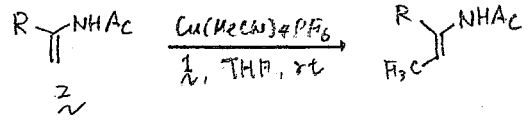
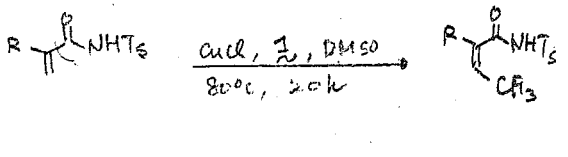
Teck-Peng Loh et al.	Nanyang Tech. Univ.	*AGCIE* (anie.201307245)	Minakata

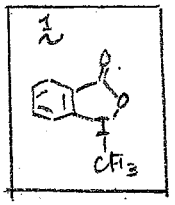
Directing-Group-Assisted Copper-Catalyzed Olefinic Trifluoromethylation of Electron-Deficient Alkenes

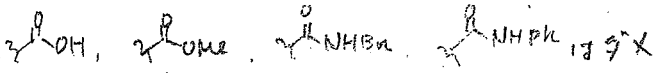
Previous work



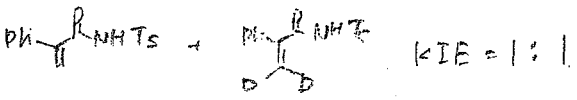
This work



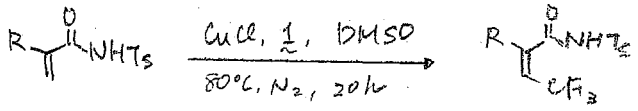




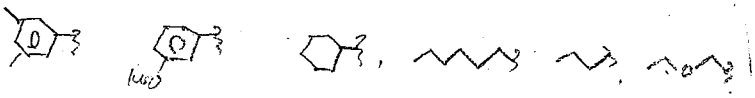
R が ▽ では目的物ができない



Best conditions, scope

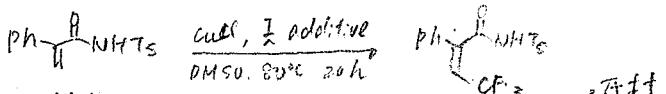


R: Ph, R' = Me, t-Bu, MeO, MeS, Me$_3$Si, Ph, Cl, F, CF$_3$, Ac



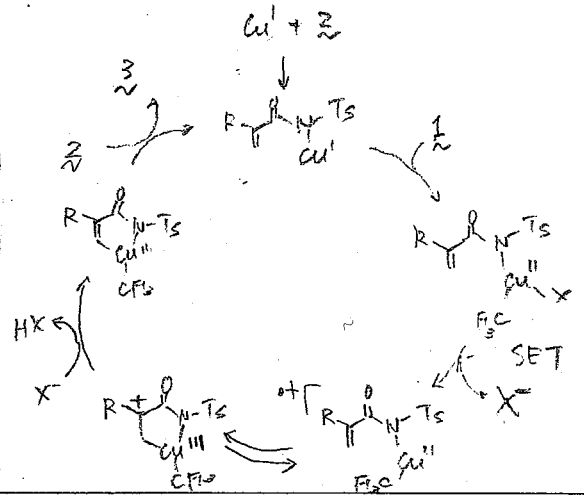
(64 ~ 97%)

control experiment



Additive		
TMPO	39	(49)
BHT	36	(15)
1,1-diphenylethylene	34	(66)

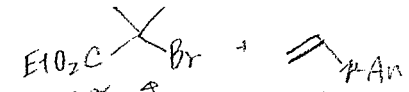
Proposed mechanism



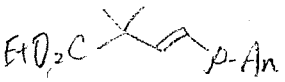
Takashi Nishikata	Yamaguchi Univ. (Japan)	*JACS* 10.1021/ja409661n	清川

An Efficient Generation of a Functionalized Tertiary-Alkyl Radical for Copper-catalyzed Tertiary-Alkylative Mizoroki-Heck type Reaction

This Work

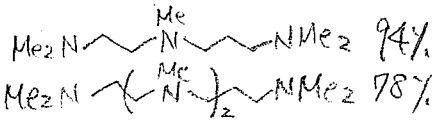


CuI (10 mol%)
TBABr (50 mol%)
toluene
amine, 20°C

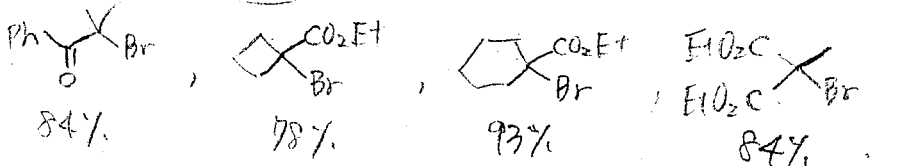


94% yield

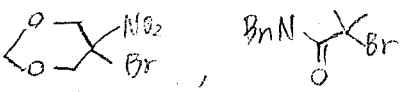
Cu 1価, amine; none NR
Et$_3$N NR
TMEDA NR



Scope: tert-alkyl halides



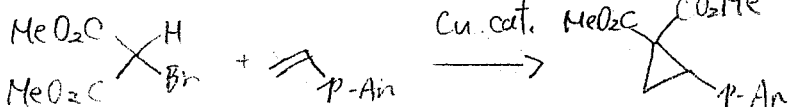
84%, 78%, 93%, 84%



79%, trace

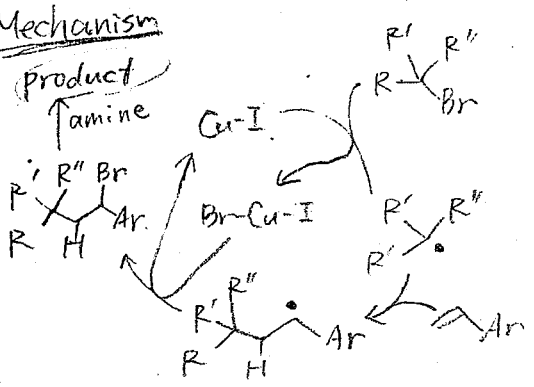
Styrenes
電子 rich 有意質のみ OK.
FG = ester, nitrile, halogen, amine, alkene, OK.

Cyclopropanation

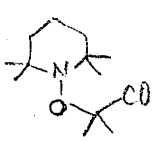


67%

Mechanism



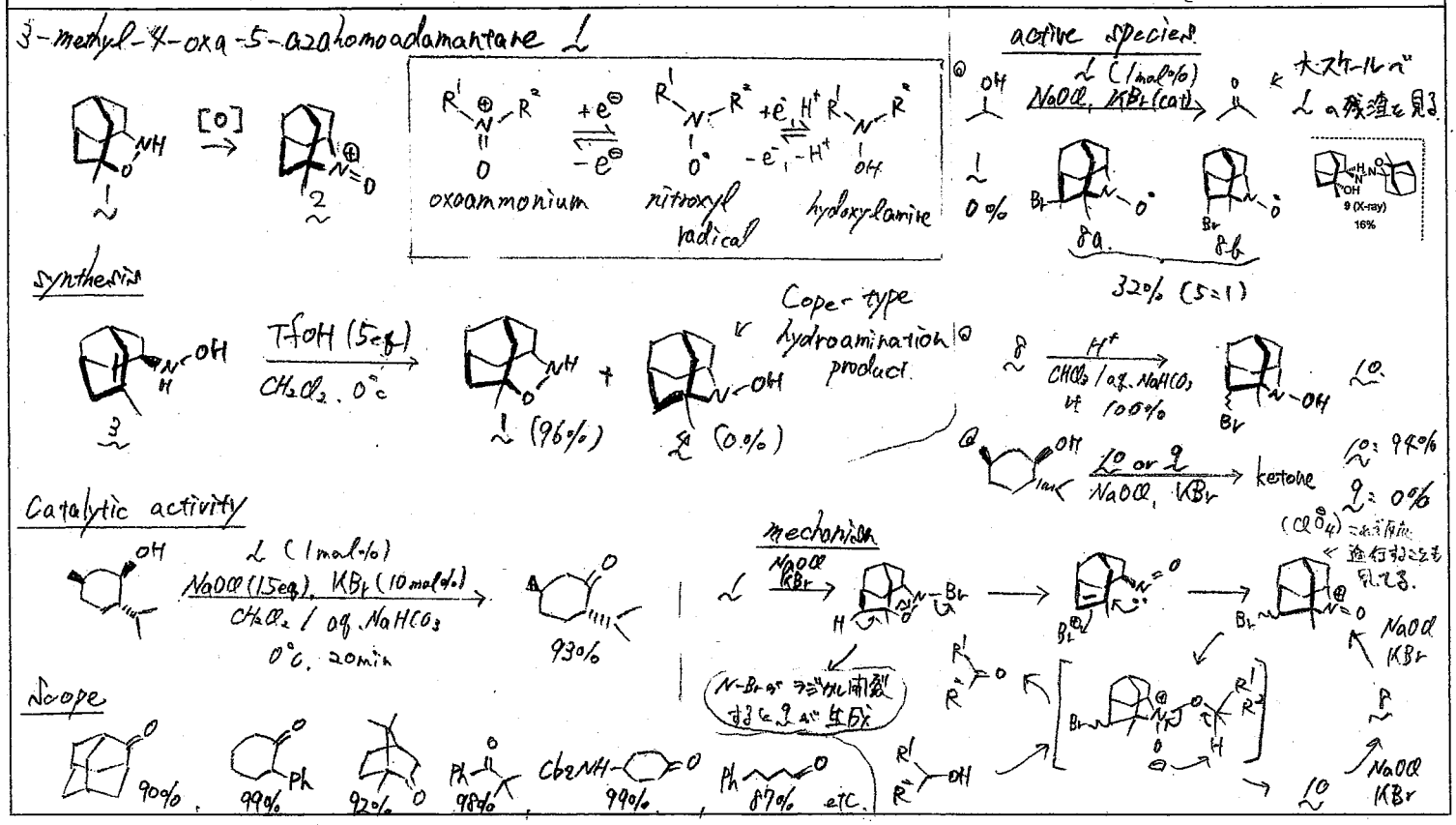
TEMPO 存在下反応させると



が生成する。

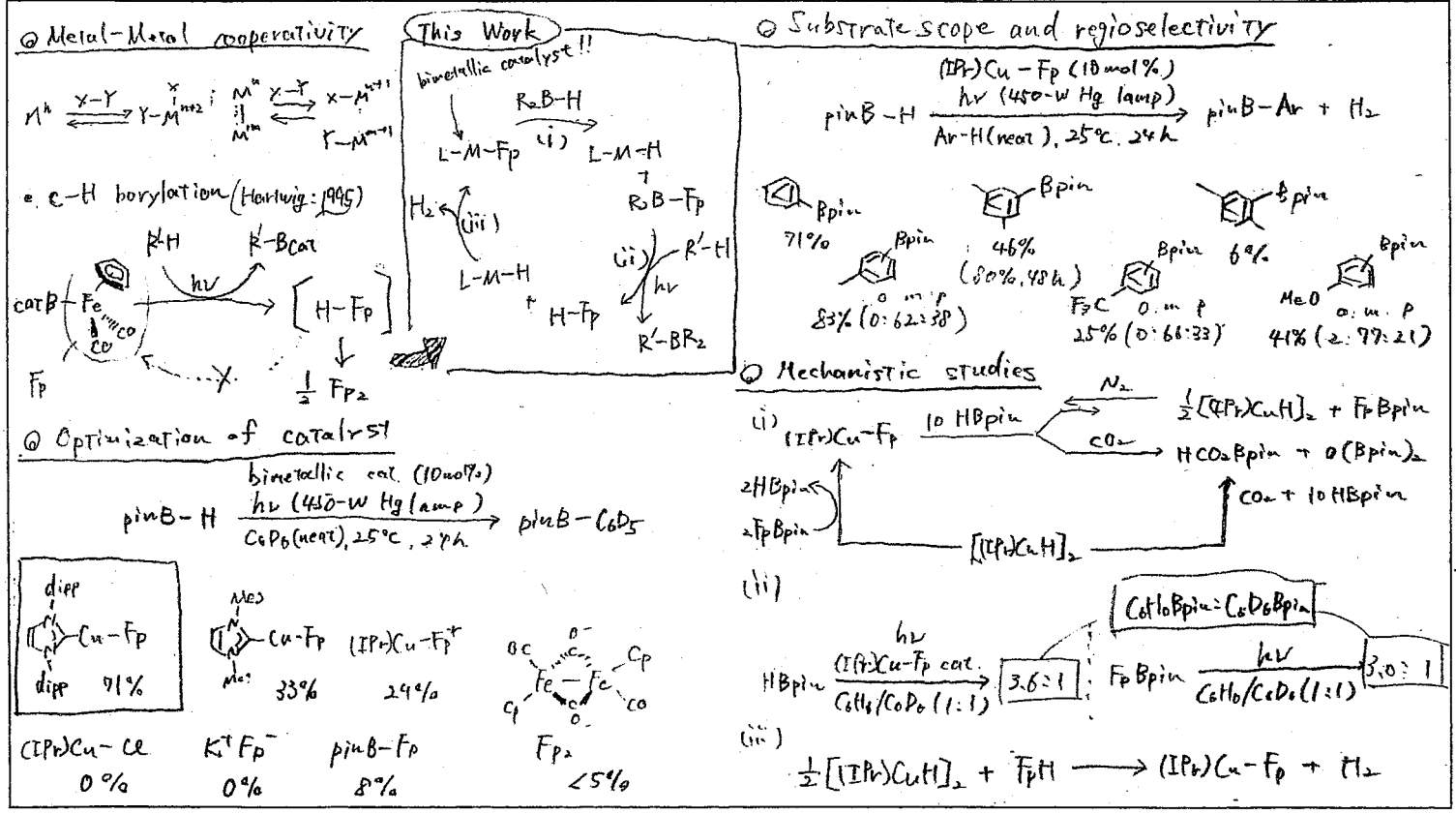
Iwabuchi, Y.	Tohoku University (Japan)	*ACIE* anie.201307144	Okumura

3-Methyl-4-Oxa-5-Azahomoadamantane: Alkoxyamine-Type Organocatalyst for Alcohol Oxidation



Mankad, N. P. et al.	University of Illinois	JACS DOI: 10.1021/ja408861p	M2 榎島

Base Metal Catalysts for Photochemical C-H Borylation That Utilize Metal-Metal Cooperativity



Aiko Fukazawa
Shigehiro Yamaguchi

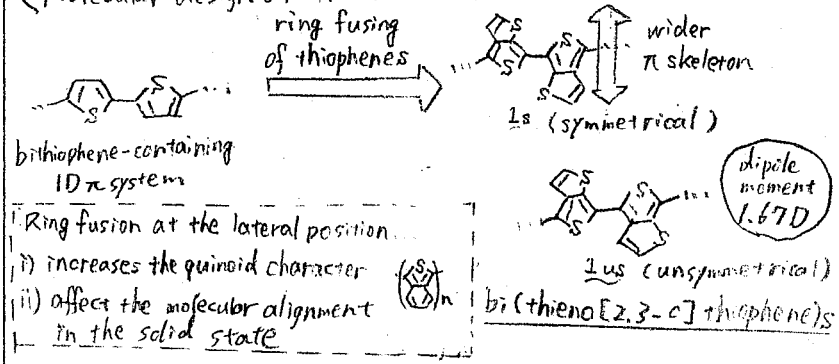
Nagoya University (Japan)

Angew. Chem. Int. Ed.
DOI: 10.1002/anie.201306523

M2 岡崎

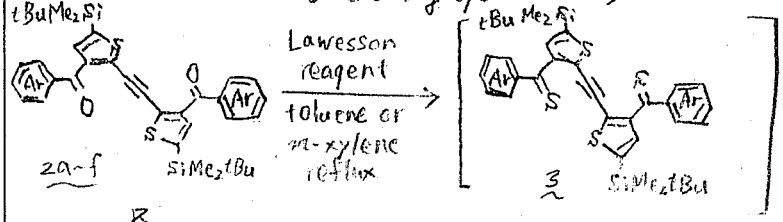
Diarylated Bi(thieno[2,3-c]thiophene)s: A Ring-Fusing Strategy for Controlling the Molecular Alignment of Oligoarenes

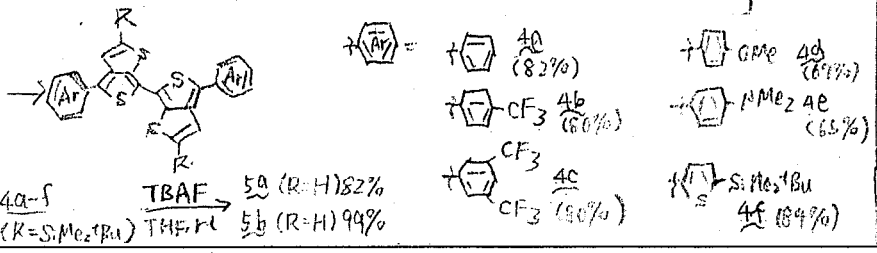
<Molecular design of the bi(thieno[2,3-c]thiophene)s>



Ring fusion at the lateral position
i) increases the quinoid character
ii) affect the molecular alignment in the solid state

<Synthesis Double 5-exo-dig cyclization>





<Pysicochemical properties>

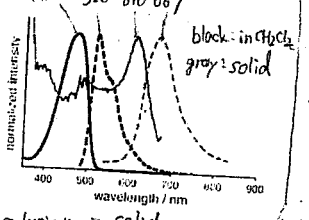
Electrochemical properties

Compound	Oxidation potential[a] $E_{1/2,ox1}$ [V][b] (E_{pa1} [V][b])	$E_{1/2,ox2}$ [V][b] (E_{pa2} [V][b])
4a	+0.23 (+0.30)	+0.86 (+0.92)
4b	+0.42 (+0.51)	+1.02 (+1.11)
4c	+0.53 (+0.59)	+1.10 (+1.12)
4d	+0.08 (+0.13)	+0.53 (+0.57)
4e	−0.22 (−0.16)	−0.05 (+0.01)
4f	+0.12 (+0.18)	+0.63 (+0.69)

a: enhansment of EA (Ph–Ph E_{pa1} = +0.67V)
@ 4e: high electron-donating ability

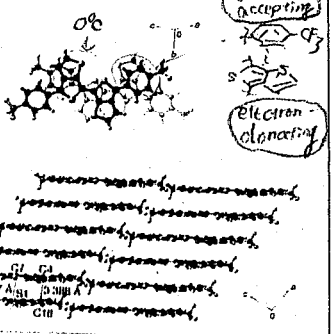
[a] 1 (1mM), TBAPF6 (0.1M), CH_2Cl_2, scan rate = 100 mV s^{-1}, E: vs. Fe/Fe^+

• Electronic spectra of 5b

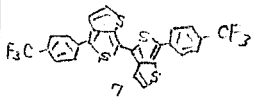


solution → solid
λab: Δ 137 nm
λem: Δ 147 nm
Φ_F: 0.09 → 0.13

X-ray structure



• Properties of 7



α-7 (red needle) recrystallized from DCE/MeCN
β-7 (more stable) (violet needle) crystallized by sublimation

@ absorption and fluorescence of 5b and 7 in CH_2Cl_2 were almost identical.
@ diffuse reflectance spectrum
5b ⇒ α-7 ⇒ β-7 (red-shifted)
@ X-ray structure
5b ≈ α-7 5b ≠ β-7
@ High hole mobility ($FEP-TRMC$)

Xihe Bi, Qun Li

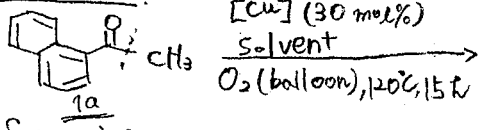
Northeast Normal University (China)

Angew. Chem. Int. Ed.
DOI: 10.1002/anie.201305010

M2 Hisakuni

Chemoselective Oxidative C(CO)–C(methyl) Bond Cleavage of Methyl Ketones to Aldehydes Catalyzed by CuI with Molecular Oxygen.

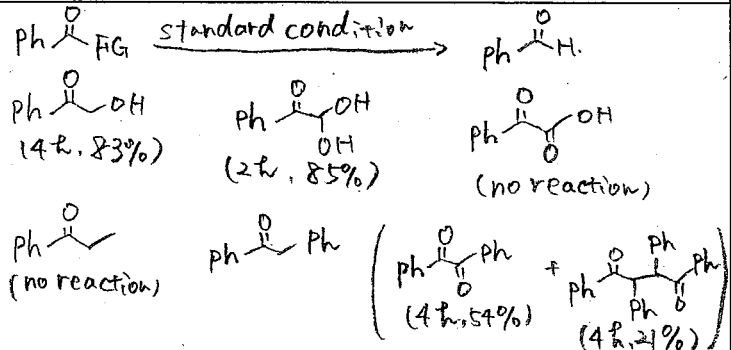
This Work



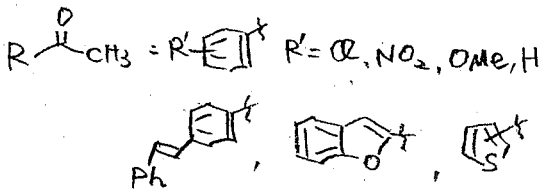
• Screening

[Cu]: (CuI), CuCl, CuOAc, $Cu(OAc)_2$, $CuCl_2$
Solvent: (DMSO), DMF, 1,2,3-TcP, CF_3Ph

• O_2 → N_2 ⇒ n.r.
• 副生成物として、CO_2 と H_2 が生成
⇒系中で蟻酸(HCOOH)が生成し、分解した為。

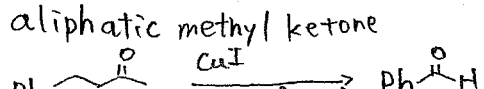


• Scope

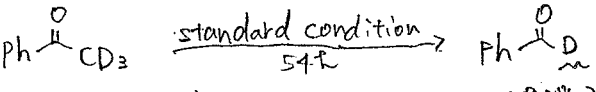


64~97%. 18 examples

aliphatic methyl ketone

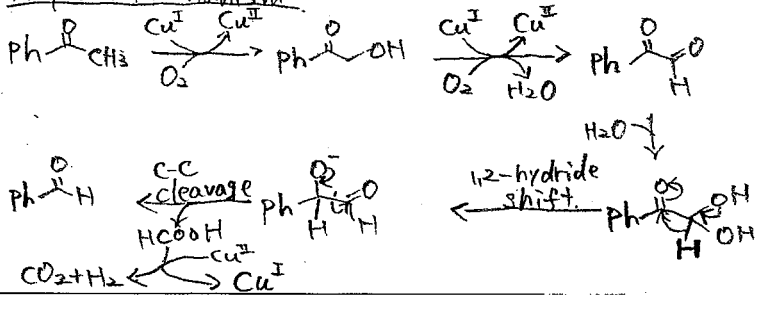


• Deuterium-labeling study



⇒ C(methyl)–H 結合の開裂が律速.

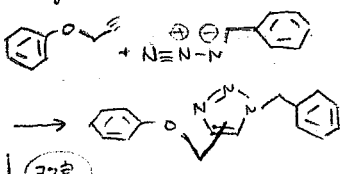
Proposed Mechanism



Yuhong Zhang	Zhejiang University	Angewandte Chemie DOI: 10.1002/anie.201306916	M1 上田

Copper-Mediated Synthesis of 1,2,3-Triazoles from N-Tosylhydrazones and Anilines

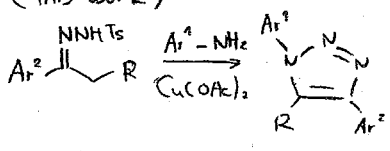
Synthesis of 1,2,3-triazoles
(従来)
- Huisgen 環化反応 (1961年)

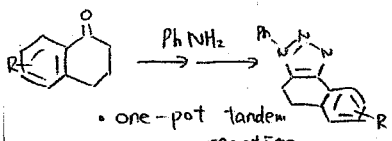


↓ 改良
- CuAAC (copper-catalyzed azid-alkyne cycloaddition)

$$R^1N_3 + \equiv\!-R^2 \xrightarrow{\text{cat. Cu}} \text{1,4-disubstituted 1,2,3-triazole}$$

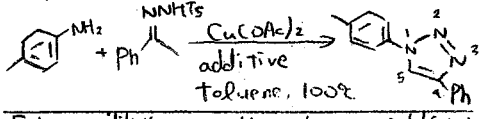
(this work)





- one-pot tandem reaction

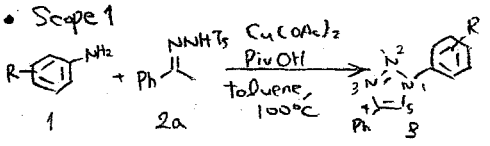
- Optimization



Entry	additive	Atmosphere	yield(%)
1	LiOtBu	Air	55
2	PivOH/LiOtBu	Air	70
3	PivOH	Air	88
4	—	Air	36
5	PivOH	Air	85
6	PivOH	Air	86
7	PivOH	N_2	42
8	PivOH	O_2	17

Piv = Pivaloyl

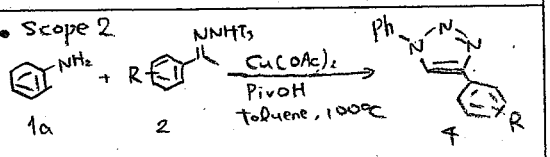
- Scope 1



1 2a 3

✓ 25 entry
✓ R=H → 73%
R=electron rich → 62~88%
R=electron-withdrawing → 37~60%
✓ 4-Br: 60% ; 4-CO$_2$Me → 39%
3-Br: 74% ; 3-CO$_2$Me → 60%

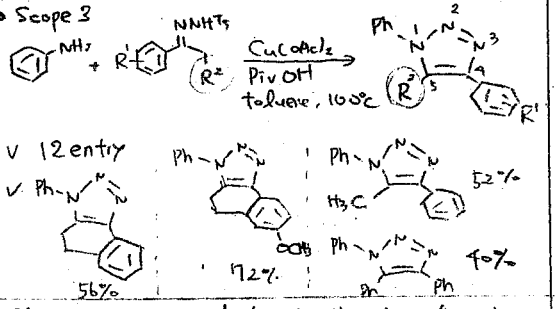
- Scope 2



1a 2 4

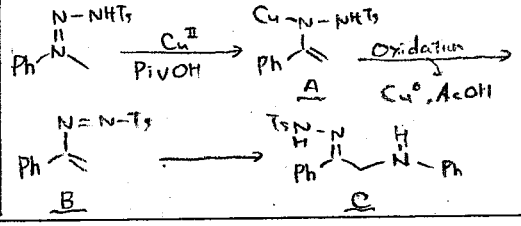
✓ 24 entry
✓ R = electron rich → 62%~90%
R = electron withdrawing → 39%~59%
✓ 立体障害の影響は 12 ほどなく オルト X9 でも良い収率. ✓ フラン, チオフェン フロセン

- Scope 3



✓ 12 entry

- Plausible intermediates in the transformation

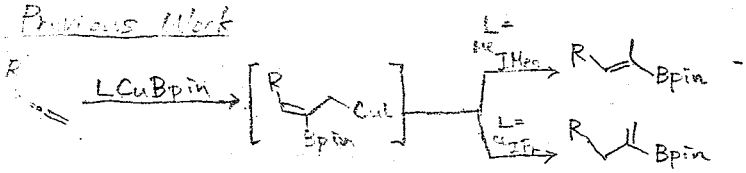


A B C

Yasushi Tsuji	Kyoto University (Japan)	ACIE 10.1002/anie.201306443	M1 [illegible]

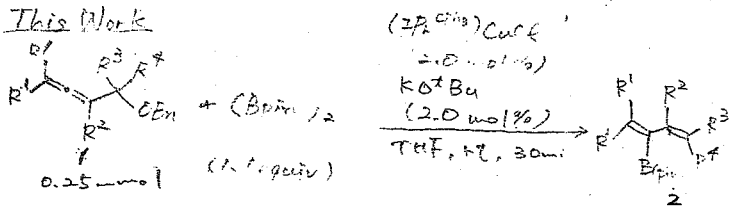
Copper-Catalyzed Borylation of α-Alkoxy Allenes with Bis(pinacolato)diboron: Efficient Synthesis of 2-Boryl 1,3-Butadienes

Previous Work



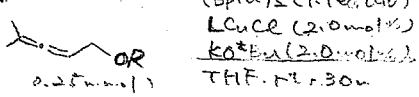
Chem. Eur. J., 2012, 18, 7215.

This Work



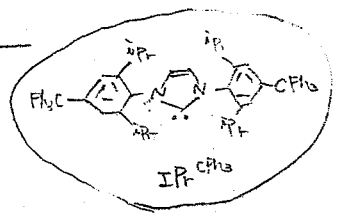
0.25 mmol (1.1 equiv)

Optimization



entry	L	OR	yield
1	xantphos	OBn	38
2	IMes		81
3	IPr		92
4	IPr^{CF_3}		95
5		O(n-C$_6$H$_{13}$)	99
6		OAc	8

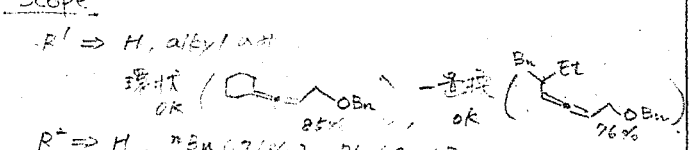
GC yields

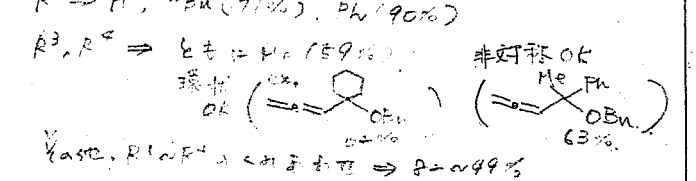


IPr^{CF_3}

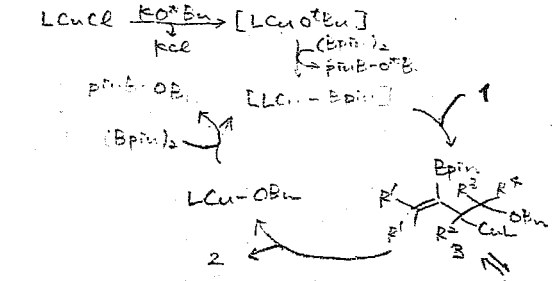
(• LCuCl は 0.01 mol% まで減らせる (98%))

Scope

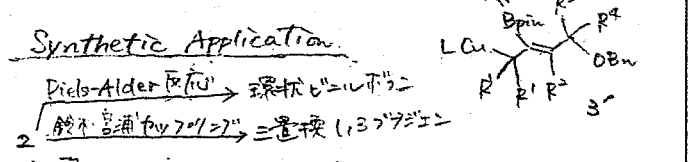




Possible Catalytic Cycle



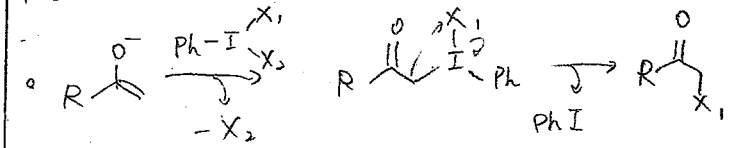
Synthetic Application

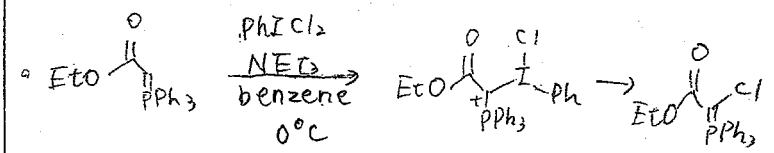


Graham K. Murphy	University of Waterloo (Canada)	JACS 10.1021/ja408678p.	M1 小坂

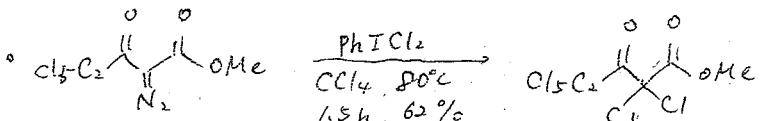
Dihaloindoarene: α,α-Dihalogenation of Phenylacetate Derivatives

超原子価ヨウ素によるカルボニルα位置換



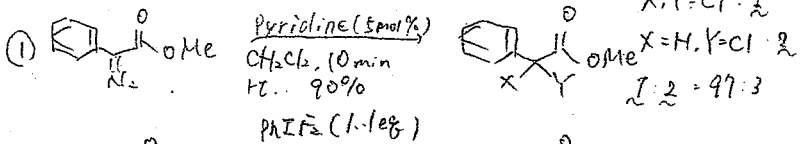


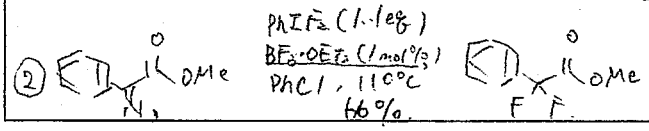
Moriarty, R.M. et al. JACS, 1984, 106, 6082.



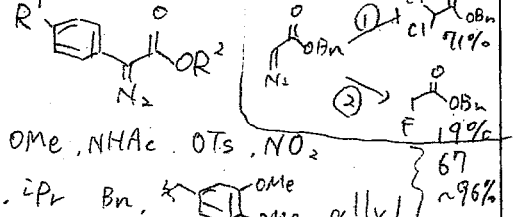
Annalen der Chemie-Justus Liebig, 1964, 675, 47.

This Work





Scope ①.

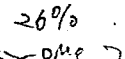


R¹ Br, OMe, NHAc, OTs, NO₂

R² Me, iPr, Bn, , allyl

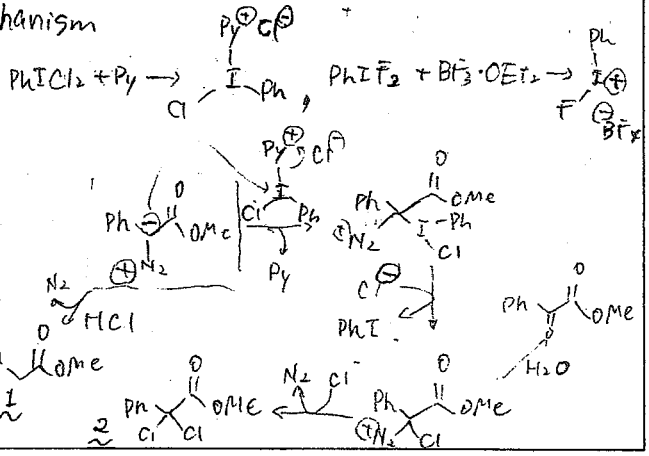
Scope ②. 上と同じ検討 66~79%.

ただし R¹=OMe, R²=Me 26%

R¹=H, R²=  0%

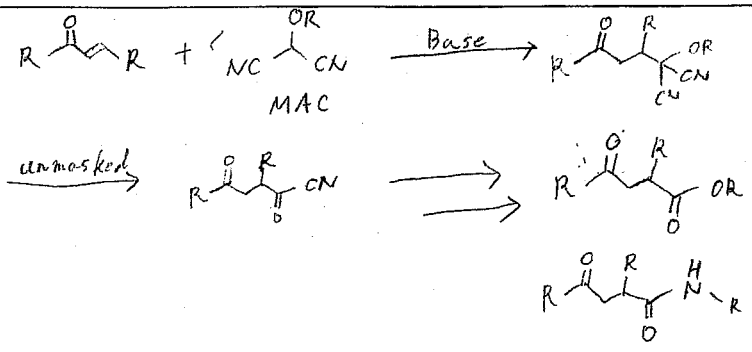
R¹=NHAc, R²=Me

Mechanism

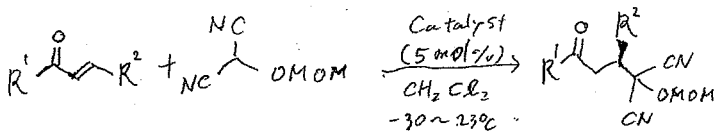


Viresh H. Rawal	University of Chicago (USA)	10.1021/ja409012q	M1 矢羽田

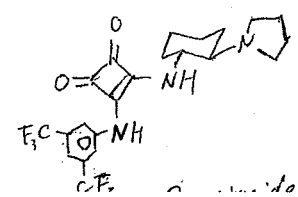
Squaramide-Catalyzed Enantioselective Michael Addition of Masked Acyl Cyanides to Substituted Enones



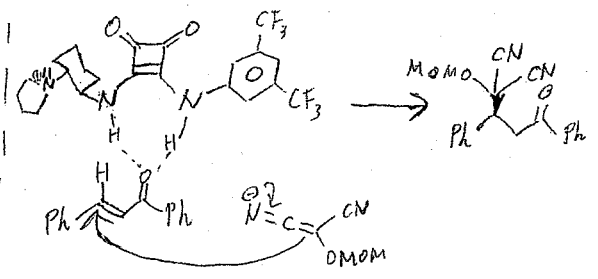
This work



Catalyst



Mechanism

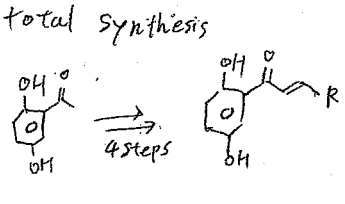


Scope

R¹… Ph, 電子供与基を持つアリール　R²… Ph, 電子求引基を持つアリール

naphthyl, 複素芳香族　アルキル基, スチリル基

total synthesis



92% ee

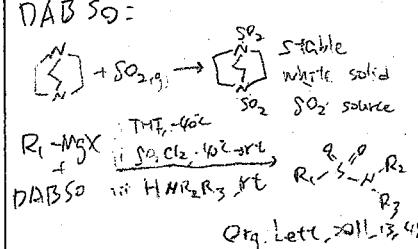
92% ee

51% overall yield

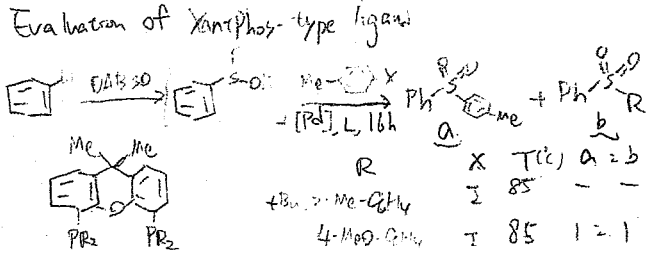
Michael C. Willis	University of Oxford	Anie.201305369	Lin

Palladium-Catalyzed Three-Component Diaryl Sulfone Synthesis Exploiting the Sulfur Oxide Surrogate DABSO

DABSO:

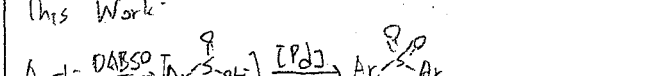


Evaluation of Xantphos-type ligand:

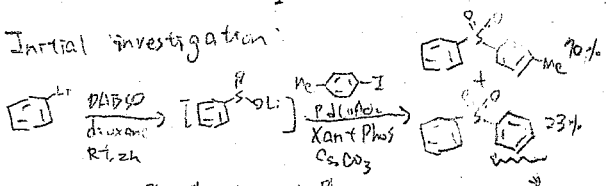


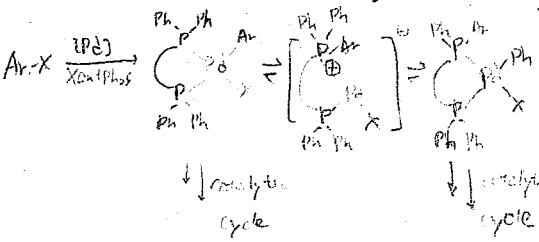
R	X	T(°C)	a : b
tBu-C6H4	I	85	— —
4-MeO-C6H4	I	85	1 : 1
4-F3C-C6H4	I	85	3 : 1
3,5-(F3C)2-C6H3	I	85	—
	Br	110	15 : 1 here condition

This Work:

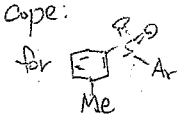


Initial investigation:



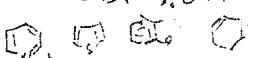


Scope:

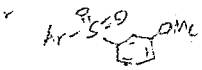


R = Me, OMe, SMe

Ar-R: NH2, NMe2, OMe, CHO, CF3, Cl, I



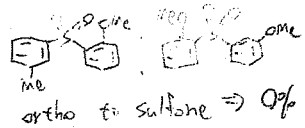
63% - 98%



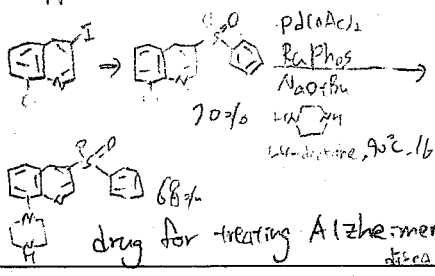
R: Me, tBu, TMS, CF3 70% - 80%

Ar-R

limitation



Application

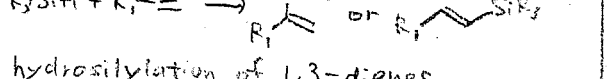


[redacted]

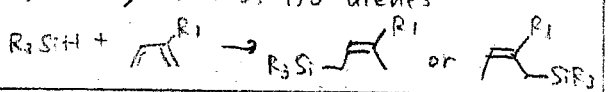
John Montgomery	University of Michigan (US)	JACS 10.1021/ja407749w	B4

Regioselective allene hydrosilylation catalyzed by N-heterocyclic carbene complexes of Nickel and Palladium

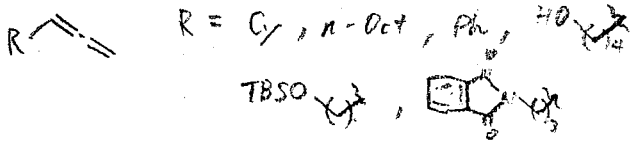
hydrosilylation of alkynes



hydrosilylation of 1,3-dienes



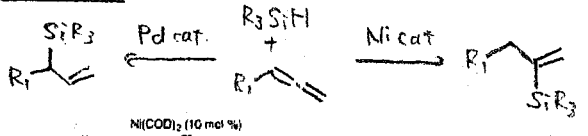
Scope

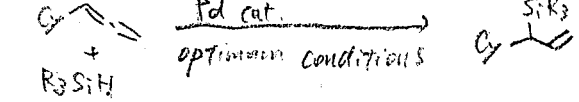


yield 62 ~ 98

regiosel. >98 : 2

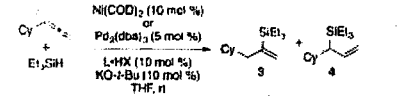
This work



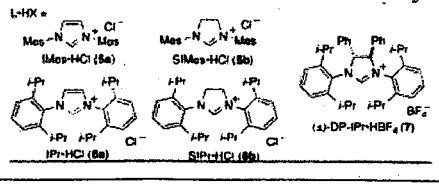


R3 = Me2Ph, Me2Bu, Me(OSiMe3)2, H(tBu)2

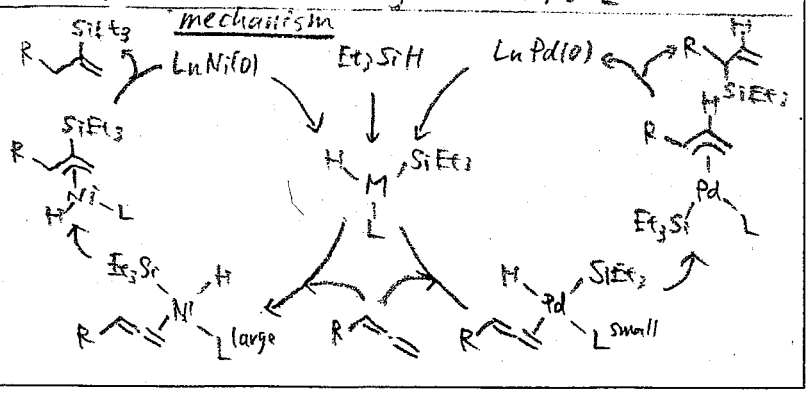
yield 75 ~ 93 regiosel. >98 : 2



entry	precatalyst	L-HX	% yield	regiosel. (3:4)	
1	Ni(COD)2	5a	22	33:67	alkenylsilane 生成
2	Ni(COD)2	5b	15	40:60	
3	Ni(COD)2	6a	58	85:15	Ligand : large
4	Ni(COD)2	6b	47	81:19	
5	Ni(COD)2	7	84	>98:<2	
6	Pd2(dba)3	7	trace	not determined	
7	Pd2(dba)3	6b	56	14:86	allylsilane 生成
8	Pd2(dba)3	6a	75	12:88	
9	Pd2(dba)3	5b	74	2:98	Ligand : small
10	Pd2(dba)3	5a	80	<2:>98	



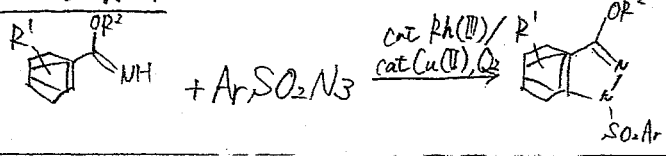
mechanism



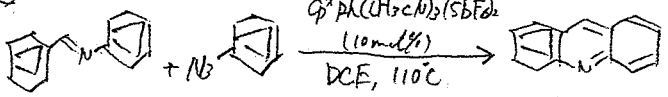
Jonathan A. Ellman	University of California	JACS, ja406131a	刘中

Facile Synthesis of Unsymmetrical Acridines and Phenazines by a Rh(III)-Catalyzed Amination/Cyclization/Aromatization Cascade

① Previous Work

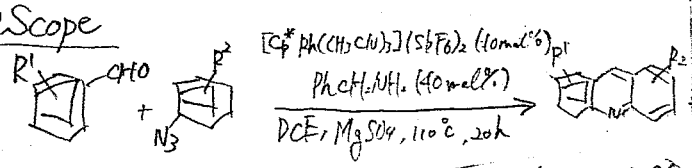


②

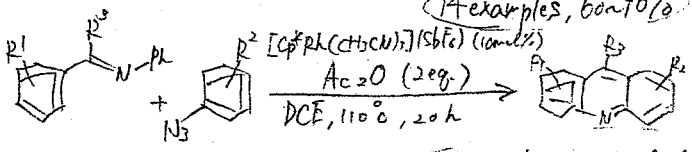


Additive	yield
none	57%
$CF_3CO_2CH_2CF_3$ (2 eq.)	71%
Ac_2O (2 eq.)	77%

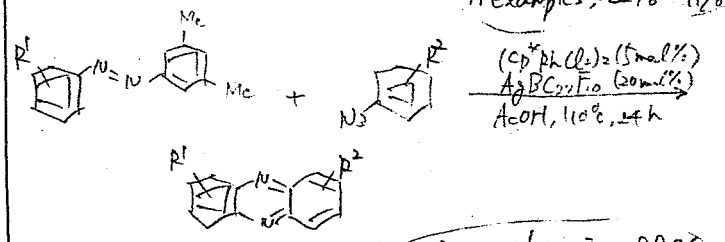
③ Scope



14 examples, 60~90%



11 examples, 32% ~ 91%



10 examples, 30~88%

④ Proposed Mechanism