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Insertion of alkynes into diterpenoid chromium aminocarbenes: synthesis of ring-C aromatic steroidal analogues

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Abstract

The insertion of alkyl- or aryl-substituted alkynes into chromium aminocarbenes derived from podocarpic acid gives good to excellent yields of cyclopentaannulated products. The presence of a heteroatom bonded directly to the alkyne lowers the yield of the indanones. Although no steroidal derivatives could be isolated from the use of acetylene or its synthons, the electron-deficient alkyne ethyl 4,4-dimethylpentyn-2-oate gave a good yield, as did ethynylferrocene. Novel diterpenoid ferrocenyl quinones were synthesised by reacting diterpenoid chromium alkoxycarbenes with ethynylferrocene. © 2001 Elsevier Science B.V. All rights reserved.

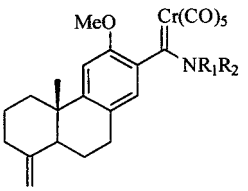
Keywords: Chromium; Aminocarbene; Diterpenoid; Alkyne; Cyclopentaannulation; Steroidal

1. Introduction

Steroids containing an aromatic ring C are relatively rare, although some have been isolated from sediments and petroleum [1]. Several have displayed fungistatic activity, while others, differing in structure only slightly from that of the cyclopentanoperhydrophenanthrene steroids, are potentially a source of anti-fertility agents [2]. Viridin [3,4], which possesses an aromatic C-ring, is a steroidal anti-fungal metabolite of the fungus *Giocladium virens*. Our previous experiences in the transformation of derivatives of podocarpic acid into ring-C aromatic steroidal analogues [5–11] provided the impetus to investigate a route using diterpenoid chromium aminocarbenes.

2. Results and discussion

We have recently reported the synthesis of six podocarpane chromium aminocarbenes **1**–**6**, possessing an exocyclic 4(18)-alkene [12]; prior oxidative decarboxylation of podocarpic acid to give this alkene was desirable, since further functionalisation of the steroidal A-ring could then be achieved using the *exo* methylene group as a chemical handle. Steroidal natural products possessing a 4(18)-alkene, albeit without an aromatic ring C, have been isolated [13–15] from natural sources, and one has shown anti-inflammatory properties in rats [16].



1: $R_1 = R_2 = H$ **4**: $R_1, R_2 = (CH_2)_2$
2: $R_1 = H, R_2 = Me$ **5**: $R_1, R_2 = (CH_2)_4$
3: $R_1 = R_2 = Me$ **6**: $R_1, R_2 = (CH_2)_2O(CH_2)_2$

Heteroatom-stabilised chromium carbene complexes possessing a π system adjacent to the carbene carbon atom are of particular synthetic value, since they allow for novel types of cyclisation reactions in which the chromium moiety acts as a template for annulation of the carbene ligand. There are relatively few examples of the formation of five-membered rings from the reaction of alkynes with aminocarbenes [17–20], since the high thermal stability of the latter often results in either low

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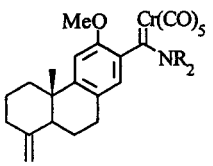
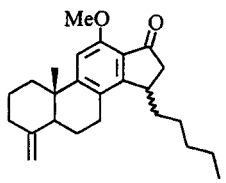
yields of the carbene annulation products or in uncontrolled loss of the transition metal [21]. The reactions are generally performed by heating the alkyne and the chromium aminocarbene in refluxing dimethylformamide (DMF) under nitrogen. The use of DMF as solvent generally affords high yields of cyclopentaannulation products [22,23], and the formation of side products is minimised compared with the use of either benzene or THF as solvent [23]. Interestingly, the product distribution has also been found to be dependent on the nature of the α,β-unsaturated substituent on the carbene; insertion of alkynes into (furyl)aminocarbenes gives a mixture of benzannulation, cyclopentaannulation and bisfuran products [24], while (aryl)aminocarbenes give only cyclopentaannulated products.

In the present work, we sought initially to establish that cyclopentaannulation would in fact occur using tricyclic podocarpane chromium aminocarbenes, and then to study the variation in the yield of the tetracyclic product with respect to the substituent(s) on the nitrogen atom. Thus, the thermolysis of each of the aminocarbenes **1**–**6** with hept-1-yne in refluxing DMF gave 12-methoxy-4-methylene-15ζ-pentyl-18-nor-5α-androsta-8,11,13-trien-17-one (**7**) (Table 1). It was observed empirically that reactions during which the solution stayed clear and pale orange resulted in high yields of insertion–cyclisation products, while those which turned a cloudy brown or orange-brown gave only low yields. In all cases, both C(15) epimers of **7** were formed in equal amounts, as shown by the presence in the ^{1}H-NMR spectrum of signals due to H(11) at 6.76 and 6.78 ppm, and by resonances due to C(17) at 204.3 and 204.6 ppm in the ^{13}C-NMR spectrum. The incorporation of a pentyl chain was confirmed by the presence of signals due to a methyl group at 14.0 ppm and methylene groups at 24.4, 27.1 (one epimer), 27.6 (one epimer), 31.8 and 34.3 ppm. The molecular formula was confirmed by the mass spectrum ($M^{+\bullet}$, 366.2551, $C_{25}H_{34}O_2$), and expulsion of methyl, ethyl, butyl and pentyl radicals was observed from the molecular ion.

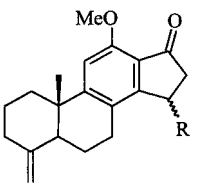
Table 1
Yield of steroidal analogue **7** vs amino substituent(s)





NR_2	(%)
NH_2	17
NHMe	22
NMe_2	51
	0
	7
	75

The data in Table 1 show that increasing methylation on the nitrogen increases the yield of the steroidal analogue. Furthermore, the morpholino-substituted carbene **6** gives the highest yield of the desired product. The previous argument [25] that increasing the steric bulk of the amino group shields the chromium from reactions leading to decomposition is reasonable considering the set of dihydroamino- (**1**), methylamino- (**2**), dimethylamino- (**3**) and morpholino- (**6**) substituted carbenes. However, the aziridinyl- (**4**) and pyrrolidinyl- (**5**) substituted carbenes gave results which did not fit this pattern. For insertion of either an alkyne or an alkene [25], 13-methoxypodocarpane chromium pyrrolidinocarbenes give less than satisfactory yields in comparison with those reported for simpler systems [22]. It is therefore suspected that there is some structural or electronic factor that decreases the stability of either the *ortho*-methoxyaryl pyrrolidinocarbenes or of intermediates arising from them during the insertion sequence. The lack of insertion products from the reaction of the aziridinylcarbene **4** with hept-1-yne was unexpected, since the analogous 19-methoxy complex gave reasonable yields from the insertion of an alkene [25]. The morpholinocarbene **6** gave the highest yield of the indanone **7**, and was therefore used in all subsequent reactions with other alkynes.

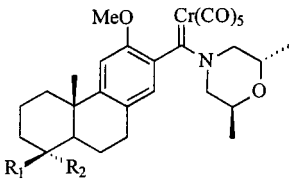


7: R = $(CH_2)_4CH_3$
8: R = $C(CH_3)_3$
9: R = CH_3

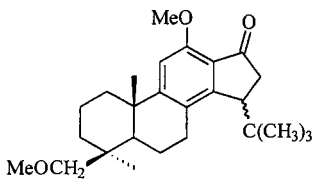
Thus, reaction of **6** with 3,3-dimethylbutyne gave 12-methoxy-4-methylene-15ζ-(1,1-dimethylethyl)-18-nor-5α-androsta-8,11,13-trien-17-one (**8**) (53%) as a (1:1) mixture of epimers. Reaction of **6** with propyne in a sealed pressure bottle (300 kPa, 125°C) gave 12-methoxy-4-methylene-15ζ-methyl-18-nor-5α-androsta-8,11,13-trien-17-one (**9**) (50%), also as a (1:1) mixture of epimers. Doublets of doublets at 2.29 and 2.32 ppm in the ^{1}H-NMR spectrum of **9** were assigned to one of the H(16) hydrogens in each epimer, but the signals due to

the other H(16) proton were obscured by those due to H(7ax) and H(7eq). Doublets of quartets at 3.35 and 3.40 ppm were characteristic of H(15). The ^{13}C-NMR spectrum showed signals at 31.9 and 31.9(5) ppm assigned to C(15) and a signal at 47.4 ppm assigned to C(16).

We sought to investigate further the variation in the yield of the cyclopentaannulated product by changing the carbene substituent from morpholino to *trans*-2,6-dimethylmorpholino, which has been used successfully in aminocarbene chemistry [26]. Reaction of 3,3-dimethylbutyne with the *trans*-2,6-dimethylmorpholinocarbene (**10**) [12] gave 12-methoxy-4-methylene-15ζ-(1,1-dimethylethyl)-18-nor-5α-androsta-8,11,13-trien-17-one (**8**) (20%) as a (1:1) mixture of epimers. Reaction of **10** with either hept-1-yne or propyne gave the 15ζ-pentyl and 15ζ-methyl androstane analogues, **7** (17%) and **9** (14%), respectively, each as a (1:1) mixture of epimers. Reaction of 3,3-dimethylbutyne with the analogous 19-methyl ether carbene **11** gave 12-methoxy-4β-methoxymethyl-4α,15ζ-dimethyl-18-nor-5α-androstan-8,11,13-trien-17-one (**12**) (8%) as a (1:1) mixture of epimers which could be separated by chromatography. That is, lower yields of the indanone derivative were obtained using the sterically more encumbered 2,6-dimethylmorpholino carbene. Since the morpholinocarbene **6** also gives superior yields compared with aminocarbenes **1**–**5** possessing less bulky groups, there is apparently an optimum size for the nitrogen substituent(s).



10: $R_1 = R_2 = CH_2$
11: $R_1 = MeOCH_2$, $R_2 = Me$



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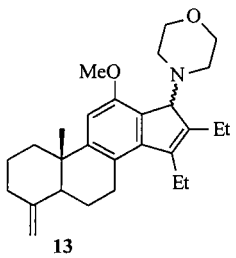

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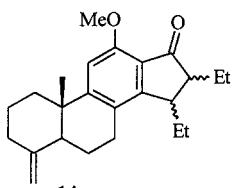

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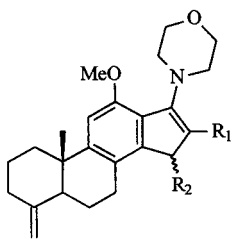
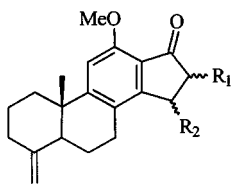
Dialkyl alkynes have been reported to give good yields of insertion products, an allylamine derivative being favoured when a morpholinocarbene is used while pyrrolidinocarbenes give the derived indanone [22]. Similar results were observed in the present work. Thermolysis of the morpholinocarbene **6** with hex-3-yne gave the allylamine derivative 12-methoxy-15,16-diethyl-4-methylene-17ζ-morpholino-18-nor-5α-androsta-8,11,13,15-tetraene (**13**) (66%). The location of the double bond was determined by 1D- and 2D-NMR experiments. The singlet at 4.05 ppm in the ^{1}H-NMR spectrum was assigned to H(17), and a COSY spectrum showed no coupling of this signal with the protons of either ethyl group. Broad signals at 2.70 (NCH_2) and 3.64 ppm (OCH_2), together with resonances at 49.8 (NCH_2) and 68.3 ppm (OCH_2) in the ^{13}C-NMR spectrum confirmed the presence of the morpholino group, and a signal at 69.4 ppm in the latter spectrum was assigned to C(17). The allylamine **13** was relatively unstable, undergoing a 1,3-hydrogen shift followed by enamine hydrolysis to give 12-methoxy-4-methylene-15ζ,16ζ-diethyl-18-nor-5α-androsta-8,11,13-trien-17-one (**14**). The indanone derivative **14** showed strong absorption due to a carbonyl group in the infrared spectrum at 1702 cm^{-1}, and signals in the ^{13}C-NMR spectrum at 207.3 and 207.4 ppm were assigned to C(17). Overlap of the signals due to H(15) and H(16) with others in the ^{1}H-NMR spectrum precluded analysis of the stereochemistry at C(15) and C(16).

Reaction of diphenylethyne with the morpholinocarbene **6** gave 12-methoxy-15ζ,16-diphenyl-4-methylene-17-morpholino-18-nor-5α-androsta-8,11,13,16-tetraene (**15**) in excellent yield (85%). An absorption at 1654 cm^{-1} in the infrared spectrum indicated an enamine double bond, and a broad singlet at 4.51 ppm in the ^{1}H-NMR spectrum, consistent with the chemical shift expected for a hydrogen bound to a doubly benzylic carbon, was assigned to H(15). Therefore, the enamine **15** was formed, rather than an allylamine.

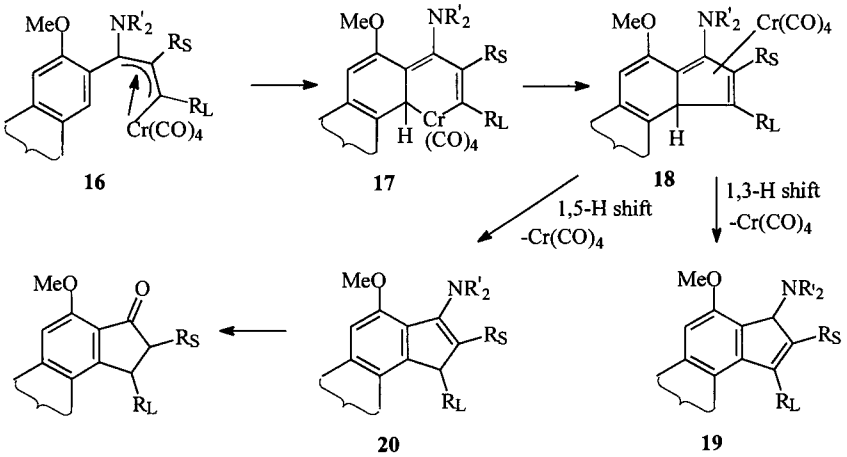


15: $R_1 = R_2 = Ph$
22: $R_1 = Ph$, $R_2 = SiMe_3$
23: $R_1 = Ph$, $R_2 = SMe$



21: $R_1 = Ph$, $R_2 = H$
24: $R_1 = H$, $R_2 = Ph$

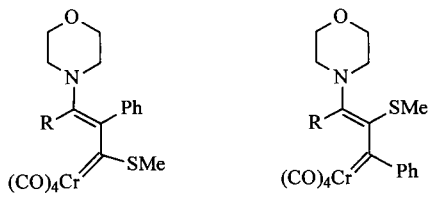
Interestingly, both enamine and allylamine derivatives have been isolated from the reaction of diphenylethyne with a morpholinocarbene [22]. The formation of an allylamine or an indanone (via an enamine) is dependent on whether the cyclopentaannulated intermediate undergoes either a 1,3- or a 1,5-hydride shift. Initial decarbonylation of the pentacarbonyl(aminocarbene) leads to a coordinatively unsaturated tetracarbonyl complex [27,28]. Insertion of the alkyne into the Cr–$C_{carbene}$ bond (Scheme 1) then gives the coordinatively saturated η^3-arylallylidene intermediate **16** [29,30], ring closure of which without CO insertion gives the chromacyclohexadiene **17**. Reductive



Scheme 1.

elimination affords the cyclopentaannulated intermediate **18**, which can undergo either a 1,3- or a 1,5-hydrogen shift to give either an allylamine **19** or an enamine **20**, respectively [18,20,31]. If the alkyne is unsymmetrical, the smaller alkyne substituent (R_S) is orientated over the carbene carbon. Therefore, in the present work the larger substituent (R_L) is expected to be directed to C(15) in the steroidal derivative.

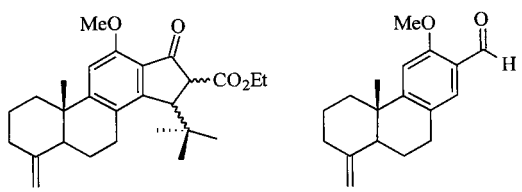
In principle, the attachment of a heteroatom to ring D could be achieved using a heteroatom-substituted alkyne. Initial studies focussed on alkynes having electron-rich heteroatom substituents, thermolysis of either (2-phenyl)trimethylsilylethyne or 1-methylthio-2-phenylethyne with the morpholinocarbene **6** giving 12-methoxy-16ζ-phenyl-4-methylene-17-morpholino-18-nor-5α-androsta-8,11,13,15-tetraene (**21**) in low yield. Neither the trimethylsilyl nor the methylthio group was retained, their reductive cleavage presumably involving a chromium hydride species. The enamine intermediates, **22** or **23**, underwent facile hydrolysis. Strong absorption at 1707 cm^{-1} in the infrared spectrum of **21** confirmed the presence of the C(17) ketone, as did signals at 203.8 and 204.1 ppm in the ^{13}C-NMR spectrum. As expected, insertion of (2-phenyl)trimethylsilylethyne into the aminocarbene proceeded with the larger group (Me_3Si) over the carbonylchromium moiety, leading to the tetracycle **21** with the phenyl group at C(16) (Scheme 1). Since a phenyl group is larger than a methylthio group, the product from 1-methylthio-2-phenylethyne was expected to be indanone **24**, having the phenyl group at C(15), rather than its 16-phenyl regioisomer **21**. This regiochemistry suggests that the methylthio group can stabilise the intermediate methylthio(enamino)carbene **25** electronically [32,33], in preference to the phenyl(enamino)carbene **26**, which would be produced if the insertion sequence was under steric control. Similar control of regiochemistry by heteroatoms has also been observed in the insertion reactions of stannylalkynes with chromium alkoxycarbenes [33].



R = 13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraenyl

Steroidal derivatives of most relevance biologically would generally not be substituted at either C(15) or C(16), and their synthesis using the present methodology would require insertion of either acetylene or a synthon of acetylene. However, thermolysis of the morpholinocarbene **6** with ethyne or trimethylsilylethyne or tributylstannylethyne gave intractable black tars; no insertion products were isolated.

Previous work has shown that the yield from an insertion reaction of an aminocarbene with an alkyne bearing an electron-deficient substituent [22,30] is dependent strongly on the choice of the alkyne [22]. In the event, heating ethyl 4,4-dimethylpentyn-2-oate with the carbene **6** gave 15ζ-(1,1-dimethylethyl)-12-methoxy-4-methylene - 16ζ - (carboxyethyl) - 18 - nor - 5α - androsta-8,11,13-trien-17-one (**27**) in good yield (54%).



The infrared spectrum showed strong absorptions due to carbonyl groups at 1734 ($C{=}O_{ester}$) and 1709 cm^{-1} ($C{=}O_{ketone}$). Signals in the ^{13}C-NMR spectrum at 168.8 and 168.9 ppm were assigned to the ester car-

bonyl carbon while those at 196.3 and 196.5 ppm were assigned to C(17). Although the ^{13}C-NMR spectrum showed at most two signals for each carbon, suggesting that only two steroidal derivatives had formed, the ^{1}H-NMR spectrum indicated that at least three were present. Singlets at 3.51 and 3.56 ppm were assigned to H(15) of two *trans* isomers, while a doublet at 3.81 ppm ($J = 2.9$ Hz) was assigned to H(15) of the *cis* isomer(s). The integration sum of these three signals was equal to that of the two-line signal at 3.72 ppm, which was assigned to the overlapping signals due to H(16) in all three stereoisomers. One of the *trans* isomers (15β-*t*-Bu, 16α-CO_2Et) crystallised from $CDCl_3$–hexanes. X-ray diffraction analysis (Fig. 1) located the *t*-butyl (larger) group at C(15) and the ester (smaller) group at C(16), regiochemistry which is consistent with the *t*-butyl group being positioned over chromium during coordination-insertion of the alkyne, thereby minimising unfavourable interactions between it and the diterpenoid residue.

The isolation also of 13-formyl-12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene (**28**) from this reaction is thought to reflect oxidative demetallation of the carbene **6** followed by reduction of the morpholino carboxamide by a chromium hydride species, leading to the aldehyde.

There is considerable medicinal and biochemical interest in steroidal derivatives bearing organometallic substituents, particularly in the treatment of hormone-dependent cancers [34]. Reaction of ethynylferrocene [35] with the morpholinocarbene **6** gave 12-methoxy-4-methylene-15ζ-ferrocenyl-18-nor-5α-androsta-8,11,13-trien-17-one (**29**) (50%) as a mixture (1:1) of epimers. The molecular ion was observed at m/z 480.1751 ($C_{30}H_{32}FeO_4$) and was the only significant peak in the mass spectrum. An intense peak at 1704 cm^{-1} in the infrared spectrum confirmed the presence of the ketone at C(17). The ^{13}C-NMR spectrum included a signal at 68.6 ppm which was assigned to the unsubstituted cyclopentadienyl ring of the ferrocene substituent.

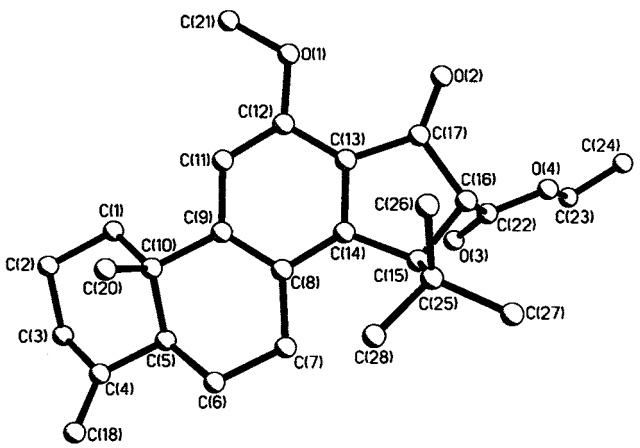
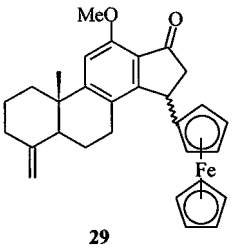


Fig. 1. The atomic arrangement in **27**.



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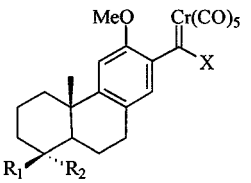
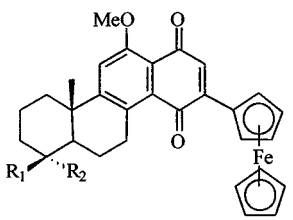
The benzannulation reaction of ethynylferrocene with two diterpenoid chromium alkoxycarbenes was also investigated, since molecules bearing both donor and acceptor sites are of current interest due to their electron-transfer properties and as potential candidates for non-linear optical materials [36–38]. Ferrocene serves as a good electron donor as well as having a reversible electrochemical redox couple. 1,4-Benzoquinones are good electron acceptors, the redox potentials being tunable by varying the electronic properties of substituents. Combining these two structural units therefore provides molecules with potentially useful electrochemical and optical properties [39].





30: R_1= $MeOCH_2$, R_2 = Me, X = OMe
32: R_1, R_2 = CH_2, X = OMe
34: R_1= $MeOCH_2$, R_2 = Me, X = SEt

31: R_1= $MeOCH_2$, R_2 = Me
33: R_1, R_2 = CH_2

Therefore, ethynylferrocene and pentacarbonyl-[(methoxy)(13 - (12,19 - dimethoxypodocarpa - 8,11,13-triene))carbene]chromium (**30**) were refluxed in THF for 25 h. The crude 1,4-diphenol product was oxidised with lead dioxide to give [6a*R*-(1α,4α,6αβ,7α,10aα)]-3-ferrocenyl - 1,4,5,6,6a,7,8,9,10,10a - decahydro - 12-methoxy-7-methoxymethyl-7,10a-dimethylchrysene-1,4-dione (**31**) (57%). Singlets at 6.85 and 7.25 ppm in the ^{1}H-NMR spectrum were assigned to the quinone hydrogen H(2) and to H(11), respectively. Signals due to the two quinone carbonyls were observed at 185.5 and 188.0 ppm in the ^{13}C-NMR spectrum, and a resonance at 70.2 ppm was assigned to the carbons of the unsubstituted cyclopentadienyl ring. Similarly, pentacarbonyl[(methoxy)(13 - (19 - norpodocarpa - 4(18),8,11,13-tetraene) carbene]chromium (**32**) gave [6a*R*-(1α,4α,6αβ,7α,10aα)] - 3 - ferrocenyl - 1,4,5,6,6a,7,8,9,10,10a - decahydro - 12 - methoxy - 7 - methylene - 10a - methylchrysene-1,4-dione (**33**) (57%). Both of the ferrocenyl diterpenoid 1,4-quinones **31** and **33** were deep green in colour. Cyclic voltammetry (0.1 mol l^{-1} solution of Bu_4NCl in MeCN, Pt disc as working electrode,

Table 2
Crystal data and structure refinement parameters for **27**

Empirical formula	$C_{27}H_{36}O_4$
Formula weight	424.56
Temperature (K)	203(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	16.0838(3)
b (Å)	17.5313(3)
c (Å)	8.6826(2)
V (Å^3)	2448.23(8)
Z	4
$D_{calc.}$ (g cm^{-3})	1.152
Absorption coefficient (mm^{-1})	0.076
$F(000)$	920
Crystal size (mm)	$0.88 \times 0.78 \times 0.06$
2θ Range (°)	1.72–25.00
Reflections collected	20457
Observed data	3298
Independent reflections	4305 [$R_{int} = 0.0385$]
Max/min transmission	0.9955, 0.9364
Refinement method	Full-matrix least-squares on F^2
R_1 (observed data)	0.0520, $wR^2 = 0.1227$
wR_2 (all data)	$R_1 = 0.0737$, $wR^2 = 0.1357$
Goodness-of-fit on F^2	1.060
Weighting scheme	calc. $w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.5456P]$ where $P = (F_o^2 + 2F_c^2)/3$
Absolute structure parameter	0.9(17)
Largest difference peak and hole (e Å^{-3})	0.24 and −0.189

Pt wire as auxiliary electrode, ferrocene as internal standard) indicated that they are electron-rich, having oxidation potentials of +0.107 and +0.104 V, respectively.

Since it is possible to tune redox properties by varying the quinone, and since the use of thiocarbenes in synthesis is largely unexplored, it was of interest to investigate the potential preparation of a 1,4-hydroxythiol rather than that of a hydroquinone. Thus, treatment of the chromium methoxycarbene **30** with ethanethiol in the presence of Na_2CO_3 gave pentacarbonyl[(ethylthio)(13 - (12,19 - dimethoxypodocarpa-8,11,13-triene))carbene]chromium (**34**) (74%). The thiocarbene **34** was then heated under reflux in THF with ethynylferrocene, acetic anhydride, triethylamine, and $BF_3{\cdot}OEt_2$ [40] for 19 h. Although treatment with lead dioxide was not attempted due to the complexity (TLC) of the crude mixture and the uncertain stability of the monothioquinone or other products towards oxidation, the ferrocenylquinone **31** was isolated in very low yield (3%). Further investigations using thiocarbenes were not undertaken.

2.1. X-ray crystal structure of **27**

Data were collected on a Siemens SMART area detector diffractometer using 0.3° frames and profile fitting. Lorentz, polarisation and absorption corrections [41] were applied and equivalent reflections averaged to give 4305 unique data. Unit cell parameters were obtained by least-squares fit to all data with $I > 10\sigma(I)$. The structure was solved by direct methods [42] and refined by full-matrix least-squares on F^2 [43]. Hydrogen atoms were placed geometrically and refined with a riding model, including free rotation for methyl groups, with thermal parameter 20% (50% for methyl groups) greater than U_{iso} of the carrier atom. All non-hydrogen atoms were refined with anisotropic thermal parameters. Refinement converged to R_1 (observed data) 0.0520. Crystal data and refinement parameters are given in Table 2 and the structure, including the absolute configuration, is shown in Fig. 1.

2.2. Summary

We have shown that ring-C aromatic derivatives of 5α androstan-17-one are accessible in high yield from the thermally promoted cyclopentaannulation reaction of podocarpane chromium morpholinocarbenes with alkyl- or aryl-substituted alkynes, ethyl 4,4-dimethylpentyn-2-oate, or ethynylferrocene. The analogous chromium methoxycarbenes reacted with ethynylferrocene to give novel ferrocenylquinones.

3. Experimental

Structures were assigned using HRMS ($\Delta < 5$ ppm) for the molecular formula, in combination with complete assignment of the ^{1}H- and ^{13}C-NMR spectra and selected infrared data.

3.1. Ethyl 4,4-dimethylpentynoate

Butyllithium (4.85 ml, 2.5 mol l^{-1}, 12.1 mmol) was added to a stirred solution of 3,3-dimethylbutyne (1.00 g, 12.2 mmol) in THF (10 ml) at −78°C. After 5 min, this solution was added dropwise to a solution of ethyl chloroformate (2.32 ml, 24.4 mmol) in THF (2 ml) at −23°C. The mixture was warmed to room temperature (r.t.), poured onto saturated aqueous ammonium chloride, and then extracted with diethyl ether (3×30 ml). The organic extracts were combined and the solvent was removed in vacuo. Kugelrohr distillation (5 mmHg, 85°C) gave ethyl 4,4-dimethylpentynoate (1.292 g, 69%) as a colourless liquid. IR (cm^{-1}): ν_{max} 1711 (C=O), 1275, 1225. ^{1}H-NMR (δ ppm): 1.29 (s, $C(CH_3)_3$); 1.31 (t, [$J = 6.9$ Hz], CH_2CH_3); 4.10–4.27 (m, OCH_2CH_3). ^{13}C-NMR (δ ppm): 13.9 (OCH_2CH_3); 29.8 ($C(CH_3)_3$);

30.6 ($C(CH_3)_3$); 61.6 (OCH_2CH_3); 63.6 ($C{\equiv}CCO_2Et$); 67.5 ($C{\equiv}CCO_2Et$).

3.2. 1-Methylthio-2-phenylethyne

Butyllithium (15.8 ml, 1.16 mol l^{-1}, 18.3 mmol) was added to a solution of phenylethyne (2.0 ml, 18.2 mmol) in THF (40 ml) at −78°C, and dimethyl disulfide (1.8 ml, 20.0 mmol) was added to the yellow-brown solution. The mixture was warmed to r.t., water (50 ml) was added, and the product was extracted with ether (150 ml). The organic extract was dried ($MgSO_4$) and the solvent was removed in vacuo. Column chromatography (hexanes) followed by Kugelrohr distillation (1.5 mmHg, 65°C) gave 1-methylthio-2-phenylethyne (2.092 g, 78%) as a pale yellow liquid. IR (cm^{-1}): ν_{max} 2927 (CH_{alkyl}), 2168 (C≡C), 1595 (C=C), 754 ($CH_{o.o.p.}$), 690 ($CH_{o.o.p.}$). ^{1}H-NMR (δ ppm): 2.45 (s, SCH_3); 7.24–7.31 (m, H_{para}, H_{meta}); 7.38–7.43 (m, H_{ortho}). ^{13}C-NMR (δ ppm): 19.3 (SCH_3); 80.8 ($C{\equiv}CSMe$); 91.7 ($C{\equiv}CSMe$); 123.3 (C_{ipso}); 127.9 (C_{para}); 128.1 (C_{meta}); 131.3 (C_{ortho}).

3.3. Reaction of pentacarbonyl[(dihydro)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (*1*) with hept-1-yne

A solution of pentacarbonyl[(dihydroamino)(13-(12-methoxy - 19 - norpodocarpa - 4(18),8,11,13 - tetraene))-carbene]chromium (**1**) (0.230 g, 0.499 mmol) in DMF (10 ml) was purged with nitrogen. Hept-1-yne (0.15 ml, 1.1 mmol) was added and the solution was heated to 120°C for 3 h. The mixture was cooled, diluted with ether (3 × 20 ml), and the organic layer was washed with water and dried ($MgSO_4$). PLC (hexanes–ether, 2:1; two elutions) gave 12-methoxy-4-methylene-18-nor-15ζ-pentyl-5α-androsta-8,11,13-trien-17-one (**7**) (31.3 mg, 17%) as a colourless oil. Found: 366.2551 [$M^{+\bullet}$]. Calc. for $C_{25}H_{34}O_2$: 366.2559 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1703 (C=O), 1597 (C=C), 1582 (C=C), 1051 (C–O–C). ^{1}H-NMR (δ ppm): 0.87 (t, [J = 6.7 Hz], $CH_2CH_2CH_3$); 0.88 (t, [J = 6.7 Hz], $CH_2CH_2CH_3$); 1.04 (s, H(20)); 1.08 (s, H(20)); 1.20–1.35 (bm, $CH_2CH_2CH_2CH_2CH_3$); 1.58 (ddd, [J = 13.0, 13.0, 4.6 Hz], H(1ax)); 1.62 (ddd, [J = 13.0, 13.0, 4.6 Hz], H(1ax)); 1.65–1.90 (m, H(2ax), H(2eq), H(6ax), $BuCH_2$); 1.95 (bdd, [J = 13.1, 6.4 Hz], H(6eq)); 2.06 (ddd, [J = 13.2, 13.2, 5.5 Hz], H(3ax)); 2.09 (ddd, [J = 13.2, 13.2, 5.5 Hz], H(3ax)); 2.20 (bd, [J = 12.4 Hz], H(5)); 2.26 (bd, [J = 12.4 Hz], H(5)); 2.28 (bd, [J = 12.3 Hz], H(1eq)); 2.40 (bd, [J = 13.1 Hz], H(3eq)); 2.41 (d, [J = 3.6 Hz], H(16) (one isomer)); 2.46 (d, [J = 3.6 Hz], H(16) (one isomer)); 2.65–2.82 (m, H(7ax), H(16) (both isomers)); 2.88 (ddd, [J = 16.5, 5.8, 1.6 Hz], H(7eq)); 2.98 (bdd, [J = 17.1, 5.0 Hz], H(7eq)); 3.20 (3 lines, [J = 8.9, 7.1 Hz], H(15)); 3.29 (3 lines, [J = 8.7, 7.7 Hz], H(15)); 3.91 (s, 12-OMe); 3.92 (s, 12-OMe); 4.63 (d, [J = 1.4 Hz], H(18)); 4.65 (d, [J = 1.3 Hz], H(18)); 4.89 (d, [J = 1.4 Hz], H(18)); 4.90 (d, [J = 1.4 Hz], H(18)); 6.76 (s, H(11)); 6.78 (s, H(11)). ^{13}C-NMR (δ ppm): 14.0 ($CH_2CH_2CH_3$); 20.7 (C(6)); 21.0 (C(6)); 22.5 (C(20)); 22.6 (C(20)); 23.5 (C(2)); 23.6 (C(2)); 24.4 ($CH_2CH_2CH_3$); 26.1 (C(7)); 27.1 ($CH_2CH_2CH_3$); 27.6 ($CH_2CH_2CH_3$); 31.8 ($CH_2CH_2CH_2CH_3$); 34.3 ($BuCH_2$); 36.0 (C(3)); 36.1 (C(3)); 37.4 (C(15)); 38.6 (C(1)); 40.6 (C(10)); 40.8 (C(10)); 44.3 (C(16)); 44.9 (C(16)); 46.9 (C(5)); 47.8 (C(5)); 55.5 (12-OMe); 106.6 (C(11)); 106.8 (C(11)); 106.9 (C(18)); 107.1 (C(18)); 122.4 (C(8)); 122.8 (C(8)); 124.1 (C(13)); 124.4 (C(13)); 149.8 (C(4)); 155.5 (C(12)); 155.6 (C(12)); 156.5 (C(9)); 156.7 (C(9)); 160.2 (C(14)); 160.3 (C(14)); 204.3 (C(17)); 204.6 (C(14)). m/z: 366 (M^+, 100), 351 (M − Me, 7), 337 (M − Et, 26); 321 (8), 309 (M − $Bu^{\bullet}$, 9); 295 (M − $C_5H_{11}^{\bullet}$, 15).

3.4. Reaction of pentacarbonyl[(methylamino)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (*2*) with hept-1-yne

A solution of pentacarbonyl[(methylamino)(13-(12-methoxy - 19 - norpodocarpa - 4(18),8,11,13 - tetraene))-carbene]chromium (**2**) (0.236 g, 0.496 mmol) in DMF (10 ml) was purged with nitrogen. Hept-1-yne was added and the solution was then heated to 120°C for 3 h. Usual workup followed by radial chromatography (hexanes–ether, 1:1) gave 12-methoxy-4-methylene-18-nor-15ζ-pentyl-5α-androsta-8,11,13-trien-17-one (**7**) (39.2 mg, 22%).

3.5. Reaction of pentacarbonyl[(dimethylamino)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (*3*) with hept-1-yne

A solution of pentacarbonyl[(dimethylamino)(13-(12-methoxy - 19 - norpodocarpa - 4(18),8,11,13 - tetraene))-carbene]chromium (**3**) (0.171 g, 0.349 mmol) in DMF (7 ml) was purged with nitrogen. Hept-1-yne (0.10 ml, 0.76 mmol) was added and the solution was heated to 120°C for 3 h. Usual workup followed by radial chromatography (hexanes–ether, 2:1) gave 12-methoxy-4-methylene-18-nor-15ζ-pentyl-5α-androsta-8,11,13-trien-17-one (**7**) (64.9 mg, 51%).

3.6. Reaction of pentacarbonyl[(aziridinyl)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (*4*) with hept-1-yne

A solution of pentacarbonyl[(aziridinyl)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (**4**) (0.268 g, 0.55 mmol) in DMF (10 ml) was purged with nitrogen. Hept-1-yne (84 μl, 0.64 mmol) was added, and the solution was heated to

120°C for 3 h. Usual workup gave an oil which was a mixture of at least 20 compounds (TLC; hexanes–ether, 1:1), all bands being of approximately equal intensity (UV).

3.7. Reaction of pentacarbonyl[(pyrrolidinyl)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (5) with hept-1-yne

A solution of pentacarbonyl[(pyrrolidinyl)(13-(12-methoxy - 19 - norpodocarpa - 4(18),8,11,13 - tetraene))-carbene]chromium (**5**) (0.214 g, 0.415 mmol) in DMF (10 ml) was purged with nitrogen. Hept-1-yne (0.15 ml, 1.1 mmol) was added and the mixture was heated to 120°C for 3 h. Extraction with ether (3 × 25 ml) followed by workup and radial chromatography (hexanes–ether, 2:1) gave 12-methoxy-4-methylene-18-nor-15ζ-pentyl-5α-androsta-8,11,13-trien-17-one (**7**) (11 mg, 7%).

3.8. Reaction of pentacarbonyl[(morpholino)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (6) with 1-hept-1-yne

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy - 19 - norpodocarpa - 4(18),8,11,13 - tetraene))-carbene]chromium (**6**) (0.280 g, 0.527 mmol) in DMF (10 ml) was purged with nitrogen. Hept-1-yne (1.14 mmol) was added and the mixture was heated to 120°C for 3 h. Usual workup and radial chromatography (hexanes–ether, 1:1) gave 12-methoxy-4-methylene-18-nor-15ζ-pentyl-5α-androsta-8,11,13-trien-17-one (**7**) (145 mg, 75%).

3.9. Reaction of pentacarbonyl[(morpholino)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (6) with 3,3-dimethylbutyne

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy - 19 - norpodocarpa - 4(18),8,11,13 - tetraene))-carbene]chromium (**6**) (0.301 g, 0.566 mmol) in DMF (10 ml) was purged with nitrogen. 3,3-Dimethylbutyne (0.30 ml, 2.4 mmol) was added and the mixture was heated to 120°C for 3.5 h. The cooled solution was diluted with ether (40 ml) and water (20 ml), and then photolysed for 24 h under a fluorescent lamp. The organic layer was washed with water (2 × 20 ml) and dried. PLC (hexanes–ether, 1:1) gave 15ζ-(1,1-dimethylethyl) - 12 - methoxy - 4 - methylene - 18 - nor - 5α-androsta-8,11,13-trien-17-one (**8**) (0.1054 g, 53%). Found: 352.2400 [$M^{+\bullet}$]. Calc. for $C_{24}H_{32}O_2$: 352.2402 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1708 (C=O), 1592 (C=C), 1580 (C=C), 1049 (C–O–C). ^{1}H-NMR (δ ppm): 0.88 (s, $C(CH_3)_3$); 0.89 (s, $C(CH_3)_3$); 1.03 (s, H(20)); 1.08 (s, H(20)); 1.59 (ddd, [J = 12.0, 12.0, 6.1 Hz], H(1ax)); 1.60 (ddd, [J = 12.0, 12.0, 6.1 Hz], H(1ax)); 1.62–1.70 (m, H(2eq)); 1.78 (qt, [J = 13.4, 4.1 Hz], H(2ax)); 1.80–1.95 (m, H(6ax), H(6eq)); 2.07 (ddd, [J = 13.4, 13.4, 5.5 Hz], H(3ax)); 2.10 (ddd, [J = 13.3, 13.3, 5.3 Hz], H(3ax)); 2.20–2.25 (m, H(5)); 2.26 (bd, [J = 11.9 Hz], H(1eq)); 2.31 (bd, [J = 11.9 Hz], H(1eq)); 2.40, bd, [J = 13.0 Hz], H(3eq)); 2.55 (ddd, [J = 17.0, 11.4, 7.4 Hz], H(7ax) (one isomer)); 2.63 (6 lines, H(16ax), H(16eq)); 2.81–2.96 (m, H(7ax) (one isomer), H(7eq)); 3.20 (dd, [J = 5.4, 2.1 Hz], H(15)); 3.26 (dd, [J = 5.6, 1.9 Hz], H(15)); 3.90 (s, 12-OMe); 3.91 (s, 12-OMe); 4.62 (d, [J = 0.9 Hz], H(18)); 4.65 (d, [J = 0.9 Hz], H(18)); 4.88 (s, H(18)); 4.90 (s, H(18)); 6.78 (s, H(11)); 6.83 (s, H(11)). ^{13}C-NMR (δ ppm): 20.8 (C(6)); 21.2 (C(6)); 22.6 (C(20)); 23.3 (C(20)); 23.4 (C(2)); 23.6 (C(2)); 26.4 (C(7)); 28.1 ($C(CH_3)_3$); 28.2 (C(7)); 28.4 ($C(CH_3)_3$); 35.8 (C(3)); 36.0 (C(3)); 36.9 ($C(CH_3)_3$); 37.6 ($C(CH_3)_3$); 38.2 (C(1)); 38.9(5) (C(1)); 40.9 (C(10)); 41.0 (C(10)); 45.0 (C(16)); 45.2 (C(16)); 47.1 (C(15)); 47.2 (C(5)); 47.8 (C(15)); 48.4 (C(5)); 55.5(0) (12-OMe); 55.5(5) (12-OMe); 106.8 (C(18)); 106.9(5) (C(11)); 107.0 (C(18)); 107.7 (C(11)); 123.4 (C(8)); 123.9 (C(8)); 125.5 (C(13)); 126.3 (C(13)); 147.9 (C(4)); 149.9 (C(4)); 154.9(9) (C(12)); 155.0(4) (C(12)); 155.9 (C(9)); 157.9 (C(14)); 158.2 (C(14)); 203.9 (C(17)); 204.1 (C(17)). m/z: 352 (M^+, 30), 296 ($M - (CH_3)_2C{=}CH_2$, 100), 295 ($M - (CH_3)_3C^{\bullet}$, 19), 281 ($296 - Me^{\bullet}$, 26), 57 ($(CH_3)_3C^+$, 23).

Repeating this reaction but omitting the photolytic decomplexation step gave 15ζ-(1,1-dimethylethyl)-12-methoxy-4-methylene-18-nor-5α-androsta-8,11,13-trien-17-one (**8**) (53%).

3.10. Reaction of pentacarbonyl[(morpholino)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (6) with propyne

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy - 19 - norpodocarpa - 4(18),8,11,13 - tetraene))-carbene]chromium (**6**) (0.256 g, 0.443 mmol) in DMF (10 ml) in a pressure bottle was purged with nitrogen and then pressurised with propyne and heated to 120°C for 1 h. Usual workup followed by PLC (hexanes–ether, 1:1) gave 12-methoxy-15ζ-methyl-4-methylene-18-nor-5α-androsta-8,11,13-trien-17-one (**9**) (69 mg, 50%) as a white foam. Found: 310.1934 [$M^{+\bullet}$]. Calc. for $C_{21}H_{26}O_2$: 310.1933 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1704 (C=O), 1598 (C=C), 1582 (C=C), 1045 (C–O–C). ^{1}H-NMR (δ ppm): 1.04 (s, H(20)); 1.09 (s, H(20)); 1.28 (d, [J = 7.0 Hz], 15-CH_3); 1.32 (d, [J = 6.9 Hz], 15-CH_3); 1.58 (ddd, [J = 12.9, 12.9, 4.7 Hz], H(1ax)); 1.65–1.90 (m, H(2ax), H(2eq), H(6ax)); 1.95 (dd, [J = 13.0, 6.2 Hz], H(6eq)); 2.06 (ddd, [J = 13.0, 13.0, 5.4 Hz], H(3ax)); 2.09 (ddd, [J = 13.3, 13.3, 5.6 Hz], H(3ax)); 2.21 (5 lines, H(5)); 2.28 (bd, [J = 10.5 Hz], H(1eq)); 2.29 (dd, [J = 2.9, 1.1 Hz], H(16) (one isomer)); 2.33 (dd, [J = 2.9,1.1 Hz], H(16) (one isomer)); 2.40 (bd, [J = 12.1 Hz], H(3eq)); 2.68–2.95 (m, H(7ax), H(7eq)

(one isomer), H(16) (both isomers)); 3.02 (dd, [$J = 17.2$, 5.2 Hz], H(7eq) (one isomer)); 3.35 (dq, [$J = 7.0$, 6.8 Hz], H(15)); 3.40 (dq, [$J = 7.0$, 6.8 Hz], H(15)); 3.63(2) (s, 12-OMe); 3.63(6) (s, 12-OMe); 4.64 (d, [$J = 1.4$ Hz], H(18)); 4.65 (d, [$J = 1.2$ Hz], H(18)); 4.89(6) (s, H(18)); 4.90 (s, H(18)); 6.76(5) (s, H(11)); 6.78 (s, H(11)). ^{13}C-NMR (δ ppm): 20.6 (C(6)); 20.8 (C(20)); 21.0 (C(6)); 22.1 (C(20)); 22.5 (15-CH_3); 22.7 (15-CH_3); 23.5 (C(2)); 23.6 (C(2)); 26.1 (C(7)); 31.9 (C(15)); 31.9(5) (C(15)); 36.0 (C(3)); 36.1 (C(3)); 38.6 (C(1)); 40.6 (C(10)); 40.8 (C(10)); 47.4 (C(16)); 47.8 (C(5)); 55.5 (12-OMe); 106.7 (C(11)); 106.8(9) (C(11)); 106.9(3) (C(18)); 107.1 (C(18)); 121.9 (C(8)); 122.3 (C(8)); 124.1 (C(13)); 124.5 (C(13)); 149.8 (C(4)); 155.7 (C(12)); 156.5 (C(9)); 156.8 (C(9)); 161.2 (C(14)); 161.3 (C(14)); 204.1 (C(17)); 204.4 (C(17)). m/z: 310 (M^+, 100), 295 ($M - Me^{\bullet}$, 13), 281 ($M - CO - H^{\bullet}$), 265 (20); 253 (44).

3.11. Reaction of pentacarbonyl[(trans-2,6-dimethylmorpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene)carbene]chromium (10) with hept-1-yne

A solution of pentacarbonyl[(*trans*-2,6-dimethylmorpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene)carbene]chromium (**10**) (75.8 mg, 0.136 mmol) in DMF (3 ml) was purged with nitrogen. Hept-1-yne (36 μl, 0.274 mmol) was added and the solution was heated to 125°C for 3 h. Usual workup followed by PLC (hexanes–ether, 1:1) gave 12-methoxy-4-methylene-15ζ-pentyl-18-nor-5α-androsta-8,11,13-trien-17-one (**7**) (8.5 mg, 17%) as a mixture (1:1) of epimers.

3.12. Reaction of pentacarbonyl[(trans-2,6-dimethylmorpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene)carbene]chromium (10) with 3,3-dimethylbutyne

A solution of pentacarbonyl[(*trans*-2,6-dimethylmorpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene)carbene]chromium (**10**) (71.2 mg, 0.127 mmol) in DMF (3 ml) was purged with nitrogen. 3,3-Dimethylbutyne (32 μl, 0.26 mmol) was added and the solution was heated to 125°C for 3 h. Usual workup followed by PLC (hexanes–ether, 1:1) gave 15ζ-(1,1-dimethylethyl)-12-methoxy-4-methylene-18-nor-5α-androsta-8,11,13-trien-17-one (**8**) (8.8 mg, 20%) as a (1:1) mixture of epimers.

3.13. Reaction of pentacarbonyl[(trans-2,6-dimethylmorpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene)carbene]chromium (10) with propyne

A solution of pentacarbonyl[(*trans*-2,6-dimethylmorpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene)carbene]chromium (**10**) (50.2 mg, 0.0897 mmol) in DMF (2 ml) was purged with nitrogen in a pressure bottle, which was then charged with propyne (300 kPa). The solution was heated to 125°C for 3 h. Usual workup followed by PLC (hexanes–ether, 1:1) gave 12-methoxy-15ζ-methyl-4-methylene-18-nor-5α-androsta-8,11,13-trien-17-one (**9**) (3.8 mg, 14%) as a mixture (1:1) of epimers.

3.14. Reaction of pentacarbonyl[(trans-2,6-dimethylmorpholino)(13-(12,19-dimethoxypodocarpa-8,11,13-triene)carbene]chromium (11) with 3,3-dimethylbutyne

A solution of pentacarbonyl[(*trans*-2,6-dimethylmorpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene)carbene]chromium (**11**) (52.4 mg, 0.0865 mmol) in DMF (1 ml) was purged with nitrogen. 3,3-Dimethylbutyne (22 μl, 0.179 mmol) was added and the solution was heated to 125°C for 3 h. Usual workup followed by PLC (hexanes–ether, 1:1) gave: (i) 12-methoxy-4β-methoxymethyl-4α,15-dimethyl-18-nor-5α-androstan-8,11,13-trien-17-one (**12**) (less polar epimer) (1.4 mg, 4%). Found: 398.2820 [$M^{+\bullet}$]. Calc. for $C_{26}H_{38}O_3$: 398.2821 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1708 (C=O). ^{1}H-NMR (δ ppm): 1.06 (ddd, [$J = 13.1$, 13.1, 4.1 Hz], H(3ax)); 1.08 (s, H(18)); 1.22 (s, H(20)); 1.30 (s, $C(CH_3)_3$); 1.45 (dd, [$J = 12.3$, 2.0 Hz], H(5)); 1.48–1.70 (m, H(1ax), H(2eq), H(6ax)); 1.78 (qt, [$J = 13.4$, 2.9 Hz], H(2ax)); 1.87 (bd, [$J = 13.3$ Hz], H(3eq)); 2.03 (bdd, [$J = 13.1$, 6.8 Hz], H(6eq)); 2.28 (bd, [$J = 12.7$ Hz], H(6eq)); 2.61 (5 lines, H(16ax), H(16eq)); 2.75–2.93 (m, H(7ax), H(7eq)); 3.18 (dd, [$J = 5.7$, 1.8 Hz], H(15)); 3.29 (d, [$J = 9.2$ Hz], H(19)); 3.33 (s, 19-OMe); 3.50 (d, [$J = 9.2$ Hz], H(19)); 3.90 (s, 12-OMe); 6.76 (s, H(11)). m/z: 398 (M^+, 34), 342 ($M - (CH_3)_2C{=}CH_2$, 100), 57 ($C(CH_3)_3^+$, 43) and (ii) 12-methoxy-4β-methoxymethyl-4α,15-dimethyl-18-nor-5α-androstan-8,11,13-trien-17-one (**12**) (more polar epimer) (1.2 mg, 4%). Found: 398.2818 [$M^{+\bullet}$]. Calc. for $C_{26}H_{38}O_3$: 398.2821 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1708 (C=O). ^{1}H-NMR (δ ppm): 1.00 (ddd, [$J = 13.1$, 13.1, 4.1 Hz], H(3ax)); 1.03 (s, H(18)); 1.25 (bs, H(20), $C(CH_3)_3$); 1.39 (dd, [$J = 12.6$, 3.3 Hz], H(5)); 1.50–1.85 (m, H(1ax), H(2ax), H(2eq), H(6ax)); 1.89 (bd, [$J = 13.8$ Hz], H(3eq)); 1.98–2.03 (m, H(6eq)); 2.30 (bd, [$J = 12.7$ Hz], H(1eq)); 2.55–2.65 (m, H(7ax), H(16)); 3.17 (ddd, [$J = 17.1$, 7.0, 2.8 Hz], H(7eq)); 3.20 (bdd, [$J = 5.8$, 1.5 Hz], H(15)); 3.32 (d, [$J = 9.2$ Hz], H(19)); 3.35 (s, 19-OMe); 3.55 (d, [$J = 9.1$ Hz], H(19)); 3.92 (s, 12-OMe); 6.77 (s, H(11)). m/z: 398 (M^+, 32), 342 ($M - (CH_3)_2C{=}CH_2$, 100), 57 ($C(CH_3)_3^+$, 17).

3.15. Reaction of pentacarbonyl[(morpholino)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (**6**) with hex-3-yne

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (**6**) (0.308 g, 0.580 mmol) in DMF (10 ml) was purged with nitrogen, followed by the addition of hex-3-yne (0.15 ml, 1.3 mmol). The solution was heated to 120°C for 3 h. Usual workup followed by radial chromatography gave 15,16-diethyl-12-methoxy-4-methylene-17ζ-morpholino-18-nor-5α-androsta-8,11,13,15-tetraene (**13**) (0.162 g, 66%). Found: 421.2987 [$M^{+\bullet}$]. Calc. for $C_{28}H_{39}O_2N$: 421.2981 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1587 (C=C), 1116. ^{1}H-NMR (δ ppm): 1.07 (t, [$J = 7.5$ Hz], CH_2CH_3); 1.08 (s, H(20)); 1.09 (t, [$J = 7.5$ Hz], CH_2CH_3); 1.16 (t, [$J = 7.5$ Hz], CH_2CH_3); 1.58 (m, H(1ax)); 1.67–1.95 (m, H(2ax), H(2eq), H(6ax), H(6eq)); 2.01–2.12 (m, H(3ax)); 2.20 (bd, [$J =$ 12.6 Hz], H(5)); 2.28 (bd, [$J = 13.4$ Hz], H(1eq)); 2.33–2.46 (m, H(3eq), CH_2CH_3); 2.63 (q, [$J = 7.5$ Hz], CH_2CH_3); 2.70 (b, NCH_2); 3.00 (ddd, [$J = 16.4$, 12.2, 5.6 Hz], H(7ax)); 3.25 (bdd, [$J = 16.3$, 4.2 Hz], H(7eq)); 3.64 (b, OCH_2); 3.83 (s, 12-OMe); 4.02 (s, H(17)); 4.05 (s, H(17)); 4.61 (s, H(18)); 4.86 (d, [$J = 1.2$ Hz], H(18)); 6.68 (s, H(11)). ^{13}C-NMR (δ ppm): 14.5 (CH_2CH_3); 14.7 (CH_2CH_3); 15.6 (CH_3CH_2); 19.2 (CH_3CH_2); 20.4 (C(6)); 20.6 (C(6)); 21.4 (C(20)); 22.8 (C(20)); 22.9 (C(2)); 23.8 (C(2)); 26.4 (C(7)); 26.5 (C(7)); 36.2 (C(3)); 39.5 (C(1)); 40.2 (C(10)); 40.3 (C(10)); 47.2 (C(5)); 47.4 (C(5)); 49.8 (NCH_2); 54.7 (12-OMe); 68.3 (OCH_2); 69.3 (C(17)); 69.4 (C(17)); 104.9 (C(18)); 105.0 (C(18)); 106.3 (C(11)); 121.3 (C(8)); 127.7(5) (C(13)); 127.9 (C(13)); 139.4 (C(16)); 139.6 (C(16)); 144.9 (C(15)); 147.1 (C(4)); 147.5 (C(4)); 148.9 (C(14)); 149.0 (C(14)); 150.7 (C(9)); 153.4 (C(12)). m/z: 421 (M^+, 10), 406 ($M - Me^{\bullet}$, 5), 392 ($M - Et^{\bullet}$, 29), 334 ($M - C_4H_9NO$, 100).

The allylamine (**13**) hydrolysed to 15ζ,16ζ-diethyl-12-methoxy-4-methylene-18-nor-5α-androsta-8,11,13-trien-17-one (**14**). Found: 352.2398 [$M^{+\bullet}$]. Calc. for $C_{24}H_{32}O_2$: 352.2402 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1702 (C=O), 1598 (C=C), 1581 (C=C). ^{1}H-NMR (δ ppm): 0.87 (t, [$J = 7.4$ Hz], CH_2CH_3); 0.93 (t, [$J = 7.4$ Hz], CH_2CH_3); 1.00 (t, [$J = 7.4$ Hz], CH_2CH_3); 1.02 (t, [$J =$ 7.4 Hz], CH_2CH_3); 1.05 (s, H(20)); 1.08 (s, H(20)); 1.36 (bq, [$J = 7.4$ Hz], CH_2CH_3); 1.39 (qd, [$J = 7.4$, 1.9 Hz], CH_2CH_3); 1.42 (qd, [$J = 7.3$, 1.9 Hz], CH_2CH_3); 1.64 (ddd, [$J = 12.6$, 12.6, 4.4 Hz], H(1ax)); 1.70–1.96 (m, H(2ax), H(2eq), H(6ax), H(6eq)); 2.06 (ddd, [$J = 12.7$, 12.7, 5.1 Hz], H(3ax)); 2.09 (ddd, [$J = 12.7$, 12.7, 5.5 Hz], H(3ax)); 2.22 (bd, [$J = 12.0$ Hz], H(5)); 2.25–2.31 (m, H(1eq), H(16)); 2.40 (bd, [$J = 12.8$ Hz], H(3eq)); 2.65–2.92 (m, H(15), H(7ax), H(7eq) (one isomer)); 2.97 (ddd, [$J = 17.0$, 6.2, 1.0 Hz], H(7eq) (one isomer)); 3.90(7) (s, 12-OMe); 3.91 (s, 12-OMe); 4.64 (d, [$J = 1.4$ Hz], H(18)); 4.65 (d, [$J = 1.4$ Hz], H(18)); 4.89(5) (bs, H(18)); 4.90 (bs, H(18)); 6.75 (s, H(11)); 6.76 (s, H(11)). ^{13}C-NMR (δ ppm): 11.4 (CH_2CH_3); 12.0(5) (CH_2CH_3); 12.1 (CH_2CH_3); 12.2 (CH_2CH_3); 20.7 (C(6)); 20.9 (C(6)); 22.6 (C(20)); 23.5 (C(2)); 23.6 (C(2)); 24.4 (CH_2CH_3); 26.0 (CH_2CH_3); 26.5 (C(7)); 26.6(6) (C(7)); 26.7 (CH_2CH_3); 28.4 (CH_2CH_3); 36.0 (C(3)); 36.1 (C(3)); 38.4 (C(1)); 38.6 (C(1)); 40.6 (C(10)); 40.8 (C(10)); 45.0 (C(5)); 46.8 (C(16)); 47.8 (C(16)); 55.4 (12-OMe); 56.0 (C(15)); 56.9 (C(15)); 106.5 (C(11)); 106.8 (C(11)); 106.9 (C(18)); 107.0 (C(18)); 121.7 (C(8)); 122.2 (C(8)); 124.3 (C(13)); 124.6 (C(13)); 149.9 (C(4)); 155.6 (C(12)); 155.7 (C(12)); 156.4 (C(9)); 156.7 (C(9)); 158.9 (C(14)); 159.2 (C(14)); 207.3 (C(17)); 207.4 (C(17)). m/z: 352 (M^+, 83), 337 ($M - Me^{\bullet}$, 9), 324 ($M - CO$, 100), 295 ($324 - Me^{\bullet}$, 33), 267 ($324 - Et^{\bullet}$, 19), 309 (18).

3.16. Reaction of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))-carbene]chromium (**6**) with diphenylethyne

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (**6**) (0.252 g, 0.474 mmol) and diphenylethyne (0.126 g, 0.707 mmol) in DMF (10 ml) was purged with nitrogen then heated to 120°C for 3 h. Usual workup followed by radial chromatography gave 12-methoxy-4-methylene-17ζ-morpholino-15,16-diphenyl-18-nor-5α-androsta-8,11,13,16-tetraene (**15**) (0.2092 g, 85%). Found: 517.2986 [$M^{+\bullet}$]. Calc. for $C_{36}H_{39}NO_2$: 517.2981 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1645 (C=N), 1601 (C=C), 737 ($CH_{o.o.p.}$), 701 ($CH_{o.o.p.}$). ^{1}H-NMR (δ ppm): 1.00 (s, H(20)); 1.03 (s, H(20)); 1.52 (ddd, [$J = 13.0$, 13.0, 4.6 Hz], H(1ax)); 1.53 (ddd, [$J =$ 13.0, 13.0, 4.6 Hz], H(1ax)); 1.58–1.98 (m, H(2ax), H(2eq), H(6ax), H(6eq)); 2.03 (ddd, [$J = 13.6$, 13.6, 4.9 Hz], H(3ax)); 2.05 (bd, [$J = 12.5$ Hz], H(5)); 2.13 (bd, [$J = 12.5$ Hz], H(5)); 2.25–2.37 (m, H(3eq)); 2.50 (ddd, [$J = 17.2$, 11.9, 7.3 Hz], H(7ax)); 2.64 (bdd, [$J = 17.3$, 3.9 Hz], H(7eq)); 2.86–2.90 (m, NCH_2); 3.02 (bt, [$J =$ 11.7 Hz], NCH_2); 3.72 (dd, [$J = 8.6$, 4.2 Hz], OCH_2); 3.92 (s, 12-OMe); 3.94 (s, 12-OMe); 4.51 (bs, H(18), H(15)); 4.61 (s, H(18)); 4.78 (s, H(18)); 4.80 (s, H(18)); 6.88–6.94 (m, H(11), Ph (3H)); 6.98 (dd, [$J = 7.8$, 1.9 Hz], H_{ortho}); 7.05–7.16 (m, Ph, 6H). ^{13}C-NMR (δ ppm): 20.8 (C(6)); 20.9 (C(6)); 22.7 (C(20)); 22.9 (C(20)); 23.7 (C(2)); 23.8 (C(2)); 26.9(5) (C(7)); 36.1 (C(3)); 36.3 (C(3)); 38.8 (C(1)); 38.9 (C(1)); 39.7 (C(10)); 39.8 (C(10)); 47.0 (C(5)); 47.4 (C(5)); 52.2 (NCH_2); 55.7(5) (12-OMe); 55.8 (12-OMe); 57.6(5) (C(15)); 57.7 (C(15)); 67.5 (OCH_2); 106.4 (C(18)); 106.6 (C(18)); 108.1 (C(11)); 108.2 (C(11)); 124.1(8) (C(8)); 124.2(4) (C(8)); 126.0 (C(13)); 126.1(5) (C(13)); 126.4 ($CH_{aromatic}$); 127.1(5) ($CH_{aromatic}$(2H)); 128.0 ($CH_{aromatic}$); 128.1 ($CH_{aromatic}$); 128.4 ($CH_{aromatic}$(2H)); 128.5 (C_{quat}); 128.8 (C_{quat}); 130.1(7) ($CH_{aromatic}$); 130.2 ($CH_{aromatic}$); 133.1

(C_{quat}); 133.6 (C_{quat}); 137.4 ($CH_{aromatic}$); 139.0 (C(16)); 139.5 (C(16)); 146.2(5) (C(17)); 146.2(5) (C(17)); 146.6 (C(4)); 146.9 (C(4)); 147.1 (C(14)); 147.2 (C(14)); 150.3(7) (C(9)); 150.4(1) (C(9)); 151.0 (C(12)); 151.1 (C(12)). *m/z*: 517 (M^+, 100), 431 ($M - C_4H_8NO$, 14).

3.17. Reaction of pentacarbonyl[(morpholino)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (6) with trimethyl-(2-phenylethynyl)silane

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy - 19 - norpodocarpa - 4(18),8,11,13 - tetraene))-carbene]chromium (**6**) (0.296 g, 0.557 mmol) in DMF (10 ml) was purged with nitrogen. Trimethyl(2-phenylethynyl)silane (0.23 ml, 1.14 mmol) was added and the solution was heated to 120°C for 3 h. Usual workup followed by PLC (hexanes–ether, 2:1) gave 12 - methoxy - 4 - methylene - 16ζ - phenyl - 18 - nor - 5α - androsta-8,11,13-trien-17-one (**21**). Found: 372.2080 [$M^{+\bullet}$]. Calc. for $C_{26}H_{28}O_2$: 372.2089 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1707 (C=O), 1599 (C=C), 1580 (C=C), 1049 (C–O–C). ^{1}H-NMR (δ ppm): 1.02 (s, H(20)); 1.03 (s, H(20)); 1.51 (ddd, [$J = 13.4$, 13.4, 6.0 Hz], H(1ax)); 1.60–2.08 (m, H(2ax), H(2eq), H(3ax), H(3eq), H(6ax), H(6eq)); 2.14 (bd, [$J = 11.9$ Hz], H(5)); 2.22–2.40 (m, H(1eq), H(3eq), H(7ax) (one isomer), H(5) (one isomer)); 2.42 (dd, [$J = 13.2$, 2.5 Hz], H(15)); 2.47–2.55 (m, H(7ax) (one isomer)); 2.57 (dd, [$J = 13.3$, 2.4 Hz], H(15)); 2.63 (ddd, [$J = 17.1$, 5.8, 1.2 Hz], H(7eq)); 3.16 (dd, [$J = 11.3$, 8.4 Hz], H(15)); 3.21 (dd, [$J = 11.4$, 8.4 Hz], H(15)); 3.97 (s, 12-OMe); 3.98 (s, 12-OMe); 4.41 (d, [$J = 8.4$ Hz], H(16)); 4.45 (d, [$J = 8.4$ Hz], H(16)); 4.54 (bs, H(18)); 4.82 (bs, H(18)); 4.84 (bs, H(18)); 6.84 (s, H(11)); 6.87 (s, H(11)); 7.04 (bd, [$J = 7.2$ Hz], H_{ortho}); 7.20 (bt, [$J = 7.0$ Hz], H_{para}); 7.24 (dd, [$J = 7.8$, 1.6 Hz], H_{meta}). ^{13}C-NMR (δ ppm): 20.5 (C(6)); 20.6 (C(6)); 22.5 (C(20)); 22.6 (C(20)); 23.5 (C(2)); 23.6 (C(2)); 26.3 (C(7)); 35.9 (C(3)); 36.1 (C(3)); 38.4 (C(1)); 38.6 (C(1)); 40.5(6) (C(10)); 40.6(3) (C(10)); 43.5 (C(15)); 43.6 (C(15)); 46.8 (C(5)); 47.1 (C(5)); 48.3 (C(16)); 48.5 (C(16)); 55.6 (12-OMe); 106.9 (C(11)); 107.1 (C(11)); 107.2 (C(18)); 107.3 (C(18)); 123.4 (C(8)); 123.5 (C(8)); 125.3 (C(13)); 125.4 (C(13)); 126.5 (C_{para}); 127.1 (C_{meta});127.3 (C_{meta});128.8 (C_{ortho}); 128.9 (C_{ortho}); 143.6 (C_{ipso}); 144.1 (C_{ipso}); 149.6(9) (C(4)); 149.7(2) (C(4)); 155.4 (C(12)); 155.5 (C(12)); 157.1 (C(9)); 157.4 (C(9)); 157.9 (C(14)); 158.2 (C(14)); 203.8 (C(17)); 204.1 (C(17)). *m/z*: 372 (M^+, 100), 357 ($M - Me^{\bullet}$, 7), 343 ($M - CO - H$, 37), 315 (18), 253 (12).

3.18. Reaction of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))-carbene]chromium (6) with 1-methylthio-2-phenylethyne

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (**6**) (0.214 g, 0.402 mmol) in DMF (8 ml) was purged with nitrogen and 1-methylthio-2-phenylethyne (0.122 g, 823 mmol) was added. The solution was heated to 120°C for 3 h. Usual workup followed by PLC (hexanes–ether, 1:1 then 7:3) gave 12 - methoxy - 4 - methylene - 16ζ - phenyl - 18 - nor - 5α - androsta-8,11,13-trien-17-one (**21**) (5.1 mg, 3%).

3.19. Reaction of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))-carbene]chromium (6) with ethyne

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy - 19 - norpodocarpa - 4(18),8,11,13 - tetraene))-carbene]chromium (**6**) (0.245 g, 0.461 mmol) in DMF (10 ml) was purged with nitrogen and then with ethyne. The pressure bottle was then pressurised with ethyne (300 kPa) and heated to 125°C for 1 h, giving a dark-red polymeric material. Usual workup gave a dark-brown oil which was dissolved in ether and decolourised with charcoal. PLC of the residue gave an unidentified product (1.8 mg).

3.20. Reaction of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))-carbene]chromium (6) with trimethylsilylethyne

Trimethylsilylethyne (0.28 ml, 1.98 mmol) was added to a nitrogen-purged solution of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))-carbene]chromium (**6**) (0.247 g, 0.499 mmol) in DMF (10 ml), and the mixture was heated at 120°C for 3.25 h. Usual workup gave a brown viscous oil, which was dissolved in ether and filtered through charcoal. PLC (hexanes–ether, 2:1) failed to yield any products. Repeating the reaction in refluxing DMF also gave intractable tars.

3.21. Reaction of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))-carbene]chromium (6) with tributylstannylethyne

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (**6**) (0.253 g, 0.476 mmol) in DMF (10 ml) was purged with nitrogen. Tributylstannylethyne (0.28 ml, 0.968 mmol) was added and the mixture was heated to 120°C for 3 h. Usual workup gave a brown polymeric oil which was decolourised with charcoal. PLC (hexanes–ether, 2:1) gave a product (0.2 mg) which was not characterised.

3.22. Reaction of pentacarbonyl[(morpholino)-(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (6) with ethyl 4,4-dimethylpentyn-2-oate

A solution of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (**6**) (0.240 g, 0.452 mmol) in DMF (10 ml) was purged with nitrogen. Ethyl 4,4-dimethylpentyn-2-oate (0.149 g, 0.966 mmol) was added and the mixture was heated to 120°C for 3 h. Usual workup followed by PLC (hexanes–ether, 1:1) gave: (i) 13-formyl-12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene (**28**) (7 mg, 6%) as colourless needles (m.p. 153–155°C). Found: 270.1651 [$M^{+\bullet}$]. Calc. for $C_{18}H_{22}O_2$: 270.1620 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1676 (C=O), 1609 (C=C). ^{1}H-NMR (δ ppm): 1.04 (s, H(20)); 1.61 (ddd, [$J = 12.8, 12.8, 4.5$ Hz], H(1ax)); 1.69–1.90 (m, H(2ax), H(2eq), H(6ax), H(6eq)); 2.07 (ddd, [$J = 12.9, 12.9, 5.5$ Hz], H(3ax)); 2.20 (bd, [$J = 12.7$ Hz], H(5)); 2.27 (bd, [$J = 12.8$ Hz], H(1eq)); 2.40 (ddd, [$J = 13.1, 4.3, 2.3$ Hz], H(3eq)); 2.85 (ddd, [$J = 16.8, 11.9, 6.5$ Hz], H(7ax)); 2.91 (ddd, [$J = 16.8, 6.4, 1.9$ Hz], H(7eq)); 3.86 (s, 12-OMe); 4.62 (d, [$J = 1.5$ Hz], H(18)); 4.88 (d, [$J = 1.5$ Hz], H(18)); 6.89 (s, H(11)); 7.55 (s, H(14)); 10.39 (s, CHO). ^{13}C-NMR (δ ppm): 21.1 (C(6)); 22.5(5) (C(20)); 23.5 (C(2)); 28.8 (C(7)); 36.1 (C(3)); 38.2(5) (C(1)); 40.4 (C(10)); 47.3(5) (C(5)); 55.6 (12-OMe); 107.1 (C(18)); 108.4 (C(11)); 122.8 (C(13)); 127.7 (C(8)); 129.3 (C(14)); 149.7 (C(4)); 156.1 (C(9)); 159.9 (C(12)); 189.7 (CHO). m/z: 270 (M^+, 100), 255 ($M - Me^{\bullet}$, 21), 227 ($255 - CO$, 42); and (ii) 16ζ-(ethylcarboxy)-15ζ-(1,1-dimethylethyl)-12-methoxy-4-methylene-18-nor-5α-androsta-8,11,13-trien-17-one (**27**) (54%); *trans* isomer as colourless crystals ($CDCl_3$–hexanes), m.p. 177–180°C. Found: 424.2614 [$M^{+\bullet}$]. Calc. for $C_{27}H_{36}O_4$: 424.2607 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1734 ($C{=}O_{ester}$), 1709 ($C{=}O_{ketone}$), 1596 (C=C), 1579 (C=C). ^{1}H-NMR (δ ppm): 0.89 (s, $(CH_3)_3C$); 0.90 (s, $(CH_3)_3C$); 1.05 (s, H(20)); 1.07 (s, H(20)); 1.11 (s, H(20)); 1.23 (t, [$J = 7.2$ Hz], OCH_2CH_3); 1.24 (t, [$J = 7.2$ Hz], OCH_2CH_3); 1.60–1.95 (m, H(1ax), H(2ax), H(2eq), H(6ax), H(6eq)); 2.08 (ddd, [$J = 12.3, 12.3, 4.6$ Hz], H(3ax)); 2.11 (ddd, [$J = 12.2, 12.2, 5.1$ Hz], H(3ax)); 2.24–2.33 (m, H(1eq), H(5)); 2.42 (bd, [$J = 11.5$ Hz], H(3eq)); 2.68 (ddd, [$J = 17.0, 12.0, 6.7$ Hz], H(7ax)); 2.90–2.97 (5 lines, H(7ax), H(7eq)); 3.29 (ddd, [$J = 17.0, 5.1, 2.1$ Hz], H(7eq)); 3.51 (s, $H(15)_{trans}$); 3.56 (s, $H(15)_{trans}$); 3.72 (2 lines, H(16)); 3.81 (d, [$J = 2.9$ Hz], $H(15)_{cis}$); 3.90 (s, 12-OMe); 3.91 (s, 12-OMe); 4.07 (dd, [$J = 13.2, 7.2$ Hz], OCH_2CH_3); 4.07(5) (dd, [$J = 13.2, 7.2$ Hz], OCH_2CH_3); 4.10 (dd, [$J = 13.2, 7.2$ Hz], OCH_2CH_3); 4.11 (dd, [$J = 13.2, 7.2$ Hz], OCH_2CH_3); 4.62 (d, [$J = 1.2$ Hz], H(18)); 4.65 (d, [$J = 1.1$ Hz], H(18)); 4.88(5) (d, [$J = 1.5$ Hz], H(18)); 4.89 (d, [$J = 1.1$ Hz], H(18)); 6.79 (s, H(11)); 6.83 (s, H(11)). ^{13}C-NMR (δ ppm): 14.0 (OCH_2CH_3); 20.8 (C(6)); 21.1 (C(6)); 22.4 (C(20)); 23.4 (C(2)); 23.5 (C(20)); 23.6 (C(2)); 26.3 (C(7)); 28.1(5) ($C(CH_3)_3$); 28.5 ($C(CH_3)_3$); 35.8 (C(3)); 36.0 (C(3)); 36.4 ($C(CH_3)_3$); 37.2 ($C(CH_3)_3$); 38.0 (C(1)); 39.0 (C(1)); 40.9(5) (C(10)); 41.1 (C(10)); 46.9 (C(5)); 48.3(5) (C(5)); 51.7 (C(15)); 51.7 (C(15)); 55.5 (12-OMe); 59.8 (12-OMe); 61.4(7) (OCH_2CH_3); 61.5(2) (OCH_2CH_3); 61.9 (C(16)); 106.9(2) (C(18)); 106.9(9) (C(18)); 107.0(2) (C(11)); 107.8 (C(11)); 121.9 (C(8)); 122.4 (C(8)); 125.7(5) (C(13)); 126.5(5) (C(13)); 149.6 (C(4)); 149.9 (C(4)); 155.5 (C(12)); 155.7 (C(12)); 156.9 (C(9)); 157.3(5) (C(9)); 158.4 (C(14)); 168.8 ($COOEt$); 168.9 ($COOEt$); 196.3 (C(17)); 196.5 (C(17)). m/z: 424 (M^+, 66), 368 ($M - CH_2{=}CMe_2$, 100), 322 ($M - (CH_3)_3C^{\bullet} - EtO^{\bullet}$, 64), 295 ($368 - EtO_2C$, 83).

3.23. Reaction of pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))-carbene]chromium (6) with ethynylferrocene

A solution of ethynylferrocene (0.144 g, 0.686 mmol) and pentacarbonyl[(morpholino)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))-carbene]chromium (**6**) (0.244 g, 0.459 mmol) in DMF (10 ml) was purged with nitrogen and then heated to 120°C for 3 h. Usual workup followed by radial chromatography (hexanes–ether, 2:1) gave 15ζ-ferrocenyl-12-methoxy-4-methylene-18-nor-5α-androsta-8,11,13-trien-17-one (**29**) (0.109 g, 50%) as an orange foam. Found: 480.1751 [$M^{+\bullet}$]. Calc. for $C_{30}H_{32}FeO_4$: 480.1752 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1704 (C=O), 1598 (C=C), 1581 (C=C), 1049 (C–O–C). ^{1}H-NMR (δ ppm): 1.00 (s, H(20)); 1.02 (s, H(20)); 1.55 (ddd, [$J = 12.6, 12.6, 4.5$ Hz], H(1ax)); 1.60–1.85 (m, H(2ax), H(2eq), H(6ax), H(6eq)); 1.99 (ddd, [$J = 13.5, 13.5, 5.5$ Hz], H(3ax)); 2.03 (ddd, [$J = 13.5, 13.5, 5.5$ Hz], H(3ax)); 2.09 (d, [$J = 13.2$ Hz], H(5)); 2.13 (d, [$J = 13.2$ Hz], H(5)); 2.19 (bd, [$J = 12.7$ Hz], H(1eq)); 2.26 (bd, [$J = 12.7$ Hz], H(1eq)); 2.36 (bd, [$J = 12.9$ Hz], H(3eq)); 2.47 (ddd, [$J = 17.4, 12.5, 6.7$ Hz], H(7ax)); 2.57 (bdd, [$J = 17.4, 7.3$ Hz], H(7eq)); 2.76 (dd, [$J = 17.0, 4.5$ Hz], H(16)); 2.94 (dd, [$J = 17.2, 5.9$ Hz], H(16)); 3.26 (bd, [$J = 5.2$ Hz], H(15)); 3.72 (bt, [$J = 1.1$ Hz], H(2′) (one isomer)); 3.77 (bt, [$J = 1.2$ Hz], H(2′) (one isomer)); 3.91 (s, 12-OMe); 3.93 (s, 12-OMe); 4.08 (b, H(2′)); 4.12 (m, H(3′)); 4.14 (s, Cp); 4.17 (s, Cp); 4.28 (bt, [$J = 1.0$ Hz], H(3′)); 4.34 (bt, [$J = 1.2$ Hz], H(3′)); 4.58 (d, [$J = 1.2$ Hz], H(18)); 4.59 (d, [$J = 1.2$ Hz], H(18)); 4.84 (d, [$J = 1.1$ Hz], H(18)); 4.86 (d, [$J = 1.1$ Hz], H(18)); 6.75 (s, H(11)); 6.80 (s, H(11)). ^{13}C-NMR (δ ppm): 20.5 (C(6)); 20.7 (C(6)); 22.4 (C(20)); 22.6 (C(20)); 23.4 (C(2)); 23.5 (C(2)); 24.5 (C(7)); 26.6 (C(7)); 35.8(5) (C(3)); 36.1 (C(3)); 36.5 (C(16)); 36.8 (C(16)); 38.4 (C(1)); 38.6 (C(1)); 40.5 (C(10)); 40.6 (C(10)); 46.6 (C(5)); 47.2 (C(5)); 49.0 (C(15)); 49.7 (C(15)); 55.5 (12-OMe); 55.6 (12-OMe); 65.8 (C(2′)); 66.3 (C(2′)); 66.5 (C(2′)); 66.6 (C(2′)); 67.5

(C(3′)); 67.8 (C(3′)); 68.6 (Cp); 69.5 (C(3′)); 70.1 (C(3′)); 91.9 (C(1′)); 93.2 (C(1′)); 106.8 (C(18)); 107.0 (C(11)); 107.2 (C(11)); 121.7(5) (C(8)); 122.1 (C(8)); 125.1 (C(13)); 125.2 (C(13)); 149.7 (C(4)); 155.4 (C(14)); 156.6(7) (C(9)); 156.7(5) (C(9)); 158.4 (C(12)); 158.9 (C(12)); 204.3(7) (C(17)); 204.4 (C(17)). *m/z*: 480 (M^+, 100).

3.24. [6aR-(1α,4α,6αβ,7α,10aα)]-3-Ferrocenyl-1,4,5,6,6a,7,8,9,10,10a-decahydro-12-methoxy-7-methoxymethyl-7-10a-dimethylchrysene-1,4-dione (31)

A solution of pentacarbonyl[(methoxy)(13-(12,19-dimethoxypodocarpa-8,11,13-triene))carbene]chromium (**30**) (0.314 g, 0.601 mmol) and ethynylferrocene (0.151 g, 0.719 mmol) in THF (15 ml) was refluxed for 25 h. The solvent was removed in vacuo and the residue was dissolved in dichloromethane (30 ml). Lead dioxide (3.042 g, 12.7 mmol) was added and the mixture was stirred at r.t. for 1 h and then filtered. Radial chromatography (hexanes–ether, 1:1) gave [6a*R*-(1α,4α,6αβ,7α,10aα)] - 3 - ferrocenyl - 1,4,5,6,6a,7,8,9,10,10a - decahydro - 12 - methoxy - 7 - methoxymethyl - 7 - 10a-dimethylchrysene-1,4-dione (**31**) (0.190 g, 57%) as a dark-green foam. Found: 552.1971 [$M^{+\bullet}$]. Calc. for $C_{33}H_{36}FeO_4$: 552.1963 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1709 (C=O), 1643, 1601 (C=C). ^{1}H-NMR (δ ppm): 1.04 (ddd, [$J = 13.5, 13.5, 4.1$ Hz], H(8ax)); 1.08 (s, 7-Me); 1.28 (s, 10a-Me); 1.47 (dd, [$J = 12.8, 1.7$ Hz], H(6a)); 1.48 (ddd, [$J = 12.8, 12.8, 4.0$ Hz], H(10ax)); 1.60–1.75 (m, H(9eq), H(6ax)); 1.77 (qt, [$J = 13.9, 3.6$ Hz], H(9ax)); 1.89 (bd, [$J = 13.4$ Hz], H(8eq)); 2.13 (m, H(6eq)); 2.31 (bd, [$J = 12.7$ Hz], H(10eq)); 3.25–3.33 (m, H(5ax), H(5eq)); 3.28 (d, [$J = 9.2$ Hz], 7-CH_2OMe); 3.35 (s, 7-CH_2O*Me*); 3.52 (d, [$J = 9.2$ Hz], 7-CH_2OMe); 3.98 (s, 12-OMe); 4.14 (s, Cp); 4.54 (10 lines, H(2′)); 4.89 (5 lines, H(3′)); 4.98 (5 lines, H(3′)); 6.85 (s, H(2)); 7.25 (s, H(11)). ^{13}C-NMR (δ ppm): 19.2 (C(9)); 19.4 (C(6)); 25.6 (10a-Me); 27.5 (7-Me); 30.6 (C(5)); 35.7 (C(8)); 37.9 (C(10a)); 39.6 (C(7), C(10)); 50.2 (C(6a)); 56.4 (12-OMe); 59.4 (7-CH_2O*Me*); 69.4(5) (C(3′)); 69.5(5) (C(3′)); 70.2 (Cp); 71.4(8) (C(2′)); 71.5(4) (C(2′)); 76.0 (7-Me); 76.2 (C(1′)); 114.5(5) (C(2)); 119.7 (C(12a)); 129.4 (C(4b)); 131.2 (C(11)); 133.6 (C(4a)); 149.8 (C(10a)); 157.3 (C(12)); 158.7(5) (C(3)); 185.5(5) (C=O); 188.0 (C=O). *m/z*: 552 (M^+, 100). $E_{1/2}$ (V) −1.330; 0.107.

3.25. [6aR-(1α,4α,6αβ,7α,10aα)]-3-Ferrocenyl-1,4,5,6,6a,7,8,9,10,10a-decahydro-12-methoxy-7-methylene-10a-methylchrysene-1,4-dione (33)

A solution of pentacarbonyl[(methoxy)(13-(12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene))carbene]chromium (**31**) (0.252 g, 0.529 mmol) and ethynylferrocene (0.130 g, 0.619 mmol) in THF (10 ml) was refluxed for 19 h. The solvent was removed in vacuo and the residue was dissolved in dichloromethane (20 ml). Lead dioxide (2.54 g, 10.6 mmol) was added and the mixture was stirred for 30 min at r.t. and then filtered. Radial chromatography (hexanes–ether, 1:1) gave [6a*R*-(1α,4α,6αβ,7α,10aα)]-3-ferrocenyl-1,4,5,6,6a,7,8,9,10,10a - decahydro - 12 - methoxy - 7 - methylene-10a-methylchrysene-1,4-dione (**33**) (0.154 g, 57%) as a dark-green foam. Found: 506.1550 [$M^{+\bullet}$]. Calc. for $C_{31}H_{30}FeO_3$: 506.1544 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 1704 (C=O), 1643, 1601 (C=C). ^{1}H-NMR (δ ppm): 1.10 (s, 10a-Me); 1.59 (ddd, [$J = 12.7, 12.7, 4.8$ Hz], H(10ax)); 1.66–1.88 (m, H(9ax), H(9eq), H(6ax), H(6eq)); 2.01 (m, H(8ax)); 2.09 (dd, [$J = 13.1, 5.4$ Hz], H(6a)); 2.27 (bd, [$J = 12.4$ Hz], H(10eq)); 2.41 (bd, [$J = 13.2$ Hz], H(8eq)); 3.20–3.31 (m, H(5ax), H(5eq)); 3.98 (s, 12-OMe); 4.14 (s, Cp); 4.54 (6 lines, [$J = 1.4$ Hz], H(2′)); 4.55 (6 lines, [$J = 1.4$ Hz], H(2′)); 4.66 (d, [$J = 1.4$ Hz], 7-CH_2); 4.89 (5 lines, [$J = 1.3$ Hz], H(3′)); 4.91 (d, [$J = 1.3$ Hz], 7-CH_2); 4.99 (5 lines, H(3′)); 6.86 (s, H(2)); 7.27 (bs, H(11)). ^{13}C-NMR (δ ppm): 21.2 (C(6)); 22.8 (10a-Me); 23.5 (C(9)); 29.2 (C(9)); 35.8 (C(8)); 38.9 (C(10)); 40.8 (C(10a)); 46.7 (C(6a)); 56.4 (12-OMe); 69.4 (C(3′)); 69.6 (C(3′)); 70.2 (Cp); 71.5 (C(2′)); 71.6 (C(2′)); 76.2 (C(1′)); 107.2 (7-CH_2); 115.3 (C(2)); 119.9 (C(12a)); 129.4 (C(4b)); 131.1 (C(11)); 133.9 (C(4a)); 149.4 (C(7)); 149.8 (C(10a)); 156.0 (C(12)); 157.2 (C(3)); 184.5 (C=O); 187.8 (C=O). *m/z*: 506 (M^+, 52), 480 (100), 442 ($M - Cp^{\bullet} + H$, 20). $E_{1/2}$ (V) −1.317; 0.104.

3.26. Pentacarbonyl[(ethylthio)(13-(12,19-dimethoxypodocarpa-8,11,13-triene))carbene]chromium (34)

Ethanethiol (50 μl, 0.67 mmol) and sodium carbonate (0.100 g, 0.943 mmol) were added to a solution of pentacarbonyl[(methoxy)(13 - (12,19 - dimethoxypodocarpa-8,11,13-triene))carbene]chromium (**30**) (0.295 g, 0.565 mmol) in isopropanol (4 ml) at 0°C. The suspension was stirred at 0°C for 1 h and then at r.t. for 21 h. The red-brown solution was extracted with diethyl ether, and the extracts were washed with water, and dried ($MgSO_4$). Solvent was removed by passing a constant stream of dry nitrogen over the solution in a well-ventilated fumehood. Radial chromatography (hexanes–ether; 9:1) gave pentacarbonyl[(thioethyl)(13-(12,19 - dimethoxypodocarpa - 8,11,13 - triene))carbene]-chromium (**34**) (0.232 g, 74%) as a viscous red-black oil, the ratio of the two rotamers being ca. 1.2:1. Found: 552.1293 [$M^{+\bullet}$]. Calc. for $C_{27}H_{32}CrO_7S$: 552.1274 [$M^{+\bullet}$]. IR (cm^{-1}): ν_{max} 2055 (s, C≡O), 1990 (sh, C≡O), 1937 (br, C≡O). ^{1}H-NMR (δ ppm): 1.01 (m, H(3ax)); 1.05 (s, H(18)); 1.11 (t, [$J = 7.7$ Hz], SCH_2CH_3); 1.20(7) (s, H(20)); 1.21 (s, H(20)); 1.22 (s, H(20)); 1.46 (bt, [$J = 12.9$ Hz], H(1ax)); 1.60–1.80 (m, H(2ax), H(5), H(2eq), H(6ax)); 1.88 (bd, [$J = 13.1$ Hz], H(3eq)); 1.97 (m, H(6eq)); 2.27 (b, H(1eq)); 2.67–2.90 (m, H(7ax),

H(7eq)); 2.71 (q, [$J = 7.7$ Hz], SCH_2CH_3); 3.25 (d, [$J = 9.2$ Hz], H(19)); 3.27 (d, [$J = 9.2$ Hz], H(19)); 3.33 (s, 19-OMe); 3.33(9) (s, 19-OMe); 3.34(1) (s, 19-OMe); 3.52 (d, [$J = 9.2$ Hz], H(19)); 3.54 (d, [$J = 9.2$ Hz], H(19)); 3.74 (s, 12-OMe); 6.14 (s, H(14)); 6.16 (s, H(14)); 6.76 (s, H(11)). ^{13}C-NMR (δ ppm): 12.0 (SCH_2CH_3); 19.2 (C(2)); 19.4 (C(6)); 25.6 (C(20)); 25.7 (C(20)); 27.6 (C(18)); 30.2 (C(7)); 30.3 (C(7)); 30.4 (C(7)); 36.0 (C(3)); 38.0 (C(4), C(10)); 38.7 (SCH_2CH_3); 38.8 (SCH_2CH_3); 39.1 (C(1)); 51.1 (C(5)); 51.2 (C(5)); 51.3 (C(5)); 55.1 (12-OMe); 59.4 (19-OMe); 75.9 (C(19)); 76.1 (C(19)); 106.4 (C(11)); 106.6 (C(11)); 106.9 (C(11)); 118.0(8) (C(14)); 118.1(4) (C(14)); 126.8 (C(13)); 128.7 (C(8)); 144.0 (C(9)); 144.1 (C(9)); 150.2 (C(12)); 215.9 ($C{\equiv}O_{cis}$); 229.0 ($C{\equiv}O_{trans}$); 362.4 ($C_{carbene}$). m/z: 552 (M^+, 4), 524 (M − CO, 9), 496 (M − 2CO, 3); 468 (M − 3CO, 8); 440 (M − 4CO, 55), 412 (M − 5CO, 52), 384 (43), 377 (33), 361 (81), 331 (35), 315 (412 − Cr − $MeOCH_2$, 100).

3.27. Reaction of pentacarbonyl[(thioethyl)(13-(12,19-dimethoxypodocarpa-8,11,13-triene))-carbene]chromium (34) with ethynylferrocene

A solution of pentacarbonyl(ethylthio)(13-(12,19-dimethoxypodocarpa - 8,11,13 - triene)) - carbene]-chromium (**34**) (0.164 g, 0.297 mmol), triethylamine (0.210 ml, 1.51 mmol), $BF_3{\cdot}Et_2O$ (0.21 ml, 1.71 mmol) and ethynylferrocene (0.129 g, 0.614 mmol) in THF (10 ml) was refluxed for 19 h. The solvent was removed in vacuo, the residue was dissolved in ether and the solution was washed with water and dried ($MgSO_4$). PLC (hexanes–ether, 9:1) gave ethynylferrocene (75.6 mg, 59%) and a mixture of products, some fractions of the 24-component mixture were combined and re-plated on a 20×20 cm^2 TLC plate (hexanes–ether, 1:1). Recovery from the most intense deep green band gave [6a*R*-(1α,4α,6αβ,7α,10aα)] - 3 - ferrocenyl - 1,4,5,6,6a,7,8,9,10,10a-decahydro-12-methoxy-7-methoxymethyl-7-10a-dimethylchrysen-1,4-dione (**31**) (4.1 mg, 3%).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 156246 for compound **27**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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