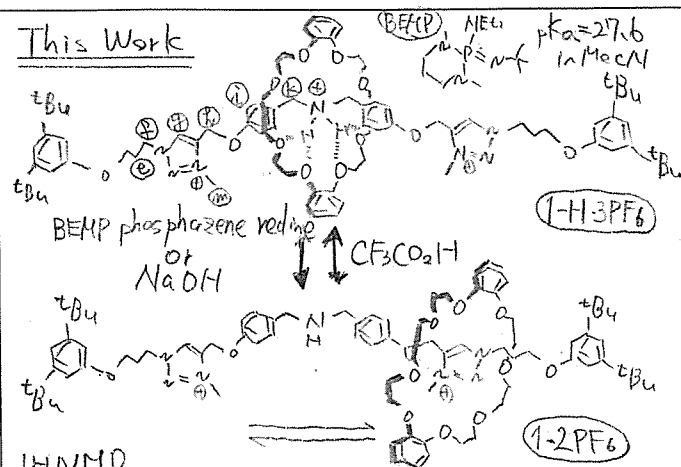




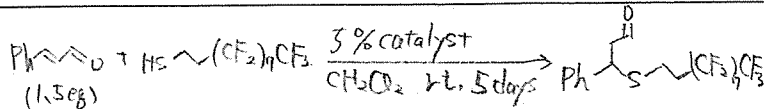
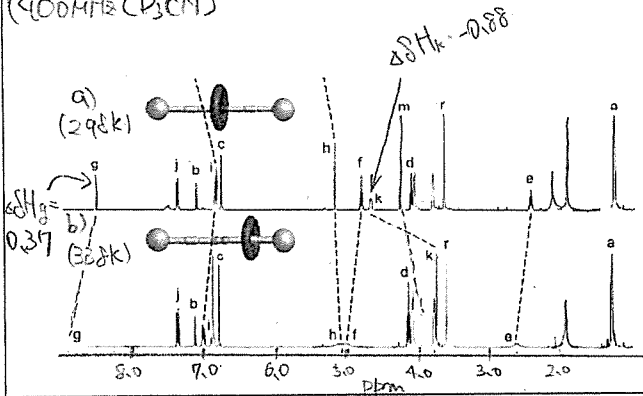
# A Rotaxane-Based Switchable Organocatalyst

## This Work



## <sup>1</sup>H NMR

( $\text{CDCl}_3$ )



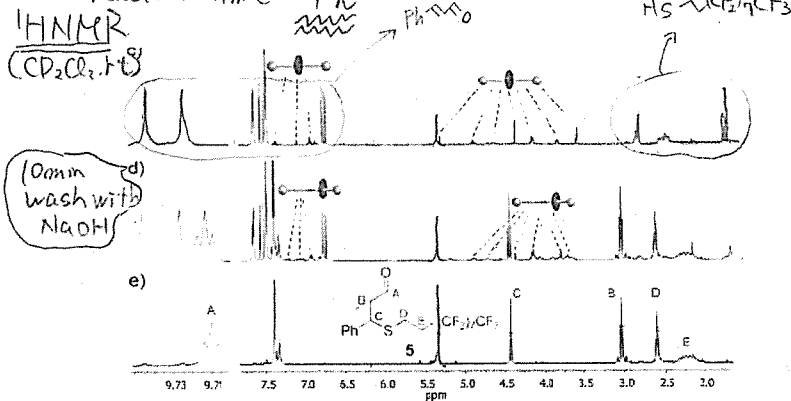
entry	cat.	yield (%)
1	no cat	no reaction
2	dibenzylamine	69%
3	1-2PF6	83%
4	1-H3PF6	no reaction
5 <sup>a</sup>	1-2PF6 / 1-H3PF6 + (10 min NaOH) wash	66%
6	no cat. + (10 min NaOH) wash	traces

$\text{K}_2\text{CO}_3$  (aq) 20% deprotonate catalyst

<sup>a</sup> reaction time: 1 h

## <sup>1</sup>H NMR

( $\text{CD}_2\text{Cl}_2$ )



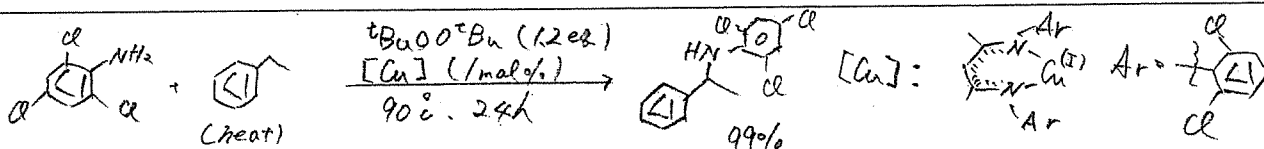
Timothy H. Warren

Georgetown Univ. (USA)

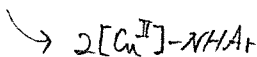
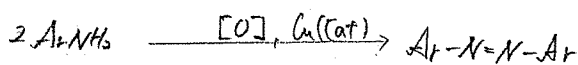
DOI:10.1021/anie201201921

Okumura

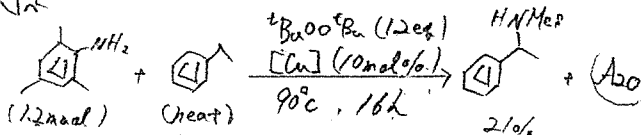
## Catalytic C-H Amination with Aromatic Amines



## Oxidation of Aromatic Amines



实际

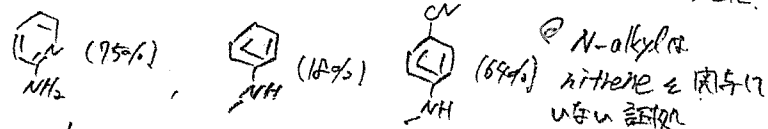
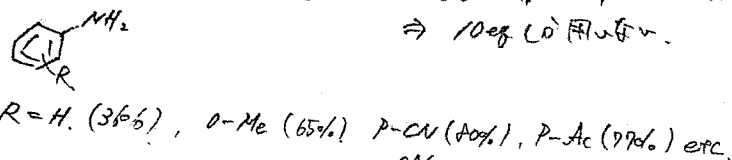
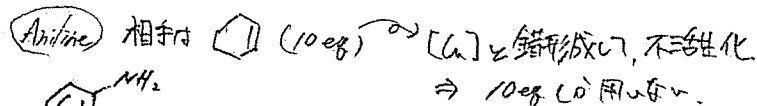
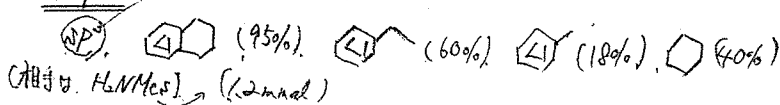


↓ optimization

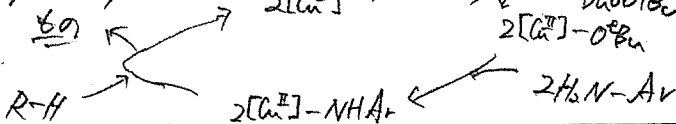
- [Cu] 在减少
- 基团 (heat) 在增加
- 电子不足与 aniline 在增加

## SCOPE

20 mL 用 0.3



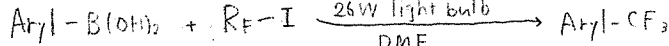
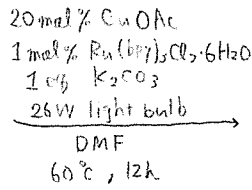
catalytic cycle





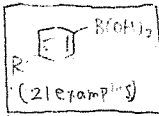
Merging Visible-Light Photocatalysis and Transition-Metal Catalysis in the Copper-Catalyzed Trifluoromethylation of Boronic Acids with CF<sub>3</sub>I

This Work



光、CuOAc, Ru cat. の 3 1 → 2 まで 無 電 気 反 応 性 無 事 進 行 。

Scope ① (R<sub>F</sub> = CF<sub>3</sub>)

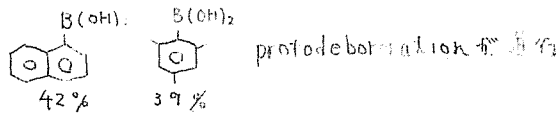


R: Ph, H, OMe, <sup>t</sup>Bu, CF, CN, I, F.  
60-90% yield

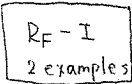
Heteroaryl



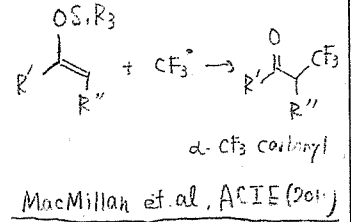
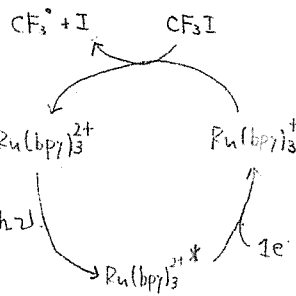
Limitation



Scope ② (Aryl = 1,4-phenylene)



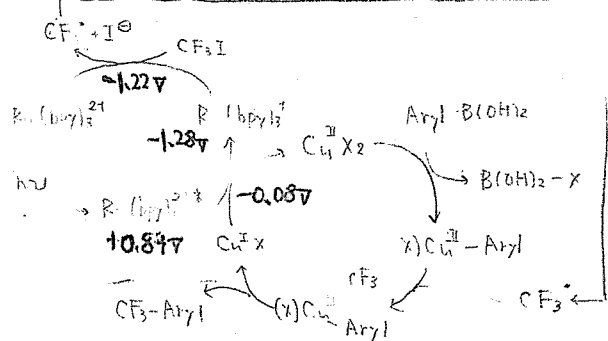
R<sub>F</sub> = C<sub>4</sub>F<sub>9</sub> 67%  
R<sub>F</sub> = C<sub>10</sub>F<sub>21</sub> 71%  
ただし、CuOAc が 0.5 ~ 1 eq. 必要



4F 反応は「CF<sub>3</sub>」が 3,4 3 3 - 2 に 注目。

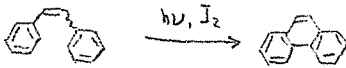
CF<sub>3</sub> 代 換 反 応 の 機 理

Possible Mechanism

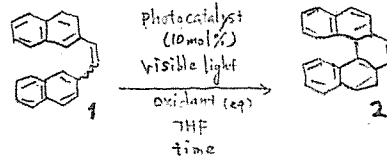
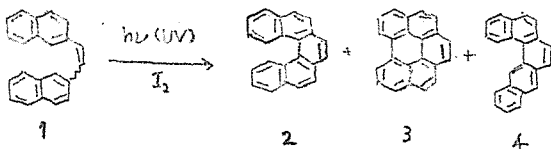


Toward a Visible Light Mediated Photocyclization: Cu-Based Sensitizers for the Synthesis of [5]Helicene

スカルベン誘導体への UV 照射による光環化反応はヘリセン誘導体合成の主な手法である。

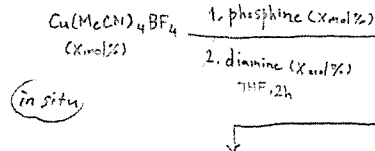


しかしこの手法は以下のような副生成物が生じる。これが問題である。

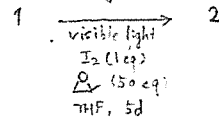


副生成物なし

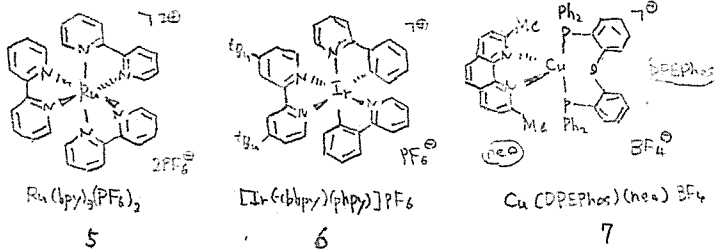
光が少なくていいから



in situ



entry	photo-catalyst	oxidant (eq)	time (cd)	yield (%)
1	5	I <sub>2</sub> (1), O <sub>2</sub> (5);	3	<10
2	6	I <sub>2</sub> (1), Δ (50);	3	<10
3	7	I <sub>2</sub> (1), Δ (50);	5	30-40
4	7	I <sub>2</sub> (0.1), O <sub>2</sub> (1 atm);	5	38
5	7	DDQ (2);	3	21
6	7	*B <sub>2</sub> O <sub>3</sub> (4); Δ; 3		29



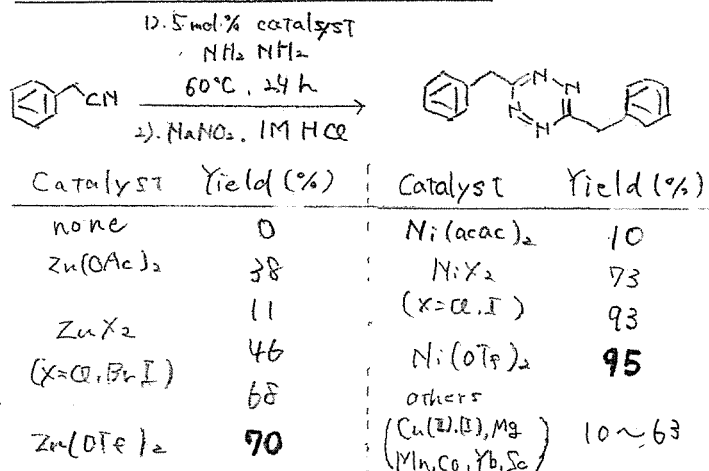
entry	phosphine	diamine	X	yield (%)
1	DPEPhos	neo	10	32
2	DPEPhos	neo	50	56
3	DPEPhos	himida	10	40
4	DPEPhos	himida	25	47
5	XantPhos	neo	10	50
6	XantPhos	neo	25	57 (51)
7	XantPhos	himida	10	36

batch flow, 120 h 42%, 10 h 40%

R=H 0%, R=OMe 23%

# Metal-Catalyzed One-Pot Synthesis of Tetrazines Directly from Aliphatic Nitriles and Hydrazine

## Survey of metal catalysts



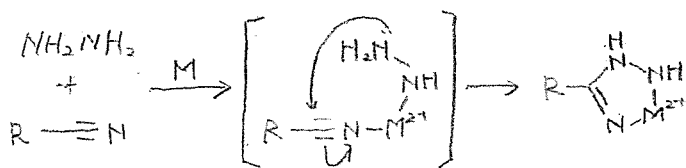
## Synthesis of tetrazines from nitriles

1. 5 mol% catalyst  
 $\text{NH}_2\text{NH}_2$   
 $60^\circ\text{C}, 24\text{h}$   
 2.  $\text{NaNO}_2, 1\text{M HCl}$

catalyzed by Ni or Zn

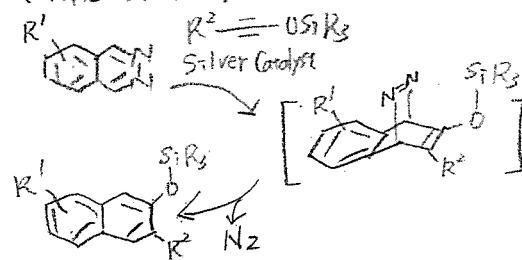
Entry	R'	R''	Cat.	Yield (%)
1	$\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_2\text{CH}_2\text{CH}_3$	Zn	59
2	$t\text{Bu}$	$t\text{Bu}$	Zn	24
3	$\text{Boc}$	$\text{Me}$	Ni	58*
4	$\text{Ar}$	$\text{Me}$	Ni	41~70
5	alkyl	$\text{Me}$	Zn	36~40
6	$\text{BocHN}$	$\text{Me}$	Ni	36
7	$\text{Ph}$	$\text{CH}_2\text{CH}_2\text{CH}_3$	Zn	12
8	$\text{HO}$	$\text{TMS}$	Zn	30*
9	$\text{Ar}$	$\text{NH}$ $\text{H}-\text{C}=\text{N}-\text{NH}_2$	Ni, Zn	64~74**

## Plausible catalytic role of the metal

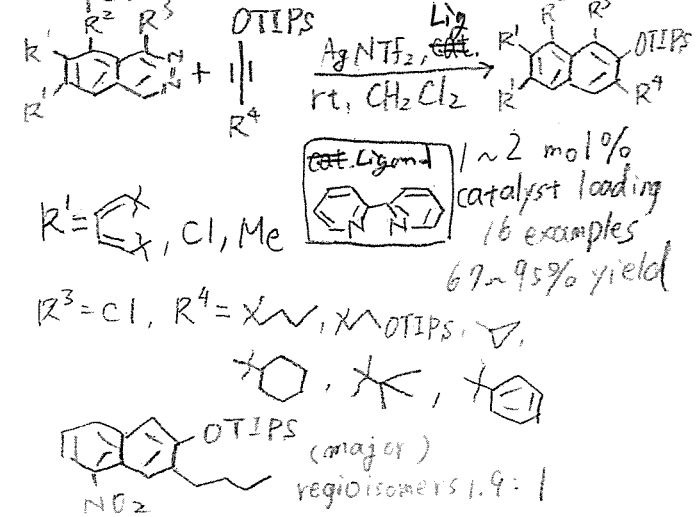


# Silver-Catalyzed Formal Inverse Electron-Demand Diels-Alder Reaction of 1,2-Diazines and Siloxy Alkynes

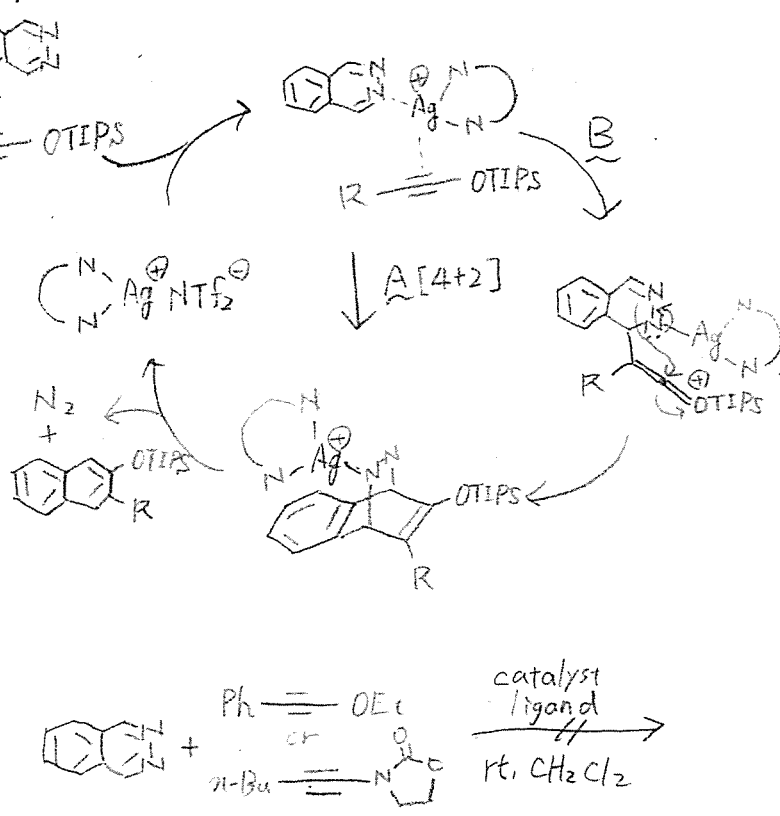
## <This Work>



## <Scope>



## <Proposed Reaction Mechanism>



Bright White Light Emission from Ultrasmall Cadmium Selenide Nanocrystals

今までは...

CdSe nanocrystal (~2nm)  
 白色発光するが発光素子として  
 商業的に利用するには、  
 蛍光量子収率が低い(8~9%)。

this work

CdSeの蛍光量子収率の向上  
 ... トルエン溶液をカルボン酸で処理。  
 ギ酸が最も高い値 (Max: 45%)  
 ・ある程度持続(41%  $\xrightarrow{15\text{ days}}$  30%)

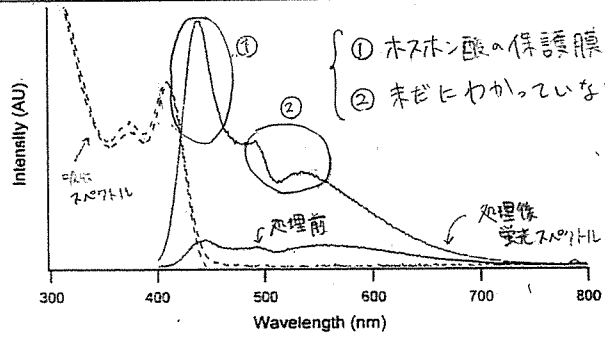
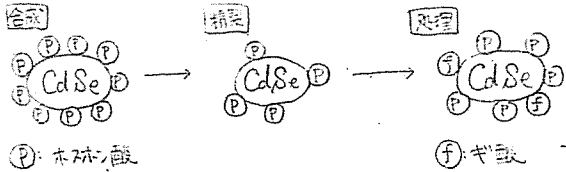


Fig. 1 ギ酸処理前後のスペクトル

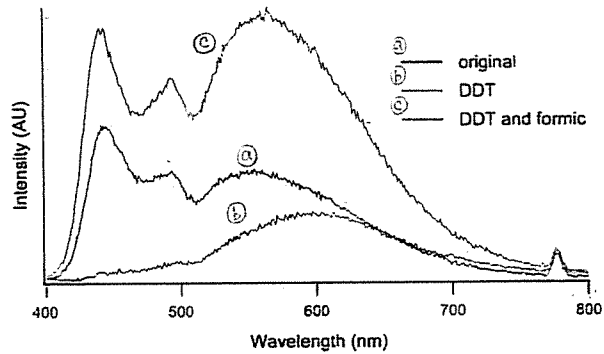


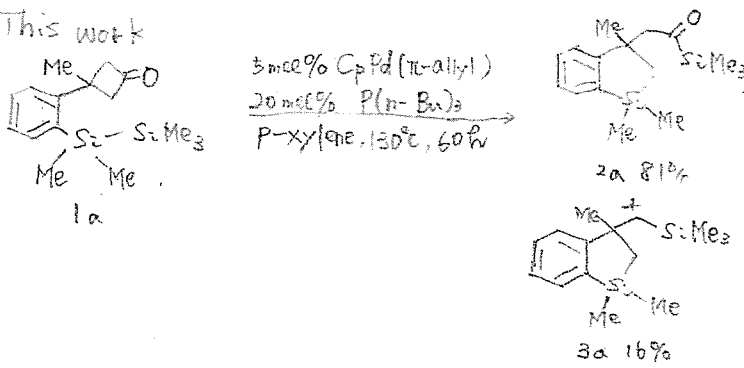
Fig. 2 DDT (ドデカチオール)の存在による変光スペクトル

白色だが、  
 青色(①)の強度  
 が大きい。

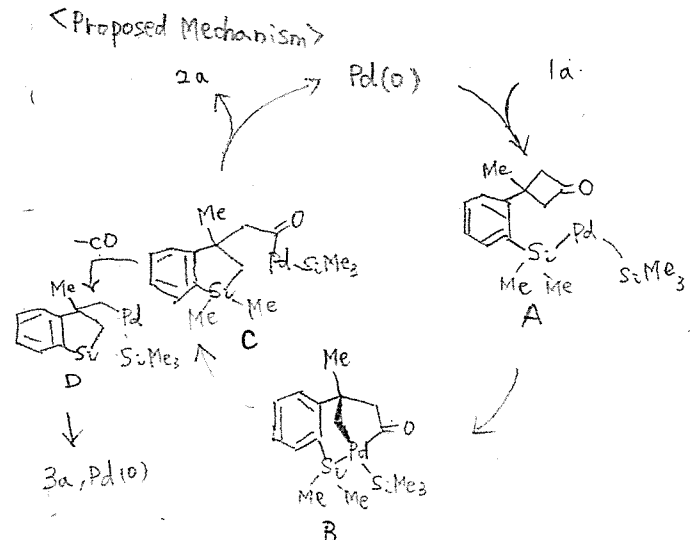
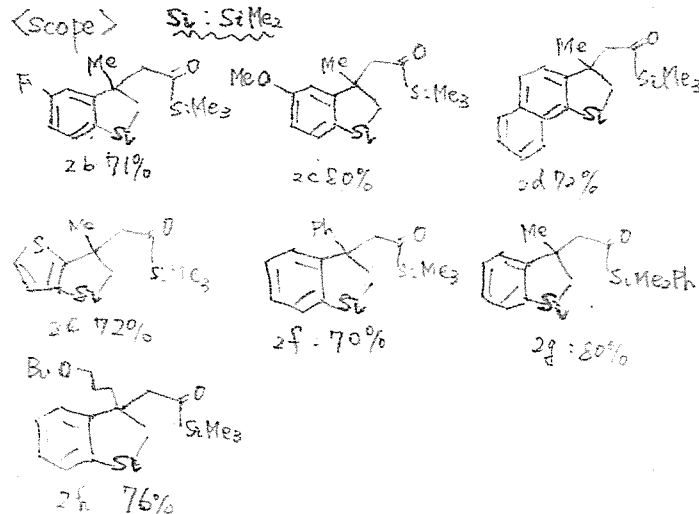
DDTがCd表面の  
 ホズホン酸と置換  
 → Fig. 1の①が減少  
 ↓  
 平衡状態を  
 白色発光に。

Intramolecular  $\sigma$ -Bond Metathesis Between Carbon-Carbon and Silicon-Silicon bonds

This work

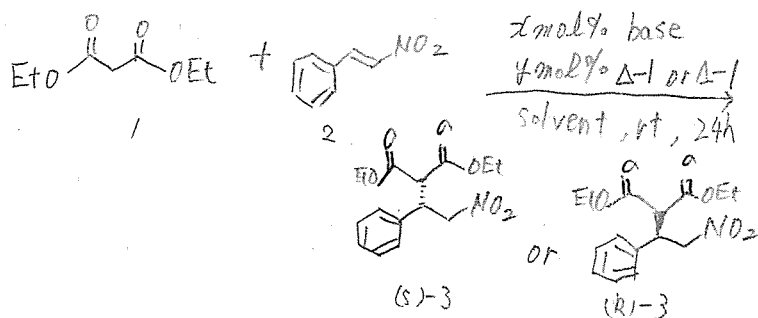
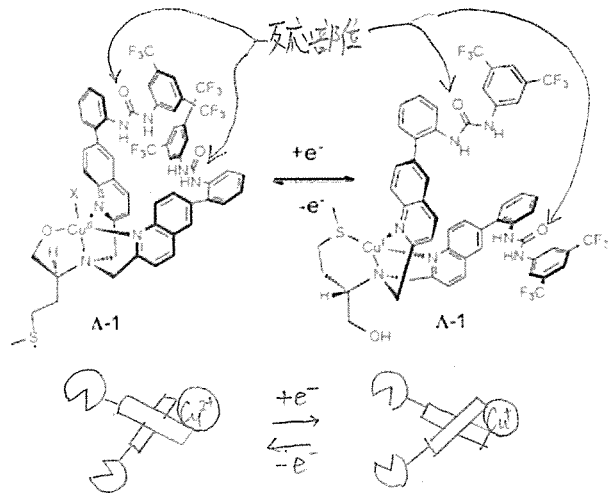


① This was not observed in reaction mixture.  
 ② direct decarbonylation of cyclobutane unit under Rh catalyzed reaction  
 ③ 5 remained intact under the same reaction condition  
 • initial activation  
 X cyclobutane  
 O disilane



A Redox-Reconfigurable, Ambidextrous Asymmetric Catalyst

銅イオンの酸化数により  
エナンチオ選択性を変える



solvent: toluene, THF, MeCN, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, hexane  
 → MeCN で 収率は低いから Δ-1, Δ-1 で  
 共に高い 選択性

base: NEt<sub>3</sub>, DIPEA, DABCO, DBU, DMAP  
 → 収率は変わらないから NEt<sub>3</sub> が 高い 選択性

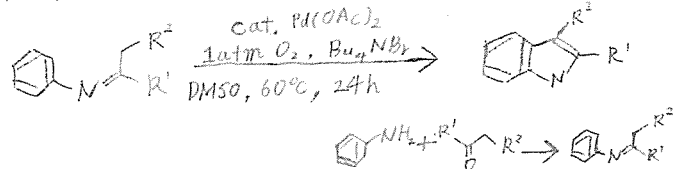
loading concentration: (Δ-1)

entry	X	Y	% ee	% yield	ALS-3
1	10	5	72	55	
2	10	10	70	50	
3	2	0.5	62	67	
4 <sup>a</sup>	10	5	20	44	

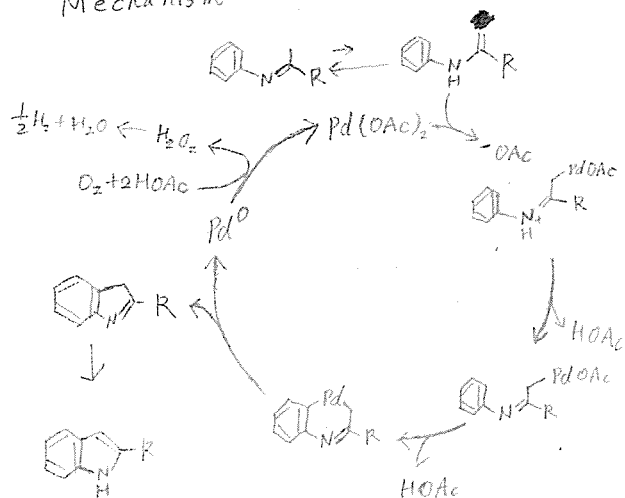
solvent: MeCN  
 base: NEt<sub>3</sub>  
 % ee: chiral HPLC analysis  
 % yield: isolated yield  
 a: 90 metal

Palladium-Catalyzed Aerobic Oxidative Cyclization of *N*-Aryl Imines:  
Indole Synthesis from Anilines and Ketones

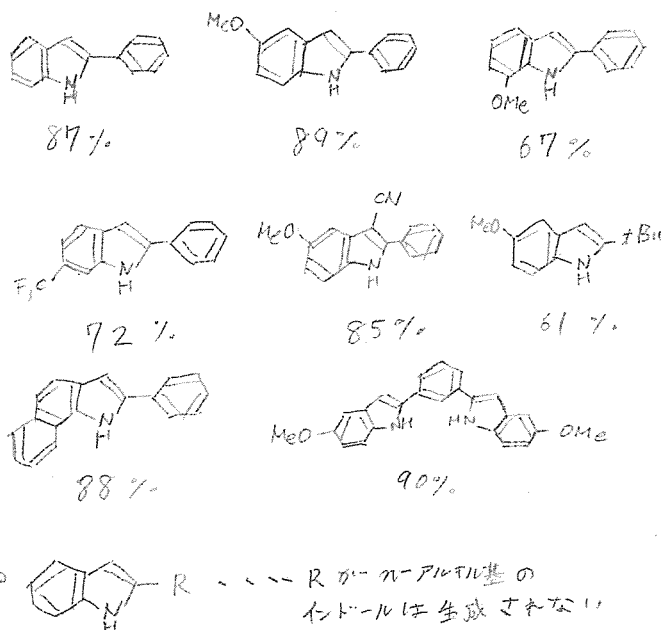
This work



Mechanism



Scope



○ R が *n*-Pr 以上の  
 インドールは生成できなかった  
 ○ 7-ポジットではインドールは生成できなかった