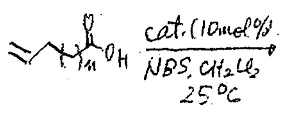
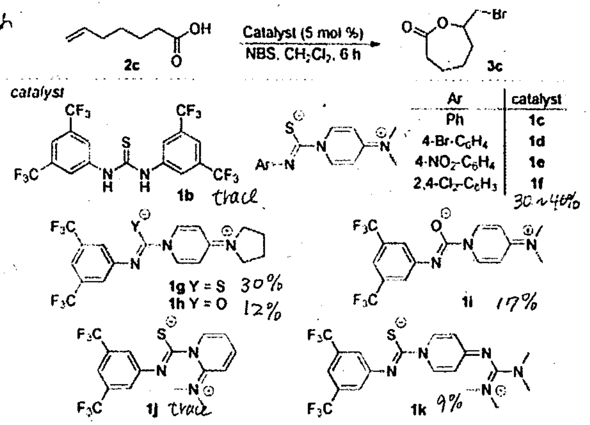
Ying-Yeung Yeung et al.	National University of Singapore	***JACS*** (ja307210n)	Minakata

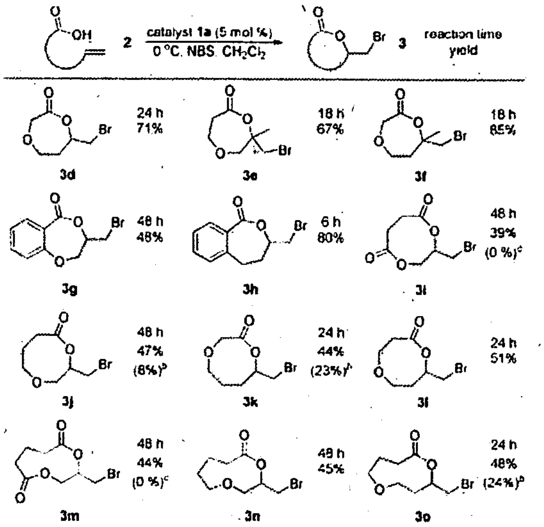
Efficient Medium Ring Size Bromolactonization Using a Sulfur-Based Zwitterionic Organocatalyst

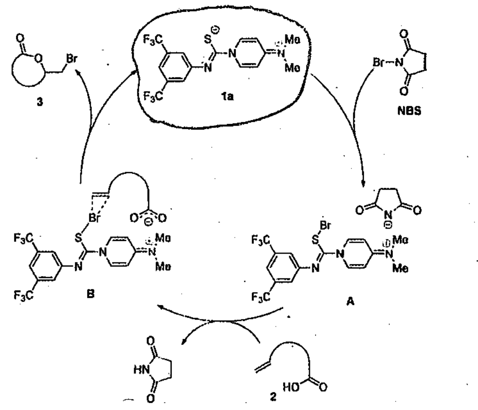


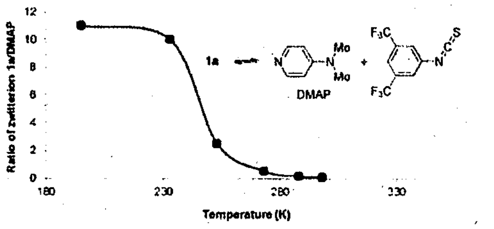
cat.	n	time(h)	yield(%)
none	1	54	99
1a	1	0.75	92
DMAP	1	5	69
DABCO	1	3	92
1a	2	6	89

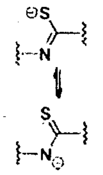


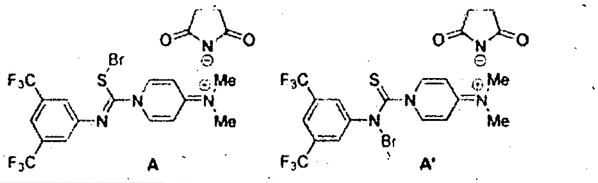
1a cat. 25°C ⇒ 25% 0°C ⇒ 54%









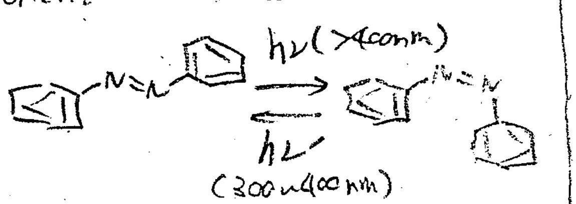


I. Aprahamian et al.	Dartmouth College, United States	*J. Am. Chem. Soc.* **2012**, *134*, 15221–15224.	Youhei Takeda

Visible Light Switching of a BF$_2$-Coordinated Azo Compound

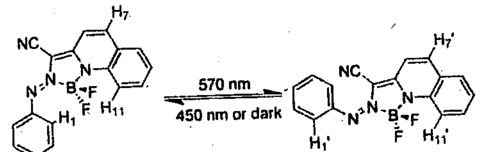
(※分子設計(特にLewis酸)に一般性ありそう。)

photo-induced trans-cis isomerization of azobenzene



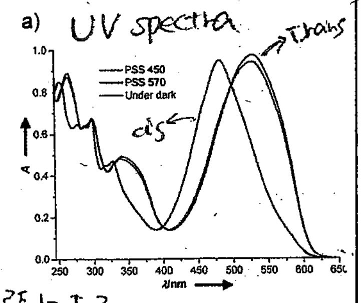
※ hν, hν' を可視光 or Δ 領域にまでずらせれば用途が増える。(生体イメージング等)

<Serendipitous discovery of the formation of azo 2>

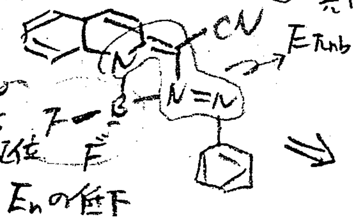


淡いピンク (trans)

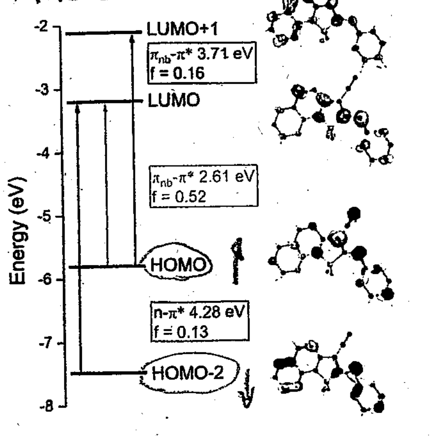
τ½ 12.5h! オレンジ (cis) (何度もくり返し可能)



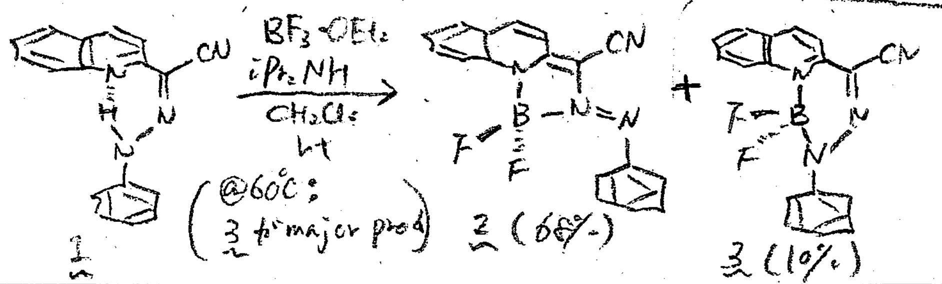
② 共役の拡張による Eπnb の向上。



① Lewis 酸の配位による En の低下

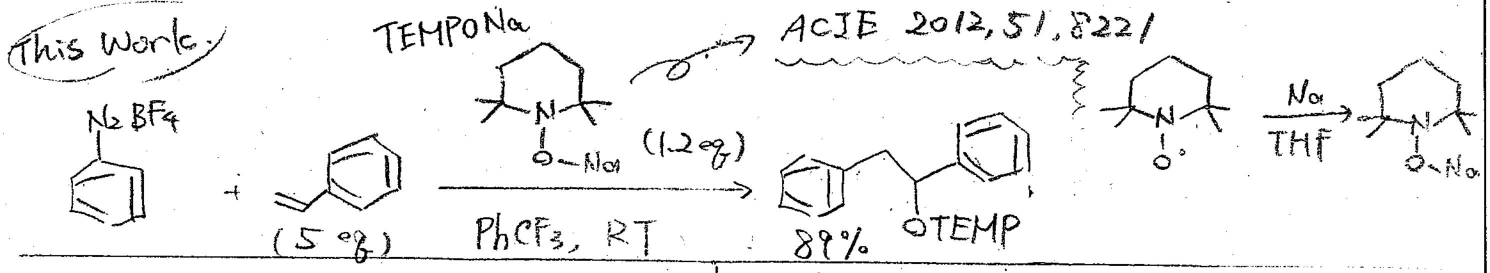


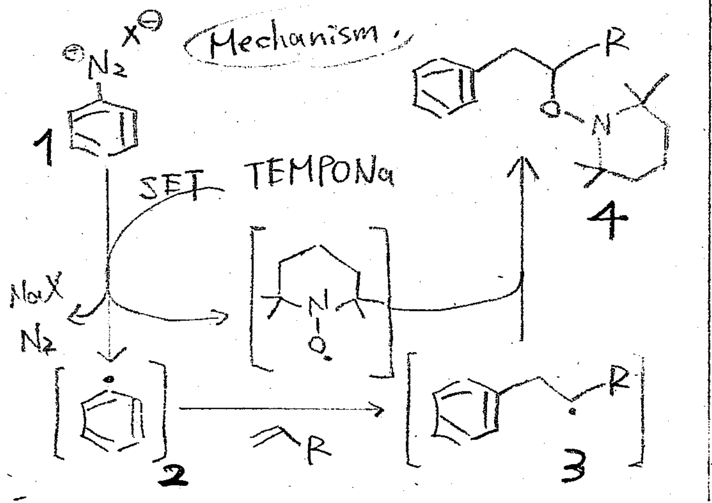
DFT-calculation

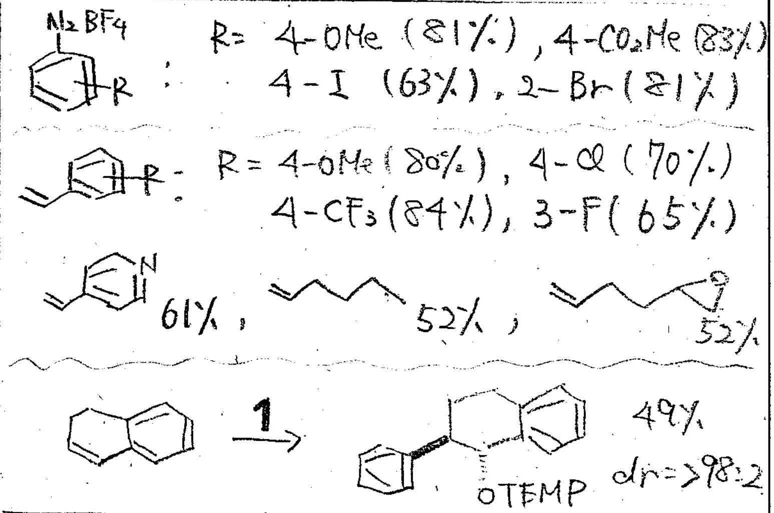


Armido Studer	University of Münster (Germany)	*JACS*, ja307638u	清川

Transition-Metal-Free Oxyarylation of Alkenes with Aryl Diazonium Salts and TEMPONa



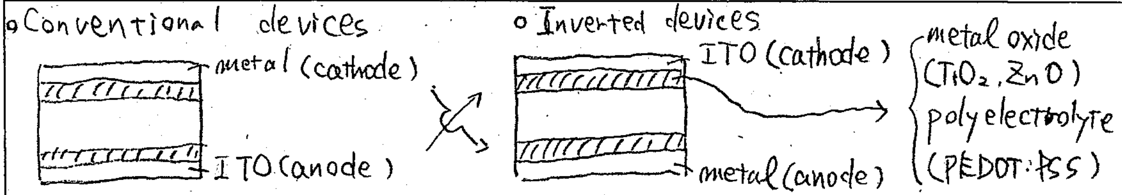




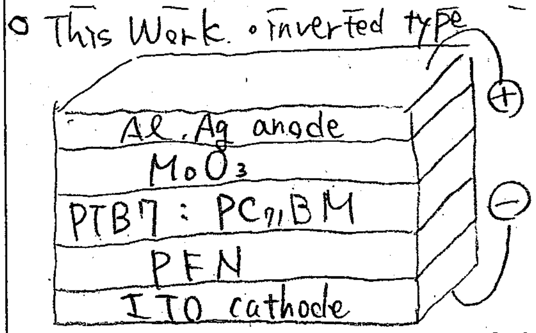
$[ArN_2^{\oplus} + TEMPO^{-} \rightarrow Ar{-}N{=}N{-}OTEMPO \rightarrow Ar^{\cdot} + N_2\uparrow + TEMPO]$

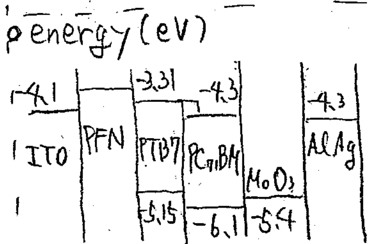
Hongbin, Wu et al	South China University of Technology	10.1038/NPHOTON.2012.190	Nagamachi

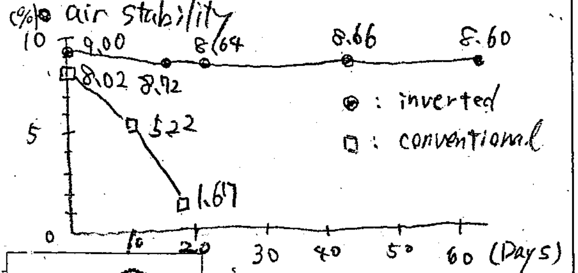
Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure

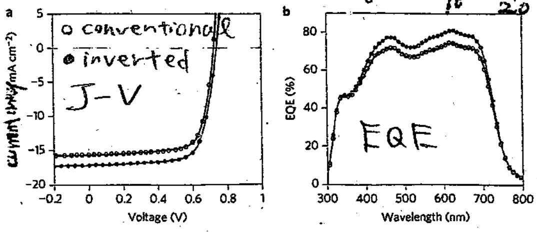


advantage
air stable
PEDOT:PSS や low-work-function metal を使う必要がない



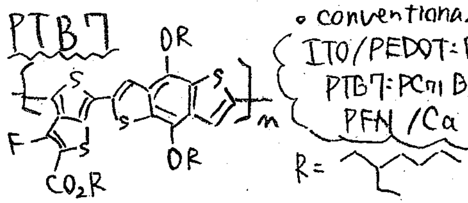




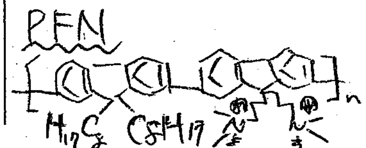


PCEは PFNの Thicknessに影響されやすい
⇒ ITOとPFNの接合面がKey.

5nm : 8.39%
10nm : 8.96%
20nm : 7.36%



- conventional device
ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/PFN/Ca/Al



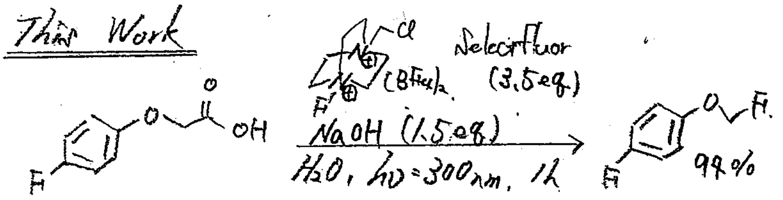
alchol-water-soluble conjucated polymer

devicetype	PCE	Jsc	FF	Voc
conventional	8.24	15.4	70.6	0.759
Inverted	9.21 (10%↑)	17.5	69.99	0.754

Glenn M. Sammis	University of British Columbia (Canada)	*ACIE* DOI:10.1002/201206352	Okumura

Photo-fluorodecarboxylation of 2-Aryoxy and 2-Aryl Carboxylic Acids

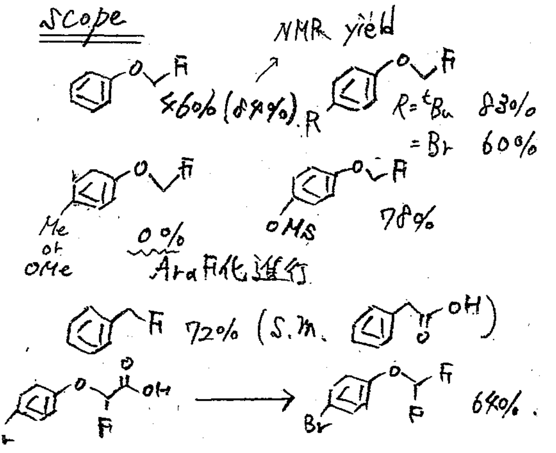
This Work



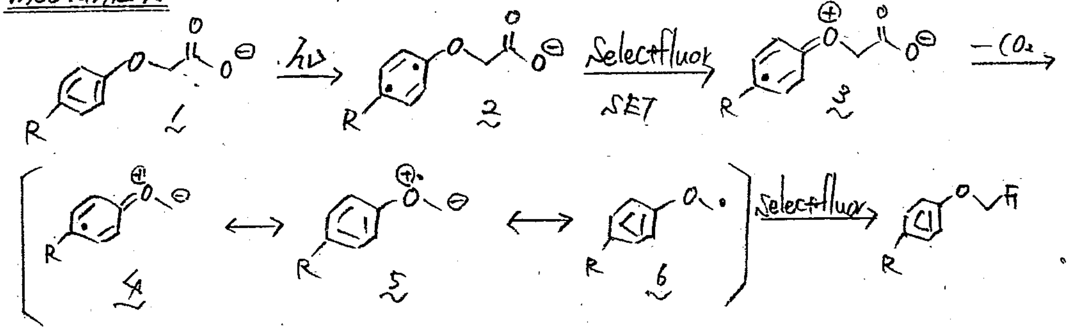
optimization

- light : 350nm (47%), sunlight (42%), tungsten lamp (4%)
- F source : $\mathrm{Py{-}\overset{\oplus}{F}{-}Py\ {}^{\ominus}BF_4}$ (0%), $\mathrm{F{-}N(SO_2Ph)_2}$ (28%)
- 難溶な基質は MeCNを co-solvent に添加

Scope



mechanism

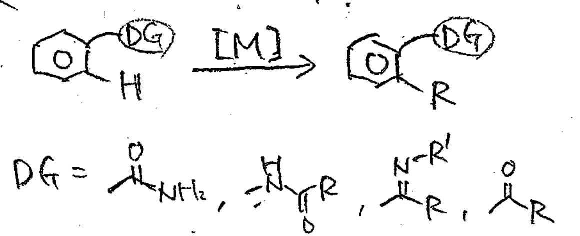


- hypofluorite は NMR より観られない。
- 1 より 2 の方がより良い電子ドナー
- アルキルカルボン酸では進行しない

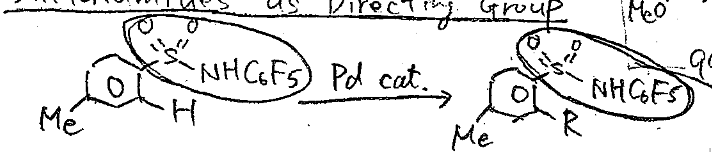
Nicolai Cramer et al.	Laboratory of Asymmetric Catalysis and Synthesis (Switzerland)	*Angew. Chem. Int. Ed.* 10.1002/anie.201206191	池田

Access to Sultams by Rhodium(III)-Catalyzed Directed C–H Activation

〈C–H Activation〉

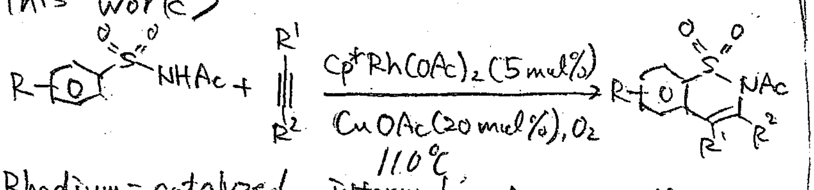


Sulfonamides as Directing Group



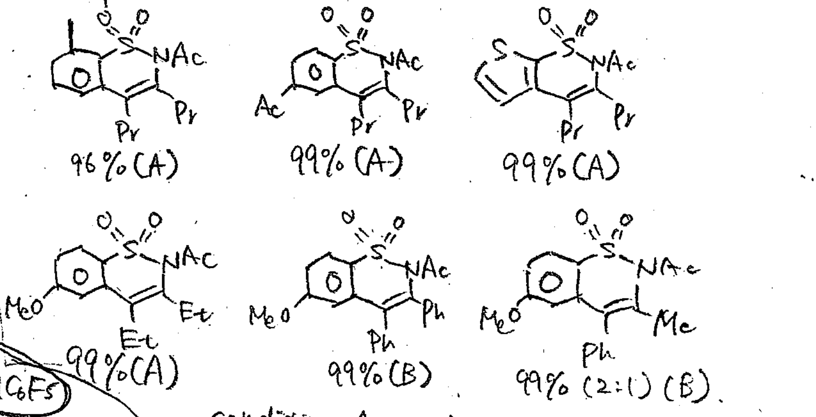
Yu, J.-Q. et al. JACS (2011)

〈This work〉

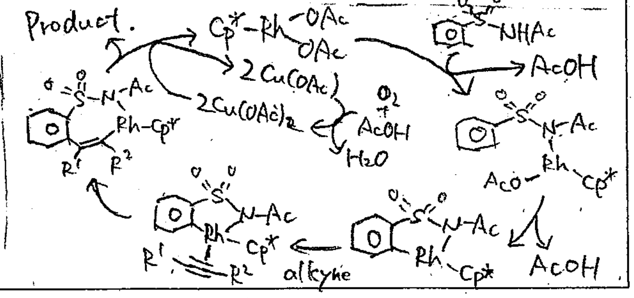


Rhodium-catalyzed Intermolecular reaction

〈Scope〉



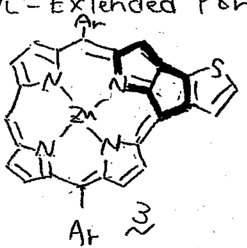
condition A : solvent ; tAmOH
condition B : solvent ; toluene



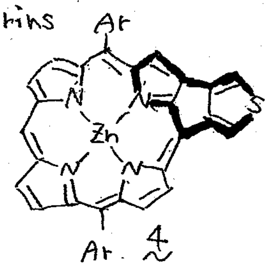
Matsuo, Y. et al	University of Tokyo (Japan)	ja30829991	M2 Kawai

Synthesis of Thieno-Bridged Polphyrins: Changing the Antiaromatic Contribution by the Direction of the Thiophene Ring

・π-Extended Porphyrins

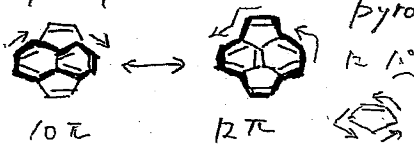


3
18π aromatic
20π antiaromatic



4
18π aromatic
24π weak antiaromatic

∘ Pyracylene

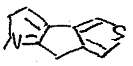


pyracylene の5員環 に パラトロピック環電流

反芳香族性

AICD plot = 3 の5員環にパラトロピック環電流

3



4

NICS(0) : +30.5 ppm　　+13.1 ppm

∘ porphyrin macrocycle の NICS(0)

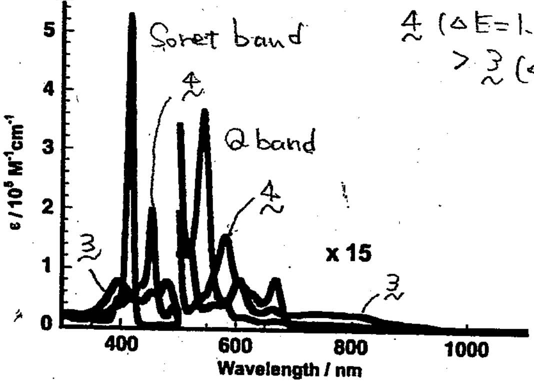
3 = −10.1 ～ −13.6 ppm　3 > 4　↙ 20π

4 : −14.6 ～ −16.1 ppm　3の方が反芳香族性の寄与が大きい。

∘ ^{1}H NMR

β位と meso位のプロトンは、3 の方が 4 より高磁場に観測された。

∘ UV-Vis-NIR



4 (ΔE = 1.93 eV) > 3 (ΔE = 1.59 eV)

4 : fluorescence maxima = 674 nm, Φ = 0.009

3 : No fluorescence

∘ S_1 の lifetime : 4 (790 ps) > 3 (850 fs, 7.5 ps)

3 における $S_1 \rightarrow S_0$ の無輻射遷移がすみやかに起る。

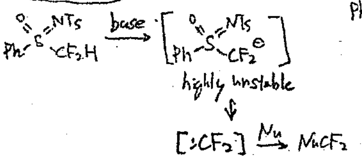
3 の強い反芳香族性により、フロンティア軌道が不安定化

4 は24π系にSを含むため弱い反芳香族性

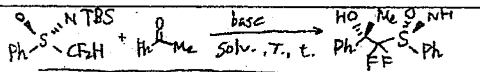
Hu, J. *et al.*	Chinese Academy of Sciences (CHN)	JACS :ja308419a	M2 矢野

Tuning the Reactivity of Difluoromethyl Sulfoximines from Electrophilic to Nucleophilic: Stereoselective Nucleophilic Difluoromethylation of Aryl Ketones

Previous Work



Tsをもっと電子求引性の弱い基に変えることでカルバニオンの寿命を延ばす。

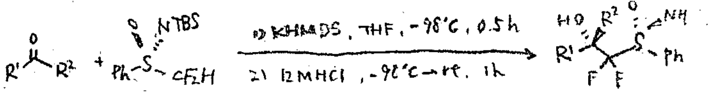


base	solv.	T (℃)	t (h)	yield (%)	dr
NaHMDS	THF	−78	3	37	87/13
KHMDS	THF	−78	3	67	90/10
KHMDS	THF/HMPA	−78	3	48	57/43
KHMDS	THF	−98	0.5	82	93/7
*KHMDS	THF	−98	0.5	99(88)	93/7

sulfoximide : ketone : base = 1.0 : 1.5 : 1.2

* のとき　1.0 : 1.5 : 1.8

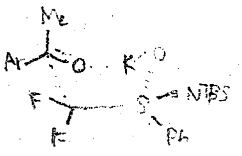
・Difluoromethylation



11 examples

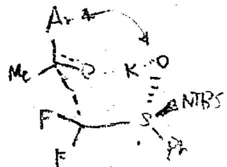
62% ～ 88% yield　80/20 ～ 93/7 dr

Proposed TSs



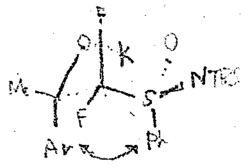
A

favored



B

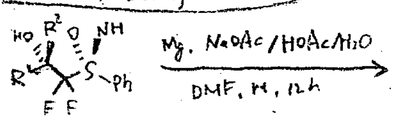
disfavored



C

disfavored

・Reductive Desulfoximination

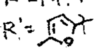


R¹ = Ph, R² = Me 77%

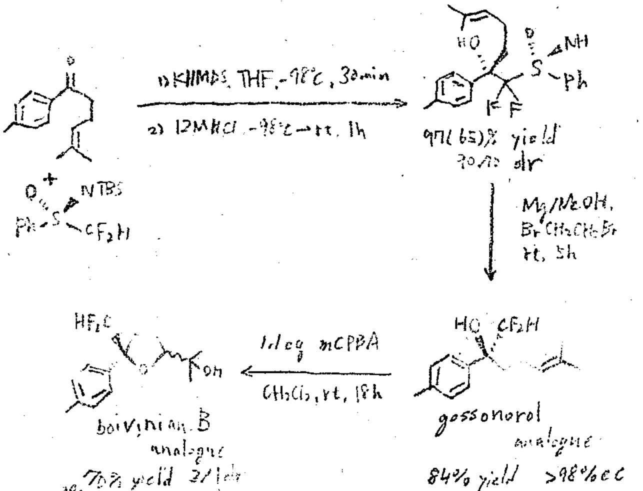
R¹ = 4-FC$_6$H$_4$, R² = Me 68%

R¹ = 2-MeOC$_6$H$_4$, R² = Me 90%

R¹ = Ph, R² = ^{n}Pr 83%

R¹ = , R² = Me 84%

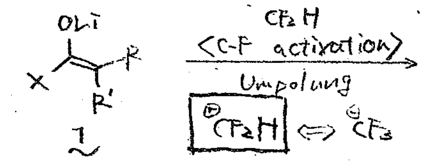
R¹ = 4-BrC$_6$H$_4$, R² = H 68%



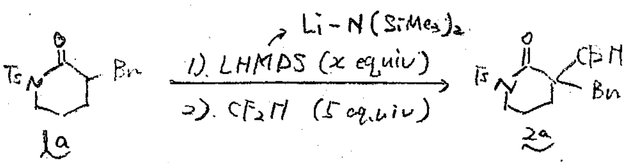
Koichi Mikami et al.	Tokyo Institute of Technology	Angewandte DOI: 10.1002/anie.201203588	M1 榎島

Umpolung of Fluoroform by C-F Bond Activation: Direct Difluoromethylation of Lithium Enolates

☆ Unpolung 極性転換



○ effects of the amount of lithium amide

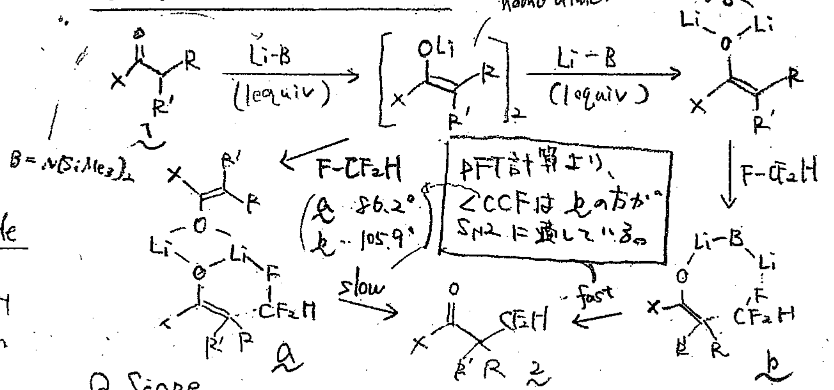


Entry	x [equiv]	T [°C]	t [h]	Yield [%]*
1	1	-78	14	17
2	2	-78	14	45
3	3	-78	14	25
④	2	rt	6	64
5	3	rt	6	24

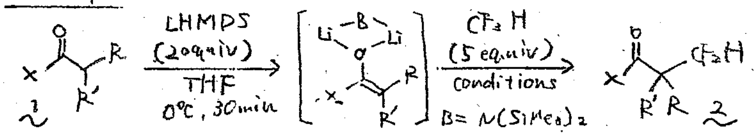
* The yields were determined by ^{19}F NMR

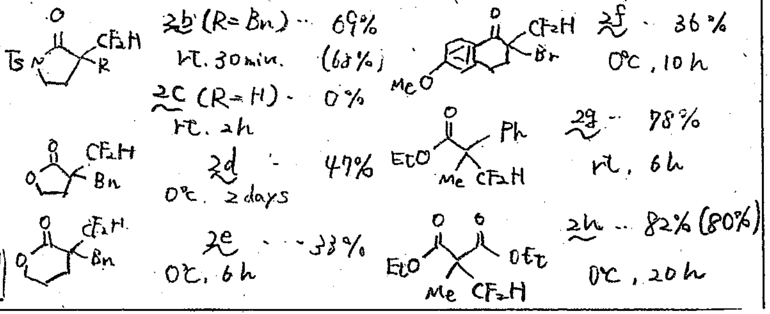
☆ 1当量 < 2当量 > 3当量 ⇒ $\boxed{\text{2当量がベスト!!}}$

○ Plausible Mechanism



○ Scope





2b (R = Bn) … 69% (68%) rt, 30 min.

2c (R = H) · 0% rt, 2h

2d · 47% 0°C, 2 days

2e … 33% 0°C, 6h

2f · 36% 0°C, 10h

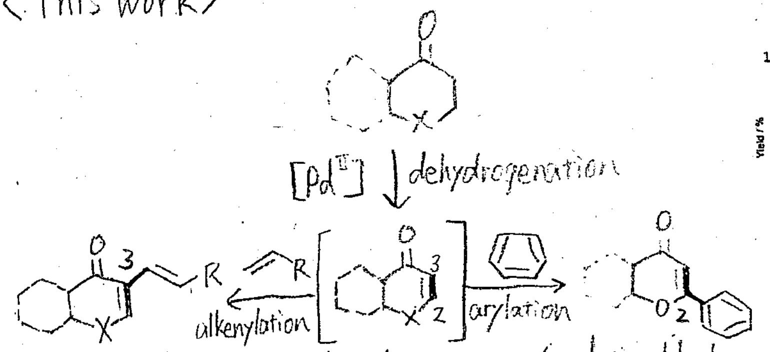
2g · 78% rt, 6h

2h … 82% (80%) 0°C, 20h

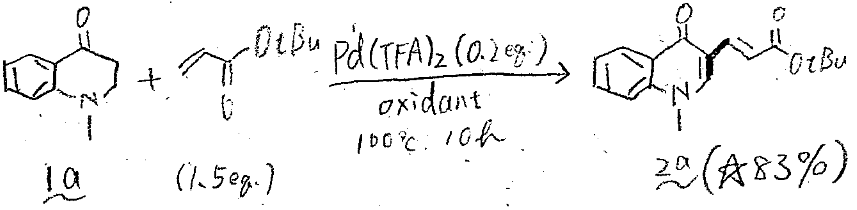
Sungwoo Hong	Korea Advanced Institute of Science and Technology (Korea)	Angew. Chem. Int. Ed. DOI: 10.1002/anie.201206610	岡崎

Palladium-Catalyzed Dehydrogenation/Oxidative Cross-Coupling Sequence of β-Heteroatom-Substituted Ketones

<This work>



<Optimization of the dehydrogenation/oxidative Heck reaction>



Cu (3eq.)

Cu(OAc)2

Cu(TFA)2·nH2O

☆ CuCO3·Cu(OH)2

Ag (3eq.)

AgOAc

(oxidative decomposition of 1a)

Solvent

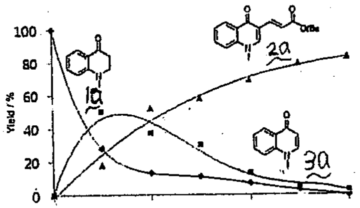
DMF

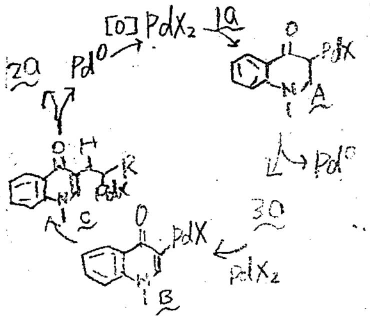
1,4-dioxane

☆ PivOH

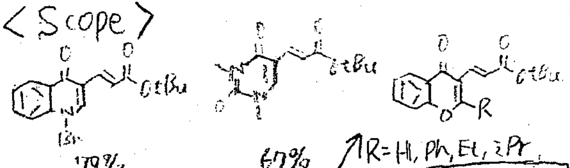
AcOH

<Proposed mechanistic pathways>





<Scope>



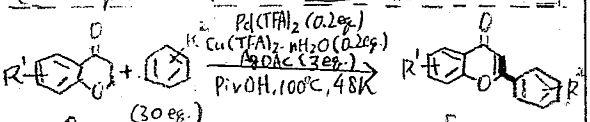
79%

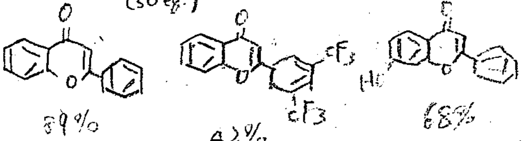
67%

R = H, Ph, Et, iPr

Pd(OAc)2 (0.2eq.), Cu(OAc)2 (0.2eq.), Ag2CO3 (3eq.), PivOH, 110°C, 18~16h

(8 examples 50~93%)





89%

42%

68%

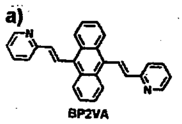
(16 examples 42~89%)

Wenjing Tian	Jilin University	ACIE, 10.1002/anie.201204660	西田

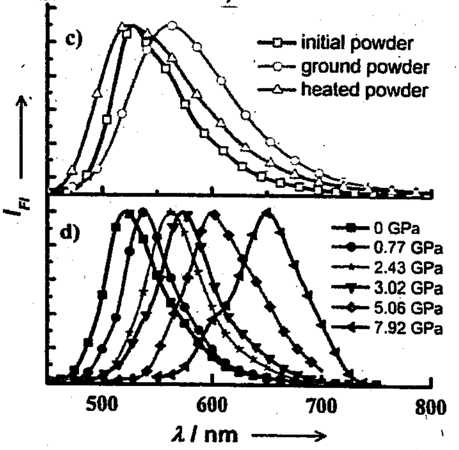
Piezochromic Luminescence Based on the Molecular Aggregation of 9,10-Bis((E)-2-(pyrid-2-yl)vinyl) anthracene

外部圧力を変化 (0 GPa → 7.92 GPa)
↓
分子の配列の仕方が変化
↓
発光スペクトルが変化. (528 nm → 652 nm
green red)

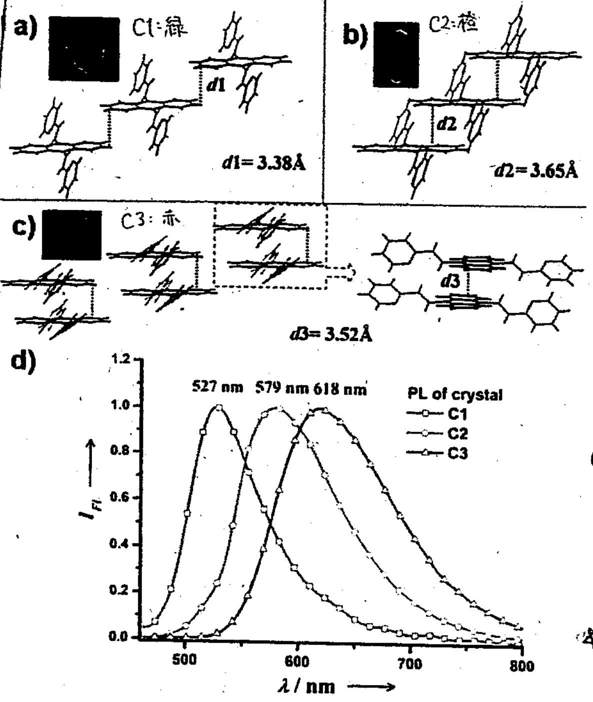
a)



← 今回使用した分子
grinding と heating (160°C) で可逆的に発光スペクトルが変化。



発光色の異なる3種類の単結晶



C1: アントラセン面同士の π-π interaction がほとんどない。
分子間での軌道の重なりも少ない。

$\begin{cases} \lambda_{max} = 527\,nm\ (green) \\ \Phi_F = 0.48 \end{cases}$

C2: アントラセン面が約40%重なっており軌道の重なりが生じている。
弱い π-π interaction。

$\begin{cases} \lambda_{max} = 579\,nm\ (orange) \\ \Phi_F = 0.37 \end{cases}$

C3: アントラセン面がほとんど重なっており.
強い π-π interaction。

$\begin{cases} \lambda_{max} = 618\,nm\ (red) \\ \Phi_F = 0.28 \end{cases}$

※ 外部圧力をかけた時もこのような分子の配列の変化が生じていると考えている。

Matthias Driess	**Technische Universität Berlin (Germany)**	**ACIE, 10.1002/anie.201205840**	**M1 Hisakuni**

The Elusive Silyliumylidene $[ClSi:]^+$ and Silathionium $[ClSi{=}S]^+$ Cations Stabilized by Bis(Iminophosphorane) Chelate Ligand

Silyliumylidene $[RSi:]^+$
(R = H, halogene, organo groups)
→ building blocks, Lewis acid catalysts として利用

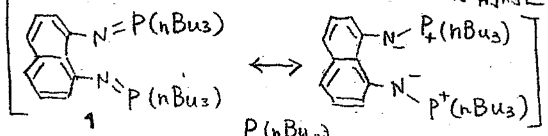
- The first isolabe silyliumylidene cations.

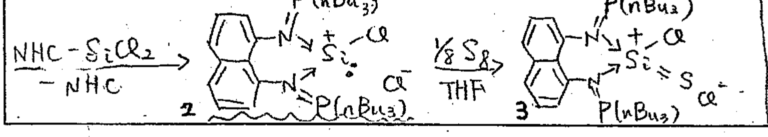
$$(Me_5C_5)_2Si: + Me_5C_5H_2^+B(C_6F_5)_4^- \xrightarrow[CH_2Cl_2]{}$$

$$\underbrace{Me_5C_5Si:^+B(C_6F_5)_4^-} + 2Me_5C_5H$$

- This Work

The synthesis of the isolable $[ClSi:]^+$
→ Cl は求核剤Rで置換できるので、$[ClSi:]^+$は他の $[RSi:]^+$ を合成するのに有用な前駆体となる。





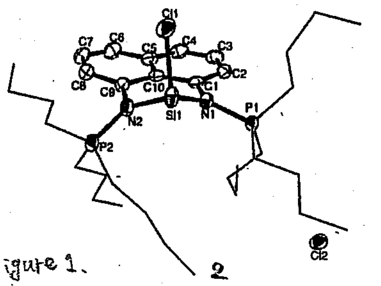


Figure 1. 2

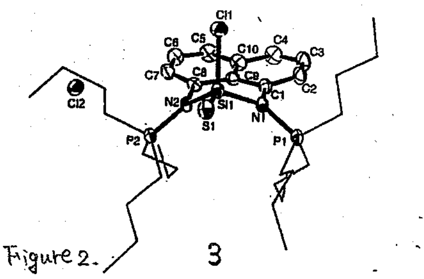


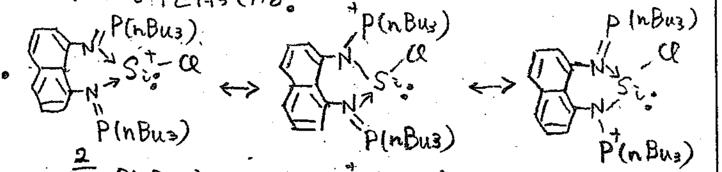
Figure 2. 3

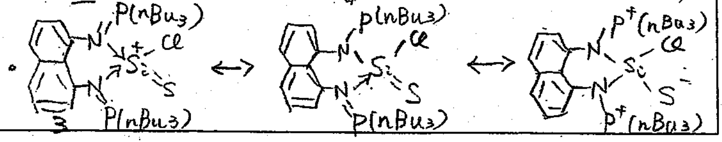
P1−N1 : 1.666Å, P2−N2 : 1.659Å
→ P−N 単結合(1.75−1.80Å)とP=N 二重結合 (1.51−1.57Å) の中間
→ 正電荷は非局在化

- Si 中心は四面体型配位になっている.
- 配位数が増加しているのに Si−Cl の距離は 2 にくらべて短くなっている。(3 : 2.087Å, 2 : 2.171Å)

NPA の結果 : P上に正電荷, N上に負電荷、Si上に正電荷を持っている。

NHC = IPr

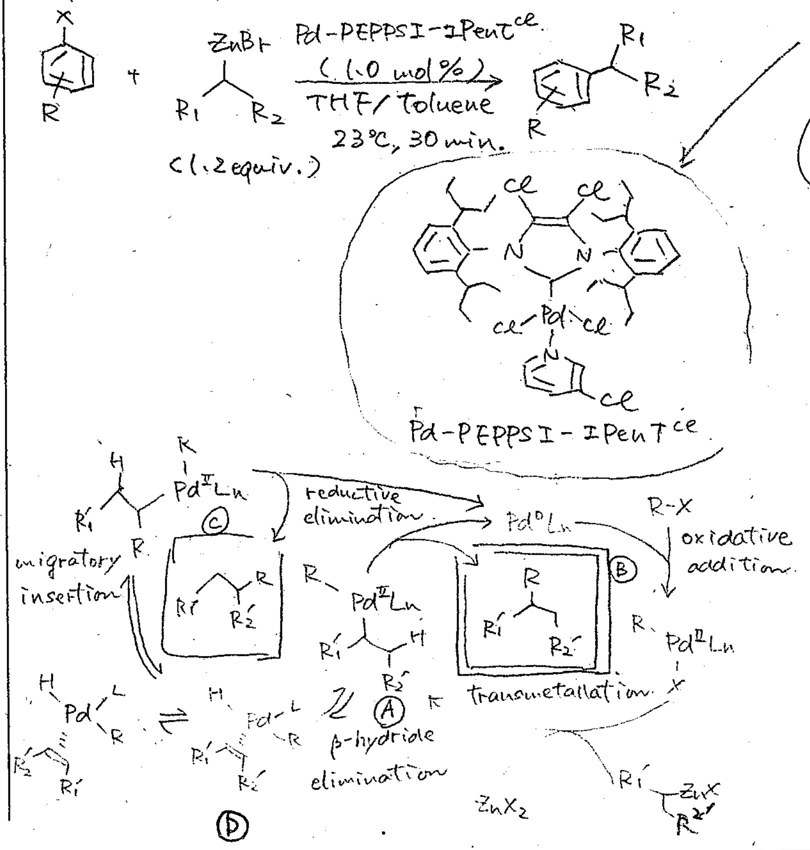




Michael G. Organ	York University (Canada)	Angew. Chem. Int. Ed. DOI: 10.1002/anie.201205747	B4 黒田

Pd-PEPPSI-IPent^{cl}: A Highly Effective Catalyst for the Selective Cross-Coupling of Secondary Organozinc Reagents

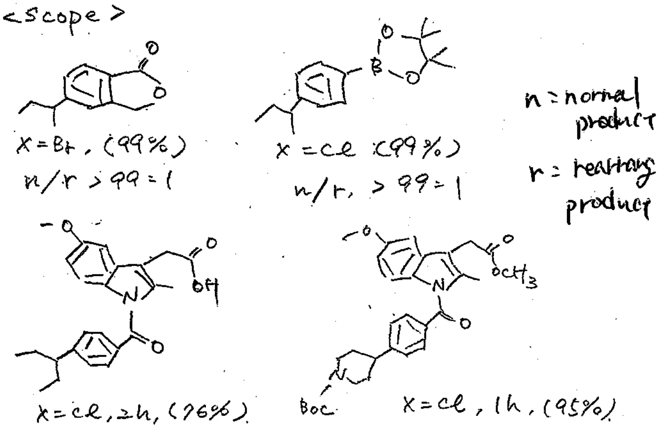
<This Work>



catalyst → ・嵩高い
・電子密度小さい

(← DFT計算
TSⒶ → Ⓑ < TSⒶ → Ⓟ)

<scope>



X = Br, (99%)
n/r > 99:1

X = cl (99%)
n/r > 99:1

X = cl, 2h, (76%)
2 equiv of zinc
n/r > 99:1

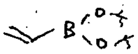
X = cl, 1h, (95%)
n/r > 99:1

n: normal product
r: rearranged product

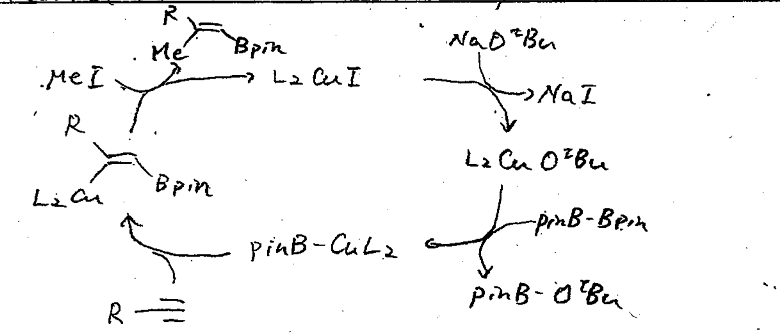
薬学, 医学に関する化合物の
合成にも応用可能

Moriora Tortosa	Universidad Autónoma de madrid (スペイン)	JACS 10.1021/ja307670k	B4 小坂

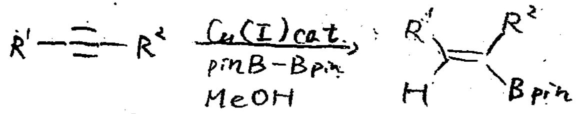
Copper(I)-Catalyzed Formal Carboboration of Alkynes; Synthesis of Tri- and Tetra substituted Vinylboronates

ビニルボロン酸 

・鈴木・宮浦カップリング
・共役付加
などに利用可能で、複雑な分子への
足がかりとなる.
⇒ 3 or 4 置換体を合成する方法がほしい.

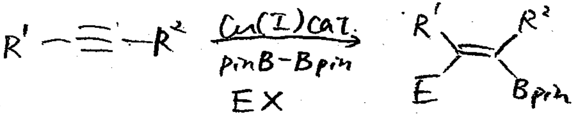


ヒドロホウ素化.



$$R^1-\equiv-R^2 \xrightarrow[\text{pinB-Bpin, MeOH}]{\text{Cu(I)cat.}}$$

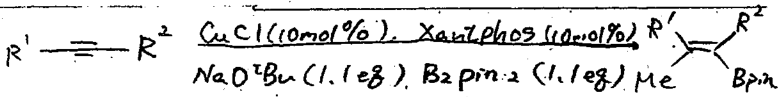
カルボホウ素化 (This work)



$$R^1-\equiv-R^2 \xrightarrow[\text{pinB-Bpin, EX}]{\text{Cu(I)cat.}}$$

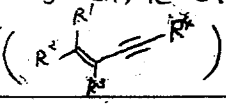
(E = Me, Allyl, Bn)

※末端アルキンにおいては Me, Bn のみ



$$R^1-\equiv-R^2 \xrightarrow[\text{NaO}^t\text{Bu (1.1eq), B}_2\text{pin}_2\text{ (1.1eq), MeI (4.0eq), THF}]{\text{CuCl (10mol\%), Xantphos (10mol\%)}}$$

- R' = Ar, R² = Hのとき, 12 examples 66~83%
  o- や p- 位の電子供与性基がよい.
- R' = Ar, R² = Me or Ph 3 examples 50~70%
  65°C の熱をかける
- R' = アルキル, R² = H 3 examples 56~59%
  プロパルギル位にエーテルが必要.
- 1,3-enyne を用いた場合, 5 examples 52~77%

() ・位置異性体が生成する例もある
・3 or 4 置換ビニルボロン酸が生成