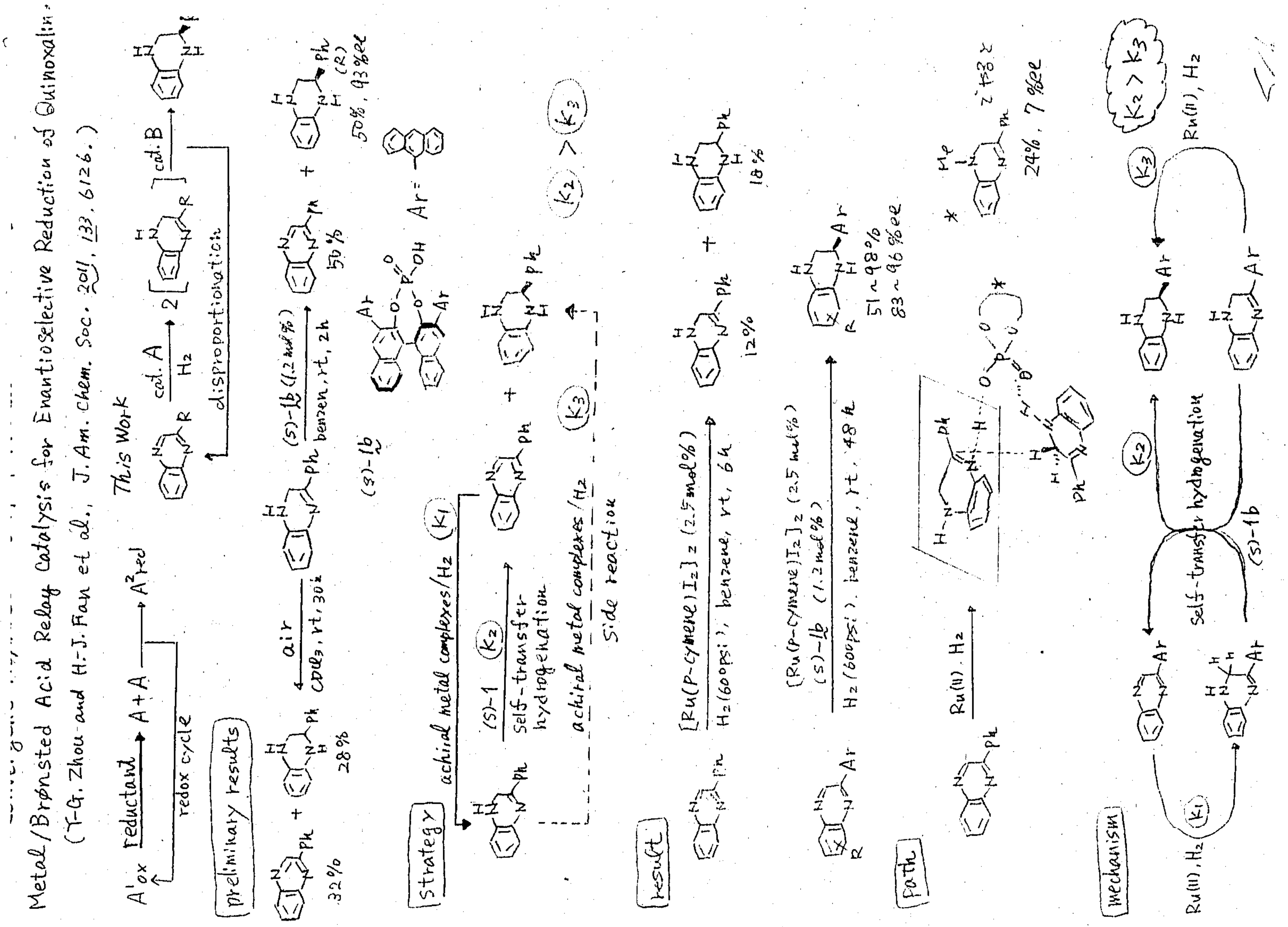
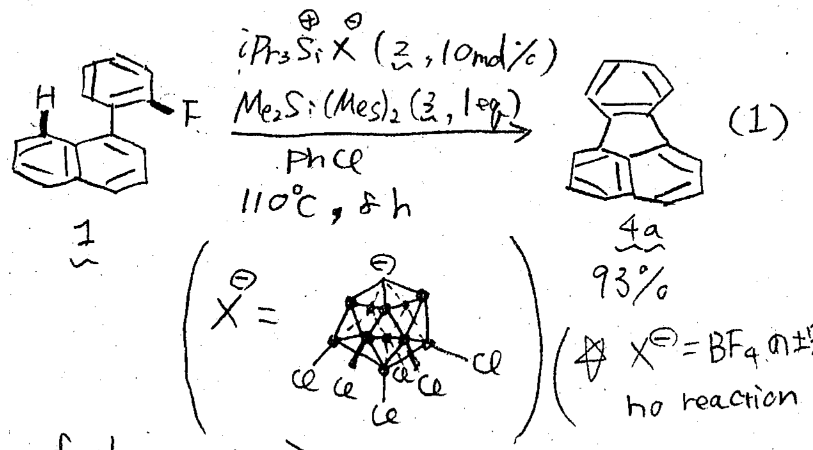




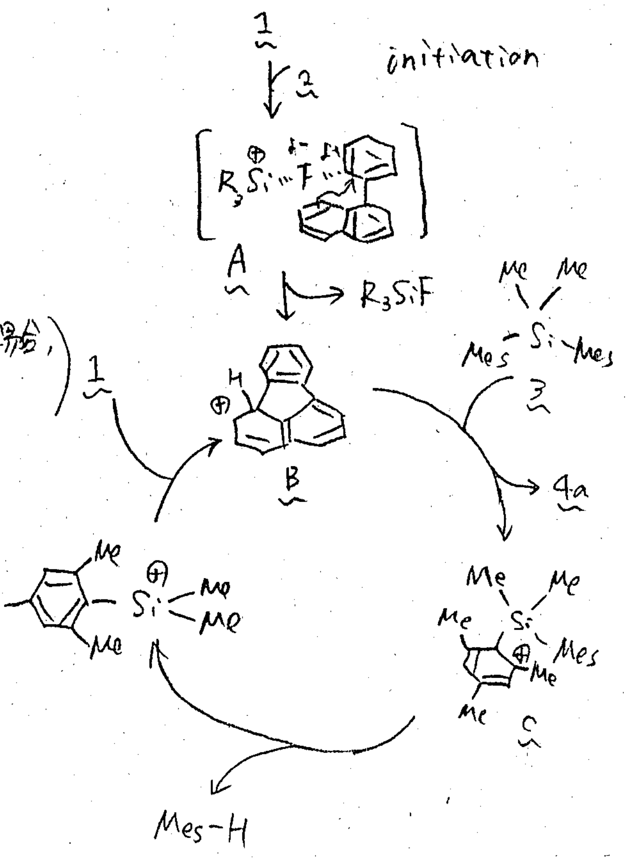

## "Proton-Catalyzed, Silane-Fueled Friedel-Crafts Coupling of Fluoroarenes"

Allemann, O.; Duttwyler, S.; Romanato, P.; Baldridge, K. K.; Siegel, J. S.* *Science* **2011**, *332*, 574-577.

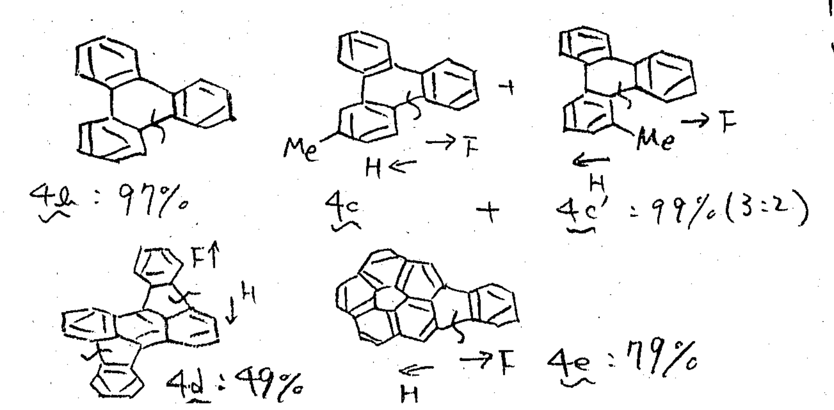
◎ C-F結合を活性化しながらのFriedel-Crafts反応




<Plausible Mechanism>




<Scope of the reaction>



Lewis acid-catalyzed formal [3+2] cycloadditions of N-tosyl aziridines with electron-rich alkenes via selective carbon-carbon bond cleavage

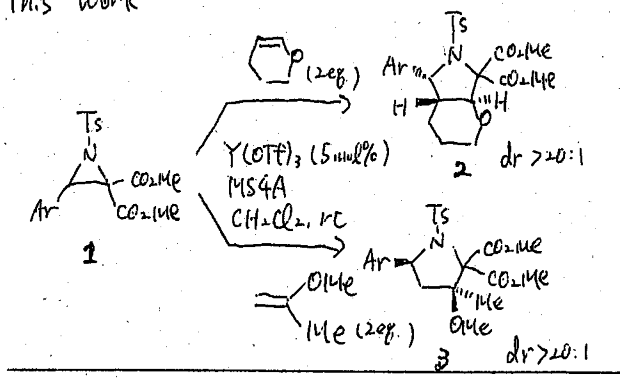
D3 村上

Lei Li, Xingxing Wu and Junliang Zhang* (East China Normal University)

Chem. Commun. 2011, 47, 5049-505

---

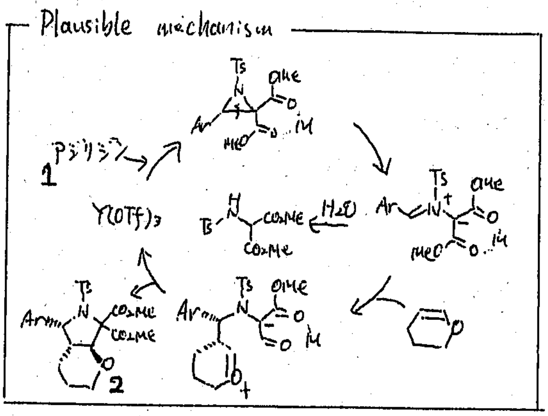
This work




| Ar = | | |
|---|---|---|
| Ph | 1h | 81% |
| 4-ClC6H4 | 2h | 82% |
| 4-BrC6H4 | 2h | 78% |
| 4-NO2C6H4 | 2.5h | 74% |
| 4-MeC6H4 | 1h | 83% |
| 2-BrC6H4 | 2h | 68% |

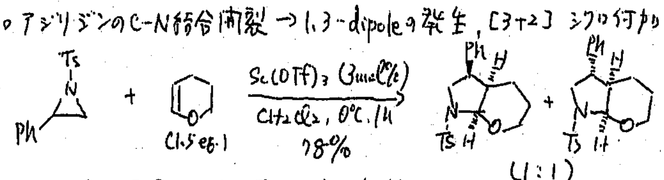
| Ar = | | |
|---|---|---|
| Ph | 2h | 70% |
| 4-BrC6H4 | 2h | 68% |
| 4-MeC6H4 | 2h | 69% |

Plausible mechanism

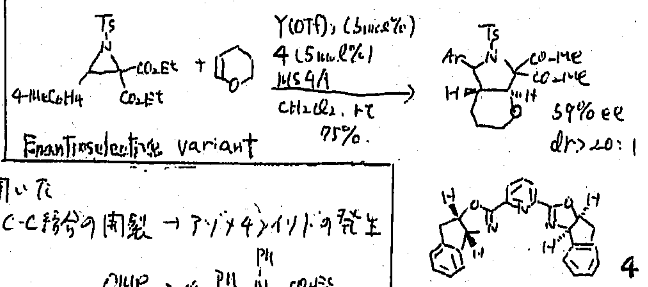



Previous works

○アジリジンのC-N結合開裂 → 1,3-dipoleの発生、[3+2] シクロ付加

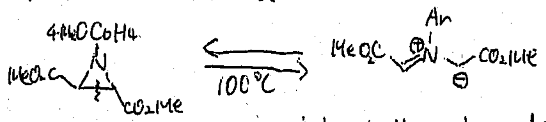



Yadav, J.S. et al. Tetrahedron Lett. 2001, 42, 9089-9092




Enantioselective variant

○アジリジンのC-C結合開裂 → アゾメチンイリドの発生

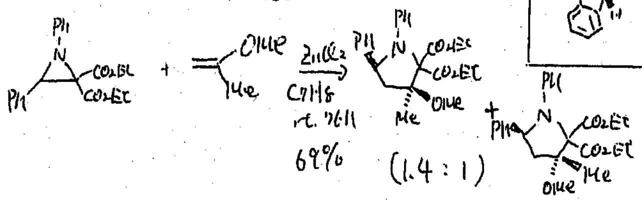



※ harsh thermal condition

29 kcal/mol

Mäder, H et al Angew Chem Int Ed Engl 1969, 8, 602-604

○ルイス酸を用いた
アジリジンのC-C結合の開裂 → アゾメチンイリドの発生




Johnson, J.S. et al. J. Am. Chem. Soc. 2004, 126, 2294-2295

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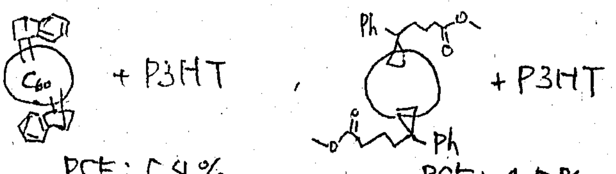
D2 長町俊希

## 1,4-Fullerene Derivatives: Tuning the Properties of the Electron Transporting Layer in Bulk-Heterojunction Solar Cells

Alessandro Varotto, Neil D. Treat, Jang Jo, Christopher G. Shuttle, Nicolas A. Batara, Fulvio G. Brunetti, Jung Hwa Seo, Michael L. Chabinyc, Craig J. Hawker, Alan J. Heeger, and Fred Wudl*. DOI: 10.1002/anie.201100029

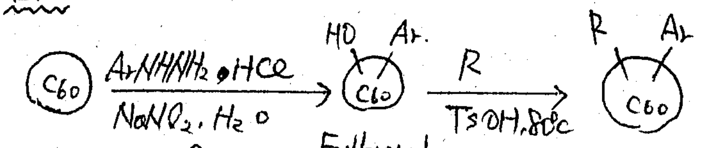
○有機薄膜太陽電池
現在、8.3%のPCEを達成。
(Konarka Technologies, Inc)

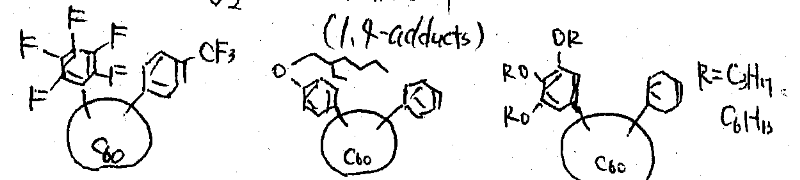
previous work



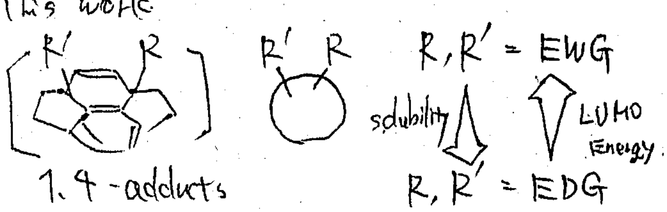

JACS, 2010, 132, 1377) (Adv. Mater. 2008, 20, 2116)

1 合成

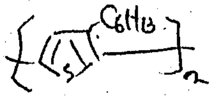



This work




Donor : P3HT




○UV-vis

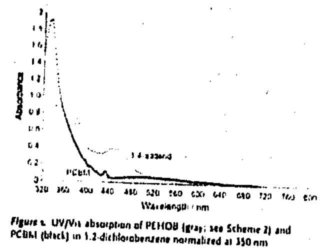


Figure 1. UV/Vis absorption of PEHOB (gray; see Scheme 2) and PCBM (black) in 1,2-dichlorobenzene normalized at 350 nm

• HOMO/LUMO

| | HOMO | LUMO |
|---|---|---|
| PCBM | -6.00 | -4.30 |
| PEHOB | -5.86 | -4.29 |
| PTHOB | -5.82 | -4.24 |
| PF8 | -6.35 | -4.65 |

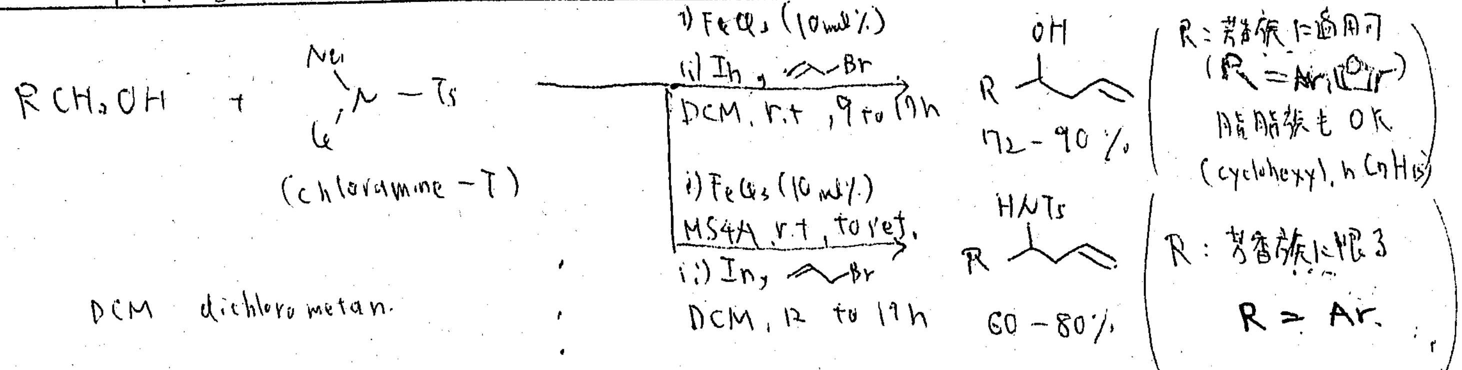
• device performance

| | Jsc | Voc | FF | PCE |
|---|---|---|---|---|
| PCBM | 8.13 | 0.54 | 0.65 | 2.81 |
| PTPOB | 6.16 | 0.61 | 0.62 | 2.34 |
| PTHOB | 3.[illegible] | 0.[illegible] | 0.[illegible] | 1.15 |

Lewis Acid - Catalyzed Oxidative Allylation: A New Approach for the Synthesis of Homoallylic Alcohols and Amines Directly from Alcohols.

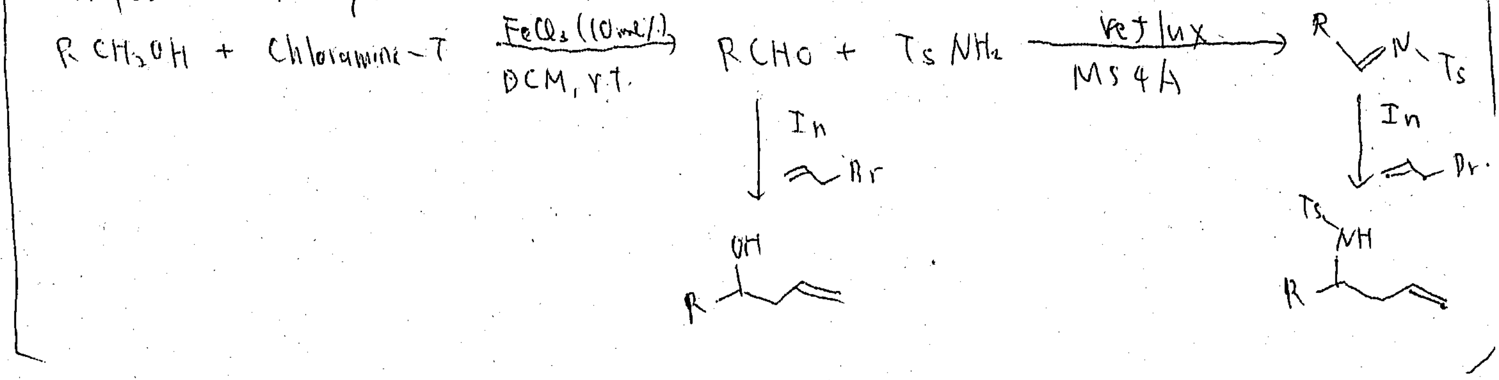
D1 早川

Dhal S. Yadav et al. Adv. Synth. Catal. 2011, 353, 695-70




DCM dichlorometan.

Proposed Pathway.



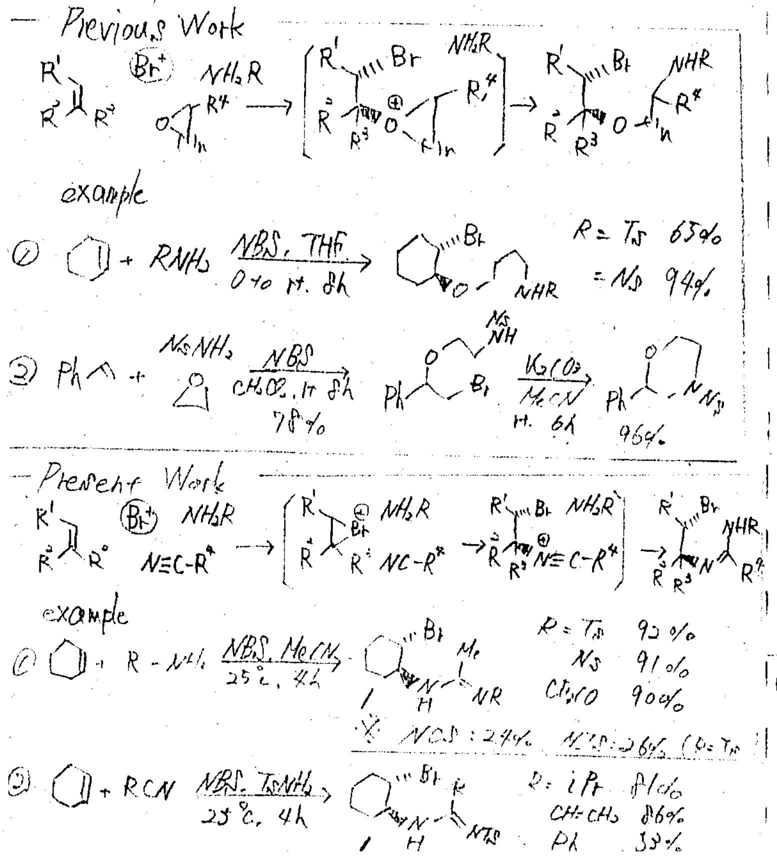

---

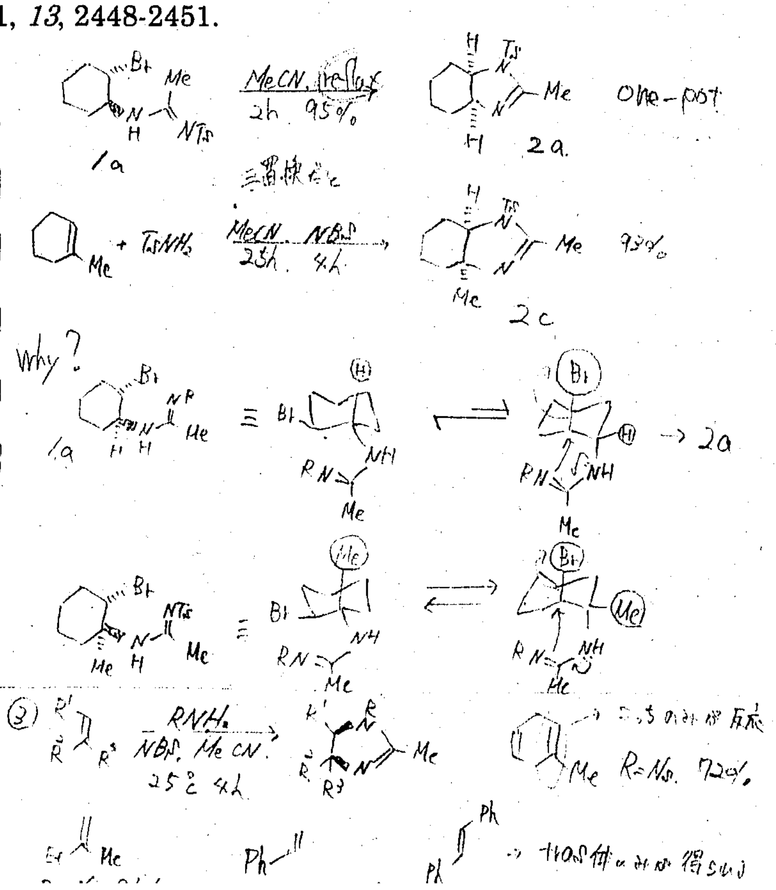
**N-Bromosuccinimide Initiated One-Pot Synthesis of Imidazoline**

M2 奥村壮太

Zhou, L.; Zhou, J.; Tan, C. K.; Yeung, Y.-Y.

*Org. Lett.* 2011, *13*, 2448-2451.



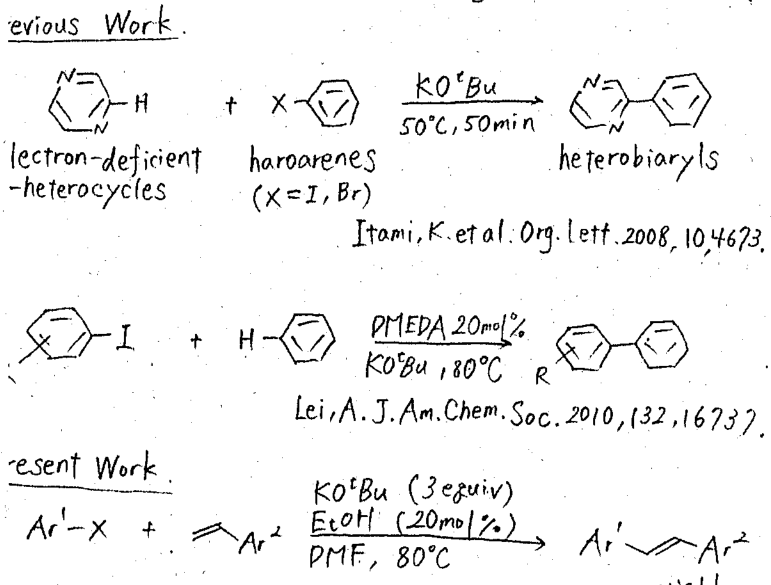



CT 2011/05/07 M2 MitaniYuki

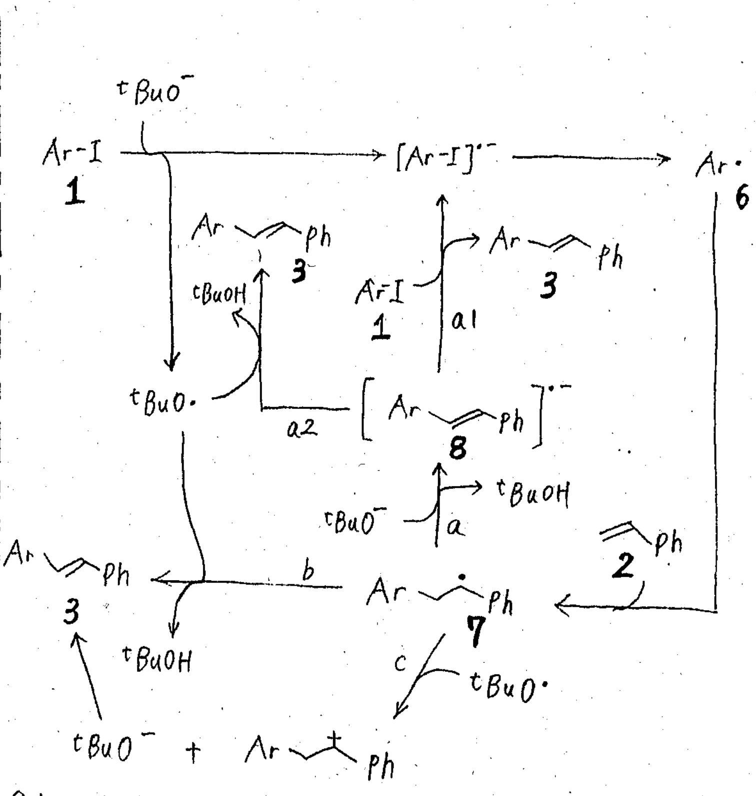
## Mizoroki-Heck-Type Reaction Mediated by Pottasium tert-Butoxide

Shirakawa, E.; Zhang, X.; Hayashi, T.

*Angew. Chem. Int. Ed.* **2011** (DOI: 10.1002/anie.201008220)




| Ar'-X | Ar² | yield |
|---|---|---|
| Ph-I | Ph | 66 |
| 4-MeOC6H4-I | Ph | 65 |
| 4-CF3C6H4-I | Ph | <1 |
| 4-MeC6H4-Br(α) | Ph | 2 (<1) |
| for 2-napthyl-Br (α) | Ph | 65, 76 (63, 83) |
| 4-vinylC6H4-Br(α) | Ph | 62(61) |
| 4-MeC6H4-I | 4-MeOC6H4 | 56 |
| 4-MeC6H4-I | 4-CF3C6H4 | <1 |

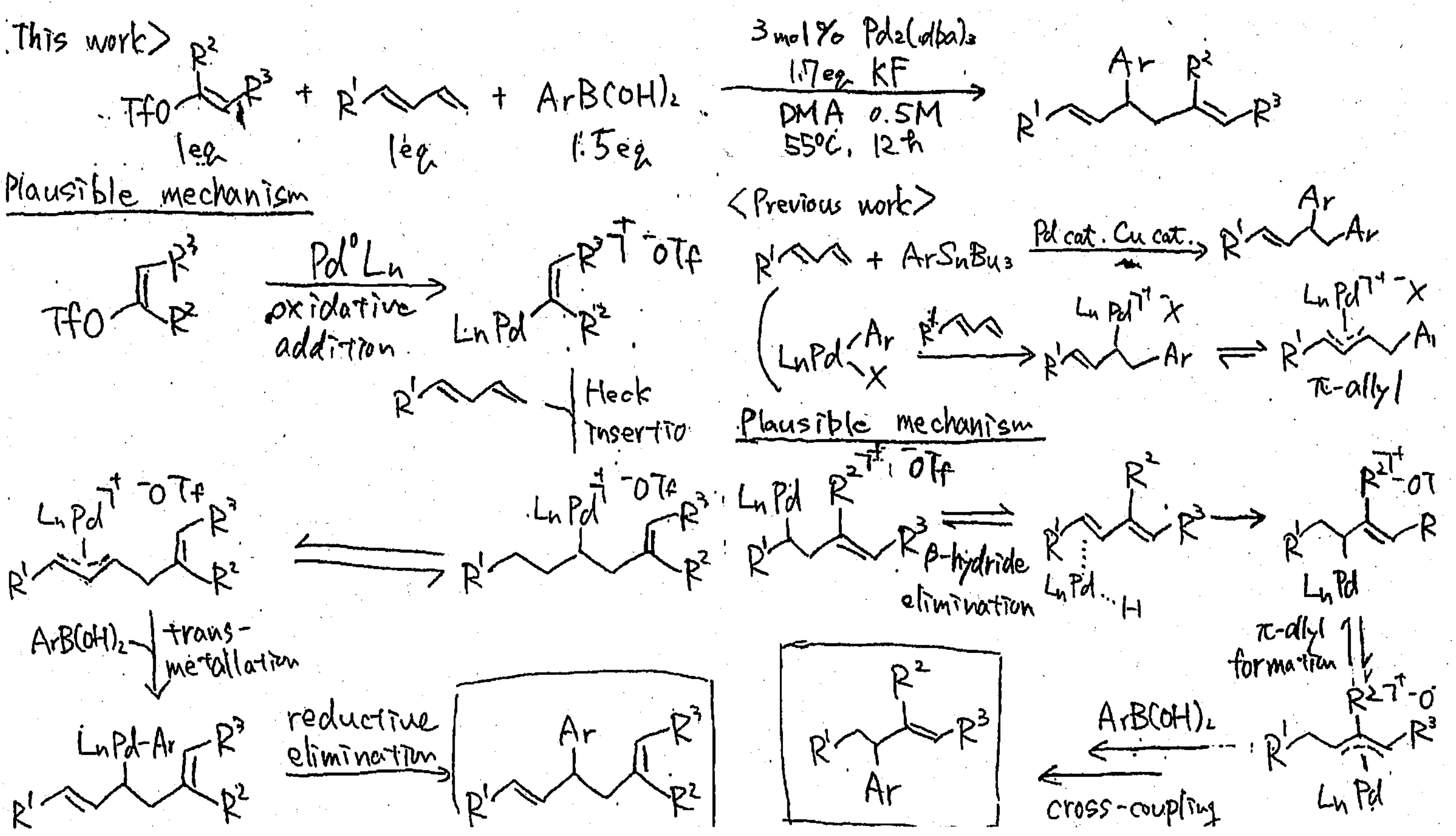


Scheme 1. A plausible reaction mechanism.

## A Palladium-Catalyzed Three-Component Cross-Coupling of Conjugated Dienes or Terminal Alkenes with Vinyl Triflates and Boronic Acids

Yuki Ikeda

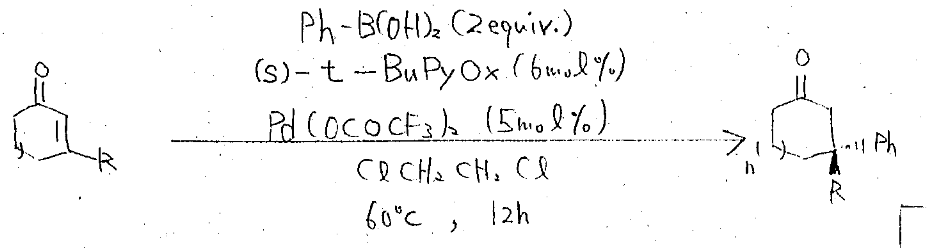
Liao, L.; Jana, R.; Urkalan, K. B.; Sigman, M. S. *J. Am. Chem. Soc.* *(10.1021/ja201358b)*



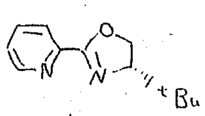
## Palladium-Catalyzed Asymmetric Conjugate Addition of Arylboronic Acids to Five-, Six-, and Seven-Membered β-Substituted Cyclic Enones Enantioselective Construction of All-Carbon Quaternary Stereocenters

*Hajime Kawai*

Brian M. Stoltz *et al.* *J. Am. Chem. Soc.* **2011**, *133*, 6902-6905



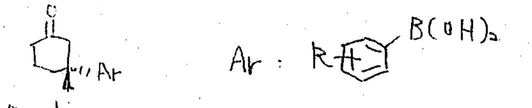

(S)-t-BuPyOx



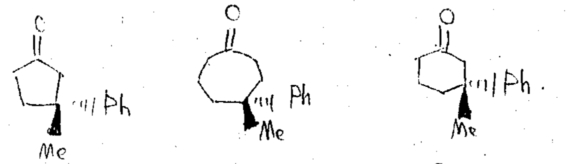

: easily prepared

The first palladium-catalyzed asymmetric conjugate addition of arylboronic acids to β-substituted cyclic enones.
This transformation is tolerant to air and water.

α, β-不飽和カルボニルへの共役付加による不斉四級炭素の構築
1) Feringa, Alexakis, Hoveyda
Cu 触媒 + highly reactive organometallic reagents
2) Hayashi et al.
Rh触媒 + $Ar_4BNa$ or $(ArBO)_3$
今回、安価で取り扱い容易な $ArB(OH)_2$ を求核剤として用いている。




| Product R | Yield | ee |
|---|---|---|
| 4-Me- | 99% | 87% |
| 4-MeO- | 58% | 85% |
| 4-Ac- | 99% | 96% |
| 3-Me- | 99% | 91% |
| 3-NO2- | 40% | 92% |




| | | |
|---|---|---|
| 84% | 85% | 99% |
| 91% ee | 93% ee | 93% ee |

---

## Practical C-H Functionalization of Quinones with Boronic Acids

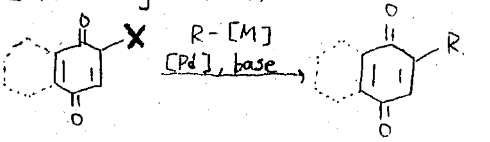
M1 錦織 克聡

Yuta Fujiwara, Victoriano Domingo, Ian B. Seiple, Ryan Gianatassio, Matthew Del Bel, and Phil S. Baran

J. Am. Chem. Soc. 2011, 133, 3292-3295

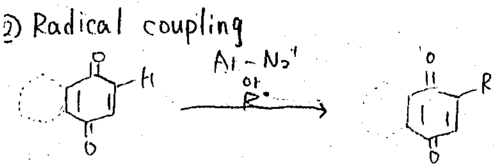
<Common Pathways to Substituted Quinones>

① Prehalogenation



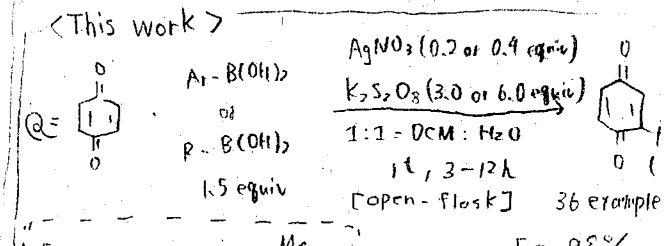

欠点
- Requires prehalogenation
- Quinones act as ligand

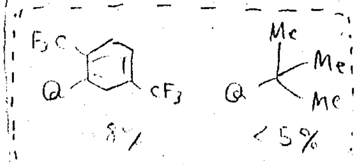
② Radical coupling




欠点
- Difficult to synthesize Ar-N2+

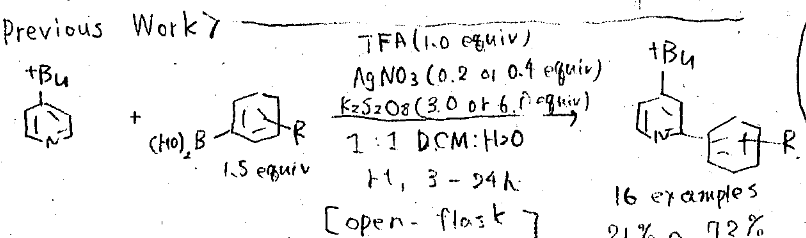
<This work>



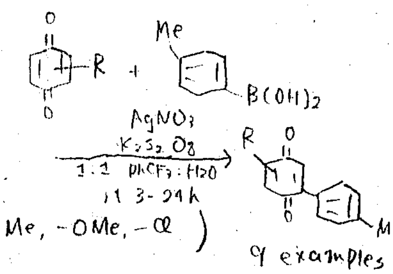




electron poor and steric hindered

<Previous Work>

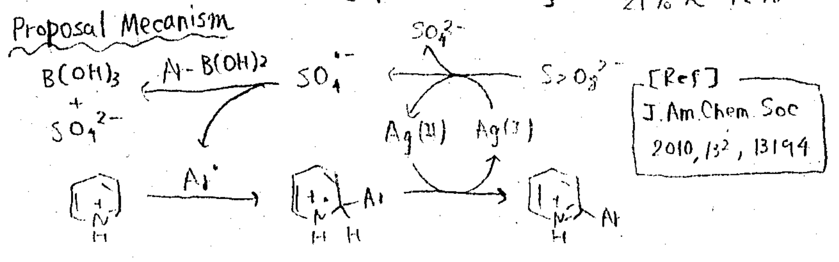



(R = -Me, -F, -X(Br, I), -OMe, -CO2Me, -CN, NO2, -CF3)



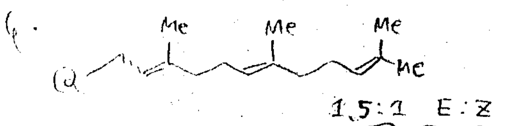

(R = -Me, -OMe, -Cl)
9 examples

Proposal Mecanism




[Ref]
J. Am. Chem. Soc. 2010, 132, 13194

筆者は本反応はラジカル機構を提唱している




1.5:1 E:Z

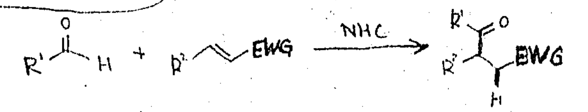
## N-Heterocyclic Carbene (NHC)-Catalyzed Intermolecular Hydroacylation of Cyclopropene

M1 矢野 知樹

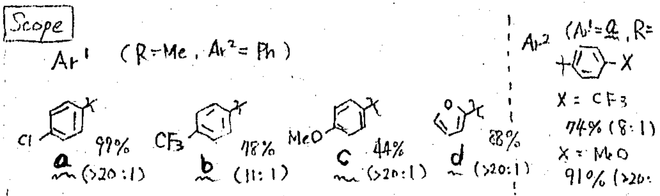
Xavier Bugaut, Fan Liu, and Frank Glorius*

doi /10.1021/ja202594g

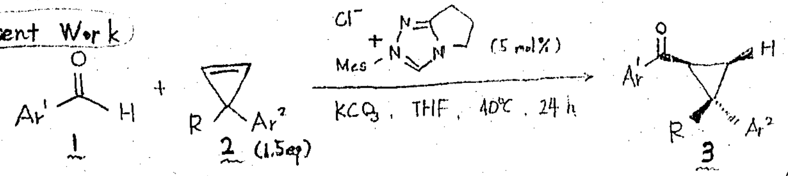
**Stetter Reaction**

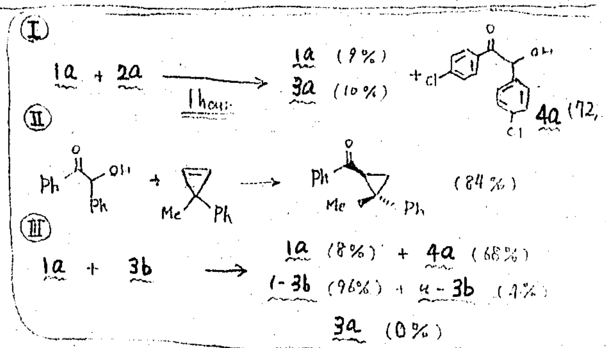


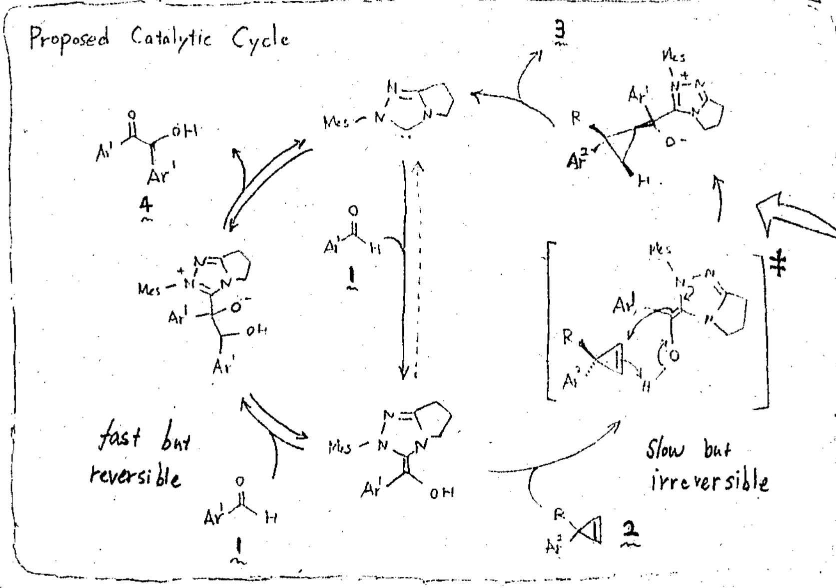

**Scope**

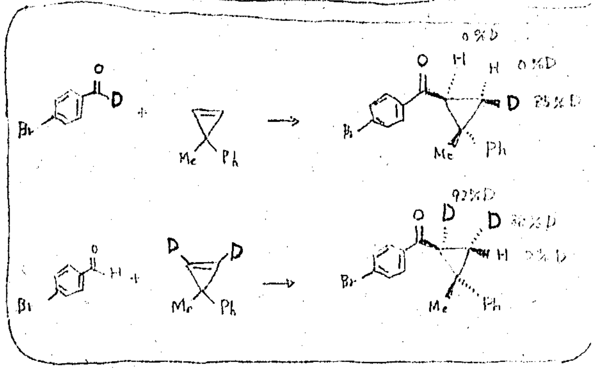



**Present Work**



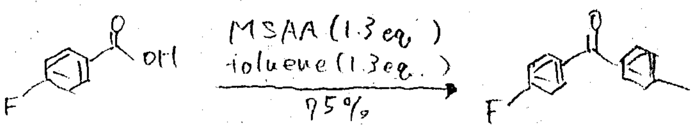




## "Greener" Friedel-Crafts Acylations: A Metal- and Halogen-Free Methodology

B4 榎島 悟

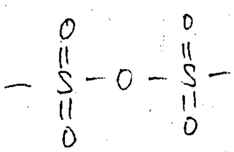
(Mark C. Wilkinson, Organic Letter, DOI: 10.1021/ol2004825)

### ◎ This work

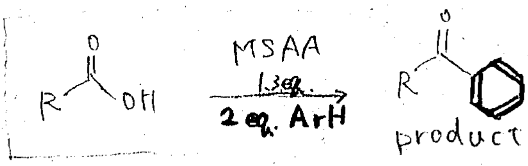



E factor = 4, 20% mass productivity
↓
(kg waste per kg product)

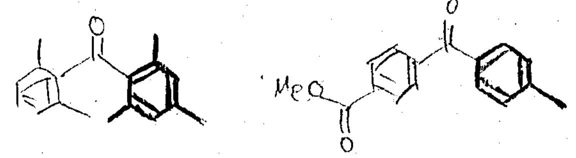
MSAA (methanosulfonic anhydride)



### ◎ Scope of reaction

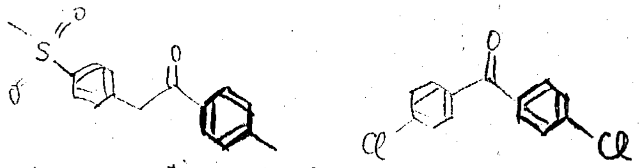



product



yield 87%

isomer ratio 86:14
yield 63%

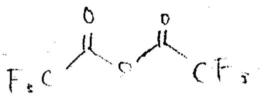


isomer ratio 91:9
yield 69%

isomer ratio 86:14
yield 53%

### ◎ Previous work

試薬に TFAA (trifluoroacetic anhydride)



を使用していた。

- 触媒が必要 ($BF_3 \cdot OEt_2$ etc)
- 副生成物の処理
- 求核剤が電子richなものに限られる。

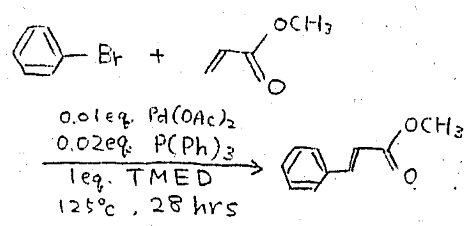
A Domino Approach (Hydrolysis/Dehydrohalogenation/Heck Coupling) for the Synthesis of Styrene Sulfonate Salt

*Saori Tone*

G. K. Surya Prakash, Parag V. Jog, Hema S. Krishnan, and George A. Olah

JACS. 2011, 133, 2140

Heck反応




触媒サイクル

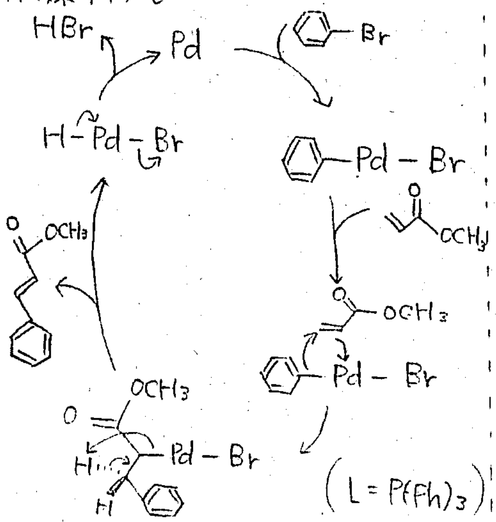
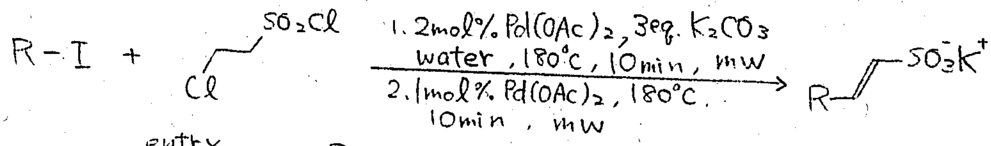
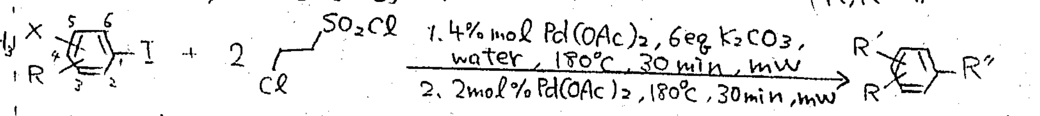



Table 1. Synthesis of Sulfonate Salts




| entry | R = | % yield |
|---|---|---|
| 1 | $C_6H_5$ – | 85 |
| 2 | 3-$NO_2$-$C_6H_4$ – | 89 |
| 3 | 2-$OCH_3$-$C_6H_4$ – | 83 |
| 4 | 2,6-diMe-$C_6H_3$ – | 61 |
| 5 | 2-COOH-$C_6H_4$ – | 0 |
| 6 | Naphthyl – | 89 |
| 7 | 2-pyridyl – | 10 |
| 8 | 3-pyridyl – | 66 |

Table 2. Synthesis of Disulfonate Salts (R′, R″ = CH=CH–$SO_3^-K^+$)




| entry | R = | X = | R′ = | % yield |
|---|---|---|---|---|
| 9 | H | 2-I | 2-R′ | 75 |
| 10 | H | 3-I | 3-R′ | 68 |
| 11 | H | 4(4′-Iodo-$C_6H_4$) | R′-$C_6H_4$ | 29 |
| 12 | 2,3,5,6-Tetra-F | 4-I | 4-R′ | 41 |
| 13 | 2,3,5,6-Tetra-Me | 4-I | 4-R′ | 59 |