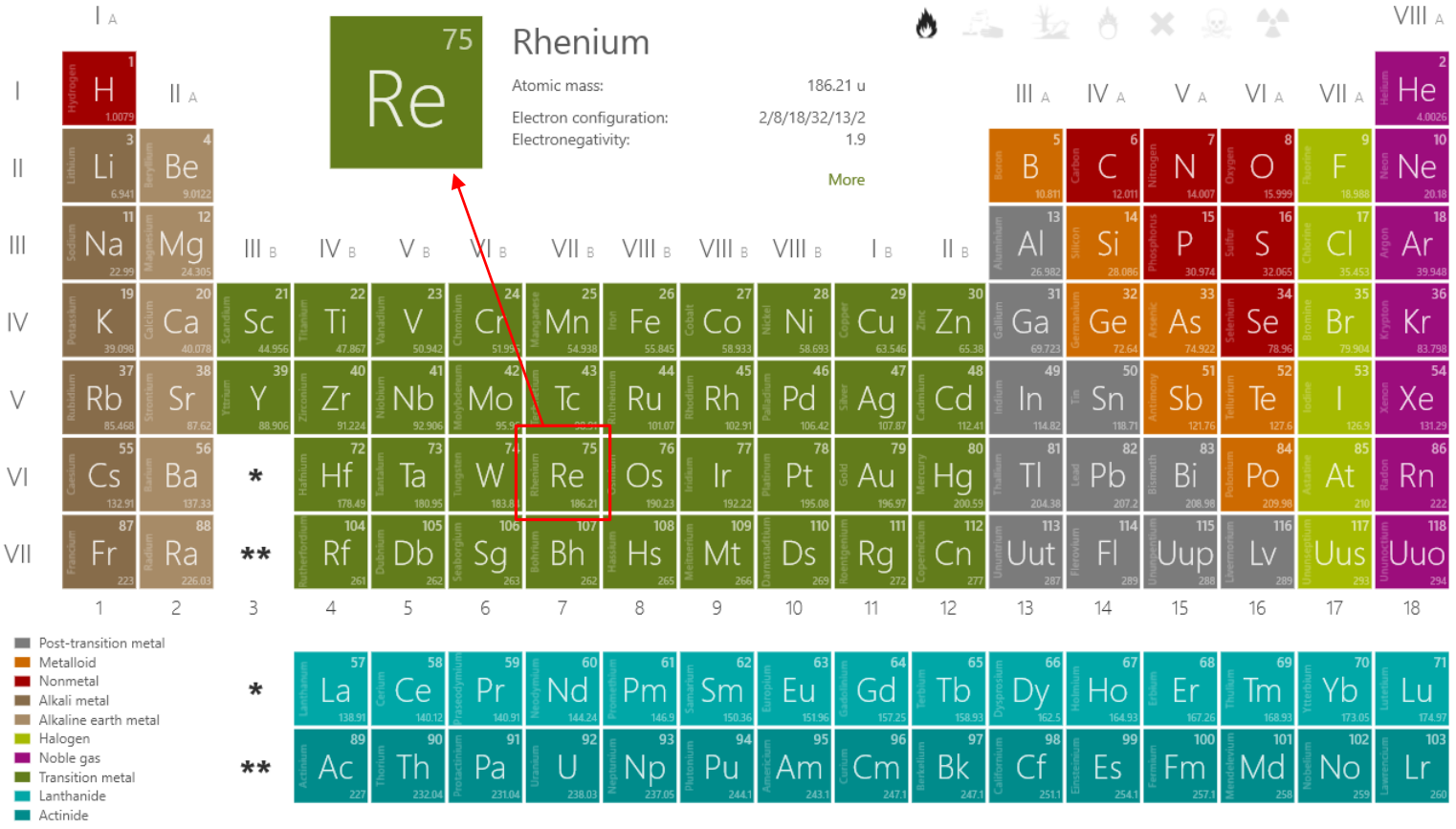
# Organic Reactions catalyzed by rhenium carbonyl complexes

Fanyang Mo
Dong group seminar
Feb. 26, 2014

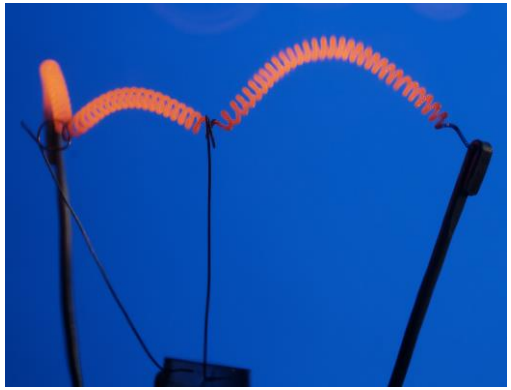
Ref: Kuninobu, Y.; Takai, K. *Chem Rev.* **2011**, *111*, 1938.

# Periodic Table




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

# General Applications in Industry



Filament

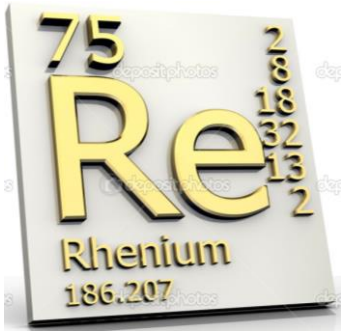
Jet engine

Petroleum purification
(Platinum-rhenium catalysts)

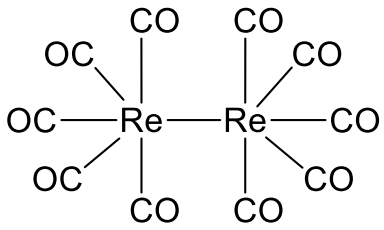
(high melting point 3186 °C)

# Contents

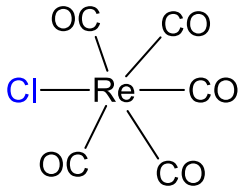
# 1. Introduction



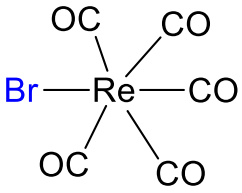

[Xe] $4f^{14}$ $5d^5$ $6s^2$



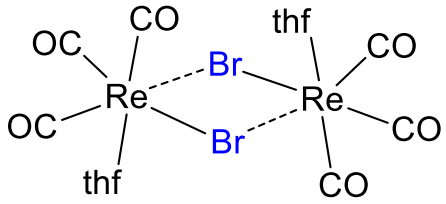

$Re_2(CO)_{10}$



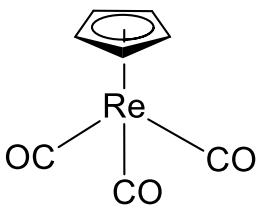

$ReCl(CO)_5$



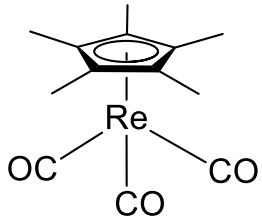

$ReBr(CO)_5$




$[ReBr(CO)_3(thf)]_2$




$CpRe(CO)_3$




$Cp^*Re(CO)_3$

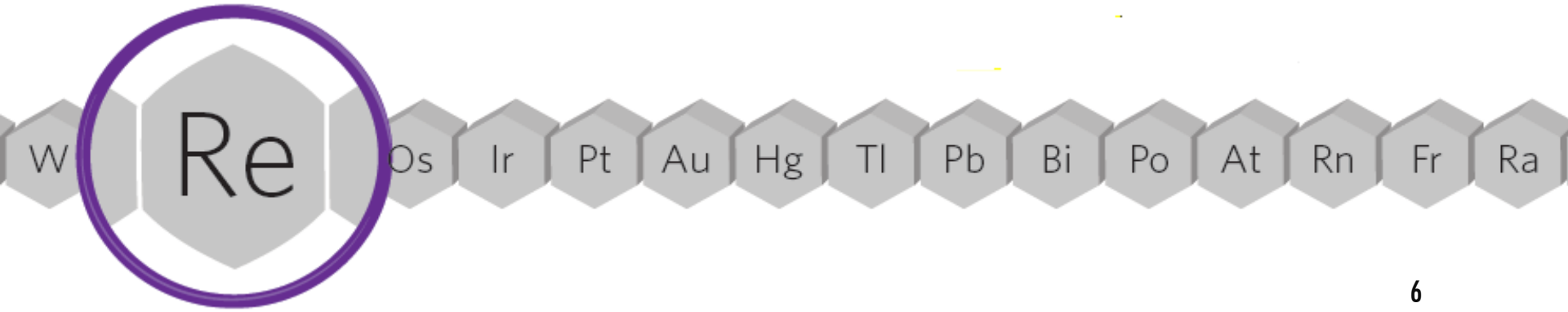
Four notable features

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

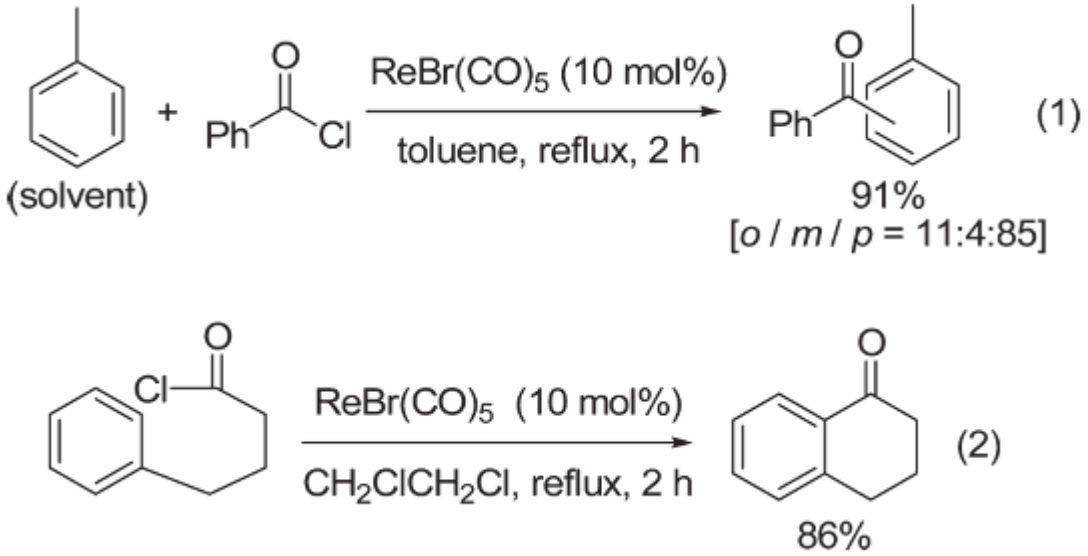
Commercially available Rhenium carbonyl complexes.

# 2. C—C bond formation

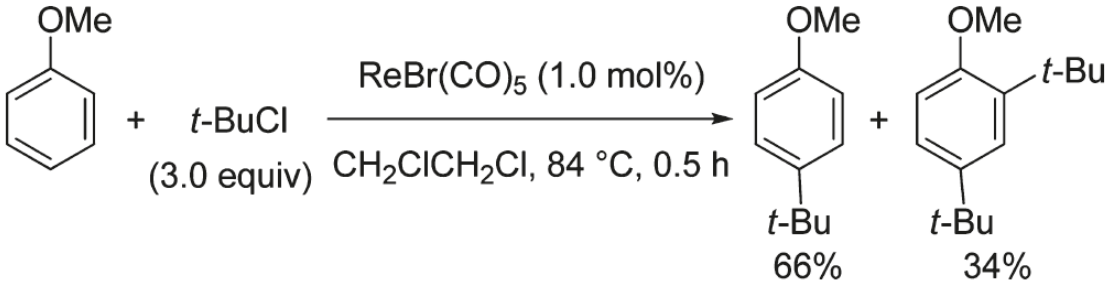
- 2.1 Friedel-Crafts
- 2.2 Nucleophilic addition
- 2.3 Annulations
- 2.4 C—H bond activation
- 2.5 C—C bond cleavage



# 2.1 Friedel-Crafts Reactions

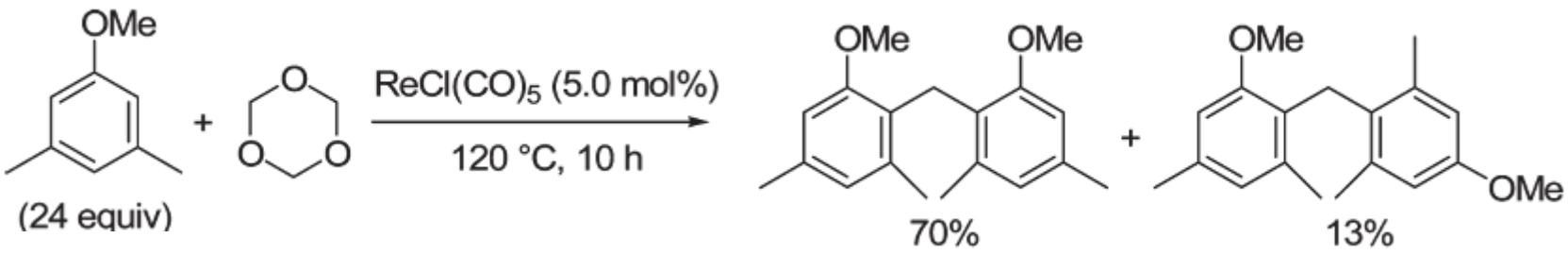



Kusama, H.; Narasaka, K. *Bull. Chem. Soc. Jpn*. **1995**, *68*, 2379.

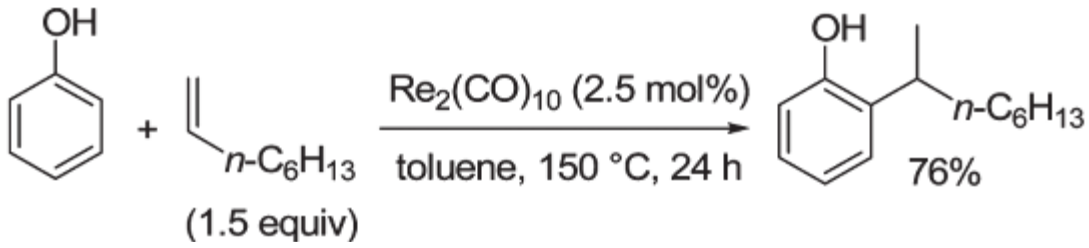



Nishiyama, Y.; Kakushou, F.; Sonoda, N. *Bull. Chem. Soc. Jpn*. **2000**, *73*, 2779.

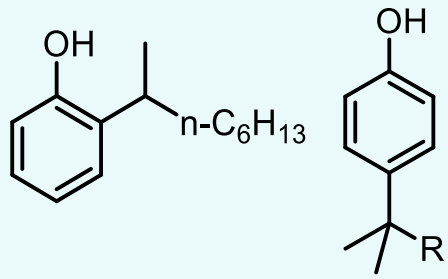
# 2.1 Friedel-Crafts Reactions

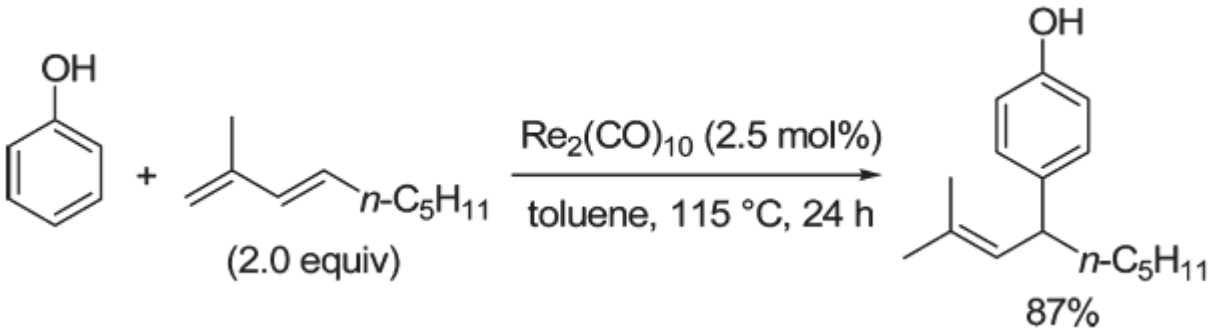



Hua, R.; He, J.; Sun, H. *Chin. J. Chem*. **2007**, *25*, 132.




- Regio-selectivity

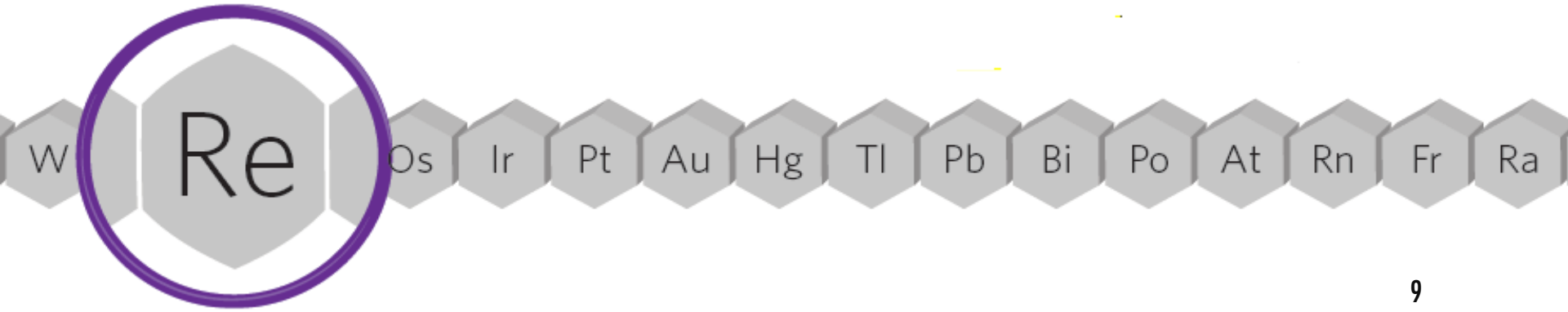


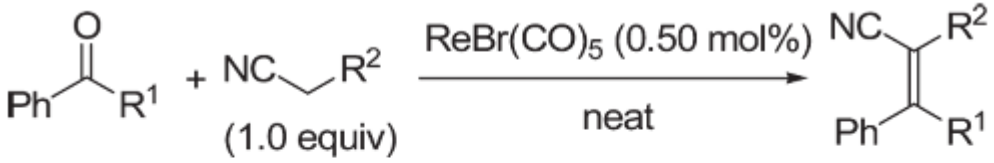

Kuninobu, Y.; Matsuki, T.; Takai, K. *J. Am. Chem. Soc*. **2009**, *131*, 9914.

# 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



# 2.2 Nucleophilic addition to carbonyl compounds

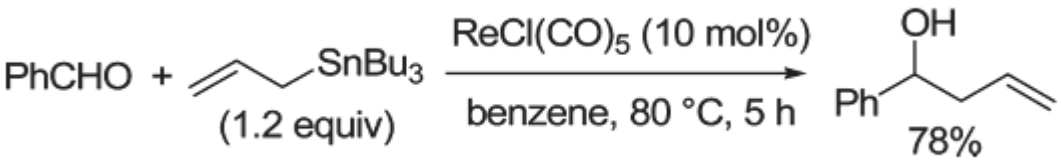



Knoevenagle condensation

| $R^1$ | $R^2$ | conditions | yield / % |
|---|---|---|---|
| H | CN | 110 °C, 1.5 h | 90 |
| H | $CO_2Et$ | 110 °C, 2 h | 88 |
| Me | $CO_2Et$ | 130 °C, 70 h | 45 [*E*/*Z* = 3/2] |

- No solvent
- No base

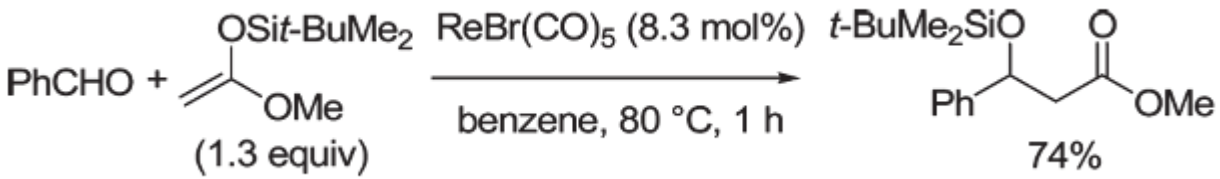
Zuo, W.-X.; Hua, R.; Qiu, X. *Synth*. *Commun*. **2004**, *34*, 3219.




| Entry | Re complex | Solvent | Yield (%)[a] |
|---|---|---|---|
| 1 | $ReBr(CO)_5$ | Benzene | 83 |
| 2 | $ReBr(CO)_5$ | Toluene | 80 |
| 3 | $ReCl(CO)_5$ | Benzene | 75 |
| 4 | $ReBr(CO)_4(PPh_3)$ | Benzene | 27 |
| 5 | $Re_2(CO)_{10}$ | Benzene | Trace |
| 6 | $CpRe(CO)_3$ | Benzene | Trace |
| 7 | $ReBr(CO)_5$ | $CH_2ClCH_2Cl$ | 72 |
| 8 | $ReBr(CO)_5$ | $CHCl_3$ | 54 |
| 9 | $ReBr(CO)_5$ | THF | 0 |
| 10 | $ReBr(CO)_5$ | $CH_3CN$ | 0 |
| 11 | $ReBr(CO)_5$ | $CH_3OH$ | 23 |

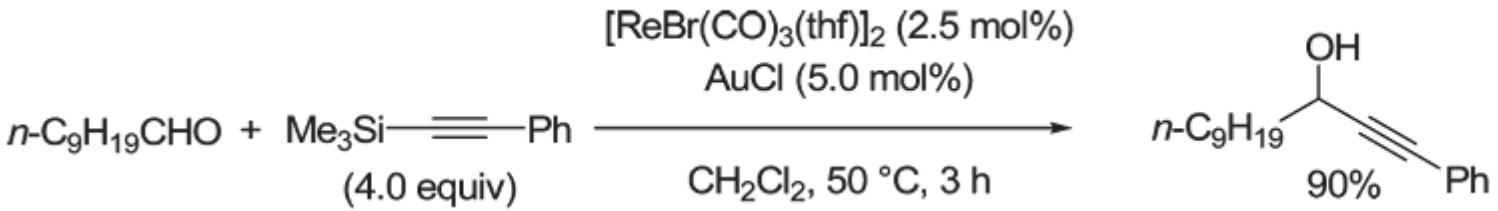
Nishiyama, Y.; Kakushou, F.; Sonoda, N. *Tetrahedron Lett*. **2005**, *46*, 787.

# 2.2 Nucleophilic addition to carbonyl compounds

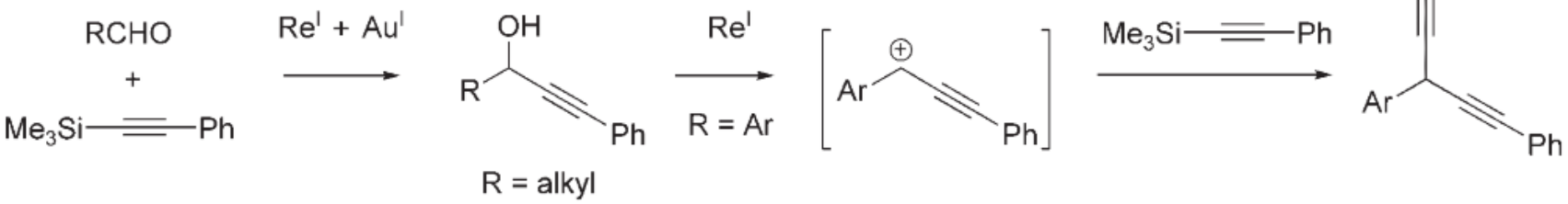



Mukaiyama Aldol reaction

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



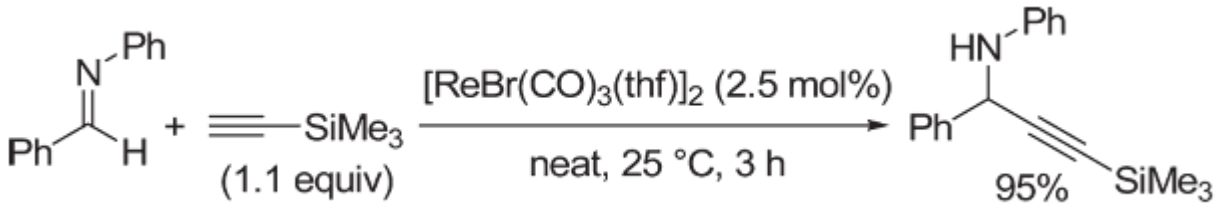

- Mechanism:



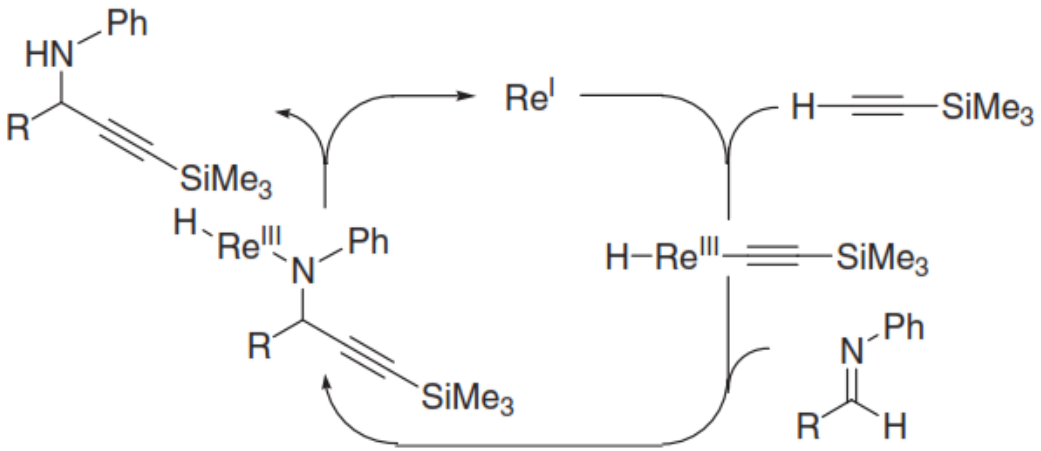

Kuninobu, Y.; Ishii, E.; Takai, K. *Angew. Chem., Int. Ed*. **2007**, *46*, 3296.

# 2.2 Nucleophilic addition to carbonyl compounds

- Imine as electrophile




- Mechanism:

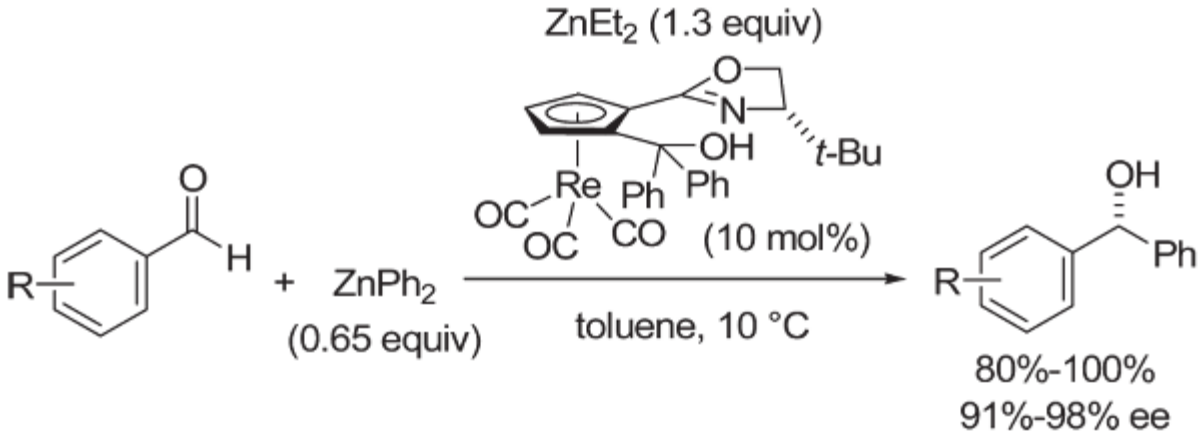



*For H-alkynyl-rhenium complexes, see:*
a) K.-W. Lee; W. T. Pennington; A. W. Cordes; T. L. Brown, *J. Am. Chem. Soc*. **1985**, *107*, 631. b) K.-W. Lee; T. L. Brown, *Organometallics* **1985**, *4*, 1025.

Kuninobu, Y.; Inoue, Y.; Takai, K. *Chem. Lett*. **2006**, *35*, 1376

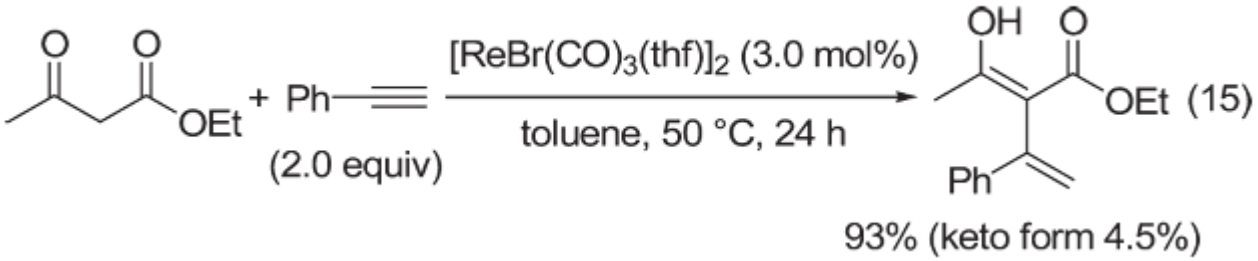
# 2.2 Nucleophilic addition to carbonyl compounds

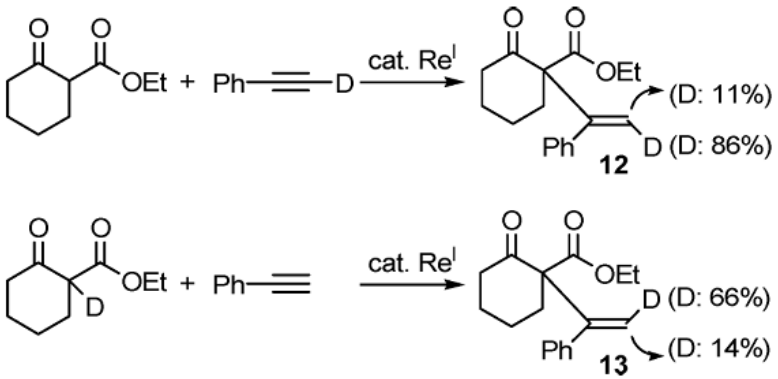
- Enantioselective addition

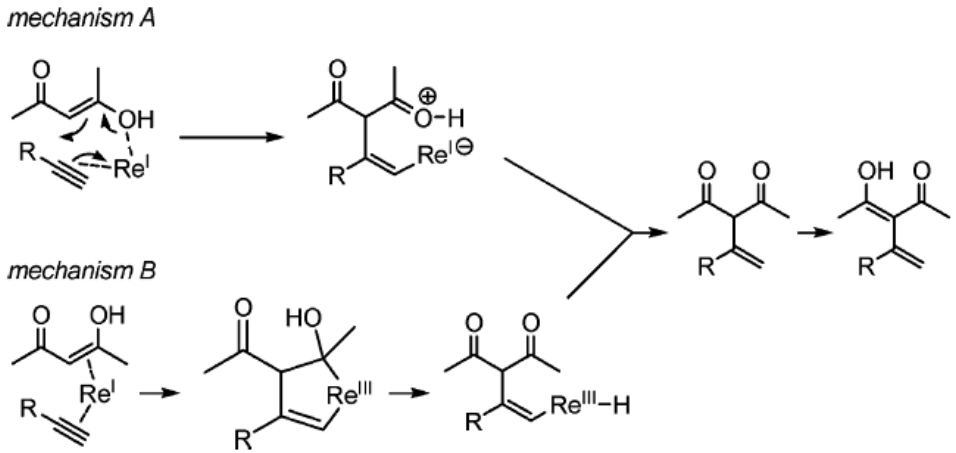


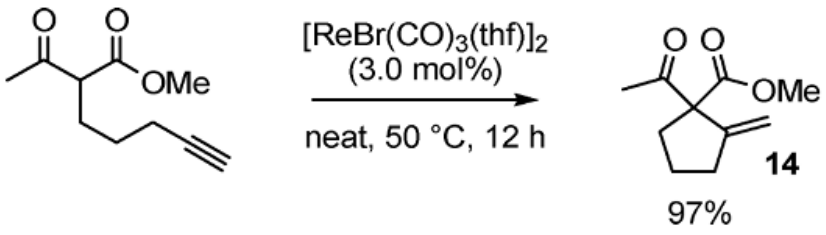

Bolm, C.; Kesselgruber, M.; Hermanns, N.; Hildebrand, J. P.; Raabe, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1488.

# 2.2 Nucleophilic addition to C—C unsaturated bond



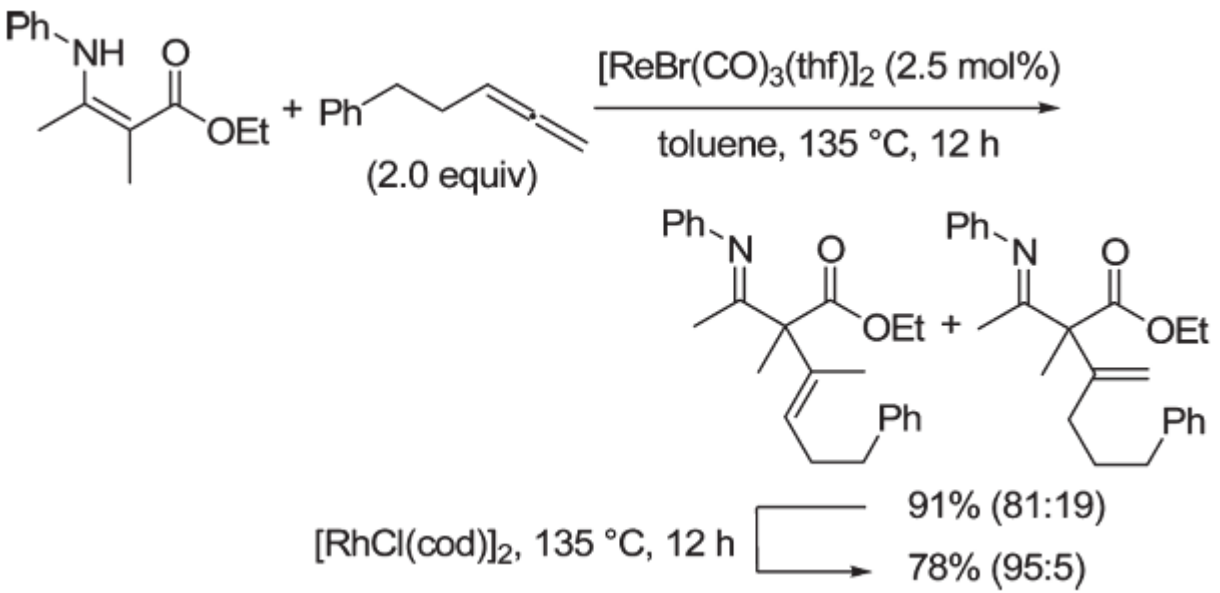




Kuninobu, Y.; Kawata, A.; Takai, K. *Org. Lett.* **2005**, *7*, 4823

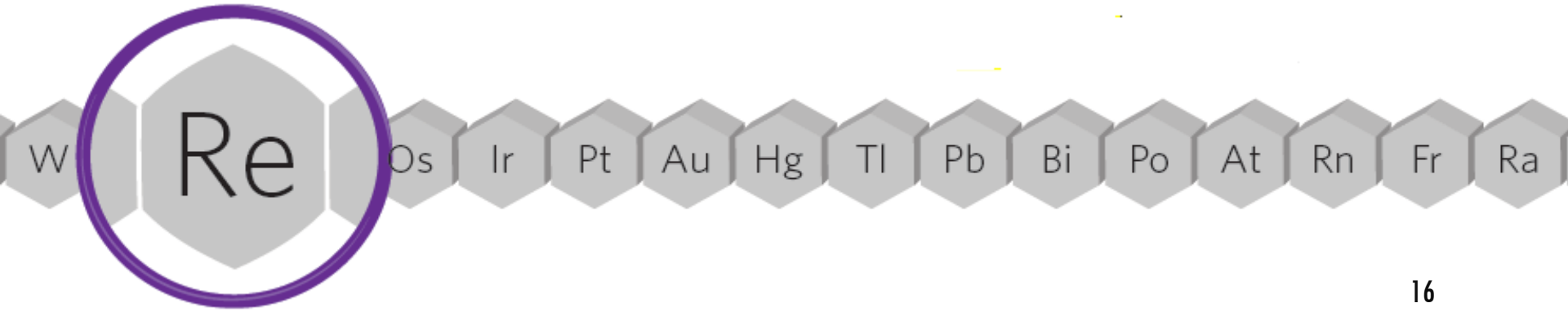
# 2.2 Nucleophilic addition to C—C unsaturated bond



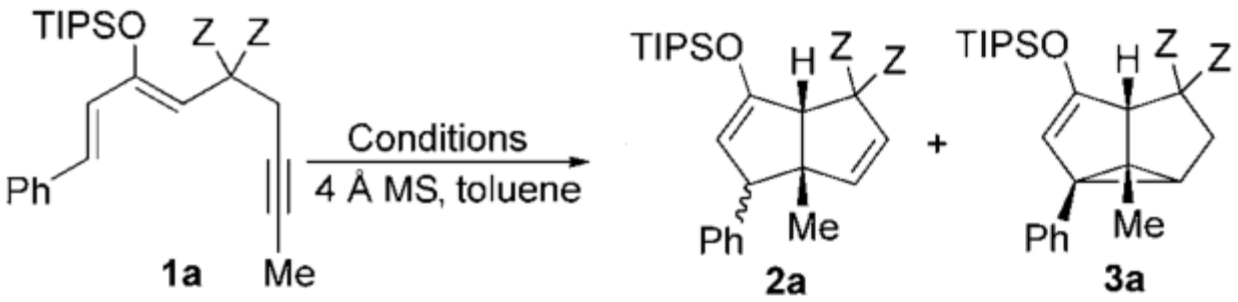

Kuninobu, Y.; Yamashita, A.; Yamamoto, S.-i.; Yudha, S. S.; Takai, K. *Synlett* **2009**, 3027.

# 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



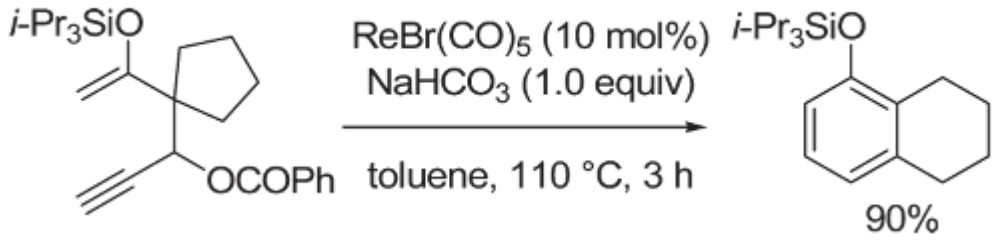

| Conditions | *t* [h] | Yield (**2a**+**3a**) [%] | **2a**(α:β):**3a** |
|---|---|---|---|
| $[W(CO)_6]$ (10 mol%), *hν* | 4 | 88 | 86(9:1):14 |
| $[PtCl_2]$ (10 mol%), 70°C | 48 | 67 | 59(1.3:1):41 |
| $[AuBr_3]$ (10 mol%), RT | 24 | 79 | 65(7.7:1):35 |
| $[ReCl(CO)_5]$ (10 mol%), *hν* | 3 | 98 | 91(12.5:1):9 |
| $[ReCl(CO)_5]$ (0.5 mol%), *hν* | 16 | 92 | 86(4.2:1):14 |

Z = $CO_2Me$, TIPS = triisopropylsilyl, MS = molecular sieves.

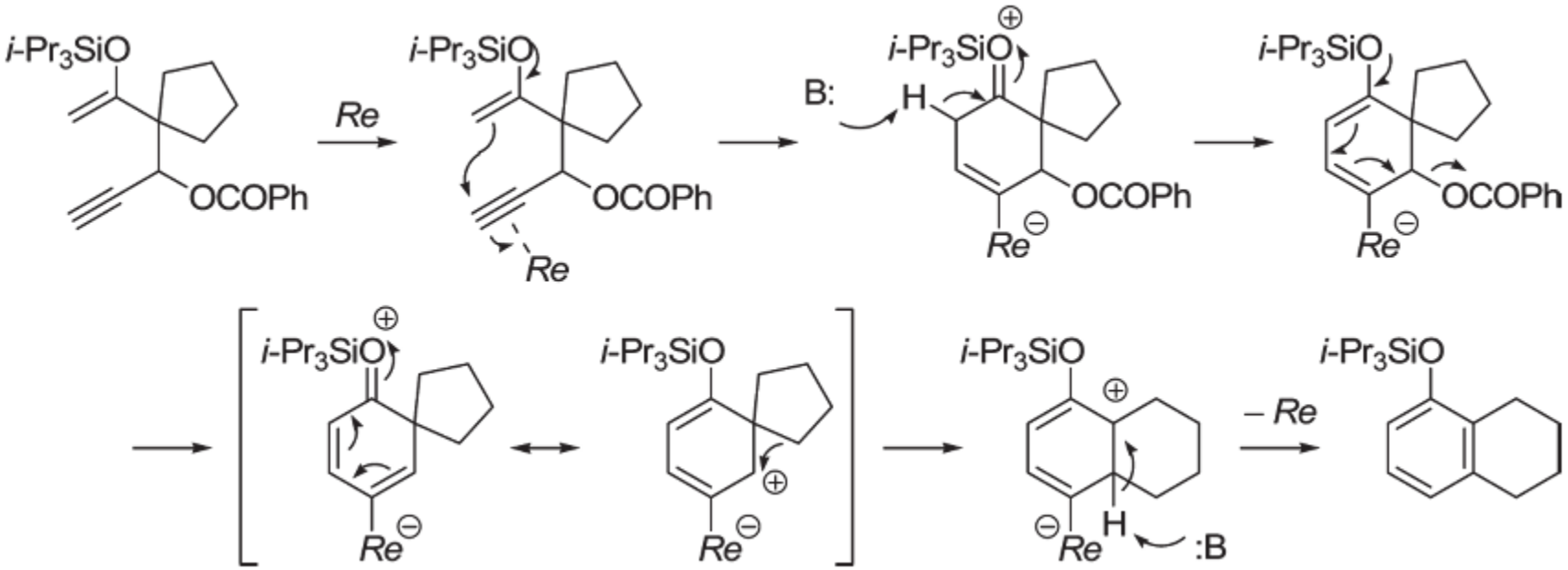
Quiz1: The mechanisms for both 2a and 3a formation?

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

# 2.3 Annulations



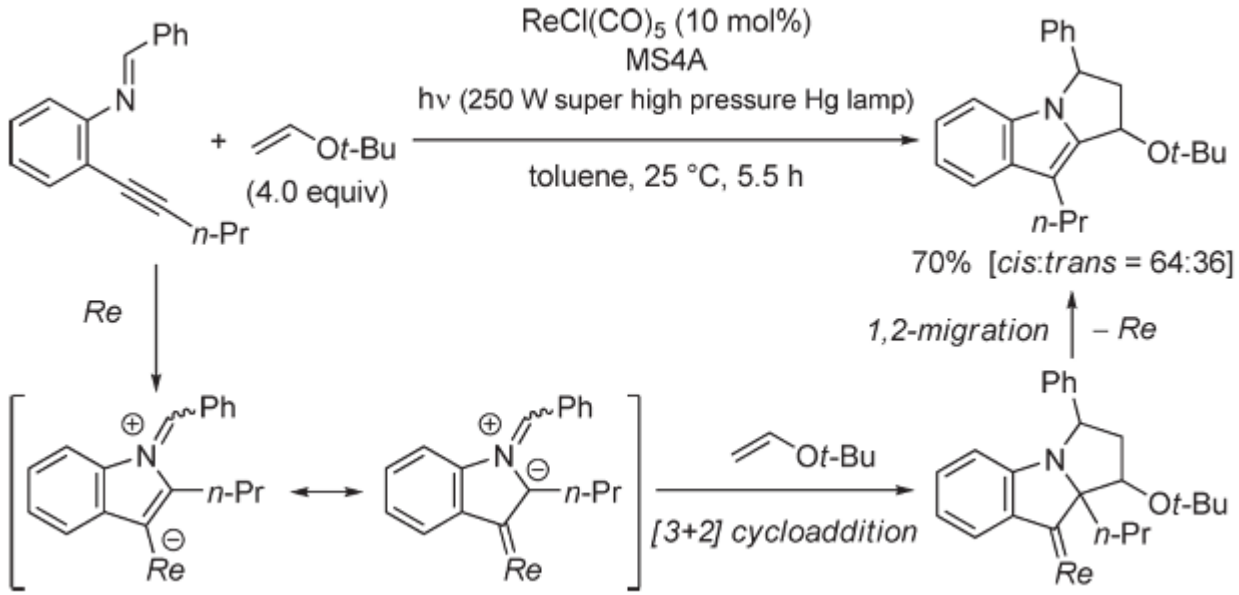

- Mechanism:




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

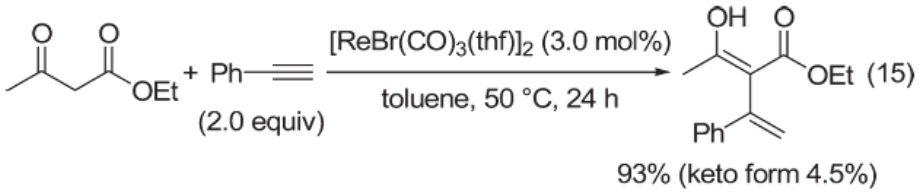
# 2.3 Annulations

- [3+2]

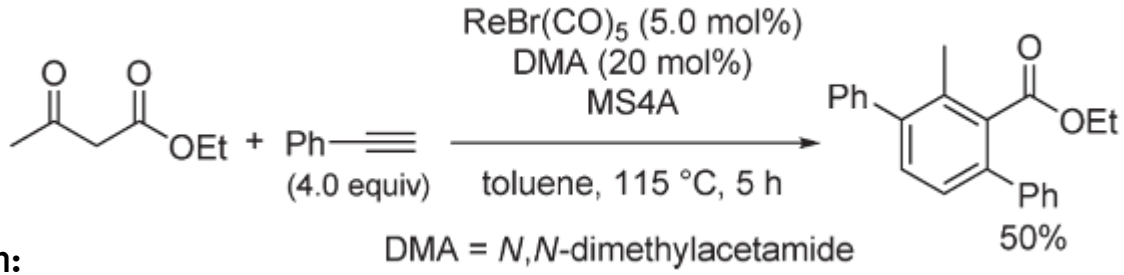



Kusama, H.; Miyashita, Y.; Takaya, J.; Iwasawa, N. *Org. Lett.* **2006**, *8*, 289.

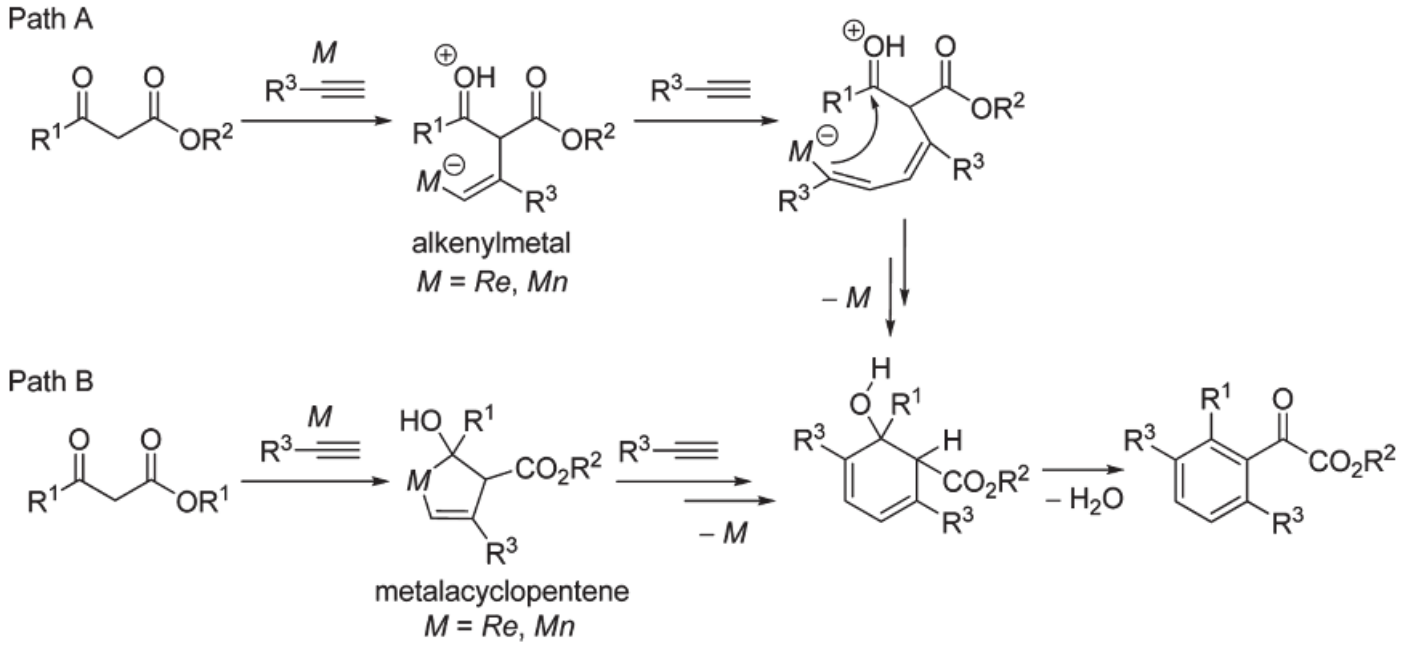
# 2.3 Annulations




OL 2005
Slide 14

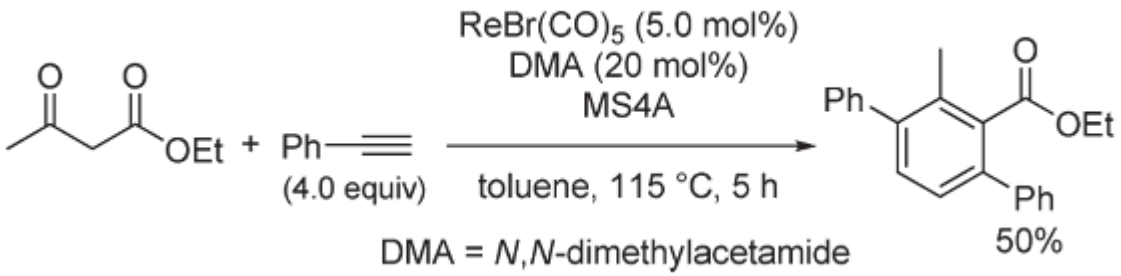



- Mechanism:



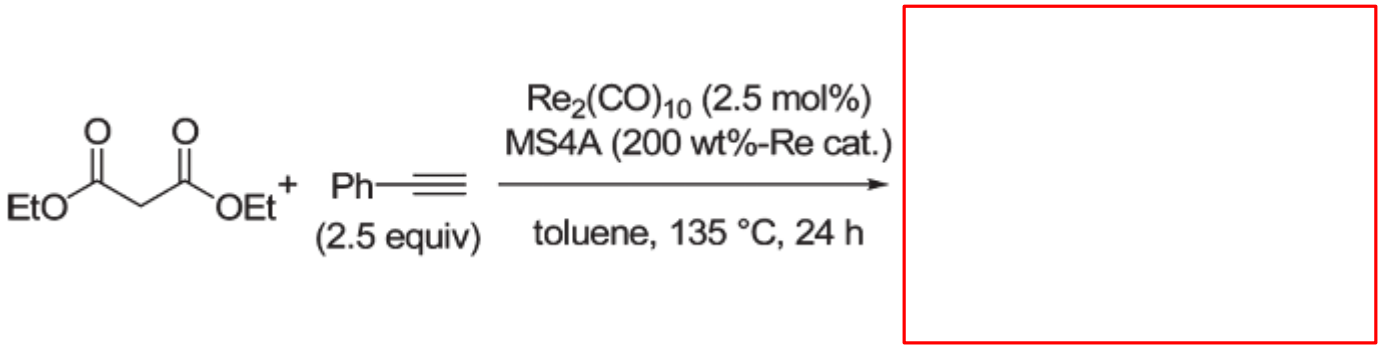

Kuninobu, Y.; Nishi, M.; Yudha, S. S.; Takai, K. *Org. Lett.* **2008**, *10*, 3009.
Tsuji, H.; Yamagata, K.-i.; Fujimoto, T.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 7792.

# 2.3 Annulations




Previous slide

Quiz 2:




Product 54%

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

# 2. C—C bond bond formation

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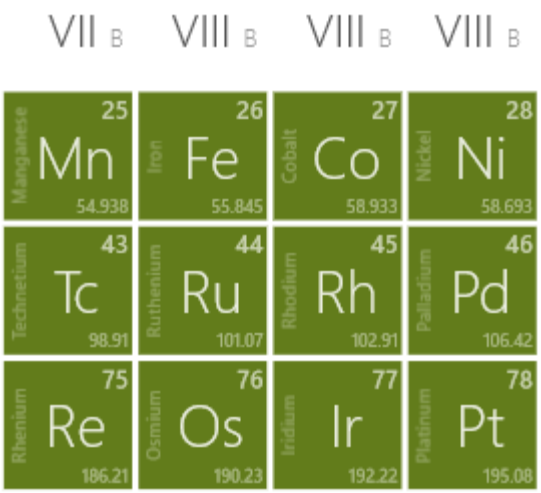
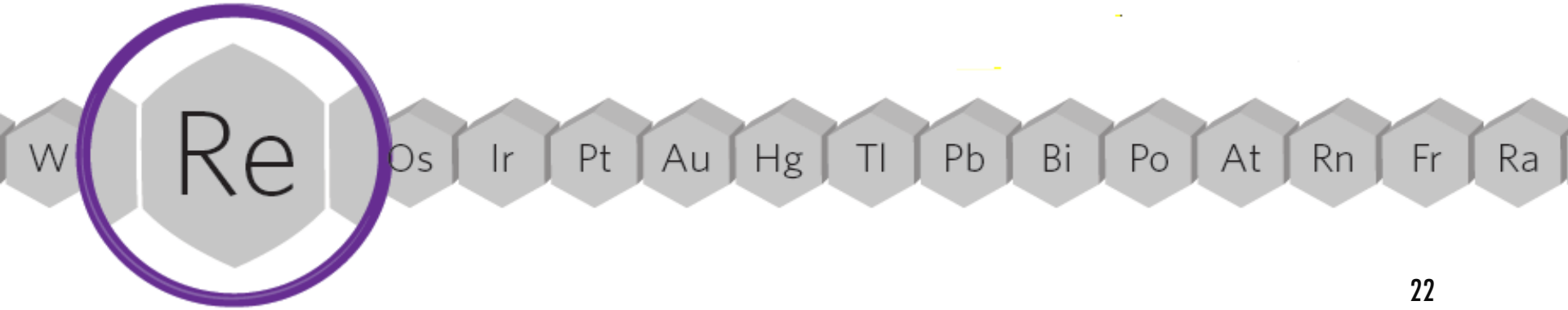
- 2.5 C—C bond cleavage



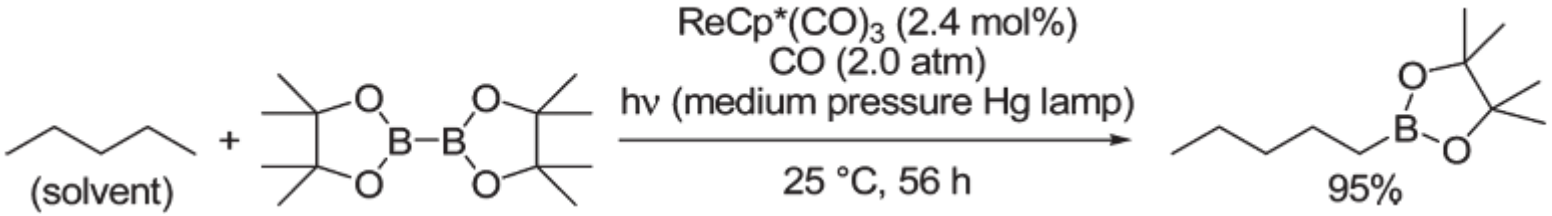

***Re(0,I), Ru(0), Rh(I)***

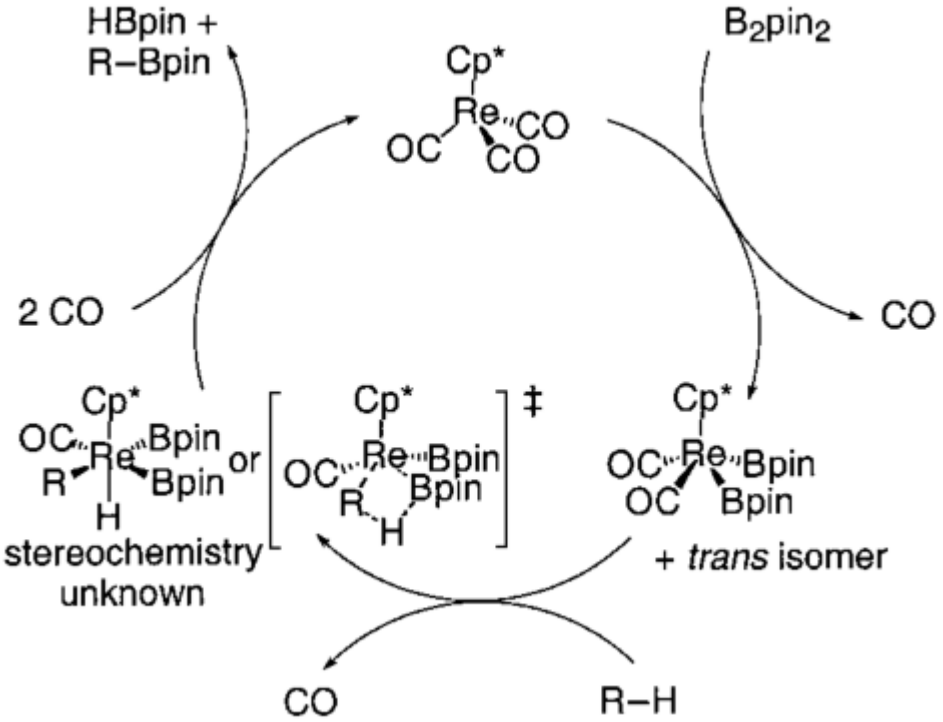
***Rh(III), Pd(II)***



# 2.4 C—H bond activation

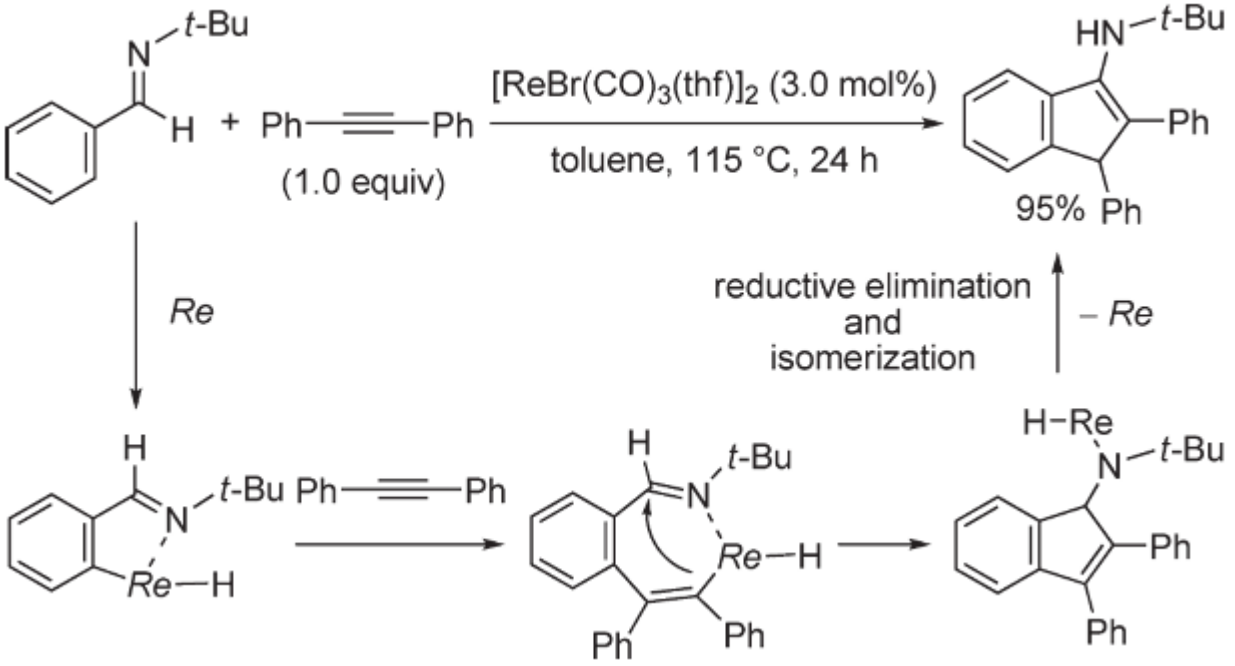
- Sp3 C—H borylation



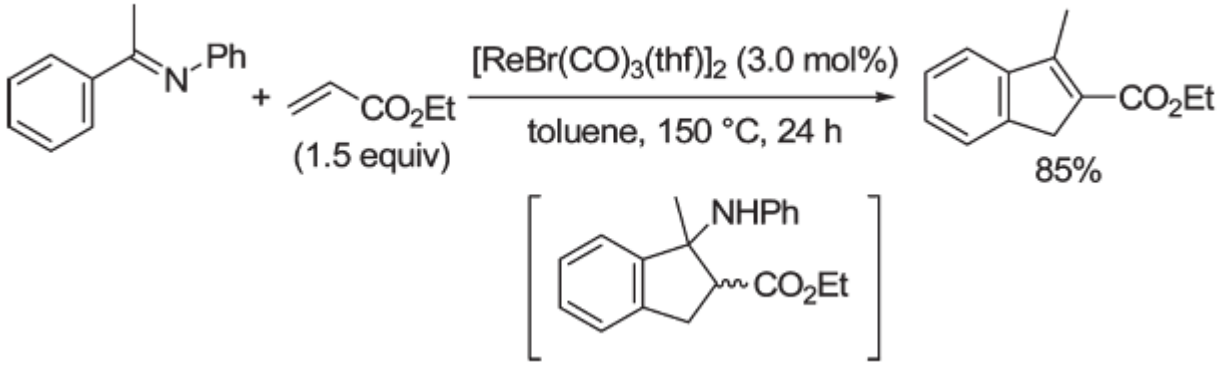




Chen, H.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3391.

# 2.4 C—H bond activation

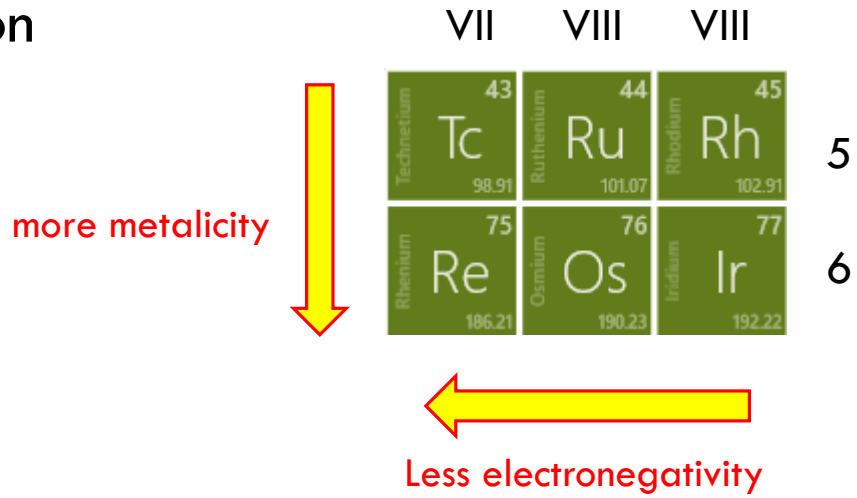


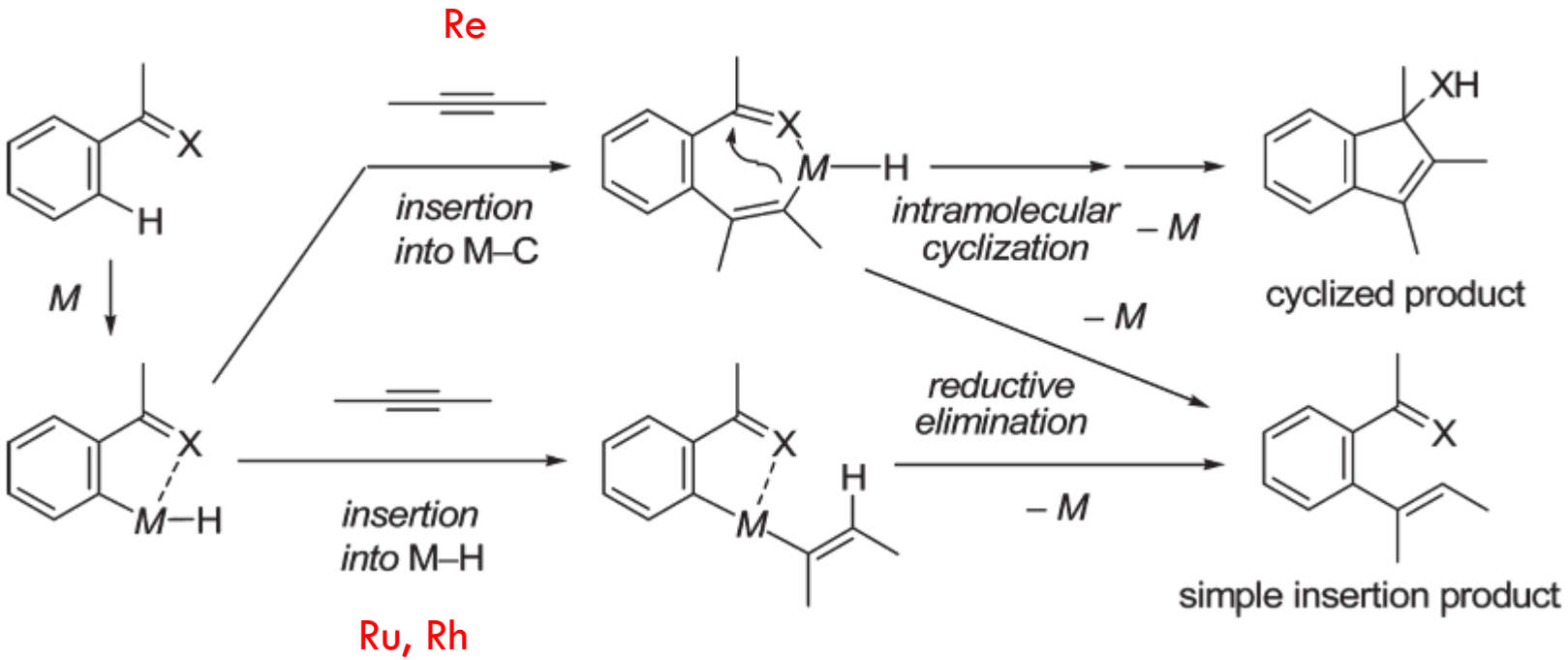

Kuninobu, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc*. **2005**, *127*, 13498.




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

# 2.4 C—H bond activation

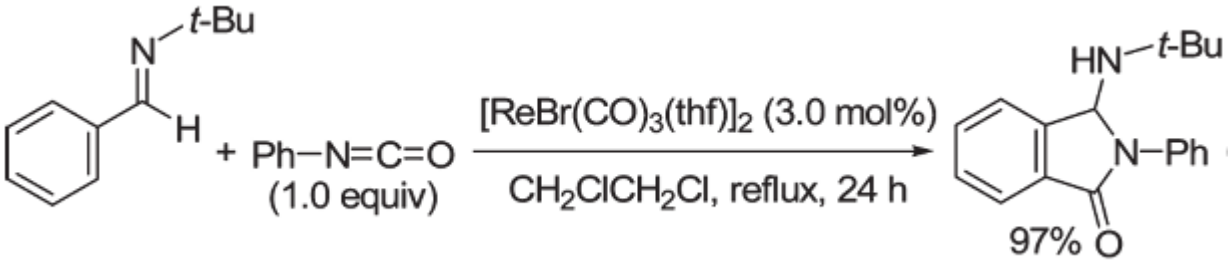


# 2.4 C—H bond activation

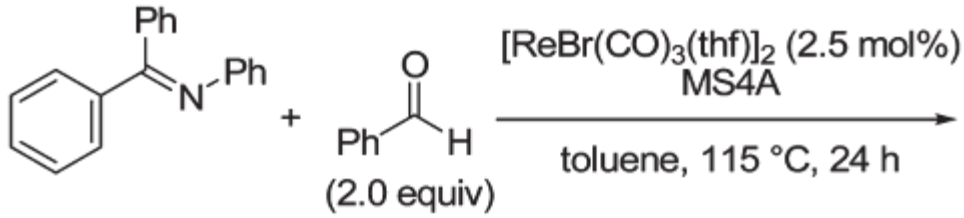
- Addition to polar unsaturated bonds

## Isocyanates




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

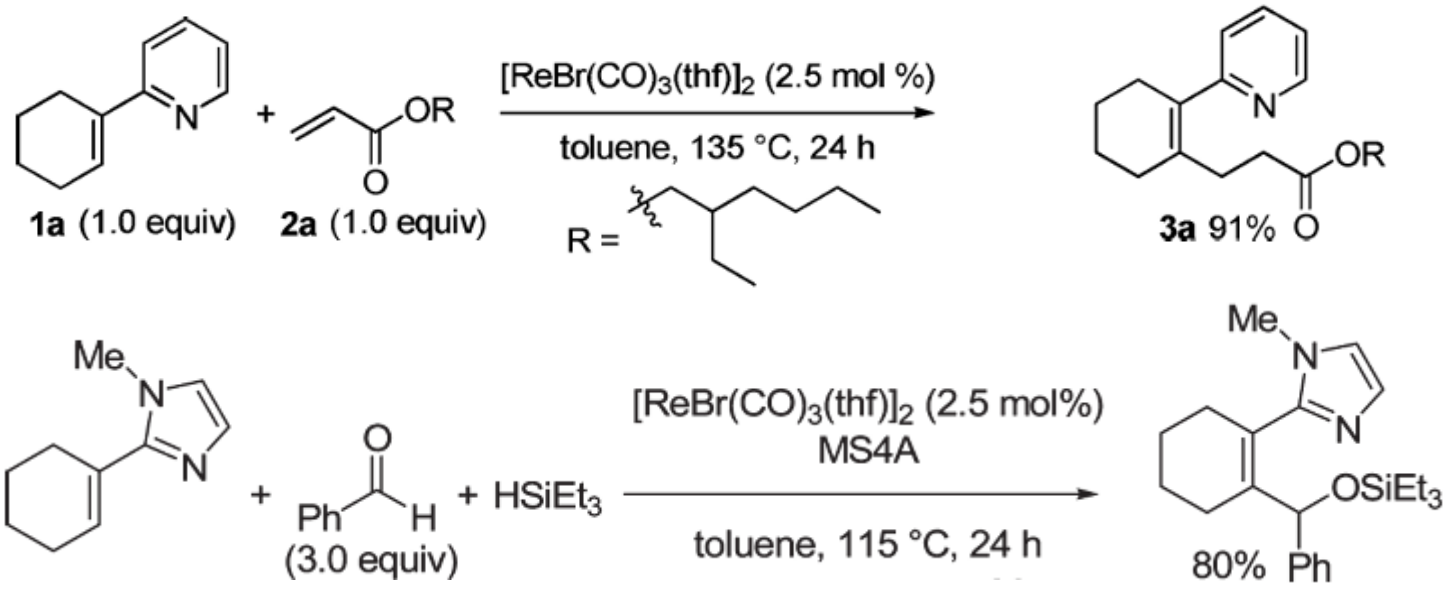
## Aldehydes

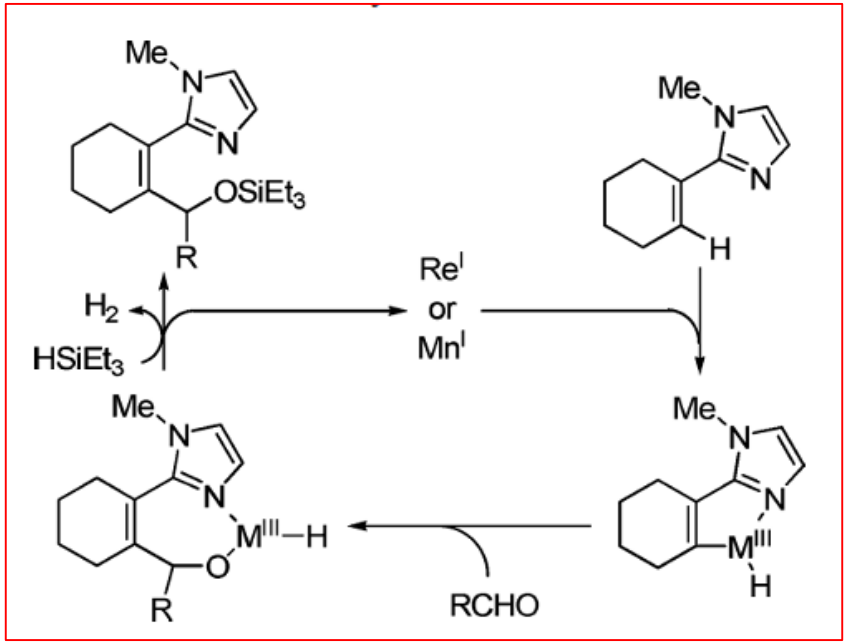



Quiz 3

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

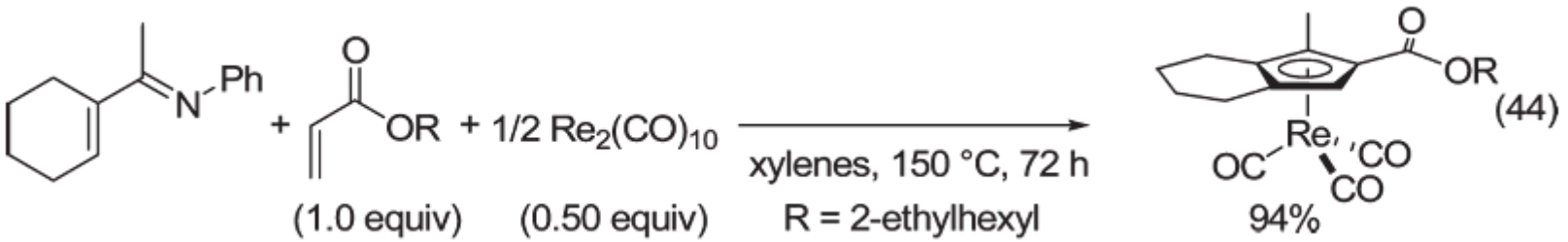
# 2.4 C—H bond activation



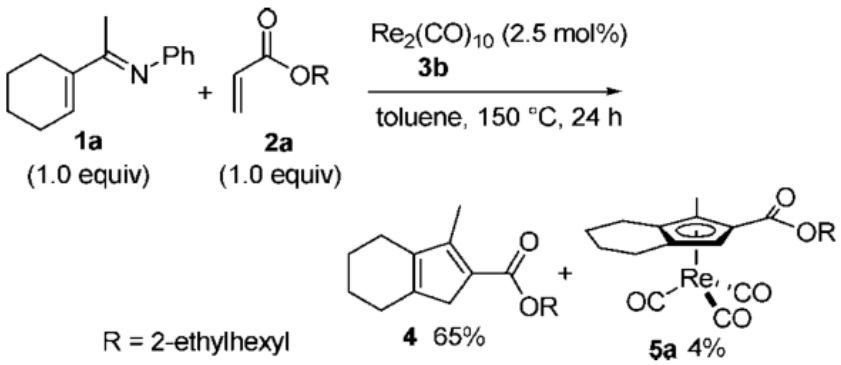




Kuninobu, Y.; Fujii, Y.; Matsuki, T.; Nishina, Y.; Takai, K. *Org. Lett.* **2009**, *11*, 2711.

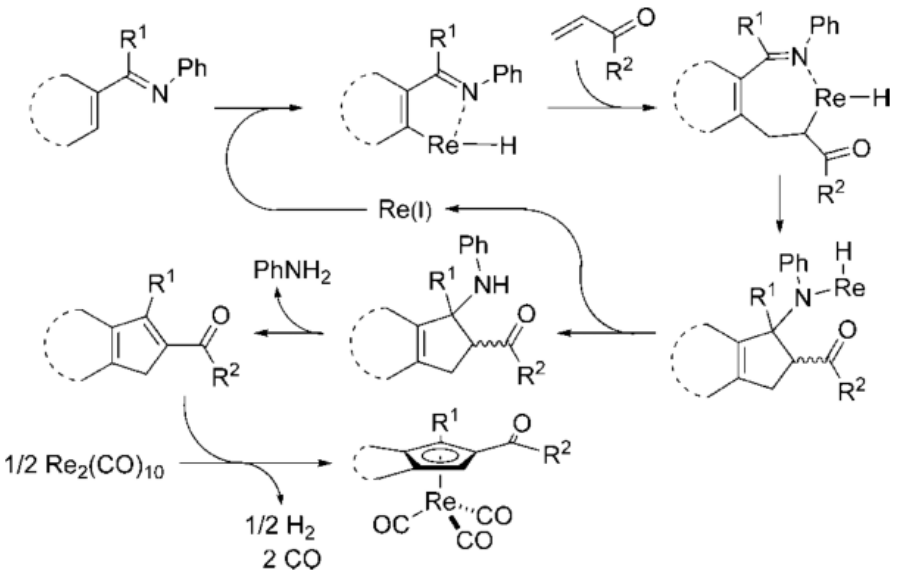
# 2.4 C—H bond activation




- Discovery



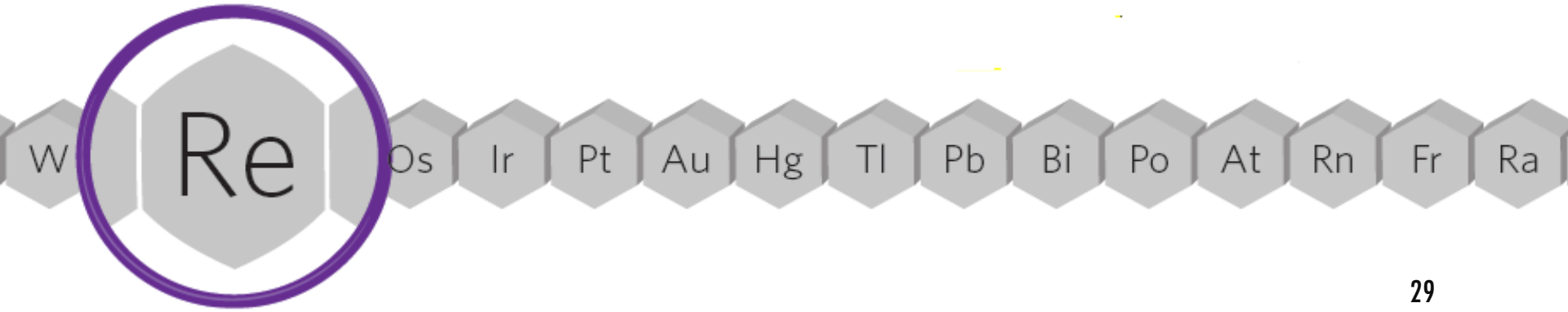

- Mechanism



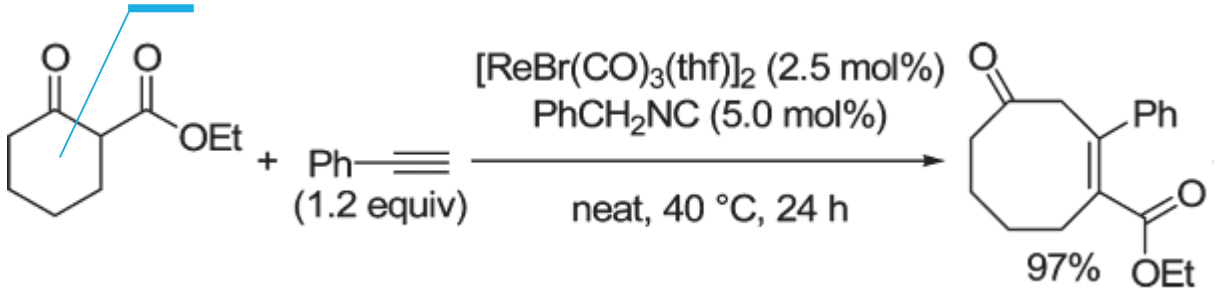

Kuninobu, Y.; Nishina, Y.; Matsuki, T.; Takai, K. *J. Am. Chem. Soc*. **2008**, *130*, 14062.

# 2. C—C bond formation

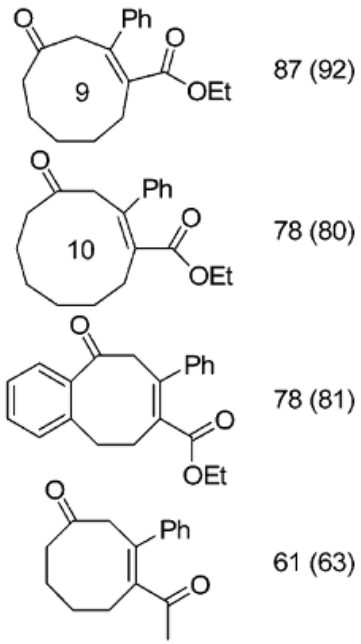
- 2.1 Friedel-Crafts
- 2.2 Nucleophilic addition
- 2.3 Annulations
- 2.4 C—H bond activation
- 2.5 C—C bond cleavage



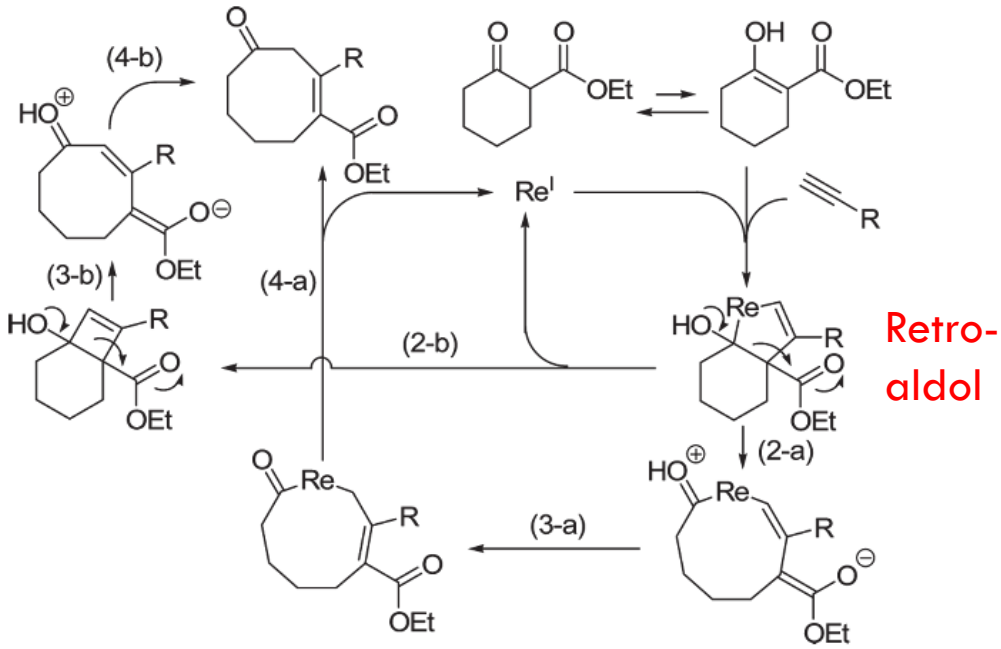
# 2.4 C—C bond cleavage




- Substrate scope

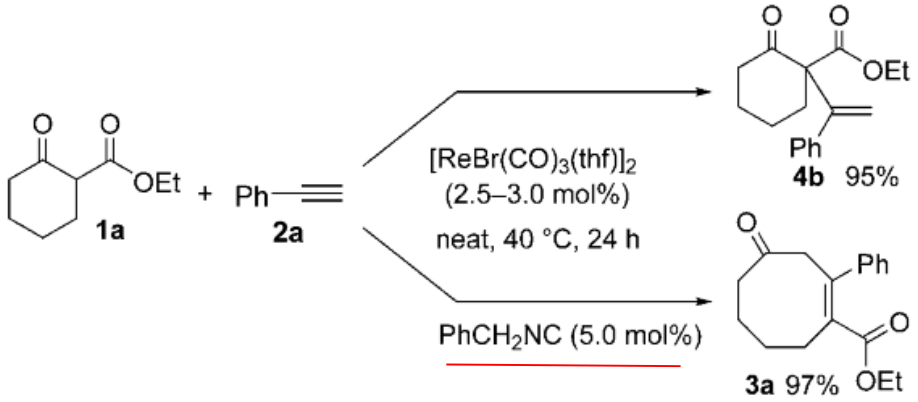



- Mechanism



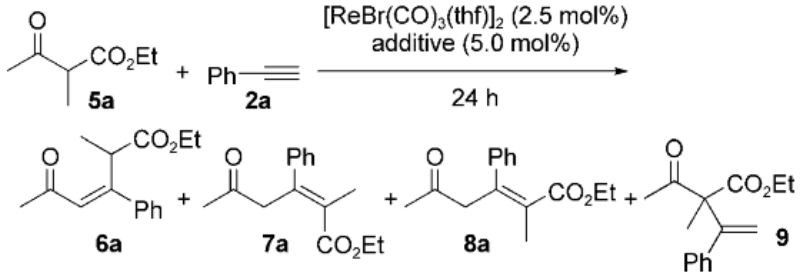

Kuninobu, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 11368.

# 2.4 C—C bond cleavage




OL 2005

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[b] | THF | neat | 50 | 65 | 34 |
| 8 | 2,6-*i*Pr$_2$C$_6$H$_3$NC | neat | 50 | 76 | 15 |

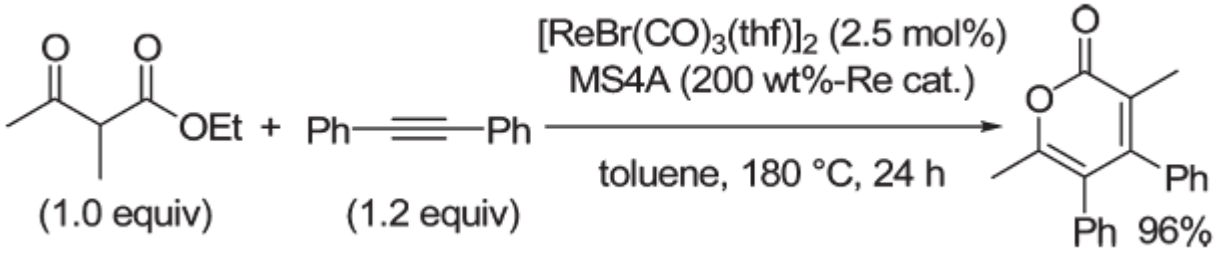
[a] **2a** (1.2 equiv). [b] THF (20 mol %).

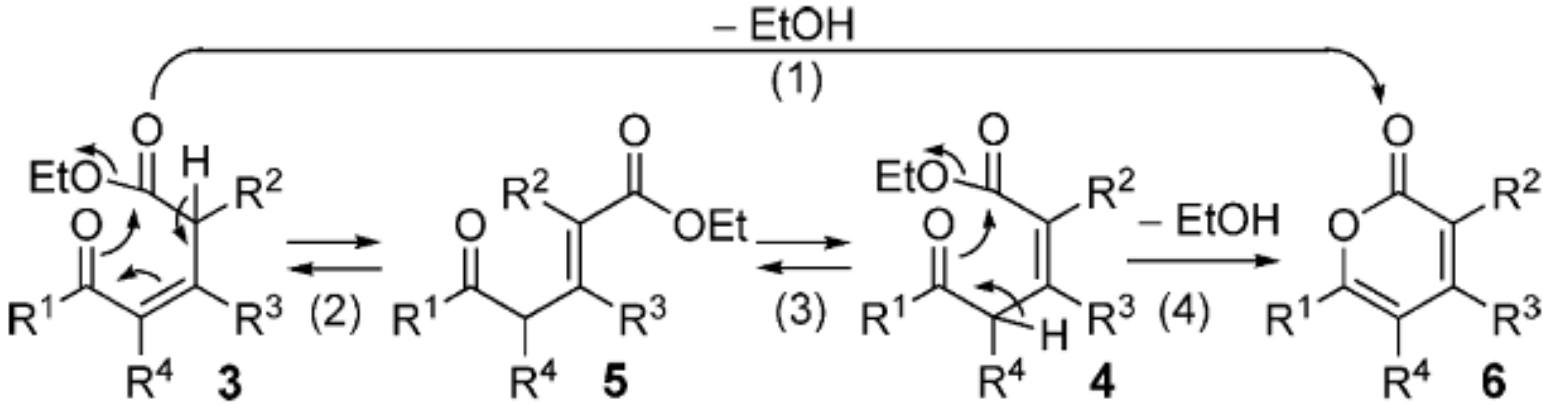
$[ReBr(CO)_3(thf)]_2 \xrightarrow{THF} [ReBr(CO)_3(thf)_2]$

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

Kuninobu, Y.; Kawata, A.; Nishi, M.; Yudha, S. S.; Chen, J.-j.; Takai, K. *Chem. Asian J.* **2009**, *4*, 1424.

# 2.4 C—C bond cleavage




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

# Contents

# 4. Conclusion

***Prior to 2000***

Used as **hard Lewis acid** catalysts

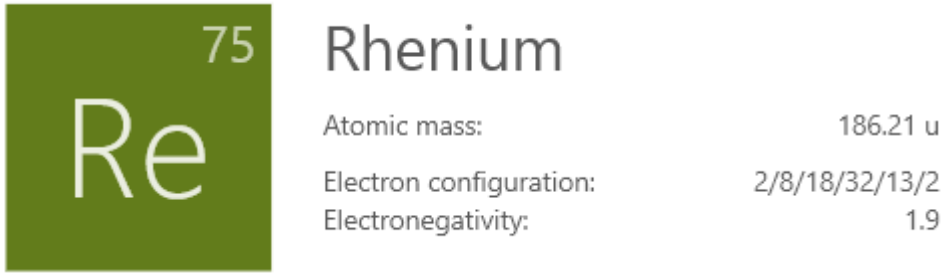
- Friedel-Crafts reactions
- Aldol reactions
- Knoevenagel reactions

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

***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**

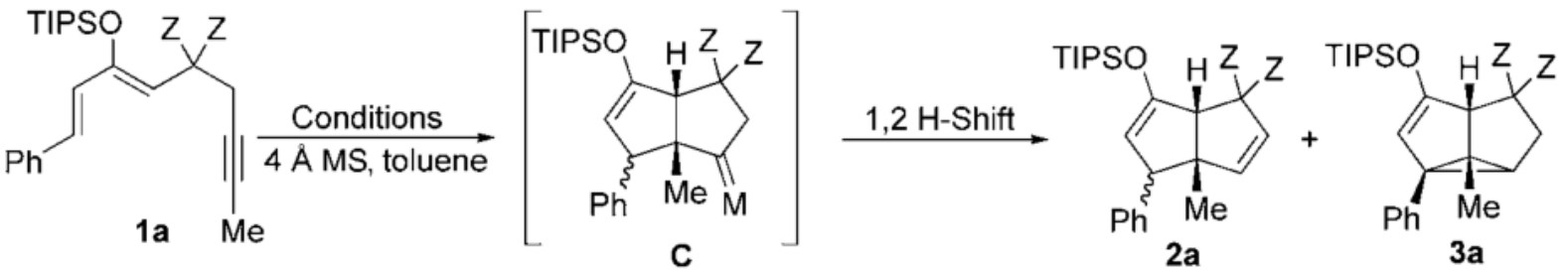
***Since 2005***

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

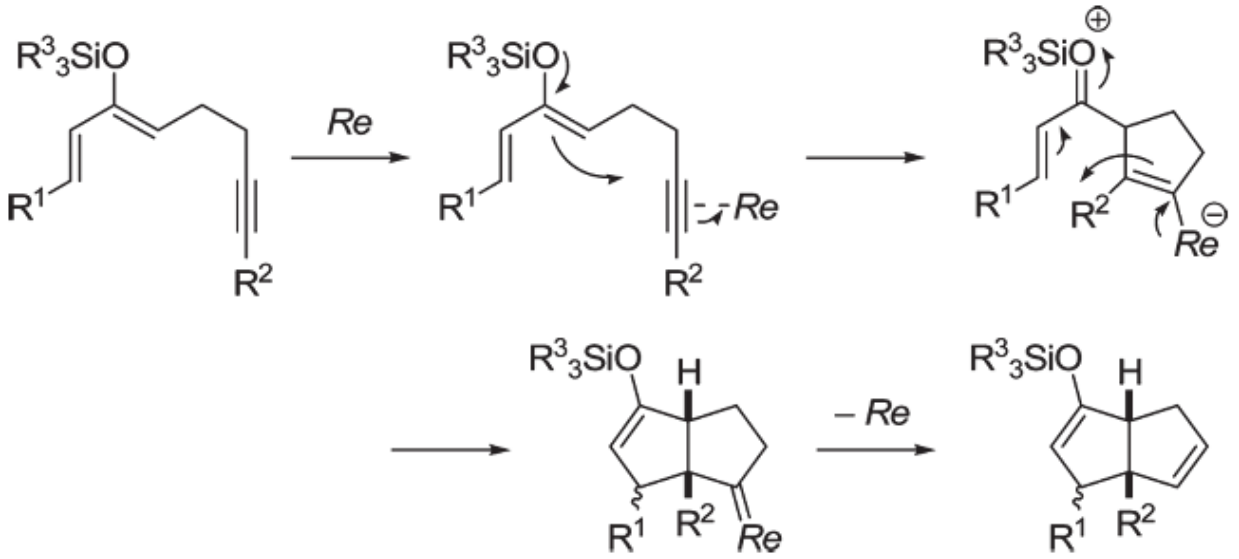
- C-H oxidative addtion
- Unique reactivity

# Thank you!

# Answers for quiz 1

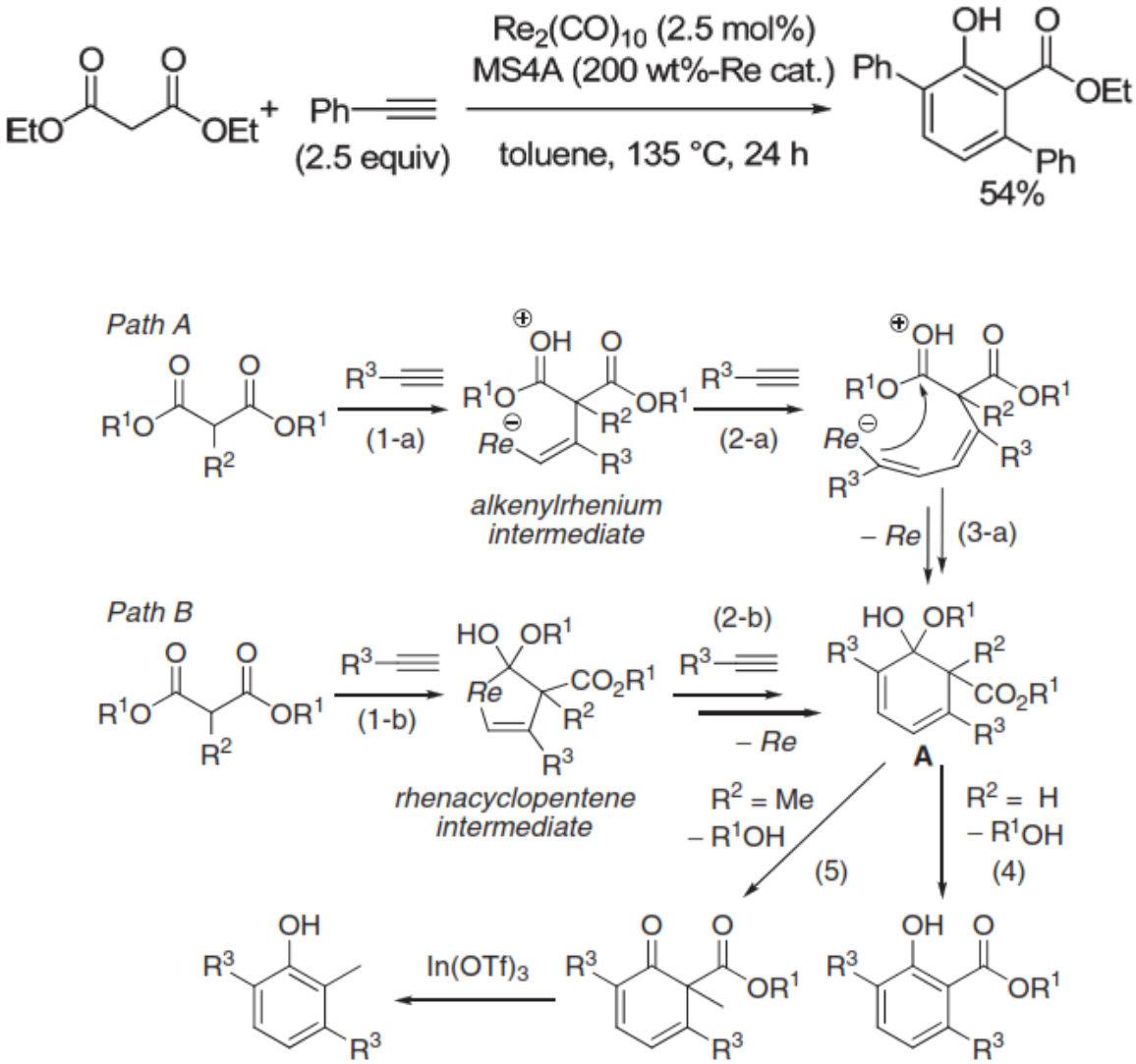



**Scheme 2. Proposed Mechanism for the Formation of Bicyclo[3.3.0]octane Derivatives**



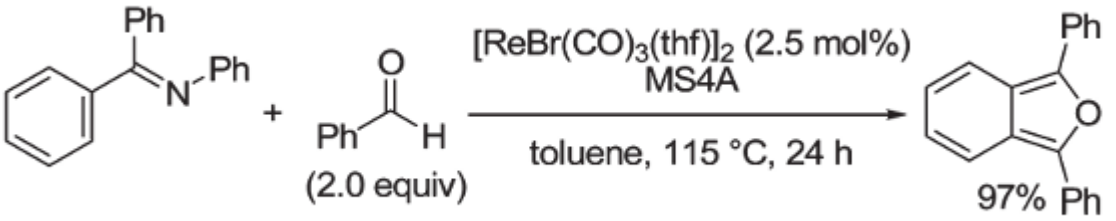

Kusama, H.; Yamabe, H.; Onizawa, Y.; Hoshino, T.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 468.

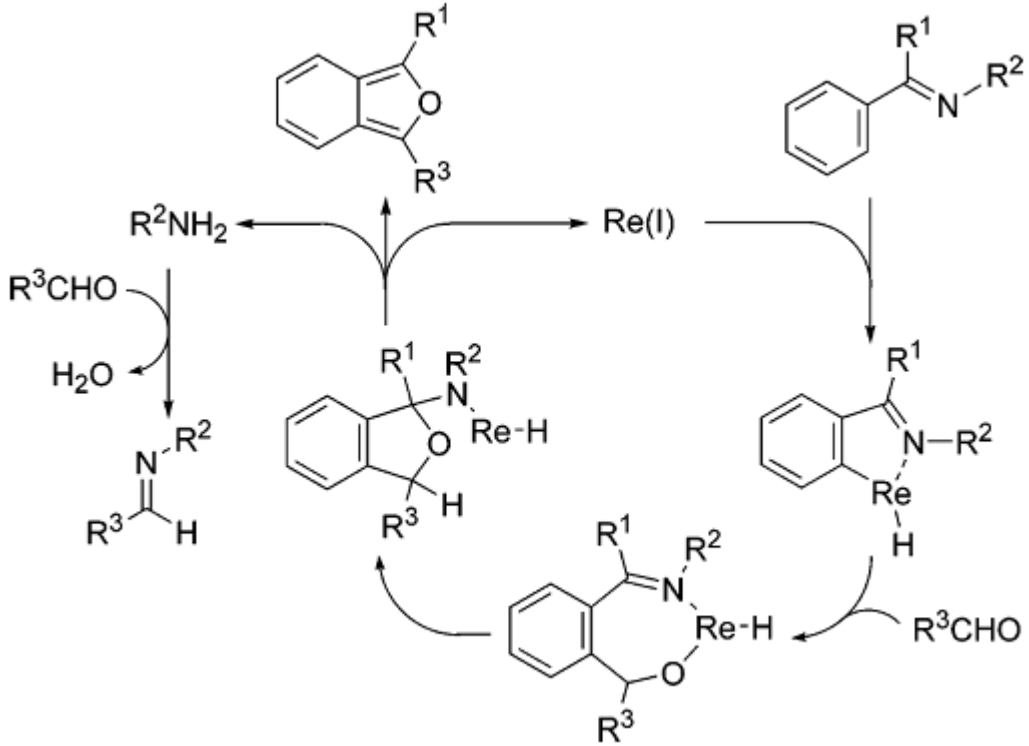
# Answers for quiz 2




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

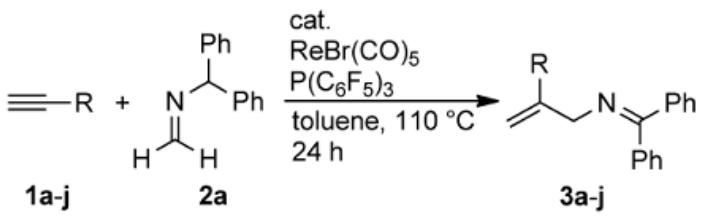
# Answers for quiz 3



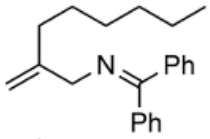
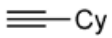
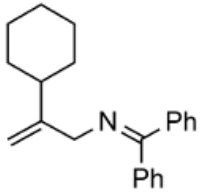
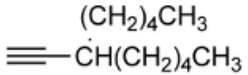
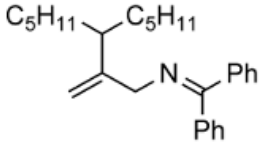



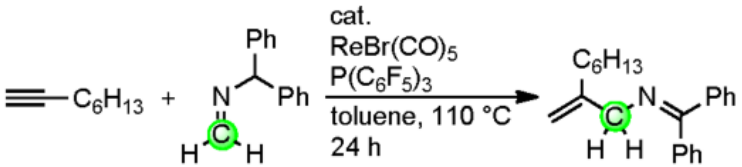

Kuninobu, Y.; Nishina, Y.; Nakagawa, C.; Takai, K. *J. Am. Chem. Soc*. **2006**, *128*, 12376.

# 2.2 Nucleophilic addition to carbonyl compounds

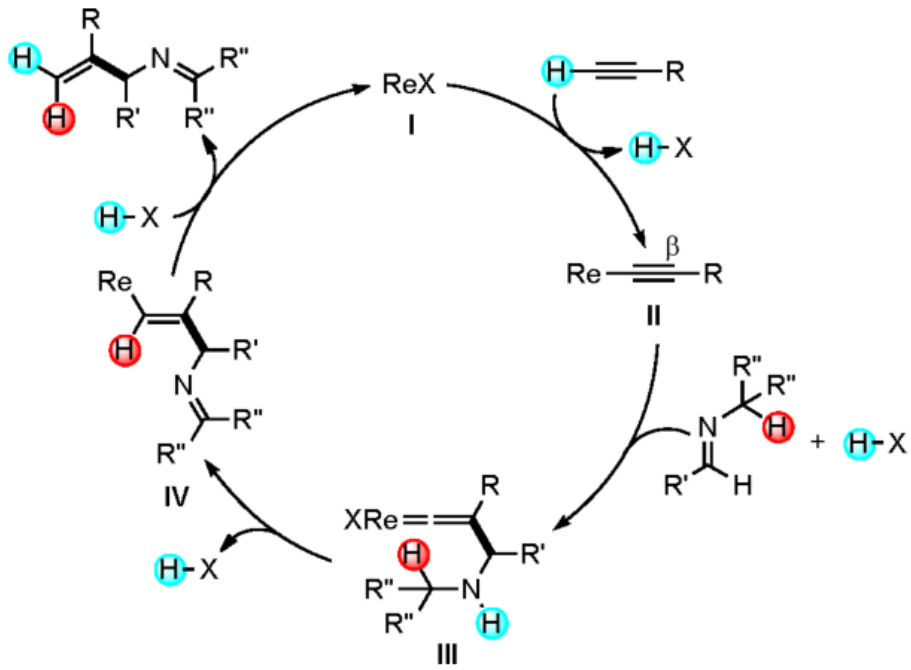


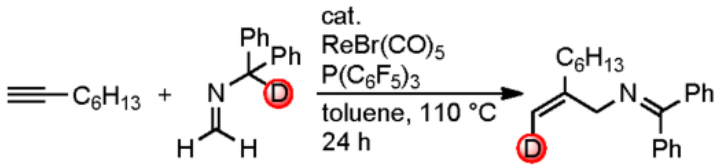

1a-j + 2a → 3a-j

| entry | alkyne | product | | yield (%)[b] |
|---|---|---|---|---|
| 1 |  **1a** |  | **3a** | 73 |
| 2 |  **1b** |  | **3b** | 72 |
| 3 |  **1c** |  | **3c** | 66 |




**1a** **2a-*13C*** **3a-*13C*** 70%

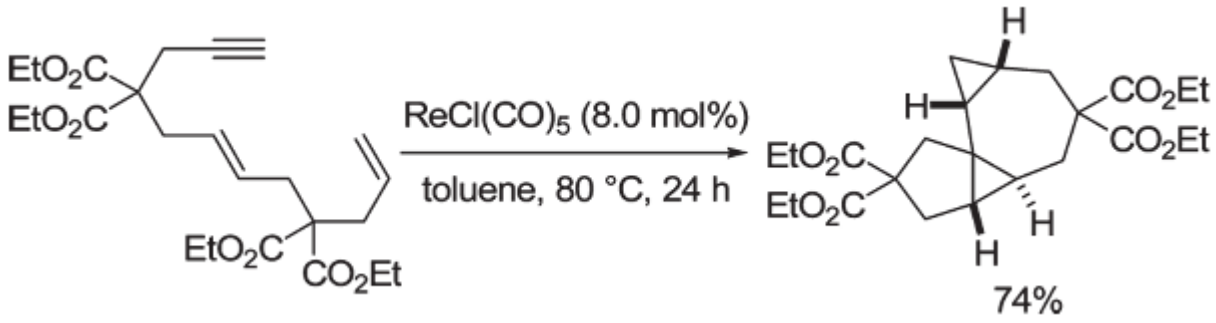


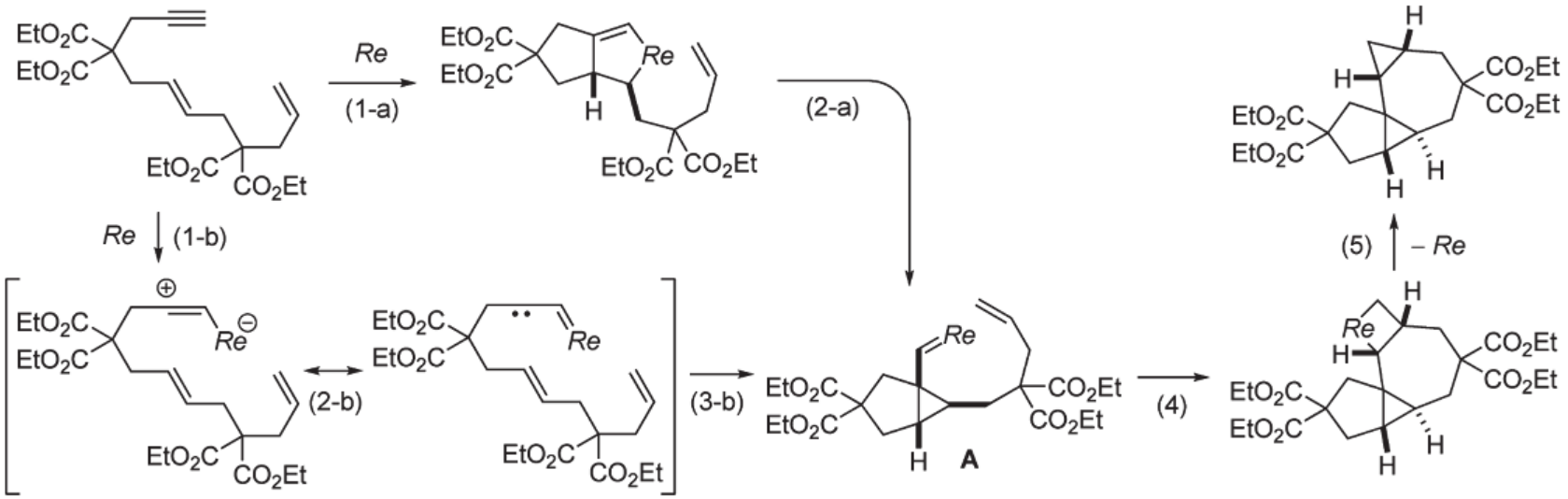

**1a** **2a-*d*** (99% D) **3a-*Z*-*d*** 71% (99% D)

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

# 2.3 Annulations

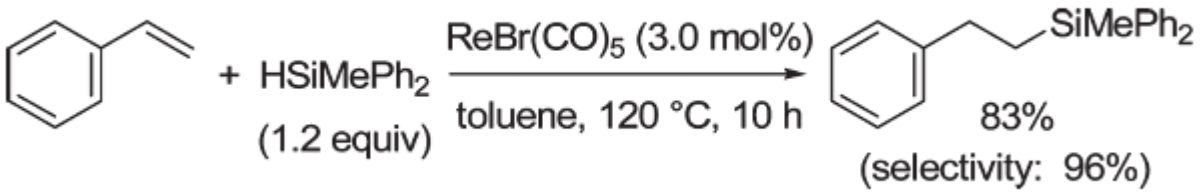



- Mechanism:

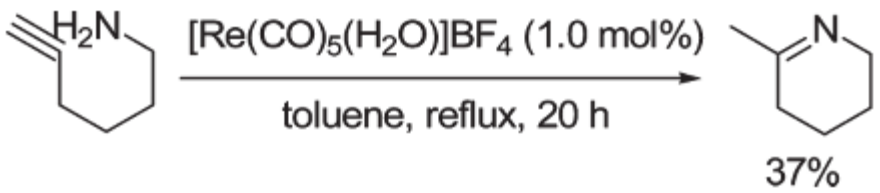



Chatani, N.; Kataoka, K.; Murai, S. *J. Am. Chem. Soc.* **1998**, *120*, 9104.

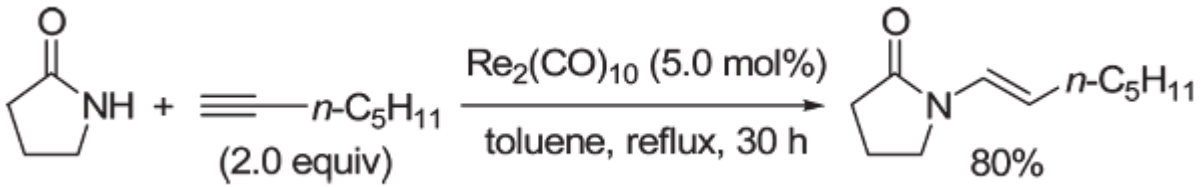
# 3. C—hetero bond formation




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.