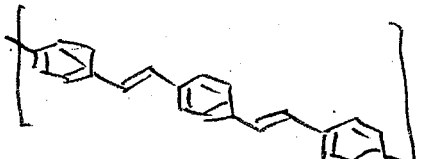


Electron-Deficient Poly(*p*-phenylene vinylene) Provides Electron Mobility over $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under Ambient Conditions

<This Work>

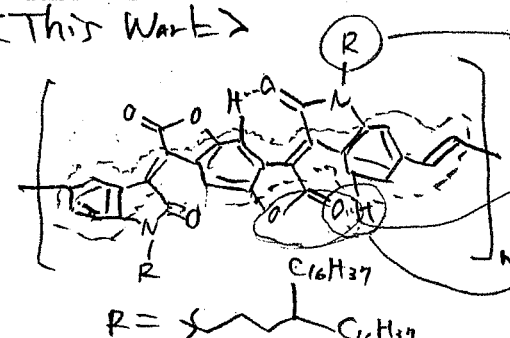


① PPV (poly(*p*-phenylene vinylene))
LED材料としては優秀
LAL, FET材料としては?

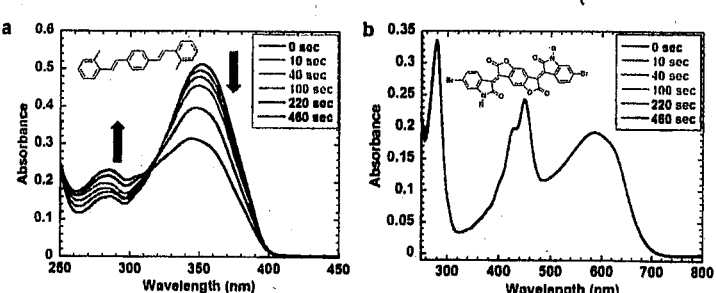
hole mobility: $10^{-5} - 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
electron " : $10^{-5} - 10^{-9}$

1Aの移動度の理由

- UVIに対する cis-trans異性化
- C-C single bondの自由回転による conformationの自由度が高い
- 分子間相互作用が低い
- LUMOが高い (-2.7 - -3.2 eV)

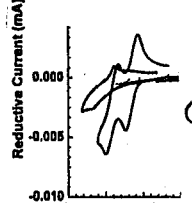


① side chain: 溶解性向上, 加工容易
② 電子引寄せ: LUMO ↓
③ 水素結合: 平面性向上



☆ CV

HOMO/LUMO = -6.12 / -4.10 eV (cf. PPV)
-5.2 / -2.7 eV

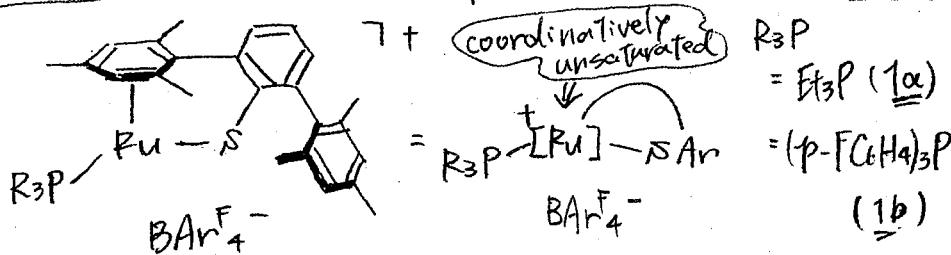


Me(max) $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (ambient cond.)

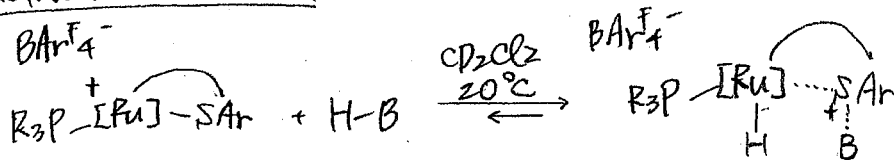
OKTOP

Catalytic Generation of Borenum Ions by Cooperative B-H Bond Activation: The Elusive Direct Electrophilic Borylation of Nitrogen Heterocycles with Pinacolborane

tethered Ru(II) thiolate complex. (Ohki, Tatsumi 2008)

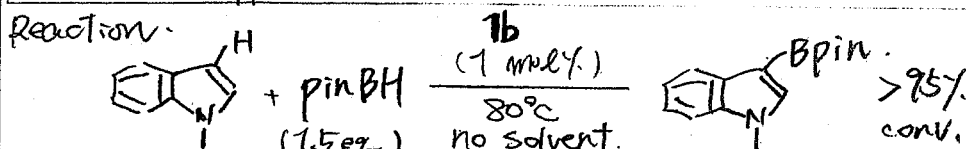


activation of B-H.

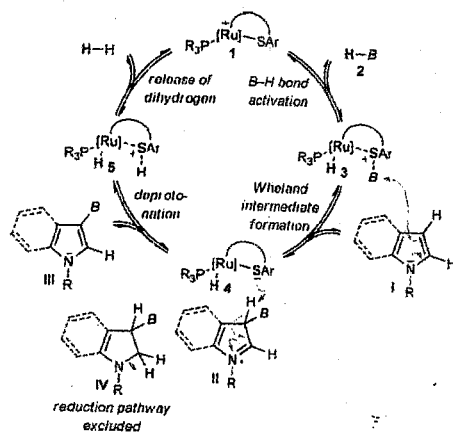


H-B	H-B	H-B + 1a	H-B + 1b
(<i>q</i> -BBN) ₂	1.5	-11.9 (α)	-11.8 (α)
pinBH	3.8 (β)	-8.9 (α)	-8.1 (α)

¹H NMR / ppm.

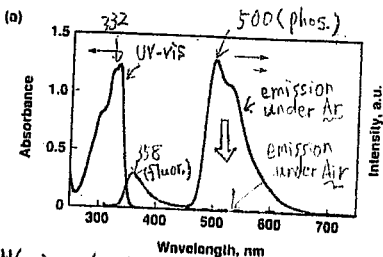
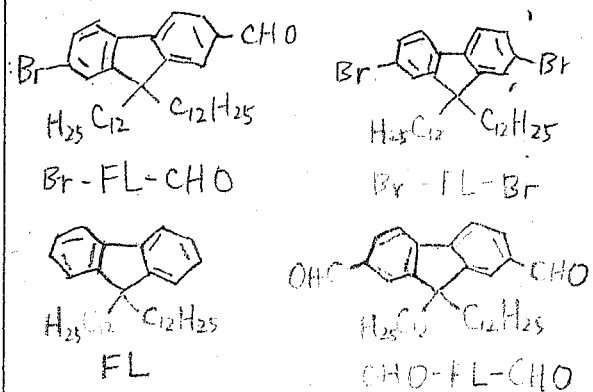


mechanism.

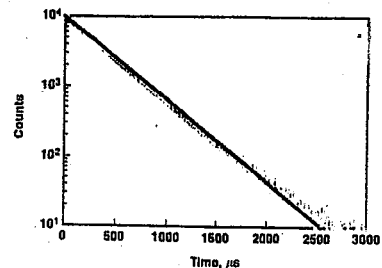


• N-Me 1つは -11, EtO-11
が適用可.
• solvent 2) Et₂
反応が非常に速い
• cat. 1a は不活性
borenum ionの求電子性
が低いため.
(*q*-BBN)₂ は適用可)

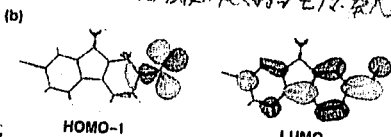
Phosphorescence from pure organic fluorine derivative in solution at room temperature



UV-vis and emission spectra of Br-FL-CHO (4.9×10^{-5}) in $CHCl_3$ at 298 K
 (0.1% 溶液の極限濃度まで測定可能) \rightarrow ICT 特性あり
 (濃度比比例で最大強度が増加) \rightarrow E12 型



Emission lifetime of Br-FL-CHO observed at 500 nm in $CHCl_3$ at 298 K
 τ (life time) = 255 μ s

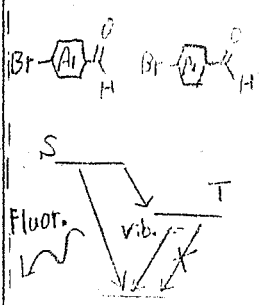


TDDFT with B3LYP/6-31G* of Br-FL-CHO
 S-S 遷移: $n-\pi^*$ 遷移

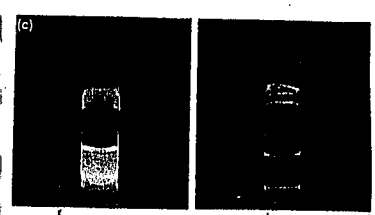
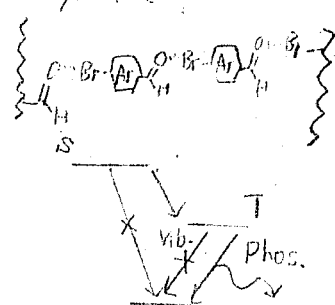
	Absorption (nm) (ϵ ($M^{-1} cm^{-1}$))	Emission (nm)	$\Phi(S_1)$ (eV)
FL	342 (2.0×10^4)	314	3.95
Br-FL-CHO	332 (4.0×10^4)	358, 500*	3.46, 2.46*
Br-FL-Br	342 (1.2×10^4)	321	3.86
CHO-FL-CHO	354 (3.7×10^4)	412	3.01

* Observed only under Ar atmosphere. * The singlet energy levels of the fluorine derivatives. * The triplet (T₁) energy level of Br-FL-CHO.

Solution



Crystalline



under Ar in $CHCl_3$ at 298 K
 under air

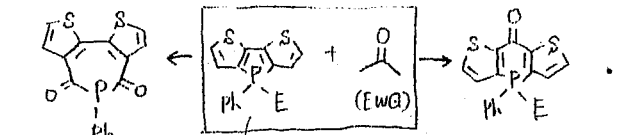
$\Phi_p(CHCl_3, 298K) = 5.9\%$
 $\Phi_p(2-Me-THF, 277K) = 35\%$

Br, CHO 基がリノル酸光の吸収を促進
 \rightarrow したがって、この化合物は、より効果的に光を吸収する
 FL or Br-FL-CHO + PMMA + $CHCl_3$ $\xrightarrow{drop. cast}$ FL + PMMA / Br-FL-CHO + PMMA
 blue / bright green
 空气中、5日間放置して、少し光が弱くなる

Kim, J. et al. Nat. Chem. 2011, 3, 205-1

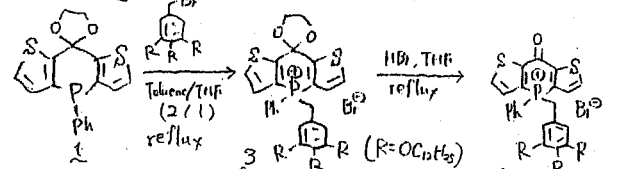
Phosphine Lipids: A Successful Marriage between Electron-Acceptor and Self-Assembly Features

Introduction



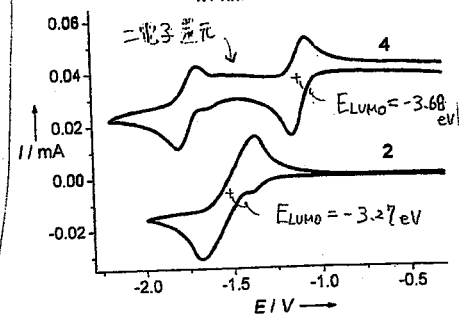
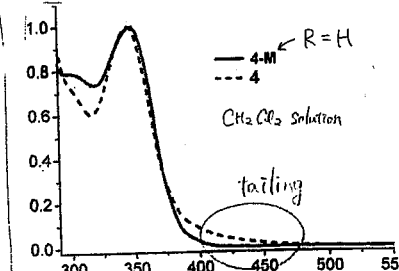
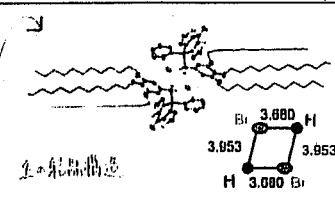
J. Am. Chem. Soc. 2013, 135, 1137.
 Angew. Chem., Int. Ed. 2004, 43, 6197.
 This Work (n-type material)

Synthesis



液晶
 ...分子の配列制御が可能
 (分子の性質に大きく影響)

	液晶性	m.p. (°C)	decomposition (°C)
3	X	185	225
4	○	215	227
5	○	146	235



二分子間でのπ-π相互作用と
 π-σ相互作用の相互作用による
 (C-H...Br: 3.95 Å, 3.68 Å)
 \Rightarrow T_m の m.p. が高い

ジロキシ基が無いもの R-H (R=H) と
 比較して吸収末端側の tailing による。
 \Rightarrow ジロキシ基は分子内電荷移動
 { 電子供与: ジロキシ基
 電子受容: リン骨格

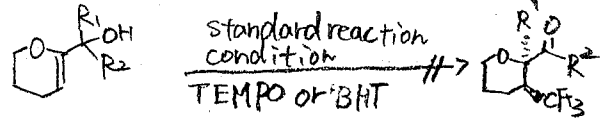
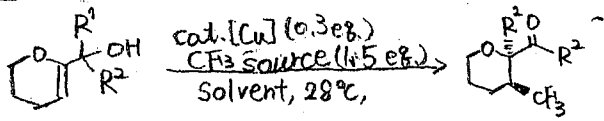
\bullet CH_3OH 溶液に代ると少し blue shift

この材料の光発光性は劣る。
 理由は m.p. と分解点、近い
 ため、融解~凝固を数回
 繰り返すと分解してしまう。
 \downarrow
 Br[⊖] の配位能力が弱い Br[⊖] の
 カウンターイオンとして、分子の
 m.p. 付近で分解してしまう。
 融解と分解が同時に起こる。

\bullet 2×10^{-3} M in CH_2Cl_2 solution with 0.1 M nBu₄NPF₆
 \bullet 可逆なリド... electron acceptor として機能

Copper-Catalyzed Tandem Trifluoromethylation/Semipinacol Rearrangement of Allylic Alcohols.

This Work.



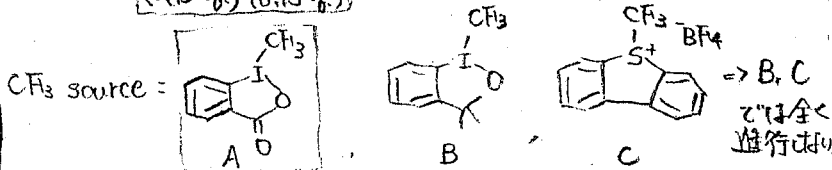
TEMPO-CF₃ or BHT-CF₃ 加ひして



CF₃ ラジカルが系中で生じてる。

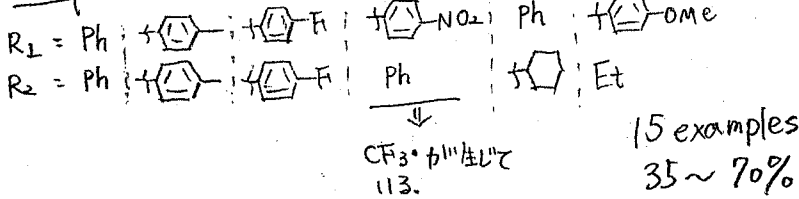
Optimization

Catalyst: CuBr/CuOAc (0.3 eq.), CuBr, CuOAc, CuCl, CuOTf·0.5C₆H₆ (0.15 eq.) (0.15 eq.)

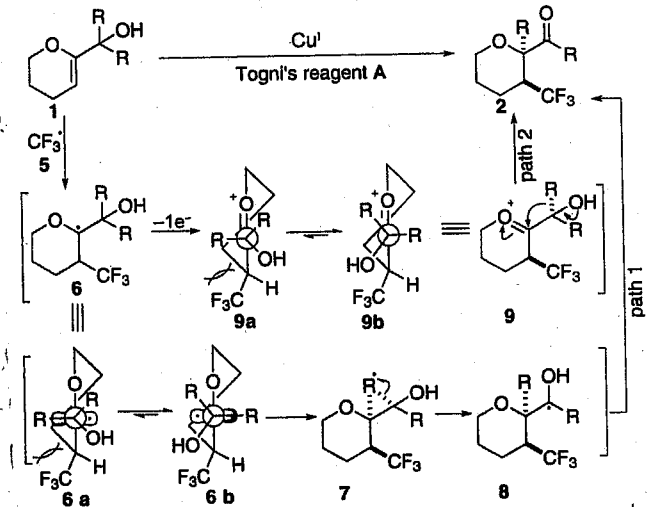


Solvent: CH₂Cl₂, CH₃CN, CH₃OH, toluene

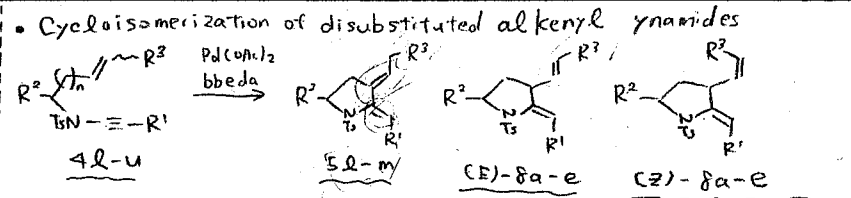
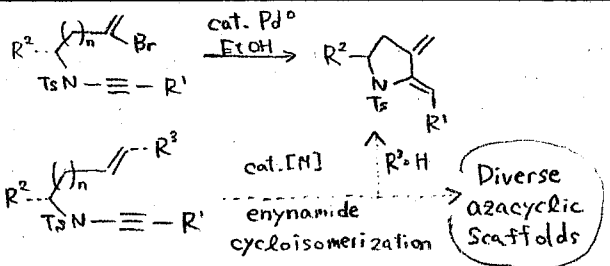
Scope



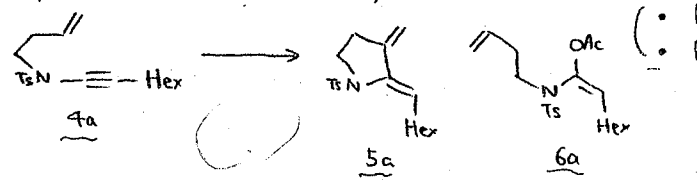
Proposed mechanism.



Palladium- and Ruthenium-Catalyzed Cycloisomerization of Enynamides and Enynhydrazides: A Rapid Approach to Diverse Azacyclic Frameworks.

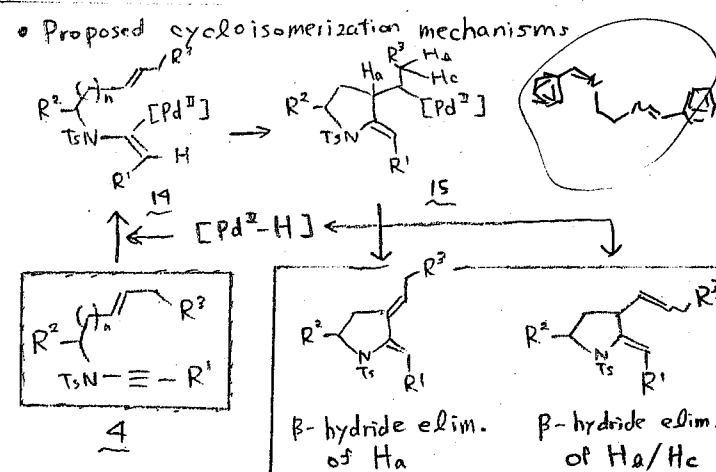


Optimization of enynamide cycloisomerization



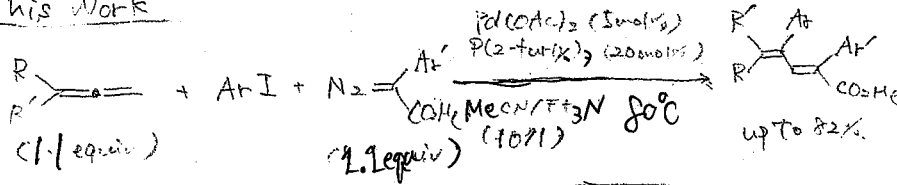
Entry	Catalyst system	t	5a/4a/6a
1	Pd(OAc) ₂ / bbeda	10 min	100:0:0
2	[Pd(OAc) ₂ (PPh ₃) ₂]	10 min	98:0:2
3	[Pd(OAc) ₂ ·iPr ₂ P(O-tol) ₃] ₂	1 h	31:62:7
4	Pd(OAc) ₂	1 h	66:29:9
5	[Pd ₂ (dba) ₃]·CH ₂ Cl ₂ /AcOH	1 h	50:49:1
6	[Pd ₂ (dba) ₃]·CH ₂ Cl ₂ /AcOH/bbeda	10 min	99:0:1
7	[Pd ₂ (dba) ₃]·CH ₂ Cl ₂ /AcOH/PCO-tol	1 h	19:69:11
8	[Cp*Ru(cod)Cl]	1.5 h	100:0:0

- 1,3-diene & 1,4-diene 生成 93%
- R³ to E alkene → E-1,4-dienes to major product
- R³ to Z alkene → E-1,4-dienes to major product
- R³ to E Ph → E-1,3-dienes to major product
- R³ to Z Ph → Z-1,3-dienes to major product

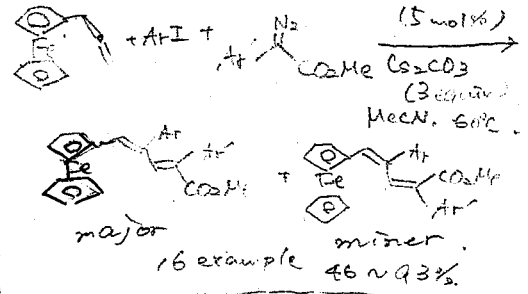


Palladium-Catalyzed Three-Component Reaction of Allenes, Aryl Iodides and Diazo Compounds: Approach To 1,3-Dienes

This Work



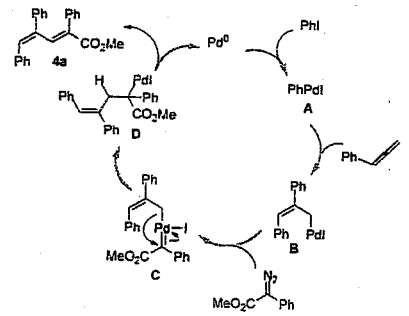
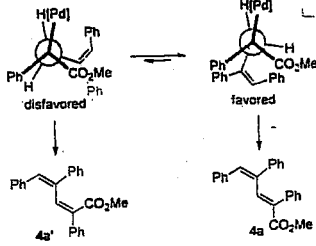
Application



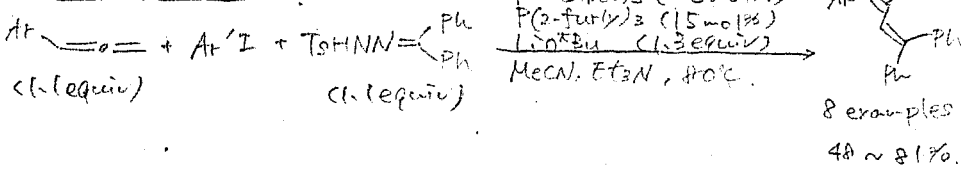
Scope

- (R, R') = (4-MeC₆H₄, H) 71%
- (4-ClC₆H₄, H) 74%
- (4-MeOC₆H₄, H) 54%
- (Ph, Ph) 55%
- Ar = EDG, EWG 62 ~ 82%
- Ar' = 3 or 4-Me, 3 or 4-Cl, 3 or 4-MeO, 2-F, 4-NO₂ Trace

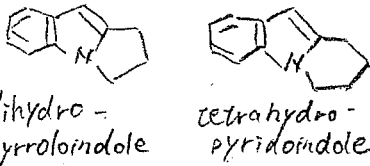
Plausible mechanism



Diazo Compound



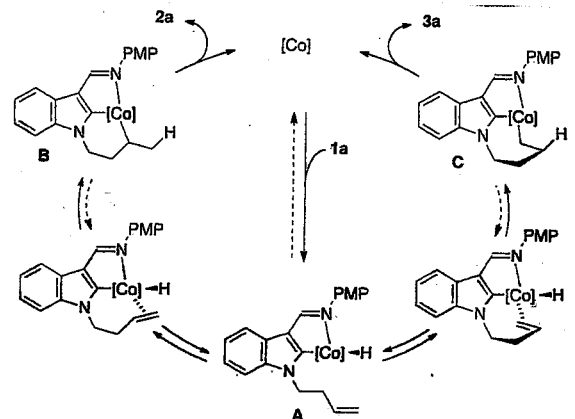
Cobalt-Catalyzed Intramolecular Olefin Hydroarylation Leading to Dihydropyrroloindoles and Tetrahydropyridoindoles



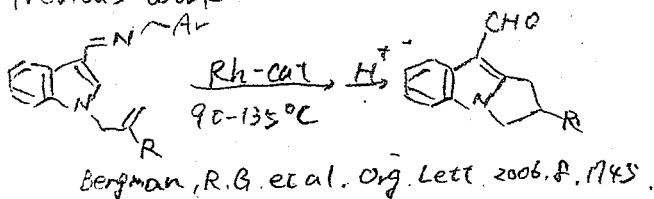
Scope

Ligand	Major Product	Yield (%)
IPr		99 (48:1)
SIMes		75 (1.2:1)
R = (C ₆ H ₅) ₂ Ph, IPr		78 (9:1)
R = Et, SIMes		51 (9:1)
IPr		90
ZPL		73 (9:1)

Mechanism



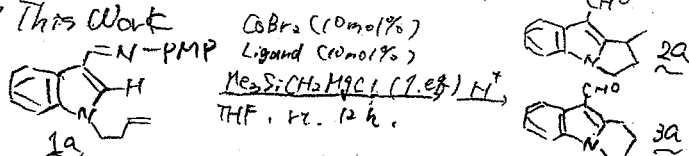
Previous Work



• S-endo-Type.

• 5-endo, 6-endo 选择性

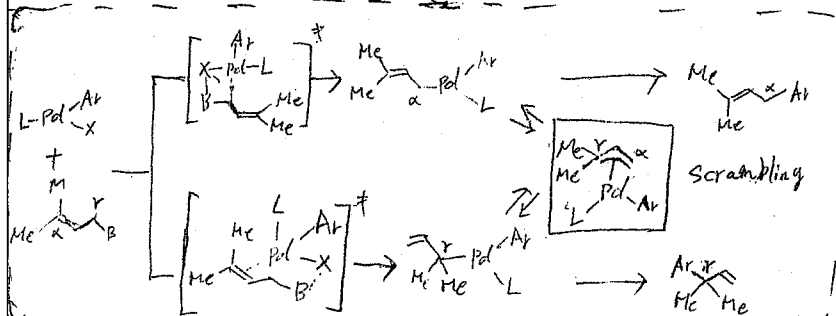
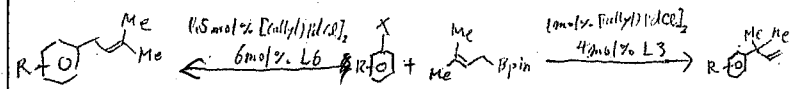
This Work



Entry	Ligand	Yield (2a:3a)
1	SIMes·HCl	84 (4:1)
2	IPr·HCl	85 (2:1)
3	SIPr·HCl	86 (1:5)
4	IPr·HCl	63 (1:5)

Ligand-Controlled Palladium-Catalyzed Regiodivergent Suzuki-Miyaura Cross-Coupling of Allylboronates and Aryl Halides

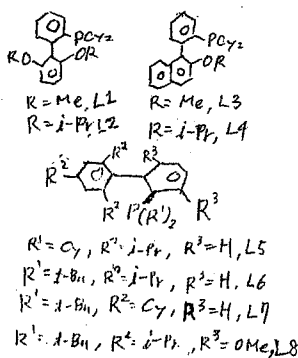
This work



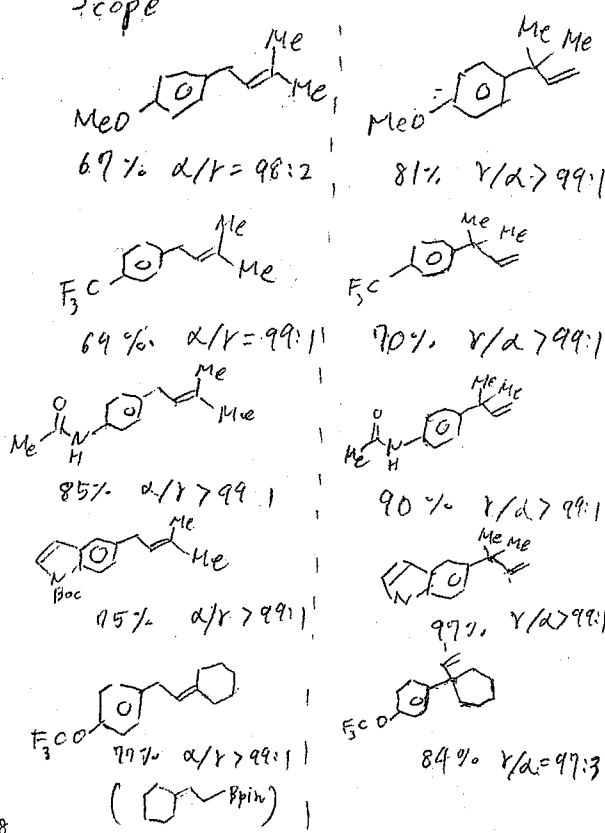
Ligand Evaluation

Reaction conditions: Allylboronate + Ar-X, PdCl₂(dppf)₂, THF, K₂PO₄ (1.0), 40-70°C, 12h.

L	d/r	Yield of a (%)	Yield of b (%)
L1	<1:99	<1	55
L2	1:99	<1	42
L3	<1:99	<1	99
L4	17:83	16	7
L5	90:10	63	7
L6	98:2	84 (in MeCN)	<1
L7	88:12	59	7
L8	46:54	6	7



Scope



Alexander Breder

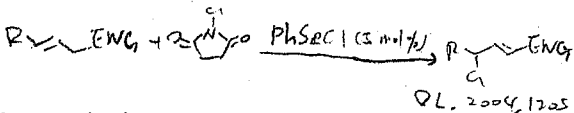
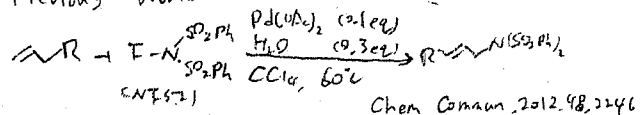
Georg-August-Universität Göttingen

Anie.201303662

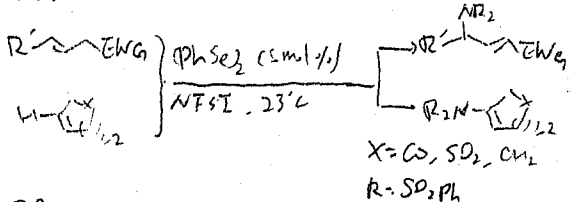
Lin

Direct Oxidative Allylic and Vinylic Amination of Alkenes through Selenium Catalysis

Previous Work



This Work

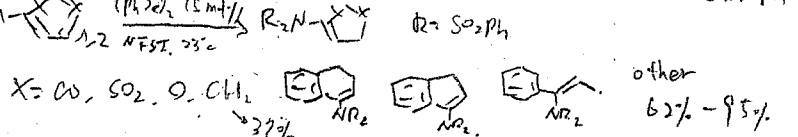
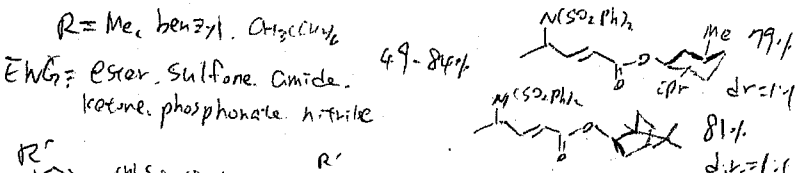
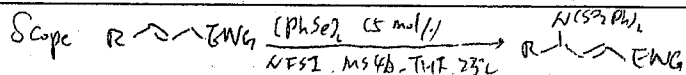


Optimization

Reaction conditions: Alkene + N(SO₂Ph)₂, PhSe₂ (5 mol%), THF, 23°C.

PhSe ₂	solv.	additive	Yield (%)
(PhSe) ₂	THF	-	64 ⇒ by-product
(PhSe) ₂	THF	MS4A	84
(PhSe) ₂	Et ₂ O	MS4A	64
(PhSe) ₂	MeCN	MS4A	60
-	THF	MS4A	0

Other [Se]: (i-Pr)₂Se₂ 55%, (CF₃)₂Se₂ 48%



Mechanism Studies:

