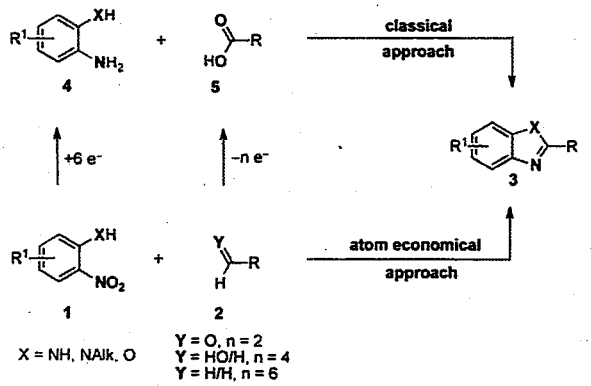
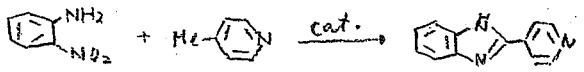
Thanh Binh Nguyen et al.	CNRS (France)	*JACS*, **2013**, *135*, 118	Minakata

Iron Sulfide Catalyzed Redox/Condensation Cascade Reaction between 2-Amino/Hydroxy Nitrobenzenes and Activated Methyl Groups: A Straightforward Atom Economical Approach to 2-Hetarylbenzimidazoles and -benzoxazoles



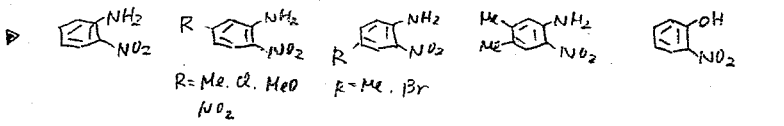
Optimization



cat. (mol%)	conditions	conversion(%)
—	150°C, 72h	0
FeS(10)	150°C 16 h	30
$FeSO_4 \cdot 7H_2O/Na_2S$ (10/10)	150°C, 16 h	30
Fe(10), S(10)	150°C 16h	95

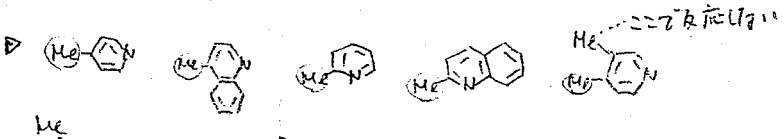
$FeSO_4 \cdot 7H_2O$(10), $Fe(NO_3)_3 \cdot 9H_2O$(10), Fe(acac)$_3$(10), $FeCl_3$(10) ··· ×
S(10) ·· × Fe(10) ·· ×

Scope

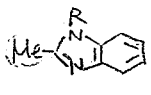


R=Me, Cl, MeO
NO_2

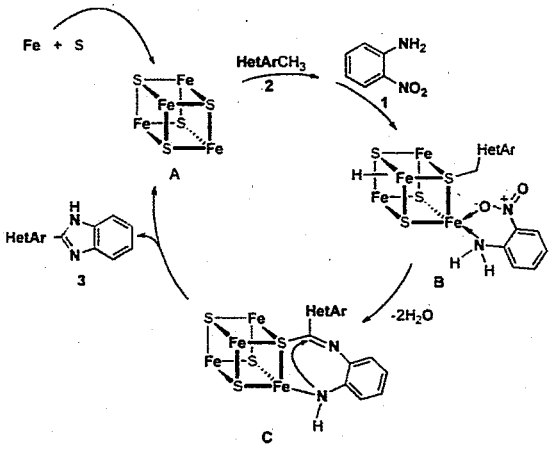
R=Me, Br



no reaction

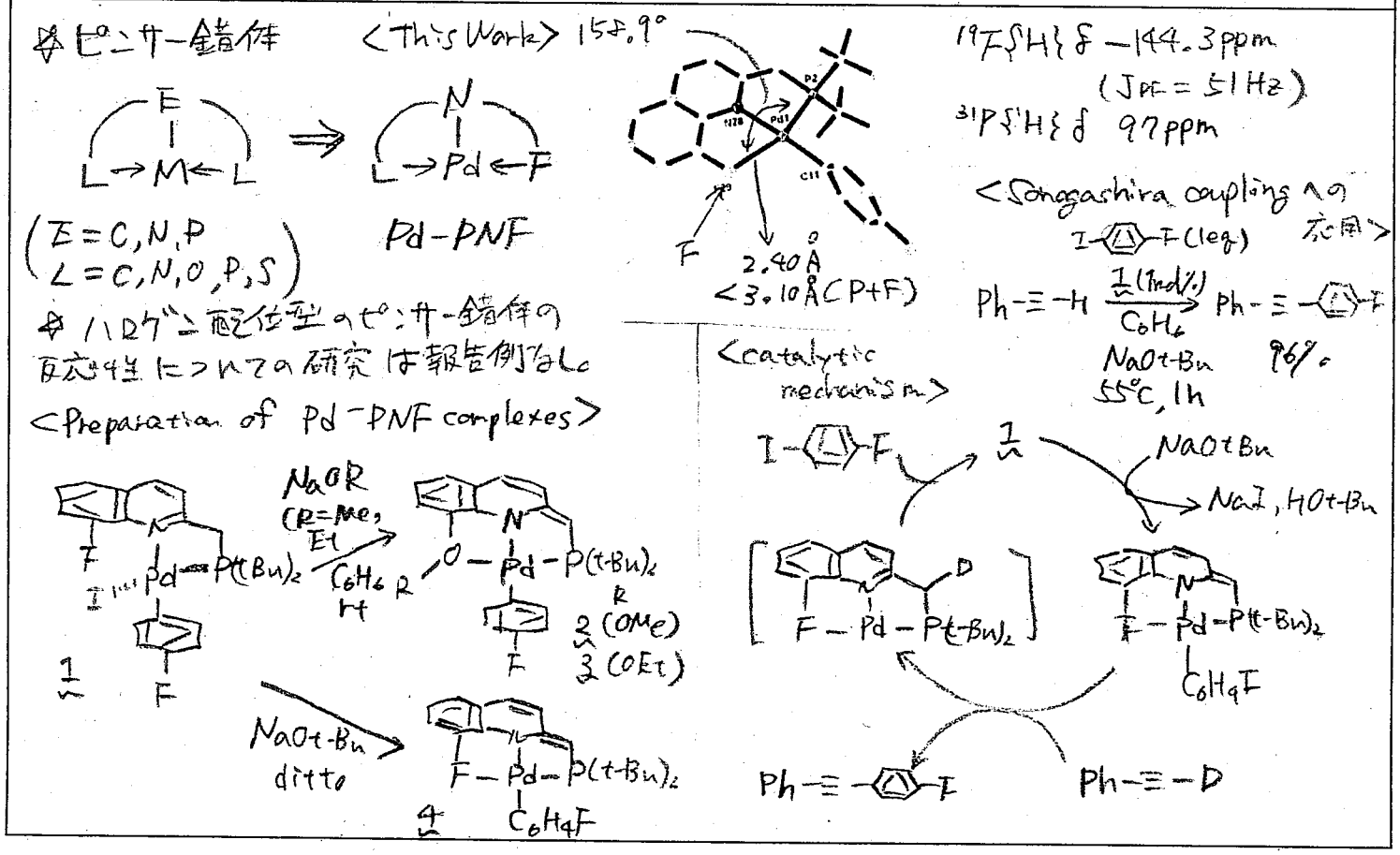


R=H, Me



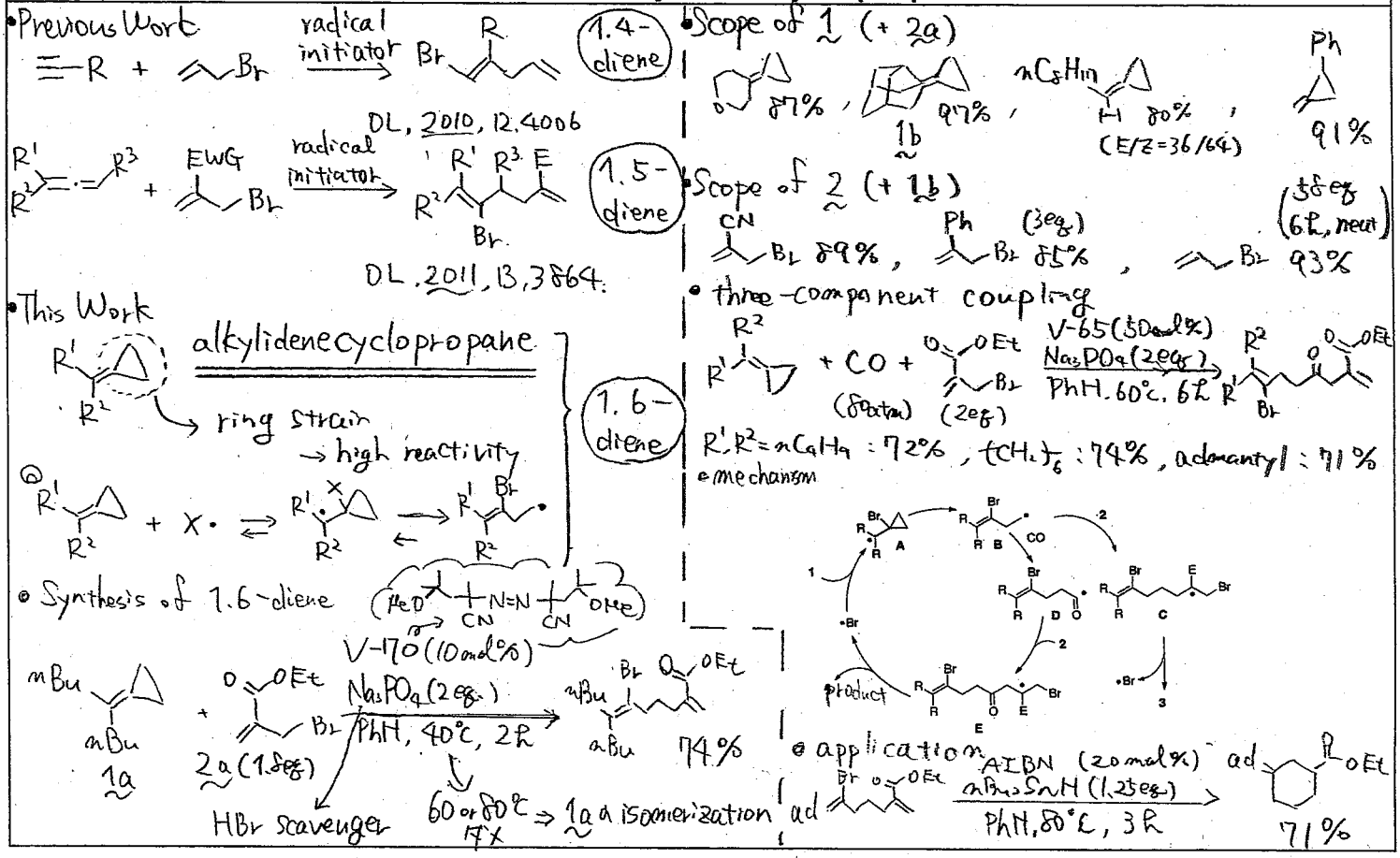
Arkadi Vigalok	Tel Aviv University, Israel	*J. Am. Chem. Soc. ASAP* Doi: 10.1021/ja310782kl	Youhei Takeda

Evidence for Metal–Ligand Cooperation in a Pd–PNF Pincer-Catalyzed Cross-Coupling



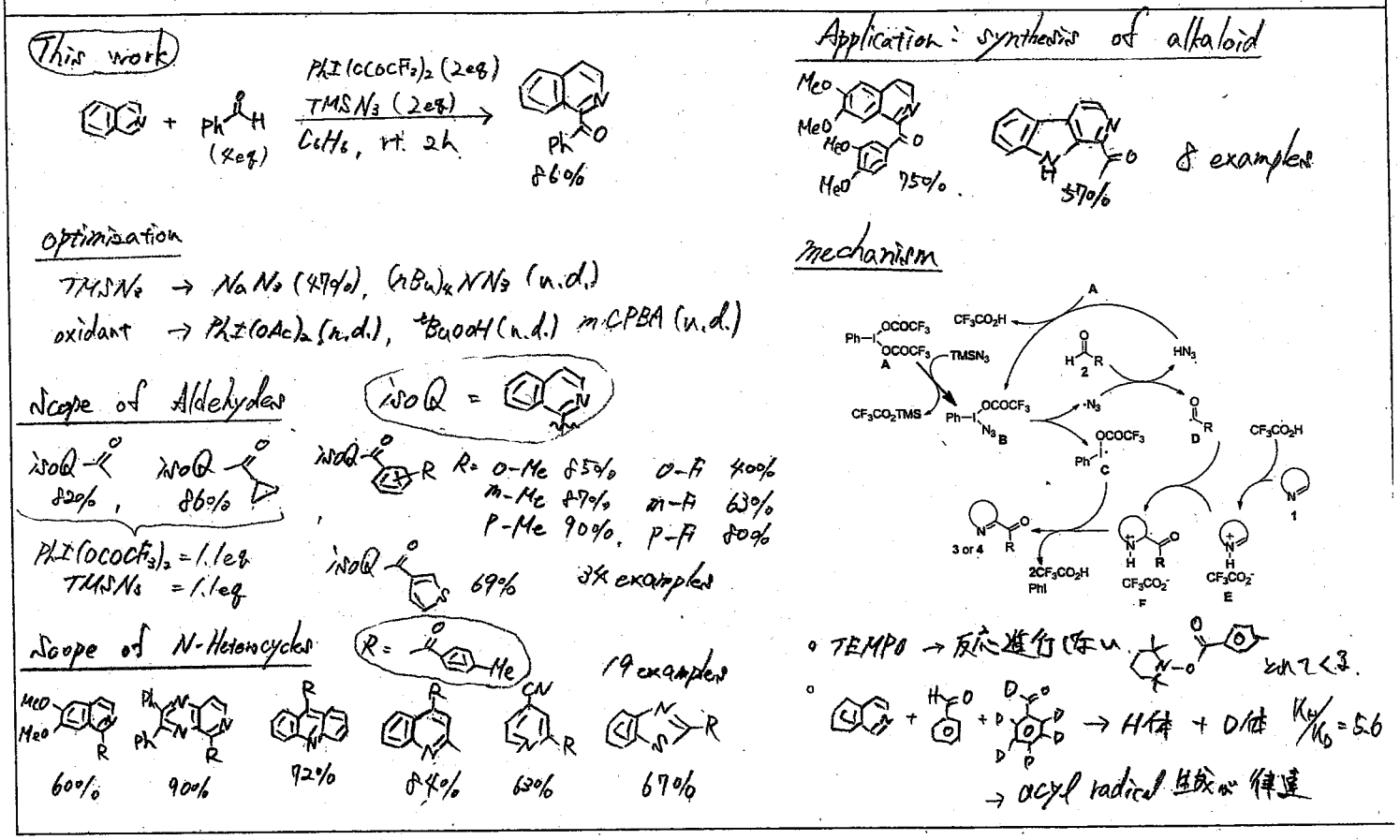
Ilhyong Ryu et al.	Osaka Prefecture University (Japan)	JACS ja311821h	Nagamachi

Bromine Radical-Mediated Sequential Radical Rearrangement and Addition Reaction of Alkylidenecyclopropane



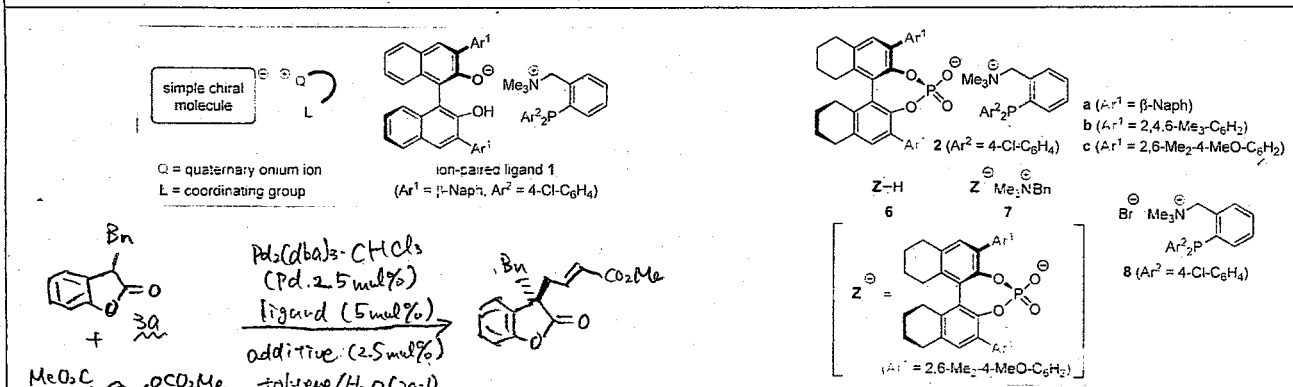
Andrey P. Antonchick	Max-Planck Institute of Molecular Physiology	ACIE (anie.201208851)	Okumura

Metal-Free Cross-Dehydrogenative Coupling of Heterocycles with Aldehydes

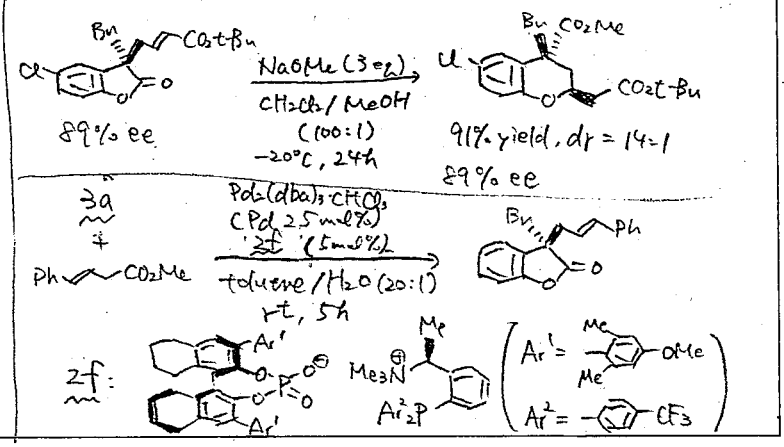


Takashi Ooi *et. al.*	Nagoya University (Japan)	*J. Am. Chem. Soc.* (10.1021/ja312125a)	Ikeda

Exploiting the Modularity of Ion-Paired Chiral Ligands for Palladium-Catalyzed Enantioselective Allylation of Benzofuran-2(3H)-ones

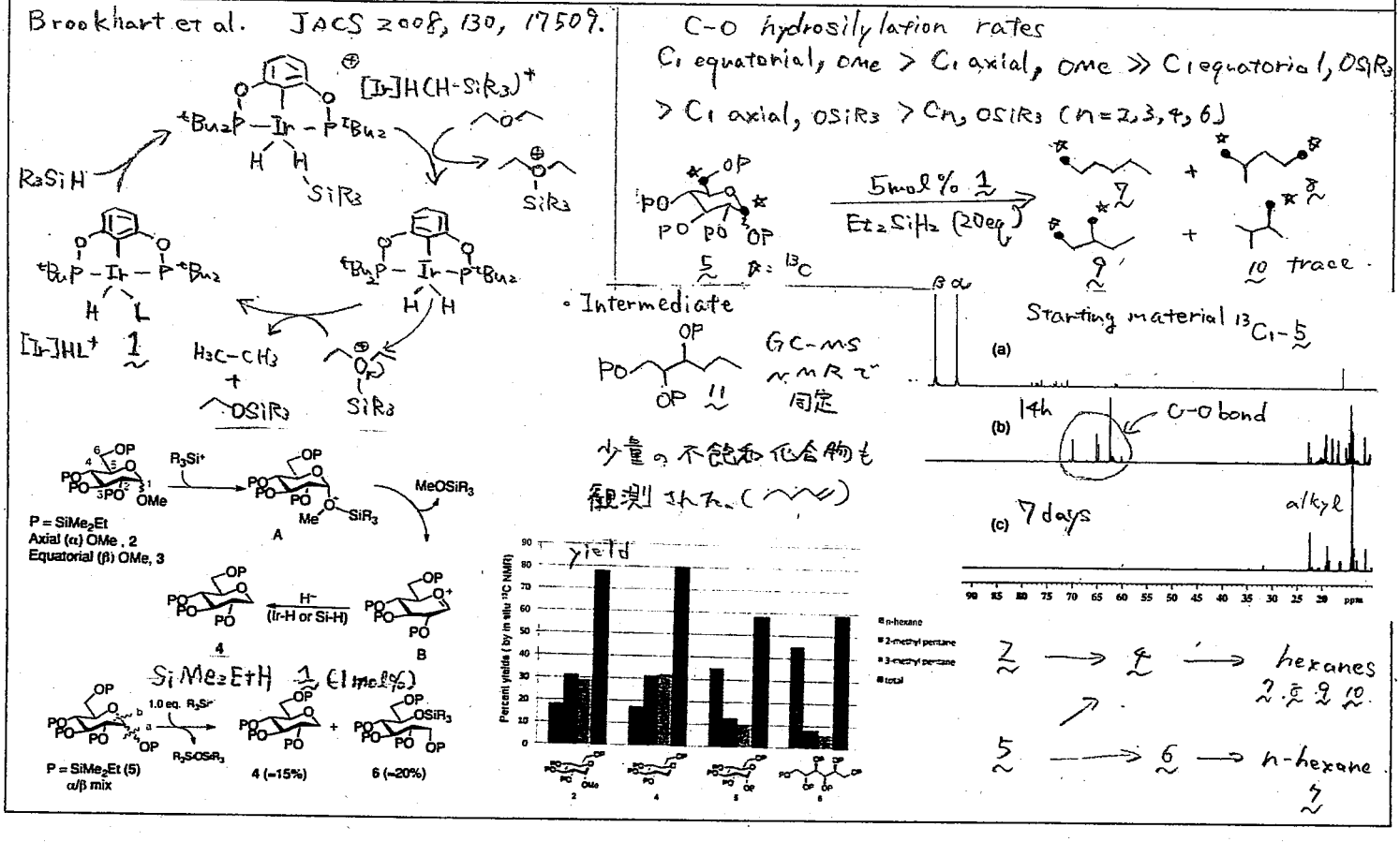


entry	ligand	additive	% yield	% ee
1	1	none	79	22
2	2a	none	78	80
3	2b	none	68	82
4	2c	none	81	90
5	P(4-α-C6H7)3	6	14	<1
6	P(4-α-C6H4)3	7	30	<1
7	8	6	43	−19



Iridium-Catalyzed Hydrosilylative Reduction of Glucose to Hexane(s)

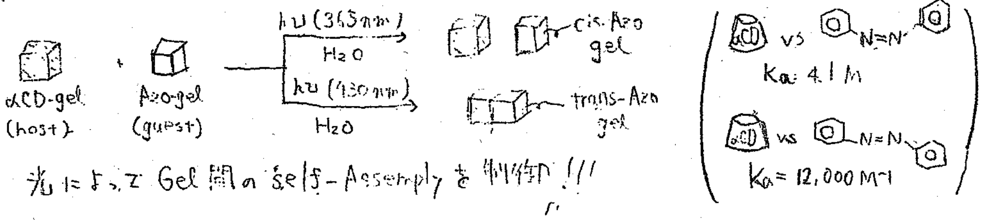
Gagne, M. R.	University of North Carolina at Chapel Hill (United States)	ja3110494l	Kawai



Akira Harada et al	Osaka University (JPN)	*Nature Communications* (DOI: 10.1038/ncomms2280)	M2 錦織

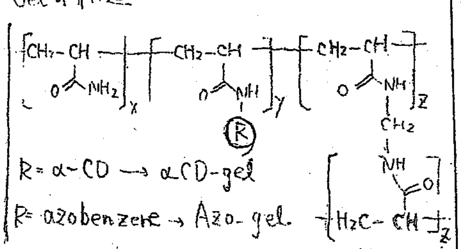
Expansion-Contraction of photoresponsive artificial muscle regulated by host-guest interactions

Previous Work : Harada et al. Nature Communications, 3, 603, (2012)

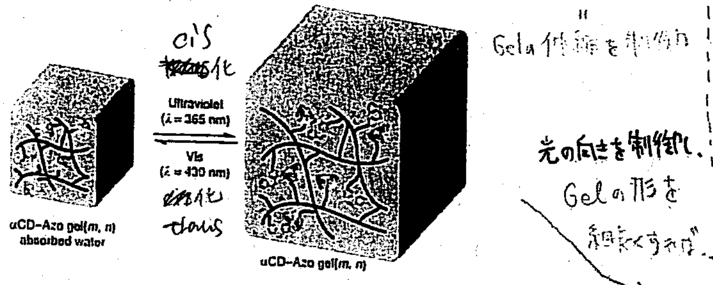


光によってGel間のSelf-Assemblyを制御!!!

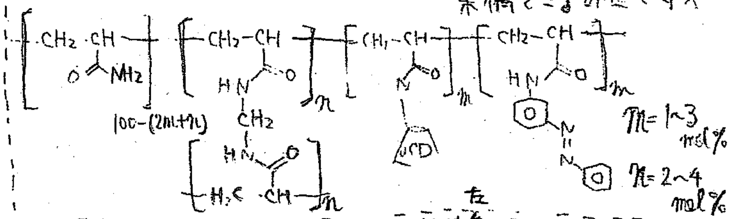
Gelの構造



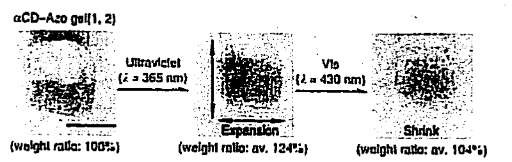
This Work 光によってGel内のHost-Guest作用を制御 = Gelの伸縮を制御

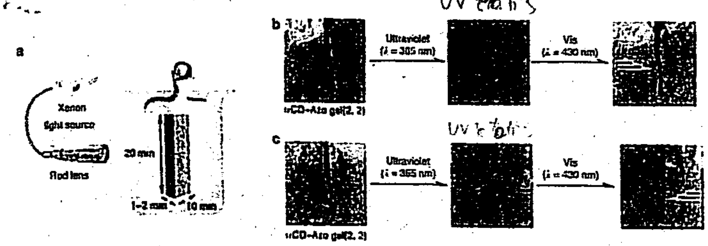


αCD-Azo gel ポリマー鎖間で共有結合的・非共有結合的に架橋できる部位を導入



光の向きを制御し、Gelの形を細かくすれば



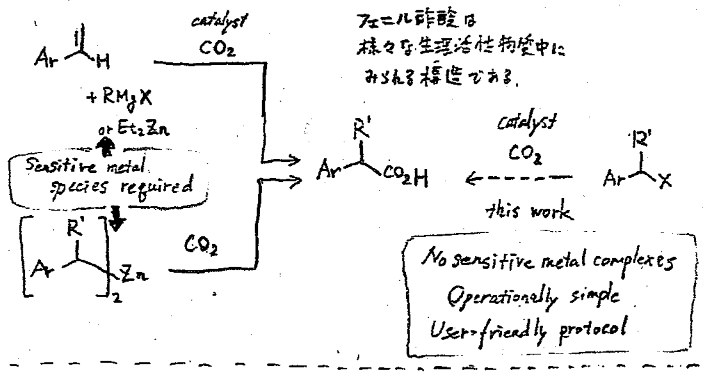


n=4のとき、伸縮変化は小さく、n=2のとき大きかった。

Martin, R. *et al.*	Institute of Chemical Research of Catalonia (ESP)	JACS doi: 10.1021/ja311045f	M2 矢野

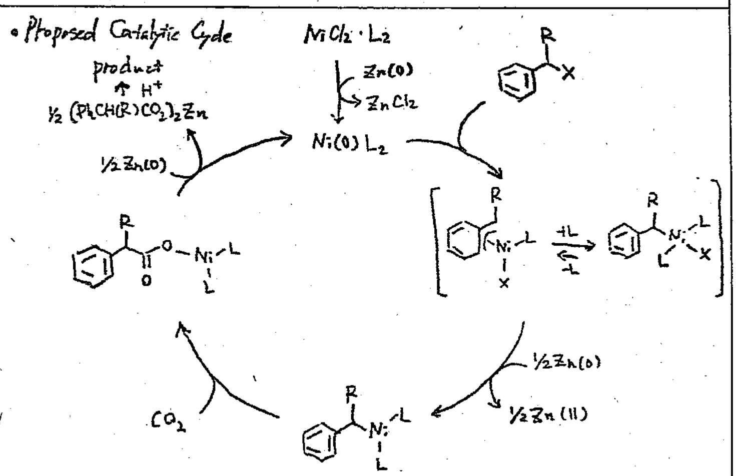
Ni-Catalyzed Direct Carboxylation of Benzyl Halides with CO_2

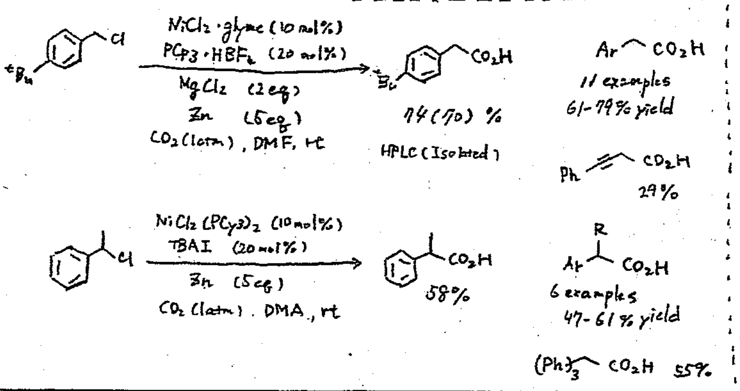
• Synthesis of Phenylacetic Acids



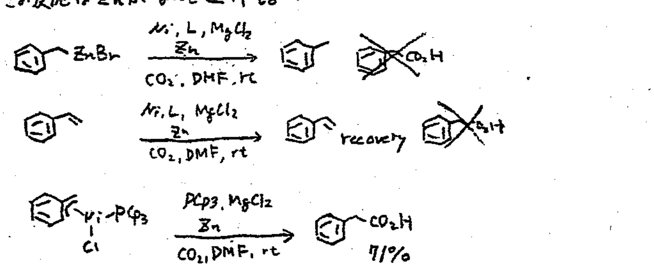
フェニル酢酸は様々な生理活性物質中にみられる構造である。

• Proposed Catalytic Cycle





この反応はZnがないと進行しない



A Ogawa et al	Osaka Prefecture University	Angew 10.1002/anie.201207383	M1 榎島

Synthesis and Properties of Perfluoroalkyl Phosphine Ligands: Photoinduced Reaction of Diphosphines with Perfluoroalkyl Iodides

① Perfluoroalkylated phosphine ligands

$[R_f(CH_2)_2]_3P$ (1a)　$(p\text{-}R_fC_6H_4)_3P$ (1b)　R_fR_2P (2) ← This work

② reaction of perfluoroalkyl iodides with diphosphines

$R_f\text{-}I$ (3) + $(R_2P)_2$ (4) $\xrightarrow[CDCl_3,\ rt,\ 12h \rightarrow 60°C,\ 5h]{h\nu\ (\lambda>330nm),\ S_8\ (2.6\ equiv)}$ $R_f\text{-}PR_2$ (5)

- isolated yields of 5 : 60 ~ 89% (R = Ph) : 53% (R_f = C_6F_{13}, R = tBu)

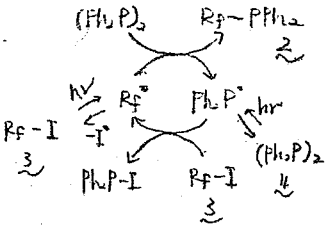
$R_f\text{-}I$ (3) + $(Ph_2P)_2$ (4a) $\xrightarrow[CDCl_3,\ rt,\ 12h]{h\nu\ (\lambda>330nm)}$ $\xrightarrow[MeOH]{\text{extraction with FC-72}}$ $R_f\text{-}PH_2$ (2)

$R_f = C_{10}F_{21}$: 90%, $C_{12}F_{25}$ 94%
C_8F_{17} : 41%, C_6F_{13} : 19%
(Fc-72 : perfluorohexane)

$n\text{-}C_{10}F_{21}\text{-}I$ (3a) + $(Ph_2P)_2$ (4a) $\xrightarrow{\text{reaction conditions}}$ $n\text{-}C_{10}F_{21}PPh_2$ (2a)

- under dark, $CDCl_3$, rt, 12h : 8%
- sunlight, $CDCl_3$ rt 10h : 91%
- AIBN (1.3 equiv), C_6H_6, 80°C, 6h : 90%

③ reaction pathway



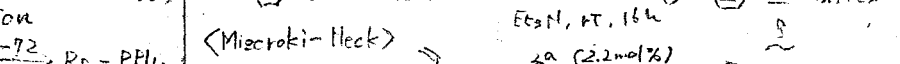
④ ligand exchange

$[PdCl_2(MeCN)_2]$ + $n\text{-}C_{10}F_{21}PPh_2$ (2a) → $CDCl_3$ → $[PdCl_2(n\text{-}C_{10}F_{21}PPh_2)_2]$ (7a)

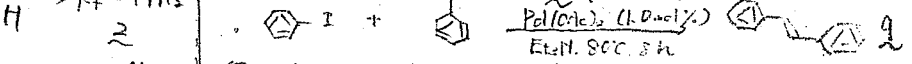
X線あり。

⑤ coupling reactions using ligand 2a

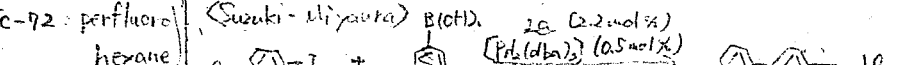
<Sonogashira>



<Mizoroki-Heck>



<Suzuki-Miyaura>

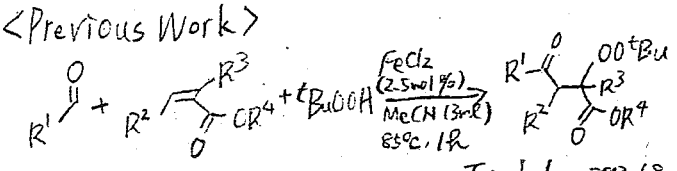


Product	Without 2a	1st run with 2a	1st recycle	2nd recycle	3rd recycle	4th recycle
5	< 1%	99%	99%	99%	99%	98%
9	18%	89%	89%	89%	88%	83%
10	40%	89%	98%	85%	—	—

Zhiping Li	Renmin University of China (China)	Chem. Asian J. DOI: 10.1002/asia.202000973	M1 岡崎

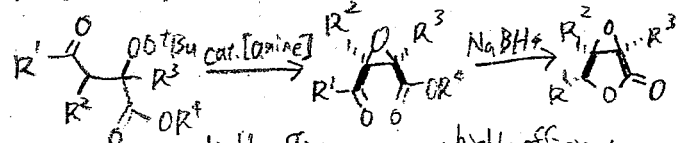
Efficient and Selective Synthesis of α,β-Epoxy-γ-Butyrolactones from 2-Peroxy-1,4-Dicarbonyl Compounds

<Previous Work>



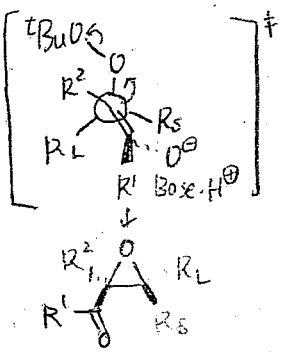
Tetrahedron 2012, 68, 10333.

<This Work>

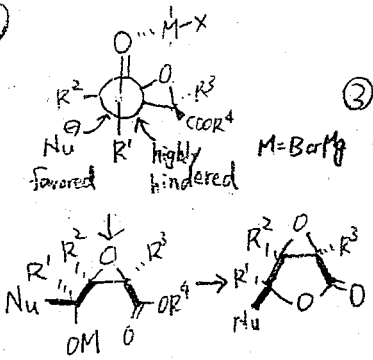


- highly efficient
- diastereoselective
- highly efficient
- stereospecific

①

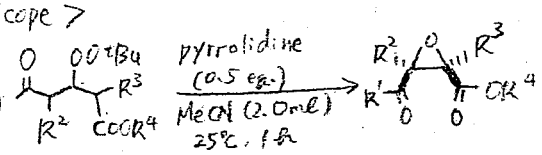


②③



<Scope>

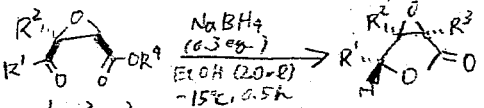
①



R^1 = Ph, 2-thienyl, cyclopropyl, Bu, Pr　R^2 = H, Me, Ph
R^3 = Me, Ph, ～, ～OMe, ～OAc, ～COOEt, ～COMe
R^4 = Me, Et, Bn, ～OH, ～//, ～

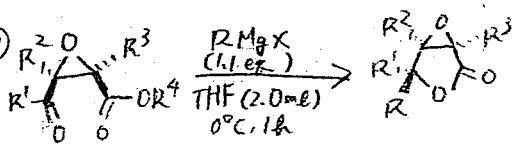
40 ~ 90%　dr: 89:11 ~ 96:4　15 examples (回置換: 4 examples)

②



R^1, R^2, R^3, R^4 上記に加えて同じ 60 ~ 94%　13 examples

③



R^1 = Ph, 2-thienyl, Pr　R^2 = H, Me　R^3 = Me, Ph, //
R^4 = Me, Et　R = Ph, p-Cl-Ph, p-MeO-Ph, Me, Et

40 ~ 99%　12 examples

n-BuLi, PhLi では選択性落ちる。

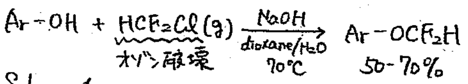
John F. Hartwig	University of Califolnia, Berkeley (USA)	ACIE 10.1002/anie.201209250	M1 西田

Synthesis of Difluoromethyl Ethers with Difluoromethyltriflate

Introduction

Ar−OCF₂H

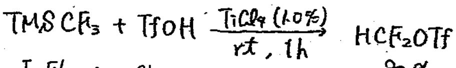
…医学的に重要な化合物（酵素阻害剤，抗菌剤，anti-HIV剤 など）



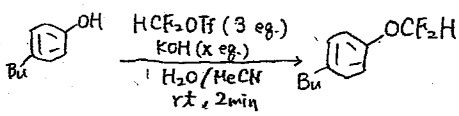
Scheme 1 J. Org. Chem. 1960, 25, 2009−2012

This work

HCF₂OTf … 非オゾン破壊性，液体

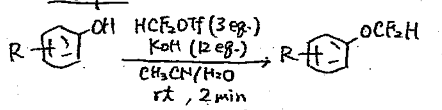


J. Fluorine Chem. 2009, 130, 667−670

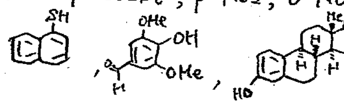


Entry	KOH (eq.)	ArOCF₂H [%]	ArOTf [%]
1	12	75	12
2	8	59	6
3	10	70	19
4	LiOH (12 eq.)	38	11
5	NaOH (12 eq.)	61	10

Scope

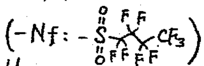


R = p-CO₂Et, p-NO₂, o-NO₂,

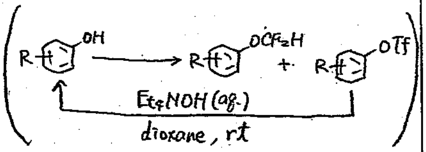


23 examples, 53 ~ 94 %

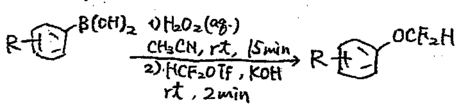
・HCF₂ONf を使うと yield up (4 examples)



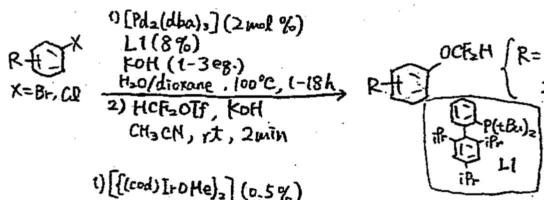
・副生成物は未反応の phenol と Aryl triflate だけ。再生可能



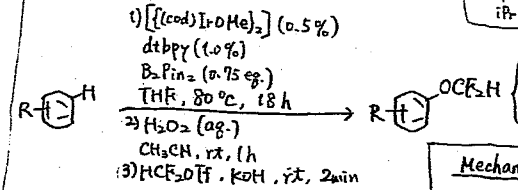
One pot



R = −Bu, −Br, −C(O)−Me, −C(O)−H, −C(O)−NMe₂ 50 ~ 86 % (すべて p位)

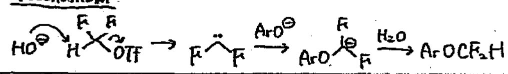


R = p-Bu, m-OMe, m-C(O)-Me, p-C(O)-H, 2,6-Me 49 ~ 71 %



R … 3,5位に置換基（エステル，アミド，ハロゲン など） 5 examples, 45 ~ 78 %

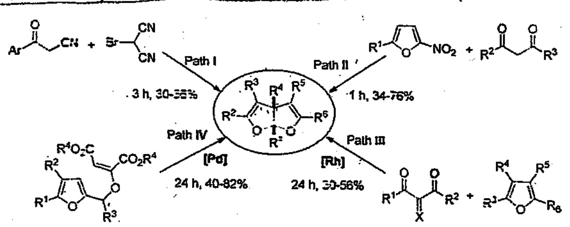
Mechanism



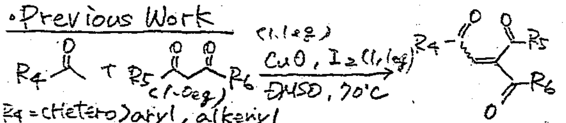
Guo-Dong Yin, An-Xin Wu	Central China Normal University / Hubei Normal University	o.l. 10.1021/ol400016c	B4 黒田

Highly Efficient Synthesis of 3a,6a-Dihydrofuro[2,3-b]furans via a Novel Bicyclization

・Methods for the synthesis of DHFF (3a,6a-Dihydrofuro[2,3-b]furans)



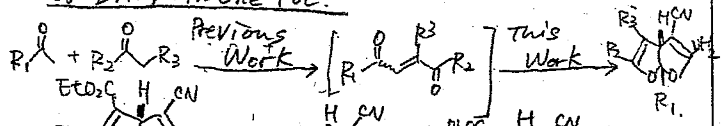
・Previous Work

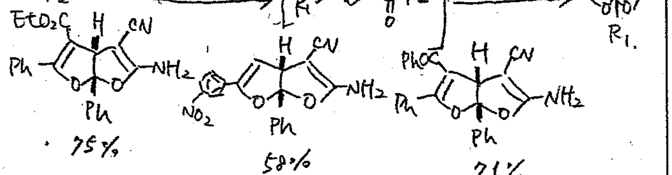


R₄ = (Hetero)aryl, alkenyl
R₅, R₆ = (Hetero)aryl, alkenyl, alkyl, alkoxyl

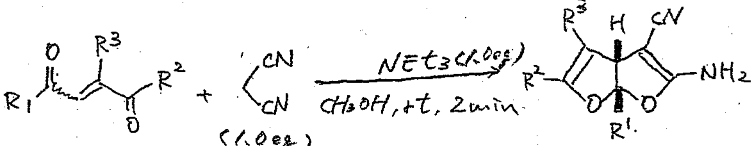
19 examples
67−89 %
(E,Z 75:25 ~ >99:1)
Org. Lett. 2010, 12, 1856−1859

・Domino Strategy for the synthesis of DHFF in One Pot.





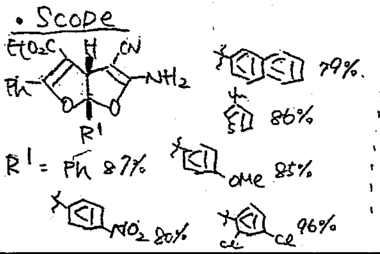
・This Work (Bicyclization reaction)

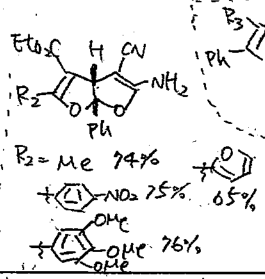


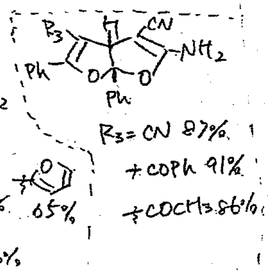
R₁ = (Hetero)aryl
R₂ = (Hetero)aryl, alkyl
R₃ = CO₂Et, CN, COPh, COCH₃

22 examples
64% ~ 96%

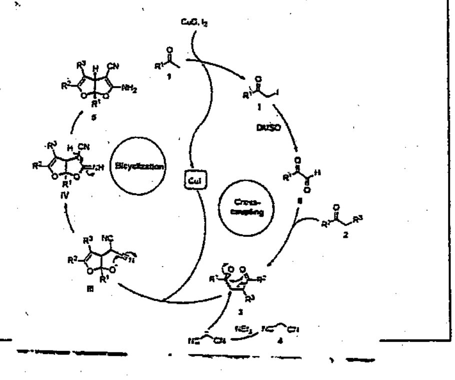
・Scope







・Proposed Mechanism



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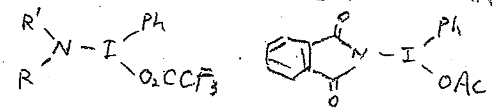
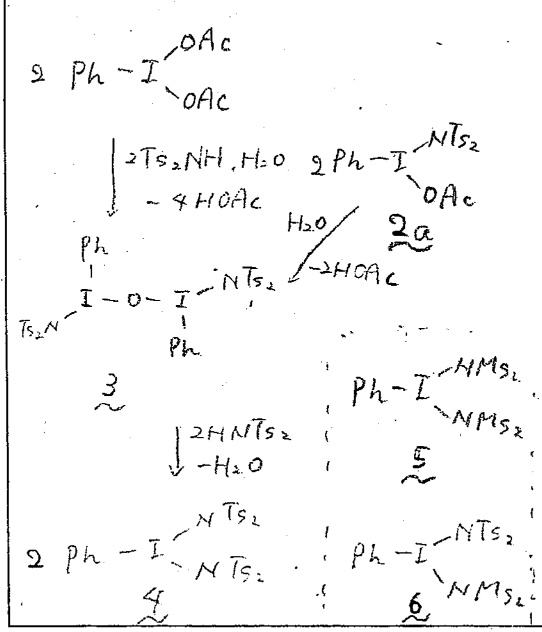
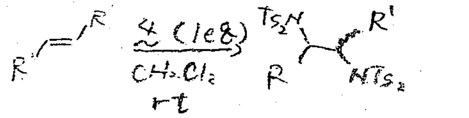
Defined Hypervalent Iodine(III) Reagents Incorporating Transferable Nitrogen Groups: Nucleophilic Amination through Electrophilic Activation.

既知のアミノ化剤としての超原子価ヨウ素

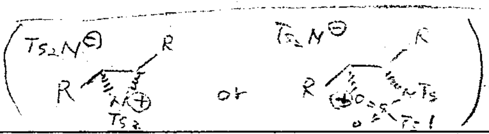


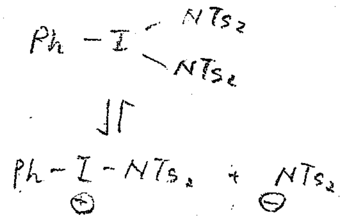
・PhI(OAc)等から得られる中間体
・構造は決まっていない





Entry	Substrate	Product	Time (min)	Yield %
1	Ph	Ts2N, Ph, NTs2	25	80
2	C6H13	Ts2N, C6H13, NTs2	50	82
3	Ph	Ts2N, Ph, NTs2	90	90
4	Ph, Ph	Ts2N, Ph, Ph, NTs2	240	66
5		NTs2, NTs2	300	72
6	Ph	Ts2N, Ph, NTs2	90	91





D化、^{15}N化した化合物でMSにおいて $[PhINTs_2]^+$、$[PhI^{15}NTs_2]^+$、$[C_6D_5NTs_2]^+$、$[C_6D_5I^{15}NTs_2]^+$のフラグメント出る。