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R1—OH + R²—C(O)—CH₂—R³ →[*t*-amyl alcohol, 18 h][*t*-BuONa (30 mol%), 120℃] R¹—O—C(O)—R²

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Journal Name

ARTICLE

Base-catalyzed Retro-Claisen Condensation: A Convenient Esterification of Alcohols via C-C Bond Cleavage of Ketones to Afford Acylating Sources

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The base-catalyzed esterification of alcohols via retro-Claisen condensation has been demonstrated for the first time. A variety of alcohols including aryl- and heteroaryl methanols as well as aliphatic ones underwent efficient acylation to give the ester products in reasonable to good yields upon isolation. Not only conventional 1,3-diketones but also strong electron-withdrawing group containing acetophenones could serve as the acylating suppliers. The synthetic protocol is operationally simple and adaptable to a broad substrate scope. It complements the existed esterification via the retro-Claisen condensation, and enlarges this benign synthetic methodology.

Introduction

Esters have been known as a fundamental class of organic compounds. And the ester groups frequently occur in numerous bioactive compounds,[1] top-sold marketing medicines[2a] (e.g., Plavix,[2b] Concerta,[2c] Xalatan[2d]), and synthetic polymers (e.g. proteins and nylons)[3]. Moreover, esters could serve as interesting building blocks for the preparation of various functionalized products.[4] Due to its multiple functions, the development of efficient esterification approaches has long been a subject of synthetic chemists. The conventional syntheses include the Tishchenko[5,6] and Fischer esterification,[7] trans-esterification,[8] and the condensation or coupling reactions of alcohols with carboxylic acids,[9] anhydrides,[10] acid halides.[11] Interestingly, the dehydrogenative esterification established in recent years directly from alcohols demonstrated an alternative approach towards the related end.[12] Although these methods are currently the most widely used, many of them suffer a number of drawbacks, such as use of less environmentally benign halogenated reagents, concentrated acid catalysts (i.e., HCl and H_2SO_4), or expensive ligands and transition-metal catalysts, which could lead to either easy equipment corrosion, or generation of toxic wastes. Therefore, there is a need for the development of acid and transition-metal catalysts free esterification approaches.

In recent years, the retro-Claisen condensation has offered a new avenue to access different type of esters. The reaction proceeds via a synergistic process of carbon-carbon (C-C) bond cleavage of ketones and alcohol acylation. Lewis acids such as $In(OTf)_3$, $FeCl_3$ and $Fe(OTf)_3$ have been proven to be efficient catalysts.[13] However，to the best of our knowledge, the usage of inexpensive base catalysts for such a transformation has not been explored yet. During the course of our study on α-alkylation of ketones,[14] the reaction of pyridin-3-ylmethanol **1a** with acetylacetone **2a** gave, instead of the anticipated α-alkylated product **3a**', but the ester **3a** exclusively (Eq.1). With

this new observation, our further investigations showed that the base (*t*-BuONa) served as a catalyst in the formation of desired product **3a**, while the ruthenium species was not involved in the reaction. Herein, we report a base-catalysed retro-Claisen condensation for the first time, providing a convenient esterification of alcohols via C-C bond cleavage of ketones to afford acylating sources.
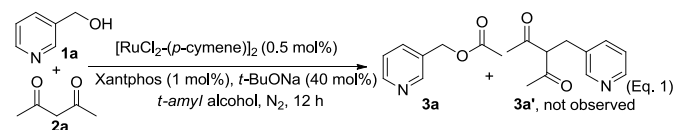

Results and discussion

Firstly, we tried to screen an efficient reaction system. The synthesis of pyridin-3-ylmethyl acetate **3a** from 3-pyridin-3-ylmethanol **1a** and acetylacetone **2a** was chosen as a model reaction to determine different reaction parameters. Initially, the reaction was performed at 120 °C for 12 h in the presence of 20 mol% of *t*-BuONa. The desired product was detected in 57% yield upon GC analysis (Table 1, entry 1). However, the reaction in absence of base gave only trace of expected product (Table 1, entry 2), indicating the base is an essential catalyst in the formation of product. Subsequently, under the same reaction conditions, replacing *t*-BuONa with a series of other inorganic and organic bases gave lower product yields (Table 1, entries 3-8). Hence, we chose *t*-BuONa as the preferred catalyst, other polar and less-polar solvents were showed to be less effective in the formation of **3a** comparing to *t*-amyl alcohol (Table 1, entries 9-11). Gratifyingly, the increase of base loading from 20 mol% to 30 mol% led to an improved product yield (Table 1, entry 12). However, a further increase could not improve the product yield any more (Table 1, entry 13). Similarly, increase or decrease of reaction temperature also

failed to result in better reaction efficiency (Table 1, entries 14-15). Finally, prolonging the reaction time from 12 h to 18 h gave a highest yield (Table 1, entry 16). Hence, the optimal reaction conditions can be as indicated in entry 16 of Table 1.

**Table 1.** Screening of optimized reaction conditions [a]
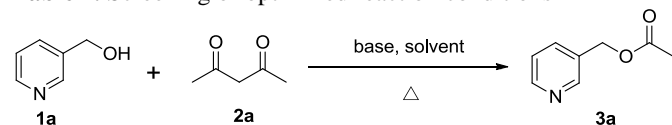
Entry	Base	Solvent	3a,Yield%[b]
1	t-BuONa	t-amyl alcohol	57
2	-	t-amyl alcohol	trace
3	K_2CO_3	t-amyl alcohol	23
4	CS_2CO_3	t-amyl alcohol	34
5	KOH	t-amyl alcohol	38
6	CH_3ONa	t-amyl alcohol	46
7	NEt_3	t-amyl alcohol	<10
8	DABCO	t-amyl alcohol	31
9	t-BuONa	DMSO	43
10	t-BuONa	DMF	41
11	t-BuONa	toluene	52
12[c]	t-BuONa	t-amyl alcohol	68
13[d]	t-BuONa	t-amyl alcohol	68
14[e]	t-BuONa	t-amyl alcohol	68
15[f]	t-BuONa	t-amyl alcohol	48
16[g]	t-BuONa	t-amyl alcohol	82

[a] Reaction conditions: Unless otherwise specified, all reactions were carried out without inert gas protection by using **1a** (1.2 mmol, **2a** (1 mmol), solvent (1 mL), temperature: 120 ℃, base (0.2 mmol), reaction time (12 h). [b] GC yield. [c] Base (0.3 mmol). [d] Base (0.5 mmol). [e] Reaction temperature: 130 ℃. [f] Reaction Temperature: 100 ℃. [g] Reaction time: 18 h

With the availability of the optimized reaction conditions in hand, we then examined the scope of the synthetic protocol. Considering the pyridyl group containing esters could often exhibit some interesting biological activities,[15] but the esterification of pyridyl methanols by employing retro-Claisen condensation has been scarcely explored. Hence, we firstly focused on the synthesis of pyridylmethyl esters. The reactions of a variety of pyridyl methanols were examined in combination with two representative alkyl and aryl 1,3-diketones (**2a**, **2b**). As shown in table 2, all the reactions proceeded smoothly and furnished desired esters in moderate to good yields upon isolation (Table 2, entries 1-10). It was found that the substitution patterns of pyridyl methanols slightly affected the product yields. Specifically, the *para*-pyridyl methanol afforded the corresponding products in higher yields than the *meta*- and *ortho*- ones (Table 2, entries 1-3 and 6-8). Meanwhile, the reactions using (2-chloropyridin-3-yl)methanol gave the products in relatively lower yields, which might be attributable to the influence of steric hindrance (Table 2, entries 5, 10). In addition, benzylic alcohols **1f** and **1g** as well as aliphatic alcohol **1h** could also been acylated to afford the desired products in good yields (Table 2, entries 11-14). Noteworthy, the reactions of (2-nitrophenyl)methanol **1f** need longer reaction time and elevated reaction temperature to afford

desirable yields. It is conceivable that the *ortho*-NO$_2$ group could significantly decrease the nucleophilicity of alcohol, thus disfavouring the acylation process (Table 1, entries 11-12).

Table 2. Base-mediated acylation or alcohols with of 1,3-diketones.[a]
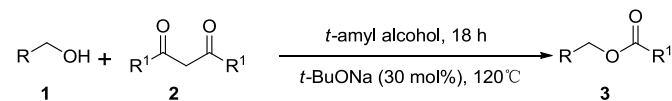
Entry	Alcohol 1	Ketone 2	3, Yield%[b]
1	**1a**	**2a：** R^1 = Me	**3a**, 70
2	**1b**	**2a**	**3b**, 74
3	**1c**	**2a**	**3c**，61
4	**1d**	**2a**	**3d**, 50
5	**1e**	**2a**	**3e**, 53
6	**1a**	**2b：** R^1 = Ph	**3f**, 75
7	**1b**	**2b**	**3g**, 78
8	**1c**	**2b**	**3h**, 66
9	**1d**	**2b**	**3i**, 60
10	**1e**	**2b**	**3j**, 65
11[c]	**1f**	**2a**	**3k**, 63
12[c]	**1f**	**2b**	

13	**1g**	**2b**	**3l**, 70
			3m, 71
14	**1h**	**2b**	**3n**, 62
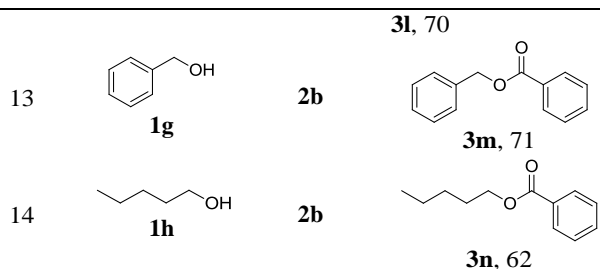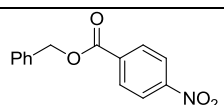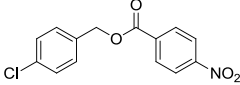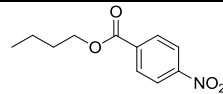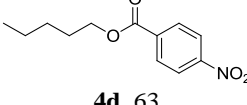
[a] Reaction conditions: Unless otherwise specified, all reactions were carried out in presence of **1** (1.2 mmol), **2** (1 mmol), solvent (1 mL), temperature (120 °C), base (0.3 mmol), reaction time (18 h).[b] Isolated Yields. [c] Temperature: 130 °C, time: 24 h.

Next, we turned our attention to employ less-reactive acetophenones for the synthetic protocol. Firstly 1-(4-nitrophenyl)ethanone **3a** in combination with a variety of alcohols was tested. As shown in table 3, all the reactions underwent efficiently to afford desired products in reasonable to good isolated yields (Table 3, entries 1-8). Simple benzylic alcohol **1g** and aliphatic ones **1j** and **1h** were proven to be effective coupling partners, giving desired products in good yields (Table 3, entries 1, 3 and 4). Moreover, chloride-containing alcohols (**1i**, **1k**) as well as pyridyl methanols (**1a**, **1b** and **1d**) could also be transformed into the corresponding esters in reasonable yields (Table 3, entries 2 and 5-8). However, the reactions of acetophenone **3b**, 1-(4-methoxyphenyl)ethanone **3c** and 1-(4-fluorophenyl)ethanone **3d** failed to yield even trace of expected products (Table 3, entries 9-11), attributing to the acetophenones lacking an strong electron-withdrawing group disfavor of the C-C bond cleavage between the carbonyl group and the α-position.

Table 3. Base-catalyzed esterfication alcohols with acetophenones[a].

$$R{-}CH_2OH + R^2{-}C(O)CH_3 \xrightarrow[\text{t-amyl alcohol, 18 h}]{\text{t-BuONa (30 mol\%), 120℃}} R{-}CH_2{-}O{-}C(O){-}R^2$$

1   **3**   **4**

1i: R = 4-Cl-C$_6$H$_4$;
1j: R = n-propyl;
1k: R = 4-Cl-C$_6$H$_4$CH$_2$;

3a: R^2 = 4-NO$_2$-C$_6$H$_4$;
3b: R^2 = Ph;
3c: R^2 = 4-OMe-C$_6$H$_4$;
3d: R^2 = 4-Cl-C$_6$H$_4$;

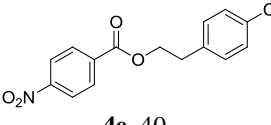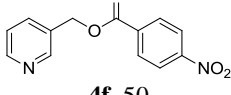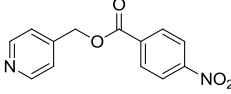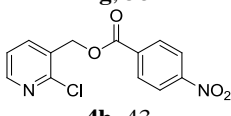| Entry	Alcohol **1**	Ketone **3**	**4**, Yield%[b]
1	**1g**	**3a**	**4a**, 62
2	**1i**	**3a**	**4b**, 50
3	**1j**	**3a**	**4c**, 63
4	**1h**	**3a**	**4d**, 63
5[c]	**1k**	**3a**	**4e**, 40
6	**1a**	**3a**	**4f**, 50
7	**1b**	**3a**	**4g**, 58
8	**1d**	**3a**	**4h**, 43
9	**1g**	**3b**	-
10	**1g**	**3c**	-
11	**1g**	**3d**	-

[a] Reaction conditions: Unless otherwise specified, all reactions were carried out without inert gas protection by using **1** (1.2 mmol), **3** (1 mmol), solvent (1 mL), temperature (120 °C), base (0.3 mmol), reaction time (18 h). [b] Yields of isolated pure product. [c] Temperature: 130 °C, reaction time : 24 h.

Finally, unsymmetrical 1-phenylbutane-1,3-dione **2c** was used in combination with pyridin-2-ylmethanol **1c** to investigate the reaction chemoselectivity, which could lead to two possible isomers **3c** and **3h**. Interestingly, except for the generation acetophenone **3b**, ester **3c** and **3h** were observed in a ratio of 10 : 1. The selectivity is associated with the sterically less hindered acyl moiety favor the acylation of alcohol.
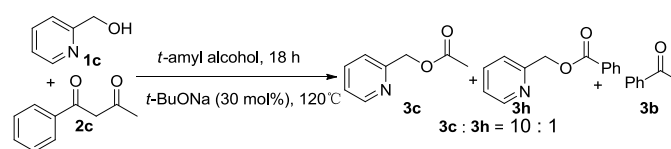
Scheme 1. The esterification of dissymmetric 1,3-diketone and alcohols

Based on the retro-Claisen condensation,[16] a plausible pathway for the generation of esters from alcohols and ketones is depicted in scheme 2. The reaction initiated with t-BuONa-induced deprotonation of alcohol **1** to form alkoxy anion **A**, **A** undergoes a nucleophilic attack to the carbonyl group of ketone and affords intermediate **B**. Then, by abstracting a proton from

the *in-situ* formed *t*-BuOH, the thermodynamic favorable C-C bond cleavage of **B** in a retro-Aldol manner would afford the desired product, regenerate the *t*-BuONa catalyst and release the side product R³Me, respectively.
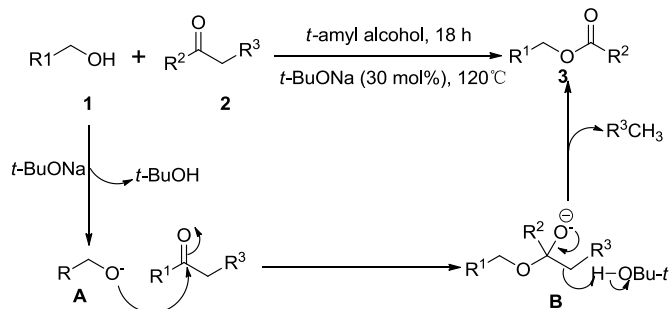
Scheme 2. Proposed mechanism for the esterfication of keones

Conclusions

In summary, we have demonstrated a base-catalyzed esterification of alcohols via retro-Claisen condensation for the first time. A variety of alcohols including aryl- and heteroaryl methanols as well as aliphatic ones underwent efficient acylation to give the ester products in reasonable to good isolated yields. Not only conventional 1,3-diketones but also strong electron-withdrawing group containing acetophenones could serve as the acylating suppliers. The synthetic protocol is operationally simple and adaptable to a broad substrate scope. It complements the existed esterification via the retro-Claisen condensation, and enlarges this benign synthetic methodology.

Experimental

General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR infrared spectra (IR), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, the solid and new products were further determined by Melting points and mass spectra (MS), respectively. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Bruker Avance 400 MHz NMR spectrometer; Mass spectra were recorded on Trace DSQ GC/MS. Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a Brucker Vector 22 spectrometer; Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification.

Typical procedure for the synthesis of 3-Pyridylmethyl acetate 3a

t-BuONa (0.028 g, 0.3 mmol), 3-(Hydroxymethyl)pyridine **1a** (0.131 g, 1.2 mmol), acetylacetone **2a** (0.1g, 1 mmol) and *t*-amyl alcohol (1 mL) were added successively to a Schlenk tube, it was then closed and the resulting mixture was heated at 120 ℃ for 18 h in an oil bath. After cooling down to room temperature, the reaction mixture was then filtered and concentrated under vacuum, the obtained crude product was directly purified by preparative TLC on silica, eluting with petroleum ether (60-90 ℃): ethyl acetate (3:1) to give 3-pyridylmethyl acetate **3a** as a yellow oil (0.110 g, 75%).

Analytic data of the obtained compounds

3-Pyridylmethyl acetate (3a). Yellow oil; ^{1}H NMR (400 MHz, CDCl₃): δ 8.62 (d, *J* = 1.6 Hz, 1H), 8.58 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.70 (dt, *J* = 7.6, 2.0 Hz, 1H), 7.33-7.29 (m, 1H), 5.13 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, CDCl₃): δ 170.71, 149.67, 149.61, 136.07, 131.63, 123.47, 63.72, 20.87; IR (neat): 2926, 1746, 1579, 1481, 1381, 1364, 1235, 1027, 873, 795, 713 cm⁻¹; MS (EI, m/z): 151.11 [M]⁺.

4-Pyridylmethyl acetate (3b). Yellow oil; ^{1}H NMR (400 MHz, CDCl₃): δ 8.54 (d, *J* = 5.6 Hz, 2H), 7.20 (d, *J* = 5.2 Hz, 2H), 5.07 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, CDCl₃): δ 170.50, 149.99, 144.97, 121.94, 64.26, 20.79; IR (neat): 2930, 1746, 1606, 1563, 1417, 1383, 1365, 1234, 1045, 800 cm⁻¹; MS (EI, m/z): 151.08 [M]⁺.

2-Pyridylmethyl acetate (3c). Yellow oil; ^{1}H NMR (400 MHz, CDCl₃): δ 8.53 (d, *J* = 4.8 Hz, 1H), 7.63 (td, *J* = 8.0, 2.0 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 7.2, 5.2 Hz, 1H), 5.15 (s, 2H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, CDCl₃): δ 170.68, 155.77, 149.52, 136.76, 122.88, 121.87, 66.87, 20.91; IR (neat): 2924, 2853, 1738, 1637, 1459, 1130, 638 cm⁻¹; MS (EI, m/z): 151.11 [M]⁺.

(4-chloropyridin-2-yl)methyl acetate (3d). Yellow oil; ^{1}H NMR (400 MHz, CDCl₃): δ 8.49 (d, *J* = 5.2 Hz, 1H), 7.37 (d, *J* = 1.6 Hz, 1H), 7.25 (dd, *J* = 5.2, 1.6 Hz, 1H), 5.21 (s, 2H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, CDCl₃): δ 170.47, 157.59, 150.35, 144.91, 123.21, 122.00, 66.13, 20.85; IR (neat): 2959, 2925, 1738, 1637, 1450, 1106, 619 cm⁻¹; MS (EI, m/z): 185.97 [M+1]⁺.

(2-chloropyridin-3-yl)methyl acetate (3e). Yellow oil; ^{1}H NMR (400 MHz, CDCl₃): δ 8.36 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.82-7.72 (m, 1H), 7.33-7.24 (m, 1H), 5.21 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, CDCl₃): δ 170.40, 150.27, 149.05, 138.00, 130.51, 122.56, 62.61, 20.73; IR (neat): 2958, 2852, 1742, 1637, 1414, 1107, 992, 619 cm⁻¹; MS (EI, m/z): 185.98 [M+1]⁺.

3-Pyridylmethyl benzoate (3f). Yellow oil; ^{1}H NMR (400 MHz, CDCl₃): δ 8.62 (s, 1H), 8.53-8.44 (m, 1H), 8.02-7.89 (m, 2H), 7.67 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50-7.41 (m, 1H), 7.37-7.28 (m, 2H), 7.20 (dd, *J* = 8.0, 5.6 Hz, 1H), 5.27 (s, 2H); ^{13}C NMR (101 MHz, CDCl₃): δ 166.19, 149.61, 135.97, 133.23, 131.73, 129.72, 129.68, 128.44, 123.49, 64.11; IR (neat): 3963,

3030, 1719, 1602, 1579, 1484, 1453, 1427, 1374, 1315, 1272, 1181, 1110, 1070, 1025, 946, 796, 710 cm^{-1}; MS (EI, m/z): 214.03 [M+1]$^+$.

4-Pyridylmethyl benzoate (3g). Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.51 (d, J = 4.4 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H), 7.54-7.42 (m, 1H), 7.37-7.33 (m, 2H), 7.23 (d, J = 5.2 Hz, 2H), 5.27 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 165.00, 148.99, 144,08, 132.37, 128.70, 128.52, 127.51, 120.83, 63.59; IR (neat): 3037, 1722, 1602, 1561, 1450, 1378, 1278, 1175, 1109, 1072, 1026, 797, 714 cm^{-1}; MS (EI, m/z): 214.05 [M+1]$^+$.

2-Pyridylmethyl benzoate (3h). Brown oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.61 (d, J = 4.0 Hz, 1H), 8.13 (s, 1H), 8.11 (d, J = 1.2 Hz, 1H), 7.71 (td, J = 8.0, 2.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 2H), 7.44 (d, J = 1.2 Hz, 1H), 7.24 (dd, J = 7.2, 5.2 Hz, 1H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 166.21, 156.05, 149.48, 136.78, 133.18, 129.90, 129.80, 128.43, 122.85, 121.67, 67.22; IR (neat): 3055, 1721, 1636, 1475, 1384, 1275, 1109, 992, 756, 618 cm^{-1}; MS (EI, m/z): 214.05 [M+1]$^+$.

(4-chloropyridin-2-yl)methyl benzoate (3i). Brown oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.52 (d, J = 5.2 Hz, 1H), 8.14 (dd, J = 8.0, 1.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 8.0 Hz 3H), 7.27 (dd, J = 5.6, 2.0 Hz, 1H), 5.49 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 166.05, 157.84, 150.35, 144.95, 133.36, 129.83, 129.60, 128.52, 123.23, 121.89, 66.51. IR (neat): 3062, 3011, 1724, 1637, 1578, 1451, 1314, 1110, 709, 619 cm^{-1}; MS (EI, m/z): 248.01 [M+1]$^+$.

(2-chloropyridin-3-yl)methyl benzoate (3j). Brown solid. m.p: 81-83°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.38 (dd, J = 4.8, 1.6 Hz, 1H), 8.09 (dd, J = 8.0, 1.2 Hz, 2H), 7.85 (dd, J = 7.6, 1.2 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.32-7.25 (m, 1H), 5.46 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 166.03, 150.40, 149.14, 138.04, 133.42, 130.68, 129.76, 129.53, 128.55, 122.62, 63.05; IR (neat): 3058, 1740, 1637, 1385, 1107, 992, 619 cm^{-1}; MS (EI, m/z): 248.01 [M+1]$^+$.

2-nitrobenzyl acetate (3k). Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.00 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 5.41 (s, 2H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 170.33, 147.52, 133.77, 132.11, 129.00, 128.77, 124.99, 62.89, 20.73; IR (neat): 2959, 2925, 1723, 1575, 1437, 1312, 1108, 991, 732 cm^{-1}; MS (EI, m/z): 195.03 [M]$^+$.

2-nitrobenzyl benzoate (3l). Gray solid; m.p: 113-115°C (Lit^{16a}, 101-102 ℃); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06-7.96 (m, 3H), 7.63-7.47 (m, 3H), 7.44-7.34 (m, 3.H), 5.68 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 165.94, 147.62, 133.84, 133.42, 132.36, 129.78, 129.59, 128.93, 128.82, 128.58, 125.11, 63.35; IR (neat): 2923, 2849, 1718, 1598, 1575, 1521, 1436, 1372, 1336, 1312, 1272, 1119, 1069, 1028, 991, 860, 796, 715, 661 cm^{-1}; MS (EI, m/z): 257.05 [M]$^+$.

benzyl benzoate (3m). Light yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.40-7.21 (m, 7H), 5.28 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 166.46, 136.11, 133.06, 130.19, 129.74, 128.63, 128.41, 128.27, 128.20, 66.72; IR (neat): 3066, 3034, 1718, 1637, 1451, 1270, 1107, 710, 618 cm^{-1}; MS (EI, m/z): 211.94 [M]$^+$.

pentyl benzoate (3n). Colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.08 (s, 1H), 8.06 (d, J = 1.2 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 4.34 (t, J =6.8 Hz, 2H), 1.86-1.75 (m, 2H), 1.52-1.35 (m, 4H), 0.96 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 166.69, 132.77, 130.57, 129.54, 128.31, 65.12, 28.45, 28.21, 22.37, 13.98; IR (neat): 2958, 2932, 2361, 1720, 1637, 1451, 1384, 1107, 710, 618 cm^{-1}; MS (EI, m/z): 192.09 [M]$^+$.

benzyl-4-nitrobenzoate (4a). Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.23-8.15 (m, 4H), 7.41-7.28 (m, 5H), 5.34 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 163.52, 149.58, 134.49, 134.22, 129.81, 127.73, 127.64, 127.42, 122.53, 66.64; IR (neat): 2925, 1712, 1605, 1524, 1456, 1348, 1271, 1103, 870, 744, 715 cm^{-1}; MS (EI, m/z): 257.04 [M]$^+$.

4-chlorobenzyl-4-nitrobenzoate (4b). Yellow solid, m.p: 110-111°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.22 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 7.36-7.28 (m, 4H), 5.30 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 164.45, 150.69, 135.30, 134.67, 133.73, 130.83, 129.87, 128.98, 123.60, 66.83; IR (neat): 3054, 1732, 1637, 1399, 1107, 992, 618 cm^{-1}; MS (EI, m/z): 290.97 [M]$^+$.

butyl-4-nitrobenzoate (4c). Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.30-8.15 (m, 2H), 8.16-8.04 (m, 2H), 4.30 (m, 2H), 1.74-1.66 (m, 2H), 1.46-1.35 (m, 2H), 0.94-0.85 (m, 3H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 163.75, 149.49, 134.88, 129.64, 122.50, 64.81, 29.63, 18.21, 12.70; IR (neat): 2961, 2932, 2874, 1727, 1608, 1520, 1351, 1278, 1103, 1016, 874, 784, 720 cm^{-1}; MS (EI, m/z): 223.06 [M]$^+$.

Pentyl-4-nitrobenzoate (4d). Colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.32-8.26 (m, 2H), 8.21 (dt, J = 8.8, 2.0 Hz, 2H), 4.37 (t, J = 6.4 Hz, 2H), 1.85-1.75 (m, 2H), 1.46-1.37 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 164.76, 150.51, 135.91, 130.66, 123.52, 66.11, 28.31, 28.13, 22.32, 13.95; IR (neat): 2959, 2926, 1725, 1630, 1530, 1384, 1105, 991, 619 cm^{-1}; MS (EI, m/z): 237.08 [M]$^+$.

4-chlorophenethyl 4-nitrobenzoate (4e). Yellow solid, m.p: 103-104°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.21 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 4.50 (t, J = 6.8 Hz, 2H), 3.00 (t, J = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 164.54, 150.62, 135.90, 135.47, 132.72, 130.67, 130.21, 128.81, 123.60, 65.96, 34.47; IR (neat): 2923, 1718, 1637, 1525, 1384, 1107, 992, 618 cm^{-1}; MS (EI, m/z): 305.03 [M]$^+$.

3-Pyridylmethyl-4-nitrobenzoate (4f). Yellow solid, m.p: 133-135°C (Lit[16b], 140-142 ℃); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.67 (s, 1H), 8.57 (d, J = 4.8 Hz, 1H), 8.23 (d, J = 8.8 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 7.6 Hz, 1H), 7.29 (dd, J = 8.0, 5.2 Hz, 1H), 5.36 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 164.40, 150.73, 150.03, 149.86, 136.31, 135.06, 130.97, 130.86, 123.65, 123.64, 65.08; IR (neat): 2925, 1722, 1601, 1522, 1347, 1284, 1124, 853, 796, 716 cm^{-1}; MS (EI, m/z): 258.04 [M]$^+$.

4-Pyridylmethyl-4-nitrobenzoate (4g). Yellow solid, m.p: 143-145°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.59 (dd, J = 4.4, 1.6 Hz, 2H), 8.26 (dd, J =7.2, 2.0 Hz, 2H), 8.20 (dd, J =7.2, 2.0 Hz, 2H), 7.27 (d, J = 6.0 Hz, 2H), 5.36 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 164.25, 150.92, 150.16, 144.27, 134.85, 130.90, 123.71, 122.07, 65.54; IR (neat): 2925, 1722, 1601, 1522, 1347, 1284, 1124, 853, 796, 716 cm^{-1}; MS (EI, m/z): 258.04 [M]$^+$.

(2-chloropyridin-3-yl)methyl 4-nitrobenzoate (4h). Brown solid; m.p: 122-124°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.42 (dd, J = 4.8, 2.0 Hz, 1H), 8.31 (dt, J = 9.2, 2.0 Hz, 2H), 8.26 (dt, J = 9.2, 2.0 Hz, 2H), 7.85 (dd, J = 7.6, 2.0 Hz, 1H), 7.32 (dd, J = 7.6, 4.8 Hz, 1H), 5.51 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 164.26, 150.88, 150.82, 149.67, 138.65, 134.88, 130.92, 129.83, 123.70, 122.68, 64.12; IR(neat): 2957, 1748, 1637, 1458, 1384, 1061, 991, 619 cm^{-1}; MS (EI, m/z): 291.99 [M]$^+$.

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