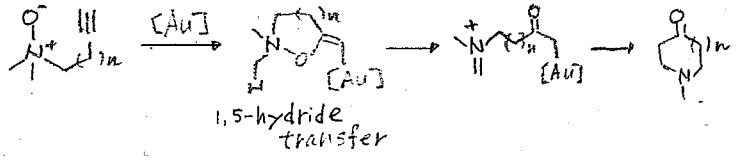
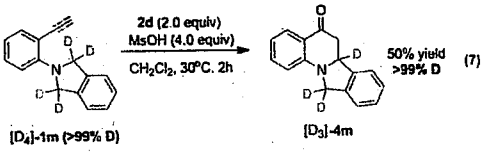
Liu-Zhu Gong et al.	Univ. of Science and Technology of China	Angew. Chem. anie. 201205062	Minakata

Metal-Free Oxidative/C(sp³)–H Functionalization of Unactivated Alkynes Using Pyridine-N-Oxide as the External Oxidant

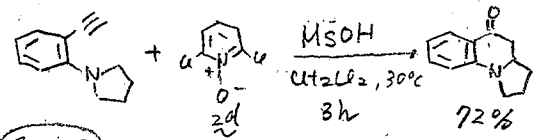
Previous Work

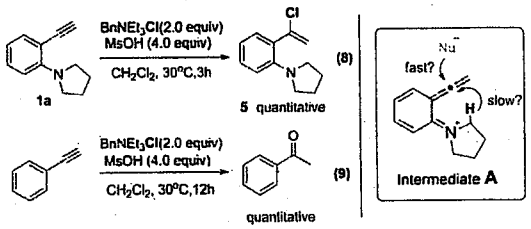
(Zhang and Houk's work)



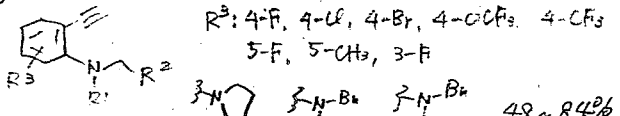


Optimization

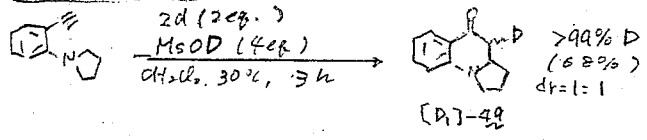


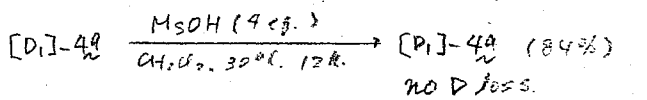


Scope

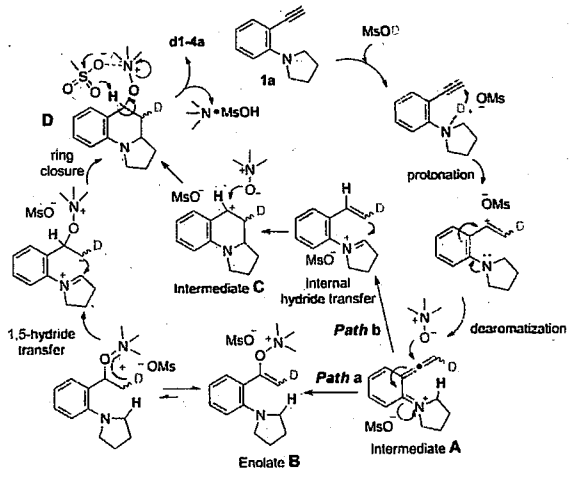


Deuterium-labeling





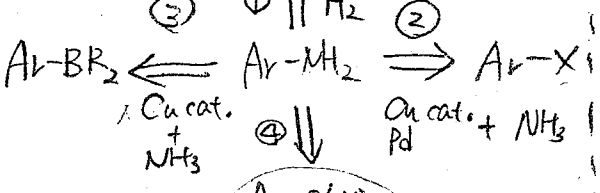
Mechanism



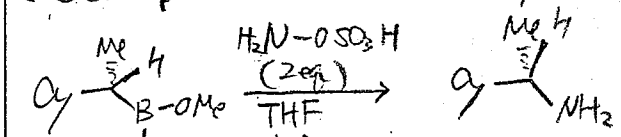
L. Kürti	University of Texas Southwestern Medical Center, USA	J. Am. Chem. Soc. (doi:10.1021/ja309637rl)	Youhei Takeda

Elusive Metal-Free Primary Amination of Arylboronic Acids: Synthetic Studies and Mechanism by Density Functional Theory

① $Ar-NH_2$ の合成法 $Ar-NO_2$

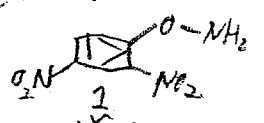


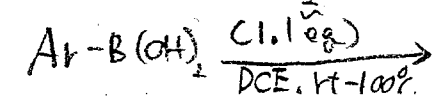
② electrophilic amination of alkylboronates



H.C. Brown, JACS, 1964, 86, 3565.

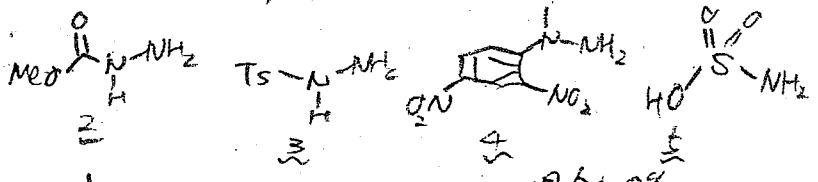
<This Work>





☆ Effect of aminating reagents

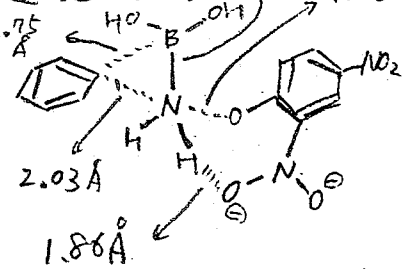
(Ar =  , 50°C, 24h)



☆ いずれの場合も0%

☆ DFT calculation

<TS state>



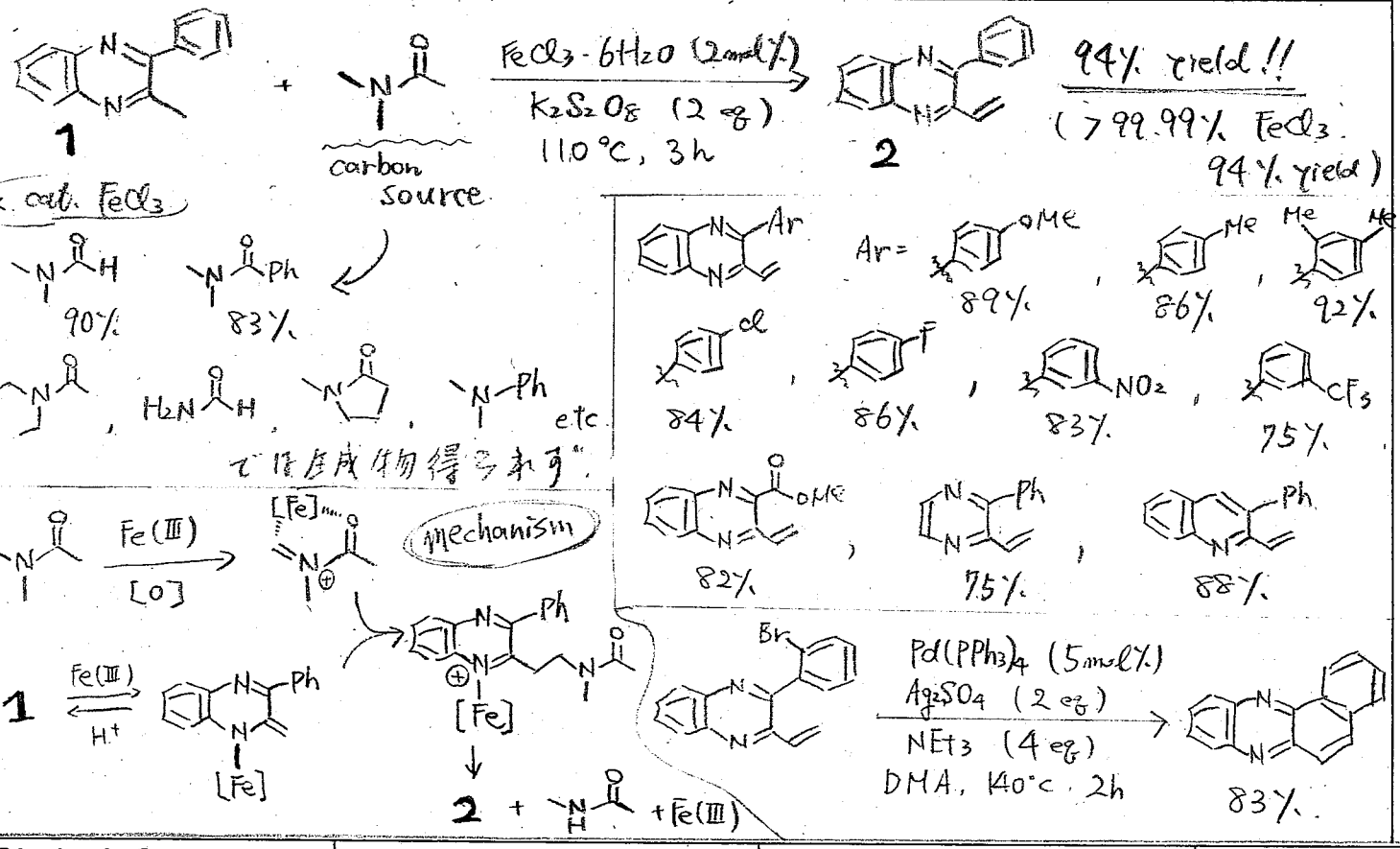
$\Delta G^{\ddagger}$ = 28.0 kcal/mol

(BDE of N-O: 29.9 kcal/mol)

エン体	$\Delta G^{\ddagger}$ (kcal/mol)	BDE (kcal/mol)
2	54~66 (CH2Cl2中)	82.1
3		74.1
4		68.4
5	31.1	52.7
6	31.6	49.4

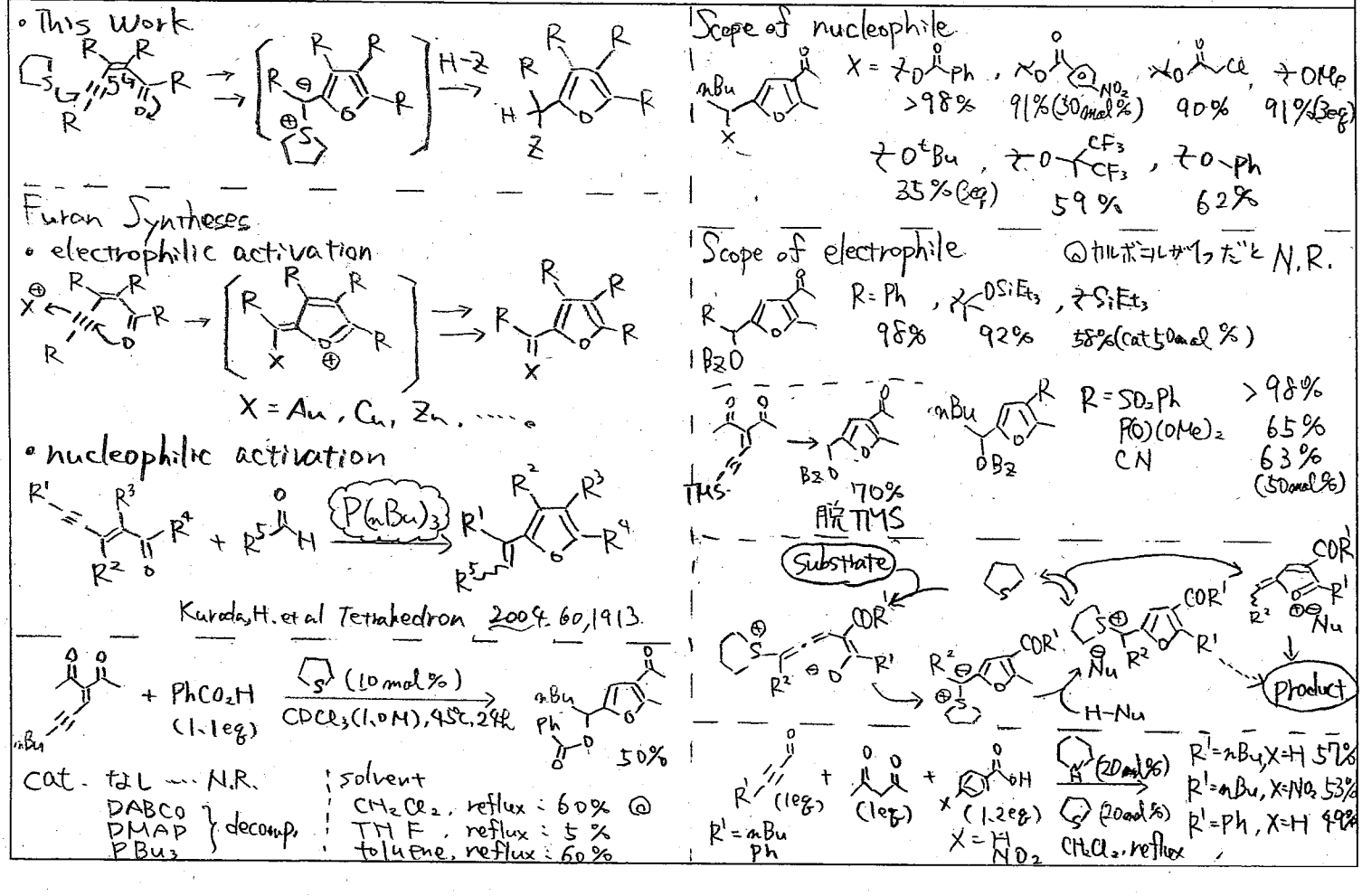
Dan-Qian Xu, Zhen-Yuan Xu	Zhejiang University of Technology (China)	*CC* 10.1039/c2cc36708d	清川

Highly Efficient Vinylaromatics Generation *via* Iron-Catalyzed *sp3* C-H Bond Functionalization CDC Reaction: A Novel Approach to Preparing Substituted Benzo[*a*]phenazines



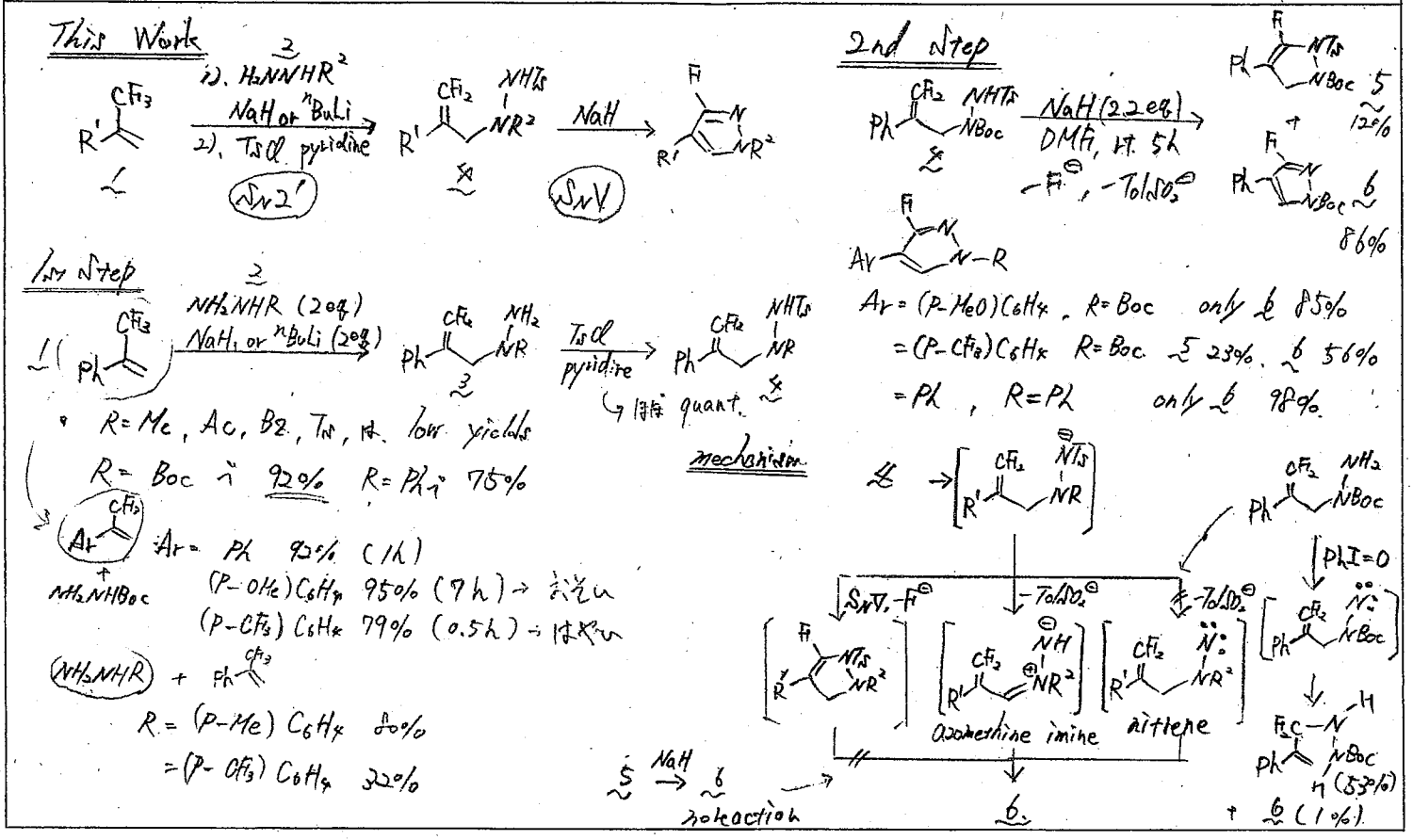
Clark, J. S. et al	University of Glasgow (UK)	anie.201207300	Nagamachi

Organocatalytic Synthesis of Highly Substituted Furfuryl Alcohols and Amines



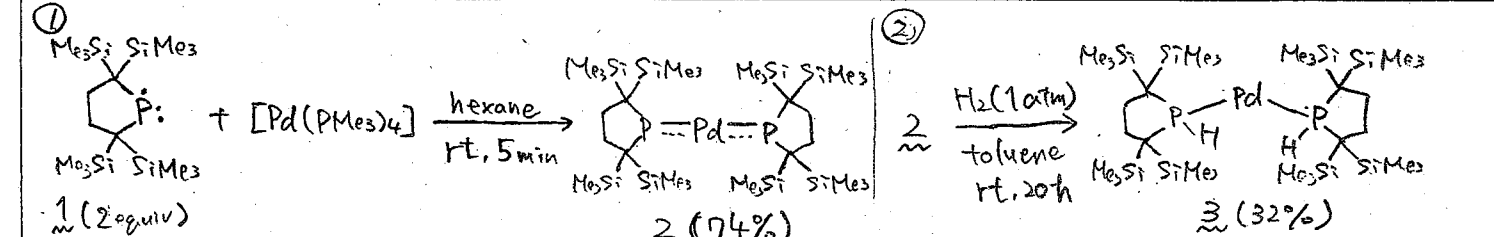
Junji Ichikawa	University of Tsukuba (Japan)	*ACIE* DOI:10.1002/anie.201206946	Okumura

Substitution of Two Fluorine Atoms in a Trifluoromethyl Groups: Regioselective Synthesis of 3-Fluoropyrazoles



Takeshi Iwamoto *et al.*	Tohoku University	*Angew. Chem. Int. Ed.* (10.1002/anie.201206997)	Yuki Ikeda

A Two-Coordinate Palladium Complex with Two Dialkylphosphinyl Ligands



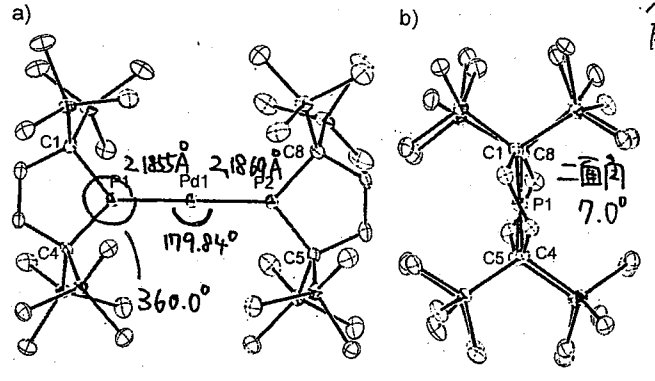
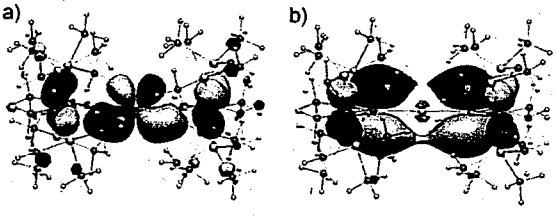


Figure 1. Molecular structure of **2** at 100 K. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. a) A perspective view. b) A view along the P1-Pd1-P2 axis.

cf. P-Pd distance of $Pd(PR_3)_2$ 2.28–2.29 Å

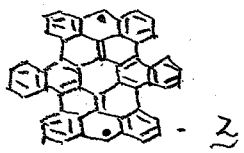


2opt の HOMO-5　　2opt の HOMO

1 の SOMO も Pd の間に π 相互作用あり

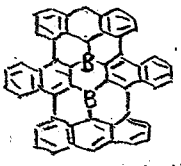
Saito, S. Yamaguchi, S.	Nagoya University (Japan)	anie.201206699	M2 Kawai

A Boron-Containing PAH as a Substructure of Boron-Doped Graphene

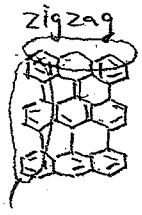


Singlet biradical

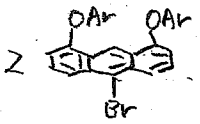
B-doping

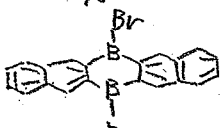


closed shell

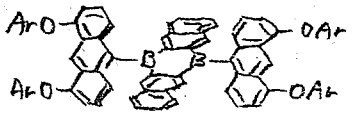


armchair





n-BuLi
Et2O
0°C → 25°C

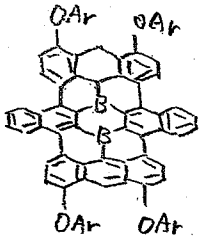


3 stable

54%

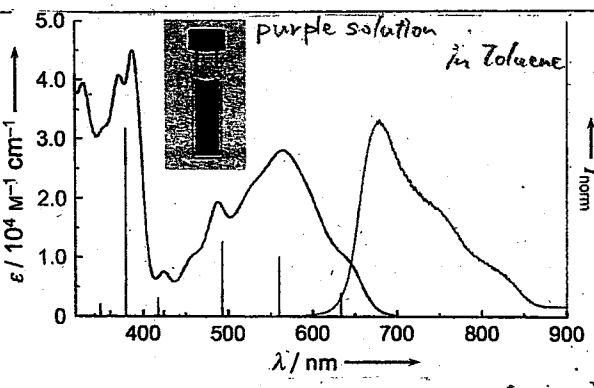
Ar = mesityl { 効率的な1,8位での環化
Aggregationを阻害

FeCl3
CH3NO2/CH2Cl2
51%

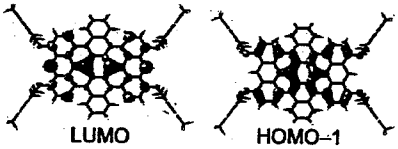


stable to air
chlorobenzene (4.8 mg mL^{-1})
o-dichlorobenzene (10.8 mg mL^{-1})

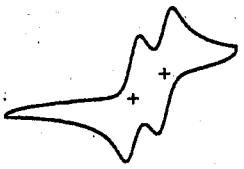
2 : ΔEs-T = 1.5 kcal/mol
1 : ΔEs-T = 34.9 kcal/mol



1a (λabs = 569, 487 nm, λem = 679 nm)
hexabenzocoronene (λabs = 392, 361 nm),
teranthene (λabs = 1054, 878 nm)



- 640 nm HOMO → LUMO
- 564 nm HOMO-1 → LUMO
- 487 nm HOMO-2 → LUMO



E_{red}^1 E_{red}^2
−1.45 V −1.66 V

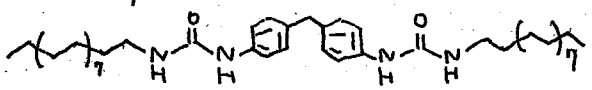
高い可逆性
Liイオン電池の電極への応用

Hui-Bi Xu et al.	Huazhong University(China)	DOI: 10.1002 / chem.201202721	M2 錦織

Supramolecular Gel-Assisted Formation of Fullerene Nanorods

☆ 超分子ゲルを用いたフラーレンナノロッドの作成

• Strategy

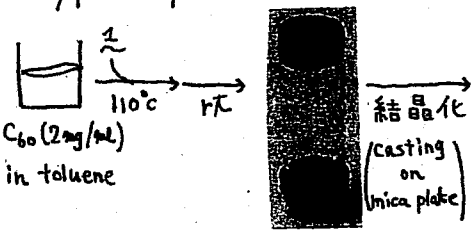


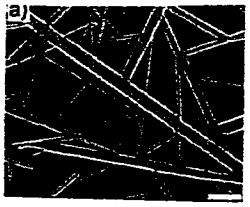
gelator 1

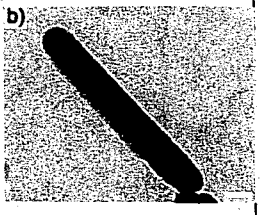
1 が、toluene中でゲル化し、ヘリカルな構造をしていると CD スペクトルにより予想 (Chem. Lett. 1996, 885)

➡ 本論文で詳細に調査。

• Typical procedure

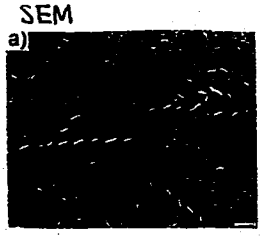


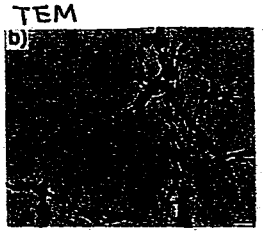




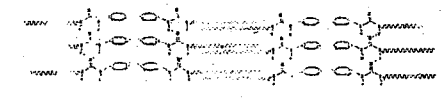
nanorod
↕ 数百nm
数 mm

※他に、SAED、EDS、HRTEMによってフラーレンナノロッドであることを確認



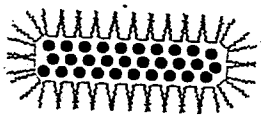


• Proposed mechanism



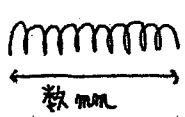
- hydrophobic interaction
- hydrophilic interaction
- Hydrogen Bonding
- π-π interaction

(C60)



(C60 nanorod)

上の結果から、1 のゲル構造が



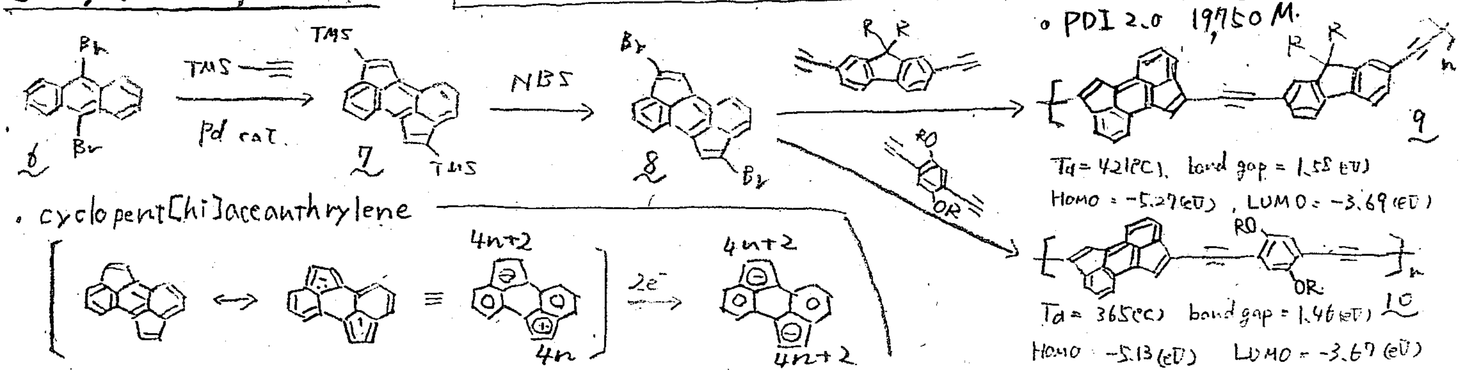
pitch が約 140 nm の helical nanobelt であると判明

➡ C60 を包むことができるのでは…?

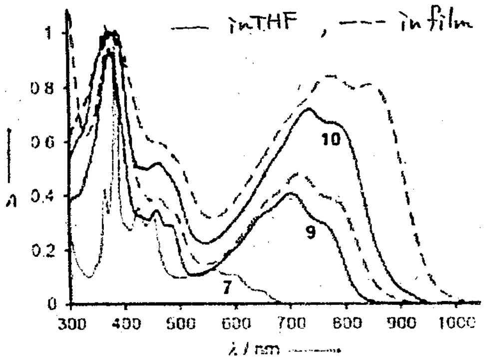
Kyle N. Plunkett	Southern Illinois University	Angew. Chem anie.201206145	M1 榎島

Electron Acceptors Based on an All-Carbon Donor-Acceptor Copolymer

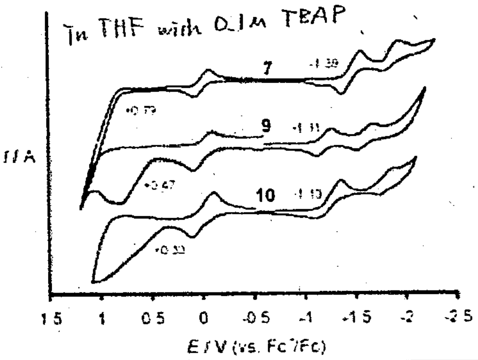
◎ synthetic pathway ※ 6 → 7 : JACS, 2012 Condition: [Pd(PPh3)2Cl2], PPh3, NEt3, benzene 110℃



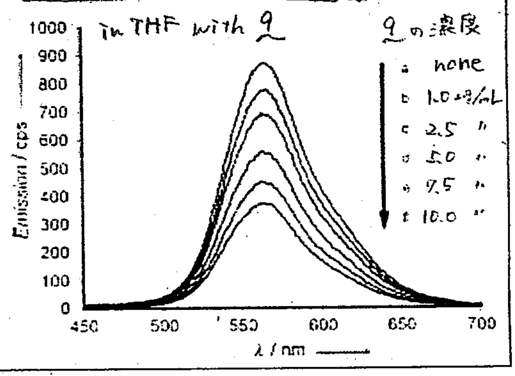
◎ UV/Vis spectrum



◎ Cyclic voltammograms



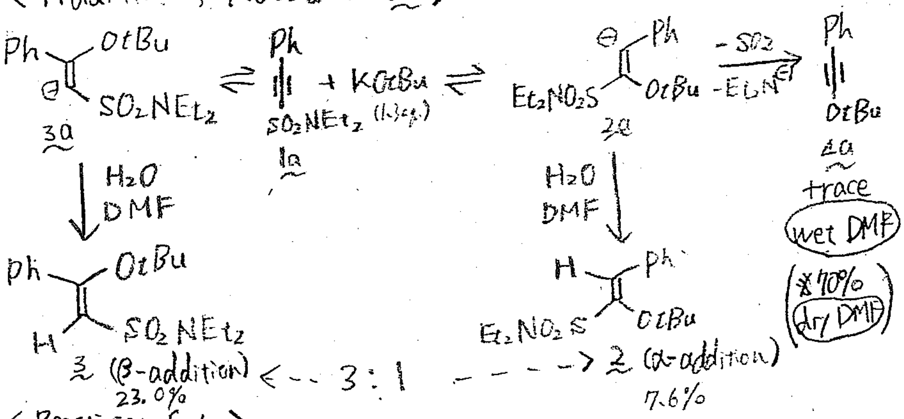
◎ Emission spectrum of P3HT



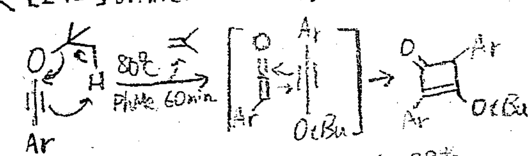
Jonathan D. Wilden	University College London (UK)	Chem. Eur. J. DOI: 10.1002/chem.201203015	M1 岡崎

Transition-Metal-Free Synthesis of Aryl-Substituted tert-Butyl Ynol Ethers through Addition/Elimination Substitution at an sp Centre

<Addition of KOtBu to 1a>

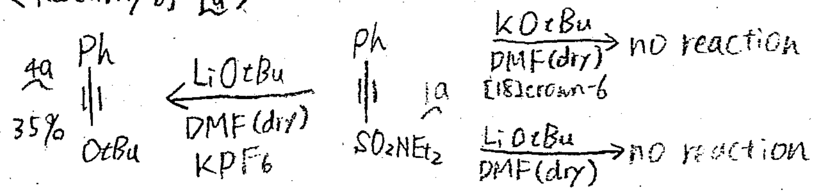


<[2+2] dimerization>

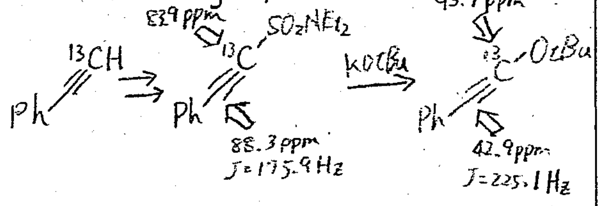


Ar = 5a Ph, 78%; 5b p-NO2, 80%; 5c p-CF3, 80%; 5d 2-Naphthyl, 75%

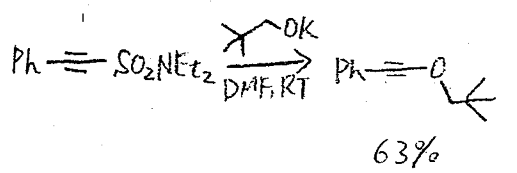
<Reactivity of 1a>



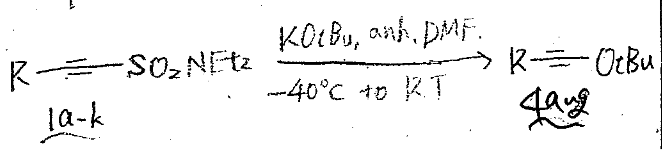
<¹³C-labelling experiment>



<Synthesis of a neopentyl ynol ether>



<Scope>



R = Ar (EWG, EDG) 59 ~ 93%

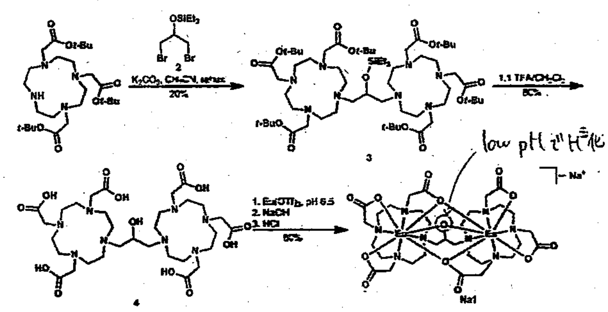
R = tBu 0%

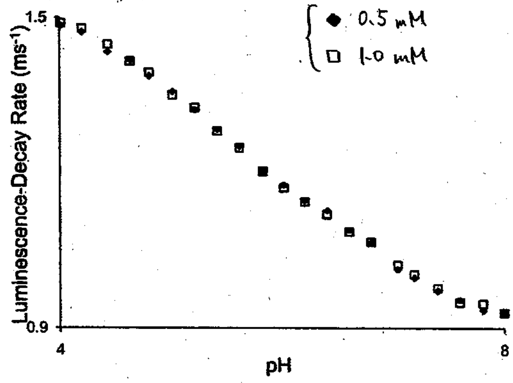
Matthew J. Allen	Wayne State University (United States)	JACS 10.1021/ja307098z	M1 西田

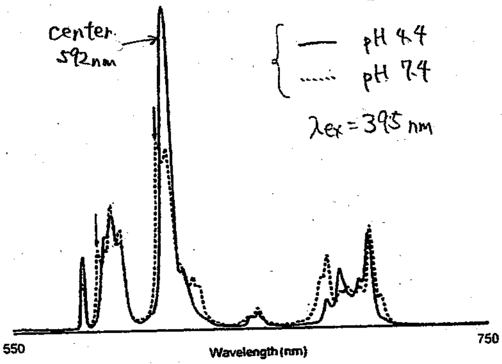
Concentration - Independent pH Detection with a Luminescent Dimetallic Eu(III) - Based Probe

蛍光プローブ
↓ … biochemical, biomedical で重要
ランタノイドを base としたプローブ
{ 蛍光波長が broad しにくい.
 蛍光寿命がながい
 (有機物を base としたものと比較)
ただし、monometallic だと低感度になることがある。
⇓
新規 dimetallic Eu(III) complex

Scheme 1. Synthetic Route to 1







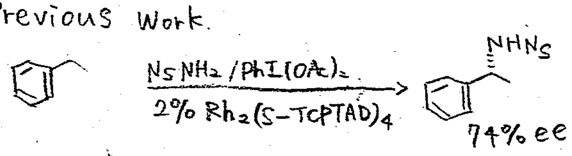
・化合物1の濃度には依存しない。
↓ 対して…
・pHが大きくなると、蛍光減衰率が下がってる。
(low pHだと架橋酸素がH⁺化され これが Eu(III)の励起状態をクエンチ。)

pH 4.4
… 許容遷移
pH 7.4 の割合が多い
… 禁制遷移が ある程度許容されてる
⇓
{ ・broadなスペクトル
 ・寿命がながい.

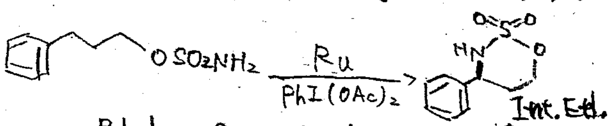
Tambar, U.K. et al	The University of Texas (USA)	JACS (ja3078516)	M1 Hisakuni

Catalytic Enantioselective Allylic Amination of Unactivated Terminal Olefins via an Ene Reaction / [2,3] - Rearrangement

Previous Work.

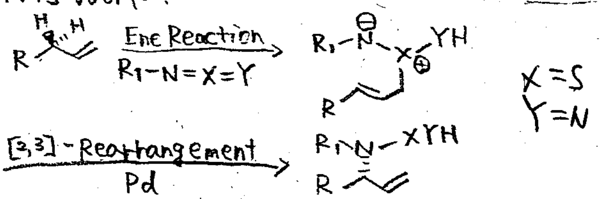


Davies, H.M.L. et al. Org. Lett. 2006, 8, 5013

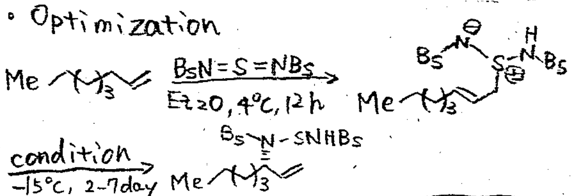


Blakey, S. et al., Angew. Chem. Int. Ed. 2008, 130, 9220

This Work.

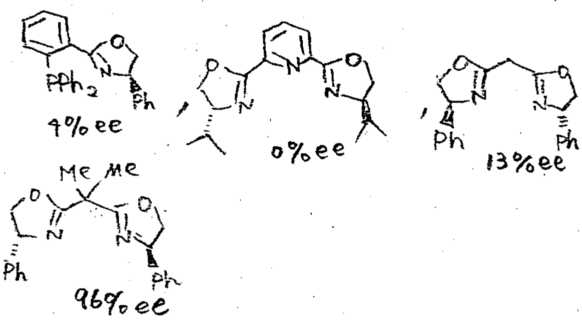


・Optimization

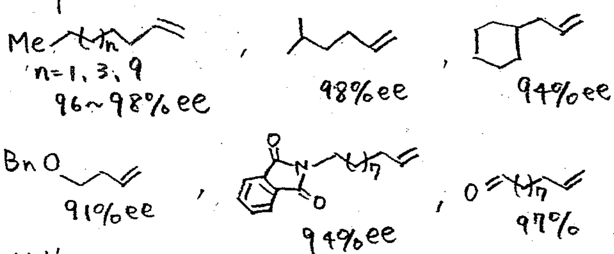


・Metal Catalyst … Pd(OAc)2, (Pd(TFA)2) (10 mol%)
・Solvent … CH2Cl2, DCE, Acetone, (MeOH)

・Ligand

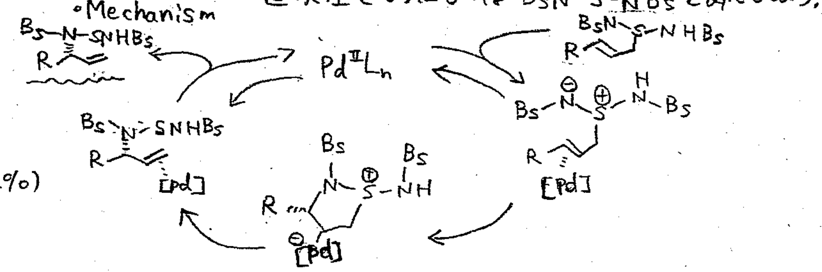


・Scope



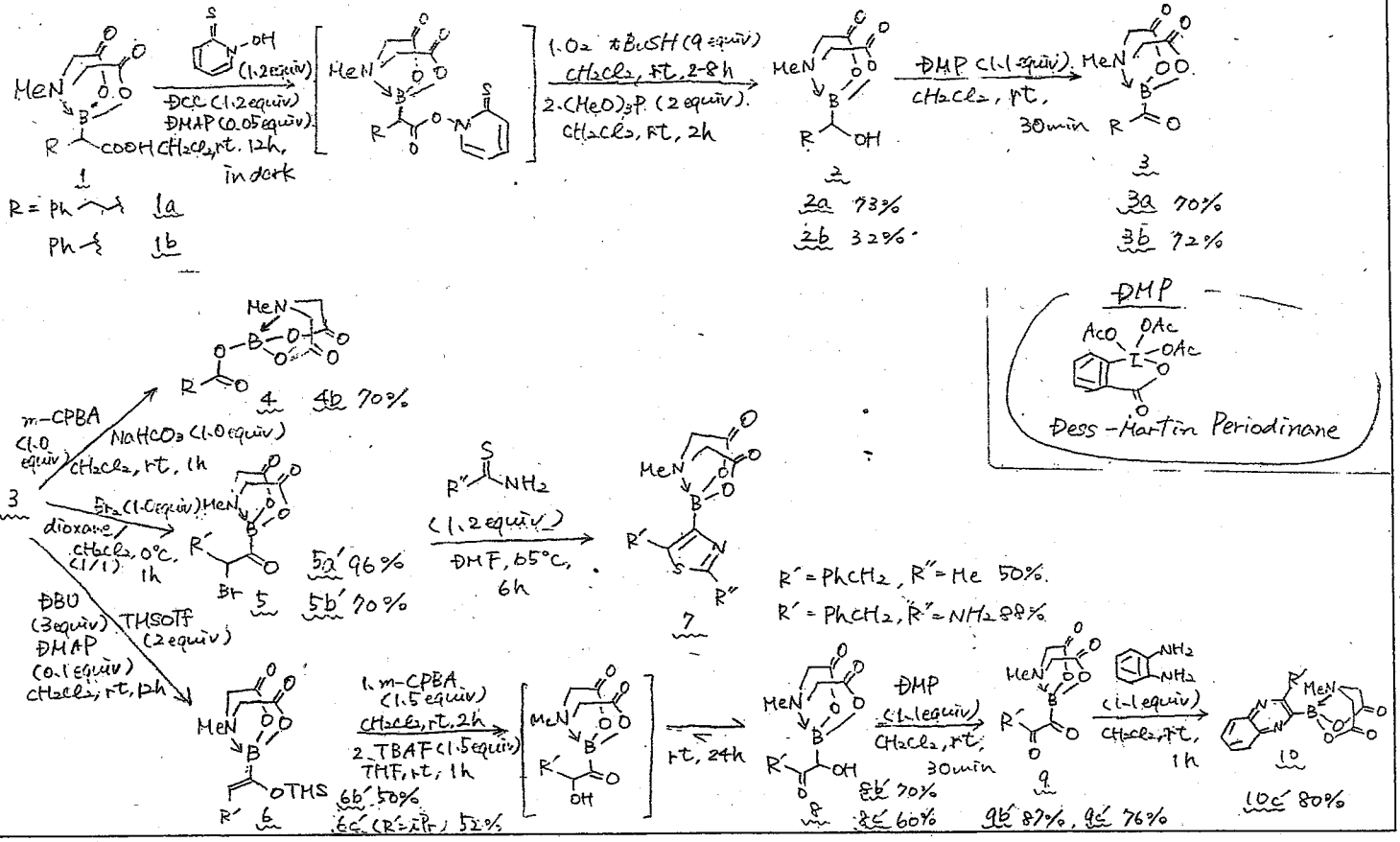
求核性の置換基をもったものは BsN=S=NBs と反応してしまう。

・Mechanism



Andrei K. Yudin	Toronto University (Canada)	Angew. chem. Int. ed DOI: 10.1002/anie.201206501	B4 黒田

Oxidative Geminal Functionalization of Organoboron Compounds



・Deracemization of α-Aryl Hydrocoumarin via Catalytic Asymmetric Protonation of Ketene Dithioacetals.

Benjamin List	Max-Planck-Institut, ドイツ	JACS 10.1021/ja309620z	B4 小坂