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A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Pnictogen-Bonding Enzymes

Giacomo Renno, Dongping Chen, Qing-Xia Zhang, Rosa M. Gomila, Antonio Frontera, Naomi Sakai, Thomas R. Ward*, and Stefan Matile*

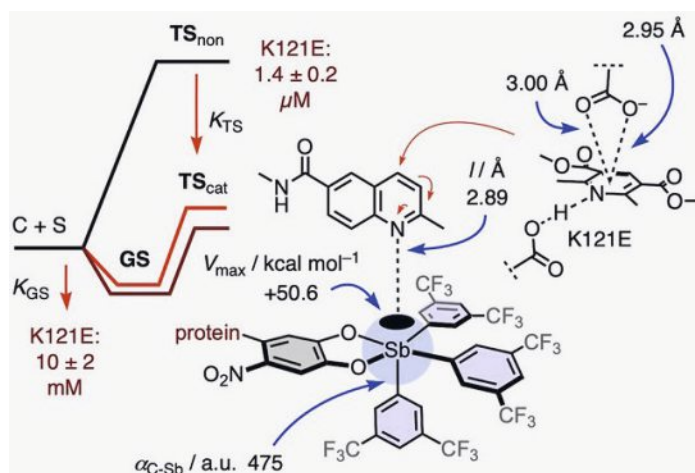
Angew. Chem. Int. Ed. **2024**, e202411347,
<https://doi.org/10.1002/anie.202411347>

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This article focuses on developing artificial enzymes that utilize pnictogen bonds, a type of non-covalent σ -hole interaction, which is rarely observed in biocatalysis. The researchers designed stibine-based pnictogen-bonding catalysts, interfaced with streptavidin mutants, to catalyze transfer hydrogenation reactions. The study highlights a significant increase in catalytic activity and stereoselectivity, with deep σ -holes on the Sb(V) center enhancing transition-state recognition by more than three orders of magnitude compared to substrate recognition. The artificial enzymes showed Michaelis-Menten kinetics, confirming their enzyme-like behavior and the potential for stereoselectivity. These findings open new possibilities for using pnictogen bonds in aqueous catalysis and demonstrate the compatibility of pnictogen-bonding interactions with complex catalytic systems, expanding the toolbox of artificial enzymes for challenging reactions.

Authors' comments:

“Collaborating with the Matile group is always a highly stimulating and productive encounter: yet another curiosity-driven project resulting from the NCCR molecular systems engineering.”



Template-dependent DNA Ligation for the Synthesis of Modified Oligonucleotides

Nazarii Sabat, Andreas Stämpfli, Steven Hanlon, Serena Bisagni, Filippo Sladojevich, Kurt Püntener, and Marcel Hollenstein*

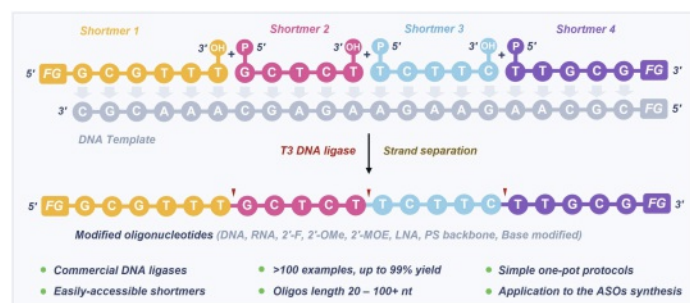
Nat. Commun. **2024**, 15, 8009,
<https://doi.org/10.1038/s41467-024-52141-8>

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This article introduces a new method for synthesizing chemically modified oligonucleotides using template-dependent DNA ligation with shortmer fragments, offering an alternative to traditional phosphoramidite chemistry and nucleoside triphosphate polymerization. The method uses T3 DNA ligase to link chemically modified shortmer monophosphates, showing high tolerance to modifications and allowing the synthesis of oligonucleotides ranging from 20 to 120 nucleotides in length. The approach is scalable, efficient, and flexible, making it suitable for creating diverse oligonucleotides for therapeutic and nanotechnology applications. Notably, this method has been applied to synthesizing clinically relevant antisense drugs and ultramers, demonstrating its potential for advancing biotechnology and therapeutic development.

Authors' comments:

“Chemically modified oligonucleotides display a large potential for therapeutic applications. We hope that our ligase-based method will meet the increasing demand for synthetic oligonucleotides and help in identifying novel drugs.”



Prepared by Cesare Berton, James Southwell, Simon Klingler, Jonas Genz, Stanislav Prytuliak, Fan Liu, Eda Nisli, Deborah Bäcker, Perle Hermant, Samy Kichou, Ben Boback, Dominik Ernst, Tiago Rosa de Araujo, Liam Wenger, Henrik Braband, and Jason P. Holland*

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CO₂ Electroreduction to Long-Chain Hydrocarbons on Cobalt Catalysts

Phil Preikschas, Jie Zhang, Ranga R. Seemakurthi, Zan Lian, Antonio J. Martín, Shibo Xi, Frank Krumeich, Haibin Ma, Y. Zhou, Núria López, Boon S. Yeo, and Javier Pérez-Ramírez

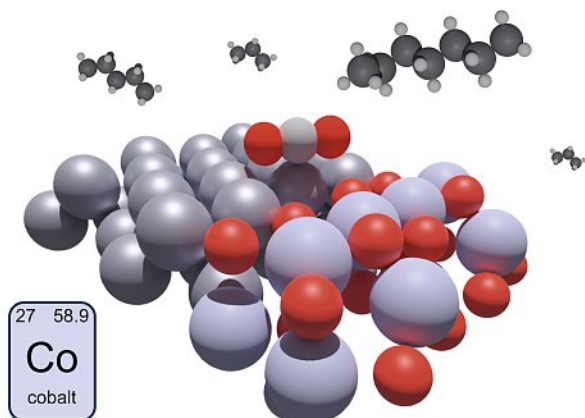
Adv. Energy Mater. **2024**, 2401447,
<https://doi.org/10.1002/aenm.202401447>.

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The study explores electrocatalytic CO₂ conversion to long-chain hydrocarbons using cobalt-based catalysts, specifically focusing on a Co₃O₄-derived material. The cobalt catalyst promotes the formation of C₁–C₇ hydrocarbons with a high chain growth probability of 0.54, outperforming any electrocatalyst and close to Fischer-Tropsch synthesis. Active sites, formed during CO₂ electrolysis at Co-Co₃O₄ interfaces, drive the enhanced chain growth. The study highlights the catalyst's ability to regenerate activity through intermittent reoxidation, preventing deactivation. The findings demonstrate significant advancements in direct electrocatalytic production of long-chain products from CO₂ and underscore the role of metal-metal oxide interfaces in sustainable energy solutions.

Authors' comments:

"This work highlights the potential of a family of materials traditionally considered inactive. This stemmed from a thorough analysis, combining all partners' diverse expertise and the exceptional platform for collaboration provided by NCCR Catalysis."



Pd-Catalyzed [3+6+3+6] Macrocyclizations of Aryl α -Diazo- β -Ketoesters

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Adv. Synth. Catal. **2024**, 366, 3029,
<https://doi.org/10.1002/adsc.202400118>.

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Palladium(II) catalysis facilitates a highly efficient synthetic route for the production of unsaturated macrocycles through a [3+6+3+6] process involving cyclic ethers and aryl α -diazo- β -ketoesters. Notably, the presence of electron-rich aryl ester functionalities precludes the use of dirhodium complexes, as these diazo decomposition catalysts induce unwanted intermolecular C(sp²)-H insertion reactions, thereby compromising the desired reaction pathways. Conversely, by employing Pd(acac)₂ under elevated concentration conditions (1 M), a diverse array of eighteen-membered macrocycles can be synthesized utilizing both aryl and alkyl diazo precursors, as has been demonstrated on 16 distinct examples. The rationale for the choice of catalysts, either for electrophilic aromatic substitution (rhodium) or ylide (palladium) pathways, is elucidated through computational analyses.

Authors' comments:

"This article demonstrates the power of metal-carbene and metal-bound ylide chemistry to influence and control subsequent reactivity. Traditionally, in our hands, clear distinction is made with Rh(II) and Ru(II) complexes. Herein, Pd(II) was nevertheless necessary."

