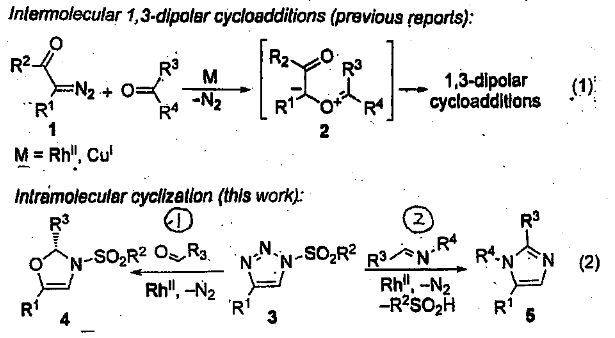
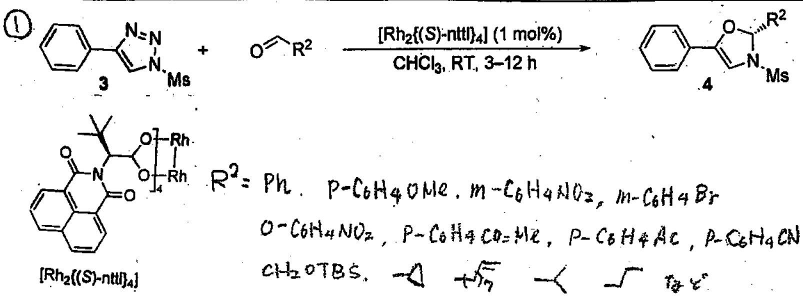
Valery V. Fokin et al.	The Scripps Research Institute	*ACIE* (anie.201206388)	Minakata

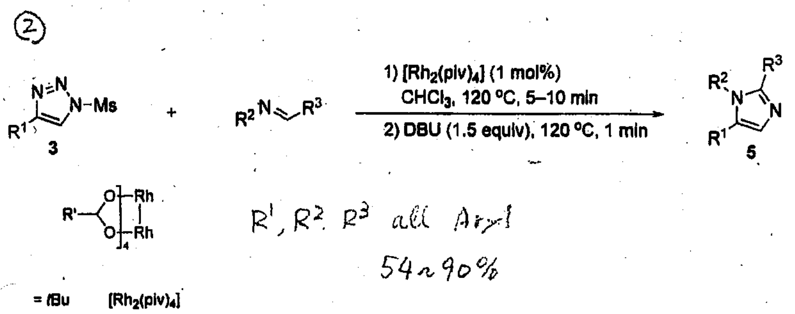
Sulfonyl-1,2,3-Triazoles: Convenient Synthones for Heterocyclic Compounds





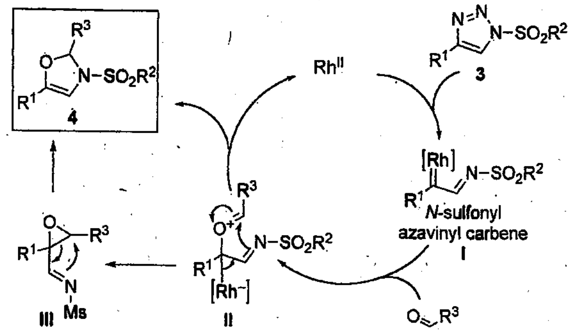
R^2 = Ph, p-C_6H_4OMe, m-$C_6H_4NO_2$, m-C_6H_4Br, o-$C_6H_4NO_2$, p-$C_6H_4CO_2$Me, p-C_6H_4Ac, p-C_6H_4CN, CH_2OTBS, など

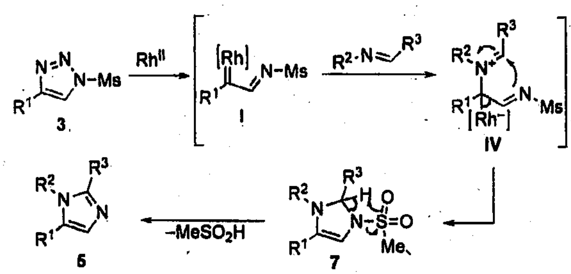
74~98%, 80~98% ee



R^1, R^2, R^3 all Aryl

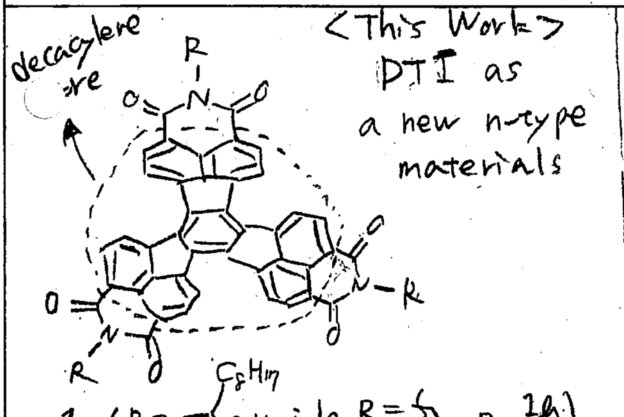
54~90%





Fred Wudl	University of California, Santa Barbara USA	*Angew. Chem., Int. Ed.* (doi:10.1002/anie.201207608)	Youhei Takeda

Self-Assembling Decacyclene Triimides Prepared Through a Regioselective Hextuple Friedel–Crafts Carbamylation

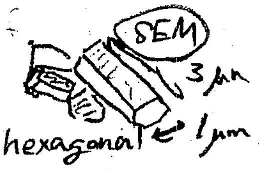


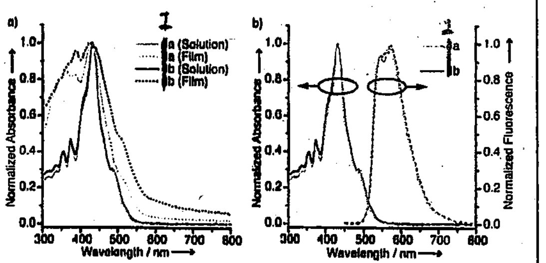
<This Work>

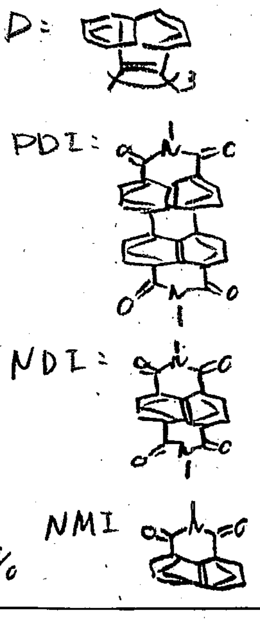
DTI as a new n-type materials

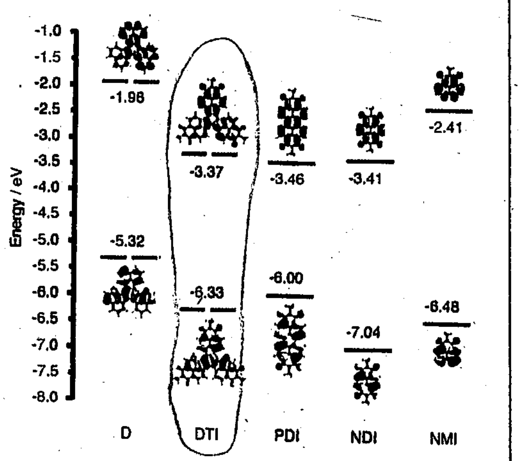
HOMO: −5.81eV

LUMO: −3.61eV







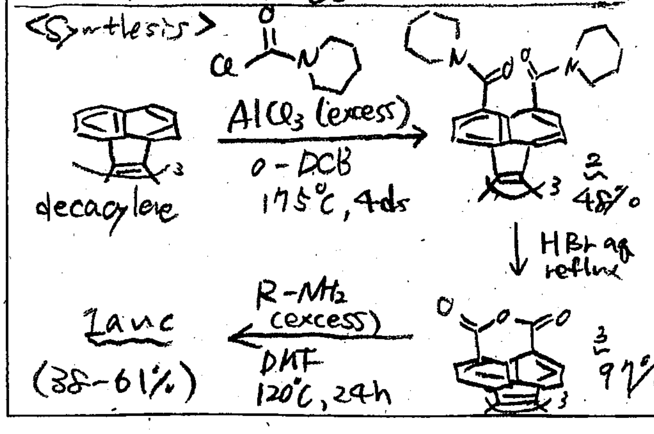


PDI, NDIとあまりLUMOに変化なし

application = solar cell (P3HTと)

PCE 1.6% (1a)

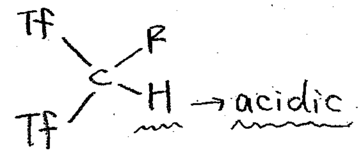
<Synthesis>



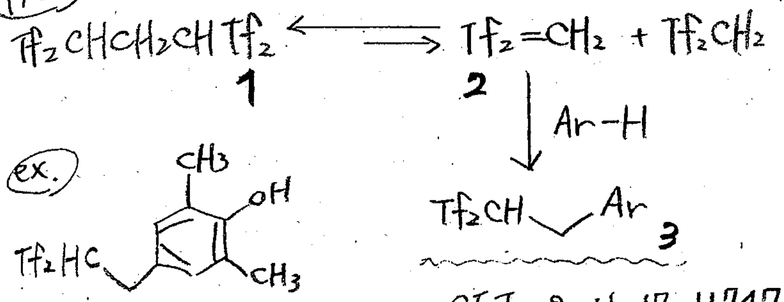
Hikaru Yanai, Takeo Taguchi	Tokyo University of Pharmacy and Life Sciences (Japan)	*ACIE* 10.1002/anie.201208809	清川

Synthesis, Characterization, and Applications of Zwitterions Containing Carbanion Moiety

Carbon acid



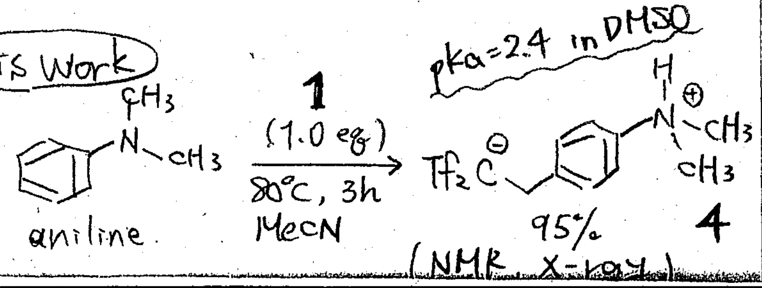
Prev.

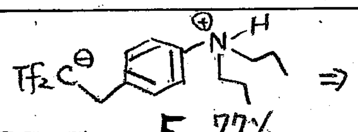


CEJ, 2011, 17, 11747

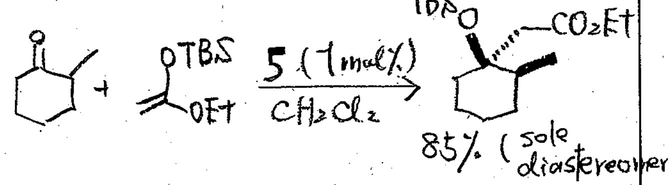
Brønsted acid cat.

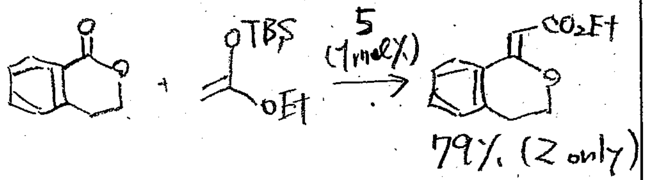
This Work

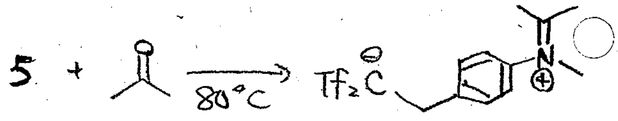




⇒ novel class of Brønsted acid.







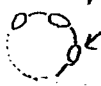
98%

stable zwitterionic iminium.

Würthner, F et al.	Universität Würzburg (Germany)	Org. Lett. ol3029115	Nagamachi

Synthesis and Properties of a Covalently Linked Angular Perylene Imide Dimer

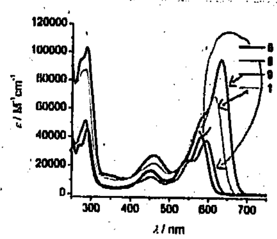
macrocyclic system



{ porphyrins
thiophenes
phenylacetylenes

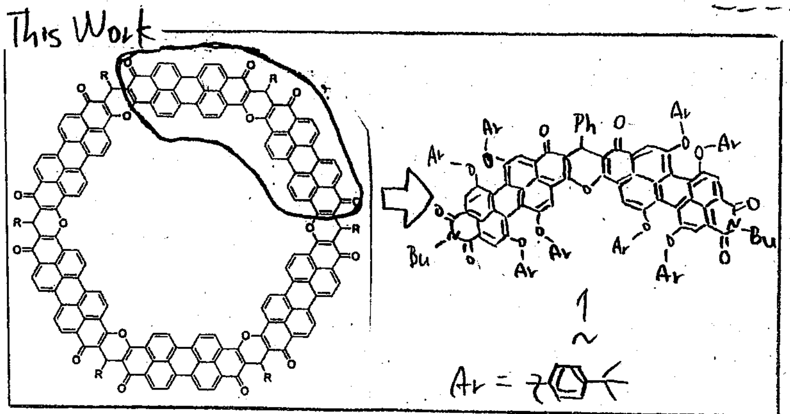
☆ Perylene Bisimidesの報告例はない。

UV-vis spectra (CH_2Cl_2, 10^{-5} M, 298K)

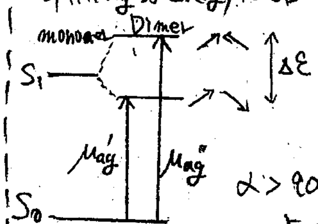


S_0-S_1	λmax (nm)	ε ($M^{-1}cm^{-1}$)	μeg (D)
6	579	40700	6.8
8	592	38100	6.
9	632	95300	11.0
1	615	69200	9.6.

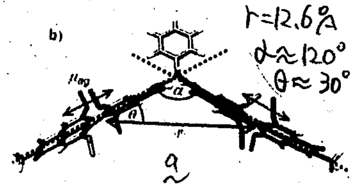
This Work



o Splitting of energy levels.

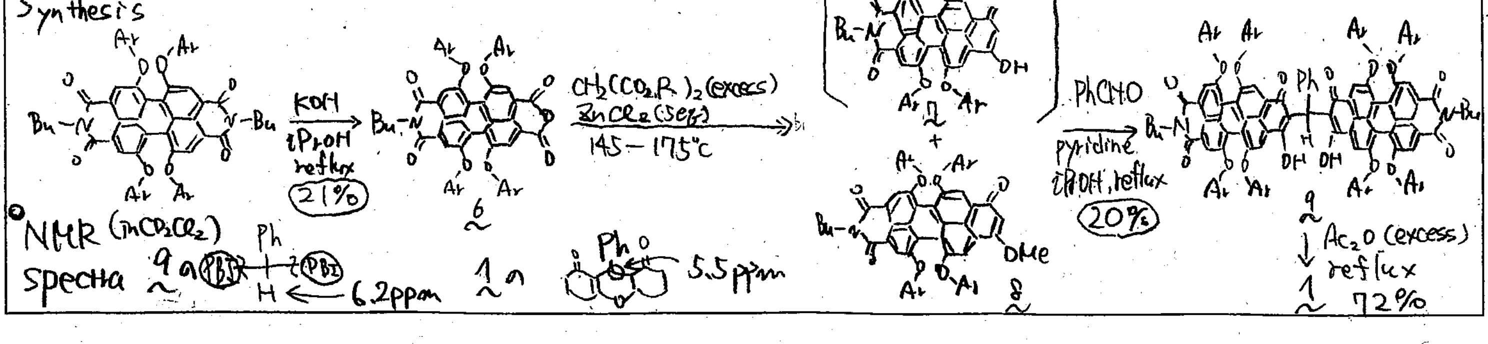


r=12.6Å
α≈120°
θ≈30°



α > 90° のため、μeg' の方が強い。よってレッドシフトのバンドの吸収帯の強度は強くなる。

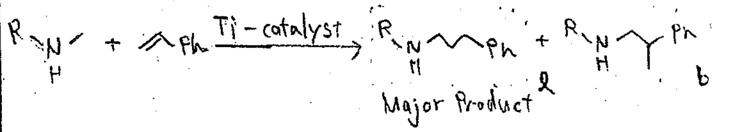
Synthesis



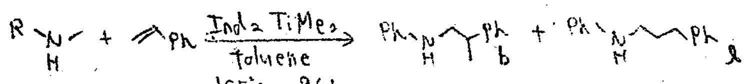
Sven Doye	Universität Oldenburg, Germany	DOI: anie.201206027	D2 早川純平

Aminopyridinato Titanium Catalysts for the Hydroaminoalkylation of Alkenes and Styrenes

<Reaction>



<Previous Work>



(Ind = η^5-indenyl)

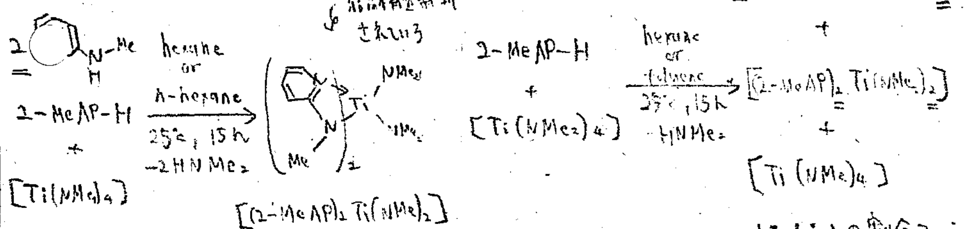
91% (b : l = 85:15)

S. Doye, Angew. Chem. Int. Ed. 2010, 49, 2626.

<In situ generated 2-aminopyridinato titanium complex>

Ti : 配位子 = 1:2

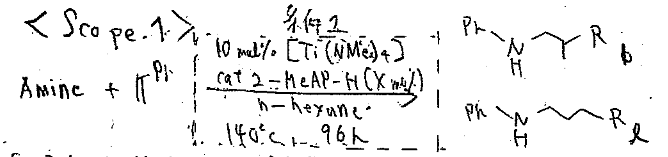
これまでにX線結晶構造解析されている Ti : 配位子 = 1:1



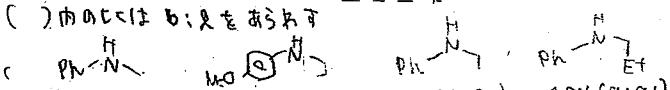
重ベンゼン NMRにて 右の構造を確認している。

1:1:1の割合で3種類が混在

<Scope.1>



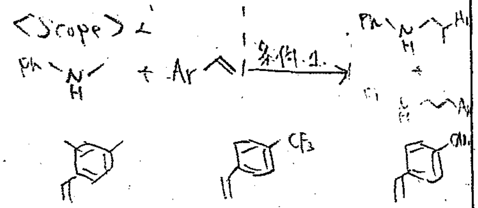
( )内の比は b:l をあらわす



X=10	79% (32:68)	50% (35:65)	51% (21:79)	48% (9:91)
X=20	76% (34:66)	15% (25:75)	32% (21:79)	4% (1:99)

X=10	22% (20:80)	5% (12:88)	26% (15:85)
X=20	5% (12:88)	17% (12:88)	8% (12:88)

<Scope> 2



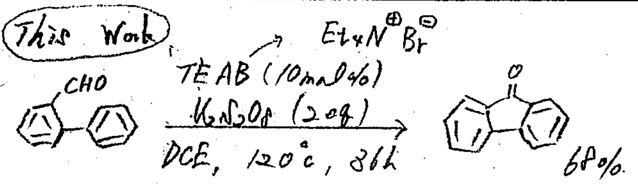
X=10	49% (44:56)	31% (19:81)	—
X=20	43% (45:55)	9% (4:96)	—

芳香族のオレフィンは分岐型が優先。
反応機構に関しては記述なし。

Frank Glorious	University of Münster	Chem. Soc. DOI: 10.1039/c2sc21823b	Okumura

Synthesis of fluorenones *via* quaternary ammonium salt-promoted intramolecular dehydrogenative arylation of aldehydes

This Work



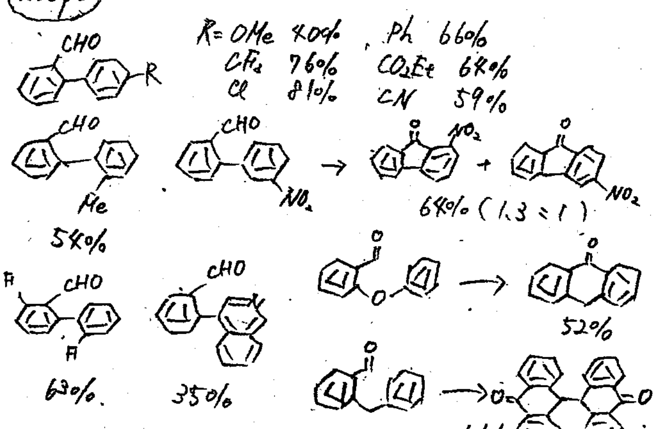
optimization

ammonium salt
- TBAB 50%
- TBAC 36%
- TBAF 33%
- TBAI 0%

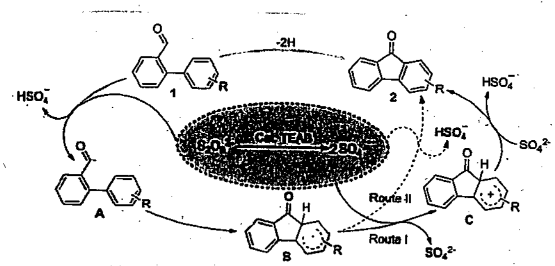
Oxidant
- $Na_2S_2O_8$ 46%
- $(NH_4)_2S_2O_8$ 34%
- Oxone 11%
- TBHP 18%

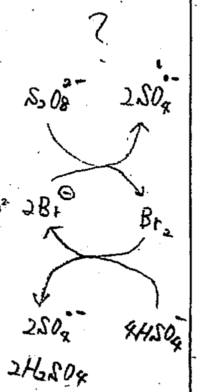
$K_2S_2O_8$ or TEAB のみでは 0%

Scope

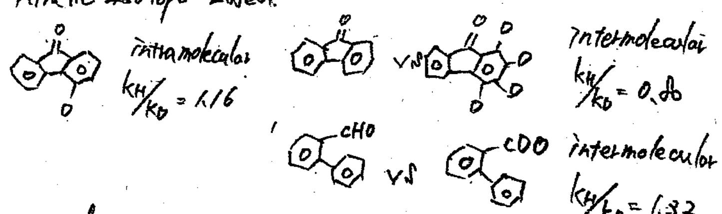


mechanism





- TEMPO存在下 → 反応進行しない
- $AgNO_3$ (20mol%) + $K_2S_2O_8$ (2eq) → 反応進行しない
- Kinetic Isotope Effect



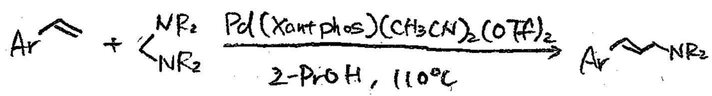
rate-determining step → X. C-H bond cleavage

↳ B → C (homolytic radical aromatic substitution)

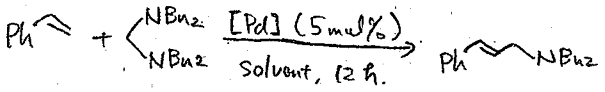
Hanmin Huang	Chinese Academy of Sciences (China)	J. Am. Chem. Soc. (10.1021/ja310848x)	Ikeda

Palladium-Catalyzed Vinylation of Aminals with Simple Alkenes: A New Strategy To Construct Allylamines

<This work>



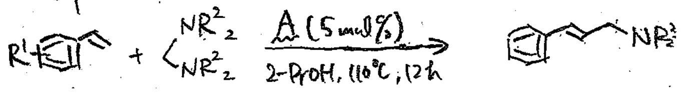
<Screening>



[Pd]	solu.	T(°C)	yield(%)
$Pd(OAc)_2$	MeOH	120	<5
$Pd(BINAP)Cl_2$	MeOH	120	30
$Pd(xantphos)Cl_2$	MeOH	120	85
A	MeOH	120	89
A	EtOH	120	75
A	2-PrOH	120	92
A	CH_3CN	120	74
A	2-PrOH	110	93

(A : $Pd(Xantphos)(CH_3CN)(OTf)_2$)

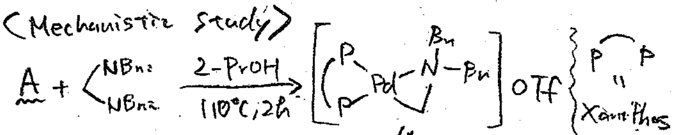
<Scope>



R^2 = Bnなど, R^1 = H, o-Me, m-Me, p-Me, p-tBu, p-OMe, p-F, p-Cl, p-CF_3, o-CO_2Me, p-NO_2 など

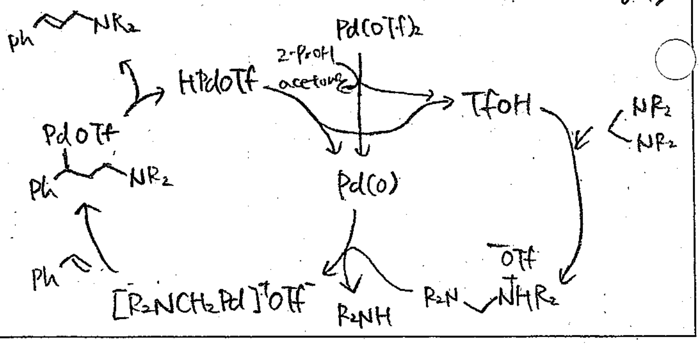
R^1 = Hなど, R^2 = Bn, Et, n-Pr, n-Bu, $-CH_2CH_2OCH_2CH_2-$ など

<Mechanistic Study>



4

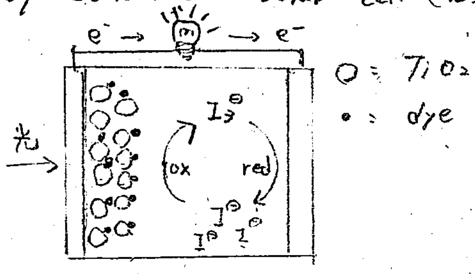
characterized by X-ray crystallography



Grätzel, M.	Swiss Federal Institute of Technology (Switzerland)	anie.201205007	Kawai

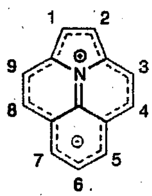
The Molecular Engineering of Organic Sensitizers for Solar Cell Application

dye-sensitized solar cell (DSC)



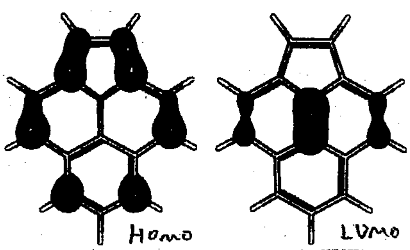
O : TiO_2
• : dye

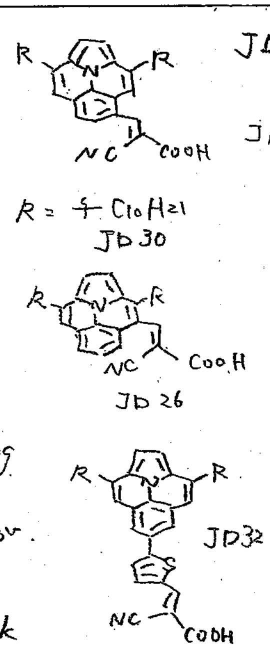
◦ Ullazine = pyrene と等電子構造

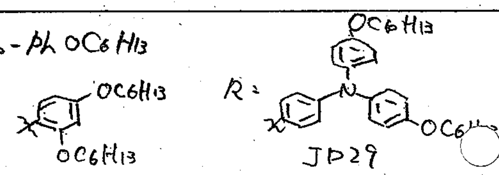


14 π-electron annulene

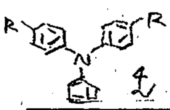
1) planar π-system
2) donating and accepting properties
3) 置換反応における反応点が多い。







Compound	λ_{max} [nm][b]	ε [$L mol^{-1} cm^{-1}$]	$E_{(0-0)}$ [eV][c]	$E_{(S+/S)}$ [V][d]	$E_{(S+/S*)}$ [V][e]
Ullazine and triarylamine					
3	393	19400	2.74	0.89	−1.85
4	299	20500	3.44	0.91	−2.53
Ullazine sensitizers					
JD21	582	28000	2.03	1.09	−0.94
JD25	598	33000	1.99	1.03	−0.96
JD26	548, 570[f]	7500[f]	2.06	1.06	−1.00
JD29	598	24000	2.00	1.09	−0.91
JD30	531	12000	2.05	1.09	−0.96
JD32	393, 540[f]	1600[f]	2.08	1.04	−1.04

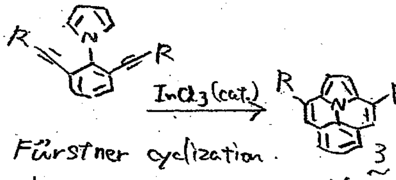


4

JD26 : loss of planarity

$E(S+/S^*) = E(S+/S) - E(0\text{-}0)$

This work



3

Fürstner cyclization

Chem. Eur. J. 2004, 10, 4556.

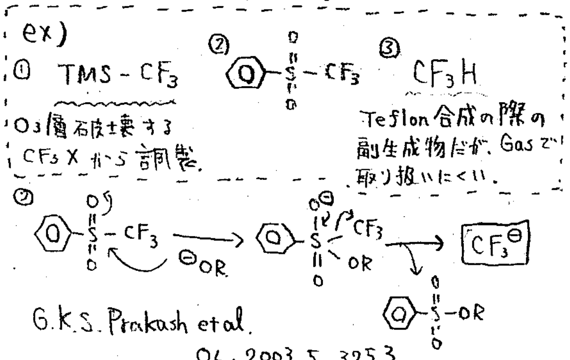
Sensitizer	V_{oc} [mV]	J_{sc} [$mA cm^{-2}$]	FF	PCE [%]
JD21	730	−15.4	0.75	8.4
JD25	807	−11.5	0.72	6.7
JD29	716	−13.3	0.70	6.7
JD30	672	−11.0	0.70	5.2
JD32	553	−3.7	0.78	1.7

David A. Colby et al	Purdue University(USA)	*OL*: 10.1021/ol303291x	M2 錦織

Amidinate Salt of Hexafluoroacetone Hydrate for the Preparation of Fluorinated Compounds by the Release of Trifluoroacetate

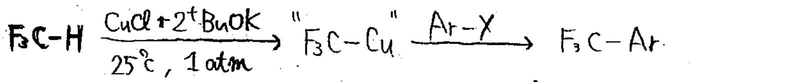
☆ Trifluoromethylating Reagent

ex)

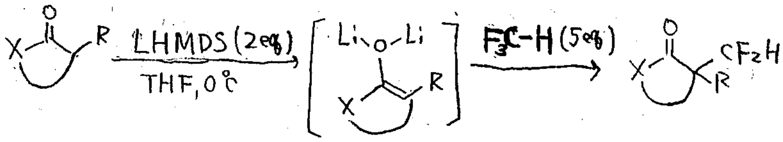


G.K.S. Prakash et al. OL, 2003, 5, 3253

③

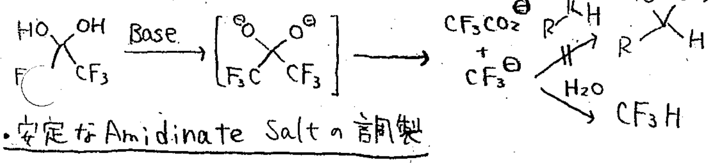


V.V. Grushin et al. 2011, 133, 20901.

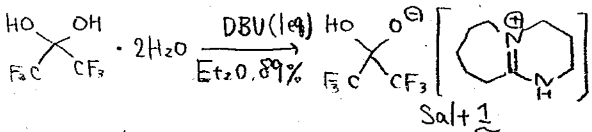


K. Mikami et al. ACIE, 2012, 51, 9535.

· Initial Experiment



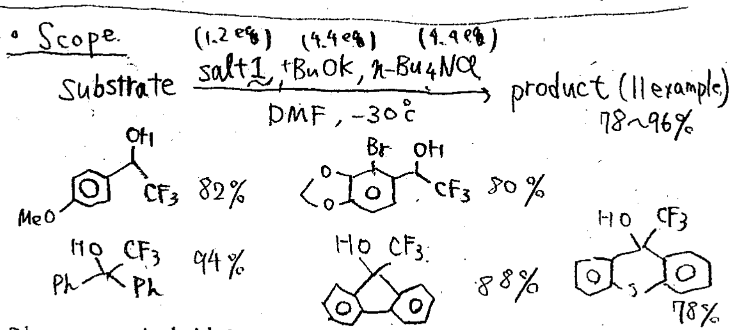
· 安定な Amidinate Salt の調製



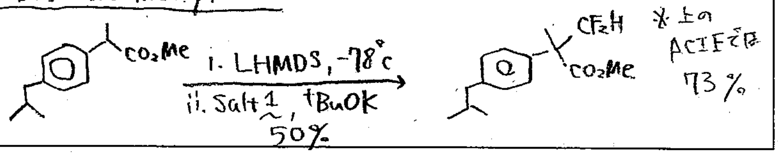
Salt 1

X-ray → 無水物と判明。Airに3ヵ月放置しても安定。

· Scope



· Difluoro methylation

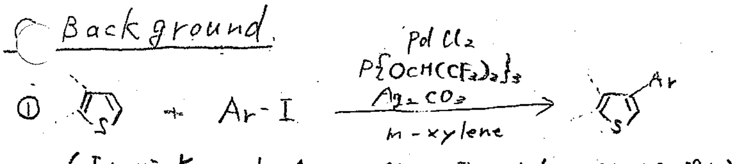


Shuichi Oi et al.	東北大学	OL DOI: 10.1021/ol3029109	M1 榎島

Pd-Catalyzed β-Selective Direct C-H Bond Arylation of Thiophenes with Aryltrimethylsilanes

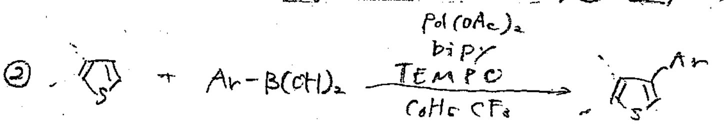
◎ Background

①



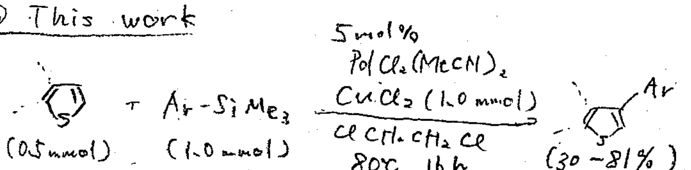
(Itami, K. et al. Angew. Chem. Int. Ed. 2010, 49, 8946)

②



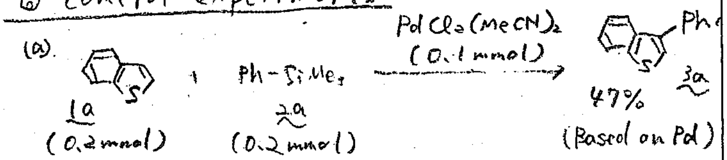
(Studer, A.; Itami, K. et al. Angew. Chem. Int. Ed. 2011, 50, 2387)

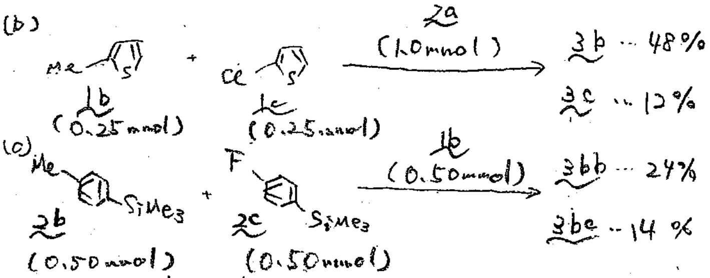
◎ This work



- $CuCl_2$ → 他の Cu(II) や Ag(I), Oxone®, [BQ] は ×。
- $-SiMe_3$ → $SiEt_3$ は ○、Si^iPr_3, $Si(OMe)_3$ などでは ×。
- Ar → 2位の置換基 ×。(2-MeC_6H_4 → 19%)
  EDG > EWG (4-$MeOC_6H_4$ → 64%, 4-$MeC(O)C_6H_4$ → 30%)
- [thiophene] → 電子不足なチオフェンは ×。

◎ control experiments

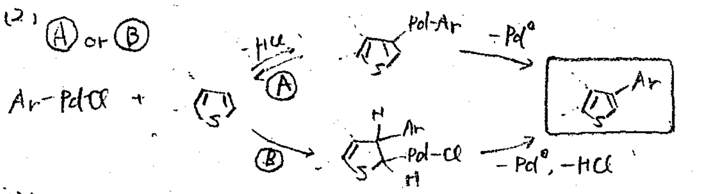




◎ Proposed mechanism

(1) $PdCl_2 + ArSiMe_3 \longrightarrow Ar\text{-}PdCl + Cl\text{-}SiMe_3$

(2) Ⓐ or Ⓑ

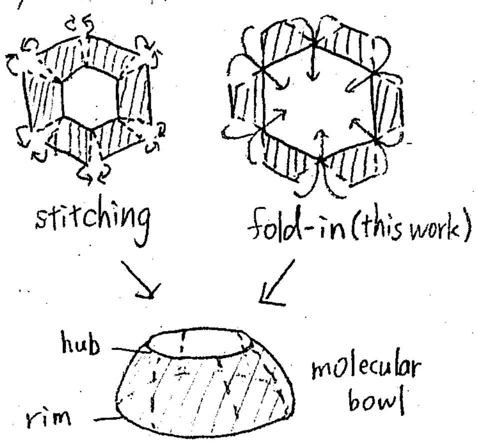


(3) $Pd^0 + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$

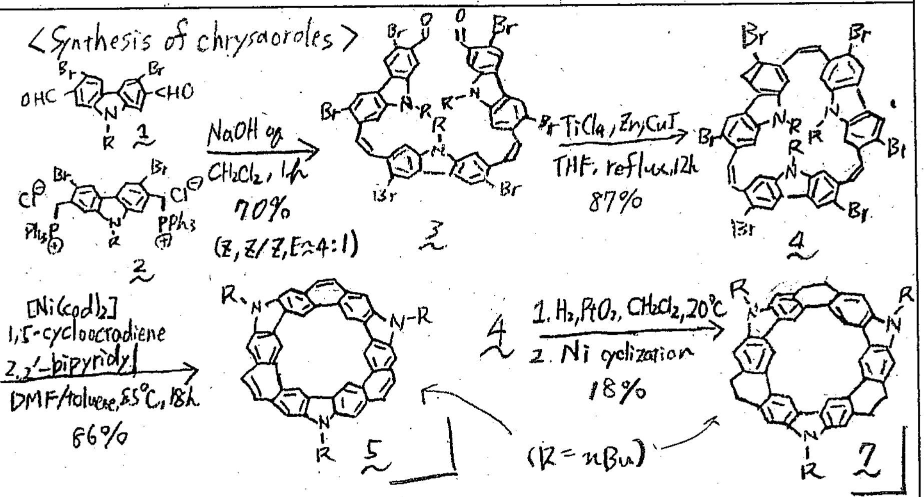
Marcin Stępień	University of Wrocław (Poland)	Angew. Chem. Int. Ed. DOI:10.1002/anie.201208547	M1 岡崎

The Fold-In Approach to Bowl-Shaped Aromatic Compounds: Synthesis of Chrysaoroles

<Synthetic approaches>



<Synthesis of chrysaoroles>



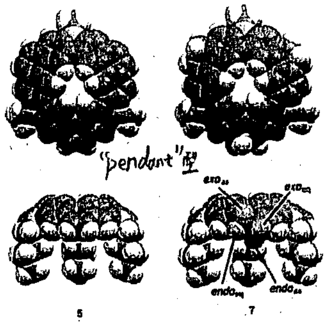
<Properties of 5 and 7>

- NMR (^1H, ^{13}C, COSY, ROESY, HSQC, HMBC) により構造を決定。

5
- 黄緑色の蛍光
- 溶液中で不安定(固体は冷蔵庫で数日保存可能)
- C_{3v} 対称

7
- エチレン部位の構造によって5より対称性は低い。(C_3 または C_1)
- VT-^{1}HNMR (170K) でピークに変化なし。

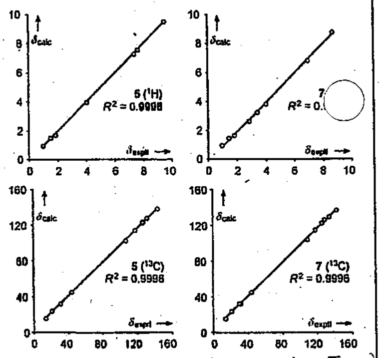
⇒ 反転は非常に速い。



DFT calculations (B3LYP/6-31G*)

計算により求めたケミカルシフトと実験値との相関がほぼ一致した。

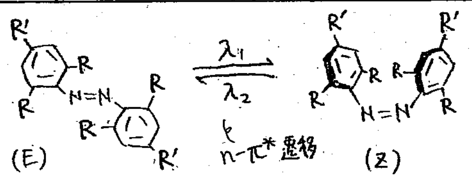
⇒ DFT計算による構造は実際の分子構造にかなり近い。



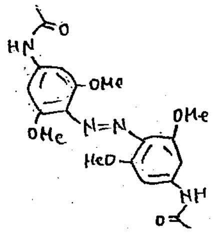
(GIAO/B3LYP/6-31G(d,p), δ_{calc})

Albert M. Brouwer, Stefan Hecht	Humboldt-Universität (Germany)	JACS 10.1021/ja310323y	M1 西田

o-Fluoroazobenzenes as Readily Synthesized Photoswitches Offering Nearly Quantitative Two-Way Isomerization with Visible Light



可視光で効率の良い可逆的な(E)-(Z)異性化を目標とした。(⟶ 生体内での応用を視野)



(E) → (Z)
λ = 530 nm, 80 %

(Z) → (E)
λ = 450-460 nm, 85 %

J. Am. Chem. Soc. 2011, 133, 19684.

この化合物では、Z体の方がE体よりも熱力学的に安定
(メトキシ基の酸素とアゾの窒素の lone pair が反発し、E体の平面性がくずれている。)

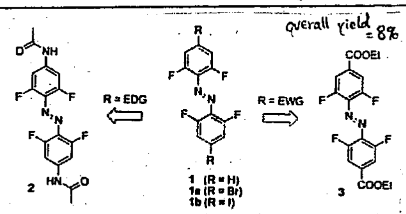
↓

アゾベンゼンの平面性を念頭においた application が数多く存在する。

→ π共役系や分子間 π-π stacking の利用

⇓

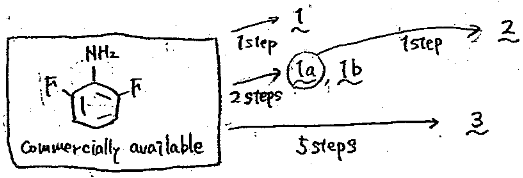
平面性の維持が必要



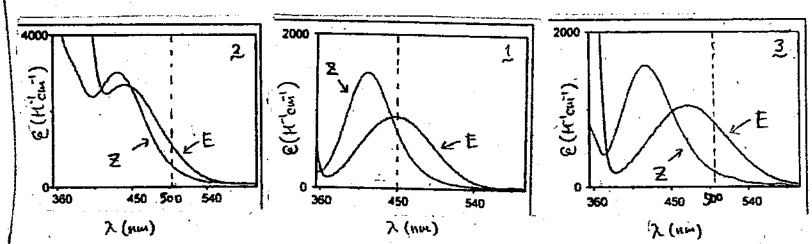
F: メトキシ基と比べて小さく アゾベンゼンは平面性を維持

p位に電子求引基(EWG)

∵ E体とZ体の n-π* 遷移の吸収波長が大きく変化。



overall yields = 8 %
(各の化合物は 1% 以下)



2	1	3
E体: λmax = 約440 nm	E体: λmax = 456 nm	E体: λmax = 469 nm
Z体: λmax = 約430 nm	Z体: λmax = 414 nm	Z体: λmax = 419 nm

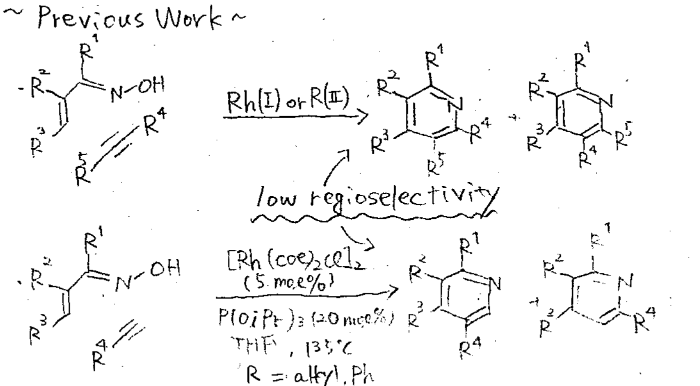
光定常状態で…

2	1	3
λ > 500 nm : Z体 85%	λ > 450 nm : Z体 91%	λ > 500 nm : Z体 90%
λ = 410 nm : E体 69%	λ = 410 nm : E体 86%	λ = 410 nm : E体 97%

Tomislav Rovis	Colorado State University (USA)	JACS DOI: 10.1021/ja3104389	M1 Hisakuni

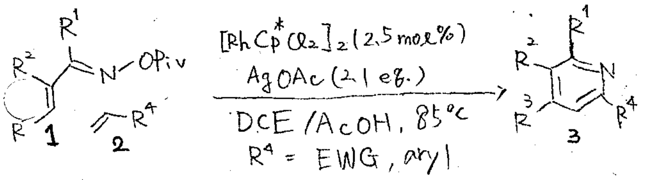
Rh(III)-Catalyzed Regioselective Synthesis of Pyridines from Alkenens and α,β-Unsaturated Oxime Esters.

~ Previous Work ~

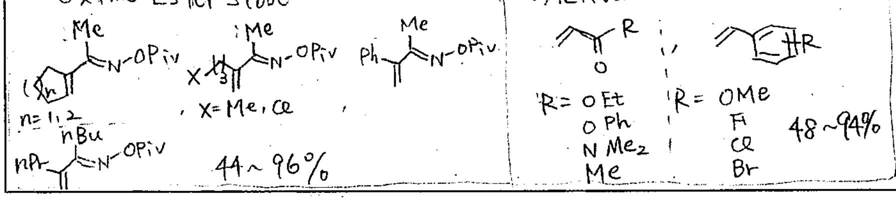


- Org. Lett. 2008, 10, 325
- J. Org. Chem. 2012, 77, 2501

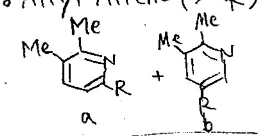
~ This Work ~



Oxime Ester Scope — Activated Alkene Scope

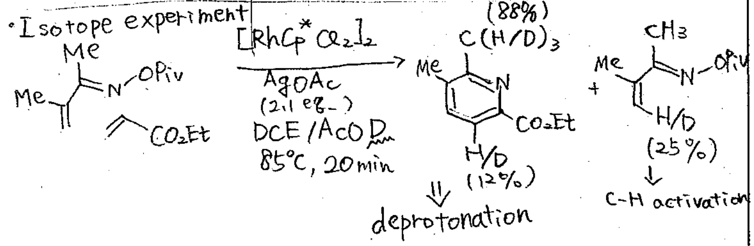


∘ Alkyl Alkene

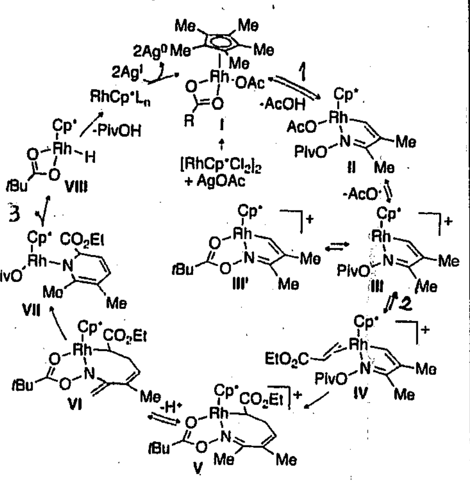


R =	nHex	CyP	Cy	tBu
(a:b)	(1:1.3)	(1.3:1)	(7.2:1)	(1:20)
	72%	67%	69%	17%

∘ Isotope experiment



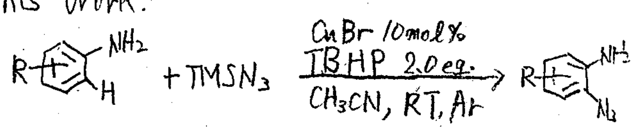
~ Proposed Mechanism ~



Conghui Tang and Ning Jiao	Peking University (China)	JACS(ja3089907)	B4 丸岡

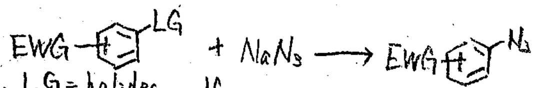
Copper Catalyzed C-H Azidation of Anilines under Mild Conditions

This Work.



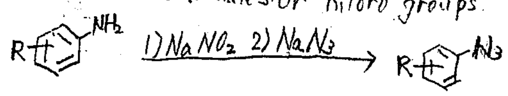
Azidation

a)

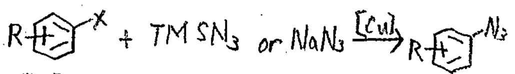


LG = halides, sulfonates or nitoro groups

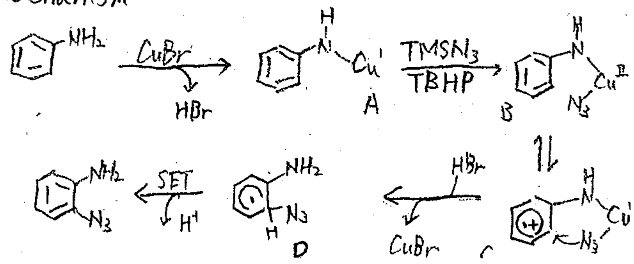
b)



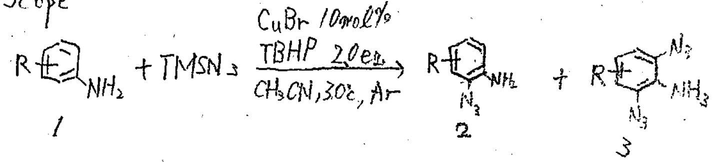
(c)

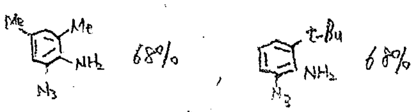


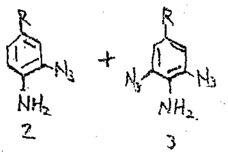
Mechanism



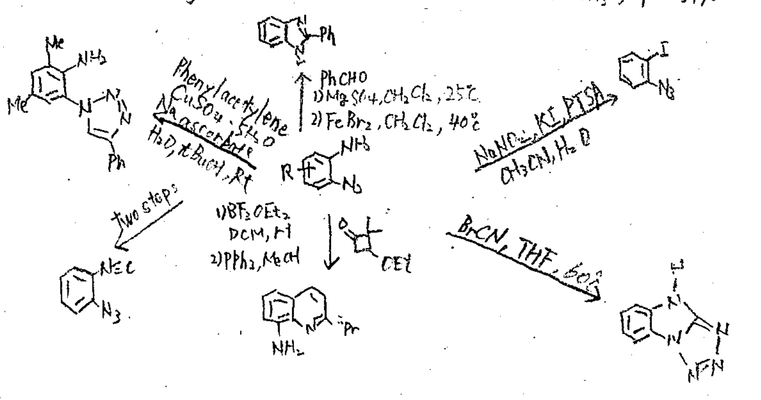
Scope





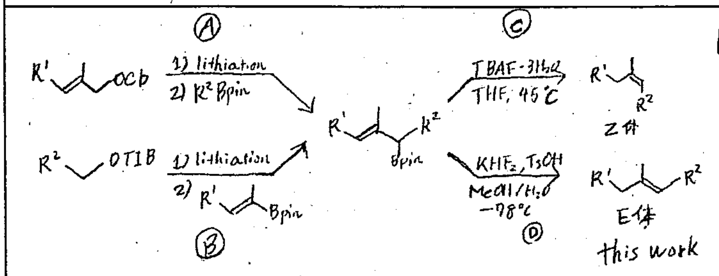


	2:3			2:3	
R = H	1.7:1	73%	R = OMe	1:1.7	61%
R = t-Bu	1:1.8	85%	R = CO2Me	2:1	63%
R = c-Hex	1:1.4	75%	R = COCH3	5:1	54%

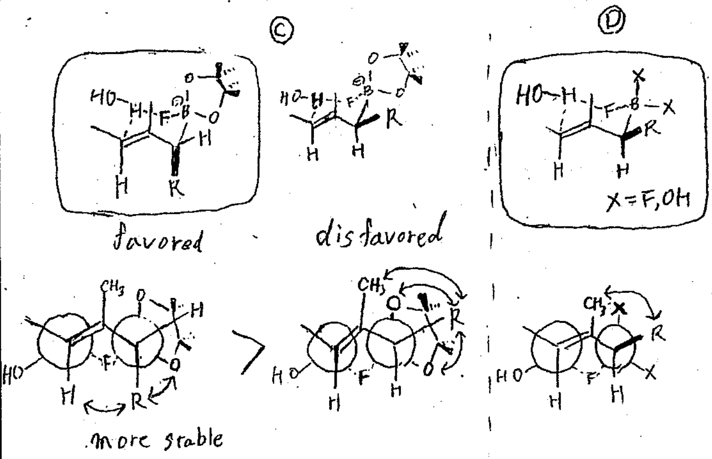


Varinder K. Aggarwal	University of Bristol (UK)	*ACIE*, anie. 201207312	B4 矢羽田

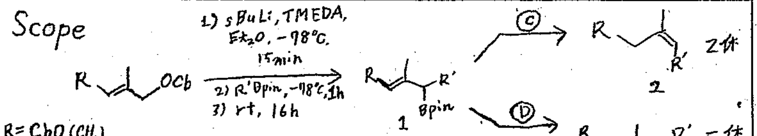
Diastereodivergent Synthesis of Trisubstituted Alkenes through Protodeboronation of Allylic Boronic Esters: Application to the Synthesis of the Californian Red Scale Beetle Pheromone



Transition States for Protodeboronation

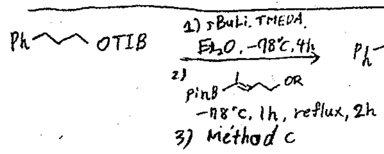


Scope



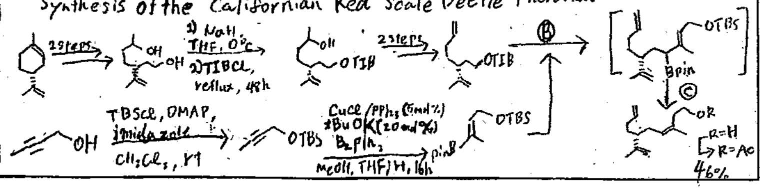
R = CbO$(CH_2)_3$

R'	Yield of 1 (%)	Method C Yield of 2 (%)	Z:E	Method D Yield of 3 (%)	Z:E
iPr	82	98	>20:1	95	1:9
$(CH_2)_2$Ph	76	99	>20:1	93	1:2
tBu	70	98	>20:1	99	1:10
Ph	73	95	>20:1	92	1:1



R	Yield (%)	Z:E
THP	68	13:1
Bn	77	14:1
TBS	74	20:1

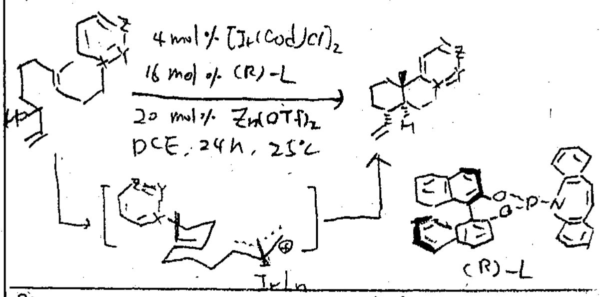
Synthesis of the Californian Red Scale Beetle Pheromon



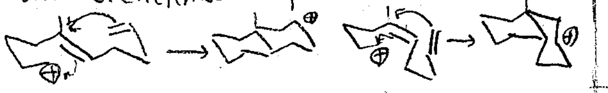
Eric M. Carreira	ETH	JACS DOI: 10.1021/ja310386m	Lin

Iridium-Catalyzed Enantioselective Polyene Cyclization

This work

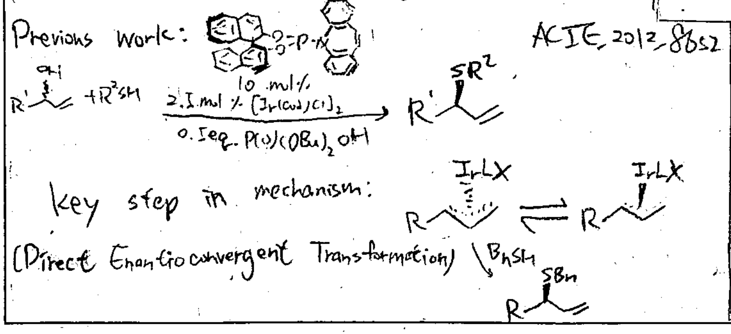


Stork-Eschenmoser postulate:



E-olefin → trans ring fusion   Z-olefin → cis ring fusion
JACS, 1955, 5068   Helv. Chim. Acta, 1955, 1890

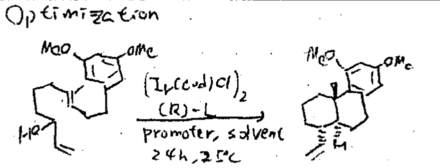
Previous work:



ACIE, 2012, 8852

(Direct Enantioconvergent Transformation)

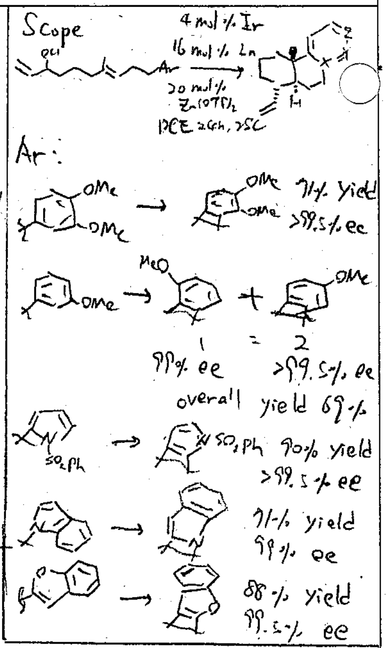
Optimization



promoter (mol%)	solv.	yield (%)	ee (%)
P(O)(OBu)2OH (50)	DCE	42	89
Bi(OTf)3 (10)	DCE	71	96
Yb(OTf)3 (10)	DCE	79	94
Zn(OTf)2 (10)	DCE	72	>99.5
Zn(OTf)2 (10)	DMF	n.r.	—
Zn(OTf)2 (10)	1,4-dioxane	8	>99.5
$\boxed{\text{Zn(OTf)}_2 \text{(20)}}$	$\boxed{\text{DCE}}$	$\boxed{90}$	$\boxed{>99.5}$

Best!

Scope



Tricyclization