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Development of Modified Pauson-Khand Reactions with Ethylene and Utilisation in the Total Synthesis of (+)-Taylorione†

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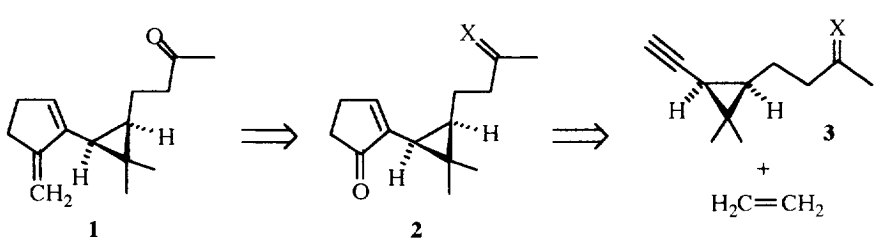
Abstract: Two complementary Pauson-Khand annulation protocols for use with the gaseous alkene, ethylene, are described. These *N*-oxide promoted reactions (10 examples) are shown to proceed under both mild autoclave conditions or, more conveniently, at atmospheric pressure. The developed methodology has been utilised as the key transformation in the total synthesis of the sesquiterpene (+)-taylorione which has been realised in a good overall yield from readily available (+)-2-carene.

INTRODUCTION

The Pauson-Khand annulation reaction,[4] for the formation of cyclopentenones from alkenes and alkynehexacarbonyldicobalt complexes, has been finding increasing use as the key transformation in the synthesis of natural products and other cyclic compounds possessing an array of functionality and skeletal frameworks.[4,5] In this context, we envisaged that this cobalt-mediated process could be employed strategically in the total synthesis of (+)-taylorione **1**, the enantiomer of the principal sesquiterpene isolated from the common leafy liverwort *Mylia taylorii*[6] (found on acidic rocks in upland areas throughout the northern hemisphere). The structure and absolute configuration of natural taylorione were determined by a combination of spectroscopic and degradation studies[7] and were, subsequently, confirmed by an inauspiciously low yielding and multistep synthesis.[8] More recently, a total synthesis of racemic taylorione has also appeared in which the latter steps are remarkably similar to those of the previously reported strategy.[9]



1 **2**

Scheme 1

Retrosynthetic analysis of (+)-taylorione **1**, with placement of some suitable protecting group on the more reactive carbonyl, leads to the 2-substituted cyclopentenone **2**, an attractive target for Pauson-Khand

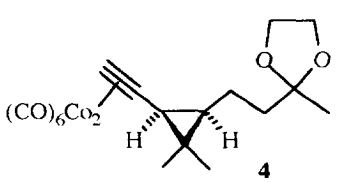
methodology (Scheme 1). Utilisation of this protocol would generate the requirement for the $Co_2(CO)_6$ complex of alkyne **3** to undergo cyclisation with ethylene gas. However, until now, when gaseous or volatile alkenes are employed in the Pauson-Khand reaction conditions of elevated temperature and pressure are required to drive this process to completion. Furthermore, the yields of the cyclopentenone products are, more commonly, only moderate.[4,10]

Faced with the general inadequacies of the known techniques and the synthetic challenge posed by using Pauson-Khand methodology towards the target structure **1**, we endeavoured to create an overall more efficient annulation protocol with the gaseous olefin ethylene. We now report, in full, our systematically optimised reaction conditions which have markedly improved annulations of this class and, in turn, show how these modified Pauson-Khand procedures have been utilised in our concise route towards the total synthesis of (+)-taylorione.[11]

RESULTS AND DISCUSSION

Initial Transformations Towards the Preparation of (+)-Taylorione: Synthesis of the (1S,3R)-Alkynehexacarbonyldicobalt Complex 4

The starting material for the synthesis of the alkyne complex **4** is (+)-2-carene **5**. This inexpensive material is readily available in an enantiopure form and provides the requisite absolute stereochemical configuration around the cyclopropyl ring for use in this total synthesis programme.



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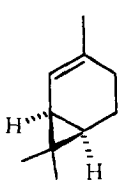
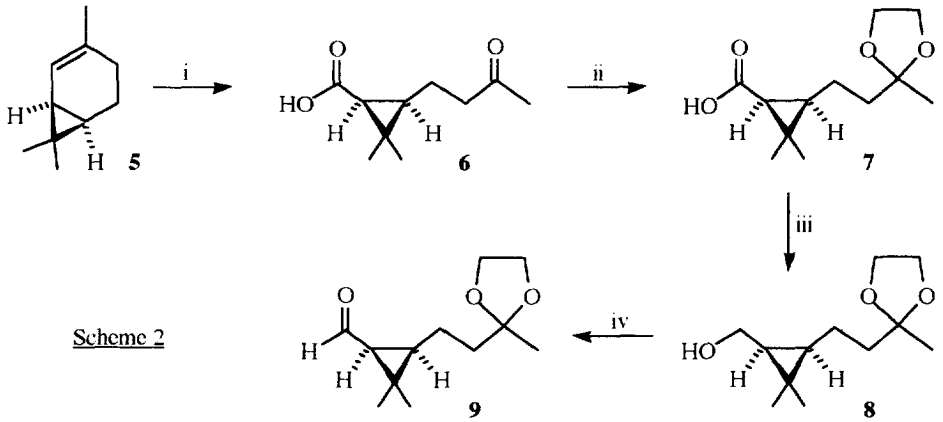


5

Using a slight modification of the known procedure,[12] ozonolysis, followed by an oxidative work up, provided the keto acid **6** (Scheme 2). This compound could be obtained in an isolated and purified yield of 60%. Such a low yield was attributed to the poor miscibility of (+)-2-carene with methanol. In turn, yields were improved by vigorously stirring the reaction mixture at room temperature for approximately 30 minutes to attain homogeneity, before cooling and commencement of ozonolysis. Using this procedure, followed by oxidation of the ozonide with basified hydrogen peroxide, led to the isolation of the crude acidic product **6** in 80% yield. This material can be used in the next synthetic step without purification.

The ketone moiety was then protected as the 1,3-dioxolane by acid-catalysed condensation with ethylene glycol under Dean and Stark conditions. This interconversion proceeded in consistently high yields (90-100%) on all occasions in either refluxing benzene or chloroform. Since the ketal product **7** proved to be unstable to storage (even at 0 °C under N_2) the ketalisation reaction had to immediately precede any further manipulations. Consequently, the carboxylic acid **7** was readily converted to the corresponding alcohol **8** by reduction with $LiAlH_4$ in THF (90%, 24h) followed by oxidation with PDC to the aldehyde **9**. The $LiAlH_4$ reduction was found to proceed more rapidly in ether but at the expense of the chemical yield (80%, 3h).



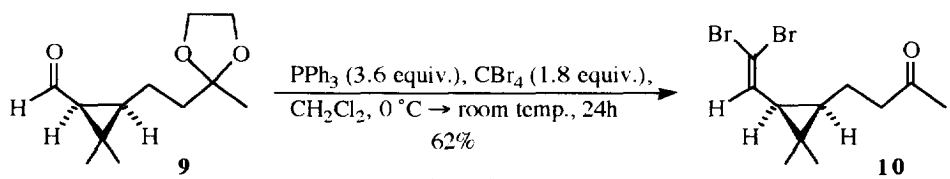
Scheme 2

Reagents and conditions: i, O_3, MeOH, -65 °C → room temp. then H_2O_2, NaOH, reflux (60%); ii, ethylene glycol, C_6H_6, *p*-TSA, reflux (96%); iii, $LiAlH_4$, THF, room temp. (90%); iv, PDC, CH_2Cl_2, 0 °C → room temp. (73%).

The subsequent partial oxidation using PDC in dichloromethane gave good yields of the aldehyde **9** on condition that the reaction was carried out immediately after the preparation of the starting material. Indeed, any delay in carrying out the transformations from keto acid **6** to aldehyde **9** causes substantial depletion of material and yield due to decomposition. Thus, aldehyde **9** was obtained in 73% yield from alcohol **8**.

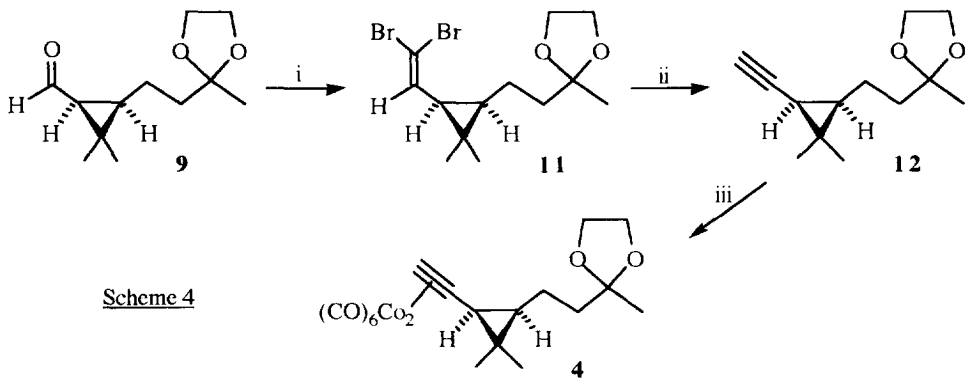
At this stage it is also worth noting that literature based procedures employing both Dibal-H[13] and *t*-hexylchloroborane dimethylsulfide complex[14] were adopted in attempts to bring about the conversion of carboxylic acid **7** to the aldehyde **9** in a single process. Unfortunately, we failed to utilise either technique to our advantage and, with this particular compound **7**, could not successfully carry out this one step transformation. Nonetheless, with efficient access to aldehyde **9**, as already described, attention was directed towards synthesis of the requisite alkyne complex **4**.

The method of choice for conversion of the aldehydic carbonyl group to the carbon-carbon triple bond of the alkyne was *via* the corresponding dibromo olefin. Since each of the standard Corey-Fuchs protocols[15] failed to give any reaction with aldehyde **9**, a modified procedure was adopted.[16] Rather unexpectedly, the initial reactions led to mixtures of products where loss of the ketal protection had at least partially occurred. On prolonged reaction, with 3.6 equivalents of PPh_3 and 1.8 equivalents of CBr_4, the product of dibromoolefination *and* deprotection, ketodibromo alkene **10**, was formed exclusively (Scheme 3).[17]



Scheme 3

In an attempt to avoid ketone generation, reactions were carefully monitored. This revealed that on addition of the first equivalent of CBr_4 to a mixture of aldehyde **9** and PPh_3, the aldehyde was almost completely consumed, with only traces of the deprotected material being formed. Subsequent addition of the second equivalent of CBr_4 and continued stirring caused deprotection to increase and, ultimately, take over as the predominant product forming process. Consequently, addition of CBr_4 (in dichloromethane), with careful chromatographic supervision, and a shorter reaction time allowed the clean transformation of aldehyde **9** to the desired dibromo olefin **11** in 84% yield (Scheme 4).[18]



Scheme 4

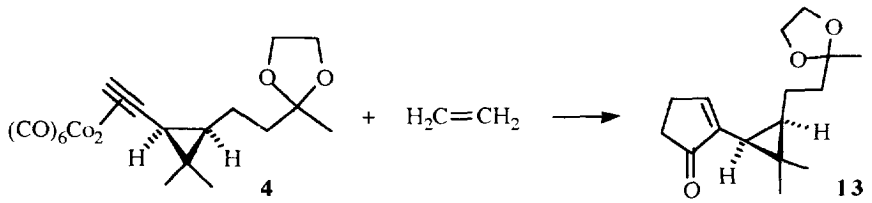
Reagents and conditions: i, PPh_3 (3.6 equiv.), CBr_4 (1.7 equiv.), CH_2Cl_2, 0 °C → room temp., 80min (84%); ii, *n*-BuLi (2 equiv.), THF, -78 °C (100%); iii, $Co_2(CO)_8$, pet. ether, room temp. (100%).

The next two reactions in our synthetic sequence proceeded without complication. The dihalo alkene **11** was converted cleanly and rapidly to the terminal alkyne **12** by treatment with 2 equivalents of *n*-BuLi followed by aqueous work up. Subsequent reaction of this alkyne with octacarbonyldicobalt at room temperature gave the dicobalt complex **4** as a deep red oil in quantitative yield. Therefore, the synthesis of the desired alkyne complex can be achieved in 7 steps from (+)-2-carene **5** with an overall yield of 42%.

Development of Mild and Efficient Pauson-Khand Reactions with Ethylene

As mentioned in the Introduction section, Pauson-Khand reactions involving gaseous olefins are considered to be somewhat less than efficient processes. More specifically, ethylene reacts readily with hexacarbonyldicobalt complexes of terminal alkynes but forcing conditions (80-160 °C, 50-120atm. initial ethylene pressure; autoclave) are required for optimum yields, typically in the 30-60% range.[4] Internal alkynes have also been employed in the Pauson-Khand reaction, under similar conditions with ethylene, showing limited success and often displaying incomplete regioselectivity in alkyne incorporation.[19]

When the alkyne complex **4** was subjected to routine literature conditions for this type of cyclisation (C_2H_4, 50atm, 80 °C, benzene) the desired cyclopentenone **13** was obtained in a, not unsurprisingly, modest yield of 38%. Despite having a facile route into compound **13**, the yield under the conditions described was unattractive, especially in terms of this total synthesis programme. At this stage we, therefore, aimed to modify our reaction techniques to both improve the yield of the transformation in hand and, in addition, establish a generally more successful method for conducting Pauson-Khand cyclisations with ethylene.



It is generally known that amine *N*-oxides mildly decarbonylate metal carbonyl species by oxidation of CO ligands to CO_2.[20,21] Furthermore, amine *N*-oxides, as additives in the Pauson-Khand reaction, have been shown to readily promote annulations in a wide range of examples both in our laboratory[22] and elsewhere.[23] In turn, when trimethylamine *N*-oxide dihydrate (TMANO.$2H_2O$) was applied to reactions between complex **4** and ethylene consistently improved annulations were achieved, but only following the establishment of systematically optimised conditions.

Study of autoclave reaction conditions for the cyclisation of the hexacarbonyldicobalt complex **4** with ethylene (benzene or toluene as solvent) in the presence of 9 equivalents of TMANO.$2H_2O$ (introduced to reactions as a methanol solution) revealed the optimum temperature for annulations to be 40 °C. Next, maintaining 40 °C as a constant temperature, the effect of pressure was investigated. It was found that the yields of the cyclopentenone **13** steadily increased with pressure of ethylene until 25-30 atmospheres was reached. Then, remarkably, the yield of cyclopentenone began to fall again as pressures approached 50 atmospheres. This finding contradicted more classical Pauson-Khand reaction patterns, where higher ethylene pressure was found to favour cyclopentenone formation.[4,10] Most surprising was the fact that the depletion in yield at 50 atmospheres, in our system, was so great that yields around or below those afforded under the classical conditions were obtained.

Under the *N*-oxide conditions employed it is envisaged that the additive is initially mildly oxidising a CO ligand to eliminate CO_2 from the starting complex. The vacant ligand site created on the Co atom is now available for complexation with the alkene, ethylene. However, it is also possible that the *N*-oxide by-product, trimethylamine, is contributing a further beneficial rôle in the reaction process; that of a donor ligand, which stabilises the intermediate unsaturated cobalt species. With this in mind, it is tempting to postulate that the higher ethylene pressures are affecting the stabilising influence imparted by the amine by-product, in turn, leading to the observed depleted yields of cyclopentenone.

In addition to the conditions already described, the concentrations of both the complex in toluene or benzene and the *N*-oxide promoter in methanol are also crucial to the success of this technique, since the initially optimised conditions gave erratic reaction rates and yields. The source of this irreproducibility was found to be due to the re-precipitation of TMANO.$2H_2O$ when added (in methanol) to the complex in hydrocarbon solvent. Therefore, the concentrations of both reagent/solvent mixtures were adjusted to allow the *N*-oxide to remain in solution throughout the entire reaction.

A further practical modification (detailed in the Experimental section) which avoided contact between the oxidant and complex until after the autoclave vessel was sealed under ethylene gas was also employed. This reduced the extent of complex decomposition prior to the introduction of ethylene. With these practical

amendments in place, the Pauson-Khand reaction between complex **4** and ethylene to give cyclopentenone **13** proceeded more rapidly in a much improved 81% yield and with excellent reproducibility.

A further discovery that has emerged from our study is that the desired cyclopentenone **13** can be formed in moderate yield even at *atmospheric pressure and room temperature* using the *N*-oxide promoted conditions developed here. Simply bubbling ethylene gas through the reaction mixture allowed cyclisation with complex **4** to occur, giving **13** in a more modest yet acceptable yield of 41%.

Since this is, to our knowledge, the first time a Pauson-Khand reaction has been successfully carried out under such mild conditions (especially at atmospheric pressure and ambient temperature) we decided to investigate the generality of these findings. Table 1 summarises our results obtained in this study along with the optimum yields (and conditions used) for each substrate as previously cited. At the outset, alkyne **14** was subjected to a systematic study similar to that undertaken with the complex of alkyne **12**. Gratifyingly, low ethylene pressures (25-30atm.) at 40 °C again provided the optimum reaction conditions. Furthermore, the same general conditions (as those developed for **4**) also provided the method of choice for cyclisation of the same alkyne complex at atmospheric pressure.

Overall, we have found that in the majority of cases under the mild autoclave techniques (Table 1, entries 1-3, 5-6, 8 & 10) significant enhancement in the yield of cyclopentenone, when compared to classical conditions, can be realised through application of our optimised conditions. Moreover, *n*-Bu_3PO has previously been used as a Pauson-Khand reaction promoter[10] (under much more vigorous conditions than those developed here); when the yields from reactions with each promoter are compared (Table 1, entries 3&4) it can be seen that we have again obtained enhanced yields . On the other hand, we acknowledge that, despite one case showing improved yields over the previously reported example, internal alkynes still give lower than desired quantities of cyclopentenones.

It is generally recognised that alkyne incorporation in the intermolecular Pauson-Khand reaction is usually completely regioselective giving the cyclopentenone product with the more bulky alkyne substituent at the 2-position.[4] However, it has been reported that in reactions between ethylene and internal alkynes product mixtures result, of which approximately 10% comprises the unexpected regioisomer, with the more bulky substituent in position 3.[19] Entries 6 and 7 (Table 1) indicate that, unlike previous reports, we have detected no presence of the minor regioisomer. It would, therefore, appear that our milder cyclisation conditions have also provided greater selectivity in alkyne incorporation reactions of this type.

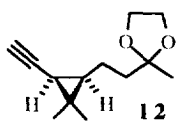
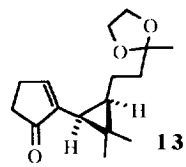
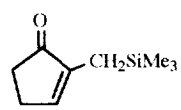
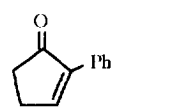
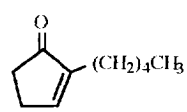
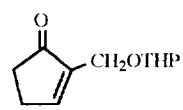
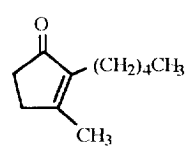
The atmospheric pressure technique of simply bubbling ethylene gas through the reaction mixture has also led to a range of satisfactory results. This protocol dispenses with the requirement for specialised autoclave equipment and enables more careful monitoring of reaction progress. Furthermore, the introduction of the amine *N*-oxide in solution can be performed over an extended period of time and, indeed, addition *via* syringe pump has led to a minor yield enhancement (Table 1, entry 3).

In general, at atmospheric pressure and room temperature, we have found that yields are comparable to those obtained by more classical thermal methods and often with shorter reaction times. Again, internal alkynes were incorporated with complete regioselectivity. Surprisingly, this milder cyclisation method afforded higher yields of enones with the complexes of THP-propargyl alcohol **17** and the MEM ether **20** than those obtained from the, generally more favourable, promoted autoclave reaction. Additionally, in the

cases of the complexes of the propargyl sulphide **21** and selenide **22** the yields from the two alternative *N*-oxide techniques were comparable.

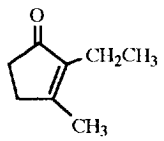
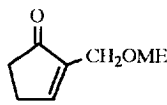
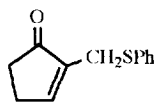
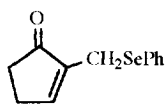
Finally, the possibility of performing the reaction under a static atmosphere of ethylene, introduced *via* balloon, rather than wastefully bubbling ethylene through the reaction mixture, was investigated with substrate **17**; a negligible decrease in yield was observed. The strategies of using slower *N*-oxide addition and static ethylene atmospheres was also utilised with alkyne **20** whilst the former method was used in the case of alkyne **22** and the latter technique with alkyne **21**.

Table 1: *N*-Oxide Promoted Pauson-Khand Reactions with Ethylene.

Entry	Alkyne	Product	Autoclave Yields	Atmospheric Pressure Yields	Optimum Thermal Conditions
1	 **12**	 **13**	81%	41%	80-90 °C, 50atm., 5h, 38%[a]
2	$HC{\equiv}CCH_2SiMe_3$ **14**		49%	38%	90 °C, 60atm., 36h, 29%[24]
3	$HC{\equiv}CPh$ **15**		71%	46% 55%[b]	110 °C, 50atm., *n*-Bu_3PO, 36h, 45%[10]
4	$HC{\equiv}C(CH_2)_4CH_3$ **16**		73%	58%	110 °C, 50atm., *n*-Bu_3PO, 36h, 70%[10]
5	$HC{\equiv}CCH_2OTHP$ **17**		22%[c]	33% 30%[d]	130 °C, 45atm., 6h, 0%[e]
6	$CH_3C{\equiv}C(CH_2)_4CH_3$ **18**		40%	23%	110 °C, 60atm., 36h, 22% (2%)[f,19]

(continued over)

Table 1: *N*-Oxide Promoted Pauson-Khand Reactions with Ethylene (cont.).

7	$CH_3C{\equiv}CCH_2CH_3$ **19**		28%	11%	110 °C, 35atm., 36h, 24% (3%)[f,19]
8	$HC{\equiv}CCH_2OMEM$ **20**		14%	29%[b,d]	80 °C, 55atm., 24h, 0%[a]
9	$HC{\equiv}CCH_2SPh$ **21**		23%	21%[d]	---[g]
10	$HC{\equiv}CCH_2SePh$ **22**		14%	13%[b]	90 °C, 50atm., 24h, 0%[a]

a: Work carried out during this programme. b: $TMANO.2H_2O$ added slowly *via* syringe pump. c: A number of alternative products were also formed in this reaction in trace amounts. d: Ethylene balloon used. e: A multicomponent product mixture resulted from which no cyclopentenone was isolated.[25] f: Yield of minor regioisomer in parenthesis. g: Reactions under the more classical conditions were not attempted, however, a yield of 7% was achieved at room temperature with no *N*-oxide additive.

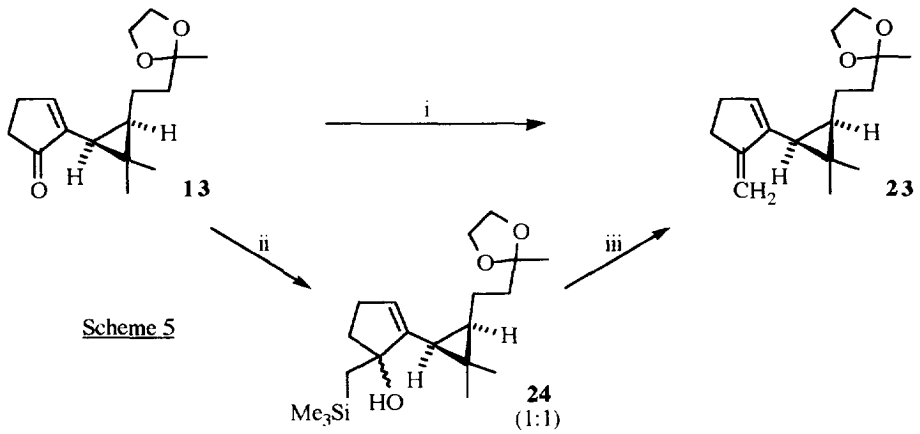
The development of this mild, convenient and higher yielding Pauson-Khand cyclisation technique using $TMANO.2H_2O$ not only provides economical access to cyclopentenone **13** but establishes two general and efficient protocols whereby alkynehexacarbonyldicobalt complexes can be cyclised with ethylene either under gentle autoclave conditions or, alternatively, at atmospheric pressure.

(+)-Taylorione; The Total Synthesis

On completion of the full investigation into the factors affecting the Pauson-Khand reaction under $TMANO.2H_2O$ promoted conditions with ethylene gas, and having subsequently achieved excellent yields of cyclopentenone **13** in a reproducible fashion, attention was turned towards the final steps in the synthetic sequence towards (+)-taylorione **1**.

A series of carbonyl methylenation studies on enone **13** found that modified Peterson olefination in the presence of $CeCl_3$[26] was the most successful method of obtaining the desired diene **23** (Scheme 5). Accordingly, cyclopentenone **13**, was reacted with dry cerium(III) chloride and trimethylsilyllithium then adsorbed onto silica. Prolonged exposure to this acidic medium gave the diene **23** in an isolated yield of 58%. In addition to this one-step technique, the intermediate β-hydroxysilanes **24** could also be isolated (as a 1:1 mixture of diastereomers) following purification on neutral alumina. Subsequently, 40% aqueous HF

(**CAUTION!**) was found to provide the optimum conditions for elimination to the single enantiomer of the diene **23**, giving a yield of 70% over the two steps.

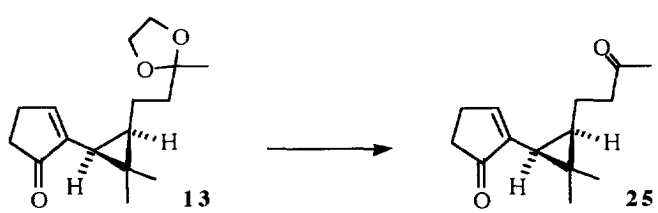


Scheme 5

Reagents and Conditions: i, $CeCl_3$, Me_3SiCH_2Li, THF, -78 °C → room temp. then SiO_2 (58%); ii, $CeCl_3$, Me_3SiCH_2Li, THF, -78 °C → room temp. then neutral Al_2O_3 purification (86%); iii, 40% aqueous HF, CH_3CN, room temp. (82%).

At this juncture it was envisaged that simple ketal hydrolysis would yield (+)-taylorione **1**. To our disappointment, and despite intense synthetic efforts, all attempts to successfully effect this seemingly simple transformation were frustrated. Following almost exhaustive application of the known techniques for ketal cleavage[27] to diene **23** (and, in a number of cases, the hydroxy silane **24**), including many especially mild methods,[28] synthesis of (+)-taylorione **1** was not realised. Indeed, in the majority of attempts, the integrity of the desired carbon skeleton was compromised (the cyclopropyl and olefinic regions suffering disruption), with, in some cases, the ketal moiety remaining intact.

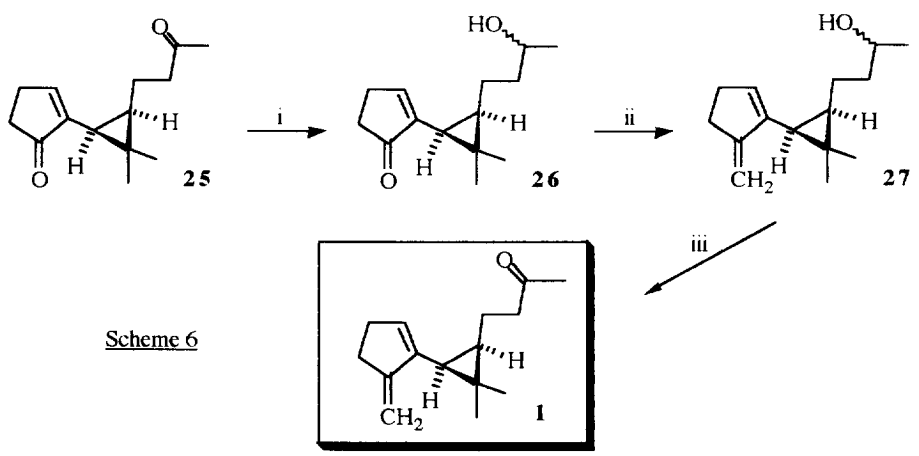
To circumvent this problem, whilst retaining the largely successful strategy used up to this point, attempts were made to remove the ketal group in compound **13**. This was achieved, with varying degrees of success, by the three methods attempted. Firstly, using the $TiCl_4$ technique of Balme and Goré at 0 °C,[28k] the diketone **25** was isolated in 79% yield. Since this procedure required stringently anhydrous conditions, the experimentally less demanding standard aqueous acidic hydrolysis method was also applied.[27] When *p*-TsOH was used with acetone, methanol and water the dione **25** was again obtained. However, in this case a reduced yield of 66% was achieved and more prominent by-product formation was apparent. The third



deprotection attempt took advantage of our developed mild and anhydrous CBr_4/PPh_3 technique for ketal cleavage.[17] Gratifyingly, when cyclopentenone **13** was treated with triphenylphosphine and carbon tetrabromide in CH_2Cl_2, from 0 °C to room temperature, the desired diketone **25** was isolated in an excellent 92% yield with negligible decomposition of the original carbon framework.

From **25** the final steps in the synthesis were then performed without complication (Scheme 6). Selective carbonyl reduction to give the hydroxy ketones **26** (89%) was achieved by application of the excellent Ward conditions[29] using $NaBH_4$ in CH_2Cl_2 with acetic acid and methanol. Modified Peterson methylenation was carried out in a similar fashion to the one-step process described for the conversion of **13** to **23**. In this instance the diene **27** was isolated in a somewhat lower yield of 47%. However, it should be noted that equivalent depression in yields have been observed for this type of transformation, in the presence of a free hydroxyl group, in similar substrates.[8,30] Finally, application of the mild, catalytic Griffith-Ley tetrapropylammonium perruthenate (TPAP) agent[31] provided optimum oxidation and gave the target molecule **1** in an excellent 91% yield. (+)-Taylorione **1** obtained by this route possessed spectroscopic data identical to those of the natural product and displayed high optical purity.

Thus, the synthesis of enantiopure (+)-taylorione **1** from the readily available chiral pool reagent, (+)-2-carene **5**, has been achieved in a concise fashion and a good overall yield of 12% through 12 synthetic transformations.



Scheme 6

Reagents and Conditions: i, $NaBH_4$, AcOH, CH_2Cl_2 and 5% MeOH, room temp. (89%); ii, $CeCl_3$, Me_3SiCH_2Li, THF, -78 °C then SiO_2 (47%); iii, TPAP, *N*-methylmorpholine *N*-oxide, crushed molecular sieves, CH_2Cl_2 (91%).

CONCLUSIONS

Following the studies presented here a milder and much more practically convenient set of complementary protocols for Pauson-Khand reactions with ethylene have been established. In most cases, the mild autoclave techniques provide the optimum yields of cyclised products. On the other hand, the atmospheric pressure reactions allow a more simple reaction set up to be adopted without the need for

autoclave facilities. Overall, yields of cyclopentenones are good when simple terminal aryl or alkyl substituted alkynes are employed. However, it should be noted that lower yields are achieved when internal alkynes or substrates bearing a propargylic heteroatom are utilised. Nonetheless, yields of cyclised products in all of theses examples represent improvements, in most cases significant, over those gained previously under the more classical thermal reaction conditions.

When the developed Pauson-Khand techniques were applied as the key transformation in routes towards (+)-taylorione **1**, the synthesis of this sesquiterpene was realised in an economical fashion from readily accessible starting materials.

EXPERIMENTAL

General information

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. THF and ether (Et_2O) was distilled from Na/benzophenone and methylene chloride (CH_2Cl_2) distilled from calcium hydride. Toluene was distilled from sodium metal and petrol (*i.e.* petroleum ether, Bp 40-60 °C), chloroform, hexane, acetone, cyclohexane were distilled prior to use. Tlc was performed using Camlab 5x20cm plastic sheets (which were cut to required size) precoated with 0.25mm silica gel containing fluorescent indicator UV_{254}. Chromatographic purification was carried out on silica gel, MN-Kieselgel 60 (0.04-0.063mm, 230-400 mesh) by flash techniques, or ungraded alumina, neutralised with ethyl acetate, washed with ethanol and water and oven dried at 150 °C. All cobalt complexes were stored under nitrogen at or below -20 °C. Proton and ^{13}C nmr were obtained at 250MHz and 62.9MHz respectively on a 250MHz Bruker WM 250. Infrared spectra were run on a Unicam Mattson 1000 series FTIR spectrometer. High resolution mass spectra were recorded on an AEI MS 9 double focusing spectrometer using an Elliot 905 computer based system, or a JEOL Instruments JMS-AX505HA Mass Spectrometer system; relative peak intensities are indicated in parenthesis. Elemental analysis was carried out on a Carlo Erba 1106 CHN analyser. Gas chromatography was performed using a Perkin Elmer F33 gas chromatograph fitted with a 2.5 metre column containing 2.5% silicon gum rubber E301 on Chromosorb G (80-100 mesh); detection was by flame ionisation and the chromatogram was produced with a SpectraPhysics Data Jet Integrator. Melting points were determined on an Gallenkamp electrothermal melting point apparatus in open capillaries and are uncorrected. Optical rotations were carried out at room temperature using a Perkin Elmer 241 Polarimeter with solution concentrations given in grammes per 100ml.

(1*S*,3*R*)-*cis*-2,2-Dimethyl-3-(3-oxobutyl)cyclopropanecarboxylic acid (6).[12a] A solution of (+)-2-carene **5** (6.08g, 44.6mmol) in MeOH (40ml) was cooled to -65 °C and stirred vigorously. Ozone was bubbled into the mixture (30-40lh^{-1}), *via* an inlet tube which reached below the surface of the liquid, for 2h. The mixture was slowly warmed to room temp., then added with care to a stirred solution of 30% aqu. NaOH (25ml) and 30% H_2O_2, and the resulting mixture refluxed for 1h. The solution was checked for peroxides (KI-starch paper). Traces of peroxides were destroyed with $Na_2S_2O_5$. The MeOH was removed *in vacuo* and the basic solution extracted with ether (2x200ml) to remove any neutral products. The aqueous solution was then

acidified with conc. HCl and extracted with ether (4x100ml). The combined organic phases were dried ($MgSO_4$), filtered, concentrated *in vacuo*, and purified by silica chromatography (eluent: petrol/ethyl acetate (1:1)) to give **6** (4.942g, 60%) as a colourless oil. IR ($CHCl_3$): 3700-2390 (br), 1724, 1689cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.8-2.2 (4H, m), 1.17 and 1.23 (both 3H, 2xs), 2.16 (3H, s), 2.43 (2H, t, J=7.3Hz), 9.80ppm (<1H, br. s).

A similar procedure can be followed with the initial mixture of (+)-carene **5** (25.0g, 185.3mmol) and MeOH (220ml) being vigorously stirred at room temp. for 30min. prior to cooling (-70 °C) and treatment with ozone (4h). Following work up in the same fashion, a crude product (yellow oil) was isolated (27.11g, 80%) and used without further purification.

(1*S*,3*R*)-*cis*-3-(2-(2-Methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropanecarboxylic acid (7).[12b] The following method is illustrative: (1*S*,3*R*)-*cis*-2,2-dimethyl-3-(3-oxobutyl)cyclopropanecarboxylic acid **6** (5.1132g, 27.73mmol) and benzene (200ml) were mixed with ethane-1,2-diol (8ml, 144mmol) and *p*-toluenesulphonic acid (50mg). Using a Dean & Stark condenser the mixture was heated to reflux overnight. After cooling to room temp., the solution was washed with water, the organic phase dried ($MgSO_4$), filtered, and the solvent was removed *in vacuo* to give **7** (6.0623g, 96%) as an unstable yellow oil. IR (neat): 3600-2500 (br), 1710cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.03-1.72 (6H, m), 1.13 and 1.21 (both 3H, 2xs), 1.29 (3H, s), 3.90 (4H, m), 7.37ppm (1H, s); $[\alpha]_D$ = +20.9 (c=0.755, ethanol).

All experiments of this class were carried out immediately before use of the carboxylic acid **7**. All yields lay between 90 and 100%.

(1*S*,3*R*)-*cis*-3-(2-(2-Methyl-1,3-dioxolan-2-yl)ethyl)-1-hydroxymethyl-2,2-dimethylcyclopropane (8).[12b] (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropanecarboxylic acid **7** (153.6mg, 0.672mmol) and dry THF (40ml) were mixed under N_2 and the solution cooled in an ice bath. Lithium aluminium hydride (69.2mg, 1.82mmol) was added slowly *via* a solid addition tube to the vigorously stirred solution. After the addition was complete, the slurry was allowed to warm to room temp. and stirring was continued overnight. The mixture was again cooled in an ice bath, and quenched sequentially with water (0.5ml), dilute NaOH (1ml) and water (1ml). Ether and solid $NaHCO_3$ were added, the precipitate removed by filtration through a pad of kieselguhr, the cake washed with ether, and the phases separated. The aqueous phase was washed with ether, the organic phases were combined, dried ($MgSO_4$), filtered, and the solvent was removed *in vacuo* to yield **8** (129.7mg, 90%) as an unstable colourless oil. IR (neat): 3600-3100 (br), 3000, 2970, 2890cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.89-1.86 (6H, m), 1.03 and 1.07 (both 3H, 2xs), 1.33 (3H, s), 2.07 (1H, br. s), 3.66 (2H, d, J=7.4Hz), 3.94ppm (4H, m).

This reaction was repeated using 5.09g, 22.3mmol of **7**, 2.72g, 71.6mmol of $LiAlH_4$ in ether under N_2 (3h) to give **8** (3.81g, 80%).

(1*S*,3*R*)-*cis*-3-(2-(2-Methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropanecarboxaldehyde (9).[12b] Pyridinium dichromate (0.64g, 1.7mmol) and dry dichloromethane (6ml) were mixed in a flame dried flask under N_2 and the resultant slurry was cooled in an ice bath. To this mixture (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-1-hydroxymethyl-2,2-dimethylcyclopropane **8** (178.8mg, 0.834mmol) was added over

5min. as a dichloromethane solution (2ml). The mixture was stirred at 0 °C for 2h, and then allowed to warm to room temp. and allowed to stir for a further 4.5h. Ether (80ml) was added, the mixture filtered through a pad of kieselguhr (with ether washing), the solvent removed *in vacuo* and the crude product purified by chromatography on silica (eluent: ether) to give **9** (130mg, 73%) as a colourless oxygen-sensitive oil. IR (neat): 3000, 2960, 2890, 1690cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 0.94-1.88 (6H, m), 1.19 and 1.32 (both 3H, 2xs), 1.36 (3H, s), 3.94 (4H, m), 9.46ppm (1H, d, J=6.3Hz); $[\alpha]_D$ = +38.4° (c=0.1640, chloroform) (*cf.* lit.[32] on the opposite enantiomer of **9**: $[\alpha]_D$ = -24° (c=0.1874, chloroform).

The aldehyde **9** was found to be rather sensitive to oxidation during storage. Conveniently, a simple wash with dilute NaOH removed any oxidation products without any detectable epimerisation at the 1*S* chiral centre. When the literature value[32] for the rotation of the opposite enantiomer is considered it is conceivable that the material used for this earlier study was slightly impure due to this oxidation process.

It should also be noted that, in our case, the 1*R*,3*R*-diastereoisomer was observed to be present in approximately 5% by ^{1}H nmr signal integration (9.30ppm, d, J=5.6Hz).

(1*R*,3*R*)-*cis*-1-(2,2-Dibromoethenyl)-2,2-dimethyl-3-(3-oxobutyl)cyclopropane (10). Triphenylphosphine was recrystallised from ethanol and dried under vacuum (<1mmHg) at 60 °C for 2h. Carbon tetrabromide was recrystallised from ethanol and dried under vacuum at room temp. for 2h. Aldehyde **9** was washed with dilute NaOH and dried over $MgSO_4$ before use.

A mixture of (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropanecarboxaldehyde **9** (708.0mg, 3.33mmol) and dichloromethane (29ml) was cooled to 0 °C, and to it was added triphenylphosphine (3.13g, 11.9mmol) by means of the solid addition tube. A dichloromethane solution (5ml) of carbon tetrabromide (1.95g, 5.89mmol) was added dropwise by injection over 50min. resulting in a yellow colouration during the addition. After 1h the mixture was warmed to room temp., and stirred overnight. Ether was added to precipitate triphenylphosphine oxide, and the mixture was filtered through a pad of silica gel, the pad thoroughly washed with ether, the solvent was removed *in vacuo* and repeated column chromatography on neutral alumina (eluent: petrol/ether (9:1)) gave **10** (668.9mg, 62%) as a colourless oil. IR ($CHCl_3$): 2988, 2956, 2931, 2874, 1712cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 0.87-1.77 (4H, m), 1.04 and 1.11 (both 3H, 2xs), 2.16 (3H, s), 2.40 (2H, t, J=7.6Hz), 6.11ppm (1H, d, J=8.8Hz); HRMS calcd for $C_{11}H_{16}Br_2O$ (M^+; $^{81}Br_2$): 325.9527, (M^+; ^{81}Br,^{79}Br): 323.9547, (M^+; $^{79}Br_2$): 321.9568. Found: 325.9515 (19.3), 323.9546 (38.5), 321.9576 (19.2); calcd for C_8H_{10} (M^+ - Ac - 2Br - Me):106.0783. Found: 106.0786 (100).

(1*R*,3*R*)-*cis*-1-(2,2-Dibromoethenyl)-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropane (11). In a similar fashion to that used for the formation of **10**, a mixture of (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropanecarboxaldehyde **9** (67.6mg, 0.318mmol) in dichloromethane (2ml) was cooled to 0 °C, and triphenylphosphine (298.7mg, 1.14mmol) was added as a solid. A dichloromethane solution (0.75ml) of carbon tetrabromide (182.9mg, 0.551mmol) was added dropwise (over 80min.) with careful tlc monitoring until the reaction was complete. The reaction was worked up immediately, in a similar manner to the above experiment to afford the desired dibromo olefin **11** (99.0mg, 84%) as a colourless oil. IR ($CHCl_3$): 3000, 2951, 2893cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 0.95-1.78 (6H, m), 1.04

and 1.12 (both 3H, 2xs), 1.33 (3H, s), 3.95 (4H, m), 6.13ppm (1H, d, J=8.8Hz); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 15.8, 20.2, 22.6, 23.6, 28.7, 31.0, 31.2, 38.7, 64.6, 87.4, 109.7, 136.0ppm; HRMS calcd for $C_{13}H_{20}Br_2O_2$ (M^+; $^{81}Br_2$): 369.9789, (M^+; ^{81}Br,^{79}Br): 3367.9810, (M^+; $^{79}Br_2$): 365.9830. Found: 3369.9777 (3.5), 367.9798 (6.8), 365.9848 (3.4); calcd for $C_4H_7O_2$: 87.0446. Found: 87.0452 (100); $[\alpha]_D$ = +34° (c=0.212, chloroform).

Reference 18 notes that in larger scale preparations of **11** a proportion of the product is present as the undesired ketone **10**. The following procedure is illustrative of how the desired ketal **11** can be isolated in uncontaminated form: Using the above procedure (for formation of **11**), the reaction was repeated using a mixture of (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropanecarboxaldehyde **9** (4.63g, 21.79mmol) and dichloromethane (100ml). Triphenylphosphine (20.10g, 76.63mmol) was added as a solid and carbon tetrabromide (10.84g, 32.68mmol) was added as a solution in dichloromethane (10ml). After the addition was complete, tlc analysis of the mixture indicated that the starting material had been consumed but that both the desired dibromo olefin **11** and the deprotected product **10** were present. The solvent was removed *in vacuo* and the bulk of the unreacted triphenylphosphine was removed by alumina column chromatography. The crude mixture of products was then mixed with benzene (250ml), ethane-1,2-diol (4ml) and a catalytic quantity of *p*-toluenesulphonic acid. The flask was fitted with a Dean & Stark apparatus and heated to reflux overnight. After cooling the bulk of the solvent was removed *in vacuo*, ether and water were added, and the phases separated. The aqueous layer was washed with ether, the organic phases combined, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Purification of the product was carried out by alumina column chromatography (eluent: petrol/ether (9:1)) to afford the desired dibromo olefin **11** (5.86g, 73%) as a colourless oil.

(1*R*,3*R*)-*cis*-3-(2-(2-Methyl-1,3-dioxolan-2-yl)ethyl)-1-ethynyl-2,2-dimethylcyclopropane (12). The following method is illustrative: A solution of (1*R*,3*R*)-*cis*-1-(2,2-dibromoethenyl)-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropane **11** (425.6mg, 1.156mmol) and dry THF (20ml) was cooled to -78 °C under nitrogen. To this *n*-BuLi (2.5M solution in hexanes, 1ml, 2.5mmol) was slowly added and the mixture stirred at -78 °C for two hours, then allowed to warm to room temp. The reaction was quenched with water (4ml), extracted with ether, the organic phase dried ($MgSO_4$), filtered, the solvent removed *in vacuo* and the crude product purified by silica chromatography (eluent: petrol/ether (9:1)) to give **12** (240.1mg, 100%) as a colourless oil. IR ($CHCl_3$): 3310, 2978, 2953, 2927, 2110cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.77 (1H, dt, J=8.5Hz, 7.1Hz), 1.07 and 1.11 (both 3H, 2xs), 1.17 (1H, dd, J=8.6Hz, 2.3Hz), 1.35 (3H, s), 1.43-1.89 (4H, m), 1.89 (1H, d, J=2.2Hz), 3.93ppm (4H, m); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 16.0, 17.4, 20.4, 21.8, 23.9, 27.8, 29.8, 38.4, 64.8, 67.8, 83.3, 110.2ppm; HRMS calcd for $C_{12}H_{17}O_2$ (M^+ - Me): 193.1228. Found: 193.1224 (5.2); calcd for C_8H_{10} (M^+ - Me - ketal): 106.0783. Found: 106.0783 (3.3); calcd for $C_4H_7O_2$: 87.0446. Found: 87.0448 (100); $[\alpha]_D$ = +8.2° (c=0.184, chloroform).

General Procedure for Preparation of Alkynehexacarbonyldicobalt Complexes.

Octacarbonyldicobalt in petroleum ether were stirred under nitrogen and a solution of the alkyne in petroleum ether was added. The resulting mixture was stirred at room temperature for approx. 4h, filtered

through a pad of kieselguhr, the solvent removed *in vacuo* and the crude residue purified by chromatography on neutral alumina to yield the desired complex.

Hexacarbonyl((1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-1-ethynyl-2,2-dimethyl-cyclopropane)dicobalt (4). The following method is illustrative of this specific transformation and the general technique described above: To a mixture of octacarbonyldicobalt (10% hexanes, 116.8mg, 0.342mmol) and petroleum ether (15ml) under N_2 was added (1*R*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-1-ethynyl-2,2-dimethylcyclopropane **12** (70.6mg, 0.339mmol) as a solution in petrol (15ml). The resulting mixture was stirred at room temp. for 1h, the solution filtered through a pad of kieselguhr, the pad washed thoroughly with petrol, the solvent removed *in vacuo* and the crude product purified by chromatography on neutral alumina (eluent: petrol/ether (9:1)) to give **4** (168mg, 100%) as a dark red oil. IR ($CHCl_3$): 2989, 2951, 2884, 2095, 2057, 2019 (Co=C=O), 1588cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.86 (1H, m), 1.07 and 1.18 (both 3H, s), 1.33 (3H, s), 1.55-1.77 (4H, m), 2.08 (1H, dd, J=8.1Hz, 0.7Hz), 3.92 (4H, m), 5.84ppm (1H, d, J=0.9Hz); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 15.6, 20.0, 24.0, 27.1, 28.8, 34.0, 34.9, 38.9, 64.9, 71.2, 94.7, 109.9, 200.6ppm; HRMS calcd for $C_{19}H_{20}Co_2O_8$ (M^+): 493.9822. Found: 493.9810 (12.9); calcd for $C_{17}H_{20}Co_2O_6$ (M^+ - 2CO): 437.9924. Found: 437.9949 (59.8); calcd for $C_{15}H_{20}Co_2O_4$ (M^+ - 4CO): 382.0025. Found: 382.0012 (83.0); calcd for $C_{13}H_{20}Co_2O_2$ (M^+ - 4CO): 326.0127. Found: 326.0113 (100); $[\alpha]_D$ = +165.6° (c=0.0163, chloroform).

Hexacarbonyldicobalt Complexes.

The known $Co_2(CO)_6$ complexes of alkynes **14**,[24] **15**,[33] **16**,[10] **17**,[25] **18**,[19] and **19**[19] were prepared according to the standard procedure laid out above.

3-((2-Methoxyethoxy)methoxy)-1-propyne (20).[34] A solution of 2-propyn-1-ol (1ml, 936mg, 17mmol) in THF (20ml) was cooled to 0 °C under N_2 and NaH added portionwise with stirring for 30min. 2-Methoxyethoxymethyl chloride (2.4ml, 2.64g, 21mmol) was added and following stirring for 5h the reaction was quenched with water (50ml), extracted with ether (4x40ml), dried ($MgSO_4$), filtered and the ether removed *in vacuo* by distillation through a Vigreux column. The crude product was then purified by distillation (75-76/8mmHg) to give 2.06g (84%) of **20**. ^1H nmr ($CDCl_3$): δ 2.41 (1H, t, J=2.4Hz), 3.39 (3H, s), 3.54-3.57 (2H, m), 3.69 (2H, m) 4.23 (2H, d, J=2.4), 4.80ppm (2H, s).

Hexacarbonyl(3-((2-methoxyethoxy)methoxy)-1-propyne)dicobalt. This complex was prepared according to the standard procedure laid out above using $Co_2(CO)_8$ (1.89g, 5.52mmol), 3-((2-methoxyethoxy)methoxy)-1-propyne **20** (702mg, 4.87mmol) in petrol (8ml); 2h reaction time; purification by silica column chromatography (eluent: petrol/ether (4:1)) to give the desired complex (1.68g, 80%). IR (CCl_4): 3096, 2985, 2927, 2888, 2836, 2097, 2061, 2029, 2017 (Co=C=O), 1544, 1451cm^{-1}; ^1H nmr ($CDCl_3$): δ 3.40 (3H, s), 3.56-3.60 (2H, m), 3.74-3.78 (1H, m), 4.75 (2H, d, J=0.9Hz), 4.86 (2H, s) 6.05ppm (1H, d, J=0.8Hz); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 59.2, 67.2, 67.7, 71.9, 76.8, 91.4, 95.1, 199.5ppm; HRMS calcd for $C_{11}H_{12}Co_2O_7$ (M^+ - 2CO): 397.9247. Found: 373.9260 (33.6); calcd for $C_{10}H_{12}Co_2O_6$ (M^+ - 3CO): 345.9298. Found: 345.9273 (100); calcd for $C_9H_{12}Co_2O_5$ (M^+ - 4CO): 317.9713. Found: 317.9666 (100);

calcd for $C_8H_{12}Co_2O_4$ (M^+ - 5CO): 289.9399. Found: 289.9416 (100); calcd for $C_7H_{12}CoO_3$ (M^+ - 6CO - Co): 203.0118. Found: 203.0063 (43.1).

2-Propyn-1-ylthiobenzene (21).[35] Sodium hydroxide (3g, 75mmol), water (40ml) and thiophenol (4.66ml, 45mmol) were stirred at room temp. and after 15min. the mixture was cooled to 0 °C and propargyl bromide (6.75g, 80% solution in toluene, 45mmol) as a solution in benzene (50ml) was added dropwise. Four drops of Adogen 464® were added and the mixture stirred vigorously for 30min. The organic phase was separated, washed with water (2x25ml) then brine (25ml), dried ($MgSO_4$) and the ether removed *in vacuo*. Distillation (60-62 °C/0.6mmHg) afforded **21** as a yellow oil (5.07g, 76%). IR (CCl_4): 3295, 3061, 2943, 2916, 1587, 1480, 1437, 1411, 1234.5cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.25 (1H, t, J=2.6Hz), 3.62 (2H, d, J=2.6Hz), 7.26-7.49ppm (5H, m).

Hexacarbonyl(2-propyn-1-ylthiobenzene)dicobalt. This complex was prepared according to the standard procedure laid out above using $Co_2(CO)_8$ (6.84g, 20mmol), 2-propyn-1-ylthiobenzene **21** (2.96g, 20mmol) in petrol (10ml); 24h reaction time; purification by alumina column chromatography (eluent: petrol) to give the desired complex (7.56g, 87%). ^1H nmr ($CDCl_3$): δ 4.39 (2H, d, J=1.1Hz), 5.82 (1H, t, J=1.1Hz), 7.22-7.43ppm (5H, m); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 38.4, 73.8, 92.1, 126.6, 129.1, 129.5, 135.6, 199.4ppm; HRMS calcd for $C_{14}H_8Co_2O_5S$ (M^+ - 1CO): 405.8757. Found 405.8911 (21.3); calcd for $C_{12}H_8Co_2O_3S$ (M^+ - 3CO): 349.8858. Found: 349.8904 (100); calcd for $C_{11}H_8Co_2O_2S$ (M^+ - 4CO): 321.8909. Found: 321.8951 (65.8); calcd for $C_{10}H_8Co_2OS$ (M^+ - 5CO): 293.8960. Found: 293.9391 (20.8).

2-Propyn-1-ylselenobenzene (22).[36] Diphenyldiselenide (2g, 6.41mmol) was dissolved in ethanol (16ml) and a mixture of sodium formaldehyde sulphoxylate (1.0g, 6.49mmol) and sodium hydroxide (1.27g, 31.8mmol) in water (6.7ml) was added. The yellow mixture was stirred for 15min. at 50 °C during which time the yellow colour faded and a precipitate formed. The mixture was cooled to 0 °C and propargyl bromide (1.77g, 80% solution in toluene, 11.9mmol) was added followed by 2 drops of Adogen 464®. After 3h stirring at 0 °C the mixture was poured into dilute HCl (30ml), extracted with ether/hexane (1:1; 3x15ml), the organic fractions washed with aqu. $NaHCO_3$ (2x50ml) and brine (2x50ml), dried (Na_2SO_4) and the solvent removed *in vacuo*. Distillation (59-61 °C/0.3mmHg) afforded **22** as a pale yellow oil (2.10g, 91%). IR (CCl_4): 3311, 3074, 3061, 2927, 2113, 1576, 1473, 1435 cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.27 (1H, t, J=2.6Hz), 3.50 (2H, d, J=2.6Hz), 7.29-7.34 (3H, m), 7.60-7.64ppm (2H, m).

Hexacarbonyl(2-propyn-1-ylselenobenzene)dicobalt. This complex was prepared according to the standard procedure laid out above using $Co_2(CO)_8$ (3.91g, 11.4mmol), 2-propyn-1-ylselenobenzene **22** (2..06g, 10.55mmol) in petrol (50ml); 14h reaction time; purification by alumina column chromatography (eluent: petrol) to give the desired complex (3.07g, 60%). ^1H nmr ($CDCl_3$): δ 4.39 (2H, s), 5.81 (1H, s), 7.27-7.35 (3H, m), 7.54-7.58ppm (2H, m); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 31.6, 74.5, 93.7, 127.9, 130.0, 130.8, 133.2, 199.9ppm; HRMS calcd for $C_{14}H_8Co_2O_5Se$ (M^+ - 1CO; ^{80}Se): 453.8201, (M^+ - 1CO; ^{78}Se): 451.8201. Found: 453.8353 (13.0), 451.8336 (6.7); calcd for $C_{12}H_8Co_2O_3Se$ (M^+ - 3CO; ^{80}Se): 397.8302,

(M^+ - 3CO; ^{78}Se): 395.8302. Found: 397.9013 (100), 395.8966 (50.7); calcd for $C_{11}H_8Co_2O_2Se$ (M^+ - 4CO; ^{80}Se): 369.8353, (M^+ - 4CO; ^{78}Se): 367.8353. Found: 369.8173 (28.1), 367.7905 (14.5).

General Procedures for Pauson-Khand Cyclisation Reactions with Ethylene

Unpromoted Thermal Reactions (General Procedure A). A benzene solution of the alkynehexacarbonyldicobalt complex was placed in steel autoclave vessel and the apparatus sealed. The vessel was purged with ethylene and, isolated under 50-55atm. of the same gaseous alkene and the resulting mixture shaken (rocked) at 80-90 °C. On completion, the vessel and mixture were cooled, filtered thorough kieselguhr, the solvent removed *in vacuo* and the product purified by column chromatography.

***N*-Oxide Promoted Reactions under Autoclave Conditions (General Procedure B).** A steel autoclave was charged with the alkynehexacarbonyldicobalt complex and toluene or benzene. A test tube was charged with TMANO.$2H_2O$ in methanol and carefully inserted into the autoclave without allowing mixture with the toluene/benzene solution. The vessel was purged twice with ethylene before being sealed under 25-35atm. of ethylene gas. The autoclave was rocked (promoting complete mixing of the autoclave contents) at 40 °C. On completion the contents of the vessel were washed out with chloroform, filtered through a pad of kieselguhr, the solvent removed *in vacuo* and the product purified by column chromatography.

***N*-Oxide Promoted Reactions at Atmospheric Pressure (General Procedure C).** A 3-necked flask, fitted with an oil bubbler, was charged with the alkynehexacarbonyldicobalt complex and benzene. Ethylene gas was bubbled through the stirred solution *via* cannula at room temp. TMANO.H_2O in methanol was added portionwise and stirring was continued at room temp. On completion the mixture was filtered through a pad of kieselguhr, the solvent removed *in vacuo* and the product purified by column chromatography.

(1*S*,3*R*)-*cis*-1-(2-Cyclopenten-1-on-2-yl)-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropane (13).

Unpromoted Thermal Reaction. General procedure A was used with the following reagents and reaction conditions: hexacarbonyl((1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-1-ethynyl-2,2-dimethylcyclopropane)dicobalt **4** (168mg, 0.339mmol), benzene (40ml), ethylene (50atm.), 80-90 °C, 5h. Following silica column chromatography (eluent: petrol/ether (2:3)) cyclopentenone **13** was isolated (34.1mg, 38%) as a pale yellow oil.

***N*-Oxide Promoted Reaction under Autoclave Conditions.** General procedure B was used with the following reagents and reaction conditions: hexacarbonyl((1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-1-ethynyl-2,2-dimethylcyclopropane)dicobalt **4** (706.4mg, 1.43mmol), toluene (8ml), TMANO.$2H_2O$ (1.43g, 12.87mmol), methanol (8ml), ethylene (25atm.), 40 °C, 24h. Following silica column chromatography (eluent: petrol/ether (2:3)) cyclopentenone **13** was isolated (306.5mg, 81%) as a pale yellow oil.

***N*-Oxide Promoted Reaction at Atmospheric Pressure**. General procedure C was used with the following reagents and reaction conditions: hexacarbonyl((1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-1-ethynyl-2,2-dimethylcyclopropane)dicobalt **4** (283.7mg, 0.547mmol), benzene (3ml), TMANO.$2H_2O$ (576mg, 5.2mmol), methanol (3ml), 18h. Following silica column chromatography (eluent: petrol/ether (2:3)) cyclopentenone **13** was isolated (62.0mg, 41%) as a colourless oil.

IR ($CHCl_3$): 2989, 2957, 2893, 1704, 1627, 1455, 1378cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.87-1.71 (6H, m), 0.97 and 1.16 (both 3H, 2xs), 1.29 (3H, s), 2.35 (2H, m), 2.57 (2H, m), 3.91 (4H, m), 7.24ppm (1H, m); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 15.4, 15.6, 20.0, 20.4, 22.3, 23.9, 26.4, 29.2, 33.8, 39.2, 64.7, 109.9, 143.4, 155.8, 210.9ppm; HRMS calcd for $C_{16}H_{24}O_3$ (M^+): 264.1726. Found: 264.1723 (13.4); calcd for $C_4H_7O_2$: 87.0446. Found: 87.0439 (100); Anal.: calcd for $C_{16}H_{24}O_3$: C 72.68, H 9.17. Found: C 72.62, H 9.30%; $[\alpha]_D$ = + 28.5° (c=0.172, chloroform).

2-(1-Trimethylsilylmethyl)-2-cyclopenten-1-one.[24]

***N*-Oxide Promoted Reaction under Autoclave Conditions**. General procedure B was used with the following reagents and reaction conditions: hexacarbonyl(trimethyl-2-propynylsilane)dicobalt (5.142g, 12.91mmol), benzene (70ml), TMANO.$2H_2O$ (12.9g, 116mmol), methanol (70ml), ethylene (25-30atm.), 40 °C, 24h. Following alumina column chromatography (eluent: petrol/ether (1:1)) 2-(1-trimethylsilyl-methyl)-2-cyclopenten-1-one was isolated (1.057g, 49%).

***N*-Oxide Promoted Reaction at Atmospheric Pressure**. General procedure C was used with the following reagents and reaction conditions: hexacarbonyl(trimethyl-2-propynylsilane)dicobalt (448mg, 1.12mmol), benzene (6ml), TMANO.$2H_2O$ (655mg, 5.9mmol), methanol (6ml), 8h. Following alumina column chromatography (eluent: petrol/ether (1:1)) 2-(1-trimethylsilylmethyl)-2-cyclopenten-1-one was isolated (72mg, 38%).

IR (neat): 3055, 2953, 2927, 2902, 1702, 1625.33cm^{-1}; ^1H nmr ($CDCl_3$): δ -0.01 (9H, s), 1.66 (2H, d, J=1.2Hz), 2.36-2.40 (2H, m), 2.53-2.58 (2H, m), 7.12-7.14ppm (1H, m); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ -1.2, 14.9, 26.4, 34.1, 144.1, 154.4, 209.9ppm.

2-Phenyl-2-cyclopenten-1-one.[10]

***N*-Oxide Promoted Reaction under Autoclave Conditions**. General procedure B was used with the following reagents and reaction conditions: hexacarbonyl(phenylethyne)dicobalt (483.8mg, 1.247mmol), toluene (7ml), TMANO.$2H_2O$ (1.26g, 11.34mmol), methanol (7ml), ethylene (25-30atm.), 40 °C, 7h. Following silica column chromatography (eluent: petrol/ether (2:1)) 2-phenyl-2-cyclopenten-1-one was isolated (140.4g, 71%) as an off-white solid.

***N*-Oxide Promoted Reaction at Atmospheric Pressure**. General procedure C was used with the following reagents and reaction conditions: hexacarbonyl(phenylethyne)dicobalt (436mg, 1.12mmol), benzene (5.5ml),

TMANO.$2H_2O$ (1.12g, 10.1mmol), methanol (5.5ml), 7h. Following silica column chromatography (eluent: petrol/ether (2:1)) 2-phenyl-2-cyclopenten-1-one was isolated (82mg, 46%) as a white crystalline solid.

This process was repeated with the following quantities of reagents and reaction conditions: hexacarbonyl(phenylethyne)dicobalt (445mg, 1.15mmol), benzene (5.6ml), TMANO.$2H_2O$ (1.15g, 10.4mmol), methanol (5.6ml), 7h. In this case the TMANO.$2H_2O$ was added over 2h by means of a syringe pump. Following silica column chromatography (eluent: petrol/ether (2:1)) 2-phenyl-2-cyclopenten-1-one was isolated (99.7mg, 55%)as a white crystalline solid.

IR (CH_2Cl_2): 3052, 2998, 2926, 1706, 1599, 1497cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.59-2.63 (2H, m), 2.70-2.75 (2H, m), 7.33-7.43 (3H, m), 7.68-7.72 (2H, m), 7.84ppm (1H, t, J=2.9Hz); Mp: 68-69 °C.

2-Pentyl-2-cyclopenten-1-one.[10]

***N*-Oxide Promoted Reaction under Autoclave Conditions.** General procedure B was used with the following reagents and reaction conditions: hexacarbonyl(1-heptyne)dicobalt (485.6mg, 1.271mmol), toluene (7ml), TMANO.$2H_2O$ (1.26g, 11.34mmol), methanol (7ml), ethylene (25-30atm.), 40 °C, 24h. Following silica column chromatography (eluent: petrol/ether (1:1)) 2-pentyl-2-cyclopenten-1-one was isolated (140.4mg, 73%) as a colourless oil.

***N*-Oxide Promoted Reaction at Atmospheric Pressure.** General procedure C was used with the following reagents and reaction conditions: hexacarbonyl(1-heptyne)dicobalt (448mg, 1.17mmol), benzene (5.7ml), TMANO.$2H_2O$ (1.17g, 10.5mmol), methanol (5.7ml), 24h. Following silica column chromatography (eluent: petrol/ether (1:1)) 2-pentyl-2-cyclopenten-1-one was isolated (103mg, 58%) as a colourless oil.

IR (neat): 2979, 2953, 2928, 2902, 1702, 1651cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.89 (3H, t, J=6.9Hz), 1.24-1.34 (4H, m), 1.45-1.51 (2H, m), 2.17 (2H, td , J=7.7Hz, 1.4Hz), 2.38-2.42 (2H, m), 2.54-2.59 (2H, m), 7.29-7.32ppm (1H, m).

2-(((Tetrahydro-2*H*-pyran-2-yl)oxy)methyl)-2-cyclopenten-1-one.

***N*-Oxide Promoted Reaction under Autoclave Conditions.** General procedure B was used with the following reagents and reaction conditions: hexacarbonyl(tetrahydro-2-(2-propynyl-1-oxy)-2*H*-pyran)dicobalt (502.6mg, 1.179mmol), toluene (7ml), TMANO.$2H_2O$ (1.19g, 10.7mmol), methanol (7ml), ethylene (25-30atm.), 40 °C, 24h. Following silica column chromatography (eluent: ether) 2-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)-2-cyclopenten-1-one was isolated (50.8mg, 22%) as a pale yellow oil.

***N*-Oxide Promoted Reaction at Atmospheric Pressure.** General procedure C was used with the following reagents and reaction conditions: hexacarbonyl(tetrahydro-2-(2-propynyl-1-oxy)-2*H*-pyran)dicobalt (384mg, 0.901mmol), benzene (4.5ml), TMANO.$2H_2O$ (900mg, 8.1mmol), methanol (4.5ml), 6h. Following alumina column chromatography (eluent: ether) 2-((tetrahydro-2*H*-pyran-2-yloxy)methyl)-2-cyclopenten-1-one was isolated (57.7mg, 33%).

This process was repeated with a balloon filled with ethylene being used to replace the bubbling technique used above. The following quantities of reagents and reaction conditions were employed: hexacarbonyl(tetrahydro-2-(2-propynyl-1-oxy)-2*H*-pyran)dicobalt (480.7mg, 1.128mmol), benzene (7ml), TMANO.$2H_2O$ (1.17g, 10.5mmol), methanol (7ml), 24h. Following silica column chromatography (eluent: ether) 2-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)-2-cyclopenten-1-one was isolated (72.5mg, 30%) as a colourless oil.

IR (CCl_4): 2939, 2867, 1705, 1643cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.52-1.88 (6H, m), 2.43 (2H, t of m, J=4.5Hz), 2.64 (2H, t of m, J=4.6Hz), 3.45-3.55 (1H, m), 3.82-3.91 (1H, m), 4.14 (1H, dd, J=13.8Hz, 1.5Hz), 4.43 (1H, dd, J=13.8Hz, 1.6Hz), 4.66 (1H, t, J=3.4Hz), 7.59-7.61ppm; $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 19.6, 25.4, 26.9, 30.7, 35.1, 61.2, 62.5, 98.9, 143.6, 159.8, 208.6ppm; HRMS calcd for $C_6H_7O_2$ (M^+ - C_5H_9O): 111.0446. Found: 111.0446 (9); calcd for $C_5H_9O_2$ (M^+ - C_6H_7O): 101.0603. Found: 101.0596 (100); calcd for C_6H_7O (M^+ - $C_5H_9O_2$): 95.0497. Found: 95.0489 (75.1); calcd for C_5H_9: 85.0653. Found: 85.0642 (79.0).

3-Methyl-2-pentyl-2-cyclopenten-1-one.[19]

***N*-Oxide Promoted Reaction under Autoclave Conditions**. General procedure B was used with the following reagents and reaction conditions: hexacarbonyl(2-octyne)dicobalt (509.5mg, 1.286mmol), toluene (7ml), TMANO.$2H_2O$ (1.27g, 11.43mmol), methanol (7ml), ethylene (25-30atm.), 40 °C, 24h. Following alumina column chromatography (eluent: petrol/ether (1:1)) 3-methyl-2-pentyl-2-cyclopenten-1-one was isolated (85.2mg, 40%).

***N*-Oxide Promoted Reaction at Atmospheric Pressure**. General procedure C was used with the following reagents and reaction conditions: hexacarbonyl(2-octyne)dicobalt (514.4mg, 1.3mmol), benzene (6.3ml), TMANO.$2H_2O$ (1.3g, 11.7mmol), methanol (6.3ml), 24h. Following alumina column chromatography (eluent: petrol/ether (1:1)) 3-methyl-2-pentyl-2-cyclopenten-1-one was isolated (49mg, 23%).

IR (neat): 2953, 2928, 2902, 2851, 1702, 1651, 1447, 1393cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.87 (3H, t, J=7.2Hz), 1.19-1.40 (6H, m), 2.05 (3H, s), 2.16 (2H, t, J=7.6Hz), 2.34-2.38 (2H, m), 2.46-2.49ppm (2H, m).

2-Ethyl-3-methyl-2-cyclopenten-1-one.[19]

***N*-Oxide Promoted Reaction under Autoclave Conditions**. General procedure B was used with the following reagents and reaction conditions: hexacarbonyl(2-pentyne)dicobalt (426.8mg, 1.205mmol), toluene (7ml), TMANO.$2H_2O$ (1.27g, 11.43mmol), methanol (7ml), ethylene (25-30atm.), 40 °C, 24h. Following alumina column chromatography (eluent: petrol/ether (2:1)) 2-ethyl-3-methyl-2-cyclopenten-1-one was isolated (41.3mg, 28%).

***N*-Oxide Promoted Reaction at Atmospheric Pressure**. General procedure C was used with the following reagents and reaction conditions: hexacarbonyl(2-pentyne)dicobalt (460mg, 1.3mmol), benzene (6.3ml), TMANO.$2H_2O$ (1.3g, 11.7mmol), methanol (6.3ml), 24h. Following alumina column chromatography (eluent: petrol/ether (2:1)) 2-ethyl-3-methyl-2-cyclopenten-1-one was isolated (17mg, 11%).

IR (neat): 2971, 2914, 2875, 2856, 1670, 1647, 1457, 1446, 1436cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 0.97 (3H, t, J=7.6Hz), 2.05 (3H, s), 2.21 (2H, q, J=7.6Hz), 2.34-2.38 (2H, m), 2.46-2.50ppm (2H, m).

2-((2-Methoxyethoxy)methoxy)-2-cyclopenten-1-one.

Unpromoted Thermal Reaction. General procedure A was used with the following reagents and reaction conditions: hexacarbonyl(3-((2-methoxyethoxy)methoxy)-1-propyne)dicobalt (306.4mg, 0.712mmol), benzene (2.3ml), ethylene (55atm.), 80 °C, 24h. No cyclopentenone product was isolated from the crude residue.

***N*-Oxide Promoted Reaction under Autoclave Conditions**. General procedure B was used with the following reagents and reaction conditions: hexacarbonyl(3-((2-methoxyethoxy)methoxy)-1-propyne)-dicobalt (301mg, 1.50mmol), benzene (3.8ml), TMANO.2H_2O (700mg, 6.3mmol), methanol (3.8ml), ethylene (35atm.), 40 °C, 24h. Following silica column chromatography (eluent: ether) 2-((2-methoxy-ethoxy)methoxy)-2-cyclopenten-1-one was isolated (19.6mg, 14%).

***N*-Oxide Promoted Reaction at Atmospheric Pressure**. General procedure C was used with the amendments that TMANO.2H_2O was added by syringe pump over 90min. and ethylene bubbling was replaced with a balloon filled with ethylene above the reaction. The reagents and reaction conditions given here were used: hexacarbonyl(3-((2-methoxyethoxy)methoxy)-1-propyne)dicobalt (305.4mg, 0.71mmol), benzene (3.8ml), TMANO.2H_2O (700mg, 6.3mmol), methanol (3.8ml), 18h. Following silica column chromatography (eluent: ether) 2-((2-methoxyethoxy)methoxy)-2-cyclopenten-1-one was isolated (40.6mg, 29%).

IR (CCl_4): 2929, 2884, 1714, 1643, 1450cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.43-2.49 (2H, m), 2.60-2.67 (2H, m), 3.40 (3H, s), 3.55-3.59 and 3.70-3.74 (both 2H, 2xm), 4.27 (2H, d, J=1.5Hz), 4.77 (2H, s), 7.59-7.62ppm (1H, m); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 27.04, 35.07, 59.22, 61.41, 67.15, 71.95, 95.54, 143.22, 160.17, 208.53ppm; HRMS calcd for $C_{10}H_{17}O_4$ (M^+ + 1): 201.1127. Found: 201.1168 (100).

2-((Phenylthio)methyl)-2-cyclopenten-1-one.[37]

***N*-Oxide Promoted Reaction under Autoclave Conditions**. General procedure B was used with the following reagents and reaction conditions: hexacarbonyl(2-propyn-1-ylthiobenzene)dicobalt (240.5mg, 0.554mmol), benzene (3ml), TMANO.2H_2O (550mg, 4.95mmol), methanol (3ml), ethylene (35atm.), 40 °C, 24h. Following silica column chromatography (eluent: petrol/ether (2:1)) 2-((phenylthio)methyl)-2-cyclopenten-1-one was isolated (26.5mg, 23%).

***N*-Oxide Promoted Reaction at Atmospheric Pressure**. General procedure C was used with the amendments that ethylene bubbling was replaced with a balloon filled with ethylene above the reaction and the reaction solvent was CH_2Cl_2 at -78 °C for 2h then room temp. for 18h. The reagents and reaction conditions given here were used: hexacarbonyl(2-propyn-1-ylthiobenzene)dicobalt (527.1mg, 1.21mmol),

CH_2Cl_2 (6.3ml), TMANO.$2H_2O$ (1.2g, 10.8mmol), methanol (6.1ml), 20h. Following silica column chromatography (eluent: petrol/ether (2:1)) 2-((phenylthio)methyl)-2-cyclopenten-1-one was isolated (51.8mg, 21%).

This reaction was repeated with ethylene bubbling and no *N*-oxide promoter at room temp. The following quantities of reagents and reaction conditions were employed: hexacarbonyl(2-propyn-1-ylthiobenzene)dicobalt (310.6mg, 0.715mmol), benzene (6ml). Following silica column chromatography (eluent: petrol/ether (2:1)) 2-((phenylthio)methyl)-2-cyclopenten-1-one was isolated (10.7mg, 7%).

IR (CCl_4): 3079, 2923, 1712, 1640, 1587, 1482, 1442cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.43-2.47 (2H, m), 2.54-2.59 (2H, m), 3.69 (2H, d, J=1.6Hz), 7.25-7.33 (5H, m), 7.40-7.42ppm (1H, m); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 26.67, 27.86, 34.74, 126.52, 129.08, 129.71, 135.91, 142.20, 160.24, 208.15ppm; HRMS calcd for $C_{12}H_{13}OS$ (M^+ + 1): 205.0687. Found: 205.0793 (38.2); calcd for $C_{12}H_{12}OS$ (M^+): 204.0609. Found: 204.0694 (100).

2-((Phenylseleno)methyl)-2-cyclopenten-1-one.

Unpromoted Thermal Reaction. General procedure A was used with the following reagents and reaction conditions: hexacarbonyl(2-propyn-1-ylselenobenzene)dicobalt (389.2mg, 0.81mmol), benzene (8.8ml), ethylene (50atm.), 90 °C, 24h. No cyclopentenone product was isolated from the crude residue.

***N*-Oxide Promoted Reaction under Autoclave Conditions**. General procedure B was used with the following reagents and reaction conditions: hexacarbonyl(2-propyn-1-ylselenobenzene)dicobalt (398.8mg, 0.829mmol), benzene (4.5ml), TMANO.$2H_2O$ (830mg, 7.47mmol), methanol (4.5ml), ethylene (30atm.), 40 °C, 24h. Following silica column chromatography (eluent: petrol/ether (1:1)) 2-((phenylseleno)methyl)-2-cyclopenten-1-one was isolated (28.6mg, 14%).

***N*-Oxide Promoted Reaction at Atmospheric Pressure**. General procedure C was used with the amendment that TMANO.$2H_2O$ was added by syringe pump over 3h. The reagents and reaction conditions given here were used: hexacarbonyl(2-propyn-1-ylselenobenzene)dicobalt (173.7mg, 0.36mmol), benzene (2.3ml), TMANO.$2H_2O$ (360mg, 3.24mmol), methanol (2.3ml), 4h. Following silica column chromatography (eluent: petrol/ether (1:1)) 2-((phenylseleno)methyl)-2-cyclopenten-1-one was isolated (11.8mg, 13%).

IR (CCl_4): 3074, 3061, 2925, 2860, 1713, 1635, 1582, 1477, 1438, 1339cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.40-2.44 (2H, m), 2.48-2.52 (2H, m), 3.62 (2H, d, J=1.0Hz), 7.13-7.18 (1H, m), 7.27-7.30 (3H, m), 7.45-7.51ppm (2H, m); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 20.20, 26.56, 34.63, 127.66, 129.21, 130.19, 133.93, 142.98, 159.16, 207.98ppm; HRMS calcd for $C_{12}H_{12}OSe$ (M^+; ^{80}Se): 252.0053, (M^+; ^{78}Se): 250.0061. Found: 252.0176 (100), 250.0188 (58.1).

(1*S*,3*R*)-*cis*-3-(2-(2-Methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethyl-1-(3-methylencyclopenten-2-yl)-cyclopropane (23) directly from 13. Crushed $CeCl_3.6H_2O$ (68.9mg, 0.185mmol) was dried (180°C, <1mmHg) for 2h and then cooled to room temp. The flask was purged with nitrogen and to the white powder

was added dry THF (2ml) and the mixture was stirred vigorously at room temp. for 2h and then cooled to -78 °C. To the slurry was added, slowly by injection, trimethylsilylmethyllithium (1M solution in pentane, 0.15ml, 0.15mmol) during which time a yellow/orange colour was observed. The mixture was stirred at -78 °C for 30min. and then (1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropane **13** (19.9mg, 0.075mmol) added as a solution in THF (1ml) by means of a double-ended needle. The reaction mixture was stirred at -78 °C for 7h and then allowed to warm slowly to room temp. *N,N,N',N'*-tetramethylethylenediamine (0.6ml, 4mmol) was added and the resulting mixture stirred at room temp. for 15min. Dilute aqu. $NaHCO_3$ solution (10ml) was added, the organic products extracted with CH_2Cl_2, dried ($MgSO_4$), filtered and flash silica gel (10g) added. The mixture was slurried, the solvent removed *in vacuo* and the powder left standing overnight. The organic product was washed from the silica with $CHCl_3$ and methanol, the solvents removed *in vacuo* and the crude product purified by silica column chromatography (eluent: petrol/ether (9:1)) to give (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethyl-1-(3-methylencyclopenten-2-yl)cyclopropane **23** (11.5mg, 0.0438mmol, 58%) as an oil. ^1H nmr ($CDCl_3$): δ 0.84-1.80 (6H, m), 0.92 and 1.16 (both 3H, s), 1.32 (3H, s), 2.40 (2H, m), 2.55 (2H, m), 3.93 (4H, m), 4.85 and 4.75 (both 1H, 2xbr.s), 5.94 (1H, br.s); $^{13}C\{^1H\}$ nmr ($CDCl_3$): δ 15.2, 19.6, 23.9, 24.5, 27.0, 28.6, 29.9, 30.5, 34.0, 37.4, 64.3, 100.5, 110.1, 134.7, 141.0, 156.2ppm; HRMS calcd for $C_{17}H_{26}O_2$ (M^+): 262.1933. Found: 262.1920 (37.4); calcd for $C_{116}H_{23}O_2$ (M^+ - Me): 247.1698. Found: 247.1678 (9.2); calcd for $C_4H_7O_2$: 87.0446. Found: 87.0452 (100).

(1*S*,3*R*)-*cis*-3-(2-(2-Methyl-1,3-dioxolan-2-yl)ethyl)-1-(3-hydroxy-3-trimethylsilylmethylcyclopenten-2-yl)-2,2-dimethylcyclopropane (24). The procedure as that used in the direct preparation of (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethyl-1-(3-methylencyclopenten-2-yl)cyclopropane **23** was used with the following quantities of reagents: $CeCl_3.2H_2O$ (1.02g, 2.7mmol), trimethylsilylmethyl-lithium (1M solution in pentane, 2ml, 2mmol) and (1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropane **13** (156.6mg, 0.592mmol) in THF. The reaction was quenched in the same fashion, extracted with dichloromethane, the organic phase dried ($MgSO_4$), filtered, the solvent removed *in vacuo* and the crude product purified by alumina column chromatography (eluent: petrol/ether (9:1)) to give (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-1-(3-hydroxy-3-trimethylsilylmethylcyclopenten-2-yl)-2,2-dimethylcyclopropane **24** (179.9mg, 86%) as a mixture of diastereoisomers (1:1). IR ($CHCl_3$): 3514, 3078, 2989, 2954, 2889, 1617, 1555, 1458, 1379cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.20 (9H, s), 0.76-1.79 (10H, m), 0.94 and 1.16 (both 3H, 2xs), 1.31 (3H, s), 1.60 (1H, s, D_2O exch.), 2.86 (2H, d, J=1.6Hz), 3.93 (4H, m), 5.82 and 6.02 (diast. (1:1), 1H, both br.s); HRMS calcd for $C_{20}H_{34}O_2Si$ (M^+ - H_2O): 334.2328. Found: 334.2342 (89.8); calcd for $C_4H_7O_2$: 87.0446. Found: 87.0427 (94.9); calcd for C_3H_9Si: 73.0473. Found 73.0463 (100).

(1*S*,3*R*)-*cis*-3-(2-(2-Methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethyl-1-(3-methylencyclopenten-2-yl)-cyclopropane (23) from 24. A teflon bottle was charged with (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-1-(3-hydroxy-3-trimethylsilylmethylcyclopenten-2-yl)-2,2-dimethylcyclopropane **24** (92.9mg, 0.263mmol) as a solution in acetonitrile (0.5ml) and the solution stirred at room temp. while aqueous hydrofluoric acid (48%w/w, 2 drops) (**CAUTION/HAZARD: The necessary precautions should be taken**

when handling this reagent) was added from a plastic pipette. The resulting mixture was stirred at room temp. for 75min., saturated aqu. $NaHCO_3$ solution (5ml) added, the organic products extracted with dichloromethane, dried ($MgSO_4$), filtered and the solvent was removed *in vacuo*. The crude product was purified by silica column chromatography on silica (eluent: petrol/ether (9:1)) to give (1*S*,3*R*)-*cis*-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethyl-1-(3-methylencyclopenten-2-yl)cyclopropane **23** (56.7mg, 82%) as an oil. Spectral details were identical to those recorded above for the same compound.

4-((1*S*,3*R*)-*cis*-1-(2-Cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)butan-2-one (25).
Titanium(IV) Chloride Technique.[28k] A flame dried flask was charged with (1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropane **13** (23.8mg, 0.090mmol) and sodium dried ether (0.5ml) under N_2. The solution was cooled to 0 °C and $TiCl_4$ (1M solution in dichloromethane, 2 drops) was added by injection. The resulting mixture was stirred for 2h, saturated aqu. $NaHCO_3$ solution (5ml) added, the organic product extracted with dichloromethane, dried ($MgSO_4$) filtered, and the solvent removed *in vacuo*. The product was purified by silica column chromatography (eluent: petrol/ether (1:1)) to give 4-((1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)butan-2-one **25** (15.7mg, 79%) as a colourless oil.

Aqueous *p*-TsOH Hydrolysis.[27] A mixture of (1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropane **13** (60.4mg, 0.228mmol), acetone (4ml), water (1ml), and *p*-toluenesulphonic acid (3mg) was stirred at room temperature for 90min., after which time, no reaction was observed by tlc analysis. The flask was fitted with a reflux condenser, and the mixture warmed to 50 °C. The reaction began to proceed slowly. The reaction proceeded more rapidly on addition of methanol (1ml). Following the total consumption of the starting material, aqu. $NaHCO_3$ was added, the organic products extracted with ether, dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by silica column chromatography (eluent: petrol/ether (1:1)) to afford 4-((1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)butan-2-one **25** (30.1mg, 66%). A number of unidentified by-products were also formed by this process.

Triphenylphosphine/Carbon Tetrabromide Technique.[17] A flame dried flask was charged with (1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)-2,2-dimethylcyclopropane **13** (30.6mg, 0.116mmol) and dry dichloromethane (2ml). The solution was cooled to 0 °C and triphenylphosphine (76.0mg, 0.299mmol) was added in one portion. Carbon tetrabromide (74.6mg, 0.225mmol) in dichloromethane (0.75ml) was then added slowly over 45min. and the resulting mixture stirred at room temp. for a further 3h. The reaction mixture was loaded directly onto a packed silica chromatography column (eluent: petrol/ether (1:1)) to afford 4-((1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)butan-2-one **25** (23.4mg, 0.106mmol, 92%) as a colourless oil.

IR ($CHCl_3$): 2957, 2926, 2865, 1702, 1625, 1454, 1442, 1433, 1407, 1377, 1362, 1304cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 0.85 (1H, dt, J=8.7Hz, 7.4Hz), 0.97 and 1.14 (both 3H, 2xs), 1.33 (1H, d, J=9.0Hz), 1.49 (2H, q, J=7.7Hz), 2.11 (3H, s), 2.34 (2H, m), 2.44 (2H, t, J=7.7Hz), 2.54 (2H, m), 7.25ppm (1H, m); ^{13}C{^{1}H} nmr

($CDCl_3$): δ 15.9, 19.7, 20.5, 22.4, 26.9, 28.7, 29.3, 30.3, 33.9, 43.9, 143.2, 156.6, 209.0, 211.1ppm; HRMS calcd for $C_{14}H_{20}O_2$ (M^+): 220.1463. Found: 220.1493 (28.5); $[\alpha]_D$ = + 28.4° (c=0.844, chloroform).

4-((1*S*,3*R*)-*cis*-1-(2-Cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)-2-hydroxybutane (26). To a mixture of 4-((1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)butan-2-one **25** (485mg, 2.20mmol) and pre-prepared solvent (5% methanol in dichloromethane, 50ml), fresh $NaBH_4$ (166mg, 6.9mmol) was added in one portion and the slurry was stirred vigorously while glacial acetic acid (282mg, 4.7mmol) in solvent (5% methanol in dichloromethane, 5ml) was added slowly. Gas was evolved. The mixture was stirred at room temp. until gas evolution ceased and the reaction was complete by tlc. The reaction mixture was then poured onto dilute aqu. $NaHCO_3$ solution (gas evolved) and the organic products were extracted with dichloromethane, dried ($MgSO_4$), filtered and the solvent was removed *in vacuo*. The product was purified by silica column chromatography (eluent: petrol/ether (1:2)) to give 4-((1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)-2-hydroxybutane **26** (435.9mg, 89%). IR ($CHCl_3$): 3464, 2976, 2927, 2876, 1702, 1625, 1460, 1378, 1295cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.75-1.50 (13H, m), 0.98 and 0.99 (diast., 3H, both s), 2.36 and 2.56 (both 2H, 2xm), 3.73 (1H, m), 7.26ppm (1H, m); ^1H nmr (C_6D_6): δ 0.78-1.56 (6H, m), 0.93 and 0.94 (diast., 3H, both s), 1.06 (3H, d, J=6.2Hz), 1.13 and 1.14 (diast., 3H, both s), 1.95 (1H, br.s), 1.89 and 1.97 (both 2H, 2xm), 3.63 (1H, m), 6.78ppm (1H, m) *cf.* spectral characteristics of analogous diastereomers.[8]

This transformation was also performed under the alternative Ward technique[29] using the following reagents and conditions: 4-((1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)butan-2-one **25** (9.2mg, 0.042mmol), dichloromethane (0.5ml), methanol (0.5ml) at -70 °C and $NaBH_4$ (3.9mg, 0.103mmol) added followed by additional $NaBH_4$ (2mg, 0.08mmol). Acetone (2ml) was added the mixture brought to room temp. and gave, following isolation and purification, 4-((1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)-2-hydroxybutane **26** (8.6mg, 93%). Unfortunately, this latter protocol proved to be irreproducible.

4-((1*S*,3*R*)-*cis*-2,2-Dimethyl-1-(3-methylenecyclopenten-2-yl)cycloprop-3-yl)-2-hydroxybutane (27). Crushed $CeCl_3.6H_2O$ (508mg, 1.36mmol) was dried (180°C, <1mmHg) for 2h and then cooled to room temp. The flask was purged with nitrogen and to the white powder was added dry THF (5ml). The resulting mixture was stirred vigorously at room temp. for 2h and was then cooled to -78 °C. To the slurry was added trimethylsilylmethyllithium (1M solution in pentane, 0.8ml, 0.8mmol), slowly by injection, during which time a yellow/orange colour was observed. The mixture was stirred at -78 °C for 30min. and 4-((1*S*,3*R*)-*cis*-1-(2-cyclopenten-1-on-2-yl)-2,2-dimethylcycloprop-3-yl)-2-hydroxybutane **26** (32.7mg, 0.147mmol) was added as a solution in THF (1.5ml) by means of a double-ended needle. After 30 minutes the mixture was allowed to warm to room temp., *N,N,N',N'*-tetramethylethylenediamine (1ml) added, the mixture stirred at room temp. for 15min., dilute aqu. $NaHCO_3$ (10ml) added, the organic products extracted with ether, and flash silica gel (2g) added. The solvent was removed *in vacuo* and the powder was left standing in air with periodic tlc monitoring. After 3h some decomposition products began to form so the silica was washed exhaustively with ether, the organic extracts dried ($MgSO_4$), filtered and the solvent was removed *in vacuo*. The crude product was purified by silica column chromatography (eluent: petrol/ether (8:1)) to give

4-((1*S*,3*R*)-*cis*-2,2-dimethyl-1-(3-methylenecyclopenten-2-yl)cycloprop-3-yl)-2-hydroxybutane **27** (15.2mg, 47%). ^{1}H nmr (C_6D_6): δ 0.96 - 1.48 (6H, m), 0.98 - 1.07 (6H, m), 1.14 and 1.19 (diast., 3H, 2xs), 1.89 (1H, br.s), 2.24 and 2.47 (both 2H, m), 3.60 (1H, m), 4.89 and 5.07 (both 1H, br.s), 5.89ppm (1H, br.s) *cf.* spectral characteristics of analogous diastereomers.[8]

4-((1*S*,3*R*)-*cis*-2,2-Dimethyl-1-(3-methylenecyclopenten-2-yl)cycloprop-3-yl)-2-butanone, (+)-taylorione (1). To a mixture of 4-((1*S*,3*R*)-*cis*-2,2-dimethyl-1-(3-methylenecyclopenten-2-yl)cycloprop-3-yl)-2-hydroxybutane **27** (40.4mg, 0.183mmol) and dichloromethane (1ml) were added *N*-methylmorpholine *N*-oxide (33.1mg, 0.28mmol) and molecular sieves (94.2mg) (oven-dried prior to use). To this slurry was added tetra-*N*-propylammonium perruthenate (TPAP) (5mg) and the resulting mixture sealed under nitrogen. After 15 minutes the mixture was loaded directly onto a pre-packed silica chromatography column (eluent: petrol/ether (9:1)) to give 4-((1*S*,3*R*)-*cis*-2,2-dimethyl-1-(3-methylenecyclopenten-2-yl)cycloprop-3-yl)-2-butanone, (+)-taylorione **1** (36.6mg, 91%). IR (CCl_4): 3075, 2945, 3735, 1720, 1630, 1452, 1410, 1378, 1360, 1299, 1250, 1200, 1161, 1125, 1076, 1005, 957, 936, 856, cm^{-1} (*cf.* IR details for enantiomer; lit. ref. 7); ^{1}H nmr (CCl_4; int. ref. TMS): δ 0.71-1.7 (4H, m), 0.91 and 1.16 (both 3H, 2xs), 2.05 (3H, s), 2.35-2.43 (4H, m and t, J=7.3Hz), 2.51 (2H, m), 4.67 and 4.76 (both 1H, 2xbr.s), 5.87ppm (1H, br.s) (*cf.* ^{1}H nmr details for enantiomer; lit. ref. 7); ^{1}H nmr ($CDCl_3$): δ 0.7-1.6 (4H, m), 0.94 and 1.16 (both 3H, 2xs), 2.15 (3H, s), 2.40-2.54 (6H, m), 4.75 and 4.84 (both 1H, 2xbr.s), 5.91ppm (1H, br.s); ^{13}C{^{1}H} nmr ($CDCl_3$): δ 15.8, 19.0, 20.8, 24.8, 27.8, 29.4, 29.5, 30.7, 44.6, 100.4, 135.9, 141.7, 157.1, 209.4ppm (*cf.* ^{13}C nmr details for enantiomer; lit. ref. 7); HRMS calcd for $C_{15}H_{22}O$ (M^+): 218.1670. Found: 218.1654 (28.4); calcd for $C_{11}H_{13}$ (M^+ - Ac - 2xMe): 145.1017. Found: 145.1012 (100); $[\alpha]_D$ = + 27.4° (c=0.84, chloroform), *cf.* $[\alpha]_D$ = -28.1° (c=1.52, chloroform) for enantiomer (see lit. ref. 7).

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REFERENCES AND NOTES

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4. For Pauson-Khand reaction reviews see: Schore, N. E. In *Comprehensive Organic Synthesis*; Trost B. M.; Fleming I. Eds.; Pergamon: Oxford, 1991; vol. 5; pp. 1037-1064. Schore N. E. *Organic Reactions*

1991, *40*, 1. Pauson, P. L.; Khand, I. U. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 2. Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.

5. Bernardes, V.; Kann, N.; Riera, A.; Moyano, A.; Pericàs, M. A.; Greene, A. E. *J. Org. Chem.* **1995**, *60*, 6670. Veretenov, A. L.; Koltun, D. O.; Smit, W. A.; Strelenko, Y. A. *Tetrahedron Lett.* **1995**, *36*, 4651. Jamison, T. F.; Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5505. Naz, N.; Al-Tel, T. H.; Al-Abed, Y.; Voelter, W. *Tetrahedron Lett.* **1994**, *35*, 8581. Marco-Contelles, J. *Tetrahedron Lett.* **1994**, *35*, 5059. Krafft, M. E.; Chirico, X. *Tetrahedron Lett.* **1994**, *35*, 4511. Clive, D. L. J.; Cole, D. C.; Tao, Y. *J. Org. Chem.* **1994**, *59*, 1396. Jeong, N.; Lee, B. Y.; Lee, S. M.; Chung, Y. K.; Lee, S.-G. *Tetrahedron Lett.* **1993**, *34*, 4023. Yoo, S.; Lee, S.-H.; Jeong, N.; Cho, I. *Tetrahedron Lett.* **1993**, *34*, 3435. van der Waals, A.; Keese, R. *J. Chem. Soc., Chem. Commun.* **1992**, 570. Takano, S.; Inomata, K.; Ogasawara, K. *J. Chem. Soc., Chem. Commun.* **1992**, 169. Rowley, E. G.; Schore, N. E. *J. Org. Chem.* **1992**, *57*, 6853. Gybin, A. S.; Smit, W. A.; Caple, R.; Veretenov, A. L.; Shashkov, A. S.; Vorontsova, L. G.; Kurella, M. G.; Chertkov, V. S.; Carapetyan, A. A.; Kosnikov, A. Y.; Alexanyan, M. S.; Lindeman, S. V.; Panov, V. N.; Maleev, A. V.; Struchkov, Y. T.; Sharpe, S. M. *J. Am. Chem. Soc.* **1992**, *114*, 5555. Krafft, M. E.; Wright, C. *Tetrahedron Lett.* **1992**, *33*, 151. Takano, S.; Inomata, K.; Ogasawara, K. *Chem. Lett.* **1992**, 443. Veretenov, A. L.; Smit, W. A.; Vorontsova, L. G.; Kurella, M. G.; Caple, R.; Gybin, A. S. *Tetrahedron Lett.* **1991**, *32*, 2109. Smit, W. A.; Buhanjuk, S. M.; Simonyan, S. O.; Shashkov, A. S.; Struchkov, Y. T.; Yanovsky, A. I.; Caple, R.; Gybin, A. S.; Anderson, L. G.; Whiteford, J. A. *Tetrahedron Lett.* **1991**, *32*, 2105. Rowley, E. G.; Schore, N. E. *J. Organomet. Chem.* **1991**, *413*, C5. Thommen, M.; Gerber, P.; Keese, R. *Chimia* **1991**, *45*, 21. Castro, J.; Sörensen, H.; Riera, A.; Morin, C.; Moyano, A.; Pericàs, M. A.; Greene, A. E. *J. Am. Chem. Soc.* **1990**, *112*, 9388. de Meijere, A.; Wessjohann, L. *Synlett* **1990**, 20. Dauben, W. G.; Kowalczyk, B. A. *Tetrahedron Lett.* **1990**, *31*, 635. Price, M. E.; Schore, N. E. *J. Org. Chem.* **1989**, *54*, 5662. Magnus, P.; Slater, M. J.; Principe, L. M. *J. Org. Chem.* **1989**, *54*, 5148. Price, M. E.; Schore, N. E. *Tetrahedron Lett.* **1989**, *30*, 5865. Schore, N. E.; Rowley, E. G. *J. Am. Chem. Soc.* **1988**, *110*, 5224. Mulzer, J.; Graske, K.-D.; Kriste, B. *Justus Liebigs Ann. Chem.* **1988**, 891. Almansa, C.; Moyano, A.; Serratosa, F. *Tetrahedron* **1988**, *44*, 2657. Almansa, C.; Carceller, E.; García, M. L.; Torrents, A.; Serratosa, F. *Synth. Commun.* **1988**, 381. Magnus, P.; Becker, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 7495. Sampath, V.; Lund, E. C.; Knudsen, M. J.; Olmstead, M. M.; Schore, N. E. *J. Org. Chem.* **1987**, *52*, 3595. Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* **1987**, *52*, 1483. Schore, N. E.; Knudsen, M. J. *J. Org. Chem.* **1987**, *52*, 569. Billington, D. C.; Kerr, W. J.; Pauson, P. L. *J. Organomet. Chem.* **1987**, *328*, 223. Hua, D. H.; Coulter, M. J.; Badejo, I. *Tetrahedron Lett.* **1987**, *28*, 5465. Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3835. Carceller, E.; García, M. L.; Moyano, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron* **1986**, *42*, 1831. La Belle, B. E.; Knudsen, M. J.; Olmstead, M. M.; Hope, H.; Yanuck, M. D.; Schore, N. E. *J. Org. Chem.* **1985**, *50*, 5215. Montãna, A.-M.; Moyano, A.; Pericas, M. A.; Serratosa, F. *Tetrahedron* **1985**, *41*, 5995. Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861. Carceller, E.; Centellas, V.; Moyano, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron Lett.* **1985**, *26*, 2475. Kenaniyan, S.; Apel, M.; Richmond, J. P.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 770. Knudsen, M. J.; Schore, N. E. *J. Org. Chem.* **1984**, *49*, 5025. Daalman, L.; Newton, R. F.; Pauson, P.

L.; Taylor, R. G.; Wadsworth, A. *J. Chem. Res.* **1984**, *(S)* 344, *(M)* 3131. Exon, C.; Magnus, P.; *J. Am. Chem. Soc.* **1983**, *105*, 2477. Billington, D. C. *Tetrahedron Lett.* **1983**, *24*, 2905. Jaffer, H. J.; Pauson, P. L. *J. Chem. Res.* **1983**, *(S)* 244, *(M)* 2201. Billington, D. C.; Pauson, P. L. *Organometallics* **1982**, *1*, 1560. Newton, R. F.; Pauson, P. L.; Taylor, R. G. *J. Chem. Res.* **1980**, *(S)* 277, *(M)* 3501.

6. Matsuo, A.; Sato, S.; Nakayama, M.; Hayashi, S. *Tetrahedron Lett.* **1974**, 3681.
7. Matsuo, A.; Sato, S.; Nakayama, M.; Hayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2652.
8. Nakayama, M.; Ohira, S.; Shinke, S.; Matsushita, Y.; Matsuo, A.; Hayashi, S. *Chem. Lett.* **1979**, 1245.
9. Speicher, A.; Eicher, T. *Synthesis* **1995**, 998.
10. Billington, D. C.; Helps, I. M.; Pauson, P. L.; Thomson, W.; Willison, D. *J. Organomet. Chem.*, **1988**, *354*, 233.
11. Some of the results presented here have been the subject of two short preliminary publications: (a) Johnstone, C.; Kerr, W. J.; Lange, U. *J. Chem. Soc., Chem. Commun.* **1995**, 457. (b) Gordon, A. R.; Johnstone, C.; Kerr, W. J. *Synlett* **1995**, 1083.
12. (a) Cocker, W.; Lauder, H. St. J.; Shannon, P. V. R. *J. Chem. Soc., Perkin Trans. 1* **1975**, 332. (b) Hammond, G. B.; Cox, M. B.; Wiemer, D. F. *J. Org. Chem.* **1990**, *55*, 128.
13. Zakharkin, L. I.; Khorlina, I. M. *J. Gen. Chem. USSR* **1964**, *34*, 1021.
14. Brown, H. C.; Cha, J. S.; Yoon, N. M.; Nazer, B. *J. Org. Chem.* **1987**, *52*, 5400.
15. Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.
16. Bestmann, H. J.; Li, K. *Chem. Ber.* **1982**, *115*, 828. Bestmann, H. J.; Frey, H. *Justus Liebigs Ann. Chem.* **1980**, 2061. Ramirez, F.; Desai, N. B.; McKelvie, N. *J. Am. Chem. Soc.* **1962**, *84*, 1745.
17. These novel conditions for carbonyl deprotection have now been developed and provide a convenient mild, neutral and anhydrous technique for the selective cleavage of ketals and acetals. This methodology is the subject of a recent communication: Johnstone, C.; Kerr, W. J.; Scott, J. S. *J. Chem. Soc., Chem. Commun.* In Press.
18. This method proved to be excellent for preparing small quantities of dibromo alkene **11**. Unfortunately, the control over the concentration of CBr_4 in the reaction mixture is diminished when the reaction is carried out on multigram scale, and again the ketodibromo olefin **10** is formed as a by-product. Thankfully, this material can be reprotected in good yield, under acid-catalysed (*p*-TSA) dehydrating conditions with ethylene glycol.
19. Billington, D. C.; Bladon, P. ; Helps, I. M.; Pauson, P. L.; Thomson, W.; Willison, D. *J. Chem. Res.* **1988**, *(S)* 326, *(M)* 2601.
20. Shen, J.-K.; Gao, Y.-C.; Shi, Q.-Z.; Basolo, F. *Organometallics*, **1989**, *8*, 2144. Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1975**, 829. Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336. Alper, H.; Edward, J. T. *Can. J. Chem.* **1970**, *48*, 1543.
21. More recently hydroxylamines have also been shown to be good decarbonylating agents of metal carbonyl derivatives: Maksakov, V. A.; Ershova, V. A. *J. Organomet. Chem.* **1995**, *485*, 69.
22. Other than the examples given in the communications relevant to this study (ref. 11(a) & (b)) see: (a) Kerr, W. J.; Kirk, G. G.; Middlemiss, D. *Synlett* **1995**, 1085. (b) Hay, A. M.; Kerr, W. J.; Kirk, G. G.; Middlemiss, D. *Organometallics* **1995**, *14*, 4986.

23. Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289. Jeong, N.; Chung, Y. K.; Lee, B. Y.; Lee, S. H.; Yoo, S.-E. *Synlett.* **1991**, 204. Chung, Y. K.; Lee, B. Y.; Jeong, N.; Hudecek, M.; Pauson, P. L. *Organometallics*, **1993**, *12*, 220. Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199.
24. Billington, D. C.; Kerr, W. J.; Pauson, P. L. *J. Organomet. Chem.* **1988**, *341*, 181.
25. Jaffer, H. J. *Ph.D. Thesis*, University of Strathclyde 1982.
26. Johnson, C. R.; Tait, B. D. *J. Org. Chem.* **1987**, *52*, 281. Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Mita, T.; Hatanaka, Y.; Yokoyama, M. *J. Org. Chem.* **1984**, *49*, 3904.
27. Greene, T. W.; Wuts, P. G. M. *Protecting Groups in Organic Synthesis*; Wiley and Sons, Inc.: New York, 2nd edn., 1991.
28. (a) Denis, J.-N.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1006. (b) Olah, G. A.; Husain, A.; Singh, B. P.; Mehrotra, A. K. *J. Org. Chem.* **1983**, *48*, 3667. (c) Jung, M. E.; Andrus, W. A.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 4175. (d) Gros, P.; Le Perchec, P.; Senet, J.-P. *J. Chem. Res.* **1995** *(S)* 196. (e) Wu, S. H.; Biao, D. Z. *Synth. Commun.* **1994**, *24*, 2173. (f) Ma; S.; Venanzi, L. M. *Tetrahedron Lett.* **1993**, *34*, 8071. (g) Chang, C.; Chu, K. C.; Yue, S. *Synth. Commun.* **1992**, *22*, 1217. (h) Mandal, A. K.; Shrotri P. Y.; Ghogare, A. D. *Synthesis* **1986**, 221. (i) Kim, K. S.; Song, Y. H.; Lee, B. H.; Hahn, C. S. *J. Org. Chem.* **1986**, *51*, 404. (j) Lipshutz, B. H.; Pollart, D.; Monforte, J.; Kotsuki, H. *Tetrahedron Lett.* **1985**, *26*, 705. (k) Balme, G.; Goré, J. *J. Org. Chem.* **1983**, *48*, 3336. (l) Lipshutz, B. H.; Harvey, D. F. *Synth. Commun.* **1982**, *12*, 267. (m) Bowers, A.; Cuéllar Ibáñez, L.; Ringold, H. J. *Tetrahedron* **1959**, *7*, 138. (n) Nishiguchi, T.; Ohosima, T.; Nishida, A.; Fujisaki, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1121. (o) Barton, D. H. R.; Magnus, P. D.; Smith, G.; Streckert, G.; Zurr, D. *J. Chem. Soc., Perkin Trans. 1* **1972,** 542. (p) Barton, D. H. R.; Magnus, P. D.; Smith, G.; Zurr, D. *J. Chem. Soc., Chem. Commun.* **1971**, 861. (q) Oku, A.; Kinugasa, M.; Kamada, T. *Chem. Lett.* **1993**, 165. (r) Tanemura, K.; Suzuki, T.; Horaguchi, T. *J. Chem. Soc., Chem. Commun.* **1992**, 979. (s) Kametani, T.; Kondoh, H.; Honda, T.; Ishizone, H.; Suzuki, Y.; Mori, W. *Chem. Lett.* **1989**, 901. (t) Huet, F.; Lechevalier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63. (u) Sterzycki, R. *Synthesis* **1979**, 724.
29. Ward, D. E.; Rhee, C. K.; Zoghaib, W. M. *Tetrahedron Lett.* **1988**, *29*, 517. It is also worth noting that diketone **25** was selectively reduced to **26** in an excellent 93% using the alternative conditions reported in this paper ($NaBH_4$, CH_2Cl_2, MeOH, -70 °C). However, this transformation under these conditions proved to be notoriously irreproducible.
30. Pattenden, G.; Whybrow, D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1046. Pattenden, G.; Whybrow, D. *Tetrahedron Lett.* **1979**, 1885.
31. Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639.
32. Crombie, L.; Kneen, G.; Pattenden, G.; Whybrow, D. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1711.
33. Greenfield, H.; Sternberg, H. W.; Friedel, R. A.; Wotiz, J. H.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 120.
34. Piers, E.; Wong, T.; Ellis, K. A. *Can, J. Chem.* **1992**, *70*, 2058.
35. Denmark, S. E.; Harmata, M. A.; White, K. S. *J. Org, Chem.* **1987**, *52*, 4031.

36. Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 3112.
37. Cohen, T.; Kosarych, Z.; Suzuki, K.; Yu, L.-C. *J. Org. Chem.* **1985**, *50*, 2965.

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