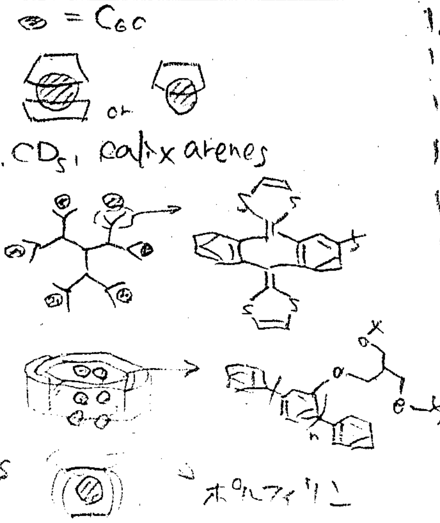
Stuparu, M. C.	University of Zürich Switzerland	*Angew. Chem., Int. Ed.* doi: 10.1002/anie.201303032	Youhei Takeda

Rationally Designed Polymer Hosts of Fullerene

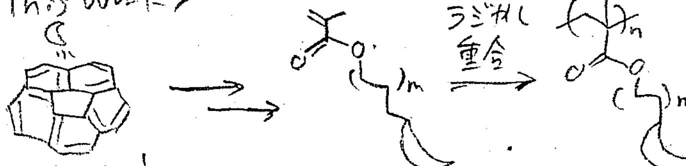
(C_{60} know receptors)

- macrocycle — e.g. CDs, calixarenes
- dendrimers
- π-conjugated oligomers
- molecular-clips — ポルフィリン

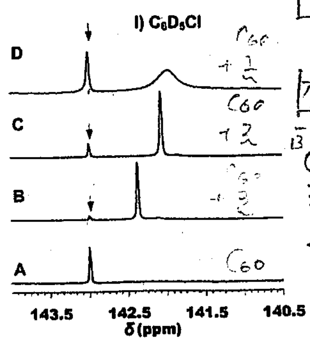


※ polymer に receptor 部位を有するものは少ない。
(PMMA, PVP は C_{60} を包接するが receptor 部位はない)

<This Work>



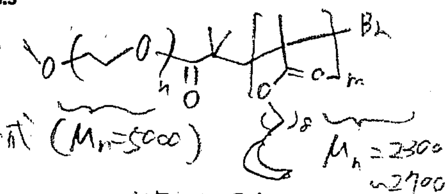
<物性, 包接挙動>



H にはすべてクロロベンゼンに可溶 (透明)
↓ C_{60}
均一な紫色の溶液。

C_{60}-rich な C_{60} を用いての ^{13}C NMR 測定 (↓は C_{60} の外部標準)
※ m が小さいほど interaction が強い。

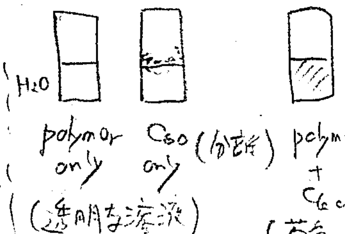
<co-polymer 合成>

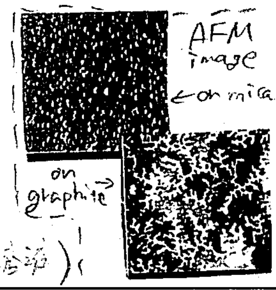


Cu 塩による ATRP 法により合成 (M_n=5000)
M_n = 2300 ~ 2700

↓ 水中への C_{60} 分散が可能に。

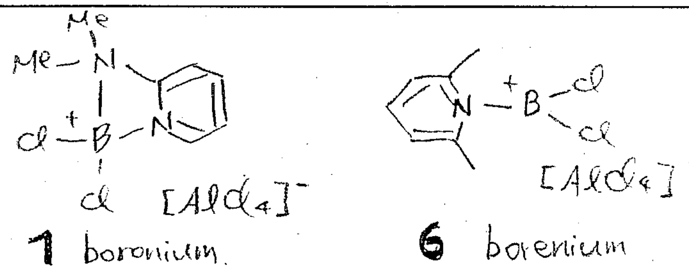
m = 1 : 3
= 4 : 3
= 7 : 3



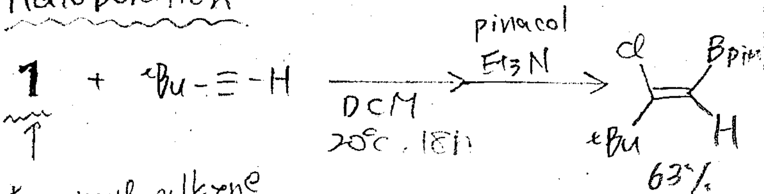


Michael J. Ingleson	University of Manchester (UK)	*ACIE* 10.1002/anie.20130269	清川

Haloboration of Internal Alkynes with Boronium and Borenium Cations as a Route to Tetrasubstituted Alkenes

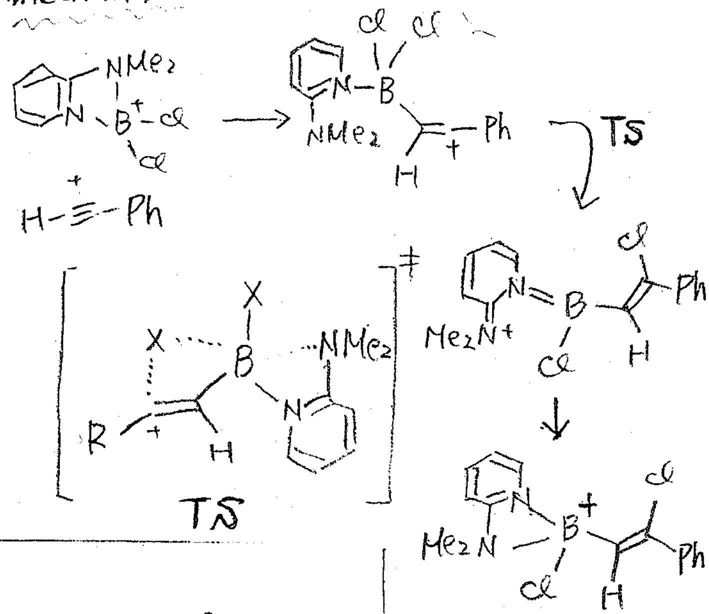


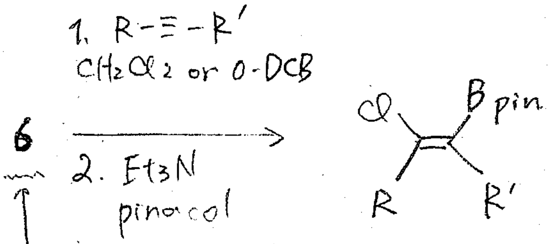
Haloboration



terminal alkyne のみ有効

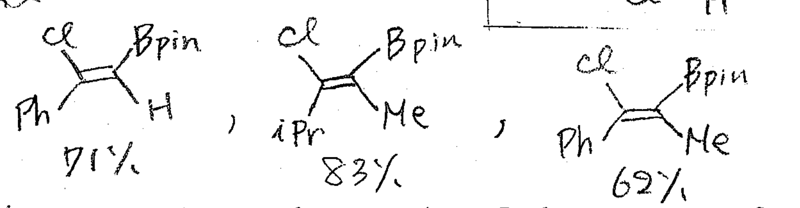
mechanism





internal alkyne も可

Scope

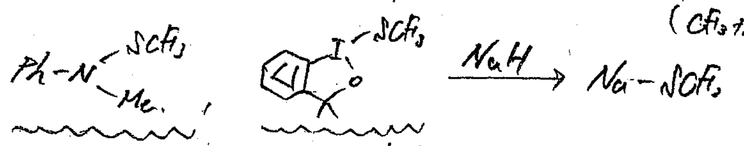


◎ product をクロスカップリングで四置換アルケンに誘導

Shibata Norio	Nagoya Institute of Technology	JACS ja3024551	粟村

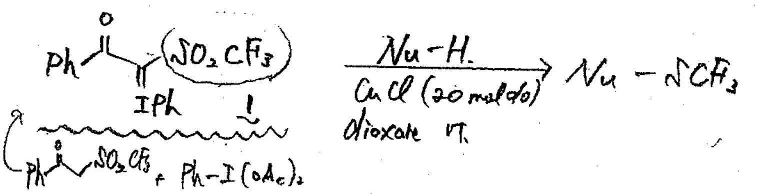
Trifluoromethanesulfonyl Hypervalent Iodonium Ylide for Copper-Catalyzed Trifluoromethylthiolation of Enamines, Indoles and β-Keto Esters

<u>General Methods for Electrophilic trifluoromethylthiolation</u> (CF_3 thiolation)

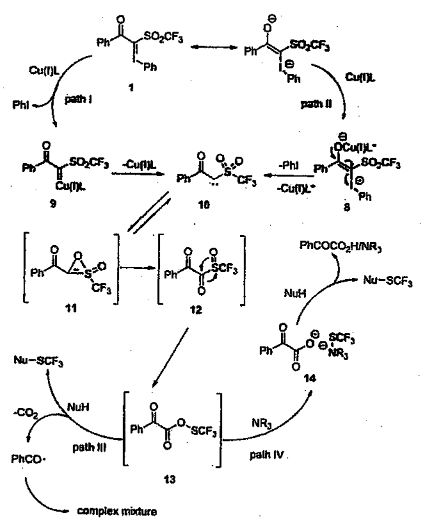


Prepared by CF_3 thiolation

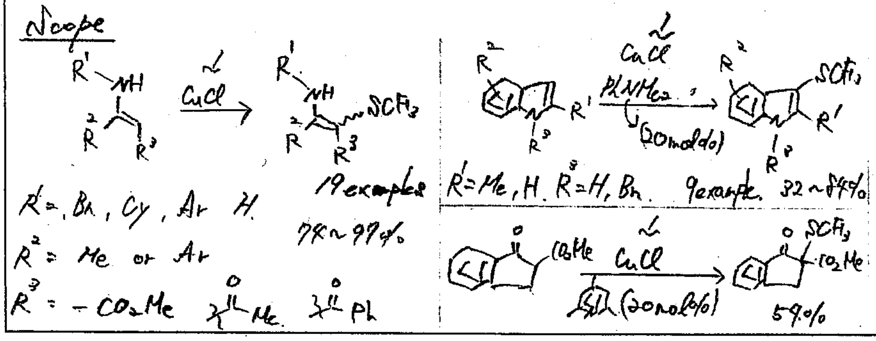
<u>Author's Method</u>



<u>mechanism</u>



<u>Scope</u>



R = Bn, Cy, Ar, H.　74~97%

R^2 = Me or Ar

R^3 = $-CO_2Me$, COMe, COPh

19 examples

R^1=Me, H. R^3=H, Bn.　9 examples　32~84%

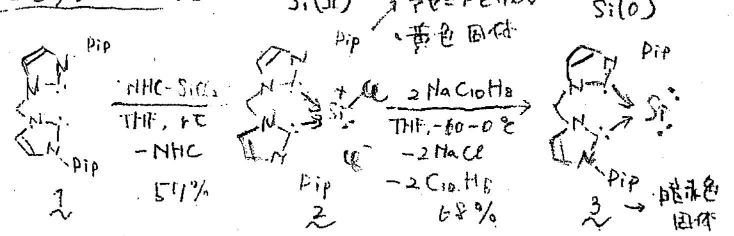
59%

- 10 は HRMS-ESI にて捕捉
- 10 ⇄ 11 は報告あり
- Path II が有力 ($FeCl_2$, $Mg(ClO_4)_2$, $Zn(OTf)_2$ でも反応進行) カルベノイドではない可能性大

M Driess et al.	Technische Universität Berlin	Angew. Chem. Int. Ed anie.201302537	M2 模島

A Cyclic Silylone ("Siladicarbene") with an Electron-Rich Silicon(0) Atom.

○ Synthesis



Si(II)　THF不溶。アセトニトリルに可溶。黄色固体

Si(0)

1 → 2: NHC-$SiCl_4$, THF, rt, −NHC, 51%

2 → 3: 2 $NaC_{10}H_8$, THF, −80~0 ℃, −2 NaCl, −2 $C_{10}H_8$, 68%

3 → 暗赤色固体

○ Molecular structures and shapes of frontier orbitals

2: Cl^- は遠くにある。(>6.42Å)

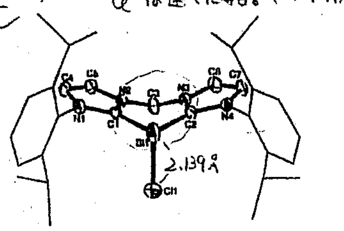


Figure 1. Molecular structure of the chlorosilyliumylidene cation of 2. Ellipsoids are set at 50% probability. H atoms and one acetonitrile lattice solvent molecule are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1-Cl1 2.139(2), Si1-C1 1.960(4), Si1-C2 1.963(4), C1-N1 1.348(5), C1-N2 1.355(5), C2-N3 1.356(5), C2-N4 1.342(5); C1-Si1-C2 88.7(2), C1-Si1-Cl1 95.8(1), C2-Si1-Cl1 97.6(1), Si1-C1-N1 126.4(3), Si1-C1-N2 127.9(3), N1-C1-N2 105.2(3), Si1-C2-N3 127.3(3), Si1-C2-N4 127.1(3), N3-C2-N4 104.9(3).

^{29}Si NMR δ = −58.4 ppm

∠C1SiC2 = 88.7°

舟型

Si−C Ave. = 1.961Å

σ orbital　π orbital

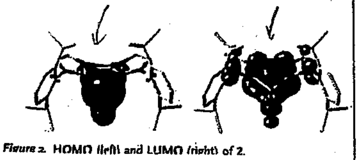


Figure 2. HOMO (left) and LUMO (right) of 2.

3: 舟型

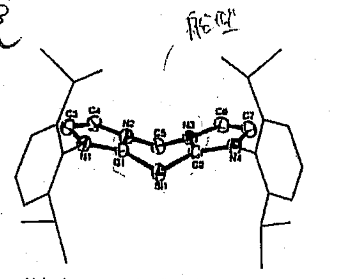


Figure 3. Molecular structure of 3. Ellipsoids are set at 50% probability. H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1-C1 1.864(1), Si1-C2 1.874(1), C1-N1 1.383(2), C1-N2 1.382(2), C2-N3 1.374(2), C2-N4 1.377(2); C1-Si1-C2 89.1(1), Si1-C1-N2 128.9(1), Si1-C1-N1 127.9(1), N1-C1-N2 103.1(1), Si1-C2-N3 128.4(1), Si1-C2-N4 127.8(1), N3-C2-N4 103.7(1).

^{29}Si NMR δ = −83.8 ppm

∠C1SiC2 = 89.1°

SiC Ave. = 1.869Å

(Si=C : 1.702~1.775Å)

π orbital　σ orbital

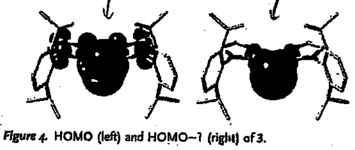
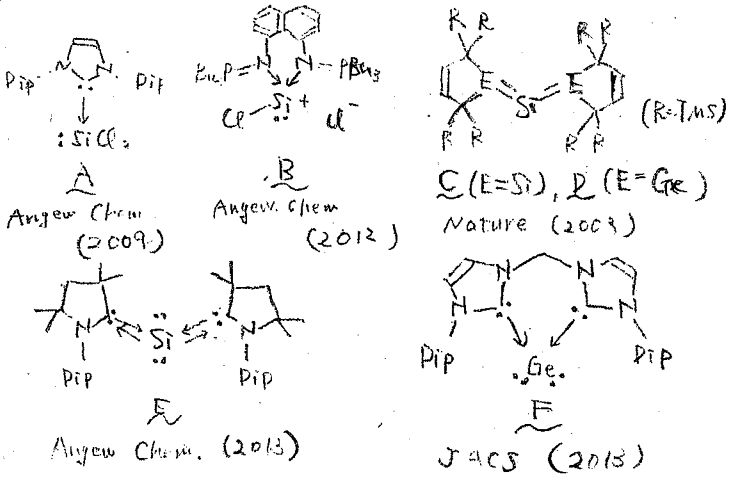


Figure 4. HOMO (left) and HOMO−1 (right) of 3.

○ Background



A　Angew. Chem. (2009)

B　Angew. Chem. (2012)

C (E=Si), D (E=Ge)　(R: TMS)　Nature (2009)

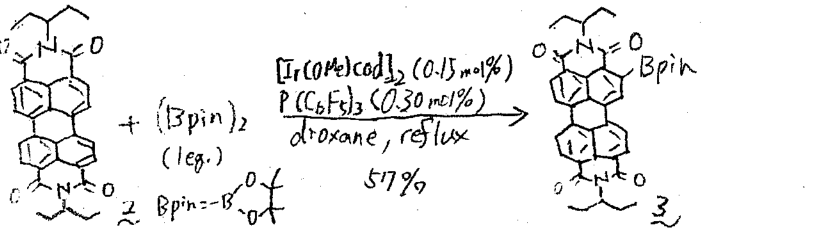
E　Angew. Chem. (2013)

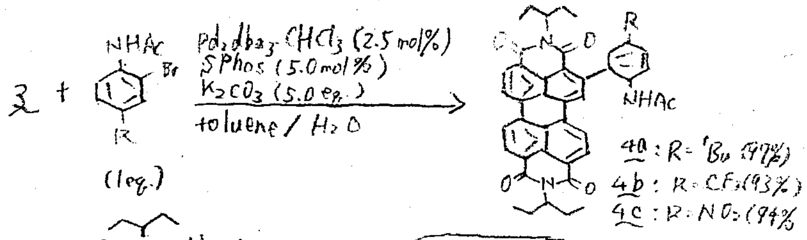
F　JACS (2013)

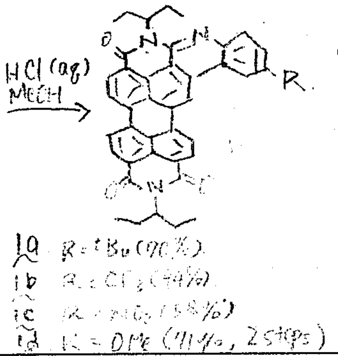
Shinokubo, H. | Nagoya University (Japan) | Org. Lett. DOI: 10.1021/ol4013168 | M2 岡崎

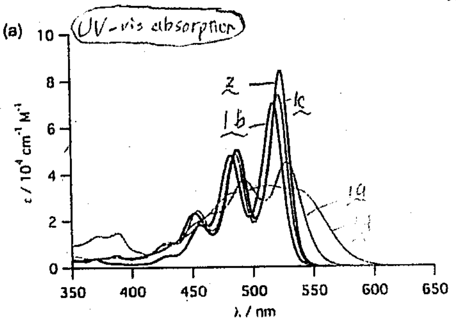
Synthesis of Pyridine-Fused Perylene Imides with an Amidine Moiety for Hydrogen Bonding

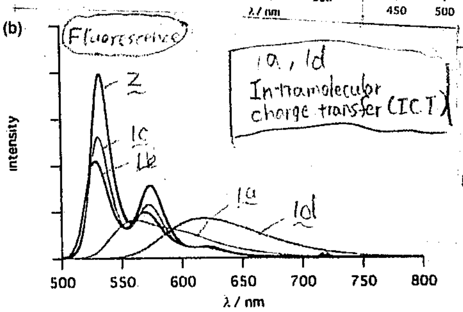
〈Synthesis of Pyridine-Fused PBIs〉



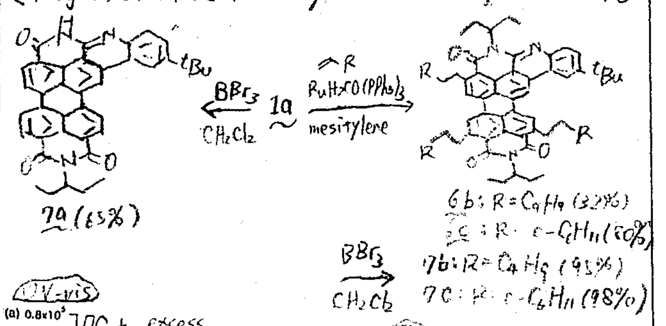


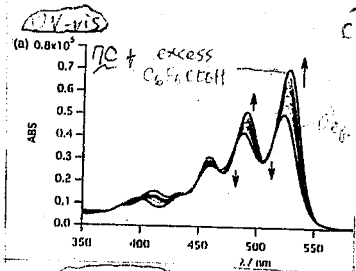


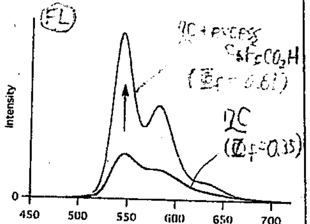


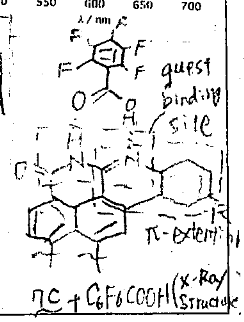


〈Regioselective Dealkylation and Alkylation of 1a〉







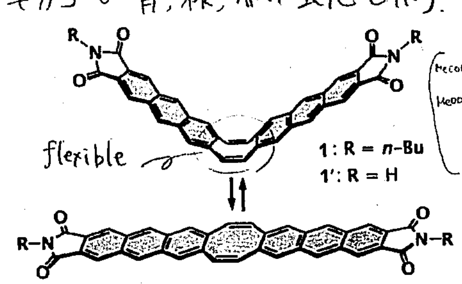


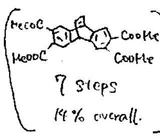
Shigehiro Yamaguchi
Stephan Irle, Shohei Saito

Nagoya University (Japan) | JACS, ASAP | M2 西田

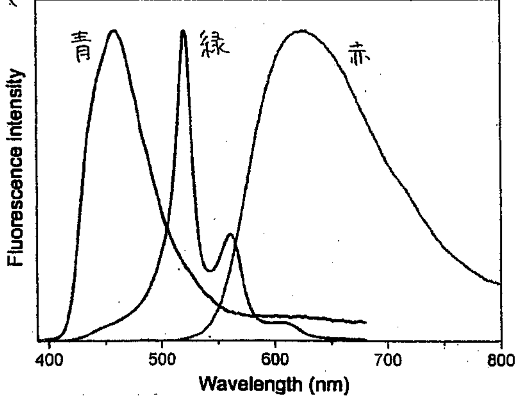
A π Conjugated System with Flexibility and Rigidity That Shows Environment-Dependent RGB Luminescence

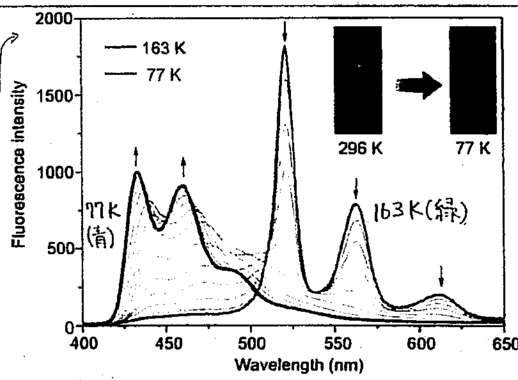
単分子で青, 緑, 赤の蛍光を示す.





- 青: 1.0 wt% in PMMA film ($\Phi = 0.09$)
- 緑: in CH_2Cl_2 ($\Phi = 0.31$)
- 赤: 結晶状態 (excimer発光) ($\Phi = 0.06$)



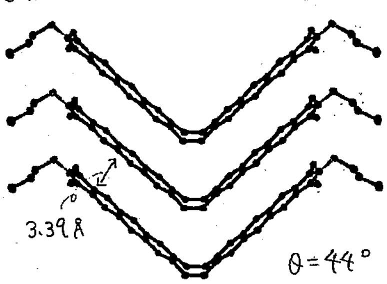


1.0×10^{-6} M in 2-methyltetrahydrofuran
低温で粘度(高)
⇓
1 の conformation が変

- $\theta = 0°$: planar (緑)
- $\theta = 22.8°$: V-shape (青)

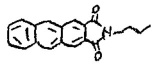
・296 Kでは 緑:青 = 12:1

◎ 結晶状態では赤色に発光 (エキシマー発光)



π-π 間距離: 3.39 Å
… 強い π-π 相互作用
(7 mg/L, CH_2Cl_2
60 mg/L, $CHCl_3$)

分子内に 2つのアントラセン部位
… 分子間での π-stack が容易
⇓
excimer や excited oligomer を形成しやすい → 赤色発光



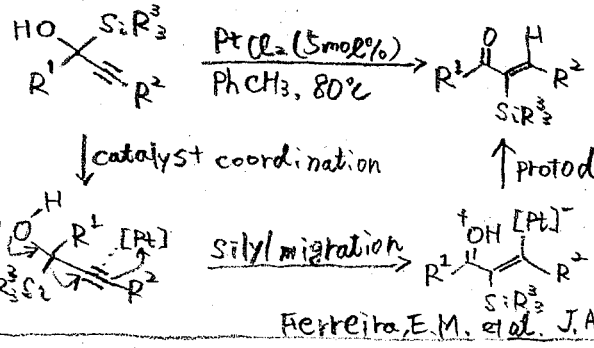
結晶状態で excimer発光 → 黄緑色発光

☆ 今後は…
光学的特性だけではなく電気化学的, 磁性的性質, キャリア移動度などに展開していく.

Eric M. Ferreira | Colorado State University (USA) | Angew. Chem. Int. Ed. DOI: 10.1002/anie.201303007 | M2 Hisakuni

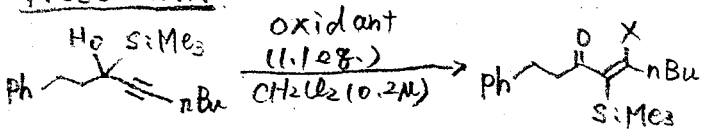
Stereoselective Synthesis of Tetrasubstituted Olefins through a Halogen-Induced 1,2-Silyl Migration.

Previous Work

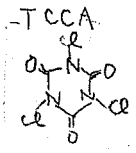


Ferreira, E. M. et al. J. Am. Chem. Soc. 2010, 132, 11926.

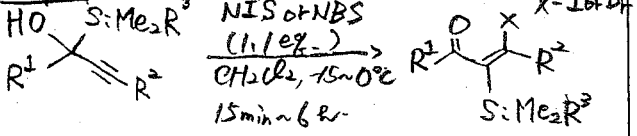
Present Work



- Oxidant
  - mCPBA, NCS, TCCA, Selectfluor ⇒ no reaction.
  - NBS (23°C) ⇒ 91% (E:Z > 19:1, X=Br)
  - NIS (0°C) ⇒ 90% (E:Z > 19:1, X=I)



Scope



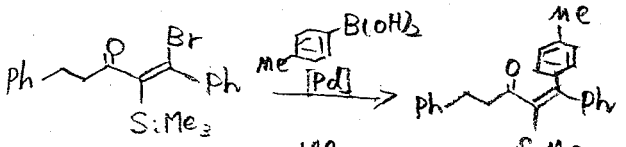
E/Z > 19:1 selectivity

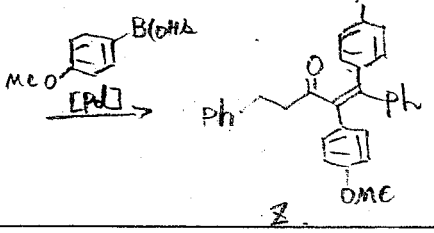
R^1 = Ph, , , TBSO

R^2 = H, nBu, CH_2OTHP, Ph, BnO

R^3 = Me, Bn, Ph

63~94%



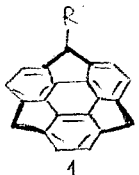


All-carbon tetrasubstituted alkenes

Hidehiro Sakurai | 総合研大 | Angewante Communication DOI: 10.1002/anie.201303139 | M1 上田

Stereoelectronic Effect of Curved Aromatic Structures: Favoring the Unexpected endo Conformation of Benzylic-Substituted Sumanene

buckybowls … フラーレンの一部を切り取ったお椀型をした分子のこと

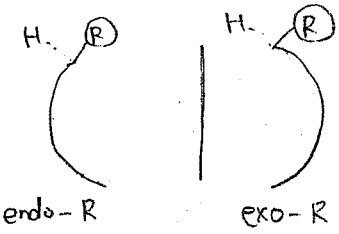


1

Sumanene (スマネン) (6員環4つ 5員環3つ C数21)

1a	R=H	1d	R=OH
1b	R=$Si(CH_3)_3$	1e	R=2,6-$(CH_3)_2C_6H_3$
1c	R=Me	1f	R=C_6H_5

★ 1の endo/exo-R conformational stability を支配する立体電子効果を、buckybowl で見出した最初の例

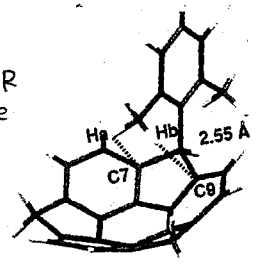


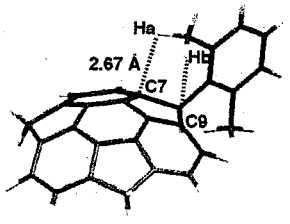
compound	R	Experimental endo-R/exo-R	conformer	ΔE	DFT	ΔE	NBO	ΔE_{NBO}
1a	H	–	–	–	–	–	–	-0.5
1b	$Si(CH_3)_3$	0 : 100	exo	–	exo-R	2.0	exo-R	4.9
1c	CH_3	81 : 19	endo	-0.9	endo-R	-1.4	endo-R	-1.1
1d	OH	90 : 10	endo	-1.3	endo-R	-2.3	endo-R	-0.9
1e	2,6-$(CH_3)_2C_6H_3$	82 : 18	endo	-0.9	endo-R	-4.6	exo-R	4.2
1f	C_6H_5	49 : 51	endo/exo	0.0	endo-R	-2.1	endo-R	-0.3

▼ 一般的には置換基Rと芳香環水素との立体反発から、exo体が安定に存在すると考えられる (1a)

▼ しかし 1c, 1d, 1e は endo-R体が、1f は 1:1 の比で安定に存在した (ΔE = E(endo R) - E(exo-R) = RTlnK)

▼ 1e は置換基とスマネン間で CH-π相互作用が存在する



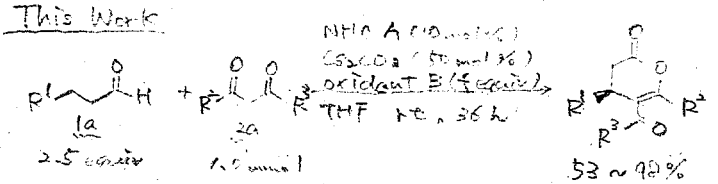


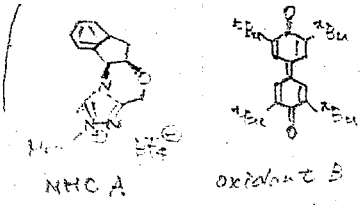
▼ 1c, 1d は C-H結合との超共役で、コンホメーションをコントロールしている

Yonggui Robin Chi	Nanyang Technological University (Singapore)	Angew. Chem. Int. Ed. DOI: 10.1002/anie.201302152	M1 黒田

Direct β-Activation of Saturated Aldehydes to Micheal Acceptors Through Oxidative NHC Catalysis

This Work





Scope

R¹ = aryl 他多数.

p-EDG, EWG : 87 ~ 93%, e.r. = 93:7 ~ 97:3

o or m 置換 = 75 ~ 96%, e.r. = 95:5

R², R³

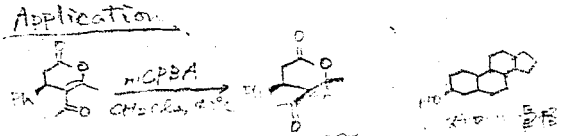
(R², R³) = (Et, Ph), (Et, Et), (Ph, Ph)

= 53 ~ 61%, e.r. = 85:15 ~ 91:9

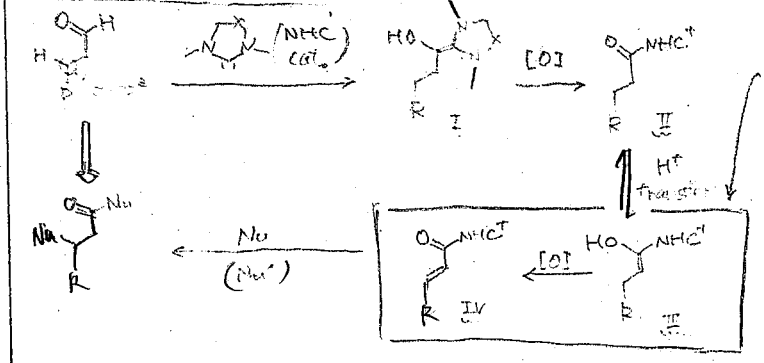
(R², R³) = (Me, MeO), (Me, EtO), (Et, EtO)

= 85 ~ 95%, e.r. = 88:12 ~ 94:6.

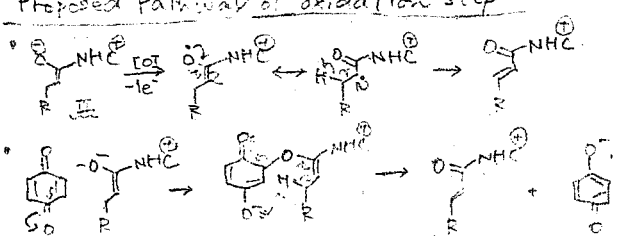
Application



Working Hypothesis



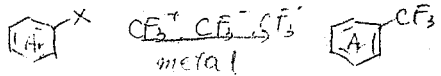
Proposed Pathway of oxidation step



Yao Fu	University of Science and Technology of China	JACS 10.1021/ja4042172	M1 山根

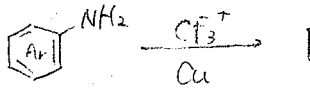
Copper-Promoted Sandmeyer Trifluoromethylation Reaction

Aromatic Trifluoromethylation



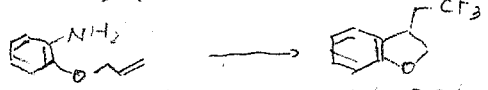
X = H, B(OH)₂, Bpin, halogen

This Work



- mild condition
- good functional group tolerance

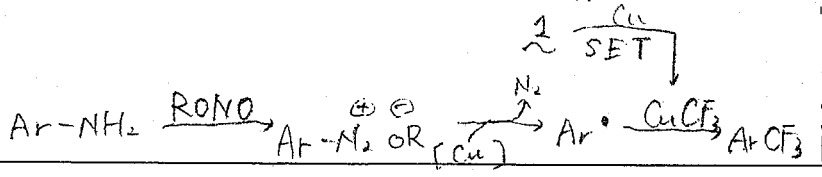
Mechanism



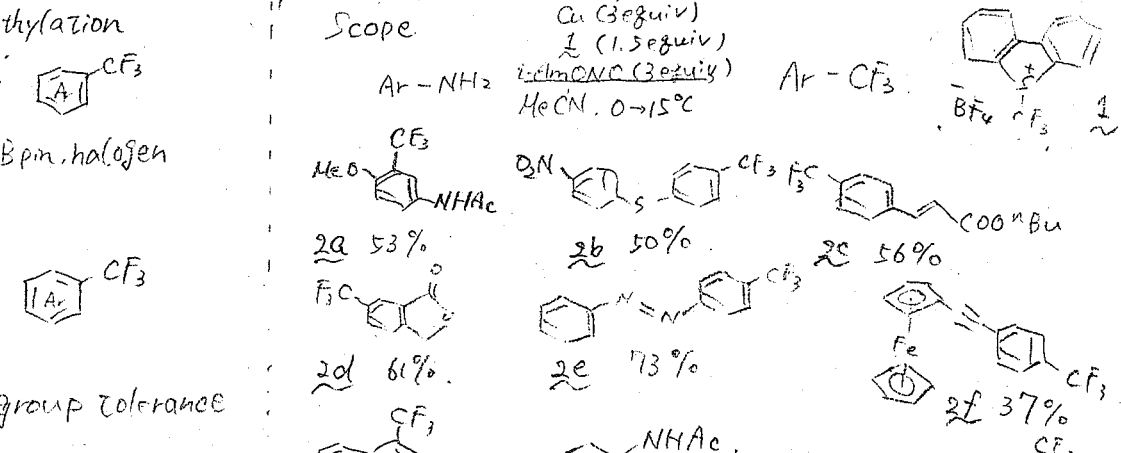
1 68%.

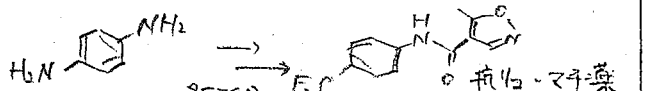
⇒ aryl radical.

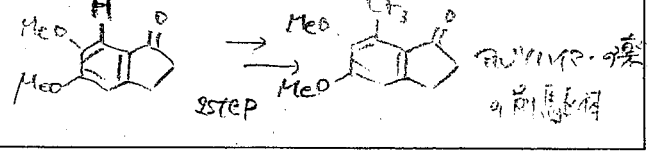
- Cu + 1 ¹⁹F NMR $CuCF_3$ (-34.72 ppm)



Scope

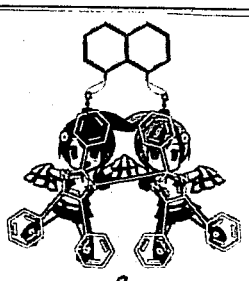




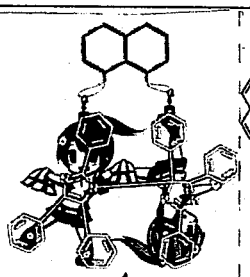


Jiro Abe	Aoyama Gakuen University (Japan)	Organic Letters 10.1021/ol401024u	M1 矢羽田

Photochromism of a Naphthalene-Bridged Imidazole Dimer Constrained to the "Anti" Conformation



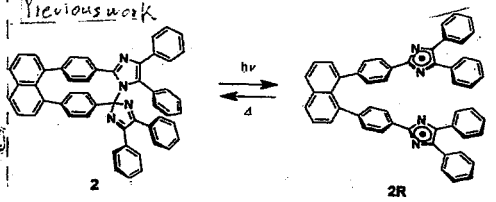
2
Previous work



1
This work

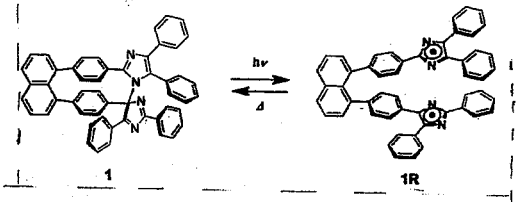
Photochromic Molecular とは
光を照射すると変色する分子⇒調光レンズ等に利用
・短時間で退色する分子はごくわずか

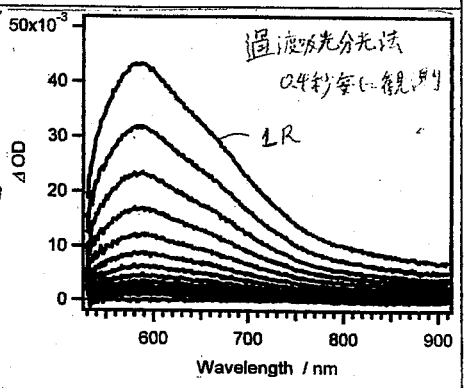
Previous work

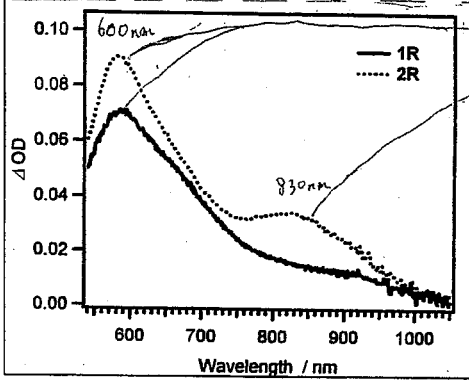


・短時間で退色
しかし、吸収帯が 500-1000nm にブロード

This work

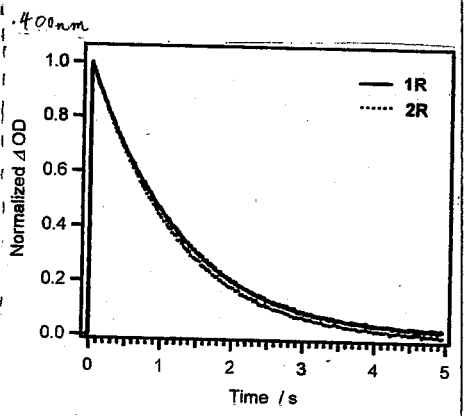






triphenylimidazolyl radical (TPIR) の典型的な吸収帯
π軌道の広がによる ラジカル-ラジカル 相互作用に
由来する吸収帯

2Rは2つのTPIRのπ軌道が完全に重なる36-
1Rは完全には重ならないため 830nm の吸収が減少
⇒ 1Rは1つの吸収帯のみを持つ。

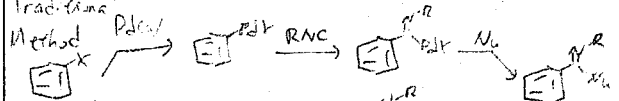


2Rほど 速い退色速度を示している。

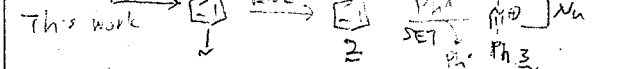
L. El Kaim P. Gámez-Montaño	ENSTA (France) Universidad de Guanajuato (Mexico)	ACIE(anie.201302659)	Lin

Three-Component Metal-Free Arylation of Isocyanides

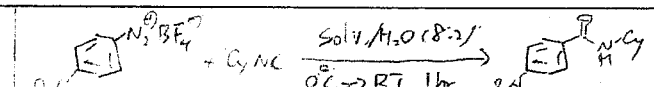
Traditional Method



in situ generation of $Ar-N_2^{\oplus}$

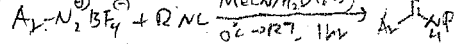


Ar: 4-$NH_2C_6H_4$, 4-ClC$_6$H$_4$, 4-MeOC$_6$H$_4$
R': Cy, tBu, $CH_2C_6H_4$-4-OMe
Yield: 19-92%



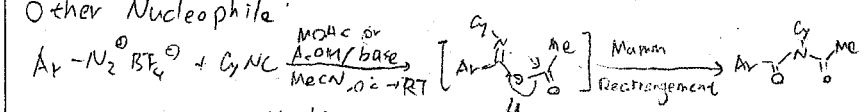
Base (1.5eq)	solv	Yield(%)
—	MeCN	
Py	MeCN	0
NEt_3	MeCN	15
NaOAc	MeCN	52
NaOAc	H_2O	45
NaOAc	Acetone	50

Scope:



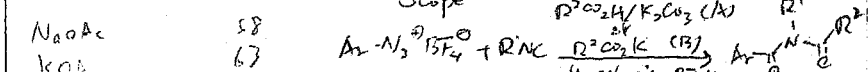
Ar: 4-ClC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-$NH_2C_6H_4$, 2-$CF_3C_6H_4$
R': Cy, tBu, $CH_2C_6H_4$-4-OMe, $CH_2C_6H_4$-4-Cl, CH_2CO_2Et,
Yield 33%-76%

Other Nucleophile



Base (1.1eq)	Yield (%)
NaOAc	58
KOAc	63
AcOH/K_2CO_3	59
AcOH/Cs_2CO_3	46

Scope

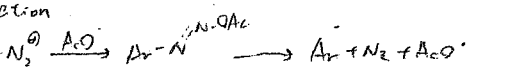


Ar: 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 2-$CF_3C_6H_4$, 4-$NO_2C_6H_4$ Yield(%)
R': Cy, $CH_2C_6H_4$-4-Cl, $CH(Ph)CO_2Me$, tBu (A) 31-76
R^2: Me, Ph, $CH_2C_6H_4$-4-F, iPr (B) 35-78

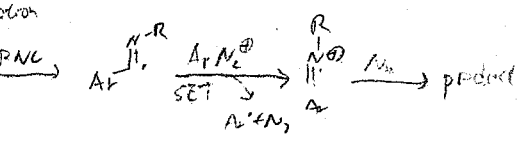
Possible mechanism

$S_{RN}1$:

Initiation



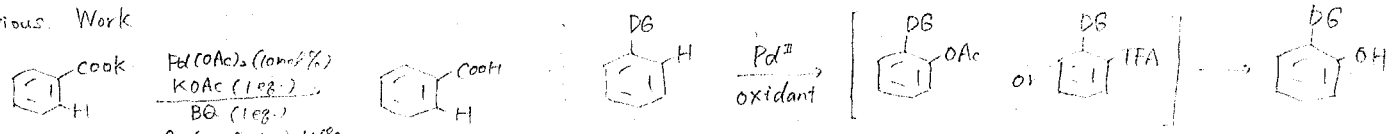
Propagation



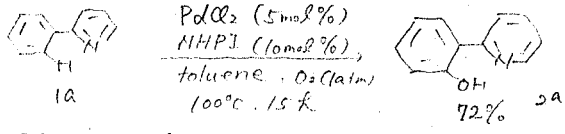
Ning Jiao	Peking University, China	ACIE, :10.1002/anie.201300957	D4 小嶋

$PdCl_2$ and N-Hydroxyphthalimide Co-catalyzed C_{sp2}-H Hydroxylation by Dioxygen Activation

◎Previous Work

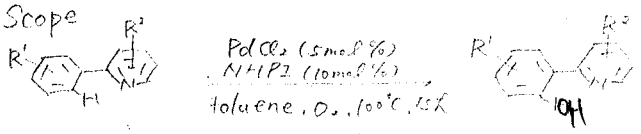


◎This Work



Pd, NHPI (or TBHP), toluene, O_2 の組み合わせ

◎Scope



- R' = p-F, Cl, Me, Ph, ^iPr, CF_3, OEt → 63~93%
  m-F → 71%
  o-OEt, O^nBu, O^iPr, OPh → 36~64%
- R^2 = 3 or 4 or 5 - Me, OMe → 53~78%

◎Mechanism

・$^{18}O_2$ を使用 → OH基のOがラベル

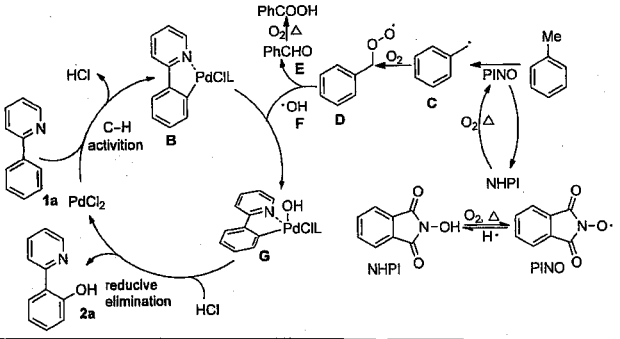
1a m-CPBA, Ar, no reaction

1a , no reaction

・EPR

toluene + NHPI ⇒ 反応系中と同じく ・OH 由来のピーク

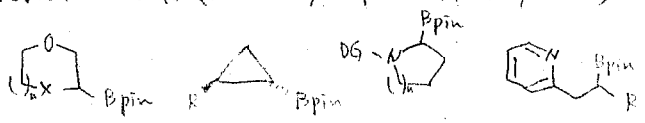
⇒ ・OH が NHPI と toluene の系から発生



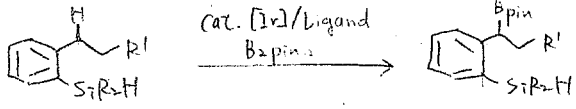
John F. Hartwig	University of California, United States	JACS, ja403462b	田中

Iridium-Catalyzed Borylation of Secondary Benzylic C-H Bonds Directed by a Hydrosilane

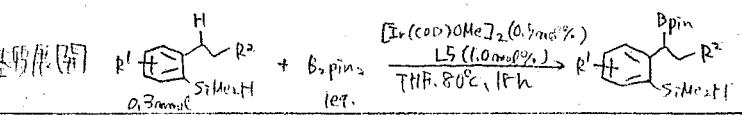
◎Previous Work (secondary (sp^3) C-H borylation)

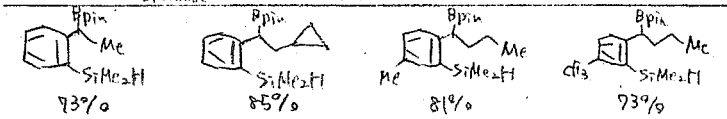


◎This Work (Silyl-directed secondary (sp^3) C-H borylation)



◎基質適用



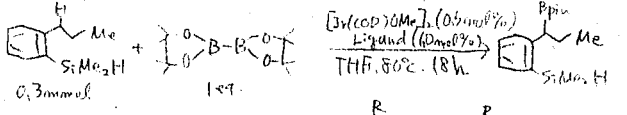


全18種

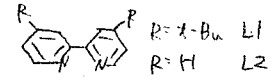
収率 50%~95%

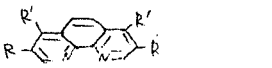
完全位置選択性

◎配位様式の決定



entry	ligand	yield (%)
1	L1	83
2	L2	61
3	L3	85
4	L4	89
5	L5	97
6	L5	9 ← H-Bpin を使用





◎Proposed Mechanism