

# Organic Reactions catalyzed by rhenium carbonyl complexes

Fanyang Mo  
Dong group seminar  
Feb. 26, 2014



# Periodic Table

ρ

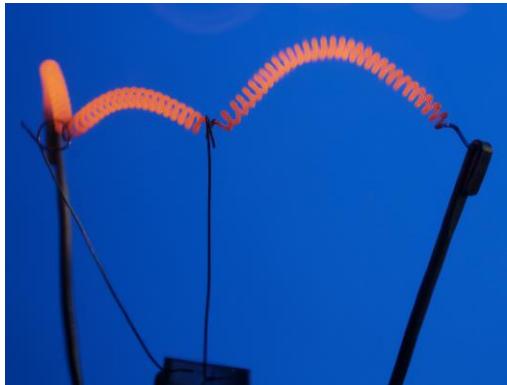
	I A																	VIII A				
I	H 1 1.0079 Hydrogen																	He 2 4.0026 Helium				
II	Li 3 6.941 Lithium	Be 4 9.0122 Beryllium																	Ne 10 20.18 Neon			
III	Na 11 22.99 Sodium	Mg 12 24.305 Magnesium																	Ar 18 39.948 Argon			
IV	K 19 39.098 Potassium	Ca 20 40.078 Calcium	Sc 21 44.956 Scandium	Ti 22 47.867 Titanium	V 23 50.942 Vanadium	Cr 24 51.99 Chromium	Mn 25 54.938 Manganese	Fe 26 55.845 Iron	Co 27 58.933 Cobalt	Ni 28 58.693 Nickel	Cu 29 63.546 Copper	Zn 30 65.38 Zinc	Al 13 26.982 Aluminum	Si 14 28.086 Silicon	P 15 30.974 Phosphorus	S 16 32.065 Sulfur	Cl 17 35.453 Chlorine	F 9 18.988 Fluorine	O 8 15.999 Oxygen	N 7 14.007 Nitrogen	B 5 10.81 Boron	He 2 4.0026 Helium
V	Rb 37 85.468 Rubidium	Sr 38 87.62 Strontium	Y 39 88.906 Yttrium	Zr 40 91.224 Zirconium	Nb 41 92.906 Niobium	Mo 42 95.95 Molybdenum	Tc 43 95.95 Technetium	Ru 44 101.07 Ruthenium	Rh 45 102.91 Rhodium	Pd 46 106.42 Palladium	Ag 47 107.87 Silver	Cd 48 112.41 Cadmium	In 49 114.82 Indium	Tl 50 118.71 Thallium	Sn 51 121.76 Tin	Sb 52 127.6 Antimony	Te 53 126.9 Tellurium	I 54 131.29 Iodine	Xe 55 131.29 Xenon			
VI	Cs 55 132.91 Cesium	Ba 56 137.33 Barium	*	Hf 72 178.49 Hafnium	Ta 73 180.95 Tantalum	W 74 183.8 Tungsten	Re 75 186.21 Rhenium	Os 76 190.23 Osmium	Ir 77 192.22 Iridium	Pt 78 195.08 Platinum	Ag 79 196.97 Silver	Hg 80 200.59 Mercury	Tl 81 204.38 Thallium	Pb 82 207.2 Lead	Bi 83 208.98 Bismuth	Po 84 209.98 Polonium	At 85 210 Astatine	Rn 86 222 Radium				
VII	Fr 87 223 Francium	Ra 88 226.03 Radium	**	Rf 104 261 Rutherfordium	Db 105 262 Dubnium	Sg 106 263 Seaborgium	Bh 107 262 Bohrium	Hs 108 265 Hassium	Mt 109 266 Meitnerium	Ds 110 269 Darmstadtium	Rg 111 272 Rutherfordium	Cn 112 277 Cn	Uut 113 287 Ununtrium	Fl 114 289 Fluorine	Uup 115 288 Ununpentium	Lv 116 289 Livermorium	Uus 117 290 Ununseptium	Uuo 118 294 Ununoctium				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18				

- Post-transition metal
- Metalloid
- Nonmetal
- Alkali metal
- Alkaline earth metal
- Halogen
- Noble gas
- Transition metal
- Lanthanide
- Actinide

*	La 57 138.91 Lanthanum	Ce 58 140.12 Cerium	Pr 59 140.91 Praseodymium	Nd 60 144.24 Neodymium	Pm 61 146.9 Promethium	Sm 62 150.36 Samarium	Eu 63 151.96 Europium	Gd 64 157.25 Gadolinium	Tb 65 158.93 Terbium	Dy 66 162.5 Dysprosium	Ho 67 164.93 Holmium	Er 68 167.26 Erbium	Tm 69 168.93 Thulium	Yb 70 173.05 Ytterbium	Lu 71 174.97 Lutetium
**	Ac 89 227 Actinium	Th 90 232.04 Thorium	Pa 91 231.04 Protactinium	U 92 238.03 Uranium	Np 93 237.09 Neptunium	Pu 94 244.1 Plutonium	Am 95 243.1 Americium	Cm 96 247.1 Curium	Bk 97 247.1 Berkelium	Cf 98 251.1 Californium	Einsteinium 99 254.1 Einsteinium	Fm 100 257.1 Fermium	Md 101 258 Mendelevium	No 102 259 Nobelium	Lr 103 260 Lawrencium

Accidentally found by Ogawa in 1908, and officially discovered by Noddack, Tacke, and Berg in 1925.

# General Applications in Industry



Filament

(high melting point 3186 °C)



Jet engine



Petroleum purification  
(Platinum-rhenium catalysts)

# Contents

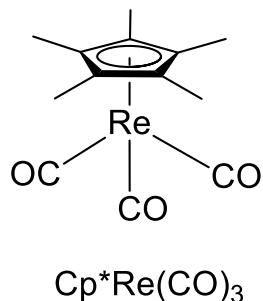
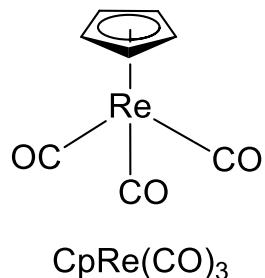
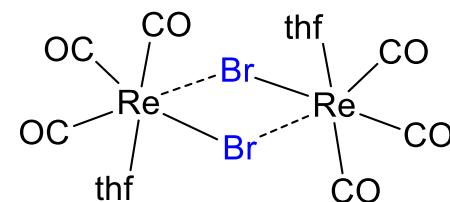
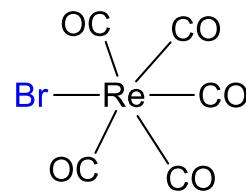
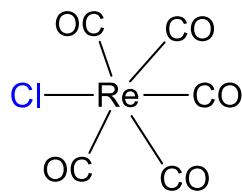
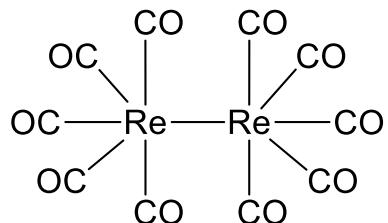
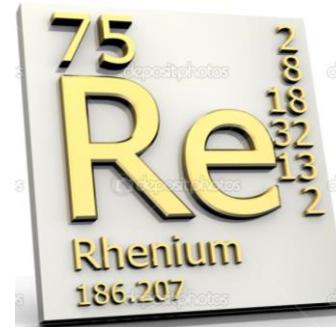
## 1. Introduction

## 2. C—C bond formation

- 2.1 Friedel-Crafts
- 2.2 Nucleophilic addition
- 2.3 Annulations
- 2.4 C—H bond activation
- 2.5 C—C bond cleavage

## 3. Conclusion

# 1. Introduction



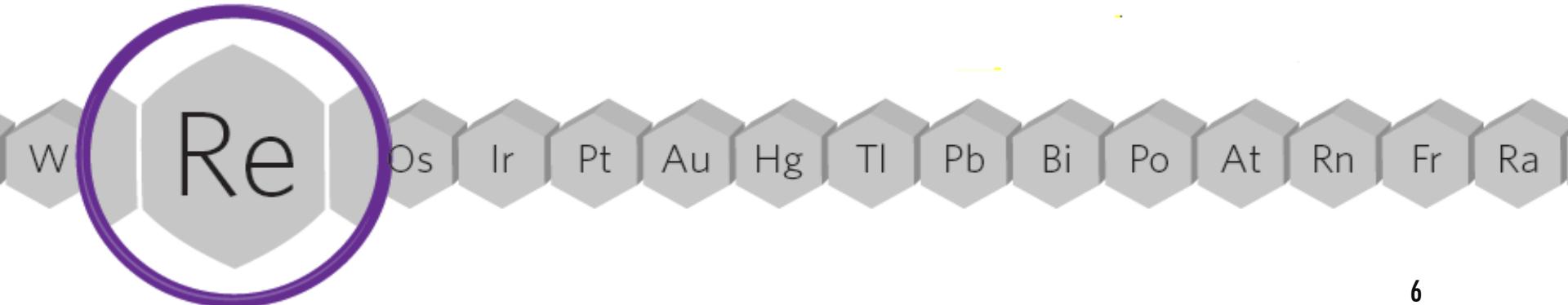
## Four notable features

- Hard Lewis acidity (O, N, halides)
- Soft Lewis acidity (unsaturated compounds)
- Ability to activate C—H bond
- Promote oxidative cyclization

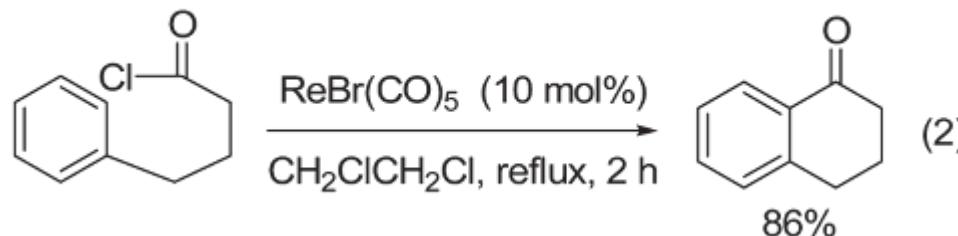
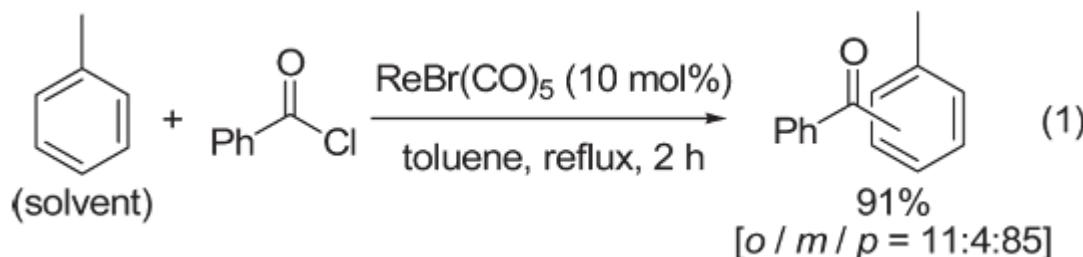
Commercially available Rhenium carbonyl complexes.

## 2. C—C bond formation

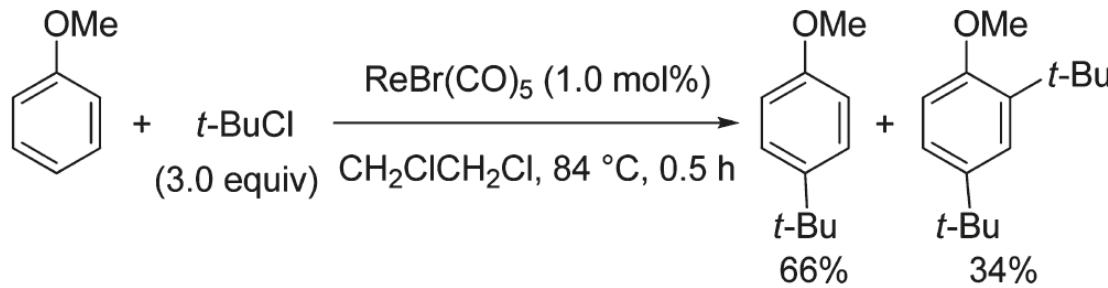
- 2.1 Friedel-Crafts
- 2.2 Nucleophilic addition
- 2.3 Annulations
- 2.4 C—H bond activation
- 2.5 C—C bond cleavage



## 2.1 Friedel-Crafts Reactions

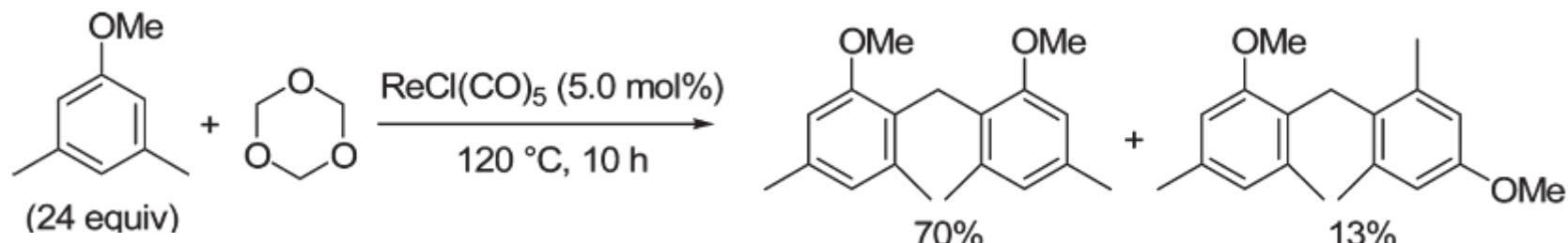


Kusama, H.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1995**, 68, 2379.



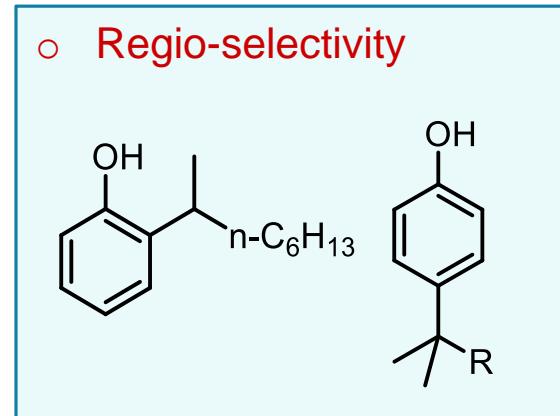
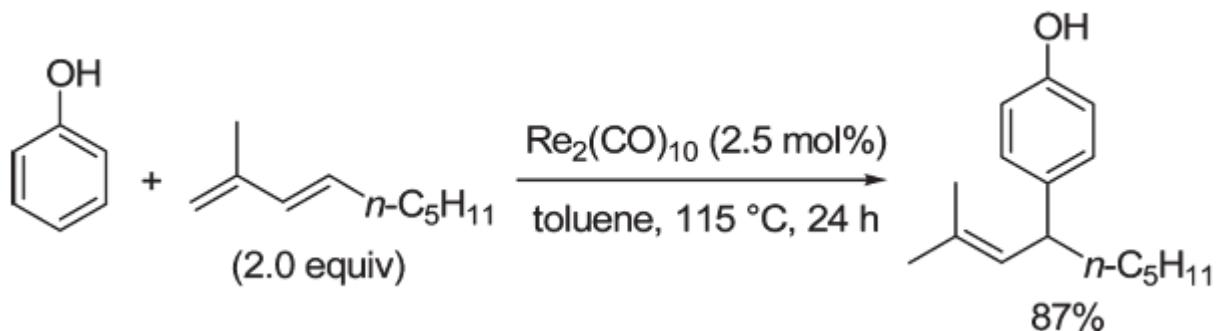
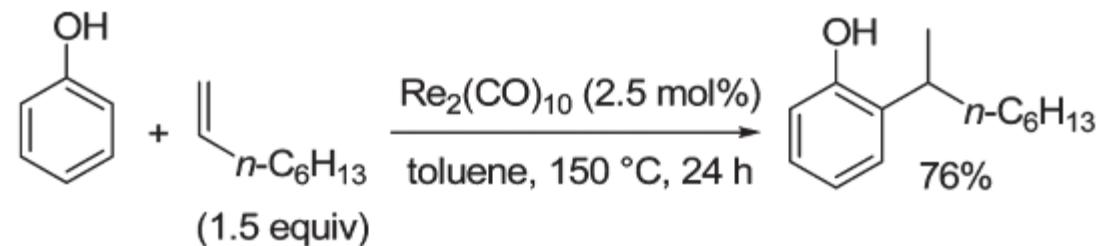
Nishiyama, Y.; Kakushou, F.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **2000**, 73, 2779.

## 2.1 Friedel-Crafts Reactions



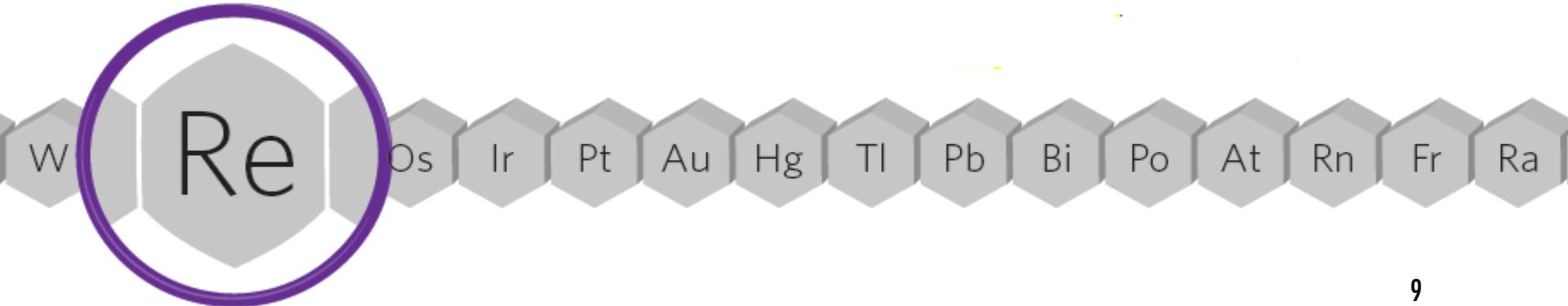
Hua, R.; He, J.; Sun, H. *Chin. J. Chem.* **2007**, 25, 132.

- Regio-selectivity

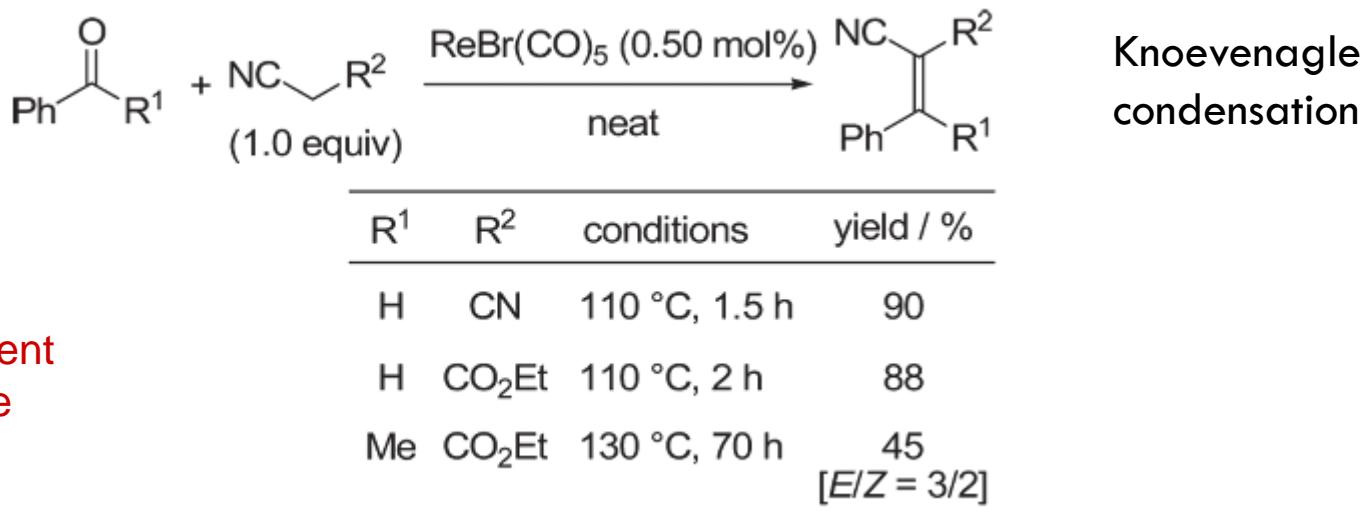


## 2. C—C bond formation

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- 2.3 Annulations
- 2.4 C—H bond activation
- 2.5 C—C bond cleavage

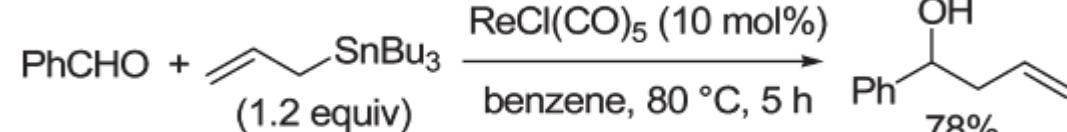


## 2.2 Nucleophilic addition to carbonyl compounds



- No solvent
- No base

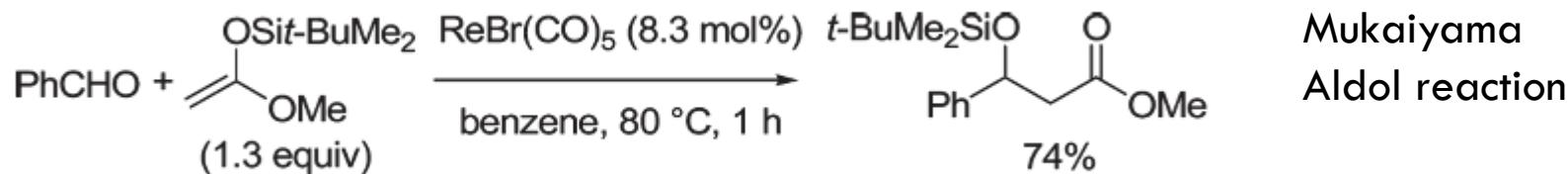
Zuo, W.-X.; Hua, R.; Qiu, X. *Synth. Commun.* **2004**, *34*, 3219.



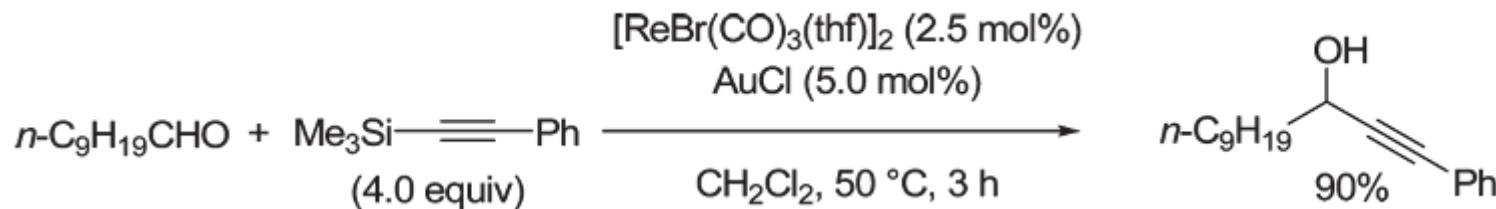
Nishiyama, Y.; Kakushou, F.; Sonoda, N.  
*Tetrahedron Lett.* **2005**, *46*, 787.

Entry	Re complex	Solvent	Yield (%) <sup>a</sup>
1	$\text{ReBr}(\text{CO})_5$	Benzene	83
2	$\text{ReBr}(\text{CO})_5$	Toluene	80
3	$\text{ReCl}(\text{CO})_5$	Benzene	75
4	$\text{ReBr}(\text{CO})_4(\text{PPh}_3)$	Benzene	27
5	$\text{Re}_2(\text{CO})_{10}$	Benzene	Trace
6	$\text{CpRe}(\text{CO})_3$	Benzene	Trace
7	$\text{ReBr}(\text{CO})_5$	$\text{CH}_2\text{ClCH}_2\text{Cl}$	72
8	$\text{ReBr}(\text{CO})_5$	$\text{CHCl}_3$	54
9	$\text{ReBr}(\text{CO})_5$	THF	0
10	$\text{ReBr}(\text{CO})_5$	$\text{CH}_3\text{CN}$	0
11	$\text{ReBr}(\text{CO})_5$	$\text{CH}_3\text{OH}$	23

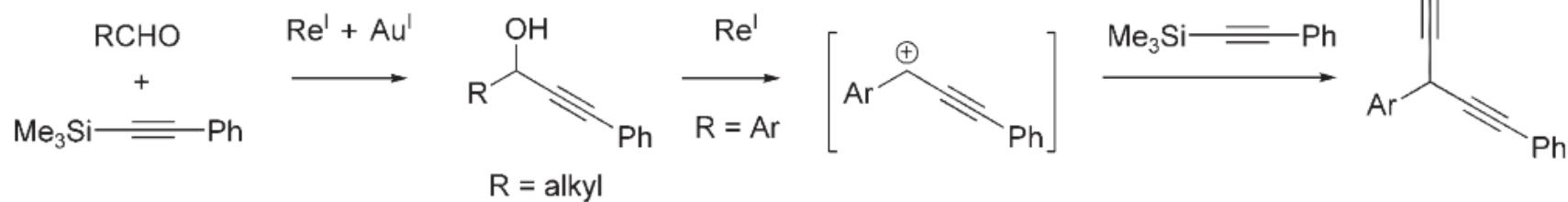
## 2.2 Nucleophilic addition to carbonyl compounds



Nishiyama, Y.; Kaiba, K.; Umeda, R. *Tetrahedron Lett.* **2010**, *51*, 793.



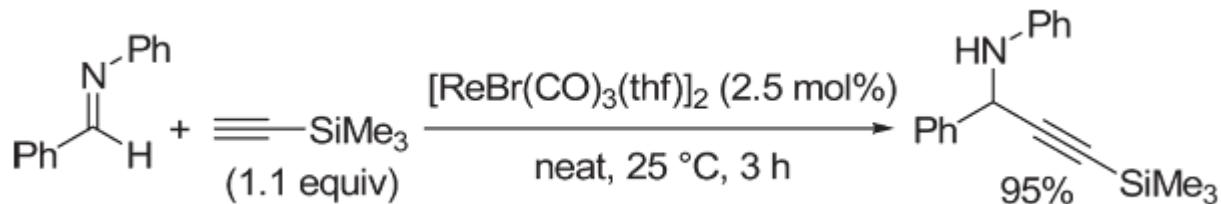
### ○ Mechanism:



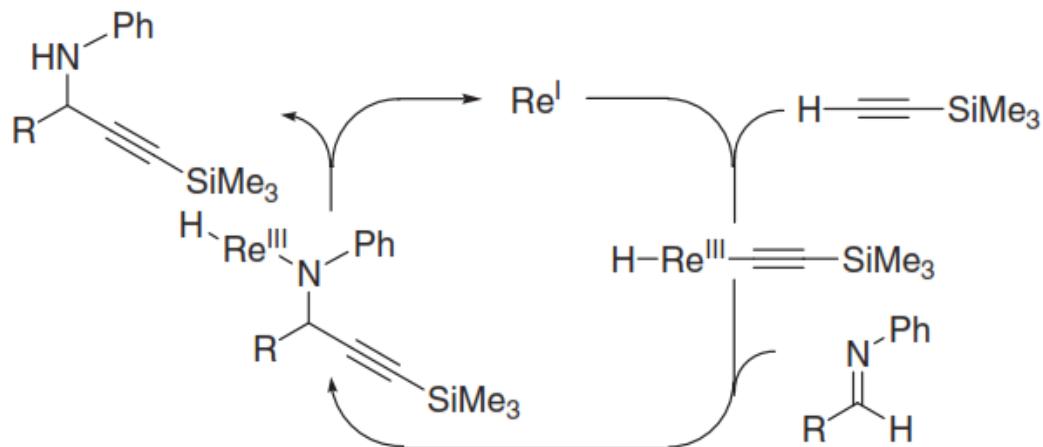
Kuninobu, Y.; Ishii, E.; Takai, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3296.

## 2.2 Nucleophilic addition to carbonyl compounds

- Imine as electrophile



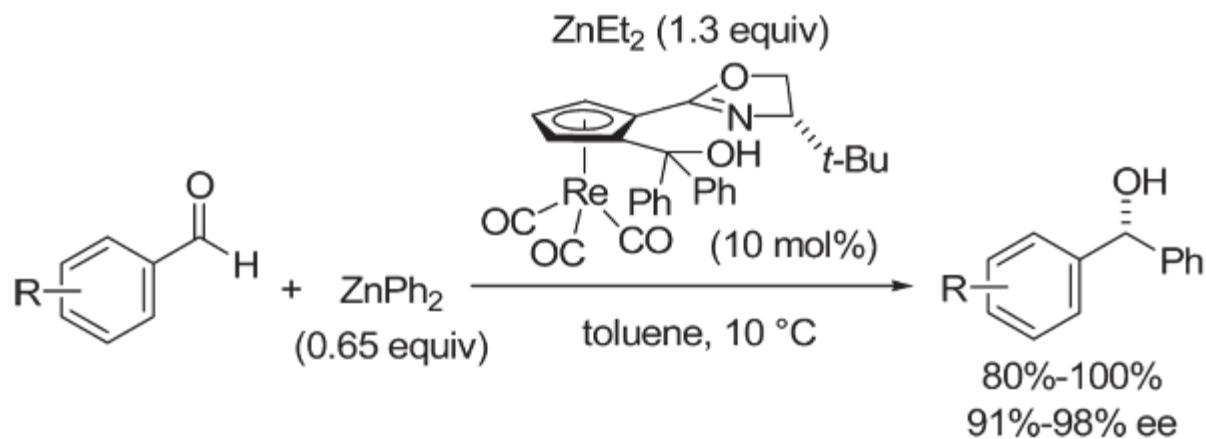
- Mechanism:



For *H*-alkynyl-rhenium complexes, see:  
a) K.-W. Lee; W. T. Pennington; A. W. Cordes; T. L. Brown, *J. Am. Chem. Soc.* **1985**, *107*, 631. b) K.-W. Lee; T. L. Brown, *Organometallics* **1985**, *4*, 1025.

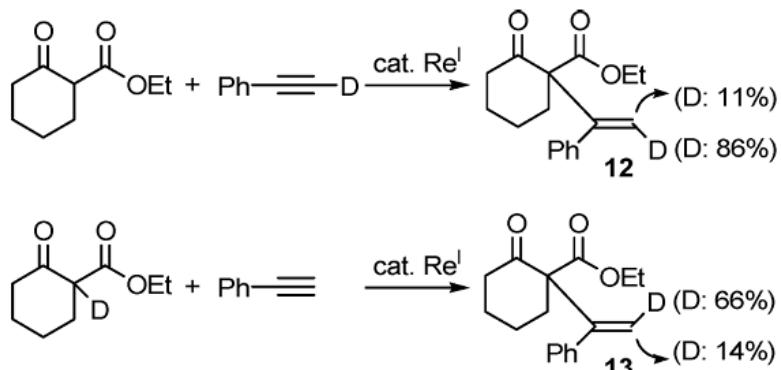
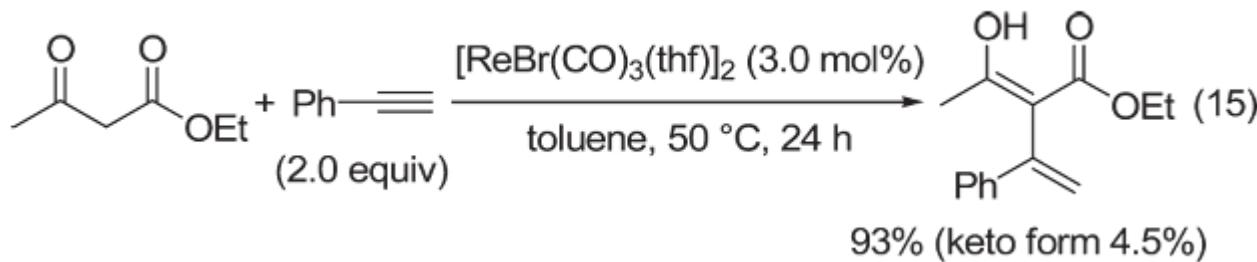
## 2.2 Nucleophilic addition to carbonyl compounds

- Enantioselective addition



Bolm, C.; Kesselgruber, M.; Hermanns, N.; Hildebrand, J. P.;  
Raabe, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1488.

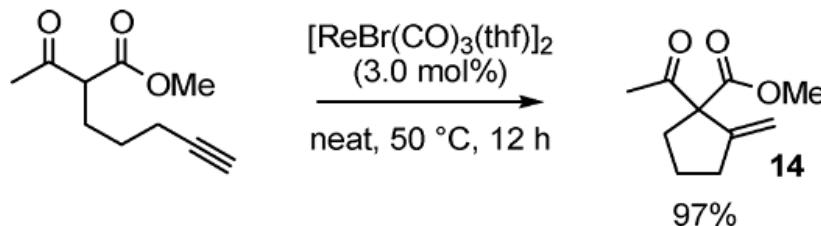
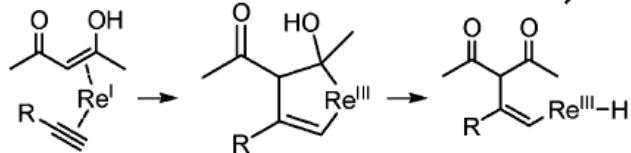
## 2.2 Nucleophilic addition to C—C unsaturated bond



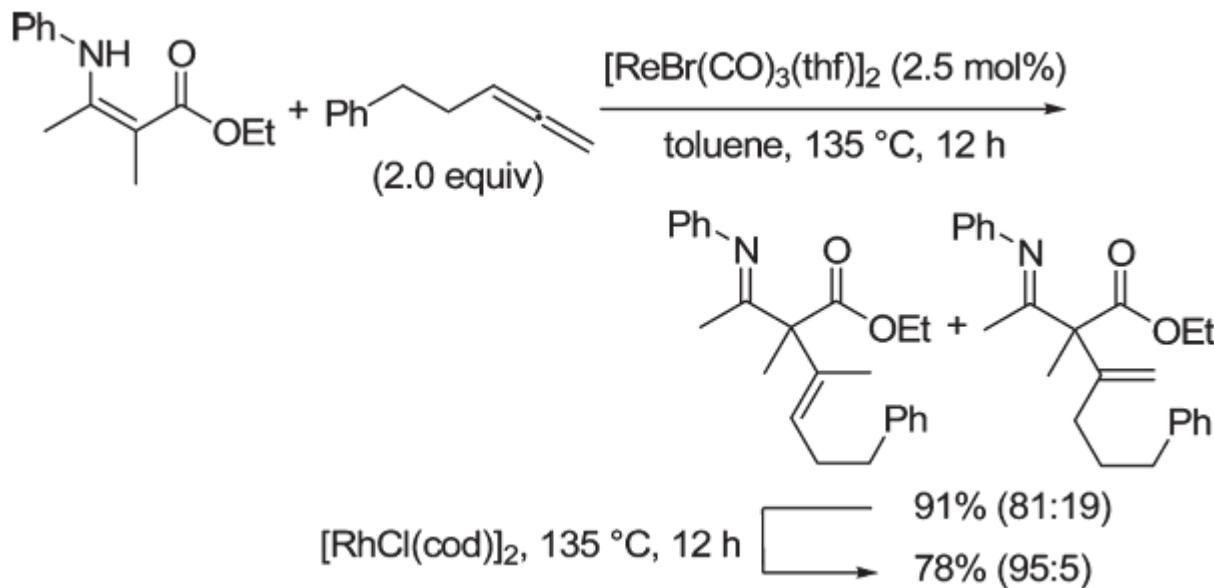
mechanism A



mechanism B



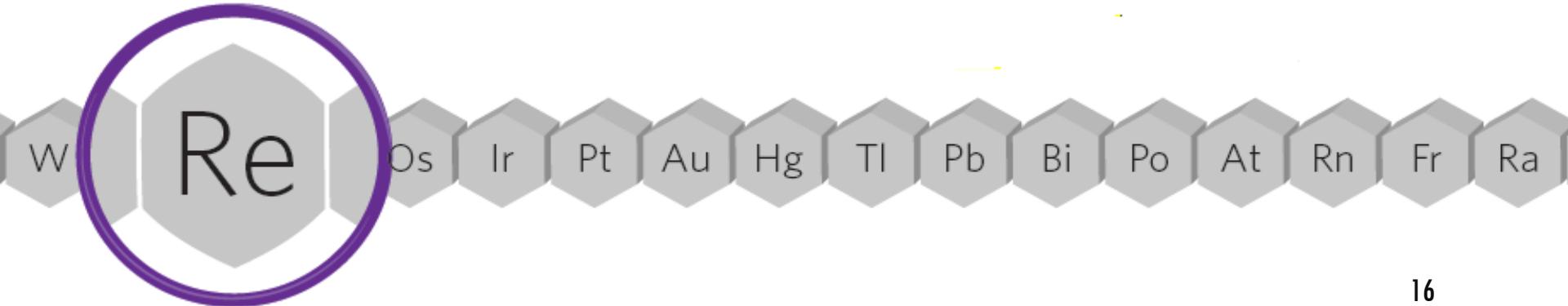
## 2.2 Nucleophilic addition to C—C unsaturated bond



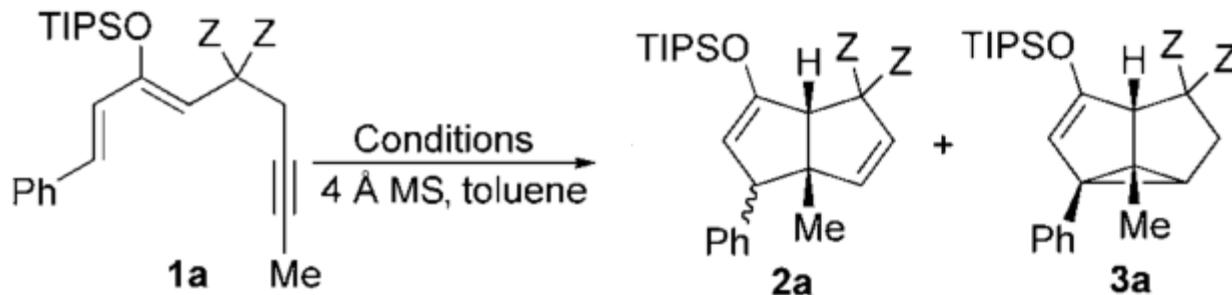
Kuninobu, Y.; Yamashita, A.; Yamamoto, S.-i.; Yudha, S. S.; Takai, K. *Synlett* **2009**, 3027.

## 2. C—C bond formation

- 2.1 Friedel-Crafts
- 2.2 Nucleophilic addition
- 2.3 Annulations
- 2.4 C—H bond activation
- 2.5 C—C bond cleavage



## 2.3 Annulations

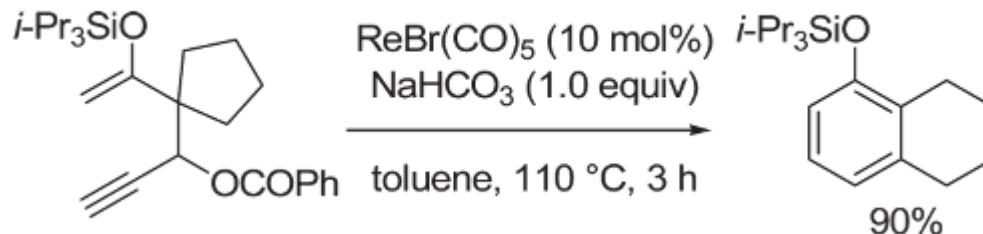


Conditions	<i>t</i> [h]	Yield ( <b>2a+3a</b> ) [%]	<b>2a</b> ( $\alpha:\beta$ ): <b>3a</b>
[W(CO) <sub>6</sub> ] (10 mol %), <i>hν</i>	4	88	86(9:1):14
[PtCl <sub>2</sub> ] (10 mol %), 70 °C	48	67	59(1.3:1):41
[AuBr <sub>3</sub> ] (10 mol %), RT	24	79	65(7.7:1):35
[ReCl(CO) <sub>5</sub> ] (10 mol %), <i>hν</i>	3	98	91(12.5:1):9
[ReCl(CO) <sub>5</sub> ] (0.5 mol %), <i>hν</i>	16	92	86(4.2:1):14

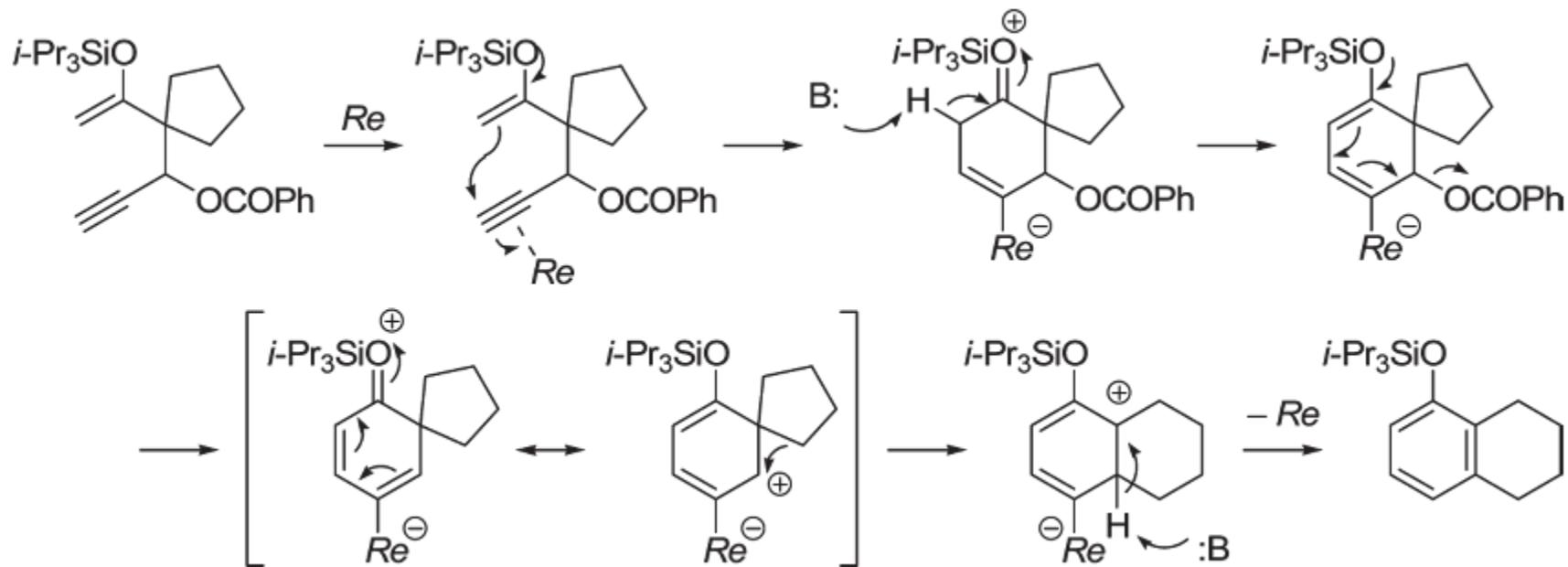
Z = CO<sub>2</sub>Me, TIPS = triisopropylsilyl, MS = molecular sieves.

Quiz 1: The mechanisms for both **2a** and **3a** formation?

## 2.3 Annulations



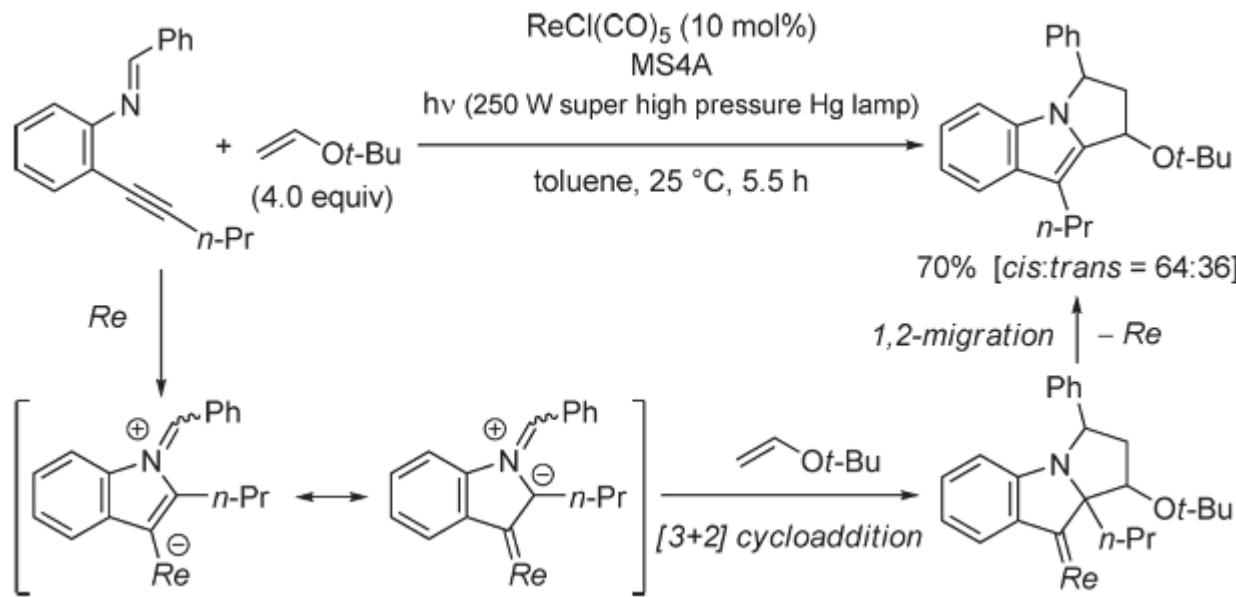
- Mechanism:



Saito, K.; Onizawa, Y.; Kusama, H.; Iwasawa, N. *Chem.-Eur. J.* **2010**, *16*, 4716.

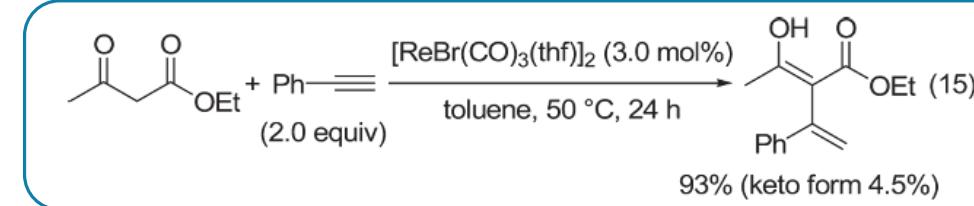
## 2.3 Annulations

- [3+2]

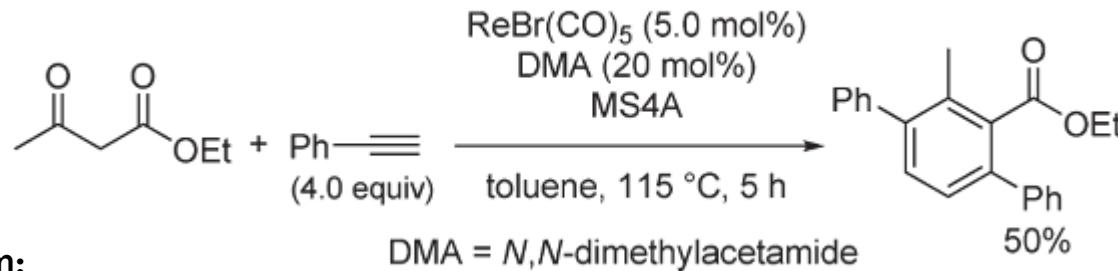


Kusama, H.; Miyashita, Y.; Takaya, J.; Iwasawa, N. *Org. Lett.* **2006**, 8, 289.

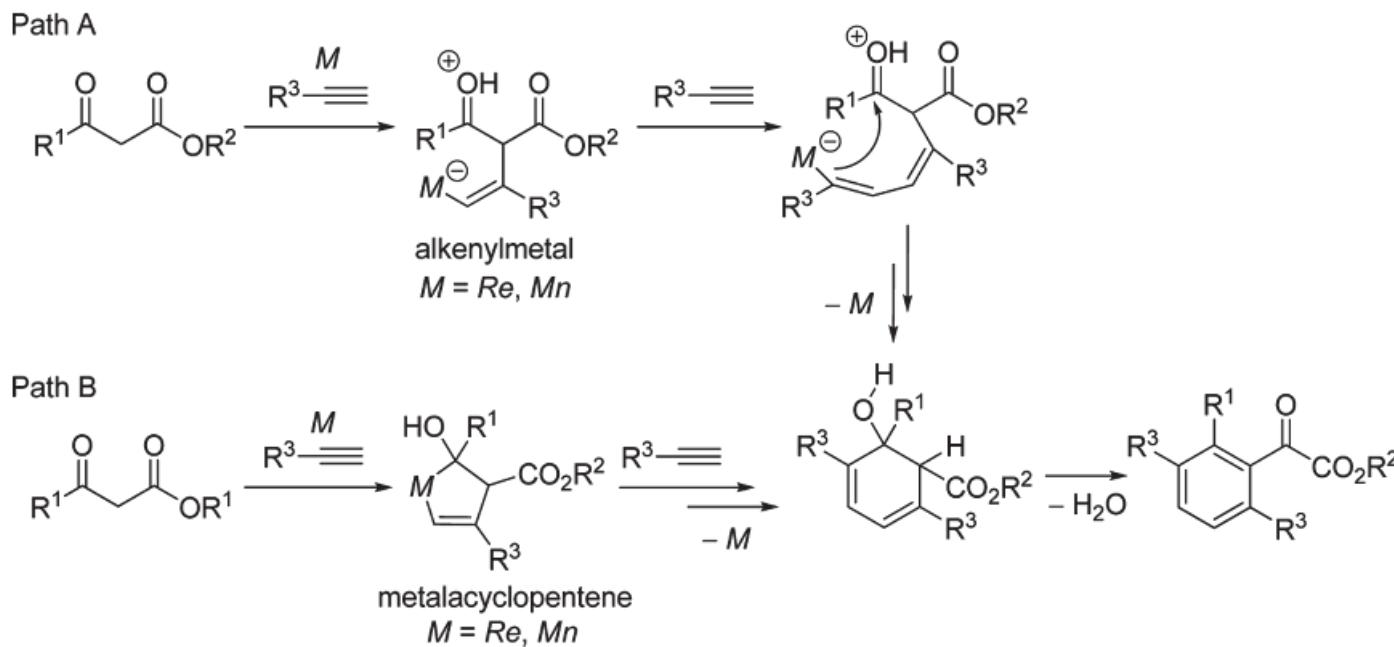
## 2.3 Annulations



OL 2005  
Slide 14



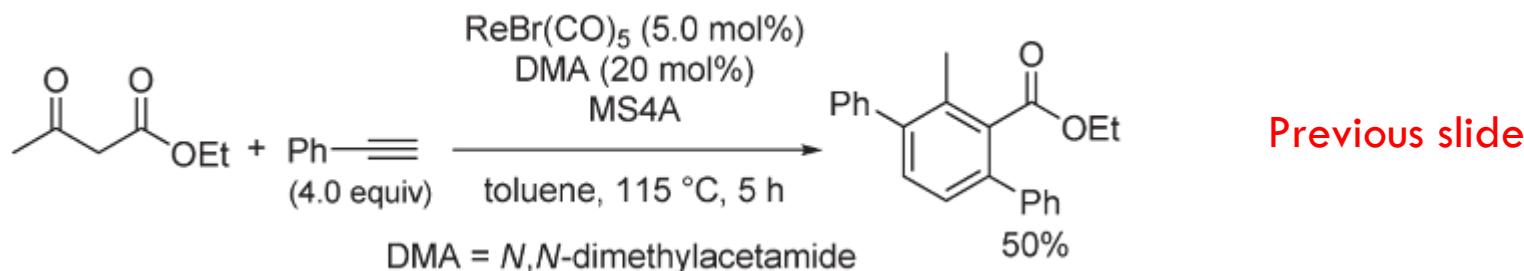
- Mechanism:



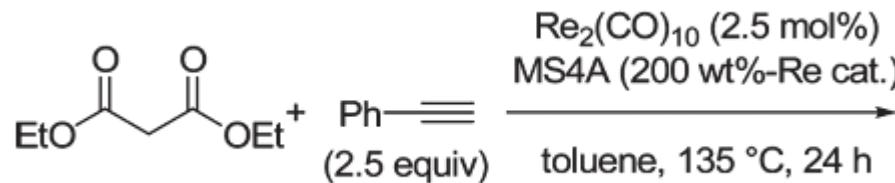
Kuninobu, Y.; Nishi, M.; Yudha, S. S.; Takai, K. *Org. Lett.* **2008**, *10*, 3009.

Tsuji, H.; Yamagata, K.-i.; Fujimoto, T.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 7792.

## 2.3 Annulations



Quiz 2:



Product 54%

Kuninobu, Y.; Iwanaga, T.; Nishi, M.; Takai, K. *Chem. Lett.* **2010**, 39, 894.

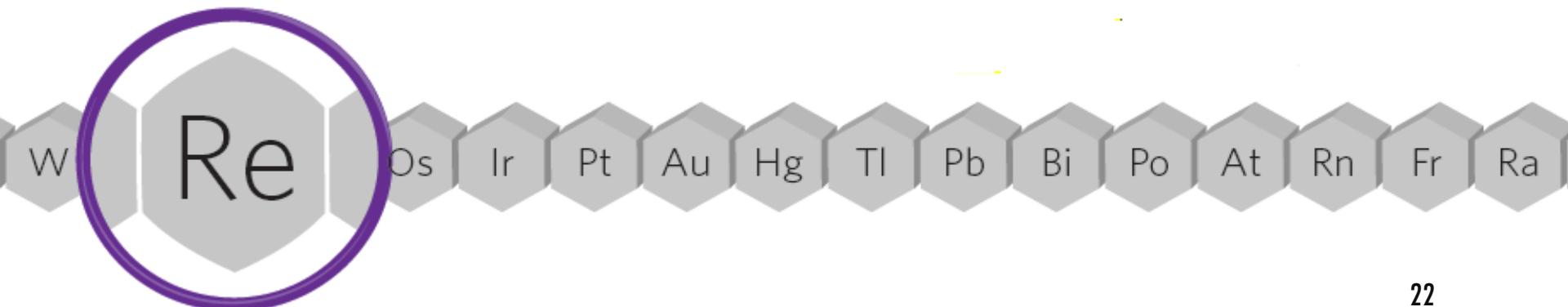
# 2. C—C bond bond formation

- 2.1 Friedel-Crafts
- 2.2 Nucleophilic addition
- 2.3 Annulations
- 2.4 C—H bond activation
- 2.5 C—C bond cleavage

VII B	VIII B	VIII B	VIII B
Manganese Mn 54.938	Iron Fe 55.845	Cobalt Co 58.933	Nickel Ni 58.693
Technetium Tc 98.91	Ruthenium Ru 101.07	Rhodium Rh 102.91	Palladium Pd 106.42
Rhenium Re 186.21	Osmium Os 190.23	Iridium Ir 192.22	Platinum Pt 195.08

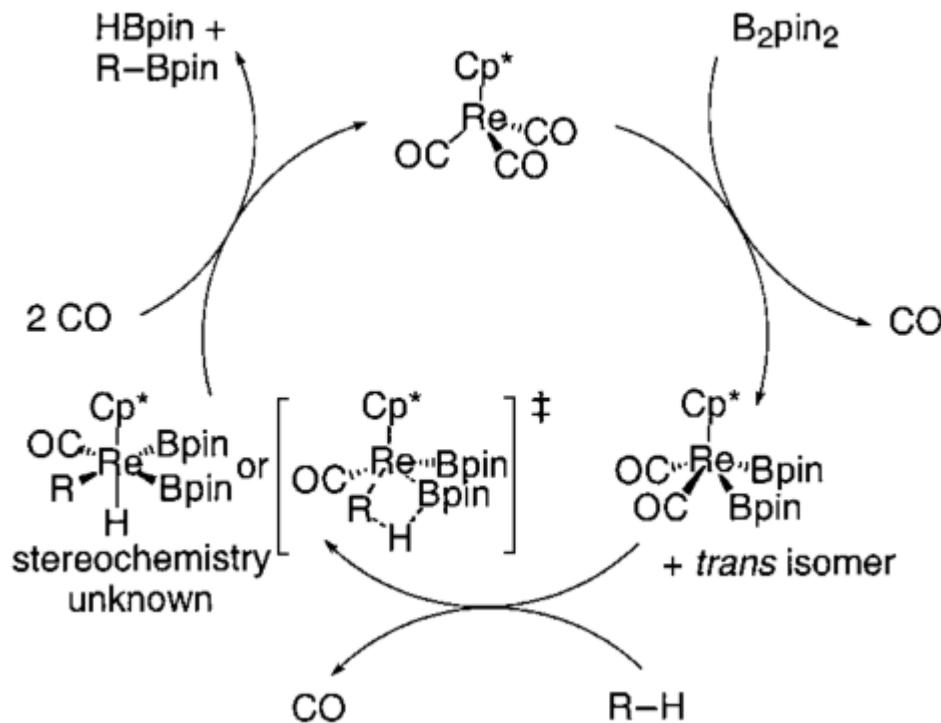
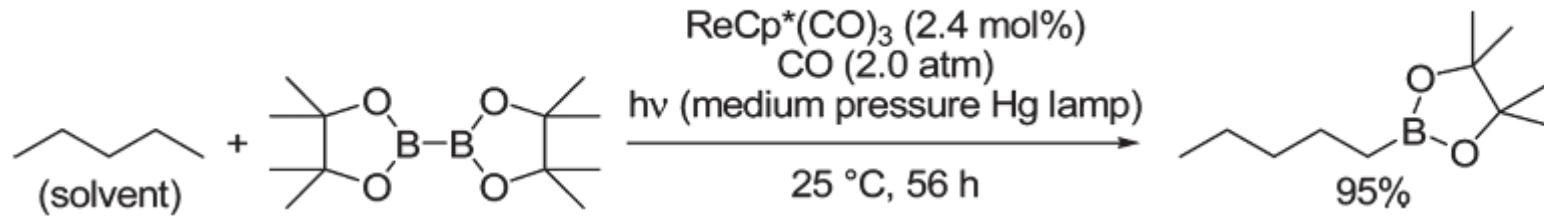
*Re(0,I), Ru(0), Rh(I)*

*Rh(III), Pd(II)*

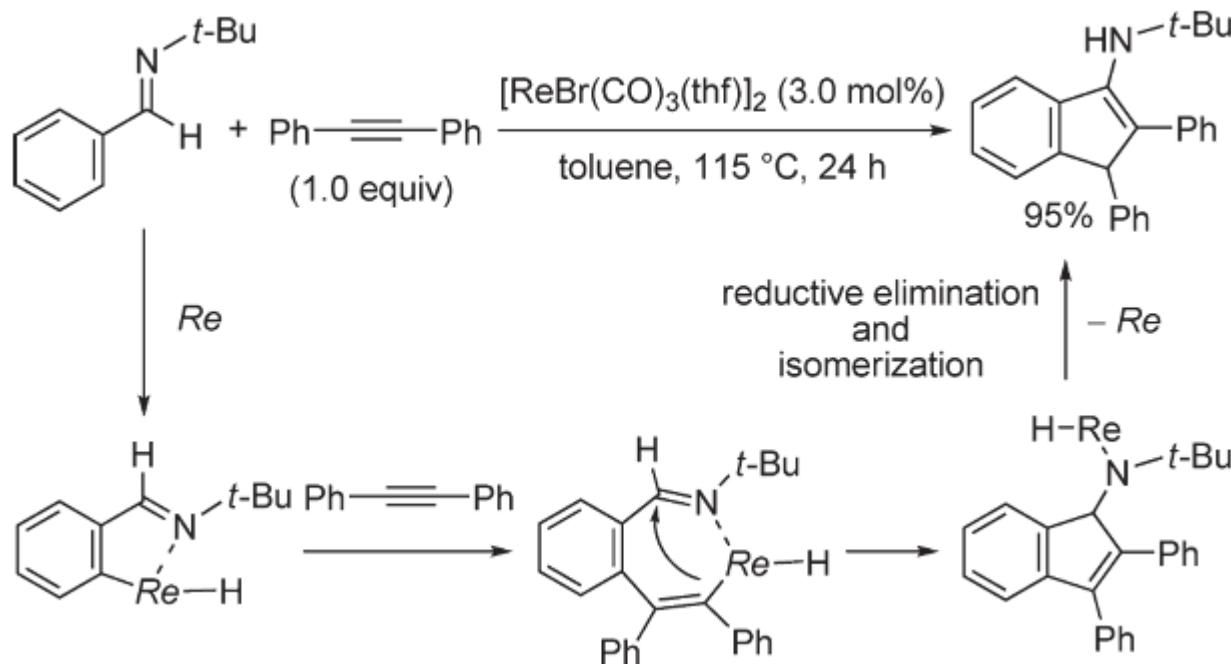


## 2.4 C—H bond activation

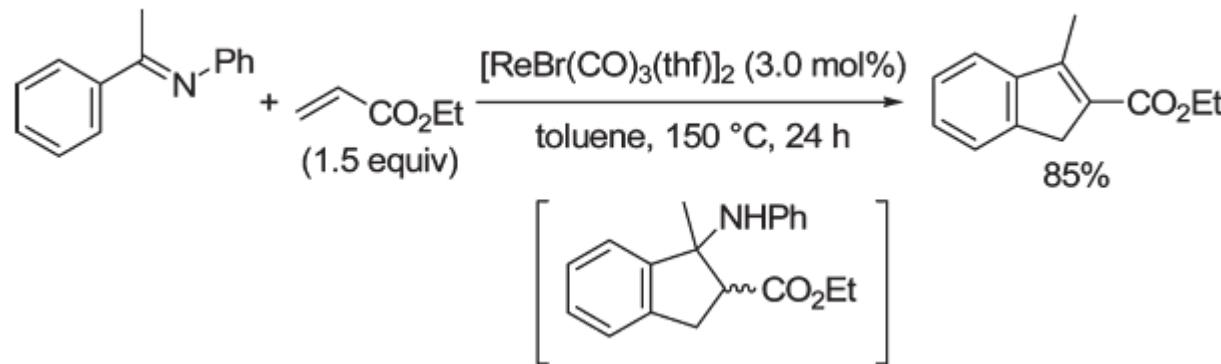
- Sp<sup>3</sup> C—H borylation



## 2.4 C—H bond activation



Kuninobu, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2005**, *127*, 13498.



Kuninobu, Y.; Nishina, Y.; Shouho, M.; Takai, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2766.

## 2.4 C—H bond activation

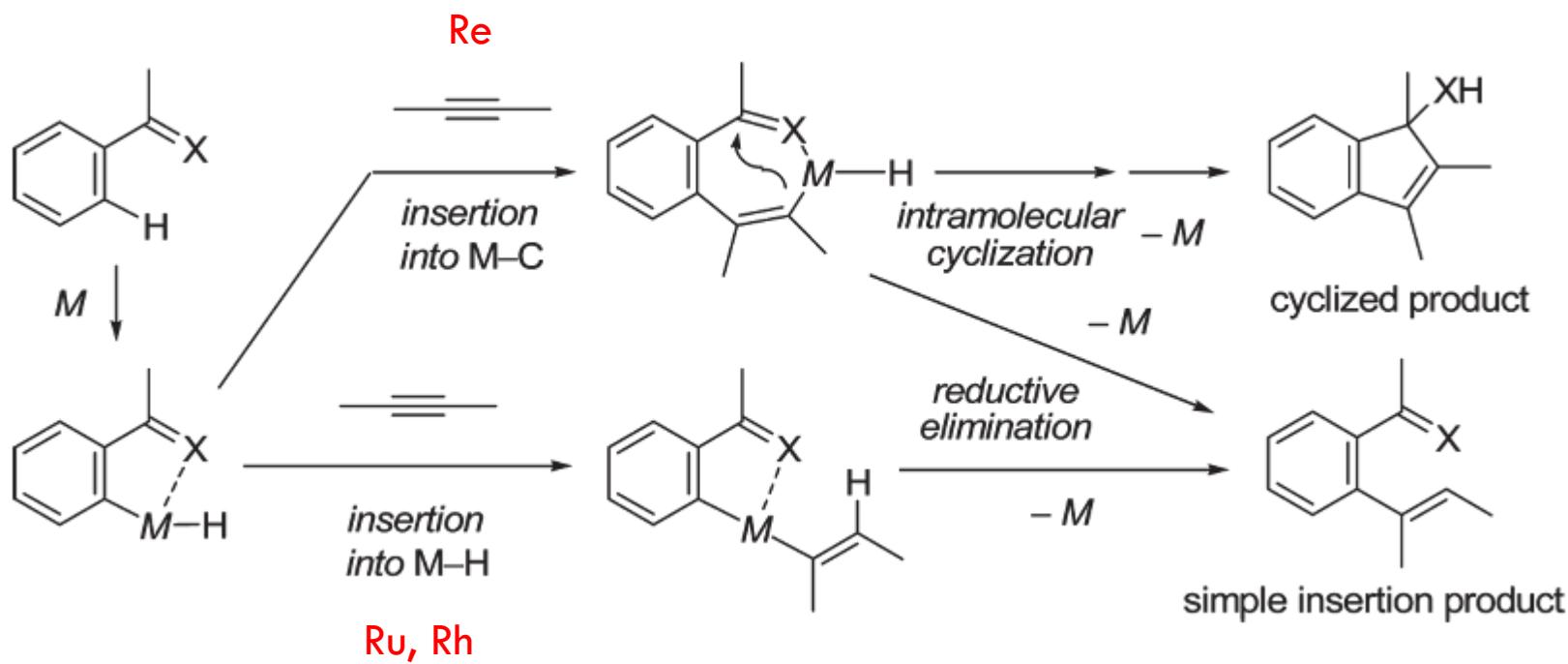
VII VIII VIII

Technetium 43 98.91	Ruthenium 44 101.07	Rhodium 45 102.91
Rhenium 75 186.21	Osmium 76 190.23	Iridium 77 192.22

5  
6

more metalicity

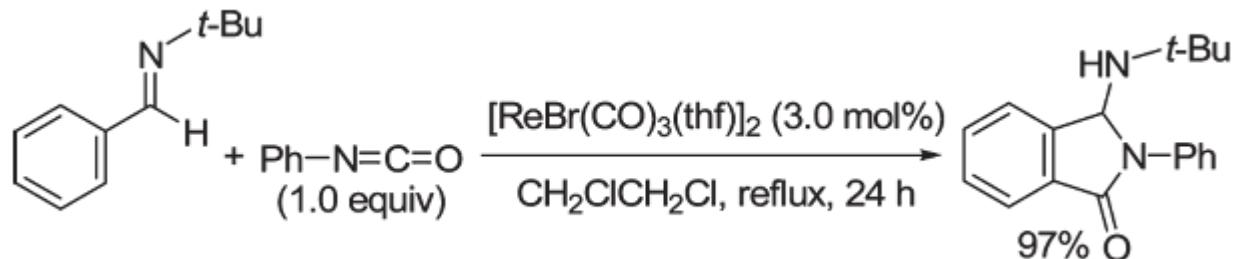
Less electronegativity



## 2.4 C—H bond activation

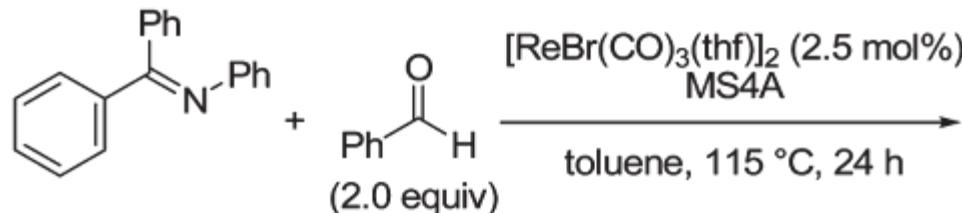
- Addition to polar unsaturated bonds

### Isocyanates



Kuninobu, Y.; Tokunaga, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2006**, 128, 202.

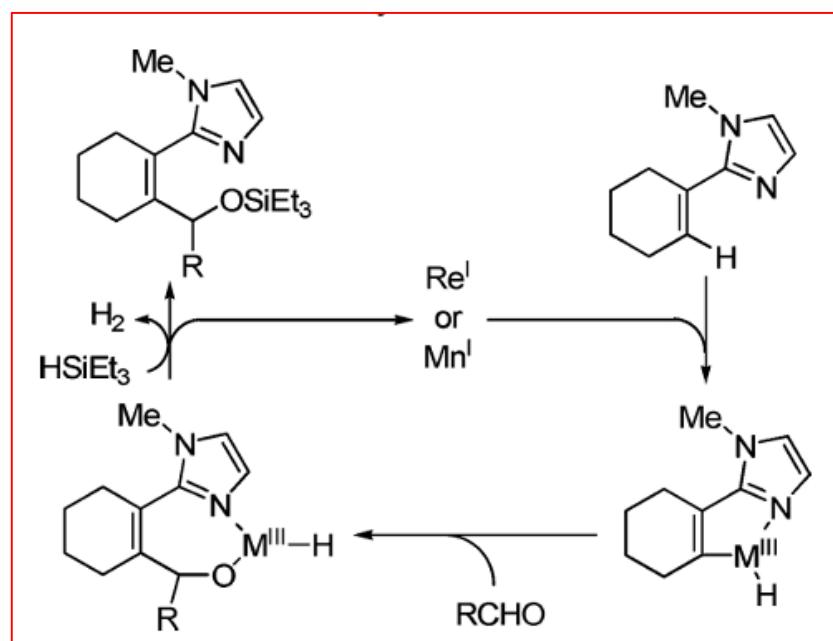
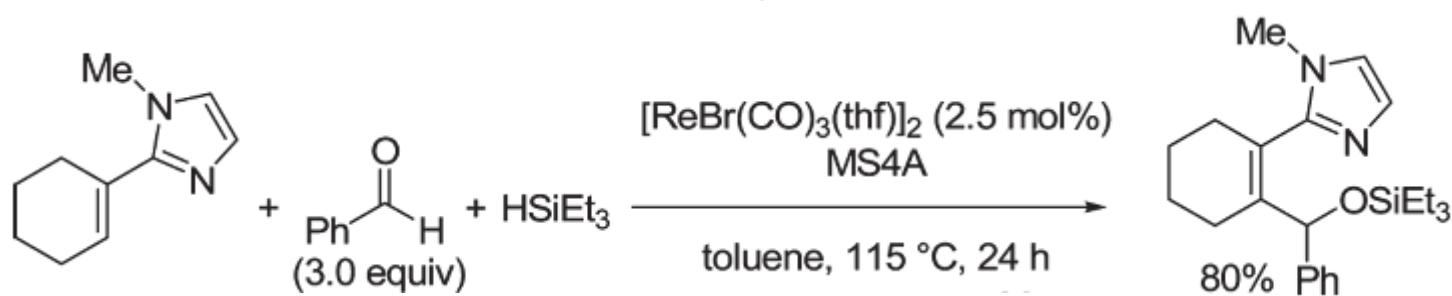
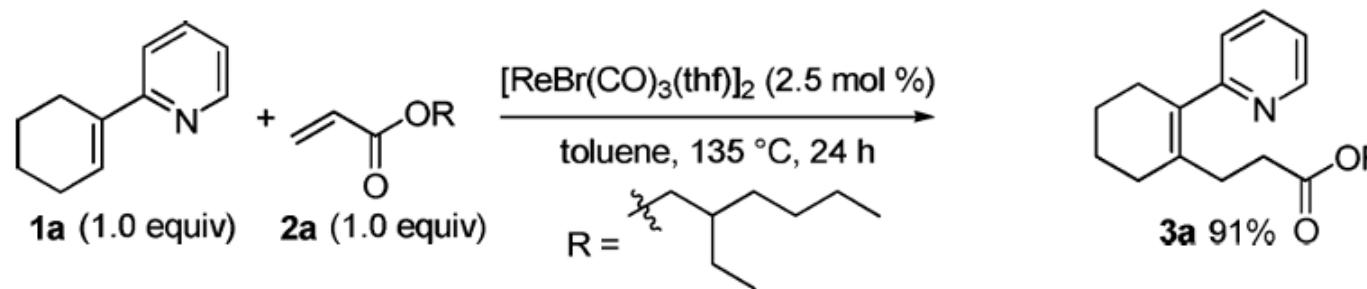
### Aldehydes



Quiz 3

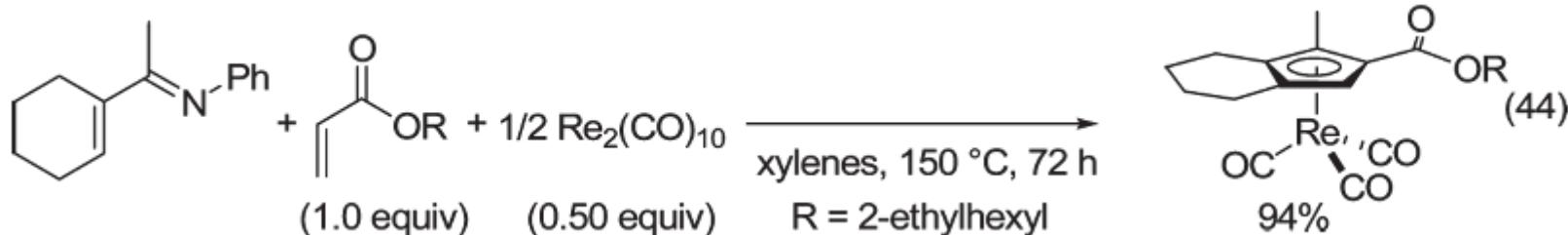
Kuninobu, Y.; Nishina, Y.; Nakagawa, C.; Takai, K. *J. Am. Chem. Soc.* **2006**, 128, 12376.

## 2.4 C—H bond activation

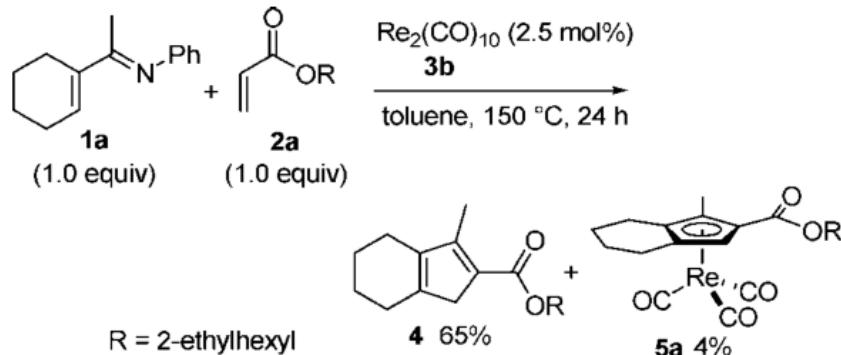


Kuninobu, Y.; Fujii, Y.; Matsuki, T.; Nishina, Y.; Takai, K. *Org. Lett.* **2009**, *11*, 2711.

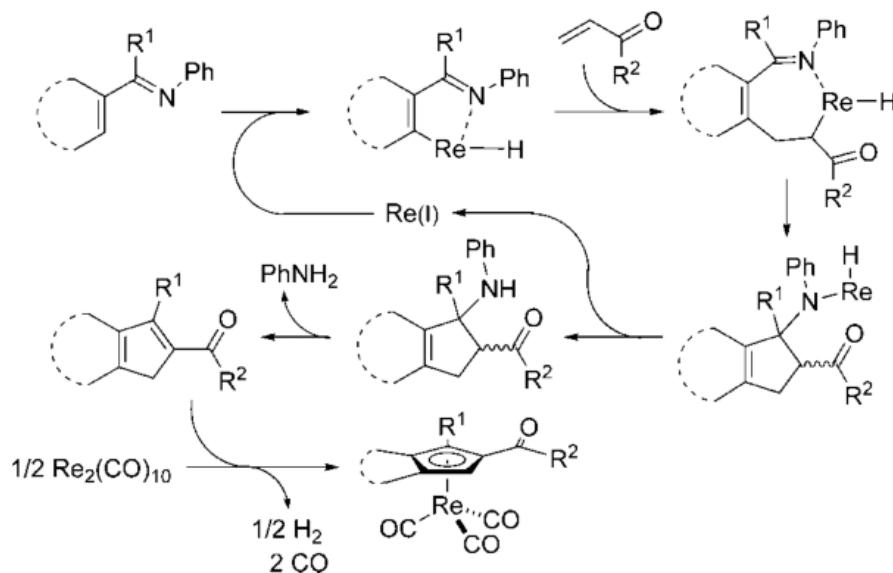
## 2.4 C—H bond activation



### Discovery



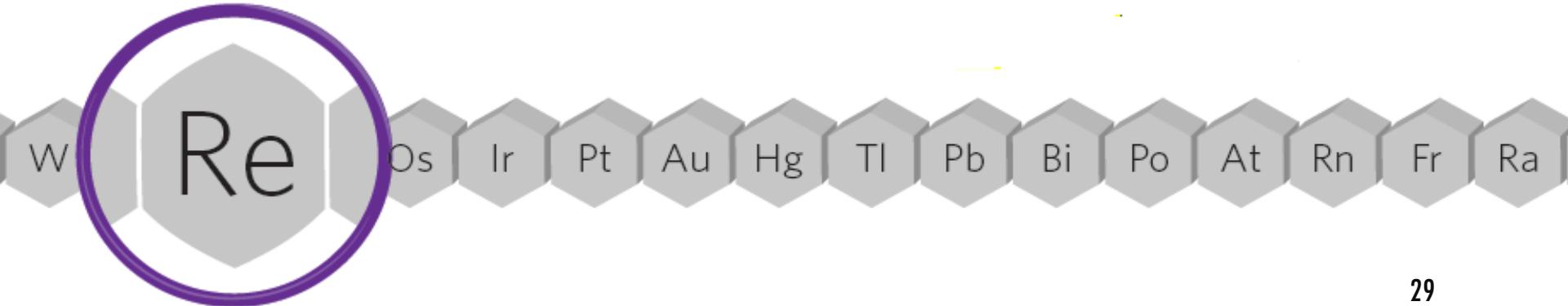
### Mechanism



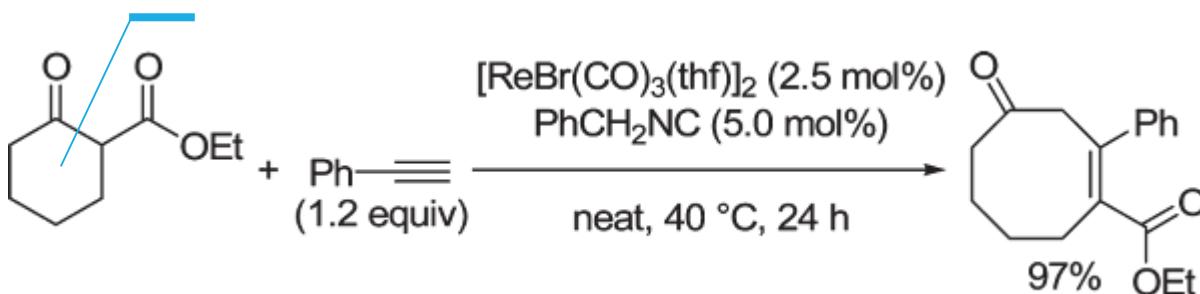
Kuninobu, Y.; Nishina, Y.; Matsuki, T.; Takai, K. *J. Am. Chem. Soc.* **2008**, *130*, 14062.

## 2. C—C bond formation

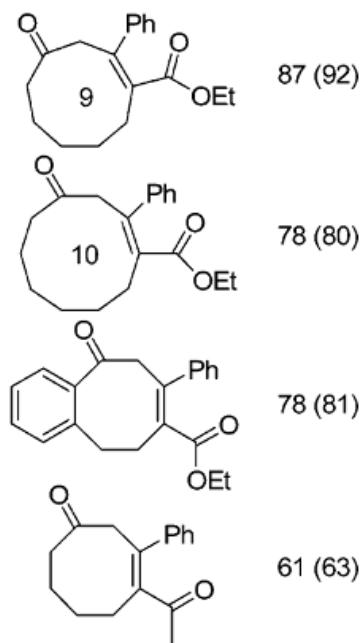
- 2.1 Friedel-Crafts
- 2.2 Nucleophilic addition
- 2.3 Annulations
- 2.4 C—H bond activation
- 2.5 C—C bond cleavage



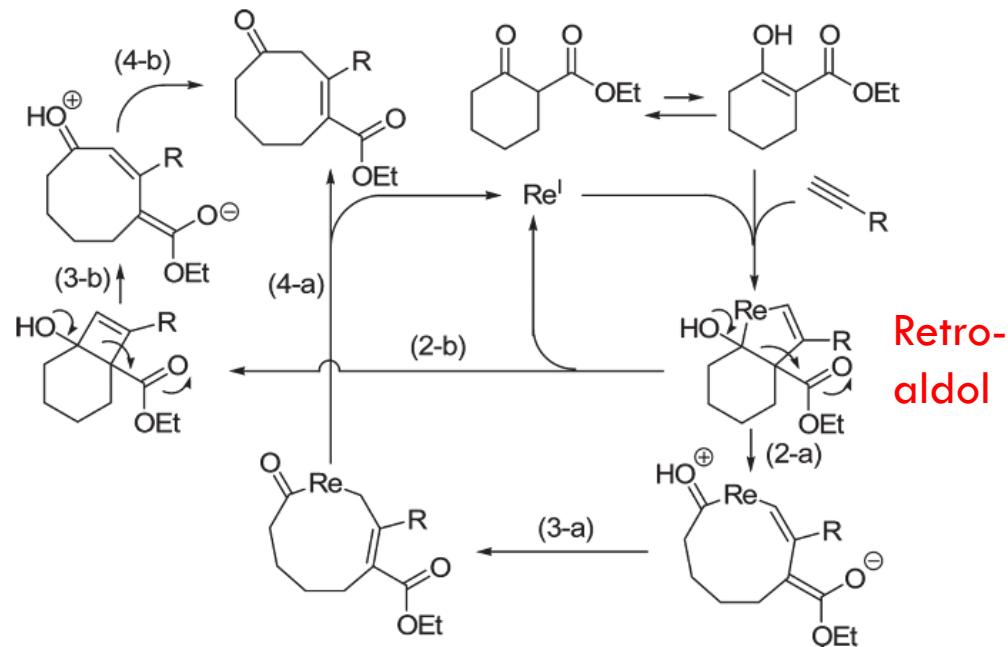
## 2.4 C—C bond cleavage



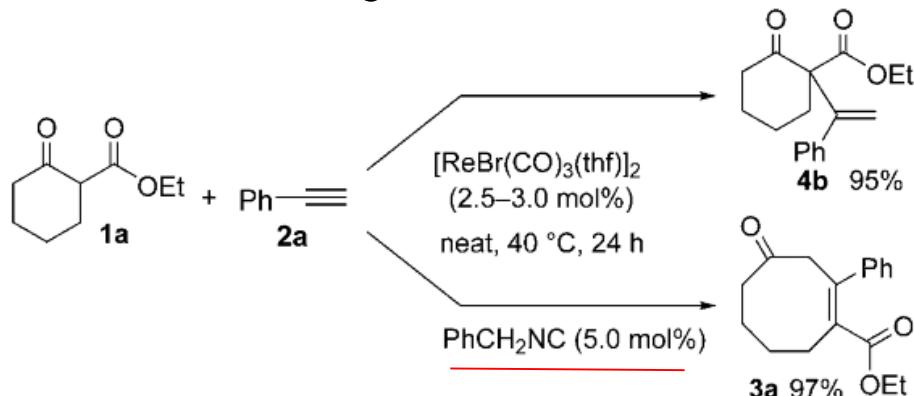
- Substrate scope



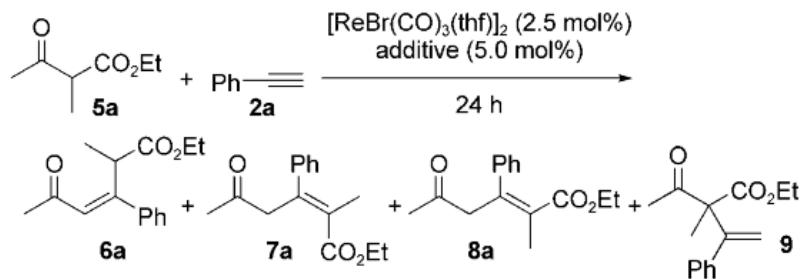
- Mechanism



## 2.4 C—C bond cleavage

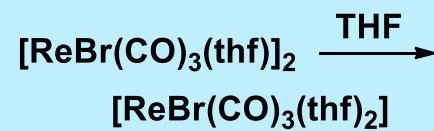


JACS 2006



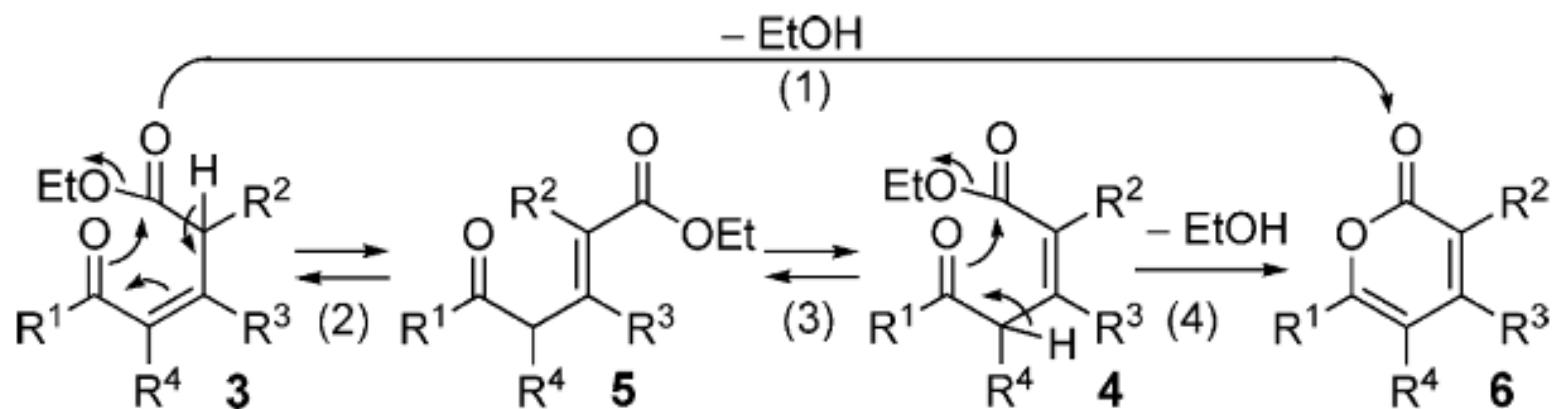
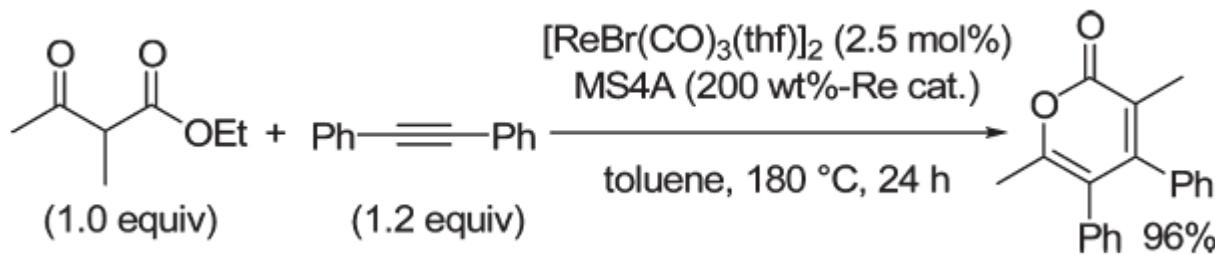
Entry	Additive	Solvent (conc./M)	Temp [°C]	Yield [%]	
				6a–8a	9
1	none	neat	50	33	66
2	none	toluene (2.0)	50	50	46
3	none	toluene (0.50)	50	77	14
4	none	toluene (0.25)	50	85	9
5	none	toluene (0.50)	80	92	<1
6	THF	neat	50	48	48
7 <sup>[b]</sup>	THF	neat	50	65	34
8	2,6-iPr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC	neat	50	76	15

[a] **2a** (1.2 equiv). [b] THF (20 mol %).



Vitali, D.; Calderazzo, F. *Gazz. Chim. Ital.* **1972**, 102, 587.

## 2.4 C—C bond cleavage



Kuninobu, Y.; Kawata, A.; Nishi, M.; Takata, H.; Takai, K. *Chem. Commun.* **2008**, 6360.

# Contents

## 1. Introduction

## 2. C—C bond formation

- 2.1 Friedel-Crafts
- 2.2 Nucleophilic addition
- 2.3 Annulations
- 2.4 C—H bond activation
- 2.5 C—C bond cleavage

## 3. Conclusion

# 4. Conclusion

## Prior to 2000

Used as **hard Lewis acid** catalysts

- Friedel-Crafts reactions
- Aldol reactions
- Knoevenagel reactions

**Not interfered by a small amount of water**

75	Rhenium
Re	
Atomic mass:	186.21 u
Electron configuration:	2/8/18/32/13/2
Electronegativity:	1.9

## Since about 2000

Have also been employed as **soft Lewis acids**

- Nucleophilic additions to alkynes or allenes
- Cycloisomerization of enynes
- Cyclization reactions

**Many similar reactions were previously known to be promoted by other transition metals**

## Since 2005

**C-H and C-C bond cleavage**

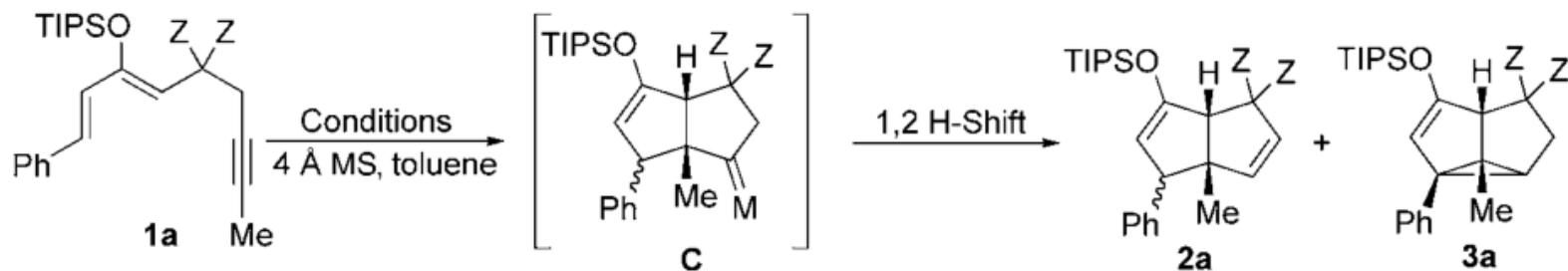
- C-H oxidative addition
- Unique reactivity

# Thank you!

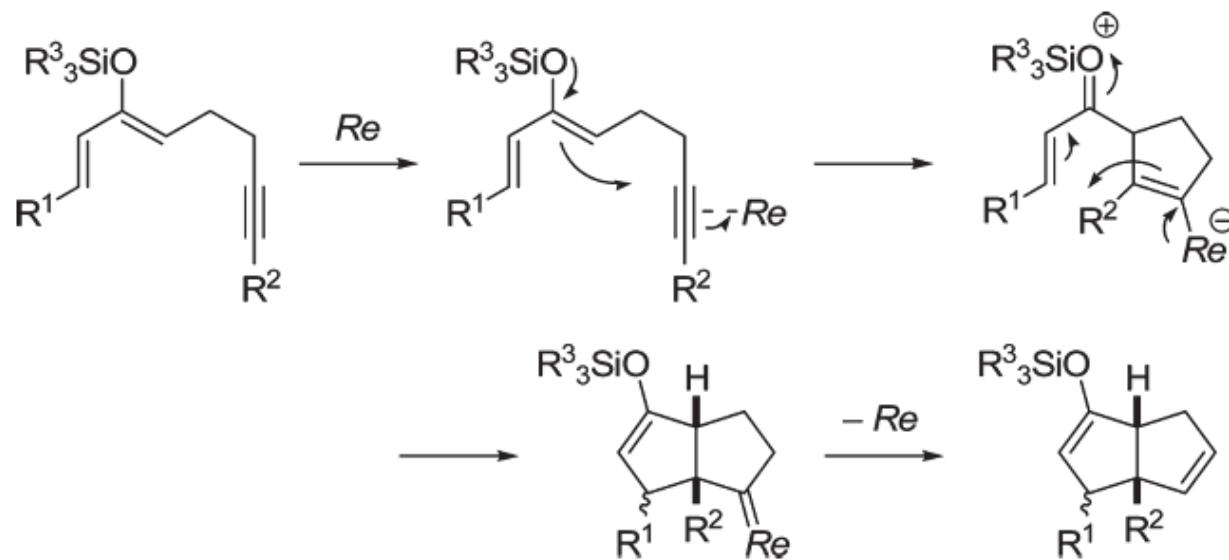




# Answers for quiz 1

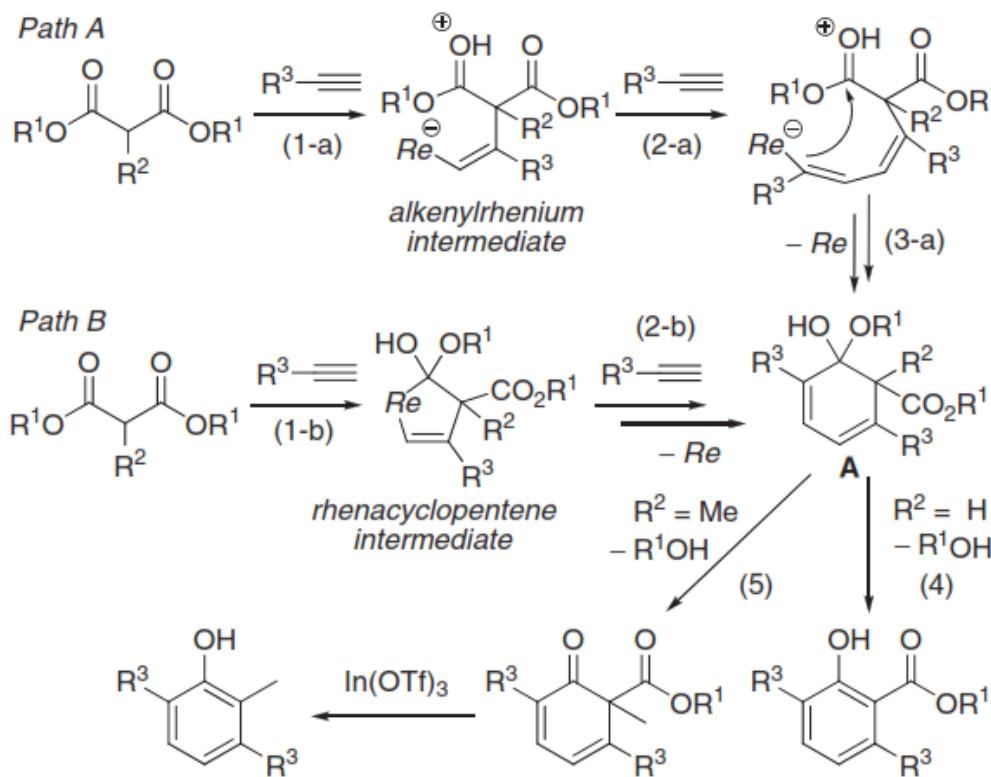
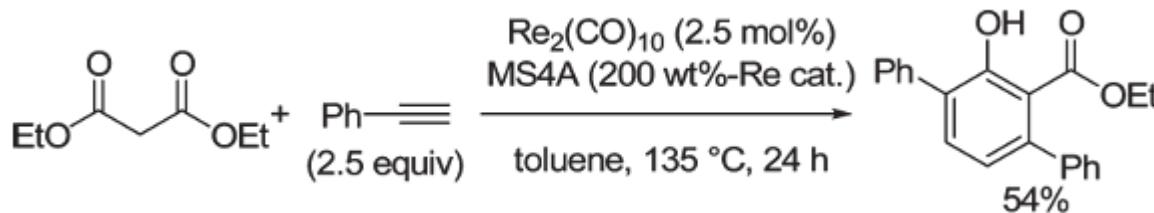


**Scheme 2.** Proposed Mechanism for the Formation of Bicyclo[3.3.0]octane Derivatives

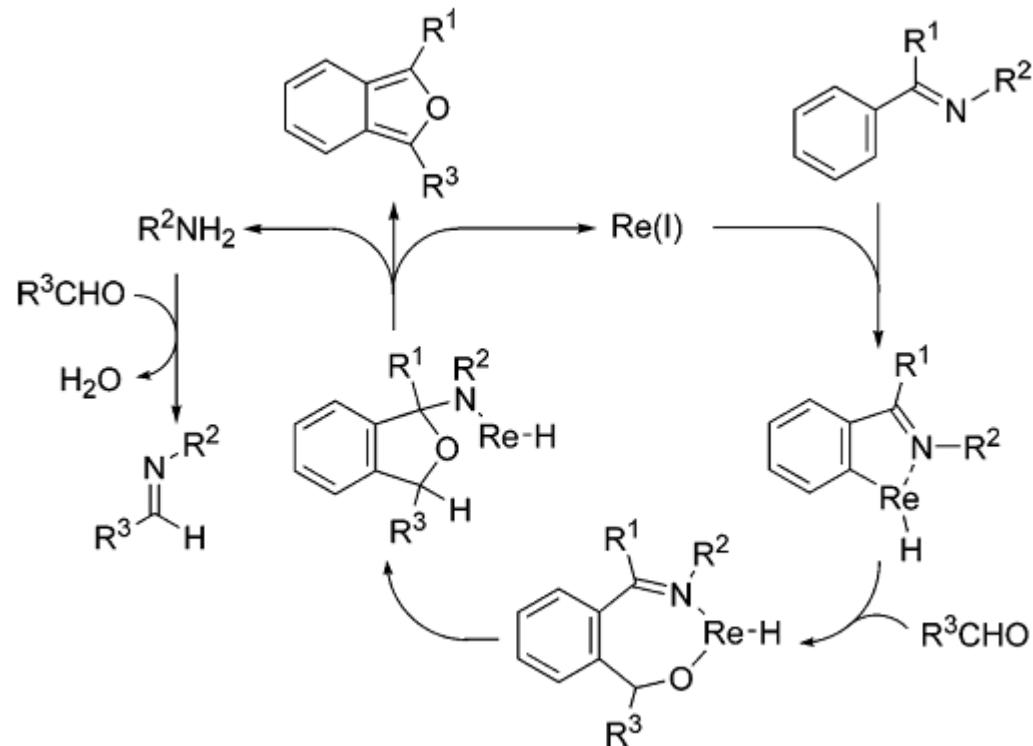
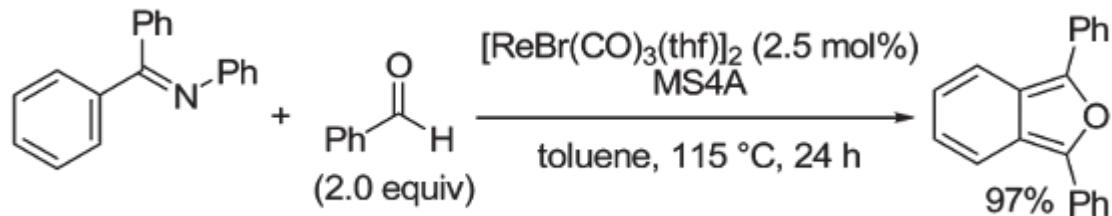


Kusama, H.; Yamabe, H.; Onizawa, Y.; Hoshino, T.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 468.

## Answers for quiz 2

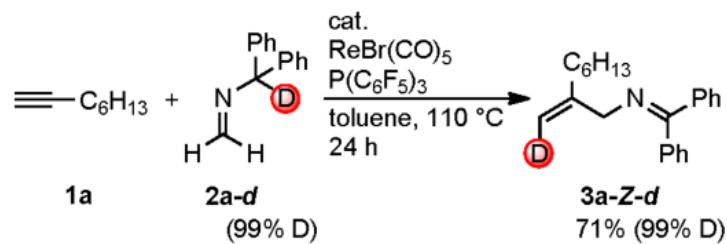
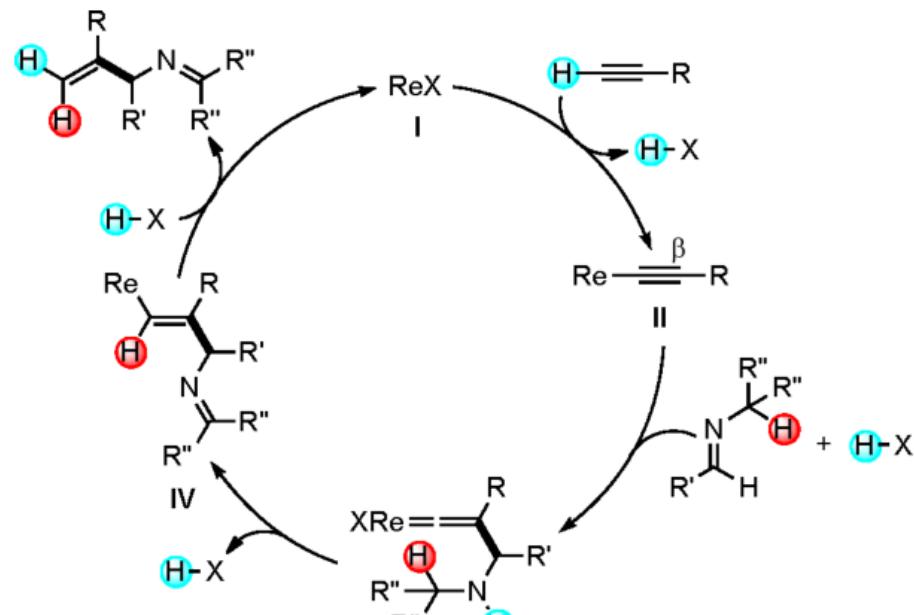


# Answers for quiz 3



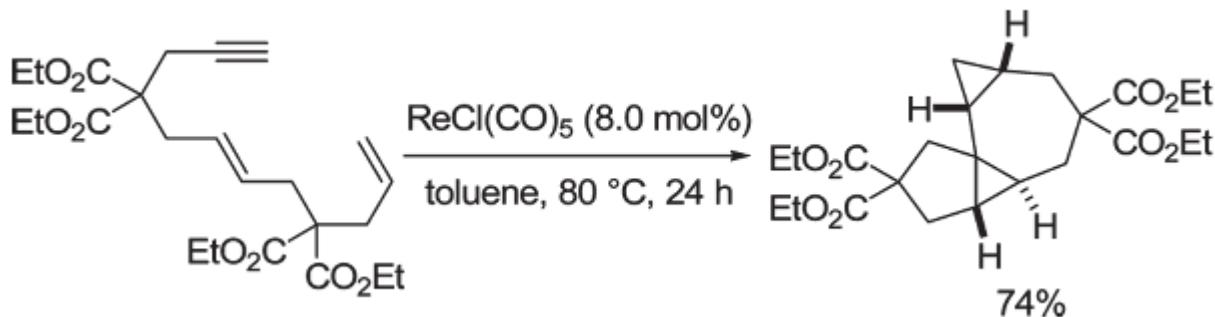
## 2.2 Nucleophilic addition to carbonyl compounds

	$\equiv R$	$+ \text{N}(\text{Ph})_2\text{H}$	$\xrightarrow[\text{24 h}]{\text{cat. ReBr(CO)}_5, \text{P}(\text{C}_6\text{F}_5)_3, \text{toluene, } 110^\circ\text{C}}$	$\text{R}-\text{CH}_2-\text{CH}=\text{N}(\text{Ph})_2$
entry	alkyne		product	yield (%) <sup>b</sup>
1	$\equiv-(\text{CH}_2)_5\text{CH}_3$ <b>1a</b>		<b>3a</b>	73
2	$\equiv\text{Cy}$ <b>1b</b>		<b>3b</b>	72
3	$\equiv\text{CH}(\text{CH}_2)_4\text{CH}_3$ <b>1c</b>		<b>3c</b>	66
	$\equiv\text{C}_6\text{H}_{13}$ <b>1a</b>	$\text{N}(\text{Ph})_2\text{H}$	$\xrightarrow[\text{24 h}]{\text{cat. ReBr(CO)}_5, \text{P}(\text{C}_6\text{F}_5)_3, \text{toluene, } 110^\circ\text{C}}$	
			$\text{C} = {}^{13}\text{C}$	70%

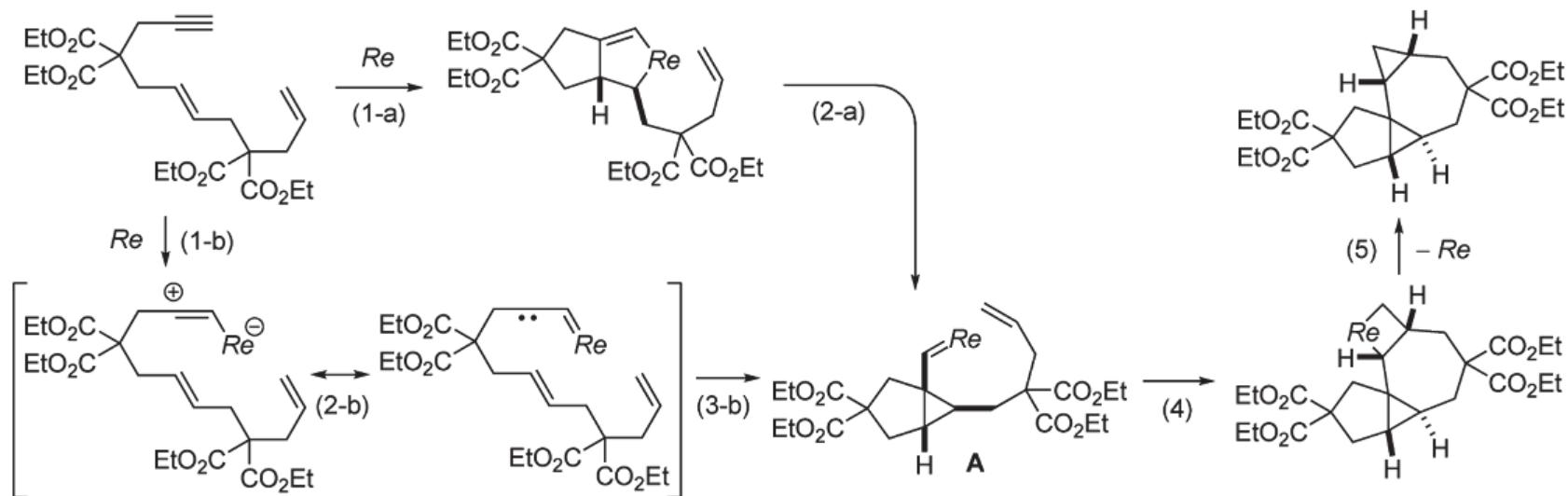


Fukumoto, Y.; Daijo, M.; Chatani, N. *J. Am. Chem. Soc.* **2012**, *134*, 8762.

## 2.3 Annulations

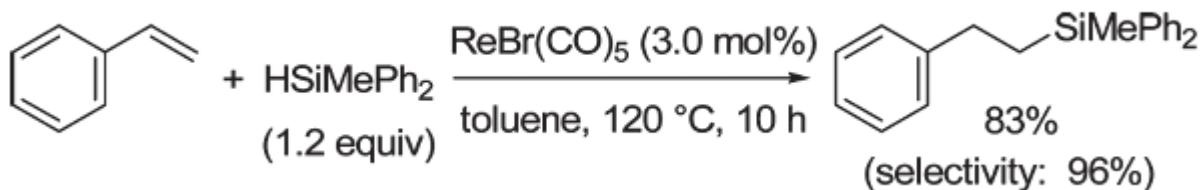


- Mechanism:

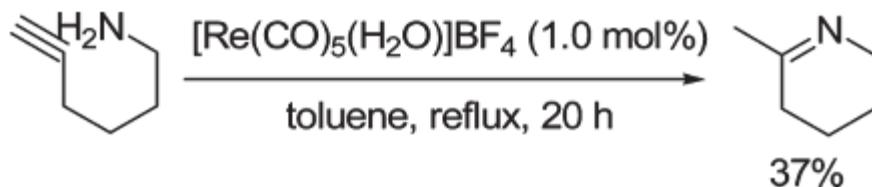


Chatani, N.; Kataoka, K.; Murai, S. *J. Am. Chem. Soc.* **1998**, *120*, 9104.

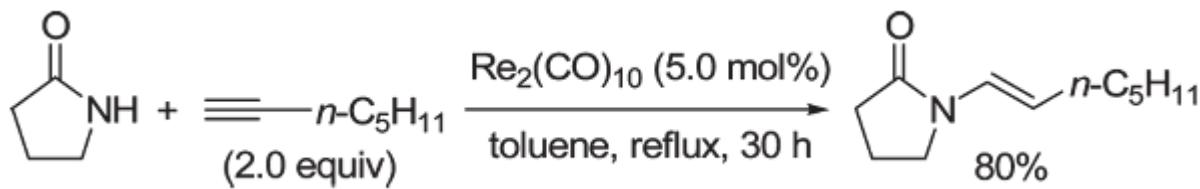
### 3. C—hetero bond formation



Zhao, W.-G.; Hua, R. *Eur. J. Org. Chem.* **2006**, 5495.



Ouh, L. L.; Müller, T. E.; Yan, Y. K. *J. Organomet. Chem.* **2005**, 690, 3774.



Yudha, S. S.; Kuninobu, Y.; Takai, K. *Org. Lett.* **2007**, 9, 5609.

