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Alkyl radical cyclization to vinylogous carbonates for the stereoselective synthesis of unsymmetrical dioxa-cage compounds: effect of conformation on the rate of cyclization versus reduction

Santosh J. Gharpure *, Suheel K. Porwal

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India

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ABSTRACT

An efficient strategy for the stereoselective construction of unsymmetrical dioxa-cage compounds containing ether linkages employing a 6-*exo-trig* alkyl radical cyclization to vinylogous carbonates is developed. The radical precursors are prepared from the diols obtained from the Diels–Alder adducts via iodoetherification followed by addition of the alcohol to the ethyl propiolate. The geometrical constrains play important role in deciding the outcome of the reaction as cyclization versus simple reduction. Formation of the mono-oxa-cage compounds via a 5-*exo-trig* intramolecular alkyl radical cyclization to olefin is also described. The dioxa-cages could also be assembled employing a tandem oxymercuration reduction-radical cyclization to vinylogous carbonates protocol with equal efficiency and with reduced number of steps.

1. Introduction

Over the years, strained organic molecules have evoked considerable interest amongst synthetic and theoretical chemists.[1] Whereas synthesis of carbacycles was focus of the early efforts, recently, developing new synthetic strategies toward heteroatom substituted bowls and cages has gained currency. These aesthetically pleasing molecules also provide opportunity for testing new reactions for their synthesis as these are strained molecules. Oxa-, aza- and thia-bowls and cages typically possess distinct hydrophilic and hydrophobic surfaces. Consequently, they were thought to be more useful than their carbon analogue as they could potentially function as ligands for chelation with metal ions. Further, it was also envisaged that they may prove to be useful in chemical transportation phenomenon.[2] It has been suggested that these molecules may be useful in the treatment of various diseases like Parkinson's and Alzheimer's disease and also as antiviral agents against influenza and the immunodeficiency virus (HIV).[3] As a result, this area of the synthesis of oxa- and aza-bowls and cages continues to flourish.[4]

Majority of the synthetic strategies reported in the literature for the synthesis of the oxa-bowls and cages dealt with syntheses of acetal/ketal containing oxa-cage compounds. These were obtained by ozonolysis of Diels–Alder adducts followed by treatment with suitable acid.[5] In addition, a few different strategies, such as intramolecular alkene-oxirane photocycloaddition,[6] transannular cyclization of suitable compounds,[7] tandem cyclization,[8] dehydration of diols with proper stereochemistry,[9] by base promoted rearrangement[10] and intramolecular etherification of an alkene bond with organoselenium reagents have been used for the synthesis of oxa-cages.[11] Interestingly, prior to initiation of our work in this area, radical-based strategies[12] were not commonly available for the synthesis of oxa- and aza-bowls and cages.[13] Vinylogous carbonates are extensively used under radical conditions for the synthesis of cyclic ethers but rarely in the synthesis of oxa-cages.[14] Herein, we describe details of a new strategy for the assembly of unsymmetrical dioxa-cage compounds containing ether linkages employing iodoetherification and alkyl radical cyclization to the vinylogous carbonate moiety as the key steps.

2. Results and discussion

In continuation of our interest on using vinylogous carbonates in the synthesis of cyclic ethers,[15] we envisioned that the unsymmetrical dioxa-cage compounds like **1** could be a new type of oxa-cage compounds containing ether linkage. Further, it was argued that these structures could be rapidly assembled from the readily available diols **2** via a short three-step sequence namely (i) iodoetherification of the diol **2**, (ii) conversion of the resultant alcohol to the vinylogous carbonate **3** followed by (iii) intramolecular 6-*exo-trig*

* Corresponding author. Tel.: +91 44 22574228; fax: +91 44 22574202; e-mail address: sjgharpure@iitm.ac.in (S.J. Gharpure).

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cyclization of alkyl radical derived from the iodide **3** to the vinylogous carbonate moiety as outlined in Fig. 1. The diols **2** can be readily prepared by stereoselective reduction of the dienones (Diels–Alder adducts), which in turn could be assembled from the cyclic dienes and the dienophiles via Diels–Alder cycloaddition reaction.

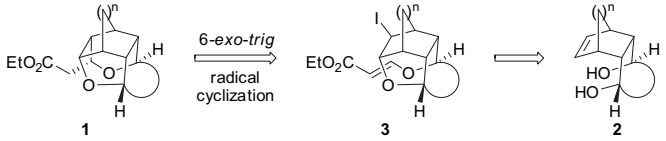


Fig. 1. Retrosynthesis for the novel oxa-cages **1**.

To test the feasibility of the approach, we undertook the synthesis of vinylogous carbonates **4a**–**g** starting from the known diols[5k,16,9c] **5a**–**g** (Table 1). Thus, iodoetherification reaction of the diol **5a** using iodine in THF–water mixture as the solvent in the presence of sodium bicarbonate furnished the iodoether **6a** in excellent yield. Treatment of the iodoether **6a** with ethyl propiolate and *N*-methylmorpholine (NMM) produced the vinylogous carbonate **4a** in 91% yield. In a similar manner, other vinylogous carbonates **4b**–**g** was prepared (cf. Table 1). In general, iodoetherification and vinylogous carbonate-formation reactions were found to be efficient in all the case. The structure of the vinylogous carbonates **4a**–**g** was established based on its spectral data.

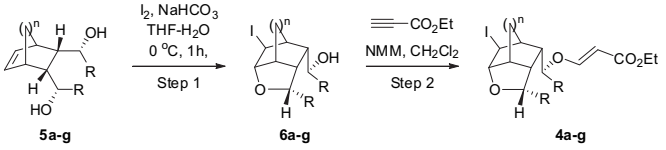
Synthesis of the vinylogous carbonate **4h** followed a slightly different sequence. Treatment of the known[17] diol **5h** with iodine in the presence of aq sodium bicarbonate resulted in the formation of the iodoether **7** via iodoetherification of the *endo* hydroxy group. Oxidation of the alcohol **7** using PCC to the ketone **8** followed by stereoselective reduction with sodium borohydride furnished the alcohol **6h** in good overall yields (Scheme 1). The iodoalcohol **6h** was then converted to the requisite vinylogous carbonate **4h** by treatment with ethyl propiolate in the presence of NMM.

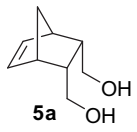
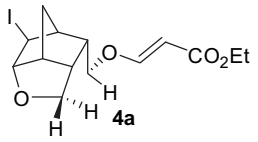
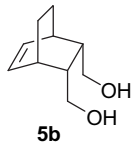
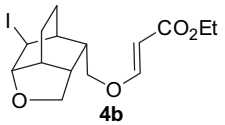
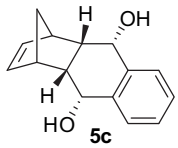
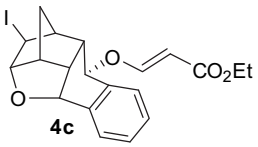
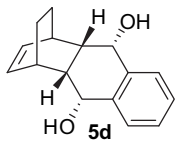
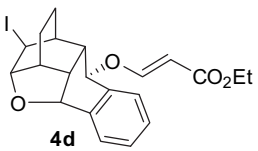
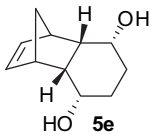
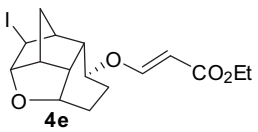
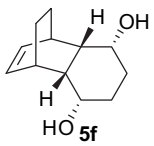
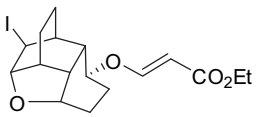
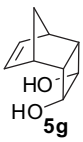
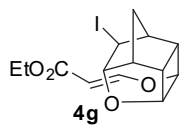
Having the vinylogous carbonates **4a**–**h** in hand, attention was turned towards the targeted radical cyclization reaction for the synthesis of the oxa-cage compound **1a**–**h**. Table 2 summarizes the outcome of this study. Thus, slow addition of a solution of $^{n}Bu_3SnH$ and AIBN in benzene to a refluxing solution of the iodide **4a** and AIBN in benzene, gratifyingly yielded the expected oxa-cage compound **1a** as the only detectable diastereomer. Only trace amounts of the uncyclized reduction product **9a** was observed (ca.<5%) (Table 2, entry 1). It must be noted here that the rate of addition of reagents and dilution had profound impact on the yield of the oxa-cage **1a**. Thus, at higher concentration and faster addition of a solution of $^{n}Bu_3SnH$ and AIBN in benzene to a refluxing solution of iodide **4a**, uncyclized reduction product **9a** was observed as the major product. Similar results were obtained for the iodide **4b**, which furnished the oxa-cage **1b** in very good yield and diastereoselectivity (Table 2, entry 2).

In a similar manner, radical cyclization of the iodides **4c**,**d** and **4g**–**h** under optimized conditions gave the oxa-cage products **1c**,**d** and **1g**–**h** in excellent yield and diastereoselectivity (Table 2, entries 3 and 4, 7 and 8). It is pertinent to mention here that the rate of addition of the reagents ($^{n}Bu_3SnH$ and AIBN) had little impact in these cases and no detectable amounts of uncyclized reduced product **9c**,**d** and **9g**–**h** were observed even at faster addition of tributyltinhydride. These experiments suggested that geometrical constrains play important role during these radical cyclizations.

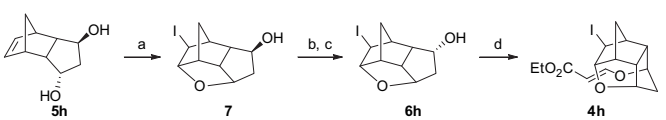
The stereochemistry of the sidearm of the oxa-cage **1d** was unambiguously established by doing single-crystal X-ray diffraction studies on the alcohol **10** (Fig. 2), which was obtained by lithium aluminum hydride (LAH) reduction of the oxa-cage **1d** (Scheme 2).[18] The stereochemistry of other oxa-cages **1a**–**c** and **1g**–**h** was assigned by analogy to the oxa-cage **1d**.

Table 1
Synthesis of the iodovinylogous carbonates **4**



Entry	Diol	Yield (%)[a]		Vinylogous carbonate
		Step 1	Step 2	
1	 **5a**	86	91	 **4a**
2	 **5b**	97	94	 **4b**
3	 **5c**	80	98	 **4c**
4	 **5d**	80	91	 **4d**
5	 **5e**	99	95	 **4e**
6	 **5f**	83	88	 **4f**
7	 **5g**	85	96	 **4g**

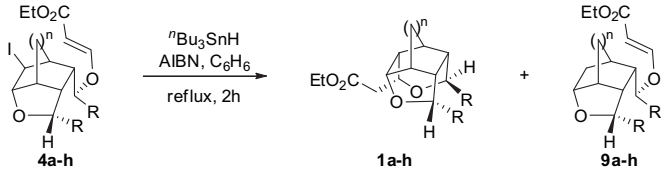
[a] Isolated yields of purified products.

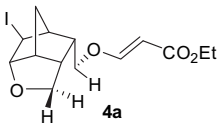
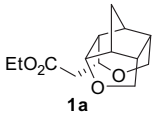
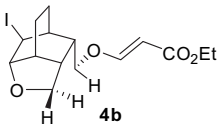
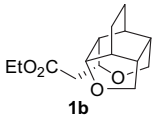
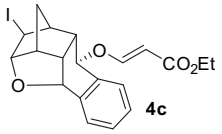
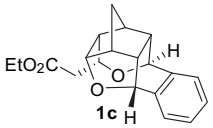
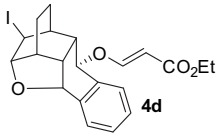
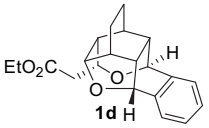
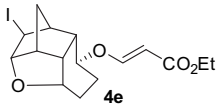
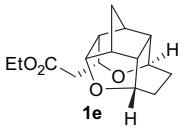
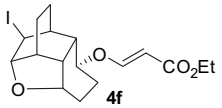
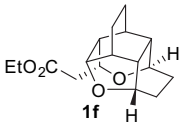
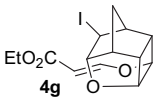
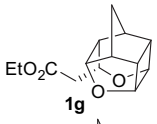
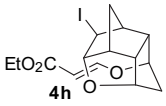
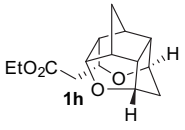


Scheme 1. Reagents, conditions and yields: (a) I_2, $NaHCO_3$, $THF–H_2O$, 0 °C, 1 h, 90%; (b) PCC, 4 Å MS, CH_2Cl_2, rt, 3 h, 88%. (c) $NaBH_4$, MeOH, 0 °C, 1 h, 96%. (d) ethyl propiolate, NMM, CH_2Cl_2, rt, 4 h, 88%.

The stereochemical outcome of these reactions could be rationalized as follows. During the radical cyclization, the alkyl radical adds to the vinylogous carbonate moiety in such a way that the vinylogous carbonate moiety is positioned '*exo*' thereby minimizing the steric interactions.

Table 2
Radical cyclization to vinylogous carbonate for synthesis of the oxa-cages **1**



Entry	Substrate	Yield (%)[a]		Oxa-cage product
		Cyclized product **1** (dr)[b]	Reduction product **9**	
1	 **4a**	86 (≥19:1)	<5[b]	 **1a**
2	 **4b**	83 (≥19:1)	<5[b]	 **1b**
3	 **4c**	90 (≥19:1)	n.d.[b]	 **1c**
4	 **4d**	84 (≥19:1)	n.d.[b]	 **1d**
5	 **4e**	<5 (n.a.)	88	 **1e**
6	 **4f**	<5 (n.a.)	75	 **1f**
7	 **4g**	88 (≥19:1)	n.d.[b]	 **1g**
8	 **4h**	83 (≥19:1)	n.d.[b]	 **1h**

[a] Isolated yields of purified products unless otherwise stated.
[b] Determined on crude reaction mixtures by ^{1}H NMR; (n.a. not applicable, n.d. not detected).

Interestingly, reaction of the iodides **4e** and **4f** under the standardized conditions furnished only the uncyclized reduction products **9e** and **9f**, respectively, as the major products and no significant amount of cyclized products could be obtained (Table 2, entries 5 and 6). All efforts to synthesize the oxa-cages **1e** and **1f** by changing solvent (toluene instead of benzene), temperature or reducing agent (hypophosphorous acid instead of tributyltinhydride) met with failure.

In order to understand this unusual behaviour, the iodide **4f** was subjected to single-crystal X-ray diffraction studies (Fig. 3).[19] The crystal structure of the iodide **4f** showed that the six membered ring bearing the vinylogous carbonate substituent in this compound has an almost locked chair conformation. The vinylogous carbonate moiety is forced on the 'outside' of the concave portion of the molecule. Due to the rigidity of the molecule, it is not able to come close to the radical obtained from the iodide thereby resulting in the formation of the uncyclized reduced product.

Close analysis of this reactivity pattern revealed some interesting observations. The iodides **4a**,**b**, which don't have any geometrical constrains, do give the corresponding cyclized products albeit at slower addition of the reagent. This can be clearly understood given

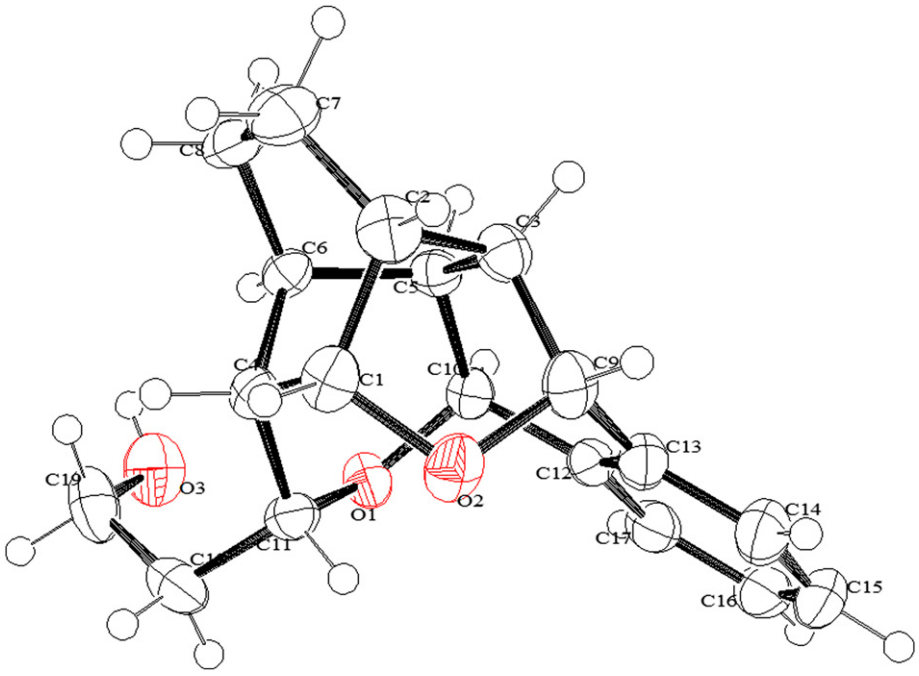
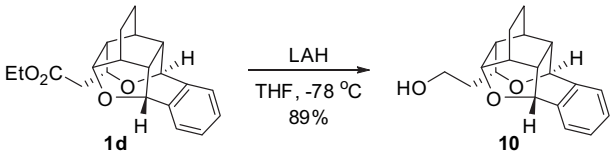


Fig. 2. ORTEP picture of the alcohol **10**.



Scheme 2.

vinylogous carbonate moiety to occupy '*endo*' orientation bringing it close to reacting radical centre during the reactions. In order to test this hypothesis of constrain in the geometry leading to efficient reactivity, it was decided to undertake synthesis of the iodides **4i**,**j**, which have two sp^3-hybridized carbons in the cyclohexane ring but are locked by another ring (an epoxide in **4i** and a bicyclic framework in **4j**). Further to understand the effect of the presence of an sp^2-hybridized carbon centre in the six membered ring, the synthesis of the iodides **4k**,**l** was planned.

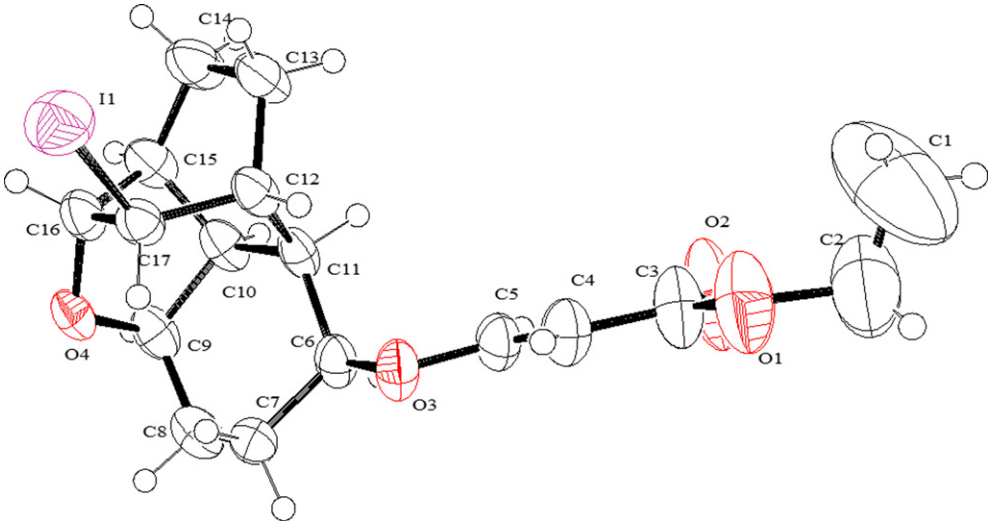
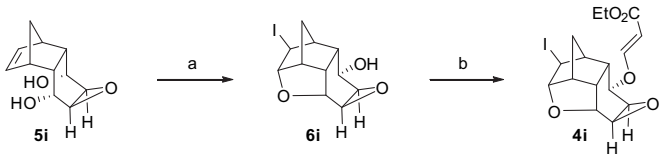


Fig. 3. ORTEP picture of the vinylogous carbonate **4f**.

that the reactive conformation requires vinylogous carbonate moiety to be oriented in a sterically unfavourable '*endo*' fashion. It was speculated that in the iodides **4g**–**h** due to smaller size of the rings bearing vinylogous carbonate moiety, the locked conformation forces the vinylogous carbonate moiety to come close to the reactive centre during radical cyclization. On the other hand, in the case of the iodides **4c**,**d**, presence of two sp^2-hybridized carbons in the cyclohexane ring significantly distort the chair conformation thereby forcing the

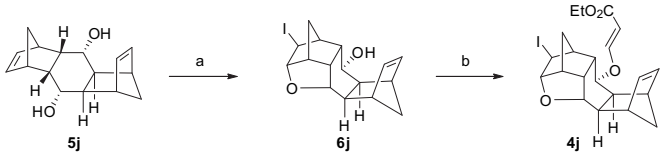
The synthesis of vinylogous carbonate **4i** started from the known[20] diol **5i**, which was subjected to iodoetherification reaction to furnish the iodoalcohol **6i** in 60% yield. Treatment of the iodoether **6i** with ethyl propiolate and *N*-methylmorpholine (NMM) produced the vinylogous carbonate **4i** in 80% yield (Scheme 3).

The synthesis of vinylogous carbonate **4j** started from the known[21] diol **5j**. Iodoetherification of the diol **5j** generated the alcohol **6j** in 68% yield. Treatment of iodoether **6j** with ethyl



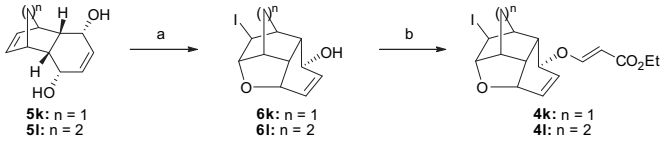
Scheme 3. Reagents, conditions and yields: (a) I_2, $NaHCO_3$, THF–H_2O, 0 °C, 1 h, 60%; (b) ethyl propiolate, NMM, CH_2Cl_2, rt, 4 h, 80%.

propiolate and *N*-methylmorpholine (NMM) produced the requisite vinylogous carbonate **4j** in 85% yield whose structure was confirmed based on its spectral data (Scheme 4).



Scheme 4. Reagents, conditions and yields: (a) I_2, $NaHCO_3$, THF–H_2O, 0 °C, 1 h, 55%; (b) ethyl propiolate, NMM, CH_2Cl_2, rt, 4 h, 85%.

Finally, the vinylogous carbonates **4k**,**l** bearing olefin were synthesized from the known[9c,5k] diols **5k**,**l** (Scheme 5). Iodoetherification of the diols **5k**,**l** to the iodo-alcohols **6k**,**l** followed by their reaction with ethyl propiolate and *N*-methylmorpholine (NMM) produced the vinylogous carbonates **4k**,**l** in good overall yield. The lower yields of iodoetherification reaction in these cases could be attributed to the presence of the additional olefin.



Scheme 5. Reagents, conditions and yields: (a) I_2, $NaHCO_3$, THF–H_2O, 0 °C, 1 h, 65% (for **6k**), 45% (for **6l**); (b) ethyl propiolate, NMM, CH_2Cl_2, rt, 4 h, 96% (for **4k**), 95% (for **4l**).

Attention was next turned towards studying the radical cyclization reaction of these iodovinylogous carbonates **4i**–**l**. Six-*exo*-*trig* radical cyclization reaction of the iodides **4i**,**j** with $^nBu_3SnH$ and AIBN in refluxing benzene gratifyingly furnished the oxa-cages **1i**,**j**, respectively, in good yields and excellent diastereoselectivity (Table 3). No detectable amounts of the uncyclized reduction products were observed in these cases. These results supported the argument that the restricted conformation of the cyclohexane ring indeed ensures that the vinylogous carbonate moiety occupies the '*endo*' orientation during the radical cyclization. Presence of the epoxide ring (in the iodide **4i**) or bicyclo[2.2.1]heptane ring fused with cyclohexane (in the iodide **4j**) provides the necessary restriction to the free rotation of the vinylogous carbonate moiety thus leading to the cyclized products. The stereochemistry of the sidearm and bicyclo[2.2.1] haptane system was unambiguously established by doing single-crystal X-ray diffraction studies on the oxa-cage **1j** (Fig. 4).[22]

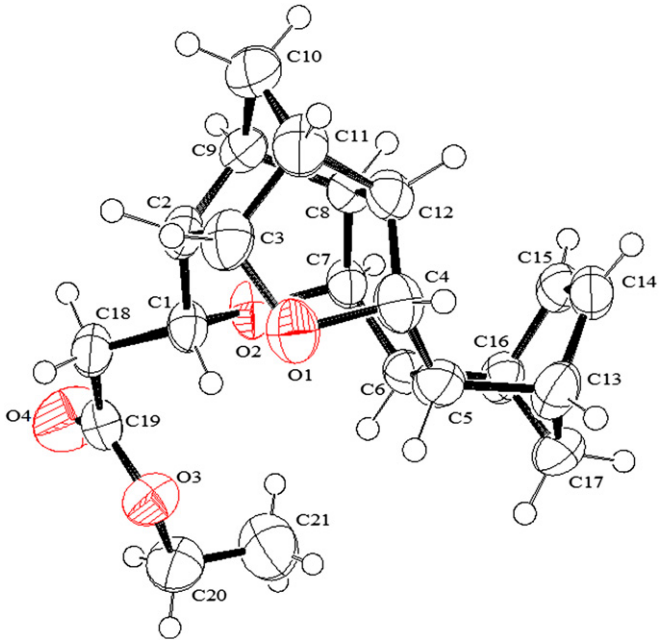
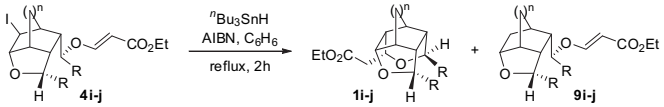
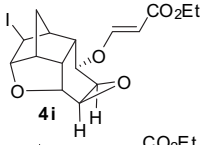
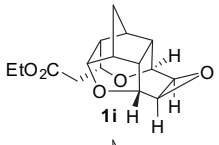
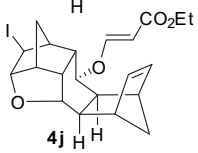
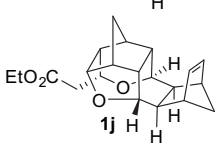


Fig. 4. ORTEP picture of the oxa-cage **1j**.

Buoyed by the success of the radical cyclization reaction for the formation of the oxa-cages **1i**,**j**, attention was turned towards the radical cyclization of the iodides **4k**,**l**. It was reasoned that the iodides **4c**,**d** gave the cyclized products due to the presence of two sp^2-hybridized carbons in the ring, which significantly distort the chair conformation. Similarly, it was expected that the iodides **4k**,**l** bearing two sp^2-hybridized carbons in the ring would furnish the corresponding oxa-cages **1k**,**l**. Thus, the iodides **4k**,**l** were subjected to the radical cyclization with $^nBu_3SnH$ and AIBN under standard conditions

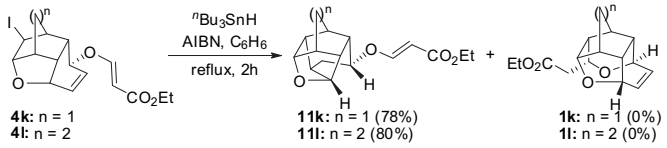
Table 3
Radical cyclization to vinylogous carbonate for synthesis of the oxa-cages **1**



Entry	Substrate	Yield (%)[a]		Oxa-cage product
		Cyclized product **1** (dr)[b]	Reduction product **9**	
1		72 (≥19:1)	n.d.[b]	
2		81 (≥19:1)	n.d.[b]	

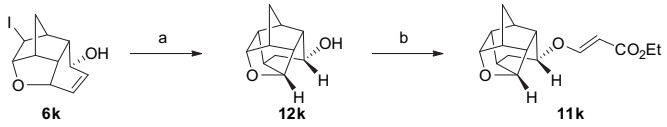
[a] Isolated yields of purified products unless otherwise stated.
[b] Determined on crude reaction mixtures by ^1H NMR; (n.a. not applicable, n.d. not detected).

(Scheme 6). Surprisingly, in these cases a totally different kind of radical cyclization ensued leading to the formation of the mono-oxa-cages **11k**,**l**, respectively, rather than the expected oxa-cages **1k**,**l**.



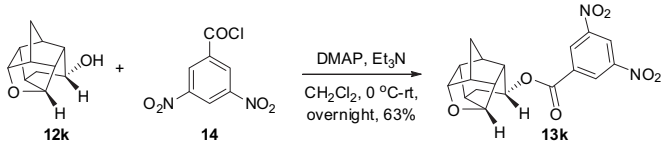
Scheme 6.

Formation of the mono-oxa-cages **11k**,**l** can be explained by a 5-*exo-trig* cyclization of the initially formed radical to cyclohexene part of the molecule rather than the desired 6-*exo-trig* cyclization to the vinylogous carbonate moiety leading to the formation of the oxa-cages **1k**,**l**. The structures of these compounds were confirmed by chemical correlation in the following manner. The iodide **6k** on radical cyclization led to the formation of the alcohol **12k** in good yields. The alcohol **12k** on reaction with ethyl propiolate and NMM lead to the formation of the monooxa-cage **11k** (Scheme 7).



Scheme 7. Reagents, conditions and yields: (a) ^{n}Bu$_3$SnH, AIBN, C$_6$H$_6$, reflux, 2 h, 80% (b) ethyl propiolate, NMM, CH$_2$Cl$_2$, rt, 4 h, 90%.

Finally, to obtain further unambiguous structural confirmation, the alcohol **12k** was converted into its 3,5-dinitrobenzoate derivative **13k** by treatment with 3,5-dinitrobenzoyl chloride (**14**), triethylamine and a catalytic amount of DMAP (Scheme 8). Single-crystal X-ray diffraction studies on the ester **13k** confirmed its structure and hence that of the monooxa-cage **11k** (Fig. 5).[23] Formation of the monooxa-cages **11k** and **11l** is particularly interesting because structurally, they contain a strained twistane framework, which further has an oxa- and a methano/ethano bridge.



Scheme 8.

Iodoetherification-reduction and oxymercuration–reduction reactions are used interchangeably many times for the synthesis of cyclic ethers. Based on this observation, an alternate disconnection based on the oxymercuration reduction protocol was envisioned. This approach relies on the fact that the reduction step in oxymercuration reduction process involves a radical intermediate. Thus, a new tandem approach for the synthesis of the oxa-cage **1** was contemplated involving a two-step sequence from the diol **2** namely (i) formation of the mono-vinylogous carbonate **15** of the diol **2** followed by (ii) oxymercuration–reduction reaction which on cyclization of the radical intermediate would form the oxa-cage **1**. During synthesis of the oxa-cages **1**, it was observed for few examples like the oxa-cages **1c**,**d**, the efficiency of cyclization is unaffected even if rate of addition of the reducing agent ^{n}Bu$_3$SnH is fast. The diol **5c** was thus selected as the substrate of choice to test this proposed oxymercuration reduction based approach for the synthesis of oxa-cage **1c** (Scheme 9). Treatment of the diol **5c** with ethyl propiolate and *N*-methylmorpholine (NMM) furnished the mono-vinylogous carbonate **15c** in 61% yield along with small amounts of the bis-addition product **16**. Treatment of the mono-vinylogous carbonate **15c** with 1 equiv of mercuric acetate in dry THF at 0 °C followed by reduction of the intermediate **17c** with sodium borohydride gratifyingly yielded the expected oxa-cage compound **1c** as the only detectable diastereomer. This study proved that the oxa-cages could be assembled in a shorter reaction sequence in excellent overall yields using oxymercuration reduction reaction and cyclization of the intermediate radical to vinylogous carbonate moiety.

3. Conclusions

In summary, a new method for the synthesis of unsymmetrical dioxa-cage compounds employing a 6-*exo-trig* alkyl radical cyclization to vinylogous carbonates has been developed. The oxa-cages are obtained with very high diastereoselectivity and in excellent yields. Moreover, it has also been established that in the cases where there is the possibility of competing 5-*exo-trig* cyclization (cf. iodides **4k**,**l**), the mono-oxa-cage compounds are formed exclusively rather than the corresponding dioxa-cage compounds. Radical cyclization to vinylogous carbonates could also be effected by employing oxymercuration reduction protocol with equal efficiency and with reduced number of steps.

4. Experimental section

4.1. General

Melting points are recorded using Sigma melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer and JASCO FT-IR-4100 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrophotometer. The chemical

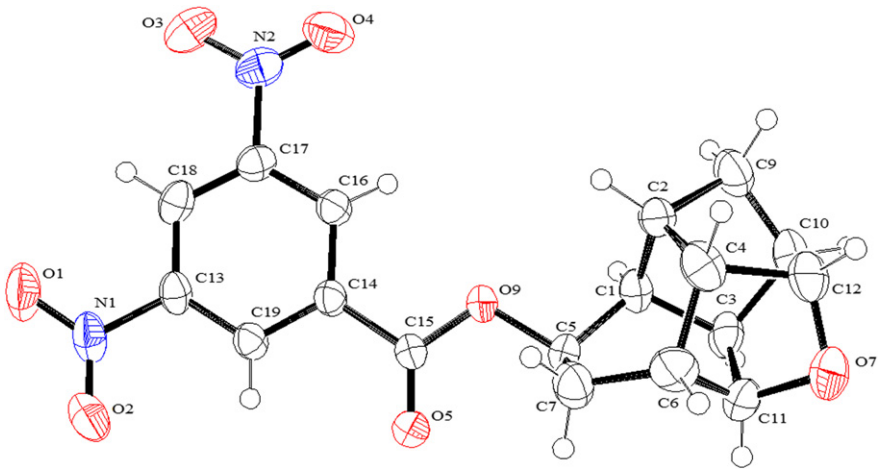
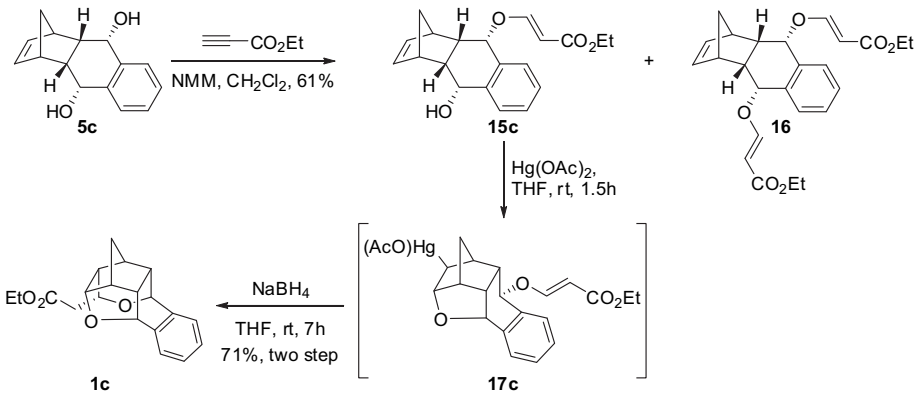


Fig. 5. ORTEP picture of the mono-oxa-cage **13k**.



Scheme 9.

shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane or residual $CHCl_3$ (7.26 ppm for ^1H) or the central line (77.16 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses. High resolution mass measurements were carried out using Micromass Q-ToF instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) was performed on glass plates (7.5×2.5 and 9×5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or $KMnO_4$ stain. Acme's silica gel (100–200 mesh) was used for column chromatography (approximately 15–20 g per 1 g of the crude product). All small-scale dry reactions were carried out using standard syringe septum technique. Low temperature reactions were conducted in a bath made of acetone and liquid nitrogen. Dry THF and dry ether were obtained by distillation over sodium-benzophenone ketyl. Dry dichloromethane and dry benzene were prepared by distilling over calcium hydride. Dry pyridine and triethylamine were obtained by distillation over KOH and stored over KOH. PCC and PDC was prepared according to literature procedure. LAH, $NaBH_4$, imidazole, ^{n}BuLi (1.6 M in hexane), PPh_3, DMAP, *m*-CPBA, 57% NaH dispersion in oil, 3,5-dinitrobenzoic acid, 1,4-benzoquinone, 1,4-naphthoquinone and $^n Bu_3SnH$ were obtained from Aldrich. Dicyclopentadiene was purchased from Fluka, zinc-dust, aq H_2O_2 and acetic acid were obtained from Merck. AIBN obtained from Spectrochem was recrystallized from ether and stored at 0–5 °C in the dark.

All the commercial reagents were used as such without further purification.

4.2. Experimental procedures

4.2.1. [(3S,3aR*,5S*,6S*,6aS*,7R*)-6-Iodohexahydro-2H-3,5-methanocyclopenta[b]furan-7-yl]methanol (**6a**).* To a cold (−10°C), magnetically stirred solution of the diol **5a** (300 mg, 1.95 mmol) in THF (12 mL) and saturated aq $NaHCO_3$ (4 mL) was added iodine (742 mg, 2.92 mmol) in portions. The reaction mixture was stirred at the same temperature for 1h (TLC control), diluted with water (15 mL) and extracted with ethyl acetate (3×20 mL). The combined organic layer was washed with brine and dried (anhyd Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:6) as eluent gave the iodoether **6a** (466 mg, 86%) as a colourless oil. R_f (2:5 EtOAc/hexane) 0.5; IR (neat): 3376, 2952, 2880, 1463, 1280, 1206, 1146, 1122, 1060, 1026, 966, 957, 943, 920, 902, 839, 761, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.73 (d, *J*=5.1 Hz, 1H), 3.82 (d, *J*=2.5 Hz, 1H), 3.72 (ABX, *J*=9.0, 0.0 Hz, 1H), 3.75–3.65 (m, 3H), 3.59 (ABX, *J*=9.0, 4.2 Hz, 1H), 2.71 (t, *J*=4.2 Hz, 1H), 2.50–2.40 (m, 2H), 2.35–2.20 (m, 1H), 2.20 (AB, *J*=11.0 Hz, 1H), 1.79 (AB, *J*=11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 89.69 (CH), 68.38 (CH_2), 60.37 (CH_2), 48.17 (CH), 46.02 (CH), 44.58 (CH), 38.45 (CH_2), 37.46 (CH_2), 33.70 (CH). HRMS (ESI, M+H^+): *m*/*z* calcd for $C_9H_{14}O_2I$ 281.0039, found 281.0034.

4.2.2. Ethyl (2E)-3-{[(3S,3aR*,5S*,6S*,6aS*,7R*)-6-iodohexahydro-2H-3,5-methano cyclopenta[b]furan-7-yl]methoxy}acrylate (**4a**).* To a magnetically stirred solution of the iodoalcohol **6a** (440 mg, 1.57 mmol) in dry CH_2Cl_2 (7 mL) were added *N*-methylmorpholine (189 μL, 1.73 mmol) and ethyl propiolate (176 μL, 1.73 mmol) at rt. The reaction mixture was stirred for 4h (TLC control). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) gave the vinylogous carbonate **4a** (540 mg, 91%) as a white solid. R_f (1:5 EtOAc/hexane) 0.5; mp: 46–47°C; IR (neat): 2973, 2882, 1702, 1621, 1464, 1396, 1367, 1324, 1283, 1232, 1200, 1124, 1096, 1035, 965, 942, 918, 826, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J*=12.6 Hz, 1H), 5.22 (d, *J*=12.6 Hz, 1H), 4.73 (d, *J*=4.8 Hz, 1H), 4.17 (q, *J*=7.1 Hz, 2H), 3.85 (d, *J*=6.1 Hz, 2H), 3.76 (d, *J*=1.9 Hz, 1H), 3.59 (s, 2H), 2.74 (br s, 1H), 2.55–2.40 (m, 3H), 2.23 (AB, *J*=11.0 Hz, 1H), 1.83 (AB, *J*=11.0 Hz, 1H), 1.27 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.67 (C), 161.86 (CH), 97.27 (CH), 89.53 (CH), 68.43 (CH_2), 68.24 (CH_2), 60.02 (CH_2), 48.13 (CH), 46.09 (CH), 41.40 (CH), 38.64 (CH), 37.60 (CH_2), 32.63 (CH), 14.48 (CH_3). HRMS (ESI, M+Na^+): *m*/*z* calcd for $C_{14}H_{19}O_4NaI$ 401.0226, found 401.0214.

4.2.3. [(3S,3aR*,6S*,7S*,7aS*,8R*)-7-Iodooctahydro-3,6-methano-1-benzofuran-8-yl] methanol (**6b**).* Reaction of the diol **5b** (486 mg, 2.89 mmol) with iodine (1.1 g, 4.34 mmol) in THF (20 mL) and saturated aq $NaHCO_3$ (6.0 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:6) as eluent furnished the iodoether **6b** (825 mg, 97%) as a pale yellow oil. R_f (3:10 EtOAc/hexane) 0.5; IR (neat): 3364, 2940, 2870, 1463, 1366, 1300, 1216, 1008, 950, 905, 852, 731, 636, 588, 546 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.49 (d, *J*=5.4 Hz, 1H), 4.13 (d, *J*=2.3 Hz, 1H), 3.76 (ABX, *J*=8.8, 0.0 Hz, 1H), 3.69 (ABX, *J*=10.2, 7.4 Hz, 1H), 3.60 (ABX, *J*=10.2, 7.4 Hz, 1H), 3.54 (ABX, *J*=8.8, 3.8 Hz, 1H), 2.45–2.30 (m, 2H), 2.20–2.05 (m, 1H), 2.05–1.95 (m, 1H), 1.90–1.80 (m, 3H), 1.75 (br s, 1H), 1.60–1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 84.78 (CH), 68.33 (CH_2), 62.40 (CH_2), 41.74 (CH), 37.30 (CH), 36.37 (CH), 36.16 (CH), 31.58 (CH), 26.69 (CH_2), 15.24 (CH_2). HRMS (ESI, M+H^+): *m*/*z* calcd for $C_{10}H_{16}O_2I$ 295.0195, found 295.0186.

4.2.4. Ethyl (2E)-3-{[(3S,3aR*,6S*,7S*,7aS*,8R*)-7-iodooctahydro-3,6-methano-1-benzo furan-8-yl]methoxy}acrylate (**4b**).* Reaction of the alcohol **6b** (753 mg, 2.56 mmol) with ethyl propiolate (286 μL,

2.82 mmol) and *N*-methylmorpholine (307 μL, 2.82 mmol) in CH_2Cl_2 (10 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:19) gave the vinylogous carbonate **4b** (940 mg, 94%) as a white solid. R_f (1:5 EtOAc/hexane) 0.6; mp: 44–46°C; IR (neat): 2946, 2874, 1705, 1624, 1465, 1446, 1368, 1325, 1284, 1234, 1202, 1135, 1026, 987, 949, 912, 830, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J=12.6 Hz, 1H), 5.21 (d, J=12.6 Hz, 1H), 4.50 (d, J=5.4 Hz, 1H), 4.16 (q, J=7.1 Hz, 2H), 4.08 (br s, 1H), 3.87 (ABX, J=9.1, 9.1 Hz, 1H), 3.76 (ABX, J=9.1, 9.1 Hz, 1H), 3.60 (ABX, J=9.0, 0.0 Hz 1H), 3.54 (ABX, J=9.0, 3.8 Hz, 1H), 2.56 (q, J=8.4 Hz, 2H), 2.40 (dt, J=7.9, 3.7 Hz, 1H), 2.20–2.05 (m, 2H), 2.02 (br s, 1H), 1.95–1.80 (m, 2H), 1.80 (br s, 1H), 1.60–1.50 (m, 1H), 1.27 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.71 (C), 161.81 (CH), 97.20 (CH), 84.52 (CH), 70.21 (CH_2), 68.26 (CH_2), 60.03 (CH_2), 38.57 (CH), 37.13 (CH), 36.01 (CH), 35.00 (CH), 31.58 (CH), 26.58 (CH_2), 15.08 (CH_2), 14.48 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{15}H_{22}O_4I$ 393.0563, found 393.0562.

4.2.5. (2S,2aR*,4S*,4aR*,5R*,9bR*,9cR*,10S*)-10-Iodo-2,2a,3,4,4a,5,9b,9c-octahydro-2,4-methanobenzo[5,6]indeno[7,1-bc] furan-5-ol (**6c**).* Reaction of the diol **5c** (200.0 mg, 0.88 mmol) with iodine (334.0 mg, 1.32 mmol) in THF (10 mL) and saturated aq $NaHCO_3$ (3.0 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:6) as eluent furnished the iodoether **6c** (248.0 mg, 80%) as a gummy solid. R_f (1:5 EtOAc/hexane) 0.6; IR (neat): 3437, 2962, 2885, 1492, 1455, 1407, 1367, 1318, 1287, 1268, 1241, 1194, 1118, 1027, 980, 950, 932, 907, 891, 874, 825, 780, 755, 722 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J=7.6 Hz, 1H), 7.40–7.25 (m, 3H), 5.18 (t, J=7.6 Hz, 1H), 4.93 (d, J=5.7 Hz, 1H), 4.80 (d, J=4.9 Hz, 1H), 3.93 (d, J=2.5 Hz, 1H), 3.02 (t, J=4.3 Hz, 1H), 2.85 (br s, 1H), 2.85–2.65 (m, 2H), 2.27 (d, J=11.0 Hz, 1H), 1.92 (d, J=6.5 Hz, 1H), 1.79 (d, J=11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 136.90 (C), 135.45 (C), 130.74 (CH), 129.20 (CH), 128.32 (CH), 127.36 (CH), 91.23 (CH), 76.99 (CH), 67.72 (CH), 51.70 (CH), 46.72 (CH), 42.84 (CH_2), 38.21 (CH), 37.18 (CH_2), 33.45 (CH). HRMS (ESI, M+Na^+): m/z calcd for $C_{15}H_{15}O_2NaI$ 377.0015, found 377.0002.

4.2.6. Ethyl (2E)-3-{[(2S,2aR*,4S*,4aR*,5R*,9bR*,9cR*,10S*)-10-iodo-2,2a,3,4,4a,5,9b,9c-octahydro-2,4-methanobenzo[5,6]indeno[7,1-bc] furan-5-yl]oxy}acrylate (**4c**).* Reaction of the alcohol **6c** (74.0 mg, 0.21 mmol) with ethyl propiolate (24 μL, 0.23 mmol) and *N*-methylmorpholine (25 μL, 0.23 mmol) in CH_2Cl_2 (6 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:6) gave the vinylogous carbonate **4c** (92.0 mg, 98%) as a colourless oil. R_f (1:5 EtOAc/hexane) 0.6; IR (neat): 2977, 2889, 1699, 1636, 1619, 1495, 1462, 1369, 1319, 1285, 1219, 1188, 1124, 1037, 988, 947, 909, 873, 830, 755, 727 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J=12.3 Hz, 1H), 7.40–7.30 (m, 4H), 5.47 (d, J=12.3 Hz, 1H), 5.45–5.40 (m, 1H), 4.95 (d, J=5.4 Hz, 1H), 4.79 (d, J=4.9 Hz, 1H), 4.21 (q, J=7.1 Hz, 2H), 3.85 (d, J=2.6 Hz, 1H), 3.05–3.00 (m 1H), 2.90–2.80 (m, 2H), 2.68 (br s, 1H), 2.25 (dt, J=11.2, 1.3 Hz 1H), 1.77 (d, J=11.2 Hz, 1H), 1.31 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.99 (C), 162.63 (CH), 135.57 (C), 132.04 (C), 130.78 (CH), 129.20 (CH), 129.17 (CH), 128.23 (CH), 98.47 (CH), 91.13 (CH), 78.77 (CH), 76.58 (CH), 60.17 (CH_2), 51.63 (CH), 46.81 (CH), 40.38 (CH), 38.14 (CH), 36.61 (CH_2), 32.12 (CH), 14.52 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{20}H_{22}O_4I$ 453.0563, found 453.0552.

4.2.7. (2S,2aR*,5S*,5aR*,6R*,10bR*,10cR*,11S*)-11-Iodo-2a,3,4,5,5a,6,10b,10c-octahydro-2H-2,5-methanoanthra[9,1-bc]furan-6-ol (**6d**).* Reaction of the diol **5d** (500.0 mg, 2.07 mmol) with iodine (787.0 mg, 3.10 mmol) in THF (18 mL) and saturated aq $NaHCO_3$ (6 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent furnished the iodoether **6d** (605.0 mg, 80%) as a gummy solid. R_f (1:5 EtOAc/hexane) 0.5; IR (neat): 3269, 2945, 2922, 2883, 2822, 1491, 1464, 1455, 1373, 1357, 1339, 1321, 1307, 1267, 1201, 1184, 1042, 1019, 1003, 910, 882, 870, 859, 790, 750, 742, 710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J=7.1 Hz, 1H), 7.40–7.25 (m, 3H), 4.98 (t, J=7.1 Hz, 1H), 4.86 (d, J=5.2 Hz, 1H), 4.54 (d, J=5.0 Hz, 1H), 4.10–4.05 (m, 1H), 2.80–2.70 (m, 2H), 2.35–2.15 (m, 3H), 1.99 (d, J=7.6 Hz, 1H), 1.91 (td, J=7.6, 3.1 Hz 2H), 1.70–1.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 136.57 (C), 135.96 (C), 130.46 (CH), 128.82 (CH), 128.07 (CH), 125.41 (CH), 86.34 (CH), 75.11 (CH), 68.49 (CH), 40.40 (CH), 40.32 (CH), 37.33 (CH), 37.25(CH), 30.11 (CH), 27.98 (CH_2), 15.45 (CH_2). HRMS (ESI, M+Na^+): m/z calcd for $C_{16}H_{17}O_2NaI$ 391.0171, found 391.0183.

4.2.8. Ethyl (2E)-3-{[(2S,2aR*,5S*,5aR*,6R*,10bR*,10cR*,11S*)-11-iodo-2a,3,4,5,5a,6, 10b,10c-octahydro-2H-2,5-methanoanthra[9,1-bc]furan-6-yl]oxy}acrylate (**4d**).* Reaction of the alcohol **6d** (140.0 mg, 0.38 mmol) with ethyl propiolate (43 μL, 0.42 mmol) and *N*-methylmorpholine (46 μL, 0.42 mmol) in CH_2Cl_2 (4 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:10) gave the vinylogous carbonate **4d** (161.0 mg, 91%) as a gummy solid. R_f (1:5 EtOAc/hexane) 0.5; IR (neat): 2941, 1709, 1693, 1640, 1632, 1620, 1390, 1368, 1321, 1281, 1190, 1125, 1094, 1023, 1005, 970, 907, 834, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J=12.3 Hz, 1H), 7.45–7.30 (m, 4H), 5.48 (d, J=12.3 Hz, 1H), 5.22 (d, J=7.3 Hz, 1H), 4.91 (d, J=5.9 Hz, 1H), 4.51 (d, J=4.8 Hz, 1H), 4.19 (q, J=7.1 Hz, 2H), 3.95 (br s, 1H), 2.91 (t, J=8.0 Hz 1H), 2.85–2.75 (m, 1H), 2.35–2.25 (m, 1H), 2.20–2.10 (m, 2H), 1.90 (td, J=7.6, 2.1 Hz, 2H), 1.65–1.55 (m, 1H), 1.30 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.92 (C), 162.14 (CH), 136.11 (C), 131.85 (C), 130.67 (CH), 128.81 (CH), 128.74 (CH), 125.39 (CH), 99.04 (CH), 86.43 (CH), 79.69 (CH), 74.35 (CH), 60.15 (CH_2), 40.27 (CH), 37.76 (CH), 36.58 (CH), 36.00 (CH), 30.14 (CH), 27.58 (CH_2), 15.22 (CH_2), 14.52 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{21}H_{24}O_4I$ 467.0719, found 467.0725.

4.2.9. (2S,2aR*,4S*,4aR*,5R*,7aS*,7bR*,8S*)-8-Iododecahydro-2,4-methanoindeno[7,1-bc] furan-5-ol (**6e**).* Reaction of the diol **5e** (395.0 mg, 2.19 mmol) with iodine (835.0 mg, 3.29 mmol) in THF (18 mL) and saturated aq $NaHCO_3$ (6 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:4) as eluent furnished the iodoether **6e** (667.0 mg, 99%) as a white crystalline solid. R_f (1:5 EtOAc/hexane) 0.3; mp: 98–100°C; IR (neat): 3365, 2950, 2884, 1462, 1348, 1272, 1206, 1223, 1149, 1131, 1119, 1065, 1048, 1032, 1019, 999, 964, 936, 914, 875, 849, 820, 779, 743, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.77 (d, J=5.0 Hz, 1H), 4.29 (d, J=2.4 Hz, 1H), 4.10 (br s, 1H), 3.96 (dt, J=11.5, 6.8 Hz, 1H), 2.87 (t, J=4.0 Hz, 1H), 2.67 (br s, 1H), 2.40–2.25 (m, 2H), 2.17 (AB, J=10.9 Hz, 1H), 1.97(dq, J=14.4, 6.5, 3.2 Hz, 1H), 1.75–1.60 (m, 4H), 1.50–1.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 89.99 (CH), 75.98 (CH), 69.98 (CH), 49.99 (CH), 45.45 (CH), 43.23 (CH), 39.75 (CH), 37.91 (CH_2), 35.14 (CH), 26.81 (CH_2), 26.12 (CH_2). HRMS (ESI, M+H^+): m/z calcd for $C_{11}H_{16}O_2I$ 307.0195, found 307.0196.

4.2.10. Ethyl (2E)-3-{[(2S,2aR*,4S*,4aR*,5R*,7aS*,7bR*,8S*)-8-iododecahydro-2,4-methanoindeno[7,1-bc]furan-5-yl]oxy}acrylate (**4e**).* Reaction of the alcohol **6e** (309.0 mg, 1.01 mmol) with ethyl propiolate (113 μL, 1.11 mmol) and *N*-methylmorpholine (121 μL, 1.11 mmol) in CH_2Cl_2 (12 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent gave the vinylogous carbonate **4e** (385.0 mg, 95%) as a white solid. R_f (1:5 EtOAc/hexane) 0.5; mp: 84–86°C; IR (neat): 2971, 2886, 1701, 1638, 1619, 1463, 1368, 1323, 1282, 1192, 1119, 1062, 1024, 979, 964, 934, 923, 896,

875, 826, 780, 731, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J=12.5 Hz, 1H), 5.32 (d, J=12.5 Hz, 1H), 4.79 (d, J=5.1 Hz, 1H), 4.30–4.10 (m, 3H), 4.16 (q, J=7.1 Hz, 2H), 2.89 (tq, J=4.8, 1.4 Hz, 1H), 2.55 (br s, 1H), 2.48 (ddd, J=10.3, 8.0, 3.5 Hz, 1H), 2.35 (dt, J=9.6, 4.6 Hz, 1H), 2.18 (AB, J=11.1 Hz, 1H), 2.03 (dq, J=14.6, 3.5 Hz, 1H), 1.85–1.75 (m, 2H), 1.65 (AB, J=11.1 Hz, 1H), 1.50–1.40 (m, 1H), 1.27 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.07 (C), 161.55 (CH), 98.16 (CH), 89.91 (CH), 80.49 (CH), 75.49 (CH), 59.95 (CH_2), 49.98 (CH), 45.53 (CH), 40.54 (CH), 39.85 (CH), 37.81 (CH_2), 34.16 (CH), 26.33 (CH_2), 22.74 (CH_2), 14.50 (CH_3). HRMS (ESI, M+Na^+): m/z calcd for $C_{16}H_{21}O_4NaI$ 427.0382, found 427.0396.

4.2.11. (2S,2aR*,5S*,5aR*,6R*,8aS*,8bR*,9S*)-9-Iododecahydro-2H-2,5-methanonaphtho [1,8-bc]furan-6-ol (**6f**).* Reaction of the diol **5f** (300 mg, 1.55 mmol) with iodine (589 mg, 2.32 mmol) in THF (18 mL) and saturated aq $NaHCO_3$ (6 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:6) as eluent furnished the iodoether **6f** (410 mg, 83%) as a white crystalline solid. R_f (1:5 EtOAc/hexane) 0.4; mp: 136–138°C; IR (neat): 3411, 3388, 2934, 2872, 1464, 1371, 1356, 1273, 1206, 1174, 1073, 1053, 1034, 1017, 1000, 977, 937, 913, 887, 867, 801, 743 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.51 (d, J=5.4 Hz, 1H), 4.50–4.45 (m, 1H), 3.98 (q, J=3.0 Hz, 1H), 3.85–3.75 (m, 1H), 2.52 (t, J=7.8 Hz, 1H), 2.30–2.15 (m, 4H), 1.98 (dq, J=14.3, 3.1 Hz, 1H), 1.85–1.75 (m, 2H), 1.75–1.45 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 84.70 (CH), 75.29 (CH), 70.52 (CH), 41.34 (CH), 39.25 (CH), 38.74 (CH), 38.22 (CH), 29.34 (CH_2), 27.96 (CH), 26.89 (CH_2), 25.74 (CH_2), 15.41 (CH_2). HRMS (ESI, M+H^+): m/z calcd for $C_{12}H_{18}O_2I$ 321.0352, found 321.0359.

4.2.12. Ethyl (2E)-3-{[(2S,2aR*,5S*,5aR*,6R*,8aS*,8bR*,9S*)-9-iododecahydro-2H-2,5-methanonaphtho[1,8-bc]furan-6-yl]oxy}acrylate (**4f**).* Reaction of the alcohol **6f** (210.0 mg, 0.66 mmol) with ethyl propiolate (73 μL, 0.72 mmol) and *N*-methylmorpholine (79 μL, 0.72 mmol) in CH_2Cl_2 (10 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent gave the vinylogous carbonate **4f** (241.0 mg, 88%) as a white solid. R_f (1:5 EtOAc/hexane) 0.6; mp: 105–107°C; IR (neat): 2934, 1701, 1639, 1619, 1467, 1446, 1369, 1322, 1283, 1227, 1198, 1123, 1096, 1037, 1018, 1002, 971, 955, 931, 913, 903, 887, 870, 833, 805, 770, 730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J=12.4 Hz, 1H), 5.28 (d, J=12.4 Hz, 1H), 4.52 (d, J=5.2 Hz, 1H), 4.45 (br s, 1H), 4.15 (q, J=7.1 Hz, 2H), 4.10–3.95 (m, 2H), 2.64 (t, J=8.0 Hz, 1H), 2.30–2.15 (m, 3H), 2.12 (br s, 1H), 2.08–1.98 (m, 1H), 1.85–1.70 (m, 4H), 1.60–1.40 (m, 2H), 1.26 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.04 (C), 161.24 (CH), 98.28 (CH), 84.60 (CH), 81.43 (CH), 74.87 (CH), 59.95 (CH_2), 39.10 (CH), 38.80 (CH), 38.05 (CH), 37.52 (CH), 29.13 (CH_2), 28.20 (CH), 26.42 (CH_2), 22.37 (CH_2), 15.17 (CH_2), 14.50 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{17}H_{24}O_4I$ 419.0719, found 419.0712.

4.2.13. (1S,1aR*,3S*,3aR*,5S*,5aR*,5bR*,6S*)-6-Iodooctahydro-3,5-methano-2-oxacyclobuta [cd]pentalen-1-ol (**6g**).* Reaction of the diol **5g** (144 mg, 0.95 mmol) with iodine (289 mg, 1.14 mmol) in THF (12 mL) and saturated aq $NaHCO_3$ (4 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:6) as eluent furnished the iodoether **6g** (223 mg, 85%) as a colourless liquid. R_f (3:10 EtOAc/hexane) 0.5; IR (neat): 3381, 3033, 2965, 2881, 1460, 1343, 1320, 1268, 1228, 1208, 1176, 1145, 1129, 1101, 1079, 1057, 1023, 991, 974, 959, 941, 921, 899, 885, 846, 812, 775, 732, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.01 (d, J=5.2, 1.2 Hz, 1H), 4.86 (d, J=2.4 Hz, 1H), 4.55 (ddd, J=7.2, 4.0, 3.2 Hz, 1H), 4.40 (dd, J=7.6, 5.2 Hz, 1H), 2.90–2.80 (m, 1H), 2.80–2.70 (m, 1H), 2.70–2.65 (m, 2H), 2.38 (AB, J=10.8 Hz, 1H), 2.09 (s, 1H), 1.73 (AB, J=10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 91.04 (CH), 82.58 (CH), 68.26 (CH), 47.17 (CH), 45.99 (CH), 45.09 (CH), 41.42 (CH_2), 41.30 (CH), 34.11 (CH). HRMS (ESI, M+H^+): m/z calcd for $C_9H_{12}O_2I$ 278.9882, found 278.9887.

4.2.14. Ethyl (2E)-3-{[(1S,1aR*,3S*,3aR*,5S*,5aR*,5bR*,6S*)-6-iodooctahydro-3,5-methano-2-oxacyclobuta[cd]pentalen-1-yl]oxy}acrylate (**4g**).* Reaction of the alcohol **6g** (178 mg, 0.64 mmol) with ethyl propiolate (72 μL, 0.70 mmol) and *N*-methylmorpholine (78 μL, 0.70 mmol) in CH_2Cl_2 (4.0 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent gave the vinylogous carbonate **4g** (230 mg, 96%) as a white solid. R_f (3:10 EtOAc/hexane) 0.7; mp: 45–47°C; IR (neat): 2976, 1704, 1644, 1621, 1463, 1368, 1322, 1280, 1233, 1187, 1130, 1095, 1045, 1023, 978, 955, 920, 900, 889, 854, 816, 774, 754, 710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J=12.8 Hz, 1H), 5.25 (d, J=12.8 Hz, 1H), 5.01 (d, J=4.8 Hz, 1H), 4.75 (dd, J=7.6, 4.4 Hz, 1H), 4.57 (d, J=2.4 Hz, 1H), 4.51 (dd, J=7.6, 4.8 Hz, 1H), 4.16 (q, J=7.2 Hz, 2H), 3.03 (ddd, J=10.4, 8.0, 3.2 Hz, 1H), 2.87 (q, J=5.6 Hz, 1H), 2.75 (t, J=5.2 Hz, 1H), 2.67 (d, J=5.6 Hz, 1H), 2.45 (AB, J=11.2 Hz, 1H), 1.79 (AB, J=11.2 Hz, 1H), 1.27 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.40 (C), 159.53 (CH), 98.70 (CH), 91.12 (CH), 81.02 (CH), 74.47 (CH), 60.11 (CH_2), 45.87 (CH), 45.74 (CH), 45.52 (CH), 42.25 (CH), 41.47 (CH_2), 32.38 (CH), 14.46 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{14}H_{18}O_4I$ 377.0250, found 377.0258.

4.2.15. (2S,2aR*,4S*,4aR*,5R*,6aS*,6bR*,7S*)-7-Iodooctahydro-2H-2,4-methanopentaleno [1,6-bc]furan-5-ol (**7**).* Reaction of the diol **5h** (450 mg, 2.71 mmol) with iodine (826 mg, 1.2 mmol) in THF (20 mL) and saturated aq $NaHCO_3$ (7 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:4) as eluent furnished the iodoether **7** (710 mg, 90%) as a gummy solid. R_f (3:10 EtOAc/hexane) 0.3; IR (neat): 3388, 2959, 2925, 2883, 1461, 1427, 1335, 1283, 1228, 1200, 1180, 1116, 1096, 1030, 986, 936, 901, 869, 819, 803, 749, 685 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.70 (d, J=4.8 Hz, 1H), 4.44 (t, J=5.2 Hz, 1H), 4.37 (ddd, J=7.2, 5.6, 1.6 Hz, 1H), 3.87 (d, J=2.4 Hz, 1H), 3.00 (dt, J=10.0, 5.2 Hz, 1H), 2.75 (td, J=5.2, 0.8 Hz, 1H), 2.65–2.50 (m, 3H), 2.33 (AB, J=10.8 Hz, 1H), 1.95–1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 90.30 (CH), 84.29 (CH), 72.96 (CH), 57.07 (CH), 49.75 (CH), 49.25 (CH), 48.21 (CH_2), 46.81 (CH), 41.06 (CH_2), 34.09 (CH). HRMS (ESI, M+H^+): m/z calcd for $C_{10}H_{14}O_2I$ 293.0039, found 293.0043.

4.2.16. (2S,2aR*,4S*,4aR*,6aS*,6bR*,7S*)-7-Iodooctahydro-5H-2,4-methanopentaleno[1,6-bc]furan-5-one (**8**).* To a stirred solution of alcohol **7** (40 mg, 0.14 mmol) in CH_2Cl_2 (4 mL) were added 4 Å MS (200 mg) and PCC (59 mg, 0.27 mmol). The reaction mixture was stirred at rt for 3 h. It was filtered through Celite pad and filtrate was concentrated under reduced pressure. Purification of the residue on a silica gel column using ethyl acetate–hexanes (1:6) as eluent furnished the ketone **8** (35 mg, 88%) as a white solid. R_f (3:10 EtOAc/hexane) 0.5; mp: 84–86°C; IR (neat): 2964, 2883, 1731, 1459, 1387, 1329, 1288, 1265, 1224, 1195, 1170, 1152, 1117, 1084, 1030, 979, 934, 901, 883, 874, 810, 792, 729, 682 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.83 (d, J=5.2 Hz, 1H), 4.67 (t, J=4.8 Hz, 1H), 3.64 (d, J=2.8 Hz, 1H), 3.19 (dt, J=10.0, 5.2 Hz, 1H), 2.95 (t, J=5.2 Hz, 1H), 2.85–2.75 (m, 2H), 2.62 (ABX, J=19.2, 0.0 Hz, 1H), 2.53 (ABX, J=19.2, 4.8 Hz, 1H), 2.41 (ABX, J=11.2, 0.0 Hz, 1H), 1.95 (ABX, J=11.2, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 217.65 (C), 90.38 (CH), 79.92 (CH), 53.65 (CH), 51.03 (CH_2), 49.24 (CH), 48.12 (CH), 46.80 (CH), 40.89 (CH_2), 32.49 (CH).

4.2.17. (2S,2aR*,4S*,4aR*,5S*,6aS*,6bR*,7S*)-7-Iodooctahydro-2H-2,4-methanopentaleno [1,6-bc]furan-5-ol (**6h**).* To a cold (−10°C), magnetically stirred solution of the ketone **8** (450 mg, 1.55 mmol) in methanol (20 mL) was added $NaBH_4$ (59 mg, 1.55 mmol) portion

wise. The reaction mixture was stirred at the same temperature for 1 h. The solvent was removed under reduced pressure and the residue was diluted with water. The aqueous layer was extracted with ethyl acetate (4×20 mL), the combined organic layer was washed with brine and dried (anhyd Na_2SO_4). Evaporation of the solvent under reduced pressure and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:4) as eluent gave the alcohol **6h** (437 mg, 96%) as a white solid. R_f (3:10 EtOAc/hexane) 0.3; mp: 132–134°C; IR (neat): 3386, 2959, 2882, 1461, 1433, 1344, 1317, 1284, 1267, 1203, 1165, 1145, 1101, 1054, 1034, 1002, 983, 950, 932, 903, 833, 873, 854, 819, 800, 783, 730, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.81 (d, J=5.2 Hz, 1H), 4.65–4.50 (m, 1H), 4.55 (d, J=2.8 Hz, 1H), 4.34 (t, J=6.0 Hz, 1H), 2.83 (dt, J=10.4, 5.6 Hz, 1H), 2.80–2.75 (m, 1H), 2.75–2.65 (m, 1H), 2.60 (ABXY, J=16.4, 10.4, 6.4 Hz, 1H), 2.56 (d, J=6.4 Hz, 1H), 2.35 (AB, J=10.8 Hz, 1H), 1.99 (ABXY, J=16.4, 4.4, 0.0 Hz, 1H), 1.82 (AB, J=10.8 Hz, 1H), 1.64 (d, J=3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 90.69 (CH), 82.62 (CH), 73.00 (CH), 52.55 (CH), 50.42 (CH), 49.94 (CH), 47.62 (CH_2), 46.06 (CH), 40.22 (CH_2), 35.78 (CH). HRMS (ESI, M+H^+): m/z calcd for $C_{10}H_{14}O_2I$ 293.0039, found 293.0043.

4.2.18. Ethyl (2E)-3-{[(2S,2aR*,4S*,4aR*,5S*,6aS*,6bR*,7S*)-7-iodooctahydro-2H-2,4-methanopentaleno[1,6-bc]furan-5-yl]oxy}acrylate (**4h**).* Reaction of the alcohol **6h** (45 mg, 0.15 mmol) with ethyl propiolate (17.0 μL, 0.17 mmol) and *N*-methylmorpholine (19.0 μL, 0.17 mmol) in CH_2Cl_2 (2.5 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:5) as eluent gave the vinylogous carbonate **4h** (53.0 mg, 88%) as a colourless oil. R_f (3:10 EtOAc/hexane) 0.4; IR (neat): 2974, 1702, 1640, 1618, 1462, 1368, 1321, 1283, 1269, 1229, 1196, 1126, 1094, 1036, 1000, 964, 947, 932, 902, 874, 820, 783, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J=12.8 Hz, 1H), 5.18 (d, J=12.8 Hz, 1H), 4.79 (d, J=5.2 Hz, 1H), 4.70–4.60 (m, 1H), 4.37 (t, J=5.6 Hz, 1H), 4.30 (d, J=2.4 Hz, 1H), 4.16 (q, J=7.2 Hz, 2H), 2.95–2.85 (m, 2H), 2.85–2.75 (m, 1H), 2.64 (ABXY, J=16.8, 10.8, 6.4 Hz, 1H), 2.52 (br s, 1H), 2.36 (AB, J=11.2 Hz, 1H), 2.17 (ABXY, J=16.8, 4.0, 0.0 Hz, 1H), 1.84 (AB, J=11.2 Hz, 1H), 1.28 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.75 (C), 161.48 (CH), 97.89 (CH), 90.57 (CH), 81.94 (CH), 81.72 (CH), 60.04 (CH_2), 50.86 (CH), 50.46 (CH), 49.78 (CH), 45.78 (CH), 44.72 (CH_2), 40.33 (CH_2), 34.27 (CH), 14.48 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{15}H_{20}O_4I$ 391.0406, found 391.0410.

4.2.19. Ethyl (1R,4R*,4aS*,6R*,7S*,7aR*,10S*)-octahydro-7,4,6-(epoxyethane[1,2,2]triyl) cyclopenta[c]pyran-1-ylacetate (**1a**).* To a magnetically stirred, refluxing solution of the vinylogous carbonate **4a** (108.0 mg, 0.29 mmol) and AIBN (9.5 mg, 0.06 mmol) in dry benzene (25 mL) was added a solution of $^nBu_3SnH$ (154 μL, 0.57 mmol) and AIBN (9.5 mg, 0.06 mmol) in dry benzene (20 mL) over a period of 2 h under nitrogen atmosphere. The reaction mixture was further refluxed till completion (ca. 3 h, TLC control). It was then cooled, diluted with Et_2O (50 mL), washed with 2% aq NH_3 (4×5 mL) and brine and the organic layer was dried (anhyd Na_2SO_4). Evaporation of the solvent under reduced pressure and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent furnished the oxa-cage **1a** (62 mg, 86%) as a colourless oil. R_f (3:20 EtOAc/hexane) 0.5; IR (neat): 2940, 2871, 1730, 1459, 1382, 1309, 1288, 1245, 1173, 1144, 1110, 1096, 1078, 1070, 1032, 1018, 980, 959, 942, 926, 911, 853, 791, 764, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.35 (dd, J=7.6, 4.8 Hz, 1H), 4.20–4.05 (m, 2H), 4.04 (ABX, J=12.0, 0.0 Hz, 1H), 3.99 (ABX, J=8.0, 0.0 Hz, 1H), 3.90 (ddd, J=7.6, 5.6, 2.0 Hz, 1H), 3.70–3.65 (m, 2H), 2.92 (ABX, J=15.6, 7.8 Hz, 1H), 2.65–2.60 (m, 1H), 2.63 (ABX, J=15.6, 5.6 Hz, 1H), 2.38 (dt, J=9.6, 4.4 Hz, 1H), 1.95–1.85 (m, 2H), 1.56 (ddd, J=5.2, 2.8 Hz, 1H), 1.47 (AB, J=10.6 Hz, 1H), 1.32 (AB, J=10.6 Hz, 1H), 1.24 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 172.39 (C), 79.21 (CH), 71.61 (CH), 69.12 (CH_2), 65.75 (CH_2), 60.44 (CH_2), 50.05 (CH), 41.42 (CH), 40.84 (CH), 39.29 (CH), 38.95 (CH_2), 37.14 (CH), 33.07 (CH_2), 14.32 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{14}H_{21}O_4$ 253.1440, found 253.1447.

4.2.20. Ethyl (1R,4R*,4aS*,7R*,8S*,8aR*,11S*)-octahydro-1H-8,4,7-(epoxyethane[1,2,2] triyl)isochromen-1-ylacetate (**1b**).* Reaction of the iodide **4b** (108.0 mg, 0.28 mmol) with $^nBu_3SnH$ (148 μL, 0.55 mmol) and AIBN (18.0 mg, 1.1 mmol) in benzene (40 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:16) as eluent furnished the dioxa-cage **1b** (61.0 mg, 83%) as a colourless oil. R_f (3:20 EtOAc/hexane) 0.6; IR (neat): 2934, 2867, 1727, 1465, 1367, 1310, 1248, 1225, 1174, 1113, 1093, 1067, 1026, 995, 954, 908, 879, 854, 815, 732 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.24 (dd, J=7.5, 4.7 Hz, 1H), 4.20–4.10 (m, 2H), 4.08 (dd, J=12.6, 1.4 Hz, 1H), 4.02 (d, J=7.6 Hz, 1H), 3.86 (ddd, J=7.6, 5.7, 2.1 Hz, 1H), 3.59 (dd, J=11.3, 2.1 Hz, 1H), 3.53 (dd, J=7.5, 4.1 Hz, 1H), 2.95 (ABX, J=15.8, 7.5 Hz, 1H), 2.74 (ABX, J=15.8, 5.7 Hz, 1H), 2.30 (dt, J=10.0, 4.0 Hz, 1H), 1.88 (t, J=3.7 Hz, 1H), 1.85–1.40 (m, 6H), 1.31 (br s, 1H), 1.24 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 172.51 (C), 76.09 (CH), 75.92 (CH), 69.65 (CH_2), 68.78 (CH_2), 60.39 (CH_2), 41.40 (CH), 39.72 (CH_2), 39.60 (CH), 38.35 (CH), 35.38 (CH), 32.39 (CH), 25.41, (CH_2), 16.27 (CH_2), 14.34 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{15}H_{23}O_4$ 267.1596, found 267.1590.

4.2.21. Ethyl (2R,3R*,3aS*,5R*,5aR*,6R*,10bS*,10cR*,12S*)-3,3a,4,5,5a,6,10b,10c-octa hydro-2H-6,3,5-(epoxymethanetriyl)benzo[h]cyclopenta[de]chromen-2-ylacetate (**1c**).* Reaction of the iodide **4c** (100.0 mg, 0.22 mmol) with $^nBu_3SnH$ (119 μL, 0.44 mmol) and AIBN (15.0 mg, 0.10 mmol) in benzene (22 mL) as described for the oxa-cage **1a** followed by purification of the residue on silica gel column using ethyl acetate–hexanes (1:8) as eluent furnished the dioxa-cage **1c** (65.0 mg, 90%) as a colourless oil. R_f (1:5 EtOAc/hexane) 0.6; IR (neat): 2954, 2872, 1731, 1644, 1458, 1368, 1326, 1304, 1280, 1175, 1138, 1109, 1083, 1058, 1041, 1024, 988, 972, 961, 916, 843, 811, 784, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.25 (m, 4H), 5.17 (d, J=7.4 Hz, 1H), 4.92 (d, J=4.1 Hz, 1H), 4.23 (dd, J=8.1, 5.0 Hz, 1H), 4.05 (qd, J=7.2, 1.2 Hz, 2H), 3.99 (td, J=6.8, 2.8 Hz, 1H), 3.03 (br s, 1H), 2.60–2.50 (m, 2H), 2.51 (ABX, J=15.0, 6.4 Hz, 1H), 2.50–2.40 (m, 1H), 2.44 (ABX, J=15.0, 7.2 Hz, 1H), 1.80–1.70 (m, 2H), 1.56 (d, J=12.0 Hz, 1H), 1.14 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.23 (C), 136.61 (C), 135.61 (C), 131.90 (CH), 129.69 (CH), 129.31 (CH), 128.57 (CH), 80.76 (CH), 77.52 (CH), 70.87 (CH), 62.60 (CH), 60.34 (CH_2), 51.67 (CH), 44.39 (CH), 44.22 (CH), 42.28 (CH_2), 34.62 (CH), 34.16 (CH), 33.74 (CH_2), 14.30 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{20}H_{23}O_4$ 327.1596, found 327.1605.

4.2.22. Ethyl (2R,3R*,3aS*,6R*,6aR*,7R*,11bS*,11cR*,13S*)-2,3,3a,4,5,6,6a,7,11b,11c-decahydro-7,3,6-(epoxymethanetriyl)dibenzo[de,h]chromen-2-ylacetate (**1d**).* Reaction of the iodide **4d** (120.0 mg, 0.26 mmol) with $^nBu_3SnH$ (139 μL, 0.52 mmol) and AIBN (17.0 mg, 0.10 mmol) in benzene (40 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:10) as eluent furnished the dioxa-cage **1d** (73 mg, 84%) as a white solid. R_f (1:5 EtOAc/hexane) 0.6; mp: 94–96°C; IR (neat): 2931, 2864, 1728, 1460, 1381, 1271, 1260, 1247, 1173, 1100, 1077, 1060, 1041, 1004, 987, 920, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.30 (m, 4H), 5.08 (d, J=8.4 Hz, 1H), 4.74 (d, J=2.8 Hz, 1H), 4.49 (ddd, J=8.0, 5.8, 0.8 Hz, 1H), 4.15 (dd, J=6.6, 6.0 Hz, 1H), 4.08 (q, J=7.1 Hz, 2H), 2.52 (ABX, J=14.6, 5.8 Hz 1H), 2.44 (ABX, J=14.6, 8.0 Hz 1H), 2.40–2.30 (m, 3H), 1.99 (br s, 1H), 1.90–1.80 (m, 2H), 1.75–1.65 (m, 3H), 1.18 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.38 (C), 136.94 (C), 136.13 (C), 130.60 (CH), 129.37 (CH), 129.26 (CH), 128.39 (CH), 77.78 (CH), 77.23 (CH), 72.82 (CH), 65.45 (CH), 60.38 (CH_2), 41.68 (CH_2), 41.51 (CH), 40.93 (CH), 40.58 (CH), 32.42 (CH), 23.95 (CH_2), 22.40 (CH), 16.43 (CH_2),

14.34 (CH_3). HRMS (ESI, M+H^+): *m*/*z* calcd for $C_{21}H_{25}O_4$ 341.1753, found 341.1745.

4.2.23. Ethyl (2E)-3-[(2R,2aR*,4R*,4aS*,5R*,7aS*,7bR*)-decahydro-2,4-methanoindeno [7,1-bc]furan-5-yloxy]acrylate (**9e**).* Reaction of the iodide **4e** (90.0 mg, 0.22 mmol) with $^nBu_3SnH$ (120 μL, 0.44 mmol) and AIBN (15.0 mg, 0.10 mmol) in benzene (25 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent furnished the oxa-cage **9e** (55 mg, 88%) as a colourless oil. R_f (1:5 EtOAc/hexane) 0.5; IR (neat): 2941, 2854, 1702, 1638, 1618, 1462, 1442, 1368, 1323, 1279, 1229, 1216, 1188, 1123, 1072, 1026, 974, 954, 927, 878, 831, 792, 742 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J*=12.4 Hz, 1H), 5.27 (d, *J*=12.4 Hz, 1H), 4.37 (dd, *J*=7.1, 5.5 Hz, 1H), 4.30–4.20 (m, 1H), 4.20–4.10 (m, 1H), 4.14 (q, *J*=7.1 Hz, 2H), 2.85 (td, *J*=5.1, 1.1 Hz, 1H), 2.40–2.25 (m, 2H), 2.21 (br s, 1H), 2.05–1.85 (m, 3H), 1.80–1.60 (m, 2H), 1.74 (dd, *J*=14.0, 3.2 Hz, 1H), 1.55–1.40 (m, 1H), 1.42 (d, *J*=14.0 Hz, 1H), 1.25 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.30 (C), 162.10 (CH), 97.59 (CH), 81.97 (CH), 79.87 (CH), 75.14 (CH), 59.82 (CH_2), 49.76 (CH), 41.16 (2×CH), 37.81 (CH_2), 36.97 (CH_2), 35.56 (CH), 27.08 (CH_2), 22.51 (CH_2), 14.52 (CH_3). HRMS (ESI, M+H^+): *m*/*z* calcd for $C_{16}H_{23}O_4$ 279.1596, found 279.1599.

4.2.24. Ethyl (2E)-3-[(2R,2aR*,5R*,5aS*,6R*,8aS*,8bR)-decahydro-2H-2,5-methanonaphtho [1,8-bc]furan-6-yloxy]acrylate (**9f**).* Reaction of the iodide **4f** (80.0 mg, 0.19 mmol) with $^nBu_3SnH$ (103 μL, 0.38 mmol) and AIBN (13.0 mg, 0.08 mmol) in benzene (35 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent furnished the oxa-cage **9f** (42.0 mg, 75%) as a colourless oil. R_f (1:5 EtOAc/hexane) 0.5; mp: 66–68°C; IR (neat): 2935, 2866, 1702, 1638, 1618, 1462, 1441, 1369, 1322, 1283, 1242, 1202, 1187, 1161, 1123, 1093, 1075, 1045, 1026, 996, 979, 956, 908, 867, 829, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J*=12.4 Hz, 1H), 5.27 (d, *J*=12.4 Hz, 1H), 4.20–4.10 (m, 3H), 4.10–3.95 (m, 2H), 2.30–2.15 (m, 3H), 2.00 (d, *J*=14.6 Hz, 1H), 1.90–1.55 (m, 7H), 1.52 (d, *J*=13.8 Hz, 1H), 1.45–1.30 (m, 2H), 1.26 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.27 (C), 161.75 (CH), 97.74 (CH), 82.78 (CH), 75.56 (CH), 74.45 (CH), 59.84 (CH_2), 40.16 (CH), 39.56 (CH), 38.82 (CH), 37.66 (CH_2), 30.72 (CH_2), 27.26 (CH_2), 22.10 (CH_2), 20.34 (CH), 16.06 (CH_2), 14.52 (CH_3). HRMS (ESI, M+H^+): *m*/*z* calcd for $C_{17}H_{25}O_4$ 293.1753, found 293.1754.

4.2.25. Ethyl (1R,1aR*,2R*,3aS*,4R*,5R*,6aS*,6bS*,7S*)-octahydro-1H-1,2,4-(epoxymethanetriyl)-6-oxacyclobuta[cd]inden-5-ylacetate (**1g**).* Reaction of the iodide **4g** (64 mg, 0.17 mmol) with $^nBu_3SnH$ (92 μL, 0.34 mmol) and AIBN (11.0 mg, 0.08 mmol) in benzene (20 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:10) as eluent furnished the oxa-cage **1g** (37 mg, 88%) as a colourless oil. R_f (3:10 EtOAc/hexane) 0.6; IR (neat): 2960, 2872, 1729, 1461, 1375, 1342, 1275, 1249, 1222, 1203, 1177, 1162, 1138, 1096, 1076, 1029, 1011, 992, 966, 942, 904, 849, 823, 789, 771, 708 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.86 (t, *J*=7.2 Hz, 1H), 4.75–4.65 (m, 1H), 4.55 (dd, *J*=7.6, 2.8 Hz, 1H), 4.25–4.20 (m, 1H), 4.20–4.10 (m, 2H), 2.75 (br s, 3H), 2.61 (ABX, *J*=14.8, 8.0 Hz, 1H), 2.43 (ABX, *J*=14.8, 6.0 Hz, 1H), 2.27 (br s, 1H), 1.91 (dd, *J*=7.6, 3.2 Hz, 1H), 1.62 (s, 1H), 1.51 (s, 1H), 1.26 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.43 (C), 83.23 (CH), 82.17 (CH), 68.78 (CH), 68.12 (CH), 60.63 (CH_2), 48.88 (CH), 45.51 (CH), 42.95 (CH), 42.01 (CH_2), 40.75 (CH), 36.56 (CH_2), 30.57 (CH), 14.34 (CH_3). HRMS (ESI, M+H^+): *m*/*z* calcd for $C_{14}H_{19}O_4$ 251.1283, found 251.1280.

4.2.26. Ethyl (2R,3R*,3aS*,5R*,5aR*,6S*,7aR*,7bS*,9S*)-decahydro-6,3,5-epoxymethanetriyl pentaleno[1,6-bc]pyran-2-ylacetate (**1h**).* Reaction of the iodide **4h** (55 mg, 0.14 mmol) with $^nBu_3SnH$ (76 μL, 0.28 mmol) and AIBN (10.0 mg, 0.06 mmol) in benzene (20 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:8) as eluent furnished the oxa-cage **1h** (30.0 mg, 83%) as a colourless oil. R_f (3:10 EtOAc/hexane) 0.4; IR (neat): 2953, 2872, 1731, 1461, 1421, 1370, 1320, 1268, 1238, 1209, 1175, 1160, 1128, 1086, 1032, 982, 963, 945, 925, 870, 814, 787, 763, 747 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.48 (t, *J*=8.4 Hz, 1H), 4.38 (t, *J*=4.4 Hz, 1H), 4.33 (t, *J*=7.0 Hz, 1H), 4.15 (d, *J*=8.4 Hz, 1H), 4.14 (q, *J*=7.2 Hz, 2H), 2.82 (t, *J*=4.4 Hz, 1H), 2.75–2.60 (m, 2H), 2.59 (ABX, *J*=14.8, 7.0 Hz, 1H), 2.45 (ABX, *J*=14.8, 7.0 Hz, 1H), 2.29 (ABXY, *J*=16.0, 0.0, 0.0 Hz, 1H), 2.14 (br s, 1H), 1.92 (ABXY, *J*=16.0, 8.4, 4.4 Hz, 1H), 1.72 (AB, *J*=10.4 Hz, 1H), 1.70–1.65 (m, 1H), 1.57 (AB, *J*=10.4 Hz, 1H), 1.25 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.49 (C), 81.79 (CH), 80.54 (CH), 75.06 (CH), 63.46 (CH), 60.46 (CH_2), 52.76 (CH), 50.59 (CH), 44.87 (CH), 44.17 (CH_2), 43.61 (CH), 42.37 (CH_2), 37.74 (CH_2), 32.63 (CH), 14.37 (CH_3). HRMS (ESI, M+H^+): *m*/*z* calcd for $C_{15}H_{21}O_4$ 265.1440, found 265.1441.

4.2.27. 2-[(2R,3R*,3aS*,6R*,6aR*,7R*,11bS*,11cR*,13S*)-2,3,3a,4,5,6,6a,7,11b,11c-Decahydro-7,3,6-(epoxymethanetriyl)dibenzo [de,h]chromen-2-yl]ethanol (**10**).* To a cold (−10 °C) suspension of LAH (18.0 mg, 0.47 mmol) in dry THF (3 mL) was added a solution of the ester **1d** (80.0 mg, 0.24 mmol) in dry THF (3 mL). The reaction mixture was stirred at rt for 1 h. It was recooled to 0 °C and wet Na_2SO_4 was slowly added with vigorous stirring. After 0.5 h milky solution appeared, which was filtered through the cintered funnel and slurry was washed with additional ethyl acetate (3×5 mL). Evaporation of the solvent under reduced pressure and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:4) as eluent furnished the alcohol **10** (62.0 mg, 89%) as a white solid. R_f (2:5 EtOAc/hexane) 0.3; mp: 115–117°C; IR (neat): 3411, 3028, 2928, 2863, 1493, 1460, 1381, 1274, 1261, 1204, 1195, 1103, 1060, 1036, 1017, 999, 985, 960, 922, 885, 821, 804, 752, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.25 (m, 4H), 5.09 (d, *J*=8.4 Hz, 1H), 4.74 (d, *J*=2.6 Hz, 1H), 4.34 (dd, *J*=9.7, 2.6 Hz, 1H), 4.13 (t, *J*=6.3 Hz, 1H), 3.68 (q, *J*=5.4 Hz, 2H), 3.12 (t, *J*=5.4 Hz, 1H), 2.45–2.30 (m, 3H), 2.03 (br s, 1H), 1.95–1.80 (m, 2H), 1.80–1.70 (m, 4H), 1.51 (dq, *J*=14.0, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 136.84 (C), 135.96 (C), 130.52 (CH), 129.49 (CH), 129.21 (CH), 128.50 (CH), 77.63 (CH), 77.25 (CH), 72.75 (CH), 70.18 (CH), 62.20 (CH_2), 42.37 (CH), 40.80, (CH), 40.50 (CH), 38.84 (CH_2), 32.46 (CH), 24.00 (CH_2), 22.83 (CH), 16.38 (CH_2). HRMS (ESI, M+H^+): *m*/*z* calcd for $C_{19}H_{23}O_3$ 299.1647, found 299.1653.

4.2.28. (2S,2aR*,4S*,4aR*,5S*,5aR*,6aS*,6bR*,6cR*,7S*)-7-Iododecahydro-2,4-methano oxireno[5,6]indeno[7,1-bc]furan-5-ol (**6i**).* Reaction of the diol **5i** (600 mg, 3.09 mmol) with iodine (786 mg, 3.09 mmol) in THF (20 mL) and saturated aq $NaHCO_3$ (7 mL) as described for the iodoether **6a** and purification of the residue on silica gel column using ethyl acetate–hexanes (1:4) as eluent furnished the iodoether **6i** (600 mg, 60%) after two steps as a pale yellow colour solid. R_f (3:10 EtOAc/hexane) 0.6; mp: 126–128°C; IR (neat): 3435, 2968, 2884, 1460, 1335, 1315, 1287, 1270, 1225, 1210, 1165, 1121, 1101, 1066, 1041, 983, 968, 956, 944, 922, 885, 860, 834, 819, 803, 772, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.78 (d, *J*=4.8 Hz, 1H), 4.50–4.40 (m, 2H), 3.97 (d, *J*=2.8 Hz, 1H), 3.39 (t, *J*=3.2 Hz, 1H), 3.14 (d, *J*=3.6 Hz, 1H), 2.85–2.80 (m, 1H), 2.69 (br s, 1H), 2.34 (td, *J*=10.0, 3.2 Hz, 1H), 2.28 (dt, *J*=10.0, 5.2 Hz, 1H), 2.12 (AB, *J*=11.2 Hz, 1H), 2.02 (d, *J*=4.8 Hz, 1H), 1.59 (AB, *J*=11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 90.71 (CH), 74.64 (CH), 63.92 (CH), 54.69 (CH), 53.90 (CH), 49.88 (CH), 46.92 (CH), 39.26 (CH), 35.65 (CH_2), 33.67 (CH), 33.53 (CH). HRMS (ESI, M+H^+): *m*/*z* calcd for $C_{11}H_{14}O_3I$ 320.9988, found 320.9986.

4.2.29. Ethyl (2E)-3-{[(2S,2aR*,4S*,4aR*,5S*,5aR*,6aS*,6bR*,6cR*,7S*)-7-iododecahydro-2,4-methanooxireno[5,6]indeno[7,1-bc]furan-5-yl]oxy}acrylate (**4i**).* Reaction of the alcohol **6i** (214 mg, 0.67 mmol) with ethyl propiolate (75 μL, 0.73 mmol) and *N*-methylmorpholine (80 μL, 0.73 mmol) in CH_2Cl_2 (5.0 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on

a silica gel column using ethyl acetate–hexanes (1:9) as eluent gave the vinylogous carbonate **4i** (220 g, 80%) as a white crystalline solid. R_f (1:5 EtOAc/hexane) 0.5; mp: 80–82°C; IR (neat): 2979, 2888, 1702, 1641, 1620, 1462, 1369, 1319, 1282, 1194, 1125, 1050, 970, 944, 921, 887, 859, 835, 822, 773, 727 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J=12.6 Hz, 1H), 5.38 (d, J=12.6 Hz, 1H), 4.77 (d, J=4.8 Hz, 1H), 4.64 (d, J=10.0 Hz, 1H), 4.48 (dd, J=5.6, 2.8 Hz, 1H), 4.18 (q, J=7.2 Hz, 2H), 3.83 (d, J=2.8 Hz, 1H), 3.42 (t, J=2.8 Hz, 1H), 3.21 (d, J=3.6 Hz, 1H), 2.90–2.80 (m, 1H), 2.57 (br s, 1H), 2.42 (td, J=10.0, 3.2 Hz, 1H), 2.31 (dt, J=10.0, 5.2 Hz, 1H), 2.13 (AB, J=11.2 Hz, 1H), 1.59 (AB, J=11.2 Hz, 1H), 1.28 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.47 (C), 161.35 (CH), 99.04 (CH), 90.61 (CH), 74.21 (CH), 73.93 (CH), 60.21 (CH_2), 53.70 (CH), 51.61 (CH), 49.81 (CH), 46.85 (CH), 37.50 (CH), 35.63 (CH_2), 33.48 (CH), 31.76 (CH), 14.47 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{16}H_{20}O_5I$ 419.0356, found 419.0354.

4.2.30. (2S,2aR*,4S*,4aS*,5S*,5aS*,6R*,9S*,9aR*,9bR*,9cR*,11S*)-11-Iodo-2,2a,3,4,4a,5,5a, 6,9,9a,9b,9c-dodecahydro-2,4:6,9-dimethanobenzo[5,6]indeno[7,1-bc]furan-5-ol (**6j**).* Reaction of the diol **5j** (450.0 mg, 1.8 mmol) with iodine (702.0 mg, 2.8 mmol) in THF (20 mL) and saturated aq $NaHCO_3$ (7 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent furnished the iodoether **6j** (378.0 mg, 55%) as a white solid. R_f (1:5 EtOAc/hexane) 0.7; mp: 152–154°C; IR (neat): 3442, 3056, 2965, 2888, 1685, 1457, 1417, 1370, 1328, 1309, 1255, 1220, 1174, 1158, 1118, 1066, 1025, 964, 936, 904, 861, 814, 784, 737 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.11 (br s, 2H), 4.62 (d, J=5.1 Hz, 1H), 4.33 (d, J=2.4 Hz, 1H), 4.00 (dd, J=9.7, 3.6 Hz, 1H), 3.95 (d, J=4.8 Hz, 1H), 3.04 (br s, 1H), 2.89 (br s, 1H), 2.80–2.70 (m, 2H), 2.56 (br s, 1H), 2.27 (dt, J=10.1, 3.8 Hz, 1H), 2.19 (td, J=10.1, 3.6 Hz, 1H), 2.13 (AB, J=11.0 Hz, 1H), 1.93 (dt, J=10.1, 4.8 Hz, 1H), 1.60 (AB, J=11.0 Hz, 1H), 1.36 (br s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 136.69 (CH), 136.04 (CH), 88.38 (CH), 78.33 (CH), 69.45 (CH), 50.29 (CH), 50.01 (CH_2), 48.66 (CH), 48.44 (CH), 46.41 (CH), 46.16 (CH), 45.58 (CH), 42.21 (CH), 37.45 (CH_2), 37.37 (CH), 36.45 (CH). HRMS (ESI, M+H^+): m/z calcd for $C_{16}H_{20}O_2I$ 371.0508, found 371.0509.

4.2.31. Ethyl (2E)-3-{[(2S,2aR*,4S*,4aS*,5S*,5aS*,6R*,9S*,9aR*,9bS*,9cR*,11S*)-11-iodo-2,2a,3,4,4a,5,5a,6,9,9a,9b,9c-dodecahydro-2,4:6,9-dimethanobenzo[5,6]indeno[7,1-bc] furan-5-yl]oxy}acrylate (**4j**).* Reaction of the alcohol **6j** (200.0 mg, 0.65 mmol) with ethyl propiolate (73 μL, 0.71 mmol) and *N*-methylmorpholine (78 μL, 0.71 mmol) in CH_2Cl_2 (5 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:19) as eluent gave the vinylogous carbonate **4j** (249.0 mg, 85%) as a colourless oil. R_f (1:5 EtOAc/hexane) 0.8; IR (neat): 2966, 1701, 1635, 1616, 1462, 1368, 1337, 1318, 1282, 1193, 1124, 1040, 1013, 938, 908, 829, 781, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J=12.4 Hz, 1H), 6.14 (br s, 2H), 5.28 (d, J=12.4 Hz, 1H), 4.58 (d, J=5.2 Hz, 1H), 4.26 (dd, J=10.6, 2.2 Hz, 1H), 4.20–4.10 (m, 1H), 4.16 (q, J=7.1 Hz, 2H), 3.96 (d, J=4.4 Hz, 1H), 3.03 (br s, 1H), 2.88 (br s, 1H), 2.80–2.70 (m, 2H), 2.44 (br s, 1H), 2.40 (dt, J=9.5, 3.0 Hz, 1H), 2.30 (td, J=10.6, 3.8 Hz, 1H), 2.11 (AB, J=11.0 Hz, 1H), 1.90 (dt, J=9.8, 4.6 Hz, 1H), 1.59 (AB, J=11.0 Hz, 1H), 1.37 (br s, 2H), 1.28 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.15 (C), 162.28 (CH), 137.60 (CH), 134.98 (CH), 97.93 (CH), 87.91 (CH), 81.06 (CH), 77.81 (CH), 59.97 (CH_2), 50.05 (CH_2), 50.05 (CH), 49.28 (CH), 48.22 (CH), 46.41 (CH), 45.28 (CH), 41.84 (CH), 39.44 (CH), 37.19 (CH), 37.00 (CH_2), 35.60 (CH), 14.54 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{21}H_{26}O_4I$ 469.0876, found 469.0873.

4.2.32. (2S,2aR*,4S*,4aR*,5R*,7aS*,7bR*,8S*)-8-Iodo-2,2a,3,4,4a,5,7a,7b-octahydro-2,4-methanoindeno[7,1-bc]furan-5-ol (**6k**).* Reaction of the diol **5k** (501.0 mg, 2.8 mmol) with iodine (714.0 mg, 2.8 mmol) in THF (20 mL) and saturated aq $NaHCO_3$ (7.0 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:7) as eluent furnished the iodoether **6k** (556.0 mg, 65%) as a white solid. R_f (3:10 EtOAc/hexane) 0.7; mp: 106–108°C; IR (neat): 3388, 2955, 2890, 1462, 1365, 1332, 1311, 1289, 1265, 1210, 1187, 1169, 1153, 1114, 1098, 1035, 1012, 984, 961, 953, 907, 846, 824, 799, 753, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.95 (ddd, J=10.2, 4.7, 2.4 Hz, 1H), 5.79 (dd, J=10.2, 2.4 Hz, 1H), 4.81 (d, J=4.7 Hz, 1H), 4.65–4.55 (m, 1H), 4.33 (t, J=5.5 Hz, 1H), 4.17 (d, J=2.6 Hz, 1H), 2.87 (td, J=5.2, 1.4 Hz, 1H), 2.76 (br s, 1H), 2.65–2.55 (m, 1H), 2.45 (td, J=9.5, 3.0 Hz, 1H), 2.22 (AB, J=11.0 Hz, 1H), 1.67 (AB, J=11.0 Hz, 1H), 1.63 (d, J=5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 331.64 (CH), 129.04 (CH), 92.11 (CH), 72.14 (CH), 65.72 (CH), 51.81 (CH), 47.09 (CH), 42.50 (CH), 36.35 (CH_2), 35.86 (CH), 31.77 (CH). HRMS (ESI, M+Na^+): m/z calcd for $C_{11}H_{13}O_2NaI$ 326.9858, found 326.9853.

4.2.33. Ethyl (2E)-3-{[(2S,2aR*,4S*,4aR*,5R*,7aS*,7bR*,8S*)-8-iodo-2,2a,3,4,4a,5,7a,7b-octahydro-2,4-methanoindeno[7,1-bc]furan-5-yl] oxy}acrylate (**4k**).* Reaction of the alcohol **6k** (255.0 mg, 0.84 mmol) with ethyl propiolate (94 μL, 0.92 mmol) and *N*-methylmorpholine (101 μL, 0.92 mmol) in CH_2Cl_2 (10 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent gave the vinylogous carbonate **4k** (324.0 mg, 96%) as a colourless oil. R_f (3:20 EtOAc/hexane) 0.5; IR (neat): 2978, 2900, 1706, 1639, 1620, 1463, 1402, 1369, 1320, 1282, 1192, 1128, 1041, 963, 915, 831 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J=12.5 Hz, 1H), 6.07 (ddd, J=10.2, 4.8, 2.4 Hz, 1H), 5.80 (dd, J=10.2, 2.4 Hz, 1H), 5.32 (d, J=12.5 Hz, 1H), 4.85–4.80 (m, 2H), 4.36 (t, J=5.5 Hz, 1H), 4.17 (q, J=7.1 Hz, 2H), 4.12 (d, J=2.3 Hz, 1H), 2.88 (t, J=4.7 Hz, 1H), 2.68–2.61 (m, 2H), 2.56 (td, J=2.8 Hz, 1H), 2.21 (AB, J=11.1 Hz, 1H), 1.65 (AB, J=11.1 Hz, 1H), 1.28 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.86 (C), 161.59 (CH), 131.06 (CH), 126.69 (CH), 98.39 (CH), 92.04 (CH), 75.95 (CH), 71.65 (CH), 60.08 (CH_2), 51.68 (CH), 47.22 (CH), 39.90 (CH), 36.13 (CH_2), 35.86 (CH), 30.73 (CH), 14.49 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{16}H_{20}O_4I$ 403.0406, found 403.0395.

4.2.34. (2S,2aR*,5S*,5aR*,6R*,8aS*,8bR*,9S*)-9-Iodo-2a,3,4,5,5a,6,8a,8b-octahydro-2H-2,5-methanonaphtho[1,8-bc]furan-6-ol (**6l**).* Reaction of the diol **5l** (500.0 mg, 2.6 mmol) with iodine (661.0 mg, 2.6 mmol) in THF (25 mL) and saturated aq $NaHCO_3$ (8 mL) as described for the iodoether **6a** and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:7) as eluent furnished the iodoether **6l** (372.0 mg, 45%) as a gummy solid. R_f (1:5 EtOAc/hexane) 0.4; IR (neat): 3400, 3028, 2941, 1466, 1374, 1304, 1221, 1200, 1176, 1146, 1079, 1061, 1034, 1019, 1002, 978, 947, 905, 888, 873, 811, 775, 745, 717 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.93 (ddd, J=10.3, 4.0, 2.8 Hz, 1H), 5.79 (ddd, J=10.3, 1.7, 0.8 Hz, 1H), 4.55 (t, J=2.8 Hz, 1H), 4.49 (d, J=4.8 Hz, 1H), 4.46 (d, J=4.8 Hz, 1H), 4.23 (t, J=4.1 Hz, 1H), 2.60–2.50 (m, 2H), 2.25–2.10 (m, 3H), 1.90–1.80 (m, 2H), 1.65–1.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 131.98 (CH), 129.27 (CH), 86.80 (CH), 70.89 (CH), 66.18 (CH), 40.26 (CH), 39.03 (CH), 37.56 (CH), 35.76 (CH), 30.22 (CH), 27.74 (CH_2), 15.30 (CH_2). HRMS (ESI, M+Na^+): m/z calcd for $C_{12}H_{15}O_2NaI$ 341.0015, found 341.0012.

4.2.35. Ethyl (2E)-3-{[(2S,2aR*,5S*,5aR*,6R*,8aS*,8bR*,9S*)-9-iodo-2a,3,4,5,5a,6,8a,8b-octahydro-2H-2,5-methanonaphtho[1,8-bc]furan-6-yl]oxy}acrylate (**4l**).* Reaction of the alcohol **6l** (173.0 mg, 0.54 mmol) with ethyl propiolate (61 μL, 0.60 mmol) and *N*-methylmorpholine (65 μL, 0.60 mmol) in CH_2Cl_2 (5 mL) at rt as described for the vinylogous carbonate **4a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent gave the vinylogous carbonate **4l** (215.0 mg, 95%) as a colourless oil. R_f (1:5 EtOAc/hexane) 0.5; IR (neat): 2945, 1705,

1640, 1620, 1466, 1404, 1369, 1320, 1283, 1192, 1130, 1095, 1078, 1042, 1023, 1005, 973, 913, 872, 814, 777 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J=12.5 Hz, 1H), 6.03 (dt, J=10.4, 3.7 Hz, 1H), 5.80 (d, J=10.4 Hz, 1H), 5.30 (d, J=12.5 Hz, 1H), 4.67 (dd, J=7.2, 1.8 Hz, 1H), 4.53 (br s, 1H), 4.50 (d, J=4.8 Hz, 1H), 4.27 (t, J=5.0 Hz, 1H), 4.17 (q, J=7.1 Hz, 2H), 2.69 (t, J=7.7 Hz, 1H), 2.65–2.55 (m, 1H), 2.20–2.10 (m, 2H), 2.10 (br s, 1H), 1.90–1.80 (m, 2H), 1.60–1.50 (m, 1H), 1.27 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.80 (C), 160.91 (CH), 131.00 (CH), 127.06 (CH), 98.75 (CH), 86.85 (CH), 76.45 (CH), 70.57 (CH), 60.09 (CH_2), 40.09 (CH), 36.45 (CH), 36.32 (CH), 35.39 (CH), 30.46 (CH), 27.46 (CH_2), 15.10 (CH_2), 14.50 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{17}H_{22}O_4I$ 417.0563, found 417.0565.

4.2.36. Ethyl (2R,3R*,3aS*,5R*,5aR*,6R*,6aS*,7aR*,7bS*,7cR*,9S*)-decahydro-2H-6,3,5-(epoxymethanetriyl)cyclopenta[de]oxireno[h]chromen-2-ylacetate (**1i**).* Reaction of the iodide **4i** (96 mg, 0.23 mmol) with $^nBu_3SnH$ (124 μL, 0.46 mmol) and AIBN (15.0 mg, 0.10 mmol) in benzene (30 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:8) as eluent furnished the oxa-cage **1i** (48 mg, 72%) as a colourless oil. R_f (1:4 EtOAc/hexane) 0.5; IR (neat): 2959, 2874, 1731, 1456, 1368, 1272, 1246, 1220, 1174, 1111, 1071, 1062, 1039, 993, 969, 926, 872, 822, 807, 775, 719, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.60–4.55 (m, 2H), 4.38 (td, J=6.8, 3.2 Hz, 1H), 4.15 (q, J=7.2 Hz, 2H), 4.14 (d, J=8.4 Hz, 1H), 3.40 (t, J=4.0 Hz, 1H), 3.14 (t, J=3.6 Hz, 1H), 2.82 (t, J=4.0 Hz, 1H), 2.61 (ABX, J=15.2, 6.8 Hz, 1H), 2.49 (ABX, J=15.2, 6.8 Hz, 1H), 2.26 (br s, 1H), 2.25–2.10 (m, 2H), 1.75–1.65 (m, 1H), 1.47 (AB, J=10.8 Hz, 1H), 1.36 (AB, J=10.8 Hz, 1H), 1.26 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.19 (C), 80.03 (CH), 75.19 (CH), 67.14 (CH), 63.58 (CH), 60.55 (CH_2), 50.67 (CH), 50.54 (CH), 49.96 (CH), 43.89 (CH), 42.47 (CH_2), 37.58 (CH), 33.84 (CH), 31.06 (CH_2), 30.85 (CH), 14.40 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{16}H_{21}O_5$ 293.1389, found 293.1382.

*4.2.37. Oxa-cage (**1j**).* Reaction of the iodide **4j** (89.0 mg, 0.19 mmol) with $^nBu_3SnH$ (103 μL, 0.38 mmol) and AIBN (13.0 mg, 0.08 mmol) in benzene (32 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent furnished the dioxa-cage **1j** (53 mg, 81%) as a colourless crystalline solid. R_f (3:20 EtOAc/hexane) 0.5; mp: 55–57°C; IR (neat): 2957, 2869, 1732, 1454, 1379, 1336, 1272, 1260, 1247, 1163, 1108, 1080, 1052, 1038, 1008, 959, 912, 856, 831, 811, 780, 736, 719, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.00 (br s, 2H), 4.30 (td, J=6.7, 2.6 Hz, 1H), 4.20–4.05 (m, 4H), 3.93 (dd, J=7.8, 5.0 Hz, 1H), 2.90 (br s, 1H), 2.80–2.70 (m, 3H), 2.53 (ABX, J=14.9, 7.3 Hz, 1H), 2.41 (ABX, J=14.9, 6.3 Hz, 1H), 2.38 (dd, J=9.7, 3.5 Hz, 1H), 2.14 (br s, 1H), 1.86 (tt, J=10.8, 3.5 Hz, 1H), 1.74 (dt, J=10.8, 4.2 Hz, 1H), 1.55–1.50 (m, 1H), 1.45–1.35 (m, 2H), 1.35–1.30 (m, 2H), 1.24 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.52 (C), 136.20 (CH), 133.66 (CH), 78.05 (CH), 77.67 (CH), 70.56 (CH), 63.15 (CH), 60.34 (CH_2), 50.71 (CH_2), 50.68 (CH), 49.46 (CH), 47.60 (CH), 44.26 (CH), 42.59 (CH_2), 42.33 (CH), 41.73 (CH), 39.39 (CH), 34.22 (CH), 32.90 (CH), 31.94 (CH_2), 14.39 (CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{21}H_{27}O_4$ 343.1909, found 343.1912.

4.2.38. Ethyl (2E)-3-[(2R,2aS*,4R*,5S*,5aS*,7R*,7aS*,7bR*,8R*)-decahydro-2,5,7-(methanetriyl)indeno[1,7-bc]furan-4-yloxy]acrylate (**11k**).* Reaction of the iodide **4k** (105.0 mg, 0.26 mmol) with $^nBu_3SnH$ (141 μL, 0.52 mmol) and AIBN (17.0 mg, 0.10 mmol) in benzene (45 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent furnished the monooxa-cage **11k** (56 mg, 78%) as a colourless oil. R_f (3:20 EtOAc/hexane) 0.6; IR (neat): 2973, 2880, 1704, 1639, 1618, 1455, 1368, 1309, 1277, 1186, 1123, 1094, 1074, 1038, 1013, 973, 949, 916, 905, 835, 771, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J=12.4 Hz, 1H), 5.20 (d, J=12.4 Hz, 1H), 4.54 (dd, J=4.8, 4.0, Hz, 1H), 4.29 (t, J=7.9 Hz, 1H), 4.24 (d, J=4.3 Hz, 1H), 4.14 (q, J=7.2 Hz, 2H), 2.46 (br s, 1H), 2.30–2.17 (m, 3H), 2.08 (q, J=5.8 Hz, 1H), 1.75–1.65 (m, 3H), 1.49 (AB, J=10.8 Hz, 1H), 1.25 (t, J=7.2 Hz, 3H), 1.22 (AB, J=10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.11 (C), 161.44 (CH), 97.62 (CH), 85.00 (CH), 77.96 (CH), 75.64 (CH), 59.87 (CH_2), 47.84 (CH), 44.15 (CH), 39.60 (CH), 39.31 (CH), 38.98 (CH), 33.96 (CH), 31.49 (CH_2), 24.33 (CH_2), 14.49 (CH). HRMS (ESI, M+H^+): m/z calcd for $C_{16}H_{21}O_4$ 277.1440, found 277.1430.

4.2.39. Ethyl (2E)-3-[(2R,2aS*,4R*,5S*,5aS*,8R*,8aS*,8bR*,9R*)-decahydro-2H-2,5,8-(methanetriyl)naphtho[1,8-bc]furan-4-yloxy]acrylate (**11l**).* Reaction of the iodide **4l** (135.0 mg, 0.32 mmol) with $^nBu_3SnH$ (175 μL, 0.65 mmol) and AIBN (22.0 mg, 0.14 mmol) in benzene (30 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:10) as eluent furnished the monooxa-cage **11l** (76 mg, 80%) as a colourless oil. R_f (1:5 EtOAc/hexane) 0.6; IR (neat): 2937, 2867, 1705, 1639, 1619, 1447, 1368, 1323, 1284, 1231, 1214, 1189, 1170, 1126, 1069, 1047, 1006, 981, 911, 882, 866, 854, 831, 812, 762, 736, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J=12.5 Hz, 1H), 5.20 (d, J=12.5 Hz, 1H), 4.40 (br s, 1H), 4.35 (br s, 1H), 4.16 (q, J=7.2 Hz, 2H), 4.08 (t, J=8.2 Hz, 1H), 2.22 (ddd, J=14.0, 9.2, 4.6 Hz, 1H), 2.16–2.04 (m, 2H), 2.00–1.88 (m, 3H), 1.82 (d, J=5.1 Hz, 1H), 1.78–1.50 (m, 4H), 1.40–1.30 (m, 1H), 1.27 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.17 (C), 161.47 (CH), 97.73 (CH), 79.09 (CH), 78.39 (CH), 77.69 (CH), 59.92 (CH_2), 41.22 (CH), 40.94 (CH), 38.66 (CH), 36.64 (CH), 35.85 (CH), 25.04 (CH_2), 25.04 (CH), 22.09 (CH_2), 17.08 (CH_2), 14.52 (CH_3). HRMS (ESI, M+Na^+): m/z calcd for $C_{17}H_{22}O_4Na$ 313.1416, found 313.1409.

4.2.40. (2R,2aS*,4R*,5S*,5aS*,7R*,7aS*,7bR*,8R*)-Decahydro-2,5,7-(methanetriyl)indeno [1,7-bc]furan-4-ol (**12k**).* Reaction of the iodoalcohol **6k** (100.0 mg, 0.33 mmol) with $^nBu_3SnH$ (177 μL, 0.66 mmol) and AIBN (22.0 mg, 0.14 mmol) in benzene (40 mL) as described for the oxa-cage **1a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes (1:4) as eluent furnished the oxa-cage **12k** (47 mg, 80%) as a colourless oil. R_f (3:10 EtOAc/hexane) 0.3; IR (neat): 3391, 2969, 2875, 1451, 1342, 1310, 1274, 1259, 1094, 1076, 1050, 1024, 1009, 997, 975, 959, 914, 905, 856, 837, 781, 770, 743, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.52 (t, J=4.2 Hz, 1H), 4.22 (d, J=5.1 Hz, 1H), 4.05 (t, J=8.5 Hz, 1H), 2.43 (br s, 1H), 2.35–2.30 (m, 1H), 2.20–2.10 (m, 2H), 2.06 (q, J=5.6 Hz, 1H), 1.70–1.60 (m, 1H), 1.60–1.45 (m, 4H), 1.23 (d, J=10.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 85.00 (CH), 78.20 (CH_2), 65.03 (CH), 48.24 (CH), 47.68 (CH), 40.25 (CH), 39.69 (CH), 39.55 (CH), 33.64 (CH), 31.63 (CH_2), 27.51 (CH_2). HRMS (ESI, M+H^+): m/z calcd for $C_{11}H_{15}O_2$ 179.1072, found 179.1071.

4.2.41. (2S,2aR*,4S*,4aS*,5R*,7S*,7aR*,7bR*,8R*)-5-{[1-(3,5-Dinitrophenyl)vinyl]oxy} decahydro-2,4,7-(methanetriyl)indeno[7,1-bc]furan (**13k**).* To a cold (0 °C), magnetically stirred solution of the alcohol **12k** (65.0 mg, 0.36 mmol) and DMAP (13.0 mg, 0.11 mmol) in dry CH_2Cl_2 (2 mL) was added dry Et_3N (153 μL, 1.1 mmol) followed by 3,5-dinitrobenzoyl chloride (**14**) (126.0 mg, 0.55 mmol) and the resulting mixture was stirred overnight at rt. Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:9) as eluent furnished the ester **13k** (85.0 mg, 63%) as a light pale yellow solid, which was crystallized from CH_3CN. R_f (3:10 EtOAc/hexane) 0.7; mp: 165–167°C; IR (neat): 3102, 2968, 2880, 1725, 1628, 1597, 1542, 1461, 1344, 1284, 1273, 1169, 1096, 1075, 1012, 992, 976, 951, 905, 837, 786, 774, 730, 729, 721 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.22 (t, J=2.0 Hz, 1H), 9.14 (d, J=2.4 Hz, 2H), 5.37 (t, J=8.6 Hz, 1H), 4.60 (t, J=4.2 Hz, 1H), 4.35 (d, J=4.4 Hz, 1H), 2.52 (br s, 1H), 2.45–2.30 (m, 3H), 2.19 (q, J=5.6 Hz, 1H), 1.85–1.75 (m, 3H), 1.58 (AB, J=10.8 Hz, 1H), 1.31 (AB, J=10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 162.36 (C), 148.80 (C), 134.41 (C), 129.53 (CH), 122.47 (CH),

85.08 (CH), 77.94 (CH), 72.04 (CH), 47.89 (CH), 44.05 (CH), 39.68 (CH), 39.50 (CH), 39.06 (CH), 34.31 (CH), 31.60 (CH_2), 24.26 (CH_2).

4.2.42. Ethyl (2E)-3-{[(1S,4R*,4aS*,9R*,9aR*,10S*)-10-hydroxy-1,4,4a,9,9a,10-hexahydro-1,4-methanoanthracen-9-yl]oxy}acrylate (**15c**).* To a magnetically stirred solution of the diol **5c** (375 mg, 1.64 mmol) in dry CH_2Cl_2 (15 mL) and THF (5 mL) were added *N*-methylmorpholine (192 μL, 1.81 mmol) and ethyl propiolate (167 μL, 1.64 mmol) at rt. The reaction mixture was stirred for further 4 h (TLC control). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexanes (1:19) gave first bis-vinylogous carbonate **16** (155 mg, 22%) as a white solid. further elution with ethyl acetate–hexanes (1:19) gave mono-vinylogous alcohol **15c** (325 mg, 61%) as a colourless oil. R_f (3:20 EtOAc/hexane) 0.3; IR (neat): 3447, 3065, 2978, 2932, 2867, 1689, 1638, 1622, 1457, 1372, 1324, 1290, 1198, 1136, 1042, 963, 910, 886, 818, 778, 758, 732, 696, 668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J=12.4 Hz, 1H), 7.32 (d, J=7.4 Hz, 1H), 7.28 (t, J=7.2 Hz, 1H), 7.22 (t, J=7.2 Hz, 1H), 7.13 (d, J=7.4 Hz, 1H), 5.45 (d, J=12.4 Hz, 1H), 5.30–5.20 (m, 2H), 5.14 (d, J=7.0 Hz, 1H), 4.91 (d, J=6.5 Hz, 1H), 4.18 (q, J=7.1 Hz, 2H), 3.10 (ddd, J=10.3, 7.0, 3.4 Hz, 1H), 3.05–2.95 (m, 2H), 2.96 (br s, 1H), 1.70 (br s, 1H), 1.32 (br s, 2H), 1.29 (t, J=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.06 (C), 162.16 (CH), 138.68 (C), 134.13 (C), 133.75 (CH), 133.45 (CH), 127.92 (CH), 127.08 (CH), 122.99 (CH), 122.85 (CH), 98.67 (CH), 80.12 (CH), 68.83 (CH), 60.03 (CH_2), 50.32 (CH_2), 45.24 (CH), 44.73 (CH), 44.36 (CH), 42.20 (CH), 14.51 (CH_3). HRMS (ESI, M+Na^+): m/z calcd for $C_{20}H_{22}O_4Na$ 349.1416, found 349.1413.

4.2.43. Diethyl (2E,2′E)-3,3′-[(1R,4S*,4aR*,9S*,9aS*,10R*)-1,4,4a,9,9a,10-hexahydro-1,4-methanoanthracene-9,10-diylbis(oxy)]bisacrylate (**16**).* R_f (3:20 EtOAc/hexane) 0.6; mp: 122–124 °C; IR (neat): 2980, 2926, 1701, 1640, 1622, 1457, 1370, 1322, 1283, 1192, 1126, 1038, 970, 911, 888, 834, 759, 734, 702, 668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J=12.4 Hz, 2H), 7.30–7.10 (m, 4H), 5.52 (d, J=12.4 Hz, 2H), 5.16 (d, J=6.4 Hz, 2H), 5.14 (t, J=1.2 Hz, 2H), 4.22 (q, J=7.2 Hz, 4H), 3.25–3.10 (m, 2H), 2.99 (s, 2H), 1.32 (t, J=7.2 Hz, 6H), 1.35–1.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.88 (2×C), 162.11 (2×CH), 133.93 (2×C), 133.61 (2×CH), 127.70 (2×CH), 122.60 (2×CH), 98.95 (2×CH), 79.15 (2×CH), 60.04 (2×CH_2), 49.81 (CH_2), 45.30 (2×CH), 41.44 (2×CH), 14.51 (2×CH_3). HRMS (ESI, M+H^+): m/z calcd for $C_{25}H_{29}O_6$ 425.1964, found 425.1979.

4.2.44. Ethyl (2R,3R*,3aS*,5R*,5aR*,6R*,10bS*,10cR*,12S*)-3,3a,4,5,5a,6,10b,10c-octa hydro-2H-6,3,5-(epoxymethanetriyl)benzo[h]cyclopenta[de]chromen-2-ylacetate (**1c**).* To a cold (−10°C), magnetically stirred solution of the mono-vinylogous alcohol **15c** (83 mg, 0.25 mmol) in dry THF (8 mL) was added $Hg(OAc)_2$ (81 mg, 0.25 mmol) and the reaction mixture was stirred at same temperature for 1 h. After complete consumption of the starting material, $NaBH_4$ (19 mg, 0.51 mmol) was added and the reaction mixture was stirred for 7 h at rt. Then it was quenched with water and extracted with ethyl acetate (3×10 ml). The combined organic layer was washed with brine and dried (anhyd Na_2SO_4). Evaporation of the solvent under reduced pressure and the purification of the residue on a silica gel column using ethyl acetate–hexanes (1:8) as eluent furnished the oxa-cage **1c** (59 mg, 71%) as a colourless oil after two steps. The compound thus prepared gave spectral data (IR, ^1H/^{13}C NMR and HRMS) identical to that described earlier.

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Supplementary data

Supplementary data related to this article can be found online version, at doi:10.1016/j.tet.2010.11.098.

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19. Crystal data for the iodide **4f**: Formula: $C_{17}H_{23}IO_4$; unit cell parameters: a=11.4189(3), b=6.5937(2), c=23.3105(7), β=99.552(10); space group: *P*2(1)/*c*; CCDC number 793509.
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23. Crystal data for the oxa-cage **13k**: $C_{18}H_{16}N_2O_7$; unit cell parameters: a=29.6325(10), b=5.9688(2), c=21.6208(8), β=121.391(3), space group: *C*(2)/*c*; CCDC number 652178.