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Copper-Catalyzed Oxidative C–O Bond Formation of 2-Acyl Phenols and 1,3-Dicarbonyl Compounds with Ethers: Direct Access to Phenol Esters and Enol Esters

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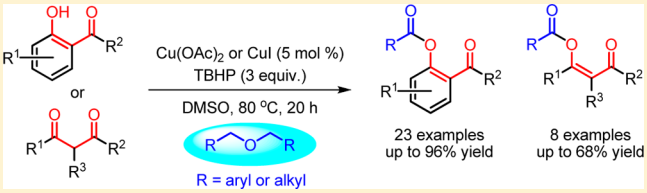
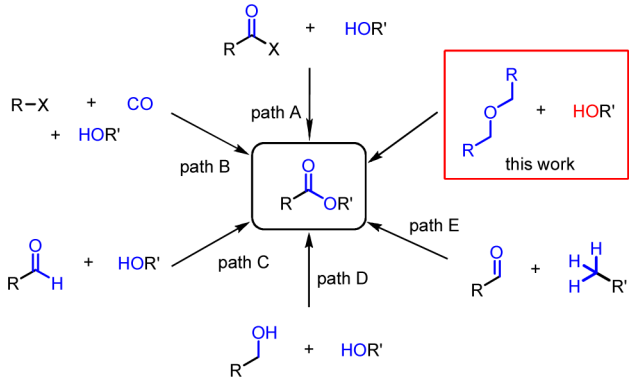
Supporting Information

ABSTRACT: A copper-catalyzed oxidative coupling of 2-carbonyl-substituted phenols and 1,3-dicarbonyl compounds with a wide range of dibenzyl or dialkyl ethers is described. This protocol provides an efficient preparation of phenol esters and enol esters in good yields with high chemoselectivity. This method represents an alternative protocol for classical esterification reactions.



Ester groups are the highly important and abundant scaffolds found in natural products, medicinally relevant molecules, and functional materials.[1] The traditional methods for the synthesis of ester groups rely on the reaction of preactivated acid derivatives, such as acyl halides, anhydrides, and activated esters, with alcohols in the presence of a stoichiometric amount of bases (Scheme 1, path A).[2] An alternative protocol involves transition-metal-catalyzed coupling reactions using aryl halides, carbon monoxide, and alcohols (Scheme 1, path B).[3] Recent efforts have been devoted toward the oxidative coupling between aldehydes and alcohols based on the use of stoichiometric amounts of metal oxidants ($KHSO_5$ and MnO_2), *N*-heterocyclic carbene activation, and a transition-metal-mediated process (Scheme 1, path C).[4] Another attractive protocol is the cross dehydrogenative coupling (CDC)[5] between two different alcohols using Ru,[6] Rh,[7] Ir,[8] Pd,[9] and Cu[10] catalysts, which represents a step forward toward an economical and sustainable process (Scheme 1, path D). Recently, efficient Cu-catalyzed and transition-metal-free protocols for the formation of benzylic esters have been developed to allow a CDC involving alkylbenzenes as coupling partners (Scheme 1, path E).[11] In the past decade, copper-catalyzed C–H functionalizations have emerged as promising new catalytic transformations because copper catalysts are inexpensive, readily available, insensitive to air, and easy to handle, compared to other transition-metal catalysts.[5,12] Notably, the combination of copper salts and peroxides as oxidants was well-known to facilitate the functionalizations of sp^3 carbon, especially the sp^3 carbon atom near to a nitrogen atom.[13] In addition, C–H bond functionalization of ethers and related oxygen-containing compounds under copper catalysis has been recently explored.[14]

Scheme 1. Synthetic Protocol for the Preparation of Ester Groups



Recently, we found that dibenzyl ethers can play a key role as new carbonyl sources for acylation reaction of arene C–H bonds catalyzed by palladium(II) metal.[15] In continuation of our efforts for the development of catalytic C–H functionalizations,[16] we herein disclose the copper-catalyzed oxidative esterification of 2-carbonyl-substituted phenols and 1,3-dicarbonyl compounds with a range of dibenzyl or dialkyl ethers to afford the corresponding phenol esters and enol esters. To our knowledge, it is the first method of catalytic esterfication from the ether oxidation level.

In our initial study, 1-(4-fluoro-2-hydroxyphenyl)ethanone (**1a**) and di(2-methylbenzyl)ether (**2a**) were selected for the optimization of reaction conditions. After detailed screening of reaction conditions, we found that the best result was obtained by using 5 mol % $Cu(OAc)_2$ and 3 equiv of *tert*-butyl hydroperoxide (TBHP) in DMSO (1 mL) at 80 °C to afford our desired product **3a** in 74% yield (see Supporting

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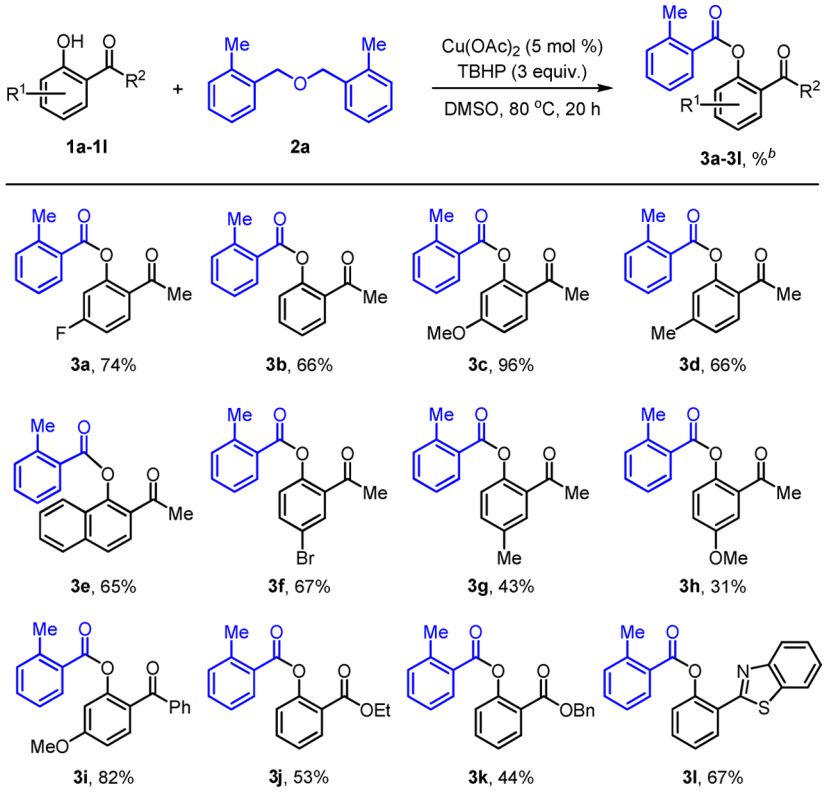
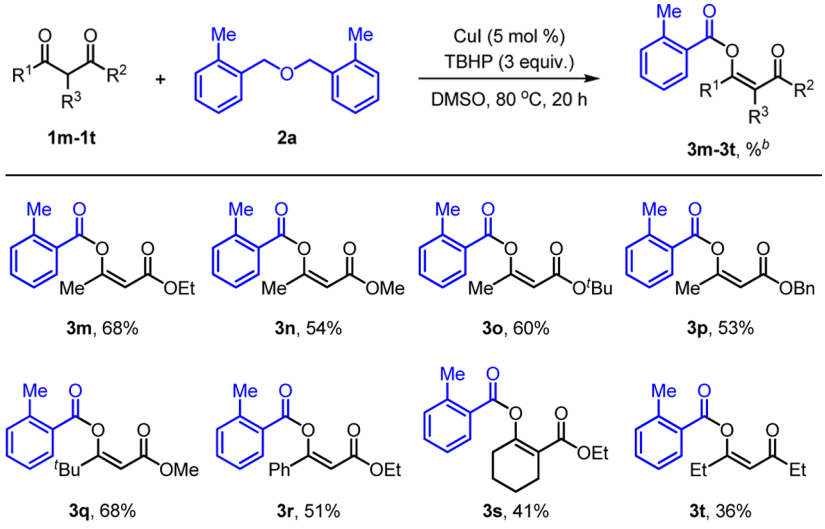
Table 1. Scope of 2-Carbonyl-Substituted Phenols[a]



[a]Reaction conditions: **1a−1l** (0.3 mmol), **2a** (0.6 mmol), $Cu(OAc)_2$ (5 mol %), TBHP (3 equiv), DMSO (1 mL) at 80 °C for 20 h in pressure tubes. [b]Isolated yield by flash column chromatography.

Table 2. Scope of 1,3-Dicarbonyl Compounds[a]



[a]Reaction conditions: **1m−1t** (0.3 mmol), **2a** (0.6 mmol), CuI (5 mol %), TBHP (3 equiv), DMSO (1 mL) at 80 °C for 20 h in pressure tubes. [b]Isolated yield by flash column chromatography.

Information for optimization table). Under the optimized reaction conditions, the scope of 2-carbonyl-substituted phenols was examined, as shown in Table 1. The coupling of dibenzylic ether **2a** and *para*-substitituted-2-hydroxyacetophenones **1a−1d** with electron-rich and electron-deficient groups was found to be favored to afford the products **3a−3d** in high yields. Notably, sterically hindered naphthol **1e** smoothly reacted with **2a** to produce compound **3e** in 65% yield. In addition, it was found that 2-hydroxyacetophenone **1f** with a bromo moiety at the *meta* position was a suitable substrate for this transformation, whereas **1g** and **1h** with electron-donating groups (Me and OMe) were less reactive under present reaction conditions. Further examination revealed that 2-hydroxybenzophenone **1i** and 2-hydroxybenzoates **1j** and **1k** were well tolerated under current reaction conditions. Finally, compound **1l** with benzothiazole moiety instead of carbonyl group at the *ortho* position of phenol underwent smoothly esterification reaction to provide **3l** in 67% yield.

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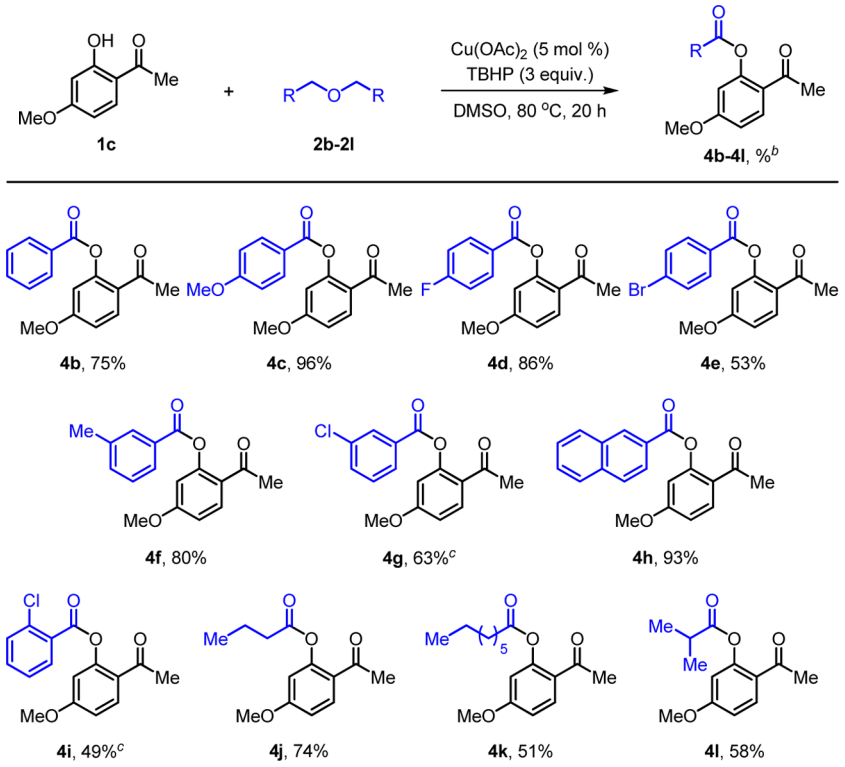
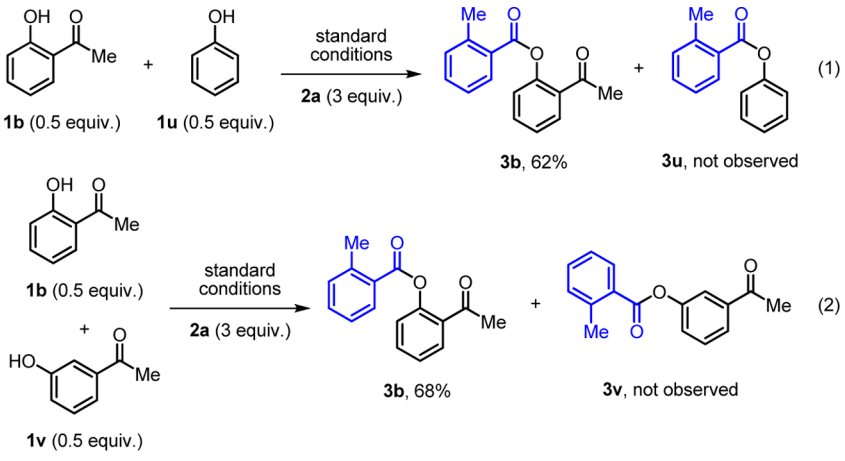
Table 3. Scope of Ethers[a]



[a]Reaction conditions: **1c** (0.3 mmol), **2b**–**2l** (0.6 mmol), $Cu(OAc)_2$ (5 mol %), TBHP (3 equiv), DMSO (1 mL) at 80 °C for 20 h in pressure tubes. [b]Isolated yield by flash column chromatography. [c]$Cu(OAc)_2$ (10 mol %), TBHP (6 equiv).

Scheme 2. Crossover Experiments



In previous literature, 1,3-dicarbonyl compounds were used as interesting substrates for catalytic C–O bond-formation reaction in the presence of aldehydes or formamides to yield the various enol esters or enol carbamates.[17] Thus, we sought to expand our substrate scope from 2-carbonyl-substituted phenols to 1,3-dicarbonyl compounds because the enol tautomer of the diketone moiety has structural similarities to 2-acyl phenolic compounds. To our pleasure, ethyl acetoacetate (**1m**) was coupled with ether **2a** under the standard conditions to afford our desired product **3m** in 54% yield. After further optimization of reaction conditions, we found that CuI was found to be a good catalyst in this transformation to afford **3m** in 68% yield (Table 2). In general, the reaction of β-keto esters **1n**–**1r** with **2a** afforded the desired products **3n**–**3r** in moderate to good yields, while α,β-disubstituted keto ester **1s** and 1,3-diketone **1t** were less reactive. It should be mentioned that all reactions furnished the (*Z*)-enol esters as major products, which were confirmed by ^{1}H NMR analysis and NOE experiments.

Subsequently, a series of dibenzyl or dialkyl ethers **2b**–**2l** were subjected to reaction with **1c** (Table 3). Dibenzylic ethers **2b**–**2i** with electron-rich and electron-deficient groups (OMe, Me, F, Cl, and Br) reacted with 2-hydroxy-4-methoxyacetophenone (**1c**) to afford the coupling products in moderate to high yields. Particulary, this process was tolerated by halogen groups as versatile functionalities for further cross-coupling reaction. To our pleasure, this process is not limited to dibenzylic ethers.[18] Dialkyl ethers **2j**–**2l** also participated in the

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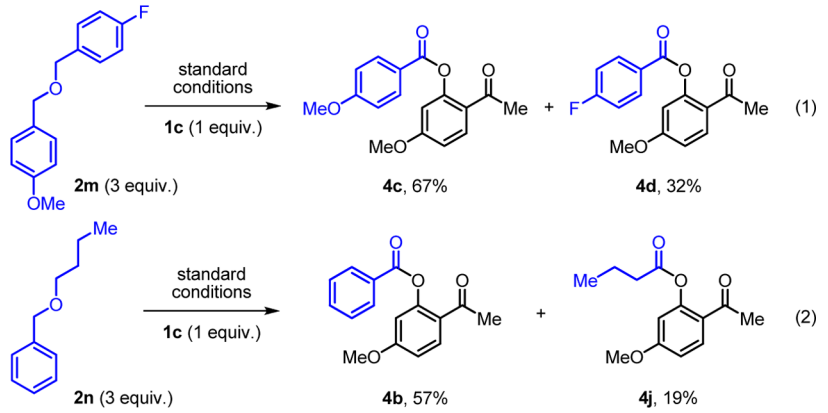
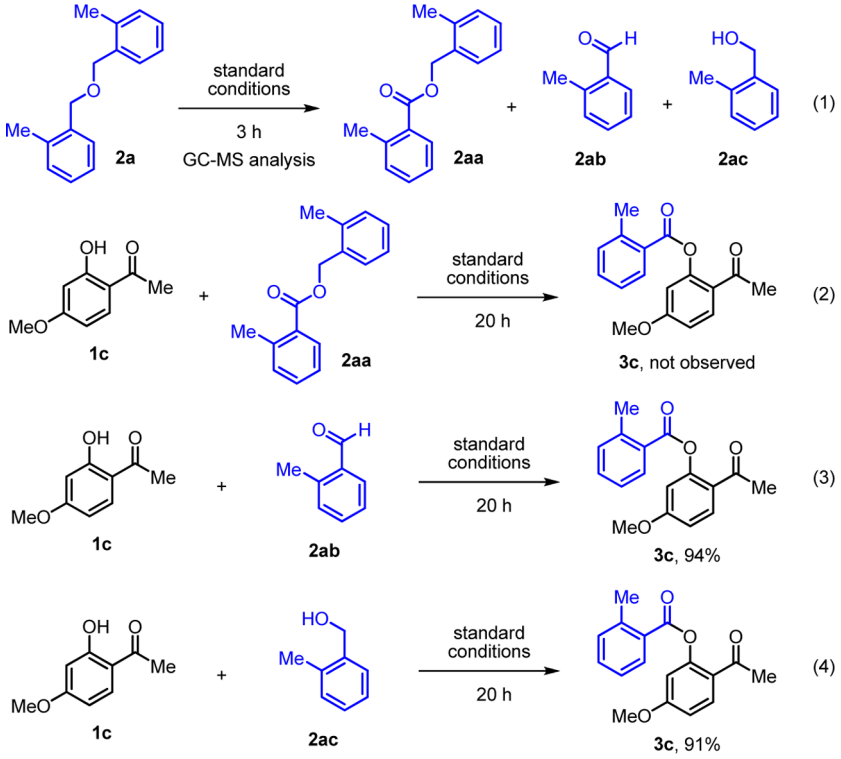
Scheme 3. Intramolecular Competition Experiments



Scheme 4. Control Experiments



coupling reaction to furnish the corresponding products **4j** (74%), **4k** (51%), and **4l** (58%).

To gain a mechanistic insight, some crossover experiments were carried out under standard reaction conditions (Scheme 2). Exposure of ether **2a** to equimolar quantities of 2-hydroxyacetophenone (**1b**) and phenol (**1u**) provided a single product of **3b** in 62% isolated yield, but no esterification of **1u** was observed (Scheme 2, eq 1). In addition, competition experiment between 2-hydroxyacetophenone (**1b**) and 3-hydroxyacetophenone (**1v**) led to no formation of **3v** (Scheme 2, eq 2). Thus, no observation of compounds **3u** and **3v** indicates that the bidentate coordination of substrate to copper center might be one of the key factors for the initiation of the catalytic cycle.

Intramolecular competition experiments using unsymmetric dibenzylic ether **2m** or alkylbenzyl ether **2n** were performed to illustrate the chemoselectivity of this transformation (Scheme 3). Exposure of **2m** to **1c** under standard reaction conditions provided a separable mixture of **4c** and **4d** in a 2:1 ratio (Scheme 3, eq 1). In addition, the reaction of **2n** with **1c** afforded a product distribution of 3:1 between **4b** and **4j** (Scheme 3, eq 2). These results may reveal that the kinetic stability of radical intermediates derived from ethers primarily influences the site selectivity.

To further examine the possible mechanism, some related experiments were performed (Scheme 4). First, the reaction of dibenzylic ether **2a** in the absence of 2-hydroxyacetophenone under standard reaction conditions was conducted, and the reaction progress was monitored by GC−MS analysis. After the reaction was carried out at 80 °C for 3 h, we could observe the formation of *o*-tolylaldehyde (**2ab**) and *o*-methylbenzyl alcohol (**2ac**), as well as ester **2aa** (Scheme 4, eq 1).[19] Thus, we further examined the esterification of **1c** using **2aa** under standard reaction conditions but observed no formation of the esterificated compound **3c** (Scheme 4, eq 2). In addition, treatment of **1c** with aldehyde **2ab** or alcohol **2ac** provided the

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desired product **3c** in high yields, respectively (Scheme 4, eqs 3 and 4). Although it is not clear about the formation of ester **2aa** at this point,[20] we believe that the C−O bond of the ester cannot be cleaved to afford the corresponding aldehyde and alcohol under the present reaction conditions.

Finally, to understand the generation of the acyl radical intermediate, the reaction between **1c** and **2a** with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical scavenger was conducted.[21] A substantial decrease of yield was detected in a dose-dependent manner (see Supporting Information for details). These collective data can be explained by a radical pathway that benzylic or alkyl radicals can be generated by the radical initiator TBHP under a copper salt. The formed benzylic or alkyl radicals may be rapidly converted to the corresponding acyl radicals, which can be trapped by a copper-substrate complex to give an esterification product. A plausible reaction mechanism is shown in Supporting Information. First, Cu(II) catalyst can form complex **I** with 2-carbonyl-substituted enol **1**. The reactive benzoyl radicals[22] derived from ether **2** by TBHP and a catalytic amount of copper catalyst can react with complex **I** by single electron transfer to produce Cu(III) complex **II**.[23] Finally, reductive elimination of intermediate **II** affords the desired product **3** and Cu(I) catalyst, which can be reoxidized to Cu(II) by TBHP.

In conclusion, a carbonyl-group-assisted copper-catalyzed oxidative esterification of 2-carbonyl-substituted phenols and 1,3-dicarbonyl compounds with dibenzyl or dialkyl ethers has been described. Further detailed mechanistic investigations regarding benzyl ethers as acyl equivalents are in progress.

EXPERIMENTAL SECTION

General Procedure for the Esterification of 2-Carbonyl-Substituted Phenols. To an oven-dried sealed tube charged with **1a** (46.2 mg, 0.3 mmol, 100 mol %), $Cu(OAc)_2$ (2.7 mg, 0.015 mmol, 5 mol %), and TBHP (0.16 mL, 0.9 mmol, 300 mol %, 5.5 M in decane) in DMSO (1 mL) was added **2a** (135.8 mg, 0.6 mmol, 200 mol %). The reaction mixture was allowed to stir at 80 °C for 20 h. After cooling at room temperature, the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2; *n*-hexane/EtOAc = 15:1) provided **3a** (61 mg, 0.222 mmol) in 74% yield.

2-Acetyl-5-fluorophenyl 2-Methylbenzoate (3a). Yield: 74% (60 mg). Colorless oil. R_f = 0.17 (*n*-hexane/EtOAc = 15:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.20 (dd, J_1 = 7.8, J_2 = 1.3 Hz, 1H), 7.91 (d, J = 6.3 Hz, 1H), 7.51 (td, J_1 = 7.6, J_2 = 1.4 Hz, 1H), 7.36−7.32 (m, 2H), 7.09−7.06 (m, 1H), 6.97 (dd, J_1 = 8.9, J_2 = 2.5 Hz, 1H), 2.67 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 196.0, 165.1, 165.0 (d, J_{C-F} = 254.3 Hz), 151.2 (d, J_{C-F} = 10.7 Hz), 141.8, 133.2, 132.3 (d, J_{C-F} = 10.3 Hz), 132.0, 131.4, 127.8 (d, J_{C-F} = 3.1 Hz), 127.7, 126.1, 113.3 (d, J_{C-F} = 21.0 Hz), 111.9 (d, J_{C-F} = 23.9 Hz), 29.6, 21.8. IR (KBr): υ 2967, 2851, 1740, 1687, 1602, 1491, 1458, 1413, 1356, 1287, 1228, 1145, 1111, 1029, 973, 885, 816, 732 cm^{-1}. HRMS (quadrupole, EI) *m*/*z* calcd for $C_{16}H_{13}FO_3$ $[M]^+$ 272.0849, found 272.0852.

2-Acetylphenyl 2-Methylbenzoate (3b). Yield: 66% (51 mg). Colorless oil. R_f = 0.20 (*n*-hexane/EtOAc = 15:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.21 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 7.86 (dd, J_1 = 7.7, J_2 = 1.6 Hz, 1H), 7.60−7.58 (m, 1H), 7.49 (td, J_1 = 7.4, J_2 = 1.3 Hz, 1H), 7.38−7.32 (m, 3H), 7.22 (dd, J_1 = 8.0, J_2 = 1.0 Hz, 1H), 2.67 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 197.7, 165.6, 149.3, 141.6, 133.4, 132.9, 132.0, 131.4, 131.3, 130.2, 128.2, 126.1, 126.0, 124.0, 29.6, 21.8. IR (KBr): υ 2927, 2581, 1737, 1686, 1602, 1574, 1480, 1446, 1356, 1283, 1241, 1190, 1133, 1071, 1028, 954, 837, 733 cm^{-1}. HRMS (quadrupole, EI) *m*/*z* calcd for $C_{16}H_{14}O_3$ $[M]^+$ 254.0943, found 254.0945.

2-Acetyl-5-methoxyphenyl 2-Methylbenzoate (3c). Yield: 96% (82 mg). Pale yellow oil. R_f = 0.26 (*n*-hexane/EtOAc = 3:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.23 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.48 (td, J_1 = 7.4, J_2 = 1.4 Hz, 1H), 7.35−7.31 (m, 2H), 6.86 (dd, J_1 = 8.7, J_2 = 2.5 Hz, 1H), 6.72 (d, J = 2.5 Hz, 1H), 3.86 (s, 3H), 2.68 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.8, 165.6, 163.8, 151.6, 141.5, 132.8, 132.5, 131.9, 131.4, 128.3, 126.0, 123.6, 111.7, 109.4, 55.7, 29.3, 21.8. IR (KBr): υ 2932, 2840, 1738, 1677, 1605, 1568, 1497, 1458, 1356, 1288, 1233, 1189, 1125, 1031, 962, 884, 733 cm^{-1}. HRMS (quadrupole, EI) *m*/*z* calcd for $C_{17}H_{16}O_4$ $[M]^+$ 284.1049, found 284.1053.

2-Acetyl-5-methylphenyl 2-Methylbenzoate (3d). Yield: 66% (53 mg). Pale yellow oil. R_f = 0.17 (*n*-hexane/EtOAc = 15:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.21 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.48 (td, J_1 = 7.4, J_2 = 1.4 Hz, 1H), 7.35−7.32 (m, 2H), 7.17−7.16 (m, 1H), 7.03 (d, J = 6.3 Hz, 1H), 2.67 (s, 3H), 2.52 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 197.0, 165.8, 149.5, 144.8, 141.5, 132.8, 131.9, 131.3, 130.5, 128.4, 128.3, 126.8, 126.0, 124.5, 29.5, 21.8, 21.4. IR (KBr): υ 2624, 2857, 1737, 1682, 1612, 1456, 1355, 1247, 1219, 1138, 1038, 965, 816, 732 cm^{-1}. HRMS (quadrupole, EI) *m*/*z* calcd for $C_{17}H_{16}O_3$ $[M]^+$ 268.1099, found 268.1098.

2-Acetylnaphthalen-1-yl 2-Methylbenzoate (3e). Yield: 65% (59 mg). Yellow oil. R_f = 0.20 (*n*-hexane/EtOAc = 15:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.44 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 8.03 (dd, J_1 = 8.4, J_2 = 0.7 Hz, 1H), 7.93−7.89 (m, 2H), 7.83 (d, J = 8.6 Hz, 1H), 7.63−7.60 (m, 1H), 7.57−7.54 (m, 2H), 7.43−7.38 (m, 2H), 2.71 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 197.8, 165.4, 146.7, 142.1, 136.4, 133.2, 132.2, 131.5, 128.5, 127.9, 127.8, 127.5, 127.4, 127.2, 126.2, 126.0, 125.2, 123.0, 30.1, 22.0. IR (KBr): υ 2924, 2851, 1738, 1685, 1598, 1463, 1356, 1230, 1191, 1132, 1067, 1018, 813, 731 cm^{-1}. HRMS (quadrupole, EI) *m*/*z* calcd for $C_{20}H_{16}O_3$ $[M]^+$ 304.1099, found 304.1098.

2-Acetyl-4-bromophenyl 2-Methylbenzoate (3f). Yield: 67% (67 mg). Colorless oil. R_f = 0.39 (*n*-hexane/EtOAc = 10:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.18 (dd, J_1 = 7.8, J_2 = 1.2 Hz, 1H), 7.95 (s, 1H), 7.68 (dd, J_1 = 8.5, J_2 = 2.4 Hz, 1H), 7.50 (td, J_1 = 7.4, J_2 = 1.3 Hz, 1H), 7.36−7.32 (m, 2H), 7.11 (d, J = 8.6 Hz, 1H), 2.66 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 196.2, 165.2, 148.3, 141.8, 136.1, 133.2, 133.0, 132.9, 132.1, 131.3, 127.7, 126.1, 125.8, 119.2, 29.6, 21.8. IR (KBr): υ 2925, 2857, 1738, 1690, 1598, 1470, 1389, 1355, 1286, 1235, 1190, 1134, 1066, 1026, 873, 732 cm^{-1}. HRMS (quadrupole, EI) *m*/*z* calcd for $C_{16}H_{13}BrO_3$ $[M]^+$ 332.0048, found 332.0045.

2-Acetyl-4-methylphenyl 2-Methylbenzoate (3g). Yield: 43% (35 mg). Colorless oil. R_f = 0.29 (*n*-hexane/EtOAc = 10:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.20 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 7.65 (s, 1H), 7.48 (td, J_1 = 7.4, J_2 = 1.4 Hz, 1H), 7.39−7.37 (m, 1H), 7.35−7.31 (m, 2H), 7.10 (d, J = 8.1 Hz, 1H), 2.66 (s, 3H), 2.53 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 197.8, 165.8, 147.1, 141.5, 135.8, 134.0, 132.8, 131.9, 131.3, 131.0, 130.6, 128.3, 126.0, 123.7, 29.7, 21.8, 20.8. IR (KBr): υ 2924, 2851, 1737, 1686, 1577, 1487, 1355, 1241, 1192, 1133, 1035, 872, 733 cm^{-1}. HRMS (quadrupole, EI) *m*/*z* calcd for $C_{17}H_{16}O_3$ $[M]^+$ 268.1099, found 268.1097.

2-Acetyl-4-methoxyphenyl 2-Methylbenzoate (3h). Yield: 31% (26 mg). Pale yellow oil. R_f = 0.18 (*n*-hexane/EtOAc = 10:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.20 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 7.49 (td, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.35−7.32 (m, 3H), 7.14−7.10 (m, 2H), 3.86 (s, 3H), 2.66 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 197.4, 166.0, 157.7, 142.8, 141.6, 132.9, 132.0, 131.2, 128.2, 126.0, 124.8, 119.0, 114.5, 55.8, 29.8, 21.8. IR (KBr): υ 2923, 2853, 1736, 1688, 1576, 1486, 1458, 1356, 1283, 1240, 1187, 1134, 1036, 870, 734 cm^{-1}. HRMS (quadrupole, EI) *m*/*z* calcd for $C_{17}H_{16}O_4$ $[M]^+$ 284.1049, found 284.1053.

2-Benzoyl-5-methoxyphenyl 2-Methylbenzoate (3i). Yield: 82% (85 mg). Light yellow solid. Mp = 91−94 °C. R_f = 0.13 (*n*-hexane/EtOAc = 15:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.76−7.74 (m, 2H), 7.71 (dd, J_1 = 7.8, J_2 = 1.2 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H), 7.47−7.44 (m, 1H), 7.39−7.36 (m, 3H), 7.21 (d, J = 7.7 Hz, 1H), 7.15 (t, J = 7.3 Hz, 1H), 6.88 (dd, J_1 = 8.6, J_2 = 2.5 Hz, 1H), 6.83 (d, J = 2.4 Hz, 1H), 3.89 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 194.2, 165.1, 163.0, 151.0, 141.3, 138.4, 132.7, 132.6, 132.4, 131.6,

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131.1, 129.6, 128.2, 127.8, 125.6, 124.2, 111.3, 109.1, 55.7, 21.7. IR (KBr): υ 2930, 2835, 1735, 1650, 1605, 1572, 1500, 1448, 1319, 1270, 1233, 1160, 1098, 1028, 912, 881, 848, 732 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{22}H_{18}O_4$ $[M]^+$ 346.1205, found 346.1206.

2-(Ethoxycarbonyl)phenyl 2-Methylbenzoate (3j). Yield: 53% (45 mg). Colorless oil. R_f = 0.29 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.26 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 8.08 (dd, J_1 = 7.8, J_2 = 1.6 Hz, 1H), 7.60 (td, J_1 = 7.5, J_2 = 1.7 Hz, 1H), 7.48 (td, J_1 = 7.4, J_2 = 1.3 Hz, 1H), 7.37−7.31 (m, 3H), 7.21 (dd, J_1 = 8.0, J_2 = 1.0 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 2.68 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 165.7, 164.8, 150.6, 141.5, 133.6, 132.7, 131.9 (two carbons), 131.5, 128.3, 126.0, 125.9, 124.1, 124.0, 61.2, 21.9, 13.9. IR (KBr): υ 2977, 2928, 2868, 1736, 1720, 1605, 1575, 1452, 1366, 1290, 1241, 1197, 1133, 1078, 1030, 733 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{16}O_4$ $[M]^+$ 284.1049, found 284.1053.

Benzyl 2-(2-Methylbenzoyloxy)benzoate (3k). Yield: 44% (46 mg). Yellow sticky oil. R_f = 0.33 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.18 (dd, J_1 = 8.2, J_2 = 1.4 Hz, 1H), 8.12 (dd, J_1 = 7.9, J_2 = 1.6 Hz, 1H), 7.63−7.61 (m, 1H), 7.47 (td, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.36 (td, J_1 = 7.7, J_2 = 1.1 Hz, 1H), 7.30−7.23 (m, 8H), 5.24 (s, 2H), 2.61 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 192.8, 165.7, 164.6, 150.7, 141.5, 135.4, 133.9, 132.6, 132.0, 131.8, 131.5, 128.4, 128.3, 128.2, 126.0, 125.9, 124.1, 123.8, 67.0, 21.8. IR (KBr): υ 2929, 2851, 1720, 1605, 1574, 1452, 1375, 1288, 1244, 1197, 1072, 1028, 732 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{22}H_{18}O_4$ $[M]^+$ 346.1205, found 346.1204.

2-(Benzo[d]thiazol-2-yl)phenyl 2-Methylbenzoate (3l). Yield: 67% (69 mg). Colorless sticky oil. R_f = 0.48 (*n*-hexane/EtOAc = 5:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.39−8.37 (m, 2H), 7.94 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.58−7.53 (m, 2H), 7.45−7.33 (m, 6H), 2.67 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 165.4, 162.6, 153.0, 148.6, 141.9, 135.4, 133.0, 132.0, 131.8, 131.5, 130.4, 128.3, 126.6, 126.4, 126.2, 126.0, 125.2, 124.0, 123.3, 121.4, 22.0. IR (KBr): υ 2978, 2857, 1740, 1603, 1574, 1482, 1433, 1264, 1240, 1188, 1134, 1104, 1024, 965, 729 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{21}H_{15}NO_2S$ $[M]^+$ 345.0824, found 345.0831.

General Procedure for the Esterification of 1,3-Dicarbonyl Compounds. To an oven-dried sealed tube charged with **1m** (39.0 mg, 0.3 mmol, 100 mol %), CuI (2.9 mg, 0.015 mmol, 5 mol %), and TBHP (0.16 mL, 0.9 mmol, 300 mol %, 5.5 M in decane) in DMSO (1 mL) was added **2a** (135.8 mg, 0.6 mmol, 200 mol %). The reaction mixture was allowed to stir at 80 °C for 20 h. After cooling at room temperature, the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2; *n*-hexane/EtOAc = 10:1) provided **3m** (51 mg, 0.203 mmol) in 68% yield.

(*Z*)-4-Ethoxy-4-oxobut-2-en-2-yl 2-Methylbenzoate (3m).[18] Yield: 68% (51 mg). Colorless oil. R_f = 0.26 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.10 (dd, J_1 = 7.7, J_2 = 1.2 Hz, 1H), 7.45−7.43 (m, 1H), 7.30−7.27 (m, 2H), 5.70 (s, 1H), 4.08 (q, J = 7.0 Hz, 2H), 2.64 (s, 3H), 2.13 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 164.0, 163.8, 159.9, 141.2, 132.6, 131.8, 131.4, 128.2, 125.8, 108.7, 60.0, 21.8, 21.7, 14.0. IR (KBr): υ 2980, 2933, 1720, 1668, 1602, 1576, 1440, 1379, 1287, 1250, 1190, 1132, 1037, 831, 732 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{14}H_{16}O_4$ $[M]^+$ 248.1049, found 248.1053.

(*Z*)-4-Methoxy-4-oxobut-2-en-2-yl 2-Methylbenzoate (3n). Yield: 54% (38 mg). Colorless oil. R_f = 0.30 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.10 (dd, J_1 = 7.7, J_2 = 1.1 Hz, 1H), 7.44 (td, J_1 = 7.4, J_2 = 1.4 Hz, 1H), 7.30−7.27 (m, 2H), 5.71 (s, 1H), 3.63 (s, 3H), 2.64 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 164.1, 164.0, 160.4, 141.2, 132.6, 131.7, 131.3, 128.3, 125.9, 108.2, 51.2, 21.8, 21.6. IR (KBr): υ 2952, 1723, 1675, 1602, 1576, 1436, 1379, 1336, 1288, 1250, 1194, 1133, 1039, 986, 922, 831, 734 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{13}H_{14}O_4$ $[M]^+$ 234.0892, found 234.0883.

(*Z*)-4-*tert*-Butoxy-4-oxobut-2-en-2-yl 2-Methylbenzoate (3o). Yield: 60% (50 mg). Colorless oil. R_f = 0.27 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.09 (dd, J_1 = 7.7, J_2 = 1.1 Hz, 1H), 7.44 (td, J_1 = 7.4, J_2 = 1.4 Hz, 1H), 7.29−7.27 (m, 2H), 5.61 (s, 1H), 2.64 (s, 3H), 2.09 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 163.9, 163.1, 157.9, 141.3, 132.6, 131.8, 131.4, 128.3, 125.8, 110.7, 80.4, 28.0, 21.8, 21.5. IR (KBr): υ 2977, 2932, 1739, 1717, 1668, 1602, 1575, 1456, 1367, 1291, 1211, 1164, 1129, 1041, 1024, 964, 831, 733 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{20}O_4$ $[M]^+$ 276.1362, found 276.1372.

(*Z*)-4-(Benzyloxy)-4-oxobut-2-en-2-yl 2-Methylbenzoate (3p). Yield: 53% (49 mg). Colorless sticky oil. R_f = 0.33 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.08 (dd, J_1 = 8.4, J_2 = 1.5 Hz, 1H), 7.47−7.45 (m, 1H), 7.30−7.27 (m, 7H), 5.79 (s, 1H), 5.11 (s, 2H), 2.63 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 163.9, 163.5, 160.5, 141.3, 135.7, 132.6, 131.7, 131.4, 128.4, 128.2, 128.1, 128.0, 125.8, 108.5, 66.0, 21.8, 21.7. IR (KBr): υ 2921, 2852, 1722, 1668, 1602, 1455, 1379, 1331, 1248, 1188, 1131, 1027, 829, 732 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{19}H_{18}O_4$ $[M]^+$ 310.1205, found 310.1205.

(*Z*)-1-Methoxy-4,4-dimethyl-1-oxopent-2-en-3-yl 2-Methylbenzoate (3q). Yield: 68% (56 mg). Colorless oil. R_f = 0.40 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.07 (dd, J_1 = 8.6, J_2 = 1.4 Hz, 1H), 7.44 (td, J_1 = 7.4, J_2 = 1.4 Hz, 1H), 7.31−7.26 (m, 2H), 5.80 (s, 1H), 3.62 (s, 3H), 2.64 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 169.5, 164.8, 164.1, 141.1, 132.4, 131.8, 131.1, 128.7, 125.8, 104.2, 51.2, 37.6, 27.4, 21.6. IR (KBr): υ 2972, 2912, 1747, 1724, 1653, 1603, 1459, 1434, 1328, 1270, 1237, 1171, 1087, 1040, 844, 731 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{20}O_4$ $[M]^+$ 276.1362, found 276.1369.

(*Z*)-3-Ethoxy-3-oxo-1-phenylprop-1-enyl 2-Methylbenzoate (3r). Yield: 51% (48 mg). Pale brown oil. R_f = 0.24 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.28 (d, J = 7.8 Hz, 1H), 7.66−7.64 (m, 2H), 7.50−7.47 (m, 1H), 7.45−7.39 (m, 3H), 7.35−7.31 (m, 2H), 6.37 (s, 1H), 4.16 (d, J = 7.0 Hz, 2H), 2.66 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 164.2, 164.1, 157.9, 141.7, 133.7, 132.9, 131.9, 131.5, 130.9, 128.8 (two carbons), 127.9, 126.0, 106.8, 60.3, 21.8, 14.1. IR (KBr): υ 2979, 2934, 1739, 1716, 1638, 1599, 1578, 1448, 1367, 1331, 1276, 1224, 1162, 1058, 1027, 850, 763, 733 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{19}H_{18}O_4$ $[M]^+$ 310.1205, found 310.1208.

2-(Ethoxycarbonyl)cyclohex-1-enyl 2-Methylbenzoate (3s). Yield: 41% (35 mg). Colorless oil. R_f = 0.34 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.06 (dd, J_1 = 8.4, J_2 = 1.4 Hz, 1H), 7.43 (td, J_1 = 7.4, J_2 = 1.4 Hz, 1H), 7.28−7.26 (m, 2H), 4.06 (q, J = 7.1 Hz, 2H), 2.64 (s, 3H), 2.48−2.45 (m, 2H), 2.38−2.36 (m, 2H), 1.81−1.78 (m, 2H), 1.73−1.70 (m, 2H), 1.03 (t, J = 7.1 Hz, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 165.9, 164.8, 155.2, 141.2, 132.5, 131.8, 131.3, 128.5, 125.8, 118.2, 60.4, 29.3, 25.3, 22.1, 21.9, 21.8, 13.9. IR (KBr): υ 2935, 2863, 1731, 1701, 1660, 1602, 1577, 1457, 1372, 1284, 1233, 1187, 1119, 1073, 1055, 1031, 857, 733 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{20}O_4$ $[M]^+$ 288.1362, found 288.1349.

(*Z*)-5-Oxohept-3-en-3-yl 2-Methylbenzoate (3t). Yield: 36% (27 mg). Colorless oil. R_f = 0.21 (*n*-hexane/EtOAc = 15:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.08 (d, J = 7.9 Hz, 1H), 7.44 (td, J_1 = 7.4, J_2 = 1.3 Hz, 1H), 7.30−7.28 (m, 2H), 5.97 (s, 1H), 2.63 (s, 3H), 2.50 (q, J = 7.2 Hz, 2H), 2.41 (q, J = 7.1 Hz, 2H), 1.18 (t, J = 7.4 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 198.1, 164.1, 161.8, 141.3, 132.6, 131.8, 131.2, 128.3, 125.9, 113.6, 37.0, 28.5, 21.7, 10.5, 7.8. IR (KBr): υ 2975, 2937, 1736, 1699, 1630, 1458, 1377, 1286, 1235, 1166, 1131, 1059, 1019, 843, 733 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{15}H_{18}O_3$ $[M]^+$ 246.1256, found 246.1255.

2-Acetyl-5-methoxyphenyl Benzoate (4b):[10] Yield: 75% (61 mg). Colorless oil. R_f = 0.29 (*n*-hexane/EtOAc = 3:1). ^1H NMR (700 MHz, $CDCl_3$): δ 8.21 (dd, J_1 = 8.3, J_2 = 1.2 Hz, 2H), 7.89 (d, J = 8.8 Hz, 1H), 7.66−7.64 (m, 1H), 7.54−7.51 (m, 2H), 6.88−6.73 (m, 1H), 6.72 (s, 1H), 3.86 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.6, 165.1, 163.7, 151.7, 133.7, 132.4, 130.3, 129.3, 128.7, 123.5, 112.0, 109.2, 55.7, 29.5. IR (KBr): υ 2923, 1734, 1676, 1604, 1567, 1497, 1425, 1356, 1320, 1237, 1159, 1124, 1056, 1021, 962, 884, 702 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{14}O_4$ $[M]^+$ 270.0892, found 270.0891.

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2-Acetyl-5-methoxyphenyl 4-Methoxybenzoate (4c). Yield: 96% (87 mg). Yellow oil. R_f = 0.19 (*n*-hexane/EtOAc = 3:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.18−8.15 (m, 2H), 7.88 (d, J = 8.8 Hz, 1H), 7.01−6.99 (m, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.70 (s, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.7, 164.7, 164.1, 163.7, 151.8, 132.5, 132.3, 128.6, 121.6, 113.9, 112.0, 109.2, 55.7, 55.5, 29.7. IR (KBr): υ 2923, 2841, 1731, 1678, 1603, 1510, 1463, 1422, 1357, 1319, 1251, 1161, 1126, 1068, 1025, 964, 845, 761 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{16}O_5$ $[M]^+$ 300.0998, found 300.0996.

2-Acetyl-5-methoxyphenyl 4-Fluorobenzoate (4d). Yield: 86% (74 mg). Colorless oil. R_f = 0.31 (*n*-hexane/EtOAc = 3:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.24−8.22 (m, 2H), 7.88 (d, J = 8.7 Hz, 1H), 7.25−7.18 (m, 2H), 6.87 (dd, J_1 = 8.7, J_2 = 2.5 Hz, 1H), 6.71 (s, 1H), 3.87 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.6, 166.2 (d, J_{C-F} = 253.6 Hz), 164.2, 163.8, 151.5, 132.9 (d, J_{C-F} = 9.0 Hz), 132.5, 125.7 (d, J_{C-F} = 2.5 Hz), 123.3, 115.9 (d, J_{C-F} = 22.3 Hz), 111.9, 109.3, 55.7, 29.2. IR (KBr): υ 2939, 2840, 1737, 1677, 1605, 1507, 1425, 1357, 1321, 1257, 1239, 1137, 1126, 1067, 1010, 963, 845, 733 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{13}FO_4$ $[M]^+$ 288.0798, found 288.0796.

2-Acetyl-5-methoxyphenyl 4-Bromobenzoate (4e). Yield: 53% (55 mg). White solid. Mp = 106−108 °C. R_f = 0.36 (*n*-hexane/EtOAc = 3:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.07−8.05 (m, 2H), 7.88 (d, J = 8.8 Hz, 1H), 7.66−7.65 (m, 2H), 6.87 (dd, J_1 = 8.8, J_2 = 2.5 Hz, 1H), 6.71 (d, J = 2.5 Hz, 1H), 3.86 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.5, 164.5, 163.8, 151.4, 132.6, 132.0, 131.8, 128.9, 128.4, 123.1, 112.0, 109.3, 55.8, 29.1. IR (KBr): υ 2983, 1738, 1679, 1608, 1591, 1486, 1424, 1397, 1357, 1262, 1164, 1127, 1069, 1010, 964, 844, 731 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{13}BrO_4$ $[M]^+$ 347.9997, found 347.9999.

2-Acetyl-5-methoxyphenyl 3-Methylbenzoate (4f). Yield: 80% (68 mg). Pale yellow oil. R_f = 0.33 (*n*-hexane/EtOAc = 3:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.03−8.01 (m, 2H), 7.89 (d, J = 8.8 Hz, 1H), 7.46−7.25 (m, 2H), 6.86 (dd, J_1 = 8.8, J_2 = 2.5 Hz, 1H), 6.71 (s, 1H), 3.85 (s, 3H), 2.49 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.7, 165.3, 163.7, 151.7, 138.5, 134.6, 132.4, 130.8, 129.2, 128.6, 127.4, 123.6, 112.0, 109.2, 55.7, 29.5, 21.3. IR (KBr): υ 2922, 2846, 1735, 1677, 1606, 1568, 1425, 1356, 1321, 1258, 1182, 1125, 1065, 1025, 964, 896, 822, 732 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{16}O_4$ $[M]^+$ 284.1049, found 284.1052.

2-Acetyl-5-methoxyphenyl 3-Chlorobenzoate (4g). Yield: 63% (57 mg). Pale yellow oil. R_f = 0.15 (*n*-hexane/EtOAc = 5:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.18 (s, 1H), 8.17−8.08 (m, 1H), 7.89 (d, J = 8.7 Hz, 1H), 7.62−7.60 (m, 1H), 7.46 (t, J = 7.9 Hz, 1H), 6.89−6.71 (m, 1H), 6.71 (s, 1H), 3.87 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.5, 164.0, 163.8, 151.4, 134.8, 133.7, 132.6, 131.2, 130.3, 129.9, 128.4, 123.0, 112.0, 109.3, 55.8, 29.1. IR (KBr): υ 2921, 2851, 1732, 1685, 1601, 1481, 1447, 1356, 1248, 1195, 1175, 1057, 1022, 954, 846, 756, 701 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{13}ClO_4$ $[M]^+$ 304.0502, found 304.0507.

2-Acetyl-5-methoxyphenyl 2-Naphthoate (4h). Yield: 93% (89 mg). Colorless oil. R_f = 0.34 (*n*-hexane/EtOAc = 3:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.21 (dd, J_1 = 8.5, J_2 = 1.6 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.6 Hz, 1H), 7.91 (d, J = 1.9 Hz, 2H), 7.64−7.62 (m, 1H), 7.59−7.56 (m, 1H), 6.89 (dd, J_1 = 8.8, J_2 = 2.5 Hz, 1H), 6.78 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.7, 165.3, 163.8, 151.8, 135.9, 132.5, 132.4, 132.2, 129.6, 128.7, 128.5, 127.8, 126.8, 126.6, 125.5, 123.6, 112.0, 109.3, 55.7, 29.5. IR (KBr): υ 2934, 2840, 1734, 1677, 1606, 1569, 1503, 1464, 1424, 1356, 1262, 1187, 1126, 1068, 952, 819, 732 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{20}H_{16}O_4$ $[M]^+$ 320.1049, found 320.1050.

2-Acetyl-5-methoxyphenyl 2-Chlorobenzoate (4i). Yield: 49% (45 mg). Pale yellow oil. R_f = 0.11 (*n*-hexane/EtOAc = 5:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.20 (dd, J_1 = 7.7, J_2 = 1.4 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.53−7.48 (m, 2H), 7.43−7.40 (m, 1H), 6.88 (dd, J_1 = 8.7, J_2 = 2.5 Hz, 1H), 6.75 (d, J = 2.4 Hz, 1H), 3.88 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.7, 163.8, 163.6, 151.2, 134.4, 133.2, 132.5, 132.3, 131.2, 129.0, 126.8, 123.1, 112.0, 109.4, 55.8, 29.0. IR (KBr): υ 2925, 2581, 1750, 1678, 1607, 1568, 1466, 1436, 1357, 1258, 1236, 1126, 1030, 963, 887, 742 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{13}ClO_4$ $[M]^+$ 304.0502, found 304.0500.

2-Acetyl-5-methoxyphenyl Butyrate (4j). Yield: 74% (53 mg). Pale yellow oil. R_f = 0.36 (*n*-hexane/EtOAc = 3:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.82 (d, J = 8.7 Hz, 1H), 6.81 (dd, J_1 = 8.8, J_2 = 2.5 Hz, 1H), 6.58 (s, 1H), 3.84 (s, 3H), 2.61 (t, J = 7.4 Hz, 2H), 2.50 (s, 3H), 1.83−1.77 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.7, 172.0, 163.7, 151.4, 132.4, 123.2, 111.5, 109.3, 55.7, 36.2, 29.1, 18.0, 13.7. IR (KBr): υ 2964, 2875, 1760, 1677, 1606, 1568, 1499, 1425, 1356, 1255, 1241, 1124, 1066, 1025, 966, 813, 749 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{13}H_{16}O_4$ $[M]^+$ 236.1049, found 236.1049.

2-Acetyl-5-methoxyphenyl Octanoate (4k). Yield: 51% (45 mg). Colorless oil. R_f = 0.47 (*n*-hexane/EtOAc = 3:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.82 (d, J = 8.8 Hz, 1H), 6.81 (dd, J_1 = 8.7, J_2 = 2.5 Hz, 1H), 6.58 (s, 1H), 3.84 (s, 3H), 2.62 (t, J = 7.4 Hz, 2H), 2.49 (s, 3H), 1.78−1.74 (m, 2H), 1.43−1.25 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.7, 172.2, 163.6, 151.5, 132.4, 123.2, 111.5, 109.3, 55.7, 34.4, 31.6, 29.2, 29.1, 28.9, 24.5, 22.6, 14.0. IR (KBr): υ 2926, 2856, 1762, 1678, 1606, 1568, 1500, 1464, 1425, 1356, 1256, 1126, 1068, 1026, 965, 813, 749 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{24}O_4$ $[M]^+$ 292.1675, found 292.1681.

2-Acetyl-5-methoxyphenyl Isobutyrate (4l). Yield: 58% (41 mg). Colorless oil. R_f = 0.22 (*n*-hexane/EtOAc = 5:1). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.81 (d, J = 8.7 Hz, 1H), 6.81 (dd, J_1 = 8.7, J_2 = 2.5 Hz, 1H), 6.56 (s, 1H), 3.84 (s, 3H), 2.90−2.84 (m, 1H), 2.49 (s, 3H), 1.35−1.34 (m, 6H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 195.8, 175.3, 163.6, 151.5, 132.3, 123.4, 111.5, 109.1, 55.7, 34.2, 29.1, 18.7. IR (KBr): υ 2975, 2935, 1756, 1678, 1606, 1569, 1500, 1466, 1356, 1319, 1255, 1125, 1066, 1025, 965, 905, 810, 734 cm^{-1}. HRMS (quadrupole, EI) m/z calcd for $C_{13}H_{16}O_4$ $[M]^+$ 236.1049, found 236.1045.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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