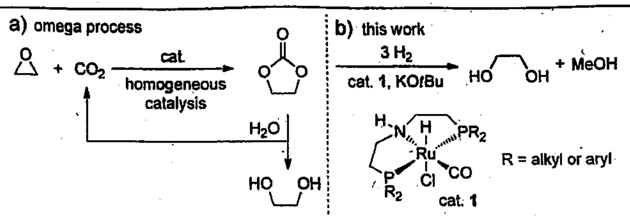
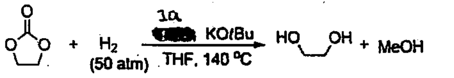
Kuiling Ding et al.	Shanghai Institute of Org. Chem.	*ACIE* (anie.201207781)	Minakata

Catalytic Hydrogenation of Cyclic Carbonates: A Practical Approach from CO_2 and Epoxides to Methanol and Diols

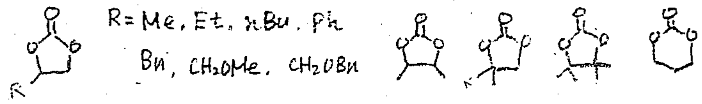




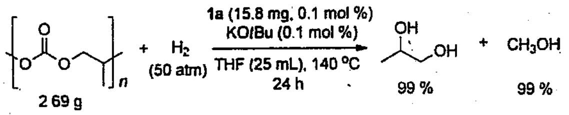
cat. 1g : R = Ph
1g と KOtBu は等量

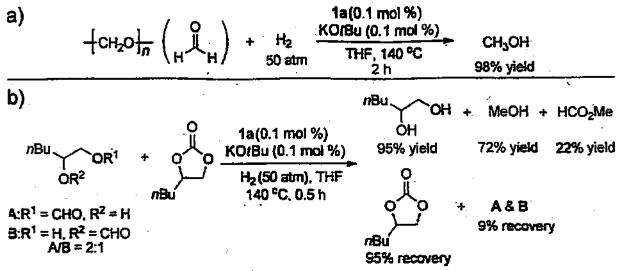
1a (0.01 mol%) 48h >99% >99%
1a (0.001 mol%) 72h 87% 84% (H_2: 60 atm)

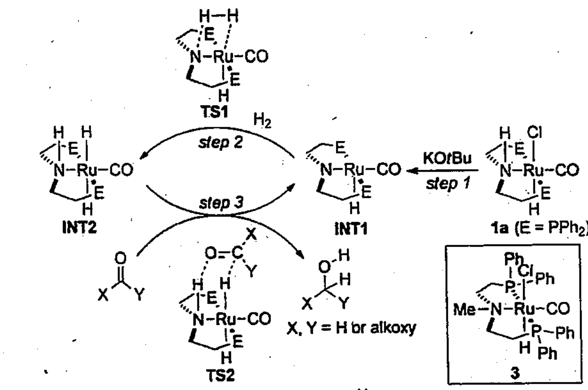
Scope

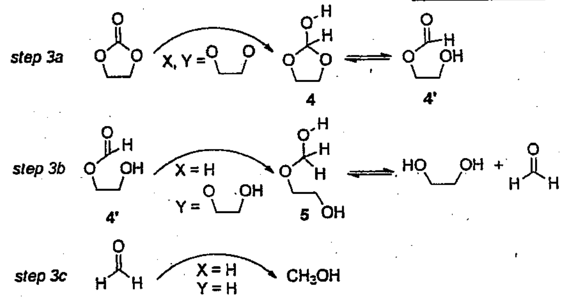


95 ~ 99%







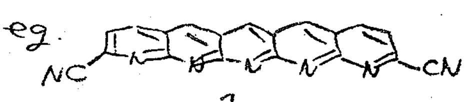


Qichun Zhang	Nanyang Technological University, Singapore	*J. Am. Chem. Soc. ASAP* (doi: 10.1021/ja310131kl)	Youhei Takeda

Synthesis and Physical Properties of Four Hexazapentacene Derivatives

※ aza acenes : candidates for n-type organic materials

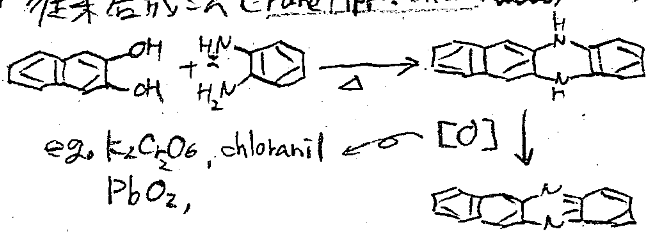
eg.



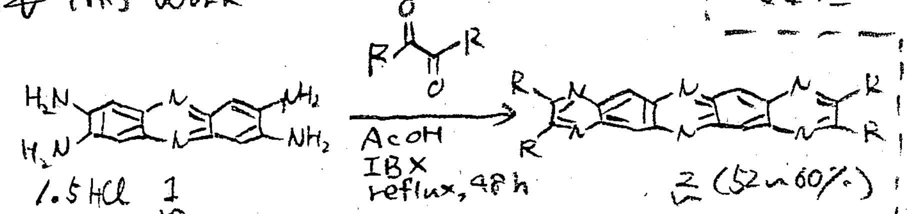
EA 3.27 eV　3 < EA < 4 が理想

JACS 2007, 129, 1805.

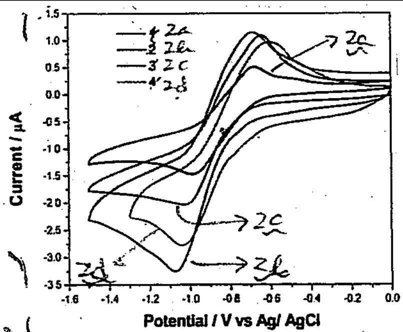
※ 従来合成法 (Pure Appl. chem. 2010, 953.)

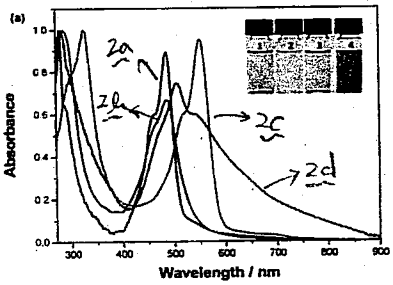


※ This Work



(R = Me: 2a, Et: 2b, [structure]: 2c, [structure]: 2d)





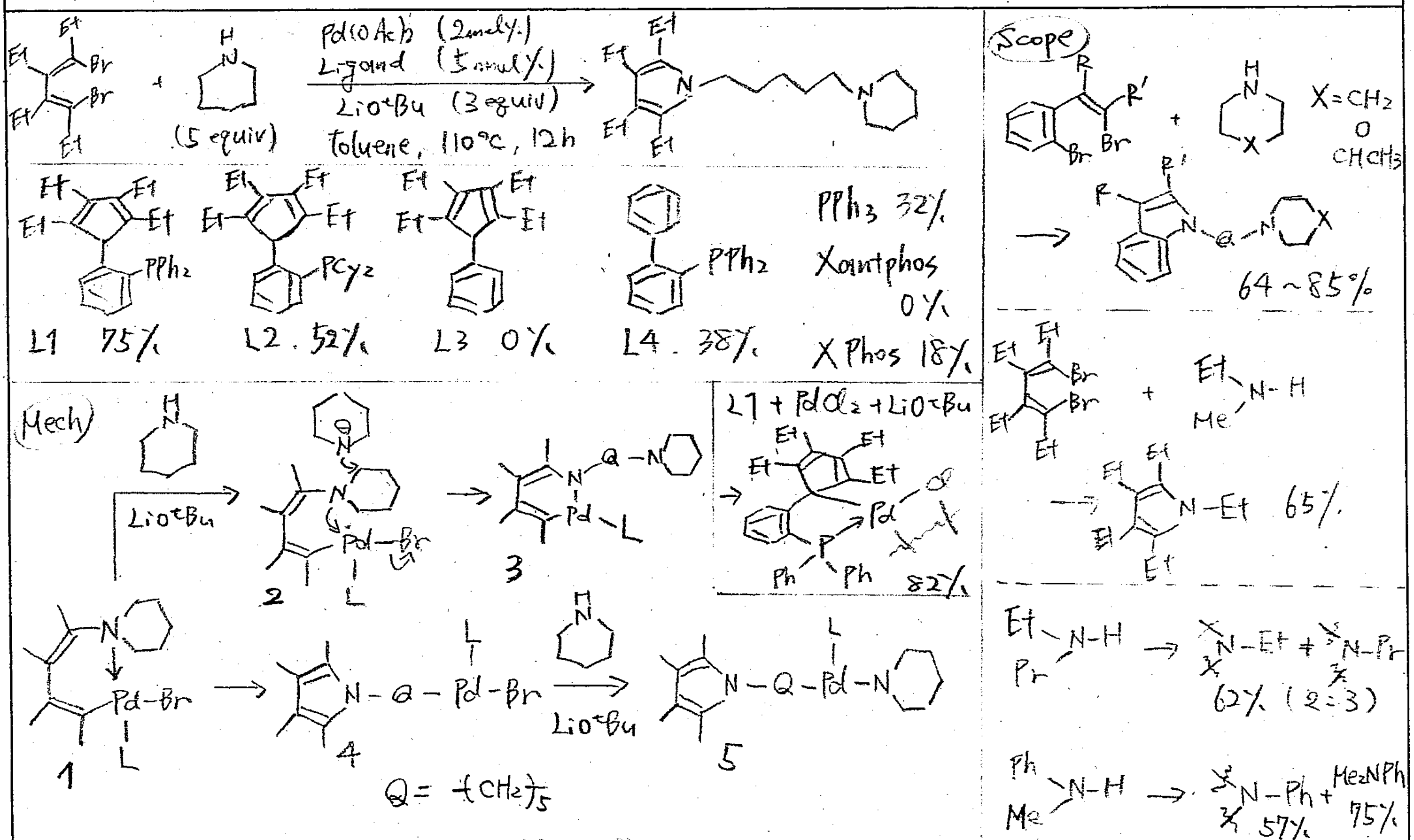
UV absorption spectra in DMF

※ HOMO が対応する acene に対して著しく低い → air に対する安定性

Compd	HOMO/eV	LUMO/eV	ΔE/eV
2a	−6.12	−3.57	2.55
2b	−6.08	−3.53	2.55
2c	−6.03	−3.58	2.45
2d	−5.84	−3.59	2.25
cf.			
pentacene	−5.14	−3.37	1.77
hexacene	−4.96	−3.56	1.57

Zhenfeng Xi	Peking University (China)	*JACS* 10.1021/ja308950d	清川

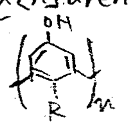
Cyclopentadiene−Phosphine/Palladium-Catalyzed Cleavage of C−N Bonds in Secondary Amines: Synthesis of Pyrrole and Indole Derivatives from Secondary Amines and Alkenyl or Aryl Dibromides



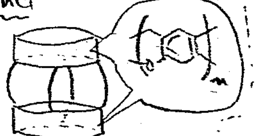
Chiu Sheng-Hsien	National Taiwan University	ol3027957	Nagamachi

Hemicarceplex Formation With a Cyclotriveratrylene-Based Molecular Cage Allows Isolation of High-Purity (≥99.0%) C_{70} Directly from Fullerene Extract

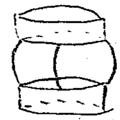
• calix[n]arene 林



• carcerand 牢籠



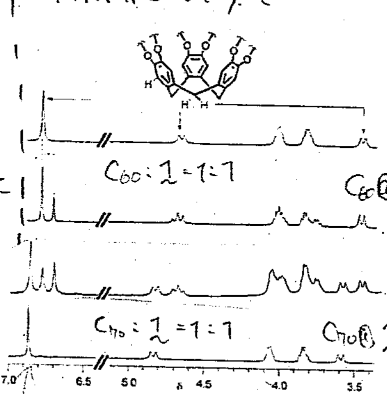
o hemicarcerand



o cavity 内の分子を取り出すには carcerand を壊す必要あり

☆ 熱により分子の出し入れが可能

o ^{1}H NMR study ($CDCl_2CDCl_2$, 298K)



1 ではシフトは見られない

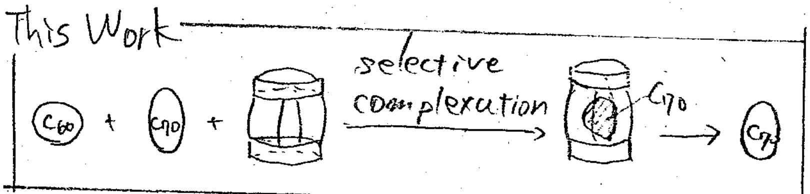
C_{60}@1 単離できない。

fulleren extract + 1 after heating 333K for 48h

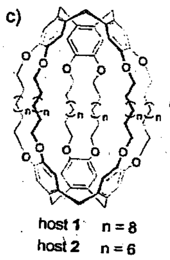
カラムで単離可能

ESI Mass: m/z = 2569.3

This Work



今回の Host Molecule



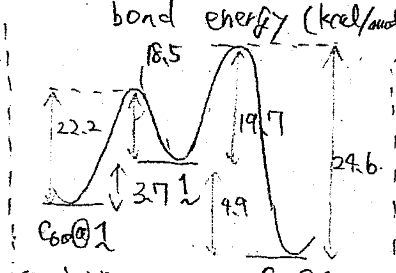
7 steps

total yield

n=8 ; 0.8%

n=6 ; 1.4%

o Constrictive and intrinsic bond energy (kcal/mol)



☆ selective separation of C_{70} from fullerene extract

1 + fullerene extract (300mg), C_{60} : C_{70} : others = 68 : 25 : 7

↓ in toluene at 303K, 12h

centrifuge

↓ in CH_2Cl_2

centrifuge

↓

pure C_{70} (6.5mg) (purity 99.0%)

↓ CH_2Cl_2 at 313K, 16h

3過、濃縮

↓

カラム

↓

濃縮

C_{60}@1 : K_a = 4200 M^{-1}

C_{70}@1 : K_a = 500 M^{-1}

association rate constant: k = 1.026 $M^{-1}s^{-1}$, k = 0.164 $M^{-1}s^{-1}$

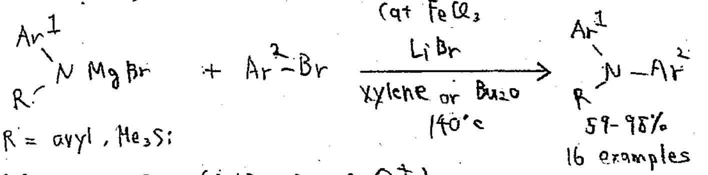
◎ 不純物に C_{76}@1 がある

ホストの n を変えて higher fullerene のみを選択的に抽出できる可能性アリ!!

Masaharu Nakamura	Kyoto University, Japan	JACS DOI: ja309845kl	D2 早川純平

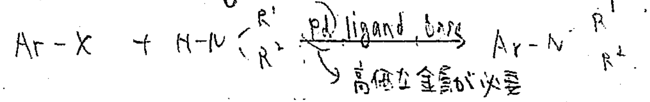
Iron-Catalyzed Aromatic Amination for Nonsymmetrical Triarylamine Synthesis

<Reaction>

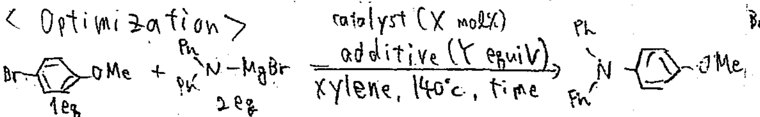


<Previous work> (トリアリールアミンの合成)

Buchwald – Hartwig Reaction



<Optimization>



entry	catalyst (X mol%)	additive (Y equiv)	time (h)	yield (%)	recovery (ブロモアニソール)
1	$FeCl_2$ (5)	none	24	10	89
2	$FeCl_2$ (5)	LiBr (0.2)	24	26	67
3	$FeCl_2$ (5)	LiBr (2.0)	12	51	41
4	$FeCl_2$ (5)	LiBr (4.0)	12	>99	0
5	$FeCl_2$ (0.5)	LiBr (4.0)	48	99	0

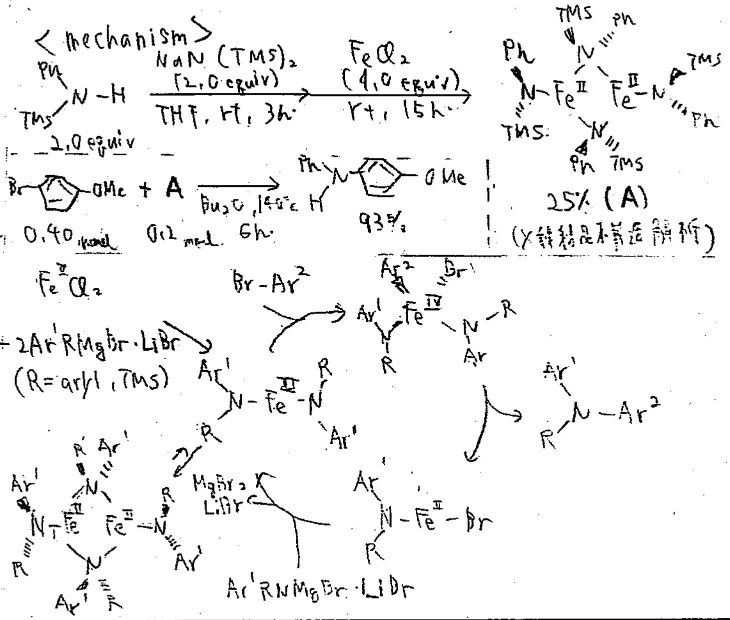
* $FeCl_2$にはppmオーダーでPd Cu Co Niが含まれるが、$PdCl_2$, $CuCl_2$, $CoCl_2$ (0.5mol%)を用いても反応は円滑に進行しない。$NiCl_2$ (0.5mol%)では88%の収率で目的のアミンが得られるものの、$FeCl_2$に含まれているNiの量0.0005mol%まで触媒を減らすと収率が8%まで低下した。

<Scope>

Ar^2 … チオフェン、ピリジン骨格も可能

エステル、ケトン、ニトリル部位が存在すれば、目的反応は円滑に進行せず、複雑な混合物を与える。

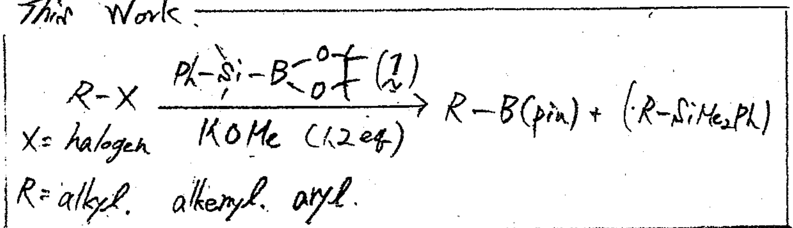
<mechanism>



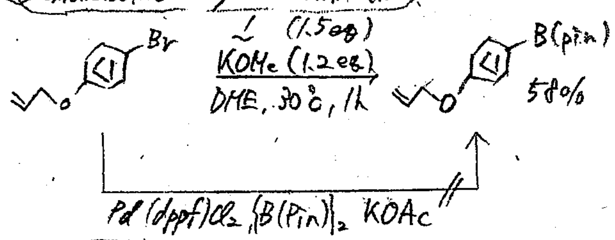
Ito Hajime	Hokkaido University	JACS DOI: 10.1021/ja309578k	Okumura

Anomalous Reactivity of Silylborane: Transition-Metal-Free Boryl Substitution of Aryl, Alkenyl, and Alkyl Halides with silylborane/Alkoxy Base Systems

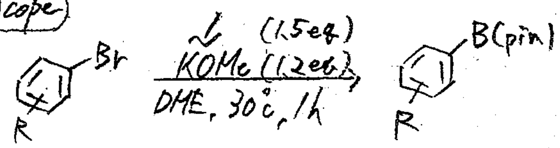
This Work



Chemoselective Boryl Substitution



Scope

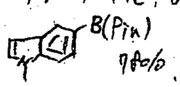


R = 4-OMe 77% (B/Si = 95:5) → X = Cl 27%, I 81%

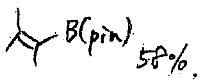
aryl = H. 68%, 4-F 63%, 4-Cl 56%

= 2-Me 67%, 3-Me 62%, 4-Me 68%

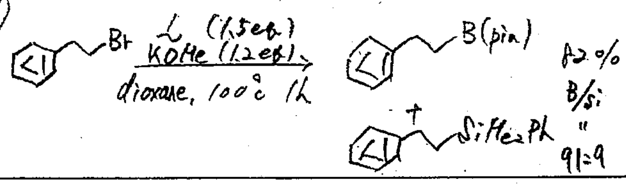
= 4-CO2Et 50%



alkenyl

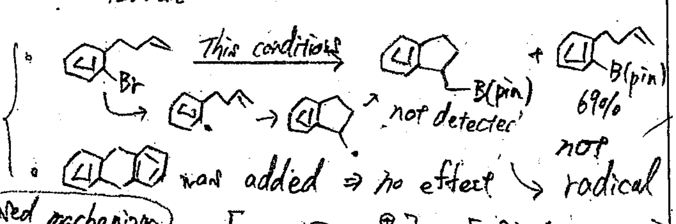


alkyl

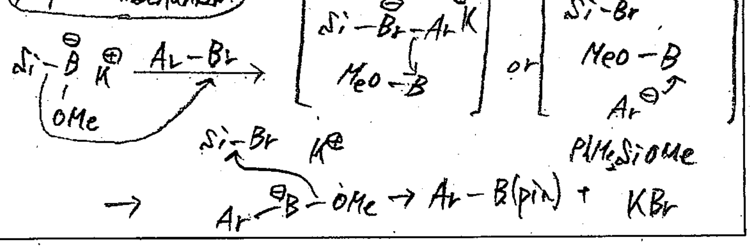


Mechanistic Study

• new reagents / labware ⇒ no effect ⇒ Metal-Free-Reaction



proposed mechanism



Matthew T. Tudge Stephen L. Buchwald *et al.*	Merck & Co., Inc. (USA) MIT (USA)	*Chem. Sci.* 10.1039/c2sc20903a	Ikeda

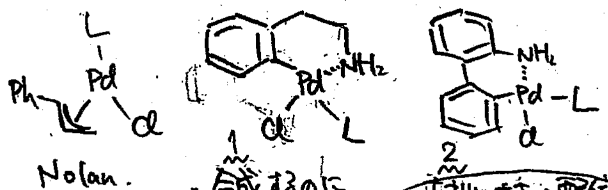
Design and preparation of new palladium precatalysts for C–C and C–N cross-coupling reactions

Pd sources

$Pd_2(dba)_3$: Pd nanoparticles と free dba 含む.
dba が反応に影響し得る。

$Pd(OAc)_2$, $PdCl_2$: Pd(0) に還元する必要がある.

⇒ 解決法 : Pre-ligated Pd(II) sources
(air and moisture stable)



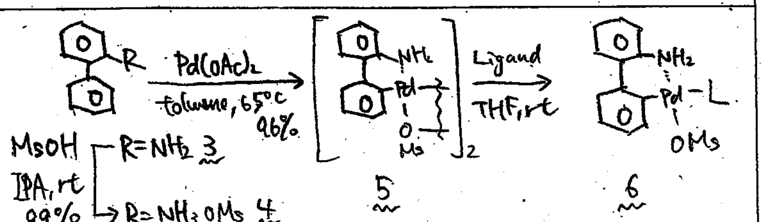
・合成するのに手間がかかる

・あまりに大きい配位子は使えない.
・溶液中安定でない.

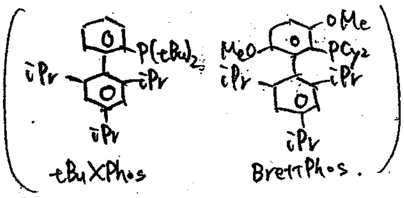
⇒ の Cl を (電子求引性のより大きいもの / non-coordinating anion) にかえる.

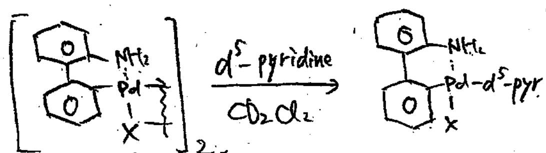
⇓

OMs (O–S(=O)(=O)–Me) が最適だった.

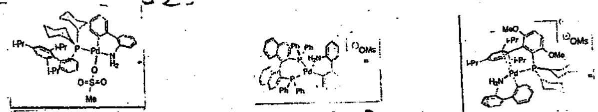


L = tBuXPhos (6b) 91%
BrettPhos (6c) 92%
XantPhos (6h) 87%
BINAP (6m) 93%





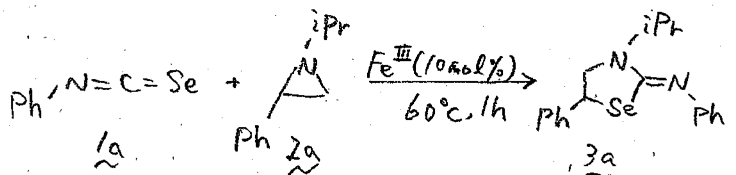
^1H NMR (NH2)
X=Cl : δ 5.53
X=OMs : δ 6.29



・Suzuki–Miyaura coupling (6a)
・α-arylation of tert-butyl acetate (6b)
・Buchwald–Hartwig amination (6c/BrettPhos, 6e/SPhos)
☆ 5 そのものもスクリーニングの際の Pd(II) source として活用できる

Punniyamurthy, T.	Indian Institute of Technology Guwahati (India)	anie.201207746	Kawai

"On Water": Efficient Iron-Catalyzed Cycloaddition of Aziridines with Heterocumulenes



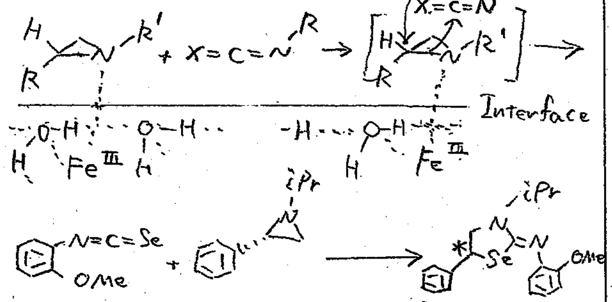
・aziridine + heterocumulenes
catalyst or stoichiometric reagent
Pd, Ni, HBF_4, Mg-MeOH, PBu_3, NaI

・Optimization

・catalyst (Fe^III)	Solvent : H_2O
$Fe(NO_3)_3 \cdot 9H_2O$	100%
$FeCl_3 \cdot 6H_2O$	87%
$Fe_2(SO_4)_3 \cdot 5H_2O$	58%
$Fe(acac)_3$	47%
no catalyst	12%

・Solvent	
H_2O	100%
CH_2Cl_2 (40°C)	n.d.
Toluene	n.d.
$(CH_2Cl)_2$	n.d.

・proposed catalytic cycle



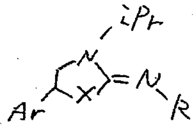
$[\alpha]_D^{20} = +21$

Scope

・isoselenocyanate (R–N=C=Se)
R = –C6H4X (X = –OMe (g scale ok) / –I / –NO2 etc)
1-naphthyl
2-fluorene
Cyclohexyl
61 ~ 93%

・aziridine (R' / N–R)
R = H, Alkyl, Ph
Bz, Boc は n.d.
R' : Ar
61% ~ 91%

・heterocumulene (R–N=C=X)
Ar–N=C=N–Ar
Ph–N=C=O
Ph–N=C=S



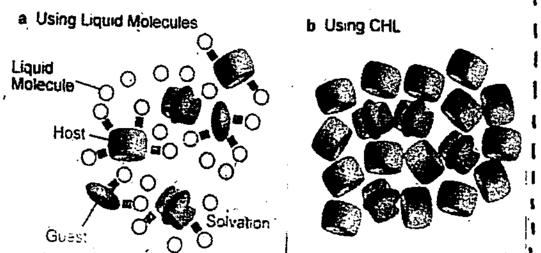
65% ~ 79%

Tadaaki Yamagishi	Kanazawa University(JPN)	*JACS*: ja310757p	M2 錦織

Cyclic Host Liquids for Facile and High-Yield Synthesis of [2]Rotaxanes

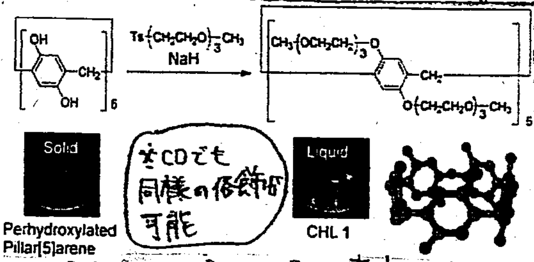
☆Liquid Host Molecules (This Work)

• Strategy



従来の H-G system → 溶媒和により、H-G の接近が妨げられる。

• Synthesis of CHLs (=Cyclic Host Liquids)



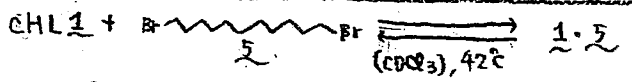
☆CDでも同様の修飾が可能

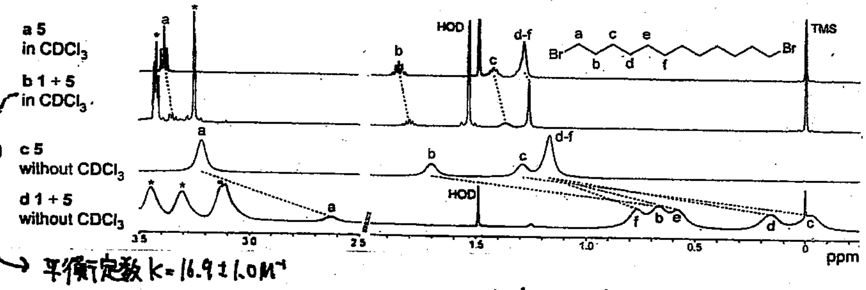
TGA & DSC: −50℃ ~ 250℃ で液相を保つ

TEO 鎖が両親媒性であるため、様々な溶媒と混和する!

(○ water, alcohols, acetone, $CHCl_3$, ethers, toluene, DMF, DMSO × Hexane)

• Complexation between CHL 1 and 1,12-dibromododecane 5

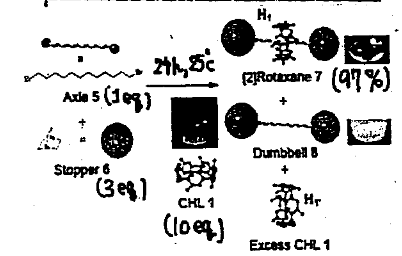




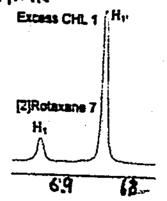
→ 平衡定数 K = 16.9 ± 1.0 M^{-1}

Neat 条件 (c,d) である場合の方が、複合化が効率的に進行!!

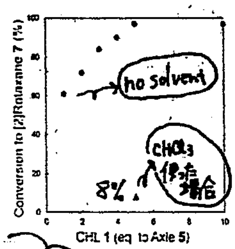
• Synthesis of [2]Rotaxane



^{1}HNMR



plot of Conversion to 7



8: acetone 洗浄で除去

1: Et_2O, Hexane を用いた洗浄により 95%以上回収可能!

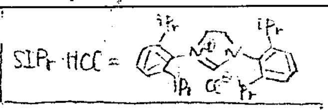
小さい K であっても CHL を用いれば効率的に Rotaxane が合成可能!

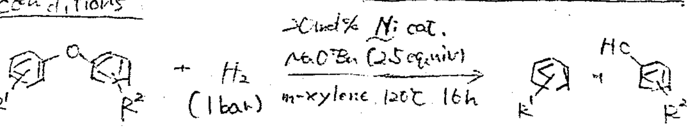
John F. Hartwig et al	University of California, Berkeley	JACS DOI: 10.1021/ja3085912	M1 榎島

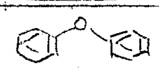
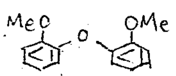
A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation

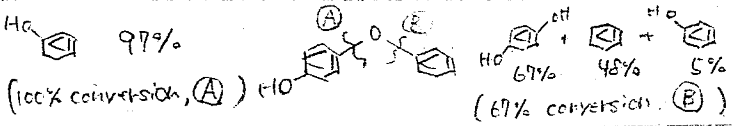
◎ Differences of Ni catalysts

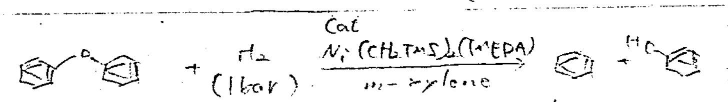
conditions





Ni = 20 mol% Ni(COD)₂ (This work)	substrate	Ni = 20 mol% Ni(COD)₂/2 SIPr·HCl
62% (48h: 99%)		99%
100%		75%
41%		100% (or 100℃: 100%)





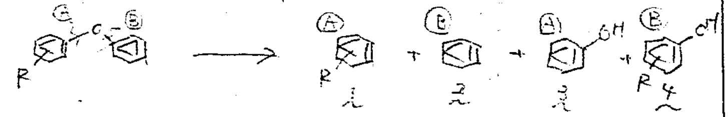
20 mol% cat, 120℃ 16h → >95% yield

2 mol% cat, 120℃ 96h → >95% yield

2 mol% cat, 140℃ 24h → 90% yield

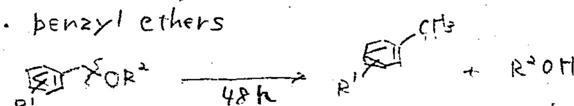
◎ Scope (Ni(CH₂TMS)₂(TMEDA) cat)

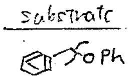
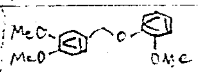
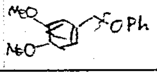
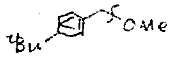
• unsymmetrical diaryl ethers



R		Ni (mol%)	time (h)	1 (%)	2 (%)	3 (%)	4 (%)
o-		10	96	22	60	17	63
m-	Me	5	48	18	82	17	75
p-		5	48	13	85	11	81
p-	tBu	5	48	3	90	3	90
o-		0.5	48	45	54	44	53
m-	OMe	10	48	21	46	22	45
p-		10	48	15	8	18	2
o-		5	48	80	9	80	—
m-	OH	10	48	75	8	75	—
p-		15	41	97	—	97	—

• benzyl ethers

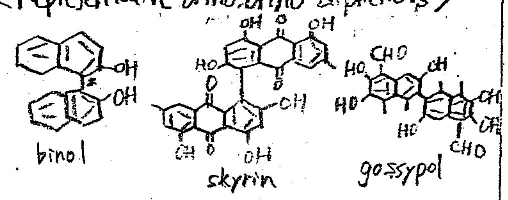


substrate	Ni (mol%)	ArCH₃ (%)	R²OH (%)	substrate	Ni (mol%)	ArCH₃ (%)	R²OH (%)
	2	98	95		0.25	93	98
	2	81	87		20	99	—

Kye-Simeon Masters
Stefan Bräse
Institute of Organic Chemistry (Germany)
Angew. Chem. Int. Ed.
DOI: 10.1002/anie.201207485
M1 岡崎

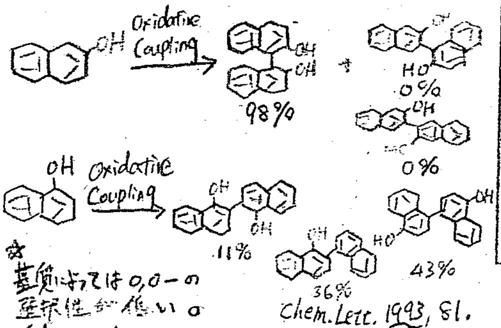
The Acetal Concept: Regioselective Access to ortho, ortho-Diphenols via Dibenzo-1,3-dioxepines

<Representative ortho,ortho-diphenols>



・天然物, 薬, 不斉配位子など数多く存在する。

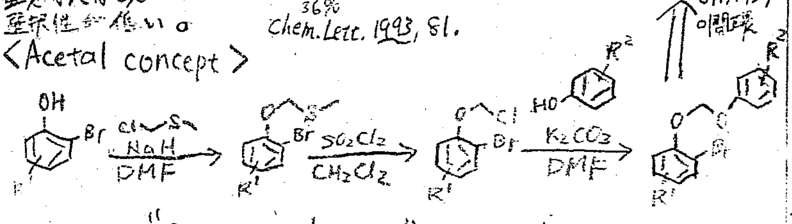
<Comparison of the dimerization of naphthols>



Chem. Lett. 1993, 81.

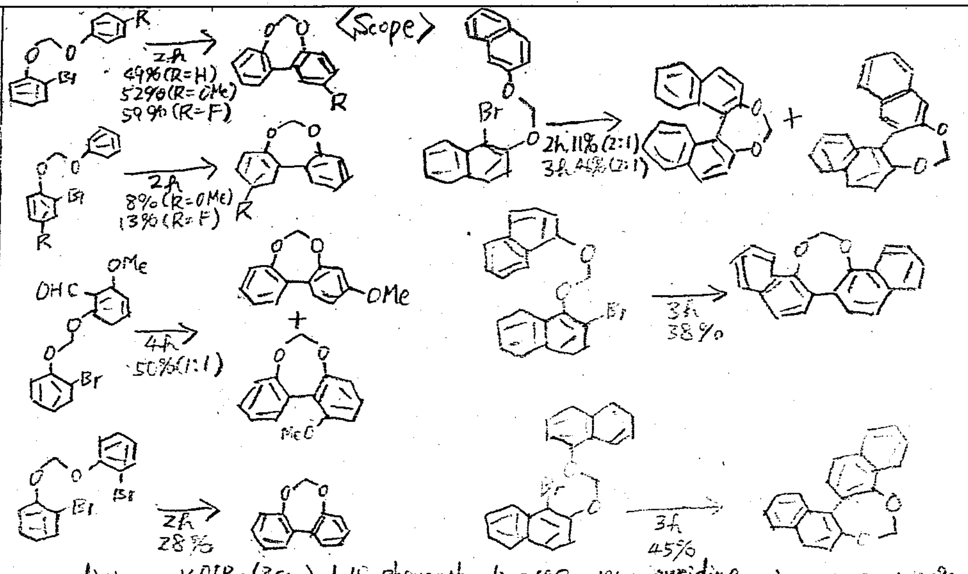
☆基質によってはo,o-の選択性が低い。

<Acetal concept>



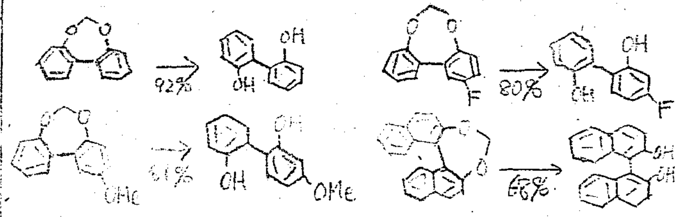
"Guillaumet's Work" Tetrahedron Lett. 2003, 44, 4219.

<Scope>



conditions: KO^tBu (3 eq.), 1,10-phenanthroline (40 mol%), pyridine, microwave at 120°C

<Hydrolysis of selected dibenzo-1,3-dioxepines>



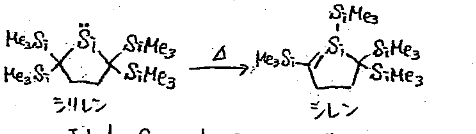
conditions: aq. HCl/EtOH (1:5), 50°C, 4~36h

Takeaki Iwamoto
Tohoku University (Japan)
JACS
10.1021/ja310391m
M1 西田

New Isolable Dialkylsilylene and its Isolable Dimer That Equilibrate in Solution

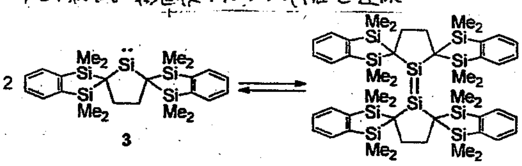
Silylenes (R_2Si)

… カルベンの類縁体。
様々な反応性が期待できる。
しかし、安定性に乏しく合成が難しい。
※無置換シリレンの単離は過去に一例のみ



Ishida, S. et al., Organometallics, 2009, 28, 919.

今回、新たに無置換シリレンの単離を達成



3 4

溶液状態で dimer (4) と平衡

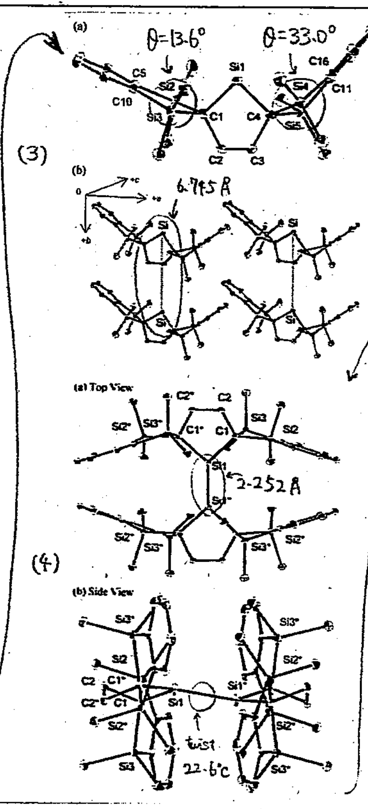
monomer (3) を再結晶 (Hex, −30°C)

⇓

monomer (3): yellow crystal
dimer (4): orange-red crystal (微量)

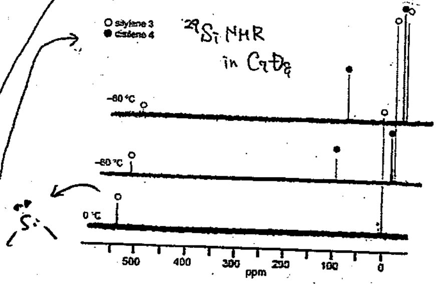
(3)

(4)

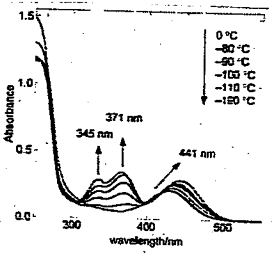


← Si1の周辺はかさ高いため、結晶構造は face to face にはならない。

Si1=Si1*はねじれているので、Si1の両隣のCは等価ではない。



・熱力学的パラメータ ($\ln K_{eq} = -\frac{\Delta H}{R}\cdot\frac{1}{T} + \frac{\Delta S}{R}$)
$\Delta H = -36 \pm 3$ kJ mol^{-1}, $\Delta S = -170 \pm 15$ J mol^{-1}



温度が下がると (4) 由来の吸収帯が出現

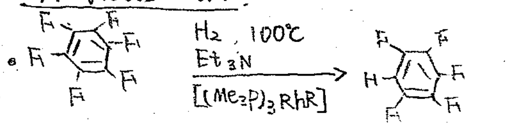
441 nm
… $\pi(Si{=}Si) \rightarrow \pi^*(Si{=}Si)$

371, 345 nm
… Siと隣接C由来の吸収
(非等価なので2種類)

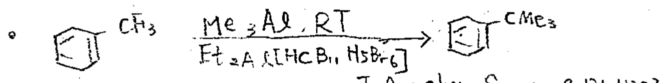
Norio Shibata | Nagoya Institute of Technology (Japan) | ACIE DOI: 10.1002/anie.201207304 | M1 Hisakuni

C-F Bond Activation of Unactivated Aliphatic Fluorides: Synthesis of Fluoromethyl-3,5-diaryl-2-oxazolidinones by Desymmetrization of 2-Aryl-1,3-difluoropropan-2-ols.

◦ Previous Work

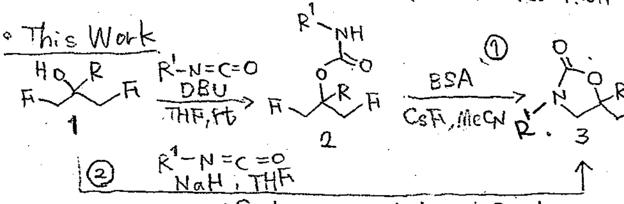


Angew. Chem. Int. Ed. 2000, 39, 3241-3244



J. Am. chem. Soc. 2009, 131, 11203

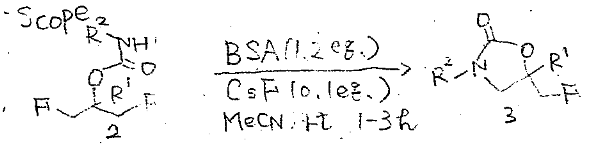
◦ This Work



Sodium-assisted C-F Bond Activation

◦ Path ① (2→3)

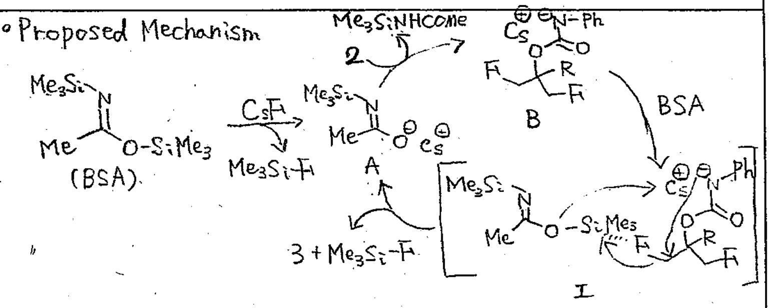
Scope



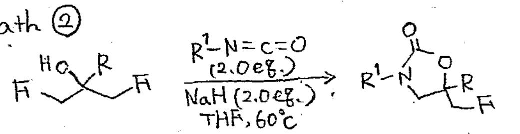
R^1 = Ph, 4-MeC6H4, 3-MeOC6H4, 4-ClC6H4   69-96%

R^2 = Ph, 4-MeC6H4, 4-BrC6H4

◦ Proposed Mechanism



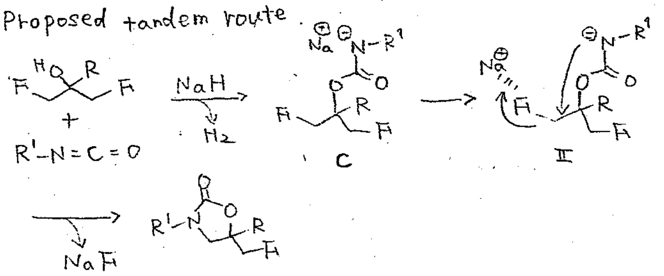
◦ Path ②



R = Ph, 4-MeC6H4, 3-MeOC6H4, 4-FC6H4, 2-naphthyl

R^1 = Ph, 4MeC6H4, 4-BrC6H4, 3-NO2C6H4, Ts

◦ Proposed tandem route



Yao Fu | University of Science and Technology of China | Angew. Chem. Int. Ed DOI: 10.1002/anie.201206681 | B4 黒田

Copper-Promoted Trifluoromethylation of Primary and Secondary Alkylboronic Acids

☆ trifluoromethylation
- transition-metal-catalyzed (Pd, Cu)
- sp^2-, sp- carbon
- allylic sp^3- carbon (recent studies)

報告されている

↓

This Work

- nonactivated sp^3-hybridized carbon

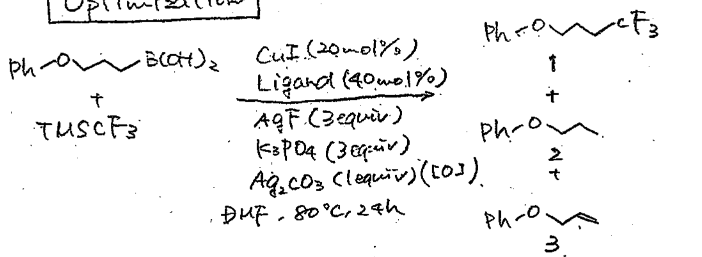
◦ primary alkyl

n-alkyl-B(OH)2 + TMSCF3 (3 equiv) — CuI (0.5 equiv), L1 (1 equiv), AgF (3 equiv), KF (3 equiv), AgBF4 (1 equiv), DMF, 80°C, 24h → n-alkyl-CF3, 36~78%, 14 examples

◦ secondary alkyl

R1R2CH-B(OH)2 + TMSCF3 (3 equiv) — CuOTf·0.5C6H6 (10 mol%), L1 (40 mol%), AgF (3 equiv), KF (3 equiv), AgOTs (1 equiv), DMF, 50°C, 24h → R1R2CH-CF3, 39-54%, 7 examples

Optimization



L1 26/24/11% (1/2/3)
L2 16/25/8% L3 18/25/9%
L4 trace/8/5% L5 14/16/10%
L6 trace/6/4% (GC yield)

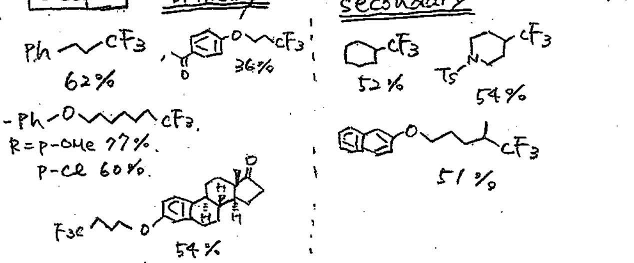
→ L1について

[O]: Ag2O, AgOAc, AgOTf, AgBF4, BQ — trace, trace, 16%, 50%, trace

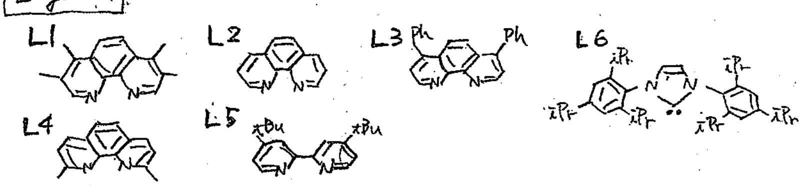
→ L1, [O] = AgBF4について

base: K2CO3, Cs2CO3, tBuOK, KF — 38%, 45%, 8%, 68% → 88% (78%)

Scope



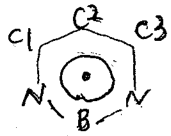
Ligand



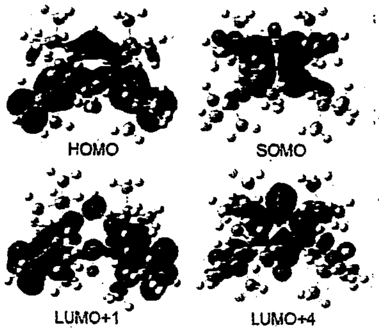
Kyoko Nozaki	東京大学（日本）	JACS 10.1021/ja3094372	B4 1枚

Synthesis and Characterization of B-Heterocyclic π-Radical and Its Reactivity as a Boryl Radical

・ホウ素中心のラジカルは5電子で不安定
・ルイス塩基などにより安定化される
ex) NHC－BR_2・　$RC_5H_4N-BH_2$・

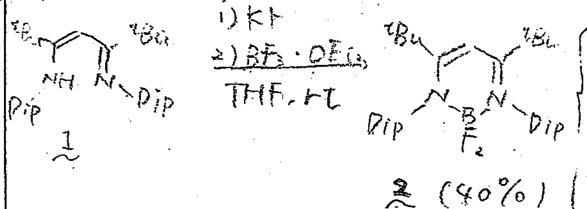


〈DFT計算〉

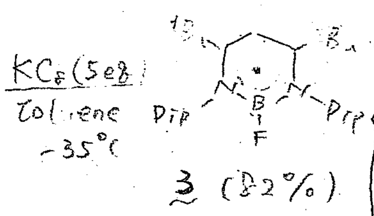


・SOMOでC−Nに反結合性
・HOMOでN−Bにπ結合性
・HOMO SOMOでC1−C2・C3にアリルラジカル性（C1 C3でスピン密度高）
・2つのLUMOでB中心と大きな軌道相互作用

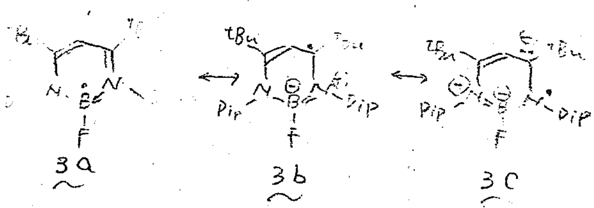
〈This work〉

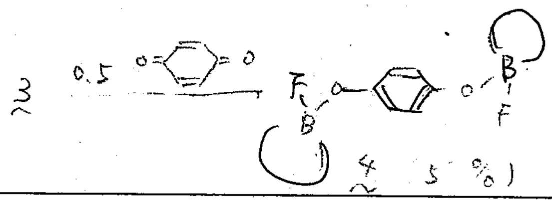


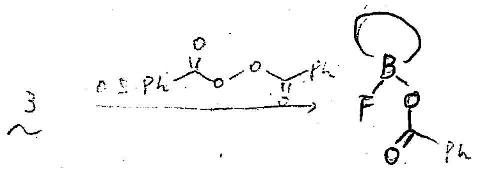
・C_{2v}（^{1}H NMR）
・singlet signal（^{19}F NMR）
・sp^3−B（B NMR）
・六員環の二面角は小さい



・sp^2−B（X-ray）
・C−Nが2より長い（電子が反結合性軌道に入っている）
・ESRスペクトルは計算値にほぼ近い







Bはスピン密度が低く反応しにくいため，嵩高いDipの立体障害を避けて3aのラジカル種からのみ反応が進行