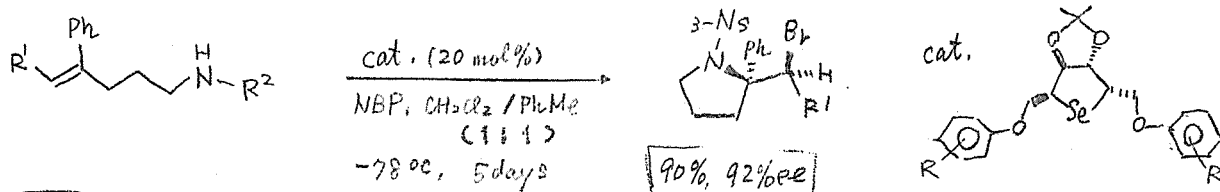


C₂-Symmetric Cyclic Selenium-Catalyzed Enantioselective Bromoaminocyclization



Screening

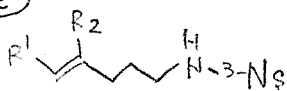
Substrate

$R^1 = \text{H, Me}$
 $R^2 = 4\text{-Ns, 2-Ns, 3-Ns}$

Cat.

$R = \text{H, 4-Me, 3,5-Me}_2, 4\text{-tBu}$
 $4\text{-iPr, 4-CMe}_2\text{Et}$

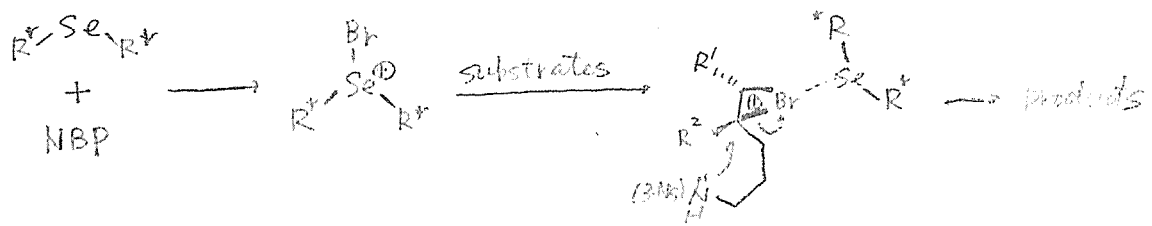
Scope



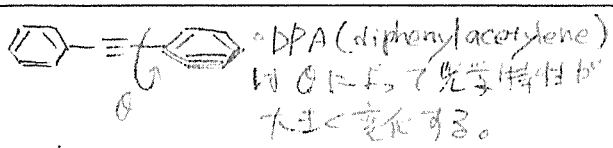
$R^1 = \text{Et, n-Pr, n-Bu, i-Bu, Bu, EtPh, allyl, homoallyl, Ph, Me}$
 $R^2 = \text{Ph, 3-ClC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 4\text{-FC}_6\text{H}_4, 4\text{-CF}_3\text{C}_6\text{H}_4, 2\text{-MeC}_6\text{H}_4, 3\text{-MeC}_6\text{H}_4, 4\text{-MeC}_6\text{H}_4$

Yield: 15 ~ 93% ee: 29 ~ 95%

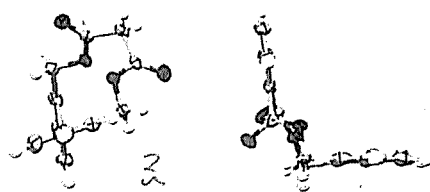
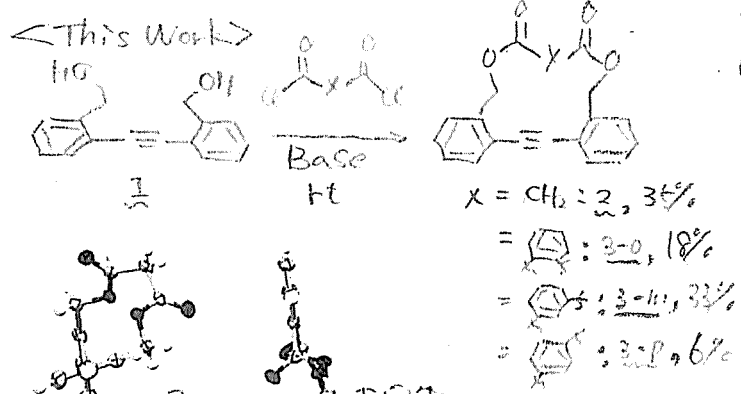
Mechanism



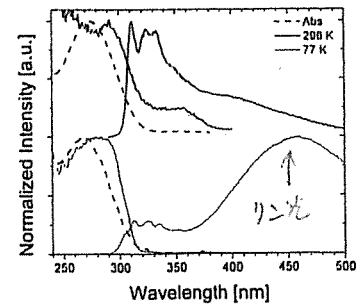
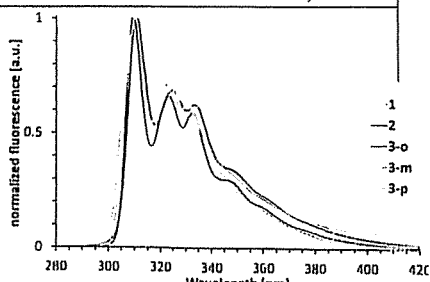
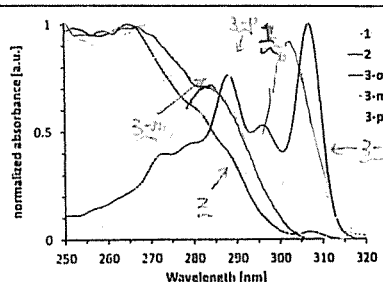
Twisted Tethered Tolanes: Unanticipated Long-Lived Phosphorescence at 77 K



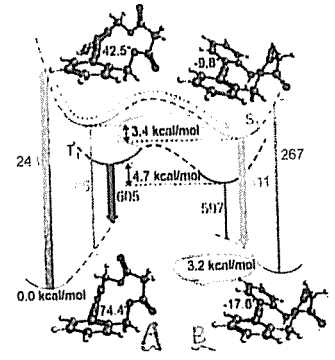
通常, $\theta = 0^\circ$ が最も安定構造
 $\theta > 90^\circ$ の報告はなし。



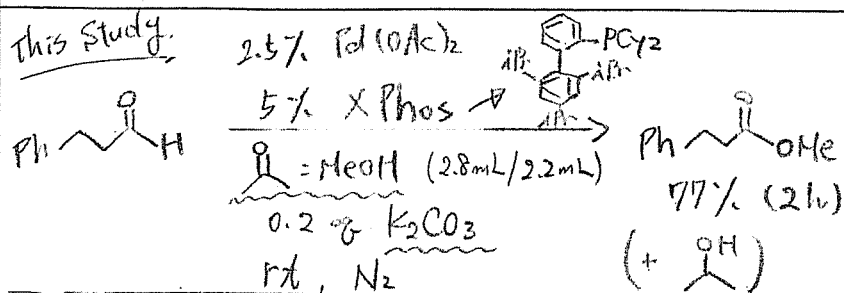
X-ray structures
 $\theta = 79.3^\circ$ $\theta = 6.2^\circ$
 $3-m: \theta = 72^\circ$



UV and FL of **2** @ 298K and @ 77K
 $\tau_{298K} < 100 \text{ ps}$
 $\tau_{77K} = 4 \text{ s!}$

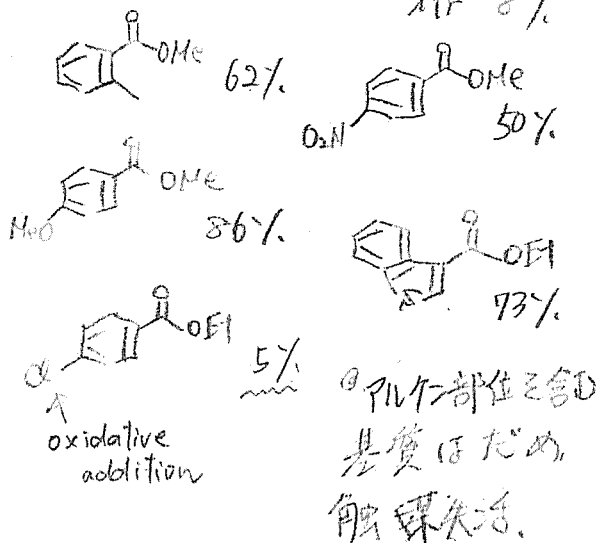
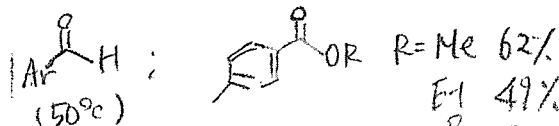
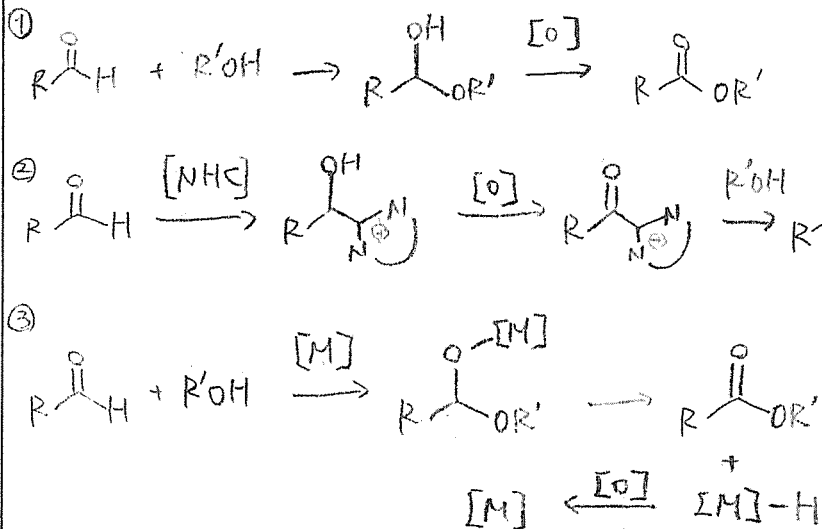


Pd-Catalyzed Aldehyde to Ester Conversion: A Hydrogen Transfer Approach



ROH: EtOH 79%, iPr-OH 60%
ABuOH 0%, sBuOH 55%
2 (50°C)

解環的 27% 5A'



Eiji Yashima et al.

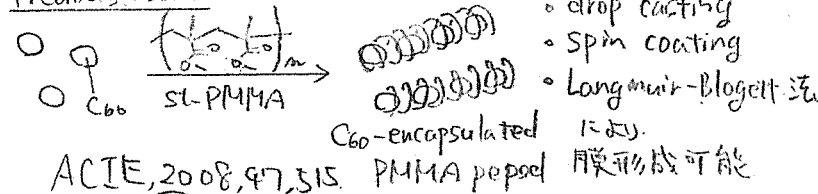
Nagoya University (Japan)

ACIE: anie.201208481

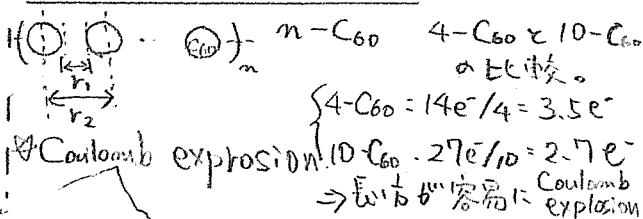
Nagamachi

Electrical Switching Behavior of a [60]Fullerene-Based Molecular Wire Encapsulated in a Syndiotactic Poly(methyl methacrylate) Helical Cavity

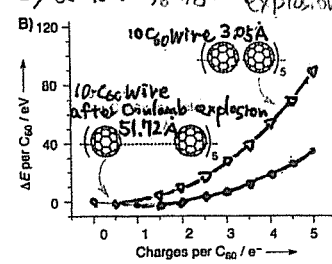
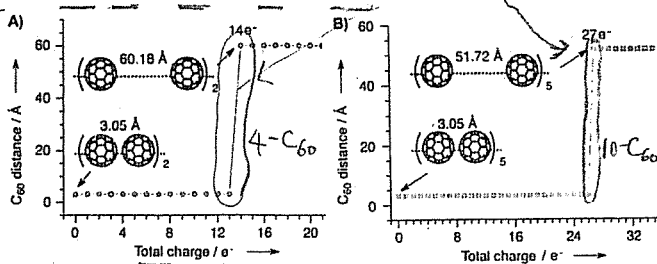
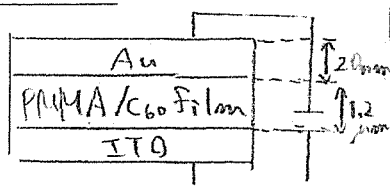
Previous Work



Quantum chemical calculation



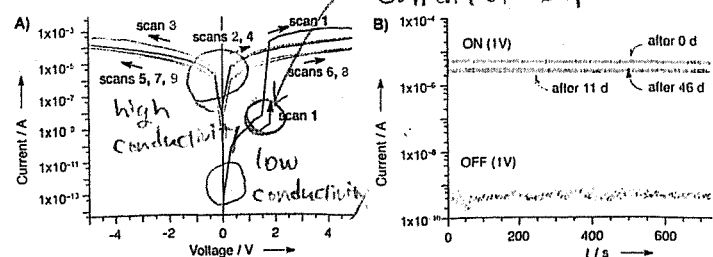
This Work



Current-Voltage characteristics and effect of operation time

Spin coating 20wt% toluene solution

1.5V での急激な Current の上昇

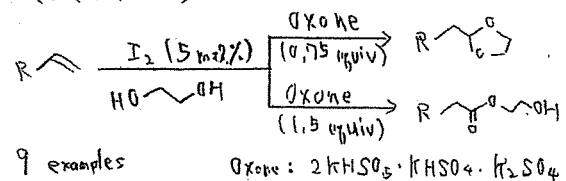


(A) 不可逆なスイッチング
徐々に電流値が下がる
scan 6 でほぼ一定。
(B) OFF の状態 (1V 未満) でのほぼ電流が流れる。
⇒ ON の状態 (1V 以上) 7000 倍の電流値
46 日後も同様

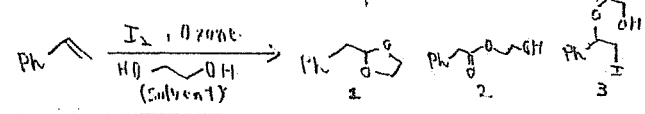
Coulomb explosion 後の電荷注入の方向が ΔE が小さいのが容易。
st-PMMA の効果により wire 内での電荷移動を制限できる。
10wt% solution at-PMMA, it-PMMA を用いた場合、この現象は見られず。

Iodine-catalyzed tandem synthesis of terminal acetals and glycol mono esters from olefins

< Reaction >



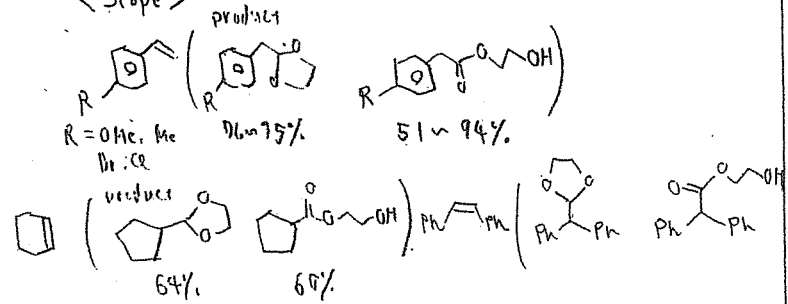
< Optimization >



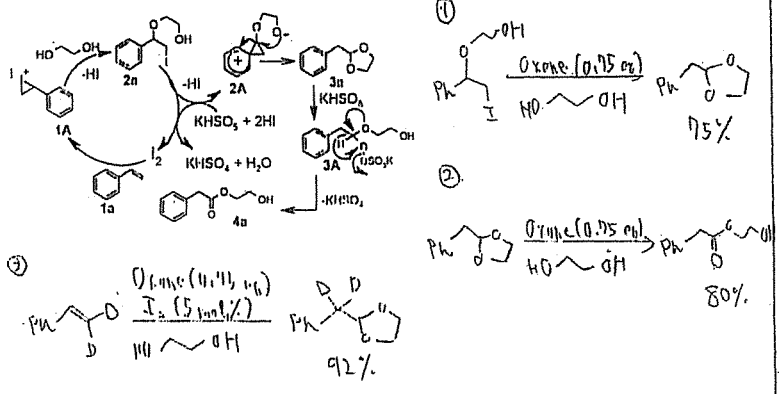
Entry	I ₂ (mol%)	Oxone (equiv)	Time (h)	yield 1	yield 2	3
1	5	0.25	24	49	0	10
2	5	0.75	1.3	95	0	0
3	5	1.5	24	0	94	0
4	100	0.25	1.3	0	0	72
5	50	0.75	1.3	85	0	12
6	170	0.75	1.3	61	0	35

* H₂O₂; O₂; TBHP 等も検討されたが、得率が悪かった。

< Scope >

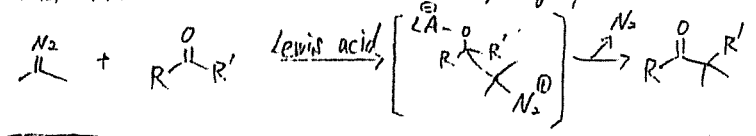


< Mechanism >

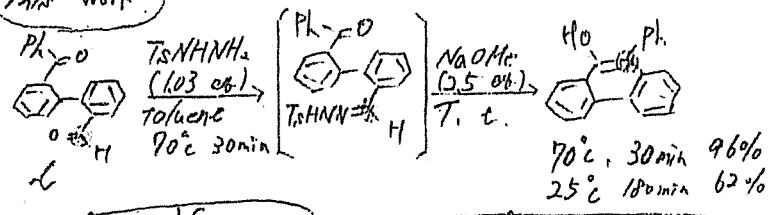


Catalyst-Free Intramolecular Formal Carbon Insertion into σ -C-C Bonds: A New Approach toward Phenanthrols and Naphthols

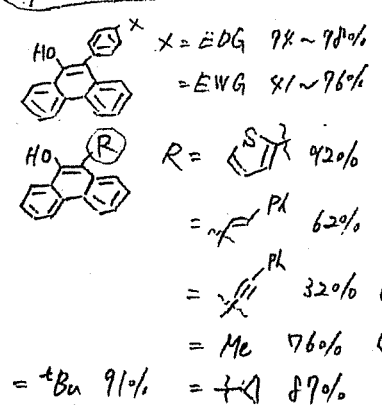
Formal diazo carbon insertion into carbonyl group



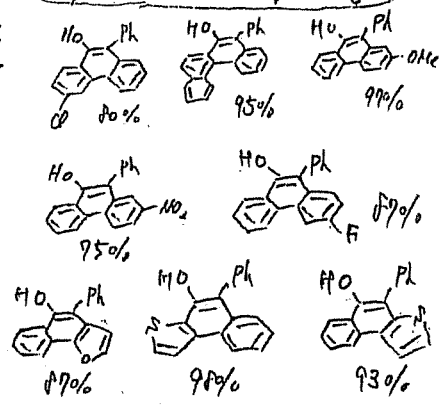
This work



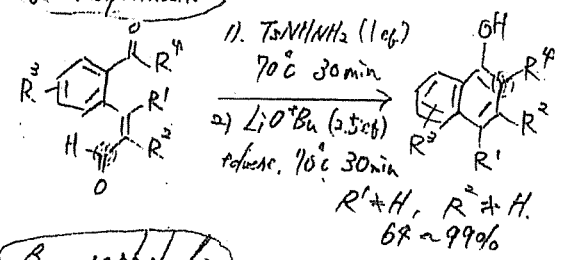
Scope of 1,2-shifting group



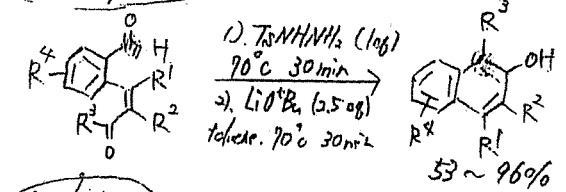
Scope of the two aryl rings



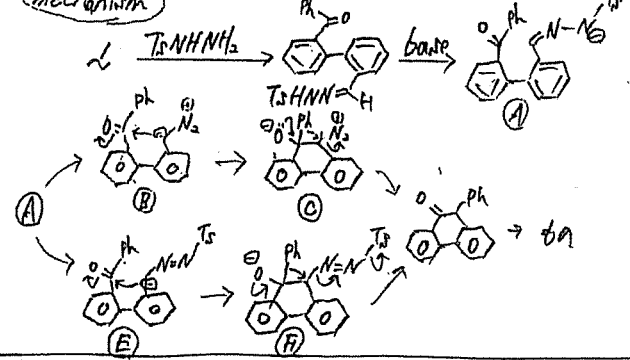
α -naphthol



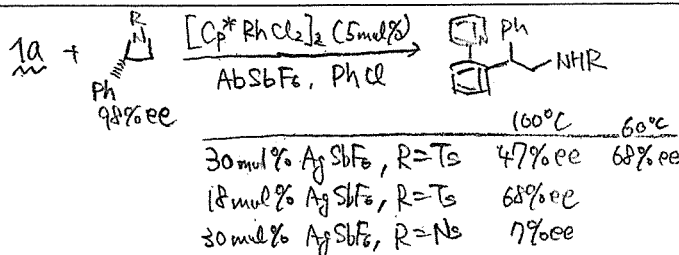
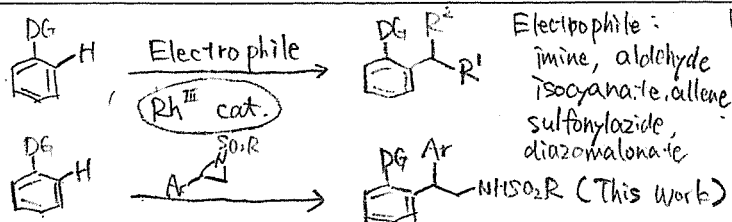
β -naphthol



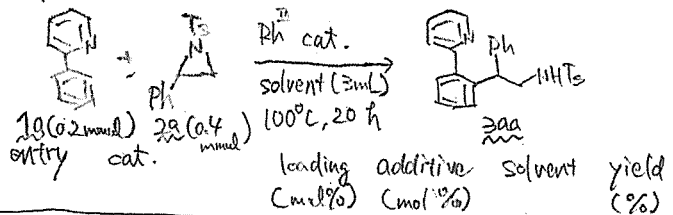
Mechanism



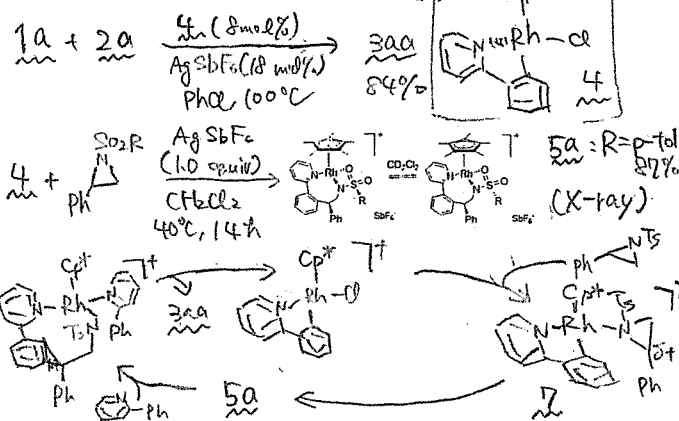
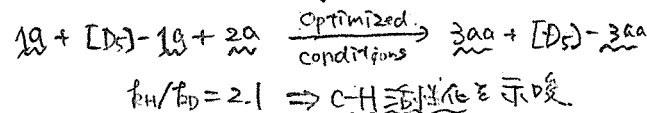
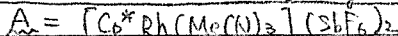
Rhodium(III)-Catalyzed C-C Coupling between Arenes and Aziridines by C-H Activation



(Optimization)

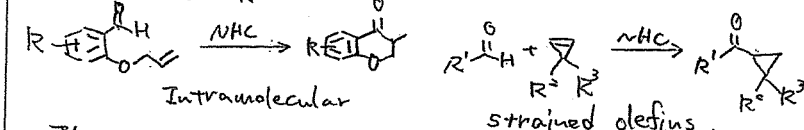


1.	A	0	-	CH ₂ Cl ₂	12
2.	[Cp*RhCl ₂] ₂	5	AgSbF ₆ (20)	CH ₂ Cl ₂	24
3.	"	5	AgSbF ₆ (30)	CH ₂ Cl ₂	80
4.	"	5	AgOAc (30)	CH ₂ Cl ₂	<5
5.	"	5	AgPF ₆ (30)	CH ₂ Cl ₂	39
6.	"	5	AgBF ₄ (30)	CH ₂ Cl ₂	47
7.	"	5	AgSbF ₆ (30)	PhCl	86

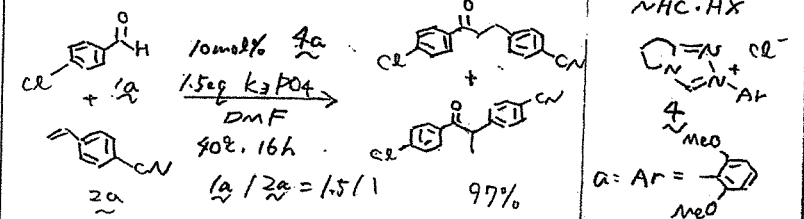


NHC-Catalyzed Hydroacylation of Styrenes

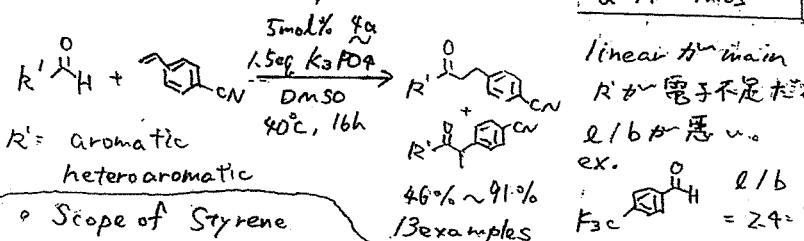
Previous work



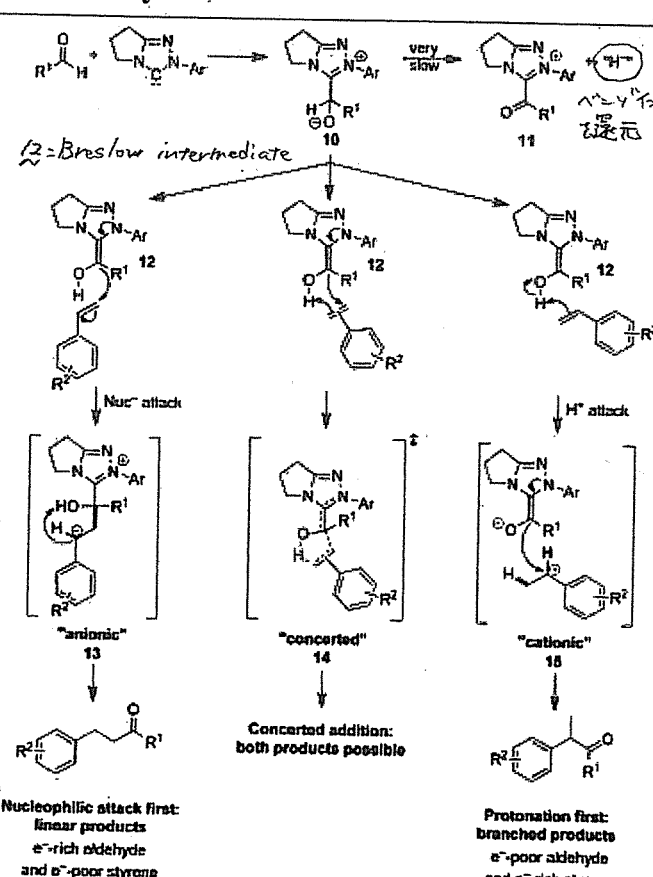
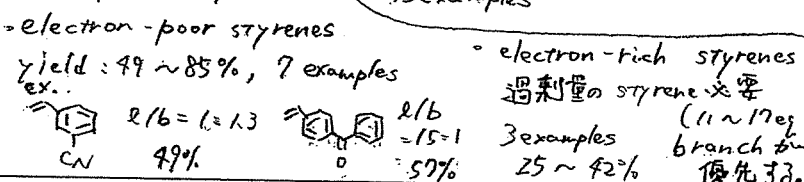
This work



Scope of the aldehyde

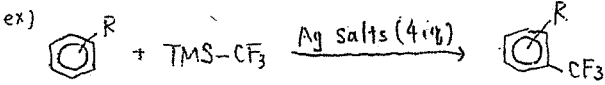


Scope of Styrene



Silver-Catalyzed Hydrotrifluoromethylation of Unactivated Alkenes with CF₃SiMe₃

• Silver-mediated trifluoromethylation



★ Stoichiometric Ag Salts

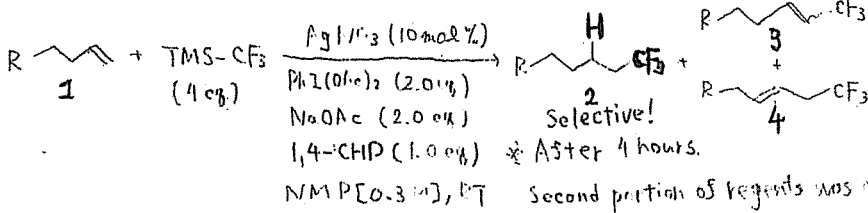
★ Limitation to the Construction of Ar-CF₃

OL, 2011, 13, 5464. Sami Said et al

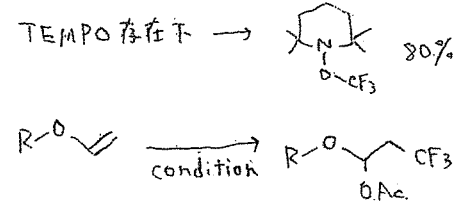
• Scope (58~82%) 23 examples

官能基許容性: amide, ester, sulfonamide, alcohol, ketone, Ar-X (Cl, Br, I), heterocycles, etc

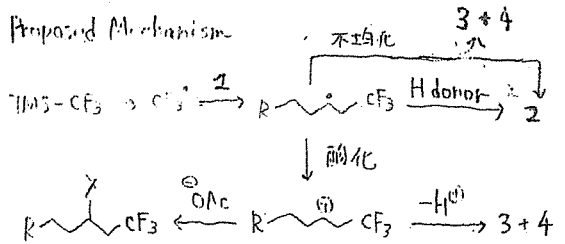
This Work



• Mechanistic Experiment



• Proposed Mechanism



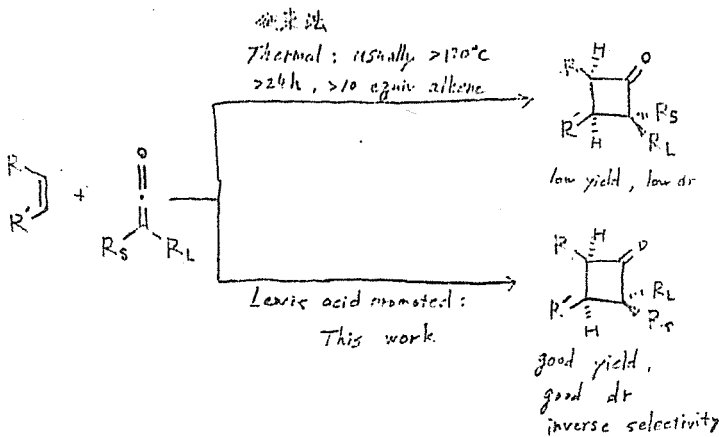
• Optimization (R = Ph)

H-donor Bu₃SnH (1.0), Et₃SiH (2.0), 1,3-dioxolane (10.0), (1,4-CHD (2.0)) 45% 100:0, (1,4-CHD (1.0)) 75% 119:3:1, (1,4-CHD (1.0+1.0)) 92% 35:2:1

1,3-dioxolane	1,4-CHD	45%	100:0
	(1,4-CHD (1.0))	75%	119:3:1
	(1,4-CHD (1.0+1.0))	92%	35:2:1

Lewis Acid-Promoted Ketene-Alkene [2 + 2] Cycloaddition

• ケテン-アルケン [2+2] 付加反応によるシクロブタンの合成



• 反応条件 (従事法 & This work 参照)

Ph-C(=O)-CH(Et)-Cl (1) $\xrightarrow[\text{CH2Cl2, 21°C, 1h}]{\text{Et3Al (1.1 eq)}}$ Ph-C(=O)-CH(Et)-Cl (2) $\xrightarrow{\text{conditions}}$ Ph-CH2-CH(Et)-CH2-C(=O)-Ph (3) + Ph-CH(Et)-CH2-CH2-C(=O)-Ph (4)

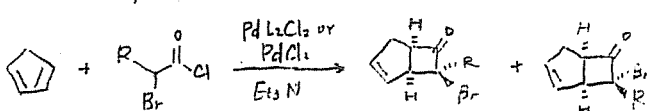
entry	temp. (°C)	time (h)	equiv of 3	LA	yield (%)	dr
1	120	48	10	—	<2	—
2	180	48	10	—	~10	~1:1
3	-78	1	2	EtAlCl ₂ (2.5 eq)	70	13:1

• Scope

付加 \rightarrow 各種のアルキル/アリール(非フェニル) ケテンと
反応可能で、58~82%の収率で、exo:endo = 7:1~20:1の生成物を得た

付加 \rightarrow 5置換, 8置換, 1,2,3-置換反応も進行した
非環式の如き dr 悪化 (2:1~3:1) 生成物も得られた

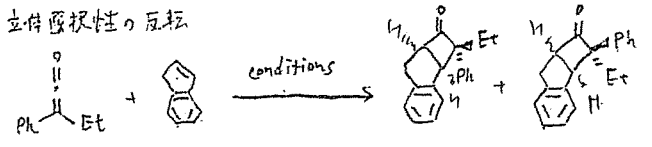
• Lewis acid promoted [2+2] の報告例 (-Ph)



α-アルキル / β-オキ ケテン = 100%

Dickinson, J. M. et al. Tetrahedron (2001)

• 立体選択性の反応

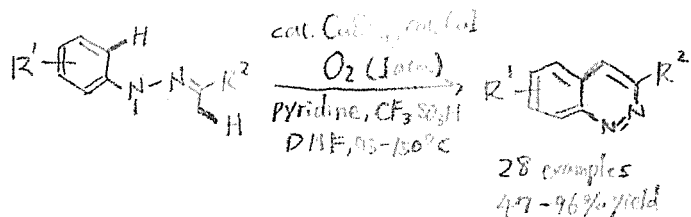


Thermal: toluene, 120°C, 24h: 1:2 dr 52% yield

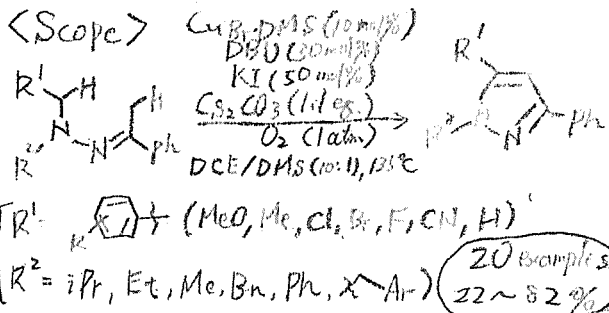
LA (EtAlCl₂): CH₂Cl₂, -78°C, 3h: 13:1 dr 65% yield

Copper-Catalyzed Aerobic Intramolecular Dehydrogenative Cyclization of N,N-Disubstituted Hydrazones through Csp³-H Functionalization

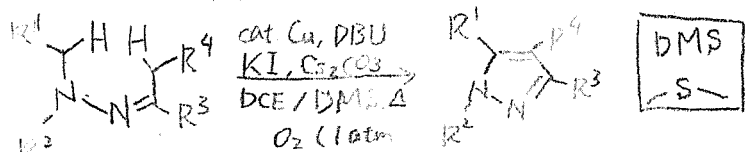
<Previous Work>



<Scope>

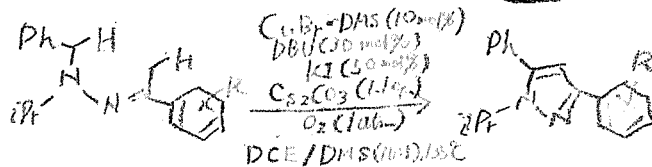
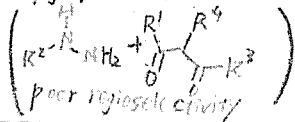


<This Work>

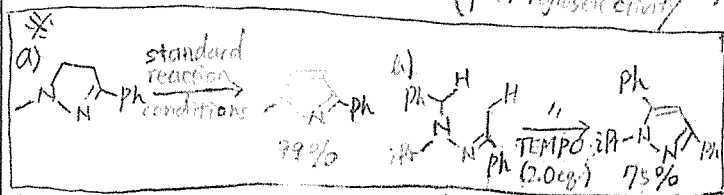
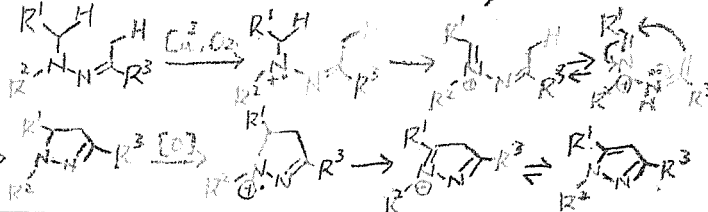


double Csp³-H bond functionalization

highly regioselective



<Plausible reaction mechanism>



An Organosilicon Cluster with an Octasilacubane Core: A Missing Silicon Cage Motif

有機 Si 化合物

- 炭素-炭素単結合系分子には見られぬ特性を発現。

(Si-Si σ結合間電子が非局在化) → σ共役している

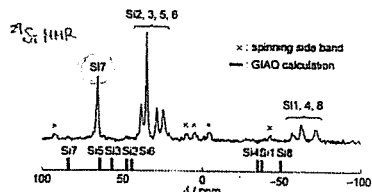
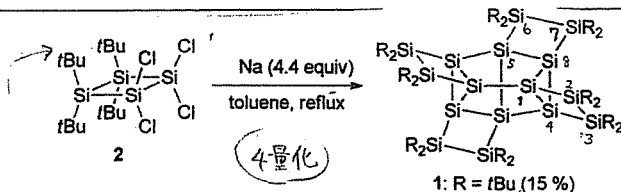
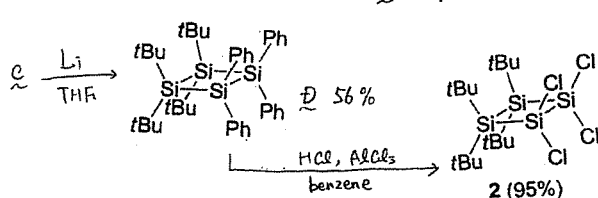
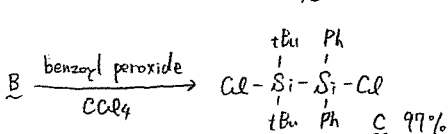
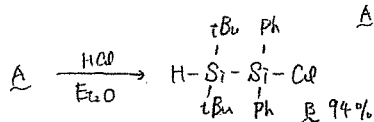
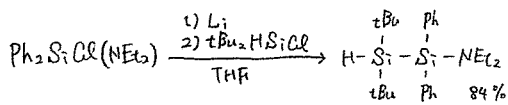


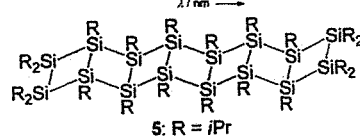
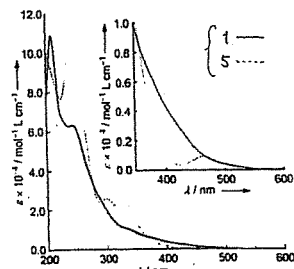
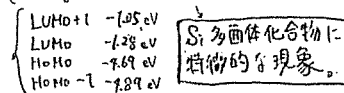
Figure 4. ²⁹Si cross polarization magic angle spinning (CP-MAS) NMR spectrum of 1 at room temperature with signals calculated by the GIAO method at the B3LYP/6-311+G(2d,p) level. Atom numbers correspond to those in Figure 2.

- Octasilacubane (三員環, 四員環, 五員環 2つずつ) Octasila cubane の異性体
- X線結晶構造決定
- ¹H NMR = 8種, ²⁹Si NMR 8種

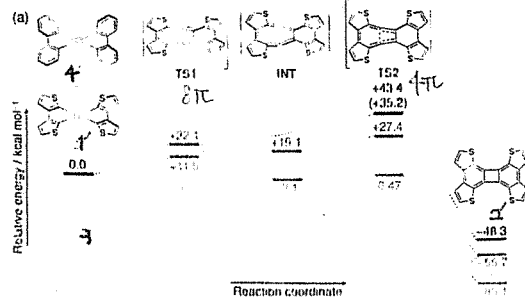
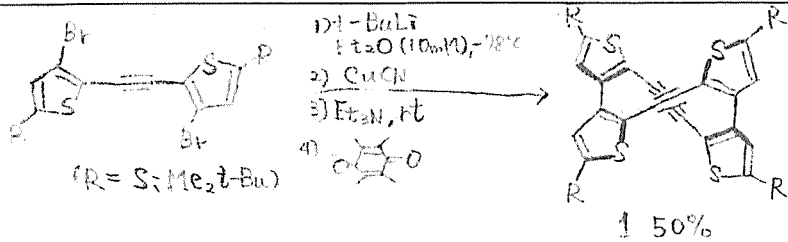
- 非経験的計算 (GIAO) と予測と比較し、中心で高磁場シフト
- Si7 の特徴的なシフト → Si7 は HOMO と LUMO 両方に寄与している。

- Si 数が同じ 1b の 1c, 1d 分子と UV/Vis と比較
- λ: 464 nm の吸収
- 分子の長軸方向に浴びると σ共役の結果発現した低エネルギー吸収

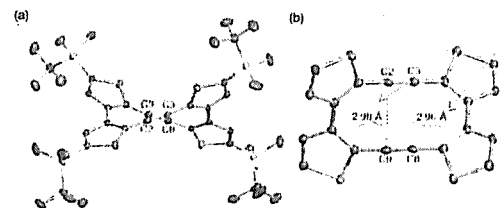
- λ: 明確な吸収は無いが 570 nm まで tailing (tailing: 各分子軌道が近接しているから)



Thiophene-Fused Bisdehydro [12] annulene That Undergoes Transannular Alkyne Cycloaddition by Either Light or Heat.



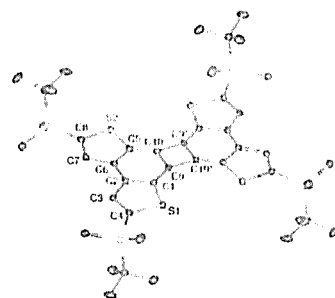
Crystal structure of 1.



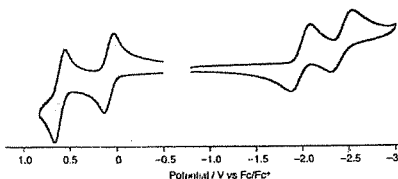
2つの炭素原子の
Vander Waals半径
の合計(3.40Å)が短い。

- 1と2の方が安定 \Rightarrow 4つの3つのN-ピロリル環により芳香族安定化
- 反転の遷移状態に依りて分子の芳香族性が失われる \Rightarrow 芳香族性はチオフェン<ベンゼン。

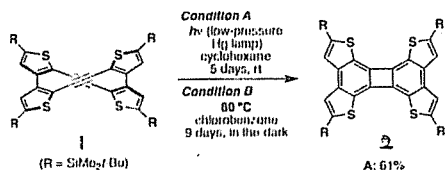
Crystal structure of 2.



- 7つの環が結合した骨格は同一平面
- THF溶液中で赤色
- CV



Cycloaddition of 1



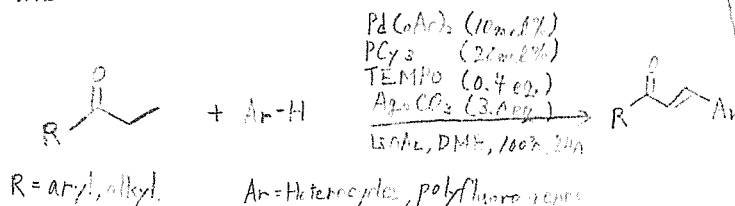
- 通常、熱的 [2+2] 付加還元反応は対称禁制過程で進む。
- 活性化エネルギーが高い。

新しい多環性のπ共役化合物

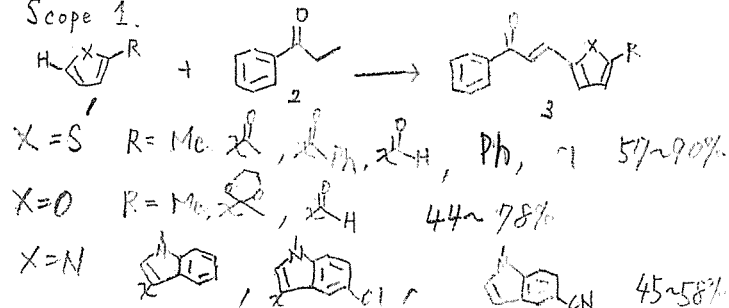
- 第一酸化還元ポテンシャルは高いHOMO
- 高いLUMOの安定性、電子受容能力

Pd-Catalyzed C-H Olefination of (Hetero)Arenes by Using Saturate Ketones as an Olefin Source

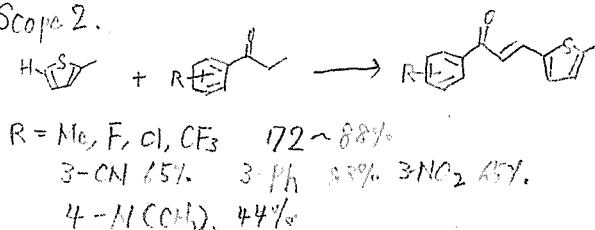
This work



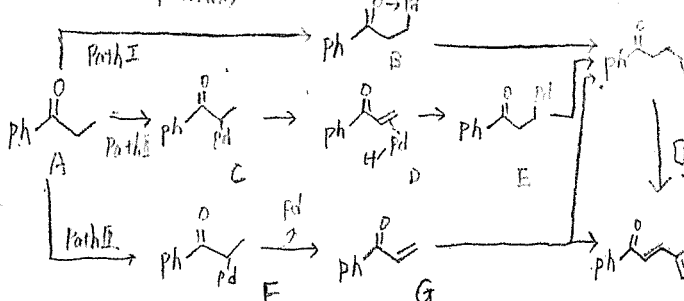
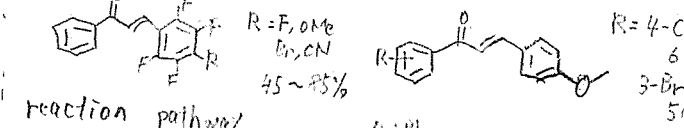
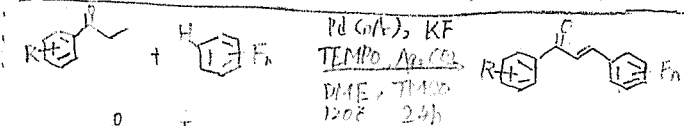
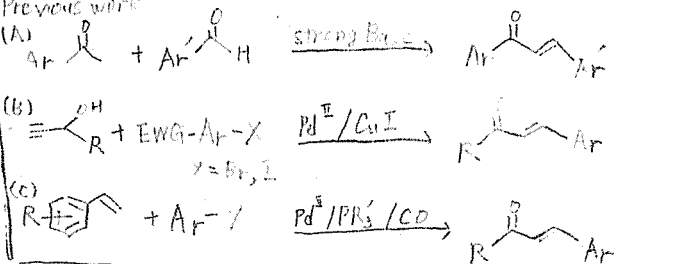
Scope 1.



Scope 2.

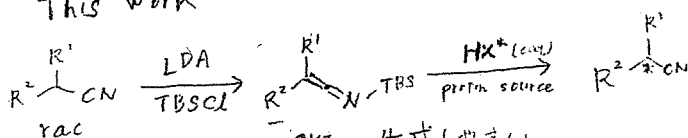


Previous work



Catalytic Asymmetric Protonation of Silyl Ketene Imines

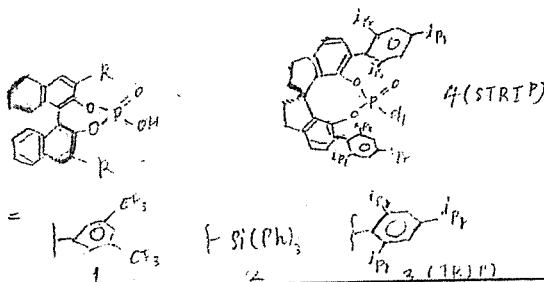
This work

SKI 生成しやすい
ラセミ化しやすい

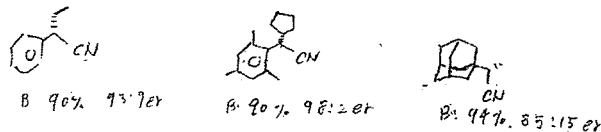
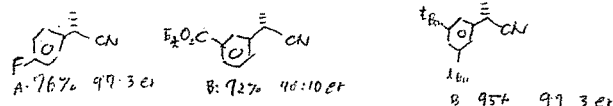
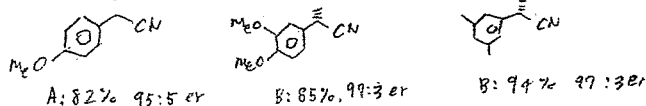
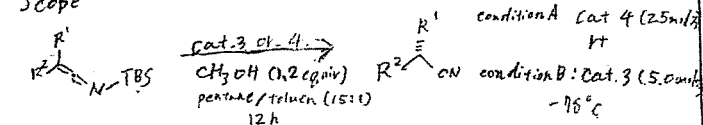
触媒の検討

entry	Cat (mol%)	conv (%)	t (h)	er
1	1 (5.0)	100	6	53:47
2	2 (5.0)	100	1	99:1
3	3 (5.0)	100	6	92:8
4	3 (5.0)	100	12	96:4
5	4 (5.0)	100	6	96:4
6	4 (2.5)	100	12	96:4

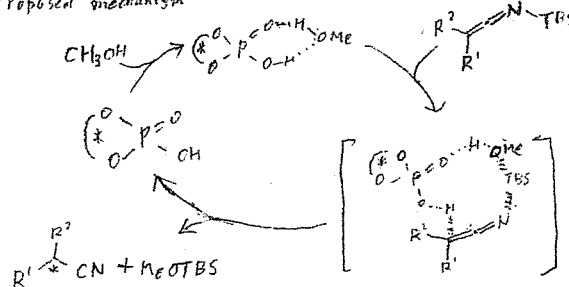
Cat



Scope



Proposed mechanism



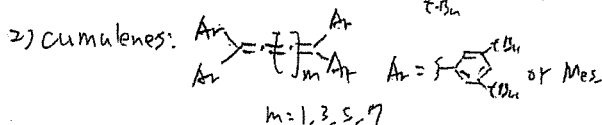
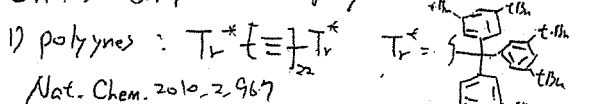
Rik R. Tykwinski

Uni. Of Erlangen-Nuremberg

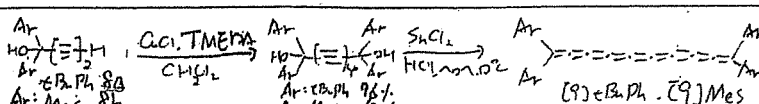
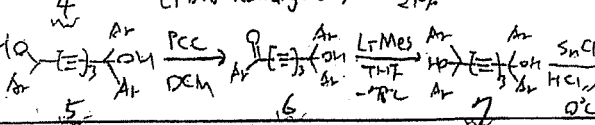
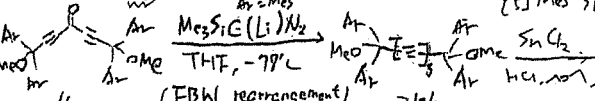
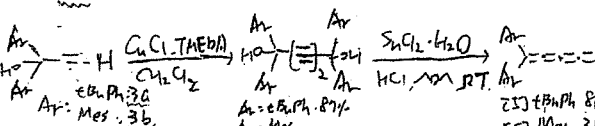
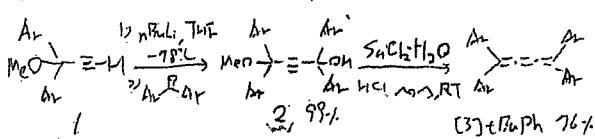
Anie.201208058

Lin

Synthesis and Structure of Tetraarylcumulenes: Characterization of Bond-Length Alternation versus Molecule Length

Chains composed of sp -hybridized carbon atoms

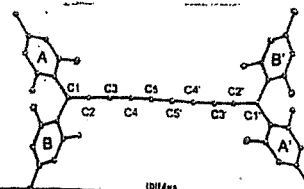
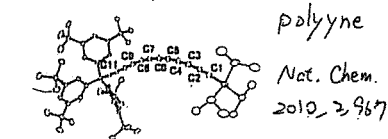
Synthesis of cumulenes 2



X-ray crystallographic analysis & UV-Vis spectra

BLA: bond-length difference
between the two central
most double bonds.

Exp.	Estimated
[3] tBuPh 0.086	
[5] tBuPh 0.054	
[5] Mes 0.048	
[7] tBuPh 0.052	[7] H 0.014
[7] Mes 0.042	
[9] Mes 0.039	[9] H 0.010



[n]	tBuPh	Mes
[3]	424	-
[5]	500	460
[7]	564	560
[9]	664	666

