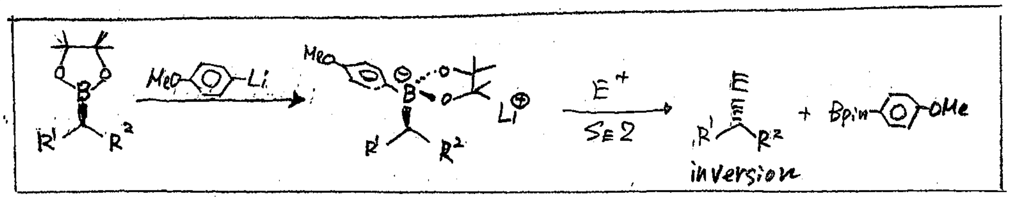
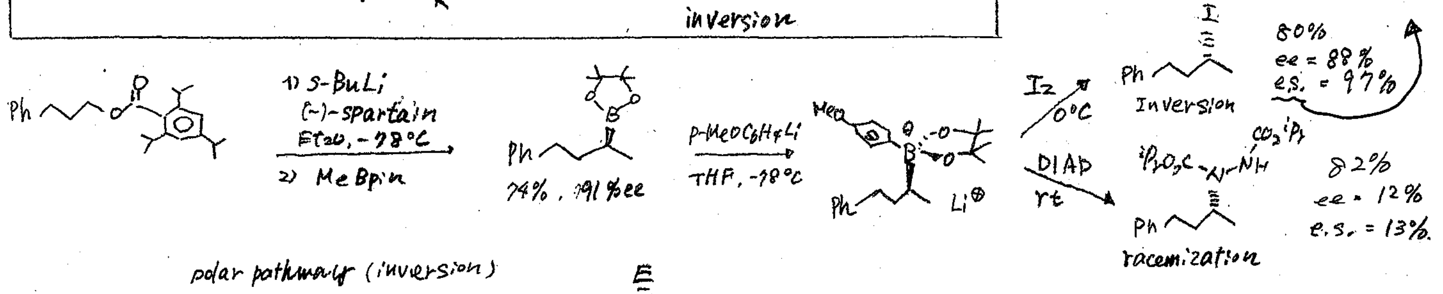
## Ate Complex of Secondary Boronic Esters as Chiral Organometallic-Type Nucleophiles for Asymmetric Synthesis

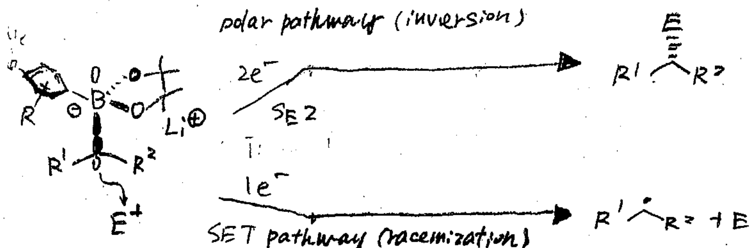
V. K. Aggarwal et al. J. Am. Chem. Soc. DOI: ja2077813 ミナカタ.





enantio specificity

立体保持率



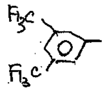
R ⇒ 電子求引基.

SET pathwayがおそくなる

⇓

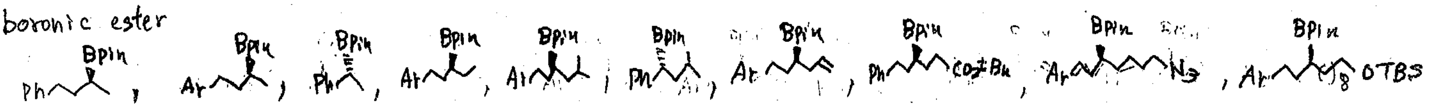
e.s.が高くなる

ex.



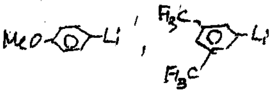
### Scope

- boronic ester



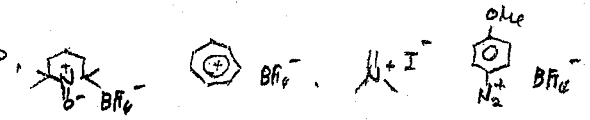
Ar = p-MeOC6H4−

- anion



- E+

I2, NIS, NBS, TCCA, DIAD, DBAD,



Yield 57~98% e.s. 66~100%

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CT 1X15

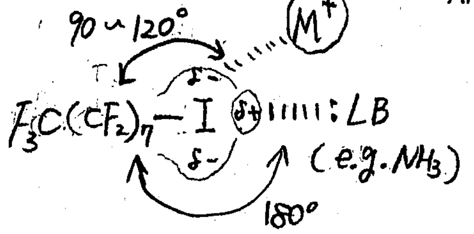
## "Halogen-Bond-Induced Activation of a Carbon–Heteroatom Bond"

Walter, S. M.; Kniep, F.; Herdtweck, E.; Huber, S. M.*

*Angew. Chem. Int. Ed.* **2011**, *50*, 7187–7191.

Youhei Takeda

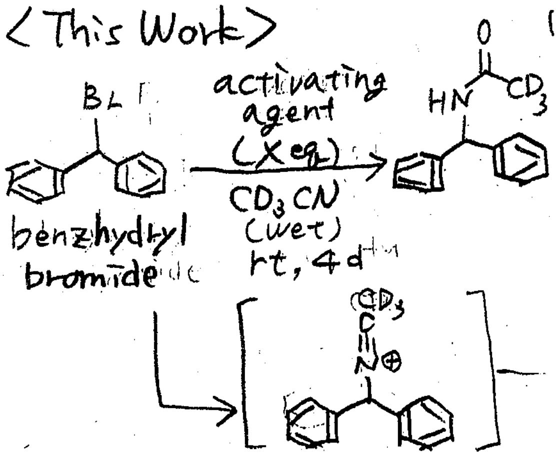
"ハロゲン結合"



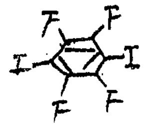
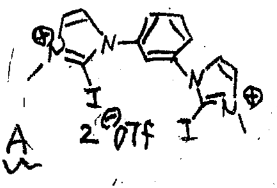
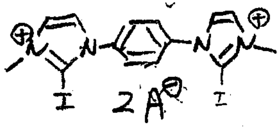
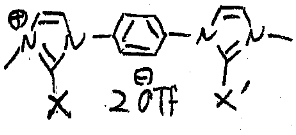
※"ハロゲン結合"を分子活性化（有機反応）に用いた例はこれまでに一例のみ

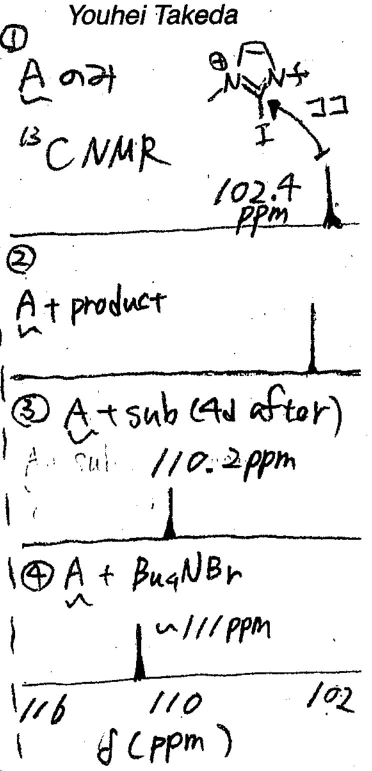
(Bolm et al. Synlett 2008, 900.)

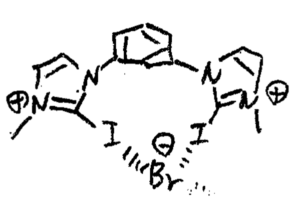
< This Work >



< Effect on activating agent >

| entry | activating agent | X eq | 1 (%) |
|---|---|---|---|
| 1 | none | − | ~5 |
| 2 | HOTf | 0.05 | 12 |
| 3 |  | 1.0 | ~5 |
| 4 |  A | 1.0 | 80 |
| 5 |  | 1.0 (A=OTf) | 85 |
| 6 |  |  | (A=BF4) 97 |
| 7 |  | 1.0 | (X=I, X'=H) 49 |
| 8 |  |  | (X=X'=H) 7 |



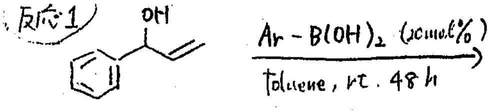


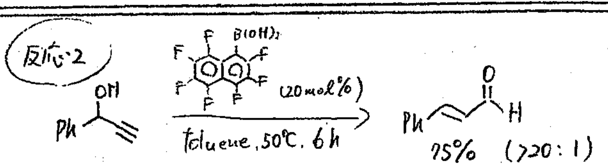
③の推定構造

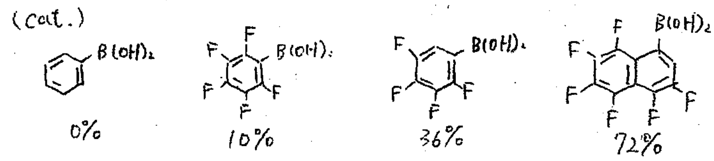
# Mild and selective boronic acid catalyzed 1,3-transposition of allylic alcohols and Meyer-Schuster rearrangement of propargylic alcohols

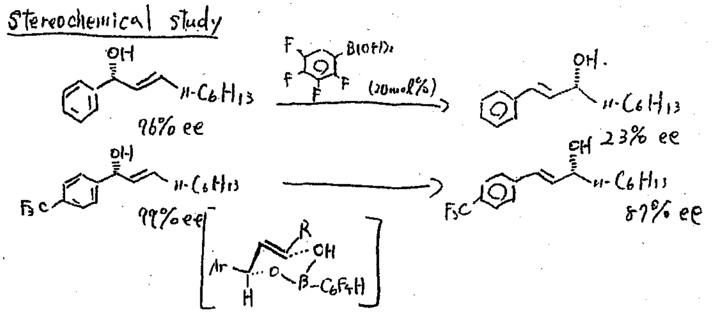
(Chem. Sci. 2011, 2, 1305-1310.)

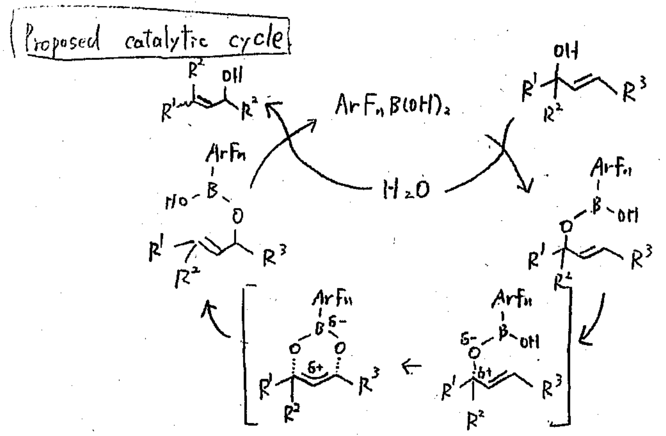
Dennis G. Hall
(University of Alberta, Canada)

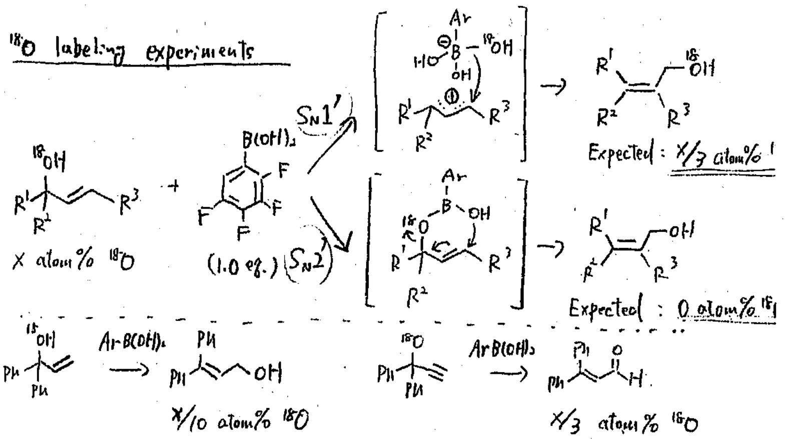












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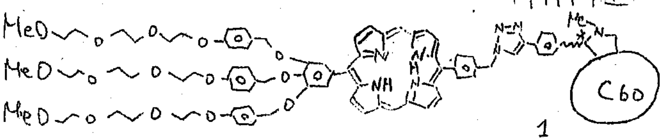
# Nanorods versus Nanovesicles from Amphiphilic Dendrofullerenes

(長町)

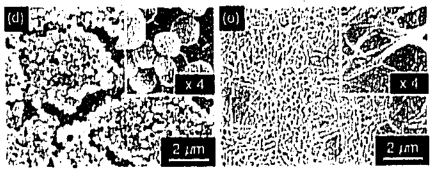
Antonio Muñoz, Beatriz M Illescas, Macarena Sánchez-Navarro, Javier Rojo, and Nazario Martín

JACS, ja206769a

フラーレン誘導体がaggregationすることの有用性



1



電荷移動度が飛躍的に向上

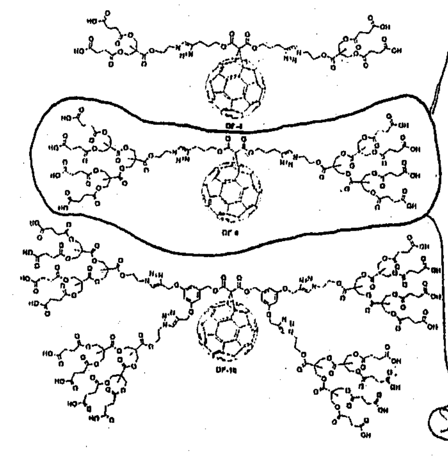
(±)1 球状ミセル

(+)1 ナノファイバー

SEM (±)-1 (+)1

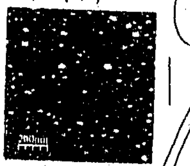
This work

カルボキシル基の異なるC₆₀誘導体



(THF/H₂O 2:7) (1.2×10⁻⁵M)

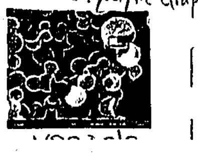
AFM



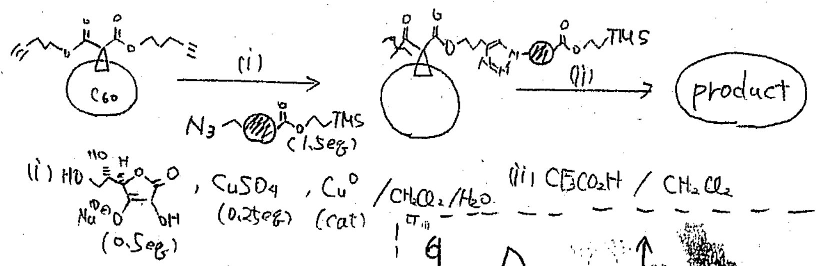
on mica

on HOPG (Highly Oriented Pyrolytic Graphite)

SEM

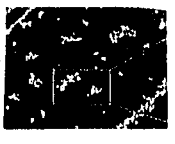


合成



(i) HO ... Na⁺ ... (0.5eq), CuSO₄ (0.25eq), Cu⁰ (cat) / CH₂Cl₂/H₂O (ii) CF₃CO₂H / CH₂Cl₂

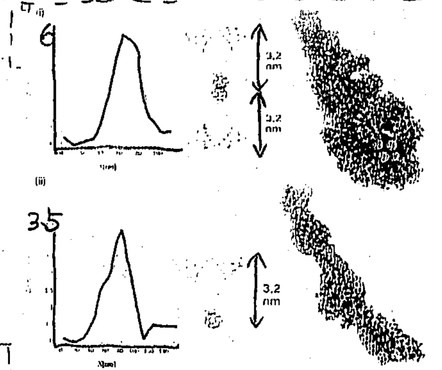
AFM



(THF 1.2×10⁻⁵M)

水の存在が重要!!

DF4, DF16では形成しない。



SEM

DF4

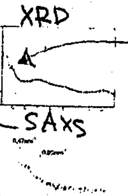
DF16

DF8

interaction

XRDより長距離の

vesicleが形成されない!



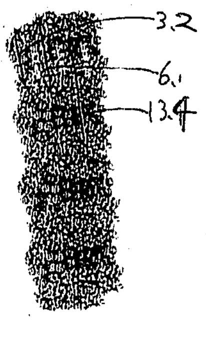
2θ=8°

$d=\frac{0.154}{2\sin(4)}=1.10\,nm$

$D=\frac{2\pi}{q}$ $q=0.47$, $0.95$

$D=13.36\,nm$, $3.2\,nm$

C₆₀-C₆₀ packing!!

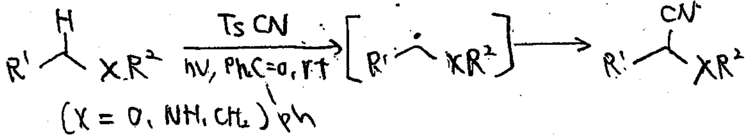


# Photochemically Induced Radical Transformation of C(sp³) – H Bonds to C(sp³) – CN Bonds

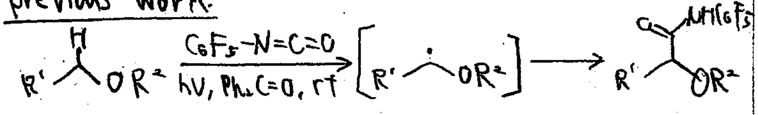
(D1 早川)

M. Inoue, et al (Tokyo Univ.) Org. Lett. ASAP
(DOI : ol 202659e)

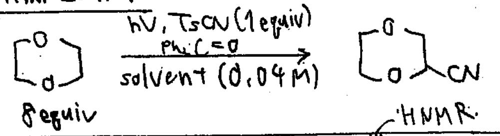
present work.



previous work.



Optimization

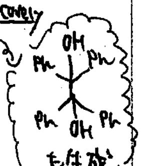


ランプ
中圧水銀灯
100W

¹HNMR

| entry | solvent | Ph₂C=O (equiv.) | t. (h) | yield (%) | Ph₂C=O (recovery) |
|---|---|---|---|---|---|
| 1 | benzene | 1 | 6 | 74 | 59 |
| 2[a] | benzene | 0 | 12 | 0 | — |
| 3 | benzene | 0.5 | 12 | 64 | <4 |
| 4 | benzene | 1 | 24 | 46 | 48 |
| 5 | dioxane | 1 | 1 | 85 | 90 |
| 6 | MeCN | 1 | 6 | 72 (63) | 87 |
| 7 | MeCN | 0.5 | 6 | 74 | 88 |

(a) TsCN (83%) 回収.

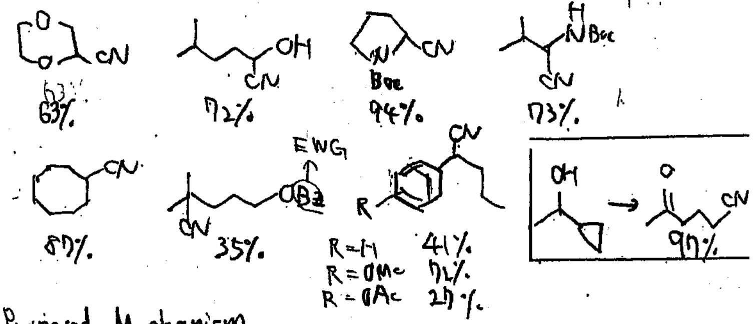


も生成

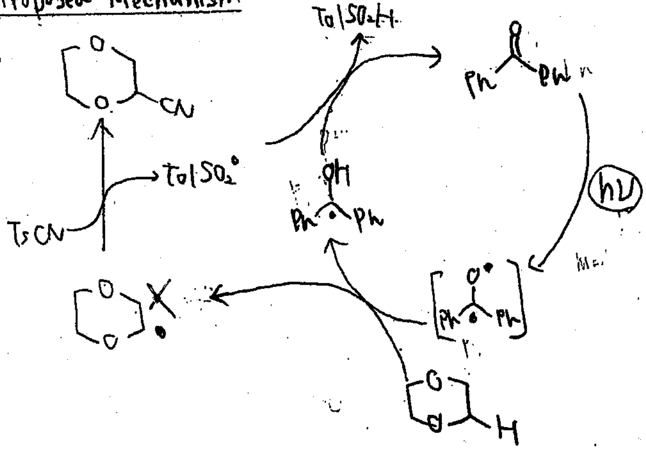
→ 回収率がよい

揮発性のため単離収率が低下

Scope. (substrate : TsCN : Ph₂C=O = 8 : 1 : 1) in MeCN



Proposed Mechanism



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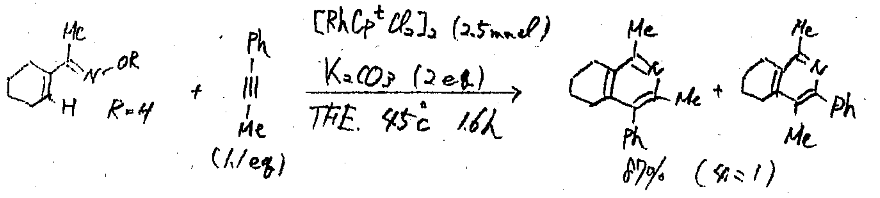
# Pyridine synthesis from oximes and alkynes via rhodium(III) catalysis :Cp* and Cpᵗ provide complementary selectivity

M2 奥村

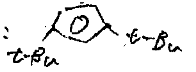
T. K. Hyster, T. Rovis

*Chem. Commun.* DOI: 10.1039/c1cc15248c

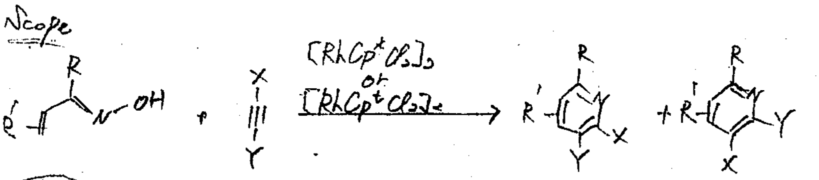


- R = Me では no reaction
- Cpᵗ の代わりに Cp* を使うと生成比が逆転
  83% (1:2)

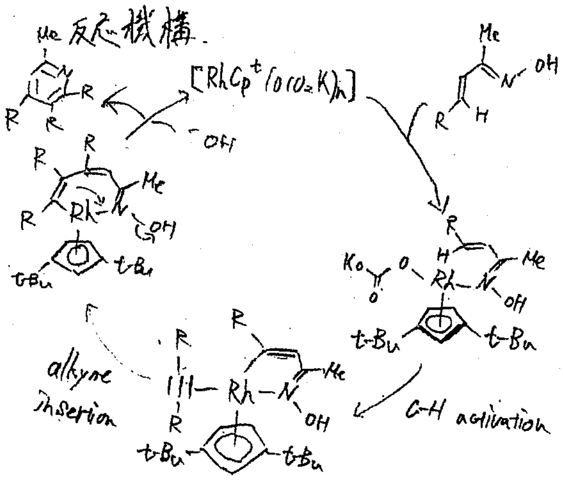
Cpᵗ :



Scope



Me 反応機構



(oxime)

R は主にアルキル、H でも反応は進行 (収率低い)

R' が アルキル, フェニル → 選択性 低い

R' が 求引基 (CF₃、エステル) で オレフィンの末端に置換されているものは 選択性高い (6.6~10 : 1)

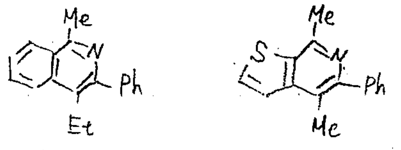
(alkyne) ※ Cp* で しか やってない

立体、電子的に差があると選択性いい

ex

X = Ph , Y = c-Pr (9.4 : 1)
= Ph = CO₂Me ( 5 : 1 )
= C₆H₄CH₃ = Me (3.5 : 1)
= Me = i-Pr (10 : 1)

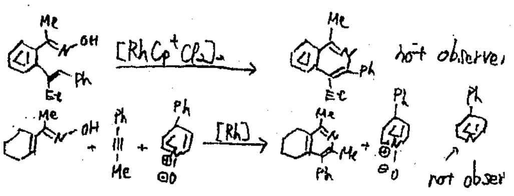
芳香環のオキシムでも反応進行



* 94% (10 : 1)

Cp* 93%
(10 : 1)
Cpᵗ 95%
(1 : 2.5)

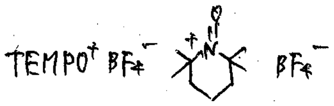
全体的に Cpᵗ を使ったときの生成比はあまり高くない



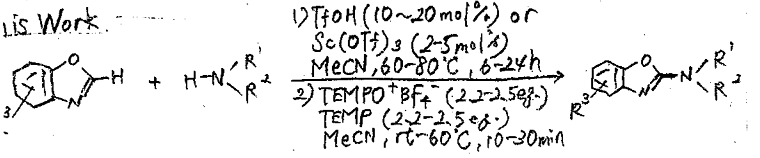
## mination of Benzoxazoles and 1,3,4-Oxadiazoles Using 2,2,6,6-Tetramethylpiperidine-*N*-oxoammonium Tetrafluoroborate as an Organic Oxidant

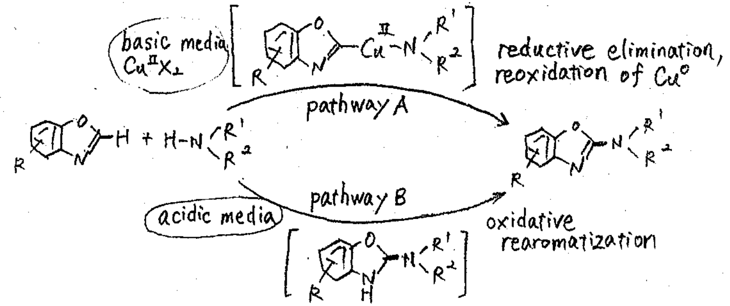
Sebastian Wertz, Shintaro Kodama, and Armido Studer*

*Angew. Chem. Int. Ed* (DOI: 10.1002/anie.201104735)



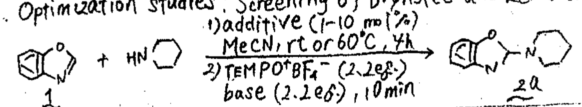
is Work



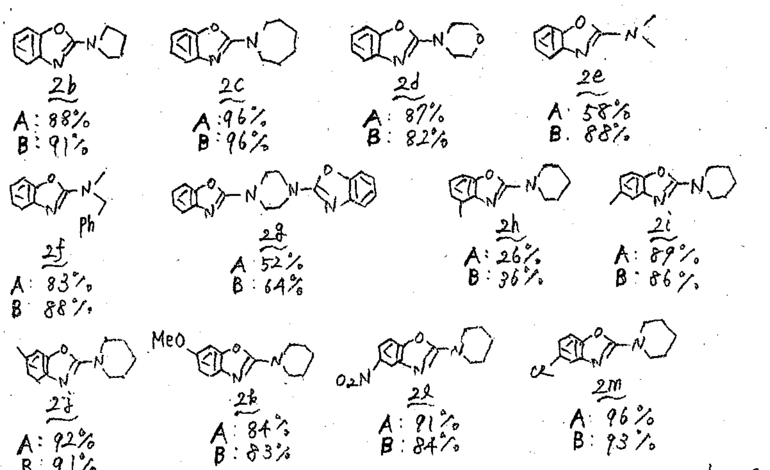


Scheme 1. Strategies for and key intermediates in the direct amination of benzoxazoles.

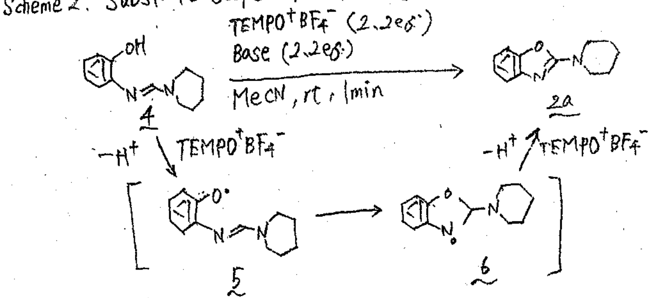
Table 1. Optimization studies: Screening of Brønsted and Lewis acids.



| entry | Additive (mol%) | T (°C) | Base | Yield (%) | |
|---|---|---|---|---|---|
| 1 | 2,6-$Cl_2C_5H_3CO_2H$ (10) | rt | 2.6-lutidine | 72 | |
| 2 | 2,6-$Cl_2C_5H_3CO_2H$ (10) | rt | TEMP | 76 | |
| 3 | 2,6-$Cl_2C_5H_3CO_2H$ (10) | 60 | TEMP | 83 | |
| 4 | TfOH (10) | 60 | TEMP | 93 | A |
| 5 | Sc(OTf)₃ (2) | 60 | TEMP | 90 | B |



Scheme 2. Substrate scope: Variation of the amine and the benzoxazole core



Scheme 3. Mechanistic studies

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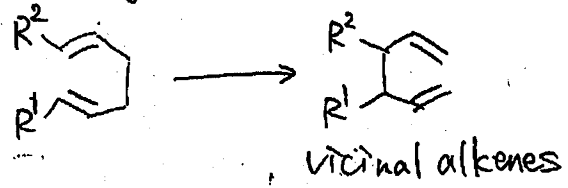
Yuki Ikeda

## Diastereocontrol in Asymmetric Allyl—Allyl Cross-Coupling: Stereocontrolled Reaction of Prochiral Allylboronates with Prochiral Allyl Chlorides

Brozek, L. A.; Ardolino, M. J.; Morken, J. P

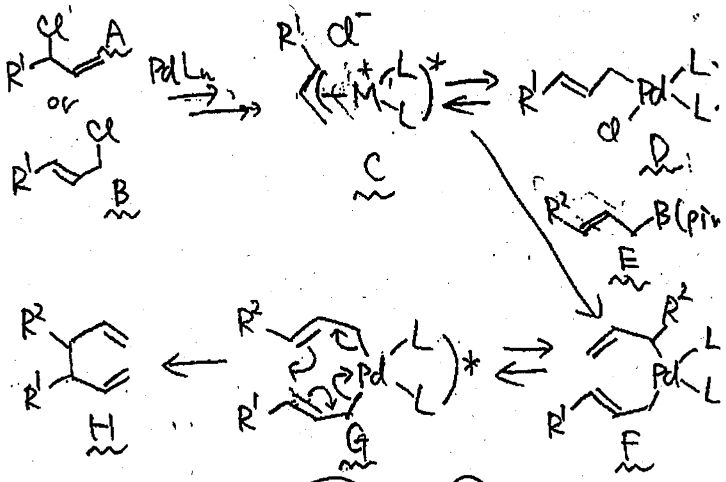
*JACS doi: 10.1021/ja2075967*

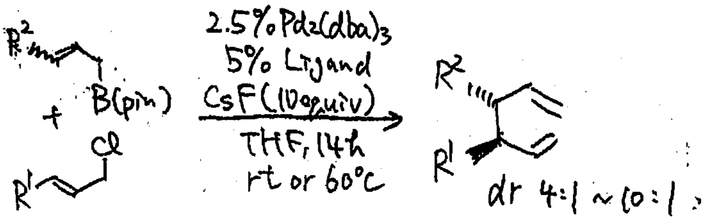
Cope rearrangement.



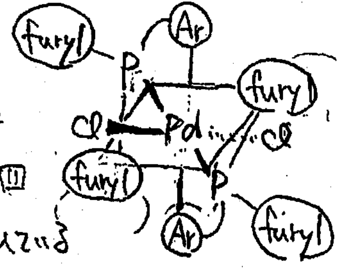
vicinal alkenes

no enantioselective variant



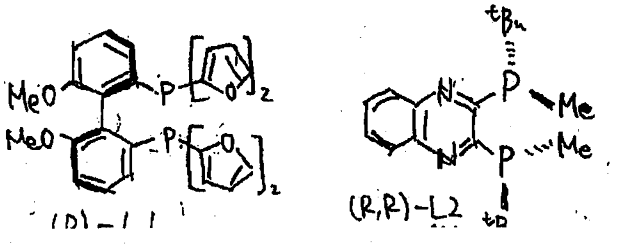


dr 4:1 ~ 10:1
ee 84 ~ 98%



X-ray structure of L1·PdCl₂

Pdを中心とする平面四角形から塩素がずれている



(R)-L1 (R,R)-L2

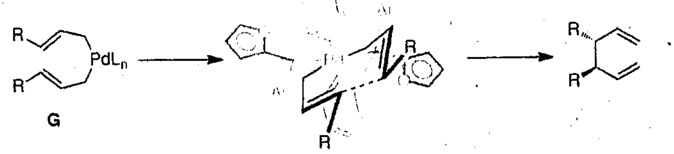


Figure 2. Model for stereochemical outcome in allyl–allyl couplings

# Efficient Ternary Blend Bulk Heterojuncion Solar Cells with Tunable Open-Circuit Voltage

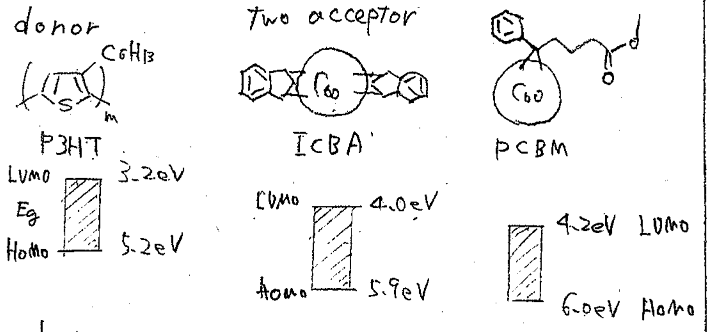
Thompson, B. *et al. J. Am. Chem. Soc.* **2011**, *133*, 14534-14537

M1 河合

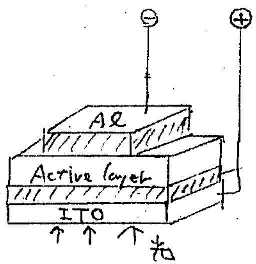
- binary blend: one donor + one acceptor
- ternary blend: 1d + 2a or 2d + 1a

binary blend の太陽電池は 10～12% の変換効率が限界と言われている。

- This work



- device



PEDOT:PSS

Jsc：短絡電流密度

Voc：開放電圧

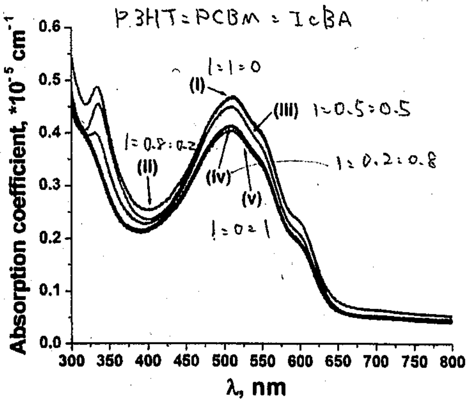
FF：曲率因子

η：光電変換効率

| P3HT:PC$_{61}$BM:ICBA | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V)$^{b}$ | FF | η (%) |
|---|---|---|---|---|
| 1:1:0$^{c}$ | 9.90 | 0.605 | 0.60 | 3.57 |
| 1:0.9:0.1$^{d}$ | 9.22 | 0.618 | 0.59 | 3.29 |
| 1:0.8:0.2$^{d}$ | 9.11 | 0.631 | 0.57 | 3.28 |
| 1:0.7:0.3$^{e}$ | 8.58 | 0.649 | 0.58 | 3.22 |
| 1:0.6:0.4$^{f}$ | 8.31 | 0.669 | 0.58 | 3.11 |
| 1:0.5:0.5$^{g}$ | 8.27 | 0.688 | 0.57 | 3.18 |
| 1:0.4:0.6$^{e}$ | 8.18 | 0.709 | 0.57 | 3.22 |
| 1:0.3:0.7$^{h}$ | 8.14 | 0.741 | 0.57 | 3.34 |
| 1:0.2:0.8$^{d}$ | 8.19 | 0.769 | 0.59 | 3.69 |
| 1:0.1:0.9$^{d}$ | 8.18 | 0.804 | 0.60 | 3.91 |
| 1:0:1$^{h}$ | 8.23 | 0.844 | 0.58 | 3.98 |

Jsc 大 ↑ 小

Voc 小 ↓ 大



EQE = 外部量子効率
吸収した光子から生まれる
電子の割合

ICBA 増 → EQE 低

UV-vis（可視光領域）

ICBA 増 → 吸光率低

光子によって生成する電子が
減ったため Jsc が下がった。

- 筆者らによる仮説

ternary system : $D_1, D_2 + A$(fullerene)

$D_1 + A$ = Voc = 0.8V Jsc = 8.0mA/cm², FF=0.6, η = 3.8%
$D_2 + A$ = 〃 0.5V 〃 14.0mA/cm² FF=0.6 η = 4.2%
$D_1 + D_2 + A$ = 〃 0.65V 〃 15mA/cm² FF=0.6 η = 5.9%

---

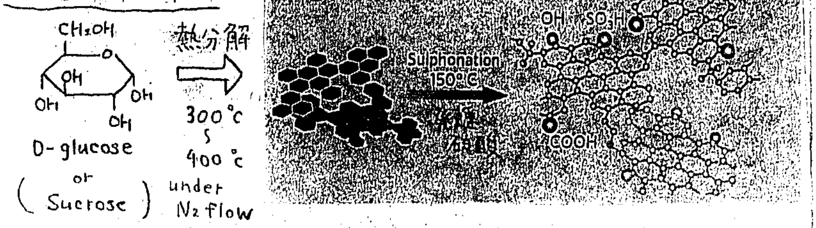
# Facile synthesis of a sulfonated carbon-silica-meso composite and mesoporous silica

Devaki Nandan, Peta Sreenivasulu, Sandeep K. Saxena and Nagbhatla Viswanadham*

Chem. Commun., 2011, 47, 11537

M1 錦織

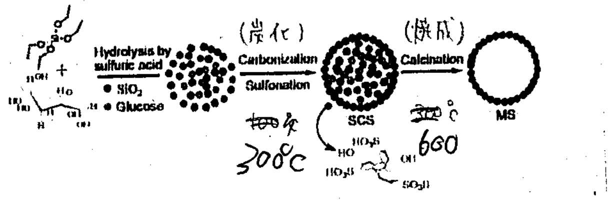
- Sugar Catalyst



☆ 熱的、化学的な安定性、強い固体酸、リサイクル可能

Toda et. al. Nature, 2005, 438, 178

- Present Work



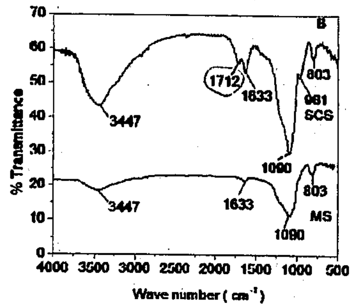
TEOS に対して 0.385 glucose : 4.8 $H_2O$ : 0.88 $H_2SO_4$ (mole 比)

☆ 界面活性剤を用いずに、メソポーラスシリカを合成

→ XRD, $N_2$ 吸脱着等温線、SEM によってメソ孔を確認

| Sample | 比表面積/m²·g⁻¹ (メソ | ・ミクロ) | 比体積/cm³·g⁻¹ | 細孔径/nm |
|---|---|---|---|---|
| SCS | 539.23 | 240.44 | 0.52 | 2.6 |
| MS | 656.47 | 0 | 0.87 | 5.3 |

IR



SCS

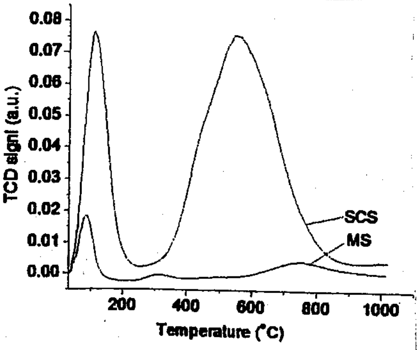
$-OSO_3H$ : 1712 cm$^{-1}$

※ 1207 cm$^{-1}$ に $-OSO_3H$ 由来のピークがでるはずだが、シリカ由来のピークで被って見えない。

MS

$-OSO_3H$ 基は消失。

TPD → アンモニアの脱離した量・温度を見る。



高温で脱離
→ 強い酸点

低温で脱離
→ 弱い酸点

SCS 強い酸点をもつ

MS 〃 をもたない

$$\text{Phenol} + \underset{(2\ \text{eq.})}{t\text{BuOH}} \xrightarrow[120\ ^\circ\text{C},\ 9\text{h}]{\text{SCS}} \text{TBP (tert-butyl phenol)}$$

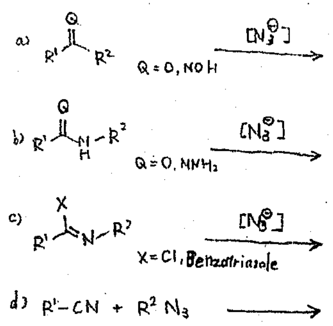
| cycle | conv. of phenol (%) | Selectivity of Product (%) | | |
|---|---|---|---|---|
| | | 2-TBP | 4-TBP | 2,4-DTPB |
| 1 | 50 | 52 | 30 | 18 |
| 2 | 48 | 52 | 31 | 17 |
| 3 | 49 | 53 | 29 | 18 |

# Implanting Nitrogen into Hydrocarbon Molecules through C-H and C-C Bond Cleavages: A Direct Approach to Tetrazoles

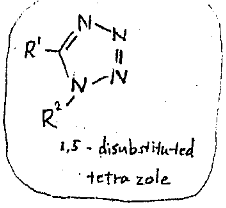
Feng Chen, Cheng Qin, Yuxin Cui, and Ning Jiao* M1 矢野

Angew. Chem. Int. Ed. 2011, 50, 1. DOI: 10.1002/anie.201105505

テトラゾールの合成法



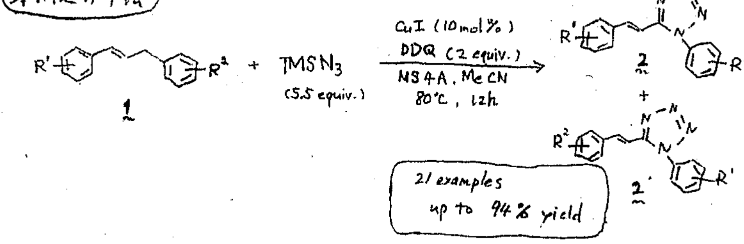
a) Suzuki, H. et al. Synthesis (1998) など
b) Zabrocki, J. et al. J. Org. Chem (1992) など
c) Artamonova, T.V. et al. Synthesis (1996) など
d) Carrillo, D. et al. J. Am. Chem. Soc (2011) など



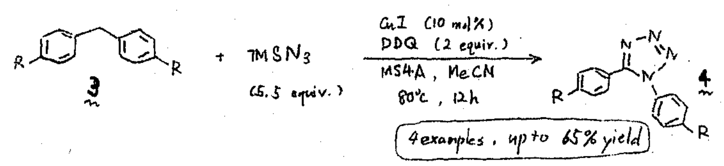
1,5 - disubstituted tetrazole

従来法では官能化された出発物質を利用している。

本論文の手法

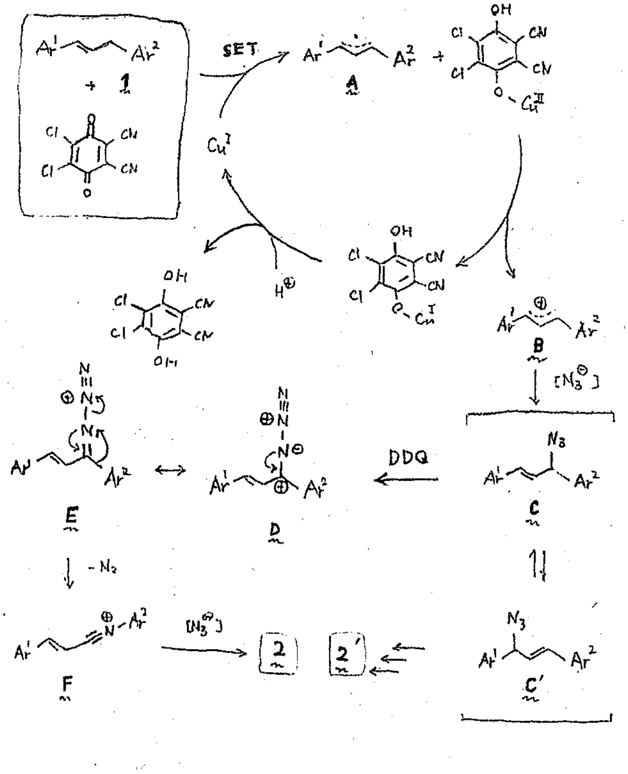


21 examples
up to 94% yield



4 examples, up to 65% yield

Proposed Pathway



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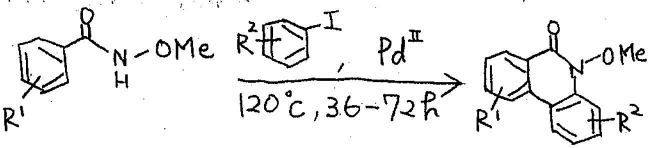
34久國

# Synthesis of Phenanthridinones from N-Methoxybenzamides and Arenes by Multiple Palladium-Catalyzed C-H Activation Steps at Room Temperature.

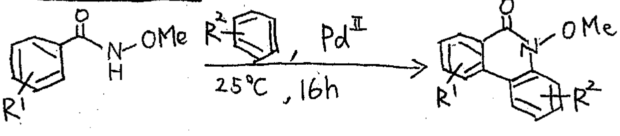
2a : $R^2$=H, $R^3$=$CH_3$
2b : $R^2$=H, $R^3$=Cl
2c : $R^2$=$CH_3$, $R^3$=CH

Previous work

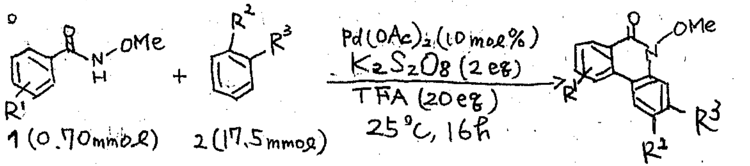


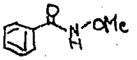
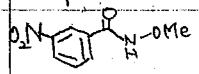
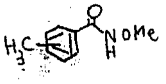
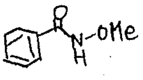
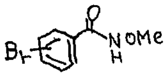
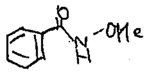
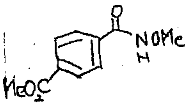
- expensive metal oxidant Ag系のoxidant
- high temperature
- long reaction time

Present work

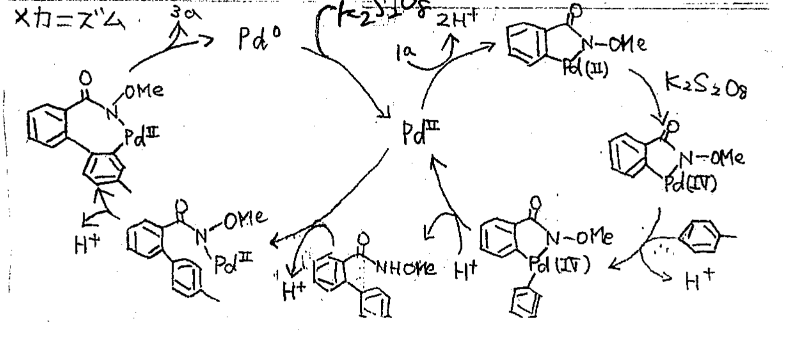


- highly regioselective
- very mild conditions
- no prefunctionalization



| 1 | 2 | Yield [%] | 1 | 2 | Yield[ |
|---|---|---|---|---|---|
|  | 2a | 92 |  | 2a | 64 |
|  | 2a | o-: 80<br>m-: 86<br>p-: 90 |  | 2b | 65 |
|  | 2a | m-: 74<br>p-: 86 |  | 2c | 83 |
|  | 2a | 89 | | | |

メカニズム



Angew. chem. Int. Ed
10.1002/anie.201104311