

# SNAPSHOTS OF SOME TOPICS OF INTEREST OF RECENT NOTABLE ADVANCES IN CHEMISTRY

- Mesoporous Niobium-Catalyzed Dehydration of Xylose to 2-Furfuraldehyde
- Synthesis of Enantiopure  $\beta$ -Boryl Allyl Nitriles
- Synthesis of Acyl Fluorides from Activated Ketones
- Activation of Carbon-Fluorine Bond at Low Temperature Using Heterobimetallic System

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# Snapshots of some topics of interest of recent notable advances in chemistry

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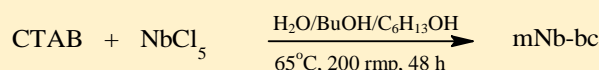
*Managing Director / Founder*

# Mesoporous Niobium-Catalyzed Dehydration of Xylose to 2-Furfuraldehyde

A reported mesoporous niobium-based catalyst prepared by microemulsion method has attracted attention because of the economic viability of its catalytic utility in dehydration of xylose to 2-furfuraldehyde that has achieved a xylose conversion of 41.2% and a selectivity of 77.1% under mild reaction conditions of 140 °C, 120 min., and catalyst-to-xylose ratio of 10%. The characterization of the catalyst showed that it has high specific surface area and acidity.

2-Furfuraldehyde constitutes an important renewable chemical product with a wide range of applications, that is derived directly from lignocellulose biomass. The ongoing research to develop the production of this compound has mainly focused on improving the performance of employed catalysts. The heterogeneous catalysts have shown better performance compared to homogeneous counterparts in the sense of, for example, environmentally friendly processes. Among these heterogeneous catalysts are niobium-based catalysts, which they demonstrated high catalytic activity, selectivity, chemical stability, and high acidity.

In this context, Gabriel *et al.* reported a mesoporous niobium-based catalyst (mNb-bc) that prepared by a simple method, avoiding the drawback of the calcination process of previously methods. This method yielded a catalyst with high surface area and acidity employing low temperatures and cetyltrimethylammonium bromide (CTAB) (Scheme 1).

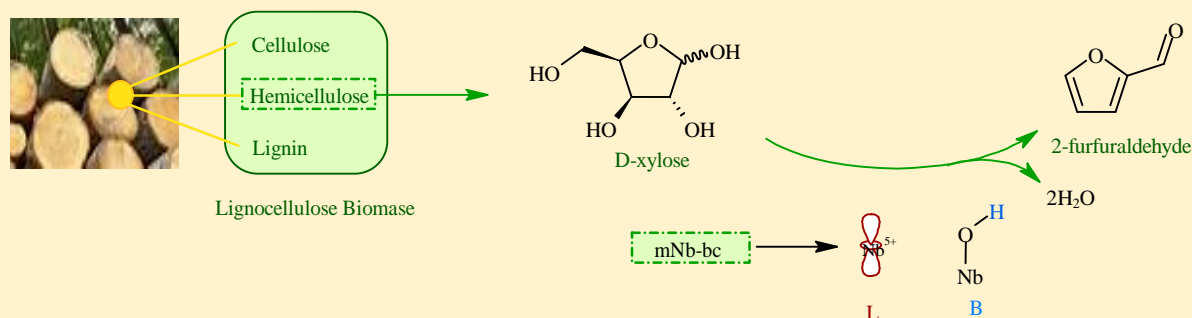


**Scheme 1.** Preparation of mesoporous niobium-based catalyst.

The characterization of mNb-bc showed that it has high specific surface area of 340 m<sup>2</sup> g<sup>-1</sup> and an average pores size of 40 Å, classified as a mesoporous material. Such high specific surface area and large pores size are the desired properties for catalysts to obtain high conversion. Furthermore, it has high acidity (65 μmol g<sup>-1</sup>). This high acidity value can promote a conversion of substrates without extensive formation of byproducts. X-ray diffraction analysis showed that it was an amorphous material. Additionally, scanning electron microscopy and energy-dispersive X-ray analyses revealed that mNb-bc has a rough surface, with high dispersion of niobium and oxygen in the material.

The mNb-bc was able to dehydrate xylose to 2-furfuraldehyde in a monophasic system using water as a green solvent, realizing a xylose conversion of 41.2% and a selectivity of 77.1% in a kinetic study proceeded

under optimized reaction conditions obtained from the  $2^3$  experimental design (140 °C, 120 min, a catalyst-to-xylose ratio (CXR) of 10%). At these reaction conditions, mNb-bc had a very high turnover number (TON) value (460) (Scheme 2).



**Scheme 2.** Dehydration of xylose to 2-furfuraldehyde. L: Lewis acid, B: Brønsted acid.

These results may pave the way to develop more stable, selective, and active catalysts under milder reaction conditions.

## Review

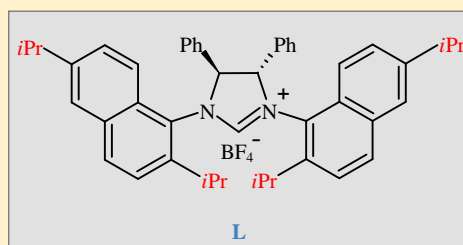
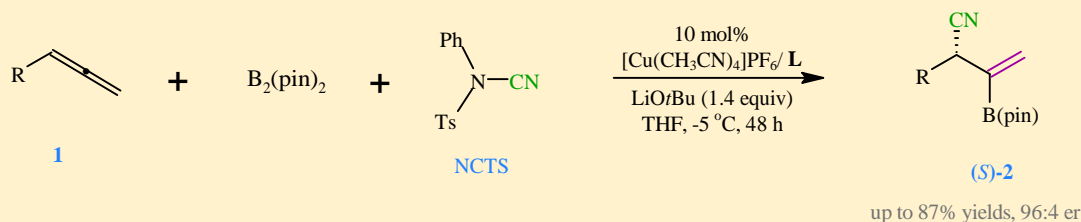
J. B. Gabriel, V. Oliveira, T. E. de Souza, I. Padula, L. C. A. Oliveira, L. V. A. Gurgel, B. Eduardo, L. Baêta, A. C. Silva, *ACS Omega* **2020**, *5*, 21392–21400.

## Synthesis of Enantiopure $\beta$ -Boryl Allyl Nitriles

Selective fine-tuning of the ligands in catalysis resulted in the preparation of enantioselective cyanoborylation of allenes. The high enantioselective  $\beta$ -boryl allyl nitriles were obtained by chiral *N*-heterocyclic carbene-copper catalysts through installation of appropriate substituents on the naphthalene ligands.

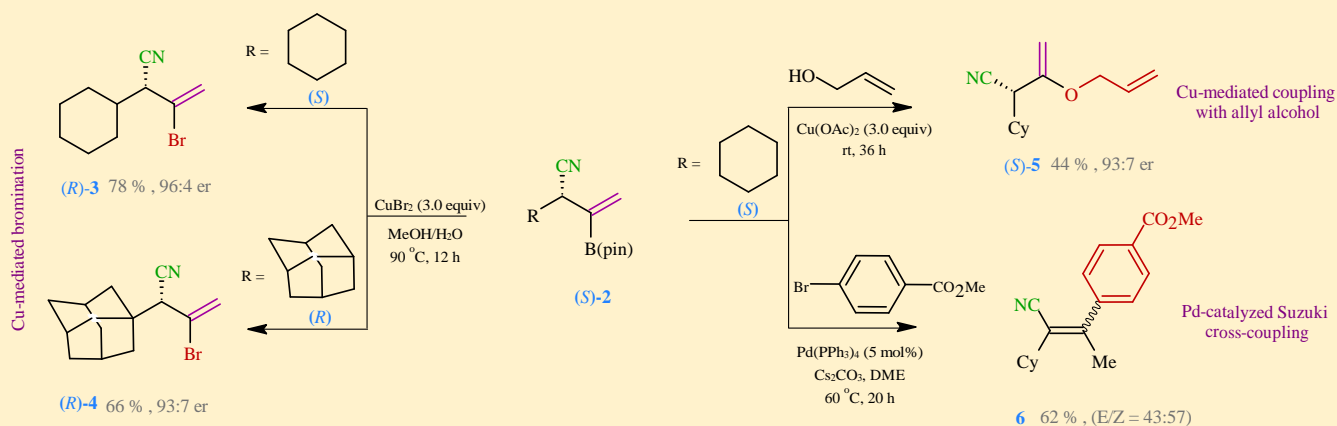
The simultaneous installation of a cyano group and a boryl unit into a C=C double bond of the allene substrate in an enantioselective fashion is of great importance due to their involvement in various chemical transformation and biologically active molecules.

In this context, Li *et al.* reported a copper-catalyzed chemo-, regio-, and enantioselective cyanoborylation of allenes, which afforded enantiopure  $\beta$ -boryl allyl nitriles efficiently. The authors demonstrated that the reaction of a variety of terminal allenes **1** with bis(pinacolate)diboron ( $B_2(\text{pin})_2$ ) and electrophilic cyanation agent, *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS), in the presence of NHC ligand based on a chiral diphenylethylene diamine backbone **L** and  $[Cu(\text{CH}_3\text{CN})_4]\text{PF}_6$  catalyst furnished chiral nitrile products (*S*)-**2** in good to excellent yields with relatively high enantioselectivity (Scheme 1). The high enantioselectivity was achieved by installing of isopropyl groups at the C2 and C6 positions of the naphthyl moiety in the newly synthesized *N*-heterocyclic carbene (NHC) ligand **L**.



**Scheme 1.** Copper-catalyzed asymmetric cyanoborylation of allenes.

The synthetic utility of this method was investigated employing a series of reactions of the obtained densely functionalized chiral nitriles which afforded a number of valuable molecules (Scheme 2).



**Scheme 2.** Synthetic applications of chiral nitriles.

Based on stoichiometric reactions and computational studies, it was revealed that the stability of the borocupration transition states determines the regioselectivity of the reaction. In addition, the enantioselectivity was controlled by the steric effects of chiral NHC ligand **L**.

This method paves the way for the development of selective catalytic processes through fine-tuning ligand design.

## Review

Z. Li, L. Zhang, M. Nishiura, G. Luo, Y. Luo, Z. Hou, *ACS Catal.*, **2020**, *10*, 11685–11692.

# Synthesis of Acyl Fluorides from Activated Ketones

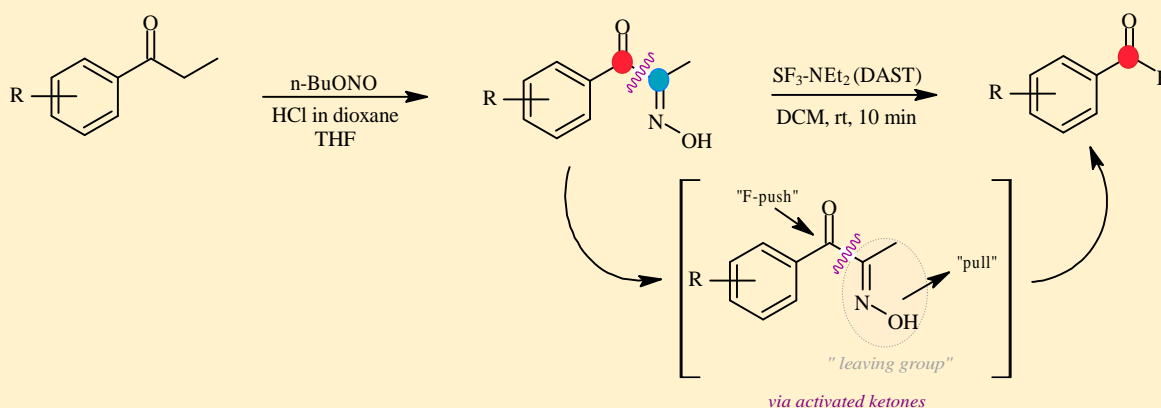
A new scope for synthesis of acyl fluorides from activated ketones as starting materials is described. The designed reaction was accomplished by the diethylaminosulfur trifluoride (DAST)-mediated Beckmann fragmentation of  $\alpha$ -oximinoketones.

Acyl fluorides constitute versatile reagents in organic synthesis owing to their reactivity and extraordinary stability compared to other types of acyl halides. Their synthetic procedures rely on the employing of carboxylic acids as starting materials in the presence of fluorinating reagents such as HF-pyridine/DCC,  $(\text{Me}_4\text{N})\text{SCF}_3$ , and  $\text{PPh}_3/\text{NBS}$  &  $\text{Et}_3\text{N}/\text{HF}$ .

A new scope for preparation of acyl fluorides is reported by Kim and Lim, that based on activated ketones as starting materials in the presence of sulfur-based fluorinating reagents. In fact, the advantage of using ketones instead of carboxylic acids as starting materials is related to their conventional functional groups as well as widely present in many biologically important molecules.

The adapted strategy is based on pull-and-push-driven fluorinative C–C bond cleavage. In the presence of a sulfur-based fluorination reagent, this bond cleavage takes place via a fluoride accepted by a ketone that is activated by an  $\alpha$ -oxime and a leaving group of an activated oxime formed by electrophilic sulfur fragment.

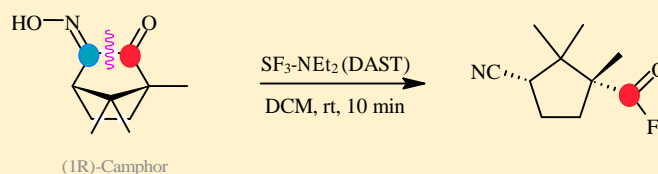
Acyl fluorides of arenes were readily accessed in one pot through  $\alpha$ -Oximation of ketones followed by the addition of diethylaminosulfur trifluoride (DAST) under mild reaction conditions in order to ensure the broad scope of tolerable functional groups (Scheme 1).



**Scheme 1.** Synthesis of acyl fluorides of arenes.



Furthermore, the substrate scope was extended from acyclic ketones to benzo-fused and aliphatic cyclic ketones (Scheme 2). The resulting acyl fluorides contain a pendant nitrile group, which allows further utilization as 1,5-, 1,6-, 1,7-, and 1,8-dicarbonyl equivalents with orthogonal reactivity.



**Scheme 2.** Synthesis of chiral acyl fluorides from chiral cyclic ketones.

Investigation of the reaction mechanism revealed that the oxime activation is initiated by the electrophilic trifluorosulfur moiety of DAST to release HF, which, in turn, adds to the activated ketone, producing a fluorohydrin that would be in equilibrium with the ketone. The reaction proceeds finally in C-C bond cleavage by the entropically favorable Beckmann fragmentation process, affording the acyl fluoride.

In the case of cyclic substrates, the fragmentation proceeds in an intramolecular fashion, affording an acyl fluoride bearing a cyano group.

The reaction features high efficiency, high chemoselectivity, a wide range of substrates with good functional group tolerance, scalability, and is potentially one-pot operative.

## Review

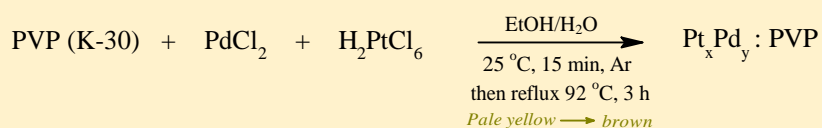
D. Kim, H. N. Lim, *Org. Lett.*, **2020**, 22, 7465–7469

# Activation of Carbon-Fluorine Bond at Low Temperature Using Heterobimetallic System

Avoiding the hard conditions required for the conversion of C-F into C-H bonds, a highly active Pt-Pd nanoalloy is underlined as a robust catalyst for the activation of C-F bonds at low temperature.

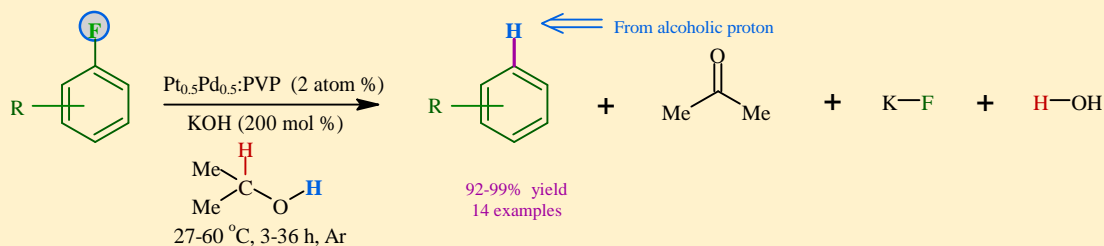
Carbon-fluorine bonds are regarded as the most inert organic functionality due to the high electronegativity of fluorine that induces a significant ionic bond character leading to the strongest and shortest sigma bond to carbon. Thus, their hydro-defluorination process at low temperature remains challenging. To overcome the use of harsh reductants at high temperature or electrochemical conditions, a novel approach was reported by Dhital *et al.* that based on employing a heterobimetallic system. In fact, alloying two metals can lead to unique catalytic activities and novel properties including stability and product selectivity owing to synergistic effects of two different metallic atoms present in the single particles.

The authors used nanoalloying of Pd with Pt as a powerful catalyst for the de-fluorination reaction at low temperature. The synthesis of Pt<sub>x</sub>Pd<sub>y</sub> nanoalloy is shown in Scheme 1.



**Scheme 1.** Preparation of Pt<sub>x</sub>Pd<sub>y</sub> nanoalloy.

De-fluorination of aryl fluorides was accomplished through the reaction of aryl fluoride with anhydrous 2-propanol as the hydrogen source in the presence of potassium hydroxide as a base and the nanoalloying catalyst Pt<sub>0.5</sub>Pd<sub>0.5</sub>:PVP using an organic synthesizer under argon conditions (Scheme 2). A wide variety of fluorides were converted into the hydroarenes in excellent yield.



**Scheme 2.** De-fluorination of aryl fluorides.

Mechanistic insight into the reaction indicated that the alcoholic proton of 2-propanol is the major hydrogen source. The oxidative addition of 2-propanol on Pd takes place before Pt activates the C-F bond taking into consideration that Pd and Pt play independent and cooperative roles to accomplish the effective activation of C-F bonds.

## Review

R. N. Dhital, K. Nomura, Y. Sato, S. Haesuwannakij, M. Ehara, H. Sakurai, *Bull. Chem. Soc. Jpn.*, **2020**, *93*, 1180–1185.