

# CATALYTIC ACTIVATION OF UNREACTIVE BOND AND ITS APPLICATION TO FUNCTIONAL MATERIALS

ISCHIA ADVANCED SCHOOL OF ORGANIC CHEMISTRY (IASOC 2012)  
September 22-26, 2012, Ischia (naples)



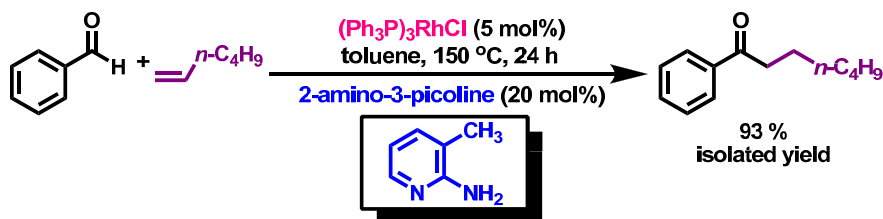
Chul-Ho Jun

Department of Chemistry  
Yonsei University, Seoul 120-749, Republic of Korea  
junch@yonsei.ac.kr

## Catalytic C-H bond Cleavage



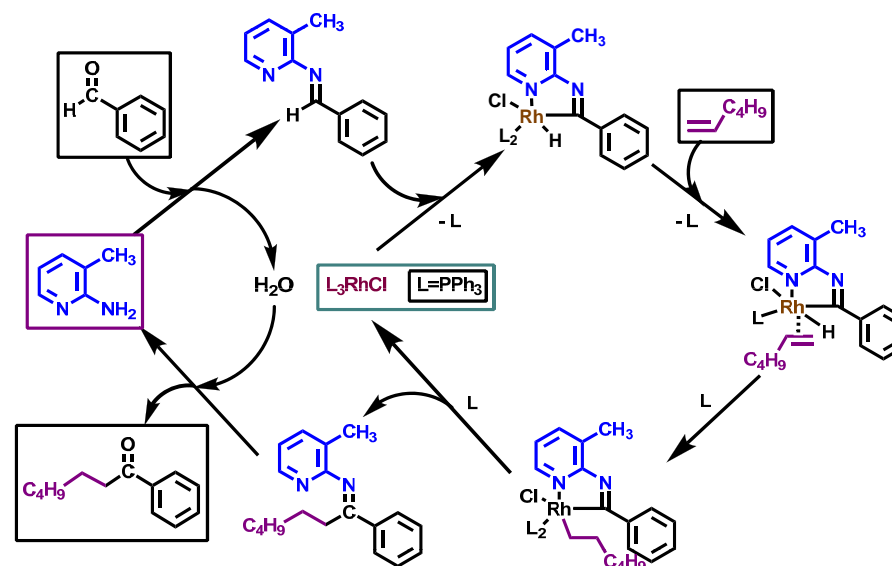
## Chelation-Assisted Hydroacylation of 1-Alkene and Aldehyde



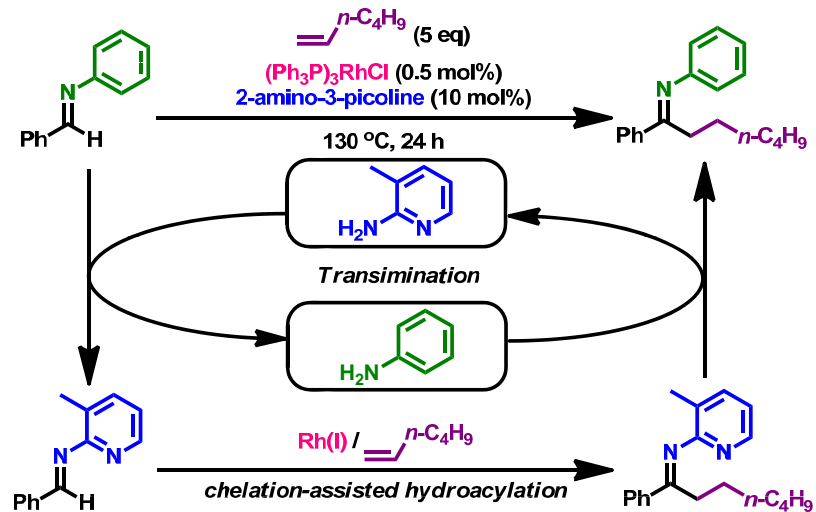
Jun, C. -H.; Lee, H.; Hong, J. -B. *J. Org. Chem.* 1997, 62, 1200



## - Mechanism



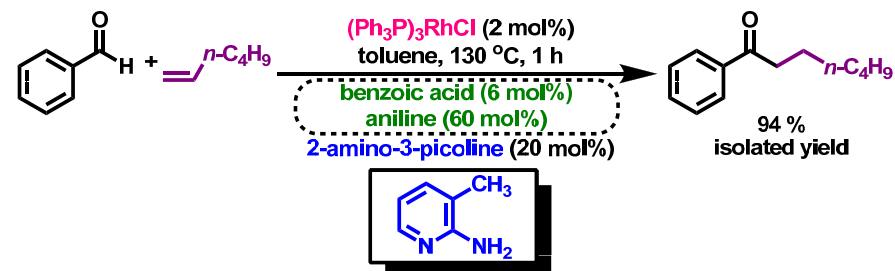
## Hydroimination through transimination



Jun, C. -H.; Hong, J. -B. *Org. Lett.* 1999, 1, 887.



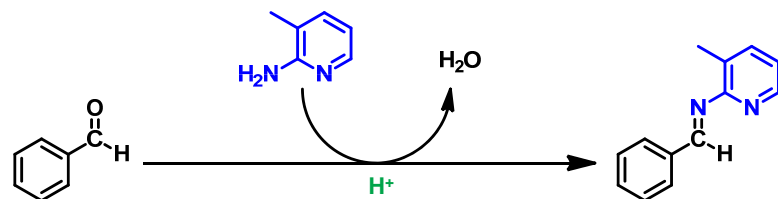
## Highly Efficient Hydroacylation of 1-Alkene and Aldehyde



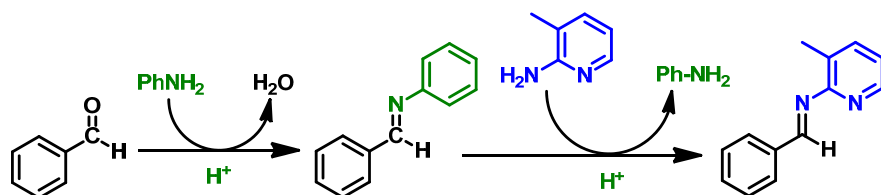
Jun, C. -H.; Lee, D. -Y.; Lee, H.; Hong, J. -B. *Angew. Chem. Int. Ed.* 2000, 39, 3070



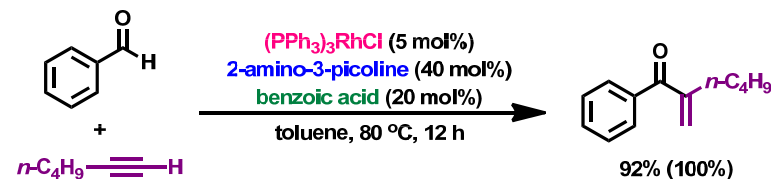
## Direct Condensation



## Transimination-Assisted Condensation



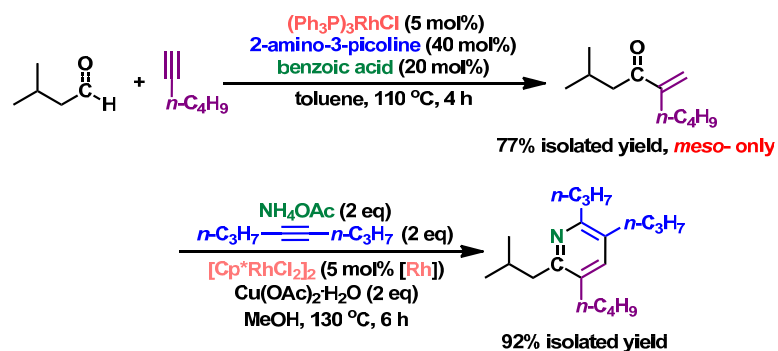
## Regioselective Chelation-Assisted Hydroacylation of Terminal Alkyne



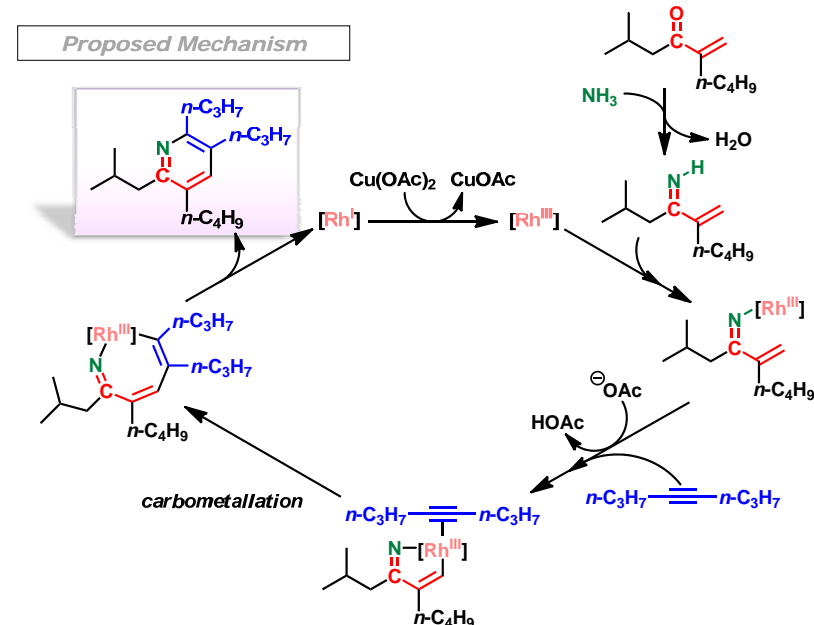
Jun, C.-H.; Lee, H.; Hong, J. B.; Kwon, B.-I., *Angew. Chem. Int. Ed.*, 2002, 41, 2146-2147



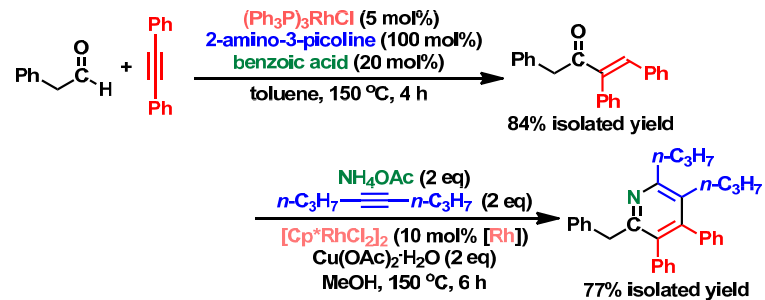
## Combination of Hydroacylation of 1-Alkyne & N-Annulation for the Synthesis of Tetrasubstituted Pyridine



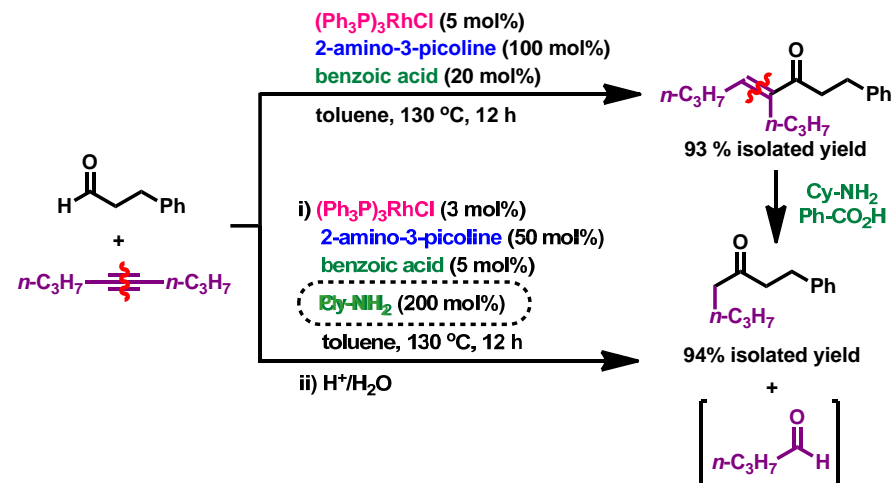
Sim, Y.-K.; Lee, H.; Park, J.-W.; Kim, D.-S.; Jun, C.-H.; submitted for publication



## Combination of Hydroacylation of Internal Alkyne & N-Annulation for the Synthesis of Peralkylated Pyridine

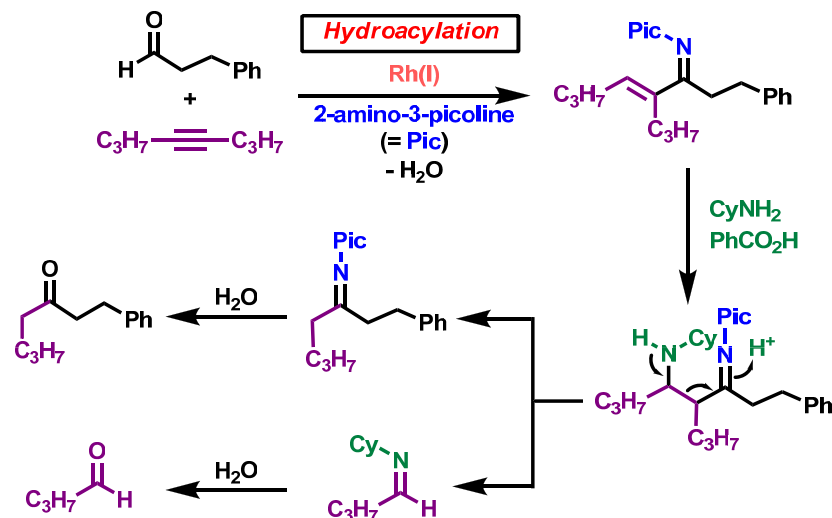


## C-C Triple Bond Cleavage of Alkyne through C-H Bond Activation

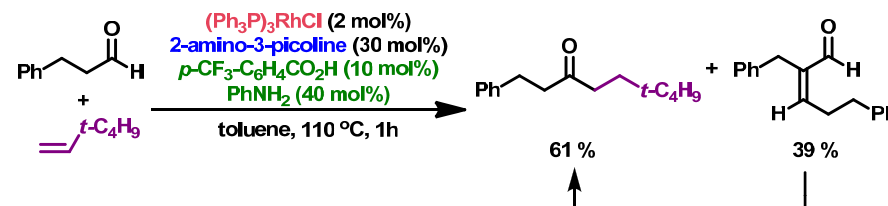


Lee, D. -Y.; Hong, B. -S.; Cho, E. -G.; Lee, H.; Jun, C. -H. *J. Am. Chem. Soc.* 2003, 125, 6372-6373

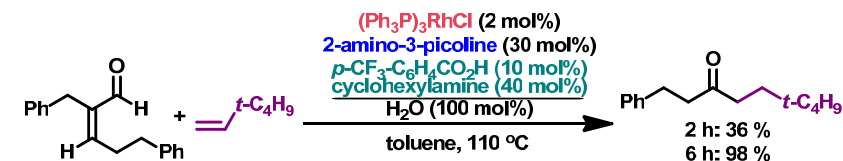
- Mechanism



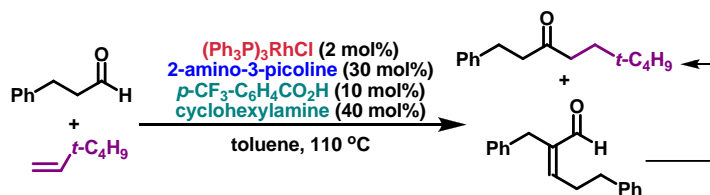
## Hydroacylation of 1-Alkene with Aliphatic Aldehyde



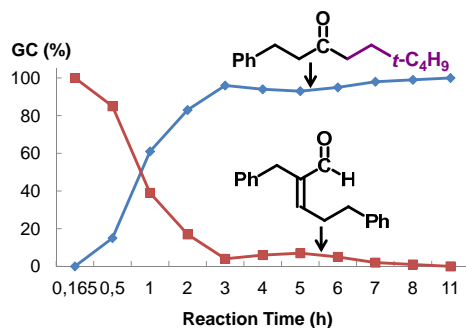
### Hydroacylation with Aldol Intermediate



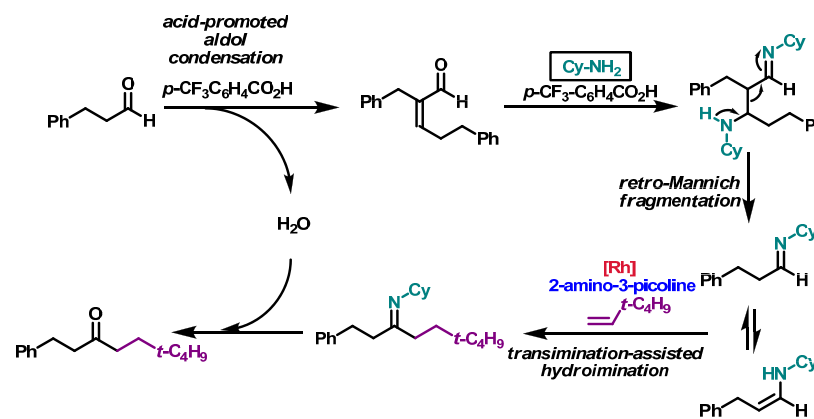
Jo, E. -A.; Jun, C. -H. *Tetrahedron Lett.* 2009, 50, 3338. (50th Anniversary)



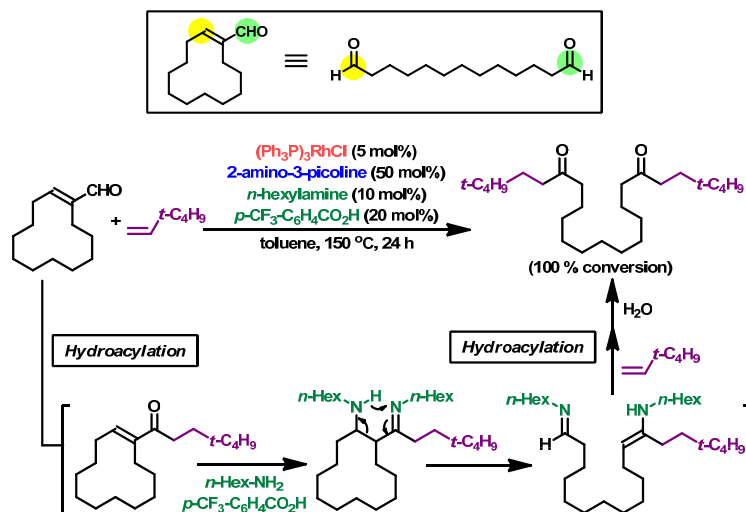
Entry	Rxn Time	GC yield (%)	
		Ph-CH <sub>2</sub> -CH <sub>2</sub> -C(=O)-CH <sub>2</sub> -CH <sub>2</sub> -Ph	Ph-CH <sub>2</sub> -CH <sub>2</sub> -C(=O)-CH=CH-Ph
1	10 min	0	100
2	30 min	15	85
3	1 h	61	39
4	2 h	83	17
5	3 h	96	4
6	4 h	94	6
7	5 h	93	7
8	6 h	95	5
9	7 h	98	2
10	8 h	99	1
11	11 h	100	0



## Mechanism of Hydroacylation with Aliphatic Aldehyde



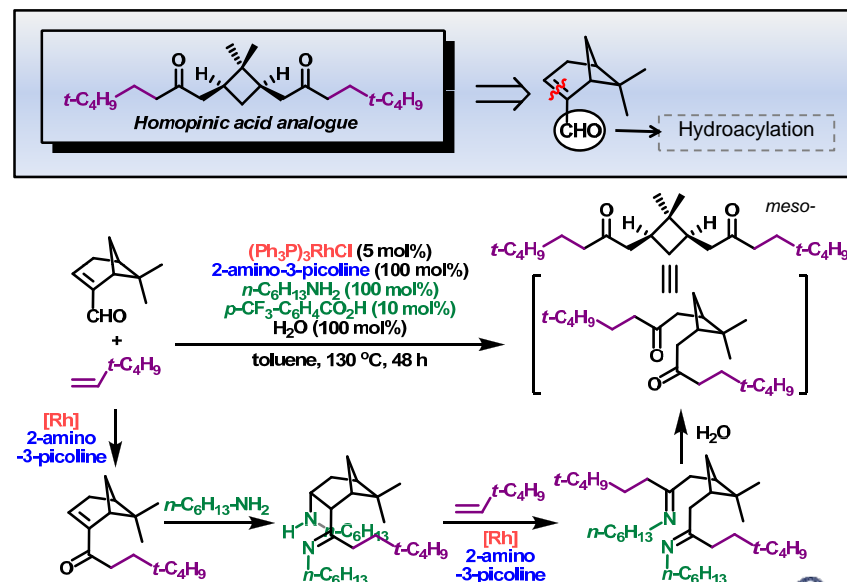
## Double Hydroacylation of 1-Alkene with 1-Cyclododecenecarboxaldehyde



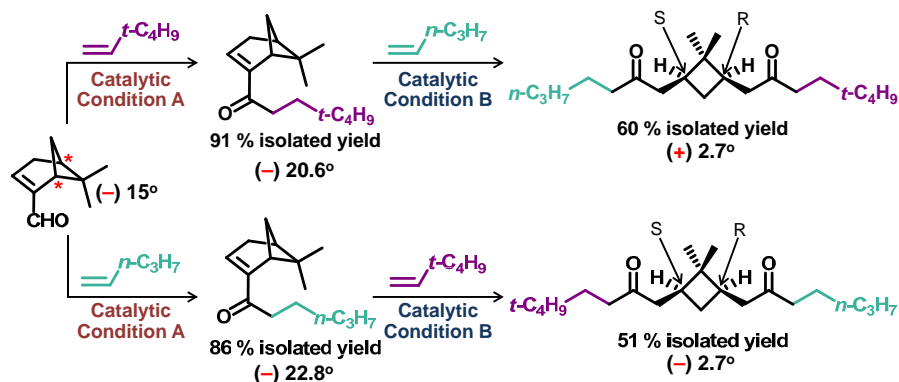
Cha, K.-M.; Lee, H.; Park, J.-W.; Lee, Y.; Jo, E.-A.; Jun, C.-H. *Chem. Asian J.* 2011, 6, 1926.



## Application of C-C Double Bond Activation: Synthesis of Homopinic Acid Analogue



## Synthesis of Chiral Homopinic Acid Analogue with Different Optical Rotation



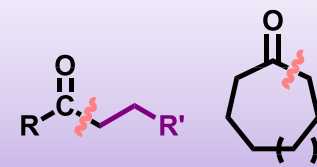
**Catalytic Condition A**  
for the hydroacylation of Myrtenal

$(\text{Ph}_3\text{P})_3\text{RhCl}$  (5 mol%)  
 $2\text{-amino-3-picoline}$  (100 mol%)  
 $p\text{-CF}_3\text{-C}_6\text{H}_4\text{CO}_2\text{H}$  (10 mol%)  
 toluene, 150 °C, 15 min ~ 1 h

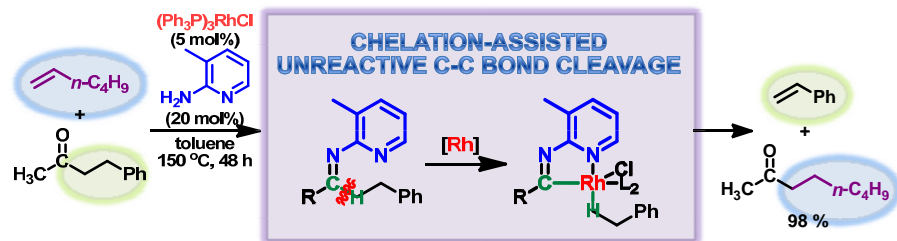
**Catalytic Condition B**  
for retro-Mannich fragmentation  
and subsequent hydroacylation

$(\text{Ph}_3\text{P})_3\text{RhCl}$  (5 mol%)  
 $2\text{-amino-3-picoline}$  (100 mol%)  
 $n\text{-C}_6\text{H}_{13}\text{NH}_2$  (100 mol%)  
 $p\text{-CF}_3\text{-C}_6\text{H}_4\text{CO}_2\text{H}$  (10 mol%)  
 $\text{H}_2\text{O}$  (100 mol%)  
 toluene, 150 °C, 24 h

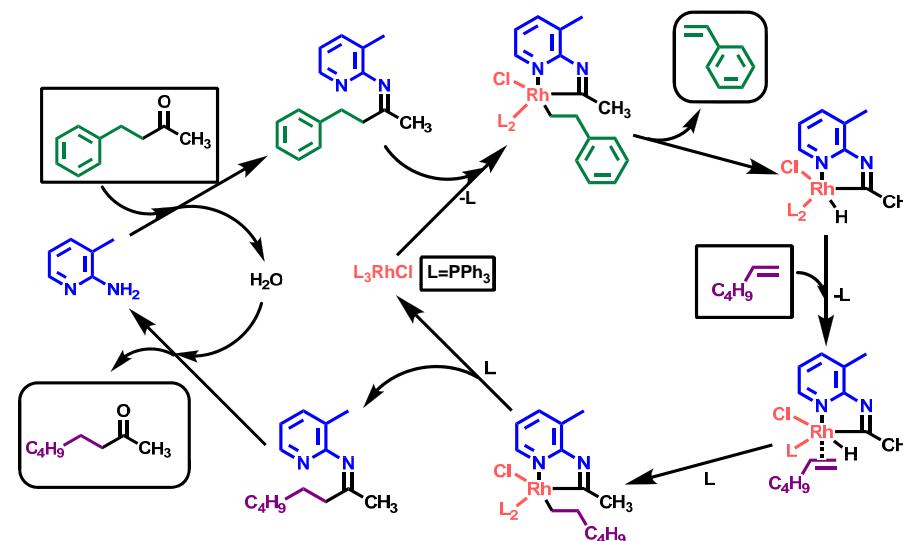
## C-C Single Bond Activation



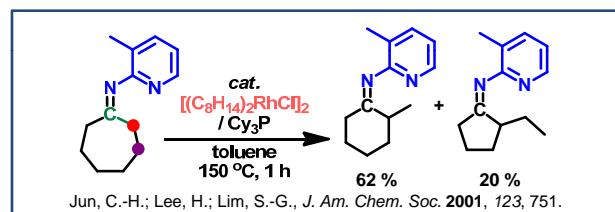
## Catalytic C-C Bond Activation



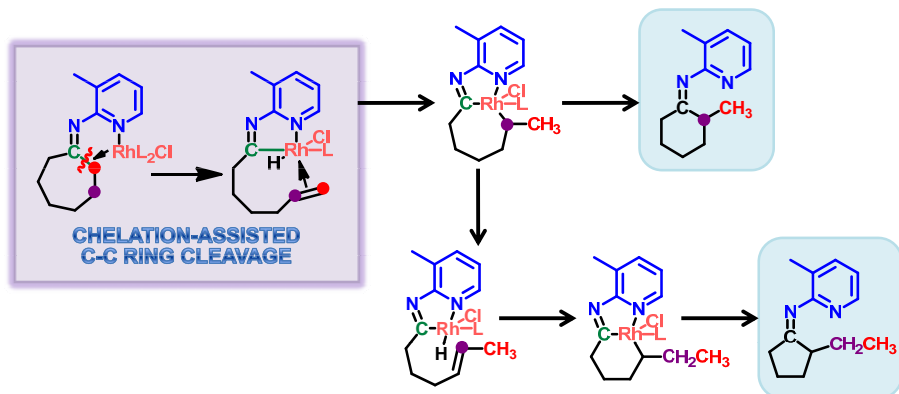
Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880.



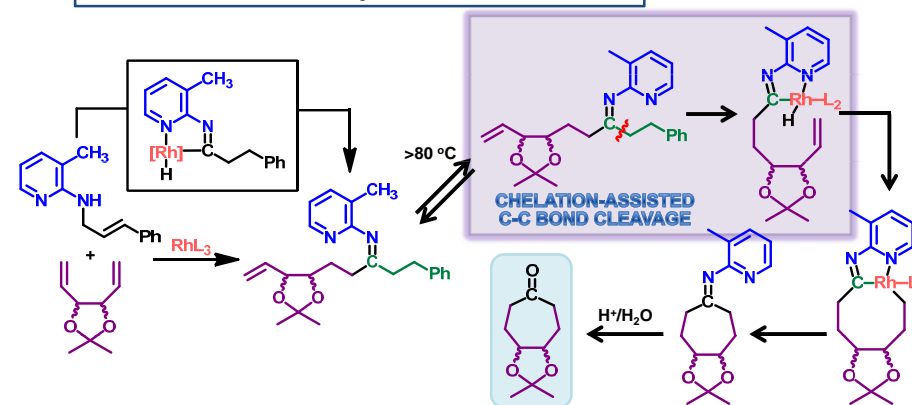
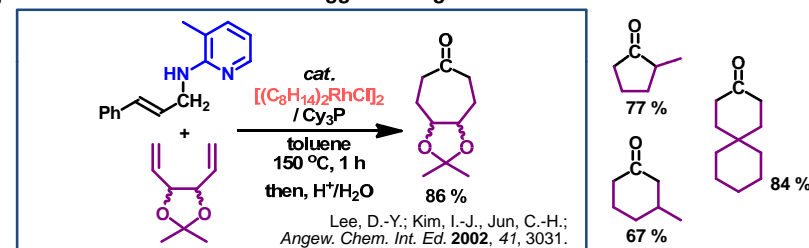
### - Application: C-C Bond Activation Promoted Ring Cleavage



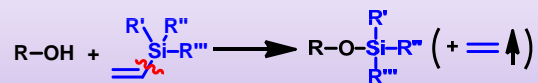
Jun, C.-H.; Lee, H.; Lim, S.-G., *J. Am. Chem. Soc.* **2001**, *123*, 751.



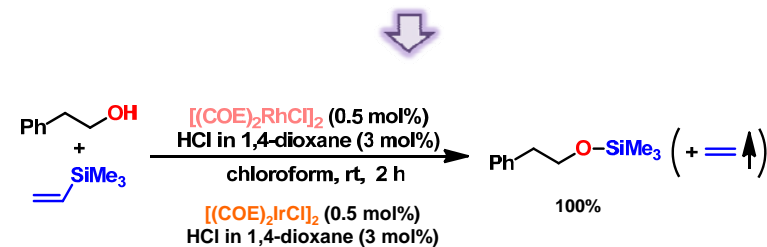
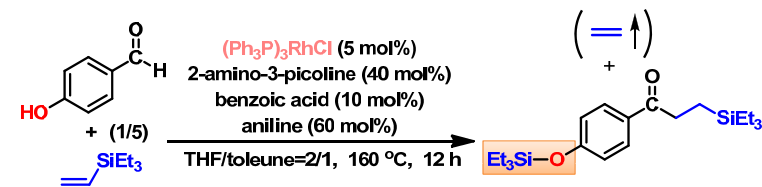
### - Application: C-C Bond Activation Triggered Ring Formation



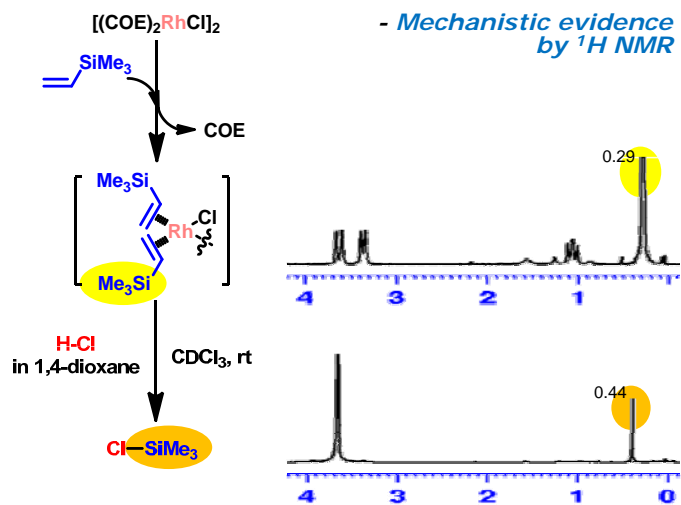
## O-Silylation with Vinylsilanes through C-Si Bond Cleavage



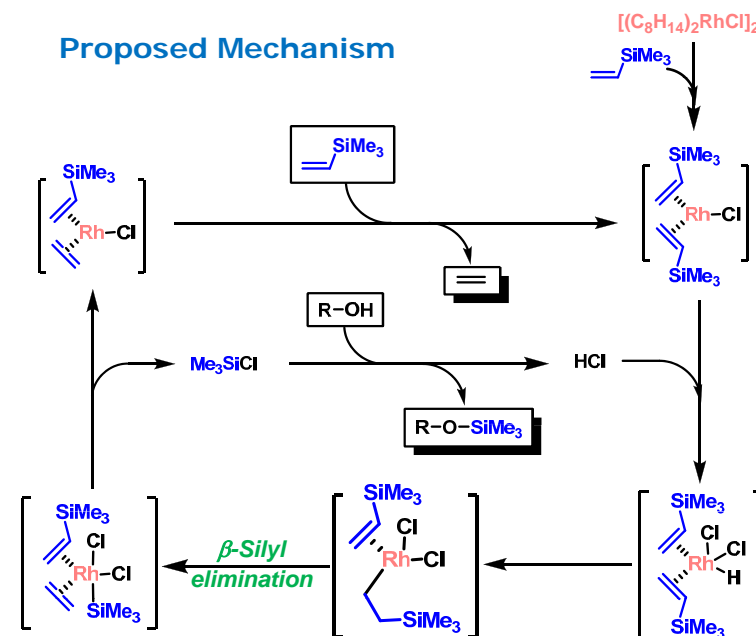
## Development of Rh(I)-Catalyzed O-Silylation



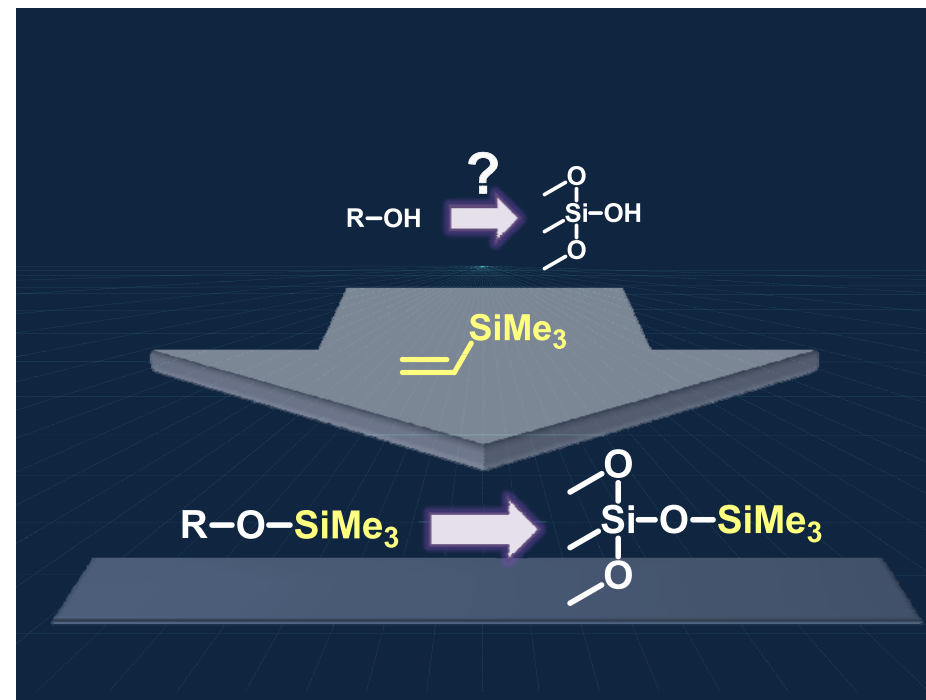
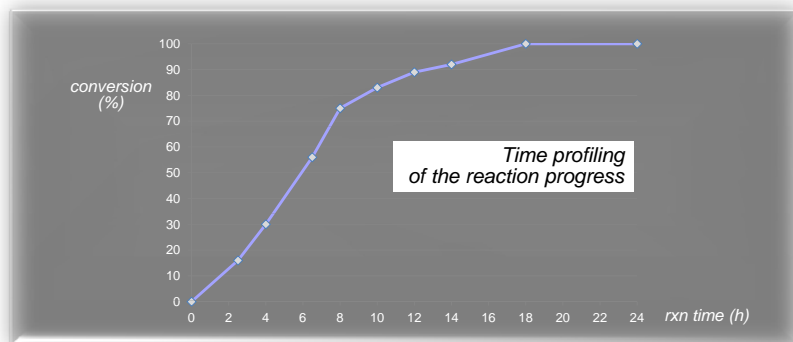
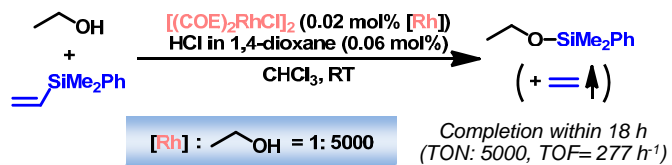
Park, J. -W.; Jun, C. -H. *Org. Lett.* 2007, 9, 4073.



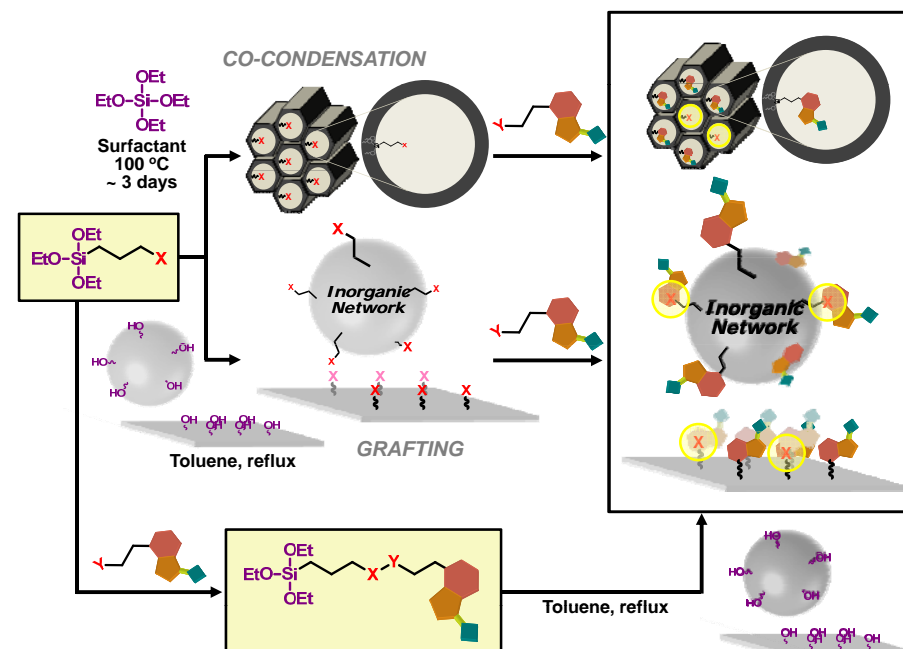
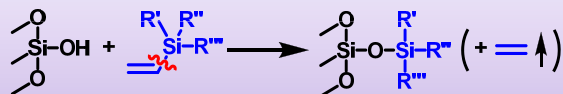
## Proposed Mechanism



## Efficiency of Catalytic Systems for O-Silylation of Alcohol



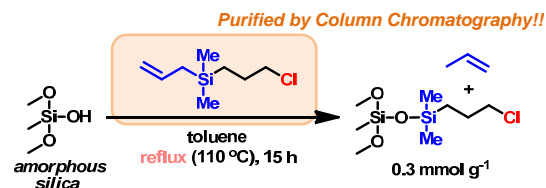
## Immobilization of Organic Functional Group onto Solid Surface



Feature Article: Park, J.-W.; Park, Y. J.; Jun, C.-H. *Chem. Commun.* 2011, 47, 4860.

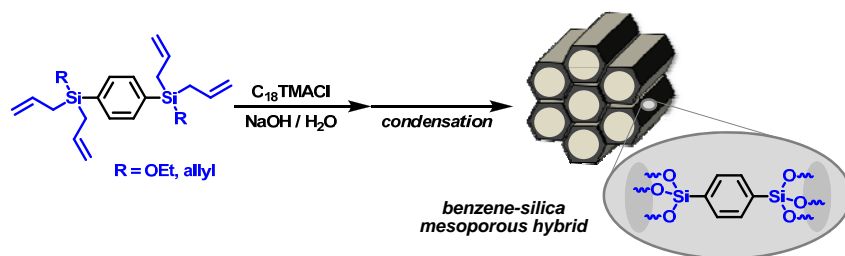


- First Grafting Study Using Allylsilane



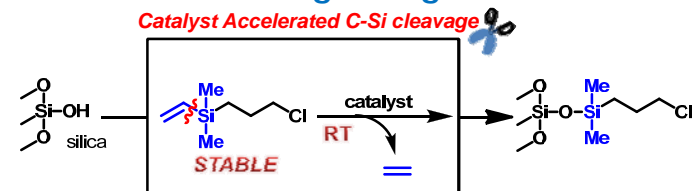
Shimada, T.; Aoki, K.; Shinoda, Y.; Nakamura, T.; Tokunaga, N.; Inagaki, S.; Hayashi, T. *J. Am. Chem. Soc.* 2003, 125, 4688.

- Preparation of Periodic Mesoporous Silica Using Allylsilane



Kapoor, M. P.; Inagaki, S.; Ikeda, S.; Kakiuchi, K.; Suda, M.; Shimada, T. *J. Am. Chem. Soc.* 2005, 127, 8174.

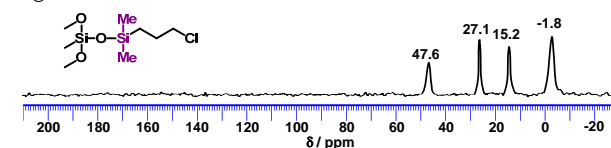
Catalytic Cleavage of C-Si Bond  
: Efficient tools for Grafting of Organic Functional Group



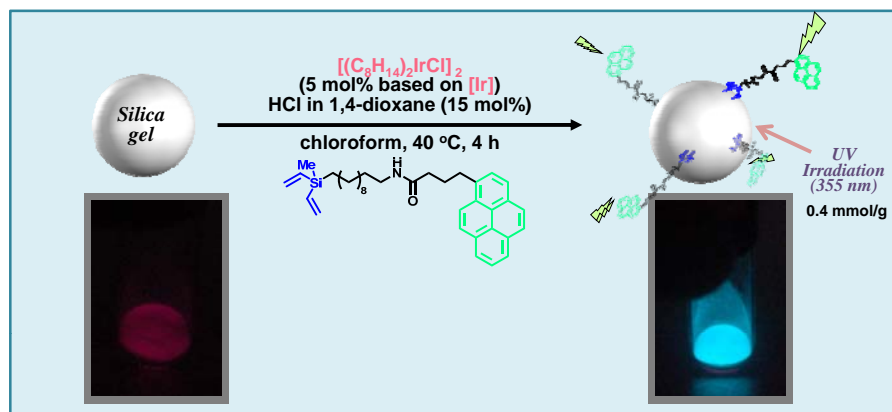
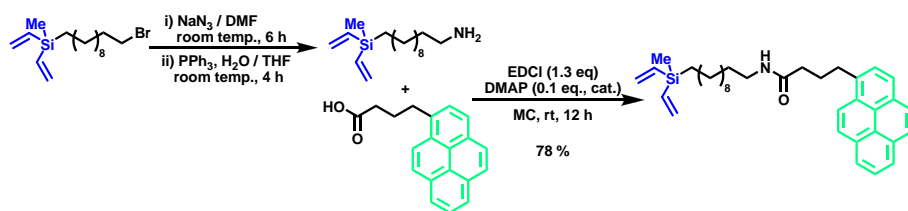
catalyst <sup>a</sup>	loading rate (mmol g <sup>-1</sup> )
none	0
[(COE) <sub>2</sub> RhCl] <sub>2</sub>	0.16
[(COE) <sub>2</sub> RhCl] <sub>2</sub> / DMA.HCl	0.91
<b>[(COE)<sub>2</sub>IrCl]<sub>2</sub> / DMA.HCl</b>	<b>0.97</b>

<sup>a</sup> 3 mol% of metal catalyst and 6 mol% of DMA.HCl were used. 4 h reaction

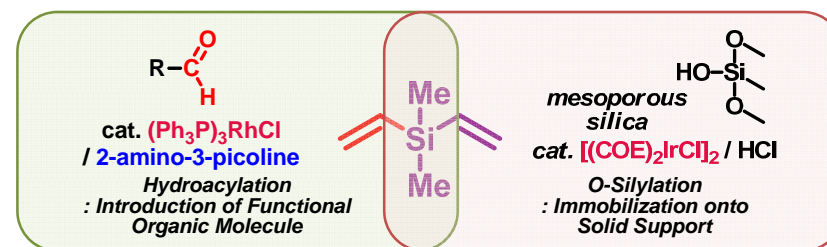
<sup>13</sup>C CP-MAS NMR



Modification of Silica Gel with Pyrene Deriv.

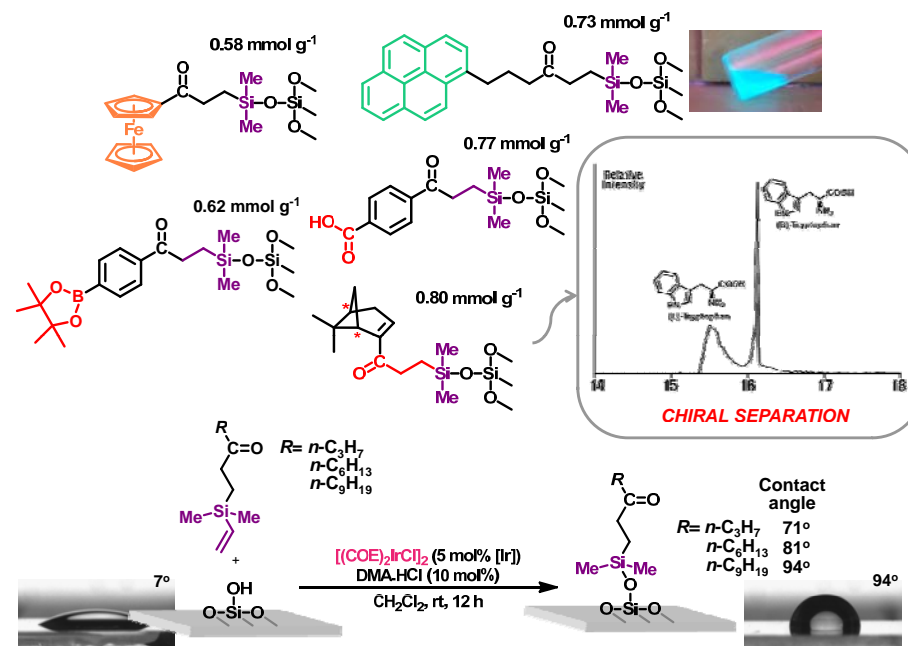
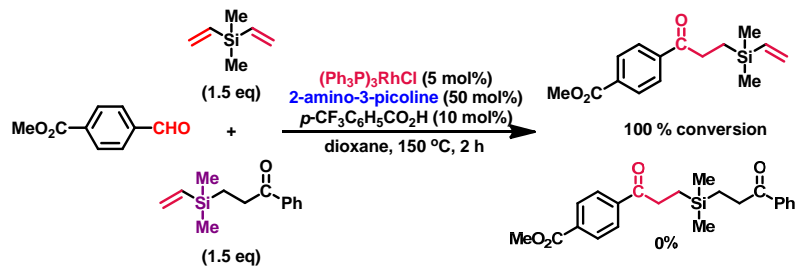
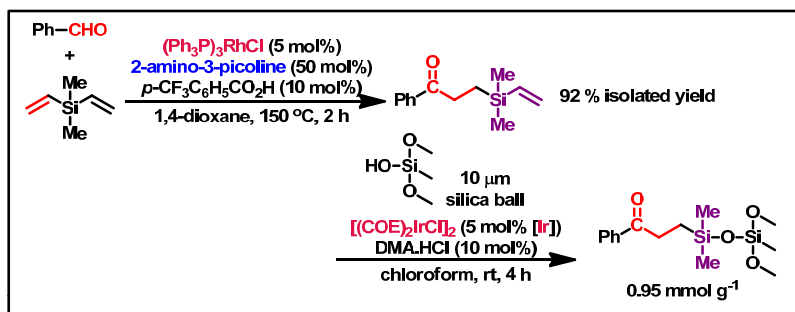


Catalytic Immobilization of Organic Molecule through Vinylsilane Coupling Reactions

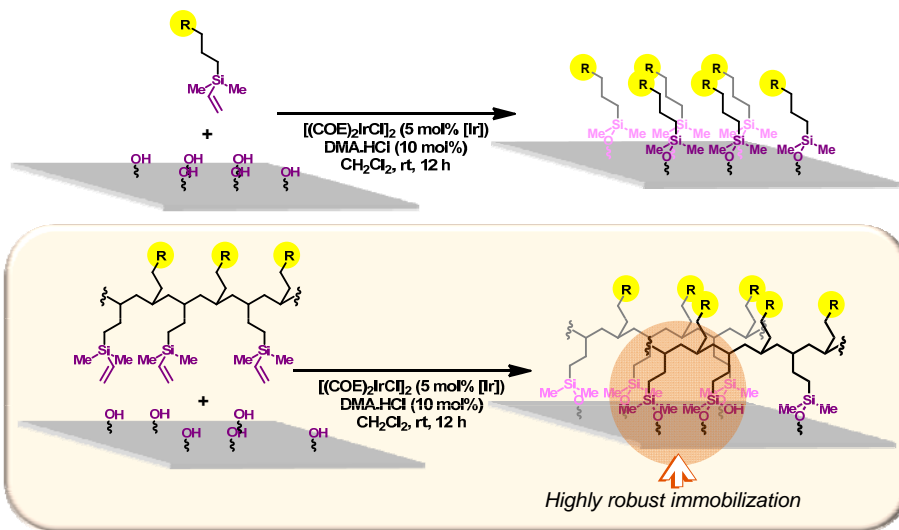


Park, J. -W.; Jun, C. -H. *J. Am. Chem. Soc.* 2010, 132, 7268.

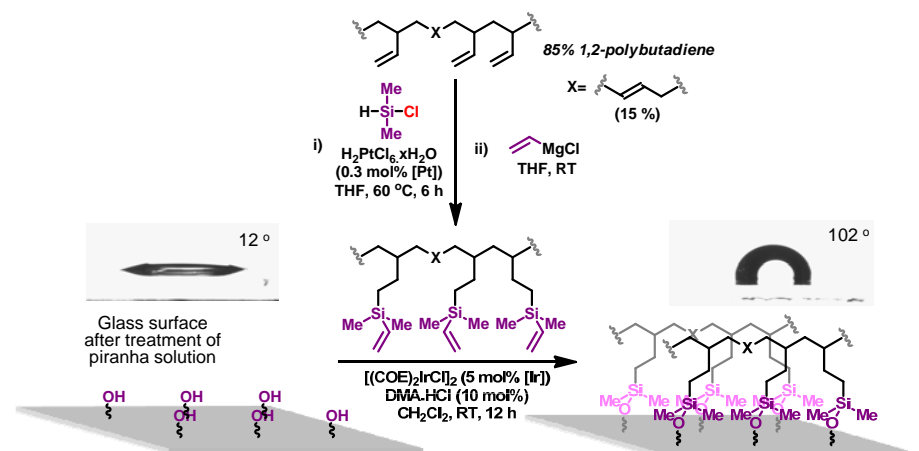




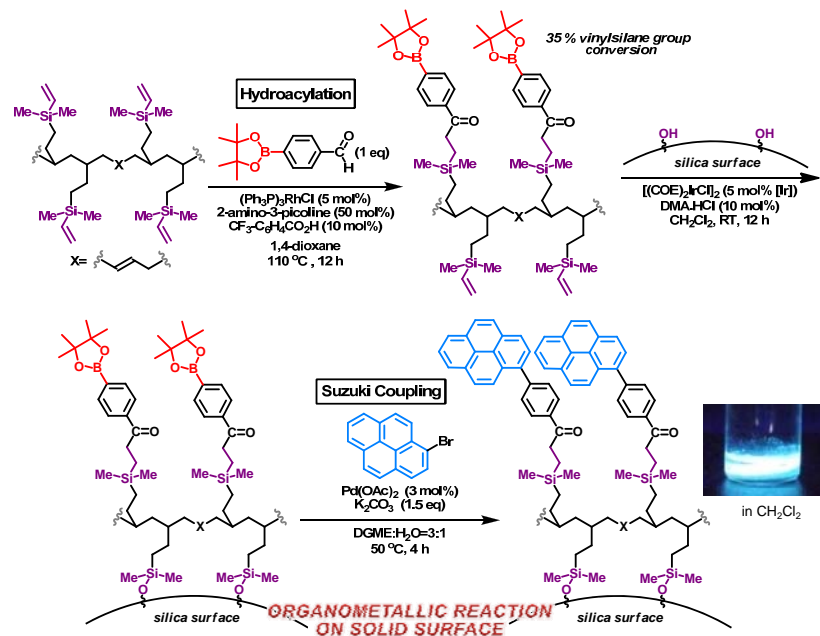
## Highly Robust Immobilization Method Using Oligomer



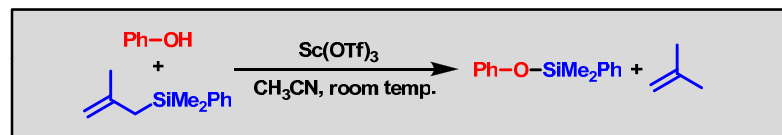
## Immobilization of Vinylsilane Oligomer



- Application

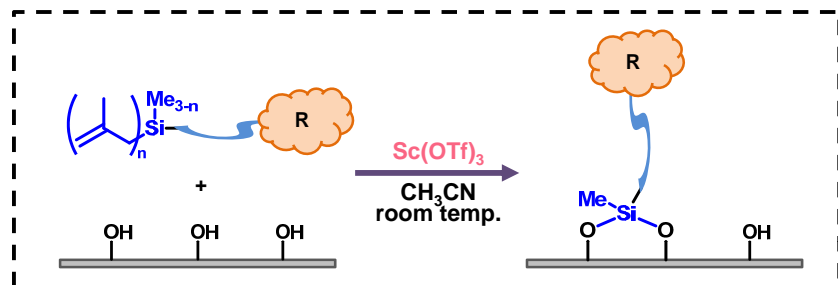
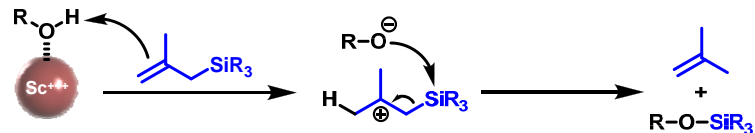


## Catalytic Grafting Using Methallylsilanes through C-Si Bond Cleavage

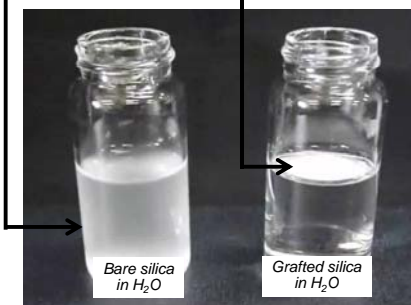
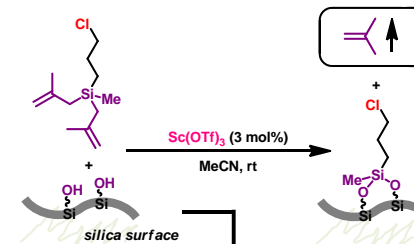


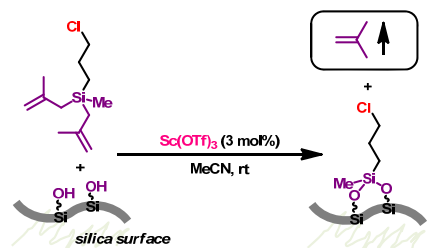
Oriyama, T. et al., *Tetrahedron Lett.* 2000, 41, 8903.

Mechanism: Increase acidity by  $\text{Sc}^{+++}$



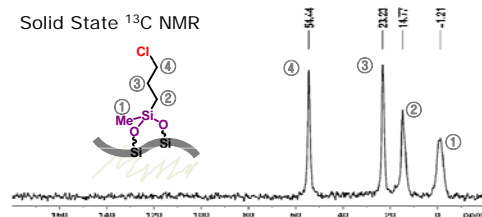
## Immobilization of Organomethallylsilane by $\text{Sc}(\text{OTf})_3$





entry	time	temp.	loading rate (mmol gr <sup>-1</sup> )
1	10 min	rt	0.85
2	30 min	rt	1.31
3	1 h	rt	1.92
4	12 h	rt	1.89

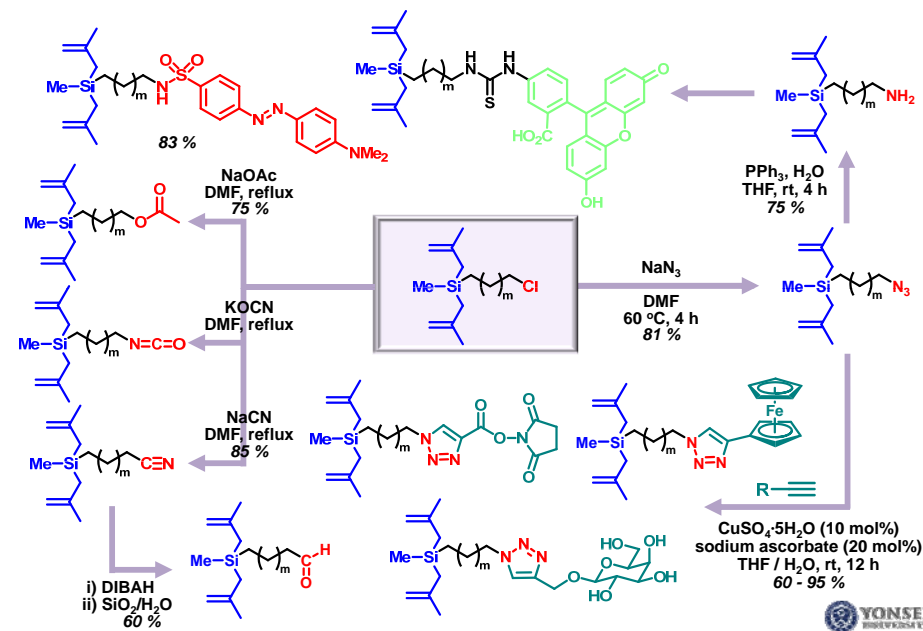
Solid State <sup>13</sup>C NMR



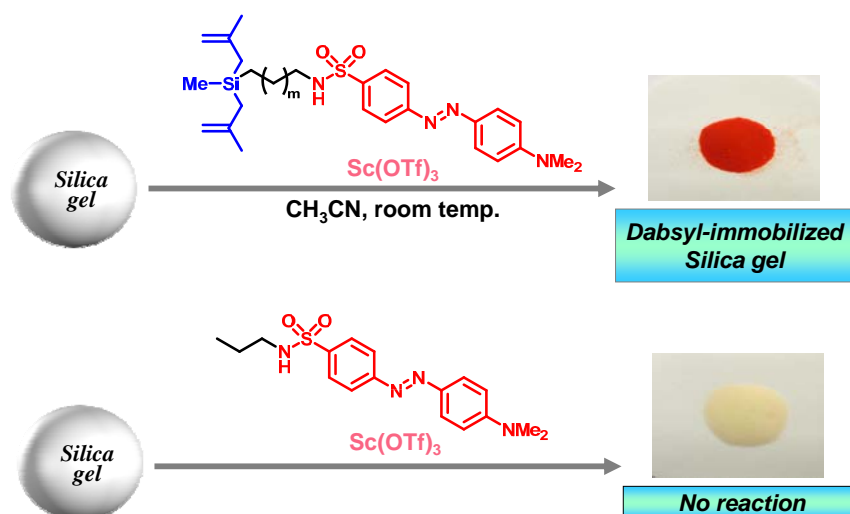
Yeon, Y. -R.; Park, Y. J.; Lee, J. -S.; Park, J. -W.; Kang, S. -G.; Jun, C. -H.  
*Angew. Chem. Int. Ed.* 2008, 47, 109-112.



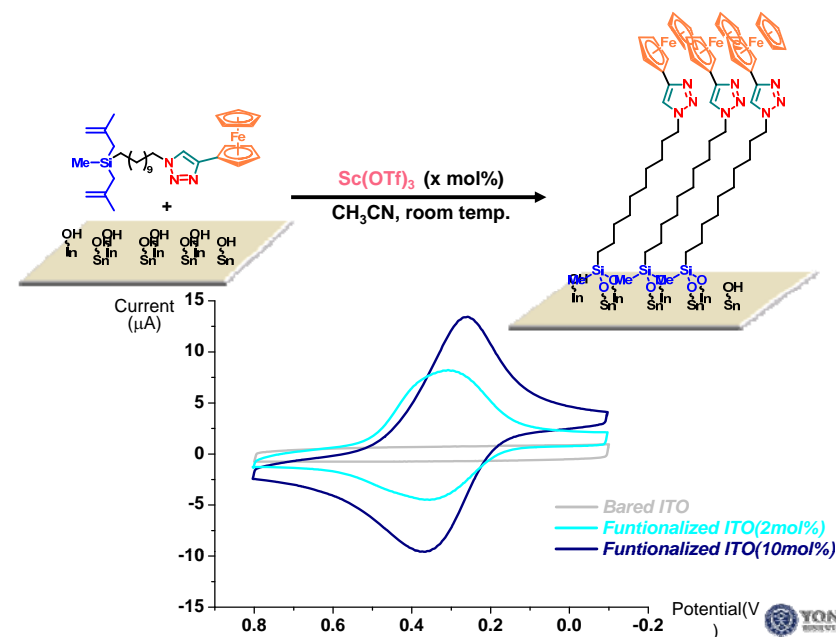
## Syntheses of Functionalized methallylsilanes

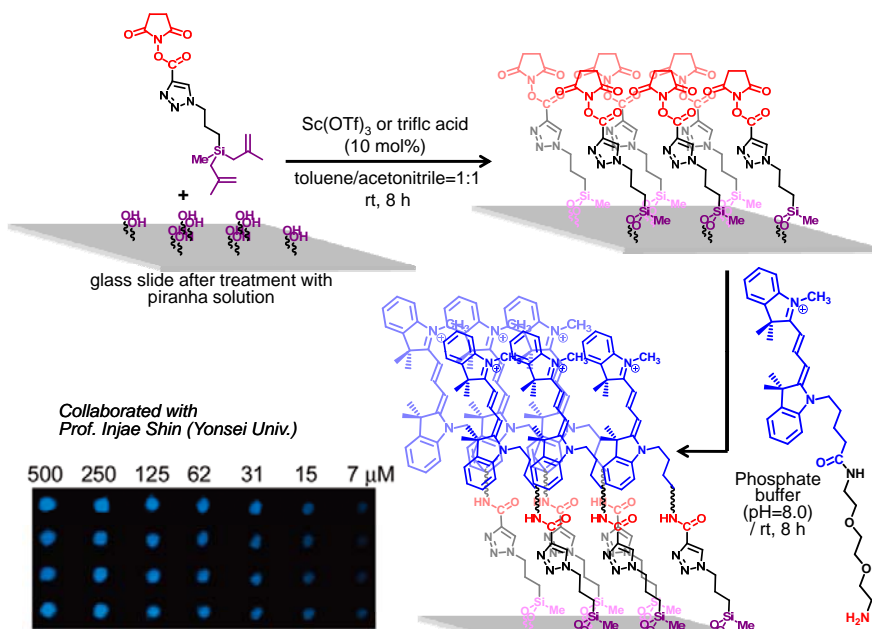


## Immobilization of DABSYL Dye onto Silica Gel

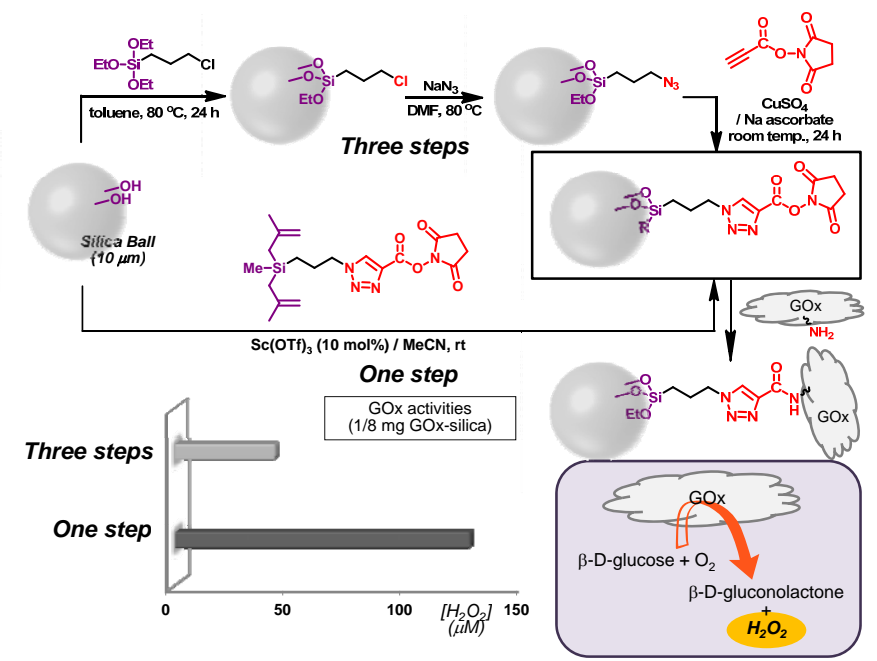


## Immobilization of Ferrocenyl Group onto ITO Glass



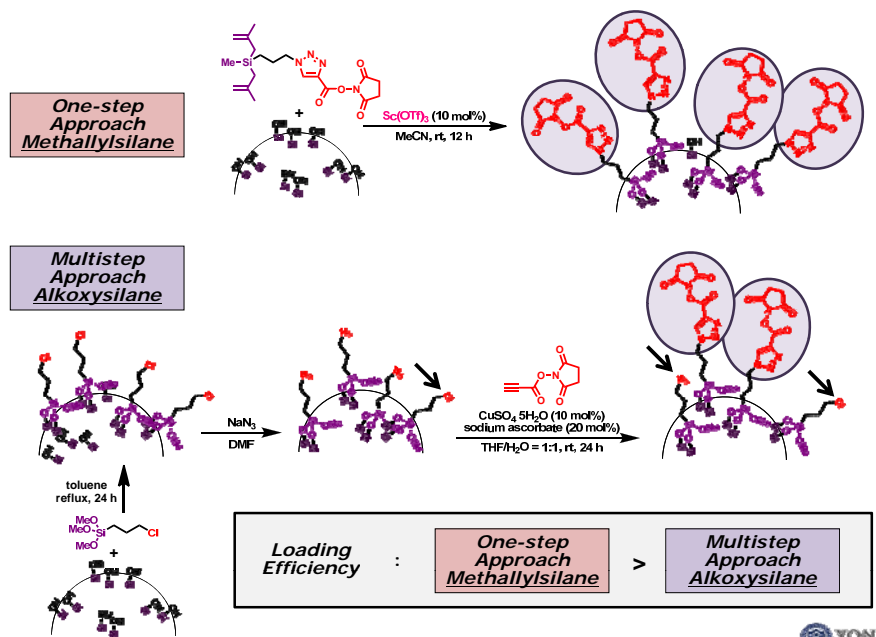


Park, S.; Pai, J.; Han, E.-H.; Jun, C.-H.; Shin, I. *Bioconjugate Chem.* 2010, 21, 1246.

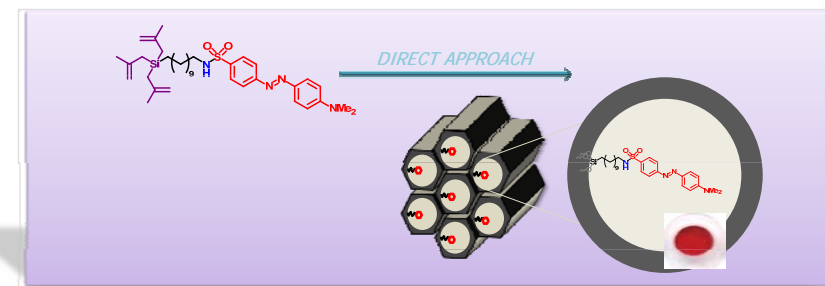


Jung, U.-Y.; Park, J.-W.; Han, E.-H.; Kang, S.-G.; Jun, C.-H. *Chem. Asian J.* 2011, 6, 638.

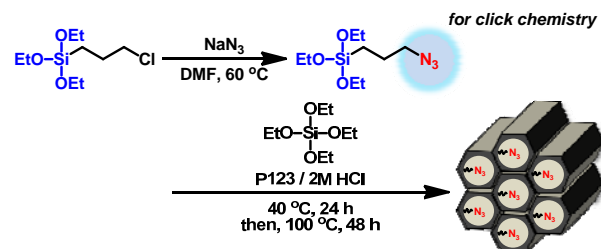
- One step Approach vs Multistep Approach



Functional Mesoporous Materials : Direct Cocondensation with Trimethylsilylamine for SBA-15



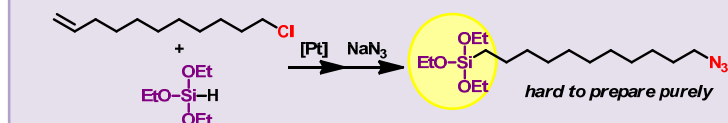
- Clickable Mesoporous Silica:  $N_3$ -Functionalized SBA-15



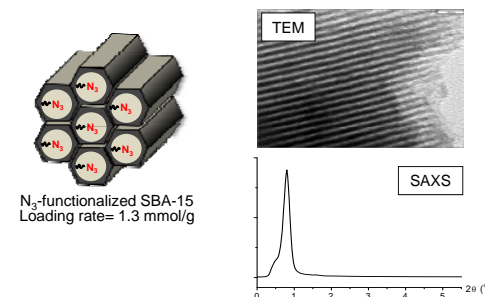
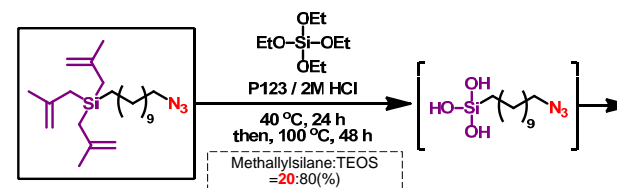
Nakazawa, J.; Stack, T. D. P. *J. Am. Chem. Soc.* **2008**, *130*, 14360.

Malvi, B.; Sarkar, B. R.; Pati, D.; Mathew, R.; Ajithkumar, T. G.; Gupta, S. S. *J. Mater. Chem.* **2009**, *19*, 1409.

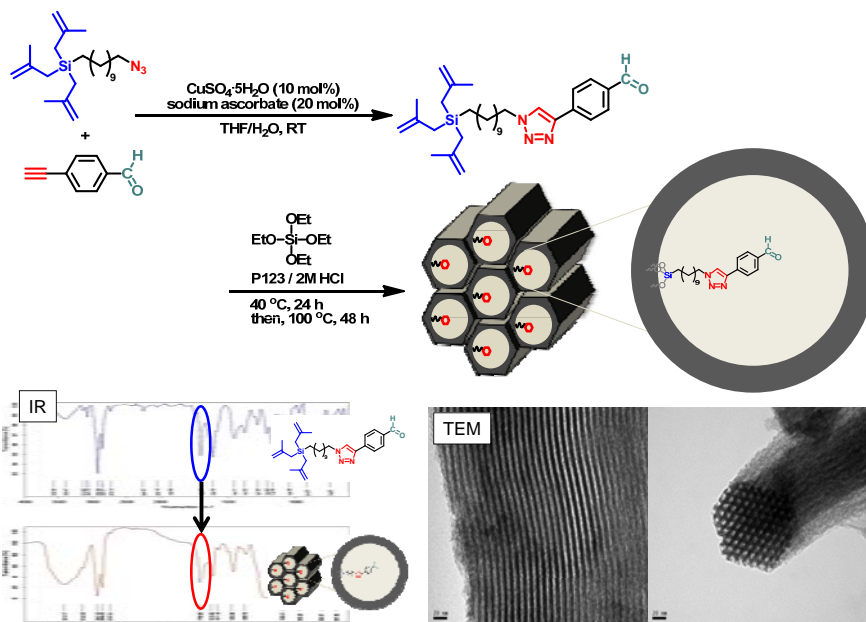
Limitation



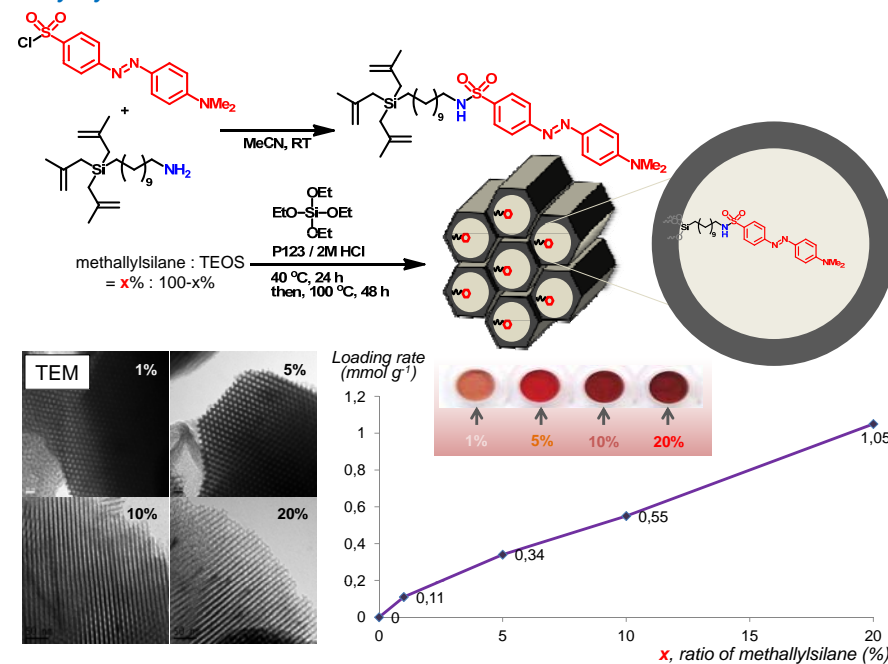
- New Approach: Trimethylsilyl silane with Long Linker



- Without click rxn on surface

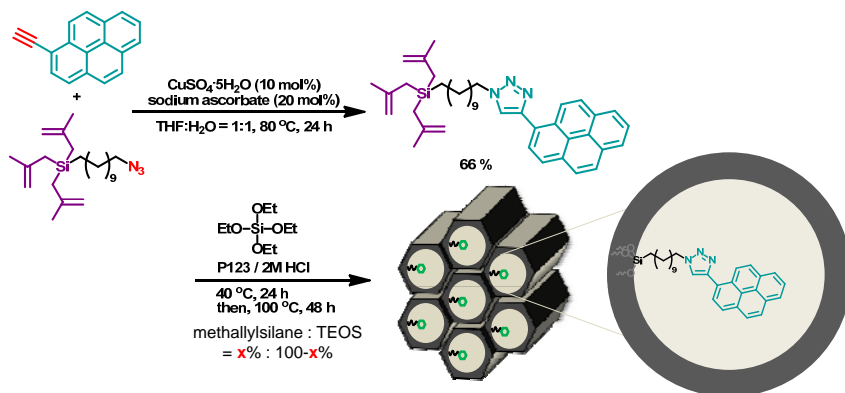


- Dabsyl-dye Functionalized SBA-15

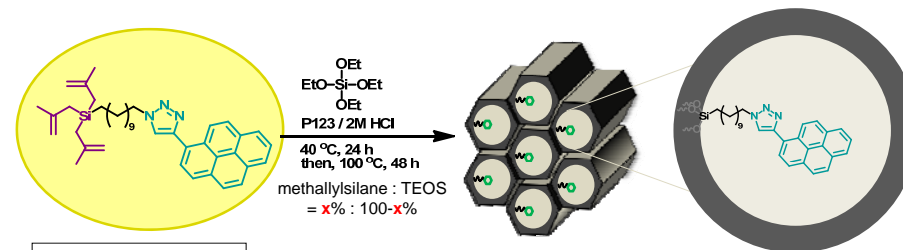
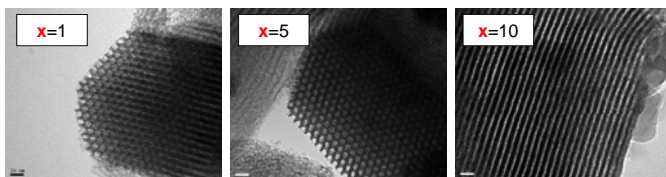




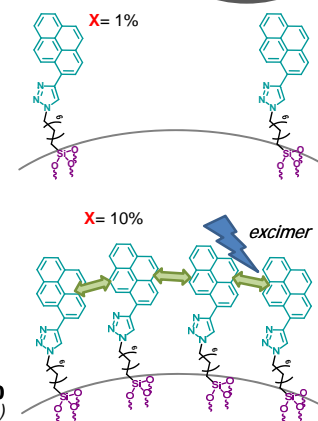
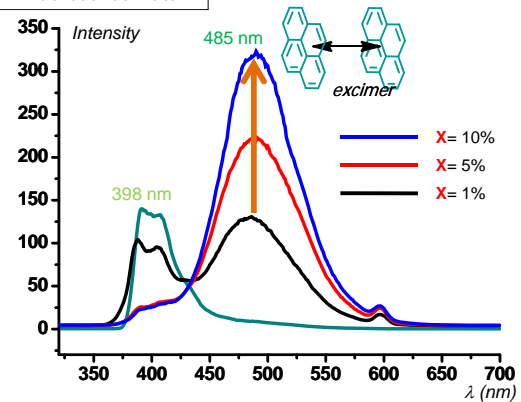
- Preparation of Pyrene-SBA from PYRENE-METHALLYLSILANE



TEM IMAGES



Fluorescence Data



## Summary

1. Chelation-assisted C-H and C-C bond cleavage can be applied for various organic transformations.
2. Catalytic C-Si bond cleavage of alkenylsilane is utilized for immobilization of functional organic molecules onto solid surface.

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