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A Straightforward Conversion of Activated Amides and Haloalkanes into Esters under Transition-Metal-Free Cs_2CO_3/DMAP Conditions

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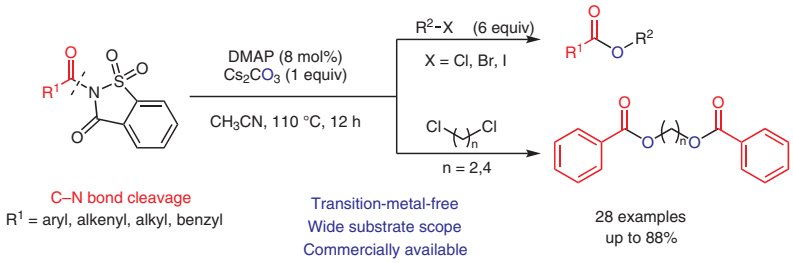

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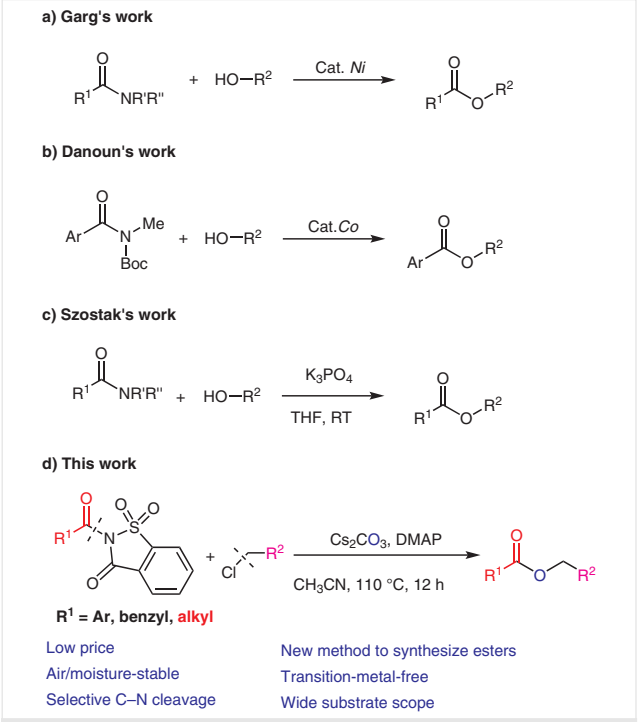
Abstract The esterification of activated amides, *N*-acylsaccharins, under transition-metal-free conditions with good functional group tolerance has been developed, resulting in C–N cleavage leading to efficient synthesis of a variety of esters in moderate to good yields. This work demonstrates that esterification may proceed by using simple *N*-acylsaccharins, haloalkanes, and Cs_2CO_3 as oxygen source.

Key words esterification, amides, metal-free, haloalkanes, C–N cleavage

Esters are ubiquitously present in most of the natural products and synthetic organic molecules. The construction of esters is an important aspect for organic chemists. Although compared to traditional methods of esterification or transesterification, Baeyer–Villiger oxidation does not need strong acid or base; a mixture of regioisomers was always observed due to the poor regioselectivity.[1] Therefore, the oxidative esterification of alcohols or aldehydes with alcohols has been a widespread concern and is an alternative to traditional methods of synthesis of esters. For example, Patel,[2] Rovis,[3] Yokayama,[4] and Konakahara[5] achieved oxidative esterification of aldehydes with alcohols by using H_2O_2, NHC, Ir complex, or iodine as oxidants or catalysts, respectively. Beyond that transition-metal-catalyzed C–H esterification provide a novel method that reduces synthetic steps and energy consumption, which is in line with green chemistry.[6]

Likewise, amides are readily available starting materials or intermediates in organic synthesis. However, the transformation of the amides to other functional groups is still a longstanding challenge due to the high activation energy of the C–N bond.[7] A pioneered strategy of cleavage of C–N bonds in amides was reported by Garg and co-workers using Ni-catalyzed synthesis of esters (Scheme 1a).[8a] Since this work, it has been rapidly followed by Danoun and co-workers who described the first Co-catalyzed conversion of *N*-Boc-amides into esters (Scheme 1b).[8h] In 2018, Szostak and co-works presented an excellent metal-free protocol for esterification of amides with broad substrate scope and functional group tolerance under exceedingly mild conditions (Scheme 1c).[9] In the previous work, the oxygen atom attached to the carbonyl groups of the ester groups is always derived from hydroxyl groups, oxidants, or carboxylic



Scheme 1 Previous studies on esterification of amides

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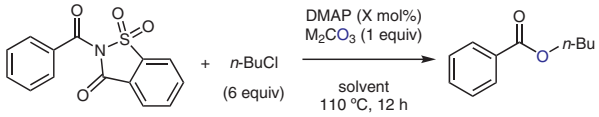
acids. In 2015, Gao and co-workers reported a novel method for the construction of esters between acyl chloride and halohydrocarbon by using Cs_2CO_3 as oxygen source with a wide scope of substrates and gram-scale.[10] Mechanistic studies suggest that the alcohol O atom rather than carbonyl O atom in the products come from Cs_2CO_3 via a free radical pathway. However, in this reaction, acyl chloride is highly active and air/moisture-unstable. Furthermore, inactive sp^3 carbons on *N*-acyl chloride are not suitable for esterification. Because of these shortcomings, acyl chlorides are incapable of synthesizing a variety of esters containing sensitive functional groups, such as epoxy and nitrile groups. Although recently the use of transition-metal-catalyzed conversions was found, these conversions require expensive catalysts and ligands.[11] According to the experience of our group,[12] we designed conversion of activated amides and haloalkanes into esters under transition-metal-free Cs_2CO_3/DMAP condition.

We initiated to investigate the esterification between *N*-benzoylsaccharin (**1a**) and chlorobutane (**2a**) in CH_3CN at 100 °C. After the investigation of the carbonate bases, Li_2CO_3, Na_2CO_3, K_2CO_3, and Cs_2CO_3, the optimal carbonate base was found to be Cs_2CO_3 (Table 1, entries 1–4). Decreasing the amount of DMAP results in the formation of ester **3aa** in 74% yield (entry 5). Without DMAP, only 60% of **3aa** was observed (entry 6). Obviously, DMAP promotes the transformation for acylation reaction and plays a role for activation of C–N bond in this transformation. Several solvents were then examined for this esterification (entries 7–10). Obviously, the carbonate base is crucial to the esterification of *N*-benzoylsaccharin with chloroalkane (entry 11). When the reaction was conducted under nitrogen atmosphere, the corresponding product **3aa** was obtained in 86% yield. This result clearly shows that oxygen does not participate in the esterification (entry 12) and the ester ^{18}O was not found in GC/MS analysis by addition of $H_2{}^{18}O$ to the reaction. When 1–2 equivalents of water were added to this reaction, it was found that the yield of the final product decreased to 33% (entry 13). Although increasing the solubility of Cs_2CO_3, the water may decompose intermediate **A** (vide infra) to benzoic acid and carbonic acid. Furthermore, carbonic acid releases water and carbon dioxide.

With the optimized reaction conditions in hand, the scope of *N*-acylsaccharins **1** was checked (Scheme 2). The yield of the ester **3ba** is slightly decreased because of the steric effect. The substituted *N*-acylsaccharins **1c–f** bearing a methoxy group at *ortho*-, *meta*-, and *para*-position of *N*-acylsaccharins were smoothly converted to esters in 60%, 80%, and 85% yield, respectively. Halogen atoms, fluorine, chlorine, and bromine are tolerated under our reaction conditions to give products **3ga**, **3ha**, and **3ia** in yields 90%, 76%, and 60%. *N*-Acylsaccharin with an electron-withdrawing group delivered the corresponding ester in 76% yield. Particularly, naphthalene, heterocycle, and *N*-cinnamoyl containing *N*-acylsaccharins were compatible with this reaction system to give the products **3ka**, **3la**, and **3ma** in 52%, 40% and 88% yield, respectively. It is especially worth nothing that the acyl groups of inactive sp^3 carbons **3na**, **3oa**, and **3pa** could also couple with **2a**. The previous reaction has not been involved in the esterification of inactive sp^3 carbons.[10]

Table 1 Optimization the Reaction Conditions[a]

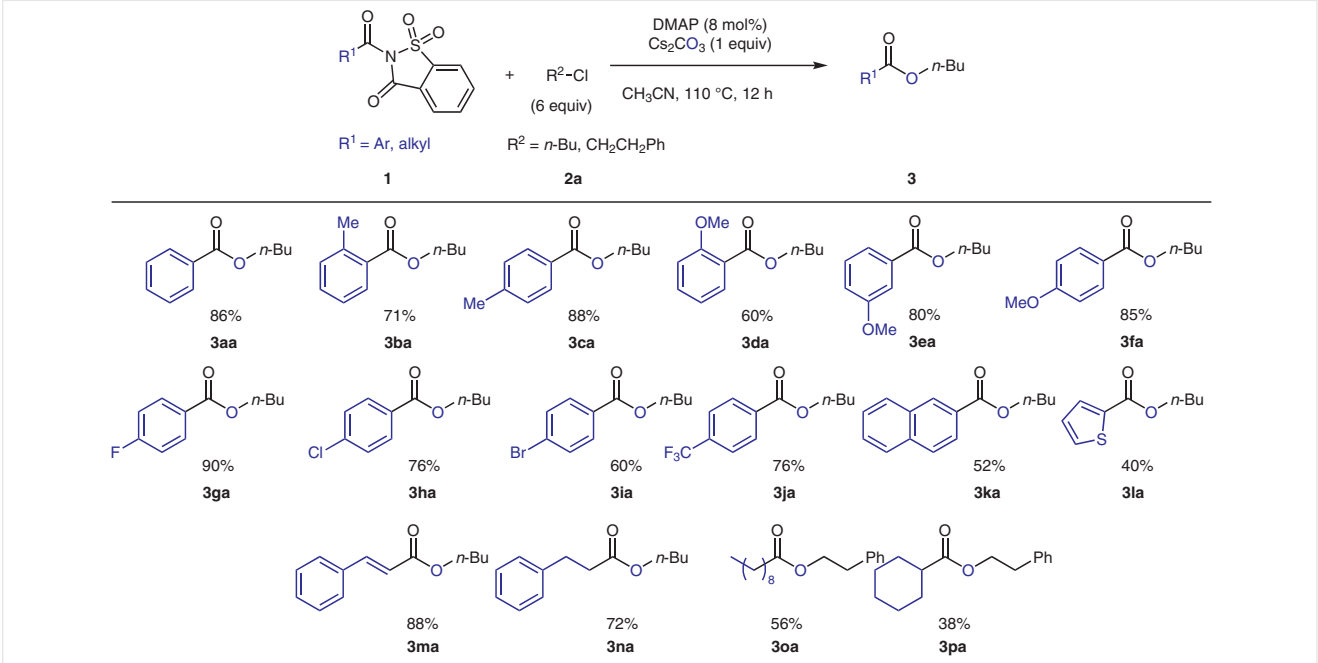


1a 2a 3aa

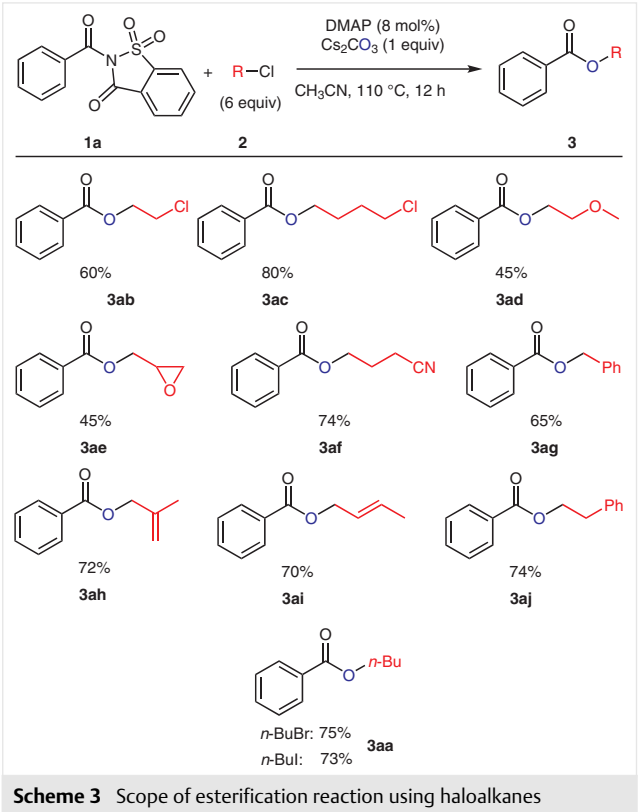
Entry	Base	DMAP	Solvent	Yield (%)[b]
1	Li_2CO_3	8	CH_3CN	0
2	Na_2CO_3	8	CH_3CN	0
3	K_2CO_3	8	CH_3CN	<5
4	Cs_2CO_3	4	CH_3CN	86
5	Cs_2CO_3	5	CH_3CN	74
6	Cs_2CO_3	–	CH_3CN	60
7	Cs_2CO_3	8	THF	<5
8	Cs_2CO_3	8	DMF	43
9	Cs_2CO_3	8	DMAc	59
10	Cs_2CO_3	8	1,4-dioxane	0
11	Cs_2CO_3	8	CH_3CN	0
12[c]	Cs_2CO_3	8	CH_3CN	86
13[d]	Cs_2CO_3	8	CH_3CN	33

[a] Reaction conditions: **1a** (0.3 mmol), base (1 equiv), DMAP (x mol%), *n*-BuCl (6 equiv), CH_3CN (2.0 mL), 100 °C, 12 h.
[b] Isolated yields.
[c] Under N_2 atmosphere.
[d] In the presence of H_2O (2 equiv).

The scope of haloalkane derivatives was also investigated (Scheme 3). The reactions of **1a** with dichloroethane and dichlorobutane under 1 equivalent of Cs_2CO_3 gave the single product **3ab** and **3ac**, respectively. The disubstituted esters **3ak** and **3al** (vide infra) were not detected. The functional groups, ether, epoxide, nitrile, and benzyl, could be assembled in the products **3ad**, **3ae**, **3af**, and **3ag** in moderate yields. No matter whether terminal or internal alkenes, esterification happened to provide both **3ah** and **3ai**. The product **3aj** was obtained by using phenyl *N*-benzoylsaccharin in 74% yield. Finally, bromobutane and iodobutane could also react as well as chlorobutane to give the corresponding ester **3aa** in 75% and 73% yield, respectively.

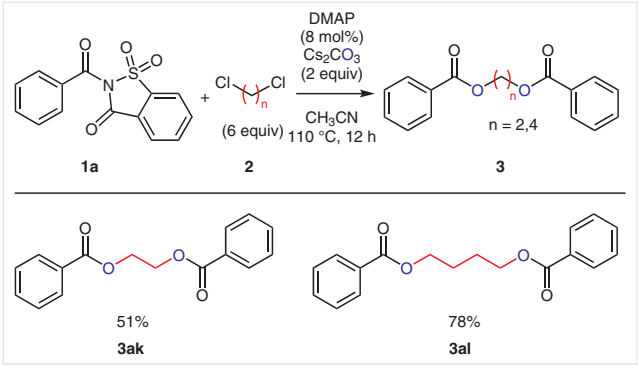


Scheme 2 Scope of esterification reaction using *N*-acylsaccharins



Scheme 3 Scope of esterification reaction using haloalkanes

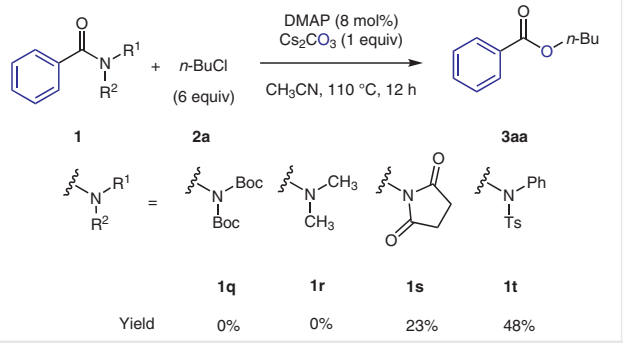
When 2 equivalents of Cs_2CO_3 were added to the reaction of **1a** with **2b** or **2c**, the disubstituted esters **3ak** and **3al** were found without formation of the expected monosubstituted ester (Scheme 4).



Scheme 4 Synthesis of disubstituted esters

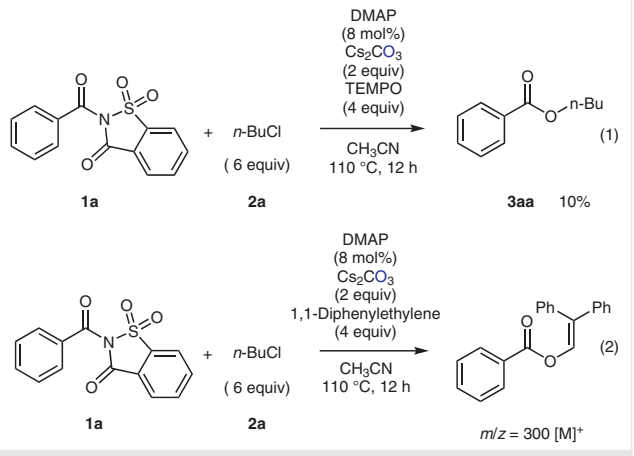
Four amides **1q**, **1r**, **1s**, and **1t** were checked in this reaction system for comparing reactivity with *N*-benzoylsaccharin (**1a**) under the same conditions (Scheme 5). No reaction occurred when **1q** and **1r** were mixed with **2a**. However, the results showed that the yield of esters from other amides **1s** and **1t** was lower than *N*-benzoylsaccharin.

To get some insights into the reaction mechanism, we carried out the reaction in the presence of 4 equivalents of TEMPO or 1,1-diphenylethylene as a radical scavenger. Accordingly, only 10% product **3aa** was observed (Scheme 6, eq 1) and the product with m/z = 300 $[M]^+$ trapped by



Scheme 5 Scope of esterification reaction using other amides

1,1-diphenylethylene was found (Scheme 6, eq 2), suggesting that the reaction proceed via the formation of radical species.



Scheme 6 Control reactions

The proposed mechanism for the esterification of *N*-acylsaccharin derivatives using haloalkanes is shown in Scheme 7. Based on the previous report,[10] nucleophilic substitution of *N*-benzoylsaccharin (**1a**) with Cs_2CO_3 gives saccharincesium and the unstable intermediate **A**, which collapses to release CO gas and form the radical intermediate **B**. Finally, the radical **B** reacts with butylsaccharin coming from saccharincesium and chlorobutane to generate product **3aa**.

In conclusion, we have developed the transition-metal-free esterification of amides by the cleavage of the amide C–N bond. This method is achieved under mild conditions with highly functional group tolerance and can be strategically employed in the synthesis of esters in moderate to good yields. Given the importance of esters, this work provides an example of the use of *N*-acylsaccharins with haloalkanes as a method for synthesis of esters.

All reactions were conducted in a sealed tube under N_2 atmosphere. All reactants reported are commercially available and have been prepared by the method reported previously. *N*-Acylsaccharins were prepared by the general method (see Supporting Information). All solvents were purchased from suppliers of China and used without any purification. Et_3N was purified by distillation with CaH_2. Flash chromatography was performed using 200–300 mesh silica gel. All products are known compounds. ^1H and ^{13}C and ^{19}F NMR data were recorded with Varian (400 MHz) spectrometers in $CDCl_3$ with TMS as an internal standard.

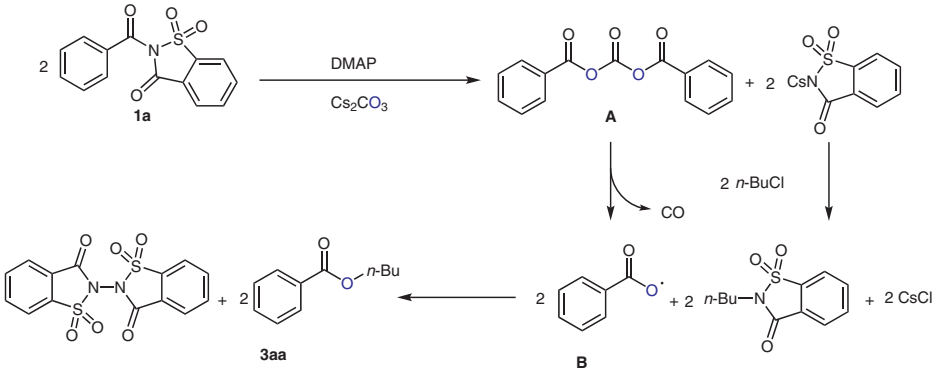
Butyl Benzoate (3aa); Typical Procedure

To a 10 mL round-bottomed flask was added *N*-benzoylsaccharin (**1a**; 86.1 mg, 0.30 mmol), DMAP (2.9 mg, 0.024 mmol), Cs_2CO_3(96.9 mg, 0.30 mmol), *n*-BuCl (**2a**; 166.7 mg, 1.80 mmol), CH_3CN (2 mL). Then, the mixture was stirred at 100 °C for 12 h. After cooling to RT, the mixture was filtered through a short pad of silica gel, and the silica gel was washed with CH_2Cl_2 (3 × 10 mL). The organic phases were combined and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EtOAc 20:1) as eluent to afforded butyl benzoate **3aa** as a colorless oil; yield: 45.9 mg (86%).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.2 Hz, 2 H), 7.58–7.51 (m, 1 H), 7.47–7.40 (m, 2 H), 4.33 (t, *J* = 6.6 Hz, 2 H), 1.79–1.71 (m, 2 H), 1.53–1.43 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

Butyl 2-Methylbenzoate (3ba)

Following the typical procedure, **3ba** was isolated as a colorless oil; yield: 40.9 mg (71%).



Scheme 7 Proposed mechanism for esterification of *N*-acylsaccharins with haloalkanes

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.8 Hz, 1 H), 7.42–7.35 (m, 1 H), 7.24 (dd, *J* = 7.2, 5.6 Hz, 2 H), 4.30 (t, *J* = 6.6 Hz, 2 H), 2.60 (s, 3 H), 1.82–1.69 (m, 2 H), 1.55–1.40 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

Butyl 4-Methylbenzoate (3ca)

Following the typical procedure, **3ca** was isolated as a colorless oil; yield: 50.7 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 4.31 (t, *J* = 6.6 Hz, 2 H), 2.40 (s, 3 H), 1.80–1.70 (m, 2 H), 1.53–1.42 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

Butyl 2-Methoxybenzoate (3da)

Following the typical procedure, **3da** was isolated as a colorless oil; yield: 37.4 mg (60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.6 Hz, 1 H), 7.50–7.41 (m, 1 H), 6.97 (dd, *J* = 7.4, 5.1 Hz, 2 H), 4.30 (t, *J* = 6.6 Hz, 2 H), 3.89 (s, 3 H), 1.77–1.70 (m, 2 H), 1.53–1.42 (m, 2 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

Butyl 3-Methoxybenzoate (3ea)

Following the typical procedure, **3ea** was isolated as a colorless oil; yield: 49.9 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.6 Hz, 1 H), 7.57 (s, 1 H), 7.38–7.30 (m, 1 H), 7.12–7.07 (m, 1 H), 4.32 (t, *J* = 6.6 Hz, 2 H), 3.85 (s, 3 H), 1.81–1.70 (m, 2 H), 1.54–1.40 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

Butyl 4-Methoxybenzoate (3fa)

Following the typical procedure, **3fa** was isolated as a colorless oil: yield: 53.0 mg (85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 4.29 (t, *J* = 6.6 Hz, 2 H), 3.86 (s, 3 H), 1.80–1.69 (m, 2 H), 1.53–1.42 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

Butyl 4-Fluorobenzoate (3ga)

Following the typical procedure, **3ga** was isolated as a colorless oil; yield: 52.9 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09–8.03 (m, 2 H), 7.15–7.05 (m, 2 H), 4.32 (t, *J* = 6.6 Hz, 2 H), 1.80–1.70 (m, 2 H), 1.53–1.42 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –106.10.

Butyl 4-Chlorobenzoate (3ha)

Following the typical procedure, **3ha** was isolated as a colorless oil; yield: 48.3 mg (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 4.32 (t, *J* = 6.6 Hz, 2 H), 1.79–1.71 (m, 2 H), 1.52–1.43 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

Butyl 4-Bromobenzoate (3ia)

Following the typical procedure, **3ia** was isolated as a colorless oil; yield: 46.3 mg (60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 4.32 (t, *J* = 6.6 Hz, 2 H), 1.81–1.69 (m, 2 H), 1.54–1.41 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

Butyl 4-(Trifluoromethyl)benzoate (3ja)

Following the typical procedure, **3ja** was isolated as a colorless oil; yield: 56.1 mg (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.2 Hz, 2 H), 7.70 (d, *J* = 8.2 Hz, 2 H), 4.36 (t, *J* = 6.6 Hz, 2 H), 1.83–1.73 (m, 2 H), 1.55–1.44 (m, 2 H), 0.99 (t, *J* = 7.4 Hz, 3 H).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.15.

Butyl 2-Naphthoate (3ka)

Following the typical procedure, **3ka** was isolated as a colorless oil; yield: 35.6 mg (52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 1 H), 8.07 (d, *J* = 8.4 Hz, 1 H), 7.96 (d, *J* = 7.6 Hz, 1 H), 7.88 (d, *J* = 8.4 Hz, 2 H), 7.63–7.50 (m, 2 H), 4.39 (t, *J* = 6.6 Hz, 2 H), 1.88–1.74 (m, 2 H), 1.58–1.47 (m, 2 H), 1.01 (t, *J* = 7.4 Hz, 3 H).

Butyl Thiophene-2-carboxylate (3la)

Following the typical procedure, **3la** was isolated as a colorless oil; yield: 22.1 mg (40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 3.6 Hz, 1 H), 7.54 (d, *J* = 4.8 Hz, 1 H), 7.13–7.06 (m, 1 H), 4.30 (t, *J* = 6.6 Hz, 2 H), 1.79–1.66 (m, 2 H), 1.54–1.39 (m, 2 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

Butyl Cinnamate (3ma)

Following the typical procedure, **3ma** was isolated as a colorless oil; yield: 53.9 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 16.0 Hz, 1 H), 7.54–7.49 (m, 2 H), 7.40–7.35 (m, 3 H), 6.44 (d, *J* = 16.0 Hz, 1 H), 4.21 (t, *J* = 6.6 Hz, 2 H), 1.73–1.65 (m, 2 H), 1.49–1.40 (m, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H).

Butyl 3-Phenylpropanoate (3na)

Following the typical procedure, **3na** was isolated as a colorless oil; yield: 44.5 mg (72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 7.4 Hz, 2 H), 7.23–7.16 (m, 3 H), 4.07 (t, *J* = 6.6 Hz, 2 H), 2.95 (t, *J* = 7.8 Hz, 2 H), 2.62 (t, *J* = 7.8 Hz, 2 H), 1.62–1.54 (m, 2 H), 1.39–1.29 (m, 2 H), 0.91 (t, *J* = 7.4 Hz, 3 H).

Phenethyl Decanoate (3oa)

Following the typical procedure, **3oa** was isolated as a colorless oil; yield: 46.4 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 2 H), 7.25–7.19 (m, 3 H), 4.28 (t, *J* = 7.2 Hz, 2 H), 2.93 (t, *J* = 7.0 Hz, 2 H), 2.28 (t, *J* = 7.6 Hz, 2 H), 1.63–1.55 (m, 2 H), 1.29–1.23 (m, 12 H), 0.88 (t, *J* = 6.8 Hz, 3 H).

Phenethyl Cyclohexanecarboxylate (3pa)

Following the typical procedure, **3pa** was isolated as a colorless oil; yield: 26.4 mg (38%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.27 (m, 2 H), 7.25–7.18 (m, 3 H), 4.28 (t, *J* = 7.0 Hz, 2 H), 2.93 (t, *J* = 7.0 Hz, 2 H), 2.27 (tt, *J* = 11.2, 1.8 Hz, 1 H), 1.86 (d, *J* = 13.2 Hz, 2 H), 1.72 (d, *J* = 11.6 Hz, 2 H), 1.65–1.60 (m, 1 H), 1.45–1.35 (m, 2 H), 1.29–1.20 (m, 3 H).

2-Chloroethyl Benzoate (3ab)

Following the typical procedure, **3ab** was isolated as a colorless oil; yield: 33.1 mg (60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.4 Hz, 2 H), 7.62–7.55 (m, 1 H), 7.49–7.42 (m, 2 H), 4.57 (t, *J* = 5.8 Hz, 2 H), 3.82 (t, *J* = 5.8 Hz, 2 H).

4-Chlorobutyl Benzoate (3ac)

Following the typical procedure, **3ac** was isolated as a colorless oil; yield: 51.0 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.2 Hz, 2 H), 7.59–7.52 (m, 1 H), 7.48–7.41 (m, 2 H), 4.36 (t, *J* = 5.8 Hz, 1 H), 3.61 (t, *J* = 6.0 Hz, 2 H), 1.99–1.90 (m, 4 H).

2-Methoxyethyl Benzoate (3ad)

Following the typical procedure, **3ad** was isolated as a colorless oil; yield: 24.3 mg (45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.2 Hz, 2 H), 7.60–7.53 (m, 1 H), 7.48–7.40 (m, 2 H), 4.48 (t, *J* = 4.8 Hz, 2 H), 3.74 (t, *J* = 4.8 Hz, 2 H), 3.44 (s, 3 H).

Oxiran-2-ylmethyl Benzoate (3ae)

Following the typical procedure, **3ae** was isolated as a colorless oil; yield: 24.0 mg (45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.0 Hz, 2 H), 7.60–7.56 (m, 1 H), 7.48–7.43 (m, 2 H), 4.66 (dd, *J* = 12.4, 3.2 Hz, 1 H), 4.18 (dd, *J* = 12.4, 6.4 Hz, 1 H), 3.41–3.29 (m, 1 H), 2.90 (t, *J* = 4.6 Hz, 1 H), 2.74 (dd, *J* = 4.8, 2.4 Hz, 1 H).

3-Cyanopropyl Benzoate (3af)

Following the typical procedure, **3af** was isolated as a colorless oil; yield: 42.0 mg (74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.6 Hz, 2 H), 7.61–7.53 (m, 1 H), 7.48–7.41 (m, 2 H), 4.43 (t, *J* = 6.0 Hz, 2 H), 2.53 (t, *J* = 7.0 Hz, 2 H), 2.18–2.10 (m, 2 H).

Benzyl Benzoate (3ag)

Following the typical, **3ag** was isolated as a colorless oil; yield: 41.3 mg (65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14–8.09 (m, 2 H), 7.61–7.54 (m, 1 H), 7.50–7.34 (m, 7 H), 5.39 (s, 2 H).

2-Methylallyl Benzoate (3ah)

Following the typical procedure, **3ag** was isolated as a colorless oil; yield: 38.0 mg (72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.2 Hz, 2 H), 7.60–7.53 (m, 1 H), 7.49–7.42 (m, 2 H), 5.08 (s, 1 H), 4.99 (s, 1 H), 4.75 (s, 2 H), 1.84 (s, 3 H).

(*E*)-But-2-en-1-yl Benzoate (3ai)

Following the typical procedure, **3ai** was isolated as a colorless oil; yield: 37.0 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09–8.02 (m, 2 H), 7.58–7.51 (m, 1 H), 7.46–7.39 (m, 2 H), 5.94–5.65 (m, 2 H), 4.90–4.75 (m, 2 H), 4.82 (dd, *J* = 55.4, 6.8 Hz, 1 H), 1.81–1.71 (m, 3 H).

Phenethyl Benzoate (3aj)

Following the typical procedure, **3aj** was isolated as a colorless oil; yield: 50.2 mg (74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.2 Hz, 2 H), 7.58–7.50 (m, 1 H), 7.46–7.38 (m, 2 H), 7.35–7.20 (m, 5 H), 4.53 (t, *J* = 7.0 Hz, 2 H), 3.02 (t, *J* = 7.0 Hz, 2 H).

Ethane-1,2-diyl Dibenzoate (3ak)

Following the typical procedure, **3aj** was isolated as a colorless oil; yield: 20.7 mg (51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.6 Hz, 4 H), 7.62–7.54 (m, 2 H), 7.47–7.42 (m, 4 H), 4.67 (s, 4 H).

Butane-1,4-diyl Dibenzoate (3al)

Following the typical procedure, **3al** was isolated as a colorless oil; yield: 34.9 mg (78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.2 Hz, 4 H), 7.63–7.51 (m, 2 H), 7.51–7.38 (m, 4 H), 4.36 (t, *J* = 5.8 Hz, 4 H), 3.61 (t, *J* = 5.8 Hz, 4 H).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690178.

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