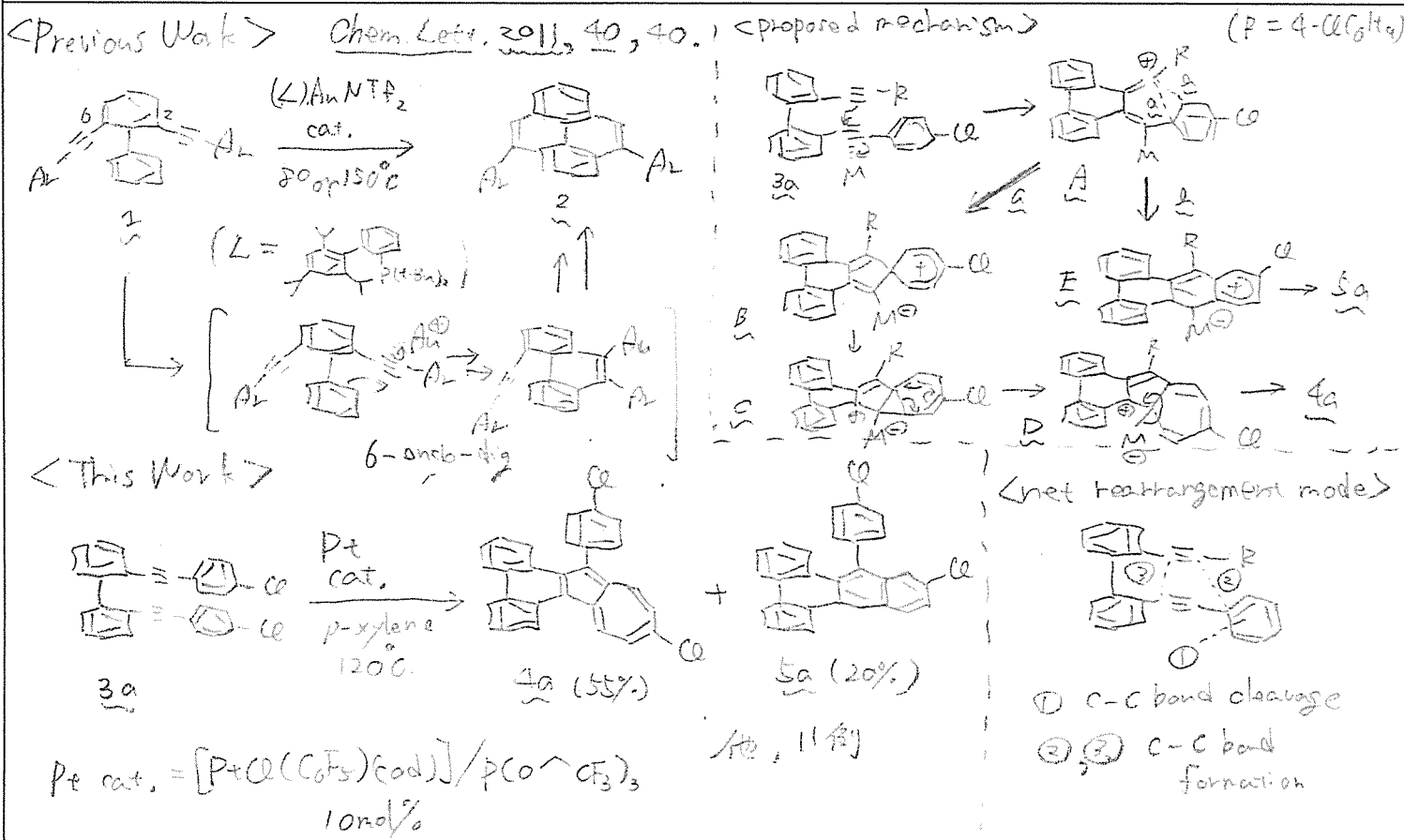
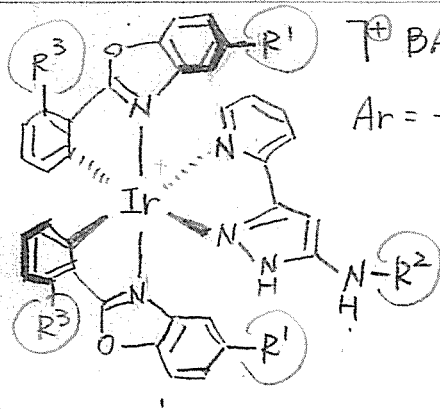
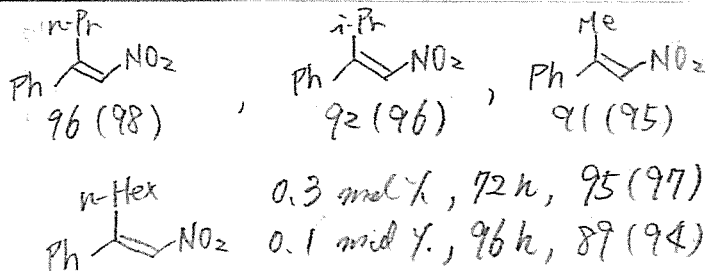
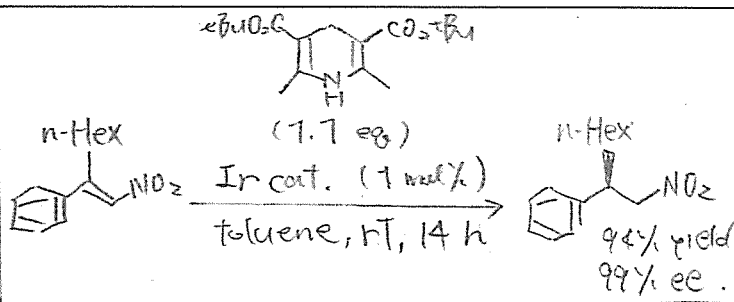
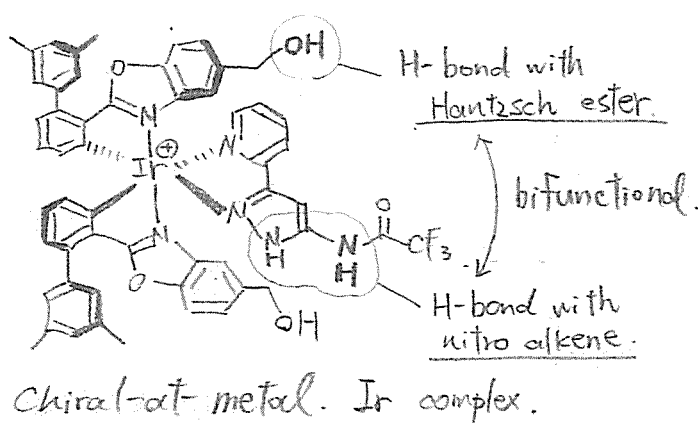


Azulenophenanthrenes from 2,2'-Di(arylethynyl)binaphenyls through C-C Bond Cleavage of a Benzene Ring



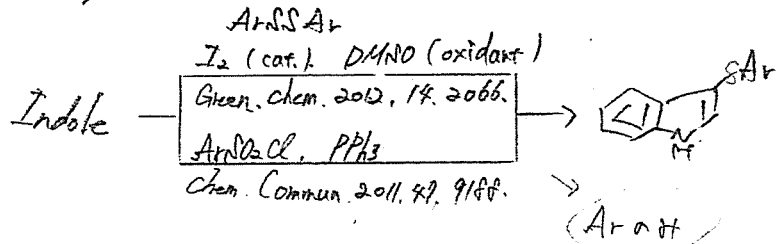
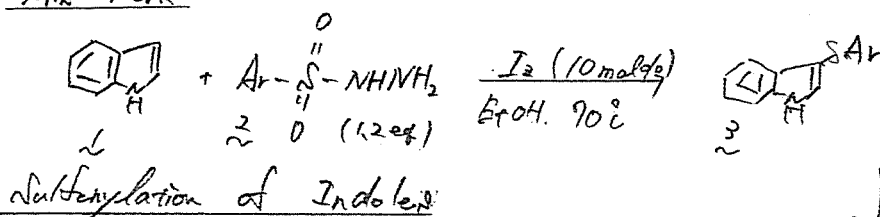
Asymmetric Catalysis with an Inert Chiral-at-Metal Iridium Complex



R ¹	R ²	R ³	yield/%	ee/%	(mol%)
CH ₂ OH	H	H	92	63	20
CH ₂ OH	nBu	H	82	70	20
CH ₂ OH	Ph	H	94	84	20
CH ₂ OH	COCF ₃	Ph	96	98	1
H	Ph	H	<20	0	20.

Iodine-Catalyzed Regioselective Sulfenylation of Indoles with Sulfonyl Hydrazines

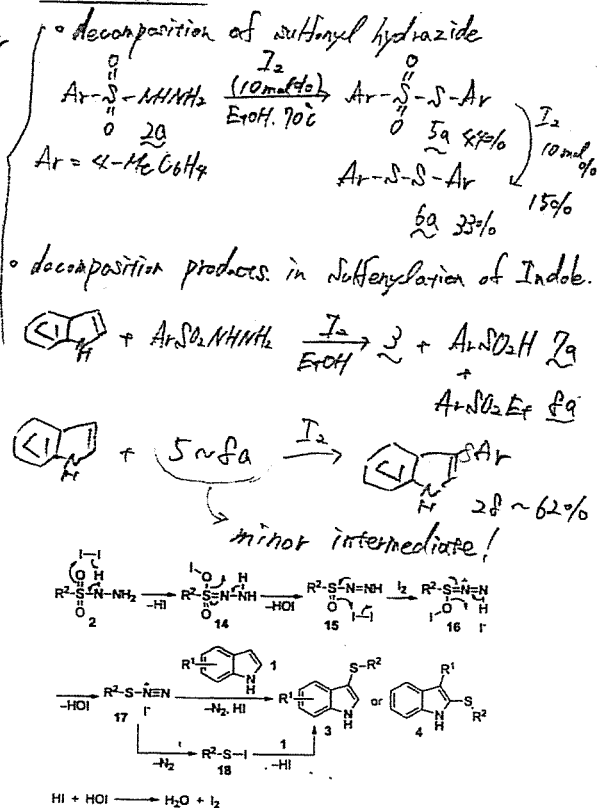
This Work



Scope

- 2nd example. 56 ~ 91%
- Alkyl sulfenyl is OK!!
- Indole 3位 置換基 好 場合 0.4 2位 i sulfenylation

Mechanism



pathway

Yasuhiro Segawa Kenichiro Itami et al.	Nagoya University	Chem. Commun. 10.1039/c3cc42655f	M2 榎島
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Pyridine-based dicarbene ligand: synthesis and structure of a bis-2-pyridylidene palladium complex

• 2-pyridylidene

c1cc[nH]c1 \leftrightarrow [H-]c1cc[n+]c1

Bis-2-pyridylidene complex \leftrightarrow 2,2'-Bipyridine complex

等電子配置

• Proposed intermediates or transition states
 [A] [B] [C]

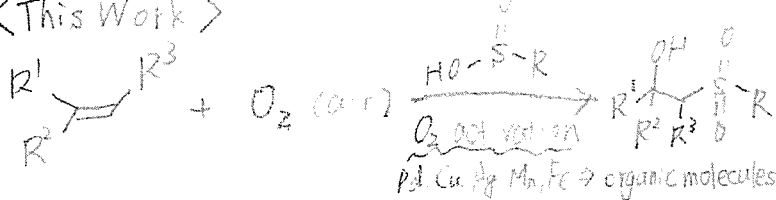
• X-ray structures
 Cl-N1: 1.365 Å
 Ni1-N2: 1.365 Å
 Ni1-N3: 2.091 Å
 Ni1-N4: 1.309 Å
 Ni1-N5: 1.352 Å
 Ni1-N6: 1.368 Å
 Ni1-N7: 2.071 Å
 Ni1-N8: 1.361 Å

• Pd is in a square planar geometry (∠ 359.29°, ∠ 359.99°)
 • Ni1-N2 炭素-H 結合は二重結合性
 • 典型的な 2-pyridylidene-M 錯体と一様

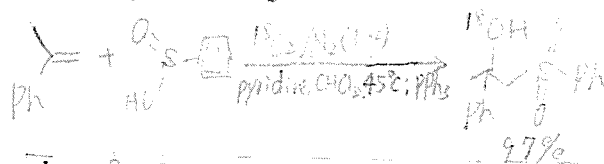
Pd(PPh₃)₄, Cs₂CO₃, THF, 100°C, 90%
 D₂O 溶液, air 中 2'-4月 安定!!

Aerobic Oxysulfonylation of Alkenes Leading to Secondary and Tertiary β -Hydroxysulfones

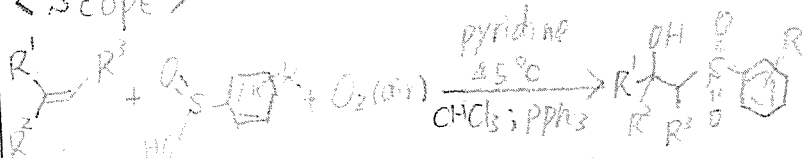
<This Work>



< ^{18}O isotope labeling experiment>



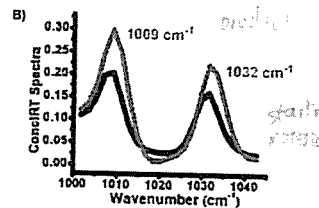
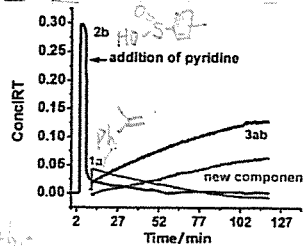
<Scope>



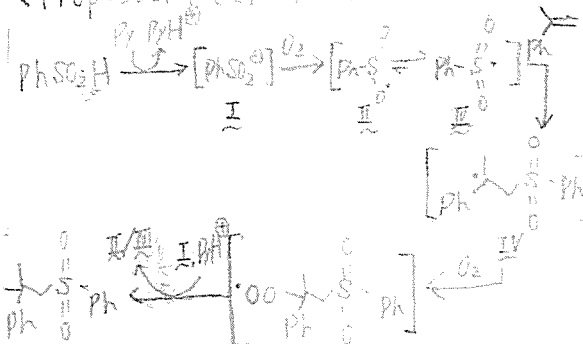
$R^1 = \text{Me}, R^2 = \text{Ph}, R^3 = \text{H}, R = \text{H}, p\text{-Me, Me, Cl, Br, Cl, F, naphthyl}$
 $R^1 = \text{Me}, R^2 = \text{H, t-Bu, Bz, NO}_2, \text{F}_3, R^3 = \text{H}, R^4 = p\text{-tolyl}$
 $R^1 = n\text{-propyl, i-propyl}, R^2 = \text{Ph}, R^3 = \text{H}, R^4 = p\text{-tolyl}$
 $R^1 = \text{H}, R^2 = \text{Ph, o/p-tolyl, p-tolyl, Cl, F}, R^3 = \text{H}, R^4 = p\text{-tolyl}$



24 examples 60~98%

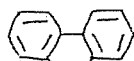


<Proposed mechanism>



Synthesis and Optical Properties of Stable Gallafluorene Derivatives: Investigation of Their Emission via Triplet States

fluorenes

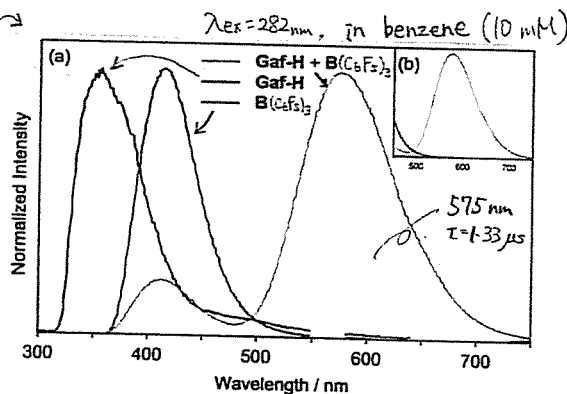
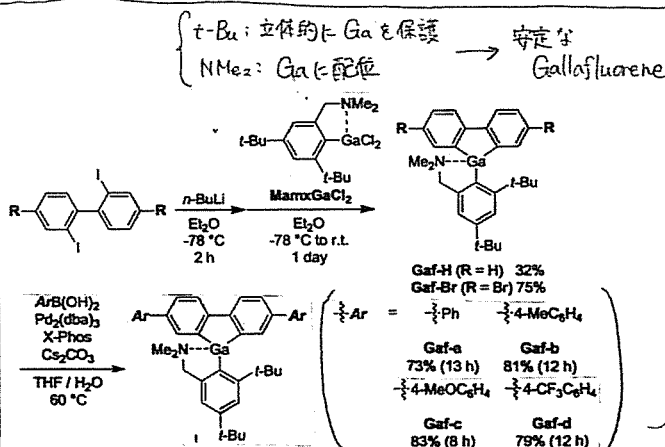


$X = \text{C, Si, B, S, Ga}$ etc.

発光特性, 寿命, 移動度に優れていることが多い。

過去に合成例はあるが光学的特性は未報告。(空气中で不安定)

安定な Gallafluorene の合成と光学的性质を報告



	$\lambda_{em}(\text{nm})$	τ	excited complex II
Gaf-H + B(C ₆ F ₅) ₃	575	1.33 μs	(exciplex)
Gaf-H	369	< 5 ns	

\rightarrow 低温 (77K) で発光 (476nm) \Rightarrow triplet exciplex

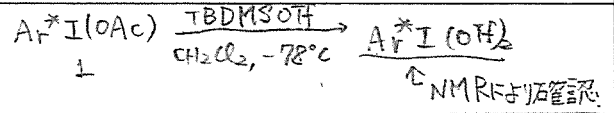
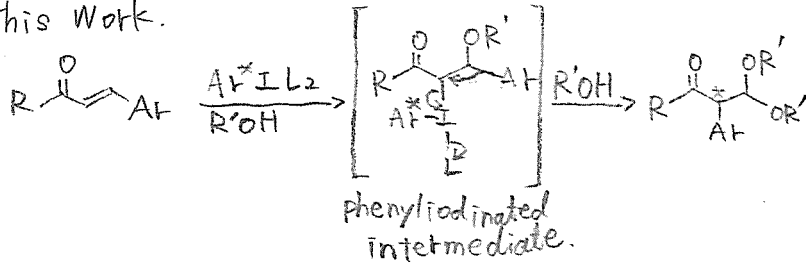
☆ Gaf-a and c と同様 exciplex を形成

☆ O₂ がトリプレットを消滅させ、575 nm の発光を消滅

\rightarrow 励起子の interaction

Stereoselective Rearrangements with Chiral Hypervalent Iodine Reagents.

This Work.



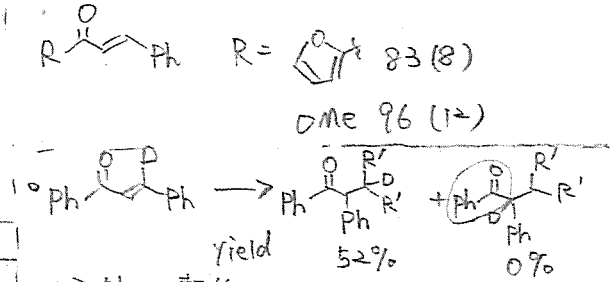
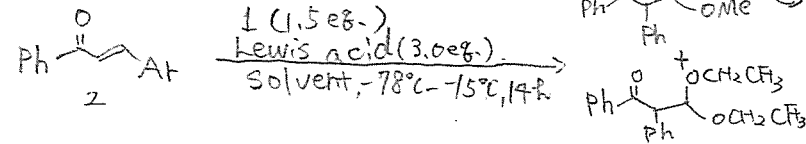
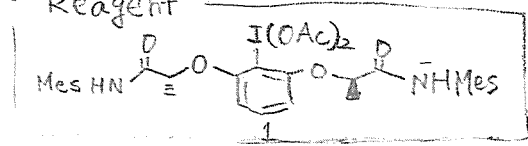
Scope

ee yield

X = F: 94 (50) NO₂: 進行しない
 Cl: 92 (38)
 Br: 91 (17)

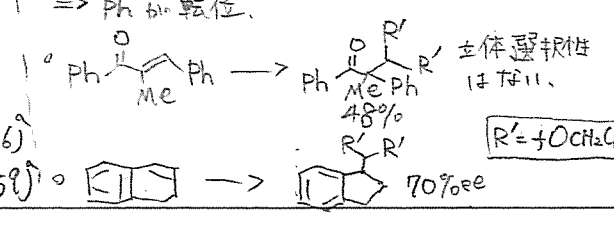
X = Me: 86 (80) tBu: 52 (65)
 iPr: 89 (68)

Reagent



Entry	Lewis acid	solvent	3ee (%)	4ee (%)
1	TBDMSOTf	CH ₂ Cl ₂ /MeOH (1=1)	12	-
2	TBDMSOTf	CH ₂ Cl ₂ , MeOH (80%)	86	-
3	TMSOTf	CH ₂ Cl ₂ , MeOH (80%)	88	-
4	TFOH	CH ₂ Cl ₂ , MeOH (80%)	91	-
5	TFOH	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1=1), MeOH (80%)	95 (28)	99
6	TFOH	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1=1)	-	69 (66)
7	TMSOTf	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1=1)	-	97 (59)

a: yields.



Guan-Wu Wang

University of Science and Technology of China

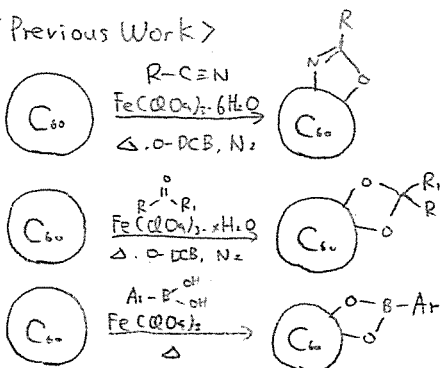
ORGANIC LETTERS

DOI: 10.1021/ol400319w

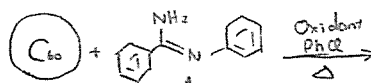
M1 上田

Synthesis and Functionalization of [60] Fullerene-Fused Imidazolines

< Previous Work >



① 反応条件



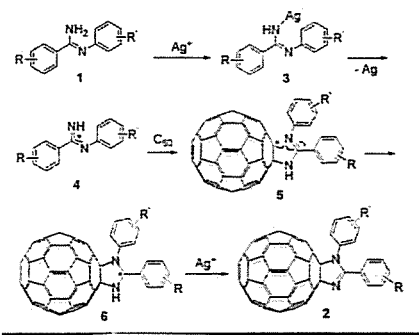
Oxidant, 温度, 時間, 比を変える
 検討した条件

Oxidant: Ag₂CO₃
 C₆₀: 1a: Oxi = 1:3:2
 Temp: 110°C
 Time: 10h

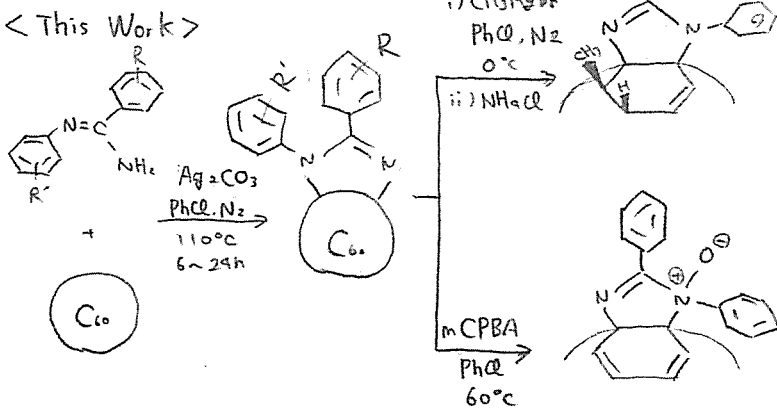
→ 56 (96)% yield

③ 反応機構

Scheme 1. Proposed Reaction Mechanism for the Formation of 2a-g



< This Work >

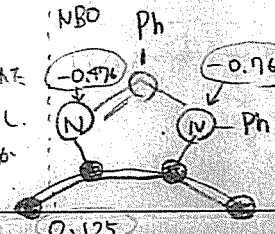


② 環にX付基, X付基, 環素を
 導入

42~54% yields

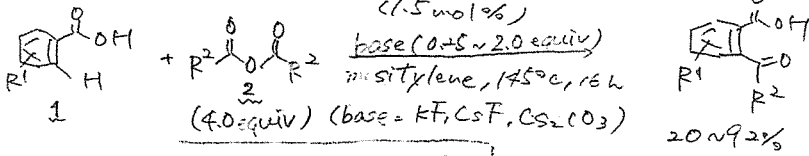
④ オルト位に置換基がある場合に、良く進行し、高収率で得ることができた。

④ 70% yield (Grignard)
 ・位置選択性



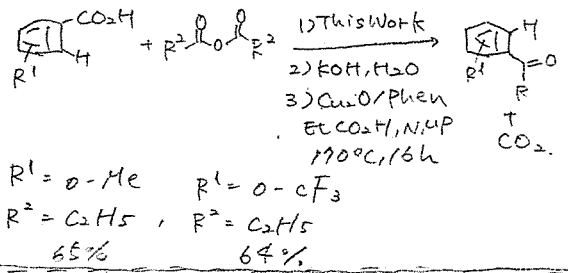
Rhodium-Catalyzed ortho Acylation of Aromatic Carboxylic Acids

This Work



Directing Group = π -alkene
 配位基 = 配位基 = 配位基

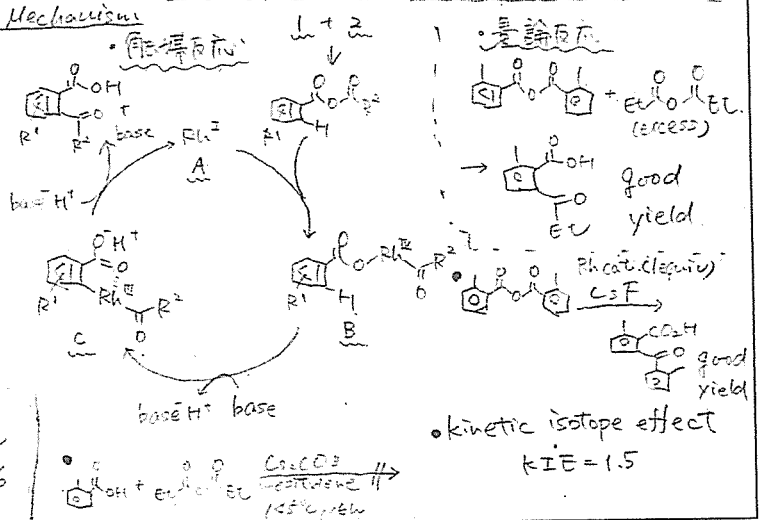
One-pot synthesis of meta-substituted ketones



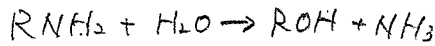
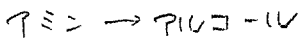
Scope

- R¹: o-Me (86%), m-Me (68%), p-Me (25%), o-Ph (87%)
- EDG (-OMe, MeO, ...): 74-92%
- EWG (-CF₃, -Cl, -Br, ...): 45-87%
- m-OH (46%), m-NMe₂ (74%)
- R²: Et (20-92%), n-Bu (82%), i-Pr (68%), t-Bu (0%)
- Yields for R¹: o-Me (88%), o-Ph (83%)

Proposed Mechanism



Direct Deamination of Primary Amines by Water To Produce Alcohols

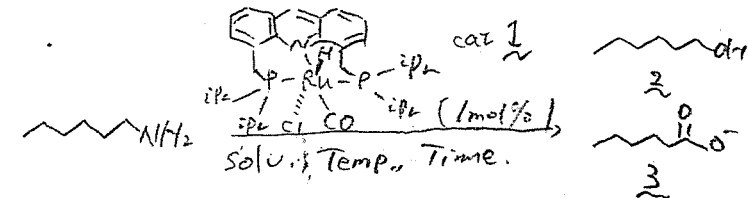
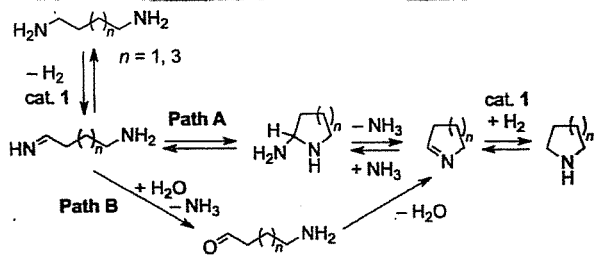
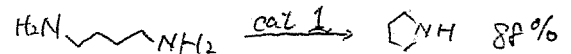
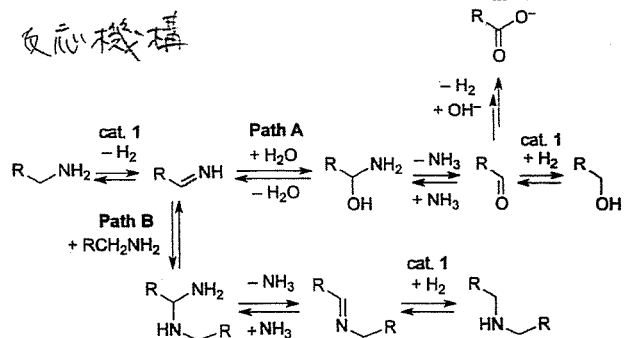


- S_N2, S_N1 - P=Oの脱離能高
- HNO₂を用いた脱アミノ化
- 生体内で起る脱アミノ化

背景展開

7-脱アミノ化, 8-脱アミノ化
 環状2級アミン - 16 examples
 (下位アミン)基のβ位にHあり(必要)

反応機構

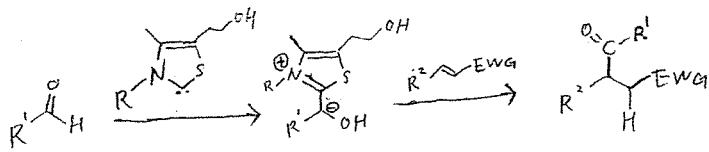


entry	solv.	Temp (°C)	Time (h)	2 (%)	3 (%)
1	H ₂ O	135	24	14	0
2	H ₂ O/dioxane	100	24	43	10
3	" (1=1)	100	72	38	23
4	"	135	24	62	13
5 (a)	"	135	48	93	<2

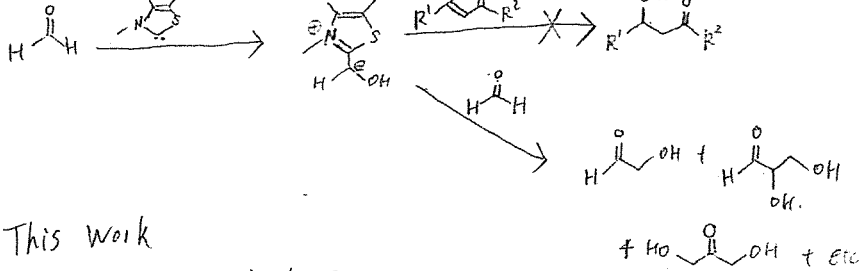
a) under H₂ (5 bar)

Catalytic Activation of Carbohydrates as Formaldehyde Equivalents
for Stetter Reaction with Enones

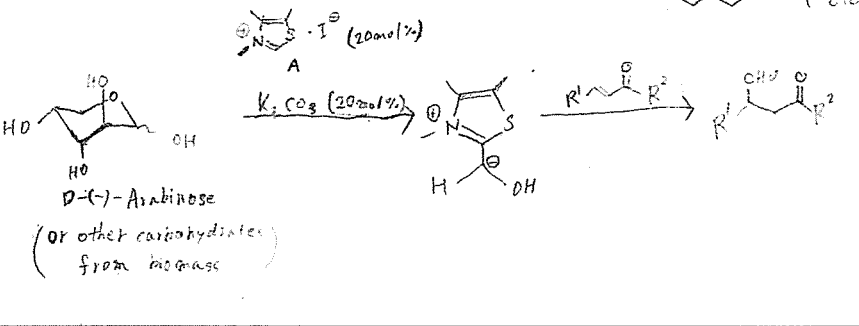
Stetter reaction



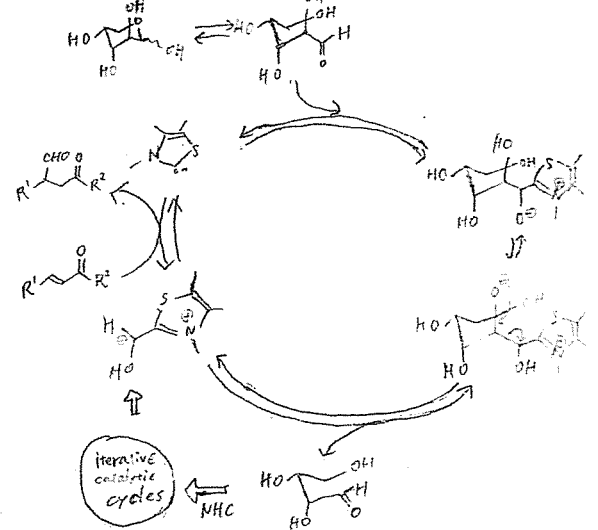
本論文にてトを用いて



This work



Mechanism



Scope

R ¹ = Ph	R ² = Ph	81%	R ¹ = Ph	R ² = p-C ₆ H ₄ CE	92%
				R ² = p-C ₆ H ₄ OCH ₃	83%
				m-C ₆ H ₄ Br	61%
				CH ₃	43%
				1-furanyl	86%
				p-C ₆ H ₄ OCH ₃	63%

Takeo Kawabata

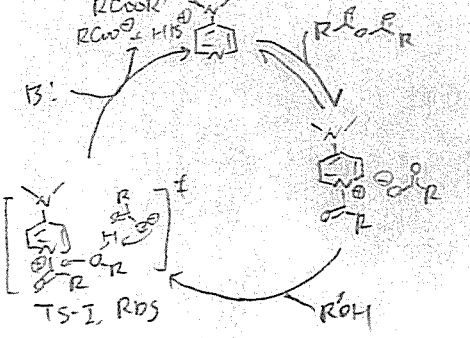
Kyoto University

ACIE, 201300665

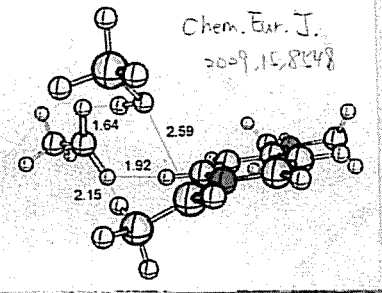
Lin

Investigation of the Carboxylate Position during the Acylation Reaction Catalyzed by Biaryl DMAP Derivatives with an Internal Carboxylate

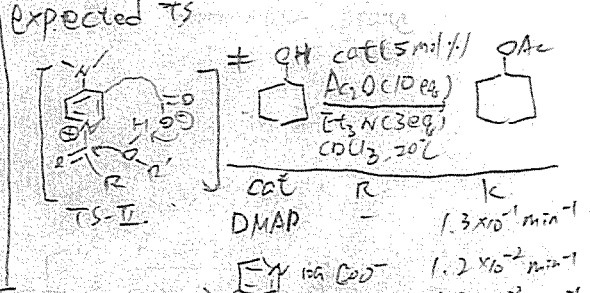
Acylation of alcohol by DMAP



Computational Exp.

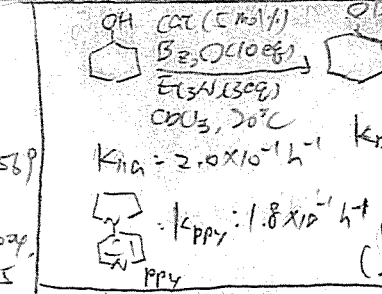


Investigation of the Carboxylate Position

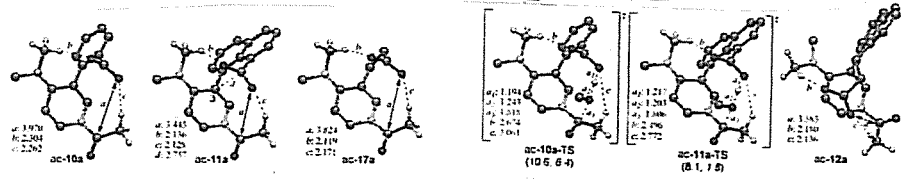


Rxn Efficiency

Acylation of 3° alcohol ACIE.
 ⇒ R₂O is faster than R₁ (1978, 56)
 Acylation of 1-2-2-propanol OL, 2004
 ⇒ R₂O is faster than R₁ 945
 ∴ Basicity R₂O > Cl⁻
 ∴ accelerate the Nu[⊖] attack of alcohol

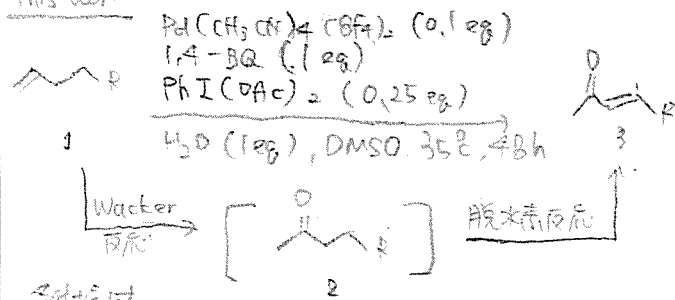


Theoretical Calculation



Terminal Olefins to Linear α,β -Unsaturated Ketones: Pd(II)/Hypervalent Iodine Co-catalyzed Wacker Oxidation-Dehydrogenation

This work



条件

- ① Pd cat.
 $\text{Pd}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$ 59%
 $\text{Pd}(\text{OAc})_2$ 3% $\text{Pd}(\text{TFA})_2$ 36%

② $\text{PhI}(\text{OAc})_2$ 量

$\text{PhI}(\text{OAc})_2$ 1.0 eq	0%
0.1 eq	38%
0.25 eq	59%
1 eq	56%

③ 1,4-BQ 量

1,4-BQ 1 eq	35%
2 eq	59%

基質展開

17 examples 51 ~ 69% (E)

- N, O を含む置換基は可.
- γ位の置換は不可



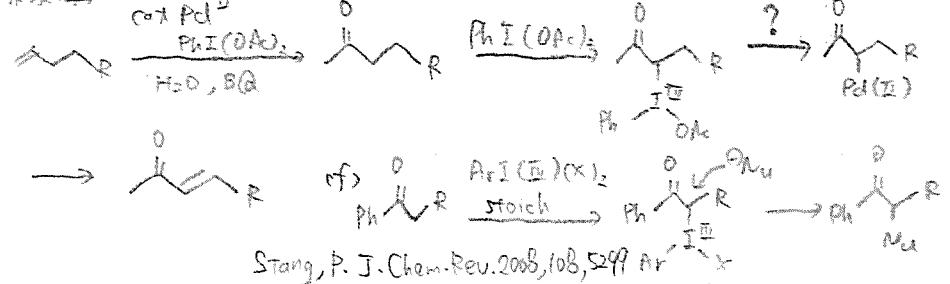
内部にβ,γ-置換は反応は進行しない (Wacker反応はβ位で進行したため)

γ位, δ位にβ,γ-置換は脱水素反応は進行しない (γ位, δ位のα-CH結合がβ位より弱いから)

β位に3級炭素の置換は脱水素反応は進行しない



機構



Catalytic Asymmetric Reductive Acyl Cross-Coupling: Synthesis of Enantioenriched Acyclic α,α -Disubstituted Ketones

多くのα,β-不飽和ケトン官能化反応

→ E/E' or E/E' 等価体を経由

そのため, C-C結合の立体化学は

① E/E' の幾何学 ② 元置換基の立体化学に依存

加えて, 非環状 α,α -置換ケトンの合成には

(1) E/E' の元置換基の選択 (2) ラセミ化の制御

が必要となる

Table 2. Substrate Scope of Benzyl Chlorides

entry	R ¹	R ²	Pdt	yield (%) ^a	ee (%) ^b
1	H	Me	3a	79	93
2 ^c	4-Me	Me	3b	74	93
3 ^c	3-Me	Me	3c	75	93
4 ^c	2-Me	Me	3d	35	72
5 ^c	4-OMe	Me	3e	56	86
6 ^d	4-Cl	Me	3f	76	91
7 ^d	4-Br	Me	3g	73	94
8 ^e	4-CF ₃	Me	3h	64	82
9 ^e	2-naphthyl	Me	3i	65	91
10	H	Et	3j	50	94
11	Cl	Et	3k	65	90
12	H	Bn	3l	79	93
13 ^f	H	CH ₂ OTBS	3m	51	89
14	H	4-pentenyl	3n	38	92
15	2,3-dihydro-1H-inden-1-yl		3o	68	78

~基質展開~

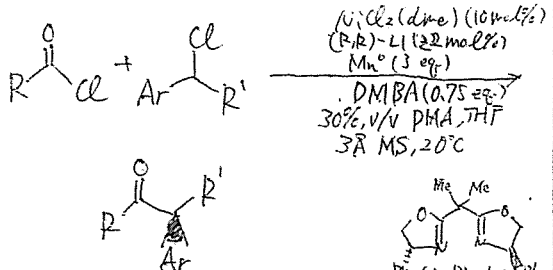
Table 3. Substrate Scope of Acid Chlorides^a

entry	R ¹	R ²	Pdt	yield (%) ^a	ee (%) ^b
1	H	Me	3a	79	93
2 ^c	4-Me	Me	3b	74	93
3 ^c	3-Me	Me	3c	75	93
4 ^c	2-Me	Me	3d	35	72
5 ^c	4-OMe	Me	3e	56	86
6 ^d	4-Cl	Me	3f	76	91
7 ^d	4-Br	Me	3g	73	94
8 ^e	4-CF ₃	Me	3h	64	82
9 ^e	2-naphthyl	Me	3i	65	91
10	H	Et	3j	50	94
11	Cl	Et	3k	65	90
12	H	Bn	3l	79	93
13 ^f	H	CH ₂ OTBS	3m	51	89
14	H	4-pentenyl	3n	38	92
15	2,3-dihydro-1H-inden-1-yl		3o	68	78

^a Isolated yield; reactions conducted on 0.2 mmol scale under a N₂ atmosphere in a glovebox. ^b Determined by SFC using a chiral stationary phase. ^c Run with 33 mol % (R,R)-L1. ^d Run with 1.25 equiv of DMBA. ^e Run in 20% v/v DMA/THF. ^f Run in 50% v/v DMA/THF.

^a Isolated yield; reactions conducted on 0.2 mmol scale under a N₂ atmosphere in a glovebox. % ee determined by SFC using a chiral stationary phase. ^b Run in 20% v/v DMA/THF. ^c Run in 10% v/v DMA/THF. ^d Run with (S,S)-L1.

~This work~



- direct ketone formation
- no stoichiometric chiral auxiliaries
- high functional group tolerance
- no epimerization of tertiary center

~予見しうる触媒サイクル~

