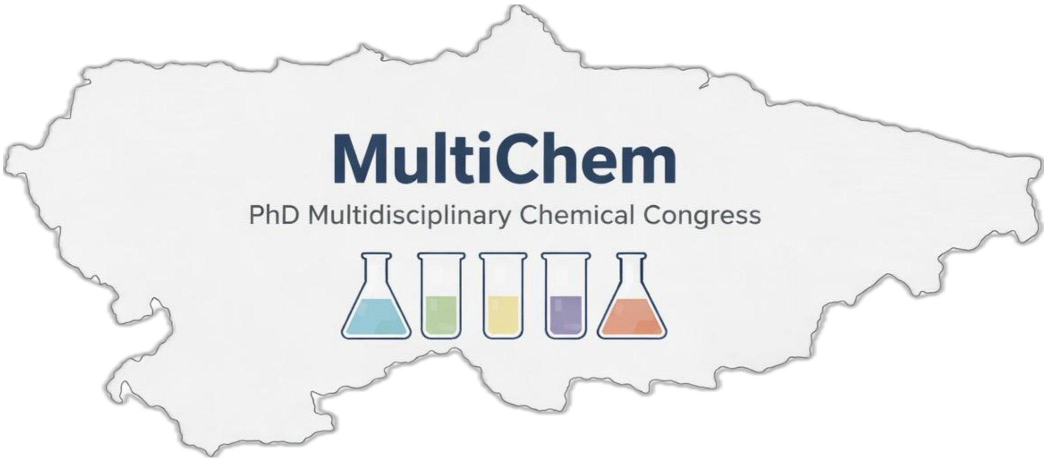
# III PhD Multidisciplinary Chemical Congress



# BOOK OF ABSTRACTS

*May 7-8th, 2026*
*Escuela Politécnica de ingeniería de Gijón (EPI)*
*University of Oviedo*

# WELCOME

We are pleased to present the third edition of the PhD Multidisciplinary Chemical Congress aimed at PhD students in Chemistry or any related area, which will take place on May 7th and 8th, 2026 at the Escuela Politécnica de Ingeniería de Gijón, Gijón (Principality of Asturias), University of Oviedo.

In this edition, as in the previous one, doctoral students are the key players of the congress, both in its organization and in the development of the event. A multidisciplinary space where we can actively participate, disseminating our scientific production and promoting collaboration between the different branches of chemistry will be created.

This congress, promoted by the Territorial Section of Asturias of the Royal Spanish Society of Chemistry, is born with the aim of making visible the Chemistry that is done in our laboratories by the younger generations.

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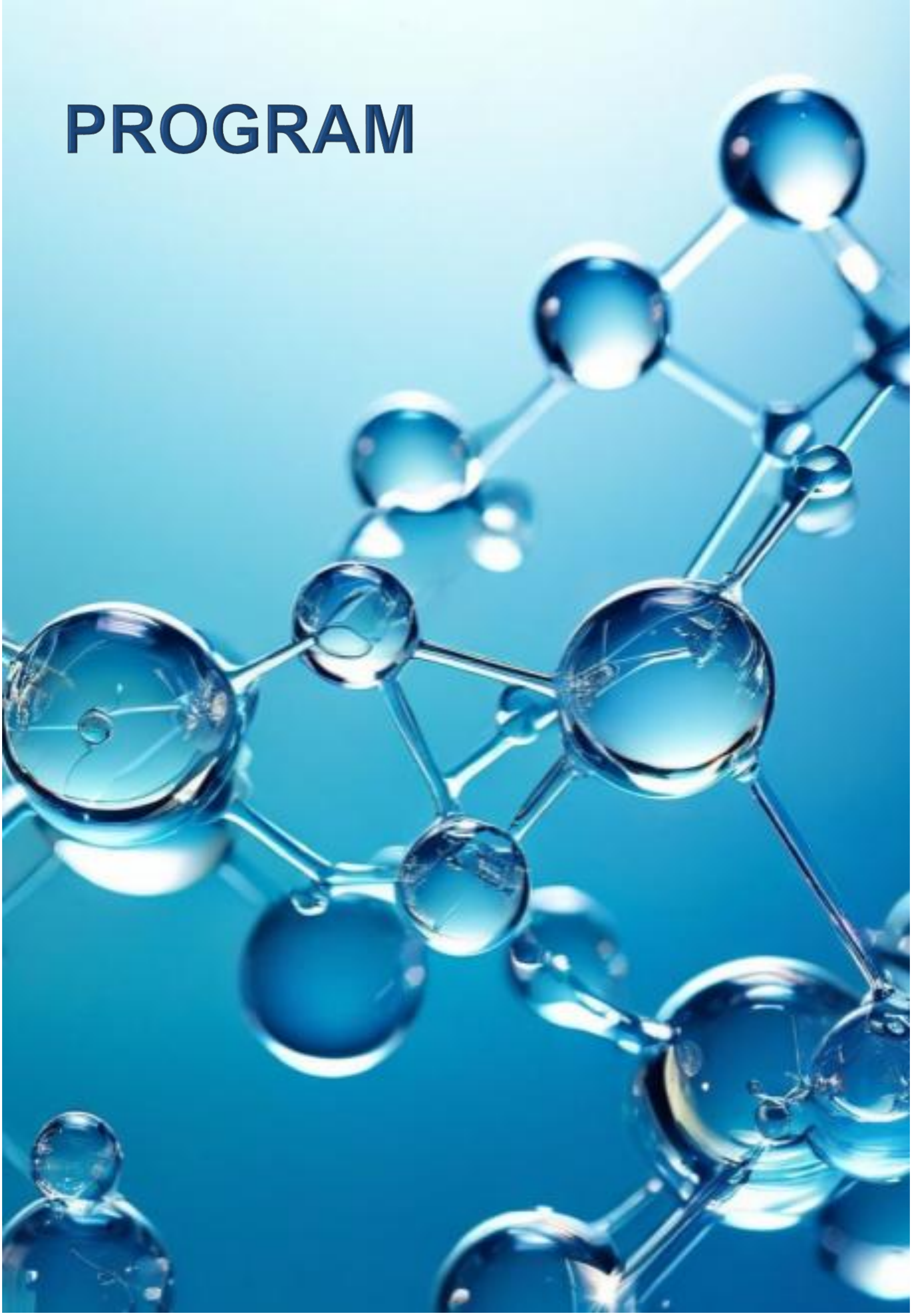

# PROGRAM

## *Thursday, May 7th*

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| **9:00 – 9:30** | **Opening Ceremony** |
| **9:30 – 11:20** | **Session 1**<br>Chairperson: Enrique Aguilar Huergo |
| **9:30 – 10:30** | **Plenary**<br>Hacking Carbon: Molecular Nanographenes at the Frontier of Atomic Design<br>*Nazario Martín León (Complutense Unisersity of Madrid)* |
| **10:30 – 10:50** | **Keynote K-1**<br>Characterization of biogenic iron nanoparticles from fly larvae and their future as supplementation<br>*Miguel Gómez Sánchez (University of Oviedo)* |
| **10:50 – 11:20** | **Flash Poster Session 1** |
| | **FP-1:** Complete pet depolymerization using ethylene glycol based deep eutectic solvents<br>*Cosimo Ricci (University of Rome)* |
| | **FP-2:** Mapping the functional landscape of cisplatin resistance in osteosarcoma using a multi-omic mathematical framework<br>*Julia Berdasco García (University of Oviedo)* |
| | **FP-3:** A Photochemical Multicomponent Strategy for the Assembly of C(sp²)–S Substituted Imidazoles<br>*Illán Tagarro Peña (University of Oviedo)* |
| | **FP-4:** Evaluation of the factors influencing the extraction of antioxidants from the microalga spirulina (*Arthrospira platensis*) using a full factorial design.<br>*Victoria Blanco Carro (University of Oviedo)* |
| | **FP-5:** Synthesis of dimethyl ether hydrogen carrying molecule catalyzed by supported heteropoly acids<br>Muhammad Adnan *(University of Oviedo)* |
| | **FP-6:** Investigation of the impact of energy supplements in the regulation of the Na/K pump of tumoral and control mammary epithelial cells<br>Teresa Rodríguez Pardo *(University of Oviedo)* |
| | **FP-7:** Filtration as a valuable alternative to ultracentrifugation for extracellular vesicle isolation using cell culture lines<br>Pablo Gutiérrez García *(University of Oviedo)* |
| | **FP-8:** Designing Bio-Based Emulsions for Controlled Release of Natural Antimicrobials<br>Elisa Fernández Sánchez *(University of Oviedo)* |

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| | **FP-9:** A Sustainable Chemoenzymatic Route to Nitriles from Primary Alcohols under Aqueous Conditions<br>Enol de Prado Fernández *(University of Oviedo)* |
| **11:20 – 12:00** | **Coffee Break – Poster Session 1** |
| **12:00 – 13:50** | **Session 2**<br>Chairperson: Mª Isabel Menéndez Rodríguez |
| **12:00 – 12:20** | **Keynote K-2**<br>Beyond Fluoride: Quantum Chemical Topology Reveals the Extreme Electronegativity of the Teflate Group<br>*Daniel Barrena Espés (University of Oviedo)* |
| **12:20 – 12:35** | **Oral O-1**<br>The Final Chelator: a Potentially Conjugable Thiocarbohydrazone That Strongly Chelates Cu(II) in a Soluble Complex Tuning Metal Redox-Activity into Selective Cytotoxicity Against Colorectal Cancer<br>*Lorenzo Verderi (University of Parma)* |
| **12:35 – 12:50** | **Oral O-2**<br>Multiplexed profiling of protein biomarkers in serum-derived extracellular vesicles using metal nanocluster-labelled antibodies<br>*Jaime Martínez García (University of Oviedo)* |
| **12:50 – 13:05** | **Oral O-3**<br>Collective interactions in ion pairs<br>*Jorge Gonzalo Alcega (University of Zaragoza)* |
| **13:05 – 13:20** | **Oral O-4**<br>Influence of Composition and Synthesis Route on CALF-20/γ-Alumina Composites for $CO_2$ Capture<br>*Daniel Felipe Ramírez Ramírez (University of Oviedo)* |
| **13:20 – 13:35** | **Oral O-5**<br>A novel electrochemical strategy for evaluating antibiotic efficacy in live bacteria: proof of concept in *Staphylococcus aureus*<br>*Diego Álvarez Rafael (University of Oviedo)* |
| **13:35 – 13:50** | **Oral O-6**<br>Production of polycyclic aromatics from components of pyrolysis oil<br>*Gvantsa Lomidze (University of Oviedo)* |
| **13:50 – 15:30** | **Lunch** |

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| **15:30 – 17:05** | **Session 3**<br>Chairperson: Javier Fernández Reynes |
| **15:30 – 15:50** | **Keynote K-3**<br>Influence of dry and wet grinding conditions on the mechanical activation process for nanoclays production<br>*Aníbal López Marín (University of Cantabria)* |
| **15:50 – 16:05** | **Oral O-7**<br>From DNA barcoding to naked-eye LAMP assays for on-site detection of seafood fraud in northern Spain<br>*María Celenza (University of Oviedo)* |
| **16:05 – 16:20** | **Oral O-8**<br>Photobiocatalytic approaches for the stereoselective preparation of chiral alcohols<br>*Laura Rodríguez Fernández (University of Oviedo)* |
| **16:20 – 16:35** | **Oral O-9**<br>Nitrogen and lanthanide co-doped polymeric Carbon Dots as versatile and innovative Nanotags for multimodal and targeted bioimaging applications<br>*Jesús Alfonso Montero García (University of Oviedo)* |
| **16:35 – 17:05** | **Flash Poster Session 2** |
| | **FP-10:** Improvement of lateral flow immunoassay sensitivity using biogenic nanoporous structures<br>*Daniela Díaz Jimenez (University of Oviedo)* |
| | **FP-11:** Wet-Oxidized Kraft Lignin as a Renewable Iron-Chelating Agent for Agricultural Applications<br>*Clara Gamonal Fernández (University of Oviedo)* |
| | **FP-12:** A Computational Exploration of N-H Bond Functionalization Driven by Geometrically Constrained Tridentate Phosphine Pincer Complexes<br>*Samuel García García (University of Oviedo)* |
| | **FP-13:** Bio-sourced nanoporous materials as functional modifiers of electrochemical transducers for enhanced biosensing<br>*Alexandra Ritta Alconz Montaño (University of Oviedo)* |
| | **FP-14:** Micro-flow liquid chromatography-ESI-QTOF for lipidomic profiling of volume-limited samples<br>*Guillermo Viejo Palenzuela (IPLA-CSIC)* |
| | **FP-15:** Understanding the role of heating rate and water dynamics in starch foam formation by thermocompression<br>*Josselyne Arely Villarroel Ayala (University of Alicante)* |

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| | **FP-16:** One-Pot Cascades for Chiral β-Hydroxy Esters via L-Cysteine Promoted Hydration<br>*Marta Menéndez González (University of Oviedo)* |
| | **FP-17:** Single-Cell Biomarker Analysis by ICP-MS and Mass Cytometry: Implications for Immunotherapy<br>*Ángela de la Rosa Díaz (University of Oviedo)* |
| | **FP-18:** Electrochemical Lateral Flow Biosensor for Rapid Pathogen Detection<br>*Mario Pérez Rodríguez (University of Oviedo)* |
| **17:05 – 17:45** | **Coffee Break – Poster Session 2** |
| **17:45 – 19:20** | **Session 4**<br>Chairperson: Manuel Plaza Martínez |
| **17:45 – 18:05** | **Keynote K-4**<br>Synthesis of Fused-Housane Derivatives via Intramolecular [2+2] Photocycloaddition<br>*David Suárez García (University of Oviedo)* |
| **18:05 – 18:20** | **Oral O-10**<br>Integrated metabolomic and transcriptomic insights into the protective role of coenzyme Q10 in a retinal hypoxia cellular model<br>*Alicia Villa Vazquez (University of Oviedo)* |
| **18:20 – 18:35** | **Oral O-11**<br>Chloride-Catalyzed Insertion of Carbon Disulfide into Nitrones for the Synthesis of Secondary Thioamides<br>*Marcos López Aguilar (University of Oviedo)* |
| **18:35 – 18:50** | **Oral O-12**<br>S-doping of sustainable carbon aerogels as anode of high-performance sodium-ion batteries<br>*Julia Trojaola Gutiérrez (INCAR-CSIC)* |
| **18:50 – 19:05** | **Oral O-13**<br>Crystal Structure Prediction of Molecular Photoswitches<br>*Lucas Martín Boujon Blanco (University of Oviedo)* |
| **19:05 – 19:20** | **Oral O-14**<br>Revalorisation of agrifood waste through solid-state fermentation: biopesticides and biostimulants production<br>Paula Siñeriz Casado *(Autonomic University of Barcelona)* |

***Friday, May 8th***

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| **9:00 – 10:30** | **Session 5**<br>Chairperson: Paula Oulego Blanco |
| **9:00 – 9:20** | **Keynote K-5**<br>Enhanced Pectin Recovery from Fruit Pomace Using Deep Eutectic Solvents: A Comparative Assessment with Acid Hydrolysis<br>*Lucía Abello Villanueva (University of Oviedo)* |
| **9:20 – 9:35** | **Oral O-15**<br>Sewing pins as electrodes for on-site ELISA readout<br>*Ana Fernández Quesada (University of Oviedo)* |
| **9:35 – 9:50** | **Oral O-16**<br>Microwave-Synthesized Nickel Aerogels for HER<br>*Francisco José Ayllón Plaza (INCAR-CSIC)* |
| **9:50 – 10:05** | **Oral O-17**<br>Photochemical Cross-Coupling of *N*-Tosylhydrazones and Boronic Acids: Difunctionalization and Multicomponent Synthesis<br>*Alvaro Valdés Maqueda (University of Oviedo)* |
| **10:05 – 10:35** | **Flash Poster Session 3** |
| | **FP-19:** Targeting cancer-associated aberrant O-glycans in pathological MUC1 with aptamers<br>*Alessandra Martucci (University of Oviedo)* |
| | **FP-20:** Towards an Integrated Understanding of Artisanal Kombucha: Biochemical, Microbiological, and Life Cycle Assessment Approach<br>*Ares Fernández Fernández (University of Oviedo)* |
| | **FP-21:** Evaluation of an Artificial Neural Network for Copper Quantification in Optical Emission Spectroscopy Using SCGD-OES<br>*Cristina López Perandones (University of Oviedo)* |
| | **FP-22:** Chemical engineering and conjugation strategies for A40s RNA aptamer to enhance structural stability and functional efficacy in Glioblastoma Multiforme<br>*Martina Mascolo (University of Naples Federico II)* |
| | **FP-23:** Pickering emulsions stabilized by cocoa bean shell using different types of oils<br>*Karla Mariuxi Villagrán Andrade (University of Oviedo)* |
| | **FP-24:** Total Synthesis of Diterpenoid Compounds<br>*Rafael García López (University of Oviedo)* |

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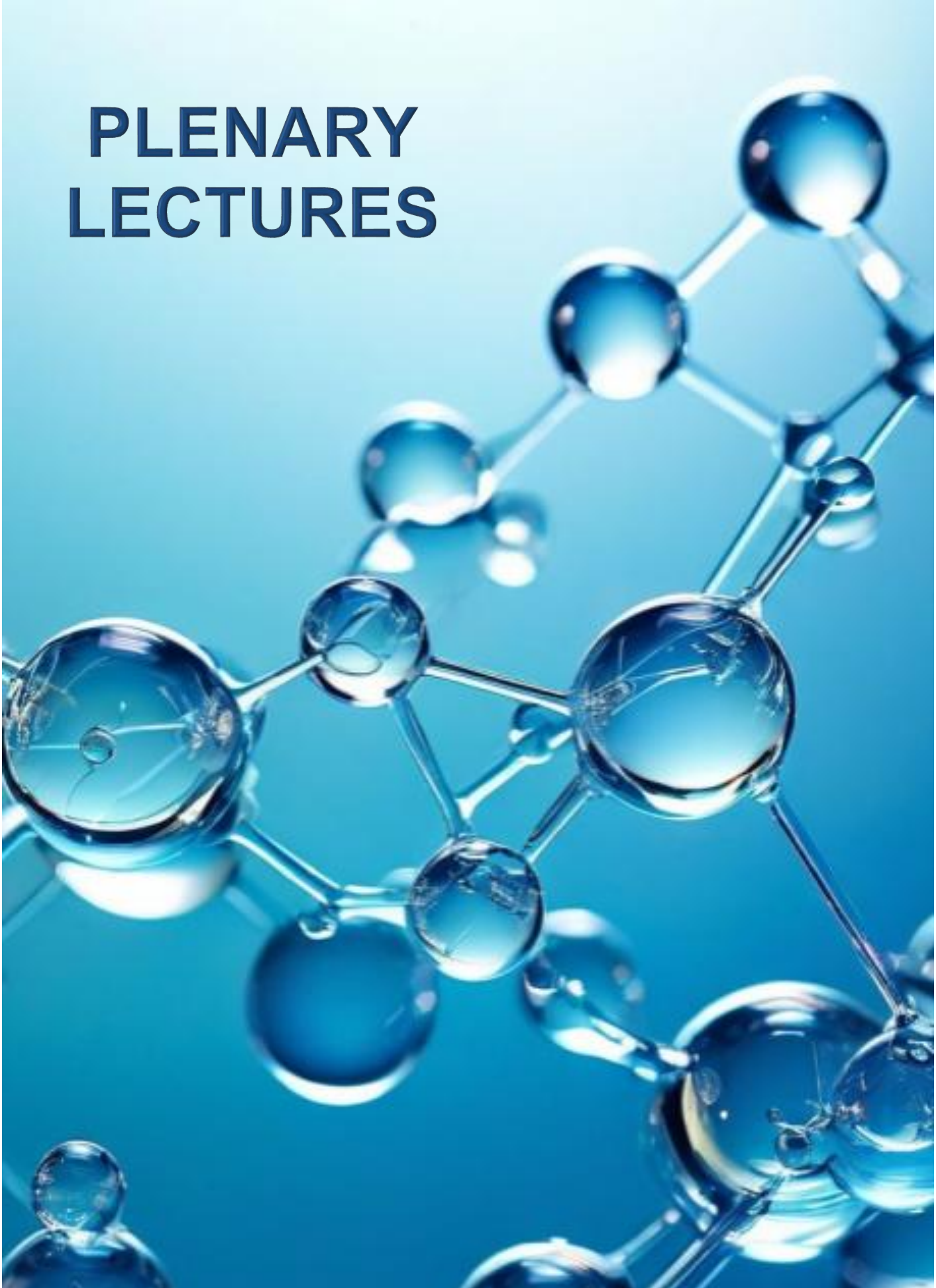
| | **FP-25:** Photochemical Oxidation of β-Hydroxynitriles: Applications in Biocatalytic Deracemization<br>*Sara Filgueira Fernández (University of Oviedo)* |
| | **FP-26:** Deep Eutectic Solvents for Sustainable Extraction of Phenolic Compounds from Hazelnut Shells<br>*Sara Rodríguez de la Fuente (University of Oviedo)* |
| | **FP-27:** Synergy of CsPbBr$_3$ perovskite nanocrystals supported on NiFe-layered double oxide enables CO$_2$ photothermal hydrogenation<br>*Kevin Mego (ITQ, UPV-CSIC)* |
| **10:35 – 11:15** | **Coffee Break – Poster Session 3** |
| **11:15 – 14:00** | **Session 6**<br>Chairperson: Mario Corte Rodríguez y Beatriz Fernández García |
| **11:15 – 11:30** | **Oral O-18**<br>Biomass-derived carbon nanoparticles for high-rate sodium storage<br>*Ángel del Blanco García (INCAR-CSIC)* |
| **11:30 – 11:45** | **Oral O-19**<br>Temperature-controlled synthesis of sustainable carbon aerogels for efficient sodium-ion battery anodes<br>*David García Pérez (INCAR-CSIC)* |
| **11:45 – 12:00** | **Oral O-20**<br>Alkaline Hydrolysis of Sewage Sludge for the Production of Protein Hydrolysates<br>*Zaira Fernández Larriet (University of Oviedo)* |
| **12:00 – 12:15** | **Oral O-21**<br>Machine Learning Tools in the Gold(I)-Catalyzed Intramolecular C(sp3)—H Bond Functionalization: Predictive Statistical Analysis<br>*Omar Arto (University of Oviedo)* |
| **12:15 – 12:30** | **Oral O-22**<br>Dynamic Colloidal Plasmonic Metasurfaces via templated self-assembly on Sb$_2$S$_3$<br>*Nineli Abramidze Kublashvili (University of Cantabria)* |
| **12:30 – 13:30** | **Plenary**<br>Beyond the PhD: Decisions and Realities of a Research Career<br>*Armando Menéndez Estrada (ASINCAR)* |
| **13:30 – 14:00** | **Closing ceremony** |

# PLENARY LECTURES



# Hacking Carbon:
## Molecular Nanographenes at the Frontier of Atomic Design

**Nazario Martín**

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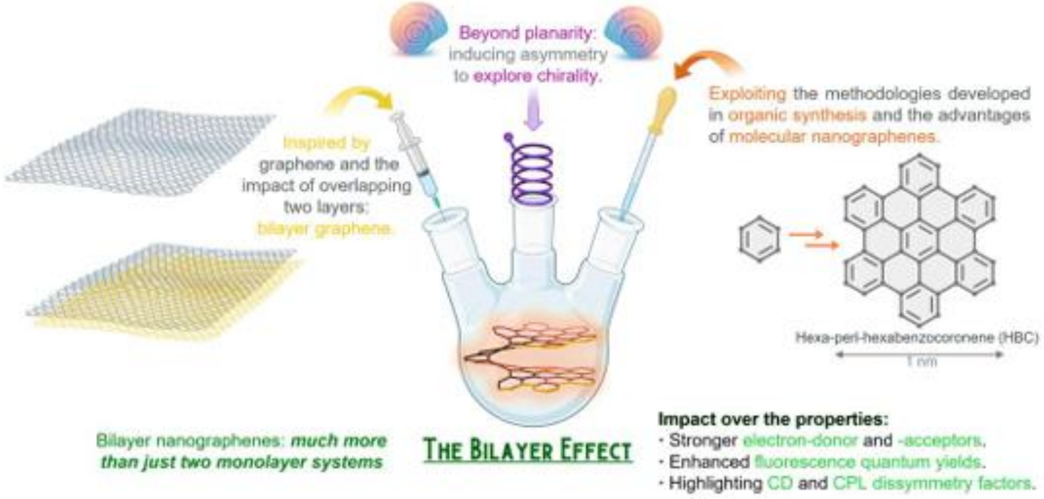
**Key words:** Nanographenes, Carbon defects, Asymmetry, Bilayer effect, Helicenes

Nanographenes (NGs) have usually been synthetized following a top-down approach by “cutting” a graphene sheet into smaller fragments using chemical or physical methods. Although this methodology starts from readily accessible bulk materials and it is easily scalable, it does not allow a fine control of the properties due to the polydisperse sizes and shapes of the final material. In contrast, the bottom-up approach in which NGs are grown up from smaller chemical entities using solution-phase benchtop organic synthesis, leads to monodisperse molecules with a precise control on the size and shape, exhibiting fine tuned optoelectronic properties.

Thus, taking advantage of the versatility that provides the set of organic reactions available, and the selectivity of these transformations depending on the reaction conditions, a large number of molecular NGs have been synthetized by design in the recent years. An example of this atomic control is the introduction of out-of-plane defects at will, namely curvature, helicity, or strain, resulting in the presence of chirality as an additional and remarkable structural control.

Along the last recent years, we have carried out the synthesis and unveiled the properties of a variety of molecular nanographenes in the search for new chiroptical and optoelectronic properties in all-carbon materials.[1-5] In this presentation some recent and amazing NGs stemming from our research group, with special emphasis on the search for enantioselectivity, will be presented and discussed. [6-10]



[1] N. Martín & C. Nuckolls, eds. “Molecular Nanographenes: Synthesis, Properties and Applications”, Wiley VCH, **2025**, 544 pp, May 2925. ISBN: 978-3-527-35322-4.
[2] P. J. Evans, et al., Angew. Chem. Int. Ed. **2018**, 57, 6774 –6779.
[3] Z. Zhou, J. M. Fernández-García, et al. Angew. Chem. Int. Ed. **2022**, 61, e20211574.
[4] P. Izquierdo-García, et al. J. Am. Chem. Soc. **2023**, 145, 11599-11610.
[5] J. Lión-Villar, et al. Nat. Chem. **2025**, 17, 1099-1106.
[6] M. Buendía-Mateos, et al. Nat. Synth. **2024**, 3, 545-553.
[7] P. Izquierdo-García, et al. J. Am. Chem. Soc. **2024**, 146, 34943−34949.
[8] J. Lión-Villar, et al., Angew. Chem. Int. Ed. **2025**, e202510209.
[9] S. Marcos López, et al., Chem. Sci., **2025**, 16, 12867–12872.
[10] P. Izquierdo-García, J. Lión-Villar, J. M. Fernández-García, N. Martín. “Bilayer nanographenes: structure, properties, and synthetic challenges", Chem. Soc. Rev. **2025**, 54, 11089–11104.

# Beyond the PhD: Decisions and Realities of a Research Career

Armando Menéndez Estrada

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**Keywords:** research careers, technology transfer, project management, doctoral training, professional development

The transition from doctoral training to a sustainable professional career in research is often perceived as a linear pathway driven primarily by scientific excellence. However, real-world trajectories frequently diverge from this expectation, requiring adaptability, strategic thinking, and the development of non-technical skills. This talk presents a personal perspective on career development in research, based on a professional path that spans academia, applied research in a technology center, and project management in a different industrial sector.

After obtaining a PhD in Analytical Chemistry from the Universidad de Oviedo, focused on direct analysis of coated solid materials using glow discharge coupled to optical emission and mass spectrometry, Armando M. transitioned to the Fundación ITMA. Over an 11-year period, research activities focused on the development and characterization of functional materials (active coatings) through thin-film deposition techniques, particularly for photovoltaic applications on diverse substrates. This stage combined research and experimental activities with active involvement in the management of national and European R&D projects.

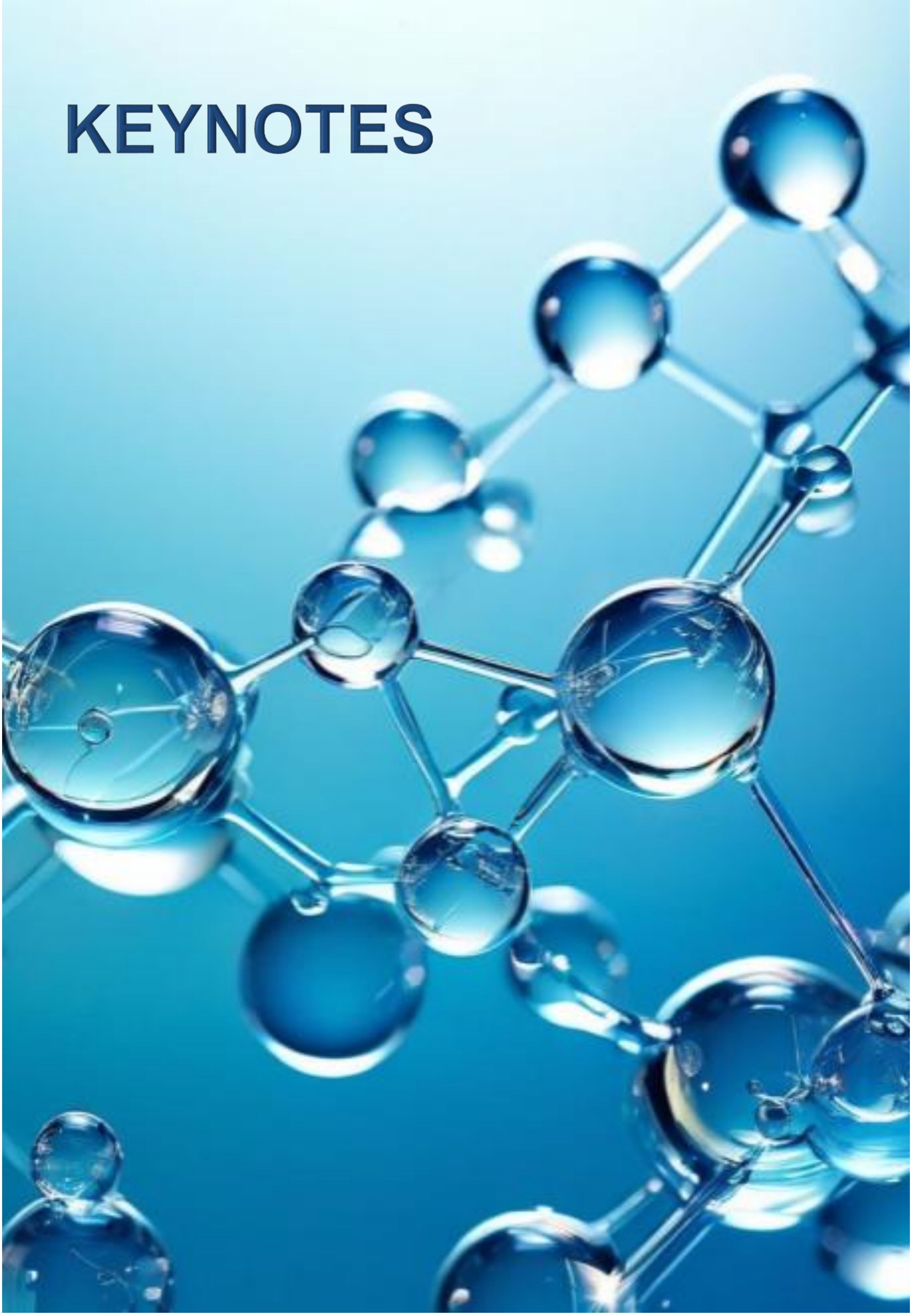
A subsequent career shift to ASINCAR marked a move away from laboratory-based research towards project management and funding strategy within the agri-food sector. This transition highlights the evolving nature of research careers and the importance of transferable skills.

The presentation will discuss key competencies acquired during doctoral and postdoctoral stages, the realities of project-based research environments, and the role of decision-making in shaping professional identity. The aim is to provide PhD students with a broader understanding of career possibilities and the skills required to navigate them.

## Acknowledgments:

The author would like to acknowledge all colleagues and collaborators who have contributed, directly or indirectly, to the professional journey described in this presentation. Special thanks are extended to the research teams at the Universidad de Oviedo (specially Rosario Pereiro and Beatriz Fernández) and Fundación ITMA (active coating research group), whose scientific rigor, collaborative spirit, and commitment to applied research played a key role in shaping both technical expertise and professional perspective. The author further acknowledges the current team at ASINCAR for providing the opportunity to continue developing a career at the interface between science, industry, and project strategy within the agri-food sector.

# KEYNOTES



# Characterization of biogenic iron nanoparticles from fly larvae and their future as supplementation

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**Keywords:** SP-ICP-MS, iron supplementation, biogenic nanoparticles.

In recent years the interest in reducing the dependence on traditional livestock meat industry has increased drastically. In this context, insect farms for human consumption are a sustainable alternative due to their nutritional value and environmental reasons [1]. Among the species breed, the Black Soldier Flight (*Hermetia illucens)* stands out not only for its capacity to recycle organic residues and transform them into protein-enriched biomass, but also for its great ability to incorporate essential elements such as iron and calcium [2]. One of the main hypotheses to explain how the larvae survive concentrations that should be toxic for them is the formation of biogenic nanoparticles (NPs) as a defense mechanism.

Because of the potential applications in food and pharmaceutical industry, these nanoparticles require a throughout characterization. In this presentation, we show a methodology capable of studying the presence of iron-containing NPs in complex biological samples (iron-enriched fly larvae) [3]. After extracting the NPs, suspensions were analyzed by Single Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICP-MS), Size Exclusion Liquid Chromatography coupled to ICP-MS (SEC-HPLC-ICP-MS) and other complementary techniques such as High-Resolution Transmission Electron Microscopy combined with Energy-Dispersive X-ray spectroscopy (HRTEM-EDX). This exhaustive analysis showed an increase in the number of iron NPs related to the supplementation provided, as well as the total iron concentration and its bioavailability. Two families of NPs were observed, where the smallest one (7 nm) is related to an analog of mammal ferritin (entoferritin), a predominant iron accumulation mechanism.

**Acknowledgments:**

MGS acknowledges Thermo Fisher Scientific for instrumental support and the Government of Asturias (SEK-25-GRU-GIC-24-061) for financial support.

**References:**

[1] A. van Huis et al. *Journal of Insects as Food and Feed*, **2021**, 7(5), 935-948.

[2] T. First et al. *Journal of Insects as Food and Feed*,**2024**, 11(7), 1187–1200.

[3] R. Álvarez-Fernández García et al. *Analyst*, **2020**, 145(4), 1457–1465.

# Beyond Fluoride: Quantum Chemical Topology Reveals the Extreme Electronegativity of the Teflate Group

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**Keywords:** Fluorine Chemistry, Teflate group, Quantum Chemical Topology, IQA, EDF

The pentafluoroorthotellurate group (-$OTeF_5$, teflate) is a strongly electron-withdrawing ligand that serves as a robust and versatile analogue of fluoride in synthetic chemistry [1]. In this work, its electronic structure and bonding characteristics are investigated using diverse quantum chemical topology (QCT) methods. Analysis of X-$OTeF_5$ systems (X = F, Cl, Br, I) combined with energy decomposition within the Interacting Quantum Atoms (IQA) framework reveals that the interaction is predominantly ionic, with limited covalent character. Complementary analyses of electron density *via* Quantum Theory of Atoms in Molecules (QTAIM), Electron Localization Function (ELF), and electron distribution functions (EDF) indicate that the electronic behaviour of teflate is comparable to that of fluorine [2].

Comparative studies within the $OEF_5$ series (E = S, Se, Te) demonstrate that teflate exhibits a group electronegativity similar to its lighter analogues [1] and exceeds that of other common fluorinated ligands, such as -$OCF_3$ and -$OC_6F_5$. These features establish teflate as a privileged ligand for stabilizing unusual chemical species and for serving as a fluoride mimic in systems where fluoride chemistry is hindered, for instance by polymerization with transition metals.

Overall, this study not only rationalizes the distinctive properties of the teflate group but also underscores the predictive power of QCT methodologies in guiding the design of novel compounds and synthetic strategies.

**Acknowledgments:**

D.B.-E. acknowledges the Spanish FICyT for a predoctoral grant (PA-23-BP22-168).

**References:**

[1] K. Seppelt, Angew. Chem. Int. Ed. Engl. **1982**, 21, 877−888.

[2] D. Barrena-Espés, Á. Martín Pendás, S. Riedel, A. Pérez-Bitrián, J. Munárriz, Inorg. Chemistry **2025**, 64, 1064−1074.

# Influence of dry and wet grinding conditions on the mechanical activation process for nanoclays production

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**Keywords:** Clay minerals, dry grinding, wet grinding, high-charge micas

Clay minerals are considered ideal adsorption materials due their high specific surface area, low-cost extraction and natural abundance. The most common clay, bentonite, is mainly composed by montmorillonite, a 2:1 layer phyllosilicate consisting by one octahedral $Al_2O_3$ sheet and two tetrahedral $SiO_2$ sheets. Recently, a group of synthetic 2:1 layer fluorosilicates know as high-charge micas (Na-*n*-micas), has attracted attention because of their exceptional adsorption properties. Furthermore, particle size of clays can be reduced by top-down approaches, allowing to increase adsorption active sites of clays by mechanical activation [1].

The aim of this research is to study the influence of dry and wet grinding on the structural and textural properties of natural and synthetic clays, treated in a planetary ball mill. Hence, montmorillonite and synthetic Na-*n*-micas ($n$ = 2, 4) were post-treated at different grinding conditions. Synthesis of Na-n-micas are achieved by NaCl melt method [2]. The as-obtained nanoclays are characterized by means of XRD, TGA, TEM, FTIR and $N_2$ adsorption isotherms.

The results show that montmorillonite structure undergo further structural damage than Na-n-micas in same dry grinding conditions, causing the complete amorphization of natural clays. Structural stability of synthetic micas can be attributed for the higher Mg(II) occupancy in the octahedral sheets. Montmorillonite reached a mean particle size of 70 nm in optimal dry grinding conditions, while Na-n-micas reduced its mean particle size to the range of 200 – 365 nm [3]. Adsorption isotherms of $N_2$ demonstrates that specific surface area can be increased by applying intensive ball milling treatment on both natural and synthetic clays. Wet grinding allows to conservation of stacking behaviour of clays.

**Acknowledgments:**

This research is funded by the NextGenerationEU Programme, under grant serial code TED2021-131305B-I00. López-Marín thanks to “Concepcion Arenal” predoctoral fellowship by Cantabria’s Government and University of Cantabria.

**References:**

[1] Baláž et al. (**2013**). Chemical Society Reviews, 42, pp. 7571 – 7637.

[2] Alba M., Castro M., Naranjo M. & Pavón E. (**2006**). J. Chem. Mater., 18, pp. 2867 – 2872.

[3] López-Marín A., Aguado F., Martín-Rodríguez R. & Perdigón A.C. (**2025**). Applied Clay Science, 277, 107969.

# Synthesis of Fused-Housane Derivatives via Intramolecular [2 + 2] Photocycloaddition

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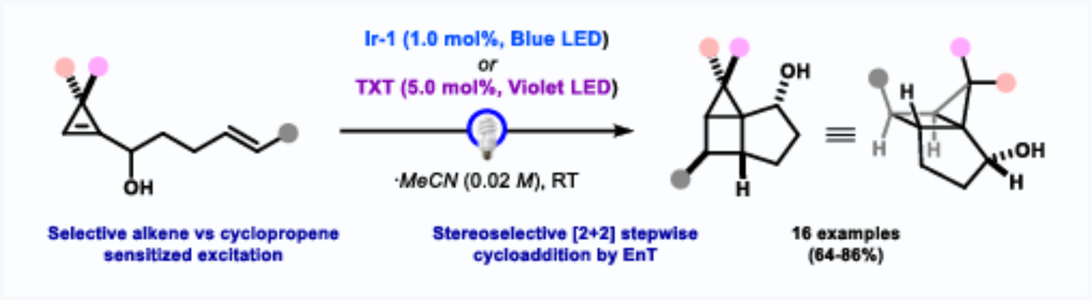
**Keywords:** Photochemistry, Cyclopropenes, Energy Transfer, Housane.

Molecules with high strain energy were paid little to no attention, being considered exotic compounds. However, they are gaining importance in medicinal chemistry, in the search for well-defined rigid 3D structures with a high Fsp$^3$ parameter. Unlike popular bicyclo[1.1.1]pentanes, their fused constitutional isomers, namely, bicyclo [2.1.0]-pentanes or housanes, have received little attention. The lack of general methods to prepare housane derivatives could explain this situation. In this work, it is described a [2 + 2] photocycloaddition of cyclopropenes bearing a styryl group to prepare fused housane derivatives. The reaction occurs via selective excitation of the styrene fragment, enabling a completely stereoselective stepwise [2+2] cycloaddition. Fused-housane derivatives with an unprecedented substitution pattern are prepared in a simple manner using convenient visible light.



**Acknowledgments:**

Support by the Spanish Government AEI (PID2022-138232NB-I00) and Principado de Asturias (AYUD0029T01, Severo-Ochoa fellowship number BP22-132 to D. S. G.) is gratefully acknowledged.

**References:** original paper

[1] David Suárez-García, Miguel A. Rodríguez, Iratxe Barbolla, and Rubén Vicente Organic Letters **2025** 27 (15), 3825-3830

# Enhanced Pectin Recovery from Fruit Pomace Using Deep Eutectic Solvents: A Comparative Assessment with Acid Hydrolysis

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**Keywords:** Acid hydrolysis; deep eutectic solvents; fruit processing residues; pectin extraction; low-methoxy pectin

Fruit processing residues, such as fruit pomace, are generated in large amounts by the agri food industry and represent both an environmental challenge and an opportunity for valorisation within a circular bioeconomy framework [1]. These residues are rich in pectin, a high-value polysaccharide widely used in food and packaging applications. However, conventional pectin extraction relies on acid hydrolysis under harsh conditions. Deep eutectic solvents (DES) have emerged as a sustainable alternative due to their low toxicity and high extraction efficiency. Therefore, the aim of this work was to compare pectin extraction from fruit pomace using acid hydrolysis and a DES-based approach, and to optimise extraction conditions and assess its structure.

Pectin was extracted from apple, pear, and orange pomace using acid hydrolysis and a choline chloride-citric acid DES system under controlled temperature (up to 90 ºC) and time conditions (up to 2.5 h). Extraction yields were calculated on a dry basis and were strongly influenced by the method employed. Acid hydrolysis resulted in recoveries of 7 ± 1 % (apple), 11 ± 4 % (pear), and 20 ± 3 % (orange), whereas DES extraction increased yields to 21.0 ± 0.1 %, 16 ± 3 %, and 35.1 ± 0.4 %, respectively. DES concentrations (2-8 %) and solid loadings (2-10 %) were evaluated, identifying 4 % DES and 4 % solid loading as optimal conditions for all residues.

FTIR analysis confirmed successful pectin extraction, while $^1$H NMR indicated a degree of esterification below 50%, classifying the pectins as low-methoxy. XRD patterns revealed an amorphous structure, whereas TGA profiles showed a single main decomposition event at ~230 ºC for DES-extracted pectins, compared to multiple degradation stages up to 415 ºC for those obtained by acid hydrolysis.

These results demonstrate that DES extraction is an efficient and sustainable strategy for pectin recovery from fruit pomace.

### Acknowledgments:

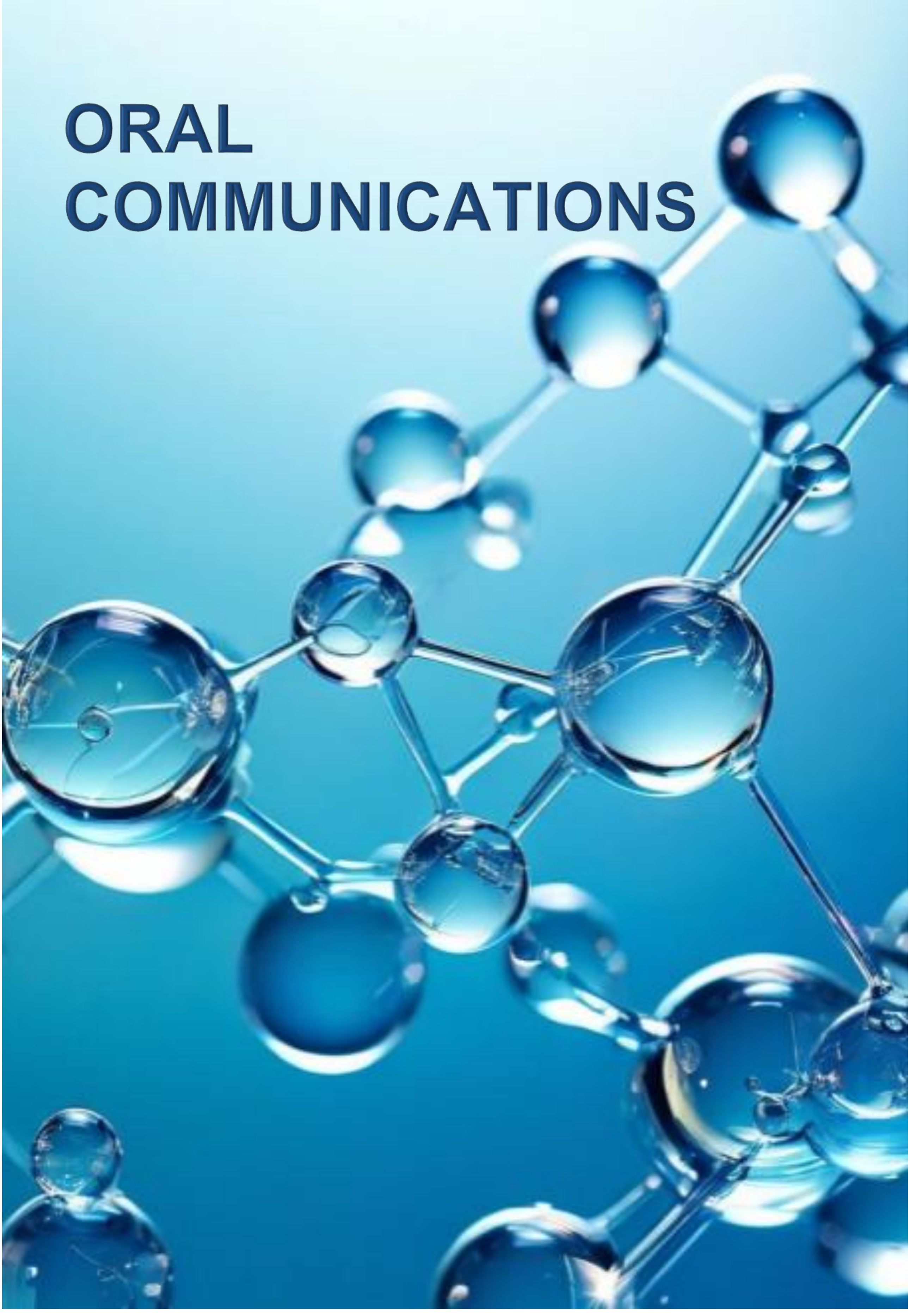
The authors acknowledge financial support from the European Union through the SuN4Med project (PCI2024-153512) and from the Agency for Science, Business Competitiveness and Innovation of Asturias (SEKUENS) through project IDE/2024/000695.

### References:

[1] P. Dubey, G. Tripathi, S. S. Mir, O. Yousuf, Trends Food Sci. Technol., **2023**, 141, 104190.

[2] H. Liu, J. Lin, Y. Hu, H. Lei, Q. Zhang, X. Tao, D. Zhang, H. Niu, J. Sci. Food Agric., **2024,** 104, 5149–5162.

# ORAL COMMUNICATIONS



# The Final Chelator: a Potentially Conjugable Thiocarbohydrazone That Strongly Chelates Cu(II) in a Soluble Complex Tuning Metal Redox-Activity into Selective Cytotoxicity Against Colorectal Cancer

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**Keywords:** Thiocarbohydrazones, Cu(II) complexes, ROS, Colorectal Cancer

The development of metal-based drug candidates hinges on chelators that integrate versatility, biological activity, synthetic accessibility, aqueous solubility, and targeted delivery potential. Thiocarbohydrazones (TCHs) have emerged as promising ligands due to their broad-spectrum biological applications and mixed hard/soft donor system (S, N, O/P)[1], enabling coordination with diverse metal ions. However, modern drug discovery demands innovative delivery strategies to enhance therapeutic efficacy and selectivity.

To address this, we designed a TCH ligand (**L**) featuring a carboxylate moiety. This functional group not only boosts the aqueous solubility of the resulting metal complexes but also enables conjugation to targeting vectors (e.g., peptides, nanoparticles), thereby improving delivery and cell selectivity. We investigated the coordination properties of **L** with Cu(II), revealing the exceptional stability of the resulting complex (**LCu**) and its potent in vitro activity.

Using ascorbate consumption and pyrogallol auto-oxidation assays, we demonstrated the pro-oxidant behavior of **LCu**. Cytotoxicity assays confirmed its efficacy against colorectal cancer cells (HT29) at 10 μM after 24 hours, with a selectivity index of 5 compared to healthy human dermal fibroblasts (HuDe). To elucidate the role of oxidative stress in its mechanism, we conducted preliminary DCFH-DA assays, which showed elevated ROS levels in HT29 cells treated with **LCu** compared to control and the free ligand (**L**). These findings support the hypothesis that **LCu** induces selective cancer cell death through ROS-mediated pathways.

In this very moment biological assays are performed to deepen the cell death modality and the consequences of ROS balance disruption, as well as conjugation to nanodelivery systems.

## References:

[1] C. Bonaccorso et al. *Pharmaceuticals* **2020**, *13*, 4.

[2] E. Falcone et al. *Metallomics* **2023**, *15*, 7.

[3] Y. Lu et al. *Appl. Organometal. Chem.* **2007**, *21*, 211-217.

# Multiplexed profiling of protein biomarkers in serum-derived extracellular vesicles using metal nanocluster-labelled antibodies

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**Keywords:** Neurodegeneration, Biomarkers, Extracellular vesicles, ICP-ToF-MS, Metal nanoclusters

Extracellular vesicles (EVs) are key mediators of intercellular communication and emerging targets for liquid biopsy approaches. In biomedical research, serum-derived EVs can provide valuable insight into physiological and pathological processes because they transport diverse molecular cargo, including proteins associated with disease states. However, the simultaneous quantification of low-abundance proteins within complex biological matrices such as blood serum remains an important analytical challenge. In this study, we implemented a highly selective and sensitive multiplexing strategy for the determination of key proteins in EVs using ICP-ToF-MS, a platform capable of high-throughput multi-element detection with minimal spectral interferences compared to conventional methods.

EVs were isolated by ultracentrifugation from blood serum obtained from a transgenic mouse model widely used in neurodegeneration research (APP/PS1 model), including animals subjected to dietary Zn supplementation. Protein determination was performed through a competitive immunoassay employing immunoprobes labelled with distinct metal-based nanoclusters (Ir, Pt, and Au) as elemental tags synthesized in our laboratory. Target proteins, previously selected through proteomic screening by LC-MS/MS of the cohorts under study, were quantified taking advantage of the high mass resolution and multi-element capabilities of ICP-ToF-MS. Preliminary results revealed differential protein expression patterns across cohorts. Although these trends require further validation with larger cohorts, the methodology demonstrates the potential of metal-tagged immunoassays combined with ICP-ToF-MS for multiplex biomarker quantitative analysis in EVs. Overall, the combination of metal nanocluster immunolabels and ICP-ToF-MS provides a scalable platform for multiplex protein analysis in EVs, supporting biomarker discovery efforts and advancing analytical strategies for precision medicine applications.

**Acknowledgments:**
This work was financially supported through project PID2022-137319OB-C21 funded by MCINN/AEI/10.13039/501100011033/ FEDER, UE and project IDE/2024/000694 by the Government of the Principality of Asturias and FEDER Program of the European Union through SEKUENS Agency. Jaime Martínez-Garcia acknowledges the Severo Ochoa Grant with reference BP21-041 from the department of science, industry and employment of the Principality of Asturias

# Collective interactions in ion pairs

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We report herein a quantum-chemical investigation into whether nominally ionic ion pairs can display collective bonding, a stabilization mode arising from distributed exchange-correlation interactions rather than a single two-center bond. Using Penetration Indices and Interacting Quantum Atoms (IQA) energy decomposition, we examined a series of ion pairs M[AX$_4$] (Fig. 1; M = Li$^+$–Cs$^+$; A = B, Fe, Co, Zn, Cd; X = –CH$_3$, –CO, –CCH, –OCH$_3$, –Cl). We found that alkali-metal tetramethylborates and several transition-metal tetrahedral anions show clear signatures of collective behavior: the direct M···A interaction is weakly covalent or even repulsive, while stabilization is dominated by exchange–correlation contributions distributed over multiple M···X contacts.

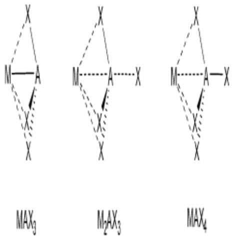

**Figure 1**. Structural motif of the studied ion pairs (MAX$_4$).

Systems bearing polarizable or electron-rich ligands (–CCH, –OCH$_3$, –Cl) exhibit low interaction-collectivity indices (ICI$_{XC}$ $\lesssim$ 0.07), whereas carbonyl-containing complexes show substantially higher values (> 0.25), consistent with more localized bonding. These results extend the concept of collective bonding into ionic environments and suggest that ion pairing, solvation, and reactivity may often be governed by multicenter exchange-correlation effects rather than purely electrostatic or classical two-center interactions.

# Influence of Composition and Synthesis Route on CALF-20/γ-Alumina Composites for $CO_2$ Capture

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**Keywords:** $CO_2$ capture; CALF-20; γ-alumina; MOF composites; breakthrough adsorption

The development of efficient solid adsorbents for post-combustion $CO_2$ capture remains a major challenge for the deployment of carbon capture technologies. Among metal-organic frameworks, CALF-20 is a promising candidate due to its scalability, durability and favorable performance under diluted and humid $CO_2$ streams [1–3]. However, its practical implementation is limited by the difficulties associated with shaping powdered materials into mechanically resistant bodies. In this work, CALF-20/γ-alumina composites were developed to improve handling, shaping and applicability in fixed-bed systems while preserving adsorption performance. The use of γ-alumina as support is attractive because of its stability and surface properties [4].

Three CALF-20/γ-alumina compositions were prepared, namely 10/90, 50/50 and 90/10 wt%, by two different routes: solvothermal synthesis in the presence of mesoporous γ-alumina and simple mechanical mixing. The materials were characterized by PXRD, TGA, FTIR, SEM and $N_2$ adsorption at 77 K. Their $CO_2$ capture performance was evaluated by gravimetric, manometric and breakthrough experiments under relevant conditions, including 15% $CO_2$ in air, 40 °C and humid streams.

SEM showed that the solvothermal route led to a more homogeneous dispersion of CALF-20 on the alumina surface, while TGA revealed enhanced thermal stability, especially at lower MOF contents. $CO_2$ adsorption capacity increased with CALF-20 loading, reaching 3.6 mmol $g^{-1}$ at 25 °C and 1 bar for the 90/10 sample. In addition, γ-alumina enabled palletization and stable operation in breakthrough tests over at least five adsorption-desorption cycles.

These results demonstrate that γ-alumina is a suitable support for CALF-20, enabling mechanically robust adsorbents with promising performance for practical post-combustion $CO_2$ capture.

## Acknowledgments:

The authors acknowledge Spanish Ministry of Science, Innovation and Universities, and the FEDER, Project MCINN-24-PID2023-148187OB-I00 (FLUDACME) for financing this work. DFR also acknowledges his FPI Scholarship (PREP2023-001162).

## References:

[1] Lin, J.-B. et al. Science 374 (**2021**) 1464–1469.

[2] Oktavian, R. et al. Nature Communications 15 (**2024**) 3898.

[3] Magnin, Y. et al. ACS Applied Nano Materials 6 (**2023**) 19963–19971.

[4] Busca, G. Catalysis Today 226 (**2014**) 2–13.

# A novel electrochemical strategy for evaluating antibiotic efficacy in live bacteria: proof of concept in *Staphylococcus aureus*

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**Keywords:** Antibiotic screening, Electrochemistry, Nanochannels, Real-time monitoring

Antibiotic resistance is an escalating global health concern, posing significant challenges for the development and effective evaluation of new therapeutic agents [1]. Conventional methods, including disk diffusion and broth microdilution, are often limited by long turnaround times and insufficient sensitivity to detect early or subtle bacterial responses [2]. There is a need for faster and more responsive analytical approaches for antibiotic screening.

Electrochemical techniques have recently attracted considerable attention. Here, we introduce a novel electrochemical strategy to evaluate antibiotic efficacy in live bacteria. The approach relies on biocompatible nanoporous alumina membranes functionalized with antibodies targeting specific secreted virulence factors from bacteria. Measurements are performed *in situ* using an indium tin oxide (ITO)-coated polyethylene terephthalate (PET) electrode positioned beneath the membrane. Antigen capture induces changes in electrochemical transport through the nanochannels, monitored in real time by chronoamperometry [3].

Proof of concept experiments were then performed using the virulence factor hyaluronidase secreted by *Staphylococcus aureus* to evaluate the dose-dependent response to streptomycin. Results were consistent with standard antibiogram methods, supporting the potential of this approach for real-time, *in vivo* evaluation of antibiotic performance and antivirulence therapies.

**Acknowledgments:**

Projects MCINN-24-PID2023-149004OB-I00, RED2022-34120-T and RED2024-153970-T funded by MCIN/AEI/10.13039/501100011033 and by "ERDF A way of making Europe" and project SEK-25-GRU-GIC-24-071 funded by the Asturias Regional Government. D. Álvarez-Rafael was supported by the "Severo Ochoa" grant (NAC-AT-PUB-ASV-2025BP24-46) from the Asturias Regional Government.

**References:**

[1] A. Karnwal A. Y. Jassim A. A. Mohammed A. R. M. S. Al-Tawaha M. Selvaraj T. Malik, Front. Microbiol. **2025**, 16, 1517772.

[2] M. Benkova O. Soukup J. Marek, J. Appl. Microbiol. **2020**, 129, 806-822.

[3] A. de la Escosura-Muñiz K. Ivanova T. Tzanov, ACS Appl. Mater. Interfaces **2019**, 11, 13140-13146

# Production of polycyclic aromatics from components of pyrolysis oil

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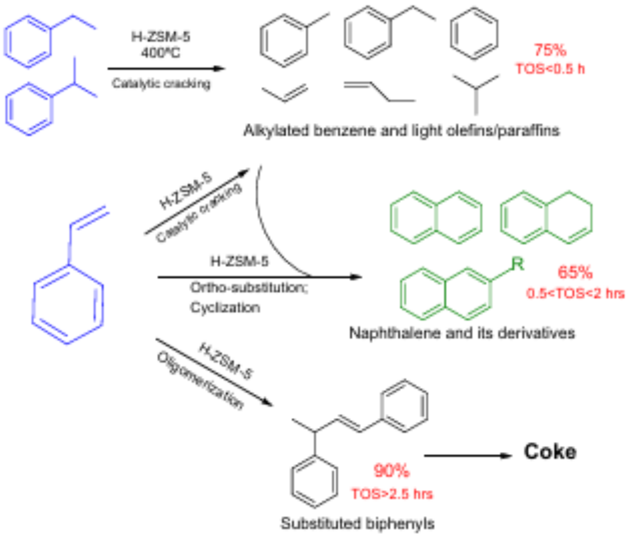
**Keywords:** styrene, condensation, zeolite, catalyst, DRIFT spectroscopy

Plastic waste poses a significant environmental challenge due to its persistence and limited recycling options. Pyrolysis has emerged as a promising strategy to convert plastic waste into valuable hydrocarbons, like naphthalene as key chemical for dyes, plasticizers, and solvent productions. However, its production still relies on fossil-derived feedstocks. This work explores a more sustainable pathway through the catalytic conversion of single ring aromatics, common in plastic pyrolysis oils, into naphthalene and related aromatics.

Experiments in a fixed-bed reactor studied the reactivity of different monoaromatics (benzene, toluene, styrene, xylene) with different zeolites and temperatures. Styrene is identified as the most promising compound, showing complete conversion with ZSM-5 and up to 80% with BETA at 400ºC.

The desired condensation competes with other reactions, including isomerization, oligomerization and cracking, see Figure 1, obtaining a complex reaction mechanism in which the porosity of the zeolite plays a crucial role. Thus, naphthalene is the main product when using ZSM-5, reaching 65% selectivity after 0.8 h, whereas with mesoporous materials such as MCM-41, biphenyls dominate greatly over other products (>75% selectivity).



Oligomers obtained by uncontrolled condensation between aromatics and light olefins (obtained by cracking) deactivate the catalyst by coking in less than 3 h. The analysis of spent catalyst demonstrates a thermal reactivation at 600ºC is enough to recover the initial activity.

These results, together with the in-situ analysis of the evolution of the catalytic surface by DRIFT spectroscopy, allow us to determine the reaction mechanism, proposing a kinetic and a deactivation model. Although a process optimization is needed, styrene produced during the pyrolysis of plastic waste is demonstrated to be a promising feedstock for obtaining naphthalene.

**Acknowledgments:**
This research has been financed by PID2023-147180OB-I00

# From DNA barcoding to naked-eye LAMP assays for on-site detection of seafood fraud in northern Spain.

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**Keywords:** LAMP; barcoding; mislabelling; traceability; seafood.

Seafood fraud represents a global issue with multiple implications, including economic losses, threats to species conservation, and risks to public health, while also undermining consumer trust in the food trade [1]. In northern Spain, the consumption of high-value marine invertebrates constitutes an important part of the economic and gastronomic identity of this area [2]. In this study, sampling was conducted in restaurants, shellfish farms, fish markets, and frozen food shops to provide an initial assessment of the extent of food fraud in the commercialisation of the native European lobster *Homarus gammarus* (Linnaeus, 1758) ("bogavante") and native razor clams of the genus *Ensis* ("navajas"). The analysis of compliance with the European Union legislative framework on food traceability revealed incomplete labelling in 83% of fresh and frozen lobster products and 10% of fresh and frozen razor clam products. DNA barcoding targeting mitochondrial *Cytochrome c oxidase subunit I* (COI) gene revealed that 4 of the 22 lobster products analysed (18%) were substituted with the non-native American lobster *Homarus americanus* (H. Milne Edwards, 1837), while 5 of the 19 razor clam products (26%) were mislabelled, or substituted with the American species *Ensis leei* (M. Huber, 2015), formerly *E. directus*. Primers for the specific identification of these species were successfully developed and tested in the laboratory using naked-eye colorimetric loop-mediated isothermal amplification (LAMP) assays. In addition, this technique was applied in a pilot on-site test, conducted in a restaurant, to enable real-time detection of food fraud. These approaches could represent a valuable tool for its use by regulatory authorities for the monitoring of seafood fraud, species conservation and safeguarding of consumer interests.

**Acknowledgments:**

Project reference: MCINN-22-PDC2022-133730-I00

**References:**

[1] Fox, M., Mitchell, M., Dean, M., Elliott, C., & Campbell, K. (**2018**). The seafood supply chain from a fraudulent perspective. Food Secur. 10, 939–963.

[2] Parrondo, M., López, S., Aparicio-Valencia, A., Fueyo, A., Quintanilla-García, P., Arias, A., & Borrell, Y. J. (**2021**). Almost never you get what you pay for: Widespread mislabeling of commercial "zamburiñas" in northern Spain. *Food Control*, *120*, 107541.

# Photobiocatalytic approaches for the stereoselective preparation of chiral alcohols

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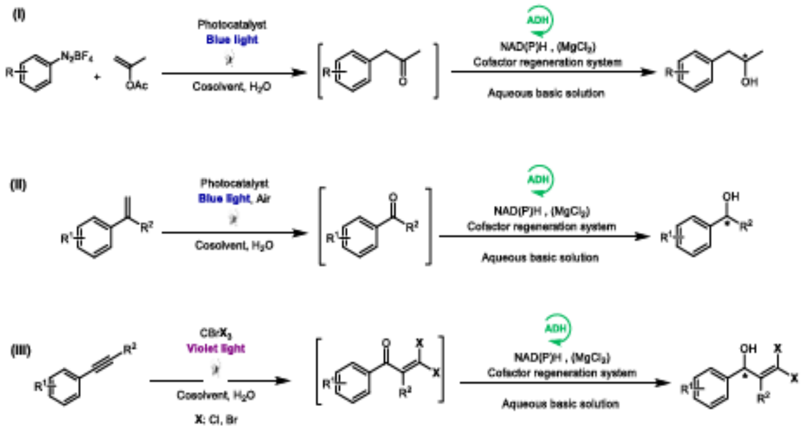
**Keywords:** Photochemistry, biocatalysis, alcohol dehydrogenase

Photochemistry and biocatalysis are complementary disciplines for accessing molecular architectures difficult to obtain by conventional synthetic methods. Their integration enables efficient and sustainable transformations under usually mild conditions [1]. This work summarizes one-pot photobiocatalytic cascades combining visible-light photochemistry with enzymatic carbonyl reduction using alcohol dehydrogenases (ADHs). These systems enable the stereoselective synthesis of optically active secondary alcohols in aqueous medium. A range of substrates is employed, including aryl diazonium salts, alkenes and alkynes. The approach highlights the versatility of photochemistry and enzymatic catalysis (Scheme 1).

The first approach discloses a two-step photobiocatalytic sequence for the stereoselective synthesis of 1-arylpropan-2-ols from aryl diazonium salts combining a light-driven Meerwein arylation with an ADH-catalyzed reduction. Building on this concept, the second strategy expands the scope of photobiocatalytic cascades by combining the photo-oxidative cleavage of alkenes into ketones with a carbonyl bioreduction step, enabling access to a broad range of secondary alcohols with high stereoselectivity. Finally, a one-pot sequential process is presented for the synthesis of optically active γ,γ-dihalo-β-enols from alkynes, in which visible-light activation generates gem-dihaloenone intermediates that are subsequently bioreduced with high efficiency [4].



**Scheme 1.** Photobiocatalytic cascades for the synthesis of optically active alcohols.

**Acknowledgments:**

Financial support from the Spanish Ministry of Science and Innovation (MCI, PID2019-109253RB-I00 and PID2022-137893OB-I00), and the Asturian Government AYUD/2021/51542.

**References:**

[1] J. Yu, B. Chen, X. Huang, Angew. Chem. Int. Ed. **2025**, 64, e202419262.

[2] L. Rodríguez-Fernández, J. Albarrán-Velo, I. Lavandera, V. Gotor-Fernández, Adv. Synth. Catal. **2023**, 365, 1883-1892.

[3] L. Rodríguez-Fernández, J. Albarrán-Velo, I. Lavandera, V. Gotor-Fernández, Adv. Synth. Catal. **2024**, 366, 900-908.

[4] L. Rodríguez-Fernández, M. Plaza, V. Gotor-Fernández, Adv. Synth. Catal. **2025**, 367,e70100.

# Nitrogen and lanthanide co-doped polymeric Carbon Dots as versatile and innovative Nanotags for multimodal and targeted bioimaging applications

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**Keywords:** Carbon Dots, Nanotags, Multimodal Bioimaging, HeLa Cells, NIH/3T3 Cells

Multimodal imaging is a cutting-edge technology where the advantages of nanoparticles are currently exploited, as the combination of several imaging agents into a unique nanotag (multifunctional nanomaterials) that allows a fast disease diagnosis. For this purpose, Carbon Dots (CDs) have been rising interest along the last years due to its tunable properties, simple synthesis procedures, outstanding photostability and extremely low toxicity compared to other quantum dots [1]. Many of doping strategies to obtain CDs with multimodal capabilities consist in the introduction of transition metal atoms in the nanostructure or even rare earth elements.

In this work, N, Gd and Yb co-doped CDs are presented as powerful nanotags for multimodal bioimaging applications [2]. The syntesized CDs were exhaustively characterized showing an intense fluorescence, multiemission and 2.5±0.3nm spherical size. Cytotoxicity assays were carried out with HeLa and NIH/3T3 cells, and our results confirmed the high biocompatibility in both, healthy and tumoral cells. After that, co-doped-CDs showed the potential application in bioimaging techniques such as fluorescence, Laser Ablation-ICP-MS by quantifying Gd and Yb; and Magnetic Resonance Imaging using these nanoparticles as potential contrast agents. Finally, doped-CDs were functionalized with an anti-mouse polyclonal antibody and targeted bioimaging studies against tumoral cells were carried out by recognizing cell membrane proteins. Our results position these nanomaterials as promising nanotools to perform multimodal bioimaging studies. Moreover, the possibility to easily functionalize these CDs with recognition biomolecules (antibodies) provides its potential as clinical tool.

## Acknowledgments:

Ministry of Science and Innovation for the project Ref. PID2020-117282RB-I00, PID2022 142323NB-I00 and PID2023-149221-B-I00RB-I00 funded by MCIN/AEI/10.13039/5011000 11033/ and by “ERDF A way of making Europe”. Government of the Principality of Asturias through the Asturias Science, Business Competitiveness and Innovation Agency, SEKUENS for the project Ref. IDE/2024/000752 .

## References:

[1] Li, H.; Yan, X.; Kong, D.; Jin, R.; Sun, C.; Du, D.; Lin, Y.; Lu, G. Recent Advances in Carbon Dots for Bioimaging Applications. Nanoscale Horiz. **2020**, 5 (2), 218–234. https://doi.org/10.1039/C9NH00476A.

[2] Li, X.; Ding, S.; Lyu, Z.; Tieu, P.; Wang, M.; Feng, Z.; Pan, X.; Zhou, Y.; Niu, X.; Du, D.; Zhu, W.; Lin, Y. Single-Atomic Iron Doped Carbon Dots with Both Photoluminescence and Oxidase-Like Activity. Small **2022**, 18 (37), 2203001. https://doi.org/10.1002/smll.202203001.

# Integrated metabolomic and transcriptomic insights into the protective role of coenzyme Q10 in a retinal hypoxia cellular model

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**Keywords:** Retinal vascular occlusions, Coenzyme Q10, Retinal hypoxia, Metabolomics, Transcriptomics

Retinal vascular occlusions (RVOs) interrupt blood flow, reducing oxygen supply and leading to hypoxia and, in many cases, cell death. For this condition, supplementation with coenzyme Q10 (CoQ10) has attracted considerable interest due to its beneficial effects on visual field in patients affected by RVOs. However, its therapeutic application is compromised by its low solubility, and liposomal encapsulation has emerged as a promising strategy to enhance cellular uptake and bioavailability.

In this study, analytical methodologies were applied to evaluate CoQ10 internalisation and molecular effects, comparing free and liposome-encapsulated forms. An integrated metabolomic (LC-HRMS) and transcriptomic (RNAseq) approach was applied in an immortalised human Müller cell line (MIO-M1) exposed to hypoxia (6 and 72 h), in the presence or absence of encapsulated CoQ10. Results revealed a higher intracellular concentration of CoQ10 in the supplemented cultures, and showed that CoQ10 modulates the cellular response to hypoxia in a time-dependent manner. At early stages, CoQ10 attenuated oxidative stress and inflammatory signalling, including the TNF and MAPK pathways. Under prolonged hypoxic conditions, CoQ10 attenuated, but did not completely reverse the changes induced in apoptosis and senescence-related pathways. These findings suggest that CoQ10 modulates key pathways involved in cell survival and stress response without fully reversing prolonged hypoxia-induced alterations, supporting its therapeutic potential in retinal vascular diseases.

**Acknowledgments:**

This work was financially supported through coordinate project PID2022-137319OB (-C21 and -C22)/Agencia Estatal de Investigación (AEI)/10.13039/501100011033 in Spain as well as the FEDER Program of the European Union (IDE/2024/000685). A. Villa-Vázquez acknowledges the Severo Ochoa Program Grant with Ref. BP22-187 (Science, Business, Training, and Employment Office, Principality of Asturias, Spain).

# Chloride-Catalyzed Insertion of Carbon Disulfide into Nitrones for the Synthesis of Secondary Thioamides

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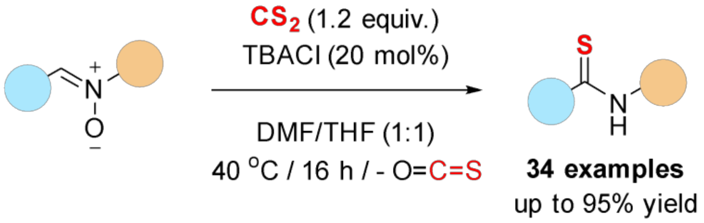
**Keywords:** Carbon disulfide, Chloride Anion, Nitrone, Thioamide, Catalysis.

Carbon disulfide is a widely used precursor in organosulfur synthesis due to its well-known electrophilic nature.[1] We have previously shown that simple chloride anions generate a nucleophilic $[Cl–CS_2]^-$ adduct that efficiently performs addition to epoxides.[2] Herein, we report its addition to a different electrophilic counterpart: nitrones.[3] This approach affords a wide range of secondary thioamides under mild conditions. These compounds are present in essential biomolecules and find application as precursors to sulfur-containing heterocycles.[4]

This methodology overcomes chemoselectivity limitations inherent to traditional sulfonating procedures (e.g., Lawesson's reagent or $P_4S_{10}$),[4] thus allowing the preparation of thioamides containing ketone, ester, amide and nitrile moieties. The reaction is scalable and has been applied to the preparation of the HIV-1 reverse transcriptase inhibitor UC-781. Moreover, DFT calculations were carried out to elucidate the reaction mechanism and to gain insight into the role and formation of the $[Cl–CS_2]^-$ adduct.



**Acknowledgments:**

PID2023-148663NB-I00, PA-22-BP21-088.

**References:**

[1] R. J. Cremlyn. An Introduction to Organosulfur Chemistry; Wiley, 1996.

[2] M. López-Aguilar, N. Ríos-Lombardía, M. Gallegos, D. Barrena-Espés, J. García-Álvarez, C. Concellón, V. del Amo. Chem. Commun. **2025**, 61, 3488–3491.

[3] M. López-Aguilar, N. Ríos-Lombardía, D. Barrena-Espés, M. Gallegos, J. García-Álvarez, C. Concellón, V. del Amo. Org. Lett. **2025**, 27, 30, 8338–8343.

[4] T. N. Hansen, C. A. Olsen. Chem. Eur. J. **2024**, 30, e202303770.

# S-doping of sustainable carbon aerogels as anode of high-performance sodium-ion batteries

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**Keywords:** sodium-ion batteries, anodes, sol-gel, sustainable carbon gels, S-doping

Sodium-ion batteries (SIBs) are emerging as a viable alternative to lithium-ion batteries (LIBs), mainly due to their independence from critical raw materials and their similar electrochemical working principles. Among the various anode candidates, hard carbons stand out as the most suitable option, thanks to the broad range of precursors and synthesis strategies available, which allows for the tunability of their physicochemical properties. In addition, to improve the electrochemical performance of hard carbons, heteroatom doping has been widely explored. In particular, S doping has been proven to introduce additional active sites and enlarge layer spacing, therefore improving reaction kinetics.[1]

Compared to biomass-derived hard carbons, synthetic approaches offer superior control over the composition and structure of the materials, allowing the fabrication of highly reproducible materials with tailored characteristics that are particularly advantageous for SIB applications.

In this work, we present an efficient and scalable process to obtain sustainable synthetic carbon aerogels to be used as anodes in SIBs. The proposed synthesis is based on the sol gel methodology assisted by microwave heating[2], using tannins, a green precursor, and glyoxal. After the synthesis, the aerogels are carbonized and functionalized with elemental sulphur through different thermal treatment strategies. With this doping, the structural and textural properties of the materials are modified without altering the gel morphology. These changes have an impact on the electrochemical performance, leading to an increase in the capacity from ~ 260 mAh g-1 (without S) to ~ 400 mAh g-1 (with S), exceeding the typical capacity of hard carbons ( ~ 300 mAh g-1).1 These findings demonstrate the beneficial role of S doping in enhancing the electrochemical performance of these types of materials.

**Acknowledgments:**

This research was funded by the 4SIBAT project, PCI2025-1632333, funded by MCIN/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR, within the framework of M-ERA.NET. DGP is grateful to the PRE2023-001408 PhD grant funded by MCIN/AEI/10.13039/501100011033 and FSE+. The authors also thank the Principado de Asturias (IDI/2024/000749).

**References:**

(1) Shao et al., Adv. Energy Sustain. Res. **2022**, 3, 2200009.

(2) Rey-Raap et al., J. Sol-Gel Sci. Technol. **2014**, 69, 488–497.

# Crystal Structure Prediction of Molecular Photoswitches

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**Crystal Structure Prediction (CSP)** aims to determine the crystal packing of a material starting only from its molecular diagram. This is a critical task since physical properties are determined by this packing, yet it remains a formidable challenge because even a simple molecule can pack in an almost infinite number of ways, requiring extensive sampling of the search space to identify all potential low-energy structures [1]. We apply CSP to stilbene, a molecular photoswitch that undergoes a light-induced solid-to-liquid transition between its stable trans and metastable cis forms. This isomerization stores both chemical energy and the latent heat of fusion, providing a high energy density ideal for Molecular Solar Thermal Energy Storage (MOST) [2]. While trans-stilbene is well-characterized, the cis phase is difficult to study as it is liquid under normal conditions.

Our hierarchical computational workflow involves: 1) generating candidate structures via stochastic exploration; 2) screening against experimental X-ray powder diffraction (XRPD) patterns using a similarity index to account for lattice deformations [3]; and 3) ranking structures via Density Functional Theory (DFT) with the XDM dispersion model. This approach balances computational speed with the high accuracy required for predicting lattice energies.

The proposed protocol was used to characterize an experimental transient crystalline polymorph of cis-stilbene obtained via cold-crystallization. Although thermodinamically stable phases were successfully identified, finding the exact match for the experimental pattern remains an ongoing challenge. Overall, our results highlight how CSP can accelerate the development of next-generation light-sensitive materials for energy applications.

**References:**

[1] G. J. O. Beran, Chem. Sci. **2023**, 14, 13290.

[2] Z. Wang et al., J. Am. Chem. Soc. **2020**, 142, 10121-10131.

[3] Otero-de-la-Roza, J. Appl. Cryst. **2024**, 57, 1401

# REVALORISATION OF AGRIFOOD WASTE THROUGH SOLID-STATE FERMENTATION: BIOPESTICIDES AND BIOSTIMULANTS PRODUCTION

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**Keywords:** SSF, Trichoderma harzianum, Pruning Waste, IAA, Circular Economy

Solid-state fermentation (SSF) has proven to be an effective solid organic waste revalorisation method due to its versatility, lower water and energy requirements, and easy integration with other valorisation strategies [1]. This work proposes a SSF process that uses different agrifood residues to produce a biostimulant (Indole-3-Acetic Acid, IAA) and a biopesticide (Trichoderma harzianum spores) simultaneously, thereby bringing an agrifood economic loop to a close.

The SSFs entailed packed bed reactors (0.5L and 22L), T. harzianum CECT 2929 inoculum, shredded apples (A) as substrate, and pallet woodchips (WCHs) and pruning waste (natural NPW– and functionalised after its use as wastewater filter –FPW, FPW_B–) as bulking agents. See Ghoreishi et al. 2024 [2] and Vargas Gil et al. 2009 [3] for the methods and materials used.

The pH (Figure 1A) and moisture content (MC, Fig. 1B) values of the combinations fall right within the ranges previously reported in similar SSF systems (pH: slightly acidic to neutral, MC: 60-70%) [1,2]. While the final yields of spore production (Fig. 1C) from 0.5L reactors match those reported earlier with other pairings (108-109) [1, 2], the 22L reactor ones surpass them (1011 vs. 108) [2]. These findings support the hypothesis that SSF would be an attractive way to revalorise these agrifood wastes and close one agrifood industry loop.

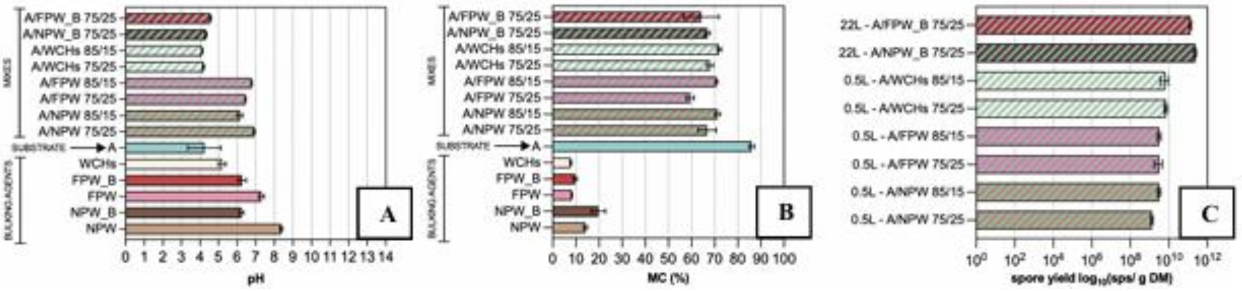

***Figure 1.*** *Selection of results. (Reactor Size -) Substrate/Bulking Agent W/W mix proportion.*

**Acknowledgments:**

This study is funded by CESAM project SSOIL (AG. nº 18). Paula S. thanks Generalitat de Catalunya for her industrial pre-doctoral grant (2024 DI 00089). Sa Canova (Spain) and Leitat Technological Centre (Spain) provided and functionalised the PW, respectively. Casas, Recuperació de Palets S.A. (Spain) provided WCHs.

**References:**

[1] A. Sala A. Artola A. Sánchez R. Barrena, Bioresour. Technol., **2020**, 296, 122322.

[2] G. Ghoreishi R. Barrena A. Sánchez X. Font, Chem. Eng. J., **2024**, 502, 158057.

[3] S. Vargas Gil S. Pastor G.J. March, Microbiol. Res., **2009**, 164, 196–205.

# Sewing pins as electrodes for on-site ELISA readout

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**Keywords:** Low-cost electroanalysis, immunoassay, ELISA, Epstein-Barr Virus, MMP9

Enzyme-Linked Immunosorbent Assays (ELISAs) remain fundamental analytical tools due to their high sensitivity, specificity, and adaptability across clinical diagnostics, food safety, and environmental monitoring. ELISA detection usually relies on optical plate readers, which provide sensitivity and ease of use. However, these instruments generally restrict ELISA deployment to laboratory environments and limit their suitability for rapid point-of-need testing.

This work introduces a electrochemical probe engineered to serve as a miniaturized and low cost alternative readout platform for standard ELISA protocols [1]. The device uses mass-produced metallic pins as electrodes, combining a carbon-modified sewing pin as the working electrode with two unmodified metallic pins as reference and counter electrodes.

The probe was applied to the quantification of two clinically relevant proteins: human IgG antibodies against the Epstein–Barr virus (EBV), and matrix metalloproteinase 9 (MMP-9), a biomarker associated with neurological damage. In both cases, the electroanalytical signal provided rapid and reliable assay readouts. Moreover, the electrochemical probe was successfully validated through its application to spiked artificial human serum samples (for anti-EBV IgG detection) and saliva samples from volunteers (for MMP-9 detection), demonstrating the feasibility of this approach as a portable alternative to optical detection.

With its low cost, operational simplicity, and seamless integration into existing ELISA workflows, this electrochemical probe represents a promising tool for expanding immunoassay testing beyond traditional laboratory settings. Its adaptability positions it as a valuable solution for decentralized diagnostics, particularly in resource-limited environments or applications requiring on-site analytical measurements.

### Acknowledgments:

This work was supported by projects PID2020-118376RA-I00 and PID2023-148375OB-I00 funded by MCIU/AEI/10.13039/501100011033/ FEDER, EU, and project IDE/2024/000694 funded by the Government of the Principality of Asturias through the Sekuens Agency, and EU through the FEDER Program. P.R.L. was supported by the "Severo Ochoa" grant (BP21-029, Government of the Principality of Asturias, Spain) and M.C.A by the "Margarita Salas" grant (MS-18, Spanish Government).

### References:

[1] P. Rioboó-Legaspi et al. ElectroELISA Probe: Low-cost and miniaturized cell for on-site electrochemical microtiter plate readout. Sens. Actuators B, **2026**. In press.

# Microwave-Synthesized Nickel Aerogels for HER

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**Keywords:** Electrocatalysis, electrolysis, hydrogen, metal aerogel, porosity

Global energy demand is rising, while fossil fuels still dominate energy supply, intensifying greenhouse gas emissions. In this context, green hydrogen is a promising energy carrier for a low-carbon economy, with water electrolysis being one of the most attractive production routes. However, current electrolyzers rely on expensive and scarce noble metals such as Pt, Ir, and Ru. In this work, we develop a series of nickel-based metal aerogels as promising electrocatalysts for the cathode reaction, namely the hydrogen evolution reaction. These materials were synthesized through a microwave-assisted sol-gel approach, which offers a faster and more efficient synthesis process [1]. In addition, we synthesized different nickel aerogels by varying the metallic precursor and drying method to evaluate how these parameters affect the final properties of the aerogel. Nickel aerogels were synthesized by a microwave-assisted sol-gel method using nickel chloride hexahydrate, nickel acetate tetrahydrate, and nickel nitrate hexahydrate as nickel precursors, besides sodium carbonate and glyoxylic acid as reduction components. After microwave treatment at 70 °C, the product was washed and dried by different methods to obtain the final aerogel. The series of nickel aerogels obtained were physicochemically and electrochemically characterized to evaluate the influence of the synthesis conditions on the electrocatalyst properties and performance. We found that the nickel precursor influences the gel morphology, from nodules to flakes, whereas the drying method mainly controls its porosity, resulting in materials within a wide range of meso-macroporosity. The nickel precursor and drying method strongly influenced the morphology and porosity of the aerogels, respectively, and these structural differences affected the final catalytic activity, with some samples showing an improved electrocatalytic performance toward the hydrogen evolution reaction (HER).

### Acknowledgments:

This research was funded by MCIN/AEI/10.13039/501100011033/FEDER-UE through the PID2022-139493OA-100 project, MITECO/IDAE, and the European Union-NextGenerationEU/PRTR through the PR H2CVAL4-C2-2023-000052 project, and by the Principado de Asturias (ID/2024/000749). NRR is grateful for the CNS2023-144627 grant funded by MCIN/AEI/10.13039/501100011033 and the European Union NextGenerationEU/PRTR.

### References:

[1] González-Lavín, J.; Arenillas, A.; Rey-Raap, N. Scalable microwave-assisted synthesis of iron oxide aerogels: Tuning morphology, crystallinity, and electrocatalytic performance. Electrochimica Acta **2025**, 547, 147927.

# Photochemical Cross-Coupling of *N*-Tosylhydrazones and Boronic Acids: Difunctionalization and Multicomponent Synthesis

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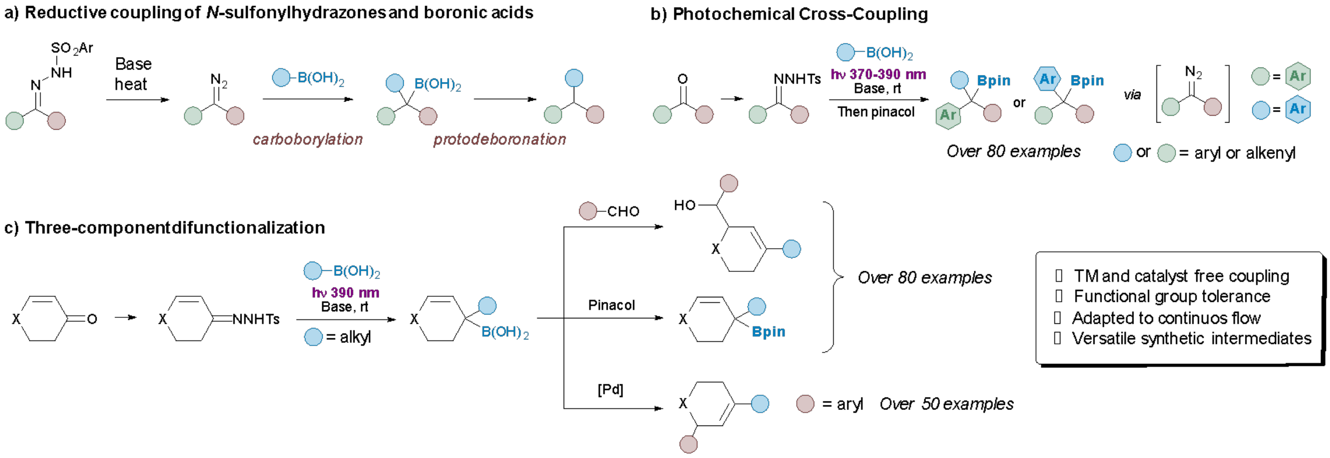
**Keywords:** Photochemistry, Metal-Free, *N*-Tosylhydrazone, Boronic Acid, Cross-coupling.

The transition-metal-free coupling of *N*-tosylhydrazones with boronic acids enables C–C bond formation via diazo intermediates but is limited by protodeboronation.[1] Herein, photochemical activation enables control over these intermediates. Visible light promotes the homologation of boronic acids under mild conditions, providing access to benzyl boronates otherwise inaccessible under thermal protocols, and enabling translation to continuous flow.[2] This platform is extended to α,β-unsaturated *N*-tosylhydrazones, affording homoallylic alcohols via a multicomponent process.[3] Additionally, the intermediates engage in palladium-catalyzed Suzuki-type couplings.[4] Overall, a unified photochemical strategy for multicomponent and catalytic transformations is established.



**Scheme 1**. Photochemical cross-coupling between *N*-tosylhydrazones and boronic acids.

**Acknowledgments:**

Agencia Estatal de Investigación grant (MCINN-23-PID2022-140635NB-I00) and a FPI predoctoral contract to Á.V.-M. (MCINN-24-PREP2022-000214).

**References:**

[1] Barluenga, J.; Tomás-Gamasa, M.; Aznar, F.; Valdés, C. *Nat. Chem.* **2009**, 1, 494.

[2] Valdés-Maqueda, Á; López, L; Plaza, M; Valdés, C. *Chem. Sci.*, **2023**, 14, 13765-13775.

[3] Valdés-Maqueda, Á; Plaza, M; Valdés, C. *Chem. Sci.*, **2024**, 15, 19626-19633.

[4] Valdés-Maqueda, Á; Plaza, M; Valdés, C. *ChemistryEurope*, **2026**, 4, e202500212.

# Biomass-derived carbon nanoparticles for high-rate sodium storage

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**Keywords:** Biomass; carbon nanoparticles; sodium-ion capacitors; sulfur doping; high-rate sodium storage

The development of sustainable electrode materials capable of fast sodium storage is essential for a new generation of post-lithium technologies, particularly for high-power sodium-ion batteries and sodium-ion capacitors. Herein, we report a simple and scalable strategy for the synthesis of carbon materials with suitable properties for use in the negative and positive electrodes of Na-ion capacitors by using a natural and abundant polyphenol such as tannic acid as carbon precursor. The negative electrode material consists of highly defective, S doped carbon nanoparticles synthesized by thermal pre-condensation at 100–200 °C (with thiourea as the crosslinker and Pluronic P123 as the structure-directing agent), pre carbonization at 600 °C and sulfur doping at 600 ºC (SCNPs). Remarkably, the size of the nanoparticles can be easily tuned (down to 20 nm) by controlling the condensation conditions.

The optimized S-doped carbon nanoparticles (pre-condensation temperature: 180 ºC, S content: 20.1%, particle size < 50 nm) possess excellent sodium-storage kinetics, reaching a reversible Na storage capacity of 544 mAh g-1 at 0.1 A g-1, retaining 222 and 153 mAh g-1 at high current densities of 5 and 10 A g-1, respectively. The positive electrode material is made up of highly porous carbon nanoparticles (2300 m2 g-1) prepared by pre-carbonization of polymeric nanoparticles at 400 ºC followed by chemical activation at 900 ºC with a benign porogen such as KHCO3. This material exhibits an anion storage capacity of 104 mAh g-1 at 0.1 A g-1, preserving 60% of that capacity at the highest rate of 10 A g-1. Na-ion capacitors were assembled with the optimized electrode materials using different positive-to-negative mass ratios. High ratios of 3-4 led to the hybrid capacitors with the best performance in terms of capacity (50 mAh g-1), rate capability (22 mAh g-1 at 10 A g-1) and cycling stability.

**Acknowledgments:**

Part of this work has been funded by national funding (project IDI/2018/000148 (FICYT/FEDER) and PID2021-123648OB-I00 (MCIN/AEI/10.13039/ 501100011033/and ERDF A way of making Europe)) and part by the Austrian Research Promotion Agency (FFG) through the COMET module project Renew4EHS (No. 892416).

# Temperature-controlled synthesis of sustainable carbon aerogels for efficient sodium-ion battery anodes

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**Keywords:** sodium-ion batteries, anodes, sol-gel, tannins, sustainable carbon gels.

The development of robust energy storage technologies is essential for the consolidation of renewable energy systems and electric mobility. Sodium-ion batteries (SIBs) are emerging as a competitive alternative to lithium-ion batteries due to the abundance of sodium and their independence from critical materials such as lithium, nickel and cobalt. Their performance strongly depends on the anode material, with disordered carbon material, especially hard carbons (HC) [1]. HC are usually obtained from biomass through routes that requires an expensive impurity-removal step. In addition, these routes often lack reproducibility and structural control. In contrast, sol-gel synthesis of disordered carbon materials offers a pathway with precise regulation of porosity, surface chemistry, and carbon ordering, enabling more consistent materials. Considering the aforementioned aspects, recent studies show that variations in structural order, defect concentration, surface area or microporosity depending on the carbonization temperatures, dramatically affecting the electrochemical performance of HC as anodes in SIBs. In this work, disordered carbon aerogels (CA) were synthesized from sustainable precursor (tannins) using a microwave-assisted sol-gel method followed by carbonization at different temperatures. The influence of the carbonization temperature on the amorphous structure, pore distribution, defect density, and surface chemistry of the CA as well as how these changes affect their electrochemical performance as anodes for SIBs, was evaluated. [2]. Optimization of the carbonization temperature enabled the synthesis of CA exhibiting electrochemical performance comparable to commercial hard carbon (HC) used in SIBs, with capacities of ~ 300 mAh $g^{-1}$, an initial coulombic efficiency of ~ 75 % (approaching ~ 100 % after the 5th cycle), and capacity retention > 92 % after 50 cycles at 50 mA g-1. These findings confirm that combining sustainable sol-gel synthesis with controlled carbonization temperature is an effective strategy for optimizing amorphous carbons for SIB anodes.

## Acknowledgments:

The authors acknowledge funding from MICIN and the EU NextGeneration EU/PRTR (PID2023-147151OB-I00, MCIN/AEI-10.13039/501100011033) and the Principality of Asturias (IDI/2024/00749). D. García acknowledges his predoctoral contract PREP2023-001408, funded by MCIN/AEI/10.13039/501100011033 and FSE+. The authors also thanks to the Principado de Asturias (IDI/2024/000749) and MCIN/AEI/10.13039/501100011033/FEDER-UE through PCI2025-163233 project.

## References:

[1] C.Wu, Y. Yang, Y. Zhang, H. Xu, X. He, X. Wu, S. Chou. Chem. Sci, **2024**, 15, 6244-6268.

[2] J. Kim, D. Yu, E. Oh, J. Jang, J. Kim, J. Yang. Carbon Lett. **2025**, 35, 351-363.

# Alkaline Hydrolysis of Sewage Sludge for the Production of Protein Hydrolysates

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**Keywords:** Alkaline hydrolysis; protein hydrolysates; sewage sludge; waste valorisation

Sewage sludge (SS), a by-product of wastewater treatment plants (WWTPs), represents a major environmental and management challenge due to the large volumes generated, together with the presence of pathogens and potentially hazardous substances [1]. In the European Union, around 10 million tons of SS on a dry basis are produced annually, requiring sustainable management strategies. Although SS is rich in organic matter and nutrients, its direct application in agriculture is limited by environmental concerns [2]. Therefore, its valorisation within a circular bioeconomy framework has gained increasing attention.

Among the possible approaches, the recovery of protein hydrolysates from SS is particularly promising due to their potential application as plant biostimulants. Thus, the aim of this work was to evaluate the effect of key operating variables on SS alkaline hydrolysis to maximise protein solubilisation and obtain hydrolysates with potential biostimulant activity.

Hydrolysis experiments were carried out at 120-200 ºC for 30 min to 4 h using sludge total solids (TS) contents of 3-10% (w/v). Calcium hydroxide was added at 0.2 g/g TS. Hydrolysis significantly enhanced organic matter solubilisation, increasing soluble TOC, proteins, and free amino acids in the liquid fraction, with soluble protein concentration reaching up to 7.6 g/L under the most suitable conditions (6.8% TS at 160ºC for 4 h). The operating conditions strongly affected hydrolysate composition: moderate conditions favoured the recovery of protein-rich fractions, whereas more severe conditions promoted the formation of short-chain carboxylic acids. Carbohydrates were also released, although to a lesser extent than proteins. Additionally, the liquid hydrolysates contained appreciable amounts of nutrients, with nitrogen, phosphorus, and potassium concentrations reaching up to 96%, 12%, and 41% of their initial contents, respectively, while heavy metals remained mainly associated with the solid fraction.

These results indicate that controlled alkaline hydrolysis is a promising strategy for converting SS into value-added hydrolysates with potential biostimulant activity.

## Acknowledgments:

The authors acknowledge financial support from the Spanish State Research Agency (AEI) through the G-Blend project (PID2024-161375OB-C21) and from the Agency for Science, Business Competitiveness and Innovation of Asturias (SEKUENS) through project IDE/2024/000695.

## References:

[1]. Zhang, X. Wang, W. Zhu, Y. Zhao, N. Wang, M. Gao, Q. Wang, Environ. Res., **2023**, 233, 116444.

[2] García, M., Urrea, J. L., Collado, S., Oulego, P., Díaz, M., Waste Manag., **2017**, 67, 278–287.

# Machine Learning Tools in the Gold(I)-Catalyzed Intramolecular C(sp3)—H Bond Functionalization: Predictive Statistical Analysis

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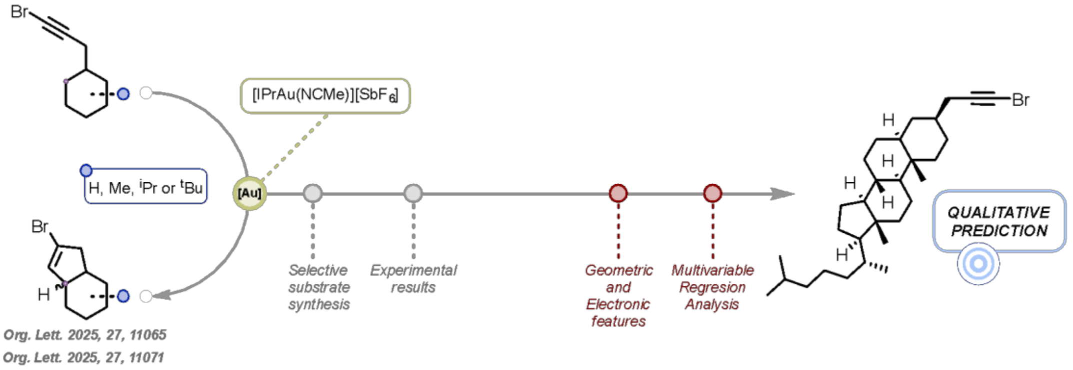
**Keywords:** Gold-catalysis, 1-Bromoalkynes, Predictive Statistical Analysis, Selectivity

Understanding the experimental outcome of a reaction is not always easy. Furthermore, the proper understanding of reaction mechanisms is essential to improve the efficiency of the process.[1] In recent years, predictive tools have gained increasing attention for their ability to rationalize and predict different types of chemical reactivity.

We have recently described the effect of the conformations[2a] in the gold(I)-catalyzed cycloisomerization of 1-bromoalkynes developed by Barrio and coworkers.[3] The use of cyclohexane derivatives displaying complex substitution patterns afforded outcomes with clear trends.[2] By using the experimental data obtained, we were able to build a model to rigorously express the factors that rule this reactivity, as well as to qualitatively predict the outcome of some complexly substituted cyclohexane derivatives.



**Scheme 1**. Graphical abstract.

## References:

[1] Deolka, S.; Dalmau, D.; Garcia Roca, A.; Vasylecskyi, S.; Samha, M. H.; Sigman, M. S., *J. Am. Chem. Soc.* **2025**, *147*, 35705–35717.

[2] a) Miguélez, R.; Arto, O.; Siera, H.; Schulte, J.; Merino, I.; Haberhauer, G.; Barrio, P., *Org. Lett.*, **2025**, *27*, 11065-11070. b) Arto, O., Miguélez, R., Siera, H., Schulte, J., Merino, I., Haberhauer, G., Barrio, P., *Org. Lett.*, **2025**, *27*, 11071-11076.

[3] Miguélez, R.; Semleit, N.; Rodríguez-Arias, C.; Mykhailiuk, P.; González, J. M.; Haberhauer, G.; Barrio, P., *Angew. Chem. Int. Ed.*, **2023**, *62*, e202305296.

# Dynamic Colloidal Plasmonic Metasurfaces via templated self-assembly on $Sb_2S_3$

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The ordered placement of plasmonic building blocks in a two-dimensional array gives rise to a collective plasmonic phenomenon known as Surface Lattice Resonance (SLR), originating from the interaction between the localized resonances of nanoparticles and diffractive modes near the Rayleigh anomaly [1]. These so-called metasurfaces present optical resonances characterized by narrow bandwidth and long lifetimes, holding great potential for a variety of applications, ranging from (bio)sensing to optoelectronics, from catalysis to photonics.

Recently, the focus has shifted towards the development of dynamic and responsive metasurfaces, exploiting the highly responsive characters of SLR to the changes in the dielectric environment surrounding the nanoparticles. In this work, we propose a colloidal tunable metasurface by self-assembling gold nanoparticles over a Phase-Change Material (PCM) compound semiconductor, antimony trisulfide (Sb2S3) [3].

Specifically, Sb2S3 is a PCM capable of thermally switching between two phases, amorphous and crystalline [2]. This phase change causes significant variations in the refractive index (n) and extinction coefficient (k), allowing post-fabrication tuning of the dielectric environment, which can be used to modulate the plasmonic response of the gold metasurface [3]. This study highlights the potential of Phase-Change Materials as active substrates for tunable colloidal plasmonic metasurfaces and paves the way for reprogrammable nanophotonic platforms [2][3].

## Acknowledgments:

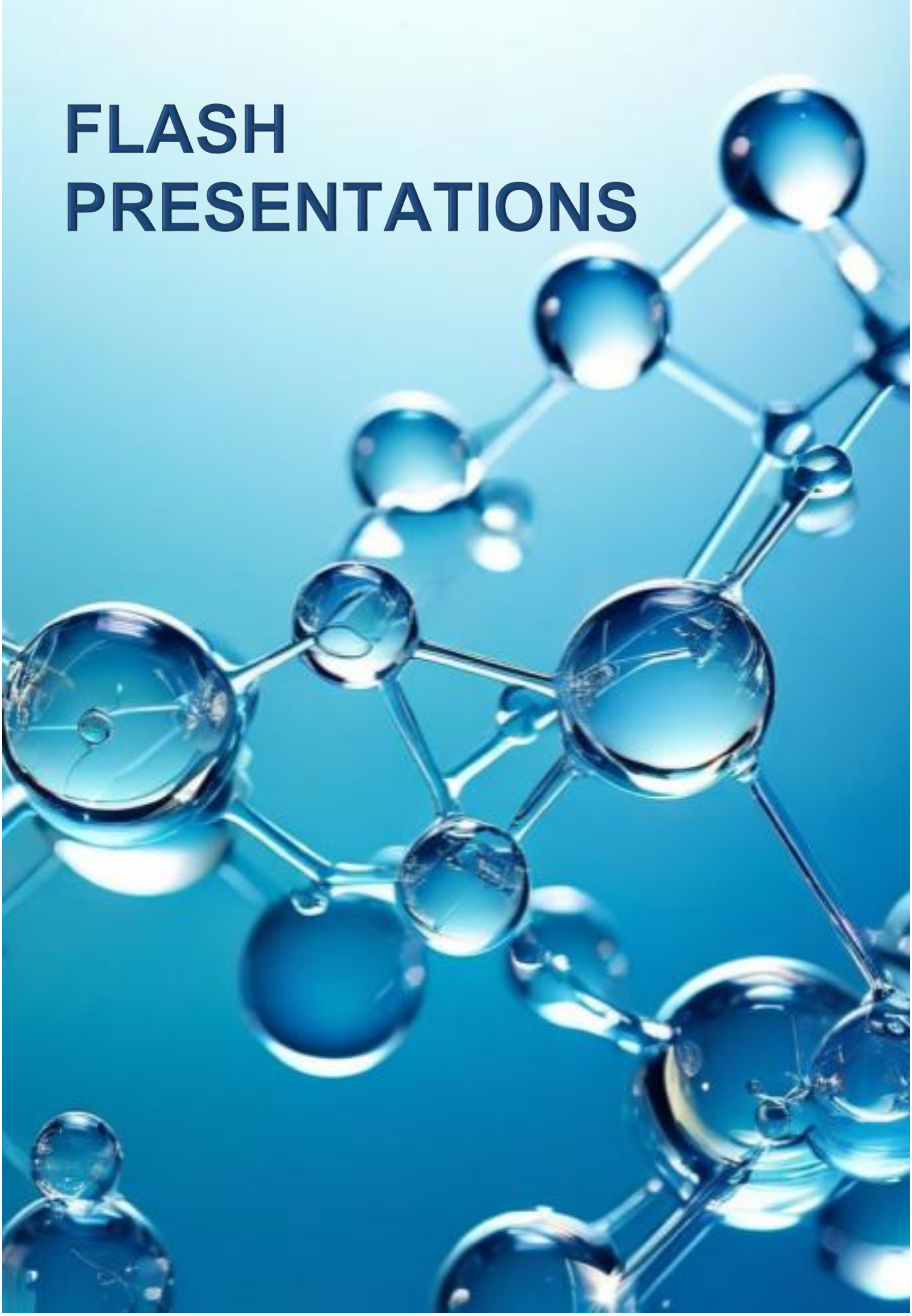
This work was funded by the European Research Council (ERC Advanced Grant 787510, 4DBIOSERS and ERC Starting Grant 101115164, NANOGROWDIRECT). L.S. acknowledges support from the Spanish Ministerio de Ciencia e Innovación y Universidades through fellowship RYC2022-037894-I.

## References:

[1] V. G. Kravets, A. V. Kabashin, W. L. Barnes and A. N. Grigorenko, Chem. Rev., **2018**, 118, 5912–5951.

[2] A. Bieganski, M. Perestjuk, R. Armand et al., Opt. Mater. Express, **2024**, 14, 862–870.

[3] M. Mayer, M. J. Schnepf, T. A. F. König, A. Fery, Adv. Optical Mater., **2019**, 7, 1800564.



# FLASH PRESENTATIONS

# COMPLETE PET DEPOLYMERIZATION USING ETHYLENE GLYCOL BASED DEEP EUTECTIC SOLVENTS

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**Keywords:** PET DEPOLYMERIZATION, DES, GREEN CHEMISTRY, POLYMER,

Polyethylene terephthalate plastic (PET) is one of the most extensively used materials worldwide due to its affordability, lightweight nature, and high durability. Proper end-of-life management is essential to address growing environmental concerns. In recent years, there has been an increasing focus on the chemical breakdown and recycling of PET materials. The primary goal of this process is the recovery of the polymer components both as ethylene glycol and as the more expensive terephthalic acid, with the purpose of using them to synthesize the virgin polymer, thus fully recycling the original waste.

The standard depolymerization reactions, albeit yielding the starting PET monomer, usually require high temperatures and long reaction times (180 °C, 24 h)[1], making the recycling process economically burdenly. Several catalyst have been developed for PET depolymerization through different mechanisms, with the effect of lowering the critical energy demand.[2]

In this study, the depolymerization of PET flakes in a KF:ethylene glycol:water deep eutectic solvent (DES) is presented. The effects of temperature, heating system, water content, and KF concentration on the depolymerization reaction were investigated. Complete depolymerization was achieved under various reaction conditions, which were then compared in terms of energy efficiency and economic feasibility. The results suggest a promising, cost-effective alternative to conventional depolymerization methods.

## References:

[1] Y. Wang, Y. Zhang, H. Song, Y. Wang, T. Deng, X. Hou, J. Clean. Prod., **2019**, 208, 1469.

[2] E. Barnard, J.J.R. Arias, W. Thielemans, Green Chem, **2021**. 23(11)

# Mapping the functional landscape of cisplatin resistance in osteosarcoma using a multi-omic mathematical framework

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**Keywords:** Osteosarcoma, cisplatin resistance, drug uptake, proteomics, single-cell ICP-MS.

Chemoresistance remains the principal obstacle to improving survival in osteosarcoma patients treated with cisplatin. While impaired drug accumulation is a known driver of resistance, its relative contribution compared to downstream adaptive processes remains unclear. To address this question, we integrated single-cell ICP-MS, DNA platination, and quantitative proteomics data from 13 osteosarcoma models and seven resistant derivatives into a mathematical framework.

Our model deconvoluted resistance into pharmacokinetics (pre-target), neutralization (on-target), and tolerance (post-target). Single-cell ICP-MS revealed significant heterogeneity in platinum accumulation; however, intracellular drug levels did not consistently correlate with cytotoxicity. Several resistant variants showed unchanged or increased platinum levels. Moreover, DNA platination did not uniformly reflect total drug burden.

Proteomic profiling validated the predictive capacity of the model, revealing that basal proteomic states strongly influence resistance. Beyond pre-existing states, resistance trajectories involved shifts from proliferative programs to metabolic reprogramming, mitochondrial reinforcement, and stress-response pathways.

Together, these results demonstrate that cisplatin resistance in osteosarcoma arises from diverse, context-dependent biological strategies rather than from a uniform reduction in drug uptake, enabling mechanistic classification and more precise therapeutic approaches.

## Acknowledgments:

This work was supported by the Plan de Ciencia, Tecnología e Innovación del Principado de Asturias/Sekuens/FEDER (grants IDE/2025/000811 to JB-G and IDE/2024/000742 to MM-B); and the Agencia Estatal de Investigación/MICINN/FEDER (grants PID2022-137222OB-I00 to MM-B and PID2022-142020OB-I00 to RR). PDG was supported by a Ramón y Cajal research grant (MCINN 24RYC2022-035568-I).

# A Photochemical Multicomponent Strategy for the Assembly of C(sp²)–S Substituted Imidazoles

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**Keywords:** Photochemistry, exciplex, C-S bond formation, organic chemistry.

We report a visible-light-driven multicomponent strategy for the synthesis of S-functionalized imidazoles from readily available organic halides, isothiocyanates, and isocyanides. The transformation proceeds under mild and photocatalyst-free conditions and displays broad substrate scope. Mechanistic investigations suggest that the process involves direct photoexcitation of in situ generated thiophenolate intermediates, leading to radical-mediated C–S bond formation. The reaction is likely governed by exciplex-type interactions rather than preassembled electron donor–acceptor complexes,[1] providing a distinct photochemical activation mode for accessing sulfur-containing heterocycles.[2]

**Acknowledgments:**

We thank the University of Oviedo (PRP-UO-PUB-ASV-2025TESIS-04), FICYT (BP21/050), Ministerio de Ciencia e Innovación of Spain (MCINN-24-RYC2022 035485-I; MCIN/AEI/10.13039/501100011033 and PID2022-139318NBI00), Generalitat Valenciana (SEJIGENT/2021/005), Agencia Sekuens; IDE/2024/000709).

**References:**

[1] I. Tagarro, H. F. Piedra, M. Plaza, Org. Chem. Front. **2025**, 12, 3920– 3941.

[2] I. Tagarro, H. F. Piedra, D. González-Pinardo, I. Fernández, I. Bosque, M. Plaza, ACS Org. Inorg. Au, **2026**, 10.1021/acsorginorgau.6c00004.

# Evaluation of the factors influencing the extraction of antioxidants from the microalga spirulina (*Arthrospira platensis*) using a full factorial design.

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**Keywords:** Spirulina; Ultrasound-assisted extraction; Antioxidants; Full factorial design; Multivariate analysis.

Microalgae are a promising source of bioactive compounds with high added value, such as proteins, pigments and polyphenols with antioxidant activity. *Arthrospira platensis* (spirulina) stands out due to its high content of phycocyanins and other metabolites with applications in the food, nutraceutical, and cosmetic sectors. Furthermore, its cultivation can be integrated into circular economy strategies by enabling the valorization of nutrient-rich waste streams and the generation of reusable biomass [1]. However, the resistance of the cell wall hinders the release of intracellular metabolites and limits the efficiency of recovery processes [2]. Therefore, the development of efficient and sustainable extraction protocols is essential within the principles of green chemistry principles.

In this study, the extraction of antioxidant compounds from spirulina was evaluated through ultrasound-assisted cell disruption using phosphate-buffered saline (PBS) as an aqueous solvent. A $3^3$ full factorial design was applied, considering the biomass-to-solvent ratio, ultrasonic amplitude, and sonication time as experimental factors. The extracts were characterized by UV–Visible spectroscopy and synchronous fluorescence spectroscopy, together with colorimetric assays to determine antioxidant capacity (DPPH), total phenolic content (Folin–Ciocalteu), and protein content (Biuret). Statistical analysis included multifactor analysis of variance (ANOVA) and principal component analysis (PCA) as a multivariate tool.

The results showed high experimental variability and the absence of statistically significant effects of the studied factors on the response variables according to ANOVA. Nevertheless, PCA applied to the absorbance and synchronous fluorescence spectra revealed trends in the data and allowed differentiation of samples mainly according to the biomass-to-solvent ratio, suggesting that this parameter influences the spectroscopic characteristics and composition of the extracts. Overall, this study highlights the potential of sustainable ultrasound-based extraction strategies for the recovery of antioxidant compounds from spirulina within the framework of green biotechnology and circular economy.

## References:

[1] Pachés Giner, M., y González Camejo, J. (**2020**). Uso de microalgas en depuración de aguas. Universitat Politècnica de València, Departamento de Ingeniería Hidráulica y Medio Ambiente.

[2] Milia, M., Pasquini, V., Addis, P., y Angioni, A. (**2025**). Eco-friendly extraction to enhance antioxidants and nutritional value in Arthrospira platensis. *Foods*, 14, 1510.

# Synthesis of dimethly ether hydrogen carrying molecule catalyzed by supported heteropoly acids

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**Keywords**: Methanol, Dimethyl ether, Heteropoly acids, Dehydration

Dimethyl ether (DME) is considered an important clean fuel and chemical intermediate because of its low particulate emissions, high cetane number, and potential used as hydrogen carrying molecule [1]. One promising pathway for DME production is the catalytic gas-phase dehydration of methanol. This reaction is typically catalyzed by solid acid catalysts that promote the formation of DME. Among the various catalytic systems studied, heteropoly acids such as phosphotungstic acid, $H_3PW_{12}O_{40}$, (PW) have attracted considerable attention due to their strong Brønsted acidity and well defined Keggin structure [2]. In this work, different supports ($SiO_2$, $ZrO_2$, SBA-15, MCM-41, etc.) have been used to support the PW by dry impregnation. Reaction tests have been performed in a fixed-bed reactor at 250ºC and 1 bar. Preliminary tests showed promising activity toward DME formation indicating that the dispersion of PW on suitable supports can significantly enhance catalytic performance. The catalyst have been characterized by different techniques to correlate catalytic performance and surface properties contributing to the development of more efficient catalysts for DME synthesis.

**Acknowledgments**:

Universidad de Oviedo

**References**:

[1] C. Peinado et al., *Chemical Engineering Journal*, **2024**.

[2] A. Alasmari et al., *Catalysis Communications*, **2023**.

# Investigation of the impact of energy supplements in the regulation of the Na/K pump of tumoral and control mammary epithelial cells

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**Keywords:** Mammary epithelial cells, energy supplements, sodium, potassium, ICP-MS

Breast cancer, which primarily originates in mammary epithelial cells, is one of the most prevalent forms of cancer worldwide. It is associated with multiple molecular and metabolic alterations that affect essential cellular processes. Among these, the regulation of intracellular ionic homeostasis plays a crucial role in cell signaling, proliferation and survival. Sodium ($Na^+$) and potassium ($K^+$) are key ions involved in maintaining cellular equilibrium through the activity of the $Na^+/K^+$- ATPase pump, which regulates their electrochemical gradients across the cell membrane [1]. Alterations in the intracellular balance of these ions have been linked to pathological conditions and, so, they can provide valuable information about cellular dysfunctions.

In this context, the present work is focused on investigating differences in the intracellular Na and K levels, that is in the regulation of the $Na^+/K^+$-ATPase pump, between healthy (HTB-125) and tumor (HTB-126) mammary epithelial cells in response to supplementation. In particular, the potential effect of two different potassium-based supplements, potassium ribosate (RK) and potassium ascorbate with ribose (RCK), on the cellular ionic regulation is explored by means of inductively coupled plasma - mass spectrometry (ICP-MS). Results show that tumor and healthy cells show differential ionic responses (i.e. different Na and K homeostasis) to potassium supplementation, since potassium-based treatments (RK and RCK) seem to increase intracellular K content in tumor cells and to reduce the Na/K ratio as compared to non-treated cells. This information is highly valuable to evaluate the effect of potassium-based treatments, specifically RCK and RK as a complementary supplement in cancer prevention and treatment.

**Acknowledgments:**

This work was financially supported through project PID2022-137319OB-C21 funded by MCINN/AEI/10.13039/501100011033/ FEDER, UE and project IDE/2024/000694 by the Government of the Principality of Asturias and FEDER Program of the European Union through SEKUENS Agency.

**References:**

[1] A. Torres-Carrillo, C. Flores-Maldonado, L. Shoshani, A. Ponce, Na+/K+-ATPase: More than an electrogenic pump, Int. J. Mol. Sci. **2024**, 25(11), 6122.

# Filtration as a valuable alternative to ultracentrifugation for extracellular vesicle isolation using cell culture lines

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**Keywords:** extracellular vesicles, cell culture, ultracentrifugation, ultrafiltration.

Extracellular vesicles (EVs) are a group of membranous particles (30-150 nm) present in all biological fluids that are secreted by cells. They play a key role in cell-to-cell communication, carrying specific information about the physiological state of the cells. For this reason, exosomes are considered very promising target molecules for diagnostic and/or therapeutic purposes [1].

At present, ultracentrifugation (UC) is the most frequently used technique for EVs isolation. It is based in a combination of different high-speed centrifugation steps, ending in a final 100,000 x g step in which the EVs are pelleted. Although the procedure takes quite a long time, exosomes can be efficiently extracted from biofluids by UC. However, in the case of cell cultures it is required large volumes of cultured-cells medium for UC experiments and, therefore, more time consuming and costly sample preparation experiments are needed.

In this context, the aim of the present work is to develop a simple and fast method for EVs isolation based on filtration, that enables to reduce sample volumes (1-3 mL) as compared to UC. For such purpose, combination of 1% tween-20 in PBS with 300 kDa centrifuge filters is proposed and compared to an established UC protocol [1]. HEK-293 and ARPE-19 cell cultures grown up in P12 wells are investigated as models of cultured-cells under study.

**Acknowledgments:**

This work was financially supported through project PID2022-137319OB-C21 and C22 funded by MCINN/AEI/10.13039/501100011033/ FEDER, UE and project IDE/2024/000694 by the Government of the Principality of Asturias and FEDER Program of the European Union through SEKUENS Agency.

**References:**

[1] J. Martinez-Garcia, *et al*,, Talanta, **2023**, 263, 124693.

# Designing Bio-Based Emulsions for Controlled Release of Natural Antimicrobials

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**Keywords:** Emulsions, antimicrobials, encapsulation, preservatives, essential oils

The growing demand for foods without synthetic preservatives has intensified interest in natural alternatives. Essential oils are candidates due to their bioactive compounds; however, their direct incorporation into food is limited by volatility, hydrophobicity and sensory impact. Encapsulation offers a means to enhance stability, release and compatibility with food products. This study evaluates the antimicrobial activity of eight natural oils1 and their encapsulation in Pickering-emulsions stabilized with pea starch[2] and several chitosans differing in molecular-weight or viscosity[3].

Emulsions were characterized by droplet size, morphology and storage stability. Antimicrobial activity was assessed through antibiograms comparing fresh and stored emulsions, to evaluate release dynamics over time.

Results demonstrate that the stabilizer strongly influences both physical stability and antimicrobial efficacy. Surfactant-based emulsions produced small and uniform droplets; however, Pickering emulsions showed comparable or superior stability.

Screening against E. coli revealed antimicrobial activity only for clove and cinnamon oils, attributed to eugenol and cinnamaldehyde[1]. Clove-oil showed strong initial inhibition that declined rapidly, whereas cinnamon-oil produced a more sustained effect, indicating slower cinnamaldehyde release. Biopolymer emulsions maintained or enhanced antimicrobial activity after storage, highlighting their potential for long-term preservation[4].

The study demonstrates that emulsion systems can encapsulate natural antimicrobials and modulate their release, offering a non-synthetic alternative of preservatives in food applications.

**Acknowledgments:**

This research was funded by MCINN, Spain (MCINN-24-PID2023 149453OB-I00) and Principado de Asturias (SEK-25-GRU-GIC-24-079).

**References:**

[1] Burt S.. IntJFoodMicrobiol. **2004**, 94(3):223-253

[2] Basiak E. et al.. Int J, Biol Macromol. **2017**, 98:348–356

[3] Liu N et al..Carbohydr. Polym. **2006**, 64, 60–65

[4] Östbring K et al.. Foods. **2021**, Jul 18; 10(7):1657

# A Sustainable Chemoenzymatic Route to Nitriles from Primary Alcohols under Aqueous Conditions

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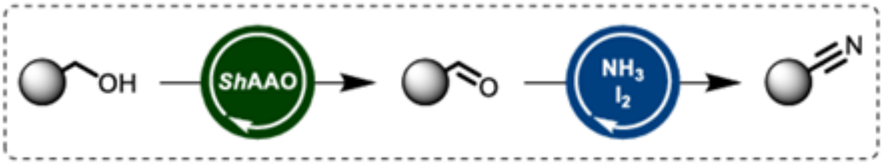
**Aryl-alcohol oxidase, Biocatalysis, Nitrile**

The nitrile functional group is a highly versatile motif in synthetic chemistry, serving both as a key intermediate for the construction of diverse heterocycles and functional groups— including amines, amides, carboxylic acids, and esters—and as a valuable structural element in its own right. Nitriles are widely encountered in fine chemicals, pharmaceuticals, agrochemicals, and fragrances.[1] Consequently, the development of efficient and sustainable methodologies for their synthesis remains an important objective in modern synthetic chemistry. Aldehydes have long been recognized as convenient precursors for nitrile formation, and numerous strategies have been reported for their conversion.[1,2,3] However, aldehydes are often toxic, unstable, and prone to degradation, which can limit their practical utility. In this context, the use of more stable surrogates such as primary alcohols—capable of generating aldehydes in situ through (enzymatic) selective oxidation—offers an attractive alternative.[4]

Aryl-alcohol oxidases (AAOs) are FAD-dependent enzymes capable of oxidizing a broad range of primary alcohols, including aliphatic, benzylic, and allylic substrates, to the corresponding aldehydes under mild conditions. Herein, we report a straightforward chemoenzymatic approach for the synthesis of nitriles from primary alcohols (Scheme 1). This strategy combines the biocatalytic oxidation of alcohols using a newly identified bacterial AAO from Streptomyces hiroshimensis[5] with a subsequent oxidative conversion mediated by an iodine–ammonia system in aqueous media. The latter promotes imine formation and oxidation, ultimately affording the corresponding nitriles through mild, scalable and operationally simple conditions.



***Scheme 1.** Graphical abstract for the chemoenzymatic synthesis of alcohols into nitriles.*

**Acknowledgements:**

PID2022-137893OB-I00, SEK-25-GRU-GIC-24-054, NAC-AT-PUB-ASV 2025 BP24-54

**References:**

1. M. J. Kim, J. Mun, J. Kim. Tetrahedron Lett., **2017**, 58, 4695–4698.
2. S. R. Mudshinge, C. S. Potnis, B. Xu, G. B. Hammond. Green Chem., **2020**, 22, 4161–4164.
3. A. Hinzmann, T. Betke, Y. Asano, H. Gröger, Chem. Eur. J., **2021**, 27, 5313–5321.
4. R. E. Ruscoe, J. I. Ramsden, N. J. Turner, Curr. Opin. Chem. Eng. **2020**, 30, 60–68.
5. P. Cinca-Fernando, C. Ascaso-Alegre, E. Sevilla, M. Martínez-Júlvez, J. Mangas-Sánchez, P. Ferreira, Appl. Microbiol. Biotechnol. **2024**, 108, 498.

# Improvement of lateral flow immunoassay sensitivity using biogenic nanoporous structures

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**Keywords:** Lateral flow immunoassay, sensitivity enhancement, nanoporous structures

Currently, growing interest in rapid analytical technologies has intensified the search for platforms capable of delivering reliable results in a brief period of time for the detection of relevant biomarkers in clinical, environmental, and industrial applications. Within these platforms, lateral flow immunoassays (LFIAs) have emerged as one of the most widely adopted solutions due to their simplicity, low cost, and suitability for Point-of-Care (PoC) use. Nevertheless, its inherent limitations in terms of sensitivity restrict its applicability in situations that require the detection of low concentrations of the target biomolecule. To address this limitation, several authors have implemented different optimizing strategies, including structural modifications to the LFIA components to reduce the limit of detection (LoD). Among these modifications, approaches such as increasing the size of the sample and conjugate pads, as well as printing wax micropillars onto the cellulose membrane to generate localized turbulence, are particularly noteworthy [1].

In this context, the present work introduces a novel modification to enhance LFIA performance by incorporating biogenic nanoporous structures into the detection zone. These structures act as a 3D matrix that increases the available surface area for antibody immobilization, improving capture efficiency and enhancing the resulting signal.

Preliminary results demonstrated that the modified strips achieved higher sensitivity than conventional formats while preserving the intrinsic advantages of LFIAs. This improvement supports their potential use in applications requiring lower LoDs, such as the determination of protein biomarkers in complex clinical samples.

**Acknowledgments:**

Projects MCINN-24-PID2023-149004OB-I00, RED2022-34120-T and RED2024-153970-T funded by MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe” and project SEK-25-GRU-GIC 24-071 funded by the Asturias Regional Government.

**References:**

[1] M. Díaz-González, A. de la Escosura-Muñiz, Anal. Bioanal. Chem. **2021**, 413, 4111-4117.

# Wet-Oxidized Kraft Lignin as a Renewable Iron-Chelating Agent for Agricultural Applications

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**Keywords:** Kraft lignin, iron chelation, wet oxidation, bio-based fertilizers

The search for sustainable alternatives to synthetic iron chelating agents is key to reducing the environmental impact of fertilization in alkaline soils. This work evaluates the potential of Kraft lignin, an abundant by-product of the pulp and paper industry, as a precursor for iron-complexing agents with lower environmental impact. To this end, lignin was modified through alkaline wet oxidation (170 °C, 70 bar, 120 min, KOH) in order to alter its structure and increase the availability of functional groups, thereby improving its solubility and its ability to coordinate Fe.

The complexation capacity was evaluated both directly in the alkaline wet oxidation effluent (EO) and in the same effluent after delignification by acid precipitation at pH 3 (FD). This delignified phase is mainly composed of oxidative degradation products of lignin, largely organic acids such as acetic, formic, and propionic acids. Complexation tests were carried out in the pH range of 6–9 (typical of calcareous soils) and Fe:C ratios between 0 and 1 mg Fe/mg TOC. Iron retention in solution was determined by ICP-MS.

The results show that EO exhibits a high iron retention capacity, especially at pH 8, where an optimal balance is achieved between deprotonation of functional groups and precipitation of ferric hydroxides. Under these conditions, a maximum concentration of 28 mg Fe/L (73% of the added iron) was obtained. Fractionated analysis revealed complementary behavior: FD contributes in the initial stages of complexation at low Fe:C ratios, whereas modified lignin (the fraction removed from EO by precipitation) dominates retention at higher ratios.

Overall, oxidized derivatives of Kraft lignin, particularly the unfractionated effluent, represent a promising renewable alternative to synthetic chelating agents in alkaline soils.

**Acknowledgments:**

Grants for Knowledge Generation Projects - 2024 Call for Proposals "Ecological processes for the conversion of lignin and sewage sludge into improved derivatives: sustainable pathways for the production of biostimulants". Acronym: NAC-ES-PUB-ASV-2025 PID2024-161375OB-C21 and Grants for Research Groups of Public R&D&I Organizations of the Principality of Asturias - 2024 Call for Proposals "Bioprocess and Reactor Technology. TBR" IDE/2024/000695. Acronym: SEK-25-GRU-GIC 24-010

**References:**

[1] J. J. Lucena, «Synthetic Iron Chelates to Correct Iron Deficiency in Plants», Iron Nutrition in Plants and Rhizospheric Microorganisms, **2006**, pp. 103-128. doi: 10.1007/1-4020-4743-6_5.

[2] M. Fuentes et al., «Supramolecular Arrangement of Lignosulfonate-Based Iron Heteromolecular Complexes and Consequences of Their Interaction with Ca2+ at Alkaline pH and Fe Plant Root Uptake Mechanisms», J. Agric. Food Chem., vol. 71, n.o 30, pp. 11404-11417, august **2023**, doi: 10.1021/acs.jafc.3c03474.

# A Computational Exploration of N-H Bond Functionalization Driven by Geometrically Constrained Tridentate Phosphine Pincer Complexes

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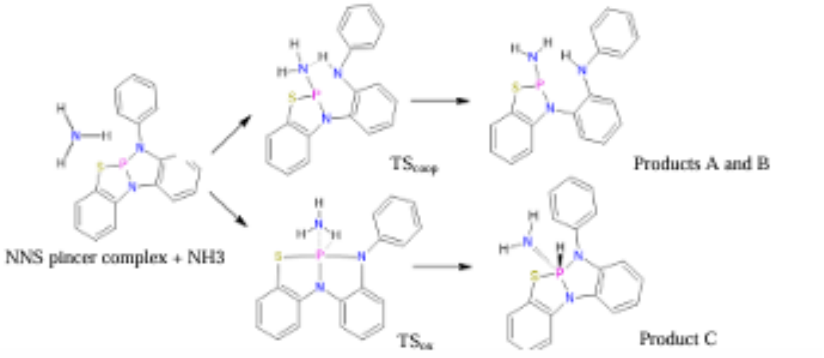
**Keywords:** N-H bond activation, Density Functional Theory, Quantum Chemical Topology

Activation and functionalization of N-H bonds has long posed a fundamental challenge in chemistry. Amines, which commonly serve as primary substrates, possess very low acidity and readily form stable Werner complexes. Several sophisticated approaches have been devised to address these issues, remaining far fewer than the diverse strategies available for activating analogous C-H/O-H bonds. Some alternatives based on cooperation between the amine and a precursor (metal-based or not) have emerged as promising avenues, coupling the breaking of the N-H bond with another process that is thermodynamically more favorable, and providing the thermodynamic driving force for the reaction [1,2].

In this context, we selected the constrained phosphine-based tridentate NNS pincer complex reported by Goicoechea et al. [2], see Scheme 1, and performed a Quantum Chemical Topology study with the aim of determining the main features of the thermodynamics and kinetics of N-H based activation on this kind of systems. Our analysis integrates the Electron Localization Function (ELF) - which allows to provide a picture of the system based on Lewis pairs - with the energetic counterpart provided by the Interacting Quantum Atoms (IQA) decomposition scheme [3]. Therefore, different substrates were considered (EWG/EDG amines, aromatic/non-aromatic), as well as several modifications on the original NNS ligand scaffold. Our results demonstrate that subtle steric and electronic tuning of the NNS pincer ligand enables more control over ammonia activation, offering new options for the development of catalysts for nitrogen fixation and ammoniation reactions.



*Scheme 1.Reaction scheme for the activation of $NH_3$ using a constrained phosphine-based tridentate NNS pincer complex [2]*

**Acknowledgments:**

Daniel Barrena Espés, Ángel Martín Pendás, Julen Munárriz

**References:**

[1] E. Khaskin, M. A. Iron, L. J. W. Shimon, J. Zhang, D. Milstein. N–H activation of Amines and Ammonia by Ru via Metal–Ligand Cooperation. J. Am. Chem. Soc. 132, 8542–8543, (**2010**).

[2] J. Abbenseth, O. P. E. Townrow, J. M. Goicoechea. Thermoneutral N–H Bond Activation of Ammonia by a Geometrically Constrained Phosphine. Angew. Chem. Int. Ed. 60, 23625–23629, (**2021**).

[3] D. Barrena-Espés, V. Polo, J. Echeverría, Á. Martín Pendás, J. Munárriz. Metal−Ligand Cooperation in N−H Activation: Bridging Electron-Pushing Formalism and Energy Descriptors. Inorg. Chem. 64, 21452−21464, (**2025**).

# Bio-sourced nanoporous materials as functional modifiers of electrochemical transducers for enhanced biosensing

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**Keywords:** Bio-sourced materials; nanoporous structures; electrochemical transducers; electrode modification; biosensing.

The performance of electrochemical biosensors largely depends on the transducer interface, where electron transfer and biomolecular interactions occur. Modifying the surface with nanostructured materials is an effective way to enhance these properties and improve detection performance [1,2].

This study examines the use of bio-sourced nanoporous materials as modifiers of electrochemical transducers. These naturally derived structures were deposited onto indium tin oxide/polyethylene terephthalate (ITO/PET) electrodes to produce porous surfaces suitable for biomolecule immobilization. Compared to conventional nanoporous membranes, such as anodic alumina, these materials offer a natural alternative.

The modified electrodes were functionalized with immunoglobulin G (IgG) as a model biomolecule. Stepwise modification was monitored using differential pulse voltammetry in the presence of a redox probe to evaluate changes in electron transfer at the electrode interface. After each modification step, a progressive decrease in current was observed, confirming successful layer incorporation and the formation of an interfacial architecture that partially hinders electron transfer.

These results suggest that bio-sourced nanoporous materials effectively modify electrochemical transducers and are a viable alternative to conventional nanoporous membranes for biosensing applications.

**Acknowledgments:**

Projects MCINN-24-PID2023-149004OB-I00, RED2022-34120-T and RED2024-153970-T funded by MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe” and project SEK-25-GRU-GIC-24-071 funded by the Asturias Regional Government.

**References:**

[1] R. Singh, R. Gupta, D. Bansal, R. Bhateria, M. Sharma, ACS Omega, **2024**, 9(7),7336-7356.

[2] D. Valero-Calvo, A. de la Escosura-Muñiz, TRAC-Trends in Anal. Chem, **2024,** 172, 117568.

# Micro-flow liquid chromatography-ESI-QTOF for lipidomic profiling of volume-limited samples

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**Keywords:** Lipidomics, Micro-flow liquid chromatography, High resolution mass spectrometry, Low sample volume

Lipids play essential roles in cellular physiology and pathology, acting as fundamental components of biological membranes, energy reservoirs, precursors of signaling molecules, and platforms for protein recruitment. In this context, lipidomics has emerged as a key discipline for the comprehensive characterization of lipid species and their biological functions, with high resolution mass spectrometry representing the cornerstone of lipid analysis. However, volume-limited samples remain a critical limitation in many biological and clinical applications [1].

To address this challenge, we developed a micro-scale liquid chromatography (MicroLC) platform coupled to an electrospray ionization quadrupole time-of-flight (ESI-QTOF) detector. Compared to conventional ultra-high-performance liquid chromatography (UPLC), the proposed method employs reduced injection volumes (0.5 µL), lower flow rates (0.75 µL min-1), and optimized ion source parameters [2,3]. Chromatographic and mass spectrometric conditions were optimized using the Ultimate SPLASHTM ONE internal standard mixture, comprising 69 isotopically labeled lipids across multiple classes, as well as the NIST SRM 1950 certified reference material. These modifications resulted in a 5-fold and 3.5-fold increase in peak area and peak height, respectively, with a modest 1.5-fold increase in peak width at half maximum (FWHM), relative to UPLC-based methods.

The performance of the method was further evaluated in biologically relevant samples with limited availability, including cell extracts from MIO-M1 and vitreous humor. Notably, enhanced lipid coverage was achieved using low sample volumes (10 µL), demonstrating the suitability of the approach for volume-restricted applications.

Overall, this MicroLC-ESI-QTOF strategy provides a robust and sensitive platform for lipidomic profiling under constrained sample conditions, and offers a promising avenue for future developments in lipid analysis.

### Acknowledgments:

This work was financially supported through project PID2022-137319OB-C22/Agencia Estatal de Investigación (AEI)/10.13039/501100011033 and the PCTI Program of the Government of the Principality of Asturias, Spain as well as the FEDER Program of the European Union (IDE/2024/000685). M. B. acknowledges financial support from grantRYC2022-035852-I funded by MICIU/AEI/10.13039/ 501100011033 and by the FSE+.

### References:

[1] Han, X. Lipidomics: Comprehensive Mass Spectrometry of Lipids; John Wiley & Sons, **2016**.

[2] Girel, S.; Galmiche, M.; Fiault, M.; Mieville, V.; Nowak-Sliwinska, P.; Rudaz, S.; Meister, I. Microflow liquid chromatography coupled to multinozzle electrospray ionization for improved lipidomics coverage of 3D clear cell renal cell carcinoma. Analytical Chemistry **2025**, 97 (9), 5109–5117. DOI: 10.1021/acs.analchem.4c06337.

[3] La Gioia, D.; Salviati, E.; Basilicata, M. G.; Felici, C.; Botrugno, O. A.; Tonon, G.; Sommella, E.; Campiglia, P. Leveraging the potential of 1.0-mm i.d. columns in UHPLC-HRMS-based untargeted metabolomics. Analytical and Bioanalytical Chemistry **2024**, 417 (13), 2837–2847. DOI:10.1007/s00216-024-05588-z.

# Understanding the role of heating rate and water dynamics in starch foam formation by thermocompression

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**Keywords:** starch foams; thermocompression; TGA; heating rate; water release kinetics

Petroleum-based polymer foams used in food packaging pose environmental concerns, motivating biodegradable alternatives such as starch-based foams. However, the mechanisms governing foam formation during thermocompression remain poorly understood, particularly the coupling between heat transfer, water state, and vapor release kinetics, which has been identified as a key factor in starch-based foaming processes [1].

In this work, the effect of heating rate on water dynamics and foam formation was investigated using potato starch formulations. In-situ temperature measurements with a thermocouple placed at the center of the mold revealed three stages: (i) an initial drop associated with gelatinization, (ii) a plateau around 100 °C due to free water evaporation, and (iii) a temperature increase linked to delayed release of bound water, promoting vapor pressure build-up and foam expansion.

Thermogravimetric analysis (2–100 °C/min) showed a strong kinetic dependence. Low heating rates (2–30 °C/min) led to gradual evaporation and drying without expansion, while high rates (≥50 °C/min) shifted water release to higher temperatures (~120 °C), indicating delayed evaporation and rapid vapor release, in agreement with previous studies on thermally induced water release in starch systems (Yang et al., 2024).

Thermocompression experiments at different mold temperatures (100–200 °C) confirmed this behavior. Lower temperatures suppressed expansion, yielding incomplete cavity filling despite identical mass. These results demonstrate that foam formation is governed by heating rate controlled water release kinetics, defining a transition from drying to foaming.

## Acknowledgments:

The authors acknowledge financial support from the Generalitat Valenciana through the PROMETEO Programme for Excellence in Research (CIPROM/2023/3)

## References:

[1] L. F. F. Gonçalves, R. L. Reis, E. M. Fernandes, Polymers, **2024**, 16, 1286.

# One-Pot Cascades for Chiral β-Hydroxy Esters via L-Cysteine Promoted Hydration

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**Keywords:** asymmetric reduction, one-pot cascade, organocatalysis.

The implementation of catalytic and atom-economy processes represents a key aspect in the design of new sustainable chemical products. We have recently demonstrated that L-cysteine (L-Cys) is an efficient and cost-effective catalyst for the hydration of activated alkynes.[1,2] Using sub-stoichiometric loadings, a broad range of β-ketosulfones, amides, and esters was obtained from the corresponding activated alkynes under aqueous conditions in a highly effective and regioselective manner.[3] At a cost of less than €0.5 per gram of catalyst, this approach constitutes a highly economical and environmentally friendly alternative to existing strategies. Moreover, the mild and biocompatible reaction conditions enable seamless integration with enzymatic processes, providing access to essential chiral synthons and further extending the applicability of this methodology within organic synthesis.

In this contribution, we report the synthesis of chiral β-hydroxy esters from a variety of aryl- and alkyl-substituted propiolic esters through a one-pot combination of organocatalytic hydration and stereoselective carbonyl reduction using ketoreductases (Figure 1). Remarkably, the approach appears to be very general and efficient, giving access to a series of hydroxy esters in good conversions and stereoselectivities.[4,5] The resulting products were subsequently employed as building blocks for the synthesis of chiral compounds of interest in pharmaceutical and chemical applications, underscoring their value as versatile intermediates in sustainable synthetic routes.

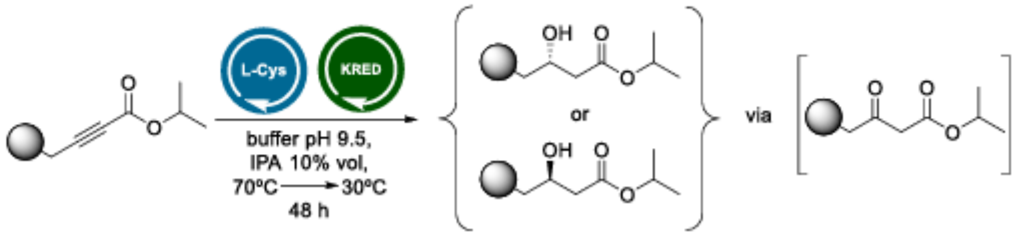

**Figure 1.** Synthesis of chiral β-hydroxy esters via one-pot sequential cascade.

**Acknowledgments:**

Financial support from PID2024-155419NB-I00 and SEK-25-GRU-GIC 24-054.

**References:**

[1] J. González-Rodríguez, S. González-Granda, I. Lavandera, V. Gotor-Fernández, J. Mangas Sánchez, Angew. Chem. Int. Ed., **2025**, 64, e202414046.

[2] L. Hintermann, A. Labonne, Synthesis, **2008**, 8, 1121-1150.

[3] M. López-Agudo, N. Ríos-Lombardía, J. González-Sabín, I. Lavandera, V.Gotor-Fernandez, ChemSusChem, **2022**, 15, e2021013.

[4] J. Muschiol, C. Peters, N. Oberleitner, M. D. Mihovilovic, U. T. Bornscheuer, F. Rudroff, Chem. Commun., **2015**, 51, 5798–5811.

[5] A. Cuetos, A. Rioz-Martínez, F. R. Bisogno, B. Grischek, I. Lavandera, G. de Gonzalo, W. Kroutil, V. Gotor, Adv. Synth. Catal., **2012**, 354, 1743-1749.

# Single-Cell Biomarker Analysis by ICP-MS and Mass Cytometry: Implications for Immunotherapy

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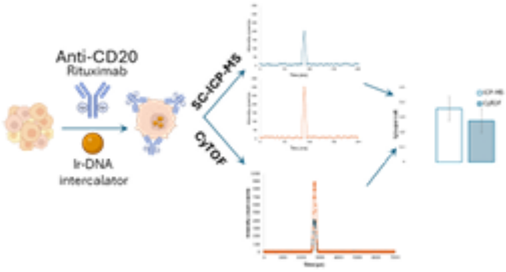
**Keywords:** Single-cell analysis ICP-MS; Mass cytometry (CyTOF); Biomarker quantification; CD20; Immunotherapy; Rituximab

Accurate determination of elemental composition at the single-cell level is fundamental for advancing biological and biomedical research. However, the use of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with non-simultaneous mass analyzers introduces methodological constraints that can affect data comparability. In this work, we systematically evaluate the conditions required to achieve consistent results between sequential and simultaneous detection modes in single-cell measurements.

Endogenous elements such as phosphorus and iron, along with iridium as an external marker, were used to assess performance under different conditions [1]. Our findings indicate that pre analytical factors, particularly cell storage and dilution, have a stronger impact on quantitative accuracy than the sample introduction system. As a case study, the interaction of the monoclonal antibody Rituximab with the CD20 antigen was investigated in MEC-1 cells using both single-cell ICP-MS and CyTOF after lutetium labeling. Both techniques yielded comparable CD20 expression levels, which were in line with previously reported data. These results highlight the feasibility of harmonizing calibration approaches across platforms and support the broader application of this methodology to the quantification of CD20 in samples from both healthy individuals and patients.



## References:

[1] Corte-Rodríguez, M.; Álvarez-Fernández, R.; García-Cancela, P.; Montes-Bayón, M.; Bettmer, J. Trac-Trends Anal. Chem. **2020**, 132, 116042.

# Electrochemical Lateral Flow Biosensor for Rapid Pathogen Detection

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**Keywords:** Electrochemical biosensor, Lateral flow immunoassay (LFIA), bacterial pathogens

Rapid detection of pathogenic bacteria is critical for food safety and clinical diagnostics. *Escherichia coli* O157:H7 and *Staphylococcus aureus* are leading causes of foodborne and healthcare-associated infections. *E. coli* O157:H7 produces Shiga-like toxins that can cause haemorrhagic diarrhea and haemolytic uremic syndrome [1], while *S. aureus* secretes heat-stable enterotoxins linked to food poisoning, skin infections, and sepsis [2]. Conventional methods such as culture, PCR, and ELISA are reliable but often slow, labour-intensive, and require specialized equipment, underscoring the need for rapid, portable alternatives.

To address this, we developed a biosensor combining lateral flow immunoassay (LFIA) with electrochemical transduction. Gold nanoparticles functionalized with biopolymers carrying an electroactive probe [3] were used as labels. Screen-printed carbon electrodes were used to directly probe the LFIA test line, allowing for a quantitative electrochemical readout proportionate to bacterial concentration. This method offers improved sensitivity without sacrificing LFIA's simplicity.

Linear response ranging from 10 to $10^2$ CFU $mL^{-1}$ and a detection limit of 3 CFU $mL^{-1}$ was obtained during validation with *E. coli* O157:H7. No cross-reactivity with non-target bacteria was confirmed by selectivity tests. Reliable performance in complicated matrices was demonstrated by recovery trials in spiked milk, water, and orange juice, which yielded recoveries between 65% and 139% with coefficients of variation below 6%. The platform's adaptability for fast identification is confirmed by ongoing work that extends it to *S. aureus*.

**Acknowledgments:**

This research was funded by the Spanish Research Agency (Agencia Española de Investigación) under Grant No. PID2023-149453OB-I00, and by Grant SEK-25-GRU-GIC-24-079 from the Principado de Asturias, Spain.

**References:**

[1] J Bai, Zhuangzhuang, et al. “A Comprehensive Review of Detection Methods for Escherichia Coli O157:H7.” TrAC Trends in Analytical Chemistry, vol. 152, (**2022**), p. 116646.

[2] Howden, Benjamin P., et al. “Staphylococcus Aureus Host Interactions and Adaptation.” Nature Reviews Microbiology, vol. 21, (**2023**), pp. 1–16.

[3] Blanco-López M.C.; Matos-González, M.; Gutiérrez-Cervelló, G.; Saweres-Argüelles, C.; Sánchez-Calvo, A.; Nanoparticles comprising a starch-iodine complex and their use for immunodetection. EP24382448.9, April 24, **2024**.

# Targeting cancer-associated aberrant O-glycans in pathological MUC1 with aptamers

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**Keywords:** SELEX, aptamers, cancer biomarker, O-glycans

Biomarkers are essential tools in oncological medicine, enabling both early detection in asymptomatic subjects and the accurate monitoring of therapeutic response[1]. Mucin 1 (MUC1) is a transmembrane glycoprotein already validated in the clinical setting as a tumour-associated antigen. Its extracellular domain contains a region of repeated motifs called Variable Number Tandem Repeats (VNTR) highly polymorphic and glycosylated. Glycosylations are a class of post-translational modifications of proteins that play a role in maintaining cellular functions. It consists of the addition of chains of carbohydrates at specific sites. The aberrant dysregulation of this machinery has been associated in recent years to the development of tumour conditions[2]. Both N- and O-glycan types undergo morphological alterations that change their functional characteristics, contributing to tumour progression by modulating cell adhesion, immune evasion, and signalling pathways[3]. The presence of aberrant glycans is a hallmark of cancer, which make them a promising non-invasive biomarker more specific than the total concentration of the protein. Among the recognition tools used in diagnostics, aptamers are recognized as valid alternatives to antibodies. Aptamers are single-stranded nucleic acids selected through an in vitro selection process (SELEX) designed to obtain the sequences with the highest affinity and selectivity for a desired target. While aptamer selection against N-glycoproteins has already been described in literature and performed in our research group against PSA protein4, targeting O-glycans with aptamers remains a field largely unexplored.

In this work, we show the selection of aptamers against one of a frequent aberrant tumor associated carbohydrate antigen (TACA) in MUC1 by designing specific counter-selection and elution steps. The goal is to provide a guidance to rationally direct the SELEX toward these specific glycans and to have a more specific tool to be used in low-cost cancer screening in plataforms and new biomarkers' development.

**Acknowledgments:**

Financially supported by STRIM EU 101169504, Spanish (PID2024-156199NB-I00) & Principado de Asturias (IDE/2024/000677) Governments

**References:**

[1] Pesch B et al, Proteins and Proteomics, 1844, 874-883 (**2014**).

[2] Lan Y et al, Mol Clin Oncol 17: 161 (**2022**).

[3] Elomaa H et al, Br J Cancer 132, 660–669 (**2025**).

[4] Díaz-Fernández A et al, Biosensors and Bioelectronics, 128, 83-90 (**2019**).

# Towards an Integrated Understanding of Artisanal Kombucha: Biochemical, Microbiological, and Life Cycle Assessment Approach

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**Keywords:** kombucha, LCA, microbiological, sequencing, phenolic compounds

The growing demand for artisanal products and clean-label foods has led to a remarkable increase in the global popularity of kombucha (García-Barón et al., 2025; Prajapati et al., 2024). In this work, an artisanal kombucha fermentation process was evaluated as a case study from biochemical, microbiological, and environmental perspectives. Physicochemical parameters were determined using spectrophotometry and chromatography, whereas microbial populations were analysed using shotgun metagenomic sequencing. Additionally, an environmental evaluation was conducted using Life Cycle Assessment (LCA) methodology implemented in SimaPro V.10 software.

No significant changes in microbial profiles were detected during fermentation; however, seasonal differences were observed among the final samples. Yeasts dominated the microbial community, and chemical composition values were within literature-reported ranges for this beverage, with ethanol levels generally below 1%. From an environmental perspective, packaging - particularly glass bottle production - was identified as the main contributor to most impact categories, and the carbon footprint value was 1.15 kg$CO_2$eq/L. These findings suggest that standardization of fermentation parameters and optimization of packaging systems are key strategies to improve both product consistency and sustainability.

## Acknowledgments:

This work was funded by the Government of the Principality of Asturias through the projects SEK-25-GRU-GIC-24-010 and IDE/2024/000704, and by CSIC grants 202370E168 and JDC2022-049850-I.

## References:

Prajapati et al. (**2024**) Multidisciplinary advances in kombucha fermentation, health efficacy, and market evolution. Archives of Microbiology 206, 366, https://doi.org/10.1007/s00203-024-04086-1.

García-Barón et al. (**2025**) Consumers' drivers of perception and preference of fermented food products and beverages: A Systematic Review. Food, 14, 713, https://doi.org/10.3390/foods14050713.

# Evaluation of an Artificial Neural Network for Copper Quantification in Optical Emission Spectroscopy Using SCGD-OES

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**Keywords:** SCGD, OES, artificial neural network.

The quantification of heavy metals is crucial due to their toxicity, environmental persistence, and risk to human health. Conventional techniques such as ICP-OES and ICP-MS offer high sensitivity and low detection limits, but they require complex and expensive instrumentation. SCGD-OES emerges as a simpler and more cost-effective alternative.

In this work, two artificial neural networks (ANNs) were used to determine copper from 1525 spectra obtained by SCGD-OES (81 concentrations, 0–40.2 ppm), divided into training, validation, and test sets. A perceptron without hidden layers and a network with a hidden layer of 200 neurons were compared, evaluating their performance against traditional linear calibration based on Cu emission lines.

Linear calibration showed wavelength dependence: the 510.6 and 521.8 nm lines exhibited low relative errors (4.88% and 4.42%) but high limits of detection (LOD) (0.4–0.9 ppm), while the more intense lines (324.7 and 327.4 nm) reduced the LOD (~0.25 ppm) at the cost of higher errors due to interferences.

The perceptron improved accuracy in interfered lines but showed high LOD values (4.2–5.14 ppm). The network with a hidden layer demonstrated greater robustness, relative errors close to 5%, and an LOD of ~1 ppm. Additionally, weight analysis allowed identification of the most relevant wavelengths, highlighting the main Cu lines.

Overall, the results demonstrate that ANNs can improve both the robustness and interpretability of spectral analysis using SCGD-OES.

## Acknowledgments:

The GELP research group acknowledges the financial support provided by the SEKUENS agency through the project SEK-25-GRU-GIC-24-075.

## References:

[1] Hoang Bao Khanh et al. (**2024**). Comparison of linear regression and interpretable ANN for copper determination using SCGD-OES. Spectrochimica Acta B, 219:107000.

# Chemical engineering and conjugation strategies for A40s RNA aptamer to enhance structural stability and functional efficacy in Glioblastoma Multiforme

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**Keywords:** Chemical engineering, RNAs, Aptamers, Cancer, Glioblastoma Multiforme

RNA aptamers are emerging therapeutic tools for the selective targeting of tumor cells due to their high affinity, specificity, low immunogenicity, and ease of production. In this project, we investigated the aptamer A40s. The A40s RNA aptamer, a 30-mer nucleotide, was selected through cell-SELEX (Systematic Evolution of Ligands by Exponential Enrichment). It binds glioblastoma stem cells (GSCs) via recognition of ephrin type-A receptor 2 (EphA2). Despite its biological activity, the parental A40s aptamer exhibits limited serum stability, with a half-life of 24 hours, which constrains its therapeutic potential. To address this limitation and potentially enhance both stability and bioactivity, we rationally designed and synthesized a library of chemically modified A40s analogues. Our strategy encompassed three distinct classes of modifications: locked nucleic acid (LNA) monomer incorporations, 2′-O-methyl substitutions, and 2′-O-MOE (2-methoxyethyl) substitutions. For each modification class, we generated four sequence variants by systematically distributing the chemical modifications across different structural domains of the aptamer: (i) complete backbone coverage, (ii) pyrimidine-selective substitution, stem-localized modifications (iii) , and (iv) loop-restricted modifications within the predicted hairpin-loop secondary structure of the aptamer. This combinatorial approach yielded a total of 12 chemically modified aptamer variants. The physico-chemical properties of all these A40s variants were evaluated for structural stability, serum resistance, nuclease resistance, maintenance of EphA2 binding affinity, and preservation of key biological functions, while ensuring the absence of undesired toxicity. The obtained results indicate that the most promising candidates within the investigated mini-library are the A40sanalogues containing the LNA variants. These compounds remain fully stable after 72 h in serum and display a markedly enhanced thermal stability of their secondary structure. Notably, they also show improved binding to EphA2 together with a stronger biological activity, resulting in higher reduction of cell viability and of stemness-related gene expression compared to the parent A40s aptamer.

**References:**

[1] **Affinito A,** et al, **2025** doi: 10.3390/biom15060768.

[2] **Diakogiannaki I,** et al**, 2025**,doi: 10.1021/acs.jcim.5c00295.

[3] **Affinito A**, et al, **2020** doi: 10.1016/j.omtn.2020.02.005

[4] **Affinito A & Quintavalle C**, et al, **2019** doi: 10.1016/j.omtn.2019.08.015**.**

# Pickering emulsions stabilized by cocoa bean shell using different types of oils

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**Keywords:** natural stabilizers, plant-based by-products, Pickering emulsions, cocoa bean shell, environmentally safe

The aim of this study is to promote the use of cocoa shell, a plant-based byproduct (derived from the chocolate industry), for the preparation of Pickering emulsions (O/W). These finely ground cocoa particles, with an approximate size of 550 nm, were able to stabilize the emulsions at different concentrations (0.1–0.5 g of cocoa particles per gram of oil used), using various types of oils as the oil phase, such as olive, soybean, cinnamon, rosemary, clove, orange, lemon, and miglyol. Notably, these particles acted as natural stabilizers without chemical modification or extraction. First, the particle size reduction process for the cocoa husk particles was optimized; for this, both knife and ball mills were used, resulting in optimal sizes of 500 nm and homogeneous samples.

The results indicated that droplet size decreased as the concentration of particles used increased until reaching a constant value (around 0.3–0.4 g/g in all cases). Additionally, a trend toward a reduction in the clarified layer formed was observed as the concentration of particles used increased.

It is important to highlight that the complex structural composition of these plant-based residues or byproducts can improve the stability of the Pickering emulsions. In addition to being environmentally safe, biocompatible, biodegradable, and healthier than conventional stabilizers.

**Acknowledgments:**

This work was supported by Ministerio de Economía y Empresa (MINECO, Spain) under Grant MCINN-24-PID2023-149453OB-I00. This study was also cofinanced by Consejería de Educación y Ciencia del Principado de Asturias (Ref. SEK-25-GRU-GIC-24-079). K. M. Villagrán-Andrade gratefully acknowledges the support of a Severo Ochoa grant (NAC-AT-PUB-ASV-2025 BP24-222) from the Principado de Asturias

**References:**

[1] Sánchez, M., Laca, A., Laca, A., & Díaz, M. (**2023**). Cocoa bean shell: a by-product with high potential for nutritional and biotechnological applications. *Antioxidants*, *12*(5), 1028. https://doi.org/10.3390/antiox12051028

[2] Gould, J., Vieira, J., & Wolf, B. (**2013**). Cocoa particles for food emulsion stabilisation. Food & Function, 4(9), 1369–1375. https://doi.org/10.1039/c3fo30181h

[3] Cuthill, H., Elleman, C., Curwen, T., & Wolf, B. (**2021**). Colloidal Particles for Pickering Emulsion Stabilization Prepared via Antisolvent Precipitation of Lignin-Rich Cocoa Shell Extract. Foods (Basel, Switzerland), 10(2), 371. https://doi.org/10.3390/foods10020371

[3] Lin, J., Han, Z., & Zeng, X.-A. (**2025**). Thermomechanically micronized sugar beet pulp: Elucidating the interaction of soluble elements and insoluble fibrous particles for enhancing emulsification. FOOD HYDROCOLLOIDS, 159, 110556. https://doi-org.uniovi.idm.oclc.org/10.1016/j.foodhyd.2024.110556

[4] Huc-Mathis, D., Almeida, G., & Michon, C. (**2021**). Pickering emulsions based on food byproducts: A comprehensive study of soluble and insoluble contents. Journal of colloid and interface science, 581, 226-237

# Total Synthesis of Diterpenoid Compounds

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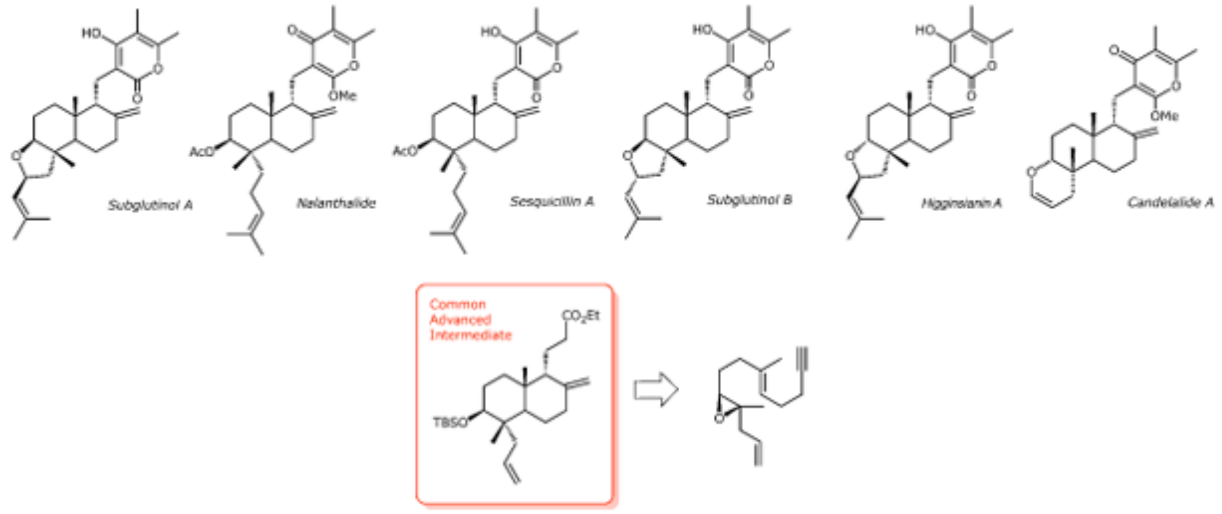
**Keywords:** total synthesis, cationic cyclization, diterpenoid compounds

Diterpenoid compounds are natural products mainly found as metabolites of fungal organisms. These compounds consist of a decalin system and an indole ring or a fully substituted α- or γ- pyrone ring, and exhibit a large number of stereocenters as well as an exocyclic alkene. Their unique structure, coupled with their potent bioactivity, makes them an interesting target for the study and development of new synthetic methods regarding their use in the pharmaceutical industry.[1]

Thus, we have designed possible synthetic routes for several naturally occurring diterpenoid pyrones and indoles, making use of a common advanced intermediate. This decalin-like intermediate would be accessible through a cationic cyclization reaction, previously developed by the group as a way of constructing enantiomerically pure scaffolds.[2] Hence, we present our studies on the synthesis of this common intermediate and our progress on the total synthesis of the final natural products.



**References:**

[1] T. Katoh. Studies in Natural Products Chemistry (Ed.: Atta-ur-Rahman), Elsevier, Oxford. **2014**, 43, Ch. 1.

[2] (a) R. Fontaneda, F. J. Fañanás, F. Rodríguez, Chemm. Commun. **2018**, 54, 11025-11028; (b) O. García Pedrero, F. Rodríguez, Chemm. Commun. 2022, 58, 1089-1099

# Photochemical Oxidation of β-Hydroxynitriles: Applications in Biocatalytic Deracemization

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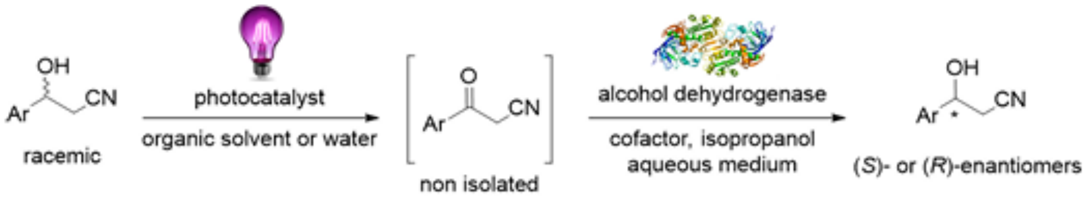
**Keywords:** photochemistry, biocatalysis, deracemization, alcohol dehydrogenase.

Enantiopure β-hydroxynitriles use in organic synthesis as chiral building blocks for the production of biologically active compounds. Biocatalysis plays an important role in its asymmetric synthesis.[1] However, kinetic resolution methods waste half of the material, making deracemization approaches valuable, converting racemic mixtures into enantiopure products. In this context, methodologies that employ catalysts, green oxidants, and mild conditions are highly desirable for large-scale applications. Thus, photochemistry emerged as a promising tool. However, current reports on the photobiocatalytic deracemization of sec alcohols still face challenges in efficiently oxidizing β-hydroxynitriles. [2-4]

In this study, we propose a one-pot two-step photobiocatalytic methodology for the efficient linear deracemization of β-hydroxynitriles (Figure). This strategy combines an initial photo oxidation step generating the corresponding ketone with a consecutive asymmetric bioreduction catalyzed by an alcohol dehydrogenase enzyme. Our approach achieves significant progress in the synthesis of enantiopure β-hydroxynitriles, overcoming the challenging oxidation step and enabling new synthetic pathways for the efficient production.



### References:

[1] E. Liardo, R. González-Fernández, N. Ríos-Lombardía, F. Morís, J. García-Álvarez, V. Cadierno, P. Crochet, F. Rebolledo, J. González-Sabín. ChemCatChem, **2018**, 10, 4676–4682.

[2] S. Filgueira, L. Rodríguez-Fernández, I. Lavandera, V. Gotor-Fernández, ChemSusChem, **2025**, 18, e202500683.

[3] A. Rudzka, N. Antos, T. Reiter, W. Kroutil, P. Borowiecki, ACS Catal., **2024**, 14, 1808–1823.

[4] J. Wang, Y. Peng, J. Xu, Q. Wu, Org. Biomol. Chem., **2022**, 20, 7765–7769.

# Deep Eutectic Solvents for Sustainable Extraction of Phenolic Compounds from Hazelnut Shells

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**Keywords:** Green Chemistry, DES, antioxidants, phenolic compounds, circular economy

Among agri-food waste, nut shells represent a valuable source of phenolic compounds, a class of bioactive metabolites with remarkable antioxidant properties, making them particularly attractive for valorization strategies. In this context, Green Chemistry promotes cleaner and more sustainable processes for the recovery of such compounds, and deep eutectic solvents (DES) have emerged as a promising alternative to conventional extractants. These mixtures, composed of a hydrogen bond acceptor and one or more hydrogen bond donors, exhibit low toxicity and high capacity to solubilize metabolites. However, their high viscosity remains one of their main limitations. Therefore, further investigation into these solvents and their applicability is essential within the framework of Green Chemistry.

To this end, a series of choline chloride-based DES were characterized and assessed as media for phenolic compounds recovery from hazelnut shells. Extractions were performed by heating and stirring under controlled conditions, while antioxidant activity and total phenolic content (TPC) of the resulting solutions were determined by DPPH and Folin-Ciocalteu assays, respectively. All DES outperformed water as an extracting agent in terms of TPC. The extraction yield depended not only on the solvent properties, but also on the hazelnut batch and the storage conditions of the extract. Notably, after 15 days under different storage conditions, the extracts preserved their phenolic content, whereas antioxidant capacity decreased, regardless of temperature or light exposure. In the case of aqueous extraction, this reduction was greater, suggesting a stabilizing effect of DES. Additionally, it was observed that higher biomass-to-solvent ratios resulted in more concentrated phenolic extracts, as expected. In contrast, increased temperatures over prolonged times led to degradation of bioactive compounds.

These results demonstrate the potential of these solvents as an effective and sustainable alternative for the extraction of bioactive compounds, highlighting their applicability in nutraceutical and cosmetic industries and contributing to the circular economy.

**Acknowledgements:**

This work was supported by PRIMA-SUN4MED (Sustainable and Novel Food Packaging based on Agro-industrial By-products and Natural Antimicrobials from the Mediterranean Area), project Section 2-2023.International Collaboration Project – Call 2024-1 MCINN-24-PCI2024-153512.

# Synergy of $CsPbBr_3$ perovskite nanocrystals supported on NiFe-layered double oxide enables $CO_2$ photothermal hydrogenation

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**Keywords:** Perovskite, nanocrystals, Layered Double Hydroxides, Photocatalysis, $CO_2$, hydrogenation

Photothermal $CO_2$ reduction is a promising strategy for converting $CO_2$ into value-added fuels using light and heat.[1,2] In this work, a $CsPbBr_3$@LDO hybrid photocatalyst was developed by assembling $CsPbBr_3$ perovskite nanocrystals onto a layered double oxide (LDO) matrix derived from $Ni_3Fe$-$CO_3$ AMO-LDH. The aim was to construct a stable heterojunction with suitable band alignment to enhance charge separation and improve solvent-free $CO_2$ hydrogenation.[3,4]

The hybrid was synthesised from the parent AMO-LDH, followed by calcination to obtain the LDO support and subsequent incorporation of $CsPbBr_3$ nanocrystals. Its photothermal catalytic performance was evaluated for $CO_2$ reduction under UV-Vis irradiation at moderate temperatures, and the material was characterised by in situ X-ray photoelectron spectroscopy and photoluminescence analyses.

$CsPbBr_3$@LDO exhibited markedly higher $CH_4$ selectivity and production than the individual counterparts and then catalysis in the dark, reaching 5.1 $mmol\cdot g^{-1}$ at 250 °C under Vis irradiation (250 $mW\cdot cm^{-2}$). The apparent quantum yield at 550 nm reached 2.39%. Reusability tests showed that the photocatalyst performed optimally at 240 °C, where the hybrid remained stable and no critical reduction of $Ni^{2+}$ occurred. In situ XPS under dark and illuminated conditions confirmed heterojunction formation and electron transfer from $CsPbBr_3$ to the LDO, while photoluminescence results indicated more efficient electron-hole separation in the hybrid.

These results demonstrate that $CsPbBr_3$@LDO is an effective and reusable photothermal catalyst for selective $CO_2$ methanation, highlighting the potential of perovskite/LDO heterojunctions for sustainable solar-driven fuel production.

**Acknowledgments:**

Financial support by the Spanish Ministry of Science and Innovation (CEX2021-001230-S grant funded by MCIN/AEI/10.13039/501100011033) is gratefully acknowledged and Direcció General de Ciència i Investigació, Consellería d'Educació Cultura i Ciencia and European Social Fund Plus for founding the project CIGE/2024/188.

**References:**

1 N. Y. Huang, H. He, S. Liu, H. L. Zhu, Y. J. Li, J. Xu, J. R. Huang, X. Wang, P. Q. Liao and X. M. Chen, *J. Am. Chem. Soc.*, 2021, **143**, 17424–17430.
2 M. Cabrero-Antonino, A. Melillo, E. Montero-Lanzuela, M. Álvaro, B. Ferrer, I. Vayá, H. G. Baldoví and S. Navalón, *Chem. Eng. J.*, 2023, **468**, 143553.
3 N. D. M. Ridzuan, M. S. Shaharun, M. A. Anawar and I. Ud-Din, *Catal. 2022, Vol. 12, Page 469*, 2022, **12**, 469.
4 S. Carenco, A. Tuxen, M. Chintapalli, E. Pach, C. Escudero, T. D. Ewers, P. Jiang, F. Borondics, G. Thornton, A. P. Alivisatos, H. Bluhm, J. Guo and M. Salmeron, *J. Phys. Chem. C*, 2013, **117**, 6259–6266.

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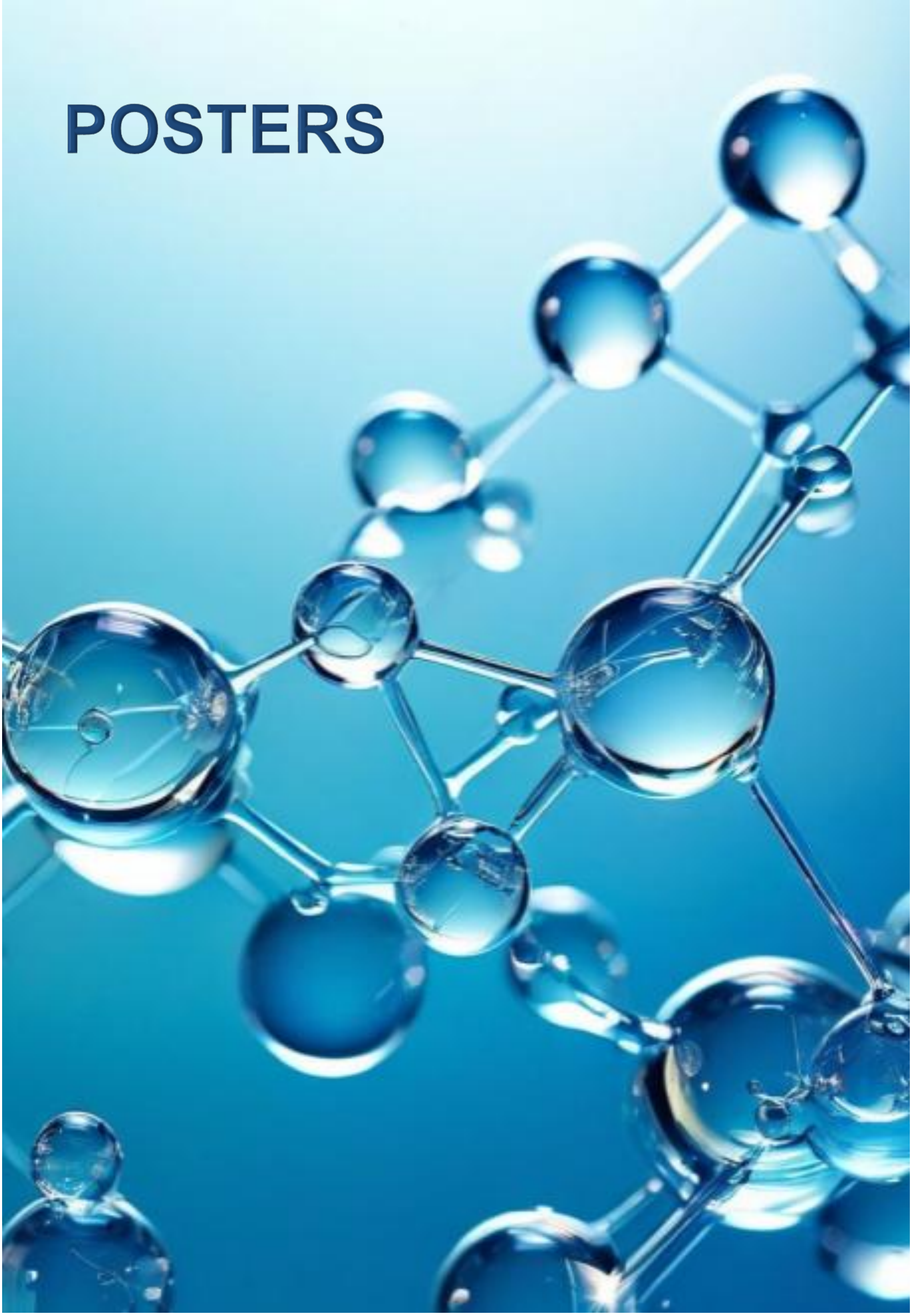

# Platinum-Based Nanotherapeutics Evaluated by Single-Cell Mass Cytometry in Complex Tumor-Blood Co-Cultures

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**Keywords:** Platinum drugs, Iron oxide nanoparticles, Mass cytometry, Single-cell analysis, Tumor microenvironment

Advanced analytical methodologies are essential to elucidate the interactions between metallodrugs and heterogeneous biological systems in precision oncology. Although platinum (Pt)-based chemotherapy remains a cornerstone of cancer treatment, systemic toxicity and limited tumor selectivity restrict its therapeutic performance. Here, we investigate iron oxide-based nanocarriers as delivery platforms for Pt drugs and evaluate their intracellular distribution in complex ex vivo tumor–immune models at single-cell resolution.

Nanocarriers were synthesized and characterized by liquid chromatography coupled to inductively coupled plasma mass spectrometry (LC-ICP-MS), enabling assessment of nanoparticle integrity and drug-loading stability. Bulk ICP-MS was used to quantify Fe and Pt content. Biological evaluation was conducted using a co-culture model mimicking intravenous administration conditions. Ovarian cancer cells (A2780) were cultured with peripheral blood (PB) cells at a 1:20 ratio and treated for 24 h with Pt-loaded nanocarriers. Single-cell uptake and phenotypic characterization were achieved using mass cytometry (CyTOF) with metal-labeled antibodies targeting tumor markers (HER2, TfR1) and a 30-marker immune panel. Results demonstrated significantly higher Pt accumulation in tumor cells compared to PB populations, confirming enhanced tumor targeting mediated by the nanocarriers. Among immune subsets, monocytes exhibited moderate Pt uptake, suggesting selective interaction with phagocytic cells. The CyTOF strategy enabled discrimination of 37 immune subpopulations and precise intracellular Pt quantification.

Overall, integrating elemental mass spectrometry with single-cell cytometry provides a powerful analytical framework for optimizing nanoparticle-based metallodrug delivery in complex biological systems.

**Acknowledgments:**

CLP gratefully acknowledges the financial support from the Spanish MICINN (Project Number PID2022-137222OB-I00).

# Enhanced spectral accuracy of GC-TOF-MS measurements in $^{13}$C-metabolic flux analysis of cancer cell line cultures

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**Keywords:** Metabolic flux analyses; 13C-labelled compounds; Multiple linear regression; Cell cultures; Prostate cancer.

The use of $^{13}$C-labelled substrates is a key tool for studying cellular metabolism [1]. $^{13}$C-metabolic flux analysis ($^{13}$C-MFA) enables quantitative reconstruction of metabolic networks through mass isotopologue distributions (MIDs) [2,3]. GC-MS, combined with silylation, is widely used due to its high resolution and metabolite coverage [4], although silicon-based derivatives can generate overlapping isotopic signals that affect accuracy [5].

In this work, we investigated biases in isotopologue distributions obtained by GC-TOF-MS. Deviations from theoretical values were attributed to partially unresolved isotopic fine structures of Si-containing derivatized metabolites and the centroiding process . To overcome this, chromatographic peaks were reconstructed using m/z profile areas instead of centroid heights, and a defined mass window was applied to capture the isotopic structure.

The method was validated using mixtures of natural and $^{13}$C-labelled standards and applied to intracellular metabolites from prostate cancer cells incubated with $^{13}C_6$-glucose, showing agreement with a GC-quadrupole MS method.

These results demonstrate that centroiding in GC-TOF-MS introduces biases in Si-derivatized metabolites. The proposed approach improves isotopologue accuracy, supporting more reliable $^{13}$C-MFA studies.

### Acknowledgments:

Daniela Pineda-Cevallos acknowledges the Principality of Asturias, Spain, for their financial support through the Severo Ochoa scholarship ref. BP22-061 and the financial support offered by ISPA and FINBA through the ISPA 2022 intramural scholarship. The Spanish Ministry of Science and Innovation is acknowledged for the funding through project PID2024-159562NB-I00.

### References:

[1] C. Jang, L. Chen and J. D. Rabinowitz, Cell, **2018**, 173, 822–837.

[2] M. R. Antoniewicz, Curr. Opin. Biotechnol., **2013**, 24, 1116–1121.

[3] Y. Wang and M. Gu, Anal. Chem., **2010**, 82, 7055–7062.

[4] Z. Lai and O. Fiehn, Mass Spectrom. Rev., **2018**, 37, 245–257.

[5] M. Fernández-Fernández, P. Rodríguez-González, D. Hevia Sánchez, P. González-Menéndez, R. M. Sainz Menéndez and J. I. García Alonso, Anal. Chim. Acta, **2017**, 969, 35–48.

# Spent coffee valorization with Deep Eutectic Solvents (DESs)

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**Keywords:** AquoDESs, DESs, Waste valorisation, Caffeine, Chlorogenic acids

Deep Eutectic Solvents (DESs) have recently emerged as promising environmentally friendly liquids for a wide range of applications. They are formed through a network of weak interactions, mainly hydrogen bonds, which hinder regular crystal lattice formation and result in liquid systems. Among them, aquoDESs are binary mixtures in which water is one of the components, whose DES nature has been confirmed by combined theoretical and experimental melting curve analyses.[1,2] Considering the framework of circular economy and sustainable processes, three aquoDES systems— glycolic acid/water (GA/$H_2O$), betaine/water (TMG/$H_2O$) and glycerol/water (Gly/H2O) were successfully applied as green extraction solvents for caffeine and chlorogenic acids from spent coffee grounds. The aquoDESs showed higher extraction efficiencies compared to water, water/ethanol mixtures, and other reported DESs. In particular betaine/water (TMG/$H_2O$) and glycerol/water (Gly/H2O), thanks to their low toxicity, related to the non-water component only, represent also promising systems, supporting the potential direct use of the obtained extracts due to the food-grade nature of the aquoDES components.[3] Green metrics confirmed the low environmental impact of the proposed methodology.

**Acknowledgments:**

NGEU–PNRR,DM117/2023 (Elison Lepore's scholarship).

**References:**

[1] E. Lepore, G. Ciancaleoni , D. Romano Perinelli, G. Bonacucina, S. Gabrielli, G. de Simone, R. Gabbianelli, L. Bordoni, M. Tiecco, Journal of Molecular Liquids, **2024**, 415, 126427.

[2] F. Pompei, E. Lepore, A. Torregrosa-Chinillach, F. Catalini, D. A. Alonso, R. Chinchilla, S. Gabrielli, C. Mannozzi, S. Vittori, M. Tiecco, Journal of Molecular Liquids, **2025**, 427, 127416.

[3] F. Pompei, G. Montillo, E. Lepore, S. Vittori, M. Tiecco, C. Mannozzi, Food and Bioprocess Technology, **2026**, 19.

# Tailoring Quinone-based Interfaces for Electrochemical DNA Biosensing

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**Keywords:** Genosensing, covalent DNA anchoring, electrogenerated quinone films.

The performance of electrochemical biosensors for nucleic acid detection strongly depends on the properties of the electrode interface used to anchor recognition elements, specifically DNA probes [1]. To analyse oligonucleotide biomarkers in biological fluids, the immobilization strategy must ensure stable DNA probe attachment while maintaining target accessibility, minimizing non-specific adsorption of biomolecules, and enabling reliable signal transduction.

In this work, we explore quinone-containing electrogenerated coatings on screen-printed carbon electrodes as reactive platforms for DNA functionalization. Quinone moieties within these films provide chemically active sites that can react with thiol-modified molecules through nucleophilic addition, generating stable covalent linkages [2,3]. Polydopamine coatings were selected as a model due to their straightforward electrochemical deposition and the presence of catechol/quinone functionalities that participate in surface coupling reactions. To characterize the reactivity and accessibility of these functional groups, a ferrocene-terminated alkanethiol was used as an electroactive probe. Electrochemical measurements were performed to assess how electrodeposition parameters influence the density and accessibility of reactive sites within the coating. Subsequently, thiolated DNA probes were immobilized, and their hybridization was examined under conditions relevant to bioanalytical applications, with emphasis on understanding how surface chemistry affects probe organization, resistance to biofouling, and the efficiency of electrochemical signal generation.

Our results show that quinone-based electrogenerated coatings provide an effective platform for the covalent immobilization of DNA probes on carbon electrodes. This approach allows the development of robust electrochemical genosensors for nucleic acid detection and offers a versatile approach for designing biofunctional interfaces for sensing applications.

**Acknowledgments:**

This work has been financially supported by the Spanish Government (Projects PID-2021-123183OB-I00 and PID2024-156199NB-I00) and Principado de Asturias (IDE/2024/000677).

**References:**

[1] T.G. Drummond, M.G. Hill, J.K. Barton, Nature Biotechnology, **2003**, 21, 1192–1199.

[2] M.L. Alfieri, A. Cariola, L. Panzella, The Journal of Organic Chemistry, **2022**, 87, 4580−4589.

[3] G. Ziyatdinova, E. Guss, E. Yakupova, Sensors, **2021**, 21(24), 8385.

# Exploring BCMA Detection Through Optimized Aptamer Design and Electrochemical Analysis

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**Keywords:** multiple myeloma, aptamers, biosensor, post-SELEX optimization

Multiple myeloma is a hematological cancer characterized by the uncontrolled proliferation of plasma cells within the bone marrow. The identification of reliable molecular biomarkers is essential for improving diagnosis and disease monitoring. Among the biomarkers associated with this pathology, B-cell maturation antigen (BCMA), a membrane-glycosylated protein overexpressed in multiple myeloma patients, stands out. However, only a limited number of recognition molecules that can detect BCMA with a level of selectivity needed for reliable analytical and diagnostic applications is currently available.

Aptamers are short single-stranded nucleic acids that can fold into well-defined 3D-structures, enabling them to bind specific targets with high affinity and selectivity. These molecules are typically generated through a conventional SELEX process, an iterative method that selects the best-binding sequences form a large initial pool. Once obtained, the aptamers can be refined by removing the non-essential nucleotides (truncation), which finally may significantly influence the affinity and overall performance of the resulting aptamers.

In this work, we carried out a SELEX procedure against BCMA using oriented protein immobilization. This selection yielded five candidates that were analysed based on predicted secondary structures and conserved sequence motifs. Two promising aptamers were subsequently optimized using the semi-automated computational platform APTAMD. [1] This tool is freely available and predicts the 3D-structures of aptamers and their truncated variants as a rational starting point to evaluate the effect of sequence shortening on target affinity. The binding performance of both the original and truncated sequences was experimentally characterized using electrochemical techniques. Finally, the most promising candidate was integrated into an electrochemical aptasensor, and its analytical performance for BCMA detection was evaluated.

### Acknowledgments:

The work has been financially supported by Spanish (PID2021 123183OB-I00, PID2024-156199NB-I00) and Principado de Asturias (IDE/2024/000677) Governments.

### References:

[1] A. Díaz-Fernández; C.S. Ciudad; N. Díaz; D. Suárez; N. de-los-Santos-Álvarez; M.J. Lobo Castañón, J. Chemi. Inf. Model. **2025**, 65 (8), 4128-4136. https://github.com/dimassuarez/APTAMD.

# Photocatalytic Transformation of *o*-Cresol to Salicylic Acid through a Salicylaldehyde Intermediate

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**Keywords:** Photocatalysis, *o*-Cresol, Salicylic Acid, Salicyaldehyde

Photocatalytic oxidation offers an environmentally friendly and sustainable approach for the transformation of aromatic compounds under mild reaction conditions [1]. Compared with conventional thermal oxidation processes, photochemical methods often require lower energy input making them attractive for green chemical synthesis. Salicylic acid and salicylaldehyde are industrially important and valuable chemicals that can be obtained through the oxidation of o-cresol. Salicylic acid is widely used as a precursor in the pharmaceutical, cosmetic, and polymer industries, while salicylaldehyde serves as an important intermediate in the synthesis of fragrances, dyes, and coordination compounds [2, 3].

In this study, the photocatalytic oxidation of o-cresol was investigated to explore its efficient conversion into value-added products. The primary objective of this work was the selective synthesis of salicylic acid. The reaction was carried out under visible light irradiation in the presence of a $CuCl_2$ ligand-to-metal charge transfer complex in acetonitrile, along with various additives, in order to evaluate their influence on the conversion of o-cresol as well as on product distribution and selectivity. The role of these additives was also examined to understand their effect on reaction efficiency and possible oxidation pathways involved in the process. Salicylaldehyde was identified as key intermediate of oxidation of o-cresol, leading to formation of salicylic acid as desired product.

**Acknowledgments:**

The authors acknowledge financial support from PID2023-147180OB-100.

**References:**

[1] S. Batsika et. al. Green Chem. **2022**, 24, 6224-6231

[2] E. Sergeev, Y. Rodikova, E. Zhizhina, Catal. Ind. **2024**, 16, 312-329

[3] D. Pisal, G. Yadav, Molecular Cat. **2020**, 491, 110991

# Study of Oscillating Reactions: The Belousov–Zhabotinsky Reaction and Other Processes of Interest

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**Keywords:** Belousov–Zhabotinsky; Briggs–Rauscher; RGB analysis; chronopotentiometry.

The Belousov–Zhabotinsky (BZ) and Briggs–Rauscher (BR) reactions were studied using two complementary techniques: chronopotentiometry, introduced here as a novel monitoring method, and RGB-based optical analysis, previously reported in the literature [1]. It has been shown that both techniques yield similar results for oscillating reactions, indicating that chronopotentiometry is suitable for their monitoring.

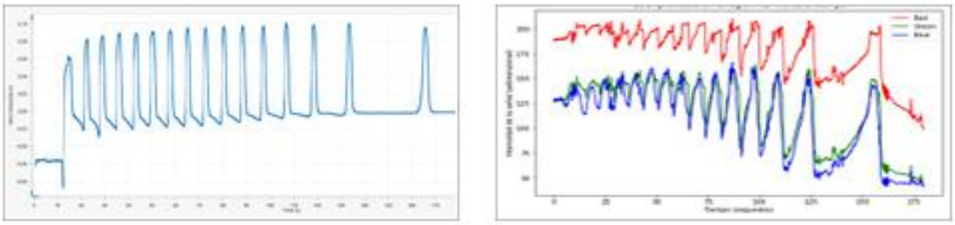

***Figure 1.*** *Chronopotentiometric (left) and RGB (right) oscillations for the same BR reaction.*

Additionally, the formation of a crystalline byproduct in the BZ reaction, identified as pentabromoketone (PBK), was observed and structurally characterized by X-ray diffraction.

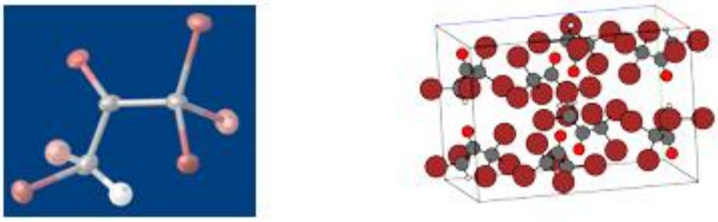

***Figure 2.*** *PBK molecule (left, obtained from XRD) and its unit cell (right, using Critic2).*

**Acknowledgments:**

The authors thank Dr. Rebeca Miranda Castro for guidance on the potentiostat–galvanostat.

**References:**

[1] B. Irina, J. Chem. Educ. **2020**, 97, 1895-1902.

# Fate of microplastics during the composting process: influence of bacterial and fungal inoculation

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**Keywords:** Compost; microplastics; bacteria; fungi; biodegradation

Organic waste treatment through anaerobic digestion and composting enables its valorization for soil amendment used in agriculture, forestry and landscaping, nurseries and gardening, and soil restoration. However, recent concerns have emerged regarding the possible presence of microplastics (MPs) in these matrices, highlighting the need for a better understanding of their potential impact on soil health.

The present study evaluates the effect of microbial inoculation on the degradation of MPs during composting. Assays were conducted over two months using digestate from anaerobic digestion of separately collected biowaste mixed with green cuttings at a 1:2 (v/v) ratio as composting feedstock. Four treatments were assessed: a non-inoculated control (i), a treatment inoculated with the bacterial strain *Comamonas testosteroni* NCIMB 8955 (ii), and two treatments inoculated with the fungal strain *Phanerochaete chrysosporium* CECT 2779 at different stages, one at the beginning of the composting process (iii) and one after the cooling phase (iv). Both microorganisms used have previously demonstrated the ability to degrade plastic material [1], [2]. Moisture, pH, temperature, and humidity were closely monitored throughout the composting assays. Samples were collected during the process to assess the presence of MPs, which were isolated by oxidizing the organic matter with hydrogen peroxide and Fenton's reagent, followed by density separation. Extracted MPs were then quantified and characterized via stereomicroscopy and Fourier-transform infrared spectroscopy (FTIR).

This study provides insight into the fate of MPs during composting and evaluates the potential of biological inoculation to enhance their degradation. This approach can improve compost quality and offers sustainable strategies to mitigate MP pollution in soils while reducing potential risks associated with organic amendments use.

**Acknowledgments:**

The authors are grateful for funding from the Government of the Principality of Asturias (SEK-25-GRU-GIC-24-010). B. A. Newrick acknowledges support from the Severo Ochoa predoctoral fellowship program (NAC-AT-PUB-ASV-2025 BP24-43). The authors also thank COGERSA SAU for providing the samples.

**References:**

[1] B.A. Newrick, D. Valdés, A. Laca, A. Laca, M. Díaz, J. Hazard. Mater., **2025**, 485, 136822.

[2] F. Wu, Z. Guo, K. Cui, D. Dong, X. Yang, J. Li, Z. Wu, L. Li, Y. Dai, T. Pan, J. Hazard. Mater., **2023**, 448, 130878.

# Direct Energy Conversion of Glyphosate in a Microfluidic Fuel Cell with Minimal Nickel-modified Anode and Metal-Free Cathode

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**Keywords:** glyphosate degradation; microfluidic fuel cell; nickel nanoclusters; energy recovery

Glyphosate contamination remains a significant environmental issue, creating a need for approaches that can remove pollutants at minimal cost. In this work, a 3D-printed microfluidic fuel cell (μFC) is used as a platform for directly converting glyphosate into electricity while simultaneously degrading it. The μFC is equipped with a Nickel-modified carbon paper anode with a low loading of Ni nanoclusters and a metal-free carbon paper cathode, operating in a mixed-media and flow-through configuration. Glyphosate oxidation takes place at the anode and is facilitated by nickel redox species, while hypochlorous acid reduction occurs at the cathode, allowing operation in galvanic mode. The system delivers a maximum power density of 0.18 mW cm-2 and achieves up to 99% degradation of glyphosate under optimized conditions, as confirmed by HPLC analysis. Overall, this work shows that microfluidic fuel cells can serve as compact and efficient systems for coupling pollutant degradation with energy generation, offering a practical alternative to conventional remediation strategies.

**Acknowledgments:**

The authors acknowledge CAPES, CNPq, FUNDECT, and FINEP for financial support.

**References:**

[1] W. B. Kira, D. F. Costa-Filho, C. R. Zanata, I. M. C. de Alcantara, J. Bettini, F. L. Souza, H. Wender, C. A. Martins, ACS Omega, 2025, 10, 19939–19949.

[2] V. B. Kimbi Yaah, S. Ahmadi, J. Quimbayo M., S. Morales-Torres, S. Ojala, Environ. Res., 2024, 240, 117477.

[3] E. V. Sierra, M. A. Méndez, V. M. Sarria, M. T. Cortés, Quím. Nova, **2008**, 31, 220–226.

[4] C. A. Martins, O. A. Ibrahim, P. Pei, E. Kjeang, Electrochim. Acta, **2018**, 271, 537–543.

[5] K. Guima, C. R. Zanata, C. A. Martins, Electroanalysis, **2024**, 36, e202300223.

# *Unlocking the Full Potential of Macroalgae Sludges: Thermochemical Pathways to Biochar, Bio-Oil and Gas*

E. Ciurcina, R. Pardo, L. Taboada-Ruiz, J. Holgado, P. Álvarez Rodríguez, M. Díaz-Somoano, B. Ruiz.

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**Keywords:** Macroalgae biowaste valorization; Flash Pyrolysis; Biochar; Biofuel.

Macroalgae processing generates significant amounts of sludge, which is often underutilized despite its potential for resource recovery. This study investigates the thermochemical conversion of macroalgae sludge via conventional and flash pyrolysis, aiming to evaluate its suitability as a feedstock for the production of value-added products. Initially, the physicochemical properties of the sludge were characterized, revealing a high ash content (≈41%) and a relatively low carbon content, with most of the inorganic fraction consisting of sand; these compositional features strongly influence its thermal behaviour. Sludge pyrolysis experiments were conducted at temperatures between 450 and 750 °C under controlled heating rates to assess the distribution and composition of biochar, bio-oil, and gas fractions. Thermogravimetric analysis indicated that the main decomposition occurs between 250 and 600 °C, associated with the degradation of proteins, carbohydrates, and lipids [1].

The results showed that process conditions significantly affect product yields. Conventional pyrolysis produced a relatively balanced distribution of products, while flash pyrolysis favoured higher biochar yields and enhanced gas production at higher temperatures. The resulting biochar exhibited very high ash content (up to 80%) and increased structural stability, suggesting strong potential for environmental applications such as soil amendment and carbon sequestration. Bio-oil presented high energy content (up to 31 MJ/kg) but was characterized by a significant presence of nitrogen-containing compounds. The composition of the gases changed with temperature, with increasing concentrations of CO, $H_2$, and $CH_4$, leading to higher energy content, particularly under flash pyrolysis conditions.

Overall, the study demonstrates that macroalgae sludge can be effectively valorized through pyrolysis, with biochar emerging as a key product due to its functional properties, while gas and bio-oil contribute to energy recovery. These findings support the development of integrated and sustainable waste-to-energy strategies for marine biomass residues.

**Acknowledgments:**

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or CINEA. Neither the European Union nor the granting authority can be held responsible for them. The work described in this publication was subsidised by Horizon Europe (HORIZON) framework through the Grant Agreement Number 101144144. Additionally, the authors thank the company ROKO S.A. for providing the industrial residue for this work.

**References:**

[1] R. Ślęzak, P. Nawrot, and S. Ledakowicz, “Pyrolysis of micro- and macroalgae in thermobalance coupled with mass spectrometer,” *Algal Res.*, **2022,** 66, 102-782.

# Turning Dairy Sludge into Value: Temperature and Pyrolysis Route as Key Drivers of Gas Yield and Composition

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**Keywords:** Dairy waste valorization; Conventional/flash pyrolysis; Biofuel; Bioenergy.

Growing dependence on non-renewable energy sources has driven the search for more sustainable alternatives. In this context, biomass pyrolysis emerges as a promising technology, enabling the valorisation of abundant, nearly carbon-neutral waste into high-value products such as biochar, bio-oil and gas for energy and industrial applications.

The dairy industry generates significant amounts of sludge, estimated at around 17.45 kg per cubic metre of processed milk [1], resulting in tens to thousands of tonnes annually. This waste poses important environmental challenges due to its high organic load, gas and odour emissions, and elevated management and transport costs, highlighting the need for effective valorisation strategies.

This study investigated the energy valorisation of dairy sludge from an Asturian industry through pyrolysis, focusing on optimising the gaseous fraction. Conventional pyrolysis (CP) and flash pyrolysis (FP) were performed at temperatures between 450 and 750 °C. CP used a heating rate of 25 °C/min, while FP involved instant heating.

Results showed that gas yield and composition strongly depend on both process type and temperature. The highest gas yield (67 vol.%) was obtained in FP at 750 °C. In CP, increasing temperature reduced $CO_2$ content (from 65% to 27%) and enhanced the formation of combustible gases such as CO (up to 17 %vol.), $H_2$ (up to 25 %vol) and $CH_4$. In FP, $CO_2$ decreased more markedly (from 73% to 14%), while combustible gases increased significantly, particularly ethylene, which rose from 0.2% to 22%.

Overall, FP gas shows high energy potential (up to 33 MJ/Kg) and a remarkable ethylene content, making it suitable not only as a fuel but also as a feedstock for the chemical industry, especially in plastic production.

## Acknowledgments:

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or CINEA. Neither the European Union nor the granting authority can be held responsible for them. The work described in this publication was subsidised by Horizon Europe (HORIZON) framework through the Grant Agreement Number 101144144. Additionally, the authors thank the company Mantequería Arias S.A. for providing the industrial residue for this work.

## References:

[1] Hu, Y.; Khomenko, O.; Shi, W.; Velasco-Sánchez, Á.; Ashekuzzaman, S. M.; Bennegadi-Laurent, N.; Daly, K.; Fenton, O.; Healy, M. G.; Leahy, J. J.; Sørensen, P.; Sommer, S. G.; Taghizadeh-Toosi, A.; Trinsoutrot-Gattin, I. Systematic Review of Dairy Processing Sludge and Secondary STRUBIAS Products Used in Agriculture. *Front. Sustain. Food Syst.* **2021**, 5:*763020*.

# Structural Control in Porous Materials via Microwave-Assisted Sol-Gel Synthesis

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**Keywords:** Sol-gel, microwave, synthetic materials.

The widespread availability of biomass waste has encouraged its use in producing carbon materials, although impurities and compositional variability limit its potential. Consequently, synthetic carbon materials derived from sustainable precursors represent a key advancement. This work focuses on developing new materials using sustainable precursors and a microwave-assisted sol–gel methodology, which enables rapid and scalable production. The influence of the solvent concentration (i.e., the dilution ratio) and synthesis temperature on the morphology and porosity has been examined to tailor the material's properties for specific applications. Carbon materials were synthesized using phloroglucinol, glyoxylic acid, and triethylenediamine (TEDA) as the main reactants [1], and water as the solvent. The reaction was carried out under microwave heating at atmospheric pressure in an open vessel. Different materials were obtained by varying the dilution degree of the precursor mixture, PAT-1250 (high dilution), PAT-120 (intermediate dilution), and PAT-20 (low dilution), and the synthesis temperature (50°C and 85°C). Physicochemical characterization shows that the materials consist primarily of spheres composed of C, H, O, and N. At 50 °C, the spheres display a broad size distribution at low dilution whilst as the dilution increases, the distribution narrows, and particle size decreases, indicating enhanced nucleation and reduced growth. At 85 °C, a similar trend is observed, but the effect of dilution is even more pronounced: the particles become smaller, and the size distribution is more uniform than at 50 °C. The results show that the degree of dilution of the precursor mixture is a key parameter for controlling the morphology, porosity, and yield of the final materials. Specifically, a higher solvent content promotes the formation of homogeneous, highly porous individual spheres, whereas lower dilutions result in larger spheres with partial particle fusion and a reduced surface area.

### Acknowledgments:

This research was funded by MCIN/AEI/10.13039/501100011033/FEDER-UE through the PID2022-139493OA-100 project, Fundación Domingo Martínez trough MACSO project, MITECO/IDAE, and the European Union-NextGenerationEU/PRTR through the PR-H2CVAL4-C2-2023-000052 project, and by the Principado de Asturias (ID/2024/000749). NRR is grateful for the CNS2023-144627 grant funded by MCIN/AEI/10.13039/501100011033 NextGenerationEU/PRTR. and the European Union

### References:

[1] A. Maetz, L. Delmotte, G. Moussa, J. Dentzer, S. Knopf, C.M. Ghimbeu, Facile and sustainable synthesis of nitrogen-doped polymer and carbon porous spheres, Green Chem. 19 (2017) 2266-2274.

# Visible light induced formation of alkenyl siloxycarbenes from α,β unsaturated acylsilanes and subsequent intramolecular cyclization

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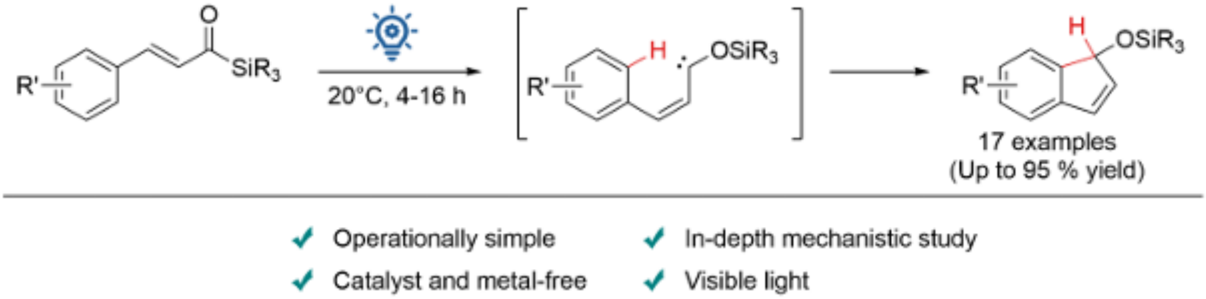
**Keywords:** Acylsilanes, Carbenes, Photochemistry, Mechanistic studies

Acylsilanes are an important class of molecules with a rich reactivity.[1] One of the most remarkable aspects of their reactivity is their ability to readily undergo a 1,2-silyl shift to generate highly reactive, nucleophilic siloxycarbenes, a reaction known as the Brook rearrangement.[1] However, reports on the transformation of α,β-unsaturated acylsilanes into siloxycarbenes have remained surprisingly scarce.[1,2] Reports on the insertion of these intermediates into unactivated C-H bonds are also significantly underrepresented in comparison to heteroatom X-H insertion reactions.[1] Herein, we report the generation of α,β unsaturated siloxycarbenes from acylsilanes by irradiation with blue light and a subsequent cyclization reaction that occurs via a formal C-H insertion, including a complete mechanistic study of the reaction.[3]



**Acknowledgments:**

Support from the Spanish Government (PID2022-140635NB-I00, PID2023-151549NB-I00, MCINN-24RYC2022-035485-I) and Principado de Asturias (IDE/2024/000709) is gratefully acknowledged.

**References:**

[1] Q. Zhao, Q. Geng, Y. Li, J. Li, Z. Liu; Org. Chem. Front. **2023**, 10, 1316-1321.

[2] Y. Li, H. Zhang, J. Li, D. Shen, Z. Liu; Org. Lett. **2022**, 24, 9163-9167.

[3] A. Álvarez, I. Rivilla, F. P. Cossío, M. Plaza, F. Rodríguez, Submitted.

# 2-[(Dimethylamino)methyl]phenyl-Stabilized Heavier Tetrylenes: Syntheses, Coordination Chemistry and Air- and Moisture-Stability

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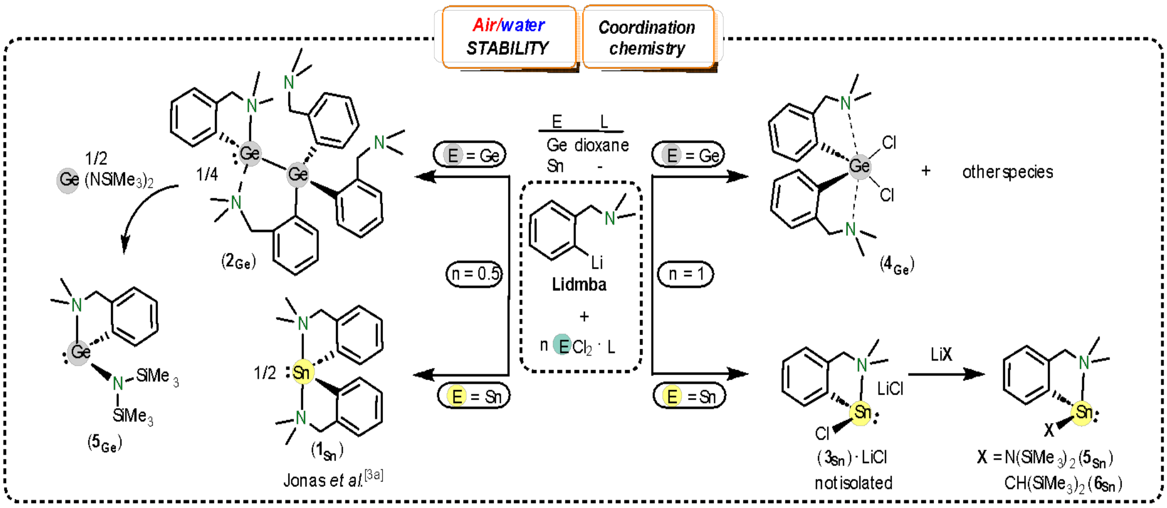
**Keywords:** heavier tetrylenes, air-stability, coordination chemistry

Heavier tetrylenes (HTs) are increasingly utilized as ligands in coordination chemistry.[1] However, their low stability towards oxygen and moisture have prevented a wider use of these compounds in catalysis, which has been rarely examined under air.[2a] To this regard, many reports have described that HTs (free or coordinated) stabilized by chelating aryl fragments bearing one or more donor groups are capable to withstand the hydrolysis of the E−C bond (E = tetrel heavy atom)[2a,b] or even to be completely air-stable.[2a] For example, the homoleptic stannylene Sn(dmba)$_2$ (**1**$_{\mathbf{Sn}}$; Hdmba = *N*,*N*-dimethylbenzylamine), reported by Jonas *et al.* in 1988,[3a] while being unstable towards oxygen,[3b] was described as inert towards hydrolysis for several hours.[3c]

Having in mind the potential of the dmba fragment (it is likely hydrolysis resistant and can be easily obtained by lithiation[3d] of the commercially available Hdmba), we describe: *(i)* our attempts to prepare unknown dmba-HT variations (the novel HTs **2**$_{\mathbf{Ge}}$, **3**$_{\mathbf{Sn}}$·LiCl, **5**$_{\mathbf{Ge}}$, **5**$_{\mathbf{Sn}}$ and **6**$_{\mathbf{Sn}}$ were prepared following different strategies; see below), *(ii)* a preliminary study of the coordination chemistry of some of the new dmba-derived HTs (gold, diiron and iridium complexes were isolated) and *(iii)* a comparison of the air/water-stability of the new HTs and HT-Ms.



## References:

[1] a) Hadlington, T. J., *Chem. Soc. Rev.* **2024**, *53*, 9738–9831. b) Zhou, Y.-P.; Driess, M., *Angew. Chem. Int. Ed.* **2019**, *58*, 3715-3728.

[2] a) Aman, M.; Dostál, L.; Růžička, A.; Tydlitát, J.; Beckmann, J.; Turek, J.; Jambor, R., *Chem. Commun.* **2021**, *57*, 12992-12995. b) Deak, N.; Madec, D.; Nemes, G., *Eur. J. Inorg. Chem.* **2020**, 2769-2790

[3]. a) Angermund, K.; Jonas, K.; Krüger, C.; Latten, J. L.; Tsay, Y. H., *J. Org. Met. Chem.* **1988**, *353*, 17-25. b) Padělková, Z.; Nechaev, M. S.; Cěrnošek, Z.; Brus, J.; Růžička, A., *Organometallics*, **1988**, *27*, 5303-

5308. c) Jastrzebski, J. T. B. H.; van Klaveren, M.; van Koten, G. *Organometallics*, **2015**, *34*, 2600-2607. d) Oakes, F. T.; Sebastian, J. J., *J. Organometl. Chem.* **1978**, *159*, 363-371.

# Air-Stability and Gold Complexes of (b-Diketiminato)germylenes

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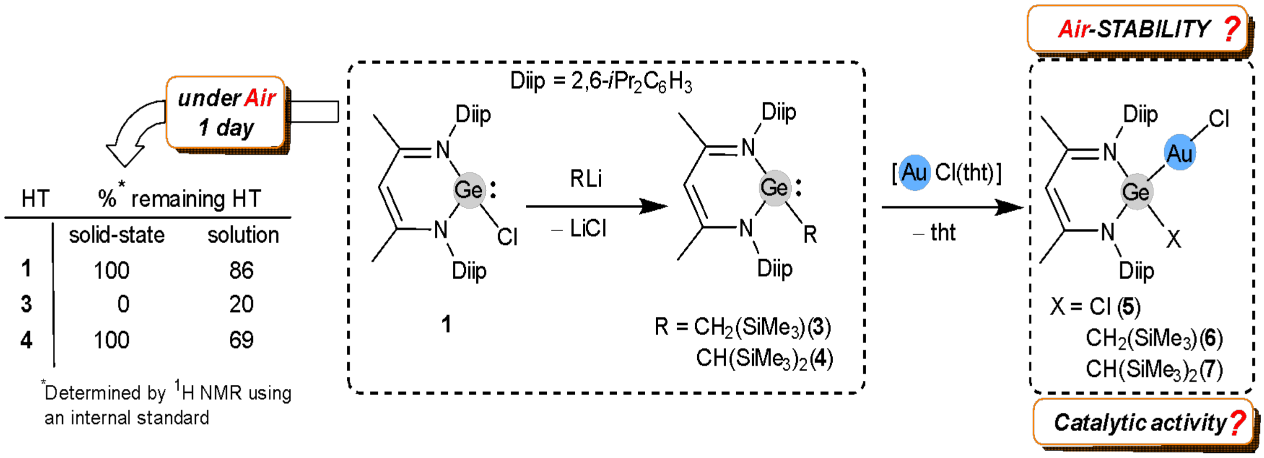
**Keywords:** heavier tetrylenes, germylenes, coordination chemistry, air stability, catalysis

Heavier tetrylenes (HTs) are increasingly used as ligands in coordination chemistry and homogenous catalysis.[1] However, the low stability towards oxygen and moisture attributed to the metal-free species and also to their complexes have prevented a wider use of these compounds in catalysis, which has been rarely examined in the absence of a protective atmosphere.[2] To this respect, some HTs have been reported to withstand reactions with water without undergoing a complete degradation (maintaining their abilities as ligands)[3a,b] or to be completely stable in air.[3c] For instance, in 2004, Roesky's group described that the reaction of the chloro(b-diketiminato)germylene $[HC\{(CMe)(NDiip)\}_2]GeCl$ (**1**; Diip = 2,6-$i$$Pr_2C_6H_3$) with water in the presence of an NHC led to the hydroxo(b-diketiminato)germylene $[HC\{(CMe)(NDiip)\}_2]GeOH$ **2**, with retention of the chelating *N,N'*-fragment.[3a] However, nothing was mentioned about the air-stability of **1** or **2**, which were prepared, as many other HTs, under an inert atmosphere.

Having in mind that hydrolysis is one of the main causes of air-instability and considering that the b-diketiminato-HT fragment has been described to be water-resistant, we now report that a study of the air-stability of compounds **1** and the novel alkyl(b-diketiminato)germylenes $[HC\{(CMe)(NDiip)\}_2]GeX$ (X = $CH_2SiMe_3$ (**3**), $CH(SiMe_3)_2$ (**4**)) has shown that **1** and **4** are much more air-stable than **3**, both in solid state and in solution.



| HT | % remaining HT* solid-state | % remaining HT* solution |
|---|---|---|
| 1 | 100 | 86 |
| 3 | 0 | 20 |
| 4 | 100 | 69 |

*Determined by $^1H$ NMR using an internal standard

**References:**

[1] a) Hadlington, T. J., *Chem. Soc. Rev.* **2024**, *53*, 9738–9831. b) Zhou, Y.-P.; Driess, M., *Angew. Chem. Int. Ed.* **2019**, *58*, 3715-3728.

[2] Aman, M.; Dostál, L.; Růžička, A.; Tydlitát, J.; Beckmann, J.; Turek, J.; Jambor, R., *Chem. Commun.* **2021**, *57*, 12992-12995.

[3] a) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M., *Angew. Chem. Int. Ed.* **2004**, *43*, 1419-1421. b) Pineda, L. W.; Jancik, V.; Colunga-Valladares, J. F.; Roesky, H. W.; Hofmeister, A.; Magull, J., *Organometallics* **2006**, *25*, 2381-2383. c) Mahawar, P.; Wasson, M. K.; Sharma, M. K.; Jha, C. K.; Mukherjee, G.; Vivekanandan, P.; Nagendran, S., *Angew. Chem. Int. Ed.* **2020**, *59*, 21377-21382.

# Boronic Esters: A new synthetic tool for boosting the tolerance of the gold(I) catalyzed cycloisomerization of 1-bromoalkynes

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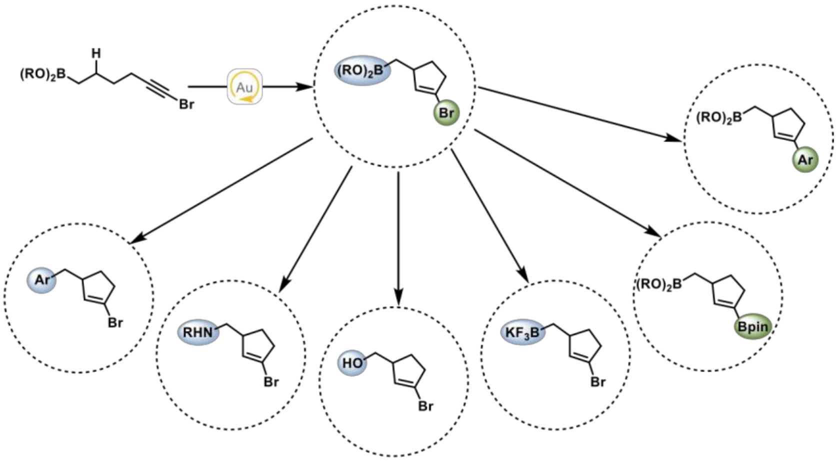
**Keywords:** Boronic esters, gold-catalysis, 1-bromoalkynes

Alkyl boronates are key intermediates in modern organic synthesis, valued for their stability, low toxicity, and exceptional versatility. Their ability to participate in a wide range of transformations, particularly carbon–carbon bond-forming reactions such as the Suzuki–Miyaura coupling, has made them indispensable tools in both academic and industrial settings.[1] In addition, alkyl boronates can undergo oxidation, homologation, and stereospecific transformations, enabling the efficient construction of complex molecular scaffolds.[2]

In our research group, the cycloisomerization of 1-bromoalkynes via gold catalysis was recently reported, affording bromocyclopentenes as valuable products.[3] A subsequent study revealed a low tolerance toward electronegative substituents near the reaction center.[4] However, the reaction showed excellent compatibility with boronic esters at any position, enabling access to novel substrates and the surpass of its main limitation. This methodology affords particularly attractive substrates that can be easily bifuncionalized.



**Scheme 1**. Graphical Abstract.

## References:

1. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.

2. Hall, D. G. *Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine*; Wiley-VCH: Weinheim, 2011.

3, Miguélez, R.; Semleit, N.; Rodríguez-Arias, C.; Mykhailiuk, P.; González, J. M.; Haberhauer, G.; Barrio, P. *Angew. Chem., Int. Ed.* **2023**, 62, No. e202305296.

4. Miguélez, R.; Arto, O.; Semleit, N.; Haberhauer, G.; Barrio, P. *Adv. Synth. Catal.* **2024**, 366, 780−789.

# Prediction and Approximate Methods for Phase Diagram Calculations: the Case of Paracetamol

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**Keywords:** polymorphism, crystal structure, CSP, vibrational effects

Paracetamol (acetaminophen) is a widely used pharmaceutical compound that exhibits pronounced solid-state polymorphism, with several crystalline forms displaying distinct structural and mechanical properties. While Forms I, II, and III are well characterized under ambient conditions,[1] additional polymorphs have been reported at high pressure and temperature, some of which still lack resolved crystal structures. This complexity makes paracetamol an excellent system for studying the interplay between thermodynamics and kinetics in molecular crystals.[2]

In this work, we present the first comprehensive phase diagram of paracetamol by combining available experimental data with thermodynamic modeling. This diagram provides a framework for understanding the complex energy landscape of this compound, offering valuable insights for crystallization design and formulation strategies. To address polymorphs with unresolved structures, we employ crystal structure prediction (CSP) methods. Furthermore, we explore the possibility of incorporating thermal contributions to the free energy using approximate approaches, such as the Einstein model or density-functional tight-binding (DFTB), enabling an efficient evaluation of vibrational effects. This combined strategy provides a consistent and computationally efficient description of the polymorphic landscape of paracetamol, offering new insights into its phase behavior and establishing a framework applicable to other molecular crystals of pharmaceutical relevance.

## References:

[1] S. J. Smith, M. M. Bishop, J. M. Montgomery, T. P. Hamilton, Y. K. Vohra, J. Phys. Chem. A, **2014**, 118, 6068–6077.

[2] A. G. Shtukenberg, M. Tan, L. Vogt-Maranto, E. J. Chan, W. Xu, J. Yang, M. E. Tuckerman, C. T. Hu, B. Kahr, Cryst. Growth Des., **2019**, 19, 4070–4080.

# Green Synthesis of Antimicrobial Nanoparticles

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**Keywords:** Green Synthesis, Metallic Oxides, Nanoparticles, Electron Microscopy.

In this study, the feasibility of utilizing green synthesis of nanoparticles was investigated based on aqueous extracts of different plants with known therapeutic properties. Different metal oxide nanoparticles were synthesized though heat-induced chemical reaction of different concentrations of the respective salts with various plants. The nanoparticles were characterized using multiple electron microscopy characterization methodologies to determine their characteristics at both the nano and microscales of dimensions. The synthesis of nanoparticle was confirmed within the 5-20 nm size range, and their composition was found to roughly match the expected composition of the nanoparticles. Successive trials indicate that the nanoparticles' characteristics are influenced by multiple factors such as pH, concentration of precursors, temperature and the final purification. Thus, we theorize that only specific combinations within small intervals of some of these values may yield a high enough concentration of nanoparticles to be deemed a success. Once this has been achieved, later tests will focus on their biocompatibility and antimicrobial properties that could be acquired from their antimicrobial precursors. This could make these nanoparticles alternatives for current antimicrobiotics and help in addressing problems such as the increased resistance of bacteria to commercial antibiotics.

**Acknowledgment:**

This research is funded through the Ramon y Cajal grant received by A.A. from the Spanish Ministry of Science and Innovation (RYC2022-038426-I).

# Accurate prediction of time-dependent density-functional theory vertical excitation energies using atom-centered potentials

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**Keywords:** BODIPY, TDDFT, electronic excitations, atom-centered potentials, B3LYP.

The accurate prediction of electronic excitations in large molecules using time-dependent density-functional theory (TDDFT) represents a challenge because common density functionals (GGA, hybrids) often yield a poor description of excited-state potential-energy surfaces. Yet, the calculation of accurate vertical singlet-singlet excitation energies is very important because it is often the first approximation to the prediction of molecular UV-Visible and fluorescence spectra. The performance of GGA and hybrid functionals for vertical excitations is particularly poor in cases when excitations have a significant charge-transfer character where, because of delocalization error, these density functional approximations severely underestimate excitation energies and, occasionally, create fictitious ("ghost") excited states. [1] A common solution for this problem within TDDFT is the use of double-hybrid functionals, but these approximations have a significantly higher computational cost and, often, properties such as excited-state atomic forces, required for geometry relaxations on an excited-state potential energy surface, are not available due to their complexity. The purpose of this study is to develop atom-centered potentials (ACP) in combination with standard hybrid functionals to improve the prediction of vertical excitation energies without affecting the computational cost.[2] ACPs were designed for the B3LYP functional with the def2-TZVPPD basis set, and trained on the QUESTDB set [3], a dataset of accurate vertical excitation energies for simple molecules. Without correction, B3LYP gives a mean-absolute-error (MAE) of 0.258 eV, which decreases to 0.159 eV upon application of the ACP, at no significant increase in cost. To demonstrate the generality of the B3LYP-ACP approach, we apply the new method to a set of BODIPY derivatives for which we gathered experimental UV-Vis absorption wavelengths.[4] The B3LYP-ACP method yields excellent results and mitigates the spurious underestimation of B3LYP. The new methodology offers a general framework for improving other functionals, and a starting point for future research. Overall, ACPs constitute a promising tool for the theoretical analysis of electronic excitations in large molecules combining computational efficiency with high accuracy.

**References:**

[1] C.Adamo, D. Jacquemin, Chem. Soc. Rev, **2013**, 42, 845-856.

[2] A. Otero-de-la-Roza, G.Dilabio, J.Chem.TheoryComput, **2020**,16, 4176−4191

[3] M.Veril et al, **2021**, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 11, e1517

[4] A. Serrano, V. Martínez-Martínez, C. Valdés, unpublished results

# Attempts to Greenly Synthesize Zinc Oxide Nanoparticles and their Structural Evaluations

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**Keywords:** Green Chemistry, ZnO, Nanoparticles, Electron Microscopy.

Green synthesis is gaining particular interest in the recent years owing to its productivity and minor bad impact on our environmental resources. In this study, an attempt was made to rely on antimicrobial plant extracts obtained from different parts of a lemon tree (*citrus x limon*), as a medium to synthesize zinc oxide nanoparticles. Different electron microscopy methodologies such as Scanning electron microscopy, High Resolution transmission electron microscopy, Electron diffraction and energy dispersive X-ray spectroscopy were used to evaluate the outcome of this green synthesis. Zinc Oxide Nanoparticles in the range 5-20nm were obtained. Further experiments are in progress to obtain purified nanoparticles with much narrower size distribution.

**Acknowledgment:**

This research is funded through the Ramon y Cajal grant received by A.A. from the Spanish Ministry of Science and Innovation (RYC2022-038426-I).

**References:**

[1] Yasser A. Sekim. Scientific reports, **2020,** 10:3445.

[2] Tu Uyen Doan Thi, RSC Adv., **2020**, 10, 23899–23907.

# Bringing light to sugars: EDA-driven C-S bioconjugation

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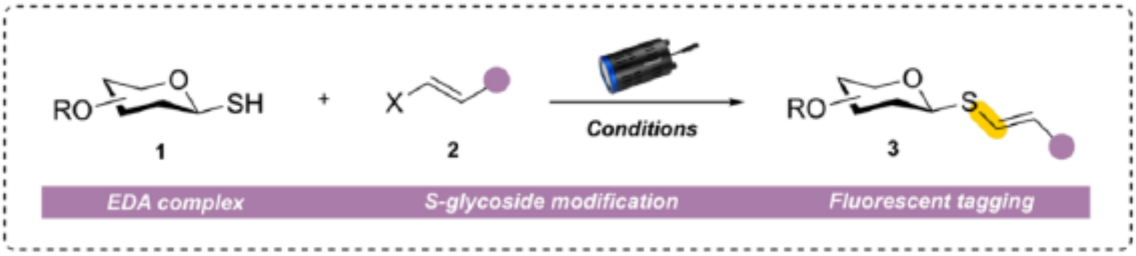
**Keywords:** *Photochemistry, bioconjugation, EDA complex, fluorescent tagging*

Bioconjugation is a key tool in chemical biology for the selective functionalization of biomolecules, particularly in fluorescence-based imaging.[1] Sulfur-containing glycoconjugates are especially attractive due to their enhanced stability and resistance to enzymatic degradation. Traditional C–S bond-forming methods often require harsh conditions, limiting their applicability to sensitive substrates. In contrast, photocatalyst-free approaches based on electron donor–acceptor (EDA) complexes enable radical generation under mild conditions via visible-light-induced single-electron transfer (SET).[2–5] Herein, we report a light-driven, catalyst-free methodology for S-glycosylation based on EDA-complex activation (Scheme 1). This approach provides efficient access to sulfur-linked glycoconjugates with broad functional group tolerance, offering a valuable platform for the synthesis of fluorescently labelled biomolecules with applications in bioimaging and chemical biology.[1]



**Scheme 1.** Catalyst-free photochemical S-glycosylation enabled by EDA complex.

**Acknowledgments:**

Financial support for this work is acknowledged to a Leonardo Grant from Fundación BBVA to M.P.

**References:**

[1] M. S. Hensley, D. Hutchings, A. Ismail, M. Tanasova, *RSC Chem. Biol*. **2025**, *6*, 987–995.

[2] M. Hornink, M. E. C. Thedy, E. Romero, *Chem. Eur. J*. **2025**, e202500284.

[3] G. E. M. Crisenza, D. Mazzarella, P. Melchiorre, J. Am. Chem. Soc. 2020, 142, 5461–5476.

[4] H. F. Piedra, C. Valdés, M. Plaza, Chem. Sci. 2023, 14, 5545–5568.

[5] H. F. Piedra, C. Valdés, M. Plaza, Adv. *Synth. Catal*. **2024**, *366*, 1422–1429.

# Stereochemical Templates for Mechanistic Studies: Gold(I)-Catalyzed C(sp3)—H Functionalization of 1-Bromoalkynes

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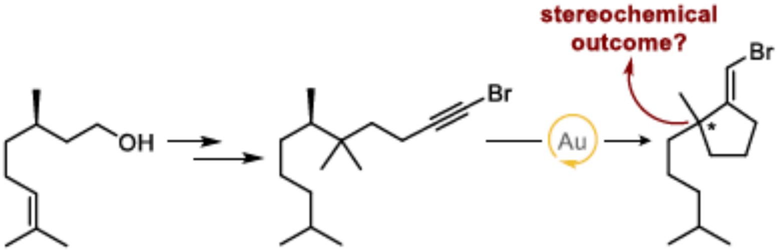
**Keywords:** Stereochemistry, gold-catalysis, 1-bromoalkynes, C(sp3)—H Functionalization

The selective functionalization of non-activated C(sp$^3$)—H bonds is still a key challenge in modern organic synthesis, as it enables the direct transformation of simple hydrocarbons into complex structures.[1] In this context, stereochemistry is not only a synthetic goal for obtaining molecules with specific biological properties but also serves as a fundamental analytical tool. Stereogenic centers enable reaction pathway tracing, as the evolution of chirality reveals the transition state's nature.

This work describes the synthesis of 1-bromoalkyne precursors derived from natural chiral pool templates, specifically terpenes. Our research utilizes this gold(I)-catalyzed cycloisomerization as a mechanistic probe, where the transfer of chirality serves as key evidence to decipher the reaction pathway.[2] Post-catalytic chemical derivatization of the products is performed to facilitate their analysis via chiral HPLC. This synthetic and analytical approach ultimately aims to investigate the reaction mechanism, using stereochemical evidence to confirm the nature of the process.[3]



**Scheme 1.** General workflow.

**Acknowledgments:**

The authors thank the Asturias Regional Government Agency (SEKUENS) for the grant "Fomento de vocaciones científicas" that supported the development of this work.

**References:**

[1] Miguélez, R.; Semleit, N.; Rodríguez-Arias, C.; Mykhailiuk, P.; González, J. M.; Haberhauer, G.; Barrio, P. *Angew. Chem., Int. Ed.* **2023**, 62, No. e202305296.

[2] Arto, O.; Miguélez, R.; Siera, H.; Schulte, J.; Merino, I.; Haberhauer, G.; Barrio, P. *Org. Lett.* **2025**, 27, 11071-11076.

[3] Arto, O.; Miguélez, R.; Moy, B.; Rodríguez-Arias, C.; Alba, P.; Siera, H.; Haberhauer, G.; Álvarez, R.; Burés, J.; Barrio, P. *Submitted*.

# Regioselective Synthesis of Stable Trisubstituted Cyclopentadienones via a Halogenation/Elimination Sequence

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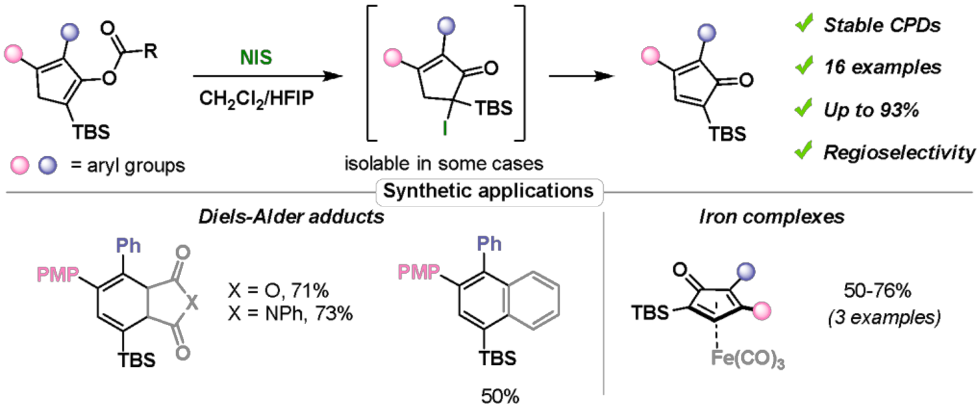
**Keywords:** cyclopentadienones, regioselectivity, cytotoxicity.

Cyclopentadienones (CPDs) are a versatile class of unsaturated compounds that have found broad applications in organic synthesis and catalysis.[1] The reaction of N-iodosuccinimide (NIS) and functionalized cyclopentadienes, previously synthetised in our group,[2] affords 2,3-diaryl-5-silylcyclopenta-2,4-dien-1-ones.[3] The reaction exhibited a reasonable scope providing the corresponding products in moderate to good yields and with complete regioselectivity.

Preliminary studies demonstrated the synthetic versatility of the resulting cyclopentadienone derivatives in the synthesis of highly substituted cyclohexadiene and benzene derivatives via Diels-Alder reaction. On the other hand, the reaction of CPDs and $Fe_2(CO)_9$ resulted in the formation of the corresponding iron tricarbonyl complexes. Preliminary studies showed that several CPDs displayed significant cytotoxicity against different cell lines.



**Scheme 1**. Synthesis and synthetic applications of CPDs.

**References:**

[1] M. A. Ogliaruso, M. G. Romanelli, E. I. Becker. Chem. Rev. **1965**, *65*, 261-367.

[2] O. Bernardo, J. González, J. Borge, L. A. López. Org. Lett. **2022**, *24*, 5203-520.

[3] P. García-Martínez, O. Bernardo, H. C. Bertrand, L. A. López, manuscript in preparation.

# Industrial oil-derived phenolic eutectic mixtures as effective solvents for the Morita-Baylis-Hillman reaction.

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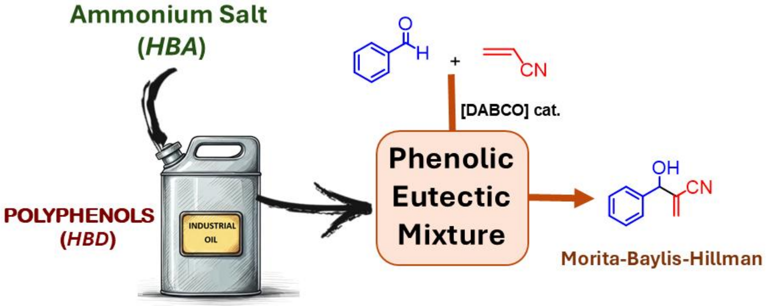
**Keywords**: Deep Eutectic Solvents, phenol extraction, industrial oil, Morita-Baylis-Hillman

Phenolic compounds, of high industrial relevance, are formed by the thermal decomposition of oxygen-containing structures present in coal during the carbonization process and are transferred into coal tar, a by-product of coke production. During subsequent coal tar processing, these compounds are mainly concentrated by distillation into the light oil fractions, where they affect the physicochemical properties of the oils. Their extraction using conventional methods, such as extraction with basic media, generates residues that, in turn, require further treatment. This work considers the use of Deep Eutectic Solvents (*DES*s) as a sustainable alternative for this extraction. In this regard, *DES*s, have demonstrated high efficiency in the extraction of phenolic compounds from complex organic matrices.[1]

Therefore, in the present work we describe the use of different quaternary ammonium salts to extract phenolic compounds from industrial oils through the formation of an [ammonium salt/phenolic mixtures] eutectic system. This approach allows, on the one hand, the extraction of valuable phenolic compounds from the treated oils and, on the other hand, the generation of eutectic mixtures derived from waste industrial oils as potential sustainable reaction media for carrying out chemical transformations of interest. In this sense, this eutectic mixture has been demonstrated to constitute an effective reaction medium for the Morita-Baylis-Hillman reaction.[2]



**References:**

[1] L. Zhao, H. Cheng, Z. Qi, Ind. Eng. Chem. Res. **2024**, 63, 10761−10772.

[2] M. Ramos-Martín, I. del Rio, J. García-Álvarez, A. Presa Soto, ChemSusChem **2026**, 19, e202501674 (1 of 9).

# Tuning Kraft Lignin and Black Liquor by Acid Selection: A Standardized Eight-Acid Study.

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**Keywords:** Black liquor, lignin, acid precipitation, valorization, biorefinery

The Kraft process generates large volumes of black liquor, a major source of lignin that remains largely underutilized despite its potential as a renewable aromatic feedstock [1]. Acid precipitation is a scalable approach for lignin recovery; however, acid selection not only affects yield but also governs lignin structure, purity and functional properties, as well as the composition of the delignified liquor [2].

In this work, a standardized comparison of eight acids, including both mineral and organic types, was performed to systematically assess their impact on lignin recovery, composition, thermal behavior, antioxidant capacity and odor profile. The results show that mineral acids promote higher recovery but generate lignins with increased inorganic content. Nitric acid exhibits a distinctive behavior, enhancing phenolic accessibility and antioxidant performance. On the other hand, organic acids produce structurally preserved lignins with significantly reduced inorganic content, making them more suitable for high-value applications

In addition, the composition of the delignified liquor is strongly influenced by acid selection, highlighting its potential as a valuable co-product for further valorization. Overall, acid choice emerges as a key tool to tailor lignin properties and optimize both solid and liquid streams for targeted biorefinery applications.

## Acknowledgements

With financial support from the Severo Ochoa Predoctoral Assistance Program. The authors acknowledge funding from the Spanish State Research Agency (AEI) - G-Blend project (PID2024-161375OB-C21) and the Asturias Agency for Science, Business Competitiveness and Innovation (SEKUENS) - project IDE/2024/000695.

## References:

[1] L. Pola, S. Collado, P. Oulego, and M. Díaz, "Kraft black liquor as a renewable source of value-added chemicals," Chemical Engineering Journal, **2022**, vol. 448.

[2] E. Amieva, L. Pola, S. Collado, P. Oulego, P. Á. Calvo, and M. Díaz, "Understanding the relationship between acid precipitation and lignin odor in Kraft Black liquor," Cleaner Chemical Engineering, **2025**, vol. 11.

# Preparation of Fatty Acid Derivatives of Carbohydrate Monomers for Incorporation into Oligonucleotides for Bioconjugation

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**Keywords:** Nucleosides; Oligonucleotides; Organic Synthesis

The field of nucleic acid therapeutics has expanded rapidly, with 24 drugs approved by the FDA, including small interfering RNAs (siRNAs), antisense oligonucleotides (ASOs), aptamers, and mRNAs. Among these, siRNAs stand out for their high specificity and potent genesilencing capability. However, their clinical translation remains limited by challenges such as inefficient cellular delivery, low nuclease stability, and potential off-target effects. To address these issues, diverse chemical modifications have been developed, enhancing siRNA stability and improving gene silencing while minimizing undesired effects.

Efficient delivery to target tissues remains a critical hurdle, requiring successful cellular uptake, endosomal escape, and in vivo activity. In this context, bioconjugation strategies have emerged as promising approaches. Conjugation of siRNAs with peptides, sugars, lipids, and other biomolecules has demonstrated improved membrane permeability, intracellular trafficking, and resistance to degradation. Notably, lipid-conjugated siRNAs have shown enhanced tissue distribution and robust RNA interference activity both in vitro and in vivo. Despite their potential, the synthesis of such conjugates is often complex, costly, and limited by challenging manufacturing processes.

Here, we present a straightforward and scalable strategy for the synthesis of fatty acid–conjugated oligonucleotide monomers compatible with automated solid-phase synthesis. This approach enables direct isolation of modified oligonucleotides, eliminating the need for postsynthetic conjugation, reducing processing time, and improving overall yields. Specifically, nucleoside derivatives functionalized with fatty acid moieties via a reactive amino group were designed and successfully incorporated into various oligonucleotide sequences. The synthetic route relies on readily accessible α- or β-cyano sugar derivatives, which are suitable for largescale production. This methodology provides an efficient platform for the development of lipidmodified oligonucleotides with potential therapeutic applications.

# Synthesis and characterization of Ru and Rh nanoclusters as innovative labels for determination of target biomolecules

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**Keywords:** Metal Nanoclusters; Immunoassays; Multimodal biomolecules detection; ICP-MS; Electroanalysis

Over the last decade, advances in nanotechnology have introduced a new class of labels known as metal nanoclusters (MNCs), with particle sizes ranging from 0.2 to 3 nm. MNCs are composed of a few to several hundred metal atoms, and their surfaces can be tailored with specific functional groups to support different chemistries. MNCs can exhibit strong fluorescence, high photostability, and good biocompatibility; therefore, they represent a promising alternative to conventional fluorescent labels used in bioanalytical applications [1]. Additionally, these small nanostructures provide high signal amplification when used as elemental labels in inductively coupled plasma - mass spectrometry (ICP-MS). Some MNCs can exhibit catalytic properties, enabling their use in electroanalytical detection techniques.

Stable MNCs of Au, Ag, Pt, Ir and Pd have been successfully used in analytical platforms, taking advantages of their performance for ICP-MS, electrochemical assays, and fluorescence detection. However, expanding the range of metal compositions remains essential to broaden their analytical applicability. The combination of multiple MNCs with ICP-MS, particularly when coupled to a time-of-flight mass analyzer, enables the simultaneous determination of several analytes. This multiplexing capability is especially attractive in clinical applications, where only low sample volumes are often available. On the other hand, the possibility of performing multimodal detection (combining fluorescence, MS, and electroanalysis) offers a versatile and robust analytical approach with improved reliability and sensitivity.

In this work, we describe the synthesis, characterization and analytical evaluation of lipoate-stabilized RuNCs and RhNCs as promising multimodal probes. The use of lipoate ligands ensures precise size control, high colloidal stability and surface functionality compatible with direct antibody bioconjugation, enabling their application in immunoassays. In both cases, fluorescence properties, catalytic activity, and signal amplification provided by ICP-MS detection were evaluated. As a case study, the IgE protein was selected as the target analyte.

**Acknowledgments:**

This work was financially supported through projectd PID2022-137319OB (-C21 and -C22) funded by MCINN/AEI/10.13039/501100011033/ FEDER, UE and IDE/2024/000694 by the Government of the Principality of Asturias and FEDER Program of the European Union through SEKUENS Agency. Clara de Lorenzo acknowledges the FPI Grant with ref. PREP2022-000181.

**References:**

[1] A. Lores-Padín, P. Menero-Valdés, B. Fernández, R. Pereiro, Anal. Chim. Acta 1128 (**2020**) 251–268.

# Development of a single-step methodology for the determination of transferrin–iron binding ratios *via* gold nanoclusters and ICP-MS: application to serum samples from stroke patients

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**Keywords:** stroke, ICP-MS, magnetic beads, gold nanoclusters

Stroke is the second leading cause of death worldwide and a major contributor to long-term disability, according to the World Health Organization (WHO). It is classified as ischemic, caused by vascular occlusion, or hemorrhagic, resulting from vessel rupture. At present, diagnosis is mainly done by computed tomography and magnetic resonance imaging since the blood–brain barrier restricts the access to clinical circulating biomarkers.

Transferrin, an iron-binding glycoprotein responsible for iron transport in plasma, can bind up to two iron ions per molecule. It is associated with oxidative stress and inflammatory processes, both implicated in stroke pathophysiology. Elevated transferrin iron saturation has been identified as a risk factor for stroke and is linked to more severe brain damage in ischemic events. Therefore, the simultaneous quantification of transferrin and its iron saturation in serum may provide valuable information for stroke differential diagnosis.

In this study, two analytical methodologies were developed for the simultaneous determination of transferrin and its bound iron using inductively coupled plasma - mass spectrometry (ICP-MS). Two sandwich immunoassay formats, magnetic beads and plate-based functionalization, were optimized and compared. Transferrin was immobilized using a monoclonal anti-transferrin antibody, and detection was carried out with a secondary antibody labelled with gold nanoclusters, enabling high signal amplification and sensitive ICP-MS quantification. Key experimental parameters, including antibody concentration, incubation time, and blocking conditions, were carefully optimized to achieve sufficient sensitivity for the determination of the transferrin and its iron bounded.

**Acknowledgments:**

This work was financially supported through project PID2022-137319OB-C21 (Ministerio de Ciencia e Inovación, Spain) and project IDE/2024/000694 of the Government of the Principality of Asturias and FEDER Program of the EU through SEKUENS Agency. Marta Marina-Latorre acknowledges a grant from "Severo Ochoa Program" with Ref. PA-23-BP22-183 funded by Principality of Asturias (Spain).

# Spin Crossover Nanoparticles

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**Keywords:** Nanoparticles, spin-crossover, sensors, information storage.

Spin Crossover (SCO) materials are pivotal for molecular electronics and data storage due to their spin-state-dependent properties. This work presents the synthesis and characterization of [Fe(Htrz)$_2$(trz)](BF$_4$) nanoparticles using IR spectroscopy and Differential Scanning Calorimetry (DSC). By employing a reverse micelle technique (sodium dioctyl sulfosuccinate/n-octane), particle size was controlled; higher surfactant ratios yielded smaller nanoparticles. DSC analysis confirmed that reducing particles to the nanometric scale significantly broadens the hysteresis loop—up to 10 °C compared to bulkier samples. This underscores the critical role of cooperativity and surface effects in bistable SCO systems. These findings advance the miniaturization of SCO-based storage, targeting the eventual development of single-molecule devices.

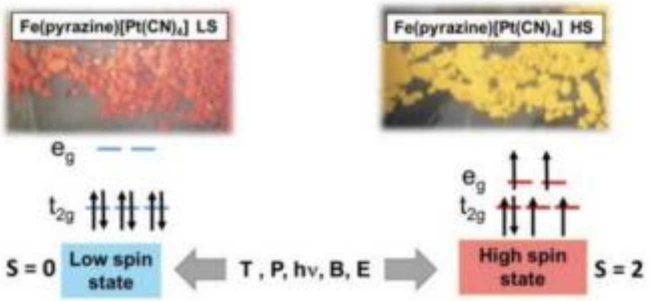

***Figure 1***. *General mechanism of SCO (example shown for a Hofmann-type clathrate).*

**Acknowledgments:**

Daniel García Vivó, professor of the Inorganic Chemistry Department of the University of Oviedo and supervisor of this project.

## References:

[1] P. Gütlich and H. A. Goodwin," Spin Crossover – An Overall Perspective," ChemInform, 36 (2), **2005**.

[2] T. Delgado and M. Villard," Spin Crossover Nanoparticles," J. Chem. Educ., 99 (2), 1026–1035, **2022**.

[3] Y. Fang et al.," Understanding of cooperative effects in molecule-based spin transition materials," Coord. Chem. Rev., 500, 215483, **2024**.

# Anionic Mo–Phosphinidene: A Gateway to Divergent Reactivity

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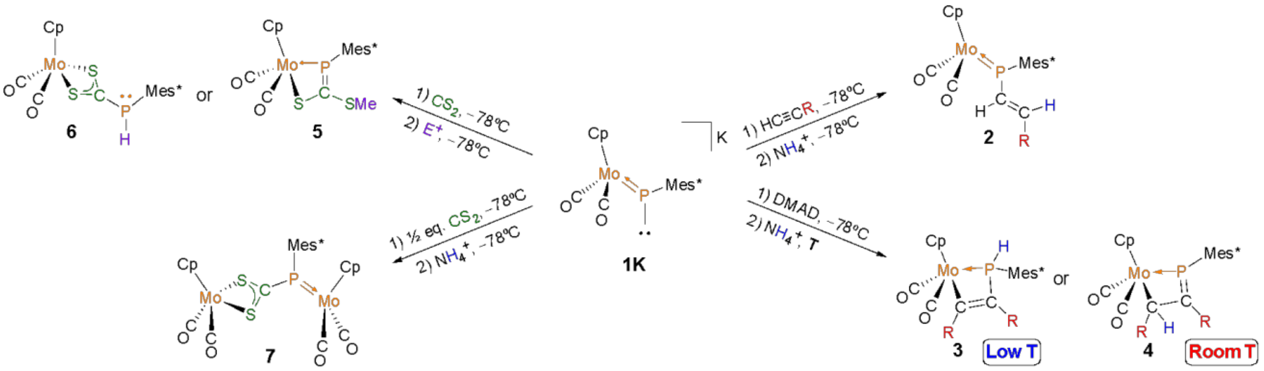
**Keywords:** phosphinidene, organometallic, anionic phosphinidene, nucleophile.

Transition metal phosphinidene complexes are a scarce family of compounds that display rich chemical behaviour, enabling novel functionalization at the P center through formation of new P–element bonds. Anionic phosphinidene complexes are even rarer, and their chemistry remains largely unexplored despite their expected higher P nucleophilicity.[1] In this context, our group recently reported the synthesis of the lithium salt of $[MoCp(CO)_2(PMes^*)]^-$ (Mes* = 2,4,6-$C_6H_2{}^tBu_3$), and its reactivity towards $[ML_nX]$ (X = Cl, Br, I) complexes, affording new heterometallic phosphinidene-bridged complexes.[2] Herein, we present further studies on the reactivity of these species towards C-based electrophiles. The potassium salt of $[MoCp(CO)_2(PMes^*)]^-$ was generated by deprotonation of $[MoCp(CO)_2\{P(H)Mes^*\}]$ with KH in THF at room temperature (**1K**). This anion reacts rapidly at −78 °C with activated alkynes. Reaction with methyl propiolate leads to regioselective P–C bond formation at the less hindered carbon, yielding a phosphorus-substituted alkene after protonation (**2**). In contrast, reaction with dimethyl acetylenedicarboxylate (DMAD) followed by protonation affords four-membered metallacycles via P–C and Mo–C bond formation, with protonation at either P (**3**) or C (**4**), with the ratio **3**/**4** being temperature-dependent. Reactivity with $CS_2$ strongly depends on conditions and subsequent electrophile. Treatment with MeI gives a phosphametallacycle with S-coordination to the metal and selective S-methylation (**5**), whereas protonation leads to formal insertion of $CS_2$ into the Mo=P bond, forming a $\kappa^2{}_{S,S'}$-dithioacetate ligand with protonation at P (**6**). Using substoichiometric $CS_2$ (0.5 equiv.) followed by protonation results in a dinuclear phosphanyl complex (**7**).



**Acknowledgments:**

We thank the MICIU/AEI of Spain for financial support (PID2021-123964NB-I00), the SCBI of the Univ. Málaga, for access to computing facilities, and the X-Ray units of the Univ. Oviedo and Santiago de Compostela, for acquisition of diffraction data.

**References:**

[1] Aktaş, H.; Slootweg, J. C.; Lammertsma, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 2102–2113.

[2] Alvarez, M. A., Burgos, M., García, M. E., García-Vivó, D., Ruiz, M. A., Vega, P. *Dalton Trans.*, **2019**, *48*, 14586.

# A DES-Based Voltammetric Sensor for CO2 Detection Exploiting pH Indicator Behavior

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**Keywords:** Deep Eutectic Solvent, pH indicator, CO2 detection, Electrochemical approach

In this study, we present a voltammetric approach for CO2 detection that exploits both the physicochemical properties of DESs and the pH-dependent electrochemical behavior of an acid–base indicator.

Deep eutectic solvents (DESs) are an emerging class of sustainable solvents characterized by good conductivity and low volatility [1], making them promising media for the development of electrochemical gas sensors. pH indicators can exist in protonated and deprotonated forms depending on the acidity of the medium, and these species exhibit different oxidation potentials; notably, the deprotonated form is oxidized at lower potentials than the protonated one [2].

The proposed sensor consists of a screen-printed carbon electrode modified with a thin DES film containing the indicator. The selected DES was reline, a mixture of choline chloride and urea in a 1:2 molar ratio, chosen for its ability to absorb CO2. Phenol red was selected as the indicator due to its suitable pKa.

The anodic voltammetric behavior of phenol red was first investigated in aqueous solution over a range of pH values, revealing a linear relationship between the anodic peak potential and pH. Subsequently, similar experiments were conducted in a deep eutectic solvent (DES) medium, where comparable behavior was observed. Based on these findings, sensors based on a reline/phenol red thin film were employed to evaluate CO2 levels in synthetic atmospheres and in the headspace of selected fruits and vegetables. The results obtained were compared with those from a nondispersive infrared (NDIR) sensor for carbon dioxide measurement.

These findings demonstrate the possibility of this approach for CO2 detection during the ripening process, highlighting its potential application for monitoring CO2 levels in food storage environments.

**Acknowledgments:**

This research was supported by co-funded resources from the European Social Fund Plus

(FSE+) under the Regional Programme of the Autonomous Region Friuli Venezia Giulia.

**References:**

[1] Abbott, Andrew P., et al. "Novel solvent properties of choline chloride/urea mixtures." Chemical communications 1 (**2003**): 70-71.

[2] González-López, Andrea, et al. "Electrochemical detection for isothermal loop-mediated amplification of pneumolysin gene of Streptococcus pneumoniae based on the oxidation of phenol red indicator." Analytical Chemistry 94.38 (**2022**): 13061-13067.

# Mannich reaction with organozinc reagents in continuous flow: experimental and computational studies

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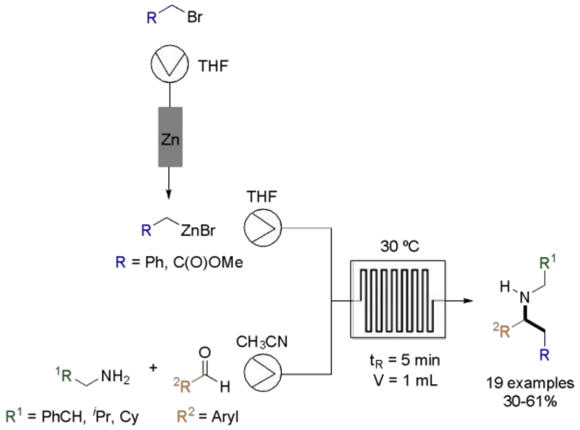
**Keywords:** Continuous flow, Mannich reactions, Organozinc reagents, DFT studies.

The Mannich reaction is essential for synthesizing pharmaceuticals, yet traditional batch methods using organozinc reagents face safety and efficiency hurdles. This research introduces a continuous-flow protocol to overcome these issues.

The two-stage system generates organozinc reagents in a packed-bed reactor before combining them with aldehydes and amines in a microchip reactor. Optimal conditions—3 equivalents at 30°C for 5 minutes—yielded secondary amines up to 61%. DFT calculations confirmed an $S_N1$ pathway involving organometallic dimers, explaining the reagent requirements. Ultimately, this integrated flow approach offers superior safety, throughput, and reproducibility compared to conventional batch synthesis.



**Scheme 1**. Continuous flow setup for representative organozinc Mannich reactions

**Acknowledgments:**

I would like to thank my research group, OSOS, particularly my supervisor, Enol López, for his guidance in this research.

**References:**

[1] R. Fan. D. Pu. L. Qin. F. Wen. G. Yao. & J. Wu, J. Org. Chem. **2007**, 72, 3149-3151.

[2] M. Pinaud. E. Gall. & M. Presset, J. Org. Chem. **2022**, 87, 4961-4964.

[3] N. Alonso. L.Z. Miller. J. De M Muñoz. J. Alcázar. & D.T. McQuade, Adv. Synth. Catal. **2014**, 356, 3737-3741.

[4] L. Fraile-González. Á. Sánchez-González. L.F. Peña. & E. López, RSC Adv. **2026**, 16, 14251-14258.

# Merging Redox Enzymes with Wittig Olefination in One-pot for the Stereoselective Synthesis of Allylic Alcohols

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**Keywords:** Allylic alcohols, Aryl-Alcohol Oxidase, Biocatalysis, Chemoenzymatic Cascade.

Aryl-alcohol oxidases (AAOs) are flavin-dependent enzymes that catalyze the selective oxidation of alcohols to the corresponding aldehydes under mild and environmentally friendly conditions[1]. In previous studies, we described the discovery and characterization of a novel AAO from Streptomyces hiroshimensis (ShAAO) and demonstrated its utility as catalyst for the scalable synthesis of aldehydes and enantioenriched intermediates via chemoenzymatic cascades[2,3].

Herein, we report the development of a three-step one-pot chemoenzymatic cascade for the stereoselective synthesis of secondary allylic alcohols. This strategy takes advantage of the compatibility of the Wittig reaction with aqueous media and its integration with biocatalytic systems[4]. Overall, it comprises the ShAAO-catalyzed oxidation of primary alcohols, in situ Wittig olefination with stabilized ylides, and a final stereoselective bioreduction of the resulting α,β-unsaturated ketones. The scope of the chemoenzymatic cascade was evaluated using a broad range of aromatic primary alcohols, as well as different ylides, demonstrating high versatility and efficiency. Furthermore, the synthetic potential of this methodology was highlighted through the stereoselective synthesis of the antiepileptic drug (R)-Stiripentol.

**Acknowledgments:**

NAC-AT-PUB-ASV-2025 BP24-53, PID2024- 155419NB-I00, SEK-25-GRU-GIC-24-054.

**References:**

1.- P. Cinca Fernando, A. Vázquez Rodríguez, J. Mangas Sánchez, M. Martínez Júlvez, E. Sevilla, P. Ferreira, Applied Microbiology and Biotechnology, **2025**, 109, 151.

2.- P. Cinca Fernando, C. Ascaso Alegre, E. Sevilla, M. Martínez Júlvez, J. Mangas Sánchez, P. Ferreira, Applied Microbiology and Biotechnology, **2024**, 108, 498.

3.- C. Ascaso Alegre, P. Cinca Fernando, T. L. Roberts, P. López Fernández, R. P. Herrera, S. C. Cosgrove, P. Ferreira, J. Mangas Sánchez, Organic Letters, **2025**, 27, 12086–12091.

4.- A. J. C. Wahart, L. N. D. Beardmore, R. A. Field, S. C. Cosgrove, G. J. Miller, Organic Letters, **2024**, 26, 6642–66

# Chemoselective Concurrent Meyer-Schuster/C-P Bond Formation Controlled by Brønsted Acidic Deep Eutectic Solvents

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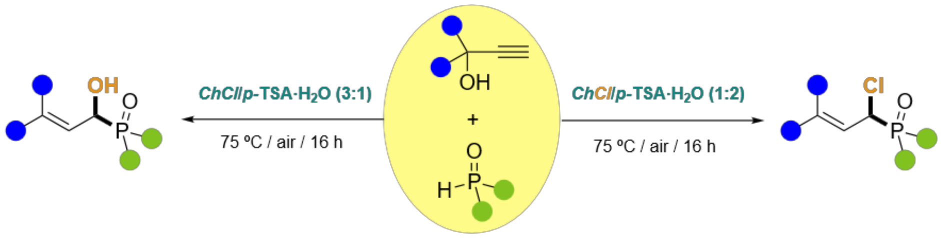
**Keywords:** Deep Eutectic Solvents, one-pot, chemoselectivity.

One-pot tandem methodologies offer powerful opportunities to enhance step economy while reducing waste, energy input and operational complexity [1], thereby directly aligning with the *Principles of Green Chemistry* [2]. Herein, we present an unprecedented fully concurrent, metal-free Meyer Schuster/C-P (and C-Cl) bond-forming protocol enabled by Brønsted Acidic Deep Eutectic Solvents (*BADESs*), which act simultaneously as solvent, promoter and chemoselectivity controller of the reaction outcome [3]. Remarkably, and just by simple modulation of the *HBA*/*HBD* ratio within the same *BADES* system, this methodology allows predictable switching between the selective formation of *α*-hydroxy or *α*-chloro allyl phosphine oxides. Moreover, the products generally precipitate from the reaction medium and can be isolated by simple filtration, thus avoiding the use of toxic and non-renewable volatile organic solvents during the synthesis or the final isolation/purification steps.



**Scheme 1**. Chemoselective one-pot tandem Meyer-Schuster/C-P (and C-Cl) bond formation promoted by different eutectic mixtures of choline chloride (*ChCl*) and *p*-toluenesulfonic acid *p*-TSA·$H_2O$.

**Acknowledgments:**

PID2023-148663NB-I00, PREP2023-001085

**References:**

[1] Y. Hayashi, *Acc. Chem. Res.* **2021**, *54*, 1385-1398.

[2] P. T. Anastas, J. C. Warner, *Green Chemistry Theory and Practice*, Oxford University Press, Oxford, **1998**.

[3] For other examples related with the use *BADESs* in organic synthesis, see: a) G. Morís-Menéndez, S. E: García-Garrido, P. García-Álvarez, A. Presa-Soto, N. Ríos-Lombardía, J. García-Álvarez, *Adv. Synth. Catal.* **2025**, *367*, e20250038; b) M. Ramos-Martín, J. García-Álvarez, A. Presa-Soto, *ChemSusChem* **2025**, *18*, e202500679.

# Hydrothermal Alkaline Treatment of Kraft Lignin: Temperature Effects on Organic Acid Production

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**Keywords:** Kraft lignin, alkaline depolymerization, organic acids, hydrothermal treatment.

Kraft lignin, the predominant byproduct of pulp and paper production (~50-60 Mt annually, <5% valorized beyond energy recovery), constitutes an abundant aromatic biomass resource with a huge potential for biorefinery applications within circular economy paradigms. Spain's ~50 paper mills generate ~400,000 t/year, representing a substantial untapped chemical feedstock with transformative potential beyond conventional combustion [1].

This investigation systematically evaluates the temperature-dependent (170, 195, 220°C) hydrothermal alkaline depolymerization of industrial Kraft lignin (10 wt% lignin, 3.5 wt% KOH) under wet oxidation conditions over an 8 h reaction time for organic acids production. Process dynamics were comprehensively characterized through total organic carbon (TOC) analysis, pH evolution tracking, UV-Vis absorbance spectroscopy at 436 nm (aromatic moieties), 525 nm (conjugated phenolics), 620 nm (polychromatic structures), and HPLC quantification of organic acids [2].

Temperature exerts decisive control over both conversion efficiency and product speciation profiles. TOC concentration increases from 4–6 g/L at 170°C (pH 8–9) to 10–13 g/L at 220°C (pH 5–6), reflecting intensified C–C bond scission counterbalanced by competing mineralization pathways. HPLC analysis identifies acetic (4-10 g/L) and formic (2-8 g/L) acids as the major products, followed by succinic (up to 6 g/L), propionic (≤2 g/L), and adipic (2 g/L) acids. The acids form sequentially: maleic/fumaric dominate early (0-50 min, 0.5-1 g/L), succinic/propionic/adipic peak during intermediate phase (80-170 min), and acetic/formic predominate in final stabilization (>200 min). Temperature-dependent yield variations reflect these sequential interconversions between acid intermediates.

UV-Vis analysis reveals two distinct colour peaks that track reaction progression, first peak at 80 minutes across all temperatures with maximum 525 nm absorbance indicating phenolic intermediate formation; second peak occurring earlier at higher temperatures (170→220°C) reflecting maximum phenolic cleavage, followed by final decolorization. This study establishes temperature-optimized wet oxidation as an industrially viable platform for high conversion of waste Kraft lignin into selective $C_2$–$C_6$ organic acid streams, providing definitive kinetic and physicochemical design criteria for sustainable biorefinery implementation.

## Acknowledgments:

The authors acknowledge funding from the Spanish State Research Agency (AEI) - G-Blend project (PID2024-161375OB-C21) and the Asturias Agency for Science, Business Competitiveness and Innovation (SEKUENS) - project IDE/2024/000695.

## References:

[1] S. Sutradhar, N. Alam, L. P. Christopher, P. Fatehi, Catalysis Today 404 (**2022**) 49–62. https://doi.org/10.1016/j.cattod.2022.08.007

[2] L. Pola, S. Collado, P. Oulego, M. Díaz, J. of Env. Chem. Eng. Volumen 7. **2019**. https://doi.org/10.1016/j.jece.2019.103472

# Turning Brewery Waste into Value: Efficient Caffeine Removal from Wastewater Using Spent Grains

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**Keywords:** lignocellulosic biowaste, biomass pretreatment, adsorption, second-generation biorefineries, microcontaminants

Contaminants of emerging concern (CECs) are receiving growing attention due to their persistence and ecological impact, as well as the recent strengthening of European wastewater regulations. Among them, caffeine is a widely detected anthropogenic marker in wastewater and a relevant target for removal due to its reported toxicity in aquatic systems. This work evaluates brewer's spent grain (BSG), a low-cost lignocellulosic by-product of the brewing industry, as an adsorbent for caffeine removal. Raw, milled, and fractionated BSG samples obtained by hot water extraction (HWE) and dilute acid hydrolysis (AH) were characterized and tested in batch adsorption experiments using 500 µg·L-1 caffeine.

Compositional analysis showed that BSG was mainly composed of hemicellulose (42.5%), followed by lignin (21.6%), cellulose (16.1%), and starch (11.1%). Fractionation altered its structure substantially: HWE preserved the polysaccharide matrix, whereas AH yielded a lignin-enriched solid. AH-treated BSG achieved the highest caffeine removal, reaching 29.2% after 24 h, while raw, milled, and HWE-treated samples showed lower performance (8.37–24.6%). This improvement is attributed to the higher lignin content, which provides aromatic and hydrophobic domains that favour interactions with caffeine.

Overall, this study demonstrates that simple fractionation strategies can significantly improve the adsorption properties of lignocellulosic waste. The results highlight the potential of BSG as a sustainable material for water treatment applications, supporting circular economy approaches by transforming industrial waste into value-added functional adsorbents.

**Acknowledgments:**

This study is part of BAPUR project, which has received funding from the M-ERA.NET 2023 call (grant agreement No 958174). Funding received from MICIU/AEI/10.13039/501100011033/UE and the European Union.

**References:**

[1] O.P. Gbenebor, O.A. Olanrewaju, M.A. Usman, S.O. Adeosun, Polymers, **2023**, 15, 1-14.

[2] S.A.L. Bachmann, K.G.P. Nunes, T. Calvete, L.A. Féris, Emergent Mater, **2023**, 6, 741-753.

[3] M. Fakioğlu, Y. Kalpaklı, RSC Adv., **2022**, 12, 26504-26513.

# Graphene-based inkjet-printed electrochemical sensors for multi-analyte detection

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**Keywords:** graphene materials, ink formulation, inkjet printing, electrochemical sensors

Electrochemical sensors have emerged as promising alternatives to conventional analytical techniques for the detection of target analytes, including biologically relevant molecules such as dopamine (DA) and water contaminants of emerging concern (WCECs) such as acetaminophen (ACF). Beyond providing reliable and accurate measurements, they offer key advantages including low cost, ease of automation and simple miniaturization, making them attractive for a wide range of applications.

Instead of traditional electrochemical sensors, such as modified glassy carbon (GCEs) and screen-printed electrodes (SPEs), inkjet-printed electrodes (IPEs) fabricated with graphene-based active materials have gained attention as an innovative technology. This novel fabrication route enables scalable and cost-effective production while improving the sensor design and providing good electrochemical performance with high selectivity and sensitivity, enabling point-of-care measurements [1].

This work focuses on the design, fabrication and optimization of IPEs with robust analytical performance for the selective detection of ACF and DA. To achieve this goal, three key aspects are examined in depth: (i) the formulation of graphene-based inks; (ii) the optimization of printing parameters, and (iii) post-processing strategies aimed at enhancing the electrochemical performance of the resulting IPEs.

**Figure1.** Ink formulation to electrochemical sensing workflow

**Acknowledgments:**

These results are part of the project PID2022-139478OB-100 funded by MICIU/AEI/ 10.13039/501100011033 y por FEDER, UE. L. Quintana also acknowledges her predoctoral contract (PREP2022-000270) associated with this project. The authors also thank SEKUENS (Principality of Asturias Government) and EU-FEDER (IDE/2024/000737) for their financial support.

**References:**

[1] G. Hanrahan, D.G. Patil, J. Wang, Electrochemical Sensors for environmental monitoring: design, development and applications, Journal of Environmental Monitoring 6 (**2004**) 657-664.

# Micro-LC-ESI-Q-TOF method for simultaneous detection of xenobiotics and metabolites in limited-volume biological matrices

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**Keywords:** micro-LC, xenobiotics, endogenous metabolites, HSS T3

Xenobiotics (e.g., PFAS and plasticizers) are components of the chemical exposome present in human biological fluids at pg/g-µg/g concentration levels, while endogenous metabolites occur at higher concentrations (ng/g-mg/g). [1] Despite their complementary value, LC-MS analyses for these compounds are typically performed separately after class-specific extractions, reducing matrix interferences but limiting applicability to low-volume samples.

In this work, a micro-LC-ESI-Q-TOF method was developed for the simultaneous detection of xenobiotics and endogenous metabolites. Two reversed-phase columns (Acquity UPLC HSS T3 and BEH C18, Waters) and a hydrophilic interaction column (Acquity UPLC BEH HILIC, Waters) were evaluated under multiple gradient programs at 0.075 mL/min in positive and negative ionization modes. A mixture of 80 xenobiotics (10 ppb) and 79 endogenous metabolites (34-1325 ppb) was used to assess chromatographic suitability for expanded chemical coverage of both compound classes. The HSS T3 column yielded the best overall performance with mobile phases consisting of 0.2% formic acid (positive ion mode) and 10 mM ammonium formate (negative ion mode) in water (A) and acetonitrile/isopropanol (B). The optimized method enabled the detection of up to 69 xenobiotics and 60 metabolites considering both ionization modes. Tandem MS analysis further allowed the annotation of 37 and 33 analytes in positive and negative ion modes, respectively, outperforming BEH C18 and HILIC columns in chromatographic and sensitivity metrics across all evaluated compounds. The method is intended for application to limited-volume biological matrices, including human tear fluid, for joint exposome and metabolome profiling.

**Acknowledgments:**

This work was financially supported through coordinate project PID2022-137319OB-C22/Agencia Estatal de Investigación (AEI/10.13039/501100011033) and the PCTI Program of the government of the Principality of Asturias, Spain as well as the FEDER Program of the European Union (IDE/2024/000685). LCAC acknowledges JAEINT_25_02505, financially supported by CSIC, programa JAE. MB acknowledges financial support from grant RYC2022-035852-I funded by MICIU/AEI/10.13039/ 501100011033 and by the FSE+.

**References:**

[1] M. Orešič et al. Environ Int. **2025**, 203, 109741.

# Development of a method for analyzing glutathione redox state in cells using LC-MS/MS with isotope dilution mass spectrometry

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**Keywords:** mass spectrometry, isotope dilution, liquid chromatography, glutathione, oxidative stress.

Glutathione (GSH) is a tripeptide that plays a fundamental role in multiple cellular processes. Under oxidative conditions, two GSH molecules can be oxidized to form glutathione disulfide (GSSG), reflecting the oxidative state of the cell. The regeneration of GSH from GSSG is carried out by the enzyme glutathione reductase. This system maintains a high GSH/GSSG ratio indicating a healthy cellular environment with low oxidative stress conditions. Alterations in the GSH/GSSG ratio can be associated with diseases such as diabetes mellitus, Alzheimer's disease and Parkinson's disease, so it can be used as an oxidative stress biomarker [1]. Due to the low concentration of GSSG relative to GSH, its determination requires a highly sensitive and reliable method. Several analytical methods have been reported to quantify both forms, however, many of these approaches suffer from limitations such as low sensitivity, lack of selectivity, time-consuming derivatization, and the risk of artificial oxidation during sample preparation. This work focuses on the development of a method for the simultaneous quantification of both analytes in cell cultures using isotope dilution mass spectrometry (IDMS). The analysis is conducted using high-performance liquid chromatography coupled to a triple quadrupole tandem mass spectrometry with electrospray ionization (LC–ESI-MS/MS). To prevent glutathione oxidation the thiol group is derivatized using N-ethylmaleimide (NEM). Optimal conditions for chromatographic separation and ESI-MS/MS detection of GSSG and GSH-NEM, as well as their labelled analogues, are presented. Satisfactory recoveries were obtained in both standards and in fortified cell culture matrix. The optimized method allows accurate, sensitive, and specific simultaneous quantification of GSSG and GSH–NEM in cell culture samples.

**Acknowledgments:**

Proyecto PID2024-159562NB-I00 financiado por MCIU / AEI / 0.13039/501100011033 / FEDER, UE. PID2023-151750NB-I00 and PREP2023-000432 (FPI).

**References:**

1. Thiel et al. (**2023**)*. Simultaneous quantitation of oxidized and reduced glutathione via LC-MS/MS to study the redox state and drug-mediated modulation in cells, worms and animal tissue. J Chromatogr B*, 1225, 123742.

# DEVELOPMENT OF A GAS CHROMATOGRAPHY COUPLED WITH TANDEM MASS ESPECTROMETRY METHOD BASED ON ISOTOPE DILUTION FOR THE ANALYSIS OF VERY LONG-CHAIN AND BRANCHED-CHAIN FATTY ACIDS IN HUMAN SERUM

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**Keywords:** fatty acids, peroxisomal disorders, gas chromatography, mass spectrometry, isotopic dilution.

The determination of fatty acids is performed within the field of lipid analysis for different purposes, such as early diagnosis and monitoring of certain diseases, or in the search for new biomarkers. Peroxisomal disorders are a group of rare genetic disorders that cause alterations in several biochemical pathways such as lipid metabolism. The main biochemical alteration observed in this disease is the accumulation of very long chain fatty acids (VLCFA) and branched-chain fatty acids (BCFA) in the brain and other tissues. Consequently, their determination in plasma and serum for diagnostic purposes has already been included in some neonatal screening programmes [1]. The development of reference methods for the determination of VLCFA, such as behenic, lignoceric and cerotic acids, and BCFA, such as pristanic (PRI) and phytanic (PHY) acids, are key tools for the validation of methodologies with lower metrological quality frequently used for the diagnosis and monitoring of peroxisomal disorders. In this context, the main objective of this work is the development of an analytical methodology for the simultaneous determination of VLCFA and BCFAs in serum samples by Isotope Dilution and Gas Chromatography coupled to Tandem Mass Spectrometry (GC-MS/MS). The sample preparation procedure will be optimised, including the derivatization process and the addition of a mixture of isotopically labelled analogues to the serum sample at the beginning of the analytical process to correct for systematic and random errors arising from sample preparation and measurement. Optimal conditions for chromatographic separation and EI-MS/MS detection of fatty acids will also be presented. Finally, the proposed methodology will be validated for the determination of fatty acids in serum samples according to CLSI (Clinical Laboratory Standards Institute) guidelines.

**Acknowledgments:**

Project MCIU-22-PID2021- 125795NB-I00 financed by por MCIU/AEI/ 0.13039/501100011033 / FEDER, UE is acknowledged.

## References:

[1] De Biase I, Tortorelli S, Kratz L, J Steinberg S, Cusmano-Ozog K, Braverman N; ACMG Laboratory Quality Assurance Committee. Laboratory diagnosis of disorders of peroxisomal biogenesis and function: a technical standard of the American College of Medical Genetics and Genomics (ACMG). Genet Med. 2020 Apr;22(4):686-697. doi: 10.1038/s41436-019-0713-9. Epub **2019** Dec 11. PMID: 31822849.

# QUANTITATIVE CHARACTERIZATION OF THYROGLOBULIN IODINATION AND ITS PROTEOFORMS

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**Keywords:** Thyroglobulin, Iodination, ICP-MS/MS

Thyroglobulin (Tg) is a key protein involved in thyroid hormone synthesis, iodine storage, and thyroid-related disorders. Its iodination, a post-translational modification involving the incorporation of iodine into tyrosine residues, plays a central role in these processes. However, quantitative characterization of Tg iodination remains analytically challenging, as current approaches are largely based on indirect measurements or immunoassays that provide averaged and method-dependent values. [1].

In this work, we present a strategy for the absolute and simultaneous quantification of sulfur (S) and iodine (I) in Tg by ICP-MS/MS. The species-independent quantitative determination of both elements enables the direct determination of Tg iodination degree by correlating I/S signal, given the known stoichiometry S:Tg from S-containing Met and Cys amino acid residues. The hyphenation of HPLC to ICP-MS/MS allows the separation of Tg proteoforms, quantified through external calibration with generic standards. Notably, this approach does not require prior enzymatic digestion nor protein-specific standards [2].

Application to human and bovine Tg has revealed a high degree of iodination heterogeneity, with proteoform populations showing different iodine contents. Comprehensive quantification of the iodination degree of Tg proteoform populations was achieved using both global integration and point-by-point analysis along the chromatographic profiles. Thus, this approach overcomes key limitations of existing methodologies and provides a robust and accurate framework for the quantitative characterization of Tg iodination, with significant potential applicability in the study of thyroid physiology and related diseases.

## Acknowledgments:

Project Ref. **PID2022-142323NB-I00**, funded by MCIN. Project Ref. **IDE/2024/000752**. LSF acknowledges the “Severo Ochoa” grant BP24-149. FCC acknowledges the “Ramón y Cajal” grant (RYC2024-048391-I)

## References:

[1] J. T. Dunn, A. D. Dunn, Biochimie, 1999, 81, 505-509. [2] F. Calderón-Celis, N. Sugiyama, M. Yamanaka, T. Sakai, S. Diez-Fernández, J. J. Calvete, A. Sanz-Medel, J. R. Encinar, Anal. Chem., **2019**, 91, 1105-1112.

# Selection of a specific DNA aptamer against Golgi Protein-73

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**Keywords:** Hepatocellular carcinoma, Aptamer, SELEX, Magnetic beads, Golgi Protein-73

Early detection of hepatocellular carcinoma (HCC) remains challenging due to the limited sensitivity of current diagnostic methods at early stages. Golgi protein-73 (GP-73), a transmembrane glycoprotein overexpressed in HCC, shows higher sensitivity and selectivity than alpha-fetoprotein. In this context, DNA aptamers represent promising alternatives to antibodies due to their high affinity and selectivity [1]. This study aims to select a GP-73-specific DNA aptamer for potential application in HCC early diagnostics.

Magnetic bead-based SELEX (MBs-SELEX) was used for aptamer selection over 16 iterative rounds, with increasing stringency achieved by varying DNA and protein concentrations, incubation time, and washing conditions. Maximal selectivity was ensured through negative selection with bovine serum albumin and counter-selection with human serum albumin and transferrin, performed both in solution and on pre-functionalized magnetic beads. After each round, DNA was amplified by PCR, and single-stranded DNA was generated via streptavidin-biotin interactions using biotinylated primers and streptavidin-coated magnetic beads. DNA quantity and purity were assessed using fluorescence-based analysis and E-Gel electrophoresis.

Enrichment analysis identified round 15 as showing the highest binding performance, while selectivity assays confirmed improved discrimination between target and non-target proteins, indicating successful enrichment of specific binders. The selected candidates will be sequenced, structurally characterized, and evaluated for binding affinity using experimental and computational approaches. The ultimate goal is to develop an electrochemical aptasensor for early HCC diagnosis, improving detection and reducing disease burden.

**Acknowledgments:**

This work was supported by the Romanian Ministry of Education and Research, project PN-IV-P1-PCE-2023-1104, grant No. 62PCE/03.01.2025, and by an internal grant from Iuliu Hațieganu University of Medicine and Pharmacy, grant No. 284/33/12.01.**2026**.

**References:**

[1] M. Casian, et al., TrAC, **2025**, 191, 118346

# Optimization and scaling of polyhydroxialkanoates (PHAs) using Dairy dissolved air flotation (DAF) sludge as a substrate.

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**Keywords:** Dairy industry, circular economy, Cupriavidus necator , PHA.

A significant amount of dairy wastewater is produced worldwide, estimated to the range from 4 to 11 million tons per year (Liu et al., 2024). These residues are processed via dissolved air flotation (DAF), separating the lipid rich fraction, called DAF-sludge from the wastewater. Due to the high fat content of DAF sludges, as well as a low nitrogen concentration, this waste is a viable feedstock for polyhydroxyalkanoate (PHA) production.

Thus, the present study aims to assess the production of PHAs by using this DAF sludge as only substrate. including the chemical characterization of the DAF waste and subsequent bioprocess optimization in lab scale and bioreactor of carbon to nitrogen (C/N) ratio, growth curve and PHA concentration. PHA produced was subsequently analysed using H-RMN and FT-IR.

Chemical characterization of DAF sludge revealed a high proportion of lipids 81% (w/w), with high percentage of palmitic, oleic and myristic acids, which are easily metabolized by C. necator (Ridella, F. et al., 2025), as well as an adequate concentration of trace elements. C/N ratio measured approximately 95 (g C/g N), which was modified using $NH_4Cl$ to obtain different C/N ratios, with a C/N of 60 being the best for PHA biosynthesis, with 3,8 g/L in flask experiments using the strain Cupriavidus necator H16. Further scaling up was done in a batch bioreactor, under controlled pH and aeration. The growth curve shows a maximum value at 54 hours, and the maximum PHA accumulation was observed at 56 hours, with a value of 84 % DCW. The final PHA production reached 7,05 g/L, nearly doubling the flask experiment's production.

PHA analysis via H-RMN and FT-IR shows similarities with commercial grade PHB. These results soundly place DAF sludge as a sustainable solution for both wastewater management and bioplastics production.

**References:**

[1] Liu, Y.-C., O'Connor, S., Paulo, L. M., Braguglia, C. M., Gagliano, M. C., & O'Flaherty, V. (**2024**). Effects of food to inoculum ratio and ultrasound pretreatment on biogas production from dissolved air flotation waste from dairy industry. Process Safety and Environmental Protection, 183, 687 697. https://doi.org/10.1016/j.psep.2024.01.058

[2] Ridella, F., Marcet, I., Rendueles, M., & Díaz, M. (**2025**). Long-chain fatty acids assole carbon source in polyhydroxyalkanoates production by Cupriavidus necator H16. Bioresource technology, 417, 131846. https://doi.org/10.1016/j.biortech.2024.131846

# Antioxidant Potential of Oca (Oxalis tuberosa) Peel Extracts from Different Varieties

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**Keywords:** Oxalis tuberosa, Phenolic compounds, Antioxidant activity

Oca (Oxalis tuberosa) is an Andean tuber whose peel represents an underutilized agro-industrial byproduct with potential as a source of natural bioactive compounds [1]. In particular, phenolic compounds present in Oca peel may contribute significantly to antioxidant activity [2], making this matrix of interest within a circular economy approach for food and health-related applications [3].

The aim of this study was to evaluate the antioxidant potential of Oca peel extracts from different varieties through the determination of total phenolic content and radical scavenging activity, complemented by a preliminary chemical characterization.

Phenolic compounds were extracted using a hydroalcoholic solution, and total phenolic content was quantified by the Folin–Ciocalteu method. Antioxidant activity was assessed using the DPPH radical scavenging assay. Additionally, ICP-MS analysis was performed to obtain an overview of the chemical profile of the extracts.

The results showed notable differences among the evaluated varieties. Total phenolic content ranged from 12.09 to 20.53 mg GAE/g extract, while antioxidant activity varied between 460.99 and 813.38 µmol TE/g extract. The variety with the highest phenolic content also exhibited the greatest antioxidant capacity, suggesting a strong correlation between these parameters. ICP-MS analysis revealed the presence of compounds potentially associated with antioxidant activity, supporting these findings.

These results highlight the potential of Oca peel as a sustainable source of natural antioxidants and reinforce the importance of valorizing agro-industrial residues for functional applications.

## Acknowledgments:

The authors gratefully acknowledge financial support from Ministerio de Ciencia e Innovación, Spain (Ref: MCINN-24-PID2023-149453OB-I00) and Regional Commission from Principado de Asturias, Spain (SEK-25-GRU-GIC-24-079).

## References:

[1] E. F. Aurora-Vigo, L. M. Paucar-Menacho, L. M. Anaya-Esparza and M. Schmiele, Oca (Oxalis tuberosa Mol.): An Andean Tuber With Promising Physicochemical, Technological and Nutritional Properties for Potential Industrial Applications, **2025**.

[2] N. Güemes-Vera, A. Bernardino-Nicanor, L. González-Cruz, S. Soto-Simental, A. Quintero-Lira and D. J. Dimas-López, Antioxidant Activity of Oxalis tuberosa Peel Extracts, **2019**.

[3] F. Oré Areche, O. M. Luque Vilca, M. Bautista Vargas, R. J. M. Yapias, A. Ruiz Rodríguez, A. Sanchez Onofre, S. Huaquipaco Encinas, J. A. J. Dominguez, A. V. S. Guarnizo, T. J. C. Rivera and J. Marcía Fuentes, Foods, **2026**, 15, 1004. DOI: 10.3390/foods15061004.

# Biocatalytic synthesis of the antiarrhythmic Procainamide using lipases

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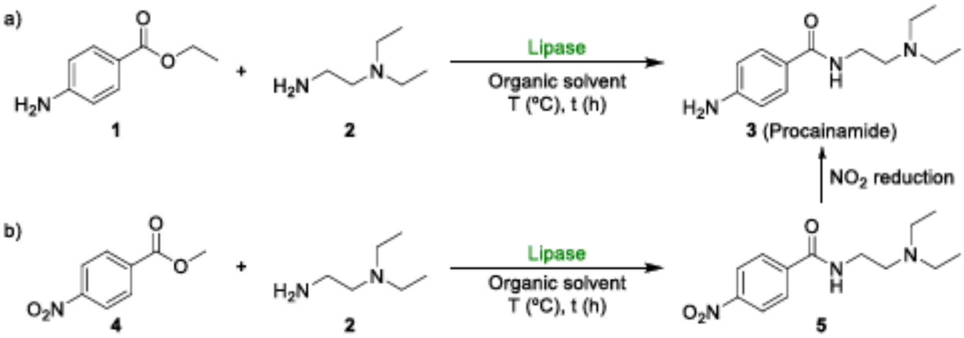
**Keywords:** Aminolysis reaction, Biocatalysis, Lipases, Organic synthesis, Procainamide

Enzymes are highly efficient and selective catalysts to carry out chemical transformations under mild reaction conditions. Among the most widely used biocatalysts are lipases, which have been extensively applied in organic synthesis, for instance towards amide syntheses, due to their catalytic versatility and stability in organic media when used in immobilized forms. In this study, a (chemo)enzymatic strategy is described for the synthesis of the drug called Procainamide, a class IA antiarrhythmic agent that acts by blocking fast sodium channels and modulating electrical conduction in the myocardium.[1] The proposed approach evaluates two complementary routes based on lipase-catalyzed aminolysis reactions using different alkyl benzoates as starting materials either bearing amino or nitro functionalities at the para position.

In the first strategy (Scheme 1a), a lipase-catalyzed aminolysis was studied over ethyl 4 aminobenzoate (**1**) using N,N-diethylethane-1,2-diamine (**2**) as nucleophile. Interestingly, *Candida antarctica* lipase type B (CAL-B) was found to be the best biocatalyst for the synthesis of the targeted amide **3**, although in general with low conversions. In the second strategy (Scheme 1b), the aminolysis process was performed between methyl 4-nitrobenzoate (**4**) and the same diamine to generate an amide intermediate 5, whose nitro group was subsequently reduced to obtain Procainamide (**3**). Procainamide was successfully synthesized and fully characterized after optimization of different variables that affect the CAL-B catalytic activity (organic solvent, temperature, time…) and exploring different approaches for nitro reduction.



***Scheme 1**. Studied (chemo)enzymatic routes towards the synthesis of Procainamide.*

## References:

[1] K. R. DeMarco, C. E. Clancy. Cardiac Na Channels: Structure to Function. Curr. Top. Membr. **2016**, 78, 287–311.

# Tracking Astrocyte Response to Ischemia in a Stroke-on-a-Chip Model via Impedimetric Immunosensing

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**Keywords:** Stroke-on-a-chip; Impedimetric immunosensor; GFAP; Astrocyte ischemia

Organ-on-a-chip technologies have emerged as advanced in vitro platforms capable of replicating key aspects of human tissue structure and function, offering valuable tools to investigate both physiological and pathological processes. In the context of stroke, these systems provide controllable environments to model ischemic injury and evaluate potential recovery strategies. Nevertheless, the monitoring of biochemical markers remains limited, with most studies relying predominantly on imaging-based analyses.

In this work, a simplified 3D stroke-on-a-chip model was combined with an impedimetric immunosensor for the detection of glial fibrillary acidic protein (GFAP), a well-established biomarker of astrocyte activation and injury. Ischemic conditions were first optimized in 2D cultures and subsequently translated into a 3D microfluidic platform based on a previously reported microvascular system, consisting of a collagen hydrogel embedded with astrocytes and a perfusable lumen connected to inlet and outlet channels[1].

The resulting model successfully reproduced key features of ischemic injury, including a significant decrease in cell viability under stroke-like conditions. The developed electrochemical sensor exhibited high sensitivity, enabling the detection of GFAP released into the culture medium. Measurements showed a strong correlation between cell death and GFAP release, confirming astrocyte activation and damage within the 3D system. Overall, this platform provides a robust approach for investigating the response of astrocytes to ischemic events by enabling simple, fast, and sensitive monitoring of protein biomarkers.

## Acknowledgments:

This work was supported by PID2023-148375OB-I00 (MCIU/AEI/10.13039/501100011033/ FEDER, EU ) and IDE/2024/000694 (PCTI, Government of the Principality of Asturias and FEDER, EU). P.R.L. acknowledges funding from the “Severo Ochoa” program (BP21-029) funded by the Government of the Principality of Asturias.

## References:

[1] Cacheux et al., STAR Protocols, **2024,** 5(2), 102950.

# Photothermal Denaturation of Proteins Induced by AuAg Nanorods for Antifouling Film Formation

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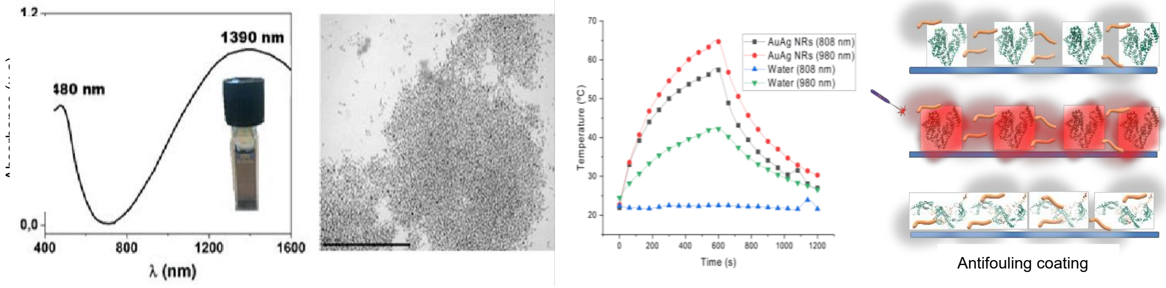
**Keywords:** AuAgNRs, LSPR, phototermal, antimicrobial.

The development of anisotropic plasmonic nanostructures with photothermal activity represents a highly attractive research field with relevant applications in biomedicine and catalysis. In this study, we present a synthetic strategy for the preparation of bimetallic Au–Ag nanorods (NRs) through the controlled reduction of the organometallic precursor $[Au_2Ag_2(C_6F_5)_4(Et_2O)_2]$. In this methodology, oleic acid functions as both a stabilizing and a shape-directing agent.[1,2] Subsequent ligand exchange with poly(ethylene glycol) methyl ether thiol (PEG-SH) provides water dispersibility and biocompatibility, while preserving the size and morphology of the plasmonic nanostructures and maintaining their outstanding plasmonic features. These include a localized surface plasmon resonance (LSPR) band in the visible region (480 nm, transverse mode) and a broad absorption band in the near-infrared region (1390 nm, longitudinal mode).



The longitudinal LSPR band of AuAgNRs enables efficient NIR-to-heat conversion, underpinning their strong photothermal performance. This property was exploited to fabricate antifouling bovine serum albumin (BSA) coatings via plasmonic heating, inducing in situ protein denaturation and yielding uniform films on functionalized silica surfaces.[3]

## References:

[1] Quintana, J., Crespo, J., Falqui, A., López-de-Luzuriaga, J. M., Olmos, M. E., Rodríguez-Castillo, M., & Monge, M. Adv. Phot.Res. **2023**, 4, 220024

[2] Crespo, J., López-de-Luzuriaga, J. M., Monge, M., Olmos, M. E., Rodríguez-Castillo, M., Cormary, B., ... & Falqui, A. (**2015**). Chemical Communications, 51(93), 16691-16694.

[3] Ma, G. J., Ferhan, A. R., Jackman, J. A., & Cho, N. J. Mat. Comm. **2020**, 1, 45.

# Optimized biopolymer sponges for microplastic capture in water

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**Keywords:** sponge, biopolymer, adsorbent, microplastic, water treatment

Microplastics (MPs) represent a major environmental concern due to their small size, low biodegradability, hydrophobicity and ability to cross biological barriers. Conventional water treatment technologies are often ineffective for MPs removal, highlighting the need for alternative approaches. Adsorbent materials such as sponges, hydrogels, and aerogels have emerged as promising candidates, as their three-dimensional hydrophobic networks provide suitable sites for MPs adsorption. In this study, biodegradable sponges were formulated and optimized using gelatin, starch, and chitosan. Each component contributes distinct physicochemical properties to the final structure. The polymers were dissolved under controlled conditions and crosslinked using citric acid and mixed at different concentrations to study their influence on the structure and characteristics of the final sponge. The sponges were characterized in terms of density, porosity, swelling ratio, and morphology (SEM). The optimized ones were then applied to model aqueous systems contaminated with MPs of varying composition and density. Sponge–water interaction was performed under manual agitation and controlled incubation to assess the effect of mechanical energy on removal efficiency. The optimized formulations demonstrated high MPs removal efficiencies under the studied conditions. However, performance varied depending on the type of microplastic, with density identified as a key factor due to its effect on particle behavior within the water column. Additionally, temperature—both during sponge curing and operation—was found to be a limiting parameter affecting material performance. These results highlight the importance of formulation and process optimization in developing biodegradable sponge-based systems for microplastic remediation. Overall, this material shows strong potential for water treatment applications and could be further extended to the removal of other types of contaminants.

## Acknowledgments:

Financial support from BiodivRestore Cofund 2020 and Agencia Estatal de Investigación (BIORESET PCI2022-133007), Ministerio de Ciencia e Innovación and the European Commission (MCINN-24-PID2023-149453OB-I00), Principado de Asturias (SEK-25-GRU-GIC-24-079) and Programa de Ayudas Severo Ochoa (NAC-AT-PUB-ASV-2025BP24-125).

## References:

[1] J. Xu et al., Chem Eng J, **2023,** 475, 146861. [2] J. Fu et al., J Hazard Mater, **2023**, 465, 131685. [3] M. Ko et al., Chemosphere, **2024**, 365, 141956.

## Characterization of Lanthanide-Doped Carbon Quantum Dots for Bioimaging

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**Keywords:** Carbon quantum dots, bioimaging, asymmetric flow field-flow fractionation (AF4), ICP-MS/MS

Carbon quantum dots (CQDs) have attracted increasing interest for bioimaging applications due to their unique physicochemical properties, including biocompatibility, low toxicity, small size, strong fluorescence and low production costs at large scale. Their surface can be easily functionalized, enabling versatile modification and conjugation strategies.

Doping CQDs with lanthanide ions further expands their functionality by introducing additional imaging capabilities beyond fluorescence, including magnetic resonance imaging (MRI) and potentially computed tomography (CT). This multimodal potential makes lanthanide-doped CQDs attractive candidates as advanced diagnostic probes. [1]

The aim of this study is to focus on the multidimensional characterization of functionalized lanthanide-doped carbon dots, with particular emphasis on controlling dopant content, size distribution, and aggregation behavior, both in isolated conditions and in biological media.

To achieve this, an analytical platform based on asymmetric flow field-flow fractionation (AF4) coupled with fluorescence, UV–visible detection, multi-angle light scattering (MALS), and inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) is employed. AF4 enables gentle separation without a stationary phase, minimizing sample alteration while providing detailed insight into nanoparticle size, composition, and stability. [2]

This approach provides a robust analytical platform for investigating doped carbon nanomaterials in biologically relevant environments.

**Acknowledgments:**

Project Ref. PID2022-142323NB-I00, funded by MCIN/AEI/10.13039/501100011033/ and by “ERDF A way of making Europe”. Project Ref. IDE/2024/000752, funded by the Government of the Principality of Asturias through the Asturias Science, Business Competitiveness and Innovation Agency, SEKUENS.

**References:**

[1] A. Salvi, S. Kharbanda, P. Thakur, M. Shandilya, A. Thakur, Carbon Trends **2024**, 17, 100407.

[2] H. S. Ferreira, B. Moreira-Alvarez, A. R. Montoro Bustos, J. Ruiz Encinar, J. M. Costa Fernández, A. Sanz-Medel, Talanta **2020**, 206, 120228.

# $FeCl_3$-Based Lewis Acidic Deep Eutectic Solvent (LADES): Selective and Efficient Promoter for the synthesis of α-chloroketones

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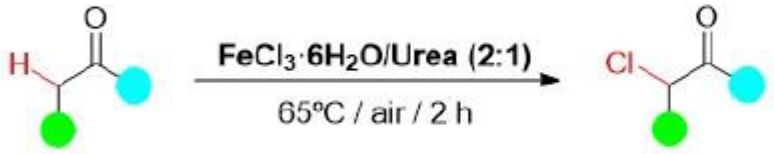
**Keywords:** Lewis Acid Deep Eutectic Solvents, Chlorination, Ketones

Deep Eutectic Solvents (DESs) have emerged as sustainable alternatives to conventional and toxic organic solvents, combining effective solvation properties with the ability to promote organic synthetic transformations within a single reaction medium.[1] In particular, Lewis Acidic Deep Eutectic Solvents (LADESs) based on metalic salts have shown considerable potential in chemical synthesis. Among them, iron-based systems have attracted special interest due to iron's low cost, high natural abundance, low toxicity and versatile redox and Lewis acidic properties, making them especially interesting as sustainable and efficient promoters in organic synthesis.[2] Herein, we present the use of an $FeCl_3$-based LADES as non-innocent reaction media for the selective and efficient synthesis of α-chloroketones (Scheme 1), compounds of high synthetic value.[3] Our system, formed by FeCl3·6H2O and urea, acts both as solvent and promoter, enabling substrate activation and modulation of reactivity. This methodology allows selective α-chlorination of ketones under mild, catalyst-free conditions in air, with good substrate scope and yields, highlighting iron-based LADESs as sustainable halogenation tools.



***Scheme 1.*** *Synthesis of α-chloroketones compounds promoted by FeCl3.6H2O:Urea (2:1).*

**References:**

[1] N. Ríos-Lombardía, J. García-Álvarez, "Deep Eutectic Solvents and Their Applications as New Green and Biorenewable Reaction Media", Ch. 20.3, pp 1619-1655, in Handbook of Solvents, Vol. 2, 4th Edition: Use, Health, and Environment, (Ed. G. Wypych), ChemTec Publishing, Toronto, **2024**.

[2] M. Ramos-Martín, N. Ríos-Lombardía, S. E. García-Garrido, A. Presa Soto, J. García-Álvarez, "Iron-Based Deep Eutectic Solvents: Versatile and Powerful Tools in Sustainable Organic Synthesis", CHIMIA **2025**, 79, 859.

[3] M. Porré, G. Pisanò, F. Nahra, C. S. J. Cazin, "Synthetic Access to Aromatic α-Haloketones", Molecules **2022**, 27, 3583.

# Physicochemical conditions that promote agmatine biosynthesis in Hafnia paralvei

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**Keywords:** U-HPLC method, Biogenic amines, Agmatine, Hafnia spp., Cheese

Agmatine is a biogenic amine formed by decarboxylation of the amino acid arginine that possesses neuromodulatory properties, which has awakened growing interest in its potential application in the development of functional foods against mental disorders such as anxiety or depression. The content of agmatine in foods is very low, so there is a need of enriching strategies to increase its presence in foods. The most consumer-acceptable strategy is the in situ production of agmatine by microorganisms. This study investigated food-related technological factors affecting agmatine production by Hafnia paralvei 7LBE7 (Casado et al., 2025). Agmatine was quantify by liquid chromatography with a previously described protocol (Redruello et al, 2013). This method based on sample derivatization with diethyl ethoxymethylmalonate, followed by ultra-HPLC, allowed for its quantification in less than 10 minutes, making this method one of the fastest ever reported. The proposed method exhibits good linearity ($R^2 > 0.995$) and sensitivity (detection limit 0.08–3.91 μM; quantification limit <13.02μM). Intraday and interday repeatability ranged from 0.35% to 1.25% and from 0.85% to 5.2%, respectively. Agmatine production by H. paralvei 7LBE7 was enhanced an acidic pH, static culture conditions, and the presence of glucose significantly-conditions typically found in fermented dairy products like cheese, whereas agitation, low temperatures, or the use of galactose and lactose reduces agmatine accumulation. These results lay the groundwork for future strategies to optimize agmatine production in fermented food matrices, with the aim of developing functional foods enriched with this bioactive amine.

**Acknowledgments:**

This research received funding from the Spanish Ministry of Economy and Competitiveness (AGL2010-18430) and from the EQUIP10-30 programme (FICYT). The work was also carried out within the framework of the project PID2020-112629RB-100, funded by the Spanish State Research Agency.

**References:**

[1] Redruello, B., Ladero, V., Cuesta, I., Álvarez-Buylla, J. R., Martín, M. C., Fernández, M., & Alvarez, M. A. (**2013**). A fast, reliable, ultra high performance liquid chromatography method for the simultaneous determination of amino acids, biogenic amines and ammonium ions in cheese, using diethyl ethoxymethylenemalonate as a derivatising agent. Food Chemistry, 139(1–4), 1029–1035. https://doi.org/10.1016/J.FOODCHEM.2013.01.071

[2] Casado, A., Fernández, E., Sánchez-Llana, E., Fernández, M., Ladero, V., & Alvarez, M. A. (**2025**). The development of a whole-cell biosensor enabled the identification of agmatine producing Hafnia spp. in cheese. International Journal of Food Microbiology, 427, 110970. https://doi.org/10.1016/J.IJFOODMICRO.2024.110970

# Nanofibrillated Cellulose from Hazelnut Shell Residues for Sustainable Packaging Applications

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**Keywords:** Nanocellulose; Hazelnut shell; Biodegradable materials; Sustainable packaging; Agro-industrial waste.

The transition towards a circular economy requires the valorization of agro-industrial waste into high-added-value products. Hazelnut shell residues are an abundant lignocellulosic by-product with high potential as a renewable cellulose source [1]. This work focuses on the extraction and purification of cellulose from hazelnut shells as a preliminary step for obtaining nanofibrillated cellulose (NFC) for biodegradable packaging applications.

The biomass was dried, milled, and sieved before successive alkaline extractions using 3% w/v NaOH at 80 °C to remove hemicellulose, part of the lignin fraction, and other extractives. The obtained pulp was then bleached using 2.7% w/v sodium chlorite in acetate buffer (pH 4.9) at 80 °C until a purified cellulose fraction with improved whiteness and structural homogeneity was obtained [2].

FTIR confirmed the progressive removal of lignin and hemicellulose, while TGA showed suitable thermal stability for further processing. Finally, the purified cellulose was subjected to TEMPO-mediated oxidation followed by high-shear homogenization to obtain stable NFC suspensions [3]. These results demonstrate that hazelnut shell residues are a viable and sustainable source for producing nanostructured cellulose intended for biodegradable food packaging materials.

## Acknowledgments:

This work was supported by PRIMA-SUN4MED (Sustainable and Novel Food Packaging based on Agro-industrial By-products and Natural Antimicrobials from the Mediterranean Area), project Section 2-2023. International Collaboration Project – Call 2024-1 MCINN-24-PCI2024-153512.

## References:

[1] M. Salgado-Ramos et al., *Ind. Crops Prod.*, **2022**, *179*, 114697.

[2] B. Deepa et al., *Materials*, 2016, *9*, 50.

[3] C. M. Chandrasekar et al., *Int. J. Biol. Macromol.*, **2025**, *333*, 148869.

# Application of 3D carbonaceous structures for metal removal

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**Keywords:** heavy metals; adsorption; 3D printing; carbonaceous materials

Heavy metal contamination in water represents a major environmental and public health concern due to its persistence, toxicity, and carcinogenic potential. These contaminants originate from both natural and anthropogenic sources [1]. Adsorption is widely applied for metal removal due to its efficiency, low cost, and operational simplicity [2]. However, conventional powdered adsorbents present limitations such as difficult separation after treatment and possible secondary contamination. To overcome these issues, three-dimensional (3D) structured adsorbents fabricated via additive manufacturing have recently been explored. In this study, 3D carbonaceous structures (agitator-type) were produced using direct ink writing (DIW) followed by carbonization. Their adsorption performance was evaluated through batch experiments using multielement and monocomponent aqueous solutions, and metal concentrations were determined by ICP-OES following standardized methods. The results showed that the 3D carbonaceous structures exhibited high and selective removal efficiencies. In multielement systems, removal percentages were 97% for Ag, 85% for Bi and 3% for Pb. In monocomponent systems, higher performance was observed for Pb (85%), while Cu removal reached 6%, indicating strong competitive adsorption effects. Additionally, in all experiments an increase in the final concentration of Ca, K, Mg, and Na was observed, suggesting ion release from the material, likely associated with leaching processes or ion-exchange mechanisms. The structured geometry enhanced mass transfer and improved accessibility to active sites, contributing to the observed adsorption behaviour. In conclusion, DIW-fabricated 3D carbonaceous structures demonstrate strong potential for selective heavy metal removal in water treatment; however, their performance is strongly influenced by ionic competition and surface chemistry, highlighting the need for further surface modification strategies.

## Acknowledgments:

The authors acknowledge the support of their respective institutions and laboratories for providing the facilities and resources necessary to carry out this research.

## References:

[1] Abraham, N., James, J., Banerji, T., & Menon, R. (**2020**). Development of a novel groundwater iron removal system using adsorptive Fe(II) process. Groundwater for Sustainable Development, 10. https://doi.org/10.1016/j.gsd.2019.100318

[2] Faria, P. C. C., Órfão, J. J. M., & Pereira, M. F. R. (**2004**). Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. Water Research, 38(8), 2043–2052. https://doi.org/10.1016/j.watres.2004.01.034

# Novel 3D adsorptive stirrers of whey-bone char to the removal of fluorides from water

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**Keywords:** Fluoride removal; Additive manufacturing; Adsorptive stirrer; Process intensification; Whey carbon

Access to safe drinking water is essential for health, and in many regions of the world, groundwater is the primary source of water and is often contaminated; fluoride ($F^-$) is one of the main contaminants found naturally in water supplies in Aguascalientes, Mexico [1]. Specifically, bone char has been widely used to remove fluorides from water, as the effectiveness of this adsorbent in fluoride removal is due to its hydroxyapatite content [2]. However, the use of powdered and/or granular bone char presents problems such as the difficulty of separating the adsorbent material after the adsorption process in batch systems, and a pressure drop in the bed may also occur in semi-continuous systems. In this study, 6 blade stirrers were designed and printed using pastes of whey, bone char, and Milli-Q water on a PRUSA MK3S+ printer modified for printing pastes; they were then cured and carbonized in a tubular furnace under an inert atmosphere. A Taguchi experimental design ($L_9$ orthogonal array) was used to manufacture the stirrers. Four variables (factors) were identified: percentage of bone char in the paste solids, print infill, carbonization temperature, and heating rate. These stirrers were tested in batch systems using a stirred, temperature-controlled reactor, with an initial $F^-$ concentration of 100 mg/L. The results indicate that these stirrers achieve an $F^-$ adsorption capacity of 4.2 mg/g, exceeding that of bone char (2.2 mg/g). These stirrers were also tested using water from a well in Palo Alto, Calvillo, Aguascalientes, Mexico, which had a fluoride concentration of 14.1 mg/L; after the adsorption process, the final concentration was 7.8 mg/L, representing a 44.7 % removal rate.

**Acknowledgments:**

The authors acknowledge the support of their respective institutions and laboratories for providing the facilities and resources necessary to develop this research.

**References:**

[1] S. M. D. U. Islam, "Electrochemical remediation of arsenic and fluoride from water: A review of the current state and future prospects," Environ Technol Innov, vol. 31, p. 103148, **2023**, doi: 10.1016/j.eti.2023.103148.

[2] S. S. A. Alkurdi, R. A. Al-Juboori, J. Bundschuh, and I. Hamawand, "Bone char as a green sorbent for removing health threatening fluoride from drinking water," Jun. 01, **2019**, Elsevier Ltd. doi: 10.1016/j.envint.2019.03.065.

# From industrial waste to bioplastics: microbial valorization by *Cupriavidus necator*

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**Keywords:** Polyhydroxyalkanoates, bioprocess, *Cupriavidus necator*, circular economy.

The generation of by-products in the food industry is currently an environmental and economic challenge of increasing relevance. The production of polyhydroxyalkanoates (PHAs) from organic residues represents a sustainable alternative for bioplastic generation within the framework of the circular economy [1]. In this study, the ability of *Cupriavidus necator* to synthesize PHAs was evaluated using three different waste-derived carbon sources in shake flask cultures: animal fat, cheese whey, and residual oil from canned tuna [2].

Fermentations were carried out at 30 °C and 150 rpm for 72 h under optimized conditions in 1 L shake flasks containing 400 mL of saline medium and 10% (v/v) inoculum. Nitrogen limitation was established to promote PHA accumulation by adjusting the medium composition with $NH_4Cl$ to reach an approximate C:N ratio of 20. Animal fat was previously extracted by Soxhlet, cheese whey was subjected to enzymatic hydrolysis with β-galactosidase as a pre-treatment step, and residual tuna oil was obtained by centrifugation of canned tuna to separate the solid and liquid phases.

PHA accumulation was determined after polymer extraction from the biomass using a chloroform–sodium hypochlorite digestion method. The recovered polymer was subsequently used to obtain films by solvent evaporation of chloroform. In terms of production, tuna oil and cheese whey reached similar maximum PHA concentrations (~4.6 g/L), whereas animal fat showed lower production (~2.7 g/L) and more limited accumulation. These differences are mainly associated with substrate bioavailability and mass transfer limitations.

Overall, these results indicate that while different residues can achieve comparable maximum PHA production, substrate bioavailability and process stability are key factors that determine overall process efficiency. Lipid-based substrates require strategies to enhance accessibility, whereas aqueous substrates such as cheese whey depend critically on efficient pre-treatment.

**Acknowledgments:**

This work was financially supported by the Scientific and Technical Research Foundation (FICYT) of the Principality of Asturias, by the project SEK-25-GRU-GIC-24-010.

**References:**

[1] Boccalon, E. et al., Front. Bioeng. Biotechnol., **2022**, 3177-3204. [2] Zhang, L. et al., Front. Bioeng. Biotechnol., **2022**, 10, 946085.

# One-Pot Stepwise and Consecutive Solvent-Free Reactions with Pd NPs

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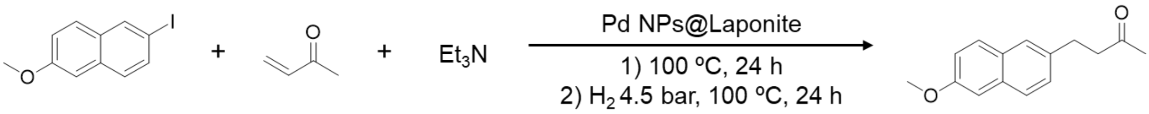
**Keywords:** Pd NPs, Laponite, Sustainability, Recoverable Catalysts, One-Pot

The design of sustainable catalytic processes requires efficient and reusable systems able to combine multiple transformations in a single sequence. Pd NPs supported on solids are attractive catalysts due to their high activity in both C–C coupling and hydrogenation reactions [1–3]. In this work, Pd NPs supported on laponite were evaluated for Heck and Sonogashira reactions followed by hydrogenation under solvent-free conditions, using both one-pot stepwise and sequential approaches.

High conversions and selectivities were obtained for a range of substrates, enabling the efficient synthesis of value-added products while avoiding intermediate purification steps. Catalyst reuse was demonstrated, although a loss of hydrogenation activity was observed after coupling reactions. This behaviour is attributed to the formation of Pd(II) species on the NP surface, as demonstrated by XPS studies, in agreement with a release and capture mechanism operating in the coupling step [4]. However, the catalytic activity for hydrogenation can be restored by simple reduction, confirming the reversible nature of this process.



**Scheme 1**. Example of one-pot stepwise synthesis of a high-value-added product..

**Acknowledgments:**

We acknowledge the financial support of the Agencia Española de Investigación (PID2021-125762NB-I00) and Gobierno de Aragón (group 23_37R).

**References:**

[1] P. T. Anastas, N. Eghbali. *Chem. Soc. Rev.* **2010**, 39, 301–312.

[2] A. V. Martínez et al. *RSC Adv.* **2015**, 5, 59983-59990.

[3] A. Leal-Duaso et al. *ACS Sustain. Chem. Eng.* **2021**, 9, 6875-6885.

[4] J. Cambronero-Arregui et al. *J. Catal.* **2026**, 458, 116860.

# Design and Application of Glycerol-Based Protic Ionic Liquids in Aza-Michael Reactions

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**Keywords:** Green chemistry; Protic Ionic Liquids; Glycerol derivatives

In recent years, research on green alternatives to traditional chemical methods has gained increasing interest and relevance. For instance, our research group has focused on the development of glycerol derivatives and their used in catalytic methods.[1]

In this study, a new family of amines synthetized from glycerol is introduced. The synthesis of various amines has been designed and optimized including primary, secondary and tertiary amines. These compounds are of interest not only because of their intrinsic properties and ability to act as organocatalysts, but also because they can be used as precursors of protic ionic liquids (PILs) when treated with strong acids. The presence of an acidic proton in the ionic liquids allows them to act as catalysts in a wide range of organic reactions.[2] In particular, we report the use of these novel PIL in aza-Michael reactions. The effect of substitution around nitrogen atom, nature of the substituents, anion of PIL and experimental conditions has been explored. Moreover, the recyclability of these catalytic system has been evaluated.

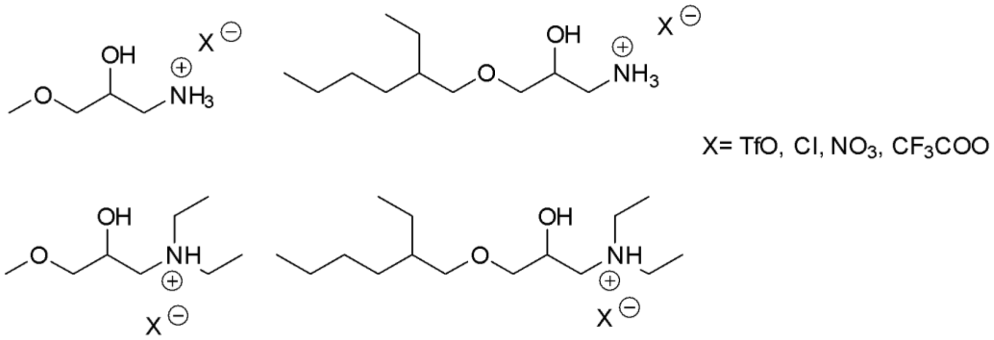

**Figure 1**. Structures of glycerol- derived protic ionic liquids (PILs) synthetized

**Acknowledgments:**

The project was funded by Agencia Estatal de Investigación (PID2021-125762NB I00), Gobierno de Aragón (E37_23R). C. D. M thanks Ministerio de Ciencia, Innovación y universidades for the grant. (FPU22/01484).

**References:**

[1] A. Leal-Duaso, P. Pérez, J. A. Mayoral, J. I. García, E. Pires, ACS Sustainable Chem. Eng., **2019**, 7, 13004–13014.

[2] J. Bailey, E. L. Byrne, P. Goodrich, P. Kavanagh, M. Swadźba-Kwaśny, Green Chem., **2024**, 26, 1092–1131.