Oxidation of acyclic alkenes and allyl and benzyl ethers with DIB/*t*BuOOH/$Mg(OAc)_2$

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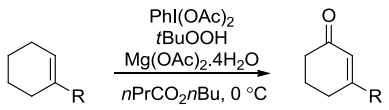
ABSTRACT

Oxidation of (11*Z*)-1′,2′-didehydrostemofoline with DIB/TBHP/ $Mg(OAc)_2$•$4H_2O$ resulted in oxidative cleavage of the C-11-C-12 double bond instead of the desired allylic oxidation of the 1-butenyl side chain. Stemofoline gave a similar result. The oxidation of more simple terminal alkenes was regioselective and gave vinyl ketones while allyl and benzyl ethers gave acrylate and benzoate esters, respectively. Allyl and benzyl ethers could be chemoselectively oxidized in the presence of a terminal alkene or benzyl group. Oxidation of an internal alkene was poorly regioselective, in contrast to the oxidation of 1-substituted cyclohexenes.

1. Introduction

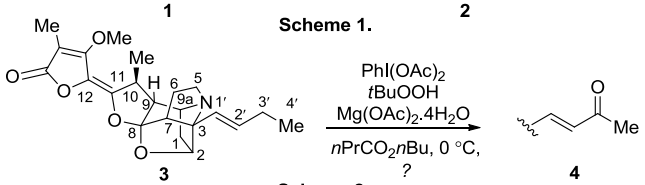
In 2010, Zhao and Yeung reported the regioselective allylic oxidation of 1-substituted cyclohexenes **1** to 3-substituted cyclohexanones **2** using diacetoxyiodobenzene (DIB), *tert*-butyl hydroperoxide (TBHP) and $Mg(OAc)_2$•$4H_2O$ in an ester solvent (Scheme 1).[1] *n*-Butyl butanoate was found to be the solvent of choice.

In connection with our studies to prepare rare *Stemona* alkaloids and analogues for biological studies,[2] starting from (11*Z*)-1′,2′-didehydrostemofoline **3**, we examined the reaction of **3** with DIB/TBHP/$Mg(OAc)_2$•$4H_2O$ with the desire to directly prepare the known enone **4** (Scheme 2). This paper reports the results of this study and related oxidation reactions on stemofoline, more simple acyclic alkenes and allyl and benzyl ethers.



1 **2**

Scheme 1.



3 **4**

Scheme 2.

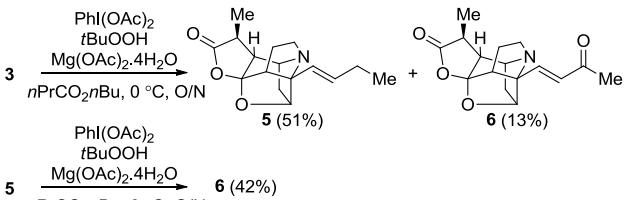
2. Results and discussion

2.1. Oxidation of (11Z)-1′,2′-didehydrostemofoline 3

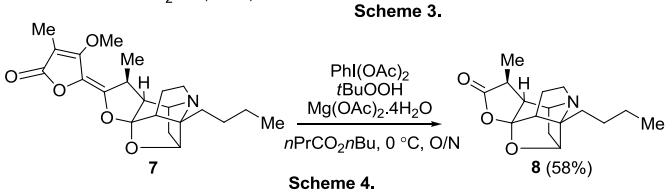
With the aim of preparing enone **4** (Scheme 2), (11*Z*)-1′,2′-didehydrostemofoline **3** was treated under the oxidation conditions reported by Zhao and Yeung.[1] Treatment of **3** in *n*-butyl butanoate with DIB (1 equiv.)/TBHP (3 equiv.)/ $Mg(OAc)_2$•$4H_2O$ (1 equiv.) at 0 °C for 15 h gave not the enone **4** but a mixture of the lactone **5** and enone **6**, a result of overall oxidative cleavage of the C-11-C-12 double bond of **3** and further side chain allylic oxidation of **5** to give **6** (Scheme 3). Purification of this mixture by column chromatography gave **5** and **6** in yields of 51 and 13%, respectively. Treatment of **5** under the same oxidative conditions gave only 20% yield of enone **6**. To improve the yield of enone **6** from **5**, the stoichiometric ratios of the reactants were systematically varied. The optimum conditions found were DIB (8 equiv.)/TBHP (24 equiv.)/ $Mg(OAc)_2$•$4H_2O$ (1 equiv.) at 0 °C for 15 h. Under these conditions the yield of enone **6** was improved to 42%. The corresponding *N*-oxides of **5** or **6** were not detected.

2.2. Oxidation of stemofoline 7

Under similar conditions to those described above for the oxidation of **3**, stemofoline **7** was converted to the known lactone **8** in 58% yield (Scheme 4). This compound was prepared previously by us by first osmium-catalyzed dihydroxylation of the C-11-C-12 double bond of **7** followed by oxidative cleavage of the result diol with $NaIO_4$ in 34% overall yield.[2]



Scheme 3.



7 **8** (58%)

Scheme 4.

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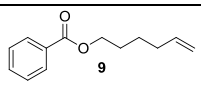
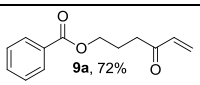
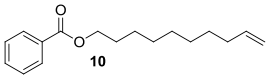
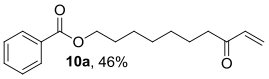
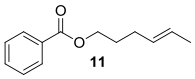
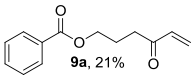
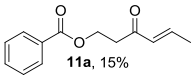
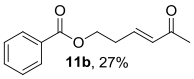
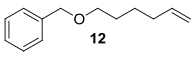
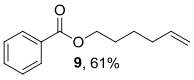
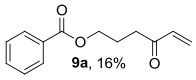
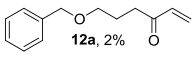
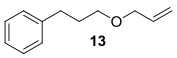
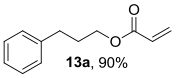
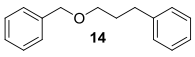
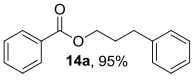
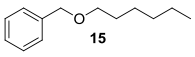
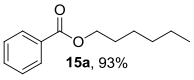
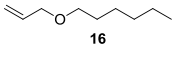
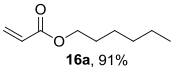
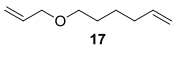
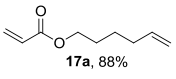
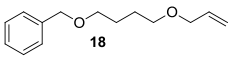
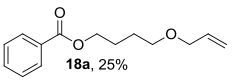
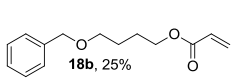
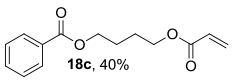
e-mail: spyne@uow.edu.au

2.3. Oxidation of simple acyclic alkenes

To further examine the potential of these oxidation conditions the allylic oxidations of simpler acyclic alkenes were studied. The results of these studies are shown in Table 1. Hex-5-enyl benzoate **9** was used as model compound to optimize the reaction conditions, which were then applied to the allylic oxidation of the other alkenes **10**−**12** shown in Table 1. The optimum reaction conditions were found to be identical to those reported by Zhao and Yeung.[1] (DIB (1 equiv.)/TBHP (3 equiv.)/$Mg(OAc)_2$•$4H_2O$ (1 equiv.) at 0 °C in *n*-butyl butanoate. The allylic oxidation reactions of the terminal alkenes **9** and **10** were regioselective and proceeded to provide the vinyl ketones **9a** and **10a**, respectively. The higher yield of enone **9a** over **10a** may be a result of formation of an intermediate involving coordination of the benzoyl ester carbonyl and the hypervalent iodine intermediate ($PhI(OOtBu)_2$). This intermediate may be able to more readily abstract, intramolecularly, the allylic H-atom in the shorter chain substrate **9**.[3] The oxidation reaction of the internal alkene **11** was not regioselective and gave a mixture of three enones (**9a**, **11a** and **11b**). Based on their isolated yields, about one third of the product (**9a**) resulted from initial oxidation at the terminal methyl group and two thirds of the products (**11a**, **b**) from initial oxidation at the internal allylic methylene group. Oxidation of the alkene **12**, gave the alkene **9** as the major product resulting from chemoselective oxidation of the benzyl ether group of **12** to a benzoate. Small amounts of doubly oxidized product (**9a**) and the enone **12a** were also isolated.

For the oxidations of substrates **13**−**18** the products were difficult to separate from the solvent *n*-butyl butanoate. Thus, ethyl acetate was used as alternative ester solvent. When allyl ether **13** was treated with DIB (1 equiv.)/TBHP (3 equiv.)/ $Mg(OAc)_2$•$4H_2O$ (1 equiv.) at 0 °C in ethyl acetate the yield of the acrylate ester **13a** was only 67%. Therefore, further optimization of the reaction conditions were carried out. It was found that by using DIB (1.5 equiv.)/TBHP (4.5 equiv.)/ $Mg(OAc)_2$•$4H_2O$ (1 equiv.) at 0 °C in ethyl acetate, the yield of **13a** was increased to 90%. This reaction was highly chemoselective and no products arising from benzylic oxidation of **13** or **13a** could be isolated. The same oxidation conditions when applied to the benzyl ether **14** gave, chemoselectively, the benzoate **14a** in 95% yield. For the substrates **15**−**18** the optimum conditions were found to be DIB (1.5 equiv.)/TBHP (6 equiv.)/$Mg(OAc)_2$•$4H_2O$ (1 equiv.). These conditions gave the benzoate ester **15a** and the acrylate esters **16a** and **17a** in improved yields of 93, 91 and 88 %, respectively over those using these reagents in a 1:3:1: molar equivalent ratio. The oxidation reaction of **18** was not chemoselective and gave a mixture of the esters **18a** and **18b** and the diester**18c**.

Table 1. Allylic oxidation of Substrates

Substrate	Product, Yield%			
 **9**	 **9a**, 72%			
 **10**	 **10a**, 46%			
 **11**	 **9a**, 21%	 **11a**, 15%	 **11b**, 27%	
 **12**	 **9**, 61%	 **9a**, 16%	 **12a**, 2%	
 **13**	 **13a**, 90%			
 **14**	 **14a**, 95%			
 **15**	 **15a**, 93%			
 **16**	 **16a**, 91%			
 **17**	 **17a**, 88%			
 **18**	 **18a**, 25%	 **18b**, 25%	 **18c**, 40%	

3. Conclusions

In conclusion, oxidation of (11*Z*)-1′,2′-didehydrostemofoline **3** with DIB/TBHP/$Mg(OAc)_2$•$4H_2O$ resulted in oxidative cleavage of the C-11-C-12 double bond instead of the desired allylic oxidation at the 1-butenyl side chain. Stemofoline **7** gave a similar result under identical oxidation conditions. The oxidation of more simple terminal alkenes was regioselective and gave vinyl ketones while allyl and benzyl ethers gave acrylate and benzoate esters, respectively. Allyl and benzyl ethers could be chemoselectively oxidized in the presence of a terminal alkene or benzyl group. Oxidation of an internal alkene was poorly regioselective, in contrast to the oxidation of 1-substituted cyclohexenes.[1] These studies further demonstrate the usefulness

and limitations of this relatively straight forward oxidation system to acyclic alkenes and benzyl and allyl ethers.

4. Experimental section

4.1. General

All ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were determined in $CDCl_3$ solution. ^{1}H NMR assignments were achieved with the aid of gCOSY and, in some cases, NOESY experiments. ^{13}C NMR assignments were based upon DEPT, gHSQC, and gHMBC experiments. Electrospray (ESI) mass spectra were obtained on a VG Autospec spectrometer. High-resolution mass spectra (HRMS) were determined on a micromass QTof2 spectrometer using polyethylene glycol or polypropylene glycol as the internal standard. Optical rotations were measured using a 1 cm cell, in a Jasco DIP-370 digital polarimeter or a 10 cm cell, in a Jasco P-2000 polarimeter. Infrared spectra were obtained as neat samples on a Shimadzu MIRacle 10 FTIR by the single reflection ATR method.

4.1.1. Starting materials

The known starting material **3** and **7** was isolated from an unidentified *Stemona* species that we reported earlier.[4] All other chemicals were purchased from commercial suppliers and were used without further purification. Dec-9-enyl benzoate **10** and (*E*)-hex-4-enyl benzoate **11** were prepared according to a literature procedures from benzoylation reactions of the commercially available alcohols.[5] Benzyl-5-hexenyl ether **12**, allyl-5-hexenyl ether **13**, benzyl-3-phenylpropyl ether **14**, benzyl hexyl ether **15**, allyoxy-3-propyl benzene **16**, allyl hexyl ether **17** and ((4-(allyloxy) butoxy) methyl)benzene **18** were prepared according to literature procedures from benzylation or allylation reactions of the commercially available alcohols.[6] Spectroscopic data of **12**[7], **13**[8], **14**[9], **15**[10], **16**[11] and **18**[8] was identical to those reported.

Dec-9-enyl benzoate **10**: colourless oil; IR ν_{max} 2927, 2855, 1719, 1270, 1111 cm^{-1}; ^{1}H NMR δ 8.04 (d, *J* = 7.0 Hz, 2H, ArH2 and 6), 7.54 (t, *J* = 7.0 Hz, 1H, ArH4), 7.43 (t, *J* = 7.0 Hz, 2H, ArH3 and 5), 5.82−5.77 (m, 1H, H9′), 4.99 (d, *J* = 17.0 Hz, 1H, H10′a), 4.93 (d, *J* = 10.0 Hz, 1H, H10′b), 4.31 (t, *J* = 7.0 Hz, 2H, H1′), 2.04 (dt, *J* = 7.0, 7.0 Hz, 2H, H8′), 1.77 (tt, *J* = 7.0, 7.0 Hz, 2H, H2′), 1.44 (dt, *J* = 7.0, 7.0 Hz, 2H, H3′), 1.41-1.32 (m, 8H, H4′, 5′, 6′ and 7′); ^{13}C NMR δ 166.7 (CO), 139.2 (C9′), 132.9 (ArC4), 130.7 (ArC1), 129.6 (ArC2 and 6), 128.4 (ArC3 and 5), 114.2 (C10′), 65.2 (C1′), 33.9(C8′), 29.5 (C2′), 29.3 (C7′), 29.1 (C6′), 29.0 (C5′), 28.8 (C4′), 26.1 (C3′); HRESIMS *m/z* 261.1846 $[MH]^+$, calcd for $C_{17}H_{25}O_2$ 261.1855.

(*E*)-Hex-4-enyl benzoate **11**: colourless oil; IR ν_{max} 2936, 2855, 1717, 1269, 1110 cm^{-1}; ^{1}H NMR δ 8.04 (d, *J* = 7.0 Hz, 2H, ArH2 and 6), 7.55 (t, *J* = 7.0 Hz, 1H, ArH4), 7.44 (t, *J* = 7.0 Hz, 2H, ArH3 and 5), 5.50−5.40 (m, 2H, H4′ and 5′), 4.32(t, *J* = 7.0 Hz, 2H, H1′), 2.14 (dt, *J* = 7.0, 7.0 Hz, 2H, H3′), 1.83 (tt, *J* = 7.0, 7.0 Hz, 2H, H2′), 1.65 (d, *J* = 7.0 Hz, 3H, H6′); ^{13}C NMR δ 166.8 (COO), 132.9 (ArC4), 130.6 (ArC1), 130.1 (C4′), 129.7 (ArC2 and 6), 128.5 (ArC3 and 5), 126.0 (C5′), 64.6 (C1′), 29.1 (C3′), 28.7 (C2′), 18.0 (C6′); HRESIMS *m/z* 205.1237 $[MH]^+$, calcd for $C_{13}H_{17}O_2$ 205.1229.

Allyl-5-hexenyl ether **17**: colourless oil; IR ν_{max} 2925, 2855, 1104, 993, 909 cm^{-1}; ^{1}H NMR δ ^{1}H NMR δ 5.95-5.87 (m, 1H, H2), 5.85−5.76 (m, 1H, H5′), 5.26 (d, *J* = 17.5, 1H, H1a), 5.16 (d, *J* = 10.0, 1H, H1b), 5.00 (d, *J* = 17.5, 1H, H6′a), 4.94 (d, *J* = 10.5 Hz, 1H, H6′b), 3.96 (d, *J* = 5.5 Hz, 1H, H3), 3.43 (t, *J* = 7.5 Hz, 1H, H1′), 2.07 (dt, *J* = 7.5, 7.5 Hz, 1H, H4′), 1.61 (tt, *J* = 7.5, 7.5 Hz, 1H, H2′), 1.46 (tt, *J* = 7.5, 7.5 Hz, 1H, H3′); ^{13}C NMR δ 138.8 (C5), 135.2 (C2), 116.7 (C1), 114.6 (C6′), 71.9 (C3), 70.3 (C1′), 33.7 (C4′), 29.3 (C2′), 25.6 (C3′); HRESIMS was non detectable.

4.2. General procedure for the DIB/TBHP protocol

To a solution of the substrate in n-butyl butanoate was added DIB (1−1.5 equiv.) and $Mg(OAc)_2$•$4H_2O$ (1 equiv.) at 0 °C. The resulting suspension was vigorously stirred and a solution of TBHP (6.0M in decane, 3−6 equiv.) was added. The solution was further stirred overnight at 0 °C (total consumption of starting material as indicated by TLC analysis) and then filtered. Diethyl ether was added to the filtrate (5 mL) and the solutiuon was washed with water (5 mL). The solution was dried ($MgSO_4$), evaporated and the residue was purified by flash column chromatography on silica gel using gradient or isocratic elution.

*4.2.1. (2S,2aR,6S,7aS,7bS,8R,9S)-7b-(1-butenyl)hexahydro-9-methyl-4H-2,2,6-(epoxy[1]propanyl[3]ylidene)furo[2,3,4-gh] pyrrolizin-10-one (**5**) and (2S,2aR,6S,7aS,7bS,8R,9S)-7b-[(1E)-buten-3-onyl]hexahydro-9-methyl-4H-2,2,6-(epoxy[1]propanyl [3]ylidene)furo[2,3,4-gh]pyrrolizin-10-one (**6**)*

The title compounds were obtained using the general procedure described above from **3** (80.4 mg, 0.21 mmol), *n*-butyl butanoate (l mL), DIB (67.3 mg, 0.21 mmol), $Mg(OAc)_2$•$4H_2O$ (44.8 mg, 0.21 mmol) and TBHP (125.4 µL, 0.63mmol). Separation of the crude reaction products by column chromatography using gradient elution from 100% EtOAc to MeOH/EtOAc (1:4) gave 29.0 mg (51%) of **5** and 8.0 mg (13%) of **6**.

5: Pale yellow gum; $[\alpha]_D^{25}$ +23 (*c* 2.3, $CHCl_3$); IR ν_{max} 2966, 2885, 1786, 1664, 1021, 968 cm^{-1}; ^{1}H NMR δ 5.79 (dt, *J* = 15.5, 6.3 Hz, 1H, H-2′), 5.49 (d, *J* = 15.5 Hz, 1H, H-1′), 4.29 (br s, 1H, H-2), 3.47 (br s, 1H, H-9a), 3.13 (ddd, *J* = 15.5, 10.5, 5.5 Hz, 1H, H-5a), 3.02 (ddd, *J* = 13.0, 8.5, 5.0 Hz, 1H, H-5b), 2.84 (d, *J* = 6.0 Hz, 1H, H-7), 2.79 (dq, 1H, *J* = 11.5, 7.0, H-10), 2.11−2.06 (m, 1H, H-3′), 1.94−1.89 (m, 1H, H-1a), 1.93−1.88 (m, 1H, H-9), 1.86−1.79 (m, 1H, H-6a), 1.80−1.74 (m, 1H, H-1b), 1.77−1.70 (m, 1H, H-6b), 1.27 (d, *J* = 7.5 Hz, 3H, H-12), 1.00 (t, *J* = 7.5 Hz, 3H, H-4′); ^{13}C NMR δ 178.4 (C-11), 133.6 (C-2′), 126.6 (C-1′), 109.3 (C-8), 83.4 (C-3), 81.0 (C-2), 61.1 (C-9a), 51.4 (C-7), 45.8 (C-9), 48.2 (C-5), 35.9 (C-10), 32.5 (C-1), 26.9 (C-6), 25.5 (C-3′), 13.6 (C-4′), 13.4 (C-12); HRESIMS *m/z* 276.1604 $[MH]^+$, calcd for $C_{16}H_{22}NO_3$ 276.1600.

6: Pale yellow gum; IR ν_{max} 2967, 2914, 1787, 1664, 1021, 967 cm^{-1}; $[\alpha]_D^{25}$ +8 (*c* 1.6, $CHCl_3$); ^{1}H NMR δ 6.80 (d, *J* = 16.0 Hz, 1H, H-1′), 6.39 (d, *J* = 16.0 Hz, 1H, H-2′), 4.40 (br s, 1H, H-2), 3.53 (br s, 1H, H-9a), 3.15−3.04 (m, 2H, H-5), 2.94 (d, *J* = 5.0 Hz, 1H, H-7), 2.79 (dq, 1H, *J* = 12.0, 7.0, H-10), 2.29 (s, 3H, H-4′), 2.04−1.98 (m, 1H, H-1a), 2.01−1.96 (m, 1H, H-9), 1.88−1.82 (m, 2H, H-6), 1.85−1.79 (m, 1H, H-1b), 1.29 (d, *J* = 6.5 Hz, 3H, H-12); ^{13}C NMR δ 198.0 (C-3′), 177.9 (C-11), 143.5 (C-1′), 130.7 (C-2′), 109.2 (C-8), 83.5 (C-3), 80.3 (C-2), 61.3 (C-9a), 52.6 (C-7), 45.7 (C-9), 48.3 (C-5), 35.9 (C-10), 32.3 (C-1), 27.9 (C-4′), 26.7 (C-6), 13.3 (C-12); HRESIMS *m/z* 290.1389 $[MH]^+$, calcd for $C_{16}H_{20}NO_4$ 290.1392.

*4.2.2. Synthesis of **6** by oxidation of ketone **5***

This was achieved by the general procedure using **5** (6.9 mg, 0.025 mmol), *n*-butyl butanoate (l mL), DIB (64.4mg, 8 equiv., 0.20 mmol), $Mg(OAc)_2$•$4H_2O$ (5.4 mg, 1 equiv., 0.025 mmol) and TBHP (120.0 µL, 24 equiv., 0.60 mmol) to give 2.6 mg (42%) of enone **6** after column chromatography using gradient elution from 100% EtOAc to MeOH/EtOAc (1:4).

*4.2.3. Oxidation of stemofoline **7***

This was achieved by the general procedure using **7** (19.3 mg, 0.05 mmol), *n*-butyl butanoate (l mL), DIB (16.1 mg, 0.05 mmol), $Mg(OAc)_2$•$4H_2O$ (10.7 mg, 0.05 mmol) and TBHP (30.0 µL, 0.15 mmol) to give 8.0 mg (58%) of the known lactone **8**, after column chromatography using gradient elution from 100% EtOAc to MeOH/EtOAc (1:4). The product was spectroscopically identical to that reported.[2]

*4.2.4. 4-Oxohex-5-enyl benzoate (**9a**).*

The title compound was obtained using the general procedure described above from **9** (22.2 mg, 0.11 mmol), *n*-butyl butanoate (l mL), DIB (34.8 mg, 0.11 mmol), $Mg(OAc)_2$•$4H_2O$ (23.2 mg, 0.11 mmol) and TBHP (64.8 µL, 0.33 mmol). Purification by column chromatography using EtOAc/ether (15:85) as eluent gave 16.9 mg (72%) of **9a**. Colourless oil; IR ν_{max} 2959, 2902, 1716, 1675, 1270, 1110 cm^{-1}; ^{1}H NMR δ 8.03 (d, *J* = 7.0 Hz, 2H, ArH2 and 6), 7.56 (t, *J* = 7.0 Hz, 1H, ArH4), 7.44 (t, *J* = 7.0 Hz, 2H, ArH3 and 5), 6.38 (dd, *J* = 17.5, 7.5 Hz, 1H, H5′), 6.25 (d, *J* = 17.5 Hz, 1H, H6′a), 5.85 (d, *J* = 7.5 Hz, 1H, H6′b), 4.37 (t, *J* = 7.0 Hz, 2H, H1′), 2.77 (t, *J* = 7.0 Hz, 2H, H3′), 2.15−2.12 (m, 2H, H2′); ^{13}C NMR δ 199.7 (C4′), 166.7 (COO), 136.6 (C5′), 133.1 (ArC4), 129.7 (ArC2 and 6), 128.6 (C6′), 128.5 (ArC1, 3 and 5), 64.3 (C1′), 36.1(C3′), 23.2 (C2′); HRESIMS *m/z* 219.1028 $[MH]^+$, calcd for $C_{13}H_{15}O_3$ 219.1021.

*4.2.5. 8-Oxodec-9-enyl benzoate (**10a**)*

The title compound was obtained using the general procedure described above from **10** (32.8 mg, 0.13 mmol), *n*-butyl butanoate (l mL), DIB (40.6mg, 0.13 mmol), $Mg(OAc)_2$•$4H_2O$ (27.0 mg, 0.13 mmol) and TBHP (75.6 µL, 0.39 mmol). Purification by column chromatography using gradient elution from 100% ether to EtOAc/ether (1:1) gave 15.7 mg (46%) of **10a**. Colourless oil; IR ν_{max} 2931, 2859, 1718, 1271, 1112 cm^{-1}; ^{1}H NMR δ 7.97 (d, *J* = 7.5 Hz, 2H, ArH2 and 6), 7.48 (t, *J* = 7.5 Hz, 1H, ArH4), 7.37 (t, *J* = 7.5 Hz, 2H, ArH3 and 5), 6.28 (dd, *J* = 17.5, 10.5 Hz, 1H, H9′), 6.14 (d, *J* = 17.5 Hz, 1H, H10′a), 5.74 (d, *J* = 10.5 Hz, 1H, H10′b), 4.24 (t, *J* = 7.0 Hz, 2H, H1′), 2.51 (t, *J* = 7.0 Hz, 2H, H7′), 1.70 (tt, *J* = 7.0, 7.0 Hz, 2H, H2′), 1.57 (tt, *J* = 7.0, 7.0 Hz, 2H, H6′), 1.41−1.38 (m, 2H, H3′), 1.34−1.25 (m, 4H, H4′ and 5′); ^{13}C NMR δ 201.1 (C8′), 166.8 (COO), 136.7 (C9′), 132.9 (ArC4), 130.6 (ArC1), 129.7 (ArC2 and 6), 128.5 (ArC3 and 5), 128.0 (C10′), 65.2 (C1′), 39.7 (C7′), 28.8 (C2′), 29.2 (C4′ and 5′), 26.0 (C3′), 24.0 (C6′); HRESIMS *m/z* 275.1647 $[MH]^+$, calcd for $C_{17}H_{23}O_3$ 275.1647.

*4.2.6. (E)-3-Oxohex-4-enyl benzoate (**11a**)*

The title compound was obtained using the general procedure described above from **11** (52.8 mg, 0.26 mmol), *n*-butyl butanoate (l mL), DIB (83.8 mg, 0.26 mmol) , $Mg(OAc)_2$•$4H_2O$ (55.8 mg, 0.26 mmol) and TBHP (156.0 µL, 0.78 mmol). Purification by column chromatography using gradient elution from 100% ether to EtOAc/ether (1:1) gave 12.0 mg (21%) of **9a**, 8.4 mg of **11a** (15%) and 15.4 mg of **11b** (27%). Compound **11b** was spectroscopically identical to that reported.[12] **11a**: colourless oil. ^{1}H NMR δ 8.00 (d, *J* = 7.0 Hz, 2H, ArH2 and 6), 7.55 (t, *J* = 7.0 Hz, 1H, ArH4), 7.43 (t, *J* = 7.0 Hz, 2H, ArH3 and 5), 6.91 (dq, *J* = 15.0, 7.0 Hz, 1H, H5′), 6.18 (d, *J* = 15.0 Hz, 1H, H4′), 4.64 (t, *J* = 7.0 Hz, 2H, H1′), 3.01 (tt, *J* = 7.0, 7.0 Hz, 2H, H2′), 1.92 (d, *J* = 7.0 Hz, 3H, H6′); ^{13}C NMR δ 197.2 (C3′), 166.6 (COO), 144.0 (C5′), 132.1 (ArC4 and C4′), 129.7 (ArC2 and 6), 128.5 (ArC1, 3 and 5), 60.4 (C1′), 38.7 (C2′), 18.5 (C6′); HRESIMS *m/z* 219.1029 $[MH]^+$, calcd for $C_{13}H_{15}O_3$ 219.1021.

*4.2.7. Oxidation of benzyl-5-hexenyl ether **12***

This was achieved by the general procedure using **12** (42.2 mg, 0.22 mmol), *n*-butyl butanoate (l mL), DIB (70.9 mg, 0.22 mmol), $Mg(OAc)_2$•$4H_2O$ (47.2 mg, 0.22 mmol) and TBHP (132.0 µL, 0.66 mmol) to give 27.2 mg (61%) of **9**, 7.8 mg of **9a** (16%) and 0.9 mg of **12a** (2%) after column chromatography using gradient elution from 100% ether to EtOAc/ether (1:9), Compound **12a** was spectroscopically identical to that reported.[13]

*4.2.8. 3-Phenylpropyl acrylate **13a***

The title compound was obtained using the general procedure described above from **13** (107.7 mg, 0.61 mmol), ethyl acetate (1 mL), DIB (296.3 mg, 1.5 equiv., 0.92 mmol), $Mg(OAc)_2$•$4H_2O$ (130.8 mg, 0.61 mmol) and TBHP (549.0 µL, 4.5 equiv., 2.75 mmol) to give 104.2 mg (90%) of **13a** after column chromatography using gradient elution from 100% ether to EtOAc/ether (1:9). Compound **13a** was spectroscopically identical to that reported.[14]

*4.2.9. 3-Phenylpropyl benzoate **14a***

The title compound was obtained using the general procedure described above from **14** (102.7 mg, 0.45 mmol), ethyl acetate (1 mL), DIB (217.4 mg, 1.5 equiv., 0.68 mmol), $Mg(OAc)_2$•$4H_2O$ (96.5 mg, 0.45mmol) and TBHP (405.0 µL, 4.5 equiv., 2.03 mmol) to give 102.5 mg (95%) of **14a** after column chromatography using gradient elution from 100% ether to EtOAc/ether (1:9). Compound **14a** was spectroscopically identical to that reported.[15]

*4.2.10. Hexyl benzoate **15a***

The title compound was obtained using the general procedure described above from **15** (108.8 mg, 0.57 mmol), ethyl acetate (1 mL), DIB (277.0 mg, 1.5 equiv., 0.86 mmol), $Mg(OAc)_2$•$4H_2O$ (122.3 mg, 0.57mmol) and TBHP (684.0 µL, 6.0 equiv., 3.42 mmol) to give 109.2 mg (93%) of **15a** after column chromatography using gradient elution from 100% ether to EtOAc/ether (1:9). Compound **15a** was spectroscopically identical to that reported.[16]

*4.2.11. Hexyl acrylate **16a***

The title compound was obtained using the general procedure described above from **16** (70.3 mg, 0.50 mmol), ethyl acetate (1 mL), DIB (241.6 mg, 1.5 equiv., 0.75 mmol), $Mg(OAc)_2$•$4H_2O$ (107.2 mg, 0.50 mmol) and TBHP (600.0 µL, 6.0 equiv., 3.0 mmol) to give 71.0 mg (91%) of **16a** after column chromatography using gradient elution from 100% ether to EtOAc/ether (1:9). Compound **16a** was spectroscopically identical to that reported.[17]

*4.2.12. Hex-5-enyl acrylate (**17a**)*

The title compound was obtained using the general procedure described above from **17** (106.8 mg, 0.76 mmol), ethyl acetate (1 mL), DIB (367.2 mg, 1.5 equiv., 1.14 mmol), $Mg(OAc)_2$•$4H_2O$ (163.0 mg, 0.76 mmol) and TBHP (912.0 µL, 6.0 equiv., 4.56 mmol). Purification by column chromatography using gradient elution from 100% ether to EtOAc/ether (1:1) gave 103.2 mg (88%) of **17a**. Colourless oil; IR ν_{max} 2959, 2902, 1716, 1675, 1270, 1110 cm^{-1}; ^{1}H NMR δ 6.40(d, *J* = 17.5, 1H, H1a), 6.12 (dd, *J* = 17.5, 10.5, 1H, H2), 5.82 (d, *J* = 10.5, 1H, H1b), 5.83−5.76 (m, 1H, H5′), 5.02 (d, *J* = 17.0, 1H, H6′a), 4.97 (d, *J* = 10.0 Hz, 1H, H6′b), 4.16 (t, *J* = 7.0 Hz, 1H, H1′), 2.09 (dt, *J* = 7.0, 7.0 Hz, 1H, H4′), 1.69 (tt, *J* = 7.0, 7.0 Hz, 1H, H2′), 1.48 (tt, *J* = 7.0, 7.0 Hz, 1H, H3′); ^{13}C NMR δ 166.7 (COO), 138.5 (C5), 130.6 (C1),

128.4 (C2), 115.0 (C6′), 64.6 (C1′), 33.4 (C4′), 28.1 (C2′), 25.3 (C3′); HRESIMS *m/z* 155.1439 $[MH]^+$, calcd for $C_9H_{15}O_2$ 155.1072.

*4.2.13. 4-(Allyloxy) butyl benzoate (**18a**), 4-(benzyloxy) butyl acrylate (**18b**) and 4-(acryloxy) butyl benzoate (**18c**)*

The title compounds were obtained using the general procedure described above from **18** (220.3 mg, 1.0 mmol), ethyl acetate (1 mL), DIB (483.2 mg, 1.5 equiv., 1.5 mmol), $Mg(OAc)_2$•$4H_2O$ (214.5 mg, 1.0 mmol) and TBHP (1,200.0 µL, 6.0 equiv., 6.0 mmol). Purification by column chromatography using gradient elution from 100% ether to EtOAc/ether.(1:1) gave 84.2 mg (25%) of **18a**, 32.8 mg of **18b** (25%) and 99.2 mg of **18c** (40%).

18a: Colourless oil; IR ν_{max} 2959, 2902, 1716, 1675, 1270, 1110 cm^{-1}; ^1H NMR δ 8.04 (d, *J* = 7.5 Hz, 2H, ArH2 and 6), 7.55 (t, *J* = 7.5 Hz, 1H, ArH4), 7.43 (t, *J* = 7.5 Hz, 2H, ArH3 and 5), 5.96−5.87 (m, 1H, H7′), 5.28 (d, *J* = 17.5 Hz, 1H, H8′a), 5.17 (d, *J* = 10.0 Hz, 1H, H8′b),4.35(t, *J* = 7.0 Hz, 2H, H1′), 3.98 (d, *J* = 5.5 Hz, 2H, H6′), 3.50 (t, *J* = 6.0 Hz, 2H, H4′), 1.87 (tt, *J* = 7.0, 6.5 Hz, 2H, H2′), 1.77 (tt, *J* = 7.0, 6.0 Hz, 2H, H3′); ^{13}C NMR δ 166.8 (COO), 135.1 (C7′), 132.9 (ArC4), 130.6 (ArC1), 129.7 (ArC2 and 6), 128.5 (ArC3 and 5), 116.8 (C8′), 71.8 (C6′), 70.0 (C4′), 64.8 (C1′), 26.4 (C3′), 25.6(C2′); HRESIMS *m/z* 235 $[MH]^+$, calcd for $C_{14}H_{19}O_3$ 235.

18b: Colourless oil; IR ν_{max} 2959, 2902, 1716, 1675, 1270, 1110 cm^{-1}; ^1H NMR δ 7.58−7.54 (m, 2H, ArH2 and 6), 7.47−7.41 (m, 1H, ArH3, 4 and 5), 6.39 (d, *J* = 17.5 Hz, 1H, H8′a), 6.15−6.08 (m, 1H, H7′), 5.80 (d, *J* = 10.0 Hz, 1H, H8′b), 4.51 (br. s, 2H, *Ph*-C<u>H</u>$_2$-O), 4.18 (t, *J* = 6.0 Hz, 2H, H4′), 3.51 (t, *J* = 6.0 Hz, 2H, H1′), 1.78 (tt, *J* = 7.0, 6.0 Hz , 2H, H3′), 1.71 (tt, *J* = 7.0, 6.0 Hz, 2H, H2′); ^{13}C NMR δ 166.5 (COO), 137.5 (ArC1), 133.0 (ArC2 and 6), 130.9 (C8′), 128.6 (C7′), 128.5 (ArC3, 4 and 5), 73.1 (*Ph*-<u>C</u>H$_2$-O), 69.8 (C1′), 64.4 (C4′), 26.3 (C2′), 25.8(C3′); HRESIMS *m/z* 235 $[MH]^+$, calcd for $C_{14}H_{19}O_3$ 235.

18c: Light brown oil; IR ν_{max} 2959, 2902, 1716, 1675, 1270, 1110 cm^{-1}; ^1H NMR δ 8.04 (d, *J* = 7.5 Hz, 2H, ArH2 and 6), 7.55 (t, *J* = 7.5 Hz, 1H, ArH4), 7.44 (t, *J* = 7.5 Hz, 2H, ArH3 and 5), 6.41 (d, *J* = 17.5 Hz, 1H, H8′a), 6.13 (dd, *J* = 17.5, 10.0, 1H, H7′), 5.82 (d, *J* = 10.0 Hz, 1H, H8′b),4.37(t, *J* = 6.0 Hz, 2H, H1′), 4.24 (t, *J* = 6.0 Hz, 2H, H4′), 1.92−1.82(m, 2H, H2′), 1.91−1.81(m, 2H, H3′); ^{13}C NMR δ 166.7 (COO), 166.3 (C6′),133.1 (ArC4), 130.9 (C8′), 130.4 (ArC1), 129.7 (ArC2 and 6), 128.5 (C7′ and ArC3 and 5), 64.5 (C1′ and 4′), 25.5 (C2′ and 3′); HRESIMS *m/z* 249.1132 $[MH]^+$, calcd for $C_{14}H_{17}O_4$ 249.1127.

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Supplementary Material

Copies of the ^1H NMR spectra of all compounds. This material is available free of charge via the internet at.