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Palladium-Catalyzed Acylation/Alkenylation of Aryl Iodide: A Domino Approach Based on the Catellani–Lautens Reaction

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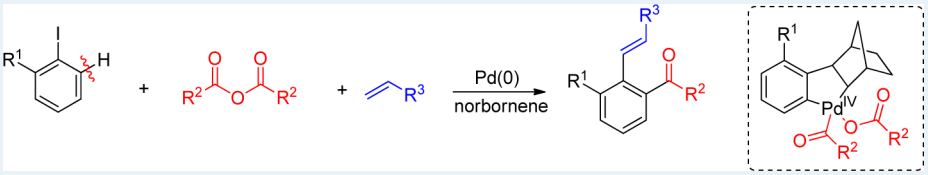
Supporting Information



ABSTRACT: A new palladium-catalyzed three-component coupling involving acylation/alkenylation of aryl iodide is reported. The reaction was carried out with readily available starting materials and gave the ortho-acylated styrene in moderate to good yields. Compared with previous Catellani–Lautens reactions, this reaction is the first example of introducing an acyl group at the ortho position of aryl iodides. The proposed Pd^{IV} complex, generated via oxidative addition of the carboxylic anhydrides, is a key intermediate for this transformation.

KEYWORDS: *palladium, Catellani–Lautens reaction, acylation, alkenylation, carboxylic anhydrides*

Aromatic ketones are fundamental building blocks in the synthesis of natural products and pharmaceutical compounds.[1] Transforming the readily available carboxylic acid derivatives into the aromatic ketone is a general approach. For example, Friedel–Crafts acylation of aromatic compounds from carboxylic acid derivatives is a classical method to synthesize these ketones (Scheme 1a).[2] The crucial drawback with this reaction is the poor regioselectivity leading to hard-to-separate isomeric mixtures. In addition, this reaction is often employed with excess Lewis acid, generating a large amount of waste. Alternatively, the acylation of arylmetal species by carboxylic acids derivatives could afford single regioisomeric aromatic ketones (Scheme 1b).[1a,3] However, these types of reactions have several potential disadvantages: (1) arylmetal reagents are air- and moisture-sensitive, (2) highly reactive arylmetal species generally are not compatible with many functional groups, and (3) the reactions need to employ cumbersome conditions to avoid the formation of tertiary alcohols. Recently, Yamamoto[4] and Gooßen[5] developed an acylation reaction of boronic acids using carboxylic acid derivatives (Scheme 1c). Such a strategy is superior to previous methods in terms of mildness of reaction conditions, efficiency, and functional group compatibility. However, transition-metal-catalyzed direct acylation of aryl C–H bonds is an attractive option. Thus far, only a few methods of direct acylation of aryl C–H bonds by carboxylic acid derivatives have been developed. These transformations rely on pyridine or carboxylic acids as a directing group (Scheme 1d).[6] Transition-metal-catalyzed acylation of aryl C–H bonds with carboxylic acid derivatives by using iodide as a pseudodirecting group is without literature precedent.

The Catellani–Lautens reaction is a remarkable methodology for aromatic C–H functionalization with palladium and norbornene as a catalyst;[7] however, to our knowledge, the functional groups are limited to alkyl, benzyl, aryl, and secondary amine.[7,8] For our interest in the Catellani–Lautens-type reaction,[9] we wish to report a palladium-catalyzed acylation of aryl C–H bonds with carboxylic acid derivatives by using iodide as a pseudodirecting group (Scheme 1e).

Our initial efforts focused on the three-component cross-coupling reaction, employing 1-iodo-2-methylbenzene (**1a**), benzoic anhydride (**2a**), and ethyl acrylate (**3a**) as substrates. The combination of $Pd(OAc)_2/PPh_3$/norbornene,[10] was chosen as the catalyst with *t*-BuOLi as base using toluene at 90 °C for 20 h (Table 1, entry 1). However, none of the cross-coupling product **4a** was detected. Similar results were obtained when the base was switched to *t*-BuONa, Na_2CO_3, or K_2CO_3 (Table 1, entries 2–4). However, it was observed that Cs_2CO_3 provided **4a** in 6% yield and $Cs(OAc)_2$ gave only trace amounts of product (Table 1, entries 5–6). With Cs_2CO_3 as the most effective base, we went on to test other reaction conditions. A series of solvents, including dioxane, MeCN, DMF, DCE, and DME were then screened. Changing the toluene to dioxane or MeCN gave comparable yields (Table 1, entries 7–8).

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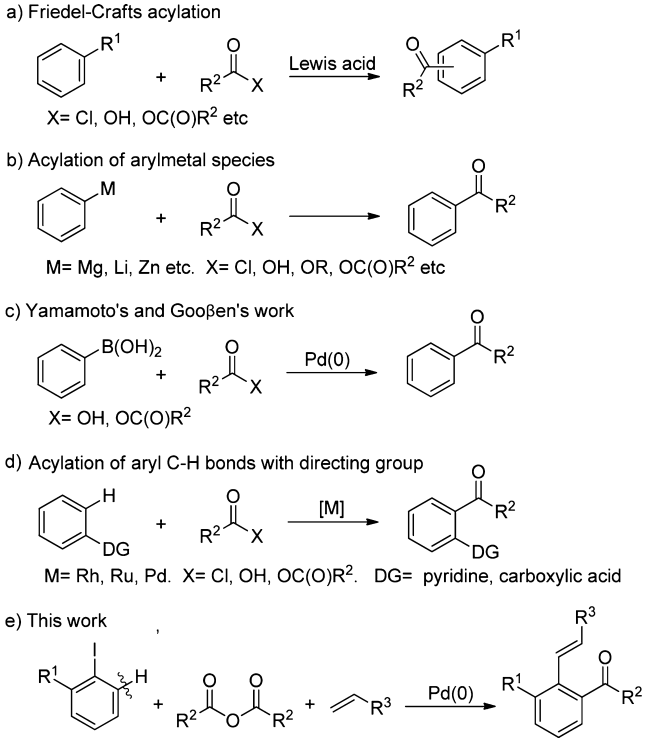
Scheme 1. Different Methods To Synthesize Aromatic Ketone with Readily Available Carboxylic Acid Derivatives As Acylating Agents

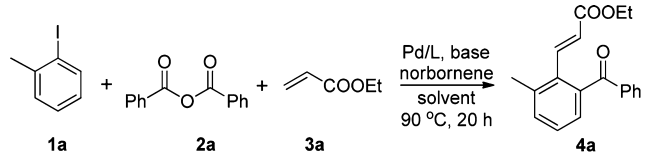


DCE and DME gave better results, and DMF was not a suitable solvent for this reaction (Table 1, entries 9−11).

Next, we investigated the influence of the palladium species and observed that $PdCl_2$ showed the best activity (Table 1, entries 12−15). Further inspection of the reaction conditions revealed that the choice of ligand had a significant effect on the yield. No reaction occurred when the reaction was performed with phen (Table 1, entry 16). Different mono and bidentate phosphine ligands were tested, and TFP was found to be the most effective (Table 1, entries 17−21). Lowering the catalyst loading to 5 mol % resulted in a diminished yield (Table 1, entry 22). Using benzoyl chloride as the acylating agent could also afford the desired product **4a**, but it was less efficient than benzoic anhydride (**2a**) (Table 1, entry 23).

First, the optimized reaction conditions established in entry 19 were applied to a series of aryl iodide **1** to examine the scope of this reaction. Both the electron-deficient and the electron-rich aryl iodides showed excellent reactivities and furnished the corresponding products in moderate to good yields. Highly sterically hindered 1-iodo-2-isopropylbenzene (**1b**) could convert into the coupling product in moderate yield (Table 2, **4-2**). The reaction of 2-iodonaphthalene (**1c**) also proceeded efficiently, delivering **4-3** in 90% yield (Table 2, **4-3**). For the electron-rich aryl iodides, increasing the amount of benzoic anhydride (**2a**) was required to improve the yield of desired products (Table 2, **4-4** and **4-5**). TBS-protected benzyl alcohol and methyl ester are compatible for this reaction (Table 2, **4-6** and **4-12**). The reaction also worked well when the aryl iodide contained a methyl group at the 3- or 4-position (Table 2, **4-7** and **4-9**). Notably, the substrates with halogen groups also worked in this transformation, which provide a possible further transition-metal-catalyzed cross-coupling for the corresponding products (Table 2, **4-8**, **4-10**, and **4-11**).

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	base	slovent	yield[b]
1	$Pd(OAc)_2/PPh_3$	*t*-BuOLi	toluene	0
2	$Pd(OAc)_2/PPh_3$	*t*-BuONa	toluene	0
3	$Pd(OAc)_2/PPh_3$	Na_2CO_3	toluene	0
4	$Pd(OAc)_2/PPh_3$	K_2CO_3	toluene	0
5	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	toluene	6
6	$Pd(OAc)_2/PPh_3$	$Cs(OAc)_2$	toluene	trace
7	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	dioxane	8
8	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	MeCN	9
9	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	DCE	13
10	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	DME	17
11	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	DMF	0
12	$Pd(PPh_3)_4/PPh_3$	Cs_2CO_3	DME	trace
13	$Pd_2(dba)_3{\cdot}CHCl_3/PPh_3$	Cs_2CO_3	DME	5[c]
14	$Pd(CH_3CN)_2Cl_2/PPh_3$	Cs_2CO_3	DME	30
15	$PdCl_2/PPh_3$	Cs_2CO_3	DME	47
16	$PdCl_2$/phen	Cs_2CO_3	DME	0[d]
17	$PdCl_2$/dppb	Cs_2CO_3	DME	53[d]
18	$PdCl_2$/DPEphos	Cs_2CO_3	DME	36[d]
19	$PdCl_2$/TFP	Cs_2CO_3	DME	88
20	$PdCl_2$/Xphos	Cs_2CO_3	DME	trace
21	$PdCl_2/[P^nBu_4]BF_4$	Cs_2CO_3	DME	trace
22	$PdCl_2$/TFP	Cs_2CO_3	DME	70[e]
23	$PdCl_2$/TFP	Cs_2CO_3	DME	72[f]

[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2a** (0.6 mmol, 2.0 equiv), **3a** (0.6 mmol, 2.0 equiv), Pd (10 mol %), ligand (20 mol %), norbornene (0.3 mmol, 1.0 equiv), base (0.90 mmol, 3.0 equiv), solvent (3 mL), 90 °C, 20 h. [b]Yield of isolated product. [c]$Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %). [d]Ligand (10 mol %). [e]$PdCl_2$ (5 mol %), ligand (10 mol %). [f]Using benzoyl chloride (0.6 mmol, 2.0 equiv) as acylating agents. Phen = 1, 10-phenanthroline, TFP = tris(2-furanyl)phosphine.

In addition, aryl iodides containing a substituent ortho to the C−H activation site were also a suitable substrate for the reaction (Table 2, **4-13**).

Next, the scope of this reaction was expanded with a range of anhydride **2**. Both aromatic and aliphatic anhydrides readily reacted with 1-iodo-2-methylbenzene (**1a**) and ethyl acrylate (**3a**) to give the corresponding product in good to moderate yields (Table 3, **4-14**−**4-24**).

Finally, the scope of this reaction was further tested with various olefins. Methyl, *tert*-butyl, and benzyl acrylates were good coupling partners in the reaction, resulting the corresponding products in moderate to good yields (Table 4, **4-25**, **4-26**, and **4-27**). Vinyl amide, methyl vinyl ketone, and acrylonitrile worked efficiently (Table 4, **4-28**, **4-29**, and **4-30**). 2-Vinylnaphthalene, ethyl 4-vinylbenzoate, and vinylpyridine are suitable Heck acceptors for the coupling reaction, and acceptable yields were obtained (Table 4, **4-31**, **4-32**, and **4-33**).

A noteworthy advantage of our method was that the reaction system could be scaled up to gram quantities, and a good yield was afforded (Scheme 2).

Using benzeneboronic acid (**5a**) as a coupling partner could afford the desired product in 38%, but the yield could not be further improved after trying many times (Scheme 3).

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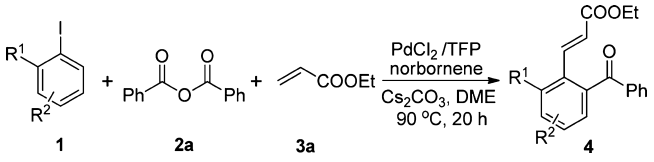
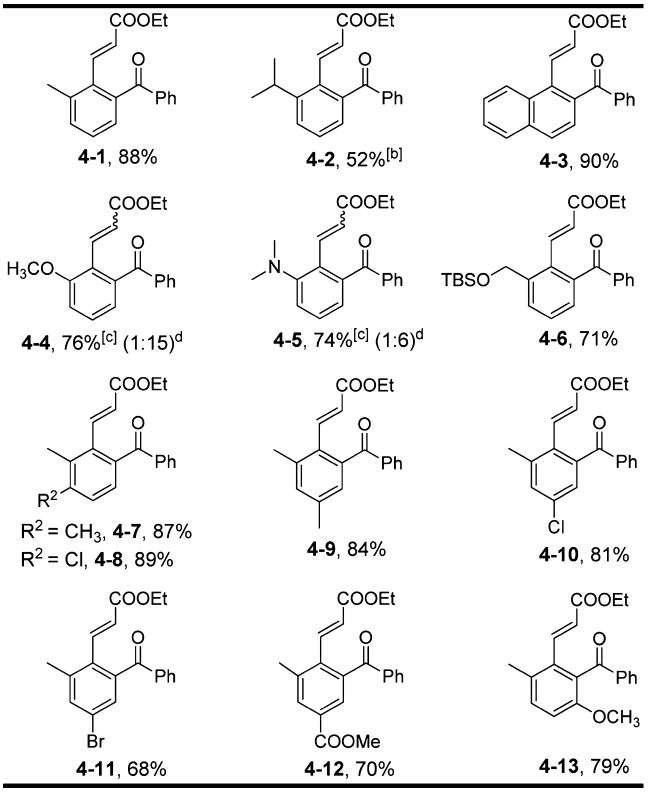
Table 2. Scope of the Reaction with Aryl Iodide 1[a]



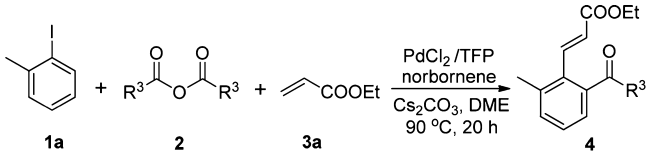


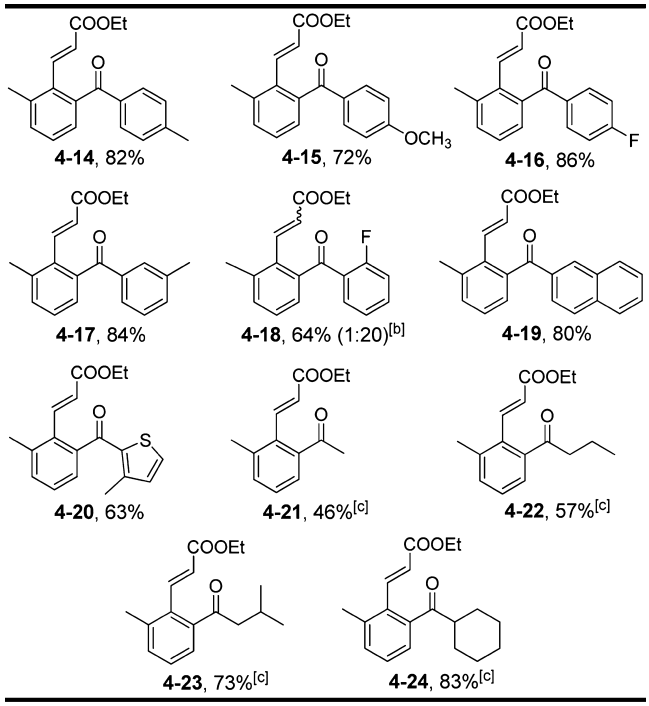
[a]Reaction conditions: **1** (0.3 mmol, 1.0 equiv), **2a** (0.6 mmol, 2.0 equiv), **3a** (0.6 mmol, 2.0 equiv), $PdCl_2$ (10 mol %), TFP (20 mol %), norbornene (0.3 mmol, 1.0 equiv), Cs_2CO_3 (0.90 mmol, 3.0 equiv), DME (3 mL), 90 °C, 20 h. Yield of isolated product. [b]The reaction was carried out at 90 °C for 14 h. [c]3.0 equiv of **2a** was employed. [d]*Z*/*E* ratio determined by ^{1}H NMR spectroscopy.

According to previous reports,[7−9,11] a possible mechanism for the formation of aromatic ketones is outlined in Scheme 4. Oxidative addition of aryl iodide to Pd(0) give complex **A**, which subsequently incorporates a norbornene to afford **B**. The intermediate **B** undergoes an ortho C−H activation to generate the palladacycle **C**. The palladium(IV) species **D**, generated from oxidative addition of anhydride **2** to **C**, undergoes a reductive elimination to give intermediate **E**. The expulsion of a norbornene from **E** affords **F**. Complexation of the alkene to **F** leads to **G**, and insertion of the alkene generates the intermediate **H**. *β*-Hydride elimination then occurs, delivering the desired ketone and palladium complex **I**. Finally, the Pd(0) catalyst regenerates by reductive elimination.

In conclusion, a new palladium-catalyzed/norbornene-mediated ortho-selective acylation of aryl iodides via C−H bond activation with readily available carboxylic anhydride as acylating source was developed. Compared with the previous method of aromatic ketones synthesis, this approach showed excellent regioselectivity. In addition, this reaction is complementary to the alkylation, benzylation, arylation,

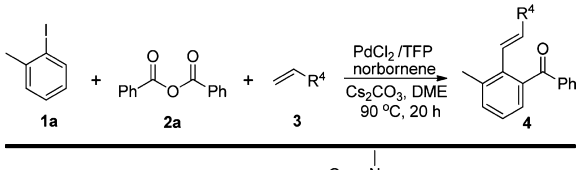
Table 3. Scope of the Reaction with Anhydride 2[a]

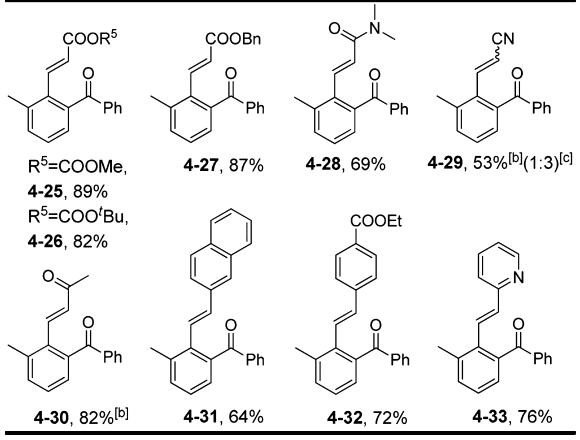




[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2** (0.6 mmol, 2.0 equiv), **3a** (0.6 mmol, 2.0 equiv), $PdCl_2$ (10 mol %), TFP (20 mol %), norbornene (0.3 mmol, 1.0 equiv), Cs_2CO_3 (0.90 mmol, 3.0 equiv), DME (3 mL), 90 °C, 20 h. Yield of isolated product. [b]*Z*/*E* ratio determined by ^{1}H NMR spectroscopy. [c]The reaction was carried out in toluene at 100 °C for 20 h.

Table 4. Scope of the Reaction with Olefin 3[a]





[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2a** (0.6 mmol, 2.0 equiv), **3** (0.6 mmol, 2.0 equiv), $PdCl_2$ (10 mol %), PPh_3(20 mol %), norbornene (0.3 mmol, 1.0 equiv), Cs_2CO_3 (0.90 mmol, 3.0 equiv), DME (3 mL), 90 °C, 20 h. Yield of isolated product. [b]The reaction was carried out at 80 °C for 20 h. [c]*Z*/*E* ratio determined by ^{1}H NMR spectroscopy.

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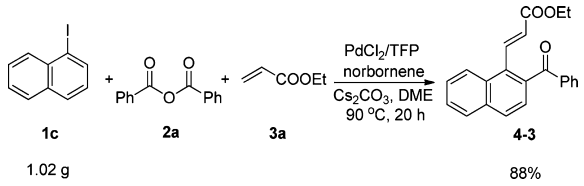
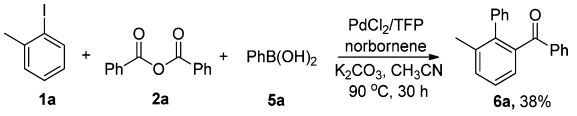
Scheme 2. Palladium-Catalyzed Gram Scale Reaction of 2-Iodonaphthalene (1c), Benzoic Anhydride (2a), and Ethyl Acrylate (3a)[a]



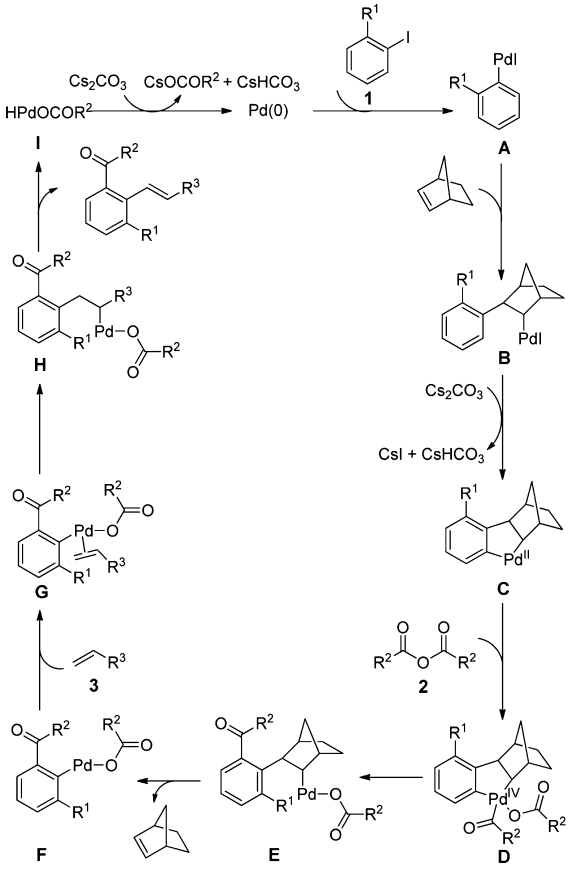
[a]Reaction conditions: **1c** (4.0 mmol, 1.0 equiv), **2a** (8.0 mmol, 2.0 equiv), **3a** (8.0 mmol, 2.0 equiv), $PdCl_2$ (10 mol %), TFP (20 mol %), norbornene (0.3 mmol, 1.0 equiv), Cs_2CO_3 (0.90 mmol, 3.0 equiv), DME (3 mL), 90 °C, 20 h. Yield of isolated product.

Scheme 3. Palladium-Catalyzed Reaction of 1-Iodo-2-methylbenzene (1a), Benzoic Anhydride (2a), and Benzeneboronic Acid (5a)[a]



[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2a** (0.6 mmol, 2.0 equiv), **3a** (0.6 mmol, 2.0 equiv), $PdCl_2$ (10 mol %), TFP (20 mol %), norbornene (0.6 mmol, 2.0 equiv), K_2CO_3 (0.90 mmol, 3.0 equiv), CH_3CN (3 mL), 90 °C, 30 h. Yield of isolated product.

Scheme 4. Proposed Mechanisms



and amination of aryl iodides in Catellani–Lautens reaction. Detailed mechanistic studies are underway and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00516.

Experimental procedures, analytical data for products, NMR spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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