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Article

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Fe-catalyzed Aerobic Oxidative C-CN Bond Cleavage of Arylacetonitriles Leading to Various Esters

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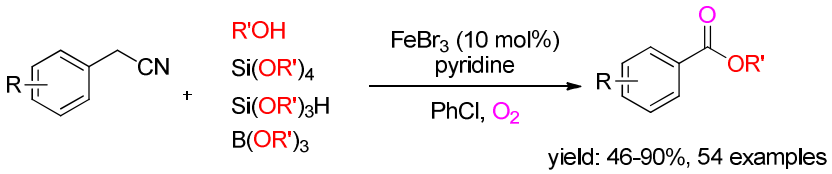
Abstract:



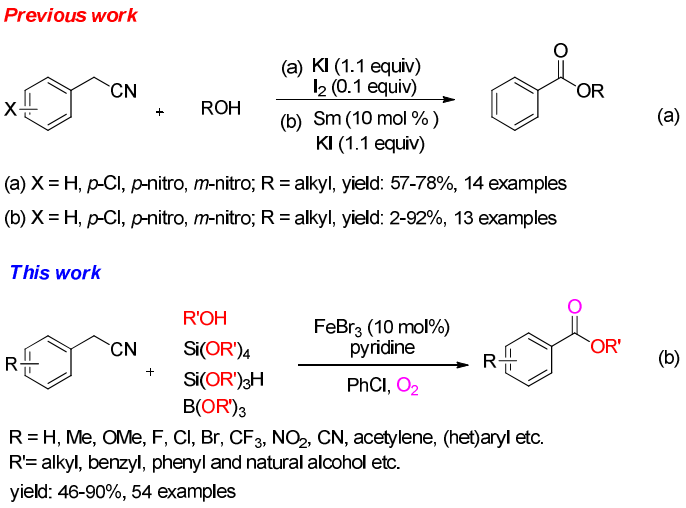
Fe-catalyzed aerobic oxidative esterifications of arylacetonitriles with alcohols, tri alkoxsilanes, silicate esters or borate esters have been developed. The acyl groups which were in-situ generated via chemoselective C(CO)-CN bond cleavage were directly used as electrophiles, leading to corresponding aryl esters in good to excellent yields under molecular oxygen when attacked by alcohols or alcohol surrogates. Dioxygen serves as both oxidant and reactant in this protocol. The reaction has a very broad substrate scope. Cheap starting materials as well as environmentally benign and inexpensive iron catalyst and ideal oxidant O_2 feature this transformation and makes it a practical and sustainable protocol to afford esters.

Introduction

Despite the high bond dissociation energy of C−CN bond (>100 kcal/mol), direct

cleavage of a C-CN bond has still attracted great attention and becomes an appealing area in modern synthetic chemistry due to its enormous potential in construction of complex moleculars.[1] Numerous transition metals, such as Ni,[2] Pd,[3] Rh[4] and Cu[5] have been extensively explored to either mediate or catalyze this transformation. Oxidative addition mechanism has successfully explained vast majority of reported C-CN bond cleavage reactions.[6] However, to the best of our knowledge, only few examples reported the C-CN bond cleavage not via oxidative addition mechanism.[7] As one of the most abundant and inexpensive transition metal salts, Fe salts are used as a catalyst for the transformations which possess both industrial significance and academic importance.[8] The -COOR moiety is a key structural motif in both natural and synthetic organic compounds, therefore various methods have been developed for the construction of esters,[9] including the acylation of alcohols and phenols. However, long duration, harsh reaction conditions (strong basic or acidic environment and anhydrous conditions) are needed when anhydrides or acyl chlorides were employed which extremely limit the functional groups tolerability, especially for phenols.[10] We envisioned that phenylacetonitrile has a great chance to be a cheap and readily available starting material for the synthesis of esters since CN group is detachable via a chemoselective cleavage of C(CO)-CN bond. For instance, Yu and his coworkers firstly reported a novel C-CN bond cleavage reaction in arylacetonitriles to afford aryl carboxylic esters by using Samarium as catalyst in one-pot process.[11] After that, iodine was used as a catalyst for this conversion reported later by the same authors as part of their continuation of these studies.[12] However, their transformations are greatly restricted due to the dependence on strong electron-withdrawing substituents on the aromatic rings (such as the nitro group) (Scheme 1a).

Therefore, it still needs a great breakthrough to establish a general, simple, and efficient method by using a variety of arylacetonitriles to lead to various esters.



Scheme 1. Ester Formation via Oxidative Decyanation of Arylacetonitriles

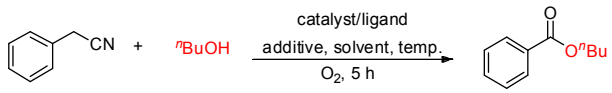
As one of our continuous interest on transition-metal-catalyzed aerobic oxidation reaction,[13] herein we would like to report an Fe-catalyzed aerobic oxidative esterification of arylacetonitriles with alcohols, or silicate esters and boric acid esters as alcohols surrogates. Esters were formed with molecular oxygen as the terminal oxidant in good to excellent yields with broad substrate scope (Scheme 1b).

Results and Discussion

Arylacetonitrile (**1a**) and n-butanol (**2a**) were selected as substrates in model reactions to probe the feasibility of the reaction between arylacetonitriles and alcohols. Based on our previous research, we initiated our study in the presence of $FeCl_3$ and pyridine in toluene at 120 ^{O}C under O_2. To our delight, the desired product **3aa** was formed in 40% yield. Further catalyst screening indicated that $FeBr_3$ showed the best catalytic reactivity among $FeCl_3$, $Fe(OAc)_2$, $FeBr_2$, $FeBr_3$, $Fe(ClO_4)_3$, $Fe(OH)_3$ and Fe_2O_3 (Table 1, entries 1-4 and Table S1 in Supporting Information). When other bases, such as thiazole and Et_3N were added to the

reaction, the desired product was obtained in very low yield (Table 1, entries 5-6, Table S2, Supporting Information), suggesting that pyridine might be irreplaceable for this reaction. The role of pyridine was not clear right now, it might acted as ligand involving in the reaction or help the leaving of proton on α-C of benzylnitriles to form the benzoyl cyanide intermediate. Solvents screening indicated that PhCl is the superior choice over toluene, DMF, DMSO, m-xylene, DME, NMP and dioxane (Table 1, entries 7-8, Table S3, Supporting Information). When temperature was increased to 130 ^{O}C, the yield increased from 75% to 98%; however, lowering the temperature to 110 ^{O}C or 100 ^{O}C only dramatically reduced the yields of desired product **3aa** (Table 1, entries 7-10). If the reactions were conducted under N_2 and air atmosphere, very low amount of product were detected (Table 1, entries 12-13). Eventually fine tuning on catalyst and ligand loadings revealed that the optimized reaction condition for 3aa was: arylacetonitrile **1a** (0.5 mmol), alcohol **2a** (1.5 mmol), $FeBr_3$ (10 mol%), pyridine (0.5 equiv), PhCl (1 mL) at 130 ^{o}C under oxygen (Table 1, entry 10).

Table 1. Optimization of the Reaction Conditions.[a]



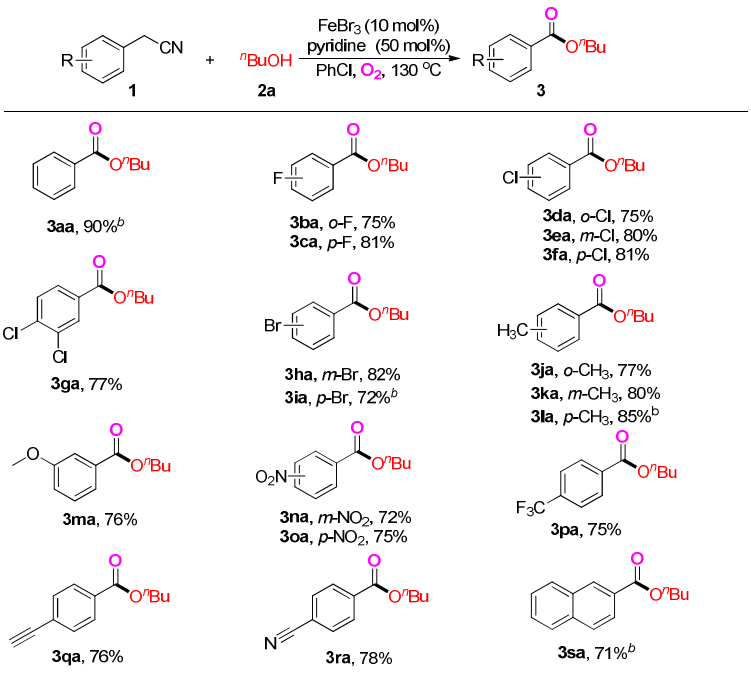
1a **2a** **3aa**

Entry	Catalyst (mol%)	Ligand (equiv)	Solvent	Temp (^{o}C)	Yield of 3aa (%)[b]
1	$FeCl_3$ (10)	pyridine (0.5)	toluene	120	40
2	$Fe(OAc)_2$ (10)	pyridine (0.5)	toluene	120	trace
3	$FeBr_2$ (10)	pyridine (0.5)	toluene	120	28
4	$FeBr_3$ (10)	pyridine (0.5)	toluene	120	62
5	$FeBr_3$ (10)	thiazole (0.5)	toluene	120	trace
6	$FeBr_3$ (10)	Et_3N (0.5)	toluene	120	trace
7	$FeBr_3$ (10)	pyridine (0.5)	PhCl	120	75
8	$FeBr_3$ (10)	pyridine (0.5)	PhCl	100	10
9	$FeBr_3$ (10)	pyridine (0.5)	PhCl	110	25
10	$FeBr_3$ (10)	pyridine (0.5)	PhCl	130	98 (90)
11	$FeBr_3$ (5)	pyridine (0.5)	PhCl	130	58
12[c]	$FeBr_3$ (10)	pyridine (0.5)	PhCl	130	trace (N_2)
13[d]	$FeBr_3$ (10)	pyridine (0.5)	PhCl	130	10 (air)
14	-	pyridine (0.5)	PhCl	130	trace
15	$FeBr_3$ (10)	-	PhCl	130	12

[a] Conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), catalyst, solvent (2 mL), temp., under O_2 in a sealed tube. [b] GC yield, the yield was listed in the parenthesis. [c] Under N_2. [d] Under air.

With the optimal reaction conditions available, the protocol was extended to different arylacetonitriles. The results were shown in table 2. The aerobic oxidative esterification of arylacetonitriles proceeded in good to excellent yields regardless of the electronic nature of the substituents on the aromatic rings: both electron-withdrawing (-Cl, -Br, -F, $-NO_2$) and electron-donating ($-CH_3$, $-OCH_3$) groups at the 4-, 3-and 2-positions are good substituents for this transformation (Table 2, entries **3ba-3oa**). Moreover, a variety of functional groups, such as trifluoromethyl, alkynyl and cyano groups were all tolerable in this reaction (Table 2, entries **3pa-3ra**). In addition, 2-naphthyl was compatible in this reaction as well to give the corresponding product **3sa** in 71% yield (Table 2, **3sa**).

Table 2. Substrate Scope for the formation of Esters from Arylacetonitriles **1** and n-BuOH **2a**.

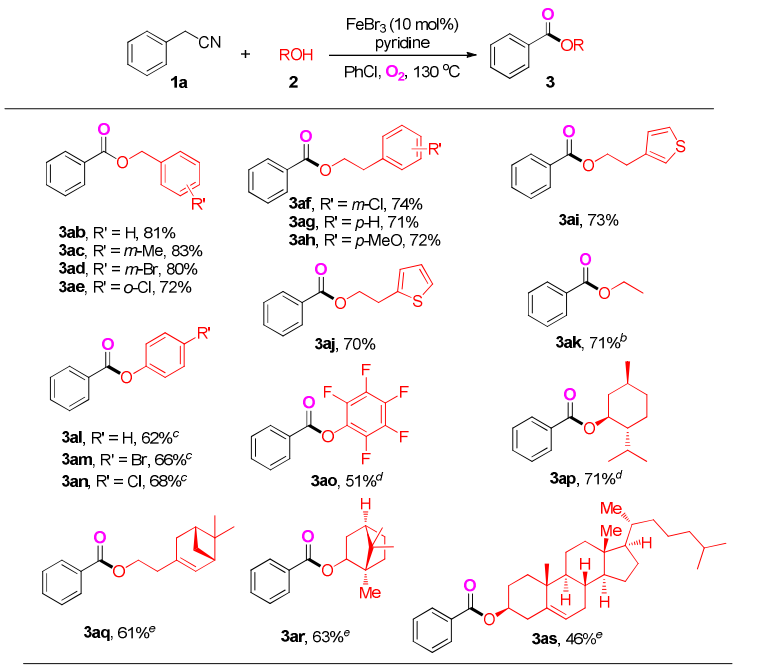


[a] Reaction conditions: arylacetonitrile **1** (0.5 mmol), *n*-butanol (**2a**) (1.5 mmol), $FeBr_3$ (10 mol%), pyridine (0.5 equiv.), PhCl (1 mL) in O_2 in a sealed tube, 130 °C, 9 h. [b] 5 h.

The scope of alcohols for this transformation was further investigated. As shown in Table 3, both phenylmethanol and 2-phenylethanol were tolerated in this esterification in spite of the types of electronic variations and positions of substituents on the aromatic rings (Table 3,

3ab-3ah). Remarkably, heteroaromatic ethanols, such as 2-thiophene ethanol and 3-thiophene ethanol, also rendered the desired esters in fair to good yields (Table 3, **3ai** and **3aj**). Significantly, p-substituted phenols and 2, 3, 4, 5, 6-pentafluorophenol which have special biological activities were also tolerable under the optimal reaction conditions to afford corresponding products (Table 3, **3al-3an**, **3ao**), which are the first cases in similar reports. Both primary and secondary aliphatic alcohol, including some natural alcohols, which are susceptible to oxidative conditions, survived well under this reaction system, generating desired products in good yields (Table 3, **3aa**, **3ak**, **3ap - 3ar**). Intriguingly, the well-known cholesterol was tolerated in this condition, **3as** was afforded in 46% yield in 20 h, fuether extension of the reaction time didn't improve its yield, probably due to the decomposition of cholesterol in the system. The success of cholesterol indicated the feasibility of using this method to achieve late-stage complex compound transformation.

Table 3. Alcohol Scope for the Formation of Esters from Phenylacetonitrile (**1a**) and alcohols **2**.

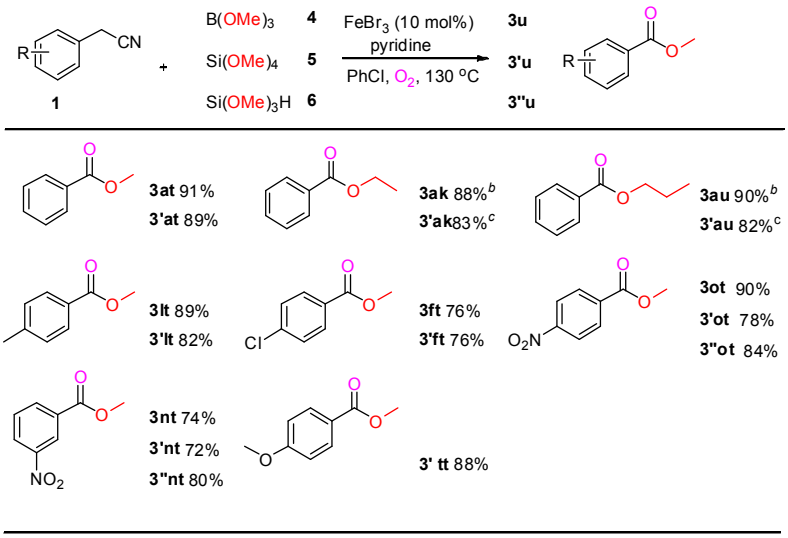


[a] Reaction conditions: 2-phenylacetonitrile (**1a**) (0.5 mmol), alcohol **2** (1.5 mmol), $FeBr_3$ (10 mol%), pyridine (0.5 equiv.), PhCl (2 mL) in O_2 in a sealed tube, O_2, 130 °C, 9 h. [b] 15 h. [c] pyridine (1.2 equiv.), 15 h. [d] 24 h. [e] 20 h.

It is worth to note that when MeOH was employed under the standard conditions, only 28% yield of desired product was obtained, suggesting that methyl ester will be a hurdle and limitation for this transformation. In order to find the key to the problem and further verify the compatibility of this system, we investigated other substrates which might be the potential MeOH surrogates. And trimethyl borate **4**, tetramethyl silicate **5** and trimethoxysilane **6** caught our eyes. To our most delight, application of the above protocol to **4**, **5** and **6** didn't encounter any problems and the corresponding desired methyl esters were formed in good to excellent yields (Table 4, **3at**, **3'at** and **3lt-3'tt**). Furthermore, Good to excellent yields was also achieved with silicate esters such as tetraethyl orthosilicate and tetrapropoxysilane and borate esters such as triethyl borate and tripropyl borate. (Table 4, **3ak**, **3'ak, 3au, 3'au**). The excellent reactivity of these three types of compounds further demonstrates the strong compatibility of this system.

Table 4. Substrate Scope for the Formation of Esters from Arylacetonitriles **1** and Borate

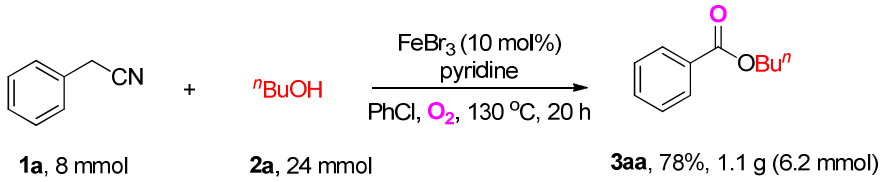
esters, Silicate esters or Trimethoxysilane.



[a] Reaction conditions: Phenylacetonitrile (**1**) (0.5 mmol), **4, 5** or **6** (1.5 mmol), $FeBr_3$ (10 mol %), pyridine (0.5 equiv), PhCl (2 mL) in O_2 in a sealed tube, O_2, 130 °C, 9 h.[b] triethyl borate and tripropyl borate were used. [c] tetraethyl orthosilicate and tetrapropoxysilane were used.

Gratifyingly, the reaction could be readily scaled up to gram scale (8 mmol) without deteriorating its efficiency (Table 5).

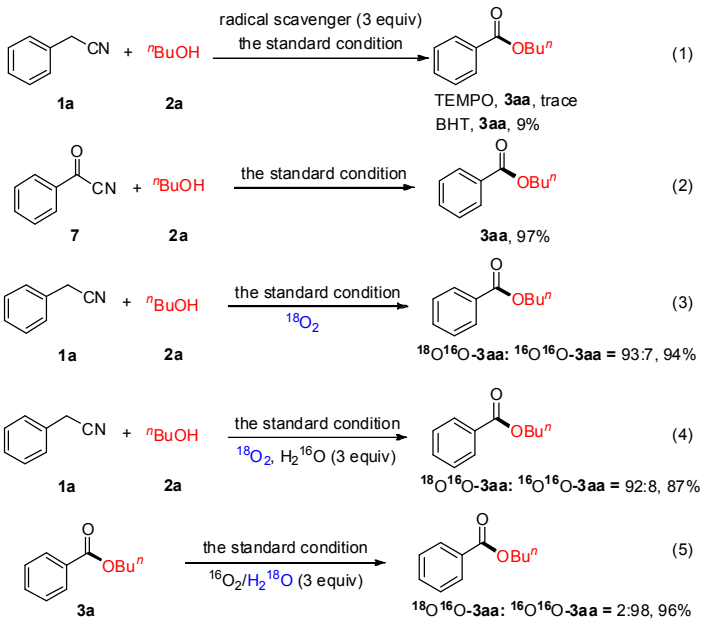
Table 5. Scale-up Reaction.



We further performed several control experiments under the standard conditions in order to probe the reaction mechanism of the ester formation. Radical trapping experiments were firstly conducted by adding 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO) and BHT into the standard conditions of arylacetonitrile (**1a**) and n-BuOH (**2a**). As shown in Scheme 2, the reaction was totally inhibited by TEMPO; with BHT as a radical trapper, the yield was decreased to 8%. The results suggested that a radical pathway should be involved in this reaction [Scheme 2, eq. (1)]. The reaction between benzoyl cyanide **7** with n-BuOH under the standard conditions was also investigated and the desired product was afforded in 97% yield

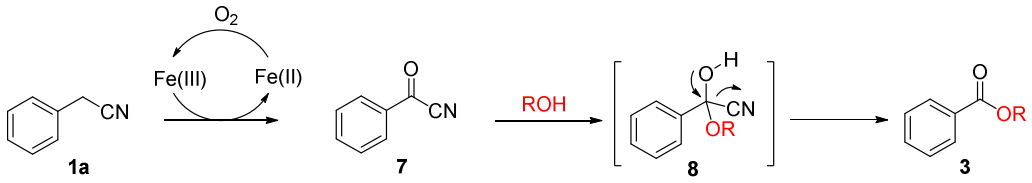
[Scheme 2, eq. (2)]. Combining with the previous report, this result demonstrated that benzoyl cyanide **7** might be the key intermediate in the transformation.

To understand the origin of the oxygen in the new carbonyl group of the desired product, isotope labeled reactions were conducted under standard conditions with $^{18}O_2$, GCMS and HRMS spectra showed that 93% $^{16}O^{18}O$-**3aa** was obtained [Scheme 2, eq.(3), Scheme S1, Supporting Information]. With the addition of 3 equivalent of H_2O under $^{18}O_2$, 92% of product was the one which contains ^{18}O [Scheme 2, eq. (4)]. With the addition of 3 equivalent of $H_2{}^{18}O$ under $^{16}O_2$, 98% of product was the one which only contains ^{16}O [Scheme 2, eq. (5)]. These three isotope labeling experiments clearly demonstrated that the oxygen was from molecular dioxygen, not from water, since one equivalent $H_2{}^{18}O$ should be obtained under $^{18}O_2$, if the oxygen was from water, unlabeled product $^{16}O^{16}O$-**3aa** should be the major one under $^{18}O_2/H_2O$ (3 equiv.) system, since H_2O is three time than $H_2{}^{18}O$. In addition, eq. (5) suggested that the incorporation of the label was not from the exchange with water since almost no ^{18}O was incorporated into the product under $^{16}O_2/H_2{}^{18}O$ (3 equiv.) system. Therefore, we have reason to believe that the oxygen atom in the new carbonyl group of the desired product was from dioxygen.



Scheme 2. Control Experiments under the Standard Conditions

On the basis of the control experiments, we proposed a plausible mechanism for the reaction (Scheme 3): arylacetonitrile is oxidized into benzoyl cyanide **7** by oxygen, which is further attacked by alcohols or alcohols surrogates (borate esters, silicate esters or trimethoxysilane) to lead to intermediate **8**, in which the cleavage of C-CN bond occurred under the optimal conditions to generate desired product **3**.



Scheme 3. Proposed Mechanism

Conclusions

In conclusion, an Fe-catalyzed aerobic oxidative esterifications of arylacetonitriles with various alcohols has been disclosed. Complex alcohols are competent candidates in this transformation and most of the corresponding desired products are obtained in good to excellent yields When MeOH was used, methyl benzoate are obtained with relatively lower

yields probably due to the low boiling point of MeOH. However, trimethyl borate, tetramethyl silicate and trimethoxysilane have been found to be excellent MeOH surrogates and showed great compatibility in this transformation as well. Other silicate esters or borate esters are also suitable for this reaction. Corresponding esters could be obtained in good to excellent yields with a very broad range of substrate scope. These protocols feature in readily accessible starting materials, inexpensive and abundant catalyst, molecular oxygen as the sole oxidant and excellent functional group tolerance. Further investigation on synthetic application and the mechanism of this reaction will be reported in due course.

EXPERIMENTAL SECTION

General information. All experiments were conducted with a sealed pressure vessel. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 500 MHz spectrometers. Chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm) as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Procedure and characterization data for products

Butyl benzoate (**3aa** CAS: 136-60-7).[13d] A sealed pressure vessel was charged with $FeBr_3$ (14.0 mg, 0.05 mmol), phenylacetonitrile (58.5 mg, 0.5 mmol), *n*-butyl alcohol (111.2 mg, 1.5 mmol), pyridine (19.8 mg, 0.25 mmol), and chlorobenzene (1 mL). The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 5 hours. Upon completion of the reaction, ethyl acetate (20 mL) was added, the green layer were washed with brine (20 mL) twice, the combined aqueous layers was extracted with ethyl acetate (20 mL) twice. The

combine organic layers were dried over anhydrous Na_2SO_4. The solvents were removed via rotary evaporator and the residue was purified with flash chromatography (silica gel, ethyl acetate: petroleum ether = 60:1) to give 81 mg of the product in 90% yield as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.3, 1.3 Hz, 2H), 7.57 – 7.49 (m, 1H), 7.47 – 7.40 (m, 2H), 1.75 (dd, J = 14.8, 6.9 Hz, 2H), 1.52 – 1.44 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.6, 132.7, 130.5, 129.5, 128.2, 64.8, 30.7, 19.2, 13.7.

Butyl 2-fluorobenzoate (**3ba** CAS: 371779-67-8).[14] The same procedure was used for 2-(2-fluorophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 73.4 mg of the product in 75% as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (m, 1H), 7.53 – 7.46 (m, 1H), 7.19 (td, J = 7.7, 1.0 Hz, 1H), 7.12 (m, 1H), 4.33 (t, J = 6.6 Hz, 2H), 1.74 (dd, J = 14.8, 6.9 Hz, 2H), 1.48 (dt, J = 15.0, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 164.5 (d, J = 3.7 Hz), 161.9 (d, J = 259.8 Hz), 134.3 (d, J = 8.9 Hz), 132.0 (d, J = 0.6 Hz), 123.9 (d, J = 3.9 Hz), 119.1 (d, J = 9.9 Hz), 116.9 (d, J = 22.5 Hz), 65.2, 30.7, 19.2, 13.7.

Butyl 4-fluorobenzoate (**3ca** CAS: 3888-64-0).[15] The same procedure was used for 2-(4-fluorophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 79.4 mg of the product in 81% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 – 7.84 (m, 2H), 7.14 – 7.07 (m, 2H), 4.31 (t, J = 6.6 Hz, 2H), 1.77 – 1.71 (m, 2H), 1.48 (dt, J = 9.2, 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 165.7 (s), 165.7(d, J = 254.5 Hz), 132.0 (d, J = 9.3 Hz), 126.8 (d, J = 3.0 Hz), 115.4 (d, J = 21.9 Hz), 65.0 , 30.8, 19.3, 13.8.

Butyl 2-chlorobenzoate (**3da** CAS: 52468-48-1).[16] The same procedure was used for 2-(2-chlorophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 79.5 mg of the product in 75% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.42 (m, 2H), 7.30 (m, 1H), 4.34 (t, *J* = 6.6 Hz, 2H), 1.78 – 1.72 (m, 2H), 1.49 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 165.9, 133.6, 132.4, 131.3, 131.0, 130.5, 126.5, 65.5, 30.7, 19.3, 13.7.

Butyl 3-chlorobenzoate (**3ea** CAS: 63987-54-2).[14] The same procedure was used for 2-(3-chlorophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 84.8 mg of the product in 80% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (t, *J* = 1.8 Hz, 1H), 7.95 – 7.90 (m, 1H), 7.52 (m, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 4.33 (t, *J* = 6.6 Hz, 2H), 1.76 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.50 – 1.45 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 165.5, 134.5, 132.8, 132.5, 129.6, 129.6, 127.6, 65.2, 30.7, 19.2, 13.7.

Butyl 4-chlorobenzoate (**3fa** CAS: 27942-64-9).[14] The same procedure was used for 2-(4-chlorophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 85.9 mg of the product in 81% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.46 – 7.36 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 1.75 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.51 – 1.43 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 165.8, 139.2, 130.9, 128.9, 128.6, 65.1, 30.1, 19.2, 13.7.

Butyl 3,4-dichlorobenzoate (**3ga** CAS: 13050-59-4).[14] The same procedure was used for 2-(3,4-dichlorophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 94.7 mg of the product in 77% yield as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.0 Hz, 1H), 7.86 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.76 (dd, *J* = 14.6, 7.2 Hz, 2H), 1.46 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 164.8, 137.4, 132.8, 131.4, 130.5, 130.3, 128.6, 65.5, 30.7, 19.2, 13.7.

Butyl 3-bromobenzoate (**3ha** CAS: 78987-67-4).[17] The same procedure was used for 2-(3-bromophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 104.1 mg of the product in 82% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (t, *J* = 1.8 Hz, 1H), 7.98 – 7.95 (m, 1H), 7.67 (m, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 4.33 (t, *J* = 6.6 Hz, 2H), 1.77 – 1.72 (m, 2H), 1.50 – 1.44 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, CDCl3) δ 165.3, 135.7, 132.5, 132.4, 129.9, 128.1, 122.4, 65.3, 30.7, 19.2, 13.7.

Butyl 4-bromobenzoate (**3ia** CAS 120047-91-8).[14] The same procedure was used for 2-(4-bromophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 5 hours. The reaction gave 92.7 mg of the product in 72% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.82 (m, 2H), 7.66 – 7.49 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 1.75 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.52 – 1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 165.95, 131.66, 131.08, 129.42, 127.89, 65.13, 30.72, 19.26, 13.76.

Butyl 2-methylbenzoate (**3ja** CAS: 65382-88-9).[18] The same procedure was used for 2-(o-tolyl) acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 73.9 mg of the product in 77% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.39 (m, 1H), 7.26 – 7.12 (m, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 2.60 (s, 3H), 1.75 (m, 2H), 1.48 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 167.8, 140.0, 131.8, 131.62, 130.5, 123.0, 125.6, 64.6, 30.8, 21.7, 19.3, 13.8.

Butyl 3-methylbenzoate (**3ka** CAS: 6640-77-3).[19] The same procedure was used for 2-(m-tolyl) acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 78 mg of the product in 80% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.7, 5.0 Hz, 2H), 7.33 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.40 (s, 3H), 1.78 – 1.71 (m, 2H), 1.51 – 1.45 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.9, 138.1, 133.5, 130.4, 130.0, 128.2, 126.6, 64.8, 30.8, 21.3, 19.3, 13.8.

Butyl 4-methylbenzoate (**3la** CAS: 19277-56-6).[14] The same procedure was used for 2-(p-tolyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 5 hours. The reaction gave 81.6 mg of the product in 85% as a light yellow oil solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.40 (s, 3H), 1.75 (m, 2H), 1.48 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.7, 143.4, 129.5, 128.98, 127.8, 64.6, 30.8, 21.6, 19.3, 13.8.

Butyl 3-methoxybenzoate (**3ma** CAS: 77201-18-4).[19] The same procedure was used for 2-(3-methoxyphenyl) acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 79.1 mg of the product in 76% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.11 – 7.06 (m, 1H), 4.32 (t, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 1.74 (dd, *J* = 14.7, 7.0 Hz, 2H), 1.47 (dt, *J* = 14.7, 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.5, 159.5, 131.8, 129.3, 121.9, 119.2, 114.1, 64.9, 55.4, 30.8, 19.3, 13.8.

Butyl 3-nitrobenzoate (**3na** CAS: 6268-25-3).[20] The same procedure was used for 2-(3-nitrophenyl) acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 80.1 mg of the product in 72% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 – 8.77 (m, 1H), 8.40 (m, 1H), 8.38 – 8.35 (m, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 4.38 (t, *J* = 6.7 Hz, 2H), 1.77 (dd, *J* = 14.8, 7.0 Hz, 2H), 1.52 – 1.45 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 164.5, 148.2, 135.2, 132.2, 129.6, 127.2, 124.5, 65.8, 30.6, 19.2, 13.7.

Butyl 4-nitrobenzoate (**3oa** CAS 120-48-9).[21] The same procedure was used for 2-(4-nitrophenyl) acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 83.6 mg of the product in 75% as a light yellow oil solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.24 (m, 2H), 8.23 – 8.17 (m, 2H), 4.37 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.74 (m, 2H), 1.52 – 1.44 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 164.7, 150.4, 135.8, 130.6, 123.5, 65.8, 30.6, 19.2, 13.7.

Butyl 4-(trifluoromethyl)benzoate (**3pa** CAS: 359803-67-1).[22] The same procedure was used for 2-(4-(trifluoromethyl) phenyl) acetonitrile. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 92.2 mg of the product in 75% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 4.36 (t, *J* = 6.6 Hz, 2H), 1.77 (m, 2H), 1.48 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 165.4, 134.29 (q, *J* = 32.6 Hz), 133.71 (d, *J* = 1.0 Hz), 125.32 (q, *J* = 3.7 Hz), 123.64 (q, *J* = 272.7 Hz), 65.38, 30.66, 19.21 , 13.68 .

Butyl 4-ethynylbenzoate (**3qa** CAS: 137790-57-9).[23] The same procedure was used for 2-(4-ethynylphenyl) acetonitrile. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 76.8 mg of the product in 76% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.56 – 7.52 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 3.22 (s, 1H), 1.76 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.47 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.98 (dd, *J* = 8.3, 6.5 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.0, 132.0, 130.5, 129.4, 126.6, 82.8, 79.9, 65.1, 30.7, 19.2, 13.7.

Butyl 4-cyanobenzoate (**3ra** CAS: 29240-34-4).[24] The same procedure was used for 4-(cyanomethyl)benzonitrile. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 79.2 mg of the product in 78% as a light yellow oil solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.07 (m, 2H), 7.78 – 7.69 (m, 2H), 4.36 (t, *J* = 6.6 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.48 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 165.0, 134.3, 132.2, 130.0, 118.0, 116.2, 65.6, 30.6, 19.2, 13.7.

Butyl 2-naphthoate (**3sa** CAS 3007-89-4).[25] The same procedure was used for 2-(naphthalen-2-yl) acetonitrile. The resulting solution was stirred at 130 °C under O_2

(monitored by TLC and GC) for 5 hours. The reaction gave 80.9 mg of the product in 71% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.61 – 7.49 (m, 2H), 4.40 (t, *J* = 6.7 Hz, 2H), 1.81 (m, 2H), 1.57 – 1.49 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.8, 135.5, 132.5, 130.9, 129.3, 128.1, 128.1, 127.8, 127.7, 126.6, 125.2, 65.0, 30.8, 19.3, 13.8.

Benzyl benzoate (**3ab** CAS 120-51-4).[26] The same procedure was used for benzyl alcohol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 85.9 mg of the product in 81% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 – 8.07 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.36 (m, 7H), 5.41 (s, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.4, 136.0, 133.0, 130.1, 129.7, 128.6, 128.4, 128.2, 128.1, 66.7.

3-methylbenzyl benzoate (**3ac** CAS: 38612-03-2).[27] The same procedure was used for 3-methylbenzyl alcohol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 92.4 mg of the product in 83% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 2H), 7.60 – 7.52 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.16 (d, *J* = 7.1 Hz, 1H), 5.34 (s, 2H), 2.38 (s, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.4, 138.3, 135.9, 133.0, 130.2, 129.7, 129.0, 128.9, 128.5, 128.3, 125.2, 66.7, 21.4.

3-bromobenzyl benzoate (**3ad** CAS：38612-14-5).[28] The same procedure was used for 3-bromobenzyl alcohol. The resulting solution was stirred at 125 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 115 mg of the product in 80% as a light yellow

oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.46 (dd, *J* = 14.7, 6.9 Hz, 3H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.28 – 7.25 (m, 1H), 5.33 (s, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.2, 138.3, 133.2, 131.3, 131.0, 130.2, 129.8, 129.7, 128.4, 126.6, 122.6, 65.7.

*2-chlorobenzyl benzoate (***3ae** CAS：882042-79-7).[29] The same procedure was used for 2-chlorobenzylalcohol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 88.6 mg of the product in 72% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.05 (m, 2H), 7.63 – 7.56 (m, 1H), 7.52 (dd, *J* = 5.7, 3.6 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.31 – 7.28 (m, 2H), 5.48 (s, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.2, 133.7, 133.1, 129.9, 129.8, 129.7, 129.6, 129.5, 128.4, 126.9, 64.0.

3-chlorophenethyl benzoate (**3af**). The same procedure was used for 3-chlorophenethyl alcohol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 96.2 mg of the product in 74% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 7.91 (m, 2H), 7.59 – 7.51 (m, 1H), 7.44 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.30 (s, 1H), 7.28 – 7.22 (m, 2H), 7.17 (dd, *J* = 6.8, 1.7 Hz, 1H), 4.53 (t, *J* = 6.9 Hz, 2H), 3.06 (t, *J* = 6.9 Hz, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.4, 139.9, 134.2, 133.0, 130.1, 129.8, 129.5, 129.1, 128.4, 127.1, 126.8, 64.9, 34.9. HRMS(MALDI DHB) m/z $[M+H]^+$ calcd for $C_{15}H_{14}O_2Cl$, 261.0677, found 261.0674.

Phenethyl benzoate (**3ag** CAS: 94-47-3).[27] The same procedure was used for phenethyl alcohol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 80.2 mg of the product in 71% as a light yellow oil liquid. ^{1}H

NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.47 – 7.41 (m, 2H), 7.34 (m, 4H), 7.29 – 7.25 (m, 1H), 4.56 (t, *J* = 7.0 Hz, 2H), 3.11 (t, *J* = 7.0 Hz, 2H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.5, 137.9, 132.8, 130.2, 129.5, 128.9, 128.5, 128.3, 126.5, 65.4, 35.2.

4-methoxyphenethyl benzoate (**3ah** CAS 174681-77-7).[27] The same procedure was used for 3-methoxyphenethyl alcohol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 92.1 mg of the product in 72% as a light yellow oil liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.56 (m, 1H), 7.47 – 7.39 (m, 2H), 7.23 – 7.16 (m, 2H), 6.90 – 6.83 (m, 2H), 4.51 (t, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 3.03 (t, *J* = 7.0 Hz, 2H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.5., 158.3, 132.8, 130.3, 129.9, 129.5, 128.3, 113.9, 65.7, 55.2, 34.3.

2-(thiophen-3-yl)ethyl benzoate (**3ai** CAS: 198278-19-2). The same procedure was used for thiophene-3-ethanol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 84.7 mg of the product in 73% as a light yellow oil liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 – 7.82 (m, 2H), 7.61 – 7.52 (m, 1H), 7.50 – 7.41 (m, 2H), 7.29 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.17 – 7.07 (m, 1H), 7.04 (dd, *J* = 4.9, 1.2 Hz, 1H), 4.54 (t, *J* = 6.9 Hz, 2H), 3.13 (t, *J* = 6.9 Hz, 2H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.5, 138.1, 132.9, 130.2, 129.5, 128.3, 128.3, 125.7, 121.6, 64.8, 29.7. HRMS (DART Positive) m/z [M+H]+ calcd for $C_{13}H_{13}O_2S$, 233.0631, found 233.0628.

2-(thiophen-2-yl)ethyl benzoate (**3aj** CAS: 1044504-84-8).[30] The same procedure was used for thiophene-2-ethanol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 81.2 mg of the product in 70% as a light yellow

oil liquid ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.62 – 7.52 (m, 1H), 7.45 (dd, *J* = 10.8, 4.7 Hz, 2H), 7.18 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.02 – 6.87 (m, 2H), 4.56 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 6.6 Hz, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.4, 140.0, 133.0, 130.1, 129.6, 128.4, 126.9, 125.6, 124.1, 65.2, 29.4.

Ethyl benzoate (**3ak** CAS 93-89-0).[31] The same procedure was used for ethanol. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 15 hours. The reaction gave 53.2 mg of the product in 71% as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.95 (m, 2H), 7.57 – 7.51 (m, 1H), 7.46 – 7.36 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.6, 132.8, 130.5, 129.5, 128.3, 60.9, 14.3.

Phenyl benzoate (**3al** CAS 93-99-2).[32] The same procedure was used for phenol. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 15 hours. The reaction gave 62.4mg of the product in 62% as a white liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.54 – 7.49 (m, 2H), 7.46 – 7.42 (m, 2H), 7.28 (dd, *J* = 10.7, 4.2 Hz, 1H), 7.24 – 7.19 (m, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 165.2, 151.0, 133.6, 130.2, 129.6, 129.5, 128.6, 125.9, 121.7.

4-bromophenyl benzoate (**3am** CAS 1523-17-7).[33] The same procedure was used for 4-bromophenol. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 15 hours. The reaction gave 90.7 mg of the product in 66% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.14 (m, 2H), 7.68 – 7.62 (m, 1H), 7.57 – 7.50 (m, 4H), 7.16 – 7.07 (m, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 164.8, 150.0, 133.8, 132.5, 130.2, 129.2, 128.6, 123.5, 119.0.

4-chlorophenyl benzoate (**3an** CAS 2005-08-5).[34] The same procedure was used for 4-chlorophenol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 15 hours. The reaction gave 78.9 mg of the product in 68% as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 8.13 (m, 2H), 7.68 – 7.63 (m, 1H), 7.55 – 7.47 (m, 2H), 7.44 – 7.35 (m, 2H), 7.21 – 7.12 (m, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 164.9, 149.4, 133.8, 131.3, 130.2, 129.5, 129.2, 128.6, 123.1.

Perfluorophenyl benzoate (**3ao** CAS 1548-84-1).[35] The same procedure was used for 2,3,4,5,6-Pentafluorophenol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 24 hours. The reaction gave 74.8 mg of the product in 51% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (m, 2H), 7.73 – 7.67 (m, 1H), 7.60 – 7.52 (m, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 162.6, 143.0 – 142.0 (m), 140.7 – 134.0 (m), 139.2 – 138.7 (m), 137.3 – 136.6 (m), 134.7, 130.7 , 128.9, 127.0.

(1R,2S,4S)-2-isopropyl-4-methylcyclohexyl benzoate (**3ap**). The same procedure was used for (±)-menthol. The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 24 hours. The reaction gave 92.3 mg of the product in 71% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 – 7.94 (m, 2H), 7.58 – 7.50 (m, 1H), 7.47 – 7.37 (m, 2H), 4.94 (m, 1H), 2.17 – 2.09 (m, 1H), 1.97 (m, 1H), 1.77 – 1.70 (m, 2H), 1.56 (m, 2H), 1.19 – 1.07 (m, 2H), 0.93 (dd, J = 6.8, 4.9 Hz, 7H), 0.80 (d, J = 7.0 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.1, 132.6, 130.8, 129.5, 128.3, 74.8, 47.3, 41, 34.3, 31.4, 26.5, 23.6, 22.0, 20.7, 16.5. HRMS(EI) m/z $[M+H]^+$ calcd for $C_{17}H_{25}O_2$, 261.1849, found 261.1847.

2-((1S,5R)-6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)ethyl benzoate (**3aq**). The same procedure was used for 3-pentanol. The resulting solution was stirred at 135 °C under O_2

(monitored by TLC and GC) for 28 hours. The reaction gave 73.3 mg of the product in 67% as a light yellow oil liquid. ^{1}H NMR (500 MHz, CDCl3) δ 8.17 – 7.91 (m, 2H), 7.59 – 7.51 (m, 1H), 7.49 – 7.38 (m, 2H), 5.41 – 5.34 (m, 1H), 4.40 – 4.27 (m, 2H), 2.46 – 2.40 (m, 2H), 2.39 – 2.35 (m, 1H), 2.33 – 2.16 (m, 3H), 2.13 (td, J = 5.7, 1.2 Hz, 1H), 2.11 – 2.07 (m, 1H), 1.27 (s, 3H), 0.84 (s, 3H).^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.5, 144.2, 132.8, 130.4, 129.5, 128.3, 118.9, 63.3, 45.8, 40.7, 38.0, 36.1, 31.7, 31.4, 26.3, 21.1. HRMS(EI) m/z $[M+H]^+$ calcd for $C_{18}H_{23}O_2$, 271.1693, found 271.1691.

(1S,2R,4R)-1,7,7,7-tetramethyl-7λ^5-bicyclo[2.2.1]heptan-2-yl benzoate (**3ar** CAS: 122922-36-5).[36] The same procedure was used for (-)-borneol. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 24 hours. The reaction gave 84.6 mg of the product in 63% as a light yellow oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.9, 0.9 Hz, 2H), 7.55 (m, 1H), 7.48 – 7.41 (m, 2H), 5.22 – 5.08 (m, 1H), 2.52 – 2.45 (m, 1H), 2.18 – 2.12 (m, 1H), 1.85 – 1.77 (m, 1H), 1.74 (t, *J* = 4.5 Hz, 1H), 1.42 (m, 1H), 1.34 – 1.29 (m, 1H), 1.13 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.97 (s, 3H), 0.92 (s, 6H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.8, 132.7, 130.9, 129.5, 128.3, 80.5, 49.1, 47.9, 45.0, 36.9, 28.1, 27.4, 19.7, 18.9, 13.6.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (**3as** CAS:604-32-0).[31] The same procedure was used for cholesterol. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 35 hours. The reaction gave 109 mg of the product in 43% yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.58 – 7.51 (m, 1H), 7.43 (dd, *J* = 10.7, 4.7 Hz, 2H), 5.42 (d, *J* = 3.8 Hz, 1H), 4.92 –

4.80 (m, 1H), 2.47 (d, *J* = 7.7 Hz, 2H), 2.05 – 1.98 (m, 3H), 1.92 (dt, *J* = 13.3, 3.4 Hz, 1H), 1.84 (m, 1H), 1.78 – 1.70 (m, 1H), 1.58 – 1.44 (m, 6H), 1.39 – 1.33 (m, 3H), 1.29 – 1.24 (m, 2H), 1.20 (dd, *J* = 16.0, 4.0 Hz, 2H), 1.15 – 1.09 (m, 4H), 1.07 (s, 3H), 1.04 – 0.99 (m, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 2.2 Hz, 6H), 0.69 (s, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 166.0, 139.6, 132.7, 130.8, 129.5, 128.2, 122.8, 74.6, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.9, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.9.

methyl benzoate (**3at** CAS:93-58-3).[37] The same procedure was used fortrimethyl borate. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 62mg of the product in 91% as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.48 – 7.41 (m, 2H), 3.92 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 167.1, 132.9, 130.1, 129.6, 128.3, 52.1.

methyl benzoate (**3'at** CAS:93-58-3).[37] The same procedure was used for trimethyl borate. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 56mg of the product in 89% as a liquid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 2H), 7.59 – 7.50 (m, 1H), 7.43 (dd, *J* = 10.8, 4.8 Hz, 2H), 3.91 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 167.0, 132.8, 130.1, 129.5, 128.3, 52.0.

propyl benzoate (**3au** CAS：2315-68-6).[38] The same procedure was used tripropyl borate. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 73 mg of the product in 90% as a colorless liquid. 1H NMR (500 MHz, CDCl3) δ 8.28 – 7.89 (m, 1H), 7.61 – 7.51 (m, 1H), 7.49 – 7.39 (m, 1H), 4.29 (t, J = 6.7 Hz,

1H), 1.90 – 1.72 (m, 1H), 1.04 (t, J = 7.4 Hz, 2H). 13C{1H} NMR (126 MHz, CDCl3) δ 166.70, 132.79, 130.53, 129.53, 128.32, 66.54, 22.13, 10.54.

methyl 4-methylbenzoate (**3lt** CAS：99-75-2).[38] The same procedure was used 2-(p-tolyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 67mg of the product in 89% as a white solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.41 (s, 3H). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 167.2, 143.5, 129.6, 129.1, 127.5, 51.9, 21.6.

methyl 4-methylbenzoate (**3'lt** CAS：99-75-2).[38] The same procedure was used 2-(p-tolyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 62mg of the product in 82% as a white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.41 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 167.2, 143.5, 129.6, 129.0, 127.4, 51.9, 21.6.

methyl 4-chlorobenzoate (**3ft** CAS: 1126-46-1).[39] The same procedure was used 2-(4-chlorophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 62 mg of the product in 76% as a white solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.44 – 7.37 (m, 2H), 3.91 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 166.2, 139.3, 130.9, 128.7, 128.6, 52.2.

methyl 4-chlorobenzoate (**3'ft** CAS: 1126-46-1).[39] The same procedure was used 2-(4-chlorophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 62 mg of the product in 76% as a

white solid,.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 2H), 7.45 – 7.36 (m, 2H), 3.91 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 166.2, 139.3, 130.9, 128.7, 128.5, 52.2.

methyl 4-nitrobenzoate (**3ot** CAS: 619-50-1).[39] The same procedure was used 2-(4-nitrophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 82 mg of the product in 90% as a white solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 – 8.15 (m, 4H), 3.97 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 165.1, 150.5, 135.5, 130.7, 123.5, 52.8.

methyl 4-nitrobenzoate (**3'ot** CAS: 619-50-1).[39] The same procedure was used 2-(4-nitrophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 71mg of the product in 78% as a white solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.24 (m, 2H), 8.20 (d, J = 7.6 Hz, 2H), 3.97 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 165.1, 150.5, 135.5, 130.7, 123.5, 52.8.

methyl 4-nitrobenzoate (**3"ot** CAS: 619-50-1).[39] The same procedure was used 2-(4-nitrophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 76mg of the product in 84% as a white solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 – 8.25 (m, 2H), 8.22 – 8.17 (m, 2H), 3.97 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 165.1, 150.5, 135.5, 130.7, 123.5, 52.8.

methyl 3-nitrobenzoate (**3nt** CAS:618-95-1).[40] The same procedure was used 2-(3-nitrophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 67mg of the product in 74% yield as a white solid.^{1}H NMR (500 MHz, CDCl3) δ 8.83 (s, 1H), 8.43 – 8.33 (m, 2H), 7.64 (t, J = 8.0 Hz,

1H), 3.97 (d, J = 0.9 Hz, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 165.1, 150.5, 135.5, 130.7, 123.5, 52.8.

methyl 3-nitrobenzoate (**3'nt** CAS:618-95-1).[40] The same procedure was used 2-(3-nitrophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 66 mg of the product in 72% yield as a white solid.^{1}H NMR (500 MHz, CDCl3) δ 8.83 (s, 1H), 8.43 – 8.33 (m, 2H), 7.64 (t, J = 8.0 Hz, 1H), 3.97 (d, J = 0.9 Hz, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 165.1, 150.5, 135.5, 130.7, 123.5, 52.8.

methyl 3-nitrobenzoate (**3"nt** CAS:618-95-1).[9c] The same procedure was used 2-(3-nitrophenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 73 mg of the product in 80% yield as a white solid.^{1}H NMR (500 MHz, CDCl3) δ 8.83 (s, 1H), 8.43 – 8.33 (m, 2H), 7.64 (t, J = 8.0 Hz, 1H), 3.97 (d, J = 0.9 Hz, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 165.1, 150.5, 135.5, 130.7, 123.5, 52.8.

methyl 4-methoxybenzoate (**3'tt** CAS:121-98-2).[39] The same procedure was used 2-(4-methoxyphenyl)acetonitrile. The resulting solution was stirred at 130 ^{o}C under O_2 (monitored by TLC and GC) for 9 hours. The reaction gave 73 mg of the product in 88% yield as white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H).^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 166.8, 163.3, 131.5, 122.6, 113.5, 55.4, 51.8.

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Notes

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ASSOCIATED CONTENT

Supporting Information

Supplementary condition screens, preliminary mechanistic studies and NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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