手性双金属催化剂发展概况

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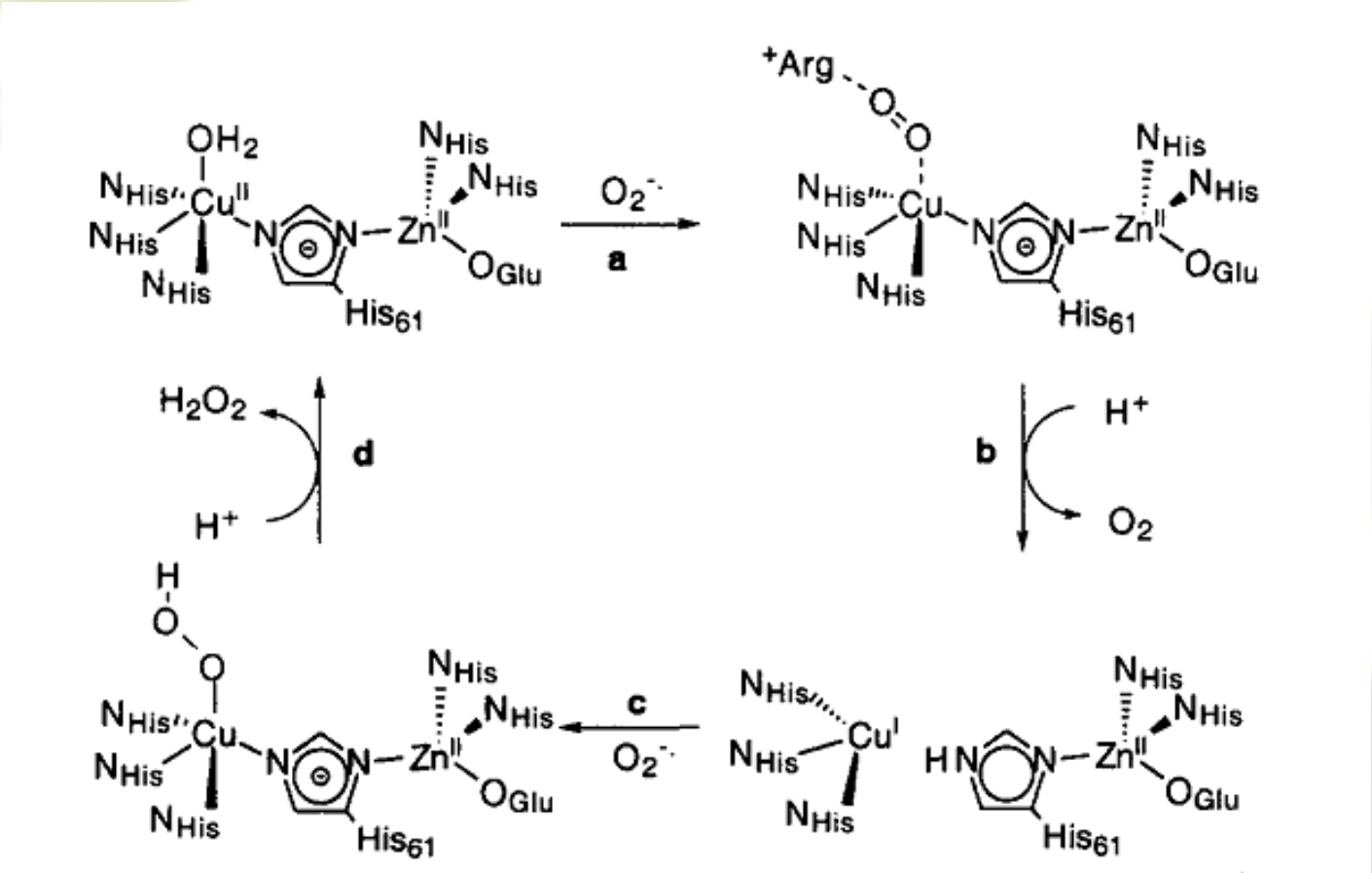
内容提要

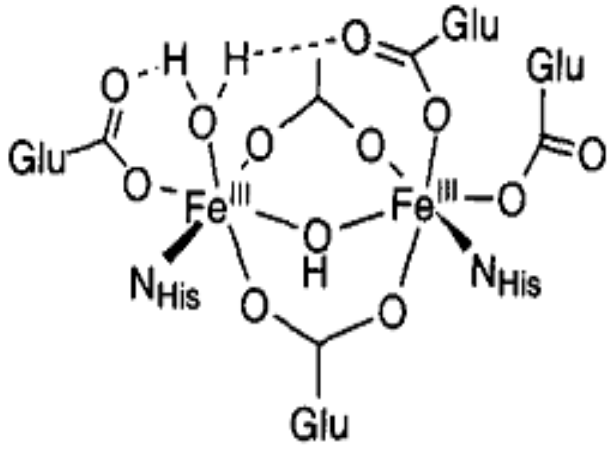
- 1 双金属酶简介
- 2 双金属催化剂分类
- 3 几类重要的手性双金属催化剂
  1） Shibasaki双杂金属催化剂
  2） Trost半冠醚氨基醇类双金属锌催化剂
  3) Jacobsen双席夫碱双金属催化剂
  4) 其它一些手性双金属催化剂

一．双金属酶SOD

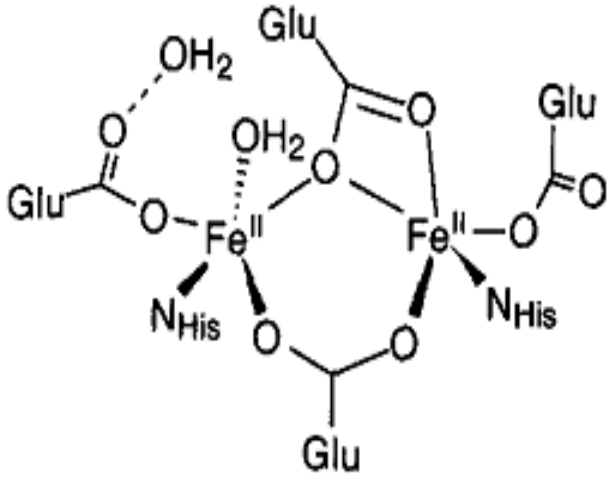


Ref 1: *Tetrahedron* 1998, 54, 12985-13011;

双金属酶MMOH



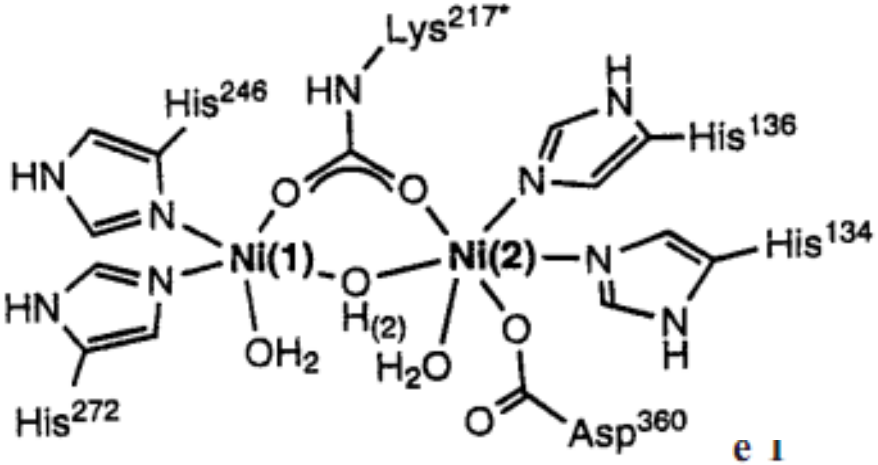
$MMOH_{ox}$

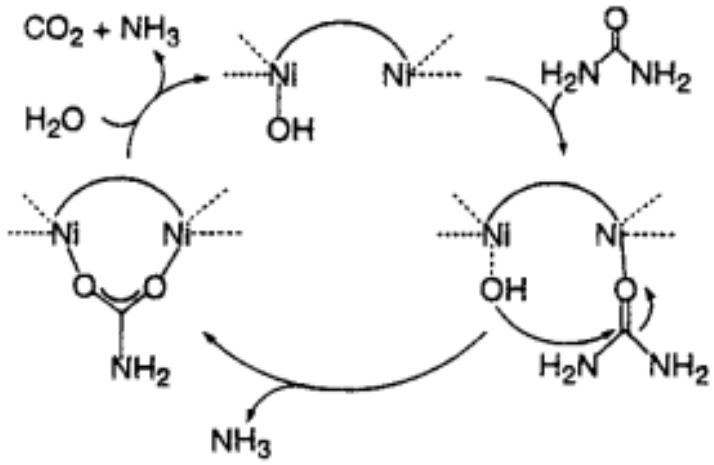


$MMOH_{red}$

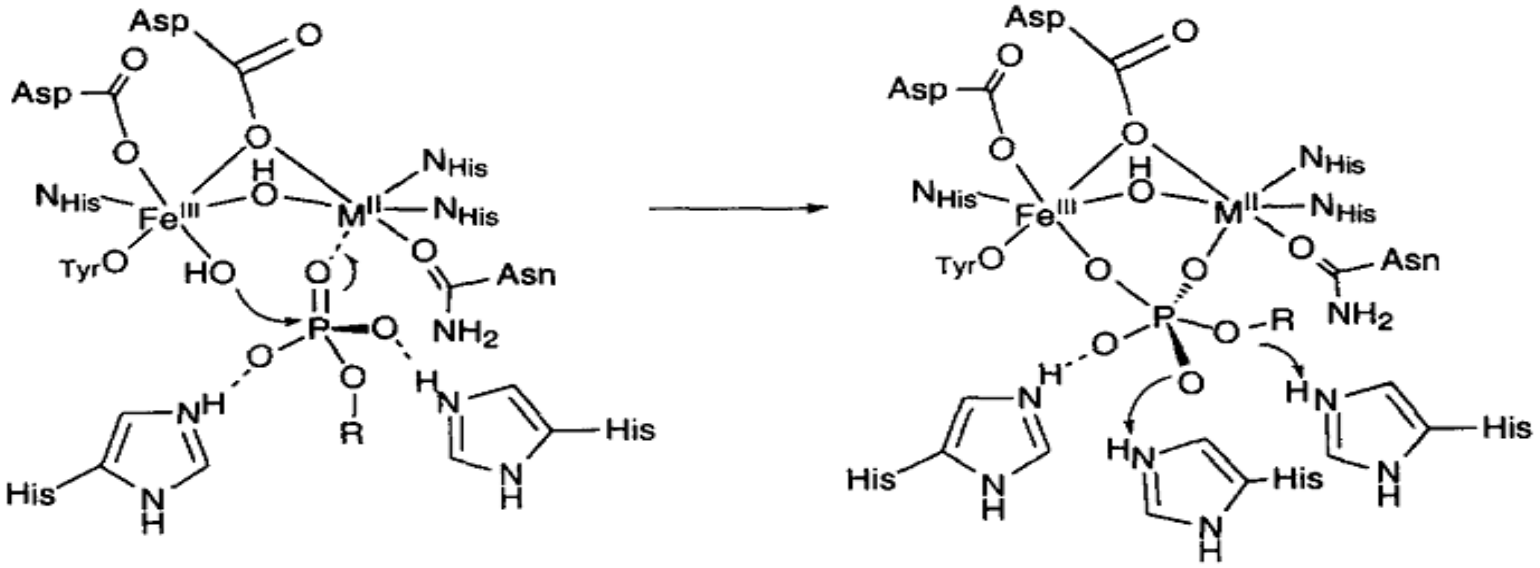
$$CH_4 + O_2 + H^+ + NADH \longrightarrow CH_3OH + H_2O + NAD^+$$

双金属酶Klebsiella aerogenes



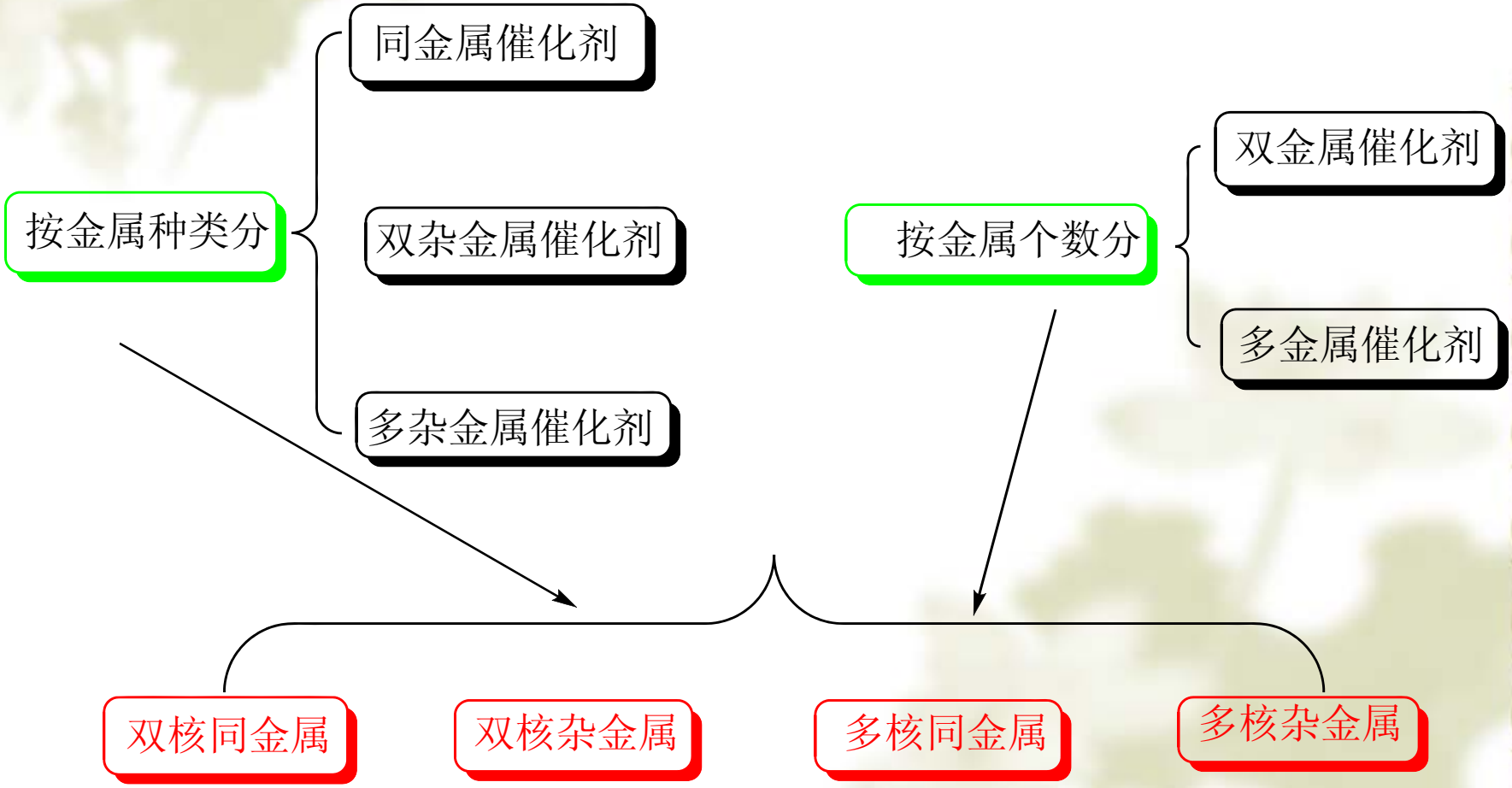


双金属酶 Purple acid phosphatase

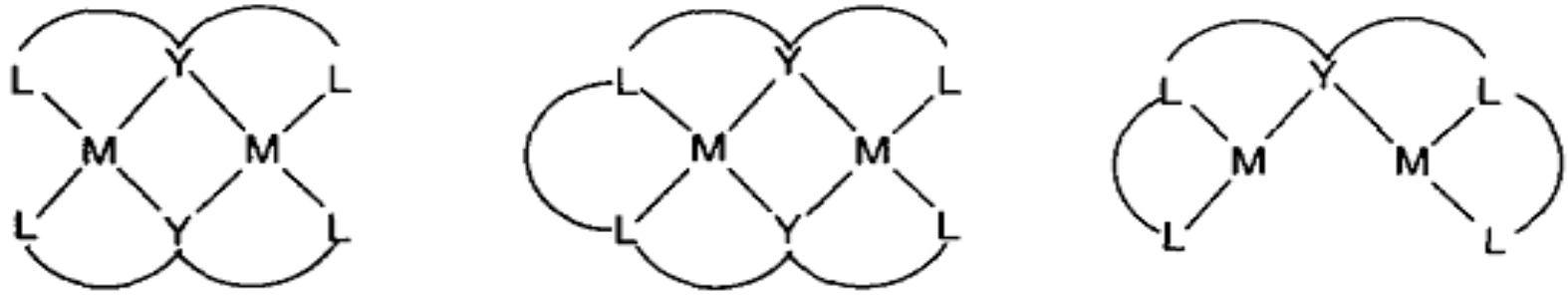


Scheme 7 Proposed mechanism for phosphate ester hydrolysis at the *kidney bean purple acid phosphatase* Fe(III)Zn(II) dinuclear site (M = Zn).

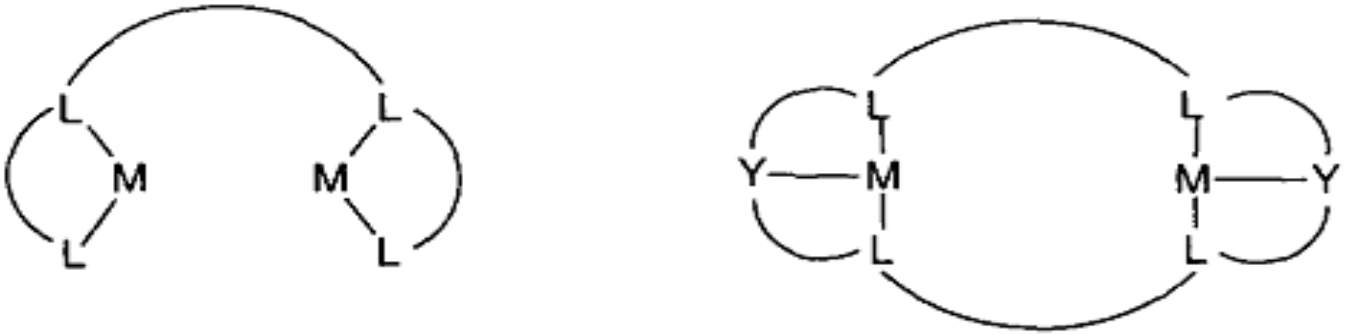
二. 双金属催化剂分类


同金属催化剂
按金属种类分
双杂金属催化剂
多杂金属催化剂
双金属催化剂
按金属个数分
多金属催化剂
双核同金属
双核杂金属
多核同金属
多核杂金属

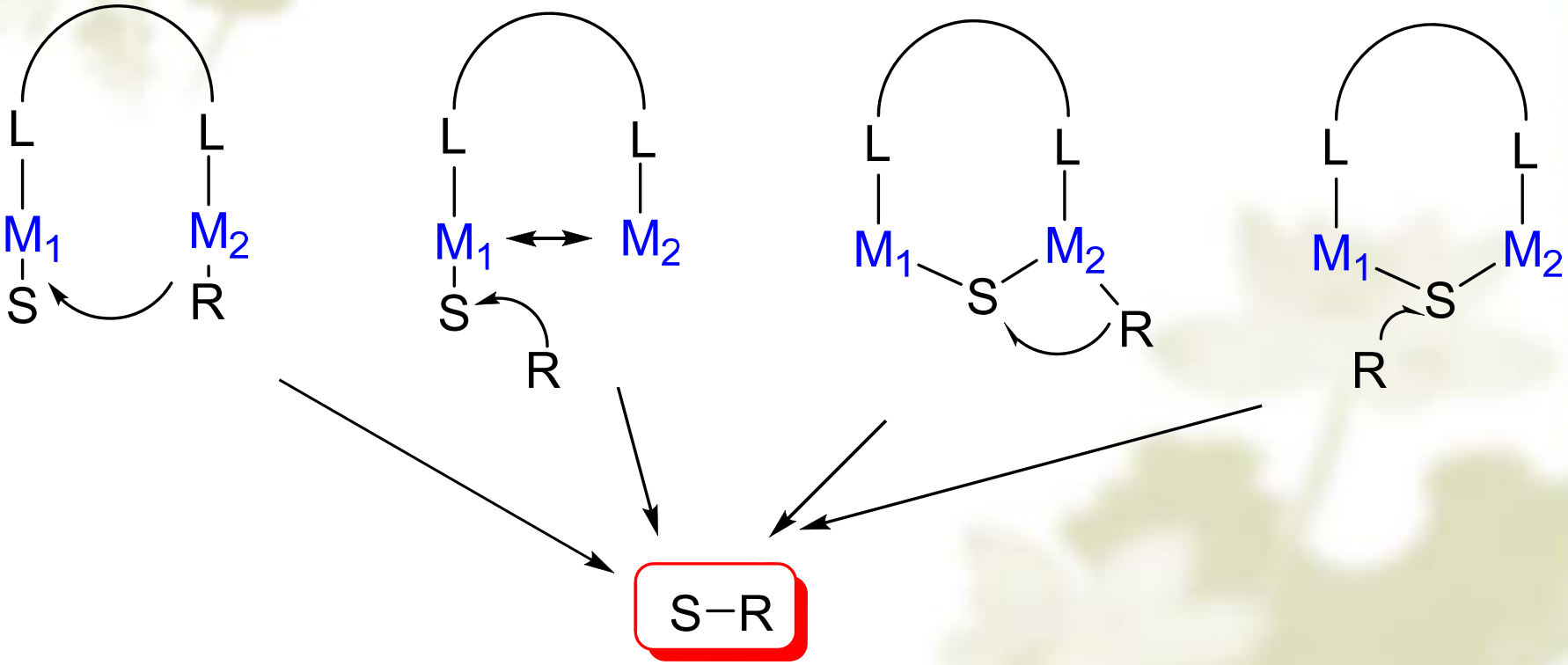
双核金属催化剂配位类型



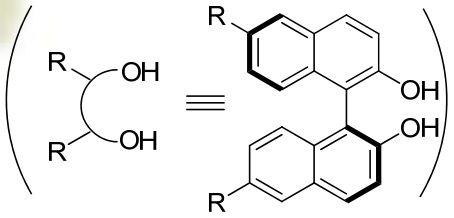
Class (a) examples of dinuclear complexes of compartimental ligands

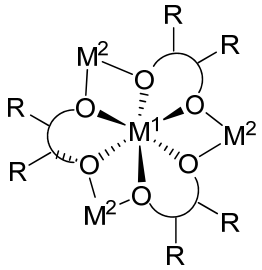


双核金属催化剂催化反应方式



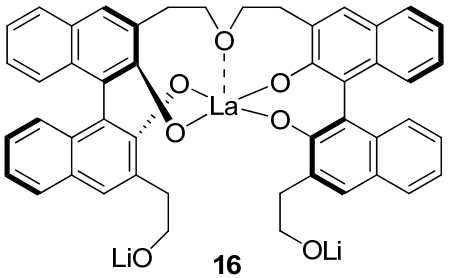
3.1 Shibasaki双杂金属催化剂





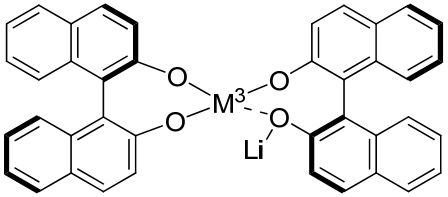
15

a M^1= La, M^2= Li;
b M^1= Sm, M^2= Na;
c M^1= Yb, M^2= H;



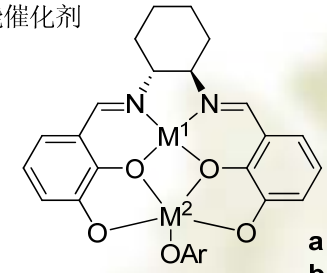
16

多核杂金属双官能催化剂



M^3= Al, Sc

17

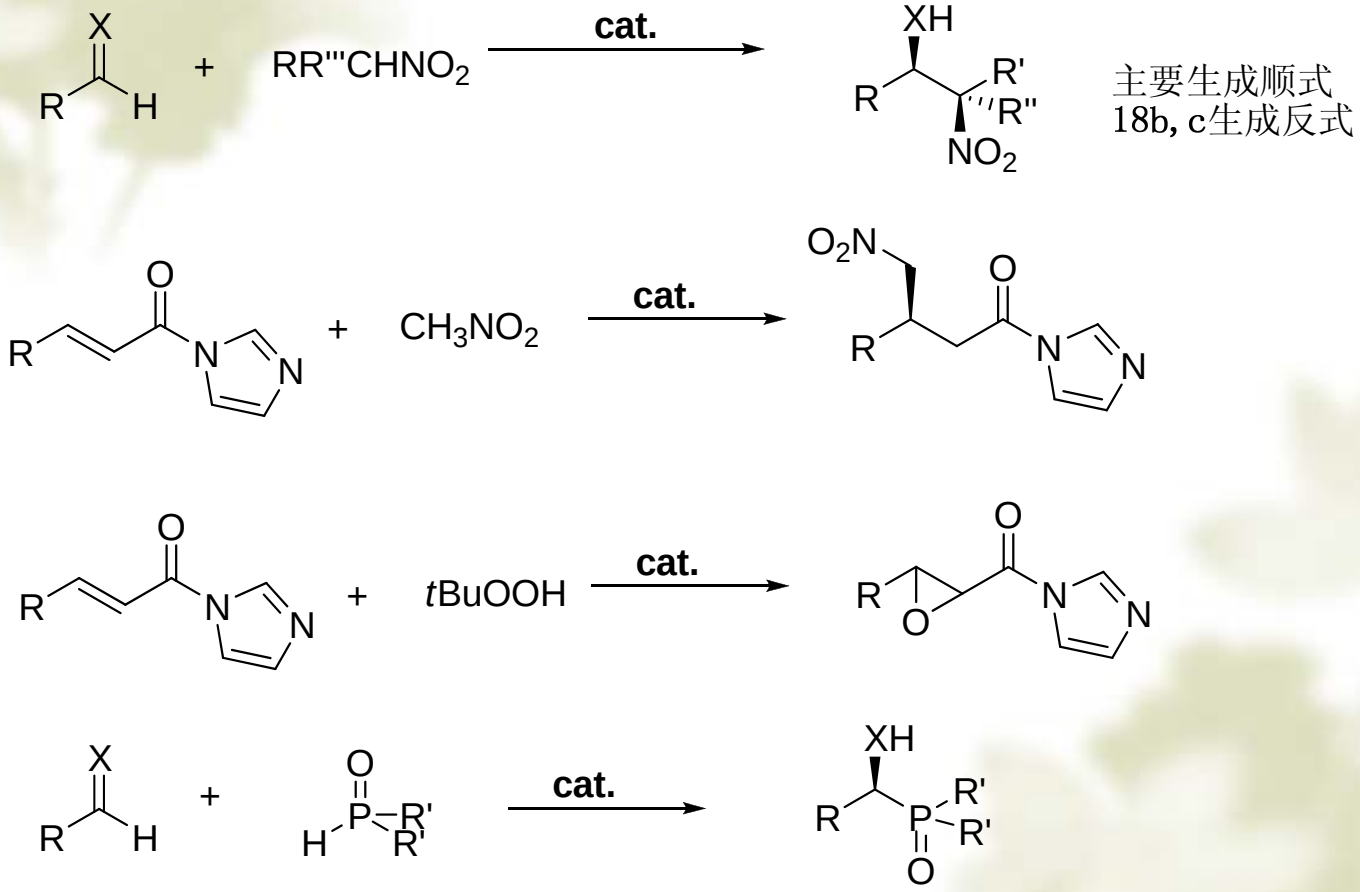


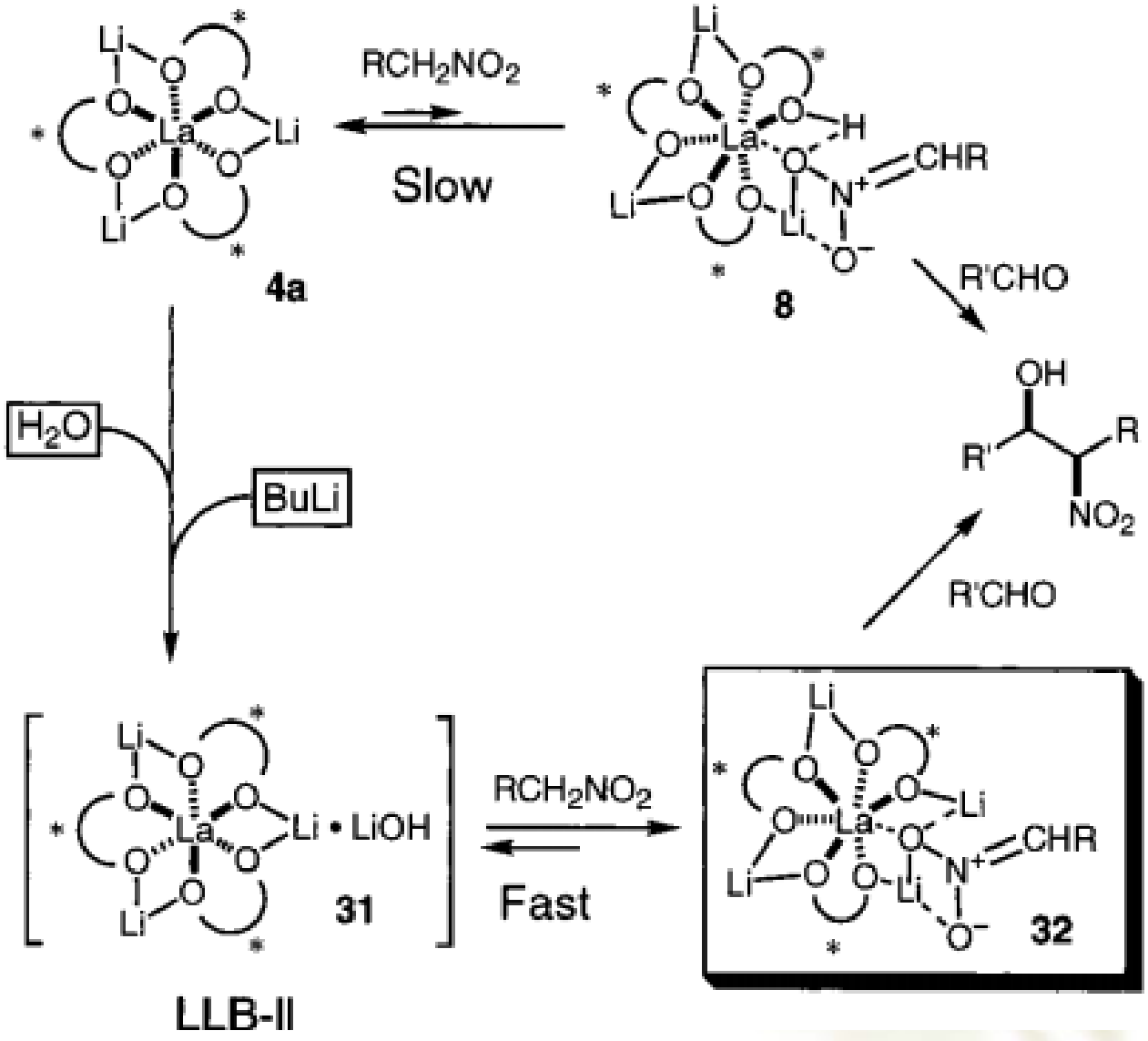
18

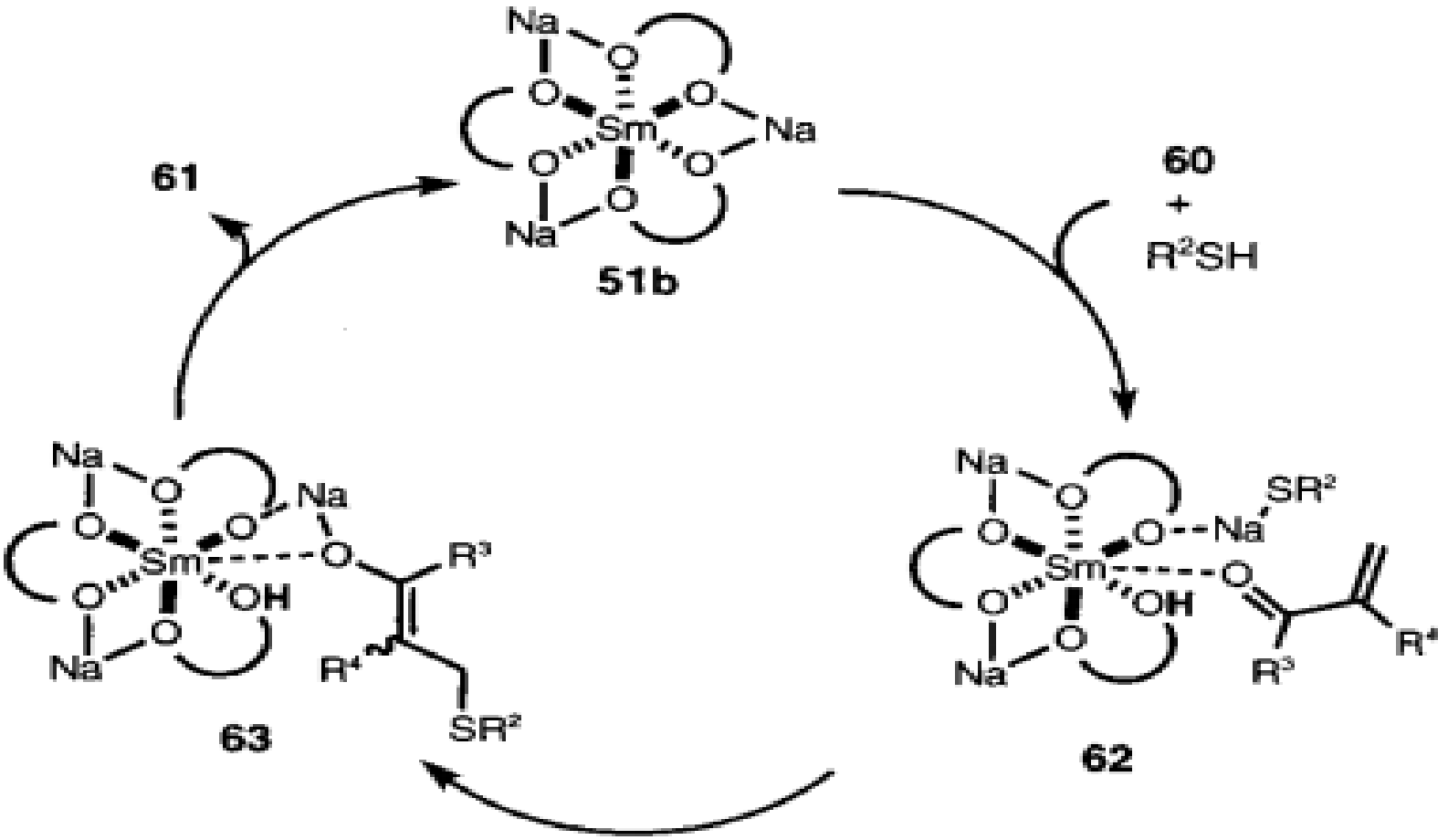
a M^1= Cu, M^2= Sm;
b M^1= Pb, M^2= La;
c M^1= Ni, M^2= Ni;

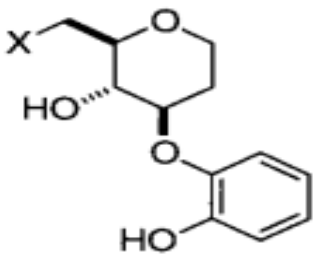
双核杂金属双官能催化剂

Ref 2: *Chem. Rev.* 2002, 102, 2187−2209


X
R
H
+
RR'''CHNO2
cat.
XH
R
R'
R''
NO2
主要生成顺式
18b, c生成反式
O
R
N
N
+
CH3NO2
cat.
O2N
O
R
N
N
O
R
N
N
+
tBuOOH
cat.
O
R
O
N
N
X
R
H
+
O
P
H
R'
R'
cat.
XH
R
P
R'
R'
O

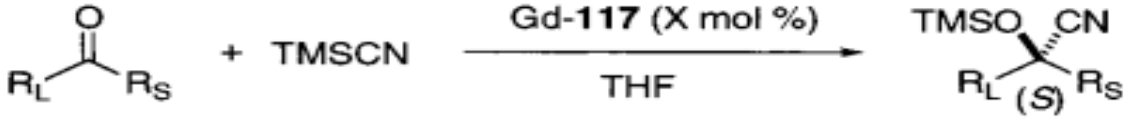

RCH2NO2
Slow
4a
8
R'CHO
OH
R
R'
NO2
R'CHO
H2O
BuLi
Li • LiOH
31
RCH2NO2
Fast
32
LLB-II


61
51b
60
+
R²SH
63
62

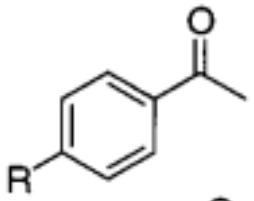


118: X = $Ph_2P(O)$
119: X = Ph_2CH

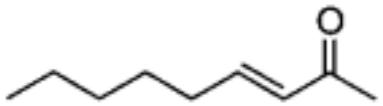
Table 25. Enantioselective Cyanosilylation of Ketones Catalyzed by Gd−117



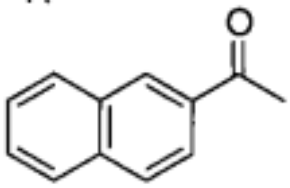
33 **120**



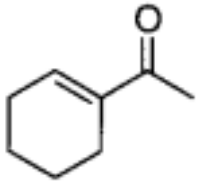
33a: R = H
33f: R = Cl



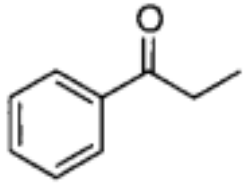
33i



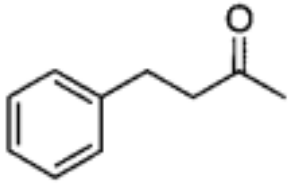
33g



33j



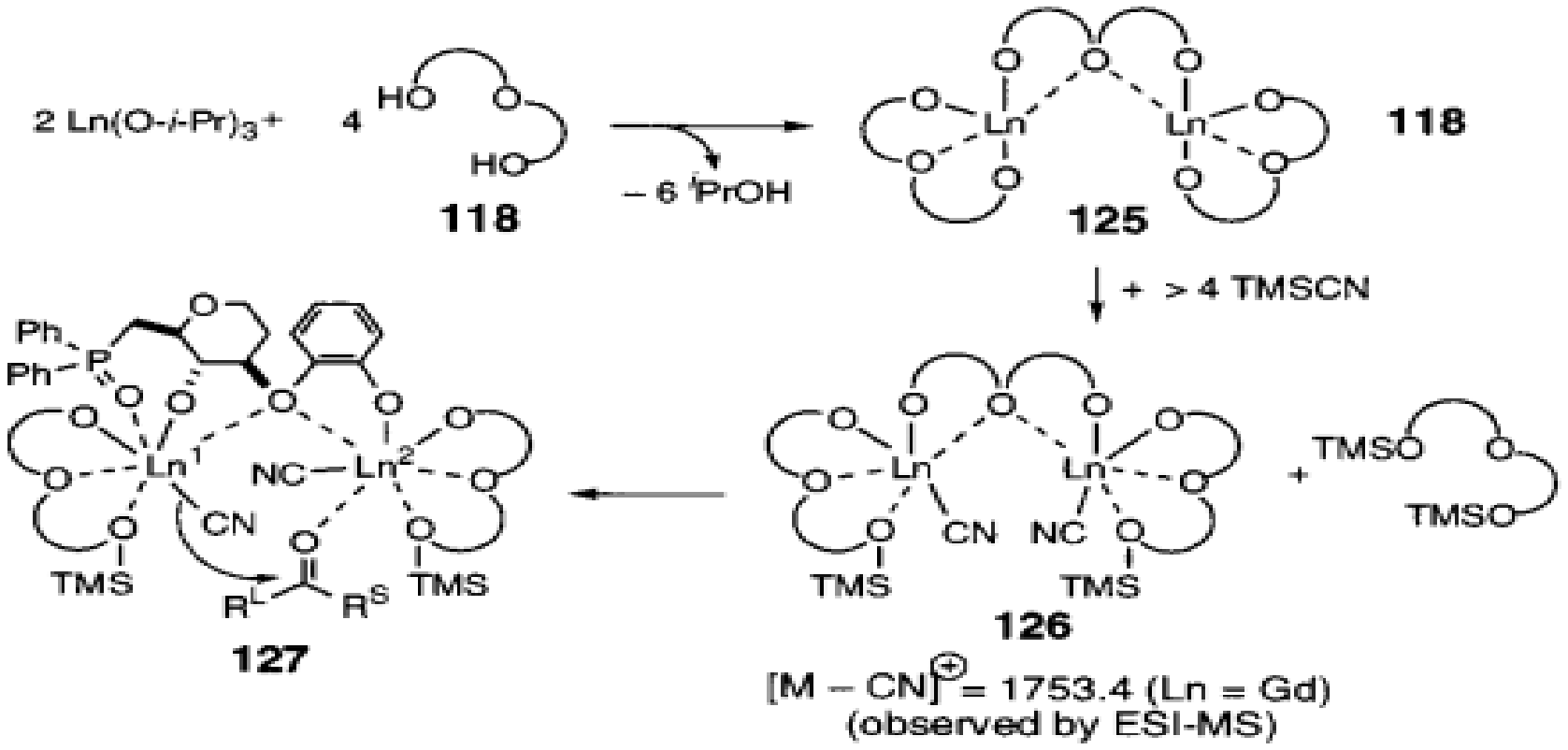
3h

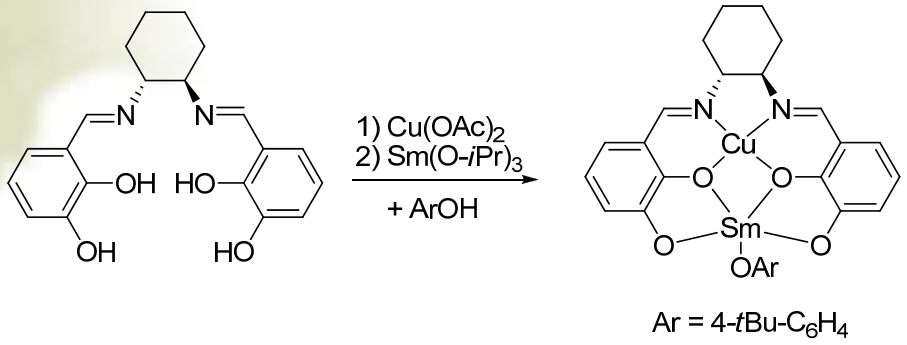


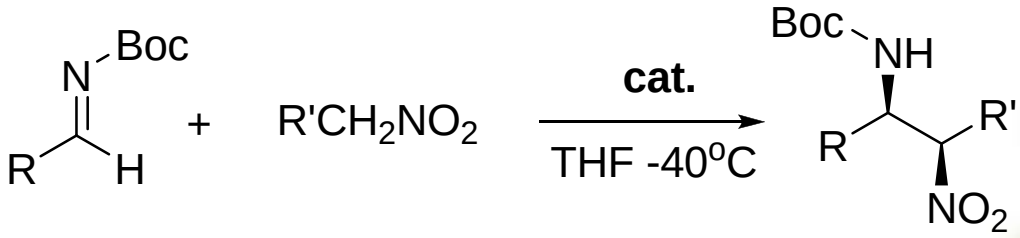
33k

entry	ketone	product	Gd (mol %)	temp (°C)	time (h)	yield (%)	ee (%)
1	**33a**	**120a**	5	−40	2	92	92 (S)
2[a]	**33a**	**120a**	10	−30	36	85	92 (R)
3	**33f**	**120b**	5	−60	55	89	89
4	**33g**	**120c**	5	−60	24	95	87
5	**33h**	**120d**	5	−60	14	93	97
6	**93f**	**120e**	10	−60	14	97	86
7	**33i**	**120f**	15	−60	18	87	80
8	**33j**	**120g**	15	−60	4	95	89
9	**33k**	**120h**	5	−60	1	90	62

[a] Reaction using a Ti catalyst. See ref 122.

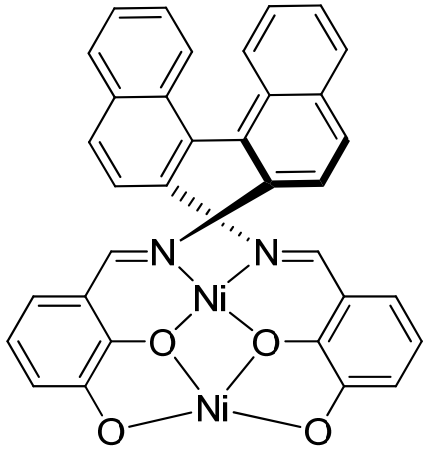

2 Ln(O-i-Pr)3 +
4
HO
HO
118
– 6 iPrOH
Ln
Ln
125
118
+ > 4 TMSCN
Ln
Ln
CN
NC
TMS
TMS
126
+
TMSO
TMSO
[M – CN]⊕ = 1753.4 (Ln = Gd)
(observed by ESI-MS)
Ph
Ph
P
Ln1
Ln2
NC
CN
TMS
TMS
RL
RS
127

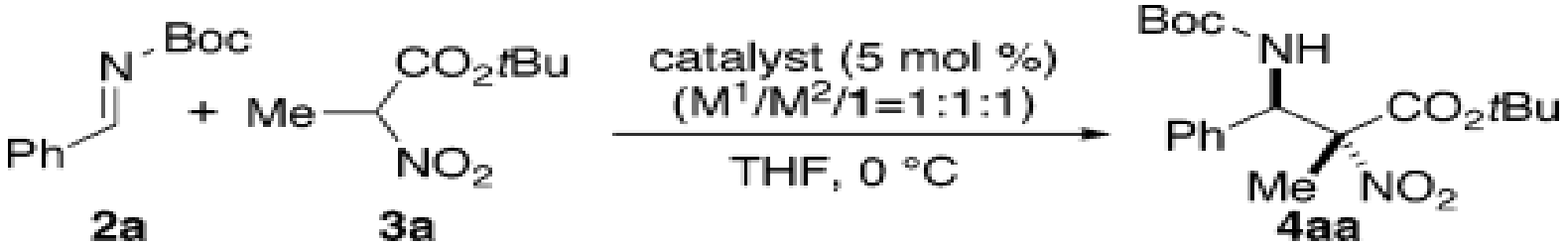




yield > 66%
dr > 20:1
ee 83-97%

Ref 3: *J. Am. Chem. Soc.* 2007, 129, 4900-4901

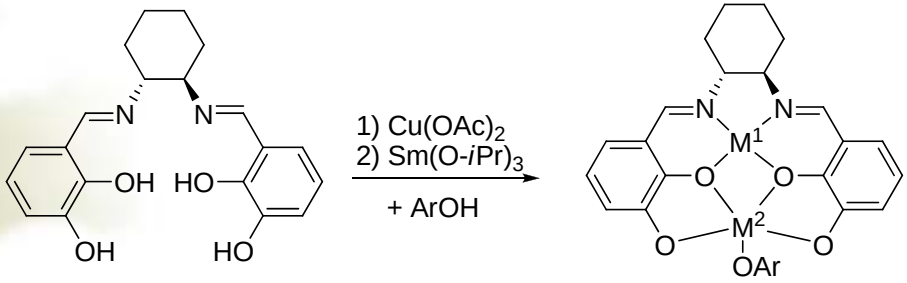




2a **3a** **4aa**

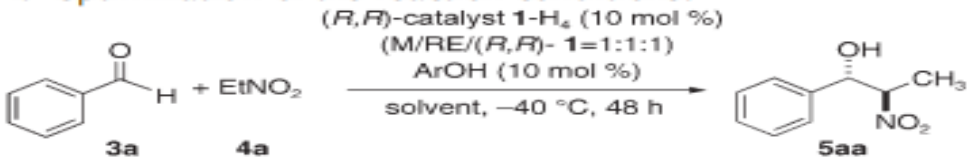
entry	metal sources M[1a]	M[2a]	Schiff base	additive	time (h)	yield[b] (%)	dr[c] (*anti*/*syn*)	% ee (*anti*)
1	Cu	Sm	**1a**	none	18	75	49:51	5
2	Ni	Sm	**1a**	none	18	36	50:50	15
3	Cu	Sm	**1b**	none	18	33	34:66	17
4	Ni	Sm	**1b**	none	18	42	61:39	59
5	Ni	Ni	**1b**	none	18	92	90:10	98
6	Cu	Cu	**1b**	none	18	95	34:66	9
7	Pd	Pd	**1b**	none	18	trace	ND	ND
8	Ni	Ni	**1b**	MS 4Å	12	95[d]	91:9	98

Ref 4: *J. Am. Chem. Soc.* 2008, *130*, 2170-2171



a M^1= Cu, M^2= Sm;
b M^1= Pb, M^2= La;

Table 1: Optimization of the reaction conditions.

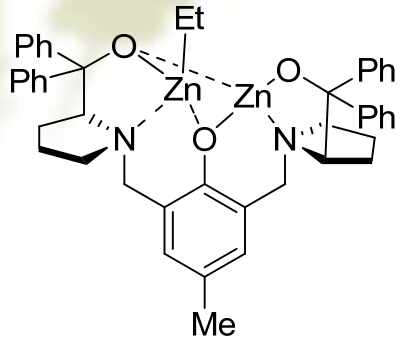


Entry	M[a]	RE[b]	ArOH	Solvent	Yield [%]	d.r. *anti*/*syn*[c]	*ee* [%][f]
1	Cu	Sm	4-*t*BuC$_6$H$_4$OH	THF	33	2.3:1	1[d]
2	Cu	Gd	4-*t*BuC$_6$H$_4$OH	THF	26	2.3:1	4[d]
3	Cu	Dy	4-*t*BuC$_6$H$_4$OH	THF	25	2.8:1	3
4	Cu	La	4-*t*BuC$_6$H$_4$OH	THF	73	2:1	28
5	Ni	La	4-*t*BuC$_6$H$_4$OH	THF	61	2:1	12
6	Zn	La	4-*t*BuC$_6$H$_4$OH	THF	30	1:2	2
7	Pd	La	4-*t*BuC$_6$H$_4$OH	THF	82	5.3:1	58
8	Pd	La	4-MeO-C$_6$H$_4$OH	THF	65	3.3:1	49
9	Pd	La	4-BrC$_6$H$_4$OH	THF	77	12:1	77
10[e]	Pd	La	4-BrC$_6$H$_4$OH	THF/xylenes	92	19:1	84

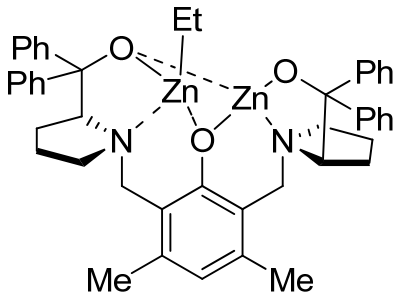
[a] $M(OAc)_2$ was used. [b] $RE(O\text{-}iPr)_3$ was used. [c] Determined by ^{1}H NMR analysis. [d] *ent*-**5aa** was the major product. [e] Reaction time was 69 h. [f] Values determined for the *anti* product.

Ref 5: *Angew. Chem. Int. Ed.* 2008, *47*, 3230-3233.

3.2 Trost半冠醚氨基醇类双金属锌催化剂

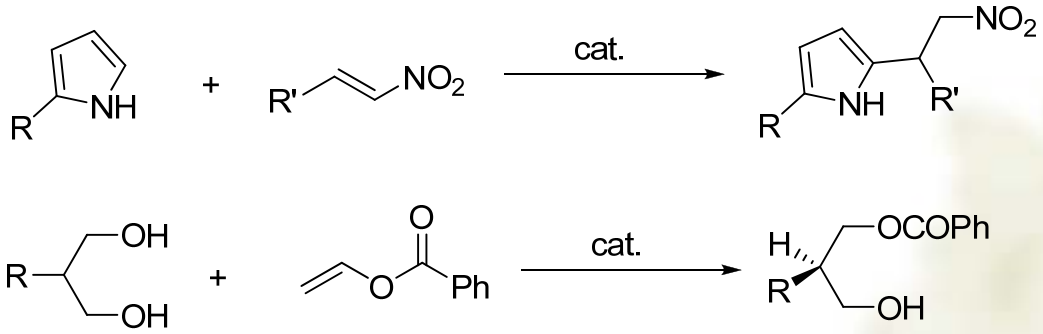


a



b

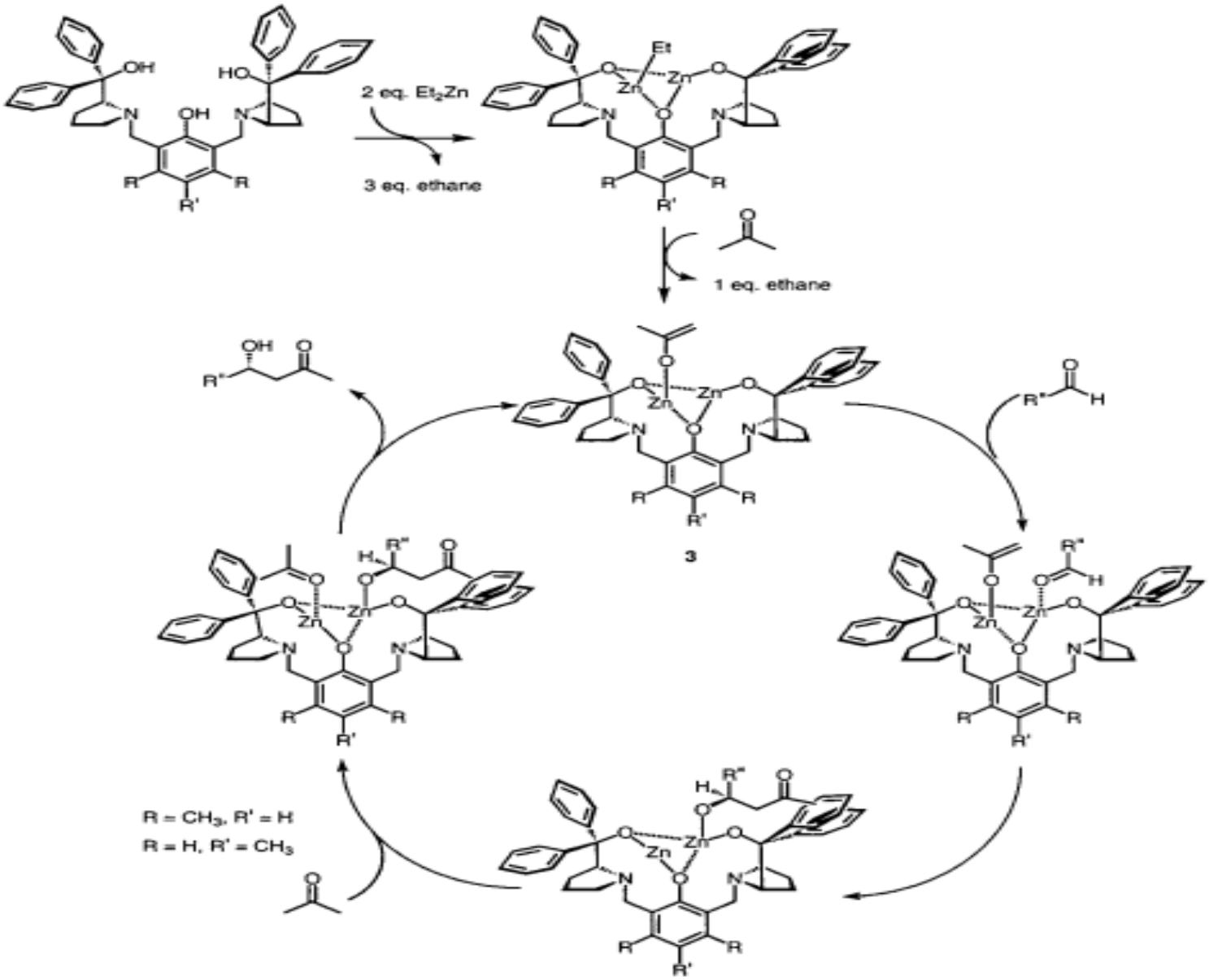
Trost 手性双金属锌催化剂



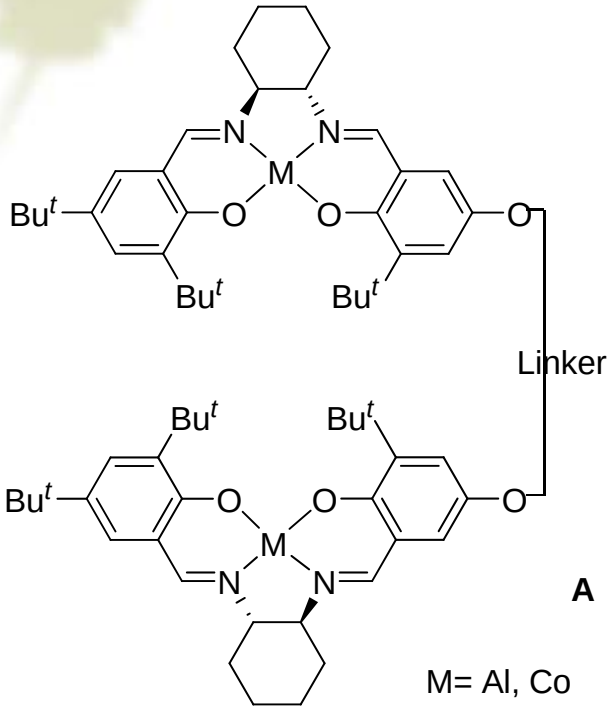
Aldol 反应

炔醛反应

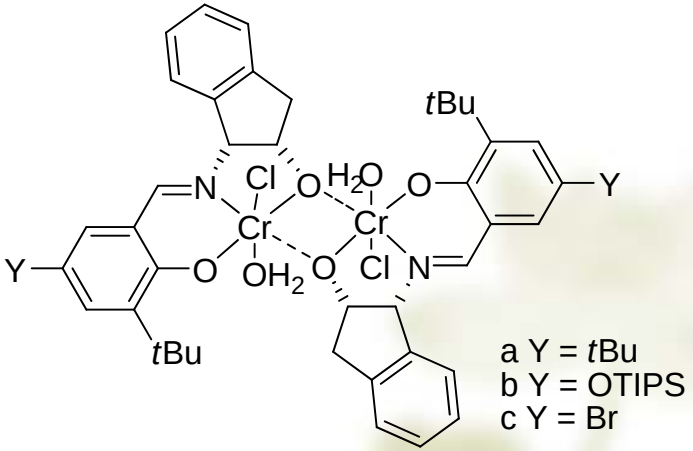
Mannich 反应


2 eq. Et2Zn
3 eq. ethane
1 eq. ethane
3
R = CH3, R' = H
R = H, R' = CH3

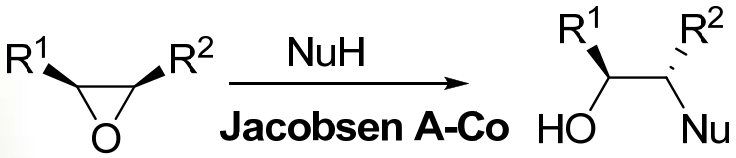
3.3 Jacobsen双席夫碱双金属催化剂



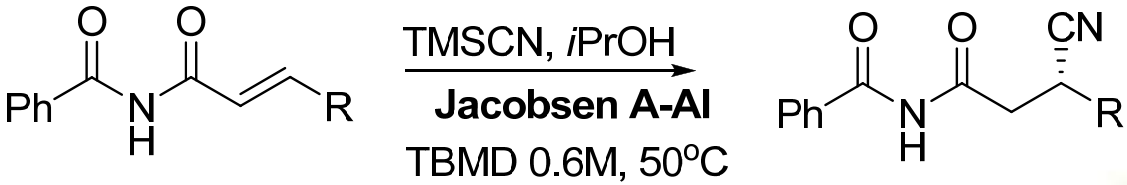
A



B



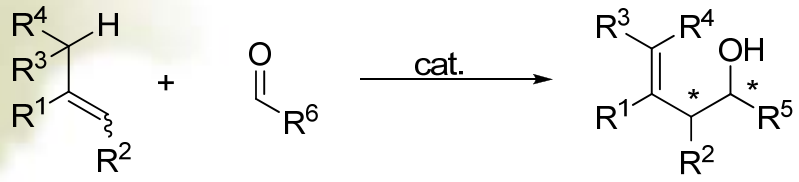
不对称催化环氧化合物开环反应

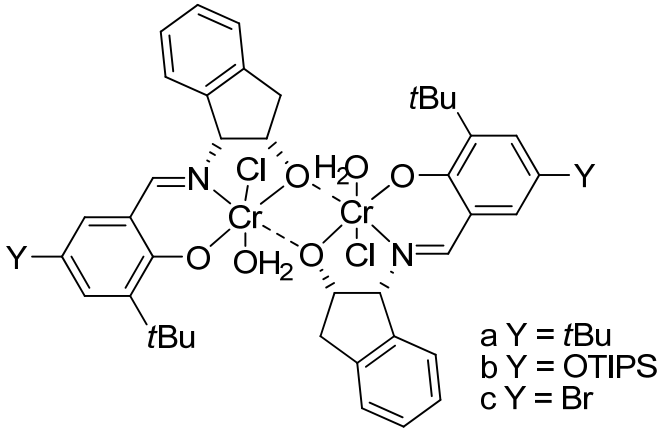


- **A-Co**主要就用于环氧化合物的开环反应，ee值都很高，且催化剂效率很高，最低用量达到了0.0004 mol%，这说明该催化剂在工业化应用中的潜力是非常大的。
- **A-Al**则应用于α,β-不饱和酰胺化合物与氰硅烷的加成反应，催化剂用量也较低，且对映选择性大多大于90%

Ref 6:
(a) Annis, D. A.; Jacobsen, E. N. *J. Am. Chem. Soc.* 1999, *121,* 4147-4154.
(b) Ready, J. M.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* 2002, *41*, 1374-1377.
(c) Mazet, C.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* 2008, *47*, 1-5.

ene 反应：



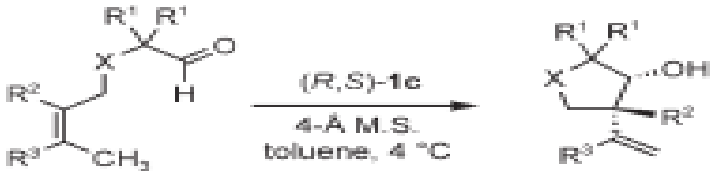


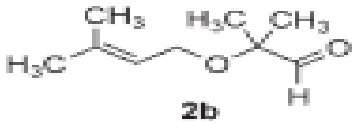
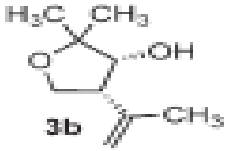
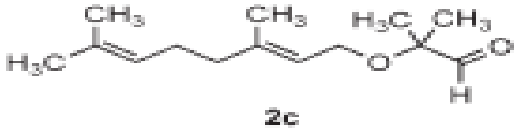
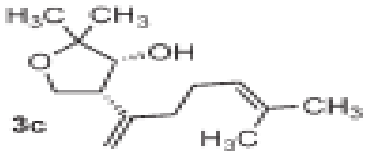
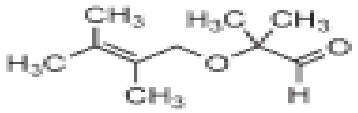
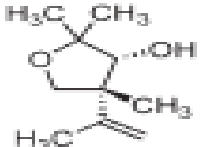
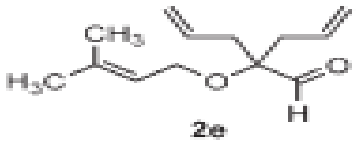
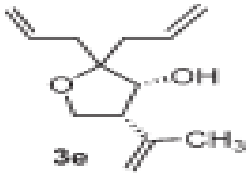
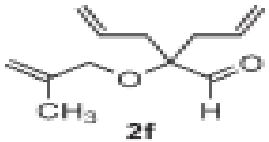
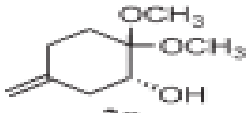
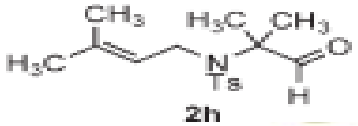
Jacobsen的席夫碱双金属铬(III)催化剂

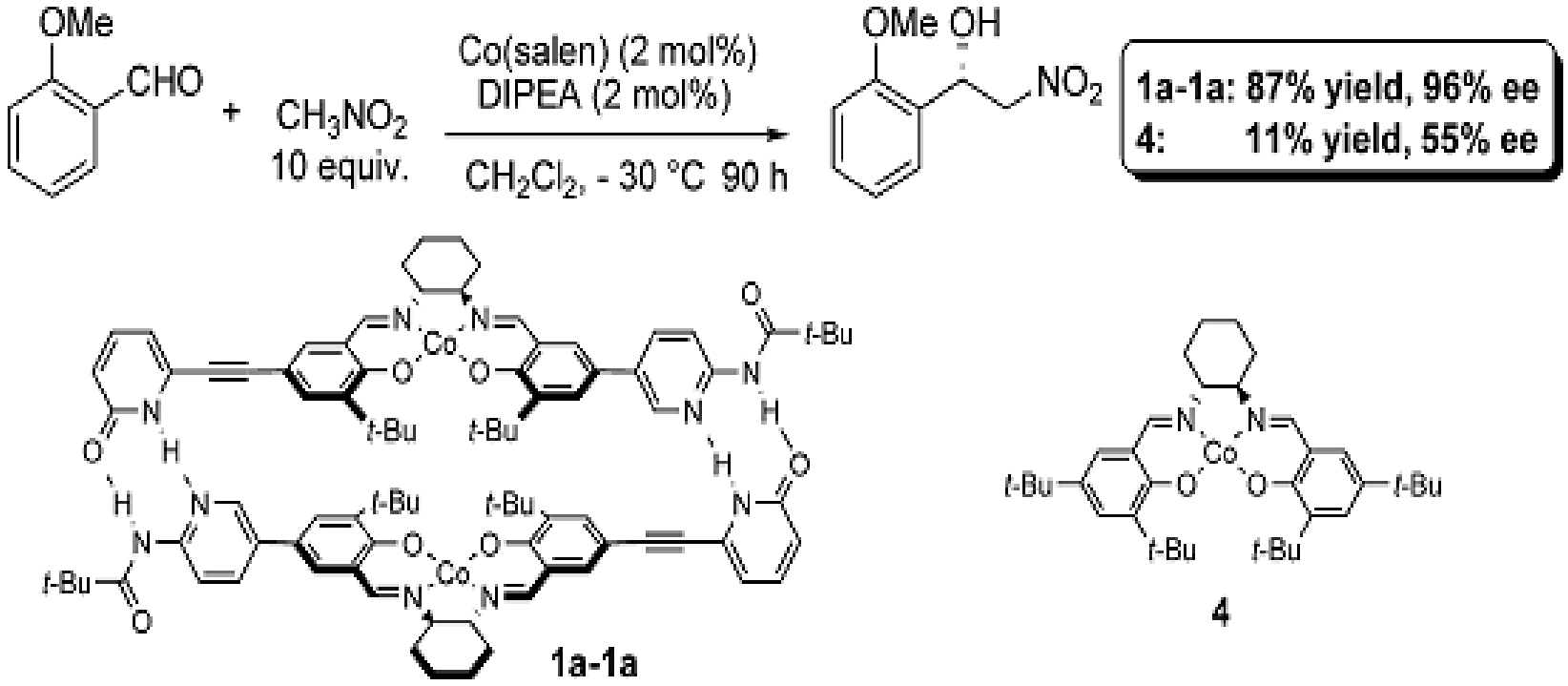
Ref 7:

(a) Grachan, M. L.; Tudge, M. T.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* 2008, *47*, 1469-1472.

(b) Ruck, R. T.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* 2003, *42*, 4771-4774

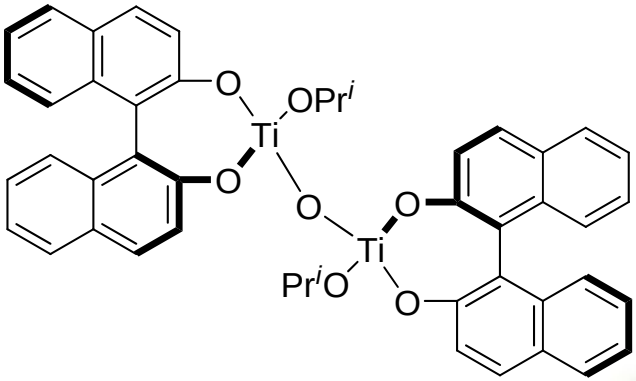


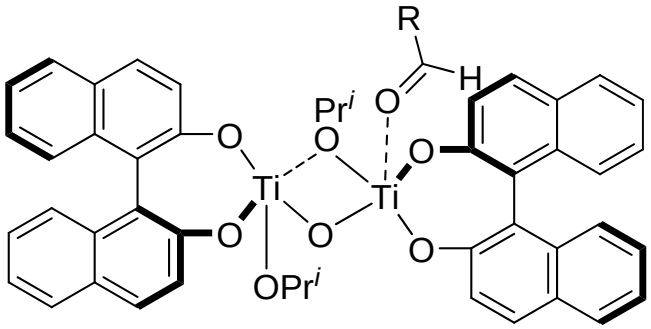
Entry	Aldehyde	Product	(R,S)-1c [mol %]	d.r.[a]	ee [%][b]	Yield [%][c]
1	 2b	 3b	0.8	> 30:1	93	77
2	 2c	 3c	1	20:1	96	94
3	 2d	 3d	5	> 30:1	75	78
4	 2e	 3e	1	> 30:1	96	96
5	 2f	 3f	5	–	93	72
6	 2g	 3g	2.5	–	94	88
7	 2h	 3h	2	> 30:1	95	98



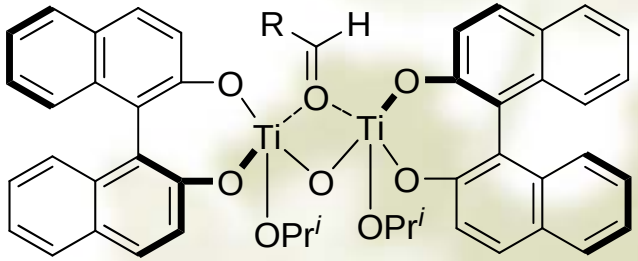
Ref 8: *J. Am. Chem. Soc*., Article ASAP • DOI: 10.1021/ja807221s

3.4 其它双金属催化剂



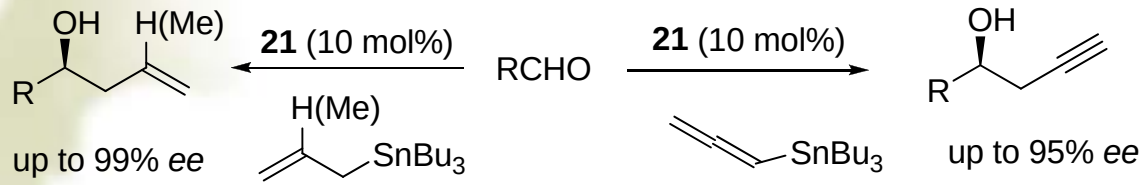


a



b

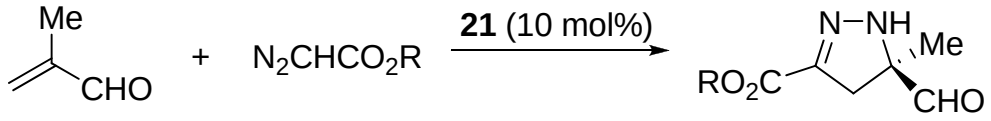
双活化羰基



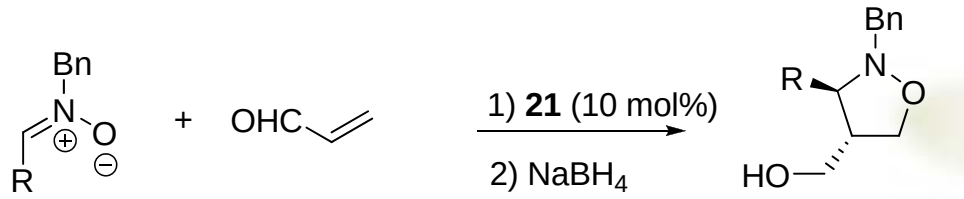
up to 99% *ee*

yield= 60~90%

up to 95% *ee*



up to 94% *ee* and 82% yield



up to 97% *ee*

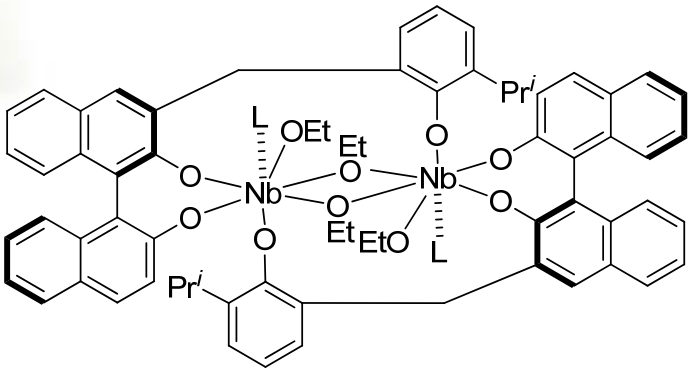
Ref 9:

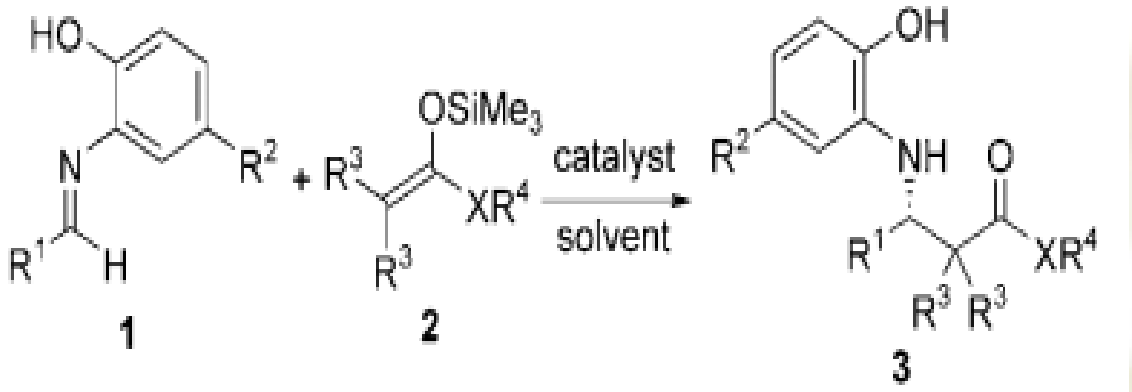
(a) Hanawa, H.; Hashimoto, T.; Maruoka, K. *J. Am. Chem. Soc.* 2003, *125*(7), 1708-1709.

(b) Hanawa, H.;Uraguchi, D.; Konishi, S.; Hashimoto, T.; Maruoka, K. *Chem. Eur. J*. 2003, *9*, 4405-4413.

(c) Kano, T.; Hashimoto, T.; Maruoka, K. *J. Am. Chem. Soc.* 2005, *127*(34), 11926-11927.

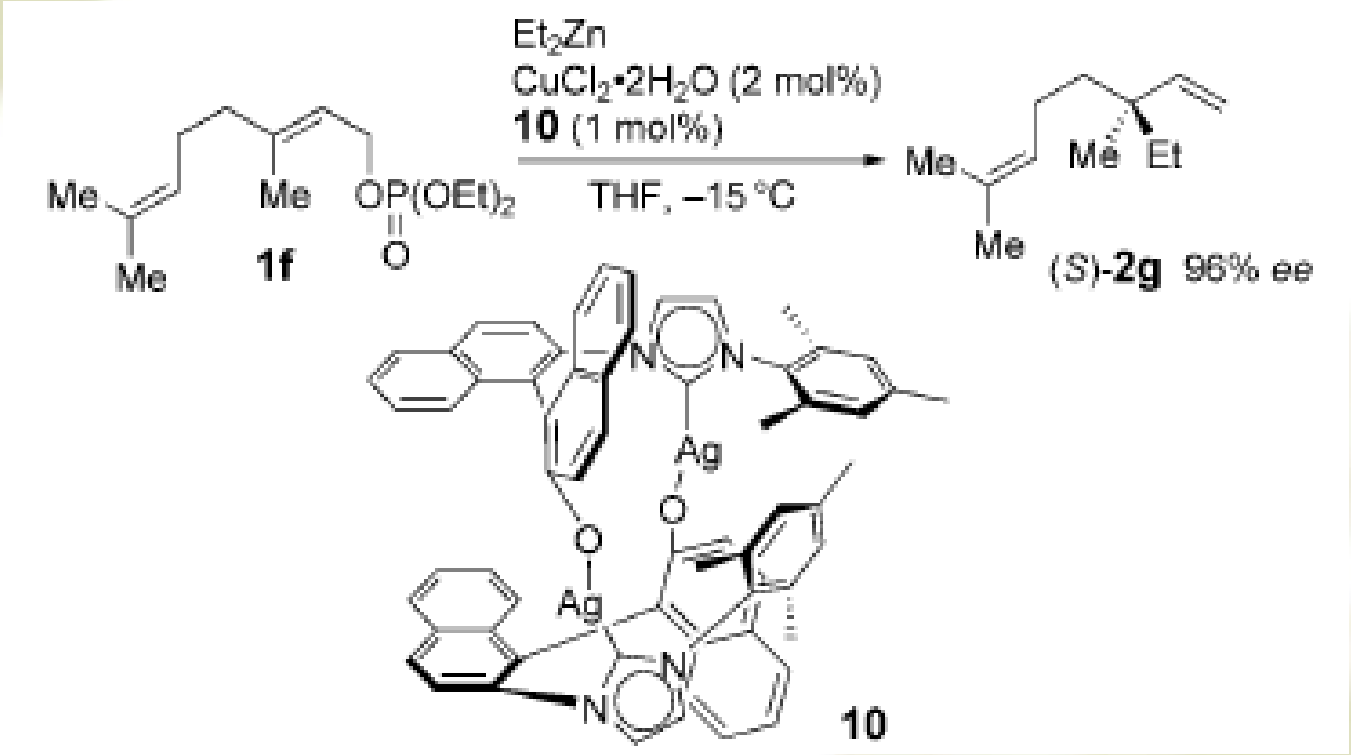
(d) Kano, T.; Hashimoto, T.; Maruoka, K. *J. Am. Chem. Soc.* 2006, *128*(7), 2174-2175.



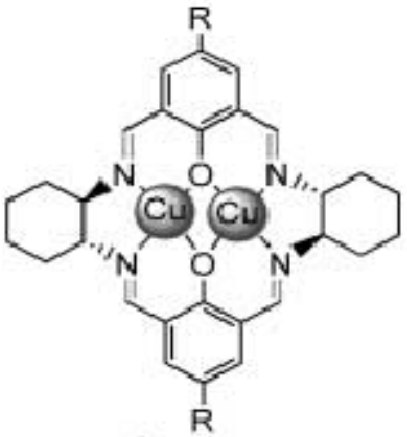


ee up to 99%

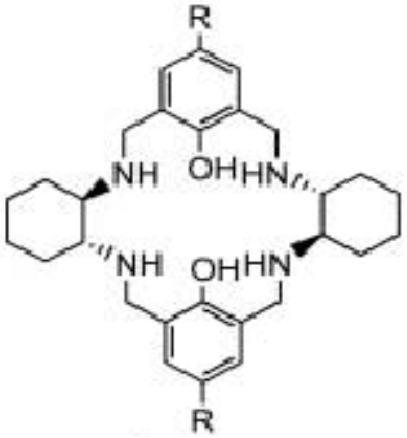
Ref 10: Kobayashi, S.; Arai, K.; Shimizu, H.; Ihori, Y.; Ishitani, H.; Yamashita, Y. *Angew. Chem. Int. Ed.* 2005, *44*, 761-764.



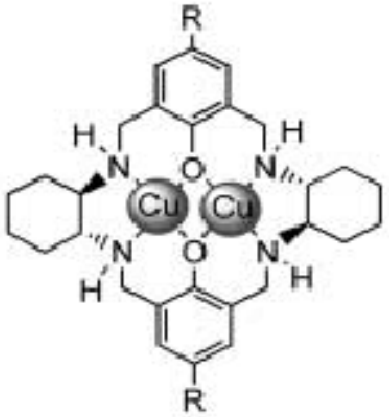
Ref 11: Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* 2004, *44*(29), 4425-4439.



1a: R = H
1b: R = Me
1c: R = *t*Bu

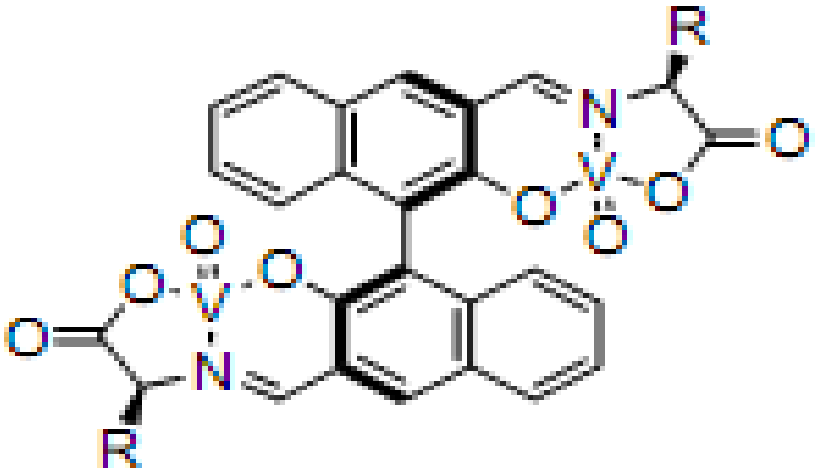


2a: R = H
2b: R = Me
2c: R = *t*Bu

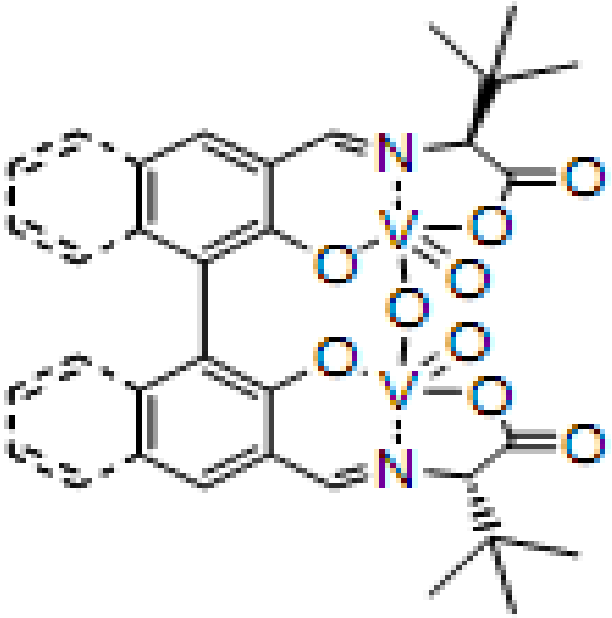


3a: R = H
3b: R = Me
3c: R = *t*Bu

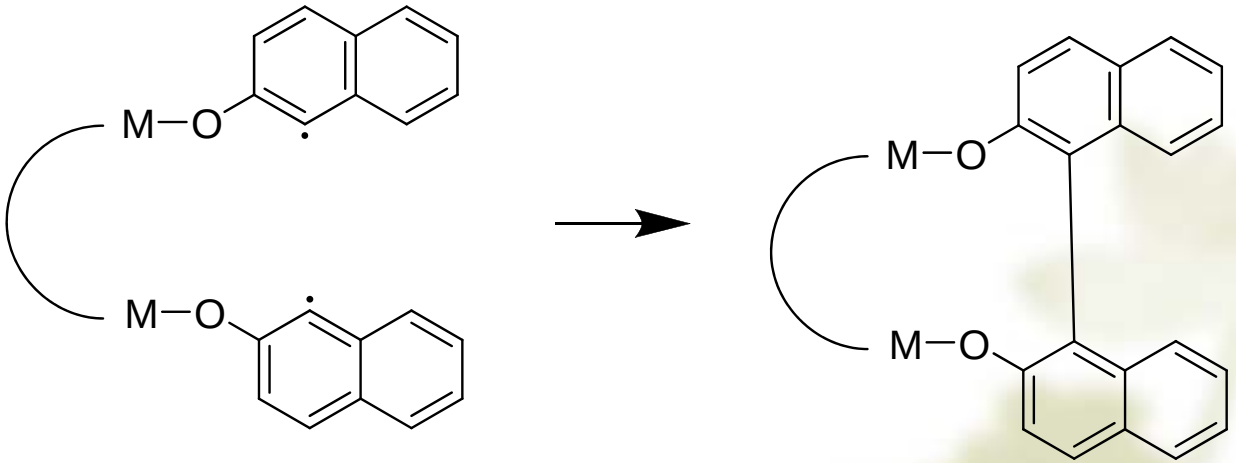
Ref 12: J, Gao;J. H. Reibenspies; A. E. Martell. *Angew. Chem. Int. Ed.* **2003,** *42*, 6008 – 6012

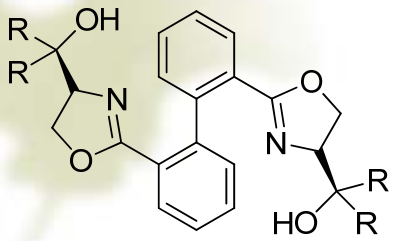


(*S*,*S*,*S*)-1



Gong's Catalyst


M—O
M—O
M—O
M—O



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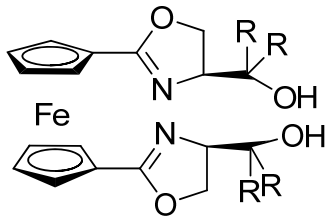

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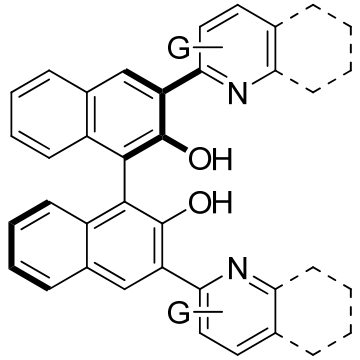
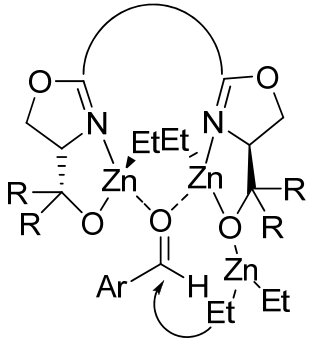
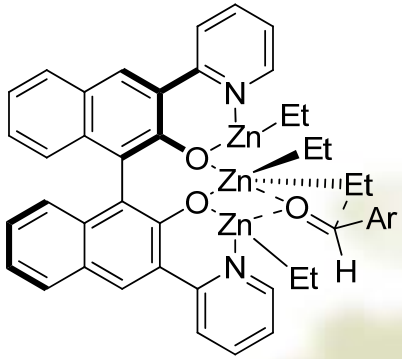


26





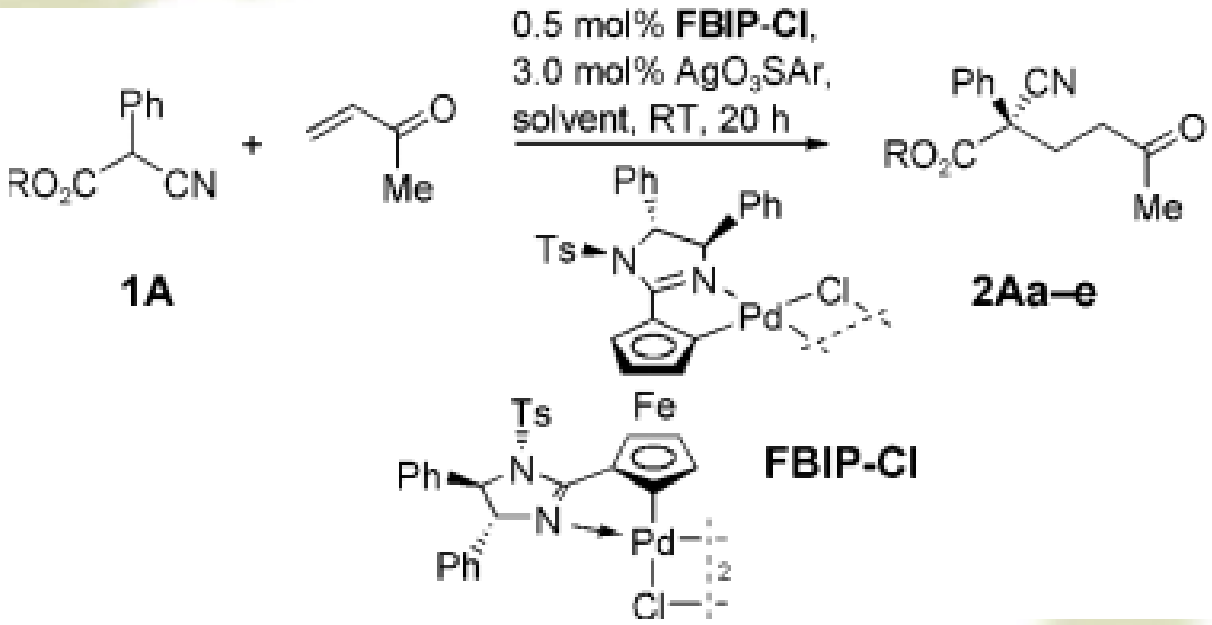
Ref 13:

(a) Hua, G.; Liu, D.; Xie, F.; Zhang, W. *Tetrahedron Lett.* 2007, *48*, 385-388.

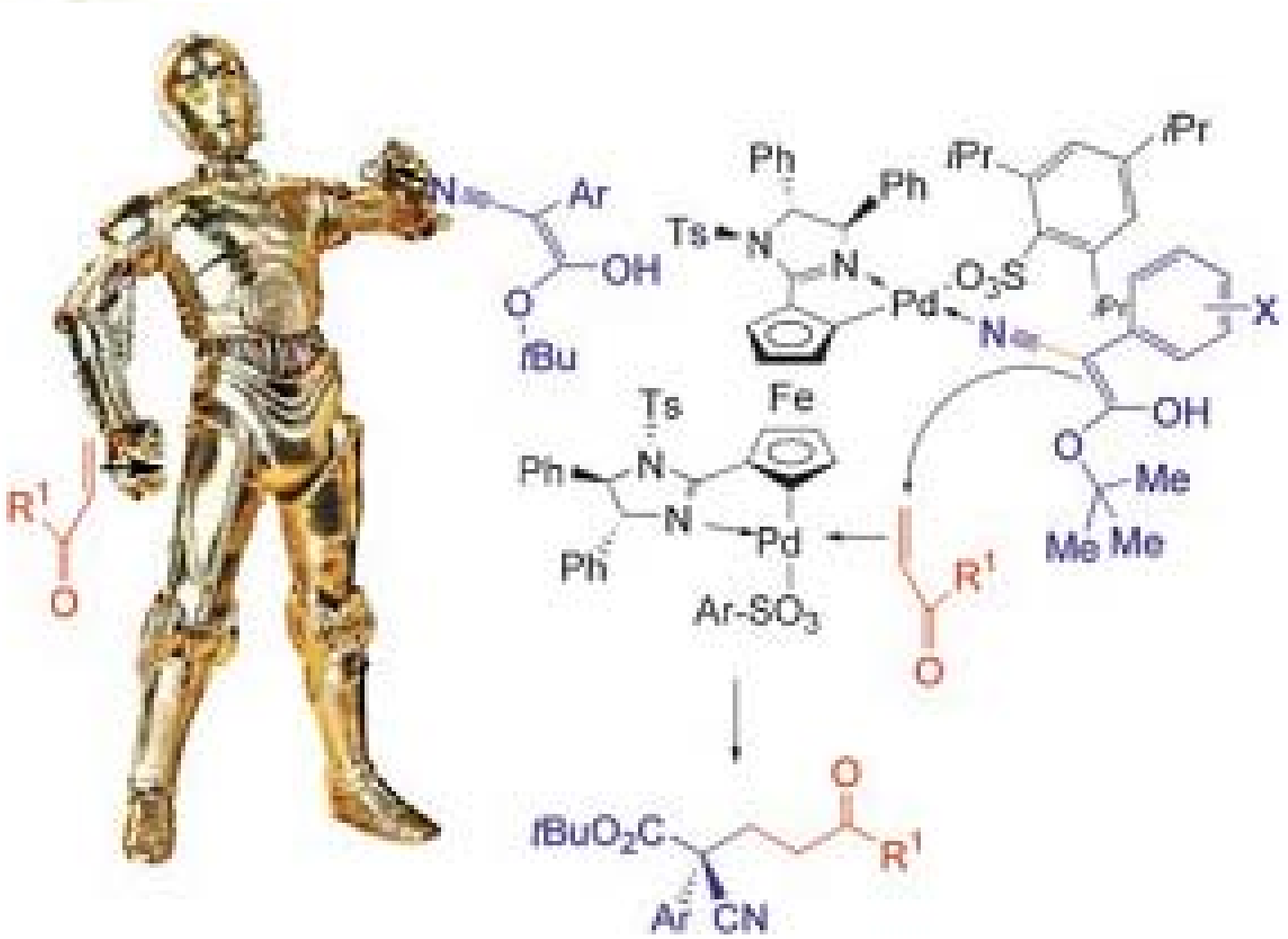
(b) Imai, Y.; Matsuo, S.; Zhang, W.; Nakatsuji, Y.; Ikeda, I. *Synlett* 2000, *2*, 239-241.

(c) Milburn, R. R.; Hussain, S. M. S.; Prien, O.; Ahmed, Z.; Snieckus, V. *Org. Lett*. 2007, *9*(22) ,4403-4406.

(d) Patrick, P.; Walailak, S.; Filisaty, V. *Org.& Bio. Chem.* **2004**, *2*, 2220.



Ref 14: S. Jautze; R. Peters. *Angew. Chem. Int. Ed*. **2008**, *47*, 9284 –9288


R1
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N
Fe
Ts
N
Ph
N
Ph
Pd
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O
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Me
R1
O
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O
R1
Ar
CN

- 谢谢收听