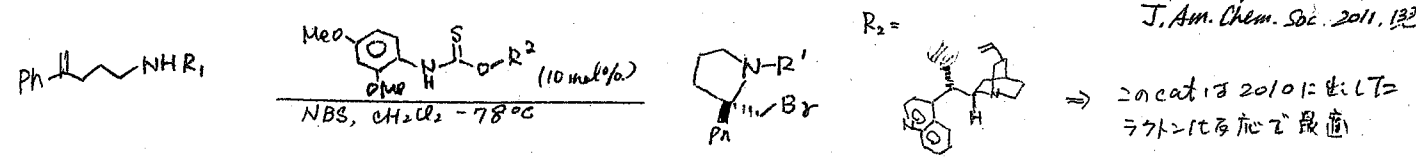


Enantioselective Bromoaminocyclization Using Amino-Thiocarbamate Catalysts

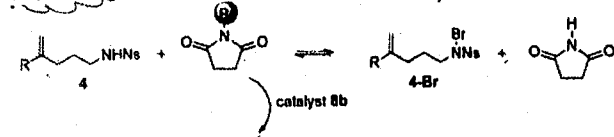
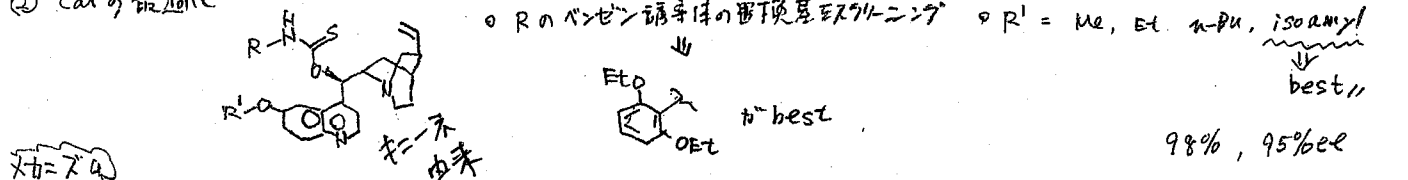
T.-T. Teng et al
(University of Singapore)
J. Am. Chem. Soc. 2011, 133, 9164.



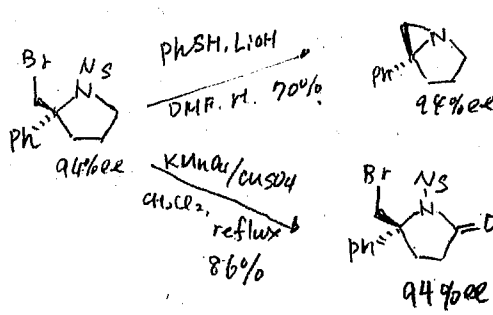
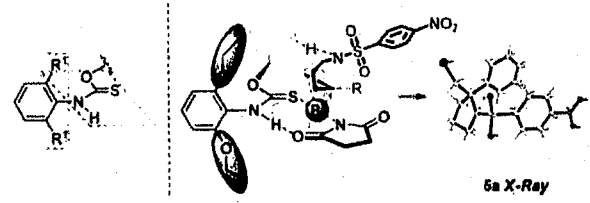
① R₁の最適化

A-NO₂C₆H₄SO₂ (4-NO₂), 3-NO₂, 2-NO₂, Boc, p-Ts, PhSO₂, 3,5-F₂C₆H₃SO₂ ⇒ 4-NO₂が best. (2Lh, 93%, 45% ee)

② catの最適化



Ar is 12 examples. 4-NO₂ is best. H & Me < c-hex. Yield: 50% yield.



CT 1625

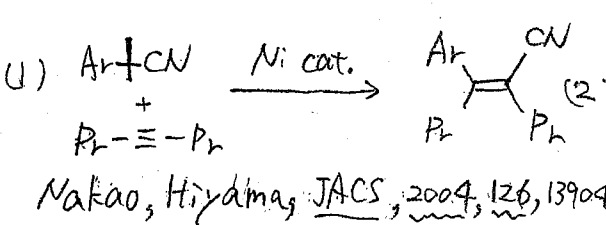
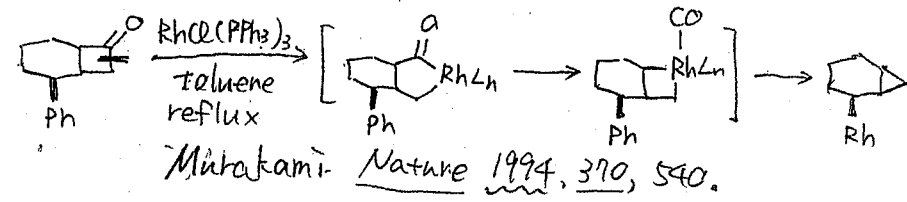
H₃C-CH₂: 90 kcal/mol M-C: 30~60 kcal/mol

Youhei Takeda

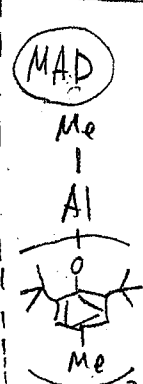
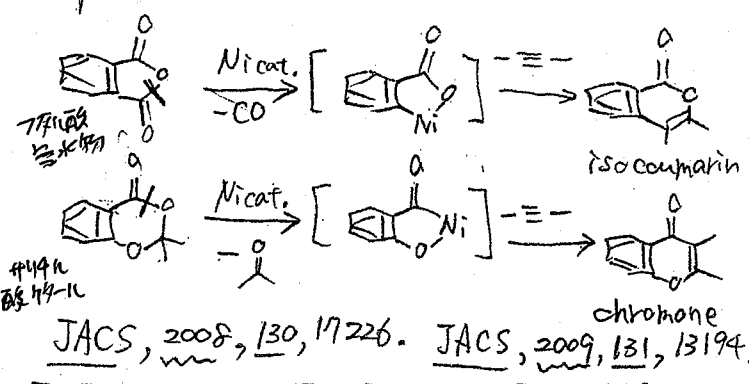
"Nickel-Catalyzed Cycloaddition of α -Arylcarboxybenzonitriles and Alkynes via Cleavage of Two Carbon-Carbon σ -Bonds"

Nakai, K.; Kurahashi, T.* Matsubara, S.* J. Am. Chem. Soc. 2011, Just Accepted (doi: 10.1021/ja.203829j)

< transition metal-catalyzed C-C bond activation >



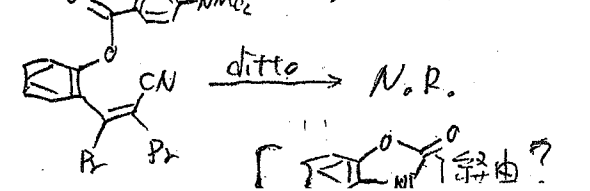
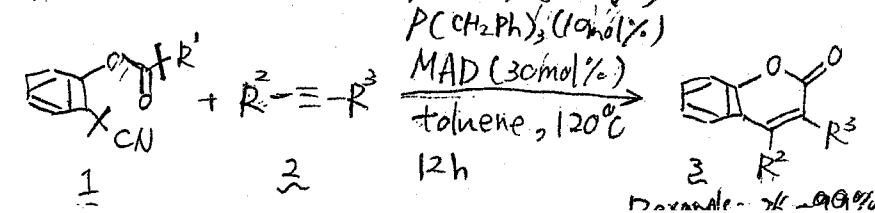
< previous work >



< Information of reaction conditions >

• R¹ = [Structure] NMe₂ が最も収率が高い。
(R² = R³ = Pr = 81%)
Alkyne E 選別用になると, Ar-CN と byproduct として得られる。
• Lewis Acid 加, nBu, AlMe₃, BPh₃ のときは, 生成物は 1% 以下

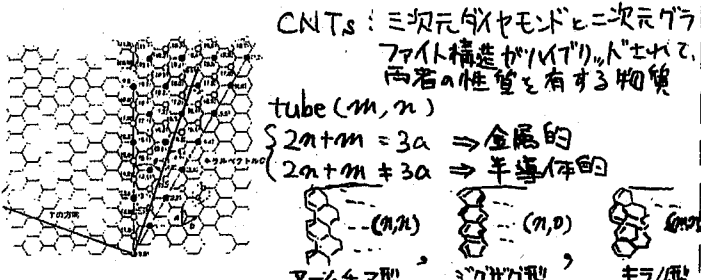
< This work >



Separation of Metallic and Semiconducting Single-Walled Carbon Nanotube Arrays by "Scotch Tape"

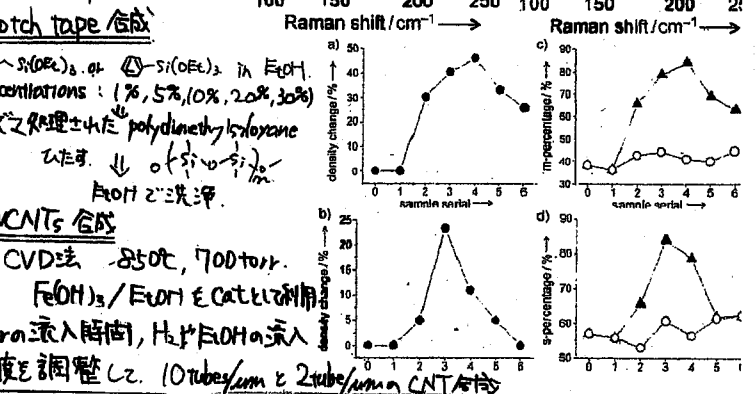
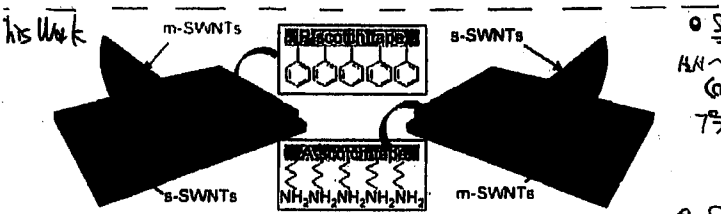
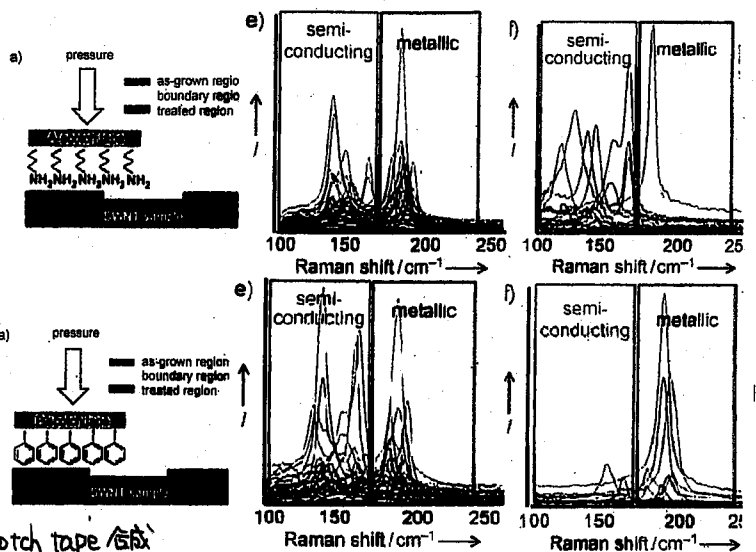
Guo Hong, Matthew Zhou, Ruoxing Zhang, Shimin Hou, Wonmook Choi, Yun Sung Woo, Jae Young Choi, Zhongfan Liu, and Jin Zhang*

Angewandte Chemie
DOI: 10.1002/anie.201101700



金属的SWCNTs (m-SWCNTs) と半導体的SWCNTs (s-SWCNTs) を分離するのは非常に重要 \Rightarrow 混在している SWCNTs を分離するのには非常に重要 \Rightarrow 混在している SWCNTs を分離するのには非常に重要

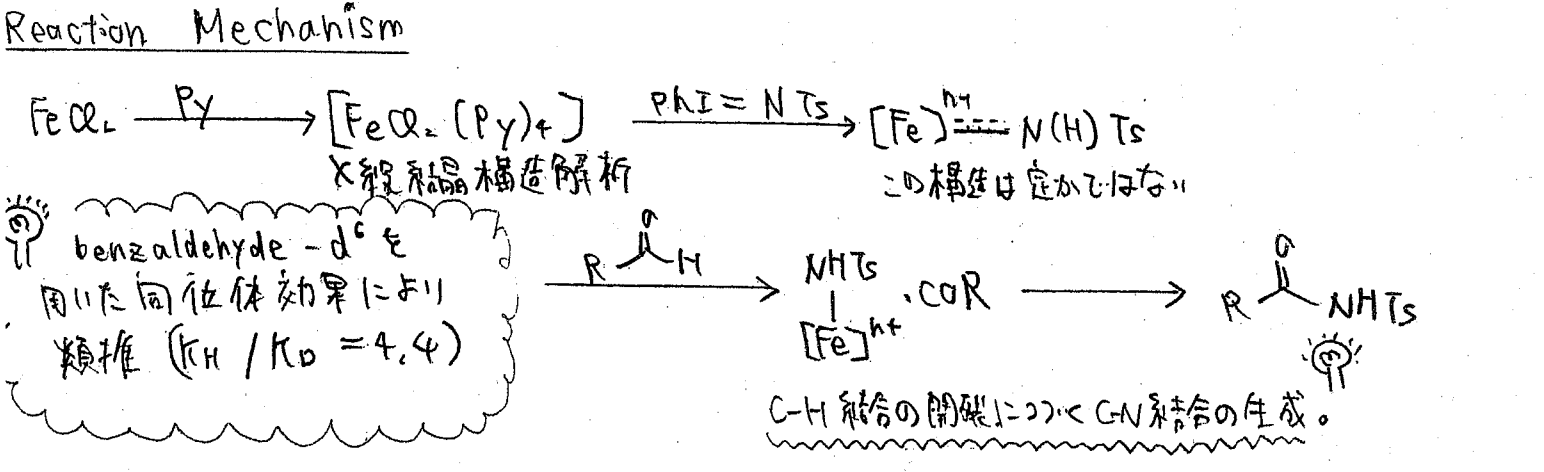
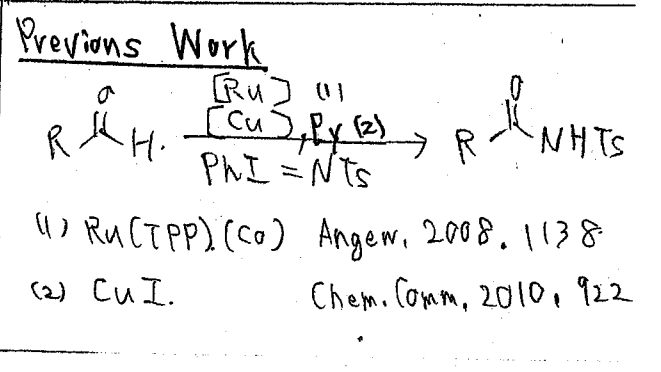
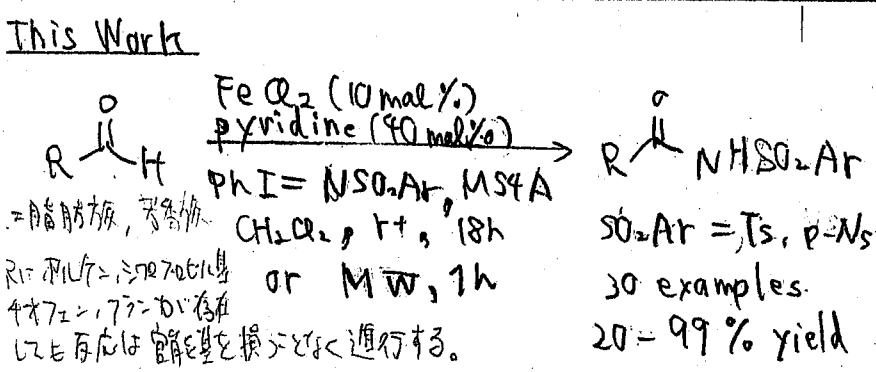
現在までに... 大きく分けて2つの手法。
 破壊する手法: ニトロソイオンの攻撃 or 酸化 or UV照射 etc.
 溶解する手法: 濃度勾配と適用する遠心分離の吸着 etc.



接着テープにアミノ基もしくはフェニル基のどちらか
 修飾することにより、容易に m-SWCNTs と s-SWCNTs を
 分離することに成功。

Iron (II) - Catalyzed Amidation of Aldehydes with Iminoiodinanes at Room Temperature and under Microwave - Assisted Conditions.

Wai Hong Chan et al J. Org. Chem. 2011. 76, 4894 早川 純平



Copper-Catalyzed Aerobic Oxidation of Hydroxamic Acids Leads to a Mild and Versatile

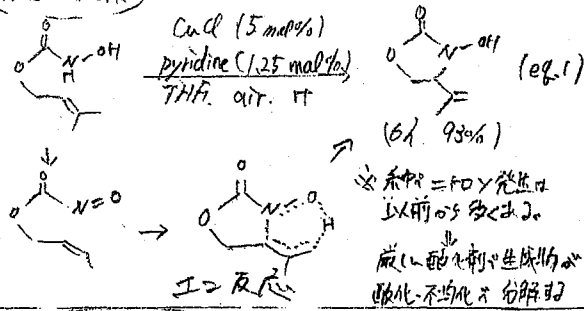
Acylnitroso Ene Reaction

Nota Okamoto

Frazier, C. P.; Engelking, J. R.; de Alaniz, J. R.*

J. Am. Chem. Soc. DOI: 10.1021/ol201173a

(This Work)



類似の酸化機構 (Marder, T. B.; Shea, K. J.; Whiting, A. Org. Lett. ANAP)

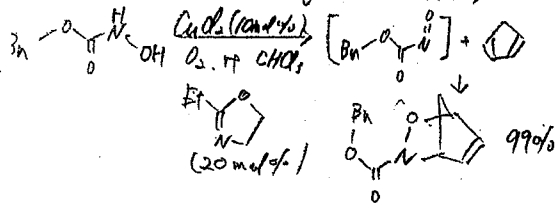


Table 1 Screening (eq 1) 反応条件

entry	cat	additive	oxidant	time	yield (%)
1	CuCl ₂	-	H ₂ O ₂	20 min	79
2	CuCl	-	H ₂ O ₂	20 min	79
3	CuCl ₂	-	air	18 h	68
4	CuCl	-	air	29 h	47
5	CuCl	pyridine	air	6 h	93

Table 2 Intramolecular Ene reaction

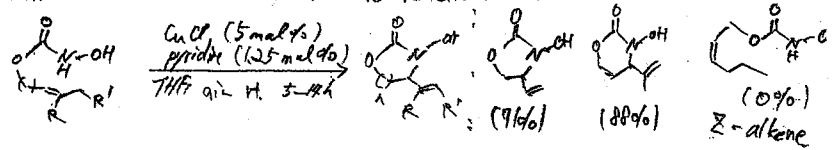


Table 3 Intramolecular Ene reaction (Screening Hydroxamic acids)

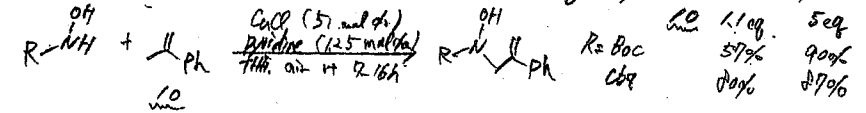
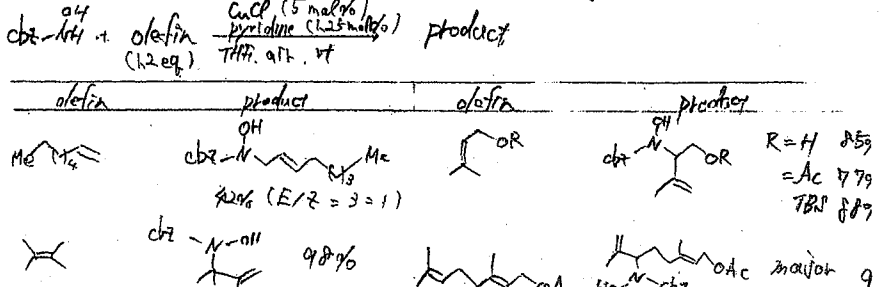
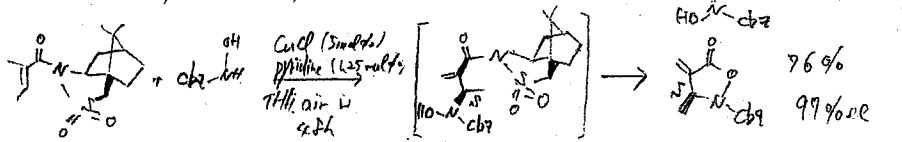


Table 4 Intermolecular Ene reaction (Screening alkenes)



Scheme 1 Asymmetric Acylnitroso Ene reaction

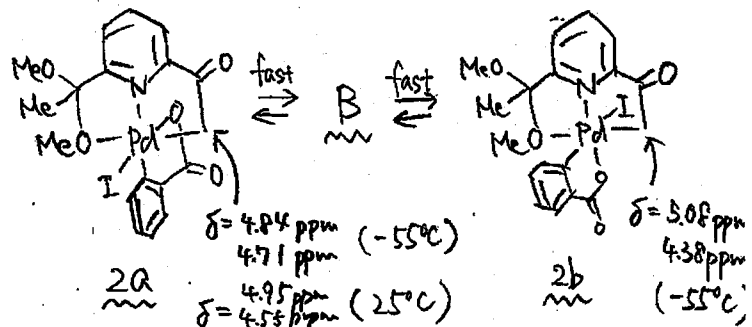
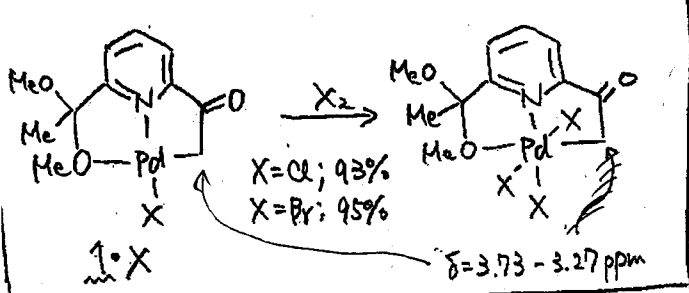


Synthesis of a Palladium(IV) Complex by Oxidative Addition of an Aryl Halide to Palladium(II) and Its Use as Precatalyst in a C-C Coupling Reaction

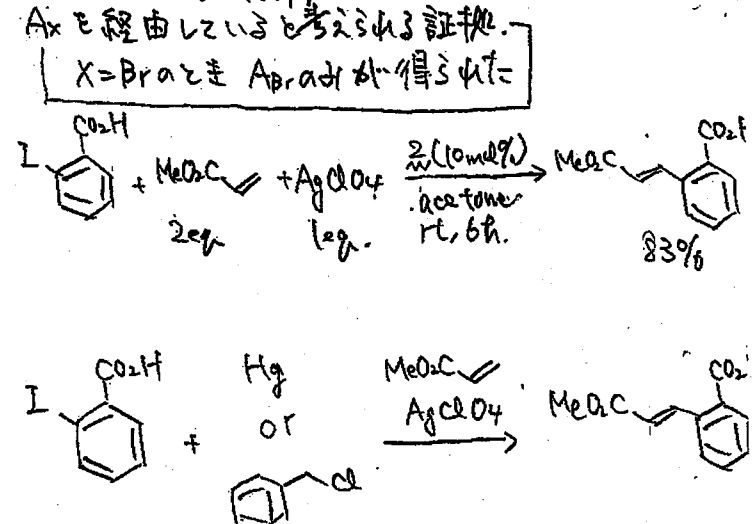
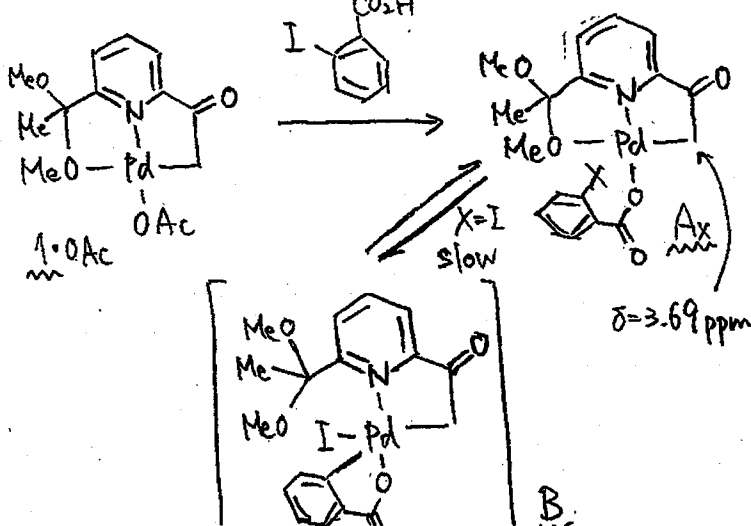
Yuki Ikeda

Vicente, J.; Arcas, A.; Julia-Hernandez, F.; Bautista, D. Angew. Chem. Int. Ed. DOI: 10.1002/anie.201102214

<Previous Work>



<This Work>

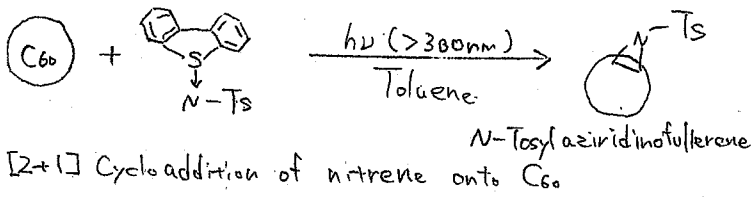


Highly Regioselective Synthesis of Bis-Aziridino[60]fullerene with Sulfilimine

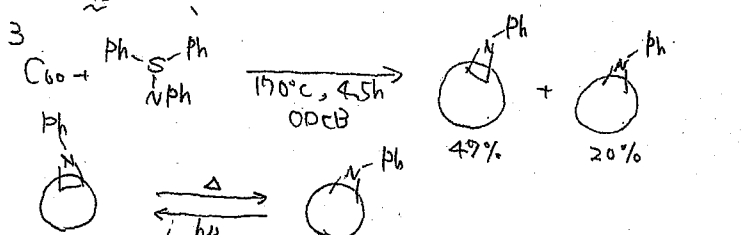
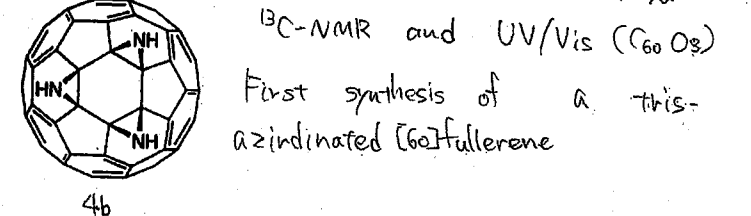
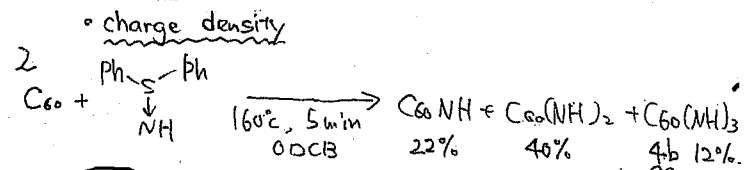
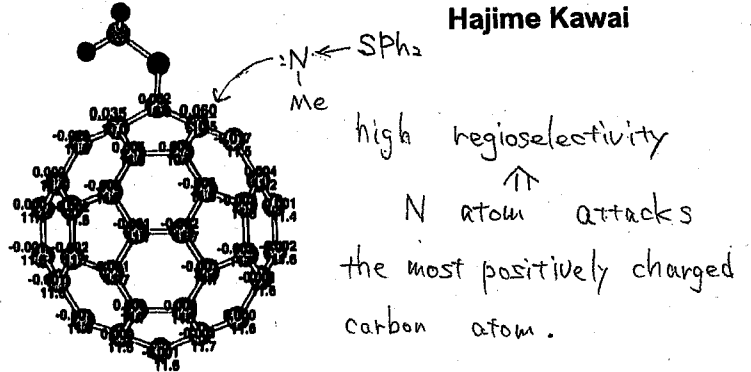
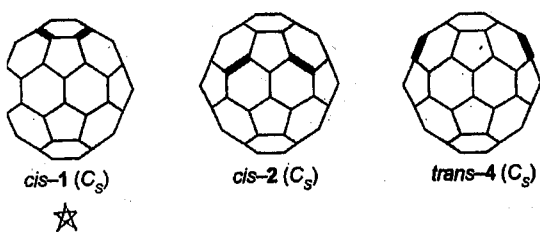
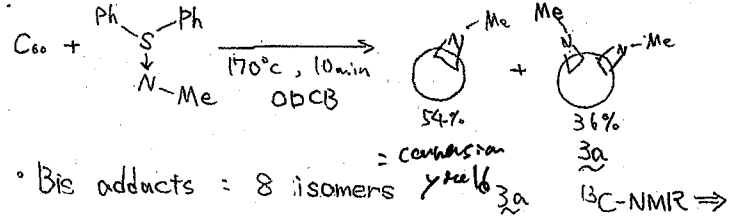
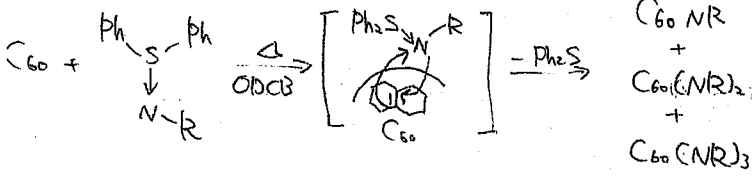
T. Akasaka, S. Nagase et al. Chem. Asian J. 2011, 6, 416-423

Hajime Kawai

Previous work (ACIE 2008, 47, 1298)



This work



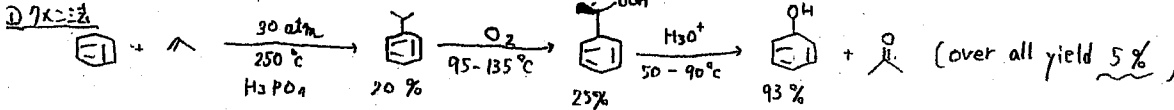
Direct, copper-catalyzed oxidation of aromatic C-H bonds with hydrogen peroxide under acid-free conditions

Ana Conde, M. Mar Díaz-Reguejo and Pedro J. Pérez DOI: 10.1039/c1cc12804c

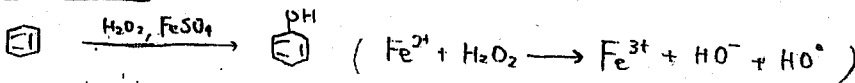
M1 錦織克聡

Chem. Commun.

代表的なFenton法



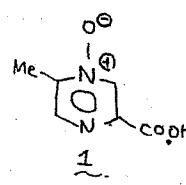
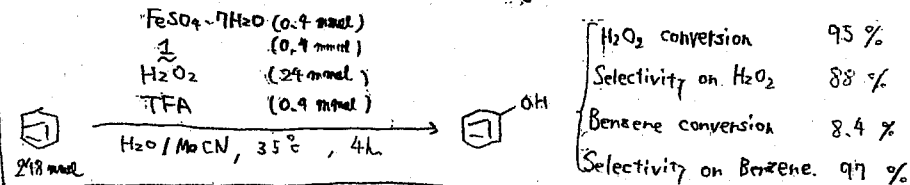
Fenton Chemistry



問題点

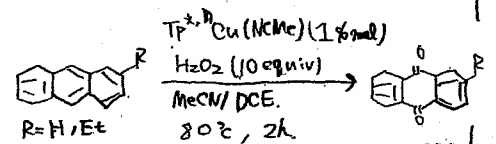
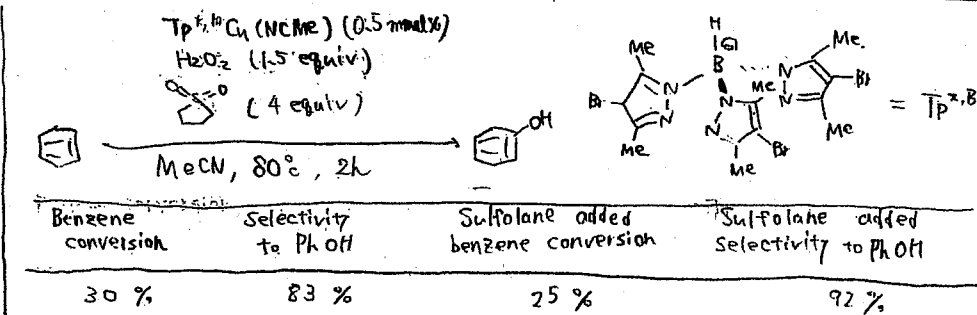
c1ccccc1-OH は c1ccccc1 より反応性が高く、over-oxidation が起きてしまう。

The best results reported (Bianchi, Vignola and co-workers)



二相系は好都合、over-oxidation が起きにくい。

Present Work



詳細な反応機構は検討中。

Catalytic Asymmetric Intermolecular Stetter Reaction of Enals with Nitroalkanes:

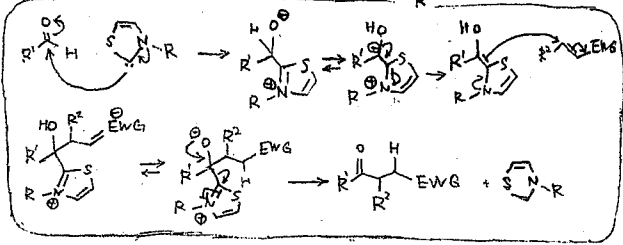
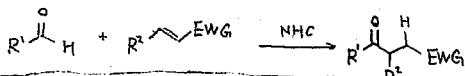
M1 矢野

Enhancement of Catalytic Efficiency through Bifunctional Additives

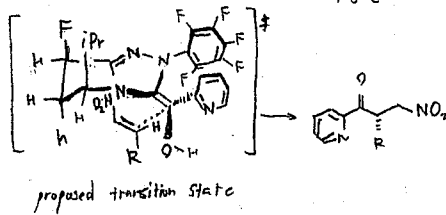
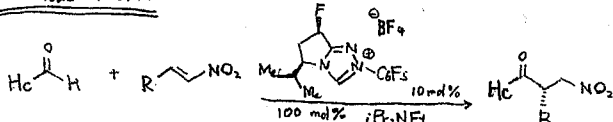
Daniel A. DiRocco and Tomislav Rovis

JACS dx.doi.org/10.1021/ja203810b

Stetter Reaction

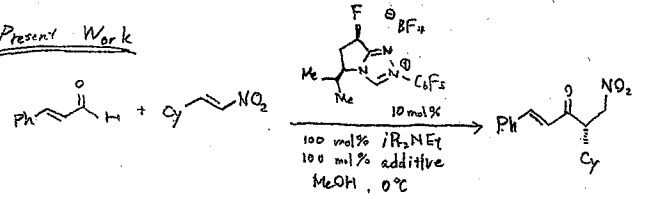


Previous Work



12 examples
62~99% yield
83~96% ee

Present Work

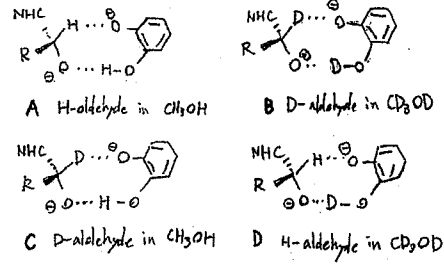


additive	time(h)	yield(%)	ee(%)
none	8	5	93
	8	8	93
	8	15	93
	2	80	93
	8	9	93

$Ph-CHO + Cy-CH=CH-NO_2$
57~98% yield
93~98% ee

$R-CHO + Cy-CH=CH-NO_2$
60~70% yield
82~86% ee

$Ph-CHO + R-CH=CH-NO_2$
75~84% yield
88~91% ee



A/B
k_H/k_D = 4.2
A/C
k_H/k_D = 2.7
A/D
k_H/k_D = 1.8

Morpholine catalyzed direct C3 alkenylation of indoles with α,β -unsaturated aldehydes

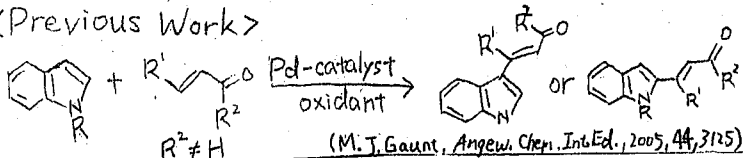
B4 岡崎

Shi-Kai Xiang, Bo Zhang, Li-He Zhang, Yuxin Cui and Ning Jiao*

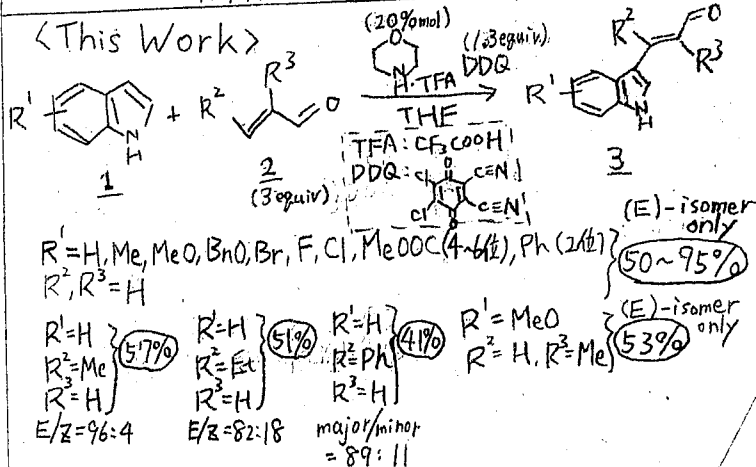
Chem Comm

DOI: 10.1039/c1cc12220g

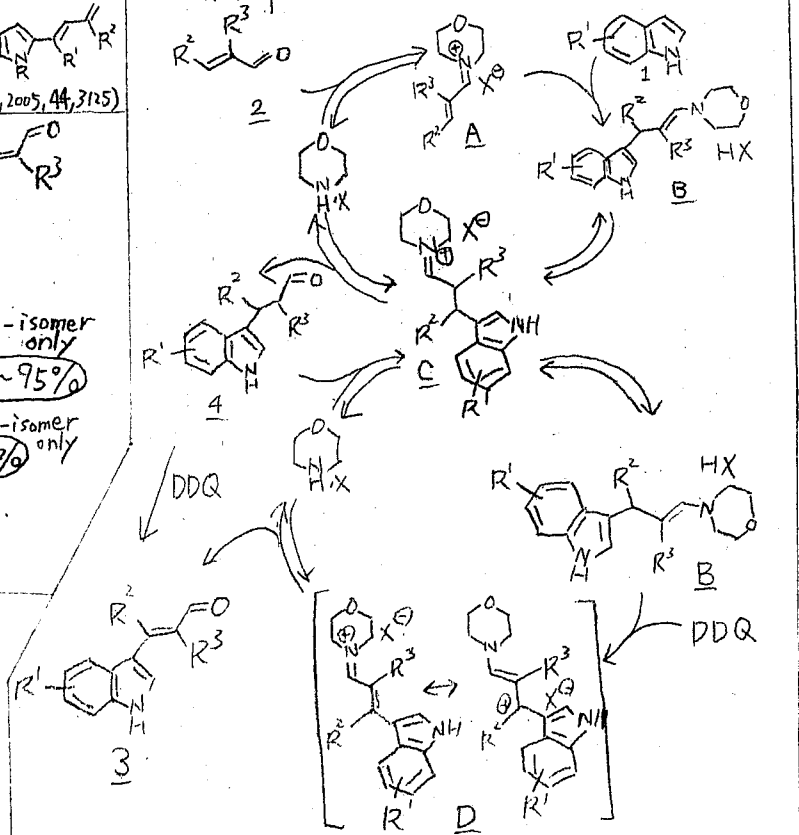
<Previous Work>



<This Work>



<Proposed Mechanism>



有機分子触媒

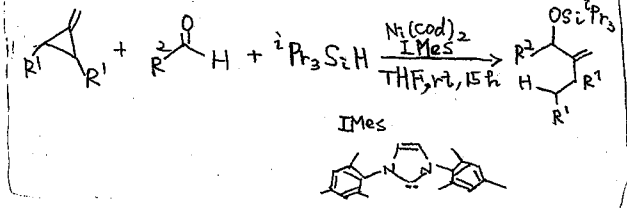
- 空気や湿気に対して安定
- 金属含有触媒に比べて、一般的に安価であり、環境への負荷が少ない。

Nickel-Catalyzed Three-Component Coupling between Aryl Aldehydes, Norbornenes, and Silanes Leading to Indanols through Atomic C-H Bond Activation of Aryl Aldehydes

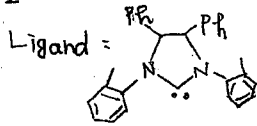
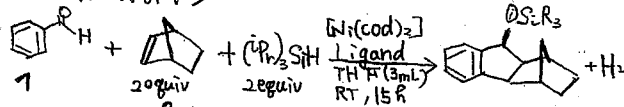
B4 久野 大地
 Angew. Chem. Int. Ed.
 DOI: 10.1002/anie.
 201101468

Kenichi Ogata, Yuka Atsumi, Da isuke Shimada, and Shin-ichi Fukuzawa

<Previous Work>



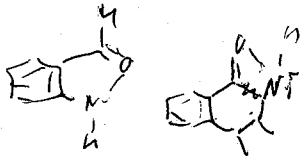
<Present Work>



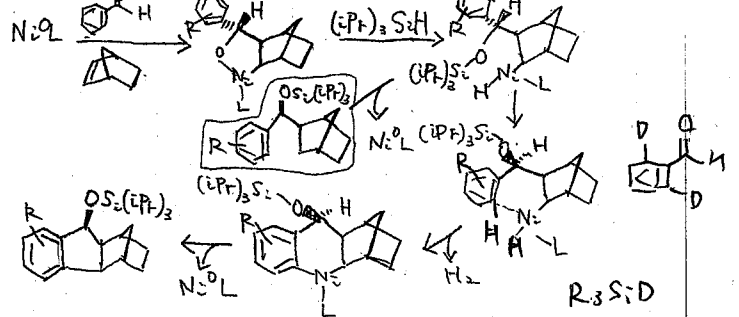
cod: cycloocta-1,5-diene

アリールアルデヒドの芳香族 C-H 活性化させて
 起こる反応の集約がなされた。

$[Ni(cod)_2]$: 0.10 mmol
 Aldehyde: 1.0 mmol
 Norbornene: 2.0 mmol
 $(iPr)_3SiH$: 2.0 mmol
 Ligand: 1.0 mmol



<Mechanism>



entry	Aldehyde	Yield (%)	entry	Norbornene	Yield (%)
1		82	1		
2		99	2		98%
3		99	3		89%
4		87	3		80%
5		77			

