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Graphical Abstract

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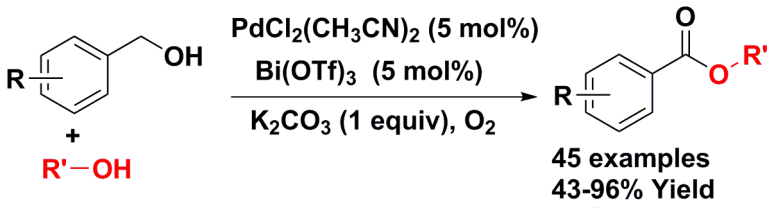

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ABSTRACT

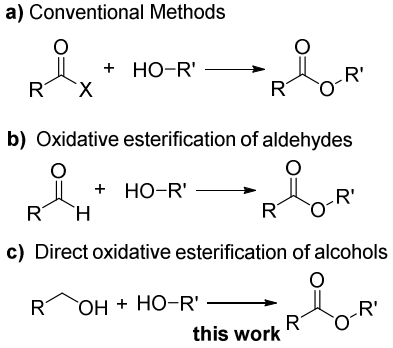
A highly efficient palladium-catalyzed approach for the direct oxidative esterification of benzylic alcohols with methanol and long-chain aliphatic alcohols under mild conditions has been achieved. This practical catalyst system exhibits a broad substrate scope and good functional group tolerance. Catalytic amount of $Bi(OTf)_3$ is used as co-catalyst to improve the activity and selectivity of the reactions. A variety of esters are obtained in yields of 43-96%.

1. Introduction

The ester group is an important functional group in organic chemistry and can be widely found in natural products, fine chemicals, pharmaceuticals and synthetic intermediates.[1] Because of their importance, the synthesis of esters has extensively attracted much attention and numerous transformations have been developed. Traditionally, the classical and common strategies for the preparation of esters involve the nucleophilic substitution of carboxylic acid derivatives (carboxylic halides, anhydrides and active esters) with alcohols (Scheme 1, a).[2] These protocols usually require stoichiometric amounts of reagents such as strong acid or basic and large amounts of unwanted by-products are produced. In recent years, considerable efforts have been devoted to the direct synthesis of esters from the oxidative esterification of aldehydes with alcohols (Scheme 1, b).[3] However, stoichiometric amounts of oxidants such as MnO_2,[4] oxone,[5] *N*-iodosuccinimide,[6] hydrogen peroxide,[7] *tert*-butyl hydroperoxide,[8] TCCA,[9] $(NH_4)_2S_2O_8$[10] or noble transition-metal catalysts including vanadium,[11] ruthenium,[12] iridium,[13] gold[14] were usually employed in this reaction. Moreover, the required aldehydes are chemical unstable. Thus, these protocols of the direct oxidative esterification of aldehydes are still environmentally unfavorable. As is well known, aldehydes can be easily prepared by the selective oxidation of alcohols and numerous methods have been developed.[15] Additionally, alcohols are inexpensive, benign and readily available chemical feedstock. Therefore, the development of one-pot process for the direct oxidative esterification of alcohols is highly desirable from both economic and environmental points of view (Scheme 1, c). However, the main challenge of this process is the selectivity between oxidation of alcohols to aldehydes and esterification. To the best of our knowledge, few works have been reported for the aerobic oxidative esterification of alcohols.[16]

Over the past few years, homogeneous and heterogeneous palladium-catalyzed oxidation reactions are of great interest and have been developed rapidly.[17] The majority of this work has focused on conversion of alcohols to aldehydes and ketones, relatively few works were carried out on the oxidative esterification of alcohols. In 2011, the group of Lei[18] and Beller[19] reported palladium-catalyzed oxidative cross-esterification of benzylic and aliphatic alcohols, respectively. In their methods, molecular oxygen was used as the terminal oxidant, and various esters were prepared in good yields. However, both of the two strategies required expensive Ag salt and special ligand, which was a disadvantage for its practical application. Subsequently, Lei also found that $PdCl_2(PPh_3)_2$ could act as the sole catalyst for the oxidative esterification of alcohols.[20] The approach used benzyl chloride as the oxidant and stoichiometric amounts of unwanted toluene were produced as by-product. Very recently, S. Stahl and coworkers described a heterogeneous Pd/charcoal in combination with bismuth(III) nitrate and tellurium metal catalyst system for the synthesis of esters.[21] Although, this catalyst system was highly efficient and readily accessible, but prevalently furnished methyl esters. Similarly, Cravotto reported Pd/C-catalyzed aerobic oxidative esterification of alcohols, but the reaction was carried out under MW irradiation and high temperature.[22] Therefore, the development of a selective, efficient and practical protocol for the aerobic oxidative direct esterification of alcohols is still desirable in both academia and industry.

Herein, we report a facile and efficient approach for the direct oxidative esterification of alcohols catalyzed by $PdCl_2(CH_3CN)_2$ with dioxygen as the environmentally benign oxidant. This protocol tolerates a variety of primary alcohols, especially long-chain aliphatic alcohols. In the present of catalytic amount of $Bi(OTf)_3$, the activity and selectivity of the reactions were significantly improved.



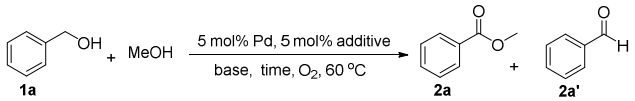
Scheme 1. Methods for the synthesis of esters.

2. Results and discussion

Initially, benzyl alcohol (**1a**) and methanol were employed as model substrates to optimize the reaction conditions using molecular oxygen as the oxidant. The optimized results including catalyst, additive, base and reaction time were summarized in Table 1. As shown in Table 1, different palladium catalysts were investigated in the present of K_2CO_3 with O_2 balloon (Table 1, entries 1-5). To our delight, $PdCl_2(CH_3CN)_2$ showed the best catalytic reactivity and the desired product **2a** was formed in 61% yield with 34% yield of aldehyde **2a'** (Table 1, entry 5). Bismuth salts have been widely used in organic synthesis, especially in oxidative esterification.[21,23] In order to improve the yield of ester **2a**, various bismuth salts such as $Bi(NO_3)_3$, $Bi(OAc)_3$, $Bi(OTf)_3$, $BiCl_3$ and Bi_2O_3 were screened (Table 1, entries 6-10). Notably, $Bi(OTf)_3$ was found to be the best co-catalyst because it significant improved the activity and selectivity of the reaction and gave the yield of **2a** up to 93%. It was obvious that $PdCl_2(CH_3CN)_2$ was crucial for the oxidative esterification of alcohols (Table 1, entry 11). Then, we investigated the influence of various bases in detail, the results revealed that K_2CO_3 was most effective for the reaction and gave good yield of **2a** (Table 1, entries 8 and 12-15). The reaction with organic base NEt_3 gave **2a** in trace yield (Table 1, entry 15). Furthermore, when the reaction was performed without base, the desired product was obtained in 62% yield (Table 1, entry 16). The reaction time could be reduced to 3 h also providing 93% yield of **2a** (Table 1, entries 17 and 18). In addition, the reaction temperature and the amount of catalyst loadings were also tested to further optimize the reaction conditions (Table 1, entries 19-23). In our hands the addition of polymethylhydrosiloxane (PMHS) as additive as reported by Xu et al.[23b] did not influence the yield of the product (Table 1, entry 24). When the reaction was carried out under air, the product was obtained in 87% yield. It was slightly lower than the reaction under oxygen.

With the optimal reaction condition in hand (Table 1, entry 17), the substrate scope and limitation of this catalytic system were examined. Firstly, we investigated the reaction of a variety

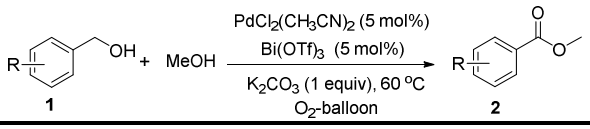
Table 1. Optimization of reaction conditions.[a]

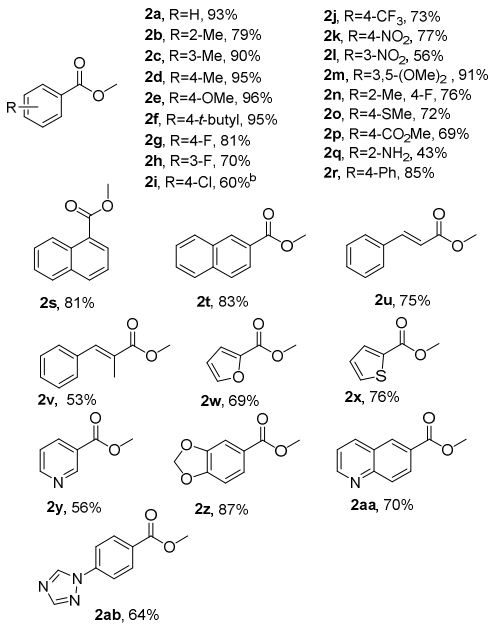


Entry	Pd-catalyst	Additive	Base	Time	Yield (%)[b] 2a	2a'
1	$PdCl_2$	-	K_2CO_3	5	-	-
2	$Pd(OAc)_2$	-	K_2CO_3	5	43	46
3	5 wt%Pd/C	-	K_2CO_3	5	39	25
4	$PdCl_2(PPh_3)_2$	-	K_2CO_3	5	52	41
5	$PdCl_2(CH_3CN)_2$	-	K_2CO_3	5	61	34
6	$PdCl_2(CH_3CN)_2$	$Bi(NO_3)_3$	K_2CO_3	5	85	11
7	$PdCl_2(CH_3CN)_2$	$Bi(OAc)_3$	K_2CO_3	5	78	17
8	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_2CO_3	5	93	<1
9	$PdCl_2(CH_3CN)_2$	$BiCl_3$	K_2CO_3	5	81	12
10	$PdCl_2(CH_3CN)_2$	Bi_2O_3	K_2CO_3	5	68	22
11	-	$Bi(OTf)_3$	K_2CO_3	5	-	-
12	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	*t*-BuOK	5	89	<5
13	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_3PO_4	5	67	23
14	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	Cs_2CO_3	5	76	18
15	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	NEt_3	5	-	45
16	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	-	5	62	16
17	**$PdCl_2(CH_3CN)_2$**	**$Bi(OTf)_3$**	**K_2CO_3**	**3**	**93**	**<1**
18	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_2CO_3	2	81	<5
19[c]	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_2CO_3	3	92	<1
20[d]	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_2CO_3	3	85	<5
21[e]	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_2CO_3	3	78	16
22[f]	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_2CO_3	3	93	<1
23[e]	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_2CO_3	5	86	10
24[g]	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_2CO_3	3	93	<1
25[h]	$PdCl_2(CH_3CN)_2$	$Bi(OTf)_3$	K_2CO_3	3	87	<5

[a] Reaction conditions: benzyl alcohol (1 mmol), 5 mol% Pd catalyst, 5 mol% additive, base (1 mmol) and MeOH (2 mL) , O_2-balloon, 60 °C , 3 h. [b] Determined by GC using internal standard. [c] Reaction at 65 °C. [d] Reaction at 55 °C. [e] 3 mol% $PdCl_2(CH_3CN)_2$. [f] 10 mol% $PdCl_2(CH_3CN)_2$ [g] 0.2 eq. polymethylhydrosiloxane(PMHS) was added. [h] Under air.

Table 2. Oxidative esterification of different benzylic alcohols with methanol. [a]



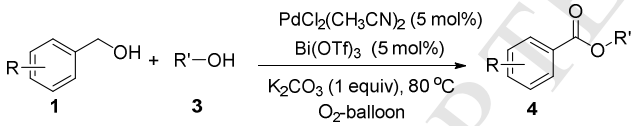


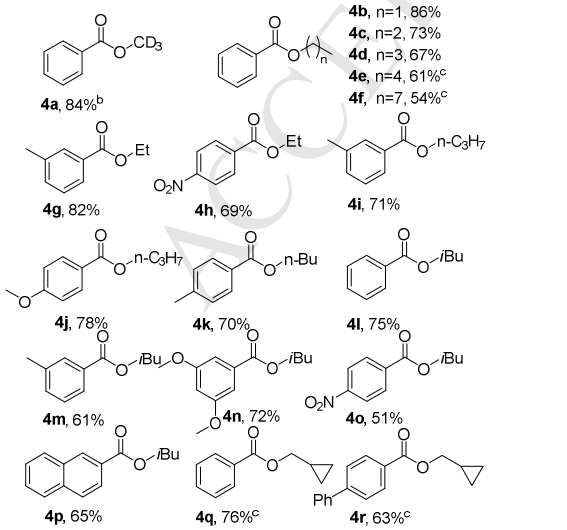
[a] Reaction conditions: **1** (1 mmol), 5 mol% $PdCl_2(CH_3CN)_2$, 5 mol% $Bi(OTf)_3$, K_2CO_3 (1 mmol) and MeOH (2 mL), 60 °C, O_2 -balloon, 3 h; Isolated yield. [b] The reaction was performed at 25 °C.

of benzylic alcohols with MeOH under standard conditions (Table 2). To our delights, both electron-donating groups and electron-withdrawing groups were well tolerated in the reactions. As is shown in Table 2, primary benzylic alcohols bearing electron-donating groups such as methyl, methoxyl, *tert*-butyl proceeded smoothly to give the desired products in 79-96% yields. (**2b-2f**). However, the electron-withdrawing groups such as -F, -Cl, $-NO_2$ and $-CF_3$ substituted benzylic alcohols provided comparably low yields of the corresponding methyl esters (**2g-2l**). Halogenated benzyl alcohols (**1i**) were susceptible to dehydrohalogenation under standard conditions and lower reaction temperature was needed to obtain the product **2i**. Disubstituted benzylic alcohols were still suitable in this transformation with good efficiency (**2m** and **2n**). Of particular note was that benzylic alcohols bearing thioether, ester and amino functional groups were smoothly converted into the desired products in 72%, 69% and 43% yields, respectively (**2o-2q**). 4-Phenylbenzyl alcohol, 1-naphthalenemethanol and 2-naphthalenemethanol furnished the corresponding methyl esters in moderate to good yields (**2r-2t**). In the case of allylic alcohol such as cinnamyl alcohol and α-methylcinnamyl alcohol were also well tolerated in this reaction (**2u** and **2v**). In addition, diverse heterocyclic and heterocyclic substituted alcohols were tested successively and the desired products were obtained in 56% - 87% yields (**2w-2ab**).

To further expand the substrate scope, we investigated the reactions of benzylic alcohols with other aliphatic alcohols. As shown in Table 3, benzyl alcohol reacted smoothly with [D_4]methanol and the product was isolated in 84% yield (**4a**). In general, a higher temperature and a longer reaction time were required for the oxidative esterification between benzylic alcohols and other long-chain aliphatic alcohols. It was worth noting that when the chain length of aliphatic alcohols increasing, the products yield reduced (**4b-4f**). Under the present reaction conditions, substituted benzylic alcohols containing either electron-donating groups or electron-withdrawing groups reacted

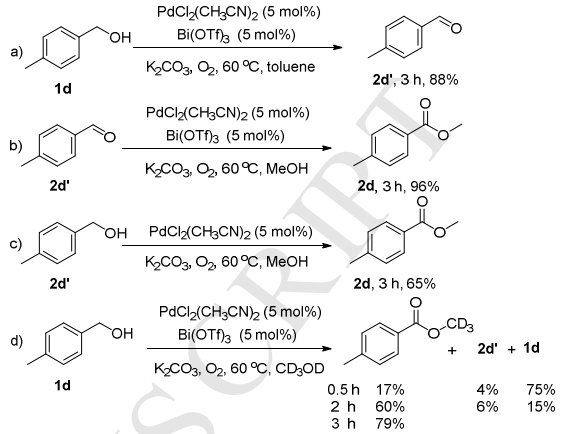
Table 3. Oxidative esterification of different benzylic alcohols with long-chain aliphatic alcohols.[a]





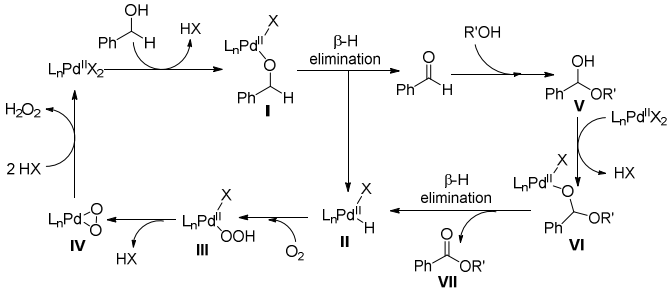
[a] Reaction conditions: **1** (1 mmol), 5 mol% $PdCl_2(CH_3CN)_2$, 5 mol% $Bi(OTf)_3$, K_2CO_3 (1 mmol) and R'OH (2 mL), 80 °C, 8 h, O_2 -balloon; Isolated yield. [b] Reaction carried out at 60 °C for 3 h. [c] Reaction carried out for 12 h.

well with aliphatic alcohols of different chain length (**4g-4k**). Then, isobutanol was introduced in this oxidative esterification and moderate to good yield of the desired products were obtained (**4l-4p**). Notably, the reaction of benzylic alcohols with sterically demanding cyclopropylmethanol was found to be effective and the respective esters were produced in 76% and 63% yields, respectively (**4q** and **4r**).



Scheme 2. Control experiments

To elucidate the reaction pathway, the following control experiments were carried out (Scheme 2). As illustrated in Scheme 2, 4-methylbenzyl alcohol was smoothly converted into 4-methylbenzaldehyde (**2d'**) with toluene serving as solvent (Scheme 2, a). When **2d'** was subjected to the standard reaction conditions, the desired ester **2d** was isolated in 96% yield (Scheme 2, b). We also carried out the reaction of oxidative esterification of 4-methylbenzyl alcohol in the absence of $Bi(OTf)_3$, only 65% yield of **2d** was obtained, which indicated that $Bi(OTf)_3$ play an important role in improving the activity and selectivity of the reaction. We suggested that bismuth could promote the formation of the hemiacetal or β-hydride elimination of intermediate **I** or **VI** to the corresponding aldehyde and ester, respectively (Scheme 3). Meanwhile, we conducted the experiment of **1d** with CD_3OD under standard conditions. After the mixture was stirred for 0.5 h and 2 h, the ^1H NMR spectrum of the reaction solution was taken (Fig S1 and S2). As shown in Fig S1 and S2, no hemiacetal was observed. When the reaction was carried out for 0.5 h, the corresponding ester, **2d'** and unreacted **1d** were observed by NMR spectroscopy in 17%, 4% and 75% yield, respectively. After the solution was stirred for 2 h, the desired ester was obtained in 60% yield by NMR spectroscopy, with 6% of **2d'** and 15% of unreacted **1d**. In addition, when the mixture was stirred for 3 h, no **1d** and **2d'** were detected (Fig S3), 79% yield of the corresponding ester was obtained. These results illustrate that aldehyde was an important intermediate of the reaction.



Scheme 3. Proposed mechanism of the oxidative esterification.

On the basis of the above-mentioned results and pertinent literatures, the reaction pathway was proposed.[18-19, 24] Firstly, the benzyl alcohol coordinated to the palladium catalyst center to form intermediate **I**. Subsequently, the intermediate **I** will undergo β-hydride elimination to give benzaldehyde and intermediate **II**. Then, reoxidation of intermediate **II** forms the active palladium catalyst. In the meanwhile, benzaldehyde reacted with aliphatic alcohols to form the hemiacetal **V**, which followed by a second palladium-catalyzed reaction to give intermediate **VI**. In the last step, another β-hydride elimination occurred to afford the desired product **VII** and intermediate **II**. Finally, the active palladium catalyst was regenerated from intermediate **II** under molecular oxygen again.

3. Conclusion

In conclusion, we have established a highly efficient $PdCl_2(CH_3CN)_2$/$Bi(OTf)_3$-catalyzed system for the oxidative esterification of benzylic alcohols with methanol and other long-chain aliphatic alcohols using dioxygen as benign oxidant. The catalyst system exhibits broad substrate scope and a variety of esters are obtained in moderate to excellent yields. The use of $Bi(OTf)_3$ additive significantly increases the activity and selectivity of the reactions. Notably, the esterification reactions of long-chain aliphatic alcohols also proceed successfully under mild conditions without the addition of ligands. In addition, a plausible reaction mechanism has been proposed and further applications of this catalytic system are under way in our laboratory.

4. Experimental section

4.1. General information

All reagents were purchased from commercial suppliers without further purification. Experiments were monitored by thin layer chromatography (TLC) and the TLC was performed on pre-coated silica gel plates. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, and the coupling constants J values are given in Hertz (Hz). Column chromatography was carried out over 200-300 mesh silica gel. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

4.2. General procedure

4.2.1. General procedure for the synthesis of **2** in Table 2.

To a 25-mL Schlenk tube equipped with a magnetic stirrer, $PdCl_2(CH_3CN)_2$ (0.05 mol, 5 mol%), $Bi(OTf)_3$ (0.05 mol, 5 mol%), K_2CO_3 (1 mmol) were added. Substrates 1 (1 mmol) and MeOH (2 mL) were added subsequently. The reaction tube was vacuumed and backfilled with oxygen (3 times). Then the reaction mixture was stirred at 60 ^{o}C for 3 h in the presence of an oxygen balloon. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate. Subsequently, the combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography with hexane/ethyl acetate to afford the corresponding products **2**.

4.2.2. General procedure for the systhesis of **4** in Table 3.

To a 25-mL Schlenk tube equipped with a magnetic stirrer, $PdCl_2(CH_3CN)_2$ (0.05 mol, 5 mol%), $Bi(OTf)_3$ (0.05 mol, 5 mol%), K_2CO_3 (1 mmol) were added. Substrates 1(1 mmol) and aliphatic alcohol (2 mL) were added subsequently. The reaction tube was vacuumed and backfilled with oxygen (3 times). Then the reaction mixture was stirred at 80 ^{o}C for 8 h in the presence of an oxygen balloon. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate. Subsequently, the combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography with hexane/ethyl acetate to afford the corresponding products **4**.

4.3. Characterization

*4.3.1. Methyl benzoate (**2a**)*[18]. Colorless oil; 90% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.85, 132.64, 129.91, 129.31, 128.09, 51.82.

*4.3.2. Methyl 2-methylbenzoate (**2b**)*[23]. Colorless oil; 79% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.7 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.24 (t, J = 7.0 Hz, 2H), 3.89 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.79, 139.90, 131.68, 131.41, 130.30, 129.30, 125.42, 51.50, 21.43.

*4.3.3. Methyl 3-methylbenzoate (**2c**)*[18]. Colorless oil; 90% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 3.91 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.02, 137.86, 133.39, 129.85, 127.98, 126.44, 51.75, 20.98.

*4.3.4. Methyl 4-methylbenzoate (**2d**)*[18]. Colorless oil; 95% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.90, 143.26, 129.33, 128.80, 127.18, 51.64, 21.35.

*4.3.5. Methyl 4-methoxybenzoate (**2e**)*[18]. Colorless oil; 96% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.61, 163.07, 131.32, 122.35, 113.34, 55.15, 51.59.

*4.3.6. Methyl 4-tert-butylbenzoate (**2f**).* Colorless oil; 95% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 3.90 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.87, 156.26, 129.18, 127.13, 125.06, 51.65, 34.80, 30.85. HRMS calcd for $C_{12}H_{16}O_2[M+H]^+$, 192.1150; found, 192.1156.

*4.3.7 Methyl 4-fluorobenzoate (**2g**)*[18]. Colorless oil; 81% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.10 (t, J = 8.2 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.88, 165.65(d, J = 253.6 Hz), 131.84 (d, J = 8.7 Hz), 126.15, 115.23(d, J = 21.6 Hz), 51.90.

*4.3.8. Methyl 3-fluorobenzoate (**2h**)*[21]. Colorless oil; 70% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.8 Hz, 1H), 7.71 (m, 1H), 7.41 (m, 1H), 7.28 – 7.23 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.71, 162.28 (d, J = 251.6 Hz), 132.04 (d, J = 6.1 Hz), 129.73 (d, J = 6.7 Hz), 125.04 (s), 119.73 (d, J = 22.1 Hz), 116.23 (d, J = 23.5 Hz), 52.11.

*4.3.9. Methyl 4-chlorobenzoate (**2i**)*[21]. Colorless oil; 67% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.95, 139.11, 130.70, 128.44, 128.07, 51.98.

*4.3.10. Methyl 4-(trifluoromethyl)benzoate (**2j**)*[21]. Colorless oil; 73% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.1 Hz,

2H), 7.70 (d, *J* = 8.1 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.59, 134.17(q, *J* =31.67 Hz), 133.09, 129.70, 125.13, 123.37 (q, *J* =271.8 Hz), 52.22.

4.3.11. Methyl 4-nitrobenzoate (**2k**)[16d]. Pale yellow solid; 77% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.9 Hz, 2H), 8.22 (d, *J* = 8.9 Hz, 2H), 3.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.92, 150.27, 135.22, 130.46, 123.29, 52.59.

4.3.12. Methyl 3-nitrobenzoate (**2l**)[16d]. Pale yellow solid; 56% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.45 – 8.34 (m, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.67, 148.00 (s), 134.99, 131.60, 129.38, 127.11, 124.30, 52.52.

4.3.13. Methyl 3,5-dimethoxybenzoate (2m)[20b]. White solid; 91% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 2.4 Hz, 2H), 6.64 (t, *J* = 2.3 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.59, 160.38, 131.74, 106.86, 105.52, 55.29, 51.96.

4.3.14. Methyl 4-fluoro-2-methylbenzoate (**2n**)[25]. Colorless oil; 76% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.5, 6.1 Hz, 1H), 6.98 – 6.86 (m, 2H), 3.88 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.73, 164.32 (d, *J* = 253 Hz), 143.64 (d, *J* = 8.0 Hz), 133.0 (d, *J* = 8.7 Hz), 125.30, 118.15(d, *J* = 21 Hz), 112.44(d, *J* = 22 Hz) , 51.53, 21.66.

4.3.15. Methyl 4-methylsulfanylbenzoate (**2o**)[21]. White solid; 72% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 3.6 Hz, 2H), 3.92 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.56, 145.16, 129.60, 126.03, 124.68, 51.72, 14.55.

4.3.16. Dimethyl terephthalate (**2p**)[21]. White solid; 69% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 4H), 3.94 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.97, 133.63, 129.26, 52.12.

4.3.17. Methyl 2-aminobenzoate (**2q**)[21]. Colorless oil; 43% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 6.65 (m, 2H), 5.72 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.34, 150.17, 133.84, 130.97, 116.42, 116.03, 110.51, 51.27.

4.3.18. Methyl biphenyl-4-carboxylate (**2r**)[18]. White solid; 85% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.97, 144.60, 138.96, 129.07, 127.88, 127.10, 126.24, 126.01, 51.08.

4.3.19. Methyl 1-naphthoate (**2s**)[20b]. Colorless oil; 81% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.7 Hz, 1H), 8.19 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.52 (m, 2H), 4.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.99, 132.81, 132.32, 130.31, 129.17, 127.49, 126.71, 126.06, 125.16, 124.79, 123.44, 51.08.

4.3.20. Methyl 2-naphthoate (**2t**)[16d]. White solid; 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.07 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.62 – 7.53 (m, 2H), 3.99 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.24, 134.50, 131.48, 130.04, 128.33, 127.20, 127.13, 126.74, 126.39, 125.61, 124.21, 51.20.

4.3.21. Methyl cinnamate (**2u**)[18]. Colorless oil; 75% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.51 – 7.53 (m, 2H), 7.40 – 7.35 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.15, 144.61, 134.14, 130.03, 128.63, 127.81, 117.56, 51.41.

4.3.22. (E)-methyl 2-methyl-3-phenylacrylate (**2v**)[23]. Colorless oil; 53% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.40 (d, *J* = 4.4 Hz, 4H), 7.33 (m, 1H), 3.82 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 138.7, 135.6, 129.4, 128.1, 128.1, 51.8, 13.8.

4.3.23. Methyl furan-2-carboxylate (**2w**)[18]. Colorless oil; 69% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.53 – 6.49 (m, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.87, 146.00, 144.36, 117.65, 111.56, 51.64.

4.3.24. Methyl thiophene-2-carboxylate (**2x**)[18]. Colorless oil; 76% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 3.4 Hz, 1H), 7.54 (d, *J* = 4.9 Hz, 1H), 7.12 – 7.05 (m, 1H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.65, 132.55, 132.42, 131.32, 126.71, 51.08.

4.3.25. Methyl nicotinate (**2y**)[26]. White solid: 56% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (d, *J* = 1.5 Hz, 1H), 8.77 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.29 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.39 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.37, 153.08, 150.55, 136.69, 125.69, 122.96, 52.06.

4.3.26. Methyl 3,4-methylenedioxybenzoate (**2z**)[21]. White solid; 87% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.46 (d, *J* = 1.5 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.03 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.17, 151.30, 147.44, 125.04, 123.91, 109.23, 107.68, 101.50, 51.76.

4.3.27. Methyl Quinoline-6-Carboxylate (**2aa**)[27]. White solid; 70% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.60 (s, 1H), 8.34 – 8.25 (m, 2H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.48 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 152.2, 149.7, 137.0, 130.7, 129.5, 128.6, 127.8, 127.1, 121.5, 52.1.

4.3.28. Methyl 4-(1,2,4-triazol-1-yl)benzoate (**2ab**). White solid; 64% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 2H), 8.13 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 152.7, 140.9, 139.9, 131.1, 129.4, 119.0, 52.1. HRMS calcd for $C_{10}H_9N_3O_2$ $[M+H]^+$, 203.0695; found, 203.0692.

4.3.29. Methyl benzoate-D$_3$ (**4a**)[19]. Colorless oil; 84% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.86, 132.62, 129.93, 129.30, 128.08.

4.3.30. Ethyl benzoate (**4b**)[19]. Colorless oil; 86% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.37, 132.52, 130.26, 129.27, 128.04, 60.67, 14.06.

4.3.31. Propyl Benzoate (**4c**)[19]. Colorless oil; 73% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.29 (t, *J* = 6.7 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.36, 132.49, 130.28, 129.24, 128.02, 66.22, 21.84, 10.20.

4.3.32. Butyl benzoate (**4d**)[19]. Colorless oil; 67% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.52 – 1.44 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.38, 132.48, 130.31, 129.25, 128.02, 64.53, 30.53, 19.01, 13.46.

4.3.33. Pentyl benzoate (**4e**)[19]. Colorless oil; 61% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.82 – 1.73

(m, 2H), 1.46 – 1.36 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.43, 132.51, 130.30, 129.27, 128.05, 64.86, 28.18, 27.95, 22.10, 13.72.

*4.3.34. Octyl benzoate (**4f**)*[18]. Colorless oil; 54% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.48 – 1.41 (m, 2H), 1.38 – 1.27 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.39, 132.49, 130.31, 129.27, 128.03, 64.86, 31.54, 28.99, 28.95, 28.48, 25.80, 22.38, 13.82.

*4.3.35. Ethyl 3-methylbenzoate (**4g**)*[28]. Colorless oil; 82% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.33 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.50, 137.78, 133.26, 130.20, 129.78, 127.92, 126.40, 60.56, 20.95, 14.05.

*4.3.36. Ethyl 4-nitrobenzoate (**4h**)*[16k]. Pale yellow oil; 69% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.42, 150.23, 135.60, 130.39, 123.23, 61.69, 13.96.

*4.3.37. Propyl 3-methylbenzoate (**4i**).* Colorless oil; 73% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.6 Hz, 2H), 7.34 (m, 2H), 4.28 (t, *J* = 6.7 Hz, 2H), 2.40 (s, 3H), 1.79 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.57, 137.80, 133.27, 130.21, 129.79, 127.94, 126.41, 66.18, 21.87, 20.98, 10.25. HRMS calcd for $C_{11}H_{14}O_2[M+H]^+$, 178.0994; found, 178.0991.

*4.3.38. Propyl 4-methoxybenzoate (**4j**)*[29]. Colorless oil; 78% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.25 (t, *J* = 6.7 Hz, 2H), 3.85 (s, 3H), 1.81 – 1.74 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.16, 162.99, 131.26, 122.71, 113.28, 65.95, 55.11, 21.90, 10.26.

*4.3.39. Butyl 4-methylbenzoate (**4k**)*[16i]. Colorless oil; 70% Yield. ^{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), 1.78 – 1.71 (m, 2H), 1.51 – 1.44 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.71, 142.34, 128.53, 127.98, 126.79, 63.59, 29.79, 20.57, 18.26, 12.73.

*4.3.40. Isobutyl benzoate (**4l**)*[18]. Colorless oil; 75% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.11 (d, *J* = 6.6 Hz, 2H), 2.09 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.55, 131.75, 129.50, 128.48, 127.28, 69.94, 26.87, 18.14.

*4.3.41. Isobutyl 3-methylbenzoate (**4m**).* Colorless oil; 61% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.34 (m, 2H), 4.10 (d, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 2.09 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.56, 137.84, 133.30, 130.22, 129.80, 127.96, 126.40, 70.69, 27.66, 21.02, 18.95. HRMS calcd for $C_{12}H_{16}O_2[M+H]^+$, 192.1150; found, 192.1142.

*4.3.42. Isobuthyl 3,5-dimethoxybenzoate (**4n**).* Colorless oil; 72% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 2.4 Hz, 2H), 6.64 (t, *J* = 2.4 Hz, 1H), 4.09 (d, *J* = 6.6 Hz, 2H), 3.82 (s, 6H), 2.07 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.03, 160.36, 132.13, 106.90, 105.05, 70.84, 55.20, 27.61, 18.89. HRMS calcd for $C_{13}H_{18}O_4[M+H]^+$, 238.1205; found, 238.1209.

*4.3.43. Isobuthyl 4-nitrobenzoate (**4o**)* [30]. Pale yellow oil; 51% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.7 Hz, 2H), 8.21 (d, *J* = 8.7 Hz, 2H), 4.16 (d, *J* = 6.7 Hz, 2H), 2.11 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.42, 150.25, 135.62, 130.37, 123.26, 71.62, 27.58, 18.86.

*4.3.44. Isobuthyl 2-naphthoate (**4p**)*[31]. Colorless oil; 65% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.09 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.56 (m, 2H), 4.19 (d, *J* = 6.6 Hz, 2H), 2.16 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.75, 134.47, 131.49, 129.89, 128.30, 127.08,1[26].72, 125.55, 124.76, 124.22, 70.12, 26.94, 18.22.

*4.3.45. Cyclopropylmethyl benzoate (**4q**)*[9]. Colorless oil; 76% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.16 (d, *J* = 7.2 Hz, 2H), 1.31 – 1.22 (m, 1H), 0.62 (q, *J* = 6.0 Hz, 2H), 0.37 (q, *J* = 4.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.47, 132.53, 130.30, 129.33, 128.04, 69.4, 9.66 , 3.03.

*4.3.46. Cyclopropylmethyl [1,1'-biphenyl]-4-carboxylate (**4r**)*[16h]. Colorless oil; 63% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 4.19 (d, *J* = 7.2 Hz, 2H), 1.30 (m, 1H), 0.64 (q, *J* = 6.0 Hz, 2H), 0.40 (q, *J* = 4.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.37, 145.30, 139.83, 129.89, 129.07, 128.68, 127.86, 127.04, 126.76, 69.44, 9.74, 3.09.

*4.3.47. 4-Methylbenzaldehyde (**2d'**).* Colorless oil; 88% Yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.71, 145.27, 133.94, 129.56, 129.43, 21.56.

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Acknowledgments should be inserted at the end of the paper, before the references, not as a footnote to the title. Use the unnumbered Acknowledgements Head style for the Acknowledgments heading.

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