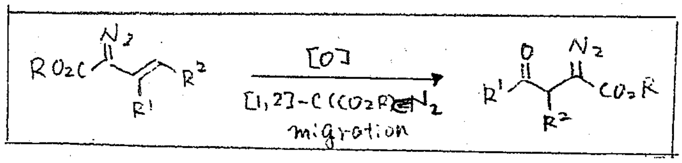
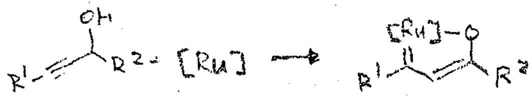
Direct Access to β-Oxodiazo Compounds by Copper(II)-Catalyzed Oxidative Rearrangement of Stabilized Vinyl Diazo Derivatives

J. Am. Chem. Soc. ja208965b

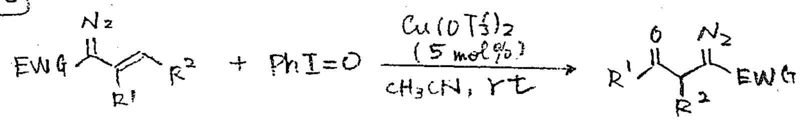
José Barluenga et al. (Univ. Oviedo)

Minakata

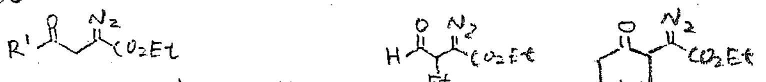




Sope



Product

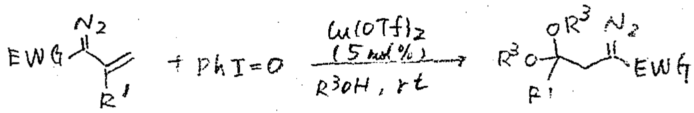


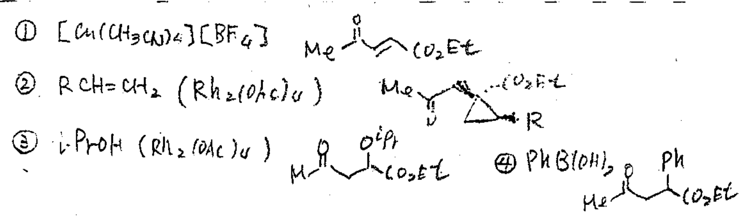
R1=Me (92%), R1=H (85%)
D (75%)

58%

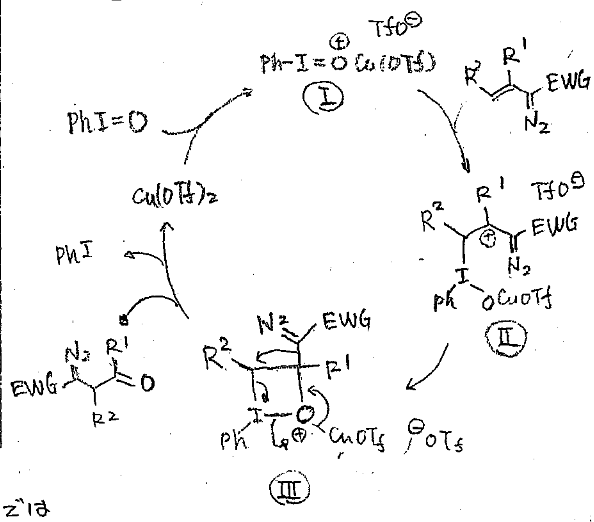
X=CH2 (66%)
=O (52%)
=NBoc (50%)

- R^2がCO2Etや末端が2置換 ⇒ NR
- この反応をアルコール中でやると

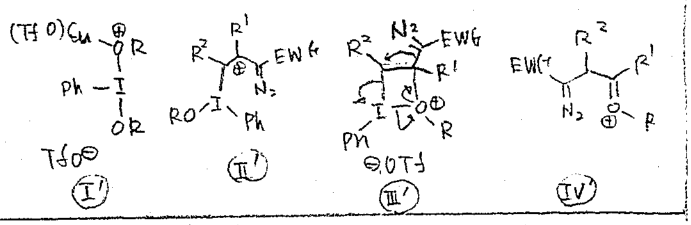




Mechanism



アルコール中では



TMP =

CT 1Y04

Youhei Takeda

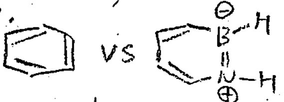
"Synthesis of BN-Fused Polycyclic Aromatics via Tandem Intramolecular Electrophilic Arene Borylation"

Hatakeyama, T.*; Hashimoto, S.; Seki, S.*; Nakamura, M.*

J. Am. Chem. Soc. ASAP (doi: ja208950c).

※芳香族化合物の C=C を B=N (等電子) で置換した化合物の研究。

ex.



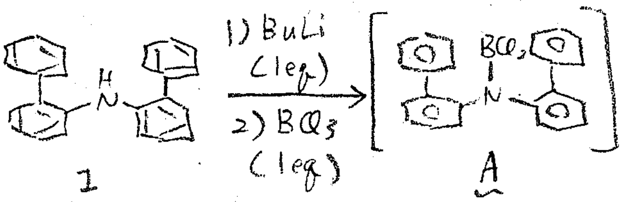
(1,2-azaborine)

Dewar et al. J. Chem. Soc. (1958)

- 分子の双極子モーメントに変化。

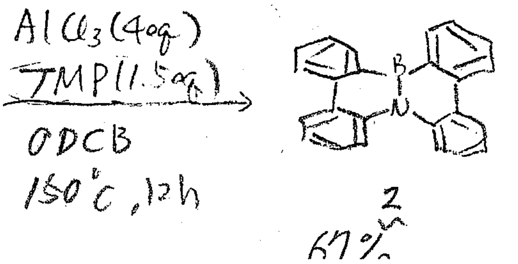
⟹ 溶解性, 物理化学的性質の変化に対する興味。

<This Work>



1

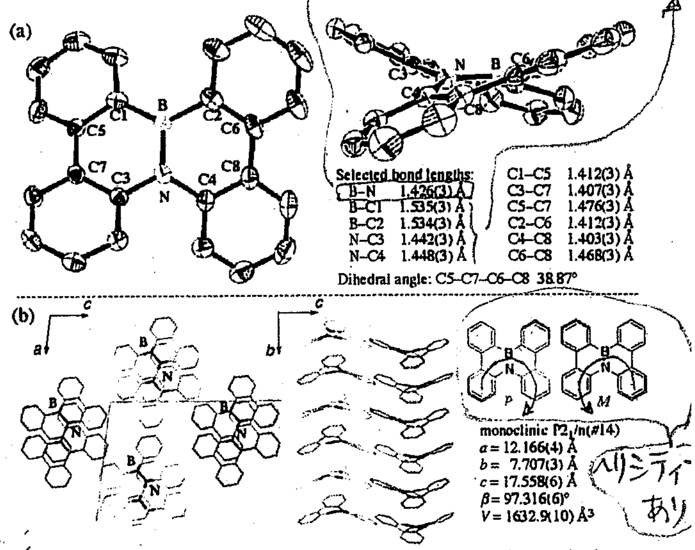
A



2

67%

※Lewis acid の例 (AlCl3, GaCl3, Zn(OTf)2) だと×。



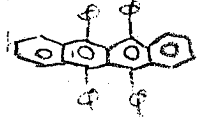
○二重結合性あり (cf. B-N bond in BN-fused は 1.45〜1.97Å) 単結合

off set 型 スタッキング

ヘリシティーあり

※TRMC (time-resolved microwave conductivity) 法による hole 移動度: 0.07 cm²V⁻¹s⁻¹

(cf.



rubrene: 0.05 cm²V⁻¹s⁻¹)

dibenzo chrysene: 0.001 cm²V⁻¹s⁻¹

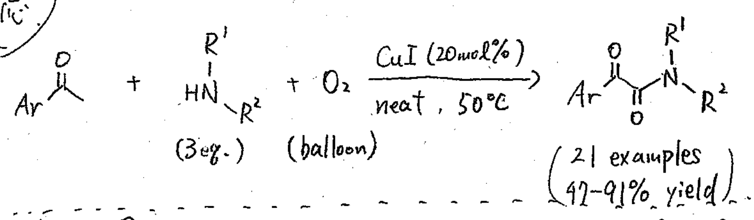
※溶解度 (AcOEt に対する)

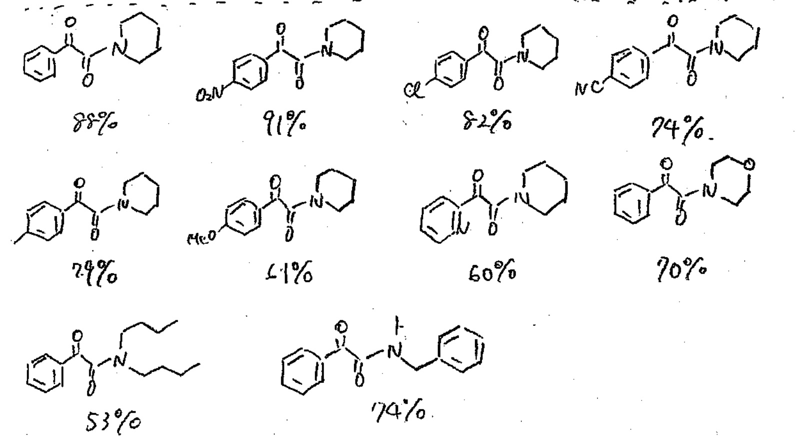
7.7 mg/mL (dibenzo chrysene: 5.0 mg/mL

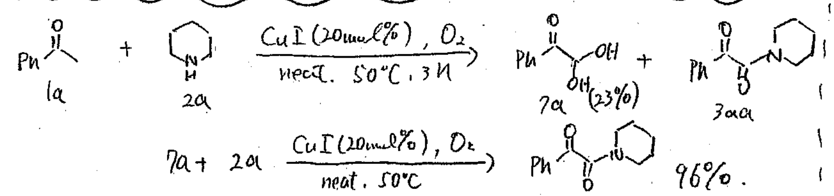
Copper-catalyzed direct oxidative synthesis of α-ketoamides from aryl methyl ketones, amines, and molecular oxygen 村上.

Jian-Xin Ji et al. (Chem. Sci. Advance Article)
(Graduate University of the Chinese Academy of Science)

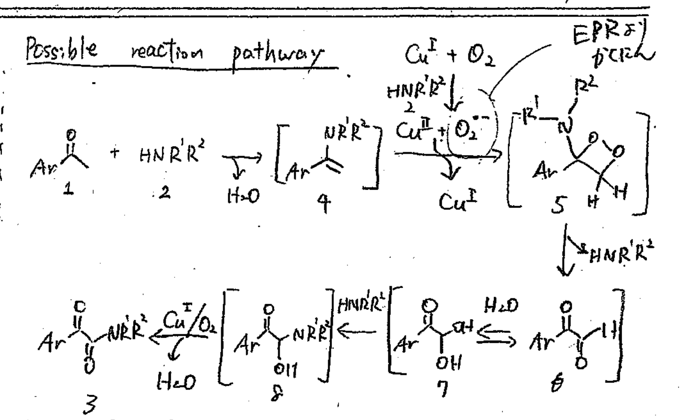
反応

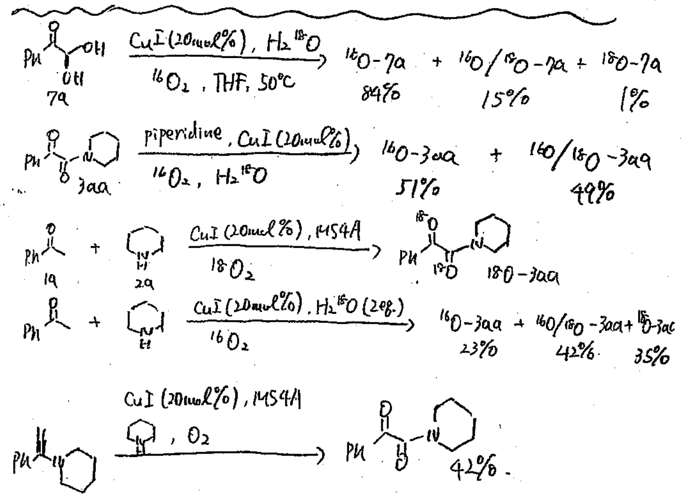






Possible reaction pathway





Enantioselective Synthesis of Endohedral Metallofullerenes 長田

Nazario Martin, Takeshi Akasaka, Shigeru Nagase et al JACS ja2062727

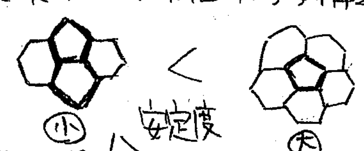
Endohedral Metallofullerene

⇒ 1つもしくはそれ以上の金属原子をフラーレンcage内にカプセルしてるもの

Isolated-Pentagon-Rule (IPR則)

5員環同士が縮環する構造は不安定。← 例外あり

ただ C_{72} だけはちがう!!



原料合成

⇒ アーク放電 ⇒ すすを1,2,4-トリクロロベンゼンで抽出 ⇒ La@C₇₂(C₆H₃Cl₂)
(ランタンを含む)

反応 Nature Chemistryの報告と同条件で…。

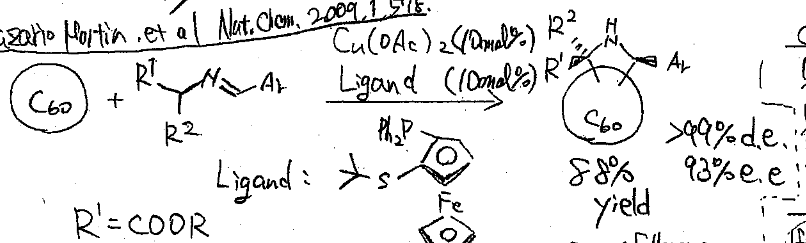
$Sc_3N@C_{80}$, $La@C_{82}$, $La_2@C_{80}$ では ✗。

(理由) HOMO-LUMOのミスマッチ

$La@C_{72}(C_6H_3Cl_2)$ 電子求引性のため反応が進行

<Previous work>

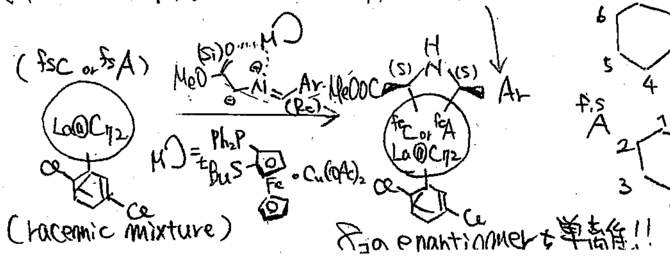
Nazario Martin, et al Nat. Chem. 2009, 1, 578.



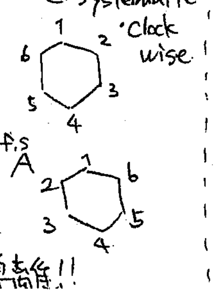
R¹ = COOR

<This work>

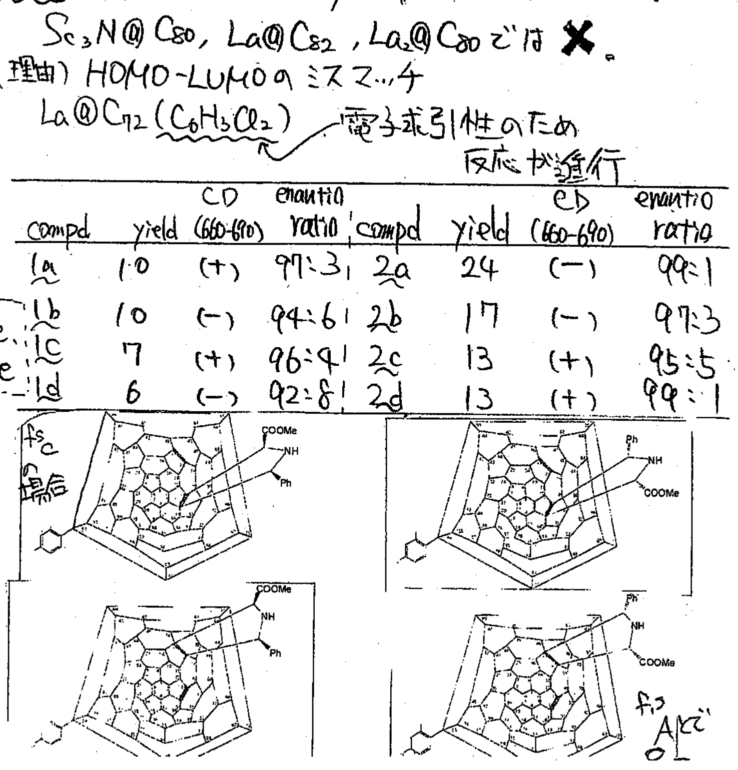
Ar = -⟨◯⟩-OMe



各 enantiomer を単離!!



compd	yield	CD (660-690)	enantio ratio	compd	yield	CD (660-690)	enantio ratio
1a	10	(+)	97:3	2a	24	(−)	99:1
1b	10	(−)	94:6	2b	17	(−)	97:3
1c	7	(+)	96:4	2c	13	(+)	95:5
1d	6	(−)	92:8	2d	13	(+)	99:1

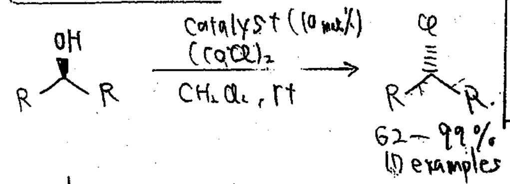


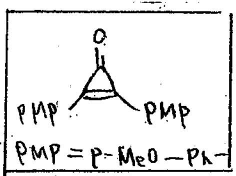
Development of a Catalytic Platform for Nucleophilic Substitution : Cyclopropenone Catalyzed Chlorodehydration of Alcohols (D1-J)

Tristan H. Lambert et al. (Columbia Univ., USA)

Angew. 2011, (anie 201104638)

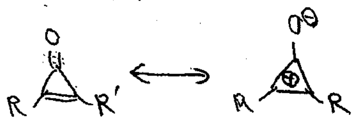
present work





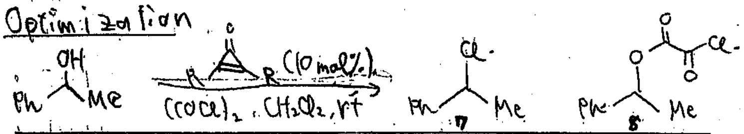
Catalyst

cyclopropenones



① 1959年 Breslowが初めて合成
② 芳香族の共鳴効果により分極
③ 安定なシクロプロペニウムの前駆体
④ 電気的、立体的な性質を置換基によって制御可能。

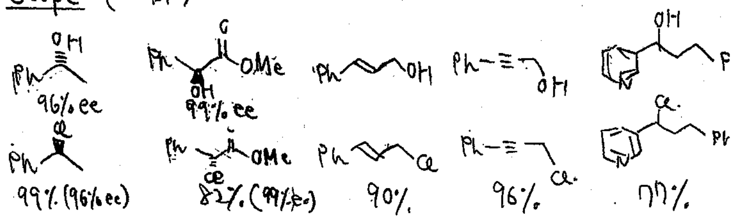
Optimization



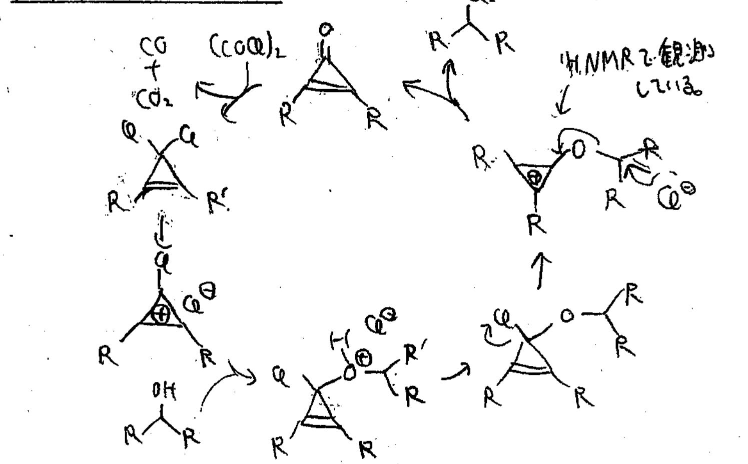
Entry	R	Catalyst conc(M)	$(COCl)_2$ Addition time(h)	7 (%)	8 (%)
1	no catalyst	—	0	0	100
2	Ph	0.1	0	68	32
3	Ph	0.1	1	75	25
4	m-NO_2Ph	0.1	1	14	86
5	p-MeOPh	0.1	1	91	9
6	p-MeOPh	0.2	1	33	67
7	p-MeOPh	0.05	1	96	4
8	p-MeOPh	0.03	1	>98	<2
9	p-MeOPh	0.03	0.25	94	6

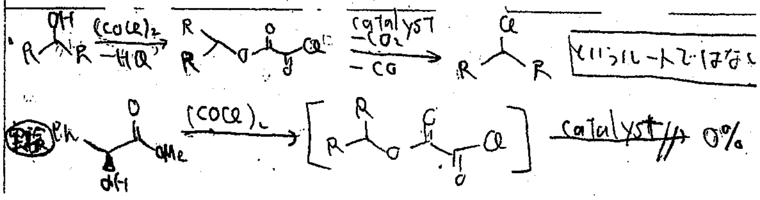
○ Rが嵩高い場合も変化なし

Scope (一部)



proposed mechanism





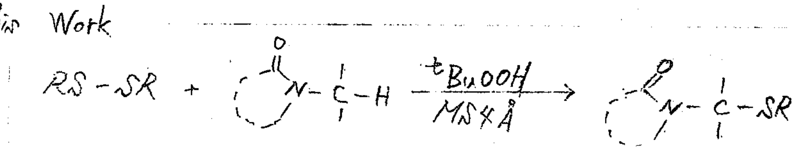
TBHP-mediated oxidative thiolation of an sp³ C–H bond adjacent to a nitrogen atom in an amide

M2 奥村

Jian-Nan Xiang, Jin-Heng Li et al.

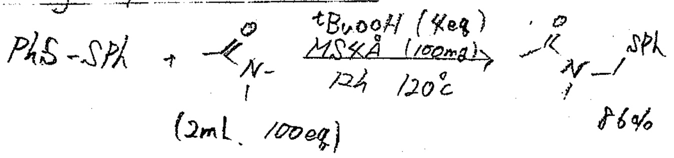
Chem. Commun. DOI: 10.1039/c1cc15397h

This Work

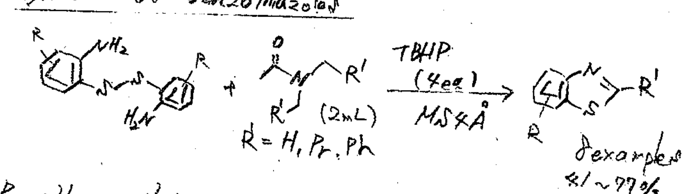


thiolation of C-H bond
← ・Cu(OAc)₂ と O₂ で アリール C-H を C-S へ
JACS (2006) JOC (2010)
・CuI / O₂ で ベンゾオキサゾールの thiolation
TL (2009)

Screening optimal conditions

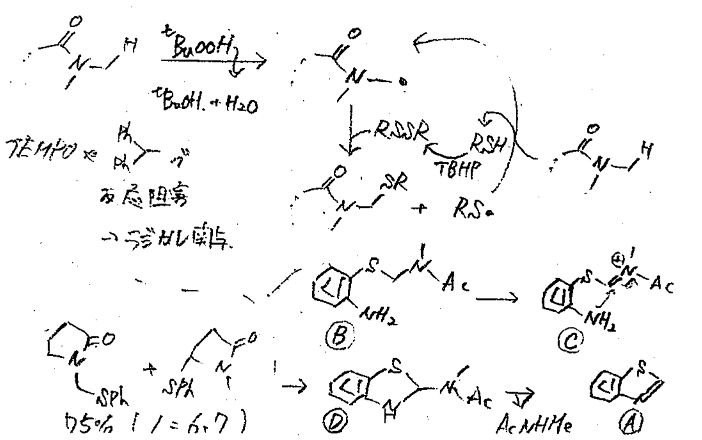


Synthesis of benzothiazoles

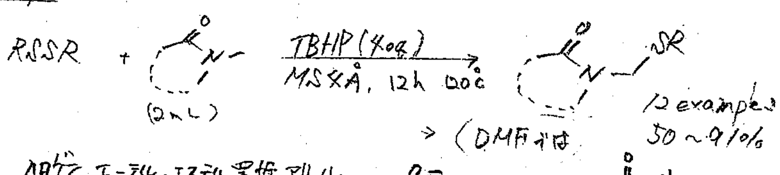


- DDQ では no reaction
- MS4Å の代わりに K_2CO_3 (0.5eq) でも反応進行
  - ↳ MS4Å は弱塩基として溶液の pH を調節している?
- 遮光条件でも反応進行

Possible mechanism



Scope

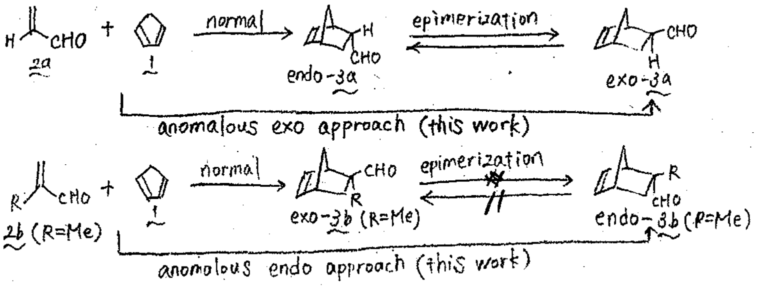


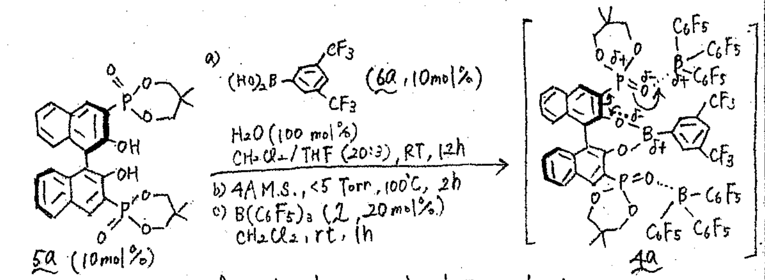
R = ハロゲン、エーテル、エステル置換 アリール
Bn (反応性低)、 ナフタ環

 Angew. Chem. Int. Ed (DOI: 10.1002/anie.201106497)

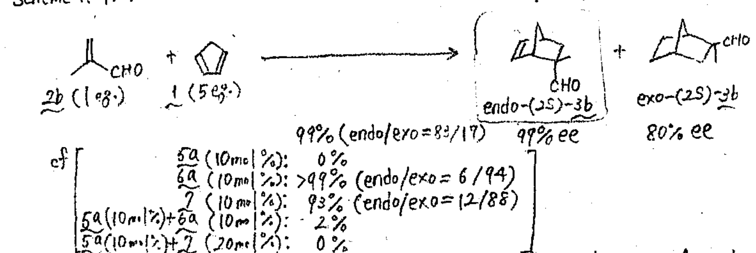
Enantioselective Diels-Alder Reaction with Anomalous endo/exo Selectivities Using Conformationally Flexible Chiral Supramolecular Catalysts

Manabu Hatano, Tomokazu Mizuno, Atsuto Izumiseki, Ryota Usami, Takafumi Asai, Matsujiro Akakura, and Kazuaki Ishihara*

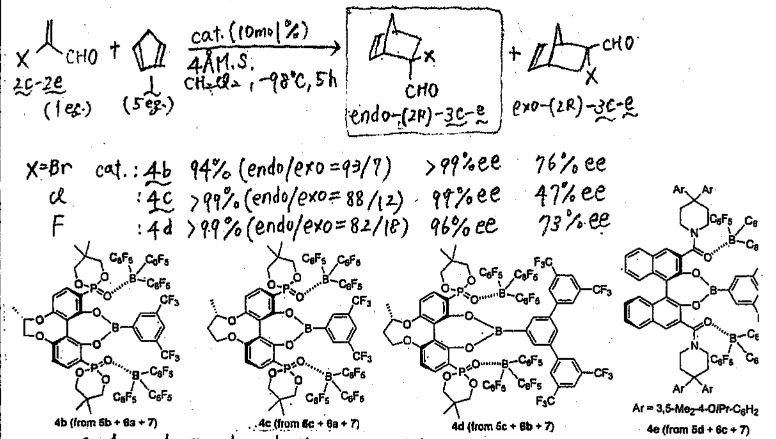




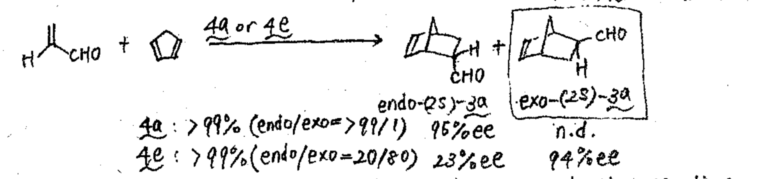
Scheme 1. Preparation of a chiral supramolecular catalyst 4a.



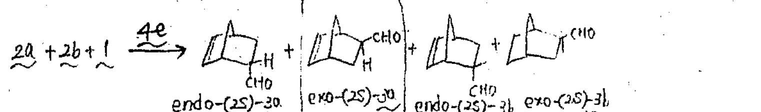
Scheme 2. Anomalous endo-selective asymmetric reaction between 1 and methacrolein (2b)



Scheme 3. Anomalous endo-selective asymmetric reactions between 1 and α-haloacrol...



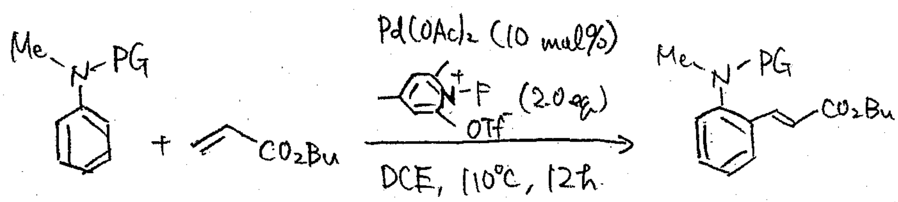
Scheme 4. Highly endo-selective and anomalous exo-selective reaction of 1 with 2a by using chiral catalysts 4a and 4e, respectively.



Scheme 5. Molecular recognition with chiral catalyst 4e in the competitive reaction of 2a and 2b.

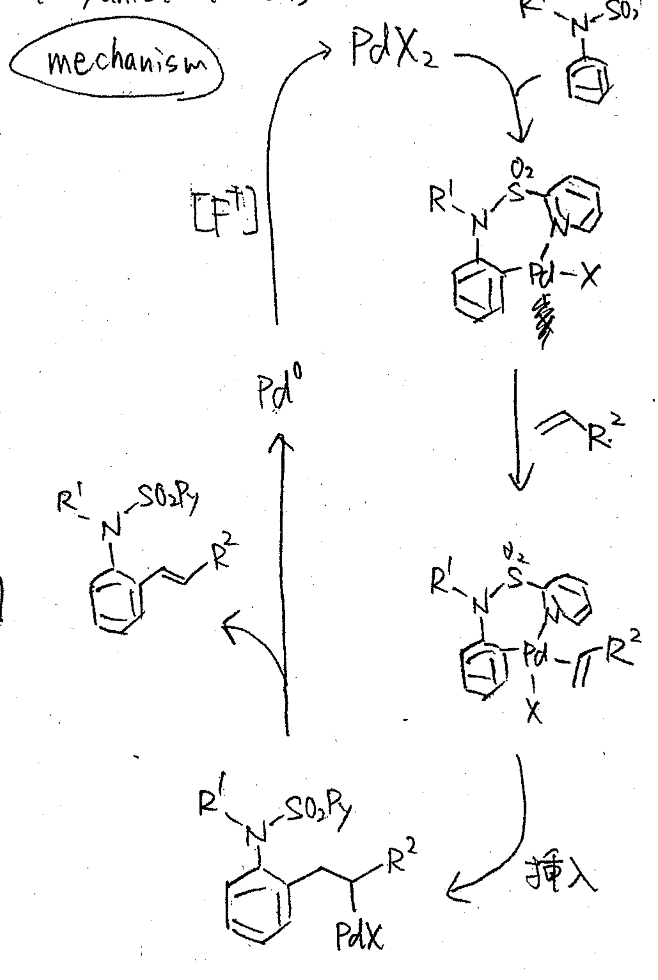
Pd^{II}-Catalyzed C-H Olefination of N-(2-Pyridyl)sulfonyl Anilines and Arylalkylamines (Carretero, J. C. et al, ACIE, 10.1002/anie.201105611)

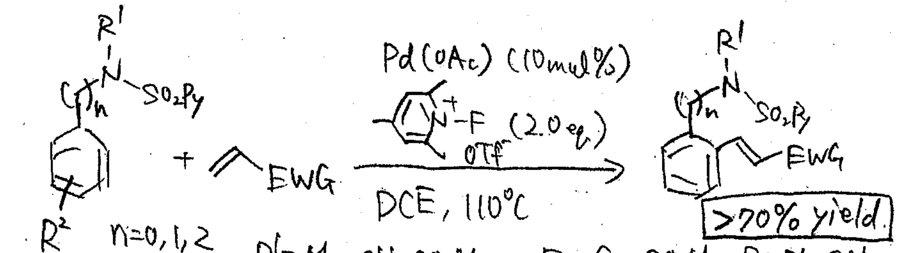
Yuki Ikeda



PG = Boc, Ts, p-Ns, (3-pyridyl)SO_2 : no reaction

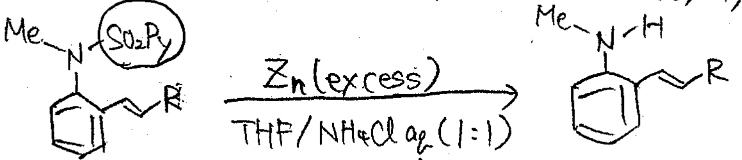
(2-pyridyl) SO_2 : 87%





R^1 = Me, CH_2CO_2Me, EWG = CO_2Me, SO_2Ph, CN

R^2 = Me, OMe, F, Cl, CO_2Me (o, m, p)



R = CO_2Bu : 72%

CN : 65%

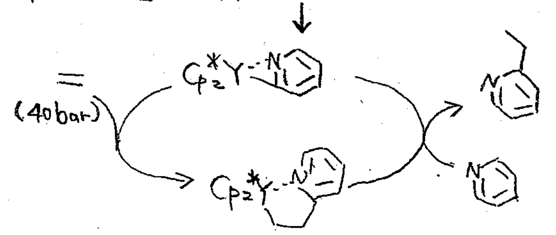
Rare-Earth-Catalyzed C-H Bond Addition of Pyridines to Olefins

Hou, Z. *et al.* *J. Am. Chem. Soc.* **2011** ASAP

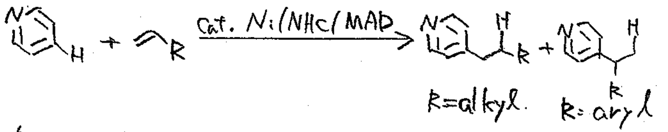
M1 Kawai

- Previous work

$(Cp^*_2YH_2)_2$ + 2pyridine — Teuben et al



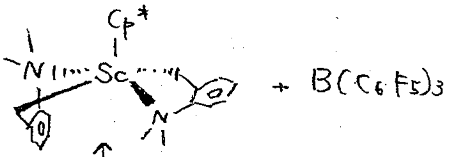
- Nakao et al



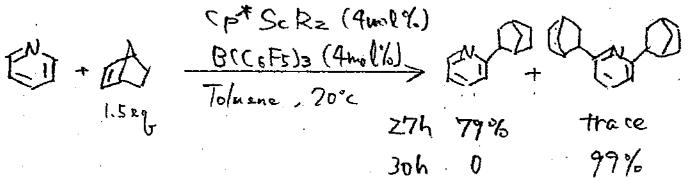
- Present work

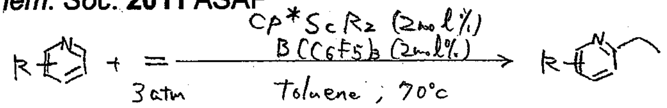
catalyst:

$C_5Me_5Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ = Cp^*LnR_2



excellent catalysts for the polymerization of Olefins.



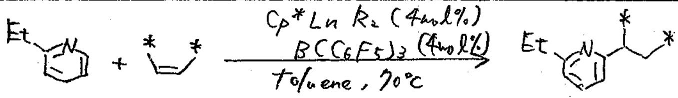


R: Me, Et, i-Pr, t-Bu — yield: 97〜99%

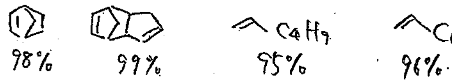
R: Br, I, Ph — yield: 91〜98%

Tetrahydroquinoline: 96% quinoline: 86%

R: t-Bu のとき catalyst: Cp^*YR_2

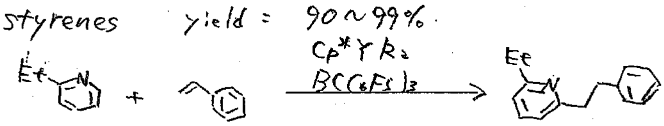


Ln = Sc

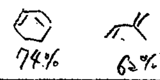


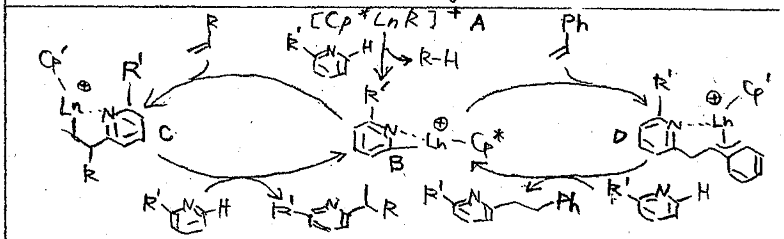
Ln: Y

styrenes yield: 90〜99%



conjugated dienes:





Low-*k* Periodic Mesoporous Organosilica with Air Walls: POSS-PMO

M1 錦織

Makoto Seino,[†] Wendong Wang,[‡] Jennifer E. Lofgreen,[‡] Daniel P. Puzzo,[‡] Takao Manabe, and Geoffrey A. Ozin[*,‡]

JACS. dx.doi.org/10.1021/ja2080136

集積回路 … 多数の素子を1つにまとめたもの
(IC) トランジスタ,抵抗,コンデンサ,コイルなど

近年の発展

・IC(主にトランジスタ)の微細化・高集積化が進む.

★メリット

電子の移動距離が少なくなり、動作速度が向上.

★デメリット

微細化による配線幅が縮小 → 配線の抵抗が上昇.

→ 配線遅延!! (配線間で電荷を蓄えてしまう)

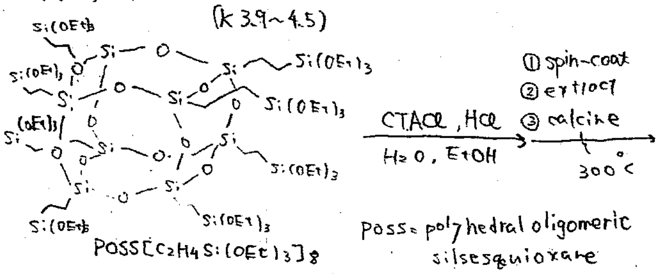
解決策

・配線間の絶縁膜を低誘電率(Low-k)なものにする.

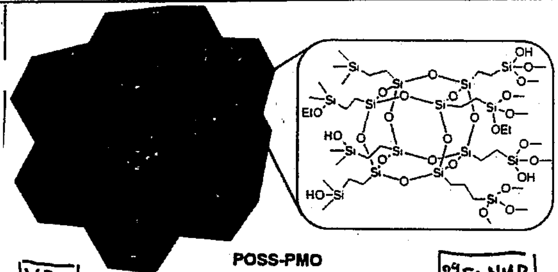
k < 2.2 のものは良いとされる.

今回の仕事

一般的な絶縁膜 SiO_2 → POSS-PMOにする.
(k 3.9〜4.5)



POSS = polyhedral oligomeric silsesquioxane

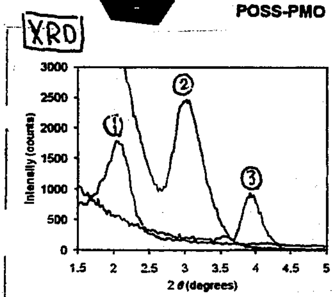


物性評価

→ XRD, TEM, ^{29}Si NMR, ^{13}C NMR, IR, TGA, EP*, SAWS*

* EP … ellipsometric porosimetry
SAWS … surface acoustic wave spectroscopy

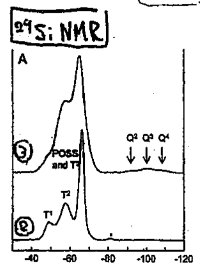
XRD



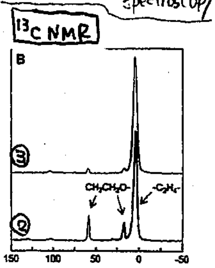
①②③へと処理する度に細孔が小さくなる.
‖
縮合反応が促進されている.

③のピークが小さい
‖
Poss由来の穴が増えて,全体として不規則化。

²⁹Si NMR



¹³C NMR



T_1 = $CSi(OSi)(OR)_2$ Q_2 = $Si(OSi)_2(OR)_2$
T_2 = $CSi(OSi)_2OR$ Q_3 = $Si(OSi)_3OR$
T_3 = $CSi(OSi)_3$ Q_4 = $Si(OSi)_4$
(R = H or Et)

・T_3 → かごが維持

・エトキシ基が②→③で消滅, 縮合している.

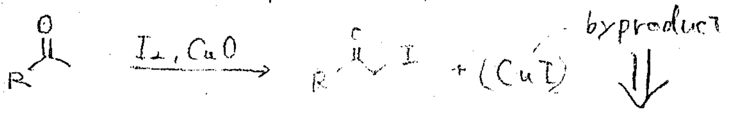
sample	Porosity (%)	ヤング率 [EP] (GPa)	[SAWS]	k
POSS-PMO film	39.0 ± 2.3	2.66 ± 0.39	3.30 ± 0.14	1.73 ± 0.05
POSS-film	4.40 ± 0.5	—	29.6 ± 3.18	2.03 ± 0.07

ヤング率が少し低いが、良いlow-kが得られた.

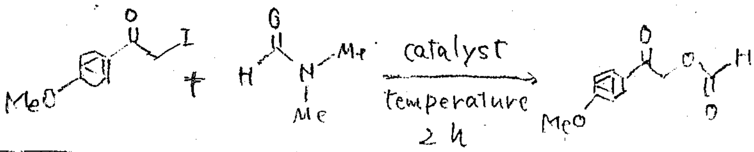
A sustainable byproduct catalyzed domino strategy: facile synthesis of α-formyloxy and acetoxy ketones via iodination/nucleophilic substitution/hydrolyzation/oxidation sequences

An-Xin Wu et al. Chem Commun. DOI: 10.1039/c1cc15819h B4 相馬 啓

<α-Iodination of ketones>

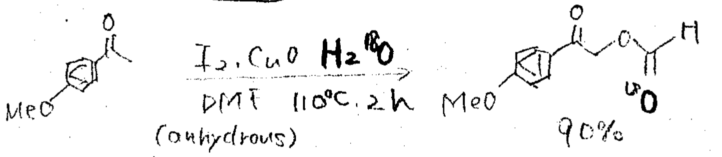


◎ Optimization



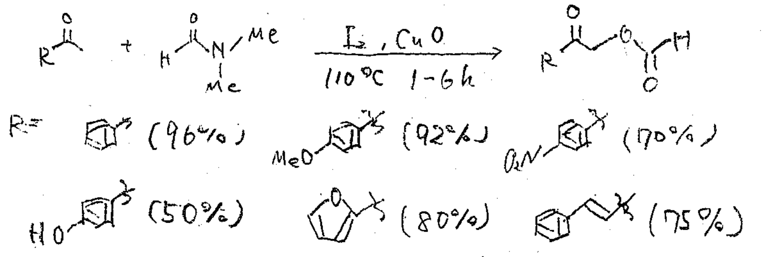
Cat. (equiv)	t (°C)	Yield (%)	Cat. (equiv)	t (°C)	Yield (%)
CuI (1.0)	90	85	$PdCl_2$ (1.0)	90	< 5
—	90	50	CuI (1.0)	110	95
CuO (1.0)	90	75	CuI (1.0)	130	93
$Cu(OAc)_2$ (1.0)	90	60	CuI (0.5)	110	**96**
CuCl (1.0)	90	< 5	CuI (0.3)	110	94
$CuBr_2$ (1.0)	90	40	CuI (0.1)	110	88

◎ Isotope labeling

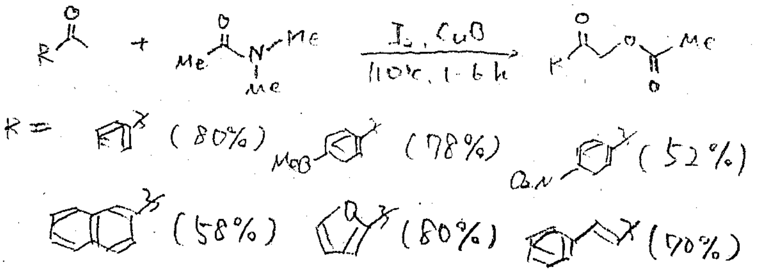


◎ Scope

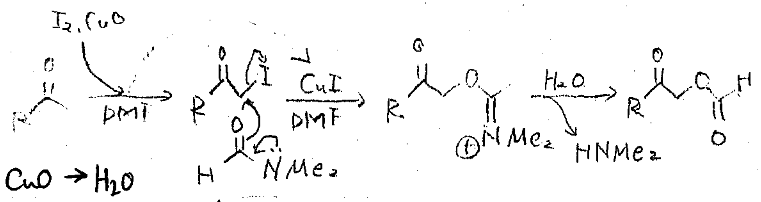
・Reaction of ketones and DMF



・Reaction of ketones and DMA



◎ Reaction Pathway



$2HI + CuO \rightarrow H_2O + CuI + \frac{1}{2}I_2$

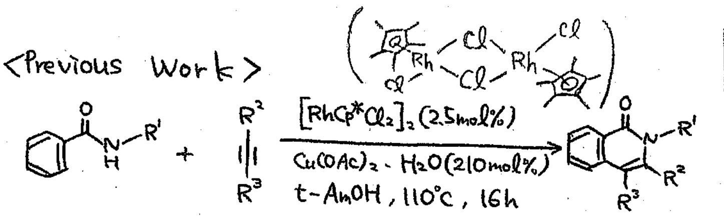
Rhodium(III)-catalyzed oxidative carbonylation of benzamide with carbon monoxide

Ya Du, Todd K. Hyster and Tomislav Rovis*

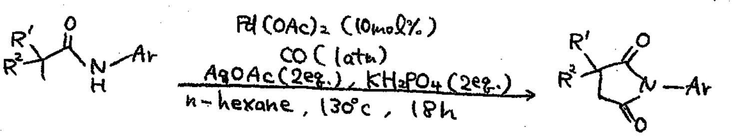
Chem. Commn, 47, 12074 (2011)
DOI: 10.1039/c1cc15843k

B4 利根

<Previous Work>



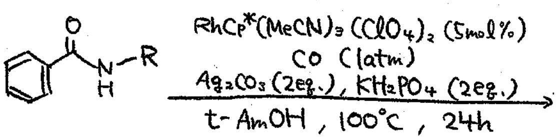
Todd K. Hyster and Tomislav Rovis, JACS, 132, 10565 (2010)

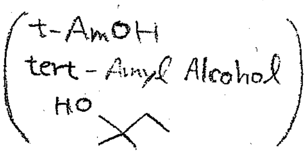


Jin-Quan Yu, et al, JACS, 132, 17378 (2010)

<This Work>

様々なアミドとCOを用いるフタルイミドの合成。





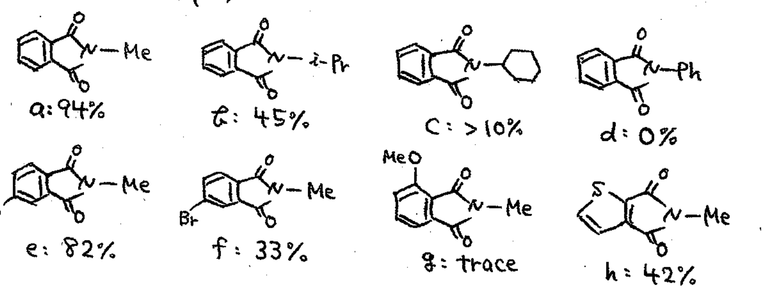
<Optimization>

catalyst : $[RhCp^*Cl_2]_2$, $RhCp^*(MeCN)_3(SbF_6)_2$, $RhCp^*(MeCN)_3(ClO_4)_2$

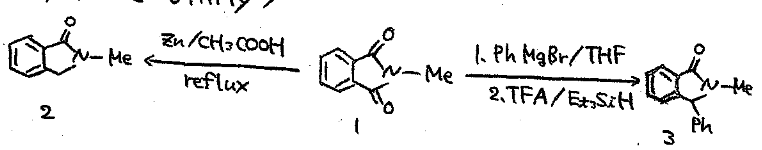
Oxidant : $Cu(OAc)_2$, AgOAc, Ag_2CO_3

Solvent : Dioxane, DCE, t-AmOH

<Reaction Scope>



<Synthetic Utility>



1 → 2 : Clemmensen 還元
1 → 3 : Grignard 試薬との反応
⇒ γ-ラクタムが生成