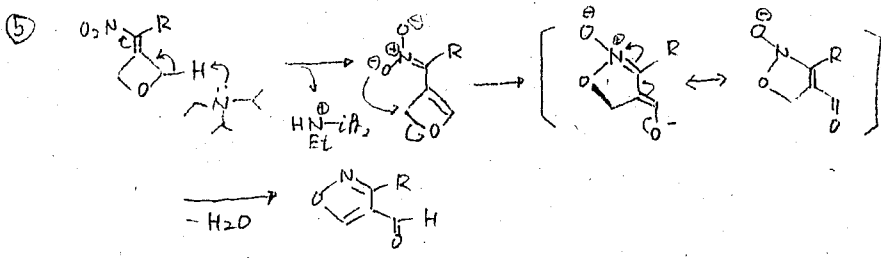
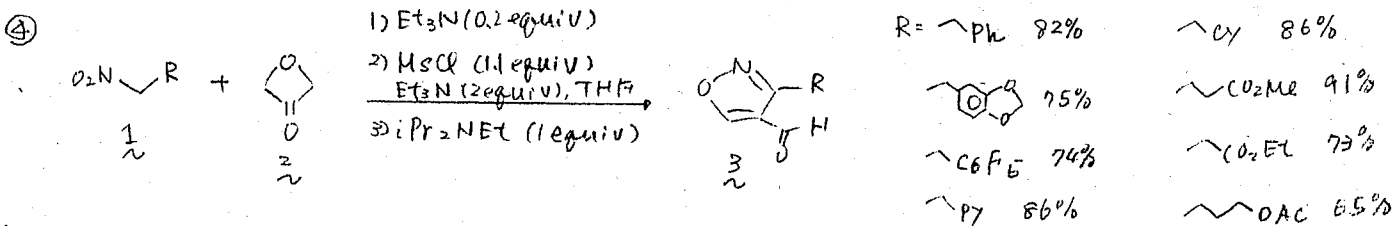
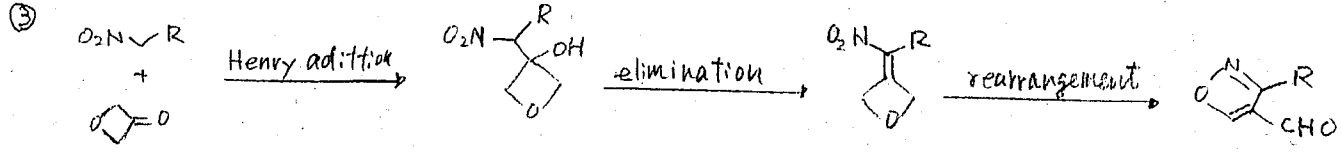
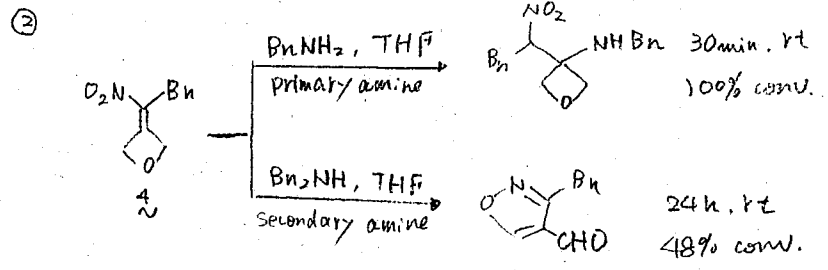
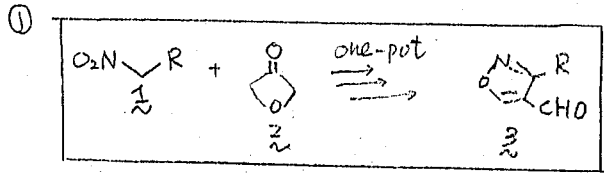


Cascade Formation of Isoxazoles: Facile Base-Mediated Rearrangement of Substituted Oxetanes

J.A. Burkhard, B.H. Tchitchanov, and E.M. Carreira (ETH) *Angew. Chem. Int. Ed.* DOI:10.1002/anie.201102260



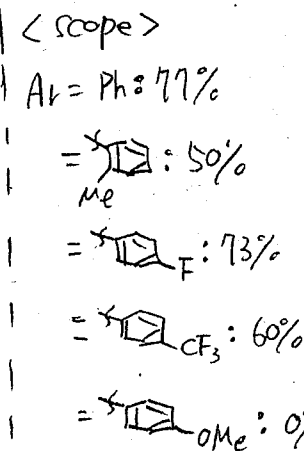
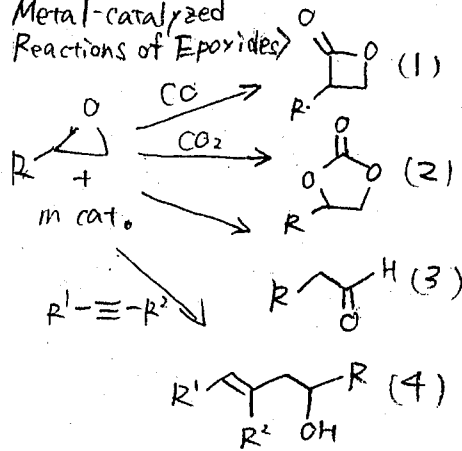
CT 1521

Youhei Takeda

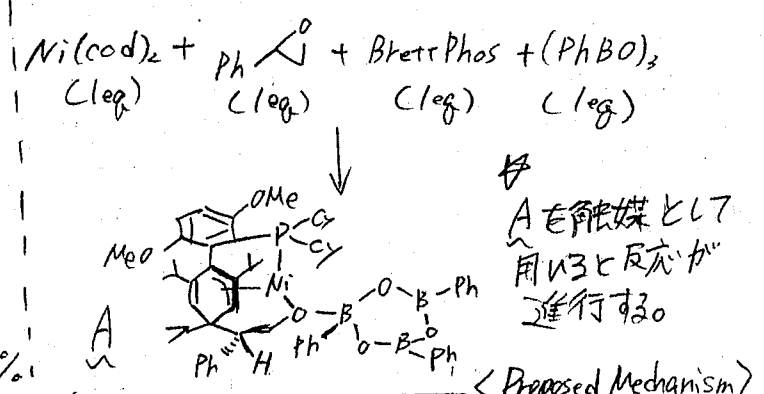
"Nickel-Catalyzed Cross-Coupling of Styrenyl Epoxides with Boronic Acids"

Nielsen, D. K.; Doyle, A. G.* *Angew. Chem., Int. Ed.* 2011, early view (doi: 10.1002/anie.201101191)

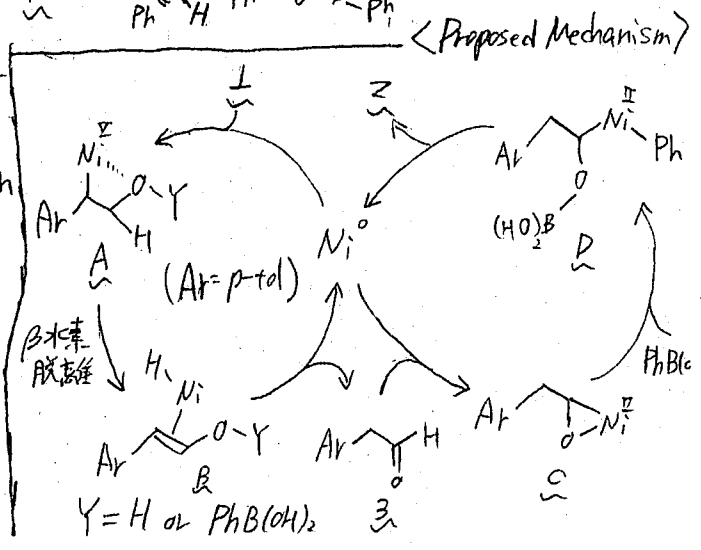
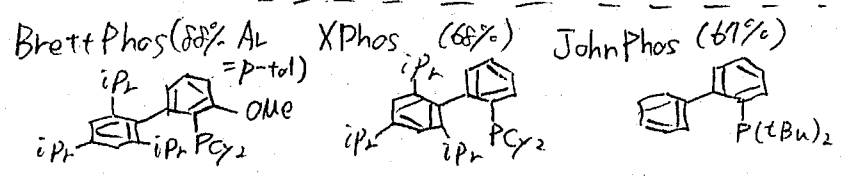
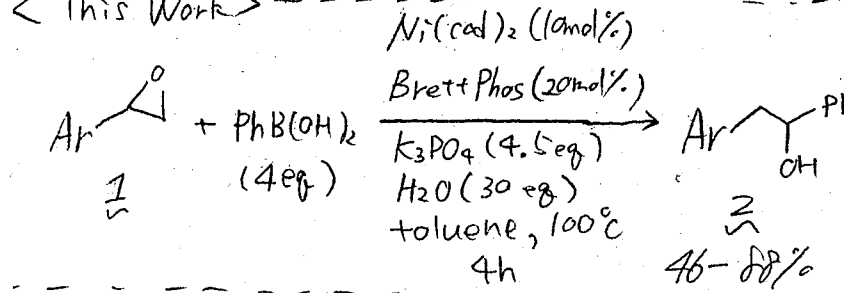
Metal-catalyzed Reactions of Epoxides



<Isolation of Catalytically Active Species>



<This Work>

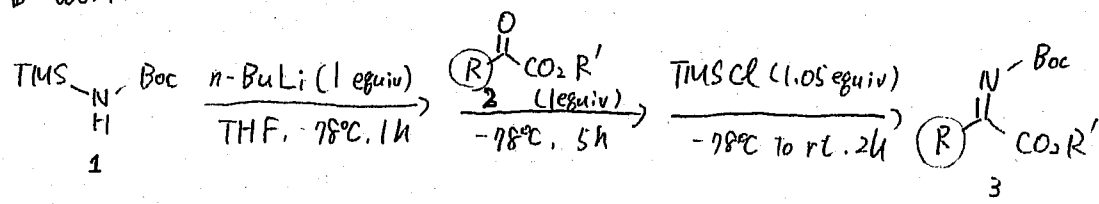


Development of a Practical Synthetic Method for *N*-tert-Butoxycarbonyl α -Ketimino Esters

Ishimoto, T.; Yamamoto, K.; Marucka, K. *Chem. Lett.* 2011, 40, 326-327.

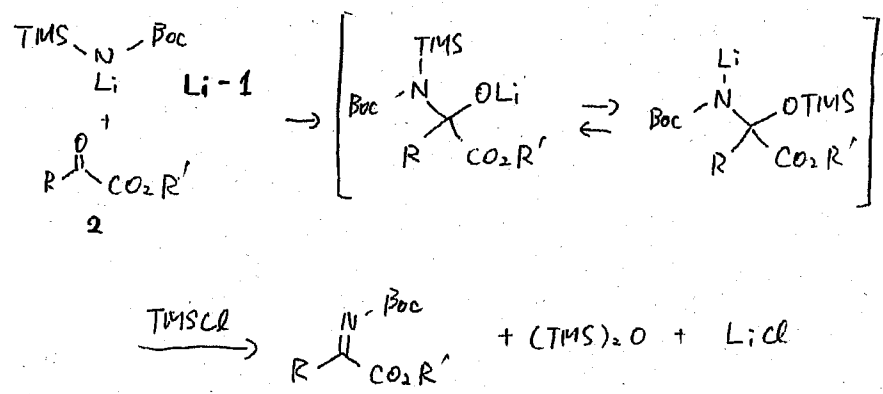
D3 村上

work.



* R is Aryl, Heteroaryl, Alkynyl etc.
 * R is Alkyl in the case, Li-1 is better, Li-1 is better than Li-2.

feasible reaction path.



Previous work. α -Ketimino ester of the type

$$\begin{array}{c} \text{O} \\ || \\ \text{CO}_2\text{Et} \end{array} + \begin{array}{c} \text{N} \text{---} \text{Boc} \\ || \\ \text{PPH}_3 \end{array} \xrightarrow[\text{THF, reflux}]{} \begin{array}{c} \text{N} \text{---} \text{Boc} \\ || \\ \text{CO}_2\text{Et} \end{array}$$

Org. Biomol. Chem. 2007, 5, 463.

本研究の着想に至る背景

$$\text{Me}_3\text{Si} \text{---} \text{N} \text{---} \text{Si} \text{---} \text{Me}_3 \xrightarrow[\text{THF, 0}^\circ\text{C}]{n\text{-BuLi}} \text{O} \text{---} \text{C} \text{---} \text{H} \xrightarrow[\text{THF}]{} \text{N} \text{---} \text{TM}$$

J. Org. Chem. 1983, 48, 289.

Proton

Proton-Driven Switching Between Receptors for C₆₀ and C₇₀

長田俊希

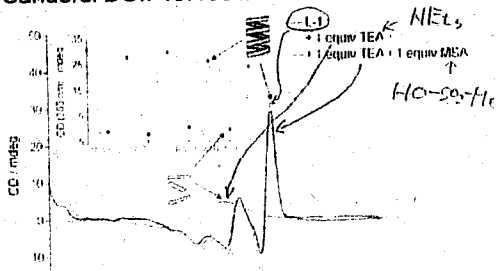
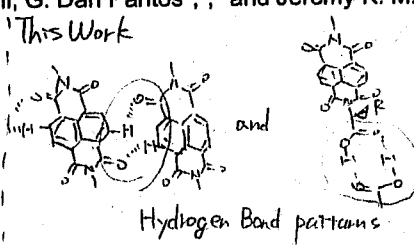
Artur R. Stefankiewicz, Emiliano Tamarin, G. Dan Pantos, * and Jeremy K. M. Sanders. DOI: 10.1002/anie.201100806

previous work

水素結合を適用する
 +14₂-7"の結合
 MeOH を入れると
 +14₂-7"が合併

L-1 R = (CH₂)₃NHBoc
 L-2 R = STH1
 L-3 R = DB21

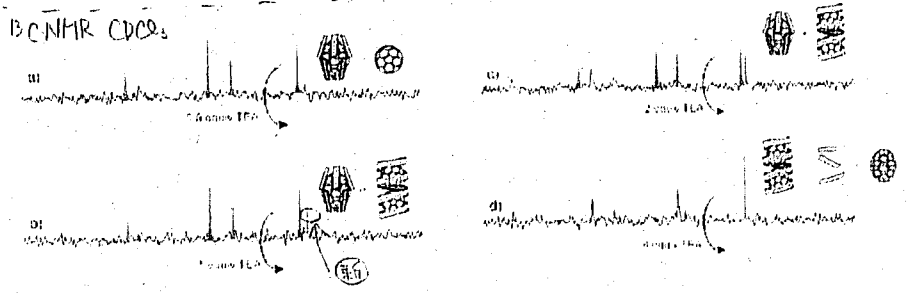
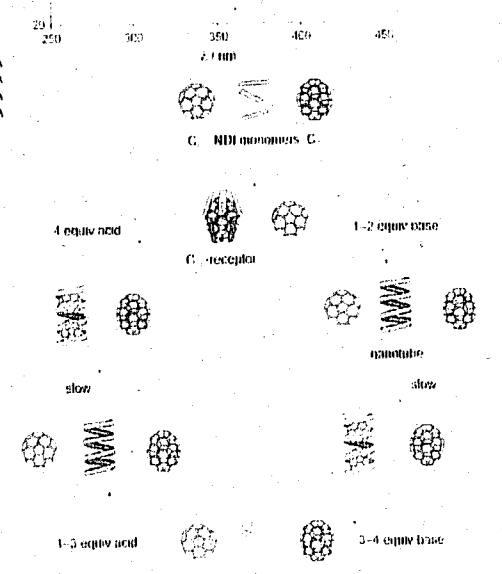
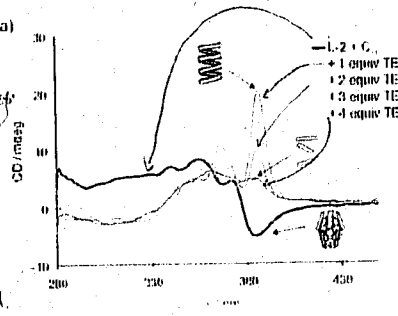
Angew. Chem. Int. Ed. 2007, 46, 144



Receptor と C₆₀ の結合
 C₆₀ の結合
 C₇₀ の結合

143, 142, 141, 140

結合を適用する
 +14₂-7"の結合
 MeOH を入れると
 +14₂-7"が合併

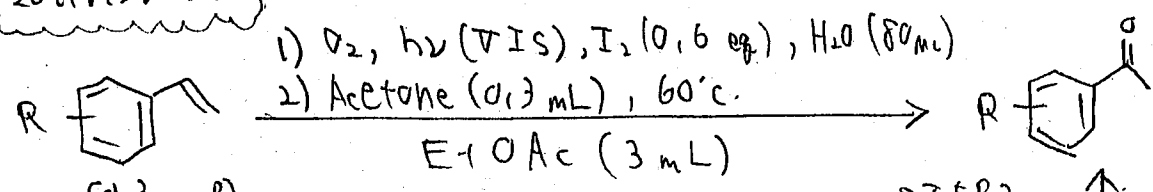


One - Pot Metal - Free Syntheses of Acetophenones from Styrenes through Aerobic Photo - oxidation and Deiodination with Iodine

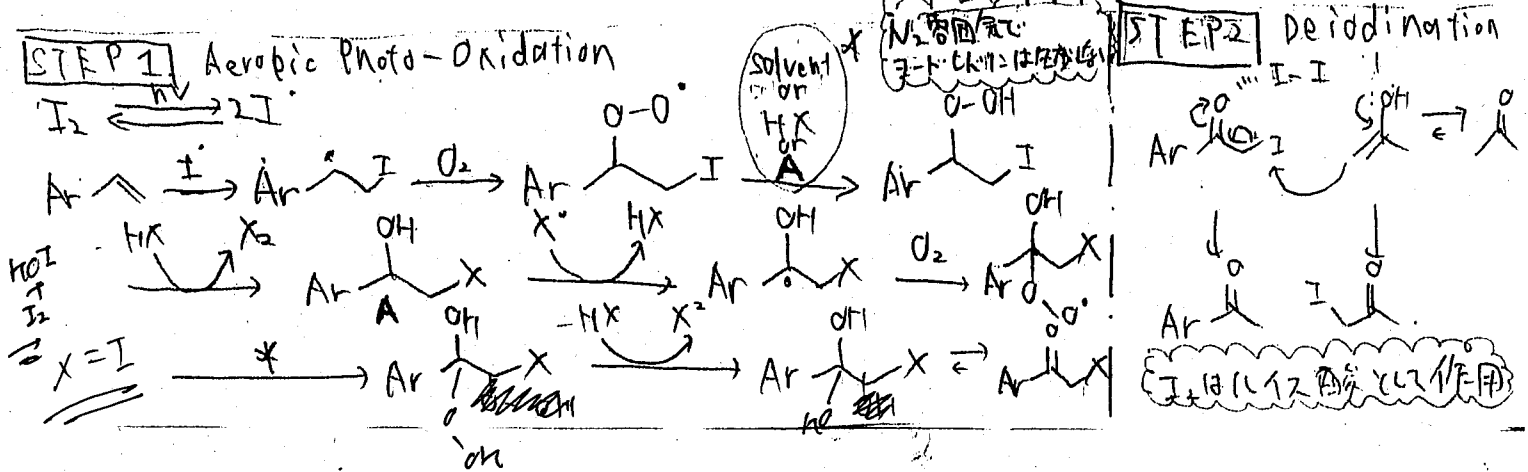
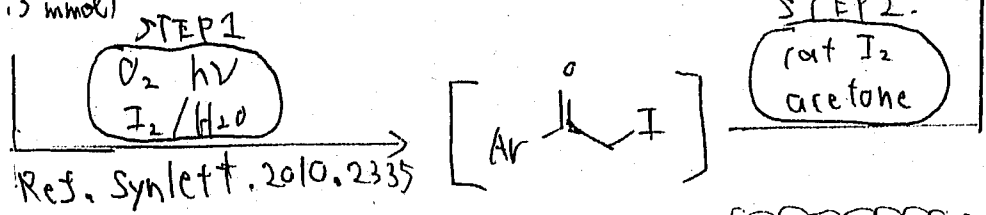
PI 早川 純平

Org. Lett.
2011.13. 2576

Akichika Itoh et al. (≠→*)



- P-H 85%
- P-tBu 85%
- P-Me 86%
- R = O-Me 42%
- P-OMe 75%
- P-Cl 85%
- P-NO₂ 76%



Sota Okumura

A straightforward one-pot multicomponent synthesis of polysubstituted pyroles

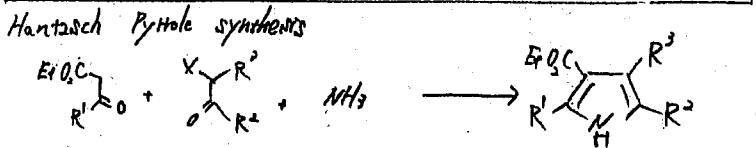
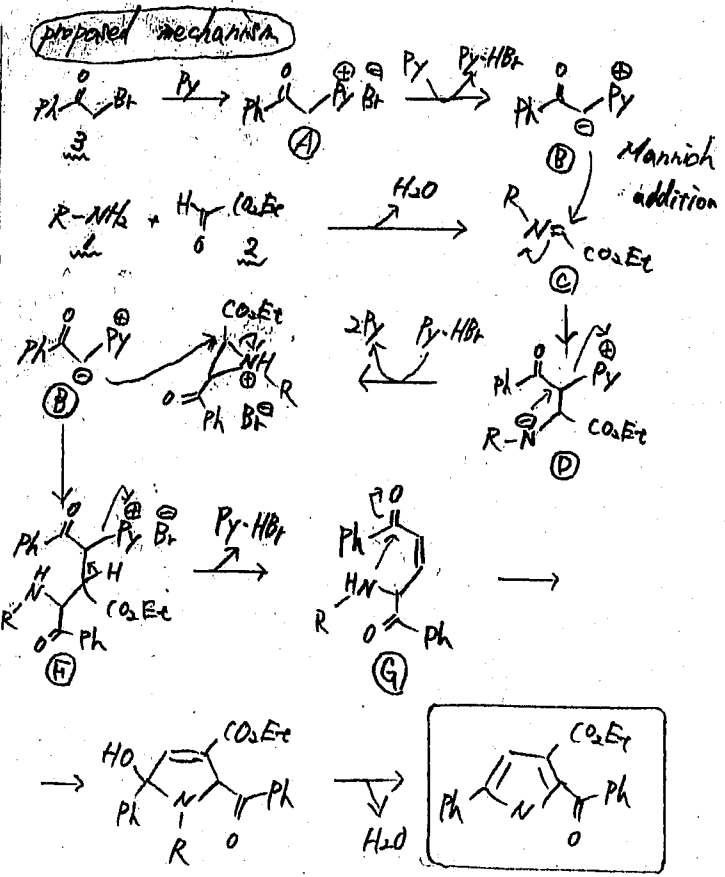
Lin, X.; Mao, Z.; Dai, X.; Lu, P.; Wang, Y. Chem. Comm. DOI: 10.1039/C1CC11363A

This Work

RNH₂ + H₂C(CO₂Et) + Ar-C(=O)-Br $\xrightarrow[\text{reflux, 12h}]{\text{NaCN, (1) (2) (3) (4) (5) (6) (7) (8) (9) (10)}}$ Polysubstituted Pyrole

基礎 - 組み合わせ

Ar = Ph, a, b, c	
R = 4-MeOC ₆ H ₄	67%
Ph	54%
4-Cl-C ₆ H ₄	50%
Cyclohexyl	35%
Bn	34%
n-Bu	24%
R = 4-MeC ₆ H ₄ , a, b, c	
Ar = 4-Cl-C ₆ H ₄	70%
4-MeC ₆ H ₄	52%
4-Bz-C ₆ H ₄	55%
R = Bn, a, b, c	
Ar = 4-Cl-C ₆ H ₄	80%
4-MeC ₆ H ₄	32%



第5回. 今日報告の反応は. 上の Hantzsch pyrole synthesis
に似た5成分生成物の合成である. EtO₂C-CH=Oの2位に
アロキ基 (X=Ar) を導入した反応である

Iron-Catalyzed Asymmetric Epoxidation of β,β -Disubstituted Enones

Yasuhiro Nishikawa and Hisashi Yamamoto

J. Am. Chem. Soc. (DOI: 10.1021/ja201873d)

Previous Work

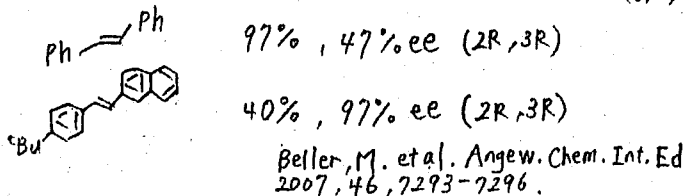
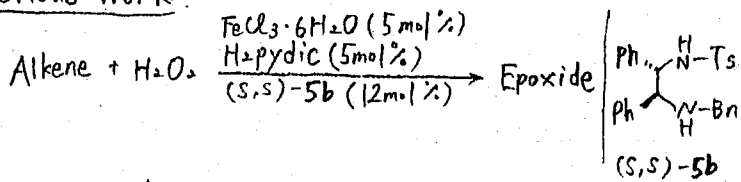


Table 1. Screening of Reaction Conditions

Reaction: metal (5mol%), ligand (X mol%), CH₃CO₂H (1.5 eq), MeCN, 0°C, 0.5 h

entry	metal	ligand (R)	X	% yield	% ee
1	FeCl ₂	L1 (H)	10	17	3
2	Fe(OTf) ₂	L1 (H)	10	95	57
3	Fe(OTf) ₂	L5 (m-xylyl)	10	88	91
4	Fe(OTf) ₂	L5 (m-xylyl)	5	73	78
5	Fe(OTf) ₂	L5 (m-xylyl)	15	25	53

This Work

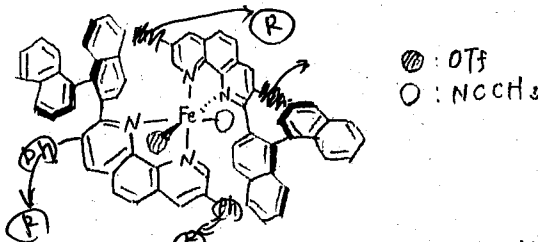
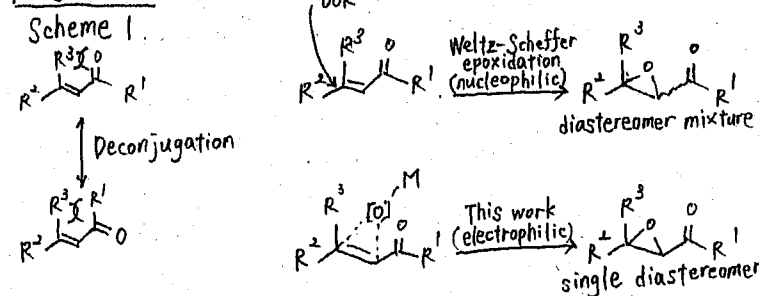


Figure 1. X-ray structure of [Fe(L3)₂(CH₃CN)(OTf)](OTf).

Table 2. Substrate Scope of Epoxidations

Reaction: L5 (10mol%)

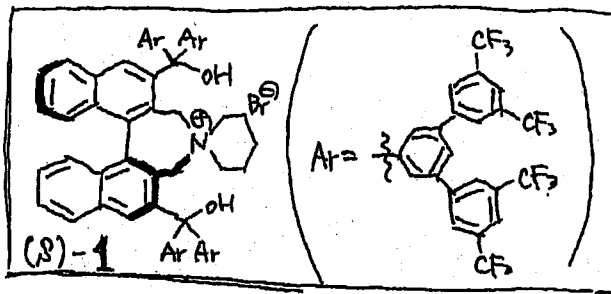
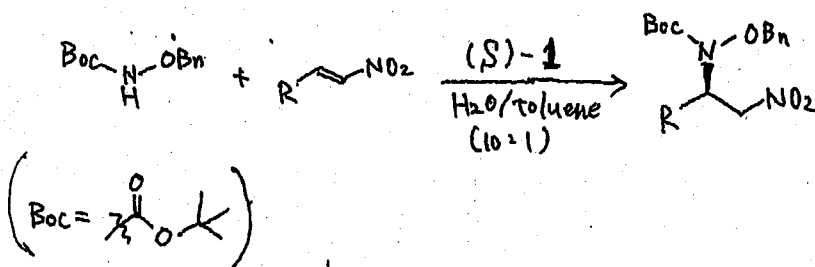
entry	R ¹	R ²	% yield	% ee
1	p-MeOC ₆ H ₄	Ph	78	90
2	p-Fc ₆ H ₄	Ph	78	92
3	Ph	p-ClC ₆ H ₄	88	92
4	Ph	2-naphthyl	45	92

Asymmetric Neutral Amination of Nitroolefins Catalyzed by Chiral Bifunctional Salts in Water-Rich Biphasic Solvent

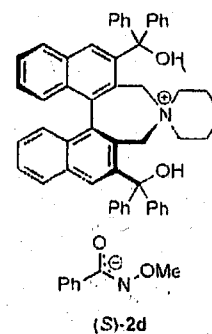
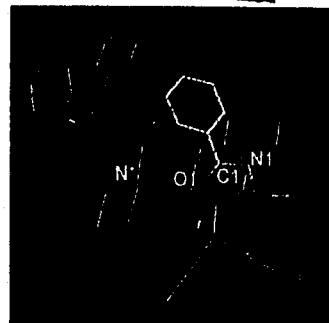
Yuki Ikeda

Wang, L.; Shirakawa, S.; Maruoka, K

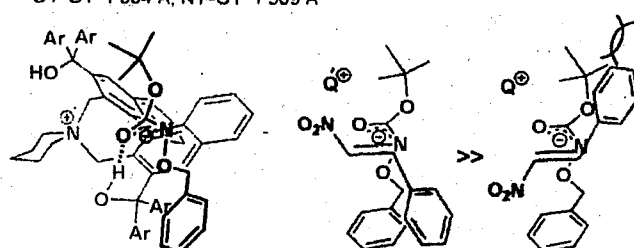
Angew. Chem. Int. Ed. DOI: 10.1002/anie.201101307



	(S)-1 (0.05mol%), 25°C	(S)-1 (1mol%), 0°C
R = 芳香環, 17口環	70-94% 90-92% ee	60-92% 91-95% ee
R = 7口キル基	95-97% 77-79% ee	99% 82-83% ee



- TBS基はこの反応に耐性がある (TBDMs) $\text{TBS} = \text{Si}(\text{Me})_2\text{Bu}$
- 酸性 and/or 塩基性に敏感な化合物が共存しても、これは分解することなく反応が進行する。

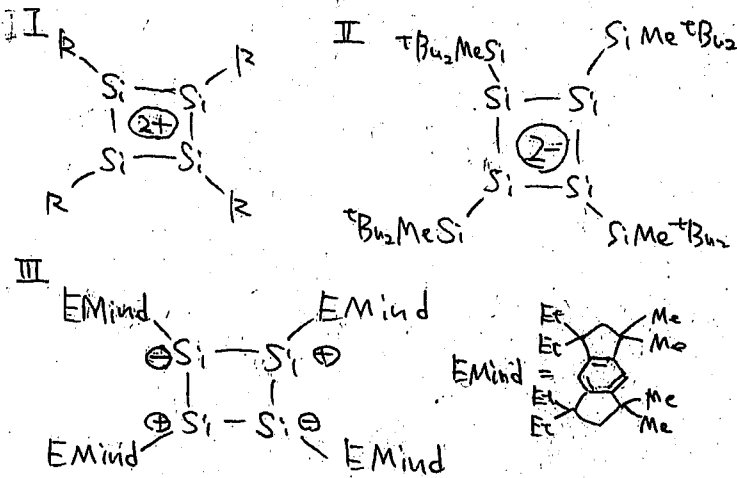


Formation of a Donor-Stabilized Tetrasilacyclobutadiene Dication by a Lewis Acid Assisted Reaction of an N-Heterocyclic Chloro Silylene

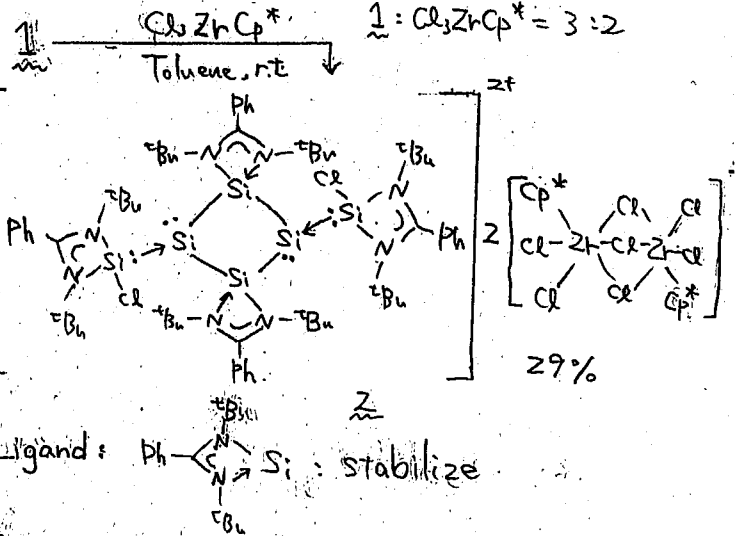
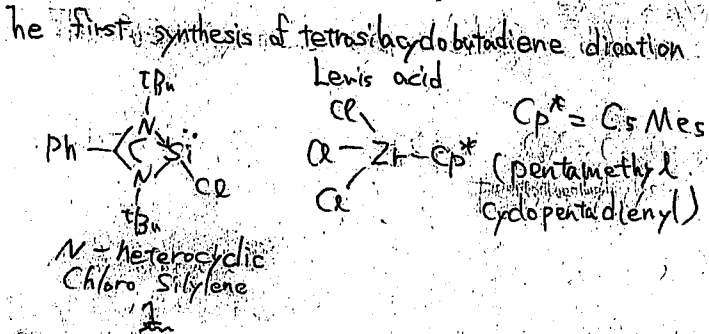
M. Driess, et al. *J. Am. Chem. Soc.*, ASAP

M1 Hajime Kawai

<Previous Work>



<This Work>



Silylene-like Si: negative charge
 Silylium-like Si: positive charge
 Six ring: ① delocalization of π electrons
 ② planer \downarrow aromatic ring (II, III = antiaromatic)
 precursor for transition-metal π -Complexes

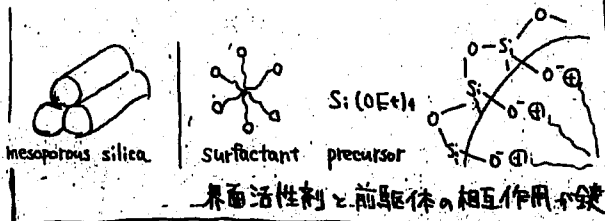
Periodic mesoporous organosilica from zwitterionic precursors

Samir EL Hankari, Blanka Motos-Pérez, Peter Hessemann, Ahmed Bouhaouss, Joël J.E. Morau
 Chem. Comm. DOI: 10.1039/c1cc11649e

本論

- 両性イオンを有するハイブリッドなメソポーラスシリカの合成
- 調整したシリカが Biginelli 反応の不均一触媒となる

一般的なメソポーラスシリカの合成



This Work

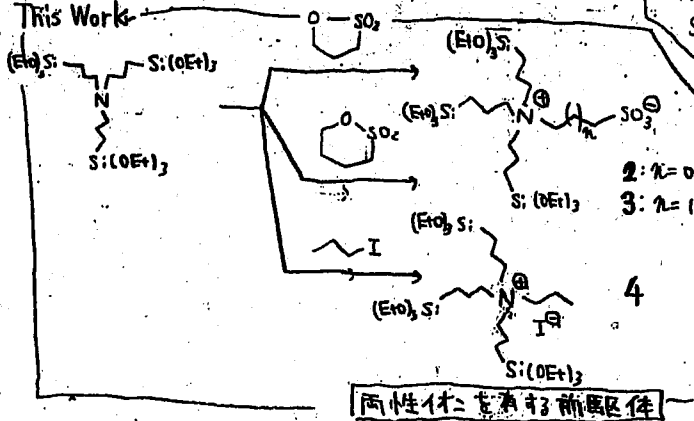


Table 1

Material	Precursor	Surfactant	SBET/m ² g	Pore diameter
A	2	CTAB	750	27
B	2	P123	403	broad
C	2	SHS	320	broad
D	3	CTAB	900	27
E	3	P123	402	broad
F	3	SHS	313	broad
G	4	CTAB	206	broad
H	4	P123	415	broad
I	4	SHS	453	<20

A, D, I \rightarrow 細孔構造
 B, C \rightarrow 粗孔構造
 (XRD, 細孔分布) 従来のメソポーラスシリカ

* CTAB ... $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ カチオン性界面活性剤
 P123 ... $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{O})_{10}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$ 中性界面活性剤
 SHS ... $\text{CH}_3(\text{CH}_2)_{11}\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$ $\text{OSO}_3^- \text{Na}^+$ アニオン性界面活性剤

Table 2

$\text{ArCHO} + \text{R}_2\text{C}=\text{O} + \text{H}_2\text{N}-\text{Mn} \xrightarrow[\text{MeCN, rt}]{\text{D(H)}} \text{ArCH}(\text{Mn})-\text{CH}_2-\text{R}$

entry	catalyst	Conv. %
1	Blank	10
2	D(H)	84
3	D(H) 2nd	75
4	D(H) 3rd	89
5	D(H) 4th	95
6	D(H) 5th	95

CTAB

その他の酸触媒との比較はない

Chelated Ruthenium Catalysts for Z-Selective Olefin Metathesis

Koji Endo and Robert H. Grubbs*

5/21 M1 矢野知樹

Olefin Metathesis



Ru-Catalyzed Z-Selective Metathesis

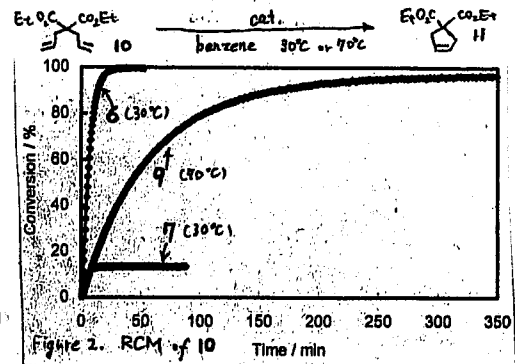
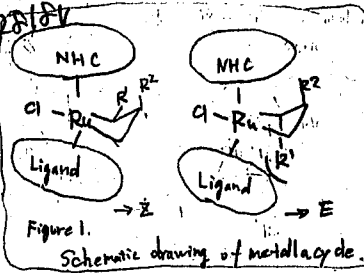
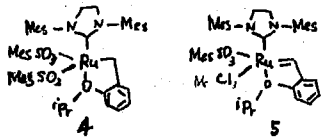
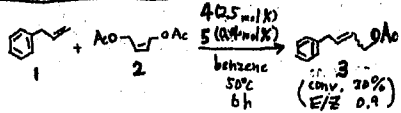
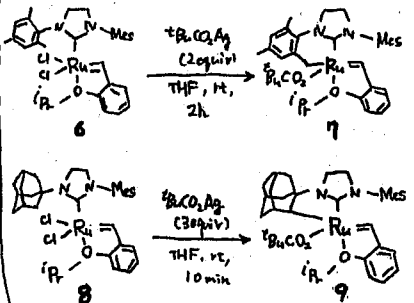


Table 1. CM.

entry	cat.	(mol%)	solvent (1 mL)	temp. (°C)	time (min)	3		12	
						conv. a (%)	E/Z ^a	conv. a (%)	E/Z ^a
1	6	(2.5)	benzene	23	30	66.3	10.7	10.2	6.86
2	8	(2.5)	benzene	23	30	0.23	2.90	NA	NA
3	7	(2.5)	benzene	23	10	57.5	1.44	3.3	1.21
4	7	(2.5)	benzene	23	60	57.4	1.44	3.0	0.69
5	9	(5.0)	benzene	70	30	32.5	0.13	14.8	0.07
6	9	(5.0)	benzene	70	120	36.4	0.12	26.0	0.06
7	9	(5.0)	THF	ref.	240	59.5	0.19	31.6	0.04
8	9	(5.0)	THF/H ₂ O (1:1 by vol.)	ref.	240	64.4	0.14	28.6	0.03
9 ^b	9	(5.0)	THF/H ₂ O	ref.	240	61.6 ^c	0.14	NA	0.03

a. Determined by GC. b. Using 1.0 mmol of 1. c. Isolated yield.

Scheme. Synthesis of catalysts



Palladium-catalyzed synthesis of indoles via ammonia cross-coupling-alkyne cyclization

Pamela G. Alsabeh, Rylan J. Lundgren, Lauren E. Longobardi and Mark Stradiotto

B4 岡崎真人
Chem Comm
DOI: 10.1039/c1cc11874a

Table 1. Scope of the Pd-catalyzed cross-coupling of ammonia or methylamine with 2-alkynyl bromobenzenes^a

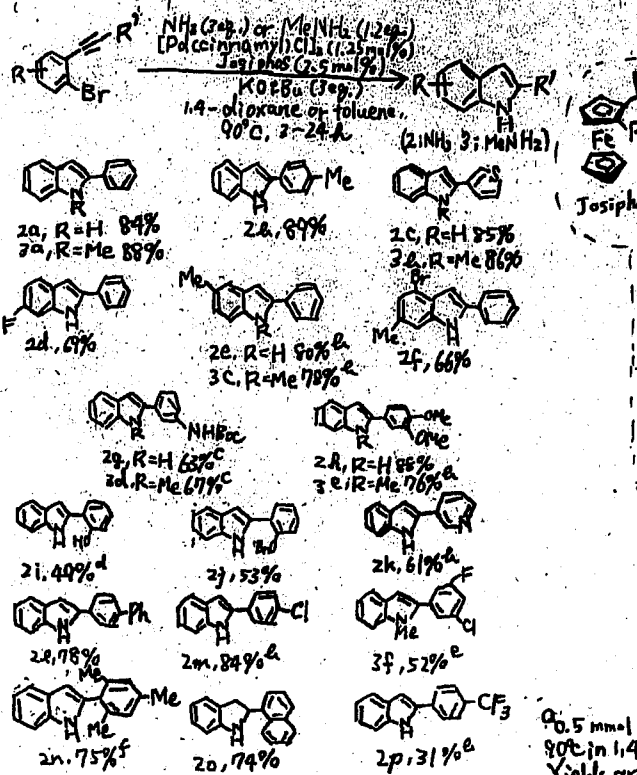
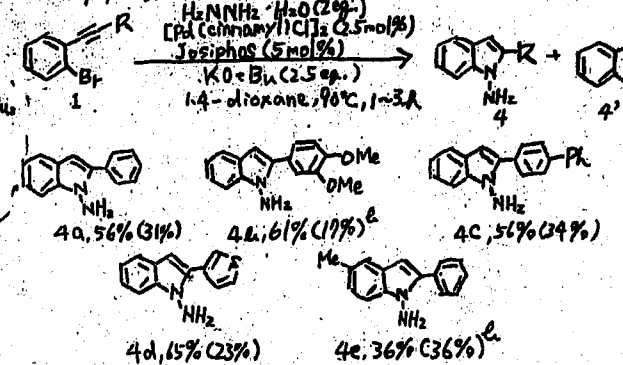


Table 2. Pd-catalyzed cross-coupling of hydrazine with 2-alkynyl bromobenzenes^a



^a 0.05 mmol scale, [Pd]/L=1:1, NH₃·H₂O=1.0 mmol, KOtBu=1.25 mmol, 90°C in 1,4-dioxane; isolated yield of 4 (4' in parentheses).
^b ¹H NMR yield of 4 (4') relative to 1,3,5-trimethoxybenzene.

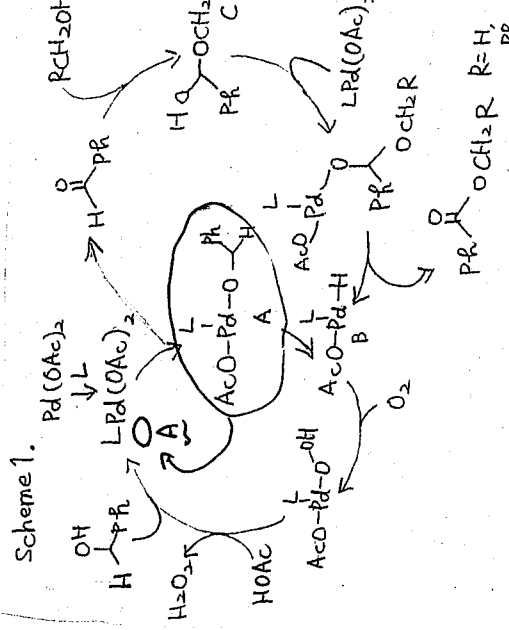
Conclusion

○ Cross-coupling and alkyne cyclizationの反応を連続して行うことが可能で、利用しやすいアルキンを7種類合成に用いることができる。
○ 4-アルキルピリジンを用いた反応も紹介されており、アルキル化の新しい手段として有用性が高い。

^a 0.5 mmol scale, [Pd]/L=1:1, NH₃=1.5 mmol or MeNH₂=0.6 mmol, KOtBu=1.5 mmol, 90°C in 1,4-dioxane (NH indoles, 3h reaction time) or in toluene (NMe indoles, 16-24h). Yields are of isolated products. ^b 5 mol% Pd used. ^c 2g = 3.5 eq. base, 3d = 4.0 eq. base. ^d From TBS-protected alcohol substrate. ^e 4.0 eq. Cs₂CO₃, 3.0 eq. KOtBu, 48h, 60°C. KOtBu, 110°C, 60h.

General and Selective Palladium-Catalyzed Oxidative Esterification of Alcohols.

久野 大地
2010/08/03



<Previous Works>
 $\text{CH}_2\text{OH} \xrightarrow[\text{RCH}_2\text{X}]{\text{Ru, Pd, Fe}}$
 additive X = NH₂, O
 化学量論量の副生成物がでる

<This Work>
 $\text{CH}_2\text{OH} \xrightarrow[\text{RCH}_2\text{OH}]{\text{Pd}}$
 additive R = H, PR
 高い選択性がある
 酸化剤として空気中のO₂を用いる。

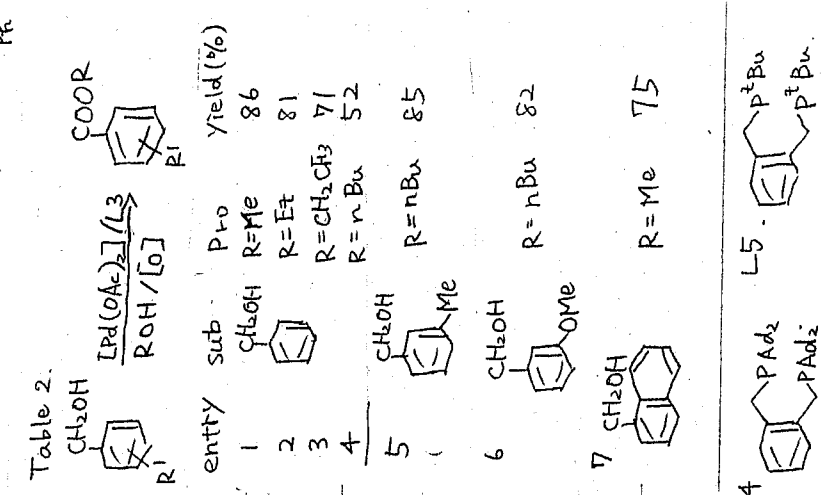


Table 1.

Entry	Additive	L	solvent	Yield (%)	
			1a	2a	3a
1	—	—	CH ₂ OH	—	—
2	—	—	CH ₂ OH	10	43
3	—	—	CH ₂ OH	62	—
4	—	—	CH ₂ OH	14	65
5	AgPF ₆	—	CH ₂ OH	49	—
6	(4nd/5)	—	CH ₂ OH	4	55
7	"	L1	CH ₂ OH	—	20
8	"	L2	CH ₂ OH	5	46
9	"	L2	CH ₂ OH	4	33
10	"	L3	CH ₂ OH	—	28
11	"	L3	CH ₂ OH	84	—
12	"	L4	CH ₂ OH	—	27
13	"	L4	CH ₂ OH	—	46
14	"	L5	CH ₂ OH	5	5
15	"	L5	CH ₂ OH	—	85

1, 2: base を用いた。Et₃N / t-Bu₃N, K₂CO₃ を用いた。

L1: Ph₂P(Ph)₂, L2: Ph₂P(Ph)(Ad), L3: Ph₂P(Ph)(Me), L4: Ph₂P(Ad)₂, L5: Ph₂P^tBu₂

Table 2.

entry	sub	Pro	Yield (%)
1	CH ₂ OH	R=Me	86
2	CH ₂ OH	R=Et	81
3	CH ₂ OH	R=CH ₂ CF ₃	71
4	CH ₂ OH	R=n-Bu	52
5	CH ₂ OH	R=nBu	85
6	CH ₂ OH	R=nBu	82
7	CH ₂ OH	R=Me	75

additive あり

