

ORGANIC CHEMISTRY

Ester dance reaction on the aromatic ring

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Aromatic rearrangement reactions are useful tools in the organic chemist's toolbox when generating uncommon substitution patterns. However, it is difficult to precisely translocate a functional group in (hetero) arene systems, with the exception of halogen atoms in a halogen dance reaction. Here, we describe an unprecedented "ester dance" reaction: a predictable translocation of an ester group from one carbon atom to another on an aromatic ring. Specifically, a phenyl carboxylate substituent can be shifted from one carbon to an adjacent carbon on a (hetero) aromatic ring under palladium catalysis to often give a thermodynamically favored, regioisomeric product with modest to good conversions. The obtained ester moiety can be further converted to various aromatic derivatives through the use of classic and state-of-the-art transformations including amidation, acylations, and decarbonylative couplings.

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INTRODUCTION

Substitution reactions on (hetero) aromatic substrates are some of the most important reactions in organic chemistry (1). However, some substitution patterns can be more difficult to forge than others based on the propensity of the positions on the (hetero) arene to engage in electrophilic, nucleophilic, or radical-based substitution. In these cases, aromatic rearrangement reactions can help access ring positions that are difficult to functionalize otherwise. Although there are many well-known aromatic rearrangements such as the Smiles, Claisen, and Bamberger rearrangements, these transformations leave behind a functional group at the carbon atom that was originally substituted in the starting material (Fig. 1A). A rarer type of aromatic rearrangement involves translocation of a functional group, in which the carbon atom bearing the functional group in the starting material loses the group entirely, and the same group is brought back to another carbon atom on the aromatic ring. One example of this type of aromatic translocation is transalkylation, which is a disproportionation of an alkyl group under Friedel-Crafts alkylation conditions, also known as a carbon-substituent rearrangement (Fig. 1B) (2–4). This reaction can translocate an alkyl substituent to another position on the same aromatic ring or onto another aromatic ring, allowing for several compounds including isomers to form from a single starting material; therefore, it is used mainly in the petrochemical industry. However, this reaction requires extremely harsh conditions and unpredictably generates a mixture of products.

An intriguing example used in the synthesis of fine chemicals is called the "halogen dance" reaction of haloarenes (Fig. 1C) (5–7). This reaction is a translocation induced by a strong base and provides a regioisomeric product via a sequence of halogen-metal exchange processes on the aromatic ring. The net effect is a removal of a halogen atom from one ring carbon and placement onto another ring carbon. Because of its practical and predictable nature, this reaction is often exploited even in the total synthesis of complex natural products (7). In an example of a simultaneous, multiple rearrangement on an aromatic ring, Eliseeva and Scott (8) observed a rearrangement of boron substituents in an iridium-catalyzed borylation with catalytic potassium *tert*-butoxide. To the best of our knowledge, there are currently no reports of a catalytic carbonyl group rearrangement. Much like the halogen dance reaction wherein a functional group is translocated from one ring carbon to another, we describe a palladium-

catalyzed translocation of an ester group on the aromatic ring, coined herein as an "ester dance" reaction.

During our recent efforts in the development of decarbonylative transformations of aromatic esters (9–13), we found that a phenyl carboxylate at the C1 position of phenyl 1-naphthoate (**1a**) migrated to the C2 position, affording phenyl 2-naphthoate (**2a**) under palladium catalysis, albeit with low conversion (18% yield of **2a**; Fig. 1D). We hypothesize that product **2a** can potentially arise from a formal 1,2-rearrangement of the ester (phenyl carboxylate) in **1a**, involving the following: (i) oxidative addition of palladium into the ester C(O)—O bond; (ii) deprotonation (*ortho* C—H bond activation of complex A) followed by decarbonylation (14), producing an aryl-palladium complex (or a η^2 -arene-palladium complex; complex B) (15–18); (iii) protonation and carbonylation; and (iv) reductive elimination. The product **2a** is thermodynamically more stable than reactant **1a** (3.7 kcal/mol lower in energy; figs. S6 and S7), and it is likely that this is a reversible reaction (19–21) that thermally converges to **2a**. The product in this experiment is an ester that can be reacted with nucleophiles using versatile reactions such as metal-catalyzed decarbonylative coupling reactions (10–13, 22–27), amidation (28), and ketone formation (29, 30) (see fig. S1 for more details). Therefore, we began to examine to develop this unprecedented reaction.

RESULTS AND DISCUSSION

After extensive investigation, we found the optimal conditions: When the reaction was conducted with 10 mole percent (mol %) PdCl₂, 20 mol % dcypt [3,4-*bis*(dicyclohexylphosphino)thiophene] (31), and K₂CO₃ (0.5 equiv) in *m*-xylene at 150°C for 24 hours, **1a** was converted to **2a** in 85% yield along with recovered **1a** (7% yield) (Table 1, standard conditions; also, see table S1). Without PdCl₂, dcypt, or K₂CO₃, the reaction completely shut down (entries 1 to 3). Other palladium salts also worked, albeit with a lower yield of **2a**; other metal salts such as NiCl₂ were ineffective (entries 4 and 5). Other electron-rich bidentate ligands such as dcyp and dcypbz were also effective, but the yields were slightly lower (entries 6 and 7). Further modifications to the phosphine ligand were detrimental (entries 8 to 13). The nature of the base played an important role, since these reactions nearly shut down completely when the base was changed from K₂CO₃ (entries 14 to 16); assisted deprotonation during the *ortho* C—H bond activation of complex A is likely to be important. When using other solvents, toluene or 1,4-dioxane showed successful reactions, but the yields were diminished (entries 17 to 19).

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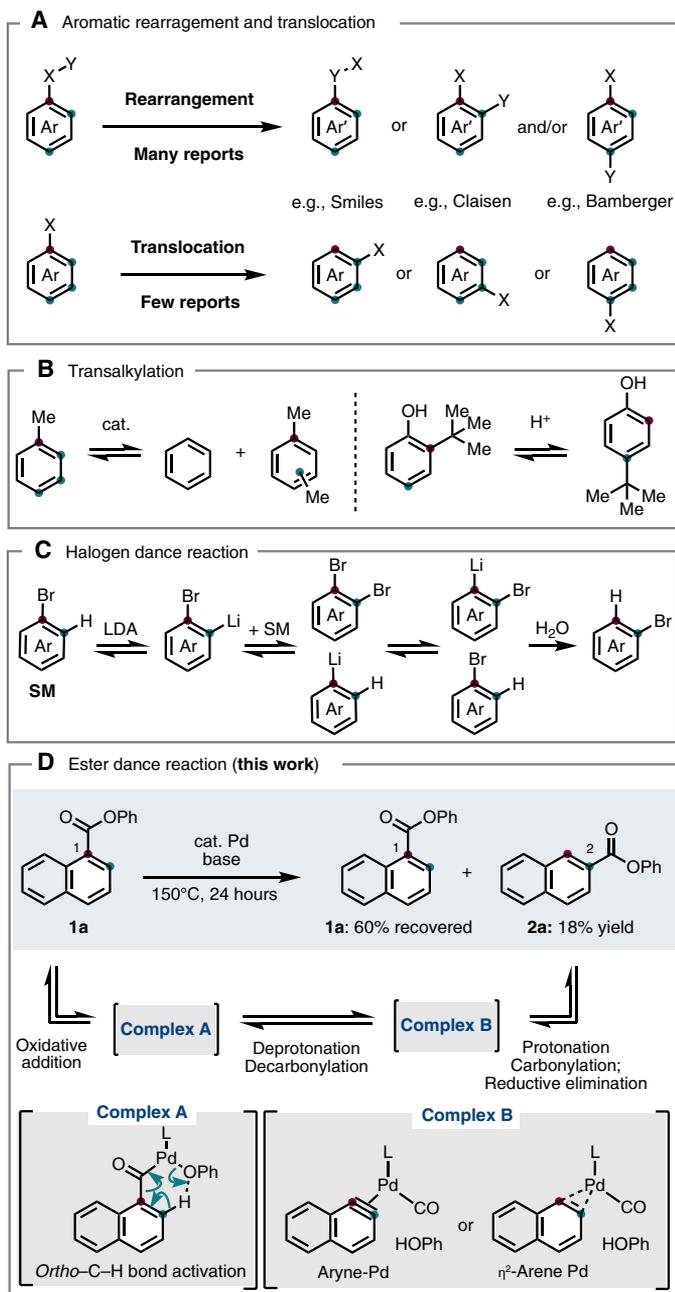


Fig. 1. Aromatic rearrangement and translocation. (A) Aromatic rearrangement and translocation. (B) Transalkylation of aromatics. (C) Halogen dance reaction of (hetero)aromatics. (D) Discovery of an ester dance reaction of aromatic esters and a plausible mechanism.

With the optimized conditions in hand, the scope of this ester dance was explored (Fig. 2; also, see the Supplementary Materials regarding the yields of recovered starting materials). In the first series of experiments, the naphthoate portion of phenyl 1-naphthoate (**1a**) was kept constant, but the phenyl group was modified. Various aryl groups such as *p*-tolyl, *m*-tolyl, and *o*-tolyl (**1b–1d**); *p*-anisyl and *m*-anisyl (**1e** and **1f**); *p*-fluorophenyl and *m*-fluorophenyl (**1g** and **1h**); and *p*-biphenyl and *m*-biphenyl (**1i** and **1j**) gave the corresponding aryl-2-naphthoates in moderate yields (**2b–2j**). Generally, this reaction formed the corresponding product **2** (42 to 71% yields) along

Table 1. Selected optimizations of reaction conditions.

Standard conditions*

Entry [†]	Deviation from the standard conditions	GC yield (%) [†] 1a	2a
1	Without PdCl ₂	74	0
2	Without dcypt	73	0
3	Without K ₂ CO ₃	86	0
4	PdBr ₂	15	51
5	NiCl ₂	55	1
6	dcype	14	72
7	dcypbz	23	67
8	dpe	78	0
9	dppt	78	0
10	BINAP	79	0
11	PCy ₃	86	0
12	ICy	67	0
13	Xphos	66	0
14 [‡]	Na ₂ CO ₃	79	6
15 [‡]	Cs ₂ CO ₃	0	0
16 [‡]	K ₃ PO ₄	65	16
17	Toluene	58	28
18	1,4-dioxane	42	44
19	DMF	6	5

***1a** (0.4 mmol), PdCl₂ (10 mol %), dcypt (20 mol %), K₂CO₃ (0.2 mmol), *m*-xylene (0.8 mL) at 150°C for 24 hours. †GC yield was determined by using *n*-decane as an internal standard. ‡Base (1.5 equiv) was added.

with recovered starting material (7 to 48% yields), as well as hydrolyzed benzoic acid derivatives. Starting materials with benzo[*d*][1,3]dioxol-5-yl (**1k**), naphthyl (**1l**), and pyridyl groups (**1m**) were tolerated under these reaction conditions, producing the corresponding regioisomers **2k–2m**. For low-yielding cases, a carboxylic acid formation occurred as a competing process (e.g., **2m**, **2u**, **2z**, and **2ab**).

Next, we examined this translocation reaction on heteroarene cores under the optimized conditions. To this end, isonicotinates (C4-carboxylated pyridines) were found to be applicable in this reaction, with the ester substituents migrating from the C4 to the C3 position of the pyridine, giving nicotinate products. The use of phenyl (**1n**), *p*-methoxyphenyl (**1o**), and *p*-fluorophenyl (**1p**) isonicotinates afforded the corresponding nicotinates **2n–2p** with moderate conversions. When an electron-donating group was present, the direction of the isomerization interestingly changed: 2-Methoxyisonicotinate (**2q**) and 2-ethoxyisonicotinate (**2r**) were obtained in 61 and 47% isolated yields from the corresponding nicotinates via this translocation reaction. *p*-Anisyl 2-methoxynicotinate (**1s**) also gave the C4 isomer **2s** in good yield. With benzo-fused heteroarenes, phenyl quinoline-4-carboxylate (**1t**) gave C3 isomer **2t** in good yield, and phenyl benzo[*b*]thiophene-2-carboxylate (**1u**) was also converted into C3 isomer **2u**, albeit with reduced yield (27%). It is worth noting that **1u**, generated from the corresponding carboxylic acid (costing \$20/g; Sigma-Aldrich), can be transformed into a much more precious carboxylic acid derivative (the acid derivative of **2u** costs \$13,300/g).

We also investigated other aromatic esters such as phenyl benzoates (**1v–1aa**). Phenyl benzoates—in which the para position of the benzoate was substituted by trifluoromethyl (**1v**), sulfonamide (**1w**), methyl

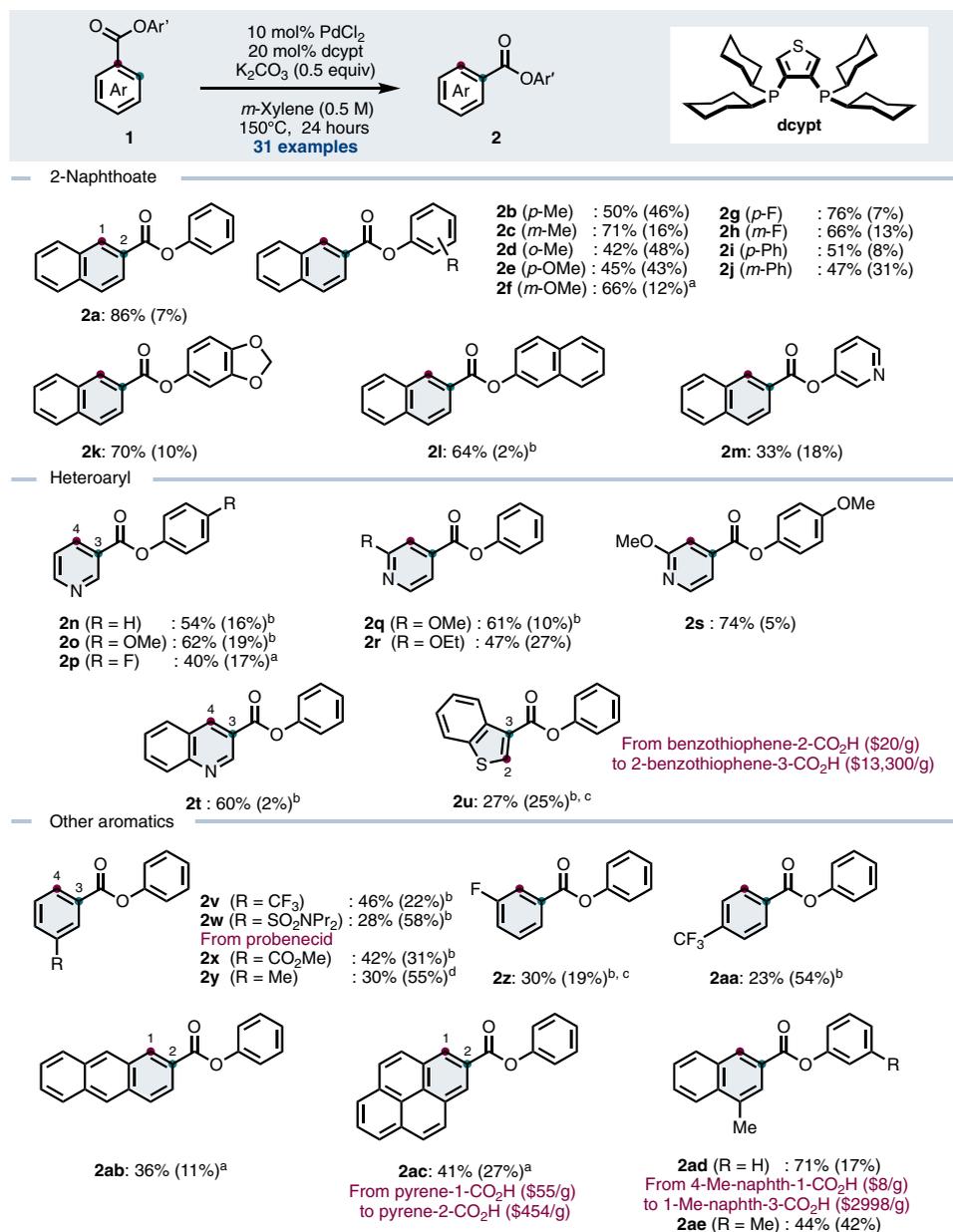


Fig. 2. Substrate scope. The numbers in parenthesis show the recovery of 1. ^aThe reaction was conducted at 160°C. ^bThe reaction was conducted at 140°C. ^cThe reaction was conducted for 36 hours. ^dThe reaction was conducted at 170°C.

ester (**1x**), or methyl (**1y**)—formed products **2v–2y** under the standard reaction conditions. Notably, **1w**, which is derivatized from probenecid (a well-known drug for the treatment of gout), can be transformed directly to its C3 isomer **2w**. *o*-Fluoro-benzoate (**1z**) and *m*-trifluoromethylbenzoate (**1z**) also allowed the ester substituent to migrate and gave the corresponding products **2z** and **2aa**, albeit with low conversions. In addition, this translocation reaction enabled the synthesis of products that are otherwise difficult to make. For example, phenyl ester **1ac** derivatized from pyrene-1-carboxylic acid (\$55/g) gave a derivative of pyrene-2-carboxylic acid (\$454/g), which is useful for pyrene-labeled fluorescent biosensors (32, 33). In addition, the corresponding carboxylic acid of aryl 4-methyl-1-naphthoates (**1ad** and **1ae**) is an inexpensive compound (\$8/g) but can be reacted under the standard

conditions to afford the C2 isomers **2ad** and **2ae** (an ester derivative of an expensive carboxylic acid, \$2998/g). Although the reaction mechanism remains unclear, we investigated (i) the reversibility of both isomers using **1v** and **2v** (Fig. 3), (ii) the electronic and steric effects of aromatic rings (table S2), and (iii) a deuterium labeling experiment (section S1). These experiments confirmed that this reaction is reversible, and deprotonation of the *ortho*-hydrogen atom occurs.

Furthermore, we demonstrated a combination of the ester dance reaction and decarbonylative coupling (Fig. 4). Phenyl 3-thiocarboxylate (**1af**) was reacted with benzothiazole (**4A**) under the optimized conditions to give **3A** in 60% yield as the major isomer (Fig. 4A and table S3). This reaction takes place because the ester dance reaction of **1af** occurs first to give phenyl 2-thiocarboxylate, followed by

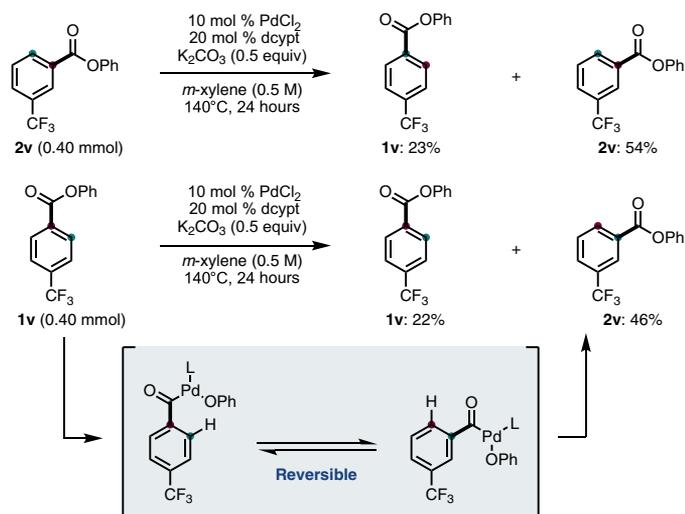


Fig. 3. Confirmation of reversibility.

decarbonylative C—H coupling under the same catalytic conditions (13). As already mentioned in Fig. 2, phenyl 4-pyridine carboxylate (**1n**) rearranges to phenyl nicotinate (**2n**). Curiously, however, in the presence of a sterically hindered diphenyl amine (**4B**), the ester dance reaction occurred in reversed fashion (from **2n** to **1n**), followed by decarbonylative amination to afford the corresponding coupling product **3B** in 62% yield (Fig. 4B and table S3). In addition, when **2t** was treated under modified standard conditions, diaryl ether **3C** was obtained in 43% yield (Fig. 4C and table S4). Although the possible intermediate **1t** is thermodynamically unstable compared with **2t**, the decarbonylative etherification occurs only at the C4 position on the quinoline ring, and therefore, **3C** was obtained with virtually complete regioselectivity (15). Last, we successfully achieved a 1,3-translocation product (i.e., two sequential translocations) from **1n** to **3n** through **2n** when we attempted to react **1n** for a longer time from 24 to 48 hours (Fig. 4D and table S4). **2n** is thermodynamically more stable than **1n** (by 0.5 kcal/mol), with **3n** bearing the highest ΔG (1.08 kcal/mol). However, the decarbonylative etherification proceeds only from the C2 position of azine carboxylates (12), and therefore, **3D** was obtained as the major isomer (see section S2 for more details). Overall, the present ester dance reaction can furnish not only thermodynamically stable regioisomers at the adjacent carbon atom but also other substitution patterns when combined with further ester-transforming reactions. We believe that this translocation will help the organic chemist synthesize (hetero)aromatic compounds that are difficult or expensive to access by providing an unconventional yet predictable synthetic approach.

MATERIALS AND METHODS

All reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. All ester dance reactions were performed in 20-ml glass vessel tubes equipped with J. Young O-ring tap and heated (IKA Plate RCT digital) in an oil bath unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents in air. Synthetic methods of all of starting materials are described in the data in the Supplementary Materials.

Analytical thin-layer chromatography (TLC) was performed using Silicagel 70 TLC Plate-Wako (0.25 mm). The developed chromato-

gram was analyzed by ultraviolet lamp (254 nm). Flash column chromatography was performed with Biotage Isolera equipped with Biotage SNAP Cartridge KP-Sil columns. Preparative TLC (PTLC) was performed using Wakogel B5-F silica-coated plates (0.75 mm) prepared in our laboratory. Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2010 Plus instrument equipped with an HP-5 column (30 m by 0.25 mm, Hewlett-Packard) with *n*-decane as an internal standard. High-resolution mass spectra (HRMS) were conducted on Thermo Fisher Scientific Exactive Plus (electrospray ionization and direct analysis in real time). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECS-400 (^1H , 400 MHz; ^{13}C , 101 MHz) spectrometer.

General procedure for ester dance reactions

A 20-ml glass vessel equipped with J. Young O-ring tap containing a magnetic stirring bar and K_2CO_3 (27.6 mg, 0.20 mmol, and 0.50 equiv) was dried with a heat gun in vacuo and filled with N_2 after cooling to room temperature. To this vessel were added aromatic esters **1** (0.40 mmol, 1.0 equiv), PdCl_2 (7.1 mg, 0.040 mmol, 10 mol %), and 3,4-*bis*(dicyclohexylphosphino)thiophene (dcypt: 38.1 mg, 0.080 mmol, 20 mol %). The vessel was placed under vacuum, refilled with N_2 gas three times, and then added with *m*-xylene (0.80 ml). The vessel was sealed with O-ring tap and then heated at 150°C for 24 hours with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc as an eluent and then concentrated in vacuo. The residue was purified by PTLC to afford the corresponding rearranged product **2**. The ratio of **1** and **2** was determined by ^1H NMR analysis.

Procedure for ester dance and decarbonylative C—H arylation

A 20-ml glass vessel equipped with J. Young O-ring tap containing a magnetic stirring bar and K_3PO_4 (127.4 mg, 0.60 mmol, 1.5 equiv) was dried with a heat gun in vacuo and filled with N_2 after cooling to room temperature. To this vessel were added phenyl thiophene-3-carboxylate (**1af**: 81.7 mg, 0.40 mmol, 1.0 equiv), $\text{Pd}(\text{OAc})_2$ (9.0 mg, 0.040 mmol, 10 mol %), and 3,4-*bis*(dicyclohexylphosphino)thiophene (dcypt: 38.1 mg, 0.080 mmol, 20 mol %). The vessel was placed under vacuum, refilled with N_2 gas three times, and then added with benzothiazole (**4A**: 81.1 mg, 0.60 mmol, 1.5 equiv) and *m*-xylene (1.6 ml). The vessel was sealed with O-ring tap and then heated at 150°C for 24 hours with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc as an eluent and then concentrated in vacuo. The residue was purified by PTLC (hexane/Et₂O = 20:1, five times) to afford 2-(thiophen-2-yl)benzo[*d*]thiazole (**3A**: 52.3 mg, 60% yield) and 2-(thiophen-3-yl)benzo[*d*]thiazole (**3A'**: 11.5 mg, 13% yield).

Procedure for ester dance and decarbonylative amination

A 20-ml glass vessel equipped with J. Young O-ring tap containing a magnetic stirring bar and K_3PO_4 (127.4 mg, 0.60 mmol, 1.5 equiv) was dried with a heat gun in vacuo and filled with N_2 after cooling to room temperature. To this vessel were added phenyl nicotinate (**2n**: 79.7 mg, 0.40 mmol, 1.0 equiv), $\text{Pd}(\text{OAc})_2$ (9.0 mg, 0.040 mmol, 10 mol %), and 3,4-*bis*(dicyclohexylphosphino)thiophene (dcypt: 38.1 mg, 0.080 mmol, 20 mol %). The vessel was placed under vacuum, refilled with N_2 gas three times, and then added with diphenylamine (**4B**: 101.5 mg, 0.60 mmol, 1.5 equiv) and toluene (1.6 ml). The vessel was sealed with O-ring tap and then heated at 150°C for 24 hours

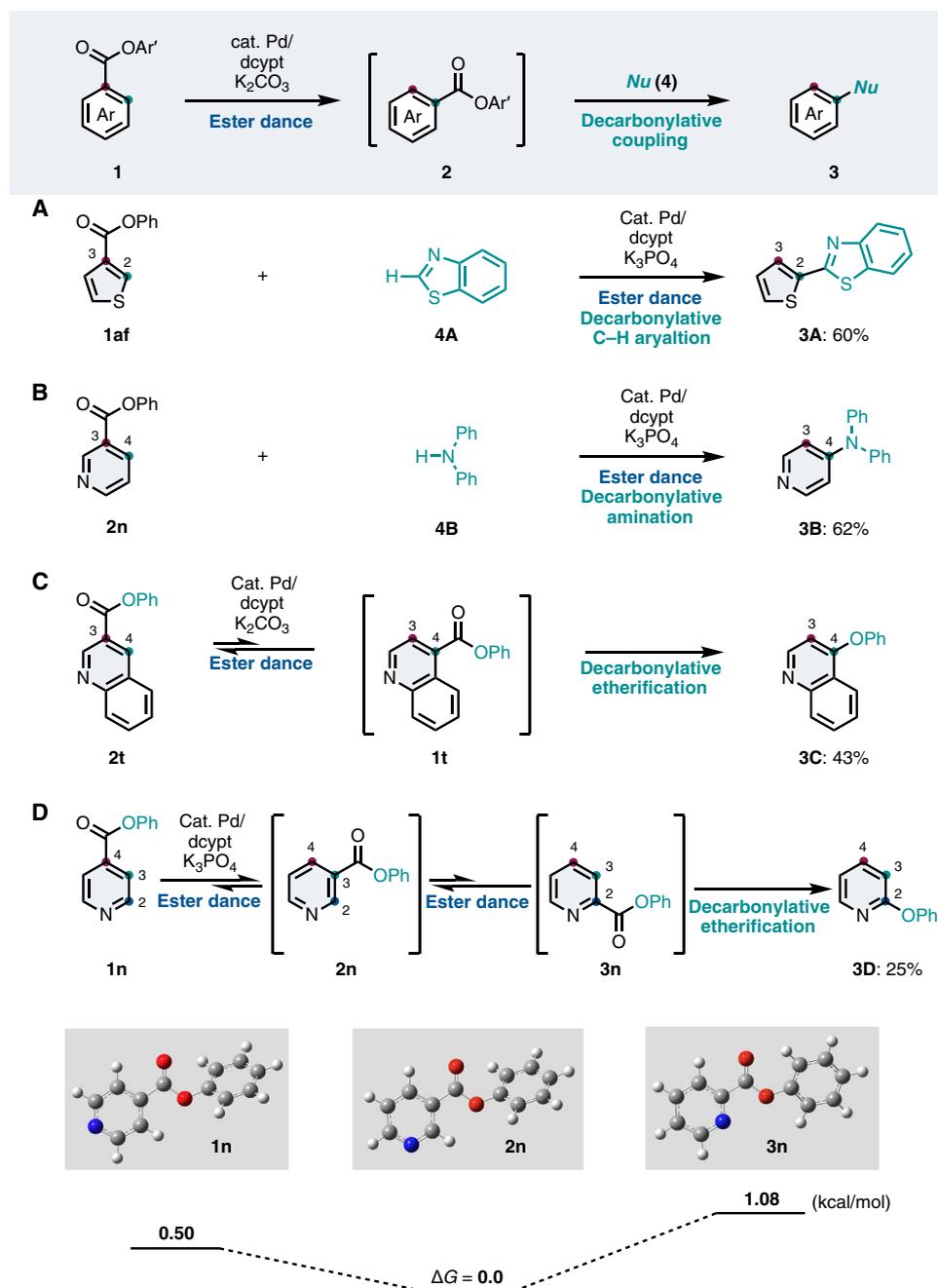


Fig. 4. Ester dance reaction followed by decarbonylative coupling. (A) Ester dance and decarbonylative C–H arylation of benzothiazole **4A**. (B) Ester dance and decarbonylative amination of **2n**. (C) Ester dance and decarbonylative etherification of **2t** via **1t**. (D) Double ester dance and decarbonylative etherification, as well as a comparison of free energies between **1n**, **2n**, and **3n**.

with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc as an eluent and then concentrated in vacuo. The residue was purified by PTLC (EtOAc) to afford *N,N*-diphenylpyridin-4-amine (**3B**: 61.2 mg, 62% yield) as a yellow solid.

Procedure for ester dance and decarbonylative etherification of **2t**

A 20-ml glass vessel equipped with J. Young O-ring tap containing a magnetic stirring bar and K_2CO_3 (27.6 mg, 0.20 mmol, 0.50 equiv)

was dried with a heat gun in vacuo and filled with N_2 after cooling to room temperature. To this vessel were added phenyl quinoline-3-carboxylate (**2t**: 99.7 mg, 0.40 mmol, 1.0 equiv), $PdCl_2$ (7.1 mg, 0.040 mmol, 10 mol %), and 3,4-bis(dicyclohexylphosphino)thiophene (dcypt: 38.1 mg, 0.080 mmol, 20 mol %). The vessel was placed under vacuum, refilled with N_2 gas three times, and then added with *m*-xylene (0.80 ml). The vessel was sealed with O-ring tap and then heated at 170°C for 24 hours with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc as an eluent and then concentrated

in vacuo. The residue was purified by PTLC (hexane/EtOAc = 4:1, twice) to afford 4-phenoxyquinoline (**3C**: 37.7 mg, 43% yield) as a colorless oil.

Procedure for ester dance and decarbonylative etherification of **1n**

A 20-ml glass vessel equipped with J. Young O-ring tap containing a magnetic stirring bar and K₃PO₄ (127.4 mg, 0.60 mmol, 1.5 equiv) was dried with a heat gun in vacuo and filled with N₂ after cooling to room temperature. To this vessel were added phenyl isonicotinate (**1n**: 79.7 mg, 0.40 mmol, 1.0 equiv), PdCl₂ (7.1 mg, 0.040 mmol, 10 mol %), and 3,4-bis(dicyclohexylphosphino)thiophene (dcypt: 38.1 mg, 0.080 mmol, 20 mol %). The vessel was placed under vacuum, refilled with N₂ gas three times, and then added with *m*-xylene (0.80 ml). The vessel was sealed with O-ring tap and then heated at 160°C for 48 hours with stirring. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel pad with EtOAc as an eluent and then concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 5:1, twice) to afford 2-phenoxy pyridine (**3D**: 17.0 mg, 25% yield) as a white solid.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/6/28/eaba7614/DC1>

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Acknowledgments: We thank K. Itami (Nagoya University), E. Ota, T. Okita (Waseda University), and Y. Ishihara (Vertex Pharmaceuticals) for fruitful discussion and critical comments. The Materials Characterization Central Laboratory in Waseda University is acknowledged for the support of HRMS measurement. We also thank the National Institute of Health Sciences in Japan for the support of NMR measurement. **Funding:** This work was supported by JSPS KAKENHI grant numbers JP19H02726, JP18H04272 (to J.Y.), JP18H04661 (Hybrid Catalysis), and JP19K15573 (to K.Mu.). **Author contributions:** J.Y. directed the projects and designed the experiments. K.Ma. and R.T. performed experiments. All authors contributed to data analysis. J.Y. wrote the manuscript with feedback from the other authors. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 3 January 2020

Accepted 22 May 2020

Published 8 July 2020

10.1126/sciadv.aba7614

Citation: K. Matsushita, R. Takise, K. Muto, J. Yamaguchi, Ester dance reaction on the aromatic ring. *Sci. Adv.* **6**, eaba7614 (2020).