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Palladium-Catalyzed Room-Temperature Acylative Suzuki Coupling of High-Order Aryl Borons with Carboxylic Acids

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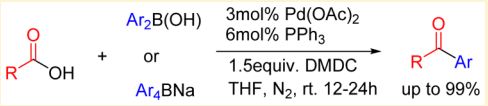
Supporting Information

ABSTRACT: This note describes a dimethyl dicarbonate-assisted, Pd(OAc)$_2$/PPh$_3$-catalyzed acylative Suzuki coupling of carboxylic acids with diarylborinic acids or tetraarylboronates for practical and efficient synthesis of sterically undemanding aryl ketones at room temperature. More than just cost-effective alternatives to aryl boronic acids, diarylborinic acids and tetraarylboronates displayed higher reactivity in the acylative Suzuki coupling. A variety of alkyl aryl ketones, including those bearing a hydroxy, bromo, or carbonyl group, could be readily obtained in modest to excellent yields.



Aryl ketones are not only key moieties of many biologically active molecules but also versatile building blocks in organic synthesis. The traditional approaches to aryl ketones often suffer from harsh reaction conditions, poor selectivities, and/or functional group compatibility.[1] Transition metal-catalyzed reactions, such as carbonylative[2] and acylative[2b,3] cross-couplings of halides and carbonyl compounds, especially carboxylic acid derivatives, have emerged with good regioselectivity and functional group compatibility and have become increasingly essential protocols for synthesis of aryl ketones. The acylative cross-coupling of carboxylic acid derivatives with aryl boronic acids (acylative Suzuki coupling) is particularly attractive because both carboxylic acids[4] and aryl boronic acids[5] are generally nontoxic, stable, easy to handle, and readily available. Great progress has been achieved on acylative Suzuki coupling with respect to acyl sources since its seminal report using acyl chlorides by Bumagin et al.[6] The milder acyl donors have been widely applied, e.g., anhydrides,[7] including *in situ*-generated ones pioneered by Gooßen[7b,8] and Yamamoto et al.,[7c,9] active esters,[10] especially the elegant Liebeskind's enzyme-mimic thiol esters,[11] and, more recently, activated amides reported by Szostak,[12] Garg,[13] and ourselves,[14] independently. The palladium-catalyzed procedures using *in situ*-generated anhydrides from carboxyl acids in the presence of an activating reagent make the acylative Suzuki coupling more practical for synthesis of aryl ketones. Besides the progress on acyl sources, a couple of transition metals other than palladium, e.g., Ru,[10a] Rh,[7a,10c] Cu,[11c,e] Ni,[13] etc., have also been found to be effective in catalyzing the acylative Suzuki coupling of anhydrides, esters, and amides. In contrast, aryl boronic acids have still overwhelmingly dominated the aryl source in acylative Suzuki coupling of carboxylic acid derivatives. In fact, even the boronic anhydrides, triaryl boroxines, were proposed to be rather unreactive in palladium-catalyzed acylative cross-couplings with carboxylic acid anhydrides.[8] Therefore, a proper amount of water had to be maintained in the system to prevent dehydration of aryl boronic acids, while excess water proved to be deleterious because of competitive hydrolysis of acyl sources and/or activating reagents for the *in situ* procedures unless some unconventional systems were used.[15] We have recently shown that high-order aryl borons, such as diarylborinic acids and tetraarylborates, could be used as cost-effective alternatives to aryl boronic acids in both traditional and acylative Suzuki coupling of aryl (pseudo)halides[16] and activated amides,[14b] respectively. Given the lower reactivity of amides as an acyl source, we rationalize that it should be more facile to couple these high-order aryl borons with the more reactive anhydrides, including the *in situ*-generated ones, through which carboxylic acids could be directly used as an acyl source. Herein, we report an efficient Pd(OAc)$_2$/PPh$_3$-catalyzed acylative Suzuki coupling of diarylborinic acids or sodium tetraarylborates with carboxylic acids via *in situ*-generated anhydrides by using dimethyl dicarbonate as an activating reagent for practical and cost-effective synthesis of aryl ketones at room temperature.

Initially, the reaction conditions developed by Gooßen et al.[8] for the coupling of aryl boronic acids with *in situ*-generated anhydrides from carboxylic acids were adopted, i.e., 3 mol % Pd(OAc)$_2$/7 mol % P(*p*-OMePh)$_3$ as the catalyst in the presence of 1.5 equiv of pivalic anhydride and 2.5 equiv of water in THF under N_2 at 60 °C. The cross-coupling of hydrocinnamic acid (**1a**) with bis(*p*-tolyl)borinic acid (**2a**) was chosen as the model for testing the reactivity of diarylborinic acids considering that diphenylborinic acid (**2b**) readily dehydrates to form anhydride [(Ph$_2$B)$_2$O] (Table 1). The desired aryl ketone 3-phenyl-1-(*p*-tolyl)propan-1-one (**3aa**) was obtained in a modest yield (60%). Substitution of tri(*p*-anisoyl)phosphine with simpler and more economical triphenylphosphine (TPP) gave almost the same yield (62%), although no reaction was observed in the absence of a phosphine ligand (Table 1, entries 1, 2, and 4).

This result is interesting because TPP was reported to be a much less efficient ligand in the corresponding reaction of aryl boronic acids,[8] implying the reactivity of borinic acids is higher than that of boronic acids in the acylative Suzuki coupling.

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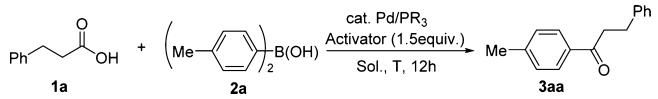
Table 1. Parameter Screening for Cross-Coupling of Hydrocinnamic Acid with Bis(*p*-tolyl)borinic Acid[a]



entry	Pd/PR_3 catalyst (mol %)	activator	H_2O (equiv)	solvent	T (°C)	yield (%)[b]
1	$Pd(OAc)_2$(3)/P(*p*-MeOPh)$_3$(7)	$(t\text{-BuCO})_2O$	2.5	THF	60	60
2	$Pd(OAc)_2$(3)/PPh_3(7)	$(t\text{-BuCO})_2O$	2.5	THF	60	62
3	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	THF	60	80
4	$Pd(OAc)_2$(3)	$(t\text{-BuCO})_2O$	2.5	THF	60	trace
5	$Pd(PPh_3)_2Cl_2$(3)	$(t\text{-BuCO})_2O$	2.5	THF	60	5
6	$Pd(PCy_3)_2Cl_2$(3)	$(t\text{-BuCO})_2O$	2.5	THF	60	68
7	Pd(dppp)Cl_2(3)	$(t\text{-BuCO})_2O$	2.5	THF	60	58
8	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	dioxane	60	65
9	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	toluene	60	28
10	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	DME	60	48
11	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	DMF	60	59
12	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	acetone	60	61
13	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	MeOH	60	73
14	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	CH_3CN	60	52
15	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	EtOAc	60	72
16	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	EtOH	60	75
17	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	*i*-PrOH	60	58
18	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	*n*-butanol	60	74
19	$Pd(OAc)_2(PPh_3)_2$(3)	$(t\text{-BuCO})_2O$	2.5	THF	rt	77[c]
20	$Pd(OAc)_2(PPh_3)_2$(3)	$(Boc)_2O$	2.5	THF	rt	35
21	$Pd(OAc)_2(PPh_3)_2$(3)	RSC	2.5	THF	rt	trace
22	$Pd(OAc)_2(PPh_3)_2$(3)	DMDC	2.5	THF	rt	96
23	$Pd(OAc)_2(PPh_3)_2$(3)	DMDC	10	THF	rt	82
24	$Pd(OAc)_2(PPh_3)_2$(3)	DMDC	–	THF	rt	99
25	$Pd(OAc)_2(PPh_3)_2$(3)	DMDC	–	THF	rt	99[d]
26	$Pd(OAc)_2$(3)/PPh_3(6)	DMDC	–	THF	rt	99[d]
27	$Pd(OAc)_2$(3)/PPh_3(6)	DMDC	–	THF	rt	34[d,e]
28	$Pd(OAc)_2$(3)/PPh_3(9)	DMDC	–	THF	rt	72
29	$Pd(OAc)_2$(3)/PPh_3(12)	DMDC	–	THF	rt	24
30	$Pd(OAc)_2$(3)/PPh_3(3)	DMDC	–	THF	rt	5
31	$Pd(OAc)_2$(1)/PPh_3(2)	DMDC	–	THF	rt	82[d]
32	$Pd(OAc)_2$(3)/PPh_3(6)	DMDC	–	THF	rt	88[d,f]
33	$Pd(OAc)_2$(3)/PPh_3(6)	DMDC	–	THF	rt	22[e,g]

[a]Reaction conditions: 1.0 mmol of **1a** with 0.6 mmol (1.2 equiv with respect to the aryl group) of **2a** in the presence of 1.5 mmol (1.5 equiv) of activator under nitrogen in an anhydrous solvent. [b]Isolated yields. [c]After 24 h. [d]ACS grade THF used directly. [e]*p*-Tolylboronic acid used. [f]One equivalent of DMDC used. [g]In air.

Therefore, we reoptimized the reaction conditions for diarylborinic acids. Using the preformed palladium acetate phosphine complex $Pd(OAc)_2(PPh_3)_2$ as a catalyst precursor, the yield of **3aa** increased to 80% under otherwise identical conditions while the other tested palladium complexes, $PdCl_2(PPh_3)_2$, $Pd(OAc)_2(PCy_3)_2$, and Pd(dppp)$(OAc)_2$, performed less efficiently (Table 1, entries 3 and 5–7). THF appeared to be the choice of solvent after the common solvents had been surveyed, e.g., dioxane (65%), toluene (28%), glyme (DME, 48%), DMF (59%), acetone (61%), MeOH (73%), CH_3CN (52%), ethyl acetate (72%), EtOH (75%), *i*-PrOH (58%), and *n*-BuOH (74%) (Table 1, entries 8–18). No increase in **3aa** yield was observed with a longer reaction time (24 h). Surprisingly, a comparable yield (77%) could be obtained when the reaction was conducted at room temperature for 24 h (Table 1, entry 19). The advantages of room-temperature organic synthesis[17] motivated us to further screen the other parameters to improve the reaction. While di-*tert*-butyl dicarbonate $(Boc)_2O$ and *N*,*N*′-disuccinimidyl carbonate (DSC) provided much lower yields, an excellent yield (96%) of **3aa** was obtained when dimethyl dicarbonate (DMDC) was used as the activating reagent (Table 1, entries 20–22). The readily removed byproducts and safety of DMDC[18] further increased the practicality of the method for synthesis of aryl ketones. The yields decreased remarkably from 96 to 82% when the amount of water was increased from 2.5 to 10 equiv with respect to carboxylic acid in the reaction system, indicating a competitive side reaction of water. In fact, a quantitative yield (99%) was obtained when no water was added (Table 1, entries 23 and 24). It is noteworthy to point out that commercial THF (ACS grade) could be used directly, showing no decease in the yield of **3aa** from that distilled from sodium/benzophenone (Table 1, entry 25). A control experiment using *p*-tolylboronic acid instead of bis(*p*-tolyl)borinic acid (**2a**) gave a low yield (34%) for **3aa** under the anhydrous condition, confirming the reactivity of diarylborinic acids was higher than that of boronic acids in the acylative Suzuki coupling (Table 1, entry 27). To the best of our knowledge, this represents the first example that diarylborinic acids showed reactivity significantly higher than that of boronic acids in palladium-catalyzed cross-couplings.

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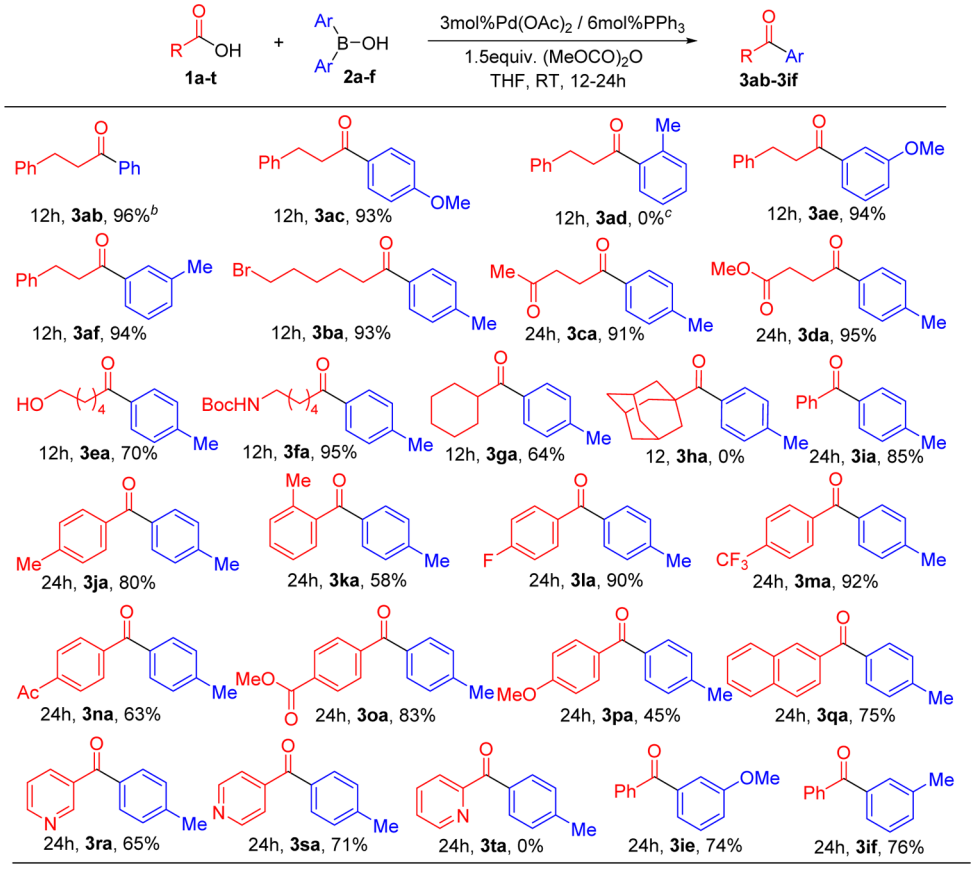
Table 2. Room-Temperature Palladium-Catalyzed Acylative Suzuki Coupling of Carboxyl Acids with Diarylborinic Acids[a]



[a]Reaction conditions: 1.0 mmol of **1** with 0.6 mmol (1.2 equiv with respect to the aryl group) of **2** under nitrogen in ACS grade THF. [b]In the form of anhydride at >90%. [c]No reaction either for bis(*o*-anisoyl)borinic acid.

More practically, the combination of 3 mol % $Pd(OAc)_2$ with 6 mol % PPh_3 worked as efficiently as $Pd(OAc)_2(PPh_3)_2$ under the optimal conditions. Gooßen et al. had reported that high phosphine/palladium ratios, e.g., P/Pd > 3, suppressed the activity of the $Pd(OAc)_2/PAr_3$ catalyst system in the corresponding reaction of arylboronic acids.[8] Similarly, significant decreases in yields of **3aa** were observed with phosphine/palladium ratios increasing to 3 (72%) and 4 (24%) (Table 1, entries 28 and 29, respectively), indicating the true catalytically active species should be a coordinatively unsaturated palladium/phosphine complex. This competitive inhibition by extra phosphine and the structure-dependent reactivity of boron partners, e.g., the activity of diarylborinic acids being higher than that of boronic acids that, in turn, are more reactive than boroxines and boronates, imply that transmetalation between palladium and boron species could be the rate-determining step in the catalytic cycle. The yields of **3aa** decreased to 82 or 88% with lower (1 mol %) catalyst or DMDC (1.0 equiv) loading, respectively. When the reaction was conducted in air, **3aa** was obtained in low yield (22%) with 4,4′-dimethylbiphenyl, which formed in a trace amount under a nitrogen atmosphere, as the major byproduct from the homocoupling of **2a** (Table 1, entry 33). The scope of the aryl ketone synthesis from carboxylic acids and diarylborinic acids was briefly investigated with respect to steric and electronic factors as well as functional groups under the optimal conditions (Table 2).

While the aryl boronic anhydrides, triaryl boroxines, were proposed to be much less reactive than acids in palladium-catalyzed acylative Suzuki coupling, the dehydrated diphenylborinic acid (**2b**) [>90% anhydride, $(Ph_2B)_2O$] gave **3ab** in 96% yield. Diarylborinic acids bearing a *meta* substituent, e.g., MeO (**2e**) and Me (**2f**), reacted similarly to their *para*-substituted analogues (**2a** and **2c**) to give **3ae** (94%) and **3af** (94%), respectively, in excellent yields. Surprisingly, *ortho*-substituted aryl borinic acids, e.g., bis(*o*-tolyl)borinic acid and bis(*o*-anisoyl)borinic acid, almost completely failed in the reaction with hydrocinnamic acid (**1a**) since we have observed that modest hindrance from diarylborinic acids could be overcome in their acylative Suzuki coupling with a variety of activated amides.[14] This sharp difference in the steric effect of the boron partner from reaction with acids to amides could be attributed to the shift of the rate-determining step in the catalytic cycle from transmetalation between boron and palladium to oxidative addition of the C−N bond of amide to palladium (*vide supra*). Alkyl aryl ketones could be isolated in good to excellent yields from alkyl carboxylic acids containing a remote common functional group, e.g., bromo (**1b**), carbonyl (**1c**), ester (**1d**), hydroxyl (**1e**), or Boc-protected amino (**1f**), although a free amino group destroyed the activating reagent DMDC. It is noteworthy that the bromo group in 6-bromohexanoic acid (**1b**) remained completely untouched by the palladium catalyst, because of the mild reaction conditions. As expected, the steric factor from carboxyl acids seriously hampered the acylative cross-coupling because pivalic anhydride could be used as the activating reagent without formation of any detectable pivalophenone. In fact, no reaction was observed for 1-adamantane carboxylic acid while

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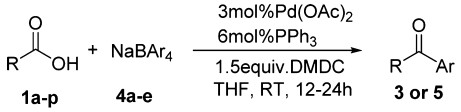
coupling of cyclohexane carboxylic acid with bis(*p*-tolyl)borinic acid gave **3ga** in a modest yield (64%). In general, the aryl carboxylic acids showed reactivities slightly lower than those of the alkyl analogues. After double reaction time (24 h), the ketone yields from the reactions of aromatic carboxylic acids even without steric hindrance were still lower than those of alkyl analogues. An electron-donating group, e.g., *p*-MeO (**1p**), or small *ortho* substituent, e.g., *o*-methyl, on the aromatic ring of benzoic acids further decreased their reactivity, providing ketones **3pa** and **3ka** in just 45 and 58% yields, respectively. Nicotinic acid [pyridine-3-carboxylic acid (**1r**)] and isonicotinic acid [pyridine-4-carboxylic acid (**1s**)] reacted with **2a** like benzoic acids to give **3ra** and **3sa** in 65 and 71% yields, respectively, while no desired product **3ta** was obtained from picolinic acid (pyridine-2-carboxylic acid) under otherwise identical conditions. Instead, a simple mixed anhydride, bis(*p*-tolyl)borinic picolinic anhydride, was isolated in 95% yield, which is obviously stabilized by the chelating N/O coordination of picolinic acid to boron and reluctant to transmetalate with palladium species, the rate-determining step in the catalytic cycle.

Utilization of tetraarylborates ($[Ar_4B]^-$) as an aryl source in arylation processes is always attractive because of their advantages over the other arylborons with respect to atom and process economies, air stability, handling, and stoichiometry. However, the stronger reducing abilities of higher-order aryl borons[19] make tetraarylborates reluctant in the transition metal-catalyzed arylation reactions unless highly reactive allylic derivatives are used.[20] Bumagin et al. have reported that sodium tetraarylborates could couple with acyl chlorides in anhydrous acetone.[21] We have observed the coupling of sodium tetraarylborates with activated amides to give aryl ketones in yields just slightly lower than those of diarylborinic and arylboronic acids.[14] Therefore, we investigated the reactivity of sodium tetraarylborates in the DMDC-assisted, $Pd(OAc)_2$/PPh_3-catalyzed acylative Suzuki coupling with carboxylic acids under the optimal conditions for diarylborinic acids (Table 3).

Table 3. Palladium-Catalyzed DMDC-Assisted Room-Temperature Acylative Cross-Coupling of Carboxyl Acids with Sodium Tetraarylborates[a]



entry	R (**1**)	Ar (**4**)	*T* (h)	yield (%)[b]
1	2-phenylethyl (**1a**)	Ph (**4a**)	12	**3ab**, 90
2	2-phenylethyl (**1a**)	*p*-MeC_6H_4 (**4b**)	12	**3aa**, 91
3	2-phenylethyl (**1a**)	*p*-$MeOC_6H_4$ (**4c**)	12	**3ac**, 85
4	2-phenylethyl (**1a**)	*m*-MeC_6H_4 (**4d**)	12	**3af**, 94
5	2-phenylethyl (**1a**)	*m*-$MeOC_6H_4$ (**4e**)	12	**3ae**, 92
6	Ph (**1i**)	*m*-MeC_6H_4 (**4d**)	24	**3if**, 72
7	Ph (**1i**)	*m*-$MeOC_6H_4$ (**4e**)	24	**3ie**, 69
8	*p*-MeC_6H_4 (**1j**)	Ph (**4a**)	24	**3ia**, 71
9	*o*-MeC_6H_4 (**1k**)	Ph (**4a**)	24	**5ka**, 54
10	*p*-$CF_3C_6H_4$ (**1m**)	Ph (**4a**)	24	**5ma**, 91
11	*p*-$MeOC_6H_4$ (**1p**)	Ph (**4a**)	24	**5pa**, 42

[a]Reaction conditions: 1.0 mmol of **1** with 0.3 mmol (1.2 equiv with respect to the aryl group) of **4** under nitrogen in ACS grade THF. [b]Isolated yields.

Representative sodium tetraarylborates, i.e., tetraphenylborate (**4a**), tetra(*p*-tolyl)borate (**4b**), tetra(*p*-anisoyl)borate (**4c**), tetra(*m*-tolyl)borate (**4d**), and tetra(*m*-anisoyl)borate (**4e**), reacted with hydrocinnamic acid (**1a**) and electronically varied benzoic acids, *p*-toluic acid (**1j**), *p*-trifluoromethyl benzoic acid (**1m**), and *p*-anisic acid (**1p**), like their diarylborinic acid analogues to offer the corresponding aryl ketones **3ab**−**3if** or **5ma**/**5pa**, albeit in slightly lower yields (Table 3, entries 1−7, 10, and 11). An *ortho* substituent on the ring of benzoic acid, *o*-toluic acid (**1k**), again decreased the yield (54%) of diarylketone (**5ka**) significantly compared with that of its *para*-substituted isomer (**1j**) in reaction with tetraphenylborate (**4a**).

In summary, an efficient palladium-catalyzed acylative Suzuki coupling of diarylborinic acids or tetraarylboronates with carboxylic acids via *in situ*-generated anhydrides by using dimethyl dicarbonate as an activating reagent is developed for practical synthesis of sterically undemanding aryl ketones under mild conditions. The reaction showed a good tolerance to common functional groups, in particular, the reactive alkyl bromide being sensitive to steric hindrance. Both diarylborinic acids and tetraarylboronates displayed reactivity significantly higher than that of the corresponding aryl boronic acids. The other features of the approach for aryl ketone synthesis include a simple catalyst system, an innocent activating reagent, and easy-to-handle yet cost-effective aryl sources. These features make the *in situ* procedure of carboxylic acids complementary to our previously reported amide approach that worked well for synthesis of sterically demanding aryl ketones under comparably rigorous conditions.

EXPERIMENTAL SECTION

General Information. All reactions were conducted under nitrogen by using standard Schlenk techniques unless otherwise stated. Commercially available chemicals were used as received. Diarylborinic acids[16a] and sodium tetraarylborates[14b] were prepared according to previously reported procedures. Column chromatography was performed on 200−300 mesh silica gal. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at ambient temperature. Chemical shifts in NMR are reported in parts per million (δ), relative to the internal standard of tetramethylsilane (TMS). The signals observed are described as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), and m (multiplets). The number of protons (*n*) for a given resonance is indicated as *n*H. Coupling constants are reported as *J* in hertz. New compound **3fa** was further characterized by HRMS.

General Procedure for Acylative Cross-Coupling of Carboxylic Acids with Diarylborinic Acids or Sodium Tetraarylborates. To a 25 mL Schlenk flask were added carboxylic acid (1.0 mmol, 1.0 equiv), diarylborinic acid (0.6 mmol, 1.2 equiv with respect to the aryl group), or sodium tetraarylborates (0.3 mol, 1.2 equiv with respect to the aryl group), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 3 mol %), PPh_3 (15.7 mg, 0.06 mmol, 6 mol %), THF (4 mL), and dimethyl dicarbonate (0.201 g, 1.5 mmol, 1.5 equiv). The mixture was stirred at room temperature for 12 or 24 h under nitrogen with the progress monitored by TLC. When completed, the reaction was quenched by water (10 mL) and the mixture extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was dried over Na_2SO_4. Removal of solvents by a rotavapor followed by purification through flash column chromatography over silica gel using an ethyl acetate/petroleum ether (60−90 °C) gradient gave product **3** or **5**.

*3-Phenyl-1-(p-tolyl)propan-1-one (**3aa**).*[14a] White solid: 0.221 g yield, 99% from reaction of hydrocinnamic acid (**1a**) with di(*p*-tolyl)borinic acid (**2a**), and 0.203 g yield, 91% from reaction of **1a** with sodium tetra(*p*-tolyl)borate (**4b**); mp 67−69 °C; ^1HNMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H), 7.31−7.17 (m, 7H), 3.26 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz,

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$CDCl_3$) δ 198.9, 143.9, 141.4, 134.4, 129.3, 128.5, 128.4, 128.2, 126.1, 40.4, 30.2, 21.7.

*1,3-Diphenylpropan-1-one (**3ab**)*.[14b] White solid: 0.202 g yield, 96% from reaction of hydrocinnamic acid (**1a**) with diphenylborinic acid or anhydride (**2a**), and 0.189 g yield, 90% from reaction of **1a** with sodium tetraphenylborate (**4a**); mp 71−72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 8.0 Hz, 2H), 7.22−7.09 (m, 5H), 3.20 (t, J = 8.0 Hz, 2H), 2.97 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 141.3, 136.9, 133.1, 128.7, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2.

*1-(4-Methoxyphenyl)-3-phenylpropan-1-one (**3ac**)*.[3c] White solid: 0.223 g yield, 93% from reaction of hydrocinnamic acid (**1a**) with di(*p*-anisoyl)borinic acid (**2c**), and 0.204 g yield, 85% from reaction of **1a** with sodium tetra(*p*-anisoyl)borate (**4c**); mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 7.32−7.20 (m, 5H), 6.91 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 3.25 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 163.5, 141.5, 130.3, 130.0, 128.5, 128.4, 126.1, 113.8, 55.5, 40.1, 30.4.

*1-(3-Methoxyphenyl)-3-phenylpropan-1-one (**3ae**)*.[22] Light yellow oil: 0.226 g yield, 94% from reaction of hydrocinnamic acid (**1a**) with di(*m*-anisoyl)borinic acid (**2e**), and 0.221 g yield, 92% from reaction of **1a** with sodium tetra(*m*-anisoyl)borate (**4e**); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53−7.48 (m, 2H), 7.37−7.18 (m, 6H), 7.09 (d, J = 6.8 Hz, 1H), 3.83 (s, 3H), 3.28 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.1, 159.9, 141.3, 138.3, 129.6, 128.6, 128.5, 126.2, 120.7, 119.6, 112.3, 55.5, 40.6, 30.2.

*3-Phenyl-1-(m-tolyl)propan-1-one (**3af**)*.[22] Light yellow oil: 0.221 g yield, 94% from reaction of hydrocinnamic acid (**1a**) with di(*m*-tolyl)borinic acid (**2f**), and 0.200 g yield, 89% from reaction of hydrocinnamic acid (**1a**) with sodium tetra(*m*-tolyl)boronate (**4d**); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76−7.73 (m, 2H), 7.33−7.19 (m, 7H), 3.26 (t, J = 7.6 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.5, 141.4, 138.4, 136.9, 133.9, 128.7, 128.6, 128.55, 128.5, 126.2, 125.3, 40.6, 30.2, 21.4.

*6-Bromo-1-(p-tolyl)hexan-1-one (**3ba**)*.[23] White solid: 0.249 g yield, 93%; mp 66−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 3.43 (t, J = 6.8 Hz, 2H), 2.97 (t, J = 6.8 Hz, 2H), 2.41 (s, 3H), 1.95−1.88 (m, 2H), 1.80−1.72 (m, 2H), 1.57−1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 143.8, 134.5, 129.3, 128.2, 38.2, 33.7, 32.7, 27.9, 23.4, 21.6.

*1-(p-Tolyl)pentane-1,4-dione (**3ca**)*.[24] White solid: 0.173 g yield, 91%; mp 59−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.26 (t, J = 6.4 Hz, 2H), 2.88 (t, J = 6.4 Hz, 2H), 2.41 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 198.1, 143.9, 134.2, 129.3, 128.2, 37.1, 32.3, 30.1, 21.6.

*Methyl 4-Oxo-4-(p-tolyl)butanoate (**3da**)*.[25] White solid: 0.196 g yield, 95%; mp 51−53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.70 (s, 3H), 3.30 (t, J = 6.8 Hz, 2H), 2.76 (t, J = 6.8 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 173.4, 144.0, 134.1, 129.3, 128.1, 51.8, 33.3, 28.1, 21.6.

*6-Hydroxy-1-(p-tolyl)hexan-1-one (**3ea**)*. White solid: 0.144 g yield, 70%; mp 72−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.67 (t, J = 6.4 Hz, 2H), 2.96 (t, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.80−1.73 (m, 3H), 1.66−1.59 (m, 2H), 1.49−1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 143.7, 134.5, 129.3, 128.2, 62.6, 38.3, 32.5, 25.5, 24.0, 21.6; HRMS (EI-TOF) m/z [M + H]$^+$ calcd for $C_{13}H_{19}O_2$ 207.1380, found 207.1379.

*6-[(tert-Butoxycarbonyl)amino]-1-(p-tolyl)hexan-1-one (**3fa**)*. White solid: 0.230 g yield, 95%; mp 67−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.58 (s, 1H), 3.15−3.10 (m, 2H), 2.95 (t, J = 7.6 Hz, 2H), 2.41 (s, 3H), 1.78−1.71 (m, 2H), 1.55−1.49 (m, 2H), 1.44−1.37 (m, 11H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 156.0, 143.7, 134.5, 129.2, 128.2, 79.0, 40.4, 38.3, 30.0, 28.4, 26.5, 24.0, 21.6; HRMS (EI-TOF) m/z [M + H]$^+$ calcd for $C_{18}H_{27}NO_3$306.2069, found 306.2063.

*Cyclohexyl(p-tolyl)methanone (**3ga**)*.[14b] White solid: 0.129 g yield, 64%; mp 63−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.27−3.20 (m, 1H), 2.40 (s, 3H), 1.89−1.81 (m, 4H), 1.74−1.71 (m, 1H), 1.54−1.25 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 143.4, 133.8, 129.3, 128.4, 45.5, 29.5, 26.0, 25.9, 21.6.

*Phenyl(p-tolyl)methanone (**3ia**)*.[14b] White solid: 0.167 g yield, 85% from reaction of benzoic acid (**1i**) with di(*p*-tolyl)borinic acid (**2a**), and 0.139 g yield, 71% from reaction of *p*-toluic acid (**1j**) with sodium tetraphenylborate (**4a**); mp 58−60 °C; ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 143.3, 138.0, 134.9, 132.2, 130.3, 130.0, 129.0, 128.2, 21.7.

*Di-p-tolylmethanone (**3ja**)*.[14b] White solid: 0.168 g yield, 80%; mp 96−97 °C; ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 4H), 7.27 (d, J = 8.0 Hz, 4H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 143.0, 135.2, 130.2, 128.9, 21.7.

*o-Tolyl(p-tolyl)methanone (**3ka**)*.[14b] Light yellow oil: 0.122 g yield, 58%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, J = 8.4 Hz, 2H), 7.40−7.36 (m, 1H), 7.30−7.22 (m, 5H), 2.42 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.4, 144.1, 139.0, 136.5, 135.1, 130.9, 130.3, 130.1, 129.2, 128.3, 125.2, 21.7, 19.9.

*4-Fluorophenyl(p-tolyl)methanone (**3la**)*.[14b] White solid: 0.193 g yield, 90%; mp 98−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 7.6 Hz, 2H), 7.15 (t, J = 8.4 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 166.5 (d, J_{CF} = 250 Hz), 143.4, 134.8, 134.1 (d, J_{CF} = 12 Hz), 132.5 (d, J_{CF} = 9.1 Hz), 130.2, 129.1, 115.5 (d, J_{CF} = 21.8 Hz), 21.7.

*p-Tolyl[4-(trifluoromethyl)phenyl]methanone (**3ma**)*.[14b] White solid: 0.243 g yield, 92%; mp 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 144.1, 141.1, 134.1, 133.4 (q, J_{CF} = 32.2 Hz), 130.4, 130.0, 129.2, 125.3 (q, J_{CF} = 3.7 Hz), 122.4, 21.7.

*1-[4-(4-Methylbenzoyl)phenyl]ethan-1-one (**3na**)*.[2c] White solid: 0.150 g yield, 63%; mp 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.67 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 195.7, 144.0, 141.8, 139.4, 134.2, 130.3, 129.9, 129.2, 128.1, 26.9, 21.7.

*Methyl 4-(4-Methylbenzoyl)benzoate (**3oa**)*.[14b] White solid: 0.211 g yield, 83%; mp 125−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 3.97 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 166.4, 143.9, 141.7, 134.3, 133.0, 130.3, 129.6, 129.5, 129.2, 52.4, 21.7.

*4-Methoxyphenyl(p-tolyl)methanone (**3pa**)*.[14b] White solid: 0.102 g yield, 45%; mp 90−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.30 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 4H), 3.94 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 153.9, 153.7, 143.4, 135.6, 134.7, 131.6, 130.2, 129.1, 120.8, 55.6, 21.7.

*Naphthalen-2-yl(p-tolyl)methanone (**3qa**)*.[11c] White solid: 0.185 g yield, 75%; mp 89−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.93−7.90 (m, 4H), 7.78 (d, J = 8.0 Hz, 2H), 7.62−7.53 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 143.2, 135.2, 132.3, 131.6, 130.4, 129.4, 129.1, 128.23, 128.20, 127.8, 126.8, 125.9, 21.7.

*p-Tolyl-3-pyridylmethanone (**3ra**)*.[26] White solid: 0.128 g yield, 65%; mp 74−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 1.6 Hz, 1H), 8.80 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 8.11 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.45 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 152.6, 150.8, 144.2, 137.2, 134.0, 133.5, 130.3, 129.3, 123.4, 21.7.

*p-Tolyl-4-pyridylmethanone (**3sa**)*.[27] White solid: 0.140 g yield, 71%; mp 94−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (dd, J_1 = 4.4 Hz, J_2 = 1.6 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.56 (dd, J_1 = 4.4 Hz, J_2 = 1.6 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 150.3, 144.8, 144.6, 133.3, 130.4, 129.4, 122.8, 21.8.

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*(3-Methoxyphenyl) (Phenyl)methanone (**3ie**).*[28] Light yellow oil: 0.157 g yield, 74% from reaction of benzoic acid (**1i**) with di(*m*-anisoyl)borinic acid (**2e**), and 0.146 g yield, 69% from reaction of **1i** with sodium tetra(*m*-anisoyl)borate (**4e**); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, J = 7.4 Hz, 2H), 7.59−7.55 (m, 1H), 7.48−7.44 (m, 2H), 7.38−7.32 (m, 3H), 7.13−7.11 (m, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.5, 159.6, 138.9, 137.6, 132.5, 130.1, 129.3, 128.3, 122.9, 118.8, 114.4, 55.5.

*(3-Methylphenyl) (Phenyl)methanone (**3if**).*[28] Light yellow oil: 0.149 g yield, 76% from reaction of benzoic acid (**1i**) with di(*m*-tolyl)borinic acid (**2f**), and 0.141 g yield, 72% from reaction of benzoic acid (**1i**) with sodium tetra(*m*-tolyl)boronate (**4d**); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, J = 7.6 Hz, 2H), 7.63−7.56 (m, 3H), 7.49−7.45 (m, 2H), 7.40−7.33 (m, 2H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.0, 138.2, 137.8, 137.6, 133.2, 132.4, 130.5, 130.1, 128.3, 128.1, 127.4, 21.4.

*Phenyl(o-tolyl)methanone **5ka**.*[14a] Light yellow oil: 0.106 g yield, 54%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, J = 8.8 Hz, 2H), 7.50 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.33−7.29 (m, 1H), 7.22 (t, J = 8.4 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.7, 138.6, 137.7, 136.8, 133.2, 131.0, 130.3, 130.2, 128.54, 128.5, 125.2, 20.0.

*Phenyl[4-(trifluoromethyl)phenyl]methanone **5ma**.*[14a] White solid: 0.227 g yield, 91%; mp 115−117 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 6.8 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.5, 140.7, 136.7, 133.7 (q, J_{CF} = 32.5 Hz), 133.1, 130.2, 130.1, 128.5, 125.3 (q, J_{CF} = 3.7 Hz), 124.0 (q, J_{CF} = 271.1 Hz).

*(4-Methoxyphenyl) (Phenyl)methanone **5pa**.*[14a] White solid: 0.890 g yield, 42%; mp 58−60 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 6.8 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.6, 163.2, 138.3, 132.6, 131.9, 130.1, 129.7, 128.2, 113.6, 55.5.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00421.

HRMS spectra of **3ea** and **3fa** and ^{1}H and ^{13}C NMR spectra of all products (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*; VCH: New York, 1989; pp 685−702. (b) Dieter, R. K. *Tetrahedron* **1999**, *55*, 4177−4236. (c) Ross, J.; Xiao, J. *Green Chem.* **2002**, *4*, 129−133. (d) Sartori, G.; Maggi, R. *Chem. Rev.* **2011**, *111*, PR181−PR214.

(2) (a) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Soc. Rev.* **2011**, *40*, 4986−5009. (b) Blangetti, M.; Rosso, H.; Prandi, C.; Deagostino, A.; Venturello, P. *Molecules* **2013**, *18*, 1188−1213. (c) Bjerglund, K. M.; Skrydstrup, T.; Molander, G. A. *Org. Lett.* **2014**, *16*, 1888−1891.

(3) For recent examples: (a) Lee, D.; Ryu, T.; Park, Y.; Lee, P. H. *Org. Lett.* **2014**, *16*, 1144−1147. (b) Wang, X.; Liu, F.-D.; Tu, H.-Y.; Zhang, A.-D. *J. Org. Chem.* **2014**, *79*, 6554−6562. For early examples: (c) Schmink, J. R.; Krska, S. W. *J. Am. Chem. Soc.* **2011**, *133*, 19574−19577 and references cited therein.

(4) Gooßen, L. J.; Rodriguez, N.; Gooßen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100−3120.

(5) Hall, D. G., Ed. *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*, 2nd ed.; Willey-VCH: Weinheim, Germany, 2011.

(6) Bykov, V. V.; Korolev, D. N.; Bumagin, N. A. *Russ. Chem. Bull.* **1997**, *46*, 1631−1632.

(7) (a) Frost, C. G.; Wadsworth, K. J. *Chem. Commun.* **2001**, 2316−2317. (b) Gooßen, L. J.; Ghosh, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 3458−3460. (c) Kakino, R.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 371−376. (d) Shen, X.-B.; Gao, T.-T.; Lu, J.-M.; Shao, L.-X. *Appl. Organomet. Chem.* **2011**, *25*, 497−501. (e) Yu, A.; Shen, L.; Cui, X.; Peng, D.; Wu, Y. *Tetrahedron* **2012**, *68*, 2283−2288.

(8) (a) Gooßen, L. J.; Ghosh, K. *Eur. J. Org. Chem.* **2002**, *2002*, 3254−3267. (b) Goossen, L. J.; Ghosh, K. *Chem. Commun.* **2001**, 2084−2085. (c) Goossen, L. J.; Winkel, L.; Doehring, A.; Ghosh, K.; Paetzold, J. *Synlett* **2002**, 1237−1240.

(9) (a) Kakino, R.; Narahashi, H.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **2001**, 1242−1243. (b) Kakino, R.; Yasumi, S.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 137−148. (c) Kakino, R.; Narahashi, H.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1333−1345.

(10) (a) Tatamidani, H.; Yokota, K.; Kakiuchi, F. N.; Chatani. *J. Org. Chem.* **2004**, *69*, 5615−5621. (b) Tatamidani, H.; Kakiuchi, F.; Chatani, N. *Org. Lett.* **2004**, *6*, 3597−3599. (c) Wang, J.; Zuo, S.; Chen, W.; Zhang, X.; Tan, K.; Tian, Y.; Wang, J. *J. Org. Chem.* **2013**, *78*, 8217−8231.

(11) (a) Liebeskind, L. S.; Srogl, J. *J. Am. Chem. Soc.* **2000**, *122*, 11260−11261. (b) Savarin, C.; Srogl, J.; Liebeskind, L. *Org. Lett.* **2000**, *2*, 3229−3231. (c) Villalobos, J. M.; Srogl, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2007**, *129*, 15734−15735. (d) Zhang, Z.; Lindale, M. G.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2011**, *133*, 6403−6410. (e) Varela-Álvarez, A.; Liebeskind, L. S.; Musaev, D. G. *Organometallics* **2012**, *31*, 7958−7968.

(12) (a) Meng, G.; Szostak, M. *Org. Lett.* **2015**, *17*, 4364−4367. (b) Meng, G.; Szostak, M. *Org. Biomol. Chem.* **2016**, *14*, YYY DOI: 10.1039/c6ob00084c.

(13) Weires, N. A.; Baker, E. L.; Garg, N. K. *Nat. Chem.* **2015**, *8*, 75−79.

(14) (a) Li, X.; Zou, G. *Chem. Commun.* **2015**, *51*, 5089. (b) Li, X.; Zou, G. *J. Organomet. Chem.* **2015**, *794*, 136−145.

(15) (a) Xin, B.; Zhang, Y.; Cheng, K. *J. Org. Chem.* **2006**, *71*, 5725−5731. (b) Mondal, M.; Bora, U. *Appl. Organomet. Chem.* **2014**, *28*, 354−358.

(16) (a) Chen, X.; Ke, H.; Chen, Y.; Guan, C.; Zou, G. *J. Org. Chem.* **2012**, *77*, 7572−7578. (b) Chen, X.; Ke, H.; Zou, G. *ACS Catal.* **2014**, *4*, 379−385. (c) Ke, H.; Chen, X.; Zou, G. *J. Org. Chem.* **2014**, *79*, 7132−7140. (d) Ke, H.; Chen, X.; Feng, Y.; Zou, G. *Sci. China: Chem.* **2014**, *57*, 1126−1131.

(17) Brahmachari, G. *Room Temperature Organic Synthesis*; Elsevier: Amsterdam, 2015.

(18) Dimethyl dicarbonate (DMDC) is a beverage preservative. See the *Food Additives Status List* of the U.S. Food and Drug Administration.

(19) (a) Turner, W. R.; Elving, P. J. *Anal. Chem.* **1965**, *37*, 207−211. (b) Geske, D. H. *J. Phys. Chem.* **1959**, *63*, 1062−1070.

(20) (a) Partyka, D. V. *Chem. Rev.* **2011**, *111*, 1529−1595. For recent examples on cross-coupling of allylic electrophiles, see: (b) Sarkar, S. M.; Uozumi, Y.; Yamada, Y. M. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 9437−9441. (c) Yamada, Y. M. A.; Sarkar, S. M.; Uozumi, Y. *J. Am. Chem. Soc.* **2012**, *134*, 3190−3198. (d) Hamasaka, G.; Sakurai, F.; Uozumi, Y. *Chem. Commun.* **2015**, *51*, 3886−3888.

(21) Bumagin, N. A.; Korolev, D. N. *Tetrahedron Lett.* **1999**, *40*, 3057−3060.

(22) Colbon, P.; Ruan, J.; Purdie, M.; Xiao, J.-L. *Org. Lett.* **2010**, *12*, 3670−3673.

DOI: 10.1021/acs.joc.6b00421
J. Org. Chem. 2016, 81, 4364−4370

(23) Holzer, M.; Ziegler, S.; Albrecht, B.; Kronenberger, B.; Kaul, A.; Bartenschlager, R.; Kattner, L.; Klein, C. D.; Hartmann, R. W. *Molecules* **2008**, *13*, 1081−1110.
(24) Biava, M.; Porretta, G. C.; Poce, G.; Supino, S.; Forli, S.; Rovini, M.; Cappelli, A.; Manetti, F.; Botta, M.; Sautebin, L.; Rossi, A.; Pergola, C.; Ghelardini, C.; Vivoli, E.; Makovec, F.; Anzellotti, P.; Patrignani, P.; Anzini, M. *J. Med. Chem.* **2007**, *50*, 5403−5411.
(25) Jo, E.-A.; Jun, C.-H. *Eur. J. Org. Chem.* **2006**, *2006*, 2504−2507.
(26) Maerten, E.; Sauthier, M.; Mortreux, A.; Castanet, Y. *Tetrahedron* **2007**, *63*, 682−689.
(27) Leventis, N.; Rawaswdeh, A. M.; Zhang, G.; Elder, I. A.; Sotiriou-Leventis, C. *J. Org. Chem.* **2002**, *67*, 7501−7510.
(28) Rao, M. L. N.; Venkatesh, V.; Banerjee, D. *Tetrahedron* **2007**, *63*, 12917−12926.

DOI: 10.1021/acs.joc.6b00421
J. Org. Chem. 2016, 81, 4364−4370