[(NHC)Pd(OAc)$_2$]: Highly Active Carboxylate Pd(II)–NHC (NHC = N-Heterocyclic Carbene) Precatalysts for Suzuki–Miyaura and Buchwald–Hartwig Cross-Coupling of Amides by N–C(O) Activation

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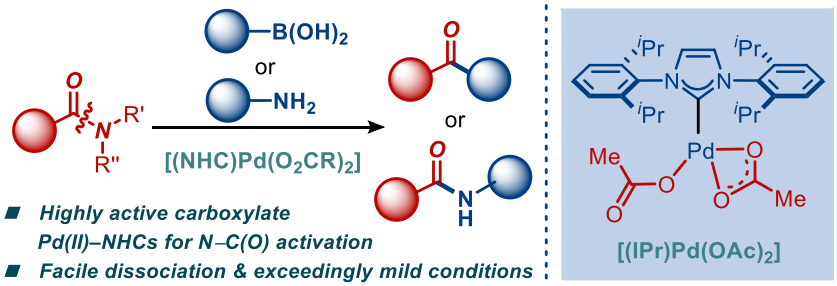
Supporting Information



ABSTRACT: In the past eight years, the selective cross-coupling of amides by N–C(O) bond activation has emerged as a highly attractive manifold for manipulation of the traditionally unreactive amide bonds. In this *Special Issue* on *Next-Generation Cross-Coupling Chemistry*, we report the Suzuki–Miyaura and Buchwald–Hartwig cross-coupling of amides by selective N–C(O) cleavage catalyzed by bench-stable, well-defined carboxylate Pd(II)–NHC (NHC = N-heterocyclic carbene) catalysts, [(NHC)Pd(O$_2$CR)$_2$]. This class of Pd(II)–NHCs promotes the cross-coupling under exceedingly mild room temperature conditions owing to the facile dissociation of the carboxylate ligands to form the active complex. These readily accessible Pd(II)–NHC precatalysts show excellent functional group tolerance and are compatible with a broad scope of amide activating groups. Considering the mild conditions for the cross-coupling and the facile access to carboxylate Pd(II)–NHC complexes, we anticipate that this class of bench-stable complexes will find wide application in activation of amide N–C(O) and related acyl X–C(O) bonds.

Introduction

The amide bond represents one of the most important functional groups throughout the realm of organic chemistry, including the synthesis of natural products, advanced functional materials and best-selling pharmaceuticals.[1-2] However, activation of the amide N–C(O) bond has been historically considered a major challenge owing to the amidic resonance ($n_N \rightarrow \pi^*_{C=O}$ barrier to rotation in planar amides, 15-20 mol/kcal).[3] The last eight years have witnessed an explosion of interest in activating amide bonds by ground-state-destabilization, where the amidic resonance is decreased by amide N–C(O) bond twisting and/or electronic N-activation (Figure 1A).[3-5] This manifold permits to selectively activate common 1° and 2° amide bonds for insertion of transition metals into the N-C(O) bond to form versatile acyl–metals from amides, which can be utilized in the powerful transition-metal-catalyzed reaction pathways.[4,5] In particular, the direct cross-coupling of acyl–metals lead to highly valuable acyl products, such as ketones and amides, [5,6] while decarbonylation results in the formation of aryl–metals, which can be utilized in the synthesis of biaryls.[7] In this context, Pd(II)–NHCs (NHC = N-heterocyclic carbene)[8, 11] have emerged as a highly reactive class of catalysts for amide N-C(O) bond activation.[5,12] The high activity of Pd–NHCs can be ascribed to a significant σ-donating character of the N-heterocyclic carbene ancillary ligand,[8-10] which promotes the challenging oxidative addition under mild conditions and with much greater generality than common Pd–phosphine catalysts.[8-10] One of the fundamental aspects of Pd(II)–NHC catalysts is the type of ancillary throw-away ligand,[11,13] which ensures that the metal and the NHC ligand are used in the optimal 1:1 ratio as well as render the catalysts bench-stable, operationally-simple and user-friendly.[13,14]

Since 2017, our group has established that several classes of well-defined Pd(II)–NHC complexes[13,15] can be employed for activation of amide N–C(O) and related acyl bonds by selective oxidative addition of the acyl group to Pd(0),[12] including [Pd(NHC)(allyl)Cl], [Pd(IPr)(cin)Cl], [Pd(NHC)(3-Cl-py)Cl$_2$], [Pd(NHC)(1-*t*Bu-ind)Cl], [Pd(NHC)(μ-Cl)Cl]$_2$, [Pd(NHC)(acac)Cl], and [Pd(NHC)(AN)Cl$_2$] (AN = aniline) complexes (Figure 1B).[15]

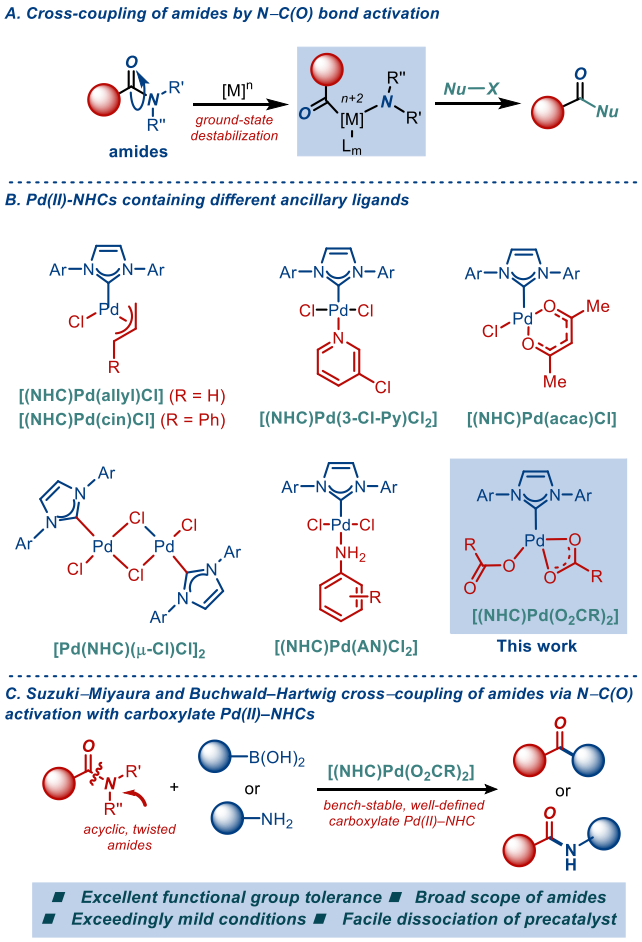


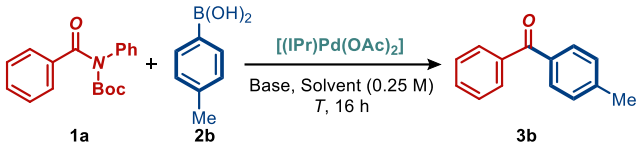
Figure 1. (a) Cross-coupling of amides by N–C(O) bond activation; (b) Pd(II)–NHCs containing different ancillary ligands; (c) This study: Suzuki-Miyaura and Buchwald–Hartwig cross-coupling of amides using well-defined carboxylate [(NHC)Pd(O_2CR)$_2$] complexes.

In general, these complexes differ by the nature of the ancillary throw-away ligand on Pd, which is removed under the reaction conditions to generate the monoligated Pd(0)-NHC complex.[14] Previous studies demonstrated that different Pd(II)–NHC complexes have unique advantages in terms of rate of activation, compatibility with the reaction conditions, substrate scope and type of amide N–C(O) bonds that can be engaged for cross-coupling reactions.[15a-e] We recognized that a class of well-defined Pd(II)–NHCs bearing carboxylates as ancillary ligands has never been used in cross-coupling reactions.[16,17] We hypothesized that the properties of the carboxylate leaving group, including the possibility of steric and electronic tuning, may be beneficial in cross-coupling of amides due to the facile dissociation of the carboxylate group.[17] Herein, we report our study on the Suzuki–Miyaura and Buchwald–Hartwig cross-coupling of amides catalyzed by bench-stable, well-defined carboxylate Pd(II)–NHC catalysts, [(NHC)Pd(O_2CR)$_2$] (Figure 1C).[16,17] Most crucially, we have established that this class of Pd(II)–NHCs promotes the cross-coupling under exceedingly mild room temperature conditions owing to the facile dissociation of the carboxylate ligands to form the active complex. Furthermore, these readily accessible Pd(II)–NHC precatalysts show excellent functional group tolerance and are compatible with a broad scope of amide activating groups. In view of the mild conditions and the facile access to carboxylate Pd(II)–NHC complexes, we anticipate that this class of bench-stable complexes will find wide application in activation of amide N–C(O) and related acyl X–C(O) bonds.

Results and Discussion

As in previous studies, the Suzuki–Miyaura cross-coupling was selected as a model reaction (Table 1). The well-defined Pd(II)–NHCs were prepared by the methods reported previously.[16b,e] A selection of carboxylate ligands included sterically- and electronically-differentiated carboxylates, such as $MeCO_2$, CF_3CO_2, $PhCO_2$, tBuCO$_2$.[16] Although our previous studies demonstrated that IPr is vastly preferred as the NHC ligand for amide N–C(O) bond activation,[12,15] related IMes and SIPr ligands were also tested. Previous studies by the Sigman[16a,b] and Nolan[16c] groups demonstrated that this class of Pd(II)–NHCs features square-planar coordination around the metal center, while the trans coordination site is occupied by water. The optimization results are summarized in Table 1.

Table 1. Optimization of the Reaction Conditions[a]



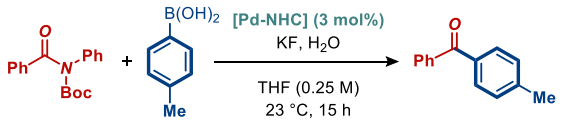
1a 2b 3b

Entry	[Pd] catalyst	[Pd] loading (mol%)	Base	Solvent	T (°C)	Yield (%)
1[b]	[(IPr)Pd(OAc)$_2$]	3.0	K_2CO_3	THF	60	41
2	[(IPr)Pd(OAc)$_2$]	3.0	K_2CO_3	THF	23	>98
3	[(IPr)Pd(OAc)$_2$]	1.0	K_2CO_3	THF	23	50
4	[(IPr)Pd(OAc)$_2$]	1.0	K_2CO_3	toluene	23	56
5	[(IPr)Pd(OAc)$_2$]	1.0	Na_2CO_3	THF	23	25
6	[(IPr)Pd(OAc)$_2$]	1.0	KOH	THF	23	6
7	[(IPr)Pd(OAc)$_2$]	1.0	K_3PO_4	THF	23	17
8	[(IPr)Pd(OAc)$_2$]	1.0	KF	THF	23	>98

[a]Conditions: amide **1a** (1.0 equiv), 4-Tol-B(OH)$_2$ (2.0 equiv), base (3.0 equiv), [Pd] (1.0-3.0 mol%), solvent (0.25 M), water (5.0 equiv), T, 16 h. [b]anhydrous conditions.

The initial promising result was obtained using K_2CO_3 as a base in the presence of [(IPr)Pd(O_2CMe)$_2$] (3 mol%) as a catalyst in THF at 60 °C under anhydrous conditions (entry 1). Pleasingly, the reaction was highly effective at room temperature using water as additive to promote transmetalation (entry 2). However, the yield decreased significantly at lower catalyst loading (entry 3). The use of toluene as a solvent was not beneficial for the reaction (entry 4). The screen of bases revealed that although Na_2CO_3, K_3PO_4 and KOH had a detrimental effect on the reaction (entries 5-7), the use of KF afforded the desired product in >95% yield without cleavage of the sensitive N-Boc activating group (entry 8).

Next, we conducted a comprehensive comparison of [(NHC)Pd(O_2CR)$_2$] precatalysts (Figure 2). As shown, [(NHC)Pd(O_2CR)$_2$] catalysts bearing $MeCO_2$, $PhCO_2$, tBuCO$_2$ groups resulted in quantitative conversion to the desired product (entries 2–4), while the acetate catalyst was the fastest-activating (entry 4).



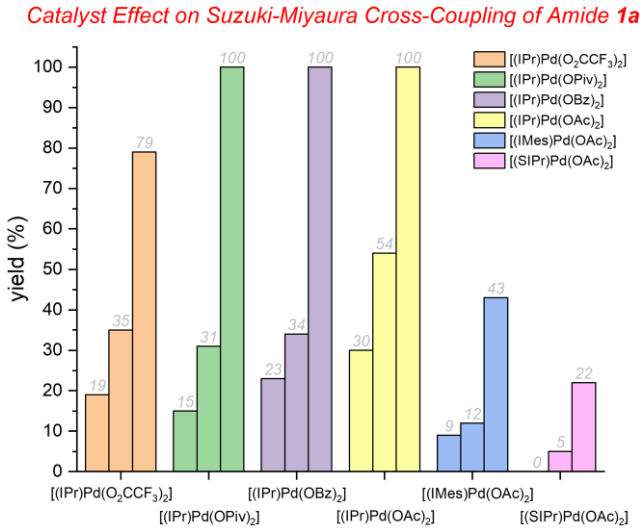
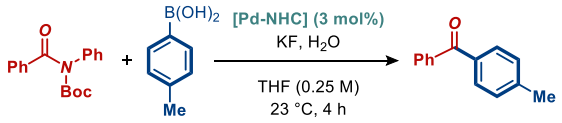


Figure 2. Catalyst effect on the Suzuki-Miyaura cross-coupling of amides using [(NHC)Pd(O$_2$CR)$_2$] precatalysts after 0.5 h, 1 h and 15 h.[a] [a]Conditions: amide (1.0 equiv), 4-Tol-B(OH)$_2$ (2.0 equiv), KF (3.0 equiv), [Pd] (3.0 mol%), 5 equiv H_2O, THF (0.25 M), 23 °C, 15 h. [Pd–NHC] = [(IPr)Pd(O$_2$CCF$_3$)$_2$], [(IPr)Pd(OPiv)$_2$], [(IPr)Pd(OBz)$_2$], [(IPr)Pd(OAc)$_2$], [(IMes)Pd(OAc)$_2$], [(SIPr)Pd(OAc)$_2$]. Note that the bars represent 0.5 h, 1 h and 15 h, respectively.



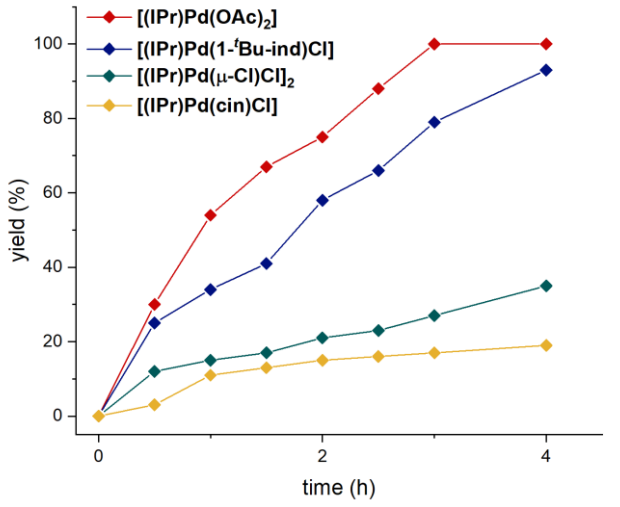


Figure 3. Kinetic studies of the Suzuki-Miyaura cross-coupling of amides using [(NHC)Pd(O$_2$CR)$_2$] precatalysts.[a] [a]Conditions: amide (1.0 equiv), 4-Tol-B(OH)$_2$ (2.0 equiv), KF (3.0 equiv), [Pd] (3.0 mol%), 5 equiv H_2O, THF (0.25 M), 23 °C, 4 h. [Pd–NHC] = [(NHC)Pd(OAc)$_2$], [(IPr)Pd(1-^{t}Bu-ind)Cl], [(IPr)Pd(μ-Cl)Cl]$_2$, [Pd(IPr)(cin)Cl].

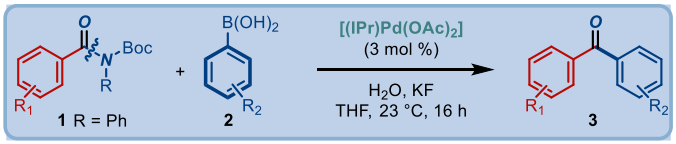
Furthermore, the trifluoroacetate catalyst resulted in high conversion (entry 1). Finally, the use of IMes and SIPr acetate catalysts gave much lower conversion that their IPr congener (entries 5-6), as expected. It is interesting to note that out of the first four complexes, [(IPr)Pd(OAc)$_2$] showed the highest reactivity, indicting that acetate is the favored ancillary ligand under these conditions. Detailed conversion curves have not been determined because [(IPr)Pd(OAc)$_2$] showed the highest reactivity (cf. Figure 3).

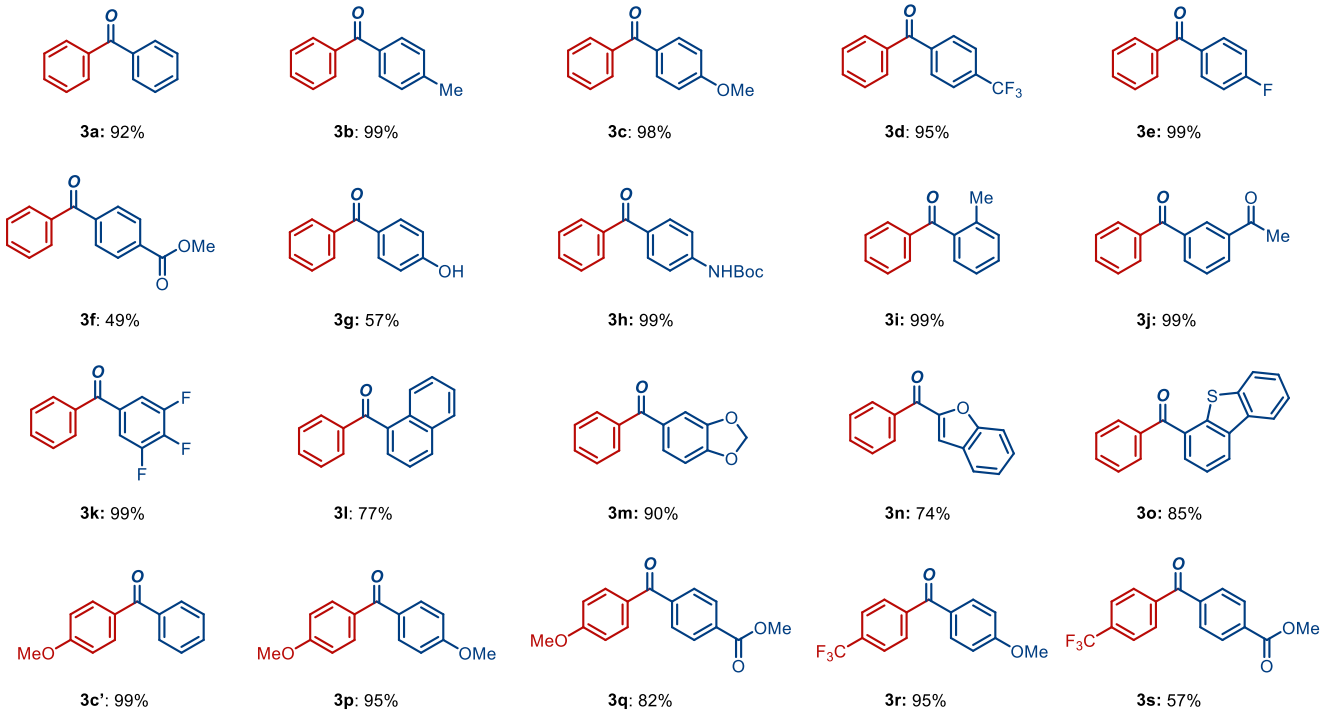
Kinetic studies were conducted to gain insight into the reactivity of [(IPr)Pd(O$_2$CMe)$_2$] as compared to other well-defined Pd(II)–NHCs (Figure 3). As shown, the carboxylate catalyst [(IPr)Pd(OAc)$_2$] outperformed [Pd(NHC)(1-*t*Bu-ind)Cl], [Pd(NHC)(μ-Cl)Cl]$_2$ and [Pd(IPr)(cin)Cl], while [Pd(NHC)(3-Cl-py)Cl$_2$] and [Pd(IPr)(acac)Cl] were unreactive under these conditions due to slow activation. Overall, the results of comparative studies are consistent with the fast activation of [(IPr)Pd(OAc)$_2$] and the role of IPr and OAc as the preferred NHC and throw-away ancillary ligand in this system, respectively.

With the optimum conditions, the substrate scope of the Suzuki–Miyaura cross-coupling of amides at room temperature catalyzed by [(IPr)Pd(O$_2$CMe)$_2$] catalyst was investigated (Scheme 1). As shown, these conditions are highly effective for the cross-coupling with a range of electronically-differentiated boronic acids, such as electron-neutral (**3a**), electron-donating (**3b**–**3c**) and electron-withdrawing (**3d**–**3f**). Importantly, electrophilic functional groups that would be problematic in the standard addition of organometallics are readily tolerated (**3f**). Furthermore, these mild conditions are compatible with acidic protons as exemplified by the substrates bearing free hydroxyl (**3g**) and amine functional groups (**3h**). Moreover, steric hindrance is well-tolerated by this system (**3i**). Meta-substitution is well-compatible (**3j**), as expected. In this case, functional group tolerance to ketones should be noted. Furthermore, challenging polyfluorinated boronic acids that are prone to protodeboronation are well-compatible with this catalyst (**3k**). Moreover, polyarenes (**3l**) and medicinally-relevant heterocycles, such as benzodioxole (**3m**), benzofuran (**3n**) and dibenzothiophene (**3o**) are well-applicable to this coupling protocol. Finally, we have systematically tested several combinations of both reaction components that contain electron-rich and electron-deficient functional groups (**3c'**–**3s**). As shown, electronically-deactivated amide performed well in the reaction, affording the cross-coupling product in quantitative yield (**3c'**). This type of deactivation is compatible with both electron-donating (**3p**) and electron-deficient nucleophiles (**3q**). Furthermore, electron-deficient amide electrophile afforded excellent yield of the cross-coupling product (**3r**). Pleasingly, this system was also compatible with the most challenging combination of electron-deficient electrophile/electron-deficient boronic acid (**3s**). Overall, these examples illustrate excellent functional group compatibility for the challenging N–C(O) amide bond cross-coupling. Importantly, the coupling is performed at practical, room temperature conditions. It is worthwhile to note that ortho-substituents on the amide bond component are well-tolerated in this coupling (see, Scheme 2, **1f**-**1g**). At this point, heterocyclic amides have not been tested. We are currently involved in a comprehensive investigation of heterocyclic substrates in the amide activation platform. These studies will be published in due course.

Next, we evaluated the compatibility of this catalyst system with various amides (Scheme 2).

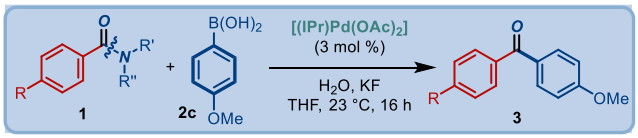
Scheme 1. Scope of the Suzuki-Miyaura Cross-Coupling of Amides by [(NHC)Pd(OAc)$_2$] Catalysis[a]

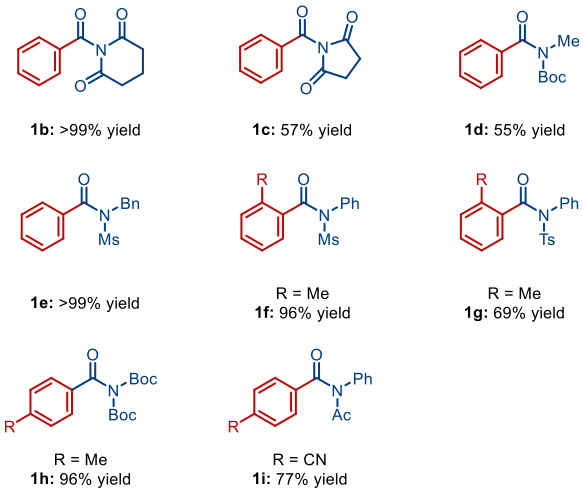




[a]Conditions: amide **1** (1.0 equiv), boronic acid **2** (2.0 equiv), [(IPr)Pd(OAc)$_2$] (3 mol%), KF (3.0 equiv), water (5.0 equiv), THF (0.25 M), 23 °C, 16 h.

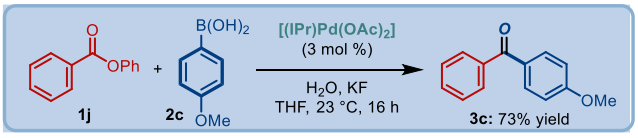
Scheme 2. Scope of the Suzuki-Miyaura Cross-Coupling of Amides by [(NHC)Pd(OAc)$_2$] Catalysis[a]





[a]Conditions: amide **1** (1.0 equiv), boronic acid **2** (2.0 equiv), [(IPr)Pd(OAc)2] (3 mol%), KF (3.0 equiv), water (5.0 equiv), THF (0.25 M), 23 °C, 16 h. See experimental section for details.

Scheme 3. Suzuki–Miyaura Cross-Coupling of Esters by O–C(O) Activation by [(NHC)Pd(OAc)$_2$] Catalysis[a]



[a]Conditions: ester **1j** (1.0 equiv), boronic acid **2c** (2.0 equiv), [(IPr)Pd(OAc)2] (3 mol%), KF (3.0 equiv), water (5.0 equiv), THF (0.25 M), 23 °C, 16 h.

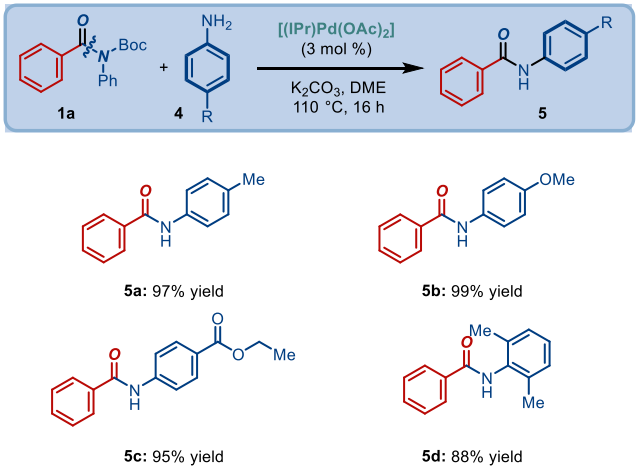
As shown, amides bearing sterically-hindered N-glutarimide (**1b**) and N-succinimide (**1c**) cyclic activating groups are compatible with this carboxylate Pd(II)–NHC catalyst system. Furthermore, N-acylic activation is broadly tolerated, including N-Boc (**1d**) as well as N-Ms (**1e–1f**) and N-Ts (**1g**) activation. Importantly, N,N-Boc$_2$ amides (**1h**) that are readily prepared from common 1° amides are well-compatible with these mild conditions. Finally, N-Ac amides that serve as versatile mono-activated acyclic amide precursors (**1j**) can also be employed in this catalyst system.

Considering the importance of activating ester O–C(O) bonds as an alternative to N-C(O) amide bond activation, we also tested the cross-coupling of phenyl benzoate (Scheme 3). Pleasingly, the [(IPr)Pd(OAc)$_2$] catalyst is also compatible with the activation of ester C(acyl)–O bonds under mild, room temperature conditions.

In view of the importance of transamidation reactions in organic synthesis, we were keen to test the activity of the [(IPr)Pd(OAc)$_2$] catalyst in acyl Buchwald–Hartwig reaction of amides (Scheme 4).[1–3] This manifold has emerged as a mild alternative to stoichiometric protocols, exploiting the versatility of the acyl–metal intermediate in ligand exchange with amines under mild base reaction conditions.[3,5] As shown, we found that this carboxylate Pd(II)–NHC catalyst is well-compatible with Buchwald–Hartwig amination using electron-neutral (**4a**), electron-donating (**4b**) as well as the challenging electron-withdrawing (**4c**) and sterically-hindered (**4d**) anilines. The functional group tolerance towards the ester group should be noted. Interestingly, high temperature is required (110 °C, 16 h) for the more challenging Buchwald-Hartwig amination using [(IPr)Pd(OAc)$_2$], which is similar to other Pd(II)–NHC precatalysts,[12b,15] while the combination of KF/THF conditions with [(IPr)Pd(OAc)$_2$] enables room temperature Suzuki–Miyaura cross-coupling.

Furthermore, the TON was determined for the Suzuki–Miyaura cross-coupling of amide **1a** of 200 (4-Me-C_6H_4-$B(OH)_2$, 0.05 mol%, 110 °C, 16 h) in THF and 388 (4-Me-C_6H_4-$B(OH)_2$, 0.05 mol%, 110 °C, 16 h) in 2-MeTHF, indicating high reactivity of the [(IPr)Pd(OAc)$_2$] catalyst.

Scheme 4. Buchwald–Hartwig Cross-Coupling of Amides by [(NHC)Pd(OAc)2] Catalysis[a]



[a]Conditions: amide **1** (1.0 equiv), aniline **4** (2.0 equiv), [(IPr)Pd(OAc)2] (3 mol%), K_2CO_3 (3.0 equiv), DME (0.25 M), 110 °C, 16 h.

Conclusions

In summary, we have reported the Suzuki–Miyaura and Buchwald–Hartwig cross-coupling of amides by selective N–C(O) cleavage catalyzed by bench-stable, well-defined carboxylate Pd(II)–NHC catalysts. Most importantly, this class of bench-stable Pd(II)–NHCs has been found to promote the cross-coupling under exceedingly mild room temperature conditions. Comparative studies between different carboxylate catalysts as well as various classes of Pd(II)–NHCs demonstrated high reactivity of [(NHC)Pd(O_2CR)$_2$] complexes. These readily accessible Pd(II)–NHC precatalysts show excellent functional group tolerance and are compatible with a broad scope of amide and ester activating groups. Considering the mild conditions for the cross-coupling and the facile access to carboxylate Pd(II)–NHC complexes, we anticipate that this class of bench-stable complexes will find wide application in activation of amide N–C(O) and related acyl X–C(O) bonds.

Experimental Section

General Methods. All compounds reported in the manuscript have been previously described in literature or prepared by the method reported previously unless stated otherwise. All boronic acids are commercially available and have been purchased from Oakwood Chemical. All catalysts used in this study are commercially available or were prepared according to literature report.[16] All experiments involving palladium were performed using standard Schlenk techniques under nitrogen or argon unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. All other general methods have been published.[15a] Oil bath as the heat source has been used for reactions that required heating. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Experimental for characterization purposes. ^{1}H NMR, ^{13}C NMR and HRMS data are reported for all new compounds.

General Procedure for the Synthesis of [(IPr)Pd(OAc)$_2$]. Literature procedure was followed.[16a] An oven-dried vial was equipped with a magnetic stir bar was charged with [Pd(IPr)(μ-Cl)Cl]$_2$ (neat, 1. 0 equiv), AgOAc (typically, 4.1 equiv). Dichloromethane (typically, 0.1 M) was added with vigorous stirring at room temperature and the reaction mixture was stirred for 16 h at 23 °C. After the indicated time, the reaction mixture was filtered through a plug of Celite and rinsed with dichloromethane. The filtrate was concentrated to afford the title product.[16a] Complexes [Pd(IPr)(μ-Cl)Cl]$_2$,[15c] [(IPr)Pd(O_2CCF_3)$_2$],[16b] [(IPr)Pd(O-piv)$_2$],[16b] [IPrPd(OBz)$_2$],[16b] [(IMes)Pd(OAc)$_2$],[16e] [(SIPr)Pd(OAc)$_2$][16e] have been previously described.

General Procedure for Suzuki-Miyaura Cross-Coupling of Amides at RT. An oven-dried vial equipped with a stir bar was charged with an amide substrate (neat, 1.0 equiv), potassium fluoride (typically, 3.0 equiv), boronic acid (typically, 2.0 equiv), [(IPr)Pd(OAc)$_2$] (3.0 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (typically, 0.25 M) and H_2O (typically, 5.0 equiv) were added with vigorous stirring at room temperature. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) to obtain conversion, selectivity, and yield using internal standards and comparison with authentic samples. Purification by chromatography on silica gel (EtOAc/hexane = 1/10) afforded the title product.

Representative Procedure for Suzuki-Miyaura Cross-Coupling of Amides at RT. 1.0 Mmol Scale. An oven-dried vial equipped with a stir bar was charged with *tert*-butyl benzoyl(phenyl)carbamate 297 mg, 1 mmol, 1.0

equiv), potassium fluoride (174 mg, 3 mmol, 3.0 equiv), 4-methoxyphenyl boronic acid (304 mg, 2 mmol, 2.0 equiv), [(IPr)Pd(OAc)$_2$] (19 mg, 0.03 mol, 3 mol%) placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (4 mL, 0.25 M) and H_2O (90 µL, 5 mmol 5.0 equiv) were added with vigorous stirring at room temperature, and the reaction mixture was stirred for 16 h at room temperature. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (80 mL), filtered, and concentrated. Purification by column chromatography on silica gel (solid loading, EtOAc/hexane: 3%-5%) afforded the title product **3c**. Yield 98% (210 mg). White solid. Characterization data are included in the section below.

General Procedure for Buchwald-Hartwig Cross-Coupling of Amides. An oven-dried vial equipped with a stir bar was charged with an amide substrate (neat, 1.0 equiv), potassium carbonate (typically, 3.0 equiv), aniline substrate (typically, 2.0 equiv), [(IPr)Pd(OAc)$_2$] 3.0 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dimethoxyethane (typically, 0.25 M) added with vigorous stirring at 110 °C temperature. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (EtOAc/hexanes = 1:5) afforded the title product. Note: the reactions have been heated in a closed vial at 110 °C. All reactions have been carried out in microwave vials with heavy-wall, Type I, Class A borosilicate. These vials are designed to withstand pressures up to 300 PSI (20 bars) and are equivalent to Fisher-Porter tube. Safety precautions should be used when heating closed reactors above the boiling point of the solvent. For the measurement of TON, the reactions were carried out at 110 °C in 2-MeTHF. Safety precautions should be taken when heating above the boiling point of the solvent.

Benzophenone (3a)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 92% yield (16.7 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.7 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.9, 137.8, 132.6, 130.2, 128.4. NMR spectroscopic data agreed with literature values.[18]

Phenyl(*p*-tolyl)methanone (3b)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), *p*-tolyboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 99% yield (19.4 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.9 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.7, 143.4, 138.1, 135.1, 132.3, 130.5, 130.1, 129.1, 128.4, 21.8. NMR spectroscopic data agreed with literature values.[19]

(4-Methoxyphenyl)(phenyl)methanone (3c)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), 4-methoxy phenylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 98% yield (20.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 163.4, 138.4, 132.7, 132.1, 130.3, 129.9, 128.3, 113.7, 55.6. White solid. NMR spectroscopic data agreed with literature values.[19]

Phenyl(4-(trifluoromethyl)phenyl)methanone (3d)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), 4-trifluoromethyl phenylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 95% yield (23.7 mg).White solid. 1H NMR (500 MHz, CDCl3) δ 7.90 (d, J = 8.0 Hz, 2H), 7.83 – 7.78 (m, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.63 (td, *J* = 7.3, 1.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, CDCl3) δ 195.7, 140.9, 136.9, 133.9 (q, J = 32.7 Hz), 133.2, 130.3, 130.2, 128.7, 125.5 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.6 Hz).^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ -63.0. NMR spectroscopic data agreed with literature values.[20]

(4-Fluorophenyl)(phenyl)methanone (3e)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), (4-fluorophenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 99% yield (19.8 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.79 – 7.75 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.5, 165.5 (d, *J* = 254.4 Hz), 137.6, 133.9 (d, *J* = 3.2 Hz), 132.8 (d, *J* = 9.2 Hz), 132.6, 130.1, 128.5, 115.6 (d, *J* = 21.9 Hz). ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ -106.0. NMR spectroscopic data agreed with literature values.[20]

Methyl 4-benzoylbenzoate (3f)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), 4-methoxycarbonylphenylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 49% yield (11.7 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 6.9 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 3.97 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.2, 166.5, 141.5, 137.1, 133.4, 133.1,

130.3, 129.9, 129.7, 128.6, 52.6. NMR spectroscopic data agreed with literature values.[21]

(4-Hydroxyphenyl)(phenyl)methanone (3g)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), (4-hydroxyphenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 57% yield (11.3 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.6 Hz, 2H), 7.78 – 7.74 (m, 2H), 7.60 – 7.55 (m, 1H), 7.48 (t, J = 7.5 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 5.58 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.8, 159.8, 138.3, 133.1, 132.1, 130.5, 129.9, 128.4, 115.3. NMR spectroscopic data agreed with literature values.[19]

***tert*-Butyl (4-benzoylphenyl)carbamate (3h)**

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), 4-((*tert*-butoxycarbonyl)amino)phenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 99% yield (29.4 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 2H), 7.78 – 7.74 (m, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.47 (dt, *J* = 7.4, 3.4 Hz, 4H), 1.54 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 152.3, 142.6, 138.2, 132.2, 132.1, 131.9, 129.9, 128.4, 117.4, 28.4. NMR spectroscopic data agreed with literature values.[22]

Phenyl(*o*-tolyl) methanone (3i)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), *o*-tolylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 99% yield (19.4 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.8, 138.8, 137.9, 136.9, 133.3, 131.1, 130.4, 130.3, 128.7, 128.6, 125.3, 20.1. NMR spectroscopic data agreed with literature values.[19]

1-(3-Benzoylphenyl)ethan-1-one (3j)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), 3-acetylphenylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 99% yield (22.2 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.99 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.61 (dt, *J* = 10.5, 7.6 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 2.65 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.5, 196.1, 138.2, 137.3, 137.2, 134.4, 133.1, 131.9, 130.2, 129.9, 128.9, 128.7, 26.9. NMR spectroscopic data agreed with literature values.[23]

Phenyl(3,4,5-trifluorophenyl)methanone (3k)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), (3,4,5-trifluorophenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 99% yield (23.3 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.1, 152.1 (dd, J = 10.3, 3.4 Hz), 150.1 (dd, J = 10.3, 3.5 Hz), 143.9 (t, J = 15.3 Hz), 141.9 (t, J = 15.4 Hz), 136.3, 133.3, 133.2 (q, J = 5.6 Hz), 129.9, 128.8, 114.7 (dd, J = 16.6, 5.4 Hz). ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ -132.3, -153.2. NMR spectroscopic data agreed with literature values.[24]

Naphthalen-1-yl(phenyl)methanone (3l)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), naphthalen-1-ylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 77% yield (17.8 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.93 (dd, J = 7.7, 1.6 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.64 – 7.57 (m, 2H), 7.56 – 7.43 (m, 5H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.2, 138.5, 136.5, 133.9, 133.4, 131.4, 131.1, 130.6, 128.6, 128.5, 127.9, 127.4, 126.6, 125.8, 124.5. NMR spectroscopic data agreed with literature values.[23]

Benzo[*d*][1,3]dioxol-5-yl(phenyl)methanone (3m)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), benzo[*d*][1,3]dioxol-5-ylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 90% yield (20.3 mg). Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.60 – 7.54 (m, 1H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.35 (m, 2H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.07 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.3, 151.7, 148.1, 138.3, 132.1, 132.1, 129.9, 128.4, 127.1, 110.1, 107.9, 102.0. NMR spectroscopic data agreed with literature values.[25]

Benzofuran-2-yl(phenyl)methanone (3n)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), benzofuran-2-ylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 74% yield(16.4 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.65 (t, 2H), 7.58 – 7.53 (m, 3H), 7.53 – 7.47 (m, 1H), 7.37 – 7.31 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 184.6, 156.2, 152.4, 137.4, 133.1, 129.6, 128.7, 128.5, 127.2, 124.1, 123.5, 116.7, 112.7. NMR spectroscopic data agreed with literature values.[26]

Dibenzo[*b,d*]thiophen-4-yl(phenyl)methanone (3o)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.1 mmol, 1.0 equiv), dibenzo[*b,d*]thiophen-4-ylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration

and chromatography the title product in 85% yield (24.5 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.9 Hz, 1H), 8.25 – 8.23 (m, 1H), 7.99 – 7.96 (m, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.59 – 7.50 (m, 5H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.0, 142.0, 141.0, 138.3, 137.6, 134.2, 132.1, 131.8, 130.4, 129.8, 128.5, 127.4, 126.0, 124.7, 123.9, 123.1, 121.6. NMR spectroscopic data agreed with literature values.[27]

(4-Methoxyphenyl)(phenyl)methanone (3c')

According to the general procedure, the reaction of *tert*-butyl (4-methoxybenzoyl)(phenyl)carbamate (0.1 mmol, 1.0 equiv), 4-methoxy phenylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 99% yield (21 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 163.4, 138.5, 132.7, 132.1, 130.3, 129.9, 128.3, 113.7, 55.7. White solid. NMR spectroscopic data agreed with literature values.[28]

Bis(4-Methoxyphenyl)methanone (3p)

According to the general procedure, the reaction of *tert*-butyl (4-methoxybenzoyl)(phenyl)carbamate (0.1 mmol,1.0 equiv), 4-methoxyphenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 95% yield (23 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 4H), 6.98 – 6.94 (m, 4H), 3.88 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 194.6, 162.9, 132.4, 130.9, 113.6, 55.6. NMR spectroscopic data agreed with literature values.[28]

Methyl 4-(4-methoxybenzoyl)benzoate (3q)

According to the general procedure, the reaction of *tert*-butyl (4-methoxybenzoyl)(phenyl)carbamate (0.1 mmol,1.0 equiv), 4-methoxycarbonylphenylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 82% yield (22.1 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.81 (dd, *J* = 16.0, 8.6 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 1H), 3.97 (s, 2H), 3.90 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 194.9, 166.5, 163.7, 142.3, 132.9, 132.8, 129.7, 129.6, 113.9, 55.7, 52.6. NMR spectroscopic data agreed with literature values.[29]

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (3r)

According to the general procedure, the reaction of *tert*-butyl phenyl(4-(trifluoromethyl)benzoyl)carbamate (0.1 mmol,1.0 equiv), 4-methoxyphenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 95% yield (26.6 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 10.0, 8.4 Hz, 4H), 7.74 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 194.4, 163.9, 141.7, 133.4 (q, *J* = 32.7 Hz), 132.8, 129.9, 129.5, 125.4 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 272.6 Hz), 113.9, 55.7. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ -62.9. NMR spectroscopic data agreed with literature values.[30]

Methyl 4-(4-(trifluoromethyl)benzoyl)benzoate (3s)

According to the general procedure, the reaction of *tert*-butyl phenyl(4-(trifluoromethyl)benzoyl)carbamate (0.1 mmol,1.0 equiv), 4-methoxycarbonylphenylboronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 57% yield (17.5 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 3.97 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 194.4, 163.9, 141.7, 133.4 (d, J = 32.7 Hz), 133.1, 132.8, 129.9, 129.5, 125.4 (q, J = 3.7 Hz), 123.9 (q, J = 272.4 Hz), 114.0, 55.7. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ -62.9. NMR spectroscopic data agreed with literature values.[31]

(4-Methoxyphenyl)(phenyl)methanone (3c, from 1b)

According to the general procedure, the reaction of 1-benzoylpiperidine-2,6-dione (0.1 mmol, 1.0 equiv), 4-methoxyphenyl boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 99% yield (21 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 2H), 7.76 (dd, J = 8.2, 1.4 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, CDCl3) δ 195.7, 163.3, 138.4, 132.7, 132.0, 130.3, 129.9, 128.3, 113.7, 55.6. NMR spectroscopic data agreed with literature values.[19]

(4-Methoxyphenyl)(phenyl)methanone (3c, from 1c)

According to the general procedure, the reaction of 1-benzoylpyrrolidine-2,5-dione (0.1 mmol, 1.0 equiv), 4-methoxyphenyl boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 57% yield (12 mg). White solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.83 (d, J = 8.5 Hz, 2H), 7.76 (dd, J = 8.0, 1.6 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.47 (t, J = 7.5 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 163.4, 138.4, 132.7, 132.0, 130.3, 129.9, 128.3, 113.7, 55.6. NMR spectroscopic data agreed with literature values.[19]

(4-Methoxyphenyl)(phenyl)methanone (3c, from 1d)

According to the general procedure, the reaction of *tert*-butyl benzoyl(methyl)carbamate (0.1 mmol, 1.0 equiv), 4-methoxyphenyl boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 55% yield (11.6 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 163.4, 138.4, 132.7, 132.0, 130.3, 129.9, 128.3, 113.7, 55.7. NMR spectroscopic data agreed with literature values.[19]

(4-Methoxyphenyl)(phenyl)methanone (3c, from 1e)

According to the general procedure, the reaction of *N*-benzyl-*N*-(methylsulfonyl)benzamide (0.1 mmol, 1.0 equiv), 4-methoxyphenyl boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 99% yield (21 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 7.4 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 163.4, 138.4, 132.7, 132.0, 130.3, 129.9, 129.1, 128.3, 113.7, 55.6. NMR spectroscopic data agreed with literature values.[19]

(4-Methoxyphenyl)(*o*-tolyl)methanone (3u, from 1f)

According to the general procedure, the reaction of 2-methyl-*N*-(methylsulfonyl)-*N*-phenylbenzamide (0.1 mmol,1.0 equiv), 4-methoxyphenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 96% yield (21.7 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.37 (td, *J* = 7.4, 1.5 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.5, 163.8, 139.3, 136.3, 132.7, 131.00, 130.7, 129.9, 128.1, 125.3, 113.8, 55.7, 19.9. NMR spectroscopic data agreed with literature values.[33]

(4-Methoxyphenyl)(*o*-tolyl)methanone (3u, from 1g)

According to the general procedure, the reaction of 2-methyl-*N*-phenyl-*N*-tosylbenzamide (0.1 mmol,1.0 equiv), 4-methoxyphenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 69% yield (19.9 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.37 (td, *J* = 7.4, 1.4 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.5, 163.8, 139.3, 136.3, 132.7, 131.0, 130.7, 129.9, 128.1, 125.3, 113.8, 55.7, 19.9. NMR spectroscopic data agreed with literature values.[33]

(4-Methoxyphenyl)(*p*-tolyl)methanone (3t, from 1h)

According to the general procedure, the reaction of *tert*-butyl(tert-butoxycarbonyl)(4-methylbenzoyl)carbamate (0.1 mmol,1.0 equiv), 4-methoxyphenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 96% yield (21.7 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.5, 163.2, 142.8, 135.6, 132.6, 130.6, 130.2, 129.0, 113.6, 55.6, 21.8. NMR spectroscopic data agreed with literature values.[32]

4-(4-Methoxybenzoyl)benzonitrile (3v from 1i)

According to the general procedure, the reaction of *N*-acetyl-4-cyano-*N*-phenylbenzamide(0.1 mmol, 1.0 equiv), (4-methoxyphenyl)boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 77% yield (18.2 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 6H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.9, 164.1, 142.2, 132.8, 132.3, 130.1, 129.1, 118.3, 115.3, 114.1, 55.8. NMR spectroscopic data agreed with literature values.[34]

(4-Methoxyphenyl)(phenyl)methanone (3c, from 1j)

According to the general procedure, the reaction of phenyl benzoate (0.1 mmol, 1.0 equiv), 4-methoxyphenyl boronic acid (2.0 equiv), H_2O (5.0 equiv), KF (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in THF (0.25 M) for 16 h at 23 °C, afforded after filtration and chromatography the title product in 73% yield (16 mg). White solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.84 (d, J = 8.5 Hz, 2H), 7.75 (dd, J = 8.0, 1.6 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.47 (t, J = 7.5 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 163.4, 138.4, 132.7, 132.0, 130.3, 129.9, 128.3, 113.7, 55.7. NMR spectroscopic data agreed with literature values.[34]

***N*-(*p*-tolyl)Benzamide (5a)**

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.10 mmol, 1.0 equiv), *p*-toluidine (2.0 equiv), K_2CO_3 (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in DME (0.25 M) for 16 h at 110 °C, afforded after filtration and chromatography the title product in 97% yield (21.4 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.1 Hz, 2H), 7.75 (s, 1H), 7.57 – 7.46 (m, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.7, 135.5, 134.4, 131.9, 129.8, 128.9, 127.1, 120.4, 21.1. NMR spectroscopic data agreed with literature values.[34]

***N*-(4-Methoxyphenyl)benzamide (5b)**

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.10 mmol, 1.0 equiv), 4-methoxyaniline (2.0 equiv), K_2CO_3 (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in DME (0.25 M) for 16 h at 110 °C, afforded after filtration and chromatography the title product in 95% yield(21.5 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.71 (s, 1H), 7.57 – 7.52 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.3, 162.7, 138.3, 129.2, 129.0, 127.3, 124.5, 120.3, 114.2, 55.6. NMR spectroscopic data agreed with literature values.[35]

Ethyl 4-benzamidobenzoate (5c)

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.10 mmol, 1.0 equiv), ethyl 4-aminobenzoate (2.0 equiv), K_2CO_3 (3.0 equiv) and [(IPr)Pd(OAc)$_2$] (3.0 mol%) in DME (0.25 M) for 16 h at 110 °C, afforded after filtration and chromatography the title product in 95% yield (25.5 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 2H), 8.03 (s, 1H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.50 (dd, *J* = 8.3, 6.8 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.3, 165.9, 142.2, 134.7, 132.4, 131.0, 129.0, 127.2, 125.4, 119.3, 61.1, 14.5. NMR spectroscopic data agreed with literature values.[35]

***N*-(2,6-Dimethylphenyl)benzamide (5d)**

According to the general procedure, the reaction of *tert*-butyl benzoyl(phenyl)carbamate (0.10 mmol, 1.0 equiv),

2,6-dimethylaniline (2.0 equiv), K_2CO_3 (3.0 equiv) and $[(IPr)Pd(OAc)_2]$ (3.0 mol%) in DME (0.25 M) for 16 h at 110 °C, afforded after filtration and chromatography the title product in 88% yield (19.8 mg). White solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.36 (s, 1H), 7.14 (q, *J* = 5.0 Hz, 3H), 2.30 (s, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.0, 135.7, 134.7, 134.0, 132.0, 128.9, 128.4, 127.6, 127.4, 18.7. NMR spectroscopic data agreed with literature values. [36]

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

^1H NMR, $^{13}C\{^1H\}$ NMR and $^{19}F\{^1H\}$ NMR spectra. 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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