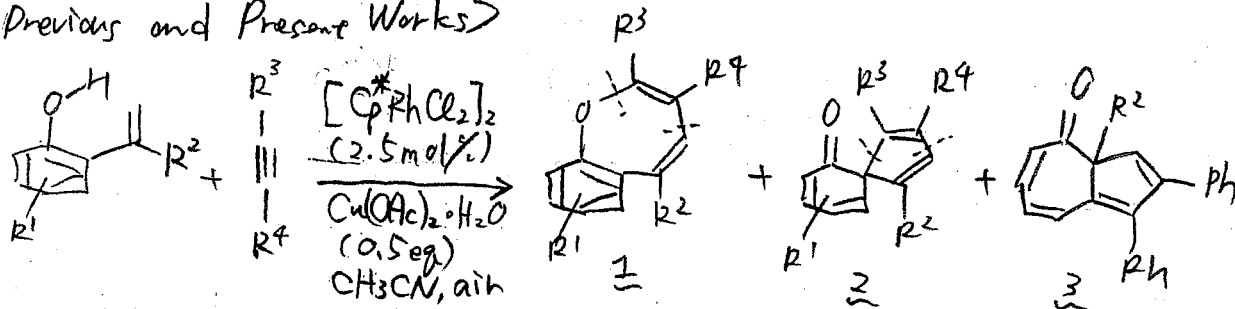


Rhodium(III)-Catalyzed Dearomatizing (3 + 2) Annulation of 2-Alkenylphenols and Alkynes

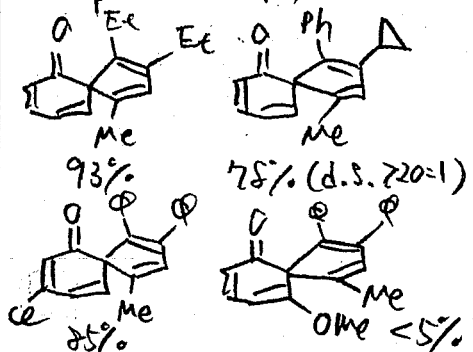
< Previous and Present Works >



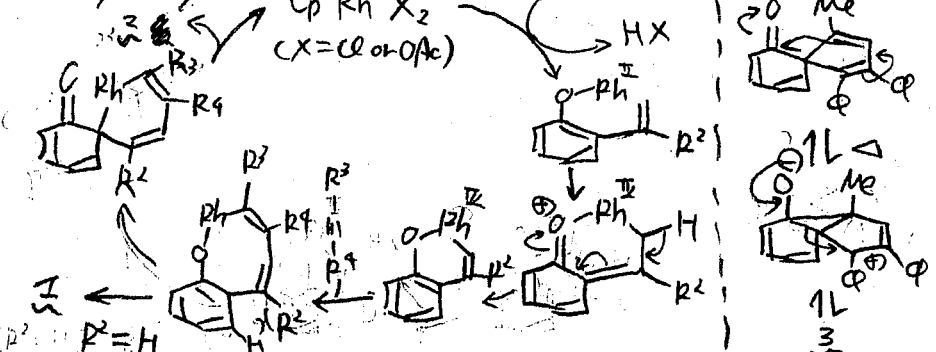
previous work: $T=85^\circ\text{C}$, $R^2=H$ **1** only (JACS, 2014, 136, 834.)

this work: $T=40^\circ\text{C}$, $R^2 \neq H$ **2** + traces of **1** (3 is 高温時に生じる).

< example of scope >

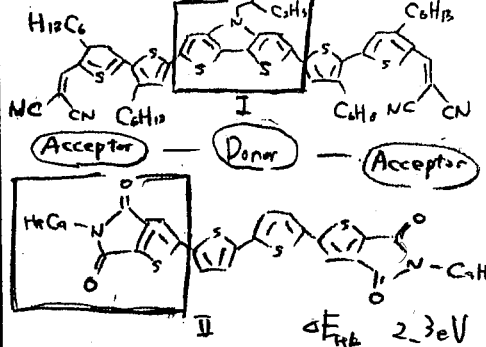


< catalytic cycle >

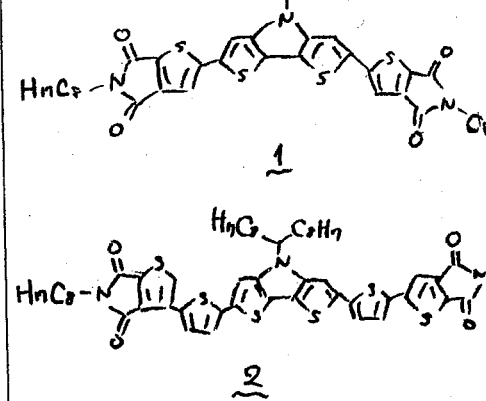


Acceptor - Donor - Acceptor Oligomers Containing Di-thieno[9,2-b:2',3'-d]pyrrole and Thieno[2,3-c]pyrrole-4,6-dione Units for Solution-Processed Organic Solar Cells

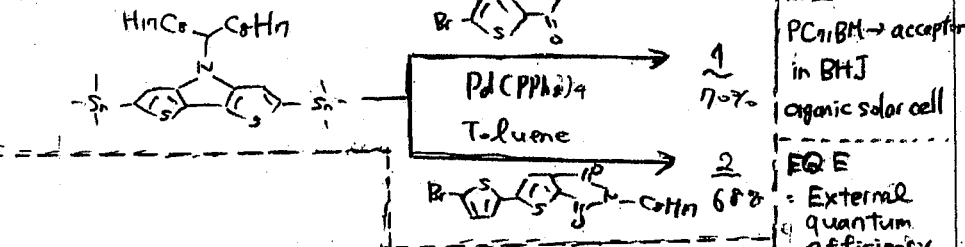
< Previous Work >



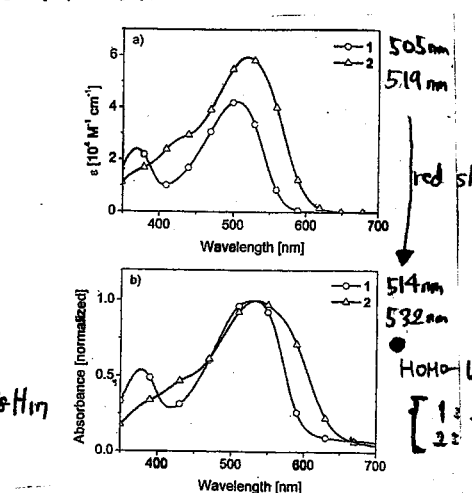
< This Work >



① Synthesis



② UV-Vis



③ J-V and EQE curves

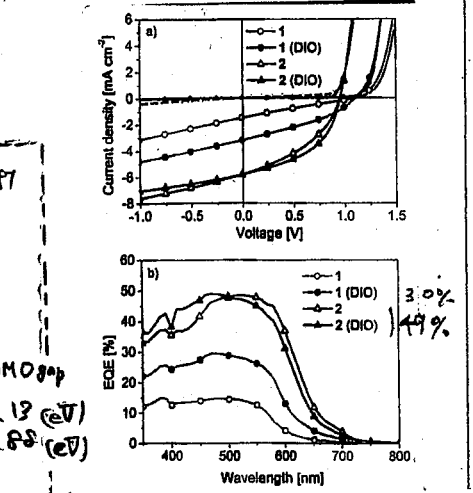


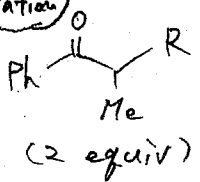
Figure 2. UV-vis absorption spectra of oligomers 1 and 2 in (a) chloroform solution and (b) thin films.

Figure 4. (a) J-V curves and (b) EQE curves of photovoltaic devices containing oligomers 1 and 2 as the donor and PC71BM as the acceptor, with and without DIO (4 mg/mL) as the additive.

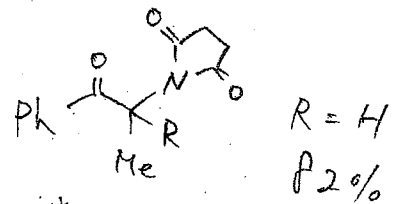
○塚原 石好, Vyanik Muhammet, 石原 一彰 | 名大院工・CREST | 2B7-06

次亜ヨウ素酸塩触媒によるカルボニル化合物のα-位ド化及びβ-ド化

Imidation



- NaI (5 mol%)
- TBHP (2 equiv)
- CS₂(O₂) (50 mol%)
- 18-crown-6 (5 mol%)
- (MeO)₂CO, rt

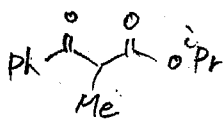


マロニ酸ジエチル OK!

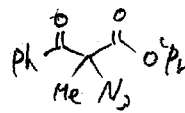


* R=H 以外の反応進行の

Azidation



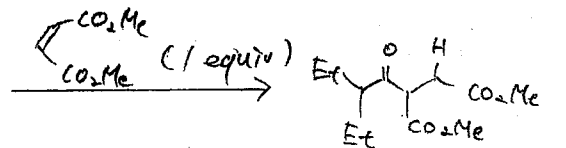
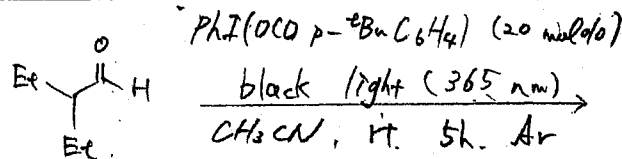
- NaN₃ (1.1 equiv)
- Bu₄N⁺I⁻ (5 mol%)
- H₂O₂ (20%, 30%)
- NH₄Cl (1 eq)
- cyclopentyl methyl ether, rt



- β-位にエチルのみ
- α位に 2° 位の R' あり
- NH₄Cl は副生する
- NaOH を取り除く

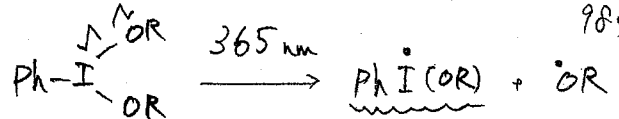
○白井 明日香, 茂木 真, 丸岡 啓二 | 京大院理 | 2B6-51

超原子価ヨウ素剤を用いた分岐鎖アルデヒドによるアルキンのヒドロアシル化反応



98%

→ α位に分岐鎖アルキル付加



このアルキル基を引抜き

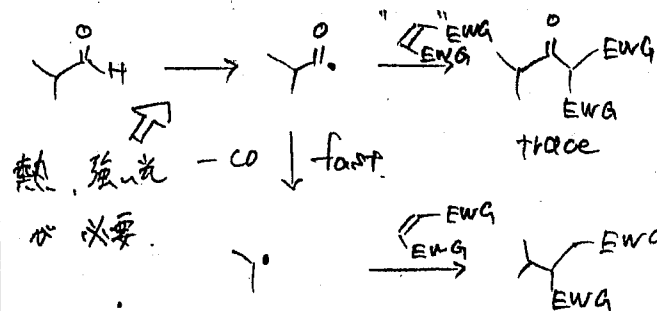
(律速)

同位体効果が見える

なぜ脱COかな?

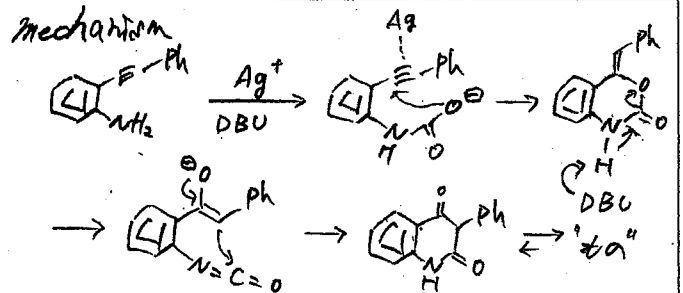
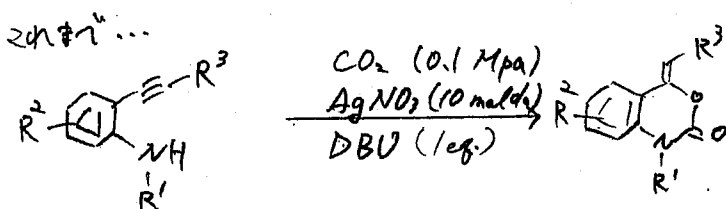
・光の波長 (365 nm 以下は選択性下)

・rt まで溫和 (0 °C 以下は、ほぼ副生成)

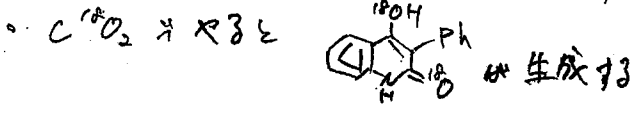
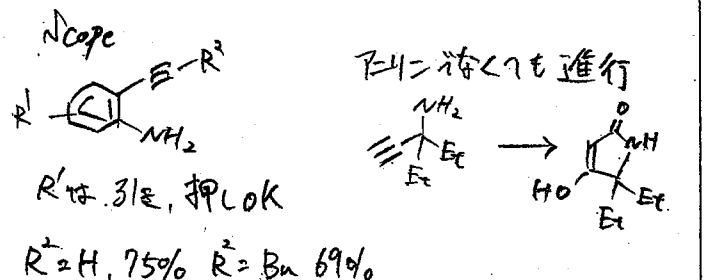
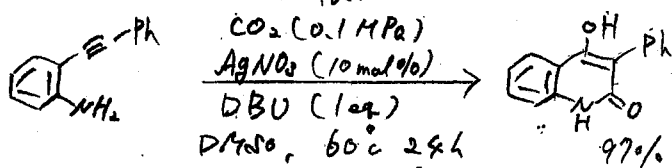


○石田 智信, ○小林 達, 菊地 善, 山田 徹 | 慶大理工 | 1B6-30 1B6-31

銀塩触媒的アルキン活性化および分子内転位によるアリールアミン誘導体のα-位炭素固定化

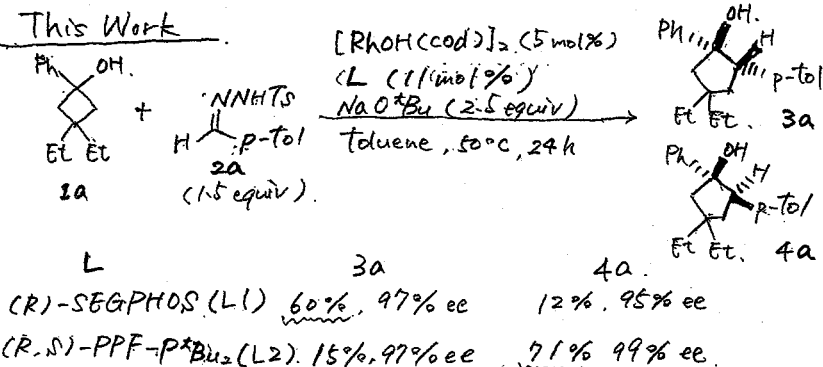


今回... R' = H だけ, 転位反応は進行しない

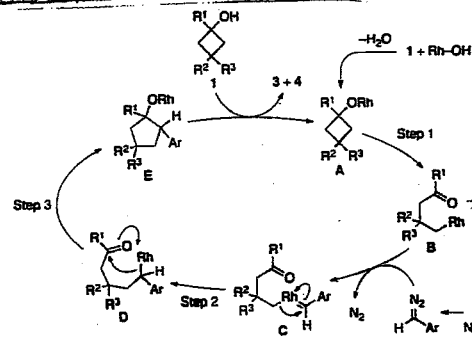


Enantioselective Insertion of a Carbenoid Carbon into a C-C Bond To Expand Cyclobutanols to Cyclopentanols

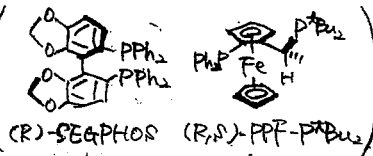
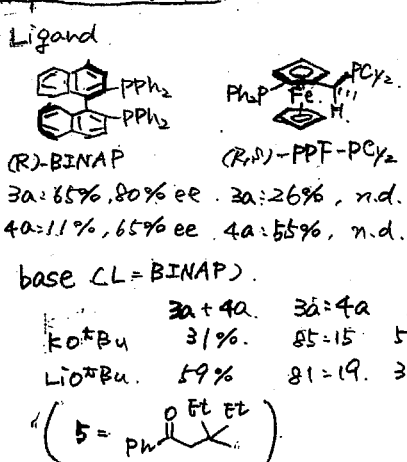
This Work



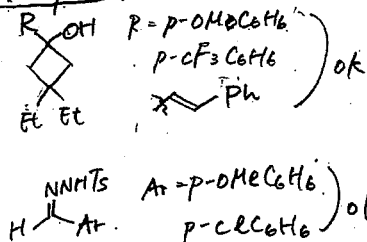
Possible Reaction Mechanism



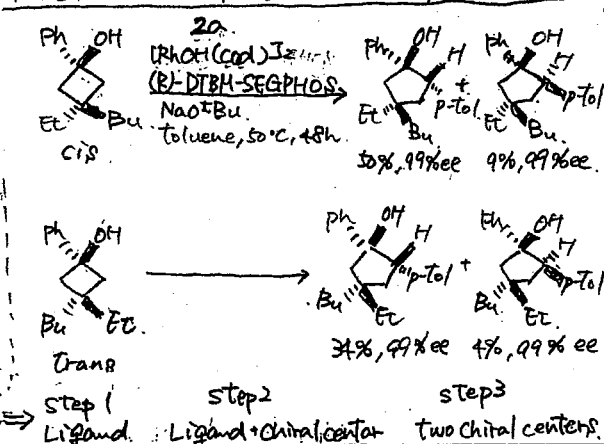
Optimization



Scope

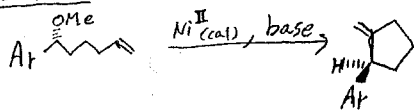


Reactions of cis- and trans-cyclobutanols

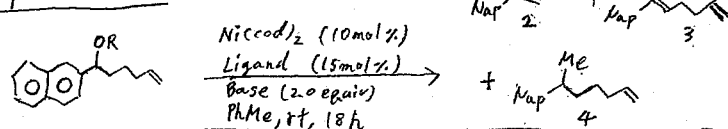


Enantiospecific Intramolecular Heck Reaction of Secondary Benzylic Ethers

This work



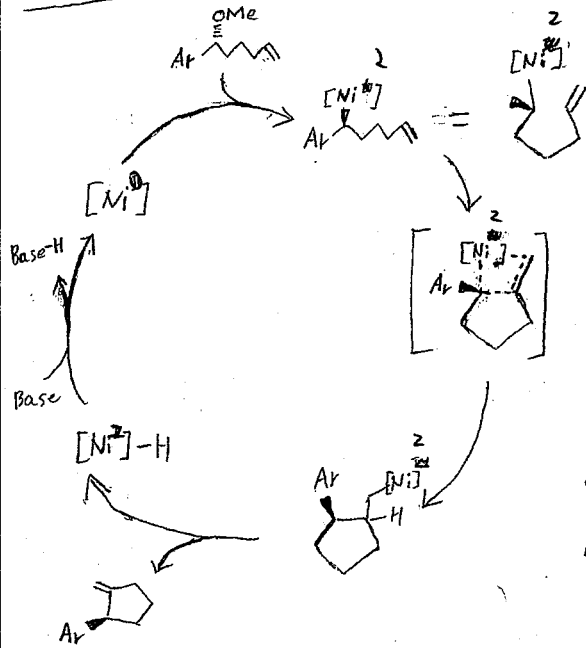
Optimization



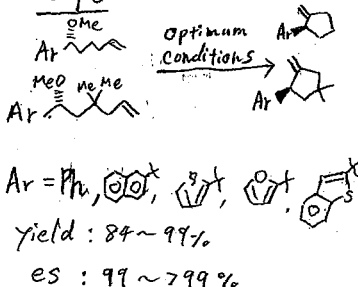
R	Ligand	base	yield (%)		
			2	3	4
Piv	PCy ₃	Cs ₂ CO ₃	<2	39	<2
Piv	PCy ₃	ZnMe ₂	7	39	<2
Me	PCy ₃	MeMgI	64	19	<2
Me	PPh ₃	MeMgI	18	96	<2
Me	PPEphos	MeMgI	4	23	47
Me	dppf	MeMgI	<2	29	66
Me	NiCl ₂ (PCy ₃) ₂ ^a	MeMgI	82	11	<2

^a NiCl₂(PCy₃)₂ was used in place of Ni(cod)₂ and added Ligand

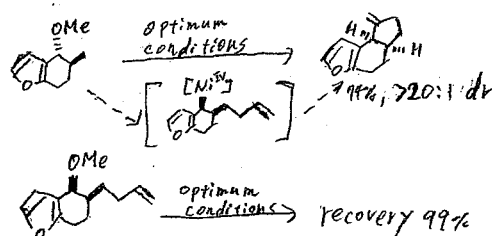
Mechanism



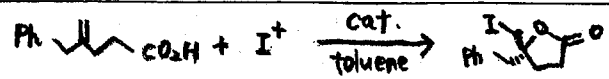
Scope



Mechanistic Study

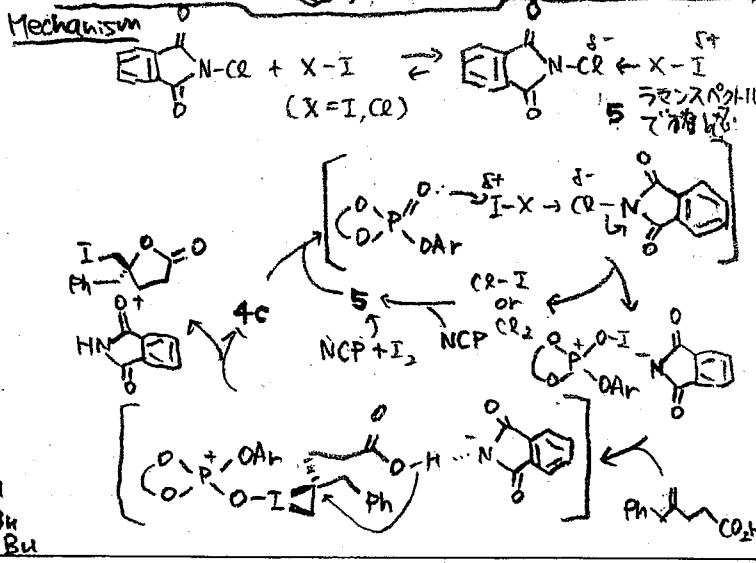
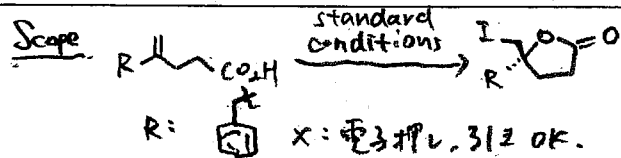
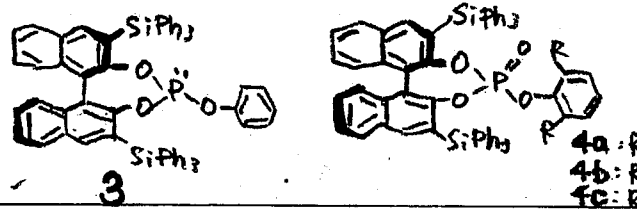


Cooperative Activation with Chiral Nucleophilic Catalysts and N-Haloimides: Enantioselective Iodolactonization of 4-Arylmethyl-4-pentenoic Acids

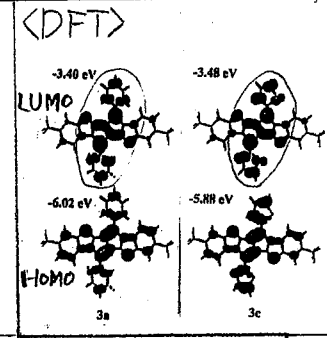
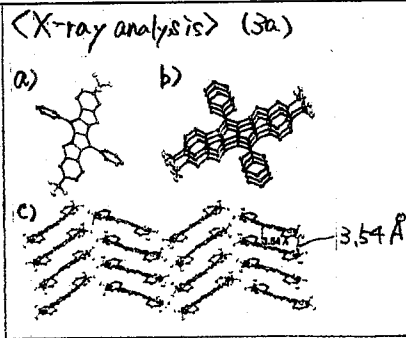
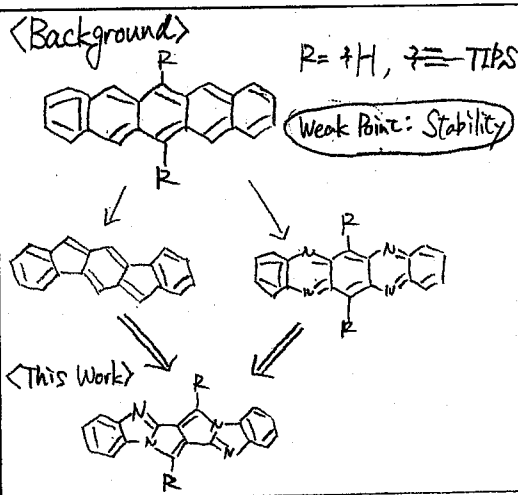


I ⁺ (equiv)	cat. (mol-%)	T (°C)	Yield (%)	ee (%)
NIS (1.1)	P(OPh) ₃ (30)	-40	60 (81)	
	3 (10)		55 (85)	
	PPh ₃		63 (80)	
	O=P(OPh) ₃		0 (100)	
	S=P(OPh) ₃		3 (100)	

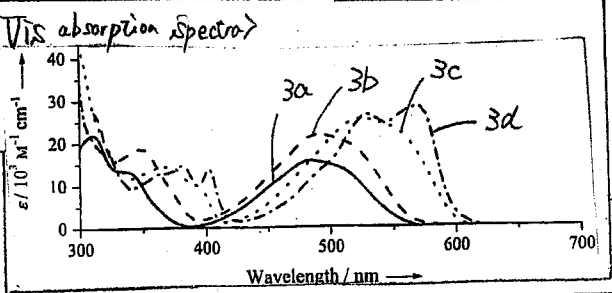
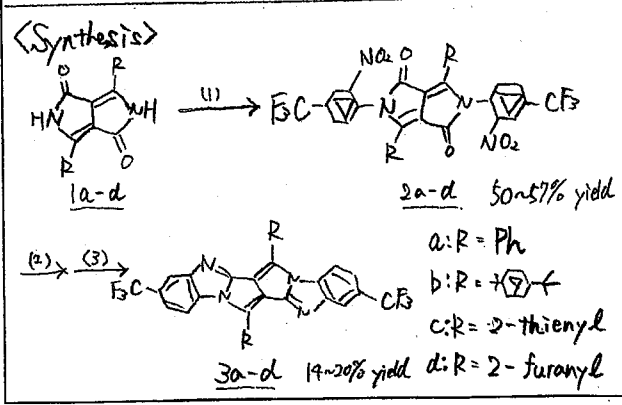
I ₂ (1.1)	NIS (1.1)	3 (30)	-78	55	30
		4a (5)		98	50
		4b (5)		99	86
		4c (5)		99	88
I ₂ (1.1)	NCS (1.1)	4c (5)		99	88
I ₂ (1.1)	NCP (1.1)	4c (5)		99	92
I ₂ (0.5)	NCP (1.5)	4c (1)		95	93



Synthesis and Properties of a New Class of Fully Conjugated Azahexacene Analogues



Stability: UV-Vis, 4 days, No degradation, 70°C heating, ¹³C NMR.



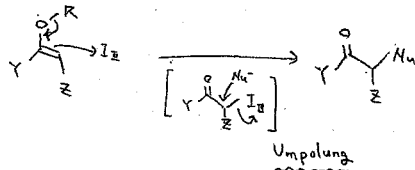
Without decomposition: No degradation of pentacene derivatives after 12 h at r.t.

Comp.	λ [nm] ^[a]	ε [M ⁻¹ cm ⁻¹]	E _{1r} [V] ^[b]	E _{1o} [V] ^[c]	LUMO [eV] ^[d]	HOMO [eV] ^[e]	E _g [eV] ^[f]	E _g [eV] ^[g]
2a	464	23800	-1.43*	1.04	-3.37	-5.84	2.47	2.42
2b	483	29600	-1.53*	0.94	-3.27	-5.74	2.47	2.39
2c	537	33000	-1.37*	0.76	-3.43	-5.56	2.13	2.22
2d	530	46700	-1.39*	0.75	-3.41	-5.55	2.14	2.27
3a	484	15700	-1.31	0.99*	-3.49	-5.79	2.30	2.23
3b	494	24900	-1.39	0.96*	-3.42	-5.76	2.34	2.20
3c	527	25500	-1.27	0.84*	-3.53	-5.64	2.11	2.06
3d	570	28500	-1.27	0.72*	-3.53	-5.52	1.99	2.08

[a]: UV-Vis [b]: [c]: [d]: LUMO-HOMO [e]: UV-Vis

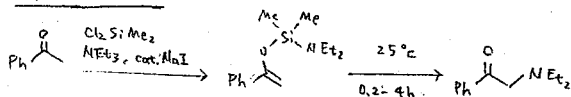
Flexible Stereoselective Functionalizations of Ketones through Umpolung with Hypervalent Iodine Reagents

This Work



Entry	Nu	Y	Z	Y	Z
1	NEt ₂	94%	92%	82%	87%
2	OH	85%	80%	72%	65%
3	OEt	83%	81%	68%	60%
4	OAc	90%	92%	91%	82%

Optimization

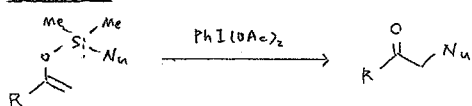


Reagent (s)	Solvent	yield (%)
PhI(OAc)CF ₃	MeCN	69
PhI(OAc)CF ₃ , BF ₃ ·OEt ₂	MeCN	< 10
PhI(OAc) ₂ , BF ₃ ·OEt ₂	MeCN ^{cat}	20
PhI(OAc) ₂ , BF ₃ ·OEt ₂	CH ₂ Cl ₂	45
I(OAc) ₃	CH ₂ Cl ₂	57
PhI(OAc) ₂	CH ₂ Cl ₂	99

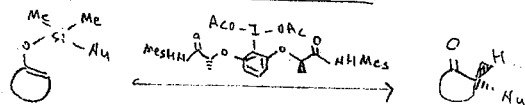
↑ 23% yield for PhI(OAc)₂ in CH₂Cl₂

cat) Reaction performed at 0°C

Scope 1.



Scope 2 (Stereo Selective Functionalization)



Nu	ee	yield	ee	yield	ee	yield
NH ₂	94%	60%	97%	76%	92%	54%
OH	90%	76%	88%	79%	90%	49%

Advantage of silyl ether

- facile to synthesize silyl ethers
- inert in most reaction
- easy to remove after reaction
- less flexible transition state → stereocontrol

Kazuhiko Semba, Yoshiaki Nakao

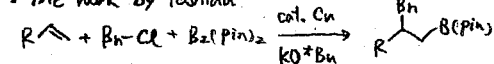
Graduate school of Engineering
Kyoto University

JACS 10.1021/ja5029556 I

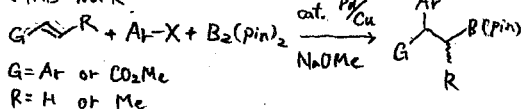
山

Arylboration of Alkenes by Cooperative Palladium/Copper Catalysis

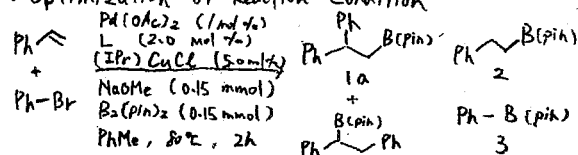
The work by Yashida



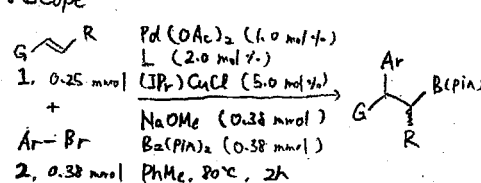
This work



Optimization of Reaction Condition

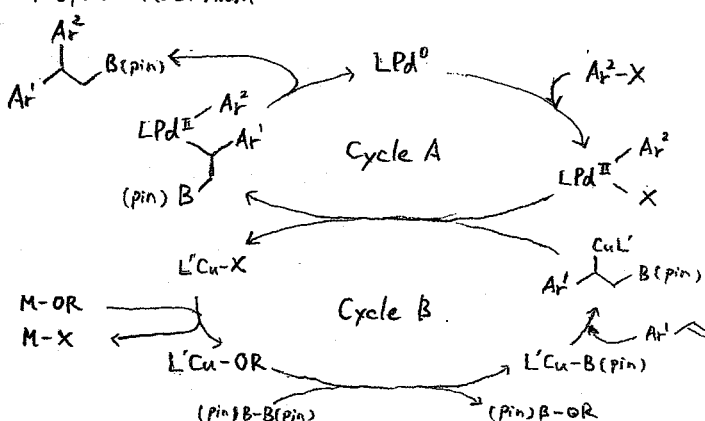


Scope



1	2	yield (%)
R = 4-OMe	Ph-Br	60
R = 4-F	"	70
R = 1,2,3,4-tetrahydroquinoline	"	71
R = MeO	Br-C ₆ H ₄ -OMe	66

Proposed Mechanism



Variation from the standard condition	yield of 1a (1a/1a')	yield of 2 (y ₂)	yield of 3 (y ₃)
none	> 95 (> 99:1)	5	8
L → PPh ₃	58 (98:2)	26	28
L → PCy ₃	84 (85:15)	9	11
L → X-Ph ₃	91 (> 99:1)	9	3
L → dppe	20 (90:10)	29	15
IPr → c ^o IPr	69 (> 99:1)	3	11
IPr → ^o IPr	95 (> 99:1)	4	7
NaOMe → LiOMe	0	0	8
NaOMe → LiO ^t Bu	> 95 (> 99:1)	0	9
NaOMe → Cs ₂ CO ₃	1	3	18
without Pd(OAc) ₂ /L	0	22	0
without (IPr)CuCl	0	0	36