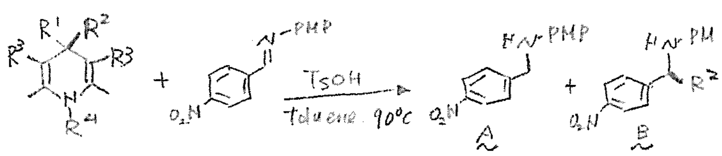
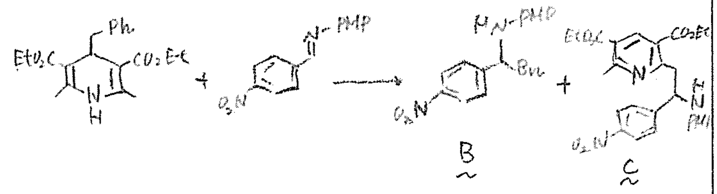
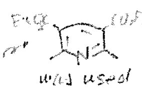
Zhuo Tang et al.	Chinese Academy Science	*ACIE* (anie.201303696)	Minakata

Alkyl Transfer from C-C Cleavage

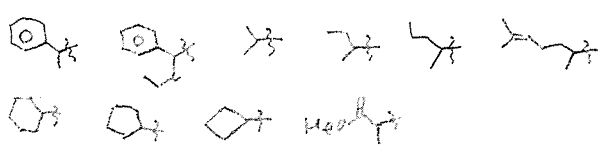


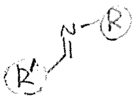
R^1	R^2	R^3	R^4	A	B
Me	Bn	CN	H	–	–
H	Bn	CN	H	80	
H	Me	CO_2Et	H	80	
H	Bn	CO_2Et	H	10	50



additive	solv.	temp (°C)	Yield (%) B	C
TsOH (30 mol%)	toluene	90	50	< 5
TsOH (30 mol%)	toluene	90	–	65 ←  was used
$BF_3 \cdot Et_2O$ (1.2 equiv)	$CHCl_3$	50	80	

R^2 : Bn, (R = 4-Cl, 2F, 4-MeO, 4-Me, 4-OH)





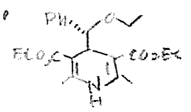
Ⓡ : –Ph, –4-$MeOC_6H_4$, –4-Cl-C_6H_4

Ⓡ' : –Ph, –4-ClC_6H_4, 2-furanyl · · ·

28 examples 70 ~ 92 %

mechanism

- TEMP. AIBN (ルイス酸なしで) 入れても阻害されない } ラジカルではない
- 光も関係ない



キラルな試薬を使っても生成物は 0 %ee

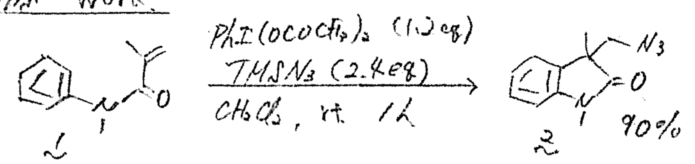
⇓

アニオン反応？

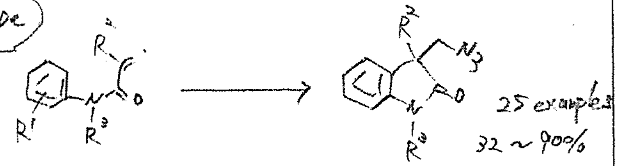
Antonchick, A. P.	Max-Planck-Institut für Molekulare Physiologie Abteilung Chemische Biologie (Germany)	ACIE. anie. 201303550	Okumura

Metal-Free Radical Azidoarylation of Alkenes: Rapid Access to Oxindoles by Cascade C-N and C-C Bond-Formation Reactions

This work



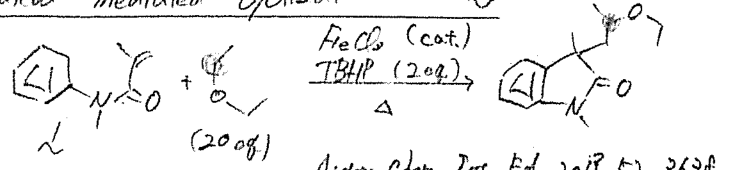
Scope



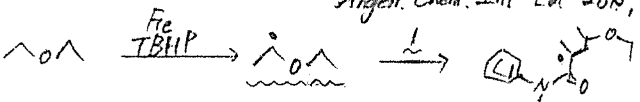
R^1, EWG, EDG, OK. メター → 位置異性体生成

R^2 = Hでは 収率低下。R^2 = Me, Ph, Bn OK
= Ac ダメ

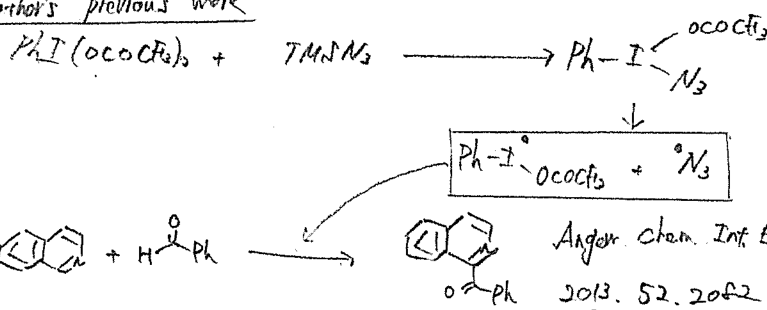
Radical-mediated cyclisation of 1



Angew. Chem. Int. Ed. 2013, 52, 3638.

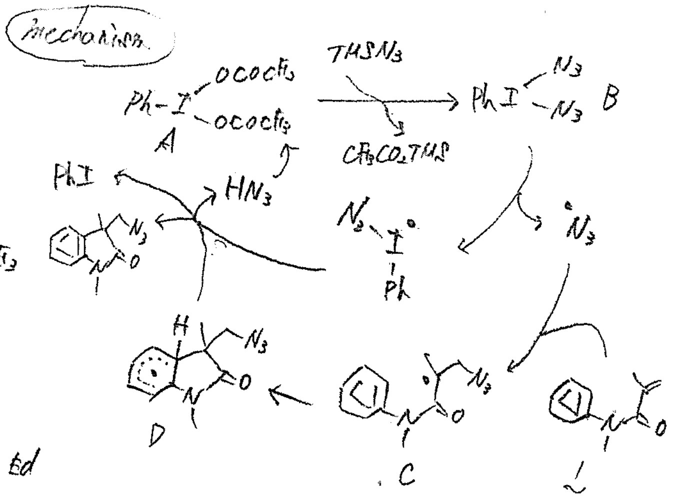


Author's previous work



Angew. Chem. Int. Ed 2013. 52. 2082

mechanism

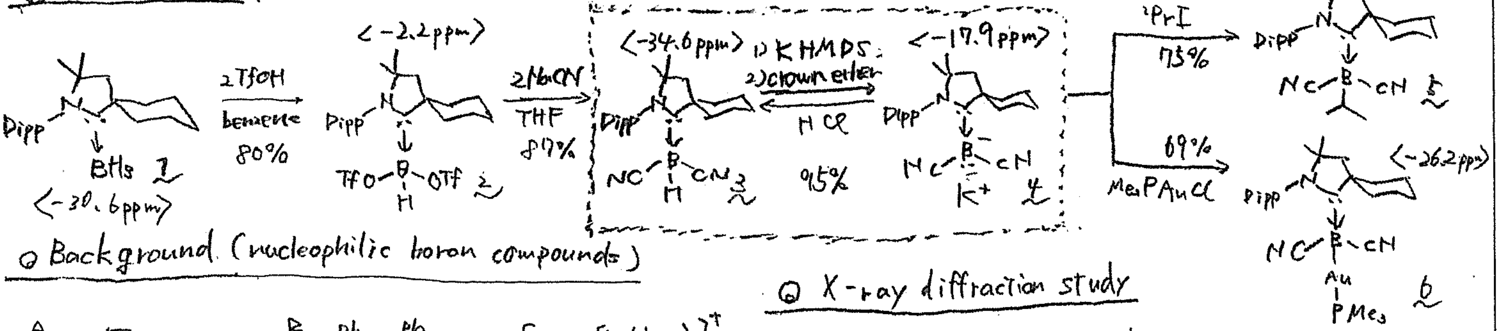


Bertrand, G. et al.	University of California San Diego	Angew. Chem. Int. Ed. 10.1002/anie. 201303457	M2 榎島

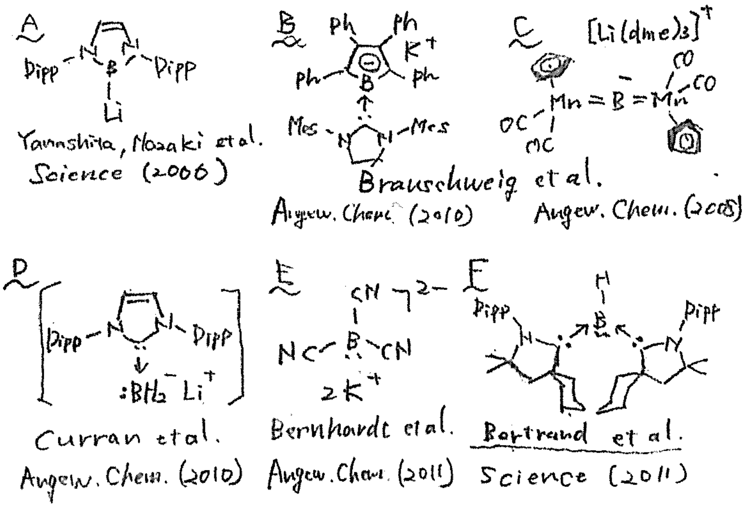
Deprotonation of a Borohydride: Synthesis of a Carbene-Stabilized Boryl Anion

◎ This work

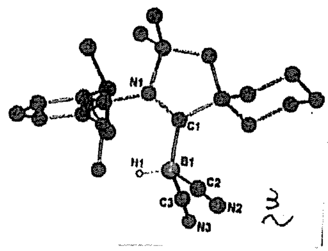
KHMDS = potassium bis(trimethylsilyl)amide



◎ Background (nucleophilic boron compounds)

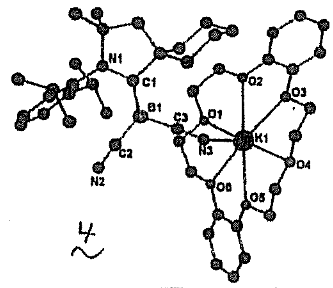


◎ X-ray diffraction study



3

B1 − C2 : 1.605(6) Å
B1 − C3 : 1.595(6) Å
B1 − C1 : 1.617(6) Å
C1 − N1 : 1.294(4) Å

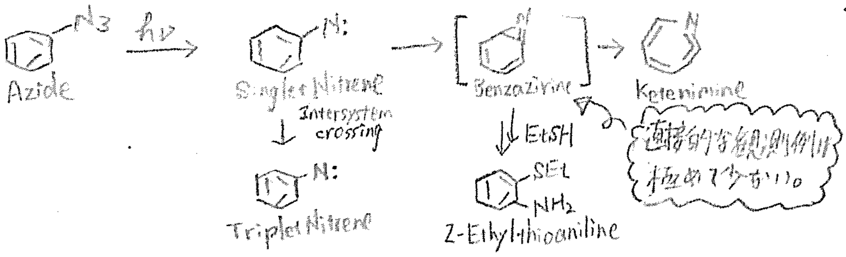


4

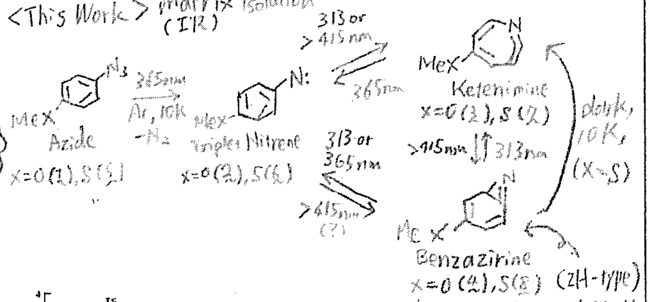
B1 − C2 : 1.553(2) Å
B1 − C3 : 1.552(2) Å
B1 − C1 : 1.473(2) Å
C1 − N1 : 1.396(2) Å

Inui, H.[1,2] McMahon, R. J.[2]	[1] Kitasato University (Japan) [2] University of Wisconsin-Madison (US)	JACS DOI: 10.1021/ja409192s	M2 岡崎

Aryl Nitrene Rearrangements: Spectroscopic Observation of a Benzazirine and Its Ring Expansion to a Ketenimine by Heavy-Atom Tunneling

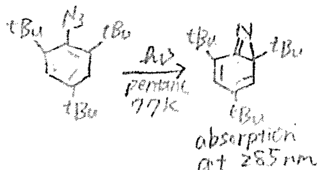


<This Work> matrix isolation (IR)

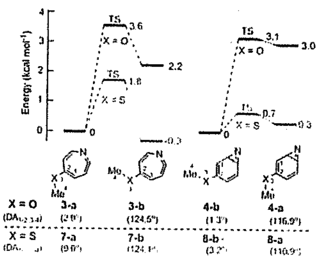


◎ laser flash photolysis

パルス光によって試料を励起して光化学反応などを誘起し、試料の光吸収率の変化を時間的に追跡して、その反応を解析する手段。



Tsao, M.-L.; Platz, M. S. J. Am. Chem. Soc. 2003, 125, 12014.

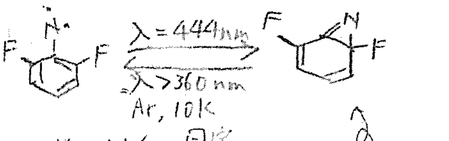


・DFT計算で求めた波数と実測値の比較
・3a, 4a のピークパターンがほぼ一致
3a (1100~1250 cm^{-1})
4a (900~1200, 1500 cm^{-1})
・7a, 7b, 8a, 8b は不明

◎ matrix isolation

不安定で反応性の高い化学種を低温で反応性の低い固体(マトリックス)の中に埋め込み、寿命を長くし観測する方法。

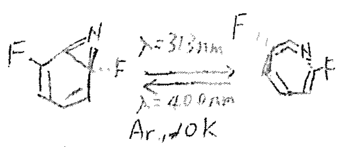
(マトリックス ⇒ Ar, N_2 など
分析方法 ⇒ 分光法)



(2F-type)

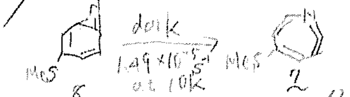
・IR, UVで同定

Morawietz, J.; Sander, W. J. Org. Chem. 1996, 61, 4351.



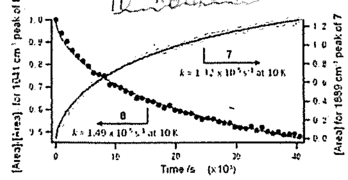
・IR, UVで同定

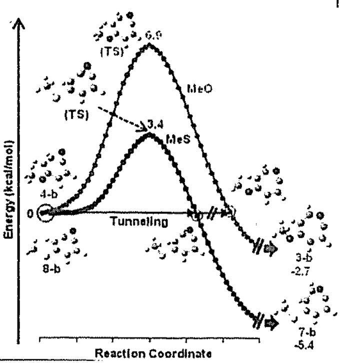
Carra, C.; Nussbaum, R.; Bally, T. ChemPhysChem 2006, 7, 1268.



計算⇒rate constant ≈ 2.09×10^{-63} s^{-1}

10^{57}倍高い値

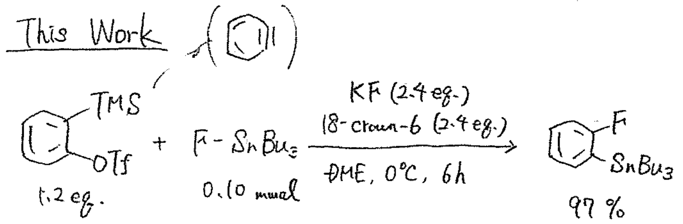




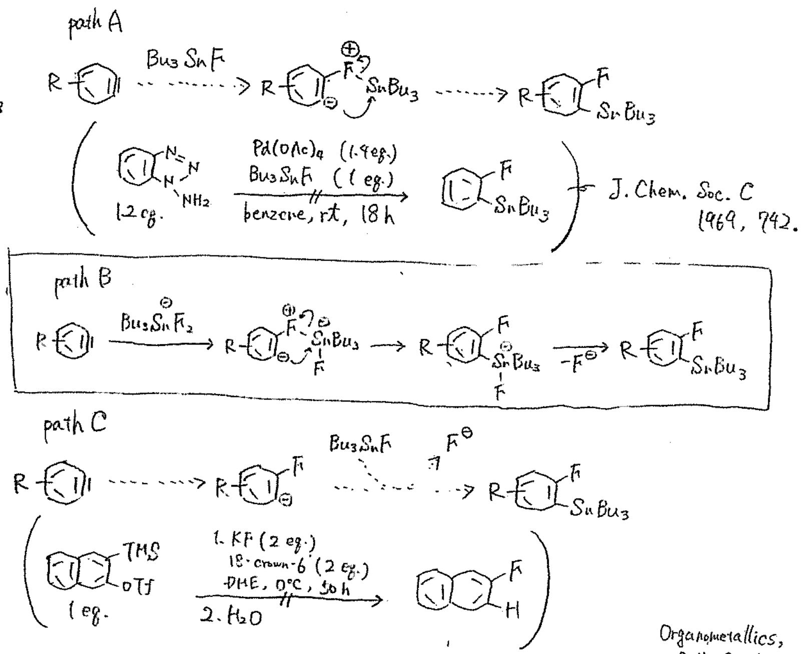
Yoshida, H	Hiroshima University (Japan)	ACIE 10.1002/anie.201302783	M2 西田

Synchronous Ar-F and Ar-Sn Bond Formation through Fluorostannylation of Arynes

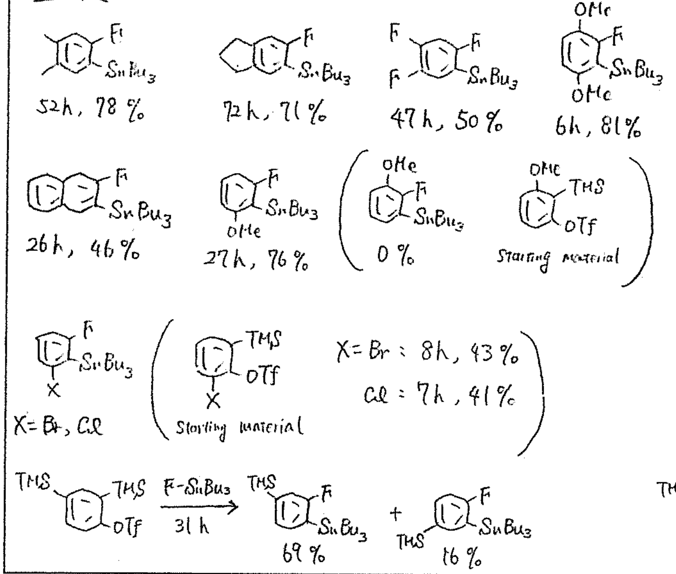
This Work



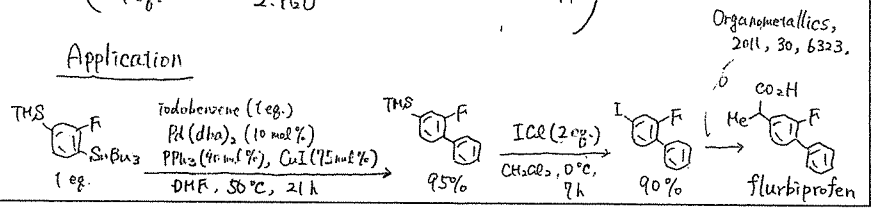
Plausible Pathways



Scope



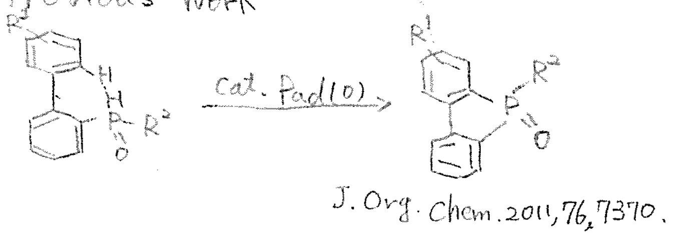
Application



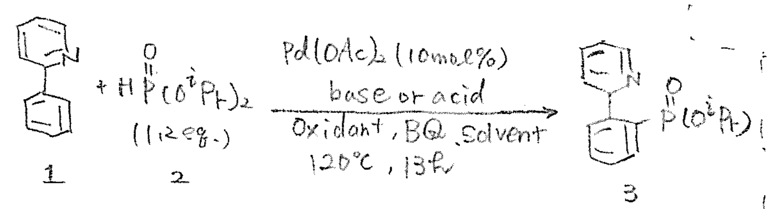
Jin-Quan Yu et al.	The Scripps Research Institute (USA)	JACS 10.1021/ja404526x	M2 Hisakuni

Pd(II)-Catalyzed Phosphorylation of Aryl C-H Bonds

Previous Work



This Work



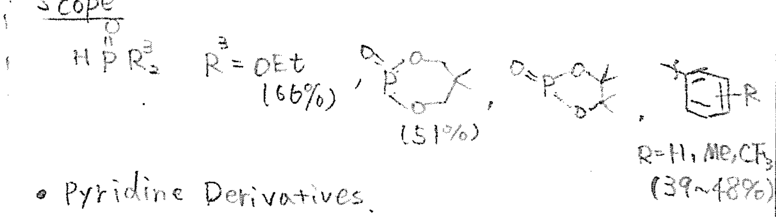
Optimization

- Solvent : (t-AmylOH), DCE, MeCN, toluen
- Oxidant : (AgOAc), AgPO4, AgCO3, Cu(OAc)2
- base/acid : (NaOAc), Na2CO3, PivOH, AcOH

⇓

3 : 84%

Scope

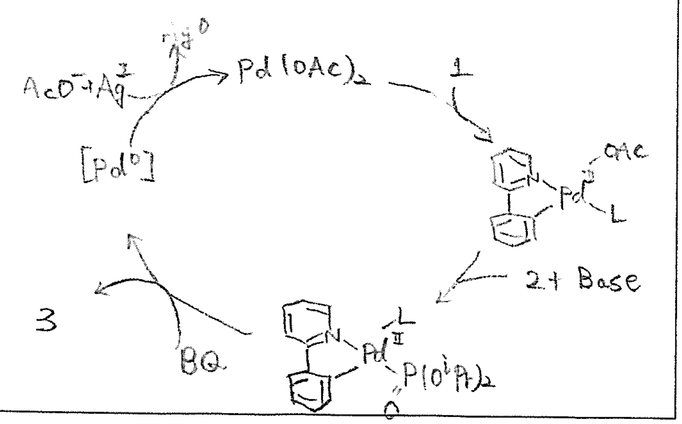


- Pyridine Derivatives

R4 = Me, OMe electron-donating group ⇒ 70~80%

F, CF3, CO2Me electron-withdrawing group ⇒ 42~58%

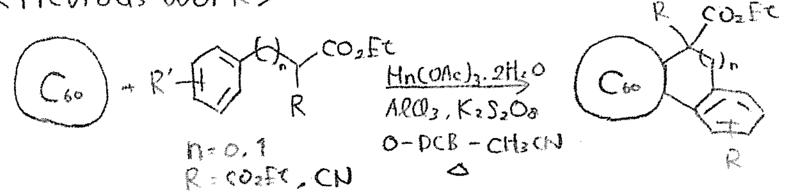
Mechanism



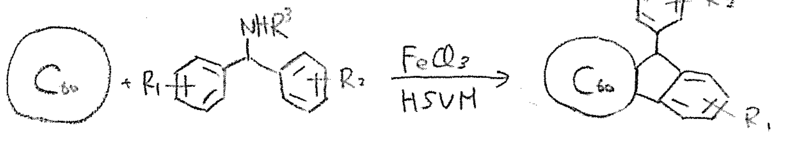
Guon-Wu Wang	University of Science and Technology of China	ORGANIC LETTERS 10.1021/ol401962	M1 上田

FeCl3-Mediated Cyclization of [60] Fullerene with N-Benzhydryl Sulfonamides under High-Speed Vibration Milling Conditions

<Previous Work>

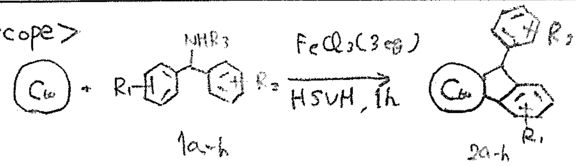


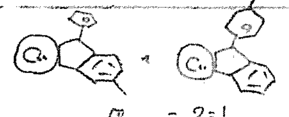
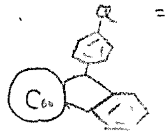
<This Work>



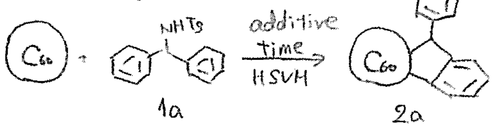
- solvent-free mechanochemical condition

<Scope>



Entry	1	2	yield
2	R1 = 4-Me, R2: H, R3 = Ts	 = 2:1	15 (35)
4	R1 = H, R2 = 4-Cl, R3 = Ts		38 (61)

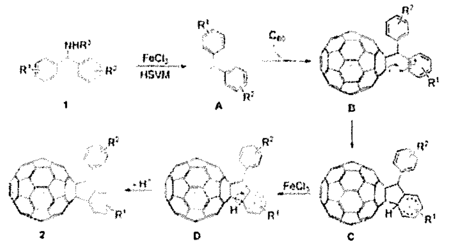
<Screening Conditions>



Entry	additive	molar ratio	time (h)	yield (%)
1	FeCl3	1:2:2	1	23 (56)
②	FeCl3	1:2:3	1	27 (66)
3	FeCl3	1:2:3	1.5	25 (60)
4	FeCl3·6H2O	1:2:2	1	trace
⋮		⋮		⋮
12				

※ molar ratio = C60 / 1a / additive
※ 5~12 は additive を様々変えたが収率は 0%　※2a は過去に報告例なし

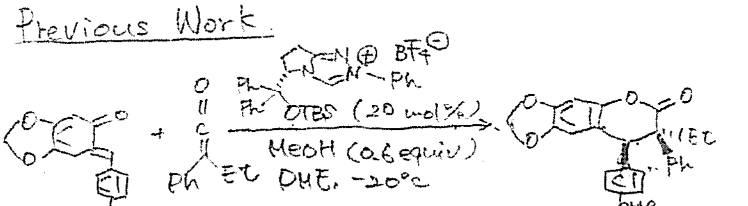
<plausible mechanism>



Song Ye. et al	Chinese Academy of Sciences (China)	Angew. Chem. Int Ed. DOI: 10.1002/anie 201303903	M1 黒田

N-Heterocyclic Carbene Catalyzed [4+3] Annulation of Enals and o-Quinone Methides: Highly Enantioselective Synthesis of Benzo-ε-Lactones

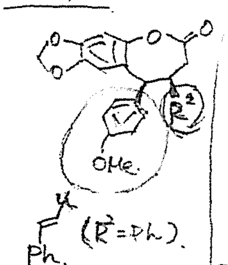
Previous Work



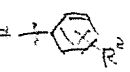
0.2 mmol　2.0 equiv.　95%, d.r. = 7:1, (cis/trans) ee cis 90% ee, trans 95% ee

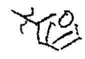
S. Ye et al. Adv. Synth. Catal 2009, 351, 2822.

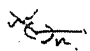
Scope



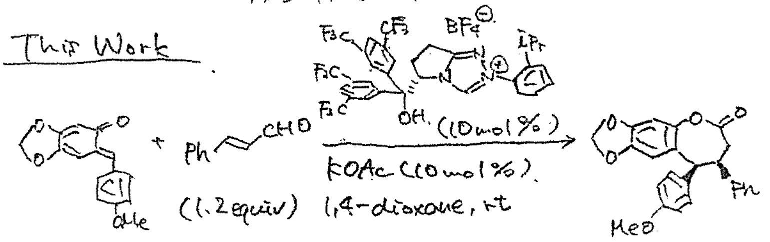
91% yield
d.r. = 3:1
ee (cis) = 93% ee

R2 = 
R3: o位, m位, p位, EDG, EWG のどれでも.
92~96% yield, d.r. = 3:1 or 4:1
ee (cis) = 81~95% ee.

R2 =  95% yield, d.r. = 5:1, ee (cis) = 94% ee.

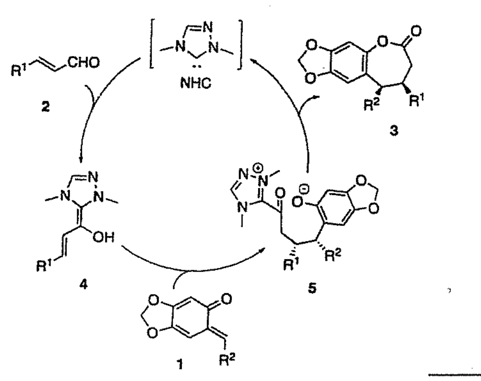
 83~97% yield. d.r. > 20:1, n=1~6. ee (cis) = 93~98% ee

This Work

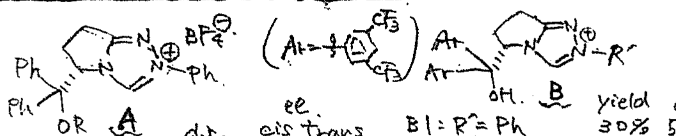


98%, d.r. 4:1, (cis/trans)
cis: 99% ee, trans: 40% ee

Proposed catalytic cycle



Optimization of NHC catalyst



	R	yield	d.r.	ee cis	ee trans
A1	R = TBS	trace	n.d.	n.d.	n.d.
A2	R = H	49%	5:1	96% ee	n.d.
B1	R′ = Ph	30%	5:1	90	15
B2	R′ = Bn	63%	2:1	84	23
B3	R′ = 2-iPrC6H4	90%	4:1	94	40

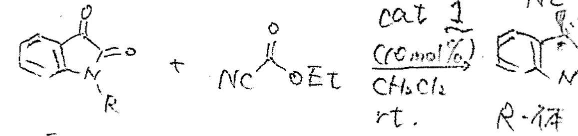
Ishihara, K	Nagoya University	Angew. Chem. Int. Ed 10.1002/anie.201303572	M1 小坂

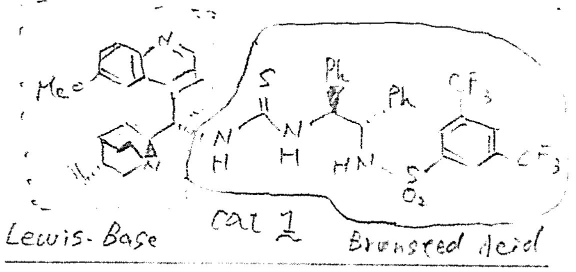
Enantioselective Cyanoethoxycarbonylation of Isatins Promoted by a Lewis Base - Brønsted Acid Cooperative Catalyst.

カルボニルの不斉シアノ化.
⇒ 4級炭素中心を構築

従来…・H-CN や Si-CN 等の
　毒性の高い原料
　・生成物が不安定

▽ This work

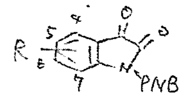




R	Yield (%)	ee (%)
Me	73	65
Bn	71	72
p-MeO-Benzyl	41	61
p-NO2-Benzyl (PNB)	94	95

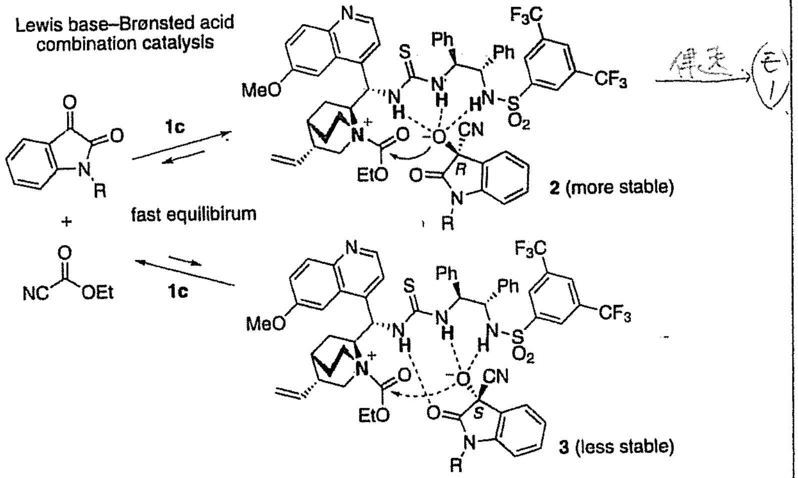
・cat 1. (5 mol%)
・MeOH (50 mol%)
・in CHCl3

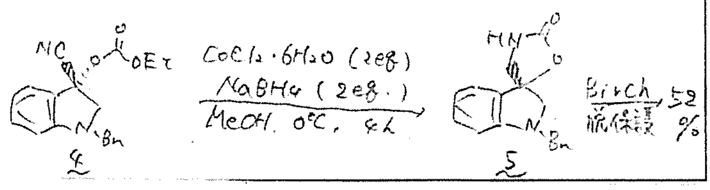
▽ Scope



・5-位に置換基 … 85～98%, 95～98% ee
・4, 5, 6, 7位のいずれかに Br … 87～98%, 94～99% ee
・5,7-位や 5 6-位の2置換 … 61～75%, 88～94% ee.

▽ Mechanism

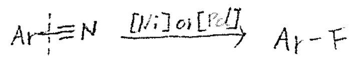




Ning Jiao	Peking University (China)	*ACIE*, anie.201303376	M1 矢羽田

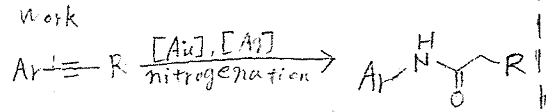
Selective C_{sp^2}–C_{sp} Bond Cleavage: The Nitrogenation of Alkynes to Amides

Previous C_{sp^2} – C_{sp} Cleavage

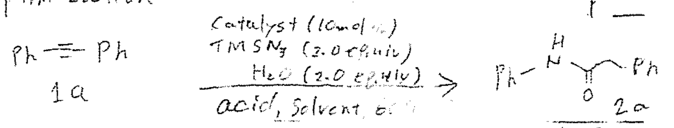


ほとんどの反応が
アリール-シアノ結合に限定

This Work

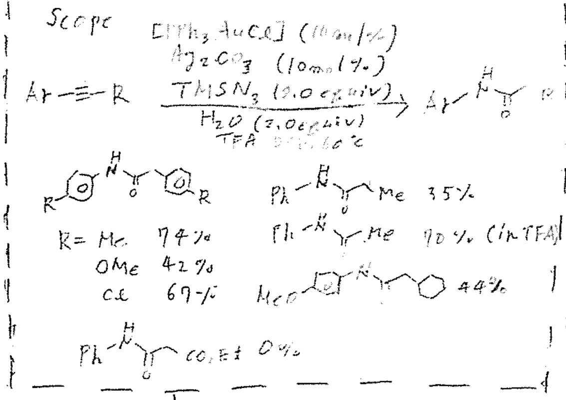


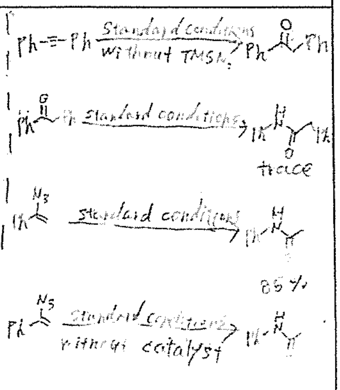
Optimization



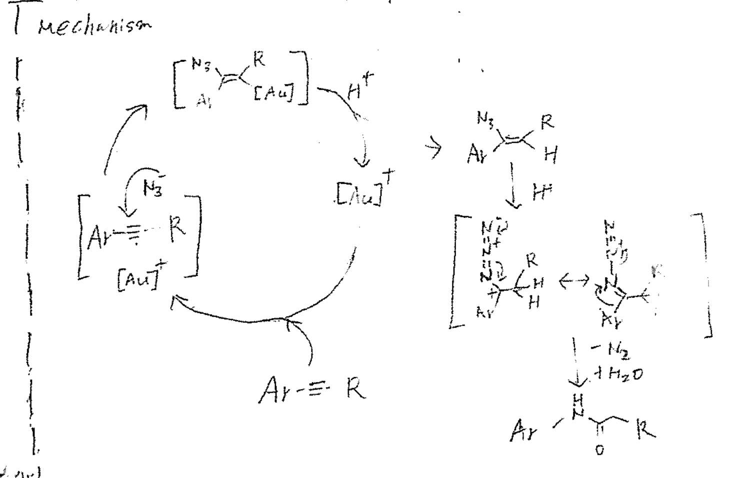
Catalyst	Acid	Solvent	Yield of 2a
Cu(OAc)2	TFA	DCE	0
PtCl4	TFA	DCE	0
AuCl3	TFA	DCE	0
[PPh3AuCl]/Ag2CO3	TFA	DCE	52
[PPh3AuCl]	TFA	DCE	9
Ag2CO3	TFA	DCE	0
[XPhosAuCl]/Ag2CO3	TFA	DCE	4
[PPh3AuCl]/Ag2CO3	TfOH	DCE	15
[PPh3AuCl]/Ag2CO3	TFA	PhCl	41
[PPh3AuCl]/Ag2CO3	TFA	DCE	72 ← TMSN3 2回に分けて添加

Scope



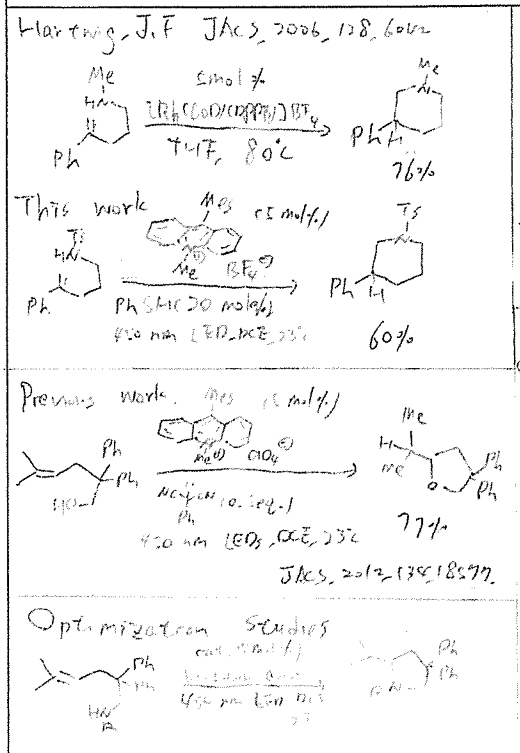


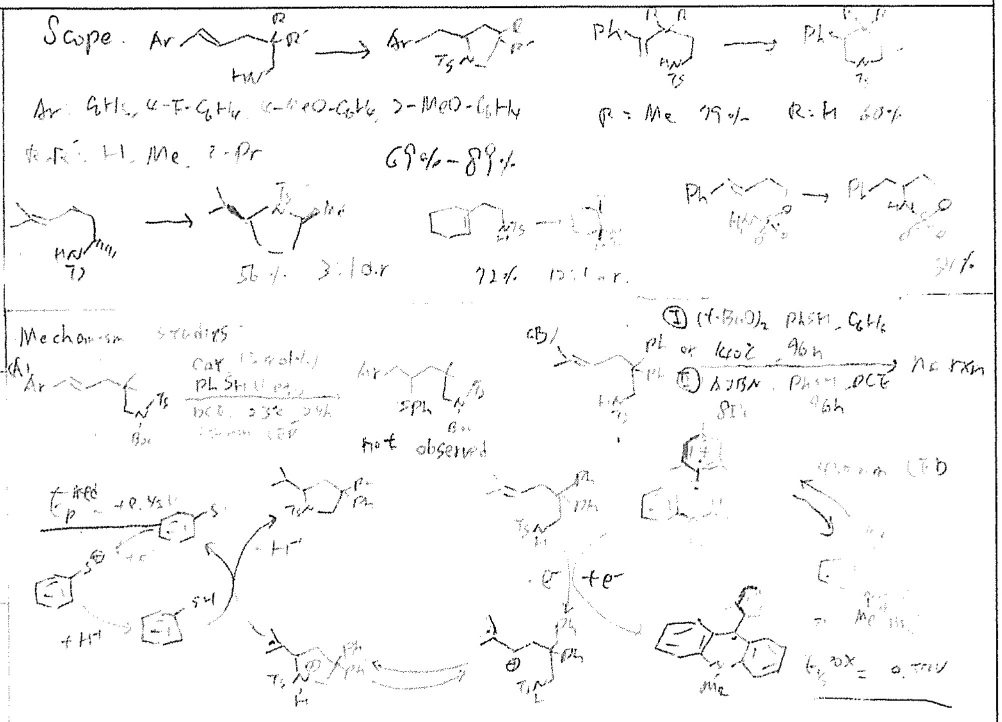
Mechanism



David A. Nicewicz	UNC Chapel Hill	ja4031616	Lin

Anti-Markovnikov Hydroamination of Alkenes Catalyzed by an Organic Photoredox System





R=Ts

H donor

1 eq PhCH2CO2H 16% 0.5 eq PhSH 66%

1 eq PhSH 41% 0.2 eq PhSH 70%

0.2 eq PhSH

R=H <5%

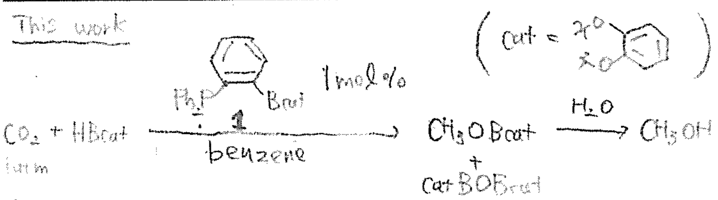
R=Bn 15%

R=Boc 65%

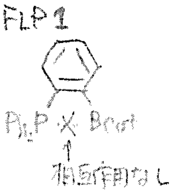
Frederic-Georges Fontaine	Laval University (Canada)	JACS, 10.1021/ja404585p	B4 永田

A Highly Active Phosphine−Borane Organocatalyst for the Reduction of CO_2 to Methanol Using Hydroboranes

This work



FLP 1



$^{31}P\{^1H\}$ NMR −4.57 ppm

$^{11}B\{^1H\}$ NMR 33.1 ppm

X線結晶構造解析

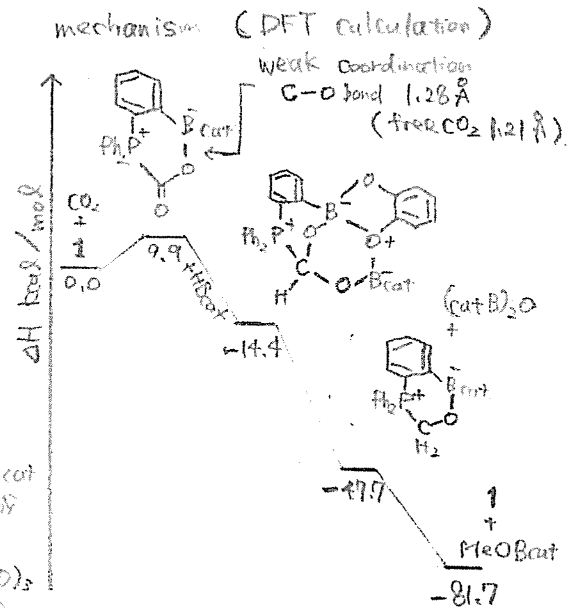
P−B 3.28 Å

entry	borane	temp(℃)	time	TON[a]	TOF (h^{-1})	yield(%)	
1	HBcat	23	24h	69	3	69	CH_3OBcat 生成
2		70	36min	86	143	86	
3			98min	92	56	92	
4	$BH_3 \cdot SMe_2$	23	14h	257	18	86	$(CH_2OBO)_3$ 生成
5		70	13min	211	973	70	
6			67min	271	242	90	

a Based on mole of B-H consumed per mole of 1

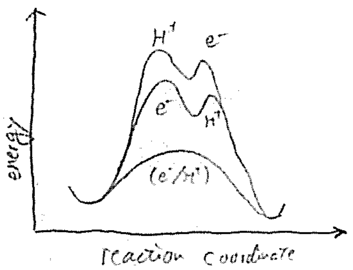
BH_3を水素源として用いた初めての例

mechanism (DFT calculation)

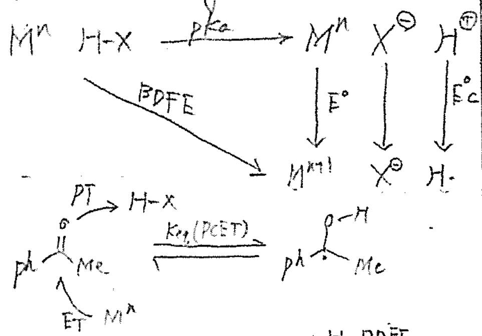


Robert R. Knowles | Princeton University JACS 10.1021/ja404354d | B4 畑中

Catalytic Ketyl-Olefin Cyclizations Enabled by Proton-Coupled Electron Transfer



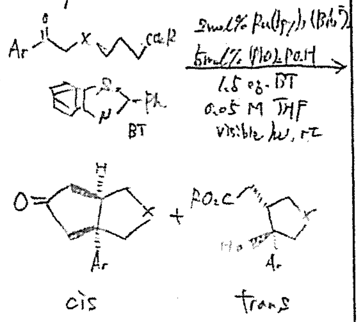
Research Design



BDFE in MeCN (kcal/mol)
$= 2.3RT\,pK_a(HX) + 23.06E^{\circ}(M^n) + 54.9$

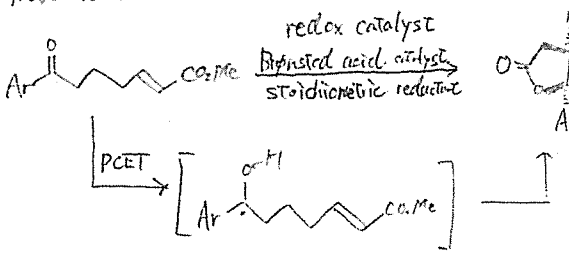
O-H BDFE
~26 kcal/mol

Scope



X = C, O, N-Ts
Yield 64~96%
cis : trans
1.2 : 1 ~ 1 : 0

This work



(PCET = Proton-Coupled Electron Transfer)

Mechanism of ketyl formation

X. electron transfer → proton transfer

X proton transfer → electron transfer

Proposed Catalytic Cycle