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Letter

Ester Transfer Reaction of Aromatic Esters with Haloarenes and Arenols by a Nickel Catalyst

Ryota Isshiki,‡ Naomi Inayama,‡ Kei Muto, and Junichiro Yamaguchi*

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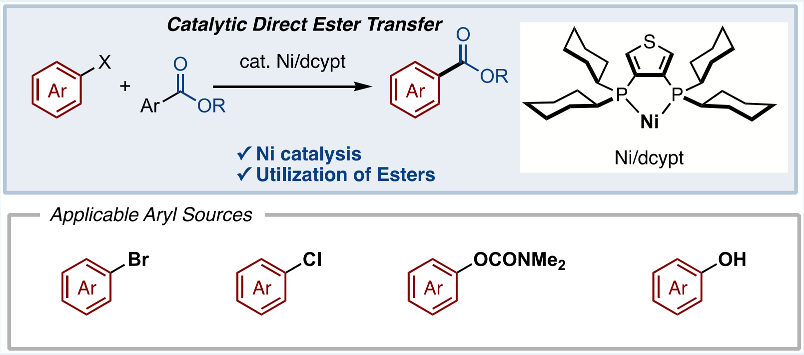

ABSTRACT: A catalytic ester transfer reaction of aromatic esters with aryl halides/arenols was developed. The present reaction can transfer an ester functional group from certain aromatic esters to haloarenes. This ester transfer reaction involves two oxidative additions—one from the C−C bond of the aromatic ester and one from the C−halogen bond of haloarenes—onto a nickel catalyst. The utilization of a Ni/dcypt catalyst capable of cleaving both chemical bonds was a key for the reaction progress. Furthermore, naphthol-based aryl electrophiles were also applicable to the catalytic system via C−O bond activation.

KEYWORDS: *aromatic ester, haloarene, phenol derivative, palladium, transfer reaction*

Development of novel substitution reactions of aromatic cores is a continually important topic in organic synthesis. Classically, C−N or C−Br bonds on arenes have been constructed by an electrophilic aromatic substitution. Cross-coupling-based strategies such as Buchwald−Hartwig amination and Ullmann condensation have also been utilized for this purpose.[1] For the synthesis of arenecarboxylic acids and related esters, the carbonylative reactions using CO have found wide use (Figure 1A).[2] However, this gaseous manipulation is preferably avoided because of its cumbersome reaction setup and toxicity. Several alternative methods using safety CO surrogates have been developed to synthesize aromatic esters while avoiding the handling of CO gas.[3]

Meanwhile, functional group metathesis reactions have been emerging as a conceptually distinct synthetic strategy.[4] In 2018, Morandi and Arndtsen independently reported a functional group metathesis of aroyl chlorides and aryl iodides catalyzed by a Pd-Xantphos complex (Figure 1B).[5] These methods used an oxidative addition and a reductive elimination of two distinct chemical bonds (C−I and C−Cl) as a reversible chemical process. Enlightened by these reports, we turned our attention to use aromatic esters instead of moisture-sensitive aroyl chlorides. Our campaign to study the decarbonylative transformation of aromatic esters revealed that the use of Ni- or Pd-dcypt (dcypt: 3,4-bis-(dicyclohexylphosphino)thiophene) catalysts was effective to formally cleave the C−C bond of aromatic esters through oxidative additions of the C(acyl)−O bond followed by decarbonylation.[6,7] Moreover, the same catalysts also enable the oxidative addition of aryl halides or arenols.[8] Thus, there is an opportunity to extend the functional group metathesis strategy to the reaction of aromatic esters with aryl halides as well as arenols. Such a reaction would also give aromatic esters as chemically stable products compared with the corresponding aroyl chlorides. We herein report our efforts toward the development of an ester transfer reaction from aromatic esters to haloarenes as well as arenols.

At the outset, we optimized reaction conditions by using 4-bromoanisole (**1A**) and phenyl nicotinate (**2a**) as model substrates (Table 1). In line with our hypothesis, under the influence of Ni(OAc)$_2$/dcypt catalyst with Zn and Na$_2$CO$_3$, the reaction of **1A** and **2a** gave the ester transferred product **3A**

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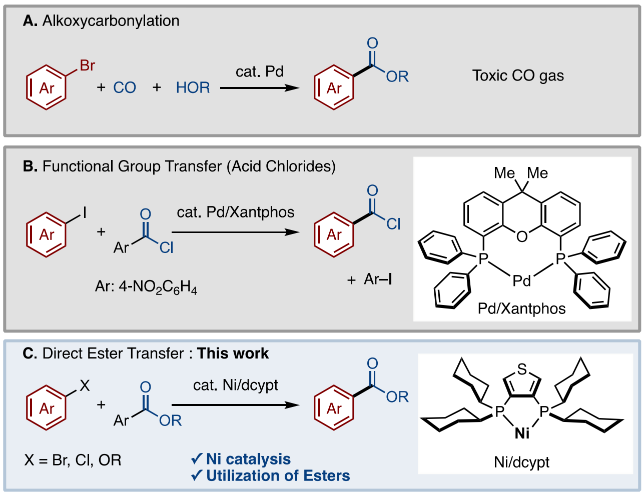
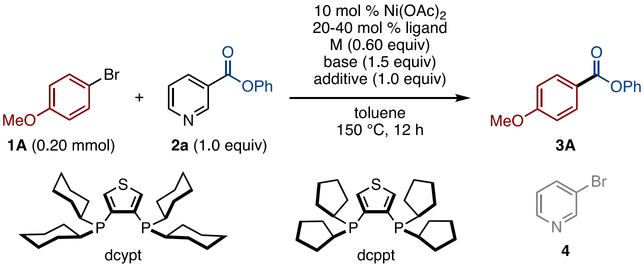


Figure 1. Catalytic synthesis of aromatic carboxylates. (A) Alkoxycarbonylation, (B) functional group transfer using acyl chlorides, and (C) direct ester transfer.

Table 1. Optimization of Reaction Conditions[a]



entry	ligand	M	base	additive	3A/%[b]
1	dcypt	Zn	Na_2CO_3	–	44
2	dcppt	Zn	Na_2CO_3	–	36
3	dcype	Zn	Na_2CO_3	–	0
4	Xantphos	Zn	Na_2CO_3	–	0
5	dppp	Zn	Na_2CO_3	–	0
6	PPh_3	Zn	Na_2CO_3	–	0
7[c]	IPr·HCl	Zn	Na_2CO_3	–	0
8	dcypt	Sn	Na_2CO_3	–	17
9	dcypt	Mn	Na_2CO_3	–	34
10	dcypt	Zn	$CaCO_3$	–	26
11	dcypt	Zn	NaOAc	–	28
12	dcypt	Zn	none	–	22
13[d]	dcypt	Zn	Na_2CO_3	–	0
14	dcypt	Zn	Na_2CO_3	DMAP	60
15	dcypt	Zn	Na_2CO_3	lutidine	45
16	dcypt	Zn	Na_2CO_3	DBU	37
17	dcypt	Zn	Na_2CO_3	DABCO	33
18	dcypt	–	Na_2CO_3	DMAP	0

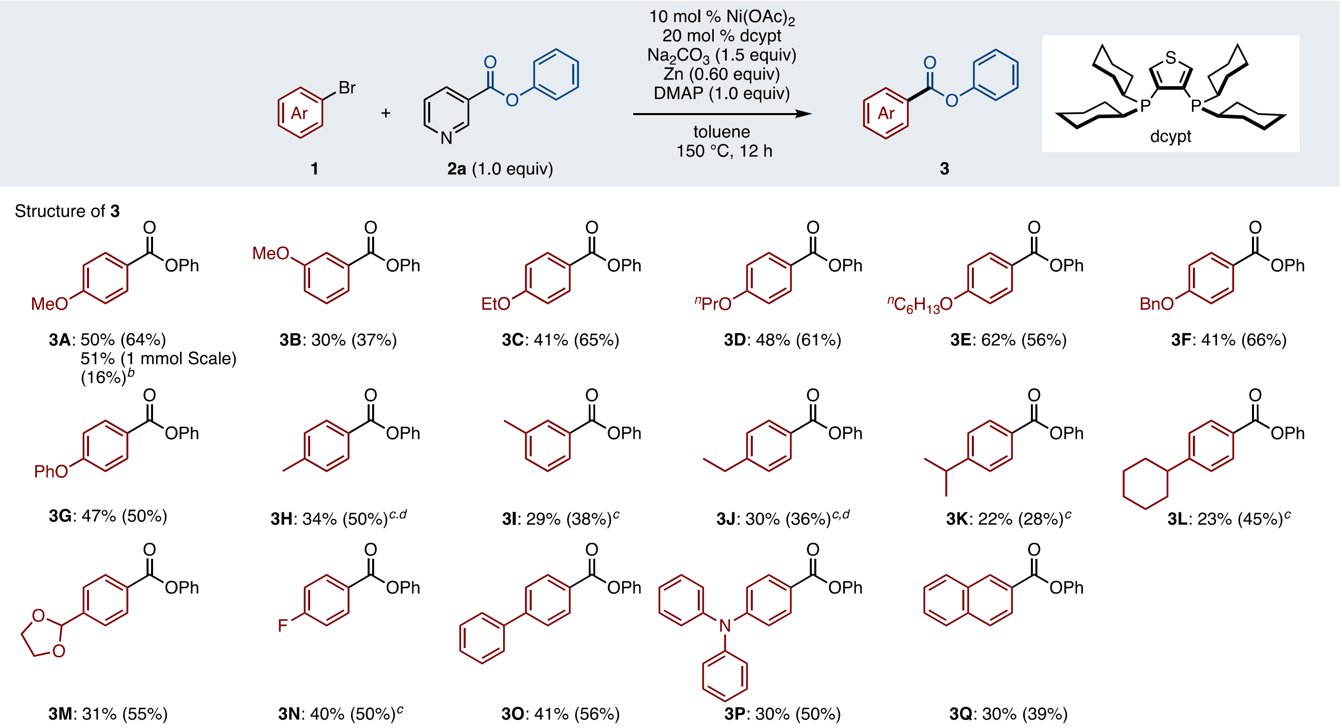
[a] Conditions: **1A** (0.20 mmol), **2a** (0.20 mmol), $Ni(OAc)_2$ (10 mol %), ligand (bidentate, 20 mol %; monodentate, 40 mol %), M (0.60 equiv), base (1.5 equiv), additive (1.0 equiv), toluene (0.80 mL), 150 °C, 12 h. [b] GC yield. [c] NaO*t*-Bu (50 mol %) was added. [d] $Pd(OAc)_2$ (10 mol %) was used instead of $Ni(OAc)_2$.

in 44% yield (Table 1, entry 1). A structurally related thiophene-based ligand dcppt (3,4-bis(dicyclopentylphosphino)thiophene), also produced **3A** in a slightly lower yield (Table 1, entry 2). Interestingly, although dcype (1,2-bis(dicyclohexylphosphino)ethane) was known to affect decarbonylative couplings,[6] this was totally ineffective in the present reaction (Table 1, entry 3). This is maybe due to the lower stability of generating Ni/dcype complex than Ni/dcypt. Xantphos, which is effective for Morandi's as well as Arndtsen's transfer reaction,[5] did not lead to the production of **3A** (Table 1, entry 4). Other typical phosphine ligands such as dppp and PPh_3 did not work at all in the present reaction (Table 1, entries 5 and 6). Although NHC-based ligands can affect the decarbonylative reaction of aromatic esters,[6] IPr did not deliver **3A** (Table 1, entry 7). Through the screening of ligands, unfortunately, Ar–Br **4** as a possible coproduct was not observed. In this study, Zn powder may act as a reductant of Ni(II) to generate the active Ni(0) species. A similar effect can be expected for Sn and Mn powder; however, they decreased the reaction yield (Table 1, entries 8 and 9).[9] Although the reaction does not seem to require the base, the addition of Na_2CO_3 improved the reaction yield (Table 1, entries 1, 10–12). Of note, we did not obtain **3A** when palladium catalysis was used instead of nickel (Table 1, entry 13). Further improvement was achieved by the addition of DMAP, in which **3A** was generated in 60% yield (Table 1, entry 14). Using another pyridine base, 2,6-lutidine also resulted in a slight improvement but not as much as when using DMAP (Table 1, entry 15). Other nucleophilic nitrogen bases, DBU and DABCO, did not increase the reaction yield (Table 1, entries 16 and 17). The reaction conditions without Zn did not generate **3A** at all (Table 1, entry 18). Through the above studies, we identified the optimized conditions as $Ni(OAc)_2$/dcypt/Zn/Na_2CO_3/DMAP catalysis.

With the optimized conditions, we next investigated the substrate scope using **2a** as an ester source (Scheme 1). First, *p*-anisyl iodide (**1A′**) instead of bromide (**1A**) was subjected to the optimized conditions; however, it was revealed that iodoarenes were not suitable, resulting in lower product yielding (16% yield). Electron-donating aryl bromides generally reacted to give the corresponding aromatic esters. *m*-Anisyl bromide (**1B**) reacted less efficiently than *p*-anisyl bromide (**1A**). Several aryl bromides with alkoxy groups including phenoxy were reacted to give the corresponding aromatic esters in moderate yields (**3C**–**3G**). Less electron-rich aryl bromides such as *m*- or *p*-alkylphenyl bromides also underwent to the present reaction, albeit affording lower yields of products **3H**–**3L** when compared with the alkoxylated arenes. Unfortunately, at this stage, *o*-substituted aryl bromides showed poor reactivity, affording the corresponding product in less than 20% yield (see the Supporting Information). Acetal (**3M**) and fluoro (**3N**) groups were tolerated under the reaction conditions. Triarylamine-based aromatic ester **3P** was successfully synthesized by the present method in 30% yield. Furthermore, naphthalene ester **3Q** was also produced.

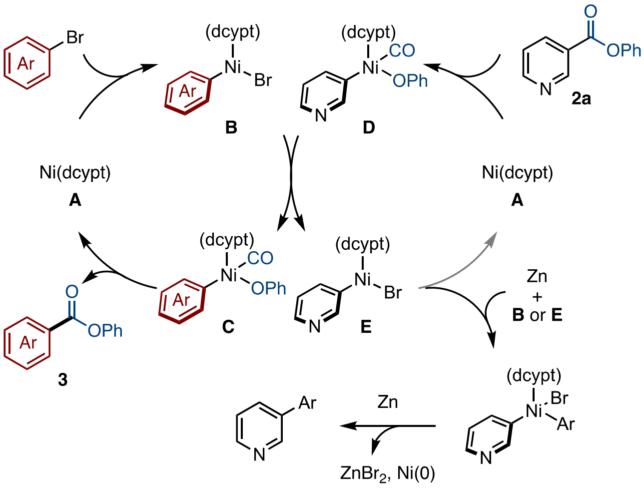
A plausible mechanism of this reaction is illustrated in Scheme 2. Ni/dcypt cleaves the C–Br bond of an aryl bromide and the C–C bond of phenyl nicotinate (**2a**) to generate Ar–Ni–Br (**B**) and Py–Ni(CO)–OPh (**D**) species, respectively. Similarly to the Arndtsen's work,[5] these intermediates could transmetalate to give Ar–Ni(CO)–OPh (**C**) and Py–Ni–Br (**E**). Reductive elimination from **C** would give ester transferred product **3**. On the other hand, reductive elimination from **E** could release bromopyridine **4** as coproduct. However, we did not detect **4** through this study. Crude analysis informed us that the reaction between **1A** and **2a** under the optimized conditions generated 3-(4-anisyl)pyridine in 20% yield along with a trace amount 3,3′-bipyridine as byproducts. This result would indicate that complex **E** reacts with **B** or **E** with the

Scheme 1. Substrate Scope[a]

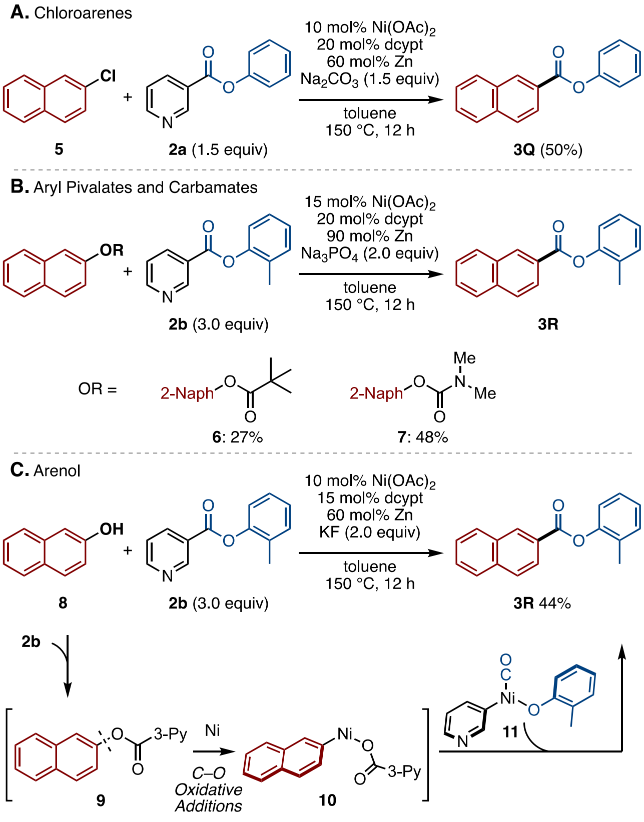


[a]Conditions: **1** (0.20 mmol), **2a** (0.20 mmol), Ni(OAc)$_2$ (10 mol %), dcypt (20 mol %), Zn powder (0.60 equiv), Na$_2$CO$_3$ (1.5 equiv), DMAP (1.0 equiv), toluene (0.80 mL), 150 °C, 12 h. Numbers in parentheses show NMR yield. [b]*p*-Anisyl iodide (**1A′**) was used instead of bromide **1A**. [c]Inseparable mixture with phenyl benzoate. Isolated yields were determined by ^{1}H NMR ratio. [d]170 °C, 24 h.

Scheme 2. Proposed Mechanism



Scheme 3. Ester Transfer using Aryl Chlorides and Arenols



action of Zn to give nickel(III)-diaryl species.[10] From this nickel species, reductive elimination occurs to give 3-arylpyridines as well as Ni(I), which would be reduced by Zn to regenerate Ni(0).[11,12] Meanwhile, the role of DMAP in this mechanism is unclear at this stage.[13] As one of the possible roles, we speculate that DMAP can form acid–base pair with in situ generating ZnBr$_2$, which might lead to catalyst deactivation.[14] This is consistent with that the addition of ZnBr$_2$ into the optimized conditions without DMAP resulted in decreasing yield of **3A** (see the Supporting Information for details).

In addition to bromoarenes, chloroarenes were found to be reactive in the present reaction (Scheme 3A). 2-Chloronaphthalene (**5**) participated in this reaction, giving **3Q** in acceptable yield (50% yield). Furthermore, the Ni/dcypt catalyst is known to oxidatively add into C−O bonds.[15] Hypothesizing that C−O-based aryl electrophiles can participate in the present system, we subjected several C−O aryl electrophiles with *o*-tolyl ester **2b** (Scheme 3B).[16]

Although the yields were moderate, we found that pivalates and carbamates underwent the ester transfer reaction under slightly modified conditions. With the success utilizing aryl pivalates in the present system, we wondered that direct esterification of Ar−OH would be possible. As expected, simple arenol **8** could be transformed to aromatic esters **3R** in 44% yield (Scheme 3C). In this case, **2b** occupies dual roles; one is an ester source, and the other is an activator of the Ar−OH group via the in situ formation of ester **9**. Subsequent oxidative addition of **9** (C(aryl)−O) to Ni/dcypt, followed by transmetalation between **10** and **11** produced **3R**. In this arenol-based reaction, we did not obtain the corresponding 3-hydroxypyridine derivatives at all.

In summary, we have developed a Ni-catalyzed ester transfer reaction between aryl halides and aromatic esters. As an alternative to aryl halides, we successfully utilized phenol-based aryl electrophiles to give ester-transferred product as well. Although the yield and scope of the method have room for improvement, the present result, particularly the utilization of Ar−OH as a starting material, could find use in synthetic chemistry as a way of creating valuable products from inexpensive feedstocks. Further studies focusing on the development of other ester transfer reactions and elucidation of the mechanism are underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c00291.

Experimental procedures and spectroscopic data for compounds including ^{1}H-, ^{13}C NMR spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

Junichiro Yamaguchi − *Department of Applied Chemistry, Waseda University, Shinjuku 169-8555, Japan;* orcid.org/0000-0002-3896-5882; Email: junyamaguchi@waseda.jp

Authors

Ryota Isshiki − *Department of Applied Chemistry, Waseda University, Shinjuku 169-8555, Japan*

Naomi Inayama − *Department of Applied Chemistry, Waseda University, Shinjuku 169-8555, Japan*

Kei Muto − *Department of Applied Chemistry, Waseda University, Shinjuku 169-8555, Japan;* orcid.org/0000-0001-8301-4384

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.0c00291

Author Contributions

‡(R.I., N.I.) These authors contributed equally.

Notes

The authors declare no competing financial interest.

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(11) In order to clarify the role of Zn, we conducted the ester transfer reaction starting from Ni(cod)$_2$ in the presence and absence of Zn powder, resulting in the generation of **3A** in 38% and 10% yield, respectively (see the Supporting Information for details). In conjunction with the result that Ni(OAc)$_2$ without Zn did not give **3A** (Table 1, entry 18), these results would support the dual role of Zn powder; one is the initiator of this reaction by the generation of Ni(0) from starting Ni(II). The other role would be a reducing agent of intermediate **E** to regenerate active Ni(0).

(12) According to this mechanism, the stoichiometric amount of Zn should be required. However, increasing the amount of Zn to 1.0 equivalent and more led to lower yielding of **3**, instead, generating homocoupled dimer of **1** as a major product.

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(16) When simple phenyl ester **2a** was used, it was found that C(aryl)-O and C(acyl)-O oxidative additions on **2a** were competitive. The *o*-methyl group probably suppressed the undesired C(aryl)-O oxidative addition by steric hindrance.

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