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Organic and hybrid systems: from science to practice

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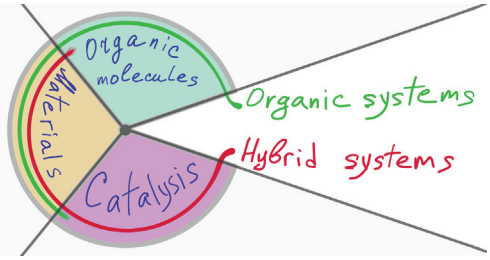
Organic systems still dominate several traditional areas of chemical science and well-known applications, such as the synthesis of pharmaceutical compounds and drugs. However, a fascinating trend has appeared recently to combine pure organic systems into advanced molecular architectures and to create hybrid molecular systems. These interdisciplinary areas, where possible connections between organic and hybrid systems may be developed, are the focus of the present review to develop valuable practical applications.



1. Introduction

In recent years, the N. D. Zelinsky Institute of Organic Chemistry has undertaken several initiatives to highlight the vital importance of organic synthesis at the intersection of fundamental and applied investigations,[1–4] including the development of new approaches for selective transformations with atomic precision,[5,6] the synthesis of novel organic and hybrid molecular systems,[7] and overcoming the challenges in the design of advanced molecular architectures.[8]

Recent initiatives on the development of rational concepts for designing new organic and hybrid molecular systems in view of the development of practical technologies[7] have largely progressed and now play key roles in providing driving forces for interdisciplinary studies. Indeed, in the first stage, the flexibility of organic synthesis procedures and fascinating diversity of readily available organic molecules have stimulated the development of task-specific components for complex hybrid systems.[7] The next stage in the development of the initiative included the identification of mechanistic challenges and focused on the synthetic handling of molecular complexity.[8] Currently, the initiative creates a research platform for the development of various research topics, as described in the present short review with a focus toward practical applications.

It should be emphasized that this is not a regular literature review. Instead, in this focus article, we discuss the progress of the ongoing initiative and analyze the possible connections with individual research projects. The development of practical applications in broad areas of medicine, new materials and catalysis represents the main aim. We believe that the stimulation of interdisciplinary research efforts and the discussion of practical requirements are needed to facilitate research in this area and improve approaches for selecting the highest priority directions to be supported by scientific funds and state institutions.

2. Organic and hybrid systems

We start the discussion with the discovery of new organic chemistry approaches stimulated by demanded applications in pharmaceutical and medical applications (Section 2.1). The discussion is followed by representative catalytic procedures (Section 2.2), where the focus is given on heterogeneous catalysis as a rapidly developing flagship of selective transformations with cost-efficient recyclable catalysts.[5] Organic synthesis solutions, provided by homogeneous catalysis, are well-described elsewhere and will not be repeated here. Finally, topics dealing with materials science and high-energy compounds are included (Section 2.3). Due to size limitations only few representative examples of the overall research initiative are covered in each section.

2.1. Chemical synthesis toward medicinal applications

Three well-known approaches were utilized in the synthesis of biologically active compounds and pharmaceutical substances: (1) the target-specific formation of new bonds; (2) the selective attachment of functional groups; (3) the optimization of carbon skeletons and introduction of chiral centers. A few chosen examples will be discussed as representative studies in this joint organic chemistry effort.

A new synthetic methodology toward 1,2-oxazine as a new scaffold for medicinal chemistry was developed. Despite the vast synthetic capabilities of modern organic chemistry, only a fractional number of available scaffolds are used in pharma-

ceuticals. In drug design, preference is usually given to so-called 'privileged scaffolds', classical basic structures, which are largely found in natural molecules and well-established pharmaceuticals. In this regard, the bioactivity of many heterocyclic systems remains unexplored. Among such systems are 1,2-oxazines, which until recently were regarded as exotic and scarcely available heterocycles not occurring in nature. This situation changed in the early 2000s, when the metabolite penicillazine possessing a 1,2-oxazine unit was isolated from the marine fungus *Penicillium sp*. In the subsequent years, many efforts were made toward the total synthesis of penicillazine and related natural N–O-containing 6-membered heterocycles as well as toward studies of their pharmacological activities.[9]

Nevertheless, non-natural 1,2-oxazines, until very recently, have not been the subject of bioactivity studies, evidently, because of their poor synthetic accessibility.[10] The developed general solution to this problem is the application of readily available cyclic nitronates **1** as direct precursors of functionalized 1,2-oxazines (Figure 1). This approach exploits the oxidative potential of *N*-oxide to achieve C–H functionalization of the alkyl group at the C-3 position through transformation of **1** to the *N*-oxyenamine system **2** and subsequent S_N' substitution of the *N*-oxy group promoted by *d*-metal cations.[11] Using this general strategy, a large array of 1,2-oxazine building blocks with various substitution patterns can be accessed.[11,12]

Biological screening of a library of 1,2-oxazines prepared in this manner revealed their high potential as anti-inflammatory and anticancer agents. A lead compound, SAB0042 (Figure 1), was found to be highly active against inflammatory bowel disease both *in vitro* and *in vivo*, which makes it an efficient analogue of the drugs sulfasalazine *etc*.[13]

A powerful technique for increasing the biological stability and efficiency of drugs is introduction of C–F bonds through the

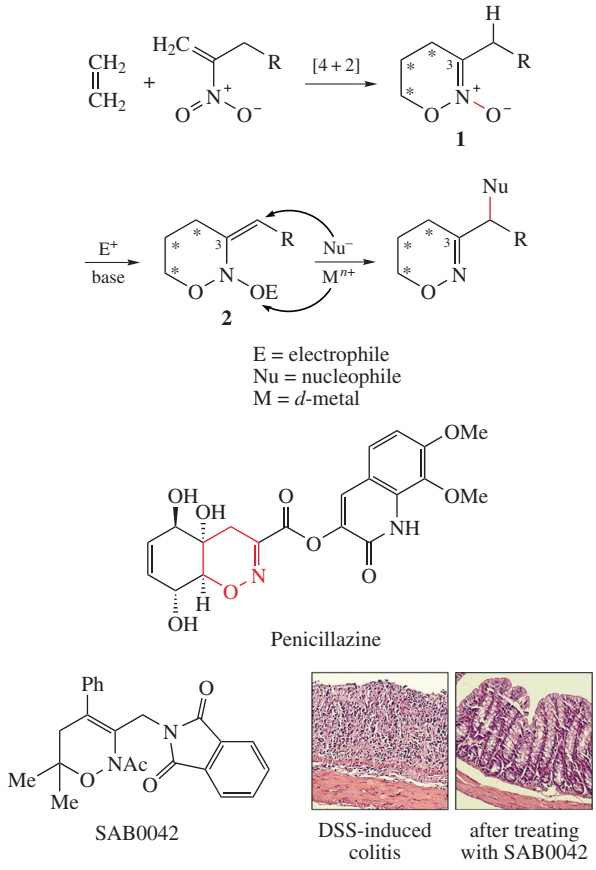


Figure 1 Suggested strategy toward the 1,2-oxazine scaffold and bioactive 1,2-oxazines.[13]

synthesis of fluorinated building blocks for medicinal chemistry. Indeed, organofluorine compounds have found widespread use in medicinal chemistry and related fields. The ability of fluorine to improve the therapeutic efficiency of substances has led to the appearance of a considerable number of fluorinated drugs for a broad spectrum of diseases, such as bacterial and viral infections, cancer and many others.

The development of methods for the synthesis of fluorinated building blocks, which are indispensable components in drug design, constitutes an important research area. Correspondingly, reactions allowing for the facile introduction of fluorinated groups by modification of common functional groups are needed.

A general concept for the synthesis of compounds bearing a difluoromethylene fragment was proposed. The key process involves the interaction of a heteroatom-centered nucleophile with difluorocarbene followed by coupling with an electrophile (Figure 2). Phosphorus- and sulfur-centered reagents, as well as halide anions, were employed as nucleophiles. A series of methods for the conversion of readily available carbonyl compounds, imines and Michael acceptors into difluoromethylated alcohols, amines, and esters were developed.[14]

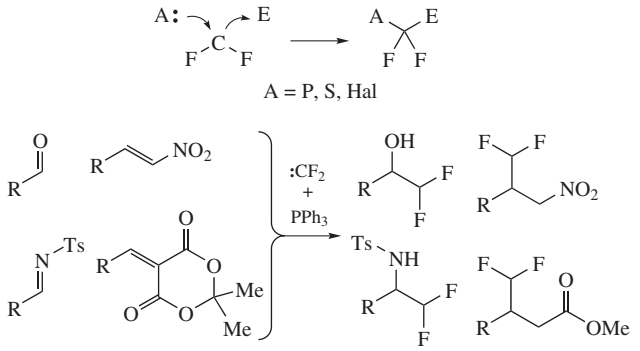
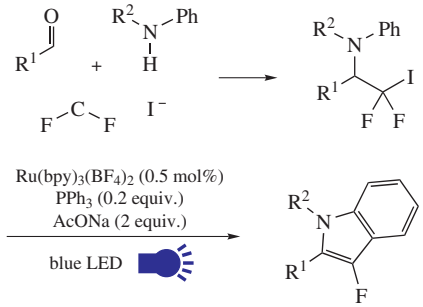


Figure 2 General concept for the use of difluorocarbene as a building block.[14–18]

When a halide ion was used as the nucleophile with respect to difluorocarbene, the reaction provided products containing the valuable mixed-halogenated fragment CF_2X. Using this protocol, alcohols and amines having bromo- and iododifluoromethyl groups were prepared.[15,16]

In the compounds derived from difluorocarbene, the carbon–heteroatom bond can be cleaved under photoredox conditions with visible light (Scheme 1). This method was applied for the synthesis of various fluorinated heterocycles.[17,18]



Scheme 1 Approach for the photoredox synthesis of fluorinated heterocycles.[17,18]

A state-of-the-art strategy for the introduction of new functional groups can be illustrated by the synthesis of peroxides to design antiparasitic and cytotoxic drugs. Organic peroxides are traditionally used as initiators of radical processes, disinfectants, and oxidants in organic synthesis and the food industry. The discovery

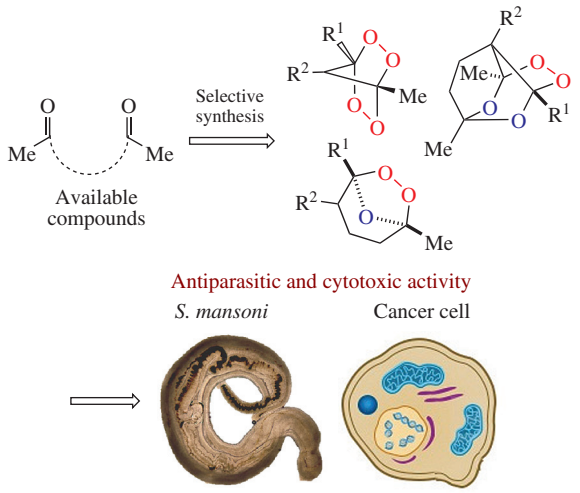


Figure 3 Selective synthesis of organic peroxides with antiparasitic and cytotoxic activities.[20,21]

of the natural peroxide artemisinin with a pronounced antimalarial activity, which awarded the Nobel Prize in 2015, started the era of medicinal chemistry of organic peroxides. Currently, the pharmacological chemistry of peroxides with antiparasitic, fungicidal, antiviral, and cytotoxic properties is intensively developed.

The focus is directed to available synthetic peroxides with simple structures possessing a broad spectrum of biological activity (Figure 3). The main challenge for the synthesis of organic peroxides from available carbonyl and unsaturated compounds is to achieve high selectivity in the reactions and high stability of the obtained peroxides. The ability to stabilize the stereoelectronic effect originating from strong anomeric $n_O \rightarrow \sigma^*_{CO}$ interactions, which provides the selectivity of the synthesis and stability of 1,2,4,5-tetraoxanes, ozonides, and tricyclic monoperoxides, was found.[19]

The antiparasitic activities of these peroxides were studied against a noteworthy parasite of humans, *Schistosoma mansoni*, a trematode with rapidly increasing drug resistance.[20] Selected tricyclic monoperoxides and ozonides showed excellent *in vitro* antischistosomal activities and were tested *in vivo* in mice harboring an adult *S. mansoni* infection. Two ozonides showed moderate worm burden reductions in mice.

The high cytotoxicity *in vitro* against prostate cancer cell lines DU145 and PC3 of synthetic tetraoxanes and ozonides was demonstrated.[21] It was found that the mechanism of cytotoxicity of these peroxides is not directly related to their oxidative properties. The obtained results make it possible to consider organic peroxides as promising antiparasitic and anticancer agents.

A rare example of a selective synthesis of peroxides from esters was demonstrated by obtaining cyclopropyl malonyl peroxide.[22] The synthesis of vicinal bisperoxides from styrenes and *tert*-butyl hydroperoxide was developed.[23] The bisperoxidation efficiently proceeded in yields from 46 to 75% with a manganese(III) acetate catalyst.

The application of $GaCl_3$ in the chemistry of cyclopropanes aimed at the design of new structures for medicinal chemistry allowed one to achieve a gradual increase of molecular complexity beginning with simple starting materials. The molecules of donor–acceptor cyclopropanes (DAC) are activated reactive three-membered carbon rings, which are very widely used in modern organic synthesis.[24] The compounds obtained on their basis are extensively applied in the construction of original structures, analogues of natural compounds and in total syntheses, as well as for the directed synthesis of molecules with pronounced biological activity.

The classical pathway of DAC transformations involves the initial generation of 1,3-zwitterionic intermediates. The usage of $GaCl_3$ allows DAC to serve as a source of gallium 1,2-zwitterions.[25] The latter species further enter reactions with various substrates followed by new cascade carbocationic processes, which allow one to produce a wide range of functionally substituted carbo- and heterocyclic structures (Figure 4). The most characteristic processes are [4+2]-annulation with unsaturated substrates,[26] cascade assembly of indenes and polycyclic lactones in the reactions with aromatic aldehydes,[27] and reactions proceeding through the preliminary isomerization of DAC into styrylmalonate intermediates.[28] The reactivity of DAC as 1,2-zwitterions is characteristic precisely with the use of gallium halides.

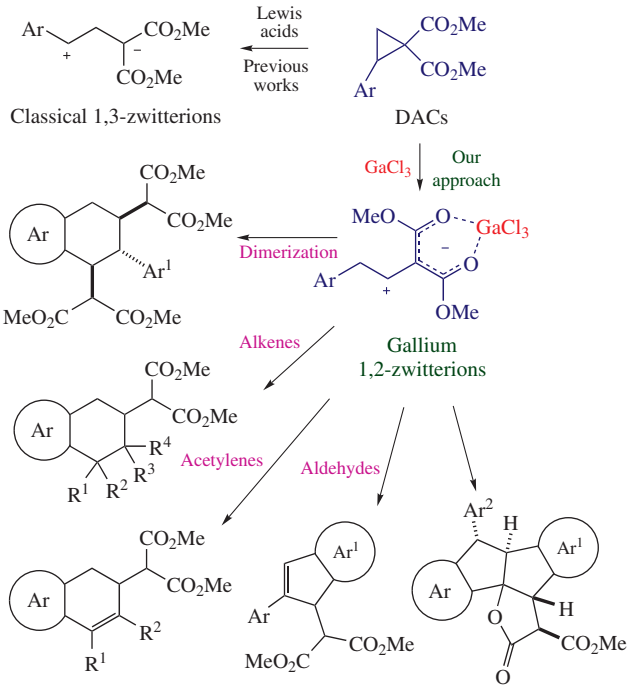


Figure 4 1,2-Zwitterionic reactivity of DACs in organic synthesis.[24–28]

The obtained compounds are of interest as key products in the synthesis of drug candidates with a specific spectrum of biological activity, including anticancer activity, as ligands for the catalysts of stereoselective polymerization of alkenes, and as precursors for the preparation of functional materials, in particular those exhibiting luminescent properties.[26–28] Primary biological tests of some of the obtained structures showed their high antimicrobial and antifungal activities, including activity against resistant strains of *Staphylococcus aureus*.

The use of $GaCl_3$ in DAC chemistry greatly expands the synthetic capabilities of this class of cyclopropanes and creates new efficient and stereoselective approaches to various polyfunctional carbo- and heterocyclic structures.

In addition to molecular complexity, chirality is a valuable aspect of many biologically active compounds. Up-to-date organocatalysis is one of the most developed strategies toward enantiomerically pure substances. Oriented organic nitrogen–oxygen systems for pharmacological applications are very promising compounds in this regard from several points of view.

α-Nitroolefins are readily available and useful intermediates in fine organic synthesis. In the presence of chiral catalysts, they can be stereoselectively converted to precursors for natural compound analogues and active pharmaceutical ingredients.[29] Metal-free catalysts are preferable in the pharmaceutical industry, as they do not contaminate products with toxic heavy metals. To meet this demand, novel C_2- and C_1-symmetric bifunctional

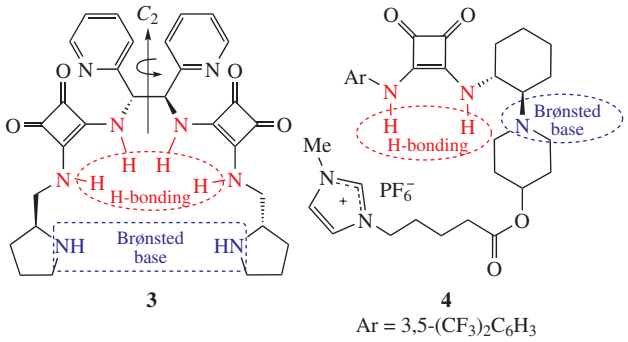


Figure 5 Bifunctional chiral diamine-squaramide organocatalysts **3** and **4**.[30,31]

organocatalysts **3**[30] and **4**[31] bearing chiral diamine and squaramide structural units were developed (Figure 5).

The key fragments of catalysts **3** and **4** acted cooperatively in asymmetric conjugate additions of C-nucleophiles to nitroolefins **5**. The Brønsted basic amino group (groups) activated a carbonyl or 1,3-dicarbonyl substrate, whereas the adjacent NH protons of the squaramide fragment (fragments) properly located the nitroolefin in the corresponding transition state *via* hydrogen bonding. As a result, the corresponding Michael adducts **6** and **7** were generated from nitroolefins **5** in nearly quantitative yield with good to excellent enantioselectivity (Scheme 2). Importantly, compound **4** efficiently promoted the reaction in a natural-like aqueous environment and could be readily recovered and reused over 30 times, retaining the activity and selectivity of the catalytic reaction.

Thus, the prepared compounds **6** were readily transformable to alkaloids (+)-ipalbidine, (+)-julandine, (–)-antofine and (–)-cryptopleurine, which exhibit potent analgetic, antimicrobial and antiviral activities. One of them is applicable for the enantioselective synthesis of (–)-venlafaxine, a new generation antidepressant drug, which is marketed as a racemate by Pfizer with the trade name of EffexorXR®. Adducts **7** could be converted to β-amino acid precursors for β-lactam antibiotics and a key intermediate in the stereoselective synthesis of useful anticonvulsant pregabalin (lyrica), which exhibits anxiolytic-like and analgesic properties while exerting very few toxic side effects. Remarkably, the method opens a practical route to the most active (*S*) enantiomer of pregabalin.

The upmost complexity of pharmaceuticals is closely related to the biomolecular carbohydrate systems providing new direction for several areas of medicine. Contrary to inorganic and hybrid organic systems,[7,8] the study of complex biomolecular systems, such as complex oligo- and polysaccharides and their glycoconjugates, includes detailed structural analysis, investigation of the biosynthesis and metabolism. Additionally, further studies involve the assessment of pharmacophore fragments that are responsible for the biological activities and the design of the corresponding bioconjugates reproducing the necessary spectrum of pharmacological properties.[32,33]

Recent studies of the first type included the systematic structural analysis of a large group of fucosylated chondroitin sulfates (FCS) from different species of sea cucumbers. These biomacromolecules were built from a [→4)-β-D-Glc*p*A-(1→3)-β-D-Gal*p*NAc-(1→]$_n$ backbone decorated by fucosyl branches and sulfates. In addition to the typical fucosyl branches attached to O-3 of Glc*p*A, unusual structural elements, such as fucosyl units attached to O-6 of the GalNAc residue (FCS from *Cucumaria frondosa*[34] and *Actinopyga mauritina*[35]) and the difucosyl fragment at O-3 of Glc*p*A (FCS from *Eupentacta fraudatrix*[36]), were found (for examples, see Figure 6). The 3-O- and 2,3-di-O-sulfated Glc*p*A units were also found in FCS from several other species of sea cucumbers.[34,36,37]

An interesting aspect of this novel type of glycosaminoglycans is related to their ability to influence blood coagulation, thrombosis and oncogenesis.[38] Thus, it was shown that all studied FCS inhibited fibrin polymerization and platelet aggregation induced

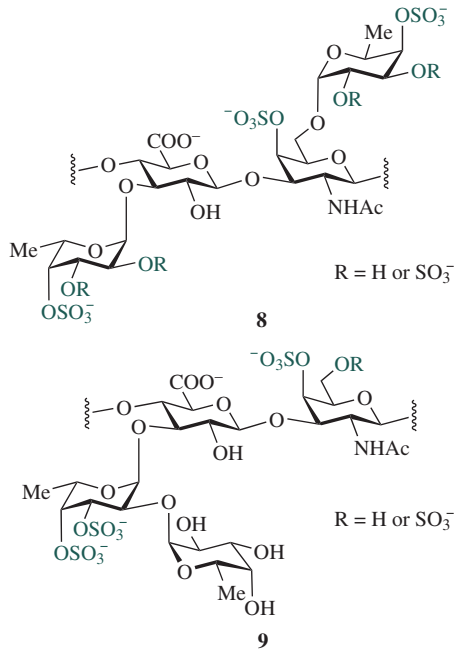
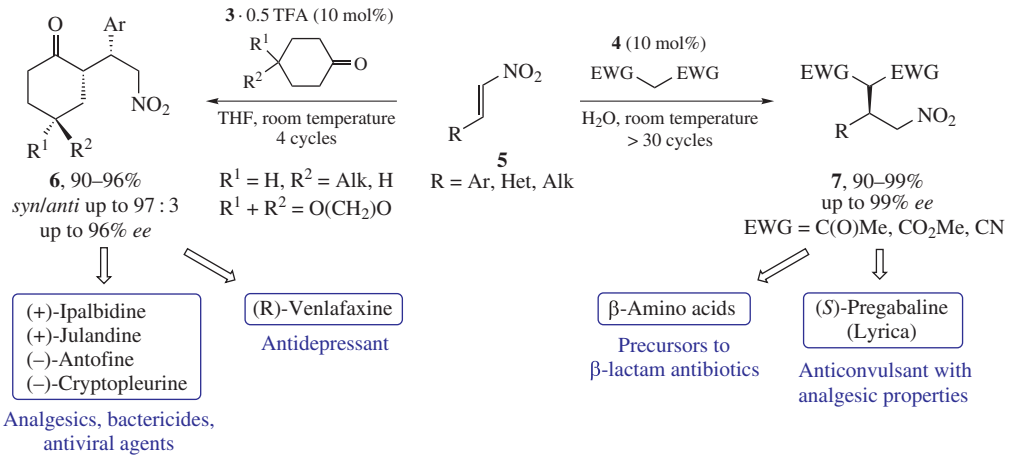


Figure 6 Structures of the fragments of fucosylated chondroitin sulfates from sea cucumbers *Cucumaria frondosa* **8**[34] and *Eupentacta fraudatrix* **9**.[36]



Scheme 2 The **3**- or **4**-catalyzed enantioselective Michael reactions of nitroolefins **5**.[30,31]

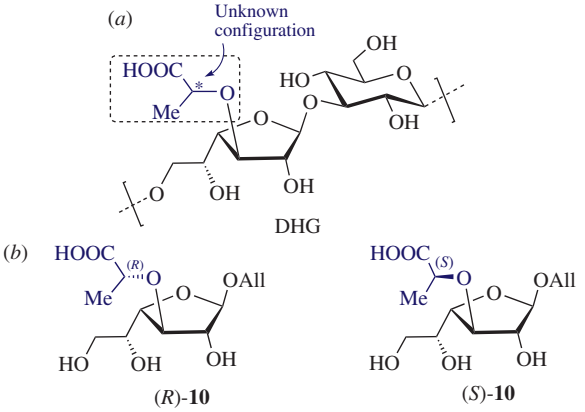


Figure 7 (*a*) Structure of the repeating unit of enterococcal DHG and (*b*) structural models (*R*)-**10** and (*S*)-**10** bearing (*R*)- and (*S*)-lactic acid substituents, respectively.[40,41]

by ristocetin. It is noteworthy that the level of biological activity depended on the structural features of FCS. Several polysaccharides demonstrated a higher effect than that of heparinoid enoxaparin currently used in medical practice as an anticoagulant.[37] These results could be considered as a base for the development of new types of anticoagulants lacking the side effects of heparinoids. The investigation of the mechanism of their activity formed the basis for the search and targeted design of glycomimetic agents.[39]

Detailed structural analysis of heteropolysaccharides often needs special synthetic models. This was the case of diheteroglycan (DHG), a polysaccharide from the pathogenic bacterium *Enterococcus faecalis*,[40,41] which is built from glucopyranosyl and galactofuranosyl units (Figure 7). The latter monosaccharide bears a lactic acid residue, and all known methods appeared to be inapplicable to assess its absolute configuration.[42] It was determined with the help of furanoside models (*R*)-**10** and (*S*)-**10**[40] prepared using a new synthetic approach, namely, pyranoside-*into*-furanoside (PIF) rearrangement.[41,43] This fruitful method (it was initially discovered as a site process during per-O-sulfation of long oligosaccharides[44]) permitted the efficient syntheses of complex oligosaccharide ligands structurally related to a number of polysaccharide antigens of clinically important fungal[45,46] and bacterial[47] pathogens. The use of these ligands opened ways toward the first-in-class glycoconjugate vaccines and immunodiagnostic assays.

Synthetic oligosaccharide probes have aided the discovery of the novel molecular mechanism of the antimicrobial action of lysozyme (one of the main agents of the immune defense system) that consists in its ability to recognize bacterial polysaccharides. The interdisciplinary study with the use of SPR, NMR, X-ray and molecular modeling methods revealed the topology of the carbohydrate–protein interaction where the oligosaccharide chain was hosted in the peptidoglycan binding cavity of lysozyme (Figure 8).[48] This discovery opens a potentially new area for the therapeutic application of lysozyme.

Currently applied in medical practice carbohydrate pneumococcal vaccines of the first and second generations comprise capsular polysaccharides (CPs) of clinically important serotypes of *Streptococcus pneumoniae* or those conjugated to a protein carrier. Biotechnological cultivation of CP producents is very laborious, while their chemical synthesis represents a much more complex task.[49] Unlike the vaccines of the first and second generations, glycoconjugated pneumococcal vaccines of the third generation are based on comprising protective epitopes, synthetic oligosaccharides of strictly defined structure, with a functional group facilitating precise conjugation to the carrier. Such vaccines are now under development and considered to be devoid of many disadvantages characteristic of CP-based vaccines.[50]

The main problem arising from the design of third-generation carbohydrate vaccines is the correct choice of oligosaccharide ligands to be included in the vaccine. To find an optimal oligosaccharide ligand related to the CP of *S. pneumoniae* serotype 14 for the design of a candidate pneumococcal vaccine, special synthetic efforts were made. In particular, tetra-, hexa- and octasaccharides representing one, 'one and a half' and two repeating units of the CP and their conjugates **11**–**13** (Figure 9) with the model protein carrier BSA were synthesized.[51,52]

The immunological activities of conjugates **11**–**13** were evaluated in a murine model. All the conjugates were immuno-

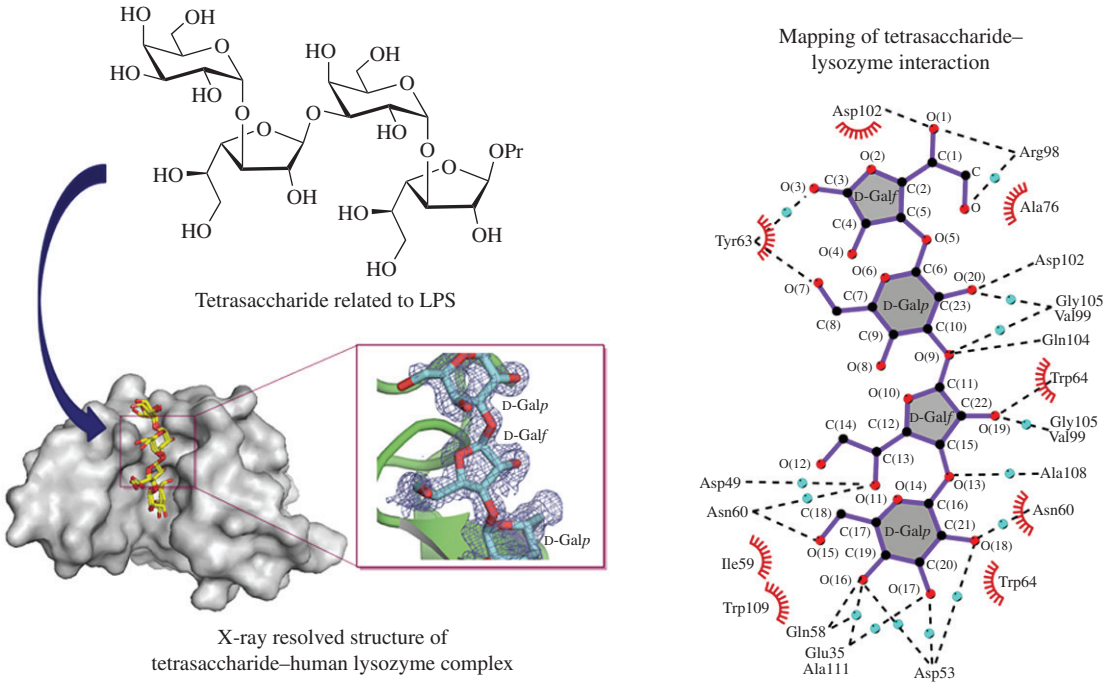


Figure 8 The structure of the synthetic tetrasaccharide related to the bacterial polysaccharide and its complex with human lysozyme, as resolved by X-ray analysis (PDB code: 5LSH).[48]

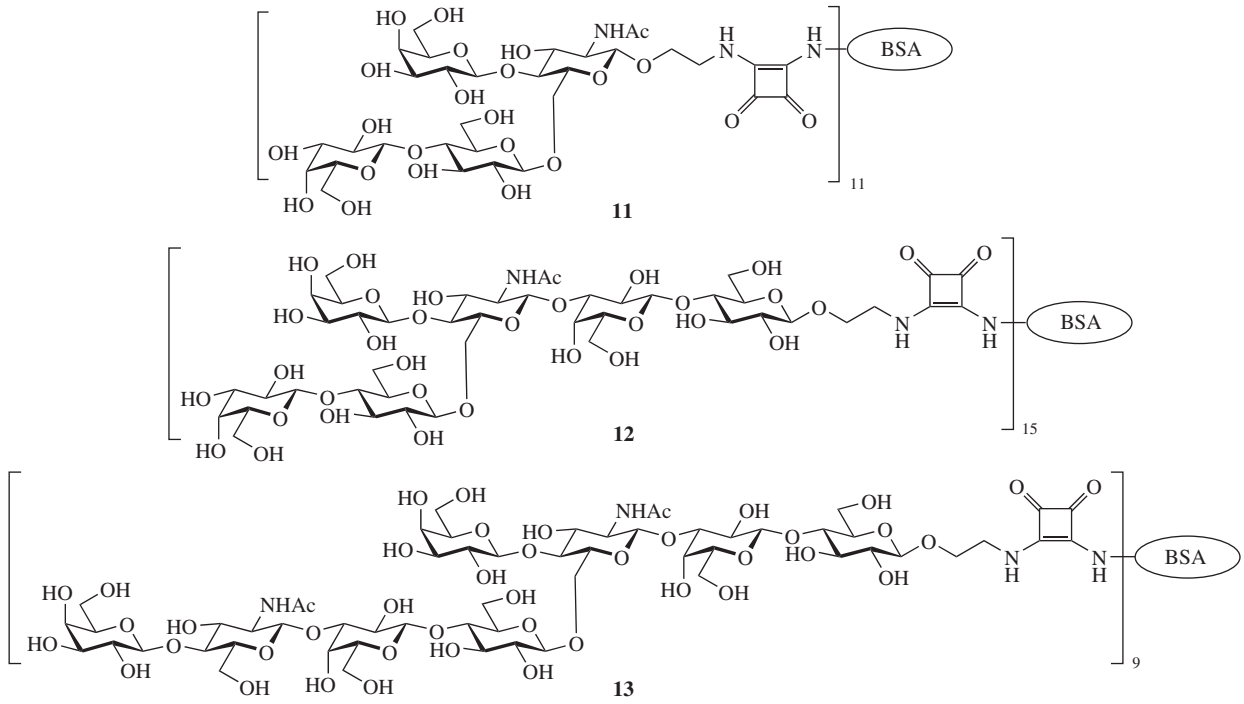


Figure 9 Structures of the oligosaccharide–BSA conjugates used to determine the optimal ligand for the glycoconjugate vaccine against *S. pneumoniae* serotype 14.[52]

genic in mice and induced the formation of IgG antibodies specific to the CP and homologous oligosaccharides but to a different extent.[52] The highest titer of antibodies specific to the homologous oligosaccharide was evoked by tetrasaccharide conjugate **11**, while the highest level of antibodies to the CP was induced by octasaccharide conjugate **13**. Hexasaccharide conjugate **12** possessed the lowest activity in both cases. The immune mouse sera to all conjugates **11**–**13** demonstrated practically equal ability to promote phagocytosis of inactivated bacterial cells of *S. pneumoniae* serotype 14. Additionally, the immune sera to glycoconjugates **11**–**13** were found to be equally active in the passive protection of mice challenged with a lethal dose of *S. pneumoniae* type 14. The activation of the innate and adaptive immunity under the action of conjugates was also investigated.[53] Decisive data for the choice of the proper oligosaccharide ligand were obtained in experiments on the active protection of mice immunized with conjugates **11**–**13** against *S. pneumoniae* type 14. It was shown that tetrasaccharide conjugate **11** possessed the highest protective activity, being as effective as the commercial pneumococcal vaccine Prevenar-13. Octasaccharide conjugate **6** was slightly less active, while hexasaccharide conjugate **12** was almost inactive in this test. Thus, the tetrasaccharide representing one repeating unit of the CP of *S. pneumoniae* serotype 14 seemed to be the best candidate for the development of the third-generation carbohydrate pneumococcal vaccine.

2.2. Catalysis

Transition-metal catalysis is a leading driving force to develop new methodologies for organic synthesis in the areas of carbon–carbon and carbon–heteroatom bond formation as well as selective functionalization. Possible applications of catalysis are very broad, starting from small molecules, such as hydrogen, water or methane, to biomolecules, such as peptides, carbohydrates and nucleic acids. In recent years, several mechanistic studies have revealed a rather complex picture of homogeneous and heterogeneous catalytic processes. Understanding of the dynamic nature of metal centers in catalytic reactions in solution developed a new perception of the concept ‘cocktail of catalysts’ (Figure 10).[54]

Re-thinking the catalyst interaction with a support led to the cutting-edge technique of spatial imaging the reactivity of carbon materials aimed to design efficient metal catalysts.[55,56] Palladium on carbon (Pd/C) catalysts are ubiquitously used in modern organic synthesis to carry out cutting-edge research and to run industrial reactions. The design of cost-efficient and eco-safe synthetic procedures is an upmost challenge in this area due to the complicated dynamic nature of the catalytic systems,[54]

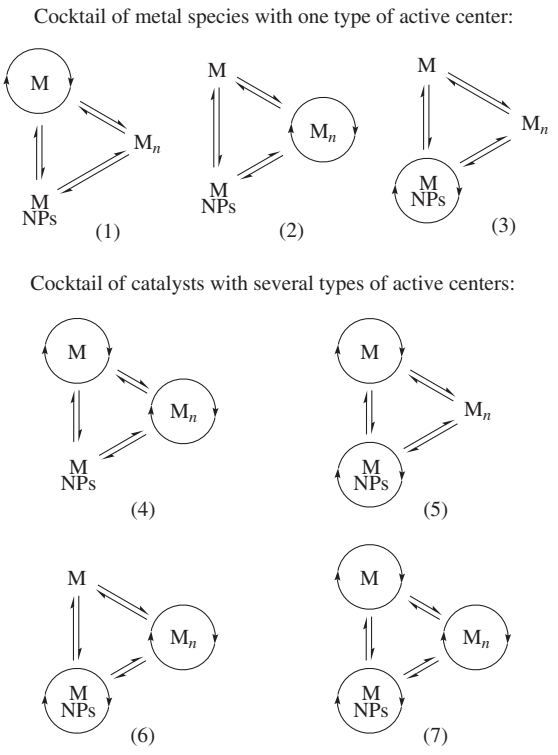


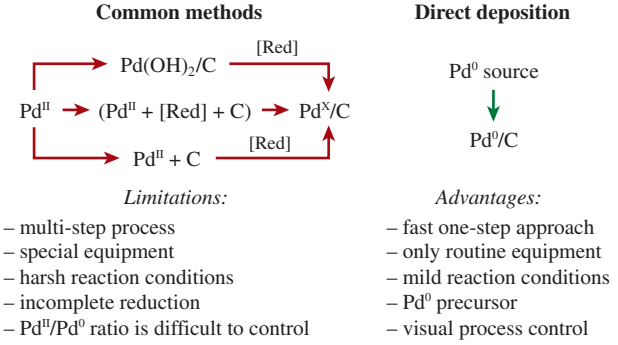
Figure 10 Cocktail of species and cocktail of catalysts in synthetic transformations [circle with arrows denotes the catalytic cycle for product formation: catalytic reactions with one type (1–3), two types (4–6) and three types (7) of active species].[54]

increasing cost of palladium and modulation of the toxicity of transition-metal species in solvent-phase reactions.[57]

The morphology and properties of supported palladium nanoparticles can be established using a variety of analytical methods, while understanding the surface properties and reactivity of a carbon support remains a challenging endeavor. It should be noted that metal nanoparticles possess high contrast in electron microscopy observations and can be easily localized, while mapping active centers on a carbon surface is not possible using direct observations.[58] The fascinating ability of metal nanoparticles to attach to specific areas of carbon materials and to maintain high visibility in regular electron microscopy studies was utilized for carrying out spatial imaging of the reactivity of the carbon surface.[57]

Based on this spatial imaging technique, experimental methodology was targeted to the step-by-step monitoring of the formation of Pd/C catalysts. Using the proposed catalyst design, a rapid preparation procedure was developed to access Pd/C catalysts.[59] Practically useful Pd/C catalysts were prepared by the direct deposition of Pd^0 centers onto the carbon surface using a commercially available Pd_2dba_3 complex as a metal source (Figure 11). The Pd/C catalyst preparation procedure required as short as 4 min of time.[59] The catalyst showed excellent performances in cross-coupling and hydrogenation reactions. Maintaining the heterogeneous nature made it possible to easily recycle and re-use the catalyst. The rapid catalyst preparation creates amazing opportunities for tuning synthetic applications and opens a new dimension for the development of the catalyst-on-demand concept.

An efficient catalyst with a single type of active center was designed for highly organized PdM intermetallic nanoparticles in selective alkyne hydrogenation. Recently, intermetallic compounds (IMCs) have been of great interest as catalytic systems for both large-scale industrial and fine organic chemical processes. IMCs offer potential opportunities for highly effective and selective catalytic systems due to their well-ordered structures and stabilities against segregation. Particularly, IMCs containing



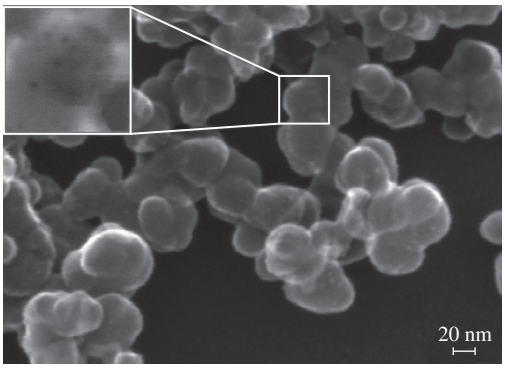


Figure 11 Comparison of the common methods of catalyst preparation with the direct deposition approach, and an electron microscopy image of a prepared Pd/C catalyst.[59]

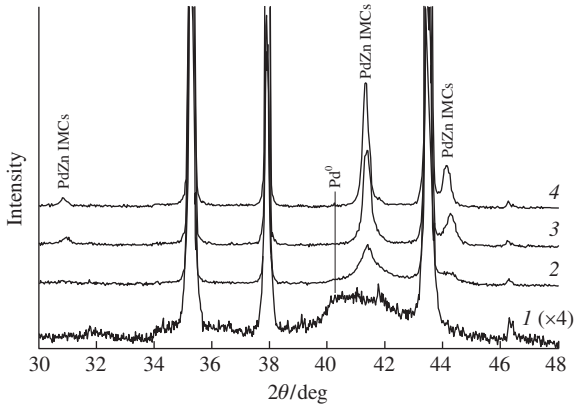


Figure 12 XRD study of PdZn IMCs formation upon reduction of PdZn/Al_2O_3 catalysts with H_2 at (*1*) 200, (*2*) 400, (*3*) 600 and (*4*) 800 °C. Compilation from ref. 63.

catalysts are promising candidates for the liquid-phase hydrogenation (LPH) of alkynes to *cis*/*trans*-olefins, which are the parent compounds for numerous synthetic applications.

Two effective preparation techniques were developed to obtain supported PdM IMCs (M = In, Zn, Ga): (1) traditional co-impregnation with the solutions of individual salts and (2) impregnation with unique PdM acetate complexes with a stoichiometric Pd : M ratio.[60–64] Excellent selectivity for olefin formation was shown for PdM catalysts in the hydrogenation of different types of alkynes (symmetrical/non-symmetrical; internal/external). Their selectivity stems from the highly ordered uniform structure of the catalyst active sites. The detailed characterization of the catalyst structure by XRD (Figure 12) and FTIR-CO revealed the formation of single Pd sites surrounded by inactive metal atoms on the surface of the IMCs nanoparticles.[60,62,63] Additionally, due to the ordered structure of the PdM active sites, the rate of the undesired alkene-to-alkane complete hydrogenation was greatly decreased, providing efficient kinetic control to the reaction (Figure 13). The synthesized intermetallic compositions offer a promising alternative to the commercial liquid-phase hydrogenation catalysts (for example, the Lindlar catalyst). Moreover, the PdIn system can serve as an efficient catalyst for the removal of alkyne impurities from industrial olefin feedstocks used for polymerization.[61,62]

Small molecule activation on heterogeneous catalysts can be even more enhanced by a strong energy impact, such as in CO_2 conversion to valuable products, under microwave or supercritical conditions. Catalytic carbon dioxide transformations are of prime importance in view of the potential industrial applications for organic syntheses.[65] One of the solutions to the problem of CO_2 sequestration is CO_2 hydrogenation, yielding methane, CO or

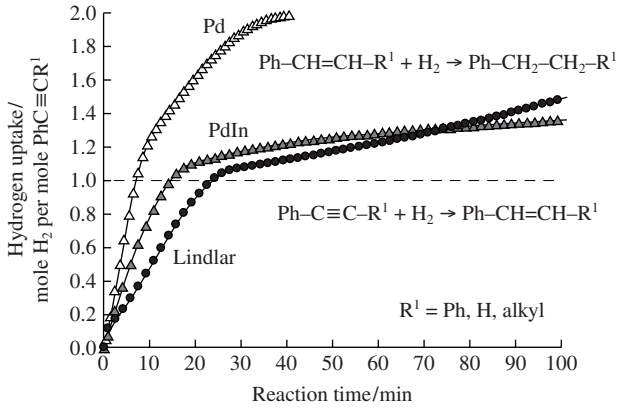


Figure 13 Hydrogen uptake *vs.* reaction time for alkyne LPH over Pd-containing catalysts. Compilation from ref. 61.

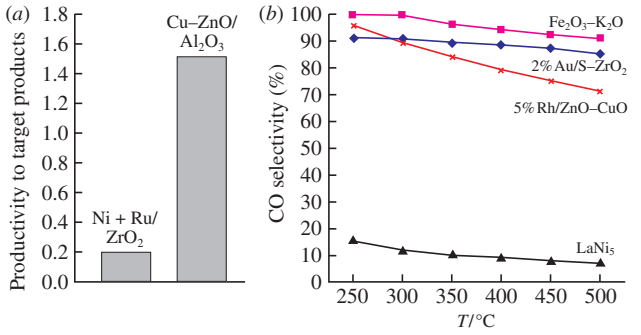


Figure 14 (*a*) Comparison of the CO_2 hydrogenation productivity to CO (20 atm, Ni + Ru/ZrO_2)[66] and MeOH (80 atm, $CuO–ZnO/Al_2O_3$)[67] and (*b*) the CO selectivity pattern for the most active catalysts.[68]

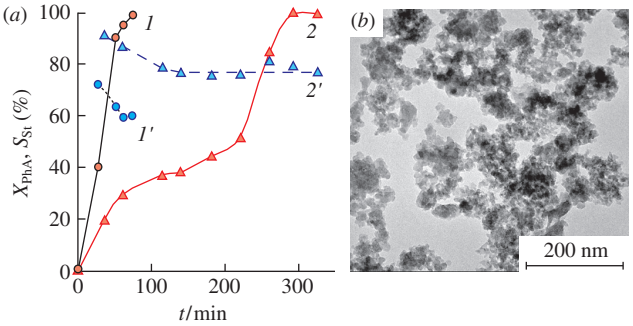


Figure 15 (*a*) Time dependence of phenylacetylene (PhA) conversion and styrene selectivity (dotted lines) over the FeO_x/HS sample calcined at 350 °C [initial PhA concentration, 0.15 M; PhA : Fe = 10 : 1; T = 105 °C; P_{H_2} = 20 bar (*1*, *1'*) or 13 bar (*2*, *2'*)], and (*b*) TEM image of FeO_x/HS calcined at 350 °C.[71–74]

methanol. Of particular interest is the conversion of CO_2 into more reactive products, CO or MeOH, which can be further converted into diverse hydrocarbons or hydroformylation, carbonylation, alkoxycarbonylation products. The development of efficient and selective catalysts is extremely important.

A comparison of different types of catalysts for the hydrogenation of carbon dioxide under supercritical conditions (80 atm, 300–500 °C) allowed one to identify catalysts with very high selectivities toward the target products (Figure 14). Catalysts possessing high activity and selectivity, such as $ZnO–CuO/Al_2O_3$, $Au/SO_4–ZrO_2$, $Fe_2O_3–K_2O$, and Ir/C, demonstrated outstanding productivity (g/g^{-1} h^{-1}) due to the specific features of supercritical CO_2 (Figure 14). The ZnO–CuO, fused $Fe_2O_3–K_2O–Al_2O_3$, and $Au/SO_4–ZrO_2$ catalysts exhibited selective formation of CO, with $Fe_2O_3–K_2O–Al_2O_3$ being the most active and selective in this reaction.

The realization of the process under microwave activation provided further benefits, as the metal nanoparticles can be heated to the reaction temperatures, while the inert carriers experience only secondary heating. This method of selective heating allows one to substantially decrease (by a factor of 5–10) the energy expenses required for activation.[69]

One of the very influential features of catalysis is the observation of new reactivity. Silica-supported iron oxide nanoparticles showed unexpected catalytic activity in the hydrogenation of phenylacetylene. The growing price and limited availability of precious metals used in catalytic hydrogenation have generated a particular need for catalysts based on iron.[70] The abundance, low cost and low toxicity of iron oxides make their use in catalysis highly sustainable and preferable compared to the commonly used Pd, Pt, Ru, Rh, and Ni catalysts for hydrogenation. For many years, iron-based catalysts have been applied for large-scale production (the Haber–Bosch process, water–gas shift reaction and Fischer–Tropsch reaction), whereas only a handful of iron-containing catalysts have been developed for use in selective hydrogenation reactions under relatively mild conditions.

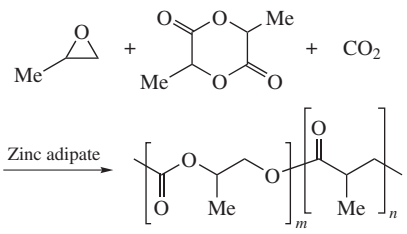
The unexpectedly high catalytic activity of silica-supported iron oxide nanoparticles was revealed for the first time in the hydrogenation of the triple C≡C bond in phenylacetylene with molecular hydrogen in the liquid phase. The FeO_x/SiO_2 catalyst was prepared *via* thermal decomposition of ammonium trioxalatoferrate. The complete hydrogenation of phenylacetylene proceeded at 100–150 °C and H_2 pressure of 6–20 bar (Figure 15). Both styrene and ethylbenzene were formed simultaneously. The selectivity to styrene depended on the H_2 pressure and the temperature of the catalyst synthesis and reached 80%.[71–74]

2.3. Materials and high-energy compounds

Materials science and the investigation of high-energy compounds have attracted much attention from researchers of different areas of chemistry and physics along with high impact industrial and practical projects. For these purposes, the development of new protocols toward polyfunctional materials is one of the primary tasks of chemical science. An important step in the sustainable direction involves the synthesis of carbon dioxide copolymers aimed to design biocompatible materials.

The catalytic conversion of the greenhouse gas carbon dioxide, an abundant, nontoxic and constantly renewable feedstock, to a variety of useful chemical products is still a challenging matter both for chemical science and industry.[75] Its utilization as a comonomer in the copolymerization with epoxides, along with other monomers of different chemical origin capable of entering the copolymer backbone within the ring-opening polymerization (ROP) mechanism, yields poly(alkylene carbonates) and their more complex derivatives. Poly(propylene carbonate) (PPC) continuously remains a promising representative of these polymer products due to simplicity of its synthesis from relatively inexpensive CO_2 and propylene oxide (PO).[76] PPC is industrially employed on a small scale as an excellent binding material, polyol compound in polyurethane manufacturing, and packaging material.[77] Its biocompatibility enables further applications as medical implants.[77]

Considering biodegradability and sustainability in relation with the end use, particularly as packaging materials and medicinal implants, PPC manifests certain restrictions. The tendency of polymers to biodegradation proves to be a more important property compared to physical-mechanical ones depending on the scope of the application. Sustainable polymers should possess 0–100% biodegradability (arbitrary scale) on demand. Ester groups incorporated into the polymer backbone are known to contribute to enhancing those properties. The most well-known example of this type of polymer is poly(lactic acid) and copolymers of lactic acid. Hypothetically, the incorporation of different amounts of ester groups into the PPC backbone might afford polymers of desired biodegradability. In this regard, the terpolymerization of CO_2, PO and L-lactide was studied.[78] The catalytic conversion of CO_2 to sustainable products was carried out by its anionic coordination terpolymerization with PO and L-lactide in the presence of zinc adipate as a catalyst, according to Scheme 3.



Scheme 3 Catalytic conversion of CO_2 to a sustainable polymeric product.[78]

A number of bulk partially crystalline terpolymers [–(PO-alt-CO_2)$_m$–(L-lactide)$_n$–] of high molecular weight with L-lactide contents from 4 to 37 mol%, depending on initial comonomers molar ratio, were synthesized, and the optimal terpolymerization conditions were determined.

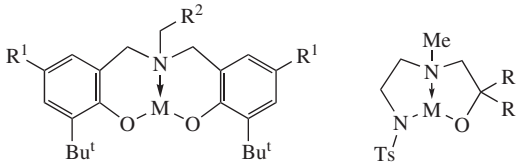
Initiation of chain growth is the key stage for accessing desired polymeric materials. The synthesis and structural characterization of novel tetrylenes were performed to optimize initiators for the polymerization of cyclic esters. The chemistry of carbene analogues of heavier group 14 elements, also called tetrylenes, has attracted great interest due to their unique properties and reactivities. Tetrylenes have been used as precursors for metal-organic chemical vapor deposition (MOCVD), as initiator catalysts in the ring-opening polymerization of cyclic esters and as an important class of ligands in coordination and organometallic chemistry.[79]

In recent years, biodegradable polymers, such as polylactide, polyglycolide, poly-ε-caprolactone and their copolymers, have attracted great attention due to ecological reasons. Moreover, polylactide has found wide application in medicine as a material for medical implants that can degrade into innocuous lactic acid in a living organism. The main synthetic method leading to such polymers is the ROP of cyclic esters, initiated by metal or metalloid compounds (complexes). Derivatives of group 14 elements, especially tin compounds, are often used in industry as initiators. The properties of the polymer strongly depend on the structure of the used initiator, whereas the structure of the ligand influences the catalytic activity of the complex. Thus, it is important to prepare novel complexes of group 14 elements that can be used as ROP initiators.[80]

Using a metathesis reaction between Lappert's tetrylene and the corresponding ligands, well-known aminobisphenoles and novel diaminoalcohols, two series of novel tetrylenes were prepared in good yields (Figure 16),[81,82] whose structures were established by X-ray diffraction and NMR spectroscopy. The structural type (monomeric, dimeric or polymeric) of these compounds strongly depended on the ligand volume and nature of the group 14 element. The preliminary investigation of the reactivity of tetrylenes based on the aminobisphenol ligands was performed. These monomeric germylenes and stannylenes easily inserted into the active C–halide bond (allyl bromide) due to oxidative addition.[83]

Sulfur management by reactive adsorption over transition-metal polycationic forms of zeolites is a useful example of a practical application of structurally organized materials. Aliphatic thiols, sulfides and disulfides are present in natural gas, crude oil and petrochemical products. Stringent desulfurization of liquid and gas streams is required by the current strict environmental regulations and the necessity to protect the environment. In this concern, adsorption and adsorbents, particularly zeolites, have earned an appreciable amount of acknowledgement.[84–87]

The reactive adsorption of sulfur compounds over transition-metal polycation-exchanged zeolites has shown to be a very efficient way for the desulfurization of hydrocarbon liquid and gaseous streams. The process consists of the physical adsorption of



M = Ge, Sn, Pb
R^1 = Me, But
R^2 = Me, 2-pyridyl

M = Ge, Sn, Pb
R = H, Ph

Figure 16 Novel tetrylenes prepared.[81,82]

Table 1 Natural gas flow desulfurization: ethanethiol, 25 ppmv; 2-methyl-2-propanethiol, 12 ppmv; diethylsulfide, 12 ppmv; LHSV, 6400 h^{-1}.[88]

Catalyst-adsorbent	Breakthrough concentration/ppb		Adsorption capacity (wt%)	
	25 °C	75 °C	25 °C	75 °C
$(Zn)_p$LSF	30	160	0.22	0.01
$(Mn)_p$LSF-71	30	28	0.27	0.20
$(Cu)_p$CaLSF	18	10	0.33	0.34
13X	880	2000	0.12	<0.01

thiols, sulfides, and disulfides and the catalytic oxidation of the adsorbed substances. The reaction does not require free oxygen participation, and DRIFTS and XAS studies confirmed that thiol oxidation proceeds through the direct involvement of transition-metal polycation superoxides. The studied adsorbents, including Zn, Mn, Cu, Cd polycation-containing zeolites X, Y, and mordenite, exhibited remarkable activities for the oxidation of sulfur compounds, resulting in a considerable increase of their total pick-up from gas and liquid hydrocarbons (Table 1).[88] The thermal regeneration of the catalyst-adsorbents under oxidizing conditions resulted in the complete restoration of their original activities and capacities for sulfur compound removal.

The design and preparation of high-energy compounds is a challenging area of modern chemistry and materials science, where optimization is performed at the molecular scale. Stable chemical products, which incorporate high-energy features, are in demand in various fields of technology. Making these molecules more sustainable from a synthetic point of view is an important task. Highly nitrated ensembles of azoles as green energetic compounds are just one of these studied examples. The chemistry of the nitro group continues to be a very active research area. Aliphatic, aromatic and heterocyclic compounds containing C–NO_2 bonds are synthetically versatile and represent valuable precursors to complex organic products. On the other hand, multi-nitro compounds are some of the most useful energetic materials for a wide variety of military, space, industrial and civilian applications as controllable storage systems for high amounts of chemical energy.

The design and synthesis of new energetic compounds with superior performances (high detonation velocity and pressure, high thermal stability and low sensitivity toward impact and friction) have drawn the interest of the scientific community over the last few decades.[89] As concern about the environmental impacts of chemicals and wastes has increased, the development of green high energetic materials has become an important area of research. As part of this challenge, a combination of good performance and an efficient balance for intramolecular redox reactions to produce carbon dioxide, water, and large volumes of environmentally friendly N_2 is necessary.

High-enthalpy nitrogen heterocycles, such as pyrazoles, triazoles, tetrazoles, furazans and tetrazines, are being applied as prime backbones to a wide range of energetic compounds that are at the forefront of high-energy research. Not surprisingly, there is still a need to develop effective methodologies for the synthesis of structurally new heterocyclic architectures to reveal novel, valuable energetic and physical properties.

Because of the combination of high nitrogen content and inherent thermal stability of the flexible linear and rigid fused ensembles of azoles, pyrazole-triazole, pyrazole-tetrazole, pyrazole-furazan and triazole-furazan were identified as attractive backbones for the sequential derivatization for developing new green energetic materials. Variation of the arrangement and type of functional groups can provide a considerable means to tune the properties of these ensembles.

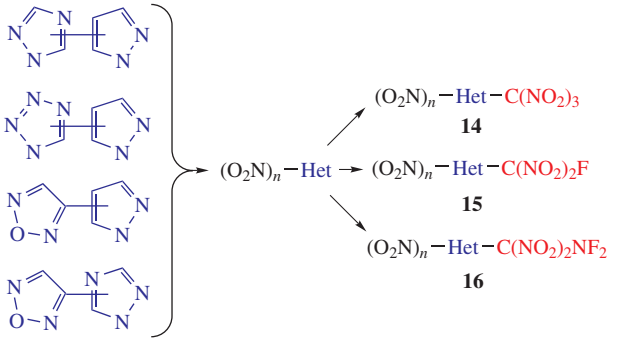


Figure 17 Nitroazoles as key building blocks for the design of novel hybrid molecular architectures.

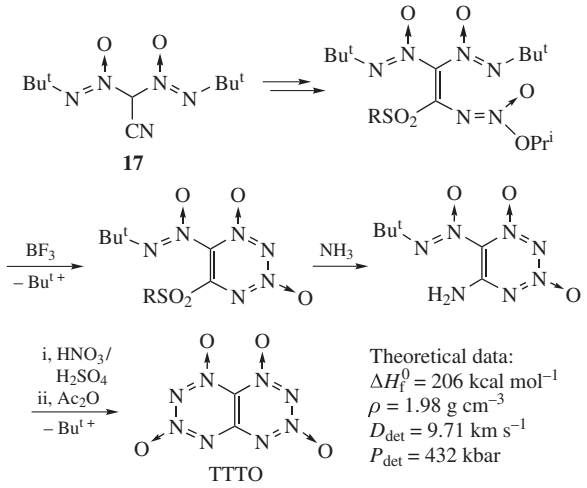
The use of nitroazoles as key materials for the preparation of novel hybrid molecular architectures with a focus on synthesizing unusual derivatives bearing *C*- or *N*-trinitromethyl, fluorodinitromethyl and difluoroaminodinitromethyl units was evaluated. An overview of this approach is shown in Figure 17.

Construction of the starting backbones is usually carried out in two or three steps or *via* a one-pot process. The second step of the transformation, nitration of the backbone for installation of one, two and three nitro groups, is achieved by a number of reagents, including HNO_3/H_2SO_4, HNO_3/Ac_2O and $HNO_3/(CF_3CO)_2O$ mixtures. The resulting nitroazoles are then N-alkylated with bromoacetone to give *N*-acetonyl products. Destructive nitration of the active methylene groups in the latter with HNO_3 or HNO_3/H_2SO_4 provides access to the target trinitromethyl compounds **14** or can be stopped at the corresponding dinitromethyl intermediates.[90,91] Finally, the dinitromethyl derivatives are converted to fluorodinitromethyl ones **15** with $FClO_3$, Selectfluor or XeF_2 as sources of fluorine. F_2NOSO_2F was employed to prepare (difluoroamino)dinitromethyl compounds **16**.[92] All stages of the transformations demonstrated good yields.

As a result, a series of oxygen- and nitrogen-rich ensembles of azoles with nitro and polynitromethyl substituents at various positions on the azole units were synthesized. It has been found that the positional isomerism plays an important role in determining the density, enthalpy of formation and thermal stability of these green energetic compounds.[90,94] The novel hybrid molecular architectures were shown to be very promising energetic materials with eco-friendly decomposition products.[90,91,93,95]

The most complex example of these materials from a synthetic point of view includes energy-rich organic nitrogen–oxygen systems. Organic compounds bearing nitrogen–oxygen bonds possess a unique combination of useful properties. The high enthalpy of formation and the presence of so-called 'active' oxygen provide them with a huge amount of accumulated chemical energy, which can be rapidly released during burning or explosion.[96] On the other hand, *N*-oxides, in particular nitro compounds, may gradually release nitric oxide, a crucial regulator for cellular metabolism useful for treating cardiovascular, nervous and other diseases,[97] under mild physiological conditions. Moreover, functionalized aliphatic nitro compounds are valuable precursors to pharmaceutically important γ-amino butyric acid (GABA) analogues and natural enzyme inhibitors used for the treatment of widespread acute and chronic diseases.[98]

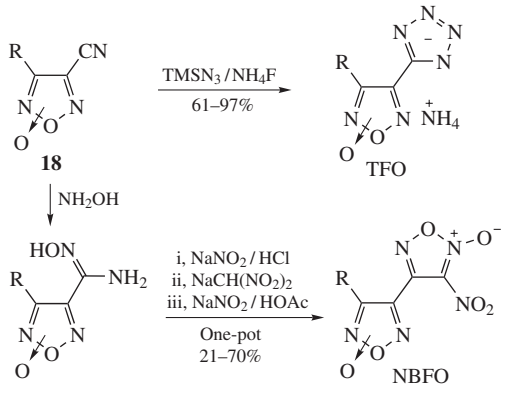
High-energy polynitrogen heterocycles bearing alternating *N*-oxide moieties are extremely promising compounds. Here, a breakthrough result was achieved by the total synthesis of the novel high-energy compound [1,2,3,4]tetrazino[5,6-*e*][1,2,3,4]-tetrazine 1,3,6,8-tetraoxide (TTTO). The backbone of this elegant C_2-symmetric molecule contains two carbon and eight nitrogen atoms. The alternating four oxygen atoms greatly stabilize the nitrogen-rich heterocyclic system, which was predicted previously based on PMO theory.[99] Furthermore, theoretical data ranked TTTO among the most powerful explosives known. In spite of numerous efforts, the synthesis of TTTO had remained a challenge for a long time. Very recently, TTTO was prepared in ten steps from 2,2-bis(*tert*-butyl-NNO-azoxy)acetonitrile **17**.[100] The synthetic strategy was based on the sequential closure of two 1,2,3,4-tetrazine-1,3-dioxide rings through the generation of oxodiazonium ions (Scheme 4). However, the total yield of TTTO was only 1%. Its synthesis clearly demonstrated the attainability and potential practical applicability of fused high-energy materials comprising the [1,2,3,4]tetrazine 1,3-dioxide unit.



Scheme 4 Developed synthesis of TTTO.[100]

Another promising class of energetic nitrogen–oxygen systems is furoxan derivatives. A series of novel hybrid structures containing energy-rich polynitrogen heterocycles (furoxan or tetrazole) attached to a furoxan ring were recently synthesized from commercially available cyanofuroxanes **18**. The [3+2]-cycloaddition of compounds **18** to ammonium azides, generated *in situ* from $TMSN_3$ and NH_4F, afforded (1*H*-tetrazol-5-yl)furoxan ammonium salts (TFOs) in up to 97% yield.[101] The cyanofuroxan-derived furoxanylamidoximes were converted to the thus far unknown 3-nitro-bisfuroxans (NBFOs) by a series of nitrozative chlorination, acylation and ring-closing reactions (Scheme 5).[102] Importantly, these reactions could be performed as a one-pot process without isolation of the reactive intermediates, providing the straightforward high-yield synthesis of energetic molecules.

Some of the prepared TFOs and NBFOs possess high enthalpies of formation and promising densities and may be considered as perspective candidates for practical application in energetic formulations (Figure 18).



R = 4-N_3, 4-NO_2, 4-MesN=N, 4-PMPN=N, 3-CN, *etc.*

Scheme 5 Developed synthesis of TFO and NBFO.[101,102]

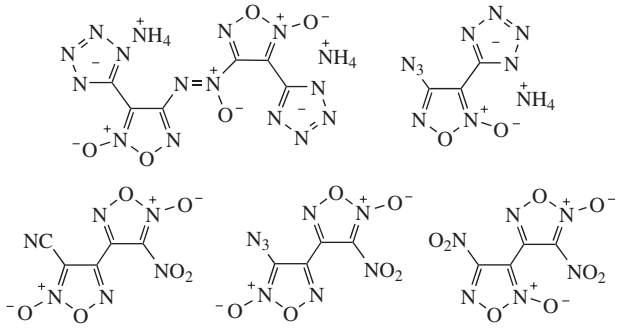
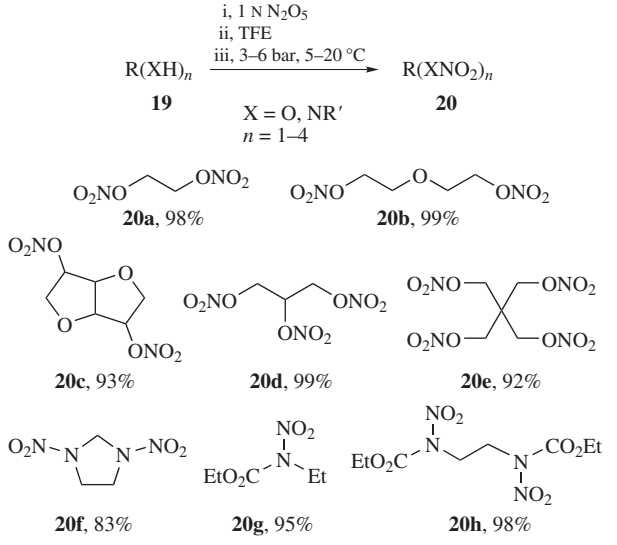


Figure 18 Molecular structures of energetic TFOs and NBFOs.[101,102]

Large-scale manufacturing of key energetic components of explosive formulations, powders, and solid propellants, which contain nitro groups, is typically based on nitration reactions. In industry, these reactions are commonly carried out by accessing mixed acids (*e.g.*, HNO_3/H_2SO_4), which serve as both nitrating agents and media.[103] As a result, huge amounts of environmentally harmful acidic wastes are produced, which require expensive and energy-consuming disposal techniques. A promising approach to address these environmental issues is to use sulfuric-acid-free dinitrogen pentoxide–liquid carbon dioxide nitrating systems.[104,105]

However, special expensive, high-pressure equipment resistant to aggressive acidic media at pressures up to 150 bar are needed to attain the patented reaction conditions. Recently, a much safer and simpler protocol was developed for O- and N-nitration reactions with N_2O_5, in which carbon dioxide was replaced with a lower freon, 1,1,1,2-tetrafluoroethane (TFE).[106] TFE is a commercially available, chemically stable compound, which can be readily liquified (as it is in freezing units) due to its remarkably low equilibrium vapor pressure (5.7 bar at 20 °C *vs*. 57.3 bar for carbon dioxide). Furthermore, it is, like carbon dioxide, practically nontoxic to humans. The developed protocols were characterized by lower explosion and fire risks as compared to common nitration methods and allowed one to synthesize various *O*- and N-polynitro compounds in high yields (Scheme 6). From a practical viewpoint, the method provides an industrially applicable pathway to produce organic nitrate- and nitramine-derived high-energy materials.



Scheme 6 The N_2O_5–TFE nitrating system for O- and N-nitration.[105,106]

3. Conclusions

In summary, research activities carried out within the present initiative highlighted several important points for analysis. Novel synthetic approaches to pharmacology-oriented and energy-rich nitrogen–oxygen systems were recently elaborated. Precursors to useful natural compounds and active ingredients of clinically important pharmaceuticals were enantioselectively prepared from readily available α-nitroalkenes in the presence of original sustainable metal-free organocatalysts. This method is attractive to the pharmaceutical industry, as it opens a practical route to most active enantiomers for medications. Another promising application of α-nitroalkenes is based on their transformation to cyclic nitronates and ultimately to functionalized 1,2-oxazines, which possess useful biological activities. Novel high-energy heterocycles (in particular, thus far challenging [1,2,3,4]tetrazino-[5,6-*e*][1,2,3,4]tetrazine 1,3,6,8-tetraoxide) were synthesized as perspective candidates for practical application in unique propellants and explosive formulations. Environmentally and explosion safe nitration procedures utilizing freon as recyclable reaction media were developed, which provide an industrially applicable pathway to the large-scale manufacturing of organic nitrates and the most powerful energetic materials bearing *N*-nitramine functionality.

The study of 3D-structure[107] and the development of new approaches toward the stereo- and regioselective synthesis of complex bioorganic determinants forms a fruitful basis for the design of indispensable molecular probes for the structural assessment of natural biologically relevant compounds as well as for studying the mechanisms of their activity, including the binding topologies to their cellular receptors. The preparation of such biomolecules opens fruitful directions for the design of novel active pharmaceutical ingredients ('API'), vaccines and immunodiagnostics of the next technological generation and even of unmet need. Such investigations are of principle importance for the development of new antibacterial and antifungal agents due to the increase of antibiotic resistance of corresponding pathogens.

The design of industrially important catalysts at the molecular level or using a single-site approach opens new cost-efficient alternatives for diverse applications, including novel processes that will be applied in industry soon. Of importance is the reduction of the content of noble metals in catalysts using cheap, abundant and nontoxic engineered nanoparticles, such as iron and other earth-abundant transition metals. The scope of the processes may include not only hydroprocessing of various organic feedstocks and CO_2 utilization but also most fine organic synthesis processes. In this concern, the use of supercritical fluids and, wherever possible, microwave irradiation may provide additional benefits to those gained using inexpensive catalysts, such as an enhancement of the space-time yield, reduction of energy expenses and, in general, prolonged lifetime of the catalyst. In the coming decade, the application of such hybrid or composite materials both upstream (purification and pretreatment of raw materials) and downstream (catalytic processes and fine purification and separation of organic products) in the commercial value chain will transform into main stream tendencies to foster wealth for future generations.

Stressed by the present initiative and by the requirements of interdisciplinary studies, an efficient approach was built to combine powerful analytical methods involving NMR spectroscopy, mass spectrometry and SEM/TEM analysis within a single research platform.[58,108] Utilization of this analytical platform advanced numerous research projects in this joint initiative, as well as in such demanded areas as biomass conversion,[109] 3D printing[110] and green synthesis.[111]

Organic synthesis provides the key building blocks and target molecules for medicinal and pharmaceutical applications. These applications are still dominated by organic compounds as drugs and active pharmaceutical ingredients (Figure 19). Hybrid molecular systems are being investigated as possible platforms for drug delivery, where nanomedicine represents a leading example.

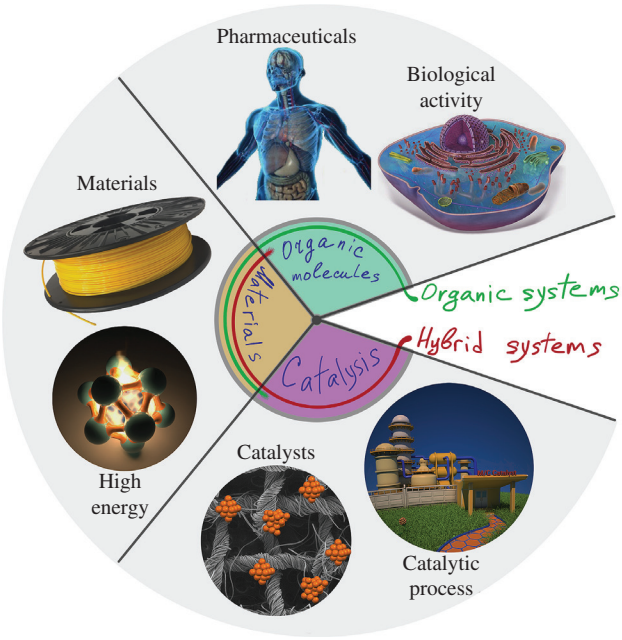


Figure 19 Summary of the applications and interconnections between organic and hybrid systems.

Real advances of such practical applications are anticipated in the future.

In contrast, the development of heterogeneous catalytic systems is exclusively based on hybrid chemical systems involving metal centers, metal nanoparticles and specific structured supports (Figure 19). The optimization of both components of a catalyst (active center and support) is a well-known traditional way to optimize a process. However, recent mechanistic findings have shown the dynamic nature of these catalytic systems, which has caused questioning of the efficiency of such catalyst optimizations. The development of heterogeneous catalysts to achieve high selectivity and to find applications in organic synthesis demands for the development of new approaches.

Both hybrid and organic systems have found excellent applications in materials science (Figure 19). Pure organic molecules, as exemplified by high-energy compounds, are still of focus and will retain highly important for practical applications. Organic polymers with a sustainable source of cost-efficient monomers require hybrid systems to initiate and carry out the polymerization. Equally important are complex metal-organic frameworks, which are among most promising hybrid materials.

The general framework for the development of molecular and hybrid organic systems, design of carbohydrate vaccines, preparation of pharmacology-oriented and energy-rich organic nitrogen–oxygen systems, development of the mechanistic understanding of dynamic catalytic reactions, study of silica-supported nanoparticles in hydrogenation, removal of sulfur compounds with zeolites, synthesis of carbon dioxide copolymers and design of biocompatible and sustainable materials was supported by the Russian Science Foundation (grant no. 14-50-00126).

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