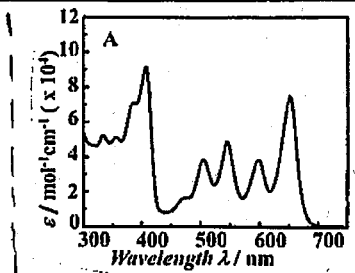


High Mobility, Air Stable, Organic Single Crystal Transistors of an n-Type Diperylene Bisimide

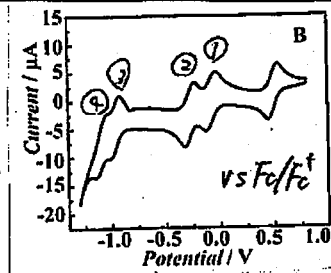
air中で安定に作動する
n型(電子輸送)材料の開発
は近年のシリコンエレクトロニクス分野
に残っている大きな課題。

分子設計: $-4.5 < \text{LUMO} < -4.0 \text{ eV}$

This Work

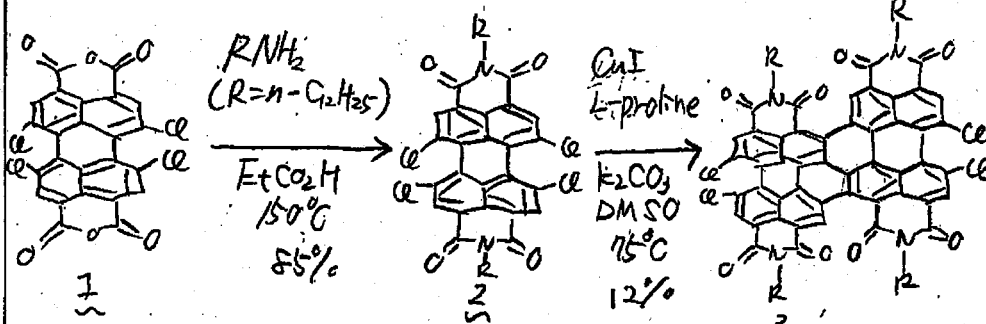


UV/vis of 3



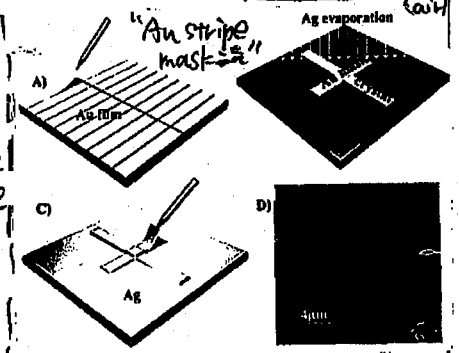
CV of 3

$\mu_e = 4.65 \text{ cm}^2 \text{Vs}^{-1}$

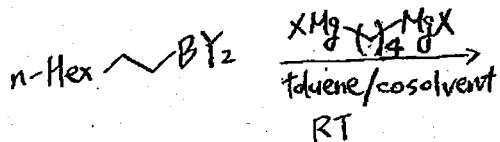


(kg scale) 合成可能

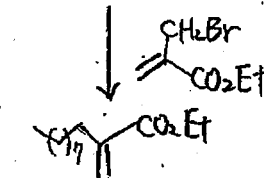
soluble in CHCl_3 , toluene, and $\text{C}_6\text{H}_5\text{-Cl}$ ($> 20 \text{ mg mL}^{-1}$) T_d (5w%) $> 389^\circ\text{C}$



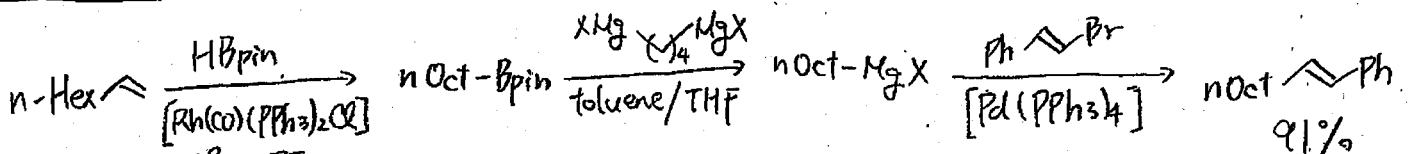
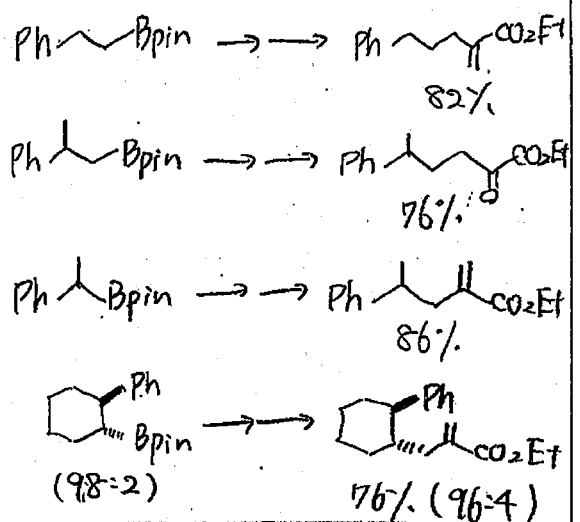
Preparation of Alkylmagnesium Reagents from Alkenes through Hydroboration and Boron-Magnesium Exchange



BY ₂	X	cosolvent	yield.
B(n-Oct) ₂	Br	Et ₂ O	85%
	Cl	THF	n.d.
9-BBN	Br	Et ₂ O	89%
	Cl	THF	n.d.
Bpin	Br	Et ₂ O	72%
	Cl	THF	93%



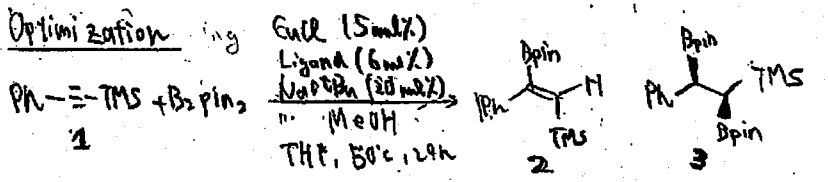
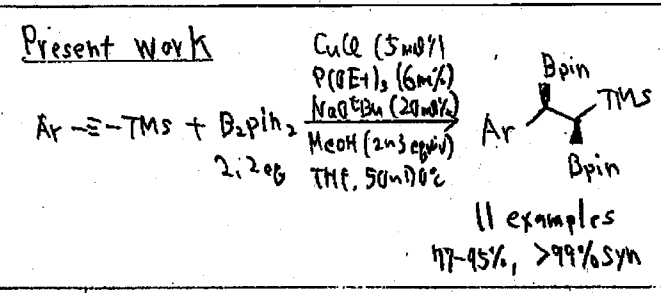
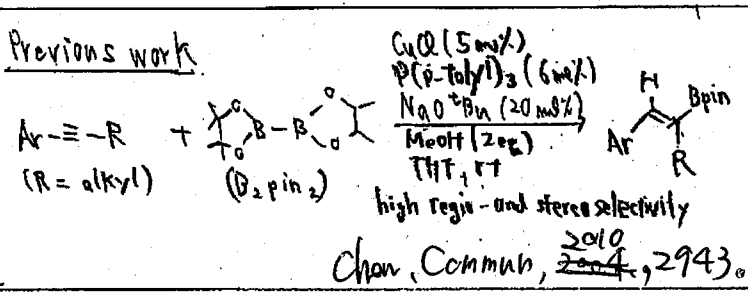
THF 溶媒での反応に成功. 応用の幅が広がる. Xの効果果については言及なし.



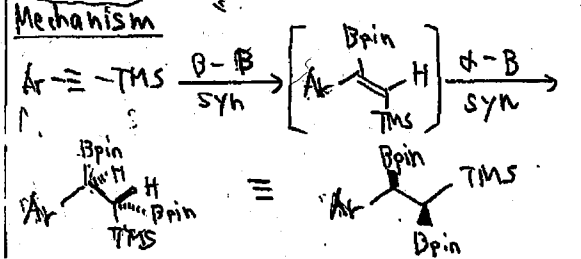
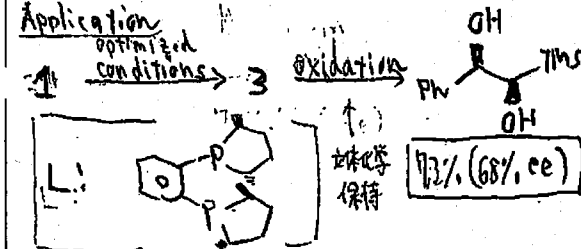
一般的な Grignard 反応剤と同様の反応性.

Fe 触媒カブリングや, Cu 触媒カブリングにも適用可能

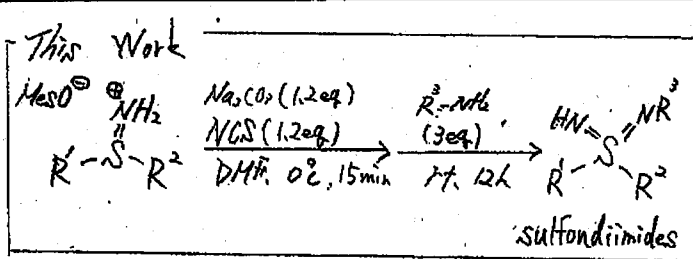
Copper-Catalyzed Double Borylation of Silylacetylenes: Highly Regio- and Stereoselective Synthesis of *Syn*-Vicinal Diboronates



entry	ligand	B ₂ pin ₂ (equiv)	MeOH (equiv)	2:3	yield of 3
1	P(p-tol) ₃	1.1	2	1.2: > 99	44
2	P(p-tol) ₃	2.2	2.2	1.1: > 99	86
3	P(OEt) ₃	2.2	2.2	1.1: > 99	89
4	P(OEt) ₃	2.2	0	-	4
5	Xantphos	1.1	1	> 99: < 1	49 (2)
6	Xantphos	1.5	2	> 99: < 1	83 (2)



Synthesis of sulfondiimines by N-Chlorosuccinimide-Mediated Oxidative Imination of Sulfiliminium Salts



• NBS, NCS は 収率
• 3, 4 は 単離 できず
• Selectfluor は 10分 = 16 早く, 3 = 2 時間 必要
• NCS は 10分 = 16 早く, 3 = 15 早く
• Selectfluor は 5 equiv 必要

Scope

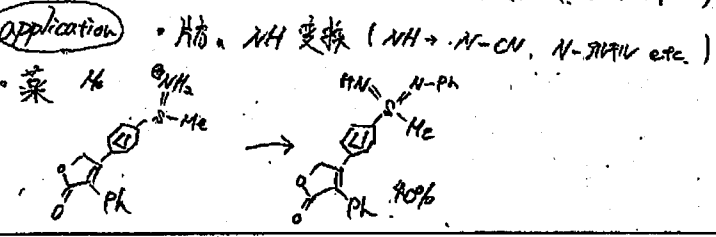
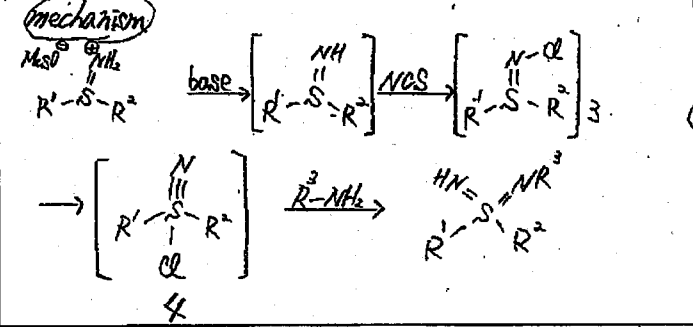
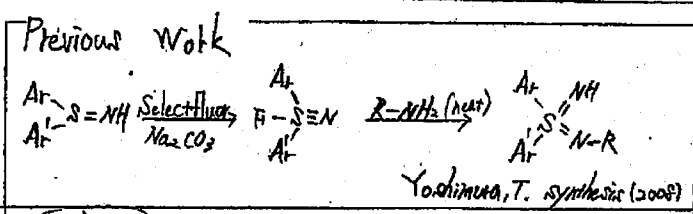
Meso⁺ NH₂ \rightarrow Ph-S(=NH)-Me \rightarrow HN=C(NR)₂

standard conditions \rightarrow 73% \rightarrow 2, 3, 4 OK

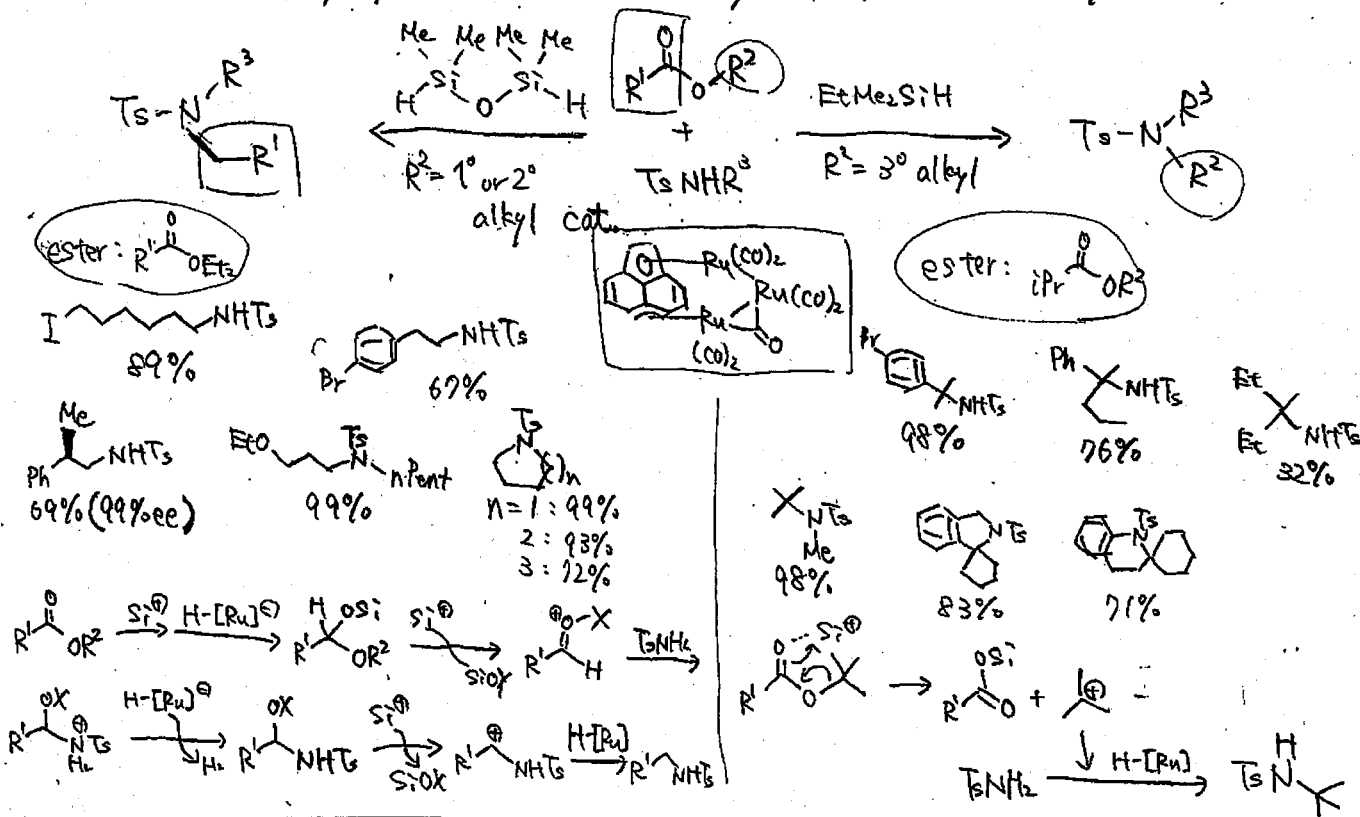
20 example: 31% ~ 80%

• R = 12 系, 脂肪族
• R = H, (7) (16) 系
• NCS 用 2 eq NH 必要

• 2 体 基本 Ph & Me (収率 40%)
Ar & Ar x 7 (16) 系

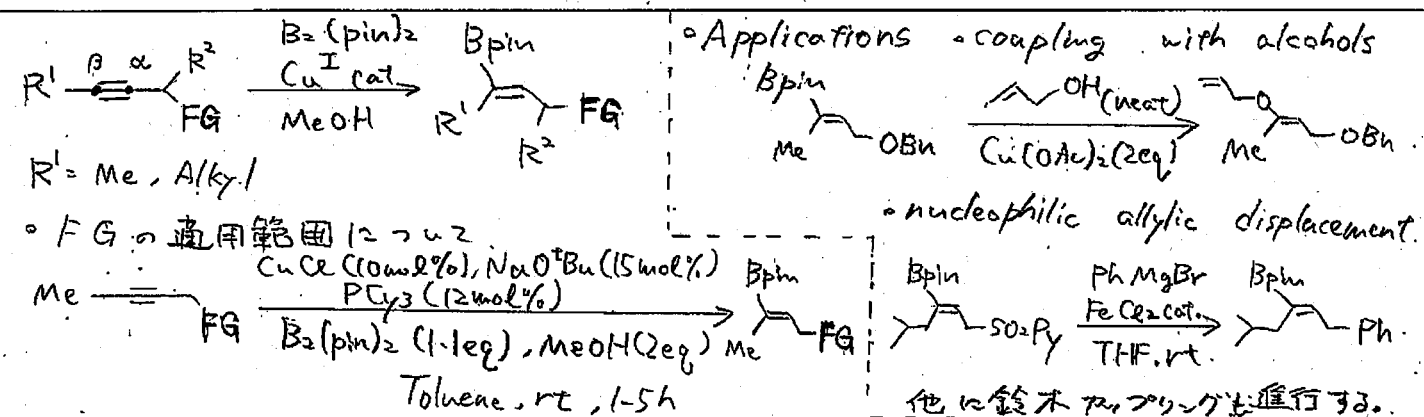


N Alkylation of Tosylamides Using Esters as Primary and Tertiary Alkyl Sources: Mediated by Hydrosilanes Activated by a Ruthenium Catalyst



Ramon Gomez Arrayas, Universidad Autonoma de Madrid (Spain), JACS (ja300627s), M2 Kawai
 Juan C. Carretero

Regiocontrolled Cu^I-Catalyzed Borylation of Propargylic Functionalized Internal Alkynes



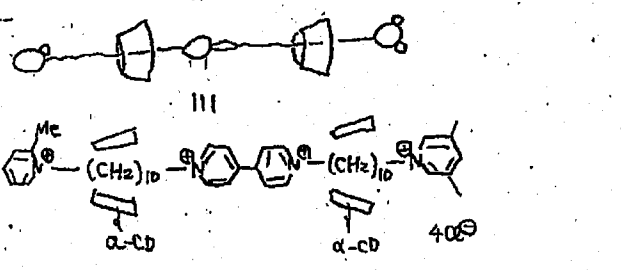
FG	α/β ratio	yield (%)
S(2-py)	<2 = 98>	82
SO ₂ Ph	<2 = 98>	98
OH	<2 = 98>	69
OBn	<2 = 98>	98
OAc	10 = 90	76
NHTs	<2 = 98>	89
CH ₂ OBn	12 = 88	72
Z-pentyne	15 = 85	30

DFT calculation results for transition states TS_α and TS_β . TS_α energy: 10.6 kcal/mol. TS_β energy: 7.9 kcal/mol. Energy difference: -42.7 kcal/mol. -43.3 kcal/mol.

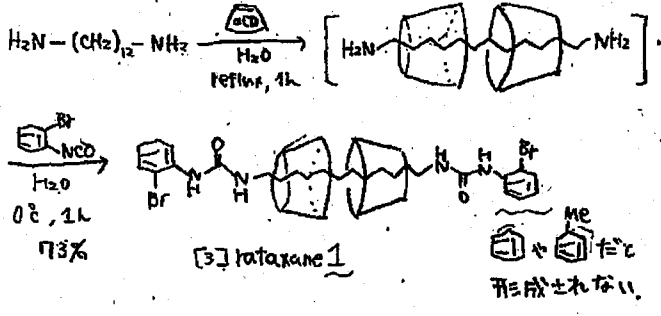
Selective Synthesis of a [3]Rotaxane, Consisting of Size-Complementary Components and Its Stepwise Deslippage

★ [3] Rotaxane の合成 (環の数 + 軸の数) → ΔS 的に不利!!

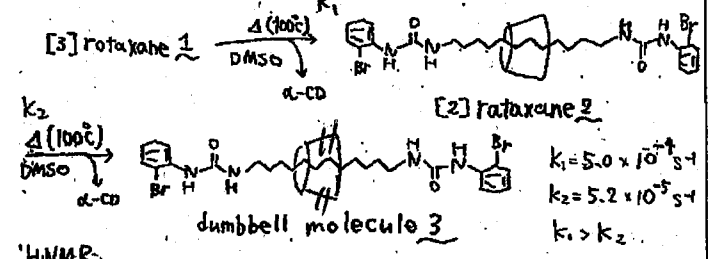
• Harada et al. (Chem. Eur. J. (2007))



• Takata et al. (This work)



Stepwise Deslippage.



¹H NMR

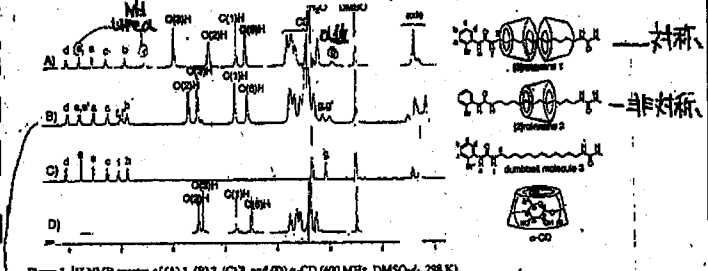
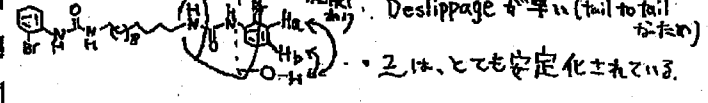


Figure 1. ¹H NMR spectra of (A) 1, (B) 2, (C) 3, and (D) α-CD (400 MHz, DMSO-d₆, 298 K).

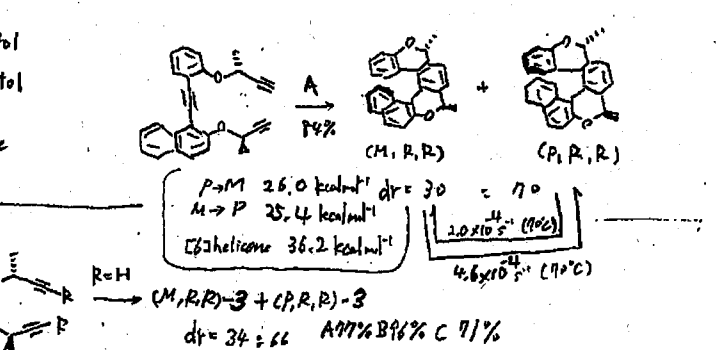
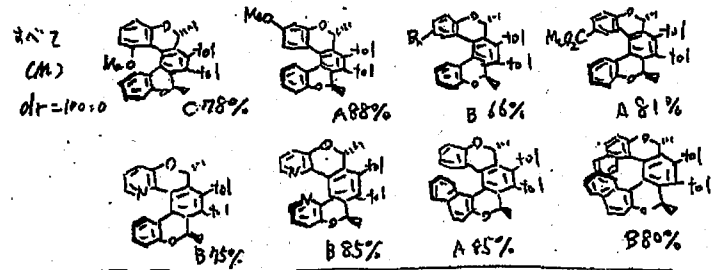
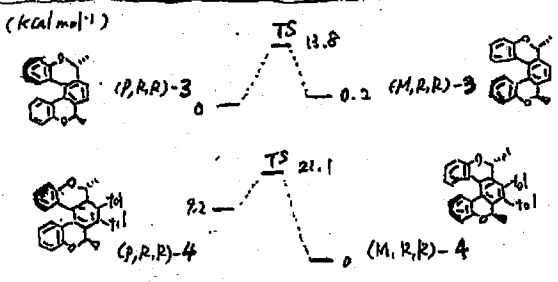
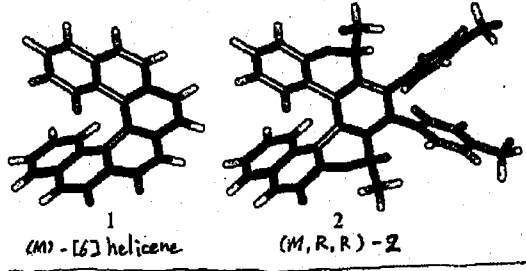
NOEST of 2



A General Approach to Optically Pure [5]-, [6]-, and [7]Heterohelicenes

ヘリセンの光学異性体の片方を選択的に合成する研究において、ヘリセン骨格の長さ、官能基に左右される手法は報告されていない。

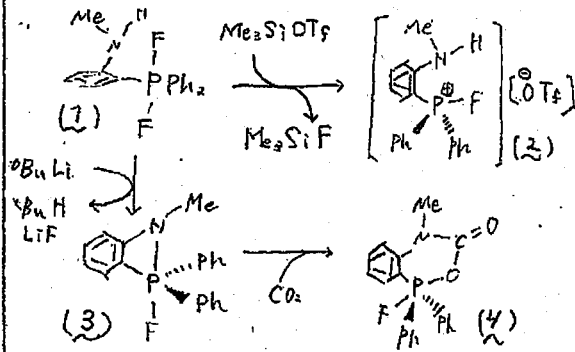
⇒ ジアステレオ選択的 [2+2+2] 環化により達成する。



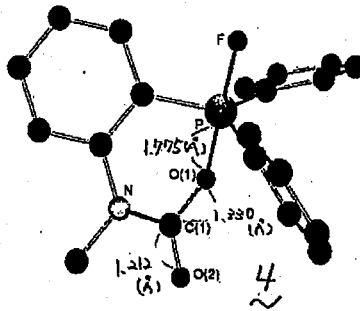
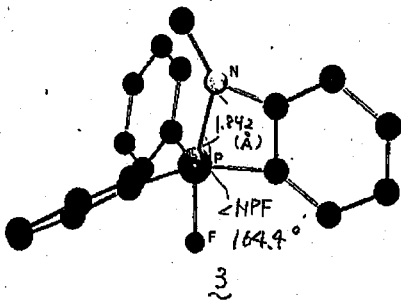
$\Delta E^\ddagger = 26.0 \text{ kcal/mol} \quad \Delta E^\ddagger = 25.4 \text{ kcal/mol}$
 $\Delta E = 36.2 \text{ kcal/mol}$
 $4.6 \times 10^{-11} \text{ s}^{-1} \quad (110^\circ\text{C})$
 $\Delta E = 34 \text{ kcal/mol} \quad A 77\% \quad B 89\% \quad C 91\%$
 $R = p\text{-tol} \rightarrow (M,R,R)\text{-}4 \quad A 81\% \quad B 89\% \quad C 91\%$
 Sum = dimethyl fumarate
 A: [CpCo(CO)] (20 mol%), PPh₃ (40 mol%), irradiated by a halogen lamp, decane, 140°C, 1h
 B: [CpCo(CO)(fumar)] (20 mol%), PPh₃ (40 mol%), microwave reactor, THF, 180°C, 20 min
 C: [Ni(Co-dh)] (20 mol%), PPh₃ (40 mol%), THF, rt, 30 min

Phosphorus as a Lewis Acid: CO₂ Sequestration with Amidophosphoranes

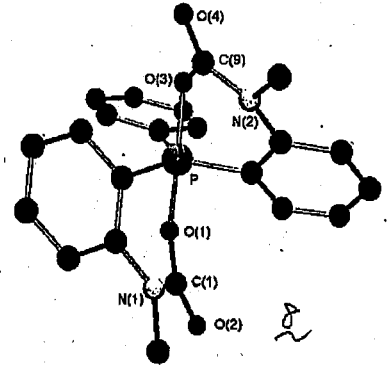
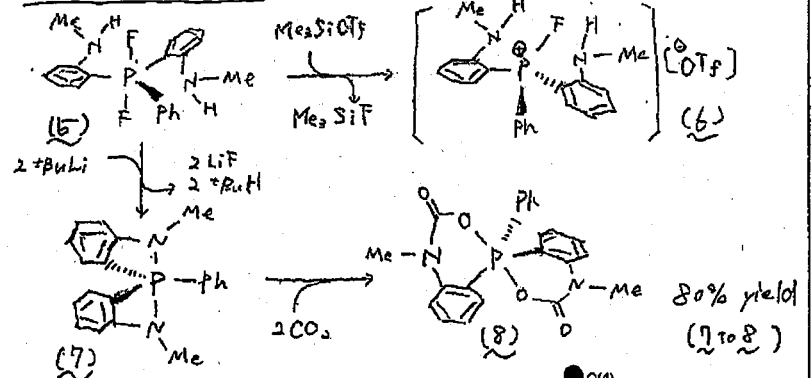
Scheme 1.



X ray structures



Scheme 2.



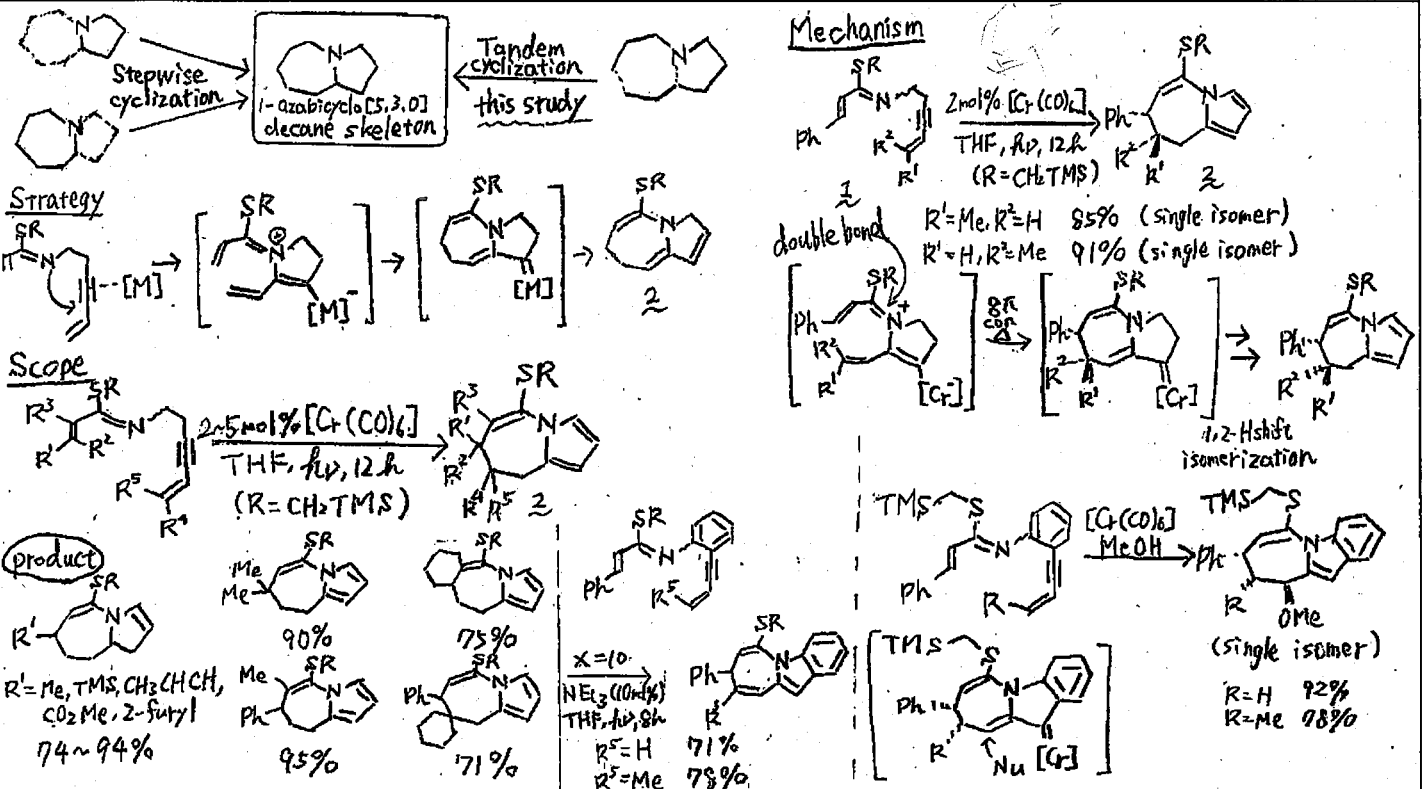
Iwasawa, N

Tokyo Institute of Technology

Angew. Chem. Int. Ed.

okazaki

10.1002/anie.201201505

Chromium(0)-Catalyzed Tandem Cyclization of α,β -Unsaturated Thioimidates Containing an Enyne Moiety

Strain Release in Organic Photonic Nanoparticles for Protease Sensing

* 癌... タンパク質分解酵素 (protease) が過剰発生する。

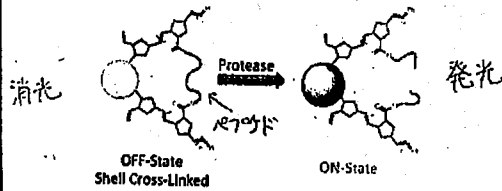
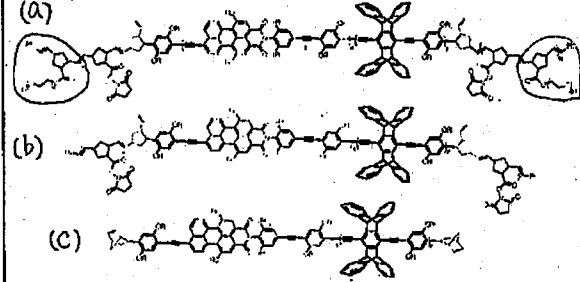


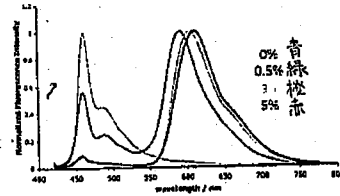
fig.1 ナノ微粒子発光標識の概略図

* 分子設計 (共役系高分子)

発光性コリモノをハイドロゲルでコーティング



* (b)の発光特性

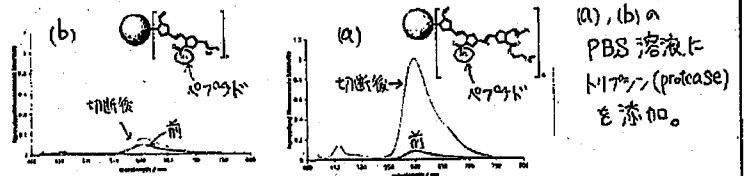


2つの発光極大

{ 454 nm... ポリマー主鎖
604 nm... ペリレン

fig.2 (b)の濃度別発光スペクトル ($\lambda_{ex} = 410\text{nm}$)
↳ 分子中のペリレン部位の濃度 (mol%)

* ペプチド切断による発光の変化



(a), (b)のPBS溶液にトリプシン (protease) を添加。

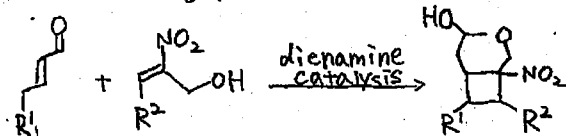
fig.3 3 mol% (a) と (b) のペプチド切断による発光の変化

(a)に関して...

トリプシンによるペプチド切断によって、発光強度が大きく増大した。

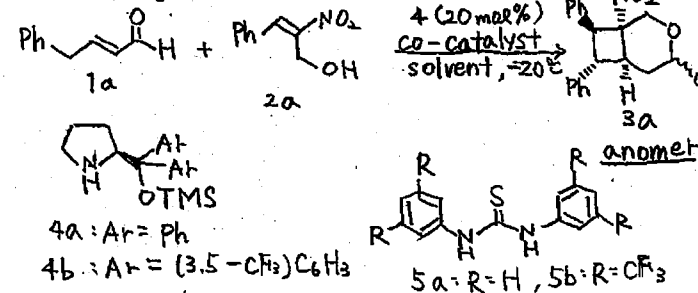
Cooperative Dienamine/Hydrogen-Bonding Catalysis: Enantioselective Formal [2+2] Cycloaddition of Enals with Nitroalkenes

~ Present Work ~



One-step synthesis of cyclobutane by [2+2] cycloaddition.

* Screening for the best conditions.

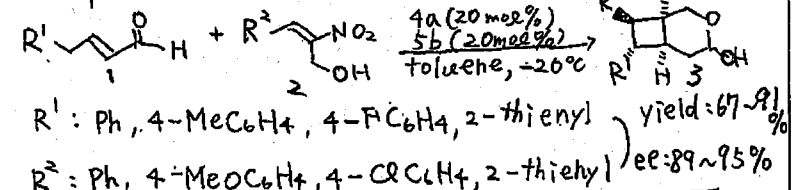


• 4 (in CHCl₃) - - - - - 4a (yield: 59%, ee: 74%)
4b (0%, -)

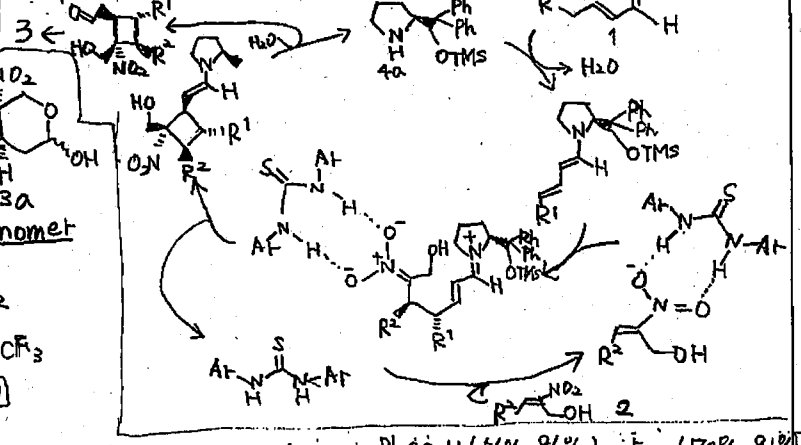
• Solvent (4a) - - - - - toluene (56%, 86%), CHCl₃ (59%, 74%)
THF, EtOH (<5%, n.d.)

• Co-catalyst + - - - - - PhCO₂H (56%, 86%), 5a (70%, 91%)
5b (86%, 91%)

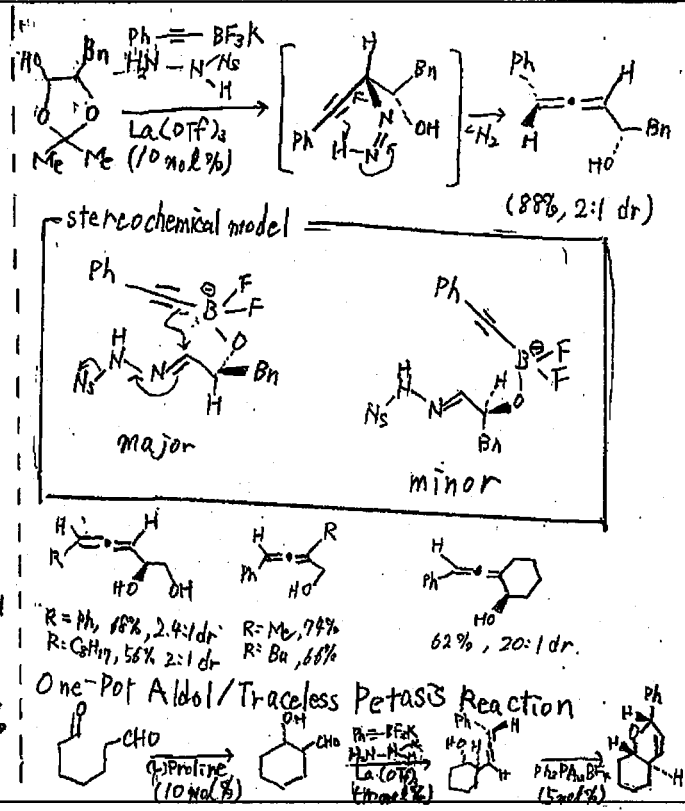
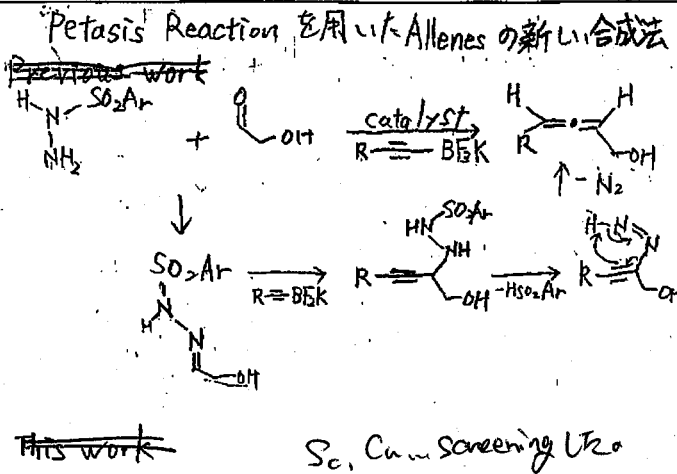
• Scope



• Proposed mechanism



A Direct Synthesis of Allenes by a Traceless Petasis Reaction



Ruthenium-Catalyzed Transfer Oxygenative Cyclization of α,ω -Dienes: Unprecedented [2+2+1] Route to Bicyclic Furans via Ruthenacyclopentatriene

