# A Group 4 Metallocene Template Synthesis of β,γ-Unsaturated ε-Hydroxy Carboxylic Acids

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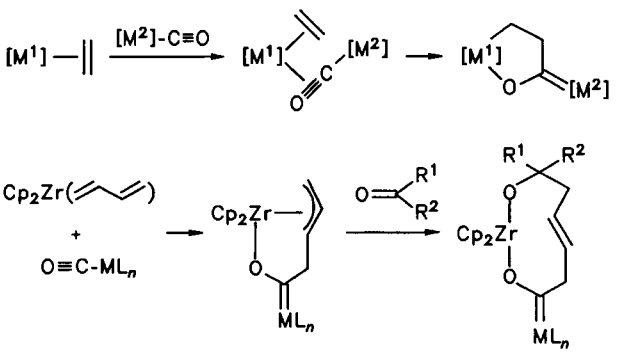
The reaction of (butadiene)zirconocene with hexacarbonyltungsten gives the metallacyclic [(π-allyl)zirconoxy]carbene complex **7**. This reagent adds to a variety of ketones to yield chiral nine-membered metallacyclic ring systems (**8**). These systems are thus formed by means of 1,4-selective coupling reactions of 1,3-butadiene with $W(CO)_6$ and an organic carbonyl compound at the zirconocene template. The ketones subjected to react with **7** include benzophenone, methyl vinyl ketone, cyclopentanone, and 3-methoxyestra-1,3,5(10)-trien-17-one (**12**). The coupling products of **7** with cyclopentanone (**8c**) and **12** (**8d-A**) were characterized by X-ray crystal structure analyses. Of the four possible diastereomeric nine-membered metallacyclic coupling products of **7** with **12** a single isomer [**8d-A** with (13'*S*,17'*R*,2,3,4-*pS*) configuration] was formed with ≥98% selectivity and isolated in 95% yield. Treatment of the complexes **8** in tetrahydrofuran with water and pyridine *N*-oxide very effectively removed both transition metals with the formation of the corresponding β,γ-unsaturated ε-hydroxy carboxylic acids. The overall reaction sequence has thus converted the steroid ketone **12** very selectively to 5-[3-methoxy-17β-hydroxyestra-1,3,5(10)-trien-17α-yl]-(*E*)-pent-3-enoic acid (**10d**).

Some time ago we reported on a novel carbene complex synthesis, the basic reaction step of which is the addition of a metal carbonyl to a reactive ($\eta^2$-alkene)- or ($\eta^2$-alkyne)-metallocene complex followed by ring closure[1]. Since then many examples of this (metaloxy)carbene complex synthesis have been reported[2]. Employing the (*s-cis/s-trans*-$\eta^4$-butadiene)zirconocene equilibrium mixture as a starting material has turned out to be very advantageous. The system reacts very rapidly with a great variety of carbonyl metal complexes to give the corresponding metallacyclic [(allyl)-zirconoxy]carbene complexes in high yield[3]. The (zirconoxy)carbene moiety is rather unreactive, although it can be converted into an ordinary M=C(R)OR' functional group. (Zirconoxy)carbene complexes can thus be regarded as *protected* Fischer carbene complexes. The presence of the zirconocene-protecting group at the carbene oxygen atom allows a variety of selective transformations to be carried out at other parts of the molecules without interfering with the M=C(R)OM' moiety. We have found that the reactive zirconium-bound allyl group in such complexes can very effectively be coupled with unsaturated organic reagents. Coupling with organic carbonyl compounds or nitriles thus gives rise to the formation of nine-membered metallacycles[4,5]. These complexes are to be regarded as the ternary coupling products of a metal carbonyl with butadiene and an organic carbonyl compound at the bis(cyclopentadienyl)zirconium template. It should be emphasized that coupling of the butadiene building block has taken place with complete 1,4-selectivity[6].

Scheme 1




For a few selected examples we have shown that the $Cp_2Zr$ template can be cleaved off hydrolytically after it has served its purpose[7]. In this paper we describe two typical examples. The [(zirconoxy)carbene]vanadium complex **1** is prepared by sequential coupling of (butadiene)zirconocene with tetracarbonyl(η-cyclopentadienyl)vanadium and pinakolone. Its hydrolysis was carried out by treatment with a stoichiometric quantity of tetra-*n*-butylammonium fluoride–trihydrate in tetrahydrofuran. The resulting acylmetallate complex (**2**) was then *O*-alkylated by Meerwein's reagent to yield the

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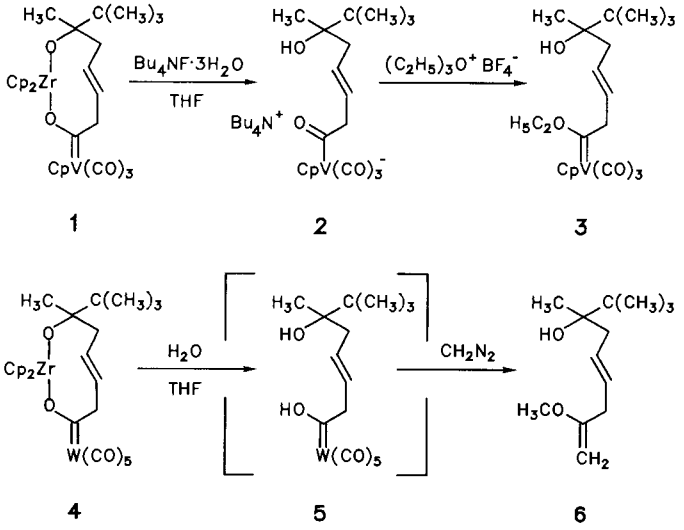
stable Fischer-type vanadium carbene complex **3**[8]. The [(zirconoxy)carbene]tungsten complex **4** was prepared by template coupling of (butadiene)zirconocene with hexacarbonyltungsten and pinakolone. Simple hydrolysis with $H_2O$ in tetrahydrofuran furnished an unstable (hydroxycarbene)tungsten complex (**5**). This reactive intermediate has turned out to be useful for the preparation of organic targets, however. When **5** is generated in the presence of a suitable trapping agent such as diazomethane[9] (which does not attack the *protected* carbene complex **4**) it is cleanly converted to the functionalized enol ether **6**[10].



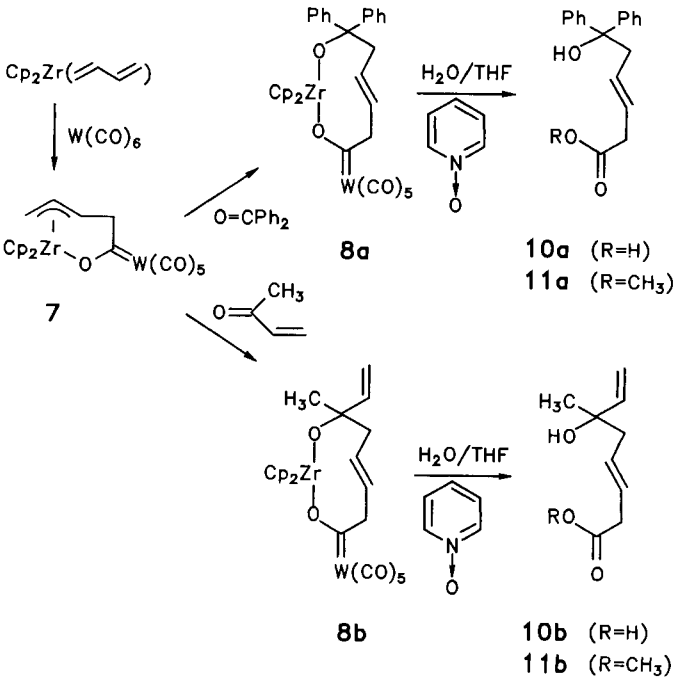

Similarly, oxidation[11] of the in situ generated hydroxycarbene complex **5** has produced the corresponding carboxylic acid. Starting from this unique example, we have tried to extend our template reaction to a widely applicable synthesis of specifically functionalized organic carboxylic acids. First representative examples are described in this account.

## Results and Discussion

We have started this study by employing two nine-membered metallacyclic (zirconoxy)carbene complexes that we have described previously[13,14]. The carbene complex **8a** was prepared in the usual way by means of a two-step reaction sequence. The reaction of (butadiene)zirconocene with hexacarbonyltungsten produced the [($\pi$-allyl)zirconoxy]carbene complex **7**. This was then treated with benzophenone to yield the nine-membered metallacycle **8a**. Optimization of our general synthesis in this case has allowed an easy preparation of the cyclic (zirconoxy)carbene complex on a 25-g scale in near to 90% isolated yield. Complex **8a** is a typical member of this general class of compounds. It contains a chiral medium-sized metallacyclic ring system. The carbon-carbon double bond which is part of the ring is *trans*-configurated. The presence of this single chirality element (planar chirality) thus leads to the occurrence of a pair of enantiomers of **8a** whose interconversion is rather slow as expected for such a metallacyclic relative of *trans*-cyclononene[12]: The activation energy of enantiomerization of **8a** has been determined as $\Delta G^{\ddagger}_{ent} \approx 17$ kcal mol$^{-1}$[13].

Complex **8a** was dissolved in tetrahydrofuran, and the solution was charged with one molar equivalent of pyridine *N*-oxide. This oxidation agent usually reacts rapidly with Fischer-type carbene complexes and converts them effectively into carboxylic esters[11]. The (zirconoxy)carbene complex **8a** exhibits a rather high acyl-metal complex character. It proves to be inert towards oxidation by pyridine *N*-oxide at room temperature. We then added ca. two molar equivalents of water to the reaction mixture to deprotect the carbene complex. Hydrolysis of the zirconium-oxygen linkages takes place rapidly under the reaction conditions. The metallacyclic ring system is cleaved and the $Cp_2Zr$ template effectively removed from the organic coupling product. We assume that a (hydroxycarbene)tungsten complex (**9a**) is generated by the hydrolysis of **8a**. This reactive Fischer-type carbene complex then reacts instantaneously with the pyridine *N*-oxide scavenger present in the solution. The $C{=}W(CO)_5$ linkage is oxidatively cleaved and the corresponding carboxylic acid obtained. We have isolated 6-hydroxy-6,6-diphenyl-(*E*)-hex-3-enoic acid (**10a**) in close to 60% yield. Subsequent esterification (diazomethane) gave **11a**.

Methyl vinyl ketone was allowed to react with **7** to give the (zirconoxy)carbene complex **8b**[14] in 93% yield. The metallacycle **8b** contains two chirality elements per molecule: The reaction of the prochiral ketone with **7** has resulted in the formation of a chiral center in addition to the planar chirality element caused by the occurrence of the *trans*-configurated carbon-carbon double bond inside the metallacyclic ring system. Therefore, a mixture of two diastereomeric metallacyclic (zirconoxy)carbene complexes is obtained whose interconversion can be achieved by a topomerization reaction of the ring system effecting an inversion process of the planar chirality element. An activation barrier of $\Delta G^{\ddagger}_{dia} \approx 16.5 \pm 0.4$ kcal mol$^{-1}$ was observed for



the interconversion of the respective **8b** diastereoisomers which were obtained in a **8b-A**: **8a-B** ratio of 60:40 [14].

The mixture of **8b** diastereoisomers was hydrolyzed ($H_2O$/THF) in the presence of pyridine *N*-oxide similarly as described above. From the reaction mixture we have isolated 6-hydroxy-6-methyl-(3*E*)-octa-3,7-dienoic acid in nearly 50% yield.

These experiments have shown us that our method can be employed to selectively introduce into a target molecule a $C_5$ side chain, which is terminated by a carboxylic acid moiety and contains a *trans* carbon-carbon double bond in its homoconjugated position, by starting from a ketone or an aldehyde. In this series of preliminary orientating experiments we wanted to clarify whether such a procedure would be principally suitable for the introduction of a functionalized side chain e. g. into the 17-position of a steroidal framework. We, therefore, had to investigate first if our carbene/template method could be applied to attach a specific side chain to a five-membered ring system by starting from a ketone.

We have treated the [(π-allyl)zirconoxy]carbene complex **7** with cyclopentanone and have obtained the nine-membered metallacyclic addition product **8c** in high yield (87%). The C=W(CO)$_5$ unit of **8c** shows characteristic $^{13}$C-NMR [δ = 332.6 (carbene C), 204.8 (*trans*-W—CO), 199.7 (*cis*-W—CO)] and IR data ($\tilde{\nu}_{CO}$ = 2058, 1975, 1909 cm$^{-1}$). The medium-sized metallacycle exhibits a persistent chirality on the $^1$H- and $^{13}$C-NMR time scale at room temperature (4.7 Tesla). This becomes evident by the occurrence of equal intensity pairs of cyclopentadienyl $^1$H/$^{13}$C resonances (δ = 6.30, 6.24/113.3, 113.0). The $C_5$ unit of **8c** originating from the cyclopentanone building block gives rise to five clearly separated $^{13}$C-NMR signals at δ = 94.9 (quart. C), 41.6, 37.8, 24.0, and 23.6 ($CH_2$). The methylene hydrogens at C-6 of the nine-membered ring system of **8c** are diastereotopic ($^1$H-NMR: δ = 4.56 and 3.00).

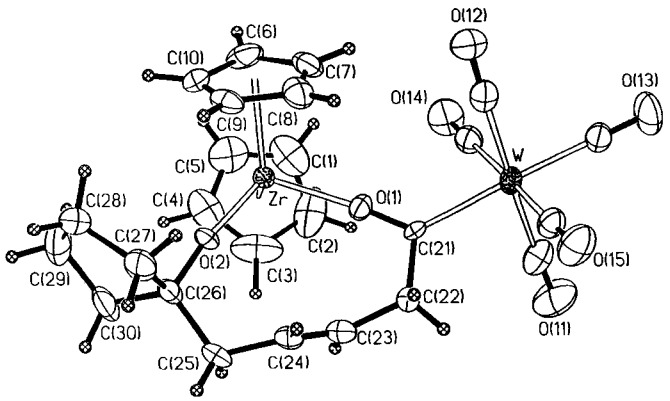



Figure 1. Molecular structure of complex **8c** (with unsystematical atom numbering scheme). Selected bond lengths [Å] and angles [°]: W—C(11) 2.037(10), W—C(12) 2.044(8), W—C(13) 1.995(10), W—C(14) 2.039(12), W—C(15) 2.040(10), W—C(21) 2.198(8), Zr—O(1) 2.100(6), Zr—O(2) 1.909(5), O(1)—C(21) 1.257(11), O(2)—C(26) 1.413(9), O(11)—C(11) 1.124(14), O(12)—C(12) 1.140(10), O(13)—C(13) 1.168(13), O(14)—C(14) 1.131(15), O(15)—C(15) 1.120(13), C(21)—C(22) 1.531(13), C(22)—C(23) 1.501(14), C(23)—C(24) 1.298(12), C(24)—C(25) 1.493(15), C(25)—C(26) 1.541(13), C(26)—C(27) 1.537(12), C(26)—C(30) 1.524(16); W—C(21)—O(1) 123.9(6), W—C(21)—C(22) 122.8(6), O(1)—C(21)—C(22) 113.3(7), C(13)—W—C(21) 178.4(3), C(22)—C(23)—C(24) 126.3(10), O(1)—Zr—O(2) 104.7(2), C(23)—C(24)—C(25) 125.4(11), Zr—O(1)—C(21) 168.9(5), Zr—O(2)—C(26) 173.3(6)

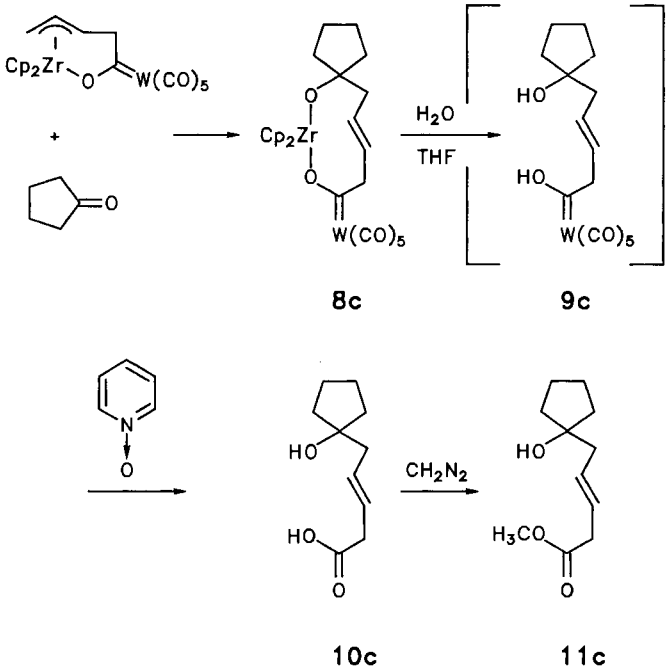
This pairwise inequivalency of groups in complex **8c** is caused by the presence of a *trans*-configurated carbon-carbon double bond inside the nine-membered ring system. In addition to the NMR spectroscopic data this was revealed by the X-ray crystal structure analysis of **8c** (Figure 1, Table 1).

Table 1. Details of the data collection and the X-ray crystal structure solution of **8c** and **8d-A**

| | **8c** | **8d-A** |
|---|---|---|
| formula | $C_{25}H_{24}O_7WZr$ | $C_{43}H_{40}O_9WZr$ |
| mol wt | 711.5 | 975.8 |
| crystal color | yellow | yellow-green |
| crystal system | monoclinic | orthorhombic |
| space group [no.] | $P2_1/c$ | $P2_12_12$ |
| *a*, Å | 11.248(2) | 20.351(4) |
| *b*, Å | 15.437(3) | 25.847(6) |
| *c*, Å | 15.519(2) | 7.819(1) |
| β, deg | 109.72(1) | --- |
| *V*, Å$^3$ | 2536.6(7) | 4112.7(14) |
| *Z* | 4 | 4 |
| cryst. dimens, mm | 0.40 x 0.45 x 0.50 | 0.28 x 0.32 x 0.45 |
| $D_{calcd}$, g cm$^{-3}$ | 1.863 | 1.589 |
| μ(MoKα), cm$^{-1}$ | 50.74 | 31.01 |
| MoKα radiation, λ, Å | 0.71073 | 0.71073 |
| diffractometer | Siemens P4 | Siemens P4 |
| monochromator | graphite | graphite |
| 2θ scan range, deg | 4-55 | 4-50 |
| temp, K | 296 | 295 |
| *T*(max)/*T*(min) | 0.327/0.213 | 0.250/0.328 |
| reflcns collected | 6045 | 7753 |
| no. of indep reflcns | 5832 | 7614 |
| indpt obsd reflcns $F_o \geq n\sigma(F_o)$ | 3843 | 3949 |
| std. reflcns | 3 std/197 reflcns | 3 std/197 reflcns |
| *R(F)*, % | 4.64 | 5.58 |
| *R(wF)*, % | 5.13 | 5.76 |
| Δ/σ(max) | 0.05 | 0.02 |
| Δ (ρ), eÅ$^{-3}$ | 0.75 | 1.15 |
| $N_o/N_v$ | 12.5 | 8.5 |
| GOF | 1.02 | 1.07 |

Complex **8c** contains a very rigid central nine-membered metallacyclic ring system. The rigidity originates mainly from the presence of the *trans*-configurated C=C bond [*d*C(23)—C(24) = 1.298(12) Å] and the specific bonding features of the endocyclic (zirconoxy)carbene moiety. The O(2)—Zr—O(1) angle is rather large at 104.7(2)°. The Zr—O(2) bond is very short [1.909(5) Å]. Together with the large C(26)—O(2)—Zr angle of 173.3(6)° this indicates a

marked additional π-bonding component of the chalcogen-metal linkage. The Zr–O(1) bond is slightly longer at 2.100(6) Å. The Zr–O(1)–C(21) angle is 168.9(5)°. The carbene carbon atom is trigonally planar coordinated with the O(1)–C(21)–C(22) plane almost bisecting with the adjacent *cis*-$(CO)_4W$ frame, as is often observed for Fischer-type carbene pentacarbonyl group 6 transition metal complexes [15]. The W–C(21) bond distance is 2.198(8) Å which is markedly longer than each of the five W–C(CO) linkages (see Figure 1). The C(21)–C(22) bond length is 1.531(13) Å which is at the high end of the typical range of $C(sp^2)$–$C(sp^3)$ single bond distances[16]. The C(21)–O(1) bond is rather short at 1.257 (11) Å [i.e. much shorter than the C(26)–O(2) linkage of 1.413(9) Å]. The short C(carbene)–O(carbene) distance is very typical of the (zirconoxy)carbene complexes in general[17]. It is indicative of a pronounced acyl-metal complex character and clearly distinguishes these (metaloxy)-carbene complexes from typical Fischer carbene complexes[15]. This structural differentiation is reflected in the pronouncedly decreased carbene complex reactivity of the (zirconoxy)carbene complexes (see above), a feature on which our specific synthetic scheme is in part based on. The spiro-annulated cyclopentane moiety of **8c** adopts an envelope conformation with the distal methylene groups oriented towards the bis(cyclopentadienyl)zirconium unit.




The carbene complex **8c** was dissolved in tetrahydrofuran containing one molar equivalent of pyridine *N*-oxide and was hydrolyzed by the addition of two molar equivalents of water. The usual workup gave a single metal-free organic product in >60% yield which was identified as 5-(1-hydroxycyclopentyl)-(*E*)-pent-3-enoic acid (**10c**). Esterification is carried out with ethereal diazomethane to give the corresponding methyl ester **11c**. Apparently, our template coupling reaction is well suited to attach a $C_5$ side chain to five-membered ring ketones. The resulting protected carbene complex **8c** is inert towards oxidation by pyridine *N*-oxide as expected but is readily hydrolyzed to a hydrocarbene complex (**9c**) which is instantaneously converted to the desired final organic product in high yield.

Next we have treated the {[(π-allyl)zirconoxy]carbene}-tungsten complex reagent **7** with 3-methoxyestra-1,3,5(10)-trien-17-one (**12**). The stereochemical characteristics of the addition of **7** to the chiral, enantiomerically pure steroidal 17-ketone are slightly more complicated than any of the coupling reactions described above; so an a priori assessment of the stereochemical features of the potential products might be useful. As outlined above, the addition of **7** to a prochiral ketone should give rise to a set of two diastereomers (each is formed as a pair of enantiomers) which are interconverted by means of inversion of the planar chirality element of the specific ring system obtained. If the ketone employed contains one or more additional chirality elements of a given persistent conformation (such as is the case of **12**) the addition reaction could principally lead to the formation of a total of four diastereomeric products. If we take the configuration of the chirality center at the steroid carbon atom C-13 (which is bearing the angular methyl substituent) as an internal reference these four diastereomeric products **8d(A-D)** will be characterized by the configurational descriptors (13′*S*, 17′*R*, 2,3,4-*pS*) (**8d-A**), (13′*S*,17′*R*,2,3,4-*pR*) (**8d-B**), (13′*S*,17′*S*,2,3,4-*pS*) (**8d-C**), and (13′*S*,17′*S*,2,3,4-*pR*) (**8d-D**) with the newly formed chirality elements being a chiral center at the steroid carbon atom C-17 and the planar chirality of the 17-spiro-annulated metallacyclic ring system (see Scheme 2 for the *systematical* numbering scheme used).

It should be noted that the diastereomers **8d-A** and **8d-B** are only distinguished from each other by the configuration of the planar chiral ring and should therefore be interconverted by a ring topomerization. From related examples[13,14] one expects an activation barrier ($\Delta G^{\neq}$) of ≈ 16–17 kcal/mol for this process. The diastereomeric pair **8d-C** and **8d-D** would be equilibrated analogously. In contrast, the mutual interconversion of any of the complexes **8d-A,B** with **8d-C,D** would require inversion at the steroid atom C17, which is a high activation energy process with breaking of a covalent bond and thus unlikely to be observed at ordinary temperature.

The reaction of the steroid ketone **12** with **7** produced a 1:1 addition product (**8d**) which was isolated in 95% yield. The crude reaction product was recrystallized to give single crystals that were suited for an X-ray crystal structure analysis. It has turned out that the crystals contain one molecule of tetrahydrofuran per molecule of **8d**. The organometallic material consists of a single diastereoisomer. As the absolute configuration of the steroid part of the molecule was known from the steroid ketone **12** employed as a starting material, the product in the crystal was identified as being the (13′*S*,17′*R*,2,3,4-*pS*)-configurated diastereomer **8d-A**. In the crystal complex **8d-A** exhibits structural parameters of the metallacyclic nine-membered ring system that are very similar to those of **8c** and many similarly structured analogs[4,7,8,13,14,17]. In **8d-A** both zirconium-to-oxygen bonds

are short [1.924(8), 2.104(11) Å]. The bonding angles at both oxygen atoms are both above 120° [168.6(9), 168.8(8)°]. Again, the carbene moiety bound to tungsten exhibits a pronounced acyl-metal complex character [*d*-O(carbene)–C(carbene): 1.269(20) Å, angle O,C,C = 113.2(13)°].

The stereochemical assignment of the diastereomer **8d-A** implies that the angular steroid methyl group at C-13 and the C–O single bond at C-17 are oriented *cis* at the steroid five-membered ring. This means that the formal nucleophilic attack of the (π-allyl)zirconium reagent **7** at the 17-keto group of the starting material **12** has occurred *trans* with respect to the adjacent angular methyl substituent. A close inspection of the adduct complexes in solution has revealed that the bulk of the product obtained from the reaction of **12** with **7** is indeed formed very selectively.

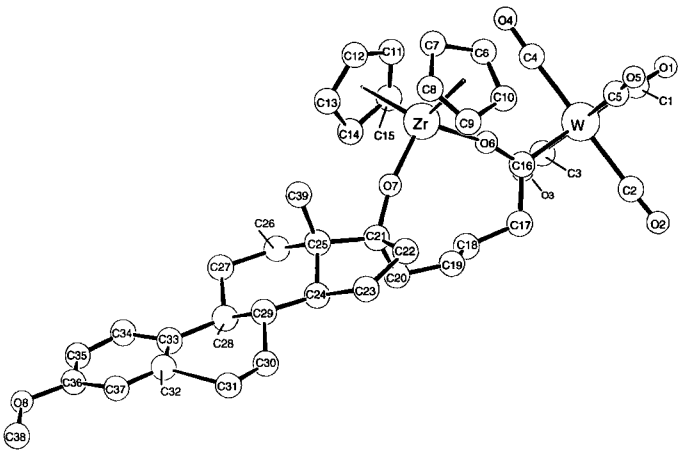
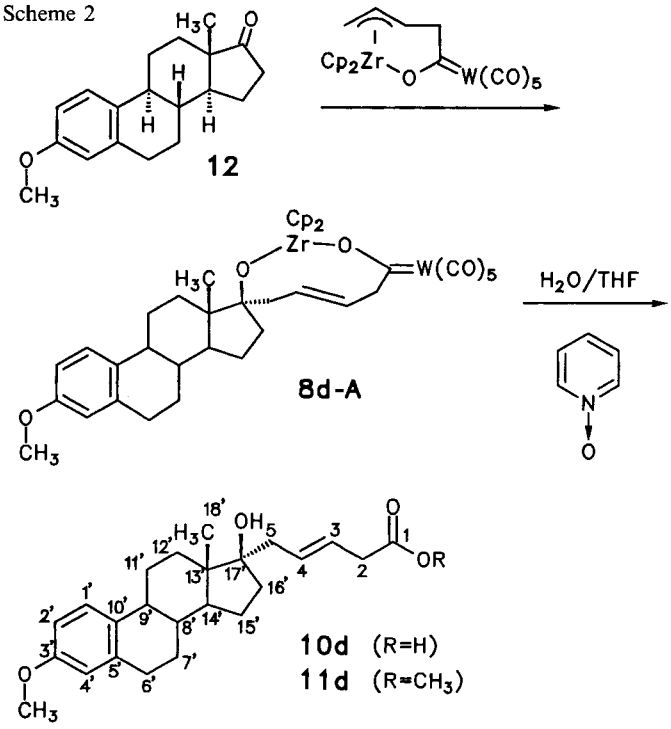



Figure 2. A view of the molecular structure of the [(zirconoxy)carbene]tungsten complex **8d-A** in the crystal (with unsystematical atom numbering scheme). Selected bond lengths [Å] and angles [°]: W–C(1) 2.052(19), W–C(2) 2.108(25), W–C(3) 2.093(22), W–C(4) 2.034(30), W–C(5) 2.052(35), W–C(16) 2.194(15), Zr–O(6) 2.104(11), Zr–O(7) 1.924(8), O(1)–C(1) 1.123(25), O(2)–C(2) 1.074(31), O(3)–C(3) 1.074(28), O(4)–C(4) 1.148(38), O(5)–C(5) 1.096(45), O(6)–C(16) 1.269(20), O(7)–C(21) 1.433(14), C(16)–C(17) 1.473(22), C(17)–C(18) 1.512(20), C(18)–C(19) 1.298(21), C(19)–C(20) 1.475(21), C(20)–C(21) 1.517(20); C(1)–W–C(16) 176.4(7), C(2)–W–C(16) 89.1(7), C(3)–W–C(16) 86.9(7), C(4)–W–C(16) 91.4(8), C(5)–W–C(16) 89.8(9), O(6)–Zr–O(7) 108.7(4), Zr–O(7)–C(21) 168.8(8), Zr–O(6)–C(16) 168.6(9), W–C(16)–C(17) 121.7(12), W–C(16)–O(6) 125.0(11), O(6)–C(16)–C(17) 113.2(13), C(18)–C(19)–C(20) 126.5(15), C(17)–C(18)–C(19) 127.4(15)

The $^1$H- and $^{13}$C-NMR spectra of a representative sample of the crude reaction product (**8d**) exhibit only a single set of resonances (e.g. δ = 6.35, 6.25/113.9, 113.0 for the cyclopentadienyl ring systems; $CDCl_3$). This immediately reveals that within the limits of the NMR detection only one of the two pairs of non-interconverting diastereomers (see above) has been formed. We then studied the $^1$H-NMR spectrum of a sample in [$D_8$]toluene at variable temperature. Only at 190 K in the 500-MHz $^1$H-NMR spectrum could we detect two additional cyclopentadienyl signals of a total of ≤2% intensity at δ = 5.89, 5.54 (under these conditions the Cp singlets of the 98% component are observed at δ = 5.77 and 5.61). We thus conclude that the addition of **7** to the 17-position of the steroid ketone **12** takes place with a very high stereoselectivity. Within the limits of the $^1$H-NMR detection the attack of the organometallic reagent takes place exclusively (i.e. >99%) from a position *trans* to the adjacent angular methyl group (at C-13). Of the two possible diastereomeric organometallic products which differ only in their configuration of the planarly chiral spiro-annulated nine-membered ring one is obtained with ≥98% selectivity under thermodynamic control. In view of the result of the X-ray crystal structure analysis, the predominant product is most likely to be assigned as the diastereoisomer **8d-A** with (13′*S*,17′*R*,2,3,4-*pS*) configuration.

Scheme 2




Hydrolysis of **8d-A** was carried out with water in tetrahydrofuran in the presence of pyridine *N*-oxide. Oxidative cleavage of the in situ liberated respective hydroxycarbene complex (**9d**) was achieved effectively. We have isolated a single diastereomer [(13′*S*,17′*R*)] of 5-[3-methoxy-17β-hydroxyestra-1,3,5(10)-trien-17α-yl]-(*E*)-pent-3-enoic acid (**10d**) in 68% yield.

These first examples show that our template carbene complex synthesis will eventually be of value for the preparation of functionalized products derived from the respective in situ generated (hydroxycarbene)metal complexes. The template synthesis is very selective in several respects: it utilizes the conjugated diene segment at the $Cp_2Zr$ unit strictly for 1,4-selective coupling. This is in contrast to other butadiene-dianion equivalents which react predominately 1,2-selectively with electrophiles[6]. In addition, coupling of the bulky [(π-allyl)zirconoxy]carbene complex reagent **7** can apparently be achieved with very high diastereoselectivities as exemplified by the reaction sequence starting from **12** as described above. The obtained "protected" nine-membered metallacyclic carbene complexes can selectively be functionalized in the α-position to the carbene ligand[7,18]. We are presently investigating whether regioselective template cou-

pling reactions can be carried out with substituted conjugated dienes at the zirconocene unit as well. This would make this type of a chain extension starting from organic carbonyl compounds an attractive method for the selective preparation of many organic target molecules.

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## Experimental

Reaction with organometallic compounds were carried out in an argon atmosphere by using Schlenk-type glassware or in a glovebox. – NMR: Bruker AC 200 P (200 MHz $^1$H; 50 MHz $^{13}$C) or Bruker AMX 500 (**8d** at variable temperature). – IR: Nicolet 5 DXC FT. – Optical rotation: Perkin-Elmer polarimeter model 241 MC, sodium vapor lamp ($\lambda = 589$ nm), ambient temperature, concentration *c* in g/100 ml. – Melting points (uncorrected): DuPont DSC 910. – Elemental analyses: Foss-Heraeus CHN-Rapid elemental analyzer. – The {[(π-allyl)zirconoxy]carbene}tungsten complex was prepared from (butadiene)zirconocene and hexacarbonyltungsten as described previously[3,13]. The nine-membered metallacycles **8a** and **8b** were synthesized as described[13,14].

*6-Hydroxy-6,6-diphenyl-(E)-hex-3-enoic Acid* (**10a**): A solution of 6.4 g (7.9 mmol) of the nine-membered metallacyclic (zirconoxy)carbene complex **8a** was dissolved in 120 ml of tetrahydrofuran. 15.6 ml (7.9 mmol) of a 0.51 M solution of pyridine *N*-oxide in tetrahydrofuran was added to the solution. Then 0.30 ml (16.7 mmol) of water was added and the mixture stirred for 2.5 h at ambient temp. Subsequently, 2 ml of water was added and all volatile components were removed in vacuo. The yellow residue was taken up in 300 ml of ether and the ether solution extracted with five 60-ml portions of a cold saturated aqueous potassium carbonate solution. The combined aqueous phases were washed with ether (3 × 100 ml) and then acidified with 2 N HCl to pH 2–3. The turbid solution was extracted with ether (5 × 100 ml). The combined organic layers were washed with brine (2 × 50 ml) and water (2 × 50 ml), then dried with sodium sulfate. The solvent was then removed in vacuo to give 1.3 g (57%) of the carboxylic acid **10a**, m.p. (DSC) 94°C. – IR (KBr): $\tilde{\nu} = 3560$, 3518, 3031, 2931, 2890, 1712, 1673, 1303, 1220, 1052, 1007, 973, 755, 700 cm$^{-1}$. – $^1$H NMR ($CDCl_3$): $\delta = 7.5-7.2$ (m, 10H, Ph), 5.69 and 5.46 (m, 2H, CH=CH), 3.06 (m, 4H, $CH_2$), OH and $CO_2H$ not observed. – $^{13}$C NMR ($CDCl_3$): $\delta = 177.1$ (C-1), 146.3 (*ipso*-C, Ph), 129.8, 128.1, 126.8, 125.9 (increased intensity) (C-3, -4 and arom. CH), 77.1 (C-6), 45.2, 37.5 (C-2, -5). – $C_{18}H_{18}O_3$ (282.3): calcd. C 76.57, H 6.43; found C 76.02, H 6.69.

*Esterification of* **10a**: A solution containing 280 mg (1.0 mmol) of **10a** in 6 ml of methanol/water (10:1) was treated with 1.25 ml (1.0 mmol) of an ethereal diazomethane solution and then stirred for 30 min at ambient temp. Volatile components were removed in vacuo, and the residue was dissolved in 10 ml of ether. The ether solution was washed twice with 2 ml of 2 N aqueous NaOH and water and then dried with magnesium sulfate. The solvent was removed in vacuo to yield 260 mg (88%) of **11a** as a white solid, m.p. (DSC) 75°C. – IR (KBr): $\tilde{\nu} = 3466$, 1718, 1438, 1364, 1317, 1207, 1193, 1174, 1064, 1014, 972, 746, 706, 695, 641, 617, 545 cm$^{-1}$. – $^1$H NMR ($CDCl_3$): $\delta = 7.5-7.2$ (m, 10H, Ph), 5.75 and 5.42 (m, 2H, CH=CH), 3.66 (s, 3H, $OCH_3$), 3.07 and 3.00 (m, 4H, $CH_2$). – $^{13}$C NMR ($CDCl_3$): $\delta = 172.0$ (C-1), 146.6 (*ipso*-C, Ph), 129.3, 127.7, 128.1, 126.8, 126.0 (C-4, -3, arom. CH), 51.8 ($OCH_3$), 45.3, 37.7 (C-2, -5), C-6 not observed. – $C_{19}H_{20}O_3$ (296.4): calcd. C 77.00, H 6.80; found C 77.19, H 6.78.

*6-Hydroxy-6-methyl-(3E)-octa-3,7-dienoic Acid* (**10b**): The carbene complex **8b** (5.8 g, 8.3 mmol) was dissolved in 80 ml of tetrahydrofuran. Then 16.3 ml (8.3 mmol) of a 0.51 M tetrahydrofuran solution of pyridine *N*-oxide was added to the obtained solution, subsequently 0.3 ml (16.7 mmol) of water, and the resulting mixture was stirred for 2.5 h at ambient temp. To the yellow solution was added an additional ml of $H_2O$, and all volatile products were removed in vacuo at room temp. The resulting yellow solid was taken up in ether (100 ml) and the acid extracted with five 50-ml portions of a saturated $NaHCO_3$ solution. After washing with ether (3 × 20 ml) the carboxylic acid was liberated with 2 N HCl at pH 2–3. The product was extracted into ether (5 × 50 ml). The ethereal solution was washed with brine (2 × 50 ml) and water (2 × 50 ml), then dried with $MgSO_4$. The solvent was removed in vacuo to give 680 mg (48%) of **10b** as a yellow oil. Treatment of 470 mg of **10b** with diazomethane as described above yielded 430 mg (86%) of the ester **11b** as a slightly yellowish oil.

**10b**: IR (NaCl): $\tilde{\nu} = 3400$, 2978, 1713, 1411, 1286, 1223, 1179, 973, 925 cm$^{-1}$. – $^1$H NMR ($CDCl_3$): $\delta = 7.0-6.5$ (br. s, 2H, OH), 5.84, 5.13, 4.98 (ABX, 3H, 7-, 8-H), 5.52 (m, 2H, 3-, 4-H), 3.00, 2.19 (m, 2H each, 2-, 5-H), 1.20 (s, 3H, $CH_3$). – $^{13}$C NMR ($CDCl_3$): $\delta = 176.6$ (C-1), 144.7, 129.6, 125.5, 112.1 (C-7, -4, -3, -8), 73.0 (C-6), 45.1, 37.6 (C-2, -5), 26.9 ($CH_3$). – $C_9H_{14}O_3$ (170.2): calcd. C 63.51, H 8.29; found C 62.80, H 8.22.

**11b**: IR (NaCl): $\tilde{\nu} = 3470$, 2977, 2955, 1740, 1437, 1411, 1361, 1310, 1259, 1168, 1120, 996, 974, 923, 691 cm$^{-1}$. – $^1$H NMR ($CDCl_3$): $\delta = 5.86$, 5.14, 4.99 (ABX, 3H, 7-, 8-H), 5.54 (m, 2H, 3-, 4-H), 3.62 (s, 3H, $OCH_3$), 3.01, 2.23 (m, 2H each, 2-, 5-H), 1.93 (br. s, 1H, OH), 1.21 (s, 3H, $CH_3$). – $^{13}$C NMR ($CDCl_3$): $\delta = 172.2$ (C-1), 144.7, 129.5, 126.0, 111.9 (C-7, -4, -3, -8), 72.4 (C-6), 51.8 ($OCH_3$), 45.3, 37.7 (C-2, -5), 27.8 ($CH_3$). – $C_{10}H_{16}O_3$ (184.2): calcd. C 65.19, H 8.75; found C 65.16, H 8.75.

*Reaction of the {[(π-Allyl)zirconoxy]carbene}tungsten Complex* **7** *with Cyclopentanone:* Complex **7** (4.3 g, 6.8 mmol) was suspended in 80 ml of toluene; then 0.6 ml (6.8 mmol) of cyclopentanone was added to the suspension and the mixture stirred for 24 h at ambient temp. The yellow mixture was filtered and the filtrate kept for 2 d at −18°C. Large crystals of **8c** were obtained [1.9 g, m.p. (DSC): 174°C; this product was used for the X-ray crystal structure analysis, for details see Table 1]. The solvent was removed from the mother liquor in vacuo. The remaining solid was washed with pentane (2 × 50 ml) and dried in vacuo: total yield of **8c**: 4.2 g (87%). – IR (KBr): $\tilde{\nu} = 3030$, 2924, 2058, 1975, 1909, 1885, 1427, 1035, 1014, 811 cm$^{-1}$. – $^1$H NMR ($CDCl_3$): $\delta = 6.30$, 6.24 (s, 5H each, Cp), 4.97 (m, 2H, CH=CH), 4.56, 3.00 (m, 2H, W=C$CH_2$), 2.14 (m, 2H, =CH$CH_2$), 1.8–1.5 (m, 8H, $[CH_2]_4$). – $^{13}$C NMR ($CDCl_3$): $\delta = 332.6$ (carbene-C), 204.8 (*trans*-CO), 199.7 (*cis*-CO), 133.1, 126.9 (CH=CH), 113.3, 113.0 (Cp), 94.9 (quart. C), 71.7 (W=C−$CH_2$), 46.8 (=CH−$CH_2$), 41.6, 37.8, 24.0, 23.6 ($[CH_2]_4$). – $C_{25}H_{24}O_7WZr$ (711.5): calcd. C 42.20, H 3.40; found C 42.47, H 3.44.

*5-(1-Hydroxycyclopentyl)-(E)-pent-3-enoic Acid* (**10c**): The carbene complex **8c** (7.7 g, 10.8 mmol) was dissolved in 200 ml of tetrahydrofuran. The solution was charged with 21.2 ml of a 0.51 M pyridine *N*-oxide solution (10.8 mmol) in tetrahydrofuran. Water (0.4 ml, 22.2 mmol) was added and the reaction mixture stirred for 2.5 h at ambient temp. Then 2 ml of water was added, and the volatile products were removed in vacuo. The yellow residue was taken up in 300 ml of ether, then 40 ml of 2 N aqueous HCl was added to the solution and the organic phase separated. The aqueous layer was extracted with additional 100 ml of ether. The combined

organic phases were extracted with four 70-ml portions of a saturated $NaHCO_3$ solution. The aqueous extract was washed with ether (3 × 30 ml) and then acidified with 2 N HCl to pH 2–3. The product was extracted with ether (3 × 100 ml), the combined extracts were washed with brine (3 × 10 ml) and water (3 × 10 ml), then dried with sodium sulfate. The solvent was removed in vacuo to yield the carboxylic acid **10c** (1.2 g, 62%) as a slightly yellowish oil. – IR (NaCl): $\tilde{\nu}$ = 3404, 3038, 2960, 2875, 1711, 1430, 1282, 1202, 1192, 973, 908, 883, 667 $cm^{-1}$. – $^1H$ NMR ($CDCl_3$): δ = 7.2–6.7 (br. s, 2H, OH), 5.58 (m, 2H, 3-, 4-H), 3.03, 2.27 (m, 2H each, $=CHCH_2$), 1.8–1.4 (m, 8H, $[CH_2]_4$). – $^{13}C$ NMR ($CDCl_3$): δ = 176.6 (C-1), 130.6, 125.2 (C-4, -3), 82.1 (quart. C), 44.1, 39.1 (double intensity), 37.7, 23.7 (double intensity, $CH_2$). – $C_{10}H_{16}O_3$ (184.2): calcd. C 65.19, H 8.75; found C 64.36, H 8.73.

The acid **10c** was purified by esterification analogously as described above. Treatment of 250 mg (1.4 mmol) of **10c** with ethereal diazomethane gave 230 mg (85%) of the ester **11c** as an oil. – IR (NaCl): $\tilde{\nu}$ = 3440, 2956, 2873, 1740, 1437, 1274, 1198, 1170, 973, 882 $cm^{-1}$. – $^1H$ NMR ($CDCl_3$): δ = 5.62 (m, 2H, 3-, 4-H), 3.65 (s, 3H, $OCH_3$), 3.04, 2.28 (m, 2H each, 2-, 5-H), 1.7 (s, 1H, OH), 1.9–1.4 (m, 8H, $[CH_2]_4$). – $^{13}C$ NMR ($CDCl_3$): δ = 172.3 (C-1), 130.5, 125.4 (C-4, -3), 81.4 (quart. C), 51.8 ($OCH_3$), 44.3, 39.3 (double intensity), 37.8, 23.8 (double intensity, $CH_2$). – $C_{11}H_{18}O_3$ (198.3): calcd. C 66.64, H 9.15; found C 66.06, H 9.12.

*Reaction of the {[(π-Allyl)zirconoxy]carbene}tungsten Complex* **7** *with 3-Methoxyestra-1,3,5(10)-trien-17-one* (**12**): To a suspension of 4.6 g (7.3 mmol) of **7** in 180 ml of toluene was added 2.1 g (7.4 mmol) of **12**. The mixture was stirred for 24 h at room temp. A small amount of a precipitate was removed by filtration and the solvent distilled from the filtrate in vacuo. The resulting yellow precipitate was washed with pentane (2 × 50 ml) and then dried in vacuo to give 6.4 g (95%) of **8d**, m.p. (DSC) 209°C (dec.). – $C_{39}H_{40}O_8WZr$ (911.7): calcd. C 50.38, H 4.42; found C 50.94, H 4.32.

The product was recrystallized from tetrahydrofuran to give crystals of **8d-A** · THF that were suited for the X-ray crystal structure analysis. – IR (KBr): $\tilde{\nu}$ = 3100, 2924, 2886, 2060, 1969, 1938, 1901, 1420, 1391, 1249, 1079, 972, 803 $cm^{-1}$. – $^1H$ NMR ($CDCl_3$): δ = 7.22, 6.73, 6.65 (m, 3H, arom. H), 6.35, 6.25 (s, 5H each, Cp), 5.3–4.8 (m, 2H, CH=CH), 4.56, 3.06 (m, 2H, metallacyclic $W=CCH_2$), 3.79 (s, 3H, $OCH_3$), 2.86 and 2.4–1.2 (m, 17H, ring CH and $CH_2$), 0.86 (s, 3H, $CH_3$), tetrahydrofuran resonances appear at δ = 3.7 and 1.8. – $^{13}C$ NMR ($CDCl_3$): δ = 331.6 (carbene C), 204.8 (*trans*-CO), 199.6 (*cis*-CO), 133.5, 127.0 (metallacyclic CH=CH), 157.6, 137.9, 132.4, 126.1, 116.0, 111.5 (arom. C), 113.9, 113.0 (Cp), 97.8 (quart. C metallacycle), 55.2 ($OCH_3$), 71.7, 49.5, 49.0, 47.1, 43.7, 41.0, 39.7, 32.8, 32.3, 29.8, 27.4, 26.5, 23.0 (CH and $CH_2$, steroid and metallacycle), 15.3 ($CH_3$). – $C_{39}H_{40}O_8WZr \cdot C_4H_8O$ (983.8): calcd. C 52.50, H 4.92; found C 52.29, H 5.07.

*X-Ray Crystal Structure Analyses of* **8c** *and* **8d-A**[19]: Crystallographic data are collected in Table 1. Crystals were mounted in nitrogen-filled capillary tubes and photographically characterized. **8c** was found to possess 2/*m* Laue symmetry and systematic absences consistent with the space group $P2_1/c$, and **8d-A** possessed *mmm* symmetry and was uniquely assigned to $P2_12_12$. To determine the correct hand for **8d-A**, a Roger test which refines a multiplicative factor for $\Delta f''$ was performed. For the hand reported the factor was 1.05(3). Both data sets were corrected for absorption effects by empirical methods. Patterson maps were used to obtain the locations of the W and Zr atoms. All non-hydrogen atoms were refined anisotropically (except for the carbon atoms of the THF solvent molecule in **8d-A** which were treated isotropically); hydrogen atoms were treated as idealized contributions. All calculations used SHELXTL-PC (ver 4.2) software (G. Sheldrick, Siemens XRD, Madison, WI).

*5-[3-Methoxy-17β-hydroxyestra-1,3,5(10)-trien-17α-yl]-(E)-pent-3-enoic Acid* (**10d**): To a solution of 1.6 g (1.7 mmol) of the carbene complex **8d** in 60 ml of tetrahydrofuran were added 3.4 ml of a 0.51 M pyridine *N*-oxide solution (1.7 mmol) in tetrahydrofuran and then 65 µl (3.6 mmol) of water. The yellow-orange solution was stirred for 2.5 h at room temp. Then 1 ml of water was added and the solvent removed in vacuo. The resulting yellow solid was dissolved in 200 ml of ether and the solution extracted with a saturated aqueous potassium carbonate solution (5 × 50 ml). The combined aqueous phases were washed with ether (2 × 50 ml) and acidified with 2 N HCl to pH 2, then extracted with ether (5 × 50 ml). The combined organic solutions were washed with brine (2 × 20 ml) and water (2 × 20 ml) and subsequently dried with sodium sulfate. The solvent was removed in vacuo and the product obtained as a white solid; yield: 450 mg (68%), m.p. (DSC) 146°C, $[\alpha]_D$ = +42.3 (*c* = 0.52, $CH_2Cl_2$). – IR (KBr): $\tilde{\nu}$ = 3445, 2938, 2868, 1713, 1612, 1504, 1451, 1380, 1322, 1308, 1303, 1284, 1255, 1182, 1162, 1109, 1039, 1024, 1011, 970, 844 $cm^{-1}$. – $^1H$ NMR ($CDCl_3$): δ = 7.18, 6.68, 6.61 (m, 3H, arom. H), 5.72 (m, 2H, 3-, 4-H), 3.76 (s, 3H, $OCH_3$), 3.13 (m, 2H, 2-H), 2.81, 2.4–1.2 (m, 17H, 5-H, steroid CH and $CH_2$), 0.90 (s, 3H, $CH_3$), OH's not observed. – $^{13}C$ NMR ($CDCl_3$): δ = 177.0 ($CO_2H$), 131.1, 125.6 (C-4, -3), 157.4, 137.9, 132.6, 126.2, 113.8, 111.4 (arom. C), 55.2 ($OCH_3$), 82.9, 68.2, 49.6, 43.8, 39.6, 46.5, 40.3, 37.7, 31.7, 29.7, 27.5, 26.3, 23.4 (C-5, -2, steroid CH and $CH_2$), 14.3 ($CH_3$). – $C_{24}H_{32}O_4$ (384.5): calcd. C 74.97, H 8.39; found C 75.28, H 8.37.

Esterification of a sample of **10d** (85 mg, 0.22 mmol) with ethereal diazomethane was carried out analogously as described above to yield 63 mg (72%) of **11d**, m.p. (DSC) 101°C, $[\alpha]_D$ = +37.2 (*c* = 0.51, $CH_2Cl_2$). – IR (KBr): $\tilde{\nu}$ = 3530, 2978, 2967, 2872, 1724, 1613, 1506, 1441, 1256, 1209, 1040, 1012, 970, 844, 823, 788 $cm^{-1}$. – $^1H$-NMR ($CDCl_3$): δ = 7.19, 6.68, 6.61 (m, 3H, arom. H), 5.71 (m, 2H, 4-, 3-H), 3.76, 3.67 (s, each 3H, $OCH_3$), 3.10 (m, 2H, 2-H), 2.81, 2.4–1.2 (m, 17H, 5-H, steroid CH and $CH_2$), 0.90 (s, 3H, $CH_3$); OH not observed. – $^{13}C$ NMR ($CDCl_3$): δ = 172.3 ($CO_2H$), 130.8, 125.3 (C-4, -3), 157.5, 138.0, 132.7, 126.3, 113.9, 111.5 (arom. C), 55.2, 51.8 ($OCH_3$), 82.7, 49.7, 46.6, 43.8, 40.3, 39.7, 38.0, 35.0, 31.8, 29.8, 27.5, 26.3, 23.5 (C-5, -2, steroid CH and $CH_2$), 14.3 ($CH_3$). – $C_{25}H_{34}O_4$ (398.5): calcd. C 75.34, H 8.60; found C 74.26, H 8.27.

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[19] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57167, the names of the authors, and the journal citation.

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