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Organomanganese complexes of podocarpic acid derivatives

Richard C. Cambie, Michael R. Metzler, Clifton E.F. Rickard, Peter S. Rutledge and Paul D. Woodgate *

Department of Chemistry, University of Auckland, Private Bag, Auckland (New Zealand)

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Abstract

Cyclomanganation reactions of podocarpic acid derivatives containing aldehyde, ketone, ester, or oxime groups as directing functionalities have been investigated. Attempted complexation of amide-containing ligands proved generally to be unsuccessful whereas benzylic ketones gave their corresponding tetracarbonyl complexes in high yields. Complexation of ligands containing either two potential sites for manganation or two potential ligating groups were also investigated and the structures of the isolated complexes established unequivocally by NMR or X-ray crystallography.

Introduction

Cyclomanganation of a range of simple aromatic and heteroaromatic ketones is well documented [1–7]. The synthesis of such tetracarbonylmanganese(I) complexes involves heating a manganese transfer reagent of the type $RMn(CO)_5$ with the substituted aromatic ligand in an inert hydrocarbon solvent. $PhCH_2Mn(CO)_5$ is generally superior to its methyl analogue, requiring shorter reflux times and usually giving fewer by-products arising from thermal decomposition of the manganating agent.

Cyclomanganated aryl ketones have been used as intermediates in the synthesis of a number of novel organic and organometallic compounds [6–9]. To provide starting materials for these reactions with the ultimate goal of achieving cyclopentaanulation of diterpenoids, we have undertaken a systematic study to define which functional groups on the aromatic ring of the dieterpenoid podocarpic acid (**1**) would afford the corresponding tetracarbonylmanganese derivatives in highest yield. This study included applying the results of earlier work [2–7] as well as investigating oximes, O-methyl oximes, and carbamyl groups as *ortho* directing functionalities.

Results and discussion

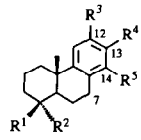
A number of ligands derived from podocarpic acid (**1**) which contained a carbonyl group at C(7) and/or a carbonyl substituent at C(13) were prepared by

Table 1

Cyclomanganation reactions of 7-oxo, 13-acetyl, and 13-methoxycarbonyl diterpenoid derivatives

Diterpenoid ligand	Manganese complex	Reflux time (h)	% yield
30	**41**	1.2	100
31	**42**	0.7	97
32	**43**	1.2	100
33	**44**	1.0	85
9	**48**	3.0	95
10	**49**	1.8	99
11	**50**	5.5	35
40	**53**	2.5	71

known procedures; these included **9** [10], **10**, **11** [11], **13**, **14**, **18** [11], **19**, **22**, **23** [12], **25** [13], **26** [14], **27**, **29**, **30** [15], **31**, **32** [16], **33** [17], **35**, **36** [15], **38**, and **39**. The 7-oxo derivative **40** [18] of dehydroabietic acid (**2**) and the 12-acetyl derivative **17** [19,20] of totarol (**3**) were also synthesised. Optimised conditions for *ortho* manganation of a 7-oxo, or 13-acetyl, or 13-methoxycarbonyl derivative involved refluxing a solution of the diterpenoid with $PhCH_2Mn(CO)_5$ (1.2 molar equiv.) in heptane (Table 1); with one exception, complexation occurred in high yield.



(1: $R^1 = CO_2H$, $R^2 = Me$, $R^3 = OH$, $R^4 = R^5 = H$
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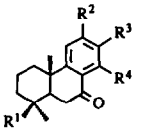
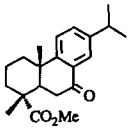
3: $R^1 = R^2 = Me$, $R^3 = H$, $R^4 = OH$, $R^5 = CHMe_2$
4: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = R^4 = R^5 = H$
5: $R^1 = CH_2OMe$, $R^2 = Me$, $R^3 = R^4 = R^5 = H$
6: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$, $R^4 = R^5 = H$
7: $R^1 = CH_2OMe$, $R^2 = Me$, $R^3 = OMe$, $R^4 = R^5 = H$
8: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$, $R^4 = Br$, $R^5 = H$
9: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$, $R^4 = COMe$, $R^5 = H$
10: $R^1 = CH_2OMe$, $R^2 = Me$, $R^3 = OMe$, $R^4 = COMe$, $R^5 = H$
11: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CO_2Me$, $R^5 = H$
12: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = H$, $R^4 = CHMe_2$, $R^3 = H$
13: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = COMe$, $R^4 = R^5 = H$
14: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = H$, $R^4 = COMe$, $R^5 = H$
15: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = R^4 = H$, $R^5 = COMe$
16: $R^1 = R^2 = Me$, $R^3 = H$, $R^4 = OMe$, $R^5 = CHMe_2$
17: $R^1 = R^2 = Me$, $R^3 = COMe$, $R^4 = OMe$, $R^5 = CHMe_2$
18: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CHO$, $R^5 = H$
19: $R^1 = CH_2OMe$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CHO$, $R^5 = H$
20: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CH_2OH$, $R^5 = H$
21: $R^1 = CH_2OMe$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CH_2OH$, $R^5 = H$
22: $R^1 = CH_2OMe$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CONMe_2$, $R^5 = H$
23: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CONEt_2$, $R^5 = H$
24: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OH$, $R^4 = R^5 = H$
25: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OCOMe$, $R^4 = R^5 = H$
26: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OCONMe_2$, $R^4 = R^5 = H$
27: $R^1 = CH_2OMe$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CHNOH$, $R^5 = H$
28: $R^1 = CH_2OMe$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CN$, $R^5 = H$
29: $R^1 = CH_2OMe$, $R^2 = Me$, $R^3 = OMe$, $R^4 = CHNOMe$, $R^5 = H$)

It has been suggested [21–23] that as an empirical guide carbonyl-containing substrates with $\nu(C{=}O) < 1700\ cm^{-1}$ in the free ligand should be amenable to cyclomanganation, with the additional requirement that an sp^2 carbon be *ortho* to the organic carbonyl to enable σ bonding to the manganese. From observations that substituted ketones with lower absorption frequencies evolved CO more rapidly during complexation procedures than those with higher frequencies, it was concluded that the lower the frequency of absorption the better the donor ability. In the present work, this relationship has been found to be valid. Thus, cyclomanganation of the 13-acetylpodocarpatriene **9** ($\nu(C{=}O) = 1670\ cm^{-1}$), was complete after only 3 h whereas the 13-methoxycarbonyl analogue **11** ($\nu(C{=}O) = 1692\ cm^{-1}$) gave an optimised complexation yield of only 35% after refluxing for 5.5 h. In the latter case increasing the reaction time resulted in a lower isolated yield.

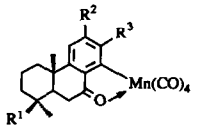


(30: $R^1 = CO_2Me$, $R^2 = R^3 = R^4 = H$
31: $R^1 = CH_2OMe$, $R^2 = R^3 = R^4 = H$
32: $R^1 = CO_2Me$, $R^2 = OMe$, $R^3 = R^4 = H$
33: $R^1 = CO_2Me$, $R^2 = OMe$, $R^3 = Br$, $R^4 = H$
34: $R^1 = CO_2Me$, $R^2 = R^3 = H$, $R^4 = CH_2Ph$
35: $R^1 = CO_2Me$, $R^2 = OMe$, $R^3 = CO_2Me$, $R^4 = H$
36: $R^1 = CO_2Me$, $R^2 = OMe$, $R^3 = COMe$, $R^4 = H$
37: $R^1 = CO_2Me$, $R^2 = OMe$, $R^3 = COMe$, $R^4 = CH_2Ph$
38: $R^1 = CO_2Me$, $R^2 = COMe$, $R^3 = R^4 = H$
39: $R^1 = CO_2Me$, $R^2 = H$, $R^3 = COMe$, $R^4 = H$)

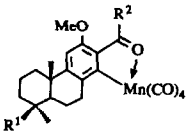


(40)

The reaction time and the excess of $PhCH_2Mn(CO)_5$ used proved to be the most important factors controlling the yield of cyclomanganated complexes. A small excess (0.2 molar equiv.) of the manganating agent was required to compensate for losses owing to thermal decomposition, and to ensure complete conversion of the diterpenoid ligands. When the reaction times were decreased, a substantial amount of non-complexed diterpenoid material was usually recovered. However, if these reaction times were extended for longer than was necessary to achieve complete conversion into the tetracarbonyl complex, side products formed in appreciable amounts. For example, whereas **30** afforded the tetracarbonyl complex **41** in 100% yield after 1.2 h, when the reaction time was increased to 2.25 h methyl 14-benzyl-7-oxopodocarpa-8,11,13-trien-19-oate (9%) was isolated in addition to the complex **41** (88%). Formation of **34** was shown to arise by reaction of the tetracarbonyl complex **41** with an additional molar equivalent of $PhCH_2Mn(CO)_5$ in refluxing heptane. The mechanism by which this product is formed has not been established, but clearly it must involve coordinatively unsaturated intermediates formed by thermal loss of CO since the coupling reaction was not observed when a solution of the tetracarbonylmanagnese complex **41** and $PhCH_2Mn(CO)_5$ was stirred at room temperature.



(41: $R^1 = CO_2Me$, $R^2 = R^3 = H$
42: $R^1 = CH_2OMe$, $R^2 = R^3 = H$
43: $R^1 = CO_2Me$, $R^2 = OMe$, $R^3 = H$
44: $R^1 = CO_2Me$, $R^2 = OMe$, $R^3 = Br$
45: $R^1 = CO_2Me$, $R^2 = OMe$, $R^3 = CO_2Me$
46: $R^1 = CO_2Me$, $R^2 = OMe$, $R^3 = COMe$
47: $R^1 = CO_2Me$, $R^2 = COMe$, $R^3 = H$)



(48: $R^1 = CO_2Me$, $R^2 = Me$
49: $R^1 = CH_2OMe$, $R^2 = Me$
50: $R^1 = CO_2Me$, $R^2 = OMe$
51: $R^1 = CO_2Me$, $R^2 = H$
52: $R^1 = CH_2OMe$, $R^2 = H$)

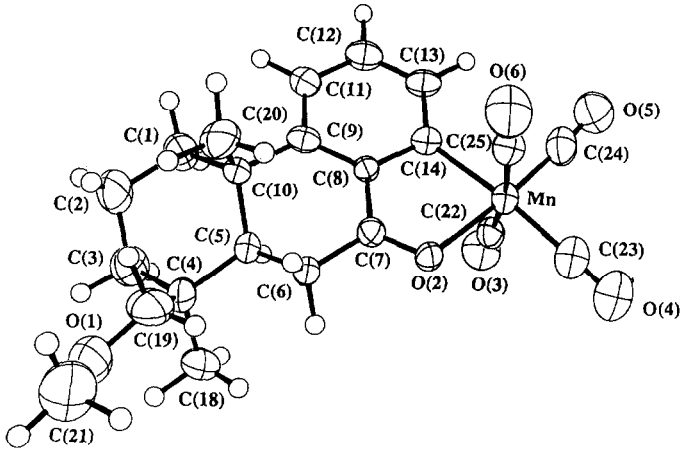


Fig. 1. Top view of compound **42** showing the atomic numbering.

A single crystal X-ray analysis of tetracarbonyl(19-methoxy-7-oxopodocarpa-8,11-13-triene-C^{14},O^{7})manganese (**42**) showed its coordination geometry to be a slightly distorted octahedron, with two of the four carbonyl ligands occupying axial positions and the remaining two being *cis* equatorial (Fig. 1).

In an attempt to improve the complexation yield of the 13-ester **50**, cyclomanganation of its 7-oxo derivative **35** was investigated. This compound should be more amenable to complexation, since ν(C=O) for the ketone was 20 cm^{-1} lower than that observed for the aryl ester carbonyl. In the event, complexation of the 7-oxo-13-ester **35** proceeded rapidly (0.75 h) to give the tetracarbonylmanganese complex **45** (99%). Moreover, in **45** the diterpenoid ligand was coordinated to manganese via the ketonic carbonyl at C(7), rather than via the aryl ester carbonyl at C(13), in accord with the expectation based on the respective IR carbonyl frequencies. This structure was confirmed by comparison of the ^{13}C NMR chemical shifts (Table 2) of the complex **45** with those of the ligand **35**. The signals of the six aromatic carbons C(8, 9, 11, 12, 13, and 14) showed the expected chemical shift differences for tetracarbonylmanganese bonding to C(14). The aryl ester carbonyl

Table 2

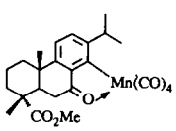
Selected ^{13}C NMR shifts (ppm) of **35** and **45**

Carbon	Ligand **35**	Complex **45**
C(7)	196.6	213.7
C(8)	123.5	133.3
C(9)	160.2	160.7
C(11)	107.2	102.6
C(12)	163.0	161.3
C(13)	118.7	134.8
C(14)	131.8	190.2
4-CO_2Me	176.8	176.2
13-CO_2Me	165.4	170.2
Mn(CO)$_4$	–	210.6, 210.8, 213.9, 219.1

bonded to C(13) showed a relatively small shift difference ($\Delta\delta$ 4.8 ppm), consistent with the introduction of $Mn(CO)_4$ at C(14), but clearly not as large as would have been expected if the ester carbonyl was ligated to the manganese atom.

The 13-acetyl-7-oxo diterpenoid **36** gave the tetracarbonyl complex **46** (93%) as well as the 14-benzyl diterpenoid **37** (4%). The chemical shift differences for the signals owing to the aromatic carbons in the ^{13}C NMR spectra of **46** versus **36** were again consistent with those of a C(14) cyclomanganated complex. However, the chemical shift differences of the two ketonic carbonyl signals could not be used to establish the structure of the manganese complex since both showed $\Delta\delta$ 10–14 ppm. Although X-ray diffraction analysis of the complex **46** showed unambiguously that the manganese was again bonded to the carbonyl oxygen at C(7), problems with disorder around Mn–C≡O in the crystal did not allow the data to be refined sufficiently to justify their publication.

With a view to eventual cyclopentaannulation of ring C across C(13)–C(14) [24,25] acetylation of methyl podocarpa-8,11,13-trien-19-oate (**4**) with $AlCl_3$/CH_3COCl afforded a mixture (4:1) (65%) of the 12-acetyl **13** and 13-acetyl **14** derivatives, and the 14-acetyl derivative **15** (3%). Treatment of **13**, **14** with $PhCH_2Mn(CO)_5$ gave a mixture (4:1) (91%) of **54, 55** which showed metal carbonyl maxima at 2074, 1973, and 1928 cm^{-1} in the IR spectrum. Both complexes showed sharp singlets in the aromatic region of the ^1H NMR spectrum, indicating clearly the presence of two *para* related hydrogens, which demands substitution at both C(12) and C(13). Cyclomanganation of the 12-acetyl-7-oxo derivative **38** afforded tetracarbonyl(methyl 12-acetyl-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^7)manganese (**47**) (85%). The ^1H NMR spectrum showed *meta* coupled doublets at 7.61 [H(11)] and 8.37 ppm [H(13)] as required for cyclomanganation involving C(7) and C(14). In contrast, the 13-acetyl-7-oxo regioisomer **39** gave the C(12)-manganated complex **56**. The structures **47** and **56** indicate that 7-oxo diterpenoid derivatives possessing an additional ketonic group bonded to the aromatic ring show preferential ligation to the C(7) carbonyl oxygen when steric constraints do not clearly favour an alternative site.



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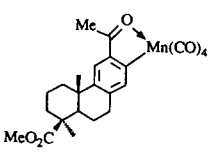

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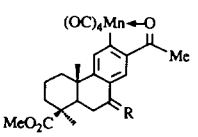
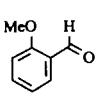


(55: R = H_2
56: R = O)



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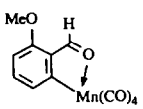

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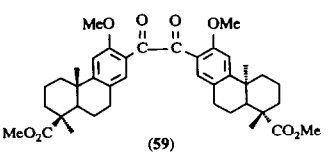
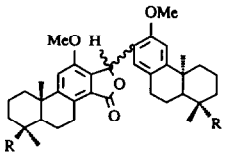


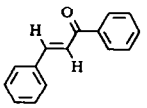
(59)

Attempted reaction of 12-acetyl-13-methoxytotara-8,11,13-triene (**17**) with $PhCH_2Mn(CO)_5$ returned only starting material (69%), presumably reflecting the steric hindrance that the methyl substituent at C(10) exerts on the only available site for cyclomanganation, C(11).

Formation of the cyclomanganated complexes from reaction of $PhCH_2Mn(CO)_5$ with 4-methoxybenzaldehyde [ν(C=O) = 1685 cm^{-1}, 33%] and 4-(dimethylamino)benzaldehyde [ν(C=O) = 1660 cm^{-1}, 61%] has been reported [22]. In contrast, benzaldehyde itself [ν(C=O) = 1700 cm^{-1}] did not undergo cyclomanganation, a failure attributed to the insufficient O-donor ability of the unsubstituted aromatic aldehyde. In the present work cyclomanganation of 2-methoxybenzaldehyde (**57**) [ν(C=O) = 1686 cm^{-1}] was achieved, albeit in an optimised yield of only 26% [25], by carrying out the complexation under a slow stream of argon so that carbon monoxide released during the complexation sequence was continuously removed. Extensive experimentation showed that optimum conditions for the formation of the aldehyde complex required the use of refluxing heptane for a relatively short time (1.5 h), reflecting the thermal instability of the complex **58**. Optimum conditions for cyclomanganation of the analogous diterpenoid-derived aldehydes **18** or **19** involved refluxing a solution in heptane for 1 h only and gave the complexes **51** (38%) and **52** (33%). In addition, a number of side products were isolated, including methyl 13-hydroxymethyl-12-methoxypodocarpa-8,11,13-trien-19-oate (**20**) (18%) and bis[13,13'-(methyl 12-methoxypodocarpa-8,11,13-trien-19-oate)]ethanedione (**59**) (5%). The presence of an aromatic ketone in **59** was indicated by a peak at 1668 cm^{-1} in the IR spectrum, and by a signal at 192.6 ppm in the ^{13}C NMR spectrum. The ^1H NMR spectrum showed two singlets in the aromatic region, as required for substitution at C(13). The mass spectrum showed the molecular ion at *m/z* 658, which gave an accurate mass measurement consistent with the formula $C_{40}H_{50}O_8$. Furthermore, the base peak was at *m/z* 329, in agreement with a symmetrical dimer. Presumably **59** arises via a radical process. It has been shown that benzylpentacarbonylmanganese will undergo thermally induced homolysis [26] and that in the absence of a suitable quenching agent the resulting radicals can dimerise to form $(PhCH_2)_2$ and $Mn_2(CO)_{10}$. Moreover, aldehyde hydrogen atoms can be abstracted by radicals to form acyl radicals which can then dimerise; such a pathway to the 1,2-diketone **59** is summarized in Scheme 1. Since homolysis of $PhCH_2Mn(CO)_5$ gives $Mn(CO)_5$ and $PhCH_2$, abstraction by either radical of the aldehyde hydrogen would afford toluene and $HMn(CO)_5$. Although any toluene formed during the reaction would have been lost in the workup procedure, $HMn(CO)_5$ could be the hydride responsible for formation of the 13-hydroxymethyl derivative **20**. Also isolated from the reaction of **18** was a mixture of the diastereoisomeric lactones **60** (26%). The mass spectrum of **60** showed the molecular ion at *m/z* 658, which gave an accurate mass measurement for $C_{40}H_{50}O_8$. The IR spectrum showed maxima at 1764 (lactone) and at 1725 cm^{-1} (aliphatic ester). The ^1H NMR and ^{13}C NMR spectra were complicated, showing significant broadening of all resonances. It is proposed (Scheme 1) that **51** undergoes an intramolecular carbonyl insertion reaction to form the acylmanganese intermediate (i), which then rearranges to form the alkylmanganese lactone derivative (ii). Coupling of this intermediate (ii) with the aryl radical (iii) formed from the parent aldehyde, leads to the lactones **60** [27,28]. Similarly, complexation of the 13-formyl-19-methoxy diterpenoid **19** with $PhCH_2Mn(CO)_5$ gave the 13-hydroxymethyl derivative **21** (12%), and the diastereoisomeric lactones **61** (24%), in addition to the complex **52**.



(60: R = CO_2Me
61: R = CH_2OMe)



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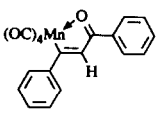
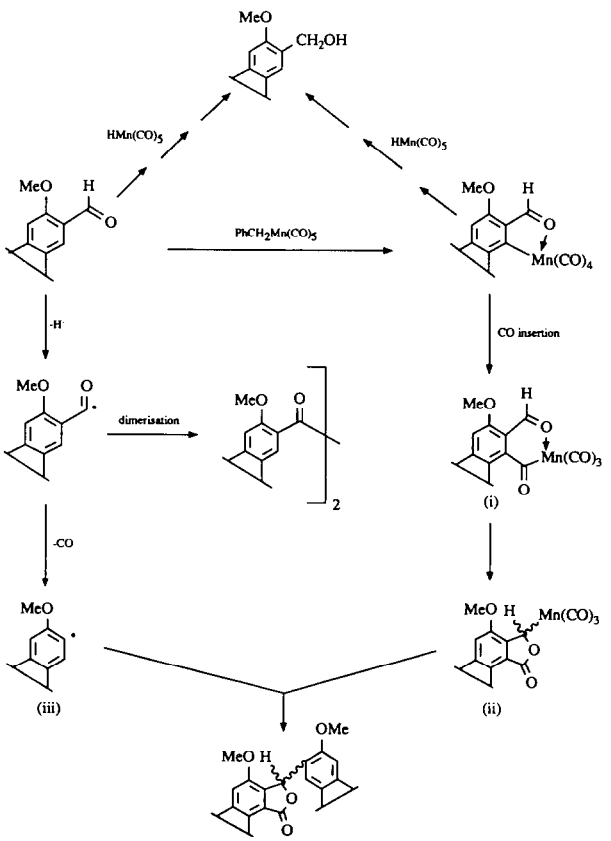


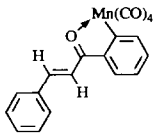
(63)

Cyclomanganation of 1,3-diphenyl-2-propen-1-one [chalcone, (**62**)] presents a competition between *ortho* metallation and *beta*-olefinic metallation. Attempted complexation with $MeMn(CO)_5$ or with $PhCH_2Mn(CO)_5$ has been reported by Cabral [4], who obtained a red precipitate which decomposed to $Mn_2(CO)_{10}$ during chromatography. Since chalcone (ν(C=O) = 1670 cm^{-1}) should form stable complex(es), its reaction with $PhCH_2Mn(CO)_5$ in heptane was repeated [4], and was monitored by TLC. Complexation did indeed occur, reaching completion after only 35 min. Flash chromatography and PLC yielded (2-benzoyl-1-phenylethene-C,O)tetracarbonylmanganese (**63**) (65%) and the *ortho* metallated aromatic analogue **64** (9%). In addition to the expected aromatic and olefinic resonances in its ^{13}C NMR spectrum, the olefinic complex **63** showed five peaks beyond 200 ppm, the lowest at 253.3 ppm; this represents a dramatic difference from the ^{13}C NMR data

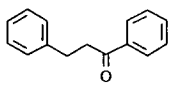


Scheme 1.

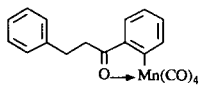
observed for cyclomanganated aromatic complexes. Cyclomanganation of the saturated analogue, **65** afforded tetracarbonyl[2-(3-phenylpropanoyl)phenyl-C,O)]-manganese (**66**) (94%).



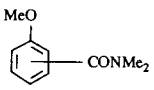
(64)



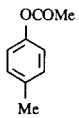
(65)



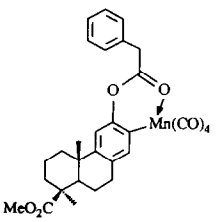
(66)



(67: *ortho*
68: *meta*
69: *para*)

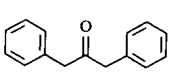


(70)

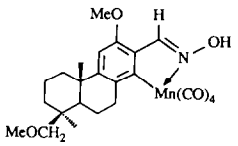


(71)

The cyclomanganation of benzamides using $PhCH_2Mn(CO)_5$ has been investigated extensively [21]. Whereas attempted *ortho* manganation of benzamide itself was unsuccessful, $C_6H_5CONR_2$ [R = Me, Et, and $(CH_2)_4$] gave rise to the expected complexes, albeit in varying yields. In the case of R = Me, quantitative conversion was achieved after 5 h at reflux temperature, while the yield for R = Et was 33% after 4 h. This decrease in yield was attributed to increased crowding adjacent to the carbonyl group. In the present work, attempted complexation of either the diterpenoid-derived *N,N*-dimethyl amide **22** or the *N,N*-diethyl homologue **23** with $PhCH_2Mn(CO)_5$ in heptane returned only the starting amides. This result was surprising since both amides show ν(C=O) near 1630 cm^{-1}. Furthermore, the *N,N*-dimethyl amide **22** should show significantly less steric hindrance to *ortho* complexation than the *N,N*-diethyl amide **23** [21]. With the intention of investigating whether the adjacent methoxy substituent was inhibiting cyclometallation in the diterpenoid case, the monocyclic *ortho*-, *meta*- and *para*-methoxy-*N,N*-dimethylbenzamides (**67**, **68**, and **69** respectively) were reacted with $PhCH_2Mn(CO)_5$ in heptane. Each amide gave (TLC) a yellow product (**68** gave two) which was less polar than the starting ligand and more polar than the manganating reagent, properties consistent with those expected for their corresponding tetracarbonyl complexes. Unfortunately, workup and flash chromatography on either silica gel or alumina under argon gave only recovered $PhCH_2Mn(CO)_5$. The yellow bands containing the putative tetracarbonylmanganese complexes became visibly less coloured as they were eluted down the columns, a clear indication that the complexes were decomposing. Although, these complexes could not be isolated, IR spectra of the crude products showed clearly the presence of tetracarbonylmanganese species. Neither the monocyclic acetate **70** nor the diterpenoid-derived acetate **25** (ν(C=O) = 1761 cm^{-1}) formed isolable *ortho* manganated complexes.



(72)



(73)

(74)

Treatment of 12-dimethylcarbamylpodocarpa-8,11,13-trien-19-oate (**26**) with $PhCH_2Mn(CO)_5$ (2 × 1.2 molar equiv.) in heptane gave **26** (71%), dibenzyl ketone (**72**), and a mixture (2:3) of **72** and a complex tentatively assigned as tetracarbonyl(methyl 12-phenylethanoyloxypodocarpa-8,11,13-trien-19-oate-C^{13}, O)manganese (**71**) (5%). Although **71** could not be separated from **72** the mixture showed maxima in the region expected for the metal carbonyl at 2077, 1990, 1980, and 1931 cm^{-1} in the IR spectrum. In addition to multiplets assigned to the hydrogens from the benzyl substituent in **72** there were singlets at 7.62 [H(11)] and 7.94 ppm [H(14)] in the aromatic region of the ^1H NMR spectrum. The methylene protons of the benzyl substituent gave rise to a singlet at 4.19 ppm. Combustion analysis of the mixture confirmed the absence of nitrogen. Formation of the complex **71** formally requires the loss of $-NMe_2$ and insertion of $-CH_2Ph$ prior to complexation. Formation of **72** is attributed to coupling between $PhCH_2^{\cdot}$ and an intermediate of the type $Mn(CO)_4COCH_2Ph$ formed by insertion of a carbonyl ligand into the $Mn-CH_2Ph$ bond. Stable manganese complexes of the type $LMn(CO)_4COCH_2Ph$ (L = phosphines, phosphites) are known [29].

Although cyclometallation of nitrogen-containing ligands is well documented [30–35], there has been no report of the *ortho* manganation of oximes. Since an oxime is an easily accessible derivative of an aldehyde, and since the diterpenoid aldehyde **19** had not provided a high yield route to its cyclomanganated complex, its oxime **27** was treated with $PhCH_2Mn(CO)_5$. However, an inseparable mixture (85:15) of the cyclomanganated oxime **73** and the 13-formyl derivative **19** was recovered in only low yield (16%). The oxime complex **73** was identified by the IR spectrum which showed four Mn–C≡O bands at 2068, 1979, 1969, and 1927 cm^{-1}, and by its ^{13}C NMR spectrum. In the mass spectrum the peak at highest mass (*m/z* 425) was assigned to $M^+ - (CH{=}N{-}OH){-}CO$, the peaks at *m/z* 397 and 369 representing successive losses of CO from *m/z* 425. Also isolated from the attempted cyclometallation reaction was the 13-cyano derivative **28** (19%), which is formally derived from the oxime by loss of water. In an attempt to decrease the amount of oxime diverted by dehydration and also to decrease the acidity of the functional group, its methyl ether **29** was used but did not form any *ortho* manganated products.

Experimental

For general experimental details see refs. 36 and 37. High field ^1H NMR spectra were determined at 400.134 MHz on a Bruker AM400 instrument operating at 9.2 T. Multiplicities were determined from DEPT spectra. Compounds from chromatography are given in order of polarity.

19-Methoxy-7-oxopodocarpa-8,11,13-triene (31)

Oxidation of 19-methoxypodocarpa-8,11,13-triene (**5**) with CrO_3 in HOAc afforded 19-methoxy-7-oxopodocarpa-8,11,13-triene (84%) which crystallized from MeOH as white rods, m.p. 60–62 °C. Anal. Found: C, 79.5; H, 9.0. $C_{18}H_{24}O_2$ calc.: C, 79.4; H, 8.9%. ν_{max} 1682 (CO), 1100 cm^{-1} (C–O–C). δ(H) 0.98 (s, $H(18)_3$); 1.02 (txd, *J* 13.5, 4.1 Hz, H(3ax)); 1.22 (s, $H(20)_3$); 1.51 (txd, *J* 13.1, 3.8 Hz, H(1ax)); 1.62 (dxp, *J* 14.1, 3.5, Hz, H(2eq)); 1.72 (qxt, *J* 13.9, 3.1 Hz, H(2ax)); 1.81 (bd, *J* 13.5 Hz, H(3eq)); 1.90 (dxd, *J* 11.9, 6.1 Hz, H(5)); 2.33 (bd, *J* 12.7 Hz,

H(1eq)); 2.70–2.80 (m, $H(6)_2$); 3.28 (s, (19-OMe)); 3.36, 3.44 (d, *J* 9.2 Hz, $H(19)_2$); 7.22 (txd, *J* 7.2, 1.0 Hz, H(13)); 7.33 (d, *J* 8.0 Hz, H(11)); 7.46 (txd, *J* 7.2, 1.5 Hz, H(12)); 7.95 (dxd, *J* 7.8, 1.4 Hz, H(14)) ppm. δ(C) 18.7 (C(2)); 23.7 (C(20)); 27.2 (C(18)); 36.2 (C(3)); 36.3 (C(6)); 37.5 (C(10)); 38.0 (C(4)); 38.1 (C(1)); 49.6 (C(5)); 59.3 (19-OMe); 76.0 (C(19)); 123.8 (C(11)); 126.1 (C(13)); 127.2 (C(14)); 130.5 (C(8)); 134.0 (C(12)); 155.9 (C(9)); 199.3 (C(7) ppm. *m/z* 272 (10, M^+), 257 (1, M – Me), 240 (15, M – MeOH), 227 (8, $M - CH_2OMe$), 211 (10), 157 (15), 145 (100).

*13-Acetyl-12,19-dimethoxypodocarpa-8,11,13-triene (**10**)*

Acetylation of 12,19-dimethoxypodocarpa-8,11,13-triene (**7**) with MeCOCl and $AlCl_3$ afforded 13-acetyl-12,19-dimethoxypodocarpa-8,11,13-triene (95%) which crystallized from hexanes/Et_2O as rods, m.p. 98–101°C. Anal. Found: C, 76.5; H 9.1. $C_{21}H_{30}O_3$ calc.: C, 76.3; H, 9.2%. ν_{max} (KBr) 1671 (CO), 1604, 1494, 1453 cm^{-1} (C=C). δ(H) 1.01 (txd, *J* 13.5, 4.0 Hz, H(3ax)); 1.03 (s, $H(18)_3$); 1.20 (s, $H(20)_3$); 1.40 (dxd, *J* 12.8, 1.9 Hz, H(5)); 1.45 (txd, *J* 13.0, 3.8 Hz, H(1ax)); 1.61–1.73 (m, H(2eq), H(6ax)); 1.74 (qxt, *J* 13.5, 3.2 Hz, H(2ax)); 1.88 (bd, *J* 13.6 Hz, H(3eq)); 1.98 (bdxd, *J* 13.4, 7.3 Hz, H(6eq)); 2.29 (bd, *J* 12.2 Hz, H(1eq)); 2.57 (s, (13-COMe)); 2.76 (dxdxd, *J* 16.7, 11.8, 7.4 Hz, H(7ax)); 2.89 (bdxd, *J* 16.7, 5.9 Hz, H(7eq)); 3.24 (d, *J* 9.1 Hz, H(19)); 3.33 (s, (19-OMe)); 3.52 (d, *J* 9.1 Hz, H(19)); 3.87 (s, (12-OMe)); 6.83 (s, H(11)); 7.43 (s, H(14)) ppm. δ(C) 19.1 (C(2)); 19.2 (C(6)); 25.4 (C(20)); 27.6 (C(18)); 29.8 (C(7)); 31.8 (13-CO*Me*); 35.8 (C(3)); 38.1 (C(10)); 38.4 (C(4)); 38.9 (C(1)); 51.0 (C(5)); 55.4 (12-OMe); 59.4 (19-OMe); 75.8 (C(19)); 107.6 (C(11)); 125.6 (C(13)); 127.3 (C(8)); 130.9 (C(14)); 156.1 (C(9)); 157.2 (C(12)); 199.5 (13-*C*OMe) ppm. *m/z* 330 (100, M^+), 315 (34, M – Me), 283 (20, 315 – MeOH), 241 (42, M – COMe–H–CH_2OMe), 203 (75), 43 (64, OCMe).

*Methyl 12-methoxy-13-methoxycarbonyl-7-oxopodocarpa-8,11,13-trien-19-oate (**35**)*

Oxidation of methyl 12-methoxy-13-methoxycarbonylpodocarpa-8,11,13-trien-19-oate (**11**) with CrO_3 in HOAc gave methyl 12-methoxy-13-methoxycarbonyl-7-oxopodocarpa-8,11,13-trien-19-oate (92%) which crystallized from $CHCl_3$/MeOH as hexagonal plates, m.p. 218–221°C. Found: C, 67.2; H, 6.9. $C_{21}H_{26}O_6$ calc.: C, 67.4; H, 7.0%. ν_{max} (KBr) 1729, 1715 (non-conj. ester CO), 1700 (conj. ester CO), 1680 (ketone CO), 1286 cm^{-1} (C–O–C). δ(H) 1.14 (s, $H(20)_3$); 1.16 (txd, *J* 13.7, 4.0 Hz, H(3ax), 1.28 (s, $H(18)_3$); 1.58 (txd, *J* 13.3, 4.1 Hz, H(1ax)); 1.74 (dxp, *J* 14.3, 3.1 Hz, H(2eq)); 2.06 (qxt, *J* 13.9, 3.6 Hz, H(2ax)); 2.07 (dxd, *J* 14.4, 3.3 Hz, H(5)); 2.32–2.37 (m, H(1eq), H(3eq)); 2.98 (dxd, *J* 18.0, 3.3 Hz, H(6eq)); 3.19 (dxd, *J* 18.0, 14.4 Hz, H(6ax)); 3.72 (s, (19-OMe)); 3.89 (s, (12-OMe)); 3.97 (s, (13-CO_2Me)); 6.94 (s, H(11)); 8.50 (s, H(14)) ppm. δ(C) 19.4 (C(2)); 21.1 (C(20)); 27.8 (C(18)); 37.1 (C(6)); 37.2 (C(3)); 38.2 (C(1)); 39.1 (C(10)); 43.8 (C(4)); 49.8 (C(5)); 51.6 (19-OMe); 52.0 (13-CO_2*Me*); 56.0 (12-OMe); 107.2 (C(11)); 118.7 (C(13), 123.5 (C(8)); 131.8 (C(14)); 160.2 (C(9)); 163.0 (C12)); 165.4 (13-*C*O_2Me); 176.8 (C(19)); 196.6 (C(7)) ppm. *m/z* 374 (100, M^+), 359 (8, M – Me), 343 (30, M – OMe), 315 (15, $M - CO_2Me$), 299 (66, 359 – HCO_2Me), 273 (16), 248 (27), 233 (34).

*Acetylation of methyl podocarpa-8,11,13-trien-19-oate (**4**)*

Acetylation of methyl podocarpa-8,11,13-trien-19-oate (**4**) with MeCOCl and $AlCl_3$ in refluxing 1,2-dichloroethane afforded after purification by PLC

(hexanes/Et_2O, 9 : 1) in order of increasing polarity (i) methyl 14-acetylpodocarpa-8,11,13-trien-19-oate (**15**) (7 mg, 3%) as a clear oil. Found: $M^{+\cdot}$, 314.1883. $C_{20}H_{26}O_5$ calc.: M, 314.1882). ν_{max} 1724 (ester CO), 1686 cm^{-1} (ketone CO). δ(H) 1.05 (s, $H(20)_3$); 1.08 (txd, J 13.7, 4.3 Hz, H(3ax)); 1.27 (s, $H(18)_3$); 1.35 (txd, J 13.3, 4.0 Hz, H(1ax)); 1.53 (dxd, J 12.3, 1.5 Hz, H(5)); 1.60–1.65 (m, H(2eq)); 1.85 (qxd, J 12.2, 6.0 Hz, H(6ax)); 2.00 (qxt, J 13.9, 3.8 Hz, H(2ax)); 2.19–2.29 (m, H(1eq), H(3eq), H(6eq)); 2.55 (s, (14-COMe)); 2.98–3.05 (m, $H(7)_2$); 3.66 (s, (19-OMe)); 7.20 (t, J 7.8 Hz, H(12)); 7.39–7.43 (m, H(11), H(13)) ppm. δ(C) 20.0 (C(2)); 20.7 (C(6)); 22.9 (C(20)); 28.4 (C(18)); 30.4 (14-CO*Me*); 30.6 (C(7)); 37.4 (C(3)); 39.0 (C(10)); 39.7 (C(1)); 43.8 (C(4)); 51.3 (19-OMe); 52.1 (C(5)); 125.4 (C(13)); 126.0 (C(12)); 129.1 (C(11)); 134.9 (C(8)); 138.8 (C(14)); 149.6 (C(9)); 177.8 (C(19)); 203.4 (14-COMe) ppm. m/z 314 (68, M^+), 299 (7, M – Me), 282 (3, M – MeOH), 267 (4, 282 – Me), 255 (5, M – CO_2Me), 239 (65, 299 – HCO_2Me), 185 (17), 159 (12), 141 (14), 115 (10), 83 (20), 43 (100, COMe); and (ii) a mixture (3 : 1) of methyl 12-acetylpodocarpa-8,11,13-trien-19-oate (**13**) and methyl 13-acetylpodocarpa-8,11,13-trien-19-oate (**14**) (0.14 g, 62%) as a white solid, m.p. 115–120°C. ν_{max} (KBr) 1717, 1708 (ester CO), 1678 (ketone CO), 1605, 1564, 1558, 1470 cm^{-1} (C=C). m/z 314 (17, M^+), 299 (27, M – Me), 239 (100, 299 – HCO_2Me), 173 (11), 43 (82, COMe). **13**: δ(H) 1.05 (s, $H(20)_3$); 1.09 (txd, J 13.5, 4.2 Hz, H(3ax)); 1.29 (s, $H(18)_3$); 1.38 (txd, J 13.3, 4.1 Hz, H(1ax)); 1.54 (dxd, J 12.3, 1.7 Hz, H(5)); 1.62–1.67 (m, H(2eq)); 1.95–2.08 (m, H(2ax), H(6ax)); 2.22 (bdxd, J 13.8, 6.1, Hz, H(6eq)); 2.29 (bd, J 13.2 Hz, H(3eq)); 2.38 (bd, J 13.0 Hz, H(1eq)); 2.56 (s, (12-COMe)); 2.83 (dxdxd, J 17.8, 12.1, 6.3 Hz, H(7ax)); 2.96 (dxd, J 17.6, 4.3 Hz, H(7eq)); 3.67 (s, 19-OMe); 7.11 (d, J 8.0 Hz, H(14)); 7.65 (dxd, J 7.9, 1.7 Hz, H(13)); 7.92 (d, J 1.5 Hz, H(11)) ppm. δ(C) 19.7 (C(2)); 20.5 (C(6)); 22.9 (C(20)); 26.4 (C(18)); 28.4 (12-CO*Me*); 32.1 (C(7)); 37.4 (C(3)); 38.5 (C(10)); 39.1 (C(1)); 43.8 (C(4)); 51.2 (19-OMe); 52.4 (C(5)); 125.3 (C(13), 125. 7 (C(11)); 129.2 (C(14)); 135.0 (C(12)); 141.4 (C(8)); 148.3 (C(9)); 177.5 (C(19)); 197.9 (12-*C*OMe) ppm. **14**: δ(H) 1.04 (s, $H(20)_3$); 1.10 (txd, J 13.4, 4.3 Hz, H(3ax)); 1.29 (s, $H(18)_3$); 1.39 (txd, J 13.5, 4.1 Hz, H(1ax)); 1.54 (dxd, J 12.3, 1.7 Hz, H(5)); 1.62–1.67 (m, H(2eq)); 1.94–2.08 (m, H(2ax), H(6ax)); 2.23 (dxd, J 14.0, 6.4 Hz, H(6eq)); 2.29 (bd, J 13.1 Hz, H(1eq), H(3eq)); 2.59 (s, (13-COMe)); 2.84 (dxdxd, J 17.2, 12.4, 6.4 Hz, H(7ax)); 2.98 (dxdxt, J 17.0, 4.8, 0.6 Hz, H(7eq)); 3.70 (s, (19-OMe)); 7.36 (d, J 8.4 Hz, H(11)); 7.65 (bs, H(14)); 7.71 (dxd, J 8.3, 1.3 Hz, H(12)) ppm. δ(C) 19.7 (C(2)); 20.7 (C(6)); 22.6 (C(20)); 26.4 (C(18)); 28.4 (13-CO*Me*); 31.9 (C(7)); 37.4 (C(3)); 38.8 (C(10)); 39.0 (C(1)); 43.8 (C(4)); 51.2 (19-OMe); 52.3 (C(5)); 125.6 (C(12)); 125.8 (C(11)); 129.2 (C(14)); 134.3 (C(14)); 134.3 (C(13)); 135.6 (C(8)); 153. 5 (C(9)); 177.5 (C(19)); 197.9 (13-*C*OMe) ppm.

*Oxidation of the mixture of **13** and **14***

Oxidation of a mixture of **13** and **14** with CrO_3 in aqueous HOAc afforded, after extensive purification by PLC (hexanes/Et_2O, 1 : 1): (i) methyl 12-acetyl-7-oxopodocarpa-8,11,13-trien-19-oate (**38**) (30%) which crystallized as rods (hexanes/Et_2O), m.p. 201–206°C. Anal. Found: C, 73.2; H, 7.6. $C_{20}H_{24}O_4$ calc.: C, 73.2; H, 7.4%. ν_{max} (KBr): 1716 (ester CO), 1689, 1686 cm^{-1} (ketone CO). δ(H) 1.13 (s, $H(20)_3$); 1.14 (txd, J 13.6, 4.0 Hz, H(3ax)); 1.26 (s, $H(18)_3$); 1.53 (txd, J 13.2, 4.0 Hz, H(1ax)); 1.72 (dxp, J 14.4, 3.2 Hz, H(2eq)); 1.99 (qxt, J 13.9, 3.5 Hz, H(2ax)); 2.05 (dxd, J 14.6, 3.2 Hz, H(5)); 2.33 (bd, J 13.4 Hz, H(3eq)); 2.48 (bd, J

12.9 Hz, H(1eq)); 2.61 (s, (12-COMe)); 3.02 (dxd, *J* 18.0, 3.2 Hz, H(6eq)); 3.25 (dxd, *J* 18.0, 14.6 Hz, H(6ax)); 3.70 (s, 19-OMe); 7.81 (dxd, *J* 8.1, 1.6 Hz, H(13)); 8.02 (d, *J* 1.4 Hz, H(11)); 8.09 (d, *J* 1.4 Hz, H(14)) ppm. δ(C) 19.5 (C(2)); 21.4 (C(20)); 26.9 (C(18)); 27.9 (12-CO*Me*); 37.3 (C(3)); 37.6 (C(6)); 38.4 (C(1)); 38.8 (C(10); 43.8 (C(4)); 49.9 (C(5)); 51.7 (19-OMe); 124.9 (C(13)); 126.1 (C(11)); 127.6 (C(14)); 133.4 (C(12)); 140.9 (C(8)); 154.5 (C(9)); 176.8 (C(19)); 197.8 (12-COMe); 198.3 (C(7)) ppm. *m/z* 328 (68, M^+), 313 (16, *M* − Me), 296 (20, *M* − MeOH), 281 (6, 296 − Me), 268 (17, *M* − HCO_2Me), 253 (79, 268 − Me), 227 (12), 213 (23), 199 (18), 187 (37), 43(100, COMe); and (ii) methyl 13-acetyl-7-oxopodocarpa-8,11,13-trien-19-oate (**39**) (12%) which crystallized from hexanes/Et_2O/$CHCl_3$ as plates, m.p. 173–176°C. Anal. Found: M^+, 328.1676. $C_{20}H_{24}O_4$ calc.: *M*, 328.1675). ν_{max} (KBr): 1723 (ester CO), 1690 cm^{-1} (ketone CO). δ(H) 1.13 (s, $H(20)_3$); 1.14 (txd, *J* 13.6, 3.8 Hz, H(3ax)); 1.27 (s, $H(18)_3$); 1.52 (txd, *J* 13.4, 4.1 Hz, H(1ax)); 1.72 (dxp, *J* 14.3, 3.2 Hz, H(2eq)); 2.03 (qxt, *J* 14.0, 3.6 Hz, H(2ax)); 2.06 (dxd, *J* 14.4, 3.3 Hz, H(5)); 2.33 (bd, *J* 13.5 Hz, H(3eq)); 2.40 (bd, *J* 12.9 Hz, H(1eq)); 2.62 (s, (13-COMe)); 3.04 (dxd, *J* 18.0, 3.2 Hz, H(6eq)); 3.25 (dxd, *J* 18.0, 14.4 Hz, H(6ax)); 3.71 (s, (19-OMe)); 7.53 (d, *J* 8.4 Hz, H(11)); 8.12 (dxd, *J* 8.4, 2.0 Hz, H(12)); 8.56 (d, *J* 2.0 Hz, H(14)) ppm. δ(C) 19.5 (C(2)); 21.2 (C(20)); 26.7 (C(18)); 27.9 (13-CO*Me*); 37.3 (C(3)); 37.5 (C(6)); 38.2 (C(1)); 39.0 (C(10)); 43.9 (C(4)); 49.8 (C(5)); 51.7 (19-OMe); 125.7 (C(11)); 127.8 (C(14)); 130.5 (C(8)); 132.8 (C(12)); 135.2 (C(13)); 159.0 (C(9)); 176.8 (C(19)); 197.3 (13-COMe); 198.0 (C(7)) ppm. *m/z* 328 (67, M^+), 313 (38, *M* − Me), 296 (19, *M* − MeOH), 281 (3, 296 − Me), 268 (17, *M* − HCO_2Me), 253 (70, 268 − Me); 202 (30), 187 (35), 161 (11), 128 (15), 101 (14), 69 (16), 43 (100, COMe).

*13-Formyl-12,19-dimethoxypodocarpa-8,11,13-triene (**19**)*

Reaction of 12,19-dimethoxypodocarpa-8,11,13-triene (**8**) with butyl dichloromethyl ether and $AlCl_3$ in nitrobenzene under argon at 0°C for 30 min and then at 5°C for 124 h followed by dilution which with dilute aqueous HCl and steam distillation afforded 13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene (87%) which crystallized from hexanes as plates, m.p. 126–129°C. Anal. Found: C, 75.8; H, 9.1. $C_{20}H_{28}O_3$ calc.: C, 75.8; H, 8.9%. ν_{max} (KBr): 1677 (CO), 1609, 1563, 1490 cm^{-1} (C=C). δ(H) 1.00 (txd, *J* 13.3, 4.1 Hz, H(3ax)); 1.03 (s, $H(18)_3$); 1.20 (s, $H(20)_3$); 1.39 (dxd, *J* 12.7, 1.8 Hz, H(5)); 1.45 (txd, *J* 13.0, 3.8 Hz, H(1ax)); 1.60–1.67 (m, H(2eq), H(6ax)); 1.72 (qxt, *J* 13.9, 3.2 Hz, H(2ax)); 1.87 (bd, *J* 13.5 Hz, H(3eq)); 1.98 (bdxd, *J* 13.4, 7.3 Hz, H(6eq)); 2.28 (bd, *J* 12.5 Hz, H(1eq)); 2.75 (dxdxd, *J* 16.8, 11.8, 7.4 Hz, H(7ax)); 2.89 (bdxd, *J* 16.8, 6.2 Hz, H(7eq)); 3.24 (d, *J* 9.1 Hz, H(19)); 3.32 (s, 19-OMe); 3.50 (d, *J* 9.1 Hz, H(19)); 3.87 (s, 12-OMe); 6.84 s, H(11)); 7.47 (s, H(14)); 10.35 (13-CHO) ppm. δ(C) 19.0 (C(2), C(6)); 25.2 (C(20)); 27.6 (C(18)); 29.7 (C(7)); 35.8 (C(3)); 38.0 (C(10)); 38.75 (C(4)); 38.82 (C(1)); 50.8 (C(5)); 55.5 (12-OMe); 59.3 (19-OMe); 75.8 (C(19)); 107.5 (C(11)); 122.6 (C(13)); 127.5 (C(8)); 129.0 (C(14)); 158.6 (C(9)); 159.9 (C(12)); 189.5 (13-CHO) ppm. *m/z* 316 (74, M^+), 301 (5, *M* − Me), 269 (14, 301 − MeOH), 241 (11), 201 (25), 189 (100), 45 (25).

*Methyl 12-dimethylcarbamylpodocarpa-8,11,13-trien-19-oate (**26**)*

A solution of methyl 12-hydroxypodocarpa-8,11,13-trien-19-oate (**24**) (1.00 g, 3.47 (mmol) in anhydrous tetrahydrofuran (15 mL) was added dropwise to a slurry

of hexanes-washed sodium hydride (0.18 g, 50% w/w dispersion, 3.82 mmol) in THF (10 mL) under argon. The mixture was then heated under reflux for 1 h after which it was allowed to cool to room temperature. Dimethylcarbamyl chloride (1.28 mL, 13.9 mmol) was added to the mixture which was then heated to reflux for 5 h. Excess of sodium hydride was discharged by the dropwise addition of MeOH and the mixture was worked up to yield a solid which was flash chromatographed (hexanes/Et_2O, 4:1) and crystallized from aqueous MeOH to give methyl 12-dimethylcarbamylpodocarpa-8,11,13-trien-19-oate (1.09 g, 87%) as needles, m.p. 128–130°C [14].

13-Formyl-12,19-dimethoxypodocarpa-8,11,13-triene oxime (27)

A solution of 13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene (**19**) (0.50 g, 1.58 mmol) and hydroxylamine hydrochloride (0.13 g, 1.90 mmol) in EtOH/pyridine (20 mL, 1:1) was heated under reflux for 2 h. The mixture was worked up, purified by PLC (hexanes/Et_2O, 4:1 and 3:2) and crystallized from $Et_2O/CHCl_3$/hexanes to give 13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene oxime as rods, m.p. 175–180°C. Anal. Found: C, 72.6; H, 8.8; N, 4.3. $C_{20}H_{29}NO_3$ calc.: C, 72.5; H, 8.8; N, 4.2%. ν_{max} (KBr): 3274 (NO–H), 1625, 1606, 1497, 1475 cm^{-1} (C=C). δ(H) 1.01 (txd, *J* 13.6, 4.1 Hz, H(3ax)); 1.04 (s, $H(18)_3$); 1.21 (s, $H(20)_3$); 1.41 (dxd, *J* 12.6, 1.7 Hz, H(5)); 1.45 (txd, *J* 13.0, 3.6 Hz, H(1ax)); 1.60–1.72 (m, H(2eq), H(6ax)); 1.73 (qxt, *J* 13.6, 3.7 Hz, H(2ax)); 1.88 (bd, *J* 13.6 Hz, H(3eq)); 1.98 (bdxd, *J* 13.2, 7.1 Hz, H(6eq)); 2.28 (bd, *J* 12.6 Hz, H(1eq)); 2.75 (dxdxd, *J* 16.8, 11.5, 7.3 Hz, H(7ax)); 2.87 (bdxd, *J* 16.7, 6.1 Hz, H(7eq)); 3.24 (d, *J* 9.1 Hz, H(19)); 3.33 (s, 19-OMe); 3.53 (d, *J* 9.1 Hz, H(19)); 3.82 (s, 12-OMe); 6.79 (s, H(11)); 7.33 (s, 13-C*H*=NOH); 7.82 (bs, 13-CH=NOH); 8.41 (s, H(14)) ppm. δ(C) 19.1 (C(2)); 19.2 (C(6)); 25.4 (C(20)); 27.6 (C(18)); 30.0 (C(7)); 35.9 (C(3)); 38.1 (C(10)); 38.3 (C(4)); 38.9 (C(1); 51.1 (C(5)); 55.6 (12-OMe); 59.4 (19-OMe); 75.9 (C(19)); 107.3 (C(11)); 118.1 (C(13)); 127.5 (C(8)); 127.8 (C(14)); 146.6 (13-CH=NOH); 153.2 (C(9)); 155.9 (C(12)) ppm. *m/z* 331 (11, M^+), 313 (37, $M - H_2O$), 268 (9, 313 – CH_2OMe), 198 (22), 186 (100), 69 (18), 45 (20).

13-Formyl-12,19-dimethoxypodocarpa-8,11,13-triene O-methyloxime (29)

A solution of 13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene oxime (**27**) (0.14 g, 0.42 mmol) and imidazole (1 mg) in THF (10 mL) was added dropwise to a stirred slurry of hexanes-washed sodium hydride (29 mg, 1.22 mmol) in THF (5 mL) and the mixture was then heated under reflux for 30 min. Methyl iodide (0.18 mL, 2.78 mmol) was injected into the mixture, which was heated for a further 1 h, after which it was allowed to cool to room temperature, and excess of NaH was quenched by the dropwise addition of MeOH. Workup gave an oil which was purified by PLC (hexanes/Et_2O, 4:1) to give 13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene *O*-methyloxime (0.13 g, 87%) as a clear oil (Kugelrohr, 120°C/0.02 mmHg). Anal. Found: C, 72.9; H, 8.9; N, 4.2. $C_{21}H_{31}NO_3$ calc.: C, 73.0; H, 9.1; N, 4.1%. ν_{max} 1615 (C=N–OMe), 1560, 1495, 1464 cm^{-1} (C=C). δ(H) 1.01 (txd, *J* 13.5, 4.1 Hz, H(3ax)); 1.04 (s, $H(18)_3$); 1.20 (s, $H(20)_3$); 1.41 (dxd, *J* 12.6, 1.8 Hz, H(5)); 1.45 (txd, *J* 13.0, 3.8 Hz, H(1ax)); 1.59–1.73 (m, H(2eq), H(6ax)); 1.73 (qxt, *J* 13.8, 3.1 Hz, H(2ax)); 1.88 (bd, *J* 13.5 Hz, H(3eq)); 1.97 (bdxd, *J* 13.3, 7.3 Hz, H(6eq)); 2.27 (bd, *J* 12.5 Hz, H(1eq)); 2.75 (bdxdxd, *J* 16.8, 11.6, 7.3 Hz, H(7ax)); 2.88 (bdxd, *J* 16.7, 6.1 Hz, H(7eq)); 3.24 (d, *J* 9.1 Hz, H(19)); 3.33 (s,

19-OMe); 3.53 (d, *J* 9.1 Hz, H(19)); 3.80 (s, 12-OMe); 3.94 (s, 13-CH=NO*Me*); 6.77 (s, H(11)); 7.43 (s, 13-C*H*=NOMe); 8.39 (s, H(14)) ppm. δ(C) 19.1 (C(2)); 19.2 (C(6)); 25.4 (C(20)); 27.6 (C(18)); 30.0 (C(7); 35.9 (C(3)); 38.0 (C(10)); 38.3 (C(4)); 38.9 (C(1)); 51.1 (C(5)); 55.7 (12-OMe); 59.4 (19-OMe); 61.7 (13-CH=NO*Me*); 75.9 (C(19)); 107.2 (C(11)); 118.1 (C(13)); 126.5 (C(14)); 127.5 (C(8)); 144.9 (13-CH=NOMe); 153.2 (C(9)); 155.9 (C(12)) ppm. *m/z* 345 (100, M^+), 330 (17, *M* − Me), 315 (10, 330 − Me), 298 (27, 330 − MeOH), 254 (24), 218 (32), 186 (27), 45 (35).

Typical complexation procedure

A solution of $PhCH_2Mn(CO)_5$ [4,38] (1.2 mol equiv.) and the organic liquid (1.0 mol equiv.) in heptane (distilled from NaH, degassed with argon, 30 mL/0.20 g of ligand unless otherwise stated) was heated under reflux (1–6 h) under positive argon pressure with the reaction progress monitored by TLC. Upon completion of the reaction the mixture was concentrated *in vacuo* and flash chromatographed on silica gel. Unreacted $PhCH_2Mn(CO)_5$ was eluted with hexanes, the diterpenoid complex was eluted with hexanes/Et_2O, and recovered (uncomplexed) organic ligand was eluted with Et_2O.

*Tetracarbonyl(methyl 7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^7)manganese (**41**)*

Methyl 7-oxopodocarpa-8,11,13-trien-19-oate (**30**) [15] (0.30 g, 1.05 mmol) and $PhCH_2Mn(CO)_5$ (0.36 g, 1.26 mmol) (1.2 h) gave tetracarbonyl(methyl 7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^7)manganese (0.47 g, 100%) as a yellow oil. Anal. Found: C, 59.0; H, 4.8. $C_{22}H_{21}MnO_7$ calc.: C, 58.4; H, 4.7%. ν_{max} 2097, 2078, 1929 (Mn–C≡O), 1727 (ester CO), 1587 (C=C), 1562 cm^{-1} (ketone CO). δ(H) 1.05 (s, $H(20)_3$); 1.13 (txd, *J* 13.7, 4.0 Hz, H(3ax)); 1.25 (s, $H(18)_3$); 1.55 (txd, *J* 13.5, 3.9 Hz, H(1ax)); 1.69–1.73 (m, H(2eq)); 2.00 (dxd, *J* 14.1, 3.3 Hz, H(5)); 1.95–2.05 (m, H(2ax)); 2.32 (bd, *J* 12.5 Hz, H(3eq)); 2.35 (bd, *J* 11.9 Hz, H(1eq)); 3.08 (dxd, *J* 18.8, 3.3 Hz, H(6eq)); 3.35 (dxd, *J* 18.8, 14.2 Hz, H(6ax); 3.70 (s, 19-OMe); 7.06 (d, *J* 7.7 Hz, H(11)); 7.38 (t, *J* 7.5 Hz, H(12)); 7.90 (d, *J* 7.3 Hz, H(13)) ppm. δ(C) 19.4 (C(2)); 21.5 (C(20)); 27.8 (C(18)); 36.2 (C(3)); 37.2 and 37.3 (C(1), C(6)); 38.2 (C(10)); 44.0 (C(4)); 51.0 (C(5)); 51.7 (19-OMe); 119.3 (C(11)); 134.9 (C(12)); 139.1 (C(13)); 139.9 (C(8)); 157.7 (C(9)); 176.8 (C(19)); 193.1 (C(14)); 211.5, 211.7, 213.0, 221.0 (Mn–C≡O); 217.0 (C(7)).

Increasing the reaction time to 2.25 h gave the complex **41** (88%) and methyl 14-benzyl-7-oxopodocarpa-8,11,13-trien-19-oate (**34**) (24 mg, 9%) as a clear oil (Kugelrohr, 172°C/0.2 mmHg). Anal. Found: C, 79.9; H, 7.4. $C_{25}H_{28}O_3$ calc.: C, 79.8; H, 7.5%. ν_{max} 1724 (ester CO), 1675 (ketone CO), 1589, 1494, 1465 cm^{-1} (C=C). δ(C) 1.11 (s, $H(20)_3$); 1.12 (txd, *J* 13.6, 4.0 Hz, H(3ax)); 1.24 (s, $H(18)_3$); 1.54 (txd, *J* 13.4, 4.1 Hz, H(1ax)); 1.71 (dxp, *J* 14.3, 3.2 Hz, H(2eq)); 2.03 (qxt, *J* 13.8, 3.6 Hz, H(2ax)); 2.03 (dxd, *J* 14.2, 4.0 Hz, H(5)); 2.30 (bd, *J* 13.5 Hz, H(3eq)); 2.35 (bd, *J* 13.2 Hz, H(1eq)); 2.89 (dxd, *J* 17.8, 4.0 Hz, H(6eq)); 3.26 (dxd, *J* 17.8, 14.2 Hz, H(6ax)); 3.69 (s, 19-OMe); 4.41, 4.51 (d, *J* 15.5 Hz, 14-CH_2Ph); 7.03 (dxd, *J* 7.2, 1.1 Hz, H(11)); 7.16–7.19 (m, *ortho*-$H)_2$, *para*-H); 7.24–7.28 (m, (*meta*-$H)_2$); 7.34 (dxd, *J* 8.1, 1.4 Hz, H(13)); 7.39 (t, *J* 8.0 Hz, H(12)) ppm. δ(C) 19.8 (C(2)); 21.6 (C(20)); 27.8 (C(18)); 37.4 (C(3)); 39.0 (C(6)); 39.2 (C(1), C(10)); 40.6 (13-CH_2–Ph); 43.9 (C(4)); 49.3 (C(5)); 51.6 (19-OMe); 123.2 (C(11)); 125.7 (*para*-C); 128.2 (*ortho*-$C)_2$; 129.1 (*meta*-$C)_2$; 129.5 (C(8)); 130.1 (C(13)); 132.6 (C(12)); 141.3, 143.0

(*ipso*-C,C(14)); 155.7 (C(9)); 177.0 (C(19)); 200.4 (C(7)) ppm. δ(H) (C_6D_6) 0.71 (txd, *J* 13.4, 3.8 Hz, H(3ax)); 0.88 (s, $H(20)_3$); 0.95 (s, $H(18)_3$); 1.17 (txd, *J* 13.3, 3.8 Hz, H(1ax), 1.44 (dxp, *J* 14.2, 3.0 Hz, H(2eq)); 1.59 (dxd, *J* 14.1, 4.1 Hz, H(5)); 1.96 (bd, *J* 14.4 Hz, H(3eq)); 2.03 (qxt, *J* 13.9, 3.5 Hz, H(2ax)); 2.20 (bd, *J* 13.6 Hz, H(1eq)); 2.90 (dxd, *J* 17.6, 4.1 Hz, H(6eq)); 3.20 (s, 19-OMe); 3.28 (dxd, *J* 17.6, 14.2 Hz, H(6ax)); 4.64, 4.86 (d, *J* 15.1 Hz, 14-CH_2Ph); 6.98–7.19 (m, H(11), H(12), H(13), (*meta*-H)$_2$, *para*-H); 7.34 (d, *J* 7.5 Hz, *ortho*-H)$_2$ ppm. δ(C) (C_6D_6) 20.1 (C(2)); 21.6 (C(20)); 27.4 (C(18)); 37.4 (C(3)); 39.0 (C(6)); 39.3 (C(10)); 39.6 (C(1)); 41.0 (14-CH_2Ph); 43.8 (C(4)); 49.1 (C(5)); 51.0 (19-OMe); 123.5 (C(11)); 126.1 (*para*-C); 128.6 (*ortho*-C)$_2$; 129.7 (*meta*-C)$_2$; 130.3 (C(8)); 130.5 (C(13)); 132.5 (C(12)); 142.0 (*ipso*-C); 143.5 (C(14)); 155.9 (C(9)); 176.6 (C(19)); 199.4 (C(7)) ppm. *m/z* 376 (100, M^+), 358 (16, $M - H_2O$), 301 (31, $M - C_6H_3$), 286 (23, M – CHPh), 283 (15), 235 (15), 212 (17), 211 (42) 91 (58, $PhCH_2$).

*Tetracarbonyl(19-methoxy-7-oxopodocarpa-8,11,13-triene-C^{14},O^7)manganese (**42**)*

19-Methoxy-7-oxopodocarpa-8,11,13-triene (**31**) (85 mg, 0.31 mmol) and $PhCH_2Mn(CO)_5$ (0.11 g, 0.38 mmol) (40 min) gave tetracarbonyl(19-methoxy-7-oxopodocarpa-8,11,13-triene-C^{14},O^7)manganese (0.13 g, 97%) which crystallized from acetonitrile as hexagonal plates, m.p. 118–120°C. Anal: Found: C, 60.6; H, 5.3. $C_{22}H_{23}O_6$ calc.: C, 60.3; H, 5.3%. ν_{max} (KBr): 2100, 2050, 1985, 1945 (Mn–C≡O), 1595 (C=C), 1555 cm^{-1} (ketone CO). δ(H) 1.03 (s, $H(18)_3$); 1.12 (txd, *J* 13.3, 4.3 Hz, H(3ax)); 1.23 (s, $H(20)_3$); 1.58 (txd, *J* 13.1, 3.8 Hz, H(1ax)); 1.64–1.77 (m, H(1eq), H(2eq), H(2ax)); 1.90 (dxd, *J* 12.3, 5.2 Hz, H(5)); 2.35 (bd, *J* 14.3 Hz, H(3eq)); 2.87–3.01 (m, $H(6)_2$); 3.31 (s, 19-OMe); 3.35, 3.53 (d, *J* 9.3 Hz, $H(19)_2$); 7.03 (d, J 7.7 Hz, H(11)); 7.37 (t, *J* 7.6 Hz, H(12)); 7.88 (dxd, *J* 7.3, 0.6 Hz, H(13)) ppm. δ(C) 18.7 (C(2)); 23.4 (C(20)); 27.6 (C(18)); 35.6 (C(6)); 36.9 (C(3)); 37.1 (C(1)); 37.7 (C(10)); 38.0 (C(4)); 51.0 (C(5)); 59.3 (19-OMe); 77.1 (C(19)); 118.5 (C(11)); 134.9 (C(12)); 138.9 (C(13)); 140.1 (C(8)); 159.5 (C(9)); 193.3 (C(14)); 211.7 (2C), 213.1, 221.1 (Mn–C≡O); 217.8 (C(7)).

*Tetracarbonyl(methyl 12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^7) manganese (**43**)*

Methyl 12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate (**32**) [16] (0.40 g, 1.27 mmol) and $PhCH_2Mn(CO)_5$ (0.43 g, 1.52 mmol) (1.2 h) gave tetracarbonyl(methyl 12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^7)manganese (0.61 g, 100%) as a yellow oil. Anal. Found: C, 57.5; H, 5.2. $C_{23}H_{23}MnO_8$ calc.: C, 57.3; H, 4.8%. ν_{max} 2091, 1980, 1932 (Mn–C≡O), 1735 (ester CO), 1589 (C=C), 1550 cm^{-1} (ketone CO). δ(H) 1.02 (s, $H(20)_3$); 1.12 (txd, *J* 13.6, 4.0 Hz, H(3ax)); 1.24 (s, $H(18)_3$); 1.55 (txd, *J* 13.4, 4.0 Hz, H(1ax)); 1.71 (dxp, *J* 14.2, 3.2 Hz, H(2eq)); 1.95 (dxd, *J* 14.0, 3.5 Hz, H(5)); 1.99 (qxt, *J* 14.0, 3.3 Hz, H(2ax)); 2.28 (bd, *J* 11.6 Hz, H(3eq)); 2.31 (bd, *J* 12.3 Hz, H(1eq)); 3.00 (dxd, *J* 18.7, 6.5 Hz, H(6eq)); 3.28 (dxd, *J* 18.7, 14.0 Hz, H(6ax)); 3.70 (s, 19-OMe); 3.94 (s, 12-OMe); 6.53 (d, *J* 2.1 Hz, H(11)); 7.41 (d, *J* 2.1 Hz, H(13)) ppm. δ(C) 19.5 (C(2)); 21.5 (C(20)); 27.9 (C(18)); 35.6 (C(6)); 37.1 (C(3)); 37.3 (C(1)); 38.3 (C(10)); 44.0 (C(4)); 51.0 (C(5)); 51.7 (19-OMe); 55.4 (12-OMe); 107.3 (C(11)); 121.9 (C(13)); 133.6 (C(8)); 159.7 (C(9)); 164.6 (C(12)): 176.9 (C(19)); 198.0 (C(14)); 211.6, 211.8, 213.2, 221.1, (Mn–C≡O); 213.2 (C(7)) ppm. *m/z* 482 (1, M^+), 423 (1, $M - CO_2Me$), 398 (3, M – 3CO), 370 (57, 398 – CO), 316 (100, $M - Mn(CO)_4 + H$), 241 (78), 201 (35), 175 (40).

*Tetracarbonyl(methyl 13-bromo-12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^{7})manganese (**44**)*

Methyl 13-bromo-12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate (**33**) [17] (80 mg, 0.20 mmol) and $PhCH_2Mn(CO)_5$ (70 mg, 0.24 mmol) (1 h) gave tetracarbonyl-(methyl 13-bromo-12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^{7})-manganese (97 mg, 85%) which crystallized from hexanes/Et_2O as yellow rods, m.p. 148–150°C (dec). Anal. Found: C, 49.4; H, 3.9. $C_{23}H_{22}BrMnO_8$ calc.: C, 49.2; H, 3.9%. ν_{max} (KBr): 2081, 1983, 1941 (Mn–C≡O), 1726 (ester CO), 1583 (C=C), 1546 cm^{-1} (ketone CO). δ(H) 1.03 (s, $H(20)_3$); 1.12 (txd, *J* 13.6, 4.0 Hz, H(3ax)); 1.23 (s, $H(18)_3$); 1.56 (txd, *J* 13.4, 4.1 Hz, H(1ax)); 1.72 (dxp, *J* 14.3, 3.1 Hz, H(2eq)); 1.93 (dxd, *J* 14.1, 3.5 Hz, H(5)); 1.99 (qxt, *J* 14.0, 3.5 Hz, H(2ax)); 2.28–2.33 (m, H(1eq), H(3eq)); 2.97 (dxd, *J* 18.8, 3.5 Hz, H(6eq)); 3.26 (dxd, *J* 18.8, 14.1 Hz, H(6ax)); 3.70 (s, 19-OMe); 3.97 (s, 12-OMe); 6.58 (s, H(11)) ppm. δ(C) 19.4 (C(2)); 21.4 (C(20)); 27.8 (C(18)); 36.0 (C(6)); 37.2 (C(3)); 37.5 (C(1)); 38.6 (C(10)); 44.0 (C(4)); 50.7 (C(5)); 51.7 (19-OMe); 56.2 (12-OMe); 104.2 (C(11)); 125.9 (C(8)); 133.5 (C(13)); 158.9 (C(9)); 161.1 (C(12)); 176.7 (C(19)); 195.8 (C(14)); 211.1, 211.3, 214.9, 220.0 (Mn–C≡O); 214.3 (C(7)) ppm. *m/z* 396/394 (17, 17; $M^+ - Mn(CO)_4 + H$), 321/319 (14, 14; 396/394 − Me − HCO_2Me), 129 (34), 57 (100).

*Tetracarbonyl(methyl 13-acetyl-12-methoxypodocarpa-8,11,13-trien-19-oate-C^{14}, O^{13})manganese (**48**)*

Methyl 13-acetyl-12-methoxypodocarpa-8,11,13-trien-19-oate (**9**) [10] (0.20 g, 0.58 mmol) and $PhCH_2Mn(CO)_5$ (0.19 g, 0.68 mmol) (3 h) gave tetracarbonyl-(methyl 13-acetyl-12-methoxypodocarpa-8,11,13-trien-19-oate-C^{14},O^{13})manganese (0.28 g, 95%) which crystallized from MeOH as yellow needles, m.p. 129–134°C (dec). Anal. Found: C, 59.1; H, 5.3. $C_{25}H_{27}MnO_8$ calc.: C, 58.8; H, 5.3%. ν_{max} (KBr): 2073, 1980, 1931 (Mn–C≡O), 1724 (ester CO), 1583 (C=C), 1550 cm^{-1} (ketone CO). δ(H) 1.11 (txd, *J* 13.6, 4.1 Hz, H(3ax)); 1.13 (s, $H(20)_3$); 1.31 (s, $H(18)_3$); 1.43 (txd, *J* 13.6, 4.3 Hz, H(1ax)); 1.55 (dxd, *J* 12.5, 1.2 Hz, H(5)); 1.67 (dxp, *J* 14.2, 2.8 Hz, H(2eq)); 1.96 (qxd, *J* 13.6, 5.4 Hz, H(6ax)); 2.06 (qxt, *J* 13.9, 5.4 Hz, H(2ax)); 2.22 (bd, *J* 12.9 Hz, H(1eq)); 2.28–2.33 (m, H(3eq), H(6eq)); 2.64 (s, 13-COMe); 2.84 (dxdxd, *J* 16.3, 12.6, 6.4 Hz, H(7ax)); 3.03 (dxdxd, *J* 16.3, 4.2, 1.4 Hz, H(7eq)); 3.68 (s, 19-OMe); 3.86 (s, 12-OMe); 6.57 (s, H(11)) ppm. δ(C) 20.1 (C(2)); 22.3 (C(6)); 22.4 (C(20)); 28.4 (C(18)); 31.3 (13-CO*Me*); 37.4 (C(3)); 38.7 (C(7)); 39.9 (C(1)); 40.0 (C(10)); 44.0 (C(4)); 51.3 (19-OMe); 51.8 (C(5)); 54.8 (12-OMe); 104.8 (C(11)); 131.8 (C(13)); 138.9 (C(8)); 155.5 (C(9)); 160.6 (C(12)); 180.0 (C(19)); 198.0 (C(14)); 211.9, 212.2, 214.9, 221.3 (Mn–C≡O); 215.2 (13-COMe) ppm. *m/z* 510 (1, M^+), 426 (3, *M* − 3CO), 398 (56, 426 − CO), 344 (100, *M* − $Mn(CO)_4$ + H), 329 (84), 269 (99), 227 (20).

*(13-Acetyl-12,19-dimethoxypodocarpa-8,11,13-triene-C^{14},O^{13})tetracarbonylmanganese (**49**)*

13-Acetyl-12,19-dimethoxypodocarpa-8,11,13-triene (**10**) (0.20 g, 0.61 mmol) and $PhCH_2Mn(CO)_5$ (0.21 g, 0.73 mmol) (1.75 h) gave (13-acetyl-12.91-dimethoxy-podocarpa-8,11,13-triene-C^{14},O^{13})tetracarbonylmanganese (0.30 g, 99%) as a yellow oil. Anal. Found: C, 60.8; H, 5.7. $C_{25}H_{29}MnO_7$ calc.: C, 60.5; H, 5.9%. ν_{max} 2074, 1975, 1929 (Mn–C≡O), 1583 (C=C), 1550 cm^{-1} (ketone CO). δ(H) 1.03 (txd, *J* 13.6, 3.9 Hz, H(3ax)); 1.08 (s, $H(18)_3$); 1.28 (s, $H(20)_3$); 1.45 (dxd, *J* 12.8, 1.6 Hz,

H(5)); 1.48 (txd, *J* 12.9, 3.7 Hz, H(1ax)); 1.65 (dxp, *J* 14.1, 3.4 Hz, H(2eq)); 1.70–1.83 (m, H(6ax), H(2ax)); 1.90 (bd, *J* 13.5 Hz, H(3eq)); 2.10 (bdxd, *J* 13.3, 7.7 Hz, H(6eq)); 2.28 (bd, *J* 12.5 Hz, H(1eq)); 2.64 (s, 13-COMe); 2.87 (dxdxd, *J* 16.7, 11.6, 7.6 Hz, H(7ax)); 3.04 (bdxd, *J* 16.7, 5.7 Hz, H(7eq)); 3.25 (d, *J* 9.1 Hz, H(19)); 3.35 (s, 19-OMe); 3.55 (d, *J* 9.1 Hz, H19)); 3.87 (s, 12-OMe); 6.59 (s, H(11)) ppm. δ(C) 19.3 (C(2)); 20.5 (C(6)); 25.4 (C(20)); 27.6 (C(18)); 31.2 (13-CO*Me*); 35.7 (C(3)); 37.8 (C(7)); 38.1 (C(10)); 38.2 (C(4)); 39.3 (C(1)); 50.1 (C(5)); 54.8 (12-OMe); 59.4 (19-OMe); 75.9 (C(19)); 103.9 (C(11)); 131.6 (C(13)); 138.4 (C(8)); 157.2 (C(9)); 160.8 (C(12)); 197.5 (C(14)); 212.0, 212.3, 214.9, 221.3 (Mn–C≡O); 215.2 (13-COMe) ppm. *m/z* 384 (9, $M^+ - 4CO$), 330 (93, 384 − Mn + H), 315 (33), 283 (21), 241 (40), 203 (77), 43 (100, MeCO).

*Tetracarbonyl(methyl 12-methoxy-13-methoxycarbonylpodocarpa-8,11,13-trien-19-oate-C^{14},O^{13})manganese (**50**)*

Methyl 12-methoxy-13-methoxycarbonylpodocarpa-8,11,13-trien-19-oate (**11**) [10] (0.20 g, 0.56 mmol) and $PhCH_2Mn(CO)_5$ (0.19 g, 0.67 mmol) (5.5 h) gave tetracarbonyl(methyl 12-methoxy-13-methoxycarbonylpodocarpa-8,11,13-trien-19-oate-C^{14},O^{13})manganese (0.10 g, 35%) which crystallized from hexanes/Et_2O as needles, m.p. 127–130°C (dec). Anal. Found: C, 56.7; H, 5.5 $C_{25}H_{27}MnO_9$ calc.: C, 57.0; H, 5.2%. ν_{max} (KBr): 2055, 1990, 1935 (Mn–C≡O), 1720 (non-ligated ester CO), 1594 (C=C), 1567 cm^{-1} (ligated ester CO). δ(H) 1.11 (txd, *J* 13.5, 4.2 Hz, H(3ax)); 1.13 (s, $H(20)_3$); 1.31 (s, $H(18)_3$); 1.44 (txd, *J* 13.2, 4.0 Hz, H(3ax); 1.56 (dxd, *J* 12.4, 1.2 Hz, H(5)); 1.66 (dxp, *J* 14.2, 2.9 Hz, H(2eq)); 1.97 (qxd, *J* 12.6, 5.4 Hz, H(6ax)); 2.05 (qxt, *J* 13.9, 3.7 Hz, H(2ax)); 2.21 (bd, *J* 12.7 Hz, H(3eq)); 2.29–2.30 (m, H(1eq), H(6eq)); 2.81 (dxdxd, *J* 16.3, 12.5, 6.4 Hz, H(7ax)); 3.01 (dxdxd, *J* 16.3, 5.5, 1.4 Hz, H(7eq)); 3.68 (s, 19-OMe); 3.82 (12-OMe); 3.94 (s, 13-CO_2Me); 6.58 (s, H(11)) ppm. δ(C) 20.1 (C(2)); 22.2 (C(6)); 22.5 (C(20)); 28.4 (C(18)); 37.4 (C(3)); 38.2 (C(7)); 39.8 (C(10)); 39.9 (C(1)); 44.0 (C(4)); 51.2 (19-OMe); 51.8 (13-CO_2*Me*); 54.2 (C(5)); 55.2 (12-OMe); 105.6 (C(11)); 119.4 (C(13)); 138.4 (C(8)); 154.7 (C(9)); 158.9 (C(12)); 180.0 (C(19)); 180.9 (13-CO_2Me); 190.2 (C(14)); 211.8, 212.2, 214.9, 222.4 (Mn–C≡O) ppm.

*Tetracarbonyl(methyl 7-oxoabieta-8,11,13-trien-18-oate-C^{14},O^7)manganese (**53**)*

Methyl 7-oxoabieta-8,11,13-trien-18-oate (**40**) [18] (0.22 g, 0.67 mmol) and $PhCH_2Mn(CO)_5$ (0.23 g, 0.80 mmol) (2.5 h) gave tetracarbonyl(methyl 7-oxoabieta-8,11,13-trien-18-oate-C^{14},O^7)manganese (0.23 g, 71%) as a yellow oil. Anal. Found: C, 61.1; H, 5.4. $C_{25}H_{27}MnO_7$ calc.: C, 60.7; H, 5.5%. ν_{max} 2090, 1980, 1930 (Mn–C≡O), 1727 (ester CO), 1590 (C=C), 1545 cm^{-1} (ketone CO). δ(H) 1.21 (s, $H(20)_3$); 1.29 (s, $H(19)_3$); 1.32 (d, *J* 5.2 Hz, $H(16)_3$, $H(17)_3$); 1.60–1.80 (m, $H(2)_2$, $H(3)_2$, H(1)); 2.32 (bd, *J* 12.3 Hz, H(1)); 2.44 (dxd, *J* 17.6, 2.7 Hz, H(6eq)); 2.62 (dxd, *J* 13.9, 2.7 Hz, H(5)); 2.73 (dxd, *J* 17.6, 13.9 Hz, H(6ax)); 3.21 (sept, *J* 6.8 Hz, H(15)); 3.67 (s, 18-OMe); 7.05 (d, *J* 8.0 Hz, H(11)); 7.41 (d, *J* 8.0 Hz, H(12)) ppm. δ(C) 16.3 (C(19)); 18.0 (C(2)); 23.7, 24.07, 24.10 (C(16), C(17), C(20)); 36.1, 36.4, 36.6 (C(1), C(3), C(6)); 37.2 (C(15)); 44.7 (C(5)); 46.6 (C(4)); 52.2 (18-OMe); 119.3 (C(11)); 131.4 (C(12)); 139.6 (C(8)); 156.5 (C(13)); 158.4 (C(9)); 177.5 (C(18)); 191.3 (C(14)); 212.0, 212.1, 214.5, 221.2 (Mn–C≡O); 216.8 (C(7)); C(10) was not detected.

*Tetracarbonyl(methyl 12-methoxy-13-methoxycarbonyl-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^{7})manganese (**45**)*

Methyl 12-methoxy-13-methoxycarbonyl-7-oxopodocarpa-8,11,13-trien-19-oate (**35**) (0.10 g, 0.27 mmol) and $PhCH_2Mn(CO)_5$ (92 mg, 0.32 mmol) (45 min) gave tetracarbonyl(methyl 12-methoxy-13-methoxycarbonyl-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^{7})manganese (0.29, g, 99%) which crystallized from hexanes/Et_2O as micro needles, m.p. 135–140°C (dec). Anal. Found: C, 55.7; H, 4.6 $C_{25}H_{25}MnO_{10}$ calc.: C, 55.6; H, 4.7%. ν_{max} (KBr): 2098, 2040, 1980, 1943 (Mn–C≡O), 1729 (ester CO), 1596 (C=C), 1540 cm^{-1} (ketone CO). δ(H) 1.03 (s, $H(20)_3$); 1.12 (txd, *J* 13.4, 4.1 Hz, H(3ax)); 1.24 (s, $H(18)_3$); 1.55 (txd, *J* 13.4, 4.1 Hz, H(1ax)); 1.72 (dxp, *J* 14.3, 3.1 Hz, H(2eq)); 1.93 (dxd, *J* 14.1, 3.5 Hz, H(5)); 2.00 (qxt, *J* 14.0, 3.5 Hz, H(2ax)); 2.29–2.33 (m, H(1eq), H(3eq)); 3.01 (dxd, *J* 18.8, 3.5 Hz, H(6eq)); 3.27 (dxd, *J* 18.8, 14.1 Hz, H(6ax)); 3.70 (s, 19-OMe); 3.88 (s, 12-OMe); 3.90 (s, 13-CO_2Me); 6.60 (s, H(11)) ppm. δ(C) 19.4 (C(2)); 21.3 (C920)); 27.8 (C(18)); 35.7 (C(6)); 37.2 (C(3)); 37.3 (C(1)); 38.7 (C(10)); 44.0 (C(4)); 50.7 (C(5)); 51.8 19-OMe); 52.1 (13-CO_2*Me*); 55.7 (12-OMe); 102.6 (C(11)); 133.3, 134.8 (C(8), C(13)); 160.7 (C(9)); 161.3 (C(12)); 170.2 (13-CO_2Me); 176.2 (C(19)); 190.2 (C(14)); 210.6, 210.8, 213.9, 219.1 (Mn–C≡O); 213.7 (C(7)).

*Tetracarbonyl(methyl 13-acetyl-12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^{7})manganese (**46**)*

Methyl 13-acetyl-12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate (**36**) (0.31 g, 0.87 mmol) and $PhCH_2Mn(CO)_5$ (0.28 g, 1.0 mmol) (1.75 h) gave (i) tetracarbonyl-(methyl 13-acetyl-12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^{7})-manganese (0.42 g, 93%) which crystallized from hexanes/Et_2O as yellow rods, m.p. 169–172°C (dec). Anal. Found: C, 57.5; H, 4.9. $C_{25}H_{25}MnO_9$ calc.: C, 57.3; H, 4.8%. ν_{max} (KBr): 2080, 1998, 1976, 1937 (Mn–C≡O), 1731 (ester CO), 1704 (non-ligated ketone CO), 1586 (C=C), 1538 cm^{-1} (ligated ketone CO). δ(H) 1.03 (s, $H(20)_3$); 1.11 (txd, *J* 13.7, 3.8 Hz, H(3ax)); 1.24 (s, $H(18)_3$); 1.55 (txd, *J* 13.3, 3.9 Hz, H(1ax)); 1.72 (dxp, *J* 14.2, 3.0 Hz, H(2eq)); 1.92 (dxd, *J* 14.0, 3.5 Hz, H(5)); 2.00 (qxt, *J* 14.0, 3.4 Hz, H(2ax)); 2.31 (bd, *J* 13.4 Hz, H(1eq), H(3eq)); 2.54 (s, 13-COMe); 3.01 (dxd, *J* 18.8, 3.5 Hz, H(6eq)); 3.27 (dxd, *J* 18.8, 14.1 Hz, H(6ax)); 3.69 (s, 19-OMe); 3.89 (s, 12-OMe); 6.59 (s, H(11)) ppm. δ(C) 19.4 (C(2)); 21.4 (C(20)); 27.8 (C(18)); 31.9 (13-CO*Me*); 35.9 (C(6)); 37.2 (C(3)); 37.4 (C(1)); 38.7 (C(10)); 44.0 (C(4)); 50.8 (C(5); 51.7 (19-OMe); 55.4 (12-OMe); 102.6 (C(11)); 133.6 (C(8)); 142.7 (C(13)); 160.4, 160.7, (C(9), C(12)); 176.7 (C(19)); 187.7 (C(14); 207.1 (13-*C*OMe); 211.1, 211.3, 213.9, 219.2 (Mn–C≡O); 213.7 (C(7)) ppm. *m/z* 374 (14, $M^+ - Mn(CO)_4 + H$); 299 (10), 69 (52), 55 (80, Mn), 41 (100); and (ii) methyl 13-acetyl-14-benzyl-12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate (**37**) (14 mg, 4%) as a clear oil. Anal. Found: M^+, 448.2241. $C_{28}H_{32}O_5$ calc.: *M*, 448.2250). ν_{max} 1724 (ester CO), 1704, 1671 (ketone CO), 1585, 1557, 1494, 1453 cm^{-1} (C=C). δ(H) 1.12 (s, $H(20)_3$); 1.13 (txd, *J* 13.5, 3.9 Hz, H(3ax)); 1.23 (s, $H(18)_3$); 1.58 (txd, *J* 13.1, 4.3 Hz, H(1ax)); 1.74 (dxp, *J* 14.4, 3.6 Hz, H(2eq)); 1.99 (dxd, *J* 14.1, 4.2 Hz, H(5)); 2.05 (qxt, *J* 14.0, 3.5 Hz, H(2ax)); 2.09 (s, 13-COMe); 2.29–2.34 (m, H(1eq), H(3eq)); 2.80 (dxd, *J* 17.9, 4.2 Hz, H(6eq)); 3.20 (dxd, *J* 17.9, 14.1 Hz, H(6ax)); 3.69 (s, 19-OMe); 3.86 (s, 12-OMe); 4.36, 4.48 (d, *J* 15.2 Hz, 14-CH_2Ph); 6.86 (s, H(11)); 7.03 (bd, *J* 7.1 Hz. (*ortho*-H)$_2$); 7.11 (txt, *J* 7.3, 2.3 Hz, *para*-H); 7.20 (txt, *J* 7.6, 1.4 Hz, (*meta*-H)$_2$) ppm. δ(C) 19.8 (C(2)); 21.5 (C(20)); 27.7 (C(18)); 32.3 (13-

CO*Me*); 35.6 (C(6)); 37.3 (C(3)); 39.1 (14-CH_2Ph, C(1)); 39.8 (C(10)); 44.0 (C(4)); 49.2 (C(5)); 51.6 (19-OMe); 55.5 (12-OMe); 105.1 (C(11)); 124.3 (C(13)); 125.6 (*para*-C); 128.0 ((*ortho*-C)$_2$); 128.8 ((*meta*-C)$_2$); 132.9 (C(8)); 140.2 (*ipso*-C); 140.7 (C(14)); 158.5 (C(9)); 158.8 (C(12)); 177.0 (C(19)); 198.7 (C(7)); 205.5 (13-*C*OMe) ppm. *m/z* 448 (80, M^+), 433 (58, M − Me), 370 (100, M − Ph), 357 (34), 43 (20, MeCO).

*Complexation of a mixture of **13** and **14***

A solution of a mixture (4 : 1) of methyl 12-acetylpodocarpa-8,11,13-trien-19-oate (**13**) and methyl 13-acetylpodocarpa-8,11,13-trien-19-oate (**14**) (0.15 g, 0.48 mmol) and $PhCH_2Mn(CO)_5$ (0.16 g, 0.57 mmol) (1.75 h) gave a mixture (4:1) of tetracarbonyl(methyl 12-acetylpodocarpa-8,11,13-trien-19-oate-C^{13},O^{12})manganese (**54**) and tetracarbonyl(methyl 13-acetylpodocarpa-8,11,13-trien-19-oate-C^{12},O^{13})manganese (**55**) (0.23 g, 91%) as a yellow oil. Anal. Found: C, 61.4; H, 6.0. $C_{24}H_{25}MnO_7 \cdot \frac{1}{3}C_6H_{14}$ calc.: C, 61.3; H, 5.8%. ν_{max} 2074, 1973, 1928 (Mn–C≡O), 1721 (ester CO), 1590 (C=C), 1570 cm^{-1} (ketone CO). *m/z* 480 (1, M^+), 396 (3, M − 3CO), 368 (57, 396–CO), 314 (22, M − $Mn(CO)_4$ + H), 299 (33), 239 (100), 173 (12), 128 (10), 43 (68, MeCO). **54**: δ(H) 1.07 (s, $H(20)_3$); 1.12 (txd, *J* 13.7, 3.7 Hz, H(3ax)); 1.31 (s, $H(18)_3$); 1.45 (txd, *J* 13.4, 3.4 Hz, H(1ax)); 1.59 (dxd, *J* 12.1, 1.0 Hz, H(5)); 1.66 (dxp, *J* 14.2, 3.0 Hz, H(2eq)); 1.98–2.09 (m, H(2ax), H(6ax)); 2.17–2.33 (m, H(1eq), H(3eq), H(6eq)); 2.56 (s, 12-COMe); 2.88 (dxdxd, *J* 17.8, 12.2, 6.3 Hz, H(7ax)); 3.02 (bdxd, *J* 17.9, 4.8 Hz, H(7eq)); 3.68 (s, 19-OMe); 7.69 (s, H(14)); 7.7 4 (s, H(11)) ppm. δ(C) 19.9 (C(2)); 20.7 (C(6)); 23.4 (C(20)); 24.3 (12-CO*Me*); 28.4 (C(18)); 32.5 (C(7)); 37.5 (C(3)); 38.1 (C(10)); 39.5 (C(1)); 44.0 (C(4)); 51.2 (19-OMe); 52.5 (C(5)); 129.1 (C(11)); 142.0 (C(14)); 143.6 (C(8), C(12)); 144.4 (C(9); 177.7 (C(19)); 185.8 (C(13)); 211.9 (2C); 212.9, 221.3 (Mn–C≡O); 215.4 (12-*C*OMe) ppm. **56**: δ (H) 7.56 (s, H(14)); 7.95 (s, H(11)) ppm.

*Tetracarbonyl(methyl 12-acetyl-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^7)manganese (**47**)*

12-Acetyl-7-oxopodocarpa-8,11,13-trien-19-oate (**38**) (18 mg, 54.9 μmol) and $PhCH_2Mn(CO)_5$ (19 mg, 65.9 μmol) (1.5 h) gave tetracarbonyl(methyl 12-acetyl-7-oxopodocarpa-8,11,13-trien-19-oate-C^{14},O^7)manganese (23 mg, 85%) as a yellow oil. Anal. Found: C, 58.8; H, 4.6. $C_{24}H_{23}MnO_8$ calc.: C, 58.3; H, 4.7%. ν_{max} 2081, 1982, 1936 (Mn–C≡O), 1728 (ester CO), 1684 (non-ligated ketone CO), 1591 (C=C), 1574 cm^{-1} (ligated ketone CO). δ(H) 1.06 (s, $H(20)_3$); 1.14 (txd, *J* 13.6, 4.4 Hz, H(3ax)); 1.25 (s, $H(18)_3$); 1.56 (txd, *J* 13.4, 4.0 Hz, H(1ax)); 1.74 (dxp, *J* 14.3, 3.1 Hz, H(2eq)); 1.992 (dxd, *J* 14.2, 3.3 Hz, H(5)); 1.995 (qxt, *J* 13.9, 3.5 Hz, H(2ax)); 2.34 (bd, *J* 13.6 Hz, H(3eq)); 2.46 (bd, *J* 13.1 Hz, H(1eq)); 2.69 (s, 12-COMe); 3.13 (dxd, *J* 19.0, 3.4 Hz, H(6eq)); 3.41 (dxd, *J* 19.0, 14.3 Hz, H(6ax)); 3.71 (s, 19-OMe); 7.61 (d, *J* 1.4 Hz, H(11)); 8.37 (d, *J* 1.4 Hz, H(13)) ppm. δ(C) 19.4 (C(2)); 21.6 (C(20)); 27.3 (C(18)); 27.9 (12-CO*Me*); 36.5 (C(3)); 37.27 (C(6)); 37.31 (C(1)); 38.4 (C(10)); 44.0 (C(4)); 50.9 (C(5)); 51.8 (19-OMe); 119.2 (C(13)); 138.1 (C(11)); 140.6 (C(12)); 142.7 (C(8)); 157.3 (C(9)); 176.7 (C(19)); 194.4 (C(14)); 199.8 (12-*C*OMe); 210.9. 211.1, 212.6, 220.9 (Mn–C≡O); 217.8 (C(7)) ppm. *m/z* 410 (1, M^+ − 3CO), 382 (11, 410 − CO), 328 (42, M − $Mn(CO)_4$ + H), 296 (16), 253 (57), 187 (24), 55 (40, Mn), 43 (100, MeCO).

Tetracarbonyl(methyl 13-acetyl-7-oxopodocarpa-8,11,13-trien-19-oate-C^{12},O^{13})manganese (56)

Methyl 13-acetyl-7-oxopodocarpa-8,11,13-trien-19-oate (**39**) (10 mg, 30.5 μmol) and $PhCH_2Mn(CO)_5$ (11 mg, 36.6 μmol) (1.5 h) gave tetracarbonyl(methyl 13-acetyl-7-oxopodocarpa-8,11,13-trien-19-oate-C^{12},O^{13})manganese (14 mg, 93%) as a yellow oil. ν_{max} 2120, 1987, 1938 (Mn–C≡O), 1729 (ester CO), 1689 (non-ligated ketone CO), 1580 cm^{-1} (br, C=C and ligated ketone CO). δ(H) 1.15–1.21 (m, H(3ax)); 1.21 (s, $H(20)_3$); 1.29 (s, $H(18)_3$); 1.65 (txd, *J* 13.5, 4.1 Hz, H(1ax)); 1.76 (dxp, *J* 14.3, 3.1 Hz, H(2eq)); 2.06 (qxt, *J* 13.8, 3.5 Hz, H(2ax)); 2.10 (dxd, *J* 14.5, 3.3 Hz, H(5)); 2.34 (bd, *J* 13.5 Hz, H(3eq)); 2.54–2.59 (m, H(1eq)); 2.66 9s, (13-COMe); 3.02 (dxd, *J* 18.1, 3.3 Hz, H(6eq)); 3.26 (dxd, *J* 18.1, 14.5 Hz, H(6ax)); 3.73 (s, 19-OMe); 8.17 (s, H(11)); 8.47 (s, H(14)) ppm. δ(C) 19.6 (C(2)); 21.3 (C(20)); 24.8 (C(18)); 28.1 (13-CO*Me*); 37.4 (C(3)); 37.5 (C(6)); 38.3 (C(1)); 39.3 (C(10)); 44.0 (C(4)); 49.7 (C(5)); 51.7 (19-OMe); 127.8 (C(8)); 129.2 (C(11)); 137.3 (C(14)); 143.8 (C(13)); 157.8 (C(9)); 177.0 (C(19)); 198.6 (C(7)); 204.4 (C(12)); 210.7, 210.8, 212.4, 220.9 (Mn–C≡O); 216.7 (13-*C*OMe) ppm.

Tetracarbonyl(2-formyl-3-methoxyphenyl-C^1,O^2)manganese (58)

1-Formyl-2-methoxybenzene (**57**) (0.11 g, 0.81 mmol) and $PhCH_2Mn(CO)_5$ (0.28 g, 0.97 mmol) (1.5 h) gave tetracarbonyl(2-formyl-3-methoxyphenyl-C^1,O^2)manganese (64 mg, 26%) which crystallized from hexanes/Et_2O as yellow micro rods, m.p. 115–130°C (dec). Anal. Found: C, 47.9; H, 2.2. $C_{12}H_7MnO_6$ calc.: C, 47.7; H, 2.3%. ν_{max} (KBr): 2081, 2006, 1977, 1927 (Mn–C≡O), 1573, 1462, 1432 (C=C), 1540 cm^{-1} (CHO). δ(H) 3.89 (s, 3-OMe); 6.57 (d, *J* 8.1 Hz, H(4)); 7.42 (t, *J* 7.6 Hz, H(5)); 7.63 (d, *J* 7.1 Hz, H(6)); 9.81 (s, OCH) ppm. δ(C) 55.2 (3-OMe); 105.5 (C(4)); 133.3 (C(6)); 136.3 (C(2)); 136.9 (C(5)); 164.8 (C(3)); 199.2 (C(1)); 204.5 (OCH); 211.2 (2C), 212.8, 221.0 (Mn–C≡O) ppm. *m/z* 302 (9, M^+), 246 (8, $M - 2CO$), 218 (18, 246 – CO), 190 (100, 218 – CO), 160 (17, 190 – CH_2O), 136 (20), 55 (45, Mn).

Tetracarbonyl(methyl 13-formyl-12-methoxypodocarpa-8,11,13-trien-19-oate-C^{14}, O^{13})manganese (51)

A solution of methyl 13-formyl-12-methoxypodocarpa-8,11,13-trien-19-oate (**18**) [11] (0.20 g, 0.61 mmol and $PhCH_2Mn(CO)_5$ (0.21 g, 0.73 mmol) (2 h) and flash chromatography gave (i) $PhCH_2Mn(CO)_5$ (12 mg); (ii) tetracarbonyl(methyl 13-formyl-12-methoxypodocarpa-8,11,13-trien-19-oate-C^{14},O^{13})manganese (70 mg, 23%) as a yellow oil. Anal. Found: C, 59.2; H, 5.3. $C_{24}H_{25}MnO_8 \cdot \frac{1}{4}C_6H_{14}$ calc.: C, 59.1; H, 5.6%. ν_{max} 2078, 1979, 1933 (Mn–C≡O), 1726 (ester CO), 1585 (C=C), 1567 cm^{-1} (aldehyde CO). δ(H) 1.12 (txd, *J* 13.7, 4.2 Hz, H(3ax)); 1.14 (s, $H(20)_3$); 1.31 (s, $H(18)_3$); 1.45 (txd, *J* 13.0, 3.7 Hz, H(1ax)); 1.56 (bd, *J* 12.4 Hz, H(5)); 1.67 (dxp, *J* 14.1, 3.0 Hz, H(2eq)); 1.97 (qxd, *J* 13.1, 5.7 Hz, H(6ax)); 2.06 (qxt, *J* 13.9, 3.1 Hz, H(2ax)); 2.20–2.31 (m, H(1eq), H(3eq), H(6eq)); 2.85 (dxdxd, *J* 16.5, 12.5, 6.3 Hz, H(7ax)); 3.03 (bdxd, *J* 16.4, 5.4 Hz, H(7eq)); 3.68 (s, 19-OMe); 3.83 (s, 12-OMe); 6.50 (s, H(11)); 9.71 (s, OCH) ppm. δ(C) 20.1 (C(2)); 22.1 (C(6)); 22.3 (C(20)); 28.4 (C(18)); 37.4 (C(3)); 38.0 (C(7)); 39.8 (C(1)); 40.3 (C(10)); 44.1 (C(4)); 51.3 (19-OMe); 51.8 (C(5)); 54.9 (12-OMe); 104.1 (C(11)); 134.0 (C(13)); 139.7 (C(8)); 157.9 (C(9)); 162.1 (C(12)); 177.9 (C(19)); 200.3 (C(14)); 204.0 (OCH); 211.6, 211.9, 214.4, 221.4 (Mn–C≡O) ppm. *m/z* 496 (1, M^+), 384 (28, $M - Mn(CO)_2 - H$), 330 (89, *M* –

$Mn(CO)_4$ + H), 255 (100, 384 − Me−CO_2Me), 227 (20), 189 (20), 129 (24); and (iii) a yellow solid (0.14 g) which was separated further by PLC (hexanes/Et_2O, 7:3) to give (a) **18** (9 mg, 5%) as a clear oil; (b) methyl 13-hydroxymethyl-12-methoxypodocarpa-8,11,13-trien-19-oate (**20**) (36 mg, 18%) as a clear oil (Kugelrohr, 120–130°C/0.15 mmHg). Anal. Found: C, 72.3; H, 8.7. $C_{20}H_{28}O_4$ calc.: C, 72.3; H, 8.5%. ν_{max} 3433 (OH), 1725 cm^{-1} (CO). δ(H) 1.04 (s, $H(20)_3$); 1.09 (txd, *J* 13.5, 4.2 Hz, H(3ax)); 1.27 (s, $H(18)_3$); 1.40 (txd, *J* 13.3, 4.0 Hz, H(1ax)); 1.52 (dxd, *J* 12.2, 1.5 Hz, H(5)); 1.64 (dxp, *J* 14.2, 3.0 Hz, H(2eq)); 1.94 (qxd, *J* 13.5, 5.5 Hz, H(6ax)); 2.01 (qxt, *J* 13.9, 3.7 Hz, H(2ax)); 2.17 (bdxd, *J* 13.8, 6.1 Hz, H(6eq)); 2.26–2.30 (m, H(1eq), H(3eq), 13-CH_2OH); 2.71 (dxdxd, *J* 16.6, 12.5, 6.0 Hz, H(7ax)); 3.21 (dxdxd, *J* 16.5, 5.5, 1.5 Hz, H(7eq)); 3.66 (s, 19-OMe); 3.82 (s, 12-OMe); 4.61 (d, *J* 6.3 Hz, 13-CH_2OH); 6.76 (s, H(11)); 6.93 (s, H(13)) ppm. δ(C) 19.9 (C(2)); 21.0 (C(6)); 22.8 (C(20)); 28.5 (C(18)); 31.1 (C(7)); 37.6 (C(3)); 38.7 (C(10)); 39.5 (C(1)); 44.0 (C(4)); 51.2 (19-OMe); 52.8 (C(5)); 55.3 (12-OMe); 61.9 (13-CH_2OH); 107.2 (C(11)); 126.6 (C(8)); 127.4 (C(13)); 129.4 (C(14)); 148.6 (C(9)); 155.7 (C(12)); 177.9 (C(19)) ppm. *m/z* 332 (100, M^+), 317 (12, *M* − Me), 299 (20, 317 − H_2O), 273 (7, *M* − CO_2Me), 257 (84, 317 − HCO_2Me), 227 (26), 191 (12), 171 (14), 69 (16), 55 (17), 41 (19); (c) bis[13,13′-(methyl 12-methoxypodocarpa-8,11,13-trien-19-oate)]ethanedione (**59**) (17 mg, 5%) as a clear oil. Anal. Found: M^+, 658.3534. $C_{40}H_{50}O_8$ calc.: *M*, 568.3506. ν_{max} 1725 (ester CO), 1668 (ketone CO), 1606, 1566, 1493, 1463 cm^{-1} (C=C). δ(H) 1.05 (s, $H(20)_3$, $H(20)_3'$); 1.10 (txd, *J* 13.4, 4.1 Hz, H(3ax), H(3ax)′); 1.29 (s, $H(18)_3$, $H(18)_3'$); 1.43 (txd, *J* 13.2, 3.9 Hz, H(1ax), H(1ax)′); 1.55 (bd, *J* 12.2 Hz, H(5), H(5)′); 1.64 (dxp, *J* 14.4, 2.8 Hz, H(2eq), H(2eq)′); 1.95 (qxd, *J* 13.0, 5.2 Hz, H(6ax), H(6ax)′); 2.02 (qxt, *J* 13.5, 3.2 Hz, H(2ax), H(2ax)′); 2.18–2.31 (m, H(1eq), H(1eq)′, H(3eq), H(3eq)′, H(6eq), H(6eq)′); 2.77 (dxdxd, *J* 16.6, 12.8, 6.1 Hz, H(7ax), H(7ax)′); 2.94 (dxd, *J* 16.6, 5.7 Hz, H(7eq), H(7eq)′); 3.57 (s, 19-OMe, (19-OMe)′); 3.67 (s, 12-OMe, (12-OMe)′); 6.83 (s, H(11), H(11)′); 7.72 (s, H(14), H(14)′) ppm. δ(C) 19.9 (C(2), C(2)′); 20.9 (C(6), C(6)′); 22.7 (C(20), C(20)′); 28.5 (C(18), C(18)′); 31.1 (C(7), C(7)′); 37.5 (C(3), C(3)′); 39.3 (C(1), C(1)′); 39.4 (C(10), C(10′); 44.0 (C(4), C(4)′); 51.3 (19-OMe, 19-OMe)′); 52.4 (C(5), C(5)′); 56.3 (12-OMe, (12-OMe)′); 110.0 (C(11), C(11)′); 121.4 (C(13), C(13)′); 128.8 (C(8), C(8)′); 130.9 (C(14), C(14)′); 156.3 (C(9), C(9)′); 158.6 (C(12), C(12)′); 177.8 (C(19), C(19)′); 192.6 (13-CO, 13-CO′) ppm. *m/z* 658 (2, M^+), 329 (100), 149 (9), 57 (54); and (d) a diastereomeric mixture (1:1) of [5a*R*-(1ζ,5aα,6β,9aβ)]-4,5,5a,6,7,8,9,9a-octahydro-11-methoxy-6-methoxycarbonyl-6,9a-dimethyl-1-[7-(1*S*-(1β,4aβ,10aα))]-1,2,3,4,4a,9,10,10a-octahydro-6-methoxy-1,4a-dimethyl-1-phenanthrene carboxylic acid methyl esterphenanthro[1,2-*c*]furan-3(1*H*)-one (**60**) (54 mg, 26%) which crystallized from Et_2O as rods, m.p. 170–190°C (dec). Anal. Found: C, 72.2; H, 7.6. $C_{40}H_{50}O_8 \cdot \frac{1}{2}C_4H_{10}O$ calc.: C, 72.5; H, 8.0%. Anal. Found: M^+, 658.3468. $C_{40}H_{50}O_8$ calc.: *M* 658.3506. ν_{max} (KBr): 1764 (lactone CO), 1725 (ester CO), 1614, 1596, 1501, 1465 cm^{-1} (C=C). δ(H) 1.01, 1.04, 1.07 ((6H), s, (9a-Me), (9a-Me)′, (4a′-Me), (4a′-Me)′); 1.19, 1.20, 1.23, 1.24 ((6-Me), (6-Me)′, (1′-Me), (1′-Me)′); 3.63 (6H), 3.64 (6H) (s, (6-CO_2Me), (6-CO_2Me)′, (1′-CO_2Me), (1′-CO_2Me)′); 6.40–6.70 (m, H(1), H(1)′, H(8′), H(8′)′); 6.79, 6.84, 6.86, 6.88 (s, H(10), H(10′, H(5′), H(5′)′) ppm. δ(C) 19.9 ((2C), 20.2 (2C), C(8), C(8)′, C(3′), C(3′)′); 20.9 ((2C)); 21.0 ((2C), C(5), C(5)′, C(10′), C(10′)′); 22.77, 22.80, 22.6 ((2C), (9a-Me), (9a-Me)′, (4a′-Me), (4a′-Me)′); 25.9, 27.4, 31.0, 31.1 (C(4), C(4)′, C(9′), C(9′)′); 28.4 (2C); 28.5 ((2C), (6-Me), (6-Me)′, (1′-Me), (1′-Me)′);

37.3, 37.5 ((2C), 37.6, C(7), C(7)', C(2'), C(2')'); 38.8 (2C); 39.7 ((2C), C(9a), C(9a)', C(4a'), C(4a')'); 39.4 (2C); 39.5, 39.6 (C(9), C(9)', C(4'), C(4')'); 43.92 (2C); 43.95 ((2C), C(6), C(6)', C(1'), C(1')'); 51.17, 51.20, 51.23, 51.3 (6-CO_2*Me*, (6-CO_2Me)', 1'-CO_2*Me*, (1'-CO_2*Me*)'); 51.9, 52.1, 52.47, 52.53 (C(5a), C(5a)', C(10a'), C(10a')'); 55.7, 55.9 (2C); 56.0 ((11-OMe), (11-OMe)', (6'-OMe), (6'-OMe)'); 106.9, 107.4 (weak, C(1), C(1)'); 108.3 (2C); 108.4 ((2C), C(10), C(10'), C(5'), C(5')'); 120.7, 121.1 (2C); 122.6 (C(3b), C(3b)', C(8a'), C(8a')'); 126.4, 127.3, 127.8, 127.9 (C(11a), C(11a)', C(7'), C(7')'); 128.4, 128.9 (C(8), C(8)'); 150.2, 150.45, 150.53, 151.0 (C(9b), C(9b)', C(4b'), C(4b')'); 155.85, 155.93, 155.99, 156.8, 156.0, 157.1 (C(3a), C(3a)', C(11), C(11)', C(6'), C(6')'); 169.1, 169.0 (C(3), C(3)'); 177.4, 177.5, 177.8, 177.9 (6-CO_2Me, (6-CO_2Me)', 1'-CO_2Me, (1'-CO_2Me)') ppm. *m/z* 658 (54, M^+), 643 (10, M − Me), 616 (11, $M - CH_2CO$), 356 (100), 296 (52), 227 (12).

Tetracarbonyl(13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene-C^{14},O^{13})manganese (52)

13-Formyl-12,19-dimethoxypodocarpa-8,11,13-triene (**19**) (0.40 g, 1.27 mmol) and $PhCH_2Mn(CO)_5$ (0.43 g, 1.52 mmol) (2 h) and flash chromatography gave (i) $PhCH_2Mn(CO)_5$ (25 mg); (ii) tetracarbonyl(13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene-C^{14},O^{13})manganese (0.18 g, 27%) as a yellow oil. Anal. Found: C, 61.0; H, 6.1. $C_{24}H_{27}MnO_7 \cdot \frac{1}{3}C_6H_{14}$ calc.: C, 61.1; H, 6.3%. ν_{max} 2077, 1980, 1933 (Mn–C≡O), 1584 (C=C), 1567 cm^{-1} (CHO). δ(H) 1.03 (txd, *J* 13.7, 4.1 Hz, H(3ax)); 1.08 (s, $H(18)_3$); 1.28 (s, $H(20)_3$); 1.45 (dxd, *J* 12.9, 1.7 Hz, H(5)); 1.49 (txd, *J* 13.0, 3.8 Hz, H(1ax)); 1.65 (dxp, *J* 14.2, 3.6 Hz, H(2eq)); 1.70–1.79 (m, H(6ax)); 1.77 (qxt, *J* 13.7, 3.4 Hz, H(2ax)); 1.90 (bd, *J* 13.5 Hz, H(3eq)); 2.09 (bdxd, *J* 13.4, 7.7 Hz, H(6eq)); 2.27 (bd, *J* 12.4 Hz, H(1eq)); 2.87 (dxdxd, *J* 16.8, 11.6, 7.6 Hz, H(7ax)); 3.03 (dxdxd, *J* 16.8, 7.1, 0.9 Hz, H(7eq)); 3.25 (d, *J* 9.1 Hz, H(19)); 3.35 (s, 19-OMe); 3.54 (d, *J* 9.1 Hz, H(19)); 3.84 (s, 12-OMe); 6.52 (s, H(11)); 9.70 (s, OCH) ppm. δ(C) 19.3 (C(2)); 20.3 (C(6)); 25.3 (C(20)); 27.6 (C(18)); 35.7 (C(3)); 37.0 (C(7)); 38.2 (C(10)); 39.3 (C(1)); 39.6 (C(4)); 50.1 (C(5)); 54.9 (12-OMe); 59.4 (19-OMe); 75.9 (C(19)); 103.1 (C(11)); 133.8 (C(13)); 139.2 (C(8)); 159.6 (C(9)); 162.3 (C(12)); 199.7 (C(14)); 203.8 (OCH); 211.7, 211.9, 214.5, 221.4 (Mn–C≡O) ppm. *m/z* 482 (1, M^+), 426 (1, $M - 2CO$), 370 (42, 426 − 2CO), 316 (75, $M - Mn(CO)_4 + H$), 269 (12), 241 (14), 189 (100), 91 (50); and (iii) a pale brown oil (0.27 g) which on PLC (hexanes/Et_2O, 8:2 then 7:3) gave (a) **19** (44 mg, 11%); (b) 13-hydroxymethyl-12,19-dimethoxypodocarpa-8,11,13-triene (**21**) (47 mg, 12%) as a clear oil (Kugelrohr, 155–160°C/0.05 mmHg). Anal. Found: C, 75.2; H, 9.2. $C_{20}H_{30}O_3$ calc.: C, 75.5; H, 9.4%. ν_{max} 3442 (OH), 1615, 1578, 1501, 1463 (C=C), 1108 cm^{-1} (C–O–C). δ(H) 1.01 (txd, *J* 13.7, 4.6 Hz, H(3ax)); 1.04 (s, $H(18)_3$); 1.21 (s, $H(20)_3$); 1.41 (dxd, *J* 12.8, 3.8 Hz, H(5)); 1.44 (txd, *J* 12.8, 3.8 Hz, H(1ax)); 1.59–1.75 (m, H(2eq), H(6ax)); 1.74 (qxt, *J* 13.8, 3.1 Hz, H(2ax)); 1.88 (bd, *J* 13.6 Hz, H(3eq)); 1.97 (bdxd, *J* 13.3, 7.1 Hz, H(6eq)); 2.29 (bd, *J* 12.9 Hz, H(1eq)); 2.33 (bs, 13-CH_2OH); 2.73 (dxdxd, *J* 16.8, 11.6, 7.1 Hz, H(7ax)); 2.85 (bdxd, *J* 16.8, 6.7 Hz, H(7eq)); 3.24 (d, *J* 9.1 Hz, H(19)); 3.33 (s, 19-OMe); 3.54 (d, *J* 9.1 Hz, H(19)); 3.83 (s, 12-OMe)); 4.61 (d, *J* 5.1 Hz, 13-CH_2OH); 6.77 (s, H(11)); 6.92 (s, H(14)) ppm. δ(C) 19.1 (C(2)); 19.3 (C(6)); 25.5 (C(20)); 27.6 (C(18)); 30.1 (C(7)); 35.9 (C(3)); 38.0 (C(4), C(10)); 39.1 (C(1)); 51.4 (C(5); 55.2 (12-OMe); 59.4 (19-OMe); 61.9 (13-CH_2OH); 75.9 (C(19)); 106.4 (C(11)); 126.4 (C(8)); 127.0 (C(13)); 129.4 (C(14)); 150.4 (C(9)); 155.6 (C(12)) ppm. *m/z* 318 (100, M^+), 303 (7, M − Me), 285

(11, M − MeOH − H), 271 (24, 303 − MeOH), 241 (61), 191 (39), 173 (12); and (c) a mixture of diastereoisomers of [5a*R*-(1ζ,5aα,6β,9aβ)-4,5,5a,6,7,8,9,9a-octahydro-11-methoxy-6,9a-dimethyl-6-methoxymethyl-1-[7-(1S-(1β,4aβ,10aα)]-1,2,3,4,4a,9,-10,10a-octahydro-6-methoxy-1,4a-dimethyl-1-methoxymethylphenanthrene]phenanthro[1,2-*c*]-furan-3(1*H*)-one (**61**) (97 mg, 24%) which crystallized from hexanes/Et_2O as rods, m.p. 140–155°C (dec). Anal. Found: $M^{+\cdot}$, 630.3862. $C_{40}H_{54}O_6$ calc.: M, 630.3920). ν_{max} (KBr): 1758 (lactone CO), 1614, 1597, 1503, 1485, 1463 cm^{-1} (C=C). δ(H) (328 K) 0.99, 1.01, 1.02, 1.03 (s, (6-Me), (6-Me)', (1'-Me), (1'-Me)'); 1.19, 1.20, 1.21, 1.23 (s, (9a-Me), (9a-Me)', (4'-Me), (4'-Me)'); 3.29, 3.30, 3.31 ((6H), 3, 6-CH_2OMe, (6-CH_2OMe)', 1'-CH_2OMe, (1'-CH_2OMe)'); 3.83 (6H); 3.98, 3.99 (s, (11-OMe), (11-OMe)', (6'-OMe), (6'-OMe)'); 6.41, 6.46, 6.49, 6.61 (bs, H(1), H(1)', H(8'), H(8')'); 6.80 ,6.81, 6.88, 6.89 (s, H(10), H(10)', H(5'), H(5')') ppm. δ(C) 18.6 (2C); 18.9 (2C); 19.3 (2C); 19.4 (2C), (C(5), C(5)', C(8), C(8)', C(3'), C(3')', C(10'), C(10')'); 25.2, 25.5, 25.6, 25.7 ((6-Me), (6-Me)', (1'-Me), (1'-Me)'); 27.51, 27.54, 27.59, 27.63 ((9a-Me), (9a-Me)', (4a'-Me), (4a'-Me)'); 25.1, 26.7 (2C); 30.0 (C(4), C(4)', C(9'), C(9')'); 38.0 (3C); 38.07 (3C); 38.09 (2C); (C(6), C(6)', C(9a), C(9a)', C(1'), C(1')', C(4a'), C(4a')'); 38.9 (2C); 39.2 (2C), (C(9), C(9)', C(4'), C(4')'); 50.3, 50.8 (2C); 51.0 (C(5a), C(5a)', C(10a'), C(10a')'); 55.7 (2C); 55.9 (2C), ((11-OMe), (11-OMe)', (6'-OMe), (6'-OMe)'); 59.3 (4C), (6-CH_2OMe, (6-CH_2OMe)', 1'-CH_2OMe, (1'-CH_2OMe)'); 75.8, 75.9 (2C); 76.0 (6-CH_2OMe, (6-CH_2OMe)', 1'-CH_2OMe, (1'-CH_2OMe)'); 107.3 (2C); 107.5 (2C), (C(10), C(10)', C(5'), C(5')'); 120.4 (2C); 120.9 (2C); 122.2 (2C); 127.4 ((2C), C(3b), C(3b)', C(11a), C(11a)', C(7'), C(7')', C(8a'), C(8a')'); 128.3 ((2C), C(8'), C(8')'); 150.6, 150.8 (C(3a), C(3a)'); 152.0, 152.2, 155.9, 156.0 (2C); 156.1, 158.6, 158.9 (C(9b), C(9b)', C(11), C(11)', C(4b'), C(4b')', C(6'), C(6')'); 169.0, 169.2 (C(3), C(3)') ppm. m/z 630 (40, $M^{+\cdot}$), 420 (45), 342 (76), 316 (31), 293 (46), 189 (47), 117 (38), 43 (100).

Table 3

Percentage yields of aldehyde complexes formed during cyclomanganation reactions with 1.2 mol equiv. of $PhCH_2Mn(CO)_5$

Complex	Solvent	Reaction time	% Yield of complexes [a]
51	Pentane	2.7 h	2
	Hexanes	2.8 h	18
	Hexanes	20 h	18
	Heptane	2.0 h	27, 33 [b]
	Octane	50 min	13
52	Heptane	1.0 h	30, 38 [b]
	Heptane	1.0 h	30 [c]
	Heptane	2.0 h	23

[a] Yields after flash column chromatography [b] The isolated yield of the aldehyde complexes increased when the reaction was scaled up to 600 mg of aldehyde. All remaining reactions were performed on 100-200 mg of aldehyde. [c] The manganating agent [$PhCH_2Mn(CO)_5$] was added in four equal portions at 15 min intervals to give a total reflux time of 1 h.

Complexation of 1,3-diphenyl-2-propen-1-one (62)

1,3-Diphenyl-2-propen-1-one (**62**) (0.50 g, 2.40 mmol) and $PhCH_2Mn(CO)_5$ (0.83 g, 2.89 mmol) (35 min) and flash chromatography gave (i) $PhCH_2Mn(CO)_5$ (57 mg); (ii) (2-benzoyl-1-phenylethene-C,O)tetracarbonylmanganese (**63**) (0.58 g, 65%) as a red-orange oil. Anal. Found: C, 61.3; H, 3.1. $C_{19}H_{11}MnO_5$ calc.: C, 61.0; H, 3.0%. ν_{max} (KBr): 2081, 1982, 1940 (Mn–C≡O), 1600, 1463, 1428 (C=C), 1538 cm^{-1} (ketone CO). δ(H) 7.38–7.41 (m, 1-*para*-H); 7.46–7.53 (m, 1-(*meta*-H)$_2$, 1-(*ortho*-H)$_2$, 2-(*meta*-H)$_2$); 7.60 (bxt, *J* 7.4 Hz, 2-*para*-H); 7.75 (s, H(2)); 8.05 (d, *J* 7.4 Hz, 2-(*ortho*-H)$_2$) ppm. δ(C) 125.2 (1-(*ortho*-C)$_2$); 128.4 (1-(*meta*-C)$_2$); 128.7 (C(2)); 128.8 (2C); 129.3 (2C), (2-(*ortho*-C)$_2$, 2-(*meta*-C)$_2$); 131.7 (1-*para*-C); 133.5 (2-*para*-C); 135.1 (2-*ipso*-C); 150.3 (1-*ipso*-C); 204.6 (*C*OPh); 210.2 (2C); 214.0, 219.4 (MnC≡O); 253.3 (C(1)) ppm. *m/z* 374 (4, M^+), 290 (15, M – 3CO), 262 (100, 290 – CO), 207 (16, M – $Mn(CO)_4$), 179 (14, 207 – CO), 132 (29), 105 (70, $PhCO^+$), 77 (52, Ph^+), 55 (32, Mn^+); and (iii) tetracarbonyl[2-(3-phenylprop-2-enoyl)phenyl-C,O]manganese (**64**) (81 mg, 9%) which crystallized from hexanes as red needles, m.p. 124–128°C (dec). Anal. Found: C, 61.5; H, 3.0. $C_{19}H_{11}MnO_5$ calc.: C, 61.0; H, 3.0%. ν_{max} (KBr): 2078, 1980, 1927 (Mn–C≡O), 1628, 1577, 1511 (C=C), 1553 cm^{-1} (ketone CO). δ(H) 7.23, 7.44 (txd, *J* 7.5, 1.2 Hz, H(4), H(5)); 7.45–7.48 (m, *para*-H, (*meta*-H)$_2$); 7.57 (d, *J* 15.6 Hz, =C*H*CO); 7.67–7.70 (m, (*ortho*-H)$_2$); 7.90 (d, *J* 15.6 Hz, PhC*H*=); 8.04, 8.16 (dxd, *J* 7.6, 0.5 Hz, H(3), H(6)) ppm. δ(C) 118.2 (=*C*HCO); 123.7 (C(4)); 128.8 ((*meta*-C)$_2$); 129.1 ((*ortho*-C)$_2$); 130.8 (*para*-C); 131.4 (C(3)); 133.5 (C(5)); 134.4 (*ipso*-C); 141.8 (C(6)); 145.3 (C(2)); 147.3 (Ph*C*H=); 195.0 (C(1)); 203.8 (=CH*C*O); 211.3 (2C); 213.3, 221.2 (Mn–C≡O) ppm. *m/z* 374 (4, M^+), 290 (13, M – 3CO), 262 (100, 290 – CO), 208 (84, M – $Mn(CO)_4$ + H), 178 (30), 131 (32), 105 (55, PhCO), 77 (70, Ph), 55 (35, Mn).

Tetracarbonyl[2-(3-phenylpropanoyl)phenyl-C,O)]manganese (66)

1,3-Diphenylpropan-1-one (**65**) (0.20 g, 0.95 mmol) and $PhCH_2Mn(CO)_5$ (0.33 g, 1.14 mmol) (2 h) gave tetracarbonyl[2-(3-phenylpropanoyl)phenyl-C,O)]manganese (0.34 g, 94%) as a yellow oil. Anal. Found: C, 60.5; H, 3.5. $C_{19}H_{13}MnO_5$ calc.: C, 60.7; H, 3.5%. ν_{max} 2081, 1980, 1934 (Mn–C≡O), 1578 (C=C), 1536 cm^{-1} (ketone CO). δ(H) 3.05 (t, *J* 7.5 Hz, PhCH_2); 3.31 (t, *J* 7.5 Hz, CH_2CO); 7.16 (bt, *J* 7.5 Hz, *para*-H); 7.18–7.25 (m, (*ortho*-H)$_2$, H(4)); 7.31 (bt, *J* 7.2 Hz, (*meta*-H)$_2$); 7.42 (bt, *J* 7.3 Hz, H(5)); 7.84 (bd, *J* 7.8 Hz, H(6)); 8.11 (bd, *J* 7.5 Hz, H(3)) ppm. δ(C) 30.8 (Ph*C*H$_2$); 39.0 (*C*H$_2$CO); 123.7 (*para*-C); 126.5 (C(6)); 128.3 ((*meta*-C)$_2$); 128.6 ((*ortho*-C)$_2$); 131.0 (C(3)); 133.7 (C(5)); 140.0 (*ipso*-C); 141.5 (C(4)); 144.9 (C(2)); 193.7 (C(1)); 211.4 (2C); 212.9, 221.0 (Mn–C≡O); 217.9 (CH$_2$*C*O) ppm. *m/z* 376 (4, M^+), 264 (83, M – 4CO), 210 (39, M – $Mn(CO)_4$ + H), 105 (100, PhCO), 91 (29, $PhCH_2$), 77 (Ph), 55 (30, Mn).

Complexation of methyl 12-dimethylcarbamylpodocarpa-8,11,13-trien-19-oate (26)

Methyl 12-dimethylcarbamylpodocarpa-8,11,13-trien-19-oate (**26**) (0.20 g, 0.56 mmol) and $PhCH_2Mn(CO)_5$ (2 × 0.21 g, 0.73 mmol) (2 h and 4 h) and flash chromatography gave (i) $PhCH_2Mn(CO)_5$ (0.17 g); (ii) a mixture (51 mg) which after PLC (hexanes/ether, 4:1) to give (a) a mixture (3:2) (32 mg) of tetracarbonyl(methyl 12-phenylethanoyloxypodocarpa-8,11,13-trien-19-oate-C^{13},O)manganese (**71**) (5%) and dibenzyl ketone (**72**) as a yellow oil. **71**: ν_{max} 2077, 1990, 1980, 1931 (sh) (Mn–C≡O), 1717 cm^{-1} (ester CO). δ(H) 1.11 (txd, *J* 13.4, 4.3 Hz,

H(3ax)); 1.12 (s, $H(20)_3$); 1.29 (s, $H(18)_3$); 1.47 (txd, *J* 13.5, 4.3 Hz, H(1ax)); 1.56 (dxd, *J* 11.8, 1.3 Hz, H(5)); 1.67 (dxp, *J* 14.1, 2.9 Hz, H(2eq)); 2.02 (qxd, *J* 12.4, 5.7 Hz, H(6ax)); 2.06 (qxt, *J* 13.9, 3.4 Hz, H(6eq)); 2.30 (bd, *J* 13.0 Hz, H(3eq)); 2.44 (bd, *J* 13.0 Hz, H(1eq)); 2.79 (dxdxd, *J* 16.4, 12.5, 5.9 Hz, H(7ax)); 2.89 (bdxd, *J* 16.5, 4.1 Hz, H(7eq)); 3.68 (s, 19-OMe); 4.19 (s, 12-OCOCH_2Ph); 7.13–7.35 (m, (*aromatic*-H)$_5$); 7.62, 7.94 (s, H(11), H(14)) ppm. δ(C) 19.9 (C(2)); 20.9 (C(6)); 22.7 (C(20)); 28.6 (C(18)); 31.7 (C(7)); 37.5 (C(3)); 39.1 (C(1)); 39.5 (C(10)); 43.5 (12-OCOCH_2Ph); 44.1 (C(4)); 51.3 (19-OMe); 52.6 (C(5)); 126.4 (C(8)); 128.8 (2C); 128.9 (2C), ((*meta*-C)$_2$, (*ortho*-C)$_2$); 127.2, 132.8, 138.4 (C(11), C(14), *para*-C); 131.5 (*ipso*-C); 142.5 (C(9)); 155.8 (C(12)); 177.7 (C(19)); 187.7 (C(13)); 211.9 (2C); 212.9, 221.5 (Mn–C≡O); 215.1 (12-O*C*OCH$_2$Ph) ppm. *m/z* 472 (1), 444 (8), 299 (100), 91 (10); and (b) dibenzyl ketone (**69**) (12 mg) as a pale yellow oil, correct IR, ^{1}H NMR, and ^{13}C NMR spectra; and (iii) **67** (0.14 g, 71%).

Complexation of 13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene oxime (27)

13-Formyl-12,19-dimethoxypodocarpa-8,11,13-triene oxime (**27**) (50 mg, 0.15 mmol) and PhCH$_2$Mn(CO)$_5$ (52 mg, 0.18 mmol) (2.5 h) and PLC (hexanes/Et$_2$O, 4 : 1) gave (i) a mixture (15 : 85) (14 mg) of **19** and tetracarbonyl(13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene oxime)manganese (**73**) (16%) as a yellow oil. ν_{max} 2068, 1979, 1969, 1927 (Mn–C≡O), 1109 cm^{-1} (C–O–C). δ(H) 1.08 (s, $H(18)_3$); 1.27 (s, $H(20)_3$); 3.25 (d, *J* 9.1 Hz, H(19)); 3.35 (s, (19-OMe)); 3.57 (d, *J* 9.1 Hz, H(19)); 3.80 (s, 12-OMe) 6.55 (s, H(11)); 8.21 (bd, *J* 9.2 Hz, 13-CH=NO*H*); 8.88 (d, *J* 10.7 Hz, 13-C*H*=NOH) ppm. δ(C) 19.4 (C(2)); 20.5 (C(6)); 25.6 (C(20)); 27.6 (C(18)); 35.7 (C(3)); 37.6 (C(7); 38.2 (C(10)); 39.2 (C(4)); 39.5 (C(1)); 50.3 (C(5)); 54.8 (12-OMe); 59.5 (19-OMe); 75.9 (C(19)); 103.1 (C(11)); 133.1 (C(13)); 138.6 (C(8)); 155.4 (C(12)); 158.0 (C(9)); 178.7 (13-CH=NOH); 186.5 (C(14)); 213.9, 214.2, 216.6, 220.2 (Mn–C≡O) ppm. *m/z* 425 (1, M^+ – CH=NOH–CO), 397 (1, 425 – CO), 369(23, 397 – CO), 189(100); and (ii) 13-cyano-12,19-dimethoxypodocarpa-8,11,13-triene (**28**) (9 mg, 19%) as a clear oil. Anal. Found: M^+, 313.2036. $C_{20}H_{27}NO_2$ calc.: *M*, 313.2042. ν_{max} 2224 (C≡N), 1608, 1562, 1498, 1460 cm^{-1} (C=C). δ(H) 1.01 (txd, *J* 13.6, 4.2 Hz, H(3ax)); 1.04 (s, $H(18)_3$); 1.20 (s, $H(20)_3$); 1.38 (dxd, *J* 12.7, 1.9 Hz, H(5)); 1.43 (txd, *J* 12.9, 4.0 Hz, H(1ax)); 1.59–1.78 (m, H(2eq), H(6ax)); 1.87 (bd, *J* 13.6 Hz, H(3eq)); 1.99 (bdxd, *J* 13.5, 7.4 Hz, H(6eq)); 2.26 (bd, *J* 12.4 Hz, H(1eq)); 2.73 (dxdxd, *J* 16.9, 11.8, 7.2 Hz, H(7ax)); 2.85 (bdxd, *J* 16.9, 5.9 Hz, H(7eq)); 3.25 (d, *J* 9.1 Hz, H(19)); 3.33 (s, 19-OMe); 3.48 (d, *J* 9.1 Hz, H(19)); 3.88 (s, 12-OMe); 6.82 (s, H(11)); 7.21 (s, H(14)) ppm. δ(C) 18.97 (C(2)); 19.00 (C(6)); 25.3 (C(20)); 27.7 (C(18)); 29.7 (C(7)); 35.9 (C(3)); 38.1 (C(10)); 38.7 (C(4)); 38.8 (C(1)); 50.7 (C(5)); 55.9 (12-OMe); 59.4 (19-OMe); 75.9 (C(19)); 99.0 (C(13)); 107.3 (C(11)); 116.9 (13-C≡N); 128.0 (C(8)); 134.0 (C(14)); 156.9 (C(9)); 159.2 (C(12)) ppm. *m/z* 313 (58, M^+), 298 (4, *M* – Me), 268 (10, 298 – CH_2O), 198 (22), 186 (100), 149 (14), 45 (20).

Unsuccessful complexations

Using the standard complexation conditions on diphenylacetylene, 13-acetyl-12-methoxytotara-8,11,13-triene (**17**) [20], 13-*N*,*N*-dimethylcarboxamido-12,19-dimethoxypodocarpa-8,11,13-triene (**22**), methyl 13-*N*,*N*-diethylcarboxamido-12-methoxypodocarpa-8,11,13-trien-19-oate (**23**), 2-methoxy-*N*,*N*-dimethylbenzamide

Table 4

Crystal data and intensity collection parameters for **42**

Formula	$C_{22}H_{23}MnO_6$
Molecular weight	438
System	Monoclinic
a (Å)	6.960(1)
b (Å)	11.466(5)
c (Å)	13.469(6)
β (°)	100.60(2)
V (Å^3)	1056.5
Temperature (K)	295
Z	2
Space group	$P2_1$
D_c (g cm^{-3})	1.38
$F(000)$	456
μ(Mo-K_α) (cm^{-1})	6.93
θ_{max} (°)	25
Total reflections	2046
Observed data	1134
Weighting scheme g	0.0005
R	0.047
R_w	0.042

Table 5

Atomic coordinates and standard deviations for **42**

Atom	x	y	z
C(1)	−0.0070(18)	−0.2904(9)	0.2922(8)
C(2)	−0.0473(20)	−0.3808(10)	0.29079(8)
C(3)	−0.1184(16)	−0.3224(11)	0.1049(9)
C(4)	0.0253(14)	−0.2350(11)	0.0746(7)
C(5)	0.0860(13)	−0.1483(8)	0.1657(6)
C(6)	0.2369(16)	−0.0598(9)	0.1447(7)
C(7)	0.2654(13)	0.0344(8)	0.2248(7)
C(8)	0.2242(12)	0.0113(7)	0.3230(6)
C(9)	0.1610(12)	−0.0998(9)	0.3481(7)
C(10)	0.1487(16)	−0.2017(8)	0.2730(7)
C(11)	0.1226(13)	−0.1143(9)	0.4450(7)
C(12)	0.1507(13)	−0.0214(10)	0.5127(7)
C(13)	0.2171(13)	0.0883(10)	0.4870(7)
C(14)	0.2535(13)	0.1064(9)	0.3903(7)
C(18)	−0.0817(16)	−0.1683(11)	−0.0175(7)
C(19)	0.2070(17)	−0.2944(10)	0.0430(8)
C(20)	0.3517(15)	−0.2587(13)	0.2948(7)
C(21)	0.3155(18)	−0.3908(12)	−0.0886(10)
C(22)	0.5940(16)	0.1871(9)	0.3750(7)
C(23)	0.4452(16)	0.3674(10)	0.2513(10)
C(24)	0.3602(16)	0.3417(11)	0.4319(9)
C(25)	0.0886(16)	0.2913(8)	0.2860(8)
Mn	0.3509(2)	0.25000(0)	0.32391(10)
O(1)	0.1496(12)	−0.3616(8)	−0.0453(6)
O(2)	0.3249(10)	0.1333(6)	0.2248(7)
O(3)	0.7372(11)	0.1454(8)	0.4090(6)
O(4)	0.4954(11)	0.4403(7)	0.2060(7)
O(5)	0.3625(12)	0.3964(8)	0.5034(7)
O(6)	−0.0710(11)	0.3131(7)	0.2664(6)

(**67**), 3-methoxy-*N*,*N*-dimethylbenzamide (**68**), 4-methoxy-*N*,*N*-dimethylbenzamide (**69**), methyl 4-methylbenzoate (**70**), methyl 12-acetoxypodocarpa-8,11,13-trien-19-oate (**25**) [16], 13-formyl-12,19-dimethoxypodocarpa-8,11,13-triene *O*-methyloxime (**29**), and cyclohex-2-en-1-one (**74**) gave no isolable cyclomanganated complexes.

X-ray crystal structure for 42

Crystals suitable for data collection were mounted on glass fibres and positioned on a Nonius CAD-4 diffractometer. Unit cell dimensions were derived from least-squares fits to the observed setting angles of 25 reflections, using monochromated Mo-K_α radiation. Intensity data collection employed the $2\theta/\omega$ technique with a total peak/background count time of 2:1. The omega scan angle was $0.80 + 0.347 \tan \theta$. Reflections were counted for 60 s or until $\sigma(I)/I$ was 0.02. Crystal alignment and decomposition were monitored throughout data collection by measuring three standard reflections every 100 measurements; no statistical variation was observed. The data were corrected for Lorentz and polarization effects and equivalent reflections averaged. Computing was carried out using the

Table 6

Interatomic distances and standard deviations for **42**

C(22)–Mn	1.851(12)
C(23)–Mn	1.854(13)
C(24)–Mn	1.786(12)
C(25)–Mn	1.864(12)
O(2)–Mn	2.060(6)
C(14)–Mn	2.047(9)
C(22)–O(3)	1.124(10)
C(23)–O(4)	1.128(12)
C(24)–O(5)	1.147(12)
C(25)–O(6)	1.122(10)
C(2)–C(1)	1.524(14)
C(10)–C(1)	1.542(12)
C(3)–C(2)	1.537(15)
C(4)–C(3)	1.524(15)
C(5)–C(4)	1.575(13)
C(18)–C(4)	1.529(14)
C(19)–C(4)	1.563(14)
C(6)–C(5)	1.524(12)
C(10)–C(5)	1.557(12)
C(7)–C(6)	1.514(12)
O(2)–C(7)	1.250(10)
C(8)–C(7)	1.429(12)
C(9)–C(8)	1.409(12)
C(14)–C(8)	1.409(12)
C(10)–C(9)	1.537(12)
C(11)–C(9)	1.389(12)
C(20)–C(10)	1.535(13)
C(12)–C(11)	1.393(13)
C(14)–C(13)	1.388(11)
O(1)–C(19)	1.412(11)
C(21)–O(1)	1.426(12)

SDP suite of programs on a PDP-11 for initial data processing, SHELXS-86 [39] and SHELX-76 [40] on an IBM 4341 or Microvax computer for structure solution and refinement. Details of crystal data and intensity data collection parameters are summarized in Table 4.

Structure solution and refinement

The structure was solved by direct methods using SHELXS-86 [39]. Refinement was by full-matrix least squares [40], minimising the function $\Sigma\omega(|F_o| - |F_c|)^2$. Atomic scattering factors were for neutral atoms. After initial isotropic refinement, anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were located from difference maps and refined with a common thermal parameter. A final electron density map showed no feature greater than 0.5 e $Å^{-3}$. Weights used were $\omega = 1/[\sigma^2(F) + gF^2]$ with final values of g as given in Table 4. The stereochemistry followed from the well-established [41] absolute configuration of the diterpenoid ligand, which is the only chiral feature in the complex.

Final atomic coordinates, bond distances, are given in Tables 5 and 6. Lists of hydrogen coordinates, thermal parameters, bond angles, and observed and calculated structure factors are available from the authors.

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