Call 2017 - Application Form

Application nr	30902231
Spokesperson-coordinator	SELS Bert
Research field	Science and Technology
Acronym	BioFact
Project title	Bio based factory: Sustainable chemistry from wood
Total budget requested	€ 3 995 166 / 4 years

CONTENT OF THIS PROPOSAL

This document contains the following parts:

- *Part 1: Consortium*
- *Part 2: General description of the proposal*
- *Part 3: Motivation and management of the consortium*
- *Part 4: Scientific section*
- *Part 5: Budget*
- *Ethical aspects*
- *Research metrics of every consortium's participants*
- *Legal statement*

Other documents attached to the application:

- *Curriculum vitae (STRICTLY up to 4 pages in Calibri Font 11pt) and publications list for the spokesperson and for each included PI and co-PI. The publication list is a free format and there is no page limitation, however one should use Calibri Font 11pt.*

- *Consent forms by Institutions of Type II, III or IV.*

- *Price offers for equipment, quotes for subcontracted tasks*

- *CVs and publication lists are attachments and not included in this document.*

- *Price offers and quotes for subcontracted tasks will only be available to the panel*

PART 1: CONSORTIUM

All administrative details of the included research groups, institutions, together with the personal details of the spokesperson-coordinator and of all included principal investigators (PI) and co-supervisors (co-PI)

Spokesperson-coordinator of the proposal: SELS Bert

Type I-FL - Centre for Surface Chemistry and Catalysis (KU Leuven)

SELS Bert	Principal Investigator Full professor (100%) KU Leuven M2S Division, Center for surface Chemistry and Catalysis (COK)
DE VOS Dirk	Co-Supervisor Full professor (100%) KU Leuven Department of Microbial and Molecular Systems (M²S)/Centre for Surface Chemistry and Catalysis (COK)

Type I-FL - Center for Molecular Modeling (Universiteit Gent)

VAN SPEYBROECK Veronique	Principal Investigator Full professor (100%) Universiteit Gent Center for Molecular Modeling

Type I-FL - Organic Synthesis (Universiteit Antwerpen)

MAES Bert	Principal Investigator Full professor (100%) Universiteit Antwerpen Chemistry Department, Laboratory of Organic Synthesis

Type I-FR - Laboratory of Organic Chemistry (Université Libre de Bruxelles)

EVANO Gwilherm	Principal Investigator Professor (100%) Université Libre de Bruxelles Laboratoire de Chimie Organique, Service de Chimie et PhysicoChimie Organiques

Type I-FR - Center for Education and Research on Macromolecules (CERM) (Université de Liège)

DETREMBLEUR Christophe	Principal Investigator Research Director of FRS-FNRS (100%) Université de Liège Chemistry/Center for Education and Research on Macromolecules (CERM)/CESAM Research Unit
DEBUIGNE Antoine	Co-Supervisor Research Associate of FRS-FNRS (100%) Université de Liège

	Chemistry/Center for Education and Research on Macromolecules (CERM)/CESAM Research Unit

Type IV - Applied Sustainable Catalytic Processes (Leibniz-Institut für Katalyse)	
BELLER Matthias	Principal Investigator Director (100%) Leibniz-Institut für Katalyse Applied Sustainable Catalytic Processes/ Applied Homogeneous Catalysi

PART 2: PROPOSAL

Identifiers

Acronym: BioFact

Project title: Bio based factory: Sustainable chemistry from wood

Short summary in Layman's terms of the project

Fossil oil depletion imposes a societal driven shift to non-edible biomass as a renewable feedstock for chemicals. Wood is among the most abundant carbon sources on earth, and is ideal to address this challenge. Wood contains (hemi)cellulose (carbohydrates) and lignin, a polymeric network of arenes. Biorefineries mostly focus on the former, using lignin only as low value fuel. This project's ambitious aim is to transform lignin into high-value chemicals and polymers, starting with the very challenging selective depolymerization of lignin. In KULeuven's 'lignin-first' concept, even before carbohydrate valorization, wood is treated in a selective way to recover just 4 biobased aromatic molecules in high yield. Next, selective catalytic (de)functionalization of the 4 molecules will lead to catechol and pyrogallol. Innovative synthetic methods (aminations, reductions, C(sp2)-O cross-coupling and C(sp2/sp3)-H functionalization) will transform these into important chemicals (substituted phenols, anilines etc). Finally, biobased chemicals are coupled with CO2 to form valuable functional polymers. Modelling, e.g. via Advanced Molecular Dynamics will allow to rationalize and even predict reactivity and selectivity in realistic operating conditions, lending strong support to the development of new concepts for transformation of aromatics.

Keywords

Research field	Science and Technology
FWO disciplines	Organic chemistry Polymer chemistry Homogeneous catalysis Heterogeneous catalysis
FNRS descriptors	Homogeneous and heterogeneous catalysis Polymer chemistry Organic chemistry
Optional keywords	lignin, biomass, biorefinery, biorenewable chemicals, C-H activation, C-O activation, zeolite, MOF, graphene-based catalyst, phenols, anilines, CO2, carbon dioxide

Ethical aspects

The form questions and responses are fully transcripted at the end of this application PDF.

I confirm that none of the issues below apply to my proposal

PART 3: MOTIVATION AND MANAGEMENT OF THE CONSORTIUM

Both motivation and management of the consortium should be addressed in a template STRICTLY up to 12 pages, Calibri Font 11pt.

PART 4: SCIENTIFIC SECTION

The description of the project should be addressed in a template STRICTLY up to 15 pages, Calibri Font 11pt).

1. Composition of the Consortium

Summary of consortium PIs and co-PIs

Participant	PI/Co-PI	PhDs past + current	Age	Pubs.	Cites*	Average cites per article	H-index*	Credentials
KULeuven	Bert Sels (PI, Coordinator)	36 + 22	44	234	9700	41	55	Director COK Ass. Ed. *ACS Sust&Eng* Board *ChemSusChem* Green Chem Award 2015
KULeuven	Dirk De Vos (Co-PI)	38 + 15	49	329	15300	39	67	Department Head Ass. Ed. *Cat. Sci. Technol.*
ULg	Christophe Detrembleur (PI)	9 + 7	43	217	6300	29	41	FNRS Research Director
ULg	Antoine Debuigne (Co-PI)	6 + 2	39	92	2400	26	28	FNRS Research Associate
ULB	Gwilherm Evano (PI)	8 + 8	40	100	3900	39	33	Editor *Lett. Org. Chem.* CNRS bronze medal 2007
UAntwerp	Bert Maes (PI)	14 + 10	42	118	2900	25	32	Head of ORSY Editor *Top. Heterocycl. Chem.*
UGent	Veronique Van Speybroeck (PI)	20 + 12	42	272	6300	23	41	Head of CMM ERC StG; ERC CoG grant
LIKAT	Matthias Beller (PI)	103+26	55	779	41800	53	105	Director of LIKAT ERC Advanced Grant

*source: Web of Science™, March 2017.

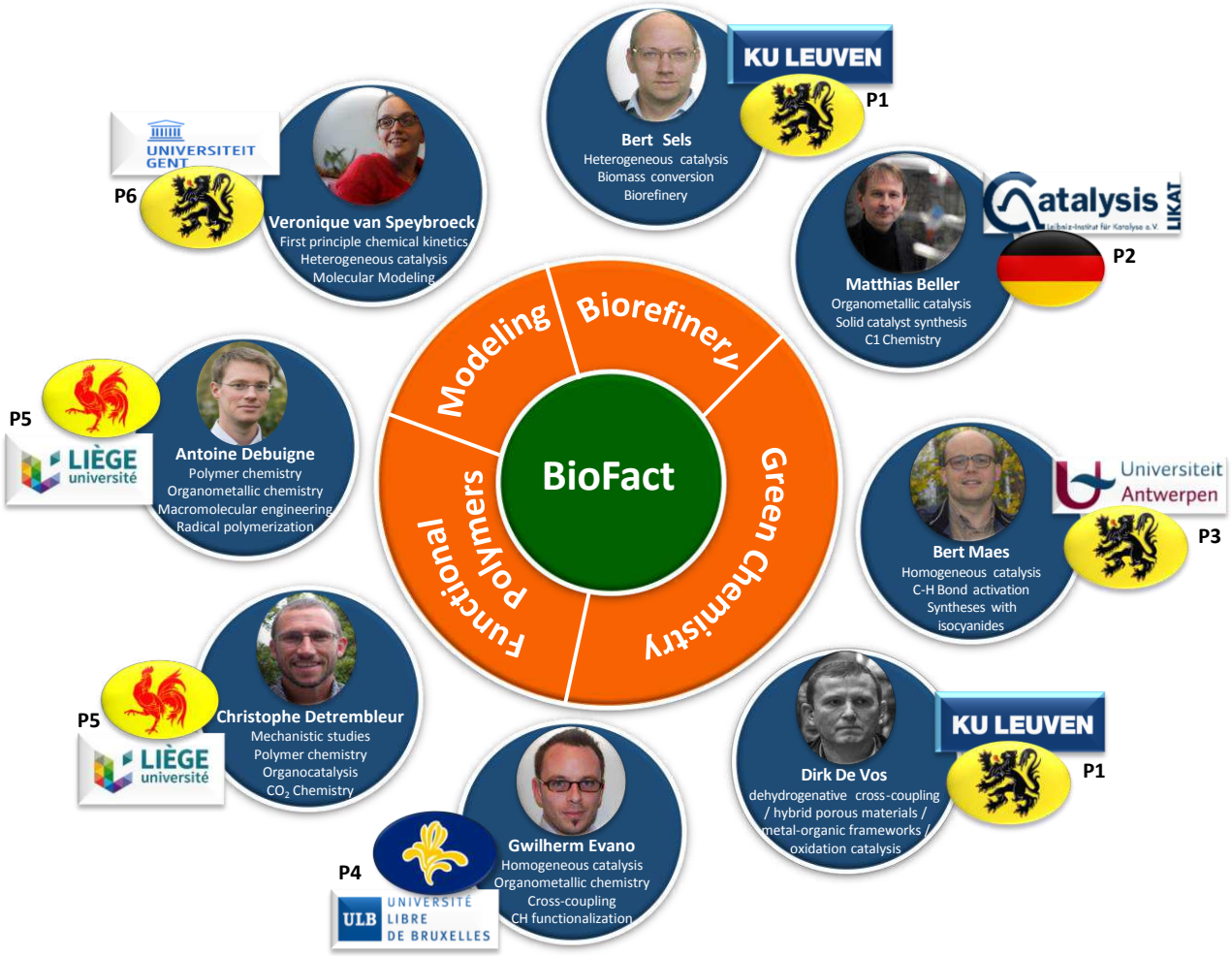
Bert F. Sels (P1, KULeuven) heads a research group on heterogeneous catalysis for future challenges in industrial organic and environmental catalysis. His focus is on the spectroscopic and kinetic study of active sites for small molecules activation (Nature 536 (2016) 317) and heterogeneous catalysis in biorefineries, as exemplified in studies on carbohydrates and lipids, or acids like lactic acid (Science 349 (2015) 78). He is the recipient of the 2015 Green Chemistry Award. Sels recently developed the reductive '**Lignin first biorefinery**', opening up fully new avenues in the high yield recovery of biobased aromatics from crude lignocellulose. This **expertise in biorefinery** excellently prepares for the carbonylation-based wood processing in **WP1**. Much of Sels' work relies on extensive mastering of acid-base and (de)hydrogenation catalysis, and most often, the subtle balance of both. This is the basis for the demethylation, dealkylation and (reductive) amination of **WP2**, and for the design of suitable building blocks for the polymers produced in **WP5**. Relying on his expertise in coordinating several similar large scale projects, Bert Sels will assume the **general coordination** of BioFact.

Dirk De Vos (P1, KULeuven) has **vast experience in catalytic oxidation reactions**, including oxygen-driven dehydrogenative cross-couplings, e.g. with homogeneous Pd catalysts. Moreover, he has a strong record in use of **porous materials** (zeolites, MOFs), especially for fine chemical transformations. These two interests now seamlessly converge in the project, with work on shape-selective C-H activations on arenes using microporous MOF and zeolite catalysts (**WP4**).

Matthias Beller (P2, LIKAT) has been for decades one of the beacons on the global catalysis scene. Starting from an organometallic background, he first championed the use of well-defined, tailored metal complexes, with a focus on cross-coupling, carbonylation, (hydro)amination, hydroformylation etc. Catalysis with the most abundant of metals, Fe, became a highlight, with e.g. (enantioselective) oxidations and reductions. He opened new paths in energy storage exploring e.g. the reversible $H_2 + CO_2 \rightleftharpoons$ formic acid reaction using well-defined complexes, even of Fe (e.g. metal pincers). He recently ventured into heterogeneous catalysis, with N-doped carbons as supports. Beller is a recipient of the Otto Roelen medal, the Leibniz price and the European Prize for

Sustainable Chemistry. Beller heads the Leibniz Institute for Catalysis Research in Rostock and in 2015 received the **ERC Advanced Grant** NaNaCat. While his insights will be beneficial for nearly the complete project, we will most strongly rely on his expertise in catalytic carbonylations in **WP1**. The carbon nitride, boron nitride or related heterogeneous catalysts will be valorized for the reductive catechol/pyrogallol transformations of **WP2**. **Beller's unique class** of metals@graphenes and metals@N-doped graphenes will be important in the cross-coupling reactions involving aryl-O bonds (**WP3**) and carbonylations (**WP1**).

Bert Maes (P3, UAntwerp) leads the UAntwerp organic synthesis division, covering the themes homogeneous catalysis, sustainable chemistry, heterocyclic chemistry and more recently biorenewables. He is a **recognized leader in catalytic C-H bond activation**, in particular for more challenging C(sp3)-H bonds. Other key research themes are catalysis with non-noble metals, synthesis and functionalization of heterocycles with e.g. isocyanides, and mechanistic studies in homogeneous catalysis. Maes will prepare lignin model compounds for **WP1**, and propose homogeneous catalysts for the dealkylations of **WP2**. The (mechanistic) insights in cross-coupling of (pseudo-)halides form the basis for the activation of aryl-O bonds with homogeneous or heterogeneous Ni catalysts in **WP3**. His profound expertise in C(sp3)-H activation will be extended from N-heterocycles to biosourced cyclohexanes, with use of 'traceless' directing groups (**WP4**). His specific expertise on sustainable synthesis of isocyanides will enable their coupling with hydroxyketones, to form monomers for the polyiminocarbonates (**WP5**). His acquaintance with green metrics will be transferred to other BioFact partners in **WP7** to allow evaluating sustainability in a method development phase, towards future scale-up.



Composition of the BioFact consortium and competences of PIs and co-PIs.

Gwilherm Evano (P4, ULB) leads the ULB Laboratory of Organic Chemistry, introducing new (homogeneous catalytic) methods into organic synthesis. Besides the development of new reagents for synthesis, his core expertise is in **non-noble metal catalysis**, e.g. in Cu-catalyzed cross-coupling, oxidative reactions and C(sp2)-H

activation. Evano's **contribution to Cu-mediated organic synthesis** is widely recognized, e.g. through the edition of a 2013 Wiley book on Cu-catalyzed cross-coupling reactions, and through **commercialization of his reagents** via Sigma-Aldrich. Evano's vast experience in cross-coupling chemistry will be the basis for the exploration of new vistas in the activation of biosourced aromatics using boronic acids or even CO_2 as an activator and leaving group (**WP3**). Within **WP4**, Evano's expertise in Cu-mediated oxidations will be crucial for the development of C(sp3)-H activation in cyclohexanols using 'traceless' DGs. His expertise in alkyne synthesis will be useful to expedite the production of alkynes for the polymerizations (**WP5**).

Christophe Detrembleur (P5, ULg) is an FNRS Research Director with vast experience in the (controlled) synthesis of **functionalized polymers** with a special emphasis on developing **innovative multifunctional materials** and related applications. Detrembleur is expert in controlled radical polymerization, e.g. in-situ nitroxide mediated polymerization and is world leader in cobalt mediated radical polymerization. He is internationally recognized for his multidisciplinary approaches, from the development of innovative synthetic tools and the understanding of reaction mechanisms, to the preparation of advanced materials. In recent years his research expanded to fully embrace sustainable concepts, including the use of **CO_2** as a supercritical solvent or foaming agent and as a **building block for polymers**. This 'green' approach will now be merged with the use of renewable, lignin-derived carbon building blocks, ultimately producing novel families of functional polyurethanes and polycarbonates in a phosgene-free manner (**WP5**).

Antoine Debuigne (P5, ULg) obtained in 2010 a highly competitive FNRS Research Associate position (success rate: 13%) at the Centre for Macromolecular Chemistry in Liège (CERM). He has a strong expertise in the preparation of macroporous polymers via emulsion-templated polymerization and **vast competence in organometallic mediated radical polymerizations (OMRP)** for precision polymer synthesis. This forms a perfect synergy with the competence of his senior colleague Detrembleur and will therefore expedite the development of new processes for the synthesis of functionalized polyethylenes (**WP5**). He devotes special attention to the controlled synthesis of polymers containing the so-called 'less activated monomers'. This is a **perfect background to the challenging co-polymerizations of methylene (imino)carbonates** with ethylene, using OMRP reagents, in **WP5**.

Veronique Van Speybroeck (P6, UGent) gained vast experience in modelling catalytic reactions, initially studying first principle kinetics using state of the art molecular modelling techniques (**ERC Starting Grant** KINPOR), and next extending this with the **ERC Consolidator Grant** DYNPOR, which develops first principle molecular dynamics simulation of complex chemical transformations in nanoporous materials. Since the onset of her scientific career, she developed models to study rates of chemical reactions and applied these on organic transformations in organic solvents and on polymerization reactions, in collaboration with various experimental partners. As such, supported by the expertise breadth of her strong team, she will computationally tackle a range of reactions in complex media, either solvents or nanoporous materials (**WP6**). In some cases the dynamics simulations for realistic operating conditions will even allow to reach a predictive level. Reaction rates and selectivities in nanoporous materials are studied with respect to reactions in **WP2** and **WP4**; computational insight will also be acquired for reactions in solvents (**WP3**, **WP4**, **WP5**).

The consortium is young by current academic standards: the five leading PIs are between 40 and 44, but most already attained the highest possible rank (Full Professor, FNRS Research Director). All PIs are already well established scientists with **excellent track records and impressive scientific output** (H-index between 32 and 55). Besides the future leaders, the consortium is supported by well-established renowned top scientists, Dirk De Vos (49 years, co-PI, H-index: 67) and Matthias Beller (55 years, PI, H-index: 105), who have extensive experience of acquiring and managing multi-partner projects.

Gender issues are important in our equal-opportunity society. A key PI, at UGhent, is female (Veronique Van Speybroeck). This relative gender imbalance will be compensated by a strong involvement of female researchers at the PhD and postdoc level, with potential to stream upward (cfr. management section). Some of the very promising female scientists in the consortium are Dr. Eugénie Roméro, Céline Guissart, Phidéline Gérard, Chunyang Zhang, Hajar Baguia, Evelien Renders, Dr. Trees De Baerdemaeker, Dr. Julianna Hajek, Prof.

Dr. Ann Ghysels, Dr. Hannelore Goossens, Dr. Xubin Wang, Dr. Zeynep Yilmaz, Dr. Annelies Dewaele, Dr. Ekatherina Makshina, Dr. Paola Ferine. We will also aim to hire at least 40% of female PhD students.

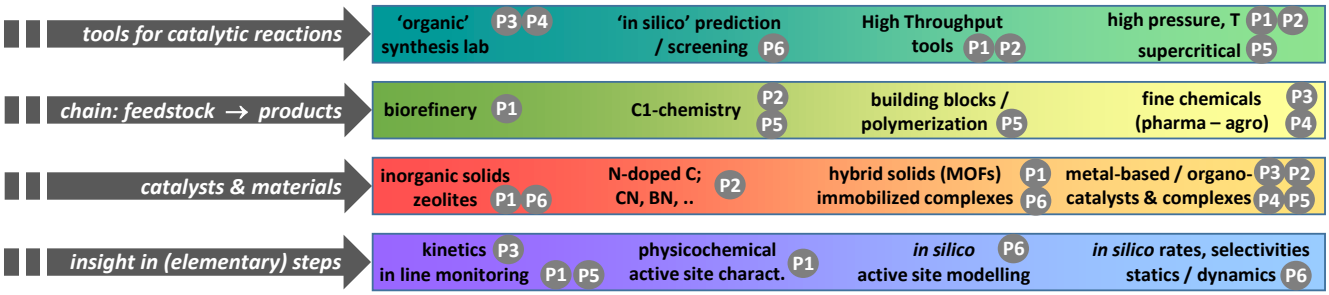
Despite the very different backgrounds, the **multidisciplinary consortium is well integrated at different levels**:

a. Complementarity along the chemical value chain, from feedstock to products:
At the start, expertise in **biorefinery** (turning molecularly complex feedstock into simpler, defunctionalized building blocks) is strongly represented by KULeuven (B. Sels, **P1**). Further down the value chain, ULg (C. Detrembleur, **P5**) is the ideal partner to integrate these building blocks into **new polymers**, preferably using CO_2 as a solvent or reactant. Finally the creativity to transform the building blocks into **fine chemicals**, **pharmaceuticals** in particular, is brought in by the high level organic synthesis of UAntwerp (B. Maes **P3**) and ULB (G. Evano, **P4**). Green processing (atom economy, step efficiency, …) is inherent all along the chain.

b. Complementarity in the toolbox of catalysts and metal complexes:
Strong expertise in **heterogeneous catalysis** is found in the Leuven group (zeolites, oxides, carbon-based catalysts: B. Sels; hybrid porous catalysts: D. De Vos; **P1**) and in the LIKAT team (with a strong new research line in N-doped graphene: M. Beller; **P2**). Different types of **homogeneous catalysis** expertise flow together in the consortium, such as Cu catalysis (ULB, Evano; **P4**), organocatalysts (ULg, Detrembleur, **P5**) and Pd or base metal catalysis e.g. Fe (UAntwerp, Maes, **P3**; LIKAT: Beller, **P2**). Organocobalts are specifically designed for the **precision synthesis of polymers** (ULg, Debuigne, **P5**). This is also an ideal line-up to turn homogeneous catalysts into heterogenized, leach-proof solid catalysts. **P6** has a proven record not only for modelling of porous materials, but also in calculations for homogeneously catalyzed reactions.

c. Complementarity in reactors and techniques for reactions:
New molecular modes of activation (e.g. alternative cross-couplings, C-H activation) require a **classical organic lab** like at **P3** or **P4** (equipped with GC(-MS), LC-MS, multinuclear high sensitivity NMR). The translation to processing of complex feedstocks calls for testing in **unusual /extreme reaction conditions** (supercritical state with CO_2 or ethylene at **P5**; pressure reactors at **P1** and **P2**) in batch or continuous mode, and in two- or three-phase operation (gas-liquid-solid). High throughput experimentation batteries at **P1**, **P2** and **P4** are complemented by **in silico screening** and **prediction of optimally selective catalysts**, e.g. zeolites, at **P6**, where also libraries of optimized structures of building blocks of e.g. zeolite catalysts are available. The high level of confidence among the PIs enables the BioFact consortium to function as a (virtual) **open lab**, in which **remote reservations** for advanced instrumentation will be enabled through on-line reservation tools.

d. Complementarity in tools for understanding catalytic mechanisms
Classical kinetic and mechanistic studies (KULeuven, UAntwerp, ULB) will be extended with fast in-line monitoring of reactions, either via FTIR (**UAntwerp**, **KULeuven**), or via **Raman** (**ULg**), including 'viewing' reactors for the study of reactions under (high) pressure (**ULg**). **KULeuven** has an extended range of advanced instrumentation for characterization of structure and active sites in **solid catalysts** (e.g. TGA-DSC-MS; FTIR with probes; in situ electronic and vibrational spectroscopy; TPD/MS; chemisorption etc). This partner has also experience with XAS at synchrotrons. Complementary computational insights are provided by **UGent**: first they model the nature of the active sites; second, the energies calculated, either via the static approach, or via the dynamics approach over complex Free Energy Surfaces, enlighten the elementary steps for reactions such as dealkylation, sp2 or sp3 C-H activation etc.



Complementarities in the BioFact consortium.

2. Management of the Consortium

2.1. Internal Research Management

a. General Vision and Risk Mitigation

We will set up a light, **agile and transparent management structure** for the multidisciplinary BioFact project. The project must be **dynamic**, to respond to **quickly changing contexts and new opportunities**, e.g.

- **breakthrough findings by the consortium** that call for a re-focused effort;
- opportunities to **hire (international) top talents** and integrate their potential into BioFact;
- answering **societal trends**; re-positioning with respect to progress of other groups worldwide;
- arising needs for specific **instrumentation** / reactors.

Most importantly, the management structure, in particular through the steering committee, will allow an adequate **risk management**. The Table below already lists a few risks that may be identified and for which some mitigation could be proposed even as of now.

WP	*Risk*	*Level*	*Mitigation*
1	Analytics may be challenging if a complex product mixture is formed upon processing real lignin feedstock and wood.	mid	If necessary, the PI will foresee additional manpower from outside the consortium to assist in the analytics.
2	Direct gas phase amination of the lignin building blocks results in unstable catalysts.	mid	A back-up strategy using H-borrowing protocols with metal catalysis will be used to form the hydroxy-anilines.
2	Direct dealkylation may be too unselective.	low	A back-up strategy using benzylic oxidation, followed by deacylation, will be tested to form catechol and pyrogallol.
3	Difficult activation of the C-O bond in the phenol-derived phosphonium carbonates.	mid	Use of phosphonium salts substituted with coordinating (directing) groups.
3	Inefficient activation of C-O bond in catechol /pyrogallol-derived arylbenzodioxaboro-l(id)es and amino analogues.	high	Activate catechols/pyrogallols as cyclic carbonates, iminocarbonates or phosphates and amino analogues.
4	Instead of dehydrogenative cross-coupling, phenols/catechols undergo radical coupling (under O_2).	mid	Protect phenols/catechols as esters (e.g. carbonate esters).
4	Cross dehydrogenative coupling does not allow to introduce a certain R type.	mid	Use RX as reactants.
4	Too slow in situ double carbonation and/or C-H activation in cyclic aminoalcohol-derived carbamates/cyclic diamine-derived urea.	high	Focus on C-H functionalization of amines via carbonation.
4	C(sp3)-H functionalization does not allow to introduce a certain R type.	high	Introduce R via C(sp2)-H functionalization followed by reduction (~ methodology of WP2).
5	Iminocarbonate cycles do not open by nucleophilic attack to C=NR bond.	mid	Nature of R will be modified and/or catalysts will be used to force the ring-opening.
5	Inhibition or lack of control of the copolymerizations.	mid	Modulating the activity of the controlling agent by the addition of coordinating molecules and the choice of the solvent
5	Formation of the 5-membered cyclic carbonate and/or formation of low molar mass PCs only.	high	Identifying appropriate catalysts and conditions to allow ring opening of the cyclic carbonate and its incorporation in the polymer chain. Focus on *trans* cyclohexanediol.

6	For organic reactions in solvent with catalyst and other additives (H-bond donors, Lewis acid), determination of collective variables might be problematic	mid	An experienced postdoc will be hired directly to benchmark various solvation models. New models for reactivity in solvents could be introduced through contacts with E.J. Meijer, P. Bolhuis and B. Ensing (UvA).
6	Determine a predictive tool to determine the reaction conditions for cyclic carbonates	high	If verification of the computational predictions fail, a small set of test reactions will be screened experimentally to refine the computational model.
	One of the PIs leaves the current position	low	High potential post-doc staff can take over

b. Management structures, key roles

The **Steering committee** (Sels / Maes / Detrembleur / Evano / Van Speybroeck/ Beller):

- Ensures that tasks are achieved in a timely way and defines corrective actions, as needed;
- Monitors budgets, in agreement with FWO-FNRS guidelines;
- Monitors WP integration: transfer of materials; transfer of compounds (e.g. as raw materials); communication between WPs;
- Monitors the scientific output, science communication and outreach activities;
- Makes decisions related to the IP protection and exploitation. To avoid unwanted IP disclosure, a publication release procedure will be installed by the Steering Committee, with a period of 15 days for internal circulation of the intended publication. Consortium members will be able to request a delay of publication in case IP protection would be jeopardized.
- Makes decisions on modifications to the research program, if required;
- Assesses the quality of the results, and assumes corrective actions; resolves conflicts between PIs, partners, should any arise.

The steering committee will meet twice a year, once at the yearly Plenary Consortium meeting. An **extraordinary Steering Committee meeting** may be called by the Coordinator or on request of at least two consortium PIs at any time.

The **Project Coordinator (B. Sels)** implements decisions of the Steering committee, with following key responsibilities:

- Administration of the project, incl. periodic annual reports and the final report;
- Coordination of the organization of the consortium meetings;
- Communication with the International Advisory Board (see below);
- Coordination of data management, including project website and project SharePoint.

To ensure optimal project performance, smaller scale project management is entrusted to **Work Package leaders**. Every WP leader will be in charge of:

- Coordination of the scientific work within his/her WP;
- Providing efficient exchange of information between partners within the WP, as well as between the interacting WPs (see the Scheme for graphical representation of interactions).
- Collecting contributions of partners for intermediate and final reports.

As an important advisory organ, an **International Advisory Board** (IAB), composed of four internationally renowned experts will be established, with the purpose of:

- providing an independent opinion on project execution;
- identifying new opportunities in the broader project context.

A tentative composition of the IAB is Prof. Michael Meier (KIT, Karlsruhe: renewables, polymers), Prof. Stephen Buchwald (MIT, Boston: homogeneous catalysis), Prof. Evert J. Meijer (UvA, Amsterdam: modeling) and Prof. François Jérôme (Poitiers: biorefinery) The IAB will receive the annual reports in advance to each yearly meeting. These reports will be a high-level overview, including sufficient information to provide evaluation and competent scientific advice without compromising the consortium IP. The IAB is expected to provide a brief

feedback within short delay. In face-to-face discussions at the yearly meeting, they can also voice their recommendations for (parallel or sequential) follow-up projects originating from BioFact. We also gladly invite the IAB members to contribute plenary lectures, at the yearly meetings or at the closing workshop.

Specific responsibilities will be given to the **Training and Communication Coordinator** (Dr. Antoine Debuigne, ULg; see also below):

- Ensuring that all BioFact-specific training activities are well announced;
- Identifying new training opportunities, such as offered by Scientific Research Communities, Universities, ITN networks of H2020, specific communities like Belgian Polymer Group, or the Belgian Organic Synthesis community, the Dutch Zeolite Association, CatBior, the COST action CHAOS (C-H activation inorganic synthesis), the International Solvay Institutes etc.;
- Initiating applications for training-based follow-up projects such as Marie Sklodowska Curie Actions of H2020, using the BioFact consortium as a core.

c. Meetings

Kick-off meeting. This meeting will be organized by the Project Coordinator in Leuven in January 2018. The teams will present their background and ongoing relevant research to the whole consortium. The steering committee will approve the detailed work plan for the first project year of the project, confirm the International Advisory Board, and the plans for data management, communication and outreach activities.

Plenary consortium meetings are organized yearly, sequentially (after the kick-off) at ULg, UGhent, ULB, UAntwerp. At each meeting, there will be about 10 presentations, adequately covering all WPs, exclusively by young scientists. **Joint presentations by partners** are strongly encouraged, with 2 presenters (from 2 different teams) jointly addressing a common research question. An ample poster session over the lunch break allows to discuss all results and brainstorm on new opportunities.

Work package meetings. To ensure frequent interactions between partners, **Work Package meetings** will be organized two additional times per year by the **WP Leaders**. Concise meeting notes will be communicated by WP leaders to the Project Coordinator and will be made available via the SharePoint.

Webinars by junior scientists. All doctoral schools provide internal research seminars, typically for a public of 15-30 junior scientists of the local research team. By live streaming (and upon consent of the local PI), these will be made accessible (as monthly '**BioFact Webinars'**) to the 5 other teams.

Closing workshop. The final yearly meeting will be coupled to an open two-day international workshop, broadly announced via all channels, and highlighting the key role of BioFact in pushing the limits for production and valorization of biobased aromatic compounds.

d. Data management and Information exchange

The coordinator at KULeuven will, in Month 1 of the project, set up a **secured collaborative internet platform** for project management. As in previous large projects that we coordinated (H2020, ..), access (login and password) will be provided according to the levels of the stakeholders (Coordinator / WP leaders and other PIs / all other senior and junior scientists). The KULeuven '**Sharepoint**' possibilities will be exploited in full. This comprises, in the access-restricted sections:

- Well-structured collection and archiving of presentations at meetings;
- Easy collection of contributions to yearly reports; archiving the reports; on-time submission;
- Structured collection of meeting minutes (boards, WPs);
- Smooth and manageable registration for plenary consortium meetings;
- (automated) e-alerting to upcoming consortium or work package meetings;
- Opportunities to create libraries
  - **libraries of chemical compounds** generated in the different WPs;
  - compound libraries will be coupled to **databases of their physical / chemical properties**;
  - procedures to prepare / process the compounds can be linked to the compounds;
  - libraries of **catalysts (homogeneous / heterogeneous)** available in the consortium;
  - libraries of relevant literature, e.g. on key reactions.

Apart from the internal information, the young (and not so young) scientists will be encouraged to share experiences, literature and other external information or any other issues via **social media** (Twitter, a BioFact Facebook group, ResearchGate or LinkedIn). In order to prevent release of information compromising the IP, a controlled release mechanism (approval by PI) will be established.

e. Reports

The coordinator edits the **yearly reports**, based on the compiled **WP reports** provided by the WP leaders. The coordinator complements reports with an analysis of issues at the consortium level, and prepares a 2 page **executive summary**, as a guide to the International Advisory Board. The Coordinator will guarantee that reporting guidelines by FNRS-FWO are timely followed.

2.2. Training and Career development activities

a. BioFact Training activities

Lectures. All guest lectures at the different host institutions will be broadly announced over the whole BioFact research community, using the Sharepoint tools. Upon consent of the guest speaker, we will enable **live streaming** to audiences at host institutions.

Training modules. The groups of the PIs constitute a large community of ca. 150 scientists. At this scale, it is rewarding to organize several workshops specifically in the BioFact frame. Two types of workshops/summer schools will be organized:

- Modules A: provide **tutorial overviews** for fresh scientists joining the field; with typically 5-8 contributions over 2 days;
- Modules B: provide **advanced coverage** of scientific-technical topics, with (optionally) hands-on training on specialized equipment or with advanced software.

An overview of the scheduled training modules, and a tentative calendar are given below:

	Topic	Host	Year
A1	Integrated biorefinery: feedstock, processing, products	KULeuven	2018
A2	Advanced molecular dynamics simulations of complex chemical transformations	UGent	2019
A3	Green chemistry and green metrics	ULB, UAntwerp	2020
B1	Cross-coupling by C-H functionalization	UAntwerp	2018
B2	Polymer processing in supercritical fluids	ULg	2019
B3	Design of catalytic solids for transformation of biobased feeds	KULeuven	2020
B4	Base metal catalysis in organic synthesis	ULB	2021

Depending on practical aspects, the training events will be open to researchers outside the project; however, priority will be given to BioFact researchers.

b. Careers of young scientists: PhDs, post-docs

- To make the PhD & post-doc positions very attractive, we will define **interdisciplinary projects**, with **co-guidance** by typically 2 PIs within the network. We will actively advertise the openings internationally, either through official channels (Euraxess, ..), or through our informal networks. We aim for a 60-40 / 40-60 gender balance of hired researchers. We will specifically aim at recruiting top students or PhDs from **renowned schools** like ETH, RWTH Aachen, Max Planck Mülheim, UPMC (Paris), LCPO (Bordeaux), ICS (Strasbourg), ICIQ Tarragona, ITQ Valencia, Imperial College, Oxford, Cambridge, UCLondon, KAIST (Korea), NUS (Singapore), DICP (Dalian, China), etc.
- (International) post-docs who are hired on BioFact can grow into a (co-)supervising role for BioFact PhD students. We will foster our excellent post-docs, so that when they have ≥ 3 years of scientific activity after their Ph.D. degree, they should be able to acquire their own follow-up grants, e.g. an ERC starting grant.

- **International exposure of researchers** will be enhanced by encouraging them to perform short term research stays abroad, whenever the need arises. Within the network, Prof. Beller's LIKAT in Rostock is an obvious hub. Other preferred sites for exchange of researchers are listed in the table below:

Mobility to	*Target expertise sought*
Ed Solomon, Stanford	advanced spectroscopy for geometric/electronic properties of active metal sites
Shannon Stahl, Wisconsin	reaction mechanisms in transition metal catalyzed reactions
Noato Chatani, Osaka	(directed) C-H functionalization of saturated and unsaturated molecules
Jim Mayer, Harvard	redox transformations in porous solids (electron, proton transfer)
Xavi Ribas & Miquel Costas, Girona	understanding mechanisms and characterizing intermediates of metal-catalyzed reactions
Evert Meijer, Amsterdam	advanced collective variables for modeling organic reactions in solvents.
Richard Catlow, UC London	expertise on modeling metal doped zeolites
Arjan Kleij, ICIQ	polymerizable CO_2-sourced synthons; CO_2/substrates catalytic coupling

  This also extends to missions to **large scientific infrastructure**. Certainly for the consortium part that is engaged in heterogeneous catalysis (Sels, De Vos), experiments at synchrotrons (Grenoble, Didcot) can be essential for getting precise insight in catalytic mechanisms (location of metal ions, intermediates etc).

2.3. Dissemination activities; international visibility

- **Publication policy:** We strive for maximal **(gold) open access** for the most important BioFact publications. All (other) scientific contributions will be made accessible on-line and free of charge to organizations external to the network through **institutional Open Access repositories** (green open access policy). Various PIs of the consortium have obtained experience with these issues in the framework of H2020 projects (ERC, ITN, EU NMP program, …).
- Our major channels of dissemination will be publications in peer-reviewed journals and lectures at scientific conferences. **Every PI is expected to publish around ten papers (quality is valued more than quantity),** of which at least four in a high IF multidisciplinary journal (such as *Chem. Sci.*, *J. Am. Chem. Soc.*, *Angew. Chem.* and *Nature* group journals), to maximize the impact of dissemination actions. At the same time, top level field-specific journals will be chosen for more specialized publications. Attendance to and active contribution to ***one international conference per year per hired researcher is envisaged.*** A mix of multidisciplinary conferences such as *EuChems*, as well as top level more specialized conferences in relevant fields (organic synthesis, biomass utilization, catalysis) will be targeted, including Tetrahedron Symposium, International Green Chemistry Symposium, CatBioR etc.
- We target for **special issues** of high-level journals devoted to **BioFact research**. Relevant journals are e.g. ACS Sustainable Chemistry & Engineering, ChemSusChem or Catalysis Science and Technology, for which BioFact PIs are either Editors or Board Members.
- The **public part of the website** (hosted in www.biofact.be) will describe consortium, grand challenges tackled in the project, and the instrumentation shared among project partners. Recent top papers will be highlighted (with a link to the open access papers); this section will obviously be continuously updated. A 'News and Events' section will announce relevant conferences and workshops, job openings at the consortium partners, etc.
- A **semiannual newsletter** will be published on the public website, but also sent to all interested colleagues, stakeholders and agencies.
- **Dissemination material** will be prepared (flyers, posters, brochures) to advertise BioFact results in the international scientific press.
- Interaction with international players: through memberships of PIs in organizing/scientific committees of international conferences (e.g. Europacat, International Symposium of Green Chemistry, European Colloquium on Heterocyclic Chemistry, Belgian Organic Synthesis Symposium (BOSS)), we will propel the research agenda and results of BioFact to the scientific forefront.

3. Five most relevant publications of included researchers

Bert Sels (P1)

1. Ennaert, T.; Van Aelst, J.; Dijkmans, J.; De Clercq, R.; Schutyser, W.; Dusselier, M.; Verboekend, D.; Sels, B. F., Potential and challenges of zeolite chemistry in the catalytic conversion of biomass. ***Chem. Soc. Rev.*** 2016, 45 (3), 584-611. (IF: 34.1; Cit: 35].
2. Snyder, B. E. R.; Vanelderen, P.; Bols, M. L.; Hallaert, S. D.; Bottger, L. H.; Ungur, L.; Pierloot, K.; Schoonheydt, R. A.; Sels, B. F.; Solomon, E. I., The active site of low-temperature methane hydroxylation in iron-containing zeolites. ***Nature*** 2016, 536 (7616), 317. (IF: 38.1; Cit: 5).
3. Van den Bosch, S.; Schutyser, W.; Vanholme, R.; Driessen, T.; Koelewijn, S. F.; Renders, T.; De Meester, B.; Huijgen, W. J. J.; Dehaen, W.; Courtin, C. M.; Lagrain, B.; Boerjan, W.; Sels, B. F., Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. ***Energ. Environ. Sci.*** 2015, 8 (6), 1748-1763. (IF: 25.4, Cit: 70).
4. Dusselier, M.; Van Wouwe, P.; Dewaele, A.; Jacobs, P. A.; Sels, B. F., Shape-selective zeolite catalysis for bioplastics production. ***Science*** 2015, 349 (6243), 78-80. (IF: 34.7; Cit: 39).
5. Op de Beeck, B.; Dusselier, M.; Geboers, J.; Holsbeek, J.; Morre, E.; Oswald, S.; Giebeler, L.; Sels, B. F., Direct catalytic conversion of cellulose to liquid straight-chain alkanes. ***Energ. Environ. Sci.*** 2015, 8 (1), 230-240. (IF: 25.4; Cit: 19).

Dirk De Vos (P1)

1. Bueken, B., Vermoortele, F., Vanpoucke, D.E.P., Reinsch, H., Tsou, C.C., Valvekens, P., De Baerdemaeker, T., Ameloot, R., Kirschhock, C., Van Speybroeck, V., Mayer, J., De Vos, D. A Flexible Photoactive Titanium Metal-Organic Framework Based on a $[Ti_3(IV)(\mu\text{-}3\text{-}O)(O)_2(COO)(6)]$ Cluster. ***Angew. Chem. Int. Ed.,*** 2015, 54(25), 13912-13917. (IF: 11.7; Cit: 1).
2. Stassen, I., Styles, M., Grenci, G., Van Gorp, H., Vanderlinden, W., De Feyter, S., Falcaro, P., Vereecken P., De Vos, D., Ameloot, R. Chemical vapour deposition of zeolitic imidazolate framework thin films. ***Nature Mater.,*** 2016, 15, 304-310. (IF: 36.5; cit: 0).
3. Van de Voorde, B., Bueken, B., Denayer, J., De Vos, D. Adsorptive separation on metal-organic frameworks in the liquid phase. ***Chem. Soc. Rev.,*** 2014, 43, 5766-5788. (IF: 34.1; Cit: 83).
4. Vermoortele, F., Bueken, B., Le Bars, G., Van de Voorde, B., Vandichel, M., Houthoofd, K., Vimont, A., Daturi, M., Waroquier, M., van Speybroeck, V., Kirschhock, C., De Vos, D.* Synthesis Modulation as a Tool To Increase the Catalytic Activity of Metal-Organic Frameworks: The Unique Case of UiO-66(Zr). ***J. Am. Chem. Soc.,*** 2013, 135, 11465-11468. (IF: 12.1; Cit: 117).
5. Dams, M., Celen, S., Jacobs P., De Vos, D.* Toward Waste-Free Production of Heck Products with a Catalytic Palladium System under Oxygen. ***Angew. Chem. Int. Ed.***, 2003, 42, 3512-3515 (IF: 11.7; Cit. 135).

Matthias Beller (P2)

1. Highly active and efficient catalysts for alkoxycarbonylation of alkenes. Dong, K.; Fang, X.; Guelak, S.; Franke, R.; Spannenberg, A.; Neumann, H.; Jackstell, R.; Beller, M., ***Nature Commun.*** 2017**,** *8*, 14117. (IF: 11.3, Cit: 0).
2. The scope and mechanism of palladium-catalysed Markovnikov alkoxycarbonylation of alkenes. Li, H. Q.; Dong, K. W.; Jiao, H. J.; Neumann, H.; Jackstell, R.; Beller, M., ***Nature Chem.*** 2016, *8*, 1159-1166. (IF: 27.9, Cit: 1).
3. Highly selective hydrogenation of arenes using nanostructured ruthenium catalysts modified with a carbon-nitrogen matrix. Cui, X. J.; Surkus, A. E.; Junge, K.; Topf, C.; Radnik, J.; Kreyenschulte, C.; Beller, M., ***Nature Commun.*** 2016**,** *7*, 11326. (IF: 11.3, Cit: 3).
4. Selective catalytic two-step process for ethylene glycol from carbon monoxide. Dong, K. W.; Elangovan, S.; Sang, R.; Spannenberg, A.; Jackstell, R.; Junge, K.; Li, Y. H.; Beller, M., ***Nature Commun.*** 2016**,** *7*, 12075. (IF: 11.3, Cit: 0).
5. Using carbon dioxide as a building block in organic synthesis. Liu, Q.; Wu, L. P.; Jackstell, R.; Beller, M., ***Nature Commun.*** 2015**,** *6*, 5933. (IF: 11.3, Cit: 136).

Bert Maes (P3)

1. Abou-Shehada, S.; Mampuys, P.; Maes, B.U.W.; Clark, J.H.; Summerton, L., An Evaluation of the Green Credentials of a Multicomponent Reaction for the Synthesis of Isothioureas Through the Use of the Holistic CHEM21 Green Metrics Toolkit. ***Green Chem.*** 2017, *19*, 249-258 (IF: 8.5, Cit: 0).
2. Morel, B.; Franck, P.; Bidange, J.; Sergeyev, S.; Smith, D.; Moseley, J.; Maes, B.U.W., Concise Xanthine Synthesis via a Double Amidination Reaction of a 6-Chlorouracil with Amidines using Base Metal Catalysis. ***ChemSusChem*** 2017, *10*, 624-628 (IF: 7.1, Cit: 0).
3. Sterckx, H.; De Houwer, J.; Mensch, C.; Caretti, I.; Tehrani, K.A.; Herrebout, W.A.; Van Doorslaer, S.; Maes, B.U.W., Mechanism of the Cu^{II}-Catalyzed Benzylic Oxygenation of (Aryl)(heteroaryl)methanes with Oxygen. ***Chem. Sci.*** 2016, *7*, 346-357 (IF: 9.1, Cit: 8).
4. Van Steijvoort, B.F.; Kaval, N.; Kulago, A.A.; Maes, B.U.W., Remote Functionalization: Palladium-Catalyzed C5(sp^3)-H Arylation of 1-Boc-3-aminopiperidine Through the Use of a Bidentate Directing Group. ***ACS Catalysis*** 2016, *6*, 4486-4490 (IF: 9.3, Cit: 1).
5. Mampuys, P.; Zhu, Y.; Vlaar, T.; Ruijter, E.; Orru, R.V.A., Maes B.U.W., Sustainable Three-Component Synthesis of Isothioureas Involving Isocyanides. ***Angew. Chem. Int. Ed.*** 2014, *53*, 13063-13068 (IF: 11.7, Cit: 18).

Gwilherm Evano (P4)

1. Theunissen, C.; Wang, J.; Evano, G., Copper-catalyzed direct alkylation of heteroarenes. ***Chem. Sci.*** 2017, 8, DOI: 10.1039/C6SC05622A. (IF: 9.1, Cit: 0).
2. Lecomte, M.; Evano, G., Harnessing the electrophilicity of keteniminium ions: a simple and straightforward entry to tetrahydropyridines and piperidines from ynamides. ***Angew. Chem. Int. Ed.*** 2016, 55 (14), 4547-4551. (IF: 11.7, Cit: 10).
3. Evano, G.; Theunissen, C.; Lecomte, M., Ynamides: powerful and versatile reagents for chemical synthesis. ***Aldrichimica Acta*** 2015, 48 (3), 59-70 (IF: 17.1, Cit: 21).
4. Theunissen, C.; Metayer, B.; Henry, N.; Compain, G.; Marrot, J.; Martin-Mingot, A.; Thibaudeau, S.; Evano, G., Keteniminium ion-initiated cascade cationic polycyclization. ***J. Am. Chem. Soc.*** 2014, 136 (36), 12528-12531. (IF: 13.0; Cit: 38).
5. Laub, H. A.; Evano, G.; Mayr, H., Hydrocarbation of C≡C bonds: quantification of the nucleophilic reactivity of ynamides ***Angew. Chem. Int. Ed.*** 2014, 53 (19), 4968-4971. (IF: 11.7; Cit: 11).

Christophe Detrembleur (P5)

1. Organocatalytic coupling of CO2 with oxetane. Alves, M.; Grignard, B.; Boyaval, A.; Méreau, R.; De Winter, J.; Gerbaux, P.; Detrembleur, C.; Tassaing, T.; Jérôme, C., ***ChemSusChem*** 2017, DOI: 10.1002/cssc.201601185. (IF: 7.1 ; Cit: 0).
2. Surface- and redox-active multifunctional polyphenol-derived poly(ionic liquid)s: controlled synthesis and characterization. Patil, N.; Cordella, D.; Aqil, A.; Debuigne, A.; Admassie, S.; Jérôme, C.; Detrembleur, C., ***Macromolecules*** 2016, 49, 7676-7691. (IF: 5.6; Cit: 0).
3. CO_2-blown microcellular non-isocyanate polyurethane (NIPU) foams: from bio- and CO2-sourced monomers to potentially thermal insulating materials. Grignard, B.; Thomassin, J.-M.; Gennen, S.; Poussard, L.; Bonnaud, L.; Raquez, J.-M.; Dubois, P.; Tran, M.-P.; Park, C. B.; Jérôme, C.; Detrembleur, C., ***Green Chem.*** 2016, 18, 2206-2215. (IF: 8.5; Cit: 9).
4. Fluorinated alcohols as activators for the solvent-free chemical fixation of carbon dioxide into epoxides. Gennen, S.; Alves, M.; Méreau, R.; Tassaing, T.; Gilbert, B.; Detrembleur, C.; Jérôme, C.; Grignard, B., ***ChemSusChem*** 2015, 8, 1845-1849. (IF: 7.1; Cit: 20).
5. Precision design of ethylene- and polar-monomerbased copolymers by organometallic-mediated radical polymerization. Kermagoret, A.; Debuigne, A.; Jérôme, C.; Detrembleur, C., ***Nature Chem.*** 2014, 6, 179-187. (IF 27.9; Cit: 30).

Antoine Debuigne (P5)

1. Simultaneous synthesis and chemical functionalization of emulsion-templated porous polymers using nitroxide-terminated macromolecular surfactants. Mathieu, K.; De Winter, J.; Jérôme, C.; Debuigne, A., ***Polym. Chem.*** 2017**,** *8*, 1850-1861. (IF 5.7; Cit: 0).

2. Controlled synthesis of poly(vinylamine)-based copolymers by organometallic-mediated radical polymerization. Dréan, M.; Guégan, P.; Detrembleur, C.; Jérôme, C.; Rieger, J.; Debuigne, A., ***Macromolecules*** 2016**,** *49*, 4817-4827. (IF 5.6, Cit: 0).

3. Precision design of ethylene- and polar-monomerbased copolymers by organometallic-mediated radical polymerization. Kermagoret, A.; Debuigne, A.; Jérôme, C.; Detrembleur, C., ***Nature Chem.*** 2014**,** *6*, 179-187. (IF 27.9; Cit: 30).

4. Effect of head-to-head addition in vinyl acetate controlled radical polymerization: why is Co(acac)2-mediated polymerization so much better? Morin, A. N.; Detrembleur, C.; Jérôme, C.; De Tullio, P.; Poli, R.; Debuigne, A., ***Macromolecules*** 2013**,** *46*, 4303-4312. (IF 5.6, Cit: 27).

5. Macroporous poly(ionic liquid)s and poly(acrylamide)s monoliths from CO2-in-water emulsion templates stabilized by sugar-based surfactants. Boyère, C.; Favrelle, A.; Léonard, A. F.; Boury, F.; Jérôme, C.; Debuigne, A., ***J. Mater. Chem. A*** 2013, 1, 8479-8487. (IF 6.6, Cit: 10).

Veronique Van Speybroeck (P6)

1. Vermoortele, F.; Bueken, B.; Le Bars, G.; Van de Voorde, B.; Vandichel, M.; Houthoofd, K.; Vimont, A.; Daturi, M.; Waroquier, M.; Van Speybroeck, V.; Kirschhock, C.; De Vos, D. E., Synthesis Modulation as a Tool To Increase the Catalytic Activity of Metal-Organic frameworks: The Unique Case of UiO-66(Zr), ***J. Am. Chem. Soc.*** 2013, 135 (31) 11465-11468, 2013 (IF: 13.0; Cit: 175).

2. Lejaeghere, K.; Bihlmayer, G.; Bjorkman, T.; Blaha, P.; Blugel, S.; Blum, V.; Caliste, D.; Castelli, I. E.; Clark, S. J.; Dal Corso, A.; de Gironcoli, S.; Deutsch, T.; Dewhurst, J. K.; Di Marco, I.; Draxl, C.; Dulak, M.; Eriksson, O.; Flores-Livas, J. A.; Garrity, K. F.; Genovese, L.; Giannozzi, P.; Giantomassi, M.; Goedecker, S.; Gonze, X.; Granas, O.; Gross, E. K. U.; Gulans, A.; Gygi, F.; Hamann, D. R.; Hasnip, P. J.; Holzwarth, N. A. W.; Iusan, D.; Jochym, D. B.; Jollet, F.; Jones, D.; Kresse, G.; Koepernik, K.; Kucukbenli, E.; Kvashnin, Y. O.; Locht, I. L. M.; Lubeck, S.; Marsman, M.; Marzari, N.; Nitzsche, U.; Nordstrom, L.; Ozaki, T.; Paulatto, L.; Pickard, C. J.; Poelmans, W.; Probert, M. I. J.; Refson, K.; Richter, M.; Rignanese, G. M.; Saha, S.; Scheffler, M.; Schlipf, M.; Schwarz, K.; Sharma, S.; Tavazza, F.; Thunstrom, P.; Tkatchenko, A.; Torrent, M.; Vanderbilt, D.; van Setten, M. J.; Van Speybroeck, V.; Wills, J. M.; Yates, J. R.; Zhang, G. X.; Cottenier, S. , Reproducibility in density functional theory calculations of solids, ***Science*** 2016, 351 (6280), 1415-aad3000-7. (IF: 34.7; Cit: 52).

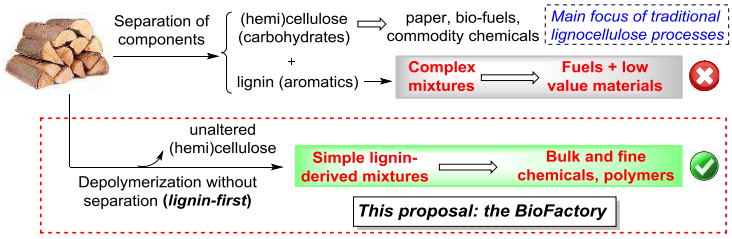
3. Van Speybroeck, V.; Hemelsoet, K.; Joos, L.; Waroquier, M.; Bell, R. G.; Catlow, C. R. A., Advances in theory and their application within the field of zeolite chemistry. ***Chem. Soc. Rev****.* 2015**,** 44 (20), 7044-7111 (IF: 33.4, Cit: 32).

4. Winne, J. M.; Catak, S.; Waroquier M.; Van Speybroeck, V., Scope and Mechanism of the (4+3) Cycloaddition Reaction of Furfuryl Cations. ***Angew. Chem. Int. Ed****.*, 2011, 50, 11990-11993 (IF: 11.709, Citations: 37).

5. Billiet, S.; De Bruycker, K.; Driessen, F.; Goossens, H.; Van Speybroeck, V.; Winne, J. M.; Du Prez, F. E., Triazolinediones enable ultrafast and reversible click chemistry for the design of dynamic polymer systems. ***Nature Chem.*** 2014, 6 (9), 815-821 (IF: 27.89, Cit: 52).

State of the art

Taking into account the depletion of crude oil reserves, the development of effective processes for the exploitation of renewable biomass as a feedstock for the chemical industry of the future is a key societal challenge. Non edible lignocellulose (from wood) is one of the most abundant biorenewable carbon sources on earth, and therefore an ideal biomass candidate. It is mainly constituted of a carbohydrate fraction (cellulose and hemicellulose) and an aromatic fraction (lignin). While the primary objective of lignocellulose biorefineries has traditionally been to maximally exploit the carbohydrate fraction to produce paper, biofuels (such as bioethanol), and various commodity chemicals,[1] the lignin fraction is instead under-utilized, and mostly used for low-value materials and fuels (when burned). However, lignin is a source of highly functionalized aromatic compounds (C-O bonds are the core linkages in the polymer), and its transformation into useful, low molecular-weight chemical building blocks would be a much more useful application for this abundant raw material. Despite this, progress in this direction has been, until recently, very limited. The reason for this lies in the chemical structure of lignin itself. Although being constituted of only 3 major monolignols, the polymeric structure of lignin is intricate and random, connected by a number of chemically similar ether linkages. Upon depolymerization, a **large variety of smaller molecules** (monomers, dimers and oligomers), which are difficult to separate and process, is obtained. These complex mixtures can only be used for non-specific applications (e.g. fuels), thus preventing the transformation of lignin into high-value chemical products.



Two main strategies have recently emerged to reduce the complexity of the mixtures obtained: 1) the use of genetic engineering to simplify the lignin structure during biosynthesis (limited variety of chemical linkages); and 2) modification of the biomass processing protocols to **increase the selectivity of the depolymerization** process.[2] Considering the reticence of society towards and the strict governmental regulation of genetically modified organisms, the second strategy is preferred, and it constitutes the foundation of this proposal. Due to the complexity of the biomass, this is a very challenging goal. The traditional lignocellulose process involves the initial separation of lignin from the carbohydrate fraction, and then its depolymerization into smaller components via oxidative or reductive transformations. This procedure results in non-selective reactions, and consequently very complex mixtures of compounds. However, it has been discovered that much higher selectivity is obtained when the depolymerization is performed on native lignocellulose (before separation of the lignin from the carbohydrates), leading to a much limited number of components in the final mixtures. This new conceptual way of processing the biomass has been labelled *lignin-first*, referring to its **primary focus on the exploitation of the lignin**, but without neglecting the valorization of the carbohydrate fraction.

KULeuven has developed a unique *lignin-first* biorefinery process from wood chips resulting in a very high carbon yield of **only 4 main monomeric arenes** (more than 50% yield based on the carbon of the lignin), while the carbohydrate structure is almost not affected, and can therefore still be processed to a variety of commodity chemicals.[3] Interestingly, considering the structural complexity of lignocellulose, these 4 compounds are very easily obtained in just three steps: a) treatment of lignocellulose with heterogeneous catalysis under a hydrogen atmosphere, b) filtration of the solid carbohydrate residue, and c) solvent recuperation and extraction from the lignin oil. **The selective depolymerization of the *lignin-first* approach, therefore, has the inherent potential to provide access to a bio-based chemical factory in the future.** However, to transform these 4 monomers into commodity, fine chemicals and polymers for the industry, new chemical transformations (synthetic methodology) are needed. Their development requires integrated experimental and theoretical fundamental research. State of the art synthetic methodology must be sustainable and in accordance with the 12 principles of green chemistry, which is a complex and very challenging goal. The use of biorenewable feedstocks is only one, though core facet, of these principles. Besides, reactions must be atom and energy efficient, avoid the use of dangerous reactants/reagents/solvents, avoid the use of protecting groups, and only produce a limited amount of (non-toxic) waste.[4] **Within this proposal, we aim at developing new, green synthetic methodology suitable for the transformation of the 4 lignin-derived monomers, obtained from an established and efficient *lignin-first* biorefinery process, into bulk/fine chemicals and polymers.** To achieve this ambitious goal, new homogeneous and heterogeneous catalytic methods will be developed by a highly complementary team with expertise in homogeneous and heterogeneous catalysis, polymer chemistry, organic synthesis and molecular modeling. The outcome of this proposal can have a major impact on the exploitation of renewable biomass in the biofactory of the future.

Objectives

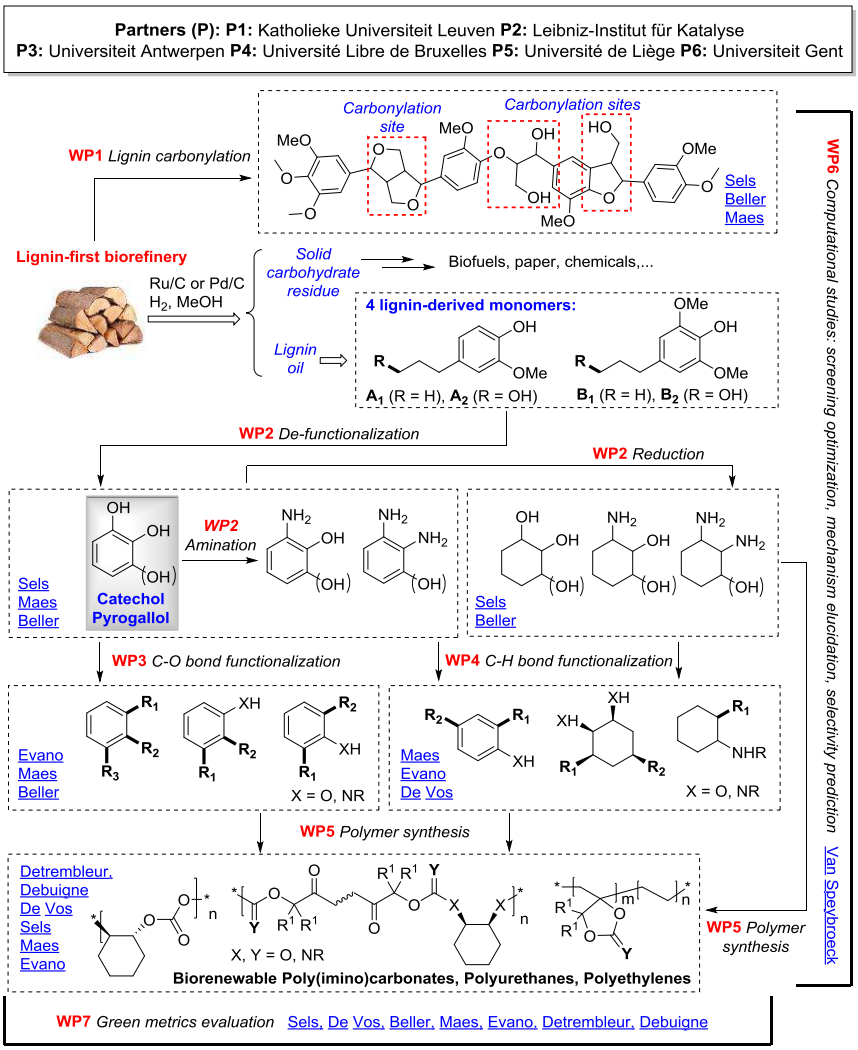
This project will involve 6 partners (P), and will be divided into 7 work packages (WP, see scheme next page for an overview).

The current chemical industry starts from crude oil and focuses on the functionalization of alkanes and arenes. Processed biomass, on the opposite, provides functionalized molecules which require a certain degree of de-functionalization to be transformed into platform molecules. The transition of oil-to-biomass based chemistry faces two

grand challenges. One is the selective synthesis of bio-based aromatic chemicals, preferably from lignin, and the second is their conversion into useful building blocks according to sustainability and green chemistry principles.[4]

Recent advancements in lignocellulosic biorefinery indicate successful depolymerization of lignin into arenes, but the research is still in its infancy. Most successful approaches, only leading to a limited number of compounds, follow the *lignin-first* concept, and rely on a selective depolymerization of lignin. While oxidative and reductive processes are currently researched in the biorefinery community, other reaction types to decompose lignin have so far been largely neglected. Within this proposal, therefore, will be explored, for the first time, the possibility of **lignin carbonylation with CO** as a valid alternative to the existing *lignin-first* technology (**WP1**).

Today the reductive *lignin-first* biorefinery is one of the most established technologies to converts lignin into soluble lignin derived arenes, yielding mainly the 4 monomeric arenes $\mathbf{A_{1\text{-}2}}$ and $\mathbf{B_{1\text{-}2}}$. More specifically, two different mixtures of 2 main products each are obtained depending on the catalyst (Pd: $\mathbf{A_1}$ and $\mathbf{B_1}$; Ru: $\mathbf{A_2}$ and $\mathbf{B_2}$).[3] Interestingly, their chemical structures have no real resemblance with the typical petrochemical alkylaromatics initially obtained from oil, as these bio-based alkyl, hydroxy and methoxy substituted benzenes feature more functionalities. This project therefore addresses the essential development of **new sustainable demethylation and dealkylation reactions** in order to get access to two attractive central building blocks, i.e. catechol (1,2-dihydroxybenzene) and pyrogallol (1,2,3-trihydroxybenzene) (**WP2**). In view of atom economy, the removed carbon chain (methyl and propyl) is preferably recovered, and should be further valorized either on itself (e.g., as methanol or propylene) or via subsequent transformations. We believe that catechol and pyrogallol have a tremendous potential to grow into important building blocks of the future bio-based factory. Here we will exploit various chemical possibilities by developing completely novel (catalytic) reactions with these two molecules to access novel building blocks, which will be useful to attain new families of bio-based polymers and materials, likely with unexpected properties. More specifically, after partial de-functionalization, the naturally provided C-O bonds in the lignin-derived building blocks will be the focal point of the chemical transformations planned, in this way taking most advantage from their pre-functionalized structures.



Nature delivers two or three C(sp2)-OH groups in the aromatic structures of catechol and pyrogallol, which are attractive for further transformation. However, due to the large C(sp2)-OH bond dissociation energy and acidity of the phenolic moiety, derivatization is typically required to activate the C(sp2)-O bond for efficient reactions. This is an important drawback, as waste resulting from both introduction and substitution of a leaving group is generated. **Direct amination of catechol and pyrogallol to hydroxyanilines** will be developed, as it allows direct introduction of nitrogen without requiring unstable nitric acid for nitration reactions. Such a condensation reaction is only known for phenol, and not for the challenging catechol and pyrogallol systems (**WP2**). Besides C-O to C-N, also transformation into C-C is important. However, cross couplings on catechol, pyrogallol and hydroxyaniline derivatives have not received attention.[5 6] The hydroxy (or amino) group *ortho* to the phenol moiety significantly deactivates these substrates for transition metal catalysis. The development of efficient, regioselective, and **sustainable consecutive C(sp2)-O bond functionalization** for these challenging systems is important to optimally utilize lignin as abundant and renewable source for the synthesis of substituted arenes. This requires the development of new activation approaches with minimal waste production (**WP3**). The *ortho* dihydroxy and hydroxyamino moiety in these substrates will for instance be exploited for consecutive **cross coupling reactions via activation with organoboron reactants**, which is an attractive yet unprecedented alternative. The substituted phenols obtained can further react in a subsequent cross coupling without relying on the known wasteful activation modes, only using CO_2 and catalytic R_4POH for in-situ activation.

The resulting substituted arenes can be further decorated via transition metal catalyzed C(sp2)-H functionalization (**WP4**). While remarkably efficient methods for the direct(ed) *ortho* functionalization of arenes have been developed, analogous processes for the *meta*- and *para*-position are rather rare. The few methods enabling the selective direct introduction of a substituent in the *para* position of an arene[7] are either restricted to the use of complex directing groups[8] or limited in scope and selectivity.[9] Development of heterogeneous catalysts, zeolites or MOFs, possessing reactive sites within well-defined spatial cavities, should allow **selective reactions at the *para* position**. Rather than using halogenated coupling partners, challenging and inherently greener **cross dehydrogenative couplings** (involving activation of two C-H bonds) with arenes, alkenes and alkynes are aimed for. These processes require an oxidant, for which O_2 will be selected based on its sustainable character.

On catechol, pyrogallol and hydroxyanilines, hydrogenation protocols with heterogeneous catalysts will be developed, yielding substituted cyclohexanes (**WP2**). Based on the chelating moieties in these aromatic substrates, as well as the necessity of diastereocontrol in the reaction, this is a non-self-evident task. Depending on catalyst and substrate, ketones and hydroxyketones can be obtained as reaction products, which can yield aminoalcohols and diamines via reductive amination. *Cis* cyclohexanediol/diamine and aminocyclohexanol can be further decorated via transition metal catalyzed C(sp^3)-H functionalization (**WP4**). This represents in itself a very challenging task, considering the high bond dissociation energy of such bonds and the necessary regio- and diastereoselectivity control.[10] The chelating *cis* diol/diamine and aminoalcohol moiety will be exploited to **temporarily install a traceless and catalytic directing group (DG)** which is expected to allow diastereoselective *cis* functionalization.[11]

A final synthetic part of the project will be based on the use of the new *lignin-first* derived building blocks for the synthesis of more sustainable and low carbon footprint plastics (**WP5**). The cyclohexanediols, -diamines and aminoalcohols can be used as monomers in the synthesis of **novel families of functional polycarbonates (PCs) and polyurethanes (PUs)**. An innovative strategy involves the use of CO_2 as reactant to prepare new cyclic carbonates, i.e. bis-(α-alkylidene cyclic carbonates), with improved features (mild reaction conditions, full regiocontrol and product selectivity). As a further improvement in the synthesis of PCs and PUs, the ambitious direct polymerization of CO_2 and diols with (organo)catalysts will also be investigated. In addition, poorly explored polyiminocarbonates (PImCs) will be synthesized starting from lignin-derived iminocarbonates. These polymers, more sensitive to hydrolysis than the corresponding PCs, are expected to provide a new class of bio-based, bio-degradable polymers. Finally, organometallic-mediated radical polymerization (OMRP) of α-methylene cyclic (imino)carbonates with ethylene will result in unique **bio-based polyethylene copolymers**, bearing pendent (imino)carbonate functionalities, allowing post functionalization of the polyethylene chain at a later stage.

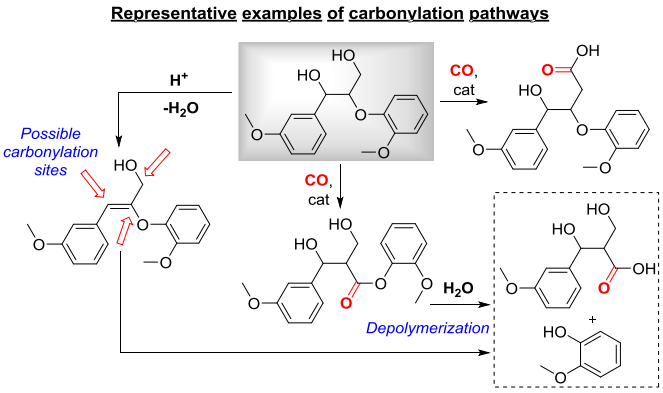
To support the development of these new synthetic methodologies, insight at the molecular level is essential. Molecular modelling will be used throughout all the synthetic WPs to facilitate reaction optimization, rationalize experimental findings, and predict chemical reactivity and selectivity (**WP6**). Theoretical methods have matured to a level where high accuracy can now be obtained. However, to reach the predictive level to unravel chemical reactivity and selectivity in complex reaction media, a thorough understanding of the free energy surface (FES) is mandatory, at conditions closely mimicking the experimental ones. The determination of free energy barriers using ab initio calculations for complex chemical transformations has become feasible, thanks to the growth in computational power and the development of advanced theoretical methods. The **mutual interaction between experimental and computational** investigations is expected to provide key insights and will speed up method development, reducing time and experimental workload.

Finally, to ensure synthetic method development to be in accordance with the green chemistry principles, the greenness of the new transformations will be assessed, during the development phase, using the recently published **green chemistry metrics** (**WP7**).[12] Besides quantitative (atom efficiency, yield, selectivity, reaction mass efficiency and mass intensity), also qualitative indications with respect to the properties of reactants/reagents/solvents used will be evaluated.

WP 1: A novel biorefinery concept: carbonylative lignin depolymerization and functionalization

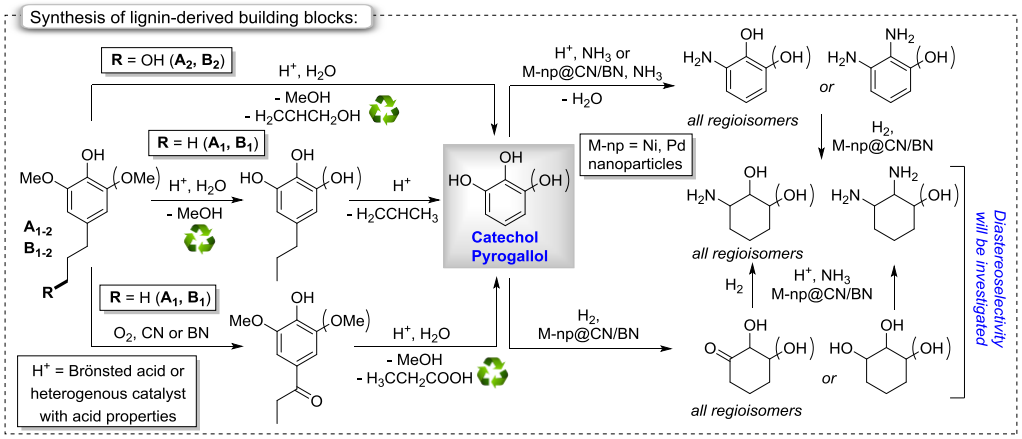
Although several oxygen based functionalities are present in the lignin structure (see scheme above), the aliphatic ethers and alcohols are expected to be reactive for catalytic carbonylation reactions with CO. Carboxylic acids and alkyl esters linkages thus formed can be easily hydrolyzed/(trans)esterified leading to new acids and esters, which constitute interesting building blocks for renewable polymers.[13] One challenging question is the reactivity difference for carbonylation between alcohols and the different outer-chain and inner-chain ether bonds. Robust classic carbonylation with metal catalysts at high temperature likely affects all these bonds, and therefore will assist both depolymerization and solubilization of the lignin, but fine-tuning of metal/ligand and additives may offer a way to handle the reactions selectively. Based on P2's expertise in carbonylations, several molecularly-defined catalysts including Pd, Ru and Rh complexes will be screened first.[14] In order to develop such innovative new technology, reactions with commercially available model systems will be initially studied (P2). Subsequently, reported model compounds that are complex enough to mirror the structural diversity in lignin will be synthesized (P3) and explored (P1, P2),[15] and finally real lignin and wood (for which the soluble carbohydrate fraction might also be carbonylated) will be investigated (P1). These reactions will reveal the functional group tolerance of the catalysts and will establish the difference in reactivity/selectivity between the

different ether/alcohol functional groups present. The use of an acid co-catalyst may be considered a key element for activation of the aliphatic alcohols and ethers via protonation, and the basicity of the ether/alcohol may be one option to impact selectivity, but it may also induce elimination reactions delivering alkenes.[14] These eliminations on one hand generate allylic alcohols/ethers and vinylic ethers which are more reactive for carbonylation. In fact, carbonylation may stabilize these unstable intermediates, preventing them to re-polymerize and to form unreactive precipitates. The anisole type ethers present in lignin are not expected to react easily, as these are less basic and not easily activated via protonation. In addition to homogeneous catalysts, heterogeneous materials will be developed. Here, we believe that metal nanoparticles @doped carbon materials constitute a suitable starting point. Large surface areas and acid-site surface modifications will be required to accommodate and activate the lignin structures at the catalyst active sites.[16] Although CO will be used first, we would also like to develop carbonylation reactions of lignin using a mixture of CO_2 and H_2 (P1, P2), both easily accessible in the future biorerfinery (from fermentation processes and water splitting with renewable energy, respectively). Such process is highly ambitious but in general feasible. In the presence of a reductant, CO_2 is in-situ transformed to CO,[17] which then undergoes the above mentioned transformations.



WP 2: Selective (de)functionalization of *lignin-first* functional aromatic building blocks

The 4 *lignin-first* derived monomers will have to go through a series of processes before being ready to be employed in C-O and C-H functionalizations (**WP3-4**) or being utilized in polymers synthesis (**WP5**). Initial dealkylation and demethylation will provide the core products catechol and pyrogallol, which will then undergo hydrogenation to cyclohexane derivatives, followed by (partial) amination, or can be aminated first to hydroxyanilines, and then reduced. To ensure the platform molecules necessary for WP3-5 are obtained in this WP, several strategies to access the different classes of compounds will be considered.



WP 2.1: C-C and C-O cleavage transformations

Although the C-C cleavage of an aromatic alkyl substituent using Brönsted solid acids like zeolites is a model example of catalytic cracking of petroleum naphtha, it has been only scarcely investigated with alkyl phenols, and not been reported for alkyl catechol and pyrogallol. Recently P1 reported a high temperature dealkylation of 4-alkylphenols to the corresponding phenol and olefins.[18] However, a great challenge is to selectively remove the alkyl chain in the presence of additional OH and OMe groups, as in the molecules resulting from the reductive *lignin-first* process (**A** and **B**). Catalytic cracking is not obvious here, due to the high reactivity of the electron-rich arene (polyarene formation) and methanol production (coke formation and undesired arene methylation). Therefore, gas phase zeolite-catalyzed dealkylation of propylcatechol and -pyrogallol yielding industrially important catechol and pyrogallol will be studied by P1, as it avoids methanol formation. Catalytic reactions will be studied in both kinetic and thermodynamic regime. It is expected that number of acid sites and pore size of the zeolite will determine activity and selectivity (isomerization and transalkylation are possible side processes). This will be investigated through diffusional and kinetic studies, supported by calculations (P6).

Considering catalytic cracking requires propylcatechol and –pyrogallol, an efficient and sustainable demethylation reaction of *lignin-first* propylguaiacol and –syringol ($\mathbf{A_1}$ and $\mathbf{B_1}$) in liquid phase is required. This is not straightforward as the classical processes typically require hazardous, expensive and (super)stoichiometric reagents (e.g. BBr_3, TMSI, HBr), which cannot be applied on a large scale.[19] In transition metal-catalyzed reduction processes with H_2, O-Me cleavage is typically plagued by C-OMe bond hydrogenolysis.[20] As the guaiacol and syringol moieties are very electron-rich, protonation with strong mineral acids or zeolites as catalysts should generate hydrolysable oxonium species yielding catechol and pyrogallol, respectively, and MeOH as by-product. To achieve demethylation through acid catalyzed hydrolysis, the reaction should be

(partly) executed in H_2O. This procedure will require high temperature but does not involve transition metals and H_2. Preliminary experiments by P3 show such catalytic demethylation is feasible.

As an alternative, the defunctionalization of 3-hydroxypropylguaiacol and –syringol (**A_2** and **B_2**), which are unsuitable for gas phase reactions, will be studied in solution (P3). Besides demethylation through hydrolysis, dealkylation of the 3-hydroxypropyl group with catalytic acid through initial elimination is expected. This delivers an alternative one-step pathway towards catechol and pyrogallol, directly applicable on the *lignin-first* derived substrates. In an attempt to replace the mineral acids for both demethylation and dealkylation in the liquid phase, P1 will design modified zeolites, stable in hot water, as previously achieved for cellulose hydrolysis.[21]

WP 2.2: Dealkylation via oxidative cleavage

A third catalytic dealkylation strategy on propylguaiacol and –syringol (**A_1** and **B_1**), which does not require initial demethylation, involves an oxidative cleavage pathway via benzylic oxidation followed by deacylation (see scheme above). The presence of the OMe and OH groups makes benzylic oxidation much more challenging than in alkylbenzenes. Homocoupling of guaiacol and syringol units, for instance, is expected as competitive pathway. As we aim to a sustainable oxidation process, O_2 will be selected as the oxidant. The free OH *para* to the propyl chain might play in our advantage as quinomethane formation activates the benzylic position. Subsequent conjugated addition of water delivers a benzylic alcohol *para* to the phenol, which can be further oxidized to ketone. However, if necessary, phenols will be protected upfront by methylation with dimethyl carbonate. Catalysts such as carbon and boron nitride (CN and BN) have been proposed to replace the typical transition metal based aerobic oxidation in liquid phase, and will therefore be evaluated (P1).[22] These are expected to be especially useful with aromatic substrates due to the peculiar surface properties (π–π interactions or defect/base site adsorption of phenol hydroxyls). Benzylic oxidation with Ce-doped zeolites in gas phase is a potential alternative route to the ketones.[23] Novel Ce zeolites will be designed via dealumination of parent zeolites, followed by selective Ce cation adsorption. Catalytic activity will be correlated with the redox properties of the zeolite, and the role of water, as reagent or competitive sorbent, will be investigated. The effect of (protected) functional groups on the substrates will be studied. Besides O_2, CO_2/O_2 mixtures will be evaluated to address synergistic effects.[24] Although the positive effect of adding CO_2 is unclear, involvement of peroxocarbonates is likely. In this respect, modifying basic sites on the catalyst surface is interesting to promote high carbonate surface coverage, hereby maximizing involvement of reactive surface peroxo species. Finally, the propanoylguaiacol and -syringol obtained can be deacylated by heating in H_2O with catalytic mineral acid or hot water-stabilized acidic zeolite (P1, P3).[21] It is expected that hydrolysis of the OMe groups will simultaneously occur also in this case (vide supra).

WP 2.3: Arene reduction to cyclic polyols and aminoalcohols

There have been several reports describing arene hydrogenation on catechols, based on Ni, Pd, Rh and Ru catalysis.[25] The challenge is the compatibility of the catalyst with the chelating moiety, which might reduce its activity and selectivity, wherein support effects can play a tremendous role. Moreover, hydrogenolysis should be avoided. Ru@N-doped carbon has proven successful in selective phenol reduction by P2.[26] Building on this result, metal nanoparticles (preferably Ni) @CN/BN materials will be designed for arene hydrogenation (P1, P2). Effect of the properties of the heterogeneous catalyst (i.e. metal morphology and dispersion, (carbon) support type and surface functionalities) on the diastereoselectivity and its tunability (through catalysis or in-situ acetalization) is a major topic here. Eventually, the methods developed should allow the selective formation of both *cis* (for WP4.2) and *trans* (for WP5.3) cyclohexanediol. The method will be extended to aminated arenes to obtain the corresponding aminocyclohexanols or diamines.

Ring hydrogenation with (partial) formation of ketones instead of only alcohols will be investigated in the liquid phase with various Ni and Pd nanoparticles @CN/BN, modified with basic sites (P1, P2). The basic surface will assist rapid enolization while the metal will promote hydrogenation of the ring. Balancing the two functions will be crucial for product selectivity. Regio- and diastereoselective aspects are metal- and support-related, and will be tuned. So far only a few transformations of di- and trihydroxybenzenes into hydroxyketones have been described,[25a] but not for the 1,2,3-isomer (pyrogallol), for which H-bond stabilization is expected to favor cyclic 2-OH-β-diketone formation.

WP 2.4: Amination of polyhydroxybenzenes and reductive amination of cyclic alcohols and hydroxyketones

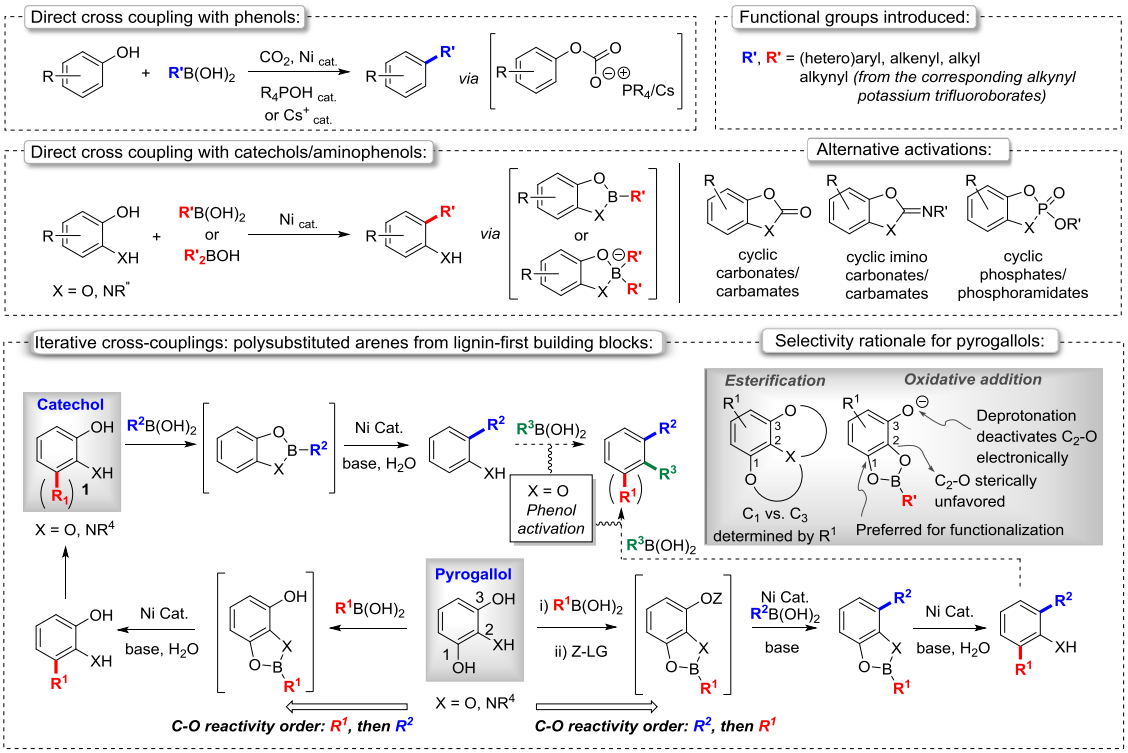
In analogy with phenol amination with NH_3,[27] high temperature (>400°C) gas phase acidic zeolite catalysis on catechol and pyrogallol can lead to *o*-hydroxyanilines via condensation, only producing water as by-product. Although these substrates are substantially more electron-rich than phenol, the additional OH groups will promote a stronger interaction with the zeolite, which would facilitate N-transfer in the amination reaction. The presence of Lewis acid or cationic sites, next to the Brönsted acid sites, is essential for substrate sorption and activation,[28] and the effect of their balance on the catalysis will be studied by spectroscopy (P1) and calculations (P6). The role of water, not studied in this context before, will be investigated with regard to catalyst stability and selectivity. As an alternative, metal catalysis following a hydrogen-borrowing strategy usually allows milder conditions for gas phase amination of phenol, and can therefore better control the selectivity to *o*-hydroxyanilines (see scheme previous page).[29] It is currently unclear whether more than one amino

group can be substituted by this strategy. Though not reported so far, Pd nanoparticles @CN/BN will have a good chance to (partially) aminate catechol and pyrogallol (P1, P2). Effect of the catalyst's surface properties (vide supra) on (regio)selectivity and its control will be a major research topic.

Metal-catalyzed amination of the aliphatic cyclohexane-1,2-diol and 1,2,3-triol using the same hydrogen-borrowing strategy can lead to the corresponding aminoalcohols. Preliminary data have shown the potential of direct amination of cyclohexane-1,4-diols in the gas phase,[30] but other diol regioisomers gave low yields. Catalytic synthesis of diamines and aminoalcohols is therefore also envisioned via reductive amination on the ketone moiety of the (hydroxy)ketones (formation of 2 ketones is also expected). This is usually based on classic heterogeneous Ni catalysis, but will be improved by introducing Ni nanoparticles @CN/BN, modified with acid sites to facilitate imine formation (P1, P2). There is still no information available about the diastereoselectivity of such reactions, and the *ortho* OH (or NH_2) will have a strong influence (molecular sorption behavior on the catalyst surface). Therefore, morphology, dispersion and support effects (type and dopants) will be studied using supported Ni catalysis.

WP 3: C(sp2)-O functionalization in *lignin-first* derived building blocks

Sequential cross-couplings reactions in lignin-derived catechol, pyrogallol and amine derivatives (with consecutive replacement of C-O by C-C bonds, e.g. pyrogallol → *ortho* substituted catechols → *ortho* disubstituted phenols → trisubstituted arenes) are aimed for as these will give access to a remarkably broad range of polysubstituted arenes that are traditionally obtained from fossil sources. This requires the development of new activation modes, avoiding/reducing waste production resulting from leaving group installation and removal in the functionalization step. Although phenols have received considerable attention, cross couplings on catechol and pyrogallol derivatives are much more challenging.[5] This is due to the presence of additional hydroxyl groups *ortho* to the phenol, which sterically and electronically deactivate the substrates for transition metal catalysis.



WP 3.1: Direct cross-couplings with phenols

In order to design a broadly applicable process for the direct cross-coupling of phenols, featuring a maximum atom-economy and not requiring stoichiometric pre-activation, in-situ activation with CO_2 and a phosphonium salt (R_4POH) will be investigated (P4). This involves the formation of an intermediate phosphonium aryl carbonate. The ability of the ionic liquid R_4POPh to "absorb" CO_2 at ambient pressure and room temperature supports the feasibility of our new approach.[31] Based on the structural similarity with aryl alkyl carbonates, known coupling partners,[5] C-O bond activation with transition metal catalysis is expected; as R_4POH is released upon cross coupling, the reaction only requires a catalytic amount of this reagent. If required, additional coordinating groups can be embedded in the R groups to facilitate activation of the C-O bond by the metal. The stabilizing effect of phosphonium cations on ionic carbonates is similar to the effect that Cs^+ cations have on ionic carbamates, i.e. facilitating the formation of carbamates from alcohols, amines and CO_2.[32] Based on the state-of-the-art in C(sp2)-O bond functionalization, Ni catalysis is preferred for this WP (P4, P3):[5] phosphines, NHCs as well as diamines will be screened as ligands for the Ni catalyst.

WP 3.2: Consecutive cross-couplings on catechols and pyrogallols

The vicinal diol moiety in catechols and pyrogallols will be exploited as a unique tool for dual substrate activation in combination with organoboron reagents (P4). In cross coupling reactions, organoboron derivatives are typically chosen as reactants based on their availability, nontoxicity, air/water stability and broad functional group compatibility.[33] Given their commercial and synthetic availability, $RB(OH)_2$ (or their esters) are usually preferred. Other than just acting as cross coupling reactants, here the boronic acid will be used to activate both C(sp2)-O bonds via (trans)esterification.[34] Moreover, borinic acids, whose condensation with catechols will generate a transient activated benzo[*d*][1,3,2]dioxaborolide,[35] featuring a tetra-coordinated boron atom, will also be explored. From a practical point of view, the development of the cross couplings with these substrates will be undertaken on isolated 2-phenylbenzo[*d*][1,3,2]dioxaborole. Once the method is optimized, in-situ activation will be studied, which can be promoted by using Lewis acids in the presence of molecular sieves or by formation of an ate complex. As two C-O bonds are simultaneously activated, we will study the regioselectivity in non-symmetrical substrates: both steric and electronic effects are expected to influence the selectivity of the C(sp2)-O bond functionalization.

The pyrogallol case is interesting as it features an additional *ortho* hydroxyl group, which is expected to be tolerated. Indeed, the base required for the cross coupling reaction deprotonates the remaining non-activated C_3-OH. This deactivates the *ortho* C_2-OB bond for oxidative addition, a position which is anyway already sterically unfavored. When the free C_3-OH in pyrogallol activated with $R'B(OH)_2$ would pose a problem, classical activation (transformation into a sulfonate, ester, carbamate, carbonate or ether) will be employed. When this group is more reactive towards oxidative addition than the C(sp2)-O in the dioxaborole, a first cross coupling occurs at C_3, which can be followed by a second one at C_1 yielding an *ortho* disubstituted phenol. Depending on the nature of the activating group, a reverse reactivity order and coupling sequence might also occur. Finally, the new synthetic methods will be extended to hydroxyanilines (P4).

When unforeseen problems arise, other new activation modes for the vicinal diol and aminoalcohol will be considered, such as cyclic carbonates/carbamates, iminocabonates or phosphates/phosphoramidates (P3). The carbonates/carbamates are the most interesting, as they potentially allow substrate activation with CO_2, which is released again in the functionalization step. A possible way to produce such carbamates and carbonates would be to react the catechols or hydroxyanilines with e.g. ethylenecarbonate or urea. However, even direct reaction with CO_2 is a viable option. While the reaction to form carbonates from CO_2 is thermodynamically strongly limited for alcohols, the analogous reaction to form carbamates is considerably more feasible. We hypothesize that large polarizable cations (like Cs^+ or R_4P^+) could again play a unique role in stabilizing the intermediate ionic carbonate.[32a]

As mentioned in WP3.1, Ni catalysis is preferred. An important goal here is that we will search for suitable heterogeneous Ni catalysts (e.g. Ni@graphenes or N-doped graphenes) (P3, P2). To the best of our knowledge, heterogeneous Ni particles @activated carbon have only been successfully used in C(sp2)-O hydrogenolysis reactions and hold great promise for reactions typically performed with homogeneous catalysis.[5] The most successful ones will also be screened for WP3.1 (P3). Insights into the selectivities in the C-O bond activation in our substrates will be gathered by studying the oxidative addition reactions with DFT calculations (P6). Moreover, calculations will be used to get an idea on the C-O bond dissociation energy of the different new activation modes versus the classical O derived leaving groups. These will be complemented by experimental data (rate constants) obtained via chronoamperometry (P3).[36] For the successful cross coupling reactions, a full catalytic cycle, taking into account the actual ligands and solvent used, will be computed to better understand the elemental steps of the process (oxidative addition, transmetallation, reductive elimination) which will give input for further optimization of the processes (P6).

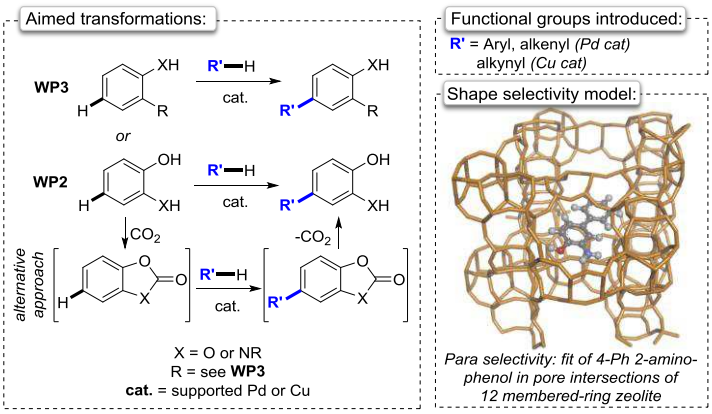
<u>WP 4: C(sp2)-H and C(sp3)-H functionalization in *lignin-first* derived building blocks</u>

Unsubstituted positions in *lignin-first* derived building blocks require new atom economic functionalization methods, aiming to minimal waste production. Transition metal catalyzed C-H functionalization opens up new alternative routes to the commonly used cross coupling reactions. While the latter typically require pre-functionalized substrates (organic (pseudo)halides) we here aim to start directly from the C-H bond.

WP 4.1: Direct *para* functionalization of C(sp2)-H bonds in phenols, anilines and arenes

Recently, P1 demonstrated that for a simple arene like toluene, a suitable zeolite can induce regioselectivity in C-H functionalization reactions, favoring rare *para* over common *ortho* substitution. Thus, for the oxidative dehydrogenative homocoupling of toluene to bitolyl, 80% *para*,*para*-selectivity was obtained with a Pd-loaded 12-membered ring zeolite; in contrast, an analogous reaction with a homogeneous catalyst in a non-constrained environment only gave 14% of the *para*,*para*-isomer.[37] This new concept will now be explored for the unusual, *para*-selective functionalization of the biobased arenes, such as the 2-substituted phenols and anilines, obtained from WP3 (P4, P1). These are ideal reactants for metal-catalyzed C-H activation due to their electron-donating substituents which greatly facilitate the initial metalation step, e.g. via a S_EAr mechanism.[38] Specifically, we aim at direct Pd or Cu catalyzed *para*-selective (hetero)arylation and alkynylation of these arenes. These dehydrogenative cross couplings[39] result in a reduction of the catalytic metal center ($Pd^{II} \rightarrow Pd^0$ or $Cu^{III} \rightarrow Cu^I$) upon product formation by reductive elimination; an oxidant therefore, preferably O_2, will be

used to reoxidize the metal. Direct *para*-alkenylation of arenes with alkenes will also be evaluated using this strategy, focusing on simple alkenes first such as styrene to minimize problems associated with regio- and stereoselectivity.



Catalyst design will focus on the introduction of a suitable metal center in a zeolite or a porous metal-organic framework[40] with well-defined docking sites for a catalytic metal, e.g. on the structural nodes of the material, or on linkers that can chelate metal ions (P1). Depending on the nature of the support, the coordinating properties of the solid matrix will vary, which will allow to increase the electrophilicity of the embedded metal and/or to stabilize organometallic intermediates and to ensure a smooth reoxidation of the metal.

We postulate that for each combination of two reactants, an optimal zeolite or MOF pore can be found, which offers a suitable spatially tight fit to the immediate precursor of the coupled product, e.g. Ar-Pd^{II}-Ar', Ar-Pd^{II}-CH=CHAr' or Ar-Cu^{III}-C≡CR. This methodology will first be evaluated with phenol and aniline, gradually increasing the complexity towards more substituted, biobased derivatives. We will carefully study the factors affecting the balance between homo- and heterocoupling, e.g. reactant ratios (affected by intraporous adsorption) or metal electrophilicity (influenced by the coordinating properties of the support). By computationally testing the fit between the pore or pore intersection and the precursor complex, we should be able to predict which zeolites or MOFs will be most promising for a certain arene-arene, arene-alkene or arene-alkyne combination (P6).

This process will later be extended to other bio-derived arenes (such as catechol and *o*-aminophenol from WP2). These might have a certain sensitivity to oxidative conditions: in case radicals are formed, one could indeed face formation of radical homocoupling products such as diphenoquinones. Using Pd^{II}, heterolytic, two-electron redox transformations are expected, which should limit such unwanted radical-induced side reactions. Nevertheless, as a safe back-up option, the C-H functionalization could be performed on suitably protected arenes such as cyclic carbonates and carbamates (see WP3).

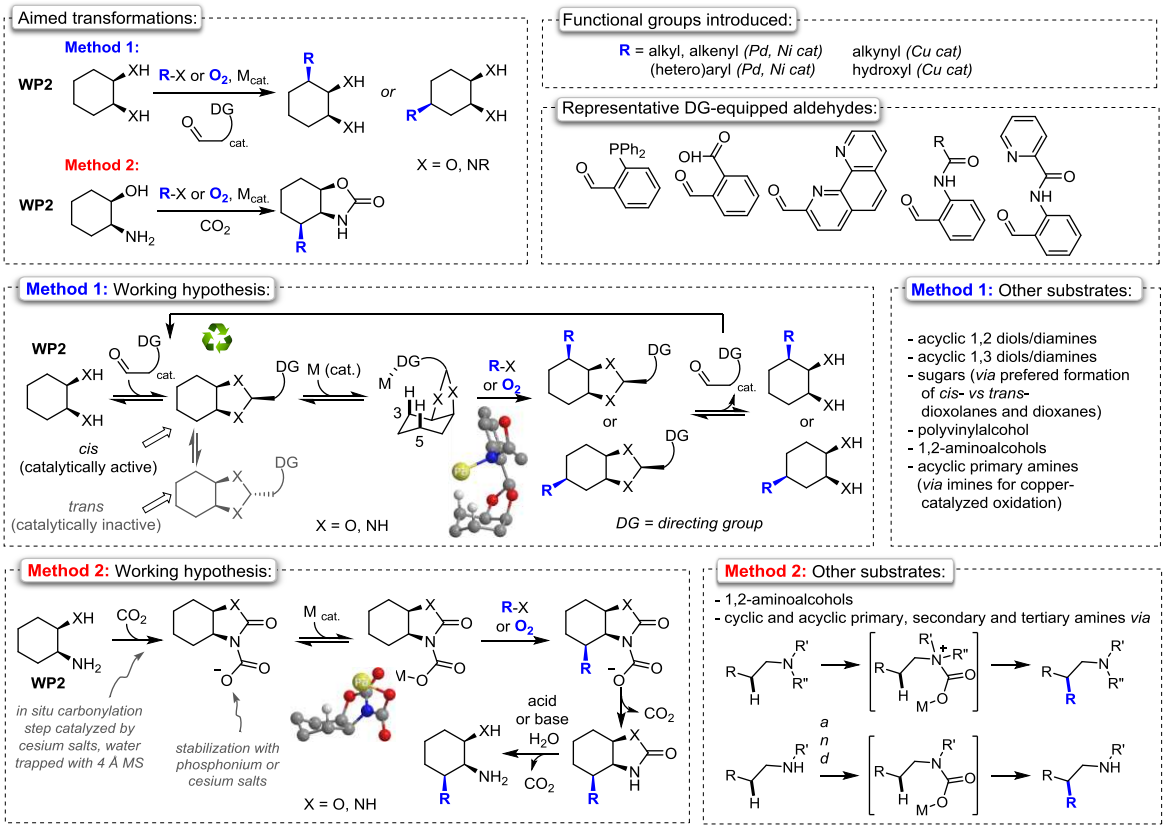
WP 4.2: Directed functionalization of C(sp3)-H bonds in diols, diamines and aminoalcohols

We envision that the temporary introduction of a traceless directing group (DG) in the cyclohexane based *cis* diol, diamine and aminoalcohol can be easily achieved via *O,O*-, *N,N*- and *N,O*-acetal formation with aldehydes embedding mono- and bidentate coordinating groups (Method 1, scheme below). Cyclic acetals will provide the required conformational rigidity to bring the metal coordinated to the DG in close proximity of the remote C(sp3)-H bond of the cyclohexane to be activated. Importantly, this approach requires the energy difference between the desired *cis* and undesired *trans* diastereoisomers obtained in the acetalization reaction to be small enough: preliminary calculations indicate sufficiently small energy differences and the DGs envisioned were found able to bring a transition metal in close proximity of remote C_3-$H_{ax.}$ and C_5-$H_{ax.}$ bonds, underlying the feasibility of our new approach. The development of these transformations will be supported by DFT calculations to pre-select the most relevant DG-equipped aldehydes by determining the energy values of the corresponding *cis* and *trans* acetals and the proximity of the transition metal to a given C(sp3)-H bond upon coordination with the *cis* isomer (P6). This intertwine between modelling and experimental work guarantees the further design and final identification of a suitable DG and catalytic system. Considering the challenging nature of the proposed strategy, catalyst screening will be performed on isolated acetals: based on the state-of-the-art in directed C(sp3)-H bond activation, Pd, Ni and Cu-based catalysts reported for other C(sp3)-H functionalization reactions will be initially evaluated (P3).[41] Processes for C(sp3)-H (hetero)arylation, alkenylation, alkynylation and alkylation will be developed using the corresponding halogenated reactants while C(sp3)-H oxidation will rely on mild and sustainable oxidants such as O_2 in the presence of Cu(II) catalysts.[42]

In a second phase the reversibility of acetal formation will be exploited for an in-situ installation of the optimal DGs, enabling the use of the DG-equipped aldehyde in catalytic amounts (P4). Although this strategy will be developed on the *lignin-first* derived *cis* cyclohexane-1,2-diol, diamine and 2-aminocyclohexanol (WP2), it will later be extended to a variety of other readily available substrates featuring these commonly encountered entities, including nucleosides and polymers such as polyvinyl alcohols (P3, P4).

In order to further diversify the molecular scaffolds obtained from the *lignin-first* derived building blocks, an alternative strategy for the direct functionalization of C(sp3)-H bonds in cyclohexane derived aminoalcohols and diamines will be explored (P4) (Method 2, scheme below). This approach is based on the in-situ formation of carbamates upon reaction of these substrates with carbon dioxide, followed by a carbonation that will enable the introduction of a temporary traceless directing group, facilitating the C-H functionalization.[43] Both steps can be promoted by the use of phosphonium[31] or Cs^+ salts,[44] as described in WP3. Final release of carbon dioxide will afford the functionalized product without the need for stepwise DG introduction/cleavage. In the case of diamines, hydrolysis is facilitated via formation of a transient isocyanate.

As in the previous case, this strategy will be extended, to demonstrate its full synthetic potential, to the direct functionalization of C(sp3)-H bonds in other substrates, with an emphasis on amines, for which there are only limited methods for their direct functionalization, without requiring additional tedious steps for the introduction/removal of a directing group (P3, P4).[11a] Although the C(sp3)-H bond functionalization on 1,2-disubstituted cyclohexanes require *cis* orientation, known hydroxyl epimerization strategies allow to easily access the *trans* isomers, of potential interest for WP5.



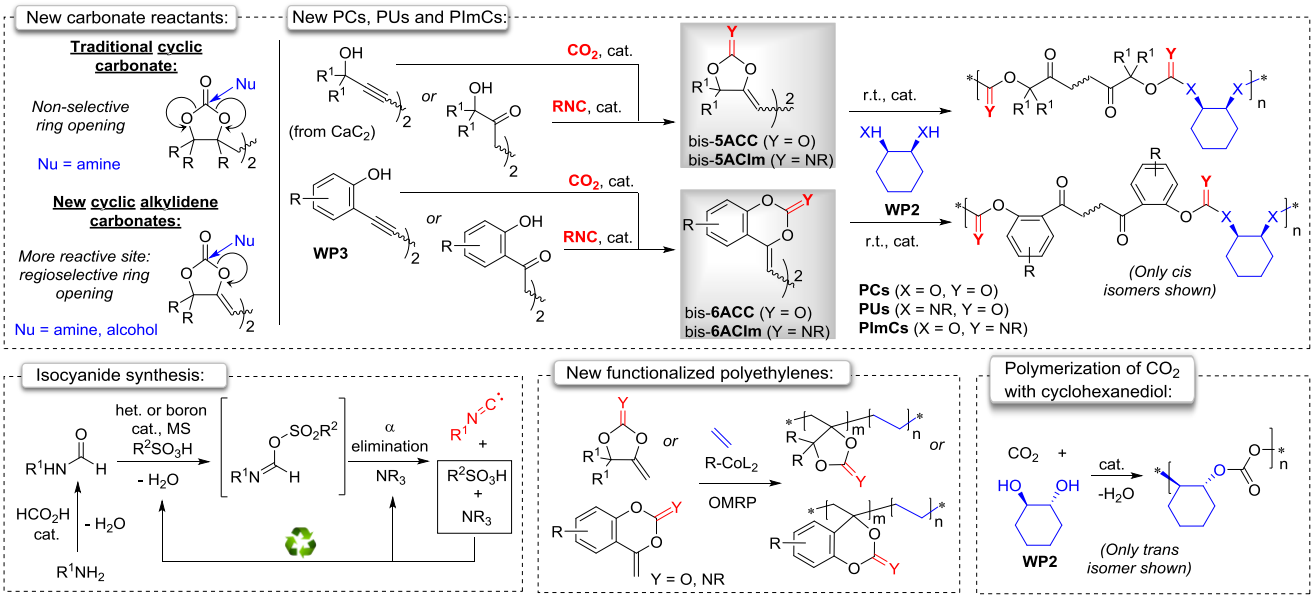
WP 5: Polymers based on *lignin-first* derived monomers

Lignin derived diol, diamine and aminoalcohol building blocks will be used as biorenewable monomers in various polymerization reactions with new bis-(α-alkylidene cyclic carbonates), obtained from CO_2 and featuring improved reactivity/selectivity versus the traditional carbonates. This will deliver a diversity of novel functional regioregular bio- and CO_2-based polyurethanes (PU) and polycarbonates (PC) in an isocyanate/phosgene free manner.[45] The *cis* or *trans* configuration of the disubstituted cyclohexanes used in polymerization is expected to influence the polymerization rate (due to different environment/steric hindrance) and the microstructure of the polymer, and therefore its final properties (thermal properties, solubility, etc.). Poorly explored imino(carbonates) analogues will also be investigated. Given the higher sensitivity to hydrolysis of these polymers compared to polycarbonates, they are more easily degradable, a valuable property in the field of biomaterials.[46] These polymers are still scarcely explored because of the lack of straightforward and sustainable synthesis routes[46] (diol + dicyanate), which will be addressed here. The new classes of (imino)carbonates available will also be exploited in precision radical copolymerization with ethylene, only requiring a controlling agent and without delivering by-products, yielding unique functional linear polyethylene polymers which can be easily post-functionalized at a later stage.

WP 5.1: Copolymerization of *lignin-first* derived monomers with (imino)carbonates

While traditional 5-membered bis-(cyclic carbonates) are inert towards reaction with alcohols and do not allow the preparation of PCs in mild conditions, these represent important CO_2-sourced starting materials for the sustainable production of isocyanate-free PUs.[45] However, their polyaddition with diamines suffers from side reactions and the absence of regiocontrol. This limits the PUs molar mass and affects their properties. Bis-(α-alkylidene cyclic carbonates) featuring an α-alkylidene moiety are expected to present an enhanced reactivity towards nucleophiles (thus allowing coupling with alcohols), while selectively forming only one regioisomer (see scheme below).[47] The driving force of the ring opening relies on the formation of an enol species which spontaneously tautomerizes into a more stable ketone.[48] In addition to facilitate the ring-opening, this tautomerization will provide functional polymers bearing ketone groups along the polymer chain. Proof-of-concept investigations by P5 carried out on a (non dimeric) α-alkylidene cyclic carbonate with model linear amines and alcohols have shown that regioselective ring opening at room temperature is feasible. The ring opening mechanism will be simulated by DFT calculations in order to come to a predictive model for the suitability of the envisioned cyclic carbonates in polymerization reactions with lignin-derived diol/diamine nucleophiles (P6). This will also

allow to predict potential side reactions. 5- and 6-membered α-alkylidene cyclic carbonates **5ACC** and **6ACC** will be prepared by (organo)catalyzed



carboxylative coupling of $CO_2$with propargylic alcohols[48a, 49] and 2-alkynylphenols,respectively (P5). The propargylic alcohols are accessible from ketones and CaC_2,[50] a cheap reactant produced on large scale by heating a mixture of lime and coke (P4). The 2-alkynylphenols will be obtained from WP3 (P4, P3). The bis-**5ACC** and bis-**6ACC** required for polymerization will be subsequently synthesized from the corresponding diynes, readily obtained by a Glaser-Hay dimerization (P4).[51] Copolymerization of these substrates with *lignin-first* derived monomers (cyclohexanediols and diamines from WP2) will be performed applying the optimized reaction conditions established for the model reactions (P5). This will allow to obtain a large structural variety of novel regioregular polymers such as poly(*oxo*-carbonates) and poly(*oxo*-urethanes), from a single bis-(α-alkylidene cyclic carbonate). Copolymerization with a mixture of cyclohexanediol and –diamine will also be considered to tentatively form innovative block-type copolymers in a one-pot process by exploiting the marked difference in reactivity between amines and alcohols, which is expected to strongly influence their order of incorporation in the polymer chain (not shown) (P5). Finally, to limit the number of synthetic steps, the *lignin-first* derived monomers will be reacted with in-situ generated cyclic carbonates (from CO_2 and dialkynols) (P5). For the *lignin-first* derived monomers, both *cis* and *trans* diastereoisomers of 1,2-disubstituted cyclohexanes, and their mixtures, will be tested, and their impact on the polymerization rate and on the polymer properties will be studied (P5). For the most interesting polymers, ring substituted derivatives obtained via C(sp3)-H activation (WP4) will be also investigated (P5).

A strategy analogous to the one described for PCs and PUs is foreseen for the synthesis of PImCs. The bis (α-alkylidene cyclic iminocarbonates) (bis-**5ACIm** and bis-**6ACIm**) will be prepared by coupling bis (α-hydroxyketones) and bis (*ortho*-acylphenols) with isocyanides (P5). Bis (α-hydroxyketones) can be obtained via regioselective hydration of the corresponding propargylic alcohols,[52] and bis (*ortho*-acylphenols) via Fries rearrangement on the respective esters (P3).

A variety of isocyanides are commercially available, and are mostly prepared by dehydration of the corresponding formamides.[53] While typically hazardous reagents are used (e.g. phosgene or triphosgene) for their synthesis, a new and greener approach will be studied here, using sulfonic acids as mediators, and generating water as the only by-product (P1, P3) (scheme, bottom left). Sulfonate ester formation will be examined by using heterogeneous (e.g. zeolites, partially oxidized BN) or homogeneous (e.g. boronic acids) Lewis acid catalysts.[54] A synthetic protocol for the reaction of hydroxyketones with RNC yielding cyclic iminocarbonates is not yet available.[55] Aerobic Ni catalysis will be studied to couple hydroxyketones with isocyanides using the sustainable reoxidant O_2 (P3). In a second phase heterogeneous Ni @carbon as well as metal-free CN and BN will be studied (P1).

WP 5.2: Precision radical copolymerization of (*lignin-first* derived) methylene (imino)carbonates with olefins

The non-dimeric methylene (imino)carbonates model compounds **5/6ACC** and **5/6ACIm** will also be utilized for the radical polymerization of their vinyl moiety (P5). Their copolymerization with other alkene monomers will result in polymers bearing pendent (imino)carbonate functionalities (scheme, bottom), which can be modified at a later stage. In particular, copolymerization with ethylene is important as it will give access to unprecedented functional linear polyethylenes. In order to precisely control the composition and architecture of the polymers, we will employ the organometallic-mediated radical polymerization (OMRP) technique developed by P5.[56] In practice, co-polymerization with ethylene will be carried out at moderate temperatures (below 50 °C) in order to disfavor side reactions like chain branching or decarboxylation. Experimental conditions will be adjusted to ensure optimal reaction control, and to precisely tune the composition of the polymer by varying the ethylene pressure. The distribution of the comonomers in the polymer chain

will also be addressed by measuring their reactivity ratios. The pendent cyclic (imino)carbonate moieties will then be exploited for post functionalization, hereby introducing different functional groups in the polyethylene chains (e.g. via ring opening with amines or by hydrolysis of the (imino)carbonate moiety). Strategies to recycle the OMRP control agent will be envisioned.

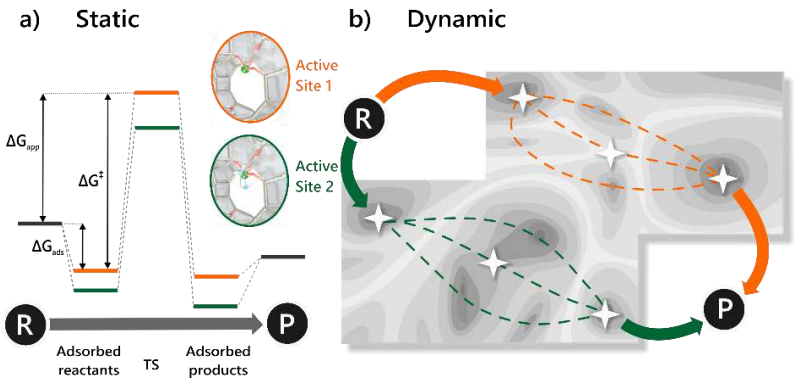
WP 5.3: Direct copolymerization of CO_2 with *lignin-first* derived diol monomers

Direct copolymerization of CO_2 with diols requires overcoming the inertness of CO_2 towards alcohols, and shift the reaction equilibrium towards the formation of the polycarbonate.[57] This copolymerization with 1,2-cyclohexanediol (*cis*- or *trans*-) is even more challenging due to the possible formation of the stable 5-membered cyclic carbonate. By the choice of an appropriate (organo)catalyst and reaction conditions, this in-situ formed cyclic carbonate is however expected to be polymerized via ring-opening polymerization (ROP) initiated by residual alcohol or water. Indeed, the polymerization of *trans*-cyclohexane-1,2-diyl carbonate has recently been demonstrated by ROP,[58] also when produced in-situ during the cyclohexene oxide/CO_2 copolymerization.[59] The *trans*-1,2-cyclohexanediol will be considered first (scheme above, bottom right). Computational modelling will guide us to identify the best operating conditions. The selection of an appropriate recyclable desiccant will also be required to remove most of the water formed. Based on the computational output, various (organo)catalysts will be then experimentally tested on model reactions (based on CO_2/cyclohexanol) in various solvents and in the presence of several desiccants (P1, P5). The best candidates will then be evaluated for the actual copolymerization (P5).

<u>WP 6: First principle simulations of chemical transformations in complex molecular environments</u>

A hierarchal modeling approach in three levels is proposed to unravel chemical reactivity and selectivity in complex reaction media at operating conditions. A continuous interaction with experimentalists will allow to efficiently develop selective chemical transformations. Initial screening of potential substrates and ligands will be performed using lower cost methods, reaction profiles will be constructed using static Density Functional Theory (DFT) methods, and reactivity at operating conditions will finally be obtained using advanced molecular dynamics methods. The research will be performed using a plethora of available program packages (Gaussian, MOLPRO, CHARMM, CP2K, VASP,…) and in-house (P6) developed software packages. This WP is performed by P6 and gives input to the different synthetic WP as indicated separately there.

Level 1: Static DFT methods to calculate reaction profiles, perform screening of potential catalysts and ligands, determine the nature of active sites in zeolites



Density Functional theory (DFT) using contemporary functionals, is the method of choice to study from first principles chemical bond formation/cleavage. However, care needs to be taken to select a proper functional for the target systems, which is capable to describe long-range interactions and the correct spin state for organometallic complexes or metal-doped zeolites.[60] For selected cases, benchmarking will be done with high level wavefunction based methods, for which P6 developed its own codes.[61] Reaction profiles and rates will initially be calculated using **static methods and Transition State theory**, where only a limited number of points on the potential energy surface is accounted for, from which free energies are determined (figure, left).[62] The conformational flexibility of the target molecules will be taken into account to ensure that the most stable energy minima are localized. Here, a prescreening of stable complexes will be performed using lower cost force field methods with P6 in-house developed force field code QuickFF.[63] Thermochemistry and reaction kinetics analysis will be performed using P6 post-processing toolkit TAMkin for normal mode analysis.

All chemical reactions in this proposal take place in a complex molecular environment such as organic solvents or a nanoporous host material, which needs to be taken up in the molecular model to obtain correct qualitative and quantitative theoretical predictions. For reactions in solvents, an implicit solvent model, where the solute is embedded in a continuum, is computationally very efficient, but fails when specific interactions between solvent and substrate take place. This can be circumvented by only considering a limited number of solvent molecules. However, still the dynamic reorganization of the solute-solvent is ignored at this level. Static DFT based methods will be used to obtain initial insight into reactivity patterns of various substrates, and more advanced calculations accounting for the dynamics of the system will be performed in Level 2-3 of the WP.

Within WP3, C(sp2)-O bond activations will be studied. Here a quick screening of potential leaving groups based on bond dissociation energies of C-O bonds will be performed, after which more specifically the reaction mechanism for oxidative additions will be studied using DFT based methods. Within WP4, a series of aldehydes for potential use as

directing groups in C(sp3)-H bond activation in diols, aminoalcohols and diamines will be screened. Their reaction with the target substrates may form *cis* or *trans* acetals, where only the *cis* is interesting for further use. Calculations will be used to screen potential aldehydes that yield a favorable isomer equilibrium. After this step, a Pd, Ni or Cu based catalyst is introduced, where it is essential that the metal can selectively approach one C-H bond. Computational studies will assist to unravel the nature of transition states and to determine the proximity of the metal to the substrate. Within WP5, initial insight into the reactivity of cyclic (imino)carbonates towards nucleophiles to produce lignin-sourced polymers will be gathered. Experimentally the reactivity of the new iminocarbonate is unknown and calculations will assist to tune the conditions to form the poly(iminocarbonates) in a regioselective manner. Also for the direct reactions of CO_2 with lignin-sourced monomers a prescreening of potential (organo)catalysts and desiccants will be performed to give insight into the reaction barriers and mechanism. For zeolite catalyzed reactions periodic DFT will be performed to unravel the **nature of the active site** in close collaboration with the experimental partners (e.g. for the Cu/Pd loaded zeolites used for C(sp2)-H activations in WP4 and the Ce-loaded zeolites for benzylic oxidations in WP2). A hierarchal approach determining the T-site position of the metal substitution/doping, the oxidation state and its coordination with guest species will be followed.[64] The coordination with guest species such as water may change the coordination sphere of the metal and will be studied in level 2.

Level 2: Molecular Dynamics methods to study the nature of intermediates in real reaction environment, and equilibrium properties under solvation

In this level, ab initio molecular dynamics simulations will be used to explore the **dynamic solvation behavior of reactants and intermediates**. The reaction medium (i.e. solvent, additives) might drastically affect chemical equilibria and stability of reaction intermediates. Within WP4, the free energy differences between the *cis* and *trans* stereoisomers formed after reaction of aldehydes to a variety of substrates will be calculated using explicit account of the solvation environment. For zeolite catalyzed reactions, the nature of the intermediates may be critically dependent on the reaction temperature, and on the loading of guest molecules within the pores of the zeolite.[65] Such insight is obtained using first principle molecular dynamics simulations that fully account for the zeolite flexibility, temperature and entropy effects. Within WP2, these techniques will be used to unravel the observed beneficial effect on the zeolite stability of adding water for the dealkylation of catechol and pyrogallol derivatives.

Level 3: Advanced Molecular Dynamics methods to study the reactivity at operating conditions and unravel competitive reaction pathways

Free energy barriers of complex chemical transformations will be studied using **advanced molecular dynamics (MD)** techniques.[66] A real challenge exists in mapping the Free Energy Surface (FES) in terms of a set of coordinates – so-called collective variables - which are representative for the reaction at real operating conditions such a realistic temperature, solvent environment, or a realistic loading with guest molecules in case of a nanoporous material. A free energy map (figure above, right) is comparable to a topographical map used when hiking the mountains, one should be able to localize the passages which are representative for making the transition from one to another stable basin. However, chemical transformations are “rare events”, and advanced MD methods (such as the metadynamics approach, umbrella sampling or the transition path) are necessary to efficiently sample the activated regions.[66-67] Herein, we will use and develop these techniques further, especially the proper choice of collective variables will be investigated.[68] The advanced MD are very challenging and computationally expensive but yield unprecedented insights into complex chemical conversions, such as the **prevalence of competitive pathways at operating conditions**, which is mandatory for predicting selectivities or proper account of entropy effects. For the dealkylation process proposed in WP2, typically occurring at high temperatures, these methods will be used to determine the selectivity conditions for isomerization versus transalkylation, and to determine the effect of water, redox properties and confinement on the benzylic oxidation on Ce-doped zeolites. For the zeolite-catalyzed, shape-selective C(sp2)-H activations in WP4, the fate of the aryl-Pd or alkynyl-Cu species can be determined, directly impacting on selectivity. For the direct copolymerization reactions of CO_2 with lignin-source monomers in WP5, these techniques will be used to give crucial information on the favored reaction mechanism for a given (organo)catalyst/desiccant combination, optimize reaction conditions, and determine the dependency on the reaction temperature, catalyst/desiccant loading and solvent.

References

1. Samec, J. S. M., *et al.*, *ChemSusChem*, 2016, **9**, 1544.
2. Rinaldi, R., *et al.*, *Angew. Chem. Int. Ed.*, 2016, **55**, 8164.
3. Sels, B. F., *et al.*, *Chem. Commun.*, 2015, **51**, 13158.
4. Anastas, P. T., *et al.*, *Green Chemistry: Theory and Practice*, Oxford University Press: New York, 1998.
5. Zeng, H., *et al.*, *ACS Catal.*, 2017, **7**, 510.
6. Examples starting from guaiacol are known: Snieckus, V., *et al.*, *J. Am. Chem. Soc.*, 2011, **133**, 6352.
7. Maiti, D., *et al.*, *Chem. Commun.*, 2016, **52**, 12398.
8. Maiti, D., *et al.*, *J. Am. Chem. Soc.*, 2015, **137**, 11888.
9. a) Gaunt, M. J., *et al.*, *Angew. Chem. Int. Ed.*, 2011, **50**, 458; b) Yu, J.-Q., *et al.*, *J. Am. Chem. Soc.*, 2011, **133**, 13864; c) Mizuno, N., *et al.*, *Angew. Chem. Int. Ed.*, 2012, **51**, 7275; d) Lloyd-Jones, G. C., *et al.*, *Science*, 2012, **337**, 1644; e) Ritter, T., *et al.*, *Nat. Chem.*, 2016, **8**, 810.
10. a) Sanford, M. S., *et al.*, *Chem. Rev.*, 2010, **110**, 1147; b) Baudoin, O., *Chem. Soc. Rev.*, 2011, **40**, 4902; c) White, M. C., *Science*, 2012, **335**, 807.

11. For rare examples of direct functionalization of C(sp3)-H bonds in amines and aminoalcohols see: a) Ge, H., *et al.*, *Nat. Chem.*, 2017, **9**, 26; b) Gaunt, M. J., *et al.*, *Nat. Chem.*, 2015, **7**, 1009.
12. a) Maes, B. U. W., *et al.*, *Green Chem.*, 2017, **19**, 249; b) Clark, J. H., *et al.*, *Green Chem.*, 2015, **17**, 3111.
13. Kasko, A. M., *et al.*, *Chem. Rev.*, 2016, **116**, 2275.
14. Beller, M., *et al.*, *Nat. Commun.*, 2017, **8**, 14117.
15. Westwood, N. J., *et al.*, *J. Am. Chem. Soc.*, 2016, **138**, 8900.
16. Beller, M., *et al.*, *Nat. Chem.*, 2013, **5**, 537.
17. Beller, M., *et al.*, *Nat. Commun.*, 2014, **5**, 3091.
18. Sels, B. F., *et al.*, *Green Chem.*, 2016, **18**, 297.
19. Weissman, S. A., *et al.*, *Tetrahedron*, 2005, **61**, 7833.
20. Zhang, Y., *et al.*, *Green Chem.*, 2016, **18**, 5510.
21. Sels, B. F., *et al.*, *ACS Catal.*, 2015, **5**, 754.
22. a) Vinu, A., *et al.*, *Chem. Soc. Rev.*, 2017, **46**, 72; b) Hermans, I., *et al.*, *Science*, 2016, **354**, 1570.
23. Murugesan, V., *et al.*, *Appl. Catal. A*, 2011, **407**, 76.
24. Suib, S., *New and Future Developments in Catalysis - Activation of Carbon Dioxide*, Elsevier, 1st edn., 2013.
25. a) Goettmann, F., *et al.*, *Chem. Commun.*, 2008, 999; b) Sajiki, H., *et al.*, *Chem. Eur. J.*, 2009, **15**, 6953; c) Karakhanov, E., *et al.*, *ChemCatChem*, 2015, **7**, 1197.
26. Beller, M., *et al.*, *Nat. Commun.*, 2016, **7**, 11326.
27. Tanabe, K., *et al.*, *J. Chem. Soc. Chem. Commun.*, 1973, 676.
28. Katada, N., *et al.*, *Stud. Surf. Sci. Catal.*, 2003, **145**, 197.
29. Wang, D., *et al.*, *Bull. Korean Chem. Soc.*, 2012, **33**, 387.
30. Baiker, A., *et al.*, *Catal. Lett.*, 1999, **61**, 111.
31. Wang, C., *et al.*, *Angew. Chem. Int. Ed.*, 2011, **50**, 4918.
32. a) De Vos, D., *et al.*, *Green Chem.*, 2008, **10**, 111; b) Zhang, Y., *et al.*, *Green Chem.*, 2013, **15**, 2086.
33. Lloyd-Jones, G. C., *et al.*, *Chem. Soc. Rev.*, 2014, **43**, 412.
34. Shi, Z.-J., *et al.*, *Angew. Chem. Int. Ed.*, 2011, **50**, 7097.
35. Taylor, M. S., *et al.*, *J. Am. Chem. Soc.*, 2011, **133**, 3724.
36. Maes, B. U. W., *et al.*, *Chem. Eur. J.*, 2015, **21**, 7858.
37. Stahl, S. S., *et al.*, *Adv. Synth. Catal.*, 2010, **352**, 3223.
38. a) Fagnou, K., *et al.*, in *Inventing Reactions*, ed. L. J. Gooßen, Springer, Berlin, 2013, pp. 91; b) Gaunt, M. J., *et al.*, *Science*, 2009, **323**, 1593.
39. Lei, A., *et al.*, *Chem. Rev.*, 2015, **115**, 12138.
40. Van Speybroeck, V., *et al.*, *Chem. Soc. Rev.*, 2017, 10.1039/C7CS00033B.
41. a) Glorius, F., *et al.*, *Chem. Soc. Rev.*, 2011, **40**, 4740; b) Chatani, N., *et al.*, *Angew. Chem. Int. Ed.*, 2013, **52**, 11726.
42. Baran, P. S., *et al.*, *J. Am. Chem. Soc.*, 2015, **137**, 13776.
43. Larrosa, I., *et al.*, *J. Am. Chem. Soc.*, 2014, **136**, 4109.
44. Saito, S., *et al.*, *Tetrahedron Lett.*, 2013, **54**, 4717.
45. Cramail, H., *et al.*, *Chem. Rev.*, 2015, **115**, 12407.
46. a) Kohn, J., *et al.*, *Biomaterials*, 1990, **11**, 666; b) Kohn, J., *et al.*, *Macromolecules*, 1989, **22**, 2029.
47. Jiang, H.-F., *et al.*, *Green Chem.*, 2007, **9**, 1284.
48. a) He, L.-N., *et al.*, *ChemSusChem*, 2015, **8**, 821; b) He, L.-N., *et al.*, *Green Chem.*, 2014, **16**, 1633.
49. Detrembleur, C., *et al.*, *ChemSusChem*, 2017, **10**, 1241.
50. Ananikov, V. P., *et al.*, *Chem. Asian J.*, 2016, **11**, 965.
51. Hua, R., in *Copper-Mediated Cross-Coupling Reactions*, ed. G. B. Evano, N., Wiley: Hoboken, 2013, pp. 456.
52. Qi, C., *et al.*, *Green Chem.*, 2014, **16**, 3729.
53. Ugi, I., *et al.*, *Angew. Chem. Int. Ed.*, 1965, **4**, 472.
54. Optimization will be based on previous synthesis protocols: Selander, N., *et al.*, *Chem. Soc. Rev.*, 2014, **43**, 2714.
55. The aerobic oxidative coupling of diamines and aminoalcohols with isocyanides has been reported: Maes, B. U. W., *et al.*, *Angew. Chem.*, 2012, **124**, 13235.
56. a) Detrembleur, C., *et al.*, *Nat. Chem.*, 2014, **6**, 179; b) Debuigne, A., *et al.*, *Polymer*, 2017, 10.1016/j.polymer.2017.01.008.
57. Tamura, M., *et al.*, *Sci. Rep.*, 2016, **6**, 24038.
58. a) Williams, C. K., *et al.*, *Nat. Chem.*, 2016, **8**, 3; b) Haba, O., *et al.*, *Polym J*, 2013, **45**, 1183.
59. Holmes, A. B., *et al.*, *Macromolecules*, 2000, **33**, 303.
60. Houk, K. N., *et al.*, *Acc. Chem. Res.*, 2016, **49**, 750.
61. Wouters, S., *et al.*, *J. Chem. Phys.*, 2014, **140**, 241103.
62. Van Speybroeck, V., *et al.*, *Chem. Soc. Rev.*, 2014, **43**, 7326.
63. Van Speybroeck, V., *et al.*, *J. Comput. Chem.*, 2015, **36**, 1015.
64. Pidko, E. A., *et al.*, *Catal. Sci. Technol.*, 2014, **4**, 2241.
65. a) Van Speybroeck, V., *et al.*, *Catal. Sci. Technol.*, 2016, **6**, 2686; b) Van Speybroeck, V., *et al.*, *J. Catal.*, 2016, **340**, 227.
66. Gervasio, F. L., *et al.*, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 771.
67. Parrinello, M., *et al.*, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 12562.
68. a) Pietrucci, F., *et al.*, *Phys. Rev. Lett.*, 2011, **107**, 085504; b) Martinez, T. J., *et al.*, *J. Chem. Theory Comput.*, 2016, **12**, 638.

Science communication and outreach activity

Development of technologies to produce added value **chemicals from biomass** is a topic of growing importance worldwide, and as such certainly suitable to attract interest of a wide community of professionals, as well as the broad public. A number of activities are proposed by the BioFact consortium to **efficiently communicate and reach out to different target groups**.

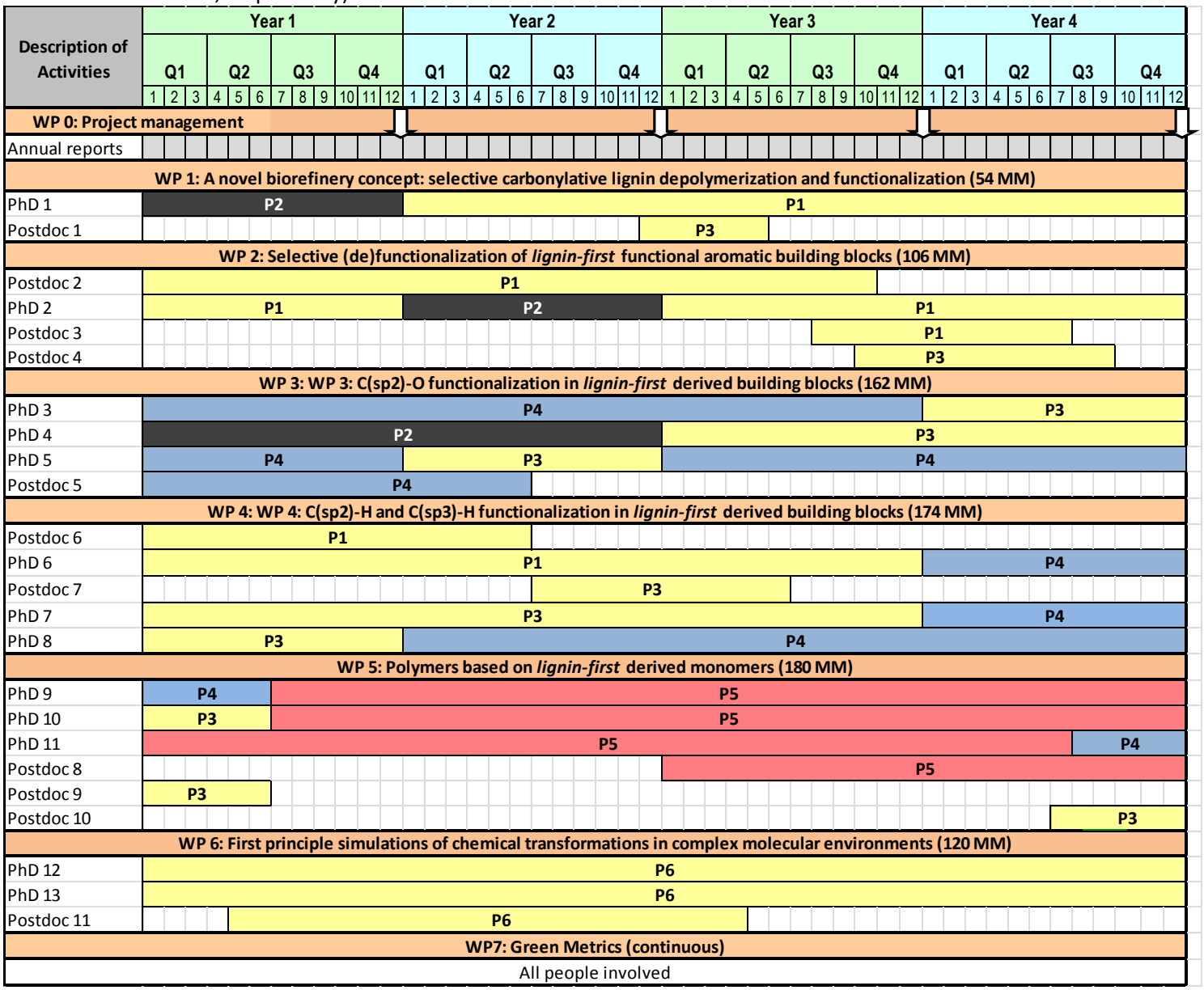
A project **newsletter** will be issued 1-2 times per year and distributed using the existing umbrella organizations for sustainable chemistry: spearhead cluster Catalisti in Flanders and Competitiveness Pole GreenWin in Wallonia. The aim will be to communicate to **chemistry-related professionals** about the newest method developments related to the production of industrially relevant classes of chemicals from wood biomass. The newsletter will also be published on the public section of the BioFact web site. A **Summer School** will be organized in May/June 2021, following the format of a recent "Chemistry as an enabler for a Sustainable Society" event organized by UAntwerpen in May 2015. The target audience will be a mix of **(young) academic and industrial researchers**. Industry will be actively involved through GreenWin and Catalisti, in order to exchange the different point of views on **green chemistry practices**. Members of the BioFact International Advisory Board will be invited to contribute with keynote lectures. Courses on important topics, such as on green chemistry metrics, to educate PhD students and postdocs will be scheduled. The **one-day annual events** such as "Day of Chemistry Education" organized by KVCV – the Flemish Royal Chemical Society, specific training organized by the CUDEC (Academic Center for the Teaching of Chemistry in Wallonia) and ULB's "Experimentarium de Chimie", will be used to promote biobased sustainable chemistry to secondary school teachers and students. In order to reach out to the **broad public**, a **blog on social media** (Facebook, Twitter) will be maintained by the PhD students/postdocs of BioFact to share their achievements in a layman style. In order to prevent release of information compromising the IP, the release mechanism (approval by a PI) will be established. In addition, two short **videos** will be made and published on **YouTube** or a similar channel. This will highlight selected project achievements related to

important sustainable chemistry issues. To the same end, the communication departments of the different organizations will publish research highlights in the respective University Magazines and on the universities websites.

Work Plan

Partners: P1: Katholieke Universiteit Leuven P2: Leibniz-Institut für Katalyse P3: Universiteit Antwerpen
P4: Université Libre de Bruxelles P5: Université de Liège P6: Universiteit Gent

Color code: Black, yellow, red and blue refer to the regional and international research location (Germany, Flanders, Wallonia and Brussels, respectively)



Total MM: 796 MM; PhDs: 13 (624 MM) of which **11 joint**, and **2 strongly interacting** with the other WPs (!)
Postdocs: 11 (172 MM) of which a mix of classical (full salary) and subsidized ones (tax free fellowships).
A postdoc can only be appointed as subsidized when fulfilling strict governmental criteria.

Staff description:

- **WP 1: A novel biorefinery concept: carbonylative lignin depolymerization and functionalization**

PhD1 (P1, P2: 48 MM) will investigate selectivity issues during lignin depolymerization and/or functionalization via carbonylation using homogeneous and heterogeneous catalysis. The person will first learn proper carbonylation strategies at P2 on simple commercially available ethers, which will be useful for reactions with advanced lignin model compounds, prepared by **Postdoc1** (P3: 6 MM), and finally with raw lignin extracts (available at P1) and wood feedstock.

- **WP 2: Selective (de)functionalization of *lignin-first* functional aromatic building blocks**

Postdoc2 (P1: 34 MM) will target the dealkylation of alkylcatechol and –pyrogallol using acidic zeolites in gas phase. Additionally, alternative dealkylation via benzylic oxidation (CN and BN materials, Ce doped zeolites), followed by deacylation of the products over acidic zeolites. **PhD2** (P1, P2: 48 MM) will synthesize (metal-doped) CN and BN materials (P1) and N-doped graphenes (P2), used throughout the whole project (WP1-3, WP5). There will be a strong focus on the modification of surface properties for the reduction and (reductive) amination reactions of catechol and

pyrogallol. **Postdoc3** (P1: 12 MM) tackles gas phase amination of catechol and pyrogallol with multifunctional acid zeolites, or with H-borrowing strategies using supported metal catalysts (e.g. metal@CN/BN materials from PhD2). Practically, WP3 and WP4 will require the anilines/amines sooner, but they are readily (commercially) available. **Postdoc4** (P3: 12 MM) will study the dealkyl- and deacylation in liquid phase (mineral acid, zeolite); zeolites provided by Postdoc 2 (P1) will also be evaluated**.**

- **WP 3: C(sp2)-O functionalization in *lignin-first* derived building blocks**

PhD3 (P4, P3, 48 MM) will optimize the $PhOPR_4$ structure for maximal CO_2 absorption (P3) and suitability of C-O oxidative addition in $PhOCO_2PR_4$ (P4). It involves cross coupling method development and scope study (P4). **PhD4** (P2, P3, 48 MM) will prepare Ni @graphenes and @N-doped graphenes (P2) for use in cross coupling with activated phenols (P3). First classical, and then new activation modes will be evaluated. Also kinetic studies (oxidative addition) on the different activation modes will be studied here. **PhD5** (P4, P3, 48 MM) will study the activation of catechol (and amino analogues) for cross coupling by boron reactants (P4). This will involve method development and scope study (P4). Alternative activation will be considered when required (P3). The person will also apply the new activation methods (PhD3, PhD5, Postdoc5) for consecutive cross coupling reactions. **Postdoc5** (P4, 18 MM) will study the activation of pyrogallol (and amino analogues), and work in close collaboration with PhD5. This will involve method development and scope study.

- **WP 4: C(sp2)-H and C(sp3)-H functionalization in *lignin-first* derived building blocks**

PhD6 (P1, P4, 48 MM) focuses on the p*ara* selective C(sp2)-H functionalization (cross-dehydrogenative couplings) of phenols, catechols and anilines with zeolites and MOFs. This involves method development (P1) and scope study (P1, P4). **Postdoc6** (P1, 18 MM) will support PhD6 by preparing MOFs/ zeolites. **PhD7** (P3, P4, 48 MM) investigates the directed C(sp3)-H functionalization on isolated DG-equipped *cis* cyclohexanediols, aminocyclohexanol and cyclohexanediamines. This involves method development and scope study (P3). Extension to other substrate classes is also included (P4). **Postdoc7** (P3, 12 MM) will support PhD7 by synthesizing DG-equipped aldehydes and investigates in situ installation of the DG on the substrates. **PhD8** (P3, P4, 48 MM) investigates the directed C(sp3)-H functionalization of *cis* aminocyclohexanol (P4) and cyclohexanediamines (P3) with CO_2. This work involves method development and scope study.

WP 5: Polymers based on *lignin-first* derived monomers

PhD9 (P5, P4, 48 MM) will investigate the synthesis of activated cyclic carbonates (P4 and P5) and their polymerization with lignin-derived monomers for producing PCs and PUs (P5). **PhD10** (P5, P3, 48 MM) is engaged in the synthesis of activated cyclic iminocarbonates (P3) (applying method Postdoc 9) and their polymerization with lignin-derived monomers to form PImCs (P5). **PhD11** (P5, P4, P48 MM) investigates the precision radical copolymerization (P5) and the post-functionalization of polymers (P4). **Postdoc8** (P5, 24 MM) will study the copolymerisation of 1,2-cyclohexanediol (*cis* and *trans*; commercial or delivered by P1 in WP2) with CO_2 using homogeneous/immobilized (organo)catalyst, in combination with a recyclable desiccant. **Postdoc9** (P3, 6 MM) focuses on the synthesis of iminocarbonates from hydroxyketones and commercially available isocyanides (method development). **Postdoc10** (P3, 6 MM) Investigates new greener ways towards isocyanide synthesis. The postdoc will receive heterogeneous catalysts of P1. PhD10 and Postdoc 9 will use commercial isocyanides.

- **WP 6: First principle simulations of chemical transformations in complex molecular environments**

PhD12 (P6, 48 MM) should start at the onset of the program, to model activation energies and reactivity profiles, and screen a set of catalysts/ligands/DGs for the C-O and C-H activation reactions in WP3 and WP4. Within WP5, reactivity of cyclic (imino)carbonates towards nucleophiles will be studies. The student should gradually use Molecular Dynamics (MD) based approaches in collaboration with Postdoc11. **Postdoc11** (P6, 24 MM) will train PhD12 and start the exploration of various intermediates in solution and the applicability of explicit MD based solvent methods. Within WP2, the *cis*/*trans* stability of acetals from aldehydes and cyclohexanediols, aminocyclohexanol and cyclohexanediamines will serve as a test case. Within WP5, the dynamic reorganization of solvent, additional hydrogen bond donors and Lewis acidity on the reactivity of cyclic carbonates will be explored. **PhD13** (P6, 48 MM) will study the nature of the active sites in a series of metal doped zeolites (Ce-doped zeolites for WP2 and Cu/Pd doped zeolites for WP4), using static DFT methods. MD methods will be used to study the nature of the intermediates under influence of water or other guest species (dealkylation processes in WP2). Advanced MD methods will be used to determine selectivity conditions for a series of zeolite catalyzed reactions within WP2, and determine shape selective conditions within WP4 for C(sp2)-H activations.

- **WP 7: Green metrics**

No staff to be appointed. Different PhD and Postdocs will perform this analysis during method development. These will be included in publications and lectures to rationalize the green 'thinking' during method development**.** Collaboration of P3 with University of York via a FWO Scientific Research Network allows implementing further advances in the current metrics, while two new journals, Nature Sustainability and ACS Sustainable Chemistry & Engineering, are planning extra emphasis on these themes.

PART 5: BUDGET

Total requested budget per cost type

	2018	2019	2020	2021	Total
Staff	€ 751 167	€ 786 167	€ 789 499	€ 738 333	€ 3 065 166
Consumables	€ 243 000	€ 208 000	€ 205 000	€ 254 000	€ 910 000
Coordination	€ 5 000	€ 5 000	€ 5 000	€ 5 000	€ 20 000
Total	**€ 999 167**	**€ 999 167**	**€ 999 499**	**€ 997 333**	**€ 3 995 166**

Total requested budget per research group and per cost category

Type I-FL - Centre for Surface Chemistry and Catalysis (KU Leuven)

	2018	2019	2020	2021	Total
Staff	€ 165 000	€ 190 000	€ 210 833	€ 137 833	€ 703 666
Consumables	€ 44 000	€ 52 000	€ 49 000	€ 52 000	€ 197 000
Coordination	€ 5 000	€ 5 000	€ 5 000	€ 5 000	€ 20 000
Total	**€ 214 000**	**€ 247 000**	**€ 264 833**	**€ 194 833**	**€ 920 666**

Type I-FL - Organic Synthesis (Universiteit Antwerpen)

	2018	2019	2020	2021	Total
Staff	€ 92 500	€ 119 167	€ 148 333	€ 197 500	€ 557 500
Consumables	€ 34 000	€ 21 000	€ 40 000	€ 61 000	€ 156 000
Total	**€ 126 500**	**€ 140 167**	**€ 188 333**	**€ 258 500**	**€ 713 500**

Type I-FL - Center for Molecular Modeling (Universiteit Gent)

	2018	2019	2020	2021	Total
Staff	€ 144 667	€ 172 000	€ 117 333	€ 90 000	€ 524 000
Consumables	€ 23 000	€ 33 000	€ 25 000	€ 34 000	€ 115 000
Total	**€ 167 667**	**€ 205 000**	**€ 142 333**	**€ 124 000**	**€ 639 000**

Type I-FR - Center for Education and Research on Macromolecules (CERM) (Université de Liège)

	2018	2019	2020	2021	Total
Staff	€ 76 000	€ 114 000	€ 199 000	€ 180 000	€ 569 000
Consumables	€ 47 000	€ 36 000	€ 51 000	€ 46 000	€ 180 000
Total	**€ 123 000**	**€ 150 000**	**€ 250 000**	**€ 226 000**	**€ 749 000**

Type I-FR - Laboratory of Organic Chemistry (Université Libre de Bruxelles)

	2018	2019	2020	2021	Total
Staff	€ 183 000	€ 101 000	€ 114 000	€ 133 000	€ 531 000
Consumables	€ 61 000	€ 33 000	€ 40 000	€ 61 000	€ 195 000
Total	**€ 244 000**	**€ 134 000**	**€ 154 000**	**€ 194 000**	**€ 726 000**

Type IV - Applied Sustainable Catalytic Processes (Leibniz-Institut für Katalyse)

	2018	2019	2020	2021	Total
Staff	€ 90 000	€ 90 000	€ 0	€ 0	€ 180 000
Consumables	€ 34 000	€ 33 000	€ 0	€ 0	€ 67 000
Total	**€ 124 000**	**€ 123 000**	**€ 0**	**€ 0**	**€ 247 000**

Budget for Staff

Budget details per research group

Type I-FL - Centre for Surface Chemistry and Catalysis (KU Leuven)

Scientist - PhD (full-time) **2018: € 0** **2019: € 45 000** **2020: € 45 000** **2021: € 45 000** **Total: € 135 000**	Motivation: PhD 1 - 36 PM (joint PhD, 12 PM at LIKAT). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 45 000** **2019: € 0** **2020: € 45 000** **2021: € 45 000** **Total: € 135 000**	Motivation: PhD 2 - 36 PM (joint PhD, 12 PM at LIKAT). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 45 000** **2019: € 45 000** **2020: € 45 000** **2021: € 0** **Total: € 135 000**	Motivation: PhD 6 - 36 PM (joint PhD, 12 PM at ULB). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - Postdoc (full-time) **2018: € 25 000** **2019: € 50 000** **2020: € 0** **2021: € 0** **Total: € 75 000**	Motivation: Postdoc 6 - 18 PM. International temporary postdoctoral researcher will be appointed. See Scientific proposal, page 14-15 for description of the research subject.
Scientist - Postdoc (full-time) **2018: € 50 000** **2019: € 50 000** **2020: € 41 667** **2021: € 0** **Total: € 141 667**	Motivation: Postdoc 2 - 34 PM. International temporary postdoc will be appointed. See Scientific proposal, page 14-15 for description of the research subject.
Scientist - Postdoc (full-time) **2018: € 0** **2019: € 0** **2020: € 34 166** **2021: € 47 833** **Total: € 81 999**	Motivation: Postdoc 3 - 12 PM. See Scientific proposal, page 14-15 for description of the research subject.

Type I-FL - Organic Synthesis (Universiteit Antwerpen)

Scientist - PhD (full-time) **2018: € 0** **2019: € 0**	Motivation: PhD 3 - 12 PM (joint PhD, 36 PM at ULB). See Scientific proposal, page 14-15 for description of the PhD subject.

2020: € 0 **2021: € 45 000** **Total: € 45 000**	
Scientist - PhD (full-time) **2018: € 0** **2019: € 0** **2020: € 45 000** **2021: € 45 000** **Total: € 90 000**	Motivation: PhD 4 - 24 PM (joint PhD, 24 PM at LIKAT). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 0** **2019: € 45 000** **2020: € 0** **2021: € 0** **Total: € 45 000**	Motivation: PhD 5 - 12 PM (joint PhD, 36 PM at ULB). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 45 000** **2019: € 45 000** **2020: € 45 000** **2021: € 0** **Total: € 135 000**	Motivation: PhD 7 - 36 PM (joint PhD, 12 PM at ULB). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 0** **2019: € 0** **2020: € 0** **2021: € 45 000** **Total: € 45 000**	Motivation: PhD 8 - 12 PM (joint PhD, 36 PM at ULB). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 22 500** **2019: € 0** **2020: € 0** **2021: € 0** **Total: € 22 500**	Motivation: PhD 10 - 6 PM (joint PhD, 42 PM at ULg). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - Postdoc (full-time) **2018: € 0** **2019: € 4 167** **2020: € 20 833** **2021: € 0** **Total: € 25 000**	Motivation: Postdoc 1 - 6 PM. International temporary postdoctoral researcher will be appointed. See Scientific proposal, page 14-15 for description of the research subject.
Scientist - Postdoc (full-time) **2018: € 0** **2019: € 0** **2020: € 12 500** **2021: € 37 500** **Total: € 50 000**	Motivation: Postdoc 4 - 12 PM. International temporary postdoctoral researcher will be appointed. See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - Postdoc (full-time)	Motivation: Postdoc 7 - 12 PM. International temporary postdoctoral researcher will be appointed. See Scientific proposal,

2018: € 0 **2019: € 25 000** **2020: € 25 000** **2021: € 0** **Total: € 50 000**	page 14-15 for description of the research subject.
Scientist - Postdoc (full-time) **2018: € 25 000** **2019: € 0** **2020: € 0** **2021: € 0** **Total: € 25 000**	Motivation: Postdoc 9 - 6 PM. International temporary postdoctoral researcher will be appointed. See Scientific proposal, page 14-15 for description of the research subject.
Scientist - Postdoc (full-time) **2018: € 0** **2019: € 0** **2020: € 0** **2021: € 25 000** **Total: € 25 000**	Motivation: Postdoc 10 - 6 PM. International temporary postdoctoral researcher will be appointed. See Scientific proposal, page 14-15 for description of research PhD subject.

Type I-FL - Center for Molecular Modeling (Universiteit Gent)

Scientist - PhD (full-time) **2018: € 45 000** **2019: € 45 000** **2020: € 45 000** **2021: € 45 000** **Total: € 180 000**	Motivation: PhD 12 - 48 PM. See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 45 000** **2019: € 45 000** **2020: € 45 000** **2021: € 45 000** **Total: € 180 000**	Motivation: PhD 13 - 48 PM. See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - Postdoc (full-time) **2018: € 54 667** **2019: € 82 000** **2020: € 27 333** **2021: € 0** **Total: € 164 000**	Motivation: Postdoc 11 - 24 PM. See Scientific proposal, page 14-15 for description of the research subject.

Type I-FR - Center for Education and Research on Macromolecules (CERM) (Université de Liège)

Scientist - PhD (full-time) **2018: € 19 000** **2019: € 38 000** **2020: € 38 000** **2021: € 38 000** **Total: € 133 000**	Motivation: PhD 9 - 42 PM (joint PhD, 6 PM at ULB). See Scientific proposal, page 14-15 for description of the PhD subject.

Scientist - PhD (full-time) **2018: € 19 000** **2019: € 38 000** **2020: € 38 000** **2021: € 38 000** **Total: € 133 000**	Motivation: PhD 10 - 42 PM (joint PhD, 6 PM at UAntwerpen). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 38 000** **2019: € 38 000** **2020: € 38 000** **2021: € 19 000** **Total: € 133 000**	Motivation: PhD 11 - 42 PM (joint PhD, 6 PM at ULB). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - Postdoc (full-time) **2018: € 0** **2019: € 0** **2020: € 85 000** **2021: € 85 000** **Total: € 170 000**	Motivation: Postdoc 8 - 24 PM. See Scientific proposal, page 14-15 for description of the research subject.

Type I-FR - Laboratory of Organic Chemistry (Université Libre de Bruxelles)

Scientist - PhD (full-time) **2018: € 0** **2019: € 0** **2020: € 0** **2021: € 38 000** **Total: € 38 000**	Motivation: PhD 6 - 12 PM (joint PhD, 36 PM at KULeuven). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 0** **2019: € 0** **2020: € 0** **2021: € 38 000** **Total: € 38 000**	Motivation: PhD 7 - 12 PM (joint PhD, 36 PM at UAntwerpen). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 38 000** **2019: € 38 000** **2020: € 38 000** **2021: € 0** **Total: € 114 000**	Motivation: PhD 8 - 36 PM (joint PhD, 12 PM at UAntwerpen). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 19 000** **2019: € 0** **2020: € 0** **2021: € 0** **Total: € 19 000**	Motivation: PhD 9 - 6 PM (joint PhD, 42 PM at ULg). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 0** **2019: € 0** **2020: € 0**	Motivation: PhD 11 - 6 PM (joint PhD, 42 PM at ULg). See Scientific proposal, page 14-15 for description of the PhD subject.

2021: € 19 000 **Total: € 19 000**	
Scientist - PhD (full-time) **2018: € 38 000** **2019: € 38 000** **2020: € 38 000** **2021: € 0** **Total: € 114 000**	Motivation: PhD 3 - 36 PM (joint PhD, 12 PM at UAntwerpen). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 38 000** **2019: € 0** **2020: € 38 000** **2021: € 38 000** **Total: € 114 000**	Motivation: PhD 5 - 36 PM (joint PhD, 12 PM at UAntwerpen). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - Postdoc (full-time) **2018: € 50 000** **2019: € 25 000** **2020: € 0** **2021: € 0** **Total: € 75 000**	Motivation: Postdoc 5 - 18 PM. International temporary postdoctoral researcher will be appointed. See Scientific proposal, page 14-15 for description of the research subject.

Type IV - Applied Sustainable Catalytic Processes (Leibniz-Institut für Katalyse)

Scientist - PhD (full-time) **2018: € 45 000** **2019: € 0** **2020: € 0** **2021: € 0** **Total: € 45 000**	Motivation: PhD 1 - 12 PM (joint PhD, 36 PM at KULeuven). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 0** **2019: € 45 000** **2020: € 0** **2021: € 0** **Total: € 45 000**	Motivation: PhD 2 - 12 PM (joint PhD, 36 PM at KULeuven). See Scientific proposal, page 14-15 for description of the PhD subject.
Scientist - PhD (full-time) **2018: € 45 000** **2019: € 45 000** **2020: € 0** **2021: € 0** **Total: € 90 000**	Motivation: PhD 4 - 24 PM (joint PhD, 24 PM at UAntwerpen). See Scientific proposal, page 14-15 for description of the PhD subject.

Consumables

Budget details per research group

Type I-FL - Centre for Surface Chemistry and Catalysis (KU Leuven)

Publication costs **2018: € 0** **2019: € 5 000** **2020: € 5 000** **2021: € 10 000** **Total: € 20 000**	Detailed description: Open Access publications costs. Motivation: In accordance with the guidelines for putting publications in open access a budget of 2500 Euro per article is foreseen. For other publications, Open Access will be provided through institutional repositories.
Research expenses **2018: € 41 000** **2019: € 43 000** **2020: € 40 000** **2021: € 39 000** **Total: € 163 000**	Detailed description: The consumables cost consists of chemicals and other consumables (e.g. cartridges for an automated chromatography system, filters, laboratory glassware and solvents (HPLC grade and pro analysis)). A part of this budget will be used for analytical characterization of the synthesized molecules (e.g. NMR and HRMS measurements which are done in a service facility). Spare parts for reactors are also covered. Motivation: Standard consumables for lab chemistry experimental work.
Travel and Accomodation costs **2018: € 3 000** **2019: € 4 000** **2020: € 4 000** **2021: € 3 000** **Total: € 14 000**	Detailed description: Registration fee, travel, accommodation. To allow the junior researcher appointed on this project to attend an international conference where the results obtained in the framework of this project will be presented. Motivation: On average 1000 EUR per conference per FTE per year is foreseen.

Type I-FL - Organic Synthesis (Universiteit Antwerpen)

Travel and Accomodation costs **2018: € 2 000** **2019: € 3 000** **2020: € 3 000** **2021: € 4 000** **Total: € 12 000**	Detailed description: Registration fee, travel, accommodation. To allow the junior researcher appointed on this project to attend an international conference where the results obtained in the framework of this project will be presented. Motivation: On average 1000 EUR per conference per FTE per year is foreseen.
Publication costs **2018: € 0** **2019: € 5 000** **2020: € 5 000** **2021: € 10 000** **Total: € 20 000**	Detailed description: Open Access publications costs. Motivation: In accordance with the guidelines for putting publications in open access a budget of 2500 Euro per article is foreseen. For other

	publications, Open Access will be provided through institutional repositories.
Research expenses **2018: € 32 000** **2019: € 13 000** **2020: € 32 000** **2021: € 47 000** **Total: € 124 000**	Detailed description: The consumables cost consists of chemicals and other consumables (e.g. cartridges for an automated chromatography system, filters, laboratory glassware and solvents (HPLC grade and pro analysis)). A part of this budget will be used for analytical characterization of the synthesized molecules (e.g. NMR and HRMS measurements which are done in a service facility). Motivation: Standard consumables for lab chemistry experimental work.

Type I-FL - Center for Molecular Modeling (Universiteit Gent)

Research expenses **2018: € 20 000** **2019: € 25 000** **2020: € 17 000** **2021: € 22 000** **Total: € 84 000**	Detailed description: Research expenses are costs for computational infrastructure, including supercomputer cluster facilities. Motivation: Standard research cost for computational work.
Publication costs **2018: € 0** **2019: € 5 000** **2020: € 5 000** **2021: € 10 000** **Total: € 20 000**	Detailed description: Open Access publications costs. Motivation: In accordance with the guidelines for putting publications in open access a budget of 2500 Euro per article is foreseen. For other publications, Open Access will be provided through institutional repositories.
Travel and Accomodation costs **2018: € 3 000** **2019: € 3 000** **2020: € 3 000** **2021: € 2 000** **Total: € 11 000**	Detailed description: Registration fee, travel, accommodation. To allow the junior researcher appointed on this project to attend an international conference where the results obtained in the framework of this project will be presented. Motivation: On average 1000 EUR per conference per FTE per year is foreseen.

Type I-FR - Center for Education and Research on Macromolecules (CERM) (Université de Liège)

Publication costs **2018: € 0** **2019: € 5 000** **2020: € 5 000** **2021: € 10 000** **Total: € 20 000**	Detailed description: Open Access publications costs. Motivation: In accordance with the guidelines for putting publications in open access a budget of 2500 Euro per article is foreseen. For other publications, Open Access will be provided through institutional repositories.
Travel and Accomodation costs	Detailed description: Registration fee, travel, accommodation. To allow the junior

2018: € 2 000 **2019: € 3 000** **2020: € 4 000** **2021: € 4 000** **Total: € 13 000**	researcher appointed on this project to attend an international conference where the results obtained in the framework of this project will be presented. Motivation: On average 1000 EUR per conference per FTE per year is foreseen.
Research expenses **2018: € 45 000** **2019: € 28 000** **2020: € 42 000** **2021: € 32 000** **Total: € 147 000**	Detailed description: The consumables cost consists of chemicals and other consumables (e.g. cartridges for an automated chromatography system, filters, laboratory glassware and solvents (HPLC grade and pro analysis)). A part of this budget will be used for analytical characterization of the synthesized molecules (e.g. NMR and HRMS measurements which are done in a service facility). Motivation: Standard consumables for lab chemistry experimental work.

Type I-FR - Laboratory of Organic Chemistry (Université Libre de Bruxelles)

Research expenses **2018: € 56 000** **2019: € 25 000** **2020: € 32 000** **2021: € 47 000** **Total: € 160 000**	Detailed description: The consumables cost consists of chemicals and other consumables (e.g. cartridges for an automated chromatography system, filters, laboratory glassware and solvents (HPLC grade and pro analysis)). A part of this budget will be used for analytical characterization of the synthesized molecules (e.g. NMR and HRMS measurements which are done in a service facility). Motivation: Standard consumables for lab chemistry experimental work.
Travel and Accomodation costs **2018: € 5 000** **2019: € 3 000** **2020: € 3 000** **2021: € 4 000** **Total: € 15 000**	Detailed description: Registration fee, travel, accommodation. To allow the junior researcher appointed on this project to attend an international conference where the results obtained in the framework of this project will be presented. Motivation: On average 1000 EUR per conference per FTE per year is foreseen.
Publication costs **2018: € 0** **2019: € 5 000** **2020: € 5 000** **2021: € 10 000** **Total: € 20 000**	Detailed description: Open Access publications costs. Motivation: In accordance with the guidelines for putting publications in open access a budget of 2500 Euro per article is foreseen. For other publications, Open Access will be provided through institutional repositories.

Type IV - Applied Sustainable Catalytic Processes (Leibniz-Institut für Katalyse)

Travel and Accomodation costs	Detailed description: Registration fee, travel, accommodation. To allow the junior

2018: € 2 000 **2019: € 2 000** **2020: € 0** **2021: € 0** **Total: € 4 000**	researcher appointed on this project to attend an international conference where the results obtained in the framework of this project will be presented. Motivation: On average 1000 EUR per conference per FTE per year is foreseen.
Publication costs **2018: € 5 000** **2019: € 5 000** **2020: € 0** **2021: € 0** **Total: € 10 000**	Detailed description: Open Access publications costs. Motivation: In accordance with the guidelines for putting publications in open access a budget of 2500 Euro per article is foreseen. For other publications, Open Access will be provided through institutional repositories.
Research expenses **2018: € 27 000** **2019: € 26 000** **2020: € 0** **2021: € 0** **Total: € 53 000**	Detailed description: The consumables cost consists of chemicals and other consumables (e.g. cartridges for an automated chromatography system, filters, laboratory glassware and solvents (e.g. HPLC grade and pro analysis)). A part of this budget will be used for analytical characterization of the synthesized molecules (NMR and HRMS measurements which are done in a service facility). Spare parts for reactors. Motivation: Standard consumables for lab chemistry experimental work.

Equipment

No budget for equipment entered

Budget for coordination costs

Budget details per research group

Type I-FL - Centre for Surface Chemistry and Catalysis (KU Leuven)

2018: € 5 000
2019: € 5 000
2020: € 5 000
2021: € 5 000
Total: € 20 000

Motivation: General coordination cost

ETHICAL ASPECTS

General information

I confirm that none of the issues below apply to my proposal

- Please specify which ethics committee(s) deal(s)/will deal with your application.
  Not applicable
- If you do not need the ethical approval(s) before the start of your project, please indicate the starting dates of the tasks/experiments subject to ethical approval.
  Description of the tasks/experiments subject to ethical approval.

Not applicable	Starting date: Not applicable
Not applicable	Starting date: Not applicable
Not applicable	Starting date: Not applicable
Not applicable	Starting date: Not applicable
Not applicable	Starting date: Not applicable
Not applicable	Starting date: Not applicable

Human Embryos/Foetuses

ETHICS ADVICE RELATED TO THESE QUESTIONS SHOULD ALWAYS BE REQUESTED BEFORE THE START OF THE RESEARCH PROJECT AS A WHOLE AND ALSO REQUIRE AN EXAMINATION BY THE FEDERAL COMMISSION FOR EMBRYOS

- Does your research involve Human Embryonic Stem Cells (hESCs)? **Not applicable**
  - Will the hESCs be directly derived from embryos within this project? **Not applicable**
  - Are the hESCs previously established cell lines? **Not applicable**
- Does your research involve the use of human embryos? **Not applicable**
- Does your research involve the use of human foetal tissues / cells? **Not applicable**

Humans

- Does your research involve human subjects? **Not applicable**
  - Are they volunteers for social or human sciences research? **Not applicable**
  - Are they persons unable to give informed consent? **Not applicable**
  - Are they vulnerable individuals or groups? **Not applicable**
  - Are they children/minors? **Not applicable**
  - Are they patients? **Not applicable**
  - Are they healthy volunteers for medical studies? **Not applicable**
- Does your research involve physical interventions on the study participants? **Not applicable**
  - Does it involve invasive techniques? **Not applicable**
  - Does it involve collection of biological samples? **Not applicable**

Human Cells/Tissues

- Does your research involve human cells or tissues (other than from Human Embryos/Foetuses)? **Not applicable**
  - Are they obtained from commercial sources? **Not applicable**
  - Do they originate from another laboratory/institution/biobank? **Not applicable**
  - Were they produced or collected by you from previous research activities? **Not applicable**
  - Are they produced or collected by you as part of this project? **Not applicable**

Personal Data

- Does your research involve personal data collection and/or processing? **Not applicable**
  - Does it involve the collection and/or processing of sensitive personal data? **Not applicable**
  - Does it involve collecting/processing of genetic information/data? **Not applicable**
  - Does it involve tracking or observation of participants? **Not applicable**
- Does your research involve further processing of previously collected personal data ('secondary use')? **Not applicable**

Animals

- Does your research involve research procedures to live non-human vertebrate animals (incl. independently feeding larval forms, foetal forms of mammals in the last trimester of their normal development and cephalopods, and also forms in earlier stages if the experiments have consequences in later stages)? **Not applicable**
  - Are they vertebrates or live cephalopods? **Not applicable**
  - Are they non-human primates? **Not applicable**
  - Are they genetically modified animals? **Not applicable**
  - Are they cloned farm animals? **Not applicable**
  - Are they endangered species? **Not applicable**

International Collaboration

- Do you plan to use local resources (e.g. animal and/or human tissue samples, genetic material, live animals, human remains, materials of historical value, endangered fauna or flora samples, etc.)? **Not applicable**
- Do you plan to import/export any material from/to other countries? **Not applicable**
  - Name of country/ies: **Not applicable**
- If your research involves low and/or lower middle income countries, are benefits-sharing measures foreseen? **Not applicable**
- Could the situation in the country put the individuals taking part in the research at risk? **Not applicable**

Environment & Health and Safety

- Does your research involve the use of elements that may cause harm to the environment, to animals or plants? **Not applicable**
- Does your research deal with endangered fauna and/or flora and/or protected areas? **Not applicable**
- Does your research involve the use of elements that may cause harm to humans, including research staff? **Not applicable**

Dual use

- Does your research have the potential for military applications? **Not applicable**

Misuse

- Does your research have the potential for malevolent/criminal/terrorist abuse? **Not applicable**

Other ethical issues

- Are there any other ethics issues that should be taken into consideration? Please specify (up to 4000 characters)
  Not applicable

RESEARCH METRICS

Type I-FL - Centre for Surface Chemistry and Catalysis (KU Leuven)

SELS Bert	Publications: 234 – Citations: 9700
Date of PhD: 03/03/2001	Source: Web of Science
	Comment: Number of publications: articles in peer-reviewed journals only. In addition, 11 book chapters and 20 patents.
DE VOS Dirk	Publications: 329 – Citations: 15300
Date of PhD: 01/03/1994	Source: Web of Science
	Comment: Number of publications: articles in peer-reviewed journals only. In addition, 23 book chapters and 47 patents.

Type I-FL - Center for Molecular Modeling (Universiteit Gent)

VAN SPEYBROECK Veronique	Publications: 272 – Citations: 6300
Date of PhD: 01/10/2001	Source: Web of Science
	Comment: Number of publications: articles in peer-reviewed journals only. In addition, 2 book chapters.

Type I-FL - Organic Synthesis (Universiteit Antwerpen)

MAES Bert	Publications: 118 – Citations: 2900
Date of PhD: 23/05/2003	Source: Web of Science
	Comment: Number of publications: articles in peer-reviewed journals only. In addition, 4 book chapters and 4 patents.

Type I-FR - Laboratory of Organic Chemistry (Université Libre de Bruxelles)

EVANO Gwilherm	Publications: 100 – Citations: 3900
Date of PhD: 28/06/2002	Source: Web of Science
	Comment: Number of publications: articles in peer-reviewed journals only. In addition, 11 book chapters.

Type I-FR - Center for Education and Research on Macromolecules (CERM) (Université de Liège)

DETREMBLEUR Christophe	Publications: 217 – Citations: 6300
Date of PhD: 02/03/2001	Source: Web of Science
	Comment: Number of publications: articles in peer-reviewed journals only. In addition, 7 book chapters and 23 patents.
DEBUIGNE Antoine	Publications: 92 – Citations: 2400
Date of PhD: 30/09/2004	Source: Web of Science
	Comment: Number of publications: articles in peer-reviewed journals only. In addition, 4 book chapters and 2 patents.

Type IV - Applied Sustainable Catalytic Processes (Leibniz-Institut für Katalyse)

BELLER Matthias	Publications: 779 – Citations: 41800
Date of PhD: 28/06/1989	Source: Scopus
	Comment: Number of publications: articles in peer-reviewed journals only. In addition, 29 book chapters and 127 patents.

LEGAL STATEMENT BY THE SPOKESPERSON-COORDINATOR

The Spokesperson-Coordinator confirms that to the best of his/her knowledge and belief, the information in this application is complete and correct.

The Spokesperson-Coordinator will inform FWO and F.R.S-FNRS immediately if the intended project cannot be carried out as foreseen or if a major change occurs that may hinder the planned implementation of the project.
The Spokesperson-Coordinator declares that he/she has read and agrees with the regulations valid for the concerned application that form an integral part of the application documents published on the FWO and F.R.S-FNRS website and that form the legal basis of the future contract. Furthermore, he/she takes note that the FWO and F.R.S-FNRS is committed to the principles of the European Charter for Researchers and the Code of Conduct for their Recruitment.

The Spokesperson-Coordinator agrees that the data required for the research grant application and follow-up are electronically stored and used by the FWO and F.R.S-FNRS. The FWO and F.R.S-FNRS will use the data provided by the Applicant according to the legal requirements of data protection in Belgium, including the use of the anonymized data for statistical purposes and reports.

The Spokesperson-Coordinator agrees that the FWO and F.R.S-FNRS will forward the full application form including their personal data to the experts involved in the evaluation of their proposal in Flanders and abroad (EU and outside EU). The panel members and experts must declare in advance that they will treat data confidentially and that they will not forward the data or the knowledge gained to anyone nor use it for their own purpose.

Furthermore, the Spokesperson-Coordinator agrees that the following information may be included in lists published by the FWO: full name of the beneficiary; nationality; e-mail address; name, birth date, host institution, degrees obtained; name of scientific contact and research unit title of research project; abstract; field of research and key words; start date and end date of the fellowship.

The Spokesperson-Coordinator declares that all information provided in the personal data section is accurate and up-to-date.