

Article

Palladium(II)-Catalyzed *ortho*-C–H-Benzoxylation of 2-Arylpyridines by Oxidative Coupling with Aryl Acylperoxides

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Abstract: A palladium(II)-catalyzed *ortho*-benzoxylation of 2-arylpyridines with aryl acylperoxides was developed. With pyridyl as directing group, the benzoxylation reaction exhibits remarkable regioselectivity and excellent functional group tolerance, providing the products in up to 87% yield.

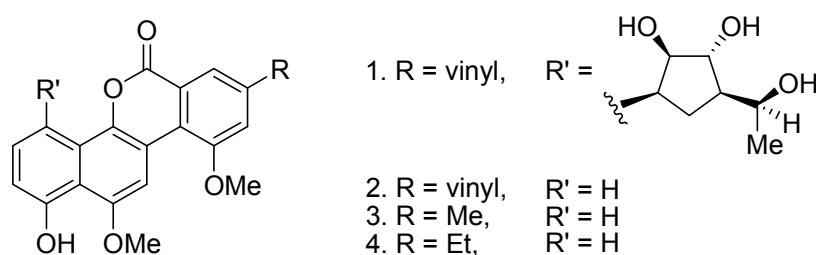
Keywords: C–H bond; oxidation; palladium

1. Introduction

Site selective direct functionalization of C–H bonds is attracting considerable current attention for developing sustainable chemical synthesis. Without relying on prefunctionalized substrates, the direct C–H functionalization approach would streamline the synthetic routes and improve atom economy. With transition metal catalysis, innovative transformations based on regioselective aryl C–H bond cleavage with the formation of C–C and C–X (X = halogen) bonds have been achieved [1–3]. Recently, significant advances have been made in the analogous transformations with C–O bond formation on arenes. For instance, the research groups of Sanford, Crabtree and Wang achieved acetoxylation of aryl C–H bonds with oxidants such as Oxone[®], PhI(OAc)₂, and K₂S₂O₈ [4–6]. The analogous acetoxylation of selected sp³ C–H bonds has also been achieved independently by Sanford, Yu and Corey [7–9]. Notably, Yu and co-workers accomplished Pd-catalyzed arene hydroxylation with dioxygen as oxidant [10]. Apart from Pd, Cu(OAc)₂ has also been shown to exhibit promising reactivities toward catalytic acetoxylation of aryl C–H bonds [11].

Compared to acetoxylation, the analogous benzoxylation is less developed [12]. Aryl benzoates are known to form structures of some natural products such as the gilvocarcins (Figure 1) [13,14]. In 2009, Cheng and co-workers reported the Rh(I)-catalyzed *ortho*-benzoxylation of 2-arylpyridines with benzoic acids [15]. Later, the same group also reported the analogous Cu(OAc)₂-catalyzed benzoxylation with benzoic anhydride and derivatives [16,17]. With a continuing interest in developing catalytic C–H bond cross coupling reactions, we have been investigating the regioselective C–C and C–N bond cross coupling reactions based on the coupling reactions of arylpalladium and –rhodium complexes with carboradicals [18–21], carbenes [22] and nitrenoids [23–25]. Previously, we described the successful development of the Pd-catalyzed decarboxylative arylation of 2-arylpyridines with aryl acylperoxides [19]. Prompted by this work, here we disclose the Pd-catalyzed regioselective benzoxylation of 2-arylpyridines with aryl acylperoxides.

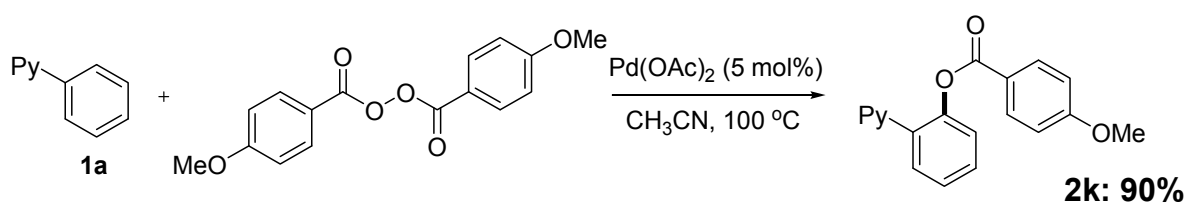
Figure 1. Examples of gilvocarcins.



2. Results and Discussion

In our earlier study on decarboxylative arylation, we found that treating 2-phenylpyridine (**1a**, 0.25 mmol) with Pd(OAc)₂ (5 mol%) with a methoxy-substituted aryl acylperoxide (4 × 0.5 equiv./0.5 h) at 100 °C for 2 h in CH₃CN (Scheme 1) furnished **2k** in 90% isolated yield. However, when simple benzoyl peroxide was employed as reagent, the analogous reaction of **1a** produced **2a** in only 7% yield. To develop a general benzoxylation reaction, we first examined the solvent effect (Table 1). With **1a** as substrate and benzoyl peroxide as reagent (4 × 0.5 equiv./0.5 h), the best result (**2a**: 49%) was obtained when xylene was employed as solvent (entry 8). As expected, toluene gave comparable results; the use of other donor solvents (e.g., dioxane, THF, DMF and DCE) produced far inferior outcomes.

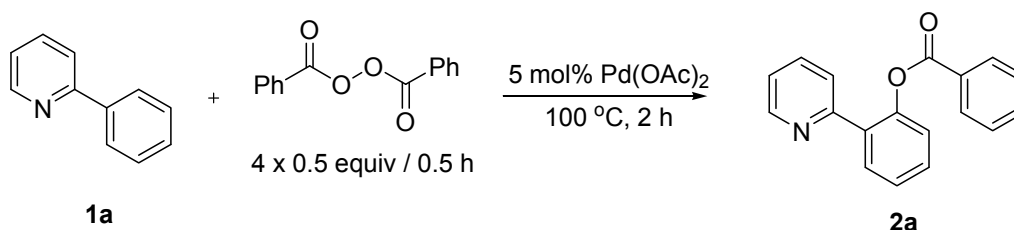
Scheme 1. Initial studies of *ortho*-C–H-arylcaboxylation by aryl acylperoxide.



We next turned to optimize other experimental parameters, and the results are summarized in Table 2. We found that when raising the reaction temperature to 120 °C led to slightly lower yield of 41% for the benzoxylation of **1a** (entry 2). Notably, further increasing the temperature to 130 °C afforded **2a** in 59% yield (entry 3). Either prolonged reaction time or higher temperature (150 °C) did not give better results (entries 4–5). After several trials, we found that employing 3.5 equiv. of benzoyl peroxide

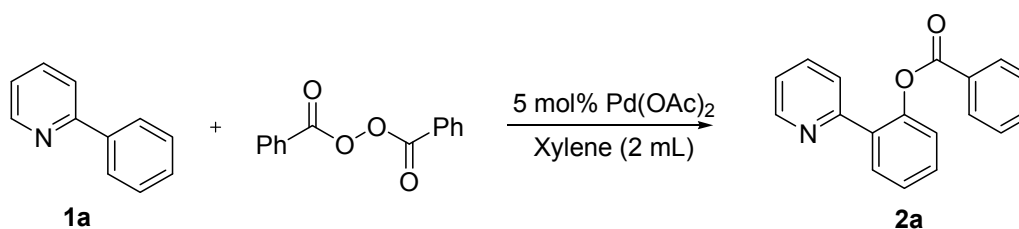
added in a batchwise fashion (7×0.5 equiv./0.5 h) improved the benzoxylation yield to 64% (entry 6). Interestingly, when dried benzoyl peroxide was employed, **2a** was obtained in 70% yield. Up to 76% yield of **2a** was obtained when 10 mol% of $\text{Pd}(\text{OAc})_2$ was employed for the benzoxylation reaction (entry 9).

Table 1. Solvent effect.



Entry	Solvent (2 mL)	GC Yield (%)
1	CH_3CN	7
2	dioxane	10
3	THF	29
4	DMF	33
5	DMA	3
6	DCE	11
7	toluene	47
8	xylene	49

Table 2. Effect of other experimental parameters.



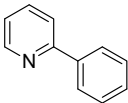
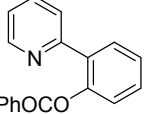
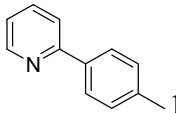
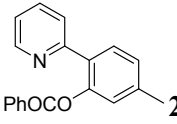
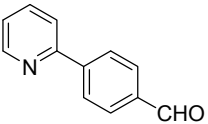
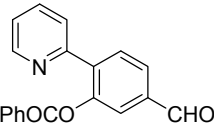
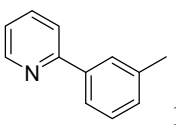
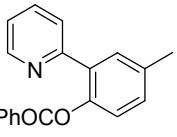
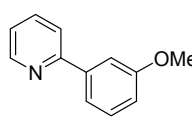
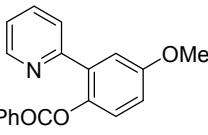
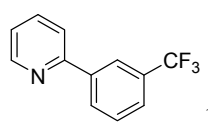
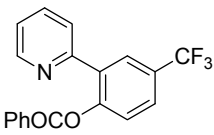
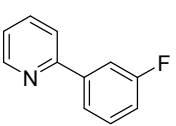
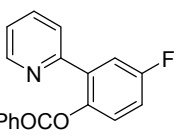
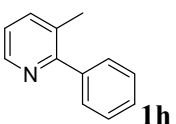
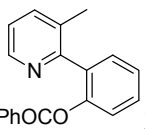
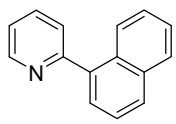
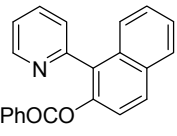
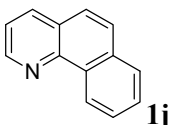
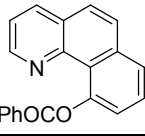
Entry	Addition method	Temp. ($^\circ\text{C}$)	Time (h)	GC Yield (%)
1	4×0.5 equiv./0.5 h	100	2	49
2	4×0.5 equiv./0.5 h	120	2	41
3	4×0.5 equiv./0.5 h	130	2	59
4	4×0.5 equiv./1 h	130	4	53
5	4×0.5 equiv./0.5 h	150	2	52
6	7×0.5 equiv./0.5 h	130	3.5	64
7	8×0.5 equiv./0.5 h	130	4	60
8 *	7×0.5 equiv./0.5 h	130	3.5	70
9 *.#	7×0.5 equiv./0.5 h	130	3.5	76

* Peroxide was washed with diethyl ether and air dry; # 10 mol% of $\text{Pd}(\text{OAc})_2$ was used.

Table 3 depicts the substrate scope study, and the Pd-catalyzed benzoxylation is broadly applicable to a variety of 2-arylpyridines. In all cases, benzoxylation occurs at the *ortho*-C-H bond to the pyridyl group. For *meta*-substituted arenes (e.g., **1d** and **1e**), benzoxylation occurred regioselectively at the less hindered *ortho*-C-H bond (entries 4–7). Apparently, those aryl groups bearing electron-donating substituent such as Me, MeO produced better yields of **2d** and **2e** (83%–87%), whereas the analogous reactions of substrates with electron-withdrawing CF_3 and F groups resulted in 54%–62% yields. Higher benzoxylation yield was also observed with **1h**, which contains a Me group on the pyridyl function. Presumably, stronger coordination of the pyridyl group would facilitate cyclopalladation,

thereby speeding up the substrate conversion. Consistent with this notion is that benzoxylation of benzoquinoline **1j** was equally facile with **2j** being obtained in 85% yield. The rigid scaffold of **1j** should lower the entropic cost for the cyclopalladation (entry 10). The molecular structure of **2i** has been established by X-ray crystallography. CCDC 933423 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk), see Supporting Information.

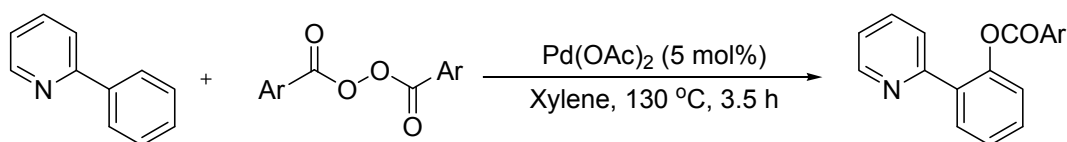
Table 3. Pd-catalyzed benzoxylation of arylpyridines ^a.

Entry	Substrate	Product	Isolated Yield (%)
1	 1a	 2a	71
2	 1b	 2b	70
3	 1c	 2c	44
4	 1d	 2d	87
5	 1e	 2e	83
6	 1f	 2f	54
7	 1g	 2g	62
8	 1h	 2h	87
9	 1i	 2i	57
10	 1j	 2j	85

^a Reaction conditions: substrate (0.5 mmol), Pd(OAc)₂ (5 mol%), peroxide (7 × 0.5 equiv./0.5 h), at 130 °C for 3.5 h in xylene (2 mL).

Table 4 depicts the scope of the aryl acylperoxides; the Pd-catalyzed benzoxylation of **1a** afforded the corresponding benzoates in 27%–81% yields. Peroxides with electron-donating (e.g., Me, MeO, EtO) and -withdrawing (e.g., CF₃) are effective reagents for the benzoxylation. Peroxides with bulky substituents such as *t*Bu and naphthalene were also tolerated with benzoates being formed in 44%–77% yields.

Table 4. Benzoxylation with various aryl acylperoxides ^a.



Entry	Ar	Isolated Yield (%)
1	4-OMe-C ₆ H ₅	54
2	3-OMe-C ₆ H ₅	69
3	2-Cl-C ₆ H ₅	43
4	3-Cl-C ₆ H ₅	73
5	2-Me-C ₆ H ₅	66
6	4-Me-C ₆ H ₅	64
7	4-F-C ₆ H ₅	55
8	4-Br-C ₆ H ₅	30
9	4-CF ₃ -C ₆ H ₅	81
10	4-OEt-C ₆ H ₅	27
11	4- <i>t</i> Bu-C ₆ H ₅	77
12	2,6-F ₂ -C ₆ H ₄	46
13	2-naphthalene	44

^a Reaction conditions: substrate (0.5 mmol), Pd(OAc)₂ (5 mol%), peroxide (7 × 0.5 equiv./0.5 h), at 130 °C for 3.5 h in xylene (2 mL).

A plausible mechanism is shown in Scheme 2. The benzoxylation is probably initiated by the pyridyl-assisted cyclopalladation of the *ortho*-C-H of the arenes. Our earlier study showed that the regioselectivity of the cyclopalladation is determined by steric factor [19]. Substrates with a *meta*-substituted group would be palladated at the least hindered site. Regarding to the nature of the palladation step, our previous studies established a linear free energy relationship ($\rho^+ = -0.74$) for the Pd-catalyzed oxidative acylation of pivylanilides, consistent with an electrophilic mechanism [21]. We conjectured that homolytic O–O cleavage of the aryl acylperoxide should afford arylcarboxy radicals [26], which would react with the palladacyclic intermediate leading to the C–O bond formation.

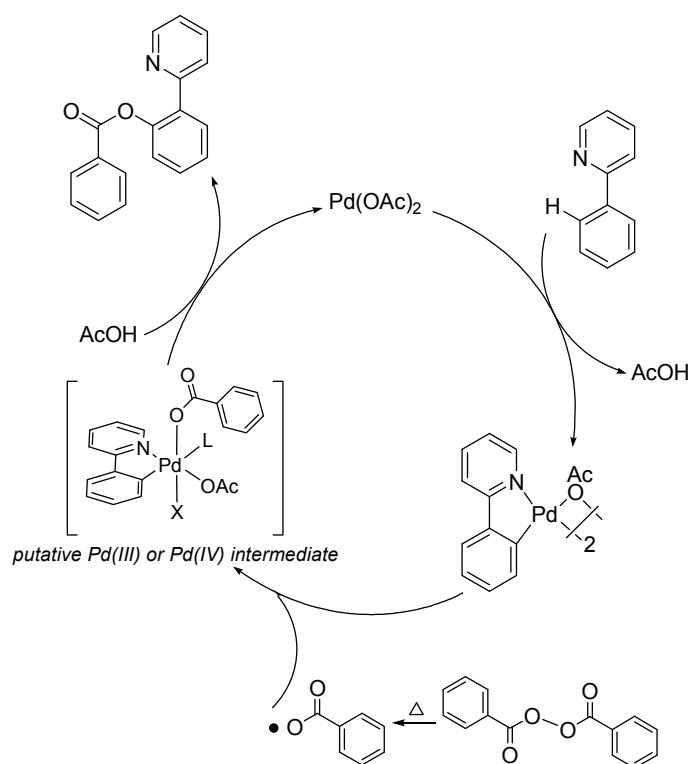
3. Experimental

3.1. General

2-Arylpyridines were prepared by reacting the corresponding arylboronic acids with 2-bromopyridines using reported procedures [27]. Aryl acylperoxides were prepared by reacting acid chlorides with hydrogen peroxide (35 wt. % in H₂O) and sodium hydroxide by the reported procedures [28]. Benzoyl peroxide (Luperox[®] A75) was obtained commercially and washed with diethyl ether and air

dry. Thin layer chromatography was performed on silica gel plates. Silica gel (Merck, 230–400 mesh) and aluminum oxide (Merck, 50–200 mesh) were used for flash column chromatography. ^1H 400 MHz) and ^{13}C -NMR spectra (100 MHz) were recorded on a Brüker DPX 400 NMR spectrometer, chemical shift (δ) valued are given in ppm and are referenced to the residual solvent peaks. Coupling constants (J) were reported in Hertz (Hz). Mass spectra and high resolution mass spectra (HRMS) were obtained on a VG Micromass Fison VG platform, a Finnigan Model Mat 95 ST instrument, or a Brüker APEX 47e FT-ICR mass spectrometer. Infrared analysis were measured on a Nicolet Magna 750 FTIR spectrometer. Melting points were measured on a Büchi B-545 melting point apparatus. The X-ray crystal structure was obtained on a Brüker CCD area detector diffractometer.

Scheme 2. Plausible mechanism of *ortho*-C-H-benzoxylation by aryl acylperoxides.

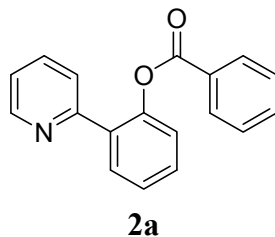


3.2. General Procedure for the Pd-Catalyzed Benzoxylation

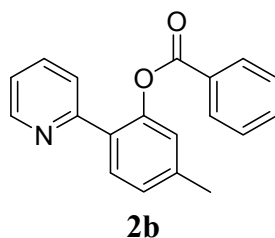
A mixture of substrate (0.5 mmol), $\text{Pd}(\text{OAc})_2$ (0.025 mmol, 5 mol%), aryl acylperoxide [1.75 mmol; addition interval: 7×0.5 equiv./0.5 h] in xylene (2 mL) was sealed in a 8-mL vial with a Teflon-lined cap. The mixture was heated at 130 °C (oil bath temperature) for 3.5 h. After cooling down to room temperature, the reaction mixture was filtered through a plug of silica gel, and the filtrate was concentrated under vacuum to afford an oily substance. The crude product was dissolved in dichloromethane and treated with saturated aqueous NaHCO_3 (3×10 mL) solution and extracted with dichloromethane (4×10 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated to dryness by a rotary evaporator. The residue was loaded to a silica gel column for purification by flash chromatography using 60% *n*-hexane/40% diethyl ether as eluent.

3.3. Characterization of Products

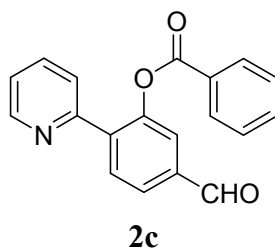
2-(Pyridin-2-yl)phenyl benzoate (2a). Yellow oil (71% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.59 (d, $J = 4.7$ Hz, 1H), 8.09 (d, $J = 7.8$ Hz, 2H), 7.78 (d, $J = 7.6$ Hz, 1H), 7.55–7.63 (m, 3H), 7.38–7.52 (m, 4H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.13–7.16 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.2 (C=O), 154.7 (C), 150.2 (C-O), 149.4 (C-H), 136.7 (C-H), 134.0 (C-H), 131.5 (C-H), 130.7 (C-H), 130.3 (C), 129.1 (C), 128.9 (C-H), 128.4 (C-H), 127.0 (C-H), 124.2 (C-H), 123.9 (C-H), 122.7 (C-H). MS (EI): 275 (M^+ , 20), 105 (100), 77 (40). HRMS (ESI): calcd. for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{H}^+$: 276.1025, found: 276.1023. IR (KBr, cm^{-1}): 1739.



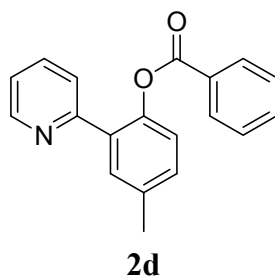
5-Methyl-2-(pyridin-2-yl)phenyl benzoate (2b). Yellow oil (70% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.57 (d, $J = 4.4$ Hz, 1H), 8.10 (d, $J = 7.5$ Hz, 2H), 7.69 (d, $J = 7.9$ Hz, 1H), 7.50–7.61 (m, 3H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.21 (d, $J = 8.3$ Hz, 1H), 6.93–6.97 (m, 1H), 2.43 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.9 (C=O), 156.2 (C), 150.1 (C-O), 149.4 (C-H), 140.8 (C), 136.7 (C-H), 134.0 (C), 131.3 (C-H), 131.0 (C-H), 130.6 (C-H), 130.2 (C), 129.1 (C-H), 128.4 (C-H), 124.2 (C), 122.5 (C-H), 122.1 (C-H), 21.9 (CH_3). MS (EI): 289 (M^+ , 40), 105 (100), 77 (40). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_2\text{H}^+$: 290.1181, found: 290.1188. IR (KBr, cm^{-1}): 1736.



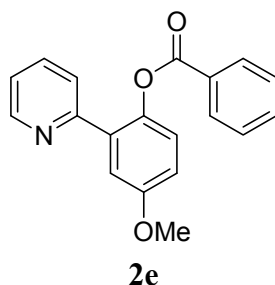
5-Formyl-2-(pyridin-2-yl)phenyl benzoate (2c). Yellow oil (44% yield based on conversion). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 10.07 (s, 1H), 8.62 (d, $J = 4.6$ Hz, 1H), 8.08 (d, $J = 7.3$ Hz, 2H), 7.95–8.00 (m, 2H), 7.91 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.83 (d, $J = 1.2$ Hz, 1H), 7.60–7.67 (m, 2H), 7.48 (d, $J = 8.2$ Hz, 1H), 7.21–7.23 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 191.5 (C=O), 165.5 (C=O), 154.9 (C), 150.5 (C-O), 146.7 (C-H), 139.6 (C-H), 137.0 (C-H), 134.5 (C), 132.5 (C-H), 130.9 (C), 129.6 (C-H), 127.4 (C-H), 126.6 (C-H), 125.2 (C-H), 123.6 (C-H), 120.7 (C-H). MS (EI): 303 (M^+ , 10), 105 (100), 77 (30). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{13}\text{NO}_3\text{H}^+$: 304.0974, found: 304.0981. IR (KBr, cm^{-1}): 1738, 1697.



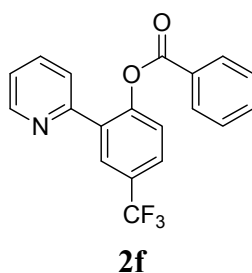
4-Methyl-2-(pyridin-2-yl)phenyl benzoate (2d). Yellow oil (87% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.61 (d, $J = 4.7$ Hz, 1H), 8.09 (d, $J = 7.4$ Hz, 2H), 7.55–7.61 (m, 4H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.28 (dd, $J = 9.0, 2.1$ Hz, 1H), 7.19 (d, $J = 8.2$ Hz, 1H), 7.12–7.15 (m, 1H), 2.44 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.9 (C=O), 156.2 (C), 150.2 (C-H), 146.6 (C), 136.7 (C-H), 134.0 (C), 133.4 (C-H), 131.9 (C-H), 130.9 (C), 130.7 (C-H), 130.1 (C-H), 129.1 (C-H), 128.4 (C-H), 124.3 (C-H), 123.6 (C-H), 122.2 (C-H), 21.5 (CH_3). MS (EI): 289 (M^+ , 30), 105 (100), 77 (30). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_2\text{H}^+$: 290.1181, found: 290.1184. IR (KBr, cm^{-1}): 1738.



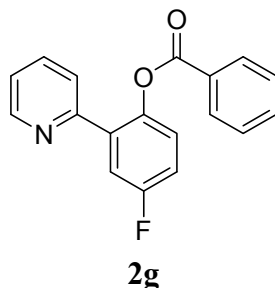
4-Methoxy-2-(pyridin-2-yl)phenyl benzoate (2e). Yellow oil (83% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.61 (d, $J = 4.7$ Hz, 1H), 8.09 (d, $J = 7.4$ Hz, 2H), 7.57–7.62 (m, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.34 (d, $J = 3.0$ Hz, 1H), 7.22 (d, $J = 8.8$ Hz, 1H), 7.13–7.17 (m, 2H), 7.02 (dd, $J = 8.8, 3.0$ Hz, 1H), 3.88 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 166.1 (C=O), 158.2 (C-O), 156.0 (C), 150.2 (C-H), 149.2 (C-O), 142.4 (C-H), 136.8 (C-H), 134.6 (C-H), 134.0 (C), 131.5 (C-H), 129.1 (C-H), 126.4 (C), 124.8 (C-H), 124.3 (C-H), 116.3 (C-H), 115.8 (C-H), 56.3 (CH_3). MS (EI): 305 (M^+ , 40), 105 (100), 77 (30). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{H}^+$: 306.1130, found: 306.1133. IR (KBr, cm^{-1}): 1737.



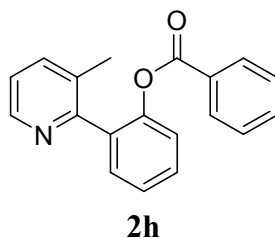
4-Methoxy-2-(pyridin-2-yl)phenyl benzoate (2f). Yellow oil (54% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.63 (d, $J = 4.5$ Hz, 1H), 8.03–8.11 (m, 2H), 7.74 (dd, $J = 8.5, 1.6$ Hz, 1H), 7.57–7.69 (m, 4H), 7.42–7.50 (m, 3H), 7.22 (d, $J = 5.3$ Hz, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.3 (C=O), 154.7 (C), 151.5 (C-O), 150.5 (C-H), 137.1 (C-H), 134.6 (C-H), 134.3 (C-H), 130.9 (C-H), 130.7 (C), 129.5 (C-H), 129.3 (C), 129.1 (C-H), 127.3 (C-H), 124.8 (C-H), 124.4 (CF_3), 123.7 (C-H), 123.5 (C-H). MS (EI): 343 (M^+ , 20), 105 (100), 77 (40). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{12}\text{NO}_2\text{F}_3\text{H}^+$: 344.0898 found: 344.0905. IR (KBr, cm^{-1}): 1739.



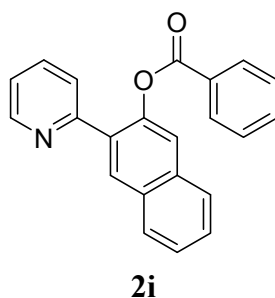
4-Fluoro-2-(pyridin-2-yl)phenyl benzoate (2g). Yellow oil (62% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.60 (d, $J = 4.7$ Hz, 1H), (d, $J = 4.7$ Hz, 1H), 8.08 (d, $J = 7.4$ Hz, 2H), 7.52–7.64 (m, 4H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.25–7.28 (m, 1H), 7.13–7.18 (m, 2H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.8 (C=O), 159.8 (C-F), 154.9 (C), 150.4 (C-H), 144.7 (C-O), 136.9 (C-H), 135.4 (C-H), 134.2 (C-H), 130.8 (C-H), 129.8 (C), 129.2 (C-H), 125.5 (C), 124.2 (C-H), 123.2 (C-H), 117.9 (C-H), 117.1 (C-H). MS (EI): 293 (M^+ , 20), 105 (100), 77 (40). HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{12}\text{NO}_2\text{F}^+$: 294.0930, found: 294.0927. IR (KBr, cm^{-1}): 1741.



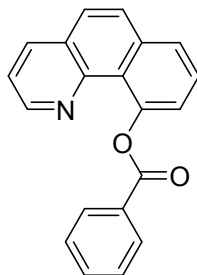
2-(3-Methylpyridin-2-yl)phenyl benzoate (2h). Yellow oil (87% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.42 (d, $J = 4.5$ Hz, 1H), 7.89 (d, $J = 7.5$ Hz, 1H), 7.26–7.54 (m, 8H), 7.04–7.07 (m, 1H), 2.21 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.0 (C=O), 155.9 (C), 148.8 (C-O), 147.1 (C-H), 138.3 (C-H), 134.0 (C-H), 133.8 (C-H), 132.6 (C), 130.9 (C-H), 130.6 (C), 130.1 (C-H), 129.7 (C), 128.8 (C-H), 126.4 (C-H), 123.3 (C-H), 123.0 (C-H), 19.5 (CH_3). MS (EI): 289 (M^+ , 30), 105 (100), 77 (40). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_2\text{H}^+$: 290.1181, found: 290.1176. IR (KBr, cm^{-1}): 1736.



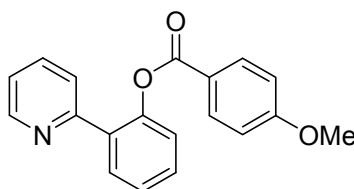
1-(Pyridin-2-yl)naphthalen-2-yl benzoate (2i). Yellow oil (57% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.77 (d, $J = 4.2$ Hz, 1H), 7.93–8.01 (m, 4H), 7.71 (t, $J = 7.6$ Hz, 1H), 7.63 (d, $J = 8.2$ Hz, 1H), 7.55–7.57 (m, 1H), 7.44–7.54 (m, 4H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.24–7.27 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.9 (C=O), 155.4 (C), 150.3 (C-O), 146.7 (C-H), 136.7 (C-H), 134.0 (C-H), 133.4 (C), 132.5 (C-H), 130.6 (C-H), 130.1 (C), 129.8 (C), 129.0 (C-H), 128.8 (C-H), 128.7 (C), 127.7 (C-H), 127.5 (C-H), 126.4 (C-H), 126.2 (C-H), 123.0 (C-H), 122.3 (C-H). MS (EI): 325 (M^+ , 50), 191 (10), 105 (100), 77 (40). HRMS (ESI): calcd. for $\text{C}_{22}\text{H}_{15}\text{NO}_2\text{H}^+$: 326.1130, found: 326.1129. IR (KBr, cm^{-1}): 1735.



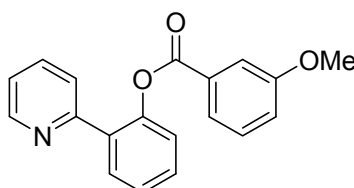
Benzo[h]quinolin-10-yl benzoate (2j). Yellow oil (85% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.39–8.42 (m, 3H), 8.08 (dd, $J = 8.0, 1.8$ Hz, 1H), 7.83–7.89 (m, 2H), 7.66–7.75 (m, 3H), 7.53–7.62 (m, 3H), 7.33 (q, $J = 4.1$ Hz, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 167.5 (C=O), 149.7 (C-O), 148.5 (C-H), 146.1 (C), 136.6 (C-H), 136.1 (C), 133.3 (C-H), 132.0 (C), 131.1 (C-H), 129.0 (C-H), 128.7 (C), 128.5 (C-H), 127.6 (C-H), 127.3 (C-H), 127.0 (C-H), 124.0 (C), 123.0 (C-H), 122.1 (C-H). MS (EI): 299 (M^+ , 40), 105 (100), 77 (30). HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{13}\text{NO}_2\text{H}^+$: 300.1025, found: 300.1024. IR (KBr, cm^{-1}): 1735.

**2j**

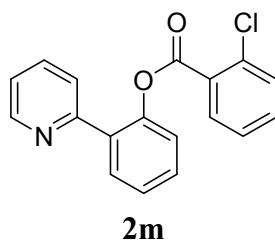
2-(Pyridin-2-yl)phenyl 4-methoxybenzoate (2k). Yellow oil (54% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.59 (d, $J = 4.5$ Hz, 1H), 8.03 (d, $J = 8.8$ Hz, 2H), 7.78 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.54–7.63 (m, 2H), 7.45 (dt, $J = 7.6, 1.5$ Hz, 1H), 7.36 (dt, $J = 7.5, 0.8$ Hz, 1H), 7.29 (dd, $J = 7.9, 0.7$ Hz, 1H), 7.11–7.14 (m, 1H), 6.91 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.4 (C=O), 164.3 (C), 156.1 (C), 150.1 (C), 148.9 (C-H), 136.6 (C-H), 133.9 (C-H), 132.8 (C-H), 131.4 (C-H), 130.2 (C), 126.8 (C-H), 123.9 (C-H), 122.6 (C), 122.2 (C-H), 119.2 (C-H), 114.3 (C-H), 56.0 (CH_3). MS (EI): 305 (M^+ , 20), 135 (100). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{H}^+$: 306.1130, found: 306.1136. IR (KBr, cm^{-1}): 1732.

**2k**

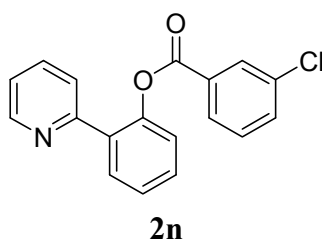
2-(Pyridin-2-yl)phenyl 3-methoxybenzoate (2l). Yellow oil (69% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.60 (d, $J = 4.1$ Hz, 1H), 7.78 (dd $J = 7.7, 1.5$ Hz, 1H), 7.69 (d, $J = 6.6$ Hz, 1H), 7.55–7.64 (m, 3H), 7.47 (dt, $J = 7.7, 1.6$ Hz, 1H), 7.35–7.41 (m, 2H), 7.32 (dt $J = 8.0, 1.0$ Hz, 1H), 7.10–7.17 (m, 2H), 3.81 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.6 (C=O), 160.2 (C), 156.1 (C), 150.2 (C), 148.9 (C-H), 136.8 (C-H), 133.9 (C-H), 131.5 (C), 131.3 (C-H), 130.3 (C-H), 130.1 (C), 127.0 (C-H), 124.3 (C-H), 123.9 (C-H), 123.2 (C-H), 122.8 (C-H), 120.7 (C-H), 115.0 (C-H), 56.0 (CH_3). MS (EI): 305 (M^+ , 20), 135 (100). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_3\text{H}^+$: 306.1130, found: 306.1134. IR (KBr, cm^{-1}): 1736.

**2l**

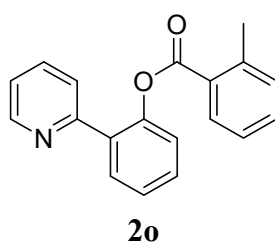
2-(Pyridin-2-yl)phenyl 2-chlorobenzoate (2m). Yellow oil (43% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.63 (d, $J = 4.7$ Hz, 1H), 7.88 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.74 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.68 (dt, $J = 7.7, 1.7$ Hz, 1H), 7.57 (d, $J = 7.8$ Hz, 1H), 7.37–7.52 (m, 4H), 7.31–7.34 (m, 2H), 7.18–7.21 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.2 (C=O), 156.4 (C), 150.2 (C-O), 148.7 (C-H), 137.0 (C-H), 135.0 (C-Cl), 134.0 (C-H), 133.6 (C-H), 132.5 (C-H), 131.8 (C-H), 131.5 (C), 130.5 (C-H), 130.0 (C), 127.2 (C-H), 124.4 (C-H), 124.0 (C-H), 122.9 (C-H), 122.1 (C-H). MS (EI): 309 (M^+ , 40), 139 (100), 111 (20). HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{12}\text{NO}_2\text{ClH}^+$: 310.0635, found: 310.0628. IR (KBr, cm^{-1}): 1742.



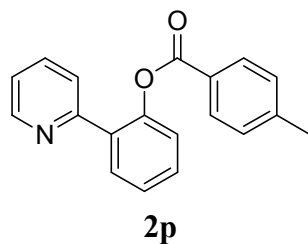
2-(Pyridin-2-yl)phenyl 3-chlorobenzoate (2n). Yellow oil (73% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.57 (d, $J = 4.6$ Hz, 1H), 8.06 (s, 1H), 7.95 (d, $J = 7.8$ Hz, 1H), 7.75 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.65 (t, $J = 7.8$ Hz, 1H), 7.53–7.57 (m, 2H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.37–7.42 (m, 2H), 7.30 (d, $J = 4.5$ Hz, 1H), 7.14–7.18 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 164.6 (C=O), 156.1 (C), 150.2 (C-O), 148.7 (C-H), 136.9 (C-H), 135.2 (C-Cl), 134.0 (C-H), 133.8 (C), 131.9 (C-H), 131.5 (C-H), 130.7 (C-H), 130.4 (C-H), 129.9 (C), 128.8 (C-H), 127.2 (C-H), 124.2 (C-H), 123.8 (C-H), 122.8 (C-H). MS (EI): 309 (M^+ , 20), 139 (100), 111 (40). HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{12}\text{NO}_2\text{ClH}^+$: 310.0635, found: 310.0640. IR (KBr, cm^{-1}): 1740.



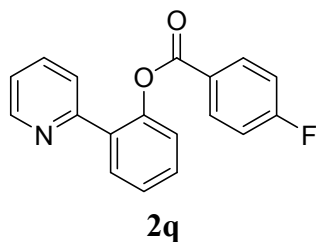
2-(Pyridin-2-yl)phenyl 2-methylbenzoate (2o). Yellow oil (66% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.61 (dd, $J = 4.8, 0.8$ Hz, 1H), 8.01 (dd, $J = 7.1, 1.3$ Hz, 1H), 7.76 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.64 (dt, $J = 7.7, 1.7$ Hz, 1H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.49 (dt, $J = 7.7, 1.6$ Hz, 1H), 7.38–7.45 (m, 2H), 7.24–7.30 (m, 4H), 7.15–7.19 (m, 1H), 2.54 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 166.3 (C=O), 156.5 (C), 150.2 (C-O), 150.0 (C-H), 141.8 (C), 136.8 (C-H), 134.2 (C-H), 133.1 (C-H), 132.7 (C-H), 132.4 (C-H), 131.5 (C-H), 130.4 (C), 129.2 (C), 128.5 (C-H), 126.9 (C-H), 126.4 (C-H), 124.1 (C-H), 122.8 (C-H), 22.2 (CH_3). MS (EI): 289 (M^+ , 10), 119 (100), 91 (40). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_2\text{H}^+$: 290.1181, found: 290.1186. IR (KBr, cm^{-1}): 1738.



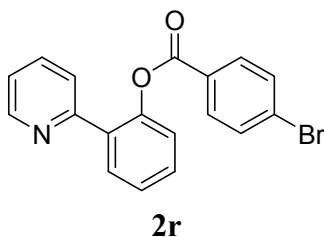
2-(Pyridin-2-yl)phenyl 4-methylbenzoate (2p). Yellow oil (64% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.60 (d, $J = 4.7$ Hz, 1H), 7.98 (d, $J = 8.1$ Hz, 2H), 7.79 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.55–7.60 (m, 2H), 7.47 (dt, $J = 7.7$, 1.5 Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 7.9$ Hz, 2H), 7.14–7.16 (m, 1H), 7.04 (t, $J = 4.7$ Hz, 1H), 2.41 (s, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.8 (C=O), 156.2 (C), 150.2 (C-O), 149.4 (C-H), 144.9 (C), 136.7 (C-H), 134.0 (C-H), 131.5 (C-H), 130.7 (C-H), 130.1 (C-H), 129.6 (C), 127.3 (C), 126.9 (C-H), 124.4 (C-H), 124.0 (C-H), 122.7 (C-H), 22.3 (CH_3). MS (EI): 289 (M^+ , 10), 119 (100), 91 (40). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{15}\text{NO}_2\text{H}^+$: 290.1181, found: 290.1173. IR (KBr, cm^{-1}): 1737.



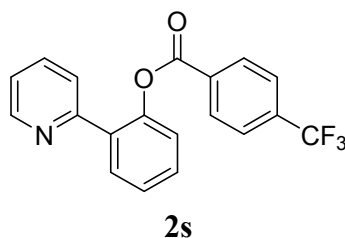
2-(Pyridin-2-yl)phenyl 4-fluorobenzoate (2q). Yellow oil (55% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.57 (d, $J = 4.2$ Hz, 1H), 8.08–8.11 (m, 2H), 7.76 (dd, $J = 7.6$, 1.5 Hz, 1H), 7.62 (dt, $J = 7.7$, 1.6 Hz, 1H), 7.53 (d, $J = 7.9$ Hz, 1H), 7.47 (dt, $J = 7.7$, 1.5 Hz, 1H), 7.39 (dt, $J = 7.5$, 0.9 Hz, 1H), 7.30 (dd, $J = 7.9$, 0.8 Hz, 1H), 7.09–7.16 (m, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 167.9 (C-F), 164.8 (C=O), 156.1 (C), 150.1 (C-O), 148.8 (C-H), 136.8 (C-H), 133.9 (C-H), 133.4 (C-H), 131.5 (C-H), 130.3 (C), 127.1 (C-H), 126.3 (C), 123.0 (C-H), 122.8 (C-H), 116.4 (C-H), 116.2 (C-H). MS (EI): 293 (M^+ , 10), 123 (100), 95 (30). HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{12}\text{NO}_2\text{FH}^+$: 294.0930, found: 294.0931. IR (KBr, cm^{-1}): 1738.



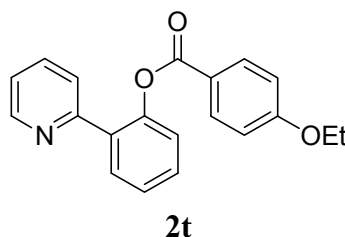
2-(Pyridin-2-yl)phenyl 4-bromobenzoate (2r). Yellow oil (30% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.56 (d, $J = 4.3$ Hz, 1H), 7.94 (d, $J = 8.5$ Hz, 2H), 7.76 (dd, $J = 7.6$, 1.4 Hz, 1H), 7.64 (dd, $J = 7.8$, 1.6 Hz, 1H), 7.46–7.53 (m, 3H), 7.40 (t, $J = 7.0$ Hz, 1H), 7.30 (d, $J = 7.8$ Hz, 1H), 7.14–7.17 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.1 (C=O), 156.2 (C), 150.2 (C-O), 148.8 (C-H), 136.9 (C-H), 133.8 (C-H), 132.5 (C-H), 132.3 (C-H), 131.9 (C-H), 130.4 (C-H), 129.3 (C), 129.1 (C), 127.2 (C-Br), 124.2 (C-H), 123.9 (C-H), 122.8 (C-H). MS (EI): 355 (M^+ , 20), 183 (100), 155 (20). HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{12}\text{NO}_2\text{BrH}^+$: 354.0130, found: 354.0133. IR (KBr, cm^{-1}): 1737.



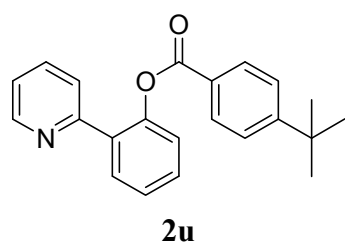
2-(Pyridin-2-yl)phenyl 4-(trifluoromethyl)benzoate (2s). Yellow oil (81% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.54 (d, $J = 4.5$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 2H), 7.71–7.82 (m, 3H), 7.64 (dt, $J = 7.8, 1.7$ Hz, 1H), 7.47–7.54 (m, 2H), 7.41 (dt, $J = 7.5, 1.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.14–7.17 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 164.7 (C=O), 156.2 (C), 150.1 (C-O), 148.7 (C-H), 137.0 (C), 135.6 (C-H), 135.2 (C-H), 133.8 (C-H), 133.4 (C), 131.5 (C-H), 131.2 (C-H), 130.5 (C), 127.3 (C-H), 125.6 (C-H), 124.1 (CF_3), 123.9 (C-H), 122.9 (C-H). MS (EI): 343 (M^+ , 40), 173 (100), 145 (50). HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{12}\text{NO}_2\text{F}_3\text{H}^+$: 344.0898, found: 344.0901. IR (KBr, cm^{-1}): 1743.



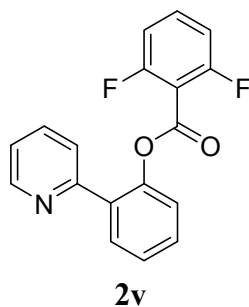
2-(Pyridin-2-yl)phenyl 4-ethoxybenzoate (2t). Yellow oil (27% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.61 (d, $J = 4.6$ Hz, 1H), 8.02 (d, $J = 8.8$ Hz, 2H), 7.78 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.54–7.63 (m, 2H), 7.47 (dt, $J = 7.6, 1.3$ Hz, 1H), 7.38 (dt, $J = 7.5, 0.9$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 1H), 7.13–7.17 (m, 1H), 6.91 (d, $J = 8.8$ Hz, 2H), 4.09 (q, $J = 7.0$ Hz, 2H), 1.44 (t, $J = 7.0$ Hz, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.5 (C=O), 163.9 (C-O), 156.2 (C), 150.3 (C-O), 149.1 (C-H), 136.7 (C-H), 134.0 (C-H), 133.0 (C-H), 131.5 (C-H), 130.3 (C), 126.9 (C-H), 124.4 (C-H), 124.1 (C-H), 122.7 (C-H), 122.2 (C), 114.9 (C-H), 64.4 (CH_2), 15.3 (CH_3). MS (EI): 319 (M^+ , 10), 207 (20), 149 (100), 121 (40). HRMS (ESI): calcd. for $\text{C}_{20}\text{H}_{17}\text{NO}_3\text{H}^+$: 320.1287, found: 320.1285. IR (KBr, cm^{-1}): 1731.



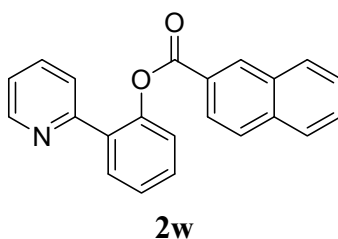
2-(Pyridin-2-yl)phenyl 4-tert-butylbenzoate (2u). Yellow oil (77% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.62 (d, $J = 4.6$ Hz, 1H), 8.04 (d, $J = 8.3$ Hz, 2H), 7.88 (d, $J = 8.3$ Hz, 2H), 7.45–7.54 (m, 2H), 7.36–7.42 (m, 2H), 7.11–7.14 (m, 1H), 1.33 (d, $J = 13.6$ Hz, 9H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 165.2 (C=O), 157.7 (C), 156.1 (C-O), 149.9 (C), 148.9 (C-H), 136.7 (C-H), 133.9 (C-H), 131.5 (C-H), 130.5 (C-H), 130.2 (C), 126.8 (C), 125.9 (C-H), 124.3 (C-H), 123.9 (C-H), 122.6 (C-H), 121.2 (C-H), 35.6 (C), 31.6 (CH_3). MS (EI): 331 (M^+ , 10), 161 (100), 146 (10). HRMS (ESI): calcd. for $\text{C}_{22}\text{H}_{21}\text{NO}_2\text{H}^+$: 332.1651, found: 332.1652. IR (KBr, cm^{-1}): 1737 cm^{-1} .



2-(Pyridin-2-yl)phenyl 2,6-difluorobenzoate (**2v**). Yellow oil (46% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.65 (d, $J = 4.4$ Hz, 1H), 7.76 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.70 (dt, $J = 7.7, 1.7$ Hz, 1H), 7.59 (d, $J = 7.9$ Hz, 1H), 7.49 (dt, $J = 7.7, 1.6$ Hz, 1H), 7.39–7.44 (m, 2H), 7.33 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.20–7.23 (m, 1H), 6.95 (t, $J = 8.3$ Hz, 2H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 162.7 (C=O), 160.7 (C-F), 156.0 (C), 150.2 (C-O), 148.3 (C-H), 136.9 (C-H), 134.1 (C-H), 134.0 (C), 131.6 (C-H), 130.5 (C-H), 127.5 (C-H), 124.4 (C-H), 123.7 (C-H), 122.9 (C-H), 112.9 (C), 112.6 (C-H). MS (EI): 311 (M^+ , 40), 141 (100), 113 (10). HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{11}\text{NO}_2\text{F}_2\text{H}^+$: 312.0836, found: 312.0841. IR (KBr, cm^{-1}): 1751.



2-(Pyridin-2-yl)phenyl 2-naphthoate (**2w**). Yellow oil (44% yield). $^1\text{H-NMR}$ (CDCl_3): δ_{H} 8.69 (s, 1H), 8.59 (d, $J = 4.8$ Hz, 1H), 8.10 (dd, $J = 8.6, 1.4$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 8.5$ Hz, 2H), 7.82 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.56–7.63 (m, 4H), 7.51 (dt, $J = 7.8, 1.6$ Hz, 1H), 7.41–7.45 (m, 1H), 7.38 (dd, $J = 7.9, 0.7$ Hz, 1H), 7.11–7.15 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 166.0 (C=O), 156.3 (C), 150.3 (C-O), 149.1 (C-H), 136.8 (C-H), 136.4 (C), 134.0 (C-H), 133.1 (C), 132.6 (C-H), 131.6 (C-H), 130.4 (C-H), 130.1 (C-H), 129.2 (C), 128.9 (C-H), 128.4 (C), 127.4 (C-H), 127.3 (C-H), 127.1 (C-H), 126.1 (C-H), 124.3 (C-H), 124.0 (C-H), 122.8 (C-H). MS (EI): 325 (M^+ , 20), 155 (100), 127 (60). HRMS (ESI): calcd. for $\text{C}_{22}\text{H}_{15}\text{NO}_2\text{H}^+$: 326.1181, found: 326.1191. IR (KBr, cm^{-1}): 1734 cm^{-1} .



4. Conclusions

In summary, we developed a Pd-catalyzed regioselective C–H benzylation reaction with aryl acylperoxides as reagents. This catalytic protocol was convenient to operate, and the product benzoates were formed in good yield with high regioselectivity and functional group tolerance.

Supplementary Materials

Supplementary materials can be accessed at: <http://www.mdpi.com/1420-3049/18/4/4403/s1>.

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Sample Availability: Not available.

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