

Regioselective Synthesis of Substituted *o*-Alkoxyphenol Derivatives through Thermal Benzannulation of Fischer (Alkenylcyclobutenyl)carbene Complexes

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A convenient, regioselective, and general synthetic method for producing highly substituted *o*-phenol-containing polycycles from Fischer (alkenylcyclobutenyl)carbene complexes has been described. The starting complexes have been synthesized by means of the [2 + 2] cycloaddition reaction of (alkenylethynyl)carbene complexes and a range of enol ethers, and in most cases, they have proven to be stable at room temperature and therefore isolable. The key step of the synthesis consists of the thermal benzannulation reaction of these novel pentacarbonyl dienyl Fischer complexes, which is an unprecedented transformation for these kinds of complexes. The unexpected behavior of (alkenylcyclobutenyl)carbene complexes has been rationalized in terms of their geometries.

Introduction

Substituted and fused phenols are commonly observed structural units in many natural products,¹ which has resulted in the development of several synthetic approaches to these compounds over the past several decades. The lack of regioselectivity shown by the classical methodologies involving the transformation of phenolic precursors² has been conveniently overcome by novel procedures that are based on selective annulations of acyclic starting materials.³ In this context, Diels–Alder⁴ and several other transition-metal-catalyzed cycloaddition reactions,⁵ Robinson annulations,⁶ electrocyclizations of dienylketene intermediates,⁷ or cycloaromatizations⁸ should be pointed out as convenient and widely employed routes to substituted phenols.

The coupling reaction of Fischer α,β -unsaturated complexes and alkynes (Dötz reaction) provides another particularly noteworthy annulation reaction leading to phenol derivatives.⁹ The process involves the initial insertion of the alkyne molecule in the metal–carbon double bond to produce unstable dienylcarbene complex intermediates (also known as metallahexatrienes) that finally afford *p*-alkoxyphenols by successive CO insertion and electrocyclization.¹⁰ Given that the process is initiated by the thermally or photochemically promoted dissociation of a CO ligand in the metal coordination sphere, the resulting dienyl complexes are coordinatively unsaturated tetracarbonyl species (Scheme 1).

Pentacarbonyl analogues to the above-mentioned intermediates of the Dötz reaction have also been described. These systems are accessible by several synthetic routes and have proven to be potentially interesting substrates for organic synthesis since they undergo selective and high-yielding transformations in mild conditions.¹¹ The photochemically driven benzannulation reaction of chromium dienylcarbene complexes is one of the most distinctive processes of pentacarbonylmetallahexatrienes and

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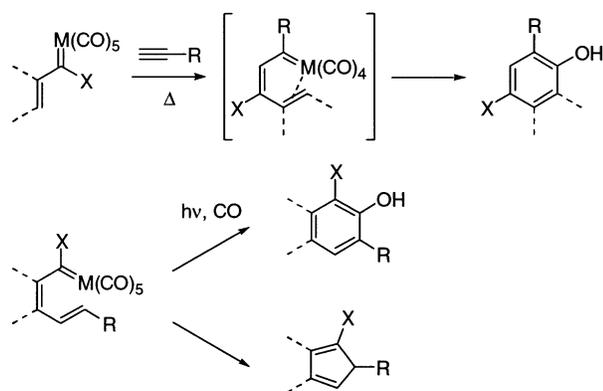
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SCHEME 1



provides another synthetic route to phenol derivatives (*o*-alkoxy-substituted, in this case). However, complexes in which one or both double bonds belong to aromatic rings have mostly been employed as starting materials.¹² *cis*-Metallahexatrienes in which none of the conjugated double bonds are contained in an aromatic ring exhibit much lower thermal stability and have to be isolated, in those cases in which this is possible, at low temperature. Cyclopentannulation is the most characteristic and commonly observed evolution path for this kind of metallahexatriene (Scheme 1).¹³

In the course of the investigation of the reactivity of Fischer (alkenylethynyl)carbene complexes toward 2-amino-1,3-butadienes, we discovered a cascade double or triple tandem ([4 + 2] cycloaddition–cyclopentannulation) process involving unstable metallahexatrienes derived from the initial [4 + 2] cycloaddition and therefore containing a cyclohexene moiety in their structure.¹⁴ We decided to extend this methodology to the preparation of polycycles starting from cyclobutene-containing dienyl complexes, but [2 + 2] cycloadducts, arising from the reaction of (alkenylethynyl)carbene complexes and cyclic enol ethers, were unreactive at room temperature. Instead of cyclopentannulation, these adducts underwent benzannulation when they were heated, thus giving rise to *o*-alkoxyphenol derivatives in a completely regioselective fashion and with good yields.¹⁵

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SCHEME 2

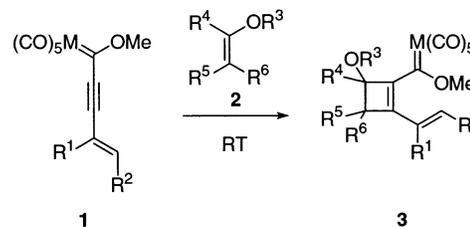


TABLE 1. Generalization of the Carbene Complex. Synthesis of 1-Metalla-1,3,5-hexatrienes **3a–m**

entry	1	M	R ¹	R ²	2	3	<i>t</i> (h)	conversn (%)	yield (%)
1	1a	W	Me	Ph	2a	3a	72	100	64
2	1b	Cr	Me	Ph	2a	3b	24	100	83
3	1c	W	Me	–CH ₂ CH ₂ CH ₂ –	2a	3c	12	100	85
4	1d	Cr	Me	–CH ₂ CH ₂ CH ₂ –	2a	3d	4	100	93
5	1e	Cr	Me	–CH ₂ CH ₂ CH ₂ CH ₂ –	2a	3e	12	100	60
6	1f	W	Me	H	2b	3f	5	100	79
7	1a	W	Me	Ph	2b	3g	24	100	87
8	1b	Cr	Me	Ph	2b	3h	120	77	52
9	1g	Cr	H	Ph	2b	3i	144	71	64
10	1c	W	Me	–CH ₂ CH ₂ CH ₂ –	2b	3j	48	100	58
11	1d	Cr	Me	–CH ₂ CH ₂ CH ₂ –	2b	3k	72	85	88
12	1e	Cr	Me	–CH ₂ CH ₂ CH ₂ CH ₂ –	2b	3l	72	69	50
13	1h	Cr	Me	–CH ₂ OAll ^a	2b	3m	48	52	79

^a All = CH₂CH=CH₂.

We envisioned the potential usefulness of this methodology for the synthesis of fused substituted phenol derivatives, and therefore, in this paper, we report the comprehensive study carried out to establish the generality and limitations of both the synthesis of stable cyclobutene-containing metallahexatrienes and their thermal benzannulation. In addition, we have carried out the transformation of the synthesized *o*-alkoxyphenol derivatives into the corresponding catechols, and proposed a rationalization for the odd behavior of these novel metallahexatrienes.

Results and Discussion

Preparation of Alkenylcyclobutenyl(alkoxy)carbene Complexes. The enol ethers initially chosen for the synthesis of (alkenylcyclobutenyl)carbene complexes were commercially available 2,3-dihydrofuran (**2a**) and 3,4-dihydro-2*H*-pyran (**2b**), given that the latter was known to undergo [2 + 2] cycloaddition to Fischer alkynyl complexes.¹⁶ According to the general procedure described in the literature for this type of process, reactions of (alkenylethynyl)carbene complexes **1** and enol ethers **2a** and **2b** were performed at room temperature, under a nitrogen atmosphere, and using an excess of olefin as solvent (Scheme 2, Table 1). Metallahexatrienes **3a–m** were obtained as single products in moderate to good yields and purified by column chromatography. In all the cases studied, compounds **3a–m** were stable at room temperature, which seemed surprising since dienylcarbene complexes arising from complexes **1**, either by [4 +

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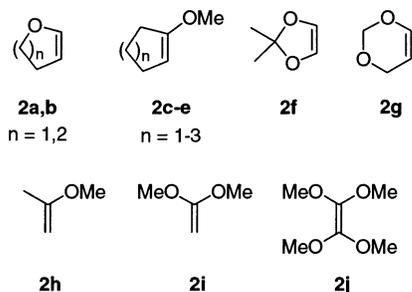


FIGURE 1.

2] cycloaddition with 1,3-butadienes or from addition of nucleophiles to their β -position, had never been isolated at such a temperature due to their fast transformation into cyclopentadiene derivatives under the reaction conditions.^{13h-1,14}

Complexes **3a–m** were obtained in typically long reaction times; in some cases, it was not possible to reach total conversion of the starting material even after the reaction mixture was stirred for several days (Table 1, entries 8, 9, and 11–14). As indicated in Table 1, cycloadditions were faster and proceeded to completion when 2,3-dihydrofuran was employed (Table 1, entries 1–5). The use of tungsten starting complexes led to total conversion in those cases in which the olefin was 3,4-dihydro-2*H*-pyran (Table 1, entries 6, 7, and 10), which was the only noticeable influence of the metal in the cycloaddition process. The structures of compounds **3** were assigned on the basis of their ¹H NMR and ¹³C NMR spectra, and the stereoselectivity in the formation of the fused cycles was determined to be *cis* by NOE experiments on compound **3j**.

Once it had been established that this methodology enabled the introduction of a wide range of substituents in the terminal double bonds of metallahexatrienes **3**, by changing alkynyl complexes **1**, we investigated the generality of the process concerning the enol ether, by testing the reaction of systems **2c–j** depicted in Figure 1 with carbene complexes **1**. Cycloadditions were carried out in the same experimental conditions described above with the exception of that involving 1,1-dimethoxyethene (**2i**), which was performed in a solution of dichloromethane because it was too exothermic to be carried out neat (Scheme 2, Table 2, entry 10). When cyclic enol ethers were employed, the process was again more favored for five-membered systems than for their six-membered analogues (Table 2, entries 2, 3, 7, and 8). Actually, it was necessary to use tungsten alkynyl complexes to accomplish the preparation of metallatrienes derived from alkenes **2d** and **2g** (Table 2, entries 3 and 8).

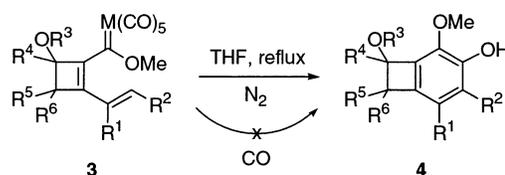
All cycloadducts **3n–y**, the same as previously described compounds **3a–m**, were isolated in moderate to high yields by flash chromatography and were found to be stable at room temperature, excluding **3w**, resulting from the reaction of **1d** and **2i**, which decomposed under the standard purification conditions and had to be directly used in the next reaction step (Table 1, entry 10). The best results were observed when 1,1,2,2-tetramethoxyethene (**2j**) was used, given that very good yields of stable metallahexatrienes **3x,y** were achieved in short reaction times (Table 2, entries 11 and 12).¹⁷

TABLE 2. Generalization of the Enol Ether. Synthesis of 1-Metalla-1,3,5-hexatrienes **3n–y**

entry	1	M	R ¹	R ²	2	3	<i>t</i> (h)	yield ^a (%)
1	1b	Cr	Me	Ph	2c	3n	48	68
2	1d	Cr	–CH ₂ CH ₂ CH ₂ –	Ph	2c	3o	48	80
3	1c	W	–CH ₂ CH ₂ CH ₂ –	Ph	2d	3p	48	66
4	1c	W	–CH ₂ CH ₂ CH ₂ –	Ph	2e	3q	12	82
5	1d	Cr	–CH ₂ CH ₂ CH ₂ –	Ph	2e	3r	6	77
6	1b	Cr	Me	Ph	2f	3s	9	67
7	1d	Cr	–CH ₂ CH ₂ CH ₂ –	Ph	2f	3t	3	78
8	1c	W	–CH ₂ CH ₂ CH ₂ –	Ph	2g	3u	72	58 ^b
9	1d	Cr	–CH ₂ CH ₂ CH ₂ –	Ph	2h	3v	6	68
10	1d	Cr	–CH ₂ CH ₂ CH ₂ –	Ph	2i	3w	12	^c
11	1b	Cr	Me	Ph	2j	3x	12	93
12	1d	Cr	–CH ₂ CH ₂ CH ₂ –	Ph	2j	3y	3	98

^a Conversion = 100%. ^b Conversion = 50%. ^c Reaction carried out in dichloromethane (concentration of **1d** 0.1 M); the cycloadduct could not be isolated and had to be directly used in the following step.

SCHEME 3



Thermal Reactivity of Alkenylcyclobutenyl(al-koxy)carbene Complexes. Synthesis of *o*-Methoxyphenol Derivatives. In a preliminary experiment, solutions of compounds **3j** and **3k** in tetrahydrofuran (THF) were refluxed until complete disappearance of the starting complex, and unexpectedly, *o*-methoxyphenol derivative **4g**, the structure of which was elucidated on the basis of its ¹H NMR and ¹³C NMR analyses, was obtained after conventional workup of the reactions (Scheme 3, Table 3, entries 9 and 10). The process involves a CO insertion followed by cyclization, and therefore, it is very closely related to the known photochemical benzannulation of chromium dienylcarbene complexes that leads to the same aromatic compounds (with regiochemistry complementary to that of the compounds obtained by the Dötz reaction).¹² However, this result constitutes the first example of a thermal benzannulation reaction of a pentacarbonyl(alkoxy)metallatriene described in the literature.^{15,18}

Complexes **3** were heated in the same experimental conditions, furnishing polycycles **4** as major products in most cases (Scheme 3, Table 3). A range of solvents could be used in the benzannulation reaction, but the best results were obtained in refluxing THF. As shown in Table 4, when solutions of metallatriene **3j** or **3k** in THF were heated at lower temperatures than the boiling point

(17) The use of **2j** in the [2 + 2] cycloaddition reaction of Fischer carbene complexes has been previously reported: Camps, F.; Llebaria, A.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Tetrahedron Lett.* **1990**, *31*, 2479.

(18) Thermal benzannulation of a tetracarbonyl-1,4,5- η^3 -dienylcarbene complex has been previously observed: Barluenga, J.; Aznar, F.; Gutiérrez, I.; Martín, A.; García-Granda, S.; Llorca-Baragaño, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 1314. Other examples of thermal benzannulation of pentacarbonyldienylcarbene complexes were reported after the preliminary communication of this work: (a) Wu, H. P.; Aumann, R.; Fröhlich, R.; Wibbeling, B. *Eur. J. Org. Chem.* **2000**, 1183. (b) Mathur, P.; Ghosh, S.; Sarkar, A.; Rheingold, A. L.; Guzei, I. *Tetrahedron* **2000**, *56*, 4995.

TABLE 3. Thermal Benzannulation of Metallahexatrienes 3. Synthesis of Phenol Derivatives 4

entry	complex	4	<i>t</i> ^a (h)	yield ^a (%)
1	3a	4a	12	89
2	3b	4a	7	72
3	3c	4b	9	77
4	3d	4b	4	56
5	3e	4c	6	46
6	3f	4d	9	79
7	3g	4e	12	60
8	3h	4e	6	55
8	3i	4f	7 (12)	56 (32)
9	3j	4g	9 (20)	59 (58)
10	3k	4g	8 (12)	72 (26)
11	3l	4h	9 (12)	69 (44)
12	3m	4i	3	77
13	3n	4j	2	90
14	3o	4k	3	95
15	3p	4l	9	70
16	3q	4m	12	83
17	3r	4m	3	90
18	3s	4n	6	72
19	3t	4o	4	67
20	3u	4p	6	65
21	3v	4q	8	72

^a Data in parentheses refer to the reactions carried out without nitrogen purge.

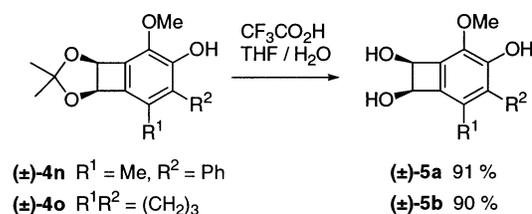
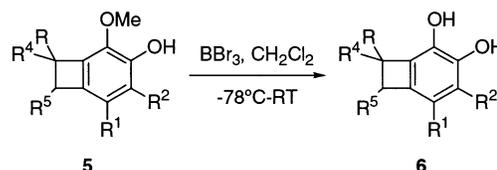
TABLE 4. Effect of the Solvent and Temperature^a

reaction conditions	3j		3k	
	yield (%)	<i>t</i> (h)	yield (%)	<i>t</i> (h)
THF, reflux	58	20	26	12
THF, 40 °C	15	48	20	28
hexane, reflux	19	48	25	24
MeCN, 65 °C	32	10	25	8

^a Yields of compound 4g isolated after total conversion of the starting complexes. The reaction times also refer to total conversion of the starting materials.

of THF, a noticeable increase in the reaction times, which implied partial decomposition of the starting complex, was observed. The use of a nonpolar solvent, such as hexane, led to the same results. However, in the more coordinating solvent acetonitrile, even though the disappearance of the starting material was slightly accelerated, a larger amount of byproducts was obtained, thus diminishing the efficiency of the process.

It has already been remarked that tetracarbonyl- and pentacarbonylmetallahexatrienes usually show different reactivity, and consequently, the behavior of dienylocarbene complexes is expected to be strongly influenced by the presence or absence of CO in the reacting mixture. With the aim of determining the effect of CO on these cyclization reactions, we heated complex 3k under a CO atmosphere, finding that most of the initial carbene complex was recovered unaltered after 9 days at 60 °C. On the other hand, when reactions were carried under a purge of nitrogen, shorter reaction times were needed, providing better yields of phenols 4 (Scheme 3, Table 3, entries 8–11). According to data displayed in Table 3, corresponding to reactions performed in the optimized conditions, metallahexatrienes arising from the cycloaddition of complexes 1 and enol ethers 2a–h underwent the benzannulation process, giving rise to phenol derivatives 4. However, complexes 3w–y, derived from ketene

SCHEME 4**SCHEME 5**

acetals 2i and 2j, decomposed when treated in the same conditions. Although both chromium and tungsten complexes provided entry to the same compounds 4, the latter required longer reaction times to be totally consumed, probably due to their higher stability (Table 3, entries 1–4, 9, and 10).

Complexes 3s and 3t bearing a dioxol moiety in their structure were particularly interesting substrates to perform the benzannulation, given that the deprotection of the acetal functionality in the final aromatic compounds 4n and 4o gave entry to 1,2-diols, which could be further modified. The hydrolysis of the acetal group was carried out with trifluoroacetic acid (TFA) in THF, and compounds 5 were obtained with high yields (Scheme 4).

We finally focused our attention on the preparation of the final products 4 in a one-pot process from alkynyl complexes 1 and enol ethers 2. The refluxing of a solution of 1 and different proportions of 2 in THF under a purge of nitrogen only afforded complex mixtures of products resulting from undesirable lateral thermal processes. However, the purification of metallahexatrienes 3 could be achieved by simple removal of the excess enol ether, once the cycloadduct was formed, followed by addition of THF and heating in the standard conditions. Polycycle 4g was synthesized by this procedure in a 48% or 51% overall yield, starting from chromium or tungsten complexes, respectively.

Synthesis of Catechol Derivatives. Preparation and Reactivity of Allyloxy- and Benzyloxy(alkynyl)-carbene Complexes. We envisioned that the synthetic potential of this methodology leading to phenols could be enhanced by removal of the methyl moiety in the final products, given that highly substituted catechols would be obtained in a regioselective manner. With that purpose, some compounds 4 were treated with boron tribromide according to the methodology described in the literature,¹⁹ and the desired diols 6 were isolated as single products in high yields (Scheme 5, Table 5). In those cases in which additional methyl ethers were present in the substrates, the treatment with boron tribromide led to the deprotection of all of them, furnishing triol systems (Table 5, entries 5 and 6). The structures of all catechol

(19) Demuyneck, M.; Clercq, P.; Vandewalle, M. *J. Org. Chem.* **1979**, *26*, 4863.

TABLE 5. Synthesis of Catechol Derivatives 6

entry	4	R ³	R ⁴	R ⁵	6	R	yield (%)
1	4a	H	O(CH ₂) ₂		6a	H	93
2	4b	H	O(CH ₂) ₂		6b	H	93
3	4e	H	O(CH ₂) ₃		6c	H	94
4	4f	H	O(CH ₂) ₃		6d	H	88
5	4j	OMe	(CH ₂) ₃		6e	OH	95

SCHEME 6

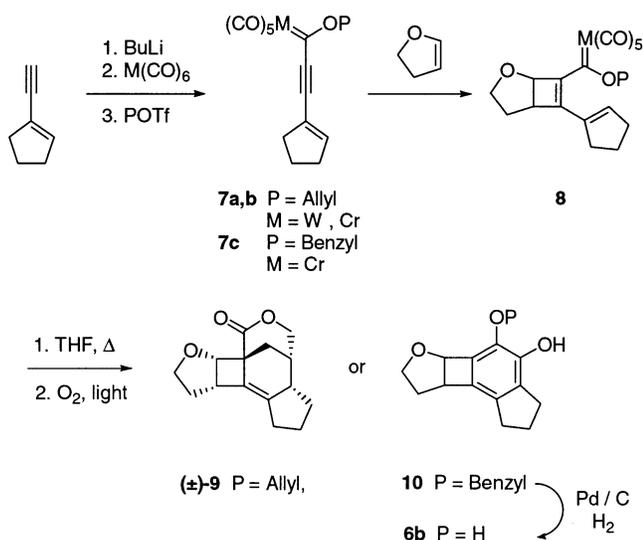


TABLE 6. Synthesis and Reactivity of Allyloxy- and Benzyloxycarbene Complexes 7

entry	7	M	P	yield (%)	8	yield (%)	product	yield (%)
1	7a	W	allyl	59	8a	97	9	49 ^a
2	7b	Cr	allyl	77	8b	79	9	55 ^a
3	7c	Cr	benzyl	<i>b</i>	8c	<i>b</i>	10 ^c	37 ^d

^a Reactions performed in a CO atmosphere. When carbene complex **8b** was heated under nitrogen purge, the yield of **9** was 41%. ^b Not isolable. ^c **10** was transformed into **6b** by hydrogenolysis (98%). ^d Yield of the overall process from crude complex **7c**.

derivatives **6** were determined by analysis of their ¹H and ¹³C NMR spectra.

The employment of 2-haloalkoxy Fischer carbene complexes as hydroxycarbene complex equivalents for the synthesis of deprotected hydroxyl compounds has been recently described by our research group,²⁰ so we decided to apply the same strategy to the direct preparation of catechol derivatives **6**. However, all the attempts directed toward the synthesis of 2-iodoalkoxy(alkynyl)carbene complexes were unsuccessful, and we resolved to position a different protective group in the starting carbene complex that similarly enabled its removal in the last step of the synthesis. Chromium and tungsten alkynylcarbene complexes **7**, bearing an allyl or benzyl moiety, were synthesized by standard methodology from M(CO)₆, the corresponding alkynyllithium, and allyl or benzyl triflate (Scheme 6, Table 6).²¹ The nature of the protective group attached to the oxygen atom in the carbene complex seemed to have a great influence on its stabil-

ity: allyl-substituted complexes **7a,b**, although not stable at room temperature for long times, could be isolated in moderate to good yields. However, the analogous system **7c** bearing a benzyl moiety quickly decomposed when chromatographic purification was attempted and could not be properly characterized.²² [2 + 2] cycloaddition of compounds **7** to 2,3-dihydrofuran afforded the desired (alkenylcyclobutenyl)carbene complexes **8**, which not only showed differential stability, the same as their precursors **7**, but also evolved to different products when they were heated in refluxing THF. Thus, allyloxy complexes **8a,b** underwent intramolecular diastereoselective [4 + 2] cycloaddition, giving rise to compound **9** after oxidative workup (Scheme 6, Table 6, entries 1 and 2).²³ Although it was possible to detect the carbene complexes initially formed in the [4 + 2] cycloaddition process, their isolation and chromatographic purification implied a great loss in the final yield of compound **9**, and oxidation by means of exposure to oxygen and sunlight was carried out in the crude mixture. The yield of the process was improved when the reaction was performed in an atmosphere of carbon monoxide (Table 6, entry 2).

On the other hand, benzyloxy complex **8c** furnished the expected *o*-benzyloxyphenol derivative **10** when it was thermally treated in THF under a purge of nitrogen (Scheme 6, Table 6, entry 3). Given the instability of both intermediates involved in this route, neither of them was isolated: the crude complex **7c** was filtered through a pad of Celite and treated with 2,3-dihydrofuran until disappearance of the starting material. Then, the excess olefin was removed in a vacuum, and crude **8c** was directly benzannulated in the usual conditions to yield *o*-benzyloxyphenol **10**. This compound was quantitatively transformed into catechol **6b** by hydrogenolysis; the overall yield of catechol derivative accomplished by this procedure was lower than that of the sequential benzannulation–methyl moiety removal, and the latter synthetic route was preferred for the preparation of the rest of compounds **6** (Table 5).

Mechanistic Proposal and Rationalization of the Results. Given the similarity of this benzannulation with both the Dötz reaction and the photochemical process that converts dienylcarbene complexes into *o*-alkoxyphenol derivatives, it seemed reasonable to propose for it an analogous mechanism, which is depicted in Scheme 7. Hence, the reaction would begin with the dissociation of a CO ligand to afford a tetracarbonylmethylhexatriene intermediate, **A**, that would give rise to a cyclohexadienone derivative, **C**, by successive CO insertion and electrocyclic ring closure. A keto–enol tautomerism and the oxidative cleavage of the tricarbonylmetal moiety attached to the aromatic ring would furnish the final phenol derivatives **4**. It is commonly accepted that the rate-determining step of this kind of reaction is the release of the CO ligand in the starting complex, which in this case would provide a rationalization for the experimental results. Thus, the nitrogen purge would facilitate the formation of the tetracarbonyl intermediate

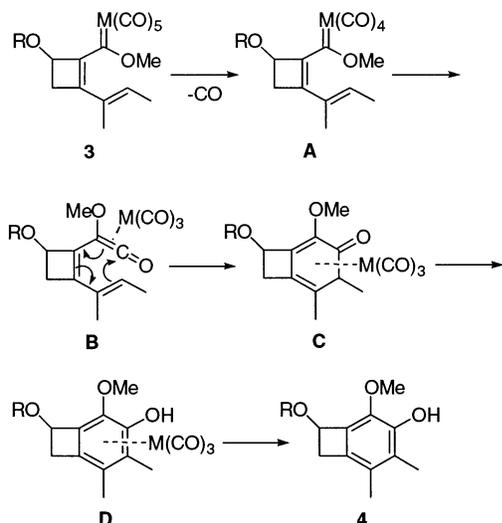
(22) The slow decomposition of alkynyl(allyloxy)carbene complexes has been reported. See ref 21.

(23) For an analogous intramolecular [4 + 2] cycloaddition reaction of Fischer carbene complexes, see: Dötz, K. H.; Noack, R.; Harms, K. *Tetrahedron* **1990**, *46*, 1235.

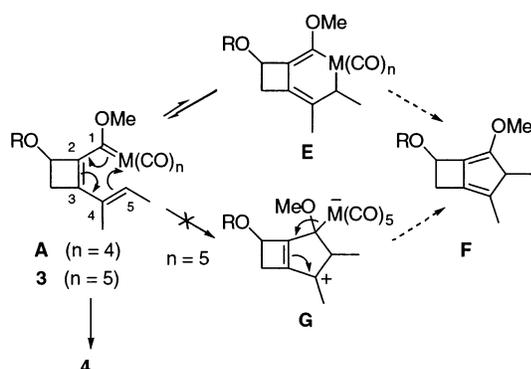
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SCHEME 7



SCHEME 8



by the removal of CO and, consequently, accelerate the reaction. On the other hand, the presence of CO would make the key intermediate revert to the starting pentacarbonyl species, avoiding the whole process.

A possible explanation for the different behavior observed for metallatrienes **3** and those generated by [4 + 2] cycloaddition of 2-amino-1,3-butadienes and complexes **1** could be based on their geometries. Our proposal is depicted in Scheme 8: we can assume that tetracarbonyl intermediate **A** is in equilibrium with metallacyclohexadiene **E**, resulting from its electrocyclicization. Given that reductive elimination of **E** to afford **F** is very disfavored due to the large angles existing between the substituents of the cyclobutene moiety, the equilibrium is displaced to the starting complex **A**, which evolves through an alternative path leading to phenol derivative **4**. An identical explanation can be applied to pentacarbonyl complexes **3**. However, it is commonly accepted that the cyclopentannulation of such compounds takes place through an initial nucleophilic attack of the terminal double bond to the carbene carbon atom to afford intermediate **G**.^{13a,14a} In the case of metallatrienes **3**, this interaction is not likely to occur since the distance between carbons C₁ and C₅ is considerably longer than that of their cyclohexene-containing analogues (Scheme 8).²⁴ Moreover, that fact would justify the stability of the (alkenylcyclobutenyl)carbene complexes at room temperature.

Conclusions

In summary, we have applied the [2 + 2] cycloaddition reaction of Fischer carbenes and enol ethers to alkenylethyne complexes to prepare cyclobutenyl-containing 1-metalla-1,3,5-hexatrienes. These complexes have shown unexpected stability at room temperature, in contrast to previously reported dienylcarbene complexes, and unusual reactivity. Upon thermal treatment, they have furnished *o*-alkoxyphenol derivatives through a process that involves CO insertion and subsequent cyclization and that did not have any precedent in the literature. We believe that the geometrical restraints introduced in the structure of the starting complexes by the cyclobutene ring are responsible for both the stability of the starting systems and the unusual reactivity they have shown.

The regioselectivity with which the reaction proceeds, as well as the broad range of possibilities of substitution in the starting substrates, convert this process into a good synthetic method of *o*-methoxyphenol derivatives. These compounds can be easily transformed into the corresponding catechols by reaction with boron tribromide, therefore increasing the potential of the methodology.

Experimental Section

General Methods. For all reactions run under a N₂ atmosphere, THF, diethyl ether, dichloromethane, toluene, and methanol were dried and distilled by standard procedures before use. Solvents used in column chromatography were distilled prior to use. All other reagents used in the reactions were of the best commercial grade available. Column chromatography was carried out on silica gel 60 (230–400 mesh). *R_f* data are referred to the mixture of solvents in which column chromatography was carried out. All melting points are uncorrected. NMR spectra were recorded at 300 or 200 MHz for ¹H and 75 or 50.3 MHz for ¹³C, with tetramethylsilane as internal standard for ¹H and the residual solvent signals as standard for ¹³C. Chemical shifts are given in parts per million. The multiplicity of the signals is indicated as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, m = multiplet. Mass spectra were obtained by EI (70 eV), FAB⁺, or MALDI-TOF. IR spectra are given in inverse centimeters.

Preparation of (Alkenylethyne)- and (Arylethyne)-carbene Complexes 1. Fischer carbene complexes **1** have already been synthesized in our research group by standard methodology from the corresponding acetylenes. Their analytical and spectroscopic data have been reported.^{14a,25}

Preparation of Enol Ethers and Ketene Acetals 2. 2,3-Dihydrofuran (**2a**), 3,4-dihydro-2*H*-pyran (**2b**), and 2-methoxypropene (**2h**) are commercially available reagents. The rest of the enol ethers and ketene acetals were prepared according to methods described in the literature: 1-methoxycyclopentene (**2c**), 1-methoxycyclohexene (**2d**), and 1-methoxycycloheptene (**2e**),²⁶ 2,2-dimethyl-1,3-dioxol (**2f**),²⁷ 2*H*-1,3-dioxine (**2g**),²⁸ 1,1-dimethoxyethene (**2i**),²⁹ and 1,1,2,2-tetramethoxyethene (**2j**).³⁰

(24) Simple molecular mechanics modeling showed that the difference between the distances C1–C5 in metallatrienes **3** and **5** is about 0.7 Å (molecular mechanics calculations were carried out using the MM2 force field; atom distance data for the pentacarbonylchromium carbene moiety were taken from an X-ray structure of a similar compound and kept fixed along the minimization).

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General Procedure for the Preparation of Fischer Dienyl Complexes. All dienylicarbene complexes **3** were synthesized by the same experimental procedure previously described by Wulff.¹⁶ 1 mmol of carbene neat with 10 mmol of the corresponding enol ether were stirred at room temperature, under a nitrogen atmosphere, until TLC analyses revealed that the starting complex had been consumed. Removal of the volatiles by vacuum (10 mmHg) and flash chromatography afforded the title compounds. Exceptionally, when 1,1-dimethoxyethene was used, 3 mmol of the cited olefin and 1 mmol of complex **1d** were dissolved in 10 mL of dry dichloromethane, and the mixture was stirred under a nitrogen atmosphere at room temperature until total consumption of the starting carbene complex was observed. The resulting adduct **3w** could not be isolated by column chromatography, so it was directly used in the next step after removal of solvents in a vacuum. Data for compounds **3a–d** and **3t,v,y** have already been reported.^{15,31}

Data for pentacarbonyl{[2,3,3a,5a-tetrahydro-4-(1-methyl-2-phenylethenyl)cyclobuta[b]furan-5-yl]methoxymethylene}tungsten(0) (3a): dark orange solid; mp 92–94 °C; yield 64%; $R_f = 0.44$ (hexane:diethyl ether:dichloromethane = 4:1:1); ¹H NMR (200 MHz, CDCl₃) δ 1.82–2.07 (m, 2H), 1.93 (s, 3H), 3.54 (dd, $J = 7.7, 3.8$ Hz, 1H), 3.90 (td, $J = 8.9, 5.6$ Hz, 1H), 4.17 (t, $J = 7.9$ Hz, 1H), 4.62 (s, 3H), 5.57 (d, $J = 3.8$ Hz, 1H), 6.92 (br s, 1H), 7.32–7.41 (m, 5H); ¹³C NMR (50.3 MHz, CDCl₃) δ 16.6 (CH₃), 27.4 (CH₂), 43.9 (CH), 66.6 (CH₂), 68.2 (CH₃), 79.1 (CH), 127.9 (CH), 128.3 (2CH), 129.4 (2CH), 131.2 (C), 136.2 (CH), 136.7 (C), 143.7 (C), 151.2 (C), 196.9 (4C), 203.4 (C), 310.7 (C); IR (CH₂Cl₂) ν 2066, 1937 cm⁻¹. Anal. Calcd for C₂₂H₁₈O₇W: C, 45.67; H, 3.14. Found: C, 45.42; H, 3.28.

Data for pentacarbonyl{[6-(cyclopentenyl)-1-methoxybicyclo[3.2.0]hepta-6-en-7-yl]methoxymethylene}chromium(0) (3o): orange oil; yield 80%; $R_f = 0.61$ (hexane:diethyl ether:dichloromethane = 4:1:1); ¹H NMR (300 MHz, CDCl₃) δ 1.30–2.70 (m, 12H), 2.90–3.40 (m, 1H), 3.23 (s, 3H), 4.66 (s, 3H), 6.12 (br s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 23.6 (CH₂), 23.6 (CH₂), 24.7 (CH₂), 31.2 (CH₂), 33.1 (CH₂), 33.2 (CH₂), 47.8 (CH), 53.0 (CH₃), 65.7 (CH₃), 94.5 (CH), 136.9 (C), 137.3 (C), 139.0 (CH), 149.6 (C), 216.2 (4C), 223.8 (C), 340.4 (C); IR (CH₂Cl₂) ν 2058, 1942 cm⁻¹. Anal. Calcd for C₂₀H₂₀CrO₇: C, 56.61; H, 4.75. Found: C, 56.83; H, 5.03.

Data for pentacarbonyl{[4-(1-cyclopentenyl)-3a,5a-dihydro-2,2-dimethylcyclobuta[d]dioxol-5-yl]methoxymethylene}chromium(0) (3t): dark red solid; mp 93–95 °C; yield 78%; $R_f = 0.30$ (hexane:dichloromethane = 5:1); ¹H NMR (300 MHz, CDCl₃) δ 1.43 (s, 3H), 1.86–2.03 (m, 2H), 2.15–2.26 (m, 1H), 2.33–2.39 (m, 1H), 2.39–2.51 (m, 2H), 4.75 (s, 3H), 5.08 (d, $J = 3.7$ Hz, 1H), 5.84 (d, $J = 3.7$ Hz, 1H), 6.47–6.48 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 23.5 (CH₂), 28.4 (CH₃), 29.0 (CH₃), 33.0 (CH₂), 33.4 (CH₂), 66.0 (CH₃), 75.9 (CH), 81.0 (CH), 137.0 (C), 137.4 (C), 143.3 (CH), 150.3 (C), 215.9 (4C), 223.6 (C), 336.5 (C); IR (CH₂Cl₂) ν 2057, 1938 cm⁻¹. Anal. Calcd for C₁₉H₁₈CrO₈: C, 53.53; H, 4.26. Found: C, 53.81; H, 4.50.

General Procedure for the Benzannulation Process. From Metallahexatrienes 3. In an optimized procedure, a solution of complex **3** (0.5 mmol) in dry THF (25 mL) was refluxed under a nitrogen purge until TLC analyses revealed total consumption of the starting material. For reactions arising from chromium complexes, addition of hexane (50 mL) and exposure to sunlight and air for 12 h, followed by flash chromatography, afforded the title compounds. For tungsten complexes, the residue was loaded directly onto a silica gel column without exposure to light and air.

From Alkynyl Complexes 1. Complex **1** was dissolved in an excess of enol ether **2** (0.5 mL), and the mixture was stirred, under a nitrogen atmosphere, until TLC analysis revealed the

formation of the corresponding cycloadduct. At that point, the remaining olefin was removed in a vacuum (10 mmHg), dry THF was added (10 mL), and the resulting solution was heated under a nitrogen purge. Phenol derivatives obtained by this procedure were purified in the same manner previously described.

Data for 2,3,5b,7,8,8a-hexahydro-5-methoxy-1H-inden[4',5':3,4]cyclobuta[1,2-b]furan-4-ol (4b): white solid; mp 155–157 °C; yield 56% or 77%; $R_f = 0.18$ (hexane:diethyl ether:dichloromethane = 6:1:1); ¹H NMR (400 MHz, CDCl₃) δ 1.70–1.88 (m, 2H), 2.09 (quint, $J = 7.2$ Hz, 2H), 2.71 (t, $J = 7.2$ Hz, 2H), 2.83 (t, $J = 7.2$ Hz, 2H), 3.63–3.70 (m, 1H), 3.93 (dd, $J = 7.8, 3.6$ Hz, 1H), 4.01 (s, 3H), 4.10 (t, $J = 8.0$ Hz, 1H), 5.44 (s, 1H), 5.58 (d, $J = 3.6$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 26.0 (CH₂), 28.8 (CH₂), 28.9 (CH₂), 29.4 (CH₂), 47.7 (CH), 58.1 (CH₃), 66.8 (CH₂), 80.5 (CH), 124.2 (C), 130.3 (C), 132.0 (C), 132.9 (C), 140.0 (C), 140.7 (C); HRMS m/z calcd for C₁₄H₁₆O₃ 232.1099, found 232.1096; LRMS (EI) m/z 232 (75), 217 (100), 189 (27), 171 (7), 128 (8), 91 (5). Anal. Calcd for C₁₄H₁₆O₃: C, 72.38; H, 6.95. Found: C, 72.32; H, 6.94.

Data for 2,3,5b,8a-tetrahydro-5-methoxy-7,7-dimethyl-1H-indeno[4',5':3,4]cyclobuta[1,2-d][1,3]dioxol-4-ol (4o): light yellow solid; mp 142–143 °C; yield 67%; $R_f = 0.32$ (hexane:ethyl acetate = 5:1); ¹H NMR (300 MHz, CDCl₃) δ 1.11 (s, 3H), 1.47 (s, 3H), 2.08–2.19 (m, 2H), 2.77–2.89 (m, 4H), 4.06 (s, 3H), 5.57 (s, 3H), 5.69 (d, $J = 3.6$ Hz, 1H), 5.85 (d, $J = 3.6$ Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 26.0 (CH₂), 28.0 (CH₃), 28.8 (CH₃), 29.0 (CH₂), 29.6 (CH₂), 58.2 (CH₃), 80.8 (CH), 81.0 (CH), 115.4 (C), 127.8 (C), 132.4 (C), 133.6 (C), 133.7 (C), 139.4 (C), 142.2 (C); HRMS m/z calcd for C₁₅H₁₈O₄ 262.1205, found 262.1208; LRMS (EI) m/z 262 (12), 204 (38), 189 (100), 187 (9), 97 (25). Anal. Calcd for C₁₅H₁₈O₄: C, 68.68; H, 6.92. Found: C, 68.47; H, 7.03.

General Procedure for the Preparation of Derivatives 5. Compounds **4n,o** (0.3 mmol) dissolved in a mixture THF/H₂O (10:1) were treated with an excess of trifluoroacetic acid (2 mL) at room temperature. After 12 h, volatiles were removed in high vacuum (0.1 mmHg), and the residue was redissolved in dichloromethane, washed with 0.5 M NaOH and saturated NaCl solutions, dried over anhydrous Na₂SO₄, and chromatographed in a 1:1 mixture of hexane and ethyl acetate to yield diols **5**.

Data for cis-2-methoxy-5-methyl-4-phenylbicyclo[4.2.0]octa-1,3,5-triene-3,7,8-triol (5a): white solid; mp 142–144 °C; yield 91%; $R_f = 0.18$ (hexane:ethyl acetate = 1:1); ¹H NMR (300 MHz, CDCl₃) δ 1.97 (s, 3H), 4.08 (s, 3H), 5.06 (d, $J = 3.1$ Hz, 1H), 5.13 (d, $J = 3.1$ Hz, 1H), 5.49 (s, 1H), 7.20–7.26 (m, 2H), 7.34–7.46 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 14.6 (CH₃), 58.0 (CH₃), 72.5 (CH), 72.8 (CH), 125.9 (C), 127.3 (CH), 128.2 (C), 128.4 (2CH), 129.7 (2CH), 131.2 (C), 136.0 (C), 136.1 (C), 140.2 (C), 143.4 (C); HRMS m/z calcd for C₁₆H₁₆O₄ 272.1049, found 272.1053; LRMS (EI) m/z 272 (23), 270 (54), 257 (68), 241 (11). Anal. Calcd for C₁₆H₁₆O₄: C, 70.57; H, 5.92. Found: C, 70.68; H, 6.11.

General Procedure for the Preparation of Catechol Derivatives 6. A solution of compound **4** (0.2 mmol) in dry dichloromethane (5 mL) was treated with an excess of boron tribromide (1.75 mmol, 1 mL of a 1.75 M solution in hexane) at –78 °C. The reaction mixture was allowed to reach room temperature over 6–7 h and then quenched with aqueous saturated NaHCO₃. The organic product was extracted twice with dichloromethane and ethyl acetate and chromatographed in a 1:1 mixture of hexane and ethyl acetate.

Data for 2,3,5b,7,8,8a-hexahydro-1H-inden[4',5':3,4]cyclobuta[1,2-b]furan-4,5-diol (6b): white solid; mp 155–157 °C; yield 93%; $R_f = 0.19$ (hexane:ethyl acetate = 1:1); ¹H NMR (300 MHz, DMSO-*d*₆) δ 1.48–1.61 (m, 1H), 1.74 (dd, $J = 12.2, 4.8$ Hz, 1H), 1.94 (quint, $J = 7.4$ Hz, 2H), 2.48–2.68 (m, 4H), 3.35–3.43 (m, 1H), 3.73 (dd, $J = 7.7, 3.4$ Hz, 1H), 3.93 (t, $J = 8.5$ Hz, 1H), 5.35 (d, $J = 3.4$ Hz, 1H), 8.01 (br s, 1H), 8.98 (br s, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 25.6 (CH₂), 28.4 (CH₂), 29.1 (CH₂), 29.4 (CH₂), 46.4 (CH), 66.0 (CH₂), 79.1 (CH), 125.9

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(C), 129.2 (C), 129.5 (C), 133.8 (C), 138.0 (C), 141.1 (C); HRMS m/z calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0944; LRMS (EI) m/z 218 (100), 203 (33), 201 (17), 190 (49), 171 (16). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.91; H, 6.22.

Preparation of Complexes 7. Butyllithium (1.6 M in hexanes, 3.3 mmol) was added dropwise to a solution of chromium or tungsten hexacarbonyl (3 mmol) and acetylene (3.3 mmol) in 10 mL of dry THF at -80°C . The mixture was allowed to reach room temperature, and the solvent was removed in a vacuum and replaced by dry dichloromethane (10 mL). Allyl or benzyl triflate was prepared by adding the corresponding alcohol (4 mmol) to a solution of pyridine (4.2 mmol) and trifluoromethanesulfonic anhydride (4.2 mmol) in dry dichloromethane (20 mL) at -25°C . The mixture was stirred at that temperature for 10 min and then poured via cannula over the solution containing the lithium acylmetalate at -10°C . Despite the fact that complexes **7a,b** slowly decomposed both neat and in solution, they could be purified by flash chromatography in hexane and stored at -5°C for short times. However, complex **8c** was filtrated through a thin pad of Celite and directly used in the subsequent cycloaddition reaction.

Data for {allyloxy[(1-cyclopentenyl)ethynyl]methylene}pentacarbonylchromium(0) (7b): red oil; yield 77%; $R_f = 0.27$ (hexane); ^1H NMR (300 MHz, CDCl_3) δ 1.87–2.06 (m, 2H), 2.42–2.44 (m, 2H), 2.58–2.61 (m, 2H), 5.09 (d, $J = 3.6$ Hz, 2H), 5.33 (d, $J = 19.4$ Hz, 1H), 5.42 (d, $J = 10.8$ Hz, 1H), 5.50–6.07 (m, 1H), 6.50–6.52 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.2 (CH_2), 34.5 (CH_2), 35.6 (CH_2), 79.5 (CH_2), 93.5 (C), 119.5 (CH_2), 124.1 (C), 131.1 (CH), 134.3 (C), 147.7 (CH), 216.1 (4C), 225.7 (C), 313.4 (C); IR (CH_2Cl_2) ν 2061, 1939 cm^{-1} . No satisfactory elemental analysis could be achieved for compound **7b** due to its slow decomposition.

Preparation of Complexes 8 and Compounds 9 and 10. Alkynyl complexes **7** were dissolved in 2,3-dihydrofuran and stirred at room temperature, under a nitrogen atmosphere, until TLC analyses revealed that the starting complex had been consumed (1–2 h), and then the volatiles were removed in a vacuum (10 mmHg). Flash chromatography in a 1:1 mixture of hexane and dichloromethane enabled the purification of compounds **8a,b**, but **8c** was directly used in the next reaction step. For the preparation of **9**, a solution of complexes **8a,b** (0.5 mmol) in THF (5 mL) was degassed by means of three freeze–pump–thaw cycles, then the atmosphere was saturated with CO, and the mixture was heated in an oil bath at 65°C for 6 h. The crude mixture was diluted 2-fold with hexane, exposed to air and sunlight, filtered, and chromatographed. Thermal benzannulation of cycloadduct **8c** to afford **10** was carried out in the standard conditions.

Data for {allyloxy[4-(1-cyclopentenyl)-2,3,3a,5a-tetrahydrocyclobuta[b]furan-5-yl]methylene}pentacarbonyltungsten(0) (8a): orange oil; yield 97%; $R_f = 0.45$ (hexane: dichloromethane = 1:1); ^1H NMR (300 MHz, CDCl_3) δ 1.71–1.98 (m, 5H), 2.30–2.43 (m, 4H), 3.31 (dd, $J = 7.7$, 1.1 Hz, 1H), 3.79–3.87 (m, 1H), 4.11 (t, $J = 8.1$ Hz, 1H), 5.30 (dd, $J =$

13.8, 6.0 Hz, 1H), 5.36 (dd, $J = 13.8$, 6.0 Hz, 1H), 5.44 (d, $J = 11.4$ Hz, 1H), 5.54 (d, $J = 12.5$ Hz, 1H), 6.13–6.26 (m, 1H), 6.46 (br s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.6 (CH_2), 27.0 (CH_2), 33.4 (CH_2), 33.6 (CH_2), 44.5 (CH), 66.3 (CH_2), 80.2 (CH), 83.2 (CH_2), 120.5 (CH_2), 131.3 (CH), 139.1 (C), 140.6 (C), 143.7 (CH), 148.6 (C), 197.1 (4C), 203.2 (C), 305.0 (C); IR (CH_2Cl_2) ν 2057, 1941 cm^{-1} ; LRMS (MALDI-TOF) m/z calcd for $C_{20}H_{18}O_7W$ 554, found 554. Anal. Calcd for $C_{20}H_{18}O_7W$: C, 43.34; H, 3.27. Found: C, 43.65; H, 2.97.

Data for (\pm)-(1S,2R,6S,12S,13S)-3,15-dioxabicyclo[11-3.1.0^{1,7}.0^{2,6}.0^{8,12}]heptadecan-7-en-16-one (9): colorless oil; yield 49% or 55%; $R_f = 0.23$ (hexane:ethyl acetate = 3:1); ^1H NMR (300 MHz, CDCl_3) δ 1.06–1.25 (m, 3H), 1.60–1.88 (m, 4H), 1.89–2.09 (m, 2H), 2.26–2.39 (m, 2H), 2.85–2.93 (m, 1H), 3.74 (td, $J = 5.4$, 2.6 Hz, 1H), 3.91 (dd, $J = 9.4$, 6.0 Hz, 1H), 4.07 (t, $J = 8.0$ Hz, 1H), 4.13–4.22 (m, 1H), 4.47 (t, $J = 9.4$ Hz, 1H), 4.84 (d, $J = 4.7$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 25.4 (CH_2), 27.9 (CH_2), 28.9 (CH_2), 31.6 (CH), 32.2 (CH_2), 36.2 (CH_2), 36.4 (CH), 49.6 (CH), 56.0 (C), 70.5 (CH_2), 71.5 (CH_2), 81.7 (CH), 126.0 (C), 142.5 (C), 178.6 (C); IR (CH_2Cl_2) ν 1752 (s) cm^{-1} ; LRMS (MALDI-TOF) m/z calcd for $C_{15}H_{18}O_3$ 246, found 246. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.02; H, 7.22.

Data for 5-benzyloxy-2,3,5b,7,8,8a-hexahydro-1H-inden[4',5':3,4]cyclobuta[1,2-b]furan-4-ol (10): yellow oil; yield 37%; $R_f = 0.36$ (hexane:ethyl acetate = 5:1); ^1H NMR (300 MHz, CDCl_3) δ 1.71–1.82 (m, 1H), 1.87 (dd, $J = 12.2$, 5.1 Hz, 1H), 2.11 (quint, $J = 7.4$ Hz, 2H), 2.73 (t, $J = 7.4$ Hz, 2H), 2.86 (t, $J = 7.4$ Hz, 2H), 3.65–3.74 (m, 1H), 3.90 (dd, $J = 7.7$, 3.4 Hz, 1H), 4.10 (dd, $J = 8.8$, 7.7 Hz, 1H), 5.27 (d, $J = 12.0$ Hz, 1H), 5.34 (d, $J = 12.0$ Hz, 1H), 5.40 (d, $J = 3.4$ Hz, 1H), 5.52 (br s, 1H), 7.35–7.45 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 26.2 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.4 (CH_2), 47.5 (CH), 66.9 (CH_2), 72.4 (CH_2), 80.5 (CH), 124.7 (C), 127.4 (2CH), 128.0 (CH), 128.5 (2CH), 130.2 (C); 132.4 (C), 133.1 (C), 137.2 (C), 139.1 (C), 140.9 (C); LRMS (MALDI-TOF) m/z calcd for $C_{20}H_{20}O_3$ 308, found 308. Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 78.02; H, 6.88.

Hydrogenolysis of 10. A mixture of compound **10** (0.2 mmol), ethanol (10 mL), and catalytical amounts of Pd/C (10%) was stirred under 1 atm of hydrogen for 24 h. Filtration through a pad of Celite and flash chromatography afforded **6b** in 98% yield.

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Supporting Information Available: Analytical and spectroscopic data for all new compounds prepared and ^{13}C NMR spectra of compounds **7a** and **7b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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