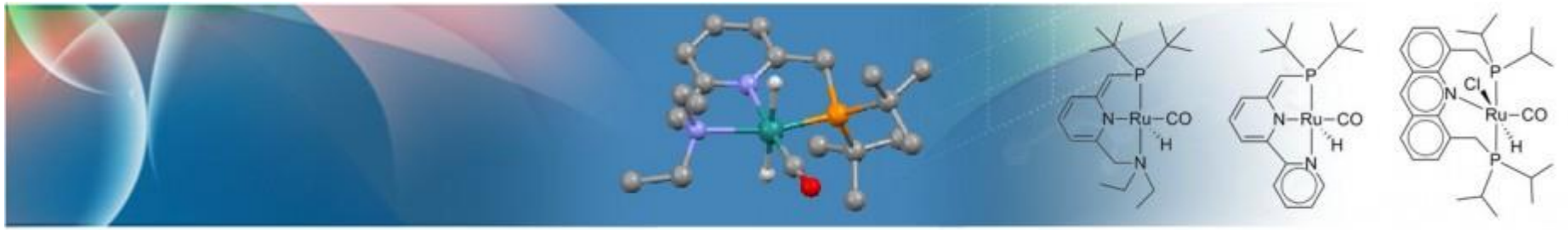


Bond Activation by Metal-Ligand Cooperation

A Selection of Prof. Milstein's Work (recent 10 years)

Fanyang Mo
Dong Group
UT Austin
Oct. 17, 2013

Ref: Prof. Milesstone's homepage: http://www.weizmann.ac.il/weizsites/milstein/

Prof. David Milstein

1976 Ph D. Hebrew University of Jerusalem

1976-1979 Postdoc Colorado State University

Discover “Stille” coupling with Prof. John Stille

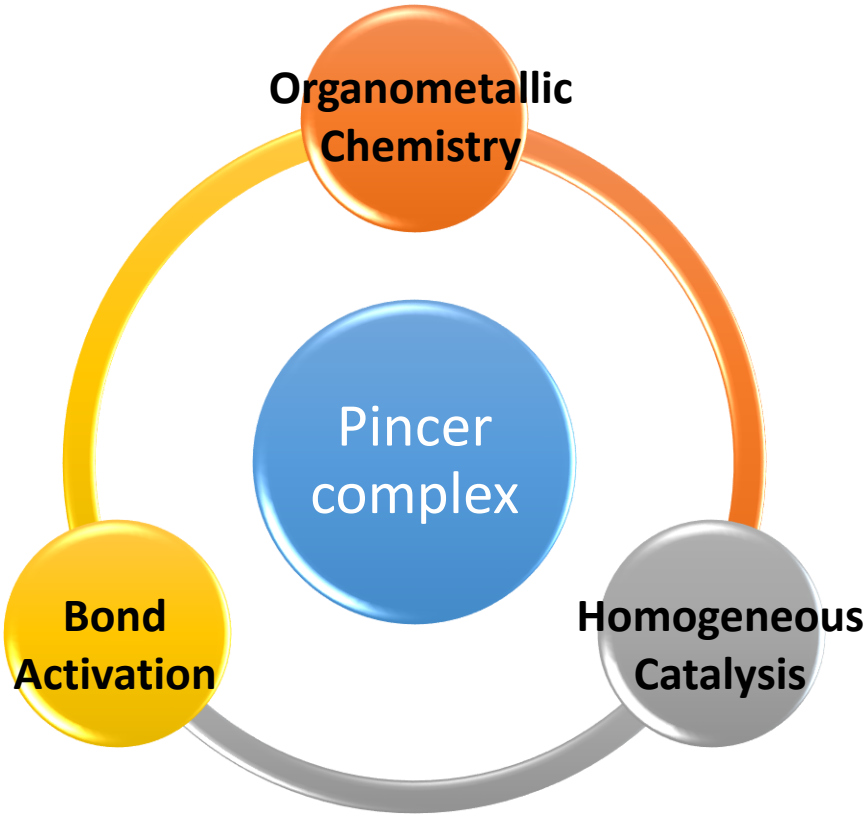
1979-1987 Group Leader DuPont Company

1987-now Professor Weizmann Institute of Science

Awards: the Kolthoff Prize by the Technion, 2002
the Israel Chemical Society Prize, 2006
the Miller Professorship, UC Berkeley, 2006
the ACS Award in Organometallic Chemistry, 2007
the RSC Sir Geoffrey Wilkinson Award, 2010
the Meitner-Humboldt Senior Award, 2011)
the Israel Prize (2012, Israel’s highest honor).

Lectureships: the Inaugural Novartis Lectureship, *Harvard Univ*, 2009
the Arthur D. Little lectureship, *MIT*, 2009
the Novartis Lectureship, *Scripps*, 2010
the Lord Lewis Lectureship, *Cambridge Univ*, 2011
the Ernest Swift Lectureship, *Caltech*, 2011
the EuCheMs Lecturer, 2012.

Research Interests: Pincer-type Tridentate Frameworks

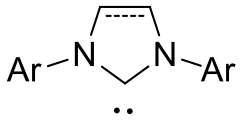


Contents

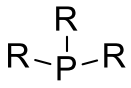
1. Introduction
2. Dehydrogenation of Alcohols to various products
3. Hydrogenation
4. Bond activation
    a. C—H bond Activation
    b. H—H bond Activation
    c. N—H bond Activation
5. Splitting Water to H_2 and O_2
6. Conclusion and Inspiration

1. Introduction

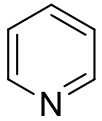
Simple and innocent ligands



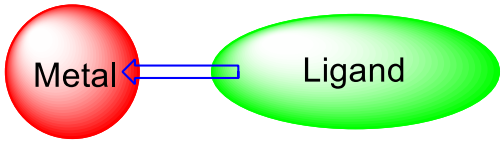
NHC



Phosphine type

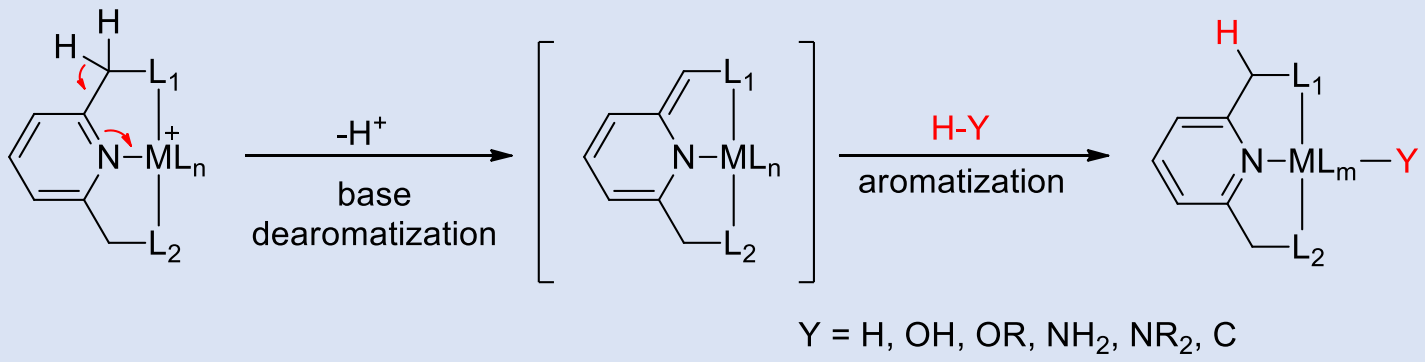


Pyridine type



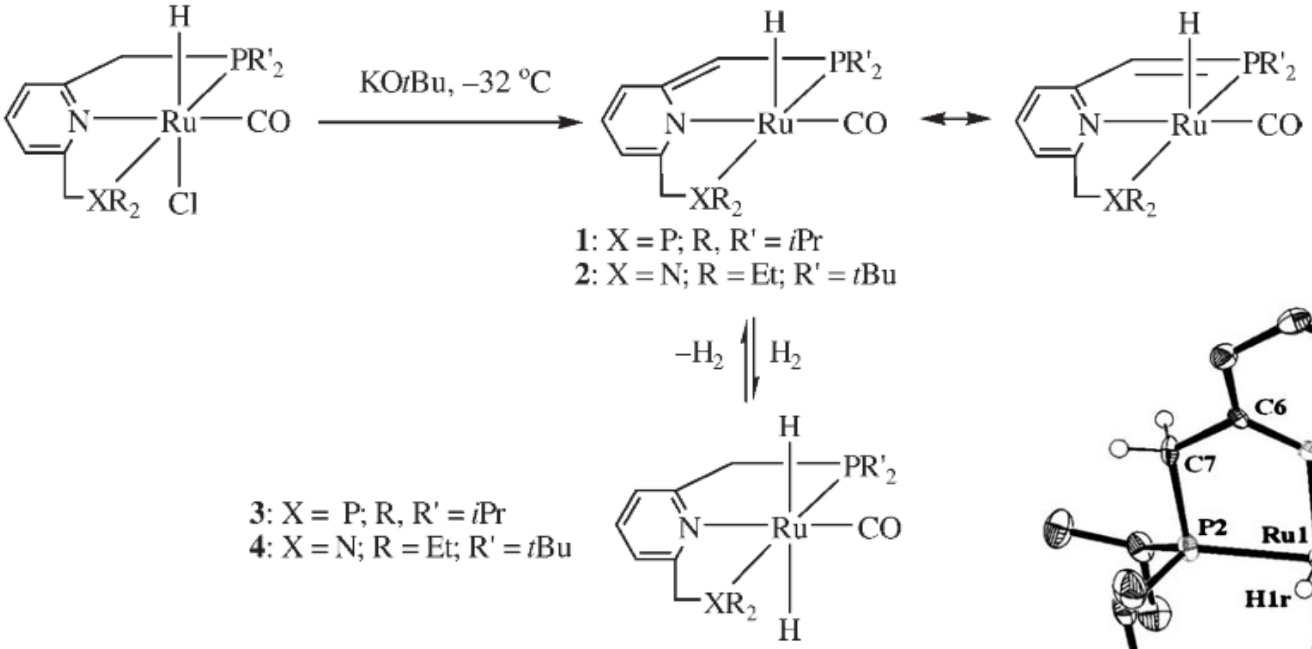
- Simply coordination
- Crucial role
- But no bond making or breaking during catalysis

Metal-Ligand Cooperation



1. Introduction

For example:



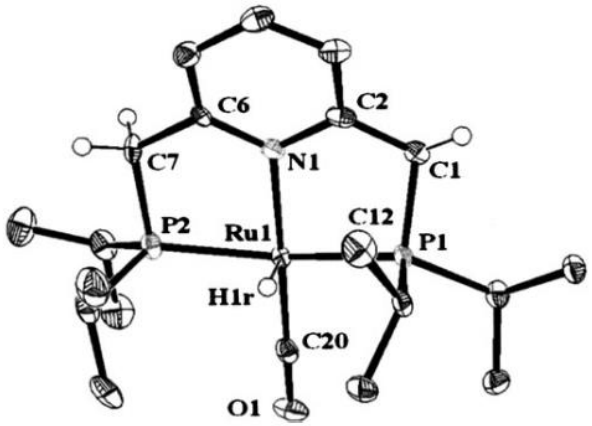
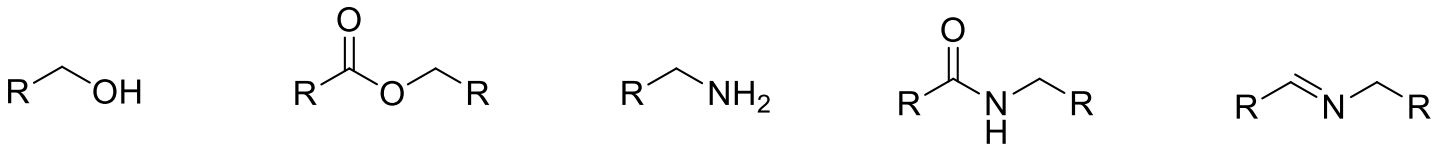


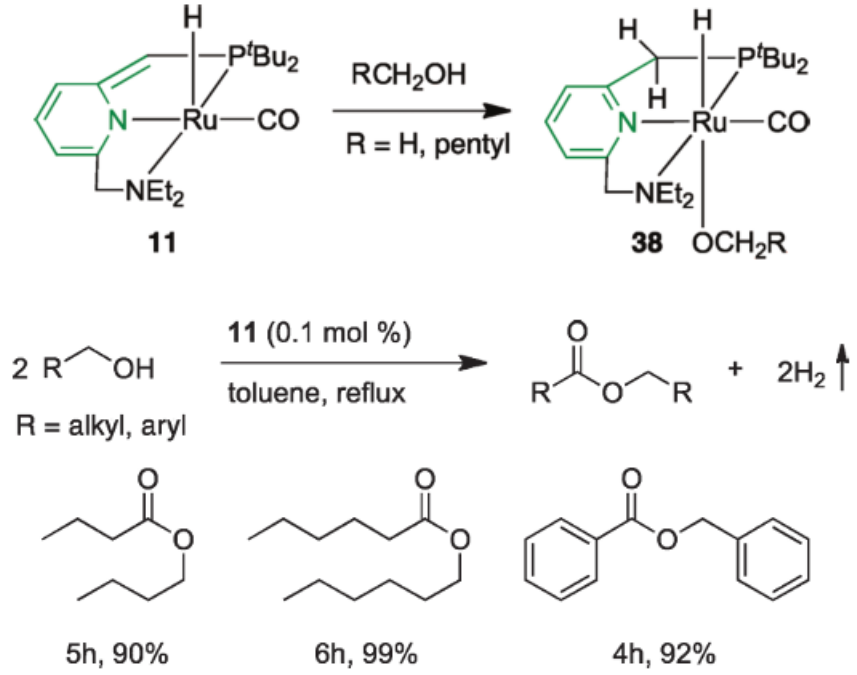
Figure 1. ORTEP diagram of a molecule of complex **1** with the thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: Ru1–C20 1.844(7), Ru1–N1 2.163(5), Ru1–P1 2.350(2), Ru1–P2 2.291(2), Ru1–H1r 1.48(11), C1–C2 1.450(9), P1–C1 1.803(6), P2–C7 1.843(7), C6–C7 1.552(9); C20-Ru1-N1 171.4(2), P1-Ru1-P2 153.1(1), H1r-Ru1-P1 72(4), H1r-Ru-P2 85(4).

Angew. Chem., Int. Ed. **2006**, *45*, 1113–1115.

2a. Dehydrogenation of Alcohols (Primary) to Esters

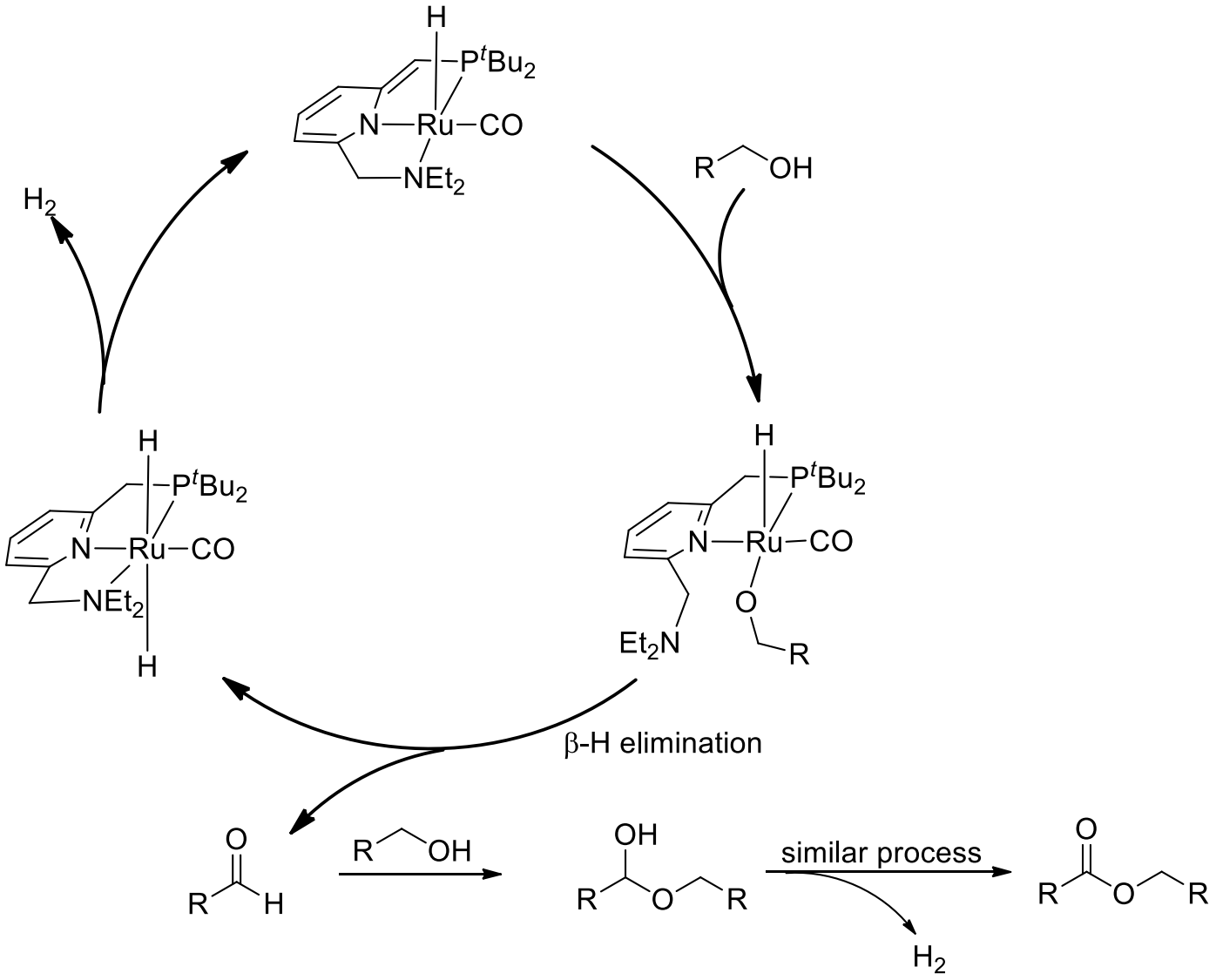


Fundamental building blocks in the chemical industry

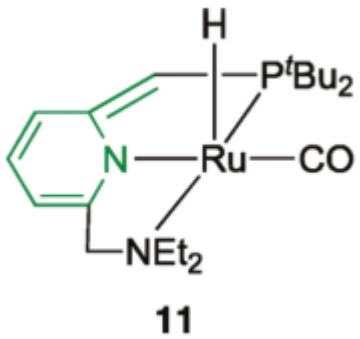


J. Am. Chem. Soc. **2005**, *127*, 10840–10840.

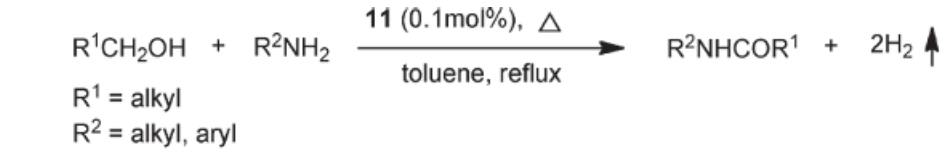
2a. Dehydrogenation of Alcohols (Primary) to Esters

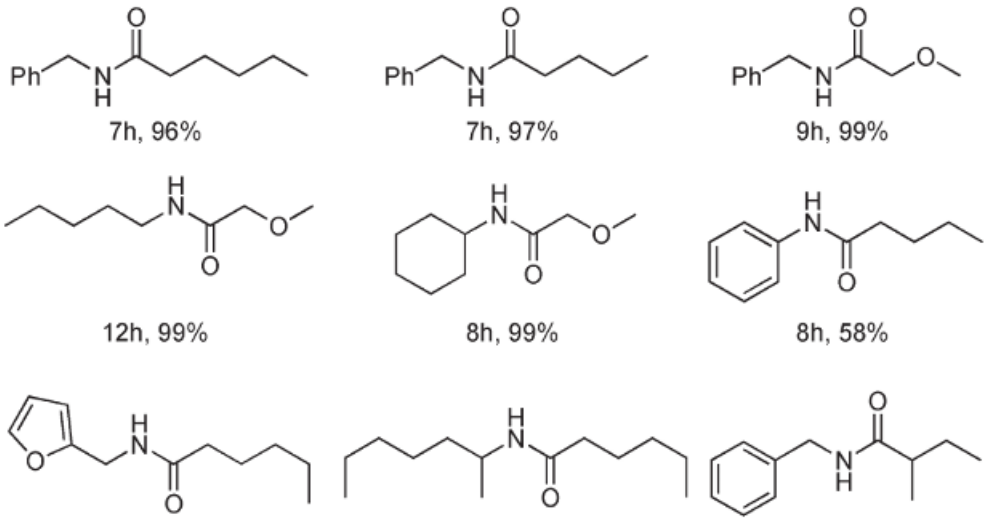


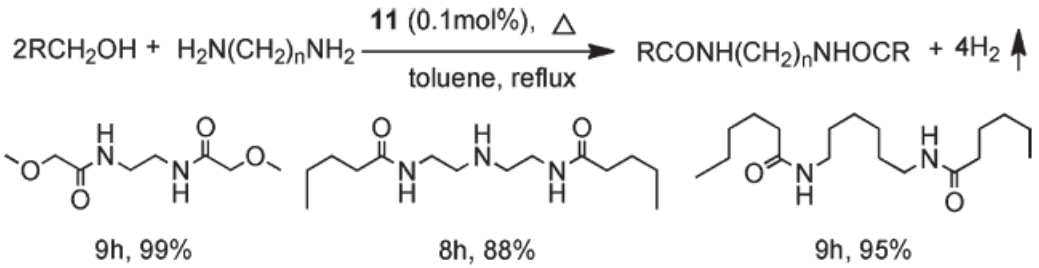
2b. Dehydrogenation of Alcohols (with Amines) to Amides



11

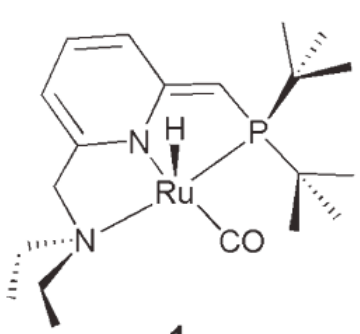






Science **2007**, *317*, 790-792.

2b. Dehydrogenation of Alcohols (and Amines) to Amides



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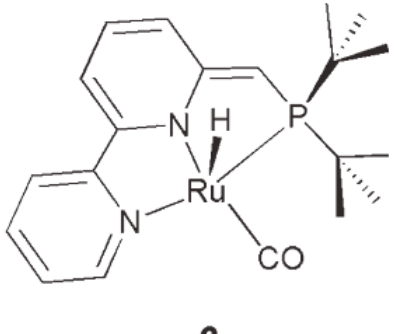
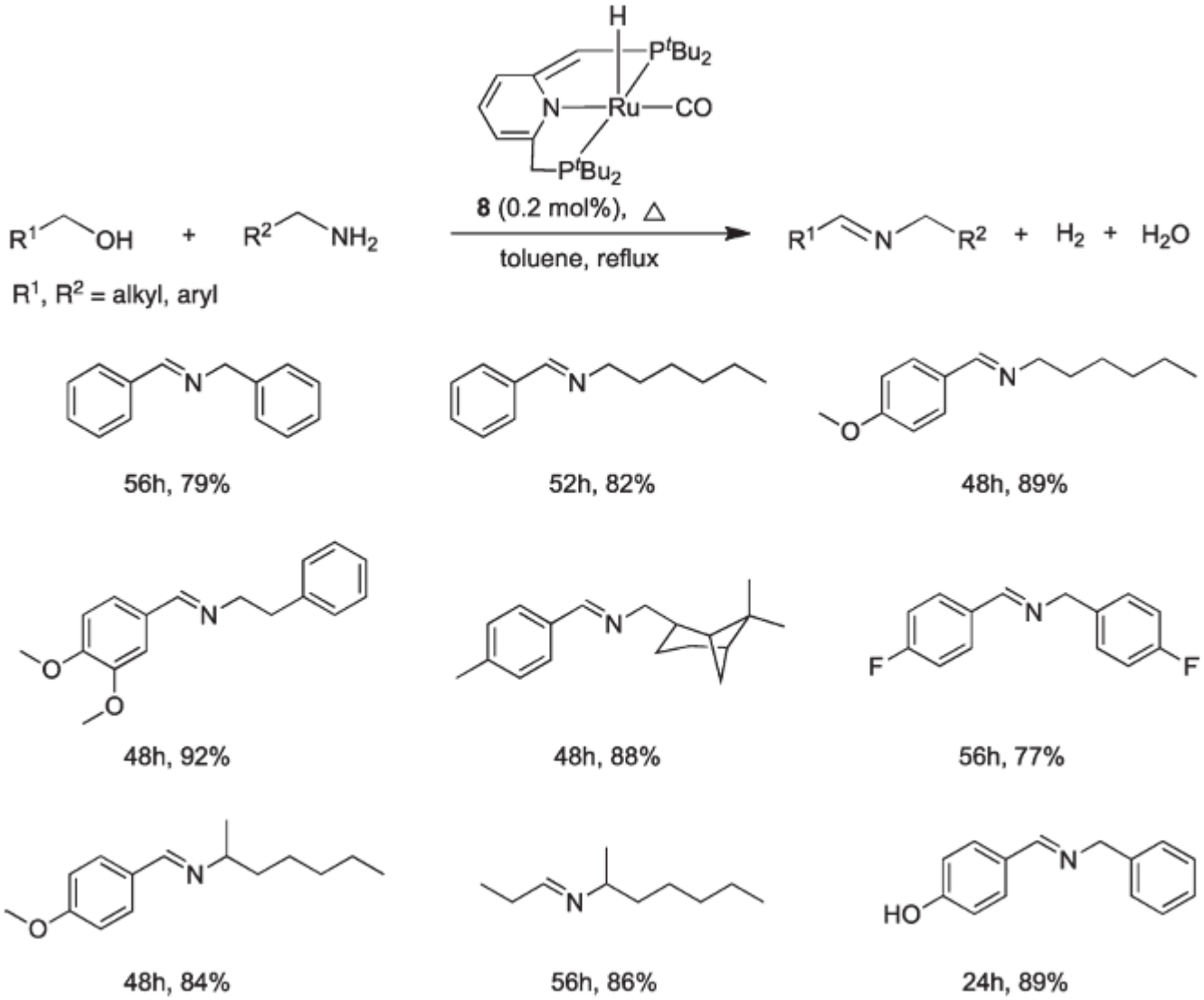


2

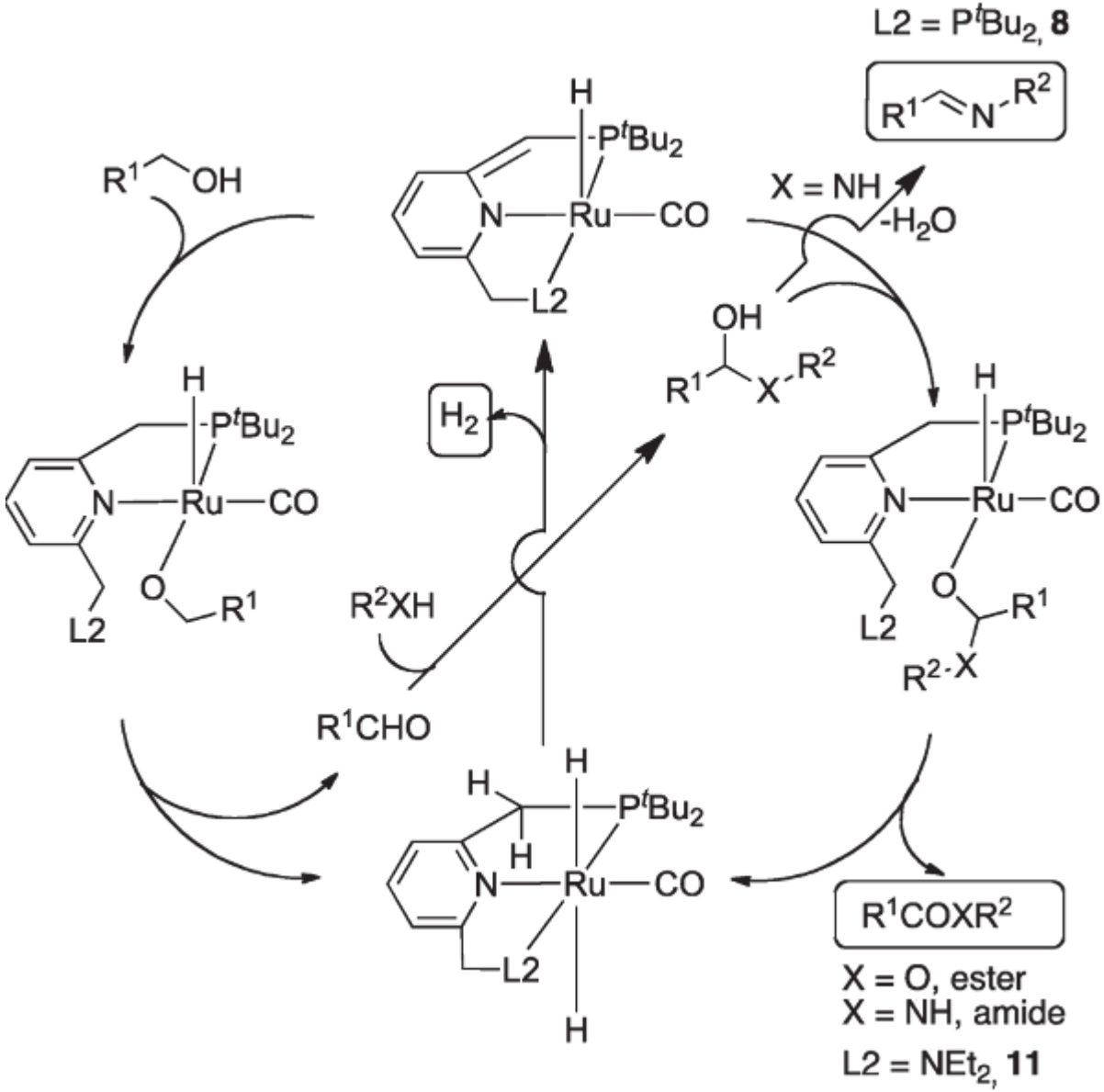
Journal of Polymer Science Part a-Polymer Chemistry, **2012**, *50*, 1755-1765.

2c. Dehydrogenation of Alcohols (and Amines) to Imines



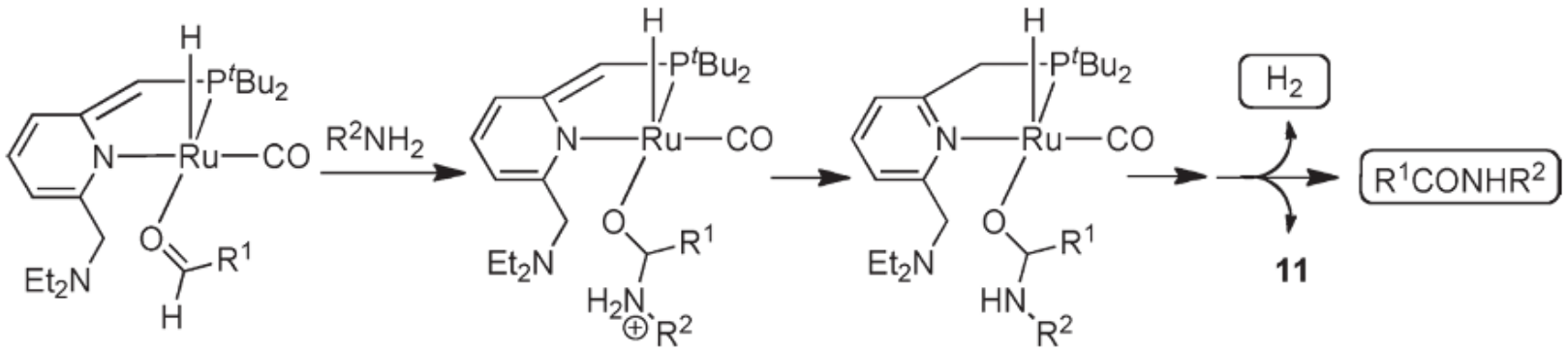
Angew. Chem., Int. Ed. **2010**, *49*, 1468-1471.

2a-c. Mechanism

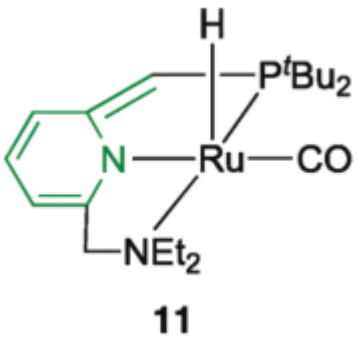


2a-c. Mechanism

When L2 is NEt_2…



2d. Amidation of Esters



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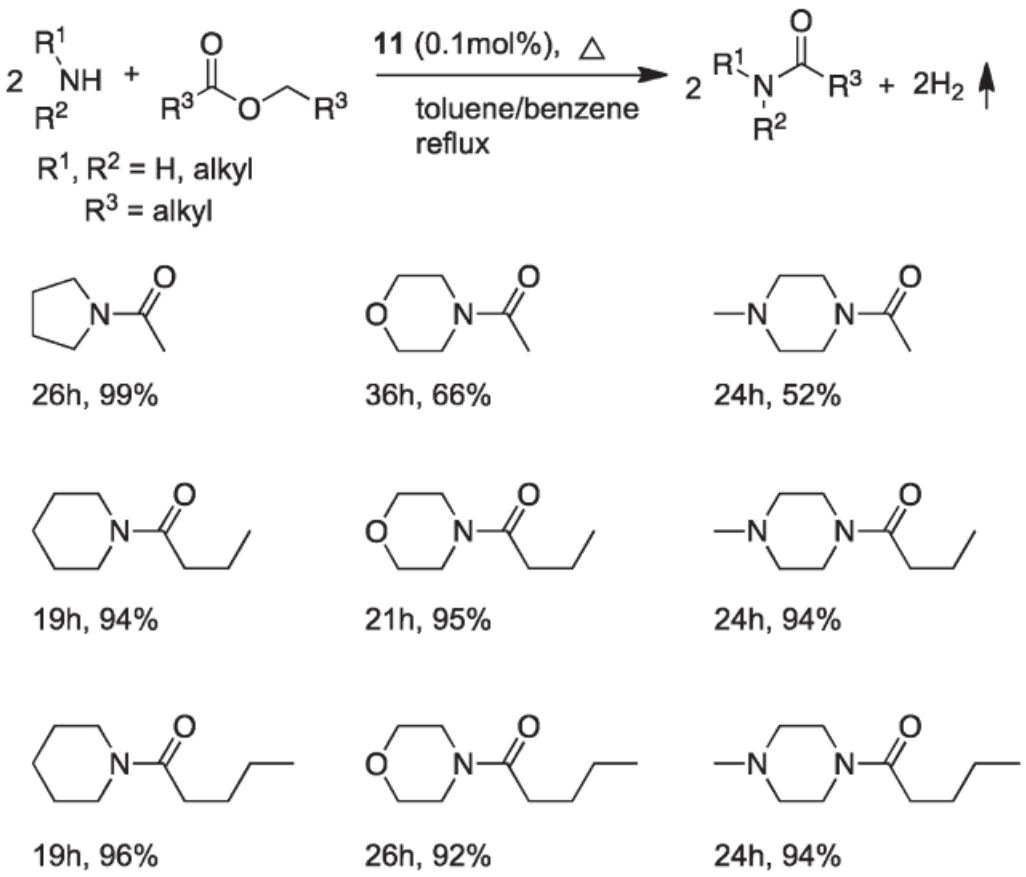
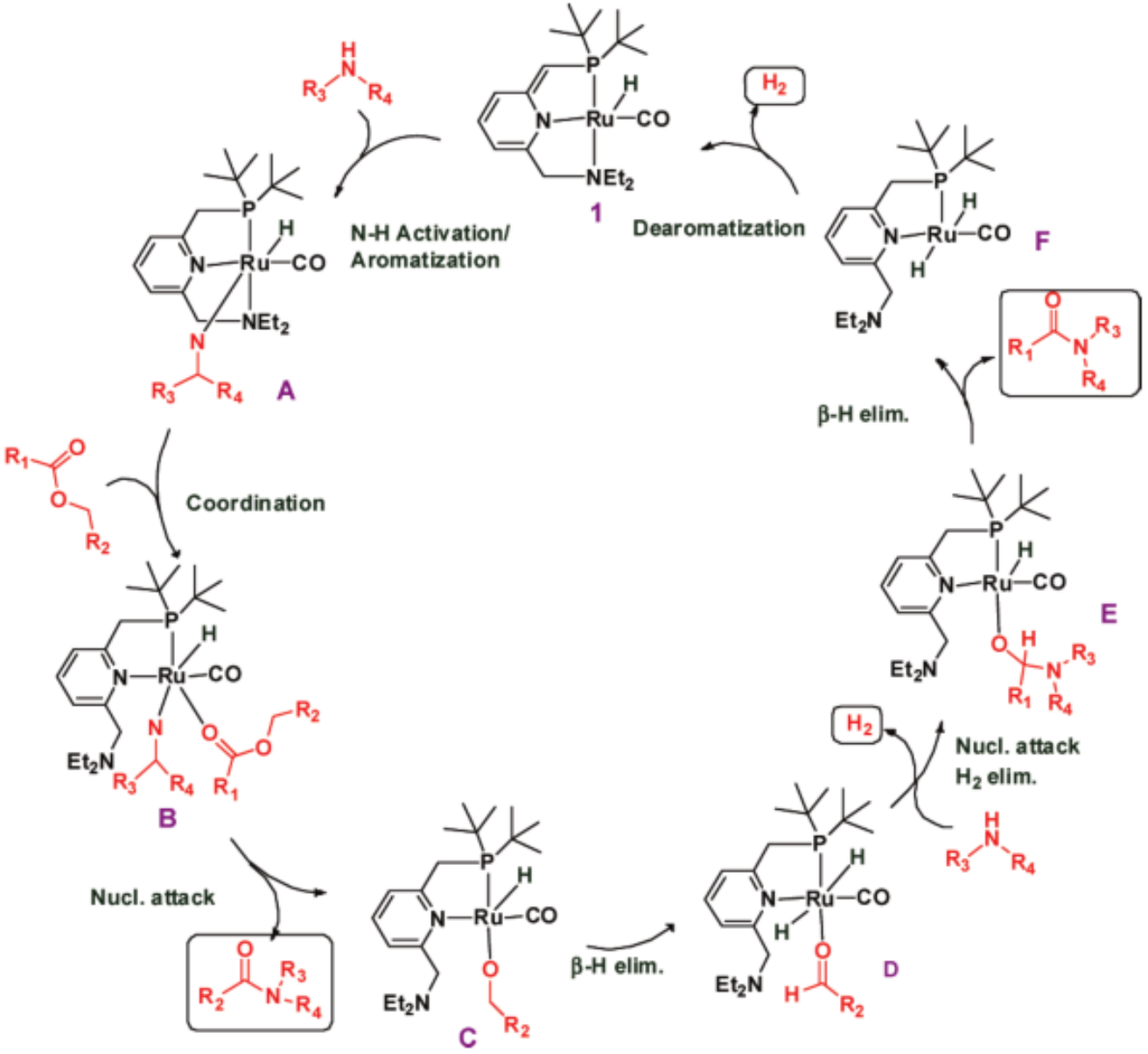
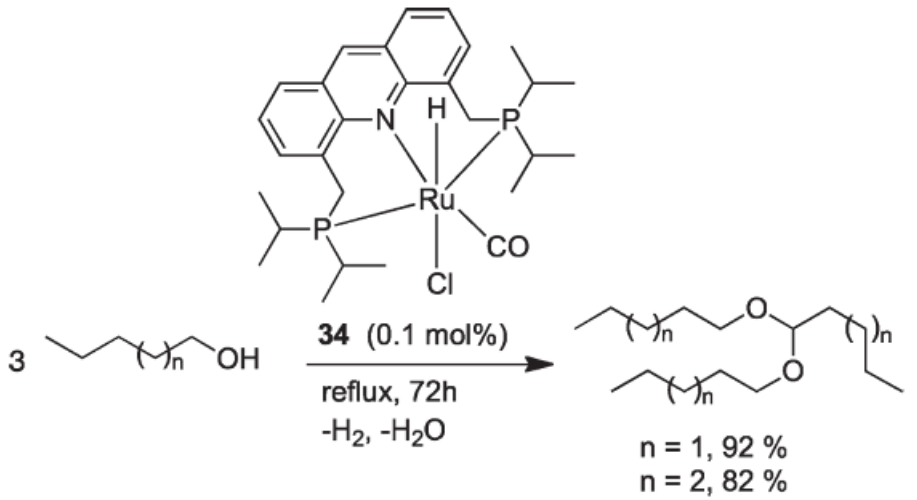


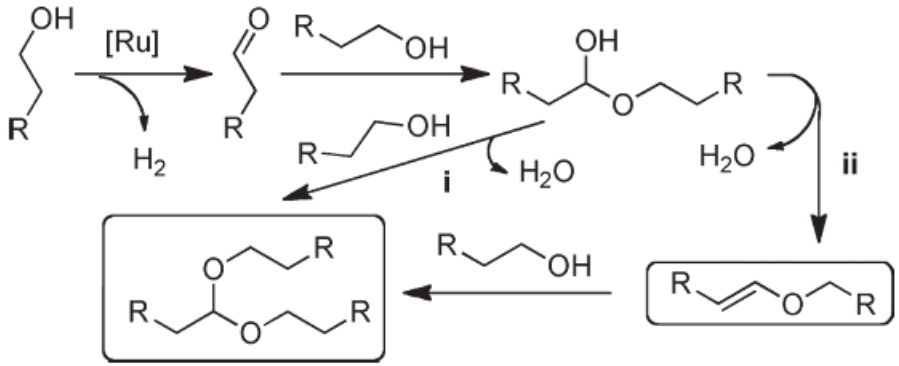
J. Am. Chem. Soc. **2011**, *133*, 1682-1685.

2d. Amidation of Esters



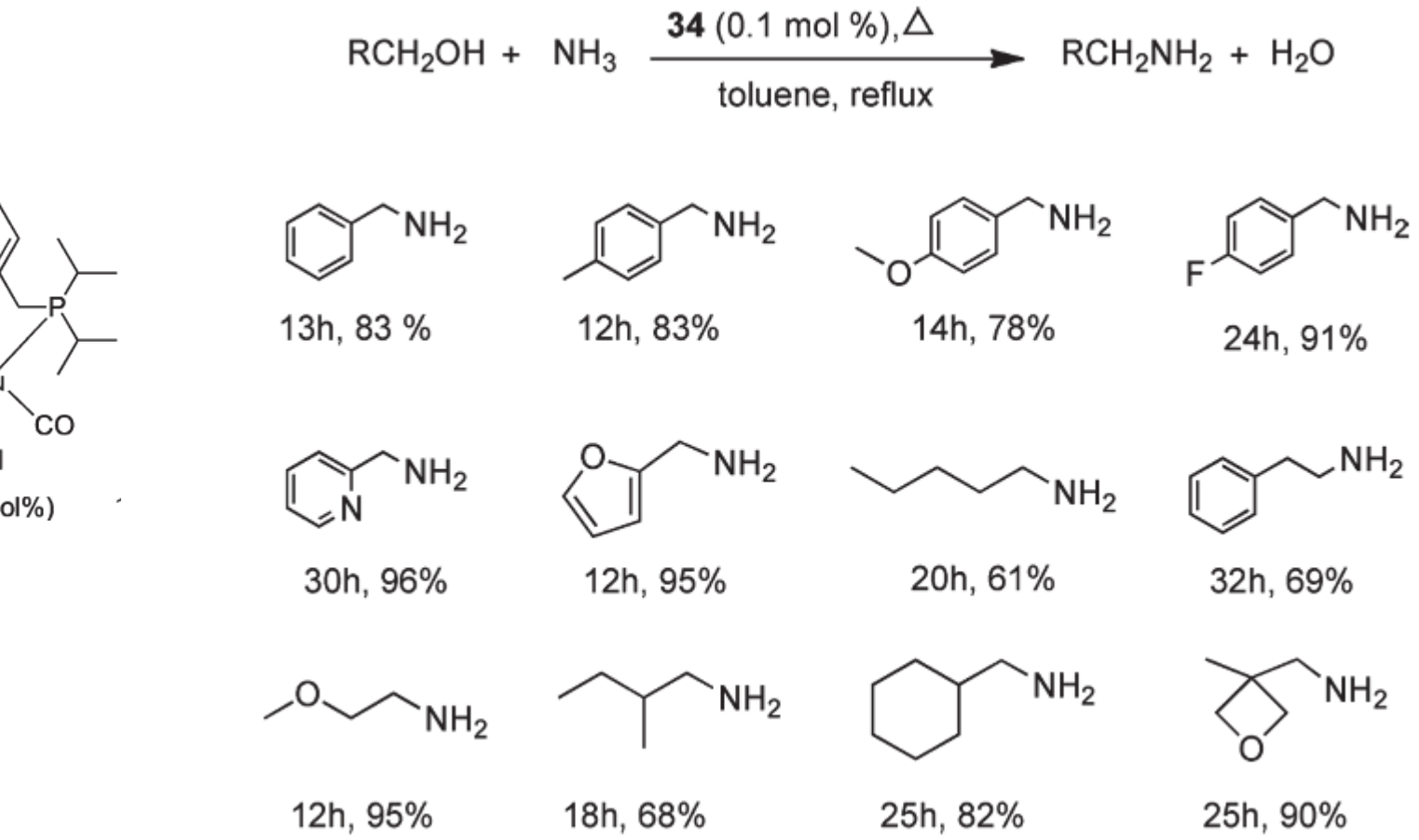
2e. Dehydrogenation of Alcohols to Acetals



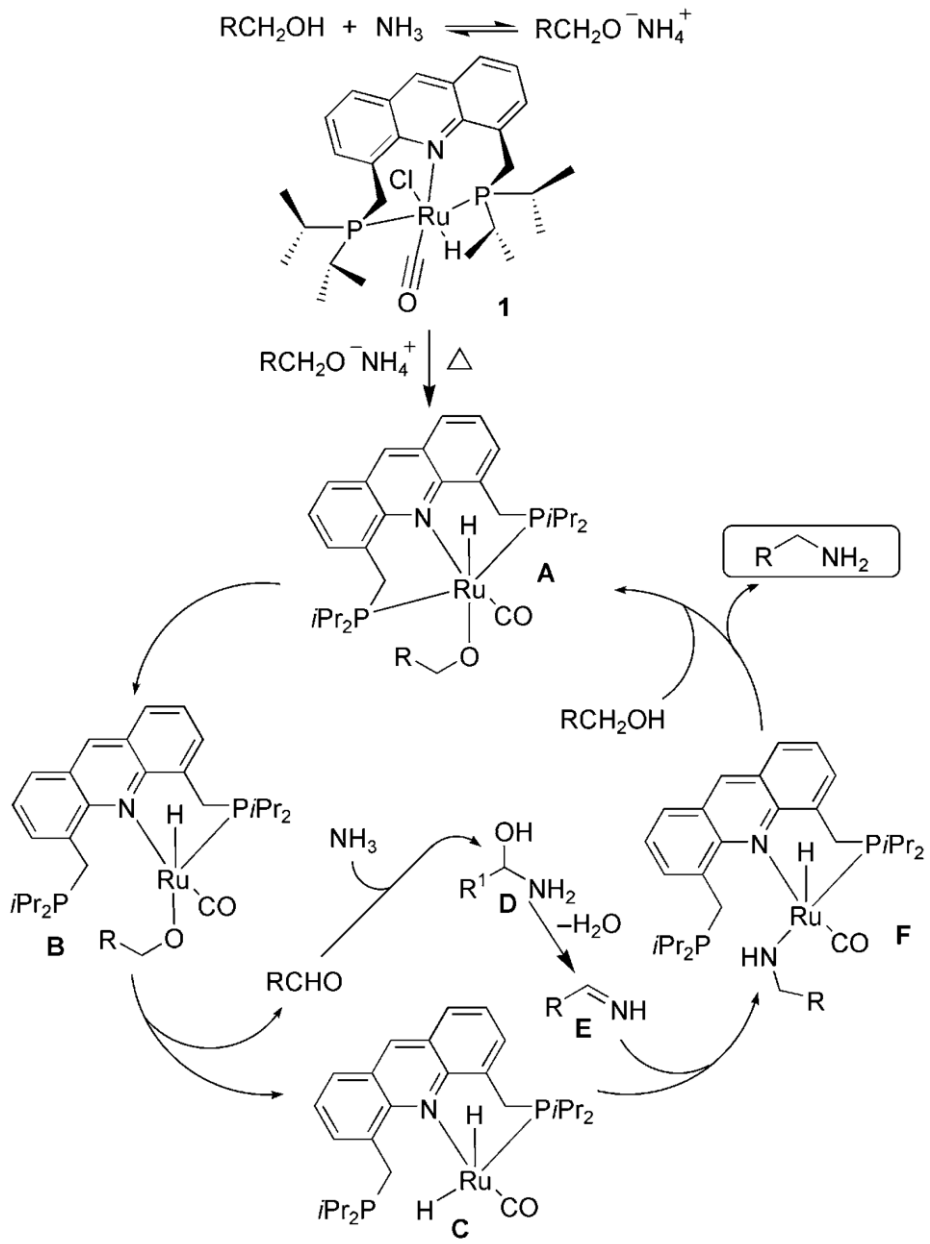


J. Am. Chem. Soc. **2009**, *131*, 3146-3147.

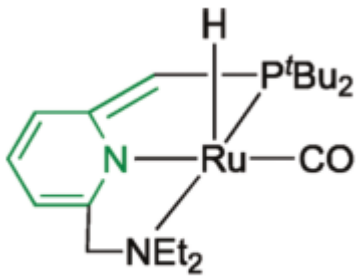
2f. Dehydrogenation of Alcohols (with ammonia) to Amines



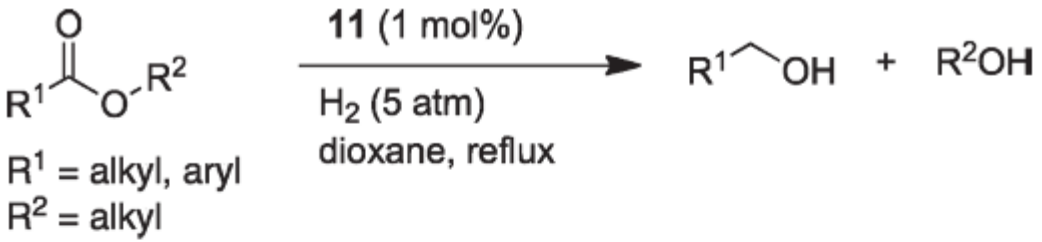
Angew. Chem., Int. Ed. **2008**, *47,* 8661-8664.


RCH2OH + NH3
RCH2O⁻NH4+
Cl
Ru
P
H
N
O
1
RCH2O⁻NH4+
△
PiPr2
iPr2P
CO
R
A
RCH2OH
R
NH2
B
NH3
OH
R1
NH2
D
–H2O
RCHO
R
NH
E
HN
F
C

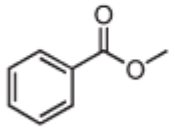
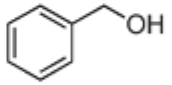
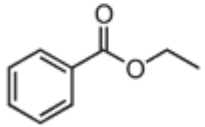
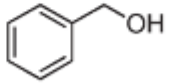
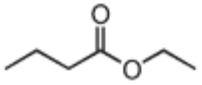
3a. Hydrogenation of Esters to Alcohols



11

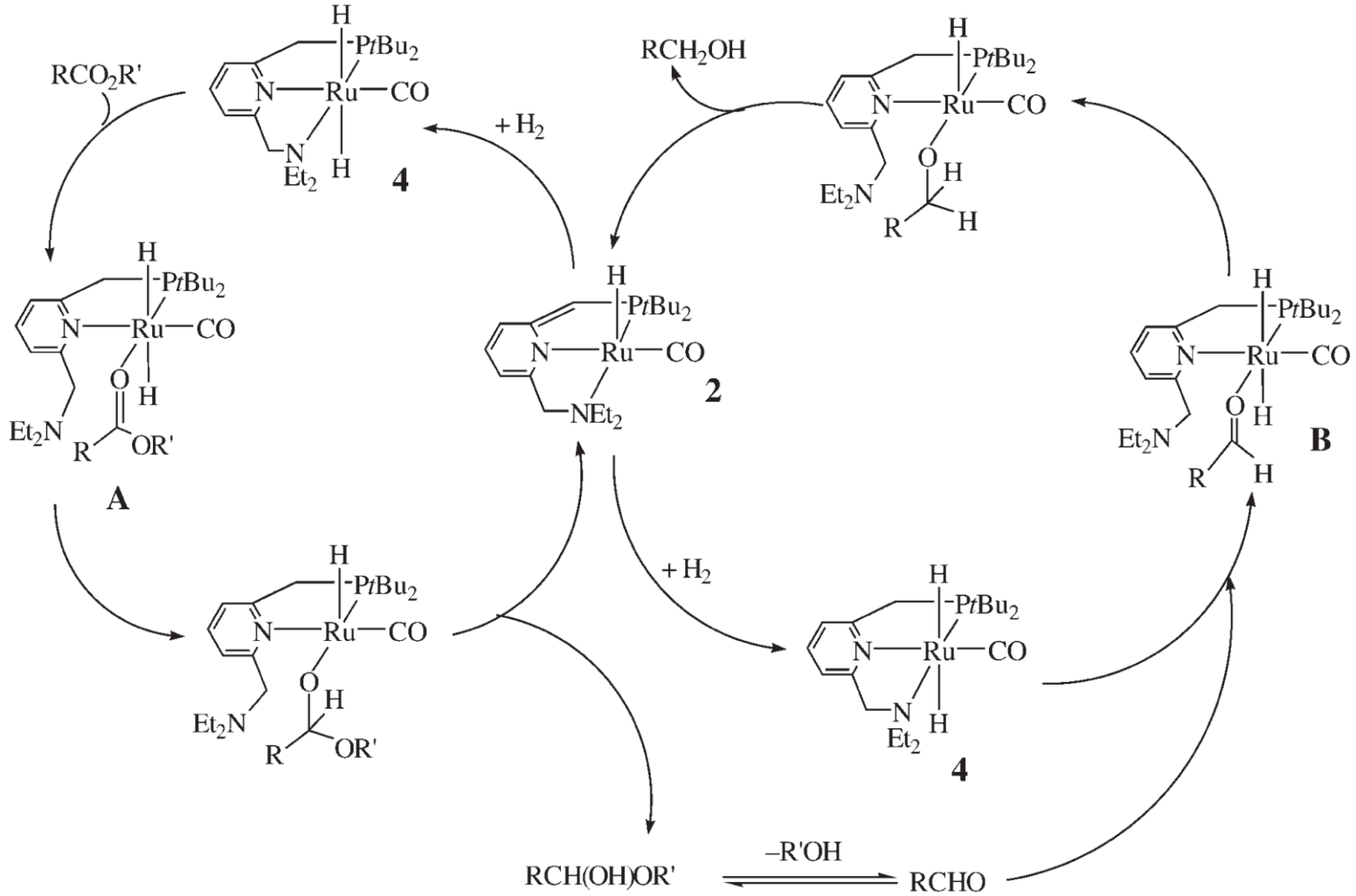


R^1 = alkyl, aryl
R^2 = alkyl

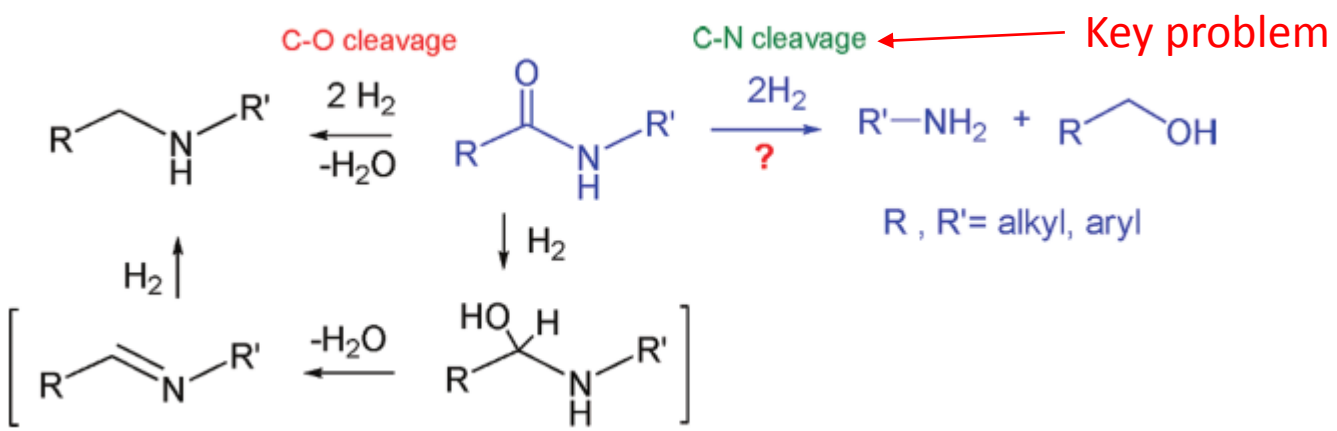
Entry	Ester	Time (h)	Conv. (%)	Alcohols (Yields, %)	
				RCH$_2$OH	R^{1}OH
1		4	100	 (97)	MeOH (100)
2		4	99.2	 (96)	EtOH (99)
3		4	100	 (98)	EtOH (98.6)

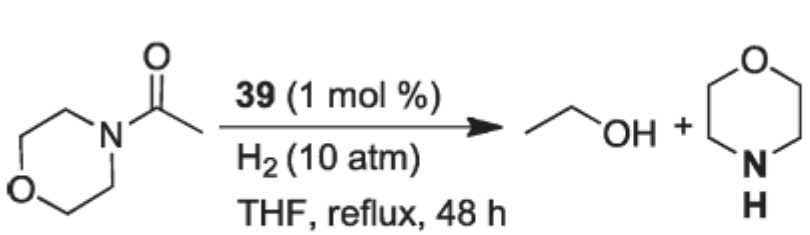
Angew. Chem., Int. Ed. **2006**, *45*, 1113-1115.

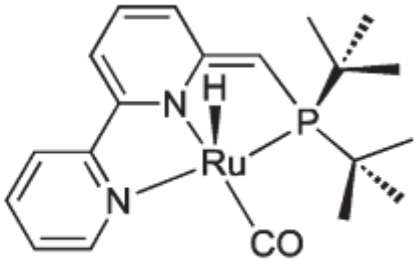
3a. Hydrogenation of Esters to Alcohols



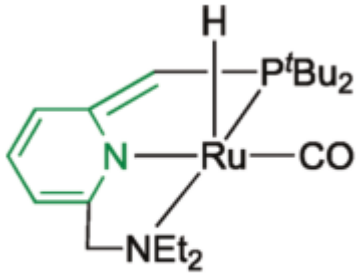
3b. Hydrogenation of Amides to Alcohols and Amines







39



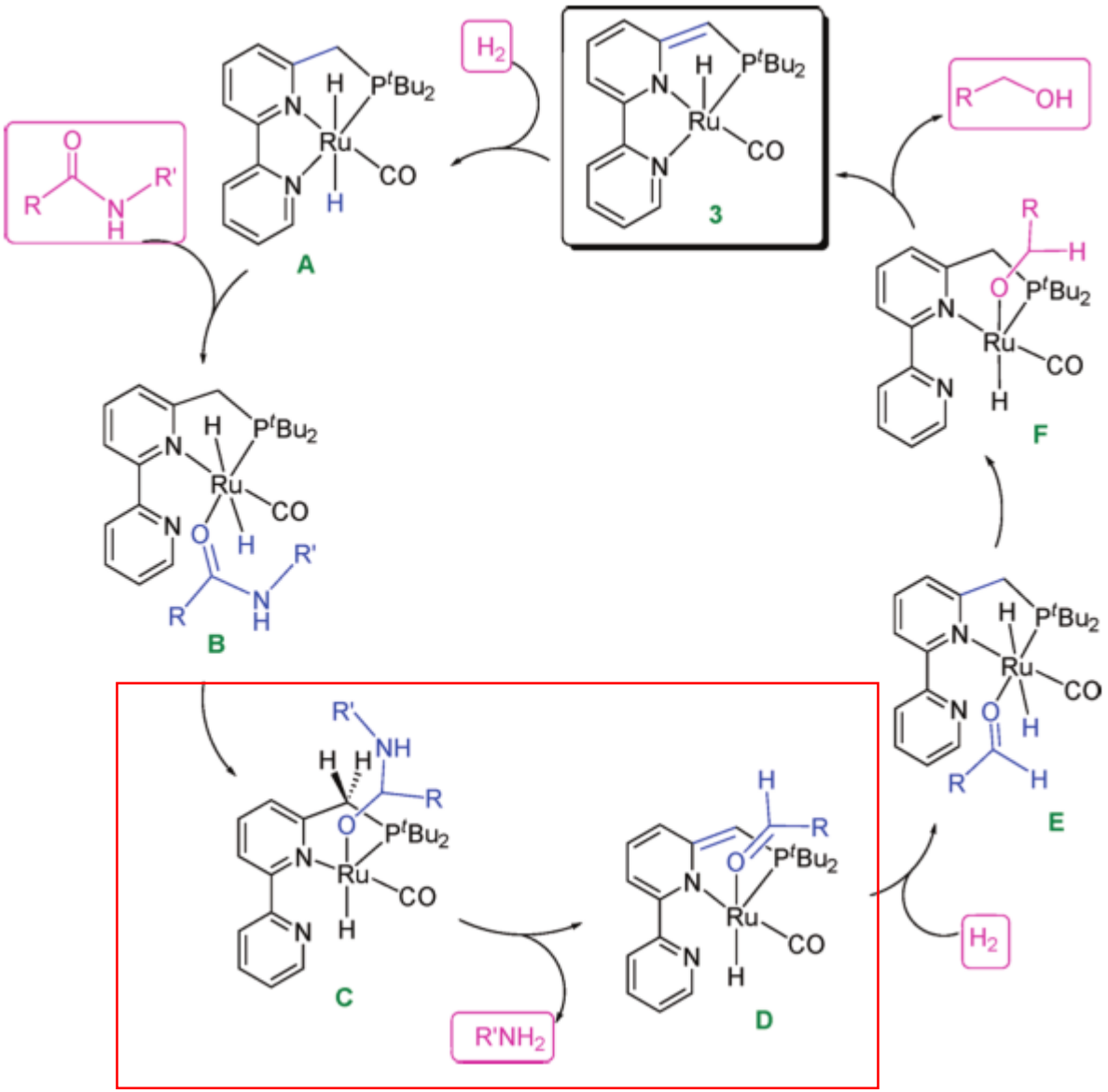
11

More efficient

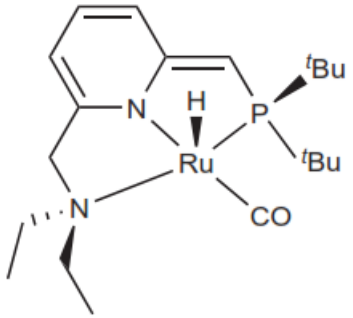
Less efficient

J. Am. Chem. Soc. **2010**, *132*:16756-16758.

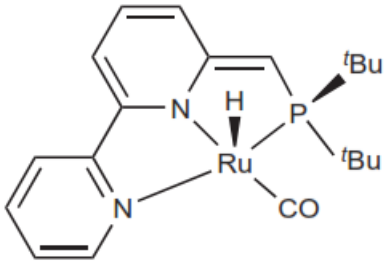
3b. Hydrogenation of Amides to Alcohols and Amines



3c. Hydrogenation of Carbonates to Methanol

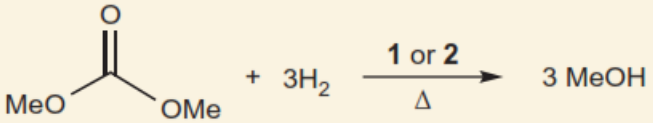


1



2

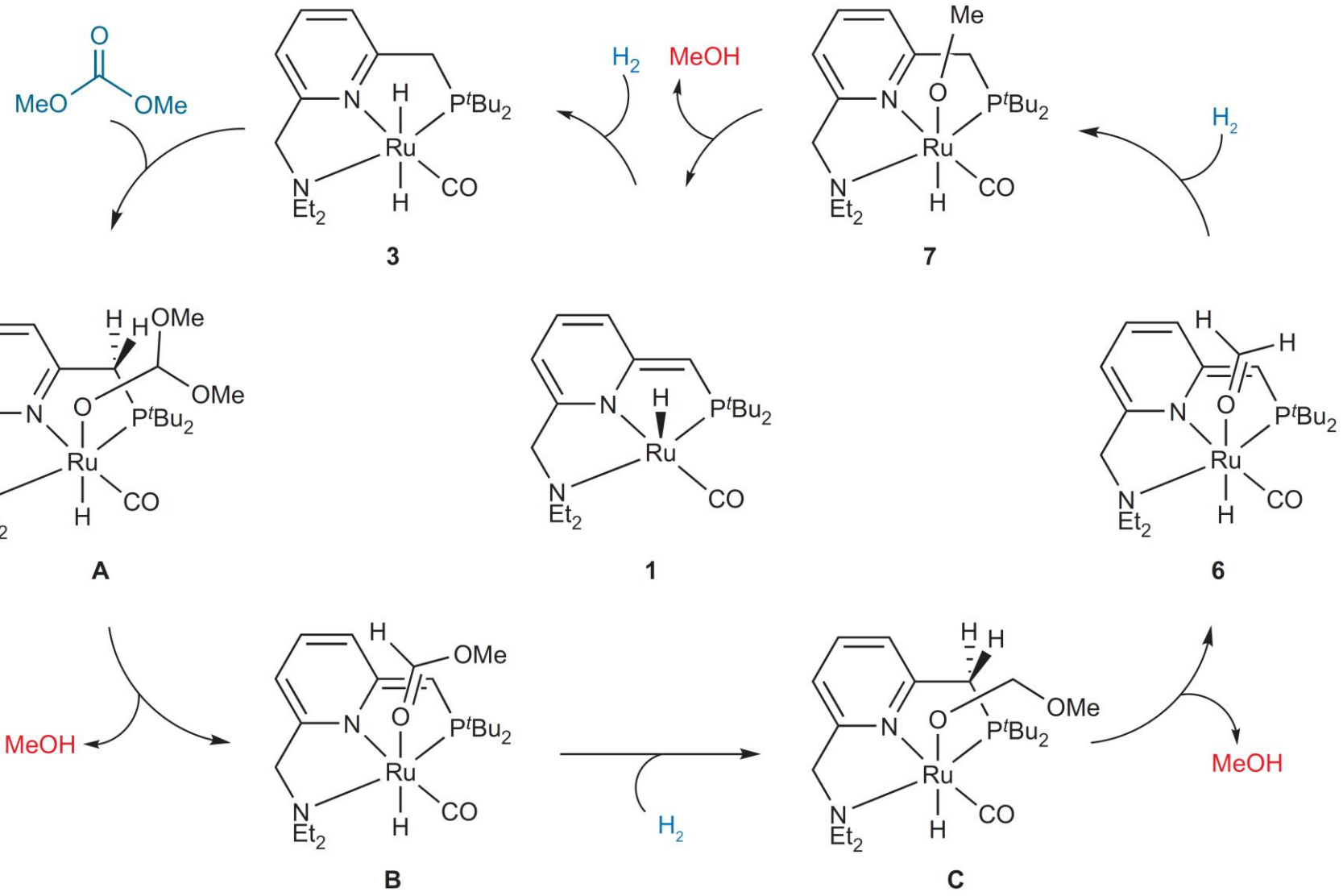
Table 1 | Hydrogenation of dimethyl carbonate to methanol.



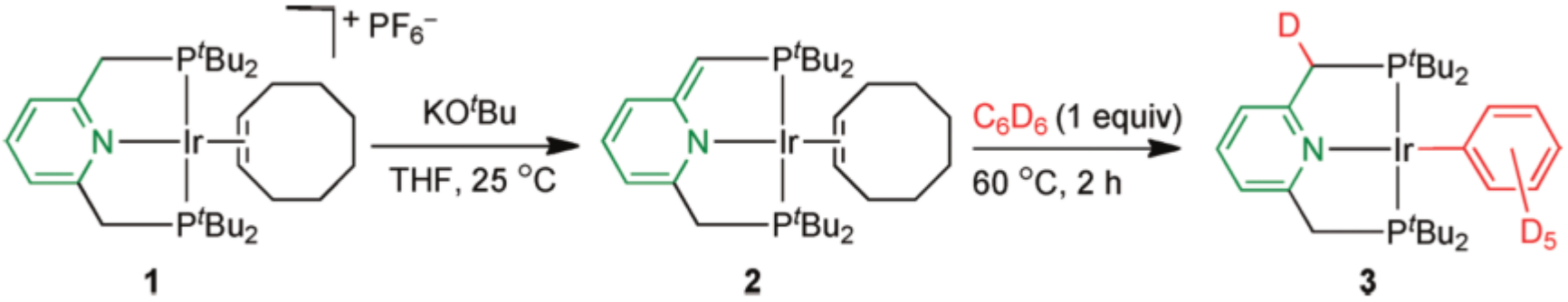
Entry	Cat.	Solvent	pH_2	Time (h)	Conv. (%)*	Yield (%)*	TON
1†	**1**	1,4-dioxane	40	3.5	>99	>99	2,500
2†	**1**	1,4-dioxane	60	1	>99	>99	2,500
3‡	**2**	THF	10	48	96	96	960
4§	**2**	THF	50	14	89	88	4,400
5¶	**2**	Neat	10	2	89	89	890
6¶	**2**	Neat	10	8	>99	>99	>990

*Yields of methanol and conversion of dimethyl carbonate were determined by gas chromatography (GC) using *m*-xylene as an internal standard. †Complex **1** (0.01 mmol), dimethyl carbonate (25 mmol) and 1,4-dioxane (20 ml) were heated in a Parr apparatus at 145 °C. ‡Complex **2** (0.01 mol) and dimethyl carbonate (10 mmol) were heated in a Fischer-Porter tube at 110 °C. §Complex **2** (0.005 mmol), dimethyl carbonate (25 mmol) and dry THF (5 ml) were heated in an autoclave at 110 °C. ¶Complex **2** (0.01 mmol) and dimethyl carbonate (10 mmol) were heated at 100 °C.

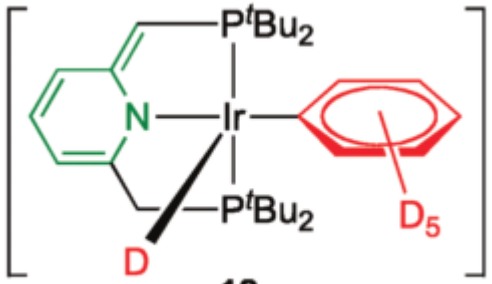
Nat. Chem. **2011**, *3*, 609.


MeO
OMe
O
N
H
Ru
P^{t}Bu$_2$
CO
Et$_2$
3
H$_2$
MeOH
Me
7
A
1
6
MeOH
B
C

4a. C—H bond Activation by PNP Ir(I) complex



1 2 3

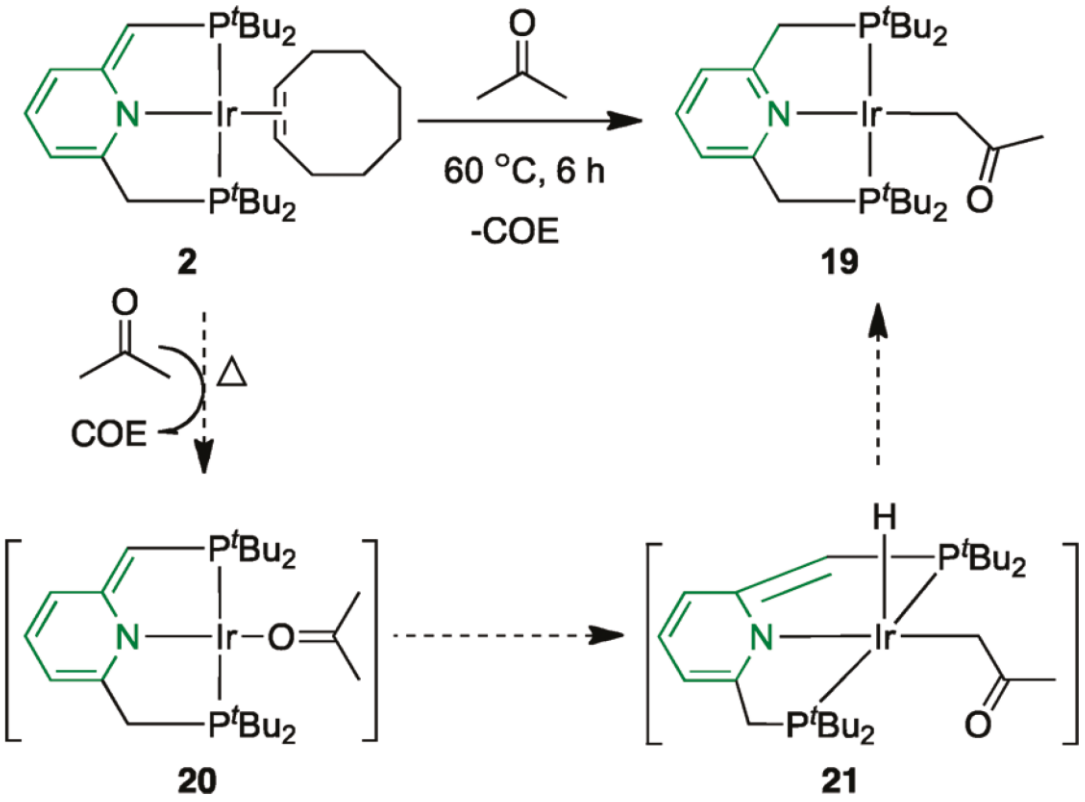


18

Not detected in this process

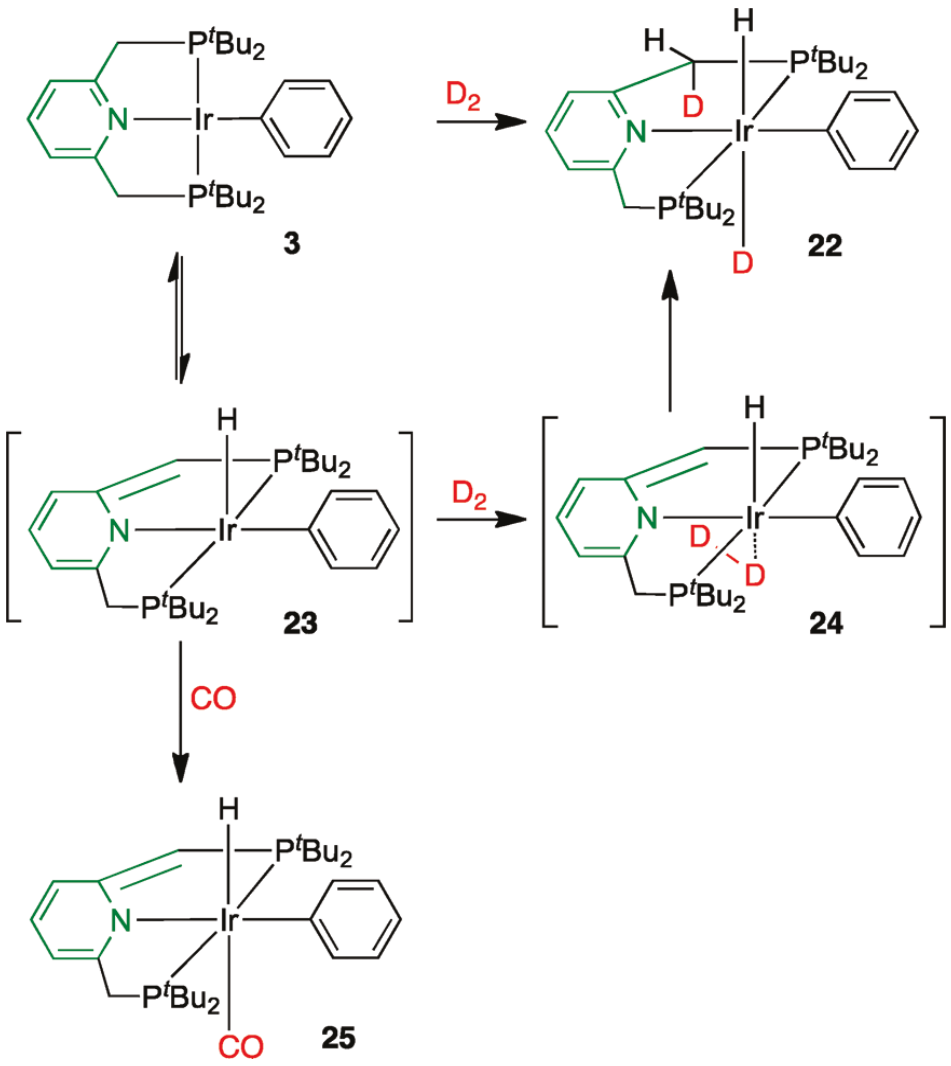
J. Am. Chem. Soc. **2006**, *128*, 15390–15391.

4a. C—H bond Activation by PNP Ir(I) complex



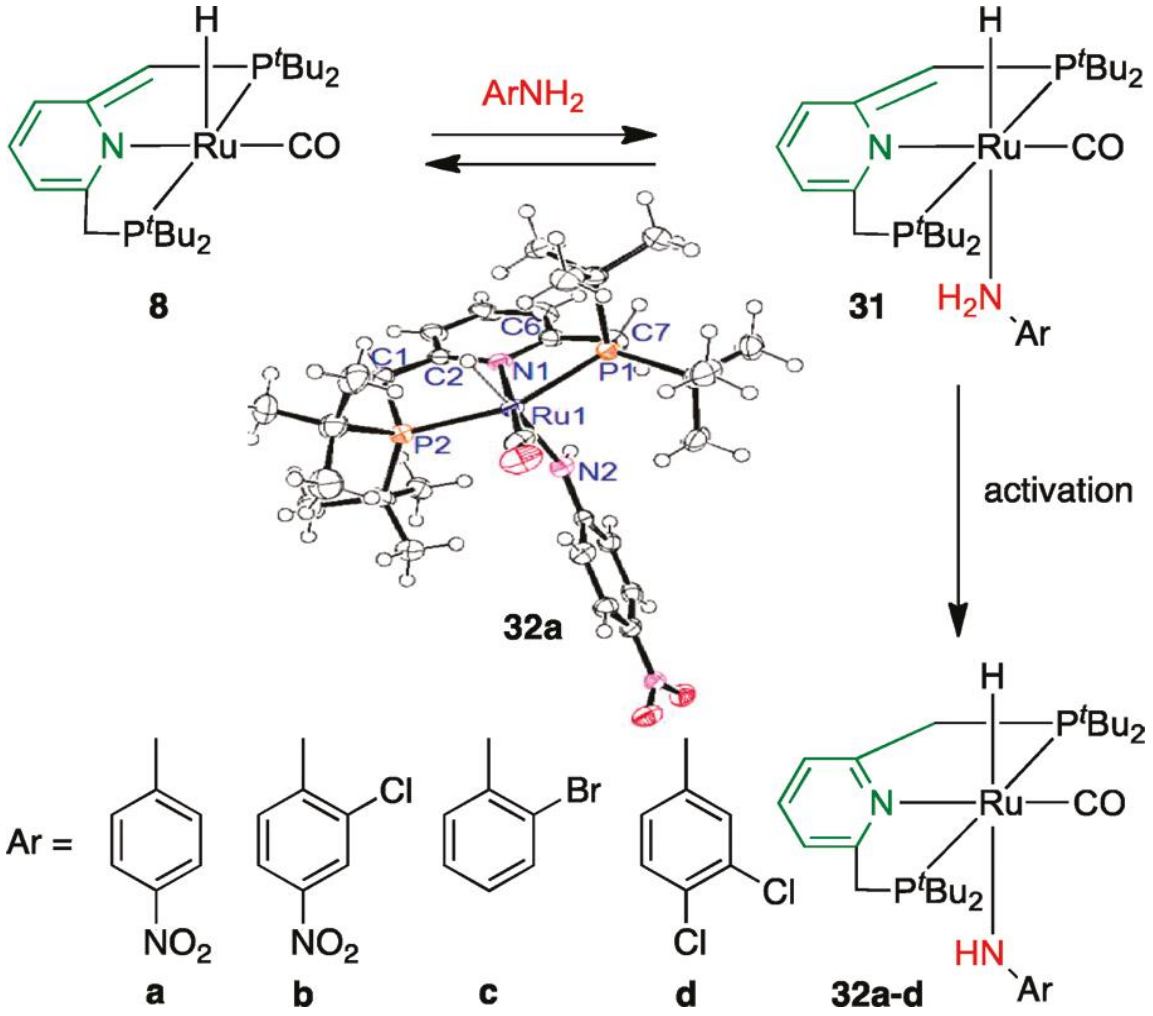
Organometallics **2010**, *29*, 3817–3827.

4b. H—H bond Activation by PNP Ir(I) complex



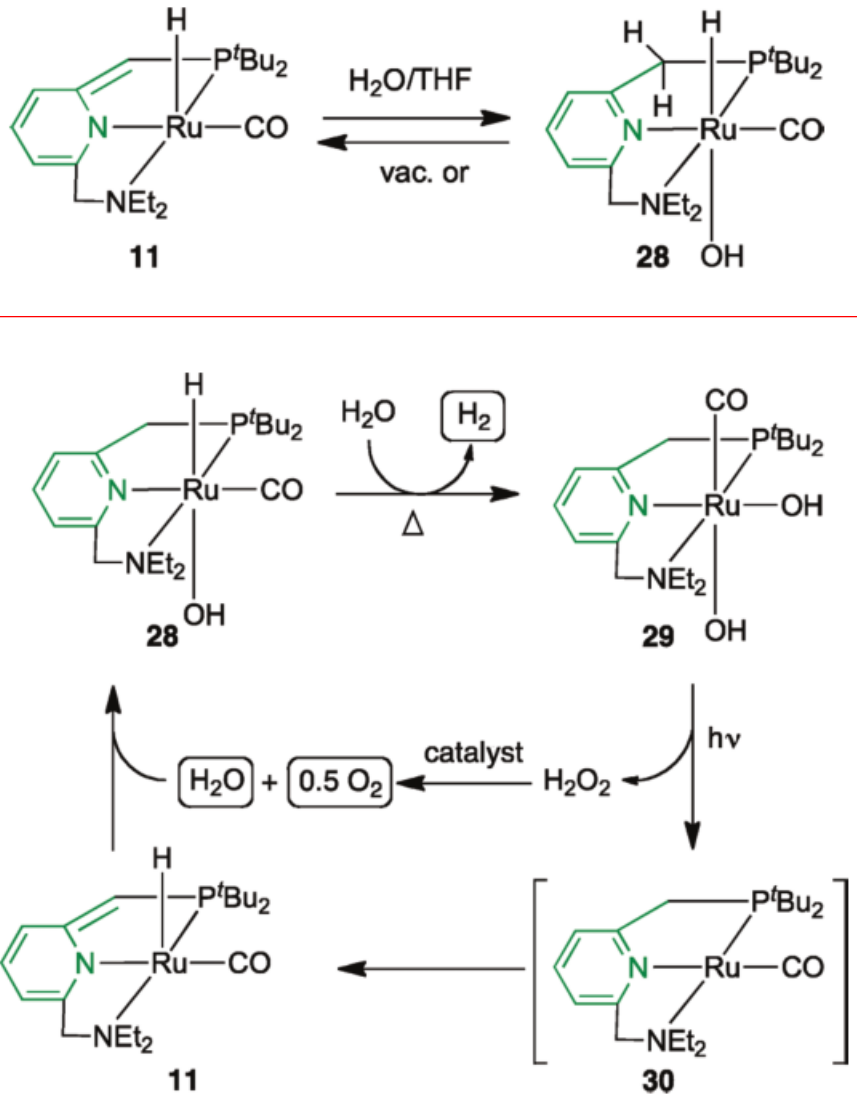
J. Am. Chem. Soc. **2006**, *128*, 15390–15391.

4c. N—H bond Activation by PNP Ru(I) complex



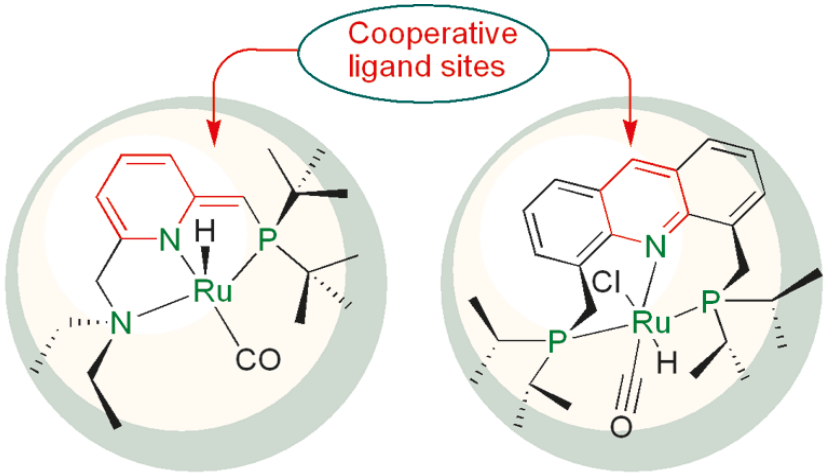
J. Am. Chem. Soc. **2010**, *132*, 8542–8543.

5. Splitting Water to H_2 and O_2



Science **2009**, *324*, 74–77.

6. Conclusion and Inspiration



I II

$$2RCH_2OH \xrightarrow{I} RCO_2CH_2R + 2H_2$$

$$R^1CH_2OH + R^2NH_2 \xrightarrow{I} R^1CONHR^2 + 2H_2$$

$$2R^1{}_2CHOH + R^2CO_2CH_2R^2 \xrightarrow{I} 2R^2CO_2CHR^1{}_2 + 2H_2$$

$$R^1CO_2CH_2R^1 + 2R^2NH_2 \xrightarrow{I} 2R^1CONHR^2 + 2H_2$$

$$R^1CO_2CH_2R^2 + 2H_2 \xrightarrow{I} R^1CH_2OH + R^2CH_2OH$$

$$3RCH_2OH \xrightarrow{II} RCH(OCH_2R)_2 + H_2 + H_2O$$

$$RCH_2OH + NH_3 \xrightarrow{II} RCH_2NH_2 + H_2O$$

Thanks!