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Facial Stereoselectivity in Lithium Dialkylcuprate Additions to Functionalized endo-Tricyclo[5.2.1.0^{2,6}]decadienones

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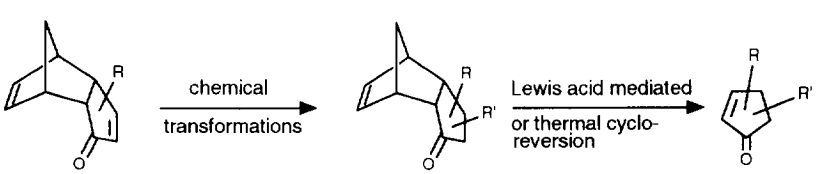
Abstract: *Lithium dialkylcuprate additions to a variety of 6-functionalized* endo-*tricyclo[5.2.1.0^{2,6}]decadienones* **4** *are described. The introduction of an alkyl or aryl ether function containing oxygen, sulfur or selenium leads to a remarkably high* endo-*stereoselectivity. The observed facial stereoselectivity of these conjugate additions to* **4** *is interpreted in steric and stereoelectronic terms.*

Introduction

Tricyclo[5.2.1.0^{2,6}]decadienones **1** have found widespread use in the synthesis of naturally occurring cyclopentanoids[1]. The basic strategy underlying this approach is depicted in Scheme 1. Chemical manipulation of **1** followed by thermal or Lewis-acid mediated [4+2] cycloreversion produces functionalized cyclopentanones **3**. Owing to their *endo* structure, most chemical modifications of **1** occur in a highly stereoselective manner ultimately leading to cyclopentenones **3** with a well-defined stereochemistry. The availability of both antipodes of **1** in enantiopure form, either by enzymatic resolution[2] or asymmetric synthesis[3] completes this strategy and makes it extremely useful for the enantioselective synthesis of a variety of natural products[1,4].

Scheme 1

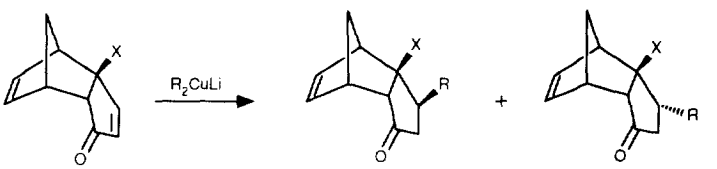


1 **2** **3**

Nucleophilic conjugate addition to the enone moiety in **1** has been studied for parent *endo*-tricyclodecadienone **4a** using a variety of nucleophiles[5,6]. Independent of the nature of the

nucleophile complete diastereoselectivity is observed in all cases to give *exo*-substituted tricyclodecenones **5a** (Scheme 2). So far no nucleophilic 1,4-additions to **4a** have been reported involving the formation of *endo*-addition product **6a**. This high stereoselectivity is the result of effective shielding of the *concave endo*-face in *endo*-tricyclodecadienones **1** by the norbornene C_8-C_9 bridge which hampers nucleophilic attack at this face and therefore promotes attack at the *exo*-face of the enone moiety. In contrast to parent tricyclodecadienone **4a**, conjugate additions of some selected organometallics to tricyclic ester **4b** were found to give mixtures of *exo*- and *endo*-addition products **5b** and **6b**[5,6]. With lithium dimethyl- and di-n-butylcuprates the *exo*-addition products **5b** (R= Me, n-Bu) are still the predominant products but a considerable amount of *endo*-products **6b** (R= Me, n-Bu) is also formed (*exo*/*endo* ratio 4:1). With lithium diphenylcuprate the *endo*-product **6b** (R= Ph) is even the major addition product[5] (ratio **5b**/**6b**= 1:2). These

Scheme 2



4a X= H **5a** **6a**
4b X= CO_2Et **5b** **6b**

results indicate that the stereochemistry of nucleophilic 1,4-additions to *endo*-tricyclodecadienones **1** is strongly affected by the substitution pattern at the *exo*-face of the molecule and the nature of the nucleophilic reagent. The substantial difference observed for the *exo*/*endo* ratios in the addition of lithium dimethyl- and di-n-butylcuprates, and lithium diphenylcuprate to **4b** indicates that besides steric effects electronic factors may play a significant role in determining the product formation.

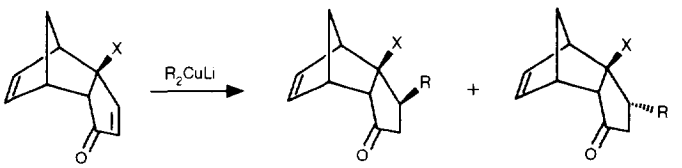
In a preceding paper[7], it was shown that tricyclic carboxylic acid **4c** (X= COOH) can be conveniently converted into the corresponding 6-halides **4d** (X= Cl, Br, I), 6-alcohol **4e** (X= OH), 6-sulfides **4g** (X= SMe) and **4h** (X= SPh), and 6-selenides **4i** (X= SePh) using the thiohydroxamic radical chemistry developed by Barton et al.[8] 6-Methoxytricyclodecadienone **4f** is readily obtained from bromide **4d** by an elimination/addition reaction using potassium hydroxide in methanol[7]. Thus, a series of 6-substituted *endo*-tricyclodecenones is available in which substituents differ in the nature of the heteroatom. As tricyclodecadienones **4** actually constitute γ-substituted cyclopentenones constrained in a rigid tricyclic system, these structures have interesting prospects to investigate the electronic and steric effect of γ-substituents of different steric size and electronic nature on conjugate addition reactions to γ-functionalized α,β-enones.

In this paper the first results on a comparative study of the 1,4-addition of lithium dimethyl- and di-n-butylcuprates to *endo*-tricyclodecadienones **4** containing an ether, thio- or selenoether function are described.

Results

For the purpose of comparison, the nucleophilic addition reactions involving 6-carboxylic ester **4b**

with both lithium dimethyl- and di-n-butylcuprate at -78°C were repeated. In both cases the chemical yields were nearly quantitative with high *exo*-stereoselectivity which was almost complete for the di-n-butylcuprate addition (Table 1). In comparison with the addition at 0 °C carried out earlier[5], a considerable increase in stereoselectivity was observed at -78°C. The somewhat higher *exo*-selectivity for



4 **5** **6**

Table 1. Diastereoselectivity of 1,4-additions of lithium dialkylcuprates to **4**

substrate	X	R_2CuLi	temp.	yield	ratio(exo **5** / endo **6**)
4a	H	Me	-78 °C	>90%	100 /-
		n-Bu	"	>90%	100 /-
4b	CO_2Et	Me	"	90%	86 /14
		n-Bu	"	90%	95 / 5
4f	OMe	Me	"	96%	23/ 77
		n-Bu	"	69%	40/ 60
4g	SMe	Me	"	97%	- /100
4h	SPh	Me	"	90%	- /100
		n-Bu	"	85%	4 / 96
4i	SePh	Me	"	89%	- /100
		n-Bu	"	86%	- /100
4j[a]	S(O)Me	Me	0 °C	98%	- /100
4k[a]	S(O)Ph	Me	"	46%	- /100

lithium di-n-butylcuprate as compared with its dimethyl analogue is merely the result of the slightly greater steric bulk of the former cuprate which disfavors *endo*-attack.

Replacing the carboxylic ester function in **4b** by a methoxy substitutent, which is sterically much less demanding (A-values 1.1-1.2 and 0.55-0.75, respectively[9]), has an enormous effect on the *exo/endo* ratio. Both with lithium dimethyl- and di-n-butylcuprate 6-methoxytricyclodecadienone **4f** gave a mixture of addition products **5f** and **6f** in excellent yield, with a preponderance of the *endo*-addition products **6f**. This result clearly shows that steric factors are less important here than electronic features. Increasing the steric size of the 6-methyl ether function by replacing the oxygen atom by sulfur as in **4g** (A-value 1.04[9]) led to complete *endo*-stereoselectivity for the addition of lithium dimethylcuprate. No *exo*-product was detected. A similar result was obtained for the addition of lithium dimethylcuprate to **4h** which contains the somewhat larger thiophenyl group (A-value 1.10-1.24[9]). Addition of lithium di-n-butylcuprate to **4h** produced again predominantly the *endo*-addition product but now a small amount (less than 4%) of

exo-product was isolated as well. Complete *endo*-stereoselectivity was observed for both the dimethyl- and n-butylcuprate addition to phenylselenide **4i**. Interestingly, due to its higher polarization selenium has a relatively low A-value (1.0-1.2)[9] despite its considerable size. Based on this consideration the phenyl selenide function is assumed to have about the same steric demand as the thiophenyl ether and ethyl ester functions as present in **4h** and **4b**, respectively.

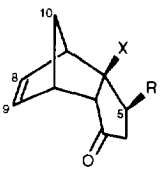
Structural assignments

The gross structures of the cuprate addition adducts **5** and **6** were deduced from their IR, NMR and MS data. Unequivocal assignment of the configuration of the newly introduced substituent at C_5, either *exo* or *endo*, was possible by comparison of the ^{1}HNMR-data of the new structures **5f,h** and **6f,g,h,i** (R= Me, n-Bu) with those of the known tricyclodecenones **5a,b** and **6a,b** (R= Me, n-Bu)[5]. Typically, the *endo*-C_5 protons in all structures **5** absorb at much high field than the *exo*-C_5 protons in tricyclodecenones **6** (Table 2). This higher field position of the *endo*-C_5 proton is clearly the result of its considerable shielding by the norbornene C_8-C_9 double bond. Obviously, such a shielding is not possible in tricyclodecenones **6**. For 6-methoxy- and 6-methylsulfanyltricyclodecenones **6f**, **6g** (R=Me) independent proof of the *endo*-configuration of the methyl group at C_5 was obtained from their 2D-^{1}H-NMR NOSY spectra (Table 3). The strong interaction observed between the C_5-methyl protons and the olefinic C_8-proton confirms that these protons are indeed within a distance of 3 Å of each other as may be expected for these structures **6f** and **6g**. Interestingly, the ^{1}H-NMR spectra of 6-phenylsulfanyltricyclodecenones **6h** (R= Me, n-Bu) were nearly identical to those of the corresponding 6-phenylselenyl compounds **6i**. Since the structure of **6i** (R= Me) has recently been secured unambiguously by X-ray diffraction analysis[11], the configuration around C_5 in the 6-sulfanyl compounds **6h** (R= Me, n-Bu) is therefore also established. Finally, with the aim to elucidate the structures of the diastereomeric tricyclic sulfoxides **6j**, which are readily obtained by oxidation of methyl sulfide **4g** followed by lithium dimethylcuprate addition *(vide infra)*, an X-ray diffraction of the major diastereomer **6j**[a] was undertaken (Figure 1). As can be seen from Figure 1 this structure again confirms the *endo*-configuration of the methyl group at C_5[11]. Interestingly, this X-ray structure shows that the methyl group of the sulfoxide group is positioned over the annelated cyclopentanone ring while the electron pair is directed toward the methylene bridge carbon C_{10}. It is evident that if this conformation has some preference in tricyclodecadienone **4j**[a], which is the precursor for **6j**[a], then addition of lithium dialkylcuprates to the enone system from the *exo*-face in **4j**[a] will be severely hindered.

Discussion

The results presented above clearly show that steric factors are not always decisive in controlling the stereochemistry of conjugate nucleophilic cuprate addition to **4**. In particular, the reversed stereoselectivity found for the lithium dialkylcuprate additions to 6-methoxytricyclodecadienone **4f** as compared with tricyclic ester **4b** unambiguously proves that electronic features dominate steric factors.

The vinylogous addition of lithium dialkylcuprates to γ-substituted cycloenones has only scarcely been studied for relative simple enones containing an alkyl or alkoxy substituent at the γ-position[12,13]. In the cases reported, cuprate addition generally occurs with high diastereoselectivity affording



5

6

Table 2. Chemical shift of selected protons in 5 and 6

product			chemical shift(ppm)	
X		R	$H_{5\text{-exo}}$	$H_{5\text{-endo}}$
5a	H	*exo*-Me		1.86
		exo-n-Bu		1.68
6a		*endo*-Me	2.40	
5b	CO_2Et	*exo*-Me		2.04
		exo-n-Bu		1.86
6b		*endo*-Me	2.44	
		endo-n-Bu	2.31	
5f	OMe	*exo*-Me		2.19
		exo-n-Bu		2.29
6f		*endo*-Me	2.63	
		endo-n-Bu	2.50	
6g	SMe	*endo*-Me	2.70	
5h	SPh	*exo*-n-Bu		2.35
		endo-Me	2.74	
6h		*endo*-n-Bu	2.56	
6i	SePh	*endo*-Me	2.76	
		endo-n-Bu	2.60	
6j[a]	S(O)Me	*endo*-Me	2.72	
6k[a]	S(O)Ph	*endo*-Me	2.73	

predominantly the *anti*-addition product. This preferred *anti*-addition is generally explained by invoking steric or electrostatic interactions which clearly disfavors *syn*-addition at the β-enone carbon in the cycloenone[13].

The exclusive formation of *exo*-addition products **5a** in the cuprate addition to parent tricyclodecadienone **4a** is in agreement with this explanation. Whereas the *exo*-face of the cyclopentenone moiety in **4a** is almost unhindered, the norbornene moiety severely hinders cuprate addition at its *endo*-face resulting in complete *exo*-addition. Increase of the steric and electrostatic demands at the

Table 3. Observed NOE-effects in **5f**, **6f**, **6g** and **6j**[a]

[Distance between H_x and the nearest hydrogen of the 5-methyl group (in Å)[a,10]]

H_x	H_1	H_2	H_{4x}	H_{4n}	H_5	H_7	H_8	H_9	H_{10a}	H_{10s}
5f	>5	3.2	2.4	3.5	2.5	4.3	>5	>5	>5	>5
6f	>5	>5	2.9	2.5	2.6	3.0	2.4	4.4	>5	5.0
6g	>5	>5	2.9	2.5	2.4	2.9	2.3	4.3	>5	5.0
6j[a]	>5	4.5	3.0	2.6	1.9	2.5	2.3	4.7	4.6	4.4

[a] A NOE-effect is expected for protons within 3 Å of the nearest proton of the methyl group. If a NOE-effect is indeed observed, the corresponding distance is underlined.

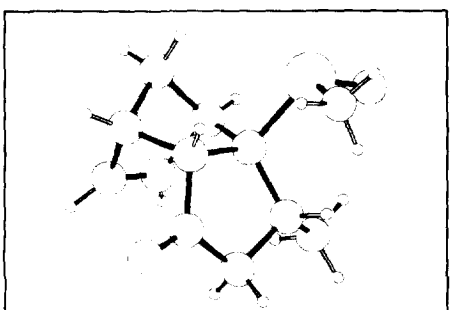


Figure 1. X-ray structure of **6j**[a]

exo-face by introducing a γ-ester function as in **4b** leads to a decrease in stereoselectivity, however, *exo*-addition is still by far the most preferred process (Table 1). A rather drastic change in stereoselectivity is observed for the cuprate addition to γ-methoxytricyclodecadienone **4f**. The major product obtained now is the *endo*-addition product **6f**. This high degree of *endo*-selectivity is certainly not primarily due to steric features since the relative steric demand of the ethoxycarbonyl group is larger than that of a methoxy group (A-values: CO_2Et>OMe)[9].

The following explanations for these observations can be envisaged. First, electrostatic repulsion between the electron-rich cuprate reagent and the lone pairs on the oxygen may give rise to a preferred *anti*-addition. Such an electrostatic repulsion is expected to be more decisive in determining the stereochemistry of cuprate addition to ethers **4f**, **4g**, **4h** and **4i** than to ester **4b** since the lone pairs on both oxygen atoms in the ester moiety can readily rotate away from the reaction center without increase of the steric hindrance at this β-enone carbon. Such an operation is not possible for the ethers **4f**, **4g**, **4h** and **4i** without considerably increasing the steric shielding of the β-enone carbon by either the methyl or phenyl group attached to the ether oxygen or sulfur.

Another possibility is stereoelectronic in nature. Assuming that the first step in the cuprate addition to the enone moiety in **4** involves the reversible formation of the corresponding *cis* and *trans*

d,π^*-complexes[14], the subsequent step, which involves either the formation of a Cu(III) β-adduct or carbocupration to form the β-alkyl copper enolate, may be strongly affected by the electronic nature of the adjacent γ-substituent. Corey and Boaz[14c] suggest that *anti*-addition may arise from hyperconjugative interaction in which the γ-heteroatom removes electron density from the d(Cu), π_3^*-enone complex or the Cu(III) β-adduct with maximum stabilization occurring in the *anti* geometry. Unfortunately, experimental data to verify this hypothesis are rather scarce and not yet convincing. This is exemplified by the recent observation that the addition of lithium dimethylcuprate to γ-methylcyclopentenone has a higher *anti*-selectivity (*anti/syn* >100:1) than that to γ-methoxycyclopentenone (*anti/syn* 42:1)[12]. Although the difference in selectivity is small, this result indicates that stereoelectronic control according to Corey's model does either not operate or does not play an important role since steric, electrostatic and stereoelectronic factors all promote *anti*-addition of the cuprate to the γ-methoxycyclopentenone which should result in at least the same high *anti*-stereoselectivity as observed for the γ-methylcyclopentenone.

An alternative stereoelectronic analysis involves interaction of the incipient bond at C_β with the nonequivalent faces of the enone system. This interaction is due to the differences in the relative stabilities of the diastereomeric transition states. According to this hypothesis (Cieplak's model[15]), which has been successfully used for the explanation of facial selectivity in 1,2-additions[16], stereoelectronic control is primarily determined by interaction of the emerging σ^*-orbital associated with the incipient bond at C_β and a suitably aligned σ-bond at C_γ. Transition state stabilization at either face is now dependent on the electron-donating ability of the respective σ-bonds at C_γ, ultimately resulting in bond formation at the face *anti* to the most electron-rich σ-bond. Applying this stereoelectronic hypothesis to γ-methoxy substituted enones *syn*-addition is expected to be the preferred process as the σ donating ability of a C-O bond is poor compared with a C-H or C-C bond[17]. Hence, the stereoelectronic control exerted by a methoxy group opposes both its steric and electrostatic effect on π-diastereofacial selectivity. This may be an explanation for the incomplete stereoselectivity observed[12] for the addition of lithium dimethylcuprate to γ-methoxycyclopentenone.

The observation of predominant *anti* stereochemistry in the cuprate addition to 6-methoxytricyclodecadienone **4f**, while for ester **4b** *syn* addition to the ester function is the main process, does not seem to be in accordance with Cieplak's hypothesis as now both sterically and stereoelectronically *syn*-addition would be the preferred reaction mode. However, it should be realized that *anti*-addition in **4f** may primarily be the result of strong repulsive electrostatic interaction between the electron-rich cuprate reagent and the methoxy oxygen lone pairs which may be of much higher weight than stereoelectronic effects. For the tricyclic thio- and selenoethers **4g**, **h** and **i** complete or almost complete diastereofacial *endo*-selectivity is observed. This increase in *endo*-selectivity as compared with the methoxy analogue may be merely the result of increased steric hindrance at the *exo*-face of the enone moiety in **4g**, **h** and **i** relative to **4f**. However, as the C-S and C-Se σ bonds are more electron donating than a C-C σ bond *anti*-addition is now also the preferred addition mode when adopting Cieplak's model. Hence, in contrast to **4f** for tricyclodecadienones **4g**, **h** and **i** steric, electrostatic and stereoelectronic effects all combine to favor the *endo*-addition product.

The tricyclic thioethers **4g** and **4h** offer a unique opportunity to further evaluate conceivable electronic effects of the γ-substituent on the cuprate additions. Transformation of the thioethers in the corresponding sulfoxides is usually a convenient reaction which changes the electronic nature of the

original sulfur substituent. Due to presence of oxygen the sulfoxide function is much more polar than a sulfide group and exerts a considerably stronger electron withdrawing inductive effect. Hence, if an appreciable electronic interaction of the γ-substituent with either the enone moiety or the incoming nucleophile would play a significant role in these cuprate additions to tricyclodecadienones **4** such an effect should certainly be reflected in either the stereoselectivity or the rate of the addition reaction.

Tricyclic methyl- and phenylsulfoxides **4j** and **4k** were readily obtained in high yield by selective oxidation of the corresponding thioethers **4g** and **4h** with sodium periodate. In both cases a mixture of diastereoisomers was isolated which could be readily separated by flash chromatography.

Addition of lithium dimethylcuprate to both sulfoxides **4j**[a] and **4k**[a] (diastereomerically pure compounds; see experimental) was considerably slower than to the corresponding sulfides **4g** and **4h**. At -78 °C no reaction was observed at all for **4j**[a] and **4k**[a] whereas for sulfides **4g** and **4h** addition of the cuprate was complete within half an hour. The temperature had to be raised to 0 °C to obtain an acceptable rate. At this temperature complete conversion of the enone was observed after 2-3 hr reaction time to give essentially only one addition product as was shown by thin layer chromatography (Table 1). The relatively low yield obtained for **6k**[a] is probably due to its thermal instability. NMR-analysis clearly revealed that cuprate addition to both **4j**[a] and **4k**[a] proceeds with high stereoselectivity to give exclusively the *endo*-5-methyltricyclodecadienones **6j**[a] and **6k**[a] (R= CH_3), respectively. No *exo*-product could be detected.

The considerably decreased reactivity of tricyclic sulfoxides **4j**[a] and **4k**[a] as compared with the corresponding sulfides presents strong evidence for significant electronic participation of the γ-substituent in the cuprate additions to the tricyclic enones **4**. By increasing the electron withdrawing ability of this substituent in going from the sulfide to the sulfoxide cuprate addition becomes apparently less favorable. The increased steric demand and electrostatic repulsive effect of the sulfoxide function as compared with the sulfide group are not relevant in this comparison as in both cases addition takes place entirely from the *endo*-face *anti* to the γ-substituent. Hence, the change in reactivity must be entirely accounted for by some electronic effect which may be attributed to electronic interaction of the sulfoxide function with the incoming nucleophile (Cieplak model). Due to the poorer electron donating ability of the C-S=O bond in comparison with C-S bond addition of the nucleophile to **4** is expected to be more facile for **4g** and **4h** than for **4j**[a] and **4k**[a] since σ-σ* overlap will be less effective in the latter cases. The alternative stereoelectronic model involving electronic interaction of the sulfoxide function with the cuprate enolate complex as suggested by Corey[14] does not seem to give a satisfactory explanation for the observed decrease in rate. On the contrary, invoking this approach, the increased electron withdrawing ability of the sulfoxide function is expected to enhance the cuprate addition rate. However, at this stage, it cannot be ruled out that both the stereochemistry and reactivity observed for cuprate additions to **4** may in some way be associated with the nature of the nucleophile, *i.e.* the copper reagent. Experiments to verify whether the nature of the nucleophile has a significant effect on both the stereochemistry and reaction rate of conjugate additions to **4** are currently underway.

In conclusion a strong directing effect of the γ-substituent on the stereoselectivity of lithium dialkylcuprate additions to γ-substituted tricyclodecenones **4** has been established. The introduction of an alkyl or aryl ether function containing oxygen, sulfur or selenium leads to a remarkably high *endo*-stereoselectivity despite the severe steric hindrance exerted by the norbornene C_8-C_9 double bond at the *endo*-face of the cyclopentenone moiety. This high facial stereoselectivity observed for tricyclodecadienones **4f-k** is

typically associated with the electronic features of the substituents which may interact electronically with either the enone-cuprate complex or with the incoming nucleophile.

Experimental

General remarks

Melting points were measured with a Reichert Thermopan microscope and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 infrared spectrometer. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AM-400 spectrophotometer, using TMS as an internal standard. For mass spectra a double focussing VG 7070E mass spectrophotometer was used. Capillary GC analyses were performed using a Hewlett-Packard 5890A gas chromatograph, containing a cross-linked methyl silicone column (25m). Flash chromatography was carried out at a pressure of ca. 1.5 bar, a column length of 15-25 cm and a column diameter of 1-4 cm, using Merck Kieselgel 60H. Elemental analyses were performed on a Carlo Erba Instruments CHNS-O 1108 Elemental analyzer. All solvents used were dried and distilled according to the standard procedures.

General procedure for cuprate addition to **4**:

A solution of RLi (ca. 2 equiv.) in hexane was gradually added to a suspension of dry CuI (ca. 1 equiv.) in dry ether at temp. below 0 °C (ice-salt) under a nitrogen atmosphere. After stirring for 15 min. at this temp., the mixture was cooled down to -78 °C. A solution of **4** (ca. 0.5 equiv.) in ether was then added. The mixture was stirred at -78 °C until the reaction was complete according to TLC (ca. 30 min.), then quenched with aqueous ammonium chloride and the aqueous phase extracted with ether (3x). The combined organic phases were washed with water (3x), dried (Na_2SO_4) and the solvent evaporated under reduced pressure. Analytical samples were obtained by flash chromatography and/or crystallization.

exo-*3-Methyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-5-one carboxylic acid ethyl ester* **5b** *(R= Me) and* endo-*3-methyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-5-one carboxylic acid ethyl ester* **6b** *(R= Me)*[5]

Following the general procedure [MeLi (1.4 ml of 1.6 M solution in hexane, 2.2 mmol), CuI (216 mg, 1.1 mmol), **4b** (110 mg, 0.5 mmol)] gave, after work-up and flash chromatography (n-hexane /EtOAc= 90/10), 105 mg (90 %) of a mixture of **5b** and **6b** in 86:14 ratio according to cap. GC.

^{1}H-NMR (400 MHz, $CDCl_3$): **5b** (R= Me): δ 6.30 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 6.20 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 4.24 (q, J=7.1 Hz, 2H, -COOC$\underline{H}_2$CH$_3$), 3.49-3.46 (m, 2H, H_6 and H_1 or H_7), 3.19-3.16 (m, 1H, H_1 or H_7), 2.31 A of AB (ddd, $J_{4x,n}$=17.3 Hz, $J_{4x,3}$=10.7 Hz, $J_{4x,6}$=1.6 Hz, 1H, H_{4x}), 2.25 B of AB (dd, $J_{4x,n}$=17.3 Hz, $J_{4n,3}$=7.9 Hz, 1H, H_{4n}), 2.09-1.99 (m, 1H, H_3), 1.69 A of AB (d, $J_{10a,s}$=8.8 Hz, 1H, H_{10s}), 1.41 B of AB (d, $J_{10a,s}$=8.8 Hz, 1H, H_{10a}), 1.32 (t, J=7.1 Hz, 3H, CH$_2$C$\underline{H}_3$), 1.04 (d, J=7.0 Hz, 3H, CH$_3$). **6b** (R= Me): δ 6.35 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 6.16 B of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 4.24-4.16 (m, 2H, -COOC$\underline{H}_2$CH$_3$), 3.49 (d, $J_{6,7}$=5.1 Hz, 1H, H_6), 3.46 (bs, 1H, H_1 or H_7), 3.23-3.21 (m, 1H, H_1 or H_7), 2.53-2.38 (m, 1H, H_3), 2.32 A of AB (ddd, $J_{4x,n}$=18.4 Hz, $J_{4x,3}$=9.4 Hz, $J_{4x,6}$=1.5 Hz, 1H, H_{4x}), 1.84 B of AB (ddd, $J_{4x,n}$=18.4 Hz, $J_{4n,3}$=11.9 Hz, $J_{4n,6}$=1.0 Hz, 1H, H_{4n}), 1.57 A of

AB (d, $J_{10a,s}$=8.7 Hz, 1H, H_{10s}), 1.42 B of AB (d, $J_{10a,s}$=8.7 Hz, 1H, H_{10a}), 1.29 (t, J=7.1 Hz, 3H, $CH_2C\underline{H}_3$), 1.21 (d, J=6.9 Hz, 3H, CH_3).

exo-*3-n-Butyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-5-one carboxylic acid ethyl ester* **5b** *(R= n-Bu) and* endo-*3-n-butyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-5-one carboxylic acid ethyl ester* **6b** *(R= n-Bu)*

Following the general procedure [BuLi (1.4 ml of 1.6 M solution in hexane, 2.2 mmol), CuI (216 mg, 1.1 mmol), **4b** (110 mg, 0.5 mmol)] gave, after work-up and flash chromatography (n-hexane /EtOAc= 90/10), 125 mg (90 %) of a mixture of **5b** and **6b** in 95:5 ratio according to ^{1}HNMR (400 MHz) and cap. GC.

^{1}H-NMR (400 MHz, $CDCl_3$): **5b** (R= n-Bu): δ 6.30 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 6.18 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 4.24 (q, J=7.2 Hz, 2H, -COOC$\underline{H}_2$CH$_3$), 3.46 (bs, 1H, H_1 or H_7), 3.40 (dd, $J_{6,7}$=4.6 Hz, $J_{4x,6}$=2.1 Hz, 1H, H_6), 3.16-3.14 (m, 1H, H_1 or H_7), 2.40 A of AB (ddd, $J_{4x,n}$=16.9 Hz, $J_{4x,3}$=12.5 Hz, $J_{4x,6}$=2.1 Hz, 1H, H_{4x}), 2.24 B of AB (dd, $J_{4x,n}$=16.9 Hz, $J_{4n,3}$=7.4 Hz, 1H, H_{4n}), 1.91-1.82 (m, 1H, H_3), 1.72 A of AB (d, $J_{10a,s}$=8.7 Hz, 1H, H_{10s}), 1.59-1.48 and 1.34-1.19 (2 x m, 1H and 5H, (C$\underline{H}_2$)$_3$CH$_3$), 1.42 B of AB (d, $J_{10a,s}$=8.7 Hz, 1H, H_{10a}), 1.32 (t, J=7.2 Hz, 3H, $CH_2C\underline{H}_3$), 0.88 (t, J=7.0 Hz, 3H, CH_3). **6b** (R= n-Bu): δ 6.32 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 6.14 B of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 4.26-4.14 (m, 2H, -COOC$\underline{H}_2$CH$_3$), 3.47 (bs, 1H, H_1 or H_7), 3.45 (dd, $J_{6,7}$=5.1 Hz, $J_{4x,6}$=1.5 Hz, 1H, H_6), 3.22-3.19 (m, 1H, H_1 or H_7), 2.40-2.27 AB (m, 2H, H_{4x} and H_{4n}), 1.93-1.77 (m, 2H, H_3 and 1H of -(C$\underline{H}_2$)$_3$CH$_3$), 1.58 A of AB (dt, $J_{10a,s}$=8.8 Hz, $J_{1,10a}\approx J_{7,10a}$ resp. $J_{1,10s}\approx J_{7,10s}\approx$1.5 Hz, 1H, H_{10s}), 1.40 B of AB (d, $J_{10a,s}$=8.8 Hz, 1H, H_{10a}), 1.42-1.15 (m, 5H of -(C$\underline{H}_2$)$_3$CH$_3$), 1.29 (t, J=7.1 Hz, 3H, $CH_2C\underline{H}_3$), 0.90 (t, J=7.1 Hz, 3H, CH_3).

6-Methoxy-exo-*5-methyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **5f** *(R= Me) and 6-methoxy*-endo-*5-methyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **6f** *(R= Me)*

Following the general procedure [MeLi (1.4 ml of 1.6 M solution in hexane, 2.2 mmol), CuI (216 mg, 1.1 mmol), **4f** (90 mg, 0.5 mmol)] gave, after work-up and flash chromatography (n-hexane /EtOAc= 80/20), 92 mg (96 %) of a colorless oil consisting of 23% of **5f** and 77% of **6f** according to ^{1}HNMR (400 MHz) and cap. GC.

^{1}H-NMR (400 MHz, $CDCl_3$): **5f** (R= Me): δ 6.25 (m, 1H, H_8 or H_9), 6.13 B of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.39 (s, 3H, OCH_3), 3.21 - 3.14 (m, 2H, H_1 and H_7), 2.81 (d, $J_{1,2}$=4.7 Hz, 1H, H_2), 2.27 (m, 1H, H_{4x}), 2.19 (m, 1H, H_5), 1.98 A of AB (d, $J_{10a,s}$=8.4 Hz, 1H, H_{10s}), 1.80 - 1.68 (m, 2H, H_{4n} and H_{10a}), 1.15 (d, J=6.8 Hz, 3H, CH_3); **6f** (R= Me): δ 6.25 (m, 1H, H_8 or H_9), 6.18 B of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.36 (s, 3H, OCH_3), 3.21-3.14 (m, 2H, H_1 and H_7), 2.75 (d, $J_{1,2}$=5.0 Hz, 1H, H_2), 2.64 (m, 1H, H_5), 2.49 A of AB (ddd, $J_{4x,n}$=18.6 Hz, $J_{4x,5}$=9.8 Hz, J=1.9 Hz, 1H, H_{4x}), 2.00 A of AB (d, $J_{10a,s}$=8.4 Hz, 1H, H_{10s}), 1.80-1.68 (m, 2H, H_{4n} and H_{10a}), 1.18 (d, J=7.0 Hz, 3H, CH_3). IR (CH_2Cl_2): υ 3010-2860 (C-H), 1740 (C=O), 1090 cm^{-1}. EI/MS: m/e (%) 127 (100, M^++1-C_5H_6), 66 (31, $C_5H_6^+$). EI/HRMS m/e: 127.0751 [calc.for $C_7H_{11}O_2$(M^++1-C_5H_6): 127.0759].

exo-*5-n-Butyl-6-methoxy*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **5f** *(R= n-Bu) and* endo-*5-n-butyl-6-methoxy*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **6f** *(R= n-Bu)*

Following the general procedure [n-BuLi (1.5 ml of 1.6 M solution in hexane, 2.3 mmol), CuI (222 mg, 1.2

mmol), **4f** (100 mg, 0.57 mmol)], gave, after work-up and flash chromatography (n-hexane /EtOAc= 80/20), 95 mg (69 %) of colorless oil consisting of 40% of **5f** and 60% of **6f** according to ^{1}HNMR (400 MHz) and cap. GC.

^{1}H-NMR (400 MHz, $CDCl_3$): **5f** (R= n-Bu): δ 6.24 A of AB (dd, $J_{8,9}$=5.5 Hz, 1H, H_8 or H_9), 6.10 B of AB (dd, $J_{8,9}$=5.5 Hz, 1H, H_8 or H_9), 3.44 (s, 3H, OCH_3), 3.14 and 3.09 (2 x bs, 2H, H_1 and H_7), 2.95 (d, $J_{1,2}$=4.6 Hz, 1H, H_2), 2.37-2.20 (m, 2H, H_{4x} and H_{4n}), 2.00-1.93 (m, 2H, H_5 and H_{10s}), 1.79-1.67 and 1.39-1.24 (2 x m, 7H), 0.91 (t, J=6.8 Hz, 3H, CH_3). **6f** (R= n-Bu): δ 6.24 A of AB (dd, $J_{8,9}$=5.7 Hz, 1H, H_8 or H_9), 6.15 B of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.8 Hz, 1H, H_8 or H_9), 3.34 (s, 3H, OCH_3), 3.14 (m, 2H, H_1 and H_7), 2.76 (d, $J_{1,2}$=5.1 Hz, 1H, H_2), 2.55-2.44 (m, 2H, H_5 and H_{4x}), 2.00-1.93 (d, $J_{10a,s}$=8.4 Hz, 1H, H_{10s}), 1.79-1.67 and 1.39-1.24 (2 x m, 8H), 0.91 (t, J=6.8 Hz, 3H, CH_3). IR (CH_2Cl_2): υ 3010-2860 (C-H), 1740 (C=O), 1090 cm^{-1}. EI/MS: m/e (%) 169 (100, M^++1-C_5H_6), 66 (100, $C_5H_6^+$). EI/HRMS m/e: 169.1227 [calc.for $C_{10}H_{17}O_2$(M^++1-C_5H_6): 169.1229].

endo-*5-Methyl-6-methylsulfanyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **6g**

Following the general procedure [MeLi (1.4 ml of 1.6 M solution in hexane, 2.2 mmol), CuI (216 mg, 1.1 mmol), **4g** (75 mg, 0.39 mmol)], gave, after work-up and flash chromatography (n-hexane /EtOAc= 90/10), 79 mg of **6g** (97 %) as a colorless crystalline solid.

6g: m.p.: 84-85 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.35 A of AB (dd, $J_{8,9}$=5.4 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 6.14 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.22 and 2.97 (2 x bs, 2H, H_1 and H_7), 2.87 (d, $J_{1,2}$=4.9 Hz, 1H, H_2), 2.69 (m, 1H, H_5), 2.31 A of AB (dd, $J_{4x,n}$=18.5 Hz, $J_{4x,5}$=9.6 Hz, 1H, H_{4x}), 2.28 A of AB (d, $J_{10a,s}$=8.3 Hz, 1H, H_{10s}), 2.18 (s, 3H, SCH_3), 1.86 B of AB (dd, $J_{4x,n}$=18.5 Hz, $J_{4n,5}$=12.4 Hz, 1H, H_{4n}), 1.67 B of AB (d, $J_{10a,s}$=8.3 Hz, 1H, H_{10a}), 1.18 (d, J=7.0 Hz, 3H, CH_3). IR (CH_2Cl_2): υ 3010-2860 (C-H), 1735 (C=O) cm^{-1}. EI/MS: m/e (%) 208 (0.6, M^+), 143 (100, M^++1-C_5H_6). EI/HRMS m/e: 208.0922 [calc.for $C_{12}H_{16}SO$(M^+): 208.0922].

endo-*5-Methyl-6-phenylsulfanyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **6h** *(R= Me)*

Following the general procedure [MeLi (0.8 ml of 1.6 M solution in hexane, 1.3 mmol), CuI (112 mg, 0.59 mmol), **4h** (100 mg, 0.38 mmol)], gave, after work-up and flash chromatography (n-hexane /EtOAc= 95/5), 93 mg (90 %) of **6h** as a colorless crystalline solid.

6h (R= Me): m.p.: 58 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55 and 7.38 (2 x m, 5H, ph-H), 6.31 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 6.13 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 3.27 and 3.08 (2 x m, 2H, H_1 and H_7), 3.01 (d, $J_{1,2}$=5.0 Hz, 1H, H_2), 2.72 (m, 1H, H_5)(dd, $J_{5,4x}$=9.5 Hz, $J_{5,4n}$=12.5 Hz from NOE irradiating CH_3), 2.45 A of AB (d, $J_{10a,s}$=8.6 Hz, 1H, H_{10s}), 2.18 A of AB (ddd, $J_{4x,n}$=18.6 Hz, $J_{4x,5}$=9.5 Hz, $J_{4x,2}$=1.5 Hz, 1H, H_{4x}), 1.78 B of AB (dd, $J_{4x,n}$=18.6 Hz, $J_{4n,5}$=12.5 Hz, 1H, H_{4n}), 1.73 B of AB (d, $J_{10a,s}$=8.6 Hz, 1H, H_{10a}), 0.94 (d, J=7.0 Hz, 3H, CH_3). IR (CH_2Cl_2): υ 3010-2820 (C-H), 1725 (C=O) cm^{-1}. EI/MS: m/e (%) 205 (100, M^++1-C_5H_6), 204 (61, M^+-C_5H_6), 189 (18, M^+-C_5H_6-CH_3), 95 (28, M^+-C_5H_6-SPh), 66 (23, $C_5H_6^+$). EI/HRMS m/e: 205.0686 [calc.for $C_{12}H_{13}SO$(M^++1-C_5H_6): 205.0684].

endo-*5-n-Butyl-6-phenylsulfanyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **6h** *(R= n-Bu)*

Following the general procedure [BuLi (1.2 ml of 1.6 M solution in hexane, 1.9 mmol), CuI (180 mg, 0.95

mmol), **4h** (140 mg, 0.55 mmol)], gave, after work-up and flash chromatography (n-hexane /EtOAc= 95/5), 145 mg (85 %) of **6h** and 5 mg (ca. 3%) of **5h**.

6h (R= n-Bu): m.p.: 50 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54 and 7.36 (2 x m, 5H, Ph-H), 6.28 A of AB (dd, $J_{8,9}$=5.4 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 6.12 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 3.26 and 3.08 (2 x bs, 2H, H_1 and H_7), 2.99 (d, $J_{1,2}$=4.9 Hz, 1H, H_2), 2.58 (m, 1H, H_5), 2.44 A of AB (d, $J_{10a,s}$=8.5 Hz, 1H, H_{10s}), 2.22 A of AB (dd, $J_{4x,n}$=18.4 Hz, $J_{4x,5}$=9.5 Hz, 1H, H_{4x}), 1.72 (m, 2H, H_{4n} and H_{10a}), 1.51 and 1.25-1.06 [2 x m, 6H, $(CH_2)_3CH_3$], 0.84 (t, J=7.0 Hz, 3H, CH_3). IR (CH_2Cl_2): υ 3010-2820 (C-H), 1725 (C=O) cm^{-1}. EI/MS: m/e (%) 312 (0.6, M^+), 247 (100, M^++1-C_5H_6), 190 (71, M^++1-C_5H_6-C_4H_9), 66 (20, $C_5H_6^+$). EI/HRMS m/e: 312.1547 [calc.for $C_{20}H_{24}SO(M^+)$: 312.1548].

5h (R=n-Bu): δ 7.53 and 7.33 (2 x m, 5H, Ph-H), 6.28 and 6.10 AB pattern (2 x dd, $J_{1,9}$=$J_{7,8}$=3.0 Hz, 2H, H_8 and H_9), 3.27 and 3.09 (2 x bs, 2H, H_1 and H_7), 3.04 (d, $J_{1,2}$=5.0 Hz, 1H, H_2), 2.45 A of AB (d, $J_{10a,s}$=8.6 Hz, 1H, H_{10s}), 2.35 and 2.03 (2 x m, 2H, H_{4x} and H_5), 1.81-0.85 [m, 8H, H_{4n}, H_{10a} and $(CH_2)_3CH_3$], 0.75 (t, J=7.3 Hz, 3H, CH_3).

endo-*5-Methyl-6-phenylselenyl*-endo-*tricyclo[5.2.1.0^{2,6}]deca-8-en-3-one* **6i**

Following the general procedure [MeLi (1 ml of 1.6 M solution in hexane, 1.6 mmol), CuI (200 mg, 1 mmol), **4i** (150 mg, 0.5 mmol)], gave, after work-up and flash chromatography (n-hexane /EtOAc= 95/5), 140 mg (89 %) of **6i** as a white solid.

6i: m.p.: 61-62 °C (diisopropylether). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66- 7.29 (m, 5H, Ph-H), 6.31 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 6.12 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.27 and 3.12 (2 x brs, 3H, H_1, H_2 and H_7), 2.81-2.71 (m, 1H, H_5), 2.39 A of AB (d, $J_{10a,s}$=8.6 Hz, 1H, H_{10s}), 2.08 A of AB (dd, $J_{4x,4n}$=18.4 Hz, $J_{4x,5}$=9.5 Hz, 1H, H_{4x}), 1.78 B of AB (dd, $J_{4x,4n}$=18.4 Hz, $J_{4n,5}$=12.5 Hz, H_{4n}), 1.76 B of AB (d, $J_{10a,s}$=8.6 Hz, 1H, H_{10a}), 0.98 (d, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 218.8 (quat.), 137.7/137.5/136.0/129.2/129.1 (tert.), 128.2/63.6 (quat.), 62.8 (tert.), 53.4 (sec.), 52.4 (tert.), 49.4 (sec.), 48.3 (tert.), 39.7 (tert.), 14.6 (prim.). IR (CH_2Cl_2): υ 3080-3020 (C-H, unsat.), 3010-2860 (C-H, sat.), 1730 (C=O) cm^{-1}. EI/MS: m/e (%) 318 (9, M^+), 252 (77, M^+-C_5H_6), 161 (45, M^+-SePh), 133 (59, M^+-SePh-CO), 95 (100, M^+-SePh-C_5H_6), 66 (53, $C_5H_6^+$). EI/HRMS m/e: 318.0524 [calc.for $C_{17}H_{18}O^{80}Se$ (M^+): 318.0523].

6-Methylsulfinyl-endo-*tricyclo[5.2.1.0^{2,6}]dec-4,8-dien-3-one* **4j**

A solution of $NaIO_4$ (3 equiv.) in water (20 ml) was added dropwise to a solution of sulfide **4g** (1.5 mmol) in methanol (25 ml) with stirring at room temp. After 1 hour the reaction mixture was filtered and methanol was evaporated under reduced pressure to gave an oil. Flash chromatography (EtOAc/methanol = 80/20) gave 183 mg **4j^a** (58%) and 102 mg **4j^b** (33%) as colorless crystalline solids.

4j^a: m.p.: 135 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.65 (d, $J_{4,5}$=5.8 Hz, 1H, H_5), 6.35 (d, $J_{4,5}$=5.8 Hz, 1H, H_4), 6.09 A of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.1 Hz, 1H, H_8 or H_9), 6.05 B of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.7 Hz, 1H, H_8 or H_9), 3.47 and 3.31 (2 x bs, 2H, H_1 and H_7), 2.81 (d, $J_{1,2}$=4.6 Hz, 1H, H_2), 2.56 (s, 3H, $SOCH_3$), 2.15 A of AB (d, $J_{10a,s}$=9.3 Hz, 1H, H_{10s}), 1.87 B of AB (d, $J_{10a,s}$=9.3 Hz, 1H, H_{10a}). IR (CH_2Cl_2): υ 3010-2860 (C-H), 1705 (C=O) cm^{-1}. EI/MS: m/e (%) 208 (0.5, M^+), 145 (100, M^+-$SOCH_3$), 127 (15, M^+-C_5H_6-CH_3), 117 (59, M^+-$SOCH_3$-CO), 79 (84, M^+-$SOCH_3$-C_5H_6), 66 (11,C_5H_6). EI/HRMS m/e: 208.0559 [calc.for $C_{11}H_{12}SO_2(M^+)$: 208.0558].

4j[b]: m.p.: 111 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, $J_{4,5}$=5.8 Hz, 1H, H_5), 6.29 (d, $J_{4,5}$=5.8 Hz, 1H, H_4), 6.10 A of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 6.06 B of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.8 Hz, 1H, H_8 or H_9), 3.34 (bs, 1H, H_1 or H_7), 3.21 (d, $J_{1,2}$=4.5 Hz, 1H, H_2), 3.05 (bs, 1H, H_1 or H_7), 2.82 (s, 3H, $SOCH_3$), 2.17 A of AB (d, $J_{10a,s}$=9.2 Hz, 1H, H_{10s}), 1.83 B of AB (d, $J_{10a,s}$=9.2 Hz, 1H, H_{10a}). IR (CH_2Cl_2): υ 3010-2860 (C-H), 1705 (C=O) cm^{-1}. EI/MS: m/e (%) 208 (0.7, M^+), 145 (100, M^+-$SOCH_3$), 127 (10, M^+-C_5H_6-CH_3), 117 (43, M^+-$SOCH_3$-CO), 79 (55, M^+-$SOCH_3$-C_5H_6), 66 (7, C_5H_6). EI/HRMS m/e: 208.0555 [calc.for $C_{11}H_{12}SO_2(M^+)$: 208.0558].

endo-*5-Methyl-6-methylsulfinyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **6j**[a]

A solution of MeLi (1.2 ml of a 1.6 M solution in hexane, 1.9 mmol) in hexane was gradually added to a suspension of dry CuI (200 mg, 1 mmol) in dry ether at temp. below 0 °C (ice-salt) in a nitrogen atmosphere. After stirring for 15 min., a solution of **4j**[a] (100 mg, 0.48 mmol) in THF was added. The mixture was then stirred at 10 °C until the reaction was complete according to TLC (ca. 2h). The mixture was quenched with aqueous ammonium chloride and the aqueous phase extracted with ether (3x). The combined organic phases were washed with water (3x), dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. Flash chromatography (EtOAc/methanol= 9/1) gave 107 mg (98 %) of **6j**[a] as a colorless crystalline solid.

6j[a]: m.p.: 154 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.51 A of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 6.30 B of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.58 and 3.25 (2 x bs, 2H, H_1 and H_7), 2.80 (d, $J_{1,2}$=4.8 Hz, 1H, H_2), 2.72 (m, 1H, H_5), 2.59 (s, 3H, $SOCH_3$), 2.49 A of AB (ddd, $J_{4x,n}$=18.9 Hz, $J_{4x,5}$=9.9 Hz, $J_{4x,2}$=1.1 Hz, 1H, H_{4x}), 2.16 A of AB (d, $J_{10a,s}$=9.1 Hz, 1H, H_{10s}), 1.94 B of AB (dd, $J_{4x,n}$=18.9 Hz, $J_{4n,5}$=11.3 Hz, 1H, H_{4n}), 1.67 B of AB (d, $J_{10a,s}$=9.1 Hz, 1H, H_{10a}), 1.24 (d, J=6.9 Hz, 3H, CH_3). IR (CH_2Cl_2): υ 3010-2860 (C-H), 1735 (C=O) cm^{-1}. CI/MS: m/e (%) 225 (10, M^++1), 161 (100, M^+-$SOCH_3$), 133 (41, M^+-$SOCH_3$-CO), 95 (25, M^+-$SOCH_3$-C_5H_6). EI/HRMS m/e: 224.0869 [calc.for $C_{12}H_{16}SO_2(M^+)$: 224.0871].

6-Phenylsulfinyl-endo-*tricyclo[5.2.1.0^{2,6}]dec-4,8-dien-3-one* **4k**

A solution of $NaIO_4$ (3 equiv.) in water (20 ml) was added dropwise to a solution of sulfide **4h** (450 mg, 1.77 mmol) in methanol (25 ml) with stirring at room temp. After 1 hour the reaction mixture was filtered and methanol was evaporated under reduced pressure to gave an oil. Flash chromatography (EtOAc/methanol = 80/20) gave 300 mg of **4k**[a] (63%) and 100 mg of **4k**[b] (31%) as colorless crystalline solids.

4k[a]: m.p.: 190 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55-7.44 (m, 6H, H_5 and Ph-H), 6.04-5.99 (m, 2H, H_8 and H_9), 5.87 (d, $J_{4,5}$=5.8 Hz, 1H, H_4), 3.68 and 3.35 (2 x bs, 2H, H_1 and H_7), 2.64 (d, $J_{1,2}$=4.6 Hz, 1H, H_2), 2.32 A of AB (d, $J_{10a,s}$=9.4 Hz, 1H, H_{10s}), 1.97 B of AB (d, $J_{10a,s}$=9.3 Hz, 1H, H_{10a}); ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 205.3 (quat.), 158.3 (tert.), 140.2 (quat.), 139.3/135.3/134.2/131.9/129.0 x2/125.5 x2 (tert.), 80.5 (quat.), 53.0 (tert.), 50.8 (sec.), 46.3 x2 (tert.). IR (CH_2Cl_2): υ 3010-2820 (C-H), 1710 (C=O) cm^{-1}. EI/MS: m/e (%) 270 (0.4, M^+), 145 (100, M^+-SOPh), 79 (63, M^+-SOPh-C_5H_6), 66 (5, $C_5H_6^+$). EI/HRMS m/e: 270.0715 [calc.for $C_{16}H_{14}SO_2(M^+)$: 270.0715].

4k[b]: m.p.: 120 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66-7.62 and 7.60-7.27 (m, 5H, Ph-H), 6.81 (d, $J_{4,5}$=5.8 Hz, 1H, H_5), 6.14 (d, $J_{4,5}$=5.8 Hz, 1H, H_4), 6.07 A of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz,

1H, H_8 or H_9), 5.87 B of AB (dd, $J_{8,9}$=5.5 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.41 (bs, 1H, H_1 or H_7), 3.33 (d, $J_{1,2}$=4.6 Hz, 1H, H_2), 3.00 (bs, 1H, H_1 or H_7), 2.40 A of AB (d, $J_{10a,s}$=9.1 Hz, 1H, H_{10s}), 1.91 B of AB (d, $J_{10a,s}$=9.1 Hz, 1H, H_{10a}); ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 206.1 (quat.), 155.8/141.1 (tert.), 140.3 (quat.), 136.1/133.5/131.9/129.1x2/125.5x2 (tert.), 80.9 (quat.), 53.0 (tert.), 51.1 (sec.), 46.4/46.0 (tert.). IR (CH_2Cl_2): υ 3010-2820 (C-H), 1710 (C=O, conj.) cm^{-1}. EI/MS: m/e (%) 270 (0.5, M^+), 145 (100, M^+-SOPh), 117 (80, M^+-SOPh-CO), 79 (85, M^+-SOPh-C_5H_6), 66 (7, $C_5H_6^+$). EI/HRMS m/e: 270.0715 [calc.for $C_{16}H_{14}SO_2(M^+)$: 270.0715].

endo-*5-Methyl-6-phenylsulfinyl*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **6k**[a]

A solution of MeLi (0.6 ml of a 1.6 M solution in hexane, 0.95 mmol) in hexane was gradually added to a suspension of dry CuI (100 mg, 0.5 mmol) in dry ether at temp. below 0 °C (ice-salt) under a nitrogen atmosphere. After stirring for 15 minutes, a solution of **4k**[a] (50 mg, 0.18 mmol) in THF was added. The mixture was stirred at 10 °C until the reaction was complete according to TLC (ca. 2h). The mixture was then quenched with aqueous ammonium chloride and the aqueous phase extracted with ether (3x). The combined organic phases were washed with brine (3x), dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. Flash chromatography (EtOAc/methanol= 80/20) gave 48 mg (46%) of **6k**[a] as a colorless solid.

6k[a]: m.p.: 105 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 and 7.54 (2 x m, 5H, ph-H), 6.44 A of AB (dd, $J_{8,9}$=5.3 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.2 Hz, 1H, H_8 or H_9), 6.25 B of AB (dd, $J_{8,9}$=5.3 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 3.63 and 3.28 (2 x bs, 2H, H_1 and H_7), 2.95 (d, $J_{1,2}$=4.7 Hz, 1H, H_2), 2.73 (m, 1H, H_5), 2.35 A of AB (d, $J_{10a,s}$=9.1 Hz, 1H, H_{10s}), 2.17 A of AB (ddd, $J_{4x,n}$=18.8 Hz, $J_{4x,5}$=10.0 Hz, $J_{4x,2}$=1.4 Hz, 1H, H_{4x}), 1.75 B of AB (dd, $J_{4x,n}$=18.8 Hz, $J_{4n,5}$=11.2 Hz, 1H, H_{4n}), 1.76 B of AB (d, $J_{10a,s}$=9.1 Hz, 1H, H_{10a}), 1.09 (d, J=7.0 Hz, 3H, CH_3). IR (CH_2Cl_2): υ 3010-2820 (C-H), 1730 (C=O) cm^{-1}. EI/MS: m/e (%) 287 (0.7, M^++1), 221 (3, M^++1-C_5H_6)), 161 (100, M^+-SOPh), 133 (47, M^+-SOPh-CO), 95 (92, M^+-C_5H_6-SPh), 66 (30, $C_5H_6^+$). EI/HRMS m/e: 286.1028 [calc.for $C_{17}H_{18}SO_2(M^+)$: 286.1028].

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