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Palladium-Catalyzed Addition of Potassium Aryltrifluoroborates to Aliphatic Nitriles: Synthesis of Alkyl Aryl Ketones, Diketone Compounds, and 2-Arylbenzo[*b*]furans

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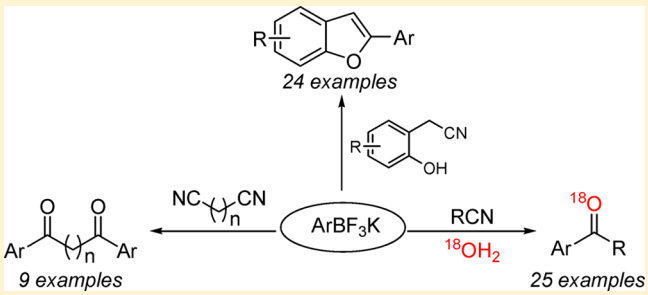
Supporting Information

ABSTRACT: A palladium-catalyzed addition of potassium aryltrifluoroborates to aliphatic nitriles has been developed, leading to a wide range of alkyl aryl ketones with moderate to excellent yields. Moreover, several dinitriles (e.g., malononitrile, glutaronitrile, and adiponitrile) were applicable to this process for the construction of 1,3-, 1,5-, or 1,6-dicarbonyl compounds. The scope of the developed approach is successfully explored toward the one-step synthesis of 2-arylbenzo[*b*]furans via sequential addition and intramolecular annulation reactions. The methodology accepted a wide range of substrates and is applicable to library synthesis.



INTRODUCTION

Transformations of nitriles play an important role in both the laboratory and industry due to their well-recognized chemical versatility.[1] However, the nitrile group is generally inert in organometallic reactions, and thus acetonitrile or benzonitrile usually participate as solvents or ligands[2] in many metal-catalyzed reactions. The insertions of nitrile groups from Grignard reagents[3] and organolithium reagents[4] are powerful tools for the construction of arylketones and heterocyclic compounds, but the rigorous conditions of these reactions have restricted their applications and the variety of substrates. Transition-metal-catalyzed insertion of nitriles offers an attractive route for the creation of novel carbon−carbon and carbon−heteroatom bonds. While rhodium,[5] palladium,[6] and nickel[7] complexes have been investigated to catalyze addition reactions of arylboronic acids to the nitrile group, the substrate scope is usually limited to aromatic nitriles[6,7] and activated nitriles (e.g., cyanoformate[5a] and (benzyl-/arylsulfonyl)-acetonitriles[5b]). Compared to the reactions of aromatic nitriles, nucleophilic addition reactions of aliphatic nitriles are limited by poor electrophilic activation that is insufficient to perform the addition. On the other hand, aliphatic nitriles tend to be deprotonated in the presence of palladium catalysts leading to α-arylation products,[8] making the addition reaction of aliphatic nitriles more difficult to perform than that of aromatic nitriles. Thus, the development of a practical and general approach to alkyl aryl ketones and heterocyclic compounds using aliphatic nitriles as substrates remains a challenging area for exploration.

Organoboron compounds and particularly boronic acids are useful reagents for carbon−carbon bond formation with various electrophiles in the presence of transition metals.[9] Although having advantages such as low toxicity and ease of handling, boronic acids often dimerize and trimerize to form boronic acid anhydrides and boroxines,[10] which hinder the direct purification and the determination of the exact stoichiometry of these reactions. Recently, potassium organotrifluoroborates, with superior features such as higher air- and moisture-stability,[11] have been investigated as alternatives to boronic acid derivatives that easily undergo protodeboronation.[12] To the best of our knowledge, the application of potassium organotrifluoroborates in transition-metal-catalyzed addition of nitriles has not been reported thus far.

As part of the continuing efforts in our laboratory toward the development of novel transition-metal-catalyzed addition or coupling reactions with organoboron reagents,[13,14] we herein explored the potential of palladium-catalyzed addition of potassium organotrifluoroborates to a nitrile group, which is usually more challenging than an aldehyde[14a] or acyl chloride[14b] group. This chemistry has provided a new method for the synthesis of alkyl aryl ketones (or dicarbonyl compounds) by Pd-catalyzed addition of potassium aryltrifluoroborates to aliphatic nitriles (or dinitriles) and the one-step synthesis of 2-arylbenzo[*b*]furan derivatives (Scheme 1). Successful addition of aliphatic nitriles would extend the substrate scope in palladium-catalyzed addition reactions.

RESULTS AND DISCUSSION

We began our study by examining the reaction between acetonitrile (**1a**) and potassium phenyltrifluoroborate (**2a**) to

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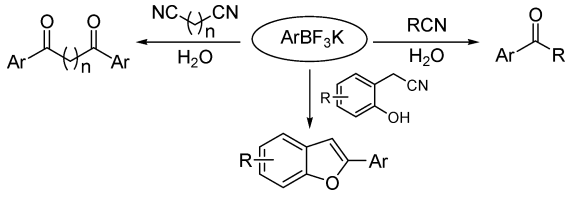
Scheme 1. Pd-Catalyzed Addition of $ArBF_3K$ to Aliphatic Nitriles

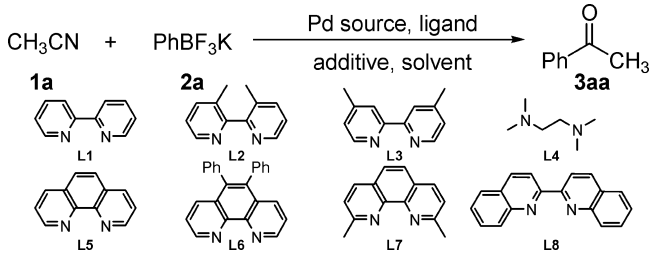


obtain the optimal reaction conditions (Table 1). Through the screening process, no target product was detected using K_2PdCl_4 as the palladium source with a variety of parameters. However, we were delighted to find that the yield of acetophenone (**3aa**) could be improved to 21% when the combination of $PdCl_2$, 2,2′-bipyridine (**L1**), and CF_3COOH was employed in toluene under a N_2 atmosphere (Table 1, entry 1). Encouraged by this promising result, we further adjusted reaction parameters including palladium sources, ligands, additives, and solvents. Among the palladium sources used, $Pd(CF_3CO_2)_2$ exhibited the highest catalytic reactivity in 41% yield (Table 1, entries 2−11). Subsequently, the effect of solvents was examined (Table 1, entries 3 and 12−19). The most effective solvents were 2-MeTHF, dioxane, ethanol, and THF, surpassing toluene, DMF, DMSO, xylene, and H_2O. The use of THF as solvent greatly increased the yield of the reaction (98%, Table 1, entry 19). The role of the THF in the reaction is not clear.[15] THF is known to be a unique ligand in many useful Pd(II) transformations.[16]

The influence of the ligand on the reaction efficiency was also noteworthy (Table 1, entries 19−26); when 2,2′-bipyridine (**L1**), 3,3′-dimethyl-2,2′-bipyridine (**L2**), 4,4′-dimethyl-2,2′-bipyridine (**L3**), 1,10-phenanthroline (**L5**), and 5,6-diphenyl-1,10-phenanthroline (**L6**) were used as the ligand, **3aa** was obtained in 98, 91, 82, 78, and 81% yields, respectively. Other ligands, including N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (**L4**), 2,9-dimethyl-1,10-phenanthroline (**L7**) and 2,2′-biquinoline (**L8**), were less efficient. No desired product was observed in the absence of $Pd(CF_3CO_2)_2$ or ligand (Table 1, entries 27−28). Replacement of TFA[17] with other acids, including CF_3SO_3H, *p*-$MeC_6H_4SO_3H$, $PhCO_2H$, and H_2SO_4, resulted in lower yields (Table 1, entries 19 and 29−32).

Having the optimized reaction conditions in hand, we next investigated the scope and generality of the addition reaction using various aliphatic nitriles and potassium aryltrifluoroborates. Initially, various aliphatic nitriles **1a−1k** were examined in the reaction with **2a** (Table 2). The steric effects of substituents affected the yields of the reaction to some extent. For example, nitriles bearing a relatively large group (e.g., isopropyl, cyclopropyl or tertiary butyl), such as **1b−1d**, afforded slightly lower yields of the desired products (Table 2, entries 2−4). Long-chain aliphatic nitriles such as pentanenitrile **1e** and octanenitrile **1f** were also good partners and reacted with **2a** efficiently (Table 2, entries 5, 6). Notably, treatment of 1-adamantanecarbonitrile **1g** with **2a** under the optimized conditions afforded the desired product **3ga** in 91% yield (Table 2, entry 7). However, substrate 2-iodoacetonitrile **1h** bearing an iodine group reacted with **2a** to give acetophenone in 62% yield, accompanied by a trace amount of the desired product 2-iodo-1-phenylethanone (Table 2, entry 8). The results demonstrated that different functional groups, including 4-butylthio, arylsulfonyl, and benzoyl, performed well under standard conditions (Table 2, entries 9−11). For example,

Table 1. Optimization of the Reaction Conditions[a]



entry	Pd source	ligand	additive	solvent	yield (%)[b]
1	$PdCl_2$	**L1**	CF_3CO_2H	toluene/H_2O	21
2	$Pd(OAc)_2$	**L1**	CF_3CO_2H	toluene/H_2O	35
3	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	toluene/H_2O	41
4	$Pd(PPh_3)_4$	**L1**	CF_3CO_2H	toluene/H_2O	0
5	$Pd(acac)_2$	**L1**	CF_3CO_2H	toluene/H_2O	33
6	$Pd(dba)_2$	**L1**	CF_3CO_2H	toluene/H_2O	18
7	$PdCl_2$(dppe)	**L1**	CF_3CO_2H	toluene/H_2O	0
8	$PdCl_2$(cod)	**L1**	CF_3CO_2H	toluene/H_2O	0
9	$PdCl_2(PPh_3)_2$	**L1**	CF_3CO_2H	toluene/H_2O	0
10	$PdCl_2(NH_3)_2$	**L1**	CF_3CO_2H	toluene/H_2O	20
11	$PdCl_2(Py)_2$	**L1**	CF_3CO_2H	toluene/H_2O	29
12	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	dioxane/H_2O	86
13	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	2-MeTHF/H_2O	87
14	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	DMF/H_2O	0
15	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	DMSO/H_2O	29
16	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	xylene/H_2O	41
17	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	ethanol/H_2O	83
18	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	H_2O	22
19	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	THF/H_2O	98
20	$Pd(CF_3CO_2)_2$	**L2**	CF_3CO_2H	THF/H_2O	91
21	$Pd(CF_3CO_2)_2$	**L3**	CF_3CO_2H	THF/H_2O	82
22	$Pd(CF_3CO_2)_2$	**L4**	CF_3CO_2H	THF/H_2O	0
23	$Pd(CF_3CO_2)_2$	**L5**	CF_3CO_2H	THF/H_2O	78
24	$Pd(CF_3CO_2)_2$	**L6**	CF_3CO_2H	THF/H_2O	81
25	$Pd(CF_3CO_2)_2$	**L7**	CF_3CO_2H	THF/H_2O	16
26	$Pd(CF_3CO_2)_2$	**L8**	CF_3CO_2H	THF/H_2O	15
27	-	**L1**	CF_3CO_2H	THF/H_2O	0
28	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	THF/H_2O	0
29	$Pd(CF_3CO_2)_2$	**L1**	CF_3CO_2H	THF/H_2O	63
30	$Pd(CF_3CO_2)_2$	**L1**	*p*-$MeC_6H_4SO_3H$	THF/H_2O	79
31	$Pd(CF_3CO_2)_2$	**L1**	$PhCO_2H$	THF/H_2O	19
32	$Pd(CF_3CO_2)_2$	**L1**	H_2SO_4	THF/H_2O	24

[a]Unless otherwise noted, reaction conditions were as follows: **1a** (0.4 mmol), **2a** (0.8 mmol), indicated Pd source (5 mol %), ligand (10 mol %), additive (10 equiv), solvent (2 mL), H_2O (0.4 mL), 80 °C, 36 h, N_2. [b]Isolated yield.

substrate **1j** bearing a *p*-chlorobenzenesulfonyl group afforded the corresponding product in 98% yield (Table 2, entry 10).

Next, we turned our attention to the effect of the addition reactions of various potassium aryltrifluoroborates to acetonitrile (**1a**) or isobutyronitrile (**1b**) under the standard conditions (Table 3). The electronic properties of the groups on the phenyl ring moiety of aryltrifluoroborates had some effects on the reaction. Generally, aryltrifluoroborates with an electron-donating substituent on the aryl group gave a slightly higher yield of addition products than those analogues bearing an electron-withdrawing substituent. Steric effects of substituents had an obvious impact on the yield of the reaction. A

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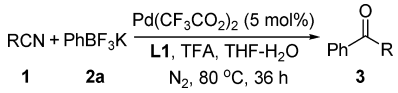
Table 2. Synthesis of Alkyl Aryl Ketones from the Addition of Potassium Aryltrifluoroborates to Aliphatic Nitriles[a]



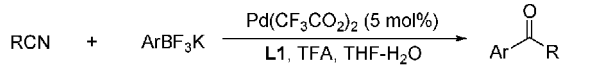
entry	RCN (1)	product (3)	yield (%)[b]
1	CH_3CN (**1a**)	(**3aa**)	98
2	(**1b**)	(**3ba**)	94
3	(**1c**)	(**3ca**)	92
4	(**1d**)	(**3da**)	81
5	*n*-BuCN (**1e**)	(**3ea**)	99
6	(**1f**)	(**3fa**)	99
7	(**1g**)	(**3ga**)	91
8	(**1h**)	(**3ha**)	62[c]
9	(**1i**)	(**3ia**)	74
10	Ar = *p*-ClC$_6$H$_4$ (**1j**)	(**3ja**)	98
11	(**1k**)	(**3ka**)	71

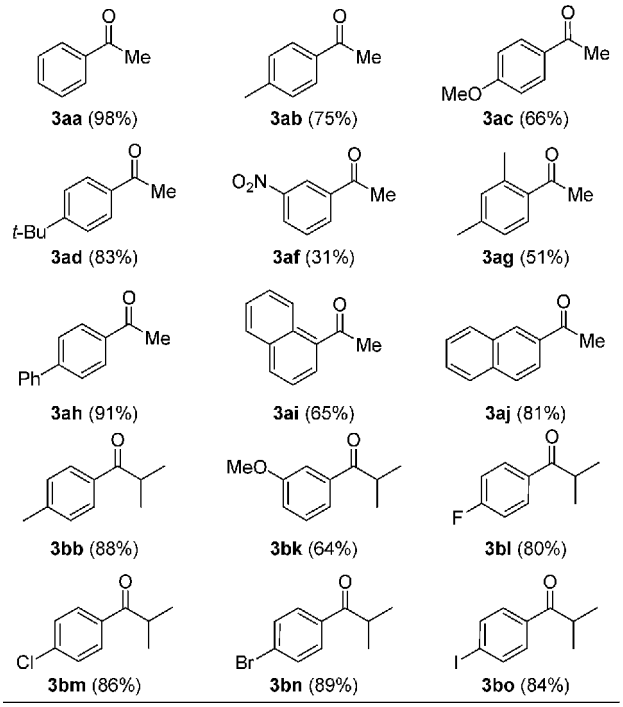
[a]Unless otherwise noted, reaction conditions were as follows: **1** (0.4 mmol), **2a** (0.8 mmol), $Pd(CF_3CO_2)_2$ (5 mol %), **L1** (10 mol %), TFA (10 equiv), THF (2 mL), H_2O (0.4 mL), 80 °C, 36 h, N_2. [b]Isolated yield. [c]Acetophenone was obtained in 62% yield.

potassium aryltrifluoroborate (**2g**) bearing an *ortho*-methyl group, for example, was treated with **1a** to afford a slightly lower yield of addition product **3ag**. Gratifyingly, substrates **2h**−**2j** bearing two benzene rings furnished the desired products **3ah**−**3aj** in moderate to good yields. It is noteworthy that the fluoro, chloro, and bromo moieties (commonly used for cross-coupling reactions) in substrates were all tolerated and afforded several halogen-containing products **3bl**−**3bo** in good yields, leading to a useful handle for further cross-coupling reactions.

The results we observed in the reactions with different nitriles encouraged us to study a new aspect of the reaction. As shown in Table 4, when several dinitriles (e.g., malononitrile, glutaronitrile, and adiponitrile) were used as the substrates, the corresponding 1,3-, 1,5-, or 1,6-dicarbonyl compounds was obtained as the products with moderate to good yields in one step. For example, the transformation of malononitrile (**1p**), glutaronitrile (**1q**), or adiponitrile (**1r**) with potassium phenyltrifluoroborate **2a** proceeded successfully to provide the corresponding products **4a**, **4d**, and **4g** in 81, 91, and 90% yields, respectively.

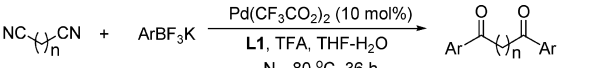
Table 3. Synthesis of Alkyl Aryl Ketones from the Addition of Potassium Aryltrifluoroborates to Acetonitrile (1a) or Isobutyronitrile (1b)[a]

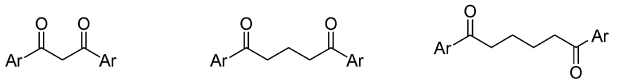




[a]Reaction conditions: **1** (0.4 mmol), **2** (0.8 mmol), $Pd(CF_3CO_2)_2$ (5 mol %), **L1** (10 mol %), TFA (10 equiv), THF (2 mL), H_2O (0.4 mL), 80 °C, 36 h, N_2. Isolated yield.

Table 4. Synthesis of 1,3- or 1,5- or 1,6-Dicarbonyl Compounds from the Addition of Potassium Aryltrifluoroborates to Dinitriles[a]





Ar = Ph, **4a** (81%)	Ar = Ph, **4d** (91%)	Ar = Ph, **4g** (90%)
Ar = *p*-MeC$_6$H$_4$, **4b** (71%)	Ar = *p*-(*t*-Bu)C$_6$H$_4$, **4e** (81%)	Ar = *p*-(*t*-Bu)C$_6$H$_4$, **4h** (73%)
Ar = *p*-ClC$_6$H$_4$, **4c** (47%)	Ar = *p*-BrC$_6$H$_4$, **4f** (87%)	Ar = *p*-ClC$_6$H$_4$, **4i** (85%)

[a]Reaction conditions: dinitriles (0.4 mmol), **2** (1.6 mmol), $Pd(CF_3CO_2)_2$ (10 mol %), **L1** (20 mol %), TFA (15 equiv), THF (2 mL), H_2O (0.4 mL), 80 °C, 36 h, N_2. Isolated yield.

As an application of this chemistry, we developed a simple and efficient approach to benzo[*b*]furans, involving one-step sequential addition and intramolecular annulation reactions of 2-(2-hydroxyphenyl)acetonitriles with potassium aryltrifluoroborates under mild conditions. A variety of 2-arylbenzo[*b*]furans were obtained in moderate to excellent yields (Table 5). Initially, various potassium aryltrifluoroborates were examined in the reaction with 2-(2-hydroxyphenyl)acetonitrile. As expected, all the reactions proceeded smoothly with a wide range of functional groups (e.g., methoxy, *tert*-butyl, naphthyl,

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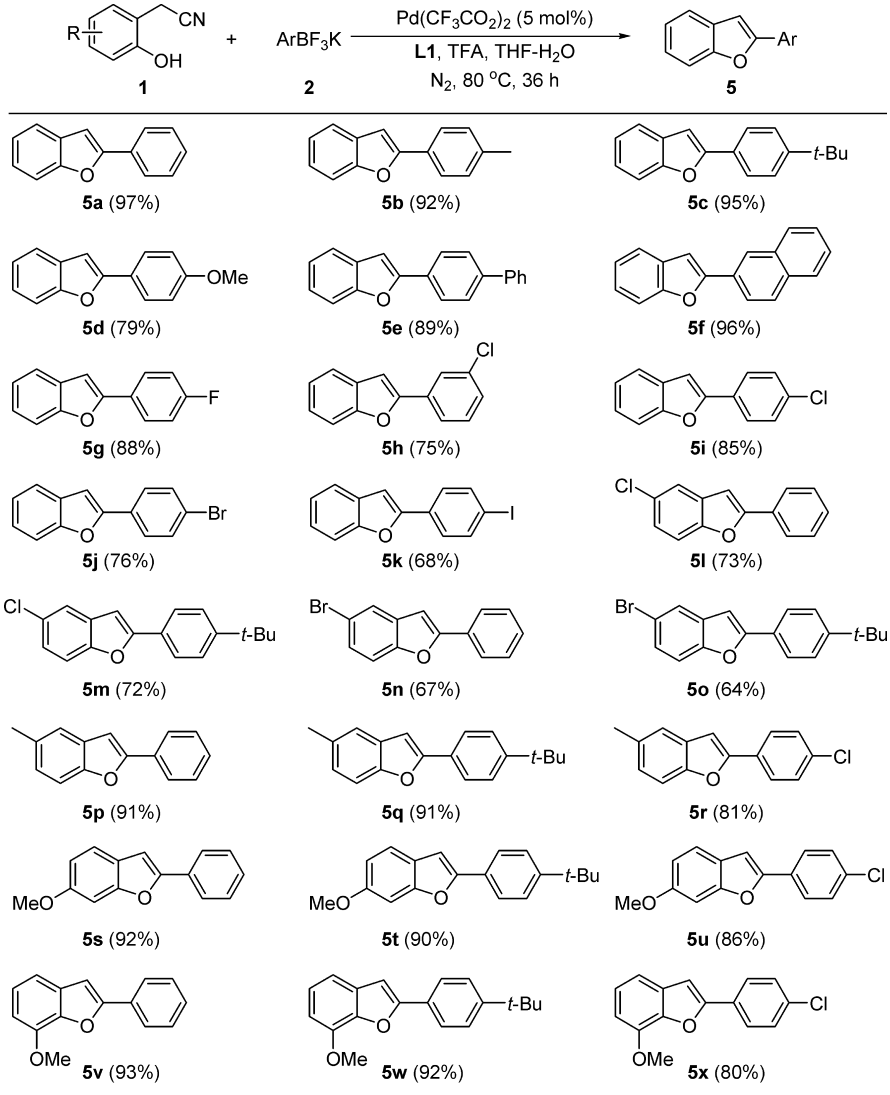
Table 5. Synthesis of 2-Arylbenzo[*b*]furans from the Addition of Potassium Aryltrifluoroborates to 2-Hydroxyphenylacetonitriles[a]



[a]Reaction conditions: 2-hydroxyphenylacetonitriles (0.4 mmol), **2** (0.8 mmol), $Pd(CF_3CO_2)_2$ (5 mol %), **L1** (10 mol %), TFA (10 equiv), THF (2 mL), H_2O (0.4 mL), 80 °C, 36 h, N_2. Isolated yield.

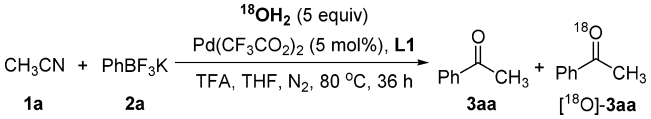
fluoro, chloro, bromo, and iodo), leading to the desired products **5a**−**5k** in moderate to excellent yields.

Moreover, several 2-(2-hydroxyphenyl)acetonitriles were also investigated. The electronic properties of the groups on the phenyl ring of 2-(2-hydroxyphenyl)acetonitriles had some effect on the reaction. Generally, the 2-(2-hydroxyphenyl)-acetonitriles possessing electron-donating groups produced the corresponding 2-arylbenzo[*b*]furans with higher yields than electron-deficient 2-(2-hydroxyphenyl)acetonitriles. For example, moderate yields of the desired products **5l**−**5o** were obtained, while good yields of **5p**−**5x** were obtained. It is worth noting that halogen-containing benzo[*b*]furans were obtained because this substrate should be subject to facile functionalization via various metal-catalyzed reactions.[18]

The present synthetic route to alkyl aryl ketones and 2-arylbenzo[*b*]furans could be readily scaled up to gram quantity without difficulty. For instance, the addition and cascade reaction at the 20 mmol scale afforded the corresponding products acetophenone (**3aa**) and 2-phenylbenzo[*b*]furan (**5a**) in 95 and 93% yields, respectively.

To understand the mechanism more clearly, labeling studies were conducted using $^{18}OH_2$. We next carried out the Pd-catalyzed reaction of acetonitrile (**1a**) and potassium phenyltrifluoroborate (**2a**) in the presence of $^{18}OH_2$ in dry THF (Scheme 2). We found that the reaction proceeded smoothly in

Scheme 2. Isotope Labeling Studies



the present of 5 equiv of $^{18}OH_2$ to provide [^{18}O]-**3aa** and **3aa** in 94% total yield. The ^{18}O-atom-containing product [^{18}O]-**3aa** was determined by GC−MS (EI) analysis (see Supporting Information).

A plausible mechanism for the formation of alkyl aryl ketones is illustrated in Scheme 3. Step (i) involves the coordination of $Pd(CF_3CO_2)_2$ with ligand to afford a Pd(II) catalyst **A**. Step (ii)

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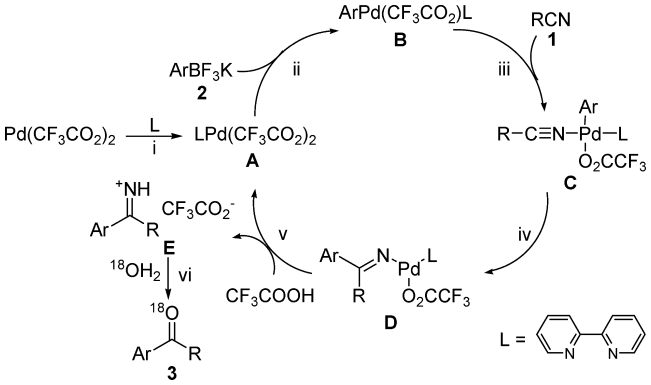
Scheme 3. Plausible Mechanism



of the proposed catalytic cycle involves the transmetalation between the Pd(II) catalyst **A** and potassium aryltrifluoroborate **2** to generate the palladium-aryl species **B**, which was followed by the coordination of aliphatic nitrile **1** giving intermediate **C**. Next, intramolecular carbopalladation of the aliphatic nitrile **1** forms the corresponding imine Pd(II) complex **D**. Finally, protonation of the imine Pd(II) complex **D** by TFA affords the ketimine intermediate **E** and regenerates the Pd(II) catalyst. Hydrolysis of the ketimine intermediate **E** delivers the corresponding alkyl aryl ketones **3** as the products.

CONCLUSIONS

In summary, we have successfully developed an efficient strategy for the palladium-catalyzed addition reaction of potassium aryltrifluoroborates with aliphatic nitriles to afford a variety of alkyl aryl ketones in moderate to excellent yields. This protocol also allows the formation of 1,3-, 1,5-, or 1,6-dicarbonyl compounds. A practical and efficient approach to a variety of 2-arylbenzo[*b*]furans in a one-pot reaction has been developed employing this synthetic protocol. This chemistry may find further applications for the rapid construction of other useful ketones or heterocyclic compounds.

EXPERIMENTAL SECTION

General Information. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz spectrometer (^{1}H at 500 MHz, ^{13}C at 125 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, and the coupling constants J are given in hertz. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. Other commercially obtained reagents were used without further purification. All reactions under nitrogen atmosphere were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300−400 mesh).

General Procedure for the Synthesis of Alkyl Aryl Ketones 3. Under N_2 atmosphere, aliphatic nitriles **1** (0.4 mmol), potassium aryltrifluoroborates **2** (0.8 mmol), $Pd(CF_3CO_2)_2$ (5 mol %), **L1** (10 mol %), TFA (10 equiv), THF (2 mL), and H_2O (0.4 mL) were successively added into a Schlenk reaction tube. The reaction mixture was stirred vigorously at 80 °C for 36 h. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated $NaHCO_3$ (2 × 10 mL) and then brine (1 × 10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired products **3**.

Acetophenone (**3aa**).[19] Colorless oil (47 mg, 98% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, J = 7.1 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 198.2, 137.2, 133.1, 128.6, 128.3, 26.6.

2-Methyl-1-phenylpropan-1-one (**3ba**).[19] Yellow oil (55.6 mg, 94% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 3.60−3.56 (m, 1H), 1.22 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 204.5, 136.3, 132.8, 128.6, 128.3, 35.4, 19.1.

Cyclopropyl (phenyl) methanone (**3ca**).[20] Yellow oil (53.8 mg, 92% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.01 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 6.8 Hz, 1H), 7.47 (t, J = 6.8 Hz, 2H), 2.69 (m, 1H), 1.25 (m, 2H), 1.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.7, 138.0, 132.7, 128.5, 128.0, 17.1, 11.6.

2,2-Dimethyl-1-phenylpropan-1-one (**3da**).[20] Yellow oil (52.6 mg, 81% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.68 (d, J = 7.3 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.4 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 209.3, 138.7, 130.8, 128.0, 127.8, 44.2, 28.0.

1-Phenylpentan-1-one (**3ea**).[21] Yellow oil (64.2 mg, 99% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.88 (d, J = 7.9 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 2H), 2.89 (t, J = 7.4 Hz, 2H), 1.68−1.62 (m, 2H), 1.38−1.30 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 199.6, 136.1, 131.8, 127.5, 127.0, 37.3, 25.5, 21.5, 12.9.

1-Phenylheptan-1-one (**3fa**).[19] Yellow oil (80.9 mg, 99% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 1.76−1.69 (m, 2H), 1.42−1.22 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 199.6, 136.1, 131.8, 127.5, 127.0, 37.6, 30.7, 28.3, 28.1, 23.4, 21.6, 13.0.

1-Adamantyl phenyl (**3ga**).[22] Yellow solid (87.5 mg, 91% yield): mp 52−53 °C (Lit. 50−52 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46 (d, J = 7.1 Hz, 2H), 7.35 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 2.0 (m, 3H), 1.94−1.93 (m, 6H), 1.70−1.64 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 210.2, 139.7, 130.1, 127.9, 127.1, 46.9, 39.1, 36.6, 28.2.

Acetophenone (**3ha**).[19] Colorless oil (29.8 mg, 62% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, J = 7.1 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 198.2, 137.2, 133.1, 128.6, 128.3, 26.6.

2-(Butylthio)-1-phenylethanone (**3ia**).[23] Yellow oil (61.7 mg, 74% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.97 (d, J = 8.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 3.77 (s, 2H), 3.56 (t, J = 7.4 Hz, 2H), 1.59−1.54 (m, 2H), 1.40−1.37 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.6, 135.3, 133.3, 128.8, 128.6, 37.1, 32.1, 31.0, 21.9, 13.6.

2-(4-Chlorophenylsulfonyl)-1-phenylethanone (**3ja**).[24] White solid (115.5 mg, 98% yield): mp 136−137 °C (Lit. 133−134 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93 (d, J = 7.3 Hz, 2H), 7.83 (d, J = 8.7 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53−7.48 (m, 4H), 4.74 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.9, 141.1, 137.1, 135.6, 134.5, 130.2, 129.5, 129.2, 129.0, 63.4.

1,3-Diphenylpropane-1,3-dione (**3ka**).[25] Yellow solid (63.7 mg, 71% yield): mp 77−78 °C (Lit. 76−77 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.99 (d, J = 7.1 Hz, 4H), 7.55 (t, J = 7.4 Hz, 2H), 7.48 (t, J = 7.4 Hz, 4H), 6.86 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.8, 135.6, 132.5, 128.7, 127.2, 93.2.

1-(4-Tolyl)ethanone (**3ab**).[26] Yellow oil (40.3 mg, 75% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 2.49 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.8, 142.8, 133.7, 128.2, 127.4, 25.5, 20.6.

1-(4-Methoxyphenyl)ethanone (**3ac**).[27] White solid (39.6 mg, 66% yield): mp 36−37 °C (Lit. 35−35.5 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.7, 163.5, 130.6, 130.4, 113.7, 55.4, 26.3.

1-(4-tert-Butylphenyl)ethanone (**3ad**).[19] Yellow oil (58.5 mg, 83% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 2.58 (s, 3H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.8, 142.8, 133.7, 128.2, 127.4, 25.5, 20.6.

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*1-(3-Nitrophenyl)ethanone (**3af**).*[28] White solid (20.4 mg, 31% yield): mp 78−79 °C (Lit. 77−79 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.77 (s, 1H), 8.43 (d, J = 8.2 Hz, 2H), 8.30 (d, J = 7.8 Hz, 2H), 7.70 (t, J = 8.0 Hz, 2H) 2.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.7, 148.5, 138.3, 133.8, 129.9, 127.4, 123.2, 26.7.

*1-(2,4-Dimethylphenyl)ethanone (**3ag**).*[29] Yellow oil (30.2 mg, 51% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (d, J = 7.7 Hz, 1H), 6.99−6.97 (m, 2H), 2.47 (s, 3H), 2.44 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.0, 141.1, 137.9, 133.7, 131.9, 128.9, 125.3, 28.3, 20.7, 20.3.

*1-(Biphenyl-4-yl)ethanone (**3ah**).*[30] White solid (71.4 mg, 91% yield): mp 116−117 °C (Lit. 116−117 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.03 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.48−7.45 (m, 2H), 7.40 (t, J = 7.3 Hz, 1H), 2.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.8, 145.8, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 26.2.

*1-(Naphthalen-1-yl)ethanone (**3ai**).*[26] Yellow oil (44.3 mg, 65% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.64 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 7.2 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.39 (t, J = 7.0 Hz, 1H), 7.34 (t, J = 7.7 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 201.8, 135.5, 134.0, 133.0, 130.2, 128.7, 128.4, 128.1, 126.5, 126.1, 124.4, 30.0.

*1-(Naphthalen-2-yl)ethanone (**3aj**).*[26] Yellow oil (55.1 mg, 81% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.42 (s, 1H), 8.00 (d, J = 8.6 Hz, 2H), 7.93 (d, J = 8.1 Hz, 1H), 7.86−7.83 (m, 2H), 7.57 (t, J = 6.9 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 198.1, 135.6, 134.5, 132.5, 130.2, 129.6, 128.5, 128.4, 127.8, 126.8, 123.9, 26.7.

*2-Methyl-1-p-tolylpropan-1-one (**3bb**).*[31] Yellow oil (57.1 mg, 88% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.58−3.50 (m, 1H), 2.41 (s, 3H), 1.21 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 204.2, 143.5, 133.7, 129.3, 128.5, 35.2, 21.6, 19.2.

*1-(3-Methoxyphenyl)-2-methylpropan-1-one (**3bk**).*[32] Yellow oil (45.6 mg, 64% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53 (d, J = 7.7 Hz, 1H), 7.49 (s, 1H), 7.37 (t, J = 7.9 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 3.85 (s, 3H), 3.57−3.49 (m, 1H), 1.21 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 204.3, 159.9, 137.7, 129.5, 120.8, 119.1, 112.8, 55.4, 35.5, 19.2.

*1-(4-Fluorophenyl)-2-methylpropan-1-one (**3bl**).*[33] Yellow oil (53.2 mg, 80% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.99 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 3.55−3.47 (m, 1H), 1.22 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 202.8, 165.5 (d, J_{C-F} = 252 Hz), 132.6, 130.9 (d, J_{C-F} = 9.1 Hz), 115.6 (d, J_{C-F} = 21.6 Hz), 35.3, 19.1.

*1-(4-Chlorophenyl)-2-methylpropan-1-one (**3bm**).*[34] Yellow oil (62.8 mg, 86% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 3.46−3.38 (m, 1H), 1.13 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.2, 139.2, 134.5, 129.7, 128.9, 35.4, 19.1.

*1-(4-Bromophenyl)-2-methylpropan-1-one (**3bn**).*[35] Yellow oil (80.8 mg, 89% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.80 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 3.51−3.43 (m, 1H), 1.19 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.3, 134.9, 131.9, 129.9, 127.9, 35.4, 19.0.

*1-(4-Iodophenyl)-2-methylpropan-1-one (**3bo**).*[36] Yellow oil (92.1 mg, 84% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 3.51−3.43 (m, 1H), 1.19 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.7, 137.9, 135.5, 129.8, 100.6, 35.4, 19.0.

General Procedure for the Synthesis of Dicarbonyl Compounds 4. Under N_2 atmosphere, dinitriles (0.4 mmol), potassium aryltrifluoroborates **2** (1.6 mmol), $Pd(CF_3CO_2)_2$ (10 mol %), **L1** (20 mol %), TFA (15 equiv), THF (2 mL), and H_2O (0.4 mL) were successively added into a Schlenk reaction tube. The reaction mixture was stirred vigorously at 80 °C for 36 h. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated $NaHCO_3$ (2 × 10 mL) and then brine (1 × 10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired products **4**.

*1,3-Diphenylpropane-1,3-dione (**4a**).*[25] Yellow solid (81.1 mg, 81% yield): mp 77−78 °C (Lit. 76−77 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.99 (d, J = 7.1 Hz, 4H), 7.55 (t, J = 7.4 Hz, 2H), 7.48 (t, J = 7.4 Hz, 4H), 6.86 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.8, 135.6, 132.5, 128.7, 127.2, 93.2.

*1,3-Di-p-tolylpropane-1,3-dione (**4b**).*[37] Yellow solid (71.7 mg, 71% yield): mp 125−126 °C (not reported); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.89 (d, J = 8.2 Hz, 4H), 7.29 (d, J = 8.2 Hz, 4H), 6.81 (s, 2H), 2.43 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.5, 143.1, 133.0, 129.4, 127.2, 92.5, 21.7.

*1,3-Bis(4-chlorophenyl)propane-1,3-dione (**4c**).*[38] Yellow solid (55.1 mg, 47% yield): mp 159−160 °C (Lit. 159−160 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.91 (d, J = 8.6 Hz, 4H), 7.46 (d, J = 8.6 Hz, 4H), 6.67 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.6, 138.9, 133.8, 129.1, 128.5, 92.9.

*1,5-Diphenylpentane-1,5-dione (**4d**).*[39] White solid (91.8 mg, 91% yield): mp 65−66 °C (Lit. 65−66 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, J = 7.3 Hz, 4H), 7.55 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.5 Hz, 4H), 3.12 (t, J = 7.0 Hz, 4H), 2.23−2.17 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 199.9, 136.9, 133.1, 128.6, 128.1, 37.6, 18.8.

*1,5-Bis(4-tert-butylphenyl)pentane-1,5-dione (**4e**).* Yellow oil (118.1 mg, 81% yield): IR (KBr, cm^{-1}) 2965, 2938, 1658, 1617, 1453; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92 (d, J = 8.4 Hz, 4H), 7.47 (d, J = 8.4 Hz, 4H), 3.09 (t, J = 7.0 Hz, 4H), 2.22−2.16 (m, 2H), 1.33 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 199.6, 156.7, 134.4, 128.1, 125.5, 37.6, 35.1, 31.1, 19.1; HRMS (ESI) calcd for $C_{25}H_{33}O_2^+$ ([M + H]$^+$) 365.2475, found 365.2488.

*1,5-Bis(4-bromophenyl)pentane-1,5-dione (**4f**).*[40] White solid (142.7 mg, 87% yield): mp 142−143 °C (not reported); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84 (d, J = 8.6 Hz, 4H), 7.60 (d, J = 8.6 Hz, 4H), 3.08 (t, J = 6.9 Hz, 4H), 2.20−2.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 198.7, 135.5, 131.9, 129.6, 128.3, 37.4, 18.5.

*1,6-Diphenylhexane-1,6-dione (**4g**).*[41] White solid (95.9 mg, 90% yield): mp 106−107 °C (Lit. 106−107 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, J = 8.3 Hz, 4H), 7.55 (t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.7 Hz, 4H), 3.04 (t, J = 7.0 Hz, 4H), 1.87−1.83 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.0, 137.0, 133.0, 128.6, 128.0, 38.4, 23.9.

*1,6-Bis(4-tert-butylphenyl)hexane-1,6-dione (**4h**).*[42] White solid (110.5 mg, 73% yield): mp 105−106 °C (not reported); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (d, J = 8.5 Hz, 4H), 7.47 (d, J = 8.5 Hz, 4H), 3.021 (t, J = 6.3 Hz, 4H), 1.86−1.81 (m, 4H), 1.34 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 199.7, 156.6, 134.4, 128.0, 125.5, 38.3, 35.0, 31.1, 24.1.

*1,6-Bis(4-chlorophenyl)hexane-1,6-dione (**4i**).*[41] Yellow solid (114.0 mg, 85% yield): mp 175−176 °C (Lit. 175−176 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.89 (d, J = 8.6 Hz, 4H), 7.43 (d, J = 8.6 Hz, 4H), 3.00 (t, J = 6.1 Hz, 4H), 1.85−1.79 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.6, 138.5, 134.2, 128.4, 127.9, 37.3, 22.7.

General Procedure for the Synthesis of 2-Arylbenzo[*b*]furans 5. Under N_2 atmosphere, 2-hydroxyphenylacetonitriles (0.4 mmol), potassium aryltrifluoroborates **2** (0.8 mmol), $Pd(CF_3CO_2)_2$ (5 mol %), **L1** (10 mol %), TFA (10 equiv), THF (2 mL), and H_2O (0.4 mL) were successively added into a Schlenk reaction tube. The reaction mixture was stirred vigorously at 80 °C for 36 h. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated $NaHCO_3$ (2 × 10 mL) and then brine (1 × 10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired products **5**.

*2-Phenylbenzo[b]furan (**5a**).*[43] White solid (75.3 mg, 97% yield): mp 119−120 °C (Lit. 121.6−122.2 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, J = 7.4 Hz, 2H), 7.57 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.10 (s, 1H); ^{13}C NMR ($CDCl_3$,

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125 MHz) δ 156.0, 154.9, 130.5, 129.3, 128.8, 128.6, 125.0, 124.3, 123.0, 120.9, 111.2, 101.3.

*2-p-Tolylbenzo[b]furan (**5b**).*[44] White solid (76.6 mg, 92% yield): mp 127−128 °C (Lit. 126−128 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.28−7.19 (m, 4H), 7.10 (s, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.3, 154.8, 138.6, 129.5, 129.4, 127.8, 125.0, 124.0, 122.9, 120.8, 111.1, 106.1, 21.4.

*2-(4-tert-Butylphenyl)benzo[b]furan (**5c**).*[45] White solid (95.1 mg, 95% yield): mp 130−131 °C (Lit. 132 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.10 (s, 1H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.2, 154.9, 151.8, 129.4, 127.8, 125.8, 124.8, 124.0, 122.9, 120.8, 111.1, 100.7, 34.8, 31.3.

*2-(4-Methoxyphenyl)benzo[b]furan (**5d**).*[46] White solid (70.8 mg, 79% yield): mp 152−154 °C (Lit. 148−150 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.26−7.19 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.87 (s, 1H) 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.0, 156.1, 154.7, 129.5, 126.4, 123.8, 123.4, 122.9, 120.6, 114.3, 111.0, 99.7, 55.4.

*2-(Biphenyl-4-yl)benzo[b]furan (**5e**).*[45] White solid (96.2 mg, 89% yield): mp 227−228 °C (Lit. 135 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.1 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.06 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.7, 155.0, 141.3, 140.5, 129.5, 129.3, 128.9, 127.6, 127.5, 127.0, 125.4, 124.4, 123.0, 120.9, 111.2, 101.5.

*2-(Naphthalen-2-yl)benzo[b]furan (**5f**).*[45] White solid (93.8 mg, 96% yield): mp 161−162 °C (Lit. 163 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.36 (s, 1H), 7.92−7.87 (m, 3H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.51−7.48 (m, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.10 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.0, 155.1, 133.5, 133.3, 129.3, 128.5, 128.4, 127.8, 127.7, 126.6, 126.5, 124.4, 123.9, 123.0, 122.8, 121.0, 111.2, 101.9.

*2-(4-Fluorophenyl)benzo[b]furan (**5g**).*[47] White solid (74.7 mg, 88% yield): mp 123−124 °C (Lit. 122−124 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84−7.81 (m, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 8.7 Hz, 2H), 6.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.9 (d, $^1J_{C-F}$ = 247 Hz), 155.1, 154.9, 129.2, 126.8 (d, J_{C-F} = 3.5 Hz), 126.7, 124.3, 123.0, 120.9, 115.9 (d, J_{C-F} = 21.8 Hz), 111.2, 101.0 (d, J_{C-F} = 1.5 Hz).

*2-(3-Chlorophenyl)benzo[b]furan (**5h**).*[45] White solid (68.6 mg, 75% yield): mp 84−85 °C (not reported); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.85 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.32−7.29 (m, 2H), 7.25−7.22 (m, 1H), 7.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.9, 154.2, 134.8, 132.1, 130.0, 128.8, 128.3, 124.8, 124.7, 123.0, 122.9, 121.0, 111.2, 102.3.

*2-(4-Chlorophenyl)benzo[b]furan (**5i**).*[48] White solid (77.7 mg, 85% yield): mp 148−149 °C (Lit. 148−149 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.30−7.21 (m, 2H), 6.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.0, 154.8, 134.4, 129.1, 129.1, 129.0, 126.2, 124.6, 123.1, 121.0, 111.2, 101.8.

*2-(4-Bromophenyl)benzo[b]furan (**5j**).*[49] White solid (83.0 mg, 76% yield): mp 154−155 °C (Lit. 159−160 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.58−7.55 (m, 3H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.01 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.0, 154.9, 132.0, 129.5, 129.1, 126.4, 124.7, 123.2, 122.6, 121.1, 111.3, 101.9.

*2-(4-Iodophenyl)benzo[b]furan (**5k**).* White solid (87.1 mg, 68% yield): mp 175−176 °C; IR (KBr, cm^{-1}) 3058, 1450; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.59−7.57 (m, 3H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.0, 154.9, 137.9, 130.0, 129.1, 126.5, 124.7, 123.2, 121.1, 111.3, 102.0, 94.1; HRMS (ESI) calcd for $C_{14}H_{10}IO^+$ ([M + H]$^+$) 320.9771, found 320.9784.

*5-Chloro-2-phenylbenzo[b]furan (**5l**).*[46] White solid (66.8 mg, 73% yield): mp 150−152 °C (Lit. 154 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.53 (s, 1H), 7.47−7.42 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 6.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.4, 153.3, 130.6, 130.0, 129.0, 128.9, 128.5, 125.1, 124.4, 120.4, 112.1, 100.8.

*2-(4-tert-Butylphenyl)-5-chlorobenzo[b]furan (**5m**).* White solid (82.0 mg, 72% yield): mp 167−168 °C; IR (KBr, cm^{-1}) 3064, 2967, 2860, 1475, 1271; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.52 (s, 1H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 6.90 (s, 1H), 1.53 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.6, 153.2, 152.3, 130.7, 128.4, 127.2, 125.8, 124.9, 124.1, 120.3, 112.0, 100.2, 34.8, 31.2; HRMS (ESI) calcd for $C_{18}H_{18}ClO^+$ ([M + H]$^+$) 285.1041, found 285.1048.

*5-Bromo-2-phenylbenzo[b]furan (**5n**).*[49] White solid (73.2 mg, 67% yield): mp 158−159 °C (Lit. 158−159 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.70 (s, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40−7.35 (m, 3H), 6.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.2, 153.6, 131.2, 129.9, 129.0, 128.9, 127.1, 125.1, 123.5, 116.0, 112.6, 100.6.

*5-Bromo-2-(4-tert-butylphenyl)benzo[b]furan (**5o**).* White solid (84.3 mg, 64% yield): mp 155−157 °C; IR (KBr, cm^{-1}) 3058, 2959, 2863, 1474, 1265; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.67 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.38−7.33 (m, 3H), 6.89 (s, 1H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.5, 153.6, 152.4, 131.4, 127.2, 126.9, 125.9, 124.9, 123.4, 116.0, 112.6, 100.1, 34.9, 31.3; HRMS (ESI) calcd for $C_{18}H_{18}BrO^+$ ([M + H]$^+$) 329.0536, found 329.0547.

*5-Methyl-2-phenylbenzo[b]furan (**5p**).*[50] White solid (75.8 mg, 91% yield): mp 127−128 °C (Lit. 128−129 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.85 (d, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.35−7.31 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.94 (s, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.1, 153.4, 132.4, 130.7, 129.4, 128.8, 128.5, 125.6, 124.9, 120.8, 110.7, 101.1, 21.4.

*2-(4-tert-Butylphenyl)-5-methylbenzo[b]furan (**5q**).* White solid (96.2 mg, 91% yield): mp 145−146 °C; IR (KBr, cm^{-1}) 3048, 2960, 2864, 1472, 1263; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.34 (s, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.89 (s, 1H), 2.43 (s, 3H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.3, 153.3, 151.7, 132.3, 129.5, 128.0, 125.7, 125.3, 124.7, 120.7, 110.7, 100.5, 34.8, 31.3, 21.4; HRMS (ESI) calcd for $C_{19}H_{21}O^+$ ([M + H]$^+$) 265.1587, found 265.1583.

*2-(4-Chlorophenyl)-5-methylbenzo[b]furan (**5r**).*[51] White solid (78.6 mg, 81% yield): mp 185−187 °C (not reported); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.40−7.39 (m, 3H), 7.35 (s, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.92 (s, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.9, 153.4, 134.2, 132.6, 129.2, 129.2, 129.0, 126.1, 125.9, 120.8, 110.7, 101.6, 21.4.

*6-Methoxy-2-phenylbenzo[b]furan (**5s**).*[52] White solid (82.5 mg, 92% yield): mp 79−81 °C (not reported); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.44−7.41 (m, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.07 (s, 1H), 6.94 (s, 1H), 6.88−6.86 (m, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.1, 156.0, 155.2, 130.8, 128.8, 128.1, 124.5, 122.6, 121.0, 112.0, 101.2, 96.0, 55.8.

*2-(4-tert-Butylphenyl)-6-methoxybenzo[b]furan (**5t**).* White solid (100.9 mg, 90% yield): mp 71−72 °C; IR (KBr, cm^{-1}) 3052, 3006, 2962, 2837, 1458, 1260; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.07 (s, 1H), 6.90 (s, 1H), 6.87−6.85 (m, 1H), 3.87 (s, 3H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.0, 155.9, 155.5, 151.3, 128.0, 125.7, 124.3, 122.8, 120.9, 111.9, 100.5, 96.5, 55.8, 34.8, 31.3; HRMS (ESI) calcd for $C_{19}H_{21}O_2^+$ ([M + H]$^+$) 281.1536, found 281.1539.

*2-(4-Chlorophenyl)-6-methoxybenzo[b]furan (**5u**).* White solid (89.0 mg, 86% yield): mp 110−111 °C; IR (KBr, cm^{-1}) 3054, 2962, 1454, 1256; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.06 (s, 1H), 6.93 (s, 1H), 6.89−6.87 (m, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$,

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125 MHz) δ 158.3, 156.0, 154.0, 133.8, 129.3, 129.0, 125.7, 122.4, 121.1, 112.2, 101.7, 95.9, 55.8; HRMS (ESI) calcd for $C_{15}H_{11}ClO_2^+$ ($[M + H]^+$) 259.0520, found 259.0519.

*7-Methoxy-2-phenylbenzo[b]furan (**5v**).*[50] White solid (83.4 mg, 93% yield): mp 80−81 °C (Lit. 79−80 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.89 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.19−7.13 (m, 3H), 7.01 (s, 1H), 6.80 (d, J = 7.6 Hz, 1H), 4.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.1, 145.4, 144.2, 131.0, 130.3, 128.6, 125.1, 123.6, 113.4, 106.7, 101.7, 56.2.

*2-(4-tert-Butylphenyl)-7-methoxybenzo[b]furan (**5w**).* White solid (103.2 mg, 92% yield): mp 87−88 °C; IR (KBr, cm^{-1}) 3048, 3007, 2837, 1460, 1265; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (d, J = 8.5 Hz, 2H), 7.45(d, J = 8.5 Hz, 2H), 7.18−7.12 (m, 2H), 6.97 (s, 1H), 6.79 (d, J = 7.6 Hz, 1H), 4.05 (s, 3H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.4, 151.8, 145.3, 144.1, 131.1, 127.6, 125.7, 124.9, 123.5, 113.3, 106.6, 101.1, 56.2, 34.8, 31.3; HRMS (ESI) calcd for $C_{19}H_{21}O_2^+$ ($[M + H]^+$) 281.1536, found 281.1537.

*2-(4-Chlorophenyl)-7-methoxybenzo[b]furan (**5x**).*[53] White solid (82.8 mg, 80% yield): mp 71−72 °C (Lit. 66 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.19−7.14 (m, 2H), 6.99 (s, 1H), 6.81 (d, J = 7.2 Hz, 1H), 4.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.0, 145.4, 144.2, 134.4, 130.8, 129.0, 128.9, 126.3, 123.8, 113.4, 106.9, 102.1, 56.2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all products and GC−MS of [^{18}O]-**3aa**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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