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A Synthesis of Oxolenes and Furans via Oxacyclopentylidene Chromium and Molybdenum Complexes

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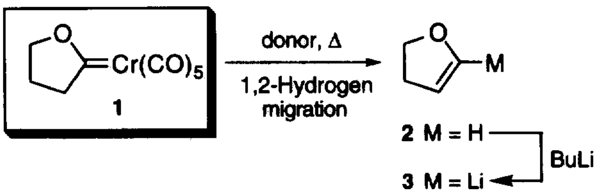
Abstract: An easy and convenient preparation of substituted oxolenes and furans by metal-assisted cyclization of alkynols using labile pentacarbonylchromium and pentacarbonylmolybdenum complexes is described.

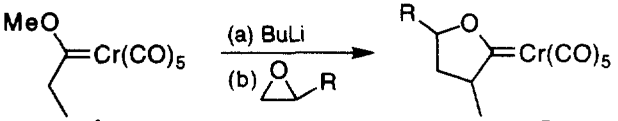
Five- and six-membered oxacyclic carbene complexes of the Fischer-type have been known for more than 20 years[1]. In contrast to the chemistry of Fischer carbene complexes in general[2,3], little work has been done to exploit the synthetic potential of this class of compounds[4-6]. With a view towards the synthesis of oxolane and oxane ring systems of various polyether antibiotics[7,8] we now report experiments aimed at the use of oxacyclopentylidene pentacarbonylchromium complexes **1** as precursors to the metallated oxolene system **3** according to the transformation depicted in Scheme 1. The base-induced 1,2-migration leading to simple enolethers has been recorded previously[9,10] but only a few examples have been described for the preparation of 2,3-oxolenes by this method[11,12]. Metal-assisted cyclisations related to those reported in this paper have been published previously by Dötz[13], McDonald[14,17], and Quayle[6].

Scheme 1



Preparation of Oxacyclopentylidene pentacarbonyl-chromium complexes. Our first attempts to prepare suitable oxacyclopentylidene pentacarbonylchromium complexes **5** by the alkylation of simple metallated Fischer carbene complexes **4** with oxirane or methyloxirane[1] (Scheme 2) gave low yields with further complications arising from competing double alkylation. A recent Lewis acid-assisted modification fared no better in our hands[5].

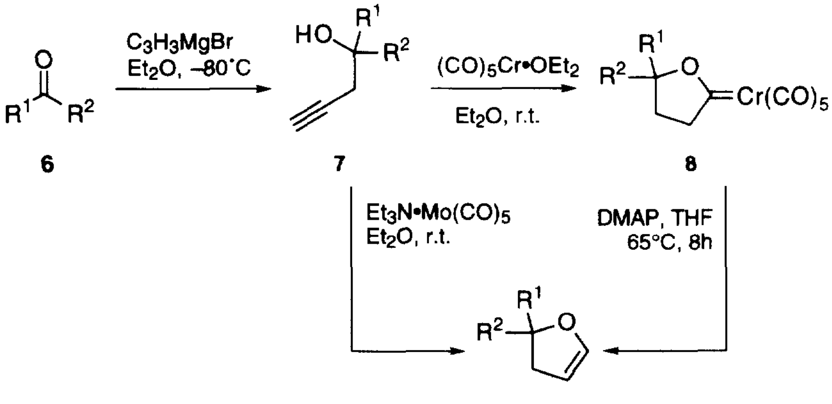
Scheme 2



4 5

Dötz[13] has described an alternative simple and convenient preparation of substituted oxacyclic carbene complexes **8** (Scheme 3) by reaction of alkynols **7** with $(CO)_5Cr{\bullet}OEt_2$ generated by irradiation of $Cr(CO)_6$ in Et_2O. The Dötz procedure proved quite general giving complexes **8a-h** in modest yield including the complex **8a** which had been prepared previously by a related method[14].

Scheme 3

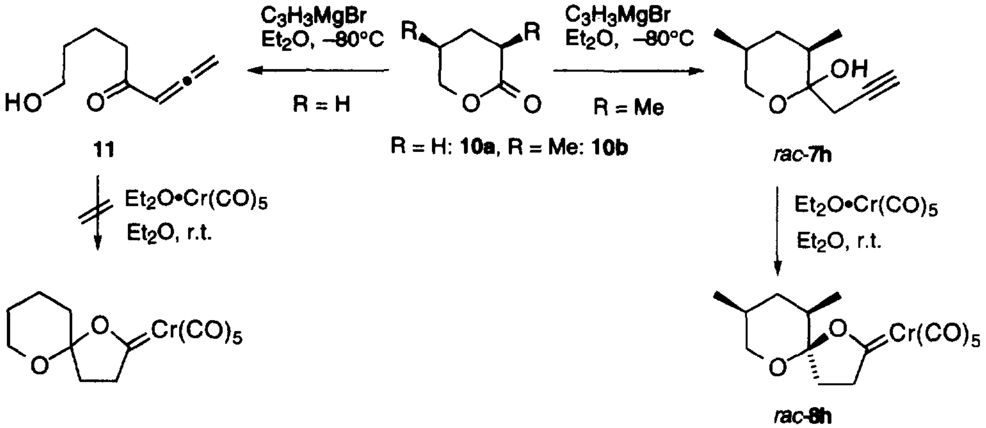


6 7 8

9

The results summarised in Table 1 show that the metal-assisted cyclisation is unaffected by the presence of C=C double bonds in the molecule (entries 4,5, and 6). Furthermore, steric hindrance does not impede cyclisation since the yields for 5,5-disubstituted carbene complexes **8d,e,g** do not differ significantly from the yield for monosubstituted complexes. Reaction of diol **7g** with $(CO)_5Cr{\bullet}OEt_2$ stopped after cyclisation of one alkynol unit, even when the $(CO)_5Cr{\bullet}OEt_2$ was present in more than twofold excess. In this case the yield of 58% is based on the alkynol used. The fact that none of the double cyclised product was isolated shows that the second cyclisation step is so slow that decomposition of the labile solvent complex can compete. Carbene complexes **8d,g** were obtained as a 1:1 mixture of diastereoisomers reflecting the ratio of diastereoisomers of the alkynols **7d,g**. Reaction of propargylmagnesiumbromide with lactone **10b** gave exclusively one diastereoisomer of hemiacetal **7h**. Metal assisted cyclisation gave the spirocyclic carbene complex **8h** as a single diastereoisomer in 48% yield. The reaction of oxan-2-one **10a** with propargylmagnesium bromide produced exclusively the allene **11**, which did not undergo cyclisation with $Et_2O{\bullet}Cr(CO)_5$ (Scheme 4).

Scheme 4



Crystal structure of **8h**. Crystals suitable for X-ray crystal structure analysis were obtained by recrystallization of **8h** from petrolether at -30°C. Figure 1 shows an ORTEP-drawing of the molecule. The oxane ring of **8h** adopts a chair conformation with the methyl groups in equatorial positions and the oxygen atom of the oxolane ring in an axial position in accord with stabilizing anomeric interactions[15]. The atoms Cr, C7, C6, O6 are all coplanar and the $Cr(CO)_5$-moiety assumes a staggered conformation relative to the carbene ligand. The bond distances of the endocyclic C-O-bonds are alternating; thus, the C6-O6 bond is 131.3 pm long (in the normal range for carbene-C-oxygen bonds[16]) whereas the C9-O6 bond (151.6 pm) is significantly longer than a normal C-O bond. The C9-O7 bond of the oxane subunit is shorter (139.0 pm) than average but the C13-O7 bond is 143.9 pm long.

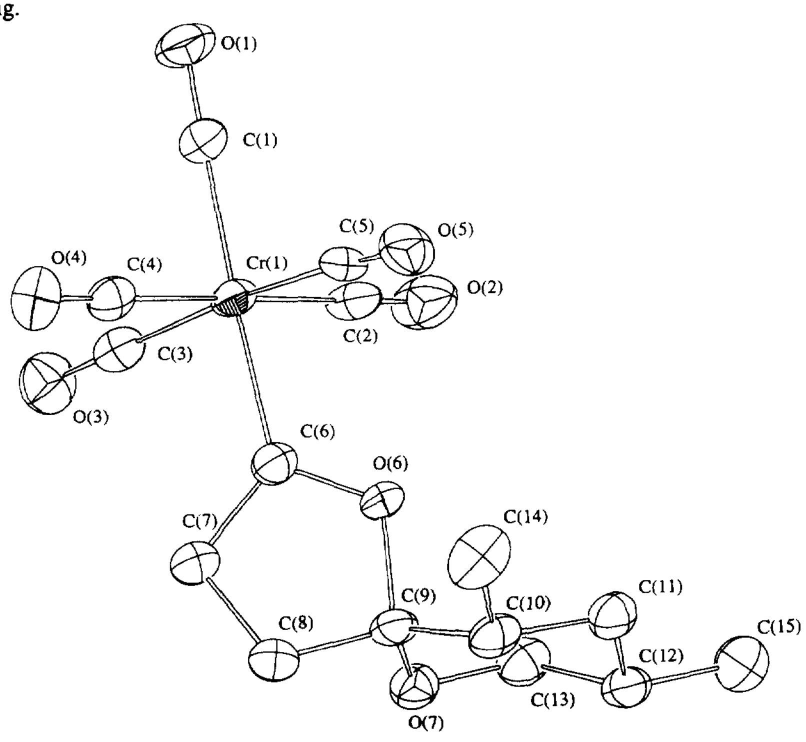
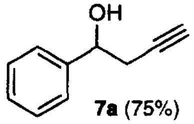
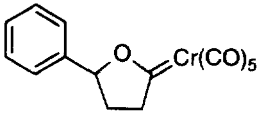
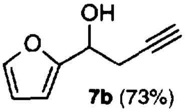
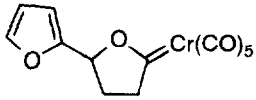
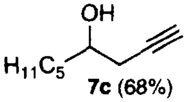
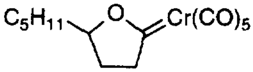
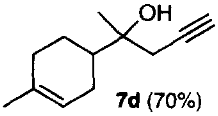
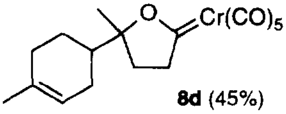
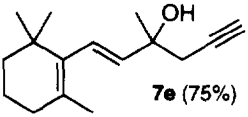
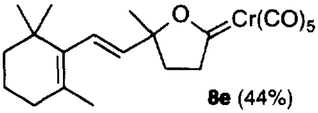
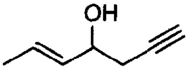
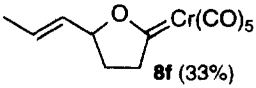
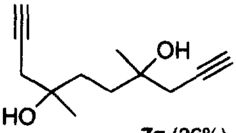
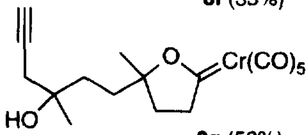
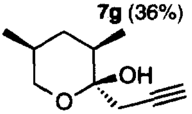
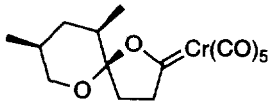


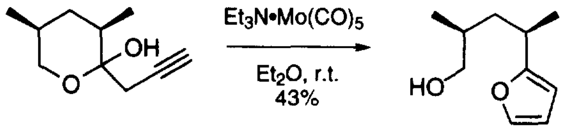
Figure 1: ORTEP-drawing of **8h** (hydrogen atoms ommitted for clarity).

Table 1. Functionalised Alkynols and Carbene Complexes

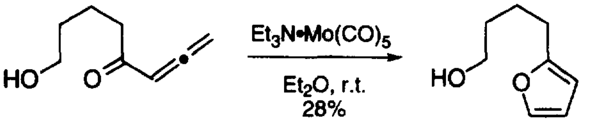
entry	alkynol (yield)	carbene complex(yield)
1	 **7a** (75%)	 **8a** (44%)
2	 **7b** (73%)	 **8b** (46%)
3	 **7c** (68%)	 **8c** (43%)
4	 **7d** (70%)	 **8d** (45%)
5	 **7e** (75%)	 **8e** (44%)
6	 **7f** (73%)	 **8f** (33%)
7	 **7g** (36%)	 **8g** (58%)
8	 *rac*-**7h** (44%)	 *rac*-**8h** (48%)

Preparation of 2,3-oxolenes via 1,2-hydrogen migration of oxacyclopentylidene pentacarbonylchromium complexes and preparation of furans from alkynyl hemiacetals. Oxolenes are usually prepared by dehydration of lactols derived from metal hydride reduction of oxolan-2-ones or reductive elimination of 3-alkoxy-2-chloro-oxolanes. In 1975 Casey and Anderson[11] showed that 2,3-oxolenes could also be prepared by the base-induced 1,2-hydrogen migration of oxacyclic carbene complexes though the method has only had limited application[12]. Recently an elegant single-step procedure for the preparation of 2,3-oxolenes by metal-assisted cyclisation of alkynols with photochemically generated $Et_3N{\bullet}Mo(CO)_5$ was published by McDonald[14,17]. The advantage of this method is, that it avoids the isolation of the intermediate carbene complex. However, the two-step procedure does not necessarily lead to the same result as the single-step procedure as will be shown for the case of hemiacetal **7h**. For the reasons outlined above, we chose the two-step Casey route in order to evaluate the use of oxacyclic carbene complexes as precursors to oxolenes. Thus, heating oxacyclic carbene complexes **8a-e** and **h** with DMAP in THF gave the substituted oxolenes **9a-e** and **h** in fair to good yield (Table 2). The method is applicable to hindered oxolenes (**9d,e**), acid-sensitive oxolene **9b** and spiroacetal **9h**. The use of DMAP in place of the usual pyridine[9,10,11] gave faster reactions and benefited from easier chromatographic workup because of the higher polarity of the $(DMAP)_n{\bullet}Cr(CO)_{6-n}$ byproducts. In the case of hemiacetal **7h** the McDonald single-step procedure[14] did not give the same result as the two-step procedure, but the 2-substituted furan **12** was formed in comparable yield (Scheme 5).

Scheme 5



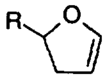
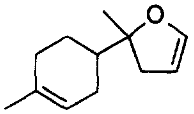
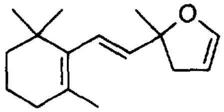
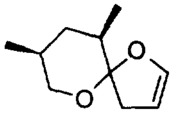
rac-**7h** *rac*-**12**



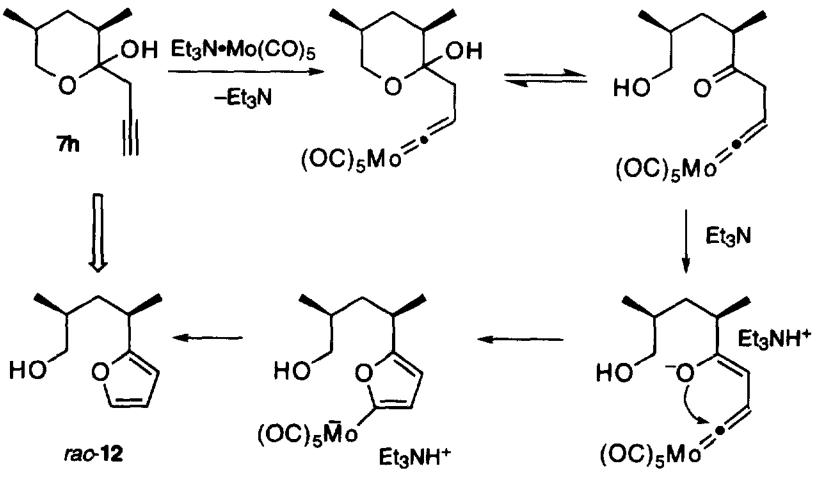
11 **13**

Furan **13** was obtained in 30% yield from allene **11** by the same procedure. A mechanistic proposal for the formation of **12** is presented in Scheme 6. The first step is the formation of an allenylidene complex and deprotonation of the alcohol function by NEt_3. In the next step a ring opening of the oxane ring by the cation may take place,[17] followed by deprotonation of the α-position to the allenylidene moiety and subsequent cyclisation to the metallated furan, which is protonated in the final step to give furan **12**.

Table 2. Functionalised 2,3-oxolenes by DMAP-induced hydrogen migration

entry	carbene complex		2,3-oxolenes (yield)
1	**8a**		**9a** R = Ph (62%)
2	**8b**		**9b** R = 2-furyl (60%)
3	**8c**		**9c** R = *n*-pentyl (56%)
4	**8d**		**9d** (73%)
5	**8e**		**9e** (55%)
6	**8h**		*rac*-**9h** (75%)

Scheme 6



In conclusion we have shown that the metal-assisted cyclisation of alkynols and subsequent base-induced 1,2-hydrogen migration is an easy and convenient method for the formation of 2,3-oxolenes. This protocol allows the formation of a variety of differently functionalised oxolenes. It is also suitable for the synthesis of spiroacetal structures, e.g. **8h** and **9h**. Spiroacetal **8h** was obtained in high diastereoselectivity and its relative configuration was determined by X-ray crystal structure analysis. We have further shown that the two-step and single-step procedures do not necessarily give the same result, as the molybdenum complex assisted cyclisation of **7h** leads to the formation of furan **12** rather than oxolene **9h**. Further aspects of this methodology and applications are currently under investigation.

EXPERIMENTAL

All experiments were conducted in dry reaction vessels in an atmosphere of dry argon or nitrogen. Hexanes were distilled from potassium hydroxide, ether and THF were distilled from sodium/benzophenone.

^{1}H-NMR spectra were recorded in $CDCl_3$ at 270 MHz or at 300 MHz with $CHCl_3$ as internal standard (δ = 7.27). ^{13}C-NMR spectra were recorded at 68 MHz or at 75 MHz with $CDCl_3$ as an internal standard (δ = 77.2). The number of coupled protons was analysed by DEPT experiments and is denoted by a number in parenthesis following the chemical shift value. IR spectra were recorded as films on NaCl plates and the peak intensities are defined as strong (s), medium (m), and weak (w). Mass spectra were obtained at 70 eV. Melting points were not corrected. All photochemical reactions were performed in a pyrex immersion cell employing a medium pressure mercury lamp as a source of UV light.

General procedure for the preparation of alkynols 7. A solution of propargylmagnesium bromide in Et_2O was prepared according to a literature procedure.[18] The titer of the solution was determined by reacting a sample of the solution with an excess of iodine in THF and titrating the unreacted iodine with thiosulfate solution. Usually solutions with a concentration of ≈1 mol•l^{-1} were obtained.
In a typical experiment the solution of the Grignard reagent was cooled to –40°C and a solution of the corresponding aldehyde, ketone or lactone (in the case of **9h** and **13**) was added dropwise. The mixture was slowly warmed to r.t. and stirred for 2 h. It was then poured onto ice water (100 mL), saturated aqueous NH_4Cl solution was added to dissolve the precipitate and the organic layer was separated. The aqueous layer was extracted with ether and dried over $MgSO_4$. After evaporation of the solvent the residue was purified by distillation at reduced pressure unless otherwise noted.

1-Phenylbut-3-yne-1-ol **7a**[19]. Obtained from benzaldehyde as a colourless oil (bp 116°C/12 mm Hg) in 77% yield: **^{1}H NMR:** δ = 7.40–7.10 (5H, m, Ph), 4.75 (1H, m, C<u>H</u>OH), 2.61 (1H, d, J = 3.3 Hz, OH), 2.51 (2H, dd, J = 6.6, 2.6 Hz, CH_2), 1.96 (1H, t, J = 2.6 Hz, $C_{sp}H$); **^{13}C NMR:** δ = 142.7 (0, *ipso*-C), 128.7 (1, Ph), 128.2 (1, Ph), 126.0 (1, Ph), 81.0 (0, C_{sp}), 72.5, 71.2 (1, CHOH and $C_{sp}H$), 29.5 (2, CH_2).

1-(2-Furyl)but-3-yne-1-ol **7b**. Obtained from furaldehyde as a colourless oil (bp 87°C/12 mm Hg) in 75% yield: **^{1}H NMR:** δ = 7.26 (1H, s, =CHO), 6.23 (2H, s, =CH–CH=), 4.74 (1H, q, J = 5.9 Hz, C<u>H</u>OH), 2.70 (1H, m, OH), 2.64 (2H, dd, J = 6.3, 2.6 Hz, CH_2), 1.96 (1H, t, J = 2.6 Hz, $C_{sp}H$); **^{13}C NMR:** δ = 154.8 (0, *ipso*-C), 142.4 (1, =CHO), 110.4 and 106.8 (1, =CH–CH=), 80.2 (0, C_{sp}), 71.3 (1, $C_{sp}H$), 66.2 (1, CHOH), 26.1 (2, CH_2); **IR:** ν = 3406(s), 3122(m), 2918(m), 2121(m), 1671(s), 1568(w), 1504(s), 1424(s), 1146(s), 1016(s), 939(m), 884(m), 856(m), 816(m), 739(m) cm^{-1}; LRMS (EI mode): m/z = 136 ($M^{+\bullet}$, 6%), 97 (100), 39 (16).

Non-1-yne-4-ol **7c**. Obtained from hexanal as a colourless oil (bp 82°C/12 mm Hg) in 68% yield: ^{1}**H NMR**: δ = 3.75 (1H, m, C**H**OH), 2.43 (1H, ddd, J = 16.5, 4.9, 2.6 Hz, C**H**$_2$–C$_{sp}$), 2.31 (1H, ddd, J = 16.5, 6.6, 2.6 Hz, C**H**$_2$–C$_{sp}$), 2.05 (1H, t, J = 2.6 Hz, C$_{sp}$–H), 2.05 (1H, (br.), OH), 1.60–1.20 (8H, m, $(CH_2)_4$), 0.89 (3H, t, J = 6.6 Hz, CH_3); ^{13}**C NMR**: δ = 81.1 (0, C$_{sp}$), 70.9 (1, C$_{sp}$H), 70.0 (1, CHOH), 36.3 (2, CH$_2$C$_{sp}$), 31.9, 27.5, 25.4, 22.7 (2, CH$_2$), 14.2 (3, CH$_3$); **IR**: ν = 3376(s), 3312(s), 2933(s), 2860(m), 2120(w), 1462(m), 1125(m), 1037(m) cm^{-1}; **LRMS** (EI mode): m/z = 101 [(M – C$_3$H$_3$)$^{+\bullet}$, 77%], 83 (100), 55 (65).

2-(1-Methylcyclohex-1-ene-4-yl)pent-4-yne-2-ol **7d**. Obtained from 4-acetyl-1-methylcyclohex-1-ene as a colourless oil (bp 130°C/12 mm Hg) in 70% yield as a 1:1 mixture of diastereoisomers: ^{1}**H NMR**: δ = 5.36 (1H, m, C=CH), 2.42 (2H, m, CH$_2$C$_{sp}$), 2.20–1.60 (11H, m, CH$_2$ + C$_{sp}$H + OH), 1.30 (1H, m, CH), 1.26 and 1.20 (3H, s, CH$_3$); ^{13}**C NMR**: δ = 134.4 and 134.0 (0, =**C**(CH$_3$)), 120.7 and 120.3 (1, =CH), 81.1 and 80.9 (0, CH$_2$**C**$_{sp}$), 73.4 (0, COH), 71.6 (1, C$_{sp}$H), 42.6 and 42.5 (1, CH), 31.3, 31.0, 30.9, 30.5, 27.1, 26.3, 24.2 (2, CH$_2$), 24.0, 23.5 (3, CH$_3$), 23.4 (2, CH$_2$), 22.8 (3, CH$_3$); **IR**: ν = 3450(s), 3301(s), 3010(m), 2915(s), 2726(w), 2117(m), 1678(w), 1440(s), 1377(s), 1349(s), 1298(s), 1252(s), 1219(s), 1159(s), 1097(s), 1070(s), 1040(s), 1020(s), 930(s), 915(s), 878(s), 840(s), 801(s), 781(s), 756(s) cm^{-1}; **LRMS** (EI mode): m/z = 178(M$^{+\bullet}$, 1%), 160(15), 145(15), 139(42), 121(100), 43(77).

6-(2-Methyl-6,6-dimethylcyclohex-1-en-1-yl)-3-methylhex-1-ene-5-yne-3-ol **7e**. Obtained from β–ionone as a colourless oil (bp 84°C/0.01 mm Hg) in 75% yield: ^{1}**H NMR**: δ = 6.14 (1H, dm, J = 16.2 Hz, C=C–C**H**=CH), 5.54 (1H, d, J = 16.2 Hz, C=C–CH=C**H**), 2.50 (2H, d, J = 2.5 Hz, CH$_2$C$_{sp}$), 2.08 (1H, t, J = 2.5 Hz, C$_{sp}$H), 2.04 (1H, br s, OH), 1.96 (2H, t, J = 6.2 Hz, C**H**$_2$–C(CH$_3$)=), 1.68 (3H, s, =C(C**H**$_3$)), 1.66–1.43 (4H, m, CH$_2$CH$_2$), 1.42 (3H, s, C(OH)C**H**$_3$), 1.00 (3H, s, C(CH$_3$)$_2$), 0.99 (3H, s, C(CH$_3$)$_2$); ^{13}**C NMR**: δ = 138.8 (1, C=C–**C**H=CH), 136.9 (0, C=**C**–CH=CH), 128.4 (0, **C**=C–CH=CH), 126.2 (1, C=C–CH=**C**H), 80.8 (0, C$_{sp}$), 72.2 (0, COH), 71.5 (1, C$_{sp}$H), 39.5 (2, CH$_2$), 34.1 (0, **C**(CH$_3$)$_2$), 33.5 and 32.7 (2, CH$_2$), 28.8, 28.7, 27.7, 21.4 (3, CH$_3$), 19.4 (2, CH$_2$); **IR**: ν = 3448(m), 3311(s), 2964–2828(s), 2119(w), 1457(m), 1374(m), 1360(m), 1275(m), 1092(m), 975(m) cm^{-1}; **LRMS** (EI mode): m/z = 232 (M$^{+\bullet}$, 4%), 193(100), 177(49).

Hept-5-ene-1-yne-4-ol **7f**. Obtained from crotylaldehyde as a colourless oil (bp 94°C/12 mm Hg) in 73% yield: ^{1}**H NMR**: δ = 5.74 (1H, dqd, J = 15.4, 6.6, 0.7 Hz, H$_3$C–C**H**=), 5.54 (1H, ddq, J = 15.4, 6.7, 1.5 Hz, H$_3$C–CH=C**H**), 4.22 (1H, m, C**H**OH), 2.45 (1H, ddd, J = 16.6, 5.5, 2.6 Hz, CH$_2$), 2.38 (1H, ddd, J = 16.6, 6.3, 2.6 Hz, CH$_2$), 2.18 (1H, s, OH), 2.04 (1H, t, J = 2.57 Hz, C$_{sp}$H), 1.70 (3H, dm, J = 6.2 Hz, CH$_3$); ^{13}**C NMR**: δ = 132.2 (1, =C), 128.0 (1, =C), 80.9 (1, C$_{sp}$H), 70.8 (1, CHOH), 27.6 (2, CH$_2$), 17.8 (3, CH$_3$); **IR**: ν = 3376(s), 3300(s), 2966(m), 2937(m), 2917(m), 2886(m), 2857(m), 2120(w), 1674(w), 1431(m), 1379(m), 1317(m), 1263(m), 1121(w), 1086(m), 1036(s), 967(s) cm^{-1}; **LRMS** (EI mode): m/z = 71[(M–C$_3$H$_3$)$^{+\bullet}$, 100%], 53(20), 43(20), 41(35), 39(25).

4,7-Dimethyldeca-1,9-diyne-4,7-diol **7g**. Obtained from hexane-2,4-dione as a colourless liquid (1:1 mixture of diastereomers, bp 120°C/0.01 mm Hg) in 36% yield: ^{1}**H NMR**: δ = 2.87 (2H, br s, OH), 2.36 and 2.35 (4H, s, CH$_2$CH$_2$), 2.05 (2H, t, J = 2.6 Hz, C$_{sp}$H), 1.72–1.57 (4H, m, CH$_2$C$_{sp}$), 1.26 and 1.25 (6H, s, CH$_3$); ^{13}**C NMR**: δ = 81.1 (0, C$_{sp}$), 71.7 (0, COH), 71.4 (1, C$_{sp}$H), 34.8, 32.5 and 32.3 (2, CH$_2$), 26.6 and 26.5 (3, CH$_3$); **IR**: ν = 3401(s), 3304(s), 2973(s), 2934(s), 2117(m), 1459(m), 1422(m), 1377(m), 1297(m), 1107(m), 1073(m), 928(m), 904(m), 877(m), 794(w), 765(m) cm^{-1}; **LRMS** (CI mode, NH$_3$): m/z = 212 [(M+NH$_4$)$^+$, 35%], 195 [(M+1)$^+$, 95], 177 (55), 159 (25), 137 (100), 119 (27).

3,5-Dimethyl-1-hydroxy-1-prop-2-ynyloxane **7h**. Single diastereoisomer obtained from lactone *rac*-**12b** as a colourless oil in 44% yield after chromatography on silica, eluant hexanes/ether mixtures of increasing polarity: **^{1}H NMR**: δ = 3.57 (1H, ddd, J = 11.0, 4.8, 2.2 Hz, CH_2O), 3.46 (1H, t, J = 11.0 Hz, CH_2O), 2.68 (1H, dd, J = 16.6, 2.6 Hz, CH_2C_{sp}), 2.51 (1H, d, J = 1.5 Hz, OH), 2.48 (1H, dd, J = 16.6, 2.9 Hz, $CH_2(C_{sp})$, 2.14 (1H, t, J = 2.6 Hz, $C_{sp}H$), 1.75 (2H, m, CH), 1.53 (1H, dm, J = 12.9 Hz, CH_2), 1.24 (1H, q, J = 12.5 Hz, CH_2), 0.93 (3H, d, J = 7.0 Hz, CH_3), 0.79 (3H, d, J = 6.6 Hz, CH_3); **^{13}C NMR**: δ = 96.4 (0, OCOH), 79.4 (0, C_{sp}), 72.1 (1, $C_{sp}H$), 67.5 (2, CH_2O), 37.1(1, $\underline{C}HCH_3$), 36.6 (2, CH_2), 31.1 (1, $\underline{C}HCH_3$), 30.8 (2, CH_2), 17.2, 17.0 (3, CH_3); **IR**: ν = 3424(s, br.), 3311(s), 2958(s), 2930(s), 2875(s), 2122(w), 1461(m), 1421(w), 1388(w), 1230(m), 1174(m), 1092(s), 1032(s), 988(s), 958(w), 901(w), 860(w), 832(w) cm^{-1}; **LRMS** (CI mode): m/z = 169 [$(M+1)^+$, 7%], 151 (100), 129 (12).

8-Hydroxyocta-1,2-diene-4-one **11**. Obtained from oxan-2-one (**10a**) as a colourless oil in 34% yield after chromatography on silica, eluant hexanes/ether mixtures with increasing polarity: **^{1}H NMR**: δ = 5.74 (1H, t, J = 6.4 Hz, $C\underline{H}$=C=CH_2), 5.22 (2H, d, J = 6.4 Hz, CH=C=$C\underline{H}_2$), 3.58 (2H, t, J = 5.9 Hz, $HOC\underline{H}_2$), 2.62 (2H, t, J = 7.0 Hz, $C\underline{H}_2$C=O), 2.33 (1H, br s, OH), 1.72–1.46 (4H, m, CH_2CH_2); **^{13}C NMR**: δ = 216.8 (0, =C=), 201.1 (0, C=O), 96.7 (1, $H\underline{C}$=C=CH_2), 79.6 (2, =CH_2), 62.3 (2, CH_2OH), 38.8, 32.1, 20.6 (2, $(CH_2)_3$); **IR**: ν = 3390(s), 3064(m), 2939(s), 2218(w), 1954(s), 1932(s), 1675(s), 1061(m), 858(m) cm^{-1}; **LRMS** (EI mode): m/z = 141 ($M^{+\bullet}$, 5%), 123 (26), 101 (90), 83 (35), 67 (55), 55 (100), 43 (40), 39 (80), 31 (60).

General procedure for the preparation of oxacyclic carbene complexes 8. In a typical experiment $Cr(CO)_6$ (660 mg, 3 mmol) was placed in the immersion cell. Et_2O (150 mL) was added and the suspension was irradiated for 3 h at –30°C to give an orange-yellow solution of $Et_2O{\bullet}Cr(CO)_5$. A solution of the alkynol **9** (4.5 mmol) in Et_2O (10 mL) was added and the mixture was stirred at r.t. for 4 h.The solvent was evaporated and the residue purified by column chromatography (SiO_2, eluant hexanes (100 mL), then hexanes/CH_2Cl_2 1/1). The orange-yellow band is collected and the pure carbene complex is obtained by evaporation of the solvent. Elution with hexanes is essential to remove unreacted $Cr(CO)_6$. Samples for microanalysis were obtained by recrystallising the carbene complex from hexanes at –30°C.

5-Phenyl-1-oxacyclopent-2-ylidene(pentacarbonylchromium) **8a**. Obtained as yellow crystals (mp 89°C) in 45% yield; **^{1}H NMR:** δ = 7.45-7.20 (5H, m, Ph), 5.95 (1H, dd, J = 8.1, 7.9 Hz, OCHPh), 3.99 (1H, ddd, J = 20.1, 8.9, 3.9 Hz, CH_2C=Cr), 3.48 (1H, dt, J = 20.1, 9.1 Hz, CH_2C=Cr), 2.36 (1H, dddd, J = 12.9, 9.3, 7.5, 3.9 Hz, CH_2), 1.80 (1H, dq, J = 12.9, 8.8 Hz, CH_2); **^{13}C NMR**: δ = 341.2 (0, C=Cr), 223.6 (0, *trans*-CO), 216.5 (0, *cis*-CO), 138.0 (0, *ipso*-C), 129.3, 129.2, 125.9 (1, Ph), 99.7 (1, CHO(Ph)), 61.4 (2, Cr=C–$\underline{C}H_2$), 29.9 (2, CH_2); **IR**: ν = 2964(w), 2063(s), 1915(s), 1496(m), 1451(m), 1399(m), 1360(m), 1332(m), 1213(m), 1182(m), 1050(m), 974(m), 758(m), 700(m) cm^{-1}; **LRMS** (EI mode): m/z = 338($M^{+\bullet}$, 64%), 310(14), 282(40), 254(51), 226(64), 198(100), 170(85), 156(25), 142(47), 104(22), 80(25), 52(69).

5-Furyl-1-oxacyclopent-2-yliden(pentacarbonylchromium) **8b**. Obtained as a red oil in 43% yield: **^{1}H NMR**: δ = 7.49 (1H, d, J = 1.8 Hz, =CHO), 6.55 (1H, d, J = 3.5 Hz, C=CH-C), 6.44 (1H, dd, 3.5, 1.8 Hz, C=C–CH=C), 6.05 (1H, t, J = 7.7 Hz, OCH(Fu)), 4.06 (1H, ddd, J = 20.1, 8.7, 5.8 Hz, CH_2CCr), 3.69 (1H, ddd, J = 20.3, 8.9, 7.5 Hz, CH_2CCr), 2.30–2,12 (2H, m, CH_2CO); **^{13}C NMR**: δ = 340.0 (0, C=Cr), 223.6 (0, *trans*-CO), 216.4 (0, *cis*-CO), 149.5 (0, =C(O)), 144.3 (1, OCH=), 111.0 and 110.9 (1, =C–C=), 92.8 (1, CHO), 61.7 (2, Cr=C–CH_2), 25.5 (2, CH_2); **IR**: ν = 3131(w), 2965(w), 2894(w), 2062(s), 1933(s), 1503(m), 1457(m), 1404(m), 1327(s), 1184(s), 1044(m), 1016(m), 974(m), 871(m), 750(m) cm^{-1}; **LRMS**

(EI mode): m/z = 328($M^{+\bullet}$, 54%), 272(17), 244(34), 216(46), 188(85), 160(42), 132(100), 108(15), 80(25), 52(53).

5-Pentyl-1-oxacyclopent-2-ylidene(pentacarbonylchromium) **8c**. Obtained as an orange-yellow oil in 43% yield: **^{1}H NMR**: δ = 5.10 (1H, d, J = 6.4 Hz, CHO), 3.86 (1H, ddd, J = 20.2, 8.8, 4.4 Hz, CH_2C=Cr), 3.46 (1H, dt, J = 20.2, 8.8 Hz, CH_2C=Cr), 2.06 (1H, m, CH_2), 1.92 (1H, m, CH_2), 1.75 (1H, m, CH_2), 1.60–1.30 (5H, m, CH_2), 0.93 (3H, br, CH_3); **^{13}C NMR**: δ = 340.1 (0, Cr=C), 223.8 (0, *trans*-CO), 216.7 (0, *cis*-CO), 100.0 (1, CHO), 60.9 (2, =C–$\underline{C}H_2$), 35.1, 31.6, 26.6, 25.1, 22.6 (2, CH_2), 14.1 (3, CH_3); **IR**: ν = 2960(m), 2935(m), 2863(m), 2064(s), 1920(s), 1460(m), 1405(w), 1359(m), 1279(w), 1213(s), 1032(m), 1009(m), 969(m), 910(w) cm^{-1}; **LRMS** (EI mode): m/z = 332 ($M^{+\bullet}$, 20%), 220 (32), 192 (100), 52(26).

5-(4-Methylcyclohex-3-enyl)-5-methyl-1-oxacyclopent-2-ylidene(penta-carbonylchromium) **8d**. Obtained as yellow crystals (mp 66°C, mixture of diastereoisomers) in 45% yield: **^{1}H NMR**: δ = 5.40 (1H, m, =CH), 3.90–3.55 (2H, m, CH_2C=Cr), 2.10–1.78 (7H, m, CH_2, CH), 1.67 (3H, m, CH_3), 1.68–1.54 (1H, m, CH_2, CH), 1.47 (3H, s, CH_3), 1.44–1.22 (1H, m, CH_2, CH); **^{13}C NMR**: δ = 336.9 (0, C=Cr), 223.7 (0, *trans*-CO), 216.8 (0, *cis*-CO), 134.4 and 134.3 (0, =C(CH_3)), 119.6 and 119.5 (1, CH=), 111.4 and 111.0 (0, C–O), 61.2 (2, $\underline{C}H_2$CCr), 43.1 (1, –CH–), 30.5, 30.4, 30.0, 29.8, 26.9, 26.7, 24.2 (2, CH_2), 23.5, 23.4, 23.1 (3, CH_3); **IR**: ν = 2968(m), 2927(m), 2063(s), 1916(s), 1382(w), 1311(m), 1290(m), 1014(s), 971(m), 909(m), 736(m) cm^{-1}; **LRMS** (EI mode): m/z = 370 ($M^{+\bullet}$, 29%), 314 (14), 286 (16), 258 (51), 230 (100), 200 (20), 174 (30), 52 (29). Calc. for $C_{17}H_{18}O_6Cr$: C 55.14, H 4.90%; found C 54.89, H 4.94.

5-Methyl-5-[(E)-2-(2,6,6-trimethylcyclohex-1-enyl)-1-ethenyl]-1-oxacyclopent-2-ylidenepentacarbonylchromium **8e**. Obtained as an orange-yellow oil in 44% yield: **^{1}H NMR**: δ = 6.12 (1H, d, J = 16.1 Hz, C=C–C$\underline{H}$=CH), 5.56 (1H, d, J = 16.1 Hz, C=C–CH=C$\underline{H}$), 3.90 (1H, ddd, J = 20.2, 8.5, 4.4 Hz, CH_2CCr), 3.56 (1H, dt, J = 20.2, 8.5 Hz, CH_2CCr), 2.00 (3H, m, CH_2), 1.80 (1H, m, CH_2), 1.74 (3H, s, CH_3), 1.64 (3H, s, CH_3), 1.60 (1H, m, CH_2), 1.46 (2H, m, CH_2), 0.99 (6H, s, C(CH_3)$_2$), 0.90 (1H, m, CH_2); **^{13}C NMR**: δ = 338.4 (0, C=Cr), 223.8 (0, *trans*-CO), 216.7 (0, *cis*-CO), 136.3 (0, C=$\underline{C}$–CH=CH), 133.5 (1, C=C–$\underline{C}$H=CH), 129.9 (0, $\underline{C}$=C–CH=CH), 128.5 (1, C=C–CH=$\underline{C}$H), 106.2 (0, $\underline{C}$(CH_3)O), 61.0 (2, $\underline{C}H_2$C=Cr), 39.3 (2, CH_2), 34.1 (0, $\underline{C}$(CH_3)$_2$), 33.4 and 32.8 (2, CH_2), 28.8 and 28.8 (3, C($\underline{C}H_3$)$_2$), 26.2 and 21.4 (3, CH_3), 19.3 (2, CH_2); **IR**: ν = 2932(m), 2867(m), 2829(m), 2064(s), 1927(s), 1649(w), 1453(w), 1378(w), 1360(m), 1360(m), 1306(m), 1168(m), 1014(m), 970(m), 909(m), 736(m) cm^{-1}; **LRMS** (EI mode): m/z = 424 ($M^{+\bullet}$, 57%), 312 (32), 284 (100), 228 (64), 204 (82), 52 (57).

5-(Propen-1-yl)-1-oxacyclopent-2-ylidene(pentacarbonyl-chromium) **8f**. Obtained as an orange-yellow oil in 33% yield: **^{1}H NMR**: δ = 5.99 (1H, dq, J = 14.9, 6.6 Hz, C$\underline{H}$CH_3), 5.56 (1H, ddm, J = 14.9, 7.8 Hz, C$\underline{H}$=CH–CH_3), 5.44 (1H, q, J = 7.8 Hz, CHO), 3.90 (1H, ddd, J = 20.1, 8.9, 4.3 Hz, CH_2CCr), 3.45 (1H, dt, J = 20.1, 8.9 Hz, CH_2CCr), 2.11 (1H, m, CH_2), 1.84 (3H, dd, J = 6.5, 1.1 Hz, CH_3), 1.63 (1H, m, CH_2); **^{13}C NMR**: δ = 339.9 (0, Cr=C), 223.7 (0, *cis*-CO), 216.6 (0, *trans*-CO), 133.3 (1, CH=CH), 127.5 (1, CH=CH), 100.2 (1, CHO), 61.4 (2, Cr=C–$\underline{C}H_2$), 27.4 (2, CH_2), 17.9 (3, CH_3); **IR**: ν = 3001–2858(m), 2064(s), 1920(s), 1672(w), 1456(w), 1404(m), 1333(m), 1186(m), 1031(m), 1003(m), 967(m), 917(w), 873(w), 807(w), 741(m) cm^{-1}; **LRMS** (EI mode): m/z = 302 ($M^{+\bullet}$, 51%), 274 (7), 246 (17), 218 (25), 190 (48), 162 (100), 134 (80), 52 (80).

5-(3-Hydroxy-3-methylhex-4-yn-1-yl)-1-oxacyclopent-2-yliden-(pentacarbonylchromium) **8g**. Obtained as an orange-yellow oil (1:1 mixture of diastereoisomers) in 58% yield: **^{1}H NMR**: δ = 3.75 (2H, m, C$\underline{H}_2$CCr), 2.40 (2H, t, J = 2.5 Hz, CH_2C_{sp}), 2.11 (1H, m, C_{sp}H), 2.00–1.58 (7H, m, 3 CH_2 + OH), 1.54 (3H, s, CH_3), 1.30 (3H, s, CH_3); **^{13}C NMR**: δ = 337.9 (0, Cr=C), 223.7 (0, *trans*-CO), 216.7 (0, *cis*-CO), 107.9

(0, –OC($CH)_3$), 80.3 (0, C_{sp}), 72.0 (0, C(CH_3)OH), 71.2 (1, $C_{sp}H$), 61.3 (2, CH_2C=Cr), 35.1, 34.6, 32.7, 31.9 (2, CH_2), 26.5, 25.8, 25.7 (3, CH_3); **IR**: ν = 3419(m), 3309(m), 2119(w), 2063(s), 1916(s), 1455(m), 1404(m), 1383(m), 1315(m), 1278(m), 1183(m), 1019(s), 971(s) cm^{-1}; **LRMS** (EI mode): *m/z* = 386 ($M^{+\bullet}$, 19%), 346 (38), 234 (54), 206 (53), 178 (82), 150 (100), 52 (65).

(5S,8R*,10S*)-8,10-Dimethyl-1,6-dioxaspiro[4,5]decanylidene-2-(pentacarbonylchromium)* **8h.** Obtained from **7h** as orange-yellow crystals in 48% yield: **^{1}H NMR**: δ = 3.80–3.70 (3H, m, CH_2O and CH_2C=Cr), 3.62 (1H, t, *J* = 11.3 Hz, CH_2C=Cr), 2.10–1.70 (5H, m, CH, CH_2), 1.56 (1H, q, *J* = 12.9 Hz, CH_2), 0.94 (3H, d, *J* = 6.6 Hz, CH_3), 0.90 (3H, d, *J* = 6.7 Hz, CH_3); **^{13}C NMR**: δ = 342.1 (0, C=Cr), 223.8 (0, *trans*-CO), 216.7 (0, *cis*-CO), 127.5 (0, O–C–O), 70.4 (2, CH_2O), 60.2 (2, CH_2C=Cr), 36.9 (2, CH_2), 36.8 (1, CH), 30.5 (1, CH), 30.5 (2, CH_2), 17.1, 16.1 (3, CH_3); **IR**: ν = 2969(m), 2933(m), 2881(m), 2063(s), 1921(s), 1462(m), 1401(w), 1383(w), 1361(w), 1338(w), 1299(m), 1246(m), 1212(m), 1191(m), 1166(m), 1123(m), 1102(m), 1080(m), 1043(m), 1026(m), 1006(m), 965(m), 902(m), 807(m), 755(m), 714(m) cm^{-1}; **LRMS** (EI mode): *m/z* = 360 ($M^{+\bullet}$, 20%), 248 (20), 220 (100), 192 (35), 52 (17); Anal.: Calc. for $C_{15}H_{16}O_7Cr$: C, 50.01%, H, 4.47. Found C, 49.82, H, 4.36.

General procedure for the formation of 2,3-Oxolenes 9. In a typical experiment, DMAP (550 mg, 4.5 mmol) was added to a solution of the carbene complex **8** in THF (15 mL). The mixture was heated to reflux for 8 h, the solvent was removed *in vacuo* and the residue extracted with hexanes. After filtration the hexanes was removed *in vacuo* and the residue purified by chromatography on silica with hexanes/ether mixtures of increasing polarity.

5-Phenyl-2,3-oxolene **9a**. Obtained from **8a** as a colourless oil in 62% yield: **^{1}H NMR**: δ = 7.40–7.20 (5H, m, Ph), 6.43 (1H, q, *J* = 2.6 Hz, =CHO), 5.49 (1H, dd, *J* = 10.7, 8.1 Hz, CHPh), 4.92 (1H, q, *J* = 2.6 Hz, OCH=CH), 3.05 (1H, ddt, *J* = 15.4, 10.7, 2.6 Hz, CH_2, H-*trans*), 2.58 (1H, ddt, *J* = 15.4, 8.4, 2.6 Hz, CH_2, H-*cis*); **^{13}C NMR**: δ = 145.5 (1, =CHO), 143.3 (0, *ipso*-C, Ph), 128.7, 127.8, 125.8 (1, Ph), 99.2 (1, OCH=CH), 82.5 (1, CHPh), 38.1 (2, CH_2); **IR**: ν = 3088(m), 3031(m), 2928(m), 2859(m), 1620(s), 1494(m), 1451(m), 1362(w), 1337(w), 1263(w), 1136(s), 1051(s), 1030(m), 939(m), 756(m), 698(s) cm^{-1}; **LRMS** (EI mode): *m/z* = 146 ($M^{+\bullet}$, 40%), 117 (100), 115 (55), 91 (45), 77 (15).

5-(2-Furyl)-2,3-oxolene **9b**. Obtained from **8b** as a colourless oil in 60% yield: **^{1}H NMR**: δ = 7.44 (1H, t, *J* = 1.5 Hz, =CH–CH=CHO), 6.36 (2H, m, =CH–CH=), 6.35 (1H, m, =CHO), 5.51 (1H, dd, *J* = 9.9, 9.2 Hz, CHO(Fu)), 5.10 (1H, q, *J* = 2.6 Hz, OCH=), 2.95 (1H, ddt, *J* = 15.1, 9.9, 2.6 Hz, CH_2), 2.88 (1H, ddt, *J* = 15.1, 9.2, 2.6 Hz, CH_2); **^{13}C NMR**: δ = 154.1 (0, *ipso*-C), 145.0 (1, =CHO), 143.0 (1, =CHO), 110.4 (1, =CH–CH=), 107.6 (1, =CH–CH=), 99.4 (1, =CH–CH_2), 75.6 (1, OCH(Fu)), 33.8 (2, CH_2); **IR**: ν = 3156(w), 2960(w), 1621(w), 909(s), 734(s) cm^{-1}; **LRMS** (EI mode): *m/z* = 137 ($M^{+\bullet}$, 100%), 109 (25), 94 (30), 81 (45).

5-Pentyl-2,3-oxolene **9c**. Obtained from **8c** as a colourless oil in 56% yield: **^{1}H NMR**: δ = 6.28 (1H, br q,, *J* = 2.2 Hz, OCH=), 4.85 (1H, q(br.), *J* = 2.2 Hz, OCH=CH), 4.52 (1H, p, *J* = 7.7 Hz, –OCH–), 2.68 (1H, ddt, *J* = 15.1, 10.2, 2.2 Hz, =CH–CH_2), 2.25 (1H, ddt, *J* = 15.1, 7.7, 2.2 Hz, =CH–CH_2), 1.80–1.20 (8H, m, $(CH_2)_4$), 0.90 (3H, t, *J* = 6.6 Hz, CH_3); **^{13}C NMR**: δ = 145.1 (1, OCH=), 99.1 (1, OCH=CH), 81.8 (1, $OCHC_5H_{11}$), 36.3, 34.9, 31.9, 25.3, 22.8 (2, CH_2), 14.2 (3, CH_3); **IR**: ν = 2931(s), 2859(s), 1619(s), 1467(m), 1379(w), 1268(w), 1140(s), 1055(s), 759(m), 703(m) cm^{-1}; **LRMS** (EI mode): *m/z* = 141 ($M^{+\bullet}$,100%), 123 (25), 81 (15), 67 (8), 55 (12).

5-(4-Methylcyclohex-3-en-1-yl)-5-methyl-2,3-oxolene **9d**. Obtained from **8d** as a colourless oil (1:1 mixture of diastereoisomers) in 73% yield: **^{1}H NMR**: δ = 6.22 (1H, q, J = 2.2 Hz, OCH=), 5.40 (1H, m, CH=C(CH_3)), 4.76 (1H, q, J = 2.5 Hz, OCH=C$\underline{H}$), 2.57 (1H, dt, J = 15.1, 2.5 Hz, OCH=CH–CH_2), 2.19 (1H, dt, J = 15.1, 2.5 Hz, OCH=CH–C$\underline{H}_2$, 1 diastereoisomer), 2.17 (1H, dt, J = 15.1, 2.5 Hz, OCH=CH–C$\underline{H}_2$, 1 diastereoisomer), 2.10–1.68 (6H, m, CH_2, CH), 1.66 (3H, s, CH_3), 1.30 (1H, m, CH_2), 1.26 (3H, s, CH_3), 1.26 (3H, s, CH_3); **^{13}C NMR**: δ = 144.3 (1, O$\underline{C}$H=), 134.3, 134.0 (0, =$\underline{C}$(CH_3)), 120.6, 120.5 (1, $\underline{C}$H=C(CH_3)), 98.4 (1, OCH=$\underline{C}$H), 89.1, 89.0 (0, –CO(CH_3)), 43.3, 43.2 (1, CH), 38.8, 37.9, 30.8, 30.7, 26.8, 26.5 (2, CH_2), 24.7, 24.0 (3, CH_3), 23.9 (2, CH_2), 23.6 (3, CH_3), 23.6 (2, CH_2), 23.6 (3, CH_3); **IR**: ν = 3102(w), 3011(m), 2965(s), 2922(s), 1622(s), 1417(s), 1373(s), 1287(s), 1260(m), 1175(s), 1060(s), 1018(m), 977(m), 918(m), 901(m), 799(m), 758(m), 704(m) cm^{-1}; **LRMS** (EI mode): *m/z* = 178 ($M^{+\bullet}$, 25%), 145 (45), 134 (58), 121 (85), 93 (75), 83 (100), 55 (30).

5-Methyl-5-[(E)-2-(2, 6, 6-trimethylcyclohex-1-en-1-yl)-1-ethenyl]-2,3-oxolene **9e**. Obtained from **8e** as a colourless oil in 55% yield: **^{1}H NMR**: δ = 6.28 (1H, m, OCH=), 6.05 (1H, d, J = 16.2 Hz, C=C–C$\underline{H}$=CH), 5.55 (1H, d, J = 16.2 Hz, C=C–CH=C$\underline{H}$), 4.80 (1H, m, OCH=C$\underline{H}$), 2.64 (1H, dm, J = 15.1 Hz, OCH=CH–C$\underline{H}_2$), 2.48 (1H, dm, J = 15.1 Hz, OCH=CH–C$\underline{H}_2$), 1.97 (2H, t, J = 6.0 Hz, =C(CH_3)–C$\underline{H}_2$–), 1.67 (3H, s, =C(C$\underline{H}_3$)), 1.60 (2H, m, CH_2–CH_2), 1.47 (3H, s, OC(C$\underline{H}$)$_3$), 1.44 (2H, m, CH_2CH_2), 0.99 (6H, s, C(CH_3)$_2$); **^{13}C NMR**: δ = 144.4 (1, OCH=), 137.9 (1, C=C–$\underline{C}$H=CH), 137.1 (0, C=$\underline{C}$–CH=CH), 128.4 (0, $\underline{C}$=C–CH=CH), 125.1 (1, C=C–CH=$\underline{C}$H), 98.3 (1, OCH=$\underline{C}$H), 86.1 (0, –O$\underline{C}$(CH_3)), 42.1, 39.6 (2, CH_2), 34.2 (0, $\underline{C}$(CH_3)$_2$), 32.8 (2, CH_2), 28.9, 28.9, 26.7, 21.4 (3, CH_3), 19.5 (2, CH_2); **IR**: ν = 2964(m), 2927(m), 2864(m), 1620(m), 1450(m), 1372(m), 1280(m), 1163(m), 1057(s), 974(m), 772(w), 701(m) cm^{-1}; **LRMS** (EI mode): *m/z* = 232 ($M^{+\bullet}$, 100%), 217 (20), 173 (30), 119 (45), 105 (30), 91 (25).

(5S,8R*,10S*)-8,10-Dimethyl-1,6-dioxaspiro[4,5]dec-2-ene* **9h**. Obtained from **8h** as a colourless oil in 60% yield: **^{1}H NMR:** δ = 6.31 (1H, q, J = 2.4 Hz, =CHO), 4.93 (1H, q, J = 2.4 Hz, OCH=C$\underline{H}$), 3.58 (1H, ddd, J = 11.0, 4.8, 2.2 Hz, CH_2O), 3.49 (1H, t, J = 11.0 Hz, CH_2O), 2.70 (1H, dt, J = 16.6, 2.4 Hz, C$\underline{H}_2$CH=), 2.42 (1H, dt, J = 16.6, 2.4 Hz, C$\underline{H}_2$CH=), 1.93–1.74 (2H, m, CH_2, CH), 1.63 (1H, m, CH_2, CH), 1.23 (1H, q, J = 12.5 Hz, CH–C$\underline{H}_2$–CH), 0.86 (3H, d, J = 7.0 Hz, CH_3), 0.82 (3H, d, J = 6.6 Hz, CH_3); **^{13}C NMR**: δ = 144.2 (1, =CHO), 110.3 (0, O–C–O), 99.4 (1, OCH=$\underline{C}$H), 68.4 (2, CH_2O), 39.6, (2, CH_2), 37.7 (1, CH), 37.0 (2, CH_2), 30.9 (1, CH), 17.2 (3, CH_3), 16.5 (3, CH_3); **IR**: ν = 3096(w), 2957(s), 2930(s), 2875(m), 1623(s), 1461(m), 1378(w), 1301(m), 1216(m), 1188(m), 1129(m), 1098(s), 1055(s), 1039(s), 824(m), 747(m), 704(m) cm^{-1}; **LRMS** (EI mode): *m/z* = 168 ($M^{+\bullet}$, 100%), 139 (19), 84 (29), 41 (20).

2-(1,3-Dimethyl-4-hydroxy-1-butyl)furan 12. A suspension of hexacarbonylmolybdenum (625 mg, 2.4 mmol) in ether (120 mL) and NEt_3 (20 mL) was irradiated in a pyrex-immersion cell at –30°C for 3 h. Hemiacetal **7h** (800 mg, 4.8 mmol) was added as a solution in ether (20 mL). Stirring at r.t. was continued for 12 h, then the solvent was evaporated, and the residue purified by chromatography on silica gel (hexanes, hexanes/Et_2O mixtures of increasing polarity) to give. **12** (340 mg, 43%) as colourless oil: **^{1}H NMR**: δ = 7.28 (1H, d, J = 1.8 Hz, OC$\underline{H}$=CH), 6.27 (1H, dd, J = 3.3, 1.8 Hz, OCH=C$\underline{H}$), 5.99 (1H, dd, J = 3.3 Hz, OCH=CH–C$\underline{H}$=), 3.44 (1H, dd, J = 10.3, 5.8 Hz, C$\underline{H}_2$OH), 3.37 (1H, dd, J = 10.3, 6.6 Hz, C$\underline{H}_2$OH), 2.94 (1H, m, C$\underline{H}$(CH_3)(Fu)), 1.79 (1H, ddd, J = 13.2, 9.6, 4.8 Hz, CH_2), 1.68 (1H, br s, OH), 1.55 (1H, m, CH, CH_2), 1.27 (1H, m, CH, CH_2), 1.25 (3H, d, J = 7.0 Hz, CH_3), 0.93 (3H, d, J = 7.0 Hz, CH_3); **^{13}C NMR**: δ = 160.3 (0, OC=), 140.8 (1, O$\underline{C}$H=CH), 110.0, 103.8 (1, =CH–CH=), 68.5 (2, CH_2OH), 39.8 (2, CH–$\underline{C}$H$_2$–CH), 33.7, 31.0 (1, CH), 20.7, 16.8 (3, CH_3); **IR**: ν = 3357(s), 3116(s), 2963(s), 2930(s), 2874(s), 1591(w), 1507(m), 1460(m), 1378(m), 1150(m), 1049(s), 1029(s), 1010(s), 987(w), 921(w), 884(w), 798(w), 730(s), 596(m) cm^{-1}; **LRMS** (EI mode): *m/z* = 168 ($M^{+\bullet}$, 32%), 135 (19), 108 (45), 95 (100), 41 (15).

1-(4-Hydroxy-but-1-yl)furan **13.** Obtained from **11** (700 mg, 5.0 mmol) and $Mo(CO)_6$ (660 mg, 2.5 mmol) following the procedure for **12**, as a colourless oil in 28% yield: **^{1}H NMR**: δ = 7.30 (1H, d, J = 2.9 Hz, OC<u>H</u>=CH), 6.28 (1H, dd, J = 2.9, 1.5 Hz, OCH=C<u>H</u>), 6.00 (1H, d, J = 2.9 Hz, OCH=CH–C<u>H</u>=), 3.65 (2H, t, J = 6.6 Hz, C<u>H</u>$_2$OH), 2.67 (2H, t, J = 7.3 Hz, CH_2–Fu), 1.79–1.56 (4H, m, CH_2CH_2), 1.90 (1H, br s, OH); **^{13}C NMR**: δ = 156.2 (0, *ipso*-C), 140.9 (1, O<u>C</u>H=CH), 110.2, 105.0 (1, =CH–CH=), 62.7 (2, CH_2OH), 32.3, 27.8, 24.4 (2, $(CH_2)_3$); **IR**: ν = 3357(s), 3119(m), 2939(s), 1596(m), 1508(m), 1458(m), 1148(m), 1058(m), 1007(m), 921(w), 885(w), 799(w) cm^{-1}; **LRMS** (EI mode): m/z = 140 ($M^{+\bullet}$, 41%), 107 (19), 94 (95), 81 (100), 53 (30).

X-Ray Structure Determination of **8h**.

Crystallographic details for **8h**: $C_{15}H_{16}O_7Cr$, F.W. = 360.28, triclinic space group $P\bar{1}$ (No. 2) with lattice parameters a = 9.929(9), b = 10.837(10), c = 8.763(9) Å, α = 108.21(7), β = 97.78(8), γ = 67.69(6) °, V = 828(1) Å^3, Z = 2, D_{calc} = 1.444 g•cm^{-3}, μ(Mo-K$_\alpha$) = 7.22 cm^{-1}. Air stable orange crystals were obtained by recrystallisation from hexanes and a crystal of approximate dimensions 0.55 x 0.30 x 0.20 mm was used for data collection at 150 K using Mo-K$_\alpha$ radiation (λ = 0.71069 Å) on a Rigaku AFC75 four-circle diffractometer. 3112 reflections were recorded (2929 unique, R_{int} = 0.046, 5° < 2Θ < 50°) and corrected for absorption (Ψ-scans) and the usual Lorentz polarisation factors. The structure was solved by heavy atom methods and refined by full-matrix least-squares refinement (on F). Hydrogen atoms were located in the electron density map and their positions refined. Using 2400 reflections ($I > 3.00\ \sigma(I)$) refinement converged at R = 0.043 (R_w = 0.047).[20]

Selected bond lengths for spiroacetal **8h** in pm: Cr-C(1) 189.5(3), Cr-C(2) 190.3(4), Cr-C(3) 189.3(4), Cr-C(4) 188.2(4), Cr-C(5) 189.8(4), Cr-C(6) 200.7(3), O(6)-C(6) 131.3(4), O(6)-C(9) 151.4(4), O(7)-C(9) 139.0(4), O(7)-C(13) 143.9(4), C(6)-C(7) 150.2(5), C(7)-C(8) 152.6(5), C(8)-C(9) 150.6(5), C(9)-C(10) 153.0(4), C(10)-C(11) 152.4(5), C(10)-C(14) 151.9(5), C(11)-C(12) 151.6(5), C(12)-C(13) 151.0(5), C(12)-C(15) 152.0(5).

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