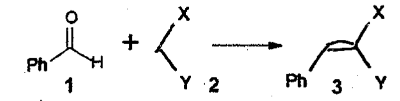
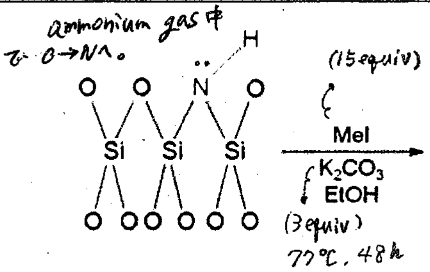
Masaru Ogura, et al.	The University of Tokyo (Japan)	***JACS*** (ja2070522)	Minakata

A Simple Modification Creates a Great Difference: New Solid-Base Catalyst Using Methylated N-Substituted SBA-15



Entry	X	Y	pKa	
2a	C≡N	C≡N	11.1	Conventional base catalysts
2b	COOEt	C≡N	13.1	
			border	
2c	COOEt	COOEt	16.4	This work

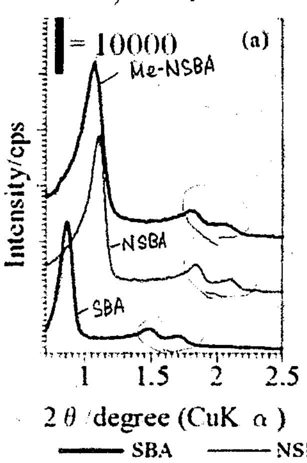


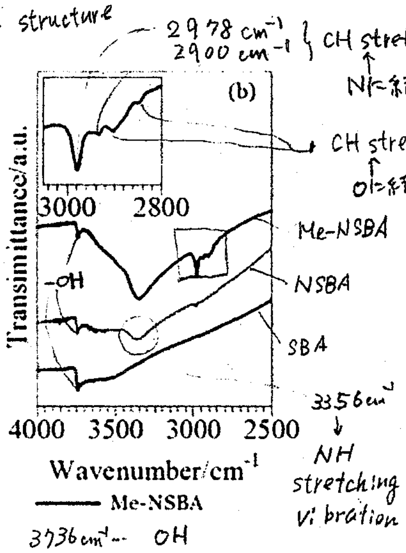
反応後、100°Cで乾燥

Elemental Analysis (NSBA, Me-NSBA)

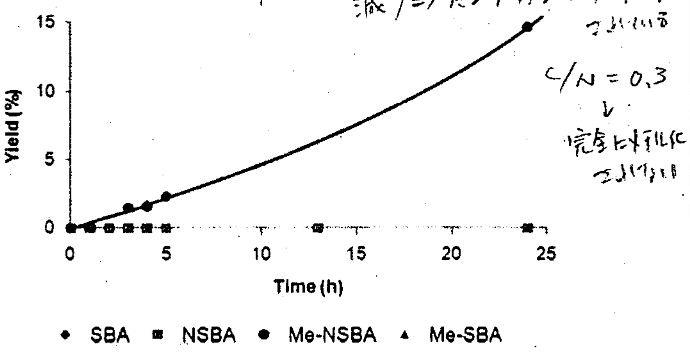
sample	N wt%	N mmol/g	C wt%	C mmol/g
NSBA	24.2	17.3	—	—
MeNSBA	18.4	13.1	3.81	3.17

hexagonal periodic structure





CH stretching
Oに結合した
⇒ OもMeにされた部分もある

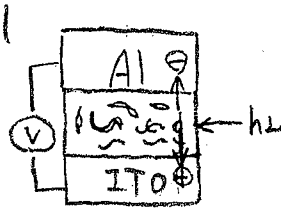


Bazan, G. C.* and Heeger, A. J.* et al.	University of California, Santa Barbara, USA	*Nature Mater.* **2012,** ***11*****, 44.**	Youhei Takeda

Solution-processed Small-molecule Solar Cells with 6.7% Efficiency

Bulk-HeteroJunktion (BHJ) solar cell

- polymer type (PCE_{max} : 7.4%)
  Adv. Mater. 2010, 22, E135.
- small molecule type (PCE_{max} : 5.2%)
  Adv. Funct. Mater. 2011, 21, 897.

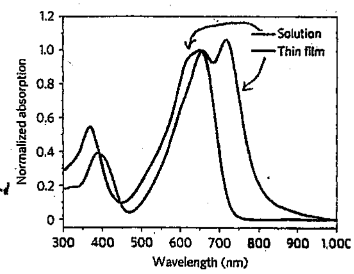


○ Properties of D

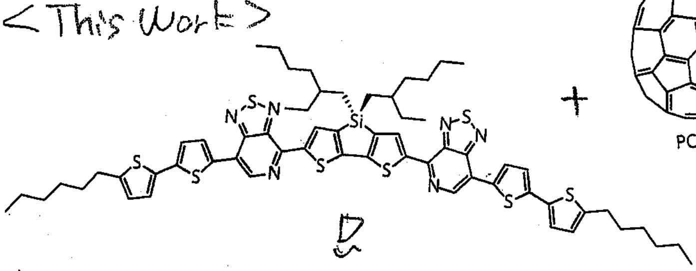
$\mu_h = 0.12\ cm^2V^{-1}s^{-1}$

on/off = 10^7

(top-contact) OFET

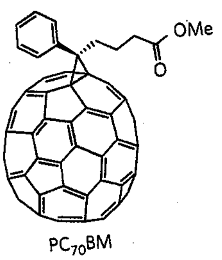


<This Work>



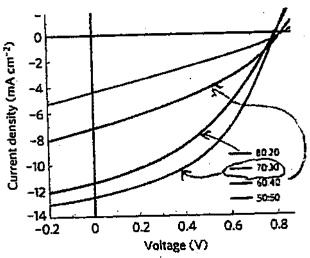
D

+

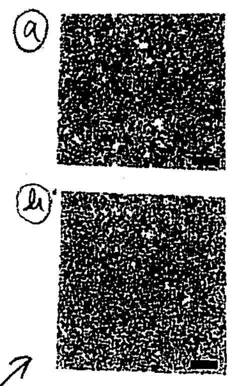


$PC_{70}BM$

A



J–V curve



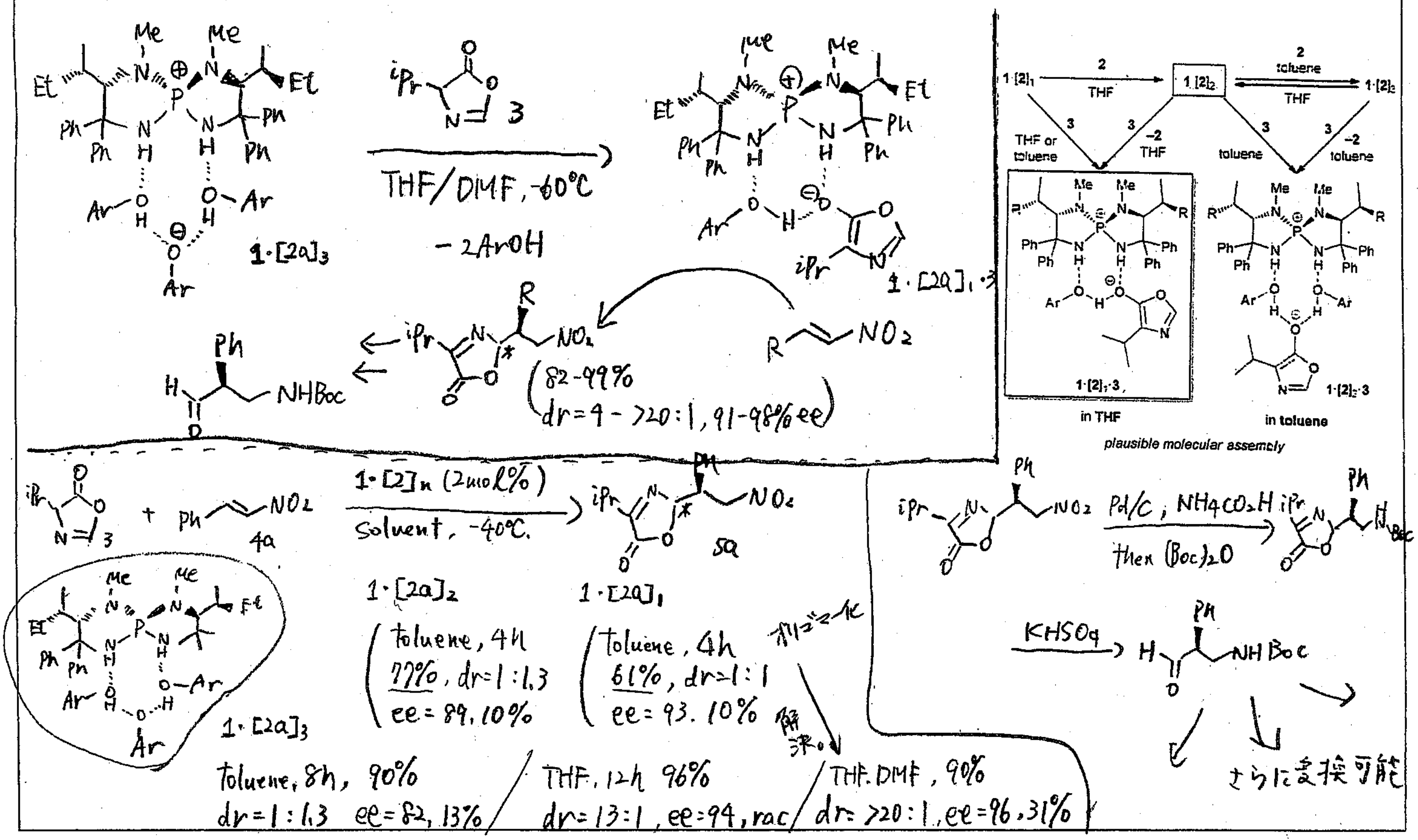
Encoded image of TEM

PCE_{max} = 6.7%!

(D : 0.7, A : 0.3, + 0.25% v/v diiodo octane) ⓐ without, ⓑ with diiodooctane

Ooi Tskashi	Nagoya University (Japan)	*Chem. Sci.* 10.1039/c1sc00678a	村上

Highly stereoselective catalytic conjugate addition of acyl anion equivalent to nitroolefins



Anna Proust	Institut Parisien de Chimie Molculaire	ACIE; DOI:anie.201106727	長町

Cyclodextrin-Induced Auto-Healing of Hybrid Polyoxometalates

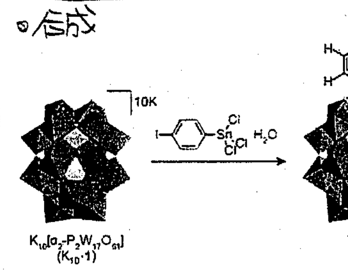
Polyoxometalates (POMs)

オキソ酸が縮合してできた陰イオンで金属元素が含まれるものもあり (ex. Mo, V, W etc…)
金属は最高酸化数まで酸化されている場合が多い ⇒ 酸化cat.として利用。
有機物とのハイブリッド ⇒ 機能材料への展開。
⇩
塩基に弱い ⤳ 金属水酸化物 → 不溶物

○This Work

CDをcapすることで aut-healing 機能を付与

○合成



Scheme 1. Synthetic route to the POM hybrid K_7·2.

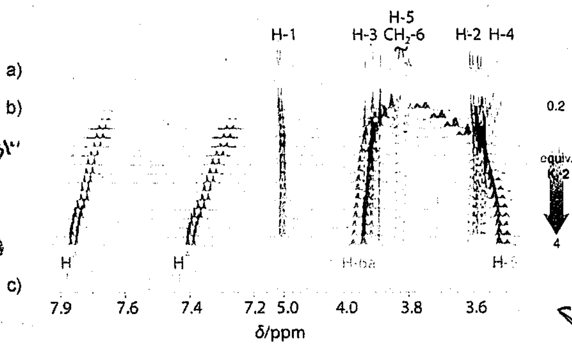
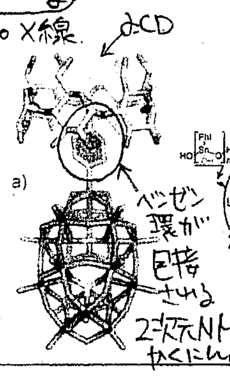
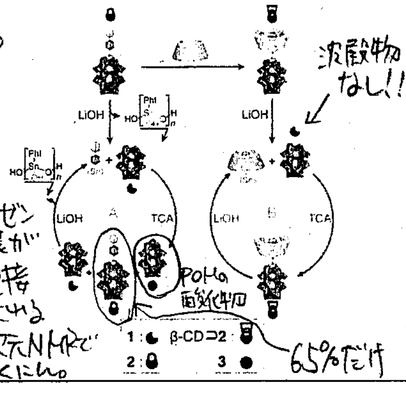
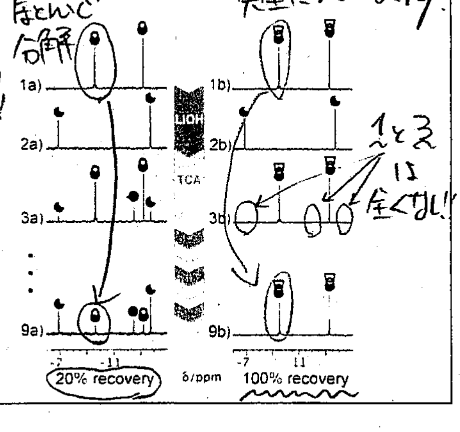


Figure 1. ^{1}H NMR spectra (400 MHz, D_2O) of β-CD (5 mM) a) before, b) after successive additions of K_7·2 (from 0.2 to 4 equiv) and c) of K_7·2 (5 mM).

Binding constant
(1020±50) M^{-1}
⇒ NMRのtimeスケールだと速すぎる。
← 平均のケミカルシフト!!



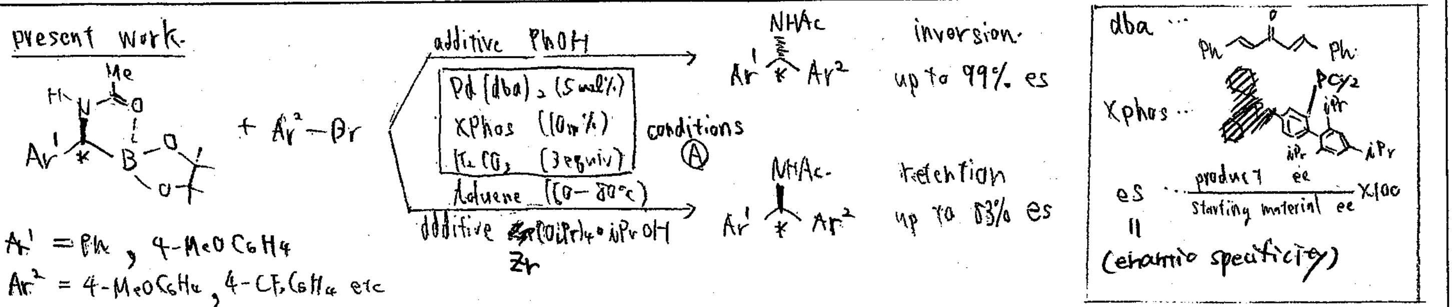




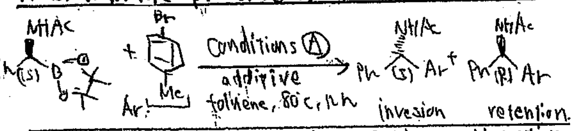
Michinori Suginome	Kyoto University, Japan	JACS DOI: ja210025q	D1 早川純平

Inversion or Retention? Effects of Acidic Additives on the Stereochemical Course in Enantiospecific Suzuki-Miyaura Coupling of α-(Acetylamino)benzylboronic Esters

present work

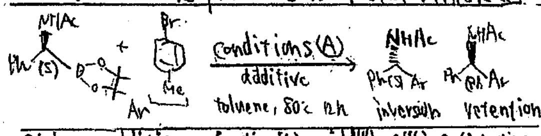


Reaction in the presence of Protic Additives



entry	additive	equiv	yield(%)	es(%)	configuration
1	—	—	87	29	inversion
2	H_2O	2	85	53	inversion
3	AcOH	2	87	61	inversion
4	PhOH	2	85	96	inversion
5	iPrOH	2	90	15	retention
6	PhOH	1	89	69	inversion
7	PhOH	3	51	99	inversion

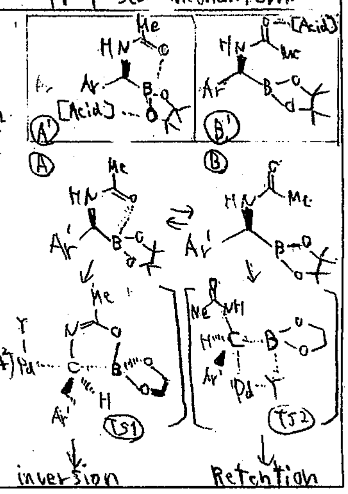
Reaction in the presence of Metal Alkoxides



entry	additive	equiv	time(h)	yield(%)	es(%)	configuration
1	$B(OiPr)_3$	2	48	74	63	Ⓡ
2	$B(OtBu)_3$	2	18	80	28	Ⓡ
3	$Ti(OiPr)_4$	2	18	74	36	Ⓡ
4	$Zr(OiPr)_4$	2	36	14	3	Ⓡ
5	$Zr(OiPr)_4$·iPrOH	2	18	10	76	Ⓡ
6	$Zr(OiPr)_4$·iPrOH	0.1	18	85	53	Ⓡ
7 a)	$Zr(OiPr)_4$·iPrOH	0.5	96	63	83	Ⓡ

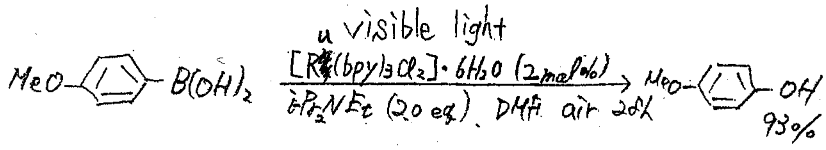
a) temp : 60°C   Ⓡ : retention

proposed mechanism

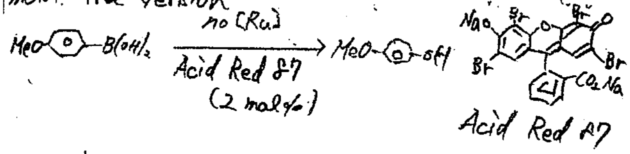


Wen-Jing Xiao	Central China Normal Univ.	Angew. Chem. Int. Ed. DOI: 10.1002/anie.201107028	M2. 奥村

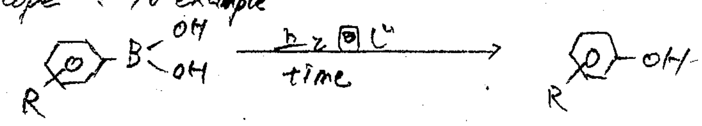
Highly Efficient Aerobic Oxidative Hydroxylation of Arylboronic Acids: Photoredox Catalysis using Visible Light.



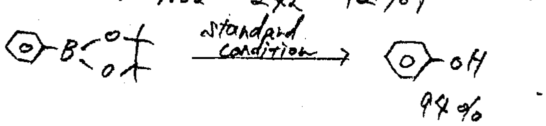
metal-free version



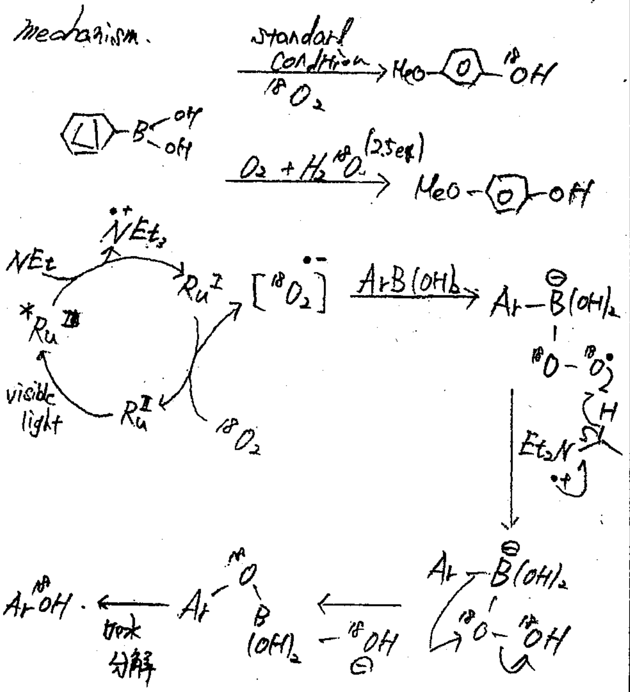
Scope : 18 example



R =	time	yield	
o-OMe	28h	72%	電子richなPhOHは合成困難
o-Me	32h	72%	
m-Me	24h	91%	
p-Me	24h	94%	
2,5-diMe	48h	69%	
o-NO_2	24h	71%	電子[illegible]は電子豊富に比べわずかに反応速い
p-CN	16h	95%	
p-COOH	24h	94%	
m-NO_2	24h	92%	



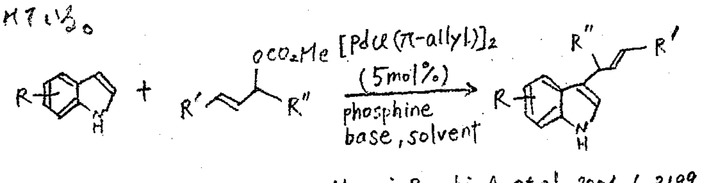
mechanism



Viresh H. Rawal	University of Chicago, United States	JACS, 10.1021/ja2095393	三谷由起

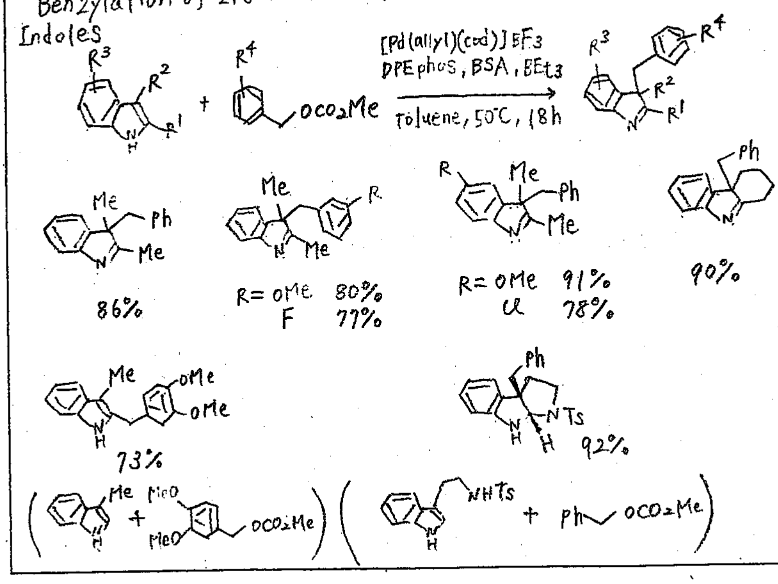
Palladium-Catalyzed C3-Benzylation of Indoles

Pd触媒を用いたインドールのC3位のアリル化はこれまでにいくつか報告されている。



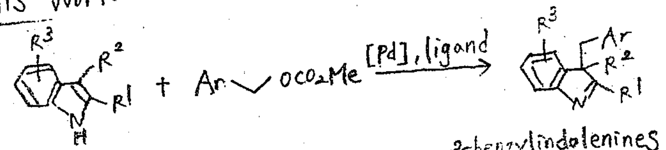
Umani-Ronchi, A. et al. 2004, 6, 3199.

Benzylation of 2,3-Disubstituted Indoles and 3-Substituted Indoles

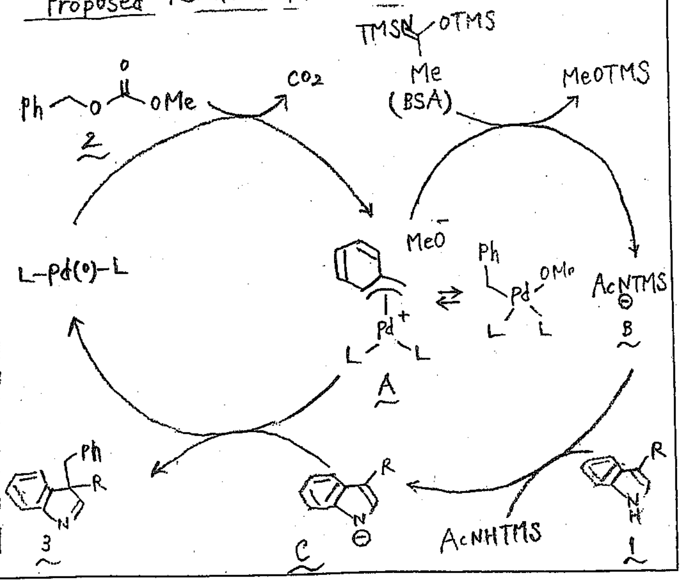


しかし、Pd触媒を用いたインドールのC3位のベンジル化はこれまで報告されていない。

This Work



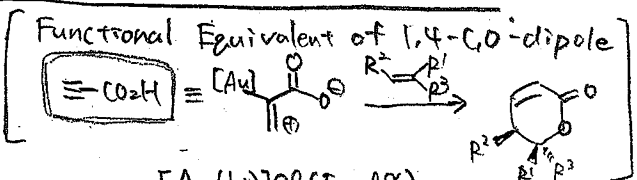
Proposed Reaction Mechanism

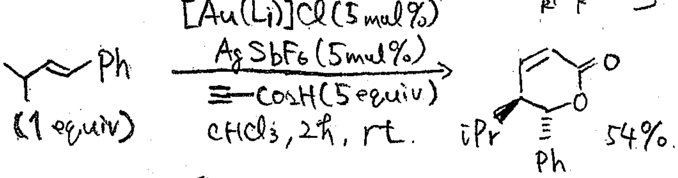


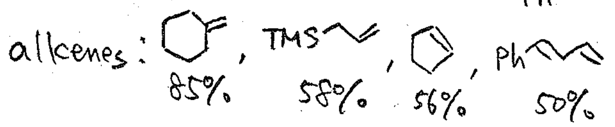
Zhi-Xiang Yu Seunghoon Shin	Peking Univ., China Hanyang Univ., Korea	*JACS* 1010.1021/ja210792e	Yuki Ikeda

Gold-Catalyzed Intermolecular Reaction of Propiolic Acids with Alkenes: [4 + 2] Annulation and Enyne Cross Metathesis

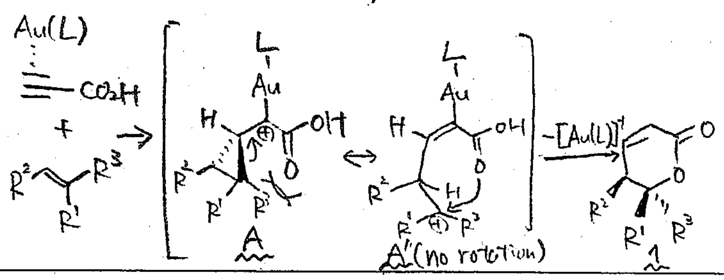
[4+2] Annulations with Alkenes



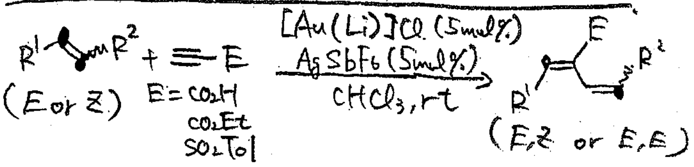


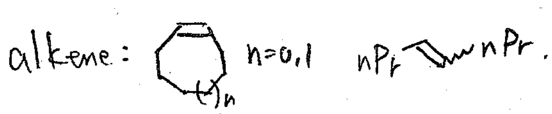


<Proposed Reaction Pathway>

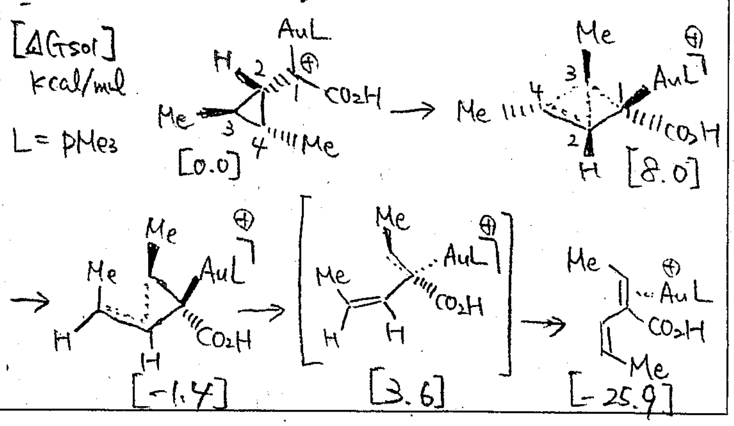


Enyne Cross Metathesis with Alkenes





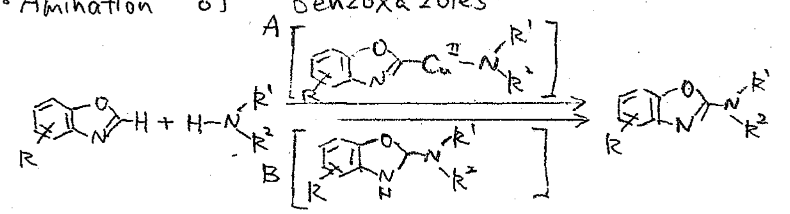
<DFT calculation>



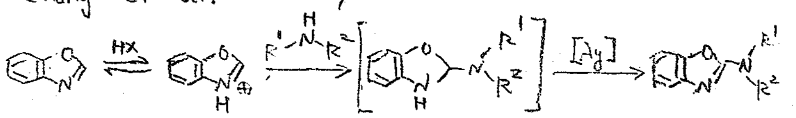
Studer, A. et al	Westfälische Wilhelms-Universität Münster	ACIE, **2011**, *50*, 11511	M1 Kawai

Amination of Benzoxazoles and 1,3,4-Oxadiazoles Using 2,2,6,6-Tetramethylpiperidine-*N*-Oxoammoium Tetrafluoroborate as an Oragnic Oxidant

• Amination of Benzoxazoles

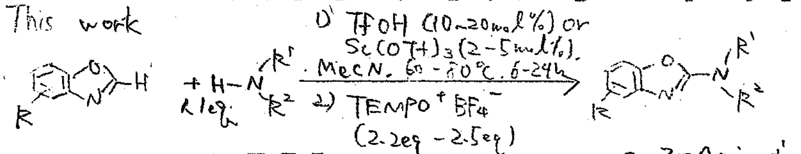


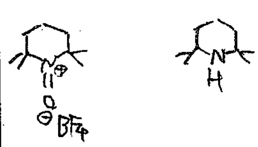
• Chang et al. (Pathway B)

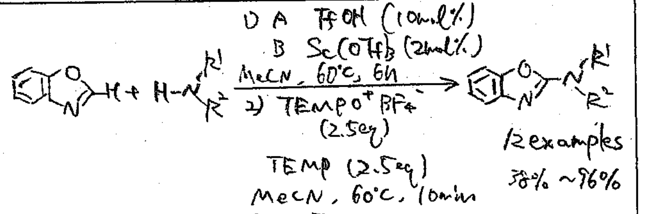


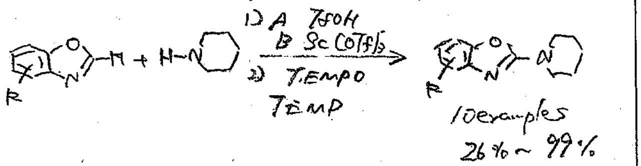
ACIE, 2009, 48, 9127-9130.

This work

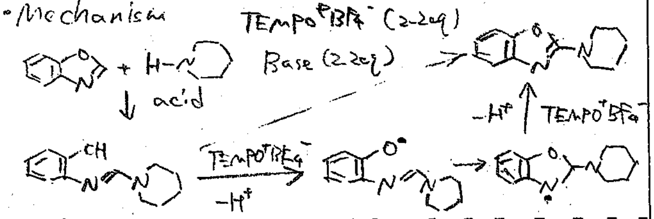




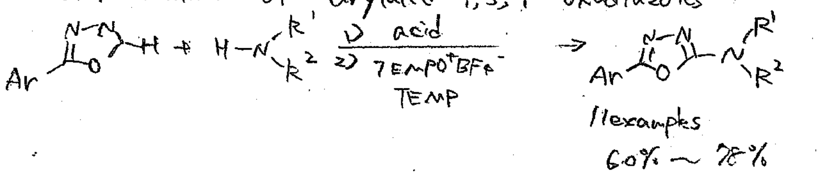




• Mechanism



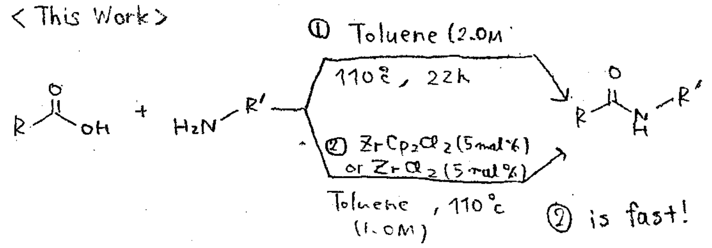
• 2-Amination of arylated 1,3,4-oxadiazoles



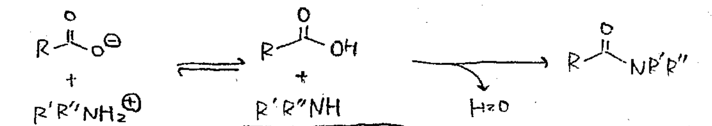
M. J. Williams	Bath University, UK	*Chem. Commun.* DOI: 10.1039/c1cc15210f	M1 錦織

Direct amide formation from unactivated carboxylic acids and amines

<This Work>



<Strategy>



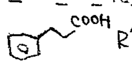
favored in polar protic solvent

favored in non-polar aprotic solvent

Supported by calculation M.R.Wilson, Eur.JOC 2011, 5981

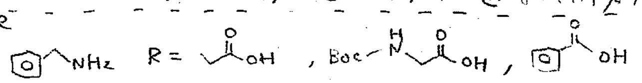
<Scope> ※括弧無いのは conversion 括弧の中は isolated yield

Carboxylic acid (6 examples)

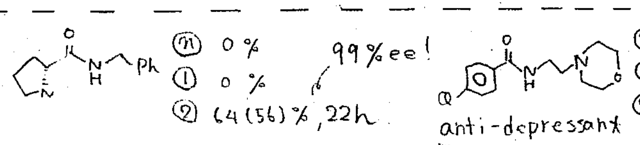


R' =	ⓝ	①	②
H_2N–CH2–Ph (benzylamine)	58 %	100 (81) %	100 (94) %, 4h
H_2N–Ph	9 %	30 %	45 %, 24h
$H_2N-C_5H_{11}$	51 %	100 (94) %	81 (71) %, 10h

Amine



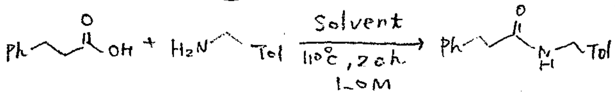
R =	ⓝ	①	②
1	79 %	100 (90) %	100 (81) %, 5h
2 (Boc)	27 %	71 %	91 (80) %, 22h
3	< 1 %	6 %	83 (72) %, 22h



ⓝ 0 % ① 0 % ② 64 (56) %, 22h 99% ee!

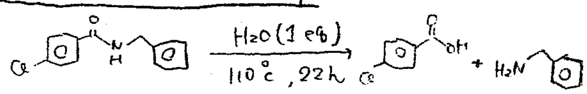
anti-depressant ⓝ 0 % ① 14 % ② 100 (55) %, 24h

• Solvent Effect.



Toluene 92 % H_2O 0 % CH_3CN 50%
DMSO 0 % 1,4-Dioxane 66 % neat 58 %

• Test of the reversibility

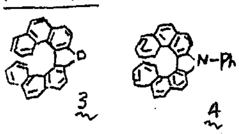


In the absence of cat ⟶ no hydrolysis.
In the presence of cat ⟶ 5 % hydrolysis.

Kyoko Nozaki	The University of Tokyo (Japan)	DOI: /anie.2011106157	M1 矢野

λ5-Phospha[7]helicenes: Synthesis, Properties, and Columnar Aggregation with One-Way Chirality

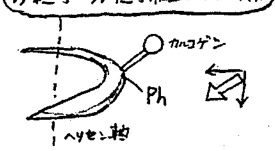
Prev. Work


3 4

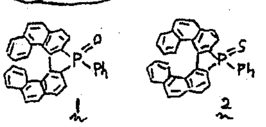
Present Work

π-π スタッキングによる 1次元カラムナー構造をつくる らせん状分子の開発

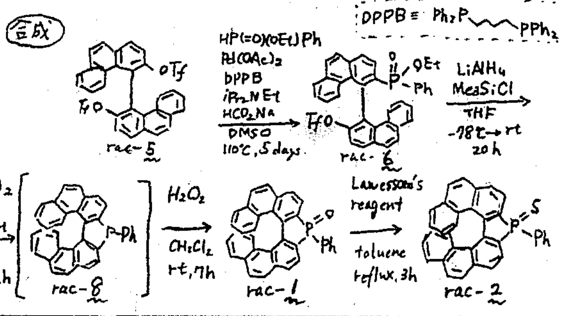
双極子-双極子相互作用の利用



目的化合物


1 2

合成



比旋光度

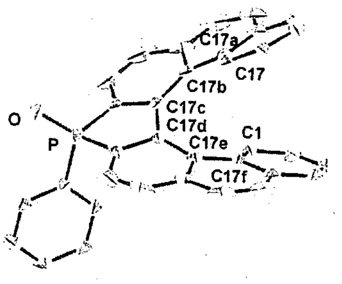
(P)-1 $[\alpha]_D$ = +3014
(P)-2 $[\alpha]_D$ = +3198
(c=0.10, $CHCl_3$)

CDスペクトル

(P)-1, (P)-2 は 他の (P)-ヘテロヘリセンと似た傾向を示した。

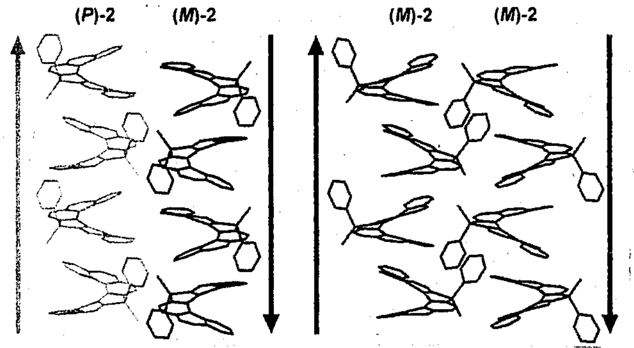
X線

rac-1, (P)-1, (M)-1
rac-2, (M)-2 を測定 ⇒ rac-1 は (M)-1のみ含んだ結晶
rac-2 は 両方含んだ結晶

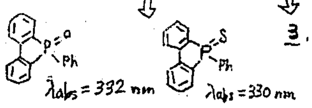


(M)-1 の ORTEP (in rac-1)

rac-2 のパッキング (M)-2 のパッキング



Helicene	λabs [nm]	λedge [nm]	λem [nm]	Stokes Shift [cm⁻¹]	HOMO [eV]	Eg [eV]
1	416	432	462	2390	-5.90	2.87
2	416	432	466	2300	-5.87	2.87



3, 4 より redshift している

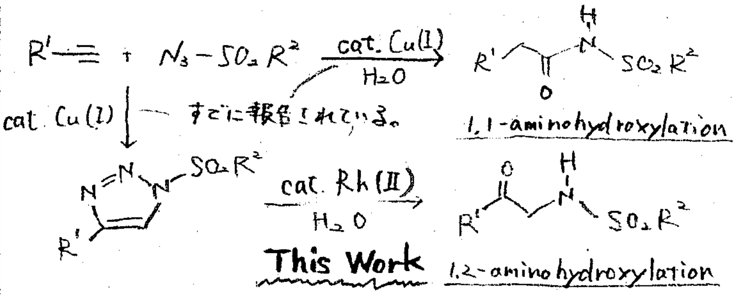
3 650 cm^{-1}
4 580 cm^{-1}

CVより

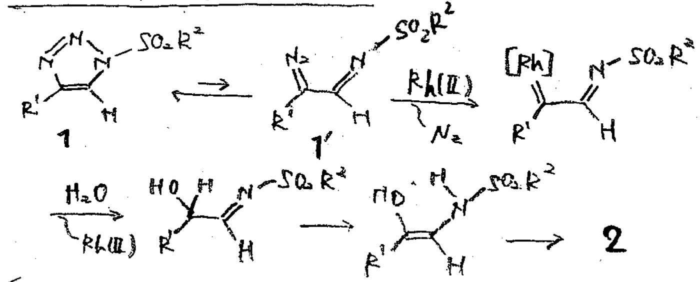
λedgeより DFTと一致

Masahiro Murakami, et al.	Kyoto University	JACS DOI: ja2104203	BY 榎島

Synthesis of α-Amino Ketones from Terminal Alkynes via Rhodium-Catalyzed Denitrogenative Hydration of N-Sulfonyl-1,2,3-triazoles

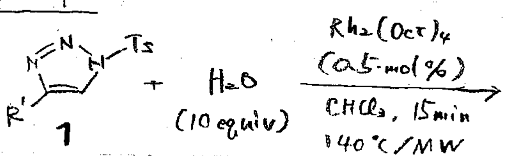


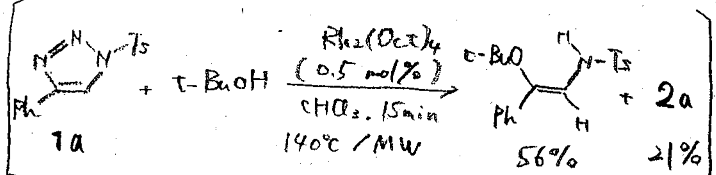
◎ Plausible Mechanism



◎ Scope

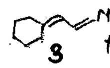
※ Oct = octanoate





R' = aryl group 1-cyclohexenyl … yield of 2 89 ~ 94%

R' = cyclohexyl . yield of 2 26% →

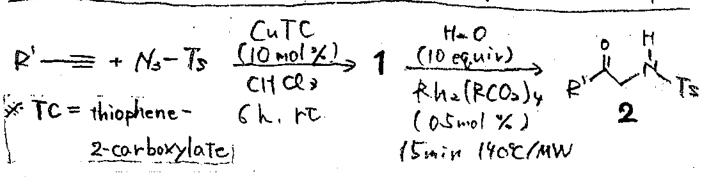

3 (62%) が生成。

condition : [Using $Rh_2(^tBuCO_2)_4$ (0.5 mol%), KOH (1 equiv), H_2O (50 equiv) in $CHCl_3$]

R' = cyclohexyl, primary alkyl group yield of 2 78 ~ 94%

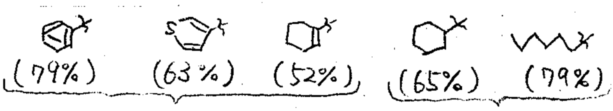
R' = H … yield of 2 38% (NaBH4 (1 equiv) を加え、2-アミノアルコールとして単離)

◎ Synthesis of 2 from terminal alkynes in one pot



※ TC = thiophene-2-carboxylate

R' =

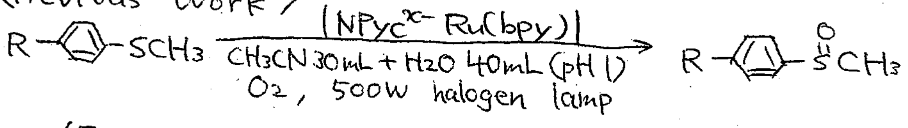


cat. = $Rh_2(Oct)_4$ (first three), $Rh_2(^tBuCO_2)_4$ (last two)

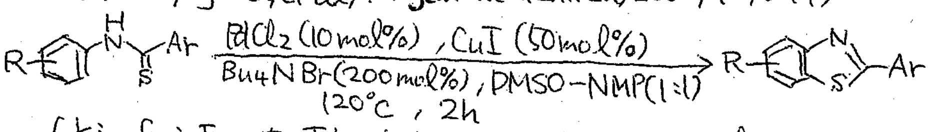
Pixu Li	Soochow University, China	*Org. Lett.*, ASAP DOI: 10.1021/ol2028866	B4 利根

Aerobic Visible-Light Photoredox Radical C-H Functionalization: Catalytic Synthesis of 2-Substituted Benzothiazoles

<Previous Work>

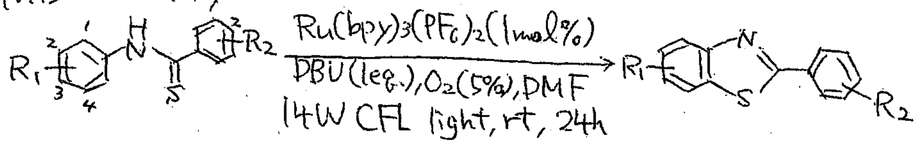


(Jyn-Myng Zen, et al, Angew. Chem. Int. Ed, 2003, 42, 577)



(Kiyofumi Inamoto, Takayuki Doi, et al, Adv. Synth. Catal, 2010, 352, 2643)

<This Work>



Scope

R_2 = H: R_1 = OMe 77~88%, R_1 = H 84%

R_1 = F, Cl, Br, I 10~91%

R_1 = CN, CO_2Me, SMe 63~89%

R_1 = H: R_2 = OMe, Cl, CN 63~86%

<Proposed Mechanism>