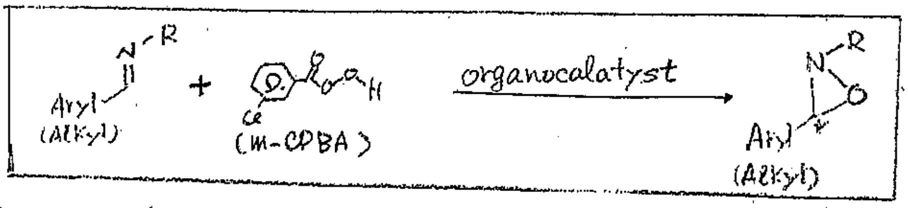
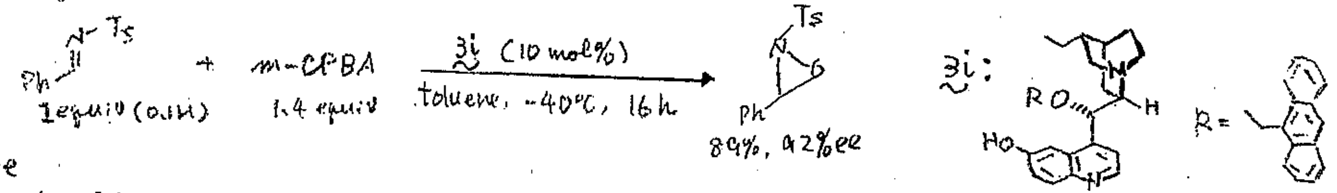
Catalytic Enantioselective Oxaziridination (K. A. Jørgensen et al.) J. Am. Chem. Soc. Doi: ja2064457

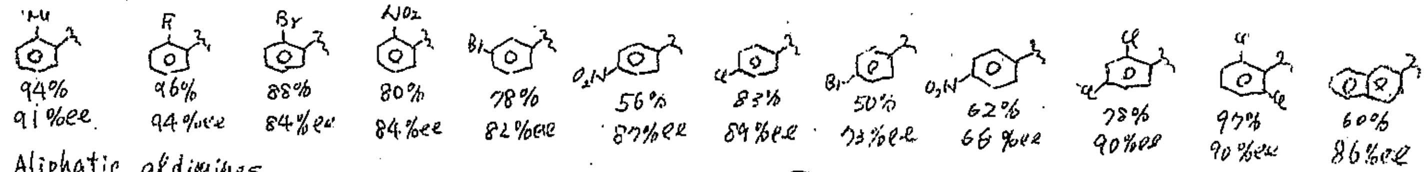


ダメな Oxidant
H_2O_2, NaOCl, Oxone®, TMPO
iodine(III)

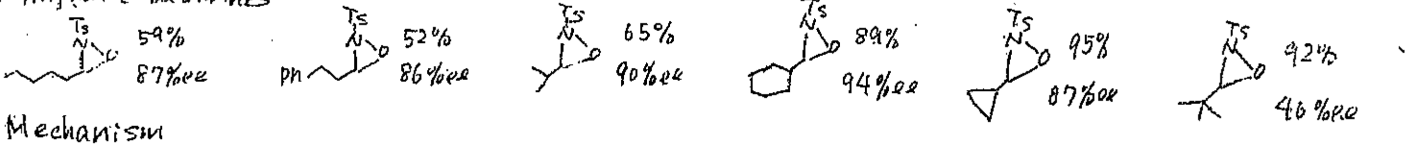
- Screening of Reaction Conditions



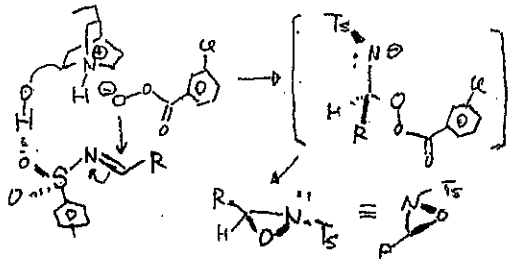
- Scope
  - Aromatic aldimines



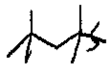
  - Aliphatic aldimines



- Mechanism
  - Catの濃度を下げても eeは少しだけ低下するのみ
    ⇓
    monomeric catalyst (active species)
    ⇑
    NMRからも確認
  - 速度論
    - ○aldimine と m-CPBAの両方に対し一次
    - ○Hammet → ρ値とeeには相関なし
    - ○競争実験 → 電子求引基が置換している aldimine は遅い
    - → Stepwise mechanism



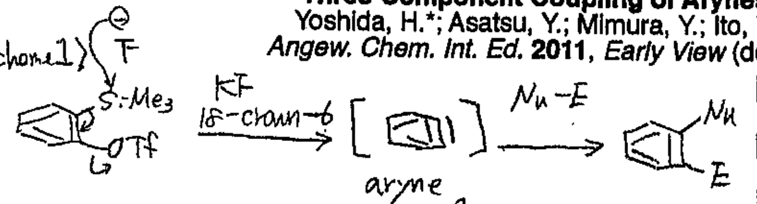
CT 1910

tOct ≡ 

"Three-Component Coupling of Arynes and Organic Bromides"
Yoshida, H.*; Asatsu, Y.; Mimura, Y.; Ito, Y.; Ohshita, J.; Takaki, K.
Angew. Chem. Int. Ed. **2011**, *Early View* (doi: 10.1002/anie.201104858)

Youhei Takeda

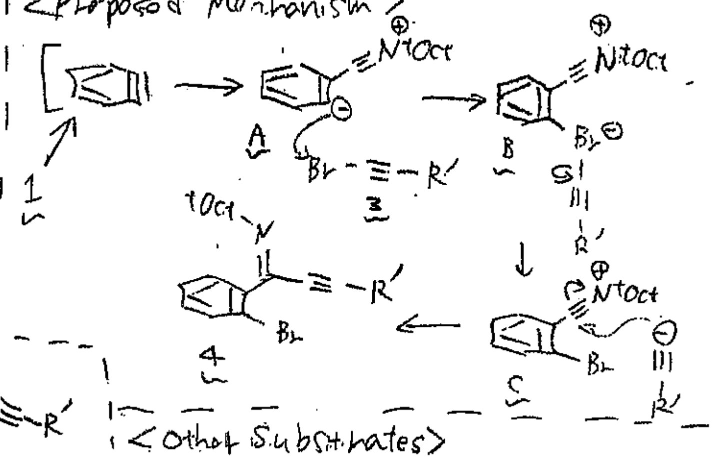
(Scheme 1)



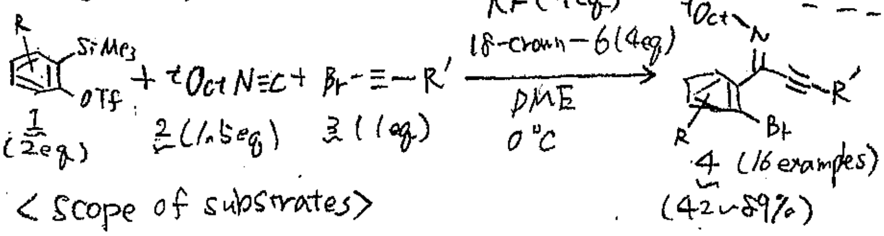
Nu-E = $(R_3Si)_2$, $(R_3Sn)_2$, X-C(=O)-R, R_2N-SiR_3.

Yoshida H. and Ohshita J.
J. Synth. Org. Chem. Jpn. 2011, 69, 877.

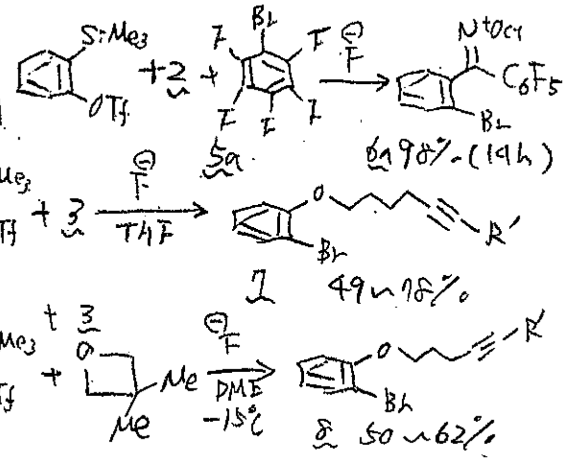
<Proposed Mechanism>



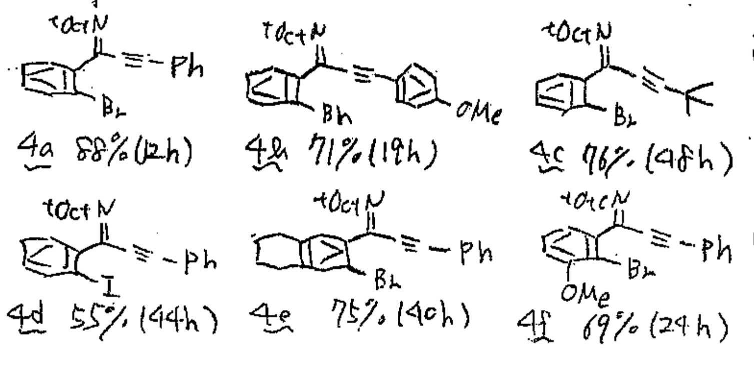
<This Work>



<Other Substrates>



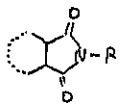
<Scope of substrates>



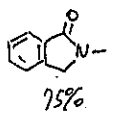
Selective Catalytic Monoreduction of Phthalimides and Imidazolidine-2,4-diones

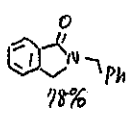
D2 村上

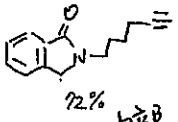
Das S ; Addis, D.; Knöpke L.R.; Bentrup, U.; Junge, K.; Brückner, A.; Beller, M.* (Angew. Chem Int. Ed.,



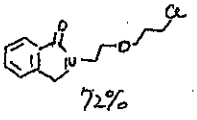
up to 78% (17 examples)

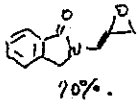


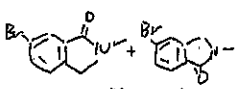


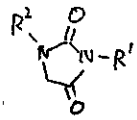


内部アルキンもOK.





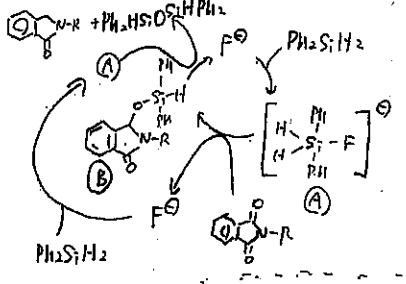


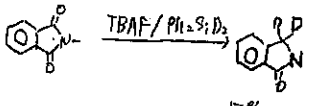


(TBAF = tetra n-butylammonium fluoride
PMHS = polymethylhydrosiloxane)

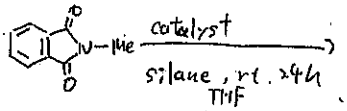
- good chemoselectivity
- operational simplicity
- functional group tolerance

Proposed reaction mechanism





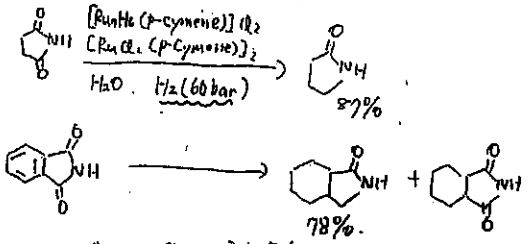
- In situ ATR-FTIR spectra
- In situ UV/Vis spectra



catalyst (mol%)	silane (equiv)	yield (%)
—	$PhSiH_3$ (2)	0
TBAF (5)	$PhSiH_3$ (2)	90
TBAF (5)	Ph_2SiH_2 (2)	80
TBAF (5)	PMHS (5)	85

catalyst (mol%)	silane (equiv)	yield (%)
TBABr (5)	PMHS (5)	0
Cs_2F (5)	PMHS (5)	35
KO^tBu (20)	PMHS (5)	25

Previous work



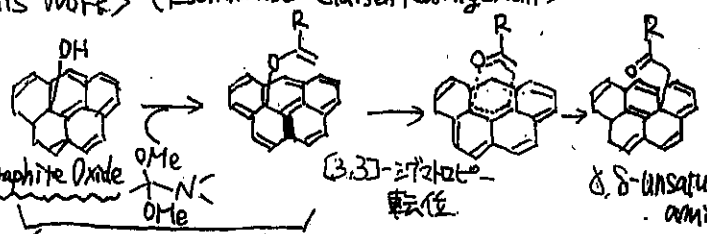
Angew. Chem Int. Ed. 2005, 117; 2059

Claisen Rearrangement of Graphite Oxide : A Route to Covalently Functionalized Graphenes

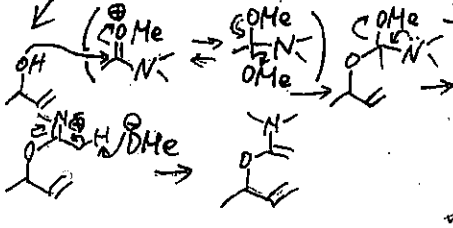
長町

William R. Collins, Wiktor Lewandowski, Ezequiel Schmois, Joseph Wallsh, and Timothy M. Swager* Angew. Chem. Int. Ed. DOI:10.1002/anie.201101371

<This Work> (Eschenmoser-Claisen Rearrangement)

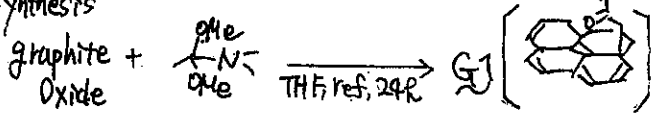


cf.



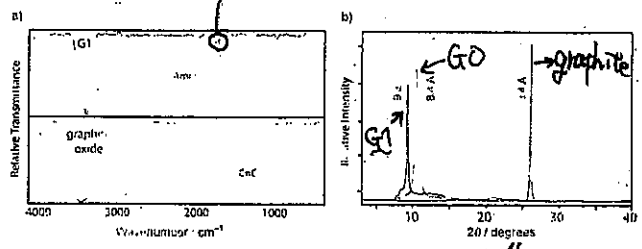
- Preperation JACS. 1958, 80, 1339
- Graphite Oxide (GO)
- Graphite Powder $\xrightarrow[H_2SO_4]{KMnO_4}$ Product

Synthesis

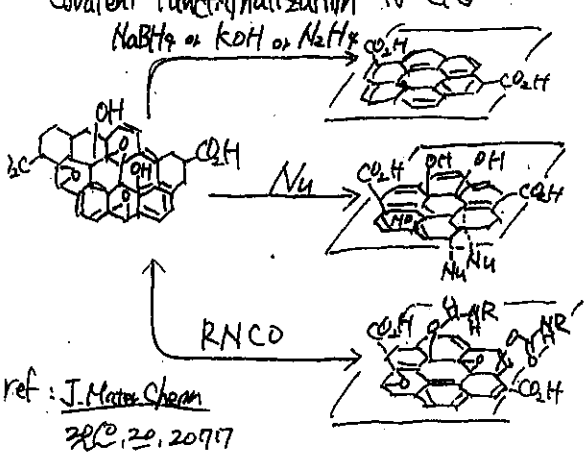


Characterization of GJ

- FT-IR
- XRD

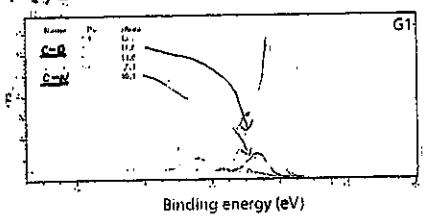


- Covalent Functionalization to GO

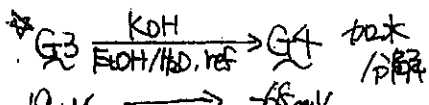


ref : J. Mater. Chem 2010, 20, 20717

XPS



Solvent / T [℃]	Atom% C : O : N	Amide/C
THF / 60	79.0 : 16.6 : 1.4	1 : 52
dioxane / 100	83.5 : 12.4 : 2.1	1 : 37
diglyme / 150	85.8 : 11.1 : 3.1	1 : 23



-19mV ⟹ -65mV (36h)
zeta potential

3.1% ⟹ 0.6%
percent of N

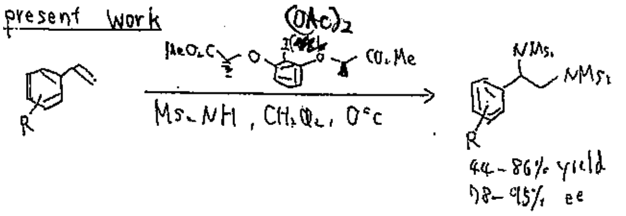
5mg/mL 溶解. 3か月は沈殿なし.

Grapheン表面のカルボキシル基のpKaにより水のpHが高い場合は分散/低い場合は凝集
↑
カルボキシル基が中性電荷

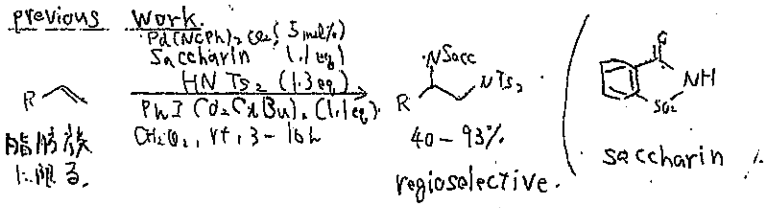
Enantioselective Metal-Free Diamination of Styrenes (D1 [illegible]) Angewandte Chem. Int. Ed.

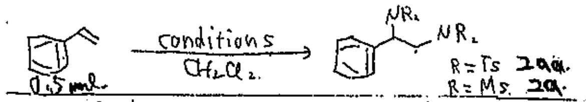
Kilian Muñiz et al (Institute of Chemical Research of Catalonia (Spain)) DOI: 10.1002/anie.201103077

present work



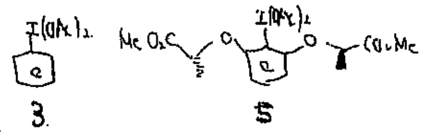
previous work





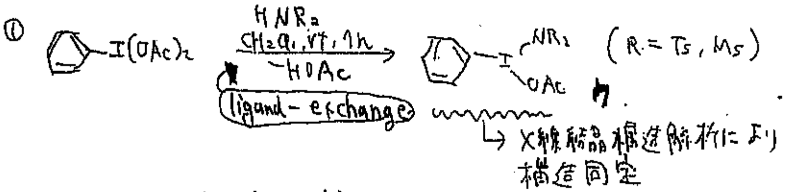
entry	Conditions	Product	yield(%)	ee
1	$(MeCN)_2PdCl_2$ (5mol%), $HNTs_2$ (1.4 equiv), saccharin (1.1 equiv) 3 (1.2 equiv), rt	2aa	45	—
2	$HNTs_2$ (1.4 equiv), 3 (1.2 equiv), rt	2aa	42	—
3	$HNTs_2$ (2.4 equiv), 3 (1.2 equiv), rt	2aa	85	—
4	$HNTs_2$ (2.4 equiv), 5 (1.2 equiv), rt	2aa	76	50
5	$HNMs_2$ (2.4 equiv), 5 (1.2 equiv), rt	2a	87	66
6*	$HNMs_2$ (2.4 equiv), 5 (1.2 equiv), 0°C	2a	86	85

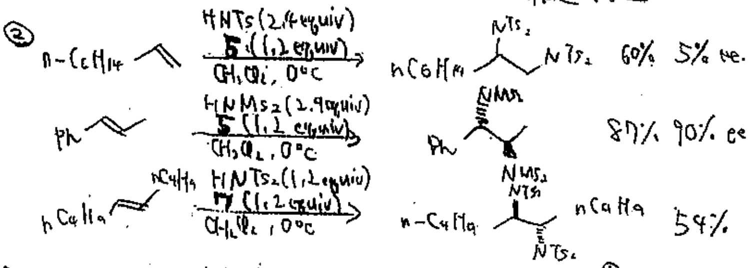
* 5 mmol scale.



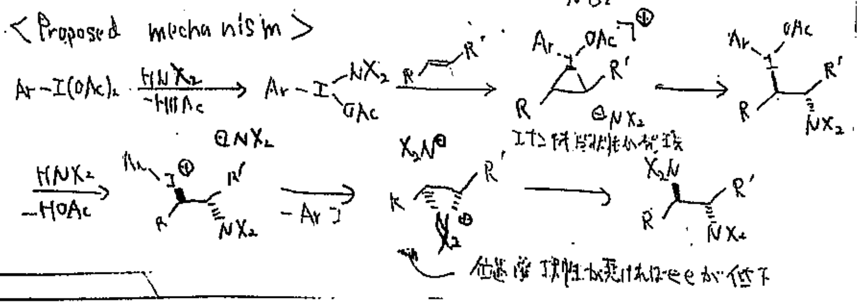
Ms = methanesulfonyl

Ts = p-toluenesulfonyl





<Proposed mechanism>



Organocatalytic, Oxidative, Intramolecular C–H Bond Amination and Metal-free Cross-Amination of Unactivated Arenes at Ambient Temperature

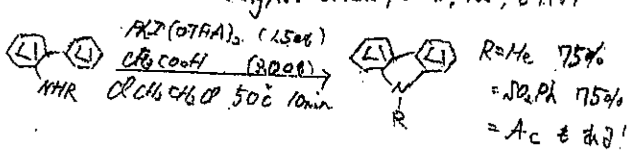
11/09/10

M2. [illegible]

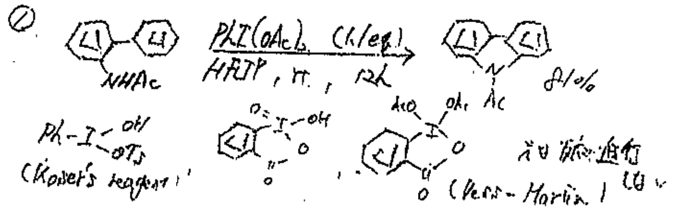
Antonchick, A. P.* Samanta, R. Kulikov, K. and Lategahn, J.

Angew. Chem., Int. Ed. **2011**, *50*, 8605.

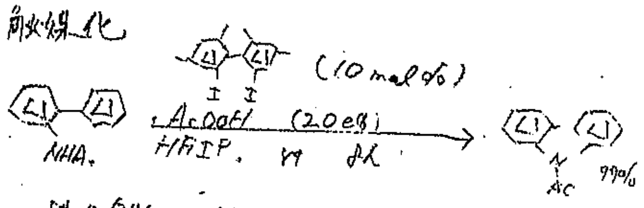
: Previous Work (Chang, S. JACS, 2011, 133, 5996)



※ Present Work



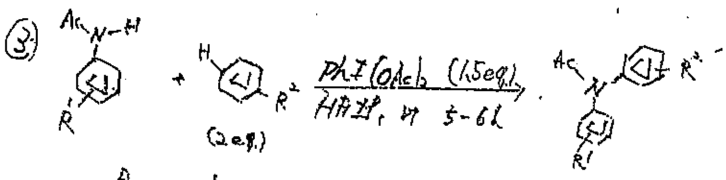
② 触媒化



・ヨウ素化合物 … PhI (51%), nBu_4NI (20%) NIS (trace)

・基質 11 examples 52 ~ 98% yield

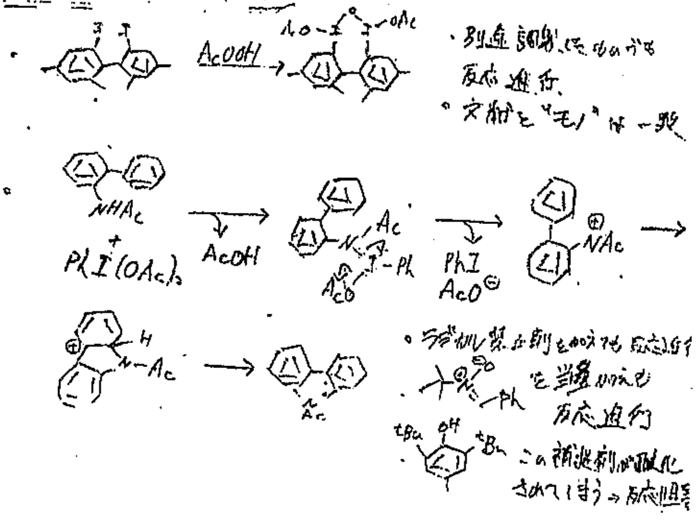
③



・ 11 examples 51 ~ 86%

・分子間では触媒での反応は進行しない (95% 原料回収)

Proposed Mechanism



・ラジカル禁止剤を加えても反応進行

・この捕捉剤が酸化されてしまう → 反応阻害

Carboxylic Acids as Traceless Directing Groups for Formal meta-Selective Direct Arylation

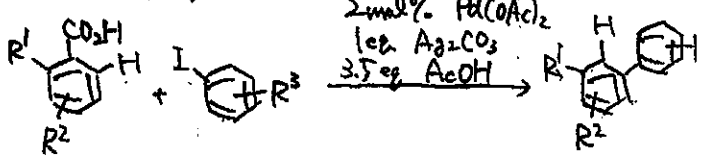
Yuki Ikeda

Cornella, J.; Righi, M.; Larrosa, I *Angew. Chem. Int. Ed.* Early Vew (DOI: 10.1002/anie.201103720)

m置換ビアリールの合成を考えると

- カップリングを用いる場合は、基質となるm置換アリールの合成に数段階必要。
- C-Hアリール化を用いると、位置選択性の制御が難しい。配向基があっても非選択的。

〈This Work〉



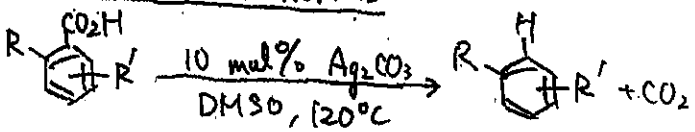
R^1= F, Cl, NO_2, CF_3, OMe

R^2= F, Cl, OMe (R^1に対して o, m, p)

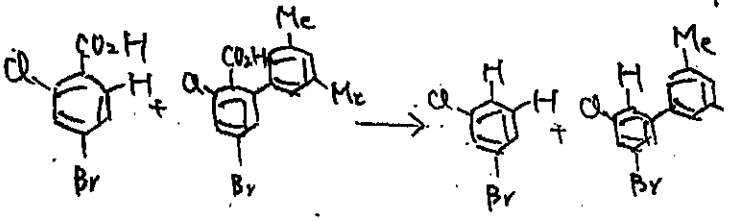
R^3= F, Cl, Br, Me, CO_2Me (I^-に対して m, p)

〈Previous Work〉

Larrosa and co-workers

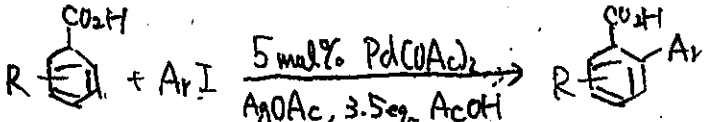


R= EWG, EDG ; R'= EWG, EDG, H



10 mol% Ag_2CO_3, DMSO, 120°C, 4h	18%	5%
1.0eq. Ag_2CO_3, AcOH, 130°C, 2h.	0%	0%
2mol% $Pd(OAc)_2$, AcOH, 130°C, 2h	0%	22%
2mol% $Pd(OAc)_2$, 1.0eq. Ag_2CO_3 AcOH, 130°C, 16h.	0%	5%

Yu and co-workers

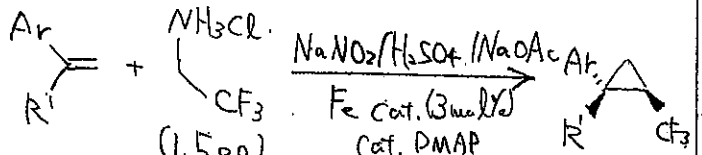


ただし、Rがo位のときはR=Meに限られる。

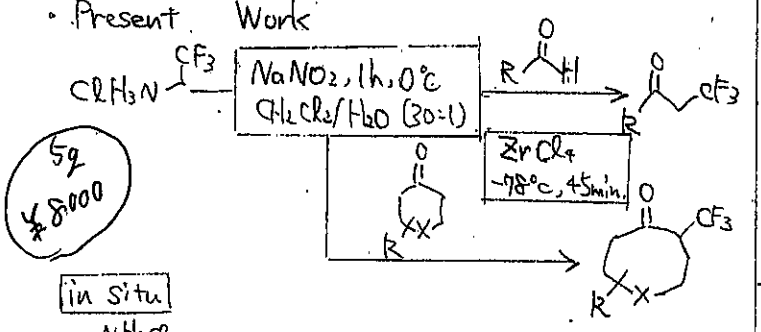
Synthesis of Trifluoro-Substituted Ketones from Aldehydes and Cyclohexanones

E. M. Carreira *et al. Angew. Chem. Int. Ed.* **2011**, *50*, Early view 溝合 萌

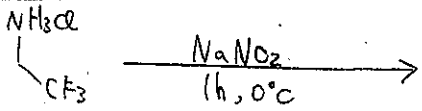
- Previous work



- Present Work



in situ



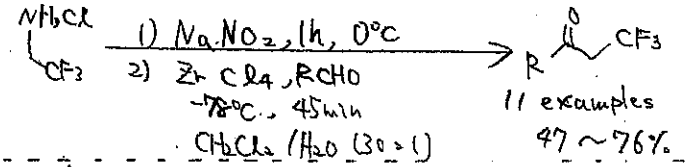
trifluoromethyl diazomethane

temp. : -78°C

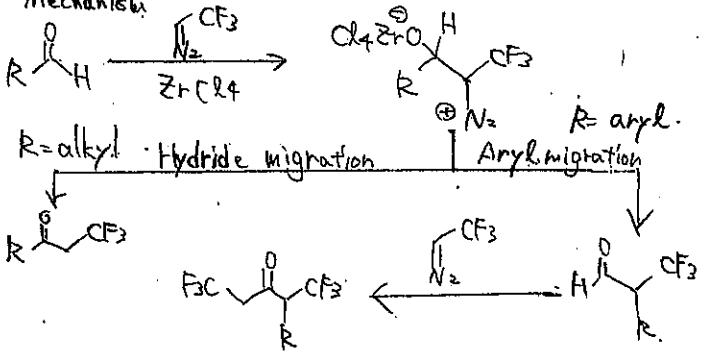
Small amount of water freeze out

Strong Lewis acid ($ZrCl_4$) が使用可能

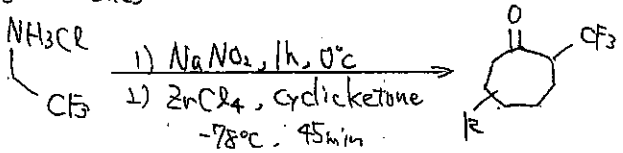
- Aldehydes



- Mechanism



- Cyclohexanones



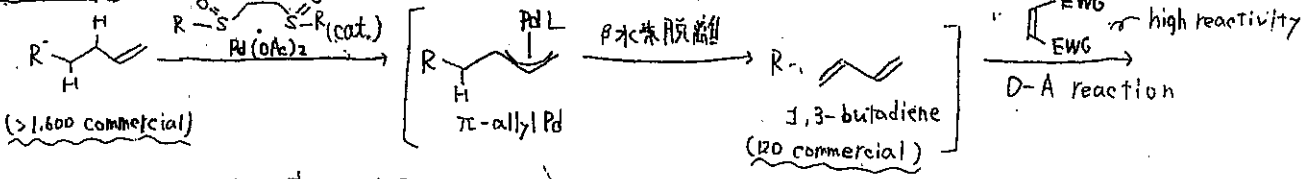
Molecular Complexity via C-H Activation : A Dehydrogenative Diels-Alder Reaction

M1 鈴織

Erik M. Stang and M. Christina White*

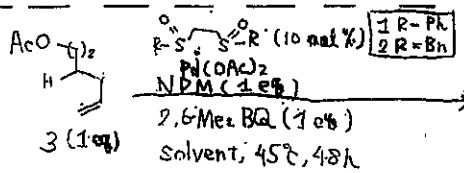
JACS. dx.doi.org/10.1021/ja2059704

Strategy



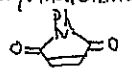
※1,3-ジエンは、反応性が高いものが多く、末端オレフィンに比べて、扱いにくい。

→ White らは、Pd(II)/sulfoxide の系からアリル位のエステル化・アミド化・アルキル化を報告している。



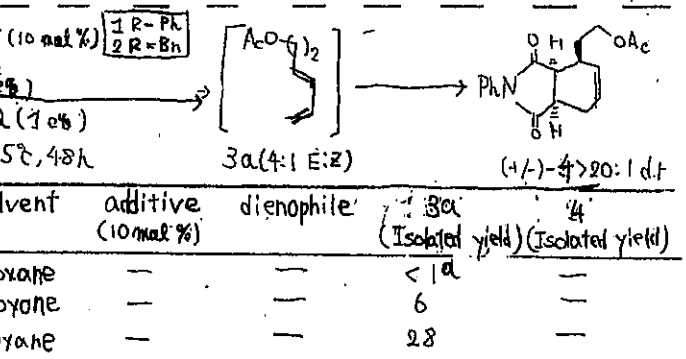
entry	catalyst	Solvent	additive (10 mol%)	dienophile	3a (Isolated yield)	4 (Isolated yield)
1	$Pd(OAc)_2$	dioxane	—	—	<1[a]	—
2	1	dioxane	—	—	6	—
3	2	dioxane	—	—	28	—
4	2	dioxane	—	NPM	<1[a]	33
5	2	DCE	—	NPM	<1[a]	52
6	2	DCE	p-NO_2BzOH	NPM	<1[a]	74
7	2	DCE	p-NO_2BzOH	—	35	—

NPM = N-phenyl maleimide.



2,6-Me_2BQ

a) GC yield.



※Pd cat なしだと 5 は完全に回収される。

※3a を NPM なしで系に入れると、15% conv. でポリマー化

⇒反応性の高い NPM が 3a を捕捉している。

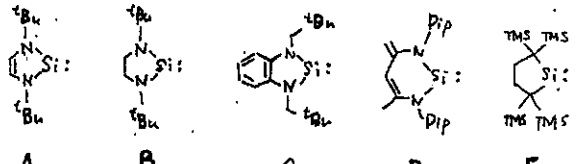
Aromatic Ylide-Stabilized Carbocyclic Silylene

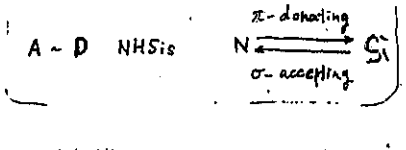
Matthew Asay, Shigeyoshi Inoue, and Matthias Driess

Angew. Chem. Int. Ed. 2011, 50, 1

DOI: 10.1002/anie.201104805

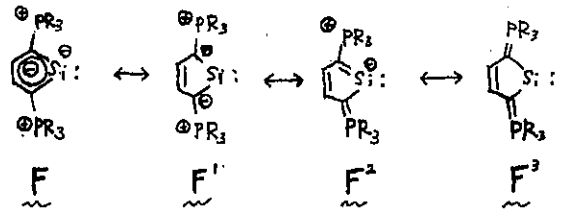
現在までに知られた環状シリレン

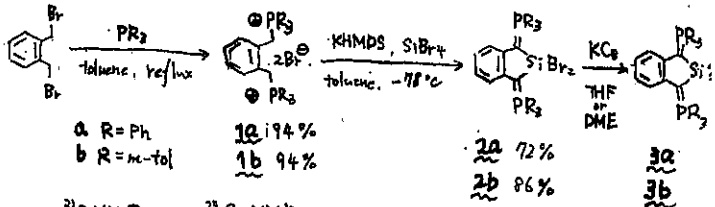




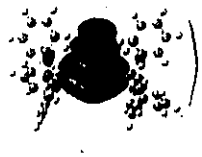
π供与能は NHSi の N に匹敵するが、σ受容能は劣る

カルバニオン置換基を導入する。





	^{31}P NMR	^{29}Si NMR	^{13}C NMR
3a	δ = 17.3 ppm	δ = 213.3 ppm (d, $^2J_{Si,P}$ = 38.5 Hz)	
2a		δ = −16.0 ppm (d, $^2J_{Si,P}$ = 29.3 Hz)	
NHSis		δ = 78-119 ppm	
E		δ = 569 ppm	
3b	δ = 18.6 ppm	δ = 212.4 ppm	δ = 90.3 ppm
2b			δ = 87.2 ppm



HOMO

HOMO−2

NHSi では lone pair を含んだ軌道が HOMO−1

LUMO

NHSi では LUMO は分上に局在化した元素を持っている。

M1 矢野 和樹

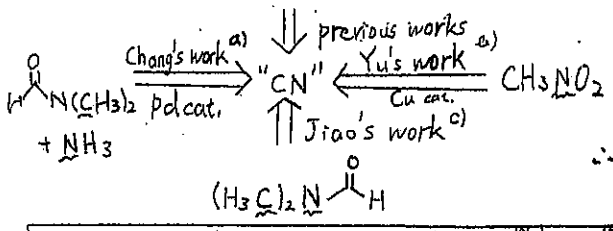
@ Copper-Mediated Cyanation of Aryl Halide with the Combined Cyanide Source

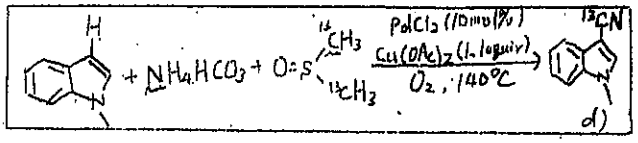
Guoying Zhang, Xinyi Ren, Jianbin Chen, Maolin Hu,* and Jiang Cheng* Org. Lett. 10.1021/ol201713b

B4 岡崎

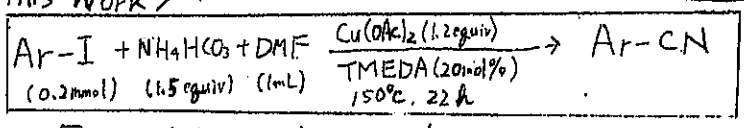
<Previous Work>

MCN (M = Cu, K, Na, Zn), $TMSCN$
$K_3Fe(CN)_6$, $(CH_2)_2C(OH)CN$





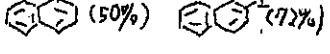
<This Work>

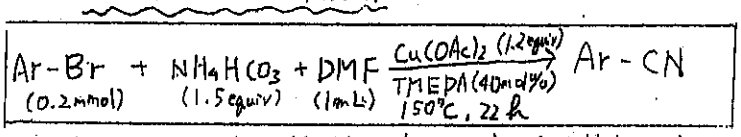


MeO-(C6H4)-I (76~87%) mono < di < tri

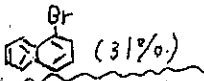
R-(C6H4)-I. R = Ph(89%), BnO(78%), OH(74%), AcNH(43%), Bu_2N(63%), Br(41%), Cl(54%), NO_2(41%), Ac(62%)

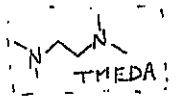
反応性 EDG > EWG





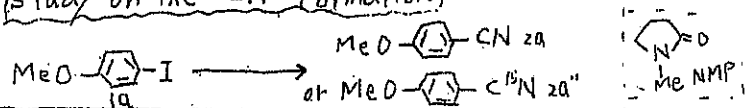
R-(C6H4)-Br, R = MeO(62%), Ph(65%), AcNH(31%), Cl(42%), Ac(38%)





まとめ
- Pd → Cu
- 基質の適用範囲が広がった。
- 毒性の少ない試薬を"CN"供与体として用いている。

Study on the "CN" Formation



entry	ammonium	ligand	solvent	Yield (%)
1	—	TMEDA	DMF	<1
2	$NaHCO_3$	〃	DMF	<5
3	NH_4HCO_3	〃	NMP	12
4	—	〃	NMP	0
5	NH_4HCO_3	〃	$HCON(CH_3)_2$	79
6	$^{15}NH_4Cl$	〃	DMF	56

a) Kim, J.; Chang, S. J. Am. Chem. Soc. 2010, 132, 10272
b) Chen, X.; Hao, X.; Goodhue, C.E.; Yu, J.-Q. J. Am. Chem. Soc. 2006, 128, 6790
c) Ding, S; Jiao, N. J. Am. Chem. Soc. 2011, 133, 12374
d) Ren, X.; Chen, J.; Chen, F.; Cheng, J. Chem. Commun. 2011, 47, 6725

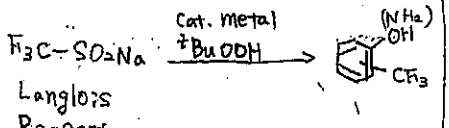
Innate C-H trifluoromethylation of heterocycles

Yining Ji, Tobias Brueckl, Phil S. Baran, et al

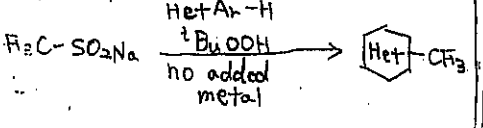
PNAS Early Edition
DOI: 10.1073/pnas.1109059108

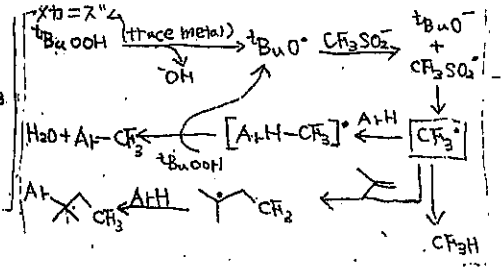
B4 久國 大土也

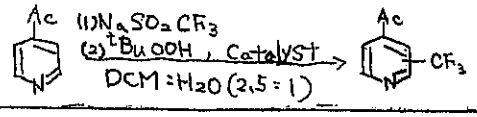
Previous Work



Present Work





① 

Entry	(1) (eq)	(2) (eq)	Cat.(eq)	Stirring (RPM)	Yield
1	3.0	5.0	$FeSO_4$(0.1)	600	74%
2	3.0	5.0	$CuSO_4$(0.1)	600	88%
3	1.0	1.0	—	600	33%
4	3.0	5.0	—	600	73%
5	3.0	5.0	—	300	79%
6	3.0	5.0	—	none	86%