

Palladium-Catalyzed C-H Activation Taken to the Limit. Flattening an Aromatic Bowl by Total Arylation

<Previous Study>

C1=CC=C2C(=C1)C(=C3C=CC=C3)C=C2 + $(PhBO)_3$ (0.67 eq) $\xrightarrow{Pd(OAc)_2 \text{ cat.}, DCE, 80^\circ C, 2h}$ C1=CC=C2C(=C1)C(=C3C=CC=C3)C=C2-Ph (50%)

<This Work>

C1=CC=C2C(=C1)C(=C3C=CC=C3)C=C2 + $(ArBO)_3$ (3.5 eq) $\xrightarrow{Pd(OAc)_2 (1.5 eq), o\text{-chlorophenyl (1.5 eq)}, DCE, 60^\circ C, \text{overnight}}$ C1=CC=C2C(=C1)C(=C3C(=C(C=C3)Ar)C=C2)Ar (6-52%)

(Ar = Ph, 47%; Ar = Cc1ccc(C)cc1, 23%; Ar = Cc1ccc(Cl)cc1, 54%)

*主, かわは. 2に5個以上のPh基が導入された分子は2つしか見つからなかったこと。 e.g. 1つはEに17個Phが入った場合, MAX 5個までしか入らない!

UV of 2a

FL of 2a (cf. 2b $\lambda_{max} = 434nm$)

X-ray structure of 2c

bowl depth (cf. corannulene: 0.27 Å!)
bowl-to-bowl inversion $\Delta G^\ddagger = 2.5 kcal/mol$ (lock)

④ → ③ → ② → ①

Visible Light Photocatalytic Synthesis of Benzothiophenes

This Work

C1=CC=C(C=C1)S(=O)(=O)N=[N+]([O-])C + C1=CC=C(C=C1)X $\xrightarrow{Green\ light, Eosin\ Y, Me^+}$ C1=CC=C(C=C1)S(=O)(=O)N=[N+]([O-])C-C1=CC=C(C=C1)X

Author's previous Work

C1=CC=C(C=C1)S(=O)(=O)N=[N+]([O-])C + C1=CC=C(C=C1)X $\xrightarrow{JACS, 2012, 134, 2958}$ C1=CC=C(C=C1)S(=O)(=O)N=[N+]([O-])C-C1=CC=C(C=C1)X

Optimized reaction conditions

C1=CC=C(C=C1)S(=O)(=O)N=[N+]([O-])C + C1=CC=C(C=C1)X $\xrightarrow{Eosin\ Y (5 mol\ %), DMSO, 20^\circ C, 14 h, LED\ 530\ nm}$ C1=CC=C(C=C1)S(=O)(=O)N=[N+]([O-])C-C1=CC=C(C=C1)X (75%)

TEMPO 15%, Cat 12%

Reaction mechanism:

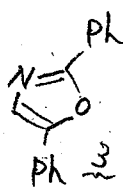
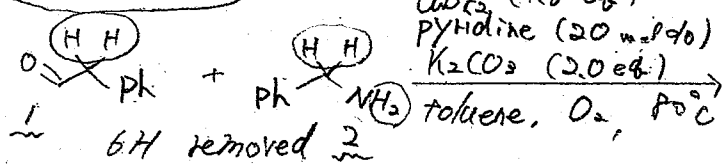
1a + C1=CC=C(C=C1)S(=O)(=O)N=[N+]([O-])C $\xrightarrow{PC^+}$ C1=CC=C(C=C1)S(=O)(=O)N=[N+]([O-])C + C1=CC=C(C=C1)S(=O)(=O)N=[N+]([O-])C

Yields:

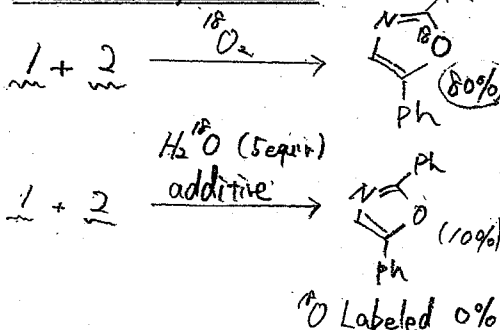
R = Me	72%	5-Ce	65%
OMe	63%	4-BL	72%
4-Ce	70%	4-F	62%
R = <chem>Cc1ccc(C)cc1</chem>		R = <chem>Cc1ccc(C)cc1</chem>	60%
R' = 4-NO ₂	81%	TMS	45%
4-OMe	72%		
3-CF ₃	62%		
R = H	61%		
4-OEt	53%		
4-Bz	55%		

Synthesis of Oxazoles through Copper-Mediated Aerobic Oxidative Dehydrogenative Annulation and Oxygenation of Aldehydes and Amines

Present Work

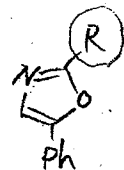


Control experiments

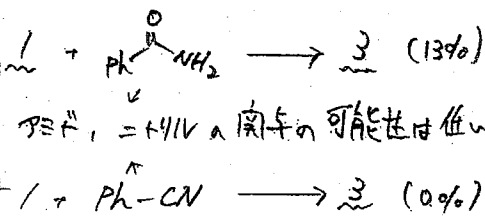


Scope

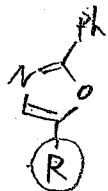
Amines



- R = Ph 82% (90%, open air)
- = 2-Me-C₆H₄ 89%
- = 3-Br-C₆H₄ 74%
- = naphthyl 89%
- = Bn 51%
- = $\text{CH}_2\text{CH}_2\text{Ph}$ 57%
- = $(\text{CH}_2)_6\text{CH}_3$ 50%
- = Me 74%

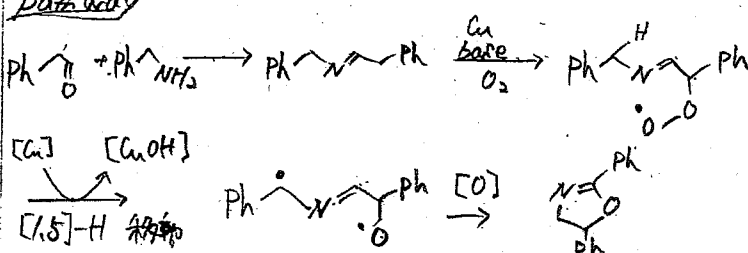


aldehydes



- R = 2-Me-C₆H₄ 68%
- = 4-OMe-C₆H₄ 72%
- = 4-F-C₆H₄ 62%
- = Me 0%

Pathway



Makoto Fujita et al.	The University of Tokyo (Japan)	J. Am. Chem. Soc. (10.1021/ja308101a)	Ikeda
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Temporary and Permanent Trapping of the Metastable Twisted Conformer of an Overcrowded Chromic Alkene via Encapsulation

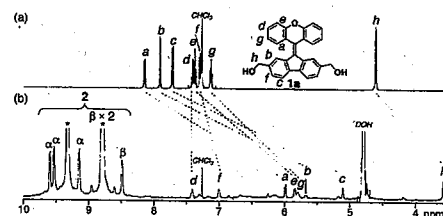
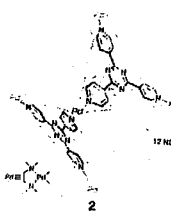
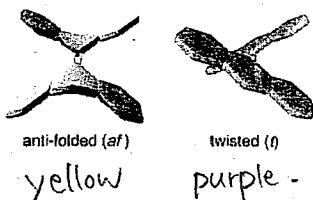
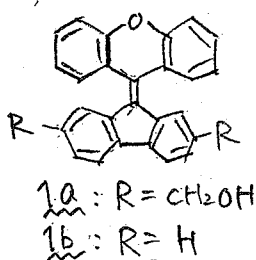


Figure 2. ¹H NMR spectra (500 MHz, 300 K) of (a) 1a in CDCl₃ and (b) 2-(t-1a) in D₂O (* labels denote signals of free cage 2).

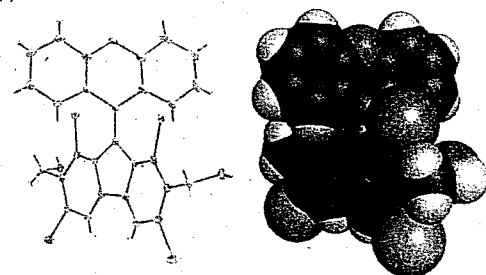
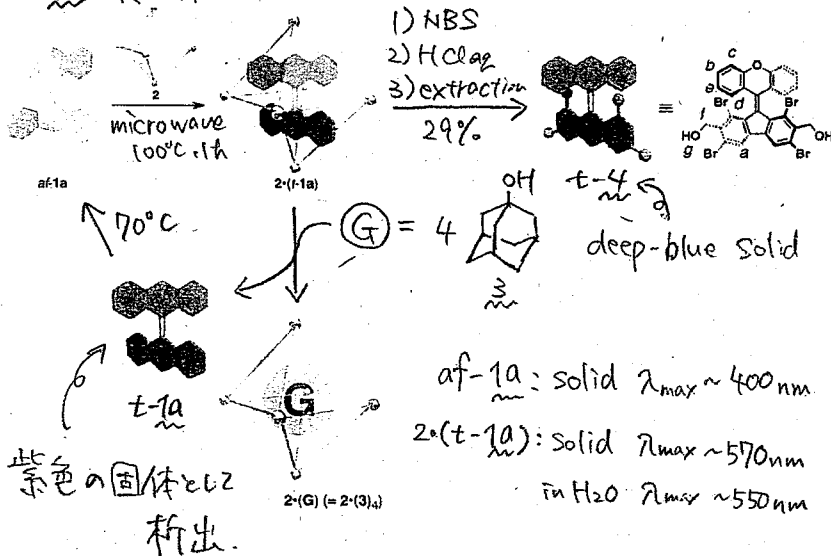


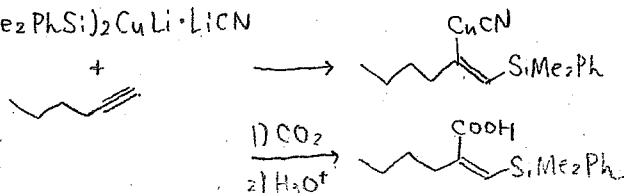
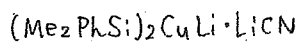
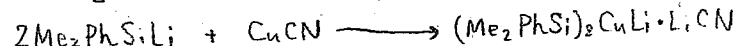
Figure 5. (a) Schematic representation of the bromination of t-1a within cage 2. (b) ¹H NMR spectrum (300 K, 500 MHz, CDCl₃) of compound t-4 obtained after purification. (c) X-ray crystal structure of t-4: (left) ORTEP drawing (ellipsoids at the 50% probability level); (right) space-filling model (C, purple; H, white; O, red; Br, orange). Solvents have been omitted for clarity.

Copper-Catalyzed Silacarboxylation of Internal Alkynes by Employing Carbon Dioxide and Silylboranes

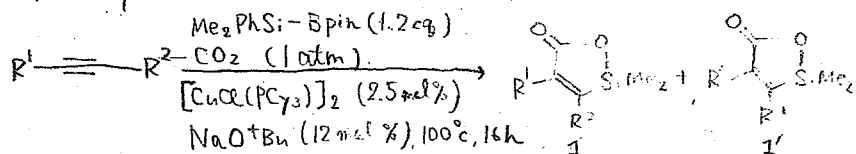
* Silacarboxylation of alkynes

< Stoichiometric Reaction >

• Fleming et al (1980) only one example!

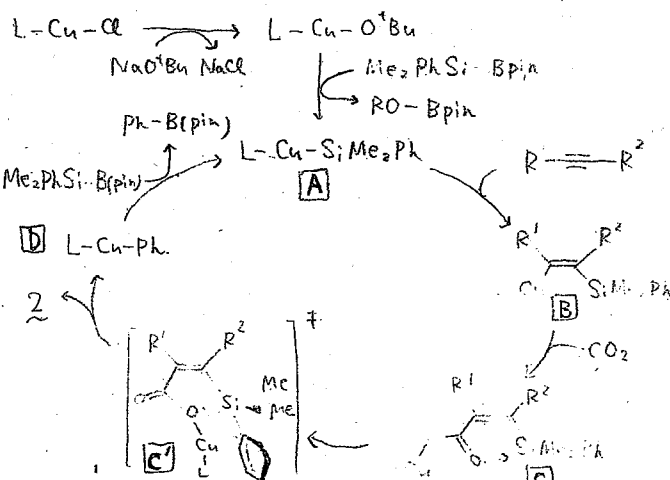


< Catalytic Reaction (This Work) >



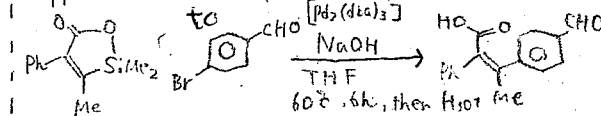
R = Ar, R' = Me or silyl, Yield: 80-97%, 2/2': 95/5 前後 (2+2')

Ar の 1,3 位に 電子供与基 求引基 があることも 進行 (-OMe, Me, Br, CO2Et)



silaboration を經由する機構の否定
 (pin)B
 ① Bu-C≡C-SiMe2Ph + CO2 $\xrightarrow[\text{NaOtBu}]{[\text{CuCl}(\text{PCy}_3)]}$ \nrightarrow
 ② silaboration LT 化合物は観察されなかった。

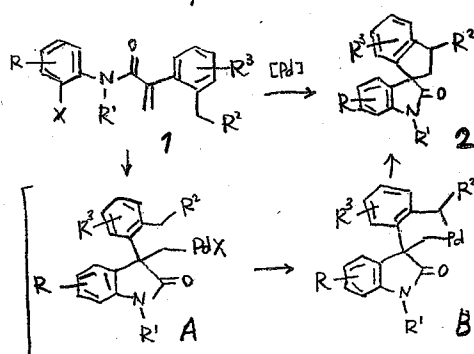
< Application for Hiyama coupling >



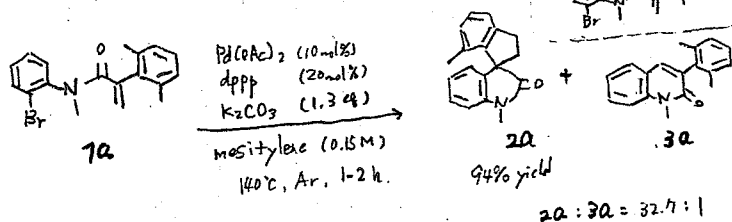
Activation of a C(sp³)-H Bond by Transient σ-Alkylpalladium(II) Complex: Synthesis of Spirooxindoles Through a Palladium-Catalyzed Domino Carbopalladation/C(sp³)-C(sp³)-C Bond-Formation Process

This Work

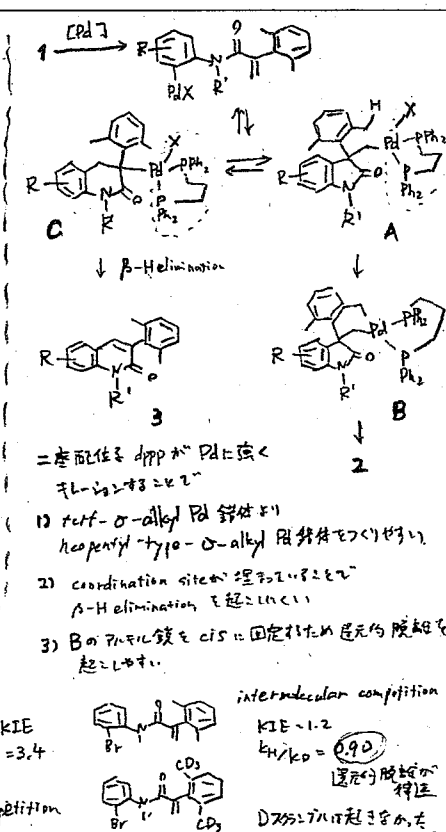
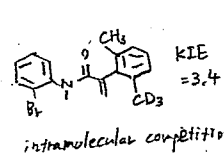
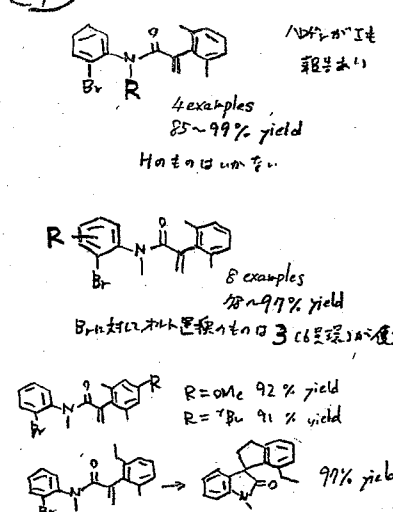
Domino carbopalladation



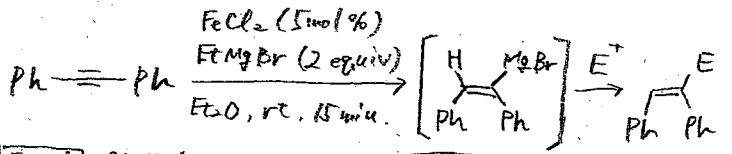
最適条件



Scope



Iron-Catalyzed Chemo- and Stereoselective Hydromagnesiation of Diarylkynes and Dienes



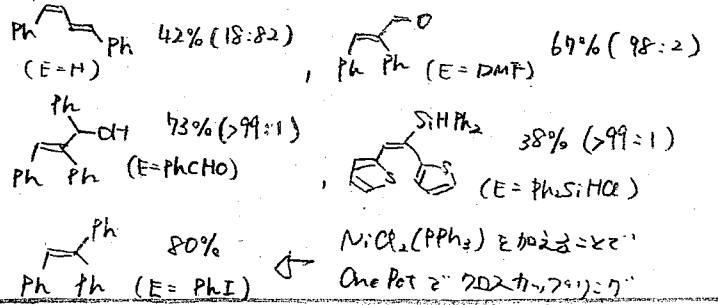
E = H: 94% (E/Z = 2:98), E = allyl: 92% (E/Z = 3:97)

• Grignard: 環状のものや Bu 等は低収率。→ EtMgBr 最適
2当量未満では低 Conversion.

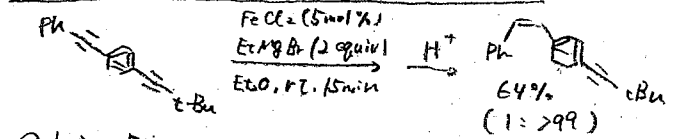
• Ligand: PBu₃ 等が反応を阻害し、反応しないう。→ $\text{P}(\text{t-Bu})_3$ 最適

Scope

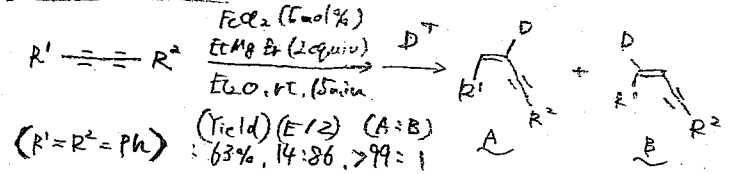
X	Yield	E/Z
(X=Me)	89%	(4:96)
(X=I)	64%	(6:94)
(X=F)	81%	(6:94)
(X=OMe)	89%	(11:89)
(X=Cl)	78%	(7:93)
(X=NMe ₂)	73%	(14:86)
(X=Br)	70%	(8:92)
(X=OH)	75%	(11:89)



① $\text{P}(\text{t-Bu})_3$ は X, Diaryl 選択的 な反応。



② 1,3-Diynes

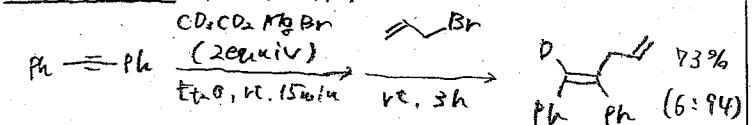


<R¹=R²=4-FC₆H₄> 63%, 11:89, 99:3

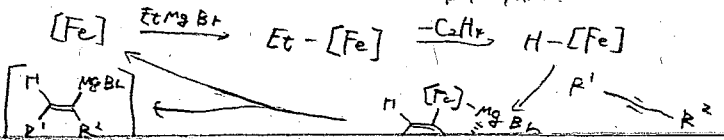
<R¹=R²=4-OMeC₆H₄> 65%, 22:78, 97:3

<R¹=Ph, R²=Me₂Si> 55%, 19:82, 98:2

③ 反応機構

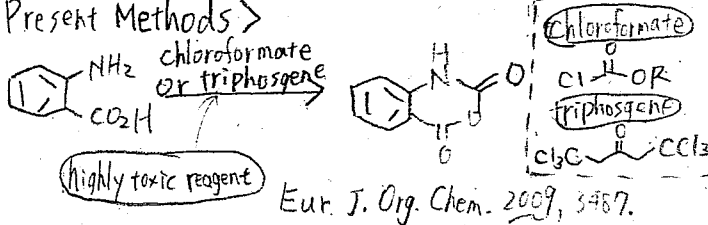


• 鉄触媒 $\text{P}(\text{t-Bu})_3$ と $\text{P}(\text{t-Bu})_3$ は β -水素 脱離

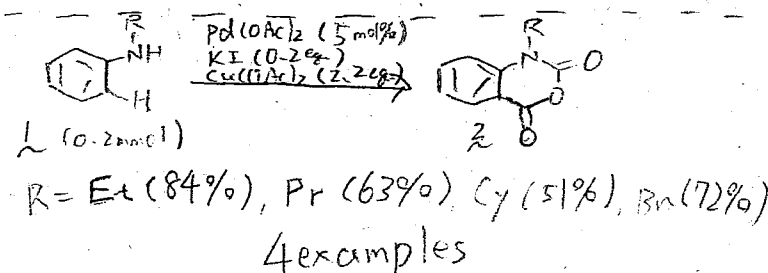
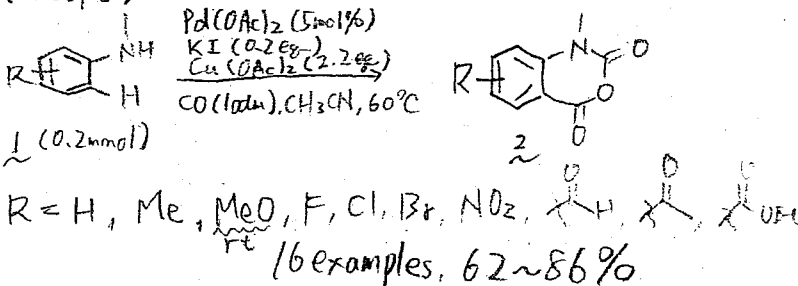


Palladium-Catalyzed Regioselective Carbonylation of C-H Bonds of N-Alkyl Anilines for Synthesis of Isatoic Anhydrides

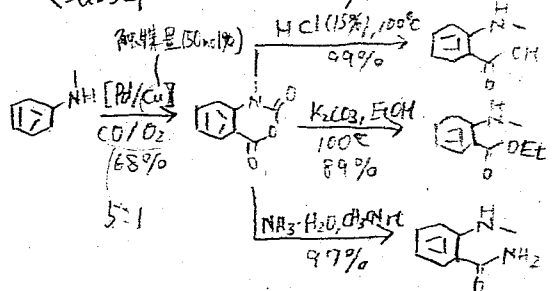
< Present Methods >



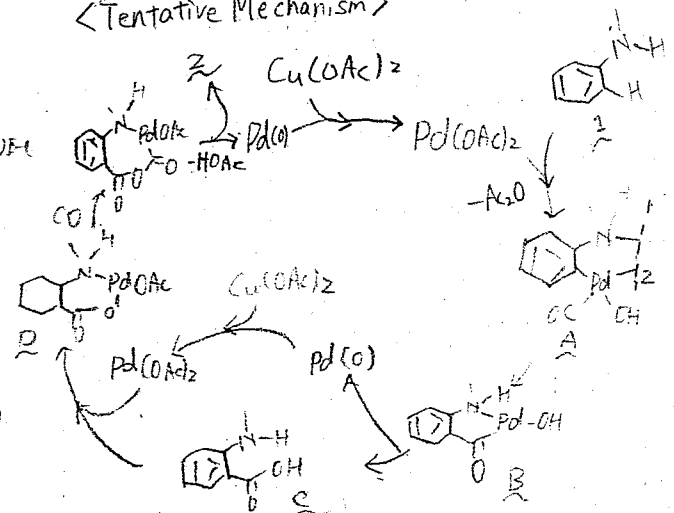
< Scope >



< Subsequent Decarboxylative Transformations >

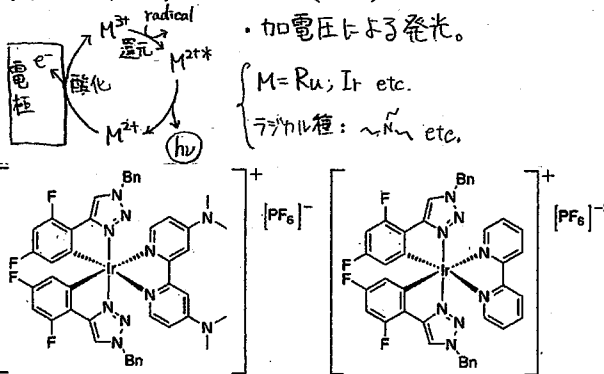


< Tentative Mechanism >

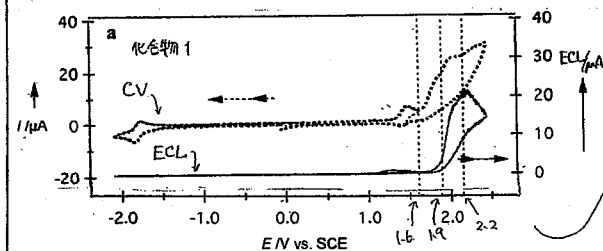


Self-Enhanced Electrochemiluminescence of an Iridium(III) Complex: Mechanistic Insight

Electrochemiluminescence (ECL): 電気化学発光



Scheme 1. Iridium(III) complexes [(dfpht)₂Ir(dmabpy)]PF₆, 1, and [(dfpht)₂Ir(bpy)]PF₆, 2.



• 4H/E/遷移金属の酸化
 $\text{P}_2\text{N}(\text{CH}_3) \rightarrow \text{P}_2\text{N}^+(\text{CH}_3) + \text{e}^-$, $\text{P}_2\text{N}^+(\text{CH}_3) \rightarrow \text{P}_2\text{N}^{2+}(\text{CH}_3) + \text{H}^+$

① $[\text{Ir}-2\text{dma}]^+ + \text{e}^- \rightarrow [\text{Ir}-2\text{dma}]^0$
 ② $[\text{Ir}-2\text{dma}]^+ \rightarrow [\text{Ir}-2\text{dma}]^{2+} + \text{e}^-$
 ③ $[\text{Ir}-2\text{dma}]^+ + [\text{Ir}-2\text{dma}]^{2+} \rightarrow [\text{Ir}-2\text{dma}]^{3+} + [\text{Ir}-2\text{dma}]^+$
 ④ $[\text{Ir}-2\text{dma}]^{3+} \rightarrow [\text{Ir}-2\text{dma}] + \text{h}\nu_1 (593\text{nm})$
 ⑤ $[\text{Ir}-2\text{dma}]^{2+} \rightarrow [\text{Ir}-2\text{dma}]^{2+} + \text{e}^-$
 ⑥ $[\text{Ir}-2\text{dma}]^{2+} \rightarrow [\text{Ir}-2\text{dma}]^{2+} + \text{H}^+$
 ⑦ $[\text{Ir}-2\text{dma}]^{2+} + [\text{Ir}-2\text{dma}]^{2+} \rightarrow [\text{Ir}-2\text{dma}]^{3+} + [\text{Ir}-2\text{dma}]^+$
 ⑧ $[\text{Ir}-2\text{dma}]^{3+} + [\text{Ir}-2\text{dma}]^+ \rightarrow [\text{Ir}-2\text{dma}]^{2+} + [\text{Ir}-2\text{dma}]^{2+}$
 ⑨ $[\text{Ir}-2\text{dma}]^{3+} \rightarrow [\text{Ir}-2\text{dma}] + \text{h}\nu_2 (608\text{nm})$
 ⑩ $[\text{Ir}-2\text{dma}]^{3+} \rightarrow [\text{Ir}-2\text{dma}]^{2+} + \text{h}\nu_3 (651\text{nm})$

ECL 測定
 Start 0V
 ↓ -1.82V (①)
 ↓ -2.10V (②, ③, ④)
 ↓ 1.20V (⑤, ⑥, ⑦, ⑧)
 ↓ 1.70V (⑨, ⑩)
 593nm, 608nm, 651nm 発光
 ↓ 2.42V 終了
 ↓ 0V 減少 end.
 (cycle可)

Rhodium-Catalyzed Ring Opening of Benzocyclobutenols with Site-Selectivity Complementary to Thermal Ring Opening

• Ring Opening of Benzocyclobutenols

proximal OH, distal

heat, hν, base → indole

Rh(I) This work → indole

• Plausible Mechanism

1a + Et → Et (4a) → indole (A) → indole (B) → indole (C)

• Conditions

1a → 2a + 3a

entry	conditions	2a	3a
1	toluene, 100°C	86	0
2	NaOH aq, dioxane, rt	87	0
3	Rh(acac)(CH ₂ CH ₂) ₂ (5 mol%), P(t-Bu) ₃ (10 mol%), toluene, 100°C	14	74
4	[Rh(OH)(cod)] ₂ (2.5 mol%), toluene, 100°C	0	89
5	[Rh(OH)(cod)] ₂ (2.5 mol%), IPr (12 mol%), toluene, 100°C	80	0

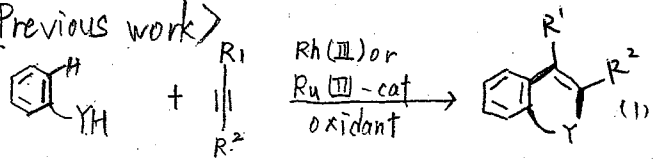
• Scope

• cyclobutenols ... (4a)

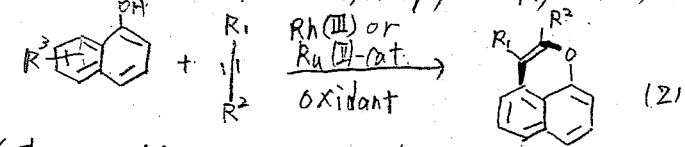
• alkynes ... (1a)

Rhodium-Catalyzed Cascade Oxidative Annulation Leading to Substituted Naphtho[1,8-bc]pyrans by Sequential Cleavage of C(sp²)-H/C(sp³)-H and C(sp²)-H/O-H Bonds

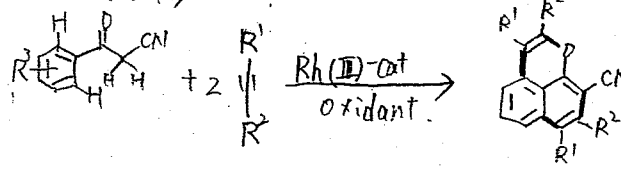
<Previous work>



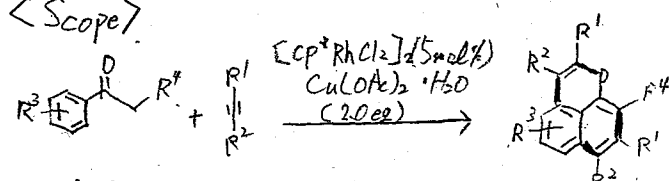
(YH = COOH, OH, NHCO_R, NHP_y, CONHR, CH=NR, etc)



<This work>



<Scope>



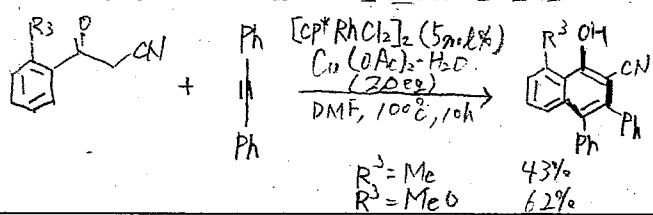
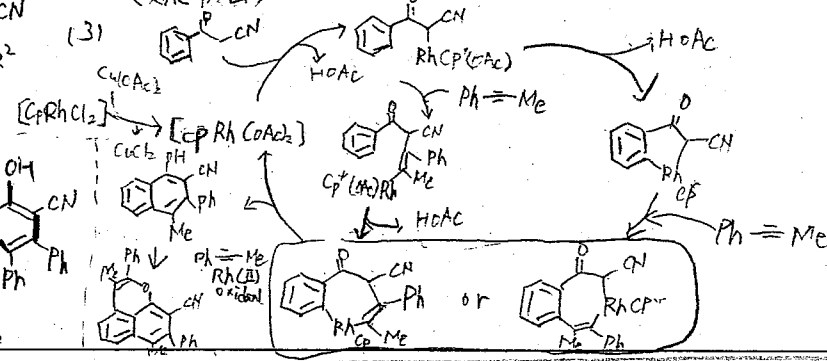
• R¹=R²=Ph, R⁴=CN
 R³: H 82%, Me 89%, Ph 91%, ^tBu 90%, MeO 91%

• R¹=R²=Ph, R³=H
 R⁴: CO₂Et 47%, NO₂ 23%, COMe 0%

• R³=H, R⁴=CN

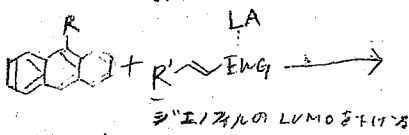
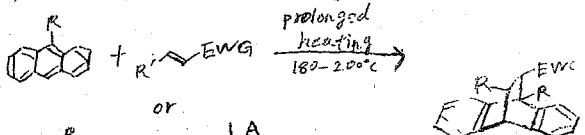
R₁, R₂ = 4-MeC₆H₄ 84%, R₁=Ph, R₂=Me 61%

<反応機構>

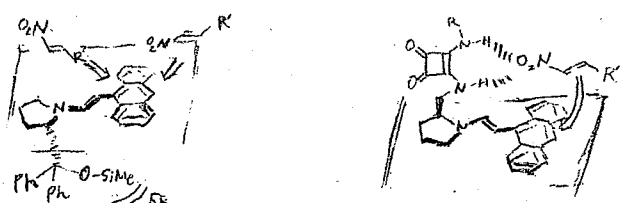
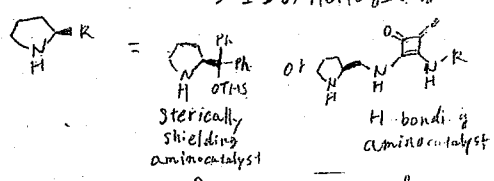
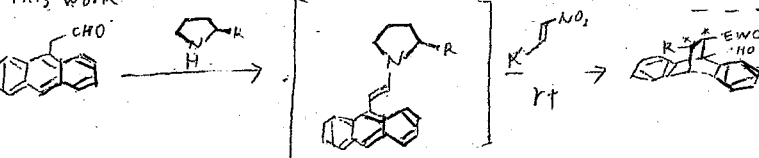


Organocatalytic Activation of Polycyclic Aromatic Compounds for Asymmetric Diels-Alder Reactions

Diels-Alder 反応



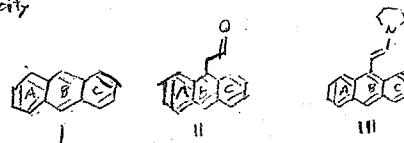
This work



Scope

Entry	Cat (anz)	R'	α [C _H]	Yield [%]	ee [%]
1	—	Ph	24	0	—
2	a (20)	Ph	16	40	-62
3	a (2)	Ph	18	95	98
4	a (2)	2-ClC ₆ H ₄	18	90	96
5	b (2)	3-NO ₂ C ₆ H ₄	18	94	97
6	b (2)	4-OMeC ₆ H ₄	48	88	97
7	a (2)	3-pyridyl	24	64	96
8	a (5)	C ₆ H ₁₁	48	83	92

Aromaticity



Structure	NICS (3) _{zz} (A, B, C)	HOMO [eV]
I	-25.3, -34.9, -25.3	-6.9
II	-24.6, -31.6, -24.0	-6.8
III	-24.2, -30.5, -24.1	-5.9