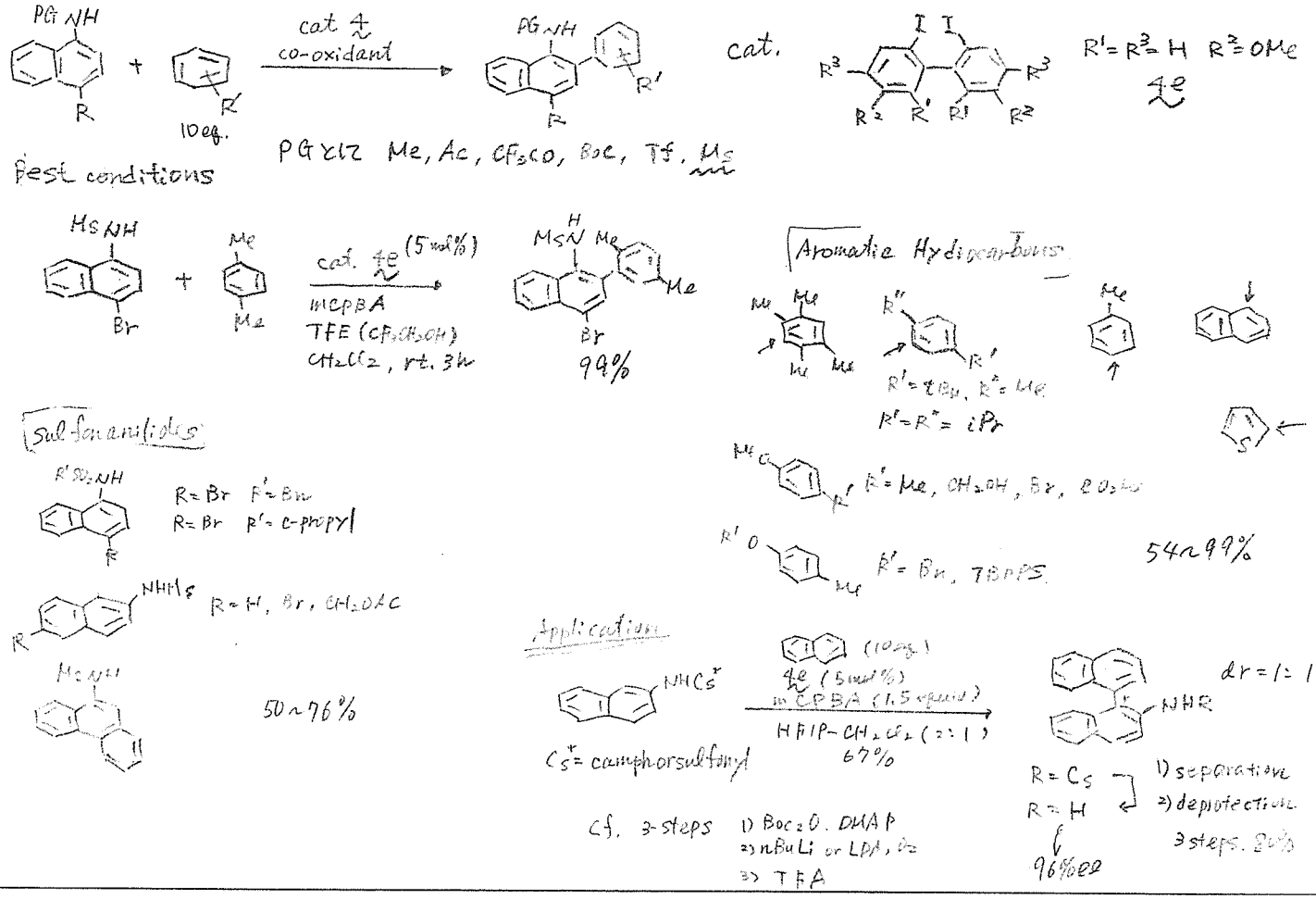
Y. Kita et al.	Ritsumeikan Univ.	*JACS* (ja.407944p)	Minakata

Organocatalytic C-H/C-H' Cross-Biaryl Coupling: C-Selective Arylation of Sulfonanilides with Aromatic Hydrocarbons

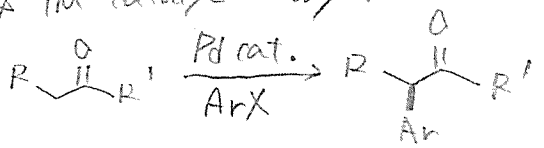


Ess, D. H.; Kürti, L. et al.	Brigham Young University, UT Southwestern Medical Center, USA	*J. Am. Chem. Soc. ASAP* doi: 10.1021/ja4074563	Youhei Takeda

Aerobic, Transition-Metal-Free, Direct, and Regiospecific Mono-α-arylation of Ketones: Synthesis and Mechanism by DFT Calculations

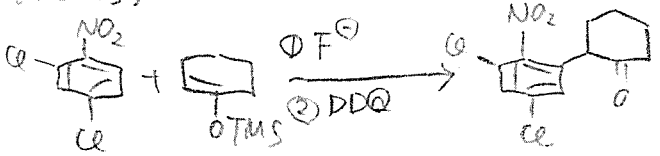
カルボニル化合物のα-アリール化

☆ TM-catalyzed arylation



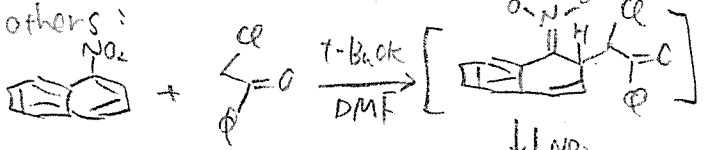
Acc. Chem. Res. 2003, 36, 234.

☆ addition to electron-deficient arenes / oxidation



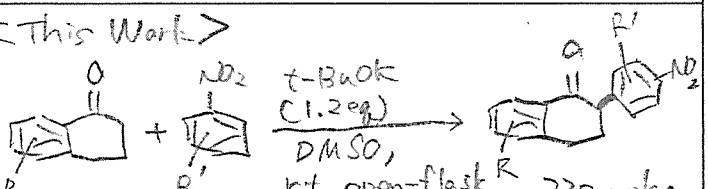
JOC, 1984, 49, 4571.

☆ others:

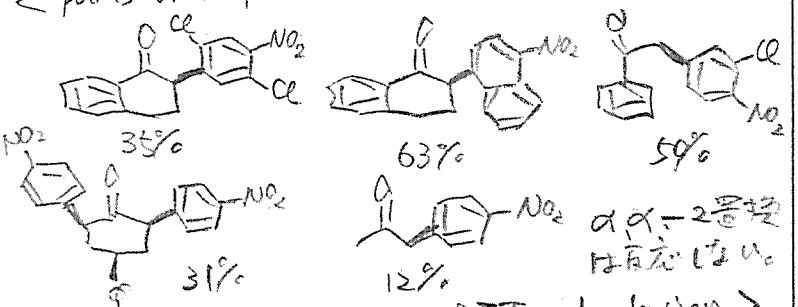


VNS
Crications nucleophilic substitution

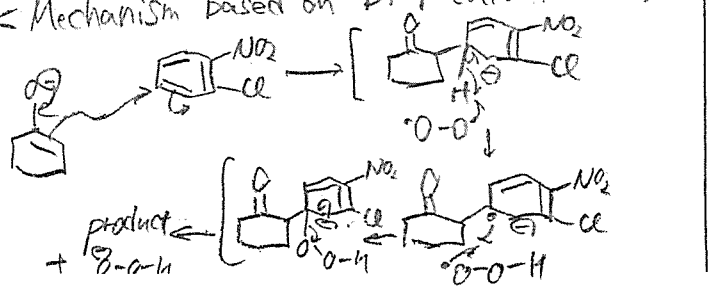
<This Work>



< parts of scope>



< Mechanism based on DFT calculation >

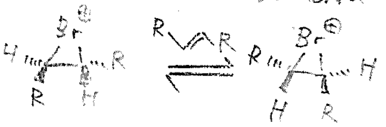


Noah Z. Burns	Stanford University (USA)	*JACS* **2013**, *135*, 12960.	Okumura

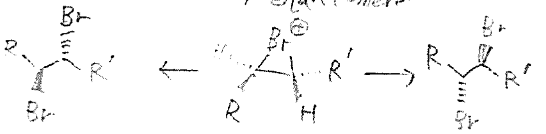
Catalytic Enantioselective Dibromination of Allylic Alcohols

Asymmetric dibromination

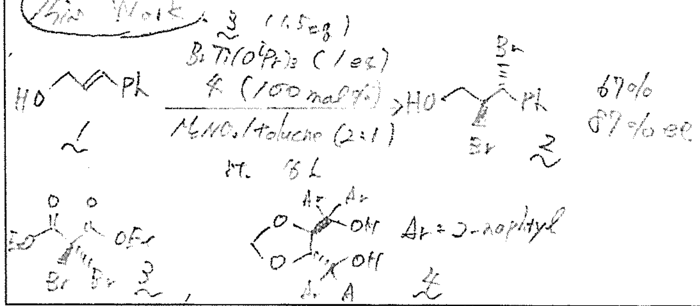
- Racemization of chiral bromonium ions



- Regioisomeric dibromide products → enantiomers

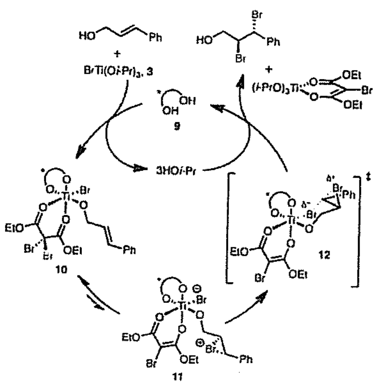


(This Work)



- Ligand (20 mol%) → 57% 76% ee, (2.5 mol%) → 53%, 34% ee
- 基質とBrTi(O^iPr)3 dropwise → yield, ee up.
- TBAB (Br^- source), BrTi(O^iPr)3 を 1eq 追加 → ee 低下
- 基質 2eq にする → ee 低下 （※鏡の単一のジアステレオマーへの…）
- HO～～Ph (1eq) 追加 → ee 低下
- ～～Ph (1eq) 追加 → 変化なし → bromonium transfer 関与しない
- ClTi(O^iPr)3 → HO～(Cl)(Br)～Ph 生成 88% ee

mechanism



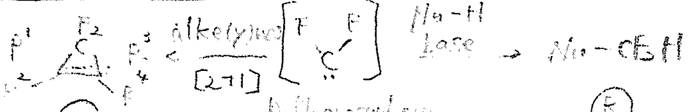
Scope

HO～～Ar
4-F, Cl, Br
-OSO2Me
CHO etc
57～90% yield
84～91% ee
20 mol% では それぞれ 5～10% 低下
ortho置換 } → yield 低下 ee 変化なし
EDG
homoallylic (75% ee)
Alkyl (55% ee) も OK

Jinbo Hu et al.	Chinese Academy of Science	anie.201306703	M2 榎島

Synthesis of *gem*-Difluorocycropropa(e)nes and O-, S-, N-, and P-Difluoromethylated Compounds with TMSCF2Br

○ Difluoromethylation



○ Difluorocarbene sources

TMSBr-Cl TMSCl (1.5 eq) —AC (0.7 eq.)→ TMSCF2Cl 80% yield ⟨Chem Comm 2011⟩

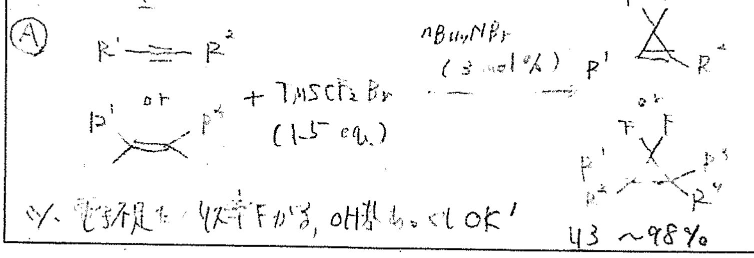
※ This work

TMSCF3 + BBr3 —52% yield, CH2Cl2, 15°C, 2 min→ TMSCF2Br

TMSCF2H + NBS —75% yield, CH2Cl2, 90°C, 48 h→

○ Scope

Ⓐ



※電子効果は収率下がる, OH基もあってもOK!

Ⓑ

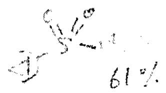
Nu-H + TMSCF2Br (2.0 eq.) —20% aq. KOH (6.0 eq.), CH2Cl2, 0°C, 0.5 h→ Nu-CF2H

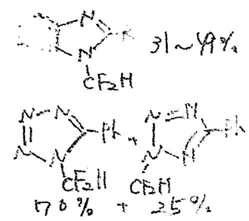
Nu = O: フェノール類 57～95%, アルコール類 42～85%

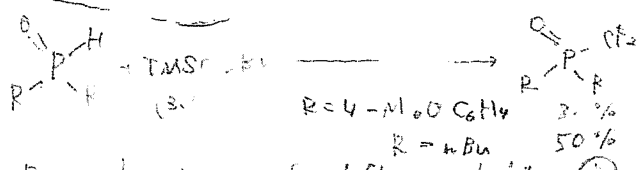
Nu = S: チオフェノール類, チオール類 ～66%

Nu = N: 31～91%

※ 電子求引基 あまり影響なし!!







○ Proposed mechanism for difluoromethylation (B)

TMSCF2Br —HO⁻, -TMSOH→ $BrCF_2^-$ ⇌ (H2O / HO⁻) HCF2Br (trace)

fast ↓ Br^-

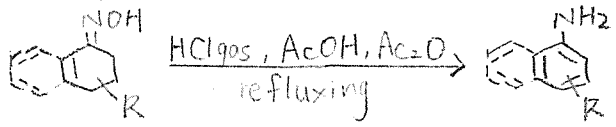
Nu-H —HO^- / H2O→ Nu^- — :CF2 → $NuCF_2^-$ —H2O, $-HO^-$→ NuCF2H

(Nu = O, S, N, or P)

Shannon S. Stahl	University of Wisconsin — Madison (United States)	J. Am. Chem. Soc. 2013, 135, 13664.	M2 岡村

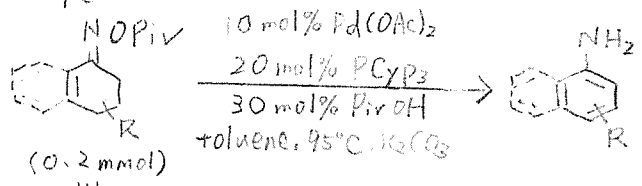
Pd-Catalyzed Semmler-Wolff Reactions for the Conversion of Substituted Cyclohexanone Oximes to Primary Anilines

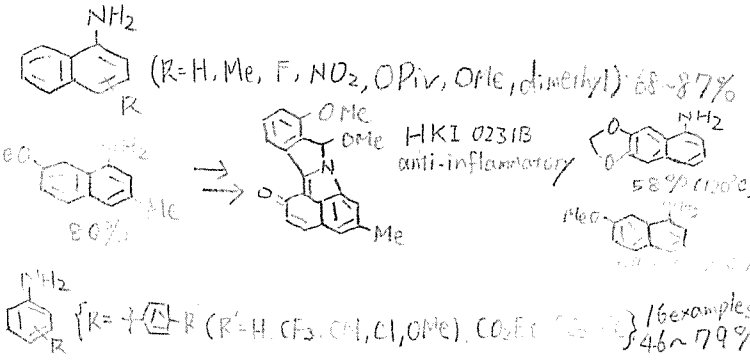
<Semmler-Wolff Reaction>



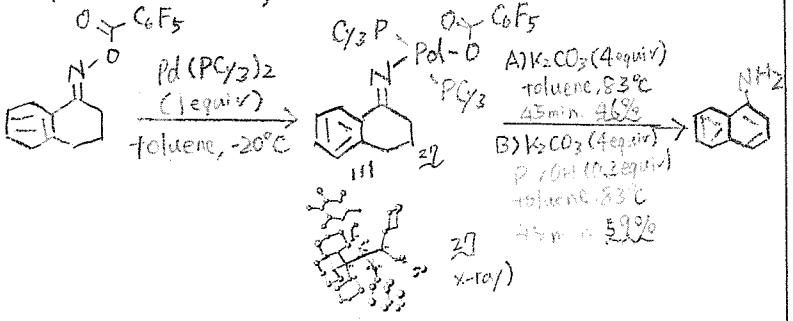
- harsh conditions → narrow scope
- low product yields (≤ 60%)

<Scope of Aromatization Reaction>

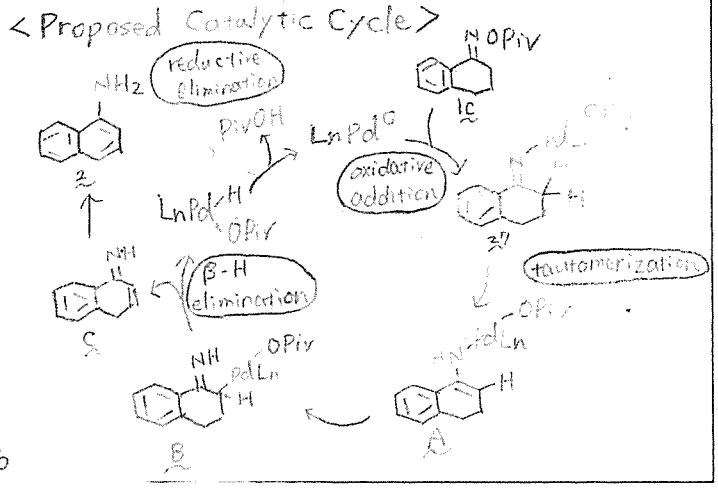




<Stoichiometric Oxidative Addition/Aromatization Sequence and X-ray-Crystal Structure of 2l>



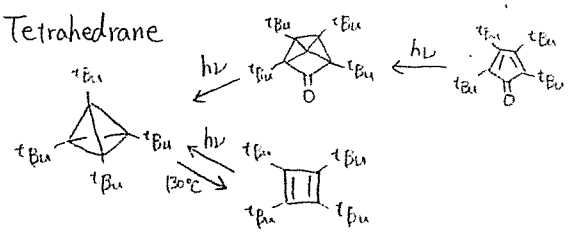
<Proposed Catalytic Cycle>



Akira Sekiguchi	University of Tsukuba (Japan)	ACIE 10.1002/anie.201304770	M2 西田

Cross-Coupling Reaction of a Highly Strained Molecule: Synthesis of σ-π Conjugated Tetrahedranes

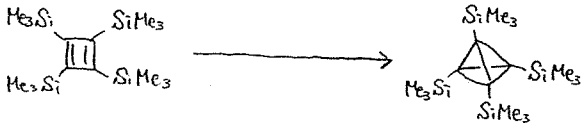
Tetrahedrane



G. Maier, et al. ACIE 1978, 17, 520

- 安定化のためにかさだかい置換基(-tBu)が必要
- 原料の合成が困難
- 低収率

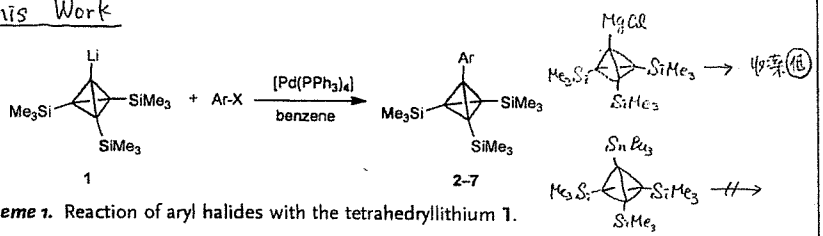
Previous Work



Entry		Solvent	Temp.	Time	Yield
1	hν/λ=254 nm	Pentane	-100 °C	100 h	10 %
2	B(C6F5)3 /0.25eq.	Toluene	rt	12 h	30 %

Heteroat. Chem. 2011, 22, 412.

This Work

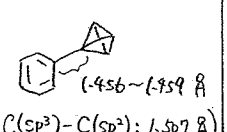


Scheme 1. Reaction of aryl halides with the tetrahedryllithium 1.

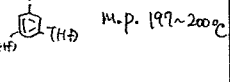
Entry	Ar-X	Product	Time [h]	Temp. [°C]	Yield [%]
1	I-Ph	THD-Ph	0.5	rt	93 (65)
2	Br-Ph		9	50	64 (53)
3	I-Ph-Br	THD-Ph-Br	0.5	rt	84 (69)
4	I-Ph-OMe	THD-Ph-OMe	0.5	rt	89 (69)
5	I-Ph-I	THD-Ph-THD	0.5	rt	(58)
6	I-Ph-I	THD-Ph-THD	0.5	rt	(65)
7	I-Ph-I	THD-Ph-THD	1	100	(50)

- 溶媒がTHFだと収率低下
- THD = TMS, TMS, TMS

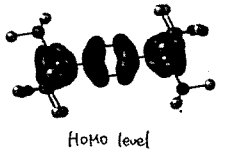
(THD-Ph-THD, THD-Ph-THD: X線により結晶構造決定)



- THDとベンゼン環の間でσ-π共役している
  ⇓
  熱安定性に優れている.



M.p. 199~200°C

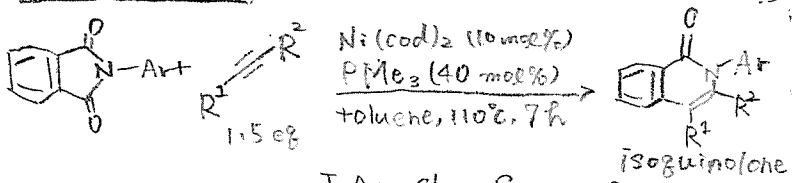


HOMO level

Seijiro Matsubara	Kyoto University (Japan)	JACS 10.1021/ja4068172	M2 Hisakuni

Nickel-Catalyzed Decarbonylative Alkylidenation of Phthalimides with Trimethylsilyl-Substituted Alkynes

Previous Work



isoquinolone

J. Am. Chem. Soc. 2008, 130, 6058.

- Scope

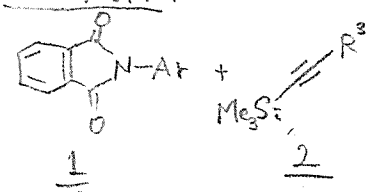
Ar : , Ph, C_6F_5 — 17 examples

R^3 : C_6H_{13}, R' (Ph, OMe, CO_2Me)

R' (H, CF_3, OMe) — 44~90%

Me_3Si ⇒ ^tBu, Me でも進行した!!

This Work

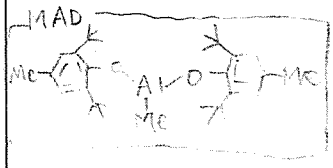


選択的に得られる。

82%

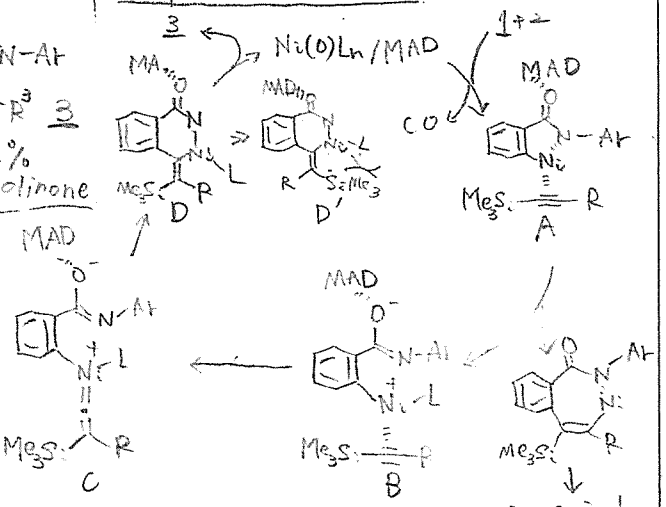
isoindolinone

- optimization
  - ligand ··· PMe_3, PMe_2Ph, $PMePh_2$, IPr
  - Lewis acid ··· MAD, $AlMe_3$, $Al(OPh)_3$, $B(C_6F_5)_3$



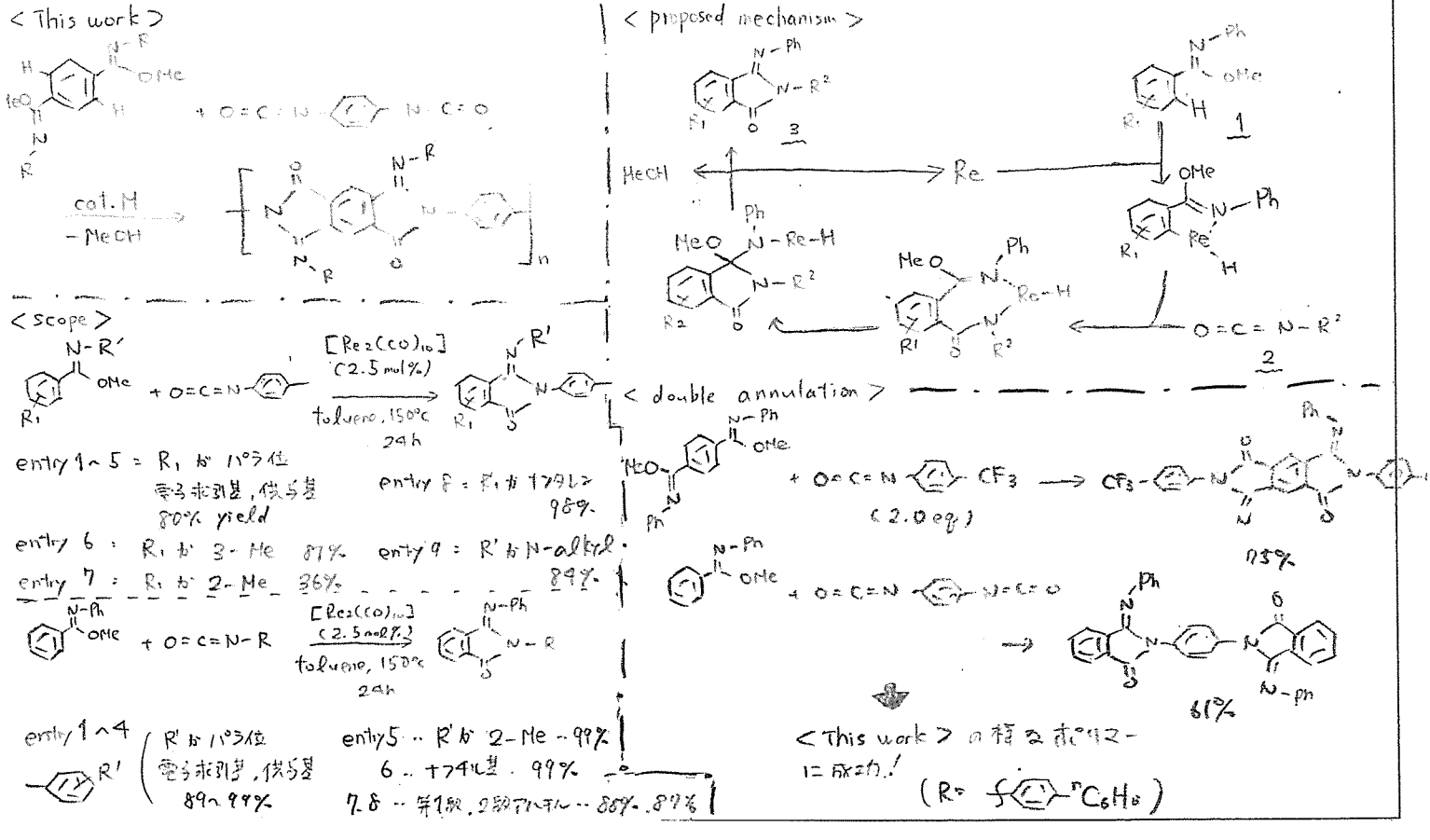
- MADは Bの形成を促進
- PMe_3は Ni^+を安定化
- $SiMe_3$と ligandの立体障害により D'ではなく Dが優先

Proposed Mechanism



Yoichiro Kuninobu	東京大学	Angewandte. Chem 10.1002/anie.201306360	M1 上田

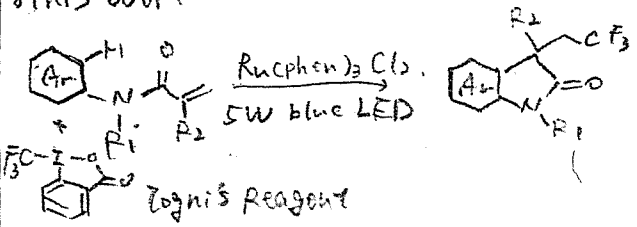
Rhenium-Catalyzed Synthesis of 3-Imino-1-isoindolinones by C-H Bond Activation Application to the Synthesis of Polyimide Derivatives



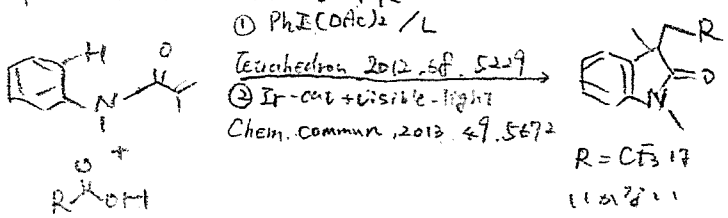
Chengjian Zhu et al. | Nanjing Univ. (China) | Chem. Eur. J 10.1002/chem.201302507 | M1 | 17枚

Visible-Light-Induced Trifluoromethylation of N-Aryl Acrylamides: A Convenient and Effective Method to Synthesize CF_3-Containing Oxindoles Bearing a Quaternary Carbon Center

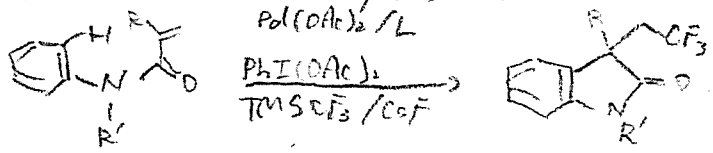
◦ This Work



◦ Author's Previous Work



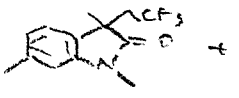
◦ Carbo-Trifluoromethylation.



Guosheng Liu, JACS, 2012, 134, 878

◦ Scope

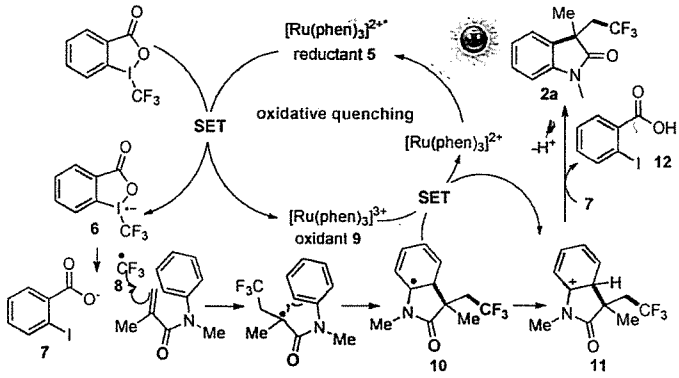
- R_1 ··· アルキル, Ph でも OK. H は 0%
- Ar ··· N の 3 位に Me がついたときのみ.



- R_2 ··· アルキル, I = Cl OK.
  $-CH_2OH$, $-CH_2-OAc$, $-CH_2-CH=CH_2$ OK

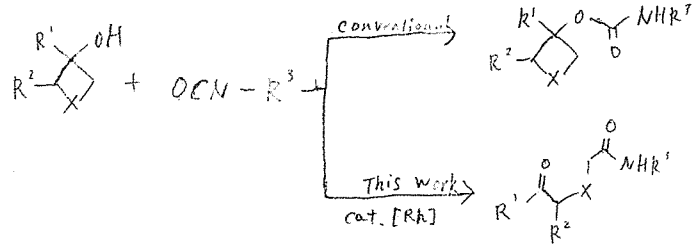
→ Example

◦ Mechanism

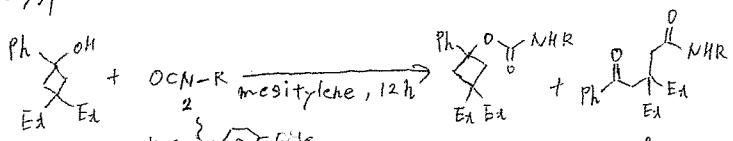


M. Murakami | Kyoto University (Japan) | DOI: 10.1002/anie.201306343 | M1 矢羽田

Reactivity Change of Cyclobutanols towards Isocyanates: Rodium Favors *C*-Carbamoylation over *O*-Carbamoylation



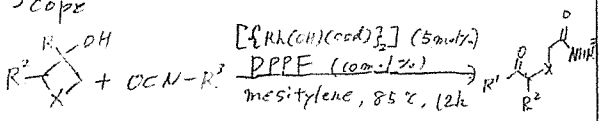
Catalyst



Entry	Catalyst (mol%)	Temp. [°C]	Yield [%] a	Yield [%] b
1	—	100	99	0
2	$[\{Rh(OH)(cod)\}_2]$ (5)	RT	99	0
3	$[\{Rh(OH)(cod)\}_2]$ (5), DPPF (10)	90	10	81
4[a]	$[\{Rh(OH)(cod)\}_2]$ (5), DPPF (10)	90	<5	89
5	$[\{Rh(OH)(cod)\}_2]$ (5), BINAP (5)	90	93	0

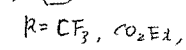
[a] Dropwise addition of 1 and 2.

Scope

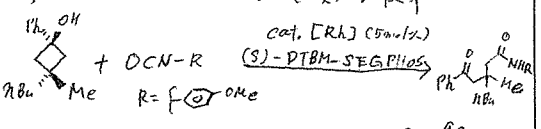


R^1 = Phenyl, 4-$MeOC_6H_4$, alkyl, vinyl

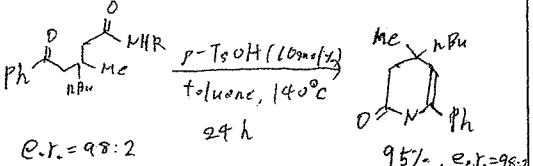
R^2 = H, alkyl

R^3 = 

X = C, O



e.r. = 98:2



e.r. = 98:2

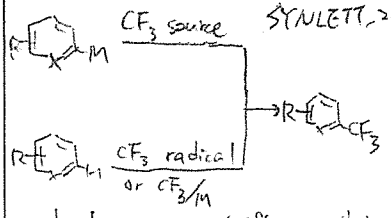
95%, e.r. = 98:2

Armido Studer	University of Münster	Anie.201306082	Lin

6-Trifluoromethyl-Phenanthridines through Radical Trifluoromethylation of Isonitriles

Previous Work:

Transition-metal catalyzed

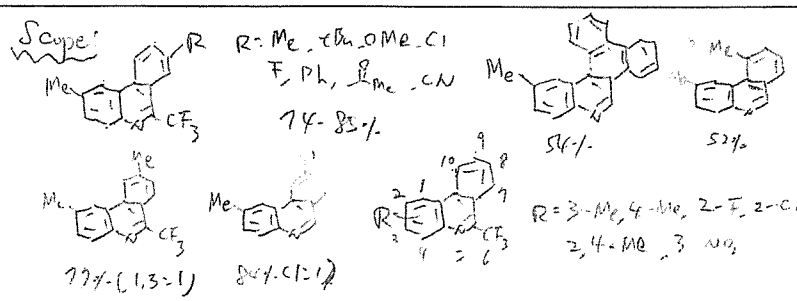


SYNLETT, 2012, 33, 2005

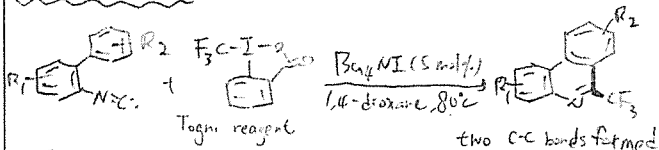
radical aromatic trifluoromethylation

ACIE, 2012, 51, 8950

Scope:



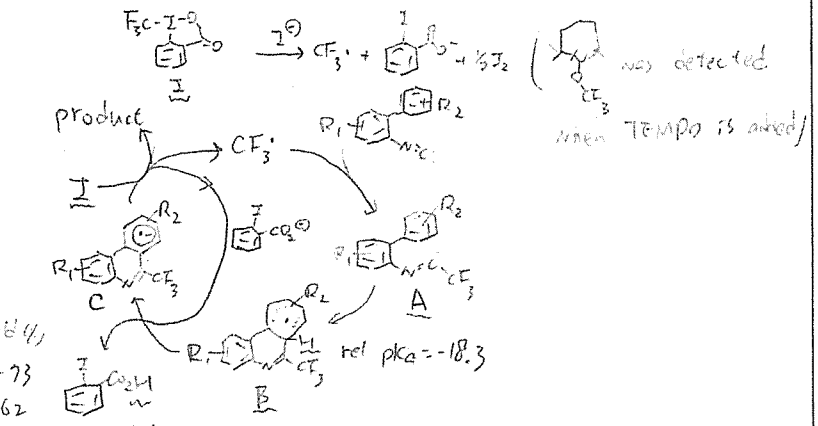
This Work:



Optimization:

Initiator (10 mol%)	solvent	T (°C)	yield (%)
CuOAc, FeCl2, FeI2, NiCl2, CuCl2, CuCl, CuBr, CuI	1,4-dioxane	70-80	56-73
	polar solvent (MeOH, CHCl3, anisen, EtOAc)		32-62
*Bu4NI (5 mol%)	1,4-dioxane	80	84

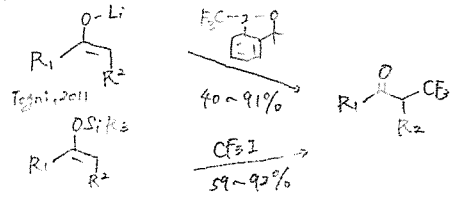
Mechanism

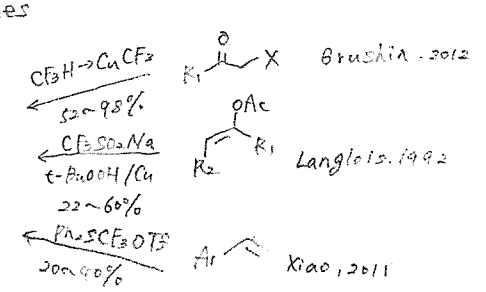


Debabrata Maiti	Indian Institute of Technology Bombay, India	ACIE, :10.1002/anie.201303576	B4 小嶋

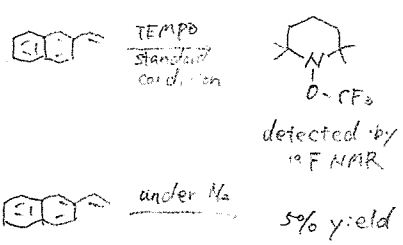
Oxidative Trifluoromethylation of Unactivated Olefins: An Efficient and Practical Synthesis of a-Trifluoromethyl-Substituted Ketones

◦ Synthesis of α-CF3 substituted ketones

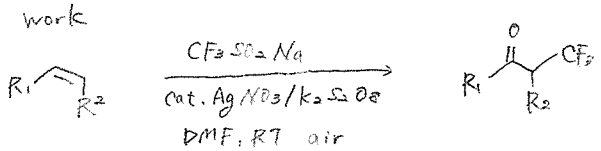


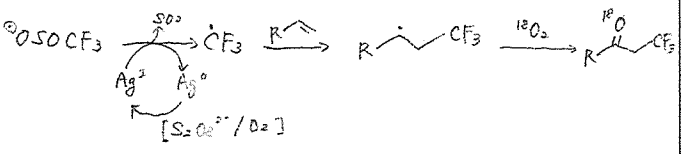


◦ Mechanism



◦ This work





◦ Scope

33 examples.