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# Highly diastereodifferentiating and regioselective [2+2]-photoreactions using methoxyaromatic menthyl cyclohexenone carboxylates



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#### 1. Introduction

Photochemical initiated cycloadditions are often used as a key step not only in natural product synthesis but also to build up key bond constructions in the complex molecule environment.<sup>1</sup> Especially the [2+2]-photoreaction of alkenones with olefins has been of great interest and well investigated, as the formed strained cvclobutane adducts are difficult to build under thermal conditions but often found as a challenging structural motive in complex synthesis.<sup>1</sup> Nevertheless photoreactions can yield in a mixture of stereo- and regioisomeric products because the reactions include excited states, short lifetimes, and weak interactions. This is why the [2+2]-photoreaction is up to now not often being found in stereoselective reaction sequences. As the [2+2]-photoreaction is a powerful tool to compose strained rings with up to four stereocenters in just one step, the stereoselective photoreaction is still challenging the researcher mind. Different approaches as solidstate photochemistry and supramolecular photochemistry,<sup>2</sup> as well as photochemical reactions using chiral auxiliaries and sensitizers<sup>3</sup> have up to now lead to great achievements in the field of asymmetric photochemical synthesis. To the chromophore or the alkene attached chiral framework has been widely used and

#### ABSTRACT

Chiral Cyclohexenone **1a** is irradiated in the presence of various alkenes to yield highly diastereodifferentiating (15,65) configurated oxobicyclo[4.2.0]octanes. For increasing the de of the reaction, we designed a new chiral auxiliary owing a methoxynaphthylmenthyl moiety **b**: cyclohexenone carboxylate **1b**. Irradiation of **1b** in the presence of various alkenes shows high diastereo- and regioselectivity, yielding (15,65)-bicyclo[4.2.0]octan-2-ones with a de of up to 96%.

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opened a promising way of inducing asymmetry in (inter- and intramolecular) photoreactions. For such kind of diastereoselective reactions, a wide range of natural products, such as menthol,<sup>4,5</sup> camphor,<sup>3a</sup> tartaric acid,<sup>6a,b</sup> and bornyl<sup>6c</sup> has been used as chiral auxiliary so far. However, generality as well as high selectivity in diastereoselective photoreactions have not yet been elucidated. We concentrated on using a menthol based chiral auxiliary attached via carboxylate bond to the irradiated enone ensuring an easy removal of the chiral auxiliary after the reaction.<sup>4</sup> So far we found that the best diastereomeric excess value (de) in a diastereodifferentiating [2+2]-photoreaction with ethylene could be achieved by attaching an 8-(*p*-substituted-phenyl)menthyl-modified chiral auxiliary (**a**) to the used cyclohexenone carboxylates. Irradiation of 8-(4methoxyphenyl)-menthyl attached cyclohexenone-carboxylate 1a conducts in the presence of the simplest alkene, ethylene, with a de up to 81%.<sup>4c</sup> We now expanded our research on developing a new chiral auxiliary (**b**) introducing even higher de in a [2+2]photoreaction. Here we report our result on [2+2]-photoreactions of chiral cyclohexenones 1a,b using methoxyarylmenthol based auxiliaries, not only in regard to its diastereoselectivity but also to its regioselectivity in the presence of various alkenes (see Fig. 1).

#### 2. Results and discussion

As we could prove,<sup>4a</sup> the 8-(*p*-methoxysubstitutedphenyl) menthyl attached cyclohexen-onecarboxylate **1a** can exist in



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**Fig. 1.** Diastereoselective [2+2]-photocycloaddition of **1a**,**b** using chiral menthyl based auxiliaries **a** and **b** in the presence of alkenes **c**–**g**, and stacked conformation of substrate in a bracket.

different conformers, among with the stacked trans form, wherein the cyclohexenone and the aryl moiety are located face to face to each other, is the most likely to be populated at low temperature (see Fig. 1). In this conformation one diastereotopic reaction side (Re-face) is shielded by the chiral auxiliary making the attack of the alkene from the Si-face side of the molecule being highly favored. For enhancing the shielding of the Re-side of the cyclohexenone, we developed a new chiral auxiliary, 6-methoxynaphthyl-menthyl (**b**), which owns a methoxynaphthyl-moiety instead of the aryl moiety. The used methoxymoiety in para-position will additionally stabilize the desired conformation by acceptor-donor interactions. Furthermore we investigated the influence of the substitution pattern of the alkene to the de-value of the photoreactions. Therefore we irradiated compounds **1a**,**b** in the presence of different alkenes as ethylene (c), 2-methylbut-2-ene, (d) 2-methylprop-2-ene ( $\mathbf{e}$ ), methacrylonitrile ( $\mathbf{f}$ ), and 2-methoxypropene ( $\mathbf{g}$ ). In general, higher substituted asymmetric alkenes are not often used in photoreactions, as due to its asymmetry the possible formation of regioisomeric products will increase, causing a decrease of the reaction's selectivity. Considering the [2+2]-photoreaction of the cyclohexenone carboxylates 1a,b to asymmetric alkenes c-g, a wide range of [2+2]-photocycloadducts is possible to be built. The primary attack from the alkene can occur from both diastereotopic sides of the cyclohexenone yielding in diastereomeric products (different in configuration at C-1 and C-6 (Fig. 2a)). If using an asymmetric alkene as the reaction partner, the amount of possible built cyclobutanes increases, as the regioselectivity of the reaction has to be concerned as well. In dependence of the orientation of the alkene toward the reacting double bond, the regioisomeric Head to Head as well as the Head to Tail product can be formed (see Fig. 2b). Fig. 2b also shows the possible diastereomeric products, which can be obtained in dependence of the substitution pattern of the alkene at the C-7 or C-8 position of the new formed cyclobutanes. Possible from this reaction resulting regio- and diastereomers are shown in Fig. 1.

#### 2.1. Photoreaction of 1a with alkenes c-g

Investigation of the influence of the alkene to the regio- and diastereoselectivity of the [2+2]-photoreaction was conducted by irradiation of **1a** in the presence of the alkenes **c**–**g**. The results are shown in Table 1. Entry 1 shows the already published data<sup>4a</sup> of **1a** with the simplest alkene ethylene (**c**) for referring. All of the shown

reactions conduct under nearly complete conversion of the cyclohexenone to yield [2+2]-photoproducts. The main product of the reaction is independently of the used alkene a *cis*-fused (15,65)oxobicyclo[4.2.0]octane. Irradiation in the presence of 2methylbut-2-ene (d) led to the formation of three products: the main product 2ad, its regioisomer 3ad as well as the diastereomer **4ad** (wherein the configuration of the bridged carbons is 1R and 6*R*), conducting with a de (concerning the diastereodifferentiating attack of the alkene 2ad/4ad) of 85% (entry 3). Photoreaction of 1a with 2-methylprop-2-ene (e) yields four products. Main product of the reaction was the 7,7-dimethyl-3-oxobicyclo[4.2.0]octane 2ae, together with the byproduct, its diastereomer 4ae, which is formed in a ratio of 8% (entry 5). Besides the cycloadducts, two 3-(2methylallyl)cyclohexanones (6ae/7ae) were found in the reaction. These products are formed by H-transfer of the primary generated biradical intermediate (see Fig. 3) and are known to be formed when 2-methylprop-2-ene as the alkene partner is employed in a [2+2]-photoreaction.<sup>7</sup>



**Fig. 2.** (a) Possible diastereomeric cyclobutanes in dependence of the attacking side of the alkene; (1) attack from the *Re*-side yielding in (1*R*,6*R*)-oxobicyclo[4.2.0]octanes and (2) attack from the *Si*-side yielding in (1*S*,65)-oxobicyclo[4.2.0]octanes. (b) Possible regioisomeric cyclobutanes built via photoreaction with asymmetric alkenes and therefrom resulting diastereomers differing in the newly built asymmetric *C*-atom (C-7/C-8) (only showed for the (1*S*,65)-configurated diastereomer).

On irradiation of **1a** in the presence of methacrylonitrile (**f**) a highly diastereoselective and regioselective reaction was observed. As the main product of the reaction the 7-methyl-5oxobicyclo[4.2.0]octane-7-carbonitrile 2af1 could be assigned. The respective diastereomer  $2af_2$  (owing a different configuration at the C-7 atom (R-configurated)) as well as the (1R,6R)-fused diastereomer 4af were found in a ratio of 14:6, respectively. Noteworthy to say is, that the reaction proceeds completely regioselective, as no Head to Tail product can be found. Using methoxypropene  $(\mathbf{g})$  as the alkene partner, a contrarious photochemical behavior was found. The main product of the reaction is the Head to Tail product **3ag**. In this case, a number of byproducts were produced but could not be assigned due to their small amount. Remarkable is that all shown photoreactions, besides being highly diastereoselective in their attack toward the enone, proceed with a high regioselectivity. Irradiation of 1a in the presence of alkenes **d**-**f** yielded the *Head to Head* adducts irrespective of the substitution pattern of the used alkenes. These products are formed via addition of the alkene from the Si-side face of the cyclohexenone in high diastereoselectivity (regarding the configuration of the bicyclic framework). The formation of the Head to Tail

Table 1	
Photocycloadditions of <b>1a</b> + <b>b</b> in the presence of	alkenes <b>c-g</b>

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	Entry	Alkene	Enone	Product ratio <sup>b</sup>	Yield <sup>c</sup> [%]	$de = \left(\frac{2ax - 4ax}{2ax + 4ax}\right)$
	1 <sup>e</sup>	=== (c)	1a	90:9 ( <b>2ac/4ac</b> )	96	81
	2		1b	100:4 ( <b>2bc/4bc</b> )	97	92
	3	(d)	1a	100:8:11 ( <b>2ad/4ad/3ad</b> )	82	85
	4		1b	100:7:25 ( <b>2bd/4bd/3bd</b> )	90	87
	5	<b></b> (e)	1a	100:8 <sup>f</sup> ( <b>2ae/4ae</b> )	85	85
	6		1b	$100:<2^{f}$ (2be/4be)	92	>95
	7	$= \swarrow^{CN}(\mathbf{f})$	1a	100:14:6 ( <b>2af<sub>1</sub>/<sup>g</sup>2af<sub>2</sub>/<sup>g</sup>4af</b> )	86	90
	8		1b	$\begin{array}{l} 100:25:<\!\!2\\ (2bf_1/^{g}\!2bf_2/^{g}\!4bf) \end{array}$	87	>95
	9	OMe (g)	1a	3ag	72	nd <sup>h</sup>
	10		1b	3bg	75	nd <sup>h</sup>

<sup>a</sup> c=0.05 mM of **1a**, c=0.005 mM of **1b** in MCH,  $-78 \degree C$ ,  $c_{(alkene)}=20$  M excess, for using gaseous alkenes **c** and **e**: bubbling of the solution for 5 min at 25 °C, irradiation time in dependence of complete conversion monitored by NMR 1.5-6 h.

Assigned from the crude NMR-mixture. Isolated yield after evaporation of the solvent and CC.

<sup>d</sup> Determined by <sup>1</sup>H NMR spectroscopy. For assigning the de-value using <sup>1</sup>H NMR, characteristic clearly separated signals caused by the proton at the C-6 atom of the cyclobutanes were used.

Ref. 4a.

<sup>f</sup> The reaction gave the products **6ae** and **7ae** additionally formed via [H]-transfer in a ratio of 2:1 (see Fig. 3).

<sup>g</sup> 2af<sub>1</sub>/2bf<sub>1</sub> and 2af<sub>2</sub>/2bf<sub>2</sub> owns a different configuration at C-7, 2af<sub>1</sub>/2bf<sub>1</sub>: S-configurated/2af2/2bf2: R-configurated. The de value is given for the diastereomeric ratio of the bridge atoms of the bicyclic framework (C-1 and C-6).

<sup>h</sup> The reaction yields various byproducts, therefore the de could not be determined (nd).



Fig. 3. Photoproducts of enones 1a.b with 2-methylprop-2-ene (e) via [H]-transfer (for 1a: product ratio of 2ae/6ae/7ae is 100:40:20; for 1b:2be/6be/7be is 100:15:15).

products could not be observed for these alkenes. The respective regioisomer (**3ax**) was only observed as a minor product using methylbut-2-ene (**d**). Alkenes **e** and **f**, which own two germinal C-atoms, which clearly differs in their steric demand, show even regioselective addition, as no Head to Tail product can be found. Using methacrylonitrile  $(\mathbf{f})$  as the alkene partner, a regioselective as well as highly diastereoselective photoreaction occurred. The main product **2af**<sub>1</sub> is built via primary binding of the cyclohexenone to

the less substituted C-atom of the alkene. The two diastereomers **2af**<sub>1</sub> and **2af**<sub>2</sub> differ thereby in their configuration at the C-7 position; **2af**<sub>1</sub>: S-configurated, **2af**<sub>2</sub>: R-configurated. Concerning the diastereoselectivity of the reaction in adding to the enones, two products (as shown in Fig. 2a) are possible to be formed. The assignment of the main products to be (15.65) configurated is based on comparison to the photoproducts of irradiating **1b** in the presence of ethylene (2bc). The cyclobutane obtained as the main product can be proven to be (15,6S) configurated by respective Xray analysis. The minor product, the (1R,6R) configurated oxobicyclo[4.2.0]octane, shows analogues signals in the <sup>1</sup>H NMR spectra. The characteristic signal of the proton at C-6 is shifted in the minor product to higher applied field. As all of the here shown crude reactions mixtures of the irradiation of 1a in the presence of different alkenes show analogues pairs of signals, the configuration of the products **2ad**-ag and **4ad**-ag are highly presumable to be alike. The configuration of the moiety at C-7 could be assigned by NOE studies of the  $\alpha$ -acidic proton of the carbonylgroup as well as for the methyl moiety at C-7. The measurements were conducted for both of the two different diastereomers and are also supported for compound **2af**<sub>1</sub> and **2af**<sub>2</sub> by NMR-Data of cyclobutanecarbonitriles.<sup>7b,d,8</sup> Based on this measurement the C-atom at C-7 has S-configuration allowing the most voluminous moiety to be located on the less hindered side of the cyclohexenone (see Fig. 4). However the described regioselectivity could not be found on irradiation of **1a** in the presence of 2-methoxyprop-1-ene (**g**). As the isolated main product of the reaction, the Head to Tail adduct 3ag, (C-8: R-configurated) could be characterized.



Fig. 4. Favored orientation of the attacking alkene toward the cyclohexenone for (a) methacrylonitrile and (b) methoxypropene and resulting configuration of the cvclobutanes.

The finding on the regioselectivity of the [2+2]-photoreaction is just opposite to the ones found for using simple cyclohexenones.<sup>7a,c,d,9</sup> For suchlike compounds mainly the electron distribution is thought to govern the reaction's regioselectivity. Using more complex molecules, the influence of the steric hindrance to the reaction will become, as well as the influence of the used solvent, predominant. An explanation for this highly regioselective and diastereoselective behavior, can be given regarding the stereochemistry of the molecule. As the Re-side is shielded by the naphthylmenthyl moiety, the attack will occur from the Si-side resulting in a highly diastereoselective reaction, which yields cis-fused (15,6S)-configurated oxo-bicyclo[4.2.0]octanes. Concerning the reaction's regioselectivity, an orientated  $\pi$ -complex between the alkene and the enone moiety is likely to be formed, to which the alkene, such as 2-methylprop-2-ene  $(\mathbf{e})$  and methacrylonitrile  $(\mathbf{f})$ will approach from the most unhindered reaction quarter (see Fig. 4) avoiding a steric hindrance with the menthyl moiety. Following ring closure reaction of the 1,4-biradical intermediate will yield the C-7 atom S-configurated product **2af**<sub>1</sub> in the case of methacrylonitrile (f). The *R*-configurated minor product **2af**<sub>2</sub> can only be obtained in a trace amount. It should also be mentioned that interestingly the Head to Head products are obtained, in sharp contrast to the results of similar photoreactions of simple cyclohexenones, where the Head to Tail products are mainly obtained. These results also show that the primary binding occurs at the  $\beta$ -atom of the enone vielding the 1.4biradical as shown in Fig. 3. Production of the ene products **6ae** and 7ae via the same biracial species also supports the primary attack of the alkene at the  $\beta$ -atom of the enone. Using methoxypropene (g) as the alkene partner, a different orientation to the reacting double bond is observed to give the Head to Tail adduct 3ag. The C-8 atom of the newly formed cyclobutane will be R-configurated, allowing the methoxygroup to avoid steric hindrance with the menthyl moiety. The reason for the different regioselectivity of this reaction might lie in the fact that the additional repulsion caused by the methoxypropene's oxygen atom suppresses the formation of the Head to Head product, but will need further investigation to be carried out. As all of the reactions of enone 1a show a diastereoselectivity (<95%), which is not satisfying for synthetic organic reactions, we now tried to increase the reaction's selectivity by irradiating the newly synthesized 6-methoxynaphthylmenthyl carboxylate 1b in the presence of the alkenes **c**–**g**.

#### 2.2. Photoreaction of 1b in the presence of alkenes c-g

The results on irradiation of **1b** in the presence of the alkenes c-g are listed in Table 1. As expected, photoreaction of compound **1b** 

Table 2
Photocycloadditions of 1b with alkene c at different temperatures

Entry	Temperature [°C]	Product ratio <sup>b</sup> ( <b>2bc/4bc</b> )	$de = \left(\!\frac{2bx-4bx}{2bx+4bx}\!\right)\!\!\%^{\!c}$
1	-100	98:2	96
2	-78	100:4	92
3	-60	93.5:6.5	87
4	-40	89.5:10.5	79
5	-20	85:15	70
6	0	81.5:18.5	63

 $^{a}$  c=0.005 mM of **1b** in MCH, –78 °C, c<sub>(alkene)</sub>=bubbling with ethylene gas for 5 min at 25 °C.

<sup>b</sup> Assigned from the crude NMR-mixture.

<sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy for assigning of the de-value using <sup>1</sup>H NMR, characteristic clearly separated signals caused by the proton at the C-6 atom of the cyclobutanes were used.

with ethylene showed a highly diastereoselective manner (entry 2). The (1*S*,*6S*)-configurated oxobicyclo[4.2.0]octane **2bc** was obtained in a diastereoselectivity of 92%. The main product of the reaction is the [2+2]-photoproduct formed via attack of the alkene from the less shielded *Si*-side of the cyclohexenone carboxylate. The absolute configuration of **2bc** could be assigned after chromatographic separation of the diastereomers by X-ray analysis (Fig. 5). Diastereodifferentiating [2+2]-photoreactions of **1b** in the presence of higher substituted alkenes **d**–**g** proceeded with the complete conversion of the starting material. The found products could be separated and assigned completely by 2D-NMR, and were characterized to be analogously formed cyclobutanes adducts to the ones



Fig. 5. ORTEP-diagram of compound 2bc.<sup>10</sup>

described above (for using **1a**). They show the same photochemical behavior concerning their regio- and diastereoselectivity (entries 3–10). Irradiation of **1b** in the presence of 2-methylprop-2-ene (**e**) and methacrylonitrile (f) yielded the main products **2be** and **2bf**<sub>1</sub>, respectively, with high regioselectivity. The formation of other regioisomers in the photoreaction of **1b** with the alkenes d-f, is suppressed due to the enhanced shielding of the *Re*-side of the molecule. This may be the reason for the high regioselectivity. Additionally an enhancement in the reaction's de (toward the diastereoselective addition to the enone) can be found. Irradiating the cyclohexenecarboxylate **1a** and **1b**, we could find, that asymmetric alkenes add regioselective as well as highly diastereoselective vielding in (15,6S)-configurated oxo-bicyclo[4.2.0]octanes. Using the alkenes **d**–**f**, the reaction gave the *Head to Head* photoproducts as the main product. The formation of the *Head to Tail* products is depressed. Moreover we could not only succeed on an improvement of the regioselectivity of the reaction but also on its diastereoselectivity when using the methoxynaphthylmenthyl auxiliary (**b**). The [2+2]-photoreaction of **1b** in the presence of alkene **d**–**f** yielded highly diastereoselective the products **2bc-2bf**, respectively.

Furthermore the effect of the temperature to the reaction was investigated by irradiating **1b** in the presence of ethylene (**c**) at different temperatures. The results are given in Table 2. Entries 1-6 clearly show that decreasing the temperature of the reacting system yields in higher de of the reaction. Irradiation at -100 °C even increases the de of the reaction to 96%. These results can be explained regarding the structure of the enone **1b**. The lower the temperature, the more likely the enone **1b** will be fixed in the closed stacked trans conformation (see Fig. 1), which induces a high shielding of one diastereotopic reaction side of the enone yielding in a high de. This stacked trans conformer can not only be stabilized by decreasing the temperature but also by the substituent at the aromatic ring. Irradiation of 1b, which owns a methoxymoiety at the naphthylring shows higher de than its unsubstituted analogue **1a** in the [2+2]-photocycloadditions. This fact clearly supports the results, which were found for the [2+2]-photoreaction of analogues methoxyphenyl- and the phenyl substituted cyclohexenone carboxylates compounds we investigated before.<sup>4a,d</sup> Herein, too, irradiation of the methoxyphenyl substituted analogue with ethylene yield in higher de than its corresponding phenyl analogue. As reported before<sup>4d</sup> the methoxymoiety at the aromatic ring seems to stabilize the stacked trans conformer by additional donor-acceptor interactions. The resulting stronger  $\pi$ -stacking between the aromatic ring and the enone causes an effective shielding of the Reside yielding in a highly diastereoselective reaction.

#### 3. Conclusion

Irradiation of **1a** in the presence of ethylene (**c**) gave the product **2ac** with a de value of 81%. For enhancing the de in [2+2]-photoreactions we designed a new menthyl-based chiral auxiliary owing a methoxynaphthyl moiety (**b**) ensuring even higher shielding of one diastereotopic side of the stacked conformer. On irradiation of **1b** in the presence of ethylene, we could succeed in finding a quantitative and highly diastereoselective reaction, which converted **1b** into the [2+2]-photocycloadduct **2bc** with a de of up to 96%.

Moreover we investigated the photochemical behavior of asymmetric alkenes in diastereodifferentiating [2+2]-photoreactions. We irradiated compound **1a** in the presence of the alkenes **d**–**f** and could prove that those reactions not only proceed with a high de but also additionally are highly regioselective. Applying the newly synthesized methoxynaphthylmenthyl attached cylohexenoncarboylate **1b** to these photoreactions, besides showing higher diastereoselectivity in addition to the enone, an increase in the reaction's regioselectivity can be observed. In conclusion we could succeed on finding a new way

to photochemically compose 7-substituted oxobicyclo[4.2.0]octanes being highly diastereo- and regioselective in their product formation by using 6-methoxynaphthylmenthyl chiral auxiliary (**b**).

#### 4. Experimental section

#### 4.1. General

All reagents were used without further purification. Air- and moisture sensitive compounds were handled under nitrogen atmosphere using Schlenk technique; Column chromatography (CC): Silica gel 60 N (SiO<sub>2</sub>; Kantokagaku mesh 63–210 µm); GC/EI-MS: Shimadzu GC2010 High-resolution Mass-spectra (HRMS): JEOL IMS-700; <sup>1</sup>H- and <sup>13</sup>C spectra: JOEL JNM-ECP 500 at 500 MHz and 125 MHz, resp.;  $\delta$  in parts per million rel to tetramethylsilane (TMS) as internal standard, J in Hertz, spin multiplicity: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and b=broad; X-ray analyses: Rigaku RAXIS-RAPID Imaging Plate diffractometer with Mo κα radiation at 296 K. Melting points: Yanaco MP-500D micro melting point apparatus. Optical rotations: JASCO DIP-1000 digital polarimeter by using the sodium D line (solvent and concentration as given); Infrared spectra (IR): JASCO FT/IR-420 spectrometer in reciprocal centimeters; HPLC (Column Oven) Hitachi L-7300 (Pump), Hitachi L-7100 (UV-vis Detector), Hitachi L-7420 and HPLC (Pump), Hitachi C 150 (UV-vis Detector), Hitachi L-7420.

#### 4.2. Starting material

4.2.1. Syntheses of **1a.b.** (-)-(1R.2S.5R)-5-Methyl-2-[1-methyl-1-(4methoxyphenyl)ethyl] cyclohexyl-3-oxo-1-cyclohexenecarboxylate (1a) was prepared according to literature procedures.<sup>4c,d</sup> (-)-(1R,2S,5R)-5-Methyl-2-[1-methyl-2-(6-methoxynaphthyl)ethyl] cyclohexyl-3-oxo-1-cyclo-hexenecarboxylate (1b) was prepared as followed. Starting from the commercial available 2-bromo-6methoxynaphthalene, (2S,5R)-2-(2-(6-methoxynaphthalen-2-yl)propan-2-yl)-5-methyl-cyclohexanone was prepared by Grignard reaction with (R)-pulgeone following Yangs procedure.<sup>11</sup> Colorless solid, yield: 66%; mp 108–111 °C;  $R_f$  (10% EtOAc/Hexane) 0.52;  $\delta_H$ (500 MHz, CDCl<sub>3</sub>): 7.74–7.65 (3H, m, CH), 7.48–7.42 (1H, m, CH), 7.15-7.10 (2H, m, CH), 3.91 (3H, s, COMe), 2.75 (1H, dd, J 12.9, 4.4 Hz, CH), 2.27–2.24 (1H, m, CH<sub>a</sub>H<sub>b</sub>), 2.04 (1H, dd, J 12.5, 12.5 Hz, CH), 1.85-1.71 (2H, m, CH<sub>a</sub>H<sub>b</sub>), 1.54 (3H, s, CMe), 1.51 (3H, s, CMe), 1.54–1.40 (2H, m, CH<sub>a</sub>H<sub>b</sub>), 1.23 (1H, dt, J 15.7, 5.3 Hz, CH<sub>a</sub>H<sub>b</sub>), 0.97 (3H, d, J 6.7 Hz, CHMe); δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 212.1, 157.3, 145.0, 132.6, 129.5, 128.7, 126.4, 125.0, 124.0, 118.6, 105.3, 59.3, 55.3, 52.4, 39.0, 36.3, 34.6, 29.1, 26.9, 23.3, 22.3; IR (KBr) 2938.0, 1710.6, 1600.6, 1454.1, 1282.7, 1269.9, 1209.2, 1159.1, 1033.7, 852.4, 809.0, 684.6; mp: 83-85 °C; HRMS (ESI): (M+Na)<sup>+</sup> found 333.1937. C<sub>21</sub>H<sub>26</sub>O<sub>2</sub>Na requires 333.1933. Reduction of the above ketone leads to the respective alcohol. For preparation of (1R,2S,5R)-2-(2-(6-methoxy naphthalen-2-yl)propan-2-yl)-5-methylcyclohexanol the substituted cyclohexanone was solved in toluene and cooled to -40 °C. Then 2 mol equiv of a 1.0 M DIBAL solution in hexane was added. The reaction mixture was allowed to warm to room temperature and stirred for additionally 12 h. After quenching with 1 N HCl and extraction with dichloromethane, followed workup (organic layers were washed with water and brine and dried over MgSO<sub>4</sub>, evaporation of the solvent) yield the crude product, which was purified by CC. Yield: 65%;  $R_f$  (17% EtOAc/Hexane) 0.24;  $\delta_H$  (500 MHz, CDCl<sub>3</sub>): 7.72-7.68 (3H, m, CH), 7.51-7.49 (1H, m, CH), 7.14-7.11 (2H, m, CH), 3.91 (3H, s, OMe), 3.58 (1H, (dd(dd)), J 10.4, 10.4, 4.0, 4.0 Hz, CHOH), 1.85-0.86 (9H, m, CH<sub>a</sub>H<sub>b</sub>, CH), 1.52 (3H, s, CMe), 1.36 (3H, s, CMe), 0.88 (3H, d, J 6.7 Hz, CHMe); δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 157.5, 146.5, 132.7, 129.4, 128.8, 127.0, 125.6, 123.1, 118.7, 105.4, 73.0, 55.3, 53.7, 45.2, 39.7, 34.9, 31.5, 28.6, 26.5, 24.3, 22.0; IR (KBr) 2944.8, 1599.7, 1379.8, 1207.0, 850.5; mp:108-111 °C; HRMS (ESI): (M+Na)<sup>+</sup> found 335.2082. C21H28O2Na requires 335.2082;  $[\alpha]_D^{29}$  –0.0368 (c 0.010, CH2Cl2).

The chiral auxiliary was then attached to the 3-oxo-1cyclohexenecarboxylic acid following the literature procedure for the preparation of  $1a^{4a}$  to give **1b**. Colorless solid, yield: 86%;  $R_f(15\%)$ EtOAc/Hexane) 0.22;  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>): 7.63 (1H, d, J 8.7 Hz, CH), 7.59 (1H, d, / 8.9 Hz, CH), 7.46 (1H, dd, / 8.7, 1.8 Hz, CH), 7.43 (1H, s, CH). 7.05 (1H, dd, / 9.0, 2.5 Hz, CH), 6.99 (1H, d, J 2.5 Hz, CH), 5.89 (1H, br s, C=CH), 5.04 (1H, ddd, / 10.7, 10.7, 4.7 Hz, OCH), 3.87 (3H, s, COMe), 2.22 (1H, m, CH), 2.03 (1H, dd, / 13.6, 3.3 Hz, CH<sub>a</sub>H<sub>b</sub>), 1.89 (1H, d(dd), / 16.7, 7.8, 4.9 Hz, CH<sub>a</sub>H<sub>b</sub>CO) 1.81-1.23 (12H, m, CH, CH<sub>a</sub>H<sub>b</sub>), 1.41 (3H, s, CMe), 1.02 (2H, m, CH<sub>a</sub>H<sub>b</sub>), 0.90 (3H, d, / 6.5 Hz, CHMe); δ<sub>C</sub> (125 MHz, CDCl<sub>3</sub>) 200.1, 165.1, 157.2, 147.6, 147.2, 132.4, 131.7, 129.0, 128.8, 126.7, 125.7, 121.9, 118.5, 105.6, 74.4, 55.4, 49.9, 41.8, 39.3, 36.9, 34.4, 31.3, 30.6, 30.3, 26.1, 23.8, 21.8, 21.4; IR (KBr) 2952.5, 1709.6, 1678.7, 1603.5, 1459.9, 1391.4, 1257.4, 1200.5, 1078.0, 1030.7, 960.4, 849.5, 810.9, 721.3; *m*/*z* (GC/EI-MS) 434 (5, M<sup>+</sup>), 199 (100), 167 (2), 158 (4), 144 (2), 95 (4), 67 (3), 55 (3%); mp:118–121 °C; HRMS (ESI):  $(M+Na)^+$  found 457.2452. C<sub>28</sub>H<sub>34</sub>O<sub>4</sub>Na requires 457.2457;  $[\alpha]_D^{29}$  –0.301 (*c* 2.1, CH<sub>2</sub>Cl<sub>2</sub>).

#### 4.3. Photocycloadditions of 1a and 1b to alkenes c-g

Photolysis was conducted using an ultrahigh pressure mercury 500 W lamp (Ushio) combined with a Unisoku CoolspeK cryostat (for analytical measurements) at -78 °C. Irradiation was carried out in a quartz cell using a Pyrex filter (>280 nm). Preparative photoreactions were carried out in a Pyrex flask (>280 nm) equipped HALOS 400 W high-pressure Hg lamp at -78 °C.

4.3.1. General procedure for photoreactions. Photoreactions were carried out by irradiation of 0.15 mmol of a 0.05 mM (0.005 mM for **1b**) N<sub>2</sub>-degassed solution of **1a,b** in methylcyclohexane (MCH) in the presence of a 20 M excess of the alkene (in the case of ethylene and 2-methylprop-2-ene a gas-saturated solution is used) at -78 °C until complete conversion of the cyclohexenone (monitored by <sup>1</sup>H NMR). After evaporation of the solvent and the excess alkene the products were separated by CC (conditions as given below) and fully characterized by <sup>1</sup>H and 2D-NMR-spectroscopy.

As the diastereoisomeric cycloadducts **3ad**, **5ad** were obtained in very small amounts only the main product of the reaction could be isolated and characterized. The assignment of these compounds as the respective diastereomers was conducted from the product mixtures' 2D-NMR data files, which shows characteristic signals for these bicyclo[4.2.0]octanes. The diastereomeric excess value (de) of the reactions was assigned (if not given differently) by <sup>1</sup>H NMR.

#### 4.3.2. Photocycloadditions of 1a

4.3.2.1. Photocycloaddition of 1a to 2-methyl-2-butene (d). A solution of 1a (0.15 mmol) was irradiated in the presence of 2methylbut-2-ene (d) for 90 min. Work up: CC, SiO<sub>2</sub>. The major product, (15,65,85)-(1R,25,5R)-2-(2-(4-methoxyphenyl) propan-2yl)-5-methylcyclohexyl7,7,8-trimethyl-5-oxobicyclo-[4.2.0]octane-1-carboxylate (2ad), elutes first to give 47.3 mg (0.104 mmol, 70%, sample includes 10% of **4ad**). R<sub>f</sub> (17% EtOAc/Hexane) 0.28; yellow oil,  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>) 7.18 (2H, d, J 8.6 Hz, CH), 6.80 (2H, d, J 8.6 Hz, CH), 4.92 (1H, ddd, J 10.7, 10.7, 4.3 Hz, OCH), 3.79 (3H, s, COMe), 3.05 (1H, s, COCHCMe<sub>2</sub>), 2.42–2.38 (1H, m, CH<sub>a</sub>H<sub>b</sub>CO), 2.30 (1H, q, J 7.3 Hz, CHMe), 2.12–1.34 (10H, m, CH<sub>a</sub>H<sub>b</sub>, CH), 1.30 (3H, s, CMe), 1.22 (3H, s, CMe), 1.18 (3H, s, CMe), 1.00–0.84 (2 H, m, CH<sub>a</sub>H<sub>b</sub>), 0.96 (3H, s, CMe), 0.94 (3H, d, J 7.3 Hz, CHMe), 0.86 (3H, d, J 6.5 Hz, CHMe), 0.79–0.76 (1H, m, CH<sub>a</sub>H<sub>b</sub>); δ<sub>C</sub> (125.0 MHz, CDCl<sub>3</sub>) 211.0, 175.6, 157.4, 143.0, 126.5, 113.3, 75.3, 55.1, 53.8, 50.2, 46.8, 44.4, 41.7, 40.3, 40.0, 39.6, 34.5, 32.6, 31.9, 31.3, 29.4, 25.0, 24.6, 21.8, 20.3, 20.0, 9.2; m/z (EI-GC/MS) 454 (M<sup>+</sup>, 1), 149 (100), 135 (3), 121 (6), 109 (3),

91 (2), 67 (2), 55 (4%); HRMS (ESI): (M+Na)<sup>+</sup> found 477.2981. C<sub>29</sub>H<sub>42</sub>ONa requires 477.2980. Compound **2ad** was followed by (1R,6S,7R)-(1R,2S,5R)-2-(2-(4-methoxyphenyl)propan-2-yl)-5methyl-cyclohexyl 7,8,8-trimethyl-5-oxobicyclo[4.2.0]-octane-1carboxylate(3ad) (Fraction still contains 37% of 2ad, characterizes as a mixture, 8.3 mg (0.017 mmol, 11%);  $R_f(17\% \text{ EtOAc/Hexane})$  0.28; yellow oil; δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 7.15 (2H, d, *J* 8.9 Hz, CH), 6.82 (2H, d, / 8.9 Hz, CH), 4.86 (1H, ddd, / 10.5, 10.5, 4.2 Hz, OCH), 3.79 (3H, s, COMe), 3.11 (1H, d, J 10.5 Hz, COCH<sub>a</sub>CHMe), 2.37–2.21 (3H, m, COCHMe, CH<sub>a</sub>H<sub>b</sub>CO, CH<sub>a</sub>H<sub>b</sub>), 2.11–1.33 (9H, m, CH<sub>a</sub>H<sub>b</sub>, CH), 1.30 (3H, s, CMe), 1.20 (3H, s, CMe), 1.09 (3H, s, CMe), 1.02 (3H, s, CMe), 1.01 (3H, d, / 6.8 Hz, CHMe), 0.89–0.79 (2 H, m, CH<sub>a</sub>H<sub>b</sub>), 0.84 (3H, d, / 6.2 Hz, CHMe), 0.75–0.66 (1H, m, CH<sub>a</sub>H<sub>b</sub>);  $\delta_{C}$  (125.0 MHz, CDCl<sub>3</sub>) 211.0, 173.3, 157.2, 142.3, 126.6, 113.3, 75.3, 55.1, 52.8, 50.5, 49.9, 43.6, 41.9, 41.5, 39.7, 38.6, 34.4, 32.1, 31.4, 31.3, 27.6, 27.1, 22.7, 21.7, 21.4, 19.9, 13.5; *m*/*z* (EI–GC/MS) 454 (M<sup>+</sup>, >1), 149 (100), 135 (4), 121 (6), 109 (3), 91 (2), 67 (2), 55 (5%).

4.3.2.2. Photocycloaddition of **1a** to 2-methylprop-2-ene (**e**). The general procedure was followed. As 2-methylprop-2-ene (e) is gaseous, the solution of **1a** was saturated with it by bubbling for 15 min. The compound 2ae elutes first to give 33.5 mg (0.076 mmol, 51%) of (1S,6S)-(1R,2S,5R)-2-(2-(4-methoxyphenyl)) propan-2-yl)-5-methylcyclohexyl 7,7-dimethyl-5-oxobicyclo[4.2.0] octane-1-carboxylate (2ae) as a yellowish oil;  $R_f$  (17% EtOAc/Hexane) 0.33; δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 7.18 (2H, d, / 8.7 Hz, CH), 6.80 (2H, d, / 8.7 Hz, CH), 4.91 (1H, ddd, / 10.7, 10.7, 4.3 Hz, OCH), 3.79 (3H, s, COMe), 2.91 (1H, s, COCH<sub>a</sub>CMe<sub>2</sub>), 2.27 (1H, ddd, J 18.9, 5.8, 5.8, COCH<sub>a</sub>H<sub>b</sub>), 2.18 (1H, ddd, J 18.9, 5.8, 5.8, COCH<sub>a</sub>H<sub>b</sub>), 2.13 (1H, d, J 12.5 Hz, CH<sub>a</sub>H<sub>b</sub>), 1.99 (1H, ddd, J 14.8, 14.8, 10.6 Hz, CHCH), 1.89–1.82 (2H, m, CH<sub>a</sub>H<sub>b</sub>), 1.85 (1H, d, / 12.5 Hz, CH<sub>a</sub>H<sub>b</sub>), 1.82-0.97 (8H, m, CH<sub>a</sub>H<sub>b</sub>, CH), 1.30 (3H, s, CMe), 1.22 (3H, s, CMe), 1.19 (3H, s, CMe), 0.96 (3H, s, CMe), 0.88 (3H, d, J 6.5 Hz, CHMe), 0.88-0.78 (1H, m, CH<sub>a</sub>H<sub>b</sub>); δ<sub>C</sub> (125.0 MHz, CDCl<sub>3</sub>) 211.3, 175.9, 157.1, 143.1, 126.4, 113.3, 75.6, 55.1, 54.7, 50.1, 42.6, 41.7, 41.3, 40.1, 39.5, 35.5, 34.5, 31.8, 31.3, 30.5, 27.8, 27.0, 26.7, 26.1, 21.8, 19.7; *m*/*z* (EI–GC/MS) 440 (M<sup>+</sup>, 1), 149 (100), 121 (7), 109 (3%); HRMS (ESI): (M+Na)<sup>+</sup> found 463.2823.  $C_{28}H_{40}ONa$  requires 463.2824;  $[\alpha]_D^{29}$  +0.4906 (*c* 1.17, CH<sub>2</sub>Cl<sub>2</sub>). This fraction was followed by (S)-(1R,2S,5R)-2-(2-(4-methoxy-phenyl) propan-2-yl)-5-methylcyclohexyl-(2-methylall-yl)-3-oxo-cyclohexane-carboxylate<sup>†</sup> (**6ae**) 14.5 mg (0.033 mmol, 22%), yellow oil;  $R_f$ (17% EtOAc/Hexane) 0.28; δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 7.22 (2H, d, J 8.8 Hz, CH), 6.83 (2H, d, J 8.8 Hz, CH), 4.87 (1H, s, C=CH<sub>a</sub>H<sub>b</sub>), 4.86 (1H, ddd, J 10.3, 10.3 4.3 Hz, OCH), 4.66 (1H, s, C=CH<sub>a</sub>H<sub>b</sub>), 3.77 (3H, s, OMe); 2.26 (1H, d, J 14.3 Hz, CH<sub>a</sub>H<sub>b</sub>C=CH<sub>2</sub>), 2.18 (1H, d, J 14.3 Hz, CH<sub>a</sub>H<sub>b</sub>), 2.13 (1H, d, J 6.7 Hz, CH<sub>a</sub>H<sub>b</sub>C=CH<sub>2</sub>), 2.31–2.09 (3H, m, CH<sub>a</sub>H<sub>b</sub>), 2.02 (1H, ddd, J 12.1, 12.1, 3.5 Hz, CH), 1.94–0.78 (11H, m, CH, CH<sub>a</sub>H<sub>b</sub>), 1.68 (3H, s, MeC=CH<sub>2</sub>), 1.30 (3H, s, CMe), 1.17 (3H, s, CMe), 0.88 (3H, d, J 6.5 Hz, CHMe); δ<sub>C</sub> (125.0 MHz, CDCl<sub>3</sub>) 209.9, 174.8, 157.1, 143.1, 140.7, 126btained in this work that the alkene attacks preferentially from the Si-side of the enone to produce 1S stereochemistry.

4.3.2.3. Photocycloaddition of **1a** to methacrylonitrile (**f**). For irradiation of **1a** in the presence of **f** the general procedure was followed to yield after evaporation of the solvent and excess alkene the complex product mixture (**2af**<sub>1</sub>/**2af**<sub>2</sub>/**4af** 100:14:6, respectively). Separation by CC gives 5.2 mg (0.012 mmol, 8% as yellow oil) of first eluting product (15,65,7*R*)-(1*R*,25,5*R*)-2-(2-(4-methoxyphenyl)propan-2-yl)-5-methylcyclo-hexyl7-cyano-7-methyl-5-oxobicyclo[4.2.0]octane-1-carboxylate) (**2af**<sub>2</sub>), *R*<sub>f</sub> (17% EtOAc/Hexane) 0.43;  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>) 7.22 (2H, d, *J* 8.8 Hz, CH), 6.77 (2H, d, *J* 8.6 Hz, CH), 5.00 (1H, ddd, *J* 10.7, 10.7, 4.4 Hz, OCH), 3.76 (3H, s, COMe), 2.97 (1H, s,

 $<sup>^\</sup>dagger\,$  Data determined by 2D-NMR-spectra analysis.

COCHCCNMe), 2.62 (1H, d, J 12.6 Hz, CNMeCCH<sub>a</sub>H<sub>b</sub>), 2.30 (1H, ddd, J 18.5, 5.8, 5.8 Hz, CHH<sub>b</sub>CO), 2.23–2.14 (2H, m, CH<sub>a</sub>H<sub>b</sub> CH), 1.98 (1H, d, J 12.6 Hz, CNMeCCH<sub>a</sub>H<sub>b</sub>), 1.87–1.15 (10H, m, CH<sub>a</sub>H<sub>b</sub>, CH), 1.31 (3H, s, CMe), 1.30 (3H, s, CCNMe), 1.15 (3H, s, CMe), 0.99-0.90 (1H, ddd, J 12.7, 13.0, 3.9 Hz, CH<sub>a</sub>H<sub>b</sub>), 0.90 (3H, d, J 6.5 Hz, CHMe);  $\delta_{C}$  (125.0 MHz, CDCl<sub>3</sub>) 206.7, 173.5, 156.9, 143.8, 126.2, 123.5, 113.3, 76.2, 55.1, 50.1, 49.3, 43.5, 41.5, 40.7, 39.9, 39.0, 34.3, 31.4, 31.0, 29.6, 29.6, 26.6, 24.3, 22.3, 21.8, 19.1; m/z (EI-GC/MS) 451 (M<sup>+</sup>, 1), 173 (1), 149 (100), 121 (7), 109 (3), 67 (2), 55 (5%); HRMS (ESI): (M+Na)<sup>+</sup> found 474.2621. C<sub>28</sub>H<sub>37</sub>NO<sub>4</sub>Na requires 474.2620;  $[\alpha]_D^{29}$  +0.3647 (c 0.18, CH<sub>2</sub>Cl<sub>2</sub>). This fraction was followed by 29.9 mg (0.066 mmol, 44%) of a yellow oil consisting of (1S,6S,7S)-(1R,2S,5R)-2-(2-(4methoxyphenyl)-propan-2-yl)-5-methylcyclohexyl7-cyano-7methyl-5-oxobicyclo [4.2.0]octane-1-carboxylate ( $2af_1$ ).  $R_f$  (17%) EtOAc/Hexane) 0.37;  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>) 7.17 (2H, d, J 8.8 Hz, CH), 6.80 (2H, d, J 8.6 Hz, CH), 4.91 (1H, ddd, J 10.7, 10.7, 4.4 Hz, OCH), 3.79 (3H, s, COMe), 3.01 (1H, s, COCH<sub>a</sub>CCNMe), 2.38 (1H, d, J 12.6 Hz, CNMeCCH<sub>a</sub>H<sub>b</sub>), 2.52 (1H, ddd, J 18.5, 5.8, 8.6 Hz, CH<sub>a</sub>H<sub>b</sub>CO), 2.34 (1H, ddd, J 18.5, 8.6, 5.8 Hz, CH<sub>a</sub>H<sub>b</sub>CO), 2.15 (1H, d, J 12.6 Hz, CNMeC-CH<sub>a</sub>H<sub>b</sub>), 2.05 (1H, ddd, J 12.3, 12.3, 3.4 Hz, CH), 2.00–1.52 (8H, m, CH<sub>a</sub>H<sub>b</sub>, CH), 1.58 (3H, s, CCNMe), 1.27 (3H, s, CMe) 1.16 (3H, s, CMe), 1.09 (1H, ddd, J 13.6, 12.6, 3.4 Hz, CH<sub>a</sub>H<sub>b</sub>), 0.97 (1H, dd, J 12.0, 12.0, 3.4 Hz, CH<sub>a</sub>H<sub>b</sub>), 0.91–0.82 (1H, m, CH<sub>a</sub>H<sub>b</sub>), 0.88 (3H, d, J 6.5 Hz, CHMe); δ<sub>C</sub> (125.0 MHz, CDCl<sub>3</sub>) 207.1, 173.6, 157.1, 143.3, 126.1, 122.6, 113.4, 76.2, 55.1, 54.0, 49.7, 43.3, 41.6, 40.7, 39.2, 39.1, 34.4, 31.4, 31.3, 29.3, 28.0, 26.7, 26.5, 26.0, 21.7, 19.6; m/z (EI-GC/MS) 451 (M<sup>+</sup>, 1), 173 (1), 149 (100), 121 (7), 109 (3), 67 (2), 55 (5%), HRMS (ESI): (M+Na)<sup>+</sup> found 474.26120.  $C_{28}H_{37}NO_4Na$  requires 474.2620;  $[\alpha]_D^{29}$  +0.4975 (c 1.38, CH<sub>2</sub>Cl<sub>2</sub>).

4.3.2.4. Photocycloaddition of **1a** to methoxypropene (**g**). Following the general procedure, irradiation of **1a** in the presence of **g** gave a complex reaction mixture. The main product (1R,6S,8R)-(1R,2S,5R)-2-(2-(4-methoxyphenyl)propan-2-yl)-5-methylcyclohexyl8-methoxy -8-methyl-5-oxobicyclo[4.2.0]-octane-1-carboxylate (3ag) could be obtained by HPLC separation, 20.3 mg (0.045 mmol, 30%). Rf (17% EtOAc/Hexane) 0.22; yellow oil,  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>) 7.15 (2H, d, J 8.8 Hz, CH), 6.82 (2H, d, J 8.8 Hz, CH), 4.92 (1H, ddd, J 10.6, 10.6, 4.3 Hz, OCH), 3.79 (3H, s, COMe), 3.30 (3H, s, OMe), 3.17 (1H, dd, J 10.2, 10.2 Hz, COCHCH<sub>2</sub>), 2.43 (1H, ddd, J 15.0, 7.5, 7.5 Hz, CH<sub>a</sub>H<sub>b</sub>CO), 2.32–2.29 (3H, m, CH<sub>a</sub>H<sub>b</sub>), 2.20–1.18 (7H, m, CH<sub>a</sub>H<sub>b</sub>, CH), 1.85 (1H, ddd, J 12.2, 12.2, 3.3 Hz, CH), 1.36 (3H, s, CMe), 1.23 (3H, s, CMe), 1.20 (3H, s, CMe); 1.22-0.81 (2H, m, CH<sub>a</sub>H<sub>b</sub>), 0.85 (3H, d, / 6.5 Hz, CHMe), 0.76-0.68 (1H, m, CH<sub>a</sub>H<sub>b</sub>);  $\delta_{C}$  (125.0 MHz, CDCl<sub>3</sub>) 210.5, 173.4, 157.2, 142.1, 126.6, 113.4, 77.3, 76.8, 58.4, 55.2, 51.4, 50.5, 41.9, 39.9, 38.4, 38.1, 36.8, 34.4, 31.8, 30.9, 27.5, 25.0, 22.9, 21.8, 21.5, 19.2; *m*/*z* (EI–GC/MS) 456 (M<sup>+</sup>, <1), 212 (2), 149 (100), 135 (17), 121 (10), 72 (25), 55 (4%); HRMS (ESI):  $(M+Na)^+$  found 479.2773.  $C_{28}H_{40}O_5Na$  requires 474.2773;  $[\alpha]_D^{29} + 0$ . 6749 (c 0.91, CH<sub>2</sub>Cl<sub>2</sub>).

#### 4.3.3. Photocycloaddition of 1b

4.3.3.1. Photocycloaddition of **1b** to ethylene (**c**). As the minor product **4bc** was obtained in only 2% yield using MCH as the solvent in the photoreaction. The isolation of the product **4bc** was conducted from a sample using dichloromethane as solvent where the product ratio of **2bc/4bc** was 1:0.3. For the separation of **2bc**, the general procedure for photochemical reactions as given was followed. CC yielded first eluting 61.6 mg (0.13 mmol, 89%) of (1*S*,6*S*)-(1*R*,2*S*,5*R*)-2-(2-(6-methoxy-naphthalen-2-yl)propan-2-yl)-5-methylcyclohexyl 5-oxobicyclo-[4.2.0]octane-1-carboxylate (**2bc**); *R*<sub>f</sub> (17% EtOAc/Hexane) 0.31; colorless crystals;  $\delta_{\rm H}$  (500 MHz, CDCl1<sub>3</sub>) 7.67–7.65 (2H, m, CH), 7.55 (1H, s, CH), 7.46–7.45 (1H, m, CH), 7.12–7.07 (2H, m, CH), 4.98 (1H, ddd, *J* 10.6, 10.6, 4.4 Hz, CH), 3.90 (3H, s, OMe), 2.82 (1H, ddd, *J* 9.2, 9.2, 6.2 Hz, COCH), 2.22 (1H, dddd, *J* 23.0, 6.7, 6.7 Hz, CH<sub>a</sub>H<sub>b</sub>CO), 2.02–1.98 (1H, m, CH<sub>a</sub>H<sub>b</sub>), 1.90–0.83 (16H, m, CH, CH<sub>2</sub>), 1.42 (3H, s, CMe), 1.26 (3H, s, CMe), 0.97 (3H, d, *J*)

6.5 Hz, CH*Me*);  $\delta_{\rm C}$  (125.0 MHz, CDCl<sub>3</sub>) 212.6, 175.1, 157.3, 146.7, 132.5, 129.3, 128.8, 126.5, 125.4, 122.6, 118.6, 105.4, 75.2, 55.3, 49.5, 48.3, 45.7, 41.7, 39.8, 38.6, 34.5, 31.3, 29.5, 28.3, 27.6, 26.9, 25.8, 21.8, 21.3, 20.5; *m*/*z* (EI–GC/MS) 462 (M<sup>+</sup>, 5), 355 (2), 286 (1), 207 (29), 199 (100), 141 (3), 67 (6%);  $[\alpha]_{29}^{29}$  +0.71 (*c* 0.80, CH<sub>2</sub>Cl<sub>2</sub>). Structure of **2bc** was determined by X-ray analysis, mp: 103–105 °C. C<sub>60</sub>H<sub>76</sub>O<sub>8</sub>; colorless block (0.30×0.25×0.15 mm); orthorhombic; space group=*P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (#19); *Z*=4; *a*=6.29568(15), *b*=24.4418(7), *c*=33.6194(8) Å; *V*=5173.3(2) Å<sup>3</sup>;  $\rho_{\rm calcd}$  1.188 g cm<sup>-3</sup>. *w*R=0.0473 and *R*=0.1251.

The second fraction consists of 33.3 mg (0.072 mmol, 48%) of (1R,6R)-(1R,2S,5R)-2-(2-(6-methoxynaphthalen-2-yl)propan-2-yl)-5-methylcyclohexyl5-oxobicyclo[4.2.0]octane-1-carboxylate (4bc) as a yellow oil;  $R_f$  (17% EtOAc/Hexane) 0.28;  $\delta_H$  (500 MHz, CDCl<sub>3</sub>) 7.69 (1H, d, J 8.6 Hz, CH), 7.66 (1H, d, J 9.7 Hz, CH), 7.55 (1H, s, CH), 7.46 (1H, dd, J 8.6, 1.9 Hz, CH), 7.11-7.06 (2H, m, 2H, CH), 4.98 (1H, ddd, J 10.6, 10.6, 4.5 Hz, OCH), 3.90 (3H, s, COMe), 2.67 (1H, dd, J 9.2, 8.8 Hz, COCH), 2.31 (1H, d(dd), J 16.9, 7.5, 5.4 Hz, CH<sub>a</sub>H<sub>b</sub>), 2.19–2.08 (2H, m, CH<sub>a</sub>H<sub>b</sub>CH<sub>a</sub>H<sub>b</sub>), 1.90–0.83 (15H, m, CH, CH<sub>a</sub>H<sub>b</sub>), 1.41 (3H, s, *CMe*), 1.27 (3H, s, *CMe*), 0.86 (3H, d, *J* 6.5 Hz, *CHMe*); δ<sub>C</sub> (125.0 MHz, CDCl<sub>3</sub>) 212.3, 175.3, 157.2, 146.6, 132.6, 129.3, 128.8, 126.6, 125.4, 122.6, 118.6, 105.4, 75.2, 55.3, 49.5, 48.2, 45.8, 41.9, 39.8, 38.7, 34.4, 31.3, 30.2, 28.0, 27.4, 26.9, 26.1, 21.8, 20.8, 20.7; *m/z* (EI–GC/MS) 462 (M<sup>+</sup>, 5), 286 (1), 207 (15), 199 (100), 141 (2), 67 (3%). HRMS (ESI):  $(M+Na)^+$  found 485.2666.  $C_{30}H_{38}O_4Na$  requires 485.2667;  $[\alpha]_D^{29}$ -1.5486 (c 0.26, CH<sub>2</sub>Cl<sub>2</sub>).

4.3.3.2. Photocycloaddition of **1b** to 2-methyl-2-butene (**d**). Irradiation of 1b in the presence of 2-methyl-2-butene (d) yields compounds 2bd, 3bd, and 4bd as a mixture. The major product, (15,65,8*R*)-(1*R*,25,5*R*)-2-(2-(6-methoxynaphthalen-2-yl)propan-2-yl) -5-methylcyclohexyl7,7,8-trimethyl-5-oxobicyclo[4.2.0]oct-ane-1-ca rboxylate (2bd) was obtained as light yellow oil; 25.3 mg (0.050 mmol, 33%).  $R_f$  (17% EtOAc/Hexane) 0.49;  $\delta_H$  (500 MHz, CDCl<sub>3</sub>) 7.66 (2H, d, J 8.6 Hz, CH), 7.55 (1H, d, / 1.0 Hz, CH), 7.44 (1H, dd, / 8.6, 1.0 Hz, CH), 7.13-7.09 (2H, m, CH), 4.99 (1H, ddd, J 10.4, 10.4, 4.6 Hz, OCH), 3.92 (3H, s, COMe), 3.05 (1H, s, COCHCMe<sub>2</sub>), 2.22 (1H, m, CHMe), 2.25-2.16 (2H, m, CH<sub>a</sub>H<sub>b</sub>CO, CH<sub>a</sub>H<sub>b</sub>), 2.09 (1H, ddd, / 12.2, 12.2, 3.6 Hz, CH), 2.10-0.96 (10H, m, CH<sub>a</sub>H<sub>b</sub>, CH), 1.76 (1H, ddd, / 13.3, 13.9, 2.6 Hz, CH), 1.40 (3H, s, CMe), 1.33 (3H, s, CMe), 1.14 (3H, s, CMe), 0.91 (3H, s, CHMe), 0.86 (3H, d, J 6.5 Hz, CHMe), 0.84 (3H, d, J 7.4 Hz, CHMe);  $\delta_{C}$  (125.0 MHz, CDCl<sub>3</sub>) 211.1, 175.8, 157.4, 146.1, 132.6, 129.5, 128.8, 126.7, 125.3, 123.1, 118.7, 105.5, 75.4, 55.4, 53.9, 49.8, 46.8, 44.4, 41.9, 40.4, 40.3, 40.0, 34.4, 32.6, 31.7, 31.1, 29.1, 27.3, 25.0, 24.6, 21.9, 20.1, 14.2; m/z (EI-GC/ MS) 504 (M<sup>+</sup>, 5), 199 (100), 185 (2), 171 (5), 158 (3), 141 (2), 81 (2), 55 (4%); HRMS (ESI): (M+Na)<sup>+</sup>, found 527.3136. C<sub>33</sub>H<sub>44</sub>O<sub>4</sub>Na requires 527.3137;  $[\alpha]_D^{29}$  +0.9661 (*c* 0.64, CH<sub>2</sub>Cl<sub>2</sub>). This fraction was followed by 5.9 mg (0.012 mmol, 8%) of (1R,6S,7R)-(1R,2S,5R)-2-(2-(6-methoxyaphtalen-2-yl) propan-2-yl)-5-methylcylohexyl7,8,8trimethyl-5oxobicyclo[4.2.0]octane-1-carboxylate (3bd) as a light yellow oil,  $R_{\rm f}$  (17% EtOAc/Hexane) 0.42;  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>) 7.67 (2H, d, J, 8.6 Hz, CH), 7.52 (1H, s, CH), 7.40 (1H, dd, J 8.6, 1.8 Hz, CH), 7.12-7.06 (2H, m, CH), 4.92 (1H, ddd, / 10.5, 10.5, 4.2 Hz, OCH), 3.90 (3H, s, OMe), 3.14 (1H, d, J 10.6 Hz, COCH<sub>2</sub>CHMe), 2.37–2.24 (3H, m, COCHMe, CH<sub>a</sub>H<sub>b</sub>, CH<sub>a</sub>H<sub>b</sub>), 2.07–1.00 (12H, m, CH, CH<sub>a</sub>H<sub>b</sub>), 1.34 (3H, s, CMe), 1.32 (3H, s, CMe), 1.08 (3H, s, CMe), 1.04 (3H, s, CMe), 1.02 (3H, d, J 6.8 Hz, CHMe), 0.83 (3H, d, J 6.3 Hz, CHMe); δ<sub>C</sub> (125.0 MHz, CDCl<sub>3</sub>) 213.5, 173.3, 157.4, 145.5, 132.6, 129.4, 128.6, 126.6, 125.3, 123.8, 118.6, 105.4, 75.4, 55.3, 52.9, 50.1, 50.0, 43.6, 41.9, 41.5, 40.5, 36.8, 34.4, 32.1, 31.4, 31.0, 27.7, 27.1, 22.6, 21.7, 21.4, 19.9, 13.5; *m*/*z*(EI–GC/MS) 504(M<sup>+</sup>, 5), 199 (100), 185 (3), 171 (5), 141 (3), 81 (2), 71 (6), 55 (7%). HRMS (ESI):  $(M+Na)^+$  found 527.3137.  $C_{33}H_{44}O_4Na$  requires 527.3137;  $[\alpha]_D^{29}$ +0.1862 (*c* 0.21, CH<sub>2</sub>Cl<sub>2</sub>).

4.3.3.3. Photocycloaddition of **1b** to 2-methylprop-2-ene (*e*). Following the general procedure in the presence of *e*, **1b** 

yielded a mixture of **2be/6be/7be** (1:0.15:0.15) with a de of >95%. Separation by CC gave the major compound (15,6S)-(1R,2S,5R)-2-(2-(6-methoxynaphtalen-2-yl)propanyl)-5methylcyclohexyl7,7-dimethyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (2be) as light yellow oil; 28.6 mg (0.058 mmol, 39%); Rf (17% EtOAc/Hexane) 0.38; δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 7.65 (2H, m, d, / 8.7 Hz, CH), 7.55 (1H, s, CH); 7.45 (1H, m, CH); 7.12-7.09 (2H, m, CH), 4.97 (1H, ddd, / 10.7, 10.7, 4.3 Hz, OCH), 3.91 (3H, s, COMe), 2.83 (1H, s, COCHCMe<sub>2</sub>), 2.17 (1H, ddd, / 12.4, 12.4, 3.2 Hz, CH), 2.15 (1H, ddd, / 17.3, 5.6, 5.6 Hz, CH<sub>a</sub>H<sub>b</sub>CO), 2.05 (1H, d, J 12.4 Hz, CH<sub>a</sub>H<sub>b</sub>), 1.90–1.86 (1H, m, CH<sub>a</sub>H<sub>b</sub>), 1.82–1.67 (2H, m, CH, CH<sub>a</sub>H<sub>b</sub>), 1.68 (1H, d, J 12.5 Hz, CH<sub>a</sub>H<sub>b</sub>), 1.62-0.99 (8H, m, CH<sub>a</sub>H<sub>b</sub>, CH); 1.41 (3H, s, CMe), 1.28 (3H, s, CMe), 1.18 (3H, s, CMe), 0.90 (3H, s, CMe), 0.88 (3H, d, J 6.4 Hz, CHMe), 0.88–0.78 (1H, m, CH<sub>a</sub>H<sub>b</sub>);  $\delta_{C}$  (125.0 MHz, CDCl<sub>3</sub>) 211.3, 176.0, 157.3, 146.5, 132.5, 129.3, 128.8, 126.5, 125.3, 122.7, 118.5, 105.5, 75.5, 55.3, 54.7, 49.5, 42.3, 41.7, 41.1, 39.9, 39.7, 35.0, 34.5, 31.8, 31.3, 30.0, 27.0, 26.9, 26.8, 26.0, 21.8, 19.4; m/z (EI-GC/MS) 490 (M<sup>+</sup>, 4), 279 (1), 199 (100), 169 (1), 158 (4), 141 (2), 56 (3%); HRMS (ESI): (M+Na)<sup>+</sup> found 513.2980. C<sub>32</sub>H<sub>42</sub>O<sub>4</sub>Na requires 513.2980;  $[\alpha]_D^{29}$  +0.5639 (c 1.8, CH<sub>2</sub>Cl<sub>2</sub>). The followed fraction consists of (1R,2S,5R)-2-(2-(6-methoxynaphthalen-2-yl)propan-2-yl)-5-methylcyclohexyl-(1S)- and (1R)-(2-methylallyl)-3-oxocyclohexane carboxylate (6be) and (7be) as light yellow oil;<sup>‡</sup> 6.9 mg (0.014 mmol, 9%) of the 1:0.9 mixture of  $R_f$  (17% EtOAc/Hexane) 0.27; δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 7.71–7.66 (2H, m, CH); 7.57 (1H, s, CH), 7.51-7.46 (1H, m, CH), 7.12-7.07 (2H, m, CH), 4.99 (1H, ddd, J 10.6, 10.6, 4.4 Hz, OCH), 3.90 (3H, s, COMe), 2.37 (1H, d, J 14.8 Hz, CH<sub>a</sub>H<sub>b</sub>C=CH<sub>2</sub>), 2.15 (1H, d, / 14.3 Hz, CH<sub>a</sub>H<sub>b</sub>), 2.02 (1H, d, / 14.8 Hz, CH<sub>a</sub>H<sub>b</sub>C=CH<sub>2</sub>), 2.16–0.86 (17H, m, CH, CH<sub>a</sub>H<sub>b</sub>), 1.62 (3H, s, MeC=CH<sub>2</sub>), 1.42 (3H, s, CMe), 1.25 (3H, s, CMe), 0.84 (3H, d, J 6.5 Hz, CHMe); δ<sub>C</sub> (125.0 MHz, CDCl<sub>3</sub>) 209.3, 174.8, 158.5, 146.7, 140.7, 132.6, 129.4, 128.8, 125.5, 122.9, 118.7, 115.6, 105.5, 76.9, 55.5, 49.6, 49.0, 47.6, 45.0, 39.5, 41.5, 40.1, 34.4, 32.9, 31.4, 27.6, 27.3, 26.1, 24.7, 24.6, 21.8, 21.5; *m/z* (EI–GC/MS) 490 (M<sup>+</sup>, 3), 199 (100), 185 (4), 158 (3), 144 (2), 107 (1), 69 (1), 55 (5%). While the stereochemistry of the C-1 atom was not determined, we assumed the major product was 1S and the minor product to be 1R configurated, according to the results obtained in this work that the alkene attacks preferentially from the Si-side of the enone to produce 1S stereochemistry.

4.3.3.4. Photocycloaddition of **1b** to methacrylonitrile (**f**). Photoreaction of **1b** in the presence of **f** yielded the product mixture  $(2bf_1/2bf_2 \ 100:25)$  with a de of >95% after evaporation of the solvent and the excess alkene. Separation by CC gave 8.5 mg (0.017 mmol, 12%) of first eluting product, (1S,6S,7R)-(1R,2S,5R)-2-(2-(6-methoxynaphthalen-2-yl)-propan-2-yl)-5-methylcyclohexyl7-cyano-7-methyl-5-oxobicyclo[4.2.0] octane-1-carboxvlate (**2bf**<sub>2</sub>) as a light yellow oil;  $R_f$  (17% EtOAc/Hexane) 0.57;  $\delta_H$ (500 MHz, CDCl<sub>3</sub>) 7.65 (1H, d, [8.7 Hz, CH), 7.62 (1H, d, [9.0 Hz, CH), 7.53 (1H, s, CH), 7.12-7.08 (2H, m, CH), 7.03 (1H, d, J 2.5 Hz, CH), 5.07 (1H, ddd, / 10.7, 10.7, 4.5 Hz, OCH), 3.91 (3H, s, OMe), 2.87 (1H, s, CHCCNMe), 2.50 (1H, d, J 13.3 Hz, CNMeCCH<sub>a</sub>H<sub>b</sub>), 2.36 (1H, ddd, J 12.1, 12.1, 3.7 Hz, CH<sub>a</sub>H<sub>b</sub>), 1.98–1.84 (3H, m, CH<sub>a</sub>H<sub>b</sub>), 1.76 (1H, d, J 13.6 Hz, CNMeCCH<sub>a</sub>H<sub>b</sub>), 1.72–0.87 (11H, m, CH<sub>a</sub>H<sub>b</sub>), 1.44 (3H, s, CCNMe), 1.23 (3H, s, CMe), 1.17 (3H, s, CMe), 0.92 (3H, d, J 6.5 Hz, CHMe); δ<sub>C</sub> (125.0 MHz, CDCl<sub>3</sub>) 206.3, 175.6, 157.3, 147.2, 131.3, 129.2, 128.7, 126.6, 125.6, 123.6, 122.1, 118.7, 105.9, 76.2, 55.4, 50.1, 48.8, 43.4, 41.2, 40.5, 29.6, 39.4, 34.3, 31.4, 29.7, 29.5, 29.2, 26.6, 23.1, 21.8, 21.4, 18.8; *m*/*z* (EI–GC/MS) 501 (M<sup>+</sup>, 5), 199 (100), 171 (5), 158 (3), 141 (2), 81 (2), 79 (2), 67 (2), 55 (5%); HRMS (ESI): (M+Na)<sup>+</sup> found 524.2776. C<sub>32</sub>H<sub>39</sub>NO<sub>4</sub>Na requires 524.2776;  $[\alpha]_D^{29}$  +0.3088 (*c* 0.16, CH<sub>2</sub>Cl<sub>2</sub>). This fraction is followed by (1S,6S,7S)-(1R,2S,5R)-2-(2-(6methoxy-naphthalen-2-yl)propan-2-yl)-5-methylcyclohexyl-7cyano-7-methyl-5-oxobicyclo[4.2.0]octane-1-carboxylate (2bf<sub>1</sub>); 38.5 mg (0.077 mmol, 51%);  $R_f$  (17% EtOAc/Hexane) 0.48;  $\delta_H$ (500 MHz, CDCl<sub>3</sub>) 7.65 (1H, d, J 9.5 Hz, CH), 7.64 (1H, d, J 9.5 Hz, CH), 7.52 (1H, s, CH), 7.44 (1H, dd, / 8.6, 1.9 Hz, CH), 7.13-7.08 (2H, m, CH), 4.95 (1H, ddd, / 10.7, 10.7, 4.5 Hz, CH), 3.91 (3H, s, OMe), 2.89 (1H, s, CHCCNMe), 2.37–2.31 (1H, m, CH<sub>a</sub>H<sub>b</sub>), 2.22 (1H, ddd, J 12.2, 12.2, 3.6 Hz, CH), 2.01 (1H, d, / 12.8 Hz, CMeCNCH<sub>a</sub>H<sub>b</sub>), 1.88 (1H, d, / 12.8 Hz, CMeCNCH<sub>a</sub>H<sub>b</sub>), 2.01–0.96 (12H, m, CH, CH<sub>a</sub>H<sub>b</sub>), 1.42 (3H, s, CCNMe), 1.38 (3H, s, CMe); 1.23 (3H, s, CMe), 0.88 (3H, d, J 6.6 Hz, CHMe); δ<sub>C</sub> (125.0 MHz, CDCl<sub>3</sub>) 207.0, 173.9, 157.5, 146.7, 132.6, 129.3, 128.8, 126.7, 125.3, 122.6, 122.5, 118.9, 105.6, 76.2, 55.5, 54.1, 49.3, 43.2, 41.8, 40.4, 39.8, 38.9, 34.5, 31.4, 31.3, 29.0, 28.6, 26.8, 26.5, 22.7, 21.9, 19.5; *m*/*z* (EI–GC/MS) 501 (M<sup>+</sup>, 4), 199 (100), 171 (5), 158 (3), 141 (2), 81 (2), 79 (2), 67 (2), 55 (5%); HRMS (ESI): (M+Na)<sup>+</sup> found 524.2776.  $C_{32}H_{39}NO_4Na$  requires 524.2777;  $[\alpha]_D^{29} + 0.05688$  (c 0.8, CH<sub>2</sub>Cl<sub>2</sub>).

4.3.3.5. Photocycloaddition of **1b** to 2-methoxypropene (g). Irradiation of 1b in the presence of f led to a complex mixture out of which the main product (1R,6S,8R)-(1R,2S,5R)-2-(2-(6-methoxynaphthalen-2-yl)propan-2-yl)-5-methylcyclohexyl 8-methoxy-8-methyl-5-oxo-bicyclo[4.2.0]octane-1-carboxylate (3bg) could be isolated in a yield of 35% (26.1 mg, 0.052 mmol) by CC. Rf (17% EtOAc/Hexane) 0.18; yellow oil,  $\delta_{\rm H}$  (500 MHz, CDCl<sub>3</sub>) 7.67 (1H, d, / 8.7 Hz, CH), 7.66 (1H, d, / 8.7 Hz, CH), 7.52 (1H, s, CH), 7.39 (1H, d, / 8.7 Hz, CH), 7.13–7.12 (1H, m, CH), 7.10 (2H, m, CH), 4.98 (1H, ddd, / 10.6, 10.6, 4.8 Hz, OCH), 3.90 (3H, s, OMe), 3.30 (3H, s, OMe), 3.18 (1H, dd, / 10.2, 10.2 Hz, CHCH<sub>a</sub>H<sub>b</sub>), 2.37 (1H, ddd, / 23.3, 5.8, 5.8 Hz, CH<sub>a</sub>H<sub>b</sub>CO), 2.29–0.80 (14H, m, CH, CH<sub>a</sub>H<sub>b</sub>), 1.37 (3H, s, CMeOMe), 1.32 (6H, s, CMe), 0.85 (3H, d, J 6.3 Hz, CHMe), 0.75-0.68 (1H, m,  $CH_aH_b$ ;  $\delta_C$  (125.0 MHz, CDCl<sub>3</sub>) 210.5, 173.4, 157.3, 145.3, 132.5, 129.4, 128.6, 126.6, 125.3, 123.3, 118.6, 105.3, 77.7, 76.8, 58.4, 55.3, 51.6, 50.0, 42.0, 40.5, 38.4, 38.0, 36.9, 34.3, 31.7, 31.4, 27.6, 25.0, 22.5, 21.8, 21.5, 19.2; *m*/*z* (EI–GC/MS) 506 (M<sup>+</sup>, 1), 434 (4), 285 (5), 212 (4), 199 (100), 185 (14), 158 (2), 141 (3), 91 (2), 72 (44), 55 (7%); HRMS (ESI):  $(M+Na)^+$  found 529.2773.  $C_{32}H_{42}O_5Na$  requires 529.2930;  $[\alpha]_D^{29}$ +0.3051 (*c* 1.5, CH<sub>2</sub>Cl<sub>2</sub>).

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<sup>&</sup>lt;sup>‡</sup> Data determined by 2D-NMR-spectra analysis.

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