# Science and Technology Group
# Annual Report FY2016

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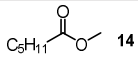
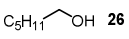
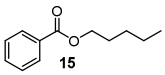
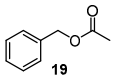
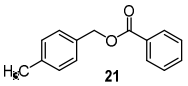
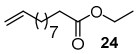
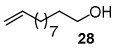
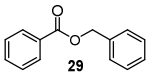
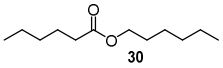
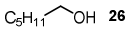
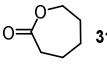
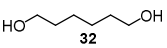
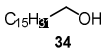
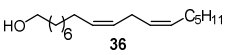
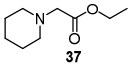
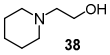
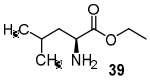
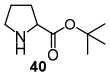
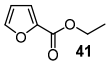
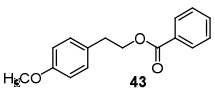
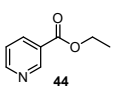
## 1 Introduction

| Entry | Ester | Product | Yield (%) |
|---|---|---|---|
| 1 |  14 |  26 | 90 |
| 2 |  15 |  27 | 90 |
| 3 |  19 |  27 | 84[a] |
| 4 |  21 |  27 | 89 |
| 5 |  24 |  28 | 90[b] |
| 6 |  29 |  27 | 74[c] |
| 7 |  30 |  26 | 87[c] |
| 8 |  31 |  32 | 58 |
| 9 | Tripalmitin (**33**) |  34 | 57 |
| 10 | Glyceryl Trilinoleate (**35**) |  36 | 16[d] |
| 11 |  37 |  38 | >95 |
| 12 |  39 | No Reaction | ------- |
| 13 |  40 | No Reaction | ------- |
| 14 |  41 |  42 | 95 |
| 15 |  43 |  27 | 15 |
| 16 |  44 |  45 | 72 |

During FY2016 I continued work on the ester metathesis and transfer hydrogenation of esters project. This paper was eventually published in the journal *ACS Catalysis* (American Chemical Society). I also presented these results at a conference in Kyoto (International Symposium on Homogenous Catalysis XX) and at the Japanese Society of Chemistry 97th annual March meeting in a 20 minute lecture format. Although the results were significant and novel, and were well received at the conferences, it proved difficult to improve on them practically and I started focusing on the synthesis of new ligands, collaboration with the Khusnutdinova unit, and searching for new catalytic reactions.

## 2 Activities and Findings

Reproduced left is a slightly modified substrate table of esters that are hydrogenated by sacrificial ethanol from the published work. This is the first ever report of effective transfer hydrogenation of esters (i.e. avoiding dangerous hydrogen gas). I tried to find a sacrificial alcohol that would give me quantitative yield and of which I would only need 1 equivalent and not 20 like with ethanol. However, after several months, the best alcohol substrate (number 38 from the table) gave only ~80% ester hydrogenation. As it is much more expensive than ethanol, I decided to focus on other projects for now. I would like to revisit transfer ester hydrogenation again for fatty acid esters such as 33 and 35, since the low yield of

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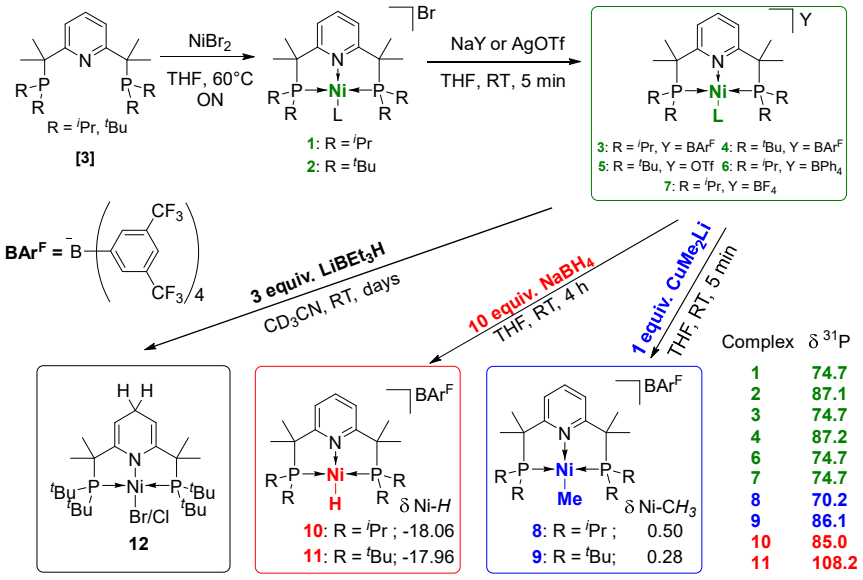
commercially important alcohols 34 and 36 there was mostly due to solubility problems. Perhaps screening biphasic conditions will lead to higher yields.

At the end of the fiscal year, as I was screening for other reactions, I discovered that esters can also react, with the right catalyst, to transform the alcohol part of the ester into a highly diastereoselective cyclopropane, which are substrates that are normally difficult to make and require several steps. The new reaction proceeds in one step however and requires 1 mol% of Ru catalyst. Alcohols can also react in this manner. Before the submission of this report, this work was not yet published, although a provisional patent has been filed as the cyclopropane motif is important in the pharmaceutical and fine chemicals industry.

## 3 Collaborations




| Complex | δ 31P |
|---|---|
| 1 | 74.7 |
| 2 | 87.1 |
| 3 | 74.7 |
| 4 | 87.2 |
| 6 | 74.7 |
| 7 | 74.7 |
| 8 | 70.2 |
| 9 | 86.1 |
| 10 | 85.0 |
| 11 | 108.2 |

A new series of ligands I prepared in collaboration with the Khusnutdinova group has been used to make a number of new nickel complexes that stabilized unusual structures and oxidation states. We are exploring the catalytic activity and properties of these complexes.

## 4 Publications and other output

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

Publication:

Dubey, Abhishek. Khaskin, Eugene. *Catalytic Ester Metathesis Reaction and its Application to Transfer Hydrogenation of Esters*, ACS Catalysis, 3998-4002, (**2016**).

Presentation:

Khaskin, E. (presenting author), Dubey, A. "'Ru' Complex Catalyzed Ester Metathesis Reaction and Its Application to Transfer Hydrogenation of Esters with Primary Alcohols" presented at the International Symposium on Homogenous Catalysis XX in Kyoto Japan July 10-15, 2016 and at the Japanese Society of Chemistry 97th annual meeting in Keio University, Yokohama, Japan March 16-19th, 2017.