

Science and Technology Group Annual Report FY2022

Eugene Khaskin

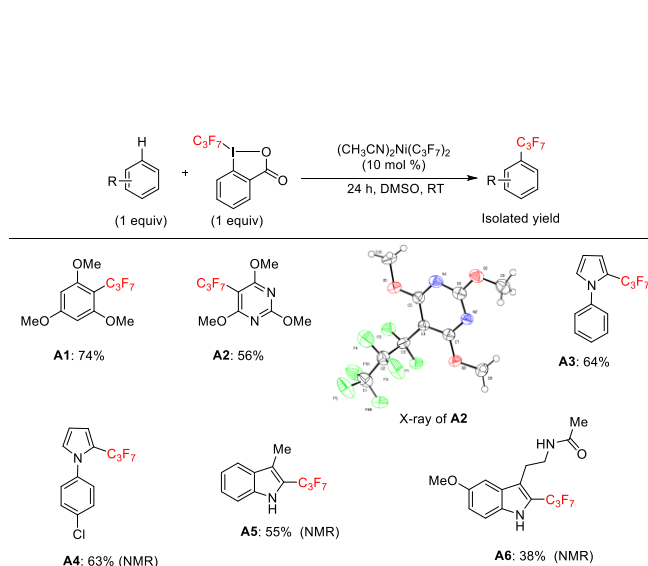
1 Introduction

During FY2022, as my main research output I published an article on the introduction of C_2F_5 and larger fluorocarbon groups onto various electron-rich arenes and heterocycles.¹ This arose from earlier published research where nickel was supported by a naphthyridine ligand to introduce a CF_3 group on these types of substrates. The reaction is important due to its potential to functionalize natural products and drugs or drug intermediates at late stages of production directly and in a mild manner. The fluorocarbon group changes the properties of the molecule and can result in metabolism/activity differences, as well as helps the molecules to transit the blood-brain barrier. In the current work we show that when a 'naked' nickel system is used without any ligands, the reaction can work well for the larger fluorocarbon groups from cheap reagents, but does not work as well with CF_3 . In addition to introducing bigger electron poor groups that change activity to a greater extent, the current protocol is simpler as it requires no ligand and no external light.

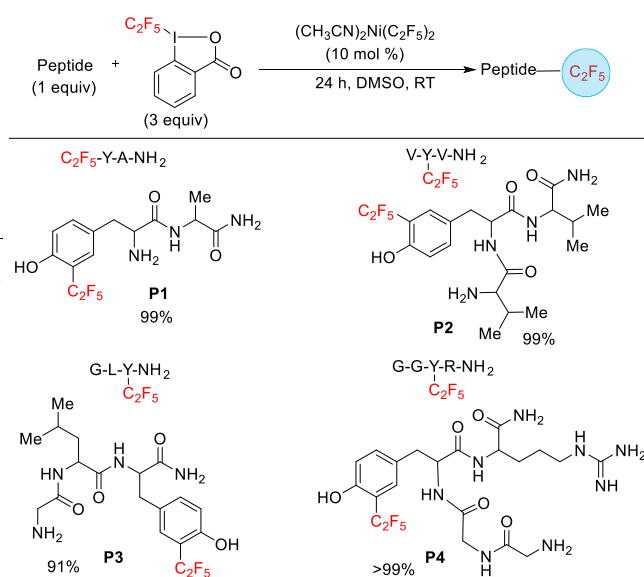
My work with OIST collaborators this year included work where a ligand designed by me was used with iron to selectively hydrogenate alkynes and I worked closely on writing this paper.² However, this work will likely be published in the next fiscal year. For other published works,³⁻⁵ I measured and solved crystal structures, helped with writing of parts of the papers, and designing and carrying out some of the experiments.

2 Activities and Findings

Due to a lack of space to discuss findings, and the happy coincidence that the main work involves the catalytic modification of organic compounds, I will include substrate tables in lieu of a greater discussion that can be found in the papers themselves. The three schemes are a summary of the fluoroalkylation work with the ligandless nickel catalyst.



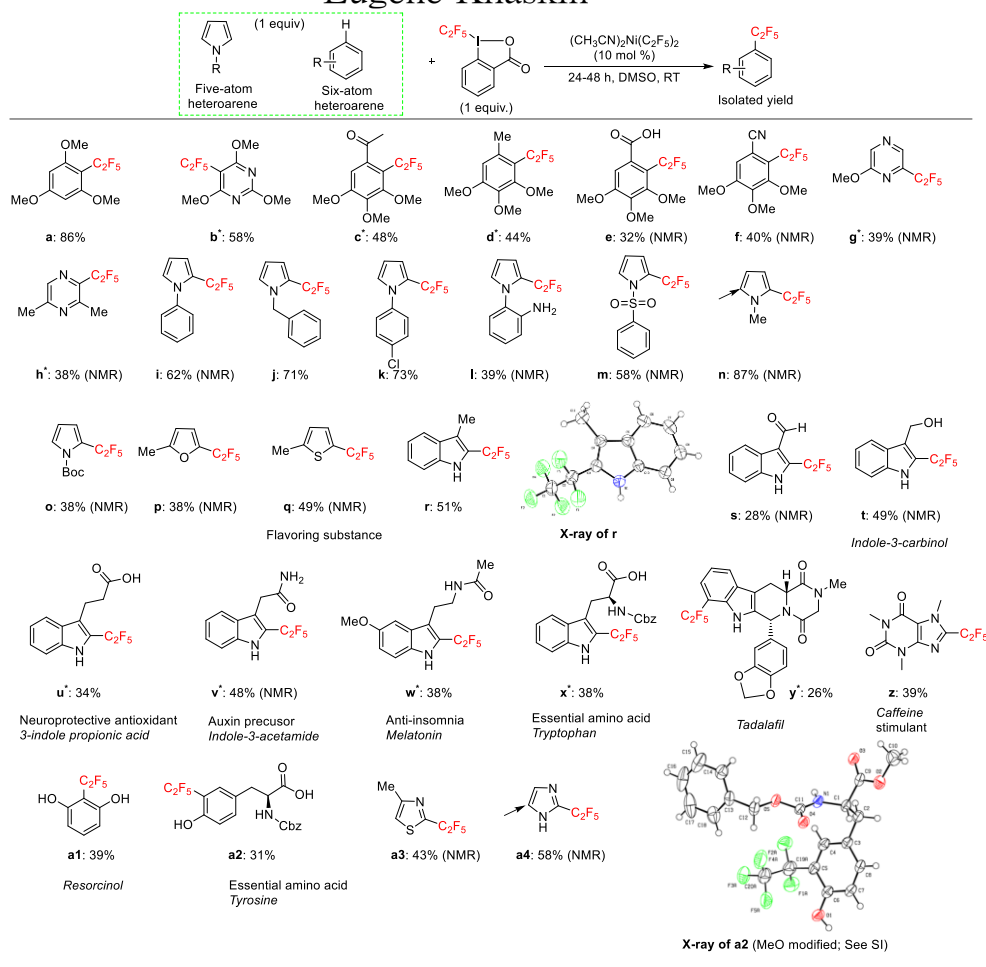
Scheme 1. Substrate scope of heptafluoropropylation.



Scheme 2. Substrate scope of peptides.

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Scheme 3. Substrate scope for pentafluoroethylation

3 Collaborations

I'm continuing my collaboration with the Khusnutdinova and Kuhn units, and trying to keep up with my foreign collaborations: Sydnese Group in Norway, Dmitry Gusev in Canada, and Sebastian Kozuch in Israel, despite the travel ban due to the coronavirus. In FY2022, I may be able to get some of the collaborators to visit me and this should result in a collaborative work being published.

4 Publications and other output

Author list, *Title*, Journal or other reference, volume information (year)

- (1) Deolka, S.; Govindarajan, R.; Vasylevskiy, S.; Roy, M. C.; Khusnutdinova, J. R.; Khaskin, E. Ligand-free nickel catalyzed perfluoroalkylation of arenes and heteroarenes. *Chem. Sci.* **2022**, *13* (44), 12971-12979.
- (2) Pandey, D. K.; Khaskin, E.; Pal, S.; Fayzullin, R. R.; Khusnutdinova, J. R. Efficient Fe-Catalyzed Terminal Alkyne Semihydrogenation by H₂: Selectivity Control via a Bulky PNP Pincer Ligand. *ACS Catal.* **2023**, *13* (1), 375-381.
- (3) Karimata, A.; Gridneva, T.; Patil, P. H.; Fayzullin, R. R.; Khaskin, E.; Lapointe, S.; Garcia-Roca, A.; Khusnutdinova, J. R. Ethylene binding in mono- and binuclear CuI complexes with tetradentate pyridinophane ligands. *Dalton Trans.* **2022**, *51* (35), 13426-13434.
- (4) Govindarajan, R.; Deolka, S.; Khaskin, E.; Fayzullin, R. R.; Pal, S.; Vasylevskiy, S.; Khusnutdinova, J. R. H₂, B-H, and Si-H Bond Activation and Facile Protonolysis Driven by Pt-Base Metal Cooperation. *Chem. - Eur. J.* **2022**, *28* (44), e202201639.
- (5) Dinh, H. M.; Gridneva, T.; Karimata, A.; Garcia-Roca, A.; Pruchyathamkorn, J.; Patil, P. H.; Petrov, A.; Sarbajna, A.; Lapointe, S.; Khaskin, E.; et al. Single and double deprotonation/dearomatization of the N,S-donor pyridinophane ligand in ruthenium complexes. *Dalton Trans.* **2022**, *51* (38), 14734-14746.