization as an example (Figure 1.c).

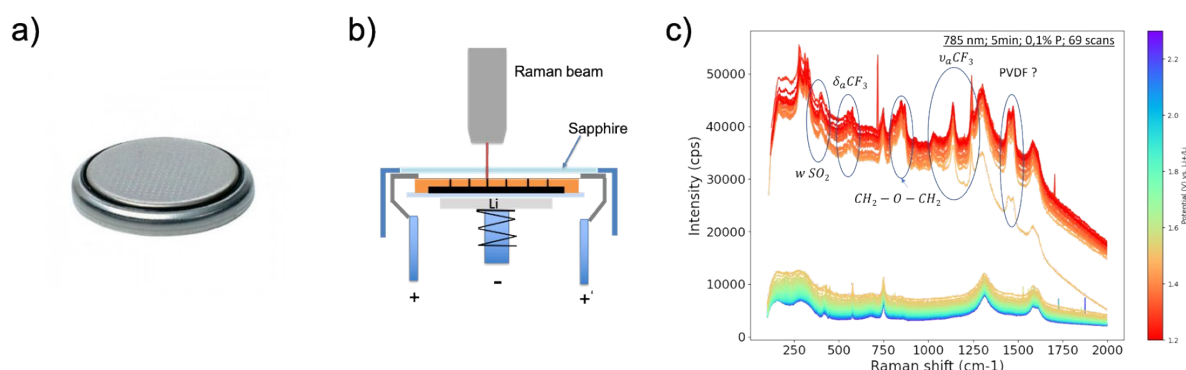


Figure 1: (a) Picture of a CR-2032 coin-type cell for LIBs; (b) Schematic representation of an *Operando* cell for Raman spectroscopy and (c) *Operando* Raman spectra obtained during the reduction of FeF<sub>3</sub> / 1M LiTFSI TEGDME / Li between 2.3 to 1.2 V vs. Li<sup>+</sup>/Li at room temperature

### REFERENCES:

- [1] H. Li, S. Guo and H. Zhou, *Journal of Energy Chemistry* 59 **2021**, 191–211
- [2] A. Krishnan, *et al.* *ACS Appl. Mater. Interfaces* **2024**, 16, 13, 16096-16105



## DEVELOPMENT OF SOLID-PHASE SYNTHESIS TO ACCESS PEPTOID OLIGOMERS CONTAINING CROWDED TERT-BUTYL SIDE CHAINS.

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In 1992, peptoids, a new class of biotic foldamers emerged [1]. Peptoids, *i.e.* *N*-substituted glycine oligomers, represent a unique class of protease-resistant peptidomimetics that closely resemble peptides. However, substitution of the amide nitrogen reduces the ability to form intramolecular hydrogen bonds and, consequently, the factors governing peptoid folding are different. Tertiary amide bonds in peptoids generally exist as *cis*- and *trans*-isomers in equilibrium. The adoption of stable secondary structures relies on the ability to control this equilibrium, which in turn depends to a very large extent on side chain chemistry (electronic factors, steric hindrance, ability to form hydrogen bonds). Our group has enriched the peptoid toolbox by proposing several *cis*-inductive side chains, and in particular the *tert*-butyl side chain [2]. Steric hindrance of the *tert*-butyl group has a profound effect on the *cis/trans* isomerism of the peptoid-amide bond, which adopts an exclusively *cis* geometry. This side chain has already shown its ability to strongly stabilise polyproline I (PPI)-type helices [3]. However, steric hindrance of the amino group of the *Nt*Bu unit has so far limited its incorporation using solution-phase protocols. Here, we report the first solid-phase syntheses of peptoids containing *Nt*Bu units, using a modified submonomer protocol. To demonstrate the effectiveness of this new protocol, we synthesized a series of homooligomers with up to 12 *Nt*Bu units and applied it to the synthesis of various peptoid oligomers with sterically demanding *N*C $\alpha$ -gem-dimethyl side chains (mimics of proteinogenic side chains) [4].

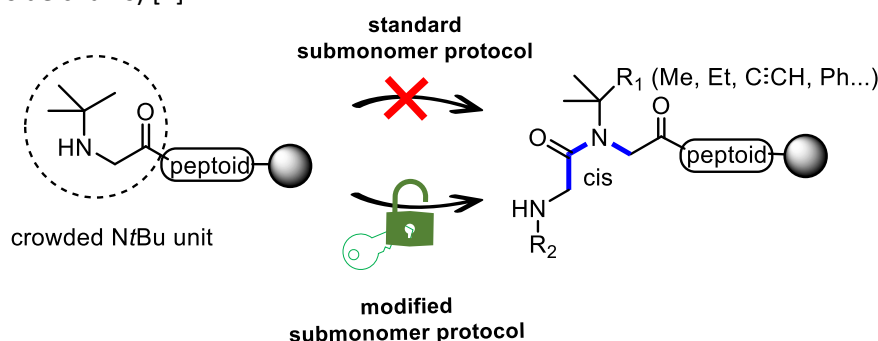


Figure 1: General scheme of solid-phase synthesis to obtain oligomers containing *tert*-butyl enclosed lateral chains

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 [2] O. Roy, C. Caumes, Y. Esvan, C. Didierjean, S. Faure, C. Taillefumier. *Org Lett.* **2013**, 15, 2246-2249.  
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## ***Exploring the potential of sewage sludge derived biochar: A sustainable approach on wastewater treatment.***

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<sup>1</sup> Université Clermont Auvergne, CNRS, Clermont Auvergne INP, ICCF, F-63000 CLERMONT-FERRAND

With the increasing water stresses in the last decade due to climate change and growing pollution, restoration of water quality for its reuse and relief of natural resources is essential. At the same time, more and more pollutants are being detected in Wastewater Treatment Plants' (WWTP) effluents, with the recent technologies being insufficient for their removal, while millions of tons of Sewage Sludge, a by-product of wastewater treatment, are produced yearly, presenting the facilities with a high disposal cost. This project aims to give answers to these two problems by thermochemically converting sewage sludge to biochar, proposing its use as a cost-effective and sustainable method for the elimination of wastewater contaminants through adsorption and photochemical processes.

For the first year of this project, biochar is characterized through ATR, SEM, EDS, TGA and DSC and tested for its potential to remove dyes, pharmaceuticals and commonly found compounds in wastewater through adsorption with promising results. Parameters such as biochar's particles size, its concentration and the contaminants' concentration are investigated for their impact on adsorption efficiency. The enhancement of biochar's performance is implicated through an assortment of physical and chemical treatment methods with alkaline, acidic treatment and UVC irradiation being amongst them. Biochar's potential contribution to the pollutant's degradation through photochemical reactions and the production of Reactive Oxygen Species (ROS) is also explored for an enhanced removal efficiency.



**Figure 1** Overview of the sources of contaminants in wastewater, the production of sewage sludge derived biochar and its application on water decontamination.

### **Acknowledgements**

This work is funded by the European Union's Horizon Europe Doctoral Networks programme under the Marie Skłodowska-Curie Actions.





## Toward a new analytical approach for monitoring ROS during homogeneous and heterogeneous AOPs.

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### Abstract:

Advanced Oxidation Processes (AOPs) offer an efficient way for water remediation and depollution. They can be used as a wastewater treatment to further decrease the concentration of concerning and refractory pollutants. AOPs can also be used to further purify drinkable water by using reactive oxygen species (ROS) to degrade most of the organic pollutants that cannot be destroyed by classical means. ROS will participate in a degradation chain with the pollutants to break it down until complete mineralization is achieved. AOPs are trendier than ever and thus their usage is more and more common. However, the mechanisms behind most AOPs remain quite unknown to this day because of the very nature of the ROS: their high reactivity.

Our work focuses on developing a method able to give information regarding the production of the ROS overtime during an AOP. This method would give hints on a temporal resolution of the concentration of the ROS in a solution through the use of specific fluorescent probes that react with a specific species. By having temporal information, an evolution of a specific ROS could be detected, giving insight on the degradation pathway, the mechanistic approach of the degradation and many more details.

Amongst the ROS active enough to degrade pollutant, the hydroxyl radical (OH<sup>\*</sup>) is of particular interest. As being one of the most reactive of all the ROS, its very short lifetime renders difficult the identification and quantification process with a traditional method using probes. This led to the development of a multi-approach method, where the radical is formed alongside its specific probe in a separate reactor from the main AOP.

For example, when studying the peroxide photolysis ( $\text{H}_2\text{O}_2 + \text{UV} \rightarrow 2 \text{OH}^*$ ), mixing the probe and the irradiated solution ex-situ proved to be inefficient regarding the quantification of OH radical. As this AOP does not produce a lot of OH<sup>\*</sup>, a very small portion was reacting with the probe, giving a weak signal. To bypass this limitation, we would irradiate both the probe and the peroxide so that the hydroxyl is formed alongside the probe and can react much more easily and in greater amounts. This proved successful and the signal was greatly improved even for low production AOPs.

The Mirror-Method approach (MiMe) works as replica of the main reactor and can be use throughout the reaction to monitor the oxidative capacity of a solution over time. This method can shed light on secondary ROS precursors production that the classical means of measurement cannot reveal as a temporal analysis of oxidative species is required. Finally, the MiMe can also be used with other probes to react specifically with other ROS such as superoxide, singlet oxygen or peroxide to give information over a complete panel of ROS during an AOP.

### Acknowledgements

This work was supported financially by a doctoral Scholarship of the UCA.





## Homogenous advanced oxidation processes for the removal of nano-plastics in water

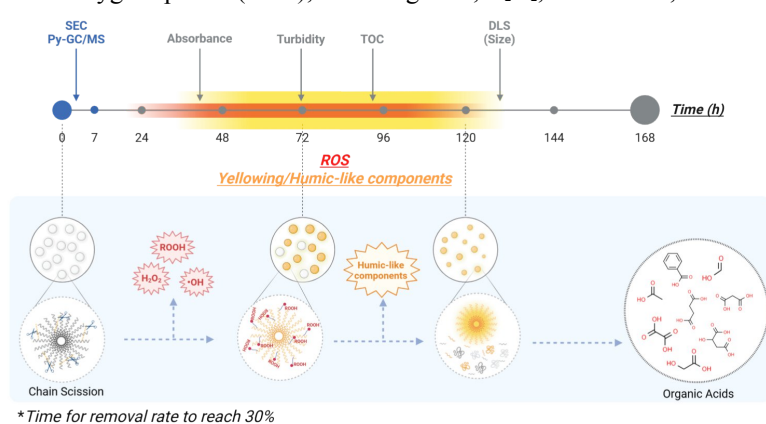
Yongrong ZOU<sup>1</sup>, Gilles MAILHOT<sup>1</sup>, Mohamad SLEIMAN<sup>1</sup>.

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During human-induced disposal or natural weathering, plastic is prone to fragmenting or degrading into small particles, which, depending on their size, can be defined as microplastics (MPs, 1  $\mu\text{m}$  to 5 mm) or nanoplastics (NPs, 1 to 1000 nm) [1]. The small-sized plastic fragments pose a greater threat to ecosystems and humans than larger plastic pieces, which has attracted global concern. In particular, there is a lack of knowledge about the environmental behavior of NPs due to the small size and complex chemical properties of NPs, and the limitations of current detection technologies. However, the current urgency lies in developing an effective and sustainable approach to degrading NPs in water.

In this study, we focused on applying different homogenous advanced oxidation processes (AOPs) for the removal of nano-sized plastics from water, evaluating the impact of different UV-induced oxidation processes on the apparent color and turbidity of the suspension, microscopic morphology, dynamic size, molar weight, UV characteristic absorption, and intermediate products. Specifically, the dynamic changes of  $\bullet\text{OH}$ ,  $\text{H}_2\text{O}_2$ , and ROOH during the reaction process were monitored using fluorescence spectrophotometer and high-performance liquid chromatography (HPLC) techniques.

The photoaging of NPs induced by photo-based AOPs is shown in the Fig.1. The light could induce NPs to generate reactive oxygen species (ROS), including  $\bullet\text{OH}$ ,  $\text{H}_2\text{O}_2$ , and ROOH, which subsequently attack the surface of NPs, resulting in the production of yellowing discoloration and humic-like components.



**Fig.1** Schematic illustration of NPs photoaging behavior in water.

The qualitative and quantitative analysis of NPs in the AOPs and quantitative monitoring of ROS can help us to understand the behavior of NPs in the environment, which also provides a scientific basis for the development of effective nano-pollution control strategies.

### Acknowledgements

This work was supported financially by ANR AOPNANOP and Chinese Scholarship Council. The authors thank Guillaume Vyard for his valuable contribution in IC/MS analysis.

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## Comparaison des déplacements chimiques calculés en *Ab initio* versus l'expérience : Application au Bore.

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L'objectif est ici de pouvoir identifier tous les pics du spectre du Bore lors de la réaction d'hydroboration. C'est à dire identifier la structure chimique du bore qui correspondra à un des pics du spectre ci-dessus. Nos références de départ seront le BH<sub>3</sub> dans le THF (produit de départ) et BF<sub>3</sub> étherate qui est la référence en RMN.

Le calcul du déplacement chimique sera fonction de la combinaison Hamiltonien/Base. Premièrement pour la géométrie optimisée du système chimique et deuxièmement pour la densité électronique au niveau du noyau qui servira à calculer l'écrantage du champs magnétique externe et ainsi obtenir le tenseur de blindage chimique.

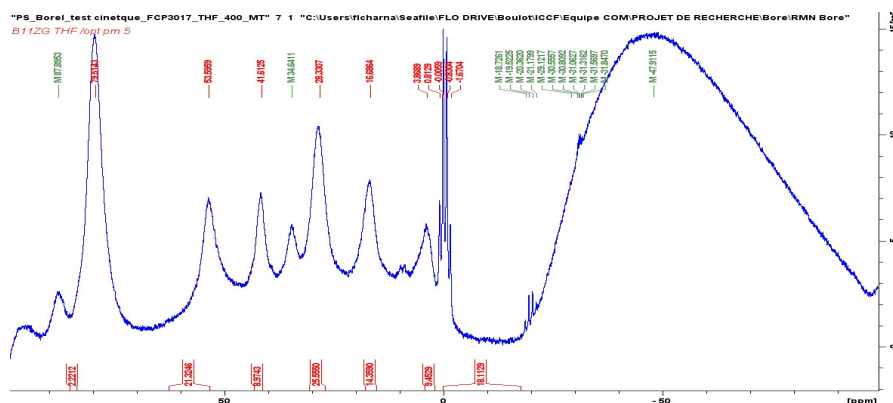


Figure 1: Spectre RMN du Bore pendant la réaction d'hydroboration.

Le bore possède une orbitale atomique vide et peut donc, dans certaine configuration chimique, jouer le rôle d'acide de Lewis vis à vis du solvant ou d'autre base de Lewis. Cela ajoute une difficulté dans l'obtention de la bonne structure chimique.

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