Decarbonylative Synthesis of Aryl Nitriles from Aromatic Esters and Organocyanides by a Nickel Catalyst

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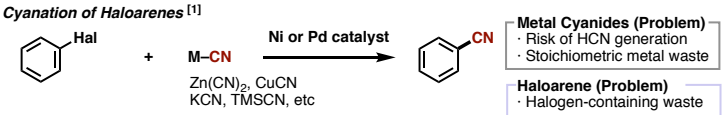
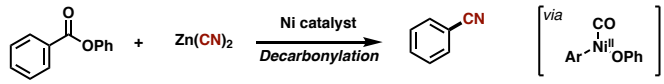
Ni- and Pd-Catalyzed Cyanation using Metal Cyanides

Cyanation of Haloarenes [1]

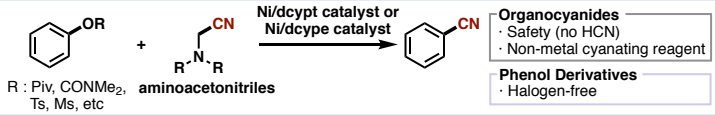


Decarbonylative Cyanation of Phenyl Esters [2]

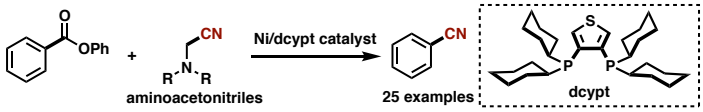


[1](a) Ellis, G. P.; Romney-Alexander, T. M. *Chem. Rev.* **1987**, *87*, 779. (b) Anbarasan, P.; Schareina, T.; Beller, M. *Chem. Soc. Rev.* **2011**, *40*, 5049. (c) Wen, Q.; Jin, J.; Zhang, L.; Luo, Y.; Lu, P.; Wang, Y. *Tetrahedron Lett.* **2014**, *55*, 1271. (d) Yan, G.; Zhang, Y.; Wang, J. *Adv. Synth. Catal.* **2017**, *359*, 4068. [2] Chatupheeraphat, A.; Liao, H.-H.; Lee, S.-C.; Rueping, M. *Org. Lett.* **2017**, *19*, 4255.

Our Previous Work[3]



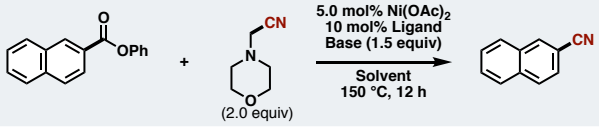
This Work[4]



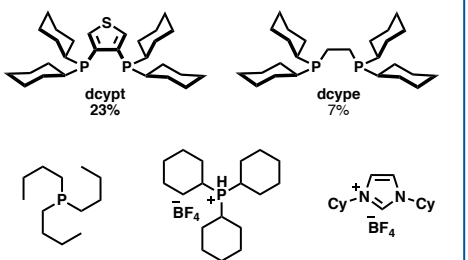
[3] Takise, R.; Itami, K.; Yamaguchi, J. *Org. Lett.* **2016**, *18*, 4428.
[4] Iizumi, K.; Kurosawa, M. B.; Isshiki, R.; Muto, K.; Yamaguchi, J. submitted.

Results

Condition Screening



Ligand



with Na_3PO_4 in 1,4-dioxane. [a] NaO*t*-Bu (20 mol%) was added.

Base

Na_2CO_3	62%[b,c]
Na_3PO_4	23%
K_3PO_4	15%
none	21%

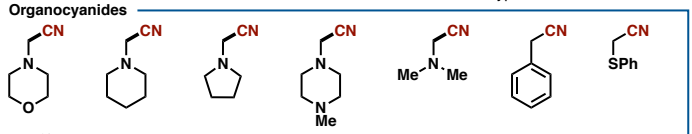
with dcypt in 1,4-dioxane.

Solvent

1,4-dioxane	62%[b,c]
toluene	63%[b]
DMF	6%

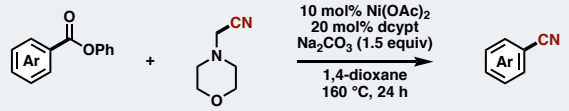
with dcypt and Na_2CO_3. [b] $Ni(OAc)_2$: 10 mol%, dcypt: 20 mol%. [c] 160 °C.

Organocyanides

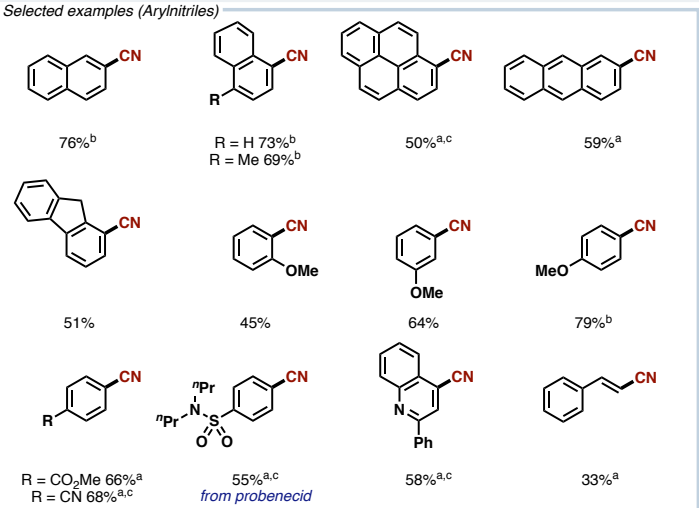


$Ni(OAc)_2$ (10 mol%), dcypt (20 mol%), Na_2CO_3 in 1,4-dioxane.

Substrate Scope

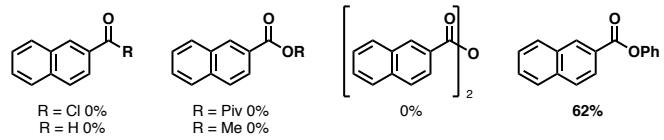


Selected examples (Arylnitriles)



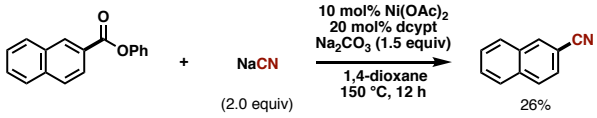
[a] 12 h. [b] Toluene instead of 1,4-dioxane. [c] 150 °C.

Reactions Using Arylcarboxylic Acid Derivatives

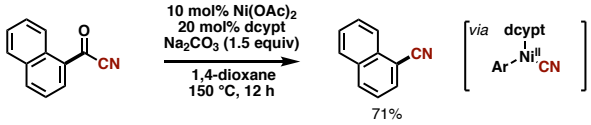


Mechanistic Studies

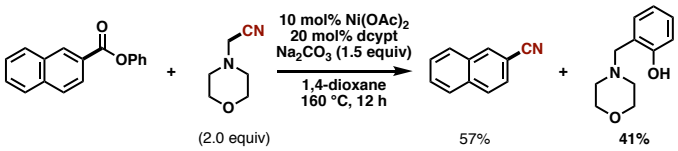
A. *Reaction with NaCN*



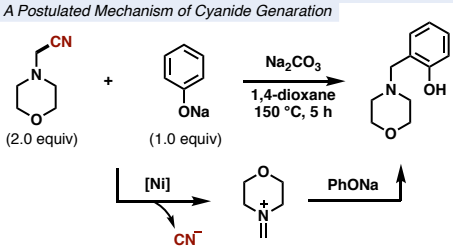
B. *Reaction of Acylnitrile*



C. *Aminoalkylphenol as a Coproduction of Aryl Nitrile*



D. *A Postulated Mechanism of Cyanide Genaration*



$Ni(OAc)_2$	dcypt	Yield/%
–	–	0
10 mol%	20 mol%	38
10 mol%	–	40

Plausible Reaction Mechanism