**Initiative
Nouvelles Réactivités
en Chimie Moléculaire**
ALLIANCE SORBONNE UNIVERSITÉ

Appel à projets
iDream 2025

Sequential degradation/valorization of lignin through catalysis - DELICAT

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Academic background

Jan. 2024 **HDR** in Organic Chemistry – Sorbonne Université, Paris
Towards new and more sustainable reactions for the synthesis of molecules of interest.

2009-2012 **PhD in Organic Chemistry** – UPMC/ENSCP Chimie ParisTech, Paris
Cycloisomerization reactions in the presence of Gold, Platinum complexes and iodogenium ions – Combinatorial approach in the presence of Platinum complexes. Acyloxylation reactions by arene C-H activation in the presence of Gold complexes.

2008-2009 **MSc in Organic Chemistry** – Université de Picardie Jules Vernes, Amiens
Green Chemistry and Organic Chemistry of natural products.

2006-2009 **French engineering diploma in Chemistry** – ESCOM, Cergy & Compiègne
Organic and General Chemistry, Process/Industrial Chemistry and Chemical engineering.

Research activities

2016-now **CNRS Research investigator** – Sorbonne Université, Paris
Institut Parisien de Chimie Moléculaire

2016 **Postdoctoral researcher** – Normandie Université, Le Havre
URCOM – under the supervision of Prof. Vincent Dalla and Dr. Catherine Taillier
Gold and N-acyliminium chemistry with ynamides.

2015 **Postdoctoral researcher** – University of Nottingham, Nottingham
Pfizer Organic Synthesis laboratory – under the supervision of Prof. Christopher J. Moody
Total Synthesis of diazonamide A.

2013-2014 **Postdoctoral researcher** – Université Libre de Bruxelles, Brussels
Laboratoire de Chimie Organique – under the supervision of Prof. Gwilherm Evano
Development of new Cu-catalyzed coupling reactions.

2009-2012 **PhD student** – Université Pierre et Marie Curie/Chimie ParisTech, Paris
Laboratoire Charles Friedel – under the supervision of Dr. Véronique Michelet and Dr. Patrick Toullec

2009 **MSc. intern** – Merck KGaA, Darmstadt
Laboratorium für medizinische Chemie, Onkologie – under the supervision of Dr. Markus Klein
Synthesis of PI3K inhibitor candidates as treatment against cancer.

5 significant publications

1) Di Matteo, M.; Gagliardi, A.; Pradal, A.; Veiros, L. F.; Gallou, F.; Poli, G. *J. Org. Chem.* **2024**, *89*, 10451.
2) Chen, T.; Lahbi, J.; Broggini, G.; Pradal, A.; Poli, G. *Eur. J. Org. Chem.* **2023**, e202201493.
3) Bassoli, S.; Schallmey, A.; Oble, J.; Poli, G.; Pradal, A. *Catal. Res.* **2022**, *2*, 36.
4) Carlet, F.; Bertarini, G.; Broggini, G.; Pradal, A.; Poli, G. *Eur. J. Org. Chem.* **2021**, 2162.
5) David, N.; Pasceri, R.; Kitson, R. R. A.; Pradal, A.; Moody, C. J. *Chem. Eur. J.* **2016**, *22*, 10867.

CURRICULUM VITAE

Franck LAUNAY

Full Professor

Age:	57 years old
Nationality :	French
Professional address :	Laboratoire de Réactivité de Surface, UMR CNRS 7197, Faculté des Sciences et Ingénierie, Sorbonne Université, 4 place Jussieu, CC 198, F-75252 Paris Cedex 05
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Member of the Société Chimique de France (SCF) - https://orcid.org/0000-0001-7504-9659

OCCUPIED POSITIONS

2010-	**Professor** / Laboratoire Réactivité de Surface (LRS) - ***RESEARCH THEMES****: Upgrading of* CO_2*, lignin and polymers / Synthesis of functionalized mesoporous silicic materials and magnesium oxides / Oxidative and reductive C-C and C-O bond cleavage / Photocatalysis* *- Inorganic Chemistry (Bachelor) / Nanoparticle Catalysis (Master) / Sustainable Chemistry (Bachelor, Master) / Projects-based Experimental Teaching (Bachelor) / Green Label (Hybrid and projects-based teaching, Bachelor).*
1999-2010	**Assistant, then Associate Professor /** Lab. Systèmes Interfaciaux à l'Echelle Nanométrique (1999-2008), then Réactivité de Surface (2009-2010)
1998-1999	**A.T.E.R. /** ENS Cachan, Lab. de Photophysique et Photochimie Supramoléculaires et Macromoléculaires
1997-1998	**A.T.E.R. /** Université Joseph Fourier (Grenoble I), Laboratoire de Chimie de Coordination au CEA/DRFMC/SCIB
1996-1997	**Associate Researcher /** Texas A & M University, USA, 20 months

CURRICULUM

2008	**HDR of Université Pierre et Marie Curie / Chemistry** Titre : *"Development of supported and unsupported catalytic systems for a more environmentally friendly chemistry "* defended on september 24th **2008**.
1991-1995*	**Doctorate from the University of Rennes I - Specialization: Chemical Sciences** PhD title : *" Catalytic oxidation using iron colloids in reverse microemulsions "* defended on september 15th **1995**. Direction : Pr H. Patin et du Dr C. Larpent, ENSC Rennes. ** Military duty*
1991	**Master of Chemistry - Molecular chemistry (University of Rennes I) / Engineering degree from the Ecole Nationale Supérieure de Chimie de Rennes**

RECHERCHE

- **100** papers, **38** oral communications, **1** educational software, **2** teaching books, **2** book chapters

- Supervision of **17** PhD candidates (**2** in progress), **30** Masters, **6** post-doctorates or temporary assistant professors, **38** others (DUT, BTS, Licence…)

2020-2023	Coordinator of a DIM Ile de France project, **"Nanoparticles of Ni and Co- or Fe-Ni strongly embedded in mesoporous silica alumina for the design of efficient lignin upgrading and reducing catalysts tunable under an oscillating magnetic field"**
2017-2022	Coordinator of the ANR OxCyCat_CO_2 project **"Sustainable catalytic process for the one-pot formation of cyclic carbonates by alkene oxidation and CO_2 cycloaddition" (ANR-17-CE06-0009)**
2012-2014	Partner of the ANR DALMATIEN project **"Dégradation des Amines Liquides et Méthodes d'Analyse : Toxicité ou Innocuité pour l'ENvironnement? " (ANR-11-SEED-06)**
2009-2012	Coordinator of the ANR MesAsColl project **"Chiral and recyclable mesoporous materials based on metal nanoparticles for the asymmetric hydrogenation of arenes " (ANR-08-CP2D-14)**

5 PUBLICATIONS RELATED TO THE PROJET

1) Efficient and selective catalytic oxidative cleavage of α-hydroxy ketones using vanadium-based HPA and dioxygen. El Aakel, L.; Launay, F.; Atlamsani, A.; Bregeault, J.-M. Chem. Commun. **2001**, 2218.

2) Nafion-supported vanadium oxidation catalysts: redox versus acid-catalyzed ring opening of 2-substituted cycloalkanones by dioxygen. El Aakel, L.; Launay, F.; Bregeault, J.-M.; Atlamsani, A. *J. Mol. Catal. A: Chem*. **2004**, *212*, 171.

3) Vanadium-substituted phosphomolybdic acids for the aerobic cleavage of lignin models-mechanistic aspect and extension to lignin. Al-Hussaini, L.; Launay, F.; Galvez, E. *Materials* **2020**, *13*, 812.

4) Alternative ball-milling synthesis of vanadium-substituted polyoxometalates as catalysts for the aerobic cleavage of C-C and C-O bonds. Al-Hussaini, L.; Valange, S.; Galvez, M.E.; Launay, F. *Dalton Trans*. **2021**, *50*, 12850.

5) Controlling C-O Aryl Hydrogenolysis vs Aryl Hydrogenation in Lignin Model Depolymerization Using Ni-, Rh- or Ni/Rh-based Silica Catalysts. Raachini, R.; Romdhane, F. Ben; Sassoye, C.; Boutros, M.; Launay, F. *ChemCatChem* **2024**, *16*, e202300948.

Résumé du projet/Summary of the project

(5 lignes)

Replacement of petroleum resources by biomass is one of the solutions envisaged to limit the overproduction of CO_2 in the atmosphere and by consequence climate change. The DELICAT project aims to that goal by proposing new heterogeneous catalysts allowing the controlled degradation of lignin, a natural and renewable source of carbon, into aromatic aldehydes and by transforming the synthons obtained into high value-added building blocks.

Support demandé/Project type

Thèse/PhD ☒
Post-doc (18 mois) ☐

Scientific description

Objectives and description of the project

Originality and innovative nature of the project:

The industrial production of molecules from petroleum-based raw material is particularly responsible of carbon dioxide release worldwide (*c.a.* 112000 tons of CO_2 in 2015 according to IEA).[1] In order to develop a more environment-friendly industrial production and at the dawn of the scarcity of petroleum, the scientific community has to rethink the production of complex organic molecules. The main solution to this problem consists in the use of renewable resources coming from plants (biomass). For that purpose, several research teams have been involved in the valorization of carbohydrates (obtained after cellulose degradation) into valuable chemicals (levulinic acid, furfural) and their derivatization products. The lignin part of lignocellulose is however **underexplored** for the production of low molecular weight compounds. This aromatic heteropolymer can be considered as a promising source of aromatic compounds as for example 50 million tons were produced per year in 2000[2] (≈ 30% of earth's non-fossil organic carbon).[3] As a result, the idea of generating complex products only using wood degradation molecules (**xylochemistry**) has very recently emerged and is very original.[4] More and more research groups these last years are actively tackling **the development of new catalytic methods to degrade lignin model compounds**, and only **very few of them reported on the use of natural lignin as the starting material**. We intend to develop **innovative environment-friendly** metal-catalyzed oxidative transformations allowing the controlled **degradation of natural lignin** and couple it to the **valorization of aldehyde synthons to obtain high value-added chemicals using cheap catalysts based on abundant metals**.

National and international context/positioning:

Nowadays, only very few research groups in France and worldwide are joining their forces to transform natural lignin obtained from wood waste into new synthons for organic synthesis.[5] Most of the current work in this field is essentially limited to degradation of lignin model compounds. Moreover, the few studies involving natural lignin degradation, allowed the detection of only a limited number of synthons, and the simple isolation of vanillin,[6] ferulic acid,[7] 4-propylcatechol and 4-propylpyrogallol.[8] Also, the concept of *xylochemistry*, *i.e.* the synthesis of compounds of synthetic interest (natural/pharmaceutical products, monomers for polymer materials,…) from only wood-derived organic chemicals, has emerged only very recently in Germany and in the US.[4a,9]

Given the current concerns about global warming, scarcity of petroleum resources and sustainability, the present collaborative integrated deconstructive/constructive project can be considered as essential for the rapid bio-based production of high value-added molecules materials such as pharmaceuticals or polymers.

Objectives and description of the project

Because the earth's fossil resources are becoming scarcer and scarcer on the planet and with the idea of developing more environment-friendly access to chemistry-based consumer goods, lignin can be seen as a serious alternative to petroleum in a near future. Based on the work already reported to prepare low molecular weight chemicals from lignin,[10] we became interested in obtaining an efficient access to these molecules through catalytic degradation, purification but also in the preparation of high value-added molecules (*i.e.* natural products, polymers) from the pure synthons obtained.

Two main steps are necessary to fulfill this goal: (a) find out catalytic conditions to efficiently degrade lignin, analyze the resulting mixtures and purify them to obtain pure synthons (**step 1**), (b) chemically transform the synthons into valuable intermediates that can be later transformed to generate molecules of interest (**step 2**). To do so, we wish to **set up a collaborative project between the Laboratoire de Réactivité de Surface** (LRS, Prof. Franck Launay – FL) and **the CASCH team at Institut Parisien de Chimie Moléculaire**

(IPCM, Dr. Alexandre Pradal – AP). The first team is specialized in the **oxidative cleavage of C-C bonds** including those of the lignin chain using oxygen and redox active catalysts and the second team works on the **valorization of the synthons** obtained after lignin degradation to get access to building blocks.

(a) Step 1 – Development of catalytic conditions for a controlled degradation of lignin.

C-C bond cleavage is a key step in a number of petro-sourced industrial processes, *e.g.* in the production of adipic acid from cyclohexane. In general, the involved strategies rely on prior C-H activation in order to facilitate oxidative C-C bond cleavage. Over the years, the LRS team has specialized in the implementation of catalytic systems operating with dioxygen, using **bifunctional catalysts involving both redox centers and Brønsted acid sites. These include vanadomolybdophosphoric acids (HPMoV)[11] as well as heterogeneous catalysts bearing sulfonic groups partially exchanged by vanadium complexes.**[12] Recently, the LRS team has shown that HPMoV-type compounds also catalyze the cleavage of C-C bonds involved in the β-O-4 linkage of lignin. In this case, the presence of a hydroxyl group in the alpha position was thought to be enough for facilitating the cleavage of the C_α-C_β bond linkage in the β-O-4 linkage.[13]

Initial experiments were carried out with lignin extracted from wheat straw (mostly containing G and S subunits with mainly β-O-4 linkages)[14] using the Organosolv process, which is known to better preserve the macromolecule. It was shown that lignin could be degraded in the presence of HPMoV under 5 bar of O_2, thus affording simple molecules among which syringaldehyde, 2-methoxybenzoquinone, *p*-hydroxybenzaldehyde and vanillin[15]. However, the yields were low. Studies on two model molecules (Figure 1) K_{1HH} (2-phenoxyacetophenone) and A_{1HH} (2-phenoxy-1-phenylethanol) were undertaken with O_2 / HPMoV showing that the carbonyl function of K_{1HH} is more suitable than the alcohol group in A_{1HH} for the implementation of the reaction under mild conditions. In the case of A_{1HH}, the reactivity was so low that activation based on ultrasound assistance had to be provided.[15]

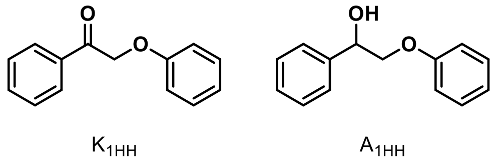

Figure 1. Structures of lignin model compounds K_{1HH} and A_{1HH}

Hence, K_{1HH} could be converted mainly into benzaldehyde and benzoic acid under atmospheric pressure of O_2[16] while the O_2 pressure had to be increased to reach significant conversion results when A_{1HH} was tested under silent conditions. Pre-oxidation of the secondary alcohol at C_α in A_{1HH} and later lignin was proposed to allow a more efficient process. As part of the DELICAT project, our colleagues from **the CASCH team at IPCM will help us to optimize the preliminary oxidation of alcohol functions first on A_{1HH}, then on lignin *via* the preparation of organocatalysts derived from TEMPO**,[17] that they used in the development of an oxidative C-H functionalization reaction.[18] Later, it is envisaged that both oxidation (step 1.a.) and degradation (step 1.b.) catalysts could be implemented simultaneously.

The objective here will be to use TEMPO-derived Bobbitt's salt and to test its substitution variants in order to optimize the oxidation of the secondary alcohol functions of A_{1HH} to get K_{1HH} and then that of the Organosolv lignin using oxygen as the primary oxidant in an acid medium (necessary for step 1.b.). This oxidation of alcohols will be monitored by GC-MS for the models and by the use of a phosphorylated derivatization reagent affording ^{31}P NMR monitoring of the oxidized lignin. Once the catalytic system (Cat_{ox}) will have been formulated, a heterogenized version will be developed by partial proton exchange on a commercial ion sulfonic exchange resin or prepared by grafting sulfonic functions onto mesoporous silica.[19] Indeed, we have already shown that proton exchange of such resins by vanadium complexes leads to heterogeneous catalysts ($Cat_{cleav.}$) affording the oxidative cleavage of C-C bonds in the presence of O_2, which is the aim of step 1.b.. These catalysts will be optimized (exchange rate since the $Cat_{cleav.}$ must include acid and redox functions) to enable the cleavage of $K1_{HH}$ and pre-oxidized lignin. The final objective will be to design a material bearing sulfonic groups whose protons will be exchanged, for the first time, by the oxoammonium component of Bobbitt's salt and the vanadium complex to achieve the overall transformation of lignin into small molecules of interest (Figure 2).

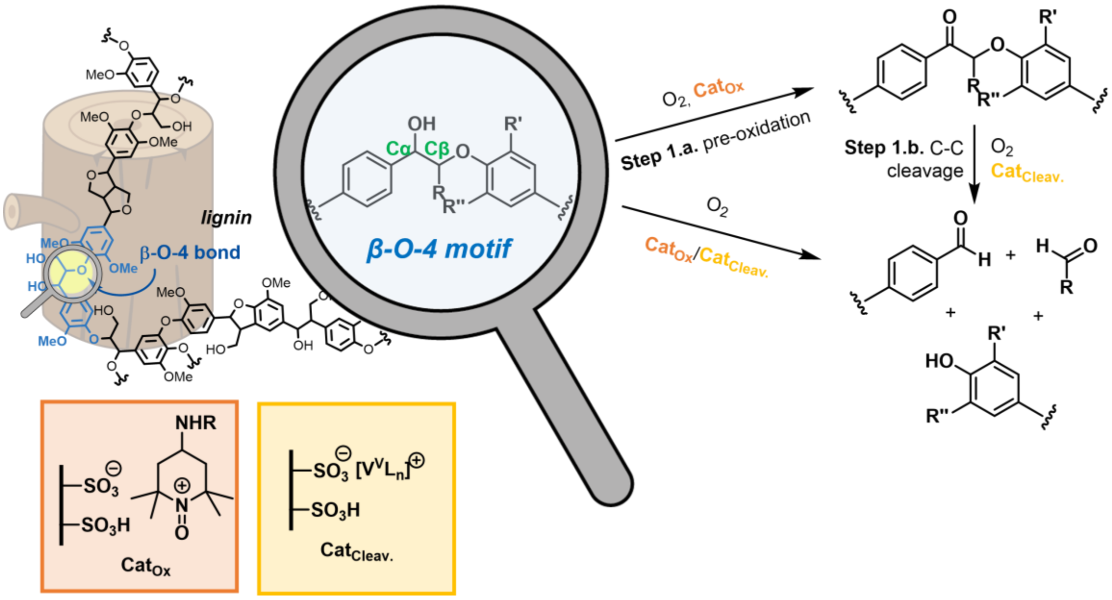

Figure 2. Lignin degradation strategy using supported catalysts.

Another part of the collaboration will involve the identification of compounds resulting from depolymerization *via* the synthesis of authentic samples. The CASCH team at IPCM is currently studying the possibility to purify lignin enzymatic degradation mixtures from another collaborative project including vanillin and syringaldehyde using automated column chromatography. As a proof of concept, it was found out separation conditions to purify a mixture of different commercial samples of the products we want to get access to from biomass. We will try to apply similar conditions to mixtures we will get within this project.

(b) Step 2 – Valorization of aldehyde degradation products *via* cobalt-catalyzed C-H acylation of arenes.

Among the synthons that could be isolated in pure state after lignin degradation, vanillin is the most abundant one.[20] Thus, in view of the fact that: a) vanillin is a known starting building block for the synthesis of a large number of aromatic targets, and b) the traditional industrial synthesis of vanillin is from fossil source, we think that the exploitation of bio-based vanillin as building block is expected to boost the synthetic interest of this molecule in the near future. This is the reason why we decided to focus on this synthon. This small molecule consists in an aromatic ring decorated by three functional groups (aldehyde, hydroxyl, and ether) and its use in synthesis is essentially based on the reactivity of the phenol or the aldehyde functions.[21] Starting from vanillin, the functionalization of the aromatic C-H bonds is well known especially on the position *ortho* to the phenol.[22] Concerning the aldehyde moiety, most of its reactivity concerns additions of carbanions to form alcohols after hydrolysis. In contrast, the direct conversion of the aldehyde function of vanillin or a derivative into a ketone by activation of the aldehyde C-H bond has been reported in a very limited number of examples.[23]

Recently, the CASCH team at IPCM became interested in the development of new transformations from biomass-based compounds (furfural, terpenes and lignin degradation products).[24] Within this collaborative project, we wish to develop a new way to get access to diarylketones in the most sustainable way possible. We plan to use a C-H activation strategy that employs a catalyst based on an abundant metal like cobalt for instance. Overall, this kind of C-H activation process is usually catalyzed mostly by Rh(I) or Ru(0) complexes.[25] The use of Co(I) catalysts has also been reported but in a low number of examples for the hydroacylation of alkenes and alkynes but never of aryl halides or boronates.[23,26] To fulfill the synthesis of diarylketones with this strategy, there will certainly be a need for a directing group (2-aminopyridines for instance) introduced in a catalytic quantity to avoid a decarbonylation side-reaction (Figure 3). As the aryl coupling partner, we will study the possibility of using haloarenes, aromatic boronic acids or derivatives and even more challenging non-pre-functionalized arenes, ideally all derived from biomass. Should this strategy work, we would apply the method to the total synthesis of (+)-mangosenone F, which possesses anticancer properties and for which no synthesis has ever been reported in the literature.[27]

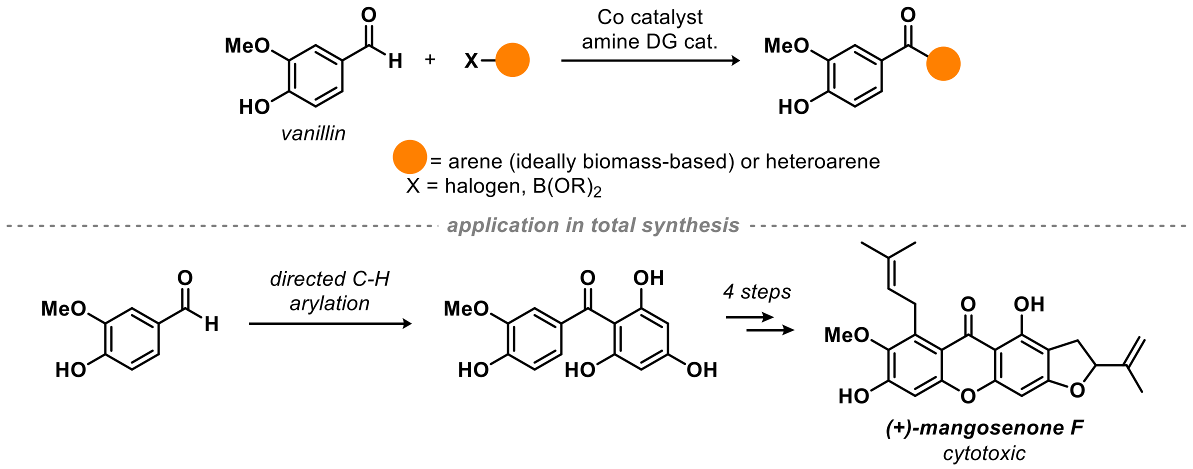

Figure 3. Project on the valorization of lignin-based aldehydes and application in the synthesis of a natural molecule.

Future projects

The DELICAT project would create a new collaboration that could be extended, in case of success, to the creation of a research consortium within a Marie Skłodowska-Curie Action-Innovative Training Network (MSCA-ITN) on lignin degradation and valorization. This kind of consortium involving research groups from all over Europe is training doctoral students and can be made in close collaboration with industrial partners. The project coordinator (AP) has some experience with such a consortium because he participated in the supervision of a PhD student involved in a MSCA-ITN program.

Feasibility. Risk assessment and management

For each step of the DELICAT project, the associated risks are detailed and fallback plans are indicated in the table below. Step 1 concerns the part on the catalytic degradation of lignin and Step 2 deals with the valorization of lignin-derived aromatic aldehydes.

Risks	**Fallback solutions**
Step 1	**Step 1**
❶ During the pre-oxidation step (step 1.a.), the re-oxidation of TEMPO derivatives by dioxygen may not be efficient enough. ❷ Heterogeneous catalysts based on an acid resin (Nafion®, Amberlyst®, etc.) partially exchanged by vanadium complexes to combine redox and acid centers may not be as efficient in the presence of lignin (step 1.b.) as with cyclohexanone derivatives, for which they have already proved their efficiency.	❶ Catalytic systems for the oxidation of alcohols based on the use of TEMPO derivatives have often been implemented in combination with non-sustainable counteranions. In the event of a difficult regeneration of the reduced forms of TEMPO derivatives by O_2, hydrogen peroxide will be used. ❷ In this case (step 1.b.), we could use homogeneous catalysts such as

❸ Ideally, it could be interesting to converge towards a material combining the Bobbitt's salt for the pre-oxidation step (step 1.a.), the acid functions and the metal for the degradation step (step 1.b.), but there are risks of incompatibilities between these three functionalities.	molybdovanadophosphoric acids (HPMoV) already tested with lignin. ❸ Failing in the implementation of a single catalytic material for steps 1.a. and 1.b. in a one-pot transformation, we could use one for each step. In that case, the two catalysts, one for pre-oxidation (step 1.a.) and one for lignin degradation (step 1.b.). could be introduced from the beginning if the temperature and O_2 pressure conditions optimized for the two separate steps 1.a. and 1.b. are compatible. Otherwise, as a last option, it is possible to add them successively.
Step 2 ❶ It may not be possible to work exclusively with lignin-based vanillin and related aldehydes if the catalytic degradation developed doesn't provide a sufficient amount of the desired compounds. ❷ For the valorization of the aldehydes, reliable C-H activation conditions have been reported with rhodium catalysts, that should be easily applicable to cobalt. The difficult part here will be to find the most suitable arene coupling partner (pre-functionalized or not).	**Step 2** ❶ If we don't manage to have a sufficient amount of lignin-based aromatic aldehydes, we can get them from commercial suppliers that provide the molecule from a natural source ❷ Shouldn't the C-H hydroacylation reaction be possible or efficient, a possibility would be to go for an arylcobalt addition[28] on the aldehyde but using a well-defined cobalt-hydride catalyst for which the CASCH team at IPCM has expertise in.[29] Contrary to the already existing procedure employing O_2 as a hydrogen acceptor at 80°C, which can pose safety problems, this one would be possible without the need for a hydrogen acceptor (namely molecular oxygen), which would make the conditions simpler and generate less waste. Should this strategy fail, we can envisage to develop the C-H activation method using rhodium catalysts.

Position of the project in regard to the iDream objectives

The DELICAT project fits within the axis n°2 "Design and engineering of complex molecular systems". In particular, it responds to the topic regarding the challenges of environmental transition. Indeed, one of the keys to reduce the CO_2 emissions in the atmosphere is the limitation in the use of fossil resources. The project meets the requirements for this challenge since we plan to use renewable resources (biomass) instead of petroleum to obtain aromatic aldehyde synthons that will be transformed after into diarylketone building blocks using step-economical and catalytic processes. The DELICAT project, coordinated by AP (PhD defended 12 years ago) is a collaboration between the "Laboratoire de Réactivité de Surface" (LRS, Sorbonne Université) represented by FL and the "Institut Parisien de Chimie Moléculaire (IPCM, Sorbonne Université) represented by AP.

Références / Bibliography

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Work program

Research program

The DELICAT project consists in eight different tasks lasting for 36 months. Seven of them are scientific deliverables and the last one concerns the preparation of the PhD manuscript. The first three tasks (16 months) will be done at LRS and will concern studies on the catalytic degradation of lignin model compounds and the application of the developed method to natural lignin. A short (3 months) middle task will concern the adaptation of known purification methods to the obtained mixtures. The three next tasks (15 months) will be done in the CASCH team at IPCM. Then, writing up the thesis manuscript should take five months at the end of the PhD and can be done either at LRS or IPCM.
The list of major deliverables as well as the Gantt chart for the DELICAT project is shown below.

List of major deliverables

N°	Deliverable title	Implied laboratory	Due date
D-1	Optimization of the oxidation of the alcohol functions of lignin models	LRS/IPCM	02/2026
D-2	Oxidations of natural lignin	LRS	07/2026
D-3	Subsequent/domino oxidation/degradation of natural lignin	LRS	12/2026
D-4	Adaptation of purification conditions	LRS/IPCM	03/2027
D-5	Development of the valorization method	IPCM	06/2027
D-6	Scope study of the developed transformation	IPCM	11/2027
D-7	Application in total synthesis	IPCM	04/2028
D-8	Thesis manuscript preparation	LRS/IPCM	09/2028

Gantt chart