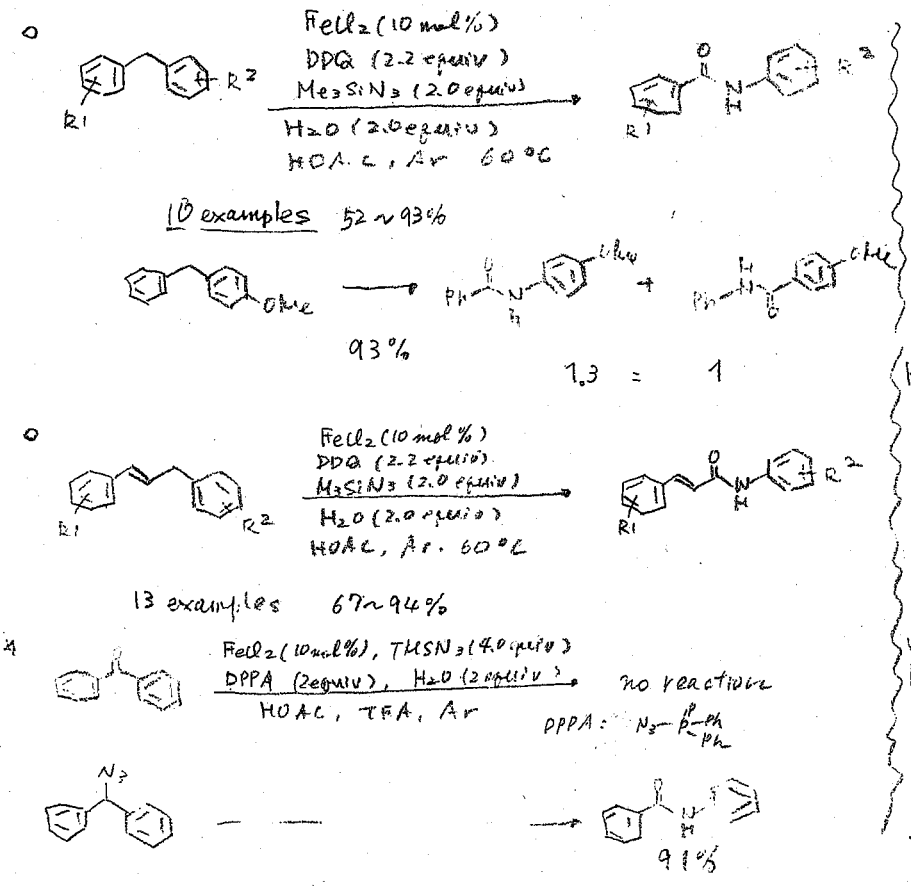
Iron-Catalyzed C–H and C–C Bond Cleavage: A Direct Approach to Amides from Simple Hydrocarbons

(Angew Chem Int Ed DOI: anie.201106112 Ning Jiao et al Peking Univ) ミーティング

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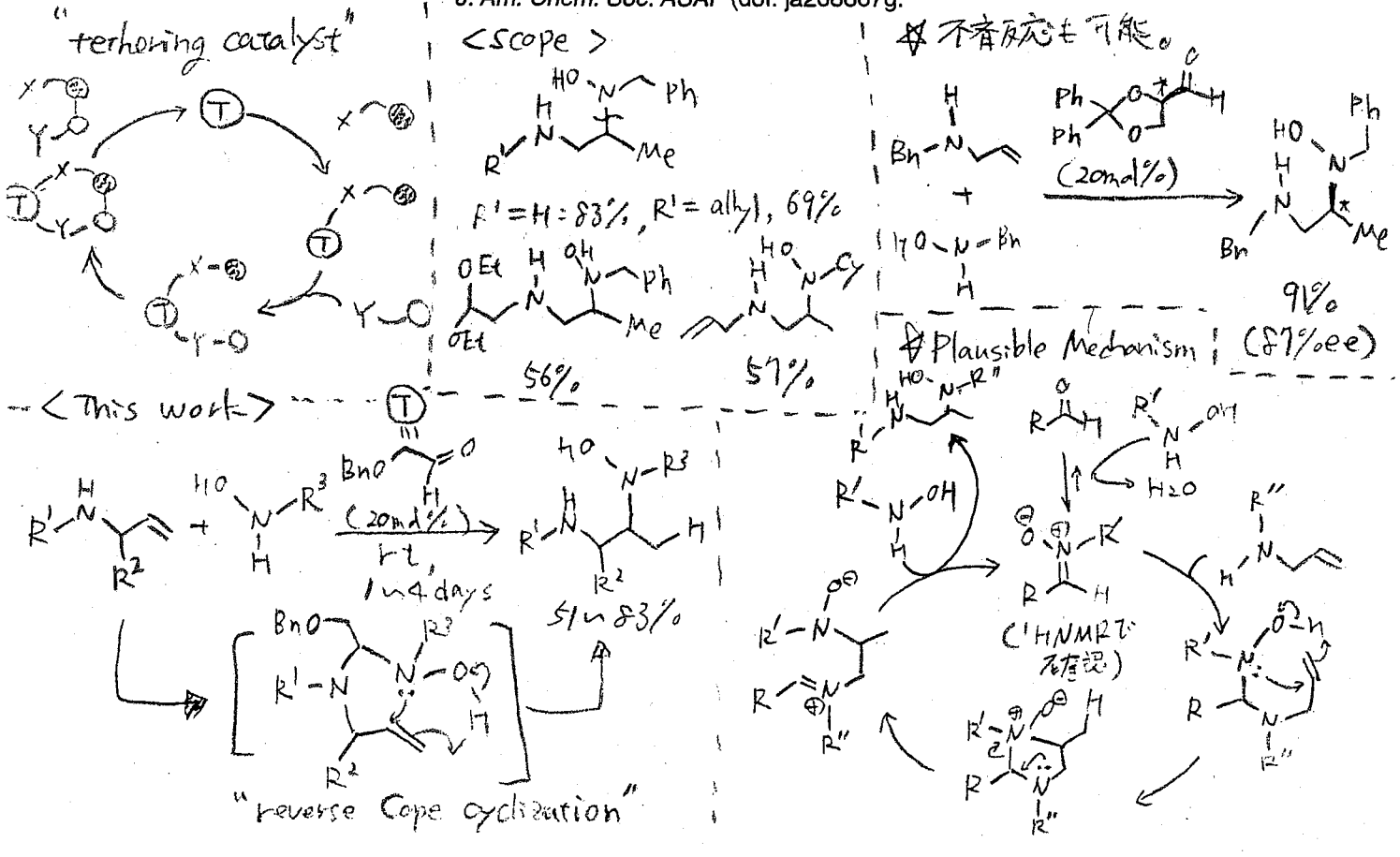
CT 1Y26 $R^1 = R^3 = Bn$ のとき, $R^2 = H$, (T) = none : 0%, Me-CHO (1eq): 41%, BnO-(=O) (1eq) = 94%, Ph-CHO (1eq): 1%, Ph-(=O)-H (1eq): 0%

" Youhei Takeda

**"A Catalytic Tethering Strategy: Simple Aldehydes Catalyze Intermolecular Alkene Hydroaminations"**

MacDonald, M. J.; Schipper, D. J.; Ng, P. J.; Moran, J.: Beauchemin, A. M.*

*J. Am. Chem. Soc. ASAP* (doi: ja208867g.

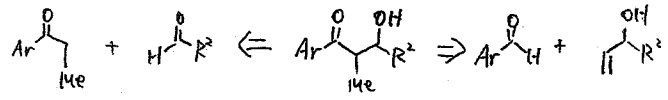


# β-hydroxy ketones prepared by regioselective hydroacylation

Dong, V. M. et al. Chem. Sci. (Advance Article)
(University of Toronto)

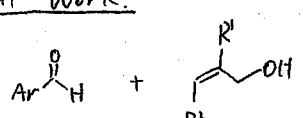
P3 村上.

## Retrosynthetic analysis of β-hydroxy ketones

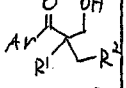


(aldol reaction) (hydroacylation)

## Present Work.

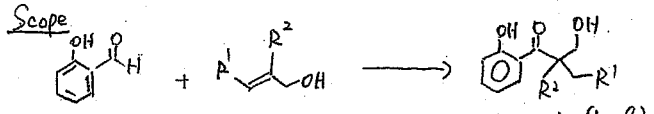


$[Rh(COD)Cl]_2$ (2.5 mol%)
$Ph_2POMe$ (25 mol%)
NaOAc (20 mol%)
cl~cl, 67°C

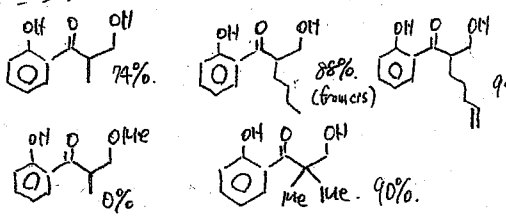


73-94%.

## Scope

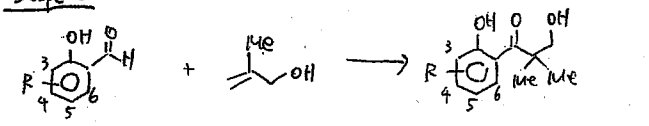


> 20:1 (b:l)

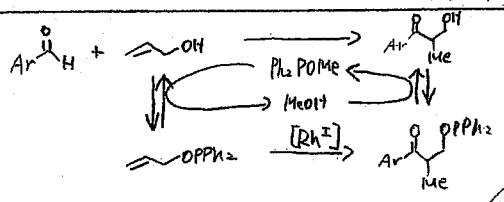


74%. 88% (6 trans) 94%. 0% 90%.

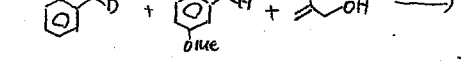
## Scope 2

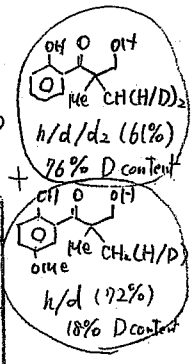


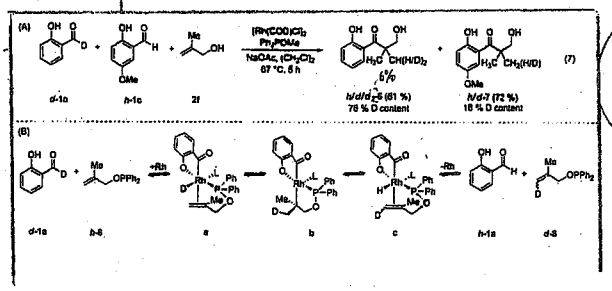
| 5-Cl | 5-OMe | 3-Me | 6-Me | 4-OH |
|---|---|---|---|---|
| 73% (5h) | 76% (6h) | 80% (5h) | 78% (5h) | 82% (7h) |



Cross-over 実験.







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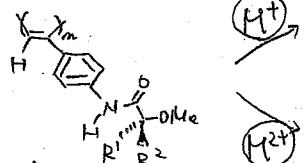
# Chiral Amplification and Helical-Sence Tuning by Mono- and Divalent Metals on Dynamic Helical Polymers

長町

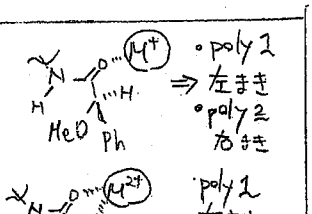
DOI: 10.1002/anie.201105769
Ricardo Riguera et al
Santiago de Compostela Univ.

① ポリマーのキラリティ
⇒ キラルセンサー, 分子メモリー
不斉触媒 ... etc. に展開可能

○ This Work



poly1, R¹=Ph, R²=H
poly2, R¹=H, R²=Ph

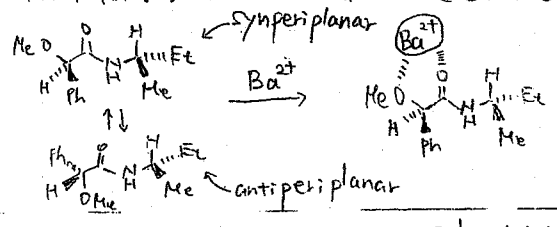


poly1 左まき
poly2 右まき

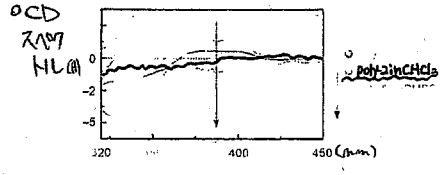
poly1 右まき
poly2 左まき

○ previous work

¹HNMRにより キラルアミンの絶対配置を $Ba^{2+}$ で固定



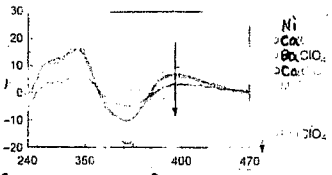
○ CD スペクトル

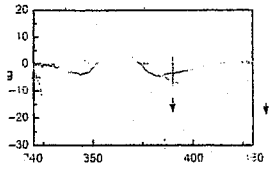


poly2 in $CHCl_3$

⇐ Solvent によって Helicity が変化。
TDDホルムでは (無)

○ TDDホルム中の poly2 に $M^{2+}$, $M^{+}$ を添加。

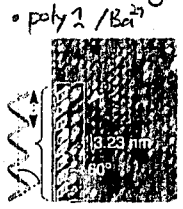


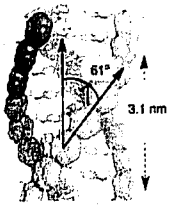


⇐ ・Cotton effects の発現 ・0.1 ($M^{2+}$)/1 (monomer) (eq/eq) で感知する!!
・$M^{2+}$ と $M^{+}$ では逆のヘリシティを確認.

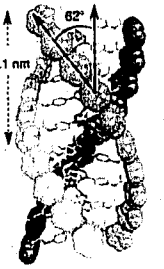
○ AFM image

・poly2/$Ba^{2+}$

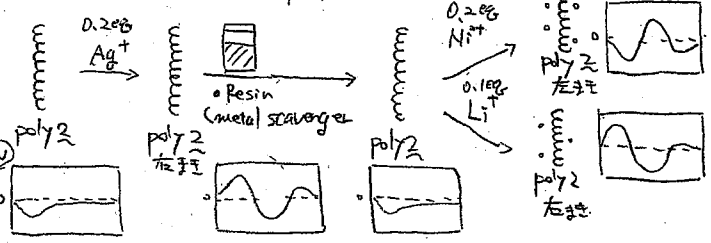




・poly2/$Ag^{+}$



○ Reversible use of poly2



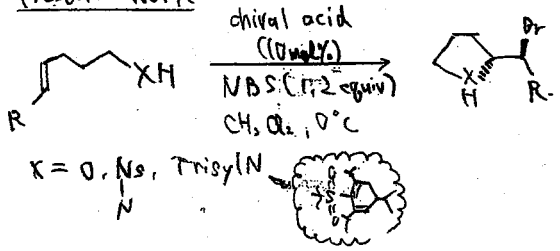
poly2 → (0.2eq $Ag^{+}$) → poly2 左まき → (Resin (metal scavenger)) → poly2 → (0.2eq $Ni^{2+}$, 0.1eq $Li^{+}$) → poly2 左まき

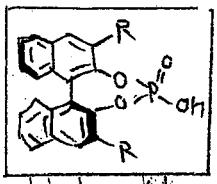
(CV) poly2 poly2 左まき poly2 poly2 左まき

# Enantioselective Bromocyclization of Olefins Catalyzed by Chiral Phosphoric Acid

Org. Lett. doi: 10.1021/ol202527g
Yian Shi et al (Colorado State University)

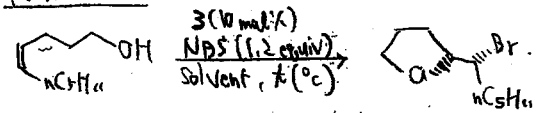
present work



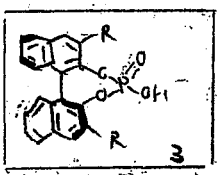



chiral acid
R = 2,4,6-($^i$Pr)$_3$C$_6$H$_2$

Optimization

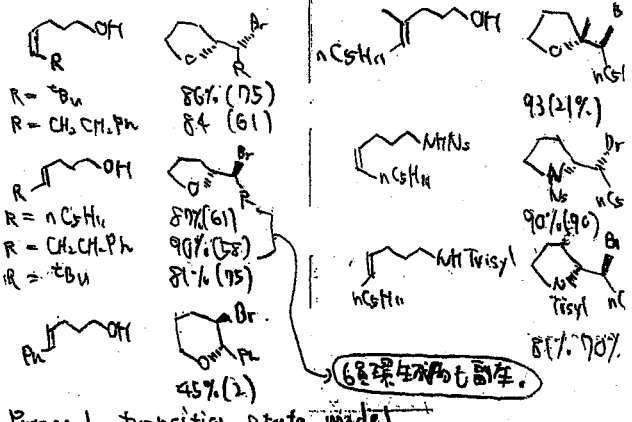



| entry | 3 | solvent | t (°C) | time (h) | yield (%) | ee (%) |
|---|---|---|---|---|---|---|
| 1 | 3a | $CH_2Cl_2$ | −60 | 48 | 83 | 10 |
| 2 | 3b | $CH_2Cl_2$ | −60 | 48 | 22 | −68 |
| 3 | 3c | $CH_2Cl_2$ | −60 | 48 | 97 | 70 |
| 4 | 3c | $CHCl_3$ | −60 | 48 | 94 | 57 |
| 5 | 3c | toluene | −60 | 48 | 45 | 50 |
| 6 | 3c | $CH_2Cl_2$ | −30 | 48 | 97 | 75 |
| ◎ 7 | 3c | $CH_2Cl_2$ | 0 | 18 | 97 | 75 |
| 8 | 3c | $CH_2Cl_2$ | rt | 6 | 3 | 71 |

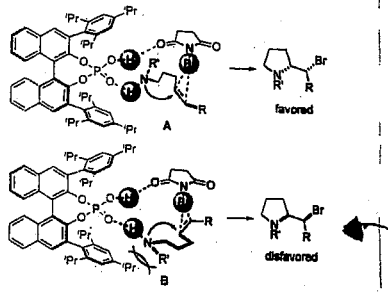


3a R = 3,5-$(CF_3)_2C_6H_3$
3b R = $SiPh_3$
3c R = 2,4,6-($^i$Pr)$_3$C$_6$H$_2$

Scope (entry 7の条件) ( )内はee. (DI型)




Proposed transition state model



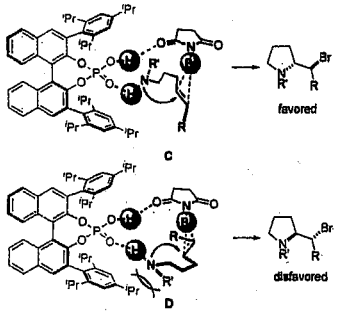
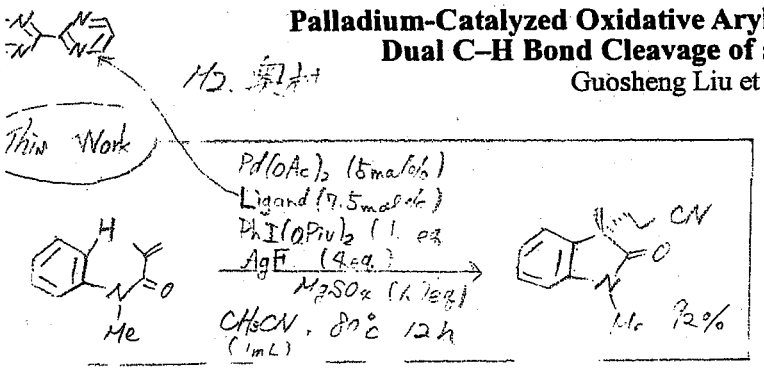



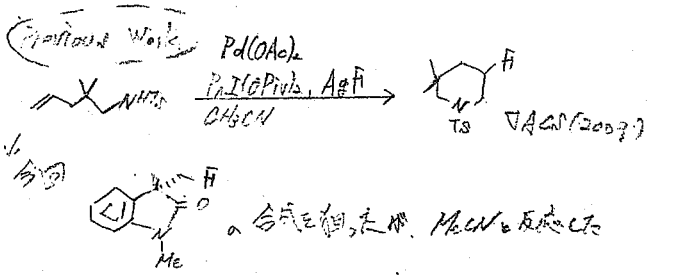

Figure 3. Proposed transition state model for bromoaminocyclization of *trans*-γ-amino-ulkenes.

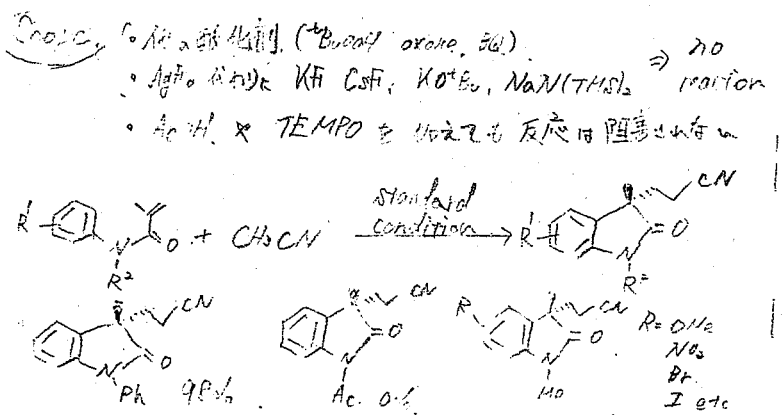
Figure 2. Proposed transition state model for bromoaminocyclization of *cis*-γ-amino-ulkenes.

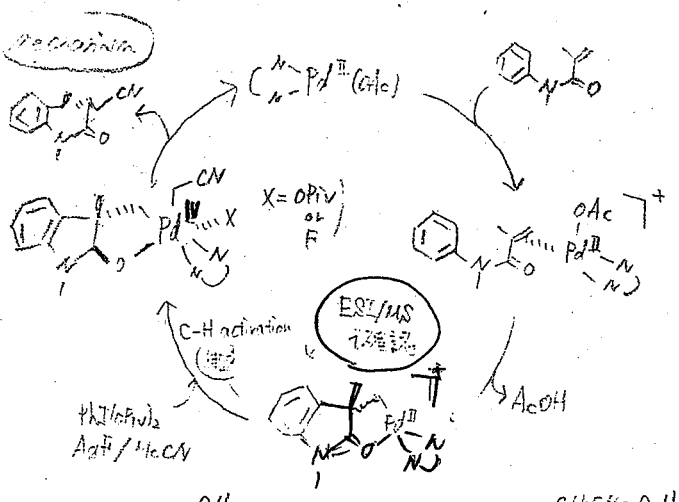
## Palladium-Catalyzed Oxidative Arylalkylation of Activated Alkenes: Dual C–H Bond Cleavage of an Arene and Acetonitrile

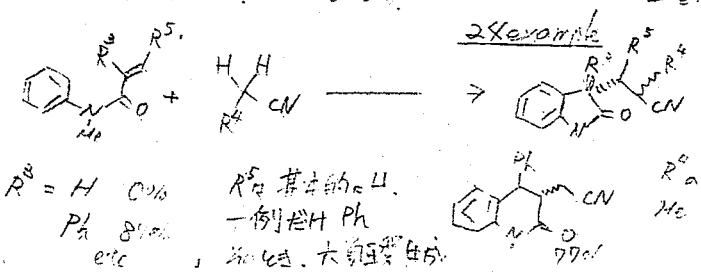
Guosheng Liu et al. *Angew. Chem. Int. Ed.*. DOI: 10.1002/anie20114575



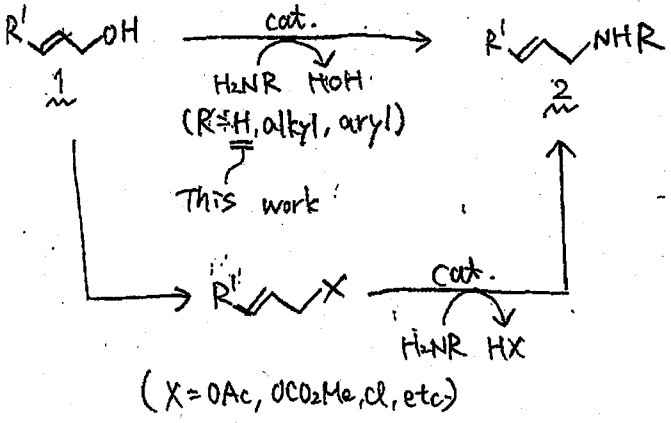



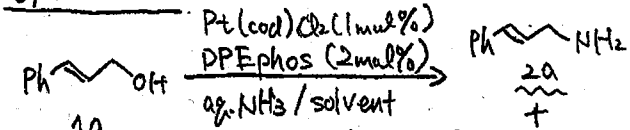
Yuki Ikeda

# Platinum-Catalyzed Direct Amination of Allylic Alcohols with Aqueous Ammonia: Selective Synthsis of Primary Allylamines

Das, K.; Shibuya, R.; Nakahara, Y.; Germain, N.; Oshima, T.; Mashima, K. *Angew. Chem. Int. Ed.* Early View (10.1002/anie.201106737)

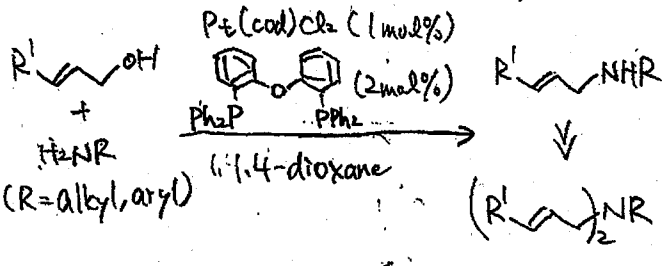


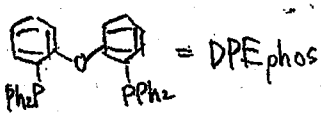

Optimization



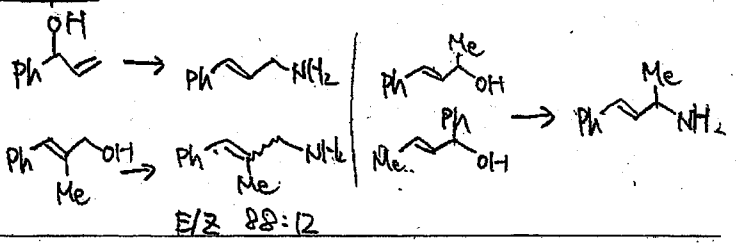

| solvent | aq. $NH_3$/solvent (equiv of $NH_3$) | 2a (%) | 2a/4a |
|---|---|---|---|
| 1,4-dioxane | 1:5 (20) | 60 | 82:18 |
| 1,4-dioxane | 1:1 (60) | 74 | 90:10 |
| 1,4-dioxane | 2:1 (80) | 51 | 94:6 |
| MeOH | 1:1 (60) | 71 | 93:7 |
| — | — (120) | 7 | 93:7 |
| 1,4-dioxane/MeOH | 3:2:1 (60) | 79 | 91:9 |

<Previous Work> OL, 2007, 9, 3371




Scope

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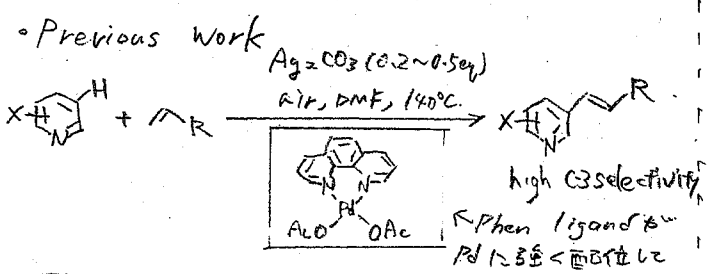
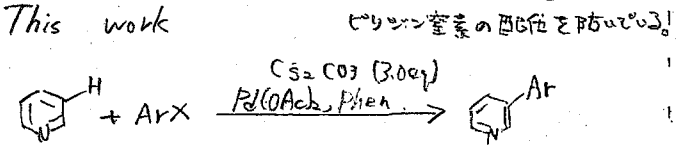
# Ligand-Promoted C3-Selective Arylation of Pyridines with Pd Catalysts: Gram-Scale Synthesis of (±)-Preclamol

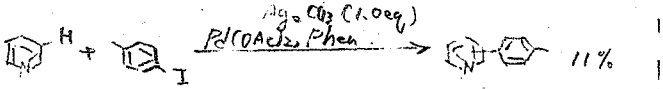
Yu, J.-Q. *et al. J. Am. Chem. Soc.* **2011**, *133*, 19090




☆これまでのピリジンのC3-C4-選択的アリール化

- Pd(0) / $PR_3$ / ArX systems
- 基質をデザインすることで選択性をコントロール

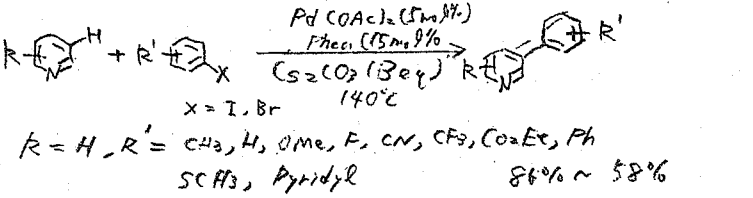



halide scavengerを代えた。

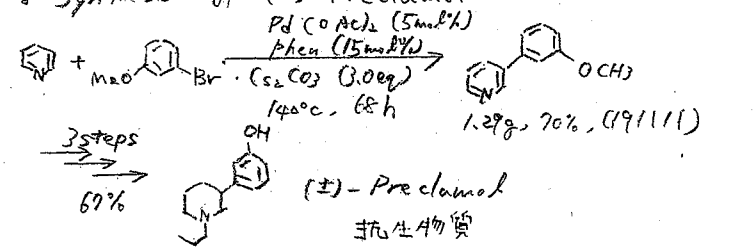
$Ag_2CO_3$ → $Cs_2CO_3$

Condition = $Pd(OAc)_2$ 5mol%, Phen 15mol%, $Cs_2CO_3$ (3.0eq)

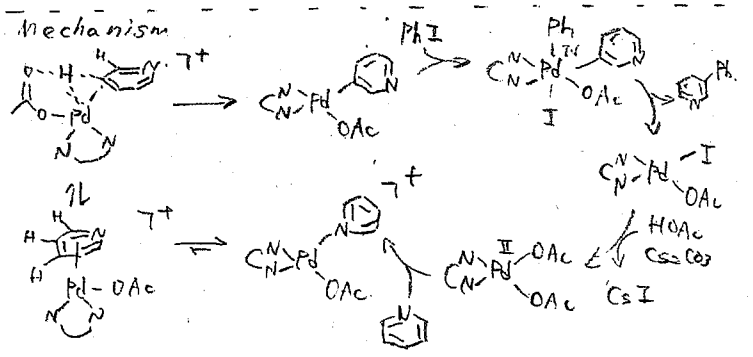
92% 38/1/1 (C3/C4/C2)




- Synthesis of (±)-Preclamol



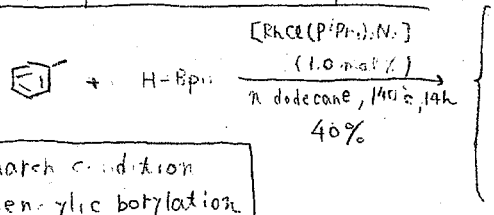

Mechanism



# Rh-Catalyzed Ortho-Selective C-H Borylation of N-Functionalized Arenes with Silica-Supported Bridgehead Monophosphine Ligands

Sawamura, M et al JACS DOI: 10.1021/ja208364a M1 錦織

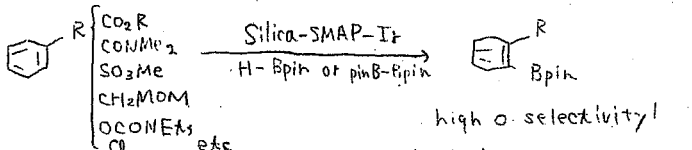
## • Rh-Catalyzed arene C-H borylation




- harsh condition
- benzylic borylation

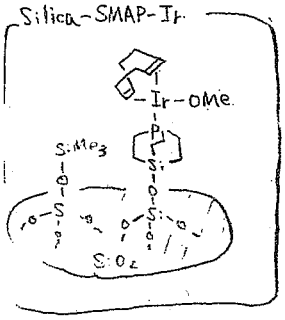
Angew Chem Int Ed (Cool)
Marder T B et al

## • Borylation using Silica-Supported Phospine Ligand (previous work)



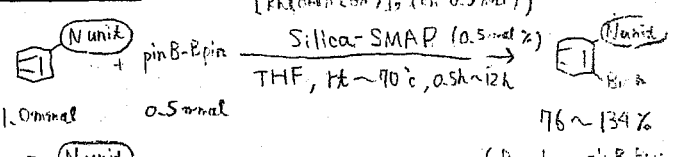

Sawamura M et al
- J Am Chem Soc 2009, 131, 5058.
- J Org Chem 2010, 75, 3855
- Org Lett. 2010, 12, 3978

Silica-SMAP-Ir

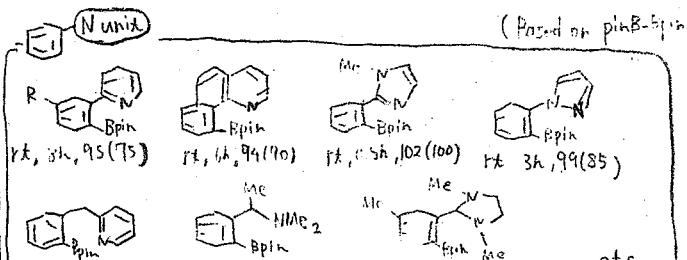



SMAP
Silicon Constrained
Monodentate
Alkyl
Phospine

## • This Work

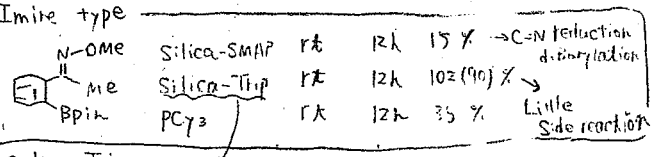



(Based on pinB-Bpin)

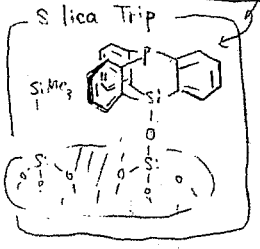



No benzylic boration was observed!

Imine type




Silica Trip




- 詳細な機構は分かっていない
- Silica-SMAP, Trip の P 原子が Rh に1つしか配位できず空の配位ができていることが全体かも...

# Catalytic Kinetic Resolution of Cyclic Secondary Amines

M1 矢野

Michael Binanzer, Sheng-Ying Hsieh, and Jeffrey W. Bode JACS DOI: 10.1021/ja209472h

## ◦ 速度論的光学分割 (Kinetic Resolution)

$S_{(R)} \xrightarrow[fast]{Cat(R)} P_{(R)}$ 片方のエナンチオマーを優先的に反応させる

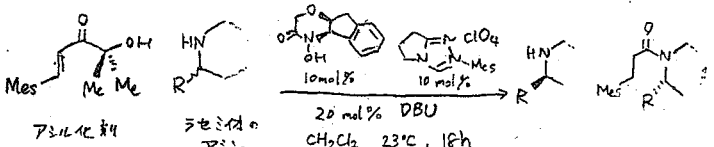
$S_{(S)} \xrightarrow[slow]{Cat(R)} P_{(S)}$

## ◦ アミンの触媒的 Kinetic Resolution

- Fu バルキーなアシル化剤を用いた反応
- Birman Miller アミンを保護した誘導体を用いた反応
- Seide 低温・低濃度での反応

第二級アミンには適用できない (Fuはインドリンを基質とした反応は行っている)

## ◦ Present Work

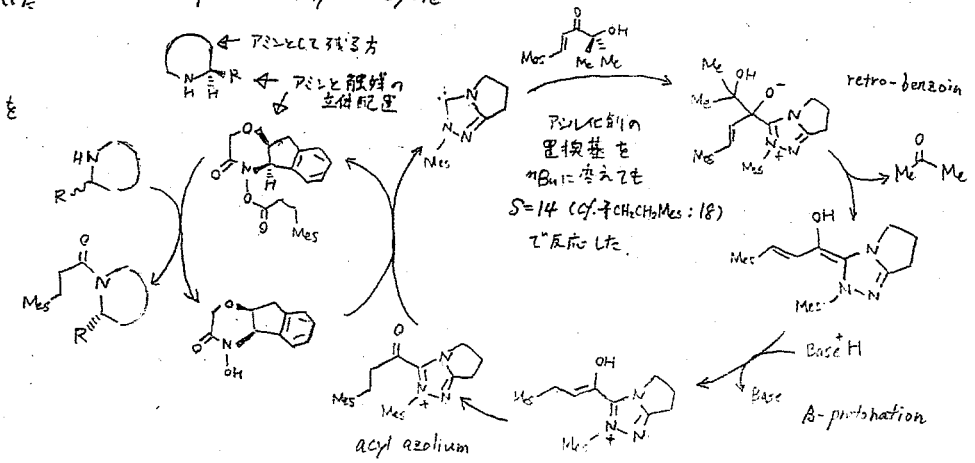



アシル化剤　ラセミ体のアミン

21 examples

$S(k_{fast}/k_{slow}) = 8 \sim 74$

## ◦ Proposed Catalytic Cycle



# Covalent Capture of Nitrous Oxide by N-Heterocyclic Carbenes

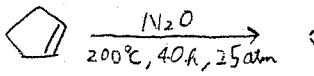
B4 岡崎

Alexander G. Tskhovrebov, Euro Solari, Matthew D. Wodrich, Rosario Scopelliti, and Kay Severin*

Angewandte DOI: 10.1002/anie.201106589.

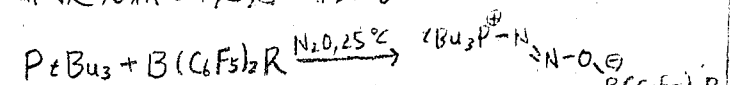
$N_2O$ $N\equiv N^{\oplus}-O^{\ominus} \leftrightarrow {}^{\ominus}N=N^{\oplus}=O$

- 高い酸化電位を持つが，反応させるためには厳しい条件が必要[a)]




Conversion 94.2%
Selectivity 97.8%

- 近年，Frustrated Lewis Pairs (FLPs) で $N_2O$ を補捉する新しい発見があった。[a)]




R = $C_6F_5$ (1), Ph (2)

Structure in the crystal

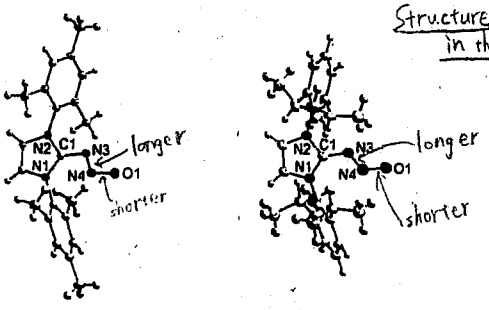
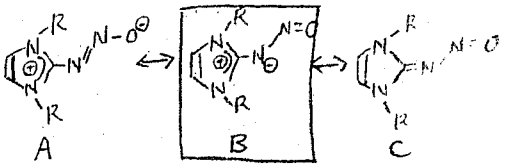


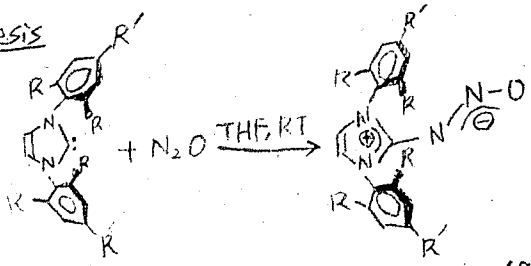

Table 1: Selected bond lengths and angles for 1 and 2.

| | 1 (exptl.) | 2 (exptl.) | 1 (theor.) | 2 (theor.) |
|---|---|---|---|---|
| C1-N1 [Å] | 1.366(2) | 1.354(4) | 1.365 | 1.361 |
| C1-N2 [Å] | 1.360(2) | 1.368(4) | 1.361 | 1.357 |
| C1-N3 [Å] | 1.360(2) | 1.358(4) | 1.323 | 1.327 |
| N3-N4 [Å] | 1.333(2) | 1.352(4) | 1.352 | 1.346 |
| N4-O1 [Å] | 1.250(2) | 1.250(4) | 1.202 | 1.205 |
| C1-N3-N4 [°] | 109.6(1) | 110.7(3) | 110.9 | 110.5 |
| N3-N4-O1 [°] | 113.1(1) | 112.9(3) | 113.9 | 114.1 |
| N4-N3-C1-N1 [°] | 25.4(2) | 39.5(5) | 24.07 | 26.25 |



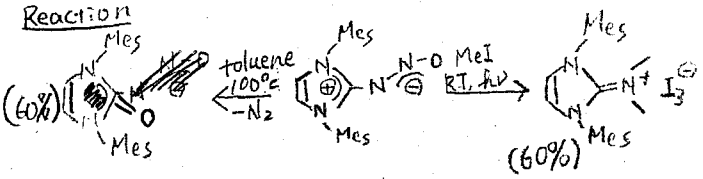

今回の仕事 NHCを使って $N_2O$ を補捉できないか？

Synthesis




1 R=R'=Me (90%)
2 R=iPr, R'=H (41%)

Reaction

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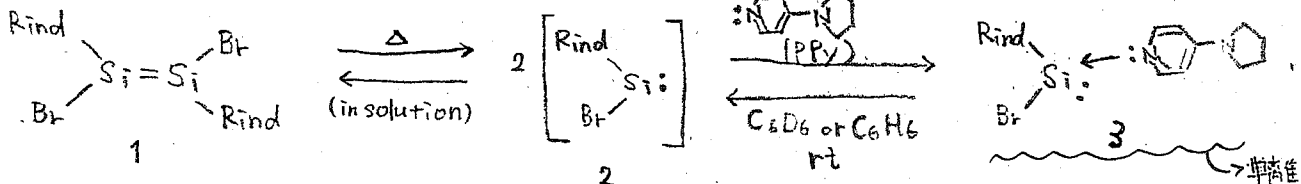
# Room-Temperature Dissociation of 1,2-Dibromodisilenes to Bromosilylenes

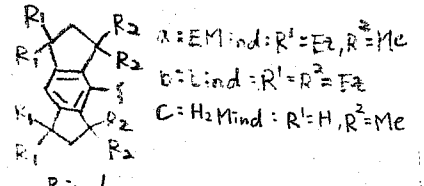
B4 久岡

Taina o, K et al)

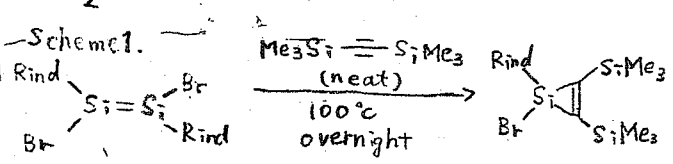
J. Am. Chem. Soc.
doi: ja209736d




→準備中・同定した




Scheme 1.




⇒ Si=Si結合が開裂して bromosilylene を中間体として反応が進行するのではないか??

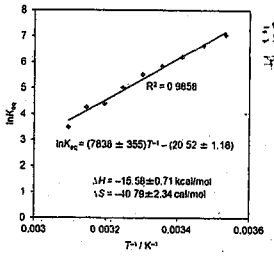
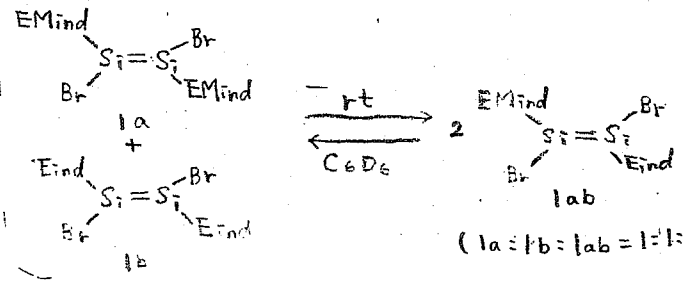



Figure S11. A plot of $\ln K_{eq}$ vs $T^{-1}$ for the equilibrium between 1a and 3a in $C_6D_6$.

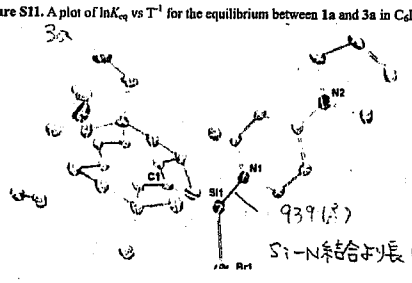
温度が下がるにつれ平衡は右に傾く。

変わり好き

Scheme 2.




(1a : 1b : 1ab = 1 : 1 : 2.9)




DFT

Si=Si 開裂エネルギー： 1c (19.2 kcal/mol) < diphenyldisilene (34.0 kcal/mol)

$\Delta E_{ST}$ value for silylene： 2c (46.4 kcal/mol) > phenylsilylene (38.2 kcal/mol)

→ 1 → 2 への反応は容易に行く