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Copper-catalyzed chemoselective oxidative *o*-aroylation of 2-acetylphenols, alkyl salicylates and 1,3-dicarbonyl compounds using styrene derivatives

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ABSTRACT

A novel copper-catalyzed chemoselective oxidative *O*-aroylation of 2-acetylphenols, alkyl salicylates and 1,3-dicarbonyl compounds with a wide range of styrene derivatives are described. This approach provides an efficient chemoselective preparation of phenol, alkyl salicylate and enol esters in good to excellent yields. This method represents an alternative protocol for the classical esterification reactions.

1. Introduction

Esterification is one of the most fundamental and basic reactions in organic synthesis because ester groups are key motifs and common building blocks present in drugs, bioactive natural products and valuable agrochemicals [1]. Aryl esters are traditionally synthesized from carboxylic acid as an acyl halide, activated esters or anhydrides with phenol derivatives. Recently, transition metal mediated esterification of functionalized hydrocarbons are some alternative strategies for the ester synthesis [2]. The cross dehydrogenative coupling (CDC) for making C-X and C–C bond is an attractive strategy because it exploits unfunctionalized starting material and is atom with step economic [3]. Various approaches for the synthesis of aryl esters with transition metals such as Pd [4], Cu[5], Rh [6], Ru[7] and Ir [8] were well known in literature.

Various CDC methods for aryl esters and carbamates synthesis have been documented in the literature [9]. However, very specifically 2-acetylphenol directing group assisted oxidative and CDC reactions for the synthesis of ester employing aryl aldehyde [path (a)] [10], dibenzyl ether [path (b)] [11a], benzyl alcohol [path (c)] [11b], 2-bromoacetophenone [path (d)] [12] and aryl alkyl [path (e)] [13] as coupling partners are documented in the literature (Scheme 1). To the best of our knowledge aryl alkenes have not yet used for the esterification of phenol derivatives. Herein, we are reporting the oxidative esterification of 2-acetylphenols and alkyl-2-hydroxybenzoates employing terminal aryl alkenes as *o*-aroyl surrogate and also its substrate scope to 1,3-dicarbonyl compounds esterification.

2. Results and discussion

We initiated this work with the possibilities in mind that aryl alkenes could be activated under oxidative conditions to furnish the coupled products. In our preliminary experiments, we used 2-acetylphenol **1a** and 4-methoxystyrene **2a** as a model substrate, *tert*-butyl hydroperoxide (TBHP) and 20 mol % of $Cu(OAc)_2$ as the catalyst. To our pleasure, we observed that when 2-acetylphenol **1a** was treated with 4-methoxystyrene **2a** in the presence of 20 mol % of $Cu(OAc)_2H_2O$, TBHP (70 wt % in H_2O) as an external oxidant and DCE as a solvent furnished the desired ester product **3aa** in 51% yield. Elimination of either TBHP or $Cu(OAc)_2$ resulted no formation of desired ester product **3aa**. Encouraged by unprecedented result, optimization of the reaction conditions was carried out to achieve the best yield of the desired ester product **3aa**. Details of various optimization reaction conditions are displayed in Table 1. Substrate

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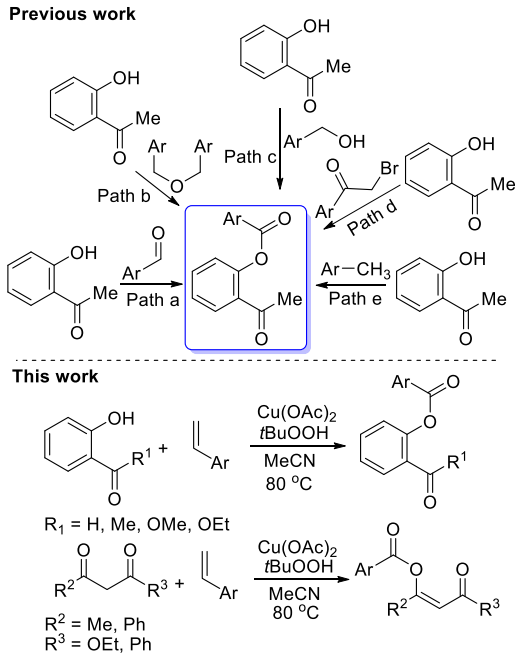
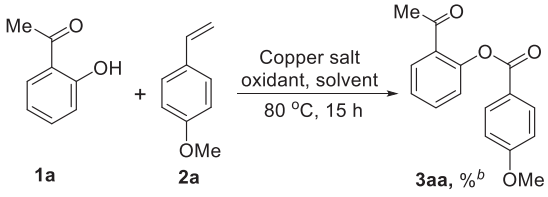


Scheme 1. C–O bond formation *via* C–H activation employing CDC and oxidative cross coupling protocols.

Table 1
Optimization of reaction conditions [a].

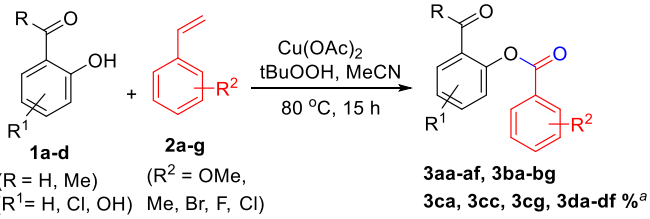


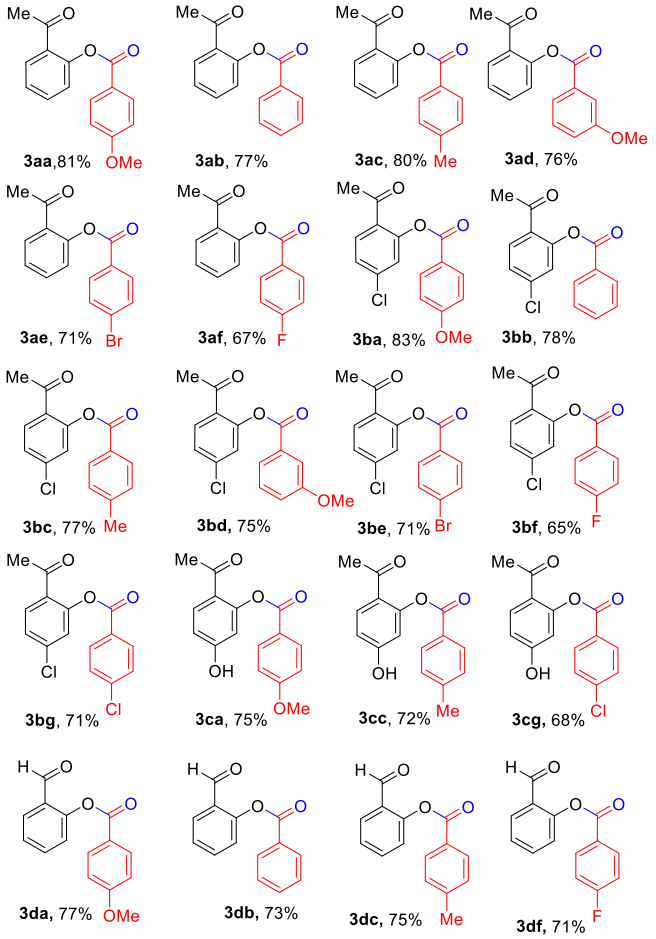
Entry	Catalyst (mol %)	Oxidant (eq.)	Solvent	Yield %
1.	$Cu(OAc)_2H_2O$	TBHP[c] (4)	DCE	51%
2.	CuI	TBHP[d] (4)	DCE	29%
3.	$CuBr_2$	TBHP[d] (4)	DCE	37%
4.	CuCl	TBHP[d] (4)	DCE	35%
5.	$Cu(OTf)_2$	TBHP[d] (4)	DCE	Trace
6.	$Cu(OAc)_2$	TBHP[d] (4)	DCE	67%
7.	$Cu(OAc)_2$	TBHP[d] (4)	DMSO	68%
8.	$Cu(OAc)_2$	TBHP[d] (4)	DMF	45%
9.	$Cu(OAc)_2$	TBHP[d] (4)	MeCN	78%
10.	$Cu(OAc)_2$	TBHP[d] (5)	MeCN	81%
11.	$Cu(OAc)_2$	Nil	MeCN	Nil
12.	Nil	TBHP[d] (5)	MeCN	Nil
13.	$Cu(OAc)_2$	H_2O_2	MeCN	<10%
14.	$Cu(OAc)_2$	$K_2S_2O_8$ (5)	MeCN	Trace
15.	$Cu(OAc)_2$	m-CPBA(5)	MeCN	Trace
16.	$Cu(OAc)_2$	Ag_2O (5)	MeCN	Trace

[a] **Reaction conditions**: 2-acetylphenol **1a** (0.5 mmol), *p*-methoxy styrene **2a** (1.0 mmol), Copper salt (20 mol %), oxidant (quantity noted), solvent (1 mL) at 80 °C for 15 h under pressure tubes. [b]Isolated yield of pure product reported.
[c] TBHP (70 wt % in H_2O).
[d] TBHP 5.5 M in decane.

2-acetylphenol **1a** 0.5 mmol), 4-methoxystyrene **2a** (1.0 mmol), catalyst $Cu(OAc)_2$ (20 mol %), TBHP oxidant in decane (5.5 M, 5.0 equiv) at 80 °C and MeCN solvent under pressure tube furnished the best results in 15 h (Table 1). These optimized reaction conditions were used for all other reactions.

We first investigated the scope of this coupling reaction for substituted 2-acetylphenol with various substituted styrene compounds **2a-g** (Scheme 2). The reaction between 2-acetylphenol and substituted styrene derivatives with electron donating and electron withdrawing group such as methoxy, methyl, bromo, chloro and fluoro were well tolerated regardless of their position on the aromatic ring and furnished the ester derivatives **3aa-ad** and **3ae-af** in good to excellent yields. We observed that the substituted styrene compounds with electron donating functional groups furnished excellent yield compared to electron withdrawing groups. However, styrene derivatives having strongly electron withdrawing group such as nitro and nitrile failed to afford the corresponding esters. This clearly suggest a significant electronic effect on the rate of reactions and hence on the product yields. Next, we tested substituted 2-acetylphenols such as chloro and hydroxy with various substituted styrene derivatives with electron donating and electron withdrawing groups such as methoxy, methyl, bromo,





Scheme 2. Oxidative coupling of 2-acetylphenols with aryl alkenes; ***Reaction conditions***: **1a-c** (0.5 mmol), 2a-g (1.0 mmol), $Cu(OAc)_2$ (20 mol %), TBHP (5 equiv) in MeCN (1.0 mL) at 80 °C for 15 h in pressure tubes. [a]Isolated yield of the pure product.

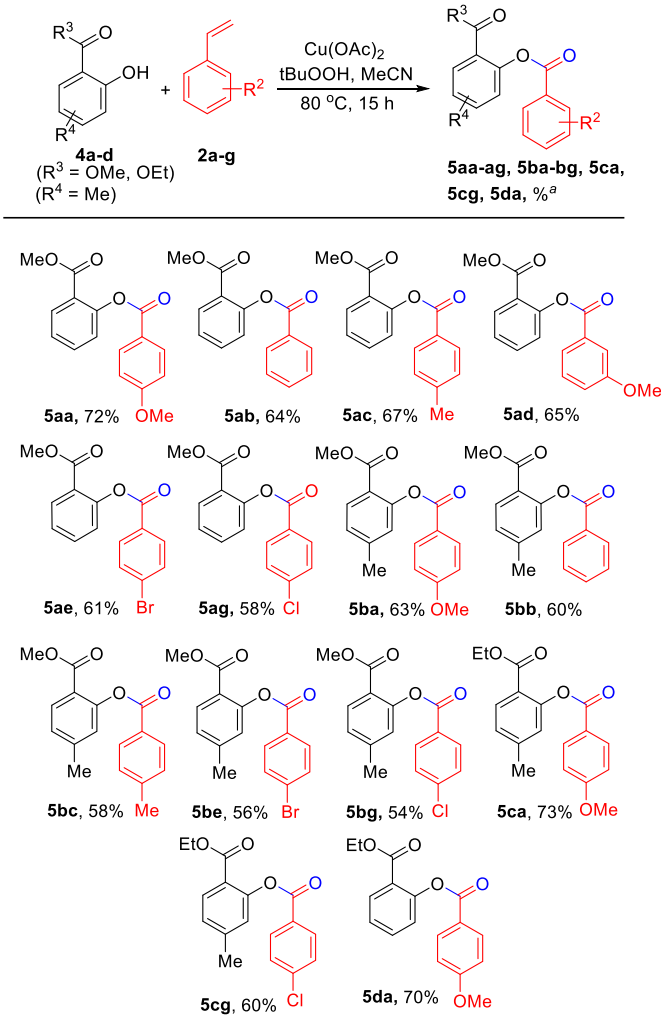
chloro and fluoro which were also well tolerated irrespective of their positions on the aromatic ring and furnished the ester derivatives **3ba-bg** and **3ca-cg** in good to excellent yields. In the presence of 3-hydroxyl group, selective protection of 2-acetylphenol afforded the ester derivative **3 cc** which shows the directing group effect in this coupling reaction. The selective protection of hydroxy functional group in the 2-acetylphenol is an important conversion in the synthesis of various biologically active natural products [14]. Next, we explored the coupling reaction of salicylaldehyde with substituted styrenes **2a-f** which also furnished the ester derivatives **3da-df** in excellent yields.

The use of salicylic acid failed to give phenol ester which clearly suggest the poor directing ability of the −COOH group. Further we explored, the scope of this coupling reaction with alkyl salicylate as directing group. To our surprise, when methyl salicylate (oil of wintergreen) **4a** was treated with substituted. styrene **2a** under the optimized reaction conditions afforded the corresponding *O*-aroylated ester product **5aa** in 72% yield (Scheme 3). To the best of our knowledge, this is the first report in which alkyl salicylate are directly coupled with substituted styrene derivatives under oxidative conditions and act as directing group.

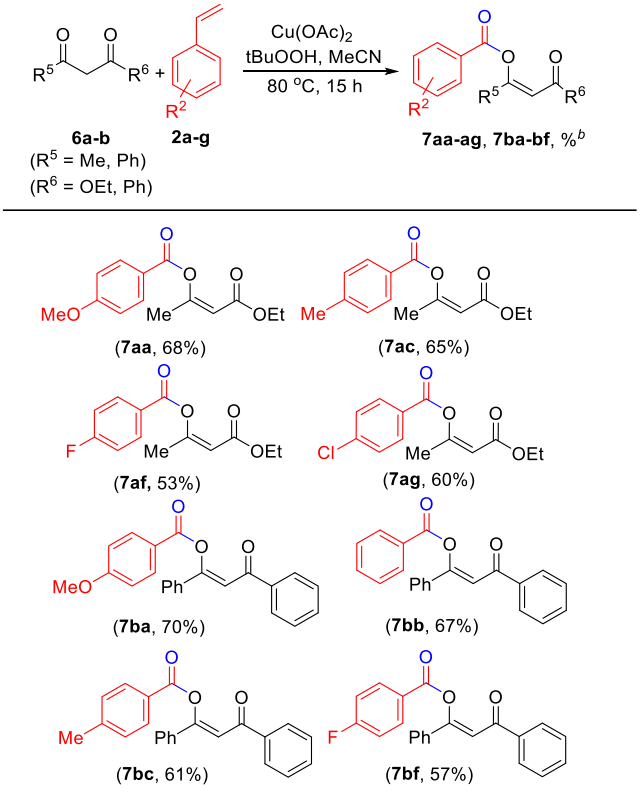
Further, we explored this coupling reaction with methyl salicylate derivatives (**4a-b**) with substituted styrene derivatives (**2a-g**) which furnished the desired ester derivatives **5aa-ag** and **5ba-bg** in good to excellent yields. Further, we tested ethyl salicylate with substituted styrenes **2a** and **2g** which were also well tolerated irrespective of their position on the aromatic ring and afforded the esters **5da**, **5ca**, and **5 cg** in good yields. The reactivity pattern of substituted styrene was found identical as in case of 2-acetylphenol as directing group, but the yields were slightly less. It may be possible due to chelating site are electron deficient.

(*Z*)-Enol form of 1,3-dicarbonyl compounds have structural analogy to those of *O*-hydroxy carbonyl and *O*-hydroxy ester compounds so far as the positioning and orientation of hydroxy and carbonyl groups are concerned [9,10a,11]. To unravel the scope and potential of this method 1,3-dicorbonyl compounds were reacted with several substituted styrene **2a-g** compounds. Methyl acetoacetate **6a** when treated with 4-methoxystyrene **2a**, p-methylstyrene **2c**, 4-fluorostyrene **2f** and 4-chlorostyrene **2g** furnished their enol ester derivatives **7aa**, **7ac**, **7af** and **7 ag** respectively, in good yield (Scheme 4). Generally, under several metal catalyzed reaction condition β-carbonyl compounds afford C(sp^3)-C(sp^3) bond rather than C(sp^3)-O bond [15]. Further, we tested the coupling of dibenzoylmethane **6b** having 1,3-dicarbonyl groups with 4-methoxystyrene **2a**, styrene **2b**, p-methylstyrene **2c** and 4-fluorostyrene **2f** which furnished the enol ester derivatives **7ba**, **7bb**, **7bc** and **7bf** in good to excellent yields. All these coupling reactions proceeded with good yields and high stereoselectivity of *Z*-enol esters with no loss in stereoselectivity which was confirmed by NOESY experiments of products **7ac**, **7af** and **7 ag**.

The key factors for the formation of esters could be the coordinating ability of the dicarbonyl with the metals. The oxidative coupling reaction between styrene and 2-acetylphenol was carried



Scheme 3. Oxidative coupling of alkyl salicylate with aryl alkene. **Reaction conditions: 4a-d** (0.5 mmol), **2a-g** (1.0 mmol), $Cu(OAc)_2$ (20 mol %), TBHP (5 equiv) in MeCN (1.0 mL) at 80 °C for 15 h in pressure tubes. [a]Isolated yield of the pure product.



Scheme 4. Oxidative coupling of styrene derivatives with β-ketoesters for the synthesis of enolesters: **Reaction conditions: 6a-b** (0.5 mmol), **2a-g** (1.0 mmol), $Cu(OAc)_2$ (20 mol %), TBHP (5 equiv) in MeCN (1.0 mL) at 80 °C for 15 h in pressure tubes. [a]Isolated Yield of the pure product.

out in the presence of TEMPO (radical quencher) which afforded traces of the desired product shows the radical type of the mechanism. Based on the observation and literature reports [16], a plausible mechanism is proposed having two paths as displayed in Scheme 5. In path-I, styrene **2b** on treatment with TBHP forms 3-phenyl-1,2-dioxetane A intermediate which undergoes oxidative dehydrogenation to afford 3-phenyl 1,2-dioxete **B** intermediate. The intermediate **B** on ring fragmentation affords phenylglyoxal **C** which finally provides benzoyl radical **D**. In path-II, Cu(II) catalyst forms a complex with 2-acetylphenol **1a** to afford the complex **E**. The benzoyl radical **D** could react with complex **E** by single electron transfer to furnish the Cu(III) complex **F** which undergoes reductive elimination to afford the product **3ab** and Cu(I) catalyst regenerated oxidized to Cu(II) by TBHP.

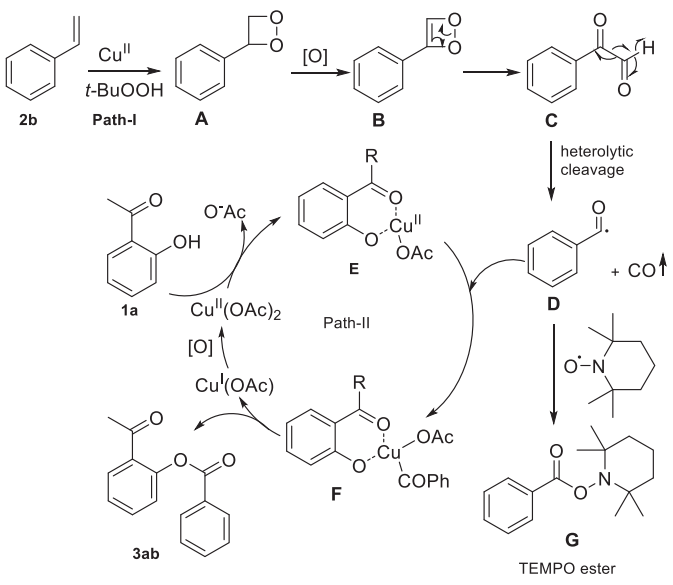
3. Conclusion

In summary, we have developed a novel chemoselective approach for the copper catalyzed direct syntheses of phenol, alkyl salicylate and enol esters in good to excellent yields employing TBHP as oxidant. The merits of our strategy are simplicity of operation, use of inexpensive, stable, and commercially available starting materials. The developed reactions are additive, base, and ligand free, proceeds under mild conditions, and can be used as an alternative approach for the classical esterification reactions.

4. Experimental section

4.1. General procedure for the synthesis of 2-acetylphenyl 4-methoxybenzoate (*3aa*)

To an oven-dried pressure tube charged with 2-acetylphenol **1a** (68.0 mg, 0.5 mmol), $Cu(OAc)_2$ (18.0 mg, 20 mol %, 0.1 mmol) and TBHP (0.50 mL, 2.50 mmol, 5.5 M in decane) in MeCN (1.0 mL) was added 4-methoxystyrene **2a** (134 mg, 1.0 mmol). The resultant reaction mixture was allowed to stir in pressure tube at 80 °C for 15 h. After completion of reaction as monitored by TLC, the reaction mixture was cooled at room temperature and evaporated onto silica gel. Purification of product by silica gel column chromatography (n-hexane/EtOAc, 15:1) furnished the 2-acetylphenyl 4-methoxybenzoate **3aa** (109 mg) in 81% yield.



Scheme 5. The plausible reaction mechanism.

4.1.1. 2-Acetylphenyl 4-methoxybenzoate (3aa) [11a]

Yield: 81% (109 mg); White solid; M.p. 131–133 °C; R_f = 0.15 (*n*-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (td, J = 9.00, 4.50 Hz, 2H), 7.85 (d, J = 8.53 Hz, 1H), 7.57 (dt, J = 7.25, 2.65 Hz, 1H), 7.35 (t, J = 7.26 Hz, 1H), 7.23 (d, J = 8.04 Hz, 1H), 7.00 (d, J = 8.55 Hz, 2H), 3.90 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 197.7, 164.8, 164.1, 149.5, 133.3, 132.4, 131.5, 130.1, 126.0, 123.9, 121.5, 114.0, 55.5, 29.9.

4.1.2. 2-Acetylphenyl benzoate (3 ab) [13a]

Yield: 77% (92 mg); Yellow gummy; R_f = 0.33 (n-hexane/EtOAc = 24:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (td, J = 7.47, 3.6 Hz, 2H), 7.86 (d, J = 6.65 Hz, 1H), 7.64 (dt, J = 7.65, 1.60 Hz, 1H), 7.57 (dt, J = 7.70, 1.30 Hz, 1H), 7.52 (t, J = 7.63 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 8.6 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 197.5, 165.1, 149.3, 133.8, 133.3, 131.2, 130.2, 129.2, 128.7, 128.6, 128.5, 126.1, 123.8, 29.7.

4.1.3. 2-Acetylphenyl 4-methylbenzoate (3ac) [13a]

Yield: 80% (102 mg); White solid; M.p. 107–109 °C; R_f = 0.30 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.49 Hz, 2H), 7.85 (dd, J = 7.78, 1.75 Hz, 1H), 7.58 (dt, J = 7.5, 1.80 Hz, 1H), 7.36 (d, J = 7.20 Hz, 1H), 7.33 (d, J = 7.70 Hz, 2H), 7.23 (d, J = 7.77 Hz, 1H), 2.53 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 197.6, 165.1, 149.5, 144.7, 133.3, 131.5, 130.3, 130.2, 129.4, 126.5, 126.0, 123.9, 29.9, 21.8.

4.1.4. 2-Acetylphenyl 3-methoxybenzoate (3ad)

Yield: 76% (102 mg); White gummy; R_f = 0.17 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 21.26, 7.70 Hz, 2H), 7.71 (s, J = 1H), 7.58 (t, J = 7.71 Hz, 1H), 7.40 (dt, J = 31.30, 7.90 Hz, 2H), 7.28–7.12 (m, 2H), 3.87 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 197.5, 165.0, 159.7, 149.3, 133.4, 131.2, 130.4, 130.2, 129.7, 126.1, 123.8, 122.6, 120.4, 114.5, 55.4, 29.7; HRMS (ESI) Calcd. for $C_{16}H_{14}O_4Na$ $[M+Na]^+$: 293.0784, found 293.0785.

4.1.5. 2-Acetylphenyl 4-bromobenzoate (3ae) [11a]

Yield: 71% (112 mg); Yellow solid; M.p. 121–124 °C; R_f = 0.24 (n-hexane/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 8.57 Hz, 2H), 7.85 (dd, J = 7.63, 1.70 Hz, 1H), 7.68–7.61 (m, 2H), 7.56 (dt, J = 8.11, 1.85 Hz, 1H), 7.35 (t, J = 7.63 Hz, 1H), 7.21 (d, J = 7.63 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 197.3, 164.5, 149.0, 133.4, 132.0, 131.9, 131.7, 131.6, 130.8, 130.3, 129.6, 128.2, 126.2, 123.8, 29.4.

4.1.6. 2-Acetylphenyl 4-fluorobenzoate (3af) [11a]

Yield: 67% (86 mg); Yellow gummy; R_f = 0.28 (n-hexane/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27–8.18 (m, 2H), 7.86 (dd, J = 7.85, 1.69 Hz, 1H), 7.57 (td, J = 7.80, 1.77 Hz, 1H), 7.36 (t, J = 7.59 Hz, 1H), 7.22 (d, J = 8.09 Hz, 1H), 7.18 (t, J = 8.55 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 197.3, 165.1 (d, J = 255.4 Hz), 164.3, 149.3, 133.6, 133.0 (d, J = 10.0 Hz), 131.1, 130.5, 126.3, 125.7, 124.0, 115.9 (d, J = 25.1 Hz), 29.6.

4.1.7. 2-Acetyl-5-chlorophenyl 4-methoxybenzoate (3ba)

Yield: 83% (126 mg); White solid; M.P.145–147 °C; R_f = 0.13 (n-hexane/EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 8.47 Hz, 2H), 7.81 (d, J = 8.46 Hz, 1H), 7.33 (dd, J = 8.42, 2.04 Hz, 1H), 7.26 (d, J = 2.04 Hz, 1H), 7.00 (d, J = 8.56 Hz, 2H), 3.90 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 196.3, 164.3, 150.1, 138.8, 132.5, 131.2, 129.8, 126.3, 124.5, 120.9, 114.1, 55.5, 29.9; HRMS (ESI) Calcd. for $C_{16}H_{13}ClO_4Na$ $[M+Na]^+$: 327.0394, found 327.0392.

4.1.8. 2-Acetyl-5-chlorophenyl benzoate (3bb)

Yield: 78% (106 mg); White solid; M. P. 72–73 °C; R_f = 0.31 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.49 Hz, 1H), 7.67 (t, J = 7.45 Hz, 1H), 7.53 (t, *J* = 7.71 Hz, 2H), 7.35 (dd, *J* = 8.54, 2.09 Hz, 1H), 7.28 (d, *J* = 2.11 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 196.2, 164.7, 150.0, 139.0, 134.1, 131.3, 130.3, 129.6, 128.8, 126.5, 124.4, 29.7; HRMS (ESI) Calcd. for $C_{15}H_{11}ClO_3Na$ $[M+Na]^+$: 297.0289, found 297.0290.

4.1.9. 2-Acetyl-5-chlorophenyl 4-methylbenzoate (3bc)

Yield: 77% (110 mg); White solid; M. p. 89–92 °C; R_f = 0.29 (n-hexane/EtOAc = 15:1); 1H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.78 Hz, 2H), 7.80 (d, *J* = 8.52 Hz, 1H), 7.32 (d, *J* = 7.72 Hz, 3H), 7.26 (s, 1H), 2.51 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 196.2, 164.7, 150.0, 145.0, 138.8, 131.2, 130.3, 129.7, 129.5, 126.4, 125.9, 124.4, 29.8, 21.7; HRMS (ESI) Calcd. for $C_{16}H_{14}O_3Na$ $[M+Na]^+$: 311.0445, found 311.0450.

4.1.10. 2-Acetyl-5-chlorophenyl 3-methoxybenzoate (3bd)

Yield: 75% (114 mg); Yellow gummy; R_f = 0.16 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 11.83, 8.02 Hz, 2H), 7.69 (t, *J* = 2.13 Hz, 1H), 7.43 (t, *J* = 7.96 Hz, 1H), 7.35 (dd, *J* = 8.53, 1.98 Hz, 1H), 7.27 (d, *J* = 1.5 Hz, 1H), 7.20 (dd, *J* = 8.25, 2.76 Hz, 1H), 3.88 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 196.2, 164.6, 159.8, 150.0, 139.0, 131.3, 130.0, 129.8, 129.6, 126.5, 124.4, 122.7, 120.6, 114.6, 55.5, 29.7; HRMS (ESI) Calcd. for $C_{16}H_{13}ClO_4Na$ $[M+Na]^+$: 327.0394, found 327.0394.

4.1.11. 2-Acetyl-5-chlorophenyl 4-bromobenzoate (3be)

Yield: 71% (125 mg); White solid; M.p. 128–130 °C; R_f = 0.34 (n-hexane/EtOAc = 19:1); 1H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.94 Hz, 2H), 7.74 (d, *J* = 8.57 Hz, 1H), 7.60 (d, *J* = 8.01 Hz, 2H), 7.29 (d, *J* = 8.43 Hz, 1H), 7.19 (d, *J* = 3.58 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 196.1, 164.2, 149.8, 139.1, 132.2, 131.8, 131.4, 129.4, 129.3, 127.8, 126.6, 124.5, 29.5.; HRMS (ESI) Calcd. for $C_{15}H_{10}BrClO_3Na$ $[M+Na]^+$: 374.9394, found 374.9390.

4.1.12. 2-Acetyl-5-chlorophenyl 4-fluorobenzoate (3bf)

Yield: 65% (95 mg); Yellow gummy; R_f = 0.26 (n-hexane/EtOAc = 19:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 8.32, 5.46 Hz, 2H), 7.75 (d, *J* = 7.77 Hz, 1H), 7.29 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.20 (d, *J* = 1.74 Hz, 1H), 7.13 (t, *J* = 8.60 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 196.3, 165.5 (d, *J* = 263.0 Hz), 164.0, 150.0, 139.2, 133.2 (d, *J* = 10.0 Hz), 131.5, 129.6, 126.8, 125.3, 124.7, 116.1 (d, *J* = 25.1 Hz), 29.5; HRMS (ESI) Calcd. for $C_{15}H_{10}ClFO_3Na$ $[M+Na]^+$: 315.0195 found 315.0180.

4.1.13. 2-Acetyl-5-chlorophenyl 4-chlorobenzoate (3bg)

Yield: 71% (109 mg); Yellow gummy; R_f = 0.24 (n-hexane/EtOAc = 19:1); 1H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.52 Hz, 2H), 7.82 (d, *J* = 8.55 Hz, 1H), 7.51 (d, *J* = 8.58 Hz, 2H), 7.36 (dd, *J* = 9.01, 2.27 Hz, 1H), 7.27 (d, *J* = 1.95 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 196.1, 164.0, 149.8, 140.6, 139.1, 131.7, 131.4, 129.3, 129.1, 127.3, 126.6, 124.4, 29.5; HRMS (ESI) Calcd. for $C_{15}H_{10}Cl_2O_3Na$ $[M+Na]^+$: 330.9962 found 330.9895.

4.1.14. 2-Acetyl-5-hydroxyphenyl 4-methoxybezoate (3ca) [2e]

Yield: 75% (107 mg); White solid; M.p. 95–97 °C; R_f = 0.22 (n-hexane/EtOAc = 9:1); ^{1}H NMR (500 MHz, DMSO-d_6/$CDCl_3$): δ 10.15 (s, 1H), 8.12 (d, J = 8.45 Hz, 2H), 7.79 (d, J = 8.68 Hz, 1H), 7.01 (dd, J = 8.79, 3.21 Hz, 2H), 6.80 (dd, J = 8.58, 2.46 Hz, 1H), 6.63 (d, J = 2.42 Hz, 1H), 3.91 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125.7 MHz, DMSO-d_6/$CDCl_3$): δ (ppm) 194.8, 164.0, 163.4, 162.1, 151.3, 131.9, 131.8, 121.7, 121.2, 113.4, 112.9, 110.5, 55.0, 28.9.

4.1.15. 2-Acetyl-5-hydroxyphenyl 4-methylbenzoate (3 cc) [2e]

Yield: 72% (97 mg); White solid; M. p.107–108 °C; R_f = 0.28 (n-hexane/EtOAc = 9:1); ^{1}H NMR (500 MHz, DMSO-d_6/$CDCl_3$) δ 10.11 (s, 1H), 8.12 (d, *J* = 8.48 Hz, 2H), 7.79 (d, *J* = 9.21 Hz, 1H), 7.01 (d, *J* = 8.48 Hz, 2H), 6.80 (dd, *J* = 9.07, 2.34 Hz, 1H), 6.63 (d, *J* = 2.11 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125.7 MHz, DMSO-d_6/$CDCl_3$): δ (ppm) 194.8, 164.0, 163.4, 162.1, 151.3, 131.9, 131.8, 121.7, 121.2, 113.4, 112.9, 110.5, 55.0, 28.9.

4.1.16. 2-Acetyl-5-hydroxyphenyl 4-chlorobenzoate (3 cg) [2e]

Yield: 68% (98 mg); White solid; M.p. 101–102 °C; R_f = 0.30 (n-hexane/EtOAc = 9:1); 1H NMR (500 MHz, DMSO-d_6): δ 10.72 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 2.41 (s, 1H); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ (ppm) 195.0, 163.6, 162.4, 150.9, 138.8, 133.2, 131.7, 129.0, 128.1, 121.2, 113.2, 110.7, 28.8.

4.1.17. 2-Formylphenyl 4-methoxybenzoate (3da) [13a]

Yield: 77% (98 mg); White solid; M.p. 75–76 °C; R_f = 0.15 (n-hexane/EtOAc = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.22 (s, 1H), 8.17 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.94 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.66 (dt, *J* = 9.2, 1.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 188.4, 164.9, 152.5, 145.0, 135.2, 130.3, 129.8, 129.4, 128.3, 126.2, 123.5, 120.8, 114.9, 55.5.

4.1.18. 2-Formylphenyl benzoate (3 db) [13a]

Yield: 73% (82 mg); Colourless liquid; R_f = 0.28 (n-hexane/EtOAc = 19:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.21 (s, 1H), 8.22 (d, *J* = 7.5 Hz, 2H), 7.94 (d, *J* = 7.0 Hz, 1H), 7.66 (dd, *J* = 7.0, 4.0 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): 188.3, 164.9, 152.2, 135.3, 134.0, 130.3, 130.2, 128.7, 128.6, 128.3, 126.4, 123.5.

4.1.19. 2-Formylphenyl 4-methylbenzoate (3dc) [12]

Yield: 75% (90 mg); White solid; M.p., 72–73 °C, R_f = 0.25 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.22 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.95 (t, *J* = 6.5 Hz, 1H), 7.66 (dt, *J* = 8.3, 2.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 3H), 2.46 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 188.4, 165.0, 152.6, 145.1, 135.3, 130.4, 129.5, 128.4, 126.4, 125.9, 123.6, 21.8.

4.1.20. 2-Formylphenyl 4-fluorobenzoate (3df) [12]

Yield: 71% (86 mg); yellow oil; R_f = 0.30 (n-hexane/EtOAc = 19:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (s, 1H), 8.25–8.26 (m, 2H), 7.94 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.68 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.21 (t, *J* = 9.5 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 188.4, 165.3 (d, *J* = 255.0 Hz), 164.0, 151.9, 135.3, 133.0, 132.7(d, *J* = 10.0 Hz), 130.4, 0128.3, 126.6, 125.0, 123.5, 115.8 (d, *J* = 16.3 Hz).

4.1.21. Methyl 2-((4-methoxy benzoyl) oxy) benzoate (5aa)

Yield: 72% (103 mg); Colourless solid, M.p. 120–122 °C; R_f = 0.20 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.29 Hz, 2H), 8.05 (d, *J* = 7.63 Hz, 1H), 7.57 (d, *J* = 7.90 Hz, 1H), 7.33 (t, *J* = 7.64 Hz, 1H), 7.23 (d, *J* = 8.27 Hz, 1H), 6.99 (d, *J* = 8.75 Hz, 2H), 3.87 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 165.0, 164.9, 163.8, 150.8, 133.6, 132.3, 131.7, 125.8, 124.0, 123.5, 121.7, 113.8, 55.4, 52.0; HRMS (ESI) Calcd. for $C_{16}H_{14}O_5Na$ $[M+Na]^+$: 309.0733, found 309.0736.

4.1.22. Methyl 2-(benzoyloxy) benzoate (5 ab) [11a]

Yield: 64% (82 mg); Colourless less liquid; R_f = 0.33 (n-hexane/EtOAc = 19:1); 1H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.52 Hz, 2H), 7.98 (d, *J* = 8.34 Hz, 1H), 7.49–7.56 (m, 2H), 7.43 (t, *J* = 7.60 Hz,

2H), 7.26 (t, J = 7.62 Hz, 1H), 7.14 (d, J = 8.28 Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 165.3, 165.0, 150.7, 133.8, 133.5, 131.8, 130.2, 129.4, 128.5, 126.0, 123.9, 123.4, 52.1.

4.1.23. Methyl 2-((4-methylbenzoyl) oxy) benzoate (5ac)

Yield: 67% (90 mg); Colourless gummy; R_f = 0.35 (n-hexane/EtOAc = 19:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 8.52 Hz, 2H), 8.06 (d, J = 7.77 Hz, 1H), 7.59 (t, J = 7.74 Hz, 1H), 7.34 (t, J = 7.25 Hz, 1H), 7.31 (d, J = 8.23 Hz, 2H), 7.22 (d, J = 7.91 Hz, 1H), 3.72 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 165.4, 165.1, 150.8, 144.3, 133.7, 131.8, 130.2, 129.2, 126.7, 125.9, 124.0, 123.5, 52.1, 21.7; HRMS (ESI) Calcd. for $C_{16}H_{14}O_4Na$ [M+Na]$^+$: 293.0784, Found 293.0785.

4.1.24. Methyl 2-((3-methoxy benzoyl) oxy) benzoate (5ad)

Yield: 65% (92 mg); Colourless liquid; R_f = 0.25 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (dd, J = 7.85, 1.90 Hz, 1H), 7.73 (d, J = 7.69 Hz, 1H), 7.63 (d, J = 2.79 Hz, 1H), 7.50 (dt, J = 8.15, 2.24 Hz, 1H), 7.33 (t, J = 8.46 Hz, 1H), 7.25 (t, J = 7.53 Hz, 1H), 7.14 (d, J = 7.95 Hz, 1H), 7.08 (dd, J = 8.39, 3.34 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 165.2, 164.9, 159.6, 150.7, 133.8, 131.8, 130.7, 129.5, 126.0, 123.8, 123.4, 122.6, 120.1, 114.5, 55.4, 52.1; HRMS (ESI) Calcd. for $C_{16}H_{14}O_5Na$ [M+Na]$^+$: 309.0733 found 309.0738.

4.1.25. Methyl 2-((4-bromobenzoyl) oxy) benzoate (5ae)

Yield: 61% (102 mg); Yellow gel; R_f = 0.34 (n-hexane/EtOAc = 19:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, J = 7.63 Hz, 3H), 7.66 (d, J = 8.37 Hz, 2H), 7.61 (t, J = 7.93 Hz, 1H), 7.36 (t, J = 7.91 Hz, 1H), 7.23 (d, J = 7.92 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 164.8, 164.7, 150.6, 133.9, 131.9, 131.7, 128.7, 128.3, 126.2, 123.8, 123.2, 52.2; HRMS (ESI) Calcd. for $C_{15}H_{11}BrO_4Na$ [M+Na]$^+$: 356.9733, found 356.9731.

4.1.26. Methyl 2-((4-chlorobenzoyl) oxy) benzoate (5 ag)

Yield: 58% (84 mg); Colourless solid, M. p. 102–104 °C; R_f = 0.37 (n-hexane/EtOAc = 19:1); 1H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 8.28 Hz, 2H), 8.08 (dd, J = 7.89, 1.78 Hz, 1H), 7.61 (td, J = 7.78, 1.75 Hz, 1H), 7.50 (d, J = 8.21 Hz, 2H), 7.37 (t, J = 7.62 Hz, 1H), 7.23 (d, J = 8.10 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 164.8, 164.5, 150.6, 140.1, 133.9, 131.9, 131.6, 128.9, 128.0, 126.2, 123.9, 123.2, 52.2; HRMS (ESI) Calcd. for $C_{15}H_{11}ClO_4Na$ [M+Na]$^+$: 313.0238 found 313.0229.

4.1.27. Methyl 2-((4-methoxybenzyol) oxy)-4-methylbenzoate (5ba)

Yield: 63% (95 mg); Colourless solid, M.p. 117–119 °C; R_f = 0.29 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 8.75 Hz, 2H), 7.95 (d, J = 8.07 Hz, 1H), 7.14 (d, J = 7.93 Hz, 1H), 7.03 (s, 1H), 7.00 (d, J = 8.75 Hz, 2H), 3.89 (s, 3H), 3.71 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 165.1, 165.1, 163.8, 150.9, 145.0, 132.3, 131.8, 126.7, 124.5, 121.9, 120.6, 113.8, 55.5, 51.9, 21.4; HRMS (ESI) Calcd. for $C_{17}H_{16}O_5Na$ [M+Na]$^+$: 323.0890, found 323.0890.

4.1.28. Methyl 2-(benzoyloxy)-4-methylbenzoate (5bb)

Yield: 60% (81 mg); Colourless gummy; R_f = 0.31 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, J = 7.41 Hz, 2H), 7.97 (d, J = 7.67 Hz, 1H), 7.62 (d, J = 7.63 Hz, 1H), 7.51 (t, J = 7.65 Hz, 2H), 7.15 (d, J = 8.12 Hz, 1H), 7.04 (s, 1H), 3.71 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 165.5, 165.0, 150.8, 145.1, 133.4, 131.8, 130.2, 129.6, 128.5, 126.9, 124.4, 120.4, 51.9, 21.4; HRMS (ESI) Calcd. for $C_{16}H_{14}O_4Na$ [M+Na]$^+$: 293.0784, found 293.0785.

4.1.29. Methyl 4-methyl-2-((4-methylbenzoyl) oxy) benzoate (5bc) [2a]

Yield: 58% (82 mg); Colorless liquid; R_f = 0.37 (n-hexane/EtOAc = 15:1); 1H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 7.93 Hz, 2H), 7.96 (d, J = 7.96 Hz, 1H), 7.31 (d, J = 7.87 Hz, 2H), 7.15 (d, J = 8.04 Hz, 1H), 7.04 (s, 1H), 3.71 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 165.5, 165.1, 150.8, 145.1, 144.3, 131.8, 130.3, 129.3, 126.9, 126.8, 124.5, 120.5, 52.0, 21.7, 21.4.

4.1.30. Methyl 2-((4-bromobenzoyl) oxy)-4-methylbenzoate (5be)

Yield: 56% (97 mg); Yellow gummy, R_f = 0.28 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$):δ 8.08 (d, J = 8.23 Hz, 2H), 7.97 (d, J = 8.06 Hz, 1H), 7.66 (d, J = 8.24 Hz, 2H), 7.17 (d, J = 8.00 Hz, 1H), 7.04 (s, 1H), 3.72 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 164.8, 164.8, 150.6, 145.3, 132.0, 131.9, 131.7, 128.7, 128.6, 127.1, 124.4, 120.3, 52.0, 21.5; HRMS (ESI) Calcd. for $C_{16}H_{13}BrO_4Na$ [M+Na]$^+$: 370.9889, found 370.9893.

4.1.31. Methyl 2-((4-chlorobenzoyl) oxy)-4-methylbenzoate (5bg)

Yield: 54% (82 mg); Colourless solid, M.p. 85–87 °C; R_f = 0.22 (n-hexane/EtOAc = 15:1); 1H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 8.27 Hz, 2H), 7.97 (d, J = 8.11 Hz, 1H), 7.49 (d, J = 8.28 Hz, 2H), 7.16 (d, J = 8.05 Hz, 1H), 7.03 (s, 1H), 3.72 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 164.8, 164.6, 150.6, 145.2, 139.9, 131.8, 131.6, 128.9, 128.1, 127.0, 124.3, 120.2, 52.0, 21.4; HRMS (ESI) Calcd. for $C_{16}H_{13}ClO_4Na$ [M+Na]$^+$: 327.0394, found 327.0394.

4.1.32. Ethyl 2-((4-methoxybenzoyl) oxy)-4-methylbenzoate (5ca)

Yield: 73% (114 mg); Colourless gel; R_f = 0.20 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 8.48 Hz, 2H), 7.96 (d, J = 8.05 Hz, 1H), 7.13 (d, J = 8.02 Hz, 1H), 7.02 (s, 1H), 6.98 (d, J = 8.66 Hz, 2H), 4.18 (q, J = 7.15 Hz, 2H), 3.87 (s, 3H), 2.40 (s, 3H), 1.08 (t, J = 7.14 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 165.0, 164.8, 163.7, 150.6, 144.8, 132.3, 131.8, 126.7, 124.4, 121.9, 121.0, 113.7, 60.8, 55.4, 21.3, 13.9; HRMS (ESI) Calcd. for $C_{18}H_{18}O_5Na$ [M+Na]$^+$: 337.1044, found 337.1047.

4.1.33. Ethyl 2-((4-chlorobenzoyl) oxy)-4-methylbenzoate (5 cg)

Yield: 60% (95 mg); Colourless solid, M.p. 106–109 °C; R_f = 0.35 (n-hexane/EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 8.40 Hz, 2H), 7.98 (d, J = 8.10 Hz, 1H), 7.48 (d, J = 8.39 Hz, 2H), 7.16 (d, J = 8.25 Hz, 1H), 7.02 (s, 1H), 4.19 (q, J = 6.89 Hz, 2H), 2.41 (s, 3H), 1.11 (t, J = 7.15 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 164.5, 164.5, 150.4, 145.0, 140.0, 131.9, 131.6, 128.9, 128.1, 127.0, 124.2, 120.7, 60.9, 21.4, 13.9; HRMS (ESI) Calcd. for $C_{17}H_{15}ClO_4Na$ [M+Na]$^+$: 341.0551, found 341.0551.

4.1.34. Ethyl 2-((4-methoxybenzoyl) oxy) benzoate (5da)

Yield: 70% (105 mg); Colourless liquid, R_f = 0.19 (n-hexane/EtOAc = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$):δ 8.17 (d, J = 8.50 Hz, 2H), 8.06 (d, J = 7.68 Hz, 1H), 7.56 (t, J = 7.90 Hz, 1H), 7.33 (d, J = 7.68 Hz, 1H), 7.20 (d, J = 8.05 Hz, 1H), 6.98 (d, J = 8.64 Hz, 2H), 4.20 (q, J = 7.43 Hz, 2H), 3.85 (s, 3H), 1.09 (t, J = 7.16 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 164.8, 164.7, 163.8, 150.5, 133.5, 132.2, 131.7, 125.8, 124.0, 123.8, 121.7, 113.7, 61.0, 55.3, 13.8; HRMS (ESI) Calcd. for $C_{17}H_{16}O_5Na$ [M+Na]$^+$: 323.0890 found 323.0859.

4.1.35. 4-Ethoxy-4-oxobut-2-en-2yl 4-methoxybenzoate (7aa)

Yield: 68% (90 mg); Colourless liquid; R_f = 0.35 (n-hexane/EtOAc = 9:1); 1H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 8.62 Hz, 2H), 6.95 (d, J = 9.15 Hz, 2H), 5.67 (s, 1H), 4.06 (q, J = 6.77 Hz, 2H), 3.86 (s, 3H), 2.13 (s, 3H), 1.10 (t, J = 7.14 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 163.8, 163.7, 163.2, 160.0, 132.2, 121.5, 113.7, 108.6, 59.9, 55.3, 21.6, 13.9; HRMS (ESI) Calcd. for $C_{14}H_{16}O_5Na$ [M+Na]$^+$: 287.0890, Found 287.0892.

4.1.36. 4-Ethoxy-4-oxobut-2-en-2-yl 4-methylbenzoate (7ac)

Yield: 65% (81 mg); Colourless liquid; R_f = 0.26 (n-hexane/EtOAc = 15:1); 1H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.86 Hz, 2H), 7.26 (d, *J* = 7.92 Hz, 2H), 5.67 (s, 1H), 4.05 (q, *J* = 7.15 Hz, 2H), 2.40 (s, 3H), 2.12 (s, 3H), 1.09 (t, *J* = 7.15 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 163.5, 163.4, 159.8, 144.1, 130.0, 129.0, 126.4, 108.6, 59.7, 21.4, 13.8; HRMS (ESI) Calcd. for $C_{14}H_{16}O_4Na$ $[M+Na]^+$: 271.0941, Found 271.0926.

4.1.37. 4-Ethoxy-4-oxobut-2-en-2-yl 4-fluorobenzoate (7af)

Yield: 53% (67 mg); Yellow gummy; R_f = 0.30 (n-hexane/EtOAc = 15:1); ^1H NMR (500 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 8.38, 5.29 Hz, 2H), 7.15 (t, *J* = 8.59 Hz, 2H), 5.70 (s, 1H), 4.06 (q, *J* = 6.90 Hz, 2H), 2.14 (s, 3H), 1.12 (t, *J* = 7.14 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 165.0 (d, *J* = 251.4 Hz), 163.7, 162.7, 159.9, 132.8 (d, *J* = 12.6 Hz), 125.6, 115.7 (d, *J* = 12.6 Hz), 108.7, 59.9, 21.5, 13.9; HRMS (ESI) Calcd. for $C_{13}H_{13}FO_4Na$ $[M+Na]^+$: 275.0690, Found 275.0685.

4.1.38. 4-Ethoxy-4-oxobut-2-en-2yl 4-chlorobenzoate (7 ag)

Yield: 60% (80 mg); Colourless liquid; R_f = 0.27 (n-hexane/EtOAc = 10:1); 1H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.17 Hz, 2H), 7.45 (d, *J* = 8.00 Hz, 2H), 5.70 (s, 1H), 4.06 (q, *J* = 6.87 Hz, 2H), 2.14 (s, 3H), 1.12 (t, *J* = 7.14 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 163.5, 162.7, 159.7, 139.9, 131.5, 128.8, 127.7, 108.8, 60.0, 21.5, 14.0; HRMS (ESI) Calcd. for $C_{13}H_{13}ClO_4Na$ $[M+Na]^+$: 291.0394, Found 291.0370.

4.1.39. 3-Oxo-1,3-diphenylprop-1-en-1-yl 4-methyoxybenzoate (7ba)

Yield: 70% (125 mg); Colourless liquid; R_f = 0.28 (n-hexane/EtOAc = 10:1); ^1H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.51 Hz, 2H), 7.96 (d, *J* = 7.59 Hz, 2H), 7.74 (d, *J* = 7.45 Hz, 2H), 7.52 (t, *J* = 7.27 Hz, 1H), 7.44 (q, *J* = 8.15, 7.61 Hz, 5H), 7.31 (s, 1H), 6.98 (d, *J* = 8.65 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 188.5, 164.0, 163.5, 157.3, 138.8, 134.2, 132.7, 132.6, 131.0, 128.9, 128.5, 128.2, 126.2, 121.5, 113.9, 110.1, 55.5; HRMS (ESI) Calcd. for $C_{23}H_{18}O_4Na$ $[M+Na]^+$: 381.1097, Found 381.1075.

4.1.40. 3-Oxo-1,3-diphenylprop-1-en-1yl benzoate (7bb) [13a]

Yield: 67% (110 mg); Colourless liquid; R_f = 0.38 (n-hexane/EtOAc = 19:1^1H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.76 Hz, 2H), 7.96 (d, *J* = 7.56 Hz, 2H), 7.75 (d, *J* = 7.49 Hz, 2H), 7.63 (t, *J* = 7.54 Hz, 1H), 7.51 (q, *J* = 7.68 Hz, 3H), 7.44 (q, *J* = 8.56, 7.42 Hz, 5H), 7.34 (s, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 188.3, 163.8, 157.2, 138.7, 134.0, 133.6, 132.7, 131.1, 130.4, 129.1, 128.9, 128.6, 128.5, 128.2, 126.2, 110.0.

4.1.41. 3-Oxo-1,3-diphenylprop-1-en-1yl 4-methylbenzoate (7bc)

Yield: 61% (104 mg); Colourless liquid; R_f = 0.35 (n-hexane/EtOAc = 19:1); ^1H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.36 Hz, 2H), 7.95 (d, *J* = 7.70 Hz, 2H), 7.74 (d, *J* = 7.51 Hz, 2H), 7.49 (d, *J* = 7.49 Hz, 1H), 7.42 (q, *J* = 8.00, 7.58 Hz, 5H), 7.32 (s, 1H), 7.29 (d, *J* = 8.20 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 188.3, 163.8, 157.2, 144.5, 138.7, 134.0, 132.6, 131.0, 130.4, 129.3, 128.8, 128.6, 128.5, 128.2, 126.4, 126.1, 109.9, 21.7; HRMS (ESI) Calcd. for $C_{23}H_{18}O_3Na$ $[M+Na]^+$: 365.1148, Found 365.1138.

4.1.42. 3-Oxo-1,3-diphenylprop-1-en-1-yl 4-fluorobenzoate (7bf)

Yield: 57% (98 mg); Yellow gummy; R_f = 0.30 (n-hexane/EtOAc = 19:1); ^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (dd, *J* = 8.56, 5.42 Hz, 2H), 7.95 (d, *J* = 7.69 Hz, 2H), 7.74 (d, *J* = 7.44 Hz, 2H), 7.52 (d, *J* = 7.13 Hz, 1H), 7.45 (q, *J* = 9.35, 7.36 Hz, 5H), 7.34 (s, 1H), 7.17 (t, *J* = 8.51 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) 188.3, 165.2 (d, *J* = 260.7 Hz), 162.9, 157.2, 138.8, 134.0, 133.2(d, *J* = 5.0 Hz), 133.0, 131.4, 129.1, 128.7, 128.3, 126.3, 125.6, 115.9 (d, *J* = 31.4 Hz), 110.1; HRMS (ESI) Calcd. for $C_{22}H_{15}FO_3Na$ $[M+Na]^+$: 369.0897, Found 369.0893.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix. ASupplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132000.

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