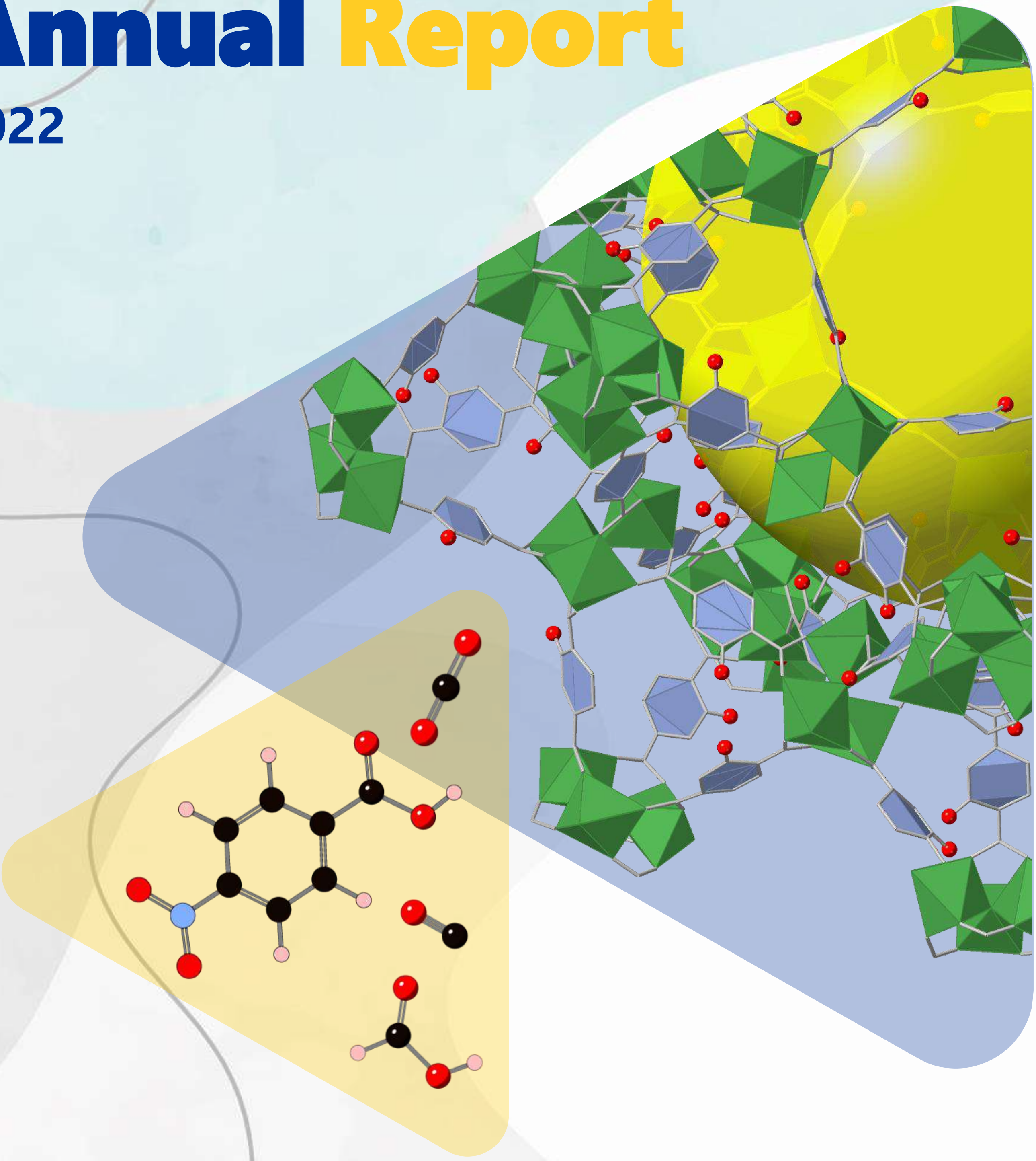
Cooperation towards a sustainable chemical industry

Annual Report

2022



CO_2PERATE Innovative Training Network
Horizon 2020 Research and Innovation Programme – Marie Skłodowska-Curie grant agreement No. 859910
Contact adress: Department of Chemistry, UiT The Arctic University of Norway, Tromsø, Norway

Cover:

The Pd^{II}*@MIL-101(Cr)-*NH_2 *catalyst (blue triangle) is a complex based on the MIL-101(Cr) metal-organic framework used for the synthesis of carboxylic acids from* CO_2 *(see our "Research Highlights" section, page 14). The building block for this complex is 4-(dihydroxyamino)benzoic acid (yellow triangle). Cover designed by Ha Phan.*

CO_2

CO_2PERATE Innovative Training Network

Cooperation towards a sustainable chemical industry

The CO_2PERATE Innovative Training Network (ITN) is funded by the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement (No. 859910). The consortium was started in February 2020 for an initial duration of four years, then extended 6 months. Our vision is simple but essential: to train a new generation of European researchers in the synthesis of indispensable molecules from sustainable carbon sources and with sustainable catalysts. This involves the development of novel and industrially relevant methods for employing CO_2 as a carbon synthon, alongside other renewable biomass, catalysed by sustainable metals.

The following 10 institutions are involved as beneficiaries:

UiT The Arctic University of Norway

Aarhus University

ICIQ Institute of Chemical Research of Catalonia

Catalysis LIKAT Leibniz-Institut für Katalyse e.V.

University of Zurich UZH

University of Oslo

Stockholm University

AstraZeneca

TOPSOE

EVONIK POWER TO CREATE

Our 2 partner organisations:

Ruhr Universität Bochum RUB

Universitat Rovira i Virgili

Contents

From the coordinator

Welcome!

We are happy to present the 3rd Annual Report of the H2020 ITN consortium CO_2PERATE. By browsing this document, you will learn about CO_2PERATE's progress and activities in 2022, research highlights, secondments, and publications. 2022 was still partially affected by the COVID pandemic, however, during the second part of the year, we were able to organize physical meetings and courses for our early-stage researchers (ESRs). Also, research visits and secondments between nodes were possible again. These visits are an important part of the ESR journey, as they allow the ESRs to gain intersectoral experience and to broaden their academic network. You can read about several of the ESR visits in this report.

Who are we?

We are an Innovative Training Network (ITN), funded under the Horizon 2020 research and innovation programme - Marie Skłodowska-Curie grant agreement No. 859910. CO_2PERATE is composed of ten Beneficiaries (three industrial & seven academic) and two Partners, across six European countries. Together we are training fifteen ESRs towards a PhD degree in chemistry, with focus on sustainable methods and substrates, in particular conversion of CO_2 to products of higher value. If you want to know more, you can email us at co2perate@uit.no or follow our daily life on social media (Twitter: @co2perate_ITN, Facebook: @co2perateITN) or on our webpage (co2perate.eu).

Three of our ESRs during a stroll in Rostock, Germany at the annual meeting 2022. Picture by M.-J. H. Halsør.

Prof. Kathrin H. Hopmann
Project Coordinator
UiT The Arctic University of Norway

Dr. Marie-J. H. Halsør
Project Manager
UiT The Arctic University of Norway

Research Highlights

Project 2: Gabriel M. F. Batista (AU)

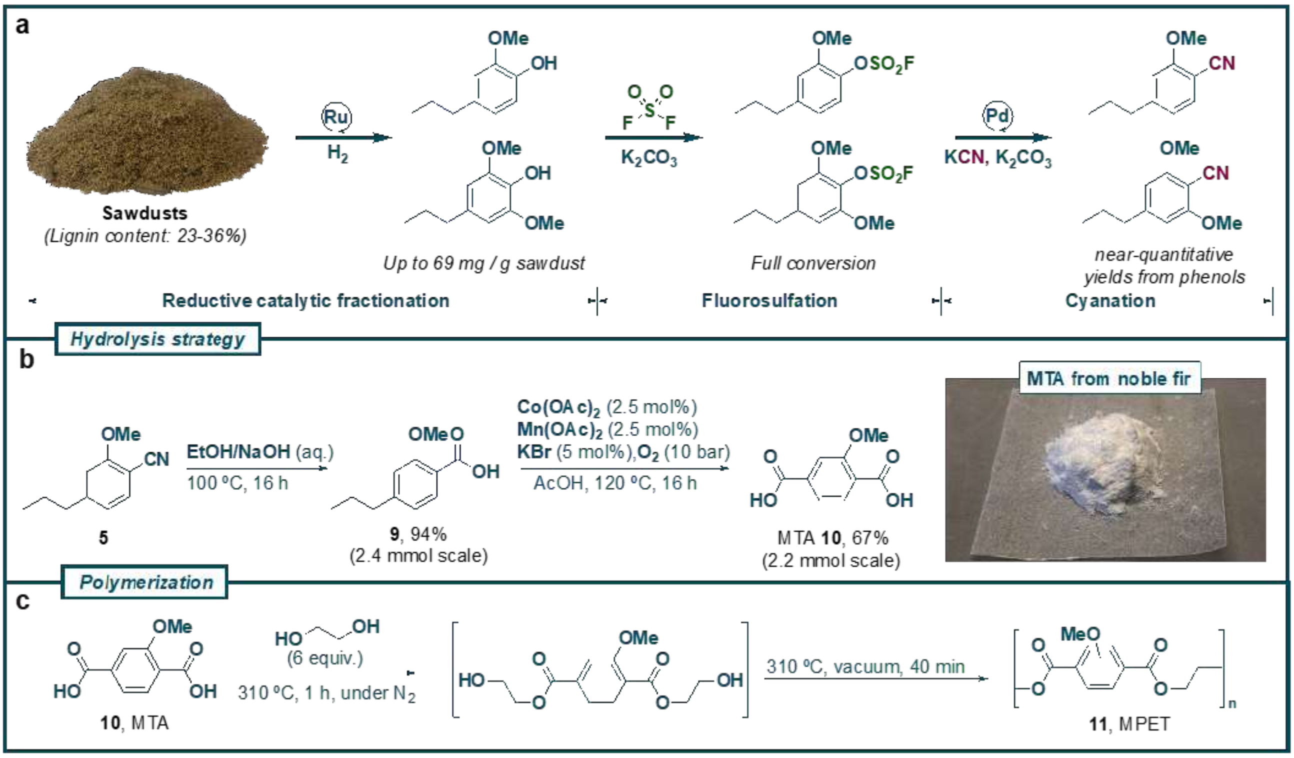
Project 2, under the supervision of Prof. Troels Skrydstrup at Aarhus University (AU), was originally titled "*Catalytic conversion of lignin to aryl carboxylic acids with CO_2*". The main purpose of this project was to develop non-precious homogeneous catalysts for oxidative addition into carbon–oxygen bonds, with the ultimate goal the cleavage of inert starting materials. A secondary objective was to investigate model lignin systems in order to study the catalytic cleavage of biaryl and methyl aryl ether bonds together with the subsequent carbon–carbon bond formation using CO_2.

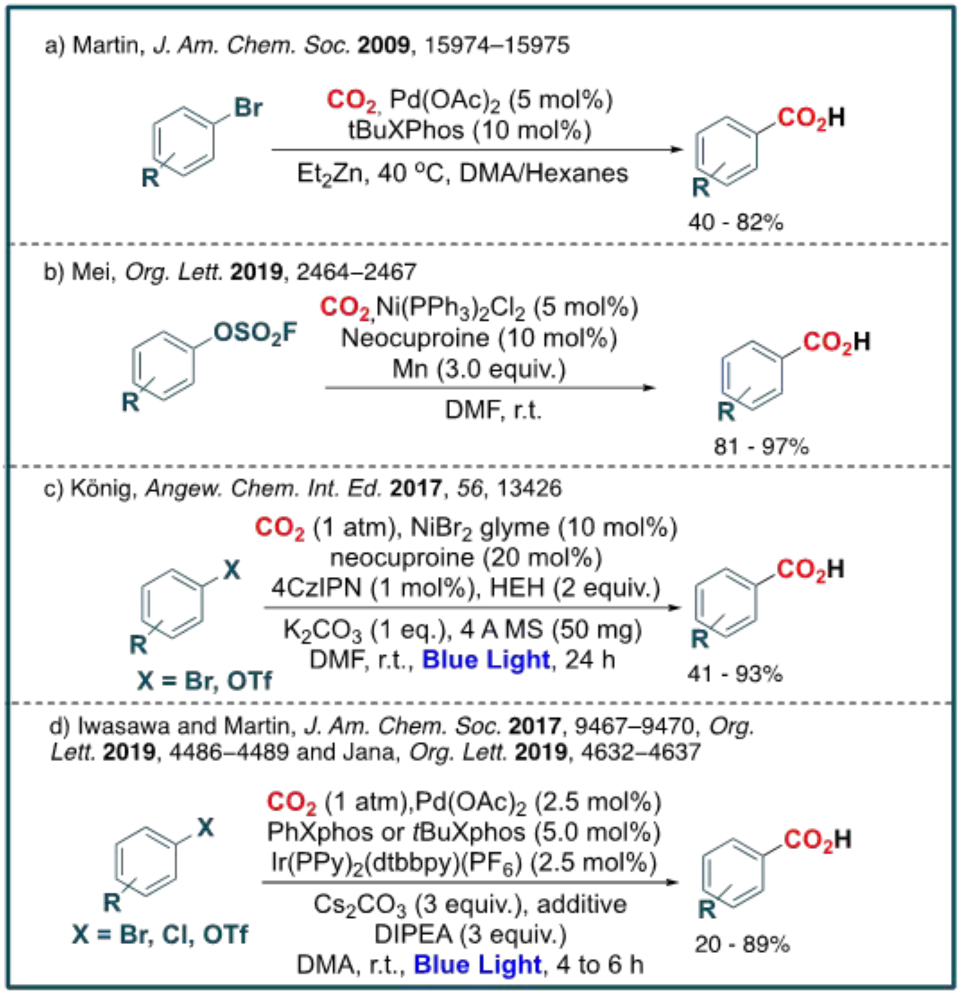
The first planned secondment of the project focused on the immobilisation of single-site carboxylation catalysts into metal-organic frameworks (MOFs), in this case catalysts responsible for the carboxylation of lignin materials.

The lignin valorization was done using a sequence of reactions in which a palladium-catalyzed cyanation followed by hydrolysis leads to the carboxylic acid (Scheme 1). A manuscript presenting this work has been submitted for publication and is currently under revision.

Once the biomass valorization had been performed in a satisfactory manner, we decided to focus on the use of CO_2 for carboxylation reactions as was originally planned, but with an emphasis on isotopic labeling. The use of near-stoichiometric CO_2 for isotopic labeling would require a selective and efficient catalyst; within the currently reported procedures, atmospheric pressures or above are required.

Scheme 1: Biomass valorization through reductive catalytic fractionation (RCF) followed by fluorosulfation, cyanation, and hydrolysis. Figure by G. M. F. Batista.





Scheme 2: Selected literature on reductive carboxylation. Figure by G. M. F. Batista.

Martin and coworkers reported several palladium- and nickel-catalyzed reductive carboxylations of aryl electrophiles (Scheme 2).[1] These carboxylation procedures called the attention of the chemical community, as they could provide a more sustainable pathway for obtaining building blocks and thus help the green transition that the chemical industry must face.

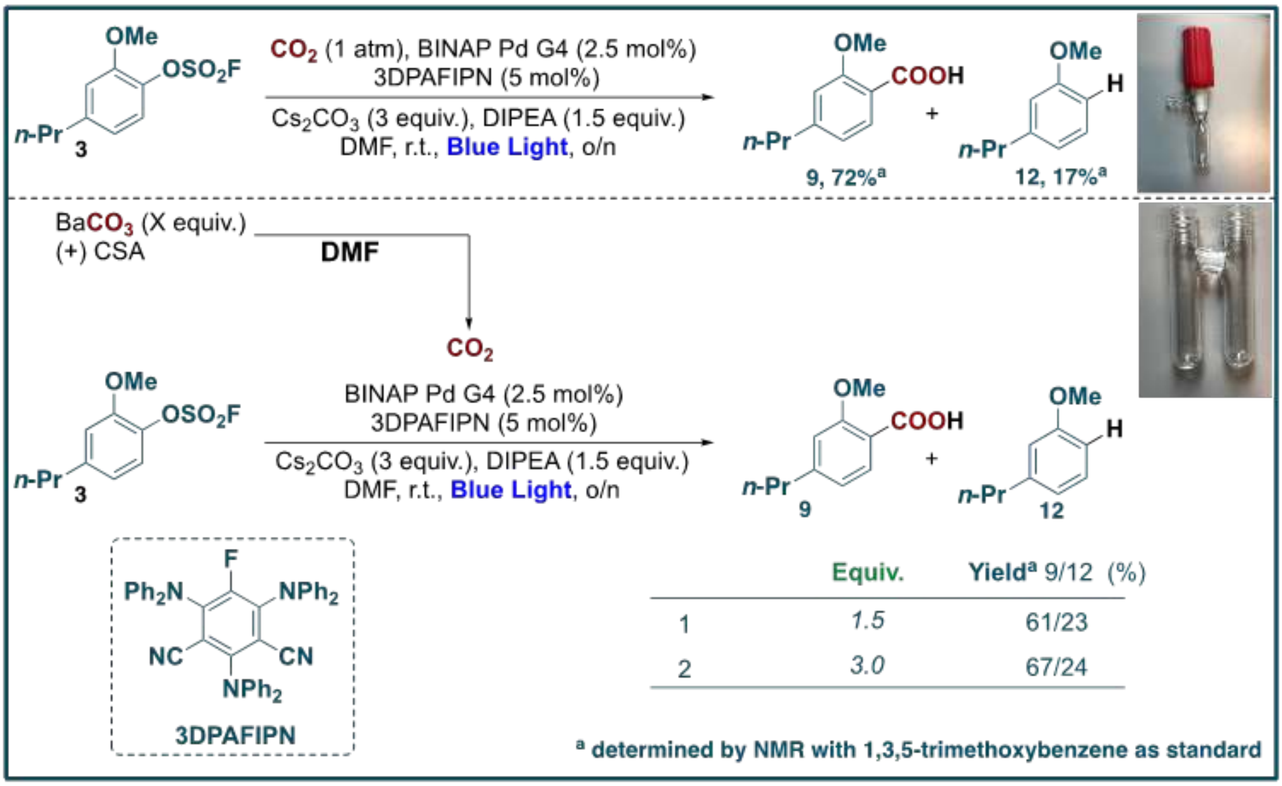
However, in a contrast to this sustainable aspect, these reactions require the use of stoichiometric amounts of metals (Mn, Zn, or transmetalation reagents such as $ZnEt_2$) to reduce the catalyst.[2,3] Tackling that problem, Martin, Iwasawa and Konig reported photoredox conditions that, instead of using stoichiometric amounts of metals, only require amines (DIPEA, Et_3N or Hantzsch ester (HEH)).[4–6]

Although this is an advantage, the procedures using palladium catalysis still require the addition of an iridium photocatalyst. In addition to this, the amines still derive from crude oil, thus increasing the carbon footprint of the overall reaction.

Enlightened by this, we decided to optimize photoredox conditions for the carboxylation of aryl fluorosulfates with the goal of avoiding using amines as sacrificial reductants as well as the iridium photocatalyst. Additionally, within most current procedures excess of CO_2 is used, and we had to adapt our method to use a near stoichiometric amount of CO_2. This enabled carbon isotope labeling in a facile manner. After optimization of the reaction conditions, we could replace the organometallic photocatalyst for an organic dye but the amine as an electron donor could not be avoided. Additionally, our procedure could be adapted for a 2-chamber glassware, in which CO_2 is released from $BaCO_3$ + Camphorsulfonic acid (CSA).[7]

As barium carbonate is commercially available in both $Ba^{13}CO_3$ and $Ba^{14}CO_3$ alternatives, the developed procedure can be used for radioactive and non-radioactive carbon isotopic labeling (Scheme 3).

With our conditions, a cheaper ligand is used compared to the ones used by Martin and Iwasawa, and we could also avoid the expensive iridium photocatalyst. Albeit lower, the reaction still requires 1.5 equivalents of DIPEA, that derive from crude oil. We therefore decided to look at alternative pathways for performing this reduction.

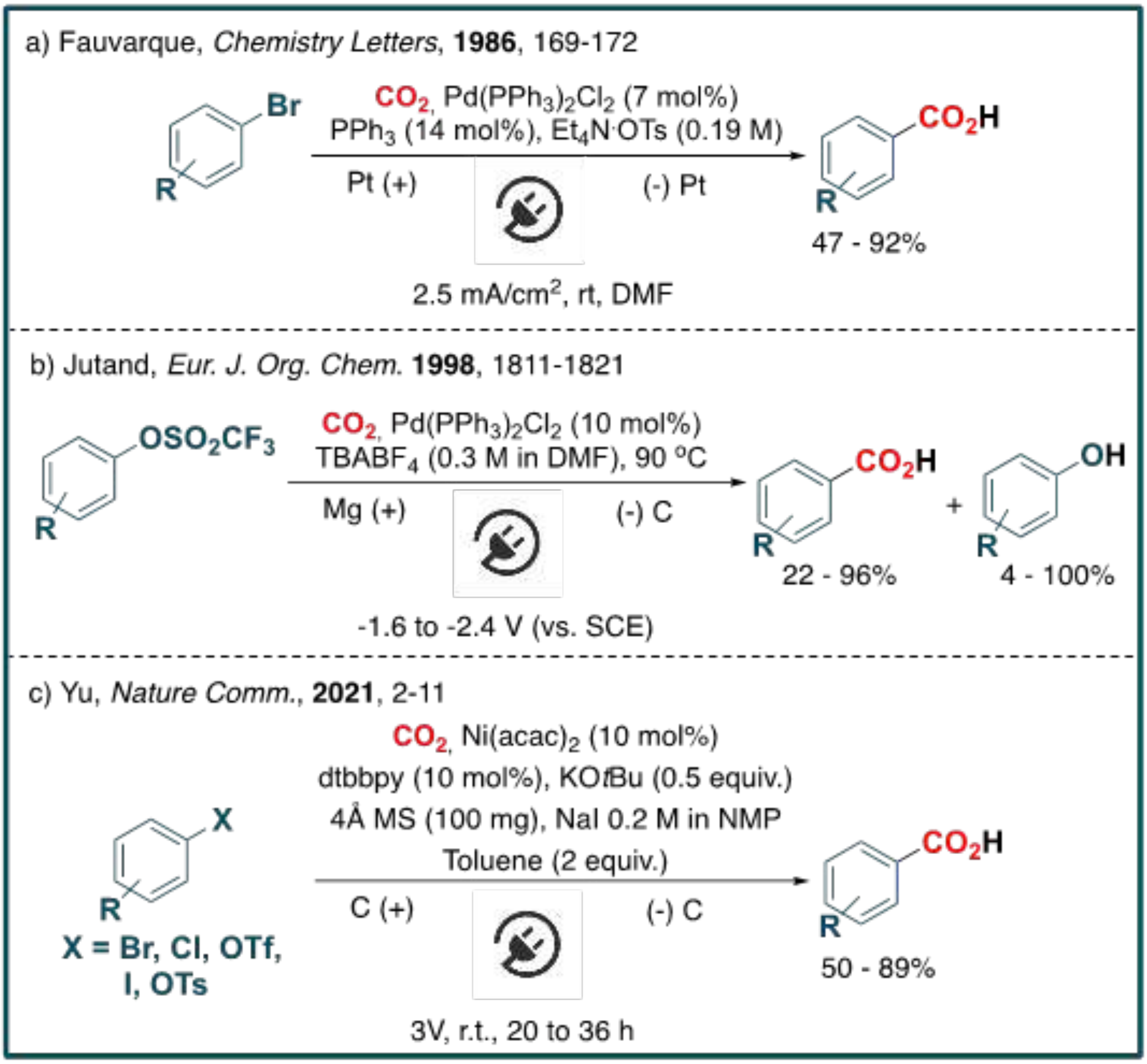


Scheme 3: Optimized conditions for a photoredox palladium catalyzed carboxylation of aryl fluorosulfates. Figure by G. M. F. Batista.

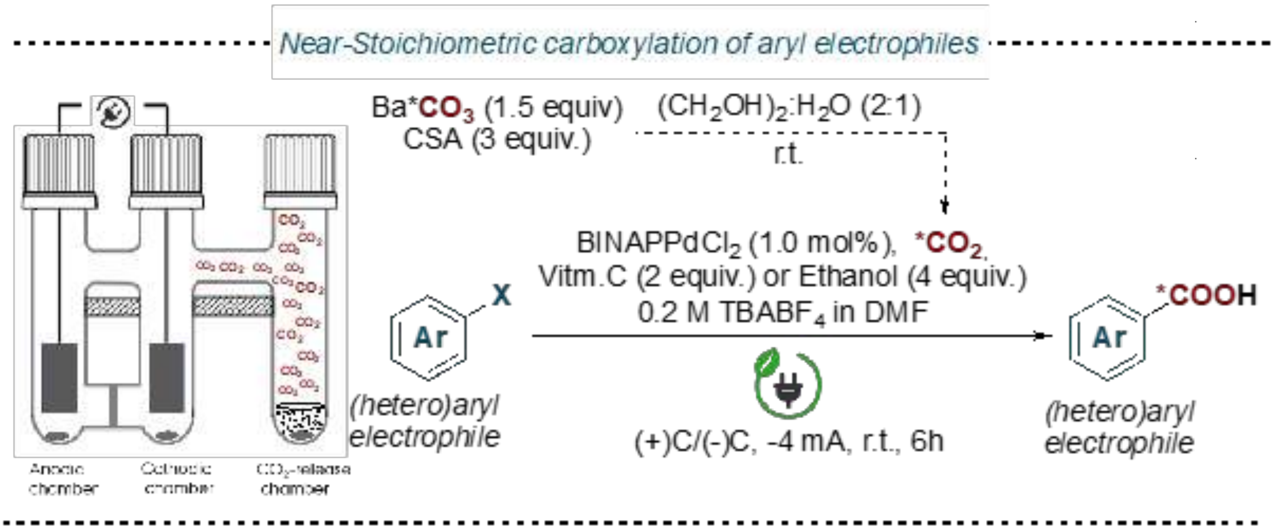
Within organic synthesis, a renaissance of electrochemical methods is ongoing due to the advantages that it can convey.[8] In our method, a reduction is required for the catalyst to turnover and an electrochemical procedure could be able to tolerate alternative sacrificial reductants. This should be feasible with a separate cell where you reduce the contact between the anodic reaction and cathodic reaction, thus circumventing side reactions that could occur due to the reactive species that can form after a single electron donation of the sacrificial reductant.

Additionally, the major side product observed for our photoredox conditions (Ar-H) should also be avoided, due to the smaller concentration of protons in the anodic chamber. This has been proposed to come from the amine, which with 2 single electron oxidations and proton release forms an iminium ion; the released proton is proposed to be the source for the Ar-H hydrogen.[9]

Looking at electrocarboxylation methods one can observe that in the late 20th century Fauvarque and Jutand made major



Scheme 4: Previous literature on electrocarboxylation of aryl electrophiles. Figure by G. M. F. Batista.



Scheme 5: Optimized conditions for a palladium catalyzed electrocarboxylation of aryl electrophiles. Figure by G. M. F. Batista.

contributions. Within these, a $(PPh_3)_2PdCl_2$ catalytic system is used for the carboxylation of aryl bromides, and triflates.[10,11] Although this was a breakthrough, the procedure could only be applied for simple substrates and only a minor scope was demonstrated.

Additionally, a state-of-the-art nickel-catalyzed electrocarboxylation was reported last year by Yu and can lead to the carboxylic acids in moderate to good yields.[12] Controversially, likewise the previously described papers it requires toluene as sacrificial electron donor which goes against the sustainable manner of the reaction. Furthermore, their procedure requires a high catalyst loading (with maximum turnover number of 8.9), besides the addition of base, molecular sieves, and other additives such as DMAP (20 mol%) and $MgBr_2$ (1.5 equiv.)), the latter being a stoichiometric amount of metal. Additionally, in the constant potential conditions, a high potential (-3 V) is applied for a long time, which could hinder functional group tolerance. Enlighted by these and based on the previously optimized photoredox conditions,[13] we turned our attention to developing a simpler method that takes into consideration the green manner of this transformation and can use near stoichiometric amounts of CO_2 in contrast to what has been previously described.

After optimization of the reaction conditions, we were pleased to find that the reaction can proceed with the use of the commercial $(BINAP)PdCl_2$ pre-catalyst with 10 times less catalyst than used by Yu, leading to a high TON of 96, currently, that is even higher than previously published papers by Martin and coworkers that depend on Et_2Zn to reduce the catalyst (Scheme 5).[3] Additionally, our conditions only require ascorbic acid (Vitamin C) as the electron donor, which can be obtained in a sustainable manner and has a comparable cost to the previously used amines. Furthermore, no additives are required besides solvent, and electrolyte thus demonstrating to be a straightforward transformation.

Moreover, an 87% Faradaic efficacy (FE) can be obtained for the **2b** molecule which is in deep contrast to the 9.5% FE obtained by Yu and coworkers for p-methoxy triflate (using the procedure: carbon felt cathode (1 cm × 1 cm × 2 cm) and a Zn plate (1 cm × 2 cm), aryl chloride/bromide 1/3 (0.3 mmol), $NiBr_2$•DME (10 mol%), 4,4'-di-tert-butyl-2,2'-bipyridine (dtbbpy, 10 mol%), DMAP, (20 mol%), KOtBu (0.5 equiv.), anhydrous $MgBr_2$ (1.5 equiv.), NaI (0.2M in NMP)). Additionally, our current conditions could be successfully applied to aryl bromide **2c** leading to eudesmic acid in 85% yield with no changes in the reaction conditions, thus demonstrating the advantage of such a procedure to tolerate both aryl bromides and fluorosulfates. Currently, a scope of 29 molecules with different functional groups is done, in which drug substrates are intended to be labeled with $^{14}CO_2$ at AstraZeneca.

The use of near stoichiometric amounts of CO_2 was evaluated, and with the use of a 3-chamber glassware and similar release conditions as previously described by Skrydstrup and coworkers[7], we could observe comparable yields to that when using 1 atm of CO_2. One aspect that is yet not fully understood is the reaction mechanism, which is currently being studied with experimental methods. The use of DFT studies as an alternative tool in the reaction mechanism study would be of great benefit, due to the modeling a better understanding of how the mechanism occurs and its barriers would be available.

Thus, our current optimized conditions for palladium catalyzed electro- or photocarboxylation of aryl electrophiles can be easily adapted to isotope labeling by release of near stoichiometric amounts of CO_2 from barium carbonate in a 2 or 3 chamber set up. Today, diverse aryl bromides are commercially available, thus facilitating the application in drug like molecules. The aryl fluorosulfates can be prepared in a reaction of the phenol with sulfuryl fluoride in basic medium. Since the oxidative addition into Ar-O bond in the phenol is not likely to occur, it can be used as a late-stage handle for the synthesis of complex molecules. Due to the high potential of our developed method for isotopic labeling of drug and drug-like molecules, we envisioned that changing my industrial secondment from Haldor Topsøe to Astra Zeneca (AZ) to perform $^{14}CO_2$ labeling would be of great benefit for the project, AZ, and the overall learning experience. The scope and mechanistic studies for this project have started and it would be ideal to go to the AZ facilities after the scope is done, to perform the $^{14}CO_2$ labeling to obtain the last results and write the manuscript. In order to finish the mechanistic studies, a change in the academic secondment from Stockholm University to the Univeristy of Oslo (UiO) was decided, as UiO Principal Investigator A. Nova works with computational chemistry and will thus be able to providance guidance for DFT studies.

1. Tortajada, A.; Juliá-Hernández, F.; Börjesson, M.; Moragas, T.; Martin, R. Transition-Metal-Catalyzed Carboxylation Reactions with Carbon Dioxide. *Angew. Chem. Int. Ed.* 2018, 57, 15948.
DOI: 10.1002/anie.201803186.

2. Ma, C.; Zhao, C.-Q.; Xu, X.-T.; Li, Z.-M.; Wang, X.-Y.; Zhang, K.; Mei, T.-S. Nickel-Catalyzed Carboxylation of Aryl and Heteroaryl Fluorosulfates Using Carbon Dioxide. *Org. Lett.* 2019, 21, 2464.
DOI: 10.1021/acs.orglett.9b00836.

3. Correa, A.; Martín, R. Palladium-Catalyzed Direct Carboxylation of Aryl Bromides with Carbon Dioxide. *J. Am. Chem. Soc.* 2009, 131, 15974.
DOI: 10.1021/ja905264a.

4. Meng, Q. Y.; Wang, S.; König, B. Carboxylation of Aromatic and Aliphatic Bromides and Triflates with CO_2 by Dual Visible-Light–Nickel Catalysis. *Angew. Chem. Int. Ed.* 2017, 56, 13426.
DOI: 10.1002/anie.201706724.

5. Shimomaki, K.; Murata, K.; Martin, R.; Iwasawa, N. Visible-Light-Driven Carboxylation of Aryl Halides by the Combined Use of Palladium and Photoredox Catalysts. *J. Am. Chem. Soc.* 2017, 139, 9467.
DOI: 10.1021/jacs.7b04838.

6. Shimomaki, K.; Nakajima, T.; Caner, J.; Toriumi, N.; Iwasawa, N. Palladium-Catalyzed Visible-Light-Driven Carboxylation of Aryl and Alkenyl Triflates by Using Photoredox Catalysts. *Org. Lett.* 2019, 21, 4486.
DOI: 10.1021/acs.orglett.9b01340.

7. Lescot, C.; Nielsen, D. U.; Makarov, I. S.; Lindhardt, A. T.; Daasbjerg, K.; Skrydstrup, T. Efficient Fluoride-Catalyzed Conversion of CO2 to CO at Room Temperature. *J. Am. Chem. Soc.* 2014, 136, 6142.
DOI: 10.1021/ja502911e.

8. Yan, M.; Kawamata, Y.; Baran, P. S. Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance. *Chem. Rev.* 2017, 117, 13230.
DOI: 10.1021/acs.chemrev.7b00397.

9. Toriumi, N.; Shimomaki, K.; Caner, J.; Murata, K.; Martin, R.; Iwasawa, N. Mechanistic Studies into Visible Light-Driven Carboxylation of Aryl Halides/Triflates by the Combined Use of Palladium and Photoredox Catalysts. *Bull. Chem. Soc. Jpn.* 2021, 94, 1846.
DOI: 10.1246/bcsj.20210151.

10. Torii, S.; Tanaka, H.; Hamatani, T.; Morisaki, K.; Jutand, A.; Peluger, F.; Fauvarque, J.-F. Pd(O)-Catalyzed Electroreductive Carboxylation of Aryl Halides, β-Bromostyrene, and Allyl Acetates with CO_2. *Chem. Lett.* 1986, 15, 169.
DOI: 10.1246/cl.1986.169.

11. Jutand, A.; Négri, S. Activation of Aryl and Vinyl Triflates by Palladium and Electron Transfer – Electrosynthesis of Aromatic and α,β-Unsaturated Carboxylic Acids from Carbon Dioxide. *Eur. J. Org. Chem.* 1998, 4, 1811.
DOI:10.1002/... (abridged link)

12. Sun, G. Q.; Zhang, W.; Liao, L. L.; Li, L.; Nie, Z. H.; Wu, J. G.; Zhang, Z.; Yu, D. G. Nickel-catalyzed electrochemical carboxylation of unactivated aryl and alkyl halides with CO_2. *Nat. Commun.* 2021, 12, 2.
DOI: 10.1038/s41467-021-27437-8.

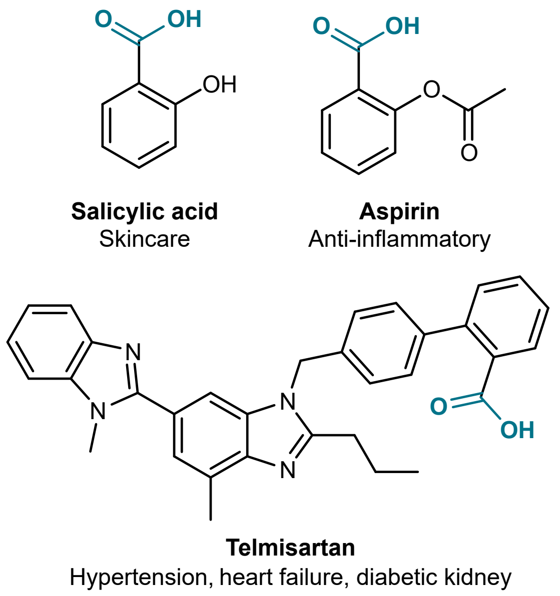
13. Tay, N. E. S.; Lehnherr, D.; Rovis, T. Photons or Electrons? A Critical Comparison of Electrochemistry and Photoredox Catalysis for Organic Synthesis. *Chem. Rev.* 2022, 122, 2487.
DOI: 10.1021/acs.chemrev.1c00384.

Project 2 is led by ESR2, Gabriel, under the supervision of main supervisor Troels Skrydstrup (AU) and co-supervisors Kathrin H. Hopmann (UiT) & Søren Tolborg (HT).

Project 3: Vu Duc Ha Phan (SU)

Project 3, titled "*Novel catalytic composites for the use of CO_2 as a one carbon synthon for organic synthesis*", is conducted at Stockholm University under the supervision of Prof. Belén Martín-Matute. This project focuses on the design and synthesis of non-precious, heterogeneous catalysts for the reduction of CO_2 to CO and carbonylation reactions.

Carboxylic acids play an important role in our society from agriculture, household products to pharmacy (Figure 1). Those compounds are mainly produced via carbonylation using pressurized toxic CO obtained from syngas which requires special equipment to reduce the risk. Other routes often require organometallic intermediates or extra reductants for direct utilization of CO_2 which are not so sustainable in mass production. Hence, finding a safe, sustainable and efficient route to synthesize carboxylic acid from CO_2 is of importance.



Salicylic acid
Skincare

Aspirin
Anti-inflammatory

Telmisartan
Hypertension, heart failure, diabetic kidney

Figure 1. Examples of carboxylic acids in pharmaceuticals. Figure by Ha Phan.

In this project, a tandem reaction including electrochemical reduction of CO_2 (eCO_2RR) with FECO up to 70% and carbonylation of aryl iodides using the ex-situ generated CO is presented (see Figure 2 on next page). Both the eCO_2RR electrode and carbonylation heterogeneous catalyst are recyclable (see Figure 3 on next page). The tandem reaction set-up is applicable to various aromatic substrates giving corresponding carboxylic acids in good to excellent yields.

References:

1. H. Phan, R. Gueret, P. Martinez-Pardo, A. Valiente-Sanchez, A. Slabon, B. Martín- Matute. Electrocatalysis-driven Tandem Catalysis for Sustainable Conversion of CO_2 to Value-Added Molecules.
Manuscript in preparation.

2. M. T. Jensen, H. H. Rønne, A. K. Ravn, R. W. Juhl, D. U. Nielsen, X. Hu, S. U. Pedersen, K. Daasbjerg & T. Skrydstrup. Scalable Carbon Dioxide Electroreduction Coupled to Carbonylation Chemistry. Nat. Commun. 2017, 8, 489.
DOI: 10.1038/s41467-017-00559-8.

3. A. Thevenon, A. Rosas-Hernández, A. M. Fontani Herreros, T. Agapie & J. C. Peters. Dramatic HER Suppression on Ag Electrodes via Molecular Films for Highly Selective CO_2 to CO Reduction. ACS Catal. 2021, 11, 8, 4530.
DOI: 10.1021/acscatal.1c00338.

The Supervisory Team of ESR3 is composed of main supervisor Belén Martín-Matute (SU) and co-supervisors Ruben Martin (ICIQ) & Chad Elmore (AZ).

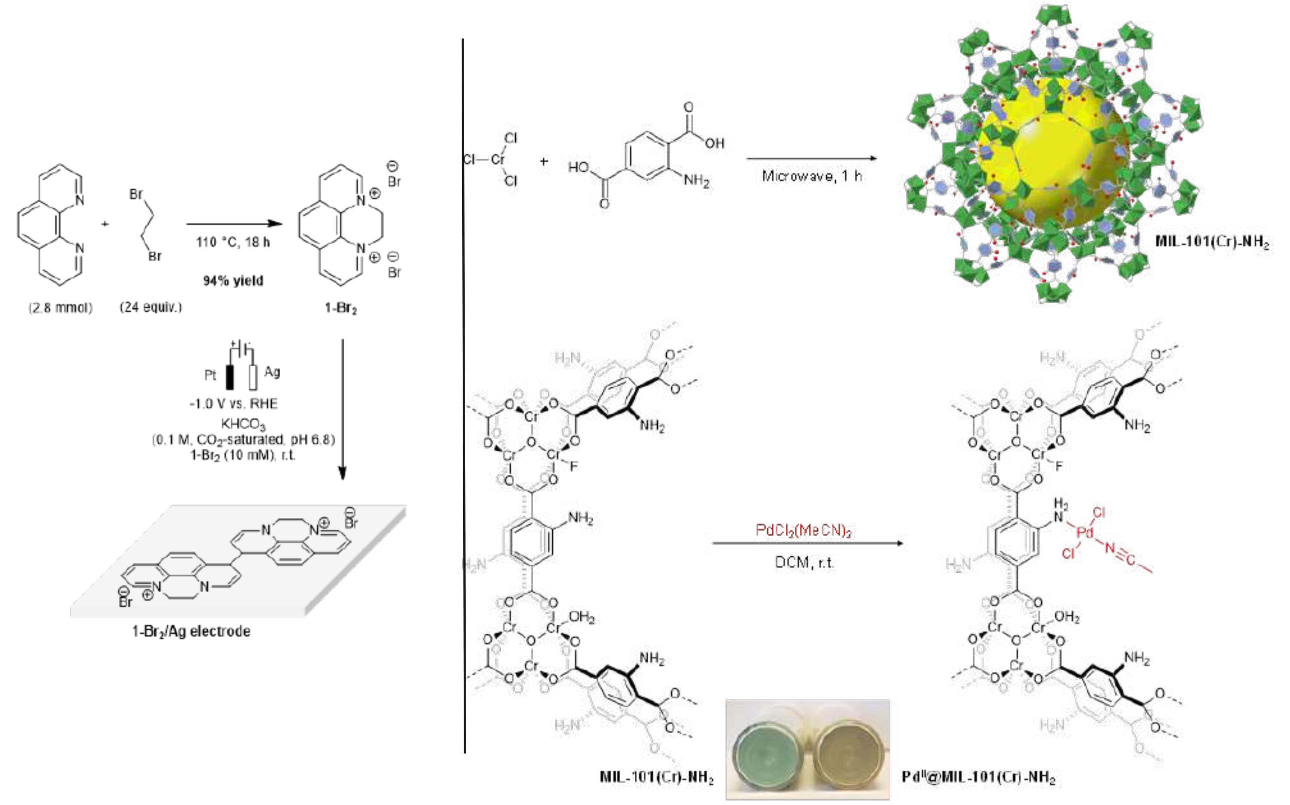


Figure 2. Tandem electrochemical reduction of CO_2 and ligand-free carbonylation of aryl iodides. Left: eCO_2RR electrode synthesis. Right: carbonylation catalyst synthesis. Figure by Ha Phan.

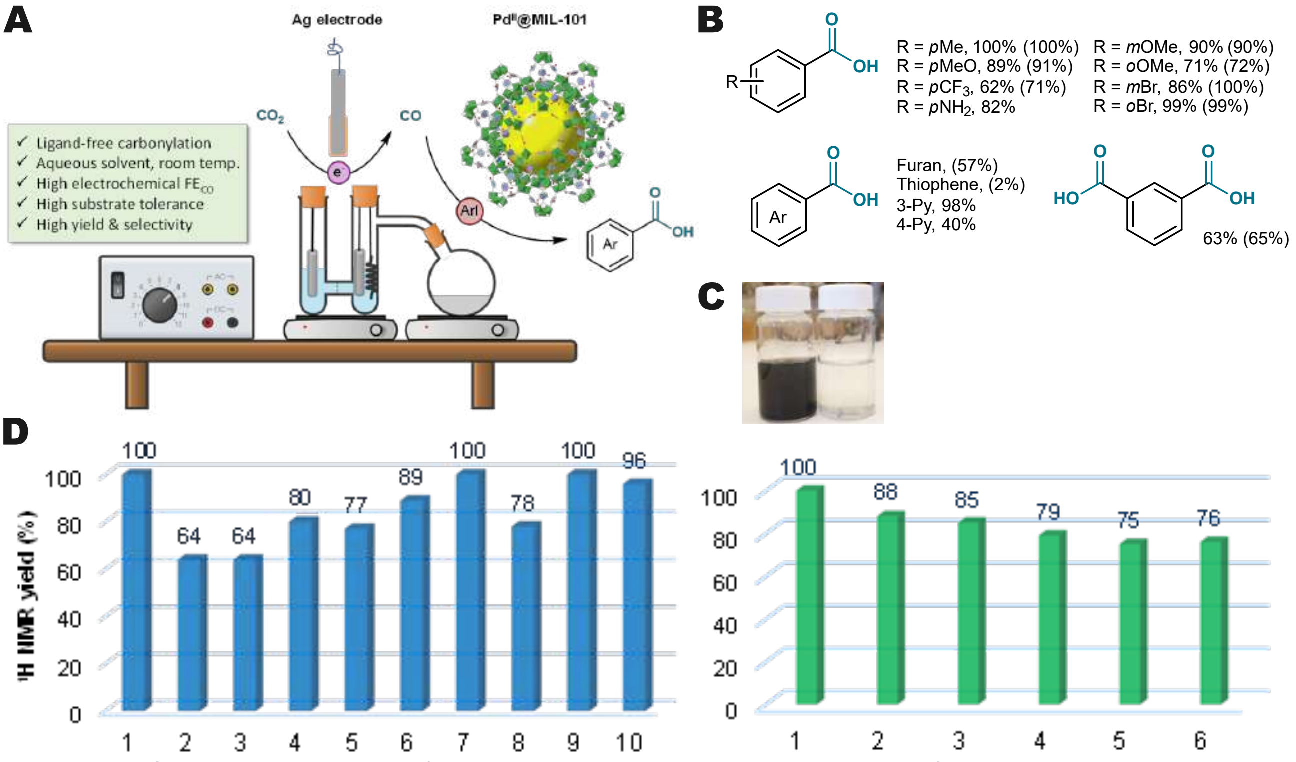


Figure 3. A: Schematic illustration of the tandem reaction setup. B: Examples of products obtained under the experiment conditions. C: the catalyst is simply removed from the reaction mixture by centrifugation. D: Yields of the recycling cycles for the Pd^{II}@MIL-101(Cr)-NH_2 (left) and the Br_2@Ag electrode (right). Figure by Ha Phan.

Project 6: Georgia Kriticou (UZH)

Project 6 has deviated from its original focus of '*Efficient synthesis of fluorine-containing oxazolidinones from atmospheric CO_2'* and has redirected it towards '*Homogeneous formation of carbamates*' as part of Work Package 2 (WP2, "Carbamates from CO_2").

This project is hosted by the University of Zurich (UZH), under the supervision of Prof. Cristina Nevado. The refocused primary goal of Project 6 revolves around the development of reliable catalytic systems for the synthesis of cyclic carbamate building blocks utilizing atmospheric CO_2 and readily available strained systems as starting materials. Use of electrocatalytic systems were initially used to perform this transformation, however, attempts as of yet have been unsuccessful.[1] Alternative approaches are currently being pursued.

Taking natural photosynthesis as an inspiration, photocatalysis has recently emerged as a powerful strategy for CO_2 transformations and attracted sustained attention from chemists, in search of developing elegant reactions to form value-added chemicals.[2] Similarly, such approaches are currently attempted in this asymmetric transformation under photocatalytic conditions and the use of Ni-catalysts.

The utilization of CO_2 as a carbon source in organic synthesis to obtain carbamates and their derivatives is particularly sought after in furthering pharmaceutical and agricultural endeavours. More specifically, the core structure of cyclic carbamates can be found in a plethora of valuable chemicals with industrial application, including Posizolid (antibiotic), Efavirenz (antiretroviral) and Toloxatone (antidepressant).[3]

Some advantages of the development of such an asymmetric methodology include the use of mild reaction conditions and the accessibility to aziridine starting materials from simple olefin feedstock or amino alcohols.

References:

1. Dunach, E.; Tascedda, P.; Electrosynthesis of cyclic carbamates from aziridines and carbon dioxide. *Chem. Comm.* 2000, 449-450.
DOI: 10.1039/a910285j.

2. Zhong, H.; Deng, F.; Lin, J.; Huang, W.; Photocatalytic Carboxylation with CO2: A Review of Recent Studies. *Asian J. Org. Chem.* 2022, 11.
DOI: 10.1002/ajoc.202200220.

3. Repo, T.; Niemi, T; Antibiotics from Carbon Dioxide: Sustainable Pathways to Pharmaceutically Relevant Cyclic Carbamates. *Eur. JOC.* 2019, 1180-1188.
DOI: 10.1002/ejoc.201801598.

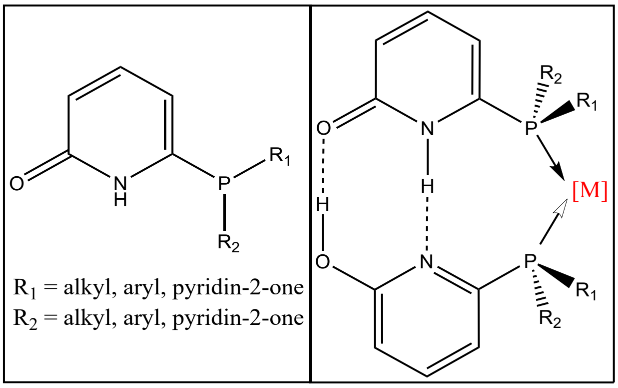
G. Kriticou is supported by C. Nevado (main supervisor, UZH), T. Skrydstrup (AU) and M. Johansson (AZ).

Project 15: Pierre Fablet (LIKAT)

Labelled as “Development of catalysts for aminocarbonylation reactions of olefins with CO_2” project 15 is aimed at the development of alternative solutions for carbonylation and aminocarbonylation reactions of olefins, with a strong focus on the use of CO_2. Following the actual trend in catalysis, investigation of different earth-abundant metals is also at the center of the topic.[1]

Based on previous research by the group of Prof. Matthias Beller and Dr. Ralf Jackstell on hydroformylation and alkoxycarbonylation, particular attention has been given to the use of non-traditional metals (i.e ruthenium) for the benchmark hydroformylation and alkoxycarbonylation of terminal olefins.[2,3]

After a benefitting collaboration with a visiting PhD student we have successfully synthesized a wide range of new heterocyclic phosphine ligands based on variations of notorious 6-Diphenylphosphinopyridin-2-(1H)-one (6-DPPon) first introduced by the Breit’s group.[4]



Synthesized analogs of 6-DPPON and self-assembling mechanism of the two tautomeric units. Figure by P. Fablet.

Empowered by such results, we have been working on the application of those novel catalytic systems to the hydroformylation of branched and terminal olefins on several substrates, hopefully leading to appreciable research output. Notably the performance of aforementioned ligands is also being assessed for several other reactions, namely CO production from CO_2 and following possible tandem catalysis applications.

References:

1. Chirik P.; Morris R. Getting Down to Earth: The Renaissance of Catalysis with Abundant Metals. *Accounts Chem. Res.* 2015, 48, 9, 2495.
DOI : 10.1021/acs.accounts.5b00385.

2. Wu L.; Liu Q.; Fleischer I.; Jackstell R.; and Beller M. Ruthenium-catalysed alkoxycarbonylation of alkenes with carbon dioxide. *Nat. Commun.*, 2014, 5, 3091.
DOI : 10.1038/ncomms4091.

3. Fleischer I.; Wu L.; Profir I.; Jackstell R.; Beller M. Towards the Development of a Selective Ruthenium-Catalyzed Hydroformylation of Olefins. *Chem. Eur. J.*, 2013, 19, 10589-10594.
DOI : 10.1002/chem.201300899.

4. Agabekov V.; Seiche W.; Breit B. Rhodium-catalyzed hydroformylation of alkynes employing a self-assembling ligand system. *Chem. Sci.*, 2013, 4, 2418-2422.
DOI : 10.1039/C3SC50725D.

Project 15 is led by ESR15, Pierre, under the supervision of their main supervisor Matthias Beller (LIKAT) and co-supervisors Ainara Nova (UiO) & Robert Franke (EV).

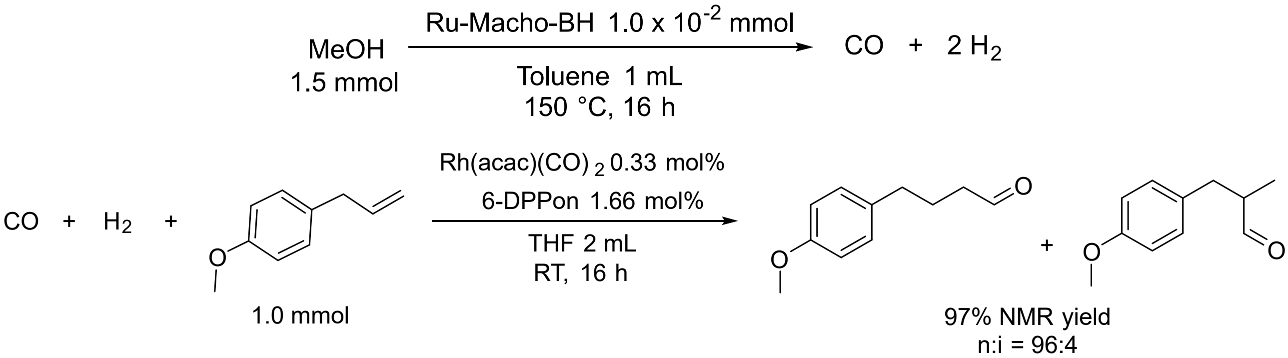
Secondments

Weiheng Huang (ESR13), LIKAT to AU

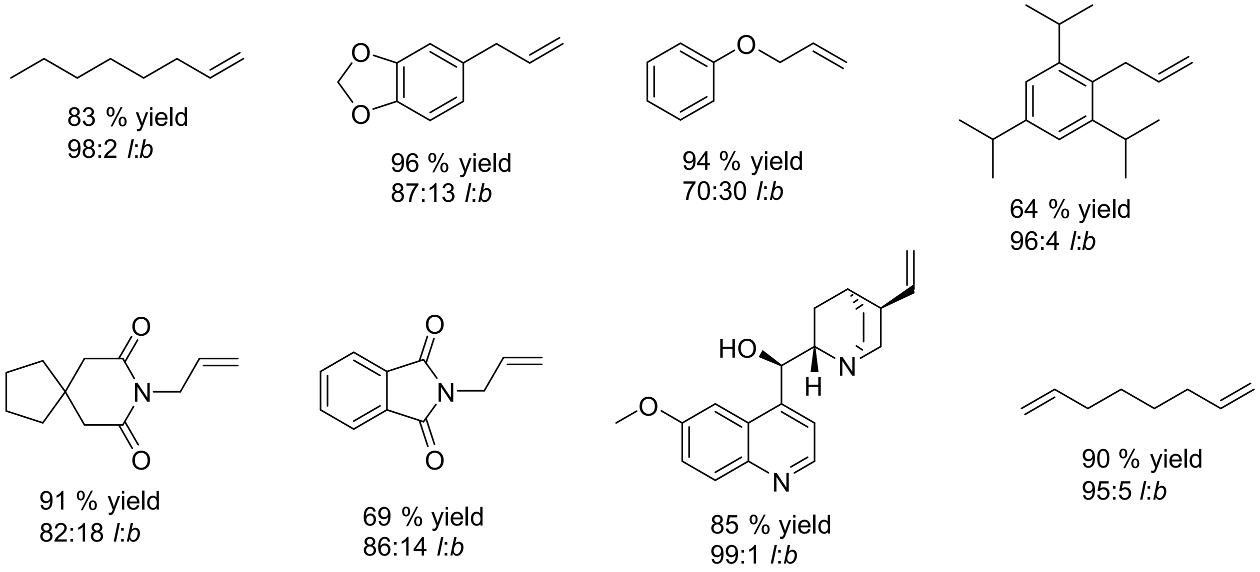
The 3 months secondment was completed at the end of March 2022 in Aarhus University. The major lab work of the secondment is the two chambers reaction. Syn gas is generated from dehydrogenation of methanol in one chamber then the hydroformylation of olefin is carried out in another chamber. The detail conditions and results are shown in scheme 1.

Due to the dehydrogenation of methanol need high temperature, the two chambers reactor was promoted (see Figure 1 next page). As the figure shown, a cool water condensation part is added into a side of reactor, the methanol dehydrogenation is launched in this side, all liquid is condensed and the syn gas could diffuse to another chamber for the hydroformylation at room temperature.

Estragole (1.0 mmol) was used as model substrate for optimizing conditions. The conditions in hydroformylation chamber were applied according to the previous work. The conditions in syn gas generation chamber were based on a recent publication of Leitner. Because of the conditions of hydroformylation are already studied before,[1] the direction of condition optimization focused on the syn gas generation chamber. The amount of methanol and Ru catalyst were investigated mainly. Different amount of methanol, solvents, temperature, and methanol dehydrogenation catalysts were tested. Finally, applying 1.5 mmol MeOH and 0.01 mmol of Ru catalyst in 1 mL toluene at 150 °C were found as the best condition for this reaction. In addition, because there is still another one equivalent of hydrogen gas was not used, then I tried to reduce the aldehyde product to alcohol in one-pot, but there was not alcohol observed after a lot of tests. Hydroaminomethylation was also tested but it did not work either.



Scheme 1. Model reaction of the two chambers reaction. Figure by W. Huang.



Scheme 2. The substrate scope under model conditions. Figure by W. Huang.

The substrate scope is still undergoing under the model conditions, and the results are shown in Scheme 2 before I left Aarhus.

The yields are the average isolated yield of two parallel experiments within 10% deviation and the n:i ratios are determined by ^{1}H NMR. There are more substrates under process. Labeling experiment and some control experiments were planned. The structure of the manuscript was discussed and we are preparing it now.

References

1. S. K. Pedersen, H. G. Gudmundsson, D. U. Nielsen, B. S. Donslund, H. C. D. Hammershøj, K. Daasbjerg, T. Skrydstrup. Main element chemistry enables gas-cylinder-free hydroformylations. *Nat. Catal.* 2020, 3, 843–850.
DOI: 10.1038/s41929-020-00510-z.

2. A. Kaithal, B. Chatterjee, C. Werlé, W. Leitner, Angew. Acceptorless Dehydrogenation of Methanol to Carbon Monoxide and Hydrogen using Molecular Catalysts. *Chem. Int. Ed.* 2021, 60, 26500.
DOI: 10.1002/anie.202110910.

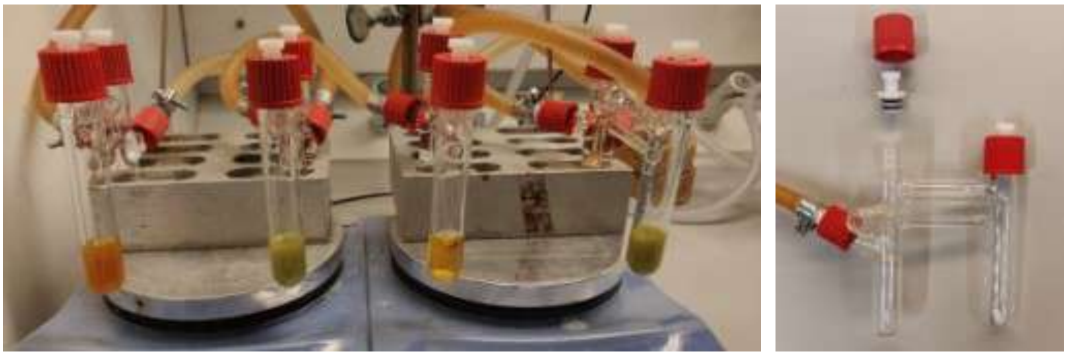


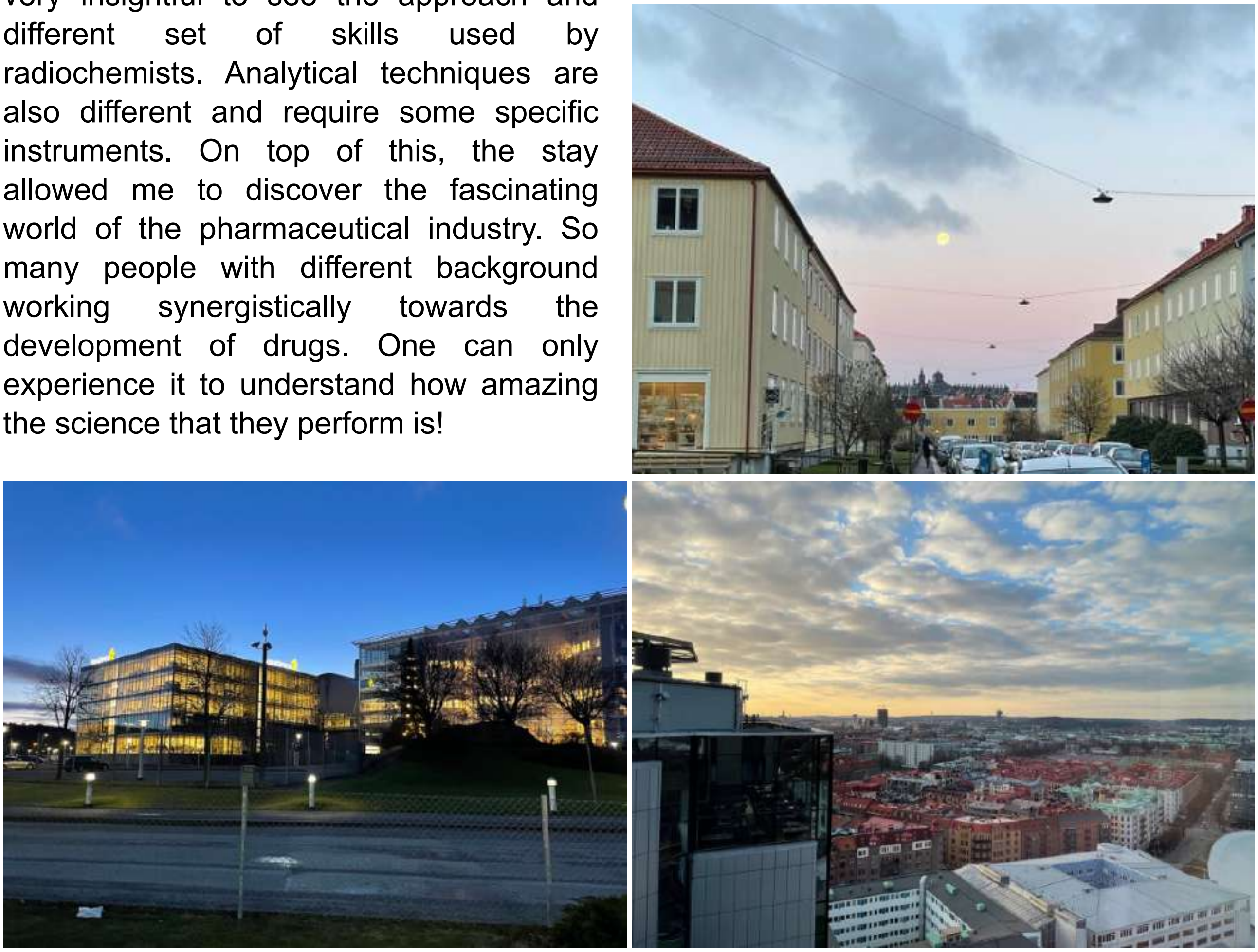
Figure 1. Pictures of promoted two chambers reactor and reactions (photos: W. Huang).

Julien Lyonnet (ESR11), ICIQ to Astrazeneca

Between January and April 2022, during my secondment at AstraZeneca in Göteborg, Sweden, I had the chance to join the team of Dr. Chad Elmore giving me my first experience with radiochemistry. Over this period, I was lucky enough to interact with many talented scientists, giving me a lot of insights on industry and chemistry as a whole. I joined the lab with the objective of using ^{14}C on the chemistry that I was performing back in Spain at ICIQ. It was very insightful to see the approach and different set of skills used by radiochemists. Analytical techniques are also different and require some specific instruments. On top of this, the stay allowed me to discover the fascinating world of the pharmaceutical industry. So many people with different background working synergistically towards the development of drugs. One can only experience it to understand how amazing the science that they perform is!

My project consisted in the carboxylation of organic halides using CO_2 reduction products as carboxylating reagents, developing a method suitable for labelling, and performing the methodology with ^{14}C.

During my free time, I was mostly walking around the city looking out for good restaurants to try, visiting nearby shores and islands, or taking the train to other cities in the country.



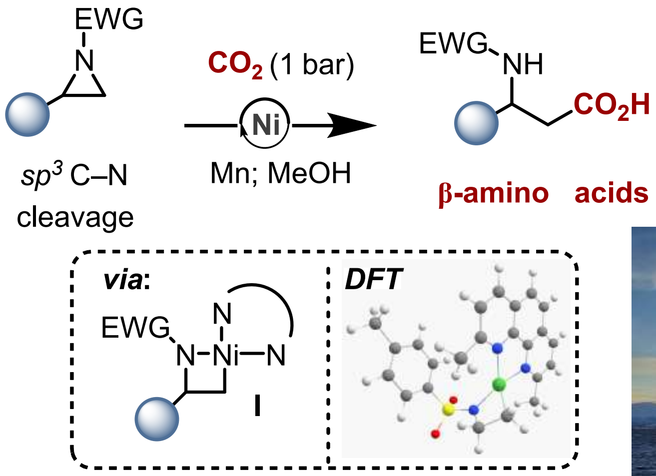
The AstraZeneca site in the early morning, Dawn with the moon in the suburbs of Göteborg, City view from a height (photos: J. Lyonnet).

Secondments

Dmitry Zimin (ESR1), ICIQ to UiT

The present secondment took place at UiT under the supervision of Prof. Kathrin Helen Hopmann. A general idea was to provide an opportunity to get expertise in a high-level *ab initio* modelling of non-precious metal-catalyzed C-C bonding of CO_2 with different modelled substrates. During the research stay, I learned how to deal with standard computational chemical software (Gaussian), how to prepare raw experimental data for computational analysis, how to proceed with computational experiments and how to interpret obtained results. As a result of the secondment, I am now able to conduct computational experiments independently, which greatly impacts my ongoing scientific research.

As a model reaction, we used the recently demonstrated Ni-catalyzed carboxylation of aziridines leading to the formation of β-amino acids. Synthetic applicability of this transformation was well explored but mechanistic aspects of this reaction are still shadowed. First, whereas a proposed reaction intermediate – a Ni-Azametallacycle I – is relatively stable with unsubstituted bipyridine and phenanthroline type of ligands, all attempts to isolate a Ni-Azametallacycle complex with sterically hindered ligands have been failed. Presence of such species was proved only with analysis by MALDI-MS technique. Taking into consideration also an enigmatic role of alcohol in the present reaction it was postulated that computational analysis of this transformation including search of potential transition states and calculation of activation energies can open up more insights about this chemical transformation.



Ni-catalyzed carboxylation of aziridines. Figure by D. Zimin.

Tromsø during the winter, shortly after the end of the polar night (photo: D. Zimin).

Kim S. Mühlfenzl (ESR12), Astrazeneca to AU

From February to June 2022, I had the opportunity to work at Aarhus University in Professor Troels Skrydstrup's group. This stay was incredibly rewarding as I was able to expand my knowledge of transition-metal catalysis and experience a new country.

During my secondment, I attended two courses where I learned a lot about advanced synthetic organic chemistry and project management. In addition to the coursework, we have started a new project looking at isotopic labeling of alkyl-aryl ketones. This motif is ubiquitous in pharmaceutically relevant compounds and is ideally suited for the incorporation of a carbon isotope. I optimized the reaction conditions for this method and was able to show that they tolerate a wide range of different substrates. In this still ongoing project, we plan to expand the scope of substrates to include some pharmaceutically relevant compounds and apply this methodology to carbon-13 and carbon-14 labeling. We would also like to confirm our proposed mechanism by mechanistic experiments and DFT calculations (ESR 8).

On the weekends, my days were filled with exploring Aarhus with its great bakeries and lovely old town, walks on the beach, and visits to Copenhagen. Moreover, I really enjoyed the group activities outside the lab, such as the canoe trip (see picture) and bowling night.

I am very grateful for this opportunity to collaborate closely with AU, AZ, and UiT and to have been part of this great research group.

The infinity bridger in Aarhus (left) and the view while on a canoe trip with the Skrydstrup Group in the region. Photos by K. S. Mühlfenzl.

Mahika Luthra (ESR10), UiO to SU

The present secondment took place at Stockholm University under the supervision of Prof. Belén Martín-Matute. The purpose was to study the incorporation of the $Mn(CO)_3bpy$ catalyst in a PCN-222 metal-organic framework (MOF), with the purpose of using it to perform the electrochemical reduction of CO_2 (see Figure 1 on the next page).

Mn-based complexes are excellent candidates for electrochemical CO_2 reduction into value-added products, like $HCOO^-$ and CO, although the selectivity of the products remains an issue.[1-2] Recently, it was discovered that the amine-substituted complex, Mn(dEAbpy) reduces CO_2 to HCOOH (FEHCOOH ~ 70%), whereas the complex without the amine is selective for CO generation under electrochemical conditions.[3] Before starting the secondment in SU, I studied the role of the amine functionality as a proton shuttle which shifts the selectivity of the homogeneous CO_2RR from CO to HCOOH using the Density Functional Theory (DFT) method.

The conductive MOF PCN-222 (Porous Coordination Network) is formed by zirconium chloride octahydrate clusters linked by units of meso-tetra porphyrin (Figure 2).[4] The Zr clusters of PCN-222 are unsaturated, which enables their post-functionalization via the Zr-carboxylate bond. The Mn complex is introduced into the linker by exploiting this unsaturation, as shown in Figure 3. It was characterized using X-Ray Diffraction (XRD) and Infrared Spectrometry (IR). The presence of Mn-N and C-O bands in the IR spectra confirmed the immobilization, and the XRD pattern shows that the MOF structure was intact during the reaction (Figure 4).

Currently, we are planning to substitute the amine to check for electrochemical CO_2 reduction. Meanwhile, I am performing DFT calculations on the computational model of the MOF to optimize the length of the amine required for the interaction.

References

1. Bourrez, M.; Molton, F.; Chardon-Noblat, S.; Deronzier, A. [Mn(bipyridyl)(CO)3Br]: An Abundant Metal Carbonyl Complex as Efficient Electrocatalyst for CO_2 Reduction. *Angew. Chem. Int. Ed.* 2011, 50 (42), 9903-9906.
DOI: 10.1002/anie.201103616.

2. Sampson, M. D.; Nguyen, A. D.; Grice, K. A.; Moore, C. E.; Rheingold, A. L.; Kubiak, C. P. Manganese Catalysts with Bulky Bipyridine Ligands for the Electrocatalytic Reduction of Carbon Dioxide: Eliminating Dimerization and Altering Catalysis. *J. Am. Chem. Soc.* 2014, 136 (14), 5460-5471.
DOI: 10.1021/ja501252f.

3. Rønne, M. H.; Cho, D.; Madsen, M. R.; Jakobsen, J. B.; Eom, S.; Escoudé, E. m.; Hammershøj, H. C. D.; Nielsen, D. U.; Pedersen, S. U.; Baik, M.-H. Ligand-controlled product selectivity in electrochemical carbon dioxide reduction using manganese bipyridine catalysts. *J. Am. Chem. Soc.* 2020, 142 (9), 4265-4275.
DOI: 10.1021/jacs.9b11806.

4. Feng, D.; Gu, Z.-Y.; Li, J.-R.; Jiang, H.-L.; Wei, Z.; Zhou, H.-C. Zirconium-Metalloporphyrin PCN-222: Mesoporous Metal-Organic Frameworks with Ultrahigh Stability as Biomimetic Catalysts. *Angew. Chem. Int. Ed.* 2012, 51 (41), 10307-10310.
DOI: 10.1002/anie.201204475.

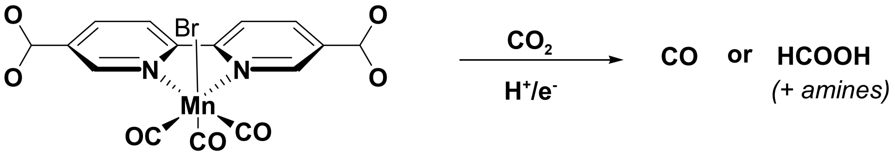


Figure 1. Incorporating Mn(CO)$_3$bpy complex into the linkers of a MOF for electrocatalytic conversion of CO_2 into CO or HCOOH. Figure by M. Luthra.

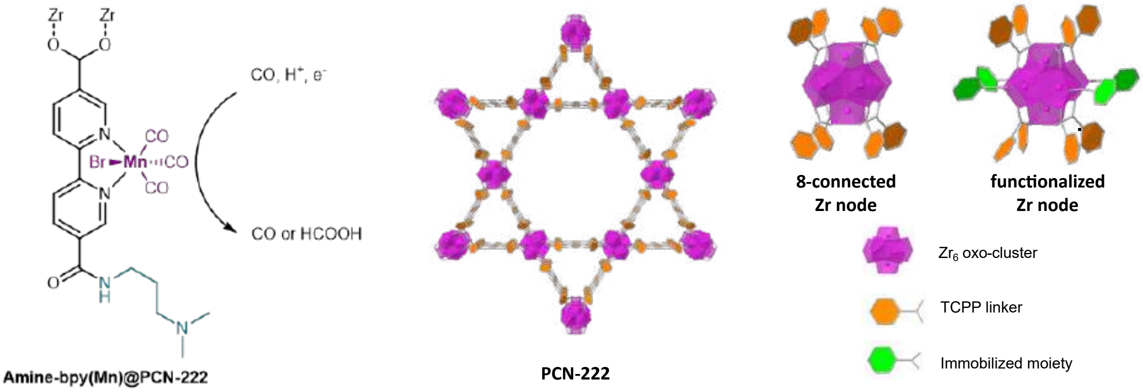


Figure 2. Schematic representation of the PCN-222 MOF with the connected Zr-clusters having Zr-carboxylate bonds for immobilization. Figure by M. Luthra.

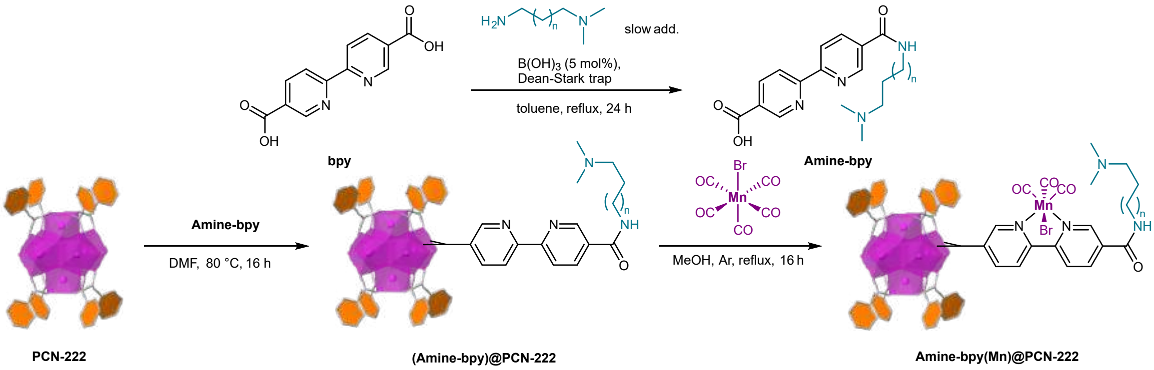


Figure 3. Synthesis procedure for Mn incorporation into the linkers of PCN-222 via Zr clusters. Figure by M. Luthra.

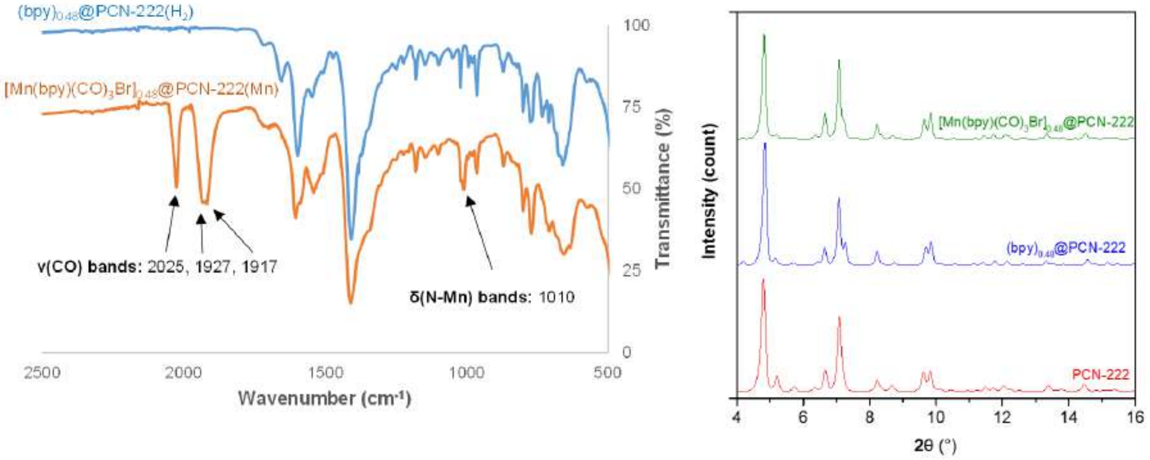


Figure 4. Characterization of Mn-incorporated MOF using X-ray Diffraction (left) and Infrared Spectrometry (right). Figure by M. Luthra.

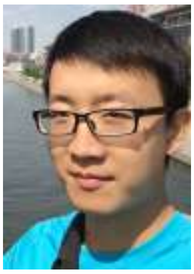
Stephanie J. Ton (ESR9): AU to Astrazeneca

In the spring of 2022, from april – june I had the opportunity to go on secondment to Astra Zeneca to work with Chad Elmore and the Isotope chemistry team. While at AZ I was working to develop aprocedure for the synthesis and use of organometallic complexes as a source of 13/14C labeling reagents. This experience was incredibly valuable to me, working in the hot lab and learning to handle radioactive material allowed me to learn a unique skill I could not have developed in an academic setting.

Not only did I get the opportunity to work with exciting new chemistry, I also had the opportunity to see the ins and outs of daily life working at a pharmaceutical company, which helped inform future career aspirations and provided me networking opportunities. While not in the lab I enjoyed exploring the many great museums, restaurants, and parks in Gothenburg. I particularly enjoyed visiting the southern archipelago islands which provided a beautiful nature retreat from the city. Overall I am very grateful to have been able to complete this secondment and work with Chad and his team!

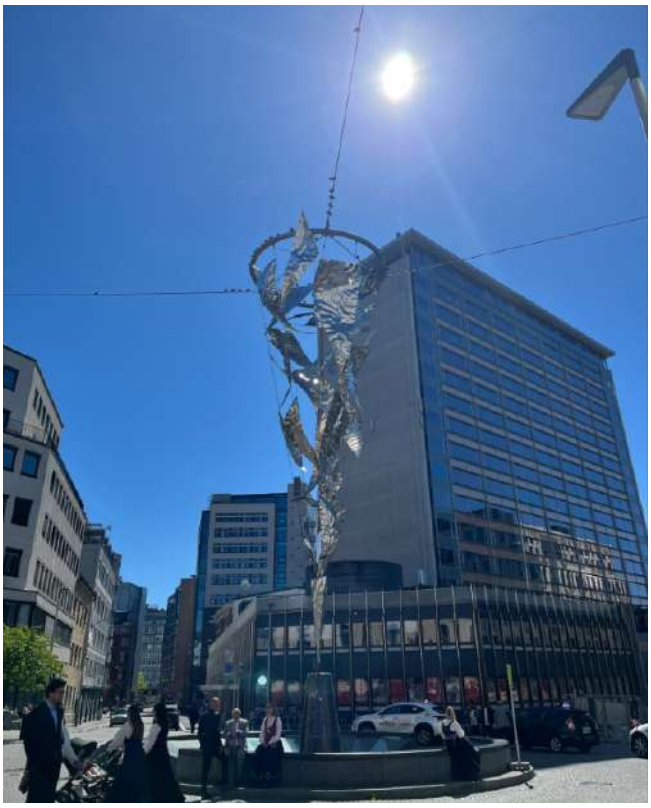
The archipelago south of Gothenburg and the Astrazeneca building entrance (insert). Photos by S. J. Ton).

Yunfei Bai (ESR4), HT to UiO



From 2022 April to July, I finished my secondment at the university of Oslo. This project focused on the catalyst testing of zeolitic materials on alkene oligomerization, which is a promising approach to producing long-chain olefins. In UiO, I did my research under the supervision of Ainara Nova Flores and Unni Olsbye. Collaboration with Ainara aims to find theoretical support for the structure change and catalytic performance of Beta zeotypes.

This work also connects with Mahika Luthra (ESR10). We worked together to build some early-stage cluster models for Sn-Beta. Catalyst tests in UiO were finished in Unni's group. She provided lots of insights into the nature of our catalytic material, and I learnt systematically about the activity evaluation of zeolite using a high-pressure reactor.
This secondment produced many interesting ideas to follow. A new collaboration between UiO and Topsøe has been planned for the spring of 2023.



The department of chemsitry at the University of Oslo (top), the "Lysfontenen" sculpture at St. Olavs plass in the city center (middle), and the parade in front of the royal castle on Norway's National Day (bottom). Photos by Y. Bai.

Kim S. Mühlfenzl (ESR12), Astrazeneca to ICIQ

From July to October 2022, I completed my research stay with Professor Ruben Martin at the ICIQ in Tarragona. During my stay, I was able to broaden my knowledge, especially about different carboxylation techniques, and to learn about a completely different culture and way of life from the one in Scandinavia.

In Professor Martin's lab, I worked on an ongoing project consisting of a four-component radical coupling with CO_2. This method allows a buildup of a high degree of complexity with three new bond formations and three stereocenters in only one step. While the protocol is already well optimized for one specific substrate class, it seems to be more challenging for another one. Therefore, I focused on optimizing the reaction conditions for another substrate class to make the procedure more general. Since CO_2 is one of the components, it may be possible to incorporate a carbon label by using labeled CO_2 for the carboxylation. This possibility will be further investigated in the future.

Besides the beautiful and historic old town, Tarragona has a lot more to offer. Therefore, I spent my free time swimming in the Mediterranean Sea, eating good food, and exploring the region. I also had the opportunity to visit the rice fields for the famous “paella” and vineyards hidden in the mountains. A special experience for me was the festivities in honor of “Sant Magí” and “Santa Tecla”, two saints of the city. During those festivities, parades of giants, dances, “fire-runs” (correfoc), and “human castles” (castells) take place.

I am truly thankful for the opportunity to not only learn a lot about chemistry but also about a new culture and country during this secondment.

Festivities in hornor of “Santa Tecla”. Left to right: the “fire-run” (correfoc), “human towers” (castells), and parade of the Giants (photos: K. S. Mühlfenzl).

Mahika Luthra (ESR10), UiO to HT

The present secondment took place at Haldor Topsøe under the supervision of Dr. Esben Taarning. The purpose was to study the incorporation of tin in beta zeolite metal-organic frameworks.

Beta Zeolite (BEA) is one of the first zeolites discovered. It has a complex structure consisting of an intergrowth of distinct structures, Polymorph A, B, and C (Figure 1a).[1] All the intergrowths contain a 3-D network of 12-ring pores. This zeolite has been demonstrated to be industrially important in several hydrocarbon conversion reactions, including cracking, hydrocracking, alkylation, and biomass conversion.

BEA has nine crystallographically different positions, which are named T-sites. It is possible to substitute Sn-atoms into all these T-sites using industrial processes[2] which give rise to Lewis acidity in the zeolite (Figure 1b).[3] During my secondment at Haldor Topsøe with Dr. Esben Taarning, I calculated the distortion in the lattice of Polymorph A after a heteroatom like Sn is substituted in place of a Si using Periodic DFT methods.

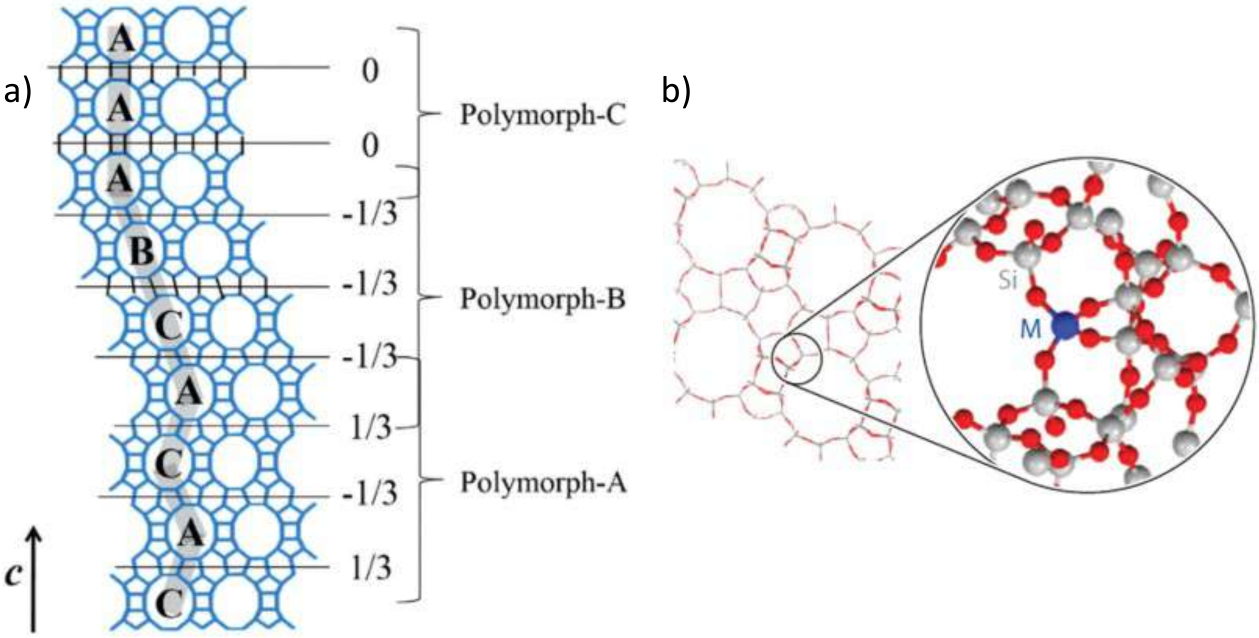


Figure 1. a) Representation of the different intergrowths of the Beta Zeolite, b) Heteroatom insertion into the framework of the zeolite to form Lewis acidic sites. Figure by M. Luthra.

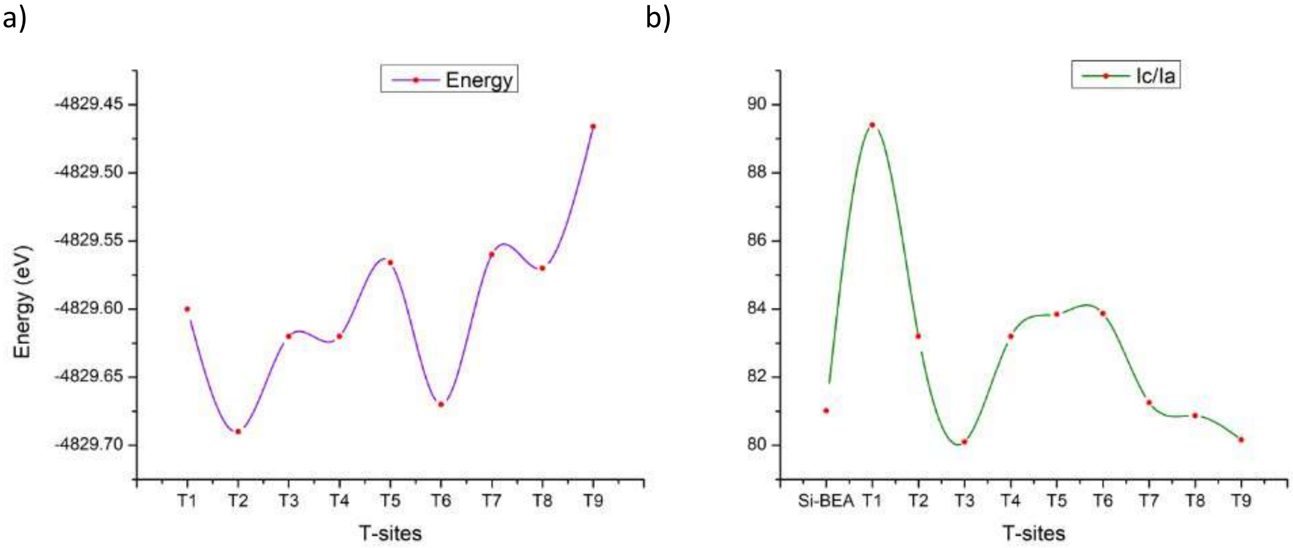


Figure 2. Analysis of a) Thermodynamic energies and b) Ic/Ia parameters of the unit cell after substitution of Sn in the Beta Zeolite framework at different T-sites. Figure by M. Luthra.

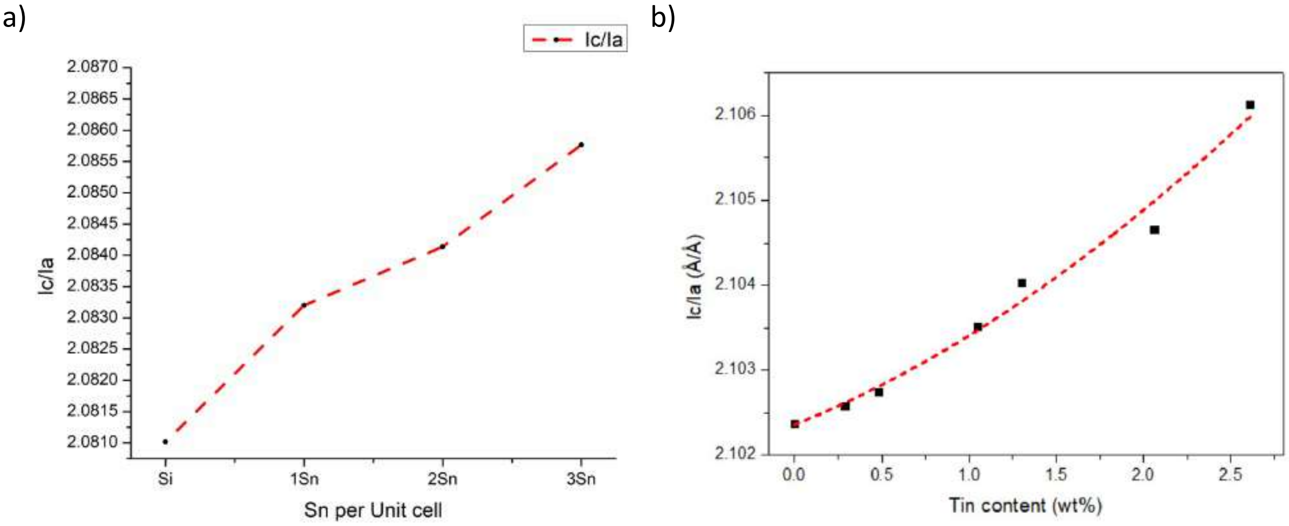


Figure 3. Comparison between the Ic/Ia unit cell parameters from a) DFT calculations and b) Experimental calculations of Ic/Ia by increasing Sn loading in the unit cell. Figure by M. Luthra.

Polymorph A was considered for the DFT calculations. Si was substituted by Sn at all the different T-sites separately. Different parameters like energy (eV) and unit cell parameters (Ic/Ia ratio) were calculated and it was found that the T2-site was thermodynamically most preferable for the Sn substitution (Figure 2).

In addition to that, the unit cell distortion was analyzed by tracking the change in the lattice parameter Ic/Ia of the unit cell. The experimental findings have revealed that increasing the Sn load in the framework of the zeolite increases the value of Ic/Ia parameters. On similar lines, with DFT calculations, it was found that increasing the number of Sn atoms per unit cell increases Ic/Ia ratio, thus confirming the experimental results (Figure 3).

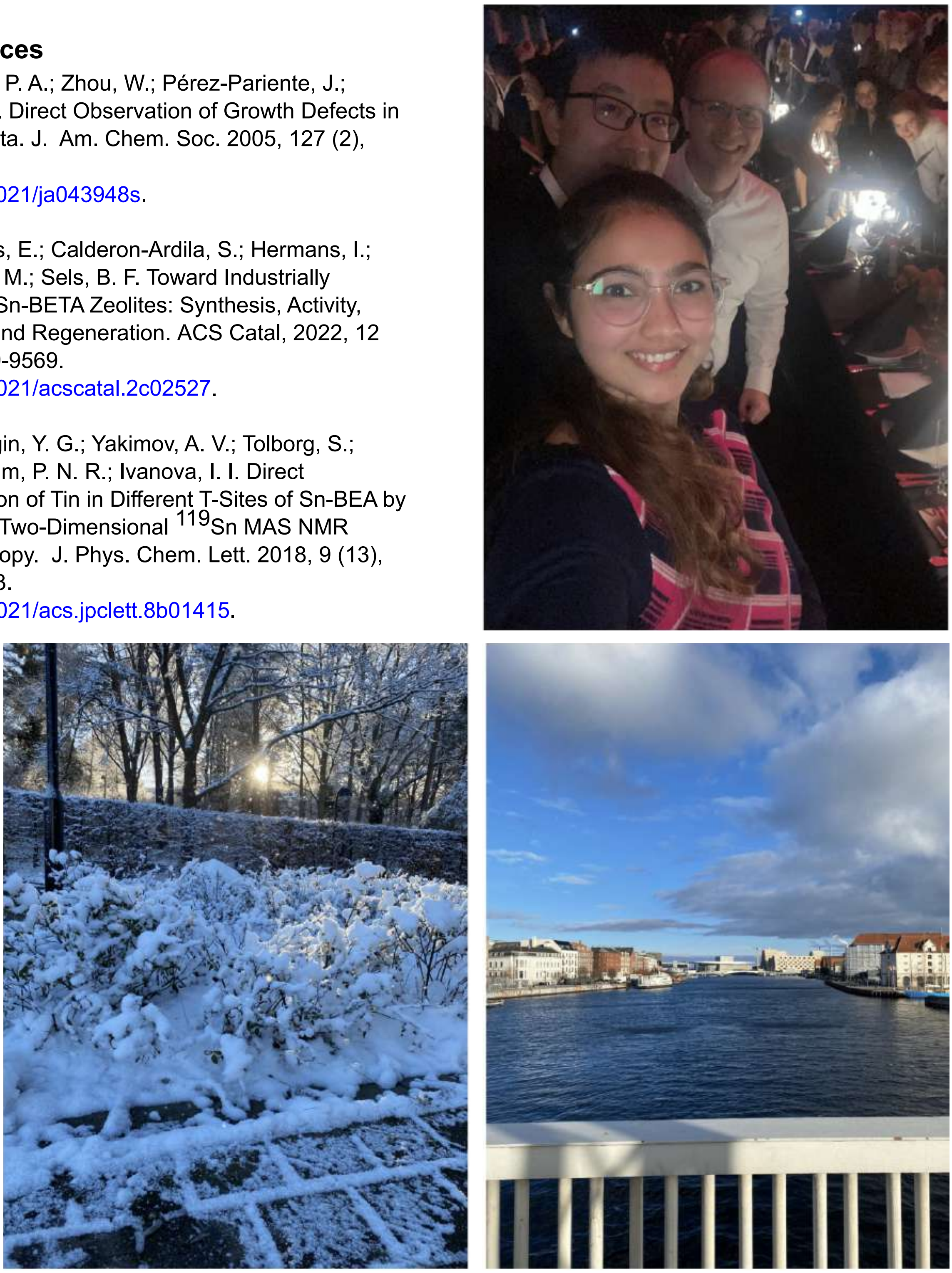
As a future plan, we will study in detail the defects created in the BEA framework in response to different perturbations like hydrolysis, calcination, destannation (Sn removal), etc.

References

1. Wright, P. A.; Zhou, W.; Pérez-Pariente, J.; Arranz, M. Direct Observation of Growth Defects in Zeolite Beta. J. Am. Chem. Soc. 2005, 127 (2), 494-495.
DOI: 10.1021/ja043948s.

2. Peeters, E.; Calderon-Ardila, S.; Hermans, I.; Dusselier, M.; Sels, B. F. Toward Industrially Relevant Sn-BETA Zeolites: Synthesis, Activity, Stability, and Regeneration. ACS Catal, 2022, 12 (15), 9559-9569.
DOI: 10.1021/acscatal.2c02527.

3. Kolyagin, Y. G.; Yakimov, A. V.; Tolborg, S.; Vennestrøm, P. N. R.; Ivanova, I. I. Direct Observation of Tin in Different T-Sites of Sn-BEA by One- and Two-Dimensional ^{119}Sn MAS NMR Spectroscopy. J. Phys. Chem. Lett. 2018, 9 (13), 3738-3743.
DOI: 10.1021/acs.jpclett.8b01415.



Top: The obligatory selfie with the HT CO$_2$PERATE members Y. Bai and E. Taarning. Bottom: Lyngby during the winter (left) and sommer (right). Photos by M. Luthra.

Activities

2022 at a glance

Our main focus for 2022 was providing our ESRs with transferable skills within entrepreneurship, in the form of a network-wide course as well as an innovation competition. The originally chosen course, supposed to be held at UiT in the spring of 2022, was re-scheduled several times and most of our ESRs instead joined either a course held at Aarhus University (AU) during the summer or the orginal course held at UiT in December 2022 (see page 36). The innovation competition is still ongoing, and the results will be announced at the occasion of the Winter School, which is postponed to the begining of 2023.

In September, we had the pleasure of gathering mostly in person for the 2022 edition of our Annual Meeting in Rostock, Germany. The meeting was hosted by the Leibniz Institute for Catalysis (LIKAT) and was focused on the progress of our ESRs, with each of them giving a talk about the status of their project. The meeting was also the occasion for all physically present to spend some time together after almost three years of digital meetings, which was very welcomed. You can read more about it from page 37.

2022 seems to be the year our Innovative Training Network (ITN) really fell into place, with gradually lifted travel restrictions and our 15th Early-stage researcher (ESR) officially joining the network (you can read more about Pierre in his interview on page 43).

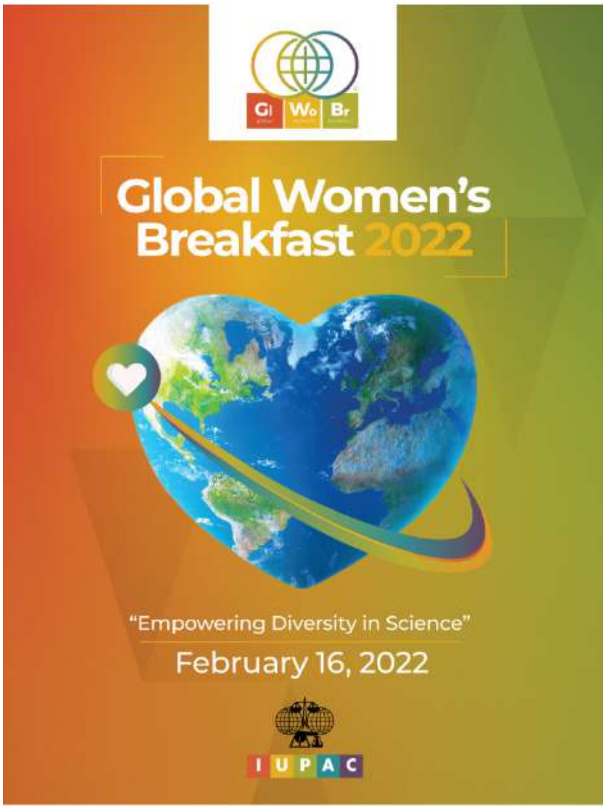
We kicked-off 2022 on the 16th of February with our participation to IUPAC's Global Women's Breakfast (GWB), for which we organised, together with the NordCO2 consortium, a hybrid seminar with a digital lecture and physical breakfast events at several locations in the Nordic countries (more about it on page 34). The week after that, we had a belated annual meeting for 2021, which was held purely as a digital meeting. For this event, we kept things short and simple and gave the main stage to research, with the purpose of not only getting an overview of the research effort within the ITN, but also to stimulate scientific discussions for each of our Work Packages. You can read all about it on page 36.

Global Women's Breakfast 2022

Each year, the International Union of Pure and Applied Chemistry (IUPAC) leads the organisation of the event "Global Women's Breakfast" (GWB), which is described as follows:
"The aim is to celebrate the accomplishments of Women in Science and to inspire younger generations to pursue careers in science. Women and men from all types of science organizations come together to share breakfast either virtually or in person. A central goal is also to establish an active network of both men and women to overcome the barriers to gender equality in science. The Global Breakfast facilitates the formation of communities on a local, regional, and international scale to effectively share ideas and strategies for progress." (source: IUPAC website).

Together with the Nordic Consortium for CO_2 Conversion, NordCO_2, CO_2PERATE participated to this event by organising a digital seminar accompanied by physical breakfast events in Oslo, Stockholm, and Helsinki. Considering that the institutions taking part in NordCO_2 and CO_2PERATE are mostly from Nordic countries, where gender equality is higher than in other parts of the world, we chose to broaden our scope to talk about diversity in research environments.

The event was chaired by Associate Prof. Ainara Nova (UiO), and the main guest was Prof. Emeritus Christina Moberg from the KTH Royal College of Technology, Stockholm, Sweden. C. Moberg gave an inspiring talk titled "*Empowering Diversity in Science: Strength lies in differences, not in similarities*" after a quote from Stephen R. Covey. She first highlighted several key points about the marginalisation of scientists as well as the related biases in our field, then proceeded to demonstrate how diversity is inherently linked to the quality of our work environments, our research, and our research outputs. The talk was followed by a discussion with the audience as well as invited guests Prof. Adela Muñoz Paez from the university of Seville (Spain) and Prof. Unni Olsbye (UiO).



The poster from the GWB 2022 event (source: IUPAC).

A moment in time during the meeting, showing the groups attending at each location (capture by A. Muños Paez).

Empowering Diversity in Science

Strength lies in differences, not in similarities

(Stephen R. Covey)

Christina Moberg

KTH Royal Institute of Technology

Speaker Christina Moberg and invited guests Adela Muñoz Paez and Unni Olsbye.

More about the subject of our GWB 2022 event:

Menon, B.R.K. The missing colours of chemistry. Nat. Chem. 13, 101–106 (2021).
DOI: 10.1038/s41557-020-00632-8.

Freeman, R., Huang, W. Collaboration: Strength in diversity. Nature 513, 305 (2014).
DOI: 10.1038/513305a.

Urbina-Blanco, C.A. A Diverse View of Science to Catalyse Change. J. Am. Chem. Soc. 142, 34, 14393–14396 (2020).
DOI: 10.1021/jacs.0c07877.

Reisman, S.E., Sarpong, R., Sigman, M.S., Yonn, T.P. Organic Chemistry: A Call to Action for Diversity and Inclusion. J. Org. Chem. 85, 16, 10287–10292 (2020).
DOI: 10.1021/acs.joc.0c01607.

Powell, K. These labs are remarkably diverse - here's why they're winning at science. Nature 558, 19-22 (2018).
DOI: 10.1038/d41586-018-05316-5.

Activities

Annual Meeting 2021

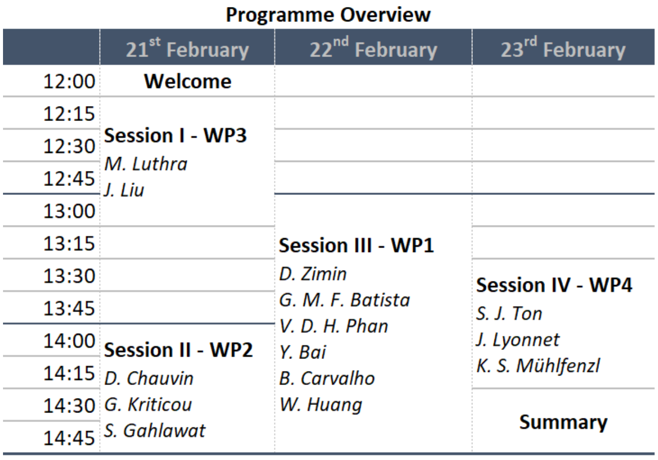
The 2021 edition of our Annual Meeting was postponed to 2022 in the hopes of holding a physical meeting at Aarhus University (AU). However, we had to transfer it to a digital platform due to travel restrictions remaining in effect at several of the institutions participating in our network.

Considering that, after almost two years of digital meetings, the interest for them had declined, we chose to keep things short an simple...with the goal of organising more social activities at the occasion of later meetings.

We gave the main stage to scientific discussions with four sessions dedicated to each of the research work packages, with early-stage researchers (ESRs) giving presentations and Work Package (WP) leaders directing the discussions. By doing this, we were able to give a network-wide update on the status of individual research projects and the progress made in each WP.

Composition of Work packages

	WP1	WP2	WP3	WP4
Leader	**R. Martin**	**C. Nevado**	**B. Martin-Matute**	**C. S. Elmore**
Supervisors	T. Skrydstrup B. Martin-Matute E. Taarning K. H. Hopmann M. Beller	K. H. Hopmann	A. Nova R. Franke M. Beller	T. Skrydstrup R. Martin
ESRs	D. Zimin G. M. F. Batista V. D. H. Phan Y. Bai B. Carvalho W. Huang	D. Chauvin G. Kriticou S. Gahlawat	M. Luthra J. Liu P. Fablet	S. J. Ton J. Lyonnet K. S. Mühlfenzl



Programme Overview

	21st February	22nd February	23rd February
12:00	**Welcome**		
12:15	**Session I - WP3** *M. Luthra* *J. Liu*		
12:30			
12:45			
13:00		**Session III - WP1** *D. Zimin* *G. M. F. Batista* *V. D. H. Phan* *Y. Bai* *B. Carvalho* *W. Huang*	
13:15			**Session IV - WP4** *S. J. Ton* *J. Lyonnet* *K. S. Mühlfenzl*
13:30			
13:45			
14:00	**Session II - WP2** *D. Chauvin* *G. Kriticou* *S. Gahlawat*		
14:15			
14:30			**Summary**
14:45			

The programme for the CO$_2$PERATE Annual Meeting was intentionally minimalist, focusing on a scientific update and giving ample time for discussions about our research (figure: M.-J. H. Halsør).

Entrepreneurship course

Also affected by the pandemic was our Entrepreneurship course, for which the ESRs were supposed to join the course scheduled for the spring semester at UiT The Arctic University of Norway. The course was cancelled, and we found an alternative course at AU, held between the 25th of July and the 5th of August 2022. The course was given as a part of the Summer University programme at AU, and 11 out of our 15 ESRs were able to join.

The four ESRs that were not able to take the Entrepreneurship course in Aarhus in the summer where able to join a course in Tromsø, the very one that was cancelled in the spring. It was held from the 5 to the 9 of December.

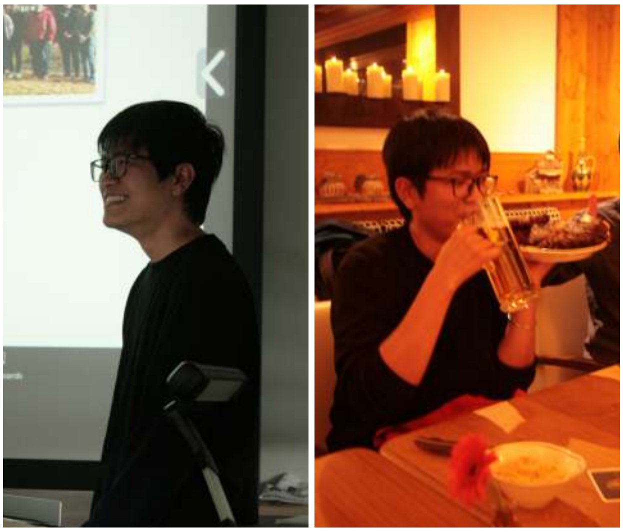
Annual Meeting 2022

Our long awaited, first physical annual meeting was hosted by the Leibniz Institute for Catalysis (LIKAT) at their location in Rostock, Germany. This time, we focused on ESR presentations given that all 15 of our ESRs were present, some meeting the rest for the very first time physically.

The "Sieben stolze Schwestern küsst das eine Meer" fountain, the Kröperliner tower disapearing in the heights, and street art at the intersection of Kröpeliner Straße and Pädagogienstraße in Rostock, Germany (photos: M.-J. H. Halsør).

We started the meeting with an opening speech by our host, CO_2PERATE Principal Investigator (PI) Matthias Beller. This was followed by a session with presentations from WP1 by ESR1 Dmitry Zimin, ESR2 Gabriel Martins Ferreira Batista, ESR3 Vu Duc Ha Phan, ESR4 Yunfei Bai and local ESR13 Weiheng Huang. After the ESR presentations, we had a talk by CO_2PERATE PI Robert Franke (Evonik, EV) and co-supervisor Per-Ola Norrby (Astrazeneca, AZ).

For our first dinner together, we went to the steakhouse Old Western, where we enjoyed burgers and very, very big portions of ribs.



ESR3, Ha, enjoys a well-deserved reward after presenting (photos: M.-J. H. Halsør).

The ITN getting ready for action: before the official start of the meeting, we had the opportunity to start by having lunch together as well as a few moments to gather ourselves (photo: M.-J. H. Halsør).

On the second day of the meeting, ESR presentaions were given by ESR5 Bjørn Carvalho, ESR14 Jiali Liu, ESR6 Georgia Kriticou, ESR7 Doriane Chauvin and ESR8 Sahil Gahlawat. Local researcher Si-Shun Yan also gave a talk about photocatalytic dicarboxylation of unactivated alkenes with CO_2 within the visible spectrum.

After lunch, technical problems prevented us to present the innovation competition, and we had instead an impromptu Q&A session led by Project Manager Marie-J. H. Halsør. The session, held without any PI present, focused on feedback from the ESRs about the ITN in general, around the theme "How does the ITN work for you?".

Our programmed resumed afterwards with the tour of the LIKAT facilities, and we even had time to take new group pictures before heading to the day's restaurant, the italian-themed L'Osteria.

Top: The CO_2PERATE table at dinner (left) and LIKAT researcher Si-Shun Yan (right). Bottom: The 2022 group picture. Photos: M.-J. H. Halsør.

For the last day of the meeting, we had presentations by ESR10 Mahika Luthra, local ESR15 Pierre Fablet, ESR9 Stephanie Ton, ESR11 Julien Lyonnet and ESR12 Kim Saskia Mühlfenzl. The presentaions were followed by the final talk of the meeting, given by local Professor Evgenii V. Kondratenko. His talk was titled "Fundamentals for tailored preparation of environmentally firendly catalysts for efficient propane dehydrogenation to propene".

After lunch, it was time to say goodbye for 2022, with the promise to meet again in 2023!

ITN ESR Digital Meetings

Our ESRs are a tight-knit group who communicates regularly. Since the travel restrictions due to the pandemic were lifted at the beginning of 2022, they have been able to meet physically during meetings and secondments. It was thus not necessary anymore to have digital meetings, and they decided to discountinue them later in 2022.

Supervisory Board Meetings

The CO_2PERATE SB met twice in 2022, in May and October. As usual, the implementation of the action was discussed regarding the scientific progress of the research projects and the activities of the network. In additon, we submitted our first periodic report to the European Commission in April, which was approved before the summer.

What's next in CO_2PERATE?

We are now in full swing and looking forward to the research that will be done during 2023 as well as, hopefully, the first group PhD defenses.

Concerning activities, we had to postpone the planned Winter School of 2022 as well as the Innovation Competition. The school was supposed to be organised at SU with the theme "Heterogeneous catalysis and Industrial scale-up". The CO_2PERATE Innovation Competition is a network-wide challenge where our ESRs are asked to use the knowledge and skills they acquired at the Entrepreneurship course to propose ideas for new businesses. Unfortunately, the delays we encountered with the Entrepreneurship course meant that we had to push back this activity. The competition was officially launched in December 2022.

To cope with these changes, the CO_2PERATE Supervisory Board decided to the follwing: the school will still be organised by SU, but in collaboration with ICIQ. It will be held in Spain in March 2023 and will feature the wrap-up of the Innovation Competition.

Originally planned in 2023 was the "CO_2 day", taking advantage of an existing event at SU. The local event was cancelled and we are looking for an alternative activity.

In addition, we planned to hold a course on "Intellectual property rights and patent applications" at AZ as well as the Annual Meeting 2023 at ICIQ, both scheduled around the summer. The course and the Annual Meeting will be held at AZ in June 2023, as we are already travelling to Spain in March.

Student Interview

Pierre Fablet (ESR15), Leibniz Institue for Catalysis

Pierre obtained his Master's degree from the Université Paris Saclay, France. In his free time, he enjoys hiking, reading and playing chess.

Why did you join CO_2PERATE?

Set aside my personal affinity with the topic, I was first attracted by the strong interface this project is aiming to develop between industry and academia. As it turns out, the numerous collaborations and expertise it offers to ESRs has become an excellent foundation for a research network able to tackle thorny environmental questions. Moreover, I believe the perspective for PhD student to not only be trained in a cross-disciplinary fashion, but also supported through by the network and to further career prospects, is an immense advantage.

What is your project about?

My project can be summed up by the development of catalysts for amino carbonylation and carbonylation reactions of olefins with CO_2. In a blend of ligand synthesis of new phosphine ligands and selection of cheap and abundant metals, it aims at developing new homogeneous catalytic conditions for industrially relevant processes, such as hydroformylation and ultimately further opening the way for CO_2.

Tell us about your institution/country you are currently in.

I am conducting my research at the Leibniz Institute für Katalyse (LIKAT), based in Rostock which is among the oldest and largest facility for catalysis. As a European and surely global hub for homogeneous and heterogeneous catalysis, the institute benefits from a strong and large pool of very talented researchers. With the opening this year of a third building on the Südstadt campus, it keeps expanding providing attractive resources and opportunities for local and visiting scientists alike.

Although weather on the Baltic Sea is far from what I'm used to (-7°C winters), Mecklenburg-Vorpommern is a naturally gifted region (i.e Rügen) that thrives with activity. Rostock is a perfect middle point between busier cities and their strict opposite, and the proximity of Berlin, Hamburg and Denmark (by ferry) makes spare time all the more enjoyable.

Supervisory Team: main supervisor Matthias Beller (LIKAT) and co-supervisors Ainara Nova (UiO) & Robert Franke (EV).

People

Aarhus University

Troels Skrydstrup
Professor
leader WP5

Gabriel M. F. Batista
ESR 2

Stephanie Ton
ESR 9

Astrazeneca

Charles S. Elmore
Senior Director
leader WP4 and SB

Kim S. Mühlfenzl
ESR 12

Per-Ola Norrby
Principal Scientist
Co-supervisor

Malvika Sardana
Senior Scientist
Co-supervisor

Markus Artelsmair
Senior Scientist
Co-supervisor

Magnus Johansson
Principal Scientist
Co-supervisor

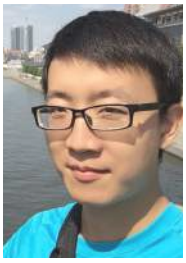
Evonik

Robert Franke
Professor
CO_2PERATE PI

Jiali Liu
ESR 14

Haldor Topsoe

EsbenTaarning
Senior Researcher
leader WP7



Yunfei Bai
ESR 4

Søren Tolborg
R&D Manager
Co-supervisor

People

Institute of Chemical Research of Catalonia

Rubén Martín
Professor
leader WP1

Dmitry Zimin
ESR 1

Julien Lyonnet
ESR 11

Leibniz Institute for Catalysis

Matthias Beller
Professor
CO$_2$PERATE PI

Weiheng Huang
ESR 13

Pierre Fablet
ESR 15

Stockholm University

Belén Martín-Matute
Professor
leader WP3

V. D. Ha Phan
ESR 3

University of Oslo

Ainara Nova
Associate Professor
leader WP6

Mahika Luthra
ESR 10

Michelle Cascella
Professor
Co-supervisor

David Balcells
Senior Researcher
Co-supervisor

Abril Castro Aguilera
Researcher
Co-supervisor

UiT The Arctic University of Norway

Kathrin H. Hopmann
Professor
Coordinator, leader WP8

Bjørn Carvalho
ESR 5

Sahil Gahlawat
ESR 8

Annette Bayer
Professor
Co-supervisor

Luca Frediani
Professor
Co-supervisor

Marie-J. H. Halsør
PhD
Project Manager

University of Zürich

Cristina Nevado
Professor
leader WP2
University of Zürich

Georgia Kriticou
ESR 6

Doriane Chauvin
ESR 7

Publications 2022

Astrazeneca: K. S. Mühlfenzl (ESR12)

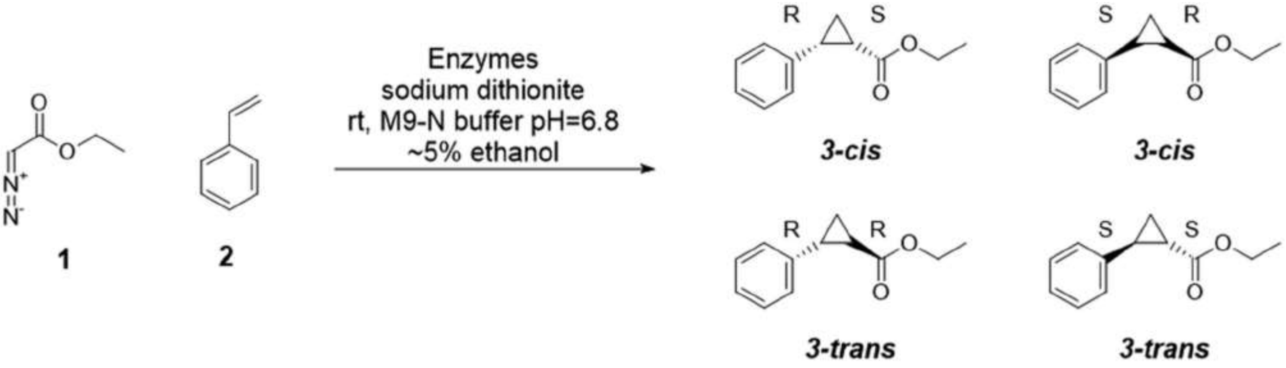
Exploring the enzyme-catalyzed synthesis of isotope labeled cyclopropanes

Malvika Sardana, Kim S. Mühlfenzl, Sylvia T. M. Wenker, Christian Åkesson, Martin A. Hayes, Charles S. Elmore, Subhash Pithani

Journal of Labelled Compounds and Radiopharmaceuticals 2022; 65 (4): 86- 100.

Publication Date: 7th of January 2022

https://doi.org/10.1002/jlcr.3962



Evonik and LIKAT: J. Liu (ESR14)

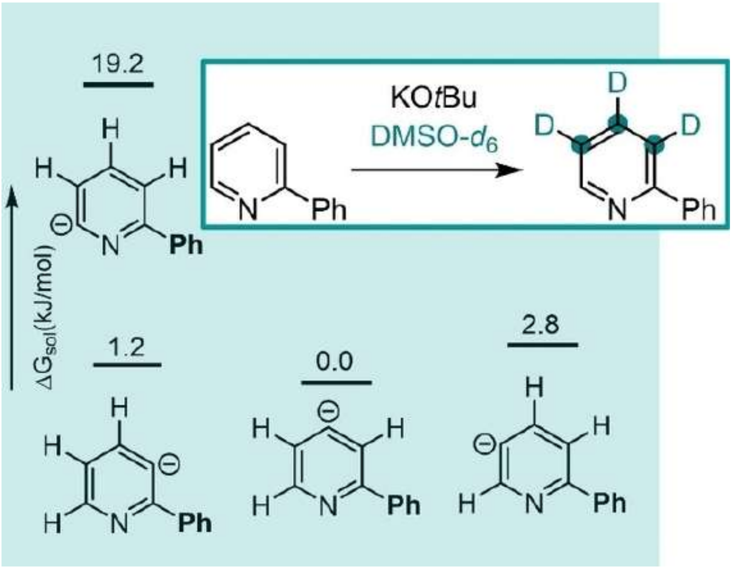
Base-Mediated Remote Deuteration of N-Heteroarenes – Broad Scope and Mechanism

Sara Kopf, Jiali Liu, Prof. Dr. Robert Franke, Dr. Haijun Jiao, Dr. Helfried Neumann, Prof. Dr. Matthias Beller

European Journal of Organic Chemistry 2022, e202200204.

Publication Date: 15th of March 2022

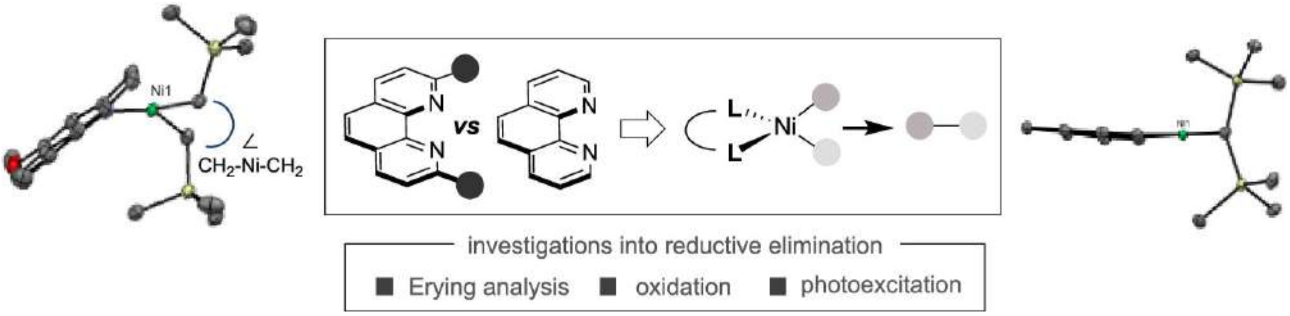
https://doi.org/10.1002/ejoc.202200204



AU and ICIQ : S. J. Ton (ESR9)

Reductive Elimination from Sterically Encumbered Ni–Polypyridine Complexes

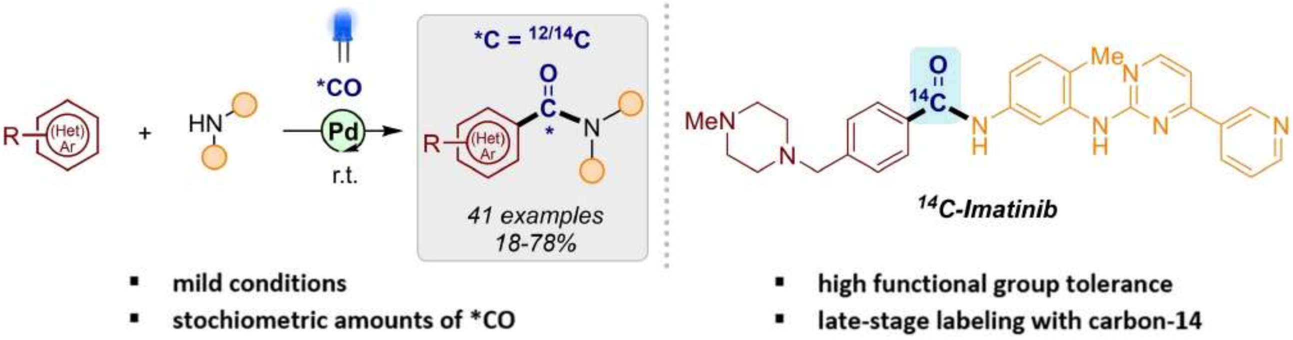
Craig S. Day, Stephanie J. Ton, Ryan T. McGuire, Cina Foroutan-Nejad, and Ruben Martin
Organometallics 2022, 41, 19, 2662–2667
Publication Date: 21st of September 2022
https://doi.org/10.1021/acs.organomet.2c00362



Astrazeneca: K. S. Mühlfenzl (ESR12)

Visible-Light Enabled Late-Stage, Room-Temperature Aminocarbonylation of Aryl Iodides with Labeled Carbon Monoxide

Kim S. Mühlfenzl, Dr. Malvika Sardana, Prof. Troels Skrydstrup, Dr. Charles S. Elmore
ChemistrySelect 2022, 7, e202203582
Publication Date: 8h of December 2022
https://doi.org/10.1002/slct.202203582



CO_2PERATE Innovative Training Network

Horizon 2020 Research and Innovation Programme – Marie Skłodowska-Curie grant agreement No. 859910

Contact adress: Department of Chemistry, UiT The Arctic University of Norway, Tromsø, Norway