DOI: 10.1002/adsc.201300436

Palladium-Catalyzed Direct Alkoxycarbonylation of Aromatic C–H Bonds *via* Selective C–C Cleavage of α-Keto Esters

Wei Zhou,[a] Pinhua Li,[a] Yicheng Zhang,[a] and Lei Wang[a,b,*]

[a] Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, People's Republic of China
Fax: (+86)-561-309-0518; phone: (+86)-561-380-2069; e-mail: leiwang@chnu.edu.cn
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, People's Republic of China

Received: May 18, 2013; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300436.

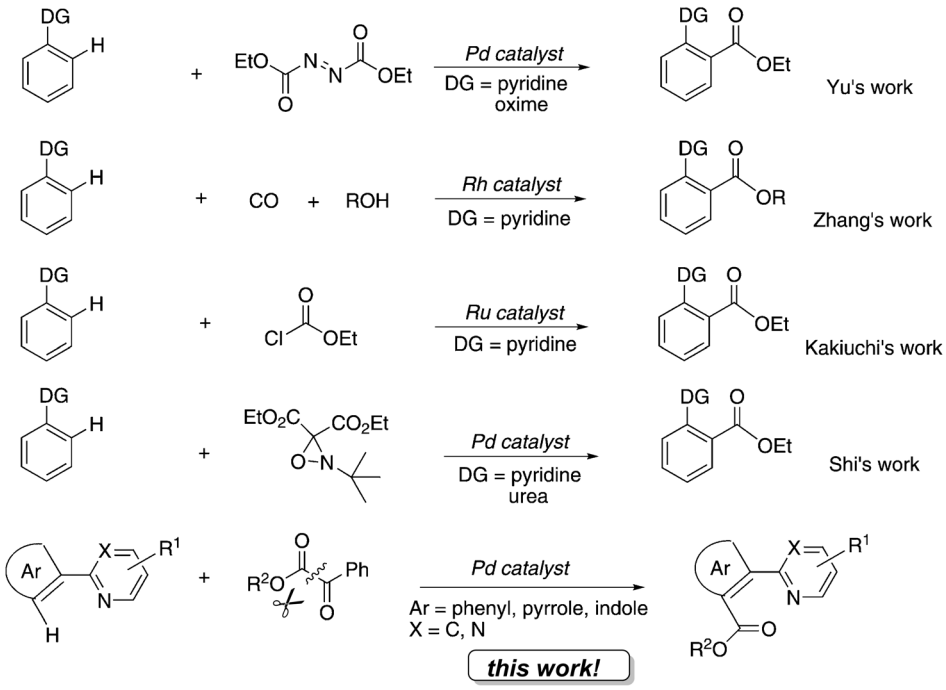
Abstract: A novel palladium-catalyzed direct alkoxycarbonylation of 2-arylpyridines, 2-arylquinolines, benzo[*h*]quinolines, 2-phenylpyrimidines, *N*-pyrimidine pyrroles and *N*-pyrimidine indoles *via* aromatic C–H bond activation and selective C–C cleavage of α-keto esters has been developed. The method has the advantages of wide functional group tolerance, high selectivity, broad range of substrates and good yields.

Keywords: alkoxycarbonylation; C–C bond cleavage; C–H bond activation; α-keto esters; palladium catalysts

Introduction

Esters are very important in the chemical and pharmaceutical industries, and they have been widely used in the production of valuable compounds, such as polymers, fragrances, fatty acids, etc.[1] There are two well-known traditional approaches for the preparation of esters. One is based on the reaction of activated acid derivatives (acyl chlorides and anhydrides) with alcohols,[2] and the other is the transition metal-catalyzed cross-coupling reaction of aryl halides with carbon monoxide.[3] However, the above methods have the drawbacks of multiple-step reactions, and necessity to handle a hazardous gas which is often under high pressure, and pre-functionalized substrates are needed in some cases. Therefore, exploiting a simple and efficient strategy to access esters is highly desirable.

Recently, the direct alkoxycarbonylation of simple C–H bonds,[4] a method involving C–H bond activation and functionalization, has received much attention in the construction of the ester group on account of its atom economy and simplified procedure in comparison with the traditional strategies.[5,6] For the purpose of obtaining selective activation and functionalization of the C–H bond to a C–CO_2R group, significant achievements have been made by means of directing functional groups in the presence of a catalyst.[7] In 2008, Yu reported the palladium-catalyzed oxidative ethoxycarbonylation of the aromatic C–H bond with diethyl azodicarboxylate.[8] In 2009, Zhang and co-workers developed the rhodium-catalyzed direct oxidative carbonylation of the aromatic C–H bond with CO and alcohol.[9] In the same year, the ruthenium-catalyzed direct alkoxycarbonylation of the C–H bond with carbamoyl chlorides was accomplished by Kakiuchi and co-workers.[10] In 2011, Shi and co-workers also achieved ethoxycarbonylation of the aromatic C–H bond *via* C–C bond cleavage of oxaziridine.[11] Most recently, we have developed an efficient carbo-acylation reaction of the aromatic C–H bond with α-diketones *via* Pd-catalyzed C–H activation and C–C bond cleavage for the synthesis of aryl ketones.[12] However, there is hardly any formation of the desired alkoxycarbonylation products in the reactions of 2-phenylpyridine with dimethyl oxalate or diethyl oxalate. Very recently, Tan and co-workers reported a Pd-catalyzed direct alkoxycarbonylation of anilides using glyoxylates for the synthesis of anthranilic esters.[13] Inspired by Tan's work, we envisioned that α-keto esters could be utilized as the alkoxycarbonylation reagents in the palladium-catalyzed aromatic C–H bond alkoxycarbonylation. To our delight, 2-phenylpyridine reacted with ethyl benzoylformate smoothly and generated the corresponding (2′-alkoxycarbonyl)-2-phenylpyridines in good yields. To develop an alternative and concise pathway to the direct alkoxycarbonylation of the aromatic C–H bond, herein we wish to report this novel and efficient Pd-catalyzed direct alkoxycarbonylation of aromatic C–H bonds



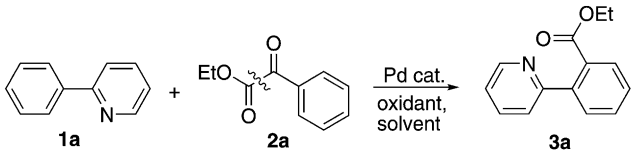
Scheme 1. The direct alkoxycarbonylation of the aromatic C–H bond.

through selective C–C cleavage of α-keto esters (Scheme 1). As far as we know, this is the first example that utilizes α-keto esters as the alkoxycarbonylation reagents in the palladium-catalyzed aromatic C–H bond alkoxycarbonylation of 2-arylpyridines, 2-arylquinolines, benzo[*h*]quinolines, 2-phenylpyrimidines, *N*-pyrimidine pyrroles and *N*-pyrimidine indoles.

Results and Discussion

In order to realize the direct alkoxycarbonylation of the C–H bond *via* selective C–C bond cleavage of α-keto esters, 2-phenylpyridine (**1a**) and ethyl benzoylformate (**2a**) were selected as model substrates. At the beginning, an intensive screening of Pd salts was investigated under the conditions of THF as solvent and *tert*-butyl hydroperoxide (TBHP) as oxidant. To our delight, $Pd(OAc)_2$ exhibited the highest activity among the Pd sources tested in Table 1, and the desired product **3a** was isolated in 81% yield (Table 1, entry 1). Other Pd sources, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PCy_3)_2Cl_2$, $Pd(CH_3CN)_2Cl_2$, and $Pd(PPh_3)_4$ were less effective and **3a** was obtained in 57–73% yields (Table 1, entries 2–6). Then, a variety of solvents were examined and the results indicated that THF was the best reaction medium. Other solvents, such as diglyme, dioxane, toluene and NMP gave the inferior yields of **3a** in 17–66% (Table 1, entries 7–10). However, when the model reaction was carried out in DCE, DMSO or DMF, no desired product **3a** was detected (Table 1, entries 11–13). In addition, the influence of oxidants on the reaction was explored. Among the tested organic oxidants, including *tert*-

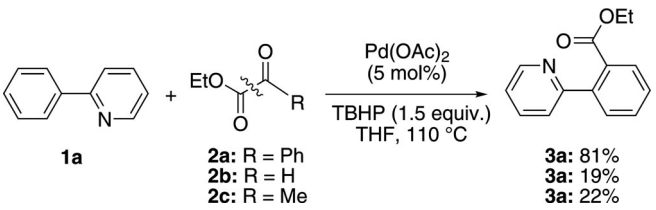
Table 1. Optimization of the reaction conditions.[a]



Entry	Pd catalyst	Solvent	Oxidant	Yield [%][b]
1	$Pd(OAc)_2$	THF	TBHP	81
2	$PdCl_2$	THF	TBHP	73
3	$Pd(PPh_3)_2Cl_2$	THF	TBHP	71
4	$Pd(PCy_3)_2Cl_2$	THF	TBHP	66
5	$Pd(CH_3CN)_2Cl_2$	THF	TBHP	59
6	$Pd(PPh_3)_4$	THF	TBHP	57
7	$Pd(OAc)_2$	diglyme	TBHP	66
8	$Pd(OAc)_2$	dioxane	TBHP	53
9	$Pd(OAc)_2$	toluene	TBHP	23
10	$Pd(OAc)_2$	NMP	TBHP	17
11	$Pd(OAc)_2$	DCE	TBHP	0
12	$Pd(OAc)_2$	DMSO	TBHP	0
13	$Pd(OAc)_2$	DMF	TBHP	0
14	$Pd(OAc)_2$	THF	DBHP	71
15	$Pd(OAc)_2$	THF	TBPB	22
16	$Pd(OAc)_2$	THF	DTBH	33
17	$Pd(OAc)_2$	THF	PAA	39

[a] *Reaction conditions:* 2-phenylpyridine (**1a**, 0.50 mmol), α-keto ester (ethyl benzoylformate, **2a**, 0.75 mmol), Pd catalyst (5.0 mol%), oxidant (0.75 mmol), solvent (anhydrous, 2.0 mL), sealed tube, 110 °C, 12 h.

[b] Isolated yields.



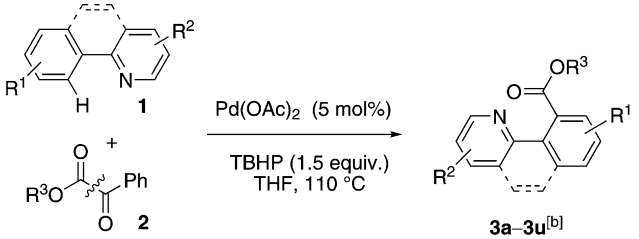
Scheme 2. The reactivity of **2a**, **2b** and **2c** with **1a**.

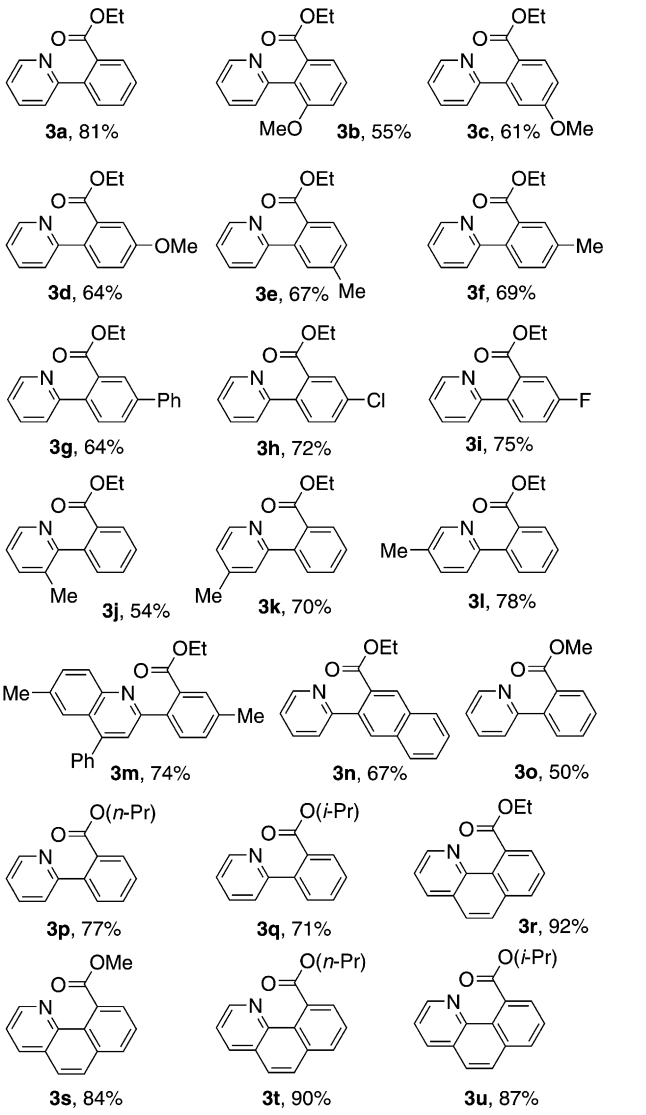
butyl hydroperoxide (TBHP), α,α-dimethylbenzyl hydroperoxide (DBHP), *tert*-butyl peroxybenzoate (TBPB), di-*tert*-butyl peroxide (DTBP), and peroxyacetic acid (PAA), TBHP (anhydrous) was the most effective one (Table 1, entries 14–17). Further optimization of the reaction conditions demonstrated that the model reaction was completed in THF (sealed tube) at 110 °C for 12 h.

As a source of the ethyloxycarbonyl group *via* C–C cleavage of α-keto esters, ethyl 2-oxoacetate (**2b**)[14] and ethyl 2-oxopropanoate (**2c**) were much less reactive compared with ethyl benzoylformate (**2a**) (Scheme 2).

Under the optimized reaction parameters [$Pd(OAc)_2$ (5.0 mol%) as the catalyst, TBHP (anhydrous, 1.5 equiv.) in THF at 110 °C for 12 h], we turned our attention to an investigation of the scope of the alkoxycarbonylation reactions between arylpyridines and α-keto esters. As can be seen from Table 2, the reactions of arylpyridines with α-keto esters indicated wide functional group tolerance, broad range of substrates, high selectivity and good yields of the desired products. 2-Phenylpyridines with an electron-donating group, such as MeO or Me on the phenyl rings reacted with ethyl benzoylformate (**2a**) smoothly and generated the direct alkoxycarbonylation products **3b–f** in 55–69% yields. Meanwhile, 2-phenylpyridines with an electron-withdrawing group, including Cl and F on the phenyl rings also exhibited high reactivity and generated **3h** and **3i** in 72% and 75% yields, respectively. Moreover, a phenyl substituent on 2-phenylpyridine was also well tolerated and the expected product **3g** was obtained in 64% yield. On the other hand, 2-phenylpyridines with Me on the pyridine rings also reacted with **2a** and gave the corresponding product **3j–l** in 54–78% yields. An obvious *ortho*-position effect was observed in the reactions (**3b** and **3j**). It was gratifying to find that the special substrates, 6-methyl-4-phenyl-2-(*p*-tolyl)quinoline and 2-(naphthalen-2-yl)pyridine also participated in the reactions and afforded the direct alkoxycarbonylation products **3m** and **3n** in 74% and 67% yields under the optimized reaction conditions. Notably, a series of α-keto esters, such as methyl benzoylformate, ethyl benzoylformate, propyl benzoylformate and isopropyl benzoylformate also reacted with 2-phenylpyridine and benzo[*h*]quinoline smoothly and the corresponding products **3o–u** were obtained in 50–92% yields, and ethyl benzoylformate showed the highest reactivity. It should be noted that the reactivity of benzo[*h*]quino-

Table 2. The scope of 2-arylpyridines and benzoylformates.[a]

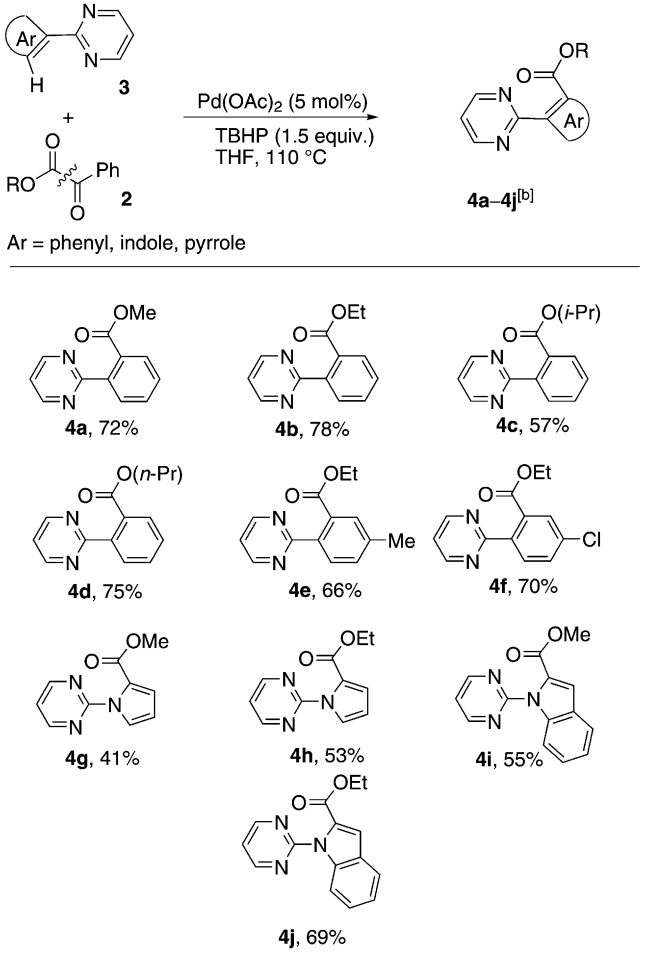




[a] *Reaction conditions:* arylpyridine or quinoline (**1**, 0.50 mmol), α-keto ester (**2**, 0.75 mmol), $Pd(OAc)_2$ (0.025 mmol), anhydrous TBHP (0.75 mmol), anhydrous THF (2.0 mL), sealed tube, 110 °C, 12 h.

[b] Isolated yields.

Table 3. The scope of 2-arylpyrimidines and benzoylformates.[a]



[a] *Reaction conditions:* 2-arylpyrimidine (**3**, 0.50 mmol), α-keto ester (**2**, 0.75 mmol), $Pd(OAc)_2$ (0.025 mmol), anhydrous TBHP (0.75 mmol), anhydrous THF (2.0 mL), sealed tube, 110 °C, 12 h.

[b] Isolated yields.

line is higher than that of 2-phenylpyridine when they reacted with α-keto esters (**3a** *vs.* **3r**, **3o** *vs.* **3s**, **3p** *vs.* **3t**, **3q** *vs.* **3u**). The higher reactivity of benzo[*h*]quinoline may result from its planar structure.[14,15]

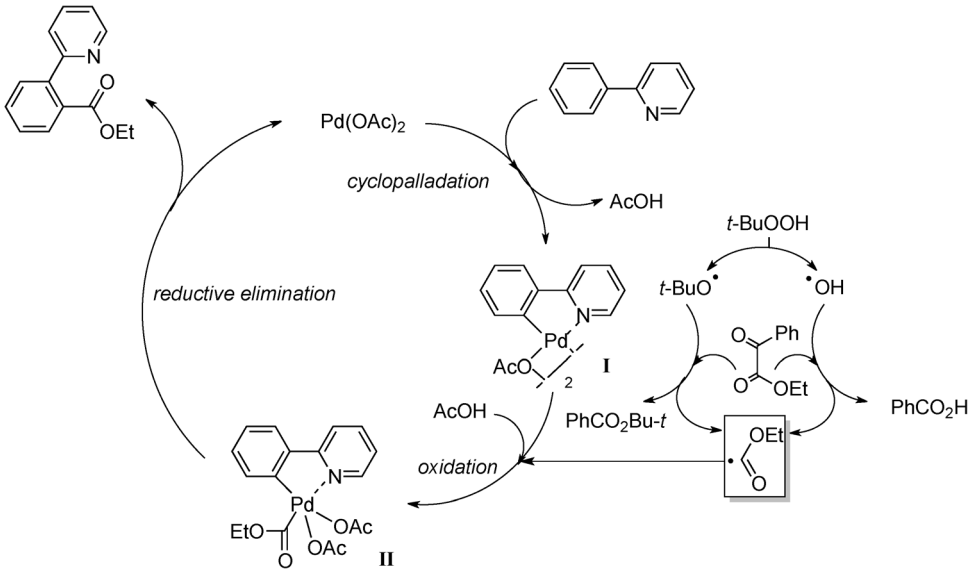
Furthermore, pyrimidine, which is similar to pyridine in molecular structure, was also explored as the directing group for the direct C–H bond alkoxycarbonylation. As can be seen from Table 3, pyrimidine is an efficient directing group and the alkoxycarbonylation generated the corresponding products (Table 3, **4a**–**j**) in moderate to good yields under the standard conditions.

A series of α-keto esters, such as methyl benzoylformate, ethyl benzoylformate, isopropyl benzoylformate and propyl benzoylformate reacted with 2-phenylpyrimidine smoothly and the desired products **4a**–**d** were obtained in 57–78% yields. Moreover, 2-phenylpyrimidines with Me or Cl on the phenyl rings reacted with ethyl benzoylformate and afforded the alkoxycarbonylation products **4e** and **4f** in 66% and 70% yields, respectively. For the aims of broad substrates scope, we turned our attention to the alkoxycarbonylation of heteroarenes, such as pyrrole and indole through the direct C–H bond functionalization. As shown in Table 3, *N*-pyrimidinylpyrrole and *N*-pyrimidinylindole also worked efficiently and gave the corresponding alkoxycarbonylation products **4g**, **4h**, **4i** and **4j** in 41%, 53%, 55% and 69% yields, respectively. This direct alkoxycarbonylation of heteroarenes methodology was valuable for the further transformation of the obtained pyrrole and indole derivatives. However, finding a suitable direct C–H bond alkoxycarbonylation system for those substrates which contain directing groups including ketones, acetamides, oximes, imines and azobenzenes is a great challenge up till now.

During the separation of products in the model reaction, *tert*-butyl benzoate and benzoic acid were also isolated as by-products. What is more, when a radical scavenger, 2,2,6,6-tetramethylpiperidyl 1-oxyl or ascorbic acid was added to the model reaction,[16] the direct C–H bond alkoxycarbonylation was almost completely shut down, suggesting that this reaction may involve a radical process. Although the exact mechanism is still not clear at present, a possible reaction mechanism was shown in Scheme 3. Firstly, a cyclopalladated dimer intermediate **I** by a chelate-directed C(benzene)–H activation of 2-phenylpyridine with $Pd(OAc)_2$ was formed. The obtained **I** then reacted with ethoxycarbonyl radical, which was generated *in situ* by the reaction of ethyl benzoylformate with TBHP,[12,17] providing a reactive Pd(IV) intermediate **II**.[14,18] Finally, carbon-carbon bond formation through a reductive elimination of **II** generated the corresponding product and regeneration of Pd(II) species for the next run. It is important to note that there is no carbon-acylation product, (2′-benzoyl)-2-phenylpyridine was formed in the reaction of 2-phenylpyridine and ethyl benzoylformate. This is probably the superior reactivity of ethoxycarbonyl radical to benzoyl radical in the reaction.[12,17]

Conclusions

In conclusion, a novel and efficient Pd-catalyzed direct alkoxycarbonylation of aromatic C–H bonds *via* selective C–C cleavage of α-keto esters to aromatic esters has been developed. In the presence of TBHP and $Pd(OAc)_2$, the reactions of 2-arylpyridines, 2-arylquinolines, benzo[*h*]quinolines, 2-phenylpyrimidines, *N*-pyrimidinylpyrroles and *N*-pyrimidinylindoles with diverse benzoylformates proceeded smoothly to generate the desired alkoxycarbonylation



Scheme 3. Proposed reaction mechanism.

products in good yields. The method has the advantages of wide functional group tolerance, high selectivity, broad range of substrates and excellent selectivity. The detailed mechanistic study and its further application are currently underway.

Experimental Section

General Considerations

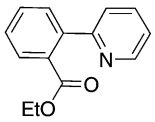
All the reactions of 2-arylpyridines and α-keto esters were carried out under an air atmosphere. THF was dried over sodium and freshly distilled. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS instrument using ESI. 2-Arylpyridines were prepared by Suzuki coupling[19] from boronic acids with 2-bromopyridine. 6-Methyl-4-phenyl-2-(*p*-tolyl)quinoline[20] was prepared by tandem reaction of the corresponding aldehyde, alkyne, and amine. General chemicals and solvents were purchased from commercial suppliers and used without further purification.

Typical Procedure for the Alkoxycarbonylation of 2-Arylpyridine

Under an air atmosphere, a sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with 2-phenylpyridine (**1a**, 0.50 mmol), ethyl benzoylformate (**2a**, 0.75 mmol), $Pd(OAc)_2$ (0.025 mmol), anhydrous *t*-BuOOH (TBHP, 0.75 mmol), and freshly distilled THF (2.0 mL). The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 110 °C for 12 h. After the reaction was completed, it was cooled to room temperature and quenched with water and extracted with ethyl acetate. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate) to give the desired product ethyl 2-(pyridin-2-yl)benzoate (**3a**).

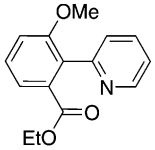
Characterization Data for all Products

Ethyl 2-(pyridin-2-yl)benzoate (3a):[8] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.64$ (d, $J = 4.8$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H),



7.76–7.72 (m, 1H), 7.57–7.54 (m, 2H), 7.48–7.44 (m, 2H), 7.27–7.24 (m, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 1.05 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 168.65$, 158.80, 148.88, 140.91, 136.07, 131.73, 130.96, 129.68, 128.18, 122.77, 121.90, 60.82, 13.71.

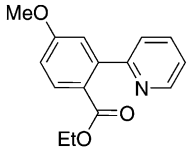
Ethyl 3-methoxy-2-(pyridin-2-yl)benzoate (3b): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.64$ (d, $J = 4.8$ Hz, 1H), 7.74–7.69



(m, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.45–7.40 (m, 2H), 7.25–7.22 (m, 1H), 7.13 (d, $J = 8.4$ Hz, 1H), 4.03 (q, $J = 7.2$ Hz, 2H), 3.76 (s, 3H), 0.98 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 167.76$, 156.99, 156.02, 148.76, 135.25,

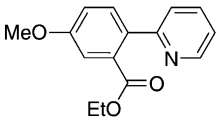
133.20, 130.28, 129.17, 125.12, 121.97, 121.65, 114.26, 60.66, 56.03, 13.66; HR-MS (ESI): m/z = 258.1133 ([MH]$^+$), calcd. for $C_{15}H_{16}NO_3$: 258.1130.

Ethyl 4-methoxy-2-(pyridin-2-yl)benzoate (3c):[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 4.4 Hz, 1H),



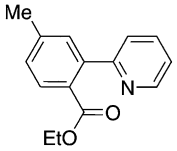
7.90 (d, J = 8.4 Hz, 1H), 7.74–7.70 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.29–7.25 (m, 1H), 7.00–6.95 (m, 2H), 4.09 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.58, 161.76, 159.33, 148.79, 143.78, 135.83, 132.23, 123.24, 123.16, 121.96, 115.41, 113.61, 60.48, 55.48, 13.76.

Ethyl 5-methoxy-2-(pyridin-2-yl)benzoate (3d):[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (d, J = 4.8 Hz, 1H),



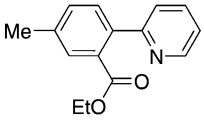
7.73–7.69 (m, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 2.8 Hz, 1H), 7.23–7.20 (m, 1H), 7.09–7.06 (m, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.88 (s, 3H), 1.05 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.70, 159.49, 158.48, 148.85, 136.02, 133.36, 133.08, 130.98, 122.60, 121.51, 116.87, 114.61, 60.97, 55.54, 13.72.

Ethyl 4-methyl-2-(pyridin-2-yl)benzoate (3e):[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, J = 4.4 Hz, 1H), 7.78 (d, J =



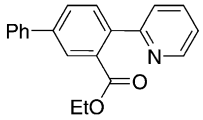
8.0 Hz, 1H), 7.74–7.69 (m, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 7.27–7.23 (m, 2H), 4.11 (q, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.36, 159.25, 148.87, 141.58, 141.31, 135.83, 130.61, 130.01, 128.80, 128.54, 122.98, 121.78, 60.63, 21.34, 13.73.

Ethyl 5-methyl-2-(pyridin-2-yl)benzoate (3f:)[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, J = 4.8 Hz, 1H), 7.73–7.69



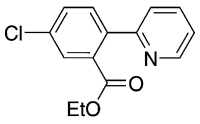
(m, 1H), 7.65 (s, 1H), 7.44–7.41 (m, 2H), 7.35–7.33 (m, 1H), 7.24–7.21 (m, 1H), 4.12 (q, J = 7.2 Hz, 2H), 2.42 (s, 3H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.75, 158.67, 148.66, 138.20, 137.93, 136.04, 131.57, 131.50, 130.16, 129.60, 122.73, 121.68, 60.71, 20.88, 13.66.

Ethyl 4-(pyridin-2-yl)-[1,1′-biphenyl]-3-carboxylate (3g): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (d, J = 4.4, 1H), 8.09



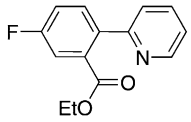
(s, 1H), 7.81–7.75 (m, 2H), 7.69–7.64 (m, 3H), 7.54–7.47 (m, 3H), 7.42–7.38 (m, 1H), 7.30–7.27 (m, 1H), 4.19 (q, J = 6.8 Hz, 2H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.74, 158.40, 148.94, 141.26, 139.63, 139.52, 136.15, 132.31, 130.21, 129.41, 128.86, 128.37, 127.83, 127.10, 122.77, 121.96, 60.97, 13.76; HR-MS (ESI): m/z = 304.1343 ([MH]$^+$), calcd. for $C_{20}H_{18}NO_2$: 304.1338.

Ethyl 5-chloro-2-(pyridin-2-yl)benzoate (3h):[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, J = 4.4 Hz, 1H), 7.81 (d, J =



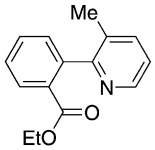
1.6 Hz, 1H), 7.77–7.73 (m, 1H), 7.54–7.48 (m, 2H), 7.44 (d, J = 7.6 Hz, 1H), 7.29–7.26 (m, 1H), 4.15 (q, J = 7.2 Hz, 2H), 1.08 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.39, 157.60, 149.03, 139.25, 136.25, 134.38, 133.27, 131.04, 130.93, 129.71, 122.73, 122.22, 61.25, 13.72.

Ethyl 5-fluoro-2-(pyridin-2-yl)benzoate (3i): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, J = 4.4 Hz, 1H), 7.76–7.72



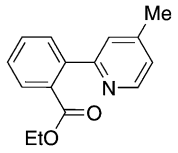
(m, 1H), 7.56–7.51 (m, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.28–7.22 (m, 2H), 4.15 (q, J = 7.2 Hz, 2H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.27 (d, J = 2.5 Hz), 162.23 (d, J = 247.7 Hz), 157.80, 148.87, 137.41 (d, J = 3.5 Hz), 136.22, 133.59 (d, J = 17.4 Hz), 131.64 (d, J = 7.9 Hz), 122.82, 122.05, 117.89 (d, J = 21.7 Hz), 116.76 (d, J = 23.5 Hz), 61.19, 13.66; HR-MS (ESI): m/z = 246.0933 ([MH]$^+$), calcd. for $C_{14}H_{13}FNO_2$: 246.0930.

Ethyl 2-(3-methylpyridin-2-yl)benzoate (3j):[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.8 Hz, 1H), 8.06 (d, J =



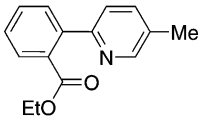
8.0 Hz, 1H), 7.61–7.54 (m, 2H), 7.50–7.46 (m, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.22–7.19 (m, 1H), 4.07 (q, J = 7.2 Hz, 2H), 2.12 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.89, 159.59, 146.08, 141.80, 137.15, 131.89, 131.13, 130.42, 129.99, 129.87, 127.91, 122.12, 60.66, 19.13, 13.69.

Ethyl 2-(4-methylpyridin-2-yl)benzoate (3k):[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, J = 4.8 Hz, 1H), 7.82 (d, J =



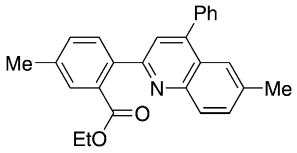
7.6 Hz, 1H), 7.54–7.53 (m, 2H), 7.46–7.42 (m, 1H), 7.29 (s, 1H), 7.08 (d, J=4.8 Hz, 1H), 4.14 (q, J=7.2 Hz, 2H), 2.40 (s, 3H), 1.07 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.76, 158.60, 148.68, 147.11, 141.00, 131.85, 130.85, 129.60, 129.56, 128.04, 123.59, 122.90, 60.78, 20.99, 13.73.

Ethyl 2-(5-methylpyridin-2-yl)benzoate (3l): ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.47 (s, 1H), 7.81 (d, J=8.0 Hz, 1H),



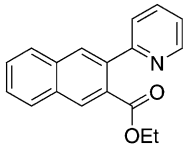
7.56–7.53 (m, 3H), 7.46–7.42 (m, 1H), 7.36 (d, J=8.0 Hz, 1H), 4.16 (q, J=7.2 Hz, 2H), 2.38 (s, 3H), 1.10 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.77, 155.94, 149.33, 140.90, 136.65, 131.73, 131.43, 130.90, 129.68, 129.59, 127.94, 122.22, 60.83, 18.14, 13.80; HR-MS (ESI): m/z= 242.1185 ([MH]$^+$), calcd. for $C_{15}H_{15}NO_2$: 242.1181.

Ethyl 5-methyl-2-(6-methyl-4-phenylquinolin-2-yl)benzoate (3m): ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.08 (d, J=



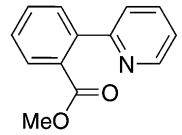
8.4 Hz, 1H), 7.69 (d, J=5.6 Hz, 2H), 7.62 (d, J=7.6 Hz, 1H), 7.57–7.50 (m, 7H), 7.40 (d, J=8.0 Hz, 1H), 4.13 (q, J= 6.8 Hz, 2H), 2.49 (s, 3H), 2.46 (s, 3H), 0.94 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=169.06, 157.29, 147.56, 146.81, 138.43, 138.34, 138.33, 136.22, 131.87, 131.70, 131.58, 130.29, 129.83, 129.56, 129.47, 128.49, 128.20, 125.27, 124.27, 121.41, 60.85, 21.76, 21.03, 13.77; HR-MS (ESI): m/z=382.1812 ([MH]$^+$), calcd. for $C_{26}H_{24}NO_2$: 382.1807.

Ethyl 3-(pyridin-2-yl)-2-naphthoate (3n):[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.67 (d, J=4.4 Hz, 1H), 8.39 (s, 1H),



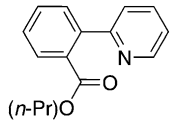
8.00 (s, 1H), 7.95 (d, J=7.6 Hz, 1H), 7.89 (d, J=7.6 Hz, 1H), 7.79–7.75 (m, 1H), 7.60–7.54 (m, 3H), 7.28–7.25 (m, 1H), 4.20 (q, J=7.2 Hz, 2H), 1.10 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.66, 158.90, 148.85, 137.43, 136.15, 133.98, 132.08, 130.74, 129.56, 129.31, 128.49, 128.03, 127.97, 127.05, 122.78, 121.73, 60.93, 13.77.

Methyl 2-(pyridin-2-yl)benzoate (3o):[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.65 (d, J=4.8 Hz, 1H), 7.82 (d, J= 7.6 Hz, 1H), 7.77–7.73 (m, 1H), 7.57–7.54 (m, 2H), 7.48–7.44 (m, 2H), 7.27–7.24 (m, 1H), 3.68 (s, 3H); ^{13}C NMR



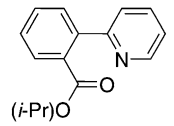
(100 MHz, $CDCl_3$): δ=169.16, 158.51, 148.98, 140.86, 136.14, 131.45, 131.05, 129.69, 129.64, 128.22, 122.64, 121.98, 51.90.

Propyl 2-(pyridin-2-yl)benzoate (3p): ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.63 (d, J=4.4 Hz, 1H), 7.83 (d, J=



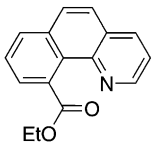
7.6 Hz, 1H), 7.74–7.69 (m, 1H), 7.53 (d, J=4.0 Hz, 2H), 7.46–7.43 (m, 2H), 7.24–7.21 (m, 1H), 4.03 (t, J=6.4 Hz, 2H), 1.48–1.39 (m, 2H), 0.73 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.74, 158.72, 148.88, 140.81, 136.03, 131.75, 130.86, 129.67, 129.62, 128.11, 122.66, 121.86, 66.50, 21.51, 10.13; HR-MS (ESI): m/z=242.1185 ([MH]$^+$), calcd. for $C_{15}H_{16}NO_2$: 242.1181.

Isopropyl 2-(pyridin-2-yl)benzoate (3q):[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.63 (d, J=4.4 Hz, 1H), 7.83 (d, J=



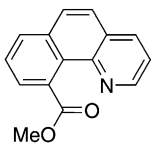
7.6 Hz, 1H), 7.75–7.71 (m, 1H), 7.56–7.51 (m, 2H), 7.47–7.43 (m, 2H), 7.27–7.23 (m, 1H), 5.08–4.99 (m, 1H), 1.08 (d, J=6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.14, 158.95, 148.92, 140.83, 136.02, 132.20, 130.78, 129.68, 129.61, 128.12, 122.83, 121.84, 68.37, 21.40.

Ethyl benzo[*h*]quinoline-10-carboxylate (3r):[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.90 (d, J=4.0 Hz, 1H), 8.14 (d, J=



8.0 Hz, 1H), 7.97–7.94 (m, 1H), 7.80 (d, J=8.8 Hz, 1H), 7.71–7.70 (m, 3H), 7.51–7.48 (m, 1H), 4.63 (q, J=7.2 Hz, 2H), 1.45 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=172.22, 147.58, 144.99, 135.42, 133.89, 132.47, 129.88, 129.20, 127.60, 127.31, 126.84, 126.05, 125.98, 121.85, 61.36, 14.18.

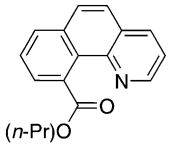
Methyl benzo[*h*]quinoline-10-carboxylate (3s): ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.92 (d, J=4.0 Hz, 1H), 8.17–8.15



(m, 1H), 7.98–7.96 (m, 1H), 7.82 (d, J=8.8 Hz, 1H), 7.73–7.70 (m, 3H), 7.52–7.49 (m, 1H), 4.09 (s, 3H); ^{13}C NMR

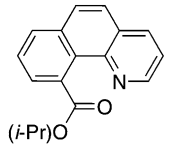
(100 MHz, $CDCl_3$): δ = 172.74, 147.92, 144.95, 135.52, 133.91, 132.09, 129.37, 127.74, 127.64, 127.34, 126.91, 126.06, 126.02, 121.92, 52.40; HR-MS (ESI): m/z = 238.0872 ($[MH]^+$), calcd. for $C_{15}H_{12}NO_2$: 238.0868.

Propyl benzo[*h*]quinoline-10-carboxylate (3t): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (dd, J = 4.0, 1.2 Hz, 1H), 8.10–



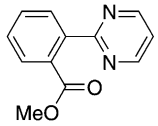
8.08 (m, 1H), 7.90–7.88 (m, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.65–7.62 (m, 3H), 7.45–7.42 (m, 1H), 4.44 (t, J = 6.8 Hz, 2H), 1.82–1.73 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.23, 147.53, 144.86, 135.31, 133.77, 132.44, 129.06, 127.50, 127.48, 127.18, 126.71, 125.89, 121.74, 66.95, 21.71, 10.43; HR-MS (ESI): m/z = 266.1184 ($[MH]^+$), calcd. for $C_{17}H_{16}NO_2$: 266.1181.

Isopropyl benzo[*h*]quinoline-10-carboxylate (3u):[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (dd, J = 4.4, 1.6 Hz,



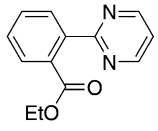
1H), 8.14 (d, J = 8.0 Hz, 1H), 7.95–7.93 (m, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.72–7.68 (m, 3H), 7.51–7.48 (m, 1H), 5.63–5.53 (m, 1H), 1.49 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.62, 147.35, 145.08, 135.38, 133.93, 132.93, 129.06, 127.63, 127.47, 127.32, 126.83, 126.12, 125.93, 121.83, 68.78, 21.86.

Methyl 2-(pyrimidin-2-yl)benzoate (4a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 4.8 Hz, 2H), 8.01 (d, J =



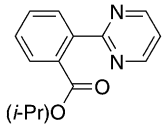
8.0 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.59–7.55 (m, 1H), 7.52–7.48 (m, 1H), 7.22–7.19 (m, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.66, 165.49, 156.73, 137.94, 132.65, 130.68, 129.84, 129.50, 128.86, 118.99, 52.00; HR-MS (ESI): m/z = 215.0824 ($[MH]^+$), calcd. for $C_{12}H_{11}N_2O_2$: 215.0821.

Ethyl 2-(pyrimidin-2-yl)benzoate (4b):[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J = 4.8 Hz, 2H), 7.98 (d, J =



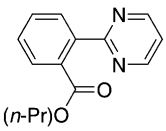
7.6 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.60–7.56 (m, 1H), 7.53–7.49 (m, 1H), 7.24–7.21 (m, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.09, 165.85, 156.72, 138.14, 132.90, 130.66, 129.83, 129.46, 129.01, 118.96, 60.97, 13.86.

Isopropyl 2-(pyrimidin-2-yl)benzoate (4c): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, J = 4.8 Hz, 2H), 7.95 (d, J =



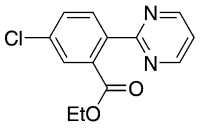
7.6 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.57–7.53 (m, 1H), 7.51–7.47 (m, 1H), 7.22–7.20 (m, 1H), 5.16–5.07 (m, 1H), 1.16 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.50, 165.89, 156.71, 138.00, 133.27, 130.47, 129.77, 129.36, 128.94, 118.92, 68.47, 21.48; HR-MS (ESI): m/z = 243.1132 ($[MH]^+$), calcd. for $C_{14}H_{15}N_2O_2$: 243.1134.

Propyl 2-(pyrimidin-2-yl)benzoate (4d): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J = 4.8 Hz, 2H), 7.98 (d, J =



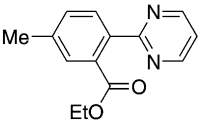
7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.60–7.56 (m, 1H), 7.53–7.50 (m, 1H), 7.24–7.21 (m, 1H), 4.12 (t, J = 6.4 Hz, 2H), 1.58–1.49 (m, 2H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.25, 165.89, 156.76, 138.16, 132.98, 130.66, 129.88, 129.48, 129.03, 118.97, 66.71, 21.64, 10.29; HR-MS (ESI): m/z = 243.1131 ($[MH]^+$), calcd. for $C_{14}H_{15}N_2O_2$: 243.1134.

Ethyl 5-chloro-2-(pyrimidin-2-yl)benzoate (4e): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, J = 4.8 Hz, 2H), 7.98 (d, J =



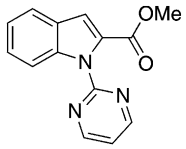
8.4 Hz, 1H), 7.67 (d, J = 0.80 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.23–7.21 (m, 1H), 4.23 (q, J = 6.8 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.97, 164.55, 156.76, 136.11, 135.75, 134.64, 131.27, 130.51, 128.90, 119.15, 61.35, 13.81; HR-MS (ESI): m/z = 263.0589 ($[MH]^+$), calcd. for $C_{13}H_{12}ClN_2O_2$: 263.0587.

Ethyl 5-methyl-2-(pyrimidin-2-yl)benzoate (4f): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 4.8 Hz, 2H), 7.92 (d, J =



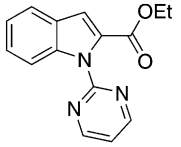
7.6 Hz, 1H), 7.52 (s, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.20–7.17 (m, 1H), 4.22 (q, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.51, 165.64, 156.65, 139.86, 135.11, 133.05, 131.20, 129.82, 129.45, 118.72, 60.93, 21.09, 13.87; HR-MS (ESI): m/z = 243.1131 ($[MH]^+$), calcd. for $C_{14}H_{15}N_2O_2$: 243.1134.

Methyl 1-(pyrimidin-2-yl)-1*H*-indole-2-carboxylate (4g): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J = 4.8 Hz, 2H),



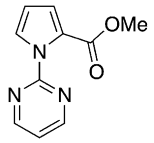
8.18 (d, $J=8.4$ Hz, 1H), 7.71 (d, $J=7.6$ Hz, 1H), 7.43–7.39 (m, 1H), 7.36 (s, 1H), 7.29–7.26 (m, 1H), 7.21–7.19 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=162.50$, 158.05, 157.48, 138.55, 129.98, 127.57, 126.26, 122.56, 122.34, 117.93, 114.12, 113.48, 51.97; HR-MS (ESI): $m/z=254.0928$ ($[MH]^+$), calcd. for $C_{14}H_{12}N_3O_2$: 254.0930.

Ethyl 1-(pyrimidin-2-yl)-1*H*-indole-2-carboxylate (4h): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.78$ (d, $J=4.8$ Hz, 2H),



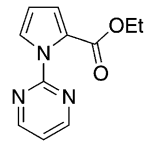
8.16 (d, $J=8.4$ Hz, 1H), 7.70 (d, $J=8.0$ Hz, 1H), 7.42–7.36 (m, 2H), 7.29–7.25 (m, 1H), 7.21–7.18 (m, 1H), 4.32 (q, $J=6.8$ Hz, 2H), 1.28 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=162.04$, 158.03, 157.54, 138.49, 130.40, 127.57, 126.15, 122.50, 122.28, 117.89, 113.93, 113.39, 60.93, 14.03; HR-MS (ESI): $m/z=268.1088$ ($[MH]^+$), calcd. for $C_{15}H_{14}N_3O_2$: 268.1086.

Methyl 1-(pyrimidin-2-yl)-1*H*-pyrrole-2-carboxylate (4i): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.72$ (d, $J=4.4$ Hz, 2H),



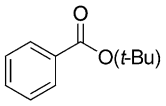
7.53 (br, 1H), 7.23–7.21 (m, 1H), 7.02–7.01 (m, 1H), 6.31 (br, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 161.74, 158.23, 157.09, 127.52, 124.36, 120.31, 118.75, 110.29, 51.55; HR-MS (ESI): $m/z=204.0775$ ($[MH]^+$), calcd. for $C_{10}H_{10}N_3O_2$: 204.0773.

Ethyl 1-(pyrimidin-2-yl)-1*H*-pyrrole-2-carboxylate (4j): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.72$ (d, $J=4.4$ Hz, 2H),

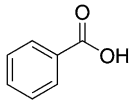


7.52 (br, 1H), 7.23–7.21 (m, 1H), 7.02–7.01 (m, 1H), 6.31 (br, 1H), 4.26 (q, $J=7.2$ Hz, 2H), 1.27 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=161.35$, 158.20, 157.18, 127.31, 124.81, 120.12, 118.71, 110.24, 60.44, 14.14; HR-MS (ESI): $m/z=218.0933$ ($[MH]^+$), calcd. for $C_{11}H_{12}N_3O_2$: 218.0930.

***tert*-Butyl benzoate:** ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 8.01 (d, $J=7.2$ Hz, 2H), 7.55–7.51 (m, 1H), 7.44–7.41 (m, 2H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.77$, 132.37, 132.04, 129.39, 128.14, 80.92, 28.18.



Benzoic acid: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=11.65$ (s, 1H), 8.16 (d, $J=7.6$ Hz, 2H), 7.66–7.62 (m, 1H), 7.52–7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=172.44$, 133.79, 130.21, 129.37, 128.47.



Acknowledgements

This work was financially supported by the National Science Foundation of China (No. 21172092).

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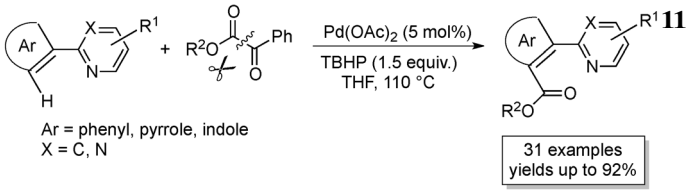
Palladium-Catalyzed Direct Alkoxycarbonylation of Aromatic C–H Bonds *via* Selective C–C Cleavage of α-Keto Esters



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