Stereoselective Intramolecular Copper(I)-Catalyzed [2 + 2]-Photocycloadditions. Enantioselective Synthesis of (+)- and (−)-Grandisol[1]

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This work deals with copper(I)-catalyzed intramolecular [2 + 2]-photocycloadditions of 1,6-diene derivatives. The bridgehead carbons C-1 and C-5 of the resulting bicyclo[3.2.0]heptanes are generated stereoselectively by using chiral starting material, chiral catalysts, or chiral auxiliaries. The irradiation of (*S*)-**3** leads to enantiomerically pure **4** and **5** which opens a new synthetic route to enantiomerically pure (+)- and (−)-grandisol **9**. The use of chiral copper complexes as catalysts delivers enantiomeric excesses below 5%. The reason for these small excesses is a low reactivity of the chiral copper complexes, as confirmed by CD-spectroscopic measurements. Malic acid or amino carboxylic acid derivatives as chiral auxiliaries yield the bicyclic alcohols **4** and **5** with enantiomeric excesses up to 15%. The employment of a chiral diol as an auxiliary delivers a chiral ketal **36**, and the resulting ketone **7** exhibits enantiomeric excesses up to 60%.

Introduction

The intramolecular copper(I)-catalyzed [2 + 2]-photocycloaddition of 1,6-diene derivatives was first described by Evers and Mackor in 1978[2] and was then extensively investigated by Salomon and co-workers.[3] It is a very convenient procedure to prepare bicyclo[3.2.0]heptane derivatives because high yields are obtained, the reaction is regioselective to 1,6-dienes, and only small amounts of nontoxic reagents are required. Due to these properties, the reaction was used as the key step in natural product syntheses, e.g. of panasinsene,[4] grandisol,[5,6] or robustadials.[7]

During the reaction of the diene **1** to the bicyclo[3.2.0]-heptane **2** up to four stereogenic centers are generated (Scheme 1). Although this photocycloaddition is an appropriate tool for special synthetic problems, there are no investigations dealing with the stereoselective generation of these stereogenic centers up to now. This paper presents investigations using chiral catalysts, chiral auxiliaries, and an enantiomerically pure diene derivative to generate the bridgehead carbons at C-1 and C-5 stereoselectively.

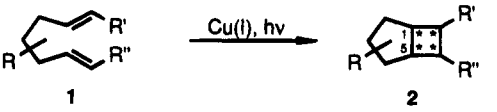
Results and Discussion

For several reasons, we focussed our investigations on the stereoselective generation of the bridgehead carbons at C-1 and C-5. First, a selective generation of the centers at C-6 and C-7 relative to the bridgehead carbons C-1 and C-5 is not possible.[8] Obviously, a copper(I)-catalyzed *cis*/*trans*-isomerization at the double bond occurs before cycloaddition,[9] or the isomerization proceeds during the photocycloaddition (see mechanism of the reaction[3a]).

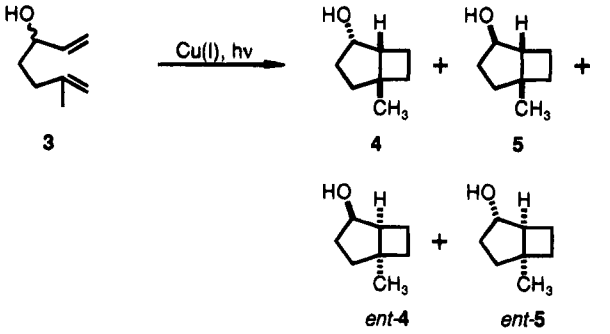
To enable a comparison of the different methods and to facilitate the analysis of the product ratios, the photocycloaddition of the dienol **3** to the diastereoisomeric bicyclic alcohols **4** and **5** was used as a "test system" (Scheme 2). The enantiomeric excesses of **4** and **5** were detected by using a chiral capillary GLC column which enables a very exact detection even of very small or very high excesses.

At first, enantiomerically pure dienol **3** was synthesized and converted into a chiral compound of known stereochemistry to identify the absolute configuration of the resulting bicyclic alcohols **4** and **5**. In addition, the influence of chiral catalysts and chiral auxiliaries on the

Scheme 1



Scheme 2



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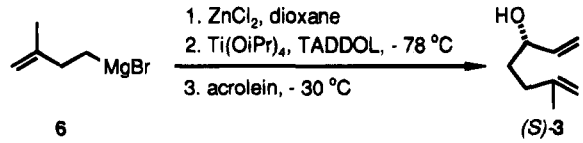
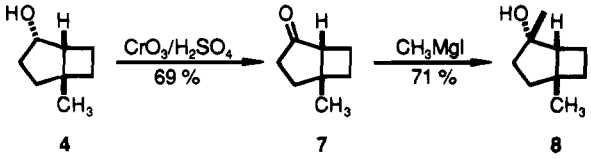
Scheme 3



Scheme 4



stereochemistry of the reaction products **4** and **5** was investigated.

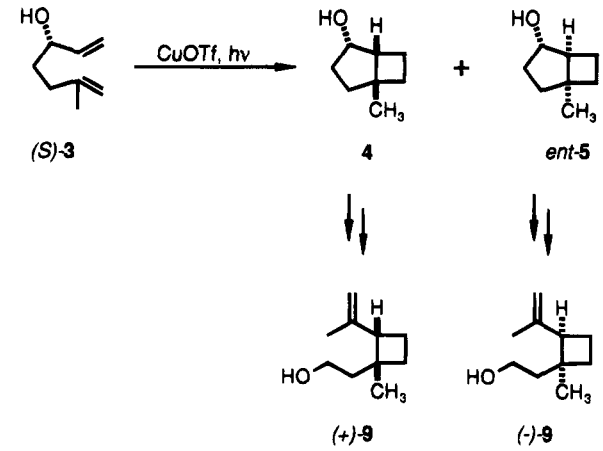
Enantiomerically pure dienol 3 was synthesized by a procedure of Seebach et al. by using a chiral titanium catalyst.[10] The Grignard compound **6**, which is generated from the corresponding alkenyl bromide, was converted into the alkenyl zinc compound. Subsequent treatment with titanium tetraisopropoxide, (4*R*,5*R*)-2,2-dimethyl-α,α,α′,α′-tetranaphth-2-yl-1,3-dioxolane-4,5-dimethanol (TADDOL)[10b] and acrolein yielded the dienol (*S*)-**3** (Scheme 3).

To determine the enantiomeric excess, the dienol (*S*)-**3** was converted into the bicyclic alcohols **4** and **5** by irradiating (*S*)-**3** in the presence of copper(I) trifluoromethanesulfonate–benzene complex (CuOTf). GLC-analysis of **4** and **5** reveals an enantiomeric excess >98% for both. Seebach et al. obtained nearly the same result for a similar compound.[10b] Because of this fact and the high excess, racemization reactions during the cycloaddition can be ruled out. Seebach et al. predict the (*S*)-configuration for the resulting secondary alcohol, if (4*R*,5*R*)-TADDOLs are used. On the other hand the dienol **3** had never been synthesized enantiomerically pure before. To determine the absolute configuration, diastereomer **4** was converted into a compound of known stereochemistry after separation of the two diastereoisomers. Oxidation of **4** yielded a ketone which was treated with methylmagnesium iodide to yield the enantiomerically pure bicyclic alcohol **8**, which had already been synthesized by Rosini et al.[5c,d] This sequence proves the absolute configuration at C2 and C5 and by inference C1 of alcohol **4** (Scheme 4).

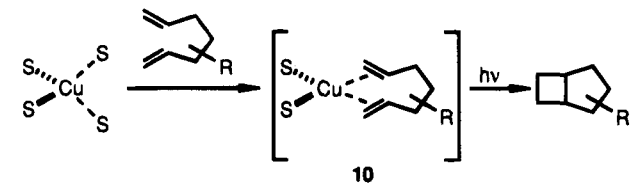
Grandisol is one of four components of grandlure, the pheromone of the male boll weevil (Anthonomus grandis).[11] Because of its unique structure, it has been the subject of many synthetic investigations.[12] It has already been synthesized enantioselectively pure several times, but the chiral information has never been introduced by an enantioselective transition metal-catalyzed reaction.[13] The enantioselective synthesis of (*S*)-**3** described above opens a new synthetic route to (+)- and (−)-grandisol **9** (Scheme 5).

The two diastereoisomeric alcohols **4** and *ent*-**5** can be separated by semipreparative HPLC or column chromatography, and after separation **4** would lead to (+)-grandisol and *ent*-**5** would lead to (−)-grandisol according to the procedure which has been described in detail by us earlier.[6]

Scheme 5



Scheme 6



Chiral Catalysis. During the copper(I)-catalyzed [2 + 2]-photocycloaddition via the intermediate **10**, two olefinic double bonds are coordinated to the copper ion[3a] while the other coordination sites of the copper ion are probably occupied by solvent molecules (*S*) (Scheme 6). The replacement of the solvent molecules by a chiral, bidentate ligand and subsequent irradiation should induce enantiomeric excesses at the generated bridgehead carbons.

Nitrogen-containing chiral ligands seem to be especially promising, because they deliver excellent stereoselectivities in other reactions[14] and, moreover, mixed complexes containing nitrogen ligands, copper, and olefins have already been isolated.[15] Therefore we investigated several chiral, bidentate ligands: (1*S*,9*S*)-dimethyl 5-cyanosemicorrin-1,9-dicarboxylate,[16] (4*S*,4′*S*)-4,4′-diisopropyl-2,2′-methylenebisoxazoline,[17a–d] (4*S*,4′*S*)-4,4′-diisopropyl-2,2′-bisoxazoline **12**,[17b–d] (4*R*,4′*R*)-4,4′-diethyl-2,2′-bisoxazoline (**13**), 2,2-bis[2-(4*S*)-isopropyloxazolinyl)-propane,[17b,e] (4*S*)-2-(2-hydroxyphenyl)-4-isopropyloxazoline (**11**)[18] (4*S*)-2-(3-*tert*-butyl-2-hydroxyphenyl)-4-isopropyl-oxazoline, (−)-diethyl tartrate, and (4*R*,5*R*)-α,α,α′,α′,2,2-hexamethyl-1,3-dioxolane-4,5-dimethanol.[19] In the presence of the chiral ligands, the irradiation time was

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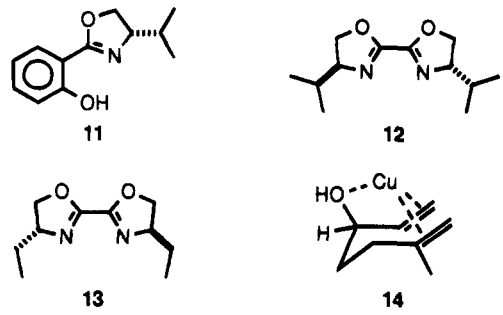
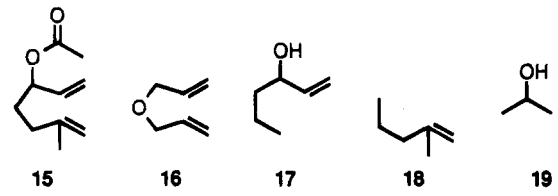
Scheme 7



Scheme 8



remarkably enhanced. In the case of the nitrogen-containing ligands, no reaction occurs if the copper/ligand ratio exceeds two. The copper complexes containing anionic chiral ligands are destroyed during irradiation, as confirmed by UV-measurements. The oxazoline derivatives **12** and **13** induce low enantiomeric excesses <5%; the other ligands did not exhibit any excess.

These negative results may have several causes: (a) The chiral ligands are not suitable to induce enantioselectivity. (b) The affinity of the copper ion to the diene moiety is decreased by the chiral ligand. (c) The chiral copper complex exhibits low reactivity, compared to the copper ion coordinated to solvent molecules.

Cause a seems not to be very likely, because the ligands have induced high enantiomeric excesses in other reactions.[14] The chiral centers are close to the catalytic center so they should strongly influence the stereoselective generation of the bridgehead carbons.

To decide between b and c, we studied the CD-spectra of the copper(I) complexes of **11** and **12** while successively adding olefinic ligands. If the olefins are coordinated to the copper ion after addition, the coordination sphere of the copper ion is changed, and this should induce a change in the CD-spectrum.[20] To draw a conclusion which part of the dienol **3** is responsible for spectral changes, compounds **15**–**19** were also investigated.

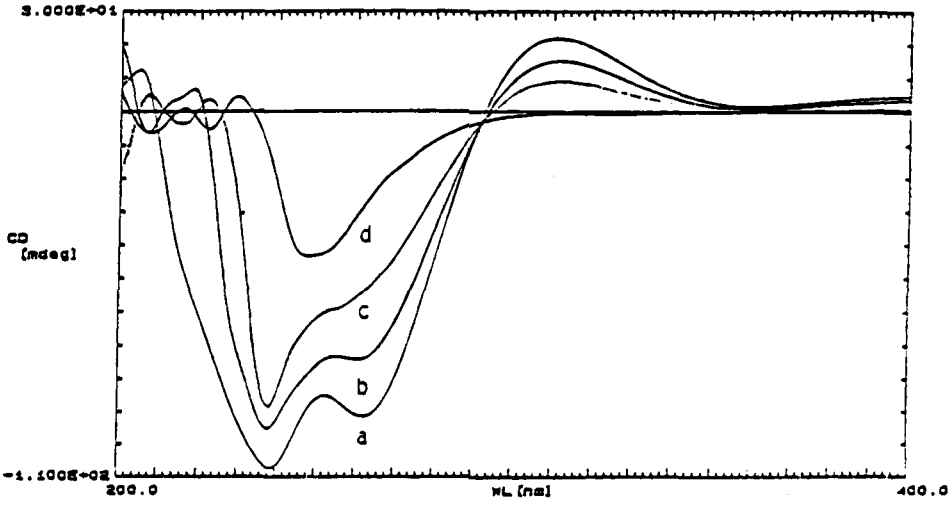
The CD-spectra of **11** and CuOTf 1:1 in ether did not change after successive addition of any of compounds **3** or **15**–**19**. This result leads to the conclusion that there is probably no change in the coordination sphere of the chiral copper(I) complex of **11** and, consequently, the copper ion in this neutral copper complex exhibits low affinity to olefinic double bonds according to b.

In contrast, in the case of **12** and CuOTf spectral change was observed. The addition of the diolefins **3**, **15**, or **16** induced a distinct change of the CD-spectrum, as depicted for **15** in Scheme 9. Monoolefins **17** and **18** induced a small spectral change, while non-olefinic **19** caused no change. It is remarkable that the spectrum of the free ligand (λ_{max} = 231 nm) was not observed. If $Cu(OTf)_2$ was used instead of CuOTf, no spectral change occurred after addition of olefins.

This result leads to the conclusion that a change in the coordination sphere of the chiral copper(I) complex occurs, probably by exchange of the low coordinating solvent molecules by olefinic double bonds. This assertion is in agreement with isolated mixed copper(I) complexes of *cis,cis*-1,5-cyclooctadiene and 2,2′-bipyridine.[15] In contrast to the neutral copper complex of **11**, the complex of **12** is a cationic complex, explaining its higher affinity to olefinic double bonds. Because a coordination of the diene in this case is obvious, low enantiomeric excesses must be caused by a very low reactivity of these complexes according to c. This conclusion is supported by the analysis of the *endo*/*exo* selectivity of the reaction. The *endo*/*exo* product ratio usually exceeds unity, although the *endo* product is the thermodynamically less stable one. This finding is caused by a tridentate intramolecular coordination of the copper ion according to **14**, leading to the *endo*-bicyclic **4**.[3c,6] The ratio exhibits typical values for the solvent used and is not influenced by the chiral ligands. This observation indicates a preferred reaction via the solvent-coordinated copper ion.

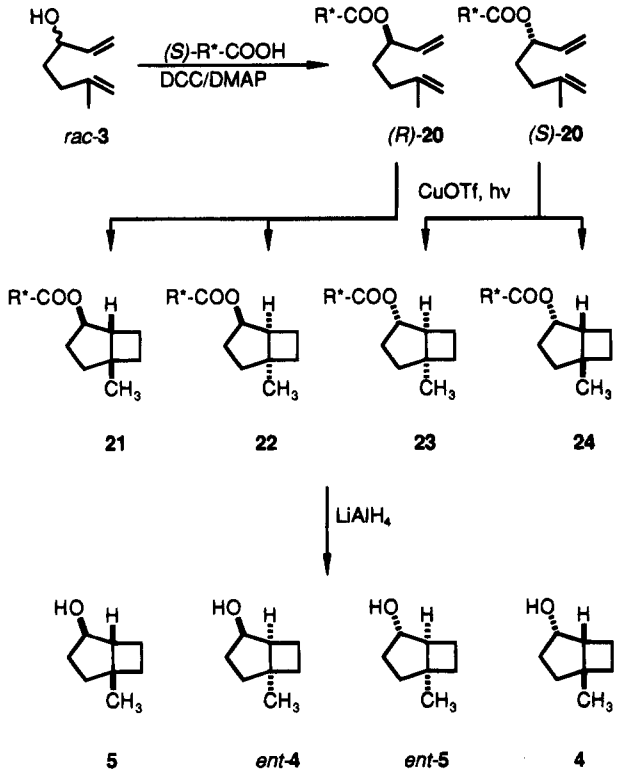
The reason for the low reactivity of the chiral copper complexes is not clear. One possible explanation could be a charge transfer between the chiral ligand and the

Scheme 9.[a] CD-Spectra of Copper(I) Complexes of 12



[a] (a) CuOTf/**12** 1:1, 0.4 mM in ether, (b) solution a + 2 μL of **15** (~26-fold excess), (c) solution a + 5 μL of **15** (~65-fold excess), (d) solution a + 20 μL of **15** (~260-fold excess).

Scheme 10



copper after excitation and not between the copper ion and the olefin. As a consequence, chiral copper complexes are not suitable for stereoselective generation of the bridgehead carbons at C-1 and C-5.

Chiral Carboxylic Acid Esters. Another alternative to achieve chiral induction during the generation of the bridgehead carbons is to attach a chiral auxiliary to the diene derivative. In the case of alcohol **3** esterification with a chiral carboxylic acid and reductive cleavage of the resulting esters after photocycloaddition offer a convenient possibility. Esterification with a chiral carboxylic acid (*S*)-R*COOH yields two diastereoisomeric dienol esters **20**, which are converted into four bicyclic esters **21**–**24** during photocycloaddition. Subsequent cleavage of these esters yields **4** and **5** (Scheme 10).

The esterification of **3** is carried out under basic conditions using DCC/DMAP,[21] because **3** is not stable under acidic conditions. The cleavage of the bicyclic esters is achieved by refluxing the esters in ether with an excess of lithium aluminum hydride.

To identify possible racemization reactions during the reaction sequence (esterification, photocycloaddition, reductive cleavage), we repeated the same procedure with enantiomerically pure (*S*)-**3** and (*S*)-*N*-(ethoxycarbonyl)-alanine (**30a**). However, less than 1% racemization was observed.

According to this sequence, several chiral carboxylic acid derivatives bearing a heteroatom that may interact with the copper ion were investigated. To obtain enantiomeric excesses of **4** and **5** after reductive cleavage of the bicyclic esters, the two diastereoisomeric dienol esters **20** have to exhibit different *endo*/*exo* selectivities during photocycloaddition.

Malic acid derivatives 25 were synthesized by known procedures[22] and converted into **26** by using DCC/DMAP. Ester **27** was generated by stirring **26b** with *p*-toluenesulfonic acid in methanol (Scheme 11).

Scheme 11

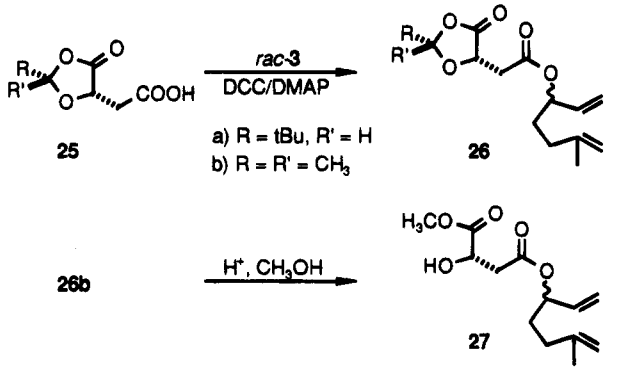


Table 1. Yields and Enantiomeric Excesses of the Bicyclic Alcohols 4 and 5 during the Copper(I)-Catalyzed [2 + 2]-Photocycloaddition of the Malic Acid Derivatives

entry	dienol ester	yield of **4** + **5** (%)[a]	ee of **4** (%)[b]	ee of **5** (%)[c]
1	**26a**	63	5 (1*R*,2*S*,5*R*)	2 (1*R*,2*R*,5*R*)
2	**26b**	73	6 (1*R*,2*S*,5*R*)	4 (1*R*,2*R*,5*R*)
3	**27**	59	4 (1*S*,2*R*,5*S*)	3 (1*S*,2*S*,5*S*)

[a] Reductive workup without isolation of **28** and **29**. [b] *ent*-**4**. [c] *ent*-**5**.

Irradiation of **26a,b** and **27** and reductive cleavage of the corresponding bicyclic esters **28a,b** and **29** according to Scheme 10 yielded bicyclic alcohols of low enantiomeric excess (ee, see Table 1). Obviously, the influence of the chiral center of the malic acid auxiliary on the generation of the bridgehead carbons is quite low.

Amino carboxylic acid derivatives which have been used as auxiliaries in other reactions[23] are more promising because the chiral center of the auxiliary is closely attached to the generated stereogenic centers in contrast to the case of the malic acid derivatives. Before carrying out the sequence, the amino moiety has to be protected for two reasons: In the presence of amine the DCC-esterification would not be successful and in addition the copper(I)-catalyzed photocycloaddition does not occur in the presence of an excess of amine. The *N*-ethoxycarbonyl group was used, because it is more stable than other alkoxycarbonyl derivatives. After esterification, the cycloaddition of **31** occurs in good yields. To avoid side reactions, to decrease the reaction time, and to enhance the yield, it is important to use 3 M lithium perchlorate solution in ether as a solvent. This extraordinary solvent has been used successfully in other reactions.[24] Usually, two irradiations were carried out. The first one to isolate the bicyclic esters **32** and the second one to detect the enantiomeric excess by direct reductive workup of the reaction mixture. To investigate the influence of the substituents at the auxiliary, several derivatives were synthesized.

The reaction of the (*S*)-*N*-(ethoxycarbonyl)alanine and -valine derivatives **31a,c** and **32a,c** can be monitored by GLC because the diastereoisomers of these derivatives

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Scheme 12

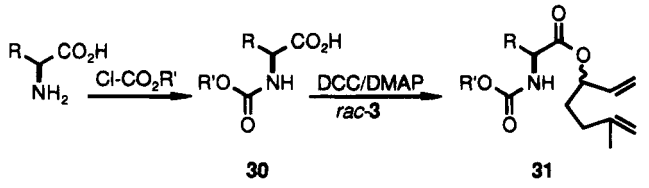


Table 2. Yields of the Bicyclic Esters 32 and Yields and Enantiomeric Excesses of the Bicyclic Alcohols 4 and 5 during the Copper(I)-Catalyzed [2 + 2]-Photocycloaddition of the Amino Carboxylic Acid Derivatives 31

entry	amino carboxylic acid ester 31	R	R′	yield of 32 (%)	yield of 4 + 5 (%)[a]	ee of 4 (%)[b]	ee of 5 (%)[c]
1	**a**) Ala	Me	Et	71	87	7	4
2	**b**) Ala	Me	Ph	86	63	7	5
3	**c**) Val	iPr	Et	79	65	10	9
4	**d**) Leu	iBu	Et	93	61	10	9
5	**e**) Phe	Bn	Et	69	55	15	14

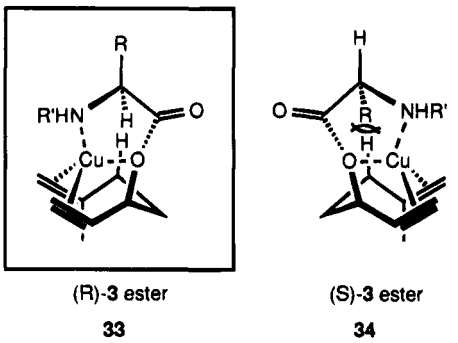
[a] Reductive workup without isolation of **32**. [b] *ent*-**4** as main enantiomer. [c] *ent*-**5** as main enantiomer.

are resolved. In these cases, the ester of (*R*)-**3** reacts much faster than the (*S*)-**3** ester and the *endo*/*exo* product ratio is higher than in the case of the (*S*)-**3** ester. The larger the substituent R at the α-carbon of the amino carboxylic acid, the higher is the *endo*/*exo* product ratio and consequently, the enantiomeric excess of **4** and **5** (see Table 2). This result is compelling, because a different *endo*/*exo* product ratio is the reason for the enantioselectivity. In contrast, the substituent R′ at the carbamate moiety does not influence the enantioselectivity. It is remarkable that the (2*R*)/(2*S*) product ratio of **32** is not 50:50, as expected, but is always shifted in favor of the (2*R*)-products.

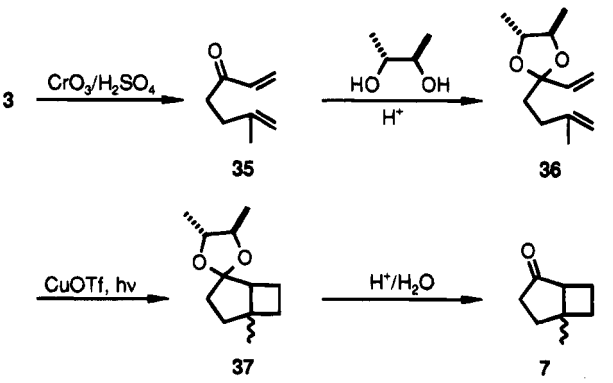
A possible explanation is offered by an intramolecular tetradentate coordination of the copper ion by the two olefinic double bonds, the oxygen of the ester, and the nitrogen of the carbamate moiety. This type of coordination should lead to the *endo* products **32**.

An intramolecular coordination by the oxygen is likely, because the *endo*/*exo* product ratio exceeds one, although the *exo* product is thermodynamically favored. In the case of the dienol, this fact is explained by an intramolecular tridentate coordination of the copper ion by the double bonds and the hydroxy group (see above) and so it should be in the case of the esters. If one assumes an additional coordination of the copper ion by the carbamate nitrogen which obviously should be rather weak, two different steric interactions at the two diastereoisomeric intermediates **33** and **34** are likely to be present as depicted in Scheme 13. In the case of **34**, a strong interaction between 5-H of the dienol site and the substituent R of the amino carboxylic acid moiety is present, while in the case of **33** two hydrogen atoms are interacting. Hence, the *endo* product of **33** is favored compared to **34**, which causes a higher *endo*/*exo* product ratio for the (*R*)-**3** esters **31**. This difference is increased if the size of R is increased. Because of the lower steric interaction, the (*R*)-**3** esters react faster. The fact that the products do not exhibit a 50:50-mixture of (2*R*)- and (2*S*)-bicyclic esters **32** cannot be explained in a satisfying manner. We suppose a more complete destruction of the (*S*)-**3** ester by UV-irradiation because its reaction rate is lower. The dienol esters **31** should be more sensitive to UV-destruction because of their higher number of chromophores compared to the bicyclic products **32**.

Scheme 13



Scheme 14



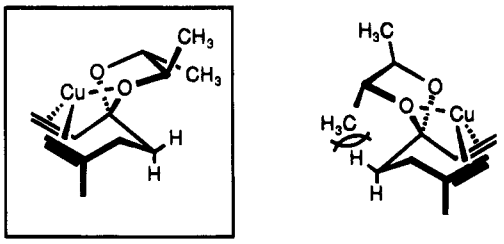
The enantiomeric excesses are quite low. Probably, the interaction between the copper ion and the carbamate nitrogen is weak and the conformational rigidity of the intermediate is small. In addition, the formation of the *exo* product does not seem to be directly influenced by the auxiliary. The enantioenrichment of the *exo* products are a consequence of the different *endo*/*exo* product ratios, which are obviously caused only by interactions of the *endo*-intermediates **33** and **34**. To overcome this problem, we decided to examine a cyclic ketal as an auxiliary.

Chiral Ketal. The dienol **3** was oxidized and the resulting ketone **35** was ketalized with a chiral, C_2-symmetric 1,2-diol. This strategy involves several advantages: the conformational rigidity of the system is enhanced, the chiral centers of the auxiliary are closer to the generated stereogenic centers, and the number of diastereoisomers is reduced. Unfortunately, the α,β-unsaturated ketone **35** is not readily ketalized. By using *p*-toluenesulfonic acid and D-(−)-2,3-butanediol, the desired ketal **36** could be isolated in 25% yield. The procedure according of Noyori,[25] as well as an attempt to ketalize with an orthoester,[26] were not successful. Attempts to ketalize **35** with (−)-diethyl tartrate were completely unsuccessful.

The copper(I)-catalyzed photocycloaddition of ketal **36** yielded two diastereoisomeric spiroketals **37** in an 80:20-ratio (Scheme 14). Acidic cleavage of these spiroketals gave the ketone **7** with an enantiomeric excess of 60%, the (1*R*,5*R*)-enantiomer being identified as the main product. To explain these results, we assume a tridentate coordination of the copper ion by the double bonds and the *endo*-oxygen of the ketal, similar to the intermediates leading to the *endo* products of the dienols and

(25) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, 1357.
(26) Roush, W. R.; Gillis, H. R. *J. Org. Chem.* **1980**, *45*, 4283.

Scheme 15



38 **39**

dienol esters. In the case of **39** an interaction between a methyl group and a hydrogen is present, while in **38** two hydrogens are interacting. Because of the lower steric interaction in the case of **38** which leads to (1*R*,5*R*)-**7** after cleavage of the corresponding ketal, the generation of this enantiomer is favored.

In polar solvents (ether, 2-propanol, 3 M lithium perchlorate solution in ether) the enantiomeric excess was about 60%, while in cyclohexane only 50% was observed. This decreased *endo*/*exo* diastereoselectivity in nonpolar solvents is similar to the behavior of the dienol **3**.[6] In ether, the *endo*/*exo* ratio of the cycloaddition was 6.8, while in cyclohexane a ratio of 2.8 was observed.

Experimental Section

HPLC: Merck Pump L-6000 or Kontron Pump 420, RI-detector Bischoff RI 8110, column 250 × 20 mm, Lichrosorb Si 60-5 or 250 × 40 mm, Lichrosorb Si 60–5 (semipreparative), 250 × 5 mm, Kontrosorb 5-Sil (analytical). GLC: Siemens Sichromat 4 with FI-detector, Spectra Physics Integrator SP 4400, and capillary column HP Ultra 2 (25 m, 0.2 mm), or Siemens Sichromat 3 with FI-detector, Spectra Physics Integrator SP 4290, and chiral capillary column Macherey & Nagel FS-Hydrodex β-PM (50 m, 0.25 mm). Because of the strong similarity of the diastereoisomers, several ^{13}C-NMR-signals are not resolved. So the number of signals listed consequently does not always correspond to the number of carbon atoms.

(*S*)-6-Methyl-1,6-heptadien-3-ol (3): In a dry apparatus under an argon atmosphere, 29.8 g (200 mmol) of 1-bromo-3-methyl-3-butene in 70 mL of dry ether was added to 4.86 g (200 mmol) of Mg. The Grignard concentration was determined by titration of a 2 mL aliquot with a solution of 764 mg of 2-butanol in 50 mL of dry toluene under argon, using 1,-10-phenanthroline as indicator. Yield: 146 mmol (73%). Under argon, the Grignard solution was added to 75 mL of a 1 M solution of $ZnCl_2$ in ether (Aldrich). The mixture was stirred for 2 h and diluted with 40 mL of dry ether. Then dry 1,4-dioxane (45 mL) was added and stirred for an additional 45 min. The precipitate was filtered under argon, and at −78 °C the resulting solution was added to a solution of 13.4 mL (45 mmol) of titanium tetraisopropoxide and 5.25 mmol of TADDOL (see above) in 75 mL of dry ether. Then, at −78 °C acrolein (2.5 mL, 37.5 mmol) was added through a septum, and the mixture was allowed to warm to −30 °C. After the reaction was complete (monitored by GLC), 80 mL of saturated NH_4Cl-solution and 200 mL of ether were added, and the white suspension was filtered through Celite 545. The organic layer was washed with water and brine, dried with $MgSO_4$, and carefully evaporated in vacuo. To separate traces of TADDOL, the crude product was suspended in pentane, stirred, filtered, and evaporated in vacuo. After column chromatography (pentane/ether 4:1), pure (*S*)-**3** (2.40 g, 51%) was obtained. Anal. Calcd for $C_8H_{14}O$ (126.20): C 76.14; H 11.18. Found: C 76.66; H 11.13. $[\alpha]^{24}_D$ = +4.84° (*c* = 2.2, $CHCl_3$). For spectroscopic data, see ref 6.

To determine the enantiomeric excess, (*S*)-**3** (70 mg) in 4 mL of a 3 M solution of $LiClO_4$ in ether was converted into **4** and **5** (see general procedure). The two bicyclic alcohols exhibit enantiomeric excesses >98% (by chiral capillary GLC).

(1*R*,2*S*,5*R*)- and (1*S*,2*S*,5*S*)-5-Methylbicyclo[3.2.0]heptan-2-ol (4 and *ent*-5). (*S*)-**3** (900 mg, 7.1 mmol) was dissolved in 30 mL of dry ether, and the solution was divided into three 10 mL portions. A 25 mg (0.1 mmol) amount of CuOTf was added to each portion, and they were irradiated in 10 mL quartz vessels. After the reaction was complete (monitored by GLC) the combined organic layers were evaporated carefully, and the crude product was chromatographed through a short column (cyclohexane/ethyl acetate 85:15) to yield 630 mg (70%) of a mixture of **4** and **5**. This mixture was separated by semipreparative HPLC (cyclohexane/ethyl acetate 85:15). (1*R*,2*S*,5*R*)-4. Anal. Calcd for $C_8H_{14}O$ (126.20): C 76.14; H 11.18. Found: C 75.82; H 11.13. $[\alpha]^{24}_D$ = −39.3° (*c* = 8.5, $CHCl_3$). (1*S*,2*S*,5*S*)-5: Anal. Calcd for $C_8H_{14}O$ (126.20): C 76.14 H 11.18. Found: C 75.65; H 11.23. $[\alpha]^{24}_D$ = −7.8° (*c* = 1.5, $CHCl_3$). For spectroscopic data see ref 6.

(1*R*,5*R*)-5-Methylbicyclo[3.2.0]heptan-2-one (7). A solution of 135 mg (1.35 mmol) of CrO_3 in 0.4 mL of water and 0.12 mL of concentrated sulfuric acid was added slowly at 0–5 °C to a solution of 170 mg (1.35 mmol) of (1*R*,2*S*,5*R*)-**4** in 1 mL of acetone. The solution was stirred for an additional 1 h at 0–5 °C, diluted with 3 mL of water, and extracted with ether. The organic layer was washed with saturated $NaHCO_3$-solution and brine and dried with $MgSO_4$. The solvent was carefully removed in vacuo to yield 118 mg (69%) of (1*R*,5*R*)-**7**. $[\alpha]^{21}_D$ = −256.2° (*c* = 5.0, $CHCl_3$). For spectroscopic data of the racemic compound see ref 6.

(1*R*,2*S*,5*R*)-2,5-Dimethylbicyclo[3.2.0]heptan-2-ol (8). In a dry apparatus under an argon atmosphere, 1.5 mL (4.5 mmol) of a 3 M solution of methylmagnesium iodide in ether (Aldrich) was diluted with 1.5 mL of dry ether. At 0–5 °C, a solution of 86 mg (0.69 mmol) of (1*R*,5*R*)-**7** in 2.5 mL of dry ether was added, and the mixture was stirred for about 16 h. At 0 °C, a saturated NH_4Cl-solution was added. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed in vacuo, and the crude product was sublimated (44–46 °C, 18 mmHg) to yield 69 mg (71%) of white crystals. Anal. Calcd for $C_9H_{16}O$ (140.23): C 77.09; H 11.50. Found: C 77.12; H 11.51. $[\alpha]^{21}_D$ = −26.2° (*c* = 2.2, CH_3OH). ^{13}C-NMR ($CDCl_3$): δ = 14.52, 27.83, 28.24, 30.97, 38.15, 39.26, 43.40, 52.77, 79.36. For further spectroscopic data see refs 5a–d.

Irradiation in the Presence of Chiral Ligands. In a dry, argon-flushed 10 mL quartz vessel, 1 mmol of $Cu(OTf)_2$ or CuOTf and 1 mmol of the chiral ligand were treated with a solution of 252 mg (20 mmol) of **3** and dodecane as internal standard in 10 mL of dry ether or cyclohexane. The vessel was sealed with a septum cap and irradiated in a merry-go-round apparatus. The reaction was monitored by GLC. Since the reaction was quite slow, it was stopped before total conversion. The reaction mixture was carefully evaporated, and the crude product was purified by HPLC (cyclohexane/ethyl acetate 90:10). The enantiomeric excess was determined by chiral GLC.

CD-Spectroscopy. For CD-spectroscopic measurements, 4 × 10^{-4} M solutions of **12**, CuOTf/**12** 1:1, and $Cu(OTf)_2$/**12** 1:1 as well as 4 × 10^{-5} M solutions of **11**, CuOTf/**11** 1:1, and $Cu(OTf)_2$/**11** 1:1 in ether were prepared under an argon atmosphere. The measurements were carried out with 900 μL each of the solutions, and the ligands **3** and **15**–**19** were added to these solutions with a 50 μL glass syringe.

6-Methyl-1,6-heptadien-3-yl Acetate (15). In a dry apparatus under an argon atmosphere, 5.14 g (40.2 mmol) of **3** and a small amount of DMAP were dissolved in 10 mL of dry pyridine. At 0 °C, a solution of 9.42 g (120 mmol) of acetyl chloride in 70 mL of dry ether was carefully added, and the mixture was stirred for about 16 h. The white precipitate was removed by filtration, and the resulting solution was extracted twice with 2 M hydrochloric acid, with saturated $NaHCO_3$-solution, and with brine. The solution was dried with $MgSO_4$ and evaporated, and the crude product was purified by column chromatography (cyclohexane/ethyl acetate 95:5). A 4.4 g (70%) amount of a colorless liquid was obtained. Anal. Calcd for $C_{10}H_{16}O_2$ (168.24): C 71.39; H 9.59. Found: C 71.13; H 9.58. ^{1}H-NMR ($CDCl_3$): δ = 1.72 (s, 3 H), 1.73–1.87 (m, 2 H),

2.00–2.08 (m, 2 H), 2.06 (s, 3 H), 4.68 (m,1 H), 4.72 (m, 1 H), 5.15–5.28 (m, 3 H), 5.78 (ddd, J = 6.4/10.6/17.1 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 21.10, 22.35, 32.11, 33.12, 74.38, 110.27), 116.70, 136.36, 144.63, 170.15. IR (neat): ν = 3050, 2910, 2820, 1730, 1635, 1430, 1360, 1225, 1095, 1010, 980, 945, 920 cm^{-1}. MS: m/z = 108 (9), 93 (51), 91 (24), 79 (26), 77 (16), 67 (12), 55 (14), 43 (100), 41 (20), 39 (35).

General Procedure for Esterification of 3. A solution of 3.7 g (18 mmol) of dicyclohexylcarbodiimide in dry dichloromethane was added to a solution of 2.0 g (16 mmol) of **3**, 18 mmol of the carboxylic acid, and a small amount of DMAP or 4-pyrrolidinopyridine in 100 mL of dichloromethane. After the reaction was complete (monitored by GLC), the white precipitate was removed by filtration. The solution was extracted three times with water, three times with acetic acid, and again with water. The organic layer was dried with $MgSO_4$, the solvent was removed in vacuo, and the crude product was purified by column chromatography.

***tert*-Butyl ketal of (1′*RS*,2*S*,5*S*)-2-hydroxysuccinic acid 4-(4′-methyl-1′-vinylpent-4′-enyl) ester 26a:** yield: 3.6 g (93%) from 12.5 mmol **3**. Anal. Calcd for $C_{17}H_{26}O_5$ (310.39): C 65.78; H 8.44. Found: C 65.66; H 8.45. (1′*S*,2*S*,5*S*)-**26a** was separated by HPLC (cyclohexane/ethyl acetate 97:3). (1′*S*,2*S*,5*S*)-**26a:** $[\alpha]^{22}_D$ = −10.4° (c = 1.1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 0.95 (s, 9 H), 1.72 (s, 3 H), 1.73–1.90 (m, 2 H), 2.04 (t, J = 7.5 Hz, 2 H), 2.73 (dd, J = 8.3/16.2 Hz, 1 H), 2.95 (dd, J = 3.8/16.2 Hz, 1 H), 4.64–4.76 (m, 3 H), 5.15–5.35 (m, 4 H), 5.79 (ddd, J = 6.4/10.5/17.0 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 22.36, 23.40, 32.03, 33.08, 34.22, 36.13, 71.77, 75.46, 109.77, 110.49, 117.18, 135.85, 144.48, 168.34, 172.21. IR (neat): ν = 3060, 2950, 2920, 2860, 1795, 1730, 1640, 1480, 1405, 1370, 1360, 1340, 1310, 1270, 1200, 1160, 1110, 1050, 960, 930, 890 cm^{-1}. **Diastereoisomeric mixture:** ^{1}H-NMR ($CDCl_3$): δ = 0.95 (s, 9 H), 1.72 (s, 3 H), 1.73–1.90 (m, 2 H), 2.04 (t, J = 7.5 Hz, 2 H), 2.73 (dd, J = 8.3/16.6 Hz, 1 H), 2.94 (dd, J = 3.8/16.6 Hz, 1 H of (1′*R*)-**26a**) 2.95 (dd, J = 3.8/16.6 Hz, 1 H of (1′*S*)-**26a**), 4.64–4.76 (m, 3 H), 5.15–5.35 (m, 4 H), 5.79 (m, 1 H). MS: m/z = 203 (4), 185 (7), 167 (6), 125 (4), 109 (78), 108 (46), 93 (100), 87 (40), 80 (32), 79 (44), 69 (42), 67 (67), 57 (58), 55 (36), 43 (26), 41 (42).

Dimethyl ketal of (1′*RS*,2*S*,5*S*)-2-hydroxysuccinic acid 4-(4′-methyl-1′-vinylpent-4′-enyl) ester 26b: yield: 2.74 g (65%) from 15 mmol **3**. Anal. Calcd for $C_{15}H_{22}O_5$ (282.34): C 63.81; H 7.85. Found: C 63.98; H 8.07. (1′*S*,2*S*)-**26b** was separated by HPLC (cyclohexane/ethyl acetate 95:5). (1′*S*,2*S*)-**26b:** $[\alpha]^{18}_D$ = −8.2° (c = 1.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 1.56 (s, 3 H,), 1.61 (s, 3 H), 1.72 (s, 3 H), 1.73–1.90 (m, 2 H), 2.00–2.08 (m, 2 H), 2.79 (dd, J = 6.8/16.6 Hz, 1 H), 2.95 (dd, J = 3.8/16.6 Hz, 1 H), 4.65-4.75 (m, 3 H), 5.78 (ddd, J = 6.4/10.5/16.9 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 22.38, 25.83, 26.76, 32.02, 33.03, 36.54, 70.73, 75.52, 110.43, 111.10, 117.23, 135.84, 144.50, 168.44, 172.00. IR (neat): ν = 3070, 2940, 2850, 1795, 1740, 1380, 1320, 1260, 1180, 1125, 890 cm^{-1}. **Diastereoisomeric mixture:** ^{1}H-NMR ($CDCl_3$): δ = 1.56 (s, 3 H), 1.61 (s, 3 H of (1′*S*,2*S*)-**26b**), 1.62 (s, 3 H of (1′*R*,2*S*)-**26b**), 1.72 (s, 3 H), 1.73–1.90 (m, 2 H), 2.00–2.08 (m, 2 H), 2.78 (dd, J = 6.8/16.6 Hz, 1 H of (1′*R*,2*S*)-**26b**) 2.79 (dd, J = 6.8/17.0 Hz, 1 H of (1′*S*,2*S*)-**26b**), 2.94 (dd, J = 3.8/16.6 Hz, 1 H of (1′*R*,2*S*)-**26b**), 2.95 (dd, J = 3.8/17.0 Hz, 1 H of (1′*S*,2*S*)-**26b**), 4.65–4.75 (m, 3 H), 5.15–5.35 (m, 3 H), 5.78–5.84 (m, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 22.34, 25.80, 26.73, 32.01, 33.02, 36.51, 70.69, 75.49, 110.43, 111.06, 117.19, 117.34, 135.77, 135.83, 144.47, 168.32, 171.95. MS: m/z = 175 (3), 174 (2), 158 (3), 157 (23), 1909 (18), 108 (34), 93 (100), 80 (37), 79 (49), 71 (28), 67 (40), 59 (80), 55 (39), 43 (81), 41 (40), 39 (22).

(1′*RS*,2*S*)-2-Hydroxysuccinic acid 1-methyl ester 4-(4′-methyl-1′-vinylpent-4′-enyl) ester 27. A solution of 7.10 g (25 mmol) of **26b** and 100 mg (0.6 mmol, 2.4 mol-%) *p*-toluenesulfonic acid in 400 mL of methanol was stirred at room temperature until the ketal moiety was completely cleaved (monitored by GLC). The solvent was removed in vacuo, and the crude product was dissolved in 300 mL of ether. The solution was extracted twice with saturated $NaHCO_3$-solution and dried with $MgSO_4$. After removal of the solvent, 4.6 g (71%) of a mixture of the diastereoisomers were obtained. Anal. Calcd for $C_{13}H_{20}O_5$ (256.30): C 60.92; H 7.87. Found: C 60.56; H 8.03. ^{1}H-NMR ($CDCl_3$): δ = 1.70 (s, 3 H), 1.60–1.90 (m, 2 H), 2.05 (m, 2 H), 2.84 (m, 2 H), 2.25 (br s, 1 H), 3.80 (s, 3 H), 4.51 (dd, J = 4.9/5.7 Hz, 1 H), 4.67 (s, 1 H), 4.73 (s, 1 H), 5.15–5.32 (m, 3 H), 5.77 (ddd, J = 6.4/10.5/17.0 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 22.33, 32.02, 33.00, 38.81, 52.69, 67.27, 75.20, 110.39, 117.11, 135.87, 144.49, 169.68, 173.68. IR (kap.): ν = 3480, 3050, 2930, 2830, 1730, 1635, 1430, 1365, 1255, 1205, 1160, 1095, 1030, 980, 920, 880 cm^{-1}. MS: m/z = 148 (12), 130 (13), 113 (15), 109 (35), 108 (24), 103 (45), 93 (100), 91 (28), 80 (30), 79 (36), 71 (26), 67 (40), 55 (25), 43 (53), 41 (29), 39 (47).

General Procedure for the Irradiation of the 6-Methyl-1,6-heptadien-3-ol Esters. 6-Methyl-1,6-heptadien-3-ol ester (1 mmol), ca. 12 mg (0.05 mmol, = 5 mol %) copper(I) trifluoromethanesulfonate–benzene complex (CuOTf), and 10 mL of a 3 M solution of $LiClO_4$ in ether were poured into an argon flushed, dry quartz vessel, and the vessel was sealed by a septum cap. The solution was irradiated in a merry-go-round apparatus until the reaction was complete (monitored by GLC). The irradiation was carried out double. The solution of the first vessel was directly reduced to determine the enantiomeric excess of the bicyclic alcohols **4** and **5**, respectively. The solution of the second vessel was used for the isolation and characterization of the diastereoisomeric bicyclic esters.

To determine the enantiomeric excess, the solution was diluted with ether, extracted with water, dried with $MgSO_4$, and evaporated. Then the solution was added to a suspension of 100 mg of $LiAlH_4$ in 10 mL of dry ether. The mixture was refluxed for 2 h and hydrolyzed with 10 mL of water and 10 mL of 1 M sulfuric acid, and the aqueous layer was extracted twice with ether. The organic layers were dried with $MgSO_4$ and carefully evaporated. The enantiomeric excess of the bicyclic alcohols was determined by chiral GLC.

To separate the diastereroisomeric bicyclic esters, the solution was diluted with ether, extracted with water, dried with $MgSO_4$, evaporated, and filtered through a short silica gel column (cyclohexane/ethyl acetate). Then, the diastereoisomers were separated by semipreparative HPLC.

***tert*-Butyl ketal of (1′*RS*,2*S*,2′*RS*,5*S*,5′*RS*)-2-hydroxysuccinic acid 4-(5-methylbicyclo[3.2.0]hept-2-yl) ester 28a:** yield: 430 mg (87%) from 494 mg (1.6 mmol) of **26a**, mixture of diastereoisomers, *endo*/*exo* = 79:21. Anal. Calcd for $C_{17}H_{26}O_5$ (310.39): C 65.78; H 8.44. Found: C 65.97; H 8.32. ^{1}H-NMR ($CDCl_3$): δ = 0.95 (s, 9 H *exo*), 0.97 (s, 9 H *endo*) 1.18 (s, 3 H *endo*), 1.24 (s, 3 H *exo*), 1.26–2.30 (m, 8 H), 2.51 (m, 1 H), 2.72 (m, 1 H), 2.88 (m, 1 H), 4.66 (m, 1 H), 4.98 (d, J = 3.8 Hz, 1 H *exo*), 5.07 (ddd, J = 7.2/9.4 Hz, 1 H *endo*), 5.17 (s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 12.64, 12.70, 16.71, 23.15, 23.25, 26.82, 29.79, 30.06, 30.97, 31.74, 31.84, 34.14, 35.79, 35.89, 36.19, 36.76, 36.83, 38.34, 38.41, 43.20, 43.98, 44.38, 48.76, 48.83, 71.10), 71.74, 77.84, 83.07, 109.62, 111.10, 168.72, 172.20. IR (neat): ν = 2960, 2850, 1795, 1730, 1480, 1405, 1360, 1340, 1310, 1280, 1210, 170, 1110, 1050, 1020, 995, 965 cm^{-1}. ***exo*-Diastereoisomers**: MS: m/z = 311 (2, M^+ + 1), 202 (10), 186 (13), 167 (5), 157 (2), 149 (5), 125 (2), 109 (100), 108 (39), 97 (32), 93 (36), 87 (34), 81 (31), 67 (36), 57 (25), 41 (52), 39 (27). ***endo*-Diastereoisomers**: MS: m/z = 202 (7), 186 (15), 167 (6), 149 (4), 135 (4), 109 (100), 108 (39), 97 (36), 93 (42), 87 (32), 81 (30), 80 (29), 67 (36), 57 (25), 41 (52), 39 (27). Irradiation and subsequent reduction: Yield: 59 mg (63%) from 230 mg (0.75 mmol) of **26a** enantiomeric excess: 2% (1*R*,2*S*,5*R*)-**4**, 5% (1*R*,2*R*,5*R*)-**5**.

Dimethyl ketal of (1′*RS*,2*S*,2′*RS*,5′RS)-2-hydroxysuccinic acid 4-(5-methylbicyclo[3.2.0]hept-2-yl) ester 28b: yield: 310 mg (69%) from 447 mg (1.6 mmol) **26b**, diastereoisomeric mixture. *endo*/*exo* = 73:27. Anal. Calcd for $C_{15}H_{22}O_5$ (282.34): C 63.81; H 7.85. Found: C 63.96; H 7.75. ^{1}H-NMR ($CDCl_3$): δ = 1.18 (s, 3 H *endo*), 1.23 (s, 3 H *exo*), 1.55 (s, 3 H), 1.61 (s, 3 H), 1.25–2.60 (m, 9 H), 2.65–2.95 (m, 2 H), 4.68 (m, 1 H), 4.93 (d, J = 4.1 Hz, 1 H *exo*), 5.06 (ddd, J = 7.5/9.4 Hz, 1 H *endo*). ^{13}C-NMR ($CDCl_3$): δ = 12.64, 12.74, 16.71, 25.71, 26.62, 26.79, 29.72, 30.03, 30.94, 31.71, 31.88, 36.26, 36.53, 36.73, 36.80, 38.28, 38.34, 43.03, 43.13, 43.91, 43.98, 44.35, 44.41, 48.63, 48.83, 70.63, 77.81, 83.09, 110.89, 168.45, 168.69, 168.79, 171.89. IR (neat): ν = 2930, 2840, 1790, 1730, 1445,

1380, 1350, 1315, 1280, 1255, 1215, 1180, 1120, 1020, 970, 930 cm^{-1}. ***exo*-Diastereoisomers:** MS: *m/z* = 267 (0.1), 226 (1), 175 (4), 174 (4), 157 (18), 109 (44), 108 (60), 97 (100), 93 (87), 81 (50), 80 (70), 67 (41), 59 (74), 55 (32), 43 (74), 41 (42). ***endo*-Diastereoisomers:** MS: *m/z* = 226 (0.3), 175 (4), 174 (3), 157 (17), 109 (42), 108 (72), 97 (78), 93 (100), 81 (44), 80 (62), 79 (53), 67 (47), 59 (85), 55 (35), 43 (86), 41 (41). Irradiation and subsequent reduction: yield: 110 mg (73%) from 336 mg (1.2 mmol) **26b**, enantiomeric excess: 4% (1*R*,2*S*,5*R*)-**4**, 6% (1*R*,2*R*,5*R*)-**5**.

(1′*RS*,2*S*,2′*RS*,5′*RS*)-2-Hydroxysuccinic acid 1-methyl ester 4-(5-methylbicyclo[3.2.0]hept-2-yl) ester 29: yield: 320 mg (78%) from 411 mg (1.6 mmol) **27**. Anal. Calcd for $C_{13}H_{20}O_5$ (256.30): C 60.92; H 7.87. Found: C 60.82; H 8.08. **Diastereoisomeric mixture:** ^{1}H-NMR ($CDCl_3$): δ = 1.11 (s, 3 H *endo*), 1.18 (s, 3 H *endo*), 1.19–1.33 (m, 1 H), 1.40–2.45 (m, 8 H), 2.63–2.78 (m, 2 H, 3-H), 3.18 (m, 1 H), 3.73 (s, 3 H *exo*), 3.74 (s, 3 H *endo*), 4.40 (m, 1 H), 4.88 (d, *J* = 4.1 Hz, 1 H *exo*), 4.98 (m, 1 H *endo*). ^{13}C-NMR ($CDCl_3$): δ = 12.77, 16.82, 26.83, 26.89, 29.78, 31.84, 38.42, 30.06, 31.00, 36.83, 38.69, 43.20, 44.01, 44.48, 48.79, 52.67, 67.33, 77.71, 82.96, 107.21, 173.71. IR (neat): ν = 3470, 2930, 2840, 1730, 1615, 1510, 1440, 1400, 1370, 1330, 1265, 1170, 1105, 1035, 1015, 995 cm^{-1}. ***exo*-Diastereoisomers:** MS: *m/z* = 257 (2, M^+ + 1), 149 (47), 131 (16), 109 (94), 108 (90), 103 (48), 97 (72), 93 (100), 81 (70), 80 (70), 79 (68), 71 (30), 67 (53), 55 (25), 43 (76), 41 (39), 39 (50). ***endo*-Diastereoisomers:** MS: *m/z* = 257 (4, M^+ + 1), 149 (100), 131 (21), 109 (89), 108 (92), 103 (33), 97 (19), 93 (50), 81 (34), 80 (30), 79 (26), 67 (31), 43 (42), 41 (20), 39 (29). Irradiation and subsequent reduction: Yield: 107 mg (59%) from 369 mg (1.45 mmol) **27**, enantiomeric excess: 4% (1*S*,2*R*,5*S*)-**4**, 3% (1*S*,2*S*,5*S*)-**5**.

General Procedure for the Synthesis of *N*-Ethoxycarbonyl Protected Amino Carboxylic Acids (30). Ethyl chloroformate (8.2 g, 75 mmol) was slowly added with stirring to a solution of 50 mmol of the amino carboxylic acid in 200 mL of 1 M $NaHCO_3$ solution. After stirring for an additional 30 min, the mixture was extracted twice with ether. At 0 °C, concentrated hydrochloric acid was added to the aqueous layer until pH = 1 was reached. The solution was extracted four times with ethyl acetate, the organic layer was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The resulting viscous oil (the white precipitate, respectively) was dried at 60 °C in vacuo (0.05 mbar).

(*S*)-*N*-(Ethoxycarbonyl)alanine (30a): yield: 13.4 g (82%) from 100 mmol (*S*)-alanine. Anal. Calcd for $C_6H_{11}NO_4$ (161.16): C 44.72; H 6.88; N 8.69. Found: C 45.01; H 6.72; N 8.85. $[\alpha]^{22}_D$ = −0.24° (*c* = 8.3, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 1.25 (t, *J* = 7.2 Hz, 3 H), 1.46 (d, *J* = 7.2 Hz, 3 H), 4.14 (m, 2 H), 4.40 (m, 1 H), 5.40 (br s, 1 H), 10.90 (br s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.43, 18.41, 49.37, 61.35, 156.21, 177.45. IR (neat): ν = 3320, 1700, 1530 cm^{-1}. MS: *m/z* = 162 (0.15, M^+ + 1), 161 (0.05, M^+), 116 (73), 88 (13), 72 (10), 45 (22), 44 (100), 43 (16), 42 (13).

(*S*)-*N*-(Phenyloxycarbonyl)alanine (30b). Due to the low solubility of phenyl chloroformate, the reaction was carried out at 50 °C in 2 M NaOH solution. The product was recrystallized from ethyl acetate/petroleum ether. Yield: 4.2 g (33%) from 5.4 g (60 mmol) (*S*)-alanine. Anal. Calcd for $C_{10}H_{11}NO_4$ (209.20): C 57.41; H 5.30; N 6.70. Found: C 57.38; H 5.34; N 6.81. $[\alpha]^{18}_D$ = −17.0 (*c* = 5.0, $CHCl_3$), mp: 122–126 °C. ^{1}H-NMR ($CDCl_3$): δ = 1.50 (d, *J* = 7.2 Hz, 3 H), 4.45 (dt, *J* = 7.2 Hz, 1 H), 5.73 (d, *J* = 7.5 Hz, 1 H), 7.11 (d, *J* = 7.9 Hz, 2 H), 7.18 (t, *J* = 7.5 Hz, 1 H), 7.33 (t, *J* = 7.7 Hz, 2 H), 10.80 (br s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 18.21, 49.66, 121.51, 125.53, 129.30, 150.73, 154.21, 177.35. IR (neat): ν = 3330, 1720, 1695, 1650 cm^{-1}. MS: *m/z* = 210 (6, M^+ + 1), 209 (12, M^+), 170 (4), 164 (7), 150 (4), 115 (7), 96 (10), 95 (18), 94 (100), 77 (16), 71 (20), 66 (28), 65 (20), 54 (17).

(*S*)-*N*-(Ethoxycarbonyl)valine (30c): yield: 14.7 g (78%) from 100 mmol of (*S*)-valine. Anal. Calcd for $C_8H_{15}NO_4$ (189.21): C 50.78; H 7.99; N 7.40. Found: C 50.57; H 8.02; N 7.49. $[\alpha]^{22}_D$ = +9.72° (*c* = 5.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 0.93 (d, *J* = 6.9 Hz, 3 H),1.00 (d, *J* = 6.9 Hz, 3 H), 1.25 (t, *J* = 6.9 Hz, 3 H), 2.21 (m, 1 H), 4.14 (q, *J* = 6.9 Hz, 2 H), 4.30 (dd, *J* = 3.7/8.8 Hz, 1 H), 5.30 (br d, *J* = 8.8 Hz, 1 H), 8.70 (br s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.41, 17.31, 18.49, 30.96, 58.73, 61.29, 156.73, 176.03. IR (neat): ν = 3320, 1700, 1530 cm^{-1}. MS: *m/z* = 144 (72), 129 (19), 116 (29), 101 (100), 98 (16), 83 (13), 74 (29), 72 (38), 56 (42), 55 (54), 46 (20), 45 (40), 44 (29), 43 (77), 42 (20), 41 (56), 39 (23).

(*S*)-*N*-(Ethoxycarbonyl)leucine (30d): yield: 6.5 g (64%) from 50 mmol (*S*)-leucine. Anal. Calcd for $C_9H_{17}NO_4$ (203.24): C 53.19; H 8.43; N 6.89. Found: C 53.48; H 8.57; N 6.63. $[\alpha]^{20}_D$ = −10.1° (*c* = 4.6, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 0.96 (d, *J* = 6.4 Hz, 6 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.50–1.82 (m, 3 H, 3-H), 4.08–4.20 (m, 2 H), 4.39 (br m, 1 H), 5.09 (d, *J* = 7.2 Hz, 1 H), 9.80 (s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.46, 21.70, 22.81, 24.76, 41.49, 52.28, 61.36, 156.45, 177.83. IR (neat): ν = 1720, 1530 cm^{-1}. MS: *m/z* = 204 (12; M^+ + 1), 158 (100), 130 (15), 102 (37), 86 (10), 74 (12), 58 (14), 43 (45), 41 (36).

(*S*)-*N*-(Ethoxycarbonyl)phenylalanine (30e): yield: 11.5 g (97%) from 50 mmol (*S*)-phenylalanine. Anal. Calcd for $C_{12}H_{15}NO_4$ (237.26): C 60.75; H 6.37; N 5.90. Found: C 60.77; H 6.47; N 5.94. $[\alpha]^{20}_D$ = 43.3° (*c* = 5.9, $CHCl_3$), mp = 81 °C. ^{1}H-NMR ($CDCl_3$): δ = 1.20 (t, *J* = 6.8 Hz, 3 H), 3.17 (m, 2 H) 4.09 (q, *J* = 6.8 Hz, 2 H), 4.67 (br m, 1 H), 5.15 (d, *J* = 7.5 Hz, 1 H), 7.15–7.33 (m, 5 H), 10.80 (br s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.41, 37.77, 54.46, 61.41, 127.12, 128.60, 129.30, 135.64, 156.19, 176.15. IR (in KBr): ν = 3320, 1720, 1680 cm^{-1}. MS: *m/z* = 238 (100; M^+), 192 (65), 164 (5), 148 (41), 131 (2), 120 (29), 91 (65), 65 (19).

Synthesis of dienol amino carboxylic acid esters according to the general procedure (see above):

(1′*RS*,2*S*)-2-[(Ethoxycarbonyl)amino]propionic acid 1-vinylpent-4-enyl ester 31a: yield: 5.43 g (67%) from 30 mmol of **3**. Anal. Calcd for $C_{14}H_{23}NO_4$ (269.34): C 62.43; H 8.61; N 5.20. Found: C 62.42; H 8.42; N 5.49. Separation of diastereoisomers by HPLC (cyclohexane/ethyl acetate 95:5). (1′*S*,2*S*)-**31a:** $[\alpha]^{22}_D$ = −13.4° (*c* = 1.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 1.24 (t, *J* = 7.2 Hz, 3 H), 1.40 (d, *J* = 7.2 Hz, 3 H), 1.72 (s, 3 H), 1.73–1.90 (m, 2 H), 2.04 (t, *J* = 7.9 Hz, 2 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 4.37 (br m, 1 H), 4.67 (s, 1 H), 4.73 (s, 1 H), 5.15–5.32 (m, 4 H); 5.78 (ddd, *J* = 6.4/10.5/17.0 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.53, 18.76, 22.35, 32.05, 33.03, 49.59, 61.01, 75.54, 110.50, 117.27, 135,81, 144.50, 156.0, 172.5. IR (neat): ν = 3320, 3060, 1720, 1640 cm^{-1}. MS: *m/z* = 162 (92), 144 (12), 116 (85), 109 (46), 93 (7), 72 (12), 44 (100), 39 (15). (1′*R*,2*S*)-**31a:** ^{1}H-NMR ($CDCl_3$): δ = 1.24 (t, *J* = 7.2 Hz, 3 H), 1.43 (d, *J* = 7.2 Hz, 3 H), 1.72 (s, 3 H), 1.74–1.90 (m, 2 H), 2.03 (t, *J* = 7.7 Hz, 2 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 4.37 (m, 1 H), 4.67 (s, 1 H), 4.73 (s, 1 H), 5.16–5.32 (m, 4 H), 5.78 (ddd, *J* = 6.4/10.5/17.1 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.50, 18.81, 22.31, 32.08, 33.02, 49.71, 59.98, 75.49, 110.56, 117.27, 135.70, 144.40, 155.77, 172.34. IR (neat): ν = 3340, 3070, 1720, 1645 cm^{-1}. MS: *m/z* = 162 (45), 144 (8), 116 (100), 109 (15), 93 (13), 72 (11), 67 (12), 44 (97), 39 (29).

(1′*RS*,2*S*)-2-[(Phenoxycarbonyl)amino]propionic acid 1-vinylpent-4-enyl ester 31b: yield: 2.77 g (73%) from 10 mmol of **3**. Anal. Calcd for $C_{18}H_{23}NO_4$ (317.39): C 68.12; H 7.31; N 4.41. Found: C 67.96; H 7.43; N 4.32 (corr). Separation of (1′*S*,2*S*)-**31b** by HPLC (cyclohexane/ethyl acetate 95: 5). (1′*S*,2*S*)-**31b:** $[\alpha]^{22}_D$ = −19.1° (*c* = 2.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 1.49 (d, *J* = 7.2 Hz, 3 H), 1.72 (s, 3 H), 1.74–1.92 (m, 2 H), 2.05 (t, *J* = 7.7 Hz, 2 H), 4.45 (m, 1 H), 4.68 (s, 1 H), 4.74 (s, 1 H), 5.18–5.37 (m, 3 H), 5.64 (d, *J* = 6.8 Hz, 1 H), 5.79 (ddd, *J* = 6.4/10.5/17.2 Hz, 1 H), 7.08–7.40 (m, 5 H). ^{13}C-NMR ($CDCl_3$): δ = 18.64, 22.36, 32.03, 33.04, 49.86, 75.85, 110,56, 117.46, 121.54, 125.39, 129.26, 135.71, 144.39, 150.90, 153.81, 172.00. IR (neat): ν = 3340, 3070, 1720, 1645, 1595 cm^{-1}. MS: *m/z* = 164 (5), 109 (23), 108 (17), 94 (100), 93 (62), 79 (32), 77 (21), 70 (62), 76 (54), 66 (33), 55 (56), 41 (39), 39 (46). **Diastereoisomeric mixture:** ^{1}H-NMR ($CDCl_3$): δ = 1.49, 1.51 (2 × d, *J* = 6.8/7.2 Hz, 3 H), 1.72 (s, 3 H), 1.74–1.92 (m, 2 H), 2.05 (t, *J* = 7.7 Hz, 2 H), 4.45 (m, 1 H), 4.68 (s, 1 H), 4.74 (s, 1 H), 5.18–5.37 (m, 3 H), 5.64 (d, *J* = 5.7 Hz, 1 H), 5.79 (ddd, *J* = 6.4/10.5/17.2 Hz, 1 H), 7.08–7.40 (m, 5 H). ^{13}C-NMR ($CDCl_3$): δ = 18.60, 18.74, 22.31, 32.01, 33.02, 49.84, 49.94, 75.82, 110.53, 110,60, 117.40, 117.47, 121.51, 125.36, 129.23, 135.57, 135.70, 144.33, 150.87; 153.76, 171.99.

(1′*RS*,2*S*)-2-[(Ethoxycarbonyl)amino]-3-methylbutanoic acid 1-vinylpent-4-enyl ester 31c: yield: 3.95 g (74%)

from 16 mmol of **3**. Anal. Calcd for $C_{16}H_{27}NO_4$ (297.40): C 64.62; H 9.15; N 4.71. Found: C 64.76; H 9.22; N 4.61 (corr). Separation of diastereoisomers by HPLC (cyclohexane/ethyl acetate 95:5). (1′*S*,2*S*)-**31c:** $[\alpha]^{20}_D = -6.9°$ (*c* = 3.4, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 0.88 (d, *J* = 6.8 Hz, 3 H), 0.98 (d, *J* = 6.8 Hz, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 1.72 (s, 3 H), 1.74–1.90 (m, 2 H), 2.04 (t, *J* = 7.1 Hz, 2 H), 2.17 (m, 1 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 4.28 (dd, *J* = 4.1/8.6 Hz, 1 H), 4.67 (s, 1 H), 4.73 (s, 1 H), 5.15 (br d, *J* = 8.6 Hz, 1 H), 5.20 (dt, *J* = 1.1/10.2 Hz, 1 H), 5.28 (d, *J* = 6.4 Hz, 1 H), 5.28 (dt, *J* = 1.1/17.7 Hz, 1 H), 5.78 (ddd, *J* = 6.4/10.2/17.7 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.49, 17.28, 19.00, 22.36, 31.30, 32.05, 32.99, 58.82, 61.06, 75.64, 110.46, 117.80, 135.86, 144.45, 155.46, 171.47. IR (neat): ν = 3340, 3070, 1720, 1645, 1520 cm^{-1}. MS: *m/z* = 297 (0.005, M^+), 190 (9), 144 (100), 116 (25), 108 (19), 98 (10), 93 (27), 79 (11), 72 (29), 67 (15), 55 (30), 41 (13). (1′*R*,2*S*)-**31c:** $[\alpha]^{22}_D = -0.7°$ (*c* = 3.7, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 0.90 (d, *J* = 6.9 Hz, 3 H), 0.99 (d, *J* = 6.9 Hz, 3 H), 1.25 (t, *J* = 6.9 Hz, 3 H), 1.72, (s, 3 H), 1.74–1.90 (m, 2 H), 2.12–2.26 (m, 2 H), 4.12 (q, *J* = 6.9 Hz, 2 H), 4.29 (dd, *J* = 3.9/8.5 Hz, 1H), 4.67 (s, 1 H), 4.73 (s, 1 H), 5.16 (br d, *J* = 8.5 Hz, 1 H), 5.20 (d, *J* = 10.6 Hz, 1 H), 5.27 (d, *J* = 6.5 Hz, 1 H), 5.27 (d, *J* = 17.1 Hz, 1 H), 5.78 (ddd, *J* = 6.5/10.6/17.1 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.49, 17.29, 19.07, 22.33, 31.28, 32.14, 33.02, 59.01, 61.06, 75.58, 110.59, 117.47, 135.73, 144.43, 156.44, 171.39. IR (neat): ν = 3340, 3070, 1720, 1645, 1515 cm^{-1}. MS: *m/z* = 297 (0.12, M^+), 190 (10), 145 (13), 144 (100), 116 (32), 108 (23), 98 (13), 93 (28), 79 (11), 72 (40), 67 (18), 55 (40), 41 (18).

(1′*RS*,2*S*)-2-[(Ethoxycarbonyl)amino]-4-methylpentanoic acid 1-vinylpent-4-enyl ester 31d: yield: 6.8 g (87%) from 25 mmol of **3**. Anal. Calcd for $C_{17}H_{29}NO_4$ (311.42): C 65.57; H 9.39; N 4.50. Found: C 65.74; H 9.55; N 4.26 (corr). Separation of diastereoisomers by HPLC (cyclohexane/ethyl acetate 95:5). (1′*S*,2*S*)-**31d:** $[\alpha]^{20}_D = -13.3°$ (*c* = 3.2, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, *J* = 6.4 Hz, 3 H), 0.96 (d, *J* = 6.4 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.40–1.70 (m, 3 H, 3-H), 1.71 (s, 3 H), 1.74–1.90 (m, 2 H), 2.04 (m, 2 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 4.36 br m, 1 H), 4.68 (s, 1 H), 4.73 (s, 1 H), 5.04 (br d, *J* = 8.3 Hz, 1 H), 5.16–5.31 (m, 3 H) 5.74 (ddd, *J* = 6.8/10.4/17.2 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.50, 21.83, 22.37, 22.84, 24.72, 32.50, 32.99, 41.88, 52.48, 61.05, 75.54, 110.45, 117.47, 135.83, 144.51, 156.17, 172.53. IR (neat): ν = 3330, 3080, 1720, 1650, 1590 cm^{-1}. MS: *m/z* = 204 (25), 158 (100), 142 (3), 130 (5), 109 (10), 102 (38), 93 (14), 67 (14), 58 (13), 44 (20), 41 (18), 39, (17). (1′*R*,2*S*)-**31d:** $[\alpha]^{22}_D = -14.2°$ (*c* = 3.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 0.95 (d, *J* = 6.4 Hz, 3 H), 0.96 (d, *J* = 6.4 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 1.40–1.70 (m, 3 H) 1.72 (s, 3 H), 1.73–1.90 (m, 2 H), 2.03 (m, 2 H), 4.11 (q, *J* = 7.2 Hz, 2 H), 4.37 (br m, 1 H), 4.67 (s, 1 H), 4.73 (s, 1 H), 5.08 (br d, *J* = 8.2 Hz, 1 H), 5.16–5.31 (m, 3 H), 5.78 (ddd, *J* = 6.0/10.5/17.3 Hz, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.47, 21.81, 22.31, 22.84, 24.79, 32.09, 33.03, 41.95, 52.61, 61.02, 75.43, 110.50, 117.23, 135.72, 144.44, 156.12, 172.46. IR (neat): ν = 3340, 3080, 1720, 1650 cm^{-1}. MS: *m/z* = 204 (35), 158 (100), 130 (3), 109 (11), 102 (36), 93 (9), 86 (10), 76 (12), 58 (13), 44 (20), 41 (17), 39 (20).

(1′*RS*,2*S*)-2-[(Ethoxycarbonyl)amino]-3-phenylpropionic acid 1-vinylpent-4-enyl ester 31e: yield: 7.3 g (87%) from 25 mmol of **3**. Anal. Calcd for $C_{20}H_{27}NO_4$ (345.44): C 69.54; H 7.88; N 4.06. Found: C 69.28; H 7.84; N 3.99 (corr). Separation of diastereoisomers by HPLC (cyclohexane/ethyl acetate 95:5). (1′*S*,2*S*)-**31e:** $[\alpha]^{20}_D = 18.4°$ (*c* = 3.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 1.22 (t, *J* = 7.2 Hz, 3 H), 1.70 (s, 3 H), 1.71–1.85 (m, 2 H), 1.98 (t, *J* = 7.9 Hz, 2 H), 3.09 (t, *J* = 5.7 Hz, 2 H), 4.09 (q, *J* = 7.2 Hz, 2 H), 4.60–4.75 (m, 3 H, 2-H), 5.08 (br d, *J* = 7.5 Hz, 1 H), 5.17–5.30 (m, 3 H, 1′-H) 5.73 (ddd, *J* = 6.8/10.6/17.3 Hz, 1 H), 7.10–7.30 (m, 5 H). ^{13}C-NMR ($CDCl_3$): δ = 14.52, 22.40, 31.98, 32.89, 38.23, 54.69, 61.11, 75.99, 110.43, 117.90, 127.03, 128.47, 129.44, 135.66, 135.76, 144.46, 155.92, 170.88. IR (neat): ν = 3340, 3080, 1720, 1645 cm^{-1}. MS: *m/z* = 238 (84), 210 (5), 192 (100), 164 (6), 148 (31), 131 (15), 120 (63), 109 (21), 108 (14), 93 (24), 91 (39), 67 (34), 55 (17), 39 (28). (1′*R*,2*S*)-**31e:** $[\alpha]^{20}_D = 15.9°$ (*c* = 3.9, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ =1.21 (t, *J* = 7.2 Hz, 3 H), 1.60–1.80 (m, 2 H), 1.95 (t, *J* = 7.7 Hz, 2 H), 3.09 (t, *J* = 5.8 Hz, 2 H) 4.08 (q, *J* = 7.2 Hz, 2 H), 4.62 (br m, 1 H), 4.65 (s, 1 H), 4.75 (s, 1 H), 5.10 (br d, *J* = 7.2 Hz, 1 H), 5.15–5.26 (m, 3 H), 5.72 (ddd, *J* = 6.4/10.6/17.1 Hz, 1 H), 7.03–7.32 (m, 5 H). ^{13}C-NMR ($CDCl_3$): δ = 14.48, 22.40, 31.94, 32.86, 38.44, 54.86, 61.10, 75.92, 110.40, 117.56, 127.06, 128.53, 129.34, 135.56, 135.83, 144.43, 155.89, 171.02. IR (neat): ν = 3340, 3080, 1720, 1645 cm^{-1}. MS: *m/z* = 238 (15), 207 (4), 192 (100), 164 (7), 148 (37), 131 (17), 120 (52), 109 (14), 108 (20), 93 (43), 91 (70), 79 (19), 67 (52), 55 (28), 41 (25), 39 (37).

Irradiation of dienol esters **31** according to the general procedure:

(1′*RS*,2*S*,2′*RS*,5′*RS*)-2-[(Ethoxycarbonyl)amino]propionic acid 5-methylbicyclo[3.2.0]hept-2-yl ester 32a: (1′*S*, 2*S*)-**32a:** yield: 251 mg (64%) from 1.5 mmol of **31a**, 66:34-mixture of diastereoisomers. Separation of diastereoisomers by HPLC (cyclohexane/ethyl acetate 95:5). (1′*R*,2*S*)-**32a:** 0.6 mmol of **31a**, Yield: 110 mg (71%), 71:29-mixture of diastereoisomers, separation by HPLC (cyclohexane/ethyl acetate 95:5). Anal. Calcd for $C_{14}H_{23}NO_4$ (269.34): C 62.43; H 8.61; N 5.20. Found: C 62.43; H 8.69; N 4.98 (corr). (1′*S*,2*S*,2′*S*,5′*S*)-**32a:** ^{1}H-NMR ($CDCl_3$): δ = 1.23 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.35 (d, *J* = 7.2 Hz, 3 H), 1.50–2.30 (m, 9 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 4.27 (m, 1 H), 4.96 (d, *J* = 3.8 Hz, 1 H), 5.18 (br s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.56, 16.75, 18.74, 26.99, 29.86, 31.78, 38.48, 44.41, 49.03, 49.60, 60.99, 83.20, 154.4, 172.2. IR (neat): ν = 1720, 1520 cm^{-1}. MS: *m/z* = 162 (12), 144 (6), 116 (100), 109 (40), 108 (28), 93 (35), 81 (70), 80 (22), 79 (29), 67 (30), 55 (20), 44 (70), 41 (21). (1′*S*,2*S*,2′*R*,5′*S*)-**32a:** ^{1}H-NMR ($CDCl_3$): δ = 1.18 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.40 (d, *J* = 6.8 Hz, 3 H), 1.50–2.20 (m, 8 H), 2.50 (m, 1 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 4.35 (m, 1 H), 5.05 (ddd, *J* = 7.2/7.2/9.8 Hz, 1 H), 5.18 (br s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 12.77, 14.59, 18.97, 26.92, 30.16, 31.10, 36.90, 43.30, 44.08, 49.65, 61.15, 78.01, 155.8, 172.9. IR (neat): ν = 1720, 1520 cm^{-1}. MS: *m/z* = 269 (1.2, M^+), 162 (18), 144 (5), 116 (100), 109 (31), 108 (39), 93 (43), 81 (53), 80 (18), 79 (23), 67 (30), 55 (18), 44 (65), 41 (20). (1′*R*,2*S*,2′*R*,5′*R*)-**32a:** ^{1}H-NMR ($CDCl_3$): δ = 1.24 (t, *J* = 7.2 Hz, 3 H), 1.25 (s, 3 H), 1.37 (d, *J* = 7.2 Hz, 3 H), 1.50–2.30 (m, 9 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 4.28 (m, 1 H), 4.95 (d, *J* = 3.8 Hz, 1 H), 5.18 (br s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.56, 16.76, 18.81, 26.96, 29.82, 31.98, 38.45, 44.07, 48.73, 49.63, 60.99, 83.23, 155.5, 172.5. IR (neat): ν = 1720, 1520 cm^{-1}. MS: *m/z* = 162 (11), 116 (100), 109 (40), 108 (32), 93 (38), 81 (68), 80 (23), 79 (26), 76 (32), 55 (20), 44 (73), 41 (21). (1′*R*,2*S*,2′*S*,5′*R*)-**32a:** $[\alpha]^{22}_D = -71.4°$ (*c* = 0.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 1.18 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.37 (d, *J* = 7.2 Hz, 3 H), 1.50–1.90 (m, 6H), 2.12 (m, 2 H), 2.51 (m, 1 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 4.35 (m, 1 H), 5.05 (dd, *J* = 7.9/8.3 Hz, 1 H), 5.19 (br s, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 12.57, 14.56, 19.08, 26.92, 30.15, 31.10, 36.84, 43.40, 44.00, 49.61, 61.01, 77.97, 155.85, 172.90. IR (neat): ν = 1720, 1520 cm^{-1}. MS: *m/z* = 269 (0.6, M^+), 162 (17), 116 (100), 109 (28), 108 (38), 93 (47), 81 (62), 80 (20), 79 (30), 70 (21), 67 (40), 55 (22), 44 (86), 41 (24). Irradiation and subsequent reduction: yield: 210 mg (87%) from 1.5 mmol **31a**. Enantiomeric excess: 7% (1*S*,2*R*,5*S*)-**4**, 4% (1*S*,2*S*,5*S*)-**5**.

(1′*RS*,2*S*,2′*RS*,5′*RS*)-2-[(Phenoxycarbonyl)amino]propionic acid 5-methylbicyclo[3.2.0]hept-2-yl ester 32b: yield: 410 mg (86%) from 1.5 mmol **31b**, 18:20:33:29-mixture of diastereoisomers. Anal. Calcd for $C_{18}H_{23}NO_4$ (317.39): C 68.12; H 7.31; N 4.41. Found: C 67.95; H 7.21; N 4.34 (corr). **Diastereoisomeric mixture:** ^{1}H-NMR ($CDCl_3$): δ = 1.17–2.55 (m, 15 H), 4.39 (m, 1 H), 4.99 (d, *J* = 3.8 Hz, 1 H *exo*), 5.09 (ddd, *J* = 7.2/10.0 Hz, 1 H *endo*), 5.63 (br s, 1 H), 7.09–7.38 (m, 5 H). ^{13}C-NMR ($CDCl_3$): δ = 12.74, 16.71, 18.60, 18.70, 18.80, 26.89, 26.96, 29.79, 30.13, 31.07, 31.78, 36.87, 38.42, 43.30 (C-5′ *endo*), 44.04, 44.38, 44.52, 48.73, 49.00, 49.84, 49.90, 78.25, 83.50, 121.55, 125.36, 129.27, 150.90, 153.80, 172.16, 172.47. (1′*S*,2*S*,2′*S*,5′*S*)-**32b:** MS: *m/z* = 318 (6, M^+ + 1), 224 (6), 210 (84), 164 (26), 109 (78), 108 (21), 94 (1009, 93 (24), 81 (62), 80 (41), 67 (48), 39 (49). (1′*S*,2*S*,2′*R*,5′*S*)-**32b:** MS: *m/z* = 318 (2, M^+ + 1), 224(4), 210 (100), 164 (20), 109 (70), 108 (30), 94 (92), 93 (22), 81 (47), 67 (45), 39 (43). (1′*R*,2*S*,2′*R*,5′*R*)-**32b:** MS: *m/z* = 318 (7, M^+ + 1), 224 (6), 210 (88), 164 (28), 109 (84), 94 (1009, 93 (21), 81 (69), 80 (40), 67 (49), 39 (50). (1′*R*,2*S*,2′*R*,5′*R*)-**32b**: MS: *m/z* = 318 (7, M^+ +

1), 224 (5), 210 (80), 164 (20), 121 (11), 109 (63), 108 (28), 94 (100), 93 (28), 81 (48), 67 (43), 39 (41). Irradiation and subsequent reduction: Yield: 110 mg (63%) from 1.5 mmol **31b**. Enantiomeric excess: 7% (1*S*,2*R*,5*S*)-**4**, 5% (1*S*,2*S*,5*S*)-**5**.

(1′*RS*,2*S*,2′*RS*,5′*RS*)-2-[(Ethoxycarbonyl)amino]-3-methylbutanoic acid 5-methylbicyclo[3.2.0]hept-2-yl ester 32c: yield: 380 mg (79%) from 1.6 mmol **31c**, 62:38 mixture of diastereoisomers, separation by HPLC (cyclohexane/ethyl acetate 97:3). (1′*R*,2*S*)-**32c**: yield: 320 mg (76%) from 1.4 mmol of (1′*R*,2*S*)-**31c**, 70:30 mixture of diastereoisomers, separation by HPLC (cyclohexane/ethyl acetate 97:3). Anal. Calcd for $C_{16}H_{27}NO_4$ (297.40): C 64.62; H 9.15; N 4.71. Found: C 64.61; H 9.11; N 4.97 (corr). (1′*S*,2*S*,2′*S*,5′*S*)-**32c:** ^{1}H-NMR ($CDCl_3$): δ = 0.85 (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 6.9 Hz, 3 H), 1.19 (s, 3 H), 1.21 (t, J = 7.1 Hz, 3 H), 1.23−1.33 (m, 1 H), 1.45−2.25 (m, 9 H), 4.07 (q, J = 7.1 Hz, 2 H), 4.17 (dd, J = 8.7/4.4 Hz, 1 H), 4.92 (d, J = 3.9 Hz, 1 H), 5.13 (br d, J = 8.7 Hz). ^{13}C-NMR ($CDCl_3$): δ = 14.50, 16.78, 17.46, 18.87, 26.83, 29.82, 31.31, 31.78, 38.52, 44.35, 48.98, 58.83, 61.02, 83.03, 156.46, 171.52. IR (neat): ν = 1720, 1520 cm^{-1}. MS: m/z = 297 (1, M$^+$), 190 (5), 172 (4), 145 (10), 144 (100), 116 (20), 109 (43), 108 (32), 93 (33), 81 (52), 79 (25), 67 (30), 55 (35). (1′*S*,2*S*,2′*R*,5′*S*)-**32c:** $[\alpha]^{22}_D$ = 41.6° (c = 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 0.83 (d, J = 6.9 Hz, 3 H), 0.89 (d, J = 6.9 Hz, 3 H), 1.11 (s, 3 H), 1.18 (t, J = 7.2 Hz, 3 H), 1.20−1.40 (m, 1 H), 1.42−2.20 (m, 8 H), 2.42 (m, 1 H), 4.05 (q, J = 7.2 Hz, 3 H), 4.18 (dd, J = 4.5/8.7 Hz, 1 H), 4.99 (ddd, J = 9.8/7.2/7.2 Hz, 1 H), 5.08 (br d, J = 7.5 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 12.96, 14.54, 17.58, 18.86, 26.92, 30.12, 31.13, 31.46, 36.95; 43.19, 44.06, 58.87, 61.06, 77.83, 156.42, 171.87. IR (neat): ν = 1720, 1515 cm^{-1}. MS: m/z = 297 (1.5, M$^+$), 190 (6), 172 (4), 145 (10), 144 (100), 116 (18), 109 (26), 108 (32), 93 (31), 81 (36), 72 (21), 67 (26), 55 (32). (1′*R*,2*S*,2′*R*,5′*R*)-**32c:** $[\alpha]^{22}_D$ = −3.4° (c = 0.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 0.89 (d, J = 7.2 Hz, 3 H), 0.96 (d, J = 6.8 Hz, 3 H), 1.24 (t, J = 7.2 Hz, 3 H), 1.25 (s, 3 H), 1.30−1.40 (m, 1 H), 1.50−2.35 (m 9 H), 4.11 (q, J = 7.2 Hz, 3 H), 4.19 (dd, J = 4.5/9.0 Hz, 1 H), 4.96 (d, J = 3.8 Hz, 1 H), 5.13 (br d, J = 9.0 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 14.55, 16.80, 17.50, 18.87, 26.93, 29.88, 31.41, 32.05, 38.48, 44.55, 48.78, 58.93, 61.07, 83.14, 156.5, 171.5. IR (neat): ν = 1720, 1515 cm^{-1}. MS: m/z = 297 (1, M$^+$), 190 (6), 172 (4), 145 (10), 144 (100), 116 (17), 109 (39), 108 (30), 93 (31), 81 (50), 79 (21), 67 (26), 55 (30). (1′*R*,2*S*,2′*S*,5′*R*)-**32c:** $[\alpha]^{18}_D$ = −55.2 (c = 4.2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 0.79 (d, J = 6.9 Hz, 3 H), 0.90 (d, J = 6.7 Hz, 3 H), 1.14 (s, 3 H), 1.20 (t, J = 7.1 Hz, 3 H), 1.25−1.35 (m, 1 H), 1.40−2.15 (m, 8 H), 2.47 (m, 1 H), 4.07 (q, J = 7.1 Hz, 2 H), 4.23 (dd, J = 4.3/9.1 Hz, 1 H), 5.05 (ddd, J = 7.4/7.4/9.7 Hz, 1 H), 5.14 (d, J = 8.5 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 12.85, 14.49, 17.18, 18.94, 26.96, 30.01, 31.12, 31.34, 36.83, 43.24, 43.91, 58.82, 61.02, 77.67, 156.48, 171.89. IR (neat): ν = 1720, 1510 cm^{-1}. MS: m/z = 297 (2, M$^+$), 190 (6), 172 (5), 145 (10), 144 (100), 116 (22), 109 (30), 108 (38), 93 (37), 81 (40), 72 (23), 67 (28), 55 (35). Irradiation and subsequent reduction: Yield: 82 mg (65%) from 1 mmol **31c**. Enantiomeric excess: 10% (1*S*,2*R*,5*S*)-**4**, 9% (1*S*,2*S*,5*S*)-**5**.

(1′*RS*,2*S*,2′*RS*,5′*RS*)-2-[(Ethoxycarbonyl)amino]-4-methylpentanoic acid 5-methylbicyclo[3.2.0]hept-2-yl ester 32d: yield: 460 mg (93%) from 1.6 mmol of **31d**, 15:18:37:30 mixture of diastereoisomers. Anal. Calcd for $C_{17}H_{29}NO_4$ (311.42): C 65.57; H 9.39; N 4.50. Found: C 65.43; H 9.52; N 4.66. **Diastereoisomeric mixture:** ^{1}H-NMR ($CDCl_3$): δ = 0.82−0.92 (m, 6 H), 1.08−2.50 (m, 17 H), 4.05 (q, J = 7.2 Hz, 2 H), 4.25 (br m, 1 H), 4.88 (d, J = 3.8 Hz, 1 H *exo*), 4.98 (m, 1 H *endo*), 5.15 (br d, J = 7.2 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 12.61, 12.67, 14.31, 14.39, 16.62, 21.80, 21.92, 22.55, 22.60, 22.67, 24.64, 26.77, 26.83, 29.71, 29.97, 30.97, 31.03, 31.66, 31.81, 36.73, 36.78, 38.35, 38.39, 41.57, 41.75, 41.84, 43.10, 43.19, 43.79, 43.96, 44.28, 44.38, 48.61, 48.83, 51.88, 52.40, 60.93, 61.25, 77.64, 77.78, 82.95, 83.03, 156.19, 157.25, 172.61, 172.91, 173.01. IR (neat): ν = 1720, 1530 cm^{-1}. (1′*S*,2*S*,2′*S*,5′*S*)-**32d:** MS: m/z = 312 (7, M$^+$ + 1), 204 (25), 186 (2), 158 (100), 130(3), 109 (12), 102 (30), 93 (6), 81 (13), 67 (12), 58 (9), 44 (14), 41 (13). (1′*S*,2*S*,2′*R*,5′*S*)-**32d:** MS: m/z = 312 (8, M$^+$ + 1), 204 (47), 186 (4), 158 (100), 130 (3), 109 (11), 108 (10), 102 (30), 93 (6), 81 (10), 67 (11), 58 (10), 44 (13), 41 (13). (1′*R*,2*S*,2′*S*,5′*R*)-**32d:** MS: m/z = 204 (17), 158 (100), 130 (3), 109 (10), 108 (10), 102 (29), 93 (12), 81 (14), 67 (16), 58 (10), 44 (13), 41 (15). (1′*R*,2*S*,2′*R*,5′*R*)-**32d:** MS: m/z = 312 (7, M$^+$ + 1), 204 (22), 186 (3), 158 (100), 130 (3), 109 (10), 102 (31), 93 (6), 81 (17), 67 (13), 58 (10), 44 (14), 41 (14). Irradiation and subsequent reduction: Yield: 100 mg (61%) from 1.3 mmol **31d**. Enantiomeric excess: 10% (1*S*,2*R*,5*S*)-**4**, 9% (1*S*,2*S*,5*S*)-**5**.

(1′*RS*,2*S*,2′*RS*,5′*RS*)-2-[(Ethoxycarbonyl)amino]-3-phenylpropionic acid 5-methylbicyclo[3.2.0]hept-2-yl ester 32e: yield: 310 mg (69%) from 1.3 mmol (2*S*,2′*S*)-**31e**, 60:40-mixture of diastereoisomers, separation by HPLC (cyclohexane/ethyl acetate 95:5). Yield: 230 mg (75%) from 0.9 mmol (2*S*,2′*R*)-**31e**, 74:26-mixture of diastereoisomers. Anal. Calcd for $C_{20}H_{27}NO_4$ (345.44): C 69.54; H 7.88; N 4.06. Found: C 69.58; H 8.09; N 4.44. (1′*S*,2*S*,2′*S*,5′*S*)-**32e:** $[\alpha]^{20}_D$ = 20.2° (c = 1.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 1.15−2.28 (m, 15 H), 3.04 (m, 2 H), 4.09 (q, J = 7.2 Hz, 2 H), 4.55 (br m, 1 H), 4.93 (d, J = 4.2 Hz, 1 H), 5.04 (br m, 1 H), 7.10−7.32 (m, 5 H). ^{13}C-NMR ($CDCl_3$): δ = 14.53, 16.81, 26.88, 29.82, 31.93, 38.36, 38.41, 44.48, 48.73, 54.72, 61.08, 83.38, 127.02, 128.52, 129.33, 135.95, 155.88, 171.08. IR (neat): ν = 1720, 1605, 1520 cm^{-1}. MS: m/z = 346 (5, M$^+$ + 1), 256 (21), 238 (29), 228 (25), 192 (100), 164 (6), 148 (33), 131 (28), 120 (45), 109 (45), 108 (20), 93 (19), 91 (45), 81 (41), 67 (40), 39 (20). (1′*R*,2*S*,2′*S*,5′*R*)-**32e:** $[\alpha]^{22}_D$ = −29.6° (c = 2.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 1.18 (s, 3 H), 1.22 (t, J = 7.2 Hz, 2 H), 1.24−1.40 (m, 1 H), 1.48−1.90 (m, 5 H), 1.98−2.14 (m, 2 H), 2.45 (m, 1 H), 3.08 (m, 2 H), 4.09 (q, J = 7.2 Hz, 2 H), 4.63 (br m, 1 H), 5.07 (br ddd, J = 7.2/9.8 Hz, 2 H) 7.07−7.32 (m, 5 H). ^{13}C-NMR ($CDCl_3$): δ = 12.85, 14.49, 26.94, 30.01, 31.12, 36.86, 38.41, 43.20, 43.90, 54.64, 61.03, 77.43, 126.95, 128.45, 129.25, 135.88, 155.84, 171.39. IR (neat): ν = 1720, 1605, 1510 cm^{-1}. MS: m/z = 256 (59), 238 (41), 211 (8), 192 (100), 164 (6), 148 (25), 131 (22), 120 (49), 109 (52), 108 (30), 93 (18), 91 (45), 81 (34), 67 (47), 55 (16), 41 (20), 39 (23). (1′*RS*,2*S*,2′*R*,5′*RS*)-**Diastereoisomeric mixture:** ^{1}H-NMR ($CDCl_3$): δ = 1.15−1.90 (m, 12 H), 1.92−2.25 (m, 2 H), 2.45 (m, 2 H *endo*), 3.08 (m, 2 H), 4.10 (q, J = 7.2 Hz, 2 H), 4.60 br m, 1 H), 4.92 (d, J = 4.2 Hz, 1H *exo*), 5.02 (ddd, J = 7.2/10.2 Hz, 1 H *endo*), 5.12 (br m, 1 H), 7.11−7.32 (m, 5 H). ^{13}C-NMR ($CDCl_3$): δ = 12.77, 14.53, 16.75, 26.86, 29.81, 30.01, 31.05, 31.87, 36.87, 38.40, 38.50, 43.16, 43.99, 44.35, 48.78, 54.67, 61.06, 78.01, 83.35, 126.99, 128.48, 129.29, 129.37, 135.97, 155.87, 171.42. IR (neat): ν = 1720, 1600, 1505 cm^{-1}. (1′*R*,2*S*,2′*R*,5′*R*)-**32e:** MS: m/z = 256 (26), 238 (30), 228(27), 192 (100), 164 (6), 148 (32), 131 (23), 120 (42), 109 (41), 108 (20), 93 (15), 91 (42), 81 (39), 67 (39), 55 (15), 39 (21). (1′*S*,2*S*,2′*R*,5′*S*)-**32e:** MS: m/z = 346 (5, M$^+$ + 1), 256 (65), 238 (66), 211 (10), 192 (100), 164 (6), 148 (23), 131 (21), 120 (51), 109 (49), 108 (30), 91 (37), 93 (17), 81 (30), 67 (42), 55 (12), 39 (20). Irradiation and subsequent reduction: yield: 108 mg (55%) from 540 mg (1.55 mmol) of **31e**. Enantiomeric excess: 15% (1*S*,2*R*,5*S*)-**4**, 14% (1*S*,2*S*,5*S*)-**5**.

Investigation of Racemization. To demonstrate, if racemization reactions occur, the reaction sequence (esterification, cycloaddition, reductive cleavage) was carried out using *ent*-**3** and **30a**. Since the diastereoisomers of **31a** and **32a** were separated by GLC, the reaction could easily be monitored by GLC.

(1′*S*,2*S*)-2-[(Ethoxycarbonyl)amino]propionic acid 1-vinylpent-4-enyl ester 31a: Esterification according to the general procedure: Yield: 320 mg (60%) from 2 mmol of (*S*)-**3**, $[\alpha]^{24}_D$ = −13.9° (c = 9.5, $CHCl_3$).

(1*RS*,2*S*,5*RS*)-5-Methylbicyclo[3.2.0]heptan-2-ol (4 and 5). Irradiation and subsequent reduction according to the general procedure: yield: 45 mg (63%) **4** and **5**, respectively, from 0.74 mmol (1′*S*,2*S*)-**31a**, *endo*/*exo* = 66:34. Enantiomeric excesses > 96% were detected by chiral GLC for both diastereoisomers.

6-Methyl-1,6-heptadien-3-one (35). A solution of 7.9 g (79 mmol) of CrO_3 in 22 mL of water and 7.1 mL of concentrated sulfuric acid was slowly added at 0−5 °C to a solution of 10.0 g (79 mmol) of **3** in 50 mL of acetone. After stirring for 1.5 h, the mixture was diluted with 90 mL of water and extracted with ether. The organic layer was extracted with

saturated $NaHCO_3$ solution and brine and dried with $MgSO_4$. The solvent was carefully removed in vacuo, and the crude product was purified by bulb to bulb distillation (95 °C, 17 mmHg) to yield 4.7 g (48%) of an unstable fluid. Anal. Calcd for $C_8H_{12}O$ (124.18): C 76.38; H 9.74. Found: C 76.36; H 9.74. ^{1}H-NMR ($CDCl_3$): δ = 1.75 (s, 3 H), 2.33 (m, 2 H), 2.74 (m, 2 H), 4.68 (m, 1 H), 4.74 (m, 1 H), 5.83 (dd, J = 10.6/1.5 Hz, 1 H), 6.23 (dd, J = 17.7/1.5 Hz, 1 H), 6.38 (dd, J = 17.7/10.6 Hz, 1 H). ^{13}C-NMR ($CDCl_3$): δ = 22.5, 31.5, 37.7, 110.1, 127.9, 136.4, 144.4, 200.0. IR (neat): ν = 3060, 1690, 1670, 1640, 1610 cm^{-1}. MS: m/z = 124 (2, M$^+$), 109 (21), 97 (2), 96 (12), 81 (28), 69 (50), 67 (12), 55 (100), 53 (10), 41 (52), 39 (18).

(*4R*,*5R*)-4,5-Dimethyl-2-(3-methylbut-3-enyl)-2-vinyldioxolane (36). **35** (2.2 g, 18 mmol), D-(−)-2,3-butanediol (3,2 g, 36 mmol), and a crystal of *p*-toluenesulfonic acid were dissolved in 20 mL of cyclohexane and refluxed in a Dean–Stark trap. After 14 h, another 1.60 mL (16 mmol) of D-(−)-2,3-butanediol and a small amount of *p*-toluenesulfonic acid were added. After 4 h, the mixture was extracted with 1 mL of saturated $NaHCO_3$ solution, and the organic layer was dried with $MgSO_4$. After removal of the solvent in vacuo the crude product was purified by bulb-to-bulb distillation (90 °C, 1 mbar) and HPLC (cyclohexane/ethyl acetate 95:5) to yield 850 mg (25%) of a colorless fluid. Anal. Calcd for $C_{12}H_{20}O_2$ (196.29): C 73.43; H 10.27. Found: C 73.52; H 10.27. $[\alpha]^{21}_D$ = −26.9 ° (c = 2.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ = 1.23 (d, J = 7.2 Hz, 3 H), 1.26 (d, J = 6.8 Hz, 3 H), 1.73 (s, 3 H), 1.85 (m, 2-H), 2.11 (m, 2 H), 3.61 (m, 2 H), 4.68 (d, J = 1.1 Hz, 2 H), 5.25 (dd, J = 10.6/1.9 Hz, 1 H), 5.40 (dd, J = 17.3/1.9 Hz, 1 H), 5.85 (dd, J = 17.3/10.6 Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ = 16.11, 16.98, 22.68, 31.24, 37.34, 77.74, 79.42, 107.93, 109.42, 114.57, 139.51, 145.71. IR (neat): ν = 1645 cm^{-1}. MS: m/z = 197 (7, M$^+$ + 1), 169 (8), 133 (5), 127 (100), 128 (8), 125 (10), 107 (5), 95 (5), 81 (5), 69 (6), 55 (35), 39 (9).

(1′*RS*,*4R*,*5R*,5′*RS*)-4,5,5′-Trimethylspiro[bicyclo[3.2.0]heptane-2′,2-1,3-dioxolane (37). Under an argon atmosphere, 0.2 g (1 mmol) of **36** and a small amount of CuOTf (~12 mg) were dissolved in dry ether and irradiated in a quartz vessel. When the reaction was complete (monitored by GLC), the solvent was removed in vacuo and the diastereoisomeric mixture was purified by short column chromatography. A colorless fluid (110 mg, 55%) was isolated, containing the two diastereoisomers in an 80:20 ratio (by chiral GLC). Anal. Calcd for $C_{12}H_{20}O_2$ (196,29): C 73.43; H 10.27. Found: C 72.99; H 10.27. ^{1}H-NMR ($CDCl_3$): δ = 1.15–1.26 (m, 9 H), 1.43–1.53 (m, 2 H), 1.68–1.97 (m, 4 H), 1.97–2.13 (m, 2 H), 2.19–2.35 (m, 1 H), 3.41–3.64 (m, 2 H 4-H). ^{13}C-NMR ($CDCl_3$): δ = 15.41, 15.24, 16.96, 17.12, 17.19, 17.39, 27.10, 30.37, 30.74, 35.69, 35.83, 37.07, 37.21, 42.87, 43.10, 49.74, 49.95, 77.75, 78.05, 78.18, 78.49, 118.04, 118.15. MS: m/z = 196 (5, M$^+$), 168 (5), 127 (100), 96 (10), 79 (10), 67 (10), 55 (55), 43 (13), 39 (15).

5-Methylbicyclo[3.2.0]heptan-2-one (7). **37** (0.5 mmol), a small amount of CuOTf (ca. 12 mg), and 10 mL of the respective solvent were irradiated in quartz vessels, until the reaction was complete (monitored by GLC). The solvent was removed in vacuo, and the residue was treated with 10 mL of water, 5 mL of THF, and a small amount of *p*-toluenesulfonic acid (In the case of 3 M $LiClO_4$ in ether, the $LiClO_4$ was extracted with water before evaporation). The mixture was stirred for 72 h, diluted with ether, extracted with saturated $NaHCO_3$ solution, and dried with $MgSO_4$, and the solvent was removed very carefully in vacuo. The crude product was purified by bulb to bulb distillation (100 °C, 16 mmHg). The enantiomeric excesses for the different solvents were determined by chiral GLC: ether 61% ee, 3 M $LiClO_4$ in ether 60% ee, 2-propanol 59% ee, cyclohexane 52% ee. (1*R*,5*R*)-**7** is generated in excess.

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