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Some Novel Electron Transfer Mediated Cascade Ring-Opening Reactions of Bicyclo[4.1.0]ketones

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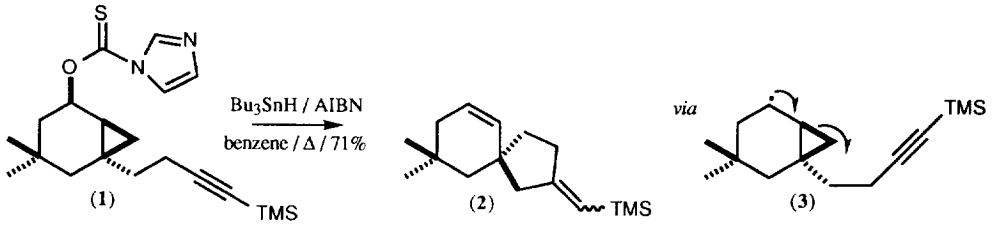
Abstract: The radical ring-opening reactions of cyclopropyl ketones, mediated by samarium (II) iodide and other electron transfer agents are described. This strategy allows tandem rearrangement cyclisation reactions and the trapping of the resultant samarium (III) enolates by a variety of electrophiles, for the construction of complex bicyclic systems.

Introduction

Preparative free radical chemistry[1] is now a firmly established strategy for the preparation of complex molecules, as demonstrated through many total syntheses.[2] Alkyl radical cyclisations are especially prominent and tandem cyclisations, as epitomised by Curran's classic synthesis of the linearly-fused triquinane hirsutene,[3] are illustrative of the power of such methodology. Less commonly employed however are the corresponding ring opening-fragmentation reactions, since in most cases these reactions are disfavoured both from a kinetic and thermodynamic standpoint. The cyclopropylcarbinyl-homoallyl radical rearrangement is however exceptional in that ring-opening is both fast and thermodynamically favoured as a result of the strain of the cyclopropane ring. Thus, ring-opening of the parent cyclopropylcarbinyl radical has been estimated to occur with a rate constant of 1.0×10^8 s^{-1} and the corresponding ring-closure at 8×10^3 s^{-1}.[4] As part of a programme designed to develop new preparatively useful methodology based on cyclopropylcarbinyl radical rearrangements, preliminary studies from these laboratories have described a tandem rearrangement-cyclisation approach toward various bicyclic skeletons, *via* tributylstannane mediated reduction of thiocarbonylimidazole derivatives of cyclopropyl carbinyl alcohols.[5]



Scheme 1

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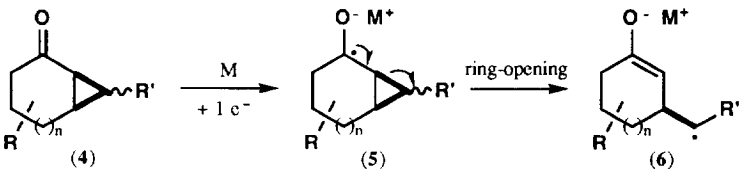
Thus, slow-addition of tributylstannane to a refluxing solution of (**1**) with AIBN as initiator, led smoothly to the spirocyclic system (**2**), via initial stereoelectronically controlled fragmentation[6] of the cyclopropyl carbinyl radical (**3**) and subsequent 5-*exo*-dig radical cyclisation (Scheme 1).

We reasoned that the overall synthetic potential of such a sequence would be considerably enhanced through the selection of a radical pathway involving single electron transfer to a cyclopropyl ketone (**4**) and subsequent rearrangement of the resultant ketyl radical (**5**) to the homoallylic radical (**6**) (Scheme 2). Intermediate (**6**) offers the potential not only for further radical reactions, such as tandem cyclisations, but also for controlled ionic reactions of the regiospecific metal enolate functionality which is also generated. An important feature of this strategy is that ring-opening occurs under stereoelectronic control[5,6] *via* opening of the exocyclic C-C bond in bicyclo[n.1.0]ketones. The regiochemistry and stereochemistry of the intermediate (**6**) is thus controlled from the initially constructed cyclopropyl ketone. Although many examples of radical additions and electron transfer reactions to cyclopropyl ketones are known,[7] problems of a second electron transfer reaction to give strongly basic dianions, and *in situ* protonation have usually precluded further controlled radical and enolate reactions. In this paper we now report in full detail the utility of tandem rearrangement / cyclisation / enolate trapping reactions of bicyclo[4.1.0]ketones, mediated by both samarium (II) iodide[8] and other reducing systems.

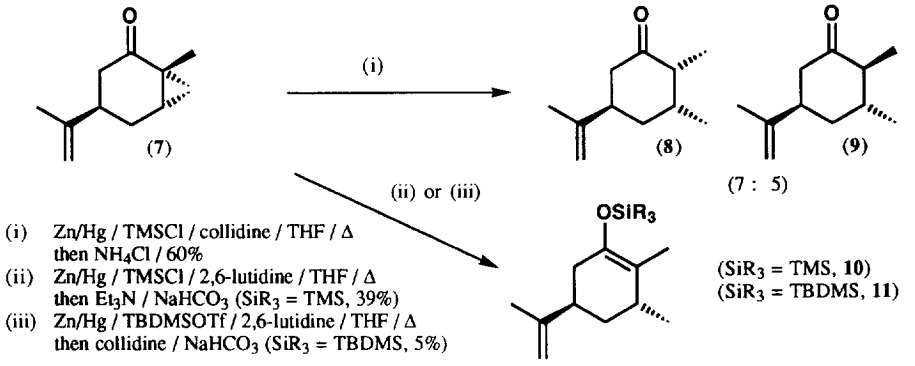


(**4**) (**5**) (**6**)

Scheme 2

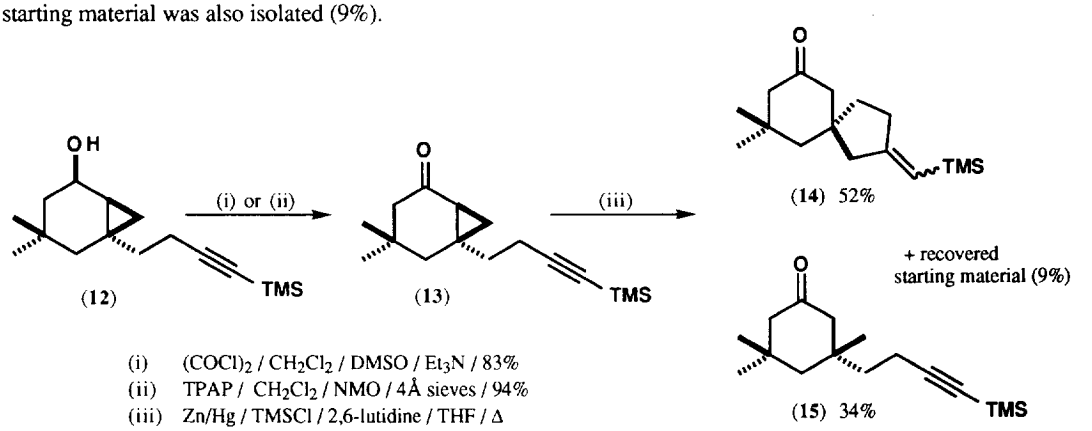
Initial Reduction Studies

Cyclopropyl ketones (**7**) and (**13**) were selected as initial substrates to investigate both enolate trapping and tandem cyclisation reactions. The cyclopropyl ketone (**7**) was expected to yield a relatively stable tetrasubstituted enolate derivative on ring-opening. Ketone (**7**) was readily synthesised in 85% yield, according to Corey's procedure, using sulfoxonium methylid chemistry.[9] Zinc / chlorotrimethylsilane (TMSCl) was chosen as the electron transfer system. This reagent combination was first described by Motherwell as a method for the deoxygenation of ketones via carbenoids under aprotic conditions.[10] In a seminal paper in the development of ketyl radical cyclisations, Corey later used zinc / TMSCl / 2,6-lutidine to achieve 5-exo-cyclisations onto alkenes, nitriles, aldehydes and oximes.[11] In the event reduction of (**7**) and hydrolytic work-up, gave a 7 : 5 mixture of the ring-opened ketones (**8**) and (**9**) in 60% overall yield, together with recovered starting material (14%) (Scheme 3). Experiments performed in the absence of a silylating reagent or in the absence of zinc amalgam gave no reaction. Hindered bases such as collidine or 2,6-lutidine were always added to avoid any proton or Lewis acid ($ZnCl_2$) catalysed side-reactions. Reduction of (**7**) under the same conditions, followed by addition of triethylamine and immediate quenching by saturated aqueous sodium bicarbonate gave the silyl enol ether (**10**) in a modest 39% yield, along with recovered starting material (18%). An attempted reaction in the presence of TBDMSCl was unsuccessful, with only starting material (**7**) being recovered even after extended reaction times. In the presence of TBDMSOTf however, a poor yield of the silyl enol ether (**10**) was obtained, not withstanding the fact that the TBDMSOTf reacts rapidly with THF under these conditions (Scheme 3).



Scheme 3

We next turned our attention to cyclisation studies of the cyclopropyl ketone (**13**), since it provided a direct comparison with the tributylstannane reduction methodology already reported (see Scheme 1). Alcohol (**12**) was readily prepared from dimedone in 4 steps, using Simmons-Smith cyclopropanation of an allylic alcohol as the key step.[5] Oxidation of (**13**) was initially accomplished using the Swern reaction, but TPAP oxidation[12] was later found to occur more reliably in 94% yield (Scheme 4). Reduction of (**13**) under the previous conditions in THF afforded a mixture of the cyclised spiroketones (**14**) and uncyclised compound (**15**) in an overall yield of 86% and a ratio of 1.5 : 1 in favour of the cyclised ketone (Scheme 4). Recovered starting material was also isolated (9%).



Scheme 4

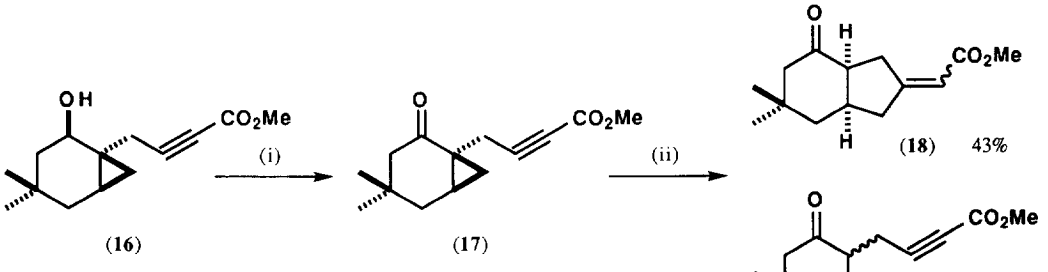
The relatively poor ratio of cyclised to uncyclised product was disappointing, but was initially considered to arise because of competing H-atom capture from the solvent. Cyclisation of 5-alkynyl radicals in a 5-*exo*-dig sense has been estimated to proceed with a rate constant of 2.8×10^4 s-1 at 25 °C and 4.6×10^4 s^{-1} at 60 °C[1e]. The rate of hydrogen atom capture from tetrahydrofuran solvent by primary alkyl radicals has been estimated to be approximately 6×10^3 s^{-1} at room temperature (pseudo-first order). We therefore decided to ascertain whether using a poorer hydrogen atom donating solvent would lead to improved yields of cyclised product (**14**).

Solvent	Temperature	Ratio of (**14**) / (**15**)	Recovered (**13**)	Isolated Yield
THF	reflux	1.5 : 1	9%	86%
THF	40 °C	2.0 : 1	-	-
THF	20 °C	2.8 : 1	-	-
DME	reflux	1.3 : 1	46%	27%
Diethyl Ether	reflux	1 : 1.7	7%	69%
THF / Benzene (1:10)	reflux	1 : 1.4	20%	59%
THF / Benzene (1:20)	reflux	1 : 1.6	9%	90%
Benzene	reflux	1 : 3.6	14%	82%

Table 1: Zinc / TMSCl Cyclisation Studies

The results for a series of different solvent mixtures are shown in Table 1 and reveal that it is indeed possible to achieve some degree of control in the spirocyclisation step. The product ratios reported are from GC analysis, but were verified by isolation of the products using column chromatography. In stark contrast to our expectations, switching to poorer hydrogen atom donating solvents, such as benzene, actually resulted in a decreased proportion of cyclised product (**14**). This solvent dependence may result from competing second electron delivery by zinc to give an organozinc species which, presumably, does not cyclise efficiently under the reaction conditions. The ratio (**14** / **15**) was also observed to decrease with increasing temperature in THF. The exact reason for these temperature and solvent variations remains unanswered however, due to the difficulty of drawing precise mechanistic conclusions from heterogeneous electron transfer reactions.

The chlorotrimethylsilane zinc system was also extended to the case of the bicyclic ketone (**17**) which possesses a pendant acetylenic ester side chain adjacent to the carbonyl group. In this instance, the bicyclic hydrindane derivative (**18**) was isolated in 43% yield, although examination of the crude reaction mixture by nmr spectroscopy also indicated that minor amounts of the uncyclised product (**19**) were also produced.



(16) (17)

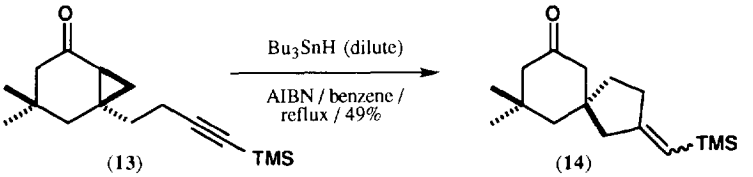
(i) $(COCl)_2$ / DMSO / CH_2Cl_2 / Et_3N / -78°C / 94%
(ii) Zn/Hg / TMSCl / collidine / THF / Δ

Scheme 5

From a practical standpoint, it should be noted that many experimental variations in the above protocol were attempted. These included the use of zinc wool, a zinc-nickel couple[13], activated Reike zinc[14], and sonochemical activation, all of which however did not result in any significant improvement.

At this stage further attempts using heterogeneous reductants were discontinued and the use of homogeneous reductants was investigated in an effort to improve the cyclisations. Initially, the use of organostannanes and organosilanes as reducing agents were investigated. Addition of silicon centred radicals to

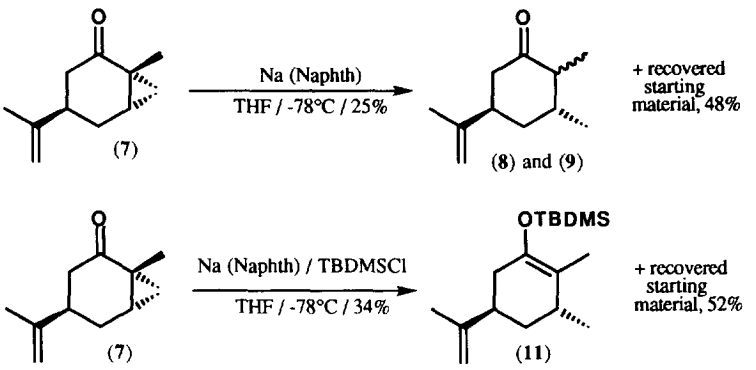
ketones is precedented,[7i, 13] but the problem with most organosilanes is that the strong Si-H bond causes chain transfer to be too slow. Attempted reduction of (**7**) with *tris*-trimethylsilylsilane (toluene / Bz_2O_2 / reflux), triethylsilane (toluene / Bz_2O_2 / reflux or benzene / AIBN / reflux) with or without t-dodecanethiol as a polarity reversal catalyst and trichlorosilane (benzene / Bz_2O_2 / sealed tube) all gave unsatisfactory results, with the isolation of a number of products in addition to significant quantities of unreacted starting material. Under the reaction conditions tested, silyl radical addition to the cyclopropyl ketone under free-radical chain conditions is inefficient and side-reactions resulting from competing addition of the silyl radicals to the alkene group of (**7**) are most probably occurring. Reactions of trialkylstannyl radicals with ketones are well known,[7j, 15] but no examples of the reduction of cyclopropyl ketones using tributylstannane with trapping of the intermediate stannyl enolates and tandem cyclisations had been undertaken. Tributylstannane reduction of (**7**) resulted in the isolation of the ring opened ketones (**8**) and (**9**) in a combined 13% yield. Reduction of (**13**) under dilute stannane conditions (0.015 M) was more successful however, resulting in clean reduction to the spirocyclic ketone (**14**) in 49% yield, along with 10% recovered starting material (Scheme 6). The formation of the spirocyclic ketone (**14**) and the complete absence of any of the uncyclised ketone (**15**) was particularly encouraging, allowing, as it did, a relatively straightforward method for the tandem rearrangement / cyclisation of cyclopropyl ketones. Unfortunately, attempts to trap out the intermediate stannyl enolates[18] gave unsatisfactory results and further investigations of the use of tributylstannane were not further pursued.



(**13**) (**14**)

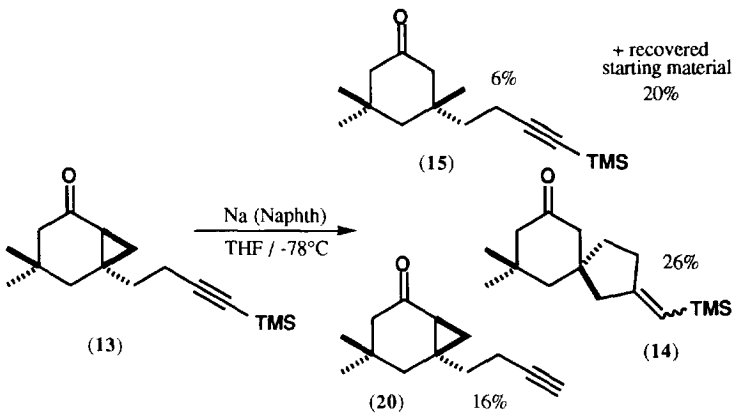
Scheme 6

The use of the strongly reducing group IA metals was next investigated. Although lithium / ammonia is too strong a reducing system because of second-electron delivery, the success of sodium naphthalenide in promoting various ketyl radical cyclisations is well documented.[19] Sodium naphthalenide, rather than lithium naphthalenide, was selected since Pradhan has reported that it is less basic (due to less disproportionation) and is therefore less efficient for α-deprotonation of ketones.[20] Thus reduction of (**7**) at -78°C was carried out by slowly adding sodium naphthalenide to the ketone until a permanent green colour persisted, affording the ring-opened ketones (**8**) and (**9**) in a combined 25% yield along with 48% recovered starting material (Scheme 7). All attempts to improve this conversion by adding better proton donors (e.g. dimethyl malonate), performing an inverse addition, or increasing the temperature, gave more complex mixtures. When the reaction was carried out in the presence of TBDMSCl, the silyl enol ether (**11**) was isolated in 34% yield, along with recovered starting material (52%) (Scheme 7).



Scheme 7

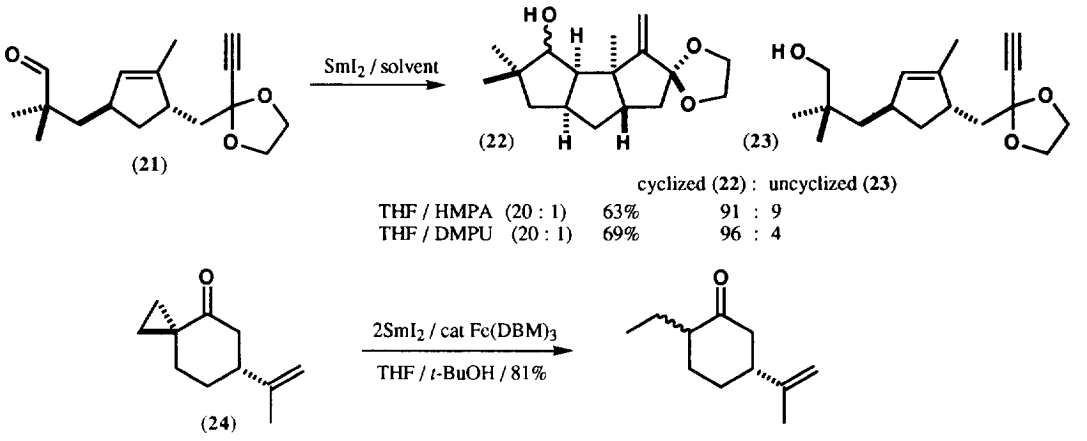
Reduction of the tandem substrate(**13**) using sodium naphthalenide gave a complex mixture of products, which included the desilylated ketone (**20**) (Scheme 8). Although, the ratio of cyclised to uncyclised material (**14 / 15**), 26 : 6, was better than in any of the zinc / TMSCl reactions, the acute problem of poor conversion which is presumably still related to competing α-deprotonation remained as an inherent limitation in the use of this class of reagents.[20]



Scheme 8

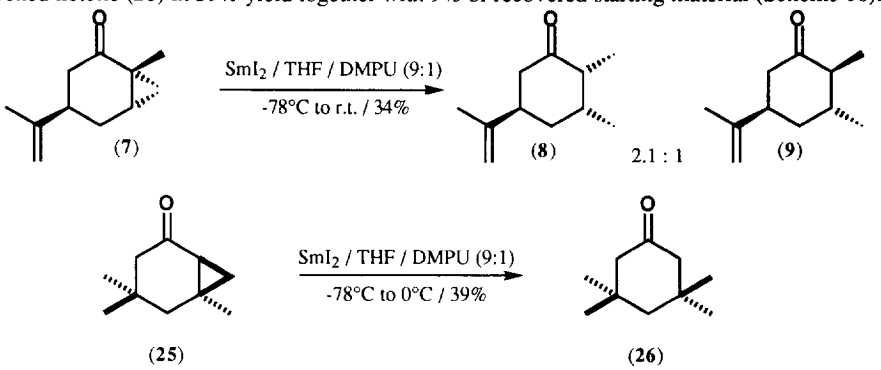
Samarium(II) Iodide Promoted Reactions

In view of the problems encountered with the previous reagent systems, we next focused on the use of samarium (II) iodide,[21] which has been widely used as an electron transfer agent for ketones and a variety of organic substrates. Although many examples of samarium (II) iodide promoted ketyl radical cyclisations are known, Curran's tandem cyclisation of alkenes (**21**),[22] using DMPU[23] and HMPA as additives was particularly encouraging (Scheme 9). In general HMPA and DMPU have both been used to improve reaction rates and yields in samarium (II) iodide reactions.[24] Curran has also successfully demonstrated cyclisations of iodoenones followed by trapping of the resultant samarium (III) enolates with aldehydes[25] and ring-opening of epoxyketones with samarium (II) iodide and methanol as an additive[26] have also been accomplished. Most recently examples of cyclobutyl and tetrahydropyryl ketones have also been reported.[27] During the course of his own studies, as part of investigations on the mechanism of samarium (II) iodide promoted intramolecular Barbier reaction, Molander had achieved a single example of ring-opening of cyclopropyl ketone (24)[28] (Scheme 9).



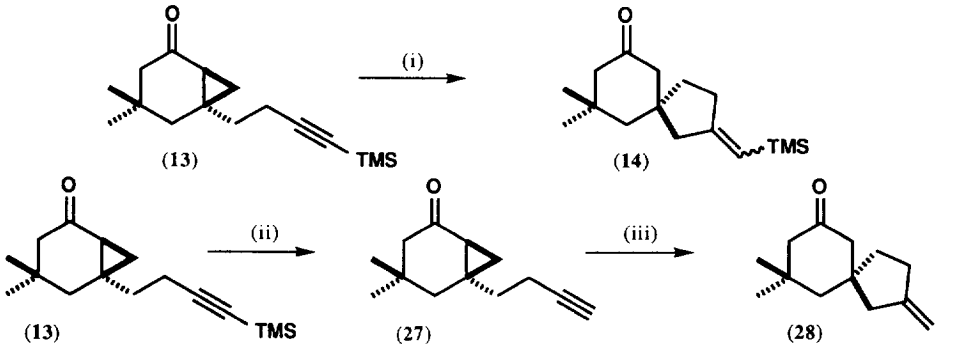
Scheme 9

In the event, samarium (II) iodide / DMPU reduction of our model cyclopropyl ketone (**7**) gave the ring-opened ketones (**8**) and (**9**) in 34% combined yield (Scheme 10). The experimental protocol followed in this and all subsequent examples was based on that employed by Curran.[22] Thus, samarium(II) iodide (approximately 0.1 M solution in tetrahydrofuran) was added to a solution of the cyclopropyl ketone in tetrahydrofuran / DMPU (9 : 1) under argon until a permanent purple / blue coloration was obtained. Reaction of cyclopropyl ketone (**7**) was rather slow at -78°C, and only at room temperature did the reaction rate increase to a reasonable level. Reduction of (**7**) with samarium (II) iodide / THF / DMPU and added t-butanol, and inverse addition of the ketone to samarium(II) iodide (2.5 equivalents), as in the Molander protocol,[28] with and without t-butanol, was less successful, with more starting material remaining. A similar reduction of (**25**) gave the ring-opened ketone (**26**) in 39% yield together with 9% of recovered starting material (Scheme 10).



Scheme 10

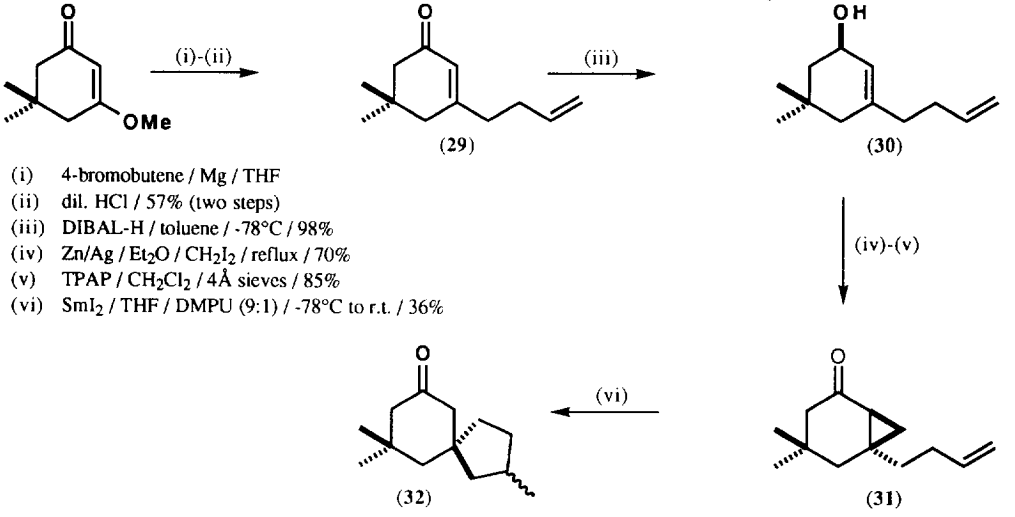
The reduction of the model cascade substrate (**13**) was then attempted under these conditions and gave the spiroketone (**14**) in a gratifying 79% isolated yield (Scheme 11). Indeed, gas chromatographic analysis of the crude mixture indicated a ratio of cyclised ketone (**14**) to uncyclised ketone (**15**) of greater than 99 : 1. In order to test whether the unprotected alkyne would also serve as a good radical trap under the reaction conditions, simple deprotection of the TMS group of (**13**) was accomplished with sodium hydroxide in methanol to give (**27**) in 96% yield. Subsequent samarium(II) iodide reduction of (**27**) then afforded the parent spirocyclic ketone (**28**) in 57% yield, free of any uncyclised material (Scheme 11).



(i) SmI_2 / THF / DMPU (9:1) / -78°C to 0°C / 79%
(ii) NaOH / MeOH / 96%
(iii) SmI_2 / THF / DMPU (9:1) / 57%

Scheme 11

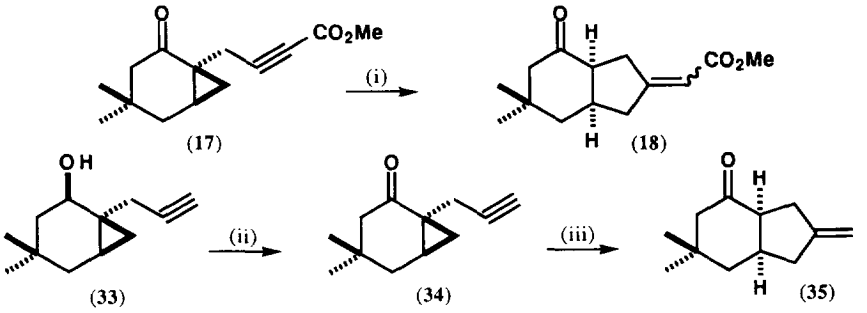
Since there were no reported examples of tandem cyclopropylcarbinyl radical cleavage and 5-*exo*-cyclisation onto unactivated alkenes, cyclopropyl ketone (**31**) was synthesised as a test substrate, using an analogous route to that employed in the synthesis of (**13**). Samarium(II) iodide / DMPU reduction of (**31**) then afforded the spirocyclic ketone (**32**) as a mixture of diastereomers in a modest 36% yield (Scheme 12).



(i) 4-bromobutene / Mg / THF
(ii) dil. HCl / 57% (two steps)
(iii) DIBAL-H / toluene / -78°C / 98%
(iv) Zn/Ag / Et_2O / CH_2I_2 / reflux / 70%
(v) TPAP / CH_2Cl_2 / 4Å sieves / 85%
(vi) SmI_2 / THF / DMPU (9:1) / -78°C to r.t. / 36%

Scheme 12

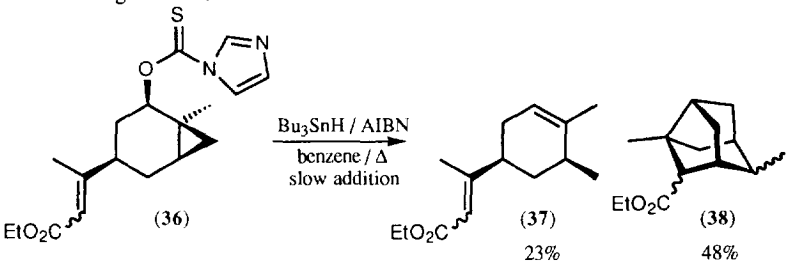
Following the earlier results obtained with (**17**) using zinc / TMSCl, extension of the samarium (II) iodide methodology to the formation of hydrindane systems was attempted. Accordingly, reduction under the standard conditions, at room temperature, afforded the bicyclo[4.3.0]ketone (**18**) in 77% yield (Scheme 13). This material had identical spectral properties to the product obtained using zinc / TMSCl (see Scheme 5). The advantage of samarium (II) iodide over zinc / TMSCl reduction is immediately apparent, since both the yield of cyclised ketone (**18**) was improved and uncyclised material was not observed. We were interested in the use of unactivated radical traps and, in particular, whether this difficult cyclisation would occur as readily as with the more activated electron-deficient alkyne (**17**). Thus, PDC oxidation of (**33**) gave the necessary precursor (**34**), which on samarium (II) iodide reduction gave the cyclised hydrindanone (**35**) in a modest 36% yield (Scheme 13).



(i) SmI_2 / THF / DMPU / -78°C to r.t. / 77%
(ii) PDC / DCM / 4Å sieves / 62%
(iii) SmI_2 / THF / DMPU / -78°C to r.t. / 36%

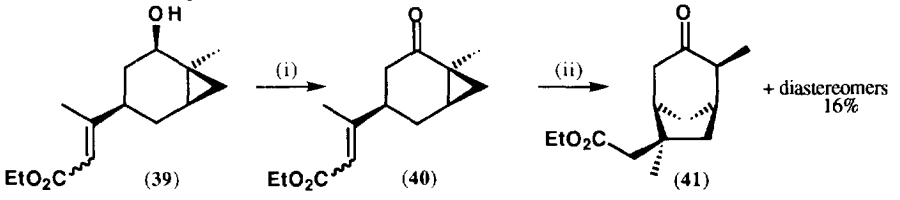
Scheme 13

Earlier studies in these laboratories had already shown that the synthesis of even more complex tricyclic skeletons via tandem radical rearrangement / cyclisation strategies was possible (Scheme 14).[5] In the case shown, the pendant alkenic side-chain of (**36**) was activated toward a conformationally demanding first 5-*exo*-trig cyclisation using an electron withdrawing carboethoxy group. However, even under slow-addition conditions complete control could not be achieved, with an approximately 1 : 2 mixture of monocyclic (**37**) to cyclised (**38**) material being obtained.



Scheme 14

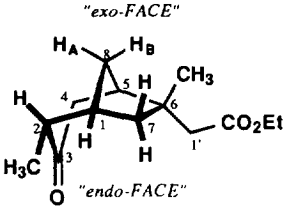
This cyclisation was therefore tested under the samarium (II) iodide reaction conditions. Accordingly, TPAP or PDC oxidation of (**39**) afforded the bicyclic cyclopropyl ketone precursor (**40**), as a mixture of E and Z isomers (17 : 3 ratio). Samarium (II) iodide / DMPU reduction of (**40**) under the usual conditions afforded a mixture of compounds, with only a small percentage of alkenic material (< 5% by crude ^1H NMR) (Scheme 15). Column chromatography then furnished the less polar, major diastereomer (**41**) in 32% yield. A further 16% of bicyclic material isolated as an inseparable mixture of the other diastereomers, showing very similar proton NMR, IR and mass spectral data to (**41**).



(i) TPAP / CH_2Cl_2 / NMO / 4Å sieves / 56%
or PDC / CH_2Cl_2 / 4Å sieves / 52%
(ii) SmI_2 / THF / DMPU (9:1) / -78°C to r.t.

Scheme 15

Confirmation of the structure of the major diastereomer was obtained using, a combination of ^{1}H, ^{13}C, DEPT, 2-D ^{1}H-^{13}C correlation and n.O.e. spectral data (Figure 1). Most significantly, irradiation of the C-2-methyl group resulted in an enhancement of H-7$_{endo}$, whilst irradiation of the C-6-methyl group gave an enhancement of the H-7$_{exo}$, but no enhancement of H-7$_{endo}$. All of these observations are consistent with the indicated structure of the major diastereomer (**41**).

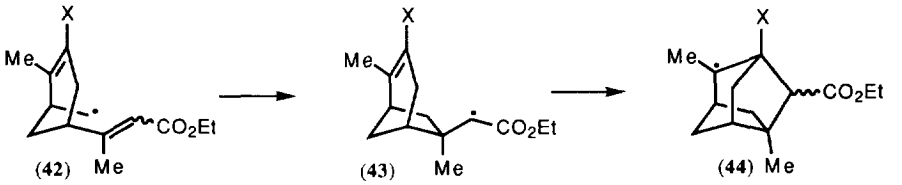


(**41**)

Irradiated	n.O.e. enhancement	Irradiated	n.O.e. enhancement
H-4$_{endo}$	H-1' (5.3%)	C-6-CH$_3$	H-7$_{exo}$ (6.1%)
	H-4$_{exo}$ (3.3%)		H-1, 5, 8$_B$ (4.8%)
H-8$_A$	H-2 (6.8%)		H-1' (2.6%)
	H-4$_{exo}$ (3.3%)	C-2-CH$_3$	H-2 (7.3%)
	H-1, 5, 8$_B$ (11.0%)		H-7$_{endo}$ (4.7%)
H-7$_{exo}$	H-7$_{endo}$ (26.8%)		H-1, 5, 8$_B$ (2.2%)
	H-1, 5, 8$_B$ (2.2%)		
	C-6-CH$_3$ (1.7%)		

Figure 1. Selected n.O.e. data for (**41**).

The preferential formation of (**41**) as the major diastereomer is in accord with our previously discussed model for cyclisation of these systems[5] (scheme 16). Thus, cyclisation of the intermediate radical (**42**) occurs via a "chair like" transition state as supported by the elegant studies of the Beckwith group[29]. In this instance however, the methylene group of the radical centre and the olefinic acceptor are required to adopt an energetically demanding pseudo 1,3 diaxial conformation for cyclisation to occur. From the case of the stannane reduction of (**36**) to the monocyclic and tricyclic products (**37**) and (**38**) respectively (scheme 14), it is clear that further cyclisation of the intermediate radical (**43**), X=H, (scheme 16) is highly efficient and does not compete with hydrogen atom capture from the stannane. In stark contrast however, samarium(II) iodide reduction of the ketone (**40**) provided the bicyclic material (**41**). Possible explanations for the differing behaviour in these two cases may reside either in the possibility that further cyclisation of the radical (**43**) X=OSmLn onto the sterically encumbered electron rich double bond of the samarium enolate is extremely slow or more probably that facile electron transfer from samarium(II) iodide to (**42**) or (**43**) (X=OSmLn) leads to the formation of a samarium ester enolate incapable of anionic cyclisation. Electron transfer to (**42**) (X=OSmLn) followed by intramolecular Michael addition would also explain the observation that monocyclic products were not isolated from the samarium(II) iodide induced reaction.

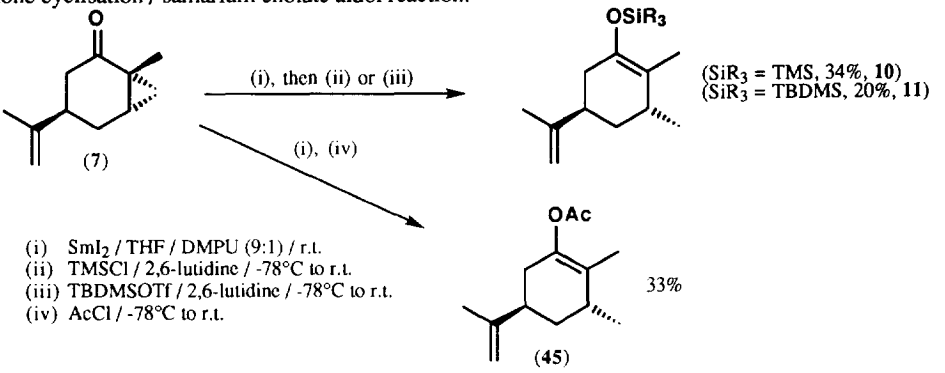


Scheme 16

The foregoing results demonstrate the effectiveness of samarium (II) iodide / DMPU as a reagent to achieve tandem rearrangement / cyclisation reactions for a variety of functionalised bicyclic skeletons. From an analysis of the yields in these reactions, it would seem that in general the presence of an intramolecular trap improves the overall yields of ring-opened products and that alkynes make more effective traps than alkenes.

Preliminary Samarium Enolate Trapping Studies

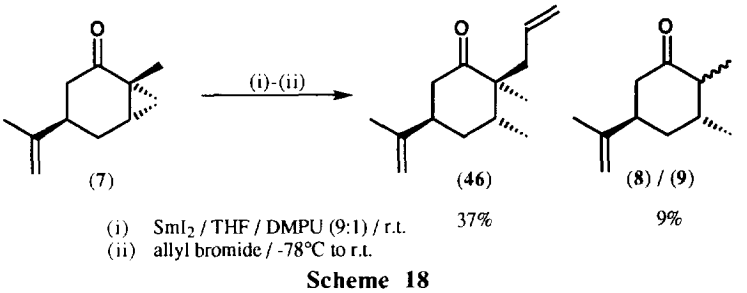
The ultimate aim of the project was not only to achieve tandem radical cyclisation reactions but also to capitalise on enolate anion chemistry through trapping of the intermediate samarium enolates with electrophiles. Few examples of such a sequential "one-pot" radical and then ionic process are known in the literature. Indeed, at the time of our initial studies, despite the popularity of samarium (II) iodide as a reductant, only a few examples of the use of samarium enolates had been reported in the literature. Examples of samarium enolate generation include samarium (II) iodide reductions of α-halocarbonyl compounds (Reformatsky reactions),[31] Imamoto's homologation of esters,[31] reductions of unsaturated carbonyls[32] and Curran's tandem iodo-enone cyclisation / samarium enolate aldol reaction.[25]



Scheme 17

Based on the mechanistic hypothesis that samarium enolates were intermediates in these reactions, simple trapping reactions were tested. Accordingly, reduction of the model substrate (**7**) and subsequent trapping with TMSCl, TBDMSOTf and acetyl chloride gave the O-trapped products, (**10**), (**11**) and (**44**) respectively (Scheme 17). To the best of our knowledge, this was the first reported example of the trapping of a samarium enolate at the oxygen atom. The yields, although modest, compare with those of the simple hydrolysis reaction (Scheme 17).

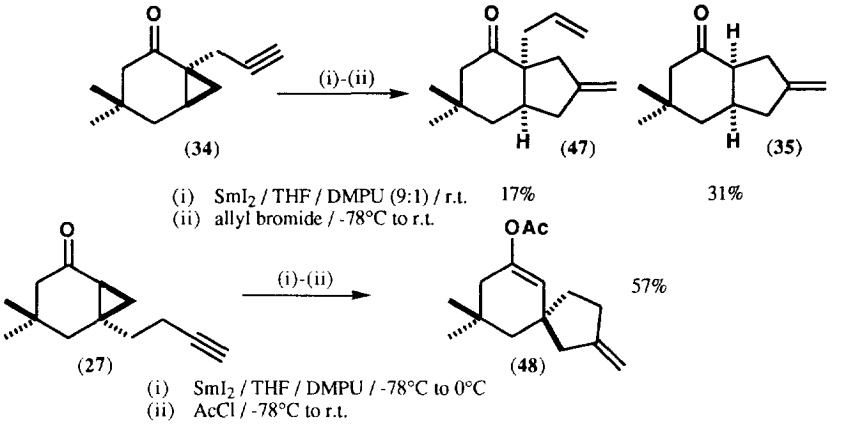
Trapping of the samarium enolate with allyl bromide afforded, the allylated product (**46**) in 37% yield, along with the hydrolysed ketones (**8**) and (**9**) in combined 9% yield (Scheme 18). This product was also formed indirectly in 39% yield, via transmetallation of the TMS enol ether (**10**) with methyl lithium and trapping with allyl bromide. The stereochemistry of the allylated product (**45**) was confirmed through n.O.e. data, and is consistent with attack from the less-hindered face of the samarium enolate.



Scheme 18

Finally, the more challenging goal of trapping samarium enolates formed from tandem cyclopropane ring-opening / intramolecular radical cyclisation reactions was addressed. Attempted sequential reduction of (**34**) and trapping with allyl bromide gave the hydrolysed ketone (**35**) in 31% yield and the desired allylated

product (**47**) in only 17% yield (Scheme 19). The stereochemistry of allylation occurred through selective trapping from the more open convex face of the bicyclic enolate intermediate, resulting in the *cis*-fused hydrindane. On a more encouraging note however, sequential reduction of (**27**) and acetyl chloride trapping afforded the spirocyclic trisubstituted enol acetate (**48**) in 57% yield, with only a very small amount of hydrolysed ketone (**28**) (Scheme 19). This example illustrates that trisubstituted samarium enolates can be successfully trapped and that no scrambling of enolate regiochemistry occurred.



Scheme 19

under the reaction conditions. This was confirmed by n.O.e. studies of (**47**), since irradiation of H-6 resulted in enhancements of H-1, H-3 and H-4, whereas irradiation of the gem-dimethyl group resulted in enhancements of H-8 and H-10.

Conclusions

In summary, we have demonstrated that the reductive ring opening of a variety of appropriately constructed bicyclo[4.1.0]ketones is a viable strategy which can be used to initiate a regio- and stereocontrolled tandem ring opening cyclisation sequence. Moreover, further synthetic advantage may be taken of the regiospecific enolate which is generated during the course of the reaction pathway. Of the electron transfer reagents studied, the samarium(II) iodide/ DMPU combination clearly emerges as the most useful in terms of avoiding the inherent problems of reagent basicity and second electron delivery which are always inherent in such an approach to radical chemistry. From a preparative standpoint, it is noteworthy that the construction of a wide variety of bicyclic skeletal types is possible and that both activated and unactivated alkenes and alkynes can be used as the intramolecular radical traps, although in general alkynes give better results.

General Experimental.

^1H and ^{13}C nmr spectra were recorded at 250 MHz and 62.5 MHz respectively on a Bruker WM-250 instrument; at 270 MHz and 67.9 MHz respectively on a Jeol GSX 270 instrument; at 400 MHz and 100 MHz respectively on a Jeol GSX 400 instrument; at 500 MHz and 125.8 MHz respectively on a Bruker AM-500 instrument, with either tetramethylsilane or residual protic solvent as the internal standard. Infrared spectra were recorded on a Perkin Elmer 983G spectrometer. Mass spectra were recorded on a VG 7070B instrument under E.I. conditions. Microanalyses were performed in the Imperial College Chemistry Department

microanalytical laboratory. Melting points were determined on a Reichert hot-stage and are uncorrected. Optical rotations were measured using an Optical Activity AA-1000 polarimeter. Diethyl ether, tetrahydrofuran were distilled from sodium - benzophenone ketyl under argon, immediately prior to use. Toluene and benzene were distilled from sodium under an atmosphere of argon immediately prior to use. Dichloromethane was distilled from phosphorus pentoxide under an atmosphere of argon immediately prior to use. Dimethyl sulphoxide and DMPU were distilled from calcium hydride at reduced pressure, and stored over 4Å molecular sieves under argon. Pyridine and triethylamine were distilled from potassium hydroxide and stored over 4Å molecular sieves under argon. 2,6-Lutidine was distilled from aluminium trichloride and stored over 4Å molecular sieves. Collidine was distilled from potassium hydroxide and stored over 4Å molecular sieves. Chlorotrimethylsilane was distilled from CaH_2 immediately prior to use and any HCl removed by storing over either sodium or polyvinylpyridine for 30 minutes. All other solvents and reagents were purified by standard means. All reactions were performed using oven dried glassware under an atmosphere of dry argon unless otherwise stated. Analytical thin layer chromatography was performed on pre-coated glass backed plates (Merck Kieselgel 60 F_{254}). Preparative column chromatography was performed at low positive pressure on Merck Kieselgel 60 (230 - 400 mesh).

Preparation of Zinc Amalgam. To a magnetically stirred solution of mercury(II) chloride (4.0 g, 14.7 mmol) in water (60 ml) containing concentrated hydrochloric acid (2.0 ml), within a conical flask (thick-walled), was added zinc powder (20.0 g, 306 mmol). This mixture was simultaneously stirred and swirled (by hand) for 10 minutes. The resulting amalgam was collected by filtration (buchner funnel) and sequentially washed with water (200 ml, containing a trace of hydrochloric acid), ethanol (200 ml) and ether (300 ml). After removal of excess solvent *in vacuo*, the amalgam was sieved through a buchner funnel (to remove any lumps of zinc) and then dried *in vacuo* (trolley-pump, < 0.5 mm Hg) for 18 hours. The amalgam was stored under argon and used within 2 weeks.

Zinc / TMSCl reduction - typical procedure. Zinc amalgam (6.5 g, 100 mmol) was flame dried with a teflon stirrer bar in a round bottomed flask with an attached condenser and then dry stirred for 30 minutes under a flow of argon. A solution of cyclopropyl ketone (1.00 mmol) and 2,6-lutidine or collidine (4.00 mmol) in tetrahydrofuran (10 ml) was added, followed by a solution of sodium dried (pre-distilled from CaH_2) trimethylsilylchloride (5 ml, 40 mmol) in tetrahydrofuran (5 ml). The mixture was stirred (flask placed off-centre from stirrer box, to allow vigorous but irregular stirring) and slowly warmed to reflux. After stirring for 24 hours, the reaction mixture was carefully quenched with water (20 ml), the solution decanted from the zinc and extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (30 ml) and brine (30 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. Purification of the resulting miture was then achieved by column chromatography (ether / petrol, silica).

(2R, 3R, 5R)-2,3-Dimethyl-5-isopropenyl-cyclohexan-1-one (8) and (2S, 3R, 5R)-2,3-dimethyl-5-isopropenyl-cyclohexan-1-one (9).[33] Cyclopropyl ketone (**7**) (245 mg, 1.49 mmol) was treated according to the general zinc / TMSCl procedure (Zn / Hg, 38.2 mmol; collidine, 4.97 mmol; TMSCl, 25.2 mmol; THF, 20 ml). Column chromatography (10% ether / petrol, florisil) afforded a mixture of the diastereomers (**8**) and (**9**) (148 mg, 60%) as a colourless oil, in an estimated (NMR) (7 : 5) ratio and recovered starting material (35 mg, 14%). Recolumning of the diastereomeric mixture (5% ether petrol, silica), achieved a partial separation of the major, less polar diastereomer (**8**) from a mixture of the two diastereomers, enriched in the minor, slightly more polar diastereomer (**9**). Less polar (**8**) (35%); ^{1}H NMR (500 MHz, $CDCl_3$) δH 4.76 (1H, m, H-2'), 4.73 (1H, m, H-2'), 2.62 (^{1}H, pm, J=6.7 Hz, H-2), 2.58 (1H, tt, J=12.4, 4.3 Hz, H-5), 2.40 (1H, ddd, J=13.0, 4.2, 2.1 Hz, H-6), 2.35-2.31 (1H, m, H-3), 2.25 (1H, td, J=13.0, 1.1 Hz, H-6), 1.87 (1H, td, J=12.7, 4.1 Hz, H-4), 1.80 (1H, dtd, 13.3, 3.5, 2.0 Hz, H-4), 1.73 (3H, s, C-1'-CH3), 0.98 (3H, d, J=6.7 Hz, C-2-CH3), 0.82 (3H, d, J=7.2 Hz, C-3-CH3); 13C NMR (125 MHz, $CDCl_3$) dC 212.97 (s, C-1), 147.63 (s, C-1'), 109.70 (t, C-2'), 48.38 (d, C-2), 46.62 (t, C-6), 41.06 (d), 37.69 (t, C-4), 36.25 (d),

20.58 (q), 13.98 (q), 11.95 (q). More polar (**9**) (25%); ^{1}H NMR (500 MHz, $CDCl_3$) dH 4.83 (1H, m, H-2'), 4.68 (1H, m, H-2'), 2.69 (1H, p, J=5.2 Hz, H-5), 2.59 (1H, ddd, J=14.5, 5.3, 1.7 Hz, H-6), 2.43 (1H, ddd, J=14.5, 5.9, 1.1 Hz, H-6), 2.01 (1H, pm, J=6.8 Hz, H-2), 1.95 (1H, dddd, J=13.3, 5.3, 3.8, 1.8 Hz, H-4), 1.73 (3H, d, J=0.7 Hz, C-1'-CH3), 1.72-1.67 (1H, m, H-3), 1.70 (1H, td, J=11.5, 4.5 Hz, H-4), 1.08 (3H, d, J=6.8 Hz, C-2-CH3), 1.03 (3H, d, J=6.4 Hz, C-3-CH3); ^{13}C NMR (125 MHz, $CDCl_3$) δC 213.53 (s, C-1), 146.94 (s, C1'), 111.68 (t, C-2'), 51.56 (d, C-2), 44.00 (t, C-6), 40.75 (d), 35.11 (t, C-4), 34.92 (d), 21.86 (q), 20.55 (q), 13.11 (q) ; m/z, (**8**) and (**9**), 166 (M^+), 151 (M+-Me), 123, 97, 95, 83, 69, 67; Observed (M+) (**8**) and (**9**): 166.1356; $C_{11}H_{18}O$ requires 166.1358.

(3R, 5R)-2,3-Dimethyl-1-(trimethylsilyloxy)-5-isopropenylcyclohex-1-ene (10). Cyclopropyl ketone (**7**) (250 mg, 1.52 mmol) was treated according to the general zinc / TMSCl procedure (Zn / Hg, 99.4 mmol; collidine, 6.05 mmol; TMSCl, 63.0 mmol; THF, 25 ml). After stirring for 13 hours, triethylamine (2.0 ml) was added and the solution poured into saturated aqueous $NaHCO_3$ solution (30 ml), decanted from the zinc and extracted with ether (3 x 50 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (30 ml), water (30 ml) and brine (30 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. The tetrahydrofuran-TMSCl derived side-products were removed by reduced pressure Kugelrohr distillation (1 mm Hg) and, the residue purified by column chromatography (0-10% ether / petrol, florisil) to afford (**10**) (140 mg, 39%) as a colourless oil. $[\alpha]_D^{20}$ +74.6° (c=1.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δH 4.73 (1H, p, J=1.5 Hz, H-2'), 4.71 (1H, m, H-2'), 2.39 (1H, m, H-5), 2.18 (1H, br p, J=6.5 Hz, H-3), 2.04-1.97 (2H, m, 2 x H-6), 1.74 (3H, s, C-2-CH3), 1.57 (3H, m, C-1'-CH3), 1.57 (1H, td, J=12.4, 5.6 Hz, H-4), 1.52-1.48 (1H, m, H4), 1.03 (3H, d, J=7.0 Hz, C-3-CH3), 0.17 (9H, s, Si(CH3)3); ^{13}C NMR (125 MHz, $CDCl_3$) δC 149.45 (s), 142.42 (s), 115.96 (s), 108.66 (t, C-2'), 37.13 (d), 35.70 (t), 35.12 (t), 33.51 (d), 20.79 (q), 19.64 (q), 14.68 (q, C-3-CH3), 0.68 (q, Si(CH3)3); m/z, 238 (M^+), 223 (M^+-Me), 195, 181, 155, 133, 73; Observed (M^+): 238.1758; $C_{14}H_{26}OSi$ requires 238.1753. and more polar recovered starting material (**7**) (30 mg, 18%).

(3R, 5R)-1-(*tert*-Butyldimethylsilyloxy)-2,3-dimethyl-5-isopropenylcyclohex-1-ene (11). Zinc amalgam (3.0 g, 46 mmol) was flame dried with a teflon stirrer bar in a round bottomed flask with an attached condenser and dry-stirred for 40 minutes under argon. A solution of cyclopropyl ketone (**7**) (164 mg, 1.00 mmol) and 2,6-lutidine (0.580 ml, 4.97 mmol) in diethyl ether (15 ml) was then added and the mixture cooled to 0°C. *Tert*-butyldimethylsilyl triflate (1.15 ml, 5.01 mmol) was then added, the reaction mixture stirred (flask placed off-centre from stirrer box, to allow vigorous but irregular stirring) for 30 minutes at 0°C and then at room temperature for 13 hours. After stirring for 13 hours, collidine (1.0 ml) was added and the solution poured into saturated aqueous $NaHCO_3$ solution (20 ml), decanted from the zinc and extracted with dichloromethane (3 x 20 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (20 ml), water (20 ml) and brine (20 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (0-10% ether / petrol, silica) afforded (**11**) (14 mg, 5%) as a colourless oil. $[\alpha]_D^{20}$ +68.1° (c=0.86, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δH 4.73 (1H, p, J=1.5 Hz, H-2'), 4.71 (1H, m, H-2'), 2.38 (1H, m, H-5), 2.18 (1H, br p, J=6.5 Hz, H-3), 2.04 (1H, ddd, J=16.4, 5.5, 0.7 Hz, H-6), 1.98 (1H, m, H-6), 1.74 (3H, s, C-2-CH3), 1.60 (3H, t, J=1.6 Hz, C-1'-CH3), 1.57 (1H, td, J=12.3, 5.6 Hz, H-4), 1.50 (1H, m, H-4), 1.04 (3H, d, J=7.0 Hz, C-3-CH3), 0.95 (9H, s, SiC(CH3)3), 0.12 (6H, s, Si(CH3)2); ^{13}C NMR (125 MHz, $CDCl_3$) δC 149.50 (s), 142.54 (s), 115.62 (s), 108.67 (t, C-2'), 37.17 (d), 35.86 (t), 35.09 (t), 33.68 (d), 25.89 (q, SiC(CH3)3), 20.80 (q), 19.64 (q), 18.23 (s, SiC(CH3)3), 14.80 (q, C-3-CH3), -3.70 (q, SiCH3), 3.88 (q, SiCH3); m/z, 280 (M^+), 265 (M^+-Me), 237, 149, 73; Observed (M^+): 280.2216; $C_{17}H_{32}OSi$ requires 280.2222.and more polar recovered starting material (**7**) (97 mg, 59%).

(1R*, 6R*)-3,3-Dimethyl-1-(4-trimethylsilylbut-3-ynyl)-bicyclo[4.1.0]heptan-5-one (13). **Method A - Swern Oxidation.** To a solution of oxalyl chloride (0.392 ml, 4.49 mmol) in dichloromethane

(20 ml) at -78°C, was added dimethyl sulphoxide (0.640 ml, 9.02 mmol) dropwise. The solution was stirred for 5 minutes and a solution of alcohol **(12)** (1.08 g, 4.08 mmol) in dichloromethane (10 ml) was added dropwise, resulting in the formation of a white precipitate. The mixture was stirred for 20 minutes, triethylamine (1.70 ml, 12.2 mmol) was added and, after stirring for a further 5 minutes at -78°C allowed to warm up to room temperature. The reaction mixture was poured into water (100 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic layers were washed with brine (100 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (20% ether / petrol, silica) gave (13) (892 mg, 83%) as a colourless crystalline solid. **Method B - TPAP oxidation**. To a stirred solution of 4-methylmorpholine N-oxide (260 mg, 2.22 mmol) and dried powdered 4Å molecular sieves (2.0 g) in dichloromethane (5 ml) was added alcohol **(12)** (385 mg, 1.46 mmol) in dichloromethane (20 ml), followed by tetrapropylammonium perruthenate (TPAP) (25 mg, 71 mmol). After 18 hours, the mixture was filtered through a pad of celite / silica and the solvent removed *in vacuo*. Column chromatography (20% ether / petrol, silica) gave (13) (360 mg, 94%) as a colourless crystalline solid (m.p. 59-61°C). ^{1}H NMR (270 MHz, $CDCl_3$) δH 2.31 (2H, t, J=7.5 Hz, 2 x H-2'), 2.01 (1H, d, J=14.4 Hz, H-4), 1.78 (1H, m, H-4), 1.67 (2H, s, 2 x H-2), 1.64-1.57 (2H, m, H-6, H-1'), 1.44 (1H, dt, J=13.9, 7.5 Hz, H-1'), 1.22 (1H, dd, J=10.7, 4.9 Hz, H-7), 0.98 (1H, td, J=4.9, 1.0 Hz, H-7), 0.95 (3H, s, CH3), 0.92 (3H, s, CH3), 0.12 (9H, s, Si(CH3)3); m/z, 262 (M^+), 247 (M^+-Me), 178, 138, 73; Found: C 73.30, H 10.20%; $C_{16}H_{26}OSi$ requires: C 73.22; H 9.99%.

(2EZ)-9,9-Dimethyl-2-[(trimethylsilyl)methylene]-spiro[4.5]decan-7-one (14) and 3,5,5-trimethyl-3-(4-trimethylsilylbut-3-ynyl)-cyclohexan-1-one (15). Cyclopropyl ketone **(13)** (79 mg, 0.302 mmol) was treated according to the general zinc / TMSCl procedure (Zn / Hg, 30.6 mmol; 2,6-lutidine,1.03 mmol; TMSCl,11.8 mmol; THF, 15 ml). Column chromatography (5-10% ether / petrol, silica) afforded in order of elution, (14) as a colourless oil and as a mixture of E and Z isomers (1 : 1); IR (film) ν_{max} 2951, 1713, 1623, 1294, 1246, 872, 838 cm^{-1}; ^{1}H NMR (500 Mhz, $CDCl_3$) dH (E and Z isomers) 5.36 (1H, m, H-1'), 2.39-2.15 (8H, m), 1.74-1.56 (4H, m) (total 12H, 2 x H-1, 2 x H-3, 2 x H-4, 2 x H-6, 2 x H-8, 2 x H-10), 1.04 (1.5H, s, C-9-CH3), 1.03 (1.5H, s, C-9-CH3), 1.02 (1.5H, s, C-9-CH3), 1.00 (1.5H, s, C-9-CH3), 0.06 (4.5H, s, Si(CH3)3), 0.05 (4.5H, s, Si(CH3)3); ^{13}C NMR (125 MHz, $CDCl_3$) δC (E and Z isomers) 211.85 (s, C-7), 211.55 (s, C-7), 159.95 (s, C-2), 159.87 (s, C-2), 120.70 (d, C-1'), 120.59 (d, C-1'), 54.42 (t), 51.49 (t), 50.49 (t), 50.16 (t), 50.01 (t), 49.85 (t), 47.26 (s), 46.94 (t), 45.84 (s), 40.71 (t), 39.23 (t), 36.41 (s), 34.05 (t), 31.07 (q), 31.00 (q), 30.28 (q), 30.07 (q), 29.61 (t), -0.30 (q, Si(CH3)3), -0.42 (q, Si(CH3)3); m/z, 264 (M^+), 249 (M^+-Me), 207, 193, 134, 73; Observed (M^+): 264.1905; $C_{16}H_{28}OSi$ requires 264.1909.and more polar **(15)** as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δH 2.23-2.18 (4H, m, H-2, H-6, 2 x H-2'), 2.14 (1H, dt, J=13.0, 1.4 Hz, H-2), 2.10 (1H, dt, J=13.0, 1.4 Hz, H-6), 1.64 (1H, ddd, J=13.8, 9.2, 7.0 Hz, H-1'), 1.61 (1H, d, J=14.5 Hz, H4), 1.56 (1H, ddd, J=13.8, 9.3, 6.9 Hz, H-1'), 1.52 (1H, dt, J=14.3, 1.2 Hz, H-4), 1.05 (3H, s, CH3), 1.03 (3H, s, CH3), 1.01 (3H, s, CH3), 0.13 (9H, s, Si(CH3)3); ^{13}C NMR (125 MHz, $CDCl_3$) dC 211.75 (s, C-1), 107.17 (s), 84.61 (s), 54.10 (t), 52.66 (t), 48.82 (t), 43.75 (t), 38.62 (s), 35.96 (s), 32.64 (q), 30.22 (q), 26.69 (q), 14.80 (t), 0.06 (s, Si(CH3)3); m/z, 264 (M^+), 249 (M^+-Me), 179, 83, 75; Observed (M^+): 264.1910; $C_{16}H_{28}OSi$ requires 264.1909.and more polar recovered starting material **(13)** (9%).

(1R*, 6R*)-4,4-Dimethyl-1-(3-carbomethoxyprop-2-ynyl)-bicyclo[4.1.0]heptan-2-one (17). To a solution of oxalyl chloride (0.167 ml, 1.9 mmol) in dichloromethane (10 ml) at -78°C, was added dimethyl sulphoxide (0.274 ml, 3.8 mmol) dropwise. The solution was stirred for 10 minutes and a solution of alcohol **(16)** (380 mg, 1.6 mmol) in dichloromethane (2 ml) was added dropwise. The cloudy solution was stirred for 20 minutes, triethylamine (0.800 ml, 5.78 mmol) was added and the mixture allowed to warm up to room temperature. Water (15 ml) was added and the mixture extracted with dichloromethane (2 x 8 ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (40% ether / petrol, silica) gave (17) (357 mg, 94%) as a colourless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δH 3.71

(3H, s, CO2CH3), 2.94 (1H, d, J=18 Hz, H-1'), 2.64 (1H, d, J=18 Hz, H-1'), 2.10 (1H, d, J=14 Hz, H-3), 1.85-1.94 (2H, m, H-5), 1.77 (1H, m, H-6), 1.56 (1H, d, J=14 Hz, H-3), 1.37 (1H, dd, J=8.8, 5.2 Hz, H-7), 1.03 (1H, t, J=5.2 Hz, H-7), 0.94 (3H, s, CH3), 0.89 (3H, s, CH3); m/z, 234 (M^+), 219 (M^+-Me), 204, 91, 41; Found: C 71.52, H 7.73%; $C_{16}H_{26}OSi$ requires: C 71.77; H 7.74%.

(8-EZ)-8-[(Carbomethoxy)methylene]-4,4-dimethyl-cis-bicyclo[4.3.0]nonan-2-one (18). Cyclopropyl ketone **(17)** (100 mg, 0.42 mmol) was treated according to the general zinc / TMSCl procedure (Zn / Hg, 30.0 mmol; collidine, 0.75 mmol; TMSCl, 25.0 mmol; THF, 10 ml). Column chromatography (10-15% ether / petrol, silica) gave (18) (42 mg, 43%) as a low melting crystalline solid and as a mixture of E / Z isomers (4 : 3, NMR); ^{1}H NMR (500 MHz, $CDCl_3$) δH (full assignment not given) 5.89 (4/7H, m, H-1'), 5.86 (3/7H, m, H-1'), 3.693 and 3.691 (3H, s, CO2CH3 both isomers), 3.16 (4/7H, dd), 2.98 (3/7H, d), 2.85 (4/7H, ddt, J=19.7, 11.0, 2.7 Hz), 2.78-2.58 (4H, m), 2.38 (1H, d, J=15.3 Hz, H-3), 2.33 (3/7H, dd, J=14.5, 0.5 Hz, H-3), 2.04-1.99 (3/7H, m), 1.47 (3/7H, m, H-5), 1.41 (4/7H, ddd, J=13.9, 5.2, 2.0 Hz, H-5), 1.33 (3/7H, dd, J=13.5, 12.5 Hz, H-5), 1.28 (4/7H, dd, J=13.5, 13.1 Hz, H-5), 1.02 (9/7H, s, CH3), 1.01 (12/7H, s, CH3), 0.93 (9/7H, s, CH3), 0.91 (12/7H, s, CH3); ^{13}C NMR (125 MHz, $CDCl_3$) dC 213.46 (s), 213.28 (s), 166.90 (s), 166.81 (s), 164.63 (s), 164.58 (s), 113.73 (d), 113.61 (d), 52.05 (d), 51.03 (q), 50.89 (d), 50.18 (t), 49.91 (t), 42.17 (t), 40.57 (t), 39.80 (t), 39.27 (t), 38.94 (d), 37.89 (d), 36.86 (t), 35.71 (s), 35.53 (s), 34.57 (t), 31.59 (q), 31.55 (q), 25.54 (q), 25.40 (q); m/z, 236 (M^+), 221 (M^+-Me), 204, 151, 119; Found: C 71.01, H 8.70%; $C_{16}H_{26}OSi$ requires: C 71.16; H 8.70%.

(2R, 3R, 5R)-2,3-Dimethyl-5-isopropenyl-cyclohexan-1-one (8) and (2S, 3R, 5R)-2,3-dimethyl-5-isopropenyl-cyclohexan-1-one (9). A solution of cyclopropyl ketone **(7)** (280 mg, 0.439 mmol), tributylstannane (0.850 ml, 3.16 mmol) and AIBN (spatula tip) in benzene (10 ml) were refluxed for 24 hours (adding 3 portions of AIBN at intervals). Carbon tetrachloride (5 ml) was added to the cooled solution, followed by a solution of iodine in ether, until a permanent yellow coloration persisted. A solution of saturated aqueous potassium fluoride (20 ml) was added, and the mixture stirred for several hours. Separation of the organic phase was followed by extraction of the aqueous layer with ether (2 x 25 ml). The combined organics were dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (5-10% ether / petrol, silica) afforded a mixture of **(8)** and **(9)** (37 mg, 13%) as a colourless oil, having identical spectral properties to those given above, and more polar recovered starting material (19 mg, 7%).

(2EZ)-9,9-Dimethyl-2-[(trimethylsilyl)methylene]-spiro[4.5]decan-7-one (14). A solution of cyclopropyl ketone **(13)** (115 mg, 0.439 mmol), tributylstannane (0.240 ml, 0.892 mmol) and AIBN (spatula tip) in benzene (30 ml) were refluxed for 39 hours (adding several portions of AIBN at intervals). Carbon tetrachloride (5 ml) was added to the cooled solution, followed by a solution of iodine in ether, until a permanent yellow coloration persisted. A solution of saturated aqueous potassium fluoride (20 ml) was added, and the mixture stirred for several hours. Separation of the organic phase was followed by extraction of the aqueous layer with ether (2 x 25 ml). The combined organics were dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (5-10% ether / petrol, silica) afforded **(14)** (57 mg, 49%), which had identical spectral properties to those given above, and more polar recovered starting material (12 mg, 10%).

(2R, 3R, 5R)-2,3-Dimethyl-5-isopropenyl-cyclohexan-1-one (8) and (2S, 3R, 5R)-2,3-dimethyl-5-isopropenyl-cyclohexan-1-one (9). To a solution of cyclopropyl ketone **(7)** (270 mg, 1.65 mmol) in tetrahydrofuran (5 ml) at -78°C was added sodium naphthalenide (1.0 M solution in tetrahydrofuran, 2.5 ml, 2.5 mmol) dropwise until a permanent green coloration persisted for 5 minutes. The solution was warmed up to room temperature and sodium naphthalenide (1.0 M solution in tetrahydrofuran, 1.0 ml, 1.0 mmol) added. The solution was stirred for a further 2 hours, quenched with water (30 ml) and extracted with ether (3 x 30 ml). The combined organics were washed with brine (30 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (5-10% ether / petrol, silica) afforded a mixture of **(8)** and **(9)**

(68 mg, 25%) as a colourless oil, having identical spectral properties to those given above, and recovered starting material (129 mg, 48%).

(3R, 5R)-1-(*tert*-Butyldimethylsilyloxy)-2,3-dimethyl-5-isopropenylcyclohex-1-ene (11). To a solution of cyclopropyl ketone (**11**) (85 mg, 0.518 mmol) and *tert*-butyldimethylsilyl chloride (170 mg, 1.126 mmol) in tetrahydrofuran (5 ml) at -78°C, was added sodium naphthalenide (1.0 M solution in tetrahydrofuran, 1.5 ml, 1.5 mmol) dropwise until a permanent green coloration persisted. The solution was warmed up to room temperature and sodium naphthalenide (1.0 M solution in tetrahydrofuran, 0.3 ml, 0.3 mmol) added. The mixture was stirred for a further 1 hour, quenched with aqueous $NaHCO_3$ solution (10 ml) and extracted with ether (3 x 10 ml). The combined organics were washed with brine (10 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (30-40 petrol - 10% ether / petrol, silica) afforded (**11**) (49 mg, 34%), which recorded spectral data identical to that given above, and recovered starting material (44 mg, 52%).

(2EZ)-9,9-Dimethyl-2-[(trimethylsilyl)methylene]-spiro[4.5]decan-7-one (14), 3,5,5-trimethyl-3-(4-trimethylsilylbut-3-ynyl)-cyclohexan-1-one (15) and (1R*, 6R*)-1-(but-3-ynyl)-3,3-dimethyl-bicyclo[4.1.0]heptan-5-one (20). To a solution of cyclopropyl ketone (**13**) (35 mg, 0.134 mmol) in tetrahydrofuran (3 ml) was added sodium naphthalenide (1.0 M solution in tetrahydrofuran, 0.3 ml, 0.3 mmol) dropwise until a permanent green coloration persisted for 5 minutes. The solution was stirred for a further 1 hour, quenched with water (10 ml) and extracted with ether (3 x 10 ml). The combined organics were washed with brine (10 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (5-10% ether / petrol, silica) afforded in order of elution, (14) (9 mg, 26%), (15) (2 mg, 6%), recovered starting material (7 mg, 20%) and (20) (4 mg, 16%) (for data on (20) see below).

Samarium(II) Iodide Reductions - Standard Protocol. To a solution of cyclopropyl ketone (0.5 mmol), in tetrahydrofuran / 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) (9 : 1, 8.0 ml) was added dropwise a solution of samarium (II) iodide (0.1 M) in tetrahydrofuran under a gentle flow of argon, until the purple coloration persisted (addition was accomplished either at the lowest tempoerature of -78°C, 0°C or room temperature, depending on which afforded rapid reaction). After 5 mins, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The solution was extracted with ether (3 x 25 ml), and the combined organics washed with water (20 ml), brine (20 ml) and dried over $MgSO_4$. Removal of the solvent *in vacuo* and column chromatography then afforded pure products.

(2R, 3R, 5R)-2,3-Dimethyl-5-isopropenyl-cyclohexan-1-one (8) and (2S, 3R, 5R)-2,3-dimethyl-5-isopropenyl-cyclohexan-1-one (9). Cyclopropyl ketone (**7**) (97 mg, 0.591 mmol) was reduced according to the standard samarium (II) iodide protocol at -78°C to room temperature. Column chromatography (5% ether / petrol, silica) afforded a mixture of (**8**) and (**9**) (33 mg, 34%) as a colourless oil (2.1 : 1), which recorded spectral data identical to that given above.

3,3,5,5-Tetramethylcyclohexan-1-one (26). Cyclopropyl ketone (**25**) (70mg, 0.461 mmol) was reduced according to the standard samarium (II) iodide protocol at -78°C to room temperature. Column chromatography (15-30% ether / petrol, silica) gave recovered starting material (6 mg, 9%) and less polar 3,3,5,5tetramethylcyclohexan-1-one (24 mg, 34%) as a volatile colourless oil. IR (film) ν_{max} 2953, 1707, 1459, 1424, 1387, 1368, 1345, 1279, 1225 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δH 2.15 (4H, s, 2 x H-2, 2 x H-6), 1.56 (2H, s, 2 x H-4), 1.04 (12H, s, 4 x CH3); 13C NMR (67.5 MHz, $CDCl_3$) δC 212.60 (s, C-1), 54.06 (t, C-2 / 6), 51.71 (t, C-4), 36.25 (s, C-3 / 5), 31.46 (q).

(2EZ)-9,9-Dimethyl-2-[(trimethylsilyl)methylene]-spiro[4.5]decan-7-one (14). Cyclopropyl ketone **(13)** (35 mg, 0.134 mmol) was reduced according to the standard samarium (II) iodide protocol at -78°C to 0°C. Column chromatography (5-10% ether / petrol, silica) gave **(14)** (28 mg, 79%) as a colourless oil, which recorded spectral data identical to that given above.

(1R*, 6R*)-1-(But-3-ynyl)-3,3-dimethyl-bicyclo[4.1.0]heptan-5-one (27). A solution of cyclopropyl ketone **(13)** (360 mg, 1.38 mmol) and sodium hydroxide (320 mg, 8.00 mmol) in methanol (10 ml) was stirred for 15 minutes. The solution was then diluted with ether (100 ml), filtered through a pad of silica and the solvent concentrated *in vacuo*. The resulting mixture was diluted with ether (50 ml), dried over $MgSO_4$ and the solvent concentrated *in vacuo*. Column chromatography (20% ether / petrol, silica) afforded **(27)** (250 mg, 96%) as a colourless oil. IR (film) ν_{max} 3290, 2998, 2953, 2865, 2116, 1687, 1463, 1447, 1383, 1366, 1346, 1306, 1282, 1246, 1225, 1076, 966, 932, 868 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δH 2.26 (2H, td, J=7.6, 2.7 Hz, 2 x H-2'), 2.01 (1H, d, J=14.3 Hz, H-4), 1.94 (1H, t, J=2.7 Hz, H-4'), 1.78 (1H, dd, J=14.4, 1.0 Hz, H4), 1.75-1.56 (2H, m, H-6, H-1'), 1.66 (2H, s, 2 x H-2), 1.44 (1H, dt, J=13.9, 7.8 Hz, H-1'), 1.22 (1H, dd, J=9.9, 4.9 Hz, H-7), 0.99 (1H, td, J=4.9, 0.9 Hz, H-7), 0.94 (3H, s, CH3), 0.91 (3H, s, CH3); m/z, 191 (MH+), 190 (M+), 189(M-H+), 175 (M^+-Me), 147, 138, 134, 133, 106, 105, 91; Observed (M^+-Me): 175.1125; $C_{12}H_{15}O$ requires 175.1123.

9,9-Dimethyl-2-methylenespiro[4.5]decan-7-one (28). Cyclopropyl ketone **(27)** (81 mg, 0.426 mmol) was reduced according to the standard samarium (II) iodide protocol at room temperature. Column chromatography (10-20% ether / petrol, silica) gave **(28)** (47 mg, 57%) as a colourless oil; IR (film) ν_{max} 3068, 2950, 2899, 1707, 1653, 1453, 1424, 1366, 1295, 1276, 1226, 877 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) dH 4.84 (1H, m, H-1'), 4,82 (1H, m, H-1'), 2.34-2.29 (2H, m), 2.26-2.14 (6H, m) [total 8H, 2 x H-1, 2 x H-3, 2 x H-6, 2 x H-8], 1.72 (1H, d, J=14.0 Hz, H-10), 1.68-1.64 (1H, m, H-4), 1.65 (1H, d, J=13.9 Hz, H-10), 1.60 (1H, dt, J=12.6, 9.7 Hz, H-4), 1.02 (3H, s, CH3), 1.00 (3H, s, CH3); 13C NMR (125 MHz, $CDCl_3$) δC 211.77 (s, C-7), 150.51 (s, C-2), 106.73 (t, C-1'), 54.39 (t), 50.35 (t), 49.87 (t), 47.30 (t), 46.70 (s), 40.17 (t), 36.40 (s), 31.05 (q), 30.06 (q), 29.87 (t); m/z, 192 (M^+), 177 (M^+-Me), 174, 159, 150, 134; Observed (M^+): 192.1510; $C_{13}H_{20}O$ requires 192.1514.followed by a mixture of the title compound **(28)** (NMR ratio suggests it comprised 3/4 of the mixture) with an unidentified impurity (total 13 mg); and more polar recovered starting material **(27)** (18 mg, 22%).

3-(3-Butenyl)-5,5-dimethyl-2-cyclohexen-1-one (29).[34] Oven dried magnesium (2.20 g, 90 mmol) was dry stirred under nitrogen for 1 hour and a single crystal of iodine added. A solution of 4-bromobutene (9.0 g, 66.7 mmol) in dry tetrahydrofuran (70 ml) was then cautiously added over a period of 90 minutes while slowly warming the reaction vessel to 30-35°C. After a further period of 1 hour at 30-35°C, a solution of 3-methoxy5,5-dimethyl-2-cyclohexen-1-one (6.90 g, 44.8 mmol) in tetrahydrofuran (15 ml) was added and the reaction mixture stirred for 2 hours. Dilute aqueous HCl (2 M, 80 ml) was then added and the reaction mixture stirred for 1 hour. The solution was carefully quenched with saturated aqueous $NaHCO_3$ until pH 7 was reached and extracted with ether (3 x 200 ml). The combined organic layers were washed with water (200 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (20-25% ether / petrol, silica) afforded **(29)** (4.53 g, 57%) as a colourless oil. IR (film) ν_{max} 2955, 1664, 1625, 1367, 1245, 903 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δH 5.84 (1H, s, H-2), 5.74 (1H, m, H-3'), 5.03-4.93 (2H, m, 2 x H-4'), 2.23 (4H, m, 2 x H-1', 2 x H-2'), 2.16 (2H, s) and 2.13 (2H, d, J=1.1 Hz) [total 4H, 2 x H-4, 2 x H-6], 0.99 (6H, s, 2 x CH3); ^{13}C NMR (100 MHz, $CDCl_3$) δC 199.90 (s, C-1), 162.92 (s, C-3), 136.88 (d, C-2), 124.84 (d, C-3'), 115.56 (t, C-4'), 50.98 (t), 43.86 (t), 37.11 (t), 33.55 (s, C-5), 30.83 (t), 28.23 (q); m/z, 178 (M+), 163 (M+-Me), 149, 122, 94, 79; Observed (M^+): 178.1358; $C_{12}H_{18}O$ requires 178.1358.

3-(3-Butenyl)-5,5-dimethyl-2-cyclohexen-1-ol (30).[34] To enone **(29)** (4.41 g, 24.8 mmol) in toluene (120 ml) at -78°C, was slowly added diisobutylaluminium hydride (1.5 M in toluene, 22.0 ml, 33.0 mmol). The solution was quenched at -78°C with water (2 ml) and allowed to warm up to room temperature.

Ethyl acetate (200 ml) and Na2SO4 (100 g) were added and the mixture stirred for 1 hour. Filtration, removal of solvent *in vacuo* and subsequent column chromatography (30-40% ether / petrol, silica) gave **(30)** (4.38 g, 98%) as a colourless oil. IR (film) ν_{max} 3319, 3074, 2948, 1665, 1637, 1449, 1362, 1025, 910 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δH 5.86-5.71 (1H, m, H-3'), 5.43 (1H, m, H-2), 5.04-4.92 (2H, m, 2 x H-4'), 4.23 (1H, m, H1), 2.21-2.00 (4H, m, 2 x H-1', 2 x H-2'), 1.84 (1H, d, J=17.1 Hz, H-4), 1.76 (1H, dd, J=12.7, 6.4 Hz, H6), 1.63 (1H, d, J=17.1 Hz, H-4), 1.49 (1H, br s, OH), 1.28 (1H, dd, J=12.7, 8.8 Hz, H-6), 0.98 (3H, s, CH3), 0.87 (3H, s, CH3); ^{13}C NMR (125 MHz, $CDCl_3$) δC 138.99 (C-3), 138.23 (C-2), 123.50 (C-3'), 114.56 (C-4'), 66.70 (C-1), 45.29, 42.37, 36.54, 31.68, 31.17, 31.04 (C-5), 26.05; m/z, 180 (M^+), 165 (M^+-Me), 162 (M^+-H2O), 151, 138, 125; Observed (M^+): 180.1518; $C_{12}H_{20}O$ requires 180.1514.

(1R*, 5S*, 6R*)-1-(But-3-enyl)-3,3-dimethyl-bicyclo[4.1.0]heptan-5-ol. Zinc powder (7.80 g, 119 mmol) was added to a stirred solution of silver acetate (200 mg, 1.20 mmol) in acetic acid (100 ml) at 80°C. The mixture was stirred for 2 minutes and the solvent decanted. The zinc-silver couple thus formed was washed with acetic acid (50 ml) and several portions of ether (each 100ml) until no smell of acetic acid remained. Freshly distilled ether (100 ml) was then poured onto the couple. Diiodomethane (3.60 ml, 44.7 mmol) was slowly added to the couple and the mixture gently warmed. A solution of the allyl alcohol **(30)** (3.60 g, 20.0 mmol) in ether (50 ml) was then slowly added and the mixture vigorously stirred at reflux for 1.5 hours. Saturated NH_4Cl solution (30 ml) was then added dropwise very cautiously to quench the reaction mixture. The solution was decanted from the zinc (washed with 100 ml of ether), the organic layer separated and the aqueous phase extracted again with ether (2 x 100 ml). The combined organic layers were washed with water (100 ml) and brine (100 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (25-30% ether / petrol, silica) gave the title compound (2.71 g, 70%) as a colourless oil. ^1H NMR (270 MHz, $CDCl_3$) δH 5.80 (1H, ddt, J=17.0, 10.4, 6.6 Hz, H-3'), 4.98 (1H, dq, J=17.2, 1.7 Hz, H-4'), 4.90 (1H, dm, J=10.2 Hz, H-4'), 4.27 (1H, dt, J=11.0, 6.1 Hz, H-5), 2.10 (2H, m, 2 x H-2'), 1.49-1.16 (5H, m, 2 x H-2, H-4, 2 x H-1'), 1.10 (1H, dt, J=8.8, 5.6 Hz, H-6), 0.85 (3H, s, CH3), 0.84 (3H, s, CH3), 0.72 (1H, dd, J=12.7, 11.5 Hz, H-4), 0.42 (1H, dd, J=8.9, 4.5 Hz, H-7), 0.25 (1H, dd, J=5.1, 4.9 Hz, H-7); m/z, 194 (M^+), 193 ($M-H^+$), 179 (M^+-Me), 176 (M^+-H2O), 161; Observed (M^+): 194.1666; $C_{13}H_{22}O$ requires 194.1671.

(1R*, 6R*)-1-(But-3-enyl)-3,3-dimethyl-bicyclo[4.1.0]heptan-5-one (31). To a stirred solution of 4-methylmorpholine N-oxide (2.34 g, 20.0 mmol) and dried powdered 4Å molecular sieves (10.0 g) in dichloromethane (20 ml) was added to the above cyclopropyl alcohol (2.40 g, 12.4 mmol) in dichloromethane (10 ml), followed by tetrapropylammonium perruthenate (TPAP) (220 mg, 0.626 mmol). After 18 hours, the mixture was filtered through a pad of celite / silica and the solvent removed *in vacuo*. Column chromatography (15% ether / petrol, silica) gave **(31)** (2.03 g, 85%) as a colourless oil. ^1H NMR (270 MHz, $CDCl_3$) δH 5.78 (1H, ddt, J=17.1, 10.3, 6.6 Hz, H-3'), 5.00 (1H, dq, J=17.1, 1.7 Hz, H-4'), 4.94 (1H, d, J=10.3 Hz, H-4'), 2.13 (2H, m, 2 x H-2'), 2.03 (1H, d, J=14.4 Hz, H-4), 1.79 (1H, d, J=14.2 Hz, H-4), 1.67 (2H, s, 2 x H-2), 1.56 (1H, ddd, J=9.5, 5.0, 1.0 Hz, H-6), 1.48 (1H, dt, J=13.7, 7.6 Hz, H-1'), 1.28 (1H, ddd, J=13.7, 9.0, 7.6 Hz, H1'), 1.16 (1H, dd, J=9.8, 4.6 Hz, H-7), 0.99 (1H, dd, J=5.4, 4.6 Hz, H-7), 0.96 (3H, s, CH3), 0.92 (3H,s, CH3); m/z, 192 (M^+), 177 (M^+-Me), 174 (M^+-H2O), 163, 159, 151, 149, 138; Observed (M^+): 192.1510; $C_{13}H_{20}O$ requires 192.1514.

[2R*, 5RS*]-2,9,9-Trimethylspiro[4.5]decan-7-one (32). Cyclopropyl ketone **(31)** (98 mg, 0.551 mmol) was reduced according to the standard samarium (II) iodide protocol at -78°C to 0°C. Column chromatography (10% ether / petrol, silica) gave (32) (36 mg, 36%) as a colourless oil and as a mixture of diastereomers (3 : 2, ^1H NMR). ^1H NMR (500 MHz, $CDCl_3$) (both diastereomers) δH 2.22 (2H, m), 2.14 (2H, s) [total 4H, 2 x H-6, 2 x H-8], 2.03-1.95 (1H, m), 1.82-1.66 (4H, m), 1.62-1.45 (2H, m), 1.24-1.00 (2H, m) [total 9H, 2x H-1, H-2, 2 x H-3, 2 x H-4, 2 x H-10], 0.996 (6/5H, s, CH3), 0.994 (9/5H, s, CH3), 0.986 (9/5H, s, CH3), 0.982 (6/5H, s, CH3), 0.97 (6/5H, dd, J=6.7, 1.0 Hz, C-2-CH3), 0.94 (9/5H, dd,

J=6.6, 1.0 Hz, C-2-CH3); ^{13}C NMR (125 MHz, $CDCl_3$) (both diastereomers) δC 212.39 (s, C-7), 212.29 (s, C-7), 54.54 (t), 54.51 (t), 53.87 (t), 52.57 (t), 51.52 (t), 51.29 (t), 49.79 (t), 49.51 (t), 47.50 (s), 46.85 (s), 41.28 (t), 40.28 (t), 36.72 (s), 34.25 (t), 33.99 (d), 32.88 (t + d), 31.23 (q), 31.00 (q), 30.18 (q), 30.09 (q), 20.96 (q), 20.78 (q); m/z, 194 (M^+), 179 (M^+-Me), 138, 123, 95, 83, 81; Observed (M^+): 194.1668; $C_{13}H_{22}O$ requires 194.1671.

8-[(Carbomethoxy)methylene]-4,4-dimethyl-cis-bicyclo[4.3.0]nonan-2-one (18). To a solution of cyclopropyl ketone **(17)** (22 mg, 0.094 mmol) in tetrahydrofuran / DMPU (9 : 1, 3.0 ml) at room temperature under argon, was added dropwise a solution of samarium(II) iodide (0.1 M in tetrahydrofuran, 2.2 ml), until a heterogeneous mauve coloration persisted. After 5 minutes the reaction mixture was poured into saturated aqueous $NaHCO_3$ solution (10 ml). The solution was extracted with ether (3 x 15 ml), and the combined organics washed with water (10 ml), brine (10 ml), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Column chromatography (10-15% ether / petrol, silica) gave (18) (17 mg, 77%) as a low melting crystalline solid and as a mixture of E / Z isomers (4 : 3, NMR), recording identical spectral properties to those recorded above.

(1R*, 6R*)-4,4-Dimethyl-1-(prop-2-ynyl)-bicyclo[4.1.0]heptan-2-one (34). To a stirred solution of 4-methylmorpholine N-oxide (730 mg, 6.24 mmol) and dried powdered 4Å molecular sieves (5.0 g) in dichloromethane (5 ml) was added alcohol **(33)** (740 mg, 4.16 mmol) in dichloromethane (20 ml), followed by tetrapropylammonium perruthenate (TPAP) (70 mg, 0.200 mmol). After 14 hours the mixture was filtered through a pad of celite / silica and the solvent removed *in vacuo*. Column chromatography (5-10% ether / petrol, silica) gave **(34)** (568 mg, 78%) as a colourless oil. ^1H NMR (500 MHz, $CDCl_3$) δH 2.83 (1H, dd, J=17.5, 2.7 Hz, H-1'), 2.52 (1H, dd, J=17.5, 2.7 Hz, H-1'), 2.11 (1H, d, J=14.1 Hz, H-3), 1.92 (1H, t, J=2.7 Hz, H-3'), 1.91-1.87 (2H, m, 2 x H5), 1.78 (1H, m, H-6), 1.56 (1H, d, J=13.2 Hz, H-3), 1.38 (1H, dd, J=8.7, 5.0 Hz, H-7), 0.97 (1H, dd, J=6.2, 5.0 Hz, H-7), 0.95 (3H, s, CH3), 0.91 (3H, s, CH3); m/z, 176 (M^+), 161 (M^+-Me), 120, 91; Observed (M^+): 176.1198; $C_{12}H_{16}O$ requires 176.1201.

4,4-Dimethyl-8-methylene-cis-bicyclo[4.3.0]nonan-2-one (35). Cyclopropyl ketone **(34)** (55 mg, 0.313 mmol) was reduced according to the standard samarium (II) iodide protocol at -78°C to room temperature. Column chromatography (5% ether / petrol, silica) gave **(35)** (20 mg, 36%) as a colourless oil. ^1H NMR (500 MHz, $CDCl_3$) δH 4.96 (1H, m, H-1'), 4.93 (1H, m, H-1'), 2.71 (1H, tdd, J=10.2, 6.0, 1.2 Hz, H-1), 2.60-2.43 (4H, m, H-6, H-7, 2 x H-9), 2.34 (1H, d, J=14.4 Hz, H-3), 2.18 (1H, dd, J=15.2, 1.3 Hz, H-7), 1.97 (1H, d, J=14.3 Hz, H-3), 1.39 (2H, m, 2 x H-5), 1.01 (3H, s, C-4-CH3), 0.90 (3H, s, C-4-CH3); ^{13}C NMR (67.5 MHz, $CDCl_3$) δC 214.47 (s, C-2), 149.28 (s, C-8), 107.72 (t, C-1'), 52.39 (d, C-1), 50.34 (t), 40.44 (t), 40.07 (t), 38.90 (d, C-6), 35.61 (s, C-4), 34.71 (t, C-5), 31.78 (q, C-4-CH3), 25.62 (q, C-4-CH3); m/z, 178 (M^+), 163 (M^+-Me), 145, Observed (M^+): 178.1358; $C_{12}H_{18}O$ requires 178.1358.

(1S, 4R, (1EZ), 6R)-4-[(2-Ethoxycarbonyl)-isopropenyl]-1-methylbicyclo[4.1.0]heptan-2-one (40). To a stirred solution of pyridinium dichromate (3.2 g, 8.5 mmol) and dried powdered 4Å molecular sieves (8 g) in dichloromethane (10 ml) was added cyclopropyl alcohol **(39)** (1.02 g, 4.29 mmol) in dichloromethane (10 ml). After 18 hours the mixture was diluted with ether and filtered through a celite / silica pad. Removal of the solvent *in vacuo* and subsequent column chromatography (20-30% ether / petrol, silica) gave **(40)** (524 mg, 52%) as a colourless oil and as a mixture of E / Z isomers (17 : 3, NMR). ^1H NMR (270 MHz, $CDCl_3$) δH 5.58 (1H, m, H-2'), 4.11 (1.7H, q, J=7.1 Hz, OCH2CH3, E-isomer), 4.10 (0.3H, q, J=7.1 Hz, OCH2CH3, Z-isomer), 2.57-2.46 (1H, m, H-4), 2.31-2.13 (3H, m, 2 x H-3, H-5), 2.09 (3H, d, J=1.2 Hz, C-1'-CH3), 1.78-1.52 (2H, m, H-5, H-6), 1.25 (2.55H, t, J=7.1 Hz, OCH2CH3, E-isomer), 1.24 (0.45H, t, J=7.1 Hz, OCH2CH3, Z-isomer), 1.19 (3H, s, C1-CH3), 1.10 (1H, dd, J=8.0, 5.0 Hz, H-7),

1.03 (1H, dd, J=5.9, 4.9 Hz, H-7); m/z, 236 (M^+), 207, 191, 163, 121, 96; Observed (M^+): 236.1412; $C_{14}H_{20}O_3$ requires 236.1412.

(1R, 2S, 5R, 6S)-6-[(1-Ethoxycarbonyl)methyl]-2,6-dimethylbicyclo[3.2.1]octan-3-one (41). Cyclopropyl ketone (40) (100 mg, 0.424 mmol) was reduced according to the standard samarium (II) iodide protocol at -78°C to room temperature. Column chromatography (10% ether / petrol, silica) gave **(41)** (30 mg, in 90% purity, the remainding 10% comprising a mixture of the diastereomers) as a colourless oil. ^1H NMR (500 MHz, $CDCl_3$) δH 4.07 (2H, qd, J=7.1, 0.7 Hz, OCH2CH3), 2.58 (1H, dt, J=16.0, 2.8 Hz, H-4), 2.44-2.40 (1H, m, H-2), 2.35 (1H, dd, J=16.0, 3.0 Hz, H-4), 2.32 (1H, d, J=15.2 Hz, H-1'), 2.25 (1H, d, J=15.3 Hz, H-1'), 2.24-2.21 (3H, m, H-1, H-5, H-8), 1.86 (1H, dd, J=10.9, 1.6 Hz, H-8), 1.53 (1H, ddd, J=14.5, 7.2, 1.5 Hz, H-7), 1.40 (1H, dd, J=14.3, 1.5 Hz, H-7), 1.21 (3H, t, J=7.1 Hz, OCH2CH3), 1.07 (3H, s, C-6CH3), 0.96 (3H, d, J=6.7 Hz, C-2-CH3); ^{13}C NMR (125 MHz, $CDCl_3$) δC 213.65 (s, C-3), 172.22 (s, C-2'), 59.96 (t, OCH2CH3), 52.08 (d, C-2), 46.19 (t, C-4), 45.91 (d, C-1 or C-5), 42.88 (t, C-1'), 42.51 (s, C-6), 42.00 (d, C-5 or C-1), 39.66 (t, C-7), 38.19 (t, C-8), 28.50 (q, C-6-CH3), 14.17 (q, OCH2CH3), 12.66 (q, C2-CH3); m/z, 238 (M^+), 223 (M^+-Me), 209 (M^+-Et), 192, 177, 165, 151, 123, 109, 74; Observed (M^+): 238.1570; $C_{14}H_{22}O_3$ requires 238.1570.and later fractions, which contained a complex inseparable mixture (18 mg) of the diastereomers **(1R, 2RS, 5R, 6RS)-6-[(1-ethoxycarbonyl) methyl]-2,6-dimethylbicyclo[3.2.1]octan-3-one** (NMR analysis suggests this mixture comprised 25% of **(41)**), which had similar ^1H NMR, IR and mass spectra to the title compound. The total percentage yield of **(41)** was therefore estimated to be 32%; with 16% of the other diastereomers.

(3R, 5R)-2,3-Dimethyl-1-(trimethylsilyloxy)-5-isopropenylcyclohex-1-ene (10). To a solution of cyclopropyl ketone (7) (86 mg, 0.524 mmol) in tetrahydrofuran / DMPU (9 : 1, 8.0 ml) at room temperature under argon, was added dropwise a solution of samarium(II) iodide (0.1 M in tetrahydrofuran, 8.6 ml), until the mauve colour persisted. The heterogeneous solution was immediately cooled to -78°C and 2,6-lutidine (0.305 ml, 2.62 mmol) and sodium dried (pre-distilled from CaH_2) trimethylsilylchloride (0.350 ml, 2.76 mmol) added. After stirring for 30 minutes at -78°C, the mixture was allowed to warm up to room temperature, stirred for 1 hour and then poured into saturated aqueous $NaHCO_3$ solution (15 ml). The solution was extracted with ether (3 x 25 ml), and the combined organics washed with water (20 ml), brine (20 ml), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Column chromatography (0-10% ether / petrol, silica) gave (10) (43 mg, 35%), which recorded spectral data identical to that given above and more polar recovered starting material (7) (12 mg, 14%).

(3R, 5R)-1-(tert-Butyldimethylsilyloxy)-2,3-dimethyl-5-isopropenylcyclohex-1-ene (11). To a solution of cyclopropyl ketone (7) (86 mg, 0.524 mmol) in tetrahydrofuran / DMPU (9 : 1, 8.0 ml) at room temperature under argon, was added dropwise a solution of samarium(II) iodide (0.1 M in tetrahydrofuran, 8.6 ml), until a mauve colour persisted. The heterogeneous solution was immediately cooled to -78°C and 2,6-lutidine (0.305 ml, 2.62 mmol) and tert-butyldimethylsilyl triflate (0.480 ml, 2.09 mmol) added, which immediately dissipated the purple colour, leaving a colourless solution. After stirring for 20 minutes at -78°C the solution became cloudy and the mixture was allowed to warm up to room temperature. The solution was further stirred for 1 hour and then poured into saturated aqueous $NaHCO_3$ solution (15 ml). The solution was extracted with ether (3 x 25 ml), and the combined organics washed with water (20 ml), brine (20 ml), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Column chromatography (0-5% ether / petrol, silica) gave (11) (30 mg, 20%) as a colourless oil, which recorded spectral data identical to that given above and more polar starting material contaminated with tert-butyldimethylsilyl triflate and tetrahydrofuran derived side-products.

(3R, 5R)-1-(Acetyloxy)-2,3-dimethyl-5-isopropenylcyclohex-1-ene (45). To a solution of cyclopropyl ketone (**7**) (86 mg, 0.524 mmol) in tetrahydrofuran / DMPU (9 : 1, 8.0 ml) at room temperature under argon, was added dropwise a solution of samarium(II) iodide (0.1 M in tetrahydrofuran, 10.5 ml), until a mauve colour persisted. The heterogeneous solution was immediately cooled to -78°C and acetyl chloride (0.400 ml, 5.63 mmol) added. After stirring for 90 minutes at -78°C the mixture was allowed to warm up to room temperature. The solution was further stirred for 45 minutes and then poured into saturated aqueous $NaHCO_3$ solution (15 ml). The solution was extracted with ether (3 x 25 ml), and the combined organics washed with water (20 ml), brine (20 ml), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Column chromatography (2.5-10% ether / petrol, silica) gave (**45**) (36 mg, 33%) as an oil. $[\alpha]_D^{20}$ 103.2° (c=0.99, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δH 4.74 (2H, m, 2 x H-2'), 2.46 (1H, m, H-5), 2.25 (1H, br p, J=6.5 Hz, H-3), 2.16-2.06 (2H, m, 2 x H-6), 2.13 (3H, s, OCOCH3), 1.73 (3H, s, C-2-CH3), 1.69 (1H, td, J=12.6, 5.7 Hz, H-4), 1.56-1.54 (1H, m, H-4), 1.53 (3H, m, C-1'-CH3), 1.09 (3H, d, J=7.1 Hz, C-3-CH3); ^{13}C NMR (125 MHz, $CDCl_3$) δC 169.02 (s, OCOCH3), 148.68 (s, C-1'), 141.37 (s), 124.14 (s), 109.13 (t, C2'), 36.75 (d), 34.65 (t), 33.56 (d), 32.49 (t), 20.82 (q), 20.78 (q), 19.29 (q), 14.32 (q, C-3-CH3); m/z, 208 (M^+), 166, 151, 148, 123, 43; Observed (M^+): 208.1467; $C_{13}H_{20}O_2$ requires 208.1463. and more polar starting material (**7**), contaminated with acetyl chloride and tetrahydrofuran derived side-products

(2S, 3R, 5R)-2-Allyl-2,3-dimethyl-5-isopropenyl-cyclohexan-1-one (46).[35] To a solution of silyl enol ether (10) (286 mg, 1.20 mmol) in tetrahydrofuran (15 ml) at -78°C was added methyl lithium (1.4 M solution in ether, 0.900 ml, 1.26 mmol). The solution was warmed to 0°C and after stirring for 10 minutes, allyl bromide (0.110 ml, 1.27 mmol) was added. After stirring for 1 hour, hexamethylphosphoramide (HMPA) (1.50 ml) was added and the mixture stirred for a further 2.5 hours. The reaction was quenched with water (50 ml) and extracted with ether (3 x 50 ml). The combined organic layers were washed with saturated aqueous $CuSO_4$ solution (4 x 50 ml), water (50 ml) and brine (50 ml), dried over $MgSO_4$ and the solvent removed *in vacuo*. Column chromatography (1-10% ether / petrol, silica) afforded in order of elution; an inseparable and unidentifiable mixture of compounds (57 mg, NMR analysis suggests that the major component of this mixture was probably O-allylated product), followed by (**46**) (96 mg, 39%); ^1H NMR (500 MHz, $CDCl_3$) δH 5.62 (1H, ddt, J=16.7, 10.4, 7.3 Hz, H-2'), 5.07-5.03 (2H, m, 2 x H-3'), 4.79 (1H, m, H-2''), 4.72 (1H, d, J=0.7 Hz, H-2''), 2.58 (1H, tt, J=10.4, 5.0 Hz, H-5), 2.49 (1H, dd, J=14.0, 10.7 Hz, H-6), 2.44-2.38 (2H, m, 2 x H-1'), 2.37 (1H, ddd, J=13.9, 4.8, 1.6 Hz, H-6), 2.08-2.02 (2H, m, H-3, H-4), 1.74 (3H, d, J=0.7 Hz, C-1''-CH3), 1.63 (1H, dtd, J=14.4, 4.5, 1.6 Hz, H-4), 0.99 (3H, s, C-2-CH3), 0.90 (3H, d, J=7.2 Hz, C-3-CH3); ^{13}C NMR (67.5 MHz, $CDCl_3$) dC 214.96 (s, C-1), 147.41 (s, C-1''), 133.47 (d, C-2'), 117.75 (t, C-3'), 110.13 (t, C-2''), 51.68 (s, C-2), 42.79 (t), 41.96 (t), 40.40 (d), 36.71 (d), 32.66 (t, C-4), 20.84 (q), 18.85 (q), 15.90 (q); m/z, 206 (M^+), 191 (M^+-Me), 163, 123, 109, 95, 81, 69, 67; Observed (M^+): 206.1671; $C_{14}H_{22}O$ requires 206.1671.and a mixture of the more polar diastereomers (**8**) and (**9**) (29 mg, 14%) (9 : 5), which recorded spectral data identical to that given above.

(2S, 3R, 5R)-2-Allyl-2,3-dimethyl-5-isopropenyl-cyclohexan-1-one (46). To a solution of cyclopropyl ketone (**7**) (86 mg, 0.524 mmol) in tetrahydrofuran / DMPU (9 : 1, 8.0 ml) at room temperature under argon, was added dropwise a solution of samarium(II) iodide in tetrahydrofuran (0.1 M, 8.2 ml), until a mauve colour persisted. The heterogeneous solution was immediately cooled to -78°C and allyl bromide (0.450 ml, 5.19 mmol) added. After stirring for 30 minutes at -78°C the mixture was allowed to warm up to room temperature. The solution was further stirred for 45 minutes and then poured into saturated aqueous $NaHCO_3$ solution (15 ml). The solution was extracted with ether (3 x 25 ml), and the combined organics washed with aqueous sodium thiosulphate solution (20 ml), water (20 ml), brine (20 ml), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Column chromatography (5-10% ether / petrol, silica) gave a mixture of (**46**) and the two diastereomers (**8**) and (**9**) (total yield 48 mg, NMR ratios indicate 37% of the allylated product (**46**) and 9% of the mixture of (**8**) and (**9**)).

1-Allyl-4,4-dimethyl-8-methylene-cis-bicyclo[4.3.0]nonan-2-one (47) and 4,4-dimethyl-8-methylene-cis-bicyclo[4.3.0]nonan-2-one (35). To a solution of cyclopropyl ketone **(34)** (110 mg, 0.625 mmol) in tetrahydrofuran / DMPU (9 : 1, 9.0 ml) at room temperature under argon, was added dropwise a solution of samarium (II) iodide (0.1 M in tetrahydrofuran, 14.6 ml), until a mauve colour persisted. The heterogeneous solution was immediately cooled to -78°C and allyl bromide (0.540 ml, 6.24 mmol) added. After stirring for 30 minutes at -78°C, the mixture was allowed to warm up to room temperature, stirred for 1 hour and then poured into saturated aqueous $NaHCO_3$ solution (15 ml). The solution was extracted with ether (3 x 25 ml), and the combined organics washed with water (20 ml), brine (20 ml), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Column chromatography (5% ether / petrol, silica) gave less polar **(47)** (23 mg, 17%) as a colourless oil. ^1H NMR (500 MHz, $CDCl_3$) δH 5.73 (1H, dddd, J=17.1, 10.2, 9.3, 5.3 Hz, H-2'), 5.04-4.96 (4H, m, 2 x H-3', 2 x H-1''), 2.70 (1H, ddt, J=13.7, 5.3, 1.5 Hz, H-1'), 2.69-2.63 (2H, m, H-7, H-9), 2.43 (1H, dt, J=11.8, 6.2 Hz, H-6), 2.36 (1H, dd, J=14.8, 0.7 Hz, H-3), 2.12 (2H, dm, J=16.2 Hz, H-7, H-9), 2.04 (1H, dd, J=14.7, 2.5 Hz, H-3), 1.91 (1H, dd, J=13.8,9.3 Hz, H-1'),1.46 (2H, m, 2 x H-5), 0.98 (3H, s, C-3-CH3), 0.84 (3H, s, C-3-CH3); ^{13}C NMR (67.5 MHz, $CDCl_3$) δC 213.92 (s, C-2), 148.71 (s, C-8), 135.16 (d, C-2'), 117.62 (t), 108.53 (t), 56.81 (s, C-1), 50.77 (t), 42.46 (t), 40.39 (d, C-6),38.52 (t), 38.02 (t), 34.91 (s, C-4), 31.71 (q, C-3-CH3), 25.42 (q, C-3-CH3); m/z, 218 (M^+), 203 (M^+-Me), 193, 185, 177 (M^+-C3H5), 121; Observed (M^+): 218.1664; $C_{15}H_{22}O$ requires 218.1671; and more polar **(35)** (34 mg, 31%), which recorded identical spectral data to that given above.

7-(Acetyloxy)-9,9-dimethyl-2-methylene-spiro[4.5]dec-6-ene (48). To a solution of cyclopropyl ketone **(20)** (91 mg, 0.479 mmol) in tetrahydrofuran / DMPU (9 : 1, 8.0 ml) at 0°C under argon, was added dropwise a solution of samarium(II) iodide (0.1 M in tetrahydrofuran, 11.5 ml), until a mauve colour persisted. The heterogeneous solution was immediately cooled to -78°C and acetyl chloride (0.350 ml, 4.92 mmol) added. After stirring for 30 minutes at -78°C the mixture was allowed to warm up to room temperature. The solution was further stirred for 50 minutes and then poured into saturated aqueous $NaHCO_3$ solution (15 ml). The solution was extracted with ether (3 x 25 ml), and the combined organics washed with water (20 ml), brine (20 ml), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Column chromatography (2.5-5% ether / petrol, silica) gave (48) (64 mg, 57%); ^1H NMR (270 MHz, $CDCl_3$) δH 5.25 (1H, m, H-6), 4.87-4.82 (2H, m, 2 x H-1'), 2.39-2.33 (2H, m, 2 x H-3'), 2.29 (2H, s, 2 x H-1),2.09 (3H, s, COCH3), 2.01 (1H, dd, J=16.5, 1.6 Hz, H-8), 1.90 (1H, dd, J=16.5, 0.9 Hz, H-8), 1.72-1.60 (2H, m, 2 x H-4), 1.42 (2H, s, 2 x H-10), 1.01 (6H, s, 2 x CH3); ^{13}C NMR (67.5 MHz, $CDCl_3$) δC169.46 (s, OCOCH3), 151.55 (s), 146.44 (s), 119.81 (d, C-6), 106.16 (t, C-1'), 48.12 (t), 47.40 (t), 43.44 (s, C-5), 40.96 (t), 40.75 (t),31.85 (s, C-9),30.25 (t), 29.97 (q), 29.00 (q), 21.16 (q, OCOCH3); m/z, 234 (M^+), 192, 177, 121; Observed (M^+): 234.1624; $C_{15}H_{22}O_2$ requires 234.1620.

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