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Note

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

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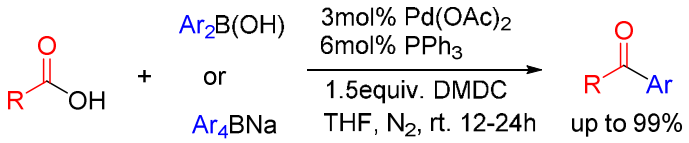


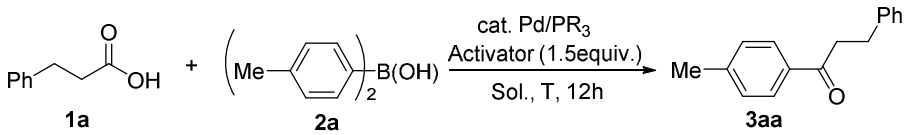
Abstract: This note describes a dimethyl dicarbonate assisted, $Pd(OAc)_2/PPh_3$ catalyzed acylative Suzuki coupling of carboxylic acids with diarylborinic acids or tetraarylboronates for practical and efficient synthesis of sterically undemanding aryl ketones at room temperature. More than just cost-effective 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 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 non-toxic, 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 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, 11e] and 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 from dehydration of aryl boronic acids while excess

water proved to be deleterious owing to 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 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 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 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. 3mol% $Pd(OAc)_2$ / 7mol%P(*p*-OMePh)$_3$ as catalyst in the presence of 1.5equiv. pivalic anhydride and 2.5equiv. water in THF under N_2 at 60^{o}C. The cross-coupling of hydrocinnamic acid (**1a**) with bis(*p*-tolyl)borinic acid (**2a**) was chosen as the model to test the reactivity of diarylborinic acids considering that diphenylborinic acid (**2b**) readily dehydrates to form anhydride ($(Ph_2B)_2O$) (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).

Table 1 Parameter screening for cross-coupling of hydrocinnamic acid with bis(*p*-tolyl)borinic acid[a]



1a 2a 3aa

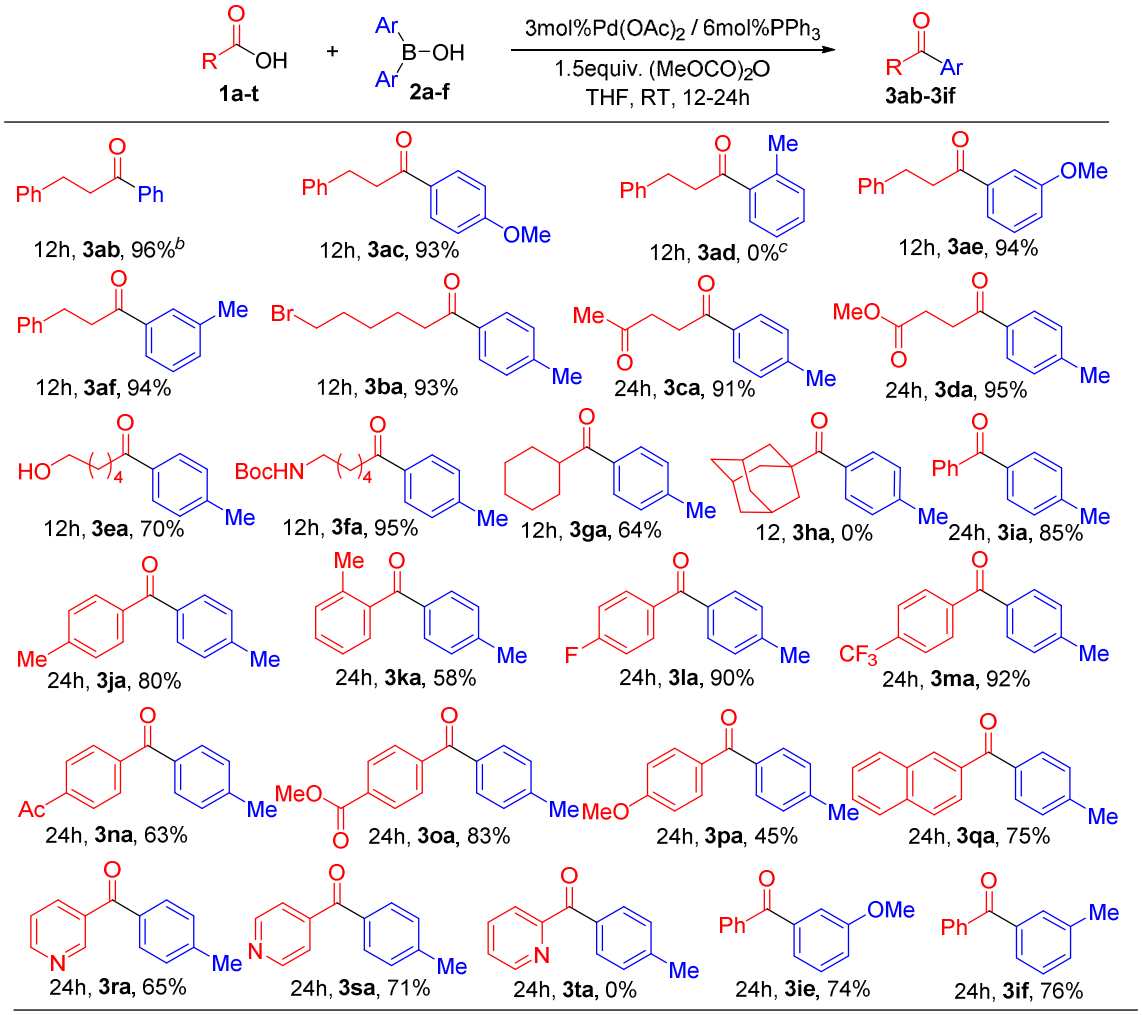
Entry	Cat. Pd/PR_3 (mol%)	Activator	H_2O(eq.)	Sol.	T.(°C)	Yield(%)[b]
1	$Pd(OAc)_2$(3) / P(*p*-MeOPh)$_3$(7)	(*t*-BuCO)$_2$O	2.5	THF	60	60
2	$Pd(OAc)_2$(3) / PPh_3(7)	(*t*-BuCO)$_2$O	2.5	THF	60	62
3	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	THF	60	80
4	$Pd(OAc)_2$(3)	(*t*-BuCO)$_2$O	2.5	THF	60	trace
5	$Pd(PPh_3)_2Cl_2$(3)	(*t*-BuCO)$_2$O	2.5	THF	60	5
6	$Pd(PCy_3)_2Cl_2$(3)	(*t*-BuCO)$_2$O	2.5	THF	60	68
7	Pd(dppp)Cl_2(3)	(*t*-BuCO)$_2$O	2.5	THF	60	58
8	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	Dioxane	60	65
9	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	Toluene	60	28
10	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	DME	60	48
11	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	DMF	60	59
12	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	Acetone	60	61
13	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	MeOH	60	73
14	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	CH_3CN	60	52
15	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	EtOAc	60	72
16	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	EtOH	60	75
17	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	*i*-PrOH	60	58
18	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	2.5	*n*-Butanol	60	74
19	$Pd(OAc)_2(PPh_3)_2$(3)	(*t*-BuCO)$_2$O	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: 1.0mmol **1a** with 0.6mmol (1.2equiv. with respect to aryl group) **2a** in the presence of 1.5mmol (1.5equiv.) activator under nitrogen in anhydrous solvent. [b] Isolated yields. [c] 24 hours. [d] ACS grade THF used directly. [e] *p*-Tolylboronic acid used. [f] 1.0 equiv. DMDC used. [g] In air.

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 higher reactivity of borinic acids than boronic acids in the acylative Suzuki coupling. Therefore, we re-optimized the reaction conditions for diarylborinic acids. Using the preformed palladium acetate phosphine complex $Pd(OAc)_2(PPh_3)_2$ as catalyst precursor, the yield of **3aa** increased to 80% under the 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, 5-7). THF appeared to be the choice of solvent after surveying the common solvents, 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 longer reaction time (24 hours). Surprisingly, a comparable yield (77%) could be obtained when the reaction was carried out at room temperature for 24 hours (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 by-products 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% with increasing the amount of water from 2.5 to 10equiv. 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 **3aa** yield 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, conforming the higher reactivity of diarylborinic acids than 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 significantly higher reactivity than boronic acids in palladium-catalyzed cross-couplings. More practically, the combination of 3mol% $Pd(OAc)_2$ with 6mol% 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 increasing the ratios of phosphine/palladium to 3 (72%) and 4 (24%) (Table 1, entries 28 and 29), 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 higher activity of diarylborinic acids than boronic acids which, in turn, are more reactive than boroxines and boronates, imply that transmetalation between palladium and boron species could be the rate-determining step in catalytic cycle. The yields of **3aa** deceased to 82% and 88% with lower (1mol%) catalyst or DMDC (1.0equiv.) 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 nitrogen atmosphere, as the major by-product from the homo-coupling 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).

Table 2 Room-temperature palladium-catalyzed acylative Suzuki coupling of carboxyl acids with diarylborinic acids[a]



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

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

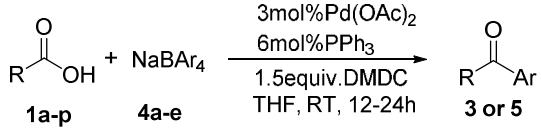
failed in the reaction with hydrocinnamic acid (**1a**) since we have observed that modest hindrance from diarylborinic acids could be overcome in their acylative Suzuki coupling with a variety of activated amides.[14] This sharp difference in steric effect of boron partner from reaction with acids to amides could be attributed to the shift of the rate-determining step in catalytic cycle from transmetalation between boron and palladium to oxidative addition of C-N bond of amide to palladium (*vide supra*). Alky 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 palladium catalyst, thanks to the mild reaction conditions. As expected, steric factor from carboxyl acids hampered seriously the acylative cross-coupling since pivalic anhydride could be used as the activating reagent without formation any detectable pivalophenone. In fact, no reaction was observed for 1-adamantane carboxylic acid while 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 slightly lower reactivities than the alkyl analogues. After double reaction time (24h), 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** similarly to 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 the 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 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 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 just slightly lower yields than 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).

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**), similarly to 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 o*rtho*-substituent on the ring of benzoic acid, *o*-toluic acid (**1k**), again decreased the yield (54%) of diarylketone (**5ka**) significantly compared with its *para*-substituted isomer (**1j**) in reaction with tetraphenylborate (**4a**).

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

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 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 albeit being sensitive to steric hindrance. Both diarylborinic acids and tetraarylboronates displayed significantly higher reactivity than the corresponding aryl boronic acids. The other features of the approach for aryl ketone synthesis include simple catalyst system, innocent activating reagent, 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 carried out 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 chromatograph was performed on 200-300 mesh silica gal. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at ambient temperature. Chemical shifts in NMR are reported in ppm (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), m (multiplets). The number of protons (n) for a given resonance is indicated as nH. Coupling constants are reported as J in Hz. 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 25mL Schlenk flask were added carboxylic acid (1.0mmol, 1.0equiv.), diarylborinic acid (0.6mmol, 1.2equiv. with respect to aryl group) or sodium tetraarylborates (0.3mol, 1.2equiv. with respect to aryl group), $Pd(OAc)_2$ (6.7mg, 0.03mmol, 3mol%), PPh_3 (15.7mg, 0.06mmol, 6mol%), THF (4mL) and dimethyl dicarbonate (0.201g, 1.5mmol, 1.5equiv.). The mixture was stirred at room temperature for 12 or 24 hours under nitrogen with the progress monitored by TLC. When completed, the reaction was quenched by water (10mL) and extracted with CH_2Cl_2 (3x10mL). The organic phase was dried over Na_2SO_4. Removal of solvents by rotavapor followed by purification through flash column chromatography over silica gel using ethyl acetate/petroleum ether (60-90^{o}C) gradient gave products **3** or **5**.

3-Phenyl-1-(*p*-tolyl)propan-1-one (**3aa**):[14a] white solid, yield: 0.221g, 99% from reaction of hydrocinnamic acid (**1a)** with di((*p*-tolyl)borinic acid (**2a**); 0.203g, 91% from reaction of **1a**

with sodium tetra(*p*-tolyl)borate (**4b**); m.p.: 67-69°C; ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm): 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, $CDCl_3$) δ(ppm): 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, yield: 0.202g, 96% from reaction of hydrocinnamic acid (**1a)** with diphenylborinic acid or anhydride (**2a**); 0.189g, 90% from reaction of **1a** with sodium tetraphenylborate (**4a**); m.p.: 71-72°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.86 (d, *J* = 7.2Hz, 2H), 7.45 (t, *J* = 7.2Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.22-7.09 (m, 5H), 3.20 (t, *J* = 8.0Hz, 2H), 2.97 (t, *J* = 8.0Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 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**):[3k] white solid, yield: 0.223g, 93% from reaction of hydrocinnamic acid (**1a)** with di(*p*-anisoyl)borinic acid (**2c**); 0.204g, 85% from reaction of **1a** with sodium tetra(*p*-anisoyl)borate (**4c**); m.p.: 96-97°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 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(ppm): 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, yield: 0.226g, 94% from reaction of hydrocinnamic acid (**1a)** with di(*m*-anisoyl)borinic acid (**2e**); 0.221g, 92% from reaction of **1a** with sodium tetra(*m*-anisoyl)borate (**4e**); ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 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(ppm): 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, yield: 0.221g, 94% from reaction of hydrocinnamic acid (**1a)** with di((*m*-tolyl)borinic acid (**2f**); 0.200g, 89% from reaction of hydrocinnamic acid (**1a)** with sodium tetra(*m*-tolyl)boronate (**4d**); ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 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(ppm): 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, yield: 0.249g, 93%; m.p.: 66-68^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.86 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.43 (t, *J* = 6.8Hz, 2H), 2.97(t, *J* = 6.8Hz, 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(ppm): 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, yield: 0.173g, 91%; m.p.: 59-60^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.88 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.26 (t, *J* = 6.4Hz, 2H), 2.88 (t, *J* = 6.4Hz, 2H), 2.41 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 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, yield: 0.196g, 95%; m.p.: 51-53^{o}C; ^{11}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.89 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.70 (s, 3H), 3.30 (t, *J* = 6.8Hz, 2H), 2.76 (t, *J* = 6.8Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 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, yield: 0.144g, 70%; m.p.: 72-73^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.86 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.67 (t, *J* = 6.4Hz, 2H), 2.96 (t, *J* = 7.2Hz, 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(ppm): 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, yield: 0.230, 95%; m.p.: 67-69^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 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* = 7.6Hz, 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(ppm): 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, yield: 0.129, 64%; m.p.: 63-65°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 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(ppm): 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, yield: 0.167g, 85% from reaction of benzoic acid (**1i)** with di((*p*-tolyl)borinic acid (**2a**); 0.139g, 71% from reaction of *p*-toluic acid (**1j**) with sodium tetraphenylborate (**4a**); m.p.: 58-60°C; ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm): 7.78 (d, *J* = 7.6Hz, 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(ppm): 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, yield: 0.168g, 80%; m.p.: 96-97°C; ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm): 7.70 (d, J = 8.0Hz, 4H), 7.27 (d, J = 8.0 Hz, 4H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 196.3, 143.0, 135.2, 130.2, 128.9, 21.7.

o-Tolyl(*p*-tolyl)methanone (**3ka)**:[14b] light yellow oil, yield: 0.122g; 58%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 7.72 (d, *J* = 8.4Hz, 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(ppm): 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, yield: 0.193g, 90%; m.p.: 98-99°C; ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm): 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(ppm): 195.1, 166.5 (d, J_{CF} = 250Hz), 143.4, 134.8, 134.1(d, J_{CF} = 12Hz), 132.5(d, J_{CF} = 9.1Hz), 130.2, 129.1, 115.5 (d, J_{CF} = 21.8Hz), 21.7.

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

1-(4-(4-Methylbenzoyl)phenyl)ethan-1-one (**3na**):[2c] white solid, yield: 0.150g, 63%; m.p.: 108-110°C; ^{1}H NMR (400 MHz,$CDCl_3$) δ(ppm): 8.05 (d, J = 8.4 Hz, 2 H), 7.84 (d, J = 8.4 Hz, 2 H), 7.72 (d, J = 8.0 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 2 H), 2.67 (s, 3 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 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, yield: 0.211g, 83%; m.p.: 125-127°C; ^{1}H NMR (400 MHz,$CDCl_3$) δ(ppm): 8.14 (d, J = 8.0 Hz, 2 H), 7.82 (d, J = 8.4 Hz, 2 H), 7.72 (d, J = 8.0 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 2 H), 3.97 (s, 3 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 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, yield: 0.102g, 45%; m.p.: 90-92°C; ^{1}HNMR (400 MHz, $CDCl_3$), δ(ppm): 7.84 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.30 (dd, J_1 = 7.6Hz, J_2 = 4.8 Hz, 4H), 3.94(s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 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, yield: 0.185, 75%; m.p.: 89-91°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 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(ppm): 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, yield: 0.128g, 65%; m.p.: 74-76°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 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(ppm) 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, yield: 0.140g, 71%; m.p.: 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 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(ppm) 194.8, 150.3, 144.8, 144.6, 133.3, 130.4, 129.4, 122.8, 21.8.

(3-Methoxyphenyl)(phenyl)methanone (**3ie**):[28] Light yellow oil, yield: 0.157g, 74% from reaction of benzoic acid (**1i)** with di(*m*-anisoyl)borinic acid (**2e**); 0.146g, 69% from reaction of **1i** with sodium tetra(*m*-anisoyl)borate (**4e**); ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 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(ppm): 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, yield: 0.149, 76% from reaction of benzoic acid (**1i)** with di((*m*-tolyl)borinic acid (**2f**); 0.141g, 72% from reaction of benzoic acid (**1i)** with sodium tetra(*m*-tolyl)boronate (**4d**); ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 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(ppm): 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, yield: 0.106g, 54%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 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(ppm): 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, yield: 0.227g, 91%; m.p.: 115-117 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 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(ppm): 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, yield: 0.890g, 42%; m.p.: 58-60 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 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(ppm): 195.6, 163.2, 138.3, 132.6, 131.9, 130.1, 129.7, 128.2, 113.6, 55.5.

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Supporting Information

HRMS of **3ea** and **3fa** and ^{1}H and ^{13}C NMR spectra of all products are available free of charge via the Internet at http://pubs.acs.org.

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