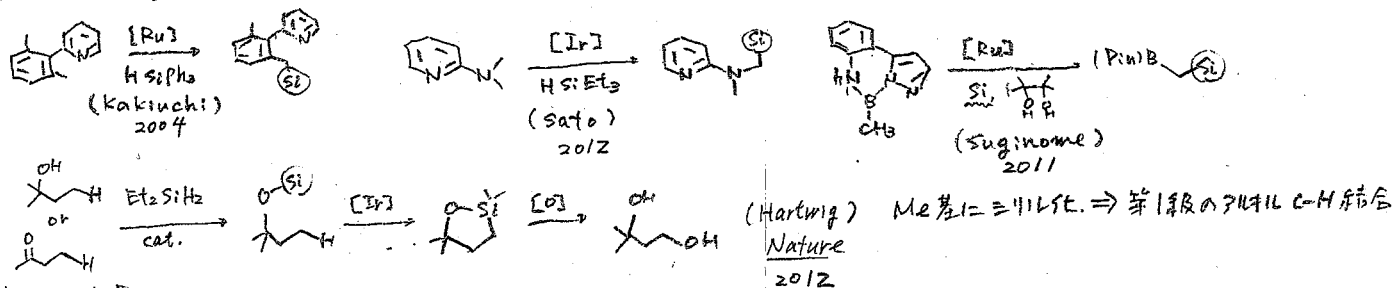
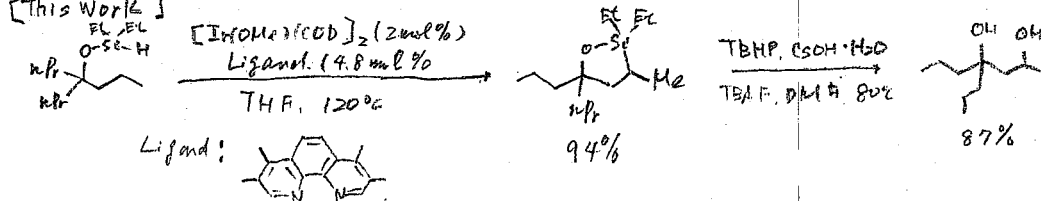


**Iridium-Catalyzed Regioselective Silylation of Secondary Alkyl C-H Bonds for the Synthesis of 1,3-Diols**

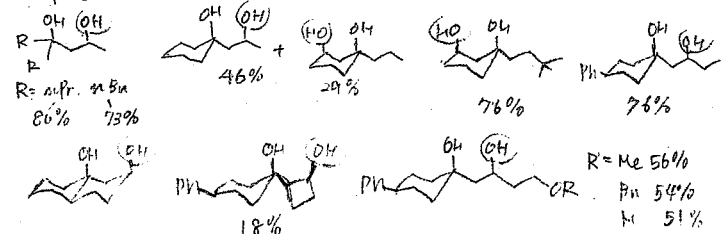
[Previous Work]



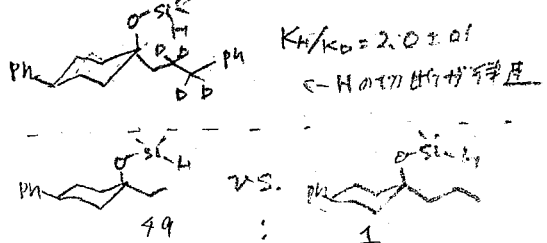
[This Work]



[Scope]



[Mechanism]



この反応は 1,3-ジオールの合成に有効である。Thorpe-Ingold効果。

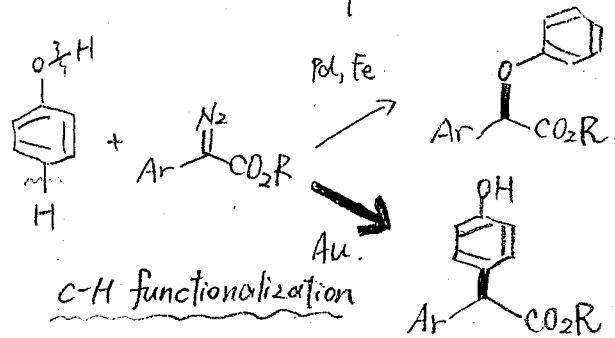


Primary C-H bondは反応しない。

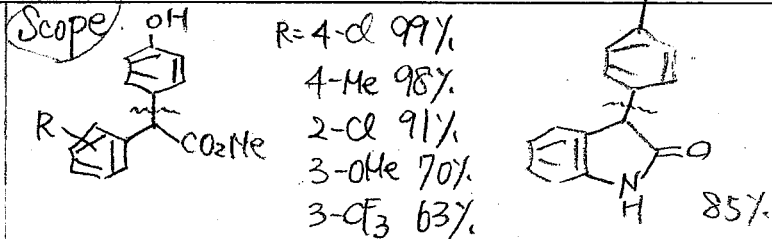
この反応は primary C-H bondよりも secondary C-H bondに選択的である。

**Highly Site-Selective Direct C-H Bond Functionalization of Phenols with  $\alpha$ -Aryl- $\alpha$ -diazoacetates and Diazooxindoles via Gold Catalysis**

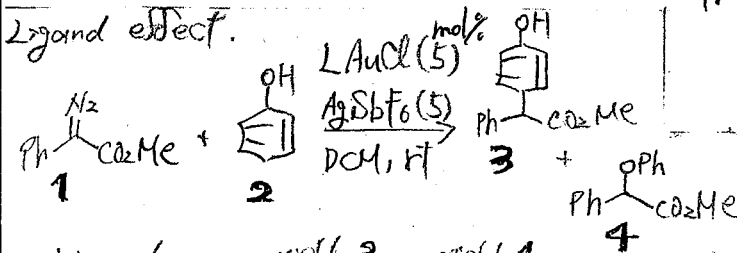
Phenol with diazo compounds.



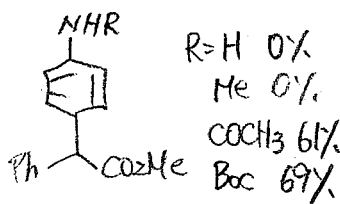
Scope



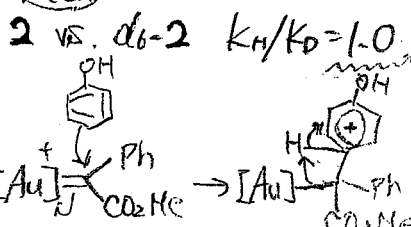
Ligand effect.



Ligand	yield 3	yield 4
PPh <sub>3</sub>	32%	46%
(EtO) <sub>3</sub> P	47%	27%
(PhO) <sub>3</sub> P	82%	0%
(2,4-tBu <sub>2</sub> C <sub>6</sub> H <sub>3</sub> O) <sub>3</sub> P	99%	0%



(Mech)



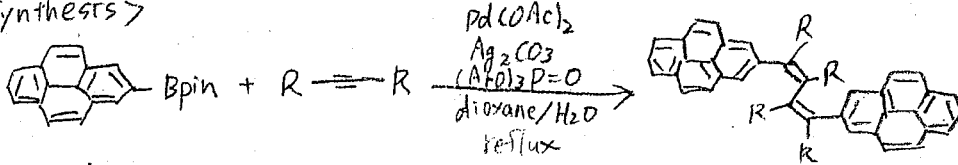
廣戸聡・小田一磨・忍久保洋

名大院工

1A7-34

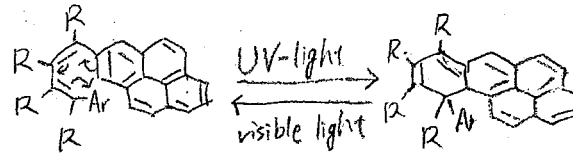
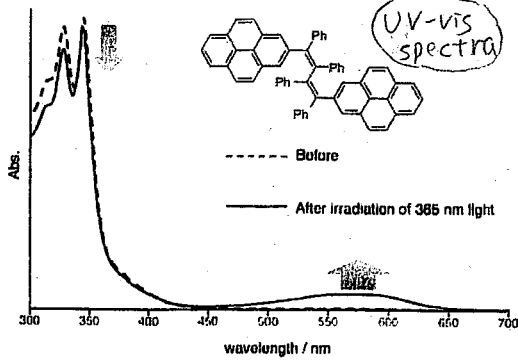
ピレン含有π共役オリゴエンの合成と物性

<Synthesis>



26% (R=Ph)  
 22% (R=C<sub>3</sub>H<sub>7</sub>)  
 14% (R=2-pyrenyl)

<Photochromism>



無色  
 無色  
 無色

-----> 紫色 (R=Ph)  
 -----> 赤紫色 (R=C<sub>3</sub>H<sub>7</sub>)  
 -----X-> 変化なし (R=2-pyrenyl)

◎ 立体障害が原因か?

<Solid state emission>

緑色の発光 (R=Ph)  
 青色の発光 (R=C<sub>3</sub>H<sub>7</sub>)

↓  
 <DFT計算>  
 ○ R=Phのとき  
 共役がπ共役とπ共役  
 分子全体に広がっている。  
 ○ R=C<sub>3</sub>H<sub>7</sub>のとき  
 ピレン上のπ共役が2倍。

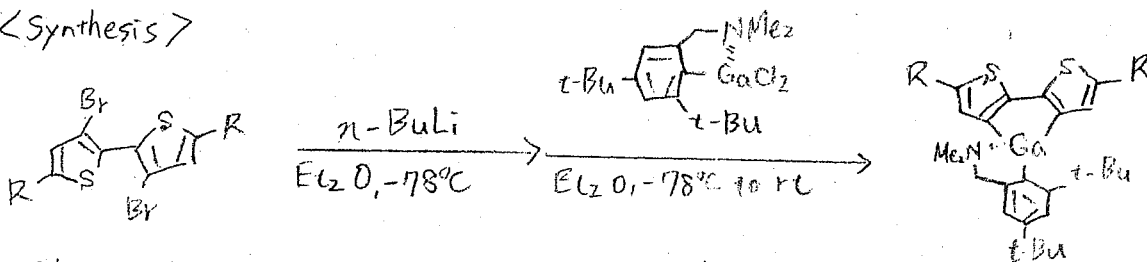
松本拓也・田中一生・中條善樹

京大院工

2A7-48

チオフェンが縮環したガロール骨格の合成とその物性

<Synthesis>



21% (R=H)  
 26% (R=TMS)

<Physicochemical properties>

	$\lambda_{ab}$ (nm)	$\lambda_{em}$	$\phi_{FL}$	HOMO(eV)	LUMO(eV)	$E_{HOMO-LUMO}$ (eV)
R=H	379	412	0.52	-5.16	-1.89	3.27
R=TMS	391	417	0.89	-5.19	-2.02	3.17
<chem>S-C6H3-S</chem>	343	362	0.13	-5.74	-2.12	3.62

X-ray analysis  
 ○ ピレン部分の  
 15°傾斜に合致  
 ○ HOMOの上昇  
 ↓  
 15°傾斜が小さく  
 なる。

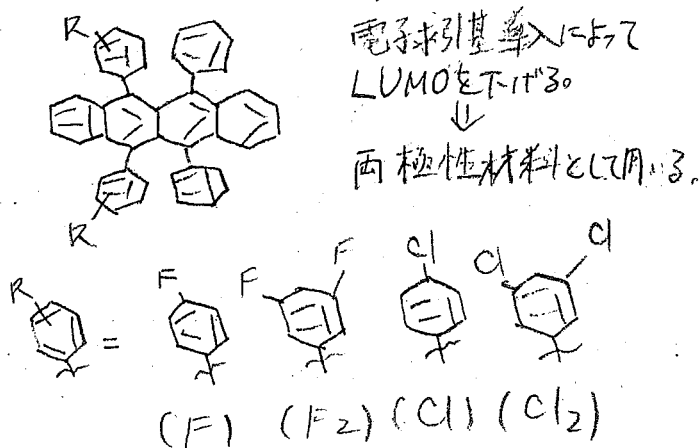
武藤裕孝・高野与一・男庭一輝・金鉄男・下谷秀和・谷垣勝巳・山本嘉則・浅尾直樹

東北大 WPI-AIMR

3A5-46

n-型特性の向上を目指した新規ルブレン誘導体の合成と物性

<Rubrene derivatives>



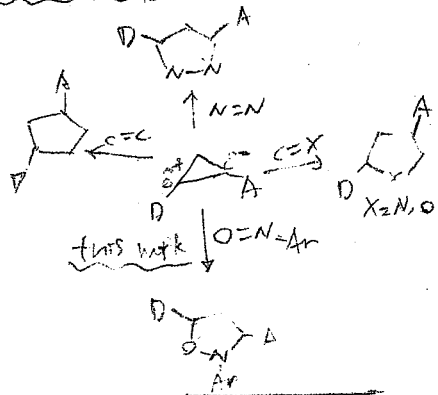
<Physicochemical properties>

	HOMO (eV)	LUMO (eV)	$E_{H1}$ (eV)	$\mu_A$	$\mu_E$
Rubrene	-5.15	-2.73	2.42	2.1	0.97
F	-5.21	-2.78	2.43	0.73	0.60
F <sub>2</sub>	-5.32	-2.87	2.45	0.02	0.043
Cl	-5.23	-2.81	2.42	0.19	0.41
Cl <sub>2</sub>	-5.33	-2.92	2.41	-	0.017

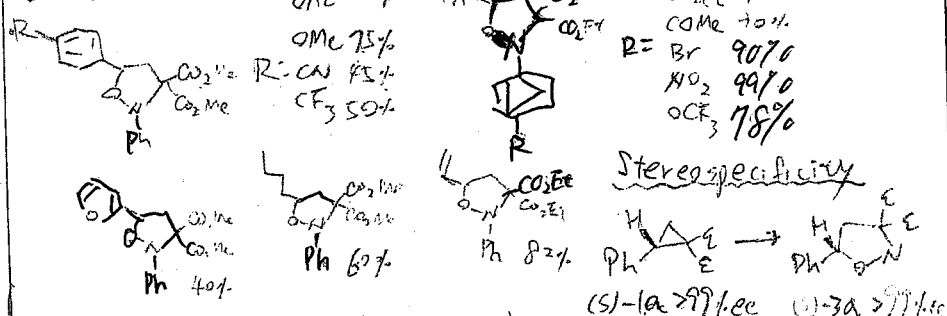
比較的高い移動度を保持しながら、LUMOを下げることに成功した。

Stereospecific Formal [3+2] Dipolar Cycloaddition of Cyclopropanes with Nitrosoarenes: An Approach to Isoxazolidines

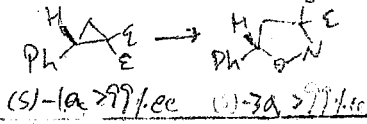
Previous Work



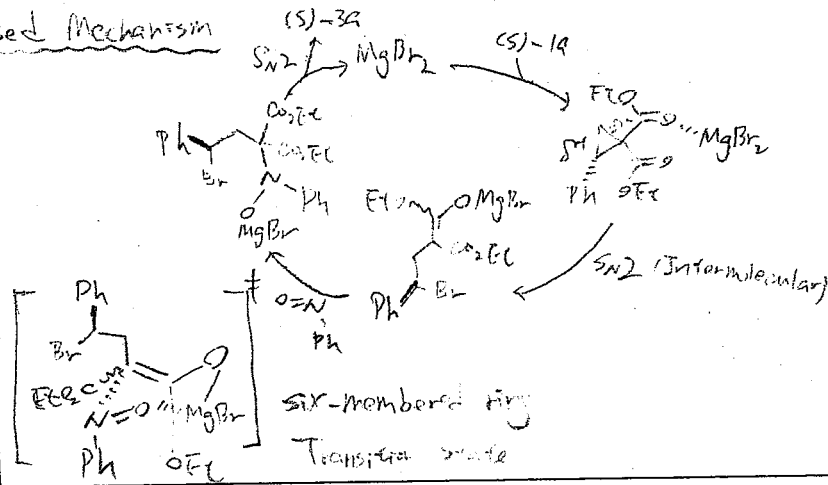
Scope



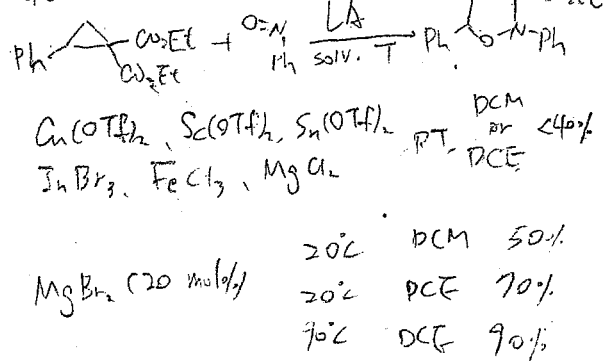
Stereospecificity



Proposed Mechanism



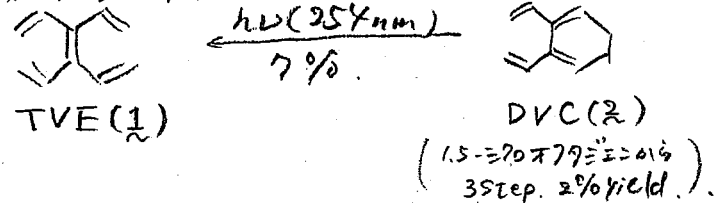
Opt. conditions



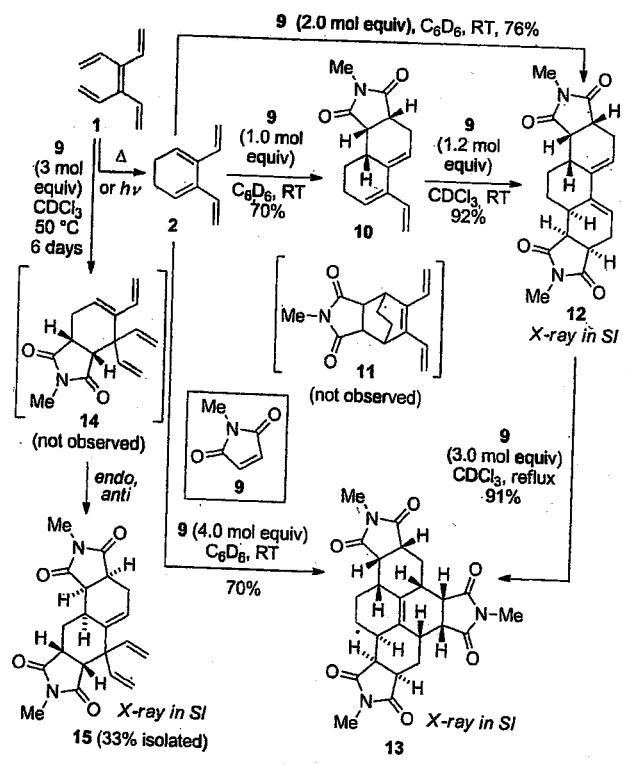
M.S. Sherburn et al. Australian National University Canberra. anie 10.1002/anie.201402840 M2 (1/2)

Tetravinylethylene

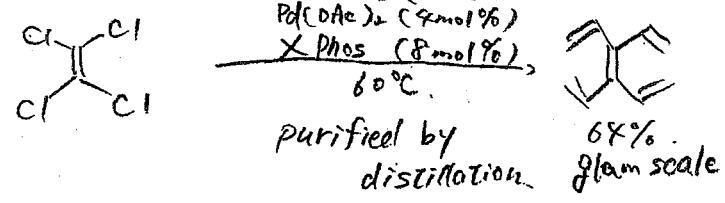
Skattebøl's work



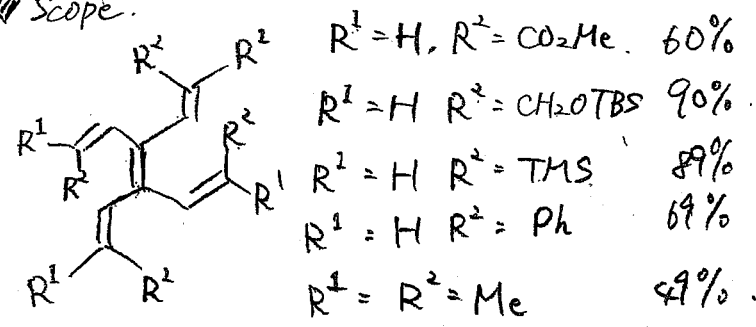
Diels-Alder Reactions using TVE (1)



This Work



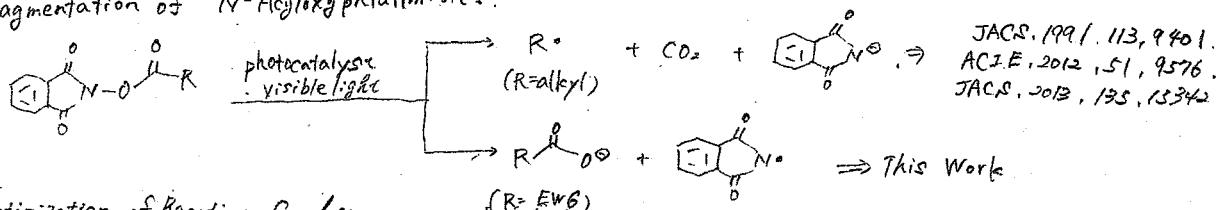
Scope



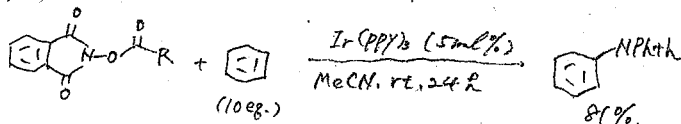
complete regio- and diastereoselectivity

# N-Acyloxypthalimides as Nitrogen Radical Precursors in the Visible Light Photocatalyzed Room Temperature C-H Amination of Arenes and Heteroarenes

Fragmentation of N-Acyloxypthalimides



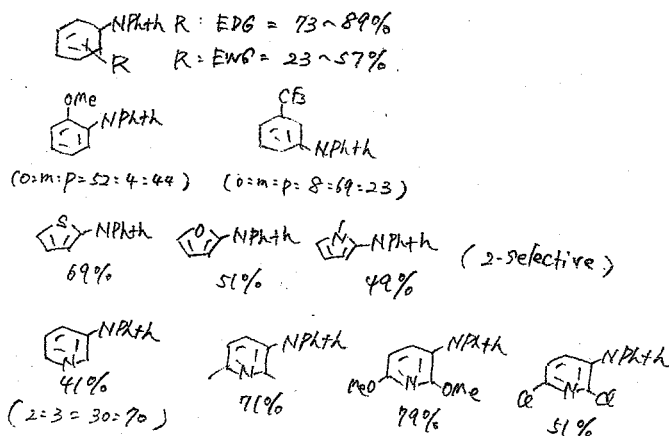
Optimization of Reaction Conditions



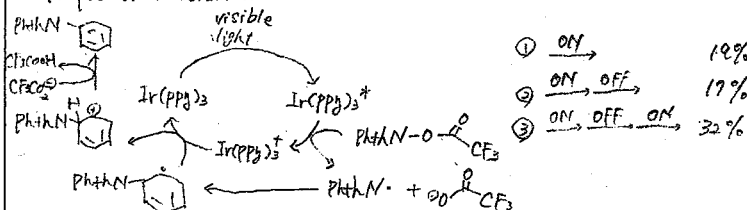
R	yield (%)	Ir cat. (mol%)	yield (%)
Me	n.r.	5	81
Ph	8	1	65
PCBPh	20	0.5	55
C <sub>6</sub> F <sub>5</sub>	53		
CF <sub>3</sub>	81		
Ts	38		

(NPhth = N1C(=O)c2ccccc12)

Scope



Proposed Mechanism



Phil S. Baran

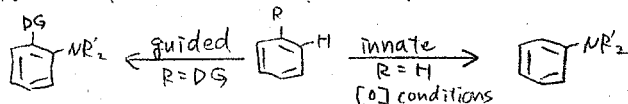
The Scripps Research Institute  
United States

JACS, ja501879c

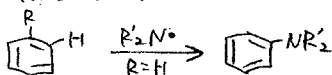
M1 田中

## A Mild, Ferrocene-Catalyzed C-H Imination of (Hetero) Arenes

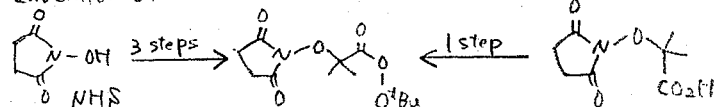
Methods for intermolecular C(sp<sup>2</sup>)-H amination



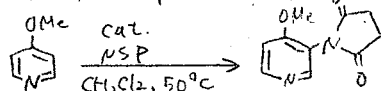
This Work



Invention of NSP

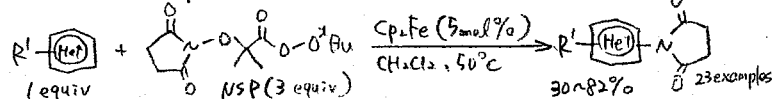


Catalyst Optimization



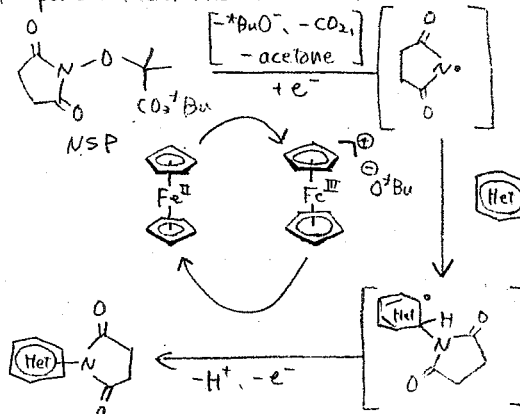
Catalyst	Yield	Catalyst	Yield
none	7	Fe(acac) <sub>3</sub>	23
Cu(I)	8-22	FeCl <sub>3</sub>	15
Cu(II)	14-26	[Cp <sup>+</sup> Fe]	39
Co(II) or Mn(II)	21-23	[Cp <sub>2</sub> Fe]	52

Substrate Scope

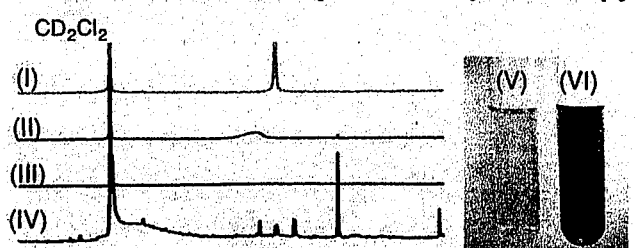


- Both arenes and heteroarenes
- Both electron rich and poor heterocycles
- Compatible with halogen and silanes
- Compatible with complex substrates

Proposed Mechanism



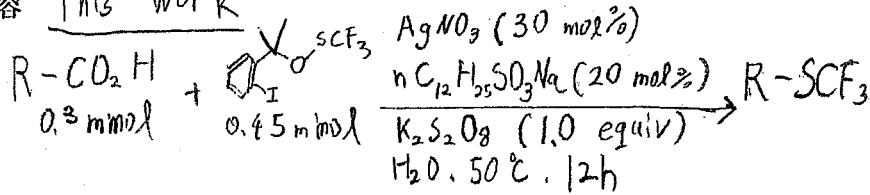
B. Mechanistic Probe by <sup>1</sup>H NMR Spectroscopy



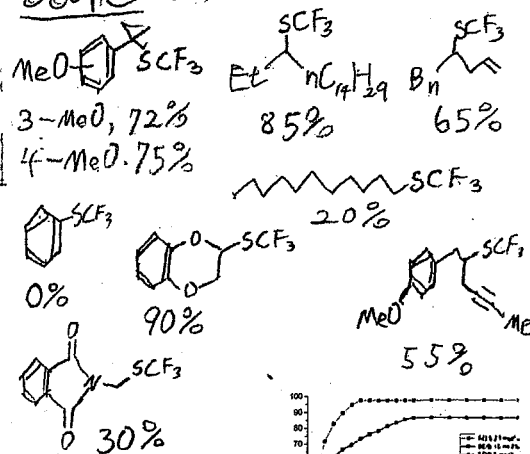
(I) Cp<sub>2</sub>Fe; (II) Cp<sub>2</sub>Fe + NSP (7) (1.75 equiv), 23 °C; (III) Heated mixture at 50 °C for 1 h; (IV) Zoomed-in image of (III); (V) Before heating; (VI) After heating.

Silver-Catalyzed Decarboxylative Trifluoromethylthiolation of Aliphatic Carboxylic Acid in Aqueous Emulsion

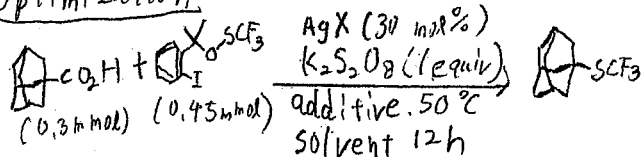
內容 This work



SCOPE (isolated product)

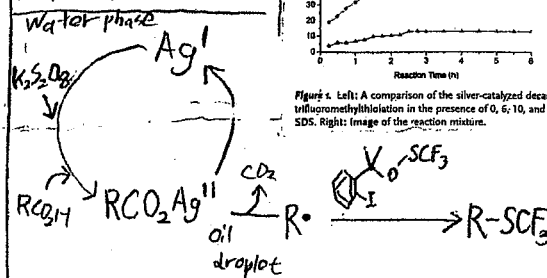


Optimization



AgX	additive	solvent	Yield by <sup>19</sup> F NMR
AgNO <sub>3</sub>	无	5% THF, CH <sub>3</sub> CN, DMF CH <sub>2</sub> Cl <sub>2</sub> , aceton, H <sub>2</sub> O 均不反应	< 12%
"	SDS (1 equiv)	CH <sub>3</sub> CN/H <sub>2</sub> O = 1:1	60%
"	" (0.2 equiv)	"	84%
"	" (" )	H <sub>2</sub> O	98%
"	" (0.1 equiv)	"	81%
"	CH <sub>3</sub> SO <sub>3</sub> Na (0.2 equiv)	"	-
"	4-(nC <sub>12</sub> H <sub>25</sub> )C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na (0.2 equiv)	H <sub>2</sub> O	70%
"	nBu <sub>4</sub> NHSO <sub>4</sub>	H <sub>2</sub> O	3%

Proposed Mechanism



S. Shang

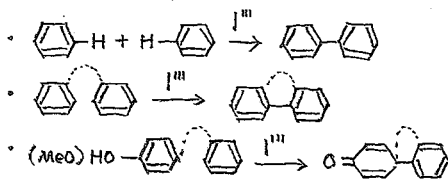
Tianjin University (China)

Angewandte  
10.1002/anie.201402925

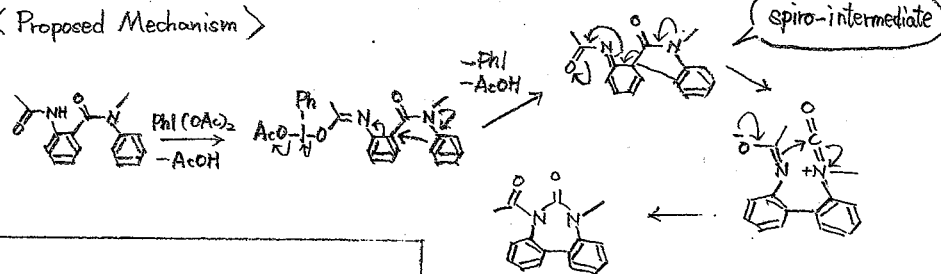
高橋

Intramolecular Metal-Free Oxidative Aryl-Aryl Coupling: An Unusual Hypervalent Iodine-Mediated Rearrangement of 2-Substituted N-Phenylbenzamide

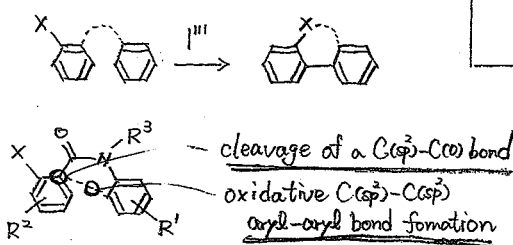
< Previous work >



< Proposed Mechanism >



< This work >



< Scope >

