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Asymmetric Approaches to Cyclopentenones in the Ni(0)-promoted Cyclocarbonylation Reaction of Allyl Halides and Acetylenes

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Abstract: Different approaches to the asymmetric synthesis of cyclopentenones by means of the $Ni(CO)_4$-promoted alkyne-allyl halide cyclization-carbonylation are reported. The use of acetylenic sulfoxides **1** has proved effective for the synthesis of acyclic, fused [5+8], and spiro [5+5], [5+7], and [5+8] cyclopentenones, whereas placement of the aryl sulfoxide on the allylic system failed to afford any cycloadduct. Homochiral fused [5+8], and spiro [5+7] and [5+8] cyclopentenones have been obtained by this methodology. Finally, a modest enantioselectivity was observed when different homochiral α-substituted carboxylates were used as ligands in our reaction system. Copyright © 1996 Elsevier Science Ltd

During recent years we have been working on the synthesis of cyclopentenones by means of the $[Ni(CO)_4]$ induced carbonylative intermolecular cyclization of acetylenes with allyl halides.[1] As a result we have been able to rationalize the different requirements concerning both the acetylene and allyl moieties to effectively control the substitution pattern as well as the regio and stereochemistry of the resulting cyclopentenones. Additionally, by the proper choice of a cyclic allylic system, this methodology has been succesfully applied to the synthesis of versatile fused and spiro cyclopentenones in a single synthetic operation in good yields and total stereocontrol.[2]

The design of an asymmetric version of this process can be envisaged along two different approaches, either by placing a proper chiral auxiliary on the acetylene or the allyl halide moiety, or, alternatively, by using an homochiral ligand as an additive in the reaction mixture (Figure 1).

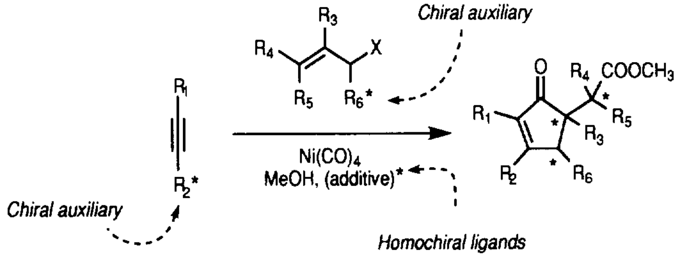


FIGURE 1

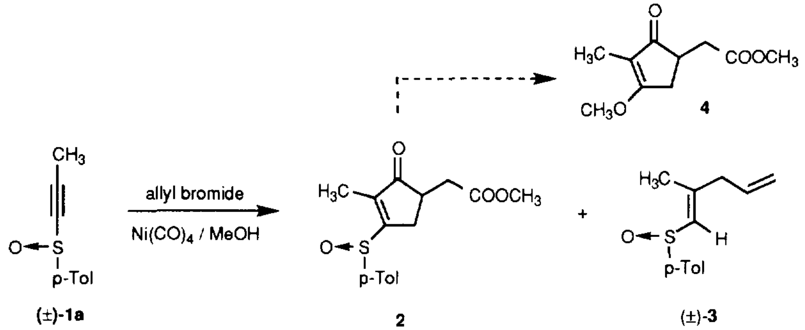
In a search for a suitable chiral auxiliary, to be placed either in the acetylenic or in the allylic moiety, the use of sulfoxides seemed promising and well documented.[3] Moreover, concerning the acetylenic moiety, we assumed, based on our previous results,[4] that the strong polarization liable to be exerted by the sulfoxide moiety on the triple bond might be an important factor not only for the regioselective outcome of the reaction but for the diastereocontrol on the new stereogenic centers arising from the insertion steps involved in the path to the final cycloadducts. On the other side, since, as shown,[5] the presence of electron withdrawing groups on the allylic moiety was compatible with the formation of cycloadducts, we also speculated on the role of a sulfoxide on the allylic system as a chiral inductor in this process. Finally, due to the sensitivity of this reaction to the presence of acetate ions,[2] we also became interested in exploring the compatibility of our reaction system with certain homochiral carboxylates as potential transient ligands in order to obtain some degree of enantioselectivity in this process.

Our preliminary results concerning the use of homochiral acetylenic sulfoxides afforded good results of enantiopure 5+8 fused and spiro cyclopentenones.[6] In this paper, we wish to report a full account of our work in this area.

Acetylenic sulfoxides.

For our initial studies, racemic acetylenic racemic sulfoxides were used. These could be easily prepared by well established methods and were able to give valuable information about the overall reaction yield, compatibility with the reaction conditions, diastereomeric ratio of the resulting cycloadducts and relative configurations of the arising stereogenic centers. The different acetylenic sulfoxides used in this study have been synthesized by standard methods as indicated in the Experimental Section.

In a preliminary experiment, acetylene (±)-**1a** was reacted with allyl bromide in MeOH under standard conditions (see Experimental), to yield cyclopentenone **2** in low yield and modest diastereoselectivity (Scheme 1). In some experiments, compound **4** was also isolated in variable yields.[7] In the presence of KOAc (1 equiv), both the yield and the diastereoselectivity were slightly increased. In all the experiments, the Michael-type adduct **3**, arising from attack of a σ-allylnickel intermediate onto (±)-**1a**, was also isolated.

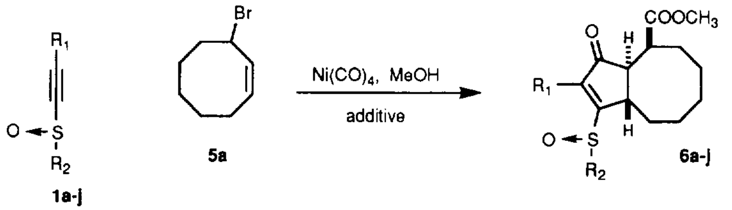


no additive: 17% (60:40) 15%
KOAc, 1 equiv.: 28% (75:25) 15%

SCHEME 1

Fused systems. The above results showed the compatibility of the sulfoxide group with our reaction system and encouraged us to perform the reaction on 3-bromocycloalkene derivatives, for which the corresponding fused bicyclic cyclopentenones had been obtained in consistently higher yields.[8] Thus, cyclocarbonylation of acetylenic sulfoxide (±)-**1a** (1 equiv) with 3-bromocyclooctene (**5a**) (2 equiv) with $Ni(CO)_4$ at room temperature in the presence of KOAc (2 equiv), afforded a separable mixture of diastereomers **6a**, epimeric at sulfur,[6] in acceptable yield (63%) and diastereoselectivity (Table 1, entry 2).

TABLE 1



Entry	Acetylene	R_1	R_2	Additive[a]	Product	dr[b]	yield %
1	(±)-**1a**	CH_3	$(C_6H_4)p\text{-}CH_3$	—	**6a**	82:18	28
2	(±)-**1a**	CH_3	$(C_6H_4)p\text{-}CH_3$	KOAc	**6a**	82:18	63
3	(±)-**1b**	CH_3	$(C_6H_4)p\text{-}NO_2$	—	**6b**	80:20	27
4	(±)-**1c**	CH_3	$(C_6H_4)p\text{-}OCH_3$	—	**6c**	77:23	20
5	(±)-**1d**	CH_3	$(C_6H_4)o\text{-}CH_3$	—	**6d**	80:20	22
6	(±)-**1e**	CH_3	CH_3	KOAc	**6e**	60:40	72
7	(±)-**1f**	CH_3	*t*-Bu	KOAc	**6f**	87:13	30 (c)
8	(±)-**1f**	CH_3	*t*-Bu	Bu_4NOAc (d)	**6f**	100:0 (e)	11
9	(+)-**1g**	*n*-Bu	$(C_6H_4)p\text{-}CH_3$	KOAc	**6g**	82:18	44
10	(±)-**1h**	CH_3OCH_2	$(C_6H_4)p\text{-}CH_3$	KOAc	**6h**	—	—
11	(+)-**1i**	TMS	$(C_6H_4)p\text{-}CH_3$	KOAc	**6i**	—	—
12	(+)-**1j**	H	$(C_6H_4)p\text{-}CH_3$	KOAc	**6j**	—	—

(a) 1 equiv. with respect to the allyl halide; (b) diastereomeric ratio based on ^1H NMR; (c) Compound **7** (44%, single diastereomer) was also isolated (see Scheme 2); (d) acetone-MeOH (5%) as solvent; (e) since the experiment was run at 1 mmol scale, the low yield does not allow to exclude other minor non detectable isomers by ^1HNMR.

The relative configuration of the major diastereomer **6a** was determined by X-ray analysis as (*SR**,3a*R**,4*R**,9a*R**), as shown in Figure 2. This configuration is in agreement with that predicted according to mechanistic considerations.[1]

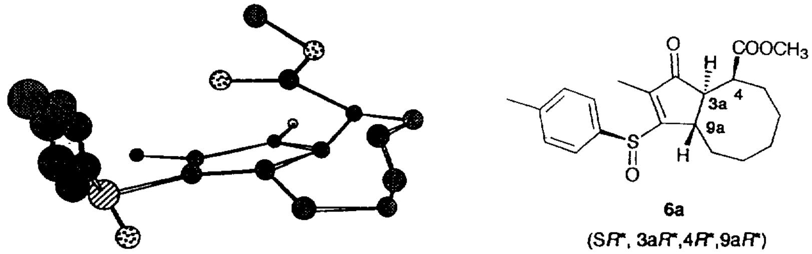
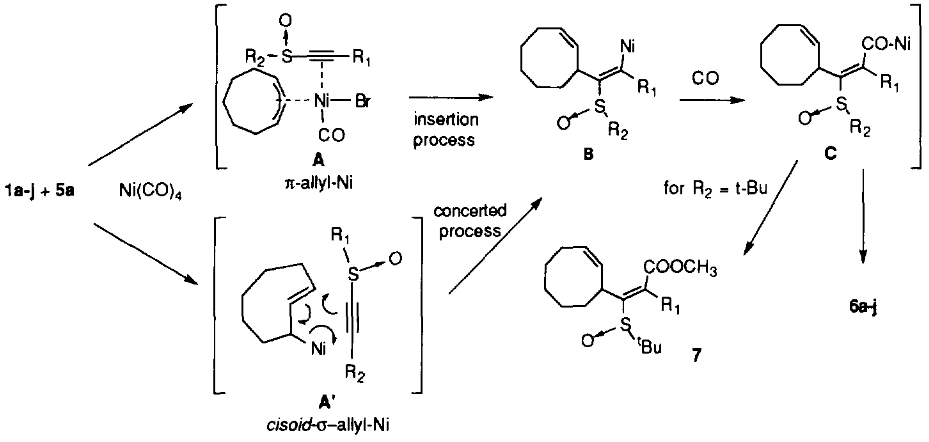


FIGURE 2

Attempts to improve the diastereomeric ratio by modification of the electronic and/or steric properties of the substituent R_2 on the sulfoxide moiety were now undertaken. Thus, replacement of the *p*-tolyl group by either the electron-poor *p*-nitrophenyl or the electron rich *p*-methoxyphenyl groups did not afford relevant improvements in either diastereoselectivity or yield (Table 1, entries 3 and 4). Similar results were achieved from the more sterically crowded *o*-tolyl group (entry 5). No significant variation of the overall yields of cycloadducts **6** was observed, which indicates a negligible role of both the electronic and steric effects of the substituents on the aromatic ring of the phenylsulfinyl moiety on the reaction course. However, steric effects appeared to be important in the reaction of alkylsufinyl derivatives. As it can be observed in Table 1, moving from *p*-tolylsulfoxide (±)-**1a** to the less sterically demanding methylsulfoxide (±)-**1e** caused an increase of the overall yield of cycloadducts **6** at the expense of the diastereomeric ratio (compare entries 2 with 6). On the contrary, the highest diastereoselectivity was found with the bulkier *t*-butylsulfinyl derivative (±)-**1f**, together with a significant drop on the reaction yield (entry 7). Interestingly, formation of the linear adduct **7** in 44% yield was also observed in this reaction. Formation of **7** can be explained by the nucleophilic attack of MeOH to the acylnickel intermediate **C** prior to the olefin insertion leading ultimately to **6f** (Scheme 2).



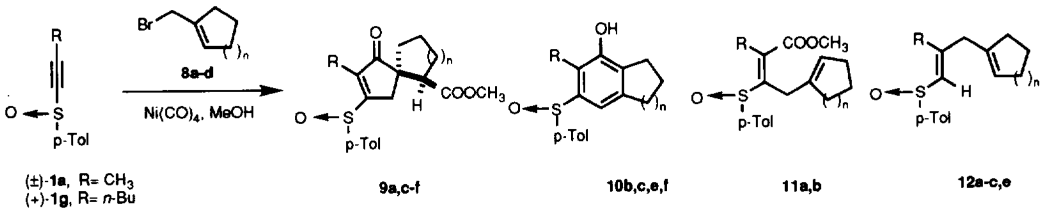
SCHEME 2

This result indicates the importance of the steric effects played by the alkylsulfinyl moiety concerning this last step. Thus, due to the steric restrictions imposed by the bulky *t*-butylsulfinyl substituent for the intramolecular acylnickel insertion on the double bond, solvolysis by MeOH becomes competitive. In order to minimize the formation of linear adduct **7**, a mixture of acetone/MeOH (5% v/v) was used as a solvent.[4] However, although no linear adduct was detected under these conditions, a complex crude mixture was obtained from which the desired cycloadducts **6f** were isolated in low overall yield. (Table 1, entry 8)

In light of these results, we decided to use *p*-tolylsulfoxide as the chiral inducer in our reaction system, due to its favourable combination of good overall reaction yield and high diastereoselectivity. Moreover, *p*-tolylsulfoxides can be obtained in enantiomerically pure form by the standard Andersen reaction [9, 20] in a straightforward way.

Attempts to explore the scope of the reaction, led us to study different alkynyl *p*-tolylsulfoxides as substrates. As it can be seen in Table 1 only acetylenes (±)-**1a** to (+)-**1g** having an alkyl chain on R_1 were tolerated. The presence of a weak electron acceptor methoxymethyl group, ((±)-**1h**), a terminal bulky group,

TABLE 2



Entry	Acetylene	Halide	n	Additive (equiv)^a	Product (%yield) (dr)^b				
1	(±)-**1a**	**8a**	1	—				**12a** (9)	**13** (50)(c)
2	(±)-**1a**	**8a**	1	KOAc (1)	**9a** (15) (60:40)		**11a** (30)	**12a** (10)	
3	(±)-**1a**	**8a**	1	KOAc (0.5)	**9a** (30) (65:35)		**11a** (10)	**12a** (18)	**13**(5)(c)
4	(±)-**1a**	**8b**	2	—		**10b** (43)	**11b** (11)	**12b** (20)	
5	(±)-**1a**	**8b**	2	KOAc (1)			**11b** (56)	**12b** (20)	
6	(±)-**1a**	**8c**	3	—	**9c** (10) (d,e)				
7	(±)-**1a**	**8c**	3	KOAc (1)	**9c** (6) (d,e)	**10c** (22)		**12c** (10)	
8	(+)-**1g**	**8c**	3	KOAc (0.5)	**9d** (17) (d,e)				
9	(±)-**1a**	**8d**	4	—	**9e** (16) (d,e)	**10e** (19)		**12e** (9)	
10	(±)-**1a**	**8d**	4	KOAc (1)			**11e** (43)	**12e** (17)	
11	(±)-**1a**	**8d**	4	KOAc (0.5)	**9e** (31) (d,e)	**10e** (14)		**12e** (17)	
12	(+)-**1g**	**8d**	4	KOAc (0.5)	**9f** (21) (d,e)	**10f** (9)			

(a) Relative to the starting halide; (b) diastereomeric ratio based on ^{1}HNMR; (c) see Scheme 3; (d) single isomer; (e) since the experiment was run at 1 mmol scale, the low yield makes not possible to exclude other minor non detectable isomers by ^{1}HNMR.

such as the trimethylsilyl group ((+)-**1i**) or a terminal acetylene ((+)-**1j**) were not compatible with this process affording in all cases complex intractable mixtures. These results confirm what we had previously observed concerning the sensitivity of this reaction towards the polarization of the acetylene.[4] On the other hand, steric effects on R_1 do not seem to play a decisive role on the reaction outcome, since going from (±)-**1a** (R_1=CH_3) to (+)-**1g** (R_1=Bu) had no effect on the diastereoselectivity while the overall yield on cycloadducts diminished only slightly (Table 1, entries 2 and 9).

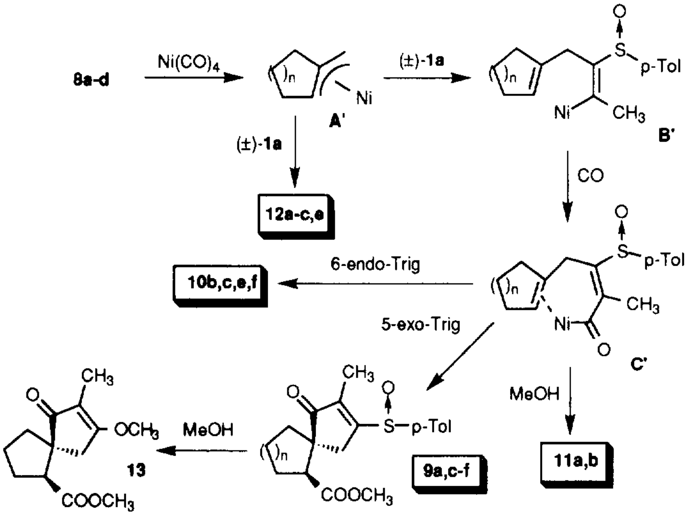
Unlike **5a**, reaction of the acetylenic sulfoxide (±)-**1a** with 3-bromocyclopentene (**5b**), 3-bromocyclohexene (**5c**), and 3-bromocycloheptene (**5d**) under standard conditions, did not afford any of the desired fused [5+5], [5+6] or [5+7] cycloadducts but products arising from acetylene coupling were observed instead. On the contrary, addition of KOAc apparently inhibited insertion of the acetylene on the putative π-allylnickel intermediate **A** (Scheme 2), since the starting acetylene was recovered in high yield. In any case, neither the starting allyl halides nor self-coupling products thereof were detected. These results are in sharp contrast with our previous observations with other alkynes as the acetylenic counterparts of these allylic systems.[2] The different behaviour of acetylenic sulfoxides could be interpreted in light of an alternative mechanism leading to **B** through a cyclic 6-electron 6-center transition state[10] **A'**, as depicted in Scheme 2. Thus, the strong triple bond polarization exerted by the sulfoxide group, might prevent coordination with the

π-allylnickel in **A**, making the cyclic transition state **A'** the operative one when acetylenic sulfoxides are involved. This mechanism would be prevented in cases where a cisoid σ-allylnickel intermediate **A'** were not attainable due to geometrical constraints, as in **5b-d**.

Spiro systems. Based on our previous work,[2] we were interested in the use of acetylenic sulfoxides for the asymmetric synthesis of spiro bicyclic cyclopentenones. A systematic survey of the reaction of sulfoxide (±)-**1a** with halomethylcycloalkenes **8a-d** was carried out, as indicated in Table 2.

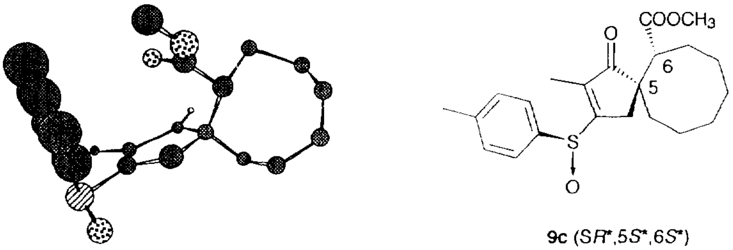
Unlike the preceding systems, product distribution in the spiro series was complicated by the competition of the two alternative 5-*exo-trig* and 6-*endo-trig* cyclization modes to give spiro cyclopentenones **9** and fused cycloadducts **10**, respectively. Moreover, monocyclic adducts **11**, resulting from acetylene insertion on the π-allylnickel intermediate followed by carbonylation and methanolysis, and **12**, arising from a Michael-type reaction between the acetylene and a sigma-alkylnickel species, were also isolated in some cases (Scheme 3).

As expected, the preference for either cyclization mode is conditioned by the steric and conformational restrictions ocurring in the cycloalkenyl moiety. Thus, for the [5+5] series, the nearly planar π-allyl system seems to favour the 5-exo-trig process leading to the spiro adduct **13** in yields up to 50% (Table 2, entry 1, and Scheme 3).[11] However, in the six member ring analogue, a combination of conformational effects and steric interactions divert the process towards the alternative 6-*endo-trig* cyclization mode leading to **10b** as the major cycloadduct (entry 4). In the seven membered allylic system, with a higher degree of conformational freedom, a 5-*exo-trig* cyclization mode to give **9c** is observed, although in low yield (entry 6). Finally, in the highly flexible 8-membered allylic system, both cyclization modes are operative, leading to **9e** and **10e** in nearly equimolar amounts (entry 9). Concerning the diastereoselectivity of the process, only one single spiro cycloadduct was observed by NMR in cyclizations leading to **9c-f**. The relative stereochemistry in this series was assigned from the X-ray analysis of **9c** (Figure 3) and was in agreement with mechanistic considerations based on our previous results.[2]



SCHEME 3

As for the fused series, the effect of KOAc on the reaction course was also tested. Thus, use of equimolar amounts of this salt with respect to the allyl halide in the [5+5] series was detrimental, since methanolysis of acylnickel intermediate **C'** (Scheme 3) prior to insertion was predominant to give **11a** as the major product together with the expected spirocycloadduct, although in modest diastereoselectivity (Table 2, entry 2). This negative effect was even more pronounced in the [5+6] and in the [5+8] series, where no cyclization adducts were found (entries 5 and 10). However, in the [5+7] series, although the postulated beneficial role of KOAc as cyclization promoter in these reactions[2] was observed, the reaction course mainly diverted towards the 6-endo cyclization mode and spirocyclopentenone **9c** was obtained in even lower yields than in the absence of this additive (compare entries 6 and 7).



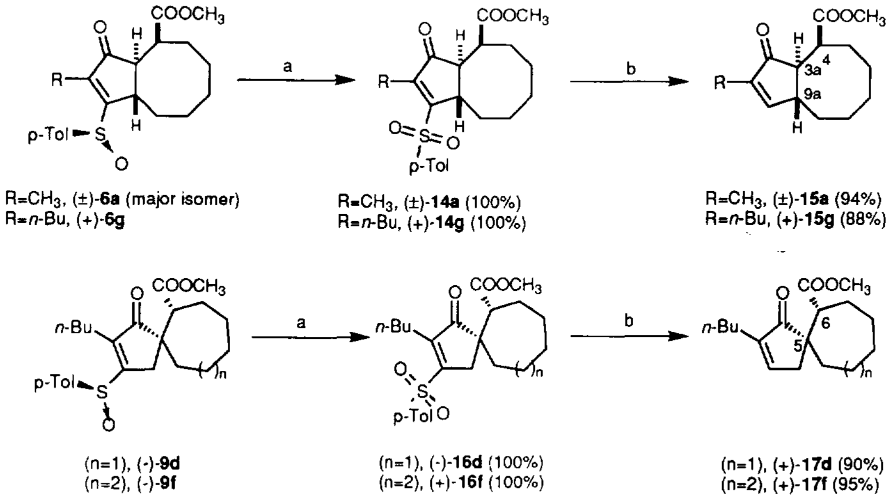
9c (*SR**,5*S**,6*S**)

FIGURE 3

In those cases where KOAc diverted the process towards the non-cyclization adducts in a major (Table 2, entry 2) or exclusive (entry 10) way, additional experiments in which the amount of KOAc was reduced to 0.5 equiv with respect to the starting allyl halide were also carried out. In both cases, a substantial improvement of the yields of the desired spirocycloadducts was observed (entry 3), with no change on the diastereoselectivity. Interestingly, in the [5+8] series, the important formation of uncyclized adduct **11e** could be completely supressed (c.f. entries 10 and 11). Although we still lack a clear model to explain the role of acetate as a ligand, it seems clear that its concentration is essential for the control of the reaction products.

Removal of the chiral auxiliary. The synthetic applicability of this methodology for the construction of homochiral cyclopentenones relies on the clean and selective removal of the vinyl sulfoxide moiety used as chiral auxiliary. Despite the well precedented examples in the literature dealing with the reductive cleavage of alkyl sulfoxides,[12] to our knowledge no examples of reduction of vinyl sulfoxides have been reported. Initial attempts carried out by treatment of (±)-**6a** with Al-Hg, under the classical conditions described for alkyl sulfoxides,[12] were unsuccessful since a complex mixture of products was obtained. We then turned our attention to the oxidation of the sulfoxide followed by reductive cleavage of the resulting vinyl sulfone, a well known process.[13-17] Thus, as depicted in Scheme 4 oxidation of (±)-**6a** with MCPBA, followed by reductive cleavage of the intermediate sulfone (±)-**14a** (Al-Hg)[14] afforded the fused [5+8] cyclopentenone (±)-**15a** in 94% overall yield.

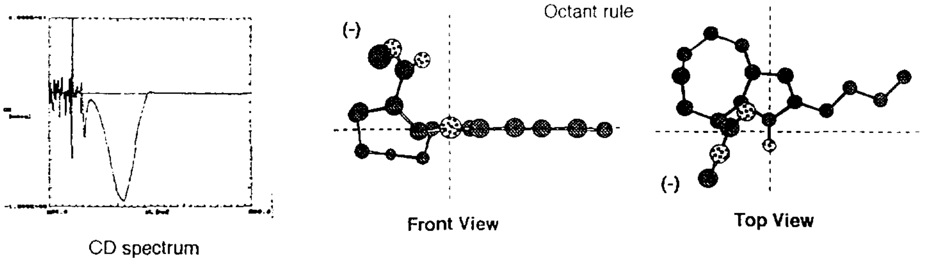
Enantioselective synthesis of cyclopentenones. The use of a homochiral acetylenic sulfoxide would enable us to confirm the required integrity of the chiral sulfur atom throughout the process. Thus, starting from acetylenic sulfoxide (*S*)-(+)-**1g**, fused ((+)-**6g**, major isomer), and spiro cyclopentenones (-)-**9d** and (-)-**9f** were obtained in 36%, 17% and 21 % isolated yields, respectively (Scheme 4). Removal of the auxiliary sulfoxide as indicated above afforded the corresponding homochiral cyclopentenones (+)-**15g**, (+)-**17d** and (+)-**17f** in high yields (88-95%).



a: MCPBA, CH_2Cl_2, rt; b: Al-Hg, THF-H_2O (10%), rfx.

SCHEME 4

Compound (+)-**15g** was analyzed by ^{1}HNMR in the presence of the chiral lanthanide shift reagent Eu(hfc)$_3$ and showed only one set of signals in comparison with (±)-**15g**, (Table 3, entry 1) which confirms the stereogenic integrity of the sulfoxide moiety in the Ni(0) promoted process. Based on the negative Cotton effect observed for (+)-**15g** in the CD spectrum, its absolute configuration could be deduced by application of the octant rule to the MMX minimized structure[18] (Figure 4), and was in agreement with that inferred from the X-ray analysis of (±)-**6a** (see above). Following an analogous procedure, the absolute configuration of spiro cyclopentenones (+)-**17d** and (+)-**17f** could be established.



CD spectrum

Front View

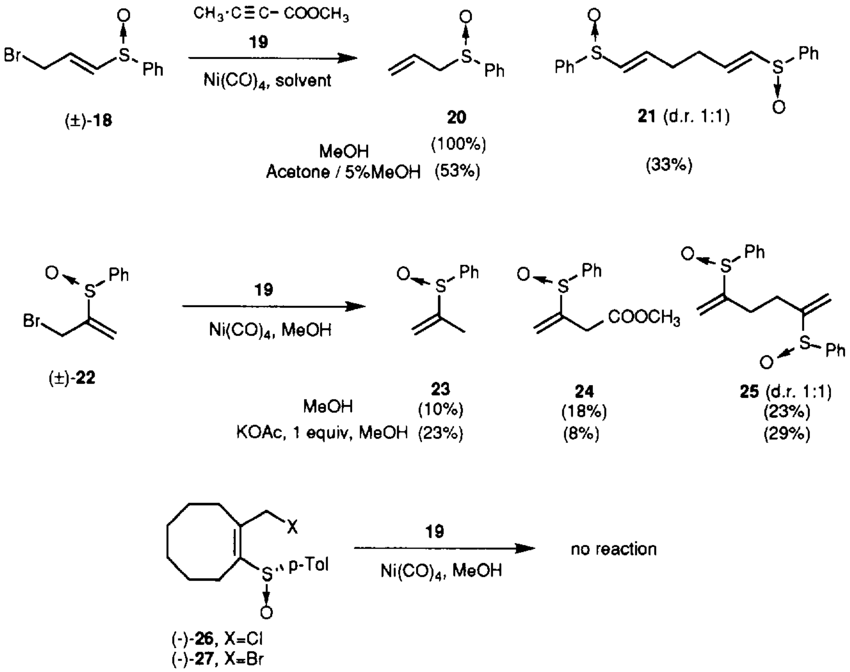
Top View

FIGURE 4

Sulfoxide on the allyl moiety

As a logical extension of this work, placement of the sulfoxide auxiliary on the π-allyl moiety was considered. Preliminary studies were carried out from racemic allyl derivatives in which the sulfoxide moiety was placed at the central ((±)-**22**, Scheme 5) or terminal carbon atoms ((±)-**18**, (-)-**26**, (-)-**27**) of the allylic system, respectively. They were synthesized in acceptable yields by a combination of standard procedures, as described in the Experimental Part.

Despite our previous studies on the effect of electron withdrawing groups at the central position of the allyl moiety,[5] no cycloadducts could be isolated from the reaction of (±)-**18** and (±)-**22** with methyl butynoate (**19**) under standard conditions. As indicated in Scheme 5, only products arising from allyl self-coupling (**21** and **25**), carbonylation (**24**) or solvolysis (**20** and **23**) were observed. Similar results and product distribution were obtained in the presence of acetate ions. Discouraging results were also obtained from allylic derivatives (-)-**26** and (-)-**27**. As above, no insertion products were detected and, in the case of (±)-**18**, the allylic sulfoxide **20** arising from protonation of the allylnickel intermediate was formed quantitatively in MeOH. Although solvolysis of the π-allyl intermediate was hampered by using a mixture of acetone/MeOH (5%) as solvent, extensive self-coupling of the allyl derivative to give **21** resulted in this case. Finally, no reaction was observed from the cyclic analogues (-)-**26** and (-)-**27**, even under the presence of KOAc as additive. These negative results indicated a higher sensitivity of the metal system towards the sulfoxide function in comparison to that observed when the sulfoxide was in the acetylenic counterpart.



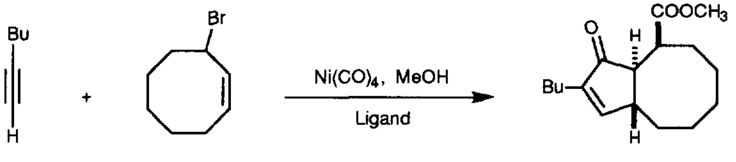
SCHEME 5

Homochiral carboxylates

The use of homochiral ligands in enantioselective processes mediated by organometallic compounds is an active field of research.[19] In this and previous studies[1] we have shown that acetate ions can be decisive for the control of the products arising from this cycloaddition process. Whatever its exact role may be, we can assume that coordination of acetate with the metal in one or more of the steps leading to the final cycloadducts is taking place. With these considerations in mind, we were interested in the study of homochiral carboxylates as potential ligands for the enantioselective synthesis of cyclopentenones.

Several inexpensive commercially available homochiral carboxylates were used in the reaction of 3-bromocyclooctene (**2a**) with alkyne **28** (Table 3). As a general trend, the change of acetate by α-hydroxy substituted carboxylates led to a significant drop in the yields of isolated fused cyclopentenone derivatives. The presence of α-amino (sodium L-alaninate), α-acetamido (sodium *N*-acetil-L-alaninate) or α-mercapto (sodium α-mercaptopropionate) groups with respect to the carboxylate moiety inhibited the process, since only traces of the corresponding cycloadduct were detected. However low, the ee obtained (below 8%) , shows that coordination of the carboxylate on the metal center is taking place in the course of the cycloaddition process.

TABLE 3



28 **5a** **15g**

Entry	Ligand	Product (% yield)	ee: (a)
1	KOAc	(±)-**15g** (80)	--
2	Na *L*-lactate	(-)-**15g** (46)	4 (A/B)
3	Na *L*-mandelate	(+)-**15g** (62)	8 (B)
4	Na (*R*)-O-acetyl mandelate	**15g** (49)	<1 (B)
5	K *L*-tartrate	**15g** (58)	<1 (A/B)

(a) Method of determination: A, polarimetry; B, ^{1}H-NMR in the presence of Eu(hfc)$_3$.

Conclusions. We report in this paper different approaches to an asymmetric version of the Ni(CO)$_4$-induced alkyne-allyl halide cyclization-carbonylation. Fused and spiro cyclopentenones have been obtained in moderate to good yields by means of acetylenic sulfoxides as auxiliaries. Among them, the *p*-tolylsulfoxide group has proved to be a suitable auxiliary for the effective diastereocontrol of the cyclization. Interestingly, the resulting cycloadducts, diastereomeric on the sulfur atom, can be separated by flash chromatography and the sulfoxide group removed by cleavage at the end of the process. Starting from homochiral acetylenic sulfoxides, this sequence allows the formation of homochiral fused and spirocyclopentenones, since chirality on the sulfur atom is preserved throughout the reaction sequence. On the contrary, placement of the sulfoxide moiety on the allylic system proved detrimental to our reaction system since no cycloaddutcs could be isolated from the reaction mixtures. Finally, although homochiral α-hydroxy carboxylates can be used as ligands in this process, the ee of the resulting cycloadducts was low.

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EXPERIMENTAL

CAUTION! $Ni(CO)_4$ is an extremely harmful chemical and special precautions have to be taken when it is used.

Elemental analyses were determined on Carlo Erba models 1107 and 1500. IR spectra were recorded on a Bomem MB-120 with Fourier transform instrument and are reported in cm^{-1}. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solutions (unless otherwise indicated) on a Varian Gemini 200 and a Varian Unity 300 spectrometers, operating at 200 and 300 MHz for ^1H and 50 and 75 MHz for ^{13}C, respectively. The chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from Me_4Si, or in ppm relative to the singlet at 7.26 ppm of $CDCl_3$ for ^1H and in ppm relative to the centre line of a triplet at 77.0 ppm of $CDCl_3$ for ^{13}C. Optical rotations were measured on a Perkin Elmer 141 polarimeter. The MS (EI) and MS (CI) spectra (70 eV) were obtained using a Hewlett-Packard 5989A mass spectrometer. High resolution MS (EI) spectra (70 eV) were obtained on a Auto Spec-Q instrument. Circular dichroism (CD) were recorded on Spectropolarimeter JASCO-720. Commercial analytical-grade reagents were obtained from commercial suppliers (Aldrich Chemie, Fluka Chemie, Janssen Chimica) and were used directly without further purification. Solvents were distilled prior to use and dried by standard methods.

•Starting materials.

Compounds (+)-**1g**,[20] **1j**,[20] **5a-d**,[2] **8a-d**[2] and (±)-**22**[21] have been described and fully characterised previously.

(±)-1-Propynyl sulfoxides (1a-1f): Starting from corresponding thiols or disulphides by reaction[22,23] with propargyl bromide, to give 1-propynyl sulfides followed by oxidation.[22,24,25] **(±)-1-Propynyl *p*-tolyl sulfoxide (1a)**: 70 % yield. R_f 0,37 (silica gel, hexane / ^{t}BuOMe 1:1). IR (film): 2920, 2192 (st C≡C), 1608, 1483, 1091, 819, 572 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.07 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 7.32 (d, 2H, J=8.2 Hz, H_{Ar}), 7.67 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 4.9 (CH_3), 21.4 (CH_3), 77.5 (C≡), 103.8 (C≡), 125.0 ($C_{Ar}H$), 130.1 ($C_{Ar}H$), 141.1 (C_{Ar}), 142.2 (C_{Ar}). **(±)-*p*-Nitrophenyl 1-propynyl sulfoxide (1b)**: 55 % yield. R_f 0.16 (silica , hexane / ^{t}BuOMe 8:2). IR (film): 3099, 2187 (st C≡C), 1601, 1583, 1525, 1470, 1348, 1089, 1053, 1006, 852, 744, 719, 680 cm^{-1}.^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.10 (s, 3H, CH_3), 7.93 (d, 2H, J=9 Hz, H_{Ar}), 8.38 (d, 2H, J=9 Hz, H_{Ar}).^{13}C-NMR (50 MHz, $CDCl_3$): δ 5.1 (CH_3), 76.6 (C≡), 103.8 (C≡), 124.6 ($C_{Ar}H$), 125.6 ($C_{Ar}H$), 149.6 (C_{Ar}), 151.0 (C_{Ar}). **(±)-*p*-Methoxyphenyl 1-propynyl sulfoxide (1c)**: 69 % yield. Rf 0.36 (silica gel , hexane / EtOAc 95:5). MS (EI) m/z 195 (M^+, 100), 178 (M-16). IR (film): 1585, 1525, 1340, 1087, 852. cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.15 (s, 3H, CH_3), 7.50 (d, 2H, J=9 Hz, H_{Ar}), 8.15 (d, 2H, J=9 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 5.2 (CH_3), 61.3 (C≡), 98.4 (C≡), 122.7 (C_{Ar}), 124.0 ($C_{Ar}H$), 125.2 ($C_{Ar}H$), 126.3 (C_{Ar}). **(±)-*o*-Tolyl 1-propynyl sulfoxide (1d)**: 50 % yield. R_f 0.27 (silica gel, hexane / EtOAc 8:2). MS (CI,) m/z 207 (M+29), 191 (M+29-16), 180 (M^++1), 163 (M^+-16, 100). IR (film): 3058, 2972, 2916, 2189 (st C≡C), 1593, 1512, 1471, 1454, 1434, 1382, 1325, 1274, 1199, 1161, 1132, 1076, 1035, 798, 757, 730, 707, 576, 555, 509, 503 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ. 2.03 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 7.19-7.25 (m, 1H, J=3.8 Hz, H_{Ar}), 7.37-7.42 (m, 2H, H_{Ar}), 7.90-7.97 (m, 1H, J=7.6 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 4.9 (CH_3), 18.1 (CH_3), 76.4 (C≡), 101.3 (C≡), 124.2 (C_{Ar}), 127.1 (C_{Ar}), 131.1 (C_{Ar}), 131.2 ($C_{Ar}H$), 135.2 (C_{Ar}), 141.8 ($C_{Ar}H$). **(±)-Methyl 1-propynyl sulfoxide (1e)**: 60 % yield. R_f 0.14 (silica gel , hexane / EtOAc 1:1). IR (film): 3058, 2972, 2916, 2189 (st C≡C), 1593, 1512, 1471, 1454, 1434, 1382, 1325, 1274, 1199, 1161, 1132, 1076, 1035, 798, 757, 730, 707, 576, 555, 509, 503 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.06 (s, 3H, CH_3), 2.90 (s, 3H, CH_3).^{13}C-NMR (50 MHz, $CDCl_3$): δ 3.8 (CH_3), 46.4 (CH_3), 76.4 (C≡), 91.7 (C≡). **(±)-tert-Butyl 1-propynyl sulfoxide (1f)**: 55 % yield. R_f 0.19 (silica gel , hexane / ^{t}BuOMe 1:1). IR (film): 2966, 2925 , 2904, 2867, 2191 (st C≡C), 1473, 1458, 1389, 1363, 1176, 1056, 1031, 572 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.32 (s, 9H, CH_3), 2.08 (s, 3H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 4.9 (CH_3), 22.8 (CH_3), 57.8 (C), 74.6 (C≡), 101.7 (C≡).

(±)-Methoxymethyl *p*-tolyl sulfoxide (1h): [26]A solution of propargyl alcohol (3.5 mmol) and 10 ml of THF was cooled to -30°C. *n*-BuLi (7.5 mmol) was added dropwise and the reaction was stirred for 30 min. A premixed solution (1h, room temp.) of bis-*p*-tolyl disulfide (3.6 mmol) and methyl iodide (11.4 mmol) in THF was then added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 1 hour. Aqueous work-up followed by SiO_2 flash chromatography (hexane / EtOAc 95:5) afforded 3-methoxypropynyl *p*-tolyl sulfide (79 % yield). Oxidation of the sulfide as described for (±)-**1a-1f** afforded (±)-**1h** (78 % yield) Rf 0.28 (silica gel , hexane /EtOAc 7:3). IR (film): 2939, 2823, 2177 (st C≡C), 1651, 1593, 1564, 1545, 1495, 1458, 1358, 1186, 1101, 1058, 1014, 1002.985, 902, 810, 617 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.41 (s, 3H, CH_3), 3.35 (s, 3H, CH_3O), 4.26 (s, 2H, CH_2), 7.33 (d, 2H, J=7.8 Hz, H_{Ar}), 7.30 (d, 2H, J=7.8 Hz, H_{Ar}).^{13}C-NMR (50 MHz, $CDCl_3$): δ 21.5 (CH_3), 58.1 (CH_3), 59.9 (CH_2), 84.4 (C≡), 99.0 (C≡), 125.1 ($C_{Ar}H$), 130.2 ($C_{Ar}H$), 140.4 (C), 142.6 (C).

(+)-(*R*)-*p*-Tolyl trimethylsilylethynyl sulfoxide (1i):[20](Trimethylsilyl)acetylene (7.8 mmol) was added to an ice-cooled solution of EtMgBr (9.76 mmol) in toluene, and the mixture was heated at reflux for 1h under nitrogen. To the ice-cooled solution a solution of *l*-menthyl-(-)-(*S*)-*p*-toluensulfinate[30] (8.0 mmol) in toluene was added dropwise, and the reaction mixture was stirred at 0°C. After 1h, the reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with ether / EtOAc / CH_2Cl_2 2:2:1 mixture. Silica gel flash cromatography (hexane/^{t}BuOMe 3:1) afforded **1i** (80 % yield). $[\alpha]^{22}_D$ +102.2 (c 0.43, $CHCl_3$). Anal. Calcd. for $C_{12}O_{16}OSSi$: C, 60.96 %; H, 6.82 %; S, 13.56%, found: C, 60.99 %; H, 6.89 %; S, 13.45 %. R_f 0.27 (silica gel, hexane / ^{t}BuOMe 3:1). IR (film): 2294, 2962, 1492, 1253, 1093, 1064, 854 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.22 (s, 9H, CH_3Si), 2.43 (s, 3H, CH_3), 7.34 (d, 2H, J=8.4 Hz, H_{Ar}), 7.69 (d, 2H, J=8.4 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ -0.9 (CH_3), 21.4 (CH_3), 90.1 (C≡), 100.1 (C≡), 125.3 ($C_{Ar}H$), 130.1 ($C_{Ar}H$), 140.4 (C_{Ar}), 142.4 ($C_{Ar}H$).

(±)-(*E*)-(3-bromo-prop-1-enyl-1-sulfinyl)-benzene (18): A solution of bromine (2.4 mmol) in CH_2Cl_2 (10 ml) was added dropwise to an ice-cooled solution of (±)-allyl phenyl sulfoxide (2.4 mmol) in CH_2Cl_2 (10 ml). After stirring at 5º for 30 min., the reaction mixture was treated with 10ml of a sat. Na_2SO_3 solution. The organic phase was dried over anh. $MgSO_4$ and the solvent removed to give 2,3-dibromopropyl phenyl sulfoxide (mixture of diastereomers) in 43% yield after flash-chromatography (hexane/EtOAc 3:1). A solution of the above mixture (2 mmol) in CH_2Cl_2 (10 ml) was treated with K_2CO_3 (3 mmol) and 18-crown-6 (5%). After stirring for 72 h. at room temperature, the solids were filtered and the solvent evaporated. The resulting residue was purified by flash-chromatography (hexane/EtOAc 6:4) to give (±)-**18** in 76% yield. R_f 0.40 (silica gel, hexane / EtOAc 6:4). IR (film): 3055, 2956, 1442, 1083, 1045, 748, 688 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 4.01 (d, 2H, J=6.8 Hz, CH_2), 6.47 (d, 1H, J=14.8 Hz, =CH), 6.56-6.78 (m, 1H, =CH), 7.46-7.55 (m, 6H, H_{Ar}), 7.55-7.65 (m, 4H, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 28.5 (CH_2), 124.6 (CH), 129.5 (CH), 131.4 (CH), 132.5 (CH), 138.9 (CH), 143.1 (C).

(-)-(*R*)-1-Chloromethyl-2-*p*-tolylsulfinyl-cyclooctene (26): Similarly prepared as described for (-)-(*R*)-1-chloromethyl--2-*p*-tolylsulfinyl-cyclohexene.[27] $[\alpha]^{22}_D$ -99.8 (c 1.52, $CHCl_3$). R_f 0.46 (silica gel, hexane / EtOAc 7:3). **IR** (film): 2925, 2854, 1448, 1080, 1045, 808 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.8–2.6 (m, 12, CH_2), 2.37 (s, 3H, CH_3), 2.2-2.6 (m, 3H), 4.31 (d, 1H, J=11 Hz), 4.97 (d, 1H, J=11 Hz), 7.26 (d, 2H, J=8.2 Hz, H_{Ar}), 7.52 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 21.2 (CH_3), 23.1 (CH_2), 25.7 (CH_2), 26.4 (CH_2), 28.7 (CH_2), 30.7 (CH_2), 31.4 (CH_2), 42.8 (CH_2), 124.3 (CH), 129.6 (CH), 138.8 (C), 140.7 (C), 143.5 (C), 145.8 (C).

(-)-(*R*)-1-Bromomethyl-2-*p*-tolylsulfinyl-cyclooctene (27): Similarly prepared as described for (-)-(*R*)-1-chloromethyl--2-*p*-tolylsulfinyl-cyclohexene.[27] R_f 0.50 (silica gel, hexane / EtOAc 7:3). IR (film): 2925, 2854, 1446, 1080, 1045, 808 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.8–2.6 (m, 12, CH_2), 2.37 (s, 3H, CH_3), 4.32 (d, 1H, J=11 Hz), 4.96 (d, 1H, J=11 Hz), 7.26 (d, 2H, J=8 Hz, H_{Ar}), 7.52 (d, 2H, J=8 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 21.2 (CH_3), 23.1 (CH_2), 25.6 (CH_2), 26.4 (CH_2), 28.7 (CH_2), 30.7 (CH_2), 31.4 (CH_2), 42.8 (CH_2), 124.3 (CH), 129.6 (CH), 138.7 (C), 140.7 (C), 143.6 (C), 145.8 (C).

•General Procedure for the Nickel-Promoted Reaction.

The mixture of allyl halide (2eq) and the acetylene (1eq) was added to a mixture of $Ni(CO)_4$ (2eq) in methanol (15 mL). In some cases (see Tables 1-3), a solution of a ligand (0.5-1 eq with respect to the allyl halide) in methanol was introduced in the reaction flask prior to the addition of $Ni(CO)_4$. The reaction mixture was stirred for 6-12 h in a thermostatized flask at (30-35°C) under an inert atmosphere closed by a Hg valve. After this time, the solution was heated at 40 °C for 1h while an inert gas (Ar) was passed through the flask to remove most of the solvent and any unreacted $Ni(CO)_4$, which was condensed and oxidised in a cold trap containing iodine connected at the outlet of the reaction flask. The remaining solvent was evaporated under vacuum, and the residue was washed (NH_4Cl saturated solution), extracted with CH_2Cl_2 and flash chromatographed to afford the products.

[3-Methyl-2-oxo-4-(*p*-tolylsulfinyl)-cyclopent-3-enyl] acetic acid methyl ester (2). Obtained from (±)-**1a** and allyl bromide. **Major diastereomer:** R_f0.38 (silica gel, hexane / EtOAc 1:1). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.04 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.60-3.10 (m, 5H), 3.54 (s, 3H, CH_3O), 7.31 (d, 2H, J=8.2 Hz, H_{Ar}), 7.48 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 9.1 (CH_3), 14.0 (CH_3), 27.7 (CH_2), 34.2 (CH_2), 41.2 (CH), 51.6 (OCH_3), 123.9 ($C_{Ar}H$), 130.1 ($C_{Ar}H$), 141.0 (C), 142.0 (C), 169.6 (C), 171.6, (C), 206.9 (CO). **Minor diastereomer:** R_f 0.31 (silica gel, hexane / EtOAc 1:1). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.06 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.60-3.10 (m, 5H), 3.64 (s, 3H, CH_3O), 7.31 (d, 2H, J=8.2 Hz, H_{Ar}), 7.48 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 9.1 (CH_3), 14.0 (CH_3), 28.2 (CH_2), 34.5 (CH_2), 41.3 (CH), 51.7 (OCH_3), 124.1 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 141.0 (C), 142.1 (C), 168.7 (C), 171.3, (C), 206.8 (CO).

(±)-(*E*)-2-Methyl-1,4-pentadienyl *p*-tolyl sulfoxide (3): R_f 0.44 (silica gel, hexane / EtOAc 1:1). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.13 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.85 (d, 2H, J=7 Hz, CH_2), 5.01-5.14 (m, 2H), 5.60-5.81 (m, 1H), 6.03-6.07 (m, 1H), 7.29 (d, 2H, J=8.4 Hz, H_{Ar}), 7.48 (d, 2H, J=8.4 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 18.7 (CH_3), 21.4 (CH_3), 43.3 (CH_2), 118.4 (CH_2), 124.0 (C-H), 129.9 (CH), 132.7 (CH), 133.0 (CH), 133.2 (CH), 140.8 (C), 141.6 (C), 150.0 (C).

(±)-(3-Methyl-4-methoxy-2-oxo-cyclopent-3-enyl)acetic acid methyl esther (4): R_f 0.35 (silica gel, hexane / EtOAc 1:1). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.56 (s, 3H, CH_3), 2.10-3.00 (m, 3H), 3.63 (s, 3H, CH$_3$O), 3.90 (s, 3H, CH$_3$O). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 6.0 (CH$_3$), 31.7 (CH$_2$), 35.4 (CH$_2$), 40.9 (CH), 51.8 (OCH$_3$), 56.7 (OCH$_3$), 172.8 (C), 183.5 (C), 205.2 (C), 213.6 (CO).

2-Methyl-3-oxo-1-(*p*-tolylsulfinyl)-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopentacycloocten-4-carboxylic acid methyl ester (6a). See Table 1. **Major diastereomer** (S*R**,3a*R**,4*R**,9a*R**): Anal. Calcd. for $C_{21}H_{26}O_4S$: C, 67.35%; H, 7.00%; S, 8.56%. Found: C, 67.40%; H, 7.10%; S, 8.43%. R$_f$0.23 (silica gel, hexane / EtOAc 7:3). IR (film): 3020, 2923, 2854, 1728 (st C=O), 1710 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.19-2.00 (m, 9H), 1.98 (d, 3H, J=2 Hz), 2.25-2.60(m, 2H), 2.38 (s, 3H, CH$_3$), 2.87-3.02 (m, 1H), 3.16-3.27 (m, 1H), 3.38 (s, 3H, CH$_3$O), 7.29 (d, 2H, J=8.2 Hz, H$_{Ar}$), 7.50 (d, 2H, J=8.2 Hz, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 9.2 (CH$_3$), 21.4 (CH$_3$), 24.1 (CH$_2$), 24.5 (CH$_2$), 26.2 (CH$_2$), 26.4 (CH$_2$), 33.4 (CH$_2$), 43.1 (CH), 44.6 (CH), 51.5 (OCH$_3$), 52.0 (CH), 124.9 (C$_{Ar}$H), 129.9 (C$_{Ar}$H), 138.1 (C), 141.5 (C), 143.8(C), 169.2 (C), 173.5 (COO), 207.3 (CO). **Minor diastereomer** (S*R**,3a*S**,4*S**,9a*S**): R$_f$ 0.26 (silica gel, hexane / EtOAc 7:3). IR (film): 3020, 2923, 2854, 1728 (st C=O), 1710 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.15-2.00 (m, 9H), 2.07 (d, 3H, J=2 Hz), 2.25-2.60(m, 2H), 2.38 (s, 3H, CH$_3$), 2.87-3.02 (m, 1H), 3.16-3.27 (m, 1H), 3.47 (s, 3H, CH$_3$O), 7.29 (d, 2H, J=8.2 Hz, H$_{Ar}$), 7.50 (d, 2H, J=8.2 Hz, H$_{Ar}$).

2-Methyl-1-(4-nitrophenylsulfinyl)-3-oxo-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopentacyclo-octen-4-carboxylic acid methyl ester (6b). See Table 1. **Major diastereomer** (S*R**,3a*R**,4*R**,9a*R**): MS (EI) m/z 405 (M), 388 (M-17), 373 (M-32), 356 (M-49), 328 (M-77,100). R$_f$ 0.36 (silica gel, hexane / EtOAc 7:3). IR (film):3097, 2945, 2923, 1718 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.00-2.00 (m, 9H), 2.14 (d, 3H, J=2.2 Hz, CH$_3$), 2.33-2.46 (m, 2H), 2.72-2.86 (m, 1H), 3.18-3.28 (m, 1H), 3.46 (s, 3H, CH$_3$O), 7.80 (d, 2H, J=9 Hz, H$_{Ar}$), 8.36 (d, 2H, J=9 Hz, H$_{Ar}$).^{13}C-NMR (50 MHz, CDCl$_3$): δ 9.6 (CH$_3$), 23.6 (CH$_2$), 24.5 (CH$_2$), 26.0 (CH$_2$), 26.1 (CH$_2$), 33.2 (CH$_2$), 43.3 (CH), 44.7 (CH), 51.8 (OCH$_3$), 51.9 (CH), 124.2 (C$_{Ar}$H), 126.0 (C$_{Ar}$H), 146.2 (C), 148.7 (C), 149.4 (C), 166.3 (C), 173.9 (COO), 206.9 (CO). **Minor diastereomer** (S*R**,3a*S**,4*S**,9a*S**): R$_f$0.36 (silica gel, hexane / EtOAc 7:3). IR (film):3097, 2945, 2923, 1718 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.00-2.00 (m, 9H), 2.13 (d, 3H, J=2,2 Hz, CH$_3$), 2.33-2.46 (m, 2H), 2.72-2.86 (m, 1H), 3.18-3.28 (m, 1H), 3.54 (s, 3H, CH$_3$O), 7.78 (d, 2H, J=9 Hz, H$_{Ar}$), 8.35 (d, 2H, J=9 Hz, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 9.7 (CH$_3$), 23.4 (CH$_2$), 24.5 (CH$_2$), 25.9 (CH$_2$), 26.0 (CH$_2$), 33.8 (CH$_2$), 42.6 (CH), 44.7 (CH), 51.9 (OCH$_3$), 52.0 (CH), 124.5 (C$_{Ar}$H), 125.4 (C$_{Ar}$H), 143.3 (C), 149.3 (C), 150.8 (C), 170.1 (C), 173.8 (COO), 206.9 (CO).

2-Methyl-1-(4-methoxy-phenylsulfinyl)-3-oxo-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopenta-cyclocten-4-carboxylic acid methyl ester (6c). See Table 1. **Major diastereomer** (S*R**,3a*R**,4*R**,9a*R**): MS (EI) m/z 374 (M-16), 358 (M-32), 345 (M-49), 325 (M-65, 100), 297. R$_f$ 0.21 (silica gel, hexane / EtOAc 7:3). IR (film): 2923, 2854, 1728 (st C=O), 1710 (st C=O) cm^{-1}.^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.15-2.00 (m, 9H), 1.94 (d, 3H, J=2 Hz), 2.25-2.60(m, 2H), 2.95-3.08 (m, 1H), 3.18-3.29 (m, 1H), 3.41 (s, 3H, CH$_3$O), 3.83 (s, 3H, CH$_3$O), 7.00 (d, 2H, J=8.2 Hz, H$_{Ar}$), 7.57 (d, 2H, J=8.2 Hz, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 9.2 (CH$_3$), 24.1 (CH$_3$), 24.5 (CH$_2$), 26.2 (CH$_2$), 26.5 (CH$_2$), 33.5 (CH$_2$), 43.1 (CH), 44.6 (CH), 51.5 (OCH$_3$), 52.6 (CH), 55.5 (CH$_3$), 144.8 (C$_{Ar}$H), 127.0 (C$_{Ar}$H), 132.5 (C), 143.2 (C), 161.7(C), 169.8 (C), 173.5 (COO), 207.3 (CO). **Minor diastereomer** (S*R**,3a*S**,4*S**,9a*S**): R$_f$ 0.21 (silica gel, hexane / EtOAc 7:3). IR (film): 2923, 2854, 1728 (st C=O), 1710 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.15-2.00 (m, 9H), 1.88 (d, 3H, J=2 Hz), 2.25-2.60(m, 2H), 2.95-3.08 (m, 1H), 3.18-3.29 (m, 1H), 3.50 (s, 3H, CH$_3$O), 3.83 (s, 3H, CH$_3$O), 7.00 (d, 2H, J=9 Hz, H$_{Ar}$), 7.57 (d, 2H, J=9 Hz, H$_{Ar}$).

2-Methyl-3-oxo-1-(*o*-tolylsulfinyl)-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopentacycloocten-4-carboxylic acid methyl ester (6d). See Table 1. **Major diastereomer (SR^*,3aR^*,4R^*,9aR^*)**: MS (EI) m/z 374 (M), 357 (M-17), 342 (M-32), 325 (M-49), 297 (100). R$_f$ 0.37 (silica gel, hexane / EtOAc 7:3). IR (film): 2923, 2852, 1726 (st C=O), 1712 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ.1.15-2.00 (m, 9H), 2.08 (d, 3H, J=1.8 Hz), 2.22 (s, 3H, CH$_3$), 2.37-2.41 (m, 1H, CH), 2.46-2.64 (m, 2H, CH), 3.16-3.23 (m, 1H, CH), 3.41 (s, 3H, CH$_3$O), 7.21 (d, 1H, J=7.2 Hz, H$_{Ar}$), 7.36-7.50 (m, 2H, H$_{Ar}$), 8.04 (dd, 1H, J=7.2 Hz, J′=1.5, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 9.3 (CH$_3$), 18.1 (CH$_3$), 24.0 (CH$_3$), 24.4 (CH$_2$), 26.2 (CH$_2$), 26.3 (CH$_2$), 33.4 (CH$_2$), 43.4 (CH), 44.5 (CH), 51.5 (OCH$_3$), 52.2 (CH), 124.9 (C$_{Ar}$H), 126.6 (C$_{Ar}$H), 130.8 (C$_{Ar}$H), 130.9 (C$_{Ar}$H), 135.8 (C), 138.3 (C), 144.6 (C), 166.1 (C), 173.5 (COO), 207.6 (CO). **Minor diastereomer (SR^*,3aS^*,4S^*,9aS^*)**. R$_f$ 0.32 (silica gel, hexane / EtOAc 7:3). IR (film): 2923, 2852, 1726 (st C=O), 1712 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): 1.15-2.00 (m, 9H), 2.13 (d, 3H, J=2 Hz), 2.54 (s, 3H, CH$_3$), 2.37-2.41 (m, 1H, CH), 2.46-2.64 (m, 2H, CH), 3.20-3.31 (m, 1H, CH), 3.44 (s, 3H, CH$_3$O), 7.21 (d, 1H, J=7.2 Hz, H$_{Ar}$), 7.36-7.50 (m, 2H, H$_{Ar}$), 8.04 (dd, 1H, J=7.2 Hz, J′=1.5, H$_{Ar}$).

2-Methyl-1-methylsulfinyl-3-oxo-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopentacycloocten-4-carboxylic acid methyl ester (6e). See Table 1. **Major diastereomer (SR^*,3aR^*,4R^*,9aR^*)**: Anal. Calcd. for C$_{15}$H$_{22}$O$_4$S: C, 60.38%; H, 7.43%; S, 10.74%; found: C, 60.53%; H, 7.53%; S, 10.59%. R$_f$ 0.40 (silica gel, hexane / EtOAc 1:1). IR (film): 2965, 2854, 1710 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.20-2.20 (m, 11 H), 1.86 (d, 3H, J=2 Hz, CH$_3$), 2.40-2.64 (m, 2H), 2.81 (s, 3H, CH$_3$), 3.67 (s, 3H,CH$_3$O). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 8.8 (CH$_3$), 24.2 (CH$_2$), 24.7 (CH$_2$), 26.3 (CH$_2$), 33.8 (CH$_2$), 38.7 (CH), 42.4 (CH), 44.6 (CH), 51.7 (OCH$_3$), 51.9 (CH), 140.2 (C), 172.0 (C), 174.0 (COO), 206.6 (CO). **Minor diastereomer (SR^*,3aS^*,4S^*,9aS^*)**: R$_f$ 0.40 (silica gel, hexane / EtOAc 1:1). IR (film): 2965, 2854, 1710 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.20-2.20 (m, 11H), 1.91 (d, 3H, J=2 Hz, CH$_3$), 2.40-2.64 (m, 2H), 2.61 (s, 3H, CH$_3$), 3.56 (s, 3H, CH$_3$O).

1-*tert*-Butylsulfinyl-2-methyl-3-oxo-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopentacycloocten-4-carboxylic acid methyl ester (6f). See Table 1. **Major diastereomer (SR^*,3aR^*,4R^*,9aR^*)**: MS (EI) m/z 284 (M-56), 268 (M-56-16), 252 (M-56-32), 236 (M-56-48), 207, 175, 147, 91, 55 (100). R$_f$ 0.18 (silica gel, hexane / EtOAc 7:3). IR (film): 2947, 2927, 1728 (st C=O), 1708 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.33 (s, 9H, CH$_3$), 1.15-2.10 (m, 11H), 1.83 (d, 3H, J=2 Hz), 2.35-2.45 (m, 1H), 2.46-2.56 (m, 1H), 2.80-3.98 (m, 1H), 3.22-3.34 (m, 1H), 3.52 (s, 3H, CH$_3$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 10.4 (CH$_3$), 23.7 (CH$_3$), 23.8 (CH$_2$), 24.6 (CH$_2$), 26.3 (CH$_2$), 26.4 (CH$_2$), 34.1 (CH$_2$), 44.4 (CH), 46.4 (CH), 51.7 (OCH$_3$), 52.2 (CH), 60.2 (CH), 144.9 (C), 167.6 (C), 174.0 (COO), 206.7 (CO). **Minor diastereomer (SR^*,3aS^*,4S^*,9aS^*)**: R$_f$ 0.18 (silica gel, hexane / EtOAc 7:3). IR (film): 2947, 2927, 1728 (st C=O), 1708 (st C=O) cm^{-1}.^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.36 (s, 9H, CH$_3$), 1.15-2.10 (m, 11H), 2.10 (d, 3H, J=2 Hz), 2.35-2.45 (m, 1H), 2.46-2.56 (m, 1H), 2.80-3.98 (m, 1H), 3.22-3.34 (m, 1H), 3.50 (s, 3H, CH$_3$).

2-Butyl-3-oxo-1-(*p*-tolyl-sulfinyl)-3a,4,5,6,7,8,9a-octahydro-3H-cyclopentacycloocten-4-carboxylic acid methyl ester (6g). See Table 1. **Major diastereomer (-)-(SS,3aS,4S,9aS)**: $[\alpha]^{22}_D$-98.6 (c 0.7, CHCl3).MS (EI) m/z 417 (M+1), 399 (M-18, 100), 367 (M-49), 339 (M-77). HRMS m/e calcd. for C$_{23}$H$_{36}$O$_4$S (M): 416.202132, found: 416.204272. R$_f$ 0.39 (silica gel, hexane / EtOAc 7:3).IR (film): 2950, 2925, 1728 (st C=O), 1710 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 0.91 (t, 3H, J=6.8 Hz, CH$_3$), 1.10-2.60 (m, 16H), 2.42 (s, 3H, CH$_3$), 2.80-2.96 (m, 1H), 3.17-3.30 (m, 1H), 3.42 (s, 3H, CH$_3$O), 7.32 (d, 2H, J=8.2 Hz, H$_{Ar}$), 7.51 (d, 2H, J=8.2 Hz, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 13.7 (CH$_3$), 21.4 (CH$_3$), 22.7 (CH$_2$), 23.6 (CH$_2$), 24.0 (CH$_2$), 24.5 (CH$_2$), 26.2 (CH$_2$), 26.5 (CH$_2$), 30.9 (CH$_2$), 33.4 (CH$_2$), 42.9 (CH), 44.5 (CH), 51.5 (OCH_3), 52.1 (CH), 124.8 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 137.8 (C), 141.3 (C), 148.8 (C), 168.5 (C), 173.4 (COO), 207.4 (CO). **Minor diastereomer (*SS*,3a*R*,4*R*,9a*R*)**: R_f 0.34 (silica gel, hexane / EtOAc 7:3). IR (film): 2950, 2925, 1728 (st C=O), 1710 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.91 (t, 3H, J=6.8 Hz, CH_3), 1.10-2.60 (m, 16H), 2.42 (s, 3H, CH_3), 2.80-2.96 (m, 1H), 3.08-3.18 (m, 1H), 3.49 (s, 3H, CH_3O), 7.32 (d, 2H, J=8.2 Hz, H_{Ar}), 7.51 (d, 2H, J=8.2 Hz, H_{Ar}).

(*E*)-3-*tert*-Butylsulfinyl-3-cyclooct-2-enyl-2-methyl acrylic acid methyl ester (7): See Table 1. MS (EI) 313 (M-1), 285 (M-28), 257 (M-57), 239 (M-57-18, 100), 207, 179, 57. R_f 0.36 (silica gel, hexane / EtOAc 7:3). IR (film): 3029, 2925, 2856, 1730 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.16 (s, 9H, CH_3), 0.08-2.20 (m, 11H), 2.05 (s, 3H, CH_3) 3.73 (s, 3H, CH_3), 5.61 (m, 2H, CH). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 18.9 (CH_3), 23.5 (CH_3), 25.7 (CH_2), 26.0 (CH_2), 26.1 (CH_2), 29.0 (CH_2), 32.1 (CH_2), 38.0 (CH_2), 51.9 (OCH_3), 58.8 (C), 130.2 (CH), 131.1 (CH), 135.8 (C), 148.2 (C), 168.7 (CO).

7-Methyl-6-oxo-8-(*p*-tolylsulfinyl)spiro[4.4]non-7-ene-1-carboxylic acid methyl ester (9a). See Table 2. **Major diastereomer (*SR**,5*S**,6*S**)**: MS (EI) 346 (M), 329 (M^+-16), 314 (M-32), 298 (M-48). HRMS m/e calcd. for $C_{19}H_{22}O_4S$ (M): 346.123811, found: 346.125295. R_f 0.24 (silica gel, hexane / EtOAc 7:3). IR (film): 3022, 2950, 2871, 1737 (st C=O), 1706 (st C=O), 1635 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.20–3.00 (m, 9H), 1.99 (t, 3H, J=2.1 Hz, CH_3), 2.38 (s, 3H, CH_3), 3.34 (s, 3H, OCH_3), 7.31 (d, 2H, J=7.8 Hz, H_{Ar}), 7.48 (d, 2H, J=7.8 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 9.3 (CH_3), 21.3 (CH_3), 23,1 (CH_2), 28.1 (CH_2), 36.3 (CH_2), 37.7 (CH_2), 51.3 (CH_3), 53.4 (CH), 55.6 (C), 124.2 (CH), 130.1 (CH), 138.2 (C), 141.0 (C), 141.9 (C), 166.7 (C), 172.8 (COO), 209.4 (CO). **Minor diastereomer (*SR**,5*R**,6*R**)**: R_f 0.24 (silica gel, hexane / EtOAc 7:3). IR (film): 3022, 2950, 2871, 1737 (st C=O), 1706 (st C=O), 1635 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.20–3.00 (m, 9H), 1.99 (t, 3H, J=2.1 Hz, CH_3), 2.38 (s, 3H, CH_3), 3.54 (s, 3H, OCH_3), 7.31 (d, 2H, J=7.8 Hz, H_{Ar}), 7.48 (d, 2H, J=7.8 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 9.3 (CH_3), 21.3 (CH_3), 23,3 (CH_2), 28.2 (CH_2), 37.3 (CH_2), 37.5 (CH_2), 51.6 (CH_3), 53.5 (CH), 56.3 (C), 124.1 (CH), 130.1 (CH), 138.5 (C), 140.5 (C), 142.1 (C), 167.3 (C), 172.9 (COO), 209.0 (CO).

(*SR,5*S**,6*S**)-2-Methyl-1-oxo-3-(*p*-tolylsulfinyl)spiro-[4.6]-undec-2-en-6-carboxylic acid methyl ester (9c)**. See Table 2. MS (EI) 432 (M), 400 (M-32), 277, 245, 217, 139, 91 (100). R_f 0.24 (silica gel, hexane / EtOAc 7:3). IR (film): 3022, 2921, 2854, 1733 (st C=O), 1708 (st C=O), 1637 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.20-2.40 (m, 11H), 2.02 (t, 3H, J=2 Hz, CH_3), 2.38 (s, 3H, CH_3), 2.54 (d, 1H, J=9,2 Hz, CH), 2.84 (dd, 1H, J=17.4 Hz, J'=1.8 Hz, CH), 3.24 (s, 3H, CH_3O), 7.29 (d, 2H, J=8.2 Hz, H_{Ar}), 7.46 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 9.5 (CH_3), 21.4 (CH_3), 23.5 (CH_2), 27.0 (CH_2), 30.2 (CH_2), 30.7 (CH_2), 37.6 (CH_2), 38.7 (CH_2), 51.0 (C), 51.5 (CH), 53.9 (CH_3), 124.3 ($C_{Ar}H$), 130.1 ($C_{Ar}H$), 138.4 (C), 141.7 (C), 141.9 (C), 165.0 (C), 174.1 (COO), 210.7 (CO).

(-)-(*SR*,5*S*,6*S*)-2-Methyl-1-oxo-3-(*p*-tolylsulfinyl)spiro-[4.6]-undec-2-en-6-carboxylic acid methyl ester (9d). See Table 2. $[\alpha]^{21}_D$-95.4 (c 1.15, $CHCl_3$). MS (EI) m/z 416 (M), 399 (M^+-16), 367 (M^+-48), 339 (M-77, 100). HRMS m/e calcd. for $C_{24}H_{32}O_4S$ (M): 416.202132, found: 416.203651. R_f 0.42 (silica gel, hexane / EtOAc 7:3), R_f 0.34 (aluminum oxide, hexane / ^{t}BuOMe 1:1) . IR (film): 2952, 2925, 2858, 1733 (st C=O), 1708 (st C=O). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.92 (t, 3H, J=6.8 Hz, CH_3) 1.20-2.90 (m, 19H), 2.39 (s, 3H, CH_3), 3.27 (s, 3H, CH_3O), 7.30 (d, 2H, J=8.2 Hz, H_{Ar}), 7.48 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 13.7 (CH_3), 21.4 (CH_3), 22.7 (CH_2), 23.6 (CH_2), 24.0 (CH_2), 27.0 (CH_2), 30.2 (CH_2), 30.4 (CH_2), 30.8 (CH_2), 37.2 (CH_2), 38.7 (CH_2), 51.3 (C), 51.3 (CH), 54.5 (CH), 53.6 (CH_3), 124,5 (CH), 130.0 (CH), 138.4 (C), 141.7 (C), 146.5 (C), 164.7 (C), 174.1 (COO), 210.8 (CO).

(SR^*,5S^*,6S^*)-2-Methyl-1-oxo-3-*p*-tolylsulfinylspiro[4.7]dodec-2-ene-6-carboxylic acid methyl ester (9e). See Table 2. R_f 0.38 (silica gel, hexane / EtOAc 7:3). R_f 0.57 (aluminium oxide, hexane / ^{t}BuOMe 1:1) . IR (film): 2921, 2854, 1731 (st C=O), 1708 (st C=O), 1483, 1294, 1082, 1051, 810 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.20–2.10 (m, 12H, CH_2), 2.02 (t, 3H, J=2.1 Hz, CH_3), 2.37 (s, 3H, CH_3), 7.29 (d, 2H, J=8.1 Hz, H_{Ar}) 7.45 (d, 2H, J=8.1 Hz, H_{Ar}). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 9.5 (CH_3), 21.3 (CH_3), 23.7 (CH_2), 25.2 (CH_2), 26.6 (CH_2), 27.7 (CH_2), 28.1 (CH_2), 33.4 (CH_2), 35.0 (CH_2), 49.1 (CH), 50.3 (C), 51.3 (CH_3), 124.3 (CH), 130.0 (CH), 138.3 (C), 141.6 (C), 142.1 (C), 164.8 (C), 175.0 (COO), 210.0 (CO).

(-)-(SR,5S,6S)-2-Butyl-1-oxo-3-*p*-tolylsulfinyl-spiro[4.7]dodec-2-ene-6-carboxylic acid methyl ester (9f). See Table 2..$[\alpha]^{22}_D$ -6.9 (c 3.6, CHCl3). MS (EI) m/z 399 (M^+-32), 367 (M^+-64, 100), 339 (M-91), 91 ($C_7H_7^+$). HRMS m/e calcd. for $C_{24}H_{31}O_3S$ (M^+-32): 399.199392, found: 399.200874. R_f 0.30 (silica gel, hexane / EtOAc 8:2), R_f 0.49 (silica gel, pentane / ether 1:1). IR (film): 2925, 2856, 1733 (st C=O), 1708 (st C=O) cm^{-1}.^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.92 (t, 3H, J=7.2 Hz, CH_3) 1.20-2.85 (m, 21H), 2.37 (s, 3H, CH_3), 3.20 (s, 3H, CH_3O), 7.29 (d, 2H, J=8.2 Hz, H_{Ar}), 7.45 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.7 (CH_3), 21.3 (CH_3), 22.8 (CH_2), 23.7 (CH_2), 24.0 (CH_2), 25.3 (CH_2), 26.7 (CH_2), 27.7 (CH_2), 27.7 (CH_2), 28.2 (CH_2), 30.3 (CH_2), 33.5 (CH_2), 34,7 (CH_2), 50.4 (C), 51.3 (CH_3), 124,5 (CH), 130.0 (CH), 138.3 (C), 141.5 (C), 146.7 (C), 164.4 (C), 175.0 (COO), 210.1 (CO).

(±)-2-Methyl-3-(*p*-tolylsulfinyl)-5,6,7,8-tetrahydro-naphthalen-1-ol (10b). See Table 2. R_f 0.22 (silica gel, hexane / EtOAc 7:3). IR (film): 3313 (broad, st O-H), 2923, 2850, 1595, 1464 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$-CD_3OD): δ 1.60–2.80 (m, 8H, CH_2), 2.11 (m, 3H, CH_3), 2.33 (m, 3H, CH_3), 7.21 (d, 2H, J=8.2 Hz, H_{Ar}), 7.45 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$-CD_3OD): δ 10.9 (CH_3), 20.7 (CH_3), 22.1 (CH_2), 22.2 (CH_2), 23.2 (CH_2), 29.2 (CH_2), 116.2 (CH), 118.8 (C), 125.6 (C), 127.6 (C), 129.6 (CH), 136.7 (C), 138.1 (C), 140.3 (C), 141.5 (C), 152.6 (C).

(±)-2-Methyl-3-(*p*-tolylsulfinyl)-6,7,8,9-tetrahydro-5H-benzocyclohepten-1-ol (10c). See Table 2. R_f 0.19 (silica gel, hexane / EtOAc 7:3). IR (film): 3263 (st O-H), 2920, 2850, 1595, 1594 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.40-2.10 (m, 6H), 2.17 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.65-3.00 (m, 4H), 6,00 (broad s, 1H, OH), 7.19 (d, 2H, J=8 Hz, H_{Ar}), 7.34 (s, 1H, H_{Ar}), 7.42 (d, 2H, J=8 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 11.9 (CH_3), 21.3 (CH_3), 26.5 (CH_2), 27.2 (CH_2), 28.0 (CH_2), 32.4 (CH_2), 36.4 (CH_2), 112.2 (C), 116.9 (CH), 120.0 (C), 125.7 (CH), 129.8 (CH), 132.9 (C), 141.3 (C), 141.5 (C), 144.0 (C), 151.3 (C).

(±)-2-Methyl-3-(*p*-tolylsulfinyl)-5,6,7,8,9,10-hexahydrobenzocycloocten-1-ol (10e). See Table 2. R_f 0.29 (silica gel, hexane / EtOAc 7:3), R_f 0.29 (aluminium oxide, hexane/^{t}BuOMe 1:1). IR (film): 3313 (broad, st O-H), 2923, 2850, 1595, 1564. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.20–1.32 (m, 2H, CH_2), 1.32–1.42 (m, 2H, CH_2), 1.56–1.70 (m, 4H, CH_2), 2.13 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.72-2.81 (s, 4H, CH_2), 5.38 (broad s, 1H, OH), 7.18 (d, 2H, J=8.1 Hz, H_{Ar}), 7.24 (s, 1H, H_{Ar}), 7.40 (d, 2H, J=8.1 Hz, H_{Ar}). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 11.5 (CH_3), 21.4 (CH_3), 24.3 (CH_2), 25.8 (CH_2), 26.2 (CH_2), 29.0 (CH_2), 32.3 (CH_2), 33.2 (CH_2), 117.2 (CH), 119.0 (C), 126.0 (CH), 129.6 (C), 130.0 (CH), 140.2 (C), 141.4 (C), 141.7 (C), 142.0 (C), 151.7 (C).

2-Butyl-3-(*p*-tolylsulfinyl)-5,6,7,8,9,10-hexahydrobenzocycloocten-1-ol (10f). See Table 2. MS (EI) m/z 328 (M), 311 (M^+-16), 241 (100), 236. R_f 0.33 (silica gel, pentane / ether 1:1). IR (KBr): 3300 (st O-H), 2950, 2920, 2840, 1595, 1590 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$-CD3OD): δ 0.79 (t, 3H, J=7.2 Hz, CH_3), 1.10-1.50 (m, 8H, CH_2), 1.52-1.70 (m, 4H, CH_2), 2.06-2.16 (m, 8H, CH_2), 2.31 (s, 3H, CH_3), 2.60

(t, 2H, J=7.6 Hz, CH$_2$), 7.18 (d, 2H, J=8.2 Hz, H$_{Ar}$), 7.22 (s, 1H, H$_{Ar}$), 7.40 (d, 2H, J=8.2 Hz, H$_{Ar}$). ^{13}C-NMR (75 MHz, CDCl$_3$-CD$_3$OD): δ 13.8 (CH$_3$), 21.3 (CH$_3$), 22.9 (CH$_2$), 24.2 (CH$_2$), 25.8 (CH$_2$), 26.1 (CH$_2$), 28.9 (CH$_2$), 31.3 (CH$_2$), 32.2 (CH$_2$), 33.2 (CH$_2$), 117.3 (CH), 124.6 (C), 126.2 (CH), 129.8 (CH), 130.1 (C), 139.6 (C), 141.5 (C), 141.9 (C), 142.0 (C), 151.5 (C).

(±)-4-Cyclopent-1-enyl-2-methyl-3-(*p*-tolylsulfinyl)-but-2-enoic acid methyl ester (11a). See Table 2. R$_f$ 0.60 (silica gel, hexane / EtOAc 7:3). IR (film): 3047, 2948, 2923, 2842, 1726 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.45–2.20 (m, 6H, CH$_2$), 2.33 (s, 6H, CH$_3$), 3.00-3.30 (m, 2H, CH$_2$), 3.64 (s, 3H, CH$_3$), 4.97 (t, 1H, J=1.8 Hz, CH), 7.21 (d, 2H, J=8 Hz, H$_{Ar}$), 7.38 (d, 2H, J=8 Hz, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 16.9 (CH$_3$), 21.1 (CH$_3$), 23.0 (CH$_2$), 24.7 (CH$_2$), 32.1 (CH$_2$), 32.1 (CH$_2$), 34.4 (CH$_2$), 51.8 (CH$_3$), 124.0 (CH), 125.9 (CH), 129.6 (CH), 133.9 (C), 139.1 (C), 140.4 (C), 140.9 (C), 149.4 (C), 167.7 (C).

(±)-4-Cyclohex-1-enyl-2-methyl-3-(*p*-tolylsulfinyl)-but-2-enoic acid methyl ester (11b). See Table 2. R$_f$ 0.53 (silica gel, hexane / EtOAc 7:3). IR (film): 3018, 2997, 2925, 2873, 2856, 1726 (st C=O), 808 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.20-1.46 (m, 4H, CH$_2$), 1.55-1.68 (m, 2H), 1.68-1.78 (m, 2H), 2.37 (s, 6H, CH$_3$), 3.06 (broad s, 2H, =C-CH$_2$-C=), 5.10 (broad s, 1H, -HC=), 7.24 (d, 2H, J=8.2 Hz, H$_{Ar}$), 7.40 (d, 2H, J=8.2 Hz, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 17.2 (CH$_3$), 21.3 (CH$_3$), 21.9 (CH$_2$), 22.6 (CH$_2$), 25.1 (CH$_2$), 27.8 (CH$_2$), 30.9 (CH$_2$), 52.0 (CH$_3$), 123.6 (CH), 124.1 (CH), 129.7 (CH), 133.7 (C), 134.7 (C), 139.3 (C), 140.9 (C), 148.5 (C), 168.0 (C).

(±)-4-Cyclooct-1-enyl-2-methyl-3-(*p*-tolylsulfinyl)-but-2-enoic acid methyl ester (11e). See Table 2. R$_f$ 0.19 (silica gel, hexane / EtOAc 7:3). IR (film): 2921, 2850, 1726 (st C=O), 1677, 1446, 1269, 1134, 1082, 1051, 1014, 808, 730 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.10-1.40 (m, 8H, CH$_2$), 1,80-1.94 (m, 4H, CH$_2$), 2.36 (s, 3H, CH$_3$), 3.37 (broad s, 3H, CH$_3$), 3.12 (broad s, 2H, CH$_2$), 3.65 (s, 3H, CH$_3$O), 4.97 (t, 1H, J=8.2 Hz, CH). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 17.3 (CH$_3$), 21.3 (CH$_3$), 25.9 (CH$_2$), 26.3 (CH$_2$), 26.3 (CH$_2$), 28.1 (CH$_2$), 28.7 (CH$_2$), 29.8 (CH$_2$), 30.2 (CH$_2$), 52.0 (CH$_3$), 124.1 (CH), 125.6 (CH), 129.7 (CH), 134.8 (C), 136.5 (C), 139.2 (C), 140.9 (C), 148.7 (C), 167.8 (C).

(±)-(*E*)-[3-(1-cyclopentenyl)-2-methyl-1-propenyl] *p*-tolyl sulfoxide (12a). See Table 2. MS (EI) m/z 261 (M$^+$), 260 (M), 243 (M$^+$-16), 212 (M-48), 183 (M-77), 91 (C$_7$H$_7^+$). R$_f$ 0.38 (silica gel, hexane / EtOAc 7:3). IR (film): 2948, 2920, 2844, 1625 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.72–2.36 (m, 6H, CH$_2$), 2.10 (s, 3H, CH$_3$), 2.39 (s, 3H, CH$_3$), 2.88 (broad s, 2H, CH$_2$), 5.42 (s, 1H, CH), 6.04 (broad s, 1H, CH), 7.29 (d, 2H, J=8.2 Hz, H$_{Ar}$), 7.46 (d, 2H, J=8.2 Hz, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 18.5 (CH$_3$), 21.3 (CH$_3$), 23.4 (CH$_2$), 32.4 (CH$_2$), 34.6 (CH$_2$), 41.1 (CH$_2$), 124.0 (CH), 127.9 (CH), 129.9 (CH), 132.9 (CH), 139.5 (C), 140.7 (C), 141.7 (C), 149.9 (C).

(±)-(*E*)-[3-(1-cyclohexenyl)-2-methyl-1-propenyl] *p*-tolyl sulfoxide (12b). See Table 2. R$_f$ 0.53 (silica gel, hexane / EtOAc 7:3). IR (film): 3018, 2997, 2925, 2873, 2856, 1726 (st C=O), 808 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.20-1.46 (m, 4H, CH$_2$), 1.55-1.68 (m, 2H), 1.68-1.78 (m, 2H), 2.37 (s, 6H, CH$_3$), 3.06 (broad s, 2H, =C-CH$_2$--C=), 5.10 (broad s, 1H, -HC=), 7.24 (d, 2H, J=8.2 Hz, H$_{Ar}$), 7.40 (d, 2H, J=8.2 Hz, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 17.2 (CH$_3$), 21.3 (CH$_3$), 21.9 (CH$_2$), 22.6 (CH$_2$), 25.1 (CH$_2$), 27.8 (CH$_2$), 30.9 (CH$_2$), 52.0 (CH$_3$), 123.6 (CH), 124.1 (CH), 129.7 (C H), 133.7 (C), 134.7 (C), 139.3 (C), 140.9 (C), 148.5 (C), 168.0 (C).

(±)-(*E*)-[3-(1-cycloheptenyl)-2-methyl-1-propenyl] *p*-tolyl sulfoxide (12c). See Table 2. R$_f$ 0.31 (silica gel, hexane / EtOAc 7:3). IR (film): 2920, 2848, 1626, 1601 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.20-1.54 (m, 4H), 1.60-1.80 (m, 4H), 1.84-2.00 (m, 2H), 2.06 (d, 3H, J=1 Hz CH$_3$), 2.38 (s, 3H, CH$_3$), 2.73 (s, 2H), 5.61 (t, 1H, J=6.4, -CH=), 6.03 (d, 1H, J=1 Hz, -CH=), 7.27 (d, 2H, J=8.2 Hz, H_{Ar}), 7.44 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 18.2 (CH_3), 21.3 (CH_3), 26.6 (CH_2), 27.0 (CH_2), 28.4 (CH_2), 32.0 (CH_2), 32.3 (CH_2), 50.1 (CH_2), 124.0 (CH), 130.0 (CH), 130.6 (C), 133.3 (C), 139.6 (C), 140.7 (C), 141.8 (C), 150.2 (C).

(±)-(*E*)-[3-(1-cyclooctenyl)-2-methyl-1-propenyl] *p*-tolyl sulfoxide (12e). See Table 2. R_f 0.28 (silica gel, hexane / EtOAc 7:3). IR (film): 2921, 2850, 1446, 1082, 1041, 811, 768 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.20-2.10 (m, 14H, CH_2), 2.09 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.76 (s, 2H, CH_2), 5.40 (t, 1H, J=8 Hz, CH). 6.04 (broad s, 1H, CH), 7.28 (d, 2H, J=8.8 Hz, H_{Ar}), 7.49 (d, 2H, J=8.8 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 18.4 (CH_3), 21.3 (CH_3), 26.2 (CH_2), 26.4 (CH_2), 26.4 (CH_2), 28.1 (CH_2), 28.3 (CH_2), 29.7 (CH_2), 47.4 (CH_2), 112.3 (C), 124.0 (CH), 128.2 (CH), 129.8 (CH), 133.2 (C), 136.1 (C), 140.7 (C), 150.3 (C).

(5*R,6*R**)-2-Methyl-1-oxo-3-methoxyspiro[4.4]dodec-2-ene-6-carboxylic acid methyl ester (13).** See Table 2. Rf= 0,24 (silica gel, hexane/EtOAc 7:3). IR (film): 2950, 2867, 1737 (st C=O), 1653 cm^{-1}. ^{1}H-RMN (200 MHz, $CDCl_3$): δ 1.54 (t, 3H, J=1.6 Hz, CH_3), 1.53-3.00 (m, 9H), 3.51 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3). ^{13}C-RMN (50 MHz, $CDCl_3$): δ 6.0 (CH_3), 23.5 (CH_2), 29.3 (CH_2), 38.0 (CH_2), 40.7 (CH_2), 51.5 (CH_3), 52.8 (CH), 55.9 (C), 56.5 (CH_3), 114.0 (C=), 173.5 (COO), 181.2 (C=), 207.1 (CO).

(3a*R,4*R**,9a*R**)-2-Methyl-3-oxo-1-(*p*-tolylsulfonyl)-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopentacyclooctene-4-carboxylic acid methyl ester (14a)**: It was prepared by oxidation of 6a with MCPBA / $CHCl_2$ at room temp[12] in 100 % yield. R_f 0.43 (silica gel, hexane / EtOAc 7:3). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.00-2.60 (m, 10H), 1.90 (d, 3H, J=2.1 Hz, CH_3), 2.42 (s, 3H, CH_3), 2.45-2.60 (m, 1H), 3.15-3.23 (m, 1H), 3.23-3.30 (m, 1H), 3.46 (s, 3H, CH_3O), 7.34 (d, 2H, J=8.4 Hz, H_{Ar}), 7.80 (d, 2H, J=8.4 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 9.5 (CH_3), 21.6 (CH_3), 24.1 (CH_2), 24.4 (CH_2), 26.2 (CH_2), 26.5 (CH_2), 33.2 (CH_2), 43.6 (CH), 44.8 (CH), 51.4 (CH), 51.7 (OCH_3), 127.7 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 137.5 (C), 144.8 (C), 145.0 (C), 165.3 (C), 173.4 (COO), 207.4 (CO).

(+)-(3a*S*,4*S*,9a*S*)-2-Butyl-3-oxo-1-(*p*-tolylsulfonyl)-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopentacycloocten-4-carboxylic acid methyl ester (14g). It was prepared by oxidation of 6g with MCPBA / $CHCl_2$ at room temp.[12] in 100 % yield. $[\alpha]^{22}_{D}$ +30.4 (c 1.0, $CHCl_3$). R_f 0.32 (silica gel, hexane / EtOAc 7:3). IR (film): 2952, 2929, 2880, 1714 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.82 (t, 3H, J=6.8 Hz, CH_3), 1.00-2.60 (m, 16H), 2.42 (s, 3H, CH_3), 3.11 (dt, 1H, J_1=11.8, J_2=3.2 Hz), 3.20-3.31 (m, 1H), 3,45 (s, 3H, CH_3O), 7.33 (d, 2H, J=8.2 Hz, H_{Ar}), 7.80 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 13.7 (CH_3), 21.6 (CH_3), 23.0 (CH_2), 24.0 (CH_2), 24.2 (CH_2), 24.4 (CH_2), 26.2 (CH_2), 26.6 (CH_2), 30.0 (CH_2), 33.3 (CH_2), 43.5 (CH), 44.7 (CH), 51.5 (CH), 51.6 (OCH_3), 127.8 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 137.6 (C), 145.0 (C), 148.9 (C), 165.0 (C), 173.3 (COO), 207.5 (CO).

(3a*R,4*S**,9a*R**)-2-Methyl-3-oxo-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopentacycloocten-4-carboxylic acid methyl ester (15a).**[28] Al (Hg)[29] was added to a solution of the sulphone **14a** in 10 % aq. THF under nitrogen and the mixture was heated at reflux. The progress of the reaction was monitored by TLC. When the reaction was completed, the mixture was filtered, concentrated to a small volume and extracted with ether. Flash chromatography of the residue afforded **15a** in 94 % yield. R_f 0.20 (silica gel, hexane / EtOAc 9:1). IR (film): 3026, 2921, 2977, 2850, 1731 (st C=O), 1706 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.80-2.20 (m, 10H), 2.23 (t, 3H, J=3.2 Hz, CH_3), 2.70-3.10 (m, 1H), 3.18-3.32 (m, 1H), 3.54 (s, 3H, CH_3O), 7.09 (broad s, 1H, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 10.1 (CH_3), 24.7 (CH_2), 25.0 (CH_2), 26.5 (CH_2), 27.1

(CH_2), 34.8 (CH_2), 42.2 (CH), 43.9 (CH), 51.5 (OCH_3), 52.3 (CH), 139.4 (C), 161.3 (CH), 174.6 (COO), 210.4 (CO).

(-)-(3a*R*,4*S*,9a*R*)-2-Butyl-3-oxo-3a,4,5,6,7,8,9,9a-octahydro-3H-cyclopentacycloocten-4-carboxylic acid methyl ester (15g). It was prepared from **14g** in 88 % yield following the same procedure as that for **15a**. $[\alpha]^{22}_D$ -7.9 (c 0.56, $CHCl_3$). CD:$[\theta]_{330}$ = -550 ($n \rightarrow \pi^*$) (c 0.040, $CHCl_3$, 22ºC). HRMS m/e calcd. for $C_{14}H_{20}O_3$ (M): 236.141245, found: 236.141920. R_f 0.56 (silica gel, hexane / EtOAc 8:2). IR (film): 2950, 2927, 2658, 1733 (st c=O), 1704 (st C=O), 1633 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.87 (t, 3H, J=6.8 Hz, CH_3), 0.90-2.29 (m, 16H), 2.86-3.00 (m, 1H), 3.16-3.32 (m, 1H), 3.54 (s, 3H, CH_3O), 7.05 (s, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 13.8 (CH_3), 22.4 (CH_2), 24.4 (CH_2), 24.8 (CH_2), 25.0 (CH_2), 26.5 (CH_2), 27.2 (CH_2), 29.7 (CH_2), 34.9 (CH_2), 42.2 (CH), 43.8 (CH), 51.4 (CH), 52.7 (OCH_3), 144.0 (C), 160.4 (CH), 174.5 (COO), 210.2 (CO).

(-)-(5*R*,6*R*)-2-Butyl-1-oxo-3-(*p*-tolylsulfinyl)-spiro[4.6]undec-2-ene-6-carboxylic acid methyl ester (16d): It was prepared by oxidation of **9d** with MCPBA / $CHCl_2$ at room temp.[12] in 100 % yield. $[\alpha]^{21}_D$ -16.9 (c 0.75, $CHCl_3$). MS (EI) m/z 432 (M), 400 (M-32), 277, 245, 217, 139, 91 ($C_7H_7^+$, 100), 55. R_f 0.41 (silica gel, hexane /EtOAc 8:2). IR (film): 2954, 2927, 2858, 1731 (st C=O), 1714 (st C=O), 1596, 1149 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.89 (t, 3H, J=6.6 Hz, CH_3) 1.08-2.73 (m, 19H), 2.44 (s, 3H, CH_3), 3.37 (s, 3H, CH_3O), 7.35 (d, 2H, J=8.2 Hz, H_{Ar}), 7.78 (d, 2H, J=8.2 Hz, H_{Ar}). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 13.8 (CH_3), 21.7 (CH_3), 23.0 (CH_2), 23.6 (CH_2), 26.8 (CH_2), 29.7 (CH_2), 30.2 (CH_2), 30.5 (CH_2), 30.7 (CH_2), 38.7 (CH_2), 43.4 (CH_2), 51.6 (C), 51.7 (CH_3), 53.5 (CH), 127.9 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 136.4 (C), 145.3 (C), 148.9 (C), 157.7 (C), 174.6 (COO), 210.7 (CO).

(+)-(5*R*,6*R*)-2-Butyl-1-oxo-3-(*p*-tolylsulfonyl)spiro[4.7]dodec-2-ene-6-carboxylic acid methyl ester (16f): It was prepared by oxidation of **9f** with MCPBA / $CHCl_2$ at room temp.[12] in 100 % yield. $[\alpha]^{21}_D$ +7.7 (c 2.4, $CHCl_3$). MS (EI) m/z 446 (M), 414 (M-32), 386 (M-32-28), 291, 259, 231 (100), 139, 91. R_f 0.39 (silica gel, hexane / EtOAc 8:2). IR (film): 2925, 2858, 1731 (st C=O), 1714 (st C=O), 1595, 1144 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.89 (t, 3H, J=6.9 Hz, CH_3), 1.20-2.00 (m, 16H), 2.26 (d, 1H, J=18 Hz, CH), 2.42 (s, 3H, CH_3), 2.67 (d, 1H, J=18 Hz, CH), 2.82 (dd, 1H, J_1=10.5 Hz, J_2=2.7 Hz), 3.32 (s, 3H, CH_3O), 7.34 (d, 2H, J=7.8 Hz, H_{Ar}), 7.77 (d, 2H, J=7.8 Hz, H_{Ar}). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.8 (CH_3), 21.7 (CH_3), 23.0 (CH_2), 23.6 (CH_2), 23.7 (CH_2), 25.3 (CH_2), 27.8 (CH_2), 28.0 (CH_2), 30.4 (CH_2), 33.3 (CH_2), 40.8 (CH_2), 49.0 (CH), 50.7 (C), 51.6 (CH_3), 127.9 (CH), 130.0 (CH), 136.4 (C), 145.2 (C), 149.0 (C), 157.4 (C), 175.0 (COO), 210.0 (CO).

(+)-(5*R*,6*R*)-2-Butyl-1-oxospiro[4.6]undec-2-ene-6-carboxylic acid methyl ester (17d). It was prepared from **16d** following the same procedure as that for **15a** in 90 % yield. $[\alpha]^{21}_D$ +18.5 (c 0.2, $CHCl_3$). CD:$[\theta]_{330}$ = -810 ($n \rightarrow \pi^*$) (c 0.080, $CHCl_3$, 22ºC). MS (EI) m/z 278 (M), 246 (M-32, 100), 218 (M-32-20), 175. HRMS m/e calcd. for $C_{17}H_{26}O_3$ (M): 278.188195, found: 278.190127. R_f 0.42 (silica gel, hexane / EtOAc 9:1). IR (film): 3022, 2952, 2925, 2856, 1737 (st C=O), 1699 (st C=O) cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.88 (t, 3H, J=7 Hz, CH_3) 1.23-2.42 (m, 16H), 2.49-2.65 (m, 3H), 3.53 (s, 3H, CH_3O), 7.03 (broad s, 1H, =CH). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 13.9 (CH_3), 22.5 (CH_3), 23.8 (CH_2), 24.8 (CH_2), 26.7 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 30.4 (CH_2), 30.7 (CH_2), 39.1 (CH_2), 43.7 (CH_2), 50.8 (C), 51.6 (CH_3), 53.4 (CH), 145.0 (CH), 152.4 (CH), 174.8 (COO), 212.7 (CO).

(+)-(5*R*,6*R*)-2-Butyl-1-oxospiro[4.7]dodec-2-ene-6-carboxylic acid methyl ester (17f): It was prepared from **14f** by the same procedure than **15a**. 95 % yield. Anal. Calcd. for $C_{18}H_{28}O_3$: C, 73.93%; H, 9.65%; found: C, 74.03%; H, 9.71%. R_f 0.41 (silica gel, hexane / EtOAc 9:1). $[\alpha]^{22}_D$ +46.1 (c 1.0, $CHCl_3$).

CD:$[\theta]_{330}$= -550 ($n\rightarrow\pi^*$) (c 0.040, CHCl$_3$, 22°C). IR (film): 2925, 1737 (st C=O), 1701 (st C=O). ^{1}H-NMR (200 MHz, CDCl$_3$): δ 0.88 (t, 3H, J=7 Hz, CH$_3$), 1.20-2.60 (m, 20 H), 2.88 (dd, 1H, J=7.8 Hz, J'=2.0 Hz), 3.52 (s, 3H, CH$_3$), 7.00 (broad s, 1H, CH). ^{13}C-NMR (50 MHz, CDCl$_3$): 13.9 (CH$_3$), 22.5 (CH$_2$), 24.0 (CH$_2$), 24.7 (CH$_2$), 25.4 (CH$_2$), 26.2 (CH$_2$), 28.0 (CH$_2$), 28.2 (CH$_2$), 30.0 (CH$_2$), 33.7 (CH$_2$), 40.9 (CH$_2$), 48.9 (CH), 50.0 (C), 51.6 (CH$_3$), 145.2 (C), 151.9 (CH), 175.6 (COO), 212.1 (CO).

(*SR**,*SR**)- and (*SR**,*SS**)-(*E*,*E*)-1,6-bis-(phenylsulfinyl)-1,5-hexadiene (21):. R$_f$ 0.05 (silica gel, hexane / EtOAc 6:4). IR (film): 3055 (broad, st O-H), 2913, 1625, 1475, 1442, 1083 1039, 748, 690 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 2.3–2.4 (m, 4H, CH$_2$), 6.24 (t, 2H, J=13.4 Hz, =CH), 6.4-6.6 (m, 2H, =CH), 7.39-7.58 (m, 10H, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 30.20 (CH$_2$), 30.22 (CH$_2$), 124.3 (CH), 124.3 (CH), 129.3 (CH), 129.3 (CH), 131.0 (CH), 131.0 (CH), 136.0 (CH), 136.0 (CH), 137.8 (CH), 137.8 (CH), 143.6 (C), 143.6 (C).

(±)-1-methylvinyl phenyl sulfoxide (23): R$_f$ 0.43 (silica gel, hexane / EtOAc 6:4). IR (film): 3058, 2972, 2918, 1672, 1442, 1081, 1049, 921, 751, 730, 690 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.69 (s, 3H, CH$_3$), 5.56 (d, 1H, J=1.6 Hz, =CH$_2$), 5.96 (s, 1H, =CH$_2$), 7.40-7.50 (m, 3H, H$_{Ar}$), 7.52-7.62 (m, 2H, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 13.3 (CH$_3$), 118.2 (=CH$_2$), 125.0 (C$_{Ar}$H), 129.1 (C$_{Ar}$H), 131.0 (C$_{Ar}$H), 142.4 (C), 150.4 (C).

(±)-3-Phenylsulfinyl-but-3-enoic acid methyl ester (24): R$_f$ 0.28 (silica gel, hexane / EtOAc 6:4). IR (film): 2952, 1739 (st C=O), 1442, 1332, 1203, 1081, 1046, 754, 690 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.69 (s, 3H, CH$_3$), 2.95 (d, 1H, J=16.4 Hz, CH$_2$), 3.14 (d, 1H, J=16.4 Hz, CH$_2$), 3.5 (s, 3H, OCH$_3$), 5.87 (d, 1H, J=0.8 Hz, =CH$_2$), 6.2 (s, 1H, =CH$_2$), 7.43-7.51 (m, 3H, H$_{Ar}$), 7.54-7.64 (m, 2H, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 32.4 (CH$_2$), 52.1 (CH$_3$), 121.5 (=CH$_2$), 125.2 (C$_{Ar}$H), 129.2 (C$_{Ar}$H), 131.3 (C$_{Ar}$H), 141.8 (C), 147.4 (C), 169.4 (COO).

(*SR**,*SR**)- and (*SR**,*SS**)-2,5-bis-phenylsulfinyl-1,5-hexadiene (25):. R$_f$ 0.10 (silica gel, hexane / EtOAc 6:4). IR (film): 3055, 2913, 1475, 1442, 1082, 1045, 925, 754, 690 cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.85–2.30 (m, 4H, CH$_2$), 5.39 (d, 2H, J=6 Hz, =CH$_2$), 5.95 (d, 2H, J=6 Hz, =CH$_2$), 3.5 (s, 3H, OCH$_3$), 5.87 (d, 1H, J=0.8 Hz, =CH$_2$), 6.2 (s, 1H, =CH$_2$), 7.37-7.53 (m, 10H, H$_{Ar}$). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 24.5 (CH$_2$), 24.6 (CH$_2$), 117.9 (=CH$_2$), 117.9 (=CH$_2$), 124.8 (C$_{Ar}$H), 124.8 (C$_{Ar}$H), 129.1 (C$_{Ar}$H), 129.1 (C$_{Ar}$H), 131.1 (C$_{Ar}$H), 131.1 (C$_{Ar}$H), 142.1 (C), 142.1 (C), 152.7 (C), 152.8 (C).

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