# Organic Syntheses via Transition Metal Complexes, CII[±]

# 1,3-Dioxycyclopentadienes from (1-Alkynyl)carbene Tungsten Complexes – Domino Cyclization/Cycloaddition Reactions

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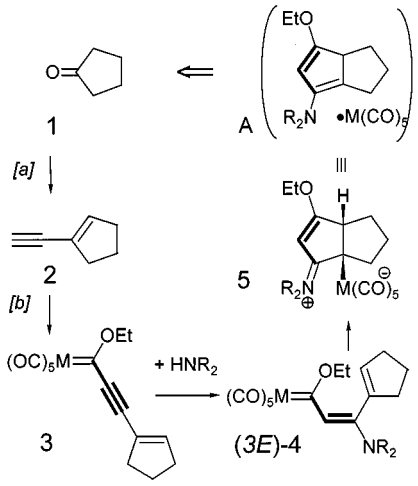
**Keywords:** (1-Alkynyl)carbene complexes / 1-Metallahexatrienes / 1,3-Dioxycyclopentadienes / (Cyclobutenyl)carbene complexes / Tungsten complexes / Domino cyclization / 1,3-Dioxytetrahydropentalenes / Spirocyclopentanes / Spirocyclobutanes

1,3-Dioxytetrahydropentalenes **9** have been generated by base-catalyzed addition of protic oxygen nucleophiles ROH **6a–g** (RO = carboxy or phenyloxy) to the [2-(1-cyclopentenyl)ethynyl]carbene tungsten complex **3**. Compounds **9** are highly reactive and afford (cyclobutenyl)carbene complexes **12a–g** through spontaneous [2+2] cycloaddition to a second molecule of the (1-alkynyl)carbene complex **3**. Thermolysis of compounds **12** was found to generate indeno[*b*]-spirotricyclo[5.3.0.0]decadienes **18** through π-cyclization of the 1-tungsta-1,3,5-hexatriene unit involving insertion of carbon monoxide into the W=C bond.

## Introduction

(1-Alkynyl)carbene complexes $(CO)_5M{=}C(OEt)$-$C{\equiv}CR$ (M = W, Cr) have been employed as stoichiometric reagents in a number of high-yielding transformations of potential use in organic synthesis.[2] In a prominent example, cyclopentadienes were generated in a [3+2] fashion by condensation of (1-alkynyl)carbene complexes with cycloalkenyl amines $(\sim)CH{=}C(\sim)NMe_2$.[3] This reaction was shown to involve the formation of amino-1-metalla-1,3,5-hexatrienes, e.g. $(CO)_5M{=}C(OEt)CH{=}C(Ph)C(\sim){=}C(\sim)(NMe_2)$, which undergo spontaneous π-cyclization to cyclopentadiene complexes.[4] A driving force for this π-cyclization of 1-metalla-1,3,5-hexatrienes is provided by amino substituents, most notably in the 6-position,[1,3,5,6] but 2-amino[7] and 4-amino substituents[7,8] were also found to favour this reaction.

The π-cyclization of 4-amino-1-metalla-1,3,5-hexatrienes has been employed as a key reaction in a metal-mediated cyclopentadiene annelation procedure starting from enolizable cycloalkanones, which is exemplified in the case of cyclopentanone **1** in Scheme 1.[8] The procedure involves initial formation of a 1-tungsta-1,5-hexadien-3-yne **3** from cyclopentanone through 1-ethynylcyclopentene (**2**) and its subsequent π-cyclization. In this particular case, cyclization was triggered by addition of a secondary amine to give first the 4-amino-1-tungsta-1,3,5-hexatriene (3*E*)-**4**, which was then transformed to the zwitterionic carbiminium pentacarbonyltungstate **5** of the 1-alkyloxy-3-amino tetrahydropentalene **A**.[8] Compounds **5** proved to be quite stable and obstinately resisted all attempts to generate 1-alkyloxy-3-aminotetrahydropentalenes by ligand disengagement under




Scheme 1. Cyclopentadiene annelation to an enolizable cycloalkanone: [a]: 1) $HC{\equiv}CH$, 2) $POCl_3/Et_3N$; [b]: 1) BuLi, 2) $M(CO)_6$, 3) $Et_3OBF_4$, M = Cr, W

mild conditions. In the course of these studies, it was found that not only 4-amino- but also 4-phosphanyl substituents are well-suited for triggering the π-cyclization of 1-metalla-1,3,5-hexatrienes of type (3*E*)-**4**. The latter reaction provided access to 1-alkyloxy-3-phosphanyltetrahydropentalene complexes, in which a pentacarbonyltungsten unit is attached to phosphorus rather than to the α-carbon atom (as has been found for the corresponding nitrogen compounds).[8] Since our method for generating 1,3-diheterocyclopentadiene skeletons was directed towards the production of metal-free systems and their application in organic synthesis, we extended our studies to the formation of 1,3-dioxycyclopentadienes, which were expected to form less stable pentacarbonyltungsten complexes than the corresponding amino or phosphanyl derivatives.

It was envisaged that formation of 1,3-dioxycyclopentadienes might be triggered by addition of a protic oxygen nucleophile ROH **6** (RO = carboxy or phenyloxy) to the C≡C

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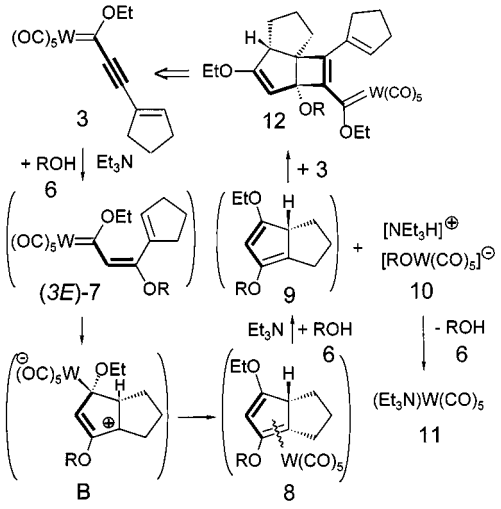
[±±] Crystal structure analysis

  1434–193X/00/0407–1183 $ 17.50+.50/0 

bond of a 1-metalla-1,5-dien-3-yne.[9] Since it was anticipated that the 1,3-dioxycyclopentadiene complexes **8** would be less stable than the corresponding 3-amino-1-alkyloxycyclopentadiene complexes **5**, it was expected that (metal-free) 1,3-dioxytetrahydropentalenes **9** would ultimately be generated following the addition of ROH compounds **6** to the [2-(1-cyclopentenyl)ethynyl]carbene complex **3** (Scheme 2).



Scheme 2. 1,3-Dioxytetrahydropentalenes **9** from [2-(1-cyclopentenyl)ethynyl]carbene complex **3** and [2+2] cycloadducts **12** derived therefrom[10]

Table 1. Starting compounds and yields of **12** given in Scheme 2

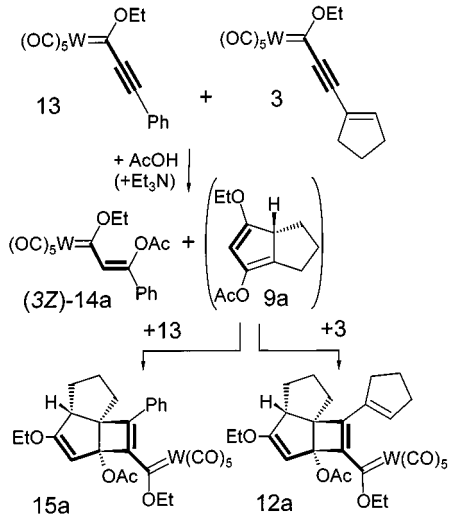
| **6**–**12** | RO | **12** [%][a] |
|---|---|---|
| **a** | MeCOO | 61 |
| **b** | $PhCH_2COO$ | 72 |
| **c** | PhCOO | 44 |
| **d** | 4-*t*Bu$C_6H_4$COO | 54 |
| **e** | MeCH=CMeCOO | [b] |
| **f** | PhO | 54 |
| **g** | 1-NaphthO | 61 |

[a] Isolated chemical yield refers to (1-alkynyl)carbene complex **3** consumed. – [b] Not isolated.

## 1,3-Dioxytetrahydropentalenes and (Cyclobutenyl)carbene Tungsten Complexes 12

Addition of a carboxylic acid **6a**–**e** or a phenol **6f**,**g** to the [2-(1-cyclopentenyl)ethynyl]carbene complex **3** was found to trigger multi-step reactions, which ultimately furnished (cyclobutenyl)carbene complexes **12a**–**g** as readily isolable products (Scheme 2, Table 1). The progress of the reactions, which were carried out using a 1:1 molar ratio of **3**:**6** in diethyl ether at 20 °C, could be monitored by observing the amount of yellow triethylammonium pentacarbonyltungstate $[Et_3NH][ROW(CO)_5]$ **10** precipitated. The formation of the red (cyclobutenyl)carbene compounds **12a**–**g** could also be monitored by TLC (Scheme 2). The reaction required base-catalysis, e.g. by triethylamine, and was found to be somewhat faster in polar than in nonpolar solvents. Since alkyl acids **6a**,**b** were seen to react faster (ca. 2 h at 20 °C in diethyl ether) than aryl acids **6c**,**d** (ca. 6 h), the initial formation of 4-oxy-1-tungsta-1,3,5-hexatrienes (3*E*)-**7** would seem to be the rate-determining step (Scheme 2). Apart from the zwitterionic carbiminium $\eta^1$-carbonylmetallates **5** (Scheme 1), the coordination mode of the corresponding oxy compounds **8** could not be established since these compounds readily lose the $W(CO)_5$ unit, which is transferred to the oxygen nucleophile **6** to give an oxy(pentacarbonyl)tungstate $[Et_3NH][ROW(CO)_5]$ **10**. The (metal-free) 1,3-dioxytetrahydropentalenes **9** thus generated under mild conditions are very reactive and readily form [2+2] adducts **12** with a second molecule of the (1-alkynyl)-carbene complex **3** present in the reaction mixture. Compounds **10** and **12** were the only detectable products in the $^1H$ NMR spectrum of a reaction mixture generated from equimolar amounts of compounds **3** and **6** in $C_6D_6$. The (cyclobutenyl)carbene complexes **12** can be isolated by chromatography on silica gel, but some loss of yield due to decomposition on the column must be allowed for (for isolated yields, see Table 1). Compounds **10** are reasonably stable in the solid state, but in solution they form $(Et_3N)W(CO)_5$ (**11**) by elimination of the starting component ROH **6**, which is thus shown to be only a temporary carrier of the $W(CO)_5$ unit. It should be noted that (cyclobutenyl)carbene complexes **12** are generated from two equivalents of (1-alkynyl)carbene complex **3**, but that the overall reaction leading to these compounds requires a 1:1 molar ratio of the reagents **3** and **6** when carried out under these mild conditions (Scheme 2).[10]

Experimental proof of the intermediacy of 1,3-dioxytetrahydropentalenes **9** as transient species was provided by a competition experiment in which two different (1-alkynyl)-carbene complexes **13** and **3** were allowed to react concomitantly with acetic acid (**6a**). This led to a mixture of cross-products **15a** and **12a**, along with 4-acetyl-1-tungsta-1,3-diene (3*Z*)-**14a** (Scheme 3).



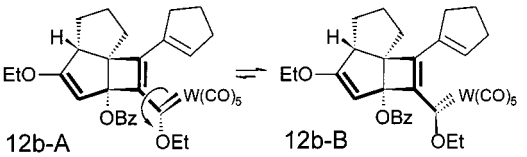
Scheme 3. Cross-reaction of 1,3-dioxytetrahydropentalene **9a** with (1-alkynyl)carbene tungsten complexes **3** and **13**

It should be noted that it is the vinyl ester, not the vinyl ether unit of compound **9**, that adds to the C≡C bond of the (1-alkynyl)carbene complex in a [2+2] fashion to give

the (4-acyloxycyclobutenyl)carbene complexes **12a** and **15a** (Scheme 3). While it has been reported that [2+2] cycloadducts of (1-alkynyl)carbene complexes are formed with vinyl ethers[2,11–13] but not with vinyl esters, even after prolonged reaction times,[11] this "normal" reactivity pattern seems to be reversed in the present situation by the strain imposed by the tetrahydropentalene skeleton and the concave shape of this molecule, as a result of which the C=C(OAc) bond becomes especially prone to *exo* addition. Note that the high diastereoselectivity of the [2+2] addition stems mainly from the specific geometry of the ring skeleton.

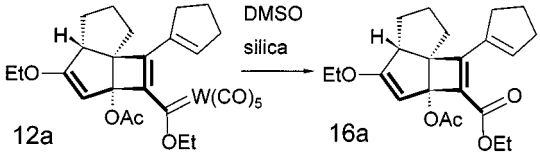
Even though 4-oxy adducts (3*E*)-**7** of the (1-alkynyl)carbene complex **3** (Scheme 2) were not directly detected in the reaction mixture, there is good evidence to suggest that they are indeed formed as intermediates of the reaction depicted in Scheme 2. Thus, it was possible to isolate an adduct (3*Z*)-**14a**, which corresponded to compound (3*E*)-**7** in all respects except for the configuration of the central C=C bond.[9]

Compounds **12** exhibit spectroscopic features typical of (4-oxycyclobutenyl)carbene tungsten complexes.[14,15] Most notably, the $^{13}C$ NMR shift of the W=C unit is observed in the range characteristic of nonconjugated 1-tungsta-1,3,5-hexatrienes, e.g. **12a**: $\delta$ = 319.4, thus indicating an apparently strong distortion of the (W=C)–(C=C) unit (which was indeed confirmed by the crystal structure analysis of compound **12b**) and consequently little $\pi$-conjugation. Two diastereomers, **12b-A** and **12b-B**, in a 2:1 molar ratio can be distinguished in the $^1H$- and $^{13}C$ NMR spectra at low temperature (223 K, 600 MHz), but line-broadening resulting from rapid interconversion of these compounds is observed at ambient temperature (Scheme 4).




Scheme 4. Interconversion of diastereomers **12b-A** and **12b-B**

The ring skeleton of compound **12a** was not affected by oxidative fission of the W=C bond with DMSO, which led to the ester **16a** (Scheme 5).




Scheme 5. Formation of ester **16a** by oxidative decomposition of the (cyclobutenyl)carbene complex **12a**

Structural details of the (cyclobutenyl)carbene complexes **12** were gleaned from a crystal structure analysis of compound **12b** (Figure 1). The W=C4–C5=C51 unit is seen to be twisted by 97.2(6)°, while the C5=C51–C52=C56 moiety adopts an almost planar *s-trans* configuration with a dihedral angle of –173.2(6)°. The cyclobutenyl ring exhibits a typical trapezoidal shape characterized by the pattern of bond lengths [C5=C51 1.339(6) Å, C5–C6 1.527(6) Å, C51–C61 1.521(6) Å, C6–C61 1.568(6) Å] and bond angles [C51–C5–C6 94.3(4)°, C5–C51–C61 94.3(4)°, C5–C6–C61 85.5(3)°, C51–C61–C6 85.9(3)°].

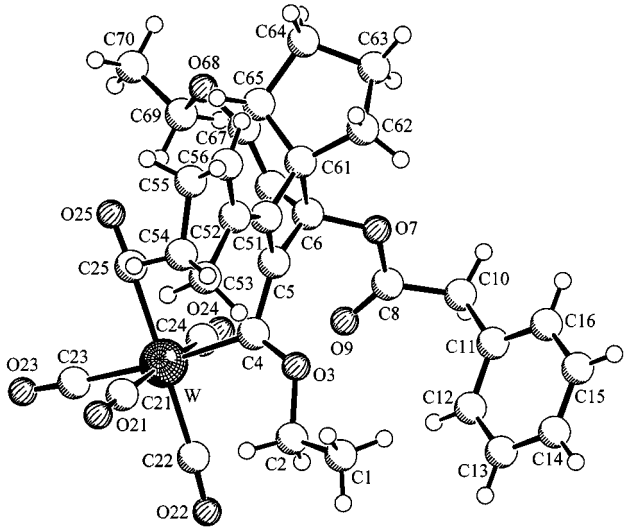



Figure 1. Molecular structure of (cyclobutenyl)carbene complex **12b** (= code 1043.aum); selected bond lengths (Å), bond angles (°) and dihedral angles (°): W–C4 2.168(5), O3–C4 1.311(5), C4–C5 1.494(6), C5–C51 1.339(6), C5–C6 1.527(6), C6–C67 1.476(6), C6–C61 1.568(6), C51–C52 1.437(6), C51–C61 1.521(6), C52–C56 1.324(7), C52–C53 1.502(7), C61–C62 1.521(6), C61–C65 1.541(6), C65–C66 1.501(7), C66–C67 1.332(7), C66–O68 1.348(5); O3–C2–C1 107.1(5), C4–O3–C2 122.6(4), O3–C4–C5 104.4(4), O3–C4–W 133.2(3), C5–C4–W 122.0(3), C51–C5–C4 133.3(4), C51–C5–C6 94.3(4), C4–C5–C6 132.3(4), O7–C6–C67 113.8(4), O7–C6–C5 114.3(3), C67–C6–C5 120.5(4), O7–C6–C61 112.5(4), C67–C6–C61 106.0(4), C5–C6–C61 85.5(3), C5–C51–C52 134.8(4), C5–C51–C61 94.3(4), C52–C51–C61 130.8(4), C56–C52–C51 126.0(5), C56–C52–C53 110.5(5), C51–C52–C53 123.5(4), C62–C61–C51 120.1(4), C62–C61–C65 105.5(4), C51–C61–C65 119.4(4), C62–C61–C6 118.9(4), C51–C61–C6 85.9(3), C65–C61–C6 105.7(4)

Compound **10d** contains a triethylammonium carboxylate ligand, which is not stable in metal-free form. Its coordination mode was characterized by a crystal structure analysis (Figure 2). The carboxylate unit is planar [as indicated by the sum of bond angles O4–C3–C31 119.7(3)° + C31–C3–O2 116.7(3)° + O4–C3–O2 123.5(3)° = 359.9°; dihedral angles W–O2–C3–O4 2.8(5)°, W–O2–C3–C31 –177.1(2)°] and its plane bisects the angle between the neighboring carbonyl groups, C6–W–O2–C3 44.3(3)°.[16] The O,C,O distances are almost equal [C3–O4 1.244(4) Å and C3–O2 1.273(4) Å], but the coordination geometries of the two oxygen atoms are strikingly different in so far as the OH–$N^+$ hydrogen bond (bond lengths N–H17 0.88 Å and H17–O4 1.79 Å) is linear (bond angle O4–H17–N 176°), while the bond to the tungsten atom is bent [W–O2–C3 121.8(2)°]. A characteristic spectroscopic feature of the OH–$N^+$ hydrogen bond is the low field proton signal of the $N^+H$ unit (e.g. **10a**: $\delta$ = 9.50).

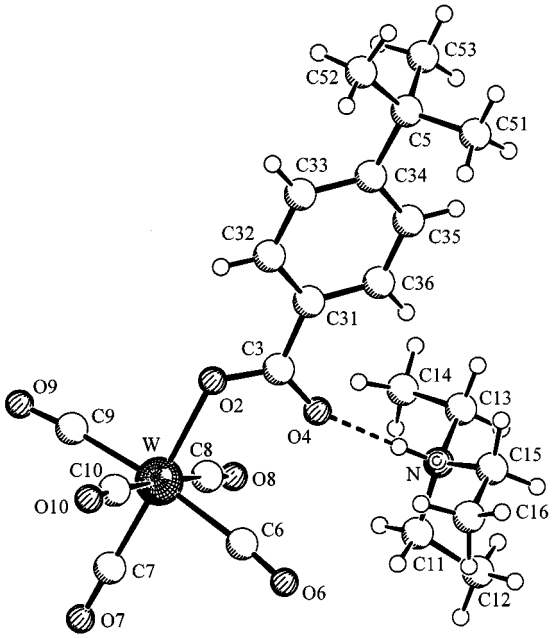
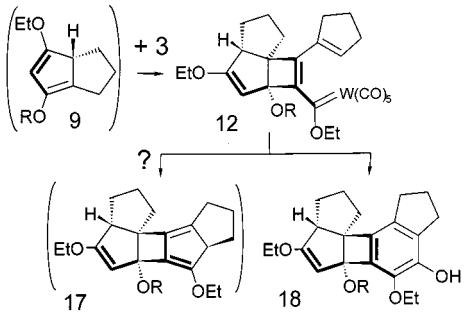



Figure 2. Molecular structure of triethylammonium carboxylate tungsten complex **10d** (= code 1050.aum); selected bond lengths (Å) and bond angles (°): C3–O4 1.244(4), C3–O2 1.273(4), O2–W 2.220(2), C6–W 2.054(5), C7–W 1.952(4), C8–W 2.029(4), C9–W 2.014(4), C10–W 2.045(4); O4–C3–O2 123.5(3), O4–C3–C31 119.7(3), C31–C3–O2 116.7(3), O2–W–C6 93.1(2), O2–W–C7 178.2(2), O2–W–C8, 91.2(1), O2–W–C9 92.3(2), O2–W–C10 89.6(2)




Scheme 6. Metal-mediated ring-closure of (cyclobutenyl)carbene complex **12** involving insertion of carbon monoxide

Table 2. Starting compounds of metal-mediated ring-closure and yields of **17** and **18** as given in Scheme 6

| **9**,**12**,**17**,**18** | RO | **17** [%] | **18** [%][b] |
|---|---|---|---|
| **a** | MeCOO | [a] | 36 + 9[c] |
| **c** | PhCOO | [a] | 18 + 10[d] |
| **e** | MeCH=CMeCOO | [a] | 35 |
| **f** | PhO | [a] | 22+ 20[c] |
| **h** | EtO | [a] | [e] |
| **i** | HO | [a] | [e] |

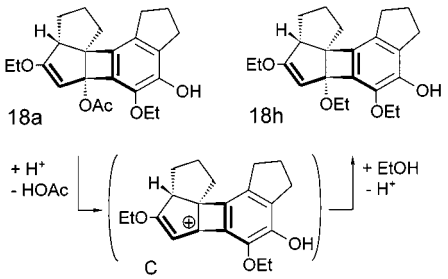
[a] Not detected. – [b] Isolated yield calculated with respect to compound **3** consumed. – [c] Isolated yield of the solvolysis product **18h** after 11 h. – [d] Isolated yield of the solvolysis product **18i** after 26 h. – [e] Supposedly generated by solvolysis of the corresponding acyl derivatives **18** on contact with silica gel.

## Indeno[*b*]-spiro-tricyclo[5.3.0.0]deca-2,5-dienes 18 by Cyclization of (Cyclobutenyl)carbene Tungsten Complexes 12

Based on general features of the π-cyclization of 1-metalla-1,3,5-hexatrienes to cyclopentadienes (Schemes 1 and 2),[4] it was anticipated that the π-cyclization would lead first to compounds **12**, subsequent π-cyclization of which would afford compounds **17**. While it was found that a cyclopentadiene ring was indeed formed in the first part of the reaction sequence, quite unexpectedly the final cyclization step was found to generate the six-membered ring products **18** rather than cyclopentadiene annelation products **17** (Scheme 6, Table 2). Unfortunately, we cannot rule out the possibility that the tetrahydropentalene system of compounds **17** might indeed have been formed but then rapidly underwent oligomerization under the reaction conditions (80 °C), whereas the more stable benzannelation products **18** survived, even during chromatography on silica gel. Since the generation of 1,2-dioxy arenes from 2-alkyloxy-1-metalla-1,3,5-hexatrienes has been reported to require UV irradiation,[17,18] but could not be induced thermally. In the present case it may be the inherent ring strain that triggers insertion of carbon monoxide into the W=C bond.

Thermolysis of the (cyclobutenyl)carbene complex **12a** in benzene at 80 °C afforded the benzannelation product **18a** together with compound **18h** (Scheme 6). Similarly, thermolysis of the (cyclobutenyl)carbene complex **12f** yielded compound **18f** and compound **18h** as a by-product. Since compound **18h** was generated in variable amounts depending on the reaction conditions, we surmised that it might result from solvolysis of the bridgehead substituent OR in an $S_N1$-type substitution involving a bis-allylic carbonium ion intermediate **C** (Scheme 7). It should be pointed out that this type of substitution would necessarily result in retention of configuration due to the specific geometry of the ring skeleton. A similar type of solvolysis reaction might account for the formation of the hydroxy derivative **18i** from compound **18c** in the reaction of benzoic acid with the (1-alkynyl)carbene complex **3**. In the latter case, hydrolysis of compound **18c** does not necessarily imply formation of an intermediate **C**, since it could also proceed by nucleophilic attack of hydroxide at the carbon atom of the carboxy group. Indeno[*b*]-spiro-tricyclo-[5.3.0.0]decadienes **18** were not only generated from compounds **12**, but also in one-pot reactions of (1-alkynyl)carbene complex **3** with oxygen nucleophiles **6** without isolation of compounds **12**.

The molecular structure of indeno[*b*]-spiro-tricyclo[5.3.0.0]deca-2,5-diene **18f** was determined by NMR techniques and was confirmed by a crystal structure analysis (Figure 3). The cyclobutenyl ring exhibits a trapezoidal shape with a typical pattern of bond lengths [C1–C8 1.594(3) Å,




Scheme 7. $S_N1$-type solvolysis of indeno[*b*]-spiro-tricyclo[5.3.0.0]-deca-2,5-dienes **18**

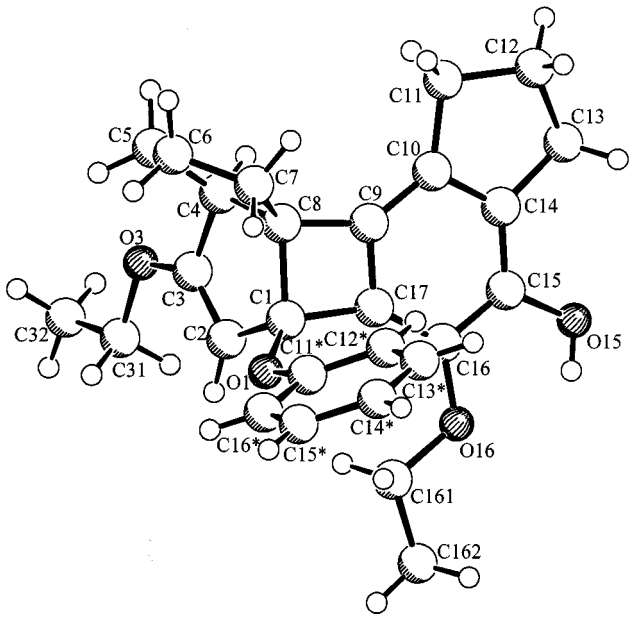



Figure 3. Molecular structure of indeno[*b*]-spiro-tricyclo[5.3.0.0]-deca-2,5-diene **18f** (= code 1103.aum); selected bond lengths (Å) and bond angles (°): C1–O1 1.436(2), C1–C2 1.495(3), C1–C17 1.543(3), C1–C8 1.594(3), C2–C3 1.334(3), C3–O3 1.356(2), C3–C4 1.503(3), C4–C5 1.540(3), C4–C8 1.558(3), C7–C8 1.531(3), C8–C9 1.511(3), C9–C10 1.376(3), C9–C17 1.397(3), C10–C14 1.398(3), C10–C11 1.508(3), C11–C12 1.537(4), C12–C13 1.536(3), C13–C14 1.508(3), C14–C15 1.387(3), C15–O15 1.375(2), C15–C16 1.407(3), C16–O16 1.368(2), C16–C17 1.388(3); O1–C1–C2 106.8(2), O1–C1–C17 121.4(2), C2–C1–C17 115.7(2), O1–C1–C8 119.6(2), C2–C1–C8 105.0(2), C17–C1–C8 86.7(2), C3–C2–C1 111.0(2), C2–C3–O3 128.8(2), C2–C3–C4 115.2(2), O3–C3–C4 116.0(2), C3–C4–C5 115.8(2), C3–C4–C8 103.4(2), C5–C4–C8 106.0(2), C9–C8–C7 122.4(2), C9–C8–C4 115.5(2), C7–C8–C4 105.6(2), C9–C8–C1 85.9(2), C7–C8–C1 120.5(2), C4–C8–C1 105.5(2), C10–C9–C17 122.1(2), C10–C9–C8 142.2(2), C17–C9–C8 95.5(2), C16–C17–C9 121.5(2), C16–C17–C1 146.0(2), C9–C17–C1 92.0(2)

C9=C17 1.397(3) Å, C8–C9 1.511(3) Å, C1–C17 1.543(3) Å] and bond angles [C17–C9–C8 95.5(2)°, C9–C17–C1 92.0(2)°, C17–C1–C8 86.7(2)°, C9–C8–C1 85.9(2)°].

## Conclusion

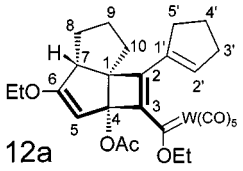
Thermal reactions of carboxylic acids and phenols with the 1-tungsta-1,5-hexadiene-3-yne **3** have been found to afford indeno[*b*]-spiro-tricyclo[5.3.0.0]decadienes through a series of steps involving a Michael-type addition of the nucleophile ROH to the C≡C of compound **3**, a π-cyclization of the adduct to give a cyclopentadiene that undergoes a [2+2] cycloaddition of compound **3**, and finally a benzannelation. 2,4-Dioxy-1-tungsta-1,3,5-hexatrienes and 1,3-dioxytetrahydropentalenes serve as key intermediates in these reactions.

## Experimental Section

**General:** All operations were carried out under an atmosphere of argon. All solvents were dried and distilled prior to use. – IR spectra were obtained on a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. – $^1$H- and $^{13}$C-NMR spectra were recorded on Bruker ARX 300 and AM 360 instruments. $^1J$(H,C), $^2J$(H,C), $^3J$(H,C) decoupling and TOCSY as well as NOE experiments were performed on Varian 400 and 600 instruments. – Elemental analyses were carried out on a Perkin–Elmer 240 elemental analyser. – Analytical TLC plates, Merck DC-Alufolien Kiesegel $60_{F240}$, were viewed under UV light (254 nm) or stained by exposure to iodine vapour. $R_f$ values refer to TLC tests on silica gel. Chromatographic purifications were performed on Merck Kieselgel 100. – Pentacarbonyl(3-cyclopentenyl-1-ethyloxy-2-propyn-1-ylidene)tungsten (**3**) was prepared according to ref.[8]

**(1*S**,4*R**,7*R**)-3-(1,1,1,1,1-Pentacarbonyl-2-ethyloxy-1-tungsta-2-ethenyl)-4-acetoxy-2-(1-cyclopentenyl)-6-ethyloxy-spiro-tricyclo-[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (12a), Triethylammonium Acetyl(pentacarbonyl)tungstate (10a), and Pentacarbonyl(triethylamine)tungsten (11):** To a solution of acetic acid (**6a**) (60 mg, 1.00 mmol) and triethylamine (80 mg, 0.80 mmol) in 1 mL of dry diethyl ether in a 2-mL screw-top vessel was added a solution of pentacarbonyl(3-cyclopentenyl-1-ethyloxy-2-propyn-1-ylidene)tungsten (**3**) (472 mg, 1.00 mmol) in 1 mL of *n*-pentane. Compound **3** was consumed within 3 h at 20 °C (TLC analysis), while compound **10a** (ca. 200 mg, 86%) was precipitated in the form of yellow air-sensitive crystals and isolated by centrifugation. The solvent was then removed in vacuo (15 Torr, 20 °C) and the residue was redissolved in 1 mL of dichloromethane. Separation by *rapid* column chromatography on silica gel (column 20 × 2 cm) eluting with dichloromethane/*n*-pentane (1:5) afforded a red main fraction containing compound **12a** [210 mg, 61%, $R_f$ = 0.7 in *n*-pentane/diethyl ether (10:1), red crystals from diethyl ether/*n*-pentane at –15 °C, m.p. 79 °C]. Chromatography had to be carried out rapidly, otherwise a noticeable decrease in the yield due to decomposition of **12a** on the silica gel column was observed. Compound **10a** was found to be stable in the solid state, but decomposed rapidly in solution to give **11** and acetic acid (**6a**).

**12a:** $^1$H NMR ($C_6D_6$): δ = 5.70 (pseudo t, 1 H, 2′-H), 5.56 (s, 1 H, 5-H), 4.51 and 4.39 (br. s, 1 H each, diastereotopic W=C–$OCH_2$), 3.78 and 3.62 (2 m, 1 H each, diastereotopic 6-$OCH_2$), 3.10 (m, 1 H, 7-H), 2.48–1.61 (m, 12 H, 8-$H_2$−10-$H_2$ and 3′-$H_2$−5′-$H_2$), 1.71 (s, 3 H, $CH_3CO$), 1.24 and 1.06 (2 t, 3 H each, 2 × $OCH_2CH_3$). − $^{13}$C NMR ($C_6D_6$): δ = 319.4 (W=C), 204.8 and 198.5 [2 $C_q$, *trans*- and *cis*-CO of $W(CO)_5$], 170.4 ($C_q$, COO), 166.8 ($C_q$, C6), 152.7 ($C_q$, br., C3), 136.3 ($C_q$, C1′), 134.8 (CH, C2′), 132.4 ($C_q$, br., C2), 97.7 (CH, C5), 92.6 ($C_q$, C4), 76.8 (dynamically broadened W=C–$OCH_2$), 65.6 (6-$OCH_2$), 61.9 ($C_q$, C1), 48.8 (CH, C7); 34.6, 33.6 and 24.0 (3 $CH_2$, C3′−C5′); 31.9, 30.7 and 26.0 (3 $CH_2$, C8−C10), 21.1 ($CH_3CO$), 14.6 (2 $OCH_2CH_3$). − IR (hexane): $\tilde{\nu}$ (rel. int.) = 2064.1 (20), 1938.9 (100) [ν(C≡O)], 1732.5 cm$^{-1}$ (80) [ν(C=O)]. − MS (70 eV); *m/z* $^{184}$W (%): 680 (20) [$M^+$], 568 (100) [$M^+$ − 4 CO], 540 (80) [$M^+$ − 5 CO]. − $C_{27}H_{28}O_9W$ (680.4): calcd. C 47.65, H 4.12; found C 47.82, H 4.35.




**10a:** $^1$H NMR ($C_6D_6$): δ = 9.50 (br. s, 1 H, $N^+H$), 2.50 (q, 6 H, 3 $NCH_2$), 1.95 (s, 3 H, $CH_3CO$), 0.80 (t, 9 H, 3 $CH_2CH_3$). − $^{13}$C NMR ($C_6D_6$): δ = 201.4 [$W(CO)_5$], 179.8 (C=O), 45.6 (3 $NCH_2$), 22.7 ($CH_3CO$), 9.2 (3 $NCH_2CH_3$).

**11:** $^1$H NMR ($C_6D_6$): δ = 2.20 (q, 6 H, 3 $NCH_2$), 0.60 (t, 9 H, 3 $NCH_2CH_3$). − $^{13}$C NMR ($C_6D_6$): δ = 201.3 and 199.1 [1:4, *trans*- and *cis*-CO of $W(CO)_5$], 52.4 (3 $NCH_2$), 13.9 (3 $NCH_2CH_3$).

**(1*S**,4*R**,7*R**)-3-(1,1,1,1,1-Pentacarbonyl-2-ethyloxy-1-tungsta-2-ethenyl)-2-(cyclopent-1-enyl)-6-ethyloxy-4-phenylacetoxy-spirotricyclo[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (12b):** 2-Phenylacetic acid (**6b**) (68 mg, 0.50 mmol) was reacted with pentacarbonyl(3-cyclopentenyl-1-ethyloxy-2-propyn-1-ylidene)tungsten (**3**) (236 mg, 0.50 mmol) in the presence of triethylamine (40 mg, 0.40 mmol) in diethyl ether/dichloromethane (1:1) as described above. After 4 h, chromatography on silica gel (column 20 × 2 cm) eluting with *n*-pentane/dichloromethane (5:1) gave a red fraction containing compound **12b** [137 mg, 72%, $R_f$ = 0.8 in *n*-pentane/diethyl ether (10:1), red crystals from diethyl ether/*n*-pentane at –15 °C; m.p. 108 °C]. Triethylammonium pentacarbonyl(phenylacetoxy)tungstate (**10b**) was isolated in the form of yellow crystals, which were not further characterized.

**12b:**[19] $^1$H NMR ($CDCl_3$, 223 K, 600 MHz, diastereomers **A** and [**B**], see Scheme 4, **A** = major product): δ = 7.34 [7.34] (m, 3 H, *o*- and *p*-H Ph), 7.26 [7.26] (m, 2 H, *m*-H Ph), 5.83 [5.75] ("s", 1 H, 2′-H), 5.28 [5.34] (s, 1 H, 5-H), 4.66 and 3.87 [4.60 and 3.85] (2 m, 1 H each, diastereotopic W=C–$OCH_2$), 3.82 [3.82] (m, 2 H, diastereotopic 6-$OCH_2$), 3.63 and 3.54 [3.69 and 3.51] (AB system, 1 H each, $^2J$ = –22 Hz each, $PhCH_2$), 2.99 [3.18] (dd, 1 H, 7-H), 2.42–1.73 [2.42–1.37] (m, 12 H, 8-$H_2$–10-$H_2$ and 3′-$H_2$–5′-$H_2$), 1.36 [1.36] (t, 6 H, 2 $CH_3CH_2O$). − $^{13}$C NMR ($CDCl_3$, 223 K): δ = 319.0 [318.4] (W=C), 204.4 [206.3] and 196.8 [197.2] [$C_q$ each, *trans*- and *cis*-CO of $W(CO)_5$], 171.1 [171.2] ($C_q$, COO), 165.9 [166.2] ($C_q$, C6), 156.2 [150.9] ($C_q$, C3), 135.0 [134.9] ($C_q$, C1′), 134.5 [134.3] (CH, C2′), 133.8 [133.4] ($C_q$, *i*-C Ph), 132.4 [131.7] ($C_q$, C2); 129.2, 128.5 and 127.0 [129.3, 128.7 and 127.3] (2:2:1, *o*-, *m*- and *p*-CH Ph), 96.5 [96.5] (CH, C5), 91.9 [92.4] ($C_q$, C4), 79.6 [75.0] (dynamically broadened W=C–$OCH_2$), 65.4 [65.5] (6-$OCH_2$), 60.5 [60.8] ($C_q$, C1), 47.3 [47.8] (CH, C7), 41.8 [42.5] ($CH_2Ph$); 33.9, 33.1 and 23.5 [33.2, 33.1 and 23.4] ($CH_2$ each, C3′−C5′); 31.3, 29.8 and 25.2 [31.7, 29.7 and 25.4] ($CH_2$ each, C8−C10), 14.7 and 14.5 [14.7 and 14.5] ($CH_3CH_2O$ each). – IR (hexane): $\tilde{\nu}$ (rel. int.) = 2063.0 (30), 1938.5 (100) [ν(C≡O)], 1731.8 $cm^{-1}$ (80) [ν(C=O)]. – MS (70 eV); *m*/*z* $^{184}$W (%): 756 (3) [$M^+$], 644 (25) [$M^+$ – 4 CO], 616 (9) [$M^+$ – 5 CO]. − $C_{33}H_{32}O_9W$ (756.4): calcd. C 52.30, H 4.23; found C 52.31, H 4.44.

**X-ray Crystal Structure Analysis of Compound 12b:** $C_{33}H_{32}O_9W$, $M_r$ = 756.44 $gmol^{-1}$, 0.25 × 0.10 × 0.05 mm, *a* = 17.924(3), *b* = 17.871(2), *c* = 9.944(2) Å, α = 90°, β = 98.17(1)°, γ = 90.00°, *V* = 3152.9(9) Å$^3$, $\rho_{calcd}$ = 1.594 $gcm^{-3}$, μ = 37.16 $cm^{-1}$, empirical absorption correction based on ψ scan data (0.780 ≤ *C* ≤ 0.999), *Z* = 4, monoclinic, space group $P2_1/c$ (No.14), λ = 0.71073 Å, *T* = 223 K, ω/2φ scans, total no. of reflections collected (±*h*, –*k*, ±*l*) 11095, $[(\sin\Theta)/\lambda]_{max}$ = 0.59 Å$^{-1}$, 5552 independent reflections and 3254 observed reflections [$I \geq 2\sigma(I)$], 390 refined parameters, *R* = 0.031, $R_w^2$ = 0.048, max. residual electron density ρ = 0.69 (–0.67) eÅ$^{-3}$, hydrogen atoms calculated and refined as riding atoms.[20]

**(1*S**,4*R**,7*R**)-3-(1,1,1,1,1-Pentacarbonyl-2-ethyloxy-1-tungsta-2-ethenyl)-4-benzoyloxy-2-(cyclopent-1-enyl)-6-ethyloxy-spirotricyclo[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (12c):** Benzoic acid (**6c**) (122 mg, 1.00 mmol) was reacted with pentacarbonyl(3-cyclopentenyl-1-ethyloxy-2-propyn-1-ylidene)tungsten (**3**) (472 mg, 1.00 mmol) in the presence of triethylamine (80 mg, 0.80 mmol) in diethyl ether/dichloromethane (1:1) at 20 °C. Workup after 15 h gave compound **12c** [164 mg, 44%, $R_f$ = 0.6 in *n*-pentane/diethyl ether (10:1); m.p. 56 °C]. Triethylammonium benzoyloxy(pentacarbonyl)tungstate (**10c**) was isolated in the form of yellow crystals, which were not further characterized.

**12c:**[19] $^1$H NMR ($C_6D_6$): δ = 8.10, 7.15 and 7.04 (2:1:2, *o*-, *p*- and *m*-H Ph), 5.73 (t, 1 H, 2′-H), 5.68 (s, 1 H, 5-H), 4.57 and 4.35 (2 br., 1 H each, diastereotopic W=C–$OCH_2$), 3.79 and 3.57 (2 m, 1 H each, diastereotopic 6-$OCH_2$), 3.17 (dd, 1 H, 7-H), 2.46–1.69 (m, 12 H, 6 $CH_2$), 1.01 and 1.05 (2 t, 3 H each, 2 × $CH_3CH_2O$). − $^{13}$C NMR ($C_6D_6$): δ = 318.21 (W=C), 203.42 and 197.07 [2 $C_q$, *trans*- and *cis*-CO of $W(CO)_5$], 171.0 ($C_q$, br., COO), 168.1 ($C_q$, C6), 164.8 ($C_q$, C3), 136.3 ($C_q$, C1′), 134.7 (CH, C2′), 132.2 ($C_q$, br., C2), 131.4 ($C_q$, *i*-C Ph); 133.2, 129.9 and 128.8 (1:2:2, CH each, Ph), 97.8 (CH, C5), 93.3 ($C_q$, C4), 78.1 (dynamically broadened W=C–$OCH_2$), 65.7 (6-$OCH_2$), 62.2 ($C_q$, C1), 48.8 (CH, C7); 34.6, 32.3 and 24.1 ($CH_2$ each, C3′−C4′); 30.7, 30.3 and 25.9 ($CH_2$ each, C8−C10), 14.6 and 14.5 ($CH_3CH_2O$ each). − IR (hexane): $\tilde{\nu}$ (rel. int.) = 2064.9 (30), 1937.9 (100) [ν(C≡O)], 1710.9 $cm^{-1}$ (80) [ν(C=O)]. – MS (70 eV); *m*/*z* $^{184}$W (%): 742 (15) [$M^+$], 630 (100) [$M^+$ − 4 CO], 602 (83) [$M^+$ − 5 CO], 446 (90). − $C_{32}H_{30}O_9W$ (742.4): calcd. C 51.75, H 4.04; found C 51.46, H 4.22.

**(1*S**,4*R**,7*R**)-3-(1,1,1,1,1-Pentacarbonyl-2-ethyloxy-1-tungsta-2-ethenyl)-4-(*p*-*tert*-butyl-benzoyloxy)-2-(cyclopent-1-enyl)-6-ethyloxy-spiro-tricyclo[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (12d) and Triethylammonium Pentacarbonyl[4-(*tert*-butyl)benzoyloxy]tungstate (10d):** To a solution of 4-(*tert*-butyl)benzoic acid (**6d**) (89 mg, 0.50 mmol) and triethylamine (40 mg, 0.40 mmol) in 1 mL of diethyl ether in a 2-mL screw-top vessel was added a solution of pentacarbonyl(1-ethyloxy-3-cyclopentenyl-2-propyn-1-ylidene)tungsten (**3**) (236 mg, 0.50 mmol) in 1 mL of *n*-pentane. The mixture was shaken for 3 min and then left at 20 °C. The starting material was consumed within 18 h at this temperature (TLC control), during which the color changed from brown to red and compound **10d** [290 mg, 96%, yellow crystals, 150 °C (dec.)] was precipitated. Chromatography of the mother liquor on silica gel eluting with *n*-pentane/dichloromethane (10:1) afforded a red fraction containing compound **12d** [216 mg, 54%, $R_f$ = 0.7 in *n*-pentane/diethyl ether (10:1), red crystals from diethyl ether/*n*-pentane; m.p. 48 °C].

**12d:**[19] $^1$H NMR ($C_6D_6$): δ = 8.04 and 7.13 (2:2, $C_6H_4$), 5.72 (t, 1 H, 2′-H), 5.70 (s, 1 H, 5-H), 4.38 and 4.35 (2 br., 1 H each, diastereotopic W=C–$OCH_2$), 3.78 and 3.56 (2 m, 1 H each, diastereotopic 6-$OCH_2$), 3.18 (dd, 1 H, 7-H), 2.48−1.65 (m, 12 H, 6 $CH_2$), 1.08 [s, 9 H, $C(CH_3)_3$], 1.03 and 1.02 (2 t, 3 H each, 2 $CH_3CH_2O$). − $^{13}$C NMR ($C_6D_6$): δ = 319.86 (W=C), 205.11 and 197.81 [2 $C_q$, *trans*- and *cis*-CO of $W(CO)_5$], 171.5 ($C_q$, br., COO), 167.2 ($C_q$, C6), 166.6 ($C_q$, C3), 157.1 ($C_q$, C1 of $C_6H_4$), 136.5 ($C_q$, C1′), 134.8 (CH, C2′), 132.4 ($C_q$, br., C2), 130.2 and 126.0 (2:2, $C_6H_4$), 128.9 ($C_q$, C4 of $C_6H_4$), 98.1 (CH, C5), 93.2 ($C_q$, C4), 78.5 (dynamically broadened W=C–$OCH_2$), 65.9 (6-$OCH_2$), 62.4 ($C_q$, C1), 49.0 (CH, C7), 45.8 ($C_q$, $CMe_3$); 35.3, 33.9 and 24.3 ($CH_2$ each, C3′−C4′); 32.6, 30.9 and 26.1 ($CH_2$ each, C8−C10), 31.3 [$CH_3$, $C(CH_3)_3$], 14.8 and 14.5 (2 × $CH_3CH_2O$). − IR (hexane): $\tilde{\nu}$ (rel. int.) = 2064.9 (30), 1939.5 (100) [ν(C≡O)], 1710.7 $cm^{-1}$ (80) [ν(C=O)]. − MS (70 eV); *m*/*z* $^{184}$W (%): 798 (4) [$M^+$], 686 (20)

[$M^+ - 4$ CO], 658 (15) [$M^+ - 5$ CO]. – $C_{36}H_{38}O_9W$ (793.5): calcd. C 54.10, H 4.76; found C 54.40, H 4.81.

**10d:** $^1$H NMR ($C_6D_6$): δ = 9.20 (v. br., 1 H, $N^+$–HO), 7.93 and 7.31 (2 H each, $C_6H_4$), 2.48 (q, 6 H, 3 $NCH_2$), 1.15 [s, 9 H, *t*-$C(CH_3)_3$], 0.87 (t, 9 H, 3 $NCH_2CH_3$). – $^{13}$C NMR ($C_6D_6$): δ = 201.5 [$W(CO)_5$], (COO),[21] 155.0 ($C_q$, C4 $C_6H_4$), 133.3 ($C_q$, C1 $C_6H_4$), 130.5 and 130.1 (2 br., CH each, diastereotopic C2 and C6 of $C_6H_4$), 125.6 and 125.4 CH each, diastereotopic C3 and C5 of $C_6H_4$), 46.0 (3 $NCH_2$), 35.1 ($CMe_3$), 31.7 [$C(CH_3)_3$], 9.5 (3 $NCH_2CH_3$). – $C_{22}H_{29}NO_7W$ (603.3): calcd. C 43.78, H 4.97, N 2.32; found C 43.78, H 4.99, N 2.17.

**X-ray Crystal Structure Analysis of Compound 10d:** $C_{22}H_{29}NO_7W$, $M_r$ = 603.31 gmol$^{-1}$, 0.5 × 0.4 × 0.1 mm, $a$ = 18.100(1), $b$ = 12.180(1), $c$ = 11.887(1) Å, α = 90°, β = 105.11(1)°, γ = 90°, $V$ = 2530.0(3) Å$^3$, $\rho_{calcd}$ = 1.584 gcm$^{-3}$, μ = 46.04 cm$^{-1}$, absorption correction via SORTAV (0.207 ≤ $T$ ≤ 0.656), $Z$ = 4, monoclinic, space group $P2_1/c$ (No.14), λ = 0.71073 Å, $T$ = 198 K, ω/2φ scans, total no. of reflections collected (±$h$, ±$k$, ±$l$) 17697, $[(\sin\Theta)/\lambda]_{max}$ = 0.71 Å$^{-1}$, 7677 independent reflections and 6631 observed reflections [$I \geq 2\sigma(I)$], 289 refined parameters, $R$ = 0.041, $R_w^2$ = 0.113, max. residual electron density ρ = 1.60 (–2.04) eÅ$^{-3}$, hydrogen atoms calculated and refined as riding atoms.[20]

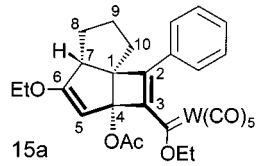
**(1*S**,4*R**,7*R**)-3-(1,1,1,1,1-Pentacarbonyl-2-ethyloxy-1-tungsta-2-ethenyl)-2-(cyclopent-1-enyl)-6-ethyloxy-4-phenyloxy-spiro-tricyclo[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (12f):** To pentacarbonyl(1-ethyloxy-3-cyclopentenyl-2-propyn-1-ylidene)tungsten (**3**) (236 mg, 0.50 mmol) and phenol (**6f**) (47 mg, 0.50 mmol) in a 2-mL screw-top vessel was added 2 mL of dichloromethane/*n*-pentane (1:1) and triethylamine (40 mg, 0.40 mmol). The mixture was shaken for 3 min. until it became homogeneous. The starting material **3** was seen to be consumed within 6 h at 20 °C (TLC control). Chromatography on silica gel (column 20 × 2 cm) eluting with *n*-pentane/dichloromethane (15:1) gave a red fraction containing **12f** [96 mg, 54%, $R_f$ = 0.7 in *n*-pentane/diethyl ether (20:1), red crystals from *n*-pentane at –20 °C; m.p. 82 °C].

**12f:**[19] $^1$H NMR ($C_6D_6$): δ = 7.16, 7.03 and 6.82 (2:2:1, Ph), 6.01 (br. "s", 1 H, 2′-H), 5.90 (s, 1 H, 5-H), 4.14 (br., 2 H, W=C–$OCH_2$), 3.78 and 3.46 (2 m, 1 H each, diastereotopic 6-$OCH_2$), 3.36 (dd, 1 H, 7-H), 2.52–1.67 (m, 12 H, 6 $CH_2$), 1.03 and 0.80 (2 t, 3 H each, 2 × $CH_3CH_2O$). – $^{13}$C NMR ($C_6D_6$): δ = 321.4 (W=C), 204.9 and 197.3 [2 $C_q$, *trans*- and *cis*-CO of $W(CO)_5$], 167.2 ($C_q$, C6), 157.2 ($C_q$, C3), 156.3 ($C_q$, *i*-C Ph), 136.7 ($C_q$, C1′), 136.4 (CH, C2′), 130.1 ($C_q$, C2); 129.7, 122.3 and 118.5 (2:1:2, Ph), 96.9 (CH, C5), 95.5 ($C_q$, C4), 77.4 (dynamically broadened W=C–$OCH_2$), 65.5 (6-$OCH_2$), 62.5 ($C_q$, C1), 49.5 (CH, C7); 34.4, 33.6, 32.9, 31.0, 26.2 and 24.0 ($CH_2$ each), 14.7 and 14.2 ($CH_3CH_2O$ each). – IR (hexane): $\tilde{\nu}$ (rel. int.) = 2066.7 (20), 1937.4 cm$^{-1}$ (100) [ν(C≡O)]. – MS (70 eV); $m/z$ $^{184}$W (%): 714 (16) [$M^+$], 658 (31) [$M^+ - 2$ CO], 574 (54) [$M^+ - 5$ CO]. – $C_{31}H_{30}O_8W$ (714.4): calcd. C 51.97, H 4.20; found C 52.09, H 4.15.

**(1*S**,4*R**,7*R**)-3-(1,1,1,1,1-Pentacarbonyl-2-ethyloxy-1-tungsta-2-ethenyl)-2-(cyclopent-1-enyl)-6-ethyloxy-4-(2-naphthyloxy)-spiro-tricyclo[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (12g):** To pentacarbonyl(1-ethyloxy-3-cyclopentenyl-2-propyn-1-ylidene)tungsten (**3**) (236 mg, 0.50 mmol) and naphthol (**6g**) (75 mg, 0.50 mmol) were added 2 mL of dichloromethane/*n*-pentane (1:1) and triethylamine (40 mg, 0.40 mmol). The mixture was shaken until homogeneous (3 min.) and then maintained at 20 °C for 8 h to give compound **12g** [116 mg, 61%, $R_f$ = 0.7 in *n*-pentane/dichloromethane (4:1), m.p. 58 °C].

**12g:**[19] $^1$H NMR ($C_6D_6$): δ = 7.89–7.46 (m, 7 H, naphthyloxy), 6.03 (br. "s", 1 H, 2′-H), 5.95 (s, 1 H, 5-H), 4.33 (br., 2 H, W=C–$OCH_2$), 4.12 and 3.76 (2 m, 1 H each, diastereotopic 6-$OCH_2$), 3.58 (dd, 1 H, 7-H), 2.89–1.94 (m, 12 H, 6 $CH_2$), 1.34 and 0.83 (2 t, 3 H each, 2 × $CH_3CH_2O$). – $^{13}$C NMR ($C_6D_6$): δ = 319.7 (W=C), 204.9 and 198.9 [2 $C_q$, *trans*- and *cis*-CO of $W(CO)_5$], 167.4 ($C_q$, C6), 155.8 ($C_q$, C3), 154.8 ($C_q$, C2 naphthyloxy), 136.2 ($C_q$, C1′), 134.8 (CH, C2′), 134.4 ($C_q$, C2); 130.0, 129.8, 127.1, 127.0, 124.6, 120.5 and 110.7 (7 CH and 2 $C_q$, naphthyloxy), 96.4 (CH, C5), 95.3 ($C_q$, C4), 77.0 (W=C–$OCH_2$), 65.5 (6-$OCH_2$), 62.8 ($C_q$, C1), 49.4 (CH, C7); 34.3, 33.5, 31.8, 30.9, 30.7, 26.1 and 23.9 ($CH_2$ each), 14.5 and 13.8 ($CH_3CH_2O$ each). – IR (hexane): $\tilde{\nu}$ (rel. int.) = 2066.1 (30), 1937.0 cm$^{-1}$ (100) [ν(C≡O)]. – MS (70 eV): $m/z$ $^{184}$W (%) = 764 (7) [$M^+$], 708 (14) [$M^+ - 2$ CO], 680 (8) [$M^+ - 3$ CO], 652 (15) [$M^+ - 4$ CO], 624 (34) [$M^+ - 5$ CO]. – $C_{35}H_{32}O_8W$ (764.5): calcd. C 55.26, H 4.19; found C 54.85, H 4.52.

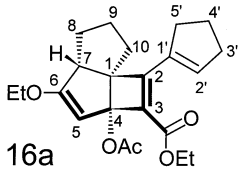
**(1*S**,4*R**,7*R**)-3-(1,1,1,1,1-Pentacarbonyl-2-ethyloxy-1-tungsta-2-ethenyl)-4-acetoxy-6-ethyloxy-2-phenyl-spiro-tricyclo-[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (15a):** To a stirred solution of acetic acid (**6a**) (60 mg, 1.00 mmol) and triethylamine (80 mg, 0.80 mmol) in 1 mL of diethyl ether in a 2-mL screw-top vessel was added a solution of pentacarbonyl(3-cyclopentenyl-1-ethyloxy-2-propyn-1-ylidene)tungsten (**3**) (236 mg, 0.50 mmol) and pentacarbonyl(1-ethyloxy-3-phenyl-2-propyn-1-ylidene)tungsten (**13**) (241 mg, 0.50 mmol) in 1 mL of *n*-pentane at 20 °C. After 4 h at this temperature, chromatographic workup gave a red fraction containing **15a** [76 mg, 44%, $R_f$ = 0.6 in *n*-pentane/diethyl ether (10:1), m.p. 123 °C] and a brown fraction containing compound (3*Z*)-**14a**.[9]



15a

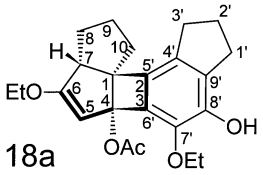
**15a:** $^1$H NMR ($C_6D_6$): δ = 7.24, 7.17 and 7.06 (2:2:1, Ph), 5.56 (s, 1 H, 5-H), 4.50 and 4.42 (2 m each br., 1 H each, diastereotopic W=C–$OCH_2$), 3.74 and 3.60 (2 m, 1 H each, diastereotopic 6-$OCH_2$), 3.22 (dd, 1 H, 7-H); 2.24, 1.99 and 1.64 (3 br. m, 2 H each, diastereotopic 8-$H_2$–10-$H_2$), 1.73 (s, 3 H, $CH_3COO$), 1.16 and 1.03 (2 t, 3 H each, 2 × $CH_3CH_2O$). – $^{13}$C NMR ($C_6D_6$): δ = 319.2 (W=C), 204.2 and 198.4 [2 $C_q$, *trans*- and *cis*-CO of $W(CO)_5$], 170.3 ($C_q$, $CH_3COO$), 166.9 ($C_q$, C6), 156.0 ($C_q$, C3), 134.8 ($C_q$, C2), 130.7 ($C_q$, *i*-C Ph); 127.8, 127.5 and 127.4 (3 br., 1:2:2, CH each, Ph), 96.0 (CH, C5), 90.8 ($C_q$, C4), 76.9 (dynamically broadened W=C–$OCH_2$), 64.2 (6-$OCH_2$ ), 60.4 ($C_q$, C1), 47.6 (CH, C7); 31.5, 29.1 and 24.0 ($CH_2$ each, C3–C5), 21.0 ($CH_3CO$), 14.6 (2 $OCH_2CH_3$). – IR (hexane): $\tilde{\nu}$ (rel. int.) = 2063.8 (30), 1939.7 (100) [ν(C≡O)], 1735 cm$^{-1}$ (80) [ν(C=O)]. – MS (70 eV); $m/z$ $^{184}$W (%): 690 (16) [$M^+$], 578 (100) [$M^+ - 4$ CO], 550 (77) [$M^+ - 5$ CO]. – $C_{28}H_{26}O_9W$ (690.4): calcd. C 48.67, H 5.30; found C 48.97, H 5.64.

**(1*S**,4*R**,7*R**)-4-Acetoxy-2-(cyclopent-1-enyl)-6-ethyloxy-3-(ethyloxycarbonyl)-spiro-tricyclo[5.3.0$^{1,7}$.0$^{1,4}$]deca-2,5-diene (16a):** Compound **12a** (180 mg, 0.24 mmol) was dissolved in 2 mL of dimethyl sulfoxide. After 6 h at 20 °C, the initially brown solution had turned yellow. Subsequent chromatography on silica gel eluting with *n*-pentane/diethyl ether (5:1) afforded a colorless fraction containing compound **16a** [79 mg, 89%, $R_f$ = 0.6 in diethyl ether/*n*-pentane (1:2)]. – $^1$H NMR ($C_6D_6$): δ = 6.11 (t, 1 H, 2′-H), 5.46 (s, 1 H, 5-H), 4.17 (m, 2 H, $COOCH_2$), 3.48 (m, 2 H, 6-$OCH_2$), 3.06 (dd, 1 H, 7-H), 2.77 and 2.62 (2 m, 1 H each), 2.21–2.12 (m, 3 H),



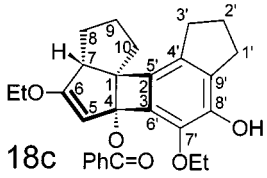

2.03–1.90 (m, 2 H), 1.74–1.62 (m, 5 H), 1.76 (s, 3 H, $CH_3CO$), 1.29 and 0.99 (2 t, 3 H each, 2 × $CH_3CH_2O$). – $^{13}C$ NMR ($C_6D_6$): δ = 169.4 ($C_q$, COO), 164 ($C_q$, C6), 149.5 ($C_q$, C3), 137.1 ($C_q$, C1′), 137.0 (CH, C2′), 136.0 ($C_q$, C2), 97.8 (CH, C5), 90.7 ($C_q$, C4), 65.1 ($COOCH_2$), 63.1 (6-$OCH_2$), 60.0 ($C_q$, C1), 49.0 (CH, C7); 33.7, 33.4 and 23.5 ($CH_2$ each, C3′–C5′); 31.4, 30.6 and 26.2 ($CH_2$ each, C8–C10), 21.4 ($CH_3CO$), 14.4 and 14.4 ($CH_3CH_2O$ each). – IR (hexane): ṽ (rel. int.) = 1752.7 $cm^{-1}$ (90) [ν(C=O)]. – MS (70 eV); *m/z* (%): 372 (10) [$M^+$], 330 (51) [$M^+ – CH_3CO$], 284 (100) [$M^+ – CH_3CO – EtO$]. – $C_{22}H_{28}O_5$ (372.5): calcd. C 70.97, H 7.53; found C 69.86,[22] H 7.77.

**(1*R**,4*R**,7*R**)-4-Acetoxy-6,7′-diethyloxy-8′-hydroxy-2′,3′-dihydro-1′*H*-indeno[5′,6′,*b*]-spiro-tricyclo[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (18a):** To acetic acid (**6a**) (36 mg, 0.60 mmol) and triethylamine (60 mg, 0.60 mmol) in 2 mL of benzene in a 5-mL screw-top vessel was added pentacarbonyl(3-cyclopentenyl-1-ethyloxy-2-propyn-1-ylidene)tungsten (**3**) (566 mg, 1.20 mmol). The vessel was flushed with argon, sealed, and heated to 80 °C for 10 h. $W(CO)_6$ was then removed by centrifugation at 20 °C and the supernatant was separated by chromatography on silica gel (column 20 × 2 cm) eluting with *n*-pentane/diethyl ether (2:1) to afford a small amount of a red fraction containing compound **12a** and colorless fraction containing compound **18a** [67 mg, 29%, $R_f$ = 0.5 in *n*-pentane/diethyl ether (3:1)]. Compound **18a** could also be generated in 47% yield by heating (cyclobutenyl)carbene complex **12a** in toluene at 80 °C for 10 h.



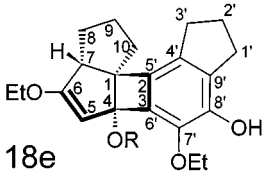

**18a:** $^1H$ NMR ($C_6D_6$): δ = 5.92 (br. s, 1 H, OH), 5.60 (s, 1 H, 5-H), 4.64 and 4.16 (2 m, 1 H each, diastereotopic 7′-$OCH_2$), 3.50 (m, 2 H, diastereotopic 6-$OCH_2$), 3.07 (dd, 1 H, 7-H), 3.01 (m, 2 H); 2.65, 2.53, 2.42 and 2.11 (4 m, 1 H each), 2.02–1.79 (m, 4 H), 1.70 (m, 2 H), 1.77 (s, 3 H, $CH_3CO$), 1.29 and 1.04 (2 t, 3 H each, 2 × $CH_3CH_2O$). – $^{13}C$ NMR ($C_6D_6$): δ = 176.4 ($C_q$, COO), 169.6 ($C_q$, C6), 144.8 ($C_q$, C7′), 135.1 ($C_q$, 8′); 134.0, 133.2 and 132.9 (3 $C_q$, 2:1:1, C4′–C6′, C9′), 98.1 (CH, C5), 93.0 ($C_q$, C4), 69.3 (7′-$OCH_2$), 65.2 ($C_q$, C1), 64.1 (6-$OCH_2$), 51.6 (CH, C7), 32.8 and 30.5 ($CH_2$ each, C1′ and C3′); 29.8, 29.6, 26.4 and 26.1 ($CH_2$ each, C2′, C8–C10), 21.4 ($CH_3CO$), 15.6 and 14.4 ($CH_3$ each, C6 and C7′ $OCH_2CH_3$). – IR (hexane): ṽ (rel. int.) = 3389 (50) [ν(OH)], 1735 $cm^{-1}$ (80) [ν(C=O)]. – MS (70 eV): *m/z* (%) = 384 (66) [$M^+$], 341 (9) [$M^+ – CH_3CO$], 325 (45) [$M^+ – CH_3COO$].

**(1*S**,4*R**,7*R**)-4-Benzoyloxy-6,7′-diethyloxy-8′-hydroxy-2′,3′-dihydro-1′*H*-indeno[5′,6′,*b*]-spiro-tricyclo[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (18c):** To benzoic acid (**6c**) (61 mg, 0.50 mmol) and triethylamine (50 mg, 0.50 mmol) in 2 mL of toluene in 10-mL round-bottomed flask was added pentacarbonyl(3-cyclopentenyl-1-ethyloxy-2-propyn-1-ylidene)tungsten (**3**) (472 mg, 1.00 mmol). The vessel was flushed with argon, sealed, and heated to 80 °C for 12 h. Subsequent chromatography afforded a small amount of a red fraction containing compound **12c** [24 mg, 6%, $R_f$ = 0.9 in *n*-pentane/diethyl ether (2:1)] and a colorless fraction containing compound **18c** [64 mg, 28%, $R_f$ = 0.5 in *n*-pentane/diethyl ether (2:1), colorless oil]. Compound **18c** could also be generated in 42% yield by heating (cyclobutenyl)carbene complex **12c** in toluene at 80 °C for 12 h.




**18c:** $^1H$ NMR ($C_6D_6$): δ = 8.21 (“d”, 2 H, *o*-H Ph), 7.12–7.03 (3 H, *p*- and *m*-H Ph), 5.87 (br. s, 1 H, OH), 5.66 (s, 1 H, 5-H), 4.63 and 4.22 (2 m, 1 H each, diastereotopic 7′-$OCH_2$), 3.47 (m, 2 H, diastereotopic 6-$OCH_2$), 3.04 (dd, 1 H, 7-H), 2.97 (m, 2 H), 2.63 (m, 1 H), 2.56–2.45 (m, 2 H), 2.14–1.64 (m, 7 H), 1.24 and 1.01 (2 t, 3 H each, 2 × $CH_3CH_2O$). – $^{13}C$ NMR ($C_6D_6$): δ = 177.5 ($C_q$, COO), 166.2 ($C_q$, C6), 145.1 ($C_q$, C7′), 135.2 ($C_q$, C8′); 134.3, 133.6, 133.5, 132.5 and 130.4 (5 $C_q$, 1:1:1:1:1, C4′–C6′, C9′ and *i*-C Ph); 133.2, 130.3 and 129.0 (1:2:2, CH each, Ph), 98.6 (CH, C5), 93.5 ($C_q$, C4), 69.5 (7′-$OCH_2$), 65.7 ($C_q$, C1), 65.2 (6-$OCH_2$), 51.9 (CH, C7), 33.6 and 31.0 ($CH_2$ each, C1′ and C3′); 30.3, 30.1, 26.8 and 26.6 ($CH_2$ each), 16.0 and 14.9 ($CH_3CH_2O$ each). – IR (hexane): ṽ (rel. int.) = 3337 (60) [ν(OH)], 1719 $cm^{-1}$ (80) [ν(C=O)]. – MS (70 eV): *m/z* (%) = 446 (18) [$M^+$], 341 (8) [$M^+ – PhCO$], 105 (100) [$PhCO^+$]. – $C_{28}H_{30}O_5$ (446.5): calcd. C 74.34, H 6.73; found C 73.94, H 6.66.

**(1*S**,4*R**,7*R**)-4-(2-Methyl-2-butenyloxy)-6,7′-diethyloxy-8′-hydroxy-2′,3′-dihydro-1′*H*-indeno[5′,6′,*b*]-spiro-tricyclo-[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (18e):** 2-Methyl-2-butenoic acid (**6e**) (75 mg, 0.75 mmol), triethylamine (70 mg, 0.70 mmol), and pentacarbonyl(3-cyclopentenyl-1-ethyloxy-2-propyn-1-ylidene)tungsten (**3**) (708 mg, 1.50 mmol) were reacted as described above for 14 h at 80 °C to give compound **18e** [111 mg, 35%, $R_f$ = 0.4 in *n*-pentane/diethyl ether (3:1), colorless oil].

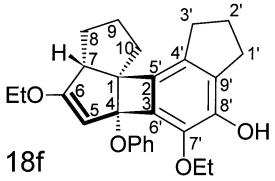



**18e:** $^1H$ NMR ($C_6D_6$): δ = 6.95 (q, 1 H, =CHMe), 5.87 (br. s, 1 H, OH), 5.65 (s, 1 H, 5-H), 4.66 and 4.20 (2 m, 1 H each, diastereotopic 7′-$OCH_2$), 3.47 (m, 2 H, diastereotopic 6-$OCH_2$), 3.05 (dd, 1 H, 7-H), 2.94 (m, 2 H), 2.61 (m, 1 H), 2.57–2.44 (m, 2 H), 2.16–1.67 (m, 7 H), 1.80 (s, 3 H, $CCH_3$), 1.38 (d, 3 H, =$CHCH_3$), 1.27 and 1.01 (2 t, 3 H each, 2 × $CH_3CH_2O$). – $^{13}C$ NMR ($C_6D_6$): δ = 177.8 ($C_q$, COO), 167.6 ($C_q$, C6), 165.4 (=CH), 145.5 ($C_q$, C7′), 138.8 ($C_q$, C8′); 137.8, 136.1, 134.7, 134.0 and 133.6 (5 $C_q$, C4′–C6′, C9′ and *i*-C Ph), 99.2 (CH, C5), 93.8 ($C_q$, C4), 70.0 (7′-$OCH_2$), 65.9 ($C_q$, C1), 65.2 (6-$OCH_2$), 52.0 (CH, C7), 33.8 and 31.3 ($CH_2$ each, C1′ and C3′); 30.6, 30.2, 27.1 and 26.8 ($CH_2$ each), 16.4 and 13.0 ($CCH_3$ each), 15.2 and 14.8 ($CH_3CH_2O$ each). – IR (hexane): ṽ (rel. int.) = 3404 (60) [ν(OH)], 1711 $cm^{-1}$ (80) [ν(C=O)]. – MS (70 eV): *m/z* (%) = 424 (57) [$M^+$], 341 (51) [$M^+$ – MeCH=C(Me)CO], 313 (66) [$M^+$ – MeCH=C(Me)CO – 28]. – $C_{26}H_{32}O_5$ (424.5): calcd. C 74.58, H 7.55; found C 74.43, H 7.76.

**(1*S**,4*R**,7*R**)-6,7′-Diethyloxy-8′-hydroxy-2′,3′-dihydro-1′*H*-4-phenyloxy-indeno[5′,6′,*b*]-spiro-tricyclo-[5.3.0$^{1,4}$.0$^{1,7}$]deca-2,5-diene (18f):** Phenol (**6f**) (47 mg, 0.50 mmol),

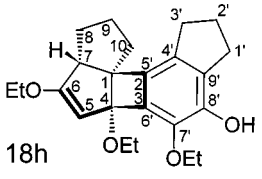
triethylamine (50 mg, 0.50 mmol), and pentacarbonyl(3-cyclopentenyl-1-ethyloxy-2-propyn-1-ylidene)tungsten (**3**) (472 mg, 1.00 mmol) were reacted as described above at 80 °C for 12 h to give a red fraction containing compound **12f** [24 mg, 7%, $R_f$ = 0.9 in *n*-pentane/diethyl ether (1:3)] and compound **18f** [46 mg, 21%, $R_f$ = 0.6 in *n*-pentane/diethyl ether (3:1), colorless solid, m.p. 121 °C]. Thermolysis of (cyclobutenyl)carbene complex **12f** (284 mg, 0.40 mmol) in toluene at 80 °C for 15 h afforded a mixture of **18f** (38 mg, 22%) and **18h** [29 mg, 20%, $R_f$ = 0.5 in *n*-pentane/diethyl ether (3:1), colorless oil].

**18f:** $^1$H NMR ($C_6D_6$): δ = 7.20, 7.04 and 6.80 (2:2:1, Ph), 5.64 (s, 1 H, OH), 5.04 (s, 1 H, 5-H), 4.12 and 4.03 (2 m, 1 H each, diastereotopic 7′-$OCH_2$), 3.51 and 3.41 (2 m, 1 H each, diastereotopic 6-$OCH_2$), 3.08 (dd, 1 H, 7-H), 2.98 (m, 2 H), 2.65 (m, 1 H), 2.56–2.46 (m, 2 H), 2.00–1.65 (m, 7 H), 1.03 and 0.98 (2 t, 3 H each, 2 × C$H_3$$CH_2$O). – $^{13}$C NMR ($C_6D_6$): δ = 163.7 ($C_q$, C6), 158.1 (*i*-C Ph), 142.8 ($C_q$, C7′), 138.4 ($C_q$, C8′), 133.1 and 132.9 (1:3, $C_q$ each); 129.3, 121.9 and 120.2 (2:1:2, Ph), 99.8 (CH, C5), 96.0 ($C_q$, C4), 66.4 (7′-$OCH_2$), 65.3 ($C_q$, C1), 65.1 (6-$OCH_2$), 32.7 and 30.9 ($CH_2$ each, C1′ and C3′); 29.7, 29.6, 27.0 and 26.3 ($CH_2$ each), 15.2 and 14.5 (*C*$H_3$$CH_2$O each). – MS (70 eV): *m*/*z* $^{184}$W (%) = 418 (55) [$M^+$], 325 (100) [$M^+$ – PhO].




**X-ray Crystal Structure Analysis of Compound 18f:** $C_{27}H_{30}O_4$, $M_r$ = 418.51 gmol$^{-1}$, 0.25 × 0.20 × 0.10 mm, *a* = 13.611(2), *b* = 10.378(3), *c* = 15.631(2) Å, α = 90.00°, β = 97.90(1)°, γ = 90.00°, *V* = 2187.0(8) Å$^3$, $\rho_{calcd}$ = 1.271 gcm$^{-3}$, μ = 6.70 cm$^{-1}$, empirical absorption correction based on ψ scan data (0.977 ≤ *C* ≤ 0.999), *Z* = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, *T* = 198 K, ω/2φ scans, total no. of reflections collected (–*h*, –*k*, ±*l*) 4634, $[(\sin\Theta)/\lambda]_{max}$ = 0.62 Å$^{-1}$, 4444 independent reflections and 3495 observed reflections [$I \geq 2\sigma(I)$], 284 refined parameters, *R* = 0.053, $R_w^2$ = 0.139, max. residual electron density ρ = 0.66 (–0.68) eÅ$^{-3}$, thermal parameters of C6 indicate disorder (not refined), hydrogen atoms calculated and refined as riding atoms.[20]

**18h**: $^1$H NMR ($C_6D_6$): δ = 5.61 (s, 1 H, OH), 4.83 (s, 1 H, 5-H), 4.40 and 4.13 (2 m, 1 H each, diastereotopic 7′-$OCH_2$), 3.58 (m, 2 H, diastereotopic 6-$OCH_2$), 3.54 and 3.47 (2 m, 1 H each, diastereotopic 4-$OCH_2$), 3.02 (dd, 1 H, 7-H), 2.98 (m, 2 H), 2.63 (m, 1 H), 2.54 (m, 1 H), 2.20 (m, 1 H), 2.01–1.63 (m, 7 H); 1.12, 1.15 and 1.05 (3 t, 3 H each, 3 × C$H_3$$CH_2$O). – $^{13}$C NMR ($C_6D_6$): δ = 163.8 ($C_q$, C6), 142.4 ($C_q$, C7′), 138.5 ($C_q$, C8′); 134.1, 133.0, 132.3 and 132.2 ($C_q$ each), 99.3 (CH, C5), 94.7 ($C_q$, C4); 66.3, 64.9 and 61.9 ($OCH_2$ each), 64.4 ($C_q$, C1), 53.0 (CH, C7), 32.0 and 31.6 ($CH_2$ each, C1′−C3′); 29.8, 29.6, 27.3 and 26.4 ($CH_2$ each); 16.0, 15.4 and 14.5 (*C*$H_3$$CH_2$O each). – MS (70 eV); *m*/*z* (%): 370 (100) [$M^+$], 341 (54) [$M^+$ – Et], 325 (70) [$M^+$ – EtO]. – $C_{23}H_{30}O_4$ (370.5): calcd. C 74.59, H 8.11; found C 74.40, H 8.48.

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[19] For the atom numbering scheme, see Experimental Section, formula **12a**.
[20] Data sets were collected on Nonius CAD4, MACH3, or KappaCCD diffractometers. Programs used: data collection Express or Collect, data reduction MolEN or Denzo-SMN, structure solution *SHELXS-86* or *SHELXS-97*, structure refinement *SHELXL-97*, graphics *SCHAKAL-92*. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-134786–1347888. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0) 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].
[21] Signal not observed probably due to dynamic line-broadening.
[22] Compound **16a** was not obtained free from traces of $W(CO)_6$.
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