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Synthesis of chiral 4-substituted 2-hydroxypent-4-enoic acid derivatives via diastereoselective ene reaction promoted by $ZnBr_2$

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Abstract—The diastereoselective carbonyl-ene reaction of various 1,1-disubstituted olefins with the chiral derivatives of glyoxylic acid, with Oppolzer's sultam **1a** and 8-phenylmenthol **1b** auxiliaries, was studied. The reaction proceeds effectively under undemanding conditions in the presence of equimolar or catalytic amount of $ZnBr_2$ in good yield and at 72–94% de. Diastereoselectivities are usually slightly better with 8-phenylmenthyl glyoxylate **1b**, however, the use of hemiacetal **1a** is preferred because the products are often crystalline.

1. Introduction

The ene reaction of olefins with glyoxylates is one of the most efficient methods for constructing α-hydroxy acids containing a double bond at the γ,δ-position, or after reduction the corresponding 1,2-diols. Such enantiomerically pure ene products are of great synthetic importance.[1,2] Usually, the asymmetric carbonyl-ene reaction can be carried out in two ways: by the application of chiral aldehydes, for example, glyoxylates[2–6] or in an enantioselective manner with chiral catalysts.[7,8] There are many catalytic systems described in the literature, of which some are highly enantioselective, for example, the complexes of BINOL-Ti(IV)[9] as well as bis-oxazoline-Cu(II).[10] An alternative approach may employ the chiral derivatives of glyoxylic acid. Some examples of the use of chiral auxiliaries in the reactions of this type are described.[2–6] Among the most effective ones, there is the Whitesell's method with application of 8-phenylmenthyl glyoxylate **1b** (Fig. 1).[4] The best results in terms of diastereoselectivity were obtained when the reaction was carried out in the presence of 1.1 equiv of $SnCl_4$ as a Lewis acid (usually >99% de).

Several years ago, we published a paper concerning the asymmetric ene reaction of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam and its hemiacetal **1a** (Fig. 1) with 1-pentene and 1-hexene.[5] The yield and diastereomeric excess were highly dependent on the Lewis acid used. The best selectivities were observed for $ZnBr_2$ (1 equiv), although the yield in this case was rather low (~50%). Recently Chen et al. reported the application of *N*-glyoxyloyl camphorpyrazolidinone in the reaction with 1,1-disubstituted olefins, catalyzed by $Sc(OTf)_3$ (0.3 equiv) with stereoselectivities usually over 74% (up to 94%).[6]

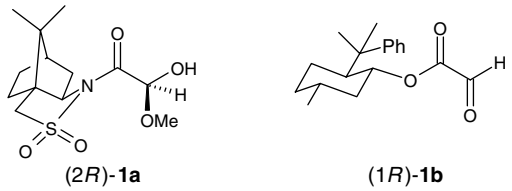

Figure 1. Chiral derivatives of glyoxylic acid used.

Herein, we report an extension of our earlier study[5] concerning the application of the easy-to-handle crystalline hemiacetal **1a**[11,12] in the $ZnBr_2$-catalyzed ene reaction with 1,1-disubstituted olefins (Scheme 1), which are more reactive than the monosubstituted alkenes. In our research group, hemiacetal **1a** was applied many times for various reactions,[12] for example, for hetero-Diels–Alder[13] and allylic additions.[14] The advantage of using the Oppolzer's sultam derived *N*-glyoxylate **1a** is that the reaction products usually appear in crystalline form, which simplifies

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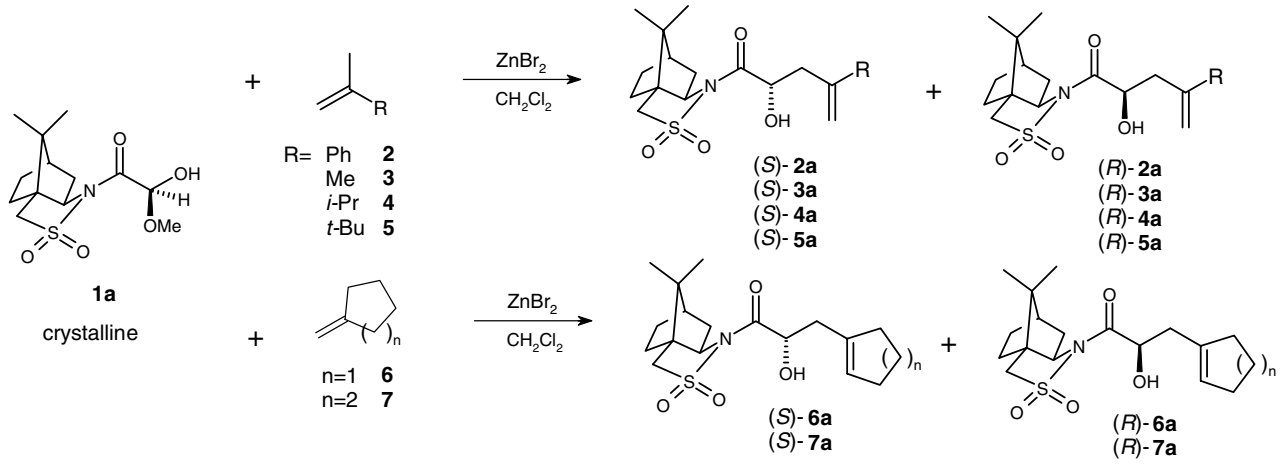


Scheme 1. Investigated ene reactions of 1,1-disubstituted olefins with crystalline hemiacetal of Oppolzer's sultam *N*-glyoxylate.

the purification of the product mixtures obtained. For comparison, we have also studied the $ZnBr_2$-catalyzed ene reaction of 8-phenylmenthyl glyoxylate **1b**. $ZnBr_2$ has many advantages over $SnCl_4$ and $Sc(OTf)_3$ as used in other studies.[4,6] As distinct from $SnCl_4$, $ZnBr_2$ is less toxic, easier to handle and does not require anhydrous conditions or low temperatures. With regards to $Sc(OTf)_3$, the use of $ZnBr_2$ is much more economical.

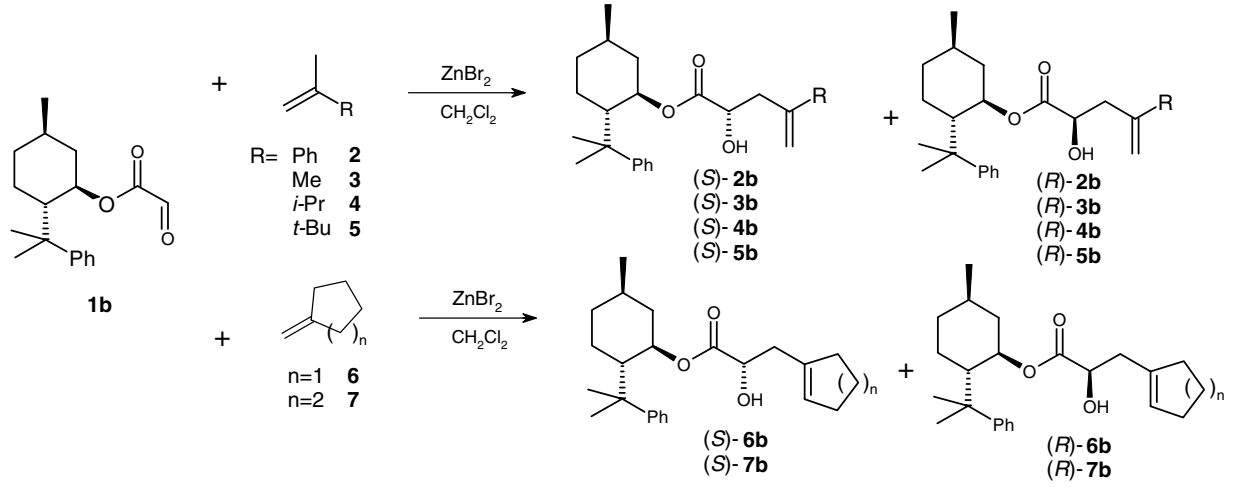
2. Results and discussion

Herein, we report the results of the diastereoselective ene reaction of reactive 1,1-disubstituted alkenes with chiral glyoxylic acid derivatives of Oppolzer's sultam **1a** (Scheme 1) and 8-phenylmenthol **1b** (Scheme 2) under undemanding conditions in the presence of $ZnBr_2$ (usually 1 equiv).

As mentioned above, $SnCl_4$ affords excellent diastereoselectivities in the ene reaction with **1b**, although it is a strong acid that can cause polymerization of the more reactive olefins, for example, 1,1-disubstituted ones. Whitesell et al.[4] demonstrated the use of **1b** in reactions with mono- and 1,2-disubstituted alkenes, and only three examples for 1,1-disubstituted olefins.

2.1. The diastereoselective ene reaction with the hemiacetal of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam 1a promoted by $ZnBr_2$

We also attempted to use $SnCl_4$ in the ene reaction, with the crystalline, easy-to-handle hemiacetal **1a**, but the stereoselectivities obtained were much lower.[5] Therefore, we focused our attention on the possibility of using in this reaction, weaker, readily accessible Lewis acids, which are easier to use than $SnCl_4$. The best results were obtained in the reaction of **1a** and 1,1-disubstituted olefins in the presence of $ZnBr_2$ (1.0–1.1 equiv) (Scheme 1 and Table 1). The reaction undergoes under mild, undemanding conditions, without the need of using dry solvents and thoroughly dried $ZnBr_2$. A small amount of water (less than 1 equiv) in $ZnBr_2$ has practically no influence on the asymmetric induction, but it helps to eliminate some byproducts and the reaction proceeds more clearly. The reaction temperature ranging from 0 to 20 °C has a small influence on the asymmetric induction, as shown in the example of



Scheme 2. Investigated ene reactions of olefins with 8-phenylmenthyl glyoxylate.

Table 1. The reaction of hemiacetal of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam (**1a**) with various 1,1-disubstituted alkenes **2**–**7**, promoted by $ZnBr_2$[a]

Entry	Alkene		$ZnBr_2$ (equiv)	Temperature (°C)	Time (h)	Product	Yield[b] (%)	de[c] (%)
1	**2**		1	20	5	**2a**	96	77
2			1	0–5	5	**2a**	92	82
3			0.2	20	60	**2a**	75	75
4	**3**		1	0–5	2	**3a**	93 (49)	86
5			0.2	20	20	**3a**	50	86
6	**4**		1	0–5	5	**4a**	92 (55) (Regioselectivity: 90:10)	79
7	**5**		1	0–5	5	**5a**	85	72
8	**6**		1	0–5	5	**6a**	89	94
9			0.2	5–20	20	**6a**	84	81
10	**7**		1	0–5	5	**7a**	92 (45)	82

[a] Conditions: The reactions were carried out using 1 mmol of hemiacetal **1a** in 5.0 mL of CH_2Cl_2, 1 equiv of $ZnBr_2$, 1.5 equiv of alkene (3 equiv of **3**).
[b] Isolated yield; the values in parentheses refer to the yields after crystallization (not optimized).
[c] The diastereomeric excess was determined by HPLC (additionally in some cases the reaction mixture was reduced to corresponding diols and de was confirmed using HPLC or GC on a chiral columns).

α-methylstyrene (Table 1, entries 1 and 2). The reactions of other 2-methylalk-1-enes **3**–**5** (R = Me, *i*-Pr, *t*-Bu, entries 4–7) as well as methylenecyclopentane **6** and methylenecyclohexane **7** (entries 8–10) have been also investigated. The best stereochemical results in this series were achieved for the least hindered substrates: isobutylene **3** (86% de) and methylenecyclopentane (94% de).

In all cases, we have obtained good asymmetric inductions (72–94% de). The stereoselectivity of the catalyzed variant of this reaction (20 mol % of $ZnBr_2$, entries 3 and 5) is similar, but the time required is much longer, and the yields are lower. The catalytic variant performs well in the case of the more reactive olefins, for example, methylenecyclopentane (entry 9). All products **2a**–**7a** are crystalline, so they can be purified in the most cases by crystallization, or by simple chromatographic methods due to large differences in their retention times.

In two cases **3a** and **7a**, crystals suitable for X-ray analysis were obtained, and the absolute configurations of the major diastereomers have been confirmed (Figs. 2 and 3). The observed direction of asymmetric induction was identical as in the reaction of hemiacetal **1a** with 1-hexene[5] or in the allylation reaction leading to unsubstituted 2-hydroxypent-4-enoic acid.[14] In the case of using the hemiacetal of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **1a**, the obtained α-hydroxy esters have (2′*S*) configuration. We can assume with a high degree of likelihood that the direction of the induction is identical for all the investigated reactions of alkanes **2**–**7** with **1a** in the presence of $ZnBr_2$.[13a]

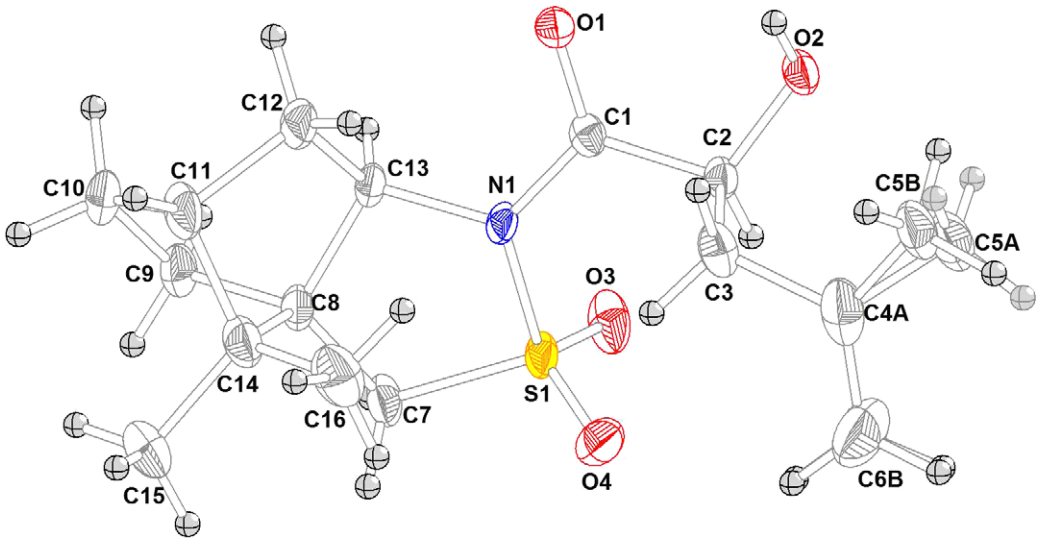


Figure 2. The X-ray crystal structure of compound (2′*S*)-**3a**.

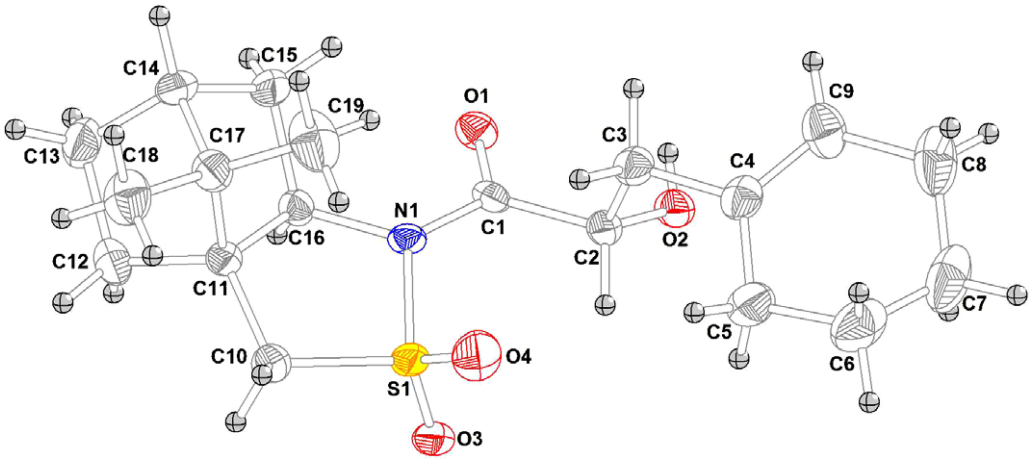


Figure 3. The X-ray crystal structure of compound (2′*S*)-**7a**.

2.2. The asymmetric ene reactions of (1*R*,2*S*,5*R*)-8-phenylmenthyl glyoxylate 1b with 1,1-disubstituted alkenes

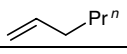
For comparison, we also investigated the possibility of using 8-phenylmenthyl glyoxylate **1b**[15] in the ene reaction with 1,1-disubstituted olefins **2**–**7** in the presence of $ZnBr_2$ (Table 2, entries 1–9). The stereoselectivities obtained for products **2b**–**7b** are usually somewhat better (83–92% de) compared to the corresponding derivatives **2a**–**7a** of the Oppolzer's sultam (72–94% de). However, the obtained products **2b**–**7b** are oils, and the diastereomers are harder to differentiate by TLC, which makes their purification difficult. On the other hand, the catalytic variant of the reaction with glyoxylate **1b** performs much better. The reactions of olefins **2**, **3** and **6** in the presence of 10 mol % $ZnBr_2$ have good yields and, most importantly, the asymmetric induction is not lowered (entries 2, 4 and 8).

Additionally, we investigated the possibility of using monosubstituted olefins, for example, 1-hexene **8** in the reaction with 8-phenylmenthyl glyoxylate in the presence of 1 equiv of $ZnBr_2$ (entry 10). This reaction proceeds much more slowly than the ones with 1,1-disubstituted olefins.

By comparison of the presented results of the ene reactions of hemiacetal **1a** and glyoxylate **1b**, one notes that the correlations between the hindrance of the olefin and the degree of the asymmetric induction are reversed. In the case of 8-phenylmenthyl glyoxylate **1b**, higher diastereoselectivities was observed for more hindered olefins. The lowest diastereoselectivity was obtained for the monosubstituted 1-hexene **8** (82% de), and the highest one for olefin **5** (92% de) bearing *tert*-butyl as one of its substituents. The ene reaction with hemiacetal **1a**, as compared with that of glyoxylate **1b**, is much slower in the catalytic version owing to the fact that Lewis acid also shifts the equilibrium towards free aldehyde form with the release of methanol.

We also checked the possibility of using $SnCl_4$ in the reaction of 8-phenylmenthyl glyoxylate with 1,1-disubstituted

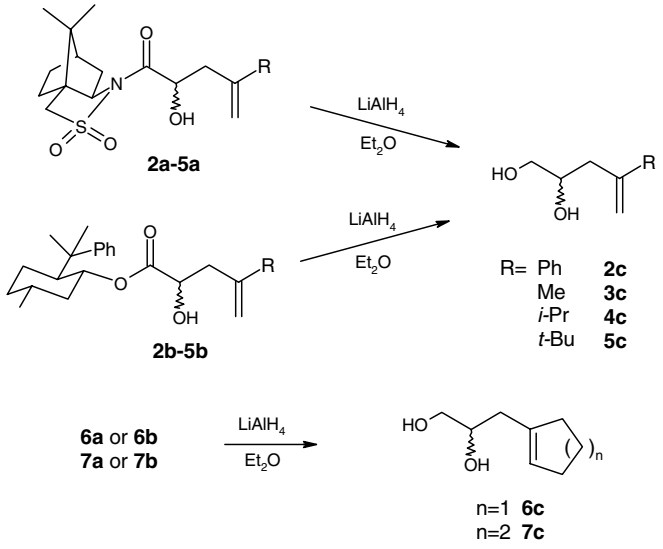
Table 2. The reaction of 8-phenylmenthyl glyoxylate **1b** with various alkenes **2**–**8**, promoted by $ZnBr_2$[a]

Entry	Alkene	$ZnBr_2$ (equiv)	Temperature (°C)	Time (h)	Product	Yield[b] (%)	de[c] (%)
1	**2** 	1	0–5	3	**2b**	95	89
2		0.1	20	24	**2b**	95	88
3	**3** 	1	0–5	2	**3b**	95	83
4		0.1	20	24	**3b**	93	81
5	**4** 	1	0–5	4	**4b**	94 (Regioselectivity: 88:12)	88
6	**5** 	1	0–5	4	**5b**	96	92
7	**6** 	1	0–5	2	**6b**	97	87
8		0.1	20	3	**6b**	93	87
9	**7** 	1	0–5	3	**7b**	97	88
10	**8** 	1	20	48	**8b**	80	82

[a] Conditions: The reactions were carried out using 1 mmol of glyoxylate **1b** in 5.0 mL of CH_2Cl_2, 1 equiv of $ZnBr_2$, 1.5 equiv of alkene (3 equiv of **3**).
[b] Isolated yield.
[c] The diastereomeric excess was determined by HPLC or GC analysis of the reduction products **2c**–**8c** on a chiral columns.

olefins **2**, **3** and **4**, which have not been studied by Whitesell et al. When olefin **2** was added to a mixture of glyoxylate **1b**/$SnCl_4$, the yield was low, probably due to competitive polymerization of the olefin. When the reaction conditions were analogous to those used by Whitesell et al.,[4] and $SnCl_4$ was added dropwise to a mixture glyoxylate/olefin at −78 °C, essentially one diastereomer **2b**, **3b** or **4b** was formed in the reaction, usually in a good yield above 75%. However, the products of olefin polymerization were also observed.

When (1*R*,2*S*,5*R*)-8-phenylmenthyl glyoxylate **1b** was used, the products formed had the same absolute (2′*S*)-configuration as in the reaction with the hemiacetal of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **1a** in the presence of $ZnBr_2$. This has been confirmed by the reduction of the ene products with Oppolzer's sultams **2a**–**7a** and 8-phenylmenthol **2b**–**7b** auxiliaries to the corresponding 1,2-diols **2c**–**7c** (Scheme 3) and chromatographical comparison on chiral phases. In the cases of **1a** and **1b**, the observed direction of induction is in accordance to the literature data for other additions and cycloadditions to those chiral derivatives of glyoxylic acid.[12–14,16]



Scheme 3. Reduction of the ene-products to the corresponding 1,2-diols.

3. Conclusions

In summary, we have found a general and undemanding method using $ZnBr_2$ as a catalyst promoter for the diastereoselective ene reaction of 1,1-disubstituted olefins with chiral glyoxylic acid derivatives of Oppolzer's sultam **1a** and 8-phenylmenthol **1b**. According to this approach, chiral α-hydroxy-acids esters containing a double bond in the γ,δ-position, being the compounds of significant synthetic interest, were obtained with good to high diastereomeric purity (72% up to 94% de). We have also compared the popular chiral auxiliaries, the Oppolzer's sultam and 8-phenylmenthol, in the ene reaction.

$ZnBr_2$ appears to be a very attractive catalyst for the ene reactions with the Oppolzer's sultam-derived hemiacetal **1a**. The products are usually crystalline and easily purified. Although $SnCl_4$ allows us to obtain very high diastereoselectivities with **1b**, the milder zinc salt seems to be also attractive in this case and is able to carry out the reaction in a catalytic variant with good yield and diastereoselectivities. The ene reaction in the cases of **1a** and **1b** is clearly and reproducibly promoted by inexpensive $ZnBr_2$ under undemanding conditions (0 °C or room temperature) without the need of using dry solvents and an inert atmosphere.

4. Experimental

4.1. General remarks

The reported NMR spectra were recorded in $CDCl_3$ using a Bruker 500 MHz or Varian Gemini 200 MHz spectrometers. Chemical shifts of ^1H NMR and ^{13}C NMR are reported as δ values relative to TMS ($\delta = 0.00$) and $CDCl_3$ ($\delta = 77.0$), respectively. The high-resolution mass spectra (HRMS) were recorded on a Mariner PE Biosystems unit using the ESI technique. The IR spectra were taken on a FT-IR Perkin Elmer Spectrum 2000. Optical rotations were measured using a JASCO P-1020 polarimeter. Analytical TLC was carried out on commercial plates coated with 0.25 mm of Merck Kieselgel 60. Preparative flash silica chromatography was performed using Merck Kieselgel 60 (230–400 mesh).

The diastereomeric ratios of the products were determined using HPLC or GC and ^1H NMR techniques. The HPLC analyses were performed on a chromatograph fitted with the diode-array detector (DAD) and Chiracel OD-H (250 × 4.6 mm, 5 μm) or AS-H (250 × 4.6 mm, 5 μm) columns eluted with *i*-propanol (2.5–10%) in hexane. The GC analyses were carried out on a Trace 2000 GC (Thermo Finnigan) apparatus equipped with a flame-ionization detector (FID) and a chiral capillary β-dex 120 column (permethyl-β-cyclodextrin, 30 m × 0.25 mm ID Supelco, Bellefonte, USA) employing nitrogen as a carrier gas. Data were collected under the following conditions: pressure of nitrogen −100 kPa, injector temperature −200 °C, detector temperature −250 °C. The oven temperature varied according to types of products.

All commercially available chemicals were used as received unless otherwise noted. Hemiacetal of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **1a** was obtained by the ozonolysis of *N*-crotonoyl-(2*R*)-bornane-10,2-sultam[11] and (1*R*,2*S*,5*R*)-8-phenylmenthyl glyoxylate **1b** was obtained by the ozonolysis of di-(1*R*,2*S*,5*R*)-8-phenylmenthyl fumarate.[15] Alkenes **2**–**8** were purchased from Aldrich.

4.2. A general procedure for the ene reactions of hemiacetal of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam 1a or (1*R*,2*S*,5*R*)-8-phenylmenthyl glyoxylate 1b promoted by $ZnBr_2$

To a stirred solution of enophiles **1a** (304 mg, 1 mmol) or **1b** (289 mg, 1 mmol) in CH_2Cl_2 (5 mL), $ZnBr_2$ (226 mg, 1 equiv or 23 mg, 10 mol %) was added in one portion at room temperature. After ca. 15 min, an appropriate olefin

(1.5 equiv; in case of **3** −3 equiv) was added at 0–5 °C to the stirred suspension, and stirring was continued for a period of time as indicated in Tables 1 and 2. The reaction was quenched with satd NH_4Cl and the aqueous layer was extracted with Et_2O (3×20 mL). The separated organic layers were combined, dried over $MgSO_4$, concentrated in vacuo and subjected to flash chromatography using hexane/AcOEt (9:1 → 8:2) as an eluent. Alternatively, in the case of using $ZnBr_2$ as a Lewis acid, the reaction mixture can be directly chromatographed without workup.

4.3. Analytical data for diastereomerically pure ene products 2a–7a and 2b–8b

4.3.1. (2′*S*)-*N*-(2′-Hydroxy-4′-phenylpent-4′-enoyl)-(2*R*)-bornane-10,2-sultam (2′*S*)-2a. Mp 105–109 °C (crystallized from Et_2O/hexane); $[\alpha]_D^{24} = -85.7$ (*c* 1.5, $CHCl_3$); IR (CH_2Cl_2): 3498, 2960, 1691, 1627, 1334, 1285, 1136, 1061, 778, 705, 536 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.45–7.42 (m, 2H), 7.32–7.29 (m, 2H), 7.27–7.23 (m, 1H), 5.39 (br s, 1H), 5.22 (d, $J = 0.7$ Hz, 1H), 4.88 (dd, $J = 8.3$, 4.2 Hz, 1H), 3.88 (dd, $J = 7.7$, 4.2 Hz, 1H), 3.48 (d_{AB}, $J = 13.8$ Hz, 1H), 3.43 (d_{AB}, $J = 13.8$ Hz, 1H), 3.21 (dd, $J = 14.4$, 4.0 Hz, 1H), 2.83 (br s, 1H), 2.70 (ddd, $J = 14.4$, 8.4, 0.7 Hz, 1H), 2.02–1.96 (m, 1H), 1.92–1.82 (m, 4H), 1.42–1.29 (m, 2H), 1.11 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 143.6, 140.6, 128.2, 127.5, 126.5, 116.4, 69.8, 65.0, 52.8, 48.8, 47.7, 44.6, 40.8, 37.9, 32.7, 26.3, 20.8, 19.8; HMRS calcd for $(M+Na)^+$ $C_{21}H_{27}NO_4SNa$: 412.1553, found: 412.1542; HPLC (Chiracel OD-H column, hexane/*i*-PrOH, 9:1, flow rate 1.0 mL/min, $\lambda = 205$ nm): t_R(minor-**2a**) = 22.8 min, t_R(major-**2a**) = 29.5 min.

4.3.2. (2′*S*)-*N*-(2′-Hydroxy-4′-methylpent-4′-enoyl)-(2*R*)-bornane-10,2-sultam (2′*S*)-3a. Mp 123–124 °C (crystallized from Et_2O/hexane); $[\alpha]_D^{24} = -114.9$ (*c* 1.5, $CHCl_3$); IR (CH_2Cl_2): 3506, 2962, 1681, 1329, 1291, 1220, 1135, 1095, 904, 760, 552 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.91–4.86 (m, 2H), 4.82 (d, $J = 0.7$ Hz, 1H), 3.94 (dd, $J = 7.7$, 4.9 Hz, 1H), 3.51 (d_{AB}, $J = 13.8$ Hz, 1H), 3.47 (d_{AB}, $J = 13.8$ Hz, 1H), 2.90 (d, $J = 7.6$ Hz, 1H), 2.65 (dd, $J = 13.8$, 3.7 Hz, 1H), 2.25 (ddd, $J = 13.8$, 9.1, 0.7 Hz, 1H), 2.09 (dd, $J = 13.8$, 7.8 Hz, 1H), 2.06–2.00 (m, 1H), 1.97–1.87 (m, 3H), 1.82 (br s, 3H), 1.47–1.41 (m, 1H), 1.39–1.34 (m, 1H), 1.14 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.5, 140.9, 114.2, 69.6, 65.0, 52.9, 48.9, 47.8, 44.6, 43.8, 38.0, 32.7, 26.4, 22.2, 20.6, 19.8; HMRS calcd for $(M+Na)^+$ $C_{16}H_{25}NO_4SNa$: 350.1396, found: 350.1393; HPLC (Chiracel OD-H column, hexane/*i*-PrOH, 9:1, flow rate 1.0 mL/min, $\lambda = 205$ nm): t_R[minor-(2′*R*)-**3a**] = 11.2 min, t_R[major-(2′*S*)-**3a**] = 19.0 min.

4.3.3. (2′*S*)-*N*-(2′-Hydroxy-5′-methyl-4′-methylene-hexanoyl)-(2*R*)-bornane-10,2-sultam (2′*S*)-4a. Mp 147–148.5 °C (crystallized from Et_2O/hexane); $[\alpha]_D^{24} = -108.8$ (*c* 0.5, $CHCl_3$); IR (CH_2Cl_2): 3455, 2962, 1675, 1460, 1335, 1286, 1169, 1138, 1107, 1061, 767, 536 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.92 (s, 1H), 4.90–4.86 (m, 2H), 3.94 (dd, $J = 7.7$, 4.9 Hz, 1H), 3.51 (d_{AB}, $J = 13.8$ Hz, 1H), 3.47 (d_{AB}, $J = 13.8$ Hz, 1H), 2.87 (d, $J = 7.4$ Hz, 1H), 2.71 (dd, $J = 14.4$, 4.0 Hz, 1H), 2.33 (septet, $J = 6.8$ Hz, 1H), 2.23 (dd, $J = 14.3$, 9.0 Hz, 1H), 2.09 (dd, $J = 13.9$, 7.7 Hz, 1H), 2.06–2.00 (m, 1H), 1.96–1.87 (m, 3H), 1.47–1.34 (m, 2H), 1.14 (s, 3H), 1.05 (d, $J = 6.8$ Hz, 3H), 1.04 (d, $J = 6.8$ Hz, 3H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.4, 150.9, 110.4, 70.0, 65.1, 52.9, 48.9, 47.8, 44.6, 40.8, 38.0, 33.0, 32.8, 26.4, 21.7, 21.5, 20.7, 19.8; HMRS calcd for $(M+Na)^+$ $C_{18}H_{29}NO_4SNa$: 378.1709, found: 378.1696; HPLC (Chiracel OD-H column, hexane/*i*-PrOH, 9:1, flow rate 1.0 mL/min, $\lambda = 205$ nm): t_R(minor-**4a**) = 11.1 min, t_R(major-**4a**) = 15.4 min.

4.3.4. (2′*S*)-*N*-(2′-Hydroxy-5′,5′-dimethyl-4′-methylene-hexanoyl)-(2*R*)-bornane-10,2-sultam (2′*S*)-5a. Mp 123–127 °C (crystallized from Et_2O/hexane); $[\alpha]_D^{24} = -93.4$ (*c* 0.4, $CHCl_3$); IR (CH_2Cl_2): 3481, 2961, 1678, 1460, 1334, 1279, 1137, 1103, 1060, 765, 537 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.03 (s, 1H), 4.97–4.93 (m, 2H), 3.96 (dd, $J = 7.6$, 5.0 Hz, 1H), 3.51 (d_{AB}, $J = 13.8$ Hz, 1H), 3.47 (d_{AB}, $J = 13.8$ Hz, 1H), 2.92 (d, $J = 6.9$ Hz, 1H), 2.71 (dd, $J = 15.5$, 4.0 Hz, 1H), 2.25 (dd, $J = 15.5$, 9.1 Hz, 1H), 2.13–2.02 (m, 2H), 1.97–1.88 (m, 3H), 1.47–1.34 (m, 2H), 1.15 (s, 3H), 1.07 (s, 9H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.4, 152.5, 108.9, 70.4, 65.1, 52.9, 48.9, 47.8, 44.6, 38.1, 36.9, 36.1, 32.8, 29.0, 26.4, 20.6, 19.8; HMRS calcd for $(M+Na)^+$ $C_{19}H_{31}NO_4SNa$: 392.1866, found: 392.1864; HPLC (Chiracel OD-H column, hexane/*i*-PrOH, 9:1, flow rate 1.0 mL/min, $\lambda = 205$ nm): t_R(minor-**5a**) = 13.1 min, t_R(major-**5a**) = 15.3 min.

4.3.5. (2′*S*)-*N*-[3′-(Cyclopent-1-enyl)-2′-hydroxy-propionyl]-(2*R*)-bornane-10,2-sultam (2′*S*)-6a. Mp 114–115 °C (crystallized from Et_2O/hexane); $[\alpha]_D^{24} = -100.7$ (*c* 1.2, $CHCl_3$); IR (CH_2Cl_2): 3513, 2949, 1681, 1422, 1336, 1298, 1214, 1137, 1062, 768, 532 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.51 (br s, 1H), 4.86 (dt, $J = 7.7$ Hz, 4.2, 1H), 3.93 (dd, $J = 7.7$, 4.9 Hz, 1H), 3.50 (d_{AB}, $J = 13.8$ Hz, 1H), 3.46 (d_{AB}, $J = 13.8$ Hz, 1H), 2.93 (d, $J = 7.6$, 1H), 2.69 (dd, $J = 14.3$, 1.7 Hz, 1H), 2.45 (dd, $J = 14.3$, 7.9 Hz, 1H), 2.37–2.25 (m, 4H), 2.08 (dd, $J = 13.8$, 7.8 Hz, 1H), 2.03–1.83 (m, 6H), 1.47–1.34 (m, 2H), 1.14 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.5, 139.2, 128.0, 70.0, 65.0, 52.9, 48.8, 47.8, 44.6, 38.0, 37.4, 35.1, 32.7, 32.4, 26.4, 23.4, 20.6, 19.8; HMRS calcd for $(M+Na)^+$ $C_{18}H_{27}NO_4SNa$: 376.1553, found: 376.1563; HPLC (Chiracel OD-H column, hexane/*i*-PrOH, 9:1, flow rate 1.0 mL/min, $\lambda = 205$ nm): t_R(minor-**6a**) = 11.7 min, t_R(major-**6a**) = 18.7 min.

4.3.6. (2′*S*)-*N*-[3′-(Cyclohex-1-enyl)-2′-hydroxy-propionyl]-(2*R*)-bornane-10,2-sultam (2′*S*)-7a. Mp 146–149 °C (crystallized from Et_2O/hexane); $[\alpha]_D^{24} = -106.1$ (*c* 1.5, $CHCl_3$); IR (CH_2Cl_2): 3523, 2927, 1683, 1331, 1287, 1134, 1093, 1060, 772, 547 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.54 (br s, 1H), 4.84 (dt, $J = 8.4$, 4.0 Hz, 1H), 3.93 (dd, $J = 7.7$, 4.8 Hz, 1H), 3.50 (d_{AB}, $J = 13.8$ Hz, 1H), 3.46 (d_{AB}, $J = 13.8$ Hz, 1H), 2.81 (d, $J = 7.5$ Hz, 1H), 2.58 (br d, $J = 13.6$ Hz, 1H), 2.16 (dd, $J = 13.6$, 8.8 Hz, 1H), 2.09 (dd, $J = 13.8$, 7.8 Hz, 1H), 2.06–1.87 (m, 8H), 1.67–1.52 (m, 4H), 1.47–1.34 (m, 2H), 1.14 (s, 3H), 0.98 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.7, 133.1, 125.5, 69.8, 65.0, 52.9, 48.8, 47.8, 44.6, 44.2, 38.1, 32.8, 28.1, 26.4, 25.3, 22.8, 22.1, 20.7, 19.8; HMRS calcd for $(M+Na)^+$ $C_{19}H_{29}NO_4SNa$: 390.1709, found: 390.1706; HPLC (Chiracel OD-H column, hexane/*i*-PrOH, 9:1, flow rate 1.0 mL/min, $\lambda = 205$ nm): t_R[minor-(2′*R*)-**7a**] = 11.3 min, t_R[major-(2′*S*)-**7a**] = 19.5 min.

4.3.7. (2′*S*)-2′-Hydroxy-4′-phenylpent-4′-enoic acid (1*R*,2*S*,5*R*)-8-phenylmenthyl ester (2′*S*)-2b. Oil; IR (CH_2Cl_2): 3505, 2955, 2924, 1724, 1600, 1444, 1265, 1214, 1092, 905, 777, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.27 (m, 5H), 7.24–7.16 (m, 4H), 7.00–6.97 (m, 1H), 5.31 (d, $J = 1.0$ Hz, 1H), 5.07 (d, $J = 1.0$ Hz, 1H), 4.84 (dt, $J = 10.8$, 4.5 Hz, 1H), 3.30–3.26 (m, 1H), 2.70 (dd, $J = 14.6$, 3.6 Hz, 1H), 2.42–2.38 (m, 2H), 2.08–2.02 (m, 1H), 1.84–1.78 (m, 1H), 1.75–1.65 (m, 2H), 1.50–1.40 (m, 1H), 1.26 (s, 3H), 1.18–1.10 (m, 1H), 1.17 (s, 3H), 0.94–0.84 (m, 2H), 0.87 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 151.5, 143.7, 140.6, 128.3, 127.9, 127.5, 126.4, 125.2, 125.1, 115.6, 75.7, 68.5, 50.3, 41.4, 40.0, 39.4, 34.4, 31.2, 29.2, 26.3, 23.4, 21.7; HMRS calcd for $(M+Na)^+$ $C_{27}H_{34}O_3Na$: 429.2400, found: 429.2420.

4.3.8. (2′*S*)-2′-Hydroxy-4′-methylpent-4′-enoic acid (1*R*,2*S*,5*R*)-8-phenylmenthyl ester (2′*S*)-3b. Oil; IR (CH_2Cl_2): 3505, 2955, 1723, 1650, 1443, 1263, 1209, 1097, 891, 765, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.26 (m, 4H), 7.18–7.11 (m, 1H), 4.87 (dt, $J = 10.8$, 4.5 Hz, 1H), 4.78 (s, 1H), 4.67 (s, 1H), 3.31–3.26 (m, 1H), 2.40 (d, $J = 5.6$ Hz, 1H), 2.14–2.08 (m, 2H), 1.97 (dd, $J = 14.2$, 8.8 Hz, 1H), 1.89–1.82 (m, 2H), 1.74–1.68 (m, 1H), 1.64 (s, 3H), 1.53–1.45 (m, 1H), 1.30 (s, 3H), 1.22–1.14 (m, 1H), 1.19 (s, 3H), 0.99–0.91 (m, 2H), 0.88 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 151.8, 141.1, 128.0, 125.3, 125.2, 113.5, 75.7, 68.2, 50.3, 42.3, 41.5, 39.4, 34.5, 31.2, 29.6, 26.2, 22.9, 22.2, 21.7; HMRS calcd for $(M+Na)^+$ $C_{22}H_{32}O_3Na$: 367.2244, found: 367.2233.

4.3.9. (2′*S*)-2′-Hydroxy-5′-methyl-4′-methylene-hexanoic acid (1*R*,2*S*,5*R*)-8-phenylmenthyl ester (2′*S*)-4b. Oil; IR (CH_2Cl_2): 3504, 2959, 2871, 1724, 1643, 1457, 1260, 1212, 1091, 979, 764, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.27 (m, 4H), 7.15–7.11 (m, 1H), 4.87 (dt, $J = 10.8$, 4.5, 1H), 4.81 (s, 1H), 4.69 (s, 1H), 3.32–3.28 (m, 1H), 2.40 (d, $J = 5.59$ Hz, 1H), 2.18 (dd, $J = 14.7$, 3.8 Hz, 1H), 2.15–2.05 (m, 2H), 1.96 (dd, $J = 14.7$, 8.7 Hz, 1H), 1.88–1.81 (m, 2H), 1.73–1.67 (m, 1H), 1.53–1.44 (m, 1H), 1.30 (s, 3H), 1.21–1.12 (m, 1H), 1.19 (s, 3H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.97 (d, $J = 6.8$ Hz, 3H), 0.96–0.86 (m, 2H), 0.88 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 151.8, 150.9, 127.9, 125.2, 125.1, 109.6, 75.6, 68.6, 50.3, 41.5, 39.5, 39.4, 34.5, 32.9, 31.2, 29.5, 26.2, 23.0, 21.7, 21.5; HMRS calcd for $(M+Na)^+$ $C_{24}H_{36}O_3Na$: 395.2557, found: 395.2575.

4.3.10. (2′*S*)-2′-Hydroxy-5′,5′di-methyl-4′-methylene-hexanoic acid (1*R*,2*S*,5*R*)-8-phenylmenthyl ester (2′*S*)-5b. Oil; IR (CH_2Cl_2): 3504, 2957, 2870, 1723, 1636, 1457, 1362, 1215, 1095, 905, 763, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.26 (m, 4H), 7.15–7.11 (m, 1H), 4.93 (s, 1H), 4.88 (dt, $J = 10.8$, 4.5 Hz, 1H), 4.71 (s, 1H), 3.41–3.37 (m, 1H), 2.38 (d, $J = 5.3$ Hz, 1H), 2.19 (dd, $J = 15.8$, 3.1 Hz, 1H), 2.12–2.06 (m, 1H), 1.95 (dd, $J = 15.8$, 9.3 Hz, 1H), 1.87–1.82 (m, 2H), 1.73–1.67 (m, 1H), 1.54–1.45 (m, 1H), 1.31 (s, 3H), 1.18–1.12 (m, 1H), 1.20 (s, 3H), 1.00 (s, 9H), 0.97–0.87 (m, 2H), 0.89 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.4, 152.6, 151.7, 128.0, 125.2 × 2, 108.5, 75.6, 69.3, 50.3, 41.5, 39.4, 36.0, 35.8, 34.5, 31.2, 29.4, 29.1, 26.3, 23.2, 21.7; HMRS calcd for $(M+Na)^+$ $C_{25}H_{38}O_3Na$: 409.2713, found: 409.2733.

4.3.11. (2′*S*)-3′-(Cyclopent-1-enyl)-2′-hydroxy-propionic acid (1*R*,2*S*,5*R*)-8-phenylmenthyl ester (2′*S*)-6b. Oil; IR (CH_2Cl_2): 3544, 2958, 1720, 1600, 1495, 1444, 1223, 1091, 1030, 977, 561 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.26 (m, 4H), 7.16–7.11 (m, 1H), 5.35 (br s, 1H), 4.85 (dt, $J = 10.8$, 4.5, 1H), 3.35–3.31 (m, 1H), 2.45 (d, $J = 5.1$, 1H), 2.29–2.24 (m, 2H), 2.21–2.06 (m, 5H), 1.86–1.79 (m, 4H), 1.73–1.66 (m, 1H), 1.53–1.42 (m, 1H), 1.29 (s, 3H), 1.20–1.12 (m, 1H), 1.19 (s, 3H), 0.96–0.87 (m, 2H), 0.87 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 151.7, 139.5, 127.9, 127.1, 125.2, 125.2, 75.6, 68.7, 50.3, 41.6, 39.4, 35.8, 35.0, 34.5, 32.3, 31.2, 29.3, 26.3, 23.4, 23.2, 21.7; HMRS calcd for $(M+Na)^+$ $C_{24}H_{34}O_3Na$: 393.2400, found: 393.2397.

4.3.12. (2′*S*)-3′-(Cyclohex-1-enyl)-2′-hydroxy-propionic acid (1*R*,2*S*,5*R*)-8-phenylmenthyl ester (2′*S*)-7b. Oil; IR (CH_2Cl_2): 3492, 2925, 1723, 1600, 1496, 1443, 1370, 1258, 1210, 1096, 764, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.26 (m, 4H), 7.15–7.12 (m, 1H), 5.36 (br s, 1H), 4.85 (dt, $J = 10.8$, 4.4 Hz, 1H), 3.32–3.28 (m, 1H), 2.37 (d, $J = 5.8$ Hz, 1H), 2.11–2.03 (m, 2H), 1.97–1.89 (m, 3H), 1.85–1.79 (m, 3H), 1.77–1.67 (m, 2H), 1.61–1.45 (m, 6H), 1.29 (s, 3H), 1.19 (s, 3H), 1.20–1.12 (m, 1H), 0.97–0.89 (m, 2H), 0.88 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.4, 151.7, 133.2, 127.9, 125.2, 125.1, 124.6, 75.6, 68.5, 50.4, 43.0, 41.7, 39.4, 34.5, 31.2, 29.2, 28.2, 26.3, 25.2, 23.3, 22.8, 22.2, 21.8; HMRS calcd for $(M+Na)^+$ $C_{25}H_{36}O_3Na$: 407.2557, found: 407.2568.

4.3.13. (2′*S*)-(4*E*)-2′-Hydroxy-oct-4′-enoic acid (1*R*,2*S*,5*R*)-8-phenylmenthyl ester (2′*S*)-8b. NMR data in agreement with those described in the literature.[4b]

4.4. Determination of the diastereomeric ratio

The compositions of the reaction mixtures in case of ene products **2a**–**7a** derived from the Oppolzer's sultam were determined independently by HPLC and by ^{1}H NMR. Both these methods suffer from a certain analytical error (HPLC because of theoretically different absorbance coefficients of both diastereomers). In all the cases, the products of the ene reactions have been reduced with $LiAlH_4$ in Et_2O to the corresponding diols **2c**–**7c** and analyzed by HPLC (**2c**, **3c**, **6c**, **7c**) or GC (**4c**, **5c**, as a isopropylidene derivatives). The obtained results were very close (±2% de) to the results of direct HPLC measurements of ene products **2a**–**7a**. In the case of 8-phenylmenthyl derivatives, the asymmetric inductions were determined after the reduction to the corresponding diols **2c**–**8c**. Isopropylidene derivatives of diols **4c**, **5c**, **8c** were obtained by treatment

of corresponding diols with acetone containing catalytic amount of *p*-toluenosulfonic acid.

4.5. Analytical data for 1,2-diols 2c–8c

4.5.1. 4-Phenylpent-4-ene-1,2-diol 2c. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.43–7.20 (m, 5H), 5.38 (d, $J = 1.4$ Hz, 1H), 5.16–5.13 (m, 1H), 3.81–3.68 (m, 1H), 3.59 (dd, $J = 11.3$, 3.1 Hz, 1H), 3.43 (dd, $J = 11.3$, 7.1 Hz, 1H), 2.8 (br s, 2H), 2.68–2.62 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 144.5, 140.3, 128.4, 127.7, 126.1, 115.3, 70.1, 66.1, 39.4; HPLC (Chiracel AS-H column, hexane/*i*-PrOH, 95:5, flow rate 1.0 mL/min, $\lambda = 205$ nm): t_R(major-**2c**) = 23.3 min, t_R(minor-**2c**) = 29.1 min.

4.5.2. 4-Methylpent-4-ene-1,2-diol 3c. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.89–4.85 (m, 1H), 4.81–4.77 (m,1H), 3.93–3.81 (m, 1H), 3.65 (dd, $J = 11.4$, 3.0 Hz, 1H), 3.46 (dd, $J = 11.4$, 7.3 Hz, 1H), 3.2 (br s, 2H), 2.26–2.08 (m, 2H), 1.77 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.9, 113.4, 69.6, 66.4, 41.6, 22.4; HPLC (Chiracel AS-H column, hexane/*i*-PrOH, 97.5:2.5, flow rate 1.0 mL/min, $\lambda =$ 205 nm): t_R[major-(2′*S*)-**3c**] = 23.3 min, t_R[minor-(2′*R*)-**3c**] = 25.1 min.

4.5.3. 5-Methyl-4-methylene-hexane-1,2-diol 4c. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.91 (br s, 1H), 4.81 (br s, 2H), 3.93–3.79 (m, 1H), 3.67 (dd, $J = 11.4$, 3.0 Hz, 1H), 3.47 (dd, $J = 11.4$, 7.0 Hz, 1H), 2.9 (br s, 2H), 2.35–2.08 (m, 3H), 1.06 (d, $J = 6.8$ Hz, 3H), 1.04 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.9, 109.6, 70.1, 66.4, 38.6, 33.5, 21.8, 21.6; GC (β-dex 120 column, analyzed as a isopropylidene derivative, $T = 90$ °C): t_R(major-**4c**) = 19.6 min, t_R(minor-**4c**) = 20.1 min.

4.5.4. 5,5-Dimethyl-4-methylene-hexane-1,2-diol 5c. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.03 (s, 1H), 4.83 (d, $J =$ 0.9 Hz, 1H), 4.00–3.87 (m, 1H), 3.71 (dd, $J = 11.2$, 3.2 Hz, 1H), 3.49 (dd, J=11.2, 7.1 Hz, 1H), 2.7 (br s, 2H), 2.24–2.17 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 153.9, 108.7, 70.7, 66.5, 36.2, 35.2, 29.1; GC (β-dex 120 column, analyzed as a isopropylidene derivative, $T = 90$ °C): t_R(minor-**5c**) = 19.8 min, t_R(major-**5c**) = 20.6 min.

4.5.5. 3-(Cyclopent-1-enyl)-propane-1,2-diol 6c. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.47 (s, 1H), 3.93–3.80 (m, 1H), 3.63 (dd, $J = 11.4$, 3.0 Hz, 1H), 3.44 (dd, $J = 11.4$, 7.3 Hz, 1H), 3.3 (br s, 2H), 2.38–2.15 (m, 6H), 1.95–1.79 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.3, 126.9, 70.2, 66.4, 35.1 ($2 \times CH_2$), 32.4, 23.3; HPLC (Chiracel AS-H column, hexane/*i*-PrOH, 95:5, flow rate 1.0 mL/min, $\lambda = 205$ nm): t_R(major-**6c**) = 13.4 min, t_R(minor-**6c**) = 16.3 min.

4.5.6. 3-(Cyclohex-1-enyl)-propane-1,2-diol 7c. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.54 (s, 1H), 3.89–3.77 (m, 1H), 3.66 (dd, $J = 11.3$, 3.2 Hz, 1H), 3.46 (dd, $J = 11.3$, 6.8 Hz, 1H), 2.3 (br s, 2H), 2.12–1.90 (m, 6H), 1.70–1.49 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 133.8, 125.1, 69.4, 66.6, 42.1, 28.4, 25.3, 22.8, 22.3; HPLC (Chiracel AS-H column, hexane/*i*-PrOH, 95:5, flow rate 1.0 mL/min,

Table 3. Crystal data and structure refinement for (2′*S*)-**3a** and (2′*S*)-**7a**

Name	(2′*S*)-**3a**	(2′*S*)-**7a**
Chemical formula	$C_{16}H_{25}NO_4S$	$C_{19}H_{29}NO_4S$
Molecular weight	327.43	367.49
T (K)	101(2)	100(2)
λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
Unit cell dimensions		
a (Å)	6.9384(2)	9.0971(6)
b (Å)	9.2281(3)	6.9065(4)
c (Å)	26.0688(9)	15.2954(10)
α (°)	90	90
β (°)	90	101.521(6)
γ (°)	90	90
V (Å^3)	1669.14(9)	941.63(10)
Z	4	2
Calculated density (Mg m^{-3})	1.303	1.296
Absorption coefficient (mm^{-1})	0.211	0.195
F(000)	704	396
Crystal size (mm)	$0.60 \times 0.20 \times 0.19$	$0.60 \times 0.30 \times 0.20$
θ Range for data collection (°)	2.70–28.73	2.88–28.69
Limiting indices	$-9 \leqslant h \leqslant 9$, $-12 \leqslant k \leqslant 12$, $-35 \leqslant l \leqslant 34$	$-11 \leqslant h \leqslant 12$, $-9 \leqslant k \leqslant 9$, $-20 \leqslant l \leqslant 20$
Reflections collected	25,415	17,782
Independent reflections (R_{int})	4149 (0.0304)	4547 (0.0223)
Completeness to θ	28.00° (99.8%)	28.00° (98.8%)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.986	1.107
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0291$, $wR_2 = 0.0735$	$R_1 = 0.0518$, $wR_2 = 0.1427$
R indices (all data)	$R_1 = 0.0366$, $wR_2 = 0.0751$	$R_1 = 0.0557$, $wR_2 = 0.1442$
Largest difference peak and hole (e Å^{-3})	0.205 and −0.257	0.881 and −0.261

$\lambda = 205$ nm): t_R[major-(2′*S*)-**7c**] = 13.1 min, t_R[minor-(2′*R*)-**7c**] = 17.0 min.

4.5.7. (4*E*)-Oct-4-ene-1,2-diol 8c. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.62–5.31 (m, 2H), 3.77–3.65 (m, 1H), 3.65 (dd, $J = 11.3$, 3.1 Hz, 1H), 3.46 (dd, $J = 11.3$, 7.2 Hz, 1H), 2.9 (br s, 2H), 2.20–2.13 (m, 2H), 2.05–1.93 (m, 2H), 1.48–1.25 (m, 2H), 0.89 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 134.3, 125.1, 71.7, 66.2, 36.7, 34.7, 22.5, 13.6; GC (β-dex 120 column, analyzed as a isopropylidene derivative, $T = 90$ °C): t_R(minor-**8c**) = 31.3 min, t_R(major-**8c**) = 31.9 min.

4.6. The X-ray structure investigations for the compounds (2′*S*)-3a and (2′*S*)-7a

The intensity data were collected using a Kuma KM4CCD κ-axis diffractometer, using the omega scan mode. The structure was solved by direct methods and refined using SHELXL. The crystal data and details of the crystal structure determinations are presented in Table 3.

The crystallographic data (excluding the structure factors) have been deposited with Cambridge Crystallographic Data Centre as supplementary publication number CCDC 626821 for compound (2′*S*)-**3a** and 626822 for compound (2′*S*)-**7a**, respectively. These data may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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