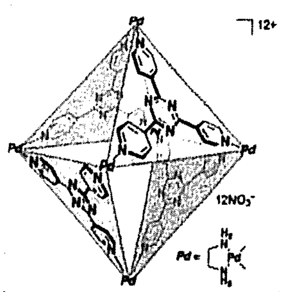
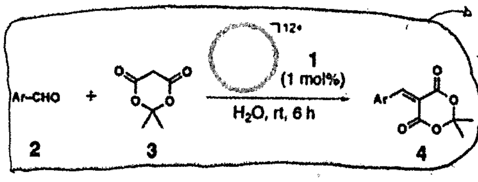
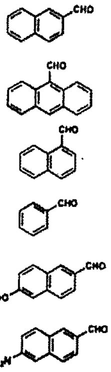
Makoto Fujita et al.	The University of Tokyo (Japan)	***JACS*** (ja2100068f)	Minakata

Cage-Catalyzed Knoevenagel Condensation under Neutral Conditions in Water





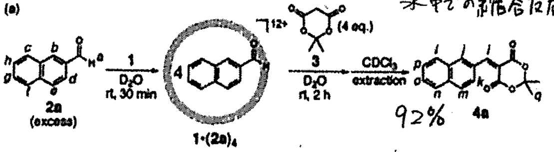


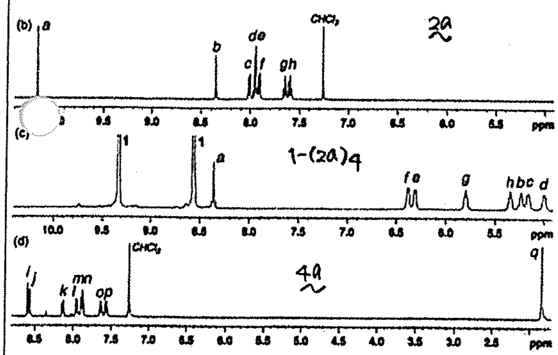
Entry	2		Yield of 4 (%)[b] in 1	without 1
1		2a	96	4
2		2b	63[c]	< 1[c]
3		2c	67[d]	15[d]
4		2d	38	26
5	MeO	2e	96	6
6	Me2N	2f	82	11

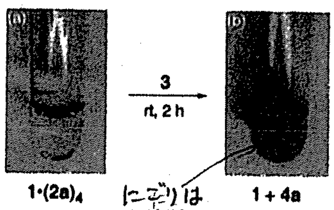
PhCHO と cage との binding が よくない。

{ 1 がないと → 4a は 2%
MeOH中で均一でやっても → 4a は 8%
⇓
ただ溶けているだけでなく、水中での縮合反応を促進

(a)

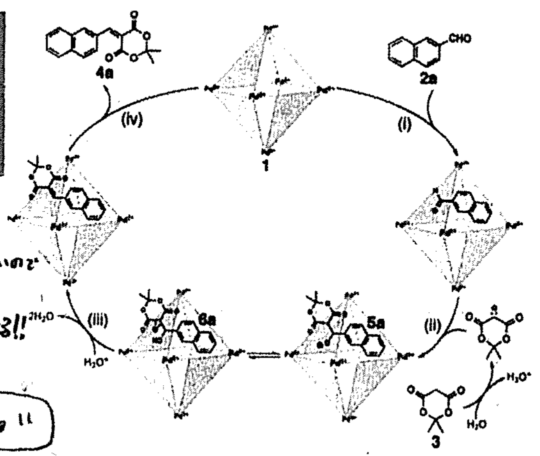






にごりは生成物 4a

4a が大きいので cage と fit しないので中から出てくる ⇒ 触媒化できる!!

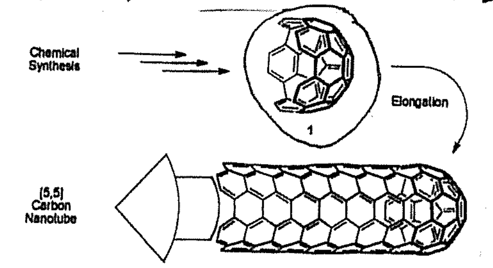


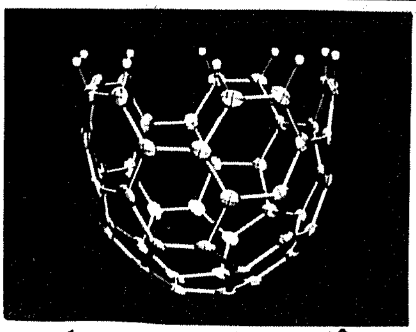
(en)Pd(NO3)2 と Ph–triazine(Ph)(Ph) をまぜて反応しても生成物はできない

Lawrence T. Scott et al.	Boston College, USA	*J. Am. Chem. Soc. ASAP* (doi: 10.1021/ja209461g)	Youhei Takeda

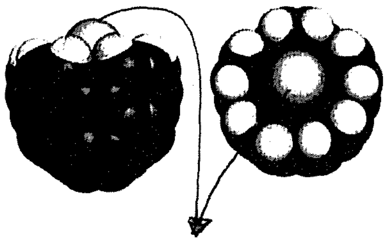
A Short, Rigid, Structurally Pure Carbon Nanotube by Stepwise Chemical Synthesis

◎ 最小のカーボンナノチューブの化学合成



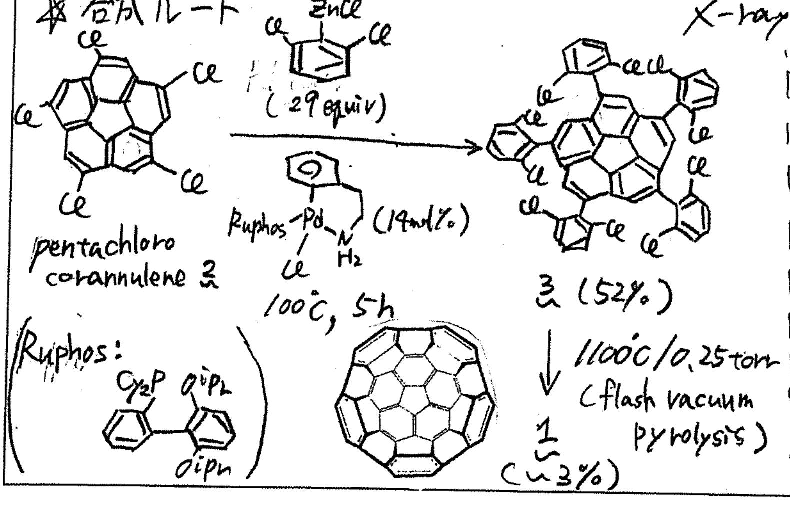


X-ray structures of 1



CS2 is included in 1

※ 合成ルート

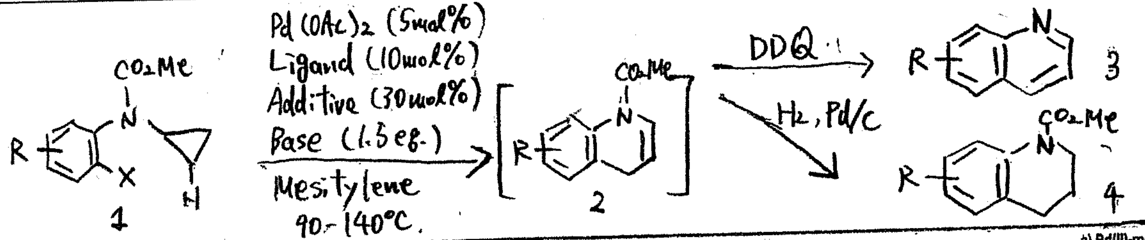


※ Properties of 1

- solubility: sufficient for routine spectroscopic analysis (CH_2Cl_2, $CHCl_3$, C_6H_6, CS_2)
- ^1H NMR: 7.63 ppm (CD_2Cl_2)
- ^{13}C NMR: 154.1, 151.5, 144.7, 137.6, 130.6, 126.4 ppm (CD_2Cl_2)
- UV-vis: λ_{max} 268, 308 nm (CH_2Cl_2) (cf. C_{60} λ_{max} 270, 329 nm)
- appearance: gold color in solution

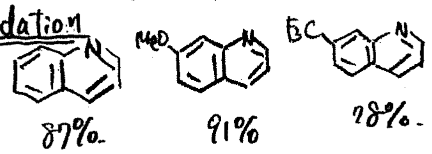
Sophie Rousseaux,* Fagnou Keith	University of Ottawa (Canada)	*Chem. Sci.* **2012**, *3*, 244-248.

Palladium(0)-catalyzed cyclopropane C–H bond functionalization: synthesis of quinoline and tetrahydroquinoline derivatives

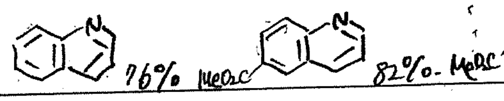


X=Br → Pd(OAc)₂ (5mol%), P(ᵗBu)₂Me·HBF₄ (10mol%), CsOPiv (30mol%), K₃PO₄ (1.5eq.)

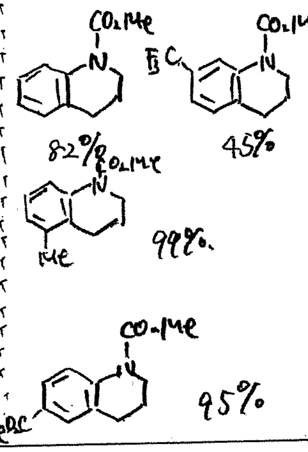
Oxidation

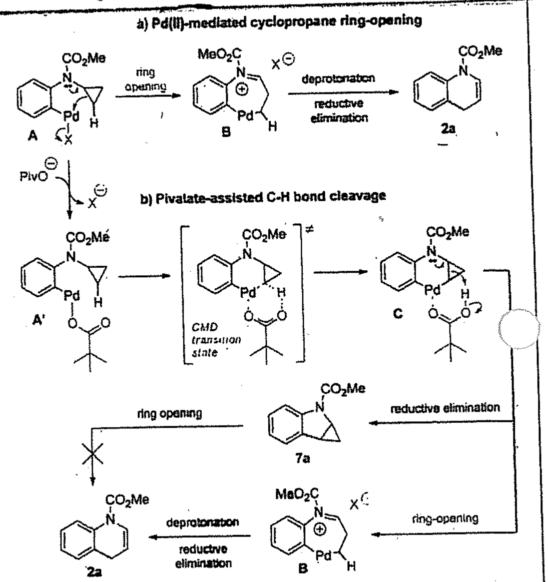


X=Cl → Pd(OAc)₂, PCy₃·HBF₄, PivOH (30mol%), Cs₂CO₃ (1.5eq.)



Reduction





Klaus Müllen et al	Max-Plank-Institut für Polymerforschung	JACS 2011, 133, 10372.	長町

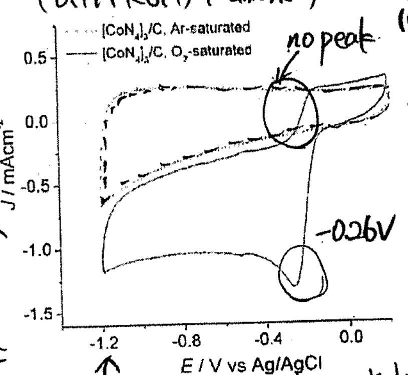
Triangular Trinuclear Metal-N4 Complexes with High Electrocatalytic Activity for Oxygen Reduction

。燃料電池 C: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
A: $H_2 \rightarrow 2H^+ + 2e^-$

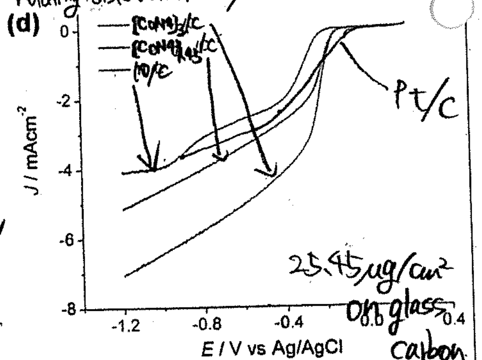
⇒ Cathode は Pt/C が一番良い。
→ 高い / COが電極を不活性化 / ドリフトが起こる etc の問題

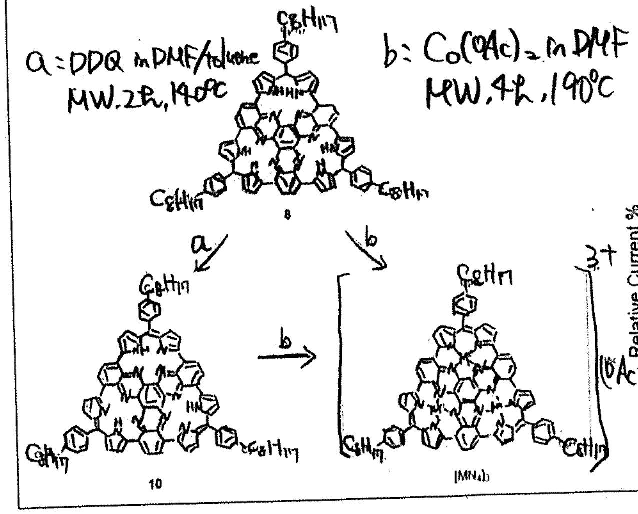
This Work Pt/C にかわる Cathode の開発

(0.1M KOH, 100mV/s)



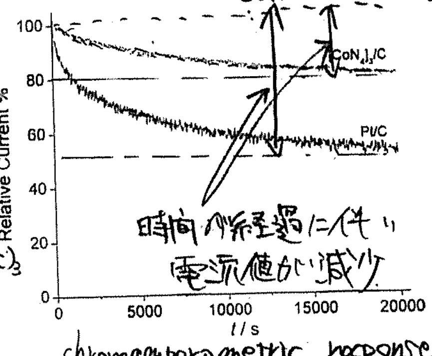
rotating disk voltammetry





電極には pyrolytic graphite で無く Carbon black を使用

- 。リガンドだけでも活性あり。
- 。Co(II)が特によい。(Feもだめ)
- 。Coの含有量で活性能に違い。



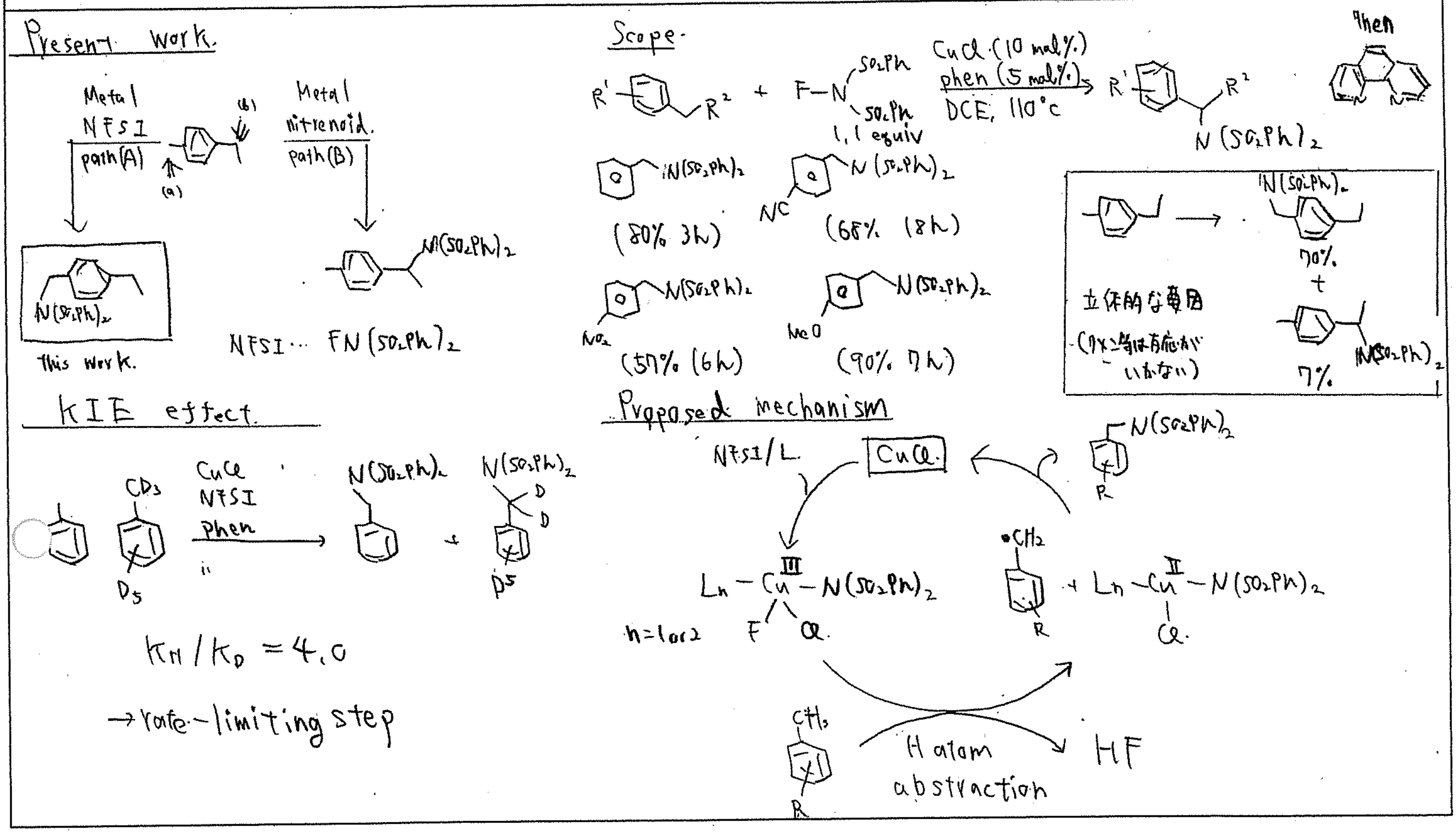
chronoamperometric response

	n	onset potential (V)	J_k ← -0.35Vで (mA/cm²)	durability
[CoN₄]₃/C	3.7	-0.14	9.63	84.0%
10/C	1.8	-0.20	3.00	73.5%
Pt/C	3.9	-0.11	4.44	52.5%

(-0.26V in O₂ saturated 0.1M KOH aq)

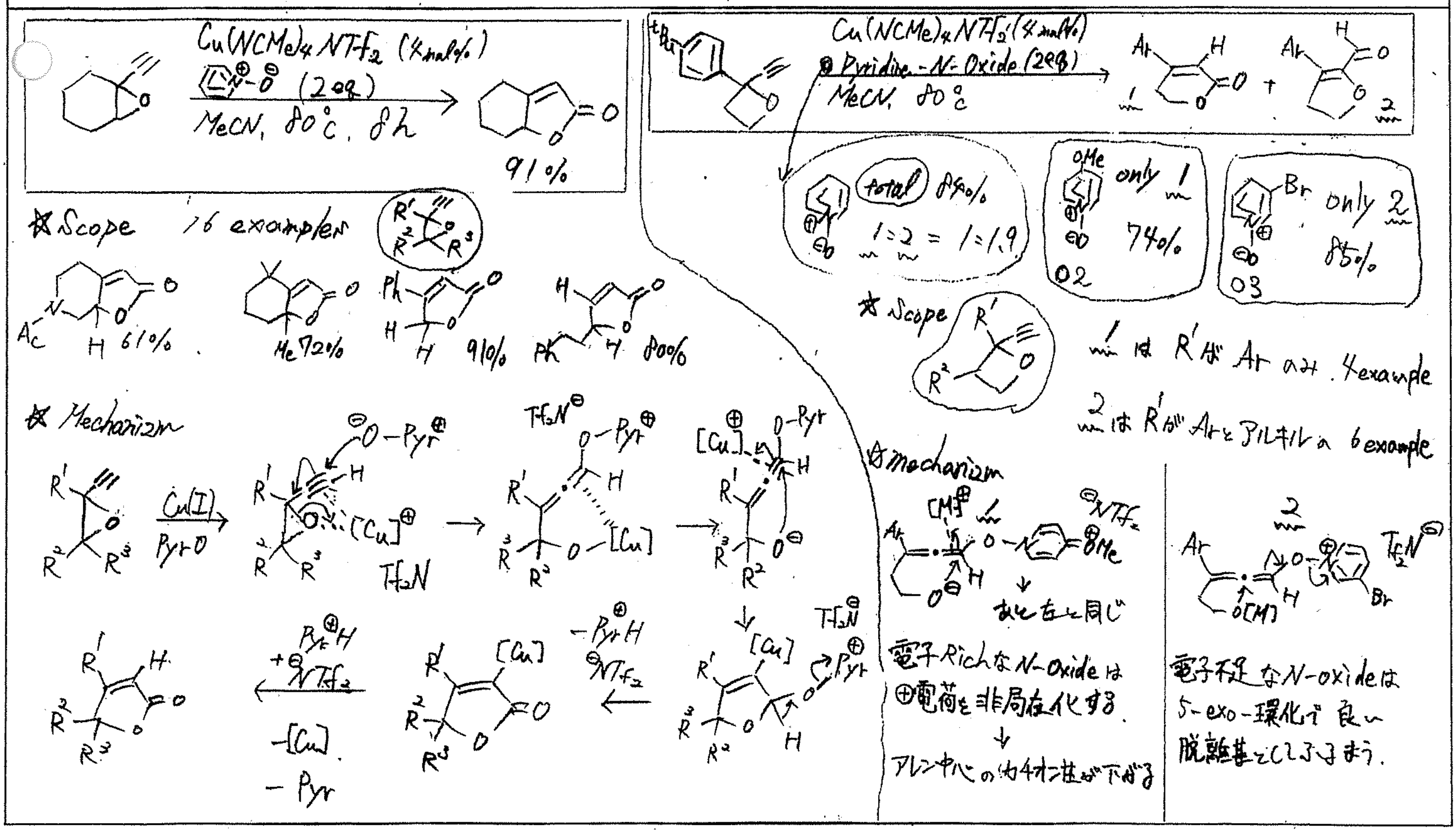
Qun Liu	Northeast Normal University, China	ACIE DOI: anie.201107427	D1 早川純平

Highly Regioselective Copper-Catalyzed Benzylic C-H Amination by *N*-Fluorobenzenesulfonimide



Fabien Gagosz	CNRS / Ecole (France)	DOI:10.1021/ja209866a	okumura

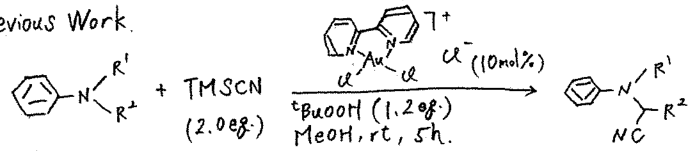
Cu(I)-Catalyzed Oxidative Cyclization of Alkynyl Oxiranes and Oxetanes



Chengjian Zhu et al.	Nanjing University, China	ACIE.10.1002/anie.201107605	三谷由起

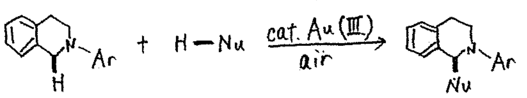
A Highly Efficient Gold-Catalyzed Oxidative C-C Coupling from C-H Bonds Using Air as Oxidant

Previous Work



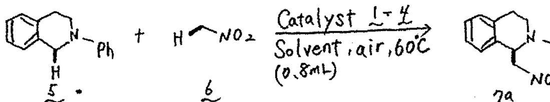
92-98% yields.

Present Work



No additional oxidant
No waste product
Short reaction time
Up to 95% yield

Table 1. Optimization of the aerobic oxidative C-C coupling reaction of amines with nitromethane



Entry	Catalyst (mol%)	Solvent	t [h]	Yield [%]
1	1a (6)	MeOH	6	48
2	1b (6)	MeOH	6	71
3	2a (6)	MeOH	6	56
4	2b (6)	MeOH	6	52
5	3 (6)	MeOH	6	45
6	4 (6)	MeOH	6	47
7	—	MeOH	6	trace
8	1b (6)	MeNO₂	3	82
9[a]	1b (6)	MeNO₂	3	86
10[a]	1b (3)	MeNO₂	3	86

a) 100μL MeOH was added.

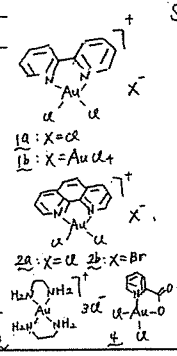
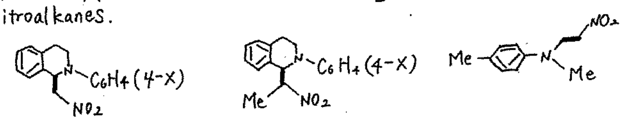
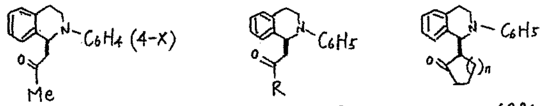


Table 2 Aerobic oxidative C-C coupling reaction of amines with nitroalkanes.



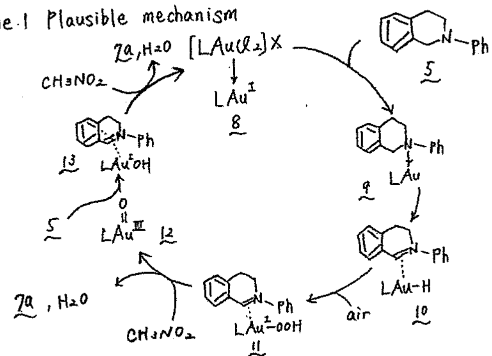
X	Yield	X	Yield		
Me	90%	H	90%		52%
OMe	87%	Me	91%		
Cl	91%	OMe	85%		
Br	88%	Br	90%		

Table 3 Aerobic oxidative C-C coupling of amines with ketones.



X	Yield	R	Yield	n	Yield
H	83%	Ph	81%	1	69%
Me	75%	nBu	80%	2	77%
OMe	78%	iBu	76%		
Cl	86%	ᵗBu	65%		
Br	80%				

Scheme 1 Plausible mechanism

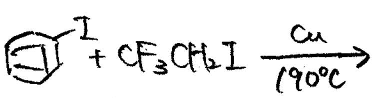


(L=2,2'-bipyridi...)

Jinbo Hu et al.	Chinese Academy of Science (Chine)	*Angew. Chem. Int. Ed.* 10.1002/anie.201106742	Yuki Ikeda

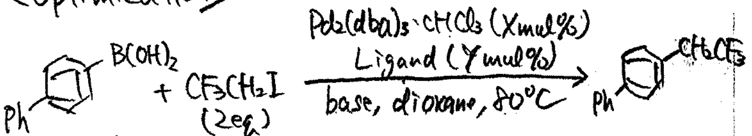
Palladium-Catalyzed 2,2,2-Trifluoroethylation of Organoboronic Acids and Enters

<Previous Work> stoichiometric process



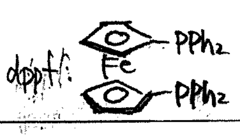
V.C.R. McLoughlin et al. Tetrahedron (1969)

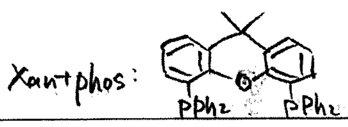
<Optimization>



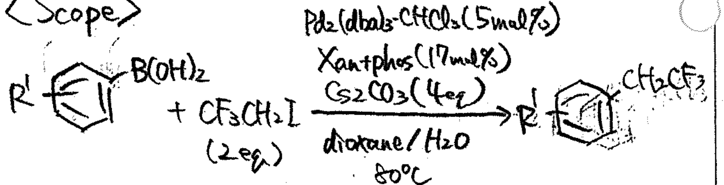
entry	Ligand	Base	H₂O (eq.)	Yield (%)
1[a]	dppf	K₃PO₄	—	4
2[a]	Xantphos	K₃PO₄	—	50
3[a]	Xantphos	Cs₂CO₃	—	59
4[a]	Xantphos	Cs₂CO₃	18	78
5[b]	Xantphos	Cs₂CO₃	18	92(81)

a: X=2.5, Y=10, Base(2.5eq.), b: X=5, Y=17, Base(4eq.)

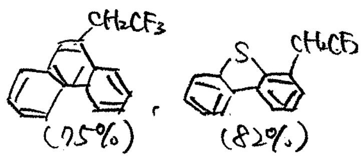




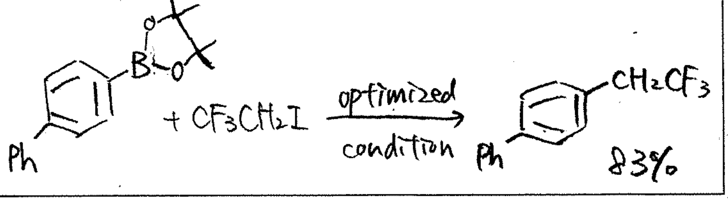
<Scope>



R = 2-NO₂ (80%), 4-CN (83%), 4-CO₂Me (71%), 4-COMe (82%),
4-CHO (70%), 4-tBu (78%), 4-OBn (75%), 4-OPh (81%),
3-NH₂ (56%), 3,5-Cl (78%),



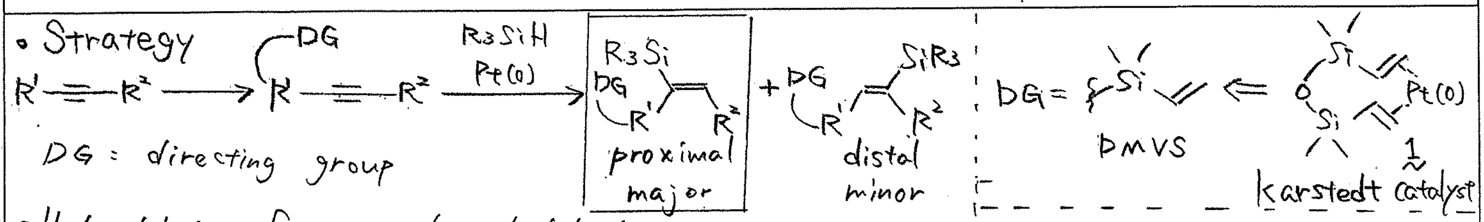
<Trifluoroethylation of aryl boronic ester>



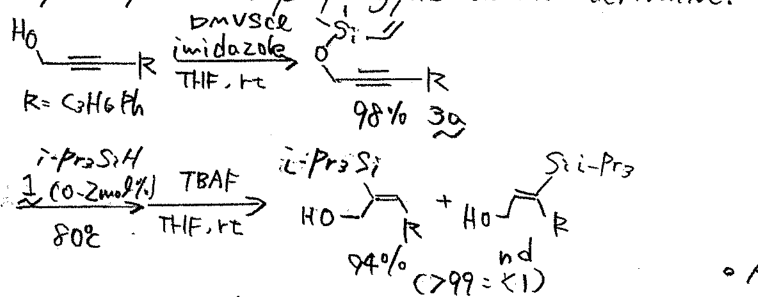
Tomooka, K. et al	Kyushu University (Japan)	JACS. 10.1021/ja209553f	M1 Kawai

Directing Group-Controlled Hydrosilylation: Regioselective Functionalization of Alkyne

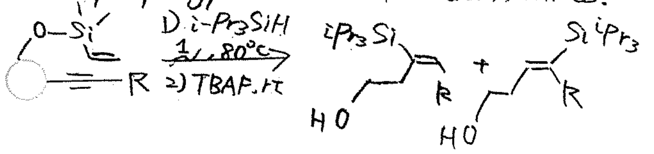
• Strategy



• Hydrosilylation of propargylic alcohol derivative.



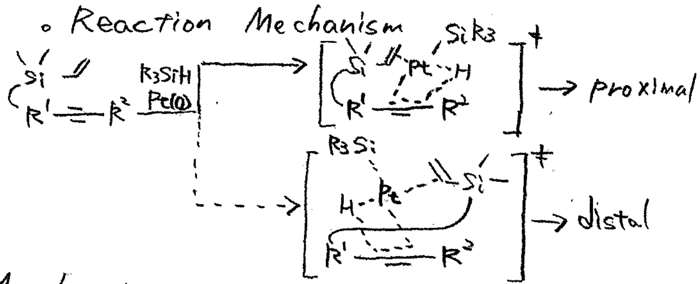
• homopropargylic alcohol derivatives.



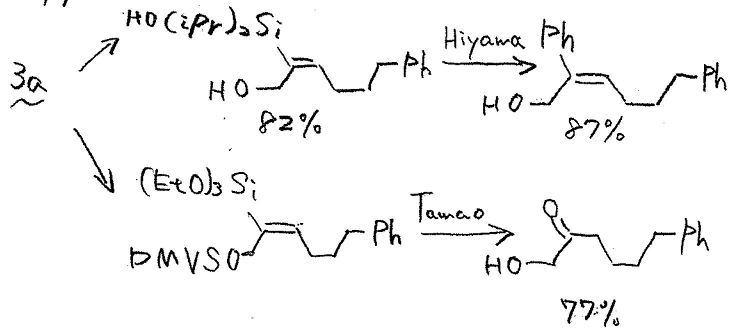
R = C3H6Ph   98%   nd

R = H   79%   nd

• Reaction Mechanism



• Applications



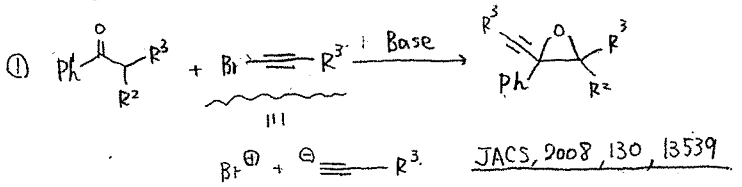
V. Gevorgyan	University of Illinois, USA	*ACIE*, DOI : 10.1002 / anie. 201106969	M1 錦織

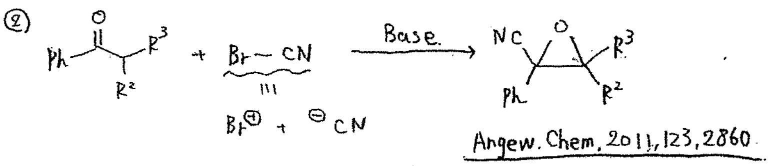
One-Pot Arylative Epoxidation of Ketones by Employing Amphoteric Bromoperfluoroarenes

Diverse reactivity of PFPBr

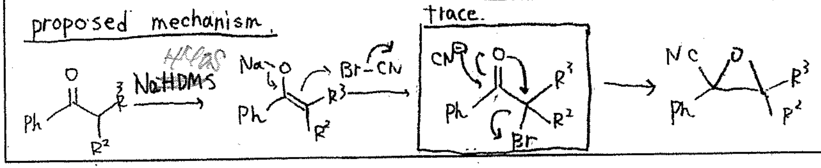
C_6F_5-Br ≡
- I. $C_6F_5^{\ominus}$ via metallation {ex. oxidative addition to Pd⁰ / alkyl Lithium reagent.
- II. $Br^{\oplus}$ via bromide abstraction {ex $[C_pFe(CO)_2]^{\ominus}$
- III. $Br^{\oplus}$ and $C_6F_5^{\ominus}$ (this report)

Previous Work

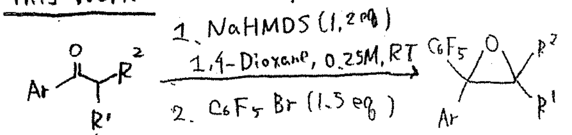




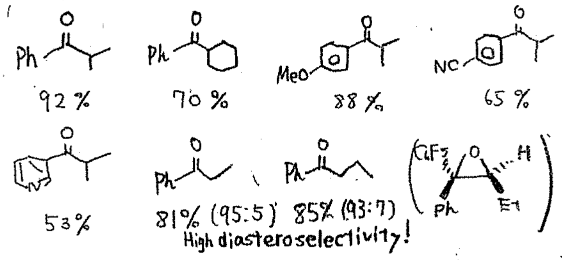
proposed mechanism.



This Work

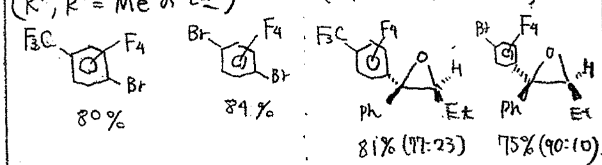


• Scope of ketones (18 examples)



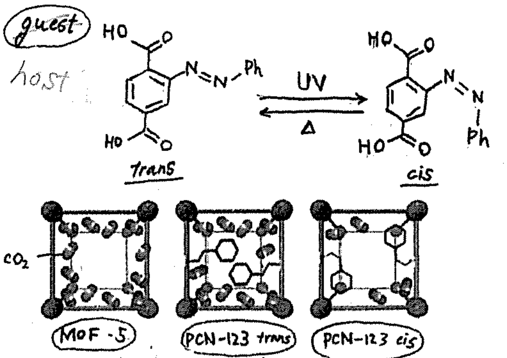
• Scope of bromopolyfluoroarenes (7 examples)

(R¹, R² = Me のとき)   (R¹, R² = H, Et のとき)



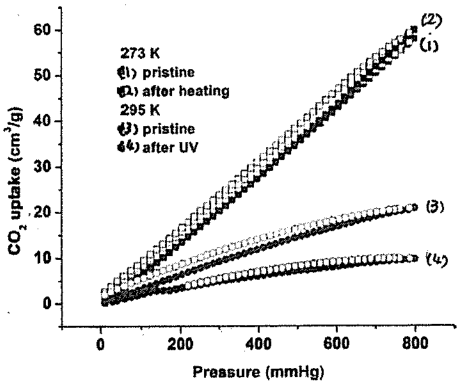
Hong-Cai Zhou	Texas A&M University (U.S.)	DOI: 10.1021/ja209197f	M1 矢野

Reversible Alternation of CO_2 Adsorption upon Photochemical or Thermal Treatment in a Metal–Organic Framework



MOF … Metal-Organic Framework
PCN … Porous Coordination Network

$Zn(NO_3)_2 \cdot 6H_2O$ + guest



0°Cで測定 (1)
↓
室温で測定 (3)

熱運動がCO_2と骨格の相互作用に打ち勝つ

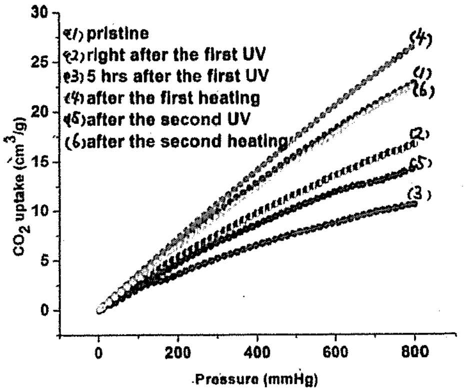
↓ UV照射
室温で測定 (4)
↓ trans化
0°Cで測定 (2)

(1)と(2)がほぼ同じことから PCN-123の骨格はアゾベンゼンの骨格の変化に対して安定である(破壊されない)

77KでのN₂吸着から孔径をみつもった。(下図)

もとのサンプルと、UV照射後加熱して再生したものの孔径の分布はほぼ同じ

孔径の分布の変化はアゾベンゼンの異性化による

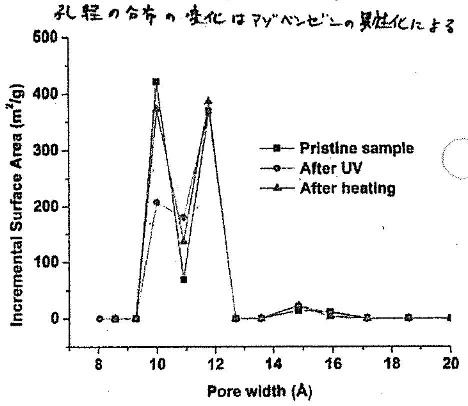


UV照射前

$22.9\ cm^3 g^{-1}$ at 1bar (1)
↓ 1h UV照射
$16.8\ cm^3 g^{-1}$ (2)
↓ 5h
$10.5\ cm^3 g^{-1}$ (3)
↓ 遮光して60°Cで22h加熱
$26.4\ cm^3 g^{-1}$ (4)
↓ 1.5h UV照射
$14.2\ cm^3 g^{-1}$ (5)
↓ □の条件で加熱
$22.4\ cm^3 g^{-1}$ (6)

(2) → (3)
UV照射に対して応答が速い
⇧ アゾベンゼンの異性化が速い

(4)が(1)より大きい。
合成の段階で(1)のアゾベンゼンはtransがほとんどだがcisも含んでいる。

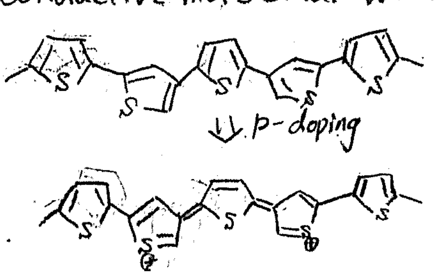


Thomas J. J. Müller	Heinrich-Heine-Universität Düsseldorf (Germany)	ChemComm 10.1039/c2cc17548g	B4 岡崎

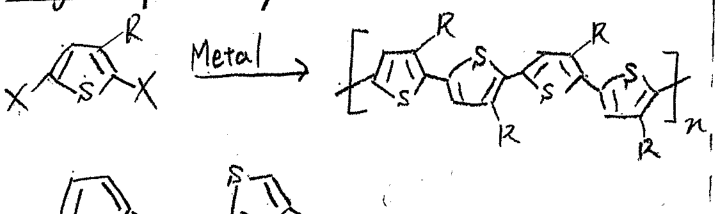
Rapid consective three-component coupling-Fiesselmann synthesis of luminescent 2,4-disubstituted thiophenes and oligothiophenes

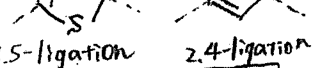
Application of thiophene

- hole transport materials in organic LEDs, field-effect-transistors and photovoltaics.
- nanostructured models of one-dimensional conductive molecular wires



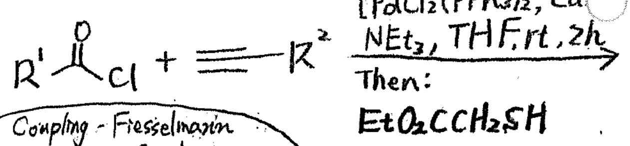
Oligothiophene syntheses



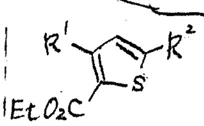


2,5-ligation major
2,4-ligation minor

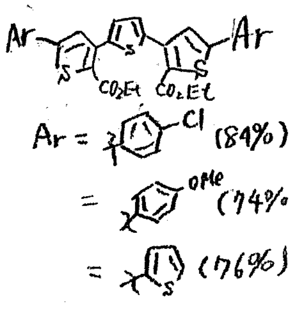
This work



Coupling-Fiesselmann Thiophene Synthesis in a one pot fashion under mild reaction conditions!

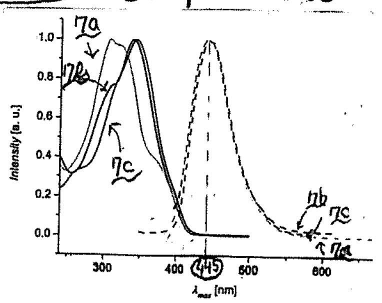


15 examples (32-97%)



Ar = (84%) 7a
= (74%) 7b
= (76%) 7c

UV spectra of 7



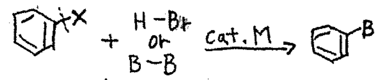
- absorption (solid lines)
- emission (dashed lines)

⇒ ☆ strong blue luminescence (solution)
☆ $\Phi_f = 8 \sim 11\%$ high fluorescence efficiency

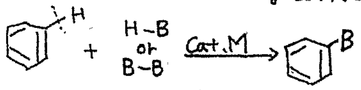
Tobisu, M.; Chatani, N. et al	Osaka University, Japan	JACS. 10.1021/ja2095975	B4 Hisakuni

Rhodium(I)-Catalyzed Borylation of Nitriles through the Cleavage of Carbon—Cyano Bonds

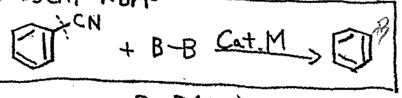
◦ Catalytic Borylation Reactions

① 

Zhu, W.; Ma, D. Org. Lett. 2005, 8, 261

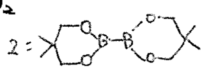
② 

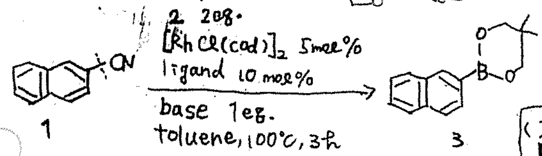
Chem. Rev. 2010, 110, 890

③ Present Work


B = B(OR)$_2$

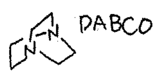
<optimization>

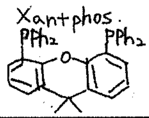




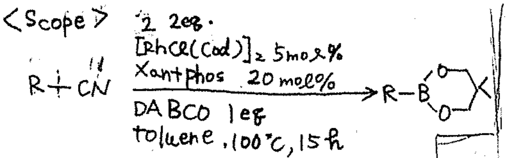
( )は反応時間を15h, ligand 20mol%

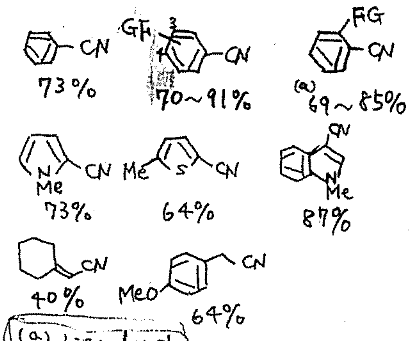
entry	base	ligand	GC yield
1	none	none	4
2	DABCO	none	10
3	DABCO	PPh$_3$	55(57)
4	DABCO	dppb	51
⑤	DABCO	Xantphos	57(86)





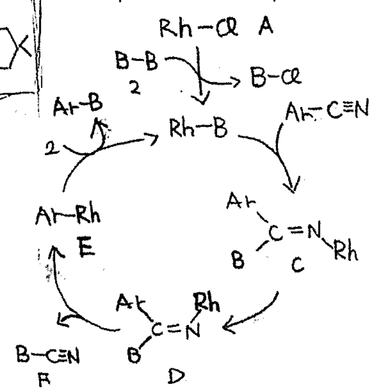
<Scope>





(a) Ligand : PPh$_3$

<Proposed Pathway>



<Synthetic Application>