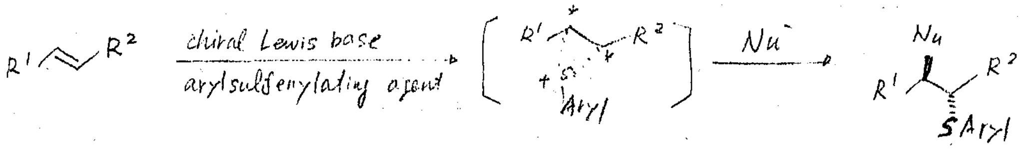
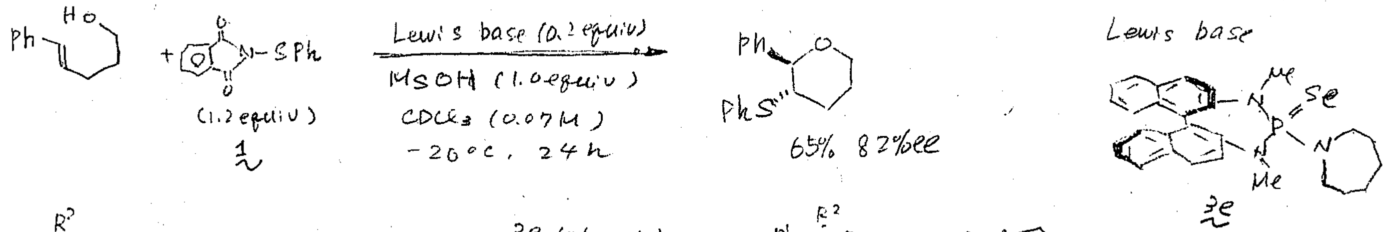
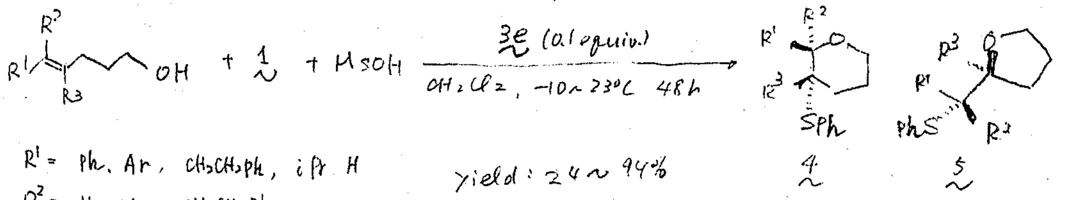
Catalytic Asymmetric Thiofunctionalization of Unactivated Alkenes J. Am. Chem. Soc.

S. E. Denmark et al DOI. Ja2064395.

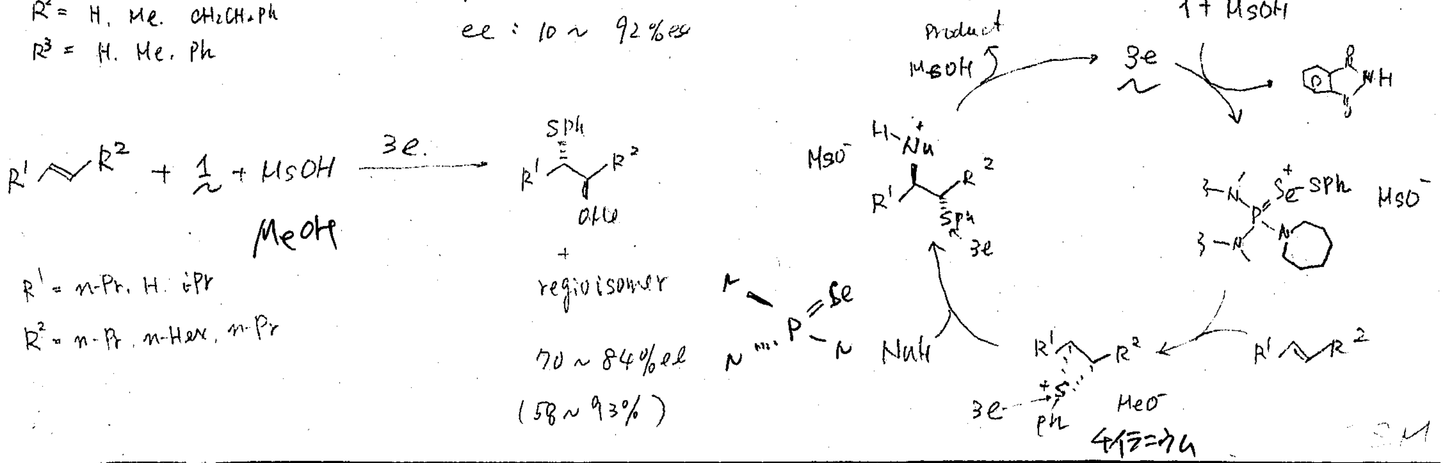






R^1 = Ph, Ar, CH_2CH_2Ph, iPr, H
R^2 = H, Me, CH_2CH_2Ph
R^3 = H, Me, Ph

yield: 24 ~ 94%
ee: 10 ~ 92%ee



R^1 = n-Pr, H, iPr
R^2 = n-Pr, n-Hex, n-Pr

CT 1X01

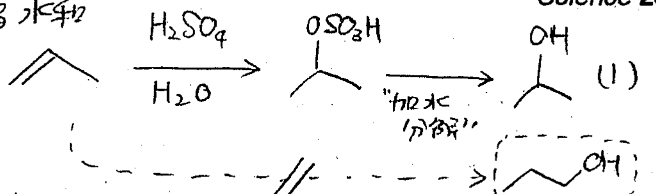
"Primary Alcohols from Terminal Olefins: Formal Anti-Markovnikov Hydration via Triple Relay Catalysis"

Youhei Takeda

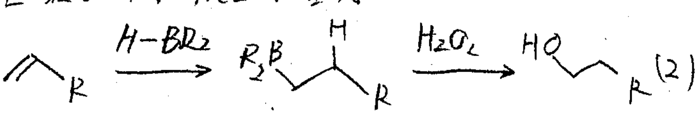
Dong, G.; Teo, P.; Wickens, Z. K.; Grubbs, R. H.*

Science **2011**, *333*, 1609–1612.

末端アルケンの酸触媒による水和

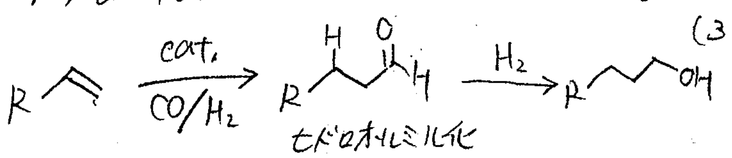


◦ 実験室的 1°アルコール合成

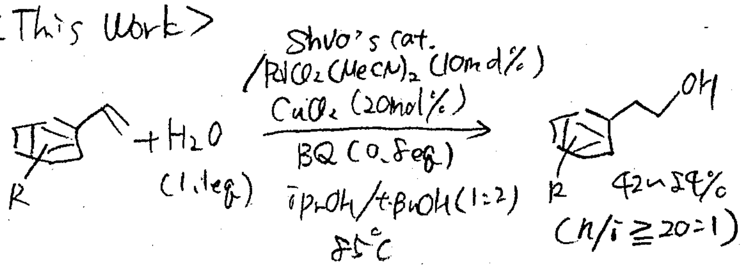


工業的には利用できない。 ⟵ { ◦ ボロン塩の副生 ◦ H_2O_2 の使用

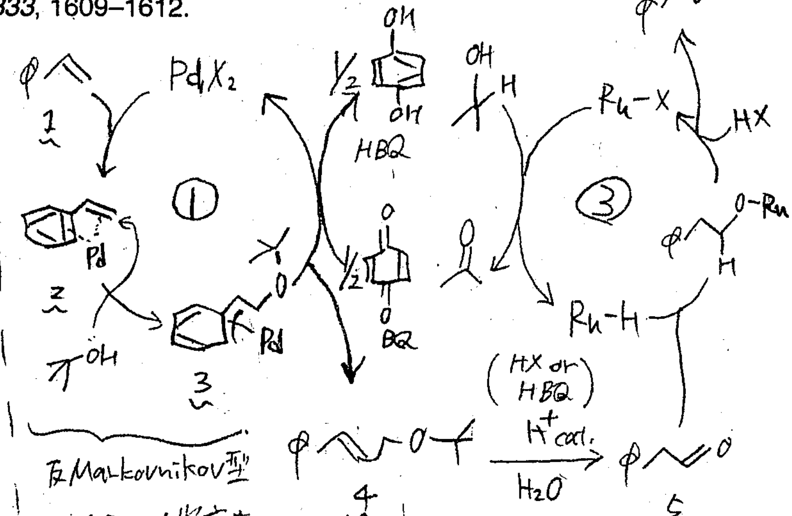
◦ "1°アルコールはどうやって製造しているのか？"



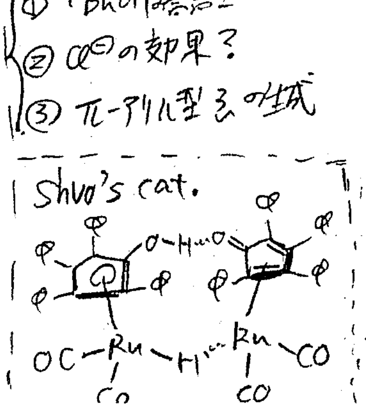
<This Work>



◦ 回収可能 (セライトで上に残るsolid



反Markovnikov型
① tBuOHの嵩高さ
② Cl⁻の効果？
③ π-アリル型3の生成



☆ control実験, D化実験からわかったこと。

◦ $CuCl_2$ は、5が還元されるのを抑える。

◦ Ru-H のHは (H) ← ココ

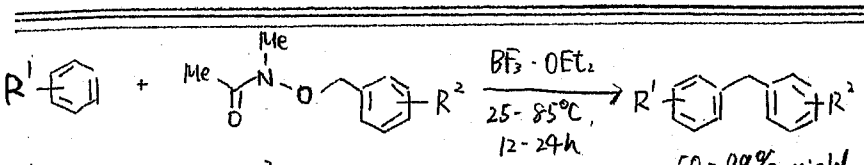
◦ 無水条件だと、4で反応がstopしている。

Friedel-Crafts Benzylation of Activated and Deactivated Arenes

Gabriel Schäfer and Jeffrey W. Bode (ETH Zürich)

(Angew. Chem. Int. Ed. Early View)

木村E.

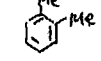
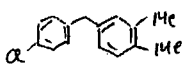
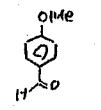
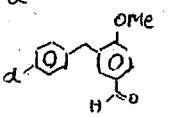


R' = H, CH₃, Cl, CF₃, CO₂Me, etc　　R² = H, CH₃, Cl, CF₃, CO₂Me, CN, NO₂

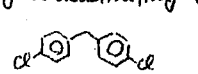
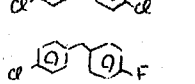
50-99% yield

○ Selected Example

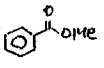
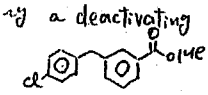
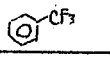
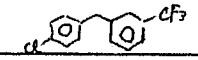
① Arenes bearing an activating ortho/para-directing gro

Arene (4eq.)	Major product	Time	yield (%)	(ratio)
		35	90	(53:47)
		50	52	(99:1)

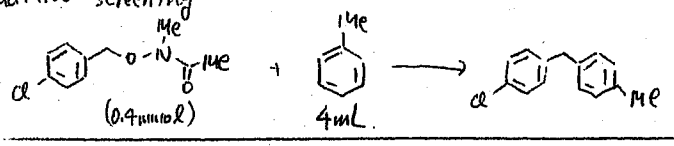
③ Arenes bearing a deactivating ortho/para-directing group

		40	76	(70:30)
		40	77	(87:13)

③ Arenes bearing a deactivating meta-directing group

		45	53	(91:9)
		45	53	(99:1)

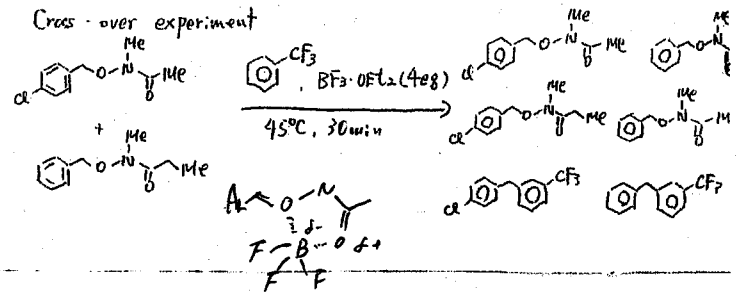
○ Additive screening



Entry	Additive	Equiv	T(°C), t(h)	yield (%) (ratio)
1	$BF_3 \cdot OEt_2$	4	25 (13)	99 (55:43:2)
2	$BF_3 \cdot OEt_2$	2	25 (22)	99 (55:43:2)
3	$BF_3 \cdot OEt_2$	0.1	25 (24)	n.r
4	$BF_3 \cdot OEt_2$ (Toluene : 1.6 mmol)	4	40 (18)	80 (54 43:3) p o m
5	$AlCl_3$	1	25 (5)	83 (48:45:7)
6	$FeCl_3$	4	25 (12)	75 (50:45:5)
7	no additive		50 (24)	n.r.

$HBF_4 \cdot OEt_2$, $B(OH)_3$, $ZnCl_2$, $Mg(acac)_2$, TMSCl, $Cu(OAc)_2$ ⇒ n.r.

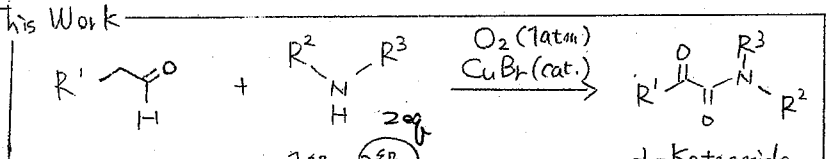
Cross-over experiment



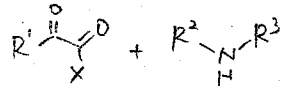
Copper-Catalyzed Aerobic Oxidative Coupling of Aryl Acetaldehydes with Anilines Leading to α-Ketoamides

Chun Zhang, Zejun Xu, Liangren Zhang, and Ning Jiao, *Angew. Chem. Int. Ed.* DOI:10.1002/anie.201105285

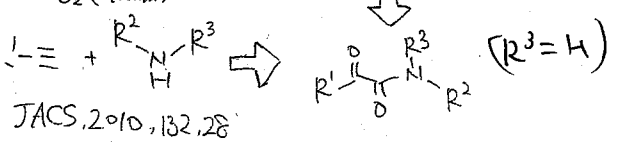
This Work



α-Ketoamide の合成法例



O_2 (1atm)



JACS, 2010, 132, 28

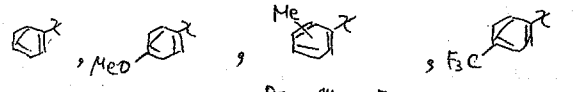
- 末端アルキンのホモカップリングのコントロールが難しい。⇒ アルキンは5当量必要!!
- アミンのRに電子求引基があると収率低下。
- 2級アミンは反応に適用不可。

○ 条件検討

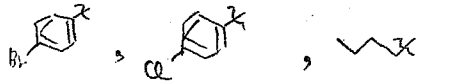
CuCl, CuOAc, 2価のCu, Solvent (benzene, DMF), Base (Na_2CO_3, NEt_3), Temp. (60°C ref) はダメ

MS4Aを使うと収率UP!!!

○ アルデヒドのR'

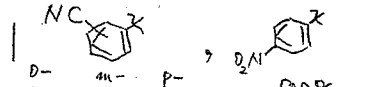


82%　83%　o- 73%　m- 71%　p- 77%　84%

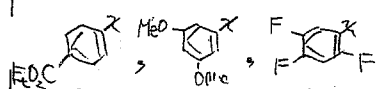


75%　78%　0%

○ アミンのR², R³



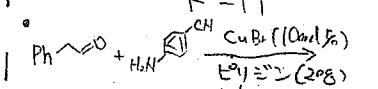
o- 70%　m- 70%　p- 82%　90%

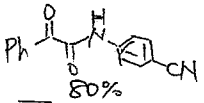


60%　35%　86%

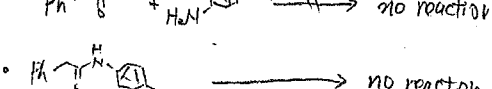
R²	R³			
	Me	 Me	 nC_5H_{11}	H
	65%		41%	0%

R³ = H

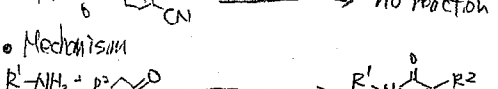




80%



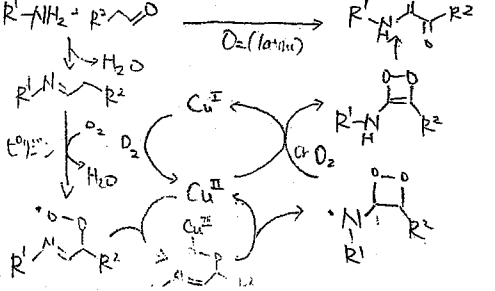
no reaction



no reaction

結果 (10mol%) ⇒ CuBr, toluene, ピリジン, rt, MS4A

○ Mechanism

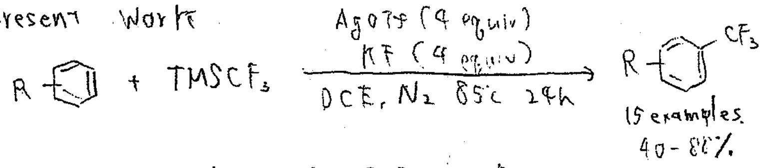


Silver-Mediated Trifluoromethylation of Arenes Using $TMSCF_3$

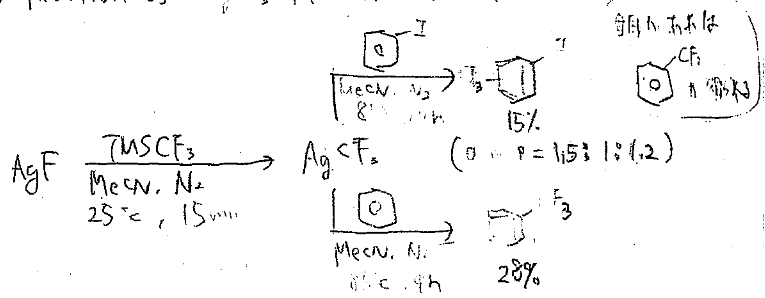
Melanie S. Sanford et al. (University of Michigan). (D1 早川)

Org. Lett, ASAP
10.1021/ol202147a

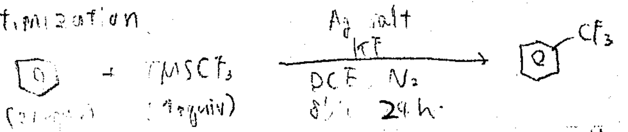
present work



① Reaction of $AgCF_3$ with PhI and Benzene

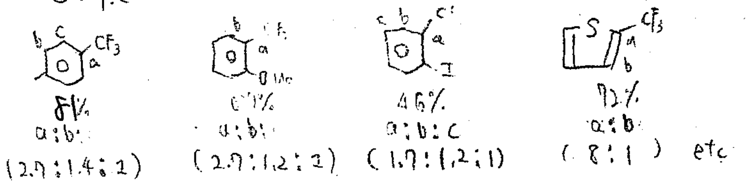


② Optimization

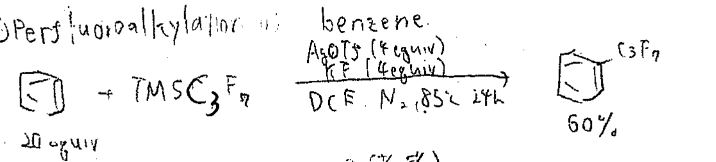


entry	metal salt	metal salt / KF equiv	yield
1	AgOAc	2/2	6
2	AgF	2/2	45
3	AgOTf	2/2	68
4	AgOTf	4/4	87
5	AgOTf	4/0	0

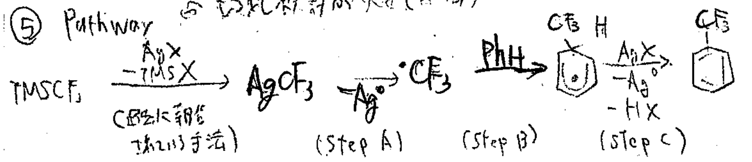
③ Scope



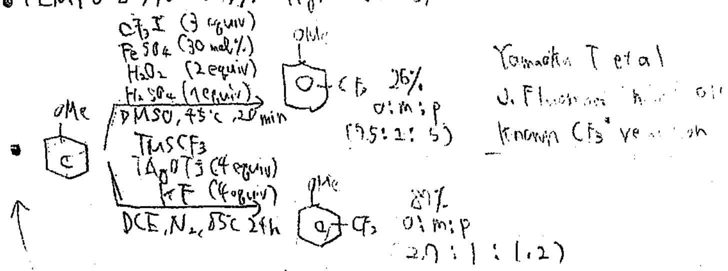
④ Perfluoroalkylation of benzene



⑤ Pathway ← もう少し検討が必要(著者)



• TEMPO 87% → 7%, light 87-75%, AIBN 87% → 57%



These results suggest against a purely free radical pathway

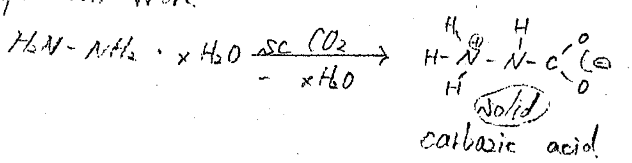
Isolation and structural characterization of the elusive 1 : 1 adduct of hydrazine and carbon dioxide

Hur, N. H. et al. Sogang University, Korea

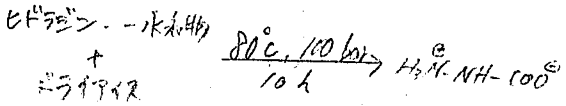
Chem. Commun. DOI: 10.1039/c1cc14542h

12 奥村

present work



(実験)



XRD測定で30日間経っても生成物変化なし

- ほとんど全ての溶媒に溶けない
- 水に対しても安定
- 空気中では昇華していく → (無水ヒドラジンとして利用)

結晶)

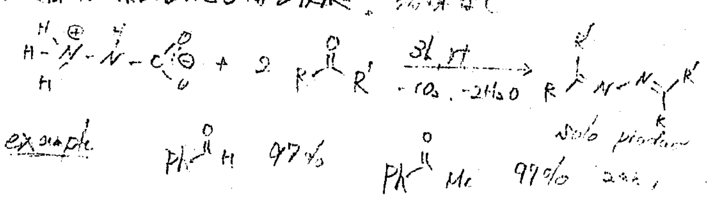
- ツイッターイオンで存在
- N-C bondが単結合と二重結合の中間
- N-N bond長は free のヒドラジンと似ている
- 2つの酸素は分子間で水素結合
  (NH_3^+ と NH から)

(固体NMR) (^1H と ^{13}C)

- 10.2 ppm と 7.2 ppm に2本のブロードピーク (積分比3 = 1)
  NH_3^+ NH
  水素結合で低磁場シフト
  COOH の H は普通 11.0~12.1 ppm NH は 6.3~10.3 ppm
- ^{13}C は 164 ppm (アミノ酸では 169~173 ppm)

(反応)

液体カルボニル化合物と反応。溶媒なし



※ $PhCH_2CH_2CHO$ で ヒドラジン一水和物を用いると副生物が見られる。(over 他の…)

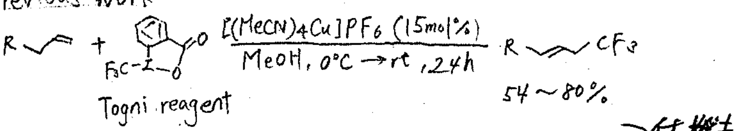
本手法の $H_3N^+-NH-CO_2^-$ では副生物は…水と二酸化炭素のみで free のヒドラジンが出ている!

Copper-Catalyzed C(sp^3)-C(sp^3) Bond Formation Using a Hypervalent Iodine Reagent: An Efficient Allylic Trifluoromethylation

Xi Wang, Yuxuan Ye, Songnan Zhang, Jiajie Feng, Yan Xu, Yan Zhang, and Jianbo Wang*

J. Am.Chem. Soc. (DOI: 10.1021/ja207775a)

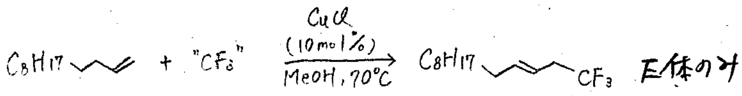
Previous Work



Z体も できる

Previous Work

Table 1 Evaluation of Different CF3 Sources



E体のみ

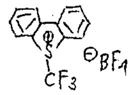
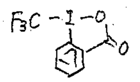
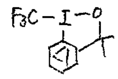
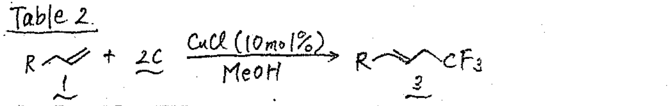
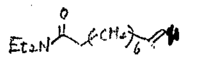
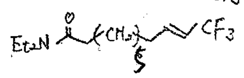
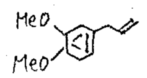
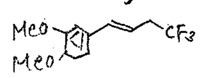
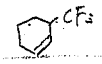
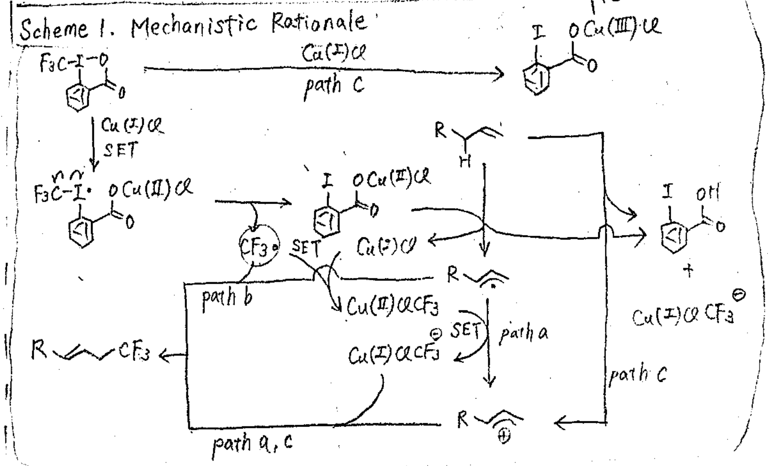
entry	"CF3" 2		yield of 3a
1	TMSCF3 (2a) (2.0eq.)/CsF (2.0eq.) PhI(OAc)2 (2.0eq.)		No Product
2	TMSCF3 (2a) (2.0eq.)/CsF (2.0eq.) tert-BuOOH (2.0eq.)		No Product
3	2b 	(1.2eq)	No Product
4	2c 	(1.75eq)	89%
5	2d 	(1.2eq)	trace

Table 2



entry	substrate 1	product 3	yield
1	TBDMSO-(CH2)7-	TBDMSO-(CH2)7- CF3	97%
2			93%
3			54%
4			44%

Scheme 1. Mechanistic Rationale

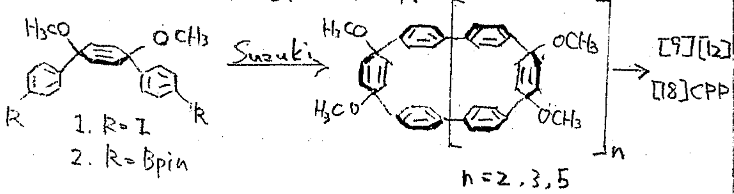


Selective Synthesis of Strained [7]Cycloparaphenylene: An Orange-Emitting Fluorophore

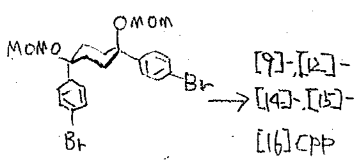
Jasti, R. *et al. J. Am. Chem. Soc.* **2011**, ASAP

M1 河合

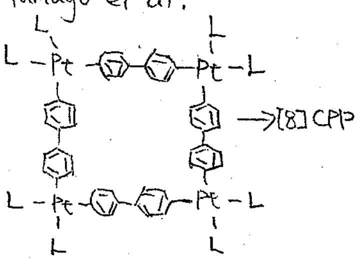
Jasti and Bertozzi et al.

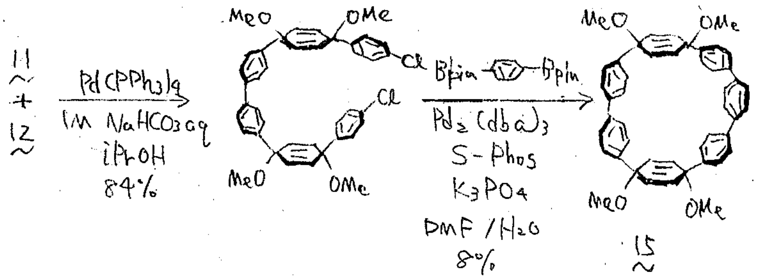


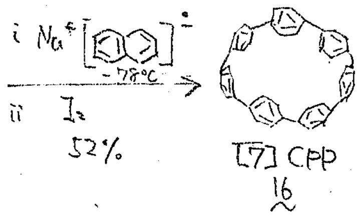
Itami et al.



Yamago et al.





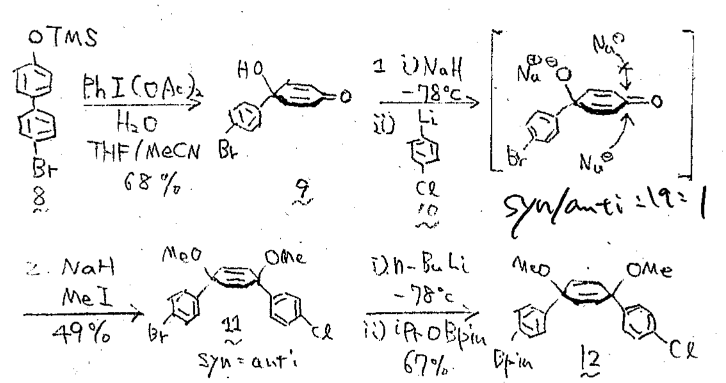


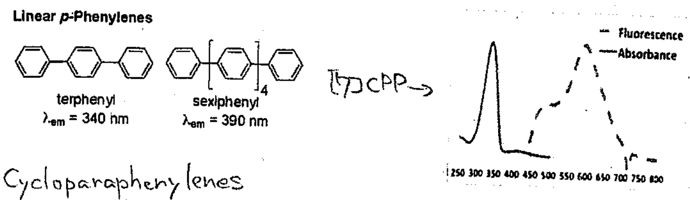
15 → 16

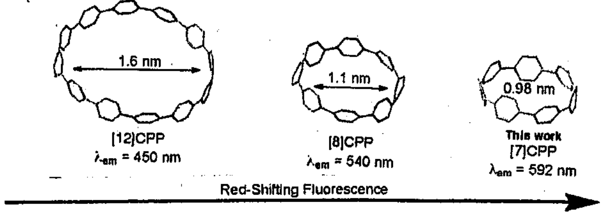
・strain energy

16kcal/mol → 83kcal/mol

・This work







吸収波長はあまりかわらない。

Palladium nanoparticles in carbon thin filmed SBA-15 nanoreactors : efficient heterogeneous catalysts for Suzuki-Miyaura cross coupling reaction in aqueous media

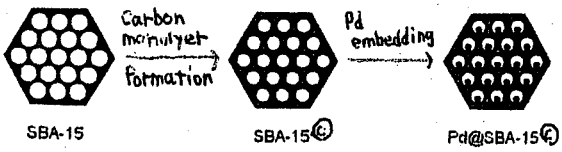
M1 鎌田

Jian Zhi, Deperg Song, Zhiwen Li, Yia Lei and Aiguo Hu

Chem. Commun., 2011, 47, 10707

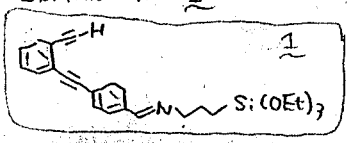
Background

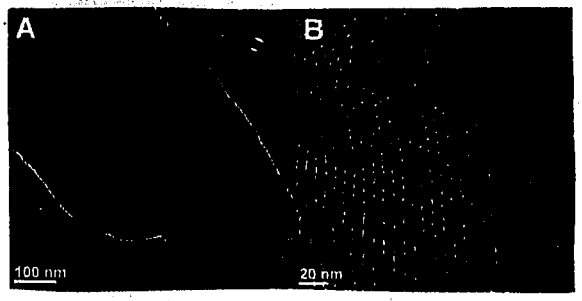
- 触媒が回収可能，再利用可能 ⇒ 不均一触媒の使用
- 水溶媒



previous work !

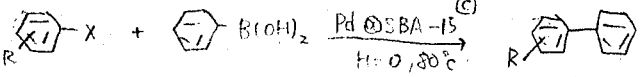
SBA-15 + 1 via Bergman Cyclization → SBA-15©





TEM images A→[110] B→[001] after removal of SBA-15.

Present Work



(X = I, Br, Cl
R = p-OMe, p-CHO, p-Me, p-COOMe p-NO2 H

Pd: 0.04 0.06 ~ 0.08 mol %

- X = Br, R = H のとき Pd@SBA-15© → 1h : 98 %
  Pd@SBA-15 → 1h : 35 % 12h : 35 % のまま

- Reusing Experiment

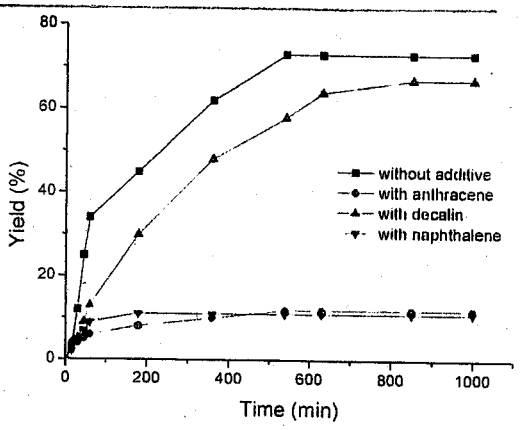
X = I, R = H Pd(0.05 mol %)@SBA-15©

Run	1st	2nd	3rd	4th	5th
Yield(%)	99	98	95	97	96

- Effect of π-π interaction

に対して 0.5eq の添加剤

デカリン → 影響少ない。
アントラセン, ナフタレン → 反応が遅くなった。
↳ 細孔内で阻害しているのでは？



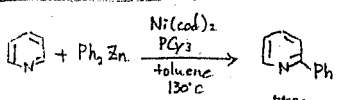
C-H Arylation of Pyridines : High Regioselectivity as a Consequence of the Electronic Character of C-H Bonds and Heteroarene Ring

M1 矢野

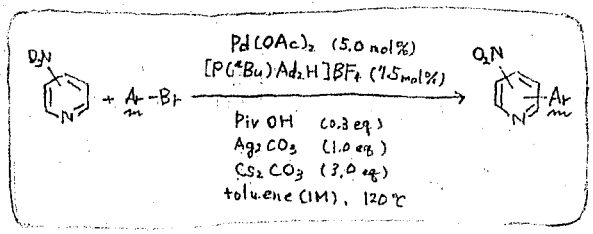
Pengfei Guo., Jung Min Joo, Souvik Rakshit, and Dalibor Sames*

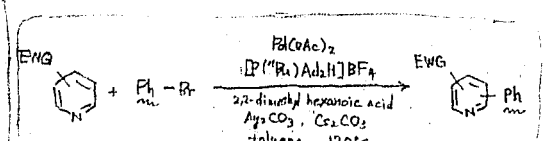
J. Am. Chem. Soc. 10.1021/ja 2060 22p

ピリジンのアリール化

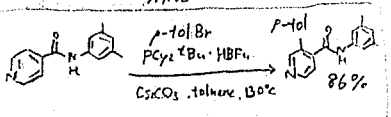


Charlani, N. et al.
J. Am. Chem. Soc. (2009)

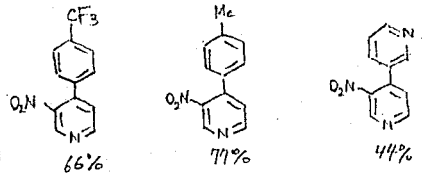


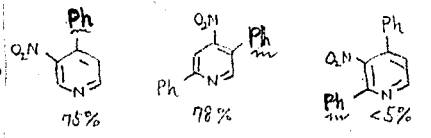


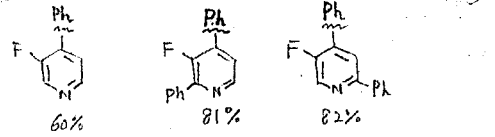
選択的に2位を置換する方法はよく研究されている。

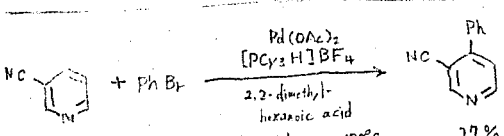


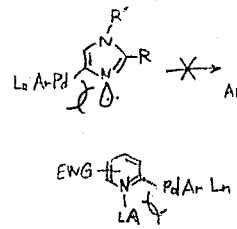
Yu, J. Q. et al.
Angew. Chem. Int. Ed. (2010)

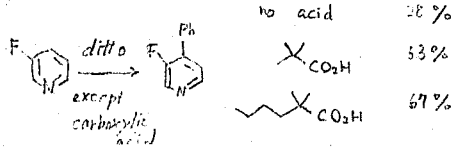


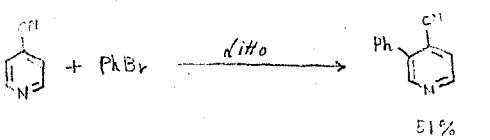








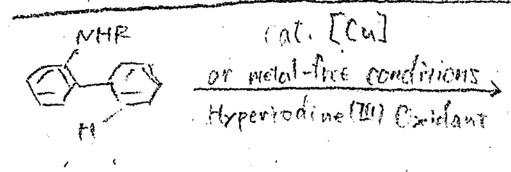




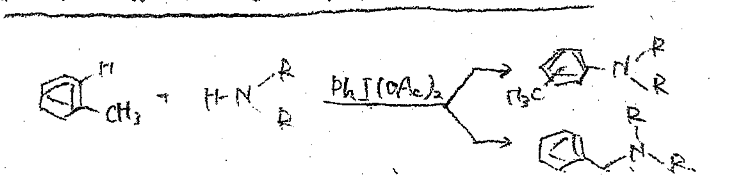
Intermolecular Oxidative C-N Bond Formation under Metal-Free Conditions : Control of Chemoselectivity between Aryl sp² and Benzylic sp³ C-H Bond Imidation

B4 [illegible]　Hyun Jin Kim, Jiyu Kim, Seung Hwan Cho, and Sukbok Chang* (DOI: 10.1021/ja209246c)

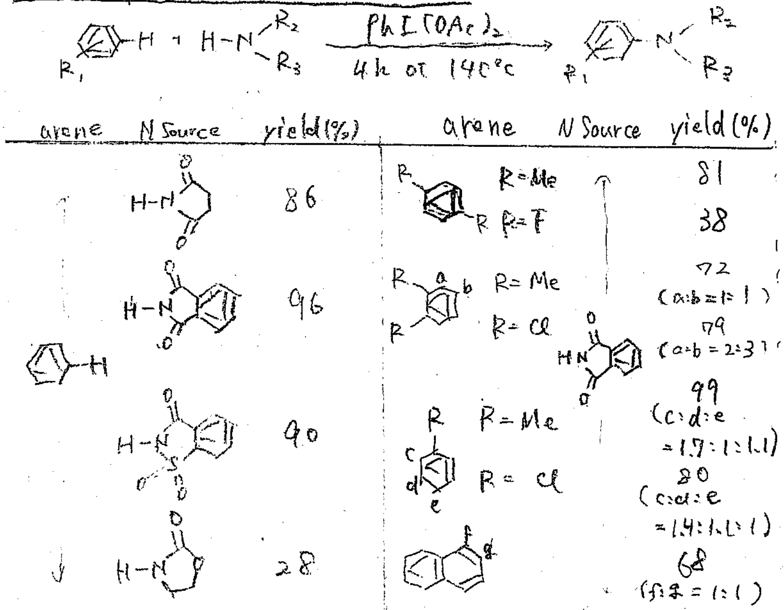
◎ Previous Work　Intramolecular reaction



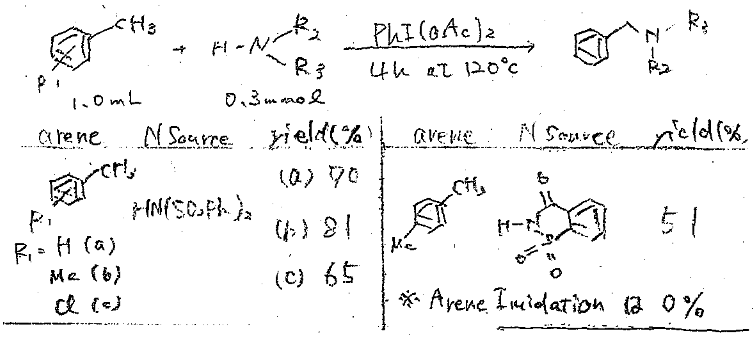
◎ This Work　Intermolecular reaction



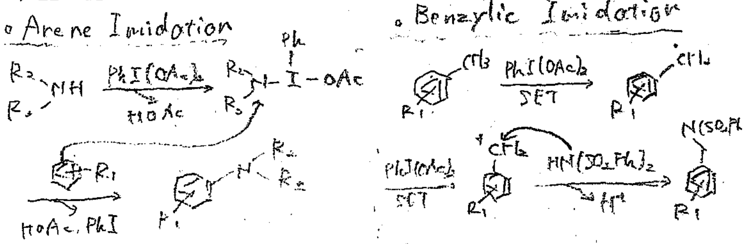
◎ Scope of Arene Imidation



◎ Scope of Benzylic Imidation



◎ Proposed Pass



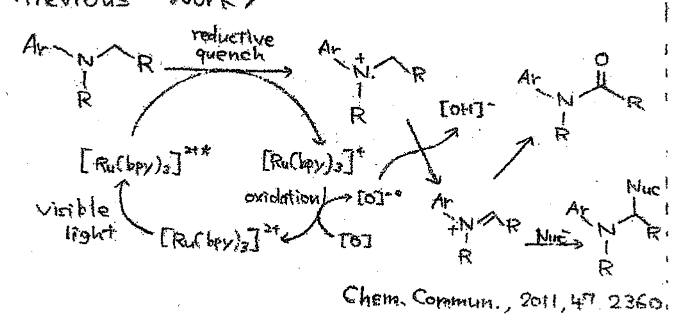
Visible light-induced intramolecular cyclization reactions of diamines: a new strategy to construct tetrahydroimidazoles

Jun Xuan, Ying Cheng, Jing An, Liang-Qiu Lu, Xiao-Xiao Zhang and Wen-Jing Xiao*

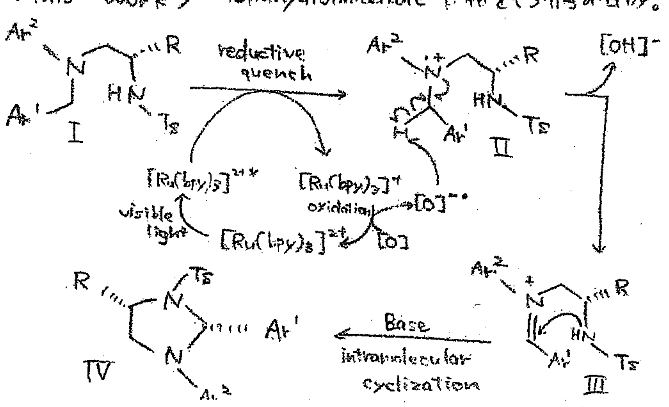
Chem. Commun.　DOI: 10.1039/C1CC12203G

B4 利根紗織

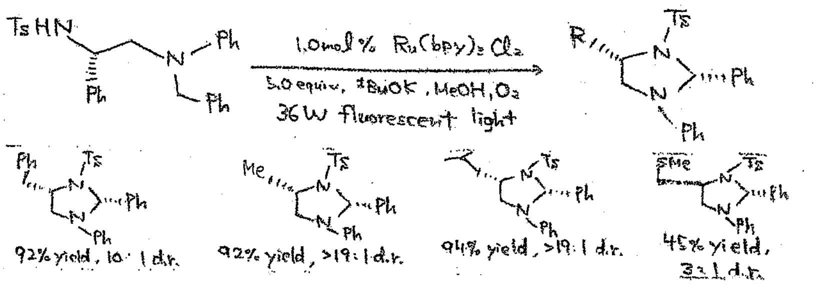
<Previous Work>



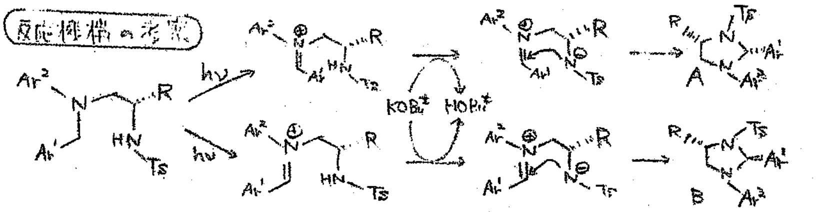
<This Work> tetrahydroimidazole 骨格をもつ分子の合成。



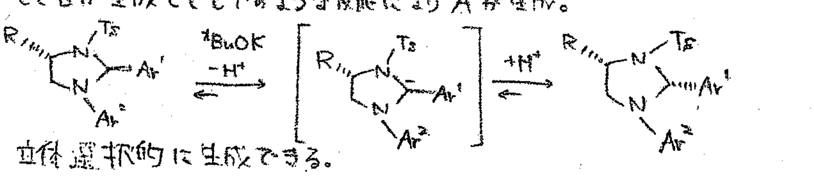
(反応条件の検討)
溶媒 → MeOH や EtOH，塩基 → ᵗBuOK，反応時間 → 48h



(反応機構の考察)



熱力学的に安定な A の方が生成しやすい。
もし B が生成しても下のような反応により A が生成。



立体選択的に生成できる。