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Stereocontrolled Palladium(0) Catalysed Cyclisation and Cyclisation/Carbonylation of Pseudoglycal Derivatives

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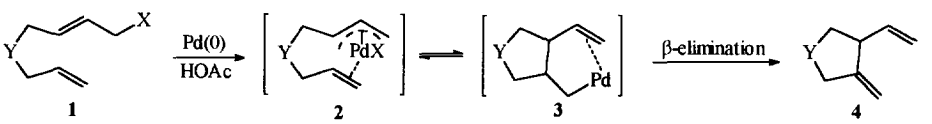
This paper is dedicated to the memory of Prof. Arthur J. Birch, a gifted teacher and innovative researcher who inspired all who were fortunate enough to cross his path.

Abstract: Pd(0) catalysed cyclisations of selected pseudoglycal 1,6-diene and 1,6-enyne derivatives provided annulated pyranoside products in a highly stereospecific fashion. Carbon monoxide insertion reactions of the cyclised σ-Pd intermediates afforded bicyclic carboxylic acids and/or bis-annulated cyclopentanone or -pentenone monosaccharide derivatives with the concomitant stereocontrolled formation of up to three C-C bonds.

INTRODUCTION

Organic chemistry has witnessed a tremendous surge[1] in the use of monosaccharide starting materials for the synthesis of a wide variety of natural products that contain carbo- and heterocyclic ring systems.[2] Particular advantage is gained by the passing of chirality from the starting materials to the products. As part of an ongoing research programme of exploring the combination of sugar templates and organometallic-promoted reactions, we have successfully accomplished the formation of stereodefined cyclopentanols from carbohydrate derivatives by SmI_2-mediated cyclisation.[3] Our Pd(0)-catalysed [2+3]-cycloaddition reactions[4] onto selected unsaturated monosaccharides have unlocked a powerful means of rapidly generating annulated carbohydrate derivatives that have been recognised as useful intermediates in the enantioselective total synthesis of many complex natural products.[5]

Cyclic carbopalladation[6] has emerged as a very versatile and powerful synthetic protocol. Palladium(0)-catalysed intramolecular 'metallo-ene' type cyclisation of 1-acetoxy-2,7-dienes (**1**) has been extensively developed by Oppolzer[7] to obtain five-membered ring compounds (Scheme 1).



1 **2** **3** **4**

Y= CH_2, NR, O, $C(CO_2CH_3)_2$, $C(SO_2Ar)_2$
X= OAc, OH, OTHP

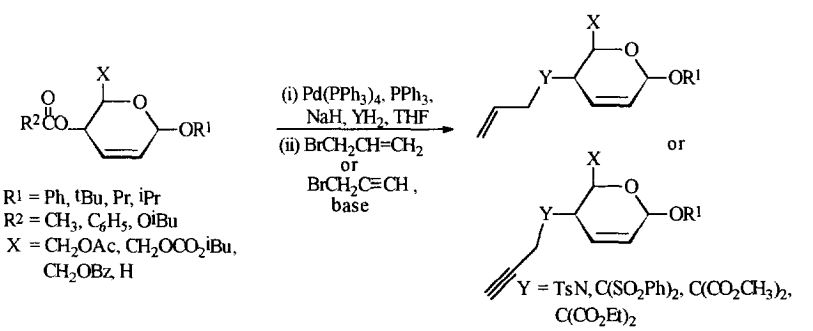
Scheme 1

Not only are these reactions regio- and stereoselective, but also entropically favoured. The experimental results are consistent with an alkene insertion into a σ-allyl- or π-allyl-palladium unit (**2**) and a subsequent β-elimination to form **4** and regenerate Pd(0). Stereoselective product formation is brought about by C-O → C-Pd → C-C chirality transfer. The findings by Oppolzer confirm that the olefin inserts into the σ- or π-allylpalladium unit in a suprafacial manner.

The purpose of this article is to disclose[8] the development and application of cyclisation and cyclisation/carbonylation reactions on selected pseudoglycal derivatives. The approach demonstrates the viability of appropriate pseudoglycal derivatives as starting materials for 'metallo-ene' cyclisation and cyclisation/carbonylation for the assembledge of chiral, highly functionalised 5,6-bicyclic systems.

RESULTS AND DISCUSSION

Preparation of starting materials The starting materials were readily prepared from the corresponding glycals, many of which are commercially available or easily prepared by known methods.[9] The incorporation of 4-amido and 4-*C*-alkyl side chains into the appropriate pseudoglycals[10] by Pd(0)-catalysed allylic substitution of the corresponding C-4 acetate or -carbonate pseudoglycals were effected according to the procedure described by Baer and Hanna[11] (Scheme 2). This was then followed by allylation or propargylation of the newly introduced side chain under standard conditions. Appropriate 4-alkoxy (**5** and **6**), amido- (**7** and **8**) and *C*-alkyl (**9**, **10**, **11** and **12**) starting materials (Table 1) were thus obtained for the investigation of the scope of 'palladium-ene' cyclisations on appropriate pseudoglycals.

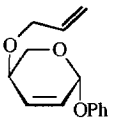
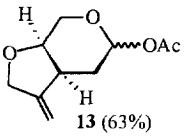
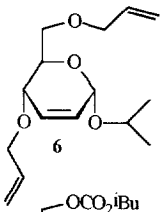
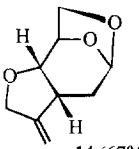
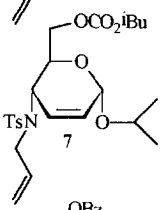
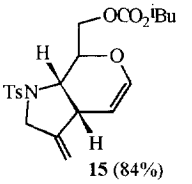
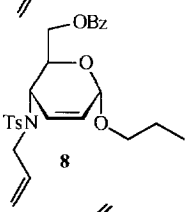
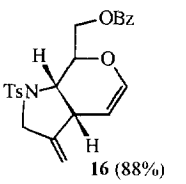
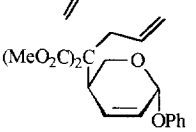
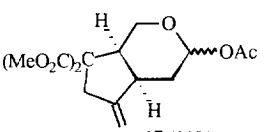
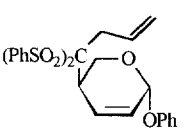
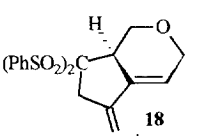
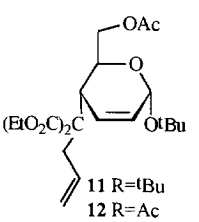
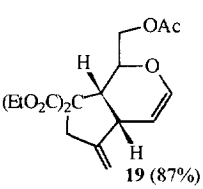


Scheme 2

'Palladium-ene' cyclisation The results summarised in Table 1 indicate that cyclisation proceeded very well to afford *cis*-fused annulated pyranoside products. The desired reactions were easily realised by stirring the pseudoglycal starting materials in glacial acetic acid[12] at 70-80 °C in the presence of a suitable palladium(0) catalyst (0.1 mol equiv.). A variety of catalysts, such as $Pd(PPh_3)_4$, palladium(II) acetate/triisopropyl phosphite, palladium(II) acetate/tributylphosphine and $Pd_2(dba)_3{\cdot}CHCl_3$/tri-*o*-tolylphosphine were exploited. Only marginal differences in product yields were obtained in most instances.

The cyclised products were obtained either in the form of glycals or their corresponding acetic acid adducts. The rate of addition of acetic acid to glycals was extremely structure dependent, pentopyranose glycals being much more susceptible to these transformations than the corresponding hexopyranose glycals.

Table 1. Palladium(0) catalysed cyclisation of pseudoglycal derivatives.

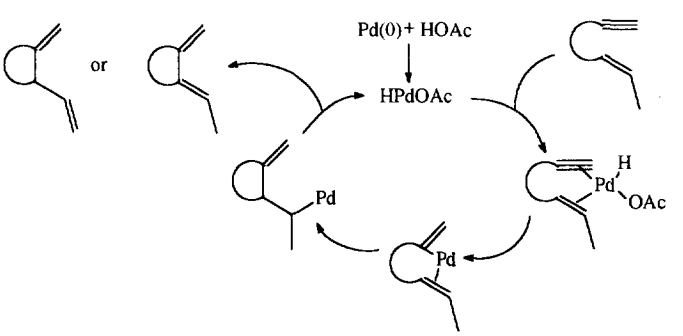
Starting material	Products (Isolated yield)
 **5**	 **13** (63%)
 **6**	 **14** (67%)
 **7**	 **15** (84%)
 **8**	 **16** (88%)
 **9**	 **17** (92%)
 **10**	 **18** + isomers (62%)
 **11** R=tBu **12** R=Ac	 **19** (87%) (60%)

The cyclisation studies were conducted with a variety of groups at the anomeric centre. Substrates bearing anomeric isopropoxy- (**7**), propoxy- (**8**) or *tert*-butoxy (**11**) groups readily cyclised (Table 1) at 80 °C to furnish the respective bicyclic products **15**, **16** and **19**. Curiously, the cyclisation of the acetate **12** was rather more sluggish to proceed to completion than the corresponding *tert*-butoxy pseudoglucal **11**. Regiospecific nucleophilic allylic substitution reactions of 2,3-unsaturated phenyl glycosides[13] in the presence of Pd(0) incited us to increase the leaving group ability of the anomeric alkoxy group by use of phenyl glycosides **5**, **9** and **10**. Indeed, these compounds underwent facile cyclisation under the optimised reaction conditions to form the respective bicyclic compounds **13**, **17** and **18**.

The reactivity of the pseudoglycal derivatives under these reactions is probably governed by stereoelectronic effects[14] where the antiperiplanar orientation of the electron lone pairs of the ring oxygen to the anomeric C-OR bond might be the main driving force in the oxidative substitution process resulting in π-allylpalladium formation. Indications are that cyclisation products are formed irrespective of the anomeric stereochemistry of the starting materials. This is in agreement with findings by Oppolzer[15] that cyclisation of *trans* disposed 'enophiles' do indeed proceed, *albeit* at a much slower rate, which implies isomerisation[16] of the intermediate Pd-η^3 complex.

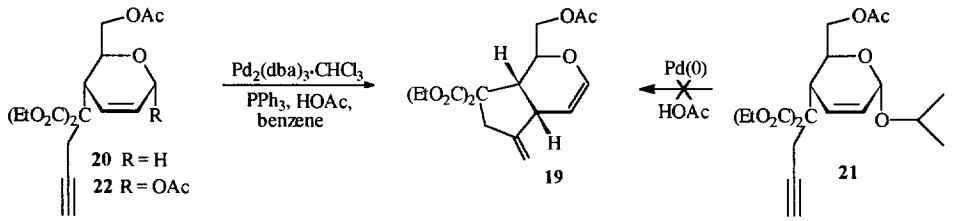
Structural assignments From the proposed reaction mechanism and inspection of *Dreiding* models, it follows that a (*Z*)-palladium-allyl unit affords only *cis*-fused products because the otherwise *trans*-substituted five-membered ring would imply a strained transition state.[7] Evidence of *cis*-fused products was apparent from the relatively small coupling constants (*J* 4-5 Hz) between the two adjacent protons on the ring junctions.

Enyne cycloisomerisation Trost[17] has illustrated the Pd-catalysed formation of dialkylidenecyclopentanes and -cyclohexanes by the versatile and highly atom economical cycloisomerisation of 1,6-enynes. The reaction is composed of three stages (Scheme 3): initiation by addition of an *in situ* generated HPdOAc species to an acetylene, propagation by intramolecular carbopalladation, and termination by *cis* β-hydride elimination.



Scheme 3

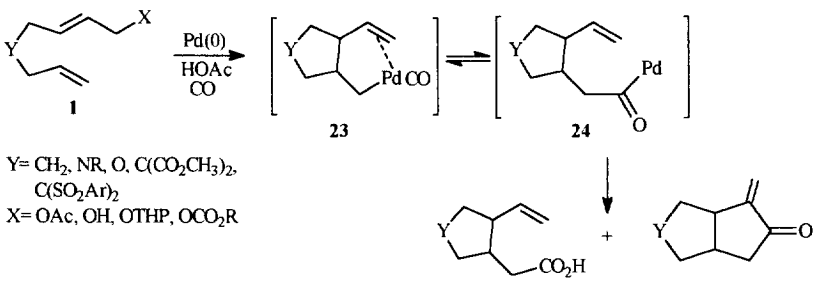
In this regard treatment of **20**[18] (Scheme 4) with $Pd_2(dba)_3$·$CHCl_3$ (0.2 mol equiv.), PPh_3 (0.4 mol equiv.) and acetic acid (0.4 mol equiv.) in benzene at room temperature for 3 hours led to the formation of the cycloadduct **19** in a yield of 81%. Unfavourable β-isopropoxy elimination was seemingly responsible for the failure of the pseudoglucal **21** to cyclise under these conditions. However, the acetate **22**[19] was converted into **19**, although more forcing conditions had to be employed than for **20**.



Scheme 4

This procedure complements recent work by Sinou and co-workers[20] where bis-annulated pyranosides were formed by polycyclisation involving an intramolecular Heck reaction.

'Palladium-ene' cyclisation/carbonylation A wealth of undiscovered synthetic potential remains in the cyclisation and carbon monoxide insertion into pyranoid (and furanoid) sugar templates. Polyfunctionalised bis-annulated pyranosides[21] were synthesised using stoichiometric amounts of $Co_2(CO)_8$ (the Pauson-Khand reaction) and have been identified as precious and advanced intermediates in the synthesis of natural products. σ-Organopalladium complexes (**23**) can be readily converted into the corresponding acylpalladium species (**24**) *via* reversible carbon monoxide insertion. A catalytic 'palladium-ene' cyclisation/carbonylation (Scheme 5) has been developed and applied by Oppolzer and co-workers[22] in natural product synthesis. Cyclisation/carbonylation has also been demonstrated to occur in the case of 1-acetoxy-2,7-enynes. The nature of the products imply that the reaction is initiated by π-allyl palladium complex formation rather than HPdOAc addition over the triple bond.



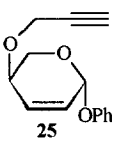
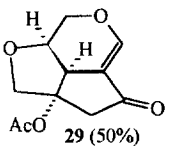
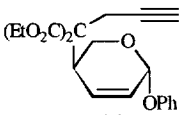
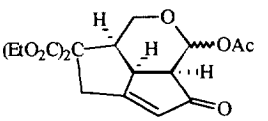
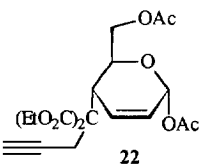
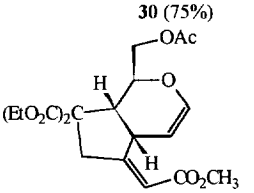
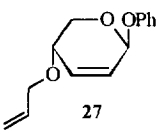
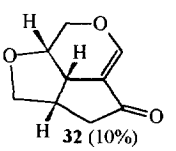
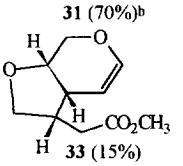
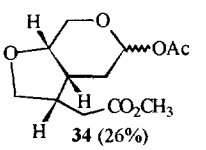
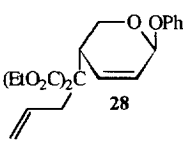
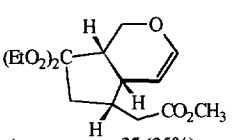
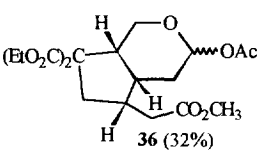
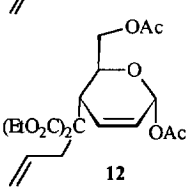
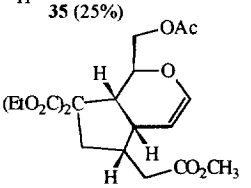
Scheme 5

Palladium catalysed carbonylation reactions of allylic acetates are commonly carried out under drastic conditions because of facile reductive elimination of the π-allyl palladium complex upon treatment with carbon monoxide.[23] We therefore anticipated suppression of the initiation step in the 'metallo-ene' cyclisation reaction in the presence of carbon monoxide. In addition, application of the cyclisation/carbonylation protocol to appropriate carbohydrate derivatives warranted consideration of observations by Oppolzer that the alkene inserts into the σ- or π-allylpalladium unit *cis* relative to the Pd atom (*i.e.* in a suprafacial manner). It followed that 1,4-*trans* substituted pseudoglycal starting materials would be the preferred substrates. These are readily obtained in the pentose series. Starting from either 3,4-di-*O*-acetyl-L-arabinal or 3,4-di-*O*-acetyl-D-xylal, the BF_3·Et_2O promoted Ferrier rearrangement in CH_2Cl_2 with phenol at -20 °C gives predominantly 1,4-*trans* substituted

pseudoglycals[24] which were further elaborated, as discussed earlier (Scheme 2), to furnish suitable starting materials.

Highly functionalised products of carbonyl insertion (Table 2) were obtained in fair to good yields upon treatment with CO, but, as was anticipated, these reactions proceeded at a much slower rate than the corresponding Pd-catalysed cyclisation reactions.

Table 2. Palladium(0) catalysed cyclisation/carbonylation of pseudoglycal derivatives.

Starting material	Products[a] (Isolated yield)
 **25**	 **29** (50%)
 **26**	 **30** (75%)
 **22**	 **31** (70%)[b]
 **27**	 **32** (10%)  **33** (15%)  **34** (26%)
 **28**	 **35** (25%)  **36** (32%)
 **12**	 **37** (58%)[b]

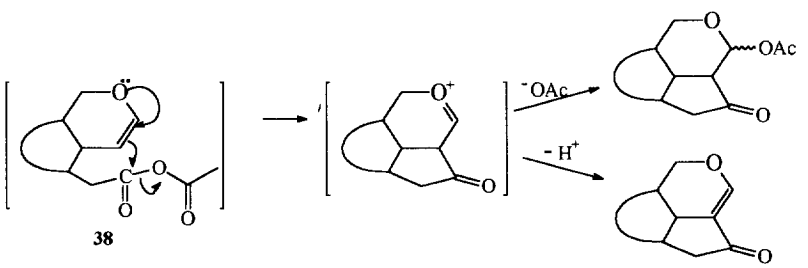
[a]Carboxylic acids were isolated as the corresponding methyl carboxylate derivatives upon treatment with an etherial solution of diazomethane in CH_2Cl_2 at 0 °C.
[b]Yield based on recovered starting material.

In a typical experiment, upon exposure to a suitable Pd(0) catalyst in acetic acid at 46 °C under 1 atmosphere of carbon monoxide, the pseudoglycal starting material underwent cyclisation/carbonylation to give the corresponding ketone and/or carboxylic acid. Solely *cis*-fused bi- and/or tricyclic pyranoids were formed. The rates and yields of cyclisation products were highly structure dependent. Here too, final products were obtained as glycals or their corresponding acetic acid adducts.

In contrast to the normal cyclisation reactions, the importance of choice of catalyst was evident. Much decomposition, even at room temperature, occurred when any of the propargyl pseudoglycal derivatives **25**, **26** or **22** were subjected to CO (1 atm) and $Pd(PPh_3)_4$ (0.1 mol equiv.) in glacial acetic acid at 46 °C. When either $Pd(OAc)_2$/triisopropyl phosphite or $Pd_2(dba)_3{\cdot}CHCl_3$/tri-*o*-tolylphosphine, however, were employed as catalysts, tlc indicated a clean course of reaction. The latter catalyst was not only very effective, but also particularly robust under the required prolonged reaction conditions. The allyl derivatives **27**, **28** and **12** exclusively furnished products of CO-insertion.

Once again the anomeric phenoxy group proved an excellent leaving group, much more so than the corresponding acetate. Prolonged reaction (24 h) of the propargyl pseudoglycal **22** yielded the α,β-unsaturated carboxylic acid, isolated as the corresponding methyl carboxylate **31** and much unreacted starting material. Similar treatment of the analogous allyl derivative **12** resulted in the formation of **37**, along with an as yet unidentified mixture of polar products.

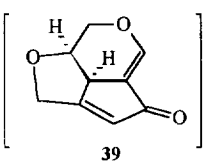
Notably, both bi- and/or tricyclic compounds were obtained from these reactions. Steric- and electronic[25] considerations rule out the possibility that the third ring of a tricyclic compound resulted from an intramolecular Pd-catalysed insertion reaction. An acid catalysed[26] intramolecular cyclisation reaction (Scheme 6) of a conceivable anhydride intermediate[27] **38** is considered more likely.



38

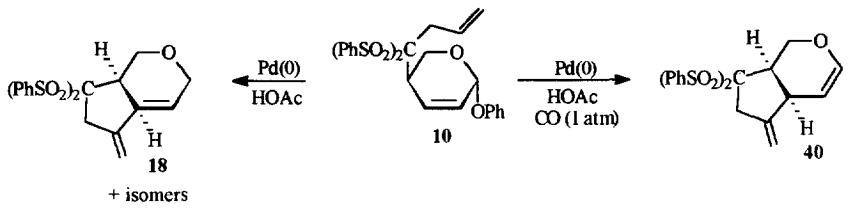
Scheme 6

In striking contrast to the other acetoxy compounds in Table 2, a different mode of acetic acid addition operated to form **29**. This acetoxy compound is seemingly derived from the exceedingly strained intermediate **39**.



39

Singularly, compound **10** underwent no carbonyl insertion, but merely cyclised to furnish **40** in a yield of 40% (Scheme 7).



Scheme 7

This is tentatively ascribed to steric congestion caused by the large SO_2Ph groups in the σ-organopalladium transition state so as to favour β-hydride elimination over CO-insertion. Interestingly, when **10** was cyclised in the absence of CO (Table 2) complete double bond isomerisation occurred to produce a rather complicated inseperable mixture of isomeric products, of which **18** was identified as major product. This phenomenon again illustrates the inhibitory influence CO exerts on hydrido-palladium addition-elimination sequences[28] needed to bring about double bond isomerisation.

Stereochemical assignments In like manner to the 'palladium-ene' cyclisation products, the accepted mechanism dictates the formation of *cis*-fused products *via* a suprafacial course. Not only did the relatively small coupling constants (*J* 4-6 Hz) between the adjacent hydrogen atoms on the ring junctions attest to all-*cis* annulated bi- and tricyclic rings, but this was also confirmed by NOE-experiments.

In conclusion, we have described a variety of cyclic carbopalladation reactions of appropriate pseudoglycal derivatives in the presence and absence of carbon monoxide for the rapid assembly of complex, chiral molecular architectures. These will no doubt find application as valuable intermediates in natural product synthesis.

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere in flamed-out glass apparatus. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ (unless otherwise stated) on a Varian VXR 200 (200 MHz) or Varian Gemini 2000 (300 MHz) spectrometer. Mass spectra, as well as accurate mass determinations, were recorded on a Finnigan-MAT 8200 mass spectrometer (70 eV). Optical rotations were obtained on a Jasco DIP 370 digital polarimeter (concentration *c* refers to g/100ml in $CHCl_3$). Melting points were taken on a Reichert Kofler hot-stage apparatus and are uncorrected. All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Solvents were purified and distilled prior to use, according to standard procedures.[29] All palladium catalysts were prepared according to literature procedures.[30,31] Diazomethane[32] was freshly prepared prior to use. Flash chromatography was conducted on silica gel (Merck Kieselgel 60, 230-400 mesh) with the indicated eluent. Unless otherwise stated, solvent systems employed for flash chromatographic techniques were mixtures of ethyl acetate and hexane in the proportions (v/v) A (1:2), B (1:3), C (1:5), D (1:8) and E (1:12).

Preparation of the 4-alkoxy pseudoglycoside starting materials **5**, **27**, **6** and **25**.

Pseudoglycals were prepared from the corresponding glycals by Ferrier rearrangement.[10] Simple deacetylation (K_2CO_3, MeOH) followed by alkylation of the hydroxyl groups by treatment with NaH (1.1 mol

equiv of a 60% oil dispersion) and either allyl- or propargyl bromide (1.1 mol equiv. per hydroxyl group) in DMF at room temperature afforded the desired compounds in excellent overall yields.

*Phenyl 4-O-allyl-2,3-dideoxy-β-D-*glycero-*pent-2-enopyranoside* (**5**) and *Phenyl 4-O-allyl-2,3-dideoxy-α-L-*glycero-*pent-2-enopyranoside* (**27**). (75% yield over 2 steps for both compounds); **5**: $[\alpha]_D^{26}$ 42.9° (*c* 1.0); NMR: δ_H 3.73 (dddd, 1H, *J* 5.1 Hz, *J* 2.7 Hz, *J* 1.3 Hz, *J* 1.3 Hz), 4.00 (ddd, 1H, *J* 12.6 Hz, *J* 1.3 Hz, *J* 1.3 Hz), 4.11 (m, 2H), 4.15 (dd, 1H, *J* 12.6 Hz, *J* 2.7 Hz), 5.21 (dddd, 1H, *J* 10.3 Hz, *J* 1.6 Hz, *J* 1.3 Hz, *J* 1.3 Hz), 5.31 (dddd, 1H, *J* 17.4 Hz, *J* 1.6 Hz, *J* 1.6 Hz, *J* 1.6 Hz), 5.74 (dd, 1H, *J* 3.3 Hz, *J* 0.9 Hz), 5.95 (dddd, 1H, *J* 17.4 Hz, *J* 10.3 Hz, *J* 5.7 Hz, *J* 5.7 Hz), 6.12 (ddd, 1H, *J* 10.2 Hz, *J* 3.3 Hz, *J* 0.9 Hz), 6.25 (dddd, 1H, *J* 10.2 Hz, *J* 5.1 Hz, *J* 0.9 Hz, *J* 0.9 Hz), 6.92-7.34 (m, 5H); δ_C 62.06, 67.02, 69.67, 91.69, 116.64, 117.43, 122.08, 127.68, 128.64, 129.52, 134.78, 157.31; *m/z*(%): 232(7), 139(71).

*Isopropyl 4,6-di-*O-*allyl-2,3-dideoxy-α-D-*erythro-*hex-2-enopyranoside* (**6**). (66% yield over 2 steps); NMR: δ_H 1.13 (d, 3H, *J* 6.3 Hz), 1.20 (d, 3H, *J* 6.3 Hz), 3.59-3.73 (m, 2H), 3.84-4.16 (m, 7H), 5.10 (dm, 2H, *J* 8.1 Hz), 5.17 (s, 1H), 5.25 (dm, 2H, *J* 17.2 Hz), 5.69 (ddd, 1H, *J* 10.2 Hz, *J* 2.3 Hz, *J* 2.3 Hz), 5.78-6.02 (m, 2H), 6.00 (d, 1H, *J* 10.5 Hz).

*Phenyl 2,3-dideoxy-4-*O-*propargyl-α-L-*glycero-*pent-2-enopyranoside* (**25**). (77% yield over 2 steps); $[\alpha]_D^{26}$ 14.8° (*c* 1.1); NMR: δ_H 2.45 (t, 1H, *J* 2.4 Hz), 3.93 (dddd, 1H, *J* 5.1 Hz, *J* 2.6 Hz, *J* 1.1 Hz, *J* 1.1 Hz), 4.01 (ddd, 1H, *J* 12.9 Hz, *J* 1.2 Hz, *J* 1.2 Hz), 4.16 (dd, 1H, *J* 12.9 Hz, *J* 2.7 Hz), 4.26 (d, 2H, *J* 2.4 Hz), 5.71 (dd, 1H, *J* 3.0 Hz, *J* 1.2 Hz), 6.14 (ddd, 1H, *J* 10.2 Hz, *J* 3.0 Hz, *J* 0.6 Hz), 6.26 (dddd, 1H, *J* 10.2 Hz, *J* 5.1 Hz, *J* 1.5 Hz, *J* 1.2 Hz), 6.80-7.31 (m, 5H); δ_C 55.69, 61.74, 66.39, 74.89, 79.54, 91.56, 116.61, 122.15, 127.04, 129.27, 129.54, 157.24; *m/z*(%): 230(4), 137(100).

Preparation of the 4-amido pseudoglycal starting materials.

The 4-amido pseudoglycal derivatives were prepared in high yields from the corresponding pseudoglycals by $Pd(PPh_3)_4$ catalysis according to the method described by Baer and Hanna.[11]

*Isopropyl 6-*O-(*isobutoxycarbonyl*)-*4-*[N-(*prop-2-enyl*)p-*toluenesulfonamido*]-*2,3,4-trideoxy-α-D-*erythro-*hex-2-enopyranoside* (**7**). The title compound was obtained from the corresponding 4,6-di-isobutoxycarbonyl pseudoglycal (388 mg, 1mmol) and *p*-toluenesulfonamide (685 mg, 4 mmol) in refluxing THF (5 ml) in the presence of $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) and PPh_3 (52 mg, 0.2 mmol). After 6 h hexane (50 ml) was added and the mixture was filtrated through a bed of Celite and evaporated. Flash chromatography (solvent A) yielded the amide as a colourless syrup (309 mg, 70%). This was taken up in THF (5 ml) and cooled to -10 °C after which time Bu_4NI (52 mg, 0.140 mmol), sodium bis(trimethylsilyl)amide (0.7 ml of 1.0 M solution in THF, 0.7 mmol) and allyl bromide (67 µl, 0.770 mmol) were added. The mixture was stirred at room temperature overnight and washed with water, extracted (CH_2Cl_2), dried (Na_2SO_4) and evaporated under reduced pressure. Flash chromatography (solvent A) afforded 7 as a colourless syrup (310 mg, 92%); $[\alpha]_D^{28}$ 46.8° (*c* 2.4); NMR: δ_H 0.92 (d, 6H, *J* 6.8Hz), 1.10 and 1.15 (2d, 6H, *J* 6.0 Hz), 1.96 (heptet, 1H, *J* 6.8 Hz), 2.41 (s, 3H), 3.49 (dd, 1H, *J* 16.0 Hz, *J* 7.6 Hz), 3.83-4.01 (m, 4H), 4.18 (ddd, 1H, *J* 9.8 Hz, *J* 5.0 Hz, *J* 3.0 Hz), 4.23-4.37 (m, 2H), 4.49 (ddd, 1H, *J* 9.8 Hz, *J* 3.0 Hz, *J* 2.0 Hz), 5.00 (m, 1H), 5.10-5.25 (m, 3H), 5.75 (ddd, 1H, *J* 10.2 Hz, *J* 3.0 Hz, *J* 2.0 Hz), 5.89 (dddd, 1H, *J* 17.2 Hz, *J* 10.0 Hz, *J* 7.6 Hz, *J* 5.0 Hz), 7.25-7.72

(m, 4H); δ_C 18.89, 21.54, 21.73, 23.32, 27.75, 47.63, 53.24, 65.86, 66.30, 70.01, 74.11, 91.83, 117.97, 127.15, 129.87, 137.28, 143.67; *m/z*(%): 422(32), 321(100), 166(67), 124(84).

Propyl 6-O-benzoyl-4-[N-(*prop-2-enyl*)p-*toluenesulfonamido*]-*2,3,4-trideoxy*-α-*D*-erythro-*hex-2-enopyranoside* (**8**). Prepared in exactly the same manner as **7** from the corresponding 4,6-dibenzoyloxy pseudoglycal. $Pd(PPh_3)_4$ catalysed allylic substition was, however, carried out in the presence of sodium bis(trimethylsilyl)amide (4 mol equiv.) to furnish **8** as a colourless syrup (55% yield over 2 steps); NMR: δ_H 0.82 (t, 3H, *J* 7.4 Hz), 1.54 (d, 2H, *J* 7.4 Hz), 2.37 (s, 3H), 3.38 (dt, 1H, *J* 6.6 Hz, *J* 9.4 Hz), 3.56 (dd, 1H, *J* 16.2 Hz, *J* 7.6 Hz), 3.63 (dt, 1H, *J* 7.0 Hz, *J* 9.4 Hz), 4.05 (dddd, 1H, *J* 16.2 Hz, *J* 5.2 Hz, *J* 1.2 Hz, *J* 1.2 Hz), 4.31-4.63 (m, 4H), 4.94 (dm, 1H, *J* 3.0 Hz), 5.15 (dm, 1H, *J* 10.0 Hz), 5.24 (ddd, 1H, *J* 10.0 Hz, *J* 3.0 Hz, *J* 2.0 Hz), 5.81-6.04 (m, 2H); δ_C 10.46, 21.48, 22.89, 47.49, 53.44, 63.64, 66.11, 70.13, 93.71, 118.02, 127.20, 128.25, 129.75, 129.87, 132.64, 135.64, 137.13, 143.76, 166.10; *m/z*(%): 426(7), 321(74), 166(100).

The *C*-alkylated pseudoglycal derivatives were prepared exactly according to the literature procedure.[11] Allylation or propargylation of the C-4 methylene groups was carried carried out in DMF at 60 °C in the presence of NaH (1.1 mol equiv. of a 60% oil dispersion) and either allyl- or propargyl bromide (1.1 mol equiv.) for 5h. Work up entailed washing with a saturated NH_4Cl solution, extraction (CH_2Cl_2), drying (Na_2SO_4), evaporation and flash chromatography.

Phenyl 4-[*bis*(*methoxycarbonyl*)*but-3-enyl*]-*2,3,4-trideoxy*-α-*L*-erythro-*hex-2-enopyranoside* (**9**). (50% yield over 2 steps); $[\alpha]_D^{19}$ -15.0° (*c* 1.0); NMR: δ_H 2.70-2.82 (m, 3H), 3.70 (s, 3H), 3.72 (s, 3H), 4.03 (d, 1H, *J* 12.3 Hz), 4.16 (dd, 1H, *J* 12.3 Hz, *J* 4.2 Hz), 5.10 (dm, 1H, *J* 10.1 Hz), 5.15 (dm, 1H, *J* 17.4 Hz), 5.48 (d, 1H, *J* 3.0 Hz), 5.65 (dddd, 1H, *J* 17.4 Hz, *J* 10.1 Hz, *J* 7.3 Hz, *J* 7.3 Hz), 6.02 (ddd, 1H, *J* 10.2 Hz, *J* 3.0 Hz, *J* 1.8 Hz), 6.21 (dd, 1H, *J* 10.2 Hz, *J* 5.4 Hz), 6.23-7.38 (m, 5H); δ_C 35.70, 37.17, 52.39, 52.67, 59.28, 59.50, 92.08, 116.81, 119.45, 122.01, 127.63, 128.66, 129.46, 132.15, 157.32, 170.45, 170.89; *m/z*(%): 346(1), 269(5), 253(89), 221(34), 193(100), 161(40), 133(64).

Phenyl 4-[*bis*(*phenylsulfonyl*)*but-3-enyl*]-*2,3,4-trideoxy*-α-*L*-erythro-*hex-2-enopyranoside* (**10**). (74% yield over 2 steps); mp 133-135 °C; $[\alpha]_D^{20}$ 85.9° (*c* 1.1); NMR: δ_H 2.96 (dd, 1H, *J* 16.8 Hz, *J* 6.0 Hz), 3.10 (dd, 1H, *J* 16.8 Hz, *J* 7.2 Hz), 3.70 (dm, 1H, *J* 11.1 Hz), 3.96 (ddd, 1H, *J* 11.1 Hz, *J* 5.1 Hz, *J* 1.5 Hz), 4.16 (dd, 1H, *J* 11.1 Hz, *J* 11.1 Hz), 5.25 (dd, 1H, *J* 16.8 Hz, *J* 1.2 Hz), 5.34 (dd, 1H, *J* 9.9 Hz, *J* 1.2 Hz), 5.51 (dm, *J* 2.9 Hz), 5.60 (ddd, 1H, *J* 10.5 Hz, *J* 2.9 Hz, *J* 2.9 Hz), 6.09-6.20 (m, 1H), 6.20 (d, 1H, *J* 10.5 Hz), 7.01-8.30 (m, 15H); δ_C 33.05, 35.51, 58.00, 92.15, 116.81, 122.16, 125.27, 128.50, 128.69, 129.54, 131.91, 132.64, 134.88, 137.47, 157.16; *m/z*(%): 275(5), 218(33), 185(11), 142(24).

*Tertiary butyl 6-*O-*acetyl-4-*[*bis*(*ethoxycarbonyl*)*but-3-enyl*]-*2,3,4-trideoxy*-α-*D*-erythro-*hex-2-enopyranoside* (**11**). (89% yield over 2 steps); $[\alpha]_D^{24}$ 45.5° (*c* 1.0); NMR: δ_H 1.18-1.25 (m, 15H), 2.05 (s, 3H), 2.70 (dd, 1H, *J* 3.6 Hz, *J* 1.8 Hz), 2.70-2.75 (m, 2H), 4.06 (dd, 1H, *J* 11.4 Hz, *J* 3.6 Hz), 4.11-4.21 (m, 4H), 4.26 (dd, 1H, *J* 11.4 Hz, *J* 8.1 Hz), 4.35 (ddd, 1H, *J* 8.1 Hz, *J* 3.6 Hz, *J* 1.8 Hz), 5.05 (dm, 1H *J* 10.2 Hz), 5.16 (dm, 1H, *J* 15.9 Hz), 5.07 (dd, 1H, *J* 2.4 Hz, *J* 0.6 Hz), 5.68 (dd, 1H, *J* 10.5 Hz, *J* 2.4 Hz), 5.66-5.74 (m, 1H), 5.83 (ddd, 1H, *J* 10.5 Hz, *J* 3.6 Hz, *J* 0.6 Hz); δ_C 13.86, 13.89, 20.85, 28.62, 28.75, 37.22, 37.42, 59.75, 61.43, 61.59, 64.29, 68.68, 74.81, 87.52, 119.13, 126.27, 130.51, 132.67, 169.72, 170.36, 170.94; *m/z*(%): 426(1), 369(10), 353(13), 279(23); HRMS calcd for $C_{22}H_{34}O_8$: 426.2254 (M^+), found 426.2226.

1,6-Di-O-*acetyl-4-[bis(ethoxycarbonyl)but-3-enyl]-2,3,4-trideoxy-α-D*-erythro-*hex-2-enopyranoside* (**12**). To a solution of **11** (993 mg, 2.410 mmol) in acetic anhydride (50 ml) was added $ZnCl_2$ (10 mg, 0.073 mmol) at 0 °C. Complete conversion of the starting material into a more polar product was witnessed after 3 h at 0 °C. The solution was washed consecutively with saturated $NaHCO_3$ and water, extracted (CH_2Cl_2), dried (Na_2SO_4) and evaporated *in vacuo*. Flash chromatography (solvent A) afforded **12** as a colourless syrup (943 mg, 95%); NMR: δ_H 1.22 (t, 3H, *J* 7.2 Hz), 1.24 (t, 3H, *J* 7.2 Hz), 2.00 (s, 3H), 2.06 (s, 3H), 2.67-2.75 (m, 3H), 4.05-4.23 (m, 5H), 4.31 (dd, 1H, *J* 11.1 Hz, *J* 8.4 Hz), 4.50 (dm, 1H, *J* 8.4 Hz), 5.11 (dd, 1H, *J* 10.2 Hz, *J* 1.8 Hz), 5.16 (dd, 1H, *J* 16.8 Hz, *J* 1.5 Hz), 5.63 (dddd, 1H, *J* 16.8 Hz, *J* 10.2 Hz, *J* 7.1 Hz, *J* 7.1 Hz), 5.87 (ddd, 1H, *J* 10.5 Hz, *J* 3.0 Hz, *J* 1.5 Hz), 6.08 (dddd, 1H, *J* 10.5 Hz, *J* 5.7 Hz, *J* 1.5 Hz, *J* 1.5 Hz), 6.11 (dd, 1H, *J* 3.0 Hz, *J* 1.5 Hz); δ_C 13.82, 13.94, 35.70, 36.64, 59.48, 61.50, 61.87, 64.98, 69.45, 86.47, 119.63, 126.11, 126.31, 131.93, 169.46, 169.96, 170.11, 170.80; *m/z*(%): 353(7), 339(5), 293(4), 279(36), 265(8), 219(9).

(*5R, 6S*)-*6-(Acetoxymethyl)-5-[bis(ethoxycarbonyl)-but-3-ynyl]-5,6-dihydro-2H-pyran* (**20**). To a solution of **21** (538 mg, 1.310 mmol) in CH_2Cl_2 (10 ml) was added $BF_3.EtO_2$ (1.965 mmol, 242 µl) and dimethylphenylsilane (1.965 mmol, 302 µl) at 0 °C and thereafter stirred at RT for 20 min. *In vacuo* evaporation and flash chromatography (solvent A) provided **20** (273 mg, 60%) as a colourless syrup; $[\alpha]_D^{23}$ 51.7° (*c* 2.6); NMR: $\delta_H(C_6D_6)$ 0.97-1.09 (m, 6H), 1.72-1.75 (m, 4H), 3.12-3.17 (m, 3H), 3.80-4.17 (m, 7H), 4.58 (dd, 1H, *J* 11.5 Hz, *J* 9.3 Hz), 4.89 (dd, 1H, *J* 9.3 Hz, *J* 4.6 Hz), 5.48-5.91 (m, 2H); δ_C 13.77, 13.91, 20.48, 23.55, 37.06, 59.39, 59.77, 62.80, 70.27, 71.93, 79.24, 120.82, 129.93, 168.20, 170.01, 170.04; *m/z*(%): 352(8).

Isopropyl 6-O-*acetyl-4-[bis(ethoxycarbonyl)but-3-ynyl]-2,3,4-trideoxy-α-D*-erythro-*hex-2-enopyranoside* (**21**). (75% yield over 2 steps); NMR: δ_H 1.08-1.26 (m, 12H), 2.00 (t, 1H, *J* 2.7 Hz), 2.05 (s, 3H), 2.90 (t, 2H, *J* 2.7 Hz), 3.02 (m, 1H), 3.90 (heptet, *J* 6.2 Hz), 4.10 (m, 7H), 5.06 (m, 1H), 5.78 (ddd, 1H, *J* 10.4 Hz, *J* 1.4 Hz, *J* 1.4 Hz), 5.86 (dm, 1H, *J* 10.4 Hz); δ_C 13.85, 13.92, 20.87, 21.82, 22.74, 22.75, 37.25, 58.88, 61.92, 62.04, 64.52, 68.55, 69.81, 71.87, 91.07, 126.62, 129.74, 168.65, 169.36, 170.81; *m/z* (%): 410(1), 351(15).

1,6-Di-O-*acetyl-4-[bis(ethoxycarbonyl)but-3-ynyl]-2,3,4-trideoxy-α-D*-erythro-*hex-2-enopyranoside* (**22**). Prepared in a similar fashion to **12** by stirring a solution of the corresponding *tert*-butoxy pseudoglucal (1.137 g, 2.682 mmol) and $ZnCl_2$ (10 mg, 0.073 mmol) in acetic anhydride (50 ml) at 0 °C. After 30 minutes the solution was washed consecutively with saturated $NaHCO_3$ and water, extracted (CH_2Cl_2), dried (Na_2SO_4) and evaporated *in vacuo*. Flash chromatography (solvent A) afforded **22** as a colourless syrup (979 mg, 89%); $[\alpha]_D^{24}$ 3.7° (*c* 1.2); NMR: δ_H 1.23 (t, 3H, *J* 7.2 Hz), 1.25 (t, 3H, *J* 7.2 Hz), 2.00 (s, 3H), 2.04 (t, 1H, *J* 2.7 Hz), 2.08 (s, 3H), 2.88 (d, 2H, *J* 2.7 Hz), 3.00 (dd, 1H, *J* 5.7 Hz, *J* 1.5 Hz), 4.05-4.26 (m, 5H), 4.36 (dd, 1H, *J* 11.1 Hz, *J* 8.4 Hz), 4.57 (dd, 1H, *J* 8.4 Hz, *J* 5.7 Hz), 5.90 (ddd, 1H, *J* 10.4 Hz, *J* 2.7 Hz, *J* 1.5 Hz), 6.12 (dd, 1H, *J* 2.7 Hz, *J* 1.5 Hz), 6.15 (ddd, 1H, *J* 10.4 Hz, *J* 5.7 Hz, *J* 1.5 Hz); δ_C 13.77, 13.91, 20.84, 21.16, 22.98, 35.52, 58.36, 61.90, 62.40, 64.90, 69.36, 72.10, 78.26, 86.39, 125.95, 126.56, 168.54, 169.34, 169.93, 170.87; *m/z*(%): 247(5), 218(3), 172(53), 146(5).

Phenyl 4-[bis(ethoxycarbonyl)but-3-ynyl]-2,3,4-trideoxy-β-D-glycero-*pent-2-enopyranoside* (**26**). (60% yield over 2 steps); $[\alpha]_D^{20}$ -11.3° (*c* 1.2), NMR: δ_H 1.25 (t, 3H, *J* 7.2 Hz), 1.26 (t, 3H, *J* 7.2 Hz), 2.03 (t, 1H, *J* 2.7 Hz), *J* 2.7 Hz), 2.97 (d, 1H, *J* 2.7 Hz), 3.02 (m, 1H), 4.14 (m, 2H), 4.21 (2q, 4H, *J* 7.2 Hz), 5.48 (d, 1H, *J*

2.8 Hz), 6.02 (ddd, 1H, *J* 10.2 Hz, *J* 2.8 Hz, *J* 1.5 Hz), 6.28 (dd, 1H, *J* 10.2 Hz, *J* 5.6 Hz), 6.92-7.29 (m, 5H); δ_C 13.85, 13.99, 23.21, 35.51, 58.08, 59.55, 61.70, 62.05, 71.86, 78.69, 92.03, 116.76, 121.92, 127.85, 128.56, 129.39, 157.32, 169.08, 169.55; *m/z*(%): 327(4), 279(100), 205(35), 190(29).

*Phenyl 4-[bis(ethoxycarbonyl)but-3-ynyl]-2,3,4-trideoxy-α-L-*glycero*-pent-2-enopyranoside* (**28**). (60% yield over 2 steps); $[\alpha]_D^{19}$ -15.6° (*c* 1.2); NMR: δ_H 1.24 (t, 3H, *J* 7.2 Hz), 1.25 (t, 3H), 2.68-2.81 (m, 3H), 4.04-4.22 (m, 6H), 5.10 (dm, 1H, *J* 10.2 Hz), 5.14 (dddd, 1H, *J* 17.1 Hz, *J* 2.1 Hz, *J* 2.1 Hz, *J* 2.1 Hz), 5.48 (dd, 1H, *J* 3.0 Hz, *J* 0.9 Hz), 5.67 (dddd, 1H, *J* 17.1 Hz, *J* 10.2 Hz, *J* 6.9 Hz, *J* 6.9 Hz), 6.01 (ddd, 1H, *J* 10.2 Hz, *J* 2.7 Hz, *J* 1.5 Hz), 6.22 (dd, 1H, *J* 10.2 Hz, *J* 5.4 Hz), 6.93-7.31 (m, 2H); δ_C 13.86, 13.97, 35.60, 36.98, 59.04, 59.52, 61.29, 61.57, 92.08, 116.75, 119.31, 121.94, 127.47, 128.94, 129.45, 132.32, 157.37, 170.08, 170.47; *m/z*(%): 281(14), 207(16).

General procedure for cyclisation of pseudoglycal derivatives.

To a solution of the appropriate pseudoglycal in glacial acetic acid was added a suitable palladium(0) catalyst (0.1 mol equiv.). The clear solution was stirred at 75-80 °C until all starting material had been consumed. Either one of two work-up procedures were employed; **A**: the solution was diluted with CH_2Cl_2 and consecutively washed with a saturated $NaHCO_3$ solution and water. The combined organic phases were then dried (Na_2SO_4) and concentrated *in vacuo* to afford a residue which was purified by flash chromatography. An alternative and slightly simpler work-up procedure **B** entailed evaporation of the solvent under reduced pressure followed by the azeotropic removal of residual acetic acid by coevaporation with toluene.

(*1*R, 4*R/S*, *6*S)-*4-Acetoxy-3,9-dioxa-7-methylidenebicyclo*[*4.3.0*]*nonane* (**13**). A solution of **5** (413 mg, 1.780 mmol) in glacial acetic acid (6 ml) was added to a neat mixture of $Pd(OAc)_2$ (40 mg, 0.178 mmol) and triisopropyl phosphite (264 µl, 1.068 mmol) and stirred at 80 °C for 2.5 h. Work-up **A** and flash chromatography (EtOAc:benzene, 1:6) afforded an inseperable anomeric mixture of products **13** (206 mg, 63%) in a ratio of *ca* 5:1 by ^{1}H NMR. Major product NMR: δ_H 1.79 (ddd, 1H, *J* 11.1 Hz, *J* 3.6 Hz, *J* 3.6 Hz), 1.90 (dd, 1H, *J* 10.9 Hz, *J* 3.6 Hz), 2.07 (s, 3H), 2.80-2.97(m, 1H), 3.85-3.98 (m, 3H), 4.29 (dt, 1H, *J* 13.5 Hz, *J* 1.9 Hz, *J* 1.9 Hz), 4.54 (ddd, *J* 13.5 Hz, *J* 3.6 Hz, *J* 2.3 Hz), 4.87-4.95 (m, 1H), 4.95-5.01 (m, 1H), 6.06 (dd, 1H, *J* 3.7 Hz, *J* 3.7 Hz); δ_C 21.07, 29.27, 36.27, 61.84, 70.42, 75.09, 90.71, 104.52, 150.95, 169.64; *m/z*(%): 198(2), 43(100); HRMS calcd for $C_{10}H_{14}O_4$: 198.0892 (M^+), found 198.0897.

(*1*R, *2*S, *6*R, *8*R)-*5-Methylidene-3,9,11-trioxatricyclo*[*6.2.1.0*^{2,6}]*undecane* (**14**). A solution of **6** (1.500 g, 5.597 mmol), $Pd_2(dba)_3$·$CHCl_3$ (480 mg, 0.835 mmol) and PPh_3 (1.3 g, 4.956 mmol) in THF (20 ml) and trifluoroacetic acid (4.2 ml, 54.115 mmol) was refluxed for 36 h. Work-up **A** followed by flash chromatography (solvent A) gave **14** (630 mg, 67%) as a colourless syrup; $[\alpha]_D^{23}$ -7.7° (*c* 1.0); NMR: δ_H 1.57 (1H, ddd, *J* 14.1 Hz, *J* 10.0 Hz and *J* 1.5 Hz), 1.91 (1H, ddd, *J* 14.1 Hz, *J* 8.6 Hz and *J* 1.8 Hz), 2.86 (1H, m), 3.68-3.86 (3H, m), 4.30 (1H, dtd, *J* 12.8 Hz, *J* 2.0 Hz and *J* 0.7 Hz), 4.64 (1H, ddd, *J* 13.3 Hz, *J* 3.7 Hz and *J* 2.2 Hz), 4.65 (1H, m), 4.85 (1H, dd, *J* 3.4 Hz and *J* 2.1 Hz), 4.93 (1H, td, *J* 2.5 Hz and *J* 1.3 Hz), 5.50 (1H, br s); δ_C 34.63, 36.21, 66.63, 71.28, 73.53, 78.42, 100.73, 104.63, 151.44; *m/z*(%): 168(23), 137(4); HRMS calcd for $C_9H_{12}O_3$: 168.0786 (M^+), found 168.0783.

(*1*S, *2*S, *6*R)-*2-Isobutoxcarboxymethyl-7-methylidene-3-oxa-9-tosylamidobicyclo[4.3.0]non-4-ene* (**15**). A solution of **7** (300 mg, 0.624 mmol) and $Pd(PPh_3)_4$ (72 mg, 0.062 mmol) in glacial acetic acid (6 ml) was stirred at 80 °C for 2 h and worked up (**A**). Flash chromatography (solvent A) furnished the crystalline **15** (220 mg, 84%); mp 101-103 °C; $[\alpha]_D^{27}$ 30.0 ° (*c* 2.0); NMR: δ_H 0.94 (d, 6H, *J* 6.8 Hz), 2.05 (heptet, *J* 6.8 Hz), 2.41 (s, 3H), 2.45 (m, 1H), 3.56 (ddd, 1H, *J* 10.2 Hz, *J* 6.2 Hz, *J* 2.4 Hz), 3.84-4.01 (m, 5H), 4.50 (dd, 1H, *J* 12.0 Hz, *J* 6.2 Hz), 4.65 (dd, 1H, *J* 12.0 Hz, *J* 2.4 Hz), 4.83 (dd, 1H, *J* 6.0 Hz, *J* 5.0 Hz), 4.88 (ddd, 1H, *J* 2.1 Hz, *J* 2.0 Hz, *J* 2.0 Hz), 5.05 (ddd, 1H, *J* 2.2 Hz, *J* 2.2 Hz, *J* 2.1 Hz), 6.39 (dd, 1H, *J* 6.0 Hz, *J* 1.6 Hz), 7.24-7.74 (m, 4H); δ_C 18.92, 21.54, 27.77, 38.30, 51.72, 55.73, 66.42, 72.53, 74.20, 98.44, 109.90, 134.24, 127.66, 129.98, 147.23, 144.13, 155.11; *m/z*(%) 421(3), 304(12), 266(76); HRMS calcd for $C_{21}H_{27}O_6NS$: 421.1559(M^+), found 421.1555.

(*1*S, *2*S, *6*R)-*2-Benzoyloxymethyl-7-methylidene-3-oxa-9-tosylamidobicyclo[4.3.0]non-4-ene* (**16**). A solution of **8** (446 mg, 0.920 mmol) and $Pd(PPh_3)_4$ (106 mg, 0.092 mmol) in glacial acetic acid (5 ml) was stirred at 80 °C for 4 h. Work up **A** followed by flash chromatography (solvent A) on deactivated silica gel (1% triethylamine) yielded the crystalline **16** (344 mg, 88%); mp 52-54 °C; $[\alpha]_D^{28}$ 9.1 ° (*c* 1.0); NMR: δ_H 2.41 (s, 3H), 2.54 (m, 1H), 3.70 (ddd, 1H, *J* 10.0 Hz, *J* 6.1 Hz, *J* 2.4 Hz), 3.87-4.20 (m, 2H), 3.97 (dd, 1H, *J* 10.0 Hz, *J* 4.6 Hz), 4.63 (dd, 1H, *J* 12.2 Hz, *J* 6.2 Hz), 4.82-4.95 (m, 2H), 4.92 (dd, 1H, *J* 12.2 Hz, *J* 2.4 Hz), 5.08 (dm, 1H, *J* 2.0 Hz), 6.41 (dd, 1H, *J* 5.9 Hz, *J* 1.5 Hz), 7.28-8.13 (m, 9H); δ_C 21.57, 38.67, 51.66, 56.22, 63.57, 72.74, 98.55, 109.88, 127.61, 128.29, 129.77, 129.99, 132.88, 143.98, 144.14, 147.35, 166.27; *m/z*(%): 425(3), 303(11), 270(84); HRMS calcd for $C_{23}H_{23}NO_5S$: 425.1297 (M^+), found 425.1306.

(*1*S, *6*R)-*4-Acetoxy-9-bis(methoxycarbonyl)-7-methylidene-3-oxabicyclo[4.3.0]nonane* (**17**). A solution of **9** (90 mg, 0.260 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) in glacial acetic acid (1 ml) were stirred at 75 °C for 5 h and worked up according to procedure **B**. Flash chromatography (solvent E) supplied an inseparable anomeric mixture **17** (75 mg, 92%). Major isomer NMR: δ_H 1.78 (ddd, 1H, *J* 14.1 Hz, *J* 6.3 Hz, *J* 6.0 Hz), 1.96-2.00 (m, 1H), 2.06 (s, 3H), 2.74 (dm, 1H, *J* 17.7 Hz), 2.83-3.07 (m, 2H), 3.39 (ddd, 1H, *J* 17.7 Hz, *J* 4.58 Hz, *J* 2.38 Hz), 3.62 (dd, 1H, *J* 12.6 Hz, *J* 6.0 Hz), 3.70 (s, 3H), 3.71 (s, 3H), 3.88 (dd, 1H, *J* 12.6 Hz, *J* 4.8 Hz), 4.94 (ddd, 1H, *J* 2.2 Hz, *J* 2.2 Hz, *J* 2.2 Hz), 5.80 (dd, 1H, *J* 6.0 Hz, *J* 3.6 Hz); δ_C 21.05, 29.46, 38.47, 38.86, 42.39, 52.87, 52.95, 59.86, 61.13, 91.18, 107.82, 149.09, 169.82, 170.80, 171.91; *m/z*(%): 312(1), 252(36), 193(35), 192(43), 133(38); HRMS calcd for $C_{15}H_{20}O_7$: 312.1209 (M^+), found 312.1216.

(*1*R)-*9-Bis(phenylsulfonyl)-7-methylidene-3-oxabicyclo[4.3.0]non-5-ene* (**18**). A solution of **10** (80 mg, 0.157 mmol) and $Pd(PPh_3)_4$ (18 mg, 0.016 mmol) in glacial acetic acid (1 ml) were stirred at 75 °C for 5 h and worked up according to procedure **B**. Flash chromatography (solvent D) furnished **18** (major product) along with other double bond isomers (40 mg, 62% combined yield); NMR of **18**: δ_H 3.08 (m, 1H), 3.30-3.44 (m, 2H), 3.91 (dd, 1H, *J* 12.4 Hz, *J* 8.4 Hz), 3.98 (dd, 1H, *J* 12.4 Hz, *J* 6.0 Hz), 4.27 (dd, 1H, *J* 11.4 Hz, *J* 11.4 Hz), 4.77 (dd, *J* 8.4 Hz, *J* 6.0 Hz), 4.94 (ddd, 1H, *J* 2.0 Hz, *J* 2.0 Hz, *J* 2.0 Hz), 5.08 (ddd, 1H, *J* 1.6 Hz, *J* 1.6 Hz, *J* 1.6 Hz), 7.63-7.74 (m, 6H), 7.95-8.15 (m, 4H); *m/z*(%): 416(2), 274(34), 149(13), 133(100); HRMS calcd for $C_{21}H_{20}O_5S_2$: 416.0752 (M^+), found 416.0741.

(*1*R, 2S, *6*S)-*2-(Acetoxymethyl)-9-bis(ethoxycarbonyl)-7-methylidenebicyclo[4.3.0]non-4-ene* (**19**)

(a) The *tert*-butoxy pseudoglucal **11** (360 mg, 0.845 mmol) and $Pd(PPh_3)_4$ (49 mg, 0.042 mmol) in glacial acetic acid (0.7 ml) was stirred at 76 °C for 12 h and worked up (**B**). Flash chromatography (solvent D) afforded **19** (193 mg, 65%). Similar treatment of **12** afforded **19** in a yield of 47%.

(b) A solution of **22** (100 mg, 0.244 mmol), glacial acetic acid (14 µl, 0.244 mmol), $Pd_2(dba)_3.CHCl_3$ (6 mg, $6.1x10^{-3}$ mmol) and tri-*o*-tolylphosphine (4 mg, 0.012 mmol) in benzene (3.5 ml) was stirred at 75 °C for 12 h. Work up according to method **B** and flash chromatography (solvent D) afforded **19** (58 mg, 68%) as a colourless syrup.

(c) A solution of **20** (158 mg, 0.450 mmol), glacial acetic acid(10 µl, 0.180 mmol), $Pd_2(dba)_3.CHCl3$ (90 mg, 0.09 mmol) and PPh_3 (45 mg, 0.18 mmol) in benzene (3 ml) was stirred at room temperature for 3 h. Work up according to method **A**, and flash chromatography (solvent D) provided **19** (365 mg, 81%); $[\alpha]_D^{25}$ -4.4° (*c* 1.2); NMR: δ_H 1.23 (t, 6H, *J* 7.2 Hz), 2.08 (s, 3H), 2.56 (ddd, 1H, *J* 17.0 Hz, *J* 2.2 Hz, *J* 2.2 Hz), 3.16 (m, 2H), 3.42 (ddd, 1H, *J* 17.0 Hz, *J* 0.9 Hz, *J* 0.9 Hz), 4.07-4.35 (m, 6H), 4.54 (dd, 1H, *J* 7.2 Hz, *J* 4.2 Hz), 4.63 (ddd, 1H, *J* 6.3 Hz, *J* 2.1 Hz, *J* 2.1 Hz), 4.95-4.97 (m, 2H), 6.12 (dd, 1H, *J* 6.3 Hz, *J* 0.6 Hz); δ_C 13.72, 13.88, 21.81, 36.39, 40.08, 43.41, 59.96, 61.66, 61.94, 64.27, 70.22, 103.33, 107.04, 140.58, 149.86, 170.51, 170.96, 171.65; *m/z*(%): 352(15), 307(6); HRMS calcd for $C_{18}H_{24}O_7$: 352.1522 (M^+), found 352.1528.

General procedure for cyclisation/carbonylation of pseudoglycal derivatives.[33]

Carbon monoxide was slowly bubbled through a capillary glass tube into a solution of the appropriate Pd(0) catalyst (0.1 mol equiv.) in glacial acetic acid at room temperature for 10 minutes. A solution of the pseudoglycal in glacial acetic acid was added and the reaction mixture stirred at 46 °C under 1 atmosphere of CO until monitoring by tlc indicated the absence of all starting material. The solvent was evaporated *in vacuo* followed by azeotropic removal of residual acetic acid by coevaporation with toluene.

(*1*R, *8*R, *11*R)-*8-Acetoxy-3,10-dioxa-6-oxotricyclo[6.2.1.0^{5,11}]undec-4-ene* (**29**). To a neat mixture of $Pd(OAc)_2$ (6 mg, 0.026 mmol) and triisopropyl phosphite (39 µl, 0.160 mmol) was added a solution of **25** (60 mg, 0.261 mmol) in acetic acid (2 ml). The solution was stirred at 46 °C for 12 h, the solvent evaporated and the residue subjected to flash chromatography (solvent C) to afford the crystalline **29** (29 mg, 50%); mp 147-151 °C; $[\alpha]_D^{20}$ 45.4° (*c* 1.2); NMR: δ_H 2.07 (s, 3H), 2.66 (d, 1H, *J* 18.3 Hz), 3.13 (d, 1H, *J* 18.3 Hz), 3.27 (dd, 1H, *J* 3.9 Hz, *J* 2.1 Hz), 4.02 (d, 1H, *J* 13.2 Hz), 4.11 (d, 1H, *J* 11.4 Hz), 4.16 (dd, 1H, *J* 11.4 Hz, *J* 1.6 Hz), 4.41 (d, 1H, *J* 13.2 Hz), 4.51 (m, 1H), 7.39 (d, 1H, *J* 2.1 Hz); δ_C 21.09, 45.94, 47.87, 65.59, 71.14, 79.08, 88.81, 110.74, 150.92, 170.58, 198.96; *m/z*(%): 224(17), 164(100); HRMS calcd for $C_{11}H_{12}O_5$: 224.0685 (M^+), found 224.0691.

(*1*S, *4*R/S, *5*R, *11*R)-*4-Acetoxy-10-bis(ethoxycarbonyl)-3-oxa-6-oxotricyclo[6.2.1.0^{5,11}]undec-7-ene* (**30**). A solution of **26** (200 mg, 0.538 mmol) in acetic acid (1.5 ml) was added to a mixture of $Pd_2(dba)_3.CHCl_3$ (28 mg, 0.027 mmol) and tri-*o*-tolylphoshine (24 mg, 0.079 mmol) in acetic acid (1 ml). The reaction mixture was stirred overnight at 46 °C under CO (1 atm) after which the solvent was evaporated. Flash chromatography (solvent C) furnished the crystalline **30** (148 mg, 75%); mp 130-132 °C; $[\alpha]_D^{19}$ -63.0 ° (*c* 1.1); NMR: δ_H 1.24 (t, 3H, *J* 7.2 Hz), 1.26 (t, 3H, *J* 7.2 Hz), 2.11 (s, 3H), 2.83 (dd, 1H, *J* 6.9 Hz, *J* 3.9 Hz), 3.10-3.18 (m, 2H), 3.32 (ddd, 1H, *J* 11.1 Hz, *J* 6.9 Hz, *J* 6.9 Hz), 3.57-3.64 (m, 2H), 3.81 (dd, 1H, *J* 11.4 Hz, *J* 7.2 Hz), 4.21 (2q, 4H, *J*

7.2 Hz), 5.79 (d, 1H, *J* 3.9 Hz), 6.02 (d, 1H, *J* 1.5 Hz); δ_C 13.90, 13.99, 21.06, 34.27, 37.16, 46.58, 49.70, 60.77, 62.29, 62.42, 63.49, 90.99, 126.74, 168.19, 169.41, 170.70, 183.36, 206.30; *m/z*(%): 366(4), 306(90), 233(33); HRMS calcd for $C_{18}H_{22}O_8$: 366.1315 (M^+), found 366.1322.

(*1*R, *2*S, *6*S)-*2-Acetoxymethyl-9-bis(ethoxycarbonyl)-7-(methoxycarbonyl)methylidene-3-oxabicyclo[4.3.0]non-4-ene* (**31**). A solution of **22** (300 mg, 0.732 mmol) in acetic acid (2 ml) was added to a mixture of $Pd_2(dba)_3$.$CHCl_3$ (39 mg, 0.038 mmol) and tri-*o*-tolylphoshine (21 mg, 0.069 mmol) in acetic acid (1 ml). The reaction mixture was stirred overnight at 48 °C under CO (1 atm). The solvent was evaporated *in vacuo* and the crude mixture dissolved in CH_2Cl_2 (1.5 ml) and treated with an etherial solution of diazomethane at 0 °C until gas evolution ceased. Evaporation and flash chromatography (solvent B) provided **31** (210 mg, 70%); $[\alpha]_D^{24}$ 11.3° (*c* 1.4); NMR: δ_H 1.22 (t, 6H, *J* 7.2 Hz), 2.08 (s, 3H), 2.67 (dd, 1H, *J* 18.6 Hz, *J* 2.1 Hz), 3.17 (d, 1H, *J* 8.7 Hz), 3.62 (ddd, 1H, *J* 18.6 Hz, *J* 1.8 Hz, *J* 1.8 Hz), 3.67 (s, 3H), 4.05-4.27 (m, 6H), 4.36 (dd, 1H, *J* 11.4 Hz, *J* 7.5 Hz), 4.62 (ddd, 1H, *J* 7.5 Hz, *J* 5.1 Hz, *J* 1.2 Hz), 4.73 (ddd, 1H, *J* 6.3 Hz, *J* 2.4 Hz, *J* 1.5 Hz), 5.80 (ddd, 1H, *J* 2.1 Hz, *J* 2.1 Hz, *J* 2.1 Hz), 6.11 (ddd, 1H, *J* 6.3 Hz, *J* 2.4 Hz, *J* 0.6 Hz); δ_C 13.70, 13.86, 20.79, 35.44, 41.59, 43.92, 51.14, 58.52, 61.84, 62.22, 64.30, 69.98, 100.70, 113.78, 141.44, 163.45, 166.19, 170.40, 170.81, 171.16; *m/z*(%): 410(2), 378(81), 291(25); HRMS calcd for $C_{20}H_{26}O_9$: 410.1577 (M^+), found 410.1585.

(*1*S, *8*S,*11*S)-*3,10-Dioxa-6-oxotricyclo*[$6.2.1.0^{5,11}$]*undec-4-ene* (**32**), (*1*S, *6*R, *7*S)-*3,9-Dioxa-7-(methoxycarbonyl)methylbicyclo[4.3.0]non-4-ene* (**33**) and (*1*S, *4*R/S, *6*R, *7*S)-*4-Acetoxy-3,9-dioxa-7-(methoxycarbonyl)methylbicyclo[4.3.0]nonane* (**34**). A solution of **27** (120 mg, 0.517 mmol) in acetic acid (2 ml) was added to a mixture of $Pd_2(dba)_3$.$CHCl_3$ (27 mg, 0.026 mmol) and tri-*o*-tolylphoshine (24 mg, 0.078 mmol) in acetic acid (1 ml). The reaction mixture was stirred overnight at 46 °C under CO (1 atm). The solvent was evaporated *in vacuo* and the crude mixture dissolved in CH_2Cl_2 (1.5 ml) and treated with small portions of an etherial solution of diazomethane at 0 °C until gas evolution ceased. Evaporation and flash chromatography (solvent C) provided **32** (9 mg, 10%), **33** (15 mg, 15%) and **34** (35 mg, 26%).

32: mp 198-203 °C; $[\alpha]_D^{26}$ -360.0° (*c* 0.8); NMR: δ_H 2.17 (d, 1H, *J* 18.3 Hz), 2.58 (dd, 1H, *J* 18.3 Hz, *J* 6.6 Hz), 3.05-3.18 (m, 2H), 3.55 (dd, 1H, *J* 9.0 Hz, *J* 6.6 Hz), 4.00 (dd, 1H, *J* 13.2 Hz, *J* 0.9 Hz), 4.14 (dd, 1H, *J* 9.0 Hz, *J* 9.0 Hz), 4.32 (m, 1H), 4.38 (dd, 1H, *J* 13.2 Hz, *J* 1.5 Hz), 7.37 (d, 1H, *J* 1.5 Hz); δ_C 38.48, 41.15, 42.01, 65.83, 72.54, 74.10, 112.12, 150.35, 203.75; *m/z*(%): 166(100); HRMS calcd for $C_9H_{10}O_3$: 166.0630 (M^+), found 166.0625.

33: NMR: δ_H 2.29 (dd, 1H, *J* 16.1 Hz, *J* 7.1 Hz), 2.44 (dd, 1H, *J* 16.1 Hz, *J* 7.1 Hz), 2.73-2.86 (m, 2H), 3.50 (dd, 1H, *J* 9.6 Hz, *J* 7.7 Hz), 3.66 (s, 3H), 3.77 (d, 1H, *J* 11.9 Hz), 3.97 (dd, 1H, *J* 7.3 Hz, *J* 7.3 Hz), 4.06 (dd, 1H, *J* 11.9 Hz, *J* 2.7 Hz), 4.28 (m, 1H), 4.56 (ddd, 1H, *J* 6.4 Hz, *J* 2.7 Hz, *J* 1.5 Hz), 6.51 (d, 1H, *J* 6.4 Hz); δ_C 32.55, 35.53, 39.63, 51.73, 66.28, 71.48, 76.81, 98.05, 146.41, 172.68; *m/z*(%): 198(34), 167(19); HRMS calcd for $C_{10}H_{14}O_4$: 198.0892 (M^+), found 198.0897.

34: $[\alpha]_D^{24}$ 75.2° (*c* 1.0); NMR: δ_H 1.55 (d, 1H, *J* 2.7 Hz), 1.60 (d, 1H, *J* 2.7 Hz), 2.06 (s, 3H), 2.28 (dd, 1H, *J* 15.9 Hz, *J* 7.8 Hz), 2.42 (dd, 1H, *J* 15.9 Hz, *J* 7.8 Hz), 2.49 (m, 1H), 2.86 (m, 1H), 3.56 (dd, 1H, *J* 8.5 Hz, *J* 8.5 Hz), 3.66 (s, 3H), 3.84 (m, 1H), 3.93 (s, 2H), 4.09 (dd, 1H, *J* 8.5 Hz, *J* 8.5 Hz), 6.15 (dd, 1H, *J* 2.7 Hz, *J* 2.7 Hz); δ_C 21.04, 24.27, 31.80, 32.36, 39.41, 51.78, 61.20, 70.44, 75.14, 90.53, 169.56, 172.46; *m/z*(%): 258(3), 199(23), 198(36); HRMS calcd for $C_{12}H_{18}O_6$: 258.1103 (M^+), found 258.1108.

(*1*R, *6*R, *7*S)-*9-Bis(ethoxycarbonyl)-7-(methoxycarbonyl)methyl-3-oxabicyclo[4.3.0]non-4-ene* (**35**) and (*1*R, *4*R/S, *6*R, *7*S)-*4-Acetoxy-9-bis(ethoxycarbonyl)-7-(methoxycarbonyl)methyl-3-oxabicyclo[4.3.0]non-4-ene* (**36**). A solution of **28** (500 mg, 1.337 mmol) in acetic acid (3.5 ml) was added to a solution of $Pd(PPh_3)_4$ (154 mg, 0.133 mmol) in acetic acid (1 ml). The reaction mixture was stirred overnight at 46 °C under CO (1 atm). The solvent was evaporated *in vacuo* and the crude mixture dissolved in CH_2Cl_2 (1.5 ml) and treated with an etherial solution of diazomethane at 0 °C until gas evolution ceased. Evaporation and flash chromatography (solvent D) furnished **35** (114 mg, 25%) and **36** (171 mg, 32%) as colourless syrups.

35: NMR: δ_H 1.22 (t, 3H, *J* 7.2 Hz), 1.24 (t, 3H, *J* 7.2 Hz), 2.09 (m, 1H), 2.26-2.50 (m, 3H), 2.75-2.85 (m, 2H), 3.33 (m, 1H), 3.65 (s, 3H), 3.88 (dd, 1H, *J* 11.1 Hz, *J* 3.3 Hz), 4.06 (dd, 1H, *J* 11.1 Hz, *J* 4.5 Hz), 4.11-4.29 (m, 4H), 4.53 (ddd, 1H, *J* 6.3 Hz, *J* 1.5 Hz, *J* 0.5 Hz), 6.40 (dd, 1H, *J* 6.3 Hz, *J* 1.8 Hz); δ_C 13.81, 13.89, 35.39, 36.79, 36.91, 43.25, 51.60, 60.23, 61.71, 61.81, 64.70, 99.43, 146.72, 170.28, 172.33, 173.14; *m/z*(%): 340(9), 309(6), 295(6), 280(17), 266(27), 220(20), 193(38), 173(100); HRMS calcd for $C_{17}H_{24}O_7$: 340.1522 (M^+), found 340.1517.

36: NMR: δ_H 1.22 (2t, 6H, *J* 7.2 Hz), 1.43-1.71 (m, 2H), 2.07 (s, 3H), 1.43-1.70 (m, 6H), 2.96 (m, 1H), 3.66 (s, 3H), 4.02-4.25 (m, 6H), 6.02 (d, 1H, *J* 3.0 Hz); δ_C 13.86, 13.94, 21.12, 24.36, 34.05, 34.86, 37.83, 37.90, 43.98, 51.63, 59.00, 59.15, 61.72, 62.25, 91.05, 169.74, 171.50, 172.43, 172.87; *m/z*(%): 400(2), 357(34), 341(75), 327(15), 281(34), 266(100), 235(25); HRMS calcd for $C_{19}H_{28}O_9$: 400.1733 (M^+), found 400.1742.

(*1*R, *2*S, *6*R, *7*S)-*2-Acetoxymethyl-9-bis(ethoxycarbonyl)-7-(methoxycarbonyl)methyl-3-oxabicyclo[4.3.0]non-4-ene* (**37**). A solution of **12** (500 mg, 1.214 mmol) in acetic acid (3 ml) was added to a mixture of $Pd_2(dba)_3.CHCl_3$ (63 mg, 0.061 mmol) and tri-*o*-tolylphoshine (37 mg, 0.122 mmol) in acetic acid (3 ml). The reaction mixture was stirred overnight at 46 °C under CO (1 atm). The solvent was evaporated *in vacuo* and the crude mixture dissolved in CH_2Cl_2 (1.5 ml) and treated with an etherial solution of diazomethane at 0 °C until gas evolution ceased. Evaporation and flash chromatography (solvent C) supplied **37** (175 mg, 35%) along with recovered starting material (200 mg, 40%); $[\alpha]_D^{24}$ -6.9° (*c* 1.0); NMR: δ_H 1.21 (t, 3H, *J* 7.2 Hz), 1.23 (t, 3H, *J* 7.2 Hz), 2.00-2.07 (m, 1H), 2.07 (s, 3H), 2.31-2.42 (m, 3H), 2.57 (dd, 1H, *J* 13.0 Hz, *J* 13.0 Hz), 2.67 (m, 1H), 3.32 (dm, 1H, *J* 7.0 Hz), 3.65 (s, 3H), 4.01 (dd, 1H, *J* 11.4 Hz, *J* 4.5 Hz), 4.08-4.26 (m, 4H), 4.32 (dd, 1H, *J* 11.4 Hz, *J* 8.4 Hz), 4.50-4.57 (m, 2H), 6.20 (dd, 1H, *J* 6.3 Hz, *J* 2.1 Hz); δ_C 13.83, 13.87, 20.83, 34.27, 34.43, 37.26, 37.95, 43.42, 51.68, 60.21, 61.89, 61.95, 64.06, 70.79, 98.00, 143.79, 170.20, 170.92, 172.47, 172.87; *m/z*(%): 412(28), 384(21), 352(28), 294(26), 279(47), 231(44), 173(99); HRMS calcd for $C_{20}H_{28}O_9$: 412.1733 (M^+), found 412.1721.

(*1*R, *6*R)-*9-Bis(phenylsulfonyl)-7-methylidene-3-oxabicyclo[4.3.0]non-4-ene* (**40**). To a neat mixture of $Pd(OAc)_2$ (11 mg, 0.049 mmol) and triisopropyl phosphite (73 µl, 0.294 mmol) was added a solution of **10** (250 mg, 0.490 mmol) in acetic acid (2 ml). The solution was stirred at 46 °C for 12 h, the solvent evaporated and the residue subjected to flash chromatography (solvent C) to afford **40** (82 mg, 40%); $[\alpha]_D^{20}$ 22.4° (*c* 1.0); NMR: δ_H 2.91-3.05 (m, 2H), 3.42 (d, 1H, *J* 18.3 Hz), 3.52 (dd, 1H, *J* 18.3 Hz, *J* 2.1 Hz), 3.73 (dd, 1H, *J* 10.8 Hz, *J* 10.8 Hz), 4.65 (ddd, 1H, *J* 10.8 Hz, *J* 4.2 Hz, *J* 1.5 Hz), 4.93 (dd, 1H, *J* 6.0 Hz, *J* 4.5 Hz), 4.99 (ddd, 1H, *J* 2.1 Hz, *J* 2.1 Hz, *J* 2.1 Hz), 5.15 (dd, 1H, *J* 2.1 Hz, *J* 2.1 Hz, *J* 2.1 Hz), 6.44 (dd, 1H, *J* 6.0 Hz, *J* 1.8 Hz), 7.26-8.08 (m, 10H); δ_C 36.52, 39.39, 43.74, 63.68, 100.17, 110.12, 128.76, 128.97, 130.54, 130.93, 134.64, 135.06,

135.69, 139.69, 144.29, 148.53; *m/z*(%): 416(2), 274(30), 133(100), 105(29); HRMS calcd for $C_{21}H_{20}O_5S_2$: 416.0752 (M^+), found 416.0758.

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