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Palladium/NHC-catalyzed tandem benzylic oxidation/oxidative esterification of benzylic alcohols with phenols

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ABSTRACT

A palladium/NHC-catalyzed tandem benzylic oxidation/oxidative esterification of benzylic alcohols with phenols to access aryl benzoate derivatives is described. The procedure tolerates a series of functional groups, such as methoxy, nitro, cyano, chloro, fluoro and bromo groups. Thus, it represents a practically alternative method to access aryl benzoate derivatives.

1. Introduction

Esterification is one of the most fundamental and important reactions in organic synthesis.[1] Although several methods have been exploited and developed, the search for new environmentally friendly, atom-efficient methods, which avoid the use of large amounts of condensing reagents and activators have attracted increasing interest.[2] From the atom-economic point of view, the oxidative couplings from aldehydes to access esters have received much attention.[3] However, long-term storage and use of aldehydes may be troublesome due to their inherent reactivity. An attractive alternative is the direct catalytic oxidation of alcohols to esters.[4] Corey detailed the two-step oxidation of allylic alcohols to esters in the presence of sodium cyanide and MnO_2.[5] Chromium[6] and iodine[7] have also been reported to oxidize alcohols to esters. However, a large excess or stoichiometric amount of a toxic oxidant was required in the above transformations. In 1987, Murahashi described a ruthenium-catalyzed oxidative transformation of alcohols and aldehydes to esters and lactones.[8] In 2002, Hiroi developed an oxidative lactonization of 1,4- or 1,5-diols catalyzed by a novel Ir catalyst.[9] Subsequently, Hartwig and Ikariya reported ruthenium-catalyzed dehydrogenative cyclization of 1,4-diols to lactones, respectively[10] Milstein designed a novel ruthenium complexes to catalyze dehydrogenation of primary alcohols to esters or acetals using a harsh condition (>150 °C).[11] Recently, Scheidt demonstrated a tandem oxidation of alcohols to esters using *N*-heterocyclic carbenes as catalysts,[12] which required super-stoichiometric amounts of MnO_2 as the oxidant. Thus, to develop a facile and versatile procedure on such transformation still remains a highly desired goal for organic chemists. Moreover, less attention has been paid to the synthesis of aryl benzoate derivatives despite their importance as building blocks of numerous active compounds.[13,14] Very recently, we developed a palladium/NHC-catalyzed oxidative esterification of aldehydes with phenols.[15] Lei and Beller developed palladium-catalzyed aerobic oxidative esterification of benzylic alcohols, respectively.[16] Herein, we report a palladium/NHC-catalyzed tandem oxidation/aromatic esterification of benzylic alcohols with phenols to access aryl benzoate derivatives, using O_2 as the clean terminal oxidant.

2. Result and discussion

Initial studies were performed by using the reaction of phenylmethanol with 4-nitrophenol under oxygen as the model reaction, employing $Pd(OAc)_2$ as the catalyst (Table 1). Only a trace of the product was formed in the absence of ligand as determined by GC–MS (Table 1, entry 1). Various precursors of *N*-heterocyclic carbene (NHC) (Fig. 1) were investigated for this reaction. To our delight, an excellent yield was obtained with **L5** (Table 1, entry 6). When the reaction was carried out under nitrogen, no product was detected by GC–MS (Table 1, entry 8). This result suggested that the oxygen played a significant role in the reaction. The choice of solvent was also crucial to the reaction and xylene appeared to be the best among the solvents (Table 1, entries 6 and 9–11). Moreover, the base used also had an important effect in the reaction and Na_2CO_3 proved to be the best. In addition, only a trace of the product was detected by GC–MS in the absence of $Pd(OAc)_2$ (Table 1, entry 6). Conducting the reaction on a 2 mmol scale provided **3aa** in an acceptable 89% yield.

Encouraged by these results, we further pursued the scope of the process with respect to the phenols. As expected, the reaction proceeded smoothly with yields ranging from good to excellent and tolerated various functional groups, such as methoxy, nitro, cyano,

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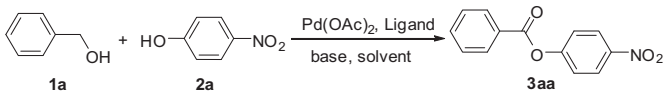
Table 1
Selected results of screening the optimal conditions



1a 2a 3aa

Entry	Ligand	Base	Solvent	Yield[a] (%)
1	—	Na_2CO_3	Xylene	Trace
2	**L1**	Na_2CO_3	Xylene	10
3	**L2**	Na_2CO_3	Xylene	16
4	**L3**	Na_2CO_3	Xylene	65
5	**L4**	Na_2CO_3	Xylene	82
6	**L5**	Na_2CO_3	Xylene	95
7	**L5**	Na_2CO_3	Xylene	Trace[b]
8	**L5**	Na_2CO_3	Xylene	81[c]
9	**L5**	Na_2CO_3	Xylene	<5[d]
10	**L5**	Na_2CO_3	DMF	<5
11	**L5**	Na_2CO_3	Toluene	43
12	**L5**	Na_2CO_3	1,4-Dioxane	30
13	**L5**	K_2CO_3	Xylene	61
14	**L5**	Cs_2CO_3	Xylene	<5
15	**L5**	$NaHCO_3$	Xylene	53
16	**L5**	*t*-BuOK	Xylene	43
17	**L5**	—	Xylene	41

[a] All reactions were run with 4-nitrophenol **2a** (0.2 mmol), phenylmethanol **1a** (0.3 mmol), base (0.1 mmol, 0.5 equiv), $Pd(OAc)_2$ (5 mol %) and ligand (10 mol %) in dry solvent (2 mL) under O_2 at 130 °C for 36 h. Isolated yields.
[b] In the absence of $Pd(OAc)_2$.
[c] Under air.
[d] Under N_2.

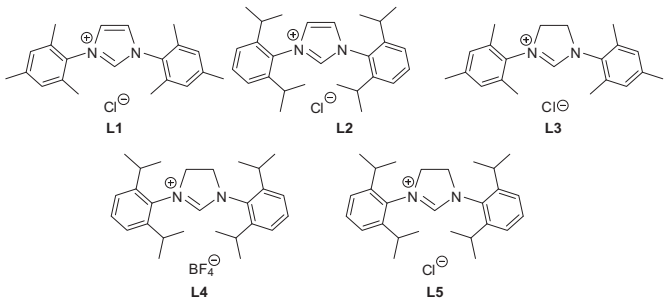
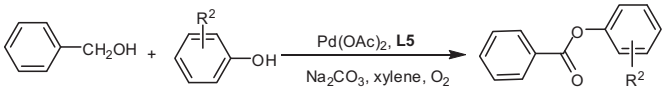


Fig. 1. Selected imidazolium salts screened.

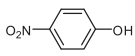
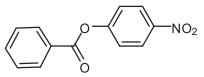
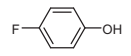
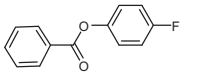
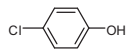
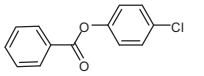
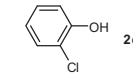
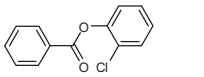
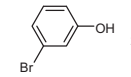
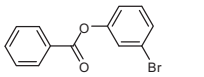
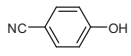
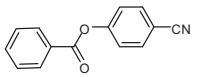
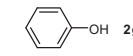
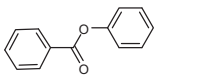
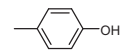
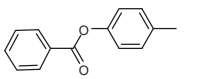
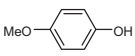
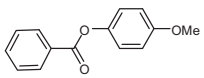
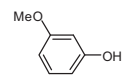
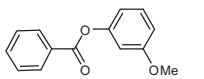
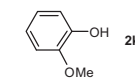
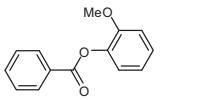
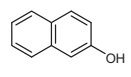
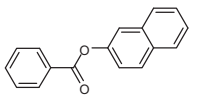
chloro, fluoro and bromo groups. Particularly, halogen-substituted phenols worked well, albeit a lower yield was obtained for bromine (Table 2, entries 2–5). The surviving halogen atom (X=Cl, Br) could be valuable for further manipulation. Generally, electron-deficient phenols reacted with phenylmethanol easily and gave the products in higher yields than electron-rich phenols (e.g., **2a**, **2b**, **2c** and **2d** vs **2h**, **2i**, **2j** and **2k**). Steric hindrance on phenols with electron-withdrawing groups had no obvious effect on the reaction (Table 2, entries 3 and 4). Nevertheless, the hindrance on phenols had a sharp effect on the reaction for those electron-rich analogues (Table 2, entries 9–11). For example, **3ak** was obtained in only 35% yield when **2k** was subjected to the procedure.

Next, we turned our attention to the scope of benzylic alcohols, and the results are shown in Table 3. Once again, the reaction proceeded smoothly with moderate to good yields and tolerated various functional groups, such as nitro, cyano, chloro, fluoro, trifluoromethyl and methoxycarbonyl groups. Generally, the benzylic alcohols possessing electron-withdrawing groups gave slightly higher yields than those of electron-donating groups (Table 3, entries 9–14). It is worth noting that a saturated ester was obtained when allyl alcohol was subjected to the procedure (Table 3, entry 14).[17]

Table 2
Palladium/NHC-catalyzed tandem benzylic oxidation/oxidative esterification of phenylmethanol with phenols



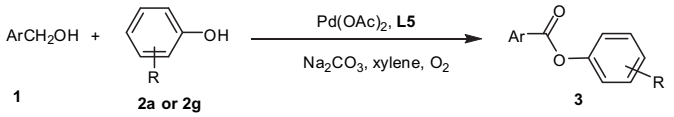
1a 2 3

Entry	Phenol 2	Product 3	Yield[a] (%)
1	 2a	 3aa	95
2	 2b	 3ab	93
3	 2c	 3ac	91
4	 2d	 3ad	89
5	 2e	 3ae	60
6	 2f	 3af	70
7	 2g	 3ag	75
8	 2h	 3ah	61
9	 2i	 3ai	64
10	 2j	 3aj	82
11	 2k	 3ak	35
12	 2l	 3al	88

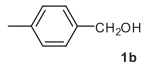
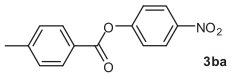
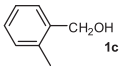
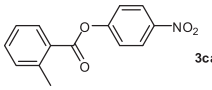
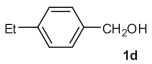
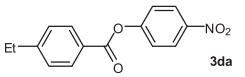
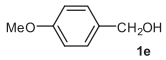
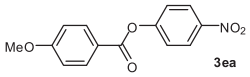
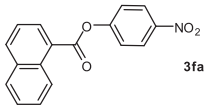
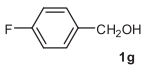
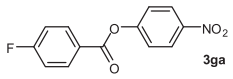
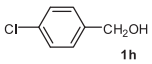
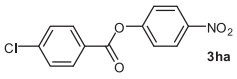
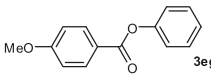
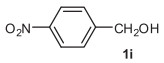
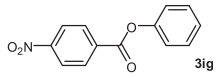
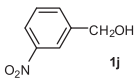
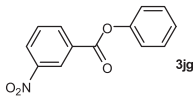
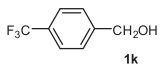
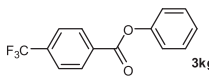
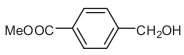
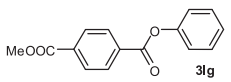
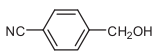
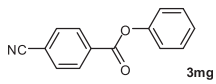
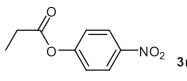
[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), **L5** (10 mol %) and Na_2CO_3 (0.1 mmol) in dry xylene (2 mL) under O_2 at 130 °C for 36 h. Isolated yield.

More experiments were carried out to gain preliminary insight into the reaction mechanism. Conversion of benzylic alcohol to the aromatic aldehyde was observed under the standard procedure by GC–MS. Moreover, when naphthalen-1-ylmethanol **1f** was subjected to the standard procedure without **L5**, 1-naphthaldehyde was isolated in 70% yield (Scheme 1).[18] These results could disclose the possibility of a tandem oxidation of benzylic alcohol to aromatic aldehyde followed by an esterification pathway. However, the mechanism in detail kept unclear in current stage.

Table 3
Palladium/NHC-catalyzed tandem benzylic oxidation/oxidative esterification of benzylic alcohols with phenols



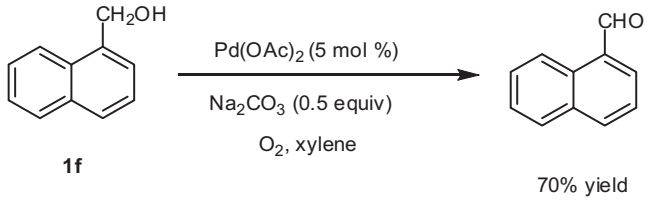
1 2a or 2g 3

Entry	Substrate 1	Product 3	Yield[a] (%)
1	 1b	 3ba	82
2	 1c	 3ca	52
3	 1d	 3da	80
4	 1e	 3ea	60
5	 1f	 3fa	82
6	 1g	 3ga	83
7	 1h	 3ha	78
8	**1e**	 3eg	46
9	 1i	 3ig	80
10	 1j	 3jg	82
11	 1k	 3kg	76
12	 1l	 3lg	65
13	 1m	 3mg	61
14	 1n	 3na	67

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), **L5** (10 mol %) and Na_2CO_3 (0.1 mmol) in dry xylene (2 mL) under O_2 at 130 °C for 36 h. Isolated yield.

3. Conclusions

In conclusion, we have developed a palladium/NHC-catalyzed tandem benzylic oxidation/oxidative esterification of benzylic alcohols with phenols to access aryl benzoate derivatives. It obviates the employment of cyanide and super-stoichiometric amounts of MnO_2. This operationally simple one-pot process uses O_2 as the clean oxidant, producing esters in good to excellent yields.



Scheme 1. $Pd(OAc)_2$-catalyzed oxidation of naphthalen-1-ylmethanol to 1-naphthaldehyde by molecular oxygen.

4. Experimental section

4.1. General procedure

^1H NMR and ^{13}C NMR spectra were measured on a 500 MHz Bruker spectrometer (^1H 500 MHz, ^{13}C 125 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in parts per million relative to TMS, the coupling constants J are given in hertz. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

4.2. Typical experimental procedure of palladium/NHC-catalyzed tandem benzylic oxidation/oxidative esterification of benzylic alcohols with phenols

Under oxygen, a reaction tube was charged with phenols (0.2 mmol), benzylic alcohols (0.3 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), **L5** (8.5 mg, 10 mol %), Na_2CO_3 (10.6 mg, 0.1 mmol) in dry xylene (2 mL). After the mixture was stirred for 36 h at 130 °C, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the product.

4.3. Analytical data of products

*4.3.1. 4-Nitrophenyl benzoate (**3aa**)*[19]. Pale yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.36 (d, J=9.0 Hz, 2H), 8.24–8.22 (m, 2H), 7.71 (t, J=7.5 Hz, 1H), 7.59–7.56 (m, 2H), 7.45 (d, J=9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.2, 155.7, 145.4, 134.2, 130.3, 128.8, 128.6, 125.3, 122.6.

*4.3.2. 4-Fluorophenyl benzoate (**3ab**)*[14h]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.19 (d, J=7.7 Hz, 2H), 7.64 (t, J=7.4 Hz, 1H), 7.51 (t, J=7.4 Hz, 2H), 7.19–7.17 (m, 2H), 7.12–7.09 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.2, 160.3 (d, J_{C-F}=242.8 Hz), 146.8 (d, J_{C-F}=2.8 Hz), 133.7, 130.2, 129.3, 128.6, 123.1 (d, J_{C-F}=8.4 Hz), 116.1 (d, J_{C-F}=23.4 Hz).

*4.3.3. 4-Chlorophenyl benzoate (**3ac**)*[20]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.19 (d, J=7.5 Hz, 2H), 7.66–7.63 (m, 1H), 7.53–7.50 (m, 2H), 7.40 (d, J=8.0 Hz, 2H), 7.17 (d, J=8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.0, 149.4, 133.8, 131.3, 130.2, 129.6, 129.2, 128.6, 123.1.

*4.3.4. 2-Chlorophenyl benzoate (**3ad**)*[21]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.25–8.24 (m, 2H), 7.68–7.65 (m, 1H), 7.55–7.49 (m, 3H), 7.36–7.33 (m, 1H), 7.30–7.28 (m, 2H). ^{13}C NMR

($CDCl_3$, 125 MHz): δ 164.3, 147.3, 133.9, 130.4, 128.9, 128.7, 127.8, 127.1, 123.9.

*4.3.5. 3-Bromophenyl benzoate (**3ae**)*[22]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.19 (d, *J*=7.5 Hz, 2H), 7.67–7.64 (m, 1H), 7.54–7.51 (m, 2H), 7.42–7.41 (m, 2H), 7.32–7.29 (m, 1H), 7.19–7.17 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.7, 151.4, 133.9, 130.5, 130.2, 129.1, 128.7, 125.3, 122.5, 120.6.

*4.3.6. 4-Cyanophenyl benzoate (**3af**)*[23]. Pale yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.12 (d, *J*=8.0 Hz, 2H), 7.67 (d, *J*=8.2 Hz, 2H), 7.60–7.59 (m, 1H), 7.48–7.45 (m, 2H), 7.30 (d, *J*=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.3, 154.3, 134.2, 133.7, 130.3, 128.8, 128.7, 122.9, 118.2, 109.9.

*4.3.7. Phenyl benzoate (**3ag**)*[14a]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.21 (d, *J*=7.5 Hz, 2H), 7.66–7.63 (m, 1H), 7.53–7.50 (m, 2H), 7.45–7.42 (m, 2H), 7.29–7.21 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.2, 151.0, 133.6, 130.2, 129.6, 129.5, 128.6, 125.9, 121.7.

*4.3.8. p-Tolyl benzoate (**3ah**)*[14a]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.20 (d, *J*=7.0 Hz, 2H), 7.63–7.49 (m, 3H), 7.25–7.09 (m, 4H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.4, 148.7, 135.5, 133.5, 130.2, 130.0, 129.7, 128.6, 121.4, 20.9.

*4.3.9. 4-Methoxyphenyl benzoate (**3ai**)*[22]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.14–8.12 (m, 2H), 7.57–7.54 (m, 1H), 7.45–7.42 (m, 2H), 7.06 (d, *J*=9.0 Hz, 2H), 6.87 (d, *J*=9.0 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.5, 157.3, 144.4, 133.5, 130.1, 129.6, 128.5, 122.4, 114.5, 55.6.

*4.3.10. 3-Methoxyphenyl benzoate (**3aj**)*[24]. Pale yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.14–8.12 (m, 2H), 7.59–7.56 (m, 1H), 7.46–7.43 (m, 2H), 7.27–7.24 (m, 1H), 6.77–6.70 (m, 3H), 3.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.1, 160.5, 151.9, 133.6, 130.2, 129.9, 129.6, 128.5, 113.9, 111.9, 107.7, 55.5.

*4.3.11. 2-Methoxyphenyl benzoate (**3ak**)*[22]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.22 (d, *J*=7.5 Hz, 2H), 7.64–7.61 (m, 1H), 7.52–7.49 (m, 2H), 7.25–7.23 (m, 1H), 7.16–7.15 (m, 1H), 7.02–6.98 (m, 2H), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.8, 151.4, 140.0, 133.4, 130.3, 129.5, 128.5, 126.9, 122.9, 120.8, 112.6, 55.9.

*4.3.12. Naphthalen-2-yl benzoate (**3al**)*[20]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.26 (d, *J*=7.5 Hz, 2H), 7.90–7.82 (m, 3H), 7.70–7.64 (m, 2H), 7.54–7.46 (m, 4H), 7.37–7.35 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.4, 148.7, 133.9, 133.7, 131.6, 130.2, 129.6, 129.5, 128.6, 127.8, 127.7, 126.6, 125.8, 121.3, 118.7.

*4.3.13. 4-Nitrophenyl 4-methylbenzoate (**3ba**)*[25]. Pale yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.26–8.24 (m, 2H), 8.01 (d, *J*=8.0 Hz, 2H), 7.35–7.33 (m, 2H), 7.27 (d, *J*=8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.3, 155.9, 145.4, 145.3, 130.4, 129.5, 125.8, 125.3, 122.7, 21.8.

*4.3.14. 4-Nitrophenyl 2-methylbenzoate (**3ca**)*[26]. Pale yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.33 (d, *J*=9.0 Hz, 2H), 8.18–8.16 (m, 1H), 7.54–7.51 (m, 1H), 7.42–7.40 (m, 2H), 7.37–7.34 (m, 2H), 2.68 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.6, 155.8, 145.4, 141.9, 133.4, 132.2, 131.3, 127.4, 126.1, 125.3, 122.7, 22.0.

*4.3.15. 4-Nitrophenyl 4-ethylbenzoate (**3da**)*[27]. Pale yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.33 (d, *J*=9.0 Hz, 2H), 8.12 (d, *J*=8.5 Hz, 2H), 7.42 (d, *J*=9.0 Hz, 2H), 7.37 (d, *J*=8.0 Hz, 2H), 2.77 (q, *J*=7.5 Hz, 2H), 1.30 (t, *J*=7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.3, 155.9, 151.5, 145.3, 130.5, 128.3, 126.0, 125.2, 122.7, 29.1, 15.2.

*4.3.16. 4-Nitrophenyl 4-methoxybenzoate (**3ea**)*[25]. Pale yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.25 (d, *J*=9.0 Hz, 2H), 8.08 (d, *J*=9.0 Hz, 2H), 7.33 (d, *J*=9.0 Hz, 2H), 6.94 (d, *J*=9.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.4, 163.9, 156.0, 145.3, 132.5, 125.2, 122.7, 120.7, 114.1, 55.6.

*4.3.17. 4-Nitrophenyl 1-naphthoate (**3fa**)*[28]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 9.01 (d, *J*=8.5 Hz, 1H), 8.50–8.35 (m, 3H), 8.21–8.15 (m, 1H), 7.96–7.94 (m, 1H), 7.70–7.47 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.6, 155.8, 145.5, 135.2, 134.0, 131.8, 131.7, 128.9, 128.6, 126.7, 125.5, 125.3, 124.6, 124.5, 122.8.

*4.3.18. 4-Nitrophenyl 4-fluorobenzoate (**3ga**)*[25]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.27–8.25 (m, 2H), 8.17–8.14 (m, 2H), 7.35–7.33 (m, 2H), 7.16–7.13 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.5 (d, J_{C-F}=255.0 Hz), 163.3155.6, 145.5, 133.0 (d, J_{C-F}=9.5 Hz), 125.3, 124.8 (d, J_{C-F}=3.0 Hz), 122.6, 116.1 (d, J_{C-F}=22.0 Hz).

*4.3.19. 4-Nitrophenyl 4-chlorobenzoate (**3ha**)*[25]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.33 (d, *J*=9.0 Hz, 2H), 8.14 (d, *J*=9.0 Hz, 2H), 7.52 (d, *J*=9.0 Hz, 2H), 7.42 (d, *J*=9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.4, 155.4, 145.5, 140.8, 131.6, 129.2, 126.9, 125.3, 122.5.

*4.3.20. Phenyl 4-methoxybenzoate (**3eg**)*[14a]. Pale yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.08 (d, *J*=8.8 Hz, 2H), 7.36–7.33 (m, 2H), 7.20–7.17 (m, 1H), 7.13–7.12 (m, 2H), 6.90 (d, *J*=8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.9, 163.9, 151.1, 132.2, 129.4, 125.7, 121.9, 121.8, 113.8, 55.5.

*4.3.21. Phenyl 4-nitrobenzoate (**3ig**)*[14g]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.33–8.28 (m, 4H), 7.41–7.38 (m, 2H), 7.26–7.23 (m, 1H), 7.18–7.16 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.3, 150.9, 150.5, 135.0, 131.3, 129.7, 126.4, 123.7, 121.4.

*4.3.22. Phenyl 3-nitrobenzoate (**3jg**)*[14a]. Pale yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 9.04 (s, 1H), 8.54–8.49 (m, 2H), 7.38 (t, *J*=8.0 Hz, 1H), 7.48–7.45 (m, 2H), 7.33–7.30 (m, 1H), 7.26–7.23 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.1, 150.5, 148.4, 135.8, 131.4, 129.9, 129.7, 128.0, 126.4, 125.1, 121.4.

*4.3.23. Phenyl 4-(trifluoromethyl)benzoate (**3kg**)*[29]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.33 (d, *J*=8.0 Hz, 2H), 7.79 (d, *J*=8.5 Hz, 2H), 7.45 (t, *J*=8.0 Hz, 2H), 7.30 (t, *J*=7.5 Hz, 1H), 7.23 (d, *J*=8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.0, 150.7, 135.0 (d, J_{C-F}=32.5 Hz), 132.9, 130.6, 129.6, 126.2, 125.6 (d, J_{C-F}=3.8 Hz), 123.1 (d, J_{C-F}=271.2 Hz), 121.5.

*4.3.24. Methyl phenyl terephthalate (**3lg**)*[14g]. White solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.27 (d, *J*=8.5 Hz, 2H), 8.16 (d, *J*=8.5 Hz, 2H), 7.46–7.43 (m, 2H), 7.29 (t, *J*=7.5 Hz, 1H), 7.23 (d, *J*=7.6 Hz, 2H), 3.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.2, 164.4, 150.8, 134.5, 133.4, 130.1, 129.7, 129.6, 126.1, 121.6, 52.5.

*4.3.25. Phenyl 4-cyanobenzoate (**3mg**)*[14h]. Pale yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.31 (d, *J*=8.0 Hz, 2H), 7.82 (d, *J*=8.0 Hz, 2H), 7.47–7.44 (m, 2H), 7.32–7.21 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.6, 150.6, 133.5, 132.4, 130.6, 129.7, 126.4, 121.4, 117.8, 117.0.

*4.3.26. 4-Nitrophenyl propionate (**3na**)*[30]. Pale yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.27 (d, *J*=7.0 Hz, 2H), 7.29 (d, *J*=7.0 Hz,

2H), 2.64 (q, J=7.5 Hz, 2H), 1.28 (t, J=7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.0, 155.5, 145.3, 125.2, 122.4, 27.7, 8.9.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.06.060.

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