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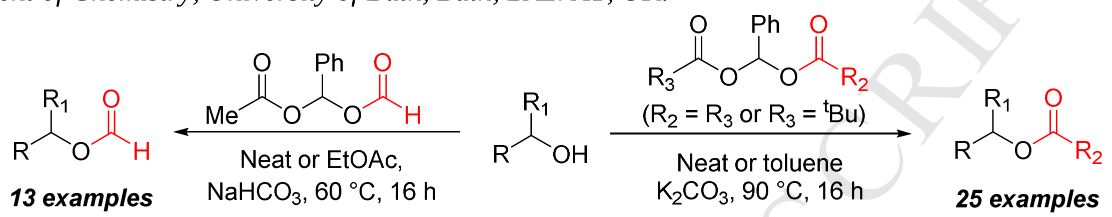

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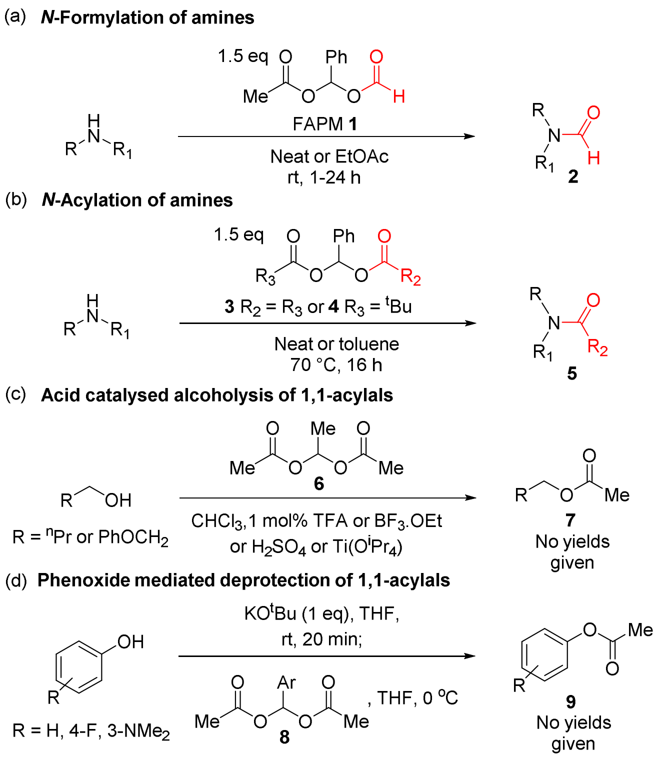
ABSTRACT

Formyloxyacetoxyphenylmethane, symmetric 1,1-diacylals and mixed 1-pivaloxy-1-acyloxy-1-phenylmethanes have been used as moisture stable *O*-formylating and *O*-acylating reagents for primary and secondary alcohols, allylic alcohols and phenols under solvent/catalyst free conditions to afford their corresponding esters in good yield.

1. Introduction

The widespread presence of ester functionalities in fine chemicals, drug molecules, natural products, polymers and biodiesels means that acylation reactions of alcohols are one of the most widely used transformations in organic chemistry.[1] Esters are also useful protecting groups that are widely used to protect acid and alcohol functionalities for the synthesis of complex natural products and drug molecules.[2] Formyl esters are particularly useful in this regard, since they are acid stable and can be hydrolysed under mild basic conditions in the presence of other ester functionality.[2b] Simple esters are traditionally prepared using Fischer esterification procedures that involve azeotropic refluxing of an alcohol in the presence of an acid catalyst.[1a] More complex esters are normally prepared through reaction of an alcohol with an activated carboxylic acid derivative, such as an acyl halide, acid anhydride or activated acyl donor.[3] However, *O*-acylation reactions of acyl chlorides and acid anhydrides are often exothermic,[4] often generating acidic by-products that are incompatible with acid sensitive functionalities. Effective catalytic trans-esterification protocols have also been developed for ester formation, however these approaches often require use of excess or irreversible acyl donor to drive the *O*-acylation reaction to completion.[5] Catalytic protocols involving Bronsted/Lewis acid catalysts, basic catalysts, metal complexes, enzymes and microwave irradiation conditions have been developed to increase the rate of *O*-acylation reactions under milder conditions.[6] Formyl esters are prepared via *in situ* generation of reactive formylating species, or through the use of stoichiometric amounts of formylating agent.[7] Although a wide range of *O*-acylation approaches are available,[1] many of these methods suffer from practical disadvantages, or harsh reaction conditions, that give low yields of ester, . Problems include long reaction times, harsh reaction conditions, poor chemoselectivities and/or regioselectivities., low functional group tolerance, the need to employ expensive, corrosive, toxic and volatile reagents, use of halogenated or environmentally unfriendly solvents, and the need to employ excess acylating reagents. All these issues can result in incomplete conversions, poor yields of ester and/or formation of by-products that can cause purification problems, particularly on a large scale. Therefore, there is still a need to develop cheap reagents for the efficient *O*-acylation of alcohol substrates, particularly if their esterification reactions can be carried out under solvent and/or catalyst free conditions.[8]

We have recently reported that formyloxyacetoxyphenylmethane **1** (FAPM) can be used as a bench stable formylating agent for the conversion of primary and secondary amines into formamides **2** under solvent free conditions at room temperature (Scheme 1a).[9a] We have also shown that structurally related 1,1-diacylals **3** and mixed 1-pivaloyl-1-acylals **4** can be used for the solvent free conversion of amines into their corresponding amides **5** (Scheme 1b).[9b] A review of the literature revealed that ethylidene diacetate **6** had previously been reported to react with primary alcohols (1-butanol, 2-phenylethanol) in $CHCl_3$ under acid catalysed conditions to afford their corresponding acetates **7** (no yields reported), acetaldehyde and acetic acid (Scheme 1c).[10] Similarly, phenoxides have been used as nucleophiles to deprotect benzal diacetates **8** to afford their corresponding benzaldehydes, phenoxy acetate **9** (no yield reported) and acetic acid as side products (Scheme 1d).[11a] Catalytic amounts of tetrabutylammonium bromide have been used to catalyse the methanolysis of 1,1-acylals to afford their corresponding aldehydes in good yield.[9b]



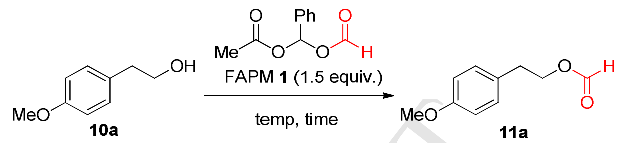
Scheme 1 (a) Formyloxyacetoxyphenylmethane (FAPM) **1** as an *N*-formylating agent for the synthesis of formamides **2**.[9a] (b) 1,1-diacylals **3** and mixed 1-pivaloxy-1-acyloxy-1-phenylmethanes **4** as *N*-acylating agents for the synthesis of amides **5**.[9b] (c) Ethylidene diacetate **6** as an *O*-acetylating agent for the synthesis of alkyl acetates **7**.[10] (d) Benzal diacetates **8** as an *O*-acetylating agent for the synthesis of phenoxy acetates **9**.[11]

Since the focus of these previous studies concentrated on using an alcohol as a nucleophile to deprotect acylals to afford their corresponding aldehydes, we decided to explore the scope and limitation of using FAPM **1** and 1,1-diacylals **3**/**4**[12] for the *O*-formylation and *O*-acylation reactions of alcohols. Consequently, we now report herein that these reagents may be used for the *O*-acylation of a range of primary and secondary alcohols under solvent/catalyst free conditions to give their corresponding formyl and acyl esters in good yield.

2. Results and Discussion

Our initial investigations focused on identifying conditions that would enable FAPM **1** to be used as a formylating agent for alcohols. Treatment of 2-(4-methoxyphenyl)ethanol **10a** with 1.5 equiv. of FAPM **1** under solvent free conditions at rt for 24 h gave only 15% conversion to 4-methoxyphenethyl formate **11a** (Table 1, Entry 1), whilst repeating the reaction at 40 °C gave an improved 64% conversion (Table 1, Entry 2). Inclusion of EtOAc as a cosolvent at 40 °C had no effect on the extent of conversion (Table 1, Entry 3), however inclusion of 2 equiv. of $NaHCO_3$ as a base resulted in improved results, affording 72% and 91% conversion to formate ester **11a** at rt (Table 1, Entry 4) and 40 °C (Table 1, Entry 5), respectively. Finally, repeating the formylation reaction using 1.5 equiv. of FAPM **1** under solvent free conditions at 60 °C for 16 h resulted in complete consumption of 2-(4-methoxyphenyl)ethanol, enabling formate ester **11a** to be isolated in 87% yield after chromatographic purification (Table1, Entry 6). There was no evidence of any competing acylation observed by ^{1}H NMR during the course of the optimisation reactions.

Table 1. Optimisation of the FAPM **1** mediated formylation reaction of 2-(4-methoxyphenyl)ethanol.

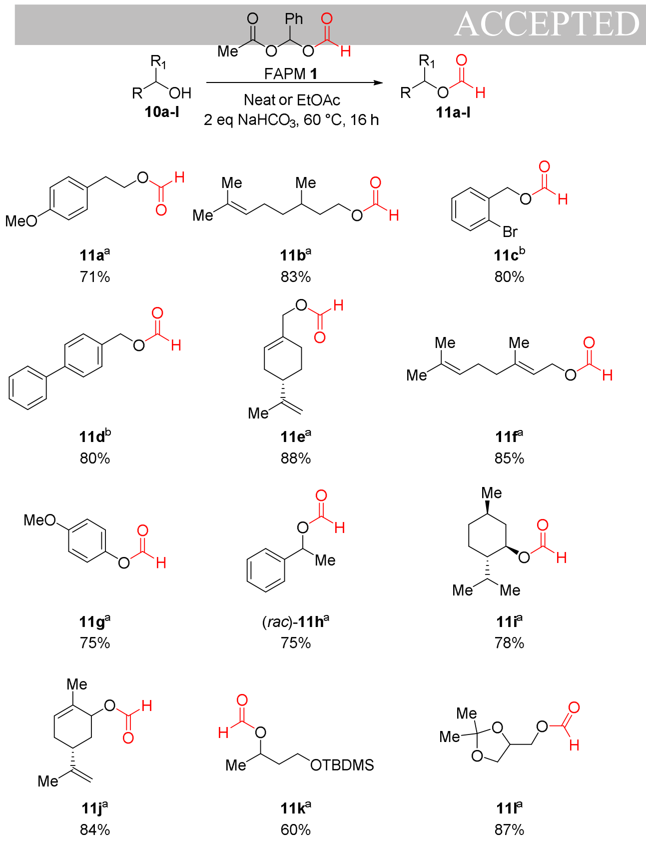


Entry	Solvent	Temp (°C)	Time (h)	Base	% Conversion
1	None	rt	24	None	15
2	None	40	24	None	64
3	EtOAc	40	24	None	66
4	None	rt	24	$NaHCO_3$ (2 equiv)	72
5	None	40	24	$NaHCO_3$ (2 equiv)	91
6	*None*	*60*	*16*	*$NaHCO_3$ (2 equiv)*	*100*

Conversion levels determined from integration of diagnostic resonances for **10a** and **11a** in the ^{1}H NMR spectra of their crude reaction products.

These optimal conditions were then applied for the *O*-formylation of a range of primary, secondary and tertiary alcohols to produce twelve formate esters **11a-l** in 60-88% yield (Scheme 2). Most of these *O*-formylation reactions were carried out by dissolving the alcohol substrates in FAPM **1** at 60 °C, addition of 2 equiv. of solid $NaHCO_3$ followed by stirring of the heterogeneous reaction mixture at 60 °C for 16 h to afford a formyl ester that were then purified by chromatography. EtOAc was added as a co-solvent when the parent alcohol was insoluble in FAPM **1**, to afford a homogeneous solution, prior to addition of insoluble $NaHCO_3$. Use of these basic reaction conditions afforded alkyl formates **11a-b**, benzylic formates **11c-d** and allylic formates **11e-f** in good 71-88% isolated yield. The ability of FAPM **1** to formylate *p*-methoxyphenol to afford reactive *p*-methoxyphenyl formate **11g** in 75% isolated yield is noteworthy. FAPM **1** also showed good reactivity towards acyclic and cyclic secondary alcohols affording their corresponding formates **11h-j** in 75-84% yield. Acid sensitive functional groups were also tolerated under these conditions, as demonstrated for the synthesis of *O*-silyl-*O*-formate ester **11k** and acetonide-*O*-formate ester **11l** in 60% and 87% yields, respectively.

Our attention then turned to investigating the potential of employing less reactive 1,1-acylal **3a** for the *O*-acetylation of alcohols. Use of our previously established base catalyzed *O*-formylation conditions (60 °C, 2 equiv. $NaHCO_3$, 16 h) for the acetylation of benzyl alcohol with 1,1-diacylal **3a** were only partially successful, affording its corresponding acetate **12a** in only 80% conversion after 16 h. However, a brief optimization study revealed that treatment of benzyl alcohol with 1.5 equiv. of 1,1-diacylal **3a** and 2 equivalents of K_2CO_3 at 90 °C for 16 h gave 100% conversion to afford acetate **12a** in 90% yield after chromatographic purification.

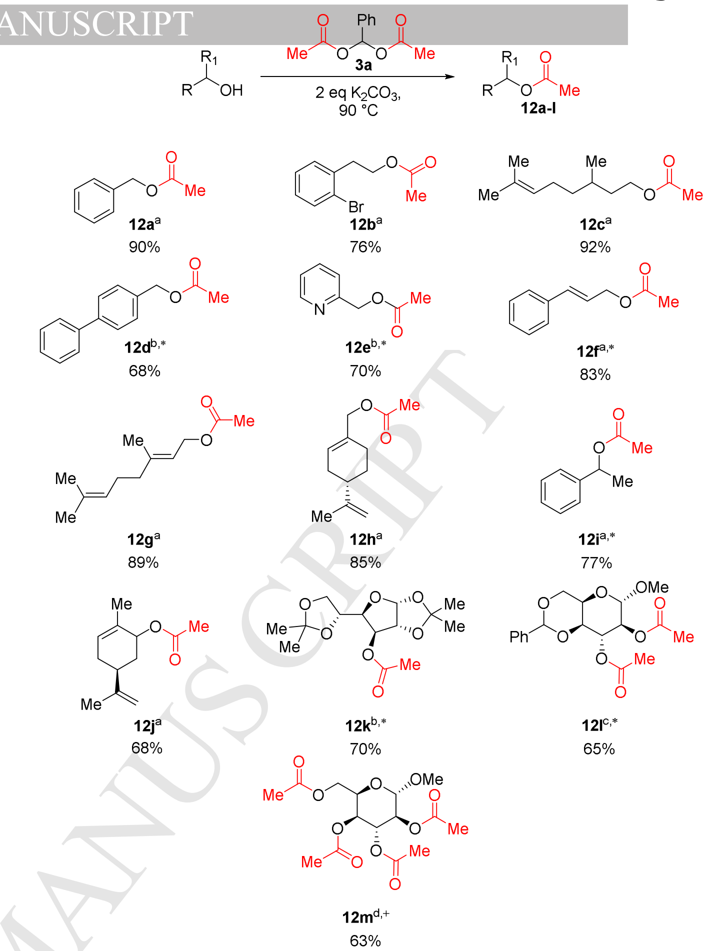


(a) 1.5 equiv. FAPM **1**, 2 equiv. $NaHCO_3$, 16 h, 60 °C. (b) 1.5 equiv. FAPM **1**, 2 equiv. $NaHCO_3$, EtOAc, 16 h, 60 °C.

Scheme 2 FAPM **1** as an *O*-formylating agent for the synthesis of formate esters **11a-l**.

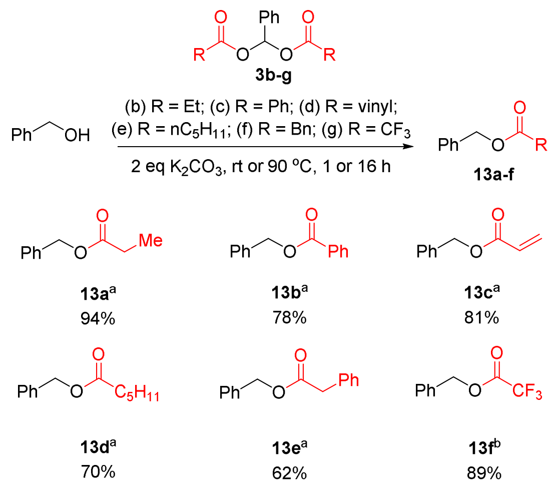
These optimal conditions were then applied for the esterification of a range of thirteen primary and secondary alcohols which gave their corresponding acetates **12a-m** in 63-92% isolated yields (Scheme 3). A wide range of different alcohol substrates were successfully *O*-acetylated to afford alkyl acetates **12a-c**, benzylic acetate **12d**, pyridyl acetate **12e** and allylic acetates **12f-h** in 68-92% yield. 1,1-Diacylal **3a** also showed good reactivity towards acyclic and cyclic secondary alcohols affording their corresponding acetates **12i-k** in 68-77% yield. Finally, use of 3 equivalents of 1,1-diacylal **3a** resulted in *bis*-acetylation of the diol fragment of methyl 4,6-*O*-benzylidene-α-D-glucopyran-oside to afford *bis*-acetate **12l** in 65% yield. Similarly, use of 6 equiv. of 1,1-diacylal **3a**, resulted in the tetra-acetylation of the tetrol fragment of methyl α-glucopyranoside to afford tetra-acetate **12m** in 63% isolated yield.

A range of 1,1-diacylal reagents **3b-g** were then used for the *O*-acylation of benzyl alcohol at 90 °C for 16 h under solvent free conditions to give five esters **13a-e** containing propionyl, benzoyl, hexanoyl, phenylacetoyl and acryloyl groups in 62-94% yields, respectively (Scheme 4). The trifluoro-1,1-diacylal reagent **3g** proved to more reactive, with trifluoroacetylation of benzyl alcohol proceeding at rt after only 1 h to afford trifluoroacetate **13f** in 89% yield.



(a) 1.5 equiv. acylal **3a**, 2.0 equiv. K_2CO_3, 16 h, 90 °C. (b) 1.5 equiv. acylal **3a**, 2.0 equiv. K_2CO_3, 24 h, 90 °C. (c) 3 equiv. acylal **3a**, 2.0 equiv. K_2CO_3, 16 h, 90 °C. (d) 6.0 equiv. acylal **3a**, 8.0 equiv. K_2CO_3, 16 h, 90 °C. (*) Toluene (2 mL) added. (+) Water (2 mL added)

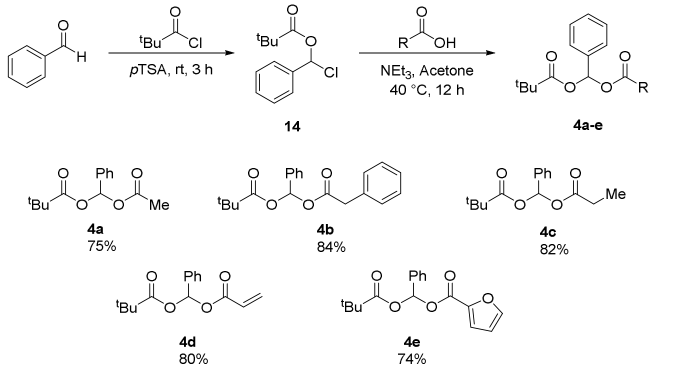
Scheme 3 1,1-Diacylal **3a** as an *O*-acylating agent for the synthesis of acetates **12a-m**.



a) 1.5 equiv. 1,1-diacylal **3a-f**, 2.0 equiv. K_2CO_3, 90 °C, 16 h. (b) 1.5 equiv. 1,1-diacylal **3g**, 2.0 equiv. K_2CO_3, rt, 1 h.

Scheme 4 Symmetric 1,1-diacylals **3b-g** as *O*-acylating agents of benzyl alcohol for the synthesis of benzyl esters **13a-f**.

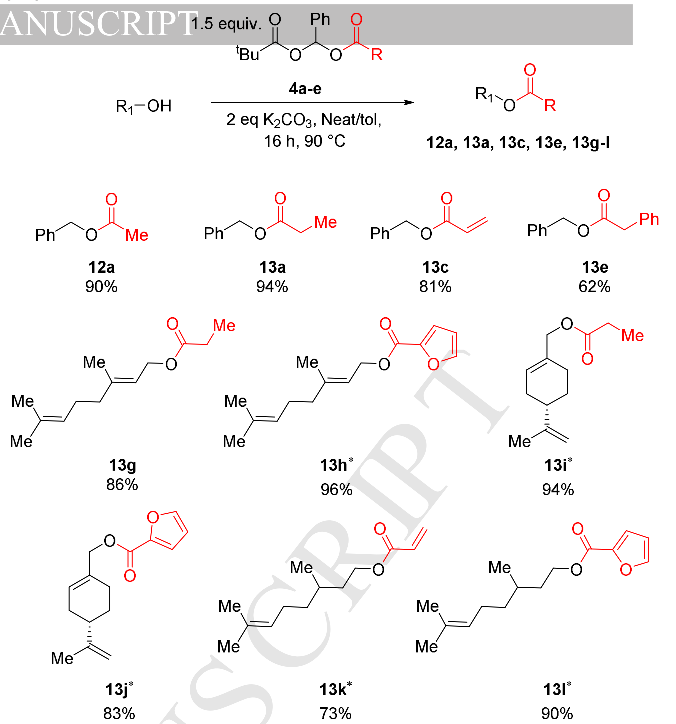
Following on from our previous success of using 1-pivaloxy-1-acyloxy-1-phenylmethanes for the *N*-acylation of amines (Scheme 1b),[9b] we next decided to investigate whether mixed 1-pivaloxy-1-acyloxy-1-phenylmethanes **4** could be used as selective *O*-acyl donors for alcohols. This would avoid wastage of one equivalent of a valuable acylating group that occurs when symmetric 1,1-acylals **3a-g** are used for *O*-acylating reagents. These mixed 1,1-diacylal reagents were prepared by treatment of benzaldehyde with 1.5 equiv. of pivaloyl chloride and a catalytic amount of *p*TSA to afford chloro(phenyl)methyl pivalate **14**,[13] that was then reacted immediately with a series of carboxylic acids and Et_3N in acetone at 40 °C to afford five mixed 1-pivaloxy-1-acyloxy-1-phenylmethanes **4a-e** in 74-84% yield (Scheme 5).[9b]



Scheme 5. Synthesis of mixed 1-pivaloxy-1-acyloxy-1-phenylmethanes **4a-e**.

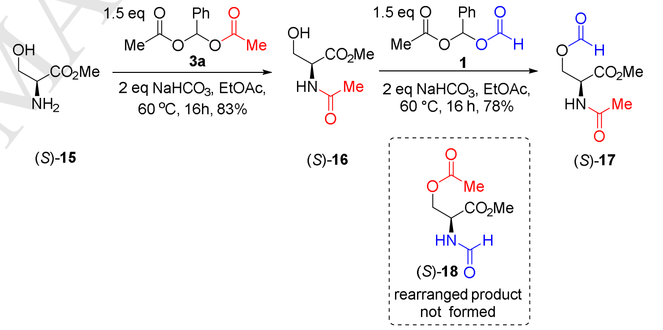
These 1-pivaloxy-1-acyloxy-1-phenylmethanes **4a-e** were then used as *O*-acylating reagents for a range of primary alkyl and allylic alcohols to give 10 primary esters (**12a**, **13a**, **13c**, **13e**, **13g-l**) in 62-96% yield (Scheme 6). Selective *O*-acyl transfer (acetyl, phenylacetyl, propionyl, acryloyl and furanoyl) was observed for all the mixed 1,1-diacylals **4a-e** employed, with no evidence of any competing *O*-pivaloyl transfer having occurred in any of these *O*-acylation reactions.

The *N*-/*O*- selectivity profiles of the acylating agent **3a** and formylating agent **1** was then investigated using L-serine methyl ester (*S*)-**15** as a bifunctional substrate. *N*-acetylation of (*S*)-**15** was performed using 1.5 equiv. of 1,1-diacylal **3a** under neutral conditions (70 °C, 16 h)[9a] to selectively afford *N*-acetyl-L-serine methyl ester (*S*)-**16** ($[\alpha]_D^{25}$ = -9.5; Lit[14a] = -10.1) as a single product in 83% yield (Scheme 7).[14] *O*-formylation of the free hydroxyl group of (*S*)-**16** was then carried out using 1.5 equiv. of FAPM **1,** using our standard basic conditions (2 equiv. $NaHCO_3$, 60 °C, 16 h, to afford *N*-acetyl-*O*-formyl-L-serine methyl ester (*S*)-**17** ($[\alpha]_D^{20}$ = -56.0) in 78% yield. We initially considered that competing base mediated *N*-/*O*-acetyl migration to afford *O*-acetyl-L-serine methyl ester might have occurred, followed by *N*-formylation to afford (*S*)-*N*-formyl-*O*-acetyl-serine methyl ester **18** as an alternative product. However, analysis of the ^{13}C NMR spectrum of the formylation product revealed resonances at δ 170.0, 169.9 and 160.3, consistent with the presence of the ester, amide and formyl ester groups of (*S*)-**17**.[9] This is in contrast to the ^{13}C NMR chemical shifts for the methyl esters and formamide groups of (*S*)-**18**, that would be expected to appear in the δ 169-174 region of its ^{13}C NMR spectrum.[9]



(*) Toluene (2 mL) added

Scheme 6. *O*-acylation reactions of 1-pivaloxy-1-acyloxy-1-phenylmethanes **4a-e** to afford esters **12a**, **13a**, **13c**, **13e**, **13g-l**



Scheme 7. Synthesis of *N*-acetyl-*O*-formyl-L-serine methyl ester (*S*)-**17**.

3. Conclusions

In summary, we have shown that formyloxyacetoxyphenyl-methane **1** and 1,1-diacylals **3** can be used as moisture-tolerant *O*-acylating reagents for primary and secondary alcohols under solvent-free conditions to afford their corresponding esters in good yields. This *O*-acylation methodology has been extended to enable mixed pivaloyl 1,1-acylals **4** to be used as efficient *O*-acylating agents for the selective transfer of a range of acyl donor groups to a wide range of alcohols. We have also demonstrated the inherent *N*-/*O*- selectivity of these acylal acylating reagents for the selective *N*-acetylation of serine methyl ester followed by *O*-formylation of its primary alcohol group to selectively afford orthogonally protected *N*-acetyl-*O*-formyl serine ester product (*S*)-**17**.

4. Experimental

Unless preparative details are given, reagents and solvents were obtained from commercial suppliers. All reactions were performed without air exclusion, at room temperature with magnetic stirring unless otherwise stated. Anhydrous $MgSO_4$ or Na_2SO_4 were used as drying agents for organic solutions. Petrol refers to petroleum ether with a boiling range of 40-60 °C. Thin layer chromatography (TLC) was carried out using Macherey-Nagel aluminium-backed plates, precoated with silica. Compounds were visualised by quenching of UV fluorescence at 254 nm or, where necessary, by staining with potassium permanganate, phosphomolybdic acid (PMA) or vanillin dip, followed by gentle heating. Purification by flash column chromatography was performed using high-purity grade 60 Å silica gel (60 Å pore size, 40-75 μm particle size). Capillary melting points were determined using a Stuart digital SMP10 melting point apparatus and are reported to the nearest °C. An Optical Activity Ltd AA-10 Series Automatic Polarimeter with a path length of 1 dm was used to measure optical rotations, with concentration (c) quoted in g/100 mL. Nuclear Magnetic Resonance (NMR) spectroscopy experiments were performed in deuterated solvent at 298 K on either a Brüker Avance 250, 300, 400 or 500 MHz spectrometer or an Agilent ProPulse 500 MHz spectrometer, with proton decoupling for all ^{13}C NMR spectra. ^{1}H and ^{13}C NMR chemical shifts, δ, are quoted in parts per million (ppm) and referenced against the residual, non-deuterated solvent peak. Ratios of formamide rotamers were determined by comparison of the integrals for equivalent peaks in their ^{1}H NMR spectra. A PerkinElmer Spectrum 100 FTIR spectrometer with Universal ATR FTIR accessory was used to record infrared (IR) spectra; with samples run neat and the most relevant, characteristic absorbances quoted as ν in cm^{-1}. High resolution mass spectrometry (HRMS) results were acquired on an externally calibrated Bruker Daltonics micrOTOF™ time-of-flight mass spectrometer coupled to an electrospray source (ESI-TOF). Molecular ions were detected in positive mode as either the protonated or sodiated form, with Bruker Daltonics software, DataAnalysis™ used to process the data. (Formyloxy)(phenyl)methyl acetate **1 and phenylmethylene diacetate 3a were** prepared using our previously described protocols.[9]

General Procedure A: *O*-formylation of alcohols

Alcohol (1.0 mmol) was added to (formyloxy)(phenyl)methyl acetate **1** (0.291 g, 1.5 mmol) and $NaHCO_3$ (0.168 g, 2.0 mmol), and the reaction stirred at 60 °C for 16 h. EtOAc (2mL) was added as a cosolvent when the alcohol substrate was insoluble in the fomylating reagent at 60 °C. The crude reaction mixture was then purified by column chromatography to give the desired formate ester.

General Procedure B: *O*-Acetylation of alcohols

Alcohol (1.0 mmol) was added to phenylmethylene diacetate **3a** (0.291 g, 1.5 mmol) and K_2CO_3 (0.270 g, 2.0 mmol) and the reaction stirred at 90 °C for 16 or 24h. Toluene or DMSO (2 mL) was added as a cosolvent when the alcohol substrate was insoluble in the formylating reagent at 60 °C. The crude reaction mixture was then purified by column chromatography to give the isolated ester.

General Procedure C: Synthesis of 1,1-diacylals

para-Toluenesulphonic acid (mono hydrate) (0.18 g, 0.94 mmol) was added to a mixture of benzaldehyde (1.0 g, 9.4 mmol) and anhydride (18.8 mmol) at rt. The reaction was stirred for 12 h and then diluted with Et_2O (50 mL) and washed with saturated Na_2CO_3 (3 x 20 mL). The organics were dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound which was used in subsequent steps without further purification unless otherwise stated.

General Procedure D: *O*-acylation of alcohols

Alcohol (1.0 mmol) was added to the acylation reagent (1.5 mmol) and K_2CO_3 (0.270 g, 2.0 mmol). Toluene (2 mL) was added as a cosolvent when the alcohol substrate was insoluble in the formylating reagent at 60 °C. The reaction was then stirred at 90 °C for 16 or 24h. The crude reaction mixture was then purified by column chromatography to give the isolated ester.

General Procedure E: Synthesis of mixed acylals

Trimethylacetyl chloride (0.813 mL, 6.60 mmol) was added dropwise to a mixture of benzaldehyde (0.489 g, 4.40 mmol) and *p*-toluenesulfonic acid (0.083 g, 0.44 mmol) at rt and the reaction mixture stirred for 3 h. The reaction was then quenched via addition of saturated $NaHCO_3$ (10 mL) and diluted with Et_2O (50 mL). The reaction was then extracted with saturated $NaHCO_3$(aq) (3 x 20 mL), the organic layer dried ($MgSO_4$) and concentrated *in vacuo* to afford chloro(phenyl)methyl pivalate **14** (1.0 g, 4.40 mmol) as a yellow oil that was carried forward to the next step without further purification. Triethylamine (0.60 mL, 4.40 mmol) was added dropwise to a solution of chloro(phenyl)methyl pivalate **14** (4.40 mmol) and carboxylic acid (4.40 mmol) in acetone (10 mL). The reaction was stirred at 40 °C for 12 h, over which time a white ppt formed. The reaction mixture was filtered through Celite® and concentrated *in vacuo* to afford a crude reaction product that was purified by silica gel chromatography to give the desired mixed acylal.

4-Methoxy phenethyl alcohol formate 11a

General procedure A was followed to afford the title compound (0.127 g, 0.71 mmol) as a clear oil in 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 1H, (C=O)*H*), 7.19 - 7.10 (m, 2H, Ar*H*), 6.91 - 6.81 (m, 2H, Ar*H*), 4.36 (t, *J* = 7.0 Hz, 2H, CH_2(OC=O)), 3.81 (s, 3H, CH_3), 2.93 (t, *J* = 7.2 Hz, 2H, CH_2CH$_2$(OC=O)). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 158.4, 129.8, 129.3, 113.9, 64.6, 55.2, 34.0.
Analytical data in accordance with the literature.[7h]

Citronellyl formate 11b

General procedure A was followed to afford the title compound (0.153 g, 0.83 mmol) as a clear oil in 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H, (C=O)*H*), 5.19 - 4.98 (m, 1H, C=C*H*), 4.29 - 4.11 (m, 2H, CH_2O(C=O)H),

2.12 - 1.83 (m, 2H,), 1.81 - 1.64 (m, 4H), 1.61 (s, 3H, C=CCH_3), 1.58 - 1.29 (m, 3H), 1.27 - 1.14 (m, 1H), 0.93 (d, J = 6.4 Hz, 3H, CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 131.4, 124.5, 62.5, 36.9, 35.3, 29.4, 25.7, 25.4, 19.3, 17.6.
Analytical data in accordance with the literature.[7h]

2-Bromobenzyl alcohol formate 11c

General procedure A was followed to afford the title compound (0.172 g, 0.80 mmol) as a yellow oil in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H, (C=O)H), 7.61 (dd, J = 1.2, 8.1 Hz, 1H, ArH), 7.45 (dd, J = 2.0, 7.8 Hz, 1H, ArH), 7.34 (dt, J = 1.2, 7.5 Hz, 1H, ArH), 7.25 - 7.20 (m, 1H, ArH), 5.31 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 134.5, 132.9, 130.1, 130.0, 127.6, 123.5, 65.2. IR (thin film) ν max (cm^{-1}): 1719 (C=O);.[14]

Biphenyl-4-methanol formate 11d

General procedure A was followed to afford the title compound (0.170 g, 0.80 mmol) as a crystalline white solid in 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.18 (t, J = 0.9 Hz, 1H, (C=O)H), 7.65 - 7.57 (m, 4H, ArH), 7.50 - 7.42 (m, 4H, ArH), 7.41 - 7.34 (m, 1H, ArH), 5.27 (s, 2H, CH_2O(C=O)). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 141.5, 140.5, 134.1, 128.9, 128.8, 127.5, 127.4, 127.1, 65.5. IR (thin film) ν max (cm^{-1}): 1702 (C=O);[15]

Perillyl alcohol formate 11e

General procedure A was followed to afford the title compound (0.159 g, 0.88 mmol) as a yellow oil in 88% yield. $[\alpha]_D^{20}$ = -62.5 in MeOH. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (s, 1H, (C=O)H), 5.86 - 5.76 (m, 1H, CH_2C=CH), 4.77 - 4.70 (m, 2H, C=CH_2), 4.57 (s, 2H, CH_2O(C=O)), 2.26 - 2.06 (m, 4H, CH_2), 2.05 - 1.94 (m, 1H, CH), 1.93 - 1.80 (m, 1H, CH), 1.75 (s, 3H, CH_3), 1.60 - 1.41 (m, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 149.4, 132.0, 126.8, 108.8, 68.0, 40.7, 30.4, 27.2, 26.3, 20.7. IR (thin film) ν max (cm^{-1}): 1722 (C=O); HRMS (ESI): m/z calculated for $C_{11}H_{16}O_2$: requires: 181.1228 for $[M+H]^+$; found: 181.1210.

Geranyl formate 11f

General procedure A was followed to afford the title compound to give the title compound (0.155 g, 0.85 mmol) as a pale yellow oil in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H, (C=O)H), 5.45 - 5.31 (m, 1H C=C$H$$CH_2$O), 5.20 - 5.00 (m, 1H, C=C$H$$CH_2$), 4.70 (d, J = 7.2 Hz, 2H, CH_2O(C=O)), 2.17-2.06 (m, 4H, CH_2CH_2), 1.76 - 1.71 (m, 3H CH_3C(CH_3)=CH), 1.71 - 1.67 (m, 3H, CH_3C(CH_3)=CH), 1.61 (s, 3H, CH_2C(CH_3)=CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 143.2, 131.9, 123.6, 117.6, 60.8, 39.5, 26.2, 25.7, 17.7, 16.5. Analytical data in accordance with literature.[18]

4-Methoxyphenol formate 11g

General procedure A was followed to afford the title compound (0.114 g, 0.75 mmol) as an orange oil in 75% yield. ^{1}H NMR (300MHz, $CDCl_3$) δ 8.30 (s, 1H, (C=O)H), 7.12 - 7.01 (m, 2H, ArH), 6.96 - 6.87 (m, 2H, ArH), 3.82 (s, 3H, CH_3). ^{13}C NMR (75MHz, $CDCl_3$) δ 159.7, 157.6, 143.3, 122.0, 114.6, 55.0. Analytical data in accordance with literature.[179]

1-Phenylethanol formate 11h

General procedure A was followed to afford the title compound (0.112 g, 0.75 mmol) as a pale yellow oil in 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (s, 1H, (C=O)H), 7.42 - 7.28 (m, 5H, ArH), 6.18 - 5.85 (m, 1H, CH(OC=O)), 1.60 (d, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (75MHz, $CDCl_3$) δ 160.4, 140.8, 128.6, 128.1, 126.1, 72.2, 22.1. Analytical data in accordance with the literature.[7h]

Menthol formate 11i

General procedure A was followed to afford the title compound (0.143 g, 0.78 mmol) as a yellow oil in 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 0.8 Hz, 1H, (C=O)H), 4.81 (dt, J = 4.3, 10.8 Hz, 1H, CH(OC=O)), 2.07 - 1.97 (m, 1H, CH), 1.91 (dtd, J = 2.6, 7.0, 13.9 Hz, 1H, CH), 1.76 - 1.64 (m, 2H, CH_2), 1.59 - 1.33 (m, 2H, CH_2), 1.14 - 0.98 (m, 2H, CH), 0.95 - 0.84 (m, 7H, CH & CH(CH_3)$_2$), 0.77 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 74.1, 46.8, 40.8, 34.1, 31.4, 26.0, 23.2, 22.0, 20.7, 16.0. Analytical data in accordance with the literature.[7a]

Carveol formate 11j

General procedure A was followed to afford the title compound as a yellow oil (0.150 g, 0.84 mmol) in 84% yield. The formate ester was obtained as a mixture of diastereomers (1:1) in the same ratio as the starting material. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 1.1 Hz, 1H, (C=O)H), 8.14 (s, 1H, (C=O)H), 5.82 - 5.75 (m, 1H), 5.68 - 5.53 (m, 2H), 5.44 - 5.37 (m, 1H), 4.78 - 4.74 (m, 2H), 4.74 - 4.70 (m, 2H), 2.40 - 2.06 (m, 5H), 2.04 - 1.82 (m, 4H), 1.76 - 1.68 (m, 10H), 1.68 - 1.63 (m, 3H), 1.61 - 1.56 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1 (α), 161.0 (β), 148.5 (α), 148.1 (β), 132.1 (α), 130.2 (β), 128.6 (α), 126.5 (β), 109.5 (α), 109.4 (β), 73.1 (α), 70.5 (β), 40.2 (α), 35.7 (β), 33.9 (α), 33.7 (β), 30.8 (α), 30.7 (β), 20.8 (α), 20.5 (β), 20.5 (α), 18.8 (β). IR (thin film) ν max (cm^{-1}): 1717 (C=O); HRMS (ESI): m/z calculated for $C_{11}H_{16}O_2$: requires: 181.1228for $[M+H]^+$; found: 181.1190.

4-((tert-butyldimethylsilyl)oxy)butan-2-yl formate 11k

General procedure A was followed to afford the title compound (0.140 g, 0.60 mmol) as a yellow oil in 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H, C(O)H), 5.20 – 5.12 (m, 1H, CHOC(O)H), 3.70 – 3.62 (m, 2H, CH_2OSiTBDMS), 1.84 (ddt, J = 13.6, 8.1, 5.5 Hz, 1H, C$H_a$$CH_b$$CH_2$OSiTBDMS), 1.79 – 1.71 (m, 1H, CH_aC$H_b$$CH_2$OSiTBDMS), 1.30 (d, J = 6.4 Hz, 3H, CH_3CH), 0.88 (s, 9H, Si$(CH_3)_2$C(CH_3)$_3$), 0.04 (s, 6H, Si(CH_3)$_2$C$(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 68.7, 59.3, 38.9, 26.0, 20.4, 18.4, -5.27, -5.29. IR (thin film) ν max (cm^{-1}): 1725 (C=O); HRMS (ESI): m/z calculated for $C_{11}H_{24}O_3Si$: requires: 255.1392 for $[M+Na]^+$; found: 255.1399.

(2,2-dimethyl-1,3-dioxolan-4-yl)methyl formate 11l

General procedure A was followed to afford the title compound (0.139 g, 0.87 mmol) as a yellow oil in 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H, C(O)*H*), 4.35 (qd, *J* = 6.2, 4.6 Hz, 1H, $CH_2CHCH_2OC(O)$), 4.26 (ddd, *J* = 11.5, 4.6, 0.9 Hz, 1H, $CH_2CHCH_aH_bOC(O)$), 4.17 (ddd, *J* = 11.5, 6.2, 0.8 Hz, 1H, $CH_2CHCH_aH_bOC(O)$), 4.10 (dd, *J* = 8.5, 6.5 Hz, 1H, $CH_aCH_bCHCH_2OC(O)$), 3.76 (dd, *J* = 8.6, 6.0 Hz, 1H, $CH_aCH_bCHCH_2OC(O)$), 1.44 (s, 3H, CH_3), 1.37 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 110.2, 73.4, 66.4, 64.3, 26.8, 25.4. IR (thin film) *v* max (cm^{-1}): 1722 (C=O); HRMS (ESI): m/z calculated for $C_7H_{12}O_4$: requires: 183.0628 for [M+Na]; found: 183.0631.

Benzyl acetate 12a

General procedure B was followed to afford the title compound (0.135 g, 0.90 mmol) as a clear oil in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 5H, Ar*H*), 5.11 (s, 2H, CH_2Ph), 2.11 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 136.0, 128.7, 128.4, 66.5, 21.2. Analytical data in accordance with literature.[20]

2-Bromophenethyl acetate 12b

General procedure B was followed to afford the title compound (0.184 g, 0.76 mmol) as a clear oil in 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 7.9, 0.9 Hz, 1H, Ar*H*), 7.29 – 7.22 (m, 2H, Ar*H*), 7.11 (ddd, *J* = 7.9, 5.1, 4.1 Hz, 1H, Ar*H*), 4.30 (t, *J* = 7.0 Hz, 2H, $CH_2OC(O)CH_3$), 3.09 (t, *J* = 7.0 Hz, 2H, ArCH_2), 2.04 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 137.3, 133.1, 131.2, 128.5, 127.6, 124.8, 63.5, 35.4, 21.1. Analytical data in accordance with literature.[21]

3,7-Dimethyloct-6-en-1-yl acetate 12c

General procedure B was followed to afford the title compound (0.178 g, 0.90 mmol) as a clear oil in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.08 (tdt, *J* = 5.8, 3.0, 1.5 Hz, 1H, C=C*H*), 4.17 – 4.01 (m, 2H, CH_2OAc), 2.04 (s, 3H, (C=O)CH_3), 1.95 (dt, *J* = 15.0, 7.7 Hz, 2H, CH_2), 1.72 – 1.62 (m, 4H, CH_2), 1.60 (d, *J* = 1.4 Hz, 3H,CH_3(C)CH_3), 1.56 – 1.27 (m, 3H, CH_3(C)CH_3), 1.18 (dddd, *J* = 13.5, 9.1, 7.5, 6.2 Hz, 1H, (C*H*CH_3), 0.91 (d, *J* = 6.4 Hz, 3H, CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 131.5, 124.7, 63.2, 37.1, 35.5, 29.6, 25.9, 25.5, 21.2, 19.5, 17.8. Analytical data in accordance with literature.[22]

[1,1'-biphenyl]-4-ylmethyl acetate 12d

General procedure B was followed to afford the title compound (0.153 g, 0.68 mmol) as a white solid in 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 4H, Ar*H*), 7.49 – 7.41 (m, 4H, Ar*H*), 7.40 – 7.32 (m, 1H, Ar*H*), 5.15 (s, 2H, CH_2), 2.13 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 141.4, 140.8, 135.0, 128.9, 127.6, 127.5, 127.3, 66.2, 21.2. Analytical data in accordance with literature.[23]

Pyridin-2-ylmethyl acetate 12e

General procedure B was followed to afford the title compound (0.105 g, 0.70 mmol) as a clear oil in 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H, Ar*H*), 7.70 (td, *J* = 7.7, 1.8 Hz, 1H, Ar*H*), 7.35 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.26 (s, 1H, Ar*H*), 5.22 (s, 2H, CH_2), 2.16 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 155.8, 149.7, 136.9, 123.0, 122.0, 67.0, 21.1. Analytical data in accordance with literature.[22]

Cinnamyl acetate 12f

General procedure B was followed to afford the title compound (0.146 g, 0.83 mmol) as a clear oil in 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (s, 5H, Ar*H*), 6.66 (dt, *J* = 15.9, 1.4 Hz, 1H, CH=C*H*CH_2), 6.29 (dt, *J* = 15.9, 6.5 Hz, 1H, C*H*=CHCH_2), 4.73 (dd, *J* = 6.5, 1.4 Hz, 2H, CH=CHCH_2), 2.11 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 136.3, 134.4, 128.7, 128.2, 126.7, 123.3, 65.2, 21.2. Analytical data in accordance with literature.[24]

(*E*)-3,7-dimethylocta-2,6-dien-1-yl acetate 12g

General procedure B was followed to afford the title compound (0.174 g, 0.89 mmol) as a waxy white solid in 89% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 5.34 (tq, *J* = 7.2, 1.3 Hz, 1H, C=C*H*CH_2O), 5.08 (tq, *J* = 5.5, 1.5 Hz, 1H, C=C*H*CH_2), 4.58 (d, *J* = 7.1 Hz, 2H, CH_2OAc), 2.16 – 1.99 (m, 7H, 2 x CH_2 and (C=O)CH_3), 1.69 (dd, *J* = 5.9, 1.3 Hz, 6H, CH_3(C)CH_3), 1.60 (d, *J* = 1.4 Hz, 3H, $CH_2C(CH_3)$=CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 142.5, 132.0, 123.9, 118.3, 61.6, 39.7, 26.4, 25.8, 21.2, 17.8, 16.6. Analytical data in accordance with literature.[22]

(*S*)-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl acetate 12h

General procedure B was followed to afford the title compound as a clear oil in 85% yield (0.165 g, 0.85 mmol). $[\alpha]_D^{20}$ = -65.5 in $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (dd, *J* = 4.6, 2.4 Hz, 1H, CH_2C=C*H*), 4.80 – 4.66 (m, 2H, C=CH_2), 4.45 (d, *J* = 1.7 Hz, 2H, CH_2OAc), 2.23 – 2.04 (m, 7H, 2 x CH_2 and (C=O)CH_3), 2.03 – 1.80 (m, 2H, CH_2), 1.74 (t, *J* = 1.1 Hz, 3H, CH_3C=CH_2), 1.54 – 1.41 (m, 1H, C*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 149.8, 132.7, 126.0, 108.9, 68.7, 40.9, 30.6, 27.4, 26.5, 21.2, 20.9. Analytical data in accordance with literature.[25]

(*rac*)-1-phenylethyl acetate 12i

General procedure B was followed to afford the title compound (0.126 g, 0.77 mmol) as a pale yellow oil in 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H, Ar*H*), 5.88 (q, *J* = 6.6 Hz, 1H, C*H*), 2.08 (s, 3H, C(O)CH_3), 1.54 (d, *J* = 6.6 Hz, 3H, CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 141.8, 128.6, 128.0, 126.2, 72.5, 22.4, 21.5. Analytical data in accordance with literature.[26]

2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl acetate (mix of isomers) 12j

General procedure B was followed to afford the title compound (0.132 g, 0.68 mmol) as a clear oil in 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (dt, *J* = 5.3, 1.8 Hz, 1H), 5.60 (dq, *J* = 5.5, 1.8 Hz, 1H), 5.45 (d, *J* = 1.5 Hz, 1H), 5.30 – 5.22 (m, 1H), 4.77 – 4.68 (m, 4H), 2.37 – 2.15 (m, 4H), 2.08 (d, *J* = 1.0 Hz, 6H), 2.02 – 1.79 (m, 3H), 1.72 (dt, *J* = 4.4, 1.1 Hz, 5H), 1.69 (dd, *J* = 2.7, 1.4 Hz, 3H), 1.64 (dp, *J* = 2.5, 1.3 Hz, 3H), 1.61 – 1.54 (m, 1H), 1.53 – 1.41 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 171.1, 148.9, 148.4, 133.0, 131.1, 128.1, 126.1, 109.5, 109.3, 73.4, 70.8, 40.4, 35.9, 34.1, 33.7, 31.0, 30.9, 21.6, 21.4, 21.0, 20.8, 20.6, 19.0. Analytical data in accordance with literature.[27]

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl acetate 12k

General procedure B was followed for 24 h to afford the title compound (0.21 g, 0.69 mmol) as a white solid in 70% yield. $[\alpha]_D^{20}$ = -32 in $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (d, *J* = 3.7 Hz, 1H, OC*H*O), 5.24 (d, *J* = 2.4 Hz, 1H, OC*H*CHOC(O)CH_3), 4.50 (d, *J* = 3.7 Hz, 1H, OC*H*C(O)CH_2), 4.25 – 4.17 (m, 2H, OCH($CHOCH_2O$)C(O)CH_3 and C*H*C(O)CH_3), 4.05 (tdd, *J* = 10.7, 7.0, 3.3 Hz, 2H, OCH_2CHO), 2.10 (s, 3H, CHC(O)CH_3), 1.52 (s, 3H, OCO(C$H_{3a}$$CH_{3b}$)), 1.41 (s, 3H, OCO($CH_{3a}CH_{3b}$)), 1.32 (s, 3H, OCO(C$H_{3a}$$CH_{3b}$)), 1.30 (s, 3H, OCO($CH_{3a}CH_{3b}$)). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 112.4, 109.5, 105.1, 83.4, 79.8, 76.3, 72.5, 67.3, 27.0, 26.8, 26.3, 25.4, 21.1. Analytical data in accordance with literature.[28]

(4a*R*,6*S*,7*S*,8*R*,8a*S*)-6-Methoxy-2-phenylhexahydropyrano[3,2-d][1,3]dioxine-7,8-diyl diacetate 12l

(4a*R*,6*S*,7*S*,8*S*,8a*R*)-6-Methoxy-2-phenylhexahydropyrano[3,2-d][1,3]dioxine-7,8-diol (0.282 g, 1.0 mmol) was added to phenylmethylene diacetate (0.582 g, 3.0 mmol) and K_2CO_3 (0.270 g, 2.0 mmol) and the reaction mixture stirred at 90 °C for 16 h. The crude reaction mixture was then purified by column chromatography to give the title compound (0.238 g, 0.65 mmol) as a white solid in 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (qd, *J* = 5.4, 4.5, 1.9 Hz, 2H, Ar*H*), 7.36 (dt, *J* = 4.6, 2.8 Hz, 3H, Ar*H*), 5.58 (t, *J* = 9.6 Hz, 1H, C*H*OCH_3), 5.51 (s, 1H, PhC*H*), 4.95 – 4.88 (m, 2H, 2 x C*H*C(O)CH_3), 4.31 (dd, *J* = 10.1, 4.7 Hz, 1H, CH_2CH(O)C*H*(O)), 3.93 (td, *J* = 9.9, 4.7 Hz, 1H, CH_2C*H*(O)CH(O)), 3.77 (t, *J* = 10.2 Hz, 1H, OC$H_a$$H_b$CHO), 3.65 (t, *J* = 9.6 Hz, 1H, OC$H_a$$H_b$CHO), 3.41 (s, 3H, OC$H_3$), 2.10 (s, 3H, C(O)C$H_3$), 2.05 (s, 3H, C(O)C$H_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 169.9, 137.0, 129.2, 128.4, 126.3, 101.7, 97.7, 79.3, 71.7, 69.1, 69.0, 62.4, 55.5, 21.0, 20.9. Analytical data in accordance with literature.[29]

(2*R*,3*S*,4*R*,5*S*,6*S*)-2-(acetoxymethyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl triacetate 12m

Methyl α-D-glucopyranoside (0.194 g, 1.0 mmol) was added to phenylmethylene diacetate (1.16 g, 6.0 mmol) and K_2CO_3 (1.10 g, 8.0 mmol) the reaction was stirred at 90 °C for 16 h. The crude reaction mixture was then purified by column chromatography to give the title compound (0.230 g, 0.63 mmol) as a white solid in 63% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48 (dd, *J* = 10.1, 9.4 Hz, 1H), 5.07 (dd, *J* = 10.2, 9.3 Hz, 1H), 4.98 – 4.84 (m, 2H), 4.26 (dd, *J* = 12.3, 4.6 Hz, 1H), 4.10 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.98 (ddd, *J* = 10.2, 4.6, 2.3 Hz, 1H), 3.41 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.3, 170.3, 169.8, 96.9, 70.9, 70.2, 68.6, 67.2, 62.0, 55.6, 20.90, 20.85, 20.8. Analytical data in accordance with literature.[8d]

Phenylmethylene dipropionate 3b

General procedure C was followed to afford the title compound (2.15 g, 9.12 mmol) as a clear oil in 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 1H, C*H*$(OCOEt)_2$), 7.51 (qd, *J* = 3.8, 1.5 Hz, 2H, Ar*H*), 7.41 (ddt, *J* = 4.3, 3.1, 1.6 Hz, 3H, Ar*H*), 2.40 (tt, *J* = 7.4, 3.6 Hz, 4H, 2 x C$H_2$$CH_3$), 1.16 (t, *J* = 7.5 Hz, 6H, 2 x CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.47, 135.81, 129.80, 128.72, 126.78, 89.72, 27.55, 8.89. IR (thin film) *ν* max (cm^{-1}): 2983 (ArC-H), 1756 (C=O); HRMS (ESI): m/z calculated for $C_{13}H_{12}O_4$: requires: 259.0946 for $[M+Na]^+$; found: 259.0995. Analytical data in accordance with literature.[30]

Phenylmethylene dibenzoate 3c

General procedure C was followed to afford the title compound (3.09 g, 9.30 mmol) as a clear oil in 99% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 – 8.06 (m, 5H, C*H* and Ar*H*), 7.75 – 7.64 (m, 3H, Ar*H*), 7.62 – 7.50 (m, 4H, Ar*H*), 7.49 – 7.40 (m, 4H, Ar*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 162.5, 134.7, 133.7, 130.7, 130.2, 129.9, 129.2, 129.0, 128.9, 128.6, 126.9, 90.8. IR (thin film) *ν* max (cm^{-1}): 3064 (ArC-H), 1722 (C=O); HRMS (ESI): m/z calculated for $C_{21}H_{16}O_4$: requires: 355.0946 for $[M+Na]^+$; found: 355.0929. Analytical data in accordance with literature.[30]

Phenylmethylene diacrylate 3d

General procedure C was followed to afford the title compound (2.12 g, 9.12 mmol) as a clear oil in 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 1H, C*H*Ph), 7.65 – 7.48 (m, 2H, Ar*H*), 7.51 – 7.36 (m, 3H, Ar*H*), 6.52 (dd, *J* = 17.3, 1.4 Hz, 2H, C$H_a$$H_b$=CH), 6.27 – 6.03 (m, 2H, CH_aH_b=C*H*), 5.93 (dd, *J* = 10.5, 1.3 Hz, 2H, $CH_a$$H_b$=CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 134.8, 132.8, 129.9, 128.8, 127.6, 126.8, 90.1. IR (thin film) *ν* max (cm^{-1}): 3040 (ArC-H), 1732 (C=O); HRMS (ESI): m/z calculated for $C_{13}H_{12}O_4$: requires: 255.0633 for $[M+Na]^+$; found: 255.0667.

Phenylmethylene dihexanoate 3e

General procedure C was followed to afford the title compound (2.89 g, 9.02 mmol) as a clear oil in 96% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 1H, C*H*Ph), 7.51 (qd, *J* = 3.7, 1.5 Hz, 2H, Ar*H*), 7.40 (ddt, *J* = 4.2, 3.1, 1.6 Hz, 3H, Ar*H*), 2.37 (td, *J* = 7.4, 2.3 Hz, 4H, 2 x (C=O)C$H_2$$CH_2$), 1.70 – 1.58 (m, 4H, 2 x (C=O)CH_2CH_2), 1.30 (dq, *J* = 7.2, 3.7, 3.3 Hz, 8H, 2 x (C=O)CH_2CH_2), 0.94 – 0.82 (m, 6H, 2 x CH_2CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 135.9, 129.8, 128.7, 126.8, 89.6, 34.2, 31.3, 24.5, 22.4, 14.0. IR (thin film) *ν* max (cm^{-1}): 2956 (ArC-H), 1752 (C=O); HRMS (ESI): m/z calculated for $C_{19}H_{28}O_4$: requires: 343.1885 for $[M+Na]^+$; found: 343.1898. Analytical data in accordance with literature.[31]

Phenylmethylene bis(2-phenylacetate) 3f

General procedure C was followed to afford the title compound (3.18 g, 8.84 mmol) as a clear oil in a 94% yield. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.69 (s, 1H, C*H*Ph), 7.43 – 7.16 (m, 15H, Ar*H*), 3.64 (s, 4H, 2 x CH_2Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5, 135.3, 133.2, 129.9, 129.5, 129.4, 128.7, 127.4, 126.7, 90.3, 41.1. IR (thin film) *ν* max (cm^{-1}): 3032, 2981 (ArC-H), 1759 (C=O); HRMS (ESI): m/z calculated for $C_{23}H_{20}O_4$: requires: 383.1259 for [M+Na]$^+$; found: 383.1259.

Phenylmethylene bis(2,2,2-trifluoroacetate) 3g

Trifluoroacetic acid (0.035 mL, 0.47 mmol) was added in a dropwise manner to a solution of benzaldehyde (0.50 g, 4.7 mmol) and trifluoroacetic anhydride (0.98 mL, 7.08 mmol) at rt. After 2 h the reaction was concentrated *in vacuo* to afford the title compound (1.4 g, 4.5 mmol) as a yellow oil in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H, Ar*H*), 7.62 – 7.45 (m, 5H, Ar*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3 (q, ^{2}JC-F = 44.7 Hz), 134.4, 131.8, 129.4, 127.0, 114.1 (q, ^{1}JC-F = 285.5 Hz), 93.8. IR (thin film) *ν* max (cm^{-1}): 1809 (C=O).

Benzyl propionate 13a

General procedure D was followed to afford the title compound (0.154 g, 0.94 mmol) as a clear oil in 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 5H, Ar*H*), 5.12 (s, 2H, CH_2Ph), 2.39 (q, J = 7.6 Hz, 2H, C$H_2$$CH_3$), 1.17 (t, J = 7.6 Hz, 3H, CH_2CH_3). C NMR (75 MHz, $CDCl_3$) δ 174.5, 136.3, 128.7, 128.3, 126.8, 66.3, 27.8, 9.3. Analytical data in accordance with literature.[32]

Benzyl benzoate 13b

General procedure D was followed to afford the title compound (0.166 g, 0.78 mmol) as a clear oil in 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 2H, Ar*H*), 7.60 – 7.48 (m, 1H, Ar*H*), 7.54 – 7.35 (m, 7H, Ar*H*), 5.38 (s, 2H, CH_2Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 136.2, 133.2, 130.3, 129.8, 128.7, 128.5, 128.4, 128.3, 66.8. Analytical data in accordance with literature.[32]

Benzyl acrylate 13c

General procedure D was followed to afford the title compound (0.131 g, 0.81 mmol) as a clear oil in 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 5H, Ar*H*), 6.45 (dd, J = 17.3, 1.4 Hz, 1H, C*H*=CH_aH_b), 6.17 (dd, J = 17.3, 10.4 Hz, 1H, CH=C$H_a$$H_b$), 5.85 (dd, J = 10.4, 1.4 Hz, 1H, CH=$CH_a$$H_b$), 5.21 (s, 2H, C$H_2$Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 136.0, 131.2, 128.7, 128.5, 128.4, 128.4, 66.5. Analytical data in accordance with literature.[32]

Benzyl hexanoate 13d

General procedure D was followed to afford the title compound (0.144 g, 0.70 mmol) as a clear oil in 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 5H, Ar*H*), 5.12 (s, 2H, CH_2Ph), 2.37 (t, J = 7.5 Hz, 2H, (C=O)C$H_2$$CH_2CH_2CH_2CH_3$), 1.71 – 1.61 (m, 2H, (C=O)CH_2C$H_2$$CH_2CH_2CH_3$), 1.31 (dq, J = 7.5, 3.8, 3.2 Hz, 4H, (C=O)CH_2CH_2CH_2C$H_2$$CH_3$), 0.91 – 0.87 (m, 3H, (C=O)$CH_2CH_2CH_2CH_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 136.3, 128.7, 128.3, 126.8, 66.2, 34.4, 31.4, 24.8, 22.4, 14.0. Analytical data in accordance with literature.[33]

Benzyl 2-phenylacetate 13e

General procedure D was followed to afford the title compound (0.140 g, 0.62 mmol) as a clear oil in 62% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 10H, Ar*H*), 5.15 (s, 2H, PhCH_2O), 3.68 (s, 2H, (C=O)CH_2Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 136.0, 134.0, 129.4, 128.7, 128.7, 128.3, 128.2, 127.2, 66.7, 41.5. Analytical data in accordance with literature.[33]

Benzyl 2,2,2-trifluoroacetate 13f

Benzyl alcohol (0.108 g, 1.0 mmol) was added to phenylmethylene bis(2,2,2-trifluoroacetate) (0.474 g, 1.5 mmol) and K_2CO_3 (2.0 mmol, 0.270 g) and the reaction stirred at rt for 1 h. The crude reaction mixture was then purified by column chromatography to give the title compound (0.181 g, 0.89 mmol) as a clear oil in 89% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 5H), 5.36 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5 (q, ^{2}JC-F = 42.5 Hz), 133.4, 129.4, 129.0, 128.8, 114.6 (q, ^{1}JC-F = 285.8 Hz), 69.7. Analytical data in accordance with literature.[34]

Acetoxy(phenyl)methyl pivalate 4a

General procedure E was followed to afford the title compound (0.82 g, 3.30 mmol) as a clear oil in 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$)) δ 7.66 (s, 1H, OC*H*O), 7.53 – 7.49 (m, 2H, Ar*H*), 7.42 – 7.39 (m, 3H, Ar*H*), 2.12 (s, 3H, C(O)CH_3), 1.23 (s, 9H, C(O)C(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$)) δ 176.4, 169.1, 135.8, 129.7, 128.7, 126.7, 89.9, 39.0, 27.0, 21.1.

Phenyl(2-phenylacetoxy)methyl pivalate 4b

General procedure E was followed to afford the title compound (1.20 g, 3.69 mmol) as a clear oil in 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 1H, OC*H*O), 7.47 – 7.43 (m, 2H, Ar*H*), 7.41 – 7.38 (m, 3H, Ar*H*), 7.31 – 7.26 (m, 5H, Ar*H*), 3.68 (s, 2H, CH_2Ph), 1.17 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 169.6, 135.7, 133.4, 129.7, 129.4, 128.7, 128.7, 127.4, 126.6, 90.0, 41.3, 38.9, 27.0. I R (thin film) *ν* max (cm^{-1}): 2995, 2983 (ArC-H), 1769, 1756 (C=O); HRMS (ESI): m/z calculated for $C_{20}H_{22}O_4$: requires: 349.1410 for [M+Na]$^+$; found: 349.1473.

Phenyl(propionyloxy)methyl pivalate 4c

General procedure E was followed to afford the title compound (0.95 g, 3.62 mmol) as a clear oil in 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 1H, OC*H*O), 7.53 – 7.49 (m, 2H, Ar*H*), 7.42 – 7.38 (m, 3H, Ar*H*), 2.40 (qd, J = 7.5, 3.0 Hz, 2H, C$H_2$$CH_3$), 1.23 (s, 9H, C(C$H_3$)$_3$), 1.16 (t, J = 7.5 Hz, 3H, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 172.5, 135.9, 129.7, 128.7, 126.7, 89.8, 39.0, 27.6, 27.0, 9.0. IR (thin film) *ν* max (cm^{-1}): 2978 (ArC-H), 1754, 1750 (C=O); HRMS (ESI): m/z calculated for $C_{15}H_{20}O_4$: requires: 287.1254 for [M+Na]$^+$; found: 287.1268.

Phenyl(pivaloyloxy)methyl acrylate 4d

General procedure E was followed to afford the title compound (0.92 g, 3.52 mmol) as a clear oil in 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 1H, OC*H*O), 7.56 – 7.51 (m, 2H, Ar*H*), 7.45 – 7.40 (m, 3H, Ar*H*), 6.50 (dd, *J* = 17.3, 1.4 Hz, 1H, C*H*=CH_aH_b), 6.15 (dd, *J* = 17.3, 10.4 Hz, 1H, CH=C$H_a$$H_b$), 5.92 (dd, *J* = 10.4, 1.4 Hz, 1H, CH=$CH_a$$H_b$), 1.23 (s, 9H, C($CH_3$)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 164.1, 135.8, 132.6, 129.8, 128.7, 127.7, 126.7, 90.0, 39.0, 27.0. IR (thin film) *ν* max (cm^{-1}): 2975, 2875 (ArC-H), 1744 (C=O); HRMS (ESI): m/z calculated for $C_{15}H_{18}O_4$: requires: 285.1097 for [M+Na]$^+$; found: 285.1149

Phenyl(2-phenylacetoxy)methyl furanoate 4e

General procedure E was followed to afford the title compound (1.00 g, 3.31 mmol) as a clear oil in 74% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, 1H, C*H*Ph), 7.61 (dd, *J* = 1.8, 0.8 Hz, 1H, C(=O)COC*H*CHCH), 7.60 – 7.55 (m, 2H, Ar*H*), 7.49 – 7.37 (m, 3H, Ar*H*), 7.29 – 7.22 (m, 1H, C(=O)COCHC*H*CH), 6.52 (dd, *J* = 3.5, 1.7 Hz, 1H, C(=O)COCHCHC*H*), 1.25 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 156.5, 147.1, 143.7 135.5, 129.7, 128.7, 126.6, 119.3, 112.0, 90.0, 38.9, 26.9. IR (thin film) ν_{max} (cm^{-1}): 2976, 2875 (ArC-H), 1769, 1741 (C=O); HRMS (ESI): m/z calculated for $C_{17}H_{18}O_5$: requires: 325.1046 for [M+Na]$^+$; found: 325.1099.

Benzyl acetate 12a

General procedure D was followed to afford the title compound (0.135 g, 0.90 mmol) as a clear oil in 90% yield. Analytical data was in accordance with **12a** synthesized using general procedure B.

Benzyl propionate 13a

General procedure D was followed to afford the title compound (0.154 g, 0.94 mmol) as a clear oil in 94% yield. Analytical data was in accordance with **13a** synthesized using general procedure B.

Geraniol propanoate 13g

General procedure D was followed to afford the title compound (0.091g, 0.43 mmol) as a clear oil in 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45 – 5.22 (m, 1H, -OCH_2C*H*=), 5.08 (q, *J* = 1.4 Hz, 1H, CH_2C*H*=C(CH_3)$_2$), 4.60 (d, 2H, -OCH_2C=), 2.33 (q, *J* = 7.6 Hz, 2H, C(=O)C$H_2$$CH_3$), 2.17 – 1.97 (m, 4H. C$H_2CH_2$C*H*=C($CH_3$)$_2$), 1.72 – 1.69 (m, 3H, CH=C(C$H_{3a}$$CH_{3b}$)$_2$), 1.68 (d, *J* = 1.3 Hz, 3H, -OCH_2CHC(CH_3)), 1.59 (dd, *J* = 5.2, 0.9 Hz, 3H, CH=C(CH_{3a}CH_{3b})$_2$), 1.14 (t, *J* = 7.6 Hz, 3H, C(=O)CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 142.2, 131.9, 123.8, 118.3, 61.3, 39.6, 27.6, 26.3, 25.7, 17.7, 16.5, 9.2. Analytical data in accordance with literature.[35]

Geranyl furanoate 13h

General procedure D was followed to afford the title compound (0.1195g, 0.48 mmol) as a clear oil in 96% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 1.8, 0.9 Hz, 1H, C(=O)COC*H*), 7.18 (dd, *J* = 3.5, 0.9 Hz, 1H, C(=O)CC*H*), 6.50 (dd, *J* = 3.5, 1.7 Hz, 1H, C(=O)CCHC*H*), 5.44 (tq, *J* = 7.1, 1.3 Hz, 1H, -OCH_2C*H*=), 5.09 (tt, *J* = 5.0, 2.8 Hz, 1H, CH_2CH_2C*H*=), 4.87 – 4.78 (m, 2H, -OCH_2), 2.16 – 1.99 (m, 4H, CH_2CH_2CH=), 1.75 (d, *J* = 1.3 Hz, 3H, CH=C(C$H_{3a}$$CH_{3b}$)), 1.67 (d, *J* = 1.3 Hz, 3H, OCH_2CH=C(CH_3), 1.60 (d, *J* = 1.3 Hz, 3H, CH=C(CH_{3a}CH_{3b})). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 146.2, 142.9, 131.9, 123.7, 117.9, 117.8, 111.8, 61.9, 60.4, 39.6, 26.3, 25.7, 17.7, 16.6. IR (thin film) ν_{max} (cm^{-1}: 2916 (ArC-H), 1716 (C=O); HRMS (ESI): m/z calculated for $C_{15}H_{20}O_3$: requires: 271.1305 for [M+Na]$^+$; found: 271.1302.

Perillyl propanoate 13i

General procedure D was followed to afford the title compound (0.098g, 0.47 mmol) as a clear oil in 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 – 5.67 (m, 1H, OCH_2C=C*H*), 4.70 (dp, *J* = 3.0, 1.3 Hz, 2H, C(CH_3)=CH_2), 4.45 (d, *J* = 1.7 Hz, 2H, OCH_2), 2.34 (q, *J* = 7.6 Hz, 2H, C(=O)CH_2), 2.22 – 2.02 (m, 4H, CH_2C(CH_2)=CCH_2), 2.01 – 1.77 (m, 1H, CH_2=C(CH_3)C*H*), 1.72 (s, 3H, CH_2=C(CH_3)), 1.47 (ddt, *J* = 12.7, 11.3, 8.5 Hz, 2H, CH_2=C(CH_3)CHCH_2), 1.13 (t, *J* = 7.6 Hz, 3H, C(=O)CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 149.6, 132.7, 125.6, 108.8, 68.3, 40.8, 30.5, 27.6, 27.3, 26.4, 20.7, 9.2. IR (thin film) ν_{max} (cm^{-1}: 2921 (ArC-H), 1736 (C=O); HRMS (ESI): m/z calculated for $C_{13}H_{18}O_2$: requires: 231.1398 for [M+Na]$^+$; found: 231.1348.

Perillyl furanoate 13j

General procedure D was followed to afford the title compound (0.1021g, 0.42 mmol) as a clear oil in 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 1.7, 0.9 Hz, 1H, C(=O)COC*H*), 7.19 (dd, *J* = 3.5, 0.8 Hz, 1H, C(=O)CC*H*), 6.51 (dd, *J* = 3.5, 1.8 Hz, 1H, C(=O)CCHC*H*), 5.84 (ddd, *J* = 5.1, 2.8, 1.4 Hz, 1H, OCH_2C=C*H*), 4.75 – 4.71 (m, 2H, C(CH_3)=CH_2), 4.71 – 4.69 (m, 2H, OCH_2), 2.25 – 2.09 (m, 4H, CH_2C(CH_2)=CCH_2), 2.08 – 1.96 (m, 1H, CH_2=C(CH_3)C*H*), 1.74 (t, *J* = 1.1 Hz, 3H, CH_2=C(CH_3)),), 1.62 – 1.19 (m, 2H, CH_2=C(CH_3)CHCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 149.6, 146.3, 144.7, 132.3, 126.3, 117.9, 111.8, 108.8, 68.8, 40.8, 30.5, 27.3, 26.4, 20.8. IR (thin film) ν_{max} (cm^{-1}: 2922 (ArC-H), 1716 (C=O); HRMS (ESI): m/z calculated for $C_{15}H_{18}O_3$: requires: 269.1148 for [M+Na]$^+$; found: 269.1145.

Citronellyl acrylate 13k

General procedure D was followed to afford the title compound (0.0772g, 0.37 mmol) as a clear oil in 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 (dd, *J* = 17.3, 1.6 Hz, 1H, C(=O)CH=C$H_a$$H_b$), 6.12 (dd, *J* = 17.3, 10.4 Hz, 1H, C(=O)C*H*=CH_aH_b), 5.82 (dd, *J* = 10.4, 1.6 Hz, 1H, C(=O)CH=$CH_a$$H_b$), 5.09 (dddd, *J* = 7.1, 5.7, 2.9, 1.4 Hz, 1H, -OCH_2CH_2CH(CH_3)CH_2CH_2C*H*=C(CH_3)$_2$), 4.32 – 3.99 (m, 2H, -OCH_2), 1.99 (td, *J* = 15.2, 13.5, 6.0 Hz, 2H, CH_2CH=C(CH_3)$_2$), 1.68 (q, *J* = 1.4 Hz, 3H, CH=C(C$H_{3a}$$CH_{3b}$), 1.60 (d, *J* = 1.3 Hz, 3H, CH=C(CH_{3a}CH_{3b}), 1.53 – 1.08 (m, 5H, CH_2C*H*(CH_3)CH_2), 0.93 (d, *J* = 6.4 Hz, 3H, CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 131.4, 130.5, 128.6, 124.6, 63.1, 36.9, 35.4, 29.5, 25.8, 25.4, 19.4, 17.7. Analytical data in accordance with literature.[36]

Citronellyl furanoate 13l

General procedure D was followed to afford the title compound (0.075g, 0.41 mmol) as a clear oil in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, J = 1.7, 0.9 Hz, 1H, C(=O)COC*H*), 7.16 (dd, J = 3.5, 0.9 Hz, 1H, C(=O)CC*H*), 6.51 (dd, J = 3.5, 1.8 Hz, 1H, C(=O)CCHC*H*), 5.09 (tt, J = 7.1, 1.5 Hz, 1H, $CH_2CH{=}C(CH_3)_2$), 4.45 – 4.24 (m, 2H, $C({=}O)COCH_2$), 2.08 – 1.90 (m, 2H, $CH_2CH{=}C(CH_3)_2$), 1.67 (q, J = 1.3 Hz, 3H, $CH{=}C(CH_{3a}CH_{3b})$), 1.60 (d, J = 1.2 Hz, 3H, $CH{=}C(CH_{3a}CH_{3b})$), 1.56 (s, 2H, $C({=}O)COCH_2CH_2$), 1.46 – 1.31 (m, 2H, $CH_2CH_2CH{=}C(CH_3)_2$), 1.30 – 1.14 (m, 1H, $-OCH_2CH_2CH(CH_3)$), 0.95 (d, J = 6.4 Hz, 3H, $-OCH_2CH_2CH(CH_3)$,). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 146.2, 144.9, 131.4, 124.5, 117.7, 111.8, 63.6, 36.9, 35.5, 29.5, 25.7, 25.4, 19.5, 17.7. IR (thin film) ν_{max} (cm^{-1}): 2970, 2926 (ArC-H), 1736 (C=O); HRMS (ESI): m/z calculated for $C_{15}H_{22}O_3$: requires: 273.1461 for $[M+Na]^+$; found: 273.1459.

(*S*)-methyl 2-acetamido-3-hydroxypropanoate 16

Et_3N (0.42 mL, 3.21 mmol) was added in a dropwise manner to (*S*)-Serine methyl ester hydrochloride salt (0.5 g, 3.21 mmol) suspended in acetone (3 mL). The reaction mixture was stirred for 10 min and then filtered through a Celite® pad. The filtrate was concentrated *in vacuo* to give (*S*)-serine methyl ester which was used without further purification. (S)-Serine methyl ester (1.0 mmol) was added to phenylmethylene diacetate **3a** (0.291 g, 1.5 mmol) and $NaHCO_3$ (0.168 g, 2.0 mmol) and EtOAc (2 mL) and the reaction was stirred at 60 °C for 16 h, followed by chromatographic purification to afford the title compound (0.428 g, 2.56 mmol) as a brown oil in 83% yield. $[\alpha]_D^{20}$ = -9.5, c = 2.0, MeOH (Lit[14a] $[\alpha]_D^{25}$ -10.1 (c 1.9, MeOH)); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52 (s, 1H, N*H*), 4.67 (dt, J = 7.3, 3.6 Hz, 1H, C*H*NH), 4.01 – 3.89 (m, 2H, CH_2OH), 3.79 (s, 3H, OCH_3), 2.81 (s, 1H, O*H*), 2.07 (s, 3H, $(C{=}O)CH_3$), ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 170.8, 63.6, 54.9, 52.9, 23.3. IR (thin film) ν max (cm^{-1}): 3291 ((C=O)NH and OH), 1738 (C=O ester), 1648 (C=O amide); HRMS (ESI): m/z calculated for $C_6H_{11}NO_4$: requires: 162.0766 for $[M+H]^+$; found: 162.0788. Analytical data in accordance with literature.[14]

(*S*)-methyl 2-acetamido-3-(formyloxy)propanoate 17

General procedure A was followed to afford the title compound (0.377 g, 2.0 mmol) as a white solid in 78% yield. m.p. 95-97 °C, $[\alpha]_D^{20}$ = -56.0, c 1.0, $CHCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (q, J = 0.9 Hz, 1H, (C=O)*H*), 6.28 (s, 1H, N*H*), 4.90 (dt, J = 7.1, 3.3 Hz, 1H, C*H*NH), 4.60 – 4.45 (m, 2H, $CH_2O(C{=}O)H$), 3.80 (s, 3H, OCH_3), 2.06 (s, 3H, $(C{=}O)CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 169.9, 160.3, 63.6, 53.2, 51.6, 23.2. IR (thin film) ν max (cm^{-1}): 3292 ((C=O)NH), 1727, 1713, 1703 (C=O); HRMS (ESI): m/z calculated for $C_7H_{11}NO_5$: requires: 190.0715 for $[M+H]^+$; found: 190.0739.

5. Conflicts of interest

The authors declare no conflicts of interest.

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7. References and Notes

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Supplementary Material