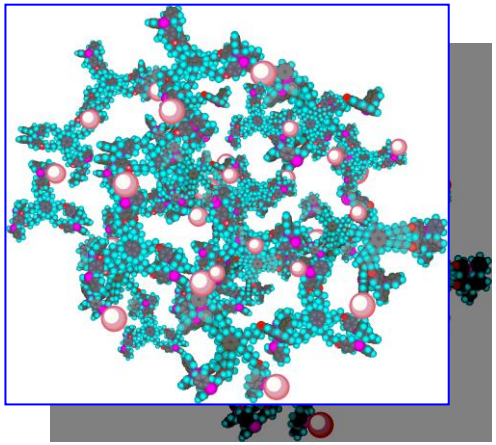
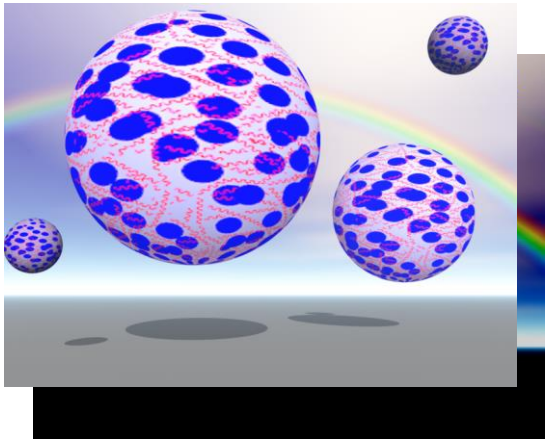
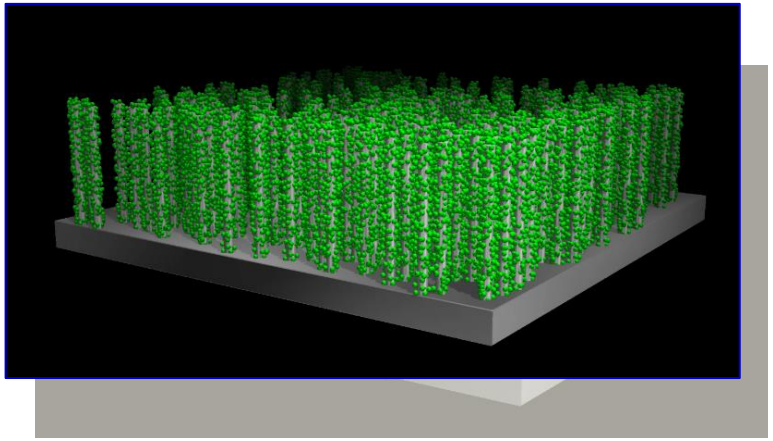
第5回SPring-8先端放射光技術による化学イノベーション
研究会／ 第62回SPring-8先端利用技術ワークショップ

高活性固定化触媒の開発と
省資源型有機変換反応への応用





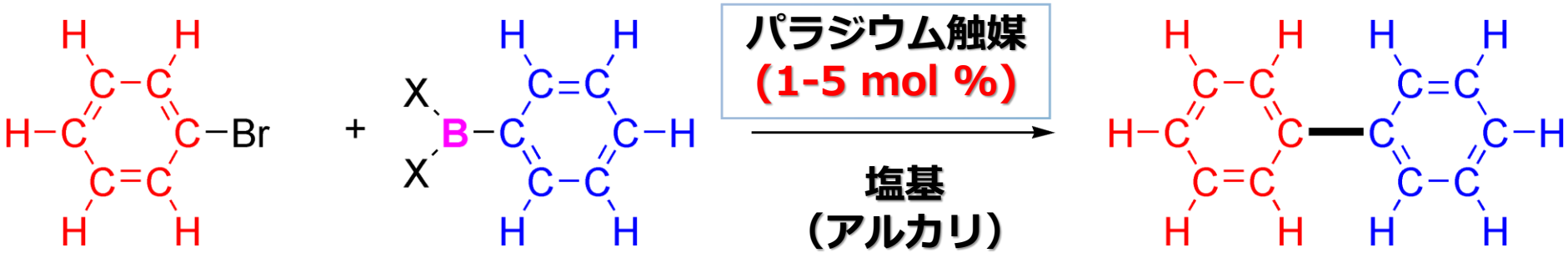


国立研究開発法人理化学研究所
環境資源科学研究センター・チームリーダー
（兼）埼玉大学大学院理工学研究科連携教授・台湾国立中興大学理学部物理学科客員教授

山田　陽一 Yoichi M. A. YAMADA

鈴木-宮浦カップリングの発見（1979 鈴木，宮浦）

非常に実用性の高いクロスカップリング反応の開発に成功した.



→ **医薬品合成，工業的利用にも容易に使用できる反応を実現**

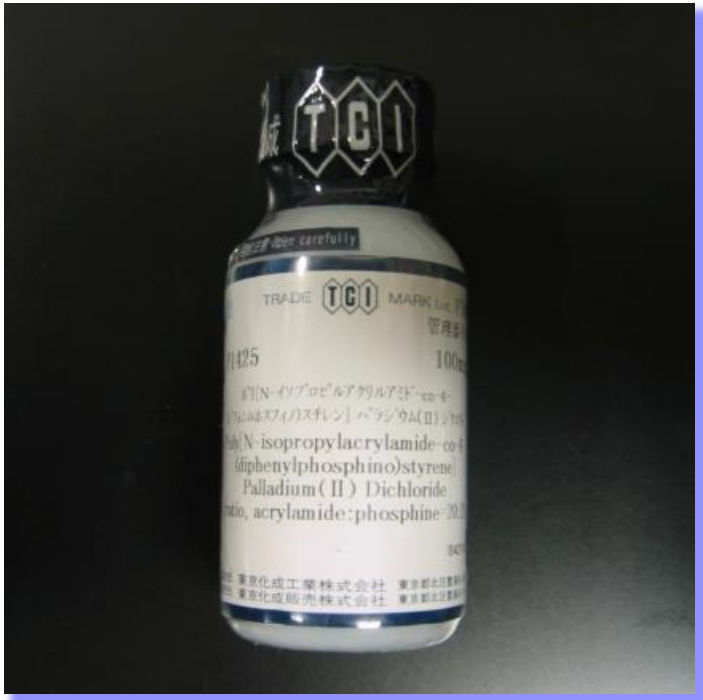
しかし、**高価なパラジウムを大量に使用**
（触媒1から生成物が20～100程度しかできない）

触媒は溶媒に溶けている（＝均一系触媒）ので、**回収・再利用が困難もしくは不可能**

➡ **SDGsに立脚した固体触媒の開発が重要**

SUSTAINABLE DEVELOPMENT GOALS
世界を変えるための17の目標

12 つくる責任 つかう責任



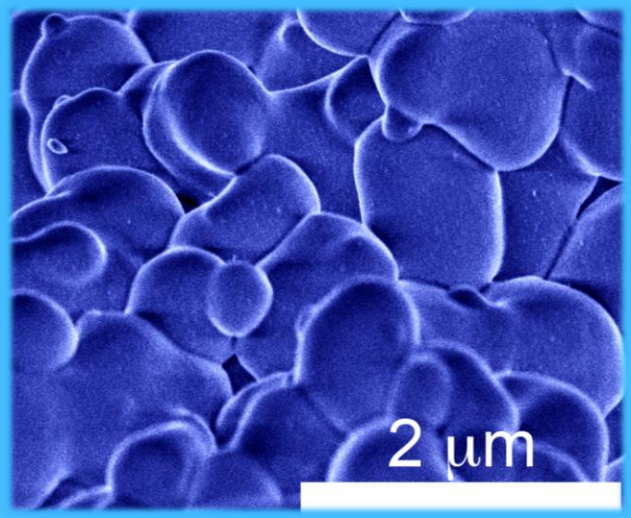
私達が開発した市販化触媒

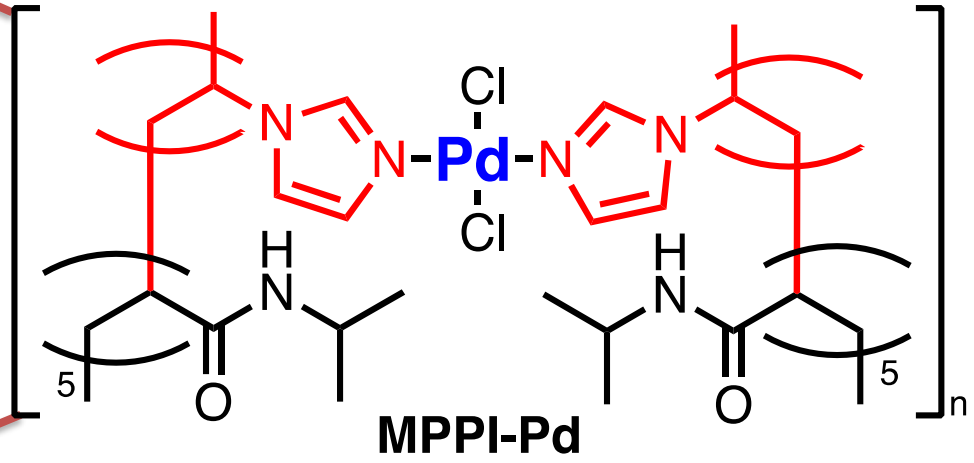
私たちが目指すグリーン固体ナノ触媒

触媒の**活性**（触媒の反応性・パワー）が高い。
触媒の**再利用**ができる
（水にも有機溶媒にも溶けない）。

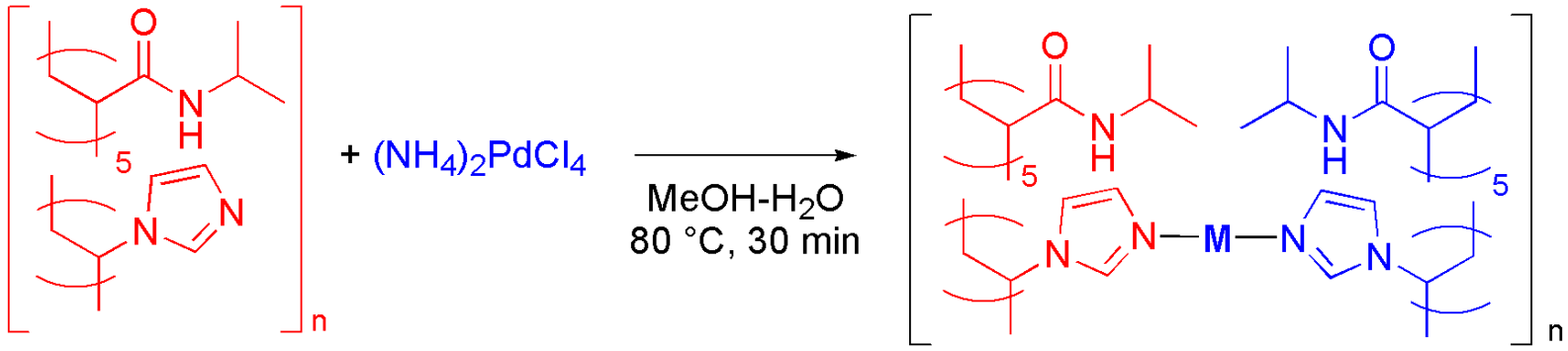
12 つくる責任 つかう責任

Polymeric Imidazole Pd Catalyst with ppm Levels





MPPI-Pd



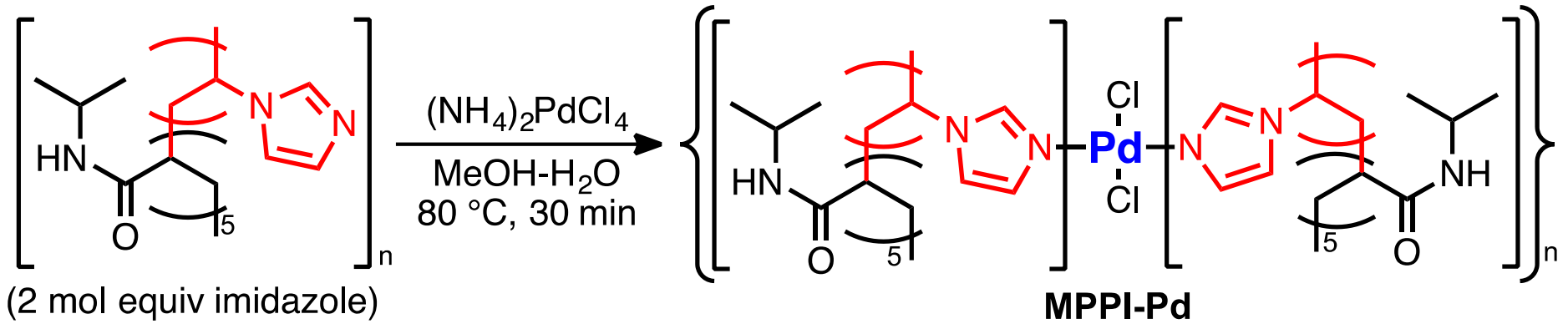
(2 mol equiv imidazole)

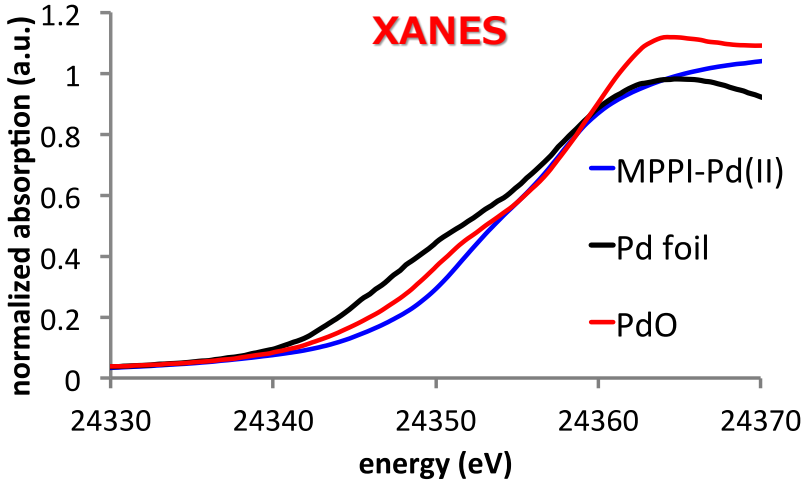
MPPI-Pd

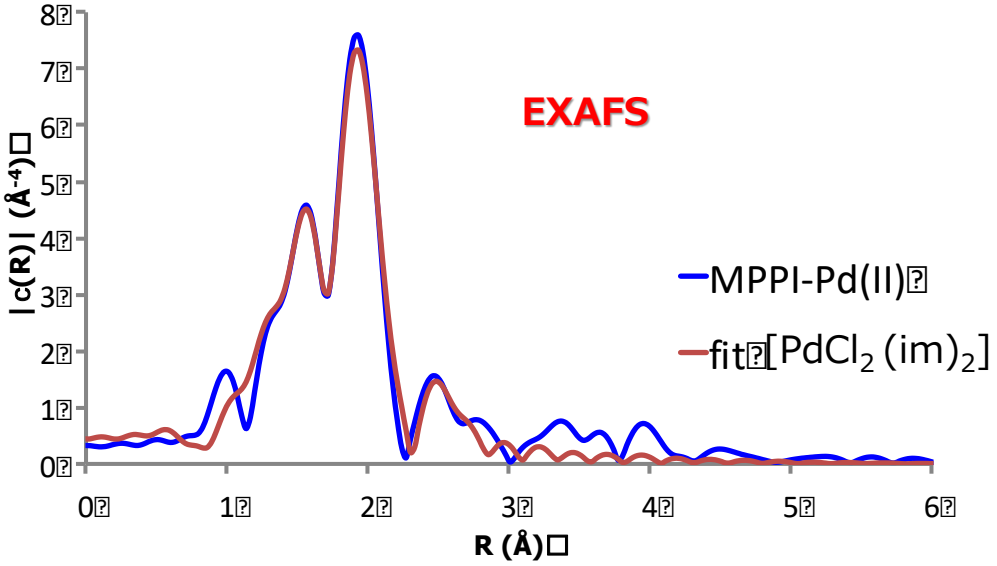
M = Pd(II)Cl_2

***Angew. Chem. Int. Ed.* 2011; *J. Am. Chem. Soc.* 2012; *ChemCatChem* 2015; *Chem Commun*. 2018**

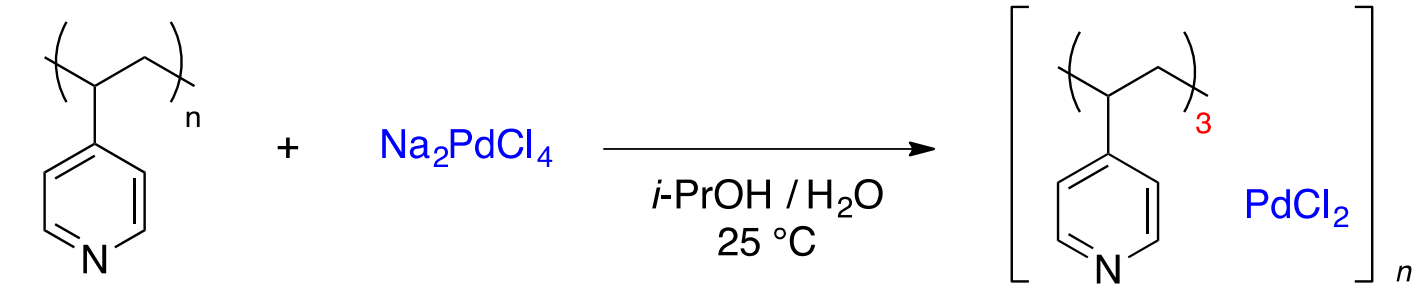
MPPI-Pd


(NH4)2PdCl4
MeOH-H2O
80 °C, 30 min
(2 mol equiv imidazole)
MPPI-Pd


XANES
normalized absorption (a.u.)
energy (eV)
MPPI-Pd(II)
Pd foil
PdO


EXAFS
|c(R)| (Å-4)
R (Å)
MPPI-Pd(II)
fit [PdCl2 (im)2]

Preparation of PVPy-Pd B

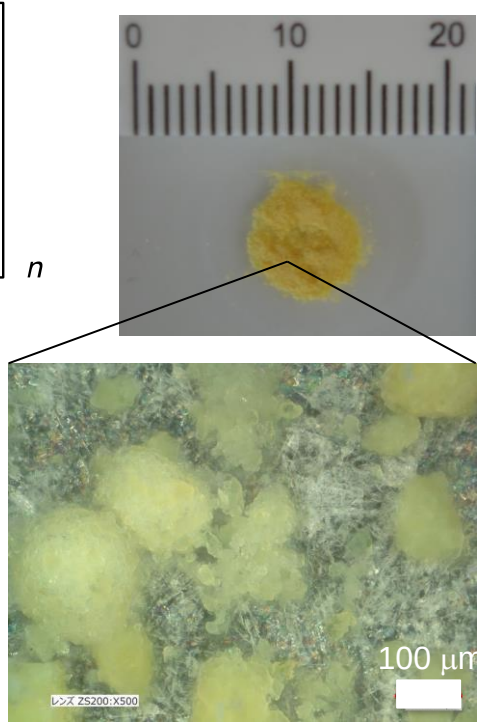


(3 mol equiv)

(1 mol equiv)

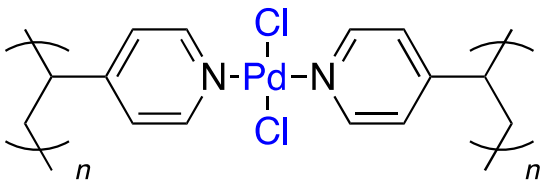
PVPy-Pd B

Py : Pd = 3 : 1



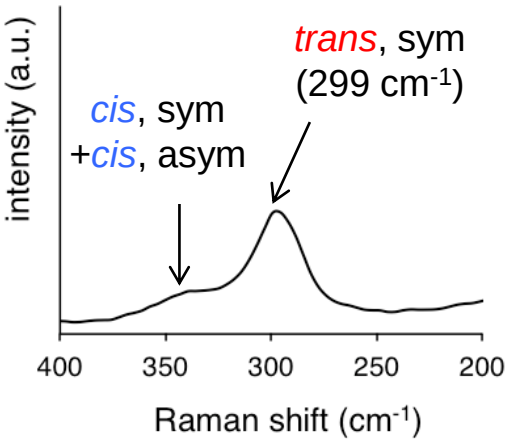
Structural Elucidation

PVPy-Pd
(Py : Pd = 3 : 1)

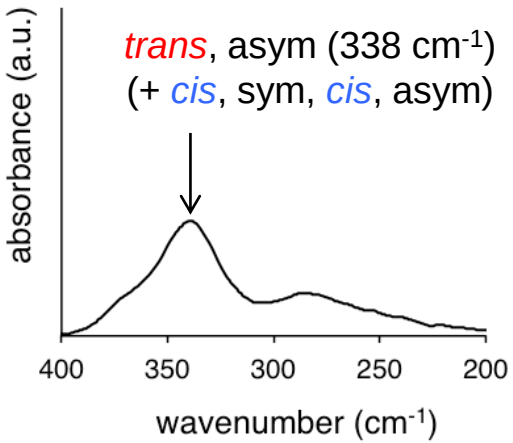


trans-$(Py)_2PdCl_2$

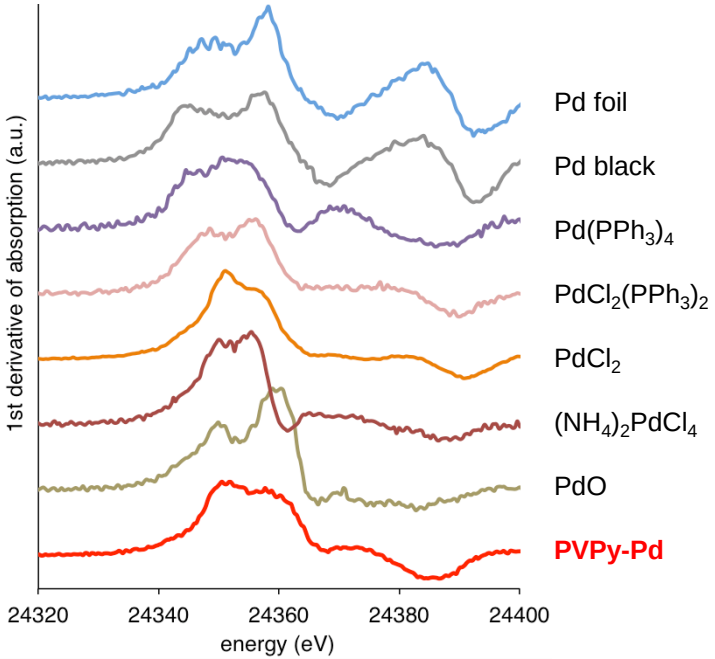
Raman (200-400 cm^{-1})



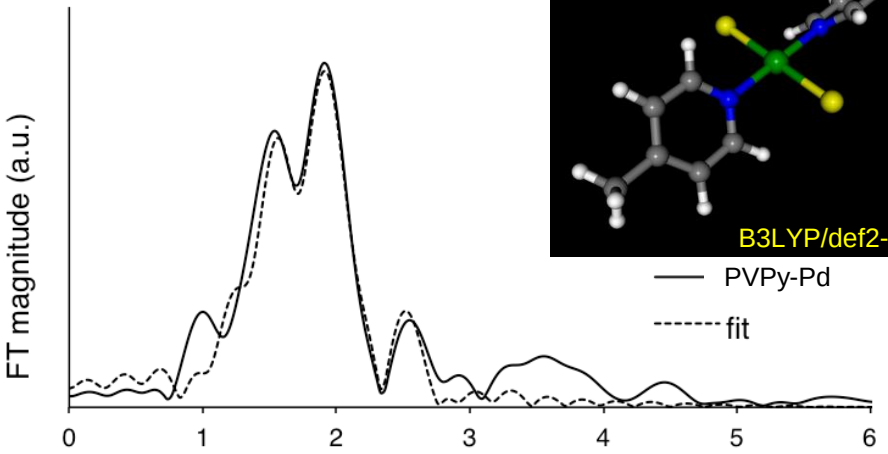
FIR (200-400 cm^{-1})



XANES spectra

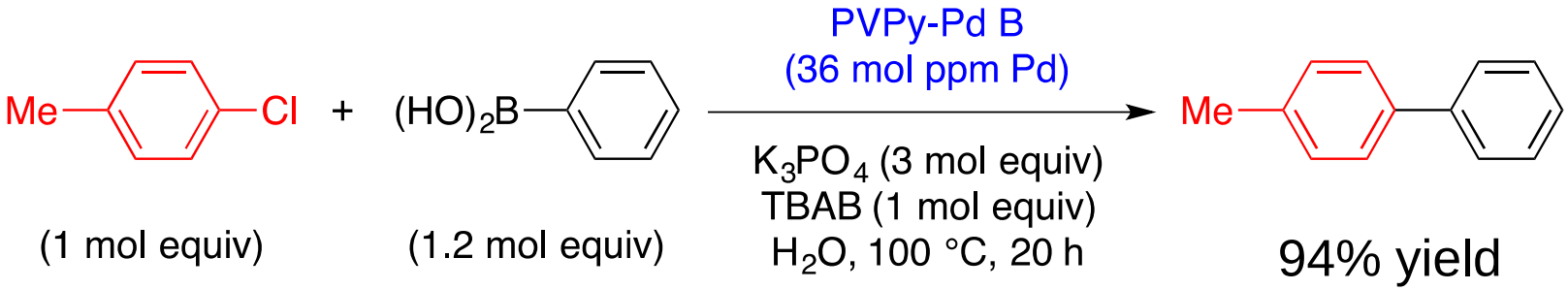


FT-EXAFS



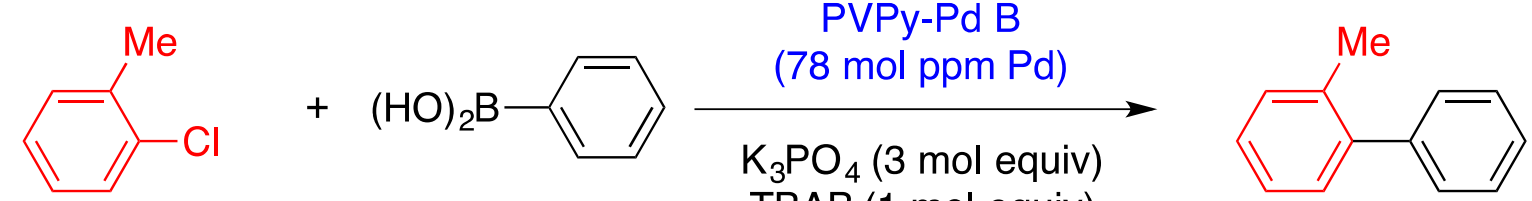
fitting parameters;
R-factor = 1.6%, R-range = 1.2-2.8 Å,
ΔE = 3.1 eV, $\Delta R(N)$ = -0.02 Å, $\Delta R(Cl)$ = -0.03 Å, $\Delta R(C)$ = -0.01 Å,
$\sigma^2(N)$ = 0.003 $Å^2$, $\sigma^2(Cl)$ = 0.004 $Å^2$, $\sigma^2(C)$ = 0.006 $Å^2$

Suzuki-Miyaura Reaction Using PVPy-Pd

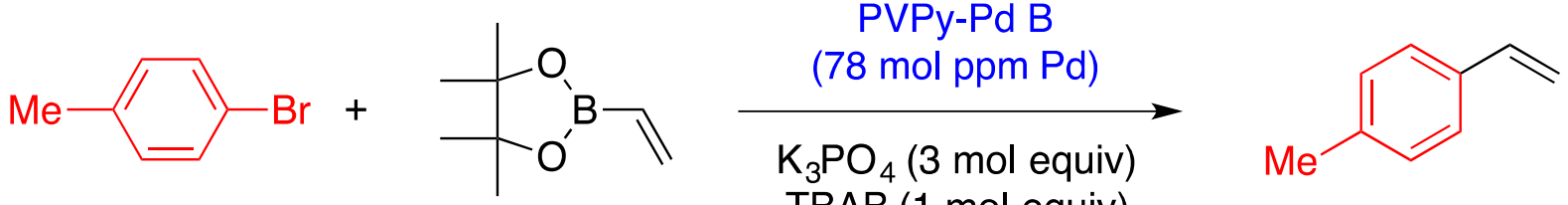


(1 mol equiv) (1.2 mol equiv) 94% yield

36 mol ppm = 0.0036 mol%

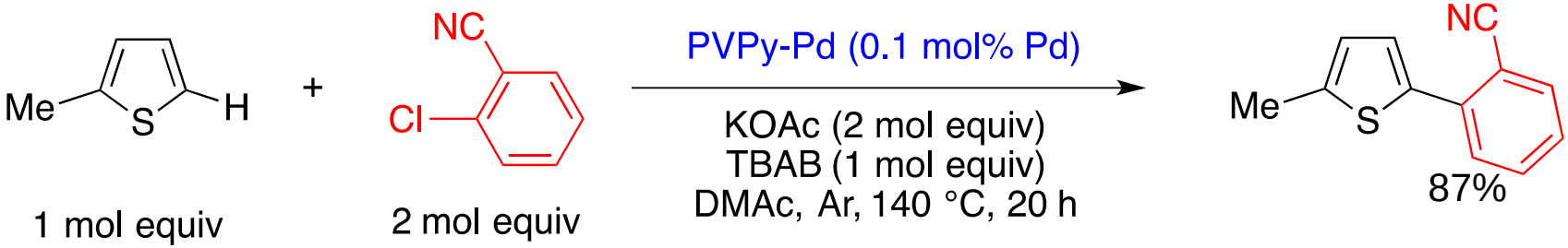


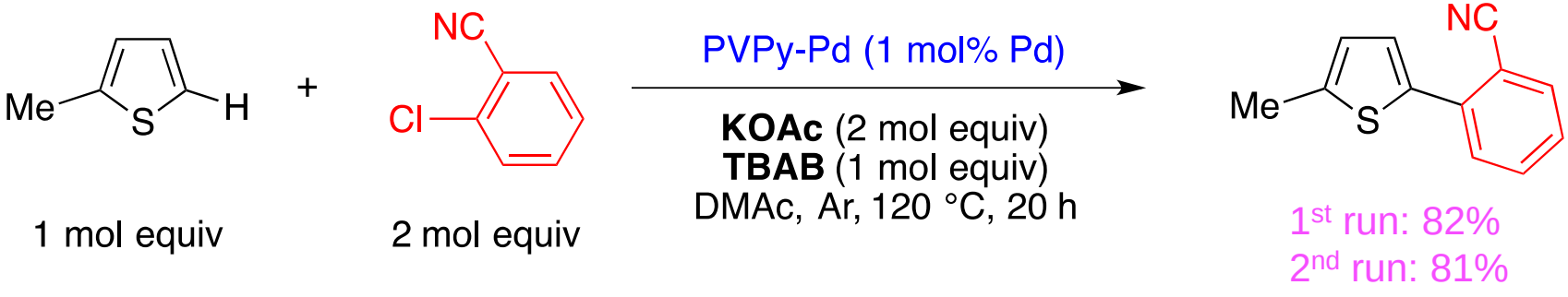
(1 mol equiv) (1 mol equiv) 82% yield



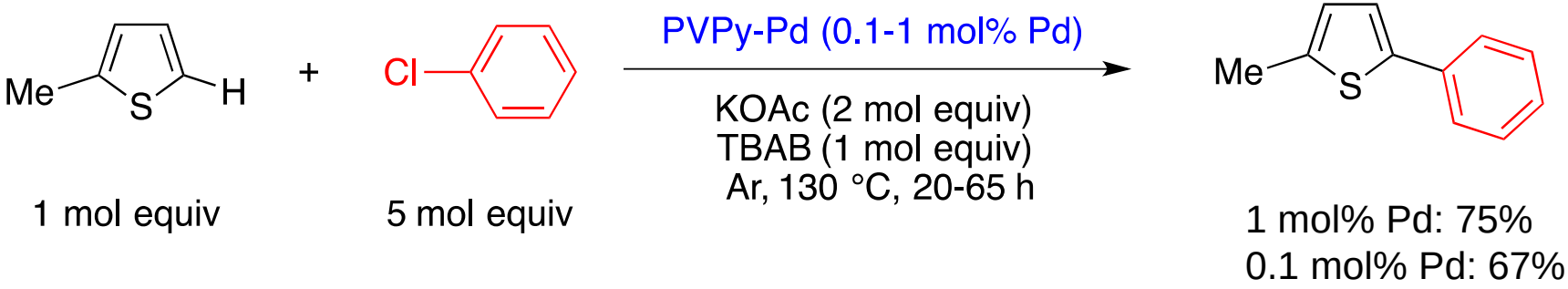
(1 mol equiv) (1.2 mol equiv) 82% yield

Direct Arylation of a Thiophene with ArCl





UV (365 nm)

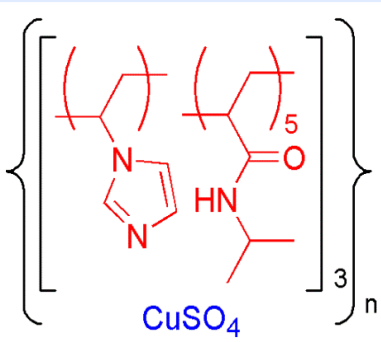


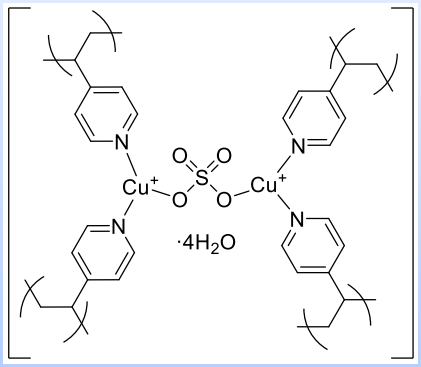
Adv. Synth. Catal. 2020

高活性自己組織化高分子銅触媒

ユビキタス元素
銅の活用

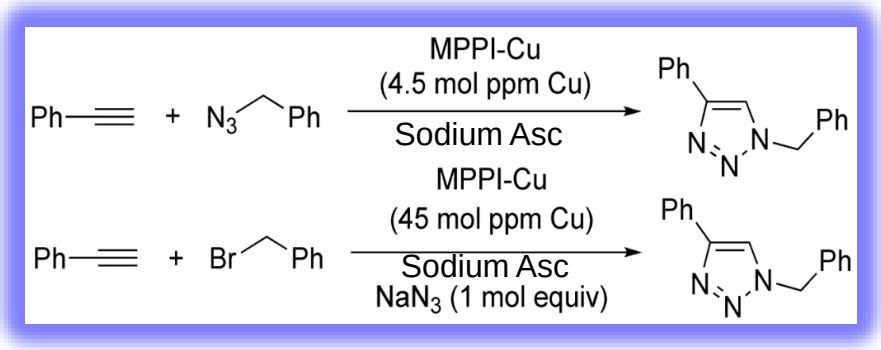
(700円/1 kg)



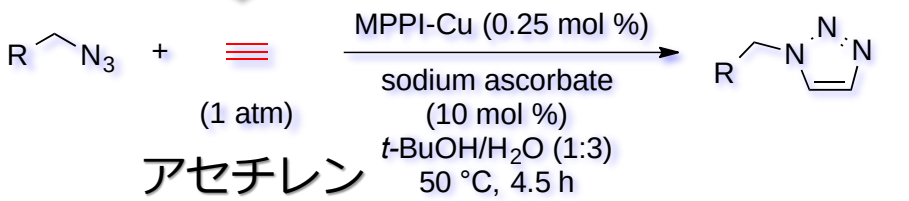


銅1から200,000の生成物

爆発性アセチレンガスの安全利用



触媒の回収・再利用を実現



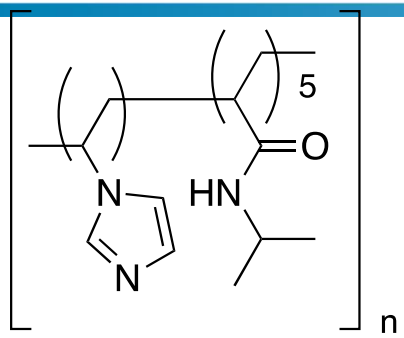
up to 96% yield
(10 examples)

アセチレン：　爆発性、高燃焼性
銅アセチリド：高い爆発性

J. Am. Chem. Soc. 2012, *Heterocycles* **2017**, OPR&D **2019**

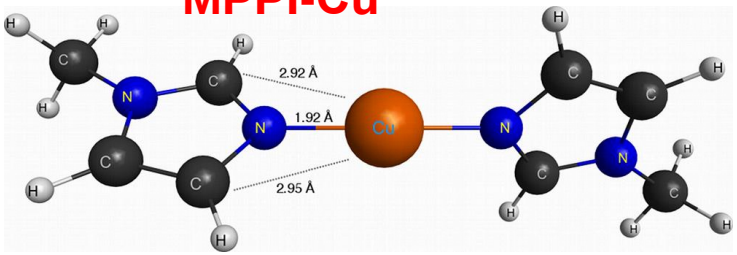
Structure of MPPI-Cu'

Cu(I) species



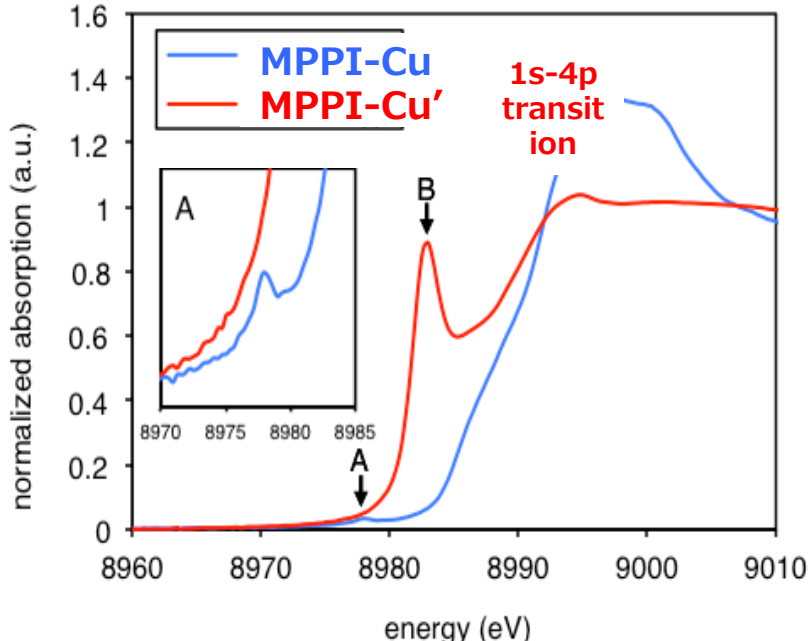
+ $CuSO_4$ —sodium ascorbate, 70 ° C, Ar→

MPPI-Cu'

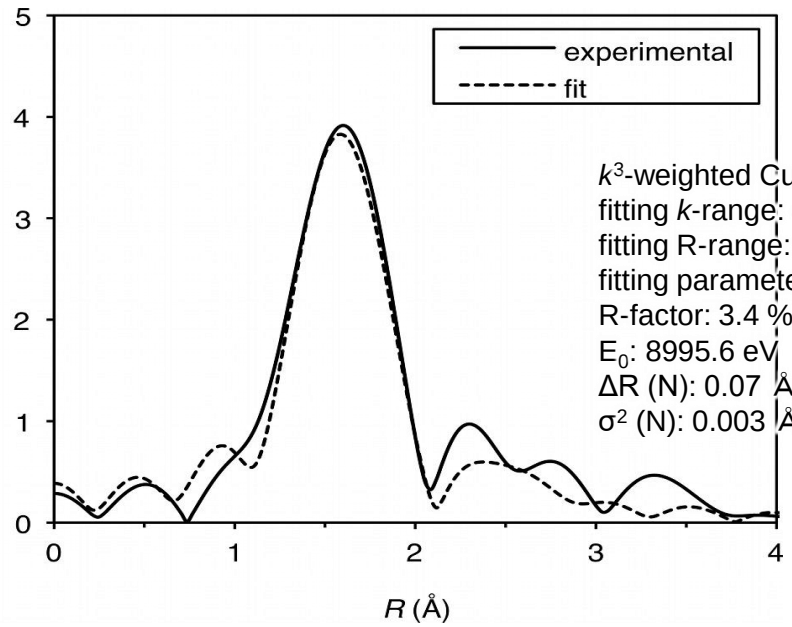


DFT-optimized structure of $[Cu^{I}(1\text{-methylimidazole})_2]^+$ (B97D/def2-SVP)

XANES of MPPI-Cu and MPPI-Cu'

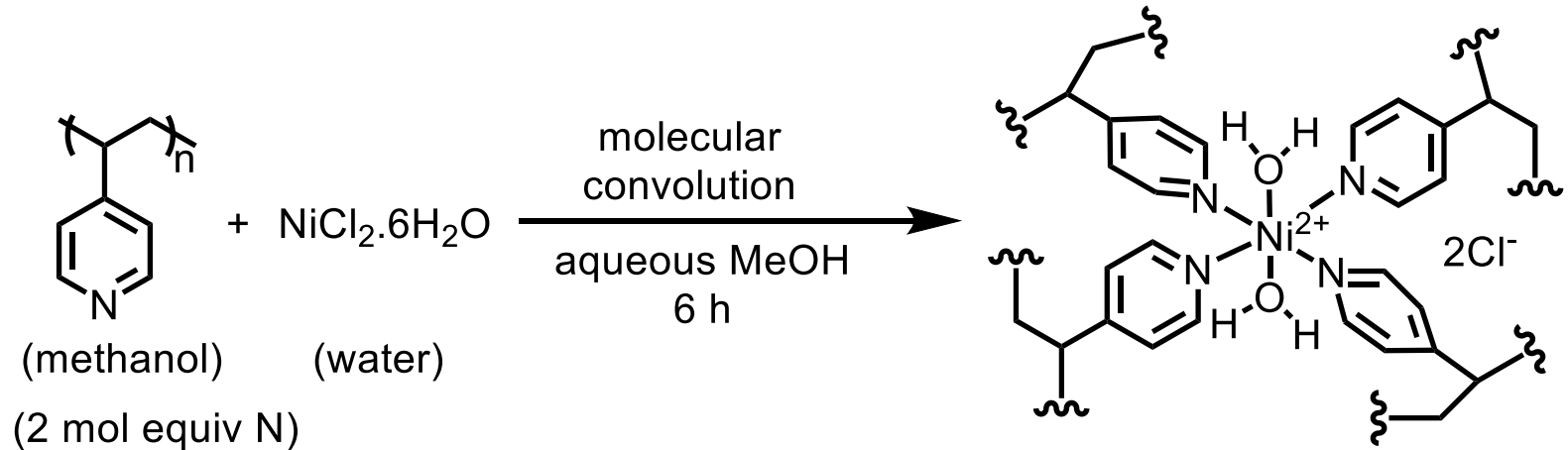


FT-EXAFS of MPPI-Cu'



k^3-weighted Cu K-edge EXAFS
fitting k-range: 4-11 $Å^{-1}$
fitting R-range: 1.2-2.9 Å
fitting parameters;
R-factor: 3.4 %
E_0: 8995.6 eV
ΔR (N): 0.07 Å, ΔR (C): 0.06 Å
σ^2 (N): 0.003 $Å^2$, σ^2 (C): 0.012 $Å^2$

Preparation of Convoluted P4VP-$NiCl_2$



(methanol) (water)

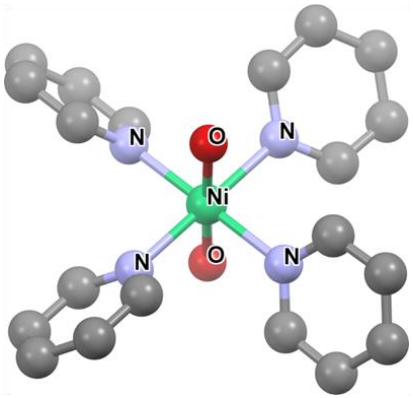
(2 mol equiv N)

poly(4-vinylpyridine) (P4VP)

P4VP-$NiCl_2$

53 wt% yield

(insoluble)

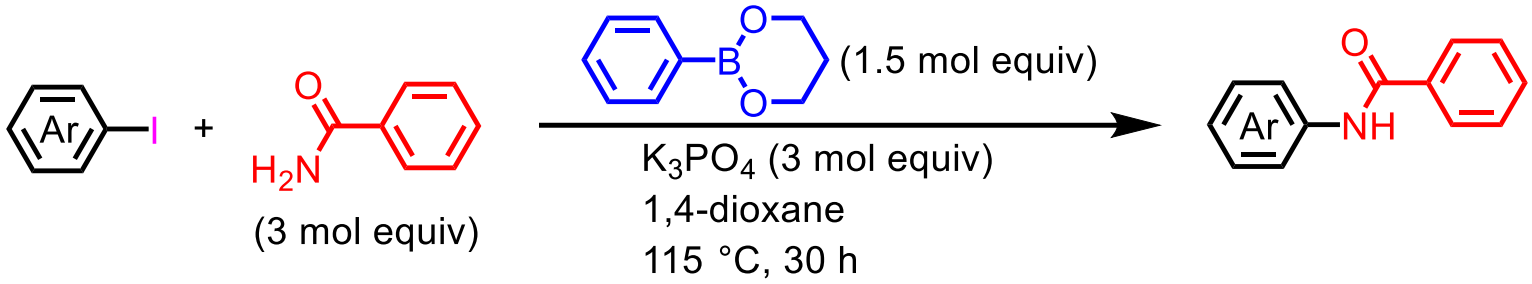


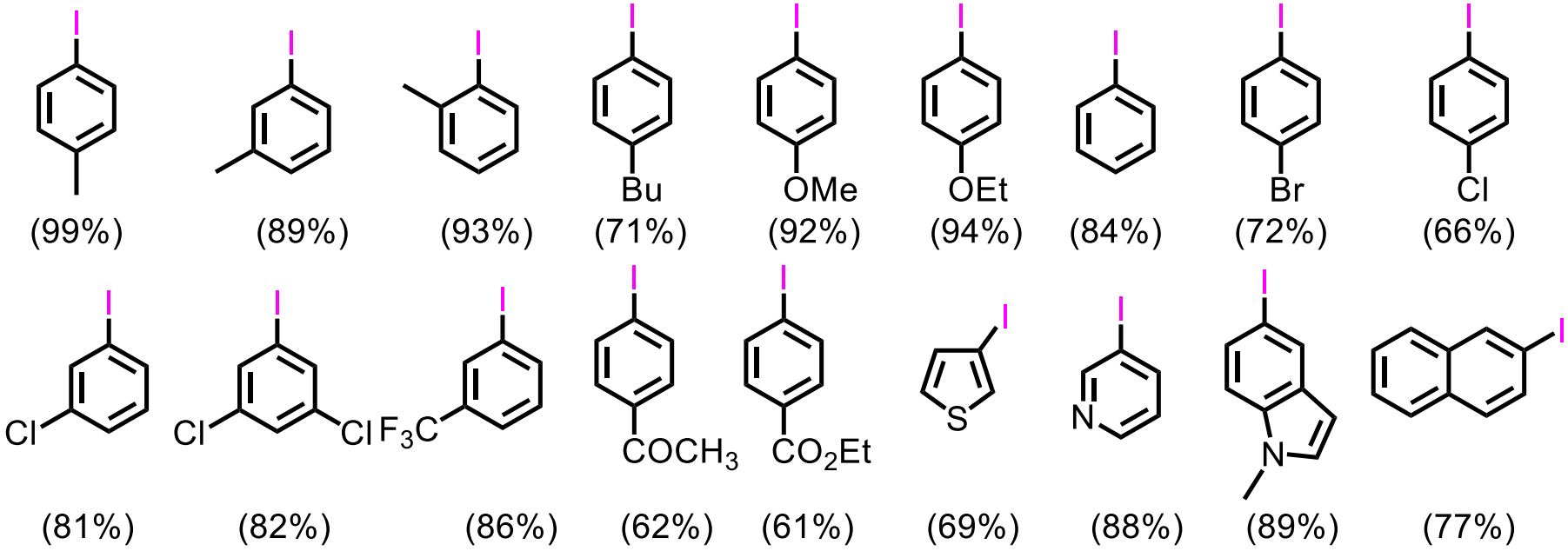
local structure near Ni of P4VP-$NiCl_2$

The catalyst is insoluble in water, methanol, ethanol, toluene, chloroform, and dioxane.

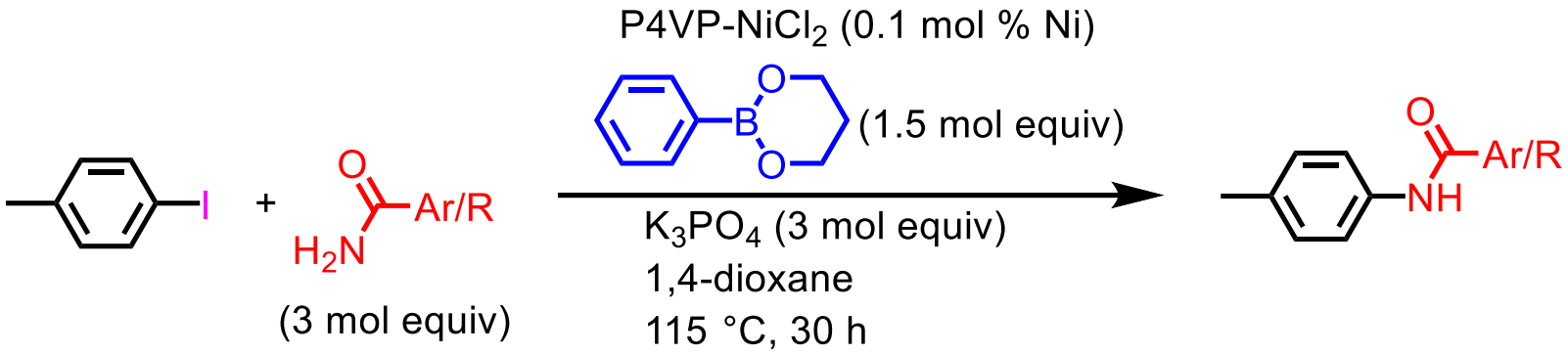
ACS Catal. **2020**, *10*, 14410

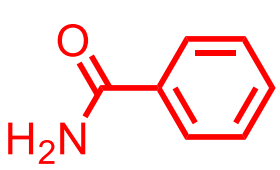
Scope of Aryl Iodide in Amidation

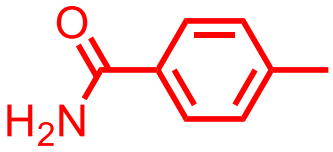


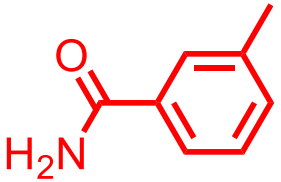


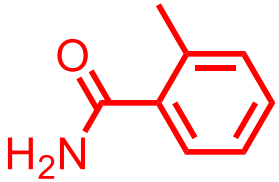
Substrate Scope of Amides

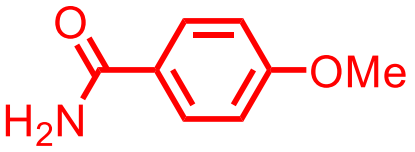


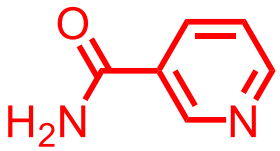

(99%)

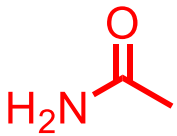

(99%)

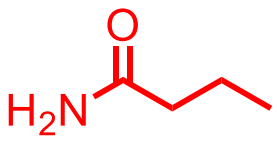

(94%)

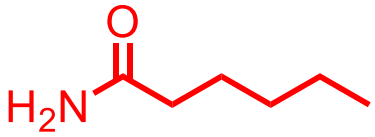

(94%)

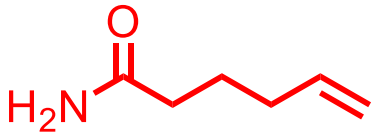

(99%)


(68%)

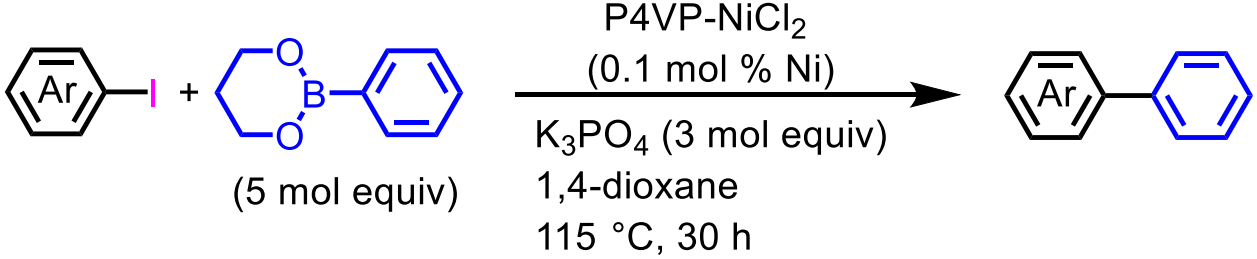

(82%)

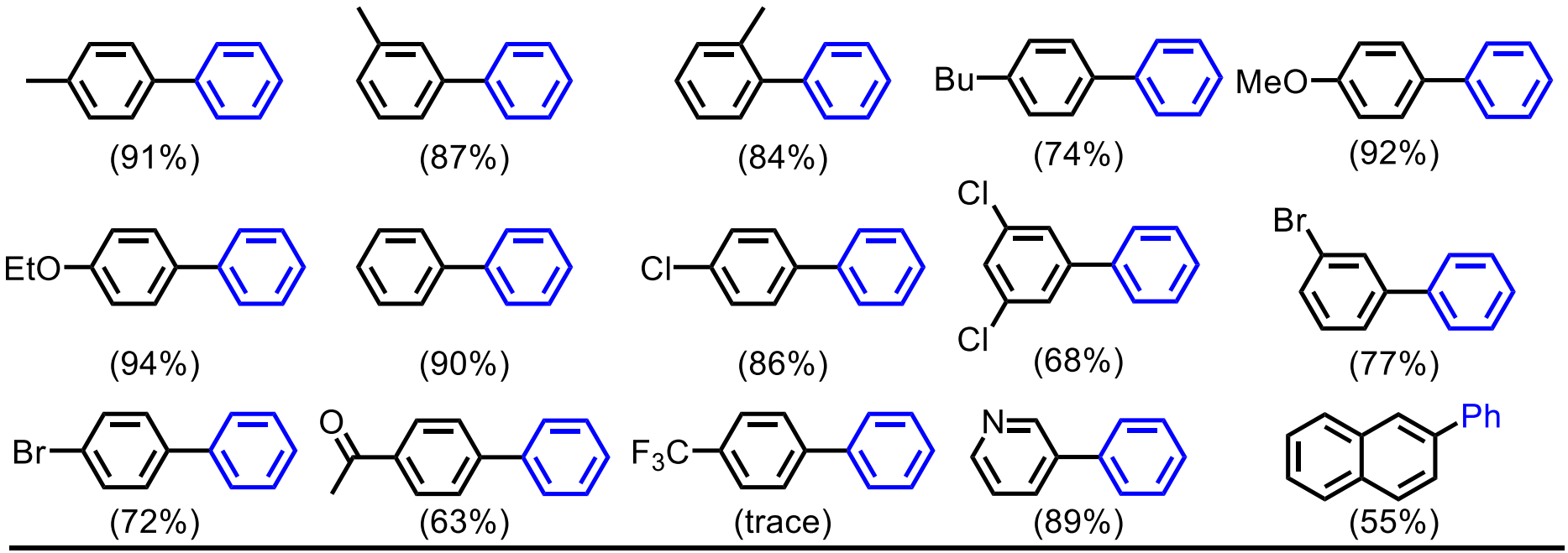

(98%)


(84%)

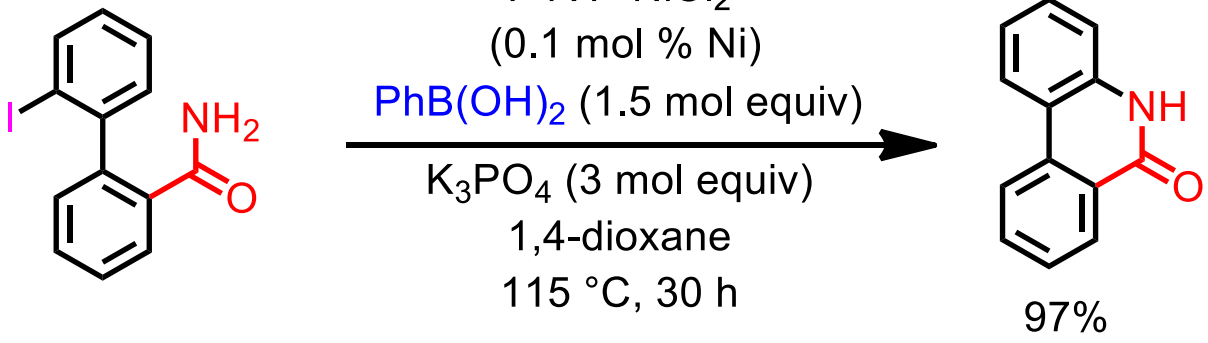

(87%)

Convoluted Polymeric Nickel-Catalyzed Suzuki-Miyaura Type Coupling



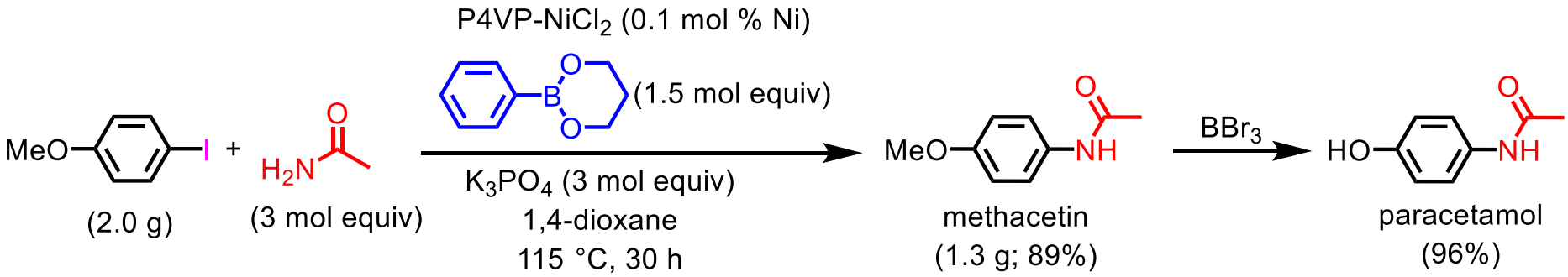


Synthesis of Phenanthridinone via Lactamization



poly(ADP-ribose) polymerase (PARP) inhibitor

Gram Scale Reaction and Synthesis of Biologically Active Molecules



(2.0 g)

(3 mol equiv)

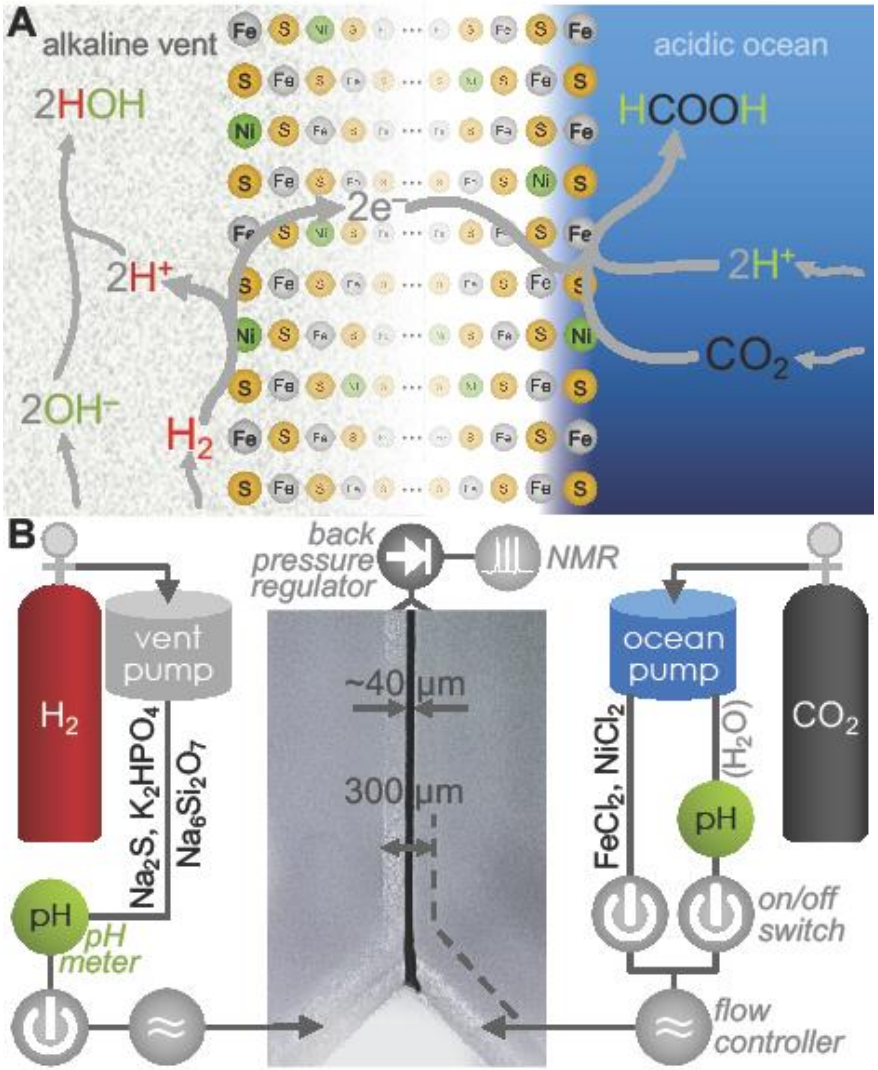
methacetin
(1.3 g; 89%)

Methacetin Breath Test (MBT) for liver function

paracetamol
(96%)

pain reliever
fever reducer

APPENDIX (CO_2変換反応)



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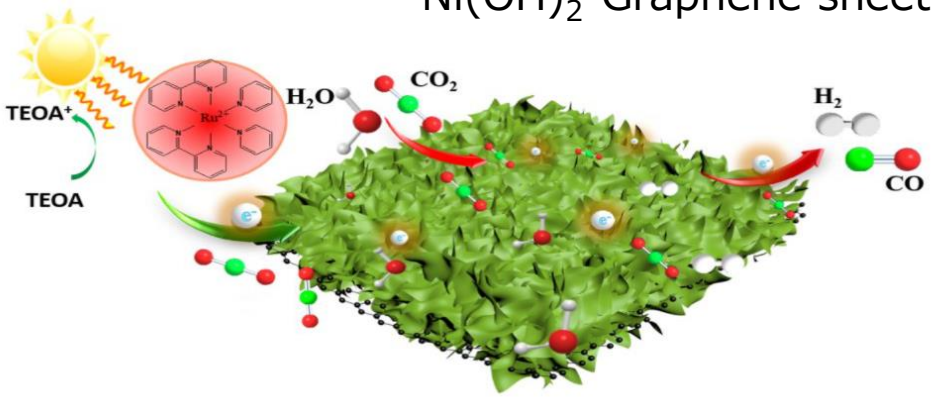
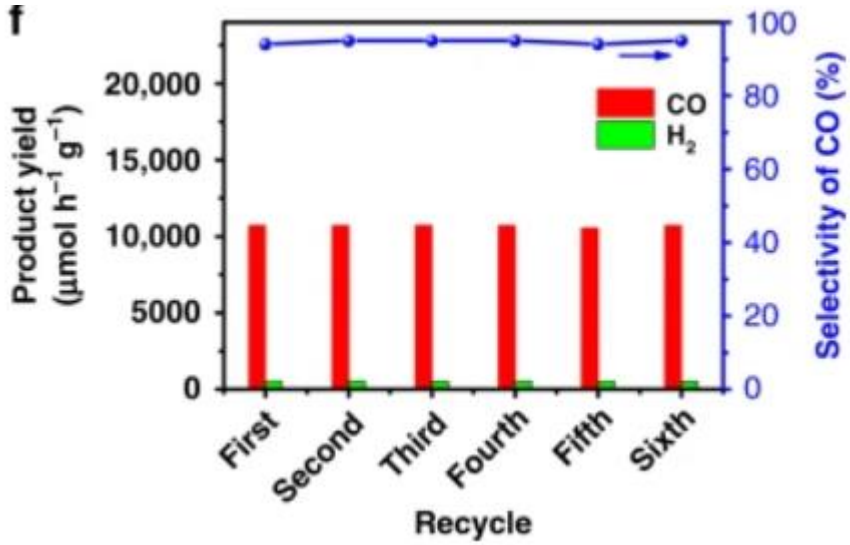
Ni(OH)$_2$-Graphene sheet





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