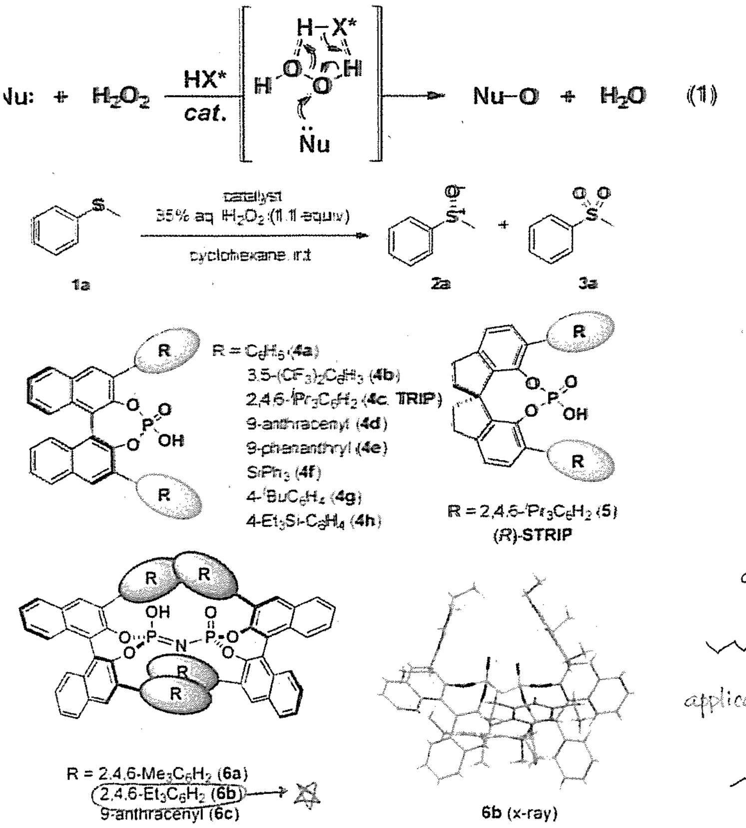
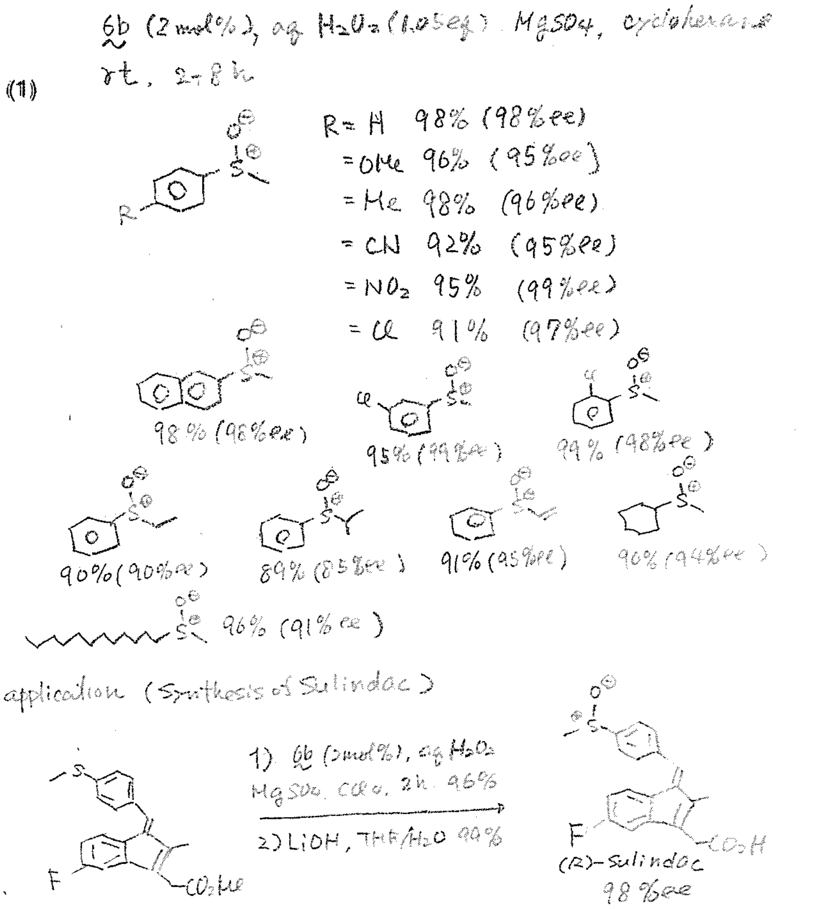
Benjamin List et al.	Max-Plank-Institute (Germany)	***JACS*** (ja3035637)	Minakata

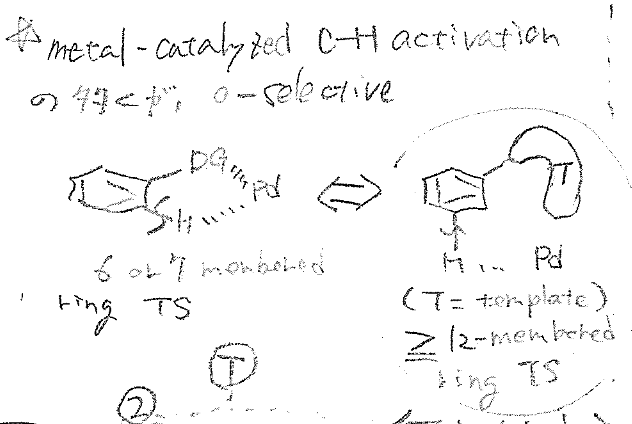
Activation of H_2O_2 by Chiral Confined Brønsted Acids: A Highly Enantioselective Catalytic Sulfoxidation

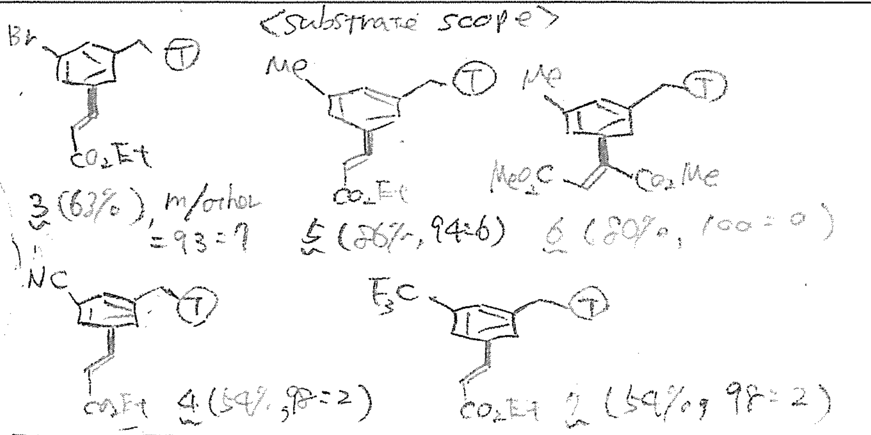


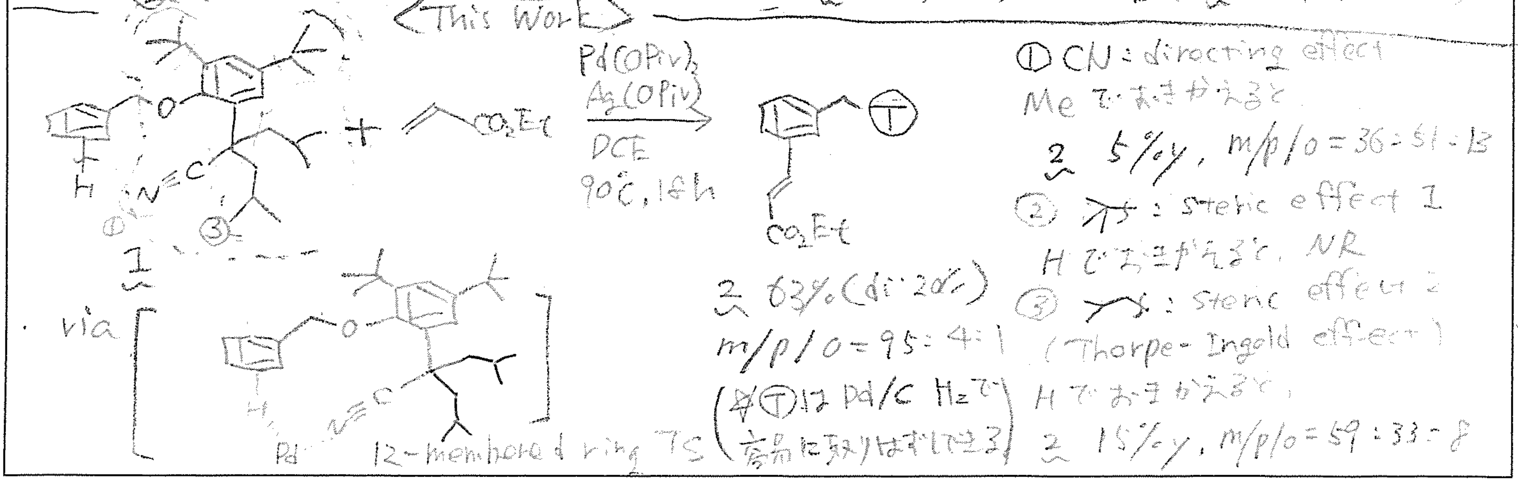


Jin-Quan Yu	The Scripps Research Institute, USA	*Nature* **2012**, *486*, 518.	Youhei Takeda

Activation of remote *meta*-C–H bonds assisted by an end-on template

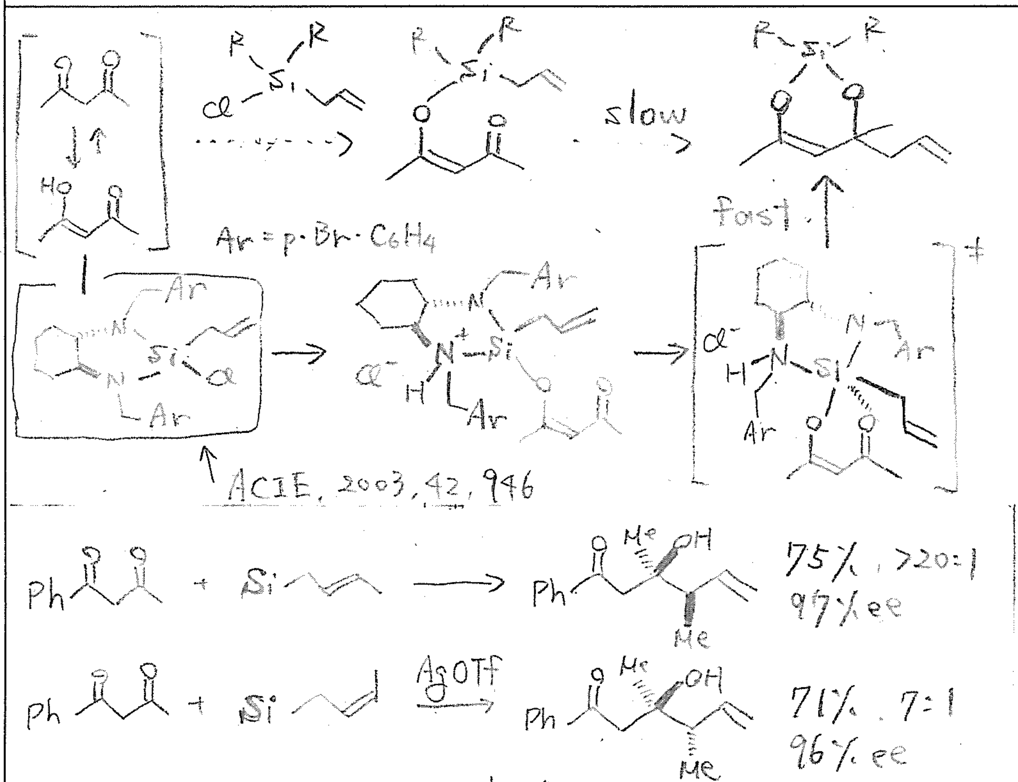






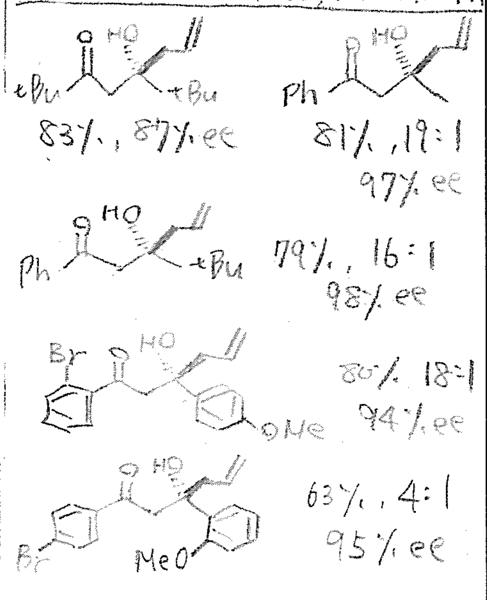
James L. Leighton	Columbia Univ. (USA)	*Nature*, 10.1038/nature11189	清川

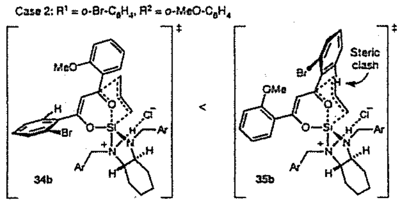
Direct and highly regioselective and enantioselective allylation of β-diketones



Si上のClをOTfに変換して
配位子交換の速さをup

conditions: $CHCl_3$, 23°C, 13-17h

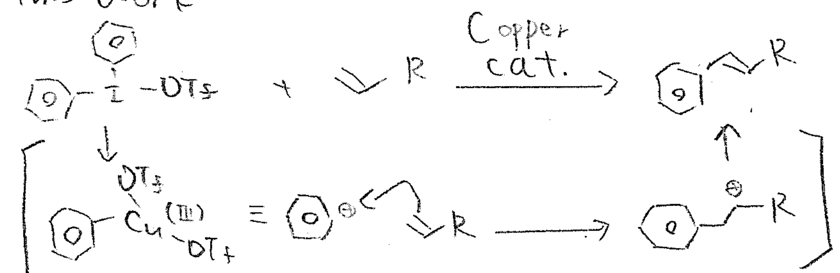




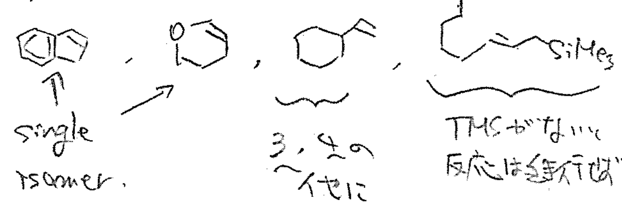
Gaunt, M. J. et al	University of Cambridge	JACS ja3039807	Nagamachi

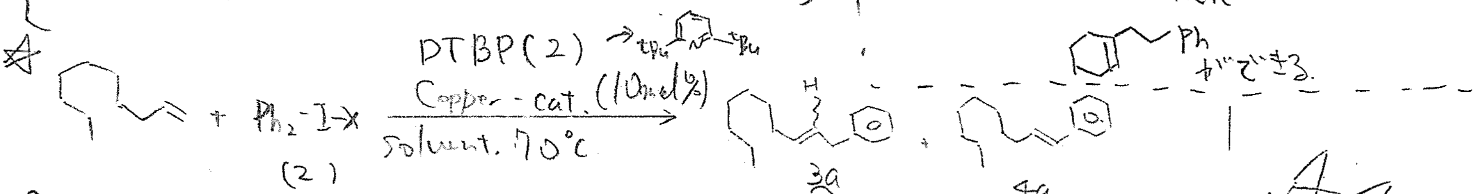
Copper-Catalyzed Alkene Arylation with Diaryliodonium Salts

This Work



Scope of Alkene
yield : 19 ~ 92%

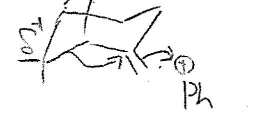




Cat. : $Cu(OTf)_2$, X = OTf, sol. CH_2Cl_2 が最適 (72%, 3a/4a = 3.5/1)

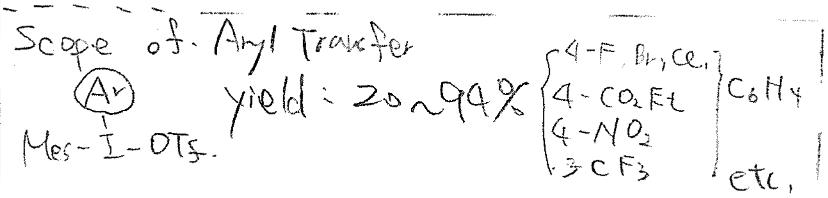
☆ Cuは(I)でも(II)でも反応は進行 (39%, 3a/4a = 1.8/1)

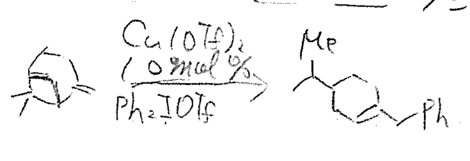
110°Cまで昇温すれば Cuなしでも反応は進行



カチオン発生とラジカルの可能性どちらかは不明

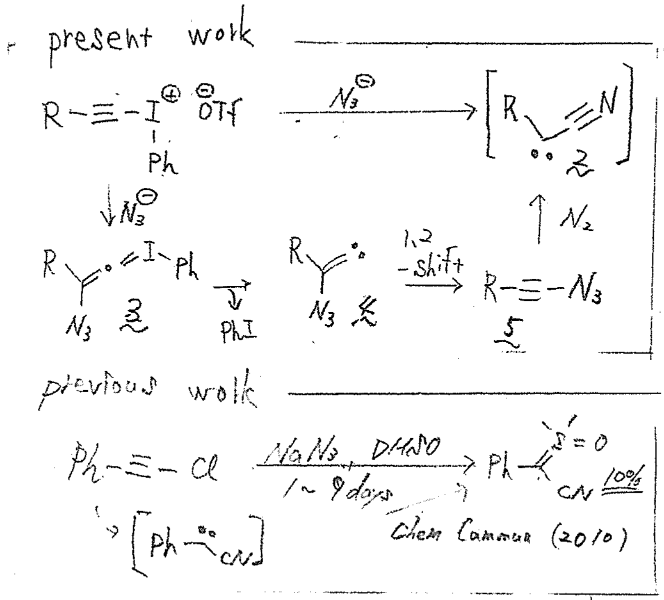
Scope of Aryl Transfer

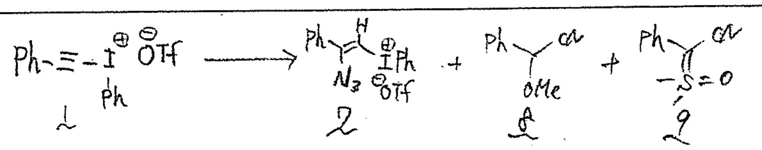




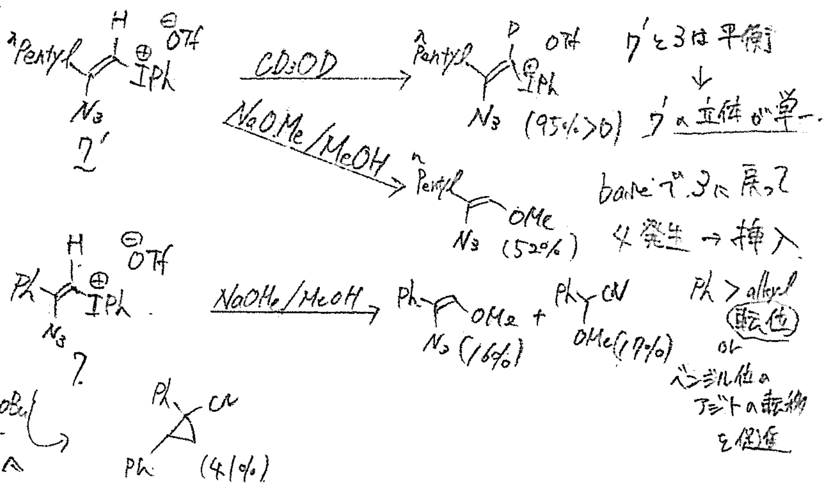
Mitchell P. Croatt	University of North Carolina (USA)	*ACIE* DOI:10.1021/anie.201203062	Okumura

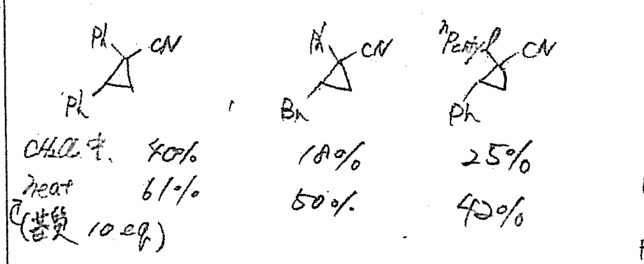
Reactions of Hypervalent Iodonium Alkynyl Triflates with Azides: Generation of Cyanocarbenes





・CH_2Cl_2/H_2O (1:1), 25°C, NaN_3 → 7 (39%) → 最初の段階を示唆.
・MeOH, 0°C NaN_3 → 8 (75%) → シアノカルベンのO-H挿入.
・Acetone, -40°C, NBu_4N_3 → 7 (42%) → C=Oへは挿入しない.
・DMSO. rt. NBu_4N_3 → 9 (27%) → Chem Commun よりは、カルベン発生効率高い

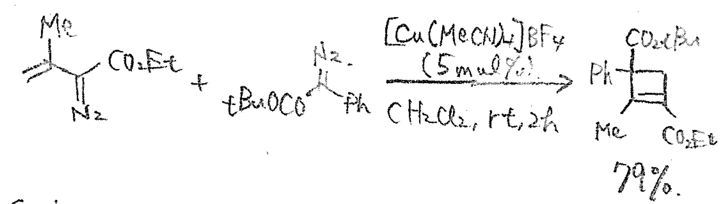




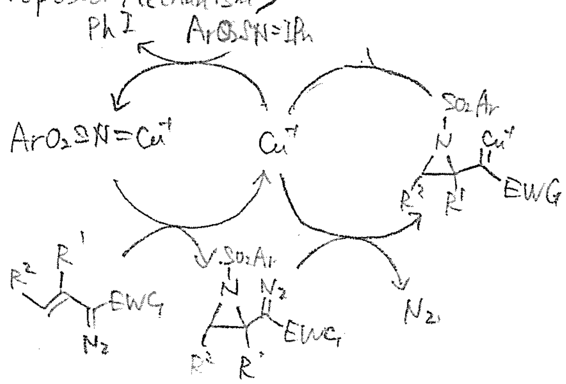
José Barluenga, Luis A. López et al	Universidad de Oviedo (Spain)	Chem. Eur. J 10.1002/chem.201200998	池田

Copper(I)-catalyzed [3+1] Cycloaddition of Alkenyldiazoacetates and Iminoiodinanes: Easy Access to Substituted 2-Azetines.

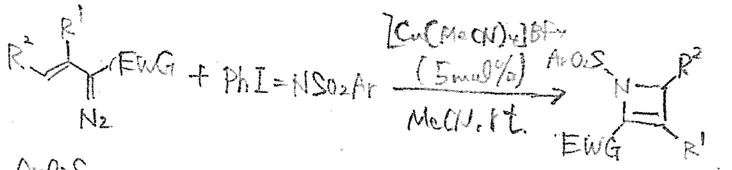
<Previous Work>

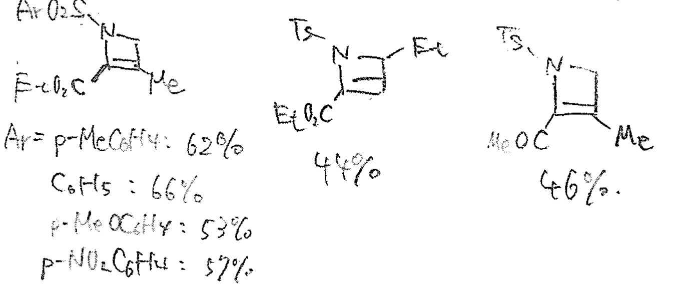


<Proposed Mechanism>

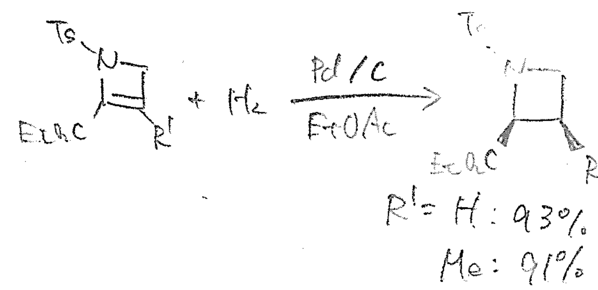


<This Work>





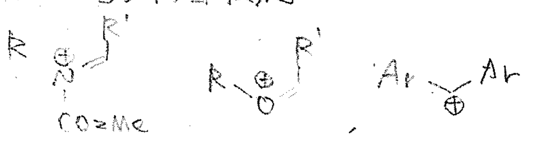
<Synthesis of Azetizine>



Jun-ichi Yoshida	Kyoto University (Japan)	anie.201202788	M2 Kawai

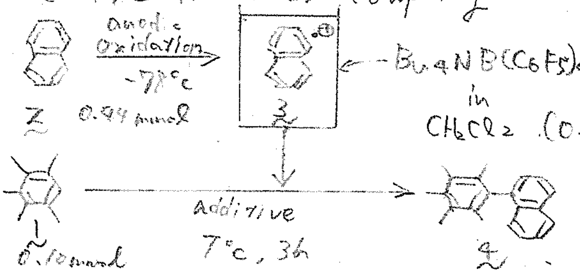
Metal- and Chemical-Oxidant-Free C-H/C-H Cross-Coupling of Aromatic Compounds: The Use of Radical-Cation Pools

・Cation-pool method
低温電子移動反応



イミニウムイオン、オキソニウムイオン、ジアリールカルベニウムイオンの発生・蓄積が達成されている。

・C-H/C-H cross-coupling

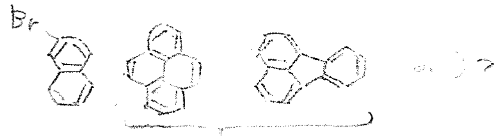


T [°C]	Additive	Yield of 4 [%]	Recovered 1 [%]
-40	-	11	40
-78		33	55
-90		27	52
-90	DME (0.3mL)	91	-

2は過剰量必要 → 系中で2と3から naphthalene dimer のラジカルカチオンが形成され、1と3の酸化反応における酸化剤として働く。

・additiveの効果
低温中での3の溶解性を高めている。

・Scope　10 examples　36〜87%
・Ar¹H（1に対応）
ベンゼン類、インドール類、ベンゾチオフェン誘導体
電子不足のものは低収率、ヨウ素を含むものもok
・Ar²H（2に対応）



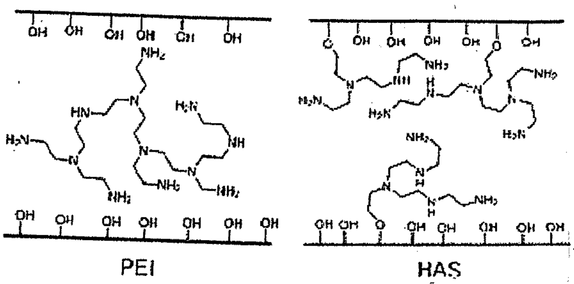
Bu4NPF6を使ってもよく進行

・regioselectivity
DFT計算により Ar¹HのHOMOの軌道係数と Ar²Hのスピン密度を算出し、位置選択性について考察している。

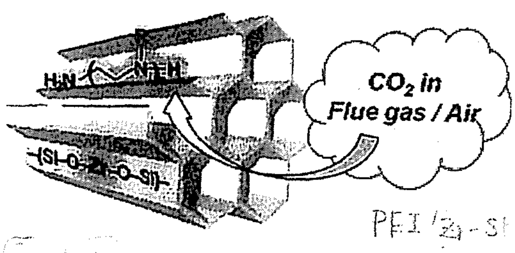
C.W.Jones et al.	Georgia University(USA)	*JACS.* : ja303136e	M2 錦織

Dramatic Enhancement of CO_2 Uptake by Poly(ethyleneimine) Using Zirconosilicate Supports

☆ CO_2 固体吸着材の開発
最近特に多いのが silica-supported amines.



・This Work



PEI/Zr-SBA-15

Zr ルイス酸 ... 空間的に分離した状態 ...
PEI ...

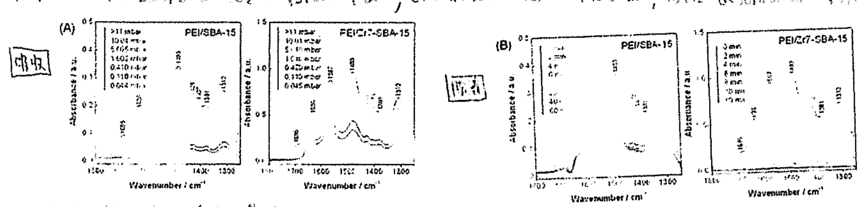
(Synthesis)（合成法はそれぞれの段階で報告あり）
P123 + ZrOCl2・8H2O + TEOS →(40°C, 1day) → Zr-SBA 15
（Zrは[illegible]）

Zr SBA + PEI →(Methanol, 1day) →(evaporation) PEI/Zr-SBA 15.

Adsorbent	Zr/Si[a] gel	Zr/Si[a] product	PEI loading[b] (wt%)	Amine content (mmol N/g)	without PEI S_{BET}[c] (m^2/g)	without PEI V_{total}[d] (cm^3/g)	without PEI d_p[e] (nm)	with PEI S_{BET}[c] (m^2/g)	with PEI V_{total}[d] (cm^3/g)	with PEI d_p[e] (nm)	Occupancy rate[f] (%)	CO_2 adsorption[g] 400 ppm (mmol CO_2/g)	CO_2 adsorption[g] 10% (mmol CO_2/g)
PEI/SBA-15	-	-	30.8	7.40	683	1.19	8.5	242	0.639	7.3	35	0.19	0.65
PEI/Zr4-SBA-15	0.05	0.038	33.0	7.92	642	1.08	8.6	205	0.460	7.3	43	0.64	1.34
PEI/Zr7-SBA-15	0.10	0.070	34.7	8.33	647	1.23	9.5	230	0.613	7.8	41	0.85	1.56
PEI/Zr11-SBA-15	0.15	0.109	33.1	7.95	601	0.692	7.0	101	0.179	5.8	67	0.83	1.41
PEI/Zr14-SBA-15	0.20	0.138	34.5	8.28	510	0.395	4.4	<1.0	<0.01	N.D.[h]	124	0.26	0.24

[a]Determined by elemental analysis. [b]Determined by TGA. [c]Calculated from the adsorption branch of the N_2 isotherm. [d]Values at $P/P_0 = 0.99$. [e]Estimated by the BdB−FHH (Frenkel−Halsey−Hill-modified Broekhoff−de Boer) method. [f]Defined by the equation [occupancy rate (%)] = [calculated aminopolymer volume ($cm^3_{polymer}/g_{SiO_2}$)]/[V_{total} of bare adsorbent (cm^3/g)] × 100%, assuming a PEI density of 1.07 cm^3/g. [g]Measured at 25 °C under dry conditions (adsorption time 12 h). [h]N.D. = not determined.

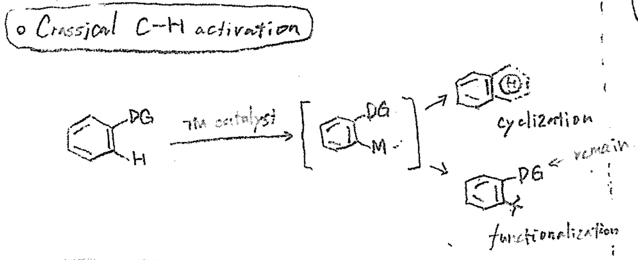
・FT-IR（adsorbed CO_2: 1310cm⁻¹付近, CH_2 deformation 1430cm⁻¹, NH_2 deformation 1570cm⁻¹）

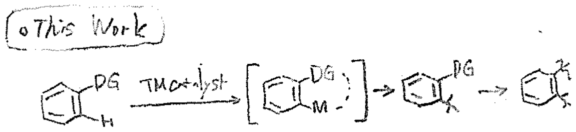


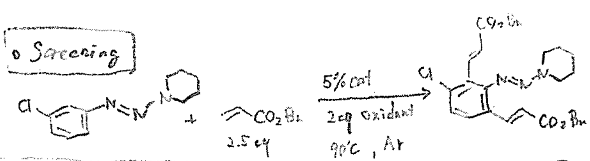
・[illegible]（110°C）
/Zr7-SBA-15 ... 吸脱着を4回繰り返しても変わらない
... /SBA ...

Huang, Y. *et al.*	Peking University (China)	ACIE anie.201203230	M2 矢野

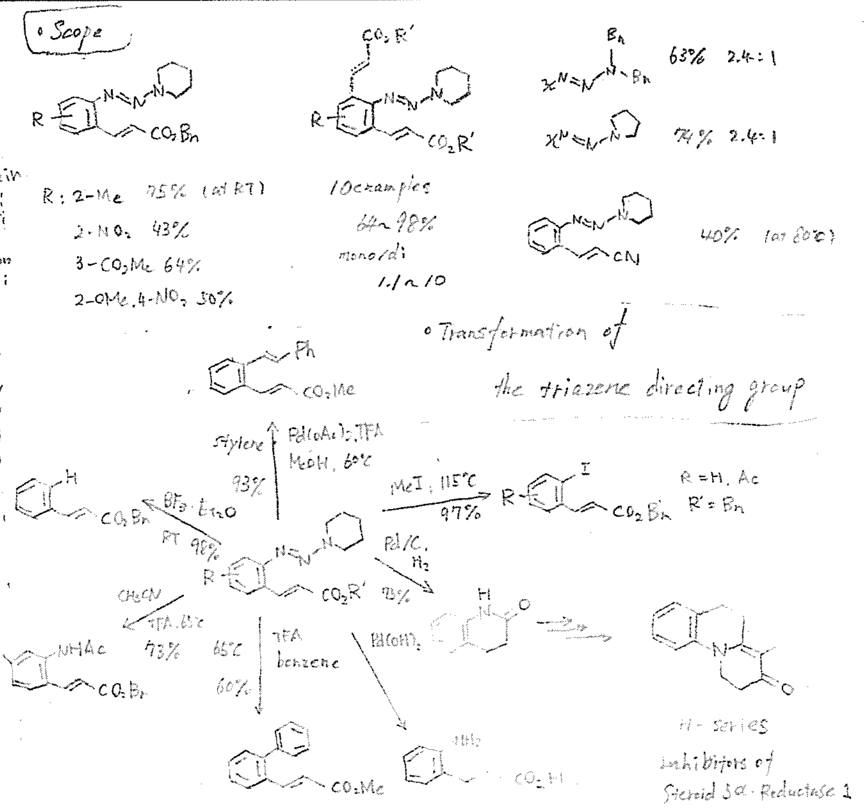
Rhodium(III)-Catalyzed C–H Activation of Arenes Using a Versatile and Removable Triazene Directing Group





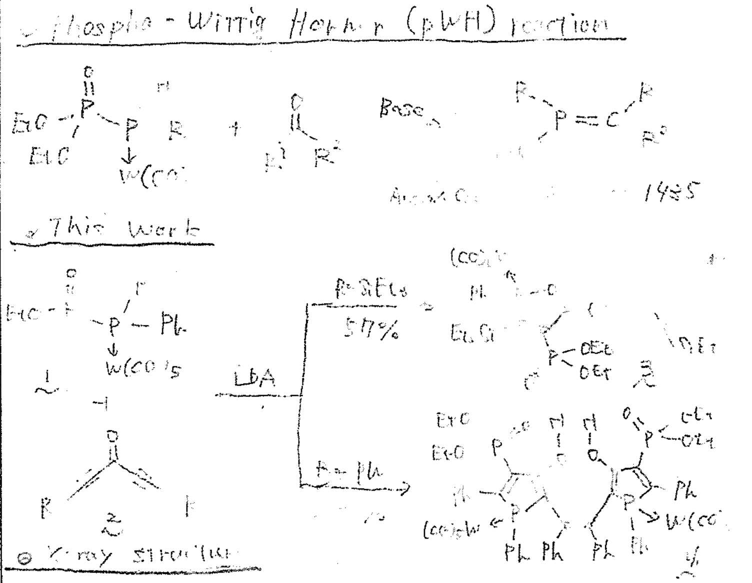


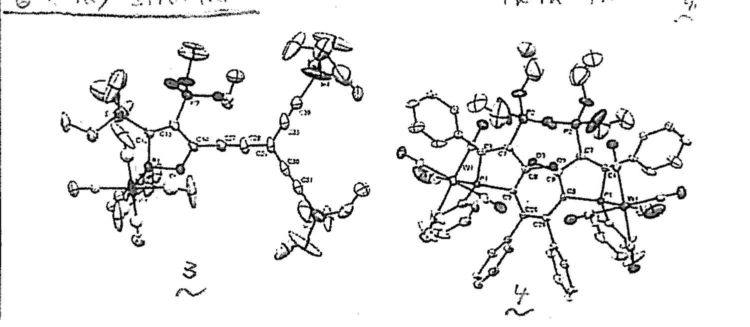
solvent	Catalyst	Oxidant	Yield (mono/di) [%]
toluene	$PdCl_2$	Ag_2CO_3	—
MeOH	$[\{Cp^*RhCl_2\}_2]$	$Cu(OAc)_2 \cdot H_2O$	43:27 (80°C)
MeOH	$[\{Cp^*RhCl_2\}_2]$	$Cu(OAc)_2 \cdot H_2O$	63:31
EtOH	$[\{Cp^*RhCl_2\}_2]$	$Cu(OAc)_2 \cdot H_2O$	35:11
DMF	$[\{Cp^*RhCl_2\}_2]$	$Cu(OAc)_2 \cdot H_2O$	45:20

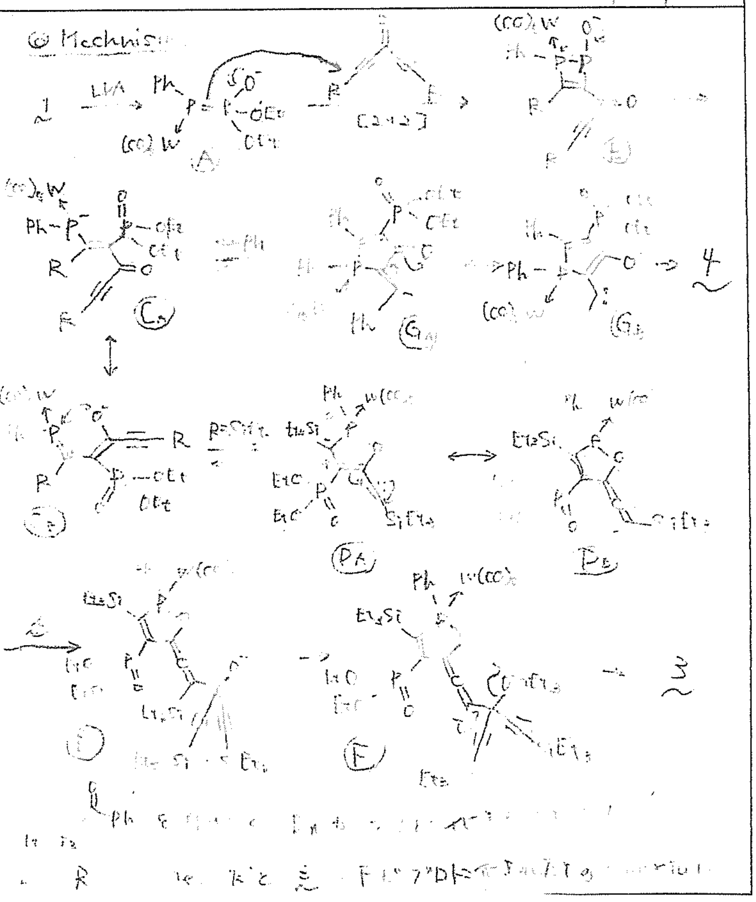


Sascha Ott et al	Uppsala University (Sweden)	Angew. DOI 10.1002/anie.201202155	M1 根島

Cascade Reactions Forming Highly Substituted, Conjugated Phospholes and 1,2-Oxaphospholes



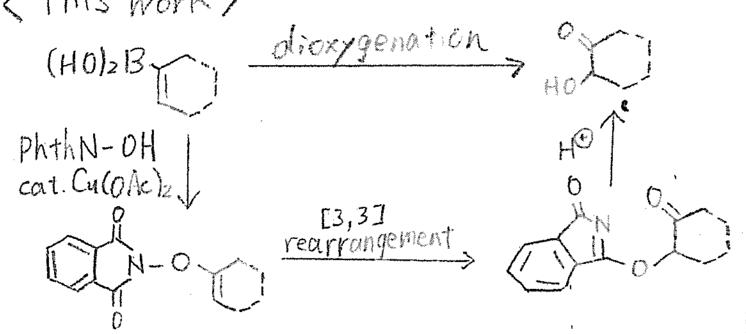




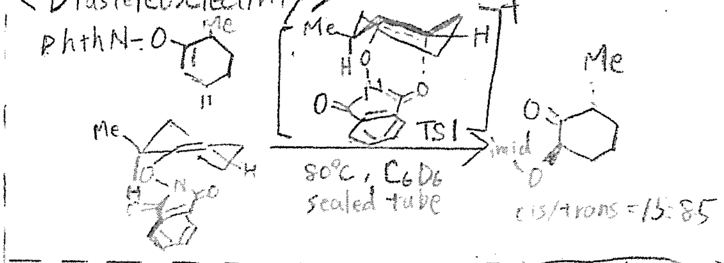
Laura L. Anderson	University of Illinois at Chicago (USA)	Angew. Chem. Int. Ed. 10.1002/anie.201202404	M1 岡崎

Preparation of α-Oxygenated Ketones by the Dioxygenation of Alkenyl Boronic Acids

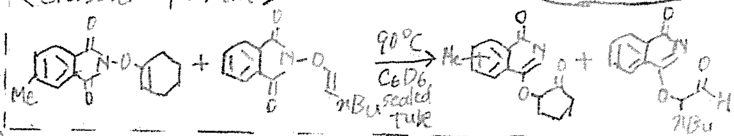
<This work>



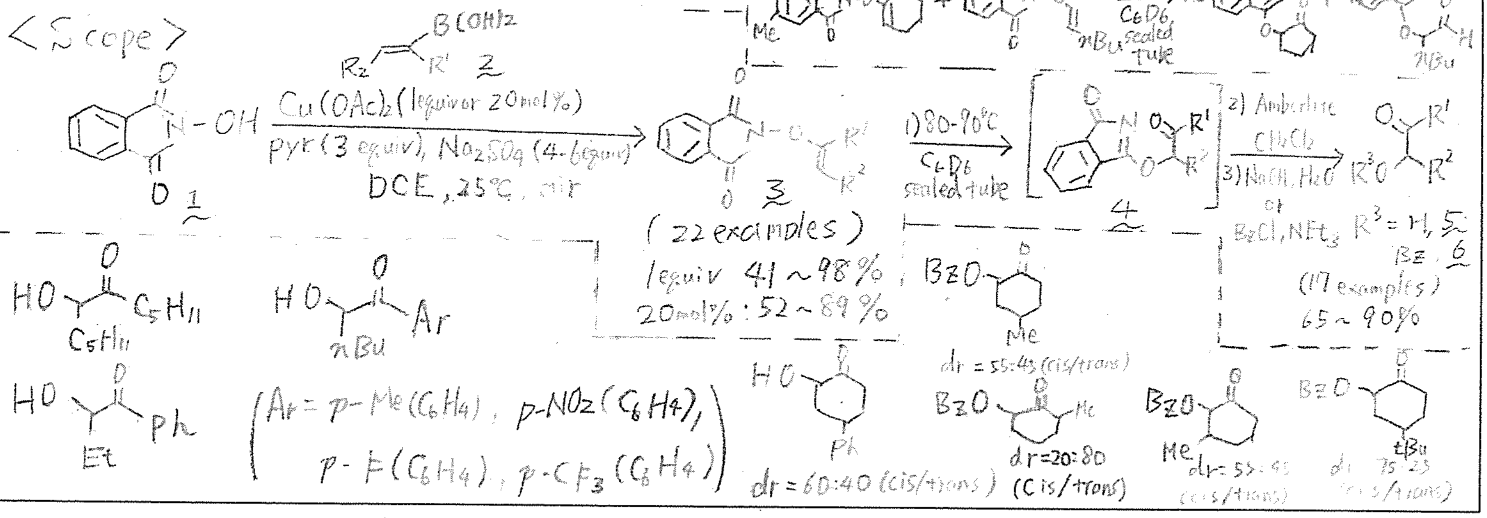
<Diastereoselectivity>



<Crossover experiment> (intramolecular)

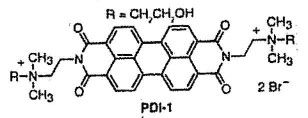


<Scope>

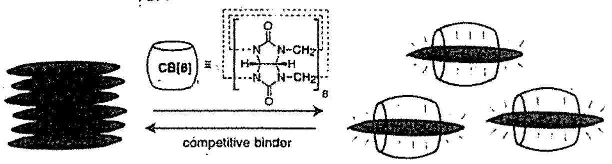


Oren A. Scherman	Cambridge (UK)	ACIE, 10.1002/anie.201202385	M1 西田

Strongly Fluorescent, Switchable Perylene Bis(diimide) Host-Guest Complexes with Cucurbit[8]uril In Water

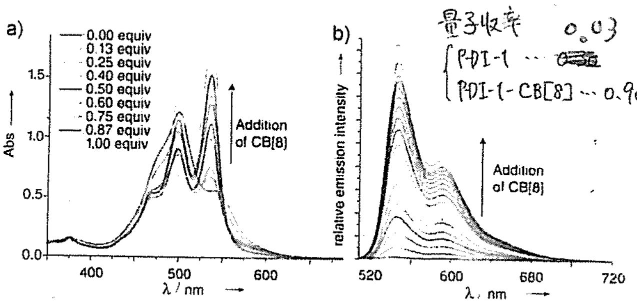


・水溶性（ジカチオン）
→しかし、水中では発光しない。



・PDI-1 水溶液に CB[8] を加えることで、π-π stacking が緩和されて蛍光を発するようになる。
（吸収も蛍光強度も、CB[8] が多いほど、大きくなる。）

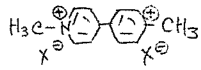
量子収率 0.03
PDI-1 … ~~0.03~~
PDI-1-CB[8] … 0.90



(a) 吸収スペクトル　(b) 蛍光スペクトル　(20μM in H2O)

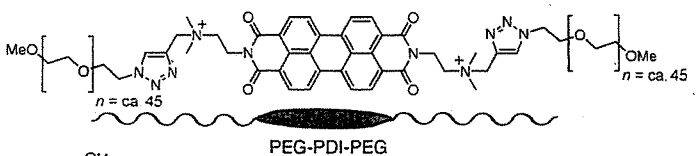
Cucurbit[8]uril (CB[8])
… 比較的大きく、PDI-1 に加えて同時にもう1分子 (2nd guest) 包摂可能。
（PDI-1 2分子は大きさ的に無理。）

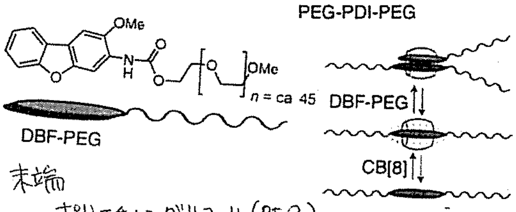
2nd guest … dimethylviologen



Azobenzen (electron-rich)

☆ ポリマーで同様に…





末端
… ポリエチレングリコール (PEG)
→ PDI-core の自己集合を妨げる。
親水性向上。

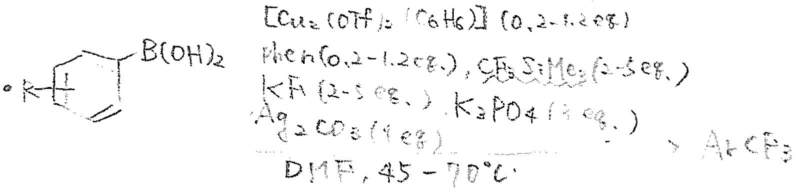
PEG-PDI-PEG を CB[8] に包摂
⇓
蛍光
↓
DBF-PEG も包摂
⇓
消光

Vladimir V. Grushin	Institute of Chemical Research of Catalonia (Spain)	ACIE, 10.1002/anie.201201613	M1 Hisakuni

Fluoroform-Derived CuCF3 for Low-Cost, Simple, Efficient, and Safe Trifluoromethylation of Aryl Boronic Acids in Air

<Previous Work>

・Ar−CH3 → Ar−CCl3 →(HF) Ar−CF3



⇒・costly oxidants (AgI), ligand drying agents, pure O2 が必要

・CF3SiMe3 が高い。(スケールを大きくすると)

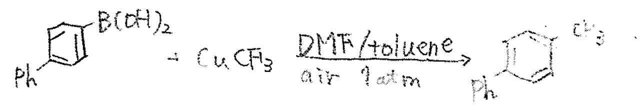
・この条件だとアリルボロン酸が容易に脱ホウ素化してしまう。

<This Work>

CuCl + 2tBuOK →(DMF, −KCl) [K(DMF)][Cu(OtBu)2]

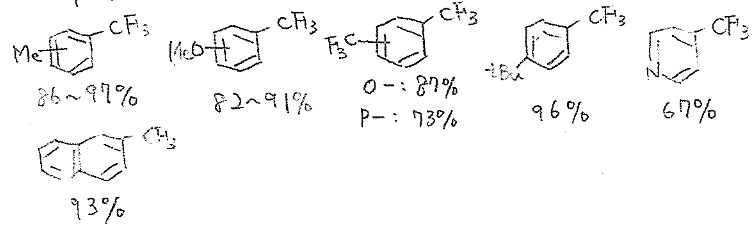
→(1. CF3H, stabilization with Et3N(HF)3) CuCF3 >90%

<Optimization>



Entry	CuCF3 (eq.)	T [°C]	t [h]	Ph2 [%]	Yield [%]
1	1.2	25	0.5	1	89
2	2	25	0.5	1	98
3	2	35	0.5	7	80
4	2	50	0.25	11	74

<Scope>



<Proposed mechanism>

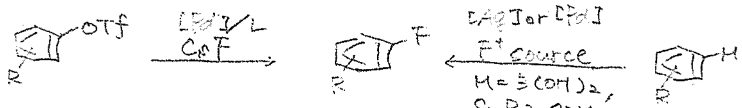
CuICF3 →(O2 (air), oxidation) CuIICF3 →(ArB(OH)2) CuII(Ar)CF3

→ Ar−CF3

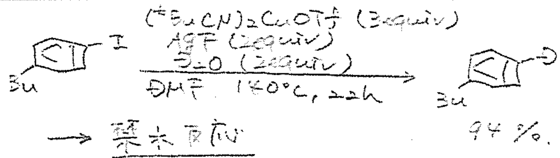
John F. Hartwig	University of California	JACS. DOI: 10.1021/ja30441 0x	B4 黒田

Copper-Mediated Fluorination of Aryl Iodides

<Reported Metal-Mediated Aryl Fluorination>

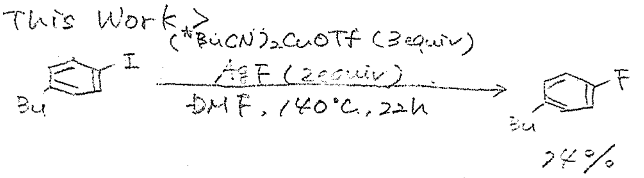


← 貴金属触媒下、電子求引基をもつ基質



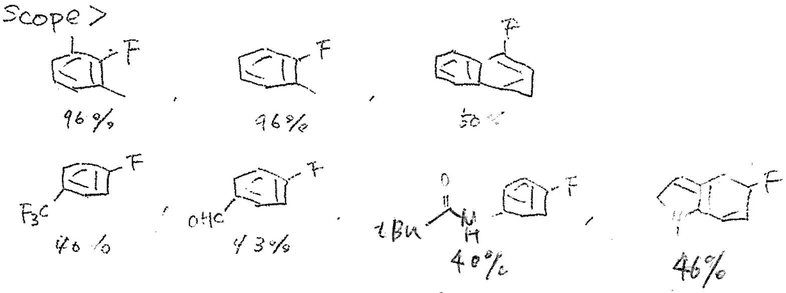
→ 架水反応

<This Work>



Cuを用いることで副反応が起こるよりも早くC−F結合を形成。

<Scope>



<Proposed Mechanism>

(tBuCN)2Cu−OTf

ArI ⇅ 酸化的付加

(tBuCN)2Cu(Ar)(I)(OTf)

AgF ↓ −AgI

(tBuCN)2Cu(Ar)(F)(OTf)

↓ 還元的脱離

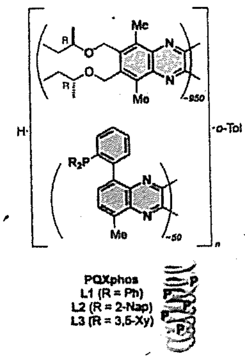
Ar−F + (tBuCN)2Cu−OTf

Michinori Suginome	Kyoto University, Japan.	JACS 10.1021/ja303506k	B4 小玉

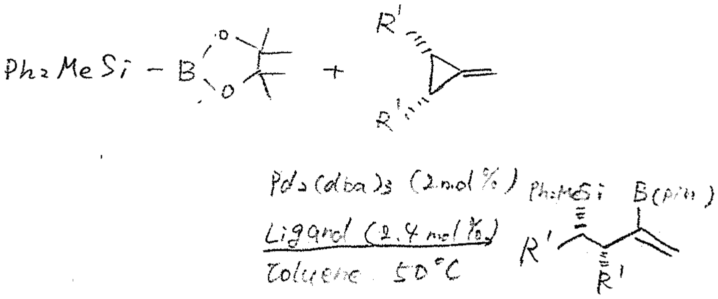
Enhanced Catalyst Activity and Enantioselectivity with Chirality-Switchable Polymer Ligand PQXphos in Pd-Catalyzed Asymmetric Silaborative Cleavage of meso-Methylenecyclopropanes

Polymer Ligand
- 反応からの回収が容易
- "Long-range steric effect" により触媒の活性を上げる

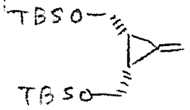
⇒ Pd触媒を用いた、ヒドロシリル化反応、鈴木・宮浦カップリング反応では高いエナンチオ選択性



〈This Work〉

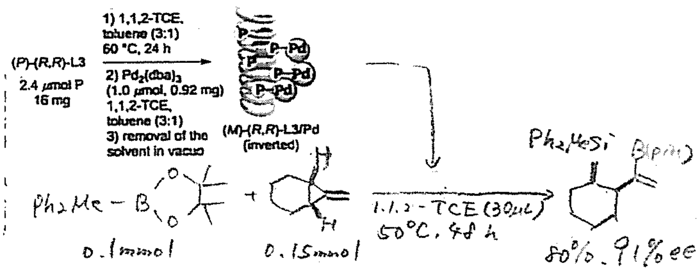


7 examples
55~97%
94~96% ee



における収率

L4	3%
L6	5%
L1	30%
L2	51%
L3	98%



最終的に Pd 0.2mol%, rtでも反応は進行
(76%, 96%ee)