Reactions of 2-Amino-1,3-butadienes and Fischer Alkynyl Carbenes: Up to Nine C–C Bonds and Seven Stereogenic Centers Created in a Stereoselective Manner through a Cascade Process

José Barluenga,* Fernando Aznar, Sofía Barluenga, Mónica Fernández, Alfredo Martín, Santiago García-Granda,* and Alejandro Piñera-Nicolás

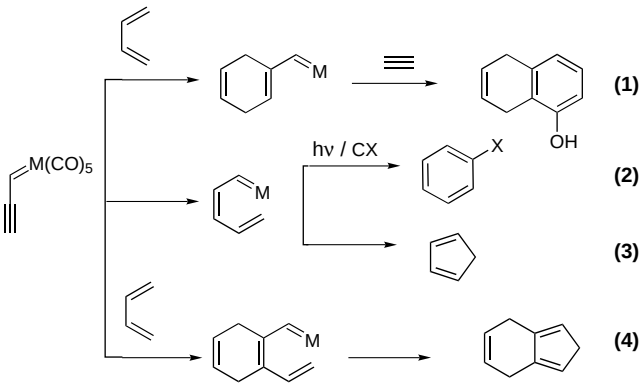
Abstract: The reactions of 2-amino-1,3-butadienes **1**, **2**, and **3** with various substituted Fischer alkynyl carbene complexes are reported. Reaction of 2-aminodienes with alkyl- or silyl-substituted complexes **4** affords cyclohexadienylcarbene complexes **5** or arylcarbene complexes **13**. However, when an aryl group is present in the carbene complex instead of the alkyl substituent, the initial [4+2] cycloaddition is followed by a cyclopentannulation to yield fluorene derivatives **15**. The reaction is highly stereoselective and occurs under mild conditions. Substitution of the starting alkynyl carbene complex with a vinyl group produces a similar tandem cycloaddition–cyclopentannulation. However, in this case, a cyclopentadiene moiety is generated and, hence, a new cycloaddition–cyclopentannulation sequence can be initiated with another molecule of the starting alkynyl complex. In this way, polycycles **35** and **42** have been synthesized by cascade double and triple [4+2] cycloaddition–cyclopentannulation processes by incorporation of two or three equivalents of the carbene complex, respectively.

Keywords: C–C bond formation · carbene complexes · cascade reactions · polycycles

Introduction

Fischer carbene complexes are useful materials for the generation of ring systems. Their chemistry has been developed to the point where there are a number of reactions that may be drawn upon for applications to problems in synthetic organic chemistry.[1] In the last few years we have been studying the behavior and synthetic applications of 2-amino-1,3-butadienes **1** and have reported their reactivity towards α,β-unsaturated carbene complexes to furnish seven-membered carbocycles through a formal [4+3] process,[2] vinylaminocarbenes through a metathesis reaction,[3] and cyclohexenyl carbene complexes through a [4+2] cycloaddition.[4] In this context, we have also reported the synthesis of 2-methyl-1,3-dimorpholino-1,3-butadiene **3**,[5] a 1,3-diamino-substituted diene that reacts with α,β-unsaturated Fischer carbene complexes to give a wide range of different products depending on the double-bond substitution pattern.[6]

On the other hand, it is well known that α,β-acetylenic carbene complexes react with a number of dienes at room temperature to yield cyclohexa-2,5-dienyl carbene complexes by the Diels–Alder reaction. These new vinyl complexes are useful starting materials for the preparation of dihydronaphthols by reaction with alkynes [Eq. (1) in Scheme 1].[7] The tandem cycloaddition and annulation reactions may be carried out one-pot and this methodology has been applied to the construction of a steroid-like skeleton with a properly designed polyynecarbene complex.[8]



Scheme 1. Reactivity of α,β-acetylenic carbene complexes.

[*] J. Barluenga, F. Aznar, S. Barluenga, M. Fernández, A. Martín
Instituto Universitario de Química Organometálica Enrique Moles
Unidad asociada al C.S.I.C., Julián Clavería 8, E-33701 Oviedo (Spain)
S. García-Granda, A. Piñera-Nicolás
Departamento de Química Física y Analítica (X-ray service)
Universidad de Oviedo, Julián Clavería 8, E-33701 Oviedo (Spain)

0947-6539/98/0411-2280 $ 17.50+.50/0

Merlic et al. published the synthesis of phenol and aniline derivatives by light-induced carbonyl or isonitrile insertion followed by cyclization in metallatriene compounds [Eq. (2), Scheme 1]; these derivatives differ in regiochemistry from those obtained through the Dötz reaction.[9]

On the other hand, the cyclopentannulation reaction was discovered as a side process in the Dötz benzannulation. This process allows cyclopentadiene derivatives to be obtained as a result of cyclization without CO insertion [Eq. (3), Scheme 1].[10] Moreover, in the reaction of arylamino carbene complexes with alkynes, indene derivatives were reported to be the main products.[11] Since then, Aumann et al. have shown several examples of cyclopentadiene formation from metallatrienes, which can be formed by treatment of alkynyl carbene complexes with enamines.[12]

We report herein our full experimental work on the study of the reactions with 2-amino-1,3-butadienes (Figure 1) and various substituted alkynyl carbene complexes (Figure 2).

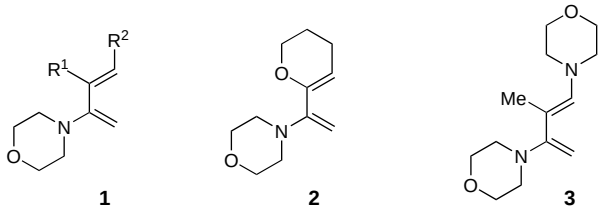


Figure 1. Structures of the 2-aminodienes used.

We found that these compounds undergo [4+2] cycloaddition, [4+2] cycloaddition followed by a cyclopentannulation,[13] [Eq. (4), Scheme 1] double tandem ([4+2] cycloaddition–cyclopentannulation),[14] and the first example of a triple tandem reaction (Diels–Alder/cyclopentannulation). In all these processes the key step is a cyclopentannulation triggered by a [4+2] cycloaddition of a diene and an alkynylcarbene complex.

Abstract in Spanish: *En esta contribución se describen las reacciones de los 2-amino-1,3-butadienos **1**, **2**, y **3** con complejos alquinil carbeno de Fischer que poseen diferente sustitución. Las reacciones de los 2-aminodienos con los complejos **4** alquil- o aril-sustituidos dan lugar a la formación de los complejos ciclohexadienilcarbeno **5** o arilcarbeno **13**. Sin embargo, cuando se coloca un grupo arilo en lugar del sustituyente alquilo, la cicloadición [4+2] inicial va seguida de un proceso de ciclopentanulación para dar lugar a los derivados del fluoreno **15**. La reacción es altamente estereoselectiva y tiene lugar en condiciones suaves. La sustitución en los complejos alquinilcarbeno iniciales con un grupo vinilo produce una reacción tándem cicloadición-ciclopentanulación similar a la anterior, sin embargo, en este caso, en los productos de este proceso aparece una estructura tipo ciclopentadienilo que puede iniciar la reacción con otra molécula de carbeno de partida. De esta forma, se han sintetizado los policiclos **35** y **42** a través de las reacciones en cascada doble- y triple-(cicloadición-ciclopentanulación) por incorporación de dos o tres equivalentes de complejo carbeno respectivamente.*

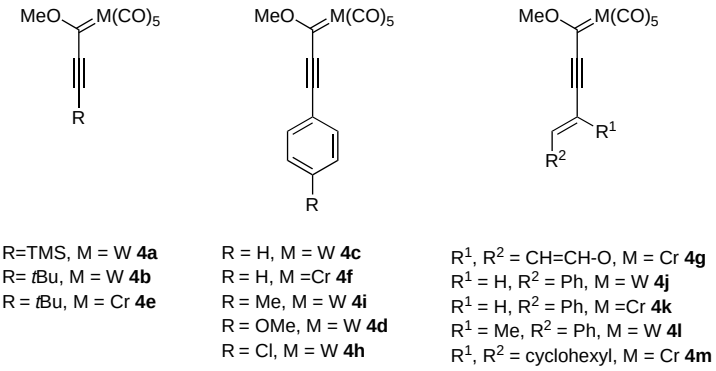
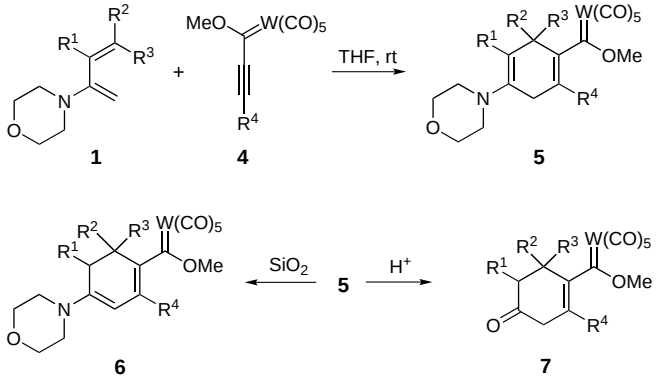


Figure 2. Structures of the alkynylcarbene complexes used.

Results and Discussion

[4+2] Cycloaddition reactions: We had previously observed that alkenyl Fischer carbene complexes react with 2-amino-1,3-butadienes to produce the corresponding [4+2] cycloadducts.[4] In a similar way, the reaction of alkyl- and trimethylsilyl-substituted alkynyl carbene complexes **4** with 2-morpholino-1,3-butadienes **1** at room temperature afforded, as expected,[7] the cyclohexadiene complexes **5** (Scheme 2,



Scheme 2. [4+2] Cycloaddition and derivations to new carbene complexes.

Table 1). The latter were obtained in high yield and isolated as yellow solids by crystallization from hexane. Elution of the crude products on silica gel yielded the purple, isomeric 1,3-

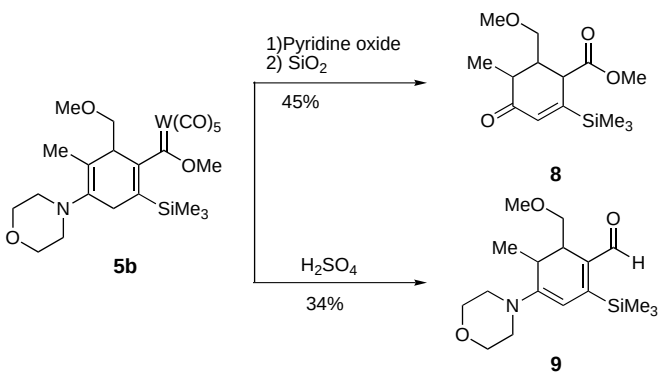
Table 1. Complexes **5**, **6**, and **7** prepared.

	Diene	Carbene	R^1	R^2	R^3	R^4	**5** [%]	**6** [%]	**7** [%]
a	**1a**	**4a**	$CH_2(CH_2)_2CH_2$		H	$SiMe_3$	95	–	80
b	**1b**	**4a**	Me	CH_2OMe	H	$SiMe_3$	95[b]	74	–
c	**1c**	**4a**	Me	H	H	$SiMe_3$	[a]	93	–
d	**1d**	**4a**	Me	H	CH_2OMe	$SiMe_3$	82[b]	–	–
e	**1a**	**4b**	$CH_2(CH_2)_2CH_2$		H	*t*Bu	71	–	40
f	**1e**	**4a**	Me	CH_2OSiMe_3	H	$SiMe_3$	95	69	[c]
g	**1e**	**4b**	Me	CH_2OSiMe_3	H	*t*Bu	73	–	[c]
h	**2**	**4b**	$O(CH_2)_2CH_2$		H	*t*Bu	90[d]	–	54

[a] The product could not be isolated because it spontaneously isomerizes to **6c**. [b] Products **5b** and **5d** are the same compound. [c] Hydrolysis of complexes **5f** and **5g** produced complexes **11f** and **11g**, respectively (see Scheme 4). [d] NMR yield, this compound could not be properly isolated.

cyclohexadienyl complexes **6** as air-stable solids. These compounds are very robust under hydrolytic and oxidative conditions, probably due to the double stabilization of the carbene by the methoxy group and the conjugated amine. On the other hand, treatment of cycloadducts **5** with 1N HCl for 1 hour afforded the ketone complexes **7**.

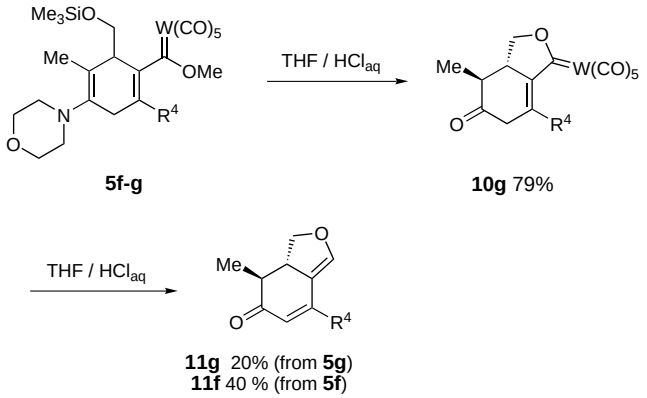
The metal can be easily removed from **5** in two ways to produce ester or aldehyde functionalities (Scheme 3). Thus, treatment of **5b** with pyridine oxide in ether followed by



Scheme 3. Transformation of carbene complexes **5** into aldehydes and esters.

chromatography on silica gel produced the keto ester **8**. On the other hand, **5b** reacted with concentrated H_2SO_4 in tetrahydrofuran overnight to afford aminoaldehyde **9**.

Adducts **5f** and **5g** (Scheme 4) present a special behavior, since under the hydrolytic conditions deprotection of the masked alkoxy group followed by cyclization takes place to



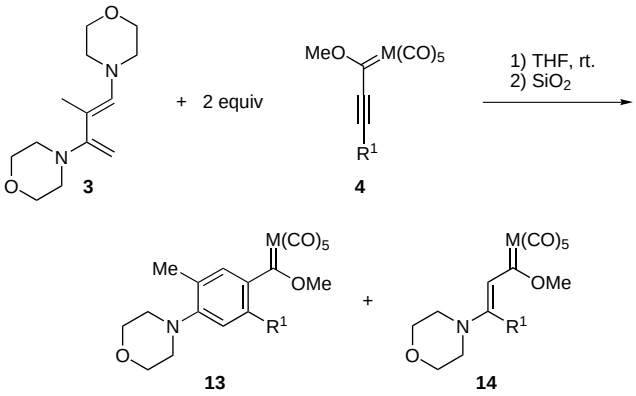
Scheme 4. Transformation of carbene complexes **5** into enolethers.

afford the bicyclic complexes **10**. Under longer reaction times these complexes undergo demetallation to afford the benzoisofuranone derivatives **11**.

As can be observed so far, the behavior of diene **2** does not present any essential difference from alkyl-substituted dienes **1**, and the higher hetero functionalization in this diene only implies a higher functionalization in the final products. However, in the reaction of diene **3** with complexes **4** the cyclohexadienyl carbene intermediates undergo aromatization very easily through morpholine elimination (Table 2, Scheme 5). Thus, complexes **13** were isolated after silica gel

Table 2. Complexes **13** prepared.

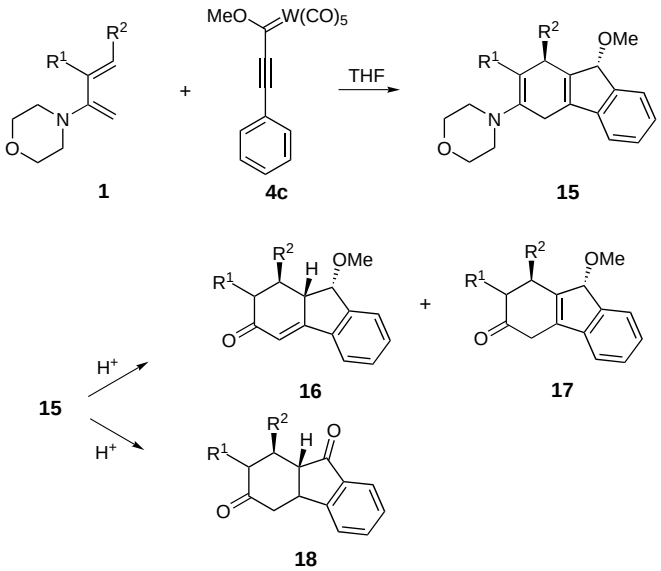
	Carbene	R^1	M	**13** [%]
a	**4a**	TMS	W	68
b	**4b**	*t*Bu	W	72
c	**4c**	Ph	W	78
d	**4d**	*p*-(MeO)Ph	W	77
e	**4e**	*t*Bu	Cr	70
f	**4f**	Ph	Cr	81



Scheme 5. [4+2] Cycloadditions with dienes **3**.

purification along with carbene complexes **14** resulting from morpholine addition to the triple bond of the starting complexes **4**.[15] In order to allow the starting diene to be fully consumed, the reaction was optimized to a diene:carbene complex ratio of 1:2.

Tandem [4+2] cycloaddition – cyclopentannulation: Reaction of aminodienes **1** and **2** with the phenyl carbene complex derivative **4c** (Scheme 6), unexpectedly afforded the fluorene derivatives **15** instead of the [4+2] cycloadducts expected. Compounds **15** were formed in excellent yield as single diastereoisomers and isolated by crystallization. Alternatively, hydrolysis of the crude products under acidic conditions



Scheme 6. Tandem [4+2] cycloaddition – cyclopentannulation.

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(THF, 3 N HCl) afforded **16**, **17**, or **18**, depending on the substitution of the diene and the carbene complex (see Table 3). Long hydrolysis times produced the diketofluorenes

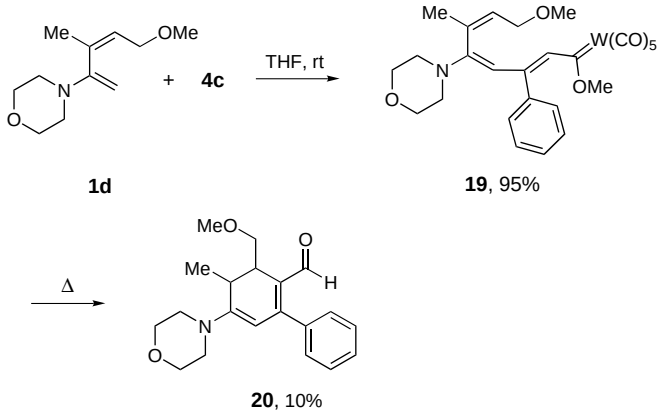
Table 3. Compounds **15**, **16**, **17**, and **18** prepared.

	R^1	R^2	Diene	t	**15** [%]	**16** [%]	**17** [%]	**18** [%]
a	Me	H	**1c**	10 min	95	75	–	50
b	Me	CH_2OMe	**1b**	5 min	95	50[b]	60[c]	51
c		$CH_2(CH_2)_2CH_2$	**1a**	15 min	92	80	–	–
d	Me	CH_2OSiMe_3	**1e**	10 min	[a]	–	83	–

[a] The corresponding compound **15d** was not isolated. [b] HCl (3 N) was used in the hydrolysis. [c] Silica gel was used for the hydrolysis of fluorene **15b**.

18 in 50 % yield (see Experimental Section), while shorter hydrolysis times afforded **16** or **17**. The relative configuration at C-8 and C-9 for **15** was postulated based on NOE experiments performed on **16b**.[13]

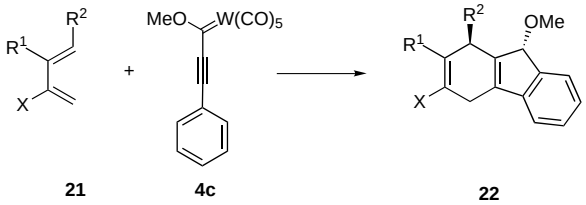
Recently, it has been reported that 2-aminodienes afford open chain products in high yield on reaction with alkynylcarbene complexes.[16] In our experiments, open chain products were only observed when diene **1d**, with *Z* configuration at the nonenaminic double bond, was used. We used the Michael-type addition of the enamine to afford the metallatetraene **19** (Scheme 7), which is stable at room temperature, but evolves into aldehyde **20** in refluxing THF. This



Scheme 7. Reaction with diene **1d** with a *Z* configuration in the nonenaminic double bond.

result also suggests a possible stepwise mechanism involving zwitterionic intermediates rather than a concerted [4+2] cycloaddition for the synthesis of compounds **5** and for the first step in the formation of fluorene derivatives **15**.

The influence of the group attached to C-2 of the diene in the reaction of **21** was studied with **4c** (Scheme 8, Table 4). In the case of the 2-methoxydiene **21a**, the reaction was



Scheme 8. Influence of the X group attached to the C-2 of the diene.

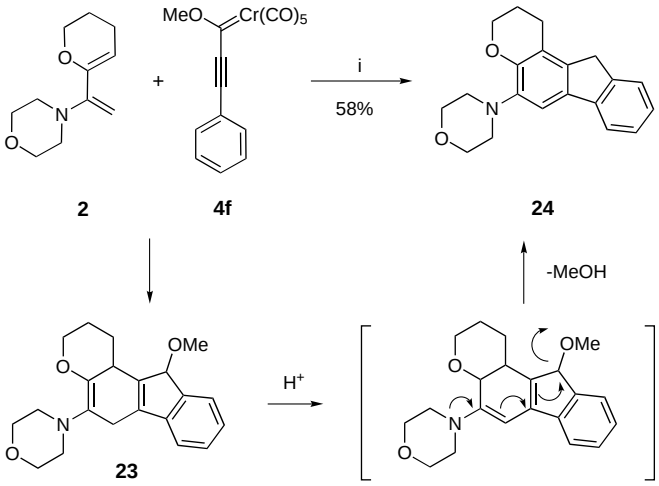
Table 4. Compounds **22** prepared.

	X	R^1	R^2	Solvent	**22** [%]
a	OMe	H	Ph	MeCN	51
b	Me	Me	H	neat	10[a]

[a] 5 % of the corresponding aromatic fluorene was isolated as a side product.

performed at room temperature (72 h) to afford **22a** in 51 % yield. When 2,3-dimethylbuta-1,3-diene **21b** was used, it was necessary to carry out the reaction at 50 °C (4 h) and only 10 % of the corresponding tricyclic system was isolated. The order of reactivity is aminodiene > alkoxydiene > unsubstituted diene. These results are in line with the expectations, since dienes react better with electrophilic reagents if their electron density is higher.

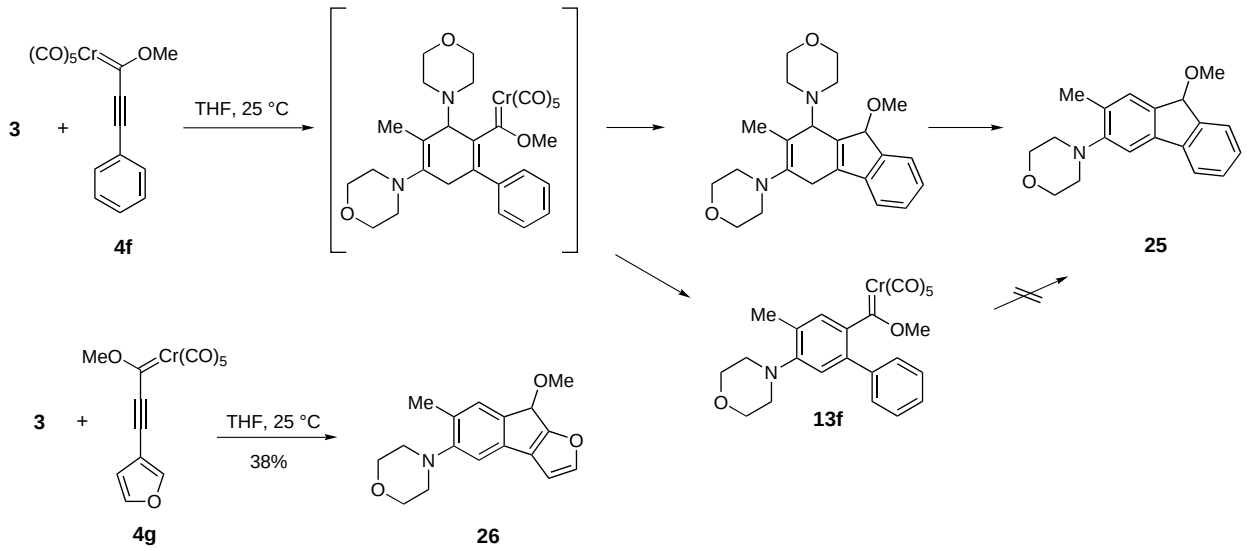
The reaction of complex **4f** with diene **2** (Scheme 9), which supports a second electron-donating group at C-3, under the same reaction conditions as used with 2-aminodienes **1**, afforded the corresponding dihydrofluorene derivative **23**, inferred by NMR analysis. The latter could not be properly



Scheme 9. Preparation of fluorene derivative **24**. i) THF, 25 °C, then toluene, TsOH 110 °C.

characterized, since attempted silica gel purification produced partial hydrolysis of the enamine moiety. Nevertheless, treatment of the crude reaction product with TsOH in toluene at 110 °C promoted elimination of methanol to afford **24**.

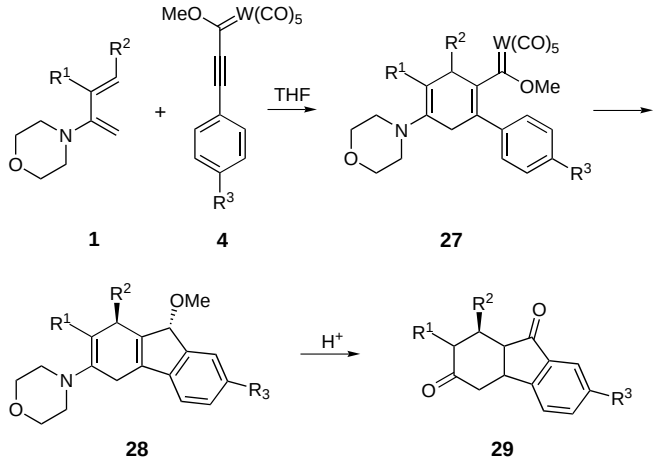
Taking these results into consideration we went back over the reaction of diene **3** with complex **4f** (Scheme 10). We observed that fluorene **25** was formed in moderate yield when the starting materials were allowed to react for a longer time at low temperature. However, in a separate experiment, when the isolated aromatic complex **13f** was warmed to 80 °C formation of **25** was not observed. Probably, this is due to the increase in activation energy required for the cyclopentannulation in a system containing two aromatic rings. This result implies that the cyclopentannulation precedes to the aromatization step by elimination of morpholine. When the reaction was performed with carbene complex **4g** the only product that could be isolated was furoindene **26**; no formation of the corresponding aromatic carbene complex could be detected.



Scheme 10. Reaction of diene **3** and carbene complexes **4d** and **4g**.

The energy required in the reaction involving the loss of aromaticity of a furyl ring must be lower than in the case of a phenyl ring, and this makes the cyclopentannulation pathway faster than the aromatization one.

The influence of substitution in the aromatic ring of complexes **4** in the reaction was investigated using various carbene complexes **4d–h** (Scheme 11, Table 5). Thus, complexes **28** were prepared by reaction with dienes **1a–c,e** at room temperature and obtained as single diastereoisomers. Complex **4d** ($R^3 = OMe$, entries **b**, **e**, **g**, Table 5) undergoes slow reaction in which the [4+2] cycloadducts cannot be observed by TLC analysis at room temperature. On the other hand, in the case of complex **4h** ($R^3 = Cl$), the cycloaddition takes place with diene **1c** (entry **c**) in a few minutes. The reaction was monitored by TLC following the disappearance of the starting material and the formation of a new spot corresponding to the [4+2] cycloadduct, which becomes purple on the TLC plate (because of enamine isomerization). However, the corresponding annulation takes 24 h to go to completion. In this case, isolation of complexes **27** was possible. The reaction was carried out in THF at room temperature for 3 min. Solvents were then removed under vacuum and the product precipitated from 2:1 hexane/ether at $-78\,^{\circ}C$ to yield analytically and spectroscopically pure **27c** in 74% yield.



Scheme 11. Influence of the susbstituents on the phenyl ring.

Table 5. Compounds **28** prepared.

	R^1	R^2	diene	R^3	carbene	*t*	**28** [%]
a	Me	H	**1c**	Me	**4i**	15 min	90
b	Me	H	**1c**	OMe	**4d**	2 d	95
c	Me	H	**1c**	Cl	**4h**	12 h	[a]
d	Me	CH_2OMe	**1b**	Me	**4i**	15 min	97
e	Me	CH_2OMe	**1b**	OMe	**4d**	8 h	94
f	$CH_2(CH_2)_2CH_2$		**1a**	Me	**4i**	15 min	95
g	$CH_2(CH_2)_2CH_2$		**1a**	OMe	**4d**	10 h	96

[a] The corresponding compound **28** was not isolated, instead compound **29** was isolated after purification in 36% yield.

The substituents at the carbene carbon and the influence of the electronic density at the metal were also investigated. Silica gel treatment of the complex **30**, generated at low temperature in situ in order to isomerize the enaminic double bond, produced a mixture of **31** and **32** (Scheme 12). We found that the new complex **32** does not undergo cyclopentannulation even at high temperature. The high electronic density at the metal is probably a major factor in the lack of reactivity of the doubly stabilized cycloadducts. Indeed, the double stabilization was not a required condition to prevent the cyclopentannulation, since simple aminolysis at $-78\,^{\circ}C$ with dimethylamine affords the aminocarbene complex **33**, which is also stable at room temperature. Warming up complex **33** in refluxing THF resulted in enamine isomerization to yield complex **34**. Again, the higher electronic density at the metal makes this complex more stable towards cyclopentannulation.

The formation of the fluorene derivatives could be rationalized through a process involving a [4+2] cycloaddition followed by a cyclopentannulation. To the best of our knowledge, this is the first example of a cyclopentannulation with the participation of an aromatic ring that takes place under such mild conditions.

The stereochemistry observed for the fluorene derivatives, together with the experimental data related to the influence of the substituents in the reaction and the previous work by

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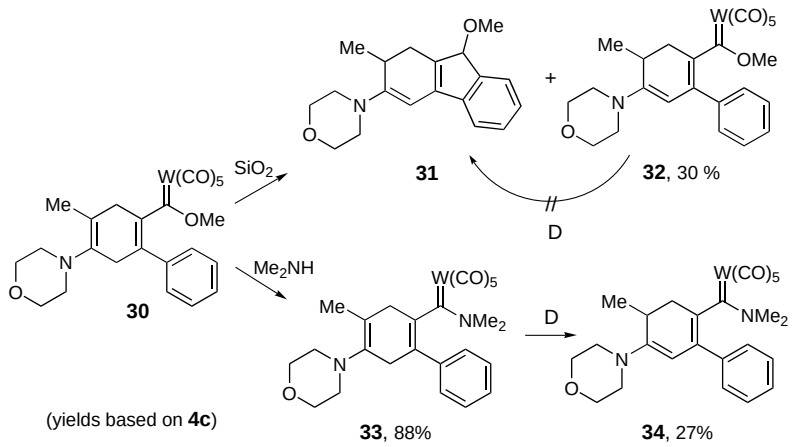
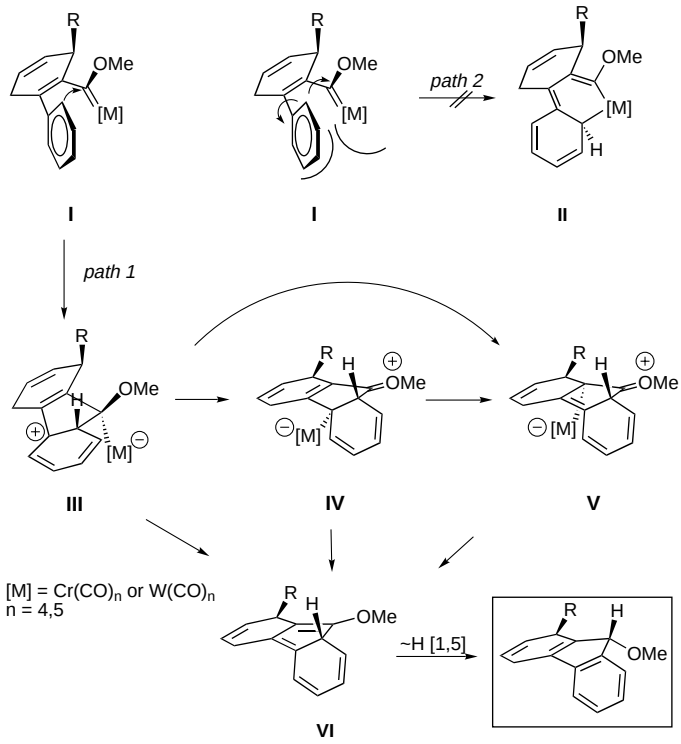


Scheme 12. Influence of the electronic density at the metal in the cyclopentannulation reaction.

Aumann et al[12] in the cyclopentannulation reactions of metallatrienes, are all in agreement with nucleophilic attack of the aryl ring on the carbene carbon for the cyclopentannulation step. The mechanism, which was in part suggested by a referee, is depicted in Scheme 13. The conformation of the

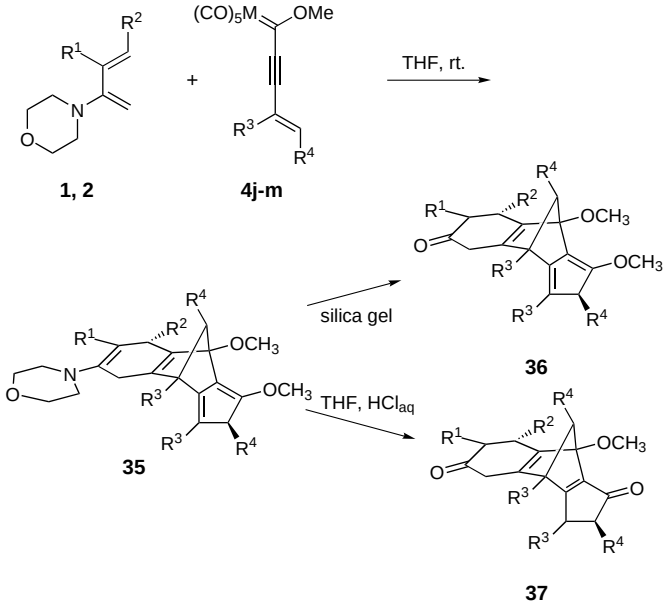


Scheme 13. Proposed mechanism for the reaction.

[4+2] cycloadduct **I**, in which the metal fragment is placed away from the substituent R, must be favored over the other rotamer in order to avoid unfavorable steric interactions. Also, steric repulsion between the phenyl group and the metal pentacarbonyl moiety will tilt the phenyl group in such a way that the distance between the upper edge of the phenyl group and the carbene carbon atom becomes shorter than the distance to the lower edge of the phenyl group (which is located on the same side of the cyclohexadiene ring as the $(CO)_5M$ fragment). Thus, attack from the ortho carbon of the phenyl ring situated in the upper edge (path 1) would produce intermediate **III** that either loses the metal or undergoes metal migration to form intermediates **IV** or **V**. In any case, elimination of the metallic fragment would produce **VI**, which recovers the aromaticity of the aryl ring by suprafacial 1,5-hydrogen shift to yield the final fluorene derivatives with the observed stereochemistry.

The other possible mechanism involves an electrocyclization followed by reductive elimination (path 2), but in this case the metal atom would attack the phenyl group at the carbon which is closest to it, that is, at the lower edge. This would lead to the formation of the diastereomer (if the reductive elimination of $M(CO)_n$ from the putative metallacyclohexadiene takes place with retention of configuration), which was not observed.

Tandem double [4+2] cycloaddition-cyclopentannulation reaction: With the aim of studying the scope of the cyclopentannulation reaction, we turned our attention to vinyl substituted alkynyl complexes. When carbene complexes **4j–m** (Scheme 14) were allowed to react with dienes **1** and



Scheme 14. Tandem reaction with vinyl-substituted alkynyl complexes.

2, no indene derivative or [4+2] cycloadduct were detected in the crude reaction mixture. Instead, complexes **35** were observed as the main products along with a significant amounts of **1**. In the light of this result, it was obvious that two equivalents of carbene had reacted with one equivalent of diene. In fact, when the reaction was carried out using two equivalents of carbene complexes **4**, compounds **35** were the only metal-free products observed (Scheme 14, Table 6). These compounds, when solids, were isolated by crystallization, otherwise, they could not be properly isolated from the mixtures by column chromatography due to partial hydrolysis

Table 6. Compounds **35**, **36**, and **37** prepared.

	R^1	R^2	Diene	R^3	R^4	M	Carbene	*t*	**35** [%]	**36** [%]	**37** [%]
a	Me	H	**1c**	H	Ph	W	**4j**	20 min	95	–	–
b	Me	H	**1c**	H	Ph	Cr	**4k**	30 min	95[a]	–	–
c	Me	CH_2OMe	**1b**	H	Ph	W	**4j**	25 min	–	–	30
d	Me	H	**1c**	Me	Ph	W	**4l**	4 days	67	–	–
e	Me	H	**1c**	$CH_2(CH_2)_2CH_2$		Cr	**4m**	2 days	86	–	–
f	Me	CH_2OMe	**1b**	$CH_2(CH_2)_2CH_2$		Cr	**4m**	6 days	85	–	51
g	Me	$CH_2Oallyl$	**1g**	$CH_2(CH_2)_2CH_2$		Cr	**4m**	4 days	–	54	–
h	$O(CH_2)_2CH_2$		**2a**	$CH_2(CH_2)_2CH_2$		Cr	**4m**	12 h	87	–	–

[a] **35a** and **35b** are the same compound.

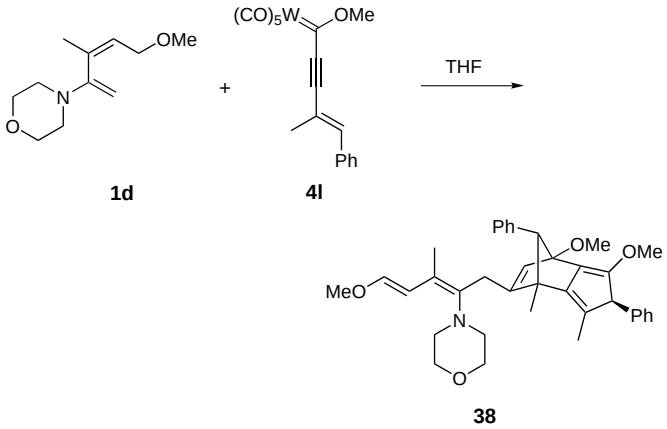
of the enamine. In these cases, the products were hydrolyzed by acidic treatment to afford compounds **36** or **37**, which were then fully characterized (Scheme 14, Table 6).

It can be observed from Table 6 that the reaction proceeded either with tungsten or chromium derivatives of carbene **4**. Substitution at the 4 position of the carbene ($R^3 \neq H$) slows down the reaction. The stereoselectivity of the process is, in most cases, very high (only one diastereoisomer was detected in the crude reaction mixtures by NMR spectroscopy) except for the reaction of diene **1b** and carbene **4j** (entry **c**, Table 6), in which a 3:1 mixture of diastereoisomers was observed even when the reaction was carried out at low temperature (−78 °C to 25 °C, 12 h). Nevertheless, the major product was isolated by crystallization. The low stereoselectivity observed for this example, in which the double bond does not form part of a cycle, can be explained considering that, in this case, the two possible intermediates **II** and **IV** in the formation of the first cyclopentadiene ring could undergo the 1,3-metal migration due to the higher flexibility of the five-membered carbocycle with respect to the fused ring system (see Scheme 13).

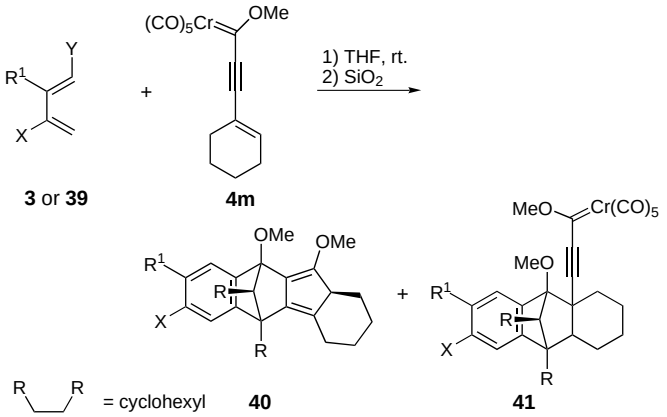
The stereochemical assignment of **35** was not possible from their NMR data because of the complexity and overlapping of significant signals. Also, it was not possible to obtain good X-ray quality crystals of these complexes, so we decided on the assignment based on hydrolysis products **37** (see Scheme 14). The first ^{13}C NMR data collected for these compounds troubled us, since we observed three low-field signals above 200 ppm and three unshielded olefinic signals, while only two low-field signals corresponding to the carbonyl carbons and four olefinic carbon signals should be expected. However, high resolution mass spectrometry and elemental analysis data were in agreement with the proposed structure. Furthermore, HMQC, HMBC, and NOESY experiments were also in agreement with the connectivity and stereochemistry of the structure shown in Scheme 14 for compounds **37**. Finally, we were able to ascertain the stereochemistry by X-ray analysis of compound **37c**.[14] The high chemical shifts observed for this compound probably arise from a strong paramagnetic effect due to the proximity of the double bonds in the molecule.

Reaction of diene **1d** with carbene complex **4l** did not take place as a [4+2] cycloaddition as had been observed with alkyl-substituted alkynyl complexes (vide supra). Instead, a Michael type addition of the enamine followed by double cyclization produced compound **38** (Scheme 15).

Reaction of diene **3** and carbene **4m** took place also under mild conditions affording the polycyclic compounds **40a** along with a small amount of the new carbene complex **41** (Scheme 16, Table 7, entry **a**). The vinyl substituent at the triple bond in the starting carbene complex again makes the cyclopentannulation faster than the aromatization through morpholine elimination allowing the cascade process to develop. Danishefsky's diene **39** possesses similar structural characteristics to diene **3**, since two electron-donor groups are in the same relative positions and can



Scheme 15. Tandem reaction with diene **1d**.



Scheme 16. Synthesis of polycyclic systems **40**.

undergo the same aromatization process by the loss of a molecule of MeOH.[17] Consistently, reaction with the alkynylcarbene **4m** produced the polycyclic system **40b**.

The formation of polycyclic compounds **35** and **40** can be explained by a double tandem [4+2] cycloaddition – cyclopentannulation. A first [4+2] cycloaddition would afford the cyclohexadienyl complexes type **I** (Scheme 17), which under-

Table 7. Compounds **40** and **41** prepared.

	X	R^1	Y	Diene	**40** [%]	**41** [%]
a	morpholine	Me	morpholine	**2**	57	9
b	TMSO	H	OMe	**39**	64[a]	–

[a] Deprotection of the hydroxyl moiety by treatment with Na_2CO_3/MeOH yield compound **40c** (87%).

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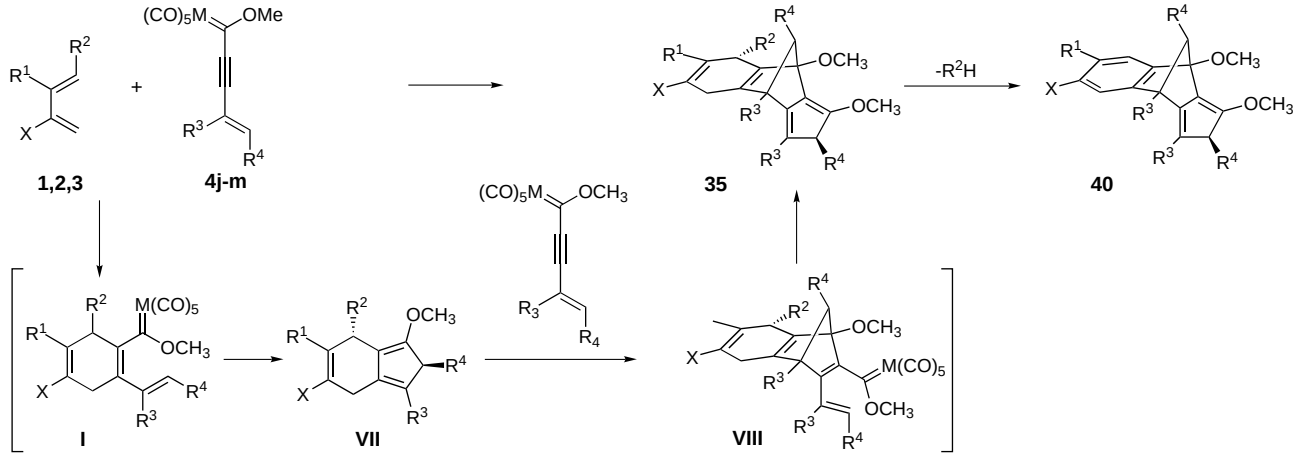

Scheme 17. Proposed mechanism for the formation of polycycles **35** and **40**.

go cyclization to yield the cyclopentadienes type **VII**. Such dienes do not rearrange, as happened with the aryl-substituted complexes, and appear to be more reactive with the starting carbene complex than the 2-aminodienes themselves, since **VII** could never be isolated or even detected by low-temperature NMR experiments. At this point, **VII** undergoes a second [4+2] process to yield **VIII**, which again cyclizes to produce the isolated polycyclic compounds **35**, or **40** after morpholine or methanol elimination in the case of dienes **3** and **39**, respectively. Finally, formation of the side product **41** can be explained by a [4+2] process of intermediate **VII** with the starting carbene complex **4**, which reacts through the cyclohexenyl double bond instead of the triple bond.

In this process six new carbon–carbon bonds and five new stereogenic centers are created in a single synthetic step and in a stereoselective manner.

Formation of **38** can be explained in a similar way (Figure 3). In this case steric hindrance due to the *Z* configuration of the nonenaminic double bond precludes cyclization after the initial Michael addition of the enamine to the triple bond of the carbene complex. Instead, intramolecular hydrogen abstraction by the α-carbon of the carbene intermediate **IX** yields the metallatriene **X** with a structure appropriate for further cyclization and [4+2] cycloaddition–cyclopentannulation to produce **38**.

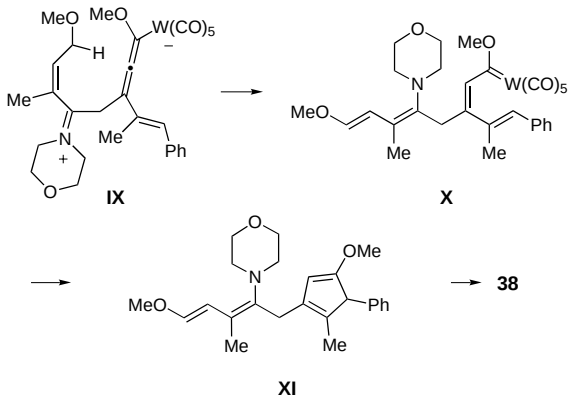

Figure 3. Michael addition of diene **1d** to a vinyl-substituted alkynyl carbene complex.

Tandem triple [4+2] cycloaddition–cyclopentannulation reaction: The reaction of dienes **1** and **2** stops after the incorporation of the first two molecules of carbene. At this step, **35** does not undergo a third cycloaddition even when warmed up in the presence of excess carbene, although **35** contains a cyclopentadiene moiety capable of incorporating a third molecule of carbene. The reason for the lack of reactivity of compounds **35** probably lies in the special arrangement of the molecule. Figure 4 shows the structures of the backbone of

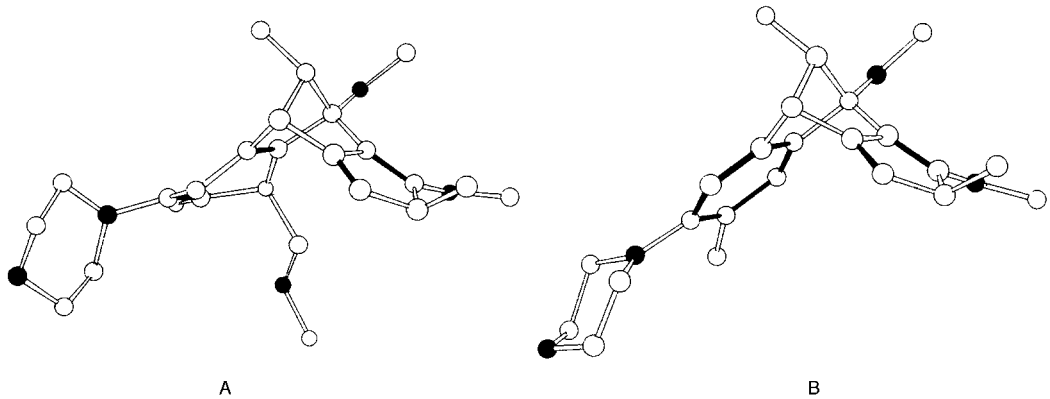

Figure 4. Structure of **35** (**A**) and **40** (**B**).

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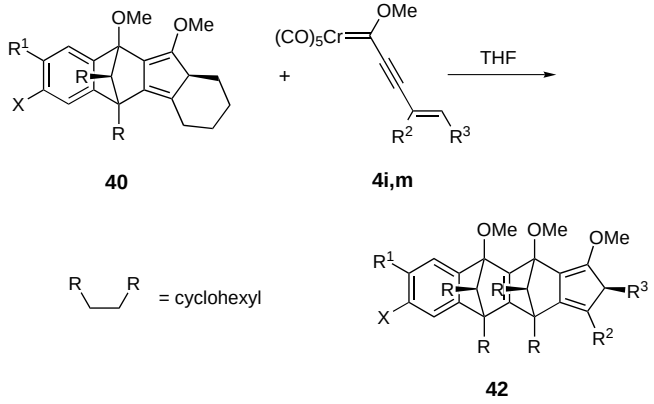
35 (**A**) and **40** (**B**) generated by MM2 molecular mechanics calculations. The bending of molecule **A** places the first cycloadduct close to the bottom face of the cyclopentadiene structure, blocking the approach of carbene **4** from this side of the molecule. Furthermore, the top face of the diene is also hindered by the group R^4 at position 2. For the same reason the approach of the carbene to the cyclopentadiene **VII** takes place from the bottom face of the diene, as derived from the stereochemistry of C-10 in **35c**.[24] On the other hand, the bottom face of the cyclopentadiene fragment of **40** should be accessible, since the first aromatic ring should be flat (molecule **B**). Thus, it should be possible to incorporate the third carbene complex with this kind of compound.

With this idea in mind, we performed the reactions of **40** with an additional equivalent of carbene complex **4i** or **4m**, which resulted in the formation of polycyclic compounds **42** in good yield (Scheme 18, Table 8).

Table 8. Compounds **42** prepared.

	X	R^1	Complex	R^2	R^3	Carbene	T[°C]	t	**42** [%][a]
a	morpholine	Me	**40a**	$CH_2(CH_2)_2CH_2$		**4m**	40 °C	48 h	76
b	TMSO	H	**40b**	$CH_2(CH_2)_2CH_2$		**4m**	25	3 days	90(59)[b]
d	morpholine	Me	**40a**	H	Ph	**4i**	25	48 h	85

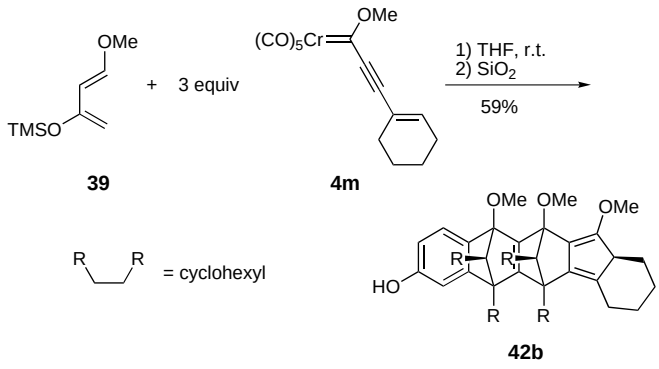
[a] Yields are referred to compounds **40** used as starting materials. Yield given in brackets is referred to diene **39** used as starting material is a one pot process. [b] Deprotection of the hydroxyl moiety by treatment with Na_2CO_3/MeOH yield compound **42c** (92%).



Scheme 18. Preparation of **42**.

An important point in the reactions of dienes **3** and **39** with 2 equivalents of carbene complex **4**, which could be deduced from the NMR analysis of the crude reaction, is the fact that **40**, with the first ring being aromatic, is present in the reaction media before SiO_2 hydrolysis. Therefore, polycyclic **42** can be obtained in a one-pot by reaction of one equivalent of diene and three of the carbene complex (Scheme 19). This reaction was carried out for Danishefsky's diene and, after seven days, **42b** was isolated as the reaction product in 59% yield. In this cascade process nine C–C bonds and seven stereogenic centers are created in stereoselective manner.

Figure 5 shows the molecular structure of **42a** obtained by an X-ray monocrystal analysis. The U-shaped structure keeps the in face of the cyclopentadiene sterically inaccessible to the dienophile, while the out face is hindered by the cyclohexenyl ring from the carbene complex. This arrangement makes the approach of another molecule of carbene difficult and, therefore, a fourth addition of carbene to the cyclopentadiene moiety has never been observed.



Scheme 19. One-pot preparation of **42**.

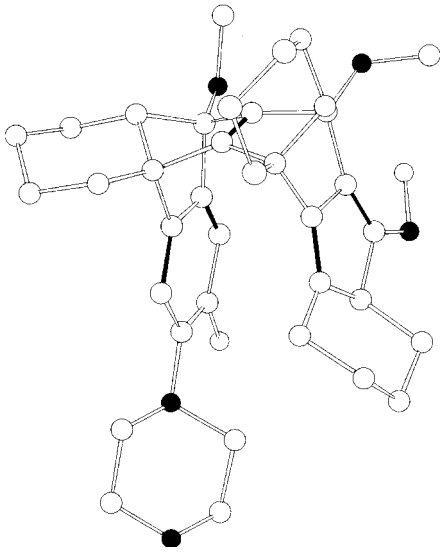


Figure 5. X-ray crystal structure of **42a**. Hydrogen atoms have been omitted for clarity.

Conclusion

We have reported a new tandem [4+2] cycloaddition–cyclopentannulation reaction of 2-amino-1,3-butadienes and Fischer alkynyl carbene complexes that produces fluorene derivatives. The reaction takes place under mild conditions and the products are obtained as single diastereoisomers. Moreover, vinyl substitution in the alkynylcarbene complex provides an entry to new polycyclic scaffolds through cascade double and triple cycloaddition–cyclopentannulation processes that can be controlled by the substitution in the 2-aminodiene.

Experimental Section

General methods: All reactions were run under N_2 atmosphere. Tetrahydrofuran (THF) and hexane were dried and distilled by standard procedures before use. Solvents used in the extractions and column chromatography were distilled prior to use. All other reagents used in the reactions were of the best commercial grade available. Column chroma-

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tography was carried out on silica gel 60 (230—400 mesh). All melting points were uncorrected. NMR spectra were recorded at 400, 300, or 200 MHz for ^{1}H and 100, 75, or 50.3 MHz for ^{13}C, with tetramethylsilane as internal standard for ^{1}H and the residual solvent signals as standard for ^{13}C. Chemical shifts are given in ppm. Mass spectra were obtained by EI (70 eV). IR spectra are given in cm^{-1}. 2-Amino-1,3-butadienes **1** and **2**[18] and Fischer carbene complexes **2a–d**[19] were prepared according to the methods described in the literature.

1-(2*H*-3,4-dihydro-6-pyranyl)morpholinoethene (**2**): 6-Ethynyl-2-*H*-3,4-dihydropyrane (10 mmol, 1.08 g) was treated with morpholine (30 mmol, 2.6 mL) to obtain **2** (1.28 g, 66 %). B.p. = 90 °C (10^{-2} Torr); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.69-1.78$ (m, 2H; CH_2 pyrane), 1.98–2.04 (m, 2H; CH_2 pyrane), 2.74 (t, ^3J(H,H) = 4.7 Hz, 4H; morpholine), 3.65 (t, ^3J(H,H) = 4.7 Hz, 4H; morpholine), 3.94 (m, 2H; CH_2O pyrane), 3.96 (s, 1H; C=CH_2), 4.37 (s, 1H; C=CH_2), 5.00 (t, ^3J(H,H) = 3.9 Hz, 1H; C=CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 20.2$ (CH_2), 22.0 (CH_2),49.5 (CH_2, morpholine), 65.9 (CH_2), 66.4 (CH_2, morpholine), 90.4 (C=CH_2), 100.2 (C=CH), 150.1 (C=C), 152.6 (C=C).

General procedure for the preparation of alkynyl carbene complexes: Fischer carbene complexes below were prepared by standard methodology[19] from the corresponding acetylenes, which were in turn prepared according to the Corey–Fuchs method.[20] These complexes can be also prepared by a modified procedure that consists of the generation of the acetylide by the Corey–Fuchs reaction in presence of the metal hexacarbonyl at −78 °C, and then allowing to react by slowly increasing the temperature overnight. This one-pot procedure provided the carbene complexes in a similar yield to that of the two step synthesis.

Pentacarbonyl[1-methoxy-3-(*p*-methoxyphenyl)propynylidene)]tungsten(0) (**4d**): Yield: 50 %. Crystallized from hexane. Black crystals; m.p. 80 °; R_f = 0.32 (hexane); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.89$ (s, 3H; CH_3O), 4.34 (s, 3H; CH_3O), 6.97 (d, ^3J(H,H) = 8.9 Hz, 2H; *p*-OMePh), 7.62 (d, ^3J(H,H) = 8,9 Hz, 2H; *p*-OMePh); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 55.5$ (CH_3O), 65.7 (CH_3O), 112.6 (C, *p*-OMePh), 114.8 (CH, *p*-OMePh), 135.5 (CH, *p*-OMePh), 162.8 (C, *p*-OMePh), 197.5 (CO), 205.5 (CO), the signals for both carbons of the triple bond, and for the carbene carbon are missing; IR (CH_2Cl_2): $\tilde{\nu} = 2066$, 1948 cm^{-1} (C≡O *cis*); $C_{16}H_{10}O_7W$ (498.1): calcd C 38.58, H, 2.02; found C 38.46, H 2.10; HRMS (EI): *m/z* calcd for $C_{16}H_{10}O_7{}^{184}W$ [M^+]: 497.9939, found 497.9932.

Pentacarbonyl[3-(3-furyl)methoxypropynylidene]chromium(0) (**4g**): 1,1-Dibromo-2-(3-furyl)ethene (10 mmol, 2.51 g) in THF was treated with $Cr(CO)_6$ (10 mmol, 2.20 g) and BuLi (20 mmol) at −78 °C. The temperature was allowed to rise to −20 °C and methyl trifluorosulfonate (20 mmol) was added. 1.53 g (47 %) of **4g** were obtained after SiO_2 purification and crystallization. Purple crystals. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.38$ (s, 3H; CH_3O), 6.58 (s, 1H; furyl), 7.54 (s, 1H; furyl), 7.88 (s, 1H; furyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 65.9$ (CH_3O), 94.8 (C≡C), 106.5 (C, furyl), 112.1 (CH, furyl), 144.4 (CH, furyl), 148.7 (CH, furyl), 216.1 (CO), 225.3 (CO), 313.7 (C=Cr); $C_{13}H_6O_7Cr$ (340.2): calcd C 47.87, H 1.87; found C 47.89, H 1.90.

Pentacarbonyl[3-(*p*-chlorophenyl)-1-methoxypropynylidene)]tungsten(0) (**4h**): Yield: 29.5 %. Crystallized from hexane. Black crystals; m.p. 104–105 °C; R_f = 0.36 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.35 (s, 3H; CH_3O), 7.42 (d, ^3J(H,H) = 8.6 Hz, 2H; *p*-ClPh), 7.56 (d, ^3J(H,H) = 8.6 Hz, 2H; *p*-ClPh); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 66.2$ (CH_3O), 119.4 (C, *p*-ClPh), 129.5 (CH, *p*-ClPh), 133.9 (CH, *p*-ClPh), 138.0 (C, *p*-ClPh), 197.2 (CO), 343.9 (C=W), both of the triple bond and one CO carbon signals are missing; IR (CH_2Cl_2): $\tilde{\nu} = 2070$, 1948 cm^{-1}; $C_{15}H_7ClO_6W$ (502.5): calcd C 35.85, H 1.40; found C 36.06, H 1.57; HRMS (EI): *m/z* calcd for $C_{15}H_7ClO_6{}^{184}W$ [M^+]: 501.9431, found 501.9424.

Pentacarbonyl[(*E*)-4-ene-1-methoxy-5-phenyl-2-pentynylene]tungsten(0) (**4j**): Yield: 54 %. Crystallized from hexane. Black crystals; m.p. 260 °C decomp; R_f = 0.58 (hexane/ethyl acetate; 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.29$ (s, 3H; CH_3O), 6.66 (d, ^3J(H,H) = 10.9 Hz, 1H; *H*C=CH), 7.38–7.56 (m, 6H; phenyl, *H*C=CH); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 65.9$ (CH_3O), 106.4 (*C*H=CH), 127.4 (CH, phenyl), 129.4 (CH, phenyl), 130.6 (C=CH), 135.3 (C, phenyl), 149.1 (C=CH), 197.4 (CO), 205.7 (CO), both of the triple bond and the carbene carbon signals are missing; IR (CH_2Cl_2): $\tilde{\nu} = 2065$, 1948 cm^{-1}; $C_{17}H_{10}O_6W$ (495.1): calcd C 41.30, H 2.03; found C 41.28, H 2.12; HRMS (EI): *m/z* calcd for $C_{12}H_{10}O^{184}W$ [$M^+ - 5$CO]: 354.0243, found 354.0220.

Pentacarbonyl[(*E*)-4-ene-1-methoxy-4-methyl-5-phenyl-2-pentynylidene]tungsten(0) (**4l**): Yield: 60 %. Crystallized from hexane. Black crystals; m.p. 103–105 °; R_f = 0.54 (hexane/ethyl acetate; 5:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.33$ (s, 3H; CH_3), 4.32 (s, 3H; CH_3), 7.41–7.45 (m, 6H; Ph, *H*C=CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 12.8$ (CH_3), 65.7 (CH_3O), 118.8 (CH_3*C*=CH), 128.0 (CH, phenyl), 128.6 (CH, phenyl), 128.8 (CH, phenyl), 135.7 (C, phenyl), 143.8 (H*C*=CCH_3), 197.4 (CO), 205.6 (CO) (both the signals for the triple bond and the carbene carbon are missing); IR (CH_2Cl_2): $\tilde{\nu} = 2067$, 1948 cm^{-1}; $C_{18}H_{12}O_6W$ (508.1): calcd C 42.52, H 2.38; found C 42.90, H 2.51; HRMS (EI): *m/z* calcd for $C_{18}H_{12}O_6{}^{184}W$ [M^+]: 508.0146, found 508.0133.

Pentacarbonyl[3-(cyclohexen-1-yl)-1-methoxypropynylidene)]chromium(0) (**4m**): Yield: 90 %. Black oil. Only stable in solution. R_f = 0.65 (hexane/ethylacetate, 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.51-1.80$ (m, 4H; 2xCH_2), 2.11–2.34 (m, 4H; 2 × CH_2), 4.32 (s, 3H; CH_3O), 6.61 (s, 1H; *H*C=C); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 20.9$ (CH_2, cyclohexenyl), 21.8 (CH_2, cyclohexenyl), 26.7 (CH_2, cyclohexenyl), 28.3 (CH_2, cyclohexenyl), 65.4 (CH_3O), 91.3 (C≡C), 120.7 (C≡C), 139.5 (C=C), 145.3 (C=CH), 216.3 (CO), 225.5 (CO), 314.4 (C=Cr); IR (CH_2Cl_2): $\tilde{\nu} = 2068$ (C≡O *trans*), 1948 cm^{-1} (C≡O *cis*).

General procedure for the synthesis of complexes 5: 2-Aminodiene **1** (1 mmol) was added to a solution of complex **4** (1 mmol) in dry THF (10 mL) at RT. The reaction mixture was stirred at RT for the time indicated and concentrated at reduced pressure (10^{-2} Torr). The reaction crude was dissolved in dry hexane, filtered through a pad of Celite and, when the complexes are solids, cooled to −20 °C overnight to induce crystallization.

Pentacarbonyl{methoxy{2-[3-trimethylsilyl-5-(*N*-morpholino)bicyclo[4.4.0]-deca-2,5-dienyl]]methylene}tungsten(0) (**5a**): Compounds **1a** (0.19 g, 1.00 mmol) and **4a** (0.45 g, 1.00 mmol) were allowed to react in THF for 5 min. The compound **5a** was isolated by crystallization form hexane (Yellow prisms). 95 % yield; m.p. 139 °C; R_f = 0.65 (hexane/ethyl acetate; 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.08$ (s, 9H; $(CH_3)_3Si$), 0.80–2.10 (m, 8H; 4 × CH_2, cyclohexyl), 2.60–2.95 (m, 6H; morpholine, CH_2), 3.26 (bd, ^3J(H,H) = 12.0 Hz, 1H; CH), 3.72 (m, 4H; morpholine), 4.55 (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = -0.04$ ($(CH_3)_3Si$), 25.8 (CH_2, cyclohexyl), 25.9 (CH_2, cyclohexyl), 27.4 (CH_2, cyclohexyl), 27.5 (CH_2, cyclohexyl), 34.7 (CH_2), 44.8 (CH), 50.4 (CH_2, morpholine), 67.2 (CH_2, morpholine), 69.3 (CH_3O), 123.1 (C=C), 126.6 (C=C), 134.6 (C=C), 197.2 (CO), 202.3 (CO), 335.2 (C=W), the vinylic carbon attached to the silicon group signal is missing; IR (CH_2Cl_2): $\tilde{\nu} = 2070$ (C≡O *trans*), 1950 cm^{-1} (C≡O *cis*); $C_{24}H_{31}O_7NWSi$ (657.5): calcd C 43.84, H 4.75, N 2.13; found C 43.92, H 4.74, N 2.33; MS EI: (*m/z*, %): (657, 1) [M^+], (629, < 1), (601, 30), (573, 8), (545, 10), (517, 57), (300, 100).

Pentacarbonyl{methoxy[3-methyl-2-methoxymethylene-4-morpholino-6-trimethylsilyl-1,4-cyclohexadienyl]methylene}tungsten(0) (**5b** or **5d**)

Method A: Compounds **1b** (0.196 g, 1.00 mmol) and **4a** (0.45 g, 1.00 mmol) were allowed to react in THF for 15 min. Compound **5b** was isolated by crystallization from hexane (Red prims). 95 % yield.

Method B: Compounds **1d** (0.196 g, 1.00 mmol) and **4a** (0.45 g, 1.00 mmol) were allowed to react in CH_3CN for 30 min. Compound **5d** was isolated by crystalization from hexane as a red solid (82 % yield; m.p. 100 °C (decomp); R_f = 0.57 (hexane/ethyl acetate; 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.10$ (s, 9H; $(CH_3)_3Si$), 1.88 (s, 3H; CH_3), 2.64 (t, ^3J(H,H) = 6.0 Hz, 4H; morpholine), 3.10–3.22 (m, s, 5H), 3.73 (t, ^3J(H,H) = 6.0 Hz, 4H; morpholine), 4.55 (s, 3H; CH_3O); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = -0.17$ ($(CH_3)_3Si$), 16.1 (CH_3), 26.8 (CH_2), 48.1 (CH), 49.9 (CH_2, morpholine), 58.6 (CH_3OCH_2), 67.2 (CH_2, morpholine), 74.4 (CH_2O), 122.9 (C=C), 126.7 (C=C), 140.7 (C=C), 197.2 (CO), 202.5 (CO), 331.4 (C=W), both the signals for the vinylic carbon attached to the silicon and the methoxy attached to the carbene carbonl are missing; IR (CH_2Cl_2): $\tilde{\nu}$ = 2070 (C≡O *trans*), 1933 cm^{-1} (C≡O *cis*); HRMS (EI): *m/z* calcd for $C_{23}H_{31}NO_8Si$ ^{184}W [M^+]: 661.1329, found 661.1327.

Pentacarbonyl{2-[3-*tert*-butyl-5-morpholino-bicyclo[4.4.0]-2,5-decadienyl]-methoxymethylene}tungsten(0) (**5e**): Compounds **1a** (0.42 g, 2.2 mmol) and **4b** (1 g, 2.2 mmol) were allowed to react in THF for 6 h. Compound **3e** was isolated by crystallization from hexane. (Yellow prisms) 71 % yield; m.p. 132 °C decomp; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.85-0.96$ (m, 2H; CH_2, cyclohexyl), 1.07 (s, 9H; $(CH_3)_3C$), 1.11–1.23 (m, 2H; CH_2, cyclohexyl), 1.34–1.62 (m, 2H; CH_2, cyclohexyl), 1.65–1.82 (m, 2H;

CH_2, cyclohexyl), 2.66 (t, ^3J(H,H) = 4.7 Hz, 4H; morpholine), 2.89 (ddd, ^3J(H,H) = 21.0, 5.2, J = 3.0 Hz, 1H; CH), 3.21 – 3.50 (m, 2H; CH_2), 3.74 (t, ^3J(H,H) = 4.3 Hz, 4H; morpholine), 4.57 (s, 3H; CH_3O); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 24.7 (CH_2, cyclohexyl), 26.1 (CH_2, cyclohexyl), 27.5 (CH_2, cyclohexyl), 27.7 (CH_2, cyclohexyl), 31.4 ((CH_3)$_3$C), 34.6 (CH_2), 37.1 ((CH_3)$_3$*C*), 45.4 (CH), 50.5 (CH_2, morpholine), 67.3 (CH_2, morpholine), 69.3 (CH_3O), 126.5 (C=C), 128.6 (C=C), 134.7 (C=C), 148.0 (C=C), 197.4 (CO), 202.6 (CO), 339.5 (C=W); IR (CH_2Cl_2): $\tilde{\nu}$ = 2067 (C≡O *trans*), 1938 cm^{-1} (C≡O *cis*); $C_{25}H_{31}NO_7W$ (641.4): calcd C 46.74, H 4.86, N, 2.18; found C 46.92, H 4.92, N 2.17; MS (EI): (*m*/*z*, %): (641, 18) [M^+], (613, < 1), (585, 10), (557, 12), (528, 28), (501, 22).

Pentacarbonyl{methoxy[3-methyl-6-trimethylsilyl-2-trimethylsilyloxymethyl-4-morpholino-3,6-cyclohexadienyl]methylene}tungsten(0) (5f): Compunds **1e** (0.255 g, 1 mmol) and **4a** (0.45 g, 1 mmol) were allowed to react in THF for 1 h. The compound **5f** was isolated as a red oil 95% yield. R_f = 0.6 (hexane/ethyl acetate; 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.01 (s, 9H; (CH_3)$_3$Si), 0.08 (s, 9H; (CH_3)$_3$Si), 1.86 (s, 3H; CH_3), 2.61 (dd, ^3J(H,H) = 5.6, 3.4 Hz, 4H; morpholine), 3.01 (br s, 2H; CH_2), 3.28 (dd, ^2J(H,H) = 9.9, ^3J(H,H) = 5.2 Hz, 1H; CH*H*O), 3.60 – 3.68 (m, 1H; C*H*HO), 3.66 (m, 1H; CH), 3.71 (dd, ^3J(H,H) = 6.0, 2.7 Hz, 4H; morpholine), 4.53 (s, 3H; CH_3O); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = – 0.82 ((CH_3)$_3$Si), – 0.07 ((CH_3)$_3$Si), 16.2 (CH_3), 27.2 (CH_2), 49.9 (CH_2, morpholine), 50.7 (CH), 63.9 (CH_2O), 67.3 (CH_2, morpholine), 67.8 (CH_3O), 122.9 (C=C), 127.4 (C=C), 141.1 (C=C), 197.2 (CO), 202.6 (CO), 331.1 (C=W), the signal for the vinylic carbon attached to the silicon is missing; IR (CH_2Cl_2): $\tilde{\nu}$ = 2068 (C≡O *trans*), 1939 cm^{-1} (C≡O *cis*); $C_{25}H_{37}NO_8SiW$: C 41.73, H 5.18, N 1.95; found C 41.88, H 5.51, N 2.93; HRMS (EI): *m*/*z* calcd for $C_{25}H_{37}NO_8Si^{184}W$ [M^+]: 719.1568, found 719.1542.

Pentacarbonyl{methoxy[6-*tert*-butyl-3-methyl-4-morpholino-2-trimethylsilyloxymethyl-3,6-cyclohexadienyl]methylene}tungsten(0) (5g): Compounds **1e** (1.27 g, 5 mmol) and **4b** (2.31 g, 4.75 mmol) were allowed to react in THF for 6 h. The compound **5g** was isolated as an oil. 71% yield; R_f = 0.51 (hexane/ethyl acetate; 8:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.05 (s, 9H; (CH_3)$_3$Si), 1.09 (s, 9H; (CH_3)$_3$C), 1.89 (s, 3H; CH_3), 2.65 (t, ^3J(H,H) = 6.0 Hz, 4H; morpholine), 2.90 – 3.00 (m, 2H; CH_2), 3.30 (dd, ^2J(H,H) = 14.7, ^3J(H,H) = 9.5 Hz, 1H; C*H*HO), 3.50 (dd, ^2J(H,H) = 14.7, ^3J(H,H) = 7.1 Hz, 1H; CH*H*O), 3.75 (t, m, ^3J(H,H) = 6.7 Hz, 5H; morpholine, CH), 4.55 (s, 3H; CH_3O); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = – 0.64 ((CH_3)$_3$Si), 16.5 ((CH_3)$_3$C), 25.5 (CH_2), 31.1 (CH_3), 37.2 ((CH_3)$_3$*C*), 48.8 (CH), 49.9 (CH_2O), 63.2 (CH_2, morpholine), 66.6 (CH_2, morpholine), 69.6 (CH_3O), 124.6 (C=C), 133.2 (C=C), 141.5 (C=C), 147.8 (C=C), 197.1 (CO), 202.5 (CO), 334.8 (C=W); $C_{26}H_{37}NO_8SiW$ (703.5): calcd C 44.39, H 5.30, N 1.99; found C 44.38, H 5.31, N 1.98; HRMS (EI): *m*/*z* calcd for $C_{26}H_{37}NO_8Si^{184}W$ [M^+]: 703.1798, found 703.1790.

General procedure for the synthesis of complexes 6: 2-Aminodiene **1** (1 mmol) was added to a solution of complex **4** (1 mmol) in dry THF (10 mL) at RT. The reaction mixture was stirred at RT overnight. Then silica gel (2 g) was added to the reaction mixture and stirred for a few minutes until the color of the solution changed from red to purple. The solvents were removed under vacuum and the residue dissolved in hot, dry and degassed hexane and crystallized at – 20 °C.

Pentacarbonyl{methoxy[5-methoxymethylene-3-methyl-4-morpholino-6-trimethylsilyl-4,6-cyclohexadienyl]methylene}tungsten(0) (6b): Compound **6b** was isolated as purple crystals: 74% yield; m.p. 152 – 153 °C; R_f = 0.10 (hexane/ethyl acetate; 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.14 (s, 9H; (CH_3)$_3$Si), 1.09 (d, ^3J(H,H) = 7.3 Hz, 3H; CH_3), 3.08 – 3.18 (m, 2H; CH, C*H*HO), 3.3 (s, 3H; C*H*$_3$OCH$_2$), 3.36 (dd, ^2J(H,H) = 9.8, ^3J(H,H) = 4.8 Hz, 1H; CH*H*O), 3.58 (t, ^3J(H,H) = 4.6 Hz, 4H; morpholine), 3.80 (t, ^3J(H,H) = 4.6, 3.9 Hz, 4H; morpholine), 3.95 (ddd, ^3J(H,H) = 9.4 ,4.9, 1.8 Hz, 1H; C*H*CH$_2$O), 4.33 (s, 3H; CH_3OC=W), 5.46 (s, 1H; CH=C); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 1.4 ((CH_3)$_3$Si), 15.6 (CH_3), 30.0 (CH), 47.0 (CH_2, morpholine), 47.3 (CH), 58.6 (CH_3O), 65.7 (CH_3O), 66.5 (CH_2, morpholine), 71.3 (CH_3OCH_2), 101.6 (HC=C), 139.0 (C=C), 158.5 (C=C), 163.7 (C=C), 199.1 (CO), 202.3 (CO) 275.7 (C=W); IR (CH_2Cl_2): $\tilde{\nu}$ = 2054 (C≡O *trans*), 1915 cm^{-1} (C≡O *cis*); $C_{23}H_{31}NO_8SiW$ (661.4): calcd C 41.77, H 4.72, N 2.12; found C 41.01, H 4.51, N 2.0; HRMS (EI): *m*/*z* calcd for $C_{23}H_{31}NO_8Si^{184}W$ [M^+]: 661.1329, found 661.1330.

Pentacarbonyl{methoxy[5-methyl-4-morpholino-2-trimethylsilyl-1,3-cyclohexadienyl]methylene}tungsten(0) (6c): Compound **6c** was isolated as purple crystals: 93% yield; m.p. 145 °C; R_f = 0.38 (hexane/ethyl acetate; 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.15 (s, 9H; (CH_3)$_3$Si), 0.93 (d, ^3J(H,H) = 7.3 Hz, 3H; CH_3), 2.65 – 2.79 (m, 1H; C*H*Me), 2.95 (dd, ^2J(H,H) = 14.6, ^3J(H,H) = 5.6 Hz, 1H; C*H*HO), 3.70 – 3.85 (m, 5H; morpholine, CH*H*O), 3.90 – 4.10 (m, 4H; morpholine), 4.33 (s, 3H; CH_3O), 5.50 (s, 1H; HC=C); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 1.17 ((CH_3)$_3$Si), 14.2 (CH_3), 30.5 (CH), 40.6 (CH_2), 46.3 (CH_2, morpholine), 65.9 (CH_3O), 66.2 (CH_2, morpholine), 101.5 (HC=C), 140.7 (C=C), 154.8 (C=C), 164.3 (C=C), 199.1 (CO), 202.7 (CO), 279.5 (C=W); IR (CH_2Cl_2): $\tilde{\nu}$ = 2054 (C≡O *trans*), 1919 cm^{-1} (C≡O *cis*); $C_{21}H_{27}NO_7SiW$ (617.4): calcd C 40.90, H 4.40, N 2.27; found C 41.30, H 4.54, N 2.26; MS EI: (*m*/*z*, %): (617, 1) [M^+], (589, < 1), (561, 42), (533, 21), (505, 3), (477, 100).

Pentacarbonyl{methoxy[3-methyl-4-morpholino-6-trimethylsilyl-2-trimethylsilyloxymethyl-4,6-cyclohexadienyl]methylene}tungsten(0) (6f): Compound **6f** was isolated as purple crystals. 69% yield; m.p. 147 – 150 °C; R_f = 0.18 (hexane/ethyl acetate; 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.06 (s, 9H; (CH_3)$_3$Si), 0.13 (s, 9H; (CH_3)$_3$Si), 1.07 (d, ^3J(H,H) = 7.3 Hz, 3H; CH_3), 3.14 – 3.49 (m, 2H; CH, C*H*HO), 3.47 – 3.56 (m, 5H; morpholine, C*H*HO), 3.74 – 3.84 (m, 5H; morpholine, C*H*CH$_2$O), 4.33 (s, 3H; CH_3O), 5.4 (s, 1H; HC=C); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = – 0.58 ((CH_3)$_3$Si), 1.39 ((CH_3)$_3$Si), 15.7 (CH_3), 29.3 (CH), 46.5 (CH_2, morpholine), 48.6 (CH), 61.2 (CH_2O), 65.8 (CH_3O), 66.3 (CH_2, morpholine), 101.4 (HC=C), 140.4 (C=C), 157.6 (C=C), 163.2 (C=C), 198.9 (CO), 202.4 (CO), 278.3 (C=W); IR (CH_2Cl_2): $\tilde{\nu}$ = 2054 (C≡O *trans*), 1921 cm^{-1} (C≡O *cis*); $C_{25}H_{37}O_8Si_2NW$: C 41.73, H 5.18, N 1.95; found C 41.67, H 5.15, N, 1.97; MS EI: (*m*/*z*, %): (719, 17) [M^+], (691, 10), (663, 11), (635, 61), (607, 22), (592, 58), (496, 100).

General method for the preparation of complexes 7: A solution of complex **5** (1 mmol) in THF (10 mL) and aqueous HCl (3 N, 10 mL) was stirred for 1 h and extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated. The crude products were chromatographed on silica gel with mixtures of hexane/ethyl acetate and crystallized from cold hexane.

Pentacarbonyl{methoxy-2-[3-trimethylsilyl-5-oxobicyclo[4.4.0]-dec-2-en-2-yl]methylene}tungsten(0) (7a): 80% yield (orange prims); m.p. 117 – 118 °C; R_f = 0.43 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.09 (s, 9H; (CH_3)$_3$Si), 1.00 – 1.50 (m, 4H; 2 × CH_2; cyclohexyl), 1.69 – 1.84 (m, 3H; cyclohexyl), 2.02 (bd, ^3J(H,H) = 13.2 Hz, 1H; CH), 2.22 (dd, ^3J(H,H) = 13.9, 11.4 Hz, 1H; CHC=C), 2.89 – 3.02 (s, dd, ^3J(H,H) = 13.8, 11.4 Hz, 3H; CHCO, CH_2O), 4.65 (br s, 3H; CH_3O); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = – 0.23 ((CH_3)$_3$Si), 24.7 (CH_2), 25.0 (CH_2), 31.1 (CH_2), 41.8 (2 × CH_2), 47.3 (CH), 51.6 (CH), 69.6 (CH_3O), 122.3 (C=C), 164.5 (C=C), 197.1 (WCO), 210.5 (CO), 202.2 (WCO), 335.7 (C=W); IR (KBr): $\tilde{\nu}$ = 2070 (C≡O *trans*), 1921 (C≡O *cis*), 1711 cm^{-1} (C=O); $C_{20}H_{24}O_7SiW$ (588.3): calcd C 40.80, H 4.10; found C 40.70, H 4.03; MS EI: (*m*/*z*, %): (588, 10) [M^+], (560, 14), (532, 12), (504, 9), (476, 38), (448, 100).

Pentacarbonyl{2-[3-*tert*-butyl-5-oxobicyclo[4.4.0]-dec-2-en-2-yl]methoxymethylene}tungsten(0) (7e): This complex was isolated as a 10:1 mixture of diasteroisomers: 40% yield; R_f = 0.47 (hexane/ethyl acetate 3:1). Spectroscopic data for the major product: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.11 (s, 9H; (CH_3)$_3$C), 1.15 – 1.45 (m, 4H; 2 × CH_2 cyclohexyl), 1.62 – 1.80 (m, 3H; cyclohexyl), 1.97 – 2.20 (m, 2H; cyclohexyl, CHC=C), 2.85 (m, 1H; CHC=O), 3.05 (s, 2H; CH_2C=O), 4.67 (s, 3H; OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 24.7 (CH_2), 25.0 (CH_2), 25.2 (CH_2), 25.4 (CH_2), 31.1 ((CH_3)$_3$C), 31.9 (CH_2), 37.1 ((CH_3)$_3$*C*), 41.6 (CH_2), 45.5 (CH), 51.4 (CH), 69.3 (CH_3), 128.0 (C=C), 149.7 (C=C), 197.3 (WCO), 201.0 (CO), 210.3 (WCO), 339.1 (C=W); IR (CH_2Cl_2): $\tilde{\nu}$ = 2070 (C≡O *trans*), 1941 (C≡O *cis*), 1714 cm^{-1}; $C_{21}H_{24}O_7W$ (572.3): calcd C 44.07, H 4.23; found C 44.35, H 4.23; HRMS (EI): *m*/*z* calcd for $C_{21}H_{24}O_7{}^{184}W$ [M^+]: 572.1035, found 572.1033.

Pentacarbonyl{2-[3-*tert*-butyl-5-oxo-7-oxabicyclo[4.4.0]-dec-2-en-2-yl]-methoxymethylene}tungsten(0) (7h): 54% yield; R_f = 0.19 (hexane/ethyl acetate; 3:1); m.p. 138 – 140 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.10 (s, 9H; (CH_3)$_3$C), 2.29 (dt, ^3J(H,H) = 4.1, 12.4 Hz, 1H; C*H*H pyranyl), 1.56 – 1.63 (m, 1H; CH*H* pyranyl), 1.63 – 1.75 (m, 1H; C*H*H pyranyl), 1.81 – 1.90 (m, 1H; CH*H* pyranyl), 3.02 (m, 1H; CH), 3.13 (d, ^2J(H,H) = 20.8 Hz, 1H, C*H*HCO), 3.25 (dd, ^2J(H,H) = 20.8 Hz, J(H,H) = 2.0 Hz; CH*H*CO), 3.45 (dt, ^2J(H,H) = 11.5 Hz, ^3J(H,H) = 5.0 Hz, 1H; C*H*HO), 3.96 (d, ^3J(H,H) = 10.5 Hz, 1H; CHO), 4.15 (dd, ^2J(H,H) = 11.5,

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4.5 Hz, 1H; CH*H*O), 4.66 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 24.5 (CH_2, pyranyl), 29.0 (CH_2, pyranyl), 30.8 (CH_3), 36.8 (C), 40.8 (*C*H_2C=CO), 43.6 (CH), 67.7 (CH_2O), 69.2 (CH_3O), 81.7 (CHO), 127.7 (C=C), 146.1 (C=C), 196.8 (CO*cis*), 201.8 (C=CO), 203.7 (CO *trans*), 336.2 (C=W); $C_{20}H_{22}O_8W$ (547.2): calcd C 41.83, H 3.86; found C 41.75, H 3.90.

Methyl-2-methoxymethyl-3-methyl-4-oxo-2-trimethylsilyl-2-cyclohexene-carboxylate (**8**): Metal complex **5b** was treated with 4 equivalents of pyridinium oxide in ether at RT for 12 h. After filtration through a pad of silica gel, **8** was isolated as a 3:1 mixture of positional isomers at the double bond. The major isomer was isolated by column chromatography with hexane/ethylacetate 10:1 as eluent. Yield: 45%. R_f = 0.33 (hexane/ethyl-acetate 10:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.12 (s, 9H; $(CH_3)_3Si$), 1.09 (d, ^3J(H,H) = 6.9 Hz, 3H; CH_3), 2.73–2.78 (m, 1H; CH), 2.86–2.95 (m, 1H; CHMe), 3.09 (dd, ^2J(H,H) = 9.5, ^3J(H,H) = 9.5 Hz, 1H; C*H*HO), 3.29 (s, 3H; CH_3O), 3.45 (dd, ^2J(H,H) = 9.5, ^3J(H,H) = 4.5 Hz, 1H; CH*H*O), 3.73–3.79 (m, s, 4H; s = CH_3O, m = CHC=C), 6.32 (s, 1H; HC=C); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = −2.46 ($(CH_3)_3Si$), 11.8 (CH_3), 40.2 (CH), 44.0 (CH), 44.6 (CH), 52.3 (CH_3OCH_2), 58.8 (CH_3OCO), 69.8 (CH_2), 137.1 (HC=C), 158.6 (C=C), 172.6 (CO), 199.3 (CO); HRMS (EI): *m/z* calcd for $C_{13}H_{21}O_4Si$ [$M^+ - CH_3$]: 269.1209, found 269.1210.

2-Methoxymethyl-3-methyl-4-morpholino-6-trimethylsilyl-1,5-cyclohexa-dienecarbaldehyde (**9**): Complex **5b** was treated with sulfuric acid (10 mL) in THF (10 mL) for 12 h. The reaction mixture was extracted with diethyl ether, and the organic layer dried with Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography with hexane/ethyl acetate 3:1. R_f = 0.23. Yield: 34% (colorless oil); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.29 (s, 9H; $(CH_3)_3Si$), 0.93 (d, ^3J(H,H) = 10.5 Hz, 3H; CH_3), 3.13–3.30 (m, 3H), 3.33 (s, 3H; OCH_3), 3.28–3.37 (m, 5H; morpholine, CH), 3.77 (t, ^3J(H,H) = 7.2 Hz, 4H; morpholine), 5.12 (s, 1H; HC=C), 9.70 (s, 1H; CHO); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 1.13 ($(CH_3)_3Si$), 16.9 (CH_3), 28.3 (CH), 37.8 (CH), 46.1 (CH_2, morpholine), 58.3 (CH_3O), 66.4 (CH_2, morpholine), 69.5 (*C*H_2OCH_3), 96.8 (HC=C), 128.3 (C=C), 159.6 (C=C), 160.9 (C=C), 188.8 (CHO); HRMS (EI): *m/z* calcd for $C_{17}H_{29}NO_3Si$ [M^+]: 323.1917, found 323.1914.

General procedure for the synthesis of complexes 10 and 11: Complex **5f** or **5g** (1 mmol) was stirred in THF (10 mL) and aqueous HCl (3N, 10 mL) for 15 min, and was extracted with diethyl ether (3 × 20 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated. The crude product was chromatographed on silica gel with a 3:1 mixture of hexane/ethyl acetate.

Pentacarbonyl[7-*tert*-butyl-4-methyl-3,3a,4,6-tetrahydro-5-isobenzofura-noneylidene]tungsten(0) (**10g**): Yield: 79% (Yellow solid); m.p. 175 °C decomp; R_f = 0.20; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.19 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 1.40 (s, 9H; $(CH_3)_3C$), 1.91 (m, 1H; *H*CCH_2O), 2.49 (dd, ^3J(H,H) = 5.1, 6.6 Hz, 1H; *H*CCW), 3.02 (dq, ^3J(H,H) = 5.1, 6.6 Hz, 1H; *H*CCMe), 4.73 (dd, ^2J(H,H) = 9.8, ^3J(H,H) = 3.5 Hz, 1H; C*H*HO), 4.89 (d, ^2J(H,H) = 9.8 Hz, 1H; CH*H*O), 6.26 (s, 1H; HC=C); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 15.2 (CH_3), 29.1 ($(CH_3)_3C$), 38.1 ($(CH_3)_3C$), 46.7 (CH), 71.0 (CH), 86.3 (CH_2O), 126.1 (C=CH), 166.5 (C=C), 198.7 (CO), 196.7 (WCO), 203.2 (WCO), 325.7 (W=C); IR (CH_2Cl_2): $\tilde{\nu}$ = 2071 (C≡O *trans*), 1948 cm^{-1} (C≡O *cis*); $C_{18}H_{18}O_7W$ (530.2): calcd C 62.42, H 5.24; found C 62.75, H 4.92; HRMS (EI): *m/z* calcd for $C_{18}H_{18}O_7{}^{184}W$ [M^+]: 530.0565, found 530.0574.

(1*S,9*R**)-5-*tert*-butyl-4,6-dien-2-methyl-8-oxabicyclo[4.3.0]nonan-3-one** (**11g**): Yield: 20% (Yellow solid); R_f = 0.40 (hexane/ethyl acetate, 10:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.10 (d, ^3J(H,H) = 6.8 Hz, 3H; CH_3), 1.24 (s, 9H; $(CH_3)_3C$), 2.23 (dq, ^3J(H,H) = 13.7, 6.8 Hz, 1H; *H*CCH_3), 3.05 (ddd, ^3J(H,H) = 13.7, 12.0, 9.0 Hz, 1H; *H*CCH_2), 3.87 (dd, ^2J(H,H) = 12.0, ^3J(H,H) = 9.0 Hz, 1H; CH*H*O), 4.70 (dd, ^2J(H,H) = 9.1, ^3J(H,H) = 9.2 Hz, 1H; *CH*HO), 5.80 (s, 1H; C=CH), 6.95 (s, 1H; C=CH); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 13.1 (CH_3), 30.2 ($(CH_3)_3C$), 36.2 ($(CH_3)_3C$), 46.1 (CH), 47.2 (CH), 74.9 (CH), 112.9 (C=C), 121.1 (C=CH), 145.8 (C=CH), 160.5 (C=C), 200.6 (CO); HRMS (EI): *m/z* calcd for $C_{13}H_{18}O_2$ [M^+]: 206.1313, found 206.1306.

(1*S,9*R**)-2-Methyl-5-trimethylsilyl-4,6-diene-8-oxabicyclo[4.3.0]nonan-3-one** (**11f**): Hydrolysis of **5f** yielded **11f**. The corresponding compound **10g** was not isolated. Yield: 40%. R_f = 0.63; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.24 (s, 9H; $(CH_3)_3Si$), 1.12 (d, ^3J(H,H) = 6.7 Hz, 3H; CH_3), 2.28 (dq, ^3J(H,H) = 13.7, 6.7 Hz, 1H; *H*CCH_3), 3.07 (ddd, ^3J(H,H) = 13.7, 12.1, 9.2 Hz, 1H; *H*CCH_2O), 3.94 (dd, ^2J(H,H) = 12.1, ^3J(H,H) = 9.2 Hz, 1H; CH*H*O), 4.74 (t, ^3J(H,H) = 9.2 Hz, 1H; CH_2O), 6.0 (s, 1H; C=CH), 6.1 (d, J(H,H) = 1.9 Hz, 1H; C=CH); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = −1.25 ($(CH_3)_3Si$), 13.2 (CH_3), 46.1 (CH), 46.3 (CH), 75.9 (CH), 117.6 (C=C), 130.9 (C=CH), 145.8 (C=CH), 152.0 (C=C), 199.1 (CO); $C_{12}H_{18}O_2Si$ (222.4): calcd C 64.80, H 8.16; found C 64.40, H 8.02; HRMS (EI): *m/z* calcd for $C_{12}H_{18}O_2Si$ [M^+]: 222.1076, found 222.1065.

Preparation of carbene complexes 13: Carbene complex **4** (2 mmol) was added to a solution of diene **3** (0.1M, 1 mmol) in THF or toluene at RT. Once the solution color turned from dark red to dark yellow the solvent was evaporated, the crude reaction mixture was filtered through a silica gel column with hexane/ethyl acetate (4:1) as eluent. Two products were obtained, the less polar one was the orange carbene complex **13**, and the second more polar one was the product resulting from the addition of morpholine to the triple bond in the starting carbene complex.

Pentacarbonyl[(5-methyl-4-morpholino-2-trimethylsilylphenyl)methoxy-methylene]tungsten(0) (**13a**): Compound **4a** (2 mmol, 928 mg) was treated with **3** (1 mmol, 238 mg) in toluene for 0.5 h to obtain 418 mg (68%). R_f = 0.59 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.26 (s, 9H; $(CH_3)_3Si$), 2.37 (s, 3H; CH_3), 3.02 (t, ^3J(H,H) = 4.7 Hz, 4H; morpholine), 3.88 (t, ^3J(H,H) = 4.7 Hz, 4H; morpholine), 4.70 (s, 3H; CH_3O), 7.14 (s, 1H; CH, Ar), 7.77 (s, 1H; CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 0.1 ($(CH_3)_3Si$), 17.5 (CH_3), 50.7 (CH_2, morpholine), 66.3 (CH_2, morpholine), 68.6 (CH_3O), 123.8 (CH, Ar), 130.5 (C, Ar), 131.8 (C, Ar), 135.6 (CH, Ar), 151.9 (C, Ar), 155.5 (C, Ar), 196.9 (CO), 202.5 (CO), 324.7 (C=W); HRMS (EI): *m/z* calcd for $C_{21}H_{25}NO_7Si^{184}W$ [M^+]: 615.0889, found: 615.0911.

Pentacarbonyl[(2-*tert*-butyl-5-methyl-4-morpholinophenyl)methoxyme-thylene]tungsten (0) (**13b**): Compound **4b** (2 mmol, 896 mg) was treated with diene **3** (1 mmol, 238 mg) in toluene for 1 h to give **13b** (431 mg, 72%); R_f = 0.42 (hexane/ethyl acetate 3:1); orange crystals; m.p. 91 °C; ^{1}H NMR (200 MHz, C_6D_6, 50 °C): δ = 1.36 (s, 9H; $(CH_3)_3C$), 2.22 (s, 3H; CH_3), 2.68 (t, ^3J(H,H) = 4.6 Hz, 4H; morpholine), 3.65 (t, ^3J(H,H) = 4.6 Hz, 4H; morpholine), 4.02 (s, 3H; CH_3O), 7.04 (s, 1H; CH, Ar), 7.22 (s, 1H; CH, Ar); ^{13}C NMR (50.3 MHz, C_6D_6, 50 °C): δ = 17.9 (CH_3), 34.2 ($(CH_3)_3C$), 37.4 ($(CH_3)_3C$), 53.1 (CH_2, morpholine), 68.0 (CH_2, morpholine), 69.1 (CH_3O), 119.7 (CH, Ar), 128.9 (CH, Ar), 129.7 (C, Ar), 141.6 (C, Ar), 150.9 (C, Ar), 152.7 (C, Ar), 199.0 (CO), 204.4 (CO), 335.6 (C=W); IR (CH_2Cl_2): $\tilde{\nu}$ = 2069 (C≡O *trans*), 1942 cm^{-1} (C≡O *cis*); $C_{22}H_{25}NO_7W$ (599.3): calcd C 44.09, H 4.20, N 2.34; found C 44.39, H 4.17, N 2.37.

Pentacarbonyl[(2-phenyl-5-methyl-4-morpholinophenyl)methoxymethyle-ne]tungsten(0) (**13c**): Compound **4c** (2 mmol, 942 mg) was treated with **3** (1 mmol, 238 mg) in toluene for 0.5 h to give **13c** (483 mg, 78%). R_f = 0.27 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.40 (s, 3H; CH_3), 3.00 (t, ^3J(H,H) = 4.5 Hz, 4H; morpholine), 3.89 (t, ^3J(H,H) = 4.5 Hz, 4H; morpholine), 4.34 (s, 3H; CH_3O), 6.90 (s, 1H; CH, Ar), 7.23–7.40 (m, 6H; phenyl, CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 18.0 (CH_3), 51.8 (CH_2, morpholine), 67.1 (CH_2, morpholine), 69.1 (CH_3O), 120.5 (CH, Ar), 127.0 (CH, Ar), 128.2 (CH, phenyl), 129.1 (CH, phenyl), 130.1 (C, Ar), 133.8 (C, phenyl), 140.8 (C, Ar), 152.0 (C, Ar), 197.0 (CO), 204.0 (CO), 327.7 (C=W); $C_{24}H_{21}NO_7W$ (619.3): calcd C 46.55, H 3.42, N 2.34; found C 46.63, H 3.43, N 2.37.

Pentacarbonyl{[5-methyl-2-(*p*-methoxyphenyl)-4-morpholinophenyl]-methoxymethylene}tungsten(0) (**13d**): Compound **4d** (2 mmol, 996 mg) was treated with diene **3** (1 mmol, 238 mg) in THF for 0.5 h to give **13d** (526 mg, 81%). R_f = 0.48 (hexane/ethyl acetate 3:1); orange crystals; m.p. 128 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.38 (s, 3H; CH_3), 3.00 (t, ^3J(H,H) = 4.5 Hz, 4H; morpholine), 3.84 (s, 3H; CH_3O), 3.89 (t, ^3J(H,H) = 4.5 Hz, 4H; morpholine), 4.39 (s, 3H; CH_3O), 6.90 (s, 1H; CH, Ar), 6.93 (d, ^3J(H,H) = 8.7 Hz, 2H; CH, *p*-methoxyphenyl), 7.13 (s, 1H; CH, Ar), 7.19 (d, ^3J(H,H) = 8.7 Hz, 2H; CH, *p*-methoxyphenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 17.9 (CH_3), 51.8 (CH_2, morpholine), 55.3 (CH_3O), 67.2 (CH_2, morpholine), 69.1 (CH_3O), 113.7 (CH, Ar), 120.4 (CH, Ar), 127.9 (C, (*p*-MeO)Ph), 129.8 (C, Ar), 130.3 (CH, (*p*-MeO)Ph), 133.0 (C, (*p*-MeO)Ph), 133.2 (C, (*p*-MeO)Ph), 141.6 (C, Ar), 151.8 (C, Ar), 158.7 (C, Ar), 197.0 (CO), 204.0 (CO), 328.4 (C=W); IR (CH_2Cl_2): $\tilde{\nu}$ = 2069 (C≡O *trans*), 1940 cm^{-1} (C≡O *cis*); MS: *m/z*: 649, 565, 509, 494; $C_{25}H_{23}NO_8W$ (649.3): calcd C 46.25, H 3.57, N 2.16; found C 46.58, H 3.56, N 2.06.

Pentacarbonyl[(2-*tert*-butyl-5-methyl-4-morpholinophenyl)methoxyme-thylene]chromium(0) (**13e**): Compound **4e** (2 mmol, 632 mg) was treated

with diene **49a** (1 mmol, 238 mg) in toluene for 1 h to give **13e** (327 mg, 70%). $R_f = 0.39$ (hexane/ethyl acetate 3:1); orange crystals; m.p. 128–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.35$ (s, 9H; $(CH_3)_3C$) 2.31 (s, 3H; CH_3), 2.98 (m, 4H; morpholine), 3.88 (m, 4H; morpholine), 4.40 (s, 3H; CH_3O), 6.62 (s, 1H; CH, Ar), 7.03 (s, 1H; CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 17.3$ (CH_3), 32.8 ($(CH_3)_3C$), 36.4 ($(CH_3)_3C$), 52.1 (CH_2, morpholine), 66.1 (CH_3O), 67.3 (CH_2, morpholine), 198.9 (CH, Ar), 125.1 (CH, Ar), 129.3 (C, Ar), 139.8 (C, Ar), 150.9 (C, Ar), 216.4 (CO), 223.7 (CO), 360.9 (C=Cr); $C_{22}H_{25}NO_7Cr$ (467.44): calcd C 56.53, H 5.39, N 3.00; found C 56.51, H 5.40, N 2.98.

Pentacarbonyl[(2-phenyl-5-methyl-4-morpholinophenyl)methoxymethylene]chromium(0) (**13f**): Compound **4f** (2 mmol, 672 mg) was treated with diene **49a** (1 mmol, 238 mg) in toluene for 20 min to give **13f** (375 mg, 77%). $R_f = 0.37$ (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.40$ (s, 3H; CH_3), 3.00 (m, 4H; morpholine), 3.89 (m, 4H; morpholine), 4.41 (s, 3H; CH_3O), 6.95 (s, 1H; CH, Ar), 7.23–7.40 (m, 6H; phenyl, CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 17.9$ (CH_3), 51.8 (CH_2, morpholine), 66.5 (CH_2, morpholine), 67.1 (CH_3O), 120.5 (CH, Ar), 127.3 (CH, Ar), 128.3 (CH, phenyl), 128.9 (CH, phenyl), 130.6 (C, Ar), 132.8 (C, phenyl), 140.1 (C, Ar), 151.4 (C, Ar), 215.7 (CO), 224.0 (CO), 355.9 (C=Cr); HRMS (EI): *m/z* calcd for $C_{21}H_{21}NO_4Cr$ [$M^+ - 3CO$]: 403.0875, found 403.0876.

General procedure for the synthesis of fluorene derivatives 15 and 28: 2-Aminodiene **1** (1 mmol) was added to a solution of complex **4** (1 mmol) in dry THF (10 mL) at RT. The reaction mixture was stirred at RT for the time indicated and concentrated at reduced pressure (10^{-2} Torr). The crude mixture was dissolved in dry diethyl ether, filtered through a pad of Celite and cooled to −20 °C overnight to induce precipitation/crystallization of $W(CO)_6$. Compounds **15** and **28**, when solid, were crystallized from cold hexane.

4,9-Dihydro-2-methyl-9-methoxy-3-morpholino-1*H*-fluorene (**15a**): 95% yield; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.85$ (s, 3H; CH_3), 2.76 (t, ^3J(H,H) = 4.7 Hz, 4H; morpholine), 2.90–3.10 (m, 2H; CH_2), 3.08 (s, 3H; CH_3O), 3.71–3.80 (m, 6H; morpholine, CH_2), 4.92 (s, 1H; *H*CCH_3), 7.12–7.19 (m, 2H; phenyl), 7.27 (d, ^3J(H,H) = 7.3 Hz, 1H; phenyl), 7.45 (d, ^3J(H,H) = 7.3 Hz, 1H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 17.5$ (CH_3), 20.7 (CH_2), 31.2 (CH_2), 50.0 (CH_2, morpholine), 52.3 (CH_3O), 67.3 (CH_2, morpholine), 83.2 (C*H*OCH_3), 117.8 (CH, Ph), 121.6 (C=C), 123.4 (CH, phenyl), 125.0 (CH, phenyl), 128.1 (CH, phenyl), 136.0 (C=C) 137.0 (C=C), 137.4 (C=C), 141.9 (C=C), 143.5 (C=C); HRMS (EI): *m/z* calcd for $C_{18}H_{23}NO_2$ [M^+]: 297.1728, found 297.1718.

(1*R,9*S**)-4,9-Dihydro-9-methoxy-1-methoxymethyl-2-methyl-3-morpholino-1*H*-fluorene** (**15b**): 95% yield; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.94$ (s, 3H; CH_3), 2.77 (t, ^3J(H,H) = 4.1 Hz, 4H; morpholine), 3.09 (s, 3H; CH_3O), 3.32 (s, 3H; CH_3O), 3.40–3.53 (m, 2H; CH_2O), 3.70–3.81 (t, m, ^3J(H,H) = 4.2 Hz, 7H; morpholine), 5.21 (s, 1H; C*H*OCH_3), 7.21–7.49 (m, 4H; phenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 15.8$ (CH_3), 20.9 (CH_2), 41.1 (CH), 50.0 (CH_2, morpholine), 52.3 (OCH_3), 58.8 (OCH_3), 67.2 (CH_2, morpholine), 74.4 (CH_2O), 82.0 (C*H*OCH_3), 117.9 (CH, phenyl), 121.9 (C=C), 123.4 (CH, phenyl), 124.9 (CH, phenyl), 127.9 (CH, phenyl), 136.6 (C=C), 139.5 (C=C), 139.9 (C=C), 142.3 (C=C), 143.3 (C=C); HRMS (EI): *m/z* calcd for $C_{21}H_{27}NO_3$ [M^+]: 341.1990, found 341.1984.

(11*R,11b*S**)-2,3,4,6,11,11b-Hexahydro-11-methoxy-5-morpholino-1*H*-benzo[*a*]fluorene** (**15c**): 92% yield; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.00–2.30$ (m, 8H; cyclohexyl), 1.83 (t, ^3J(H,H) = 4.7 Hz, 4H; morpholine), 3.06 (s, 3H; CH_3O), 3.32–3.40 (m, 3H), 3.74 (t, ^3J(H,H) = 4.7 Hz, 4H; morpholine), 5.87 (s, 1H; C*H*OCH_3), 7.12–7.22 (t, ^3J(H,H) = 7.6 Hz, 2H; phenyl), 7.00 (d, ^3J(H,H) = 7.6 Hz, 1H; phenyl), 7.00 (d, ^3J(H,H) = 7.7 Hz, 1H; phenyl); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 20.5$ (CH_2, cyclohexyl), 26.5 (CH_2, cyclohexyl), 27.4 (CH_2, cyclohexyl), 27.9 (CH_2, cyclohexyl), 34.7 (CH_2), 38.1 (CH), 50.5 (CH_2, morpholine), 52.2 (CH_3O), 67.2 (CH_2, morpholine), 80.8 (C*H*OCH_3), 117.9 (CH, Ph), 123.4 (CH, phenyl), 124.9 (CH, phenyl) 128.4 (C=C), 128.8 (CH, phenyl), 134,6 (C=C), 135.0 (C=C), 141.3 (C=C), 141.8 (C=C), 143.5 (C=C); $C_{22}H_{27}NO_2$ (337.5): calcd C 78.30, H 8.06, N 4.15; found C 78.57, H 8.02, N 4.14; HRMS (EI): *m/z* calcd for $C_{22}H_{27}NO_2$ [M^+]: 337.2041, found 337.2043.

4,9-Dihydro-2,7-dimethyl-9-methoxy-3-morpholino-1*H*-fluorene (**28a**): 90% yield; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.87$ (s, 3H; CH_3), 2.45 (s, 3H; CH_3Ph), 2.76 (t, ^3J(H,H) = 2.55 Hz, 4H; morpholine), 3.09 (s, 3H; CH_3O), 3.72–3.80 (m, 4H; morpholine), 4.90 (s, 1H; C*H*OCH_3), 7.00–7.28 (m, 3H; aryl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 17.6$ (CH_3), 20.8 (CH_2), 21.4 (CH_3Ph), 31.3 (CH_2), 50.1 (CH_2, morpholine), 52.4 (CH_3O), 67.4 (CH_2, morpholine), 83.3 (C*H*OCH_3), 117.5 (CH, aryl), 121.4 (C=C), 124.6 (CH, aryl), 128.6 (CH, aryl), 134.8 (C=C) 136.0 (C=C), 136.4 (C=C), 137.2 (C=C), 140.9 (C=C), 142.2 (C=C).

4,9-Dihydro-7,9-dimethoxy-2-methyl-3-morpholino-1*H*-fluorene (**28b**): 95% yield, m.p. 132–134 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.86$ (s, 3H; CH_3), 2.75 (t, ^3J(H,H) = 4.7 Hz, 4H; morpholine), 2.90–3.06 (s, m, 5H; s = CH_3O, CH_2), 3.65–3.80 (s, m, 9H; CH_3O, morpholine, CH_2), 4.87 (s, 1H; C*H*OCH_3), 6.79 (dd, ^3J(H,H) = 8.2, 2.5 Hz, 1H; aryl), 6.99 (s, 1H; aryl), 7.04 (dd, ^3J(H,H) = 8.2, 2.5 Hz, 1H; aryl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 17.5$ (CH_3), 20.7 (CH_2), 31.1 (CH_2), 49.9 (CH_2, morpholine), 50.0 (CH_3O), 55.6 (CH_3O), 67.2 (CH_2, morpholine), 83.0 (C*H*OCH_3), 110.9 (CH, aryl), 112.2 (CH, aryl), 117.9 (CH, aryl), 121.2 (C=C), 135.1 (C=C), 135.7 (C=C) 136.3 (C=C), 136.9 (C=C), 143.8 (C=C), 158.0 (C=C); $C_{20}H_{25}NO_3$ (327.4): calcd C 73.37, H 7.63, N 4.55; found C 73.37, H 7.70, N 4.28.

(1*R,9*S**)-4,9-Dihydro-2,7-dimethyl-9-methoxy-1-methoxymethyl-3-morpholino-1*H*-fluorene** (**28d**): 97% yield; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.82$ (s, 3H; CH_3), 2.35 (s, 3H; CH_3Ph), 2.74 (t, ^3J(H,H) = 5.5 Hz, 4H; morpholine), 3.06 (s, 3H; CH_3O), 3.20–3.50 (m, 5H; morpholine, C*H*HO), 3.70–3.80 (m, 3H), 4.14 (t, ^3J(H,H) = 5.1, 1H; CH*H*O), 5.14 (s, 1H; CHOMe), 7.00–7.08 (m, 2H; aryl), 7.26 (s, 1H; aryl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 15.8$ (CH_3), 20.9 (CH_2), 21.3 (CH_3Ph), 41.1 (CH), 50.0 (CH_2, morpholine), 52.3 (OCH_3), 58.8 (OCH_3), 67.2 (CH_2, morpholine), 74.5 (CH_2O), 81.9 (C*H*OCH_3), 117.6 (CH, aryl), 121.9 (C=C), 124.5 (CH, aryl), 128.1 (CH, aryl), 134.7 (C=C) 136.0 (C=C), 136.5 (C=C), 138.8 (C=C), 139.6 (C=C), 140.7 (C=C), 142.4 (C=C); $C_{22}H_{29}NO_3$ (355.5): calcd C 74.33, H 8.22, N 3.94; found C 74.62, H 7.89, N 4.18.

(1*R,9*S**)-4,9-Dihydro-7,9-dimethoxy-1-methoxymethyl-2-methyl-3-morpholino-1*H*-fluorene** (**28e**): 94% yield; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.83$ (s, 3H; CH_3), 2.67 (dd, ^3J(H,H) = 3.4, 5.6 Hz, 4H; morpholine), 3.09 (s, m, 5H; s = CH_3O, m = CH_2), 3.22 (s, 3H; CH_3O), 3.29–3.40 (m, 1H; C*H*HO), 3.50–3.71 (m, s, 9H; CH_3O, morpholine, CH*H*O), 5.08 (s, 1H; C*H*OCH_3), 6.71 (dd, ^3J(H,H) = 8.1, ^4J(H,H) = 2.1 Hz, 1H; aryl), 6.94–7.00 (m, 2H; aryl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 15.7$ (CH_3), 20.9 (CH_2), 41.0 (CH), 49.7 (CH_2, morpholine), 52.0 (CH_3O), 55.2 (CH_3O), 58.7 (CH_3O), 67.5 (CH_2, morpholine), 74.4 (CH_2O), 87.7 (C*H*OCH_3), 110.9 (CH, aryl), 112.1 (CH, aryl), 118.2 (CH, aryl), 121.8 (C=C), 136.1 (C=C), 136.2 (C=C), 137.6 (C=C), 139.4 C(=C), 144.2 (C=C), 158.1 (C=C); $C_{22}H_{29}NO_4$ (371.5): calcd C 71.13, H 7.87, N 3.77; found C 70.81, H 7.48, N 3.51; HRMS (EI): *m/z* calcd for $C_{22}H_{29}NO_4$ [M^+]: 371.2096, found 371.2081.

(11*R,11b*S**)-2,3,4,6,11,11b-Hexahydro-11-methoxy-9-methyl-5-morpholino-1*H*-benzo[*a*]fluorene** (**28f**): 95% yield; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.08–1.31$ (m, 4H; 2 × CH_2, cyclohexyl), 1.50–1.68 (m, 4H; 2 × CH_2, cyclohexyl), 2.38 (s, 3H; CH_3), 2.74 (t, ^3J(H,H) = 4.6 Hz, 4H; morpholine), 3.06 (s, m, 4H; s = CH_3O), 3.30–3.39 (m, 2H), 3.74 (t, ^3J(H,H) = 4.3 Hz, 4H; morpholine), 5.06 (s, 1H; C*H*OCH_3), 7.02 (d, ^3J(H,H) = 7.7 Hz, 1H; aryl), 7.10 (d, ^3J(H,H) = 7.7 Hz, 1H; aryl), 7.28 (s, 1H; aryl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 20.7$ (CH_2, cyclohexyl), 21.4 (CH_3), 26.6 (CH_2, cyclohexyl), 27.5 (CH_2, cyclohexyl), 28.0 (CH_2, cyclohexyl), 34.8 (CH_2), 38.2 (CH), 50.7 (CH_2, morpholine), 52.3 (CH_3O), 67.3 (CH_2, morpholine), 80.9 (C*H*OCH_3), 117.7 (CH, aryl), 124.7 (CH, aryl) 128.5 (CH, aryl), 128.9 (C=C), 134.6 (C=C), 134.7 (C=C), 135.2 (C=C), 140.3 (C=C), 141.0 (C=C), 142.2 (C=C); $C_{23}H_{29}NO_3$ (367.5): calcd C 75.17, H 7.95, N 3.81; found C 75.23, H 7.58, N 3.51.

(11*R,11b*S**)-2,3,4,6,11,11b-Hexahydro-9,11-dimethoxy-5-morpholino-1-*H*-benzo[*a*]fluorene** (**28g**): 96% yield; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.00–1.21$ (m, 3H; cyclohexyl), 1.40–1.61 (m, 3H; cyclohexyl), 2.10–2.19 (m, 2H; cyclohexyl), 2.60–2.68 (m, 4H), 2.96 (s, m, 4H; s = CH_3O), 3.20–3.29 (m, 2H), 3.40–3.70 (m, 4H; morpholine), 3.72 (s, 3H; CH_3O), 4.97 (s, 1H; C*H*OCH_3) 6.71 (dd, ^3J(H,H) = 8.1, ^4J(H,H) = 2.1 Hz, 1H; aryl), 6.94 (d, ^3J(H,H) = 8.1 Hz, 1H; aryl), 6.99 (d, ^3J(H,H) = 2.1 Hz, 1H; aryl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 20.6$ (CH_2, cyclohexyl), 26.4 (CH_2, cyclohexyl), 27.4 (CH_2, cyclohexyl), 27.9 (CH_2, cyclohexyl), 34.7 (CH_2), 38.1 (CH), 50.5 (CH_2, morpholine), 51.9 (CH_3), 55.2 (CH_3), 67.2 (CH_2, morpholine), 80.7 (C*H*OCH_3), 110.9 (CH, aryl), 112.3 (CH, aryl), 118.1 (CH, aryl), 128.1 (C=C), 134.3 (C=C), 135.0 (C=C), 136.4 (C=C), 138.9 (C=C), 143.7 (C=C), 158.0 (C=C).

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General procedure for the preparation 16 and 17 from the hydrolysis of 15: Fluorene **15** was dissolved in THF (10 mL) and aqueous HCl (3 N, 10 mL). The mixture was stirred for 3 h and extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (20 mL), dried over Na_2SO_4, and evaporated. The crude product was chromatographed on silica gel with a 3:1 mixture of hexane/ethyl acetate.

9-Methoxy-2-methyl-2,9,9a-trihydro-1*H*-fluorene-3-one (**16a**): Yield: 75%. $R_f = 0.30$; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.25$ (d, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 2.5–2.6 (m, 2H; CH_2), 2.90–2.99 (m, 1H; CHMe), 3.1–3.2 (m, 1H; CH), 3.6 (s, 3H; OCH_3), 4.6 (d, $^3J(H,H) = 5.1$ Hz ,1H; C*H*OCH_3), 6.3 (d, $^4J(H,H) = 3.0$ Hz, 1H; C=CH), 7.4–7.6 (m, 4H; phenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 15.6$ (CH_3), 37.2 (CH), 41.6 (CH), 49.7 (CH), 57.7 (CH_2), 86.6 (OCH_3), 117.5 (C=CH), 122.4 (CH, phenyl), 125.2 (CH, phenyl), 129.1 (CH, phenyl), 131.7 (CH, phenyl), 136.5 (C=C), 146.8 (C=C), 162.6 (C=C) 201.4 (CO); $C_{15}H_{16}O_2$ (228.3): calcd C 78.92, H 7.06; found C 78.89, H 7.04; HRMS (EI): *m/z* calcd for $C_{15}H_{16}O_2$ [M^+]: 228.1147, found 228.1150.

(1*S,2*S**,9*S**,9a*S**)-9-Methoxy-1-methoxymethyl-2-methyl-2,9,9a-trihydro-1*H*-fluorene-3-one** (**16b**): Yield: 50%. $R_f = 0.28$; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.17$ (d, $^3J(H,H) = 7.3$ Hz, 3H; CH_3), 2.75–2.84 (dq, $^3J(H,H) = 4.3$, 7.3 Hz, 1H; C*H*CH_3), 2.84–2.95 (m, 1H; C*H*CHOCH_3), 3.01 (ddd, $^3J(H,H) = 10.3$, 5.4, 2.2 Hz, 1H; C*H*CH_2OCH_3), 3.33 (s, 3H; OCH_3), 3.41 (s, 3H; OCH_3), 3.59 (m, 1H; C*H*OCH_3), 4.70 (d, $^3J(H,H) = 5.4$ Hz, 1H; CH_3OC*H*), 6,36 (d, $^3J(H,H) = 2.2$ Hz, 1H; C=CH), 7.45–7.48 (m, 2H; phenyl), 7.50–7.56 (m, 1H; phenyl), 7.66–7.68 (m, 1H; phenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 11.4$ (CH_3), 36.1 (CH), 42.0 (CH), 44.3 (CH), 55.9 (OCH_3), 58.9 (OCH_3), 72.2 (CH_2), 80.7 (CH_3OCH), 117.7 (C=CH), 123.5 (C=CH, phenyl), 126.1 (C=CH, phenyl), 129.6 (C=CH, phenyl), 130.9 (C=CH, phenyl) 138.3 (C=C), 145.8 (C=C), 163.3 (C=C), 203.5 (CO); HRMS (EI): *m/z* calcd for $C_{17}H_{20}O_3$ [M^+]: 272.1412, found 272.1398. The stereochemistry of this compound was asigned by NOE difference spectroscopy. Irradation of the methyl signal at 1.17 produced a 2.7% enhancement of the H-8′ signal at 2.99. Irradation of the H-9 signal at 4.70 produced a 7.7% enhancement of the H-8′ signal at 2.99.

(4a*S,11*S**,11a*R**,11b*R**)-2,3,4,4a,11,11a,11b-Heptahydro-11-methoxy-1*H*-benzo[*a*]fluorene-5-one** (**16c**): Yield: 80%, white solid, m.p. 146 °C; R_f = 0.14 (hexane/ethyl acetate, 10:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.17$–2.13 (m, 9H; cyclohexyl), 2.37 (d, $^3J(H,H) = 5.7$ Hz, 1H; C*H*CHOMe), 2.85 (m, 1H), 3.34 (s, 3H; OCH_3), 4.76 (d, $^3J(H,H) = 5.7$ Hz, 1H; C*H*OCH_3), 6.39 (d, $^3J(H,H) = 2.5$ Hz, 1H; HC=C), 7.43–7.68 (m, 4H; phenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 25.1$ (CH_2, cyclohexyl), 25.8 (2 × CH_2, cyclohexyl), 31.6 (CH_2, cyclohexyl), 39.0 (CH), 50.3 (CH), 56.1 (OCH_3), 80.3 (*C*HOCH_3), 118.4 (C=C), 123.4 (C=CH, phenyl), 126.2 (C=CH, phenyl), 129.5 (C=CH, phenyl), 130.8 (C=CH, phenyl), 138.6 (C=C, phenyl), 145.7 (C=C; phenyl) 163.2 (*C*=CH), 200.9 (CO); IR (CH_2Cl_2): $\tilde{\nu} = 1658$ cm^{-1} (C=O); HRMS (EI): *m/z* calcd for $C_{18}H_{20}O_2$ [M^+]: 268.1463, found 268.1465.

(1*R,2*S**,9*S**)-9-Methoxy-1-methoxymethyl-2-methyl-2,4,9-trihydro-1*H*-fluorene-3-one** (**17b**): Yield 60%. $R_f = 0.21$; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.25$ (d, $^3J(H,H) = 6.7$ Hz, 3H; CH_3), 2.78 (dq, $^3J(H,H) = 7.7$, 6.7 Hz, 1H; C*H*CH_3), 3.00–3.06 (m, 1H; CH), 3.14 (s, 3H; OCH_3), 3.19 (s, 3H; OCH_3), 3.26 (s, 2H; CH_2), 3.51 (brs, 2H; OCH_2), 5.16 (brs, 1H; C*H*OCH_3), 7.13 (d, $^3J(H,H) = 6.9$ Hz, 1H; phenyl), 7.19–7.36 (m, 2H; phenyl), 7.52 (d, $^3J(H,H) = 6.3$ Hz, 1H; phenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 11.4$ (CH_3), 36.7 (CH_2), 40.1 (CH), 44.5 (CH), 52.4 (OCH_3), 58.8 (OCH_3), 71.0 (OCH_2), 81.5 (OCH_3), 118.4 (CH, phenyl), 123.9 (CH, phenyl), 125.7 (CH, phenyl), 128.4 (CH, phenyl), 138.0 (C=C) 141.9 (C=C), 142.1 (C=C), 142.5 (C=C), 209.3 (CO); HRMS (EI): *m/z* calcd for $C_{17}H_{20}O_3$ [M^+]: 272.1412, found 272.1432.

(1*R,2*S**,9*S**)-9-Methoxy-2-methyl-2,4,9-trihydro-1-trimethylsilyloxymethyl-1*H*-fluorene-3-one** (**17d**): Yield: 83%; white solid; $R_f = 0.29$ (hexane/ethyl acetate, 10:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -0.04$ (s, 9H; $Si(CH_3)_3$), 1.2 (d, $^3J(H,H) = 6.4$ Hz, 3H; CH_3), 2.80 (dq, $^3J(H,H) = 12.7$, 6.4 Hz, 1H; C*H*CH_3), 2.92–2.94 (m, 1H; CH), 3.13 (s, 3H; OCH_3), 3.21–3.24 (m, 2H; CH_2), 3.6 (dd, $^2J(H,H) = 10.1$, $^3J(H,H) = 1.9$ Hz, 1H; C*H*O), 3.8 (dd, $^2J(H,H) = 10.1$, $^2J(H,H) = 3.5$ Hz, 1H; CH*H*O), 5.1 (brs, 1H; C*H*OCH_3), 7.1–7.4 (m, 3H; phenyl), 7.5 (d, $^3J(H,H) = 6.7$ Hz, 1H; phenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = -1.0$ ($Si(CH_3)_3$), 11.4 (CH_3), 36.7 (CH_2), 41.7 (CH), 44.5 (CH), 52.4 (OCH_3), 60.5 (OCH_2), 81.4 (*C*HOCH_3), 118.3(CH, phenyl), 123.9 (CH, phenyl), 125.6 (CH, phenyl), 128.5 (CH, phenyl), 138.6 (C=C), 141.9 (C=C) 142.2 (C=C), 142.7 (C=C), 209.2 (CO); IR (CH_2Cl_2): $\tilde{\nu} = 1658$ cm^{-1} (C=O); HRMS (EI): *m/z* calcd for $C_{19}H_{26}SiO_3$ [M^+]: 330.1651, found 330.1650.

General procedure for the preparation of fluorenedione derivatives 18 and 29: The fluorene **15** (or **28**) was dissolved in THF (10 mL) and aqueous HCl (3 N, 10 mL). The mixture was stirred overnight and extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (20 mL), dried over Na_2SO_4, and evaporated. The crude product was chromatographed in silica gel with hexane/ethyl acetate (3:1).

2-Methyl-2,4,4a,9a-tetrahydro-1*H*-fluorene-3,9-dione (**18a**): Yield: 50%; $R_f = 0.20$; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.08$ (d, $^3J(H,H) = 6.8$ Hz, 3H; CH_3), 1.56 (q, $^3J(H,H) = 13.7$ Hz, 1H; C*H*CH_3), 2.20–2.42 (m, 3H; CH, C*H*HO), 2.82 (dd, $^2J(H,H) = 15.2$, $^3J(H,H) = 6.3$ Hz, 1H; CH*H*O), 2.97 (ddq, $^3J(H,H) = 13.7$, 12.0, 2.6 Hz, 1H; C*H*CH_3), 3.70 (sept, $^3J(H,H) = 7.3$ Hz, 1H), 7.36–7.43 (m, 2H; phenyl), 7.59 (dd, $^3J(H,H) = 9.0$, 7.7 Hz, 1H; phenyl), 7.75 (d, $^3J(H,H) = 7.7$ Hz, 1H; phenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 15.7$ (CH_3), 29.7 (CH_2), 36.4 (CH), 41.6 (CH), 42.9 (CH_2), 46.1 (CH), 124.3 (CH, phenyl), 125.6 (CH, phenyl), 128.3 (CH, phenyl), 135.4 (CH, phenyl), 135.5 (C=C, phenyl), 156.5 (C=C, phenyl), 206.7 (CO), 213.3 (CO); $C_{14}H_{14}O_2$ (214.3): calcd C 78.48, H 6.59; found C 78.69, H 6.98; HRMS (EI): *m/z* calcd for $C_{14}H_{14}O_2$ [M^+]: 214.0993, found 214.0996.

(1*R,2*S**)-1-Methoxymethyl-2-methyl-2,4,4a,9a-tetrahydro-1*H*-fluorene-3,9-dione** (**18b**): Yield: 51%; $R_f = 0.16$; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.02$ (d, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 2.18 (quintet, $^3J(H,H) = 6.9$ Hz, 1HN C*H*CH_3), 2.33 (dd, $^2J(H,H) = 17.1$, $^3J(H,H) = 7.6$ Hz, 1H; C*H*HCO), 2.70 (quintet, $^3J(H,H) = 5.1$ Hz, 1H; C*H*CH_2O), 2.80–3.11 (m, 2H), 3.29 (s, 3H; OCH_3), 3.48 (dd, $^2J(H,H) = 17.8$, $^3J(H,H) = 9.5$ Hz, 1H; CH*H*CO), 3.68 (dd, $^3J(H,H) = 17.8$, 5.4 Hz, 1H; CH*H*O), 3.85 (dd, $^3J(H,H) = 15.2$, 7.6 Hz, 1H; CHC=CO), 7.31–7.41 (m, 2H; phenyl), 7.53–7.61 (m, 1H; phenyl), 7.73 (d, $^3J(H,H) = 7.6$ Hz, 1H; phenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 11.6$ (CH_3), 37.3 (CH), 40.4 (CH), 42.5 (CH), 43.5 (CH_2), 49.1 (CH), 58.8 (OCH_3), 72.0 (OCH_2), 123.9(CH, phenyl), 125.1 (CH, phenyl), 128.0 (CH, phenyl), 135.3 (CH, phenyl), 157.6 (C), 207.1 (C) 211.2 (CO); HRMS (EI): *m/z* calcd for $C_{16}H_{18}O_3$ [M^+]: 258.1256, found 258.1242.

7-Chloro-2-methyl-2,4,4a,9a-tetrahydro-1*H*-fluorene-3,9-dione (**29c**): Mixture of epimers 1:1. Yield: 36%. **29′** $R_f = 0.35$; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.15$ (d, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 2.27–2.48 (m, 4H), 2.88 (dd, $^2J(H,H) = 15.5$, $^3J(H,H) = 5.6$ Hz, 1H; C*H*HO), 3.05 (ddq, $^3J(H,H) = 7.8$, 7.7, 5.1 Hz, 1H; C*H*CH_3), 3.68–3.77 (m, 1H), 7.43 (dd, $^3J(H,H) = 8.1$, 0.8 Hz, 1H; phenyl), 7.62 (dd, $^3J(H,H) = 8.1$, 2.1 Hz, 1H; phenyl), 7.77 (d, $^3J(H,H) = 2.1$ Hz, 1H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 15.7$ (CH_3), 29.6 (CH_2), 36.0 (CH), 41.7 (CH), 42.7 (CH_2), 46.6 (CH), 124.1 (CH, phenyl), 126.8 (CH, phenyl), 134.7 (C, phenyl), 135.4 (CH, phenyl), 137.1 (C, phenyl), 154.5 (C, phenyl), 205.3 (CO), 212.7 (CO); HRMS (EI): *m/z* calcd for $C_{14}H_{13}ClO_2$ [M^+]: 248.0604, found 248.0611. **29″** $R_f = 0.34$; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.07$(d, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 2.25–2.28 (m, 1H), 2.02 (td, $^3J(H,H) = 11.6$, 6.5 Hz, 1H), 2.39 (dt, $^3J(H,H) = 14.1$, 4.3 Hz, 1H), 2.70 (dd, $^3J(H,H) = 15.9$, 6.9 Hz, 1H), 2.96 (dd, $^3J(H,H) = 15.9$, 6.9 Hz, 1H), 3.09–3.15 (m, 1H), 3.88 (q, $^3J(H,H) = 4.7$ Hz, 1H), 7.44 (d, $^3J(H,H) = 8.1$ Hz, 1H; phenyl), 7.60 (dd, $^3J(H,H) = 8.1$, 1.7 Hz, 1H; phenyl), 7.74 (d, $^3J(H,H) = 1.7$ Hz, 1H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 15.4$ (CH_3), 30.8 (CH_2), 36.3 (CH), 40.5 (CH), 41.9 (CH_2), 45.4 (CH), 123.6 (CH, phenyl), 126.7 (CH, phenyl), 134.8 (C, phenyl), 135.6 (CH, phenyl), 138.2 (C, phenyl), 154.8 (C, phenyl), 206.6 (CO), 212.3 (CO); HRMS (EI): *m/z* calcd for $C_{14}H_{13}ClO_2$ [M^+]: 248.0604, found 248.0609.

Pentacarbonyl[2-(*Z*)-6-(*E*)-6-methyl-1-methoxy-7-methoxymethyl-5-morpholino-3-phenylocta-2,4,6-trien-1-ylidene]tungsten(0) (**19**): 2-Aminodiene **1d** (1 mmol) was added to a solution of complex **4c** (1 mmol) in dry THF (10 mL) at RT. The reaction mixture was stirred at RT for a few minutes until the solution changed its color to purple, and was then concentrated at reduced pressure (10^{-2} torr). The crude reaction mixture was dissolved in dry hexane/diethyl ether (3:1), filtered through a pad of Celite and cooled to −20 °C overnight to induce crystallization of complex. Yield: 95% (purple crystals); m.p. 140 °C; $R_f = 0.12$ (hexane/ethyl acetate; 3:1); ^{1}H NMR (400 MHz,$CDCl_3$, −20 °C, TMS) $\delta = 1.31$ (s, 3H; CH_3), 3.19

(m, 4H; morpholine), 3.28 (s, 3H; OCH_3), 3.51 (dd, $^2J(H,H) = 9.7$, $^3J(H,H) = 6.5$ Hz, 1H; C*H*HO), 3.70 (dd, $^2J(H,H) = 9.4$, $^3J(H,H) = 9.7$ Hz, 1H; CH*H*O), 3.79 (m, 4H; morpholine), 4.59 (s, 3H; W=$COCH_3$), 5.18 (d, $^5J(H,H) = 2.9$ Hz, 1H; HC=C morpholine), 6.36 (s, 1H; HC=C), 7.30 (br s, 5H; phenyl), 7.35 (m, 1H;C=C*H*CH_2O); ^{13}C NMR (100 MHz,$CDCl_3$, -20 °C): $\delta = 22.6$ (CH_3), 48.7 (CH_2), 58.7 (OCH_3), 63.4 (CH_2, morpholine), 68.4 (W=$COCH_3$), 70.1 (CH_2, morpholine), 109.6 (CH), 127.8 (CH), 129.1 (CH), 129.4 (CH), 132.8 (CH), 133.8 (C), 140.9 (morpholine, C=*C*H), 143.6 (C), 149.5 (C), 160.6 (C), 198.7 (CO), 204.6 (CO), 293.2 (W=C); IR (CH_2Cl_2): $\tilde{\nu} = 2060$ (C≡O *trans*), 1932 cm^{-1} (C≡O *cis*); $C_{26}H_{27}NO_8W$ (665.4): calcd C 64.90, H 5.66, N 2.91; found C 64.10, H 5.34, N 2.71; HRMS (EI): *m/z* calcd for $C_{26}H_{27}NO_8{}^{184}W$ [M^+]: 665.1252, found 665.1238.

2-Phenyl-5-methyl-6-methoxymethyl-4-morpholino-1,3-cyclohexadiene-carbaldehyde (**20**): Compound **19** (0.5 mmol) was dissolved in THF (10 mL). The reaction mixture was warmed up to reflux. After chromatographic purification, compound **20** was isolated as an oil. Yield: 10%; $R_f =$ 0.10 (hexane/ethyl acetate; 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.09$ (d, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 3.27–3.40 (m, s, 11H; s = OCH_3), 3.76 (t, $^3J(H,H) = 5.0$ Hz, 4H; morpholine), 4.90 (s, 1H; CH), 7.27–7.40 (m, 5H; phenyl), 9.27 (s, 1H; CHO); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta =$ 17.3 (CH_3), 28.9 (CH), 37.9 (CH), 46.3 (CH_2, morpholine), 58.4 (OCH_3), 66.3 (CH_2, morpholine), 69.9 (CH_2), 96.1 (C=*C*H), 118.2 (C=C), 127.9 (C=CH), 128.9 (C=CH), 138.9 (C=C), 158.5 (C=C), 160.5 (C=C), 189.7 (CHO); HRMS (EI): *m/z* calcd for $C_{20}H_{25}NO_3$ [M^+]: 327.1831, found. 327.1834.

4,9-Dihydro-3,9-dimethoxy-1-phenyl-*1H*-fluorene (**22a**): Diene **21a** (1 mmol) was added **t**o a solution of complex **4c** (1 mmol) in dry THF (10 mL) at RT. The reaction mixture was stirred at RT for 72 h and concentrated at reduced pressure (10^{-2} Torr). The crude mixture was chromatographed on silica gel with hexane/dichloromethane (4:1). Yield: 51% (red oil); $R_f = 0.60$; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.03$ (s, 3H; OCH_3), 3.22 (d, $^2J(H,H) = 4.3$ Hz, 1H; C*H*H), 3.63 (s, 3H; OCH_3), 3.82 (d, $^3J(H,H) = 6.7$ Hz, 1H; CHPh), 4.34 (d, $^2J(H,H) = 4.3$ Hz, $J(H,H) =$ 2.9 Hz, 1H; CH*H*), 4.54 (s, 1H; C*H*OCH_3), 4.82 (d, $^3J(H,H) = 6.7$ Hz, 1H; C=CCH), 7.04–7.17 (m, 9H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 26.6$ (CH_2), 41.6 (CH), 52.5 (OCH_3), 54.4 (OCH_3), 81.2 (H*C*OCH_3), 96.6 (C=CH), 118.4 (CH, phenyl), 123.7 (CH, phenyl), 125.4 (CH, phenyl), 127.5 (CH, phenyl), 128.1 (CH, phenyl), 128.6 (CH, phenyl), 128.5 (CH, phenyl), 135.1 (C=C), 141.5 (C=C), 142.4 (C=C), 143.0 (C=C), 144.7 (C=C), 153.1 (C=C).

4,9-Dihydro-2,3-dimethyl-9-methoxy-1*H*-fluorene (**22b**): Carbene **4c** (1 mmol) and diene **21b** (2 mL) were stirred at 50 °C for 96 h. The mixture was concentrated at reduced pressure (10^{-2} Torr). The crude reaction mixture was chromatographed through a silica gel column with hexane/ethyl acetate (10:1). Yield: 10%; yellow oil; $R_f = 0.56$; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.81$ (2s, 6H; 2 × CH_3), 2.81–3.10 (m, 4H; 2 × CH_2), 3.15 (s, 3H; OCH_3), 4.97 (s, 1H; C*H*OCH_3), 7.15–7.51 (m, 4H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 18.9$ (2 × CH_3), 30.4 (CH_2), 31.7 (CH_2), 52.0 (OCH_3), 83.5 (H*C*OCH_3), 117.9 (CH, phenyl), 122.6 (C=C), 123.3 (CH, phenyl), 123.5 (C=C), 124.9 (CH, phenyl), 128.2 (CH, phenyl), 136.5 (C=C), 138.3 (C=C), 141.8 (C=C) 143.7 (C=C); $C_{16}H_{16}O$ (224.3): calcd C 85.68, H 7.19; found C 85.79, H 7.48; HRMS (EI): *m/z* calcd for $C_{16}H_{16}O$ [$M^+ - 2H$]: 224.1205, found 224.1201.

2,3-Dimethyl-9-methoxy-1*H*-fluorene (**22b′**): Yield:5%; $R_f = 0.47$ (hexane/ethyl acetate, 10:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.34$ (s, 3H; CH_3), 2.35 (s, 3H; CH_3), 3.06 (s, 3H; OCH_3), 5.56 (s, 1H; H*C*OCH_3), 7.26–7.41 (m, 3H; phenyl), 7.45 (s, 1H; phenyl), 7.46 (s, 1H; phenyl), 7.60 (dd, $^3J(H,H) = 5.2$ Hz, 1H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 20.1$ (2 × CH_3), 50.1 (OCH_3), 81.2 (H*C*OCH_3), 119.4 (C=CH), 121.0 (C=CH), 125.3 (C=CH), 126.5 (C=CH), 126.8 (C=CH), 128.8 (C=CH), 136.0 (C=C), 137.3 (C=C), 138.8 (C=C), 140.1 (C=C), 141.2 (C=C), 142.6 (C=C); HRMS (EI): *m/z* calcd for $C_{16}H_{16}O$ [M^+]: 224.1205, found 224.1197.

General procedure for reactions of dienes 2, 3, and 39: The alkynyl carbene complex **4f,g,j,m** (1, 2, or 3 mmol) was added to a solution of diene **2**, **3,** or Danishefsky's diene **39** in THF. Reaction was stirred at room temperature for the time specified in each case and the solvent was evaporated under reduced pressure. Products were purified by column chromatography in silica gel.

5-Morpholino-1,2,3,11-tetrahydrofluorene[2,1-*b*]pyrane (**24**): Compound **4f** (1 mmol, 336 mg) was treated with **2** (1 mmol, 195 mg) in toluene for 12 h. *p*-Toluensulphonic acid was added and the mixture refluxed for 1 h to give **24** (178 mg, 58%). $R_f = 0.32$ (hexane/ethyl acetate 3:1); orange crystals; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.12$ (m, 2H; CH_2, pyrane), 2.82 (m, 2H; CH_2, pyrane), 3.15 (m, 4H; morpholine), 3.65 (s, 2H; CH_2), 3.95 (m, 4H; morpholine), 4.31 (m, 2H; CH_2O, pyrane), 7.24 (t, $^3J(H,H) = 7.3$ Hz; 1H; CH, phenyl), 7.24 (s, 1H; CH, Ar), 7.34 (t, $^3J(H,H) =$ 7.3 Hz; 1H; CH, phenyl), 7.50 (d, $^3J(H,H) = 7.3$ Hz; 1H; CH, phenyl), 7.68 (d, $^3J(H,H) = 7.3$ Hz; 1H; CH, phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 21.7$ (CH_2), 22.8 (CH_2), 35.0 (CH_2), 51.5 (CH_2, morpholine), 66.4 (CH_2O), 67.1 (CH_2, morpholine), 107.3 (CH), 118.7 (CH), 119.4 (C), 124.6 (CH), 125.1 (CH), 1226.5 (CH), 133.1 (C), 137.1 (C), 140.2 (C), 142.2 (C), 142.7 (C), 147.1 (C); $C_{20}H_{21}NO_2$ (307.4): calcd C 78.15, H 6.89, N 4.56; found C 78.20, H 6.91, N 4.58.

2-Methyl-9-methoxy-3-morpholino-9*H*-fluorene (**25**): Compound **4f** (1 mmol, 336 mg) was treated with diene **3** (1 mmol, 238 mg) in THF for 6 d at -10 °C to give **25** (100 mg, 34%). $R_f = 0.40$ (hexane/ethyl acetate, 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.38$ (s, 3H; CH_3), 3.00 (t, $^3J(H,H) = 4.3$ Hz, 4H; morpholine), 3.07 (s, 3H; CH_3O), 3.90 (t, $^3J(H,H) = 4.3$ Hz, 4H; morpholine), 5.53 (s, 1H; CHOMe), 7.30 (dd, $^3J(H,H) = 7.3$ Hz, $^4J(H,H) = 1.3$ Hz, 1H; phenyl), 7.33 (s, 1H; CH, Ar), 7.38 (dt, $^3J(H,H) = 7.3$ Hz, $^4J(H,H) = 0.9$ Hz, 1H; phenyl), 7.43 (s, 1H; CH, Ar), 7.57 (d, $^3J(H,H) = 7.3$ Hz, 1H; phenyl), 7.63 (d, $^3J(H,H) = 7.3$ Hz, 1H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 18.3$ (CH_3), 52.3 (CH_2, morpholine), 52.3 (CH_3O), 67.4 (CH_2, morpholine), 81.0 (CHOMe), 110.4 (CH), 119.4 (CH), 125.3 (CH), 127.0 (CH), 128.0 (CH), 128.8 (CH), 132.1 (C), 137.3 (C), 139.6 (C), 141.1 (C), 142.8 (C), 152.3 (C(morpholine)); HRMS (EI): *m/z* calcd for $C_{19}H_{21}NO_2$ [M^+]: 295.157218, found: 295.158033.

6-Methyl-8-methoxy-5-morpholino-8*H*-indene[2,1-*b*]furane (**26**): Compound **4g** (1 mmol, 326 mg) was treated with diene **49a** (1 mmol, 238 mg) im THF for 12 h to give **26** (108 mg, 38%). $R_f = 0.40$ (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.32$ (s, 3H; CH_3), 2.93 (m, 4H; morpholine), 3.36 (s, 3H; CH_3O), 3.86 (m, 4H; morpholine), 5.13 (s, 1H; CHOMe), 6.56 (s, 1H; CH, furyl), 7.00 (s, 1H; CH, Ar), 7.23 (s, 1H; CH, furyl), 7.48 (s, 1H; CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta =$ 17.9 (CH_3), 52.1 (CH_2, morpholine), 54.6 (CH_3O), 67.2 (CH_2, morpholine), 74.7 (CHOMe), 104.8 (CH), 110.7 (CH), 127.9 (CH), 129.0 (C), 130.2 (C), 134.5 (C), 138.0 (C), 147.7 (CH), 151.5 (C), 161.3(C, morpholine); HRMS (EI): *m/z* calcd for $C_{17}H_{19}NO_3$ [M^+]: 285.1364, found: 285.1359.

Pentacarbonyl{[2-(*p*-chlorophenyl)-5-methyl-4-morpholinocyclohexa-2,5-dienyl]methoxymethylene}tungsten(0) (**27**): 2-Aminodiene **1c** (1 mmol) was added to a solution of complex **4h** (1 mmol) in THF (10 mL) at RT. The reaction mixture was stirred at RT for 3 min and concentrated at reduced pressure (10^{-2} Torr). The crude product was dissolved in a dry solution of hexane/diethyl ether (2:1), filtered through a pad of Celite, and cooled at -78 °C overnight to induce crystallization. Yield: 74%; ^{1}H NMR (400 MHz, CD_2Cl_2, -40 °C) $\delta = 1.20$ (s, 3H; CH_3), 1.90–2.31 (m, 4H; morpholine), 2.32–2.37 (m, 2H; CH_2), 2.52–2.61 (m, 2H; CH_2), 3.08–3.16 (m, 4H; morpholine), 3.94 (s, 3H; OCH_3), 6.49 (d, $^3J(H,H) = 8.9$ Hz, 2H; phenyl), 6.75 (d, $^3J(H,H) = 8.2$ Hz, 2H; phenyl); ^{13}C NMR (100 MHz, CD_2Cl_2, -20 °C) $\delta = 16.7$ (CH_3), 28.6 (CH_2), 35.5 (CH_2), 50.3 (CH_2, morpholine), 67.4 (CH_2, morpholine), 70.5 (OCH_3), 118.9 (C=C), 124.1 (C=C), 128.6 (2 × CH, phenyl), 128.9 (CH, phenyl), 130.3 (2 × CH, phenyl), 133.4 (C=C), 137.1(C=C), 139.1 (C=C), 150.1(C=C), 196.6 (CO), 204.2 (CO), 333.5 (C=W); $C_{24}H_{22}ClNO_7W$ (655.7): calcd C 43.96, H 3.38, N 2.14; found C 43.34, H 3.39, N 2.10; MS EI: (*m/z*, %): (570.9, 10) [$M^+ - 3$CO].

Pentacarbonyl{[5-methyl-4-morpholino-2-phenyl-1,3-cyclohexadienyl]-methoxymethylene}tungsten(0) (**32**): Treatment of compound **30**, generated at low temperature, with silica gel afforded a mixture of **31** and **32**. After chromatographic purification with hexane/ethylacetate (3:1), complex **32** was isolated as a purple oil. Yield: 30%; $R_f = 0.30$ (hexane/ethyl acetate, 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.11$ (d, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 3.10–3.50 (m, 7H CH_2, CH, morpholine), 3.76–3.82 (s,m, s = CH_3O; m = morpholine), 4.99 (s, 1H; C=CCH), 7.01–7.30 (m, 5H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 15.4$ (CH_3), 30.4 (CH), 39.6 (CH_2), 46.3 (CH_2, morpholine), 66.2 (CH_2, morpholine), 99.2 (NC=C*C*H), 126.6 (CH, phenyl), 127.8 (CH, phenyl), 128.6 (CH, phenyl), 134.7 (C=C), 144.4 (C=C), 145.2 (C=C), 161.7 (C=C), 198.6 (CO), 202.9 (CO), 298.7 (C=W), the signal for the methoxy group is missing; IR (CH_2Cl_2) $\tilde{\nu} = 2055$ (C≡O *trans*), 1919 cm^{-1} (C≡*cis*).

0947-6539/98/0411-2294 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 11

Pentacarbonyl{dimethylamino[5-methyl-4-morpholino-2-phenyl-1,3-cyclohexadienyl]methylene}tungsten(0) (33): Treatment of **30**, generated at low temperature, with dimethylamine at −78 °C afforded, after crystallization in dry hexane, complex **33** as yellow crystals. Yield: 88 %; m.p. 148 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.85$ (s, 3H; CH_3), 2.40–2.49 (m, 2H; CH_2), 2.70–2.75 (m, 4H; morpholine), 2.95–3.02 (m, 2H; CH_2), 3.39 (s, 3H; NCH_3), 3.68 (s, 3H; NCH_3), 3.76 (t, ^3J(H,H) = 4.3 Hz, 4H; morpholine), 7.12 (d, ^3J(H,H) = 7.7 Hz, 2H; phenyl), 7.27–7.37 (m, 3H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 16.7$ (CH_3), 28.3 (CH_2), 35.1 (CH_2), 44.4 (NCH_3), 50.2 (CH_2, morpholine), 52.8 (NCH_3), 67.3 (CH_2, morpholine), 118.6 (C=C), 121.2 (C=C), 127.0 (=CH, phenyl), 127.4 (=HC; phenyl), 128.3 (=CH, phenyl), 138.1 (C=C), 140.3 (C=C), 143.6 (C=C), 198.1 (CO), 202.7 (CO), 259.2 (C=W); IR (CH_2Cl_2) $\tilde{\nu} = 2060$ (C≡O *trans*), 1923 cm^{-1} (C≡O *cis*); $C_{25}H_{26}N_2O_6W$ (634.3): calcd C 47.34, H 4.13, N 4.42; found C 47.48, H 4.30, N 4.23; HRMS (EI): *m/z* calcd for $C_{23}H_{26}N_2O_4{}^{184}W$ [$M^+ - 2$CO]: 578.1407, found 578.1369.

Warming of compound **33** to 66 °C (refluxing THF), afforded **34**, which was isolated after chromatography (silica gel, hexane/ethyl acetate 3:1) as a yellow oil (27 % yield based on **4c**). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.07$ (d, ^3J(H,H) = 7.3 Hz, 3H; CH_3), 2.75–2.90 (m, 1H), 2.89 (s, 3H; NCH_3), 3.00–3.15 (m, 4H; morpholine), 3.24 (dd, ^3J(H,H) = 15.9, 6.9 Hz, 1H), 3.52 (s, 3H; CH_3), 3.69–3.80 (t, m, ^3J(H,H) = 5.1 Hz, 5H; t = morpholine), 5.04 (s, 1H; =CH), 7.32–7.34 (m, 5H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 18.9$ (CH_3), 29.3 (CH_2), 39.8 (CH), 45.1 (NCH_3), 47.3 (CH_2, morpholine), 53.4 (NCH_3), 66.9 (CH_2, morpholine), 99.0 (NC=C*C*H), 125.2 (C=C), 127.6 (C=CH, phenyl), 128.8 (C=CH, phenyl), 128.9 (C=CH, phenyl), 133.0 (C=C), 142.5 (C=C), 154.9 (C=C), 200.1 (CO), 203.7 (CO), 253.5 (C=W).

General procedure for the preparation of 35, 36, and 38: Diene **1** (1 mmol) was added to a solution of carbene complex **4** (2 mmol) in THF (20 mL). The reaction was monitored by TLC until complex **4** disappeared. The reaction mixture was concentrated to dryness, and the metal carbonyl formed sublimed at 40 °C (10^{-3} mm Hg). The residue was dissolved in hexane, filtered through a pad of Celite, concentrated, and crystallized or precipitated in the solvent indicated at −20 °C.

(2*R,4R*,9*S**,10*S**)-5,8-Dihydro-1,9-dimethoxy-2,10-diphenyl-4,9-methano-7-methyl-6-morpholino-2*H*-benzo[*c*]indene (35a)**: Crystallized from hexane. Yield 95 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.82$ (s, 3H; CH_3), 2.64 (t, ^3J(H,H) = 7.1 Hz, 4H; morpholine), 2.82–2.90 (m, 2H; CH_2), 3.34 (br s, 1H; CHPh), 3.41–3.44 (s, m, 5H; s = OCH_3, m = CH_2), 3.72 (t, ^3J(H,H) = 7.1 Hz, 4H; morpholine), 3.84 (s, 3H; OCH_3), 4.08 (d, ^3J(H,H) = 2.4 Hz, 1H; CH), 4.55 (d, ^3J(H,H) = 2.4 Hz, 1H; CHPh), 5.37 (d, ^3J(H,H) = 2.8 Hz, 1H; =CH), 7.25–7.35 (m, 10H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 17.6$ (CH_3), 23.1 (CH_2), 29.0 (CH_2), 50.0 (CH_2, morpholine), 50.6 (CH), 53.8 (CH), 60.4 (CH), 62.7 (OCH_3), 67.3 (CH_2, morpholine), 69.4 (OCH_3), 94.5 (*C*HOCH$_3$), 111.1 (=CH), 119.5 (C=C), 120.6 (C=C), 126.1 (CH, phenyl), 126.6 (CH, phenyl), 127.5 (CH, phenyl), 127.9 (CH, phenyl), 128.7 (CH, phenyl), 128.8 (CH, phenyl), 134.2(C=C), 136.6 (C=C), 137.6 (C=C), 137.8 (C=C), 138.5 (C=C), 152.8 (C=C), 153.5 (C=C); MS EI: *m/z* (%): 493 (45) [M^+], 478 (22), 402 (19), 323 (43), 264 (100); $C_{33}H_{35}NO_3$ (493.6): calcd C 80.29, H 7.15, N 2.84; found C 80.15, H 7.10, N 2.64.

(2*R,4*S**,9*S**,10*R**)-5,8-Dihydro-1,9-dimethoxy-2,10-diphenyl-4,9-methano-6-morpholino-3,4,7-trimethyl-2*H*-benzo[*c*]indene (35d)**: Yield 67 %. Crystallized from hexane. M.p. 150 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.34$ (s, 3H; CH_3), 1.67 (s, 3H; CH_3), 1.87 (s, 3H; CH_3), 2.54–2.67 (m, 2H; CH_2), 2.68 (t, ^3J(H,H) = 4.6 Hz, 4H; morpholine), 2.92–3.20 (m, 2H; CH_2), 3.33–3.35 (s, m, 4H; s = OCH_3, m = CHPh), 3.73–3.82 (s, m, 7H; s = OCH_3, m = morpholine), 4.24 (s, 1H; CHPh), 7.22–7.41 (m, 10H; phenyl); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 11.0$ (CH_3), 12.3 (C=C*C*H$_3$), 17.6 (C=C*C*H$_3$), 20.8 (CH_2), 29.0 (CH_2), 50.1 (CH_2, morpholine), 53.5 (PhCH), 54.3 (*C*CH$_3$), 60.0 (OCH_3), 66.3 (OCH_3), 67.3 (CH_2, morpholine), 75.0 (PhCH), 93.1 (C), 119.7 (*C*OCH$_3$), 119.8 (C=C), 120.8 (C=C), 126.3 (CH, phenyl), 126.6 (CH, phenyl), 127.7 (CH, phenyl), 127.9 (CH, phenyl), 128.6 (CH, phenyl), 130.1 (CH, phenyl), 135.1 (C=C), 136.0 (C=C), 136.2 (C=C), 137.8 (C=C), 138.7 (C=C), 148.7 (C=C), 151.2 (C=C); $C_{35}H_{39}NO_3$ (521.7): calcd C 80.64, H 7.48, N 2.68; found C 80.65, H 7.42, N 2.38; HRMS (EI): *m/z* calcd for $C_{35}H_{37}NO_3$ [$M^+ - 2$]: 521.2929, found 521.2919.

(1*S,8*R**,11*S**,18*S**)-9,11-Dimethoxy-14-methyl-15-morpholino-hexacyclo[9.6.5.0^{1,18}.0^{2,10}.0^{3,8}.0^{12,17}]docosa-2,9,12^{17},14-tetraenyl (35e)**: Precipitated from methanol. Yield: 86 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.90–1.32$ (m, 7H; cyclohexyl), 1.45–1.72 (m, 6H; cyclohexyl), 1.73–1.84 (m, s, 4H; s = CH_3), 1.91 (dd, ^3J(H,H) = 12.4, 4.7 Hz, 1H), 2.11–2.19 (m, 1H) , 2.22–2.32 (m, 1H), 2.41 (t, ^3J(H,H) = 8.2 Hz, 1H), 2.49–2.54 (m, 2H), 2.68–2.79 (m, 5H), 2.86 (dd, ^3J(H,H) = 12.0, 5.6 Hz, 1H), 3.43 (s, 3H; OCH_3), 3.72–3.75 (s, m, 7H; s = OCH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 17.5$ (CH_3), 20.6 (CH_2, cyclohexyl), 21.5 (CH_2, cyclohexyl), 23.5 (CH_2, cyclohexyl), 23.9 (CH_2, cyclohexyl), 25.2 (CH_2, cyclohexyl), 25.5 (CH_2, cyclohexyl), 25.7 (CH_2, cyclohexyl), 28.5 (CH_2, cyclohexyl), 29.4 (CH_2), 31.7 (CH_2), 50.1 (CH_2, morpholine), 50.1 (C), 52.0 (CH), 56.6 (CH), 60.3 (OCH_3), 66.6 (OCH_3), 67.4 (CH_2, morpholine), 94.0 (*C*OCH$_3$), 119.4 (C=C), 121.0 (C=C), 121.2 (C=C), 136.0 (C=C), 136.5 (C=C), 137.7 (C=C), 144.6 (C=C), 152.3 (C=C); $C_{26}H_{34}O_4$ (410.6): calcd C 79.47, H 8.74, N 3.16; found C 77.30, H 8.63, N 3.05; HRMS (EI): *m/z* calcd for $C_{29}H_{39}NO_3$ [M^+]: 449.2928, found 449.2930.

(1*S,8*R**,11*S**,13*R**,18*S**)-9,11-Dimethoxy-13-methoxymethyl-14-methyl-15-morpholino-hexacyclo[9.6.5.0^{1,18}.0^{2,10}.0^{3,8}.0^{12,17}]docosa-2,9,12^{17},14-tetraenyl (35f)**: Crystallized from hexane. Yield: 85 %; m.p. 155–157 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS) $\delta = 0.87–1.45$ (m, 5H; cyclohexyl), 1.47–1.87 (m, 7H; cyclohexyl), 2.01–2.13 (s, m, 4H; s = CH_3), 2.26–2.31 (m, 1H), 2.44–2.57 (m, 6H), 2.70–2.78 (m, 2H), 2.89 (dd, ^3J(H,H) = 21.0, 4.2 Hz, 1H), 3.09 (dd, ^3J(H,H) = 11.8, 5.4 Hz, 1H), 3.23 (s, 3H; OCH_3), 3.47 (s, 3H; OCH_3), 3.60–3.66 (m, 6H; morpholine, CH, C*H*HO), 3.80 (s, 3H; OCH_3), 3.94 (dd, ^2J(H,H) = 8.7, ^3J(H,H) = 2.7 Hz, 1H; CH*H*O); ^{13}C NMR (75 MHz, C_6D_6, 25 °C) $\delta = 16.9$ (CH_3), 20.7 (CH_2, cyclohexyl), 22.4 (CH_2, cyclohexyl), 24.0 (CH_2, cyclohexyl), 24.4 (CH_2, cyclohexyl), 25.7 (CH_2, cyclohexyl), 26.1 (CH_2, cyclohexyl), 26.4 (CH_2, cyclohexyl), 29.1 (CH_2, cyclohexyl), 32.5 (CH_2), 42.4 (CH), 50.4 (CH_2, morpholine), 52.1 (CPh), 53.6 (CH), 55.9 (OCH_3), 58.3 (OCH_3), 58.7 (CH), 67.4 (CH_2 morpholine), 68.4 (OCH_3), 74.2 (CH_2), 94.2 (*C*OCH$_3$), 121.2 (C=C), 121.4 (C=C), 125.2 (C=C), 138.1 (C=C), 139.2 (C=C), 139.4 (C=C), 145.5 (C=C), 151.1 (C=C); $C_{31}H_{43}NO_4$ (493.7): calcd C 75.42, H 8.78, N 2.84; found C 75.67, H 8.75, N 2.75.

12,14-Dimethoxy-4-morpholino-6-oxaheptacyclo[10.9.5.0^{1,26}.0^{2,11}.0^{5,10}.0^{13,21}.0^{15,20}]hexacosa-2(11),4,13,20-tetraenyl (35h): Compound **4m** (2 mmol, 632 mg) was treated with diene **3** (1 mmol, 238 mg) in THF for 12 h to give **35h** (427 mg, 87 %) as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.85–2.83$ (m, 24H), 2.92 (m, 4H; CH_2N, morpholine), 3.10 (m, 1H), 3.41 (s, 3H; CH_3O), 3.68 (m, 4H; CH_2O, morpholine), 4.10 (m, 2H; CH_2O); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 24.6$ (CH_2), 23.4 (CH_2), 23.8 (CH_2), 25.2 (CH_2), 25.3 (CH_2), 25.6 (CH_2), 25.7 (CH_2), 28.2 (CH_2), 28.5 (CH_2), 31.4 (CH_2), 31.8 (CH_2), 36.9 (CH), 50.2 (CH_2, morpholine), 51.3 (C), 53.4 (*C*HC(OMe)), 55.8 (*C*HC(OMe)), 59.3 (C(O*C*H$_3$)), 67.7 (CH_2, morpholine), 68.5 (=C(O*C*H$_3$)), 69.7 (CH_2O), 94.1 (C(OMe)), 120.7 (C), 121.7 (C), 124.9 (*C*=C(OMe)), 137.9 (C), 138.5 (C), 142.9 (C), 144.5 (C), 150.6 (C); HRMS (EI): *m/z* calcd for $C_{31}H_{41}O_4N$ 491.3035, found: 491.3024; $C_{31}H_{41}O_4N$ (491.68): calcd C 75.73, H 8.41, N 2.85 found C 75.94, H 8.54, 2.56.

(1*S,8*R**,11*S**,13*S**,14*R**,18*S**)-13-Allyloxymethyl-9,11-dimethoxy-14-methyl-hexacyclo[9.6.5.0^{1,18}.0^{2,10}.0^{3,8}.0^{12,17}]docosa-2,9,12^{17}-triene-15-one (36g)**: Diene **1e** (1 mmol) was added to a solution of carbene complex **4m** (2 mmol) in THF (20 mL). The reaction was allowed to proceed for 4 d, and then concentrated to dryness. The residue was hydrolyzed while chromatographed in silica gel with hexane/ethyl acetate (10:1) and collected the fraction of $R_f = 0.7$ (hexane/ethyl acetate 3:1); Colorless oil. Yield 54 %; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.14$ (d, ^3J(H,H) = 6.7 Hz, 3H; CH_3), 1.60–2.31 (m, 12H; cyclohexyl), 2.42–2.63 (m, 2H; cyclohexyl), 2.76–2.90 (d, m, ^3J(H,H) = 7.6 Hz, 2H), 3.37 (dd, ^2J(H,H) = 9.5, ^3J(H,H) = 2.1 Hz, 1H; C*H*HO), 3.48 (d, ^3J(H,H) = 0.9 Hz, 3H; OCH_3), 3.50–3.79 (m, 2H), 3.77 (d, ^3J(H,H) = 0.9 Hz, 2H; C=CCH$_2$O), 4.9 (dm, ^3J(H,H) = 14.0 Hz, 2H; C=CCH$_2$), 5.50–5.59 (m, 1H; =CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 11.9$ (CH_3), 21.9 (CH_2, cyclohexyl), 23.3 (CH_2, cyclohexyl), 23.7 (CH_2, cyclohexyl), 25.2 (CH_2, cyclohexyl), 25.6 (2 × CH_2, cyclohexyl), 28.4 (CH_2, cyclohexyl), 31.7 (CH_2, cyclohexyl), 35.9 (CH), 40.4 (CH), 44.6 (CH), 51.6 (C), 53.7 (CH), 55.7 (OCH_3), 58.7 (OCH_3), 67.1 (OCH_2), 71.4 (OCH_2), 93.4 (*C*OCH$_3$), 115.1 (C=CH$_2$), 119.5 (C=C), 122.1 (C=C), 134.7 (C=CH), 138.4 (C=C), 140.7 (C=C), 143.4 (C=C), 150.5 (C=C), 210.4 (CO); HRMS (EI): *m/z* calcd for $C_{29}H_{38}O_4$ [M^+]: calcd 450.2769, found 450.2770.

(1*R,4*R**,7*S**,10*S**)-1,3-Dimethoxy-8-{5-methoxy-3-methyl-2-morpholino-2-pentadienyl}-1,3-dimethyl-4,10-diphenyl-[5.2.1.0^{2,6}]tricyclodeca-2,5,7-tri-**

ene (**38**): Diene **1d** (1 mmol) was added to a solution of carbene complex **4l** (2 mmol) in THF (20 mL). The reaction was allowed to proceed for 24 h, and then concentrated to dryness. The residue was hydrolyzed while chromatographed in silica gel with hexane/ethyl acetate (10:1) and collected the fraction of $R_f = 0.3$ (hexane/ethyl acetate 3:1). Colorless oil; yield 93%; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.55$ (s, 3H; CH_3), 1.68 (s, 3H; CH_3), 1.89 (s, 3H; CH_3), 2.05 – 2.65 (m, 1H), 2.73 – 2.75 (m, 4H; morpholine), 2.76 – 2.82 (m, 1H), 3.30 – 3.48 (m, 2H), 3.50 (s, 3H; OCH_3), 3.73 (s, 3H; OCH_3), 3.74 (s, 3H; OCH_3), 3.74 – 3.90 (m, 4H; morpholine), 5.57 (d, $^3J(H,H) = 12.4$ Hz, 1H; =CH), 5.88 (brs, 1H; =CH), 6.65 (d, $^3J(H,H) = 12.4$ Hz, 1H; =CH), 7.16 – 7.50 (m, 10H; phenyl); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 11.0$ (CH_3), 12.8 (CH_3), 13.2 (CH_3), 40.4 (CH_2), 51.2 (CH_2, morpholine), 53.5 (CH), 54.0 (CCH_3), 55.5 (CH), 59.9 (OCH_3), 63.9 (OCH_3), 65.0 (OCH_3), 67.4 (CH_2, morpholine), 88.3 (*C*OCH_3), 106.4 (C=CH), 114.4 (C=CH), 119.7 (C=C), 121.3 (C=C), 121.9 (C=C), 126.6 (C=CH, phenyl), 126.7 (C=CH, phenyl), 127.8 (C=CH, phenyl), 128.3 (C=CH, phenyl), 128.6 (C=CH, phenyl), 129.4 (C=CH, phenyl), 136.1 (C=C), 137.7 (C=C), 141.1 (C), 144.5 (C=CH), 149.0 (C=C), 149.9 (C=C), 152.3 (C).

General procedure for the preparation of 37: Diene **1** (1 mmol) was added to a solution of carbene complex **4** (2 mmol) in THF (20 mL). The reaction was monitored by TLC until complex **4** disappeared. Aqueous HCl (3 N, 20 mL) was then added and the mixture stirred for 45 min. The mixture was extracted with diethyl ether, the organic layer washed with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography in hexane/ethyl acetate 3:1.

(2*R,4*S**,7*S**,8*S**,9*S**,10*R**)-2,10-Diphenyl-4,9-methano-7-methyl-9-methoxy-8-methoxymethyl-3,5,7,8-tetrahydro-1*H*-benzo[*c*]indene-1,6-dione (37c)**: $R_f = 0.18$; crystallized from hexane; m.p. 186 – 188 °C; Yield 30%.; ^{1}H NMR (400 MHz, C_6D_6, 25 °C, TMS) $\delta = 1.00$ (d, $^3J(H,H) = 10.0$ Hz, 3H; CH_3), 2.13 (quintet, $^3J(H,H) = 6.7$ Hz, 1H; C*H*CH_3), 2.55 (d, $^3J(H,H) = 2.5$ Hz, 1H; CH*H*CHPh), 2.57 (d, $^2J(H,H) = 6.1$ Hz, 1H; CH*H*CHPh), 2.68 (s, 2H; CH_2), 2.78 – 2.83 (m, 1H; C*H*CH_2O), 2.90 (s, 3H; CH_2OCH_3), 2.97 (d, $^3J(H,H) = 0.9$ Hz, 1H; C*H*CHPh), 3.11 (dd, $^2J(H,H) = 9.5$, $^3J(H,H) = 2.7$ Hz, 1H; *H*HCO), 3.51 (dd, $^2J(H,H) = 9.5$, $^3J(H,H) = 2.0$ Hz, 1H; H*H*CO), 3.55 (s, 3H; $COCH_3$), 3.74 (dd, $^3J(H,H) = 6.0$, 2.5 Hz, 1H; COCHPh), 4.24 (brs, 1H; CHPh), 7.19 – 7.29 (m, 10H; phenyl); ^{13}C NMR (100 MHz, C_6D_6, 25 °C) $\delta = 12.0$ (CH_3), 36.8 (CH_2), 40.5 (CH_2), 41.6 (CH), 44.5 (CH), 53.8 (CH), 56.0 (OCH_3), 58.8 (CH), 59.3 (OCH_3), 69.1 (OCH_2), 82.3 (CH), 98.0 ($COCH_3$), 139.4 (C=C), 141.5 (C=C), 142.2 (C=C), 147.1 (C=C), 158.4 (C=C), 196.6 (C=C), 197.4 (CO), 207.1 (CO); HRMS (EI): *m/z* calcd for $C_{30}H_{30}O_4$ [M^+]: calcd 454.2144, found 454.2160.

11-Methoxy-13-methoxymethyl-14-methylhexacyclo[9.6.5.0^{1,18}.0^{2,10}.0^{3,8}.0^{12,17}]docosa-2^{12},12^{17}-enyl-9,15-dione (37f): $R_f = 0.20$; crystallized from hexane; m.p. = 148 – 150 °C; Yield: 51%.; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.11$ (d, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 1.42 – 1.81 (m, 14H; cyclohexyl), 1.86 – 1.98 (m, 1H; cyclohexyl), 2.07 – 2.15 (m, 1H; cyclohexyl), 2.52 – 2.71 (m, 3H), 2.81 – 3.02 (m, s, 7H), 3.24 (dd, $^2J(H,H) = 9.4$, $^3J(H,H) = 2.2$ Hz, 1H; C*H*HO), 3.29 (dd, $^2J(H,H) = 9.4$, $^3J(H,H) = 2.6$ Hz, 1H; CH*H*O), 3.50 (s, 3H; OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 11.0$ (CH_3), 20.2 (CH_2, cyclohexyl), 20.7 (CH_2, cyclohexyl), 23.0 (CH_2, cyclohexyl), 23.2 (2 × CH_2, cyclohexyl), 23.5 (CH_2, cyclohexyl), 23.9 (CH_2, cyclohexyl), 25.8 (CH_2, cyclohexyl), 37.6 (CH_2),38.6 (CH), 49.9 (CH), 43.9 (CH), 52.2 (OCH_3), 55.1 (CH), 58.2 (OCH_3), 58.4 (C), 68.0 (OCH_2), 79.4 (CH), 96.0 ($COCH_3$), 142.4 (C=C), 148.0 (C=C), 156.8 (C=C), 200.4 (C=C), 204.2 (CO), 209.5 (CO); $C_{26}H_{34}O_4$: calcd C 76.06, H 8.35; found: C 75.86, H 8.13; HRMS (EI): *m/z* calcd for $C_{26}H_{34}O_4$ [M^+]: 410.2467, found 410.2457.

(1*R,8*S**,11*R**)-14-Methyl-9,11-dimethoxy-15-morpholino-2,9,12,14,16-hexacyclo[9.6.5.0^{1,22}.0^{2,10}.0^{3,8}.0^{12,17}]docosapentaenyl (40a)**: Compound **4m** (2 mmol, 632 mg) was treated with diene **3** (1 mmol, 238 mg) in THF overnight to give **40a** (255 mg, 57%). $R_f = 0.29$ (hexane/ethyl acetate 8:1); white solid; m.p. 184 – 185 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.8 – 2.0$ (m, 12H; CH_2, cyclohexyl), 2.29 (s, 3H; CH_3), 2.63 (m, 3H; CH_2, allylic, CH bridge), 2.73 (dd, $^3J(H,H) = 5.6$, 11.8 Hz, 1H; CH, cyclopentadiene), 2.92 (dd, $^3J(H,H) = 4.1$, 8.5 Hz, 4H; CH_2, morpholine), 3.60 (s, 3H; CH_3O), 3.81 (s, 3H; CH_3O), 3.88 (t, $^3J(H,H) = 4.5$ Hz, 4H; CH_2, morpholine), 6.81 (s, 1H; CH, Ar), 7.10 (s, 1H; CH, Ar); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 17.9$ (CH_3), 21.5 (CH_2), 21.7 (CH_2), 24.1 (CH_2), 25.1 (CH_2), 25.2 (CH_2), 25.7 (CH_2), 28.4 (CH_2), 31.4 (CH_2), 50.9 (C), 52.4 (CH_2, morpholine), 53.6 (*C*HC(OMe)), 55.7 (*C*HC(OMe)), 60.2 (C(OMe)), 67.4 (CH_2, morpholine), 69.0 (C=C(O*C*H_3)), 91.7 (C(OMe)), 112.4 (CH, Ar), 118.5 (*C*=C(OMe)), 121.6 (C), 122.4 (CH, Ar), 129.6 (C), 140.7 (C), 142.8 (C), 142.9 (C), 149.0 (C), 153.0 (C); MS 432 [M^+ – Me], 299, 284; $C_{29}H_{37}NO_3$ (447.3): calcd C 77.82, H 8.33, N 3.13; found C 77.55, H 7.97, N 2.80.

(1*R,8*S**,11*R**)-9,11-Dimethoxy-15-trimethylsililoxy-2,9,12,14,16-hexacyclo[9.6.5.0^{1,22}.0^{2,10}.0^{3,8}0^{12,17}]docosapentaenyl (40b)**: Compound **4m** (1 mmol, 316 mg) was treated with Danishefsky's diene **39** (1 mmol, 194 mL) in THF for 3 d to give **40b** (280 mg, 64%). $R_f = 0.67$ (hexane/ethyl acetate 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.27$ (s, 9H; $Si(CH_3)_3$), 0.85 – 2.10 (m, 10H; CH_2, cyclohexyl), 2.20 – 2.32 (m, 2H; cyclohexyl), 2.55 – 2.80 (m, 3H; CH bridge, CH_2 alyllic), 3.58 (s, 3H; CH_3O), 3.80 (s, 3H; CH_3O), 6.75 (dd, $^3J(H,H) = 7.7$ Hz, $^4J(H,H) = 2.1$ Hz, 1H; CH, Ar), 6.62 (d, $^4J(H,H) = 2.1$ Hz, 1H; CH, Ar), 7.12 (d, $^3J(H,H) = 7.7$ Hz, 1H; CH, Ar); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 0.2$ ($Si(CH_3)_3$), 21.6 (CH_2), 21.7 (CH_2), 24.1 (CH_2), 25.1 (CH_2), 25.2 (CH_2), 25.7 (CH_2), 28.4 (CH_2), 31.3 (CH_2), 50.9 (C), 53.6 (*C*HC(OMe)), 55.7 (*C*HC(OMe)), 60.1 (C(O*C*H_3)), 68.9 (=C(O*C*H_3)), 91.6 (C(OMe)), 114.0 (CH, Ar), 116.1 (CH, Ar), 118.7 (*C*=C(OMe)), 120.3 (CH, Ar), 121.9 (C), 138.8 (C), 142.6 (C), 146.1 (C), 152.8 (C), 153.4 (C); HRMS (EI): *m/z* calcd for $C_{27}H_{36}O_3Si$ [M^+]: 436.2433, found: 436.2435.

(1*R,8*S**,11*R**)-9,11-Dimethoxy-2,9,12,14,16-hexacyclo[9.6.5.0^{1,22}.0^{2,10}.0^{3,8}.0^{12,17}]docosapentaenyl-15-ol (40c)**: Compound **40b** (0.5 mmol) was treated with sodium carbonate in methanol for 2 h to give **40c** (158 mg, 87%). $R_f = 0.39$ (hexane/ethyl acetate 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.85 – 2.10$ (m, 10H; CH_2, cyclohexyl), 2.20 – 2.32 (m, 2H; cyclohexyl), 2.50 – 2.82 (m, 3H; CH bridge, CH_2 alyllic), 3.59 (s, 3H; CH_3O), 3.79 (s, 3H; CH_3O), 6.30 (brs, 1H; OH), 6.56 (dd, $^3J(H,H) = 7.9$ Hz, $^4J(H,H) = 2.0$ Hz, 1H; CH, Ar), 6.67 (d, $^4J(H,H) = 2.0$ Hz, 1H; CH, Ar), 7.11 (dd, $^3J(H,H) = 7.9$ Hz, 1H; CH, Ar); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 20.9$ (CH_2), 21.6 (CH_2), 24.1 (CH_2), 25.0 (CH_2), 25.1 (CH_2), 25.6 (CH_2), 28.3 (CH_2), 31.3 (CH_2), 50.9 (C), 53.6 (*C*HC(OMe)), 55.7 (*C*HC(OMe)), 60.2 (C(O*C*H_3)), 68.5 (=C(O*C*H_3)), 91.7 (C(OMe)), 109.5 (CH, Ar), 111.8 (CH, Ar), 119.0 (*C*=C(OMe)), 120.7 (CH, Ar), 122.2 (C), 137.7 (C), 142.4 (C), 146.3 (C), 152.6 (C), 154.4 (C); HRMS (EI): *m/z* calcd for $C_{27}H_{36}O_3Si$ [M^+]: 364.2038, found: 364.2037.

Pentacarbonyl[3-(5-methyl-4-morpholino-8-methoxy-2,4,6-pentacyclo-[6.6.5.0^{1,19}.0^{2,7}.0^{9,14}]nonadecatrien-9-yl)-1-methoxy-2-propynylidene]chromium(0) (41): Compound **4m** (2 mmol, 632 mg) was treated with **3** (1 mmol, 238 mg) in THF overnight to give **41** (57 mg, 9%). $R_f = 0.25$ (hexane/ethyl acetate 8:1); dark red solid; m.p. 178 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.9 – 1.5$ (m, 11H; CH_2, cyclohexyl rings), 1.62 (m, 3H; cyclohexyl), 1,80 (d, $^3J(H,H) = 9.4$ Hz; CH), 2.30 (dd, $^3J(H,H) = 12.5$, 5.6 Hz, 2H; CH_2), 2.34 (s, 3H; CH_3), 2.65 (dd, $^3J(H,H) = 11.2$, 4.3 Hz, 1H; CH), 2.94 (m, 4H; CH_2, morpholine), 3.58 (s, 3H; CH_3O), 3.87 (m, 4H; CH_2, morpholine), 4.38 (s, 3H; CH_3O), 6.78 (s, 1H; CH, Ar), 7.07 (s, 1H; CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 17.2$ (CH_2), 18.1 (CH_3), 18.1 (CH_2), 18.5 (CH_2), 20.4 (CH_2), 21.8 (CH_2), 24.5 (CH_2), 24.8 (CH_2), 27.3 (CH_2), 48.6 (C), 52.1 (C), 52.5 (CH_2, morpholine), 55.2 (*C*HC(OMe)), 57.2 (*C*HC(OMe)), 63.4 (OCH_3), 65.6 (OCH_3), 67.5 (CH_2, morpholine), 88.9 (C), 97.4 (C), 114.1 (CH, Ar), 114.2 (CH), 126.3 (CH, Ar), 129.6 (C), 135.9 (C), 141.8 (C), 150.1 (C), 216.4 (CO), 225.2 (CO), 317.6 (C=Cr); IR (CH_2Cl_2): $\tilde{\nu} = 2062$ (C≡O *trans*), 1954 cm^{-1} (C≡O *cis*); $C_{34}H_{37}NO_8Cr$ (639.6): calcd C 63.84, H 5.83, N 2.19; found C 63.97, H 5.94, N 1.87.

(1*R,3*S**,10*S**,12*R**,15*S**)-7-Methyl-10,12,14-trimethoxy-6-morpholino-2-(11),4,6,8,13,20-nonacyclo[10.9.5.5^{3,10}.0^{1,26}0^{2,11}.0^{3,27}.0^{4,9}.0^{13,21}.0^{15,20}]hentriacontahexaenyl (42a)**: Compound **4m** (0.5 mmol, 158 mg) was treated with compound **40a** (0.5 mmol, 223 mg) in THF for 48 h to give **42a** (452 mg, 76%). $R_f = 0.29$ (hexane/ethyl acetate 8:1); white solid; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.8 – 2.0$ (m, 22H; CH_2, cyclohexyl), 2.20 (s, 3H; CH_3), 2.30 – 2.35 (m, 4H; CH_2 allylic, CH bridge), 2.78 (m, 2H; morpholine), 2.73 (dd, $^3J(H,H) = 3.9$, 12.0 Hz, 1H; CH, cyclopentadiene), 2.94 (m, 2H; morpholine), 3.38 (s, 3H; CH_3O), 3.56 (s, 3H; CH_3O), 3.65 (s, 3H; CH_3O), 3.90 (m, 4H; CH_2, morpholine), 6.49 (s, 1H; CH, Ar), 6.86 (s, 1H; CH, Ar); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 17.7$ (CH_3), 20.7 (CH_2), 21.3 (CH_2), 21.6 (CH_2), 23.8 (CH_2), 24.0 (CH_2), 24.6 (CH_2), 25.3 (CH_2), 25.5 (CH_2), 27.2 (CH_2), 27.7 (CH_2), 30.7 (CH_2), 52.6 (C), 52.9 (CH_2, morpholine), 53.6 (*C*HC(OMe)), 54.2 (C), 54.8 (CH_3), 59.0 (*C*HC(OMe)), 65.8 (C(O*C*H_3)), 67.2 (CH_2, morpholine), 74.8 (=C(O*C*H_3)), 93.8 (C(OMe)), 97.1 (C(OMe)), 111.7 (CH, Ar), 115.3 (*C*=C(OMe)), 123.2

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(CH, Ar), 123.4 (C), 127.0 (C), 140.7 (C), 144.3 (C), 146.8 (C), 153.7 (C), 156.4 (C), 161.1 (C).

X-Ray diffraction study for 42a: Data collection, crystal, and refinement parameters were collected in Table 9. The unit cell parameters were

Table 9. Crystal data and structure refinement parameters for **42a**.

	42a
formula	$C_{39}H_{49}NO_4$
M_r	595.82
T [K]	293(2)
λ [Å]	0.71073
crystal system	triclinic
space group	$P\bar{1}$
a [Å]	9.718(3)
b [Å]	13.650(5)
c [Å]	12.68(1)
α [°]	90.25 (6)
β [°]	104.67 (8)
γ [°]	93.16 (3)
V [Å^3]	1624 (2)
Z	2
ρ_{calcd} [g cm^{-3}]	1.218
absorption coefficient [mm^{-1}]	0.072
$F(000)$	644
crystal size [mm]	0.333 × 0.167 × 0.266
θ range [°]	1.49–25.00
index ranges	$-11 \le h \le 11$ $-15 \le k \le 15$ $0 \le l \le 15$
reflections collected	6073
independent reflections	5707 [R(int) = 0.0277]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	5707/0/397
goodness-of-fit on F^2	1.024
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0641$, $wR2 = 0.1364$
R indices (all data)	$R1 = 0.1275$, $wR2 = 0.1765$
largest diff. peak/hole [e Å^{-3}]	0.210/−0.252

obtained from the least-squares fit of 25 reflections (with $\theta = 4-20°$). Data were collected with the ω-2θ scan technique with a learned profile method with a constant scan rate; the scan speed was 5.49° min^{-1}. The final drift correction factors were between 0.98 and 1.02. Profile analysis[21] was performed on all reflections. Lorentz and polarization corrections were applied and the data were reduced to F_o^2 values.[22] The structure was solved by SHELXS-90[23] (Direct methods). Isotropic full-matrix least-squares refinement on F^2 with SHELXL-93[24] converged to $R = 0.15$. The positional parameters and the anisotropic thermal parameters of the non hydrogen atoms were refined. All the hydrogen atoms were geometrically placed and refined, with their own isotropic factor, riding on their parent atoms. At this stage, with $R = 0.07$, an empirical absorption correction was applied with XABS2.[25] Maximum and minimum transmission factors were 1.00 and 0.46, respectively. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.41P]$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3)$ with $\sigma^2(F_o^2)$ from counting statistics. The maximum shift to e.d.s. ratio in the last full-matrix least square cycle was less than 0.001. The final difference Fourier map showed no peaks higher than 0.21 e Å^{-3}, nor lower than −0.25 e Å^{-3}. Atomic scattering factors were taken from International Tables for X-Ray Crystallography (1974).[26] Geometrical calculations were made with PARST.[27] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101522. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

(1*R,3*S**,10*S**,12*R**,15*S**)-10,12,14-Trimethoxy-6-trimethylsililoxy-2(11),-4,6,8,13,20-nonacyclo[10.9.5.5^{3,10}.0^{1,26}.0^{2,11}.0^{3,27}.0^{4,9}.0^{13,21}.0^{15,20}]hentriaconta-hexaenyl** (**42b**): Compound **4m** (3 mmol, 948 mg) was treated with Danishefsky's diene (1 mmol, 0.195 mL) in THF for 3 d to give **42b** (344 mg, 59%). $R_f = 0.67$ (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.24$ (s, 9H; Si(CH$_3$)$_3$), 0.82–2.20 (m, 24H; CH$_2$, cyclohexyl rings), 2.20–2.45 (m, 4H; CH bridge, CH$_2$ allylic), 2.84 (dd, ^3J(H,H) = 4.3, 11.6 Hz, 1H; CH, cyclopentadiene), 3.40 (s, 3H; CH$_3$O), 3.56 (s, 3H; CH$_3$O), 3.66 (s, 3H; CH$_3$OC=C), 6.31 (dd, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.7 Hz, 1H; CH, Ar), 6.33 (d, ^3J(H,H) = 1.7 Hz, 1H; CH, Ar), 6.84 (d, ^3J(H,H) = 7.3 Hz, 1H; CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 0.4$ (Si(CH$_3$)$_3$), 20.7 (CH$_2$), 21.3 (CH$_2$), 21.4 (CH$_2$), 23.8 (CH$_2$), 24.0 (CH$_2$), 24.5 (CH$_2$), 24.6 (CH$_2$), 25.0 (CH$_2$), 25.3 (CH$_2$), 27.2 (CH$_2$), 27.8 (CH$_2$), 30.6 (CH$_2$), 52.6 (C), 53.6 (*C*HC(OMe)), 54.1 (C), 54.7 (CH), 56.0 (CH$_3$), 59.0 (*C*HC(OMe)), 65.8 (C(O*C*H$_3$)), 74.7 (C=C(O*C*H$_3$)), 93.8 (C(OMe)), 96.9 (C(OMe)), 113.4 (CH, Ar), 113.8 (CH, Ar), 114.9 (*C*=C(OMe)), 120.5 (CH, Ar), 124.1 (C), 138.7 (C), 140.4 (C), 147.3 (C), 146.8 (C), 151.8 (C), 153.5 (C), 157.1 (C), 160.7 (C); HRMS (EI): *m/z* calcd for $C_{37}H_{48}O_4Si$ [M^+]: 584.3321, found: 584.3327.

(1*R,3*S**,10*S**,12*R**,15*S**)-10,12,14-Trimethoxy-2(11),4,6,8,13,20-nonacyclo[10.9.5.5^{3,10}.0^{1,26}.0^{2,11}.0^{3,27}.0^{4,9}.0^{13,21}.0^{15,20}]hentriacontahexaenyl-6-ol** (**42c**): Compound **42b** (0.5 mmol), was treated with sodium carbonate in methanol for 15 min to give **42c** (243 mg, 92%). $R_f = 0.39$ (hexane/ethyl acetate 3:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.82-2.20$ (m, 24H; CH$_2$, cyclohexyl rings), 2.20–2.45 (m, 4H; CH bridge, CH$_2$ allylic), 2.84 (dd, ^3J(H,H) = 4.3 Hz, ^3J(H,H) = 11.8 Hz, 1H; CH, cyclopentadiene), 3.40 (s, 3H; CH$_3$O), 3.56 (s, 3H; CH$_3$O), 3.66 (s, 3H; CH$_3$OC=C), 4.85 (br s, 1H; OH), 6.31 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 2.2 Hz, 1H; CH, Ar), 6.33 (d, ^4J(H,H) = 2.2 Hz, 1H; CH, Ar), 6.84 (d, ^3J(H,H) = 7.6 Hz, 1H; CH, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 20.7$ (CH$_2$), 21.3 (CH$_2$), 21.5 (CH$_2$), 23.8 (CH$_2$), 24.0 (CH$_2$), 24.1 (CH$_2$), 24.5 (CH$_2$), 25.2 (CH$_2$), 25.4 (CH$_2$), 27.2 (CH$_2$), 29.7 (CH$_2$), 30.5 (CH$_2$), 52.4 (C), 53.6 (*C*HC(OMe)), 54.2 (C), 54.8 (CH), 56.4 (CH$_3$), 59.0 (*C*HC(OMe)), 65.6 (C(O*C*H$_3$)), 74.2 (=C(O*C*H$_3$)), 93.9 (C(OMe)), 97.1 (C(OMe)), 108.9 (CH, Ar), 109.3 (CH, Ar), 114.4 (*C*=C(OMe)), 120.5 (CH, Ar), 124.4 (C), 137.9 (C), 140.2 (C), 147.7 (C), 152.7 (C), 153.4 (C), 157.2 (C), 160.4 (C); C_{34} H_{40} O_4 (512.7): calcd C 79.65, H 7.86; found C 79.64, H 7.88.

(1*S,3*R**,6*S**,9*R**,11*S**)-6-Phenyl-14-methyl-7,9,11-trimethoxy-15-morpholino-2(10),4,7,12,14,16-octacyclo[9.6.5.5^{3,9}.0^{1,22}.0^{2,10}.0^{3,23}.0^{4,8}.0^{12,17}]heptacosa-hexaenyl** (**42d**): Compound **4j** (0.5 mmol, 180 mg) was treated with **40a** (0.5 mmol, 223 mg) in THF for 48 h to give **42d** (462 mg, 85%). $R_f = 0.29$ (hexane/ethyl acetate 8:1); white solid; m.p. 183–184 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.01-2.10$ (m, 16H; CH$_2$, cyclohexyl rings), 2.29 (s, 3H; CH$_3$), 2.40–2.61 (m, 2H; CH bridge), 5.96 (t, ^3J(H,H) = 4.4 Hz, 4H; CH$_2$N, morpholine), 3.44 (s, 3H; CH$_3$O), 3.50 (d, ^3J(H,H) = 1.8 Hz, 1H; CH, cyclopentadiene), 3.60 (s, 3H; CH$_3$O), 3.70 (s, 3H; CH$_3$O), 3.87 (t, ^3J(H,H) = 4.4 Hz, 4H; CH$_2$O, morpholine), 4.67 (t, ^3J(H,H) = 1.8 Hz, 1H; C=CH, cyclopentadiene), 6.62 (s, 1H; CH, Ar), 6.69 (s, 1H; CH, Ar), 6.69–7.04 (m, 2H; Ph), 7.12–7.27 (m, 3H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 17.4$ (CH$_3$), 20.6 (CH$_2$), 21.0 (CH$_2$), 21.6 (CH$_2$), 23.7 (CH$_2$), 23.8 (CH$_2$), 24.4 (CH$_2$), 24.4 (CH$_2$), 25.8 (CH$_2$), 52.5 (CH$_2$, morpholine), 52.8 (C), 53.6 (*C*HC(OMe)), 54.6 (C), 54.7 (CH$_3$), 58.9 (*C*HC(OMe)), 62.0 (C(O*C*H$_3$)), 65.7 (C(O*C*H$_3$)), 67.4 (CH$_2$, morpholine), 74.5 (C=C(O*C*H$_3$)), 93.7 (C(OMe)), 97.0 (C(OMe)), 111.7 (CH, Ar), 113.4 (C=CH), 116.2 (*C*=C(OMe)), 123.2 (CH, Ar), 126.2 (CH, Ph), 127.1 (CH, Ph), 127.3 (C), 128.3 (CH, Ph), 139.8 (C), 141.5 (C), 144.5 (C), 146.6 (C), 154.2(C), 154.8 (C), 159.4 (C), 161.4 (C); HRMS (EI): *m/z* calcd for $C_{41}H_{47}NO_4$ [M^+]: 617.3505, found: 617.3484; $C_{41}H_{47}NO_4$ (617.8): calcd C 79.71; H 7.67; N 2.27; found: C 79.53; H 7.51; N 2.02.

Acknowledgments: This research was supported by the DGICYT (Grant PB92-1005). S.B gratefully acknowledges F.I.C.Y.T. for a fellowship. M.F. gratefully acknowledges M.E.C for a fellowship. Crystallographic work was partially supported by DGICYT (Grant PB96-0556).

Received: March 27, 1998 [F1070]

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