Pergamon

Tetrahedron, Vol. 53, No. 27, pp. 9323-9340, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00586-3

Enantioselective Synthesis of six Membered Carbocycles through [4+2] Cycloaddition Reactions of Chiral 2-Amino-1,3-butadienes and Tungsten Vinyl Fischer Type Carbene Complexes.

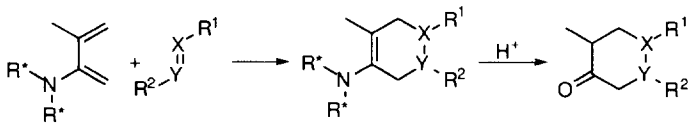
José Barluenga,* Fernando Aznar, Alfredo Martín, Sofía Barluenga.

Instituto Universitario de Química Organometálica "Enrique Moles". Universidad de Oviedo. C/ Julián Clavería S/N, 33071 Oviedo, Spain.

Abstract: 2-Amino-1,3-butadienes **1** react with carbene complexes **2** to yield, after hydrolysis, cyclohexanone derivatives. The use of chiral enantiomerically pure dienes **19** allow the access to enantio-enriched cycloadduct complexes.

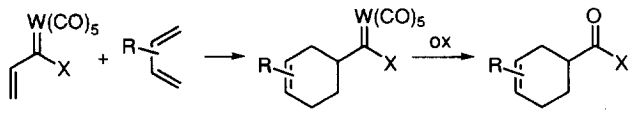
The Diels-Alder reaction[1] between 1,3-dienes and acrylates or acrylamides is the most common way of preparing cyclohexenecarboxilic acid derivatives. Furthermore, the use of chiral Lewis acids of chiral alcohol or amine derived acrylates or acrylamides have been thoroughly utilized in the enantioselective synthesis of these six membered carbocycles.[2] However, chiral dienes have been much less used[3] because of the difficulties in their preparation or in the removal of the chiral auxiliaries from the reaction products.

In our group, we have been engaged in the study of 2-amino-1,3-butadienes as reactants for organic synthesis. These readily accessible compounds[4] have been useful substrates for nucleophilic additions to electrophiles as well as for [4+2] cycloaddition reactions.[5] In addition of this, the possibility of using chiral, enantiomerically pure amines in their preparation, allowed the access to enantiomerically enriched cycloadducts through reactions with tiazolintiones, nitroolefins and imines (scheme 1).[6] Unfortunately, the 2-amino-1,3-butadienes do not react with acrylate derivatives to afford the expected carbocycles.



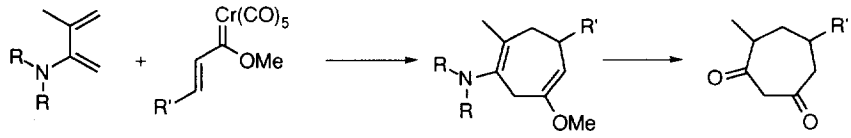
Scheme 1

In our efforts to access to the interesting 4-cyclohexanonecarboxilic acid derivatives in an enantioselective manner, we turned our attention to the reactions of 2-aminodienes with the vinylcarbene complexes. Wulff et al.[7] had reported the use of these complexes as synthons of acrylate derivatives (scheme 2). The carbene complexes react with 1,3-dienes at a rate comparable with that of the acrylate analogs catalyzed by Lewis acids and the final products can be easily converted into the ester derivatives by simple oxidation.



Scheme 2

Our first attempts with chromium complexes produced seven membered carbocycles which did not contain the metal, instead of the six membered rings (scheme 3).[8] This interesting type of products had been proposed before to arise from a tandem cyclopropanation-Cope rearrangement process,[9] although recent work have demonstrated that, with certain electron-rich dienes, the reaction is best explained by a nucleophilic attack of the diene to the carbene carbon of the complex, followed by metal migration, cyclization and metal extrusion.[10] The cycloheptadione derivatives could be obtained with our dienes in good yields.[8,11] Furthermore, when we used enantiomerically pure 2-methoxymethylpyrrolidino dienes, the seven membered carbocycles could be obtained in fair yields and good enantiomeric excesses.[6a,11]



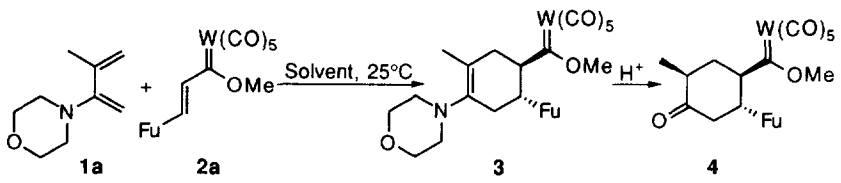
Scheme 3

In contrast with this, the vinyl tungsten complexes are more prone to give [4+2] cycloadditions and can be used to prepare six membered carbocycles in a stereoselective manner. We communicated our preliminary results of the reactions with 2-methoxymethylpyrrolidino dienes[12] and report here our full experimental work on this process.

We initiated our study with 1,3-aminodiene **1a** derived from morpholine and the tungsten carbene **2a** (scheme 4). The reaction was performed in MeOH at room temperature and went to completion after one hour. This could be observed by the transformation of the black color of the complex **2a** into the orange color of the final product. The ^{1}H-NMR spectrum of the reaction crude showed the presence of the aminocyclohexene **3** as single observable product. Unfortunately, the attempts to isolate this compound were unsuccessful due to the partial hydrolysis of the enamine under the conventional purification conditions (column chromatography, silica-gel).

The characterization of the reaction product was performed on its hydrolysis derivative **4**. Thus, the reaction crude was hydrolyzed by treatment with an aqueous 3N HCl solution in THF and purified by column chromatography. The structure of the complex **4** was deduced from its ^{1}H and ^{13}C-NMR analysis.

A closer study of the reaction conditions showed that the polarity of the solvent plays an important role in the reaction rate. Thus, the complex **2a** reacts with diene **1a** in 1h in MeOH at room temperature. In THF, a less polar solvent, the reaction takes 2 days to go to completion while in hexane, no appreciable reaction was observed after 15 days at room temperature.

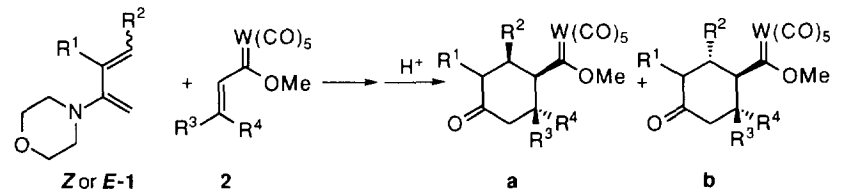


Solvent	Yield	Reaction time
Hexane	No reaction	15 days
THF	90 %	2 days
Methanol	90%	1hour

Scheme 4

These observations suggest a stepwise process, in which an attack of the enaminic carbon to the β carbon of the carbene complex, followed by rapid cyclization, is taking place. This assumption is further supported by the fact that an alkyl substituent in the position 4 of the diene enhance the reaction rate (3 min for ***E*-1b**, see below, vs 1 h for **1a** in the same conditions). Nevertheless, we have never been able to isolate or detect any open chain product in these experiments.

In order to explore how the substitution pattern in both the diene and the vinylcarbene complex would affect the reaction outcome, we performed a series of experiments varying this substitution (scheme 5). We used dienes having both the configuration *Z* and *E* at the C3-C4 double bond and carbene complexes with different groups at the β-vinylic carbon. The results are summarized in the table 1.



Scheme 5

Table 1: Tungsten cyclohexylcarbene complexes prepared:

Diene	Carbene	R^1	R^2	R^3	R^4	Prod	Yield[a] %	a:b[b,i]
1a[c]	**2a**	CH_3	H	2-Fu	H	**4**	90	
***E*-1b**[c]	**2a**	CH_3	CH_2OCH_3	2-Fu	H	**5**	52[g]	4.2:1
Z-1b[c]	**2a**	CH_3	CH_2OCH_3	2-Fu	H	**5**	61	1:3.7
***E*-1b**[c]	**2b**	CH_3	CH_2OCH_3	CH_3	H	**6**	67	>15:1
Z-1b[c]	**2b**	CH_3	CH_2OCH_3	CH_3	H	**6**	35	1:1.5
***E*-1b**	**2c**	CH_3	CH_2OCH_3	H	CH_3	**6**	67	>15:1
***E*-1c**[e]	**2a**	CH_3	$CH_2OTBDMS$	2-Fu	H	**7**	38[h]	4.7:1
Z-1c[d]	**2a**	CH_3	$CH_2OTBDMS$	2-Fu	H	**7**	65	1:2.1
***E*-1c**[d]	**2b**	CH_3	$CH_2OTBDMS$	CH_3	H	**8**	58	4.8:1
Z-1c[f]	**2b**	CH_3	$CH_2OTBDMS$	CH_3	H	**8**	53	1:1.9

Table 1: Tungsten cyclohexylcarbene complexes prepared (continuation):

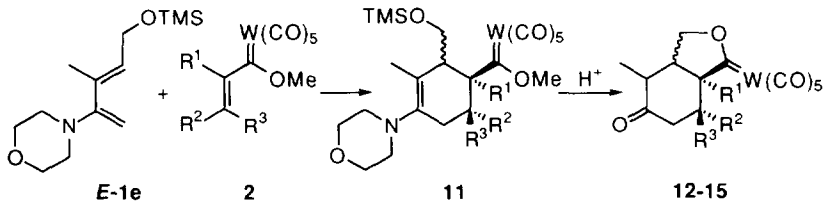
Diene	Carbene	R^1	R^2	R^3	R^4	Prod	Yield[a] %	a:b[b,i]
***E*-1b**[c]	**2d**	CH_3	CH_2OCH_3	CH_3	CH_3	**9**	48	1:2.0
***Z*-1b**[d]	**2d**	CH_3	CH_2OCH_3	CH_3	CH_3	**9**	43	1.4:1
1d[f]	**2d**	CH_2-$(CH_2)_2$-CH_2		CH_3	CH_3	**10**	49	1:8.8

(a) Yields calculated on isolated compounds after column chromatography. (b) **a**:**b** ratios based on the hydrolysis products obtained. (c) MeOH, 25° C. (d) THF, from -20 to 0° C. (e) DMF, from -50 to 0° C. (f) THF, 25° C. (g) a 35% of the seven membered carbocycle was also isolated. (h) a 55% of the seven membered carbocycle was also isolated. (i) A mixture of epymers at C3' was obtained in some cases (see experimental).

As can be seen in the table, the *E* isomer of the diene produced mainly the *cis* ("**a**") isomer of the cycloadducts while the *Z* dienes afforded the *trans* ("**b**") adducts, all corresponding to a formal *endo* approximation of the related Diels-Alder process (compounds **5**-**8**). This tendency is reverted when the β-disubstituted complex **2d** is used, being in these cases the formal *exo* adducts the major isomers (compounds **9** and **10**). The endo selectivity is specially high when carbene **2b** was enfrented to diene ***E*-1b**. The yields obtained range from moderate to good, and a specially good result was obtained when the unsubstituted diene **1a** was used.

The chemoselectivity of the reaction was always very high except when the combination of *E*-substituted dienes and carbene **2a**, bearing a furyl group at the β position, were used (compounds **5** and **7**). In these cases a considerable amount of the cycloheptadione, arising from the [4+3] cycloaddition, was obtained.[11]

An interesting observation was made from the reaction of the *Z* vinylcarbene **2c** and diene ***E*-1b**. We expected to obtain a cycloadduct with relative *cis* stereochemistry between the positions 1' and 6', resulting from the retention of the configuration in the carbene complex. Instead, we found out that the compound **7a** had been produced as a sole diastereoisomer. This complex is the same one that was obtained with the *E* carbene **2b**. Blank tests showed that the carbene was isomerizedin polar solvents in the absence of the diene in the reaction conditions, but this isomerization was slower that the reaction with the diene. This probably means that, in this case, the isomerization of the carbene is enhanced by reversible nucleophilic attack of the diene to the vinylic β carbon of the complex.



E-1e 2 11 12-15

Scheme 6

An special case in this type of reactions is presented in the scheme 6. The dienes ***E*-1e**, which bear a trimethylsilyloxymethyl group at the position 4, react with the carbene complexes to afford the adducts **11** in good yields and selectivities. The hydrolysis of these complexes give rise to the bicyclic compounds **12**-**15** (table 2). This is due to the loss of the trimethyl silyloxy group under the hydrolytic conditions, which produce the free alcohols that further react, in intramolecular fashion, by displacing the methoxy group of the carbene. As can be seen in the table 2, all the reactions were highly selective towards the formation of the "**a**" type

cycloadduct except for the β-disubstituted carbene **2c** which only produced moderate stereoselection, but towards the formal *endo* adducts, in contrast with the behavior previously observed for this complex.

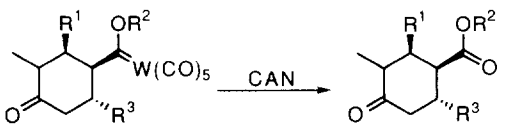
The characterization of the complexes **12a-15a** was performed by ^{1}H and ^{13}C-NMR analysis as well as nOe experiments.

Table 2: Bicyclic complexes prepared

Carbene	R^1	R^2	R^3	Comp	Yield %[a]	a:b[f]
2a	H	2-Fu	H	**12**	41[d,g]	>15:1[b]
2b	H	CH_3	H	**13**	77[e]	>15:1[b]
2d	H	CH_3	CH_3	**14**	55[e]	4.0:1[c]
2e	CH_3	H	H	**15**	61[e]	>15:1[b]

(a) The yields were calculated based on isolated products after column chromatography. (b) The a:b rations were calculated based on the proportion of the hydrolysis products obtained. (c) The selectivity was calculated based on the ^{1}H-NMR spectrum of the reaction crude. (d) DMF, 25° C. (e) THF, 25° C. (f) A mixture of epymers at C6' was obtained in some cases (see experimental). (g) Also a 40% of the cyclopropanation derived product was obtained.[11]

The cycloadduct carbene complexes can be easily transformed in the ester derivatives by oxidation (scheme 7). As an example, we tested this transformation on the complexes listed in table 3. The best results were found using CAN (cerium IV ammonium nitrate) in acetone at room temperature. The compounds **16-18** were isolated after purification by column chromatography.



Scheme 7

Table 3: Oxidation products prepared.

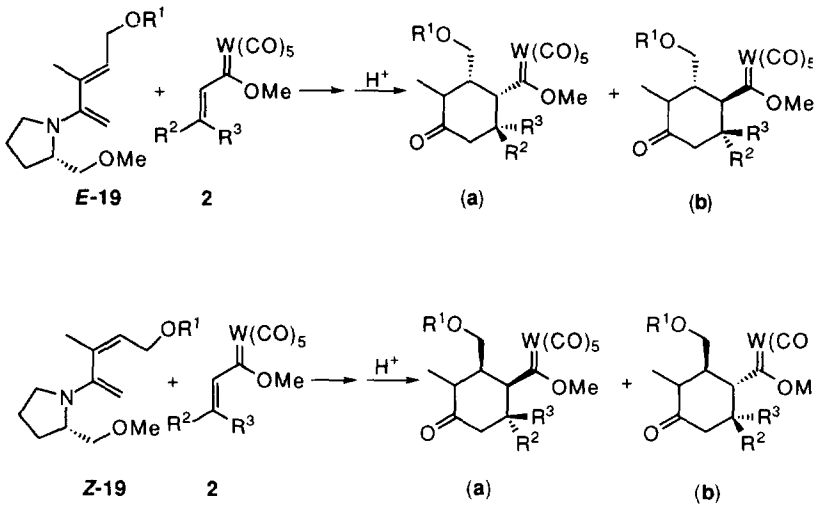
Substrate	R^1	R^2	R^3	Comp	Yield %[a]
4	H	CH_3	2-Fu	**16**	50
8a	$CH_2OTBDMS$	CH_3	CH_3	**17a**	60
13a'	CH_2-CH_2		CH_3	**18a'**	73

(a) Yield based on isolated compound after purification by column chromatography.

At the view of these results we next turned our attention to the enantioselective synthesis of the cycloadduct complexes. We chose dienes **19** derived from 2-methoxymethyl pyrrolidine because, according with our previous experience, these are the dienes we have used so far, that provide a better facial diastereoselection.

The reaction of dienes **19** and tungsten vinylcarbenes **2** afforded a mixture of the [4+2] cycloadducts along with, in some cases, a small amount of the corresponding seven membered carbocycles.[11] The hydrolysis of the reaction crudes yielded the cyclohexanone derivatives with the same spectroscopic properties that those obtained with the achiral dienes, but optically actives. The diastereoselectivities of the reactions could not be

appropriate determined from the NMR analysis of the reaction crudes and the cycloadducts could not be isolated. Because of this, the reaction crudes were hydrolyzed and the analysis performed on the ketone derivatives of the cycloadducts. The enantiomeric excesses of these compounds were determined by HPLC, using a chiral stationary phase column (chiralcell OD-H). The absolute configurations were assigned in base of those of **5a'** and **7b'**, which were determined by monocrystal X-ray crystalography using anomalous dispersion techniques.[12,13] The products obtained and their absolute configuration are represented in the scheme 8, and the results summarized in the table 4.



Scheme 8

Table 4: Tungsten cyclohexylcarbene derivatives prepared.

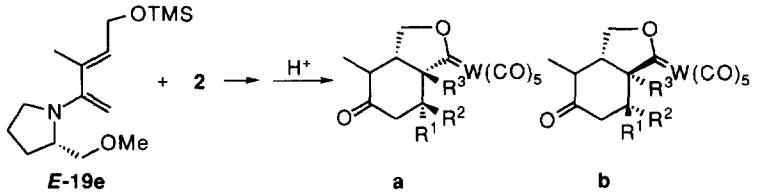
Diene	Carbene	R^1	Comp	Yield %[a]	a:b[b]	a ee(%)	b ee(%)
***E*-19b**	**2a**	CH_3	**5**	40	2.0:1	31	99
***Z*-19b**	**2a**	CH_3	**5**	45	1:2.3	94	20
***E*-19b**	**2b**	CH_3	**6**	57	4.3:1	18	82
***Z*-19b**	**2b**	CH_3	**6**	50	1:1.2	94	54
***E*-19c**	**2a**	TBDMS	**7**	28	2.5:1	5	99
***E*-19b**	**2d**	CH_3	**9**	18	<1:15		90

(a) Yields based on complexes **2** after purification by column chromatography. (b) A mixture of epymers at C3' was obtained in some cases (see experimental).

From the view of the table can be derived several consequences: The substitution at the position 4 of the dienes **19**, plays an important role in the stereochemistry of the reaction, as happened with dienes **1**. Thus, the dienes ***Z*-19** afforded mainly the products 1'-2' *cis* (**a**) while the *E*-dienes produced mainly the complexes **b**. The behavior was again the opposite when the β-disubstituted carbene **2d** was used. In this case, the compound **9b** was obtained from ***E*-19b** with high selectivity. In addition to this, the substitution at the position 4 of the diene is also important for the absolute configuration of the final products. The dienes with *E* configuration at the C3-C4 double bond produce complexes with *R* absolute configuration at position 2' while the *Z* isomers of

the diene afford cycloadducts with a *S* absolute configuration at this position.

Interestingly, the enantiomeric excesses are always high for the isomers that arise from a formal *exo* cycloaddition while the *endo* type complexes are formed with only moderate diastereoselectivity.



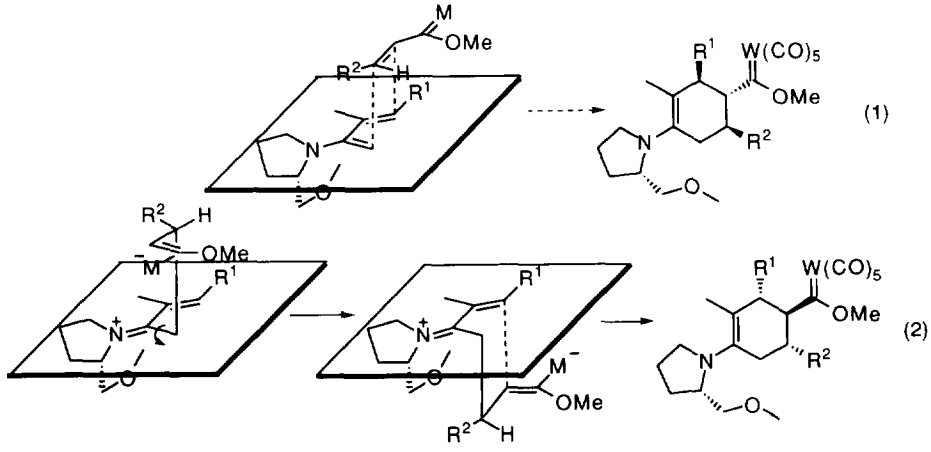
Scheme 9

Table 5: Bicyclic complexes prepared

Carbene	Comp	R^1	R^2	R^3	yield %[a]	a:b	a (e.e. %)
2b	**13**	H	CH_3	H	53	>15:1	81
2d	**14**	CH_3	CH_3	H	43	5.4:1	72
2e	**15**	H	H	CH_3	51	4.3:1	90

(a) Yields based on the starting carbene complex **2** after purification by column chromatography

The aminodienes **19e** (scheme 9), bearing the group trimethylsilyloxymethyl at the 4 position present a special behavior, in a similar way that was mentioned for their achiral counterparts. After desilylation in the hydrolytic conditions, the cycloadducts are converted into the bicyclic products **13-15** by intramolecular MeOH displacement. The results are summarized in the table 5. The cycloaddition step takes place with moderate to high stereoselectivity to afford in all cases the *endo* type adducts as the major isomers. The enantiomeric excesses for these isomers in all the cases were unexpectedly high (72-90%), compared with the results obtained with the other dienes. We have no explanation at the present time for this results, but they are probably related with conformational effects induced by the group at the position 4 of the diene.



Scheme 10

As we mentioned before, the mechanism of the reaction is unlikely to be a concerted process as derived from the influence of the solvent in the reaction rate. The absolute configuration found for the hydrolysis products of the reaction are in accordance with this previous assumption. An endo attack of the carbene complex to the less hindered face of the *E*-dienes (scheme 10, eq 1), should produce the 2' *R* isomer of the cycloadduct. In order to explain the opposite enantiomer we can imagine an attack of the diene enaminic carbon to the β-carbon of the carbene complex as shown in the equation 2 of the scheme 11. This attack is probably the slow step of the reaction, in agreement with the rate enhancement by substitution at the position 4 of the diene and the rate decrease by further substitution at the β position of the carbene. In this step the first chiral center of the adduct is created, and thus, the absolute configuration is dependent on this first attack. A rapid ring closure would then give rise to the corresponding cycloadducts.

In conclusion, we have demonstrated the versatility of the [4+2] cycloaddition reaction between the vinyl Fischer type carbene complexes and the 2-amino-1,3-butadienes. The reaction rate is highly sensitive to the reaction conditions and the stereoselectivity to the substitution pattern in both the diene and the dienophile. The enantiomeric excesses of the final hydrolysis products are always high in the formal *exo* cycloadducts, but the *endo* isomers can be obtained as well with good enantioselectivities when dienes with the appropriate substitution are used.

Acknowledgements: This work was supported by Dirección General de Investigación Científica y Técnica (DIGICYT) PB92-1005. A F.I.C.Y.T. fellowship to S. B. is gratefully acknowledged.

Experimental.

The Chromatographic purifications were carried out with silica-gel, 230-400 mesh. The TLC analysis were performed on glass plates coated with silica-gel 60 F_{245}. The reaction solvents were dried and degassed by conventional methodology and the chromatography solvents distilled prior to their use. The cycloadducts described herein are enough air stable for the time used in their purification and no special care was taken during the chromatography.The vinyl tungsten carbene complexes[7b,14] and the 2-amino-1,3-butadienes[4] were prepared by the methods described in the literature.

General procedure for the cycloaddition reactions:

A 0.12M solution of the aminodienes **1** in the indicated solvent were placed in a schlenk tube previously filled with dry nitrogen. To this solution was added one equivalent of the carbene complex **2**. The reaction is allowed to proceed at room temperature, unless otherwise indicated, until the TLC analysis shows the total consumption of the carbene **2**. The solvent is then evaporated under reduced pressure and the residue hydrolyzed by: a) elution through a short pad of silica-gel with water saturated diethyl ether, b) treatment of a THF solution of the residue with a 3N aqueous HCl solution or c) treatment of a THF solution of the residue with a pH 4.8 aqueous acetic acid / sodium acetate buffer solution. In the last cases, the mixture is then extracted with diethyl-ether, the organic layer dried with anhydrous Na_2SO_4 and concentrated. The mixture thus obtained is purified by column chromatography.

Reaction of 1a and 2a. 0.30 g of **1a** (1.96 mMol) and 0.90 g of **2a** (1.96 mMol) were reacted in MeOH for 1 h. The hydrolysis was performed by method b. After purification by column chromatography (hexane, ethyl acetate 5:1) the compound **4** (0.96 g, 90%) was isolated.

4: Pentacarbonyl {[(1'*R, 2'*R**, 5'*S**)-2'-(2-furyl)-5'-methyl-4'-oxocyclohexyl]**

methoxymethylene} tungsten (0) Yellow oil. R_f 0.29. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.07 (d, 3H, J = 6.4 Hz), 1.21-1.25 (m, 1H), 2.23 (ddd, 1H, J = 13.0, 4.1, 3.0 Hz), 2.52-2.6(m+dqd, 2H, J = 13.7, 6.4, 4.1 Hz), 2.85 (t, 1H, J = 10.8 Hz), 3.41 (m, 1H), 4.53-4.62 (s+td, 4H, J = 10.8, 3.0 Hz), 5.90 (d, 1H, J = 3.0 Hz), 6.23 (dd, 1H, J = 3.0, 1.9 Hz), 7.25 (d, 1H, J = 1.9 Hz). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 14.0 (CH_3), 36.7 (CH_2), 40.3 (CH), 43.8 (CH), 44.1 (CH_2), 70.2 (CH_3), 74.8 (CH), 105.3 (CH), 110.0 (CH), 141.5 (CH), 154.2 (C), 196.7 (C x 4), 203.0 (C), 209.2 (C), 337.5 (C). ppm. Anal. calcd for $C_{18}H_{16}O_8W$: C 39.73, H 2.96; found: C 39.58, H 2.85.

Reaction of *E*-1b and 2a. 0.24 g of ***E*-1b** (1.22 mMol) and 0.56 g of ***E*-2a** (1.22 mMol) were reacted in MeOH. Reaction time 3 min. The hydrolysis was performed by method a. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1) the compounds **5a** (0.06 g, 10%), **5a'** (0.19 g, 32 %) and **5b'** (0.06 g, 10%) were isolated along with the cycloheoptadione derivative (35%).[11]

5a: Pentacarbonyl {[(1'*R, 2'*R**, 3'*S**, 6'*R**)-6'-(2-furyl)-2'-methoxymethyl-3'-methyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0)** mp. 66-69° C (crystallized from hexane, yellow prisms). R_f 0.32 ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.12 (d, 3H, J = 6.5 Hz), 2.45 (dd, 1H, J = 6.0 Hz), 2.55-2.73 (m, 3H), 3.08-3.12 (s+m, 4H), 3.30 (dd, 1H, J = 18.9, 3.4), 3.89 (td, 1H, J = 11.6, 5.6 Hz), 4.54 (s, 3H), 4.75 (dd, 1H, J = 11.6, 3.4 Hz), 5.86 (d, 1H, J = 3.0 Hz), 6.15 (dd, 1H, J = 3.0, 2.3 Hz), 7.19 (d, 1H, J = 2.3 Hz) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 12.0 (CH_3), 36.4 (CH), 44.2 (CH), 44.5 (CH_2), 46.6 (H), 58.8 (CH_3), 68.1 (CH_2), 70.2 (CH_3), 77.5 (CH), 105.2 (CH), 110.0 (CH), 141.3 (CH), 155.2 (C), 196.9 (C x 4), 202.6 (C), 208.3 (C), 338.2 (C). ppm. IR (CH_2Cl_2) 1936, 2070. cm^{-1}.MS EI (m/e, rel. int.) (588, 2) M^+, (560,3), (504,25), (476,19), (448,24), (128,89), (115,99), (91,97), (45,100). Anal. calcd for $C_{20}H_{20}O_9W$: C 40.84, H 3.43; found: C 40.73, H 3.28.

5a': Pentacarbonyl {[(1'*R, 2'*R**, 3'*R**, 6'*R**)-6'-(2-furyl)-2'-methoxymethyl-3'-methyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0).** mp. 71-73° C. (crystallized from hexane, yellow needles). R_f 0.27. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.22 (d, 3H, J = 7.0 Hz), 2.23 (m, 1H), 2.43 (d,d, 1H, J = 15.5, 5.6 Hz), 2.65-2.73 (m, 2H), 3.17 (s, 3H), 3.24-3.29 (m, 2H), 3.66 (td, 1H, J = 7.7, 5.6 Hz), 4.56 (s, 3H), 4.86 (dd, 1H, J = 7.7, 3.9 Hz), 5.92 (d, 1H, J = 3.16 Hz), 6.19 (dd, 1H, J = 3.16, 1.9 Hz), 7.23 (d, 1H, J = 1.9 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 15.3 (CH_3), 35.1 (CH), 40.3 (CH_2), 44.3 (CH), 46.0 (CH), 58.9 (CH_3), 70.0 (CH), 70.9 (CH_3), 72.5 (CH_2), 106.1 (CH), 109.9 (CH), 141.5 (CH), 154.7 (C), 196.8 (C x 4), 202.4 (C), 211.3 (C), 339.3 (C). ppm. IR (CH_2Cl_2) 1940, 2070. cm^{-1}. HRMS calcd for $C_{20}H_{20}O_9{}^{184}W$: 588.0621; found: 588.0611. Anal. calcd for $C_{20}H_{20}O_9W$: C 40.84, H 3.43; found: C 40.78, H 3.23.

5b': Pentacarbonyl {[(1'*R, 2'*S**, 3'*R**, 6'*R**)-6'-(2-furyl)-2'-methoxymethyl-3'-methyl-4-oxocyclohexyl] methoxymethylene} tungsten (0).** mp. 107-108° C. (crystallized from hexane, orange prisms). R_f 0.19. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.10 (d, 3H, J = 7.0 Hz), 2.13 (dq, 1H, J = 7.3, 5.9 Hz), 2.38 (dd, 1H, J = 16.3, 3.9 Hz), 2.64 (qd, 1H, J =7.0, 5.7 Hz), 2.85 (dd, 1H, J = 16.3, 9.2 Hz), 3.17 (s, 3H), 3.38-3.47 (m, 2H), 4.50 (dd, 1H, J = 10.7, 7.0 Hz), 4.64 (s, 3H), 5.89 (d, 1H, J = 3.4 Hz), 6.19 (dd, 1H, J = 3.4, 1.9 Hz), 7.21 (d, 1H, J = 1.9 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) d 11.4 (CH_3), 37.9 (CH), 40.8 (CH_2), 43.0 (CH), 43.5 (CH), 58.8 (CH_3), 70.3 (CH), 72.0 (CH_2), 72.8 (CH_3), 106.0 (CH), 110.2 (CH), 141.6 (CH), 154.0 (C), 196.8 (C), 202.8 (C), 210.8 (C), 340.7 (C). ppm. IR (CH_2Cl_2) 1940, 2071. cm^{-1}. MS, EI (m/e, rel. int.) (588,3) M^+, (560,4), (532,10), (504,11), (476,13), (448,10), (155,100), (115,89), (45,98). HRMS calcd for $C_{20}H_{20}O_9{}^{184}W$: 588.0621; found: 588.0611. Anal. calcd for

$C_{20}H_{20}O_9W$: C 40.84, H 3.43; found: C 40.79, H 3.23.

Reaction of *Z*-1b and 2a. 0.24 g of ***Z*-1b** (1.22 mMol) and 0.56 g of **2a** (1.22 mMol) were reacted in MeOH for 1 h. The hydrolysis was performed by method a. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1) the compounds **5a** (0.03 g, 4%), **5a'** (0.06 g, 9 %) and **5b'** (0.34 g, 48%) were isolated.

Reaction of *E*-1b and 2b. 1.23 g of ***E*-1b** (6.24 mMol) and 2.55 g of **2b** (6.24 mMol) were reacted in MeOH for 1 h. The hydrolysis was performed by method b. After purification by column chromatography (hexane, diethyl ether 2:1) the compounds **6a** (1.83 g, 55%) and **6a'** (0.40 g, 12 %) were isolated.

6a: Pentacarbonyl {[(1'*S, 2'*R**, 3'*S**, 6'*R**)-2'-methoxymethyl-3',6'-dimethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0).** mp. 89-91° C. (crystallized from hexane, yellow prisms). *Rf* 0.22. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.86 (d, 3H, *J* = 6.4 Hz), 1.05 (d, 3H, *J* = 6.4 Hz), 1.93 (dd, 1H, *J* = 14.3, 12.8 Hz), 2.27 (dd,1H, *J* = 14.3, 5.1 Hz), 2.55-2.67 (m, 3H), 3.01 (dd, 1H, *J* = 10.2, 1.3 Hz), 3.08 (s, 3H), 3.15 (dd, 1H, *J* = 10.2, 5.7 Hz), 4.27 (dd, 1H, *J* = 11.4, 2.9 Hz, 1H), 4.61 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 11.8 (CH_3), 20.6 (CH_3), 32.3 (CH), 45.2 (CH), 46.6 (CH), 48.1 (CH_2), 58.4 (CH_3), 67.7 (CH_2), 70.4 (CH_3), 50.6 (CH), 197.2 (C x 4), 202.7 (C), 209.4 (C), 340.5 (C). ppm. IR (CH_2Cl_2) 1714, 1942, 2069. cm^{-1}. MS EI (m/e, rel. int.) (536,3) M^+, (508,3), (480,1), (452,20), (424,20), (396,23), (180,90), (133,100). Anal. calcd for $C_{17}H_{20}O_8W$: C 38.08, H 3.76; found: C 38.00, H 3.68.

6a': Pentacarbonyl {[(1'*S, 2'*R**, 3'*R**, 6'*R**)-2'-methoxymethyl-3',6'-dimethyl-4-oxocyclohexyl]methoxymethylene} tungsten (0)** mp 77-79° C. (crystallized in hexane, yellow prisms). *Rf* 0.14. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.96 (d, 3H, *J* = 6.7 Hz), 1.14 (d, 3H, *J* = 7.0 Hz), 2.10 (dd, 1H, *J* = 14.6, 7.9 Hz), 2.19-2.42 (m, 3H), 2.60 (sextet, 1H, *J* = 6.7 Hz), 3.08-3.29 (m+s, 5H), 4.32 (dd, 1H, *J* = 7.0, 4.4 Hz, 1H), 4.59 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 11.0 (CH_3), 20.8 (CH_3), 31.2 (CH), 44.0 (CH_2), 44.8 (CH), 45.9 (CH), 58.8 (CH_3), 70.2 (CH_3), 72.4 (CH_2), 73.6 (CH), 197.2 (C), 202.5 (C), 212.7 (C), 341.0 (C). ppm. IR (CH_2Cl_2) 1936, 2069. cm^{-1}. Anal. calcd for $C_{17}H_{20}O_8W$: C 38.08, H 3.76; found: C 37.97, H 3.65.

Reaction of *Z*-1b and 2b. 0.25 g of ***Z*-1b** (1.27 mMol) and 0.52 g of **2b** (1.27 mMol) were reacted in MeOH for 45 min. The hydrolysis was performed by method b. After purification by column chromatography (hexane, diethyl ether, methylene chloride 5: 1: 1) the compounds **6a** (0.09 g, 14%) and **6b** (0.14 g, 21 %) were isolated.

6b: Pentacarbonyl {[(1'*S, 2'*S**, 3'*S**, 6'*R**)-2'-methoxymethyl-3',6'-dimethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0)** mp. 74-75° C. (crystallized from hexane, yellow prisms). *Rf* 0.5 ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.00 (d, 3H, *J* = 6.0 Hz), 10.4 (d, 3H, *J* = 7.3 Hz), 2.11 (m, 3H), 2.38 (dd, 1H, *J* = 15.9, 13.8 Hz), 2.55 (dq, 1H, *J* = 12.5, 7.3 Hz), 3.18 (s, 3H), 3.3 (m, 2H), 4.14 (t, 1H, *J* = 8.6 Hz), 4.59 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 11.5 (CH_3), 20.4 (CH_3), 35.9 (CH), 44.2 (CH_2), 44.4 (CH), 45.6 (CH), 58.8 (CH_3), 70.5 (CH_3), 72.3 (CH_2), 73.9 (CH), 197.3 (C x 4), 203.1 (C), 212.2 (C), 344.17 (C). ppm. IR (CH_2Cl_2) 1715, 1941, 2071. cm^{-1}. HRMS calcd for $C_{17}H_{20}O_8{}^{184}W$: 536.0671; found: 536.0670. Anal. calcd for $C_{17}H_{20}O_8W$: C 38.08, H 3.76; found: C 38.21, H 3.66.

Reaction of *E*-1b and 2c. This reaction produced a reaction mixture identical to that obtained in the reaction of ***E*-1b** and **2b**.

Reaction of *E*-1c and 2a. 0.42 g of ***E*-1c** (1.40 mMol) and 0.64 g of **2a** (1.40 mMol) were reacted in DMF from -50° to 0° C for 2 days. The hydrolysis was performed by method a. After purification by column

chromatography (hexane, ethyl acetate 3:1) the compounds **7a** (0.30 g, 31%) and **7b'** (0.07 g, 7 %) were isolated. Also a 55% of the seven membered carbocycle was isolated.[11]

7a: Pentacarbonyl {[(1'*R, 2'*R**, 3'*S**, 6'*R**)-2'-*tert*-butyldimethylsilyloxymethyl-6'-(2-furyl)-3'-methyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0)** mp. 90-92° C. (crystallized from hexane, yellow prisms). R_f 0.61. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.01 (s, 6H), 0.83 (s, 9H), 1.13 (d, 3H, *J* = 6.7 Hz), 2.44-2.67 (m, 4H), 3.36 (d, 1H, *J* = 11.1 Hz), 3.66 (dd, 1H, *J* = 11.1, 2.9 Hz), 4.15 (td, 1H, *J* = 11.6, 6.7 Hz), 4.57 (s, 3H), 4.79 (dd, 1H, *J* = 11.6, 3.2 Hz), 5.84 (d, 1H, *J* = 3.2 Hz), 6.18 (dd, 1H, *J* =3.2, 1.9 Hz), 7.20 (d, 1H, *J* = 1.9 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ -5.8 (CH_3), 12.3 (CH_3), 18.1 (C), 25.8 (CH_3 x 3), 36.3 (CH), 44.3 (CH_2), 44.4 (CH), 46.3 (CH), 59.1 (CH_2), 70.1 (CH_3), 78.4 (CH), 105.1 (CH), 109.9 (CH), 141,2 (CH), 155.6 (C), 197.7 (C x 4), 202.5 (C), 207.5 (C), 339.7 (C). ppm. IR (CH_2Cl_2) 1944, 2071. cm^{-1}. MS EI (m/e, rel. int.) (688,<1) M^+, (172,62), (73,100). Anal calcd for $C_{25}H_{32}SiO_9W$: C 43.62, H 4.69; found: C 43.43, H 4.32.

7b': Pentacarbonyl {[(1'*R, 2'*S**, 3'*R**, 6'*R**)-2'-*tert*-butyldimethylsilyloximethyl-6'-(2-furyl)-3'-methyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0).** mp. 118-120° C. (crystallized from hexane, yellow prisms). R_f 0.44. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.01 (s, 3H), 0.03 (s, 3H), 0.86 (s, 9H), 1.10 (d, 3H, *J* = 7.0 Hz), 1.95 (m, 1H), 2.38 (dd, 1H, *J* = 17.2, 3.8 Hz), 2.68 (quintet, 1H, *J* = 7.0 Hz), 2.83 (dd, 1H, *J* = 17.2, 14.0 Hz), 3.44-3.76 (m, 3H), 4.53 (dd, 1H, *J* = 11.1, 6.0 Hz), 4.68 (s, 3H), 5.90 (d, 1H, *J* = 3.2 Hz), 6.21 (dd, 1H, *J* = 3.2, 1.9 Hz), 7.24 (d, 1H, *J* = 1.9 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ -6.0 (CH_3), -5.9 (CH_3), 11.0 (CH_3 x 3), 18.2 (C), 25.7 (CH_3), 36.8 (CH), 40.9 (CH_2), 42.0 (CH), 44.0 (CH), 62.3 (CH_2), 70.4 (CH_3), 73.8 (CH), 105.6 (CH), 110.2 (CH), 141.5 (CH), 196.6 (C x 4), 202.7 (C), 210.7 (C), 341.2 (C). ppm. IR (CH_2Cl_2) 1942, 2072. cm^{-1}. Anal calcd for $C_{25}H_{32}O_9SiW$: C 43.62, H 4.69; found: C 43.53, H 4.51.

Reaction of *Z*-1c and 2a. 0.33 g of ***Z*-1c** (1.10 mMol) and 0.51 g of **2a** (1.10 mMol) were reacted in THF from -20° to 0° C for 4 days. The hydrolysis was performed by method a. After purification by column chromatography (hexane, ethyl acetate 3:1) the compounds **7a** (0.16 g, 21%) and **7b'** (0.33 g, 44 %) were isolated.

Reaction of *E*-1c and 2b. 0.44 g of ***E*-1c** (1.48 mMol) and 0.60 g of **2b** (1.48 mMol) were reacted in THF from -20° to 0° C for 36 h. The hydrolysis was performed by method c. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1) the compounds **8a** (0.45 g, 48%) and **8b'** (0.09 g, 10 %) were isolated.

8a: Pentacarbonyl {[(1'*S, 2'*R**, 3'*S**, 6'*R**)-2'-*tert*-butyldimethylsilyloxymethyl-3',6'-dimethyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0)** mp. 75-77° C. (crystallized from hexane, orange prisms). R_f 0.58. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ -0.04 (s, 3H), -0.01 (s, 3H), 0.79 (s, 9H), 0.86 (d, 3H, *J* = 6.7 Hz), 1.08 (d, 3H, *J* = 6.7 Hz), 1.87 (dd, 1H, *J* = 15.3, 12.1 Hz), 2.30 (dd, 1H, *J* = 15.3, 5.1 Hz), 2.38-2.56 (m, 2H), 2.71-2.86 (m, 1H), 3.25 (dd, 1H, *J* = 10.8, 1.3 Hz), 3.57 (dd, 1H, *J* = 10.8, 3.5 Hz), 4.31 (dd, 1H, *J* = 11.8, 3.2 Hz, 1H).4.64 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ -6.2 (CH_3 x 2), 11.9 (CH_3), 17.9 (C), 20.9 (CH_3), 25.4 (CH_3 x 3), 32.2 (CH), 44.9 (CH), 46.2 (CH), 48.1 (CH_2), 58.7 (CH_2), 70.4 (CH_3), 81.2 (CH), 197.0 (C x 4), 202.5 (C), 208.3 (C), 324.8 (C). ppm. IR (CH_2Cl_2) 1942, 2069. cm^{-1}. HRMS calcd for $C_{22}H_{32}O_8Si^{184}W$: 636.1379; found: 636.1367. Anal. calcd for $C_{22}H_{32}O_8SiW$: C 41.52, H 5.07; found: C 41.44, H 5.00.

8b': Pentacarbonyl {[(1'*S, 2'*S**, 3'*R**, 4'*R**)-2-*tert*-butyldimethylsilyloxymethyl-3',6'-**

dimethyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0) Orange oil. R_f 0.19. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ -0.05 (s, 3H), -0.02 (s, 3H), 0.80 (s, 9H), 0.98 (d, 3H, J = 5.6 Hz), 1.03 (d, 3H, J = 7.3 Hz), 1.90-1.95 (m, 1H), 2.08-2.27 (m, 3H), 2.62 (quintet, 1H, J = 5.6 Hz), 3.55 (dd, 1H, J = 10.3, 3.4 Hz), 3.67 (dd, 1H, J = 10.3, 6.0 Hz), 4.13 (dd, 1H, J = 9.5, 7.3 Hz), 4.62 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ -5.9 (CH_3), -5.8 (CH_3), 11.0 (CH_3), 18.1 (C), 20.4 (CH_3), 25.7 (CH_3 x 3), 34.8 (CH), 42.6 (CH), 45.4 (CH), 45.6 (CH_2), 61.9 (CH_2), 70.7 (CH), 74.8 (CH), 197.1 (C x 4), 202.2 (C), 212.2 (C), 344.9 (C). ppm. IR (CH_2Cl_2) 1942, 2071. cm^{-1}. Anal. calcd for $C_{22}H_{32}O_8SiW$: C 41.52, H 5.07; found: C 41.40, H 5.01.

Reaction of *Z*-1c and 2b. 0.48 g of ***Z*-1c** (1.62 mMol) and 0.66 g of **2b** (1.62 mMol) were reacted in THF for 12 h. The hydrolysis was performed by method c. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1) the compounds **8a** (0.19 g, 18%) and **8b'** (0.36 g, 35 %) were isolated.

Reaction of *E*-1b and 2d. 0.31 g of ***E*-1b** (1.60 mMol) and 0.68 g of **2d** (1.60 mMol) were reacted in MeOH for 4 days. The hydrolysis was performed by method b. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1) the compounds **9a'** (0.14 g, 16%), **9b** (0.16 g, 18 %) and **9b'** (0.12 g, 14 %) were isolated.

9a': Pentacarbonyl {[(1'*R, 2'*R**, 3'*R**)-2'-methoxymethyl-3',6',6'-trimethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0)** mp. 120-122° C. (crystallized from hexane, yellow prisms). R_f 0.44. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.93 (d, 3H, J = 6.4 Hz), 0.96 (s, 3H), 1.07 (s, 3H), 1.84-1.92 (d+m, 2H, J = 14.2 Hz), 2.50 (d, J = 14.2 Hz, 1H), 2.73 (dq 1H, J = 12.1, 6.4 Hz), 3.21 (s, 3H), 3.35 (dd, 1H, J = 10.3, 3.9 Hz), 3.60 (dd, 1H, J = 10.3, 1.7 Hz), 4.33 (d, 1H, J = 5.2 Hz), 4.64 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 11.2 (CH_3), 28.4 (CH_3), 30.1 (CH_3), 39.1 (C), 42.3 (CH), 46.3 (CH), 51.8 (CH_2), 58.9 (CH_3), 69.8 (CH_3), 70.8 (CH_2), 76.4 (CH), 197.9 (C x 4), 202.25 (C), 212.7 (C), 348.1 (C). ppm. Anal. calcd for $C_{18}H_{22}O_8W$: C 39.29, H 4.03; found: C 39.27, H 3.97.

9b: Pentacarbonyl {[(1'*R, 2'*S**, 3'*S**)-2'-methoxymethyl-3',6',6'-trimethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0).** mp. 92-93° C. (crystallized from hexane, orange prisms). R_f 0.50. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.74 (s, 3H), 0.98 (d, 3H, J = 6.7 Hz), 1.86 (s, 3H), 1.93-2.01 (d+m, 2H, J = 12.4 Hz), 2.33-2.43 (d+dq, 2H, J = 12.4 Hz, J = 11.2, 6.7 Hz), 3.17-3.21 (m+s, 4H), 3.32 (d,d, J = 10.5, 5.4 Hz, 1H), 4.53 (d, 1H, J = 11.1 Hz), 4.60 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 11.5 (CH_3), 23.2 (CH_3), 31,5 (CH_3), 39.8 (C), 45.0 (CH), 46.7 (CH), 57.0 (CH_2), 58.8 (CH_3), 70.1 (CH_3), 71.7 (CH_2), 78.6 (CH), 197.5 (C x 4), 202.4 (C), 210.3 (C), 347.7 (C). ppm. IR (CH_2Cl_2) 1711, 1937, 2070. cm^{-1}. MS EI (m/e, rel. int.) (550,2) M^+, (522,3), (494,6), (466,7), (438,9), (410,10), (264,69), (45,100). HRMS calcd for $C_{18}H_{22}O_8{}^{184}W$: 550.0828; found: 550.0818. Anal. calcd for $C_{18}H_{22}O_8W$: C 39.29, H 4.03; found: C 39.32, H 3.93.

9b': Pentacarbonyl {[(1'*R, 2'*S**, 3'*R**)-2'-methoxymethyl-3',6',6'-trimethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0).** mp. 65-68° C. (crystallized from hexane, yellow prisms). R_f 0.56. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.86 (s, 3H), 1.05 (d, 3H, J = 7.3 Hz), 1.12 (s, 3H), 1.92 (d, 1H, J = 13.3 Hz), 2.43 (d, 1H, J = 13.3 Hz), 2.43-2.50 (m, 1H), 2.56 (quintet, 1H, J = 7.3 Hz), 3.02 (s, 3H), 3.21-3.34 (m, 2H), 4.48 (d, 1H, J = 9.9 Hz), 4.62 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 11.7 (CH_3), 24.2 (CH_3), 31.0 (CH_3), 40.2 (C), 41.5 (CH), 44.8 (CH), 53.6 (CH_2), 58.7 (CH_3), 70.2 (CH_3), 72.0 (CH_2), 74.6 (CH), 197.4 (C x 4), 202.2(C), 212.3 (C), 345.7 (C). ppm. IR (CH_2Cl_2) 1711, 1940, 2070. cm^{-1}. Anal. calcd for $C_{18}H_{22}O_8W$: C 39.29, H 4.03; found: C 39.31, H 3.90.

Reaction of *Z*-1b and 2d. 0.43 g of ***Z*-1b** (2.20 mMol) and 0.93 g of **2d** (2.20 mMol) were reacted in THF from -20° to 0° C for 4 days. The hydrolysis was performed by method b, but using H_2SO_4 instead of HCl. After purification by column chromatography (hexane, ethyl acetate 3:1) the compounds **9a** (0.23 g, 19%), **9a'** (0.07 g, 6%), **9b** (0.06 g, 5 %) and **9b'** (0.16 g, 13 %) were isolated.

9a: Pentacarbonyl {[(1'*R, 2'*R**, 3'*S**)-2'-methoxymethyl-3',6',6'-trimethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0).** mp. 90-92° C. (crystallized from hexane, orange prisms). *Rf* 0.3. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.94 (s, 3H), 1.01 (d, 3H, *J* = 6.7 Hz), 1.05 (s, 3H), 1.99 (d, 1H, *J* = 13.0 Hz), 2.26 (d, 1H, *J* = 13.0 Hz), 2.69-2.82 (m, 2H), 3.10 (dd, 1H, *J* = 9.8, 5.4 Hz), 3.12 (s, 3H), 3.29 (dd, 1H, *J* = 9.8, 4.4 Hz), 4.59-4.63 (m+s, 4H). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 11.7 (CH_3), 25.9 (CH_3), 31.1 (CH_3), 41.1 (C), 45.0 (CH), 47.2 (CH), 56.3 (CH_2), 58.2 (CH_3), 69.5 (CH_3), 70.3 (CH_2), 80.6 (CH), 197.3 (C x 4), 202.3 (C), 210.8 (C), 343.6 (C). ppm. IR (CH_2Cl_2) 1939, 2070. cm^{-1}. Anal. calcd for $C_{18}H_{22}O_8W$: C 39.29, H 4.03; found: C 39.29, H 3.95.

Reaction of 1d and 2d. 0.23 g of **1d** (1.20 mMol) and 0.51 g of **2d** (1.20 mMol) were reacted in THF for 4 days. The hydrolysis was performed by the method b. After purification by column chromatography (hexane, diethyl ether 2:1) the compound **10b** (or **10b'**) (0.29 g, 44%) was isolated. The complex **10a** (or **10a'**) was detected in the hydrolysis mixture in ca 5% but it could not be properly isolated. Its structure was proposed in function of the $^3J_{H3'H4'}$ found to be 4 Hz, corresponding to an equatorial-equatorial disposition of these hydrogens.

10b: Pentacarbonyl {2-[(1'*R, 2'*R**)-3,3-dimethyl-5-oxobicyclo[4.4.0]decyl]methoxy methylene} tungsten (0).** mp. 139-141 (crystallized from hexane, orange prisms). *Rf* 0.61. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.85 (s, 3H), 1.26 (s, 3H), 1.17-2.04 (m, 10H), 1.99 (d, 1H, *J* = 13.0 Hz), 2.47 (d, 1H, *J* = 13.0 Hz), 4.47 (d, 1H, *J* = 10.5 Hz), 4.70 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 23.2 (CH_3), 24.8 (CH_2), 25.0 (CH_2), 26.1 (CH_2), 31.2 (CH_3), 32.3 (CH_2), 40.8 (C), 45.0 (CH), 53.6 (CH), 57.2 (CH_2), 70.4 (CH_3), 82.0 (CH), 197.4 (C x 4), 202.3 (C), 209.3 (C), 350.4 (C). ppm. IR (CH_2Cl_2) 1709, 1940, 2059. cm^{-1}. HRMS calcd for $C_{19}H_{22}O_7{}^{184}W$: 546.0879; found: 546.0881. Anal. calcd for $C_{19}H_{22}O_7W$: C 41.78, H 4.06; found: C 41.85, H 3.94.

Reaction of *E*-1e and 2a. 0.41 g of ***E*-1e** (1.62 mMol) and 0.75 g of **2a** (1.62 mMol) were reacted in DMF for 2 days. The hydrolysis was performed by method b, but using H_2SO_4 instead of HCl. After purification by column chromatography (hexane, ethyl acetate 3:1) the compound **12a'** (0.36 g, 41%) was isolated. Also a 40% of the cycloheptadione derivative was isolated.[11]

12a': Pentacarbonyl {(1*R, 5*R**, 6*R**, 9*R**)-9-(2-furyl)-6-methyl-3-oxa-7-oxobicycle[4.3.0]non-2-ylidene} tungsten (0).** mp. 129-131° C (crystallized from hexane-diethyl ether, yellow prisms). *Rf* 0.25. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.99 (d, 3H, *J* = 6.5 Hz), 1.88 (dq, 1H, *J* = 11.2, 6.5 Hz), 2.31 (ddd, 1H, *J* = 11.2, 6.0, 4.7 Hz), 2.61-2.74 (m, 2H), 2.85 (d, 1H, *J* = 6.0 Hz), 4.63 (dd, 1H, *J* = 10.3, 4.7 Hz), 4.81-4.83 (m, 1H), 4.92 (d, 1H, *J* = 10.3 Hz), 6.01 (d, 1H, *J* = 3.4 Hz), 6.23 (dd, 1H, *J* = 3.4, 1.7 Hz), 7.26 (d, 1H, *J* = 1.7 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 12.8 (CH_3), 38.7 (CH), 41.2 (CH_2), 43.2 (CH), 44.2 (CH), 74.8 (CH), 88.6 (CH_2), 107.1 (CH), 110.4 (CH), 142.1 (CH), 154.3 (C), 196.4 (C), 202.6 (C), 207.4 (C), 319.1 (C). ppm. IR (CH_2Cl_2) 1942, 2073. cm^{-1}. MS, EI (m/e, rel. int.) (542,14) M^+, (514,1), (486,17), (458,38), (430,89), (402,51), (128,71), (115,100), (91,84). HRMS calcd for $C_{18}H_{14}O_8{}^{184}W$: 542.0202; found: 542.0192. Anal. calcd for $C_{18}H_{14}O_8W$: C: 39.88, H: 2.60; found: C: 39.93, H: 2.52.

Reaction of *E*-1e and 2b. 0.18 g of ***E*-1e** (0.69 mMol) and 0.28 g of **2b** (0.69 mMol) were reacted in THF for 2 days. The reaction crude was then treated with anhydrous MeOH / Na_2CO_3 for 3 hours to induce the cyclization and then was hydrolyzed by method a. After purification by column chromatography (hexane, ethyl acetate 3:1) the compound **13a'** (0.26 g, 77%), was isolated.

13a': Pentacarbonyl {(1*S, 5*R**, 6*R**, 9*R**)-6,9-dimethyl-3-oxa-7-oxobicycle[4.3.0]non-2-ylidene} tungsten (0).** mp. 135-136 °C (Crystallizad from hexane, yellow prisms). R_f 0.31. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.06 (d, 3H, J = 6.4 Hz), 1.23 (d, 3H, J = 6.9 Hz), 1.95 (dq, 1H, J = 10.5, 6.4 Hz), 2.30-2.5 (m, 2H), 2.37 (dt, 1H, J = 10.5, 5.6 Hz), 2.60 (dd, 1H, J = 5.6, 12.9 Hz), 3.70 (m, 1H), 4.70 (dd, 1H, J = 9.9, 5.6 Hz), 4.92 (d, 1H, J = 9.9 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 12.8 (CH_3), 21.0 (CH_3), 34.5 (CH), 43.2 (CH), 44.5 (CH), 45.1 (CH_2), 77.7 (CH), 88.5 (CH_2), 196.7 (C x 4), 202.9 (C), 208.9 (C), 321.2 (C). ppm. HRMS calcd for $C_{15}H_{14}O_7{}^{184}W$: 490.0252, found: 490.0248. Duplicated analysis gave high values in C for this compound. Anal. calcd for $C_{15}H_{14}O_7W$: C 36.76, H 2.88; found: C 37.33, H 3.00.

Reaction of *E*-1e and 2d. 0.30 g of ***E*-1e** (1.18 mMol) and 0.50 g of **2d** (1.18 mMol) were reacted in THF for 4 days. The hydrolysis was performed by method b but using H_2SO_4 instead of HCl. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1) the compound **14a** (0.26 g, 44%), was isolated. The compound **14b** was detected in the ^{1}H-NMR of the reaction crude (ca 11%) and quantified by integration, but could not be isolated.

14a: Pentacarbonyl {(1*R, 5*R**, 6*S**)-6,9,9-trimethyl-3-oxa-7-oxobicycle[4.3.0] nonylidene} tungsten (0).** mp. 95-97° C (crystallized from hexane, yellow prisms). R_f 0.22. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.75 (s, 3H), 0.99 (d, 3H, J = 6.7 Hz), 1.61 (s, 3H), 2.03 (d, 1H, J = 12.4 Hz), 2.58 (d, 1H, J = 12.4 Hz), 2.85 (dq, 1H, J = 7.0, 6.7 Hz), 3.00 (dddd, 1H, J = 12.4, 9.2, 7.3, 7.0 Hz), 3.97 (d, J = 7.3 Hz), 4.24 (dd, 1H, J = 10.2, 9.2 Hz), 4.68 (dd, 1H, J = 12.4, 10.2 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) d 12.2 (CH_3), 23.3 (CH_3), 33.8 (CH_3), 41.1 (CH), 41.7 (CH), 44.9 (CH), 55.0 (CH_2), 76.0 (CH), 83.9 (CH_2), 197.1 (C x 4), 203.9 (C), 209.1 (C), 325.6 (C). ppm. IR (CH_2Cl_2) 1720, 1946, 2071. cm^{-1}. HRMS calcd for $C_{16}H_{16}O_7{}^{184}W$: 504.0409; found: 504.0400. Anal. calcd for $C_{16}H_{16}O_7W$: C 38.12, H 3.20; found C 38.02, H 3.12.

Reaction of *E*-1e and 2e. 0.56 g of ***E*-1e** (2.20 mMol) and 0.90 g of **2e** (2.20 mMol) were reacted in THF for 4 days. The hydrolysis was performed by method b but using H_2SO_4 instead of HCl. After purification by column chromatography (hexane, diethyl ether, dichloromethane 2:1:1) the compounds **15a** (0.06 g, 6%) and **15a'** (0.59 g, 55%) were isolated.

15a: Pentacarbonyl {(1*S, 5*R**, 6*S**)-1,6-dimethyl-3-oxa-7-oxobicycle[4.3.0]non-2-ylidene} tungsten (0).** mp 92-95 °C (crystallized from hexane, yellow prisms). R_f 0.35. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.98 (d, 3H, J = 7.0 Hz), 1.69 (s, 3H), 1.82-2.21 (m, 4H), 2.35-2.61 (m, 2H, 2.72 (quintet, 1H, J = 7.0 Hz), 4.20 (t, 1H, J = 10.8 Hz), 4.94 (dd, 1H, J = 10.8, 8.9 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 13.1 (CH_3), 25.0 (CH_3), 31.8 (CH_2), 36.3 (CH_2), 41.0 (CH), 47.9 (CH), 69.2 (C), 86.0 (CH_2), 196.8 (C x 4), 202.8 (C), 210.2 (C), 328.3 (C). ppm. IR (CH_2Cl_2) 1717, 1944, 2072. cm^{-1}. The stereochemistry was deduced from nOe experiments. HRMS calcd for $C_{15}H_{14}O_7{}^{184}W$: 490.0252; found: 490.0246. Anal. calcd for $C_{15}H_{14}O_7W$: C 36.76, H 2.88; found: C 36.93, H 2.79.

15a': Pentacarbonyl {(1S*R, 5*R**, 6*R**)-1,6-dimethyl-3-oxa-7-oxobycicle[4.3.0]non-2-ylidene} tungsten (0).** mp. 130-131° C (crystallized from hexane, yellow prisms). R_f 0.40. ^{1}H-NMR

($CDCl_3$, 300 MHz) δ 0.99 (d, 3H, *J* = 6.4 Hz), 1.20 (s, 3H), 1.90 (ddd, 1H, *J* = 11.8, 5.5, 2.5 Hz), 2.02 (dq, 1H, *J* = 11.8, 6.4 Hz), 2.24 (ddd, 1H, *J* = 13.0, 11.4, 6.0 Hz), 2.41 (m, 2H), 2.55 (ddd, 1H, *J* = 13.3, 7.9, 5.4 Hz), 4.83 (dd, 1H, *J* = 10.8, 2.5 Hz), 4.91 (d,d, 1H, *J* = 10.8, 5.5 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 12.8 (CH_3), 23.5 (CH_3), 32.7 (CH_2), 36.4 (CH_2), 43.6 (CH_2), 48.1 (CH), 70.6 (C), 88.3 (CH_2), 196.7 (C x 4), 202.5 (C), 210.1 (C), 325.9 (C). ppm. IR (CH_2Cl_2) 1718, 1944, 2071. cm^{-1}. The stereochemistry was deduced from nOe experiments. Anal. calcd for $C_{15}H_{14}O_7W$: C 36.76, H 2.88; found: C 36.90, H 2.80.

Oxidation of the carbene complexes. Preparation of compounds 16-18.

To a solution of the metal complex in acetone are added 4 equivalents of Cerium (IV) ammonium nitrate (CAN). After 30 min the solvent is evaporated under reduced pressure. The solid thus obtained is dissolved in water and diethyl ether. The layers are separated and the aqueous phase further extracted twice with diethyl ether. The combined organics are dried with anhydrous Na_2SO_4, filtered and concentrated and the residue purified by column chromatography in silica-gel.

16: methyl (1*R, 2*R**, 5*S**)-2-(2-furyl)-5-methyl-4-cyclohexanonecarboxylate.** 0.40 g (0.74 mMol) of **4** afforded 0.09 g of **16** (50 %). *Rf* 0.28 (hexane-ethyl acetate 3:1) ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.11 (d, 3H, *J* = 6.7 Hz), 1.60-1.80 (m, 2H), 2.21.-2.37 (m, 1H), 2.57 (ddq, 1H, *J* = 13.4, 6.7, 6.4 Hz), 2.69 (d, 1H, *J* = 8.8 Hz), 3.13 (td, 1H, *J* = 8.9, 1.2 Hz), 3.40 (dq, 1H, *J* = 10.0, 8.9 Hz), 3.60 (s, 3H), 5.9 (d, 1H, *J* = 2.9 Hz), 6.2 (dd, 1H, *J* = 2.9, 1.2 Hz), 7.3 (d, 1H, *J* = 1.2 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 13.9 (CH_3), 37.9 (CH_2), 40.6 (CH), 43.4 (CH), 44.8 (CH_2), 47.6 (CH_2), 51.8 (CH), 105.0 (CH), 110.1 (CH), 141.3 (CH), 154.2 (C), 173.5 (C), 209.8 (C). ppm. Anal. calcd for $C_{13}H_{16}O_4$: C 66.09, H 6.83; found C 66.34, H 6.58.

17a: methyl (1*S, 2R*, 3*S**, 6*R**)2-*tert*-butyldimethylsilyloxymethyl-6-(2-furyl)-3-methyl-4-cyclohexanonecarboxylate.** 0.45 g of **7a** (0.71 mmol) afforded 0.14 g of **17a** (60 %). *Rf* 0.65 (hexane-ethyl acetate 3:1) ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.00 (s, 3H), 0.05 (s, 3H), 0.85 (s, 9H), 1.01 (d, 3H, *J* = 6.0 Hz), 1.13 (d, 3H, *J* = 6.8 Hz), 1.91 (dd, 1H, *J* = 15.0, 12.5 Hz), 2.28-2.52 (m, 3H), 2.65 (dd, 1H, *J* = 12.4, 3.8 Hz), 2.72-2.85 (m, 1H), 3.62-3.68 (m, 1H), 3.75 (s, 3H). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ -6.1 (CH_3 x 2), 11.7 (CH_3),18.1 (C), 21.5 (CH_3), 25.6 (CH_3 x 3), 31.0 (CH), 45.6 (CH), 45.7 (CH), 47.8 (CH_2), 51.5 (CH_3), 53.8 (CH), 59.4 (CH_2), 173.8 (C), 209.2 (C). ppm. Anal. calcd for $C_{17}H_{32}O_4Si$: C 62.15, H 9.82; found C 61.87, H 9.73.

18a': (1*S, 5*R**, 6*R**, 9*R**)-6,9-dimethyl-2,7-dioxo-3-oxabycicle[4.3.0]nonane.** 0.78 g of **13a'** (1.6 mMol) afforded 0.21 g of **18a'** (73 %). *Rf* 0.31 (hexane-ethyl acetate 1:1) ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.04 (d, 3H, *J* = 6.4 Hz), 1.07 (d, 3H, *J* = 7.0 Hz), 2.09 (dd, 1H, *J* = 14.6, 6.7 Hz), 2.19-2.33 (m, 1H), 2.42-2.57 (m, 3H), 2.64-2.75 (m, 1H), 4.15 (d, 1H, *J* = 9.8 Hz) 4.29 (dd, 1H, *J* = 9.8, 5.1 Hz). ppm. ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 12.3 (CH_3), 20.1 (CH_3), 30.0 (CH), 42.8 (CH), 43.7 (CH), 44.6 (CH_2), 45.5 (CH), 70.5 (CH_2), 176.8 (C), 210.1 (C). ppm. IR (KBr) 1711, 1765. cm^{-1}. MS EI (m/e, rel. int.) (182,14) M^+, (128,31), (100,100), (69,71), (55,15). Anal. calcd for $C_{10}H_{14}O_3$: C 65.92, H 7.74; found C 65.71, H 7.62.

Method of preparation of the enantiomericaly enriched complexes. The reactions of the chiral dienes **19** were performed in a similar way than those of the achiral dienes **1**.

Reaction of *E*-19b and 2a. 0.42 g of ***E*-19b** (1.86 mMol) and 0.86 g of **2a** (1.86 mMol) were reacted in DMF at -20° C for 4 days. The hydrolysis was performed by treating the reaction mixture with an aqueous 3N

HCl solution at -20° C for 1h. The reaction workup was performed as in method b. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1), the compounds **(-)5a** (0.21 g, 19%), **(+)5a'** (0.09g, 8%), and **(+)5b'** (0.14 g, 13%) were isolated.

(-)5a: Pentacarbonyl {[(1'*S*, 2'*S*, 3'*R*, 6'*S*)-6'-(2-furyl)-2'-methoxymethyl-3'-methyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ -11 (CH_2Cl_2, c=0.60).

(+)5a': Pentacarbonyl {[(1'*S*, 2'*S*, 3'*S*, 6'*S*)-6'-(2-furyl)-2'-methoxymethyl-3'-methyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ +28 (CH_2Cl_2, c=0.38, e.e. 31 %). HPLC: (hexane-THF 10:1, 0.9 mL/min, 36 Kg/cm^2, rt 7.9 min (major), 8.5 min (minor)).

(+)5b': Pentacarbonyl {[(1'*R*, 2'*S*, 3'*R*, 6'*R*)-6'-(2-furyl)-2'-methoxymethyl-3'-methyl-4-oxocyclohexyl] methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ +35 (CH_2Cl_2, c=0.12, e.e. 99 %). HPLC: (hexane-ethyl acetate 3:1, 0.9 mL/min, 36 Kg/cm^2, rt 5.6 min (minor), 9.2 min (major)).

Reaction of *Z*-19b and 2a. 0.50 g of ***Z*-19b** (2.22 mMol) and 1.30 g of **2a** (2.22 mMol) were reacted in DMF at -20° C for 4 days. The hydrolysis was performed by treating the reaction mixture with an aqueous 3N HCl solution at -20° C for 1h. The workup was performed as in method b. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1), the compounds **(+)5a** (0.13 g, 10%), **(-)5a'** (0.05g, 4%), and **(-)5b'** (0.40 g, 31%) were isolated.

(+)5a: Pentacarbonyl {[(1'*R*, 2'*R*, 3'*S*, 6'*R*)-6'-(2-furyl)-2'-methoxymethyl-3'-methyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ +33 (CH_2Cl_2, c=0.60).

(-)5a': Pentacarbonyl {[(1'*R*, 2'*R*, 3'*R*, 6'*R*)-6'-(2-furyl)-2'-methoxymethyl-3'-methyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ -88 (CH_2Cl_2, c=0.15, e.e. 94 %). HPLC: (hexane-THF 10:1, 0.9 mL/min, 36 Kg/cm^2, rt 7.9 min (minor), 8.5 min (major)).

(-)5b': Pentacarbonyl {[(1'*S*, 2'*R*, 3'*S*, 6'*S*)-6'-(2-furyl)-2'-methoxymethyl-3'-methyl-4-oxocyclohexyl] methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ -6 (CH_2Cl_2, c=0.12, e.e. 20 %). HPLC: (hexane-ethyl acetate 3:1, 0.9 mL/min, 36 Kg/cm^2, rt 5.6 min (major), 9.2 min (minor)).

Reaction of *E*-19b and 2b. 0.39 g of ***E*-19a** (1.73 mMol) and 0.71 g of **2b** (1.73 mMol) were reacted in THF at -20° C for 2 days. The hydrolysis was performed by method b. After purification by column chromatography (hexane, diethyl ether 2:1), the compounds **(+)6a** (0.29 g, 31%), **(+)6a'** (0.14g, 15%), and **(-)6b** (0.10 g, 11%) were isolated.

(+)6a: Pentacarbonyl {[(1'*R*, 2'*S*, 3'*R*, 6'*S*)-3',6'-dimethyl-2'-methoxymethyl-4-oxocyclohexyl]methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ +11 (CH_2Cl_2, c=0.11).

(+)6a': Pentacarbonyl {[(1'*R*, 2'*S*, 3'*S*, 6'*S*)-3',6'-dimethyl-2'-methoxymethyl-4-oxocyclohexyl]methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ +8 (CH_2Cl_2, c=0.12, e.e. 18 %). HPLC: (hexane-THF 5:1, 1.0 mL/min, 40 Kg/cm^2, rt 8.6 min (major), 9.0 min (minor)).

(-)6b: Pentacarbonyl {[(1'*S*, 2'*S*, 3'*S*, 6'*R*)-3',6'-dimethyl-2'-methoxymethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ -47 (CH_2Cl_2, c=0.12, e.e. 82 %). HPLC: (hexane-THF 15:1, 1.0 mL/min, 40 Kg/cm^2, rt 11.5 min (major), 13.0 min (minor)).

Reaction of *Z*-19b and 2b. 0.34 g of ***Z*-19b** (1.51 mMol) and 0.62 g of **2b** (1.51 mMol) were reacted in MeOH at -25° C for 2 days. The hydrolysis was performed by method b. After purification by column chromatography (hexane, diethyl ether 2:1), the compounds **(-)6a** (0.11 g, 13%), **(-)6a'** (0.08g, 10%) and **(+)6b** (0.22 g, 27%) were isolated.

(-)6a: Pentacarbonyl {[(1'*S*, 2'*R*, 3'*S*, 6'*R*)-3',6'-dimethyl-2'-methoxymethyl-4'-

oxocyclohexyl]methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ -60 (CH_2Cl_2, c=0.11, e.e. 94 %). HPLC: (hexane-THF 15:1, 1.0 mL/min, 40 Kg/cm^2, rt 9.4 min (major), 10.0 min (minor)).

(-)6a': Pentacarbonyl {[(1'*S*, 2'*R*, 3'*R*, 6'*R*)-3',6'-dimethyl-2'-methoxymethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ -42 (CH_2Cl_2, c=0.12).

(+)6b: Pentacarbonyl {[(1'*S*, 2'*S*, 3'*S*, 6'*R*)-2'-methoxymethyl-3',6'-dimethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ +26 (CH_2Cl_2, c = 0.48, e.e.= 53 %) HPLC: (hexane-THF 15:1, 1.05 mL/min, 38 Kg/cm^2, rt 13.8 min (minon), 15.8 min (major).

Reaction of *E*-19c and 2a. 0.66 g of ***E*-19c** (2.03 mMol) and 0.93 g of **2a** (2.03 mMol) were reacted in DMF at -50° C for 2 days. The hydrolysis was performed by method a. After purification by column chromatography (hexane, diethyl ether 2:1), the compounds **7a** (0.28 g, 20%) and **(-)7b'** (0.11 g, 8%) were isolated.

7a: Pentacarbonyl {[(1'*S*, 2'*S*, 3'*R*, 4'*S*)-2'-*tert*-butyldimethylsilyloxymethyl-3',6'-dimethyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0). HPLC: (hexane-THF 10:1, 0.8 mL/min, 31 Kg/cm^2, rt 5.9 min (major), 6.3 min (minor)).

(-)7b': Pentacarbonyl {[(1'*R*, 2'*S*, 3'*R*, 4'*R*)-2-*tert*-butyldimethylsilyloxymethyl-3',6'-dimethyl-4'-oxocyclohexyl] methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ -28 (CH_2Cl_2, c=0.22, e.e. 99 %). HPLC: (hexane-THF 10:1, 0.9 mL/min, 34 Kg/cm^2, rt 7.2 min (minor), 10.9 min (major)).

Reaction of *E*-19b and 2d. 0.33 g of ***E*-19b** (1.47 mMol) and 0.62 g of **2d** (1.47 mMol) were reacted in THF at -20° C for 2 days. The hydrolysis was performed by method b. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1), the compounds **(-)9b** (0.06 g, 8%) and **(-)9b'** (0.08g, 10%) were isolated.

(-)9b: Pentacarbonyl {[(1'*R*, 2'*S*, 3'*S*)-2'-methoxymethyl-3',6',6'-trimethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0). $[\alpha]_D^{20}$ -57 (CH_2Cl_2, c=0.11, e.e. 90 %). HPLC: (hexane-ethyl acetate 15:1, 1.0 mL/min, 37 Kg/cm^2, rt 9.2 min (minor), 10.0 min (major)).

(-)9b': Pentacarbonyl {[(1'*R, 2'*S**, 3'*R**)-2'-methoxymethyl-3',6',6'-trimethyl-4'-oxocyclohexyl]methoxymethylene} tungsten (0).** $[\alpha]_D^{20}$ -49 (CH_2Cl_2, c=0.33, e.e. 90 %). HPLC: (hexane-THF 10:1, 0.9 mL/min, 35 Kg/cm^2, rt 7.8 min (minor), 8.8 min (major)).

Reaction of *E*-19e and 2b. 0.56 g of ***E*-19e** (2.13 mMol) and 0.87 g of **2b** (2.13 mMol) were reacted in THF from -50° to 20° C for 36 h. The hydrolysis was performed by method b. After purification by column chromatography (hexane, ethyl acetate 3:1), the compound **(+)13a'** (0.55 g, 53%) was isolated.

(+)13a': Pentacarbonyl {(1*S*, 5*R*, 6*S*, 9*S*)-6,9-dimethyl-3-oxa-7-oxobicycle[4.3.0]non-2-ylidene} tungsten (0). $[\alpha]_D^{20}$ +39 (CH_2Cl_2, c=0.26, e.e. 81 %). HPLC: (hexane-THF 15:1, 1.0 mL/min, 37 Kg/cm^2, rt 19.0 min (minor), 24.4 min (major)).

Reaction of *E*-19e and 2d. 0.31 g of ***E*-19e** (1.18 mMol) and 0.50 g of **2d** (1.18 mMol) were reacted in THF at -20° C for 10 days. The hydrolysis was performed by method b. After purification by column chromatography (hexane, diethyl ether, dichloromethane 5:1:1), the compound **14a** (0.26 g, 43%) was isolated.

14a: Pentacarbonyl {(1*S*, 5*S*, 6*R*)-6,9,9-trimethyl-3-oxa-7-oxobicycle[4.3.0] nonylidene} tungsten (0). $[\alpha]_D^{20}$ +62 (CH_2Cl_2, c=0.35, e.e. 72 %). HPLC: (hexane-THF 15:1, 1.0 mL/min, 40 Kg/cm^2, rt 17.5 min (minor), 19.4 min (major)).

Reaction of *E*-19e and 2e. 0.83 g of ***E*-19e** (3.16 mMol) and 1.29 g of **2e** (3.16 mMol) were reacted in

DMF from -60° to 20° C for 13 h. The hydrolysis was performed by method b. After purification by column chromatography (hexane, diethyl ether, dichloromethane 2:1:1), the compounds **(-)15a** (0.29 g, 19%) and **(+)15a'** (0.49 g, 32%) were isolated. The isomers "**b**" could not be isolated but were detected and cuantified from the ^{1}H-NMR spectrum of the hydrolysis crude.

(-)15a: Pentacarbonyl {(1S*R*, 5*S*, 6*R*)-1,6-dimethyl-3-oxa-7-oxobicycle[4.3.0]non-2-ylidene} tungsten (0). $[\alpha]_D^{20}$ -102 (CH_2Cl_2, c=0.32).

(+)15a': Pentacarbonyl {(1S*R*, 5*S*, 6*S*)-1,6-dimethyl-3-oxa-7-oxobicycle[4.3.0]non-2-ylidene} tungsten (0). $[\alpha]_D^{20}$ +47 (CH_2Cl_2, c=0.67, e.e. 90 %). HPLC: (hexane-THF 12:1, 1.0 mL/min, 40 Kg/cm^2, rt 24.2 min (minor), 25.5 min (major)).

Oxidation of (+)13a': The compound **(+)13a'** was oxidized to the lactone **(+)18a'** as described for **13a'**.

(+)18a': (1*R*, 5*S*, 6*S*, 9*S*)-6,9-dimethyl-2,7-dioxo-3-oxabicycle[4.3.0]nonane. $[\alpha]_D^{20}$ +11 (CH_2Cl_2, c=0.21, 81 %).

References:

1. For recent reviews on the Diels-Alder cycloaddition reaction see (a) Carruthers, W. in *Cycloaddition reactions in Organic Synthesis*, Pergamon Press, Exeter, 1990. (b) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry* 3rd edition, Plenum Press, New York, 1991.
2. For a comprehensive review on asymmetric [4+2] cycloadditions see: Seyden-Penne, J. in *Chiral auxiliaries and ligands in asymmetric synthesis*. Wiley Interscience, New York 1995.
3. Mulzer, J.; Altenbach, H. J.; Braun, M.; Kron, K.; Reissig, H. U. *Organic Synthesys Higlights*; VCH Verlagsgesellschaft: Weinheim, 1991; pp 60-61.
4. Barluenga, J.; Aznar, F.; Valdés, C.; Cabal, M. P. *J. Org. Chem.* **1991**, *56*, 6166.
5. Barluenga, J.; Aznar, F.; Valdés, C.; Cabal, M. P. *J. Org. Chem.* **1993**, *58*, 3391. and references cited therein.
6. (a) Barluenga, J.; Aznar, F.; Valdés, C.; Martín, A. García-Granda, S.; Martín, E. *J. Am. Chem. Soc.* **1993**, *115*, 4403. (b) Enders, D.; Meyer, O.; Raabe, G. *Synthesis*, **1992**, 1242. (c) Barluenga, J.; Aznar, F.; Ribas, C.; Valdés, C.; Fernández, M.; Cabal, M. P.; Trujillo, J. *Chem. Eur. J.* **1996**, *2*, 805.
7. (a) Wulff, W. D.; Yang, D. C.; *J. Am. Chem. Soc.* **1983**, *105*, 6726. (b) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642.
8. Barluenga, J.; Aznar, F.; Martín, A.; García-Granda, S.; Salvadó, M. A.; Pertierra, P. *J. Chem. Soc., Chem. Commun.* **1993**, 319.
9. Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653.
10. (a) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pertierra, P. *J. Am. Chem. Soc.* **1996**, *118*, 695. (b) Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaría, A.; Carbajo, R. J.; López-Ortiz, F.; García-Granda, S.; Pertierra, P. *Chem. Eur. J.* **1996**, *2*, 180.
11. Barluenga, J.; Aznar, F.; Martín, A.; Vazquez, J. T.; *J. Am. Chem. Soc.* **1995**, *117*, 9419.
12. Barluenga, J.; Aznar, F.; Martín, A.; Barluenga, S.; García-Granda, S.; Paneque-Quevedo, A. A. *J. Chem. Soc., Chem. Commun.* **1994**, 843.
13. García-Granda, S.; Pérez-Carreño, E; Paneque-Quevedo, A. A.; Martín, A.; Barluenga, S. *Acta .Crys.* **1994**, C50, 1430.
14. Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.

(*Received in UK* 10 *March* 1997; *accepted* 22 *May* 1997)