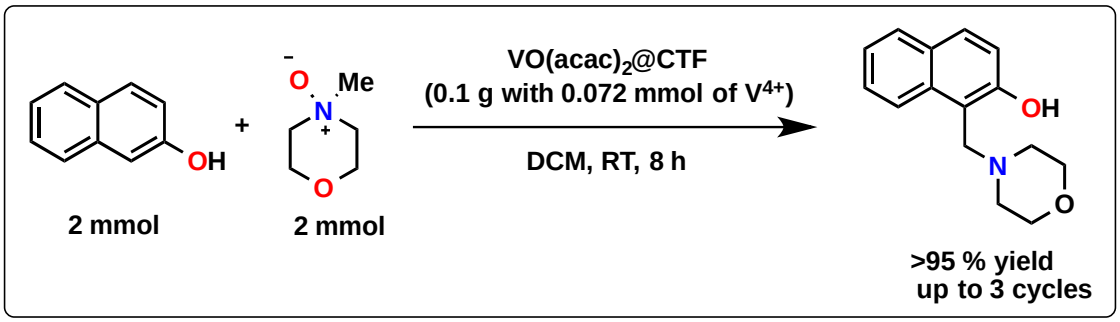
# Catalysis by Design: A Modified Mannich Type Reaction Catalyzed by $VO(acac)_2$ Supported on Covalent Triazine Framework

**Himanshu Sekhar Jena, Pascal Van Der Voort***
COMOC, Department of Chemistry, Ghent University, Ghent-9000, Belgium

Engineering porous materials such as Metal Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs) with active homogenous catalytic sites would offer new opportunities in the field of heterogeneous catalysis. Among COFs, Covalent Triazine Frameworks (CTFs) are high performance polymer materials with intrinsic repetitive triazine moieties, high surface area and regular porosity. In general, these materials are synthesized from respective nitrile monomers via either ionothermal route or by $CF_3SO_3H$ catalyzed trimerization reactions. Therefore, designing new nitrile based linkers with active binding sites (N^N, N^O, O^O, etc) and syntheses of corresponding new CTFs may offer new challenges in designing efficient heterogeneous supports for more sustainable and environment-friendly society. In this regard, novel acetylacetone based CTFs were synthesized using 4,4'-malonyldibenzonitrile under ionothermal conditions [1] using $ZnCl_2$ at different temperatures and at different molar ratios of linker and $ZnCl_2$. The resulting CTFs showed high specific surface areas (1500-2600 $m^2/g$) and high stability (>400 °C). The incorporation of highly polar acetylacetone group enhanced the interaction with $CO_2$ and $H_2$ and the CTFs showed $CO_2$ uptake up to 3.16 mmol/g at 1 bar and 273 K and $H_2$ uptake up to 1.5 wt% at 1 bar and 77 K. Additionally, $VO(acac)_2$ was incorporated on the resulting CTF by post-synthetic modification and the resulting $VO(acac)_2$@CTF showed excellent reactivity for modified Mannich-type reactions [2]. The designed $VO(acac)_2$@CTF showed higher catalytic reactivity than the homogenous catalyst with wide substrate scope and reusability. The turn over number obtained from the designed heterogeneous catalysts is three times more than the homogenous catalyst and can be reused for minimum of five repeated cycle of reactions.




**Scheme 1**. Schematic representation of modified Mannich type reaction catalyzed by $VO(acac)_2$ supported on Covalent Triazine Framework

## References

[1] Kuhn, P.; Antonietti, M.; Thomas, A.; Porous, Covalent Triazine-Based Frameworks Prepared by Ionothermal Synthesis *Angew. Chem. Int. Ed*. **2008**. *47*, 3450-3453.
[2] Hwang, D-R.; Uang, B-J.; A Modified Mannich-Type Reaction Catalyzed by $VO(acac)_2$, *Org. Lett.*, **2002**, *4*, 463-466.

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