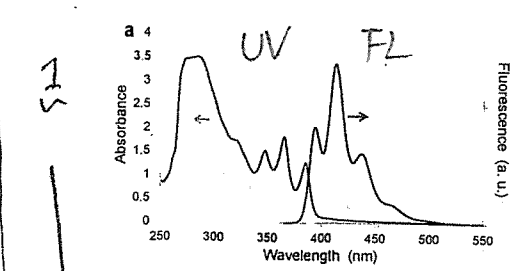
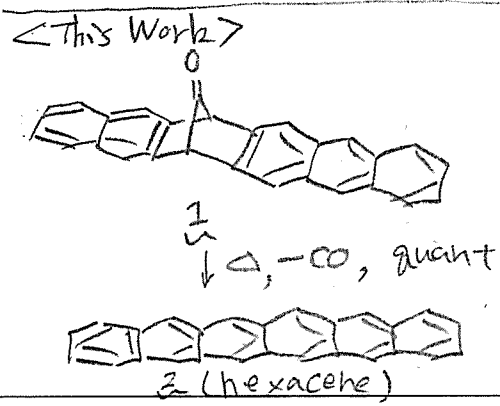
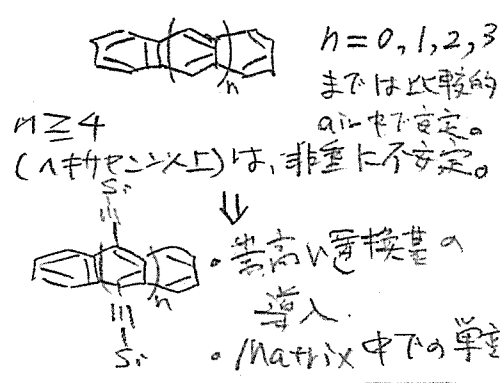


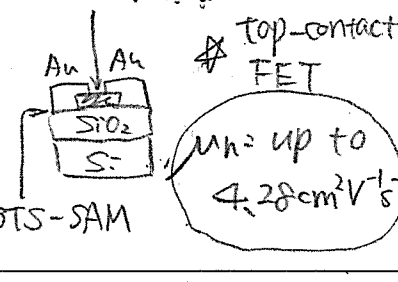
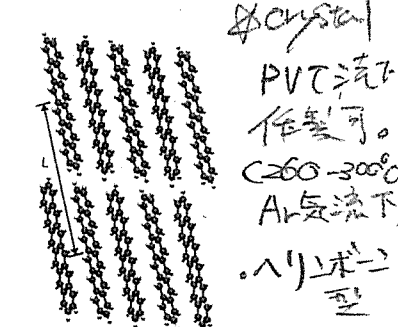
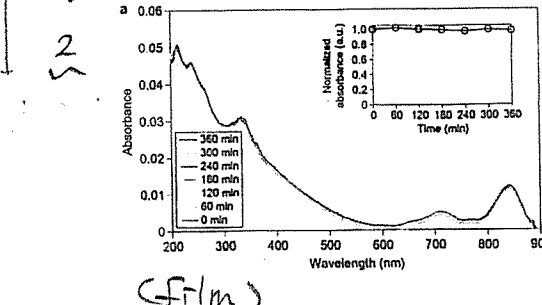
The synthesis, crystal structure and charge-transport properties of hexacene

* acene化合物は, P型有機トランジスタの候補化合物群。



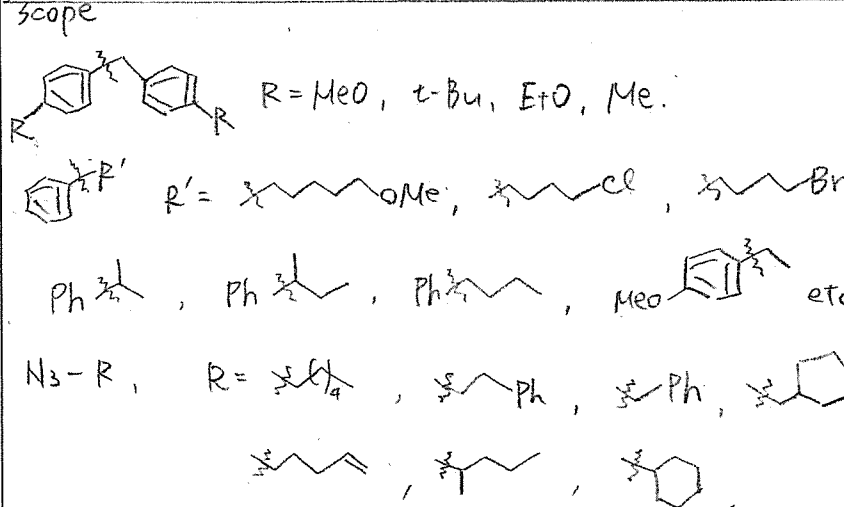
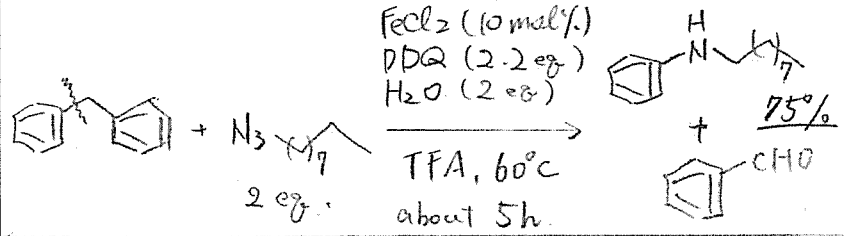
• 有機溶媒への溶解性
 高い ($CHCl_3, THF$ に対し $\sim 0.3 \text{ mg mL}^{-1}$)
 • 高い安定性 (可視光下で、半年保存可 (SC))

180°C under N_2
 (solid, or spin-coated film)

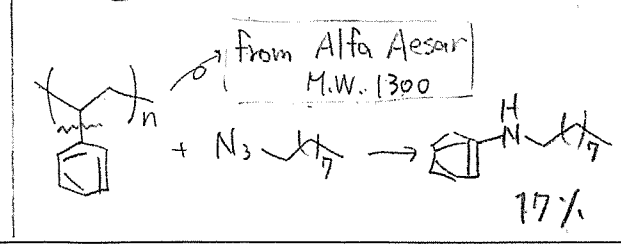
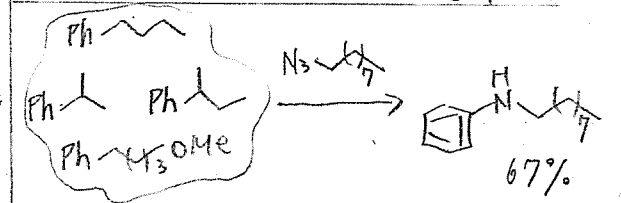
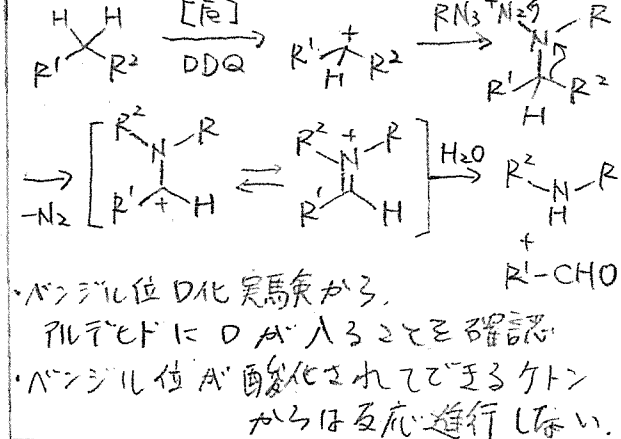


(film)
 • FT-IR (1180 cm^{-1} の $C-C$ が完全消失)
 • MALDI 空中で UV 照射すると降下は 1°C 程度でよい。

FeCl₂-Promoted Cleavage of the Unactivated C-C Bond of Alkylarenes and Polystyrene: Direct Synthesis of Arylamines



反応条件、長 out. 子 (2) 反応は進行する。
 • 酸性条件が重要。



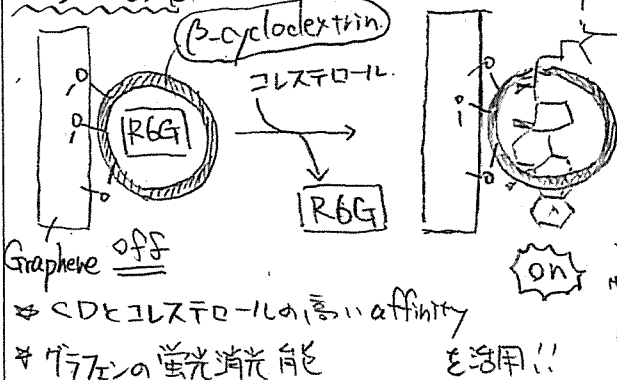
Fluorescent detection of cholesterol using β -cyclodextrin functionalized graphene

★ コレステロールの検出

コレステロール: 生体膜の構成物質
 健康なヒト: 2mg/L
 高いコレステロール値
 → 動脈硬化 etc..

種々の検出法: 電気化学的手法
 蛍光を活用する手法
 酵素を活用する手法
 → 非常に高価. 且 変性の可能性あり

This Work



β-CDとコレステロールの高い affinity
 ★ グラフェンの蛍光消光能を活用!!

合成 ~ β -Cyclodextrin 修飾 グラフェン ~

Graphene Oxide + β CD $\xrightarrow[rt, 1R]{1. NH_4OH}$ product $\xrightarrow[80\% 1R]{2. H_2NNH_2}$

ACS Nano. 2010, 7, 7001.

IR spectra: Graphene, β -CD, β -CD-G. (CD由来 C-O 72 確認)

AFM: β -CD-G, β CD. 2.5nm, 2x0.8 + 0.9, 2.5nm.

PL Intensity vs Length (nm): 450, 550, 750. コレステロール 0~30 μ M.

結合定数 1.55 M⁻¹

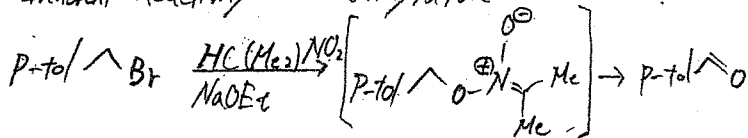
★ 血清中の他の分子が存在しても. 選択的にコレステロールを検出
 ex. NaCl, KCl, MgCl₂, amino acid, SDS.
 ★ 中性的界面活性剤は△。

Donald A. Watson	University of Delaware (USA)	JACS. DOI:10.1021/ja304561cl	Okumura
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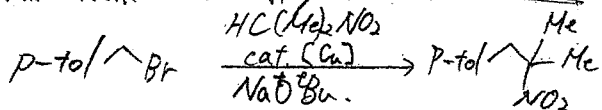
Benylation of Nitroalkanes Using Copper-Catalyzed Thermal Redox Catalysis: Toward the Facile C-Alkylation of Nitroalkanes

Alkylation of Nitronate Anions

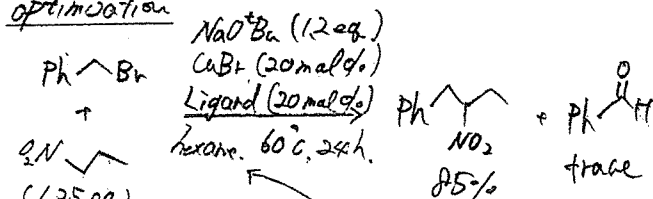
Inherent Reactivity: O-Alkylation



This Work: C-Alkylation → NET 機構.



optimization



• L =
 SETは銅と配位する
 ⇒ 水素を抜く
 配位が速 → Cu⁰が電子rich

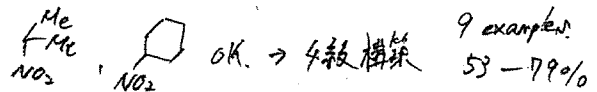
Scope

Benzyl Bromides

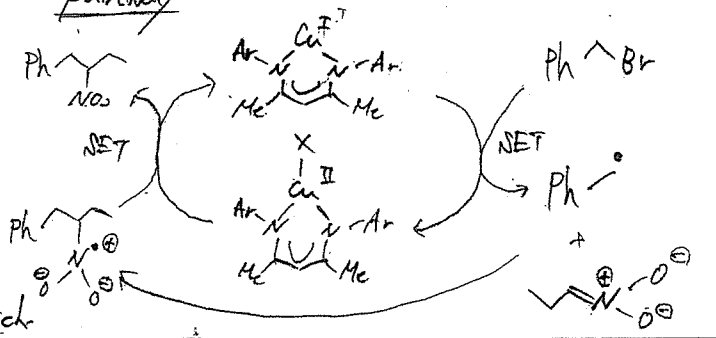
- 置換基 立体 関係なし (20 examples 89~87%)
- 複素環 (pyridine, quinoline, thiophene, ...) OK!

Nitroalkanes

- 官能基 (double bond, ketone, ester) OK!

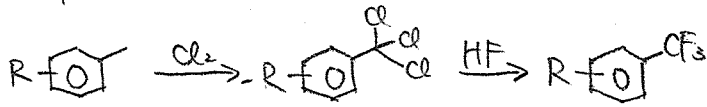


pathway

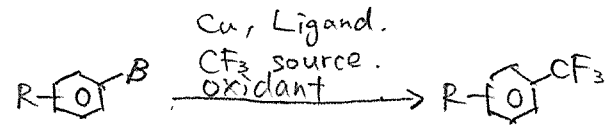


Fluoroform-Derived CuCF3 for Low-Cost, Simple, Efficient, and Safe Trifluoromethylation of Aryl Boronic in Air

<Reported Trifluoromethylation>



- o 官能基許容性が低い.
o 危険な試薬 (Cl2, HF) の使用

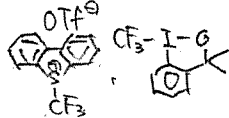


B = B(OH)2, Bpin.

Cu: Cu(OAc)2, [Cu2(OTf)2(C6H6)]...

Ligand: phen.

CF3 source: CF3SiMes.



oxidant: Ag2CO3, dry O2...

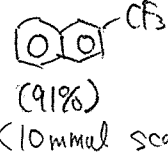
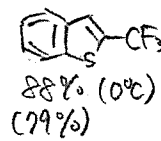
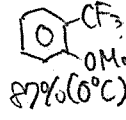
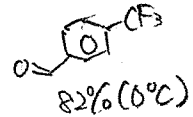
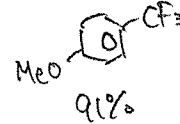
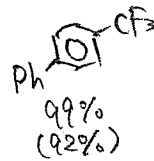
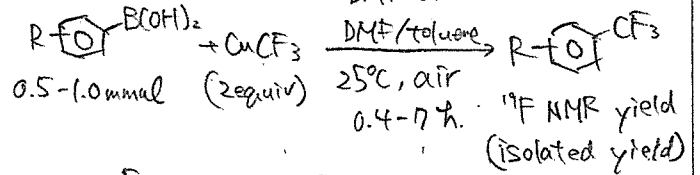
高価な試薬の使用. 27-1777 70% 困難.

<Previous Work>

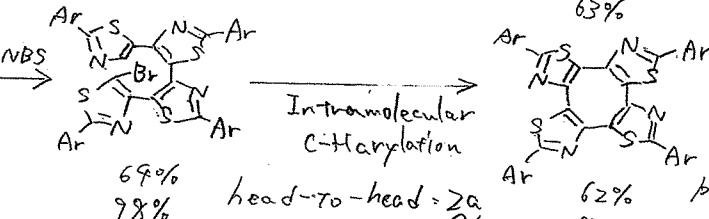
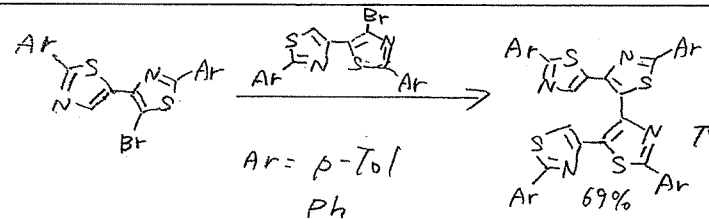


1. CF3H -> CuCF3
2. Stabilization >90% with Et3N(HF3)

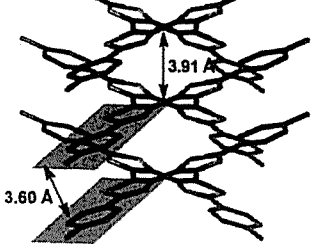
<This Work>



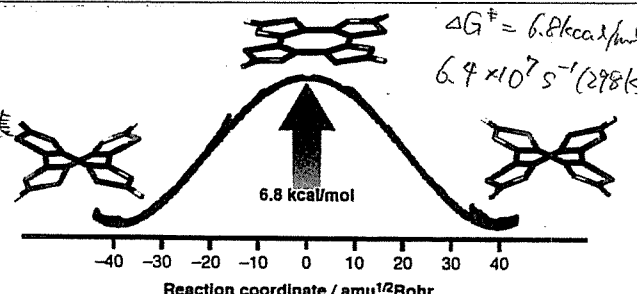
Highly Flexible pi-Expanded Cyclooctatetraenes: Cyclic Thiazole Tetramers with Head-to-Tail Connection



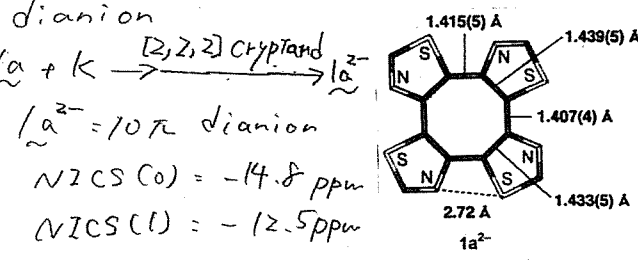
la 12 columnar stacking head-to-head の 2a 17 Columnar 構造



bent angle theta la = 29 degrees, la = 90 degrees, Tetraarene-fused COT = 38-49 degrees



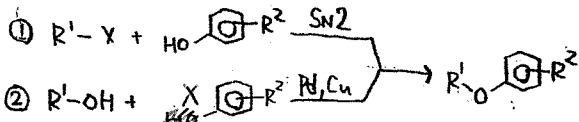
- 1) 小さな C=C-S の結合角により, COT の内角が 135 度に近くなる. -> 0 の減少
2) head-to-tail 構造での 4P4'-12 環 同士の立体障害が小さい.
3) 4P4'-12 環の導入により, 芳香族性が弱まる.



Catalytic Aerobic Synthesis of Aromatic Ethers from Non-Aromatic Precursors

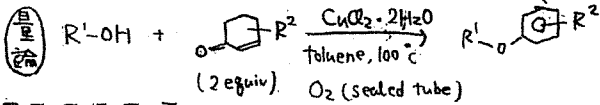
★アリールエーテルの合成

General approach

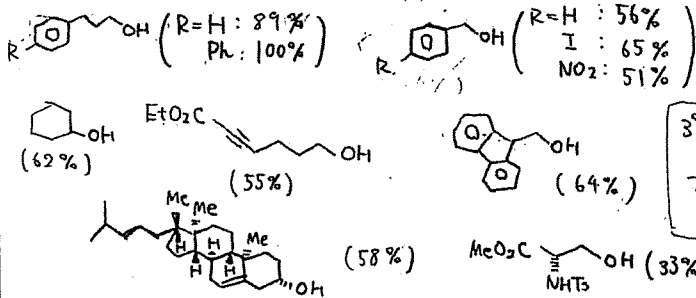


① Williamson エーテル合成 ② Pd... Buchwald-Hartwig 反応
Cu... Ullmann エーテル合成

This work

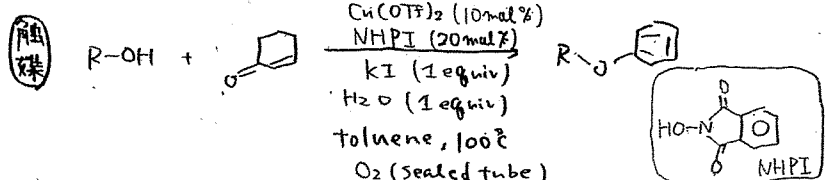
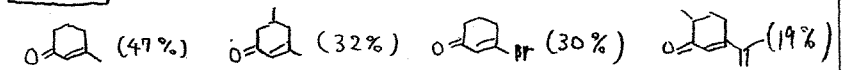


Scope ① R¹: アリール (17 examples) vs 2-エトキシフェニル



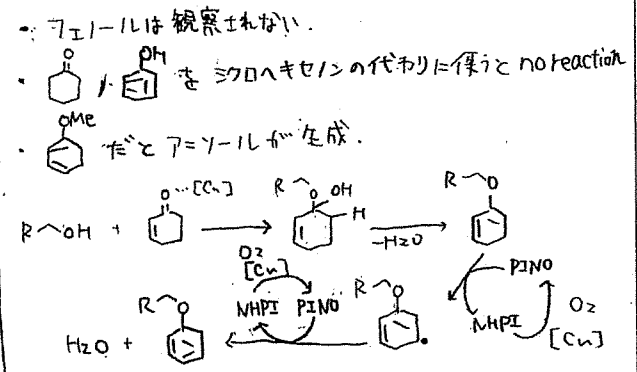
Scope ②

R²: エトキシ (6 examples) vs $Ph-OH$



アリールエーテルの合成は基質展開なし。大体、量論時と同じような収率

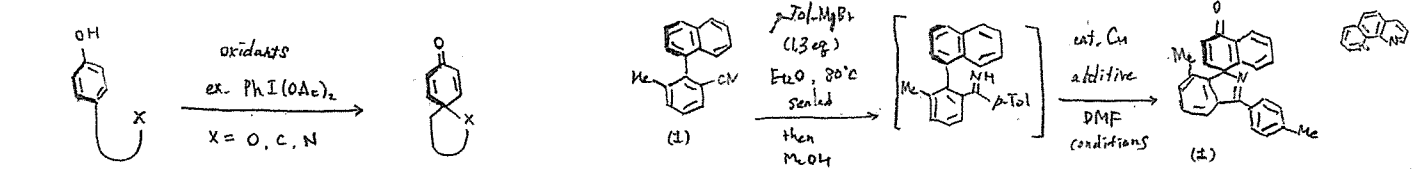
反応機構研究



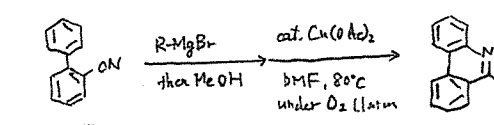
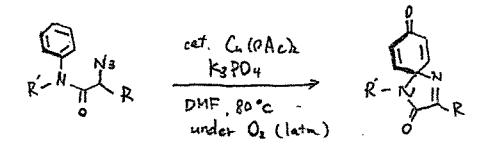
Copper-Catalyzed Aerobic Spirocyclization of Biaryl-N-H-imines via 1,4-Aminooxygenation of Benzene Rings

• Spirodienone の構築

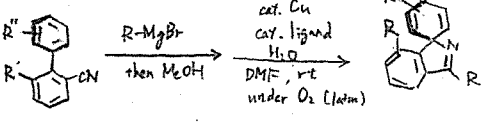
Optimization



Previous Work

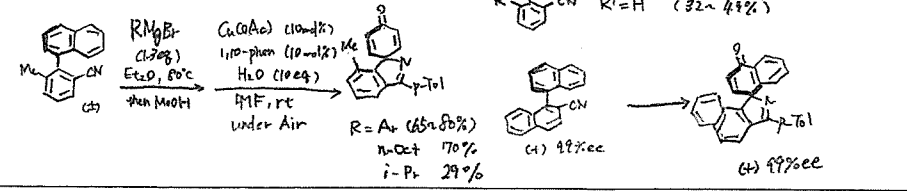


This Work

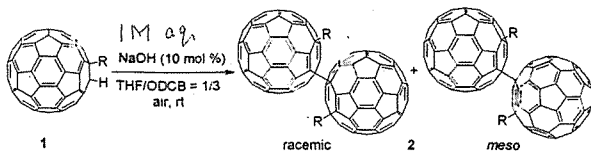


Cu salts (mol%)	additive-1 (mol%)	additive-2 (eq)	conditions	yield (%)
Cu(OAc) ₂ (20)	—	—	O ₂ , 80°C, 20h	34
Cu(OAc) ₂ (20)	1,10-phen (20)	—	O ₂ , 80°C, 3h	61
Cu Br ₂ (20)	1,10-phen (20)	—	O ₂ , 80°C, 5h	50
Cu(OAc) ₂ (20)	1,10-phen (20)	—	O ₂ , rt, 3h	55
Cu(OAc) ₂ (20)	1,10-phen (20)	H ₂ O (10)	O ₂ , rt, 3h	81
Cu(OAc) ₂ (20)	1,10-phen (20)	H ₂ O (10)	air, rt, 2h	82
Cu(OAc) ₂ (10)	1,10-phen (10)	H ₂ O (10)	air, rt, 3h	80

Scope



NaOH-Catalyzed Dimerization of Monofunctionalized Hydrofullerenes: Transition-Metal-Free, General, and Efficient Synthesis of Single-Bonded [60]Fullerene Dimers

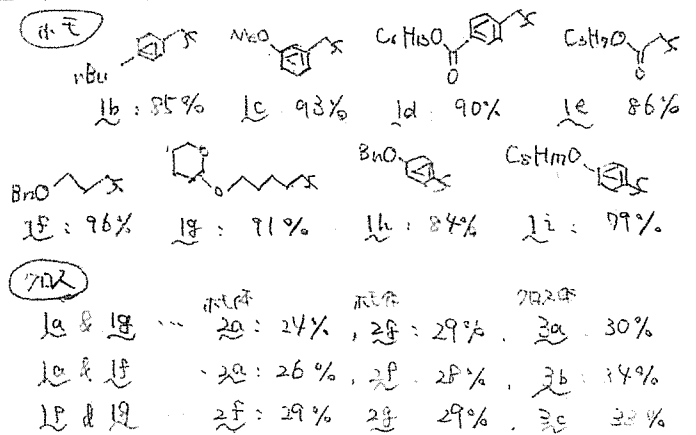


• 前報で銅(II)触媒を用いた91%の合成を報告した。
(Angew Chem Int Ed. 2012, 51, 802)
• 171124-1の触媒反応は70%以上の高収率で進む。

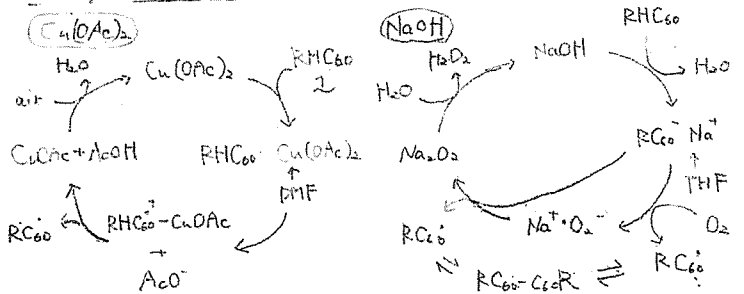
Conditions (R = Bu, Ia)

• solvent ... ODCB → 2に2は48%で1 → 48%
DMF 89%, THF 95%, MeOH 90%
trace: MeCN, CHCl₃ 0% (cosolvent: ODCB = 1/3)
• A+第四期Fは全く反応しない。
• 塩基
KOMe, KO^tBu, CsOH, KOH等、強塩基は5%以下で
有機塩基は反応しない。(Me₃NOH = 88%)
Na₂CO₃, Et₃Nは収率低い。(9%, 26%)
塩基性触媒

Scope

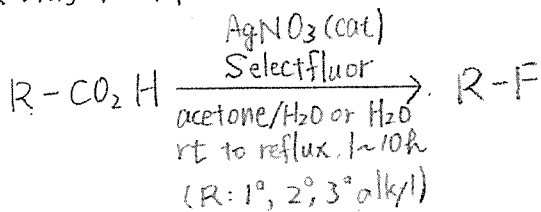


Plausible Mechanism



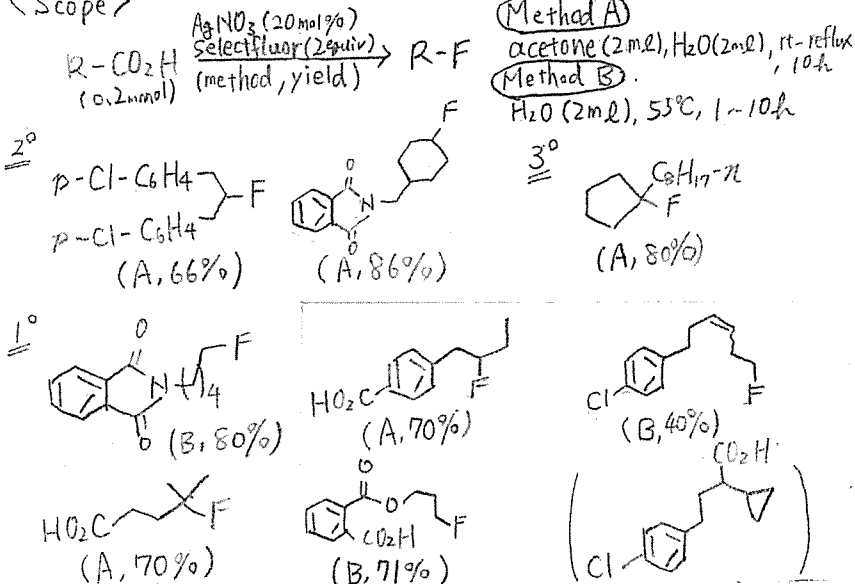
Silver-Catalyzed Decarboxylative Fluorination of Aliphatic Carboxylic Acids in Aqueous Solution

<This Work>

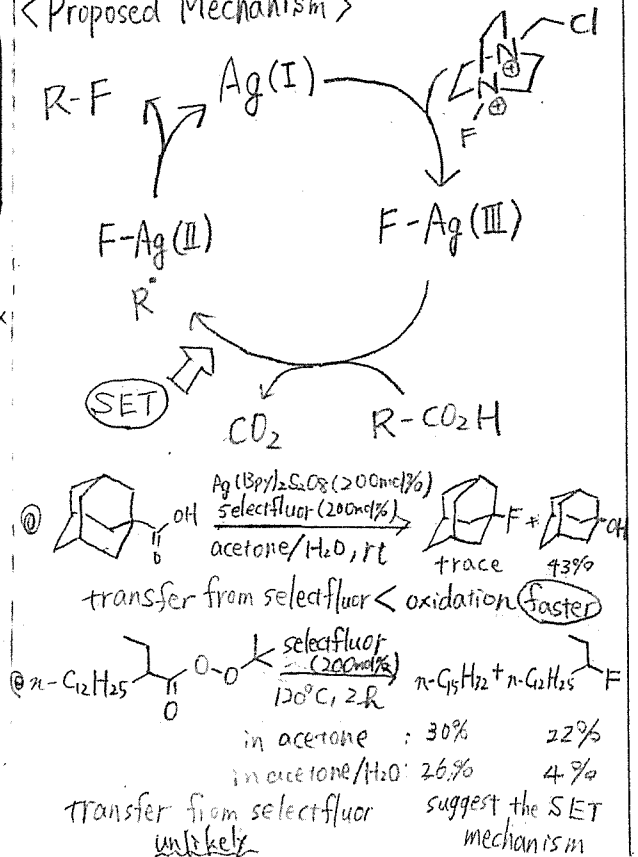


1. catalytic
2. efficient & general
3. chemoselective
4. wide functional group compatibility

<Scope>

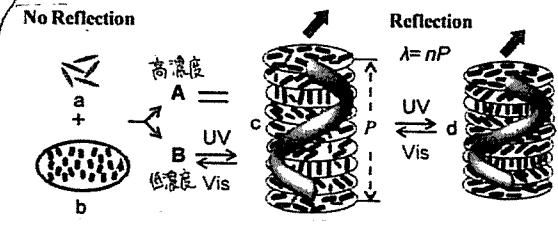
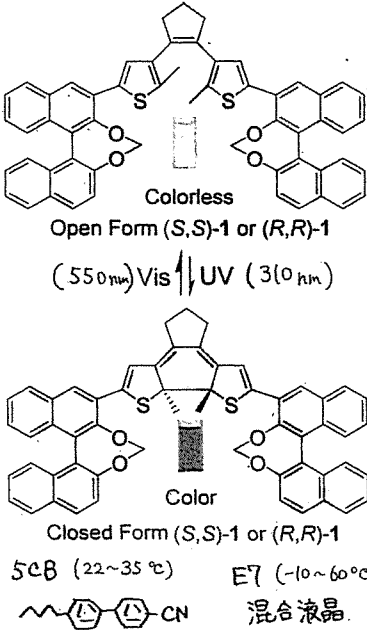


<Proposed Mechanism>

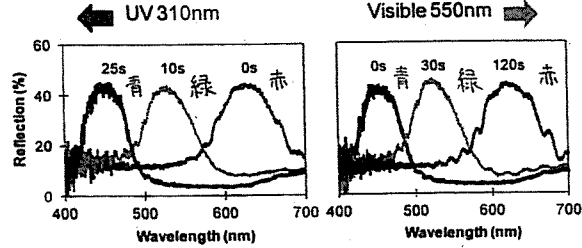


Reversible Light-Directed Red, Green, and Blue Reflection with Thermal Stability Enabled by a Self-Organized Helical Superstructure

ネマチック液晶 (SCB, E7) と dithienylethene 誘導体試薬
→ 液晶かららせんを描く。



a: dithienylethene
b: ネマチック液晶
• UV (310nm) を照射してアゲると、ピッチの長さが短くなる。
• Vis (550nm) を照射すると、元の長さに戻る。



UV (310nm) 照射
無 → 赤色
10s → 緑色
25s → 青色
Vis (550nm) 照射
無 → 青色
30s → 緑色
120s → 赤色

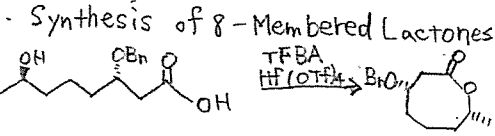
らせん構造を形成すると、特定の波長の光を反射するようになる。
→ 波長はピッチの長さで依存。
(ピッチは UV, Vis で制御可能)



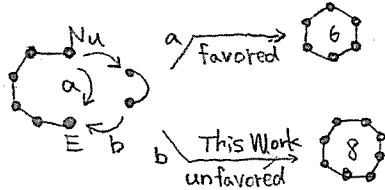
• UV照射時間を制御することで、同一平面上で異なる色の反射光を出すこともできる。
• ドーパントが低濃度 (7.7wt% in E7) →
① 熱に対して安定でらせん構造が保持される。
② UV-Vis で速やかに変化。

Synthesis of Eight-Membered Lactones: Intermolecular [6+2] Cyclization of Amphoteric Molecules with Siloxy Alkynes

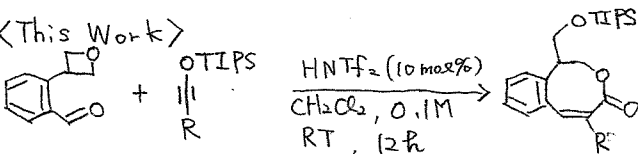
< Previous Work >



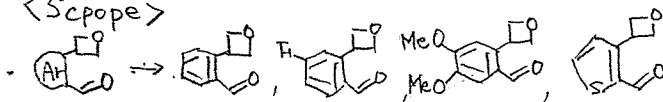
→ intramolecular reaction.



< This Work >

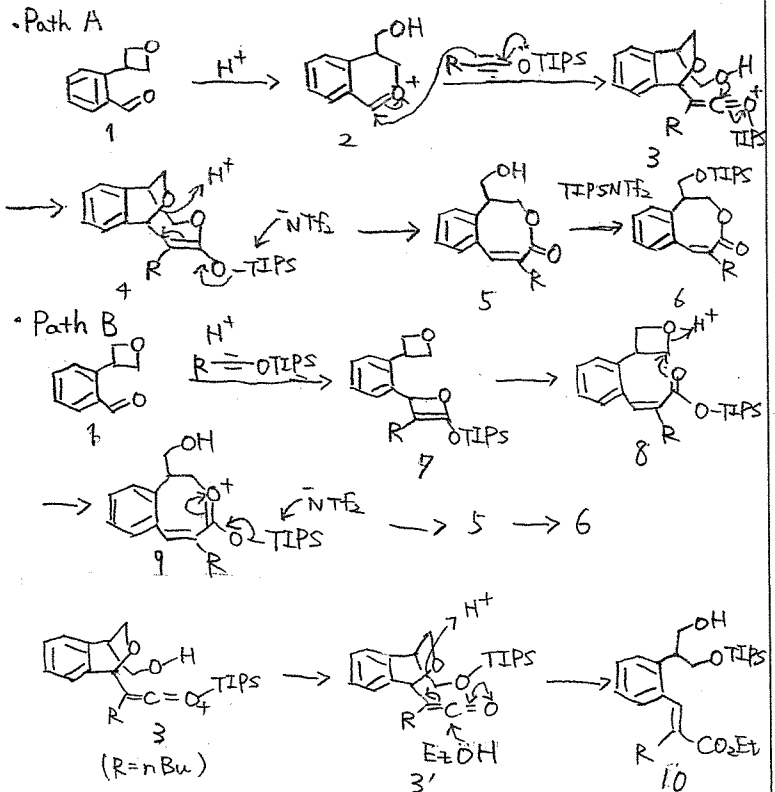


< Scope >



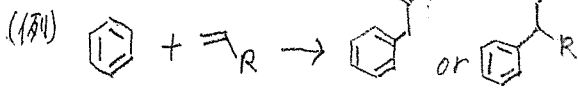
• 濃度 0.1M → 0.5M : 71% → 52% (R = nBu)

< Proposed mechanisms >



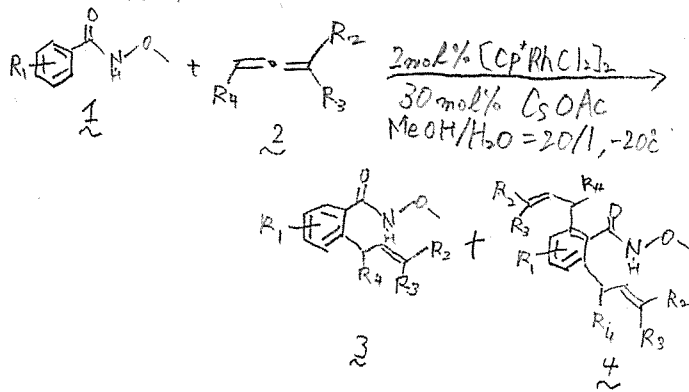
Highly selective mild stepwise allylation of N-Methoxybenzamides with allenes

Hydroarylation



一般的に高温が必要 (100°C以上)

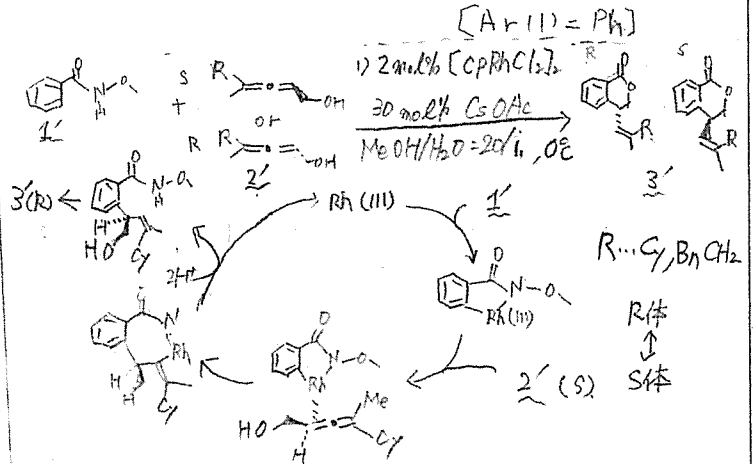
<This work>



⇒ step wise double allylation with allenes.

Ar(1) ... Ph (77%, 4%), 4-Br Ph (72%, 5%),
4-MeOPh (71%, 6%), 2-IPh (69%, 0%) etc
[R₂/R₃/R₄ = Bu/Bu/H]

R₂/R₃/R₄ ... Bu/Ph/H (62%, 2%), Bu/p-tolyl/H (56%, 2%),
-(CH₂)₅/CH₂OH (58%, 2%), Me/Me/CH₂CO₂Et (53%, 0%)

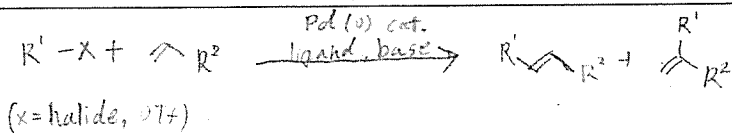


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DOI: 10.1002/anie.201201806

B4 矢野田

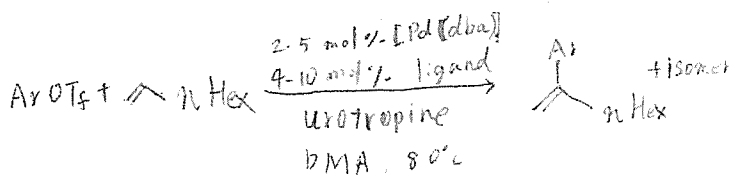
Intermolecular Mizoroki-Heck Reaction of Aliphatic Olefins with High Selectivity for Substitution at the Internal Position



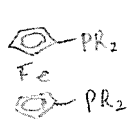
Mizoroki-Heck Reaction

α,β-不飽和炭素に電子的偏りがない
脂肪族α,β-不飽和炭素は位置選択が難しい。

This work



ligand



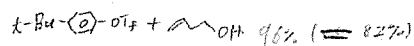
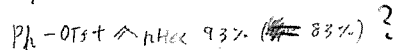
dppf: R = phenyl
dnppf: R = 1-naphthyl
dipfp: R = isopropyl

urotropine

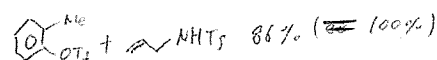
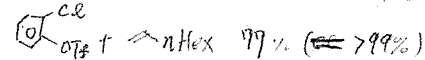


Scope

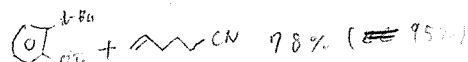
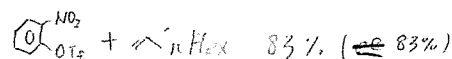
a) Aryl without ortho substituent, L = dnppf



b) Aryl with small ortho substituent L = dipfp



c) Aryl with Large ortho substituent L = dppf



DFT 計算

