Tributyltin hydride-mediated radical cyclisation of carbonyls to form functionalised oxygen and nitrogen heterocycles

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The tributyltin hydride-mediated cyclisation of unsaturated ethers and amines bearing an aldehyde or α,β-unsaturated ketone group is reported. Cyclisation proceeds *via* reversible addition of the tributyltin radical to the carbonyl double bond to form an intermediate *O*-stannyl ketyl. This nucleophilic radical can add intramolecularly to electron-rich double bonds to form substituted 5- or 6-membered rings. The efficiency of the cyclisation to form, for example, hydroxytetrahydrofurans, chromanols or quinolones, is shown to depend on the nature of the acceptor double bond and also on the stability of the intermediate *O*-stannyl ketyl. Thus, resonance-stabilised allylic or benzylic *O*-stannyl ketyl radicals have been shown, for the first time, to have a particular application in slow radical cyclisations leading to butyrolactones or pyrans.

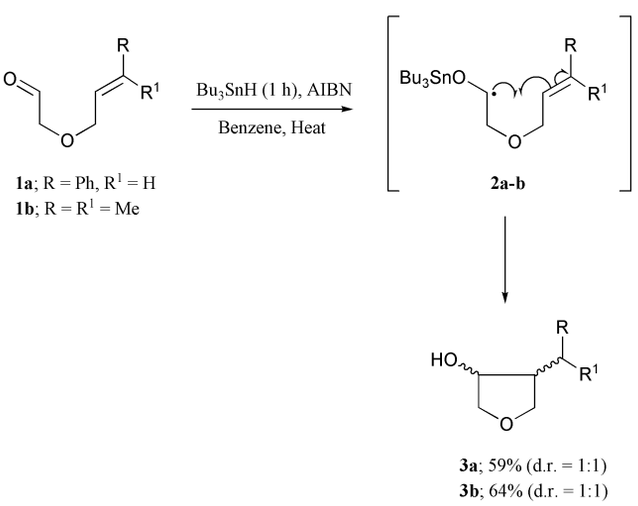
1 Introduction

The cyclisation of unsaturated organohalides, or related compounds, using tributyltin hydride has attracted considerable synthetic interest in recent years.[1] A wide variety of 5- and 6-membered rings in particular, can be prepared under mild, neutral reaction conditions using this method of cyclisation. However, one important drawback to these types of radical reaction is the loss of two functional groups (*e.g.* C–X and C=C) on cyclisation of the halide precursor to form the cyclic product. To avoid this, other methods of radical cyclisation have been developed including atom transfer reactions, which typically use hexabutylditin[2] or alternative transition metal catalysts[3] to tributyltin hydride. In contrast, Enholm and co-workers have investigated the reaction of tributyltin hydride with unsaturated aldehydes, rather than halides, to form cyclopentanes bearing a versatile hydroxy group.[4] These reactions proceed *via* addition of the tributyltin radical to the carbonyl double bond to form an intermediate *O*-stannyl ketyl, which can undergo cyclisation onto an alkene double bond. Allylic *O*-stannyl ketyls were also shown to undergo related cyclisations leading to cyclopentanes possessing a ketone group.[5] In these reactions an activating or electron-withdrawing group on the alkene double bond was found to be essential for cyclisation and related reactions have also been investigated using oxime acceptors.[6] Recently, we have extended this method of cyclisation of alkenes to the formation of substituted pyrrolidines and piperidines.[7] Both *O*-stannyl ketyls and allylic *O*-stannyl ketyls were shown to undergo cyclisation, onto electron-rich or -poor alkenes, to produce 5- or 6-membered nitrogen heterocycles. Having established that these nucleophilic radicals can undergo cyclisation on to electron-rich alkenes, we now describe the use of this method in the synthesis of hydroxy tetrahydrofurans, chromanols and quinolones.[8] Prior to this work, we were only aware of an isolated report of a related ketyl cyclisation reaction [mediated by tributyltin hydride or samarium(II) iodide] on to an electron-poor (unsaturated ester) double bond leading to a substituted tetrahydrofuran.[9]

2 Results and discussion

2.1 *O*-Stannyl ketyl cyclisations

2.1.1 Tetrahydrofurans and tetrahydropyrans. Initial work concentrated on the formation and cyclisation of aldehydes **1a**,**b** (Scheme 1). These were prepared by mono-alkylation of



1a; R = Ph, R^1 = H
1b; R = R^1 = Me

2a-b

3a; 59% (d.r. = 1:1)
3b; 64% (d.r. = 1:1)

Scheme 1

ethylene glycol using potassium hydroxide and cinnamyl bromide or prenyl bromide in DMSO,[10] followed by Swern oxidation of the resulting primary alcohols in 46–58% overall yield. The cyclisation of **1a**,**b** was then investigated by reaction with tributyltin hydride. Slow addition of tributyltin hydride (1.1 equiv.) and AIBN (0.3 equiv.) over 1 h, to a solution of **1a**,**b** (1 equiv.) in boiling degassed benzene produced the desired hydroxy tetrahydrofurans **3a**,**b** in 59–64% yield. The cyclic products were isolated as a 1 : 1 mixture of diastereoisomers (as indicated by the NMR spectra), which proved to be inseparable

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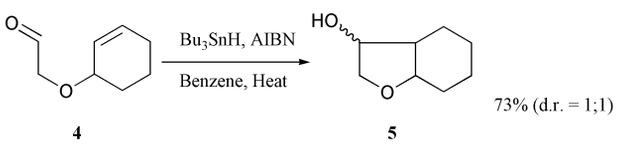
by column chromatography on silica. These reactions are expected to proceed *via* 5-*exo*-*trig* cyclisation of the intermediate *O*-stannyl ketyls **2a**,**b** followed by hydrogen-atom transfer from tributyltin hydride and hydrolysis of the tributyltin alkoxide on aqueous work-up. Interestingly, no alicyclic alcohols, derived from reaction of **2a**,**b** with tributyltin hydride, were isolated from these reactions. This contrasts with the reaction of tin hydride with (*Z*)-undec-5-enal, which showed a preference for simple reduction over cyclisation under similar reaction conditions.[4] Presumably, *O*-stannyl ketyl cyclisation to form tetrahydrofurans is faster than cyclisation to give cyclopentanes because of the introduction of an oxygen atom within the chain, which affects both the length of the chain and bond angles (*i.e.* 106.8° *versus* 109° for C–O–C and C–C–C, respectively).[11]

The synthesis of bicyclic compounds is also possible as illustrated by the cyclisation of the cyclohexenyl aldehyde **4** (Scheme 2). Under the same reaction conditions as employed for



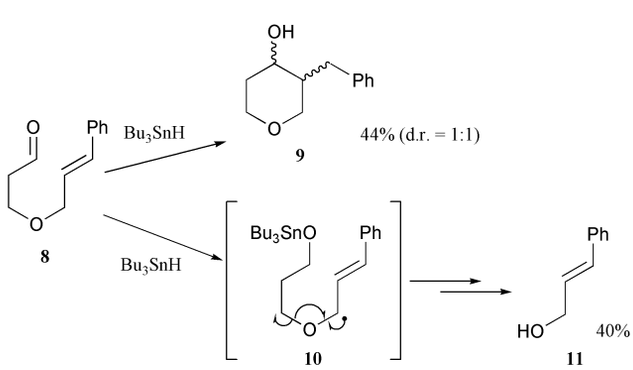
4 **5**

Scheme 2

1a,**b**, the cyclisation of **4** proceeded smoothly to afford octahydrobenzofuran **5** in an excellent 73% yield after column chromatography. This compound was isolated as an inseparable 1 : 1 mixture of diastereoisomers as indicated by both the ^{1}H and ^{13}C NMR spectra. Whereas aldehydes **1a**,**b** and **4** underwent facile cyclisation, reaction of the related ketone **6** with tributyltin hydride gave no cyclised product and only unreacted starting material was recovered. A similar result was observed on reaction of the unsaturated ester **7** with tributyltin hydride. None of the desired cyclic product was observed in the crude ^{1}H NMR spectrum and this may be attributed to the conformational effects of the ester group, which is known to lower the rate of radical cyclisation (in related systems).[12]

6 **7**

This method of cyclisation could also be applied to the formation of a tetrahydropyran (Scheme 3). Reaction of

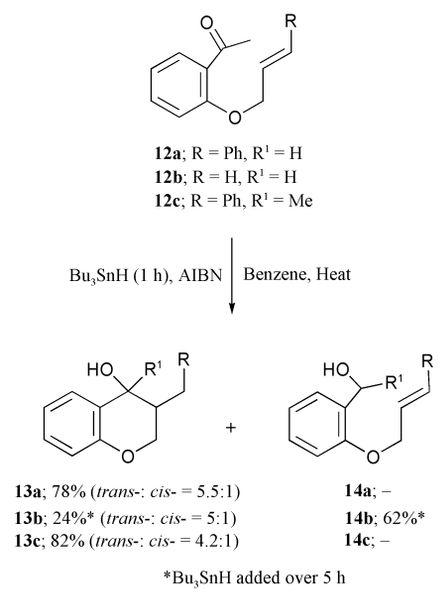


8 **9** **10** **11**

Scheme 3

aldehyde **8** with tributyltin hydride (added over 1 h) produced the desired 6-ring product **9** in 44% yield (as a 1 : 1 mixture of diastereoisomers). The lower yield of **9**, compared to tetrahydrofuran **3b**, is presumably due to the slower rate of 6-*exo*-*trig* radical cyclisation and the possibility of a competing 1,5-hydrogen atom transfer.[13] Indeed, the reaction of **8** also resulted in the isolation of cinnamyl alcohol **11** (in 40% yield), which may have been formed *via* an initial 1,5-hydrogen atom transfer. The resultant allylic radical **10** could then undergo fragmentation to form cinnamaldehyde, which may be reduced with a further equivalent of tributyltin hydride to give **11**. As for the 5-*exo* cyclisations, no simple reduction of **8** was observed and this contrasts with the related reaction of citronellal with tributyltin hydride.[4] In this case, only trace amounts of the cyclised product were isolated while the simple reduced product (citronellol) was formed in 95% yield.

2.1.2 Chromanols. The cyclisation of aromatic aldehydes was then investigated with a view to making chromanols. This novel method of cyclisation would complement the variety of other synthetic approaches, which have been developed to prepare these biologically important compounds.[14] Reaction of the benzaldehyde derivative **12a**, prepared by *O*-alkylation of 2-hydroxybenzaldehyde,[15] with tributyltin hydride (under the same conditions as for **1a**,**b**) produced chromanol **13a**, as a 5.5 : 1 mixture of separable *trans*–*cis* isomers, in an excellent 78% yield (Scheme 4). The assignment of stereochemistry was based



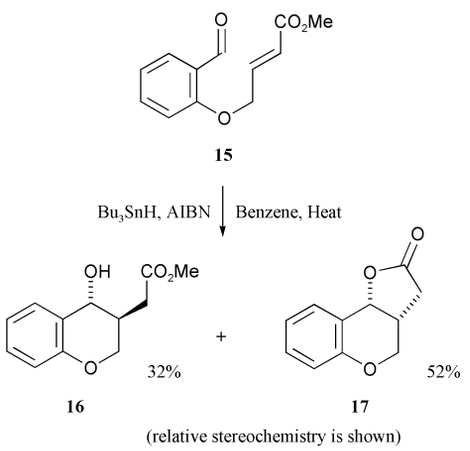
Scheme 4

on NMR data, which was compared with literature values.[16] A similar diastereoisomer ratio was observed when the tributyltin hydride was added to **12a** over 5 rather than 1 h. This contrasts with the much lower yield of 44% for tetrahydropyran **9**, which was isolated as an equal mixture of diastereoisomers. The introduction of a benzene ring, which is expected to lead to the formation of a more stable *O*-stannyl ketyl, clearly has a pronounced effect on both the efficiency and stereoselectivity of the 6-*exo*-*trig* cyclisation. Hence, the formation of a relatively stable *O*-stannyl ketyl radical, could lead to a reversible radical cyclisation,[17] which may explain the predominance of the thermodynamically more stable *trans*-isomer of **13a**.

Changing the substituents on the alkene acceptor also influences the 6-*exo* cyclisation. When the corresponding *O*-allyl derivative **12b** was treated under the same conditions the main product was benzyl alcohol **14b**, which was derived from simple reduction. Even when the tributyltin hydride was added over 5 h (rather than 1 h), benzyl alcohol **14b** was formed in 62% yield while chromanol **13b** was only isolated in 24% yield. Chromanol **13b** was isolated as an inseparable 5 : 1 mixture of diastereoisomers, the major isomer of which was tentatively assigned (from the NMR spectra) as the *trans*-isomer. Cyclisation of aromatic ketones, as well as aldehydes, is also possible as illustrated by the reaction of the acetophenone derivative

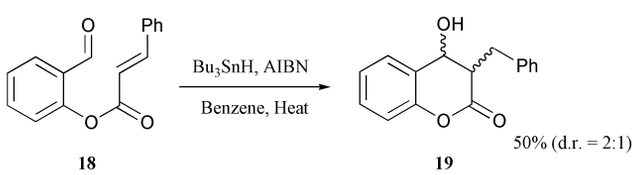
12c. This underwent cyclisation to afford chromanol **13c**, as an inseparable (4.2 : 1) mixture of diastereoisomers, in an excellent 82% yield. The relative stereochemistry of the major diastereoisomer was tentatively assigned as *trans*-, with respect to the hydroxy and benzyl groups, on the basis of NOE experiments. For example, for the major isomer, irradiation of the methyl group at C-4 resulted in an enhancement of the signals due to both benzylic hydrogens at C-3. The benzene ring clearly plays an important role in facilitating the cyclisation of ketone **12c**, as the related aliphatic ketone **6** failed to undergo 5-*exo* cyclisation under the same conditions.

The influence of the acceptor double bond was further examined by the preparation of unsaturated ester **15** (Scheme 5). On being heated with tributyltin hydride, cyclisation of



Scheme 5

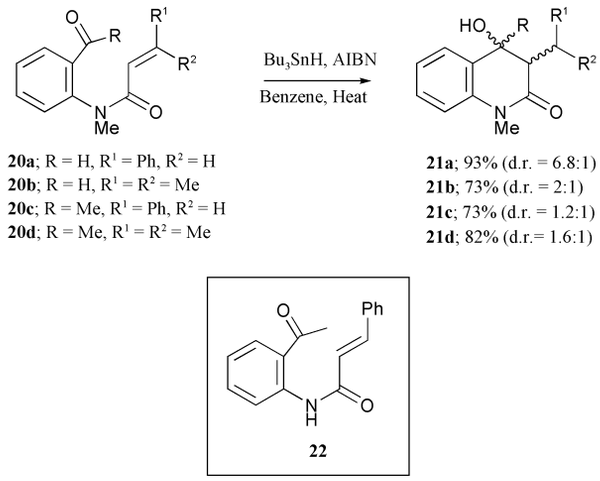
15 was observed to give an inseparable mixture of *trans*-substituted chromanol **16** and tricyclic lactone **17** (in a 1 : 1.6 ratio) in a combined 84% yield. The tricycle **17** is thought to arise *via* a second, non-radical cyclisation, which involves attack of the intermediate tin alkoxide on to the ester. None of the bicyclic *cis*-chromanol was isolated, which indicates that the lactonisation occurs rapidly under the reaction conditions. The facile cyclisation of **15**, which involves attack of the intermediate *O*-stannyl ketyl on to an electron-poor (rather than electron-rich) double bond, is therefore consistent with the efficient carbocyclisations (of unsaturated esters) reported previously.[4,5] Indeed, cyclisation on to an electron-poor double bond could also be used to prepare chromanones as illustrated by the cyclisation of ester **18** to give lactone **19** in 50% yield (as a 2 : 1 mixture of diastereoisomers) (Scheme 6).



Scheme 6

2.1.3 Quinolines. Following the successful formation of a chromanone, our attention turned to the preparation of quinolines. Quinoline alkaloids are found in the *Rutaceae* family of plants and over two hundred examples have been isolated.[18] The synthesis of these compounds is of interest because of the variety of important biological properties, including anti-bacterial, anti-fungal and anti-viral activities, which they exhibit.

Initially, amino-benzaldehydes **20a**,**b** were prepared by reduction of *N*-methyl isatoic anhydride followed by *N*-acylation and oxidation of the alcohol (Scheme 7). On reaction with tributyltin hydride both **20a** and **20b**, underwent 6-*exo* cyclisation to

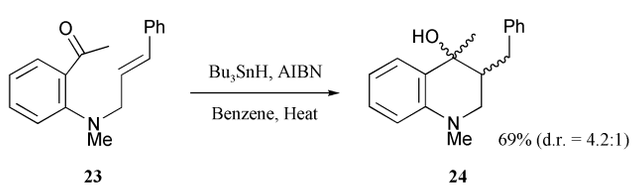


Scheme 7

form the desired hydroxy-dihydroquinolinones **21a** and **21b**, respectively. Whereas cyclisation of **20a** produced **21a** as a 6.8 : 1 mixture of diastereoisomers in 93% yield, the cyclisation of **20b** was less efficient (73%) and less stereoselective (2 : 1 mixture of diastereoisomers). The stereochemistry of the major diastereomer of **21b** was tentatively assigned as *cis* on the basis of NOE experiments (which showed a correlation between the C-3 and C-4 hydrogens).

Similar results were obtained using the 2-aminoacetophenone derivatives **20c** and **20d**. In each case, the cyclisation proceeded smoothly and, after aqueous work-up and purification *via* column chromatography, dihydroquinolinones **21c** and **21d** were isolated in excellent yield (*i.e.* 73% and 82%, respectively). Both cyclisations proceeded so as to form a similar ratio of diastereoisomers (*i.e.* 1.2 : 1 and 1.6 : 1). It should be noted that the *N*-methyl substituent plays an important role in these cyclisations, as reaction of the related secondary amide **22** with tributyltin hydride, produced only trace amounts (<3%) of the desired dihydroquinolinone. This is presumably due to the methyl group influencing the amide conformer population.[19]

Having established that unsaturated aryl amides derived from 2-aminoacetophenone undergo 6-*exo*-*trig* radical cyclisation, the synthesis and subsequent radical cyclisation of the unsaturated aryl amine **23** was also investigated (Scheme 8). Alkylation

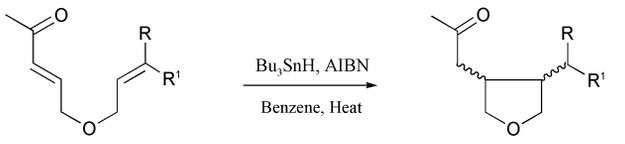


Scheme 8

of *N*-methyl-2-aminoacetophenone with cinnamyl bromide proceeded smoothly using potassium carbonate in refluxing acetone and the desired unsaturated aryl amine **23** was isolated in 64% yield. On heating **23** with tributyltin hydride and AIBN, it was pleasing to see the formation of the desired tetrahydroquinoline **24** as a 4.2 : 1 mixture of inseparable diastereoisomers in 69% yield. Cyclisation onto electron-rich, as well as electron-poor alkenes can therefore be used to prepare tetrahydroquinoline derivatives.

2.2 Allylic *O*-stannyl ketyl cyclisations

As the cyclisation of *O*-stannyl ketyls proved such an effective route to a variety of 5- and 6-ring heterocycles, our attention turned to the cyclisation of related allylic *O*-stannyl ketyls. This required the formation of precursor α,β-unsaturated ketones and compounds **25a**–**d** were readily prepared from the



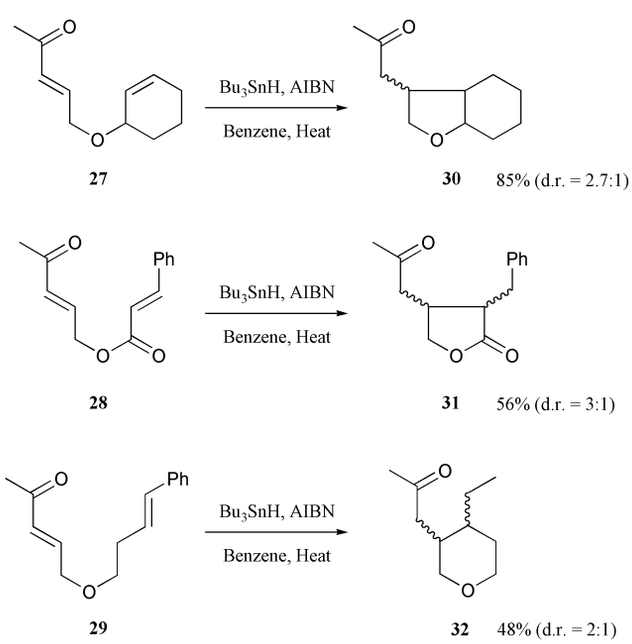
25a; R = R^1 = H
25b; R = Me, R^1 = H
25c; R = R^1 = Me
25d; R = Ph, R^1 = H

26a; 50% (*trans*-:*cis*- = 3.1:1)
26b; 80% (*trans*-:*cis*- = 3.7:1)
26c; 63% (*trans*-:*cis*- = 9.0:1)
26d; 82% (*trans*-:*cis*- = 1.8:1)

Scheme 9

corresponding aldehydes and Ph_3P=CHCOMe (Scheme 9). In each case, only the *E*-alkene isomer was formed in the Wittig reaction, as indicated by the ^{1}H NMR spectra. On reaction with tributyltin hydride, ketones **25a**–**d** underwent cyclisation to give the expected disubstituted tetrahydrofurans **26a**–**d** in 50–82% yield. The *trans*-diastereomers of **26a**–**d** were the major products isolated from each of these reactions and the stereochemistry was assigned on the basis of γ-*gauche* effects in the ^{13}C NMR spectra. For example, for **26a**, the CH_3CH carbon in the *cis*-isomer is more shielded (δ 13.4 ppm) than that in the *trans*-isomer (δ 16.6 ppm). The predominant formation of the thermodynamically more stable *trans*-isomer in each of these reactions could be explained by reversible radical cyclisation mechanisms.[3,17] Clearly, the substituents on the alkene double bond are expected to influence the reversibility of these reactions, and the electronic/steric effects of the two methyl groups could explain the surprisingly high diastereoselectivity observed for cyclisation of the trisubstituted alkene **26c**. In this case, cyclisation produces a tertiary carbon-centred radical which is expected to react less rapidly with Bu_3SnH than secondary or particularly, primary carbon-centred radicals formed on cyclisation of **26a**,**b**. The fact that the cyclisation of **26d** showed a much lower preference for the *trans*-isomer could reflect the increased stability of the intermediate benzylic radical, which is expected to lower the rate of fragmentation leading to ring-opening.

Similar cyclisations can be used to prepare bicyclic, butyrolactone and tetrahydropyran ring systems as shown by the cyclisation of methyl ketones **27**–**29** (Scheme 10). Reaction of



27 **30** 85% (d.r. = 2.7:1)

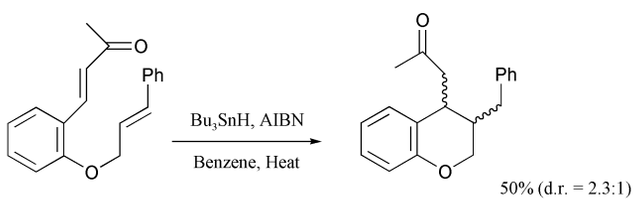
28 **31** 56% (d.r. = 3:1)

29 **32** 48% (d.r. = 2:1)

Scheme 10

27 with tributyltin hydride afforded the substituted octahydrobenzofuran **30** in 85% yield as a 2.7 : 1.0 mixture of inseparable diastereoisomers. A similar result was obtained on reaction of unsaturated ketone **28**, which produced butyrolactone **31** in 56% yield as a 3 : 1 mixture of (inseparable) *trans*–*cis* isomers, respectively. The stereochemistry was assigned on the basis of the ^{13}C NMR spectrum and confirmed by base-induced epimerisation using DBU in refluxing toluene, which produced a 10 : 1 mixture of *trans*–*cis* isomers, respectively. This contrasts with reaction of the related aldehyde **7** (under similar conditions), which did not lead to any butyrolactone. Cyclisations of similar unsaturated esters are known to be relatively slow[12] and so the intermediacy of a longer-lived allylic *O*-stannyl ketyl (compared to the *O*-stannyl ketyl) appears to be crucial, presumably because this allows time for the radical to cyclise onto the unsaturated ester double bond. An allylic *O*-stannyl ketyl can also undergo 6-*exo*-*trig* cyclisation and reaction of the unsaturated ketone **29** with tributyltin hydride afforded tetrahydropyran **32** in 48% yield (as a 2 : 1 mixture of diastereoisomers). It is of interest to note that no 4-phenylbut-3-en-1-ol, derived from a competitive 1,5-hydrogen atom abstraction mechanism, was isolated in this case. This may be attributed to the increased stability of the intermediate allylic ketyl radical compared to the radical derived from the corresponding aldehyde **8**.

Finally, the use of an allylic *O*-stannyl ketyl radical cyclisation to prepare a chroman was investigated as shown in Scheme 11. On being heated with tributyltin hydride, diene **33** underwent 6-*exo*-*trig* cyclisation to form chroman **34** in 50% yield (as a 2.3 : 1 mixture of diastereoisomers).



33 **34**

Scheme 11

3 Conclusions

This work has demonstrated that aldehydes and α,β-unsaturated ketones can undergo radical cyclisation to form substituted tetrahydrofurans, tetrahydropyrans, chromanols, quinolinones and related compounds on reaction with tributyltin hydride. The intermediate *O*-stannyl ketyls or allylic *O*-stannyl ketyls, which are nucleophilic, have been shown to cyclise onto a variety of electron-rich double bonds to give a range of 5- and 6-membered heterocycles. In general, the yields are good, particularly for the 5-*exo*-*trig* cyclisation reactions, and those involving allylic *O*-stannyl ketyls range from 50 to 85%. Many of these cyclisations are believed to be reversible, especially those involving allylic or benzylic *O*-stannyl ketyls. The importance of using these types of radical in relatively slow 6-*exo*-*trig* or unsaturated ester radical cyclisation reactions is reported for the first time.

4 Experimental

^{1}H and ^{13}C NMR spectra were recorded using a JEOL EX 270 MHz or Bruker DPX 400 MHz spectrometer; the carbon spectra were recorded at 67.5 MHz and these were assigned with the aid of DEPT and/or COSY experiments. Coupling constants (*J*) were recorded to the nearest 0.5 Hz. IR spectra were recorded on an ATI Mattson Genesis Series FT IR spectrometer or a Perkin–Elmer Paragon 1000 FT IR spectrometer. Mass spectra were recorded on a Fisons Instruments VG Analytical Autospec spectrometer system for both low and high resolution EI and CI spectra. Thin layer chromatography was performed on Merck 5554 aluminium-backed silica gel plates

and compounds were visualised by UV light or by staining with alkaline potassium permanganate solution. Column chromatography was carried out under gravity using silica gel (Fisons Matrex Silica 60, 70–200 microns or Fluorochem Ltd, Silica gel 60, 35–70 microns) and the specified eluant. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The Chemical Analytical Services Unit at the University of Newcastle performed the elemental analyses. Petroleum ether refers to the fraction of boiling range 40–60 °C. Tributyltin hydride was purchased from Lancaster Synthesis Ltd and distilled before use. Experimental procedures for the preparation of the following compounds are given in the supplementary information: (*E*)-(3-phenylprop-2-enyloxy)-ethanal **1a**; (3-methylbut-2-enyloxy)ethanal **1b**; (cyclohex-2-enyloxy)ethanal **4**; (*E*)-3-phenylprop-2-enyloxypropan-2-one **6**; (*E*)-3-(3-phenylprop-2-enyloxy)propanal **8**; (*E*)-2-(3-phenylprop-2-enyloxy)benzaldehyde **12a**; 2-allyloxybenzaldehyde **12b**; (*E*)-1-[2-(3-phenylprop-2-enyloxy)phenyl]ethanone **12c**; (*E*)-methyl 4-(2-formylphenoxy)but-2-enoate **15**; (*E*)-2-formylphenyl 3-phenylprop-2-enoate **18**; (*E*)-*N*-(2-formylphenyl)-*N*-methyl-3-phenylprop-2-enamide **20a**; *N*-(2-formylphenyl)-*N*,3-dimethylbut-2-enamide **20b**; (*E*)-*N*-(2-acetylphenyl)-*N*-methyl-3-phenylprop-2-enamide **20c**; *N*-(2-acetylphenyl)-*N*,3-dimethylbut-2-enamide **20d**; (*E*)-1-[2-(*N*-methyl-3-phenylprop-2-enylamino)phenyl]ethanone **23**; (*E*)-5-(allyloxy)pent-3-en-2-one **25a**; (3*E*)-5-[(*E*)-but-2-enyloxy]pent-3-ene-2-one **25b**; (*E*)-5-(3-methylbut-2-enyloxy)pent-3-en-2-one **25c**; (3*E*)-5-[(*E*)-3-phenylprop-2-enyloxy]pent-3-en-2-one **25d**; (*E*)-5-cyclohex-2-enyloxypent-3-en-2-one **27**; (*E*)-4-oxopent-2-enyl (*E*)-3-phenylprop-2-enoate **28**; (3*E*)-5-[(*E*)-4-phenylbut-3-enyloxy]pent-3-en-2-one **29**; (3*E*)-4-{2-[(*E*)-3-phenylprop-2-enyloxy]phenyl}-but-3-en-2-one **33**.

General procedure for tributyltin hydride mediated radical cyclisation

To a stirred solution of the aldehyde/methyl ketone (0.025 M, 0.13–0.22 g, 0.76–1.57 mmol, 1.0 equiv.) and degassed benzene (30–63 cm^3) at reflux, under an atmosphere of nitrogen/argon, was added a solution of tributyltin hydride (0.042 M, 0.24–0.50 g, 0.84–1.73 mmol, 1.1 equiv.), AIBN (0.025–0.038 g, 0.15–0.23 mmol, 0.3 equiv.) and degassed benzene (20–41 cm^3) over 1 h *via* a syringe pump. The reaction mixture was stirred at reflux until consumption of starting material was indicated by TLC analysis (4–24 h) and then cooled to rt. The benzene was then removed *in vacuo* and the resultant residue was dissolved in EtOAc (20–30 cm^3) and stirred vigorously (2–4 h) with an aqueous potassium fluoride solution (10%, 20–30 cm^3). The solution was filtered and the organic layer was separated, washed with water (2 × 20 cm^3) and brine (2 × 20 cm^3), dried over anhydrous $MgSO_4$, filtered and evaporated to dryness to afford crude product. Purification *via* column chromatography (silica) afforded the desired cyclic products (0.03–0.19 g, 24–85%).

(3*RS*,4*RS*)-4-Benzyltetrahydrofuran-3-ol 3a. Oil; 59% (1.0 : 1.0 mixture of inseparable diastereoisomers); R_f 0.25 (1 : 1, petroleum ether–EtOAc); ν_{max}/cm^{-1} (thin film) 3609 (m), 3490 (m), 2942 (m), 2867 (m), 1495 (w), 1454 (w), 1073 (m) and 1052 (m); δ_H (270 MHz, $CDCl_3$) 7.50–7.10 (5H, m, C*H*, Ar), 4.30–4.10 (1H, m, C*H*OH), 4.06–3.45 (4H, m, CH_2OCH_2), 2.95 (1H, dd, *J* 13.5 and 8.0, CH_AH_BPh), 2.80–2.50 (1H, m, CH_AH_BPh), 2.45–2.37 (1H, m, $PhCH_2CH$), 2.00–1.88 (1H, m, CHO*H*); δ_C (67.90 MHz, $CDCl_3$) 139.6 (q, Ar), 128.7 (*C*H, Ar), 128.5 (*C*H, Ar), 128.5 (*C*H, Ar), 126.3 (*C*H, Ar) and 126.1 (*C*H, Ar), 76.3 (*C*HOH), 74.4 and 71.7 (CH_2O), 49.7 ($CHCH_2Ph$), 37.4 (CH_2Ph); *m*/*z* (CI, NH_3) 196 ($M + NH_4^+$, 100%), 161 (7), 143 (6), 117 (11), 105 (9), 91 (13) and 35 (23); [Found: $M + NH_4^+$ (CI, NH_3) 196.1335. $C_{11}H_{14}O_2$ requires $M + NH_4^+$ 196.1338].

The presence of a further diastereoisomer was indicated by ^{13}C NMR spectroscopy; δ_C (67.90 MHz, $CDCl_3$) 140.3 (q, Ar), 128.7 (*C*H, Ar), 128.5 (*C*H, Ar), 128.5 (*C*H, Ar), 126.3 (*C*H, Ar) and 126.1 (*C*H, Ar), 72.4 (*C*HOH), 71.0 (CH_2CHCH_2Ph), 67.1 (CH_2CHOH), 46.4 ($CHCH_2Ph$), 31.8 (CH_2Ph).

(3*RS*,4*RS*)-4-Isopropyltetrahydrofuran-3-ol 3b. Oil; 64% (1.0 : 1.0 mixture of inseparable diastereoisomers); R_f 0.2 (2 : 1, Et_2O–petroleum ether); ν_{max}/cm^{-1} (thin film) 3416 (s, br), 2957 (s), 1469 (s) and 1077 (m); δ_H (270 MHz, $CDCl_3$) 4.32–3.70 (4H, m, OCH_2 and CCH_ACH_B and HOC*H*), 3.68–3.45 (1H, m, CCH_ACH_B), 2.12–1.48 [3H, m, C*H*C*H*$(CH_3)_2$ and HOC*H*], 1.12 (3H, d, *J* 7.0, $CHCH_3$), 1.00 (3H, d, *J* 7.0, $CHCH_3$); δ_C (67.90 MHz, $CDCl_3$) 77.0 (*C*HOH), 76.8 and 71.6 (CH_2O), 53.1 [*C*HCH$(CH_3)_2$], 30.0 [*C*H$(CH_3)_2$], 21.4 [CH(*C*H$_3)_2$], 21.0 [CH(*C*H$_3)_2$]; *m*/*z* (CI, NH_3) 148 ($M + NH_4^+$, 100%) 113 (27) and 35 (38); [Found: $M + NH_4^+$ (CI, NH_3) 148.1337. $C_7H_{14}O_2$ requires $M + NH_4^+$ 148.1338].

The presence of a further diastereoisomer was indicated by ^{13}C NMR spectroscopy; δ_C (67.90 MHz, $CDCl_3$) 72.5 (*C*HOH), 56.0 [*C*HCH$(CH_3)_2$], 26.1 [*C*H$(CH_3)_2$], 22.2 [CH(*C*H$_3)_2$], 22.0 [CH(*C*H$_3)_2$].

(3*RS*,3*aR,7*aR*)-Octahydro-1-benzofuran-3-ol 5.**[20] Oil; 73% (1.0 : 1.0 mixture of diastereoisomers); R_f 0.15 (2 : 1, isohexane–EtOAc); ν_{max}/cm^{-1} (thin film) 3397 (s, br), 2934 (s), 2863 (m), 1448 (w), 1117 (m) and 1022 (m); δ_H (270 MHz, $CDCl_3$) 4.22 (1H, dd, *J* 10.0 and 4.5, OCH_AH_B), 4.15 (1H, appt. q, *J* 3.5, OC*H*CH), 4.12–4.07 (1H, m, C*H*OH), 3.68–3.60 (1H, m, OCH_AH_B), 2.05–1.95 (1H, m, OCHC*H*), 1.80–1.08 (8H, m, $CH_2CH_2CH_2CH_2$); δ_C (67.90 MHz, $CDCl_3$) 77.8 (HO*C*H), 75.2 (O*C*H), 72.2 (OCH_2), 46.6 (OCH*C*H), 27.8 (OCH*C*H$_2$); *m*/*z* (CI, NH_3) 160 ($M + NH_4^+$, 75%), 141 (100) and 123 (60); [Found: $M + NH_4^+$ (CI, NH_3) 160.1333. $C_6H_{12}O_2$ requires $M + NH_4^+$ 160.1338].

The presence of a further diastereoisomer was indicated by ^1H and ^{13}C NMR spectroscopy; δ_H (270 MHz, $CDCl_3$) 4.55 (1H, m, C*H*OH), 4.02 (1H, dd, *J* 9.0 and 8.0, OCH_AH_B), 3.93 (1H, appt. q, *J* 3.5, OC*H*CH), 3.67–3.61 (2H, m, OCH_AH_B and OCH_ACH_B), 1.89–1.81 (1H, m, OCHC*H*), 1.40 (8H, m, $CH_2CH_2CH_2CH_2$); δ_C (67.90 MHz, $CDCl_3$) 76.7 (HO*C*H), 74.8 (O*C*HCH), 74.6 (OCH_2), 41.6 (OCH*C*H), 28.5 (OCH*C*H$_2$), 23.8 ($CH_2CH_2CH_2$), 21.0 ($CH_2CH_2CH_2$), 20.6 ($CH_2CH_2CH_2$).

(3*RS*,4*RS*)-3-Benzyltetrahydropyran-4-ol 9.[21] Oil; 44% (1.0 : 1.0 mixture of inseparable diastereoisomers); R_f 0.25 (2 : 1, isohexane–EtOAc); ν_{max}/cm^{-1} (thin film) 3520 (s), 2956 (m), 1455 (m), 1052 (m), 923 (m) and 724 (w); δ_H (270 MHz, $CDCl_3$) 7.42–7.10 (5H, m, C*H*, Ar), 3.70–3.58 (2H, m, OCH_2), 3.40 (1H, dt, *J* 11.5 and 2.5, $OCH_AH_BCH_2$), 3.10–3.00 (1H, m, $OCH_AH_BCH_2$), 2.66 (1H, dd, *J* 13.5 and 7.5, CH_AH_BPh), 2.55 (1H, dd, *J* 13.5 and 8.5, CH_AH_BPh), 2.15–1.70 (3H, m, OCH_2CH_2CHOH and $CHCH_2Ph$); δ_C (67.90 MHz, $CDCl_3$) 139.8 (q, Ar), 128.8, 128.7, 127.9 and 126.0 (*C*H, Ar), 71.8 (HO*C*H), 70.4 (CH_2O), 66.8 (CH_2O), 46.3 ($PhCH_2CH$), 35.5 ($PhCH_2CH$), 33.7 (OCH_2CH_2); *m*/*z* (CI, NH_3) 194 ($M + H^+$, 100%).

The presence of a further diastereoisomer was indicated by ^1H and ^{13}C spectroscopy; δ_H (270 MHz, $CDCl_3$) 3.10–3.00 (1H, m, CH_AH_BPh), 2.35 (1H, dd *J* 14.0 and 9.5, CH_AH_BPh); δ_C (67.90 MHz, $CDCl_3$) 139.5 (q, Ar), 128.8, 128.7, 127.9 and 126.0 (*C*H, Ar), 67.6 (CH_2O), 63.6 (CH_2O), 66.3 (HO*C*H), 43.2 ($PhCH_2CH$), 35.4 ($PhCH_2CH$), 33.6 (OCH_2CH_2).

(3*R,4*RS*)-3-Benzylchroman-4-ol 13a.**[16] White solid; 78% (5.5 : 1.0 mixture of diastereoisomers). Major diastereoisomer: R_f 0.25 (2 : 1, Et_2O–petroleum ether); m.p 137–138 °C (lit.,[16] 138–139 °C); ν_{max}/cm^{-1} ($CHCl_3$) 3603 (s), 2923 (s), 1488 (s), 1454 (s), 797 (s), 490 (s) and 683 (s); δ_H (270 MHz, $CDCl_3$) 7.34–7.13 (7H, m, C*H*, Ar), 6.90–6.85 (2H, m, C*H*, Ar), 4.52–4.48

(1H, m, C*H*OH), 4.22 (1H, dd, *J* 11.0 and 2.5, OCH_AH_B), 3.97 (1H, dd, *J* 11.0 and 4.5, OCH$_A$$H_B$), 2.72 (1H, dd, *J* 13.5 and 6.5, CH_AH_BPh), 2.54 (1H, dd, *J* 13.5 and 9.5, CH$_A$$H_B$Ph), 2.30–2.17 (1H, m, C*H*CH$_2$Ph), 1.90 (1H, s, br, O*H*); δ_C (67.90 MHz, $CDCl_3$) 154.2 (q, Ar), 139.2 (q, Ar), 130.1, 129.8, 129.1, 128.5, 126.3, 123.2, 120.9 and 116.9 (*C*H, Ar), 67.6 (*C*HOH), 64.6 (*C*H$_2$O), 41.5 (*C*HCH$_2$Ph), 34.6 (*C*H$_2$Ph); *m*/*z* (EI) 240 (M^+, 55%), 148 (100), 131 (40), 121 (55) and 91 (70); [Found: M^+ (EI) 240.1153. $C_{16}H_{16}O_2$ requires M + H^+ 240.1150].

Minor diastereoisomer: R_f 0.32 (2 : 1, Et_2O–petroleum ether); δ_H (270 MHz, $CDCl_3$) 7.42–715 (7H, m, C*H*, Ar), 7.00–6.83 (2H, m, C*H*, Ar), 4.54–4.49 (1H, m, HOC*H*), 4.18–4.07 (2H, m, OCH_2), 2.90 (1H, dd, *J* 14.0 and 8.5, OCH_AH_B), 2.70 (1H, dd, *J* 13.5 and 7.0, OCH$_A$$H_B$), 2.40–2.22 (1H, m, C*H*CH$_2$Ph), 1.73 (1H, s, CHO*H*); δ_C (67.90 MHz, $CDCl_3$) 155.1 (q, Ar), 140.2 (q, Ar), 123.0 (q, Ar), 129.6, 129.4, 128.6, 128.1, 125.8, 120.0 and 116.4 (*C*H, Ar), 64.5 (*C*H$_2$O and *C*HOH), 39.5 (*C*HCH$_2$Ph), 32.4 (*C*H$_2$Ph).

(3*RS*,4*RS*)-3-Methylchroman-4-ol 13b.[22] Oil; 24% (1.0 : 1.3 mixture of inseparable diastereoisomers); R_f 0.4 (1 : 1, isohexane–Et_2O); ν_{max}/cm^{-1} (thin film) 3398 (s, br), 2958 (m), 2926 (s), 1603 (m), 1489 (s), 1226 (s), 1047 (m) and 754 (s); δ_H (270 MHz, $CDCl_3$) 7.08–6.78 (4H, m, C*H*, Ar), 4.35 (1H, d, *J* 5.5, C*H*OH), 4.20 (1H, dd, *J* 3.0 and 11.0, OCH_AH_B), 3.90 (1H, dd, *J* 11.0 and 6.0, OCH$_A$$H_B$), 1.00 (3H, d, *J* 7.5, CHCH_3); *m*/*z* (EI) 164 (M^+, 70%), 122 (100), 106 (46), 78 (44), 41 (57); [Found: M^+ (EI) 164.0838. $C_{10}H_{12}O_2$ requires M^+ 164.0832].

The presence of a minor diastereoisomer was indicated by ^{1}H NMR spectroscopy; δ_H (270 MHz, $CDCl_3$) 1.10 (3H, d, *J* 7.5, CHCH_3).

[2-(Allyloxy)phenyl]methanol 14b. Oil; 62%. The presence of this compound was indicated by ^{1}H NMR spectroscopy; δ_H (270 MHz, $CDCl_3$) 7.08–6.78 (4H, m, CH, Ar), 6.15–5.98 (1H, m, CH=CH$_2$), 5.41 (1H, dd, *J* 16.0 and 0.3, CH=CH$_2$), 5.35 (1H, dd, *J* 10.0 and 0.3, CH=CH$_2$), 4.70 (2H, s, CH$_2$OH), 4.61–4.52 (2H, m, OCH$_2$).

(3*RS*,4*RS*)-3-Benzyl-4-methylchroman-4-ol 13c. Oil; 82% (4.0 : 1.0 mixture of inseparable diastereoisomers); R_f 0.3 (2 : 1, isohexane–EtOAc); ν_{max}/cm^{-1} (Nujol) 3407 (s), 1608 (m), 1582 (m), 1488 (s), 1453 (s), 1225 (s), 2980 (m), 2933 (m), 1043 (m), 756 (s) and 705 (m); δ_H (270 MHz, $CDCl_3$) 7.48–7.44 (1H, m, C*H*, Ar), 7.27–7.05 (6H, m, C*H*, Ar), 6.89–6.85 (1H, m, C*H*, Ar), 6.77–6.71 (1H, m, C*H*, Ar), 4.10 (1H, dd, *J* 11.5 and 3.0 OCH_AH_B), 3.82 (1H, dd, *J* 11.5 and 8.0, OCH$_A$$H_B$), 3.06 (1H, m, PhC$H_AH_B$), 2.33–2.18 (2H, m, PhCH$_A$$H_B$ and C*H*CH$_2$Ph), 1.82 (1H, s, br, CHO*H*), 1.52 (3H, s, CH_3); δ_C (67.90 MHz, $CDCl_3$) 153.0 (q, Ar), 139.8 (q, Ar), 128.9, 128.6, 128.4, 126.4, 121.0 and 117.0 (*C*H, Ar), 70.0 [*C*(CH$_3$)OH], 65.7 (O*C*H$_2$), 45.7 (*C*H$_2$Ph), 32.1 (*C*HCH$_2$Ph), 25.7 (*C*H$_3$); *m*/*z* (CI, NH_3) 254 [M(–H_2O) + H^+, 25%], 237 (100), 136 (16), 121 (16), 91 (17); [Found: M(–H_2O) + H^+, (CI, NH_3) 254.1314. $C_{17}H_{18}O_2$ requires: M(–H_2O) + H^+, 254.1307].

The presence of a minor diastereoisomer was indicated by ^{1}H and ^{13}C NMR spectroscopy: δ_H (270 MHz, $CDCl_3$) 3.97 (1H, dd, *J* 7.5 and 2.5, OCH_AH_B), 3.84 (1H, dd, *J* 8.0 and 5.0, OCH$_A$$H_B$), 2.44 (1H, dd, *J* 9.0 and 8.0, PhCH_AH_B), 2.16–2.08 (1H, m, C*H*CH$_2$Ph), 1.63 (3H, s, CH_3); δ_C (67.90 MHz, $CDCl_3$) 153.6 (q, Ar), 140.1 (q, Ar), 128.9, 128.6, 128.4, 126.4, 121.0 and 117.0 (*C*H, Ar), 69.1 [*C*(CH$_3$)OH], 65.4 (O*C*H$_2$), 44.3 (*C*H$_2$Ph), 31.6 (*C*HCH$_2$Ph), 22.9 (*C*H$_3$).

(3*R,4*S*)-Methyl 4-hydroxy-3,4-dihydro-2*H*-chromen-3-yl-acetate 16 and (3*R**,4*R*)-3a,9b-dihydro-4*H*-furo[3,2-*c*]chromen-2(3*H*)-one 17.** Oil; 84%, 1.0 : 1.6 inseparable mixture of **16** : **17**, respectively; R_f 0.25 (1 : 1, EtOAc–petroleum ether); ν_{max}/cm^{-1} (thin film) 3483 (s, br), 2953 (m), 1772 (s), 1734 (s), 1612 (m), 1585 (m), 1489 (m), 1269 (m), 1227 (s), 1165 (s), 760 (s) and 735 (s).

Chromanol **16**: δ_H (270 MHz, $CDCl_3$) 7.47–6.72 (4H, m, Ar), 4.43 (1H, d, *J* 4.5, C*H*OH), 4.30 (1H, dd, *J* 11.5 and 2.5, OCH_AH_B), 4.02 (1H, dd, *J* 11.0 and 5.0, OCH$_A$$H_B$), 3.66 (3H, s, CO$_2CH_3$), 3.04 (1H, s, br, CHO*H*), 3.00–2.90 (1H, m, OCH$_2$C*H*), 2.48–2.28 (2H, m, CHCH_AH_BCOCH$_3$); δ_C (67.90 MHz, $CDCl_3$) 172.5 (*C*O$_2$CH$_3$), 153.8 (q, Ar), 129.8 (*C*H, Ar), 129.4 (*C*H, Ar), 118.3 (*C*H, Ar), 67.3 (*C*HOH), 65.2 (O*C*H$_2$), 51.6 (CO$_2$*C*H$_3$), 36.4 (*C*HCH$_2$CO$_2$CH$_3$), 32.8 (*C*H$_2$CO$_2$CH$_3$), 30.9 (*C*H$_2$CO$_2$CH$_3$); *m*/*z* (EI) 222 (M^+, 20%), 190 (80), 148 (98), 131 (100), 121 (56), 39 (38) and 32 (40); [Found: M^+ (EI), 222.0895. $C_{12}H_{14}O_4$ requires M^+ 222.0892].

The presence of **17** was indicated by ^{1}H and ^{13}C NMR spectroscopy; δ_H (270 MHz, $CDCl_3$) 7.47–6.72 (4H, m, C*H*, Ar), 5.42 (1H, d, *J* 6.0, C*H*OCO), 4.16 (1H, dd, *J* 11.5 and 4.0, OCH_AH_B), 3.76 (1H, dd, *J* 11.5 and 9.5, OCH$_A$$H_B$), 3.00–2.90 (1H, m, OCH$_2$C*H*), 2.80 (1H, dd, *J* 17.5 and 8.5, CH_AH_BCO), 2.28–2.22 (1H, m, CH$_A$$H_B$CO); δ_C (67.90 MHz, $CDCl_3$) 175.4 (*C*=O), 154.9 (q, Ar), 131.2 (*C*H, Ar), 130.5 (*C*H, Ar), 123.0 (q, Ar), 121.7 (*C*H, Ar), 117.2 (*C*H, Ar), 74.1 (*C*HOCO), 64.6 (O*C*H$_2$), 36.4 (*C*HCH$_2$CO$_2$CH), 30.9 (CH*C*H$_2$CO); *m*/*z* (EI) 190 (M^+).

(3*RS*,4*RS*)-3-Benzyl-4-hydroxy-3,4-dihydrochromen-2-one 19. Oil; 50% (2.0 : 1.0 mixture of inseparable diastereoisomers); R_f 0.2 (2 : 1, isohexane–Et_2O); ν_{max}/cm^{-1} 3320 (s, br), 2958 (s), 1714 (s), 1610 (s), 1493 (s), 1492 (m), 1389 (m) and 1246 (m); δ_H (270 MHz, $CDCl_3$) 7.45–7.09 (9H, m, C*H*, Ar), 4.68 (1H, t, *J* 4.0, C*H*OH), 3.32–3.24 (1H, m, C*H*CH$_2$Ph), 3.05 (1H, dd, *J* 13.5 and 5.5, CH_AH_BPh), 2.75 (1H, dd, *J* 14.0 and 9.0, CH$_A$$H_B$Ph), 1.90 (1H, s, br, CHO*H*); δ_C (67.90 MHz, $CDCl_3$) 165.2 (*C*=O), 156.0 (q, Ar), 139.6 (q, Ar), 129.0 (*C*H, Ar), 128.8 (*C*H, Ar), 128.7 (*C*H, Ar), 128.1 (*C*H, Ar), 127.3 (*C*H, Ar), 124.4 (q, Ar), 126.1 (*C*H, Ar), 119.9 (*C*H, Ar), 117.3 (*C*H, Ar), 75.8 (*C*HOH), 56.6 (*C*HCH$_2$Ph), 34.4 (CH*C*H$_2$Ph); *m*/*z* (CI, NH_3) 272 (M + NH_4^+, 15%), 254 (40), 237 (100), 210 (20), 163 (15), 155 (24), 131 (15), 102 (18), 91 (14); [Found: M + NH_4^+ (CI, NH_3) 272.1287. $C_{16}H_{14}O_3$ requires M + NH_4^+ 272.1287].

The presence of a minor diastereoisomer was indicated by ^{13}C NMR spectroscopy; δ_C (67.90 MHz, $CDCl_3$) 163.8 (*C*=O), 150.8 (q, Ar), 137.3 (q, Ar), 124.4 (q, Ar), 68.2 (*C*HOH), 49.6 (*C*HCH$_2$Ph), 33.6 (CH*C*H$_2$Ph).

(3*R,4*R*)- and (3*R**,4*S*)-3-Benzyl-4-hydroxy-1-methyl-3,4-dihydroquinolin-2(1*H*)-one 21a.** Major diastereoisomer: oil; 81%; R_f 0.4 (7 : 3, EtOAc–petroleum ether); ν_{max}/cm^{-1} (thin film) 2933 (s), 2864 (s), 1689 (s), 1598 (s), 1456 (s), 1383 (m), 1286 (m), 991 (m) and 602 (m); δ_H (270 MHz, $CDCl_3$) 7.45–6.95 (9H, m, C*H*, Ar), 4.40 (1H, d, *J* 2.5, C*H*OH), 3.40 (3H, s, NCH_3), 3.20–3.12 (1H, m, C*H*CH$_2$Ph), 2.97 (1H, dd, *J* 15.0 and 6.0, PhCH$_A$$H_B$), 2.60 (1H, s, br, O*H*), 2.45 (1H, dd, *J* 15.0 and 9.0, PhCH_AH_B); δ_C (67.90 MHz, $CDCl_3$) 170.8 (*C*=O), 139.1 (q, Ar), 138.0 (q, Ar), 129.7 (*C*H, Ar), 129.0 (*C*H, Ar), 128.9 (*C*H, Ar), 128.5 (*C*H, Ar), 126.6 (*C*H, Ar), 125.4 (q, Ar), 123.3 (*C*H, Ar), 114.9 (*C*H, Ar), 68.8 (*C*HOH), 51.0 (PhCH$_2$*C*H), 34.5 (Ph*C*H$_2$), 29.6 (N*C*H$_3$); *m*/*z* (CI, NH_3) 285 (M + NH_4^+, 35%), 268 (M + H^+, 75), 250 (100), 176 (12) and 160 (45); [Found: M + H^+ (CI, NH_3) 268.1335. $C_{17}H_{17}NO_2$ requires M + H^+ 268.1338].

Minor diastereoisomer: oil; 12%; R_f 0.5 (7 : 3, EtOAc–petroleum ether); δ_H (270 MHz, $CDCl_3$) 7.45–6.90 (9H, m, C*H*, Ar), 4.44 (1H, d, *J* 3.0, C*H*OH), 3.55 (1H, dd, *J* 13.5 and 4.5, PhCH_AH_B), 3.40 (3H, s, NCH_3), 3.00 (1H, dd, *J* 13.5 and 10.0, PhCH$_A$$H_B$), 2.86–2.80 (1H, m, C*H*CH$_2$Ph); δ_C (67.90 MHz, $CDCl_3$) 170.0 (*C*=O), 139.8 (q, Ar), 139.6 (*C*H, Ar), 129.8 (*C*H, Ar), 129.3 (*C*H, Ar), 128.6 (*C*H, Ar), 128.1 (*C*H, Ar), 127.0 (q, Ar), 126.3 (*C*H, Ar), 122.9 (*C*H, Ar), 115.0 (*C*H, Ar), 66.8 (*C*HOH), 48.4 (PhCH$_2$*C*H), 31.4 (Ph*C*H$_2$), 29.8 (N*C*H$_3$).

(3*R,4*R*)- and (3*R**,4*S*)-4-Hydroxy-3-isopropyl-1-methyl-3,4-dihydroquinolin-2(1*H*)-one 21b.** Major diastereoisomer: white semi-solid; 48%; R_f 0.2 (1 : 1, EtOAc–petroleum ether); ν_{max}/cm^{-1} (thin film) 3402 (m, br), 3000 (s), 2404 (m), 1695 (s), 1598 (m), 1508 (m), 1405 (m), 1210 (s) and 900 (m); δ_H (270 MHz, $CDCl_3$) 7.42–7.22 (2H, m, C*H*, Ar), 7.13–6.93 (2H, m, C*H*, Ar), 4.70 (1H, d, *J* 3.0, C*H*OH), 3.34 (3H, s, NCH_3), 2.55 [1H, dd, *J* 9.5 and 3.0, C*H*CH(CH$_3$)$_2$], 1.59–1.32 [1H, m, C*H*(CH$_3$)$_2$], 1.00–0.80 [6H, m, CH(CH_3)$_2$]; δ_C (67.90 MHz, $CDCl_3$) 171.6 (*C*=O), 139.7 (q, Ar), 129.7 (*C*H, Ar), 129.3 (*C*H, Ar), 126.0 (q, Ar), 123.3 (*C*H, Ar), 115.0 (*C*H, Ar), 69.4 (*C*HOH), 56.8 [*C*HCH(CH$_3$)$_2$], 29.6 (N*C*H$_3$), 27.5 [*C*H(CH$_3$)$_2$], 21.2 (2 × CH$_3$); *m*/*z* (CI, NH_3) 220 (M + H$^+$, 100%), 202 (25) and 160 (15); [Found: M + H$^+$ (CI, NH_3) 220.1340. $C_{13}H_{17}NO_2$ requires M + H$^+$ 220.1338].

Minor diastereoisomer: white semi-solid; 25%; R_f 0.5 (1 : 1, EtOAc–petroleum ether); δ_H (270 MHz, $CDCl_3$) 7.42–7.27 (2H, m, C*H*, Ar), 7.12–6.90 (2H, m, C*H*, Ar), 4.92–4.89 (1H, m, C*H*OH), 3.38 (3H, s, NCH_3), 2.43–2.10 [2H, m, C*H*C*H*(CH$_3$)$_2$], 1.20–1.00 [6H, m, CH(CH_3)$_2$]; δ_C (67.90 MHz, $CDCl_3$) 170.3 (*C*=O), 139.7 (q, Ar), 129.3 (*C*H, Ar), 128.0 (q, Ar), 127.1 (*C*H, Ar), 122.8 (*C*H, Ar), 114.9 (*C*H, Ar), 68.0 (*C*HOH), 52.9 [*C*HCH(CH$_3$)$_2$], 29.6 (N*C*H$_3$), 25.4 [*C*H(CH$_3$)$_2$], 22.8 and 20.8 (2 × *C*H$_3$).

(3*R,4*S*)- and (3*R**,4*R*)-3-Benzyl-4-hydroxy-1,4-dimethyl-3,4-dihydroquinolin-2(1*H*)-one 21c.** Major diastereoisomer: white semi-solid; 40%; R_f 0.3 (1 : 1, petroleum ether–EtOAc); ν_{max}/cm^{-1} ($CHCl_3$) 3580 (s, br), 3010 (m), 1674 (s), 1603 (s), 1472 (m), 1374 (m), 1229 (w) and 702 (w); δ_H (270 MHz, $CDCl_3$) 7.62–7.51 (1H, C*H*, Ar), 7.37–6.91 (8H, m, C*H*, Ar), 3.32 (3H, s, NCH_3), 3.08–2.90 (2H, m, CH_2Ph), 2.71–2.43 [2H, m, C*H*CH$_2$Ph and C(O*H*)CH$_3$], 1.45 [3H, s, C(OH)CH_3]; δ_C (67.90 MHz, $CDCl_3$) 171.1 (*C*=O), 138.8 (q, Ar), 137.4 (q, Ar), 132.1 (q, Ar), 129.0, 128.9, 128.5, 128.3, 128.2, 126.3, 124.3, 123.6 and 114.4 (9 × *C*H, Ar), 72.1 [*C*(OH)CH$_3$], 56.1 (*C*HCH$_2$Ph), 32.9 (CH*C*H$_2$Ph), 29.4 and 29.2 [N*C*H$_3$ and C(OH)*C*H$_3$]; *m*/*z* (CI, NH_3) 282 (M + H$^+$, 100%), 264 (58), 174 (20); [Found: M + H$^+$ (CI, NH_3) 282.1491. $C_{18}H_{19}NO_2$ requires M + H$^+$ 282.1494].

Minor diastereoisomer: white semi-solid; 33%; R_f 0.4 (1 : 1, petroleum ether–EtOAc); δ_H (270 MHz, $CDCl_3$) 7.59–7.50 (1H, m, C*H*, Ar), 7.45–6.90 (8H, m, C*H*, Ar), 3.35 (3H, s, NCH_3), 3.23–3.10 (1H, m, CH_AH$_B$Ph), 3.08–2.88 (2H, m, CH_AH$_B$Ph and C*H*CH$_2$Ph), 2.30 [1H, s, br, C(O*H*)CH$_3$], 1.40 [3H, s, C(OH)CH_3]; δ_C (67.90 MHz, $CDCl_3$) 170.8 (*C*=O), 141.3 (q, Ar), 138.1 (q, Ar), 134.2 (q, Ar), 129.4, 129.2, 128.9, 128.5, 126.2, 124.0, 123.6, 115.1 (9 × *C*H, Ar), 72.5 [*C*(OH)CH$_3$], 60.6 (*C*HCH$_2$Ph), 55.5 (*C*HCH$_2$Ph), 30.9 (CH*C*H$_2$Ph), 30.1 (N*C*H$_3$), 23.5 [C(OH)*C*H$_3$].

(3*R,4*S*)- and (3*R**,4*R*)-4-Hydroxy-3-isopropyl-1,4-dimethyl-3,4-dihydroquinolin-2(1*H*)-one 21d.** Major diastereoisomer: white solid; 51%; R_f 0.25 (1 : 1, petroleum ether–EtOAc); (Found: C, 71.80; H, 8.54; N, 6.02. $C_{14}H_{19}NO_2$ requires C, 72.00; H, 8.20; N 6.00%); ν_{max}/cm^{-1} ($CHCl_3$) 3021 (s, br), 2399 (s), 1662 (s), 1602 (m), 1519 (m), 1473 (m), 1421 (m), 1369 (m), 1217 (s) and 927 (m); δ_H (270 MHz, $CDCl_3$) 7.51–7.61 (1H, m, C*H*, Ar), 7.36–7.21 (1H, m, C*H*, Ar), 7.18–7.08 (1H, m, C*H*, Ar), 7.00–6.90 (1H, m, C*H*, Ar), 3.40 (3H, s, NCH_3), 2.58 [1H, d, *J* 4.5, C*H*CH(CH$_3$)$_2$], 2.30–2.00 [1H, br s, C(O*H*)CH$_3$], 1.50 [3H, s, C(OH)CH_3], 1.47–1.20 [1H, m, C*H*(CH$_3$)$_2$], 1.10 [3H, d, *J* 7.0, CH(CH_3)$_2$], 0.56 [3H, d, *J* 7.0, CH(CH_3)$_2$]; δ_C (67.90 MHz, $CDCl_3$) 170.9 (*C*=O), 139.9 (q, Ar), 129.9 (q, Ar), 129.2, 124.5, 123.0, 114.9 (4 × *C*H, Ar), 71.3 [*C*(OH)CH$_3$], 60.2 [*C*HCH(CH$_3$)$_2$], 29.1 (N*C*H$_3$), 27.3 [*C*H(CH$_3$)$_2$], 24.1 [C(OH)*C*H$_3$], 24.1 and 18.5 [CH(*C*H$_3$)$_2$]; *m*/*z* (CI, NH_3) 234 (M + H$^+$, 100%) and 176 (20); [Found: M + H$^+$ (CI, NH_3) 234.1497. $C_{14}H_{19}NO_2$ requires 234.1494].

Minor diastereoisomer: white solid; 31%; R_f 0.4 (1 : 1, petroleum ether–EtOAc); δ_H (270 MHz, $CDCl_3$) 7.60–7.20 (2H, m, C*H*, Ar), 7.17–6.92 (2H, m, C*H*, Ar), 3.40 (3H, s, NCH_3), 3.00 [1H, s, br, C(O*H*)CH$_3$], 2.63 [1H, d, *J* 4.5, C*H*CH(CH$_3$)$_2$], 1.88–1.60 [4H, m, C(OH)CH_3 and C*H*(CH$_3$)$_2$], 1.08 [3H, d, *J* 7.0, CH(CH_3)$_2$], 0.50 [3H, d, *J* 7.0, CH(CH_3)$_2$]; δ_C (67.90 MHz, $CDCl_3$) 171.0 (*C*=O), 137.9 (q, Ar), 133.0 (q, Ar), 126.3, 123.8, 123.6, 114.3 (4 × *C*H, Ar), 72.2 [*C*(OH)CH$_3$], 60.3 [*C*HCH(CH$_3$)$_2$], 30.9 (N*C*H$_3$), 29.1 [C(OH)*C*H$_3$], 26.3 [*C*H(CH$_3$)$_2$], 24.4 and 19.3 [CH(*C*H$_3$)$_2$].

(3*RS*,4*RS*)-3-Benzyl-1,4-dimethyl-1,2,3,4-tetrahydroquinolin-4-ol 24. Oil; 69% (4.2 : 1.0 mixture of inseparable diastereoisomers); R_f 0.2 (1 : 1, petroleum ether–EtOAc); ν_{max}/cm^{-1} ($CHCl_3$) 3402 (s, br), 2929 (s), 2245 (w), 1604 (s), 1504 (s), 1344 (m), 1213 (m), 1113 (m), 910 (s) and 733 (s); δ_H (270 MHz, $CDCl_3$) 7.51–7.41 (1H, m, C*H*, Ar), 7.36–7.08 (6H, m, C*H*, Ar), 6.73–6.49 (2H, m, C*H*, Ar), 3.10–2.96 (1H, m, NCH_AH$_B$), 2.88–2.74 (1H, m, NCH$_A$$H_B$), 2.69 (3H, s, NC$H_3$), 2.22–2.00 (3H, m, C$H_2$Ph and C*H*CH$_2$Ph), 1.90 (1H, s, br, O*H*), 1.50 [3H, s, C(OH)CH_3]; δ_C (67.90 MHz, $CDCl_3$) 145.1 (q, Ar), 140.9 (q, Ar), 129.7 (q, Ar), 129.4 (*C*H, Ar) 129.3 (*C*H, Ar), 128.8 (*C*H, Ar), 128.5 (2 × *C*H, Ar), 126.2, 125.8 and 116.4 (3 × *C*H, Ar), 111.0 (*C*H, Ar), 71.7 [*C*(OH)CH$_3$], 51.4 (N*C*H$_2$CH), 46.7 (*C*HCH$_2$Ph), 39.0 (N*C*H$_3$), 33.9 (*C*H$_2$Ph), 25.8 [C(OH)*C*H$_3$]; *m*/*z* (CI, NH_3) 268 (M + H$^+$, 5%), 250 (100), 35 (12); [Found: M + H$^+$ (CI, NH_3) 268.1705. $C_{18}H_{21}NO$ requires 268.1701].

The presence of a minor diastereoisomer was indicated by ^{13}C NMR spectroscopy: δ_C (67.90 MHz, $CDCl_3$) 145.4 (q, Ar), 141.1 (q, Ar), 129.0 (q, Ar), 128.9 (2 × *C*H, Ar), 128.1 (2 × *C*H, Ar), 126.6 (*C*H, Ar), 126.4 (*C*H, Ar), 126.2 (*C*H, Ar), 116.6 (*C*H, Ar), 111.1 (*C*H, Ar), 71.3 [*C*(OH)CH$_3$], 50.9 (N*C*H$_2$CH), 45.8 (*C*HCH$_2$Ph), 39.1 (N*C*H$_3$), 33.3 (*C*H$_2$Ph), 30.4 (CO*C*H$_3$).

1-[(3*RS*,4*RS*)-4-Methyltetrahydrofuran-3-yl]propan-2-one 26a. Oil; 50% (1.0 : 3.1 mixture of inseparable diastereoisomers); R_f 0.2 (1 : 1, petroleum ether–Et_2O); ν_{max}/cm^{-1} (thin film) 2959 (s), 2929 (s), 2872 (s), 2855 (s), 1713 (s), 1363 (m), 1168 (m), 1038 (m) and 923 (m); δ_H (270 MHz, $CDCl_3$) 4.01–3.89 (2H, m, OCH_2), 3.44–3.27 (2H, m, OCH_2), 2.70 (1H, dd, *J* 17.5 and 5.0, CH_AH$_B$COCH$_3$), 2.42 (1H, dd, *J* 17.5 and 9.0, CH$_A$$H_B$COCH$_3$), 2.15 (3H, s, COC$H_3$), 2.19–2.10 (1H, m, C*H*CH$_2$COCH$_3$), 1.85 (1H, septet, *J* 7.0, CH$_3$C*H*), 1.03 (3H, d, *J* 7.0, CH_3CH); δ_C (67.90 MHz, $CDCl_3$) 208.0 (*C*OCH$_3$), 73.7 and 74.8 (2 × *C*H$_2$O), 47.0 (*C*H$_2$COCH$_3$), 42.3 (*C*HCH$_2$-COCH$_3$), 39.9 (*C*HCH$_3$), 30.3 (CH$_3$*C*O), 16.6 (*C*H$_3$CH); *m*/*z* (CI, NH_3), 143 (M + H$^+$, 100%); [Found: M + H$^+$ (CI, NH_3) 143.1070. $C_8H_{14}O_2$ requires for M + H$^+$ 143.1072].

The presence of a minor diastereoisomer was indicated by ^{1}H and ^{13}C NMR spectroscopy: δ_H (270 MHz, $CDCl_3$) 2.60 (1H, dd, *J* 16.5 and 3.5, CH_AH$_B$COCH$_3$), 0.91 (3H, d, *J* 7.0, CHCH_3); δ_C (67.90 MHz, $CDCl_3$) 208.0 (*C*OCH$_3$), 73.7 and 72.5 (2 × *C*H$_2$O), 42.1 (*C*H$_2$COCH$_3$), 37.5 (*C*HCH$_2$COCH$_3$), 35.5 (*C*HCH$_3$), 30.5 (*C*H$_3$CO), 13.4 (*C*H$_3$CH).

1-[(3*RS*,4*RS*)-4-Ethyltetrahydrofuran-3-yl]propan-2-one 26b. Oil; 80% (3.7 : 1.0 mixture of inseparable diastereoisomers); R_f 0.25 (1 : 1, petroleum ether–Et_2O); ν_{max}/cm^{-1} (thin film) 2960 (s), 2928 (s), 1713 (s), 1361 (m), 1166 (m) and 1044 (m); δ_H (270 MHz, $CDCl_3$) 4.07–3.89 (2H, m, OCH_AH$_B$), 3.49–3.32 (2H, m, OCH$_A$$H_B$), 2.71 (1H, dd, *J* 17.5 and 5.0, CH_AH$_B$-COCH$_3$), 2.50 (1H, dd, *J* 17.5 and 9.5, CH$_A$$H_B$COCH$_3$), 2.28–2.20 (1H, m, C*H*CH$_2$COCH$_3$), 2.15 (3H, s, COCH_3), 1.80–1.15 (3H, m, C*H*CH$_2$CH$_3$ and CHCH_2CH$_3$), 0.90 (3H, t, *J* 7.5, CH$_2$CH_3); δ_C (67.90 MHz, $CDCl_3$) 207.7 (*C*OCH$_3$), 73.4 and 72.9 (2 × *C*H$_2$O), 47.5 (*C*H$_2$COCH$_3$), 46.8 (*C*HCH$_2$COCH$_3$), 40.2 (*C*HCH$_2$CH$_3$), 30.1 (CO*C*H$_3$), 25.6 (CH$_3$*C*H$_2$), 12.6 (*C*H$_3$CH$_2$); *m*/*z* (CI, NH_3) 157 (M + H$^+$, 100%); [Found: M + H$^+$ (CI, NH_3) 157.1232. $C_9H_{16}O_2$ requires for M + H$^+$ 157.1232].

The presence of a minor diastereoisomer was indicated by ^{13}C NMR spectroscopy: δ_C (67.90 MHz, $CDCl_3$) 207.7 (COCH$_3$), 73.0 and 71.8 (2 × CH$_2$O), 43.2 (CHCH$_2$COCH$_3$), 41.5 (CH$_2$COCH$_3$), 36.7 (CHCH$_2$CH$_3$), 30.3 (COCH$_3$), 20.6 (CH$_3$$CH_2$), 12.8 ($CH_3CH_2$).

1-[(3*RS*,4*RS*)-4-Isopropyltetrahydrofuran-3-yl]propan-2-one 26c. Oil; 63% (9.5 : 1.0 mixture of inseparable diastereoisomers; R_f 0.3 (1 : 1, Et$_2$O–petroleum ether); ν_{max}/cm^{-1} (thin film) 2959 (s), 2931 (s), 2872 (s), 1715 (s), 1365 (m) and 938 (w); δ_H (270 MHz, $CDCl_3$) 3.95–3.90 (2H, m, OCH_2), 3.46 (1H, dd, J 9.0 and 7.0, OCH_AH$_B$), 3.36 (1H, dd, J 9.0 and 5.0, OCH$_A$$H_B$), 2.65 (1H, dd, J 17.5 and 4.5, CH_AH$_B$COCH$_3$), 2.53 (1H, dd, J 17.5 and 10.0, CH$_A$H$_B$COCH$_3$), 2.38 (1H, m, CHCH$_2$COCH$_3$), 2.16 (3H, s, COCH_3), 1.60 [1H, m, CHCH(CH$_3$)$_2$], 1.30 [1H, m, CHCH(CH$_3$)$_2$], 0.94 [3H, d, J 6.5, CH(CH_3)$_2$], 0.87 [3H, d, J 6.5, CH(CH_3)$_2$]; δ_C (67.90 MHz, $CDCl_3$) 207.8 (COCH$_3$), 73.9 (CH$_2$O), 71.1 (CH$_2$O), 51.8 (CHCH$_2$COCH$_3$), 48.9 (CH$_2$COCH$_3$), 37.9 [CHCH(CH$_3$)$_2$], 30.6 [CH(CH$_3$)$_2$], 30.0 (CH$_2$COCH$_3$), 21.3 [CH(CH$_3$)$_2$, 20.0 (CH(CH$_3$)$_2$]; m/z (CI, NH$_3$) 171 (M + H$^+$, 100%); [Found: M + H$^+$ (CI, NH$_3$) 171.1379. $C_{10}H_{18}O_2$ requires for M + H$^+$ 171.1385].

The presence of a minor diastereoisomer was indicated by ^{1}H NMR spectroscopy: δ_H (270 MHz, $CDCl_3$) 3.62 (1H, dd, J 13.0 and 9.0, OCH_AH$_B$).

1-[(3*RS*,4*RS*)-4-Benzyltetrahydrofuran-3-yl)propan-2-one 26d. Oil; 82% (1.8 : 1.0 mixture of inseparable diastereoisomers); R_f 0.4 (1 : 1, EtOAc–petroleum ether); ν_{max}/cm^{-1} (thin film) 2956 (s), 2924 (s), 2855 (m), 1717 (w), 1463 (m), 1377 (w), 1264 (w) and 1075 (w); δ_H (270 MHz, $CDCl_3$) 7.30–7.14 (5H, m, CH, Ar), 4.12 (1H, dd, J 9.0 and 7.0, OCH), 3.82 (1H, dd, J 9.0 and 7.0, OCH), 3.48 (1H, dd, J 9.0 and 7.0, OCH), 3.35 (1H, dd, J 9.0 and 7.0, OCH), 2.82–2.26 (6H, m, CHCH$_2$COCH$_3$ and CHCH$_2$Ph), 2.04 (3H, s, COCH_3); δ_C (67.90 MHz, $CDCl_3$) 207.5 (COCH$_3$), 140.1 (q, Ar), 128.6, 128.4, 128.4 and 126.1 (CH, Ar), 73.4 and 72.6 (2 × OCH$_2$), 47.3 (CH$_2$COCH$_3$), 46.5 (CHCH$_2$Ph), 40.0 (CHCH$_2$COCH$_3$), 38.9 (PhCH$_2$), 29.8 (COCH$_3$); m/z (CI, NH$_3$) 219 (M + H$^+$, 100%) and 91 (7); [Found: M + H$^+$ (CI, NH$_3$) 219.1381. $C_{14}H_{19}O_2$ requires for M + H$^+$ 219.1385].

The presence of a minor diastereoisomer was indicated by ^{1}H and ^{13}C NMR spectroscopy: δ_H (270 MHz, $CDCl_3$) 3.98 (1H, dd, J 9.0 and 7.0, OCH_AH$_B$), 3.73 (1H, dd, J 9.0 and 7.0, OCH_AH$_B$), 3.56–3.50 (2H, m, 2 × OCH$_A$$H_B$) 2.14 (3H, s, COC$H_3$); δ_C (67.90 MHz, $CDCl_3$) 207.3 (COCH$_3$), 140.1 (q, Ph), 128.6, 128.4, 128.4, 126.1 (4 × CH, Ar), 72.6 and 71.8 (2 × OCH$_2$), 42.4 (CHCH$_2$Ph), 37.0 (CHCH$_2$COCH$_3$), 41.7 (CH$_2$COCH$_3$), 33.8 (CH$_2$Ph), 30.1 (COCH$_3$).

(3*RS*,3*aR,7*aR*)-Octahydro-1-benzofuran-3-yl]propan-2-one 30.** Oil; 85% (1.0 : 2.7 mixture of inseparable diastereoisomers); R_f 0.3 (2 : 1, isohexane–EtOAc); ν_{max}/cm^{-1} (thin film) 2955 (s), 2930 (s), 2875 (s), 2865 (s), 1711 (s), 1359 (s), 1112 (s), 1050 (s), 950 (m) and 739 (m); δ_H (270 MHz, $CDCl_3$) 4.23 (1H, dd, J 9.0 and 7.0, OCH_ACH$_B$), 3.86 (1H, appt. q, J 4.5, OCHCH), 3.32 (1H, dd, J 9.0 and 7.0, OCH_AH$_B$), 2.60 (1H, dd, J 16.5 and 5.5 CH_AH$_B$COCH$_3$), 2.47 (1H, dd, J 16.5 and 8.5, CH$_A$$H_B$-COCH$_3$), 2.52–2.36 (1H, m, OCH$_2CH$), 1.84–1.72 (1H, m, OCHCH), 1.70–1.00 (8H, m, CH_2CH_2CH_2CH_2); δ_C (67.90 MHz, $CDCl_3$) 208.5 (C=O), 75.9 (OCH), 71.9 (OCH$_2$), 47.8 (CH$_2$COCH$_3$), 43.1 (OCHCH), 38.8 (CHCH$_2$COCH$_3$), 29.8 (COCH$_3$).

The presence of a minor diastereoisomer was indicated by ^{1}H NMR spectroscopy: δ_H (270 MHz, $CDCl_3$) 4.02 (1H, appt. t, J 8.5, OCH_AH$_B$), 3.98–3.82 (1H, m, OCH), 3.45 (1H, dd, J 10.0 and 8.5, OCH$_A$$H_B$), 2.80–2.70 (1H, m, C$HCH_2$COCH$_3$), 2.66–2.56 (1H, m, CH$_A$$H_B$COCH$_3$), 2.52–2.36 (1H, m, C$H_A$-H$_B$COCH$_3$), 2.00–1.91 (1H, m, OCHCH).

(3*RS*,4*RS*)-3-Benzyl-4-(2-oxopropyl)-4,5-dihydro-2(3*H*)-furanone 31. Oil; 56% (3.0 : 1.0 mixture of diastereoisomers); R_f 0.35 (1 : 1, EtOAc–petroleum ether); ν_{max}/cm^{-1} (thin film) 2918 (w), 1769 (s), 1714 (s), 1364 (m), 1188 (m), 1165 (m) and 1017 (m); δ_H (270 MHz, $CDCl_3$) 7.45–7.18 (5H, m, CH, Ar), 4.40 (1H, dd, J 9.0 and 7.5, OCH_AH$_B$), 3.73 (1H, dd, J 9.0 and 8.0, OCH_AH$_B$), 3.25 (1H, dd, J 14.0 and 4.5, PhCH_AH$_B$), 2.80 (1H, dd, J 14.0 and 8.5, PhCH$_A$$H_B$), 2.74–2.62 (1H, m, PhCH$_2$CH), 2.58–2.50 (1H, m, CH$_3$COCH$_2$CH), 2.35–2.26 (2H, m, CH$_3$COCH_2), 1.98 (3H, s, COCH_3); δ_C (67.50 MHz, $CDCl_3$) 206.1 (COCH$_3$), 177.7 (C=O), 138.1 (q, Ar), 129.3 (2 × CH, Ar), 129.1 (2 × CH, Ar), 127.3 (CH, Ar), 71.8 (CH$_2$OCO), 46.3 (CH$_2$Ph), 46.2 (PhCH$_2$$C$H), 36.2 ($CHCH_2$COCH$_3$), 35.9 ($CH_2$COCH$_3$), 30.1 (CO$CH_3$); m/z (CI, NH$_3$), 250 (M + NH$_4^+$, 45%), 233 (M + H$^+$, 100), 129 (10), 91 (22), 83 (60) and 43 (10); [Found: M + H$^+$ (CI, NH$_3$) 233.1174. $C_{14}H_{17}O_3$ requires M + H$^+$ 233.1178].

The presence of a minor diastereoisomer was indicated by ^{13}C NMR spectroscopy; δ_C (67.90 MHz, $CDCl_3$) 206.1 (COCH$_3$), 177.7 (C=O), 137.8 (q, Ar), 128.8 (2 × CH, Ar), 128.1 (2 × CH, Ar), 126.8 (CH, Ar), 71.2 (CH$_2$O), 43.3 (PhCH$_2$$C$H), 40.6 ($CH_2$Ph), 33.7 ($CHCH_2$COCH$_3$), 31.3 ($CH_2$COCH$_3$), 29.8 (CO$CH_3$).

1-[(3*RS*,4*RS*)-3-Benzyl-3,4,5,6-tetrahydro-2*H*-pyran-4-yl]-propan-2-one 32. Oil; 48% (2.0 : 1.0 mixture of inseparable diastereoisomers; R_f 0.25 (1 : 1, Et$_2$O–petroleum ether); ν_{max}/cm^{-1} (thin film) 2945 (s), 2349 (s), 1709 (s), 1400 (s), 1126 (s) and 901 (m); δ_H (270 MHz, $CDCl_3$) 7.40–7.05 (5H, m, Ar), 4.00–3.80 (1H, m, OCH_AH$_B$), 3.75–3.30 (3H, m, OCH$_A$$H_B$ and OCH_2), 2.86–2.15 (8H, m, PhCH_2CH, CH_2COCH$_3$, CHCH$_2$-COCH$_3$ and OCH$_2$CH_2), 2.12 (3H, s, COCH_3); δ_C (67.90 MHz, $CDCl_3$) 207.7 (C=O), 139.2 (q, Ar), 128.9, 128.4, 128.0, 125.8 and 125.6 (5 × CH, Ar), 71.2 and 67.3 (2 × CH$_2$O), 47.4 (CH$_2$COCH$_3$), 41.7 (CHCH$_2$Ph), 36.1 (PhCH$_2$CH), 31.8 (CH$_2$CHCH$_2$COCH$_3$), 30.3 (COCH$_3$); m/z (CI, NH$_3$), 250 (M + NH$_4^+$, 25%), 233 (M + H$^+$, 100) and 174 (20); [Found: M + H$^+$ (CI, NH$_3$) 233.1539. $C_{15}H_{20}O_2$ requires for M + H$^+$ 233.1542].

The presence of a minor diastereoisomer was indicated by ^{13}C NMR spectroscopy: δ_C (67.90 MHz, $CDCl_3$) 207.4 (C=O), 140.3 (q, Ar), 128.8, 128.4, 128.0, 125.8 and 125.6 (CH, Ar), 69.1 and 67.2 (CH$_2$O), 46.2 (CH$_2$COCH$_3$), 39.6 (CHCH$_2$Ph), 33.1 (CHCH$_2$COCH$_3$), 31.2 (CHCH$_2$Ph), 30.1 (COCH$_3$), 28.0 (CH$_2$CHCH$_2$COCH$_3$).

1-[(3*RS*,4*RS*)-3-Benzyl-3,4-dihydro-2*H*-chromen-4-yl]-propan-2-one 34. Semi-solid; 50% (2.3 : 1.0 mixture of inseparable diastereoisomers); R_f 0.2 (1 : 1, Et$_2$O–petroleum ether); ν_{max}/cm^{-1} (CHCl$_3$) 2930 (s), 2860 (s), 1709 (s), 1500 (m), 1450 (s), 1100 (m), 780 (s) and 660 (s); δ_H (270 MHz, $CDCl_3$) 7.47–6.73 (9H, m, CH, Ar), 4.12–3.83 (2H, m, OCH_2), 2.92–2.52 (4H, m, CH_2Ph and CH_2COCH$_3$), 2.50–2.32 (1H, CHCH$_2$COCH$_3$), 2.07 (3H, s, COCH_3), 1.98–1.83 (1H, m, CHCH$_2$Ph); δ_C (67.90 MHz, $CDCl_3$) 206.8 (COCH$_3$), 153.9 (q, Ar), 139.7 (q, Ar), 130.1, 129.6, 128.5, 128.4, 127.7, 126.2 (CH, Ar), 123.7 (q, Ar), 120.8, 116.8 (CH, Ar), 63.7 (OCH$_2$), 52.5 (CH$_2$COCH$_3$), 37.2 (CH$_2$Ph), 38.3 (CHCH$_2$COCH$_3$), 34.2 (CHCH$_2$Ph), 30.2 (COCH$_3$); m/z (CI, NH$_3$) 298 (M + NH$_4^+$, 100%), 281 (M + H$^+$, 28), 223 (25), 131 (10), 91 (11); [Found: M + NH$_4^+$ (CI, NH$_3$), 298.1803. $C_{19}H_{24}O_2$ requires M + NH$_4^+$ 298.1807].

The presence of a minor diastereoisomer was indicated by ^{13}C NMR spectroscopy: δ_C (67.90 MHz, $CDCl_3$) 207.1 (COCH$_3$), 67.0 (OCH$_2$), 45.2 (CH$_2$COCH$_3$), 36.9 (CH$_2$Ph), 33.5 (CHCH$_2$COCH$_3$), 30.8 (COCH$_3$).

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