A Highly Enantioselective Access to Chiral 1-(β-Arylalkyl)-1*H*-1,2,4-triazole Derivatives as Potential Agricultural Bactericides

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A series of chiral 1-(β-arylalkyl)-1*H*-1,2,4-triazole derivatives has been designed as potential antifungal agents. The target triazoles have been synthesized by using a chiral auxiliary as a controlling reagent. All of the compounds were obtained with high ee values, reaching up to 99%. Preliminary bioassay results have revealed that most of the synthesized compounds display significantly higher fungicidal activities against the species *Fusarium oxysporium*, *Rhizoctonia solani*, *Botrytis cinereapers*, *Gibberella zeae*, *Dothiorella gregaria*, and *Colletotrichum gossypii* than the commercial agent *triadimefon*. Moreover, some of the enantiomers have been found to display significant differences in activity.

Introduction. – Chirality is an important factor in pharmaceuticals, agrochemicals, and the life sciences, in general, since the living body is a highly chiral environment. Many biologically active molecules are chiral, including both naturally occurring compounds and synthetic drugs [1–4]. Nowadays, several synthetic agrochemicals, such as pyrethroid insecticides, triazole fungicides, and (aryloxy)propanoate herbicides, are marketed as their most biologically active isomers. Numerous reports describing the relative biological activities, preparations, and analyses of enantiomerically pure agrochemicals are available [5–8].

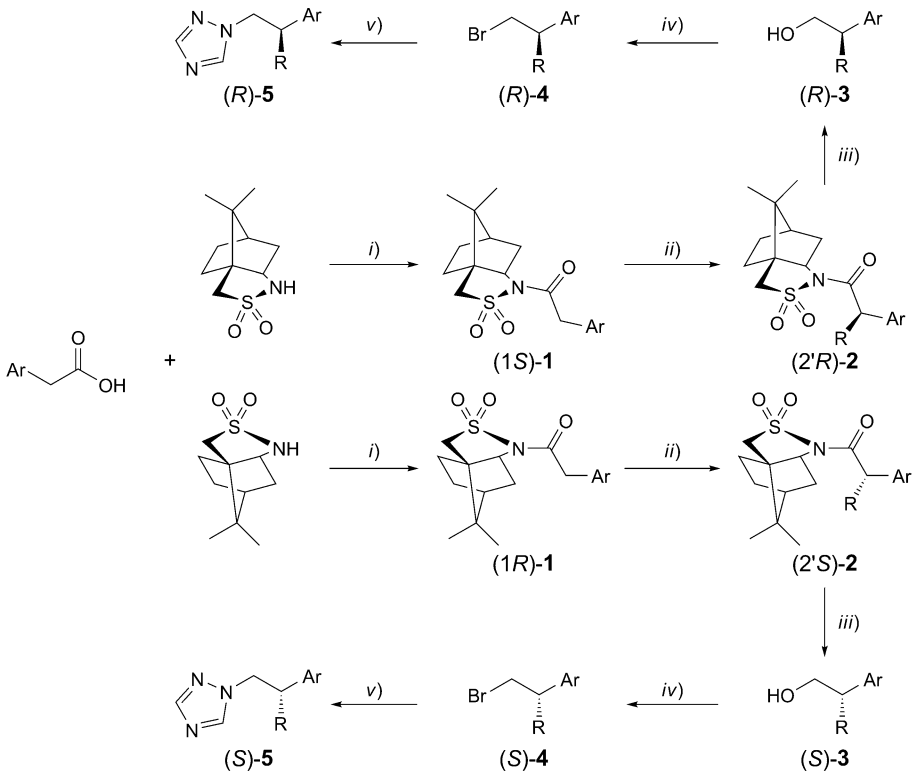
At present, a high percentage of pharmaceutical compounds are pure enantiomers, and many of them show significant enantioselective differences in their pharmacokinetics and pharmacodynamics [9][10]. There are *ca.* 650 pesticides on the market, a quarter of which exist as enantiomers [11]. Different enantiomers of chiral compounds often have different effects as drugs, and many chiral drugs must be produced with high enantiomeric purity due to potential side-effects of the other enantiomer [12][13].

The use of optically active pesticides has led to research aimed at finding new and effective methods of resolving enantiomeric mixtures. Triazole derivatives such as diniconazole, triadimefon, tebuconazole, and hexaconazole represent the most important category of fungicides to date [14–17]. These compounds are effective against a wide spectrum of crop diseases, and they all possess a stereogenic C-atom leading to two enantiomers. The influence of the configuration upon biological activity is, therefore, of particular interest in this study.

Heeres and *Backx* reported the preparation and biological activity of racemic 1-(β-arylalkyl)-1*H*-1,2,4-triazole analogs [18]; however, the goal of developing safer and

more effective chiral drugs, including medicines and agrochemicals, encouraged us to synthesize pure active enantiomers. As part of our agrochemistry program aimed at devising new routes to active chiral triazole derivatives **5** [19], we report here that exceptionally high levels of stereoselectivity can be easily achieved by steric control under standard conditions in the asymmetric alkylation of *N*-acylsultams derived from *Oppolzer*'s 10,2-camphorsultam, as depicted in *Scheme 1*. Furthermore, we have investigated the *in vitro* fungicidal activities of the resulting series of chiral 1-(*β*-arylalkyl)-1*H*-1,2,4-triazole derivatives. Preliminary *in vitro* assays have shown that almost all of the compounds **5a**–**5i** have higher fungicidal activities than the commercial agent triadimefon under the same conditions.

Scheme 1. *Synthesis of 1-(β-Arylalkyl)-1,2,4-triazole Derivatives* **5**



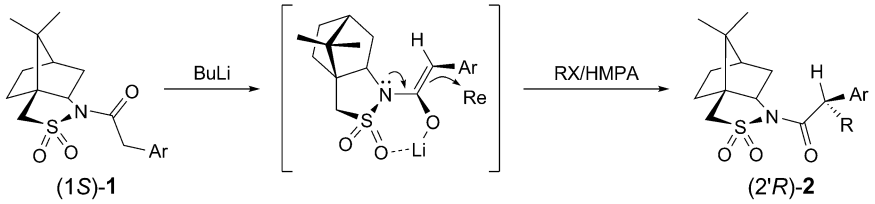
i) 1. Et_3N; 2. Me_3CCOCl, toluene, 80–110°. *ii*) 1. BuLi, THF, −78°; 2. hexamethylphosphoric triamide (HMPA)/RX (MeI, PrI, BuI, $PhCH_2Br$, CH_2=$CHCH_2Br$). *iii*) $NaBH_4$, aq. THF. *iv*) HBr. *v*) 1*H*-1,2,4-Triazole, K_2CO_3, MeCN, reflux, 5–7 h.

Results and Discussion. – 1. *Synthesis and Physicochemical Properties.* The pioneering work of *Oppolzer et al.* resulted in the development of 10,2-camphorsultam as a popular and widely used chiral auxiliary in asymmetric synthesis. The asymmetric

induction achieved by using this auxiliary is widely applied in C,C bond-formation reactions such as alkylations [20], aldol reactions [21], 1,4-additions [22], and *Diels–Alder* reactions [23]. Thus, we have applied *Oppolzer*'s 10,2-camphorsultam as a chiral auxiliary in a series of reactions under mild conditions to obtain the chiral triazole derivatives **5** with high enantiomeric purity.

The synthetic route to 1-(β-arylalkyl)-1*H*-1,2,4-triazoles **5** is outlined in *Scheme 1*. The key to the synthesis of **5** with a high enantiomeric purity was to establish the stereogenic center in the stable C(α)-alkylation products **2**. The α-alkylation reaction is most probably initiated by the chelated lithium (*Z*)-enolate intermediate, with subsequent nucleophilic attack of the alkylating reagent leading to the formation of chiral intermediates **2**. The possible mechanism of the monoalkylation reaction is depicted in *Scheme 2* [20].

Scheme 2. *Possible Mechanism of Monoalkylation Reaction with Various Alkyl Halides to Afford Compounds* **2** *with High Enantiomeric Purity*



N-Acylsultams **1** were readily obtained by acylation of camphorsultam with phenylacetic acid in the presence of pivaloyl chloride and Et_3N [24]. Deprotonation of **1** with BuLi in THF, followed by monoalkylation with benzylic or allylic halides, or even with non-activated primary alkyl iodides, in the presence of hexamethylphosphoric triamide (HMPA) at $-78°$, followed by crystallization, gave products **2** in high yields and with high diastereomeric purities [19]. Non-destructive removal of the chiral auxiliary camphorsultam under mild conditions using $NaBH_4$ in aqueous THF furnished the sultam and the alcohols **3** [25], which were then brominated with HBr. The bromo derivatives **4** were then treated with 1*H*-1,2,4-triazole in MeCN in the presence of K_2CO_3 at 60–70° for 5–7 h to give the chiral 1-(β-arylalkyl)-1*H*-1,2,4-triazoles **5** [26]. Under the experimental conditions described herein, the pure (*R*)- and (*S*)-derivatives were conveniently obtained with ee values up to 99%. The ee values and optical rotations of the target compounds are compiled in *Table 1*. The structures of all of the newly synthesized compounds were elucidated on the basis of their ^{1}H- and ^{13}C-NMR data, and elemental analyses. A detailed methodology to obtain each of the compounds **1** to **4** is given in the *Exper. Part*.

It can be seen from *Table 1* that different substituents and configurations lead to different ee values. When Ar = 4-chlorophenyl, **5c** bearing a benzyl moiety was obtained with the highest ee value. However, when Ar = 2,4-dichlorophenyl, the compounds bearing Me and Bu substituents, *i.e.*, **5f** and **5g**, respectively, were obtained with higher ee values. Furthermore, for a common R substituent such as Bu, the compounds bearing 4-fluorophenyl and 2,4-dichlorophenyl moieties, **5e** and **5g**,

Table 1. *The ee and* $[\alpha]_D^{25}$ *Values of 1-(β-Arylalkyl)-1*H*-1,2,4-Triazole Derivatives* **5**

Entry	Compound	R	Ar	Yield[a]) [%]	$[\alpha]_D^{25}$ ($c = 1$, CH_2Cl_2)	ee [%][b])
1	(*R*)-**5a**	Pr	4-Cl–C_6H_4	73	+83.7	**99**
2	(*S*)-**5a**	Pr	4-Cl–C_6H_4	71	−82.8	94
3	(*R*)-**5b**	Bu	4-Cl–C_6H_4	75	+67.5	87
4	(*S*)-**5b**	Bu	4-Cl–C_6H_4	73	−69.7	**95**
5	(*R*)-**5c**	Bn	4-Cl–C_6H_4	60	+19.7	**98**
6	(*S*)-**5c**	Bn	4-Cl–C_6H_4	58	−23.1	**99**
7	(*R*)-**5d**	Pr	4-F–C_6H_4	58	+70.2	90
8	(*S*)-**5d**	Pr	4-F–C_6H_4	60	−70.7	89
9	(*R*)-**5e**	Bu	4-F–C_6H_4	57	+59.9	**98**
10	(*S*)-**5e**	Bu	4-F–C_6H_4	59	−68.8	**99**
11	(*R*)-**5f**	Me	2,4-Cl_2–C_6H_3	54	+13.5	**99**
12	(*S*)-**5f**	Me	2,4-Cl_2–C_6H_3	56	−13.2	**97**
13	(*R*)-**5g**	Bu	2,4-Cl_2–C_6H_3	65	+20.7	**98**
14	(*S*)-**5g**	Bu	2,4-Cl_2–C_6H_3	69	−20.9	**99**
15	(*R*)-**5h**	Allyl	2,4-Cl_2–C_6H_3	59	+27.4	88
16	(*S*)-**5h**	Allyl	2,4-Cl_2–C_6H_3	62	−28.4	90
17	(*R*)-**5i**	Bn	2,4-Cl_2–C_6H_3	51	+8.3	93
18	(*S*)-**5i**	Bn	2,4-Cl_2–C_6H_3	58	−11.3	**99**

[a]) Yields of isolated products. [b]) Determined by HPLC analysis (*Chiralcel OJ-H* or *OD-H*).

respectively, exhibited the highest ee values. The configurations of compounds **5** were assigned on the basis of the absolute configurations of compounds **2**. The crystal structures of molecules (2′*R*)-**2a** and (2′*S*)-**2a** were established by X-ray crystallographic analysis and are shown in the *Figure*[1]).

2. *Antifungal Activity.* The antifungal activities of the 1-(*β*-arylalkyl)-1*H*-1,2,4-triazole derivatives **5** were evaluated by using *in vitro* agar diffusion assays, the results of which are presented in *Tables 2* and *3*. Most of the compounds showed activities in preliminary screening tests against fungal cultures when deployed at a concentration of 50 μg/ml in agar diffusion assays. All of the synthesized chiral triazole derivatives showed significant inhibitory activities against the growth of the species *Fusarium oxysporium*, *Rhizoctonia solani*, *Botrytis cinereapers*, *Gibberella zeae*, *Dothiorella gregaria*, and *Colletotrichum gossypii* compared with the commercial fungicide triadimefon.

As shown in *Table 2*, all activity screenings were performed using commercial triadimefon as a reference. Triadimefon, a broad-spectrum fungicide, was first introduced as a triazole fungicide in 1976. We used this compound as a reference to evaluate the potential activity of 1-(*β*-arylalkyl)-1*H*-1,2,4-triazole derivatives **5**. All of the synthesized compounds displayed inhibitory activities against *Botrytis cinereapers*,

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[1]) Crystallographic data for (*R*)-**2a** and (*S*)-**2a** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication (CCDC-715349 and CCDC-715350). This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +441223/336033; e-mail: deposit@ccdc.cam.ac.uk).

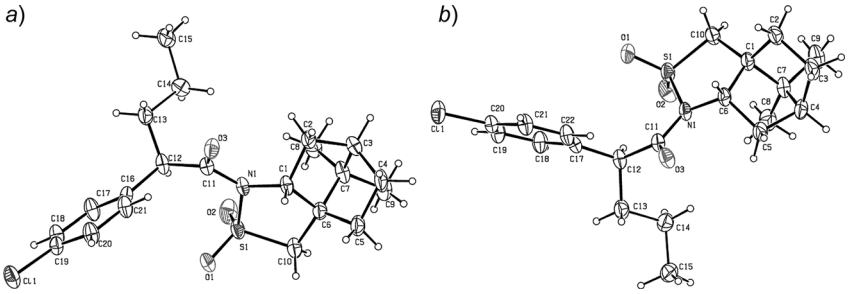

Figure. *The molecular structure of* a) *(2′*R*)*-**2a** *and* b*) (2′*S*)*-**2a**

Table 2. In vitro *Fungicidal Activities of Compounds* **5** *at 50 mg/l Concentration*[a])[b])

Compound	R	Ar	Inhibition of growth [%]					
			F. oxysporium	*R. solani*	*B. cinereapers*	*G. zeae*	*D. gregaria*	*C. gossypii*
(*R*)-**5a**	Pr	4-Cl–C_6H_4	91	98	100	85	95	100
(*S*)-**5a**	Pr	4-Cl–C_6H_4	95	99	100	70	100	100
(*R*)-**5b**	Bu	4-Cl–C_6H_4	73	99	100	78	100	100
(*S*)-**5b**	Bu	4-Cl–C_6H_4	82	99	100	74	100	100
(*R*)-**5c**	Bn	4-Cl–C_6H_4	71	86	98	73	86	100
(*S*)-**5c**	Bn	4-Cl–C_6H_4	63	86	79	70	73	96
(*R*)-**5d**	Pr	4-F–C_6H_4	98	99	100	100	100	100
(*S*)-**5d**	Pr	4-F–C_6H_4	95	99	100	89	100	100
(*R*)-**5e**	Bu	4-F–C_6H_4	95	99	100	98	98	100
(*S*)-**5e**	Bu	4-F–C_6H_4	77	96	98	74	98	100
(*R*)-**5f**	Me	2,4-Cl_2–C_6H_3	90	97	100	74	57	98
(*S*)-**5f**	Me	2,4-Cl_2–C_6H_3	93	98	89	74	98	100
(*R*)-**5g**	Bu	2,4-Cl_2–C_6H_3	91	99	100	96	100	100
(*S*)-**5g**	Bu	2,4-Cl_2–C_6H_3	91	100	100	81	100	100
(*R*)-**5h**	Allyl	2,4-Cl_2–C_6H_3	92	90	100	77	100	100
(*S*)-**5h**	Allyl	2,4-Cl_2–C_6H_3	98	99	100	81	100	100
(*R*)-**5i**	Bn	2,4-Cl_2–C_6H_3	68	94	100	78	67	98
(*S*)-**5i**	Bn	2,4-Cl_2–C_6H_3	75	90	79	73	91	92
Triadimefon			91	91	78	59	14	98

[a]) Mean values for relative inhibitions calculated from at least three determinations. [b]) Standard deviations are within the range of 1–4.

Gibberella zeae, and *Dothiorella gregaria* better than triadimefon at a concentration of 50 mg/l. In particular, for the fungus *Dothiorella gregaria*, triadimefon was found to exhibit a weak inhibition rate of only 14%, which was lower than the inhibition rates of the synthesized chiral triazole derivatives **5**. Moreover, all of the compounds, except (*S*)-**5c** and (*S*)-**5i**, showed higher inhibitory activities against *Colletotrichum gossypii* than the reference compound. The inhibitory activity of triadimefon against *Rhizoctonia solani* is lower than those of almost all of the synthesized chiral triazole derivatives, except (*R*)-**5c**, (*S*)-**5c**, (*R*)-**5h**, and (*S*)-**5i**. From these preliminary results, it

can be seen that most of the synthesized compounds exhibit high and broad-spectrum antifungal activities against the six strains tested, and the activity differences between the compounds of different configurations are insignificant. To further investigate the activity differences of the enantiomers, the test concentration was decreased to 12.5 mg/l. The inhibitory activities of compounds **5a**, **5b**, **5d**, **5e**, **5f**, and **5g** against the

Table 3. In vivo *Fungicidal Activities of Compounds* **5** *at 12.5 mg/l Concentration*[a])[b])

Compound	R	Ar	Inhibition of growth [%]					
			F. oxysporium	*R. solani*	*B. cinereapers*	*G. zeae*	*D. gregaria*	*C. gossypii*
(*R*)-**5a**	Pr	4-Cl–C_6H_4	61	86	92	61	61	91
(*S*)-**5a**	Pr	4-Cl–C_6H_4	63	97	57	31	68	88
(*R*)-**5b**	Bu	4-Cl–C_6H_4	38	91	22	34	0	87
(*S*)-**5b**	Bu	4-Cl–C_6H_4	54	92	87	38	68	87
(*R*)-**5d**	Pr	4-F–C_6H_4	88	87	78	66	55	96
(*S*)-**5d**	Pr	4-F–C_6H_4	71	95	39	55	73	92
(*R*)-**5e**	Bu	4-F–C_6H_4	79	83	26	62	45	98
(*S*)-**5e**	Bu	4-F–C_6H_4	29	90	9	21	36	75
(*R*)-**5f**	Me	2,4-Cl_2–C_6H_3	67	73	70	31	14	38
(*S*)-**5f**	Me	2,4-Cl_2–C_6H_3	79	82	22	45	77	92
(*R*)-**5g**	Bu	2,4-Cl_2–C_6H_3	79	80	98	69	45	88
(*S*)-**5g**	Bu	2,4-Cl_2–C_6H_3	63	88	100	62	95	96
Triadimefon			65	86	15	29	10	78

[a]) Mean values for relative inhibitions calculated from at least three determinations. [b]) Standard deviations are within the range of 1–4.

various fungi at this concentration are collected in *Table 3*. The results evidence that the synthesized triazole derivatives **5** exhibit higher inhibition activities than the commercial triadimefon under the same conditions. More importantly, the enantiomers display some differences in activity. For example, compound **5b** exhibits significant activity differences against *Dothiorella gregaria* and *Botrytis cinereapers*, with (*S*)-**5b** showing inhibition rates of 87 and 68%, respectively, whereas (*R*)-**5b** exhibiting inhibition rates of 22 and 0%, respectively. Enantiomers of **5a** also show distinctly different inhibition rates against *Botrytis cinereapers* and *Gibberella zeae*, with the (*R*)-enantiomer (*R*)-**5a** displaying better inhibition activity than the (*S*)-enantiomer. The activity of (*R*)-**5e** is far higher than that of (*S*)-**5e**; the inhibition rate against *Fusarium oxysporium* of the (*R*)-enantiomer is 50% higher than that of the (*S*)-enantiomer. The inhibitory activities of the enantiomers of compound **5f** against *Dothiorella gregaria* are also distinctly different, with the activity of (*S*)-**5f** being about five-fold higher than that of (*R*)-**5f**.

Conclusions. – In summary, we have achieved a highly enantioselective synthesis of 1-(β-arylalkyl)-1*H*-1,2,4-triazole derivatives utilizing camphorsultam as a chiral auxiliary. All of the compounds were obtained with high ee values reaching 87–99%. Preliminary bioassay results have demonstrated that most of these compounds

display significant wide-spectrum fungicidal activities against the species *Fusarium oxysporium*, *Rhizoctonia solani*, *Botrytis cinereapers*, *Gibberella zeae*, *Dothiorella gregaria*, and *Colletotrichum gossypii*. On the basis of the above results, the optically pure enantiomers (*R*)-**5a**, (*S*)-**5a**, (*R*)-**5d**, (*S*)-**5d**, (*R*)-**5e**, (*S*)-**5f**, (*R*)-**5g**, (*S*)-**5g**, and (*S*)-**5h** exhibited higher activities than the commercial fungicide triadimefon, and, therefore display the potential to be developed as highly potent antifungal agents.

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Experimental Part

1. *General.* Unless otherwise noted, all materials were commercially available and were used directly without further purification. All solvents were redistilled before use. *Fusarium oxysporium*, *Rhizoctonia solani*, *Botrytis cinereapers*, *Gibberella zeae*, *Dothiorella gregaria*, and *Colletotrichum gossypii* were provided by the Center for Bioassay, Central China Normal University. The enantiomeric ratio was determined by using HPLC on *Chiralcel OD-H* column and *OJ-H* column, with hexane and ^{i}PrOH as the eluent. M.p.: *Büchi B-545* melting point apparatus; uncorrected. Optical rotations: *Jasco P-1010* polarimeter. ^{1}H- and ^{13}C-NMR spectra: *Varian Mercury Plus 400* spectrometer (400 MHz) or *Varian Mercury Plus 600* spectrometer (600 MHz), resp.; the chemical shifts δ rel. to $CDCl_3$ with TMS as the internal reference. MS: *TraceMS-2000* organic mass spectrometer. Elemental analyses: *Vario ElIII CHNSO* elemental analysis instrument.

2. *Synthesis of* **1**. To a mixture of the (−)-D-10,2-camphorsultam (30 mmol) and (4-chlorophenyl)-acetic acid (60 mmol) in toluene (48 ml) was added Et_3N (120 mmol). The mixture was heated to an internal temp. of 80°. To the mixture was added a soln. of pivaloyl chloride (60 mmol) in toluene (6 mmol) at a rate to maintain an internal temp. of 80°. The mixture was then heated to 110° and stirred at this temp. for 24 h. The mixture was cooled to r.t. and was washed with 2N HCl, 5% Na_2CO_3, and brine, dried (Na_2SO_4), and filtered. The filtrate was concentrated, and the crude product was purified by crystallization or SiO_2 chromatography to afford the desired product **1** as a white solid. The analogous procedure with (+)-L-10,2-camphorsultam gave the enantiomeric products.

*(+)-(1*S*)-*N*-[2-(4-Chlorophenyl)acetyl]bornane-10,2-sultam* (=*2-(4-Chlorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]ethanone*; (1*S*)-**1a**). Yield 10.5 g (95%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90 (*s*, Me); 1.05 (*s*, Me); 1.27–1.37 (*m*, 2 H); 1.78–1.87 (*m*, 3 H); 1.95–1.97 (*m*, 2 H); 3.44 (*d*, *J* = 13.5, 2 H); 3.81–3.84 (*m*, 1 H); 3.87–3.99 (*m*, $COCH_2$); 7.16–7.23 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.73; 20.70; 38.17; 40.85; 41.06; 44.22; 44.62; 47.64; 48.35; 52.86; 65.22; 127.70; 128.49; 131.01; 131.10; 131.65; 132.95; 169.30. EI-MS: 367 (M^+). Anal. calc. for $C_{18}H_{22}ClNO_3S$ (367.89): C 58.77, H 6.03, N 3.81, S 8.72; found: C 58.53, H 5.79, N 3.69, S 8.72.

*(+)-(1*S*)-*N*-[2-(4-Fluorophenyl)acetyl]bornane-10,2-sultam* (=*2-(4-Fluorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]ethanone*; (1*S*)-**1b**). Yield 8.43 g (80%).^{1}H-NMR (400 MHz, $CDCl_3$): 0.97 (*s*, Me); 1.12 (*s*, Me); 1.34–1.42 (*m*, 2 H); 1.85–1.93 (*m*, 3 H); 2.02–2.04 (*m*, 2 H); 3.51 (*d*, *J* = 13.5, 2 H); 3.88–3.91 (*m*, 1 H); 3.95–4.06 (*m*, $COCH_2$); 6.98–7.02 (*m*, 2 arom. H); 7.25–7.29 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.77; 20.73; 38.22; 40.95; 41.18; 44.26; 44.67; 47.67; 48.38; 52.92; 65.23; 114.99; 115.23; 115.46; 128.90; 131.28; 161.94; 169.66. EI-MS: 351 (M^+). Anal. calc. for $C_{18}H_{22}FNO_3S$ (351.44): C 61.52, H 6.31, N 3.99, S 9.12; found: C 61.57, H 6.40, N 3.86, S 8.92.

*(+)-(1*S*)-*N*-[2-(2,4-Dichlorophenyl)acetyl]bornane-10,2-sultam* (=*2-(2,4-Dichlorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]ethanone*; (1*S*)-**1c**). Yield 10.26 g (85%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.99 (*s*, Me); 1.21 (*s*, Me); 1.35–1.43 (*m*, 2 H); 1.88–1.94 (*m*, 3 H); 2.04–2.06 (*m*, 1 H); 2.14–2.15 (*m*, 1 H); 3.52 (*q*, *J* = 13.7, 2 H); 3.90–3.93 (*m*, 1 H); 4.04–4.28 (*m*, $COCH_2$); 7.18–7.23 (*m*, 2 arom. H); 7.41 (*s*, 1 arom. H). ^{13}C-NMR (100 MHz,

$CDCl_3$): 19.70; 20.54; 20.68; 38.06; 39.34; 44.21; 44.61; 47.63; 48.51; 52.72; 65.17; 127.04; 129.12; 130.56; 132.62; 133.69; 135.21; 167.83. EI-MS: 401 (M^+). Anal. calc. for $C_{18}H_{21}Cl_2NO_3S$ (402.34): C 53.73, H 5.26, N 3.48, S 7.97; found: C 53.61, H 4.98, N 3.35, S 8.07.

3. *Synthesis of* **2**. A soln. of (1*R*)-**1** (0.02 mol) in anh. THF (60 ml) under N_2 was cooled to $-78°$, to which BuLi (9 ml, 2.5M in hexane) was added dropwise. After stirring for 1 h, the alkylating agents (0.1 mol) and HMPA (0.1 mol) in THF were added, then the mixture was stirred at $-78°$ for 6–8 h. The mixture was slowly warmed up to r.t., before the reaction was quenched by the addition of H_2O, and the mixture was extracted with Et_2O (3×60 ml). The combined org. phases were washed with brine, dried ($MgSO_4$), and concentrated to yield a crude oil, which was purified by crystallization or by SiO_2 chromatography to afford the desired product **2**. The enantiomeric products were prepared according to the same procedure [19].

N-*(+)-[(2*S*)-2-(4-Chlorophenyl)pentanoyl]bornane-10,2-sultam* (=*(2*S*)-2-(4-Chlorophenyl)-1-[(3a*R*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]pentan-1-one*; (2′*S*)-**2a**). White solid. M.p. 182–184°. Yield 7.79 g (95%). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.90 (*t*, *J* = 7.2, 3 H); 0.98 (*s*, Me); 1.21 (*s*, Me); 1.28–1.34 (*m*, 4 H); 1.76–1.79 (*m*, 1 H); 1.84–1.90 (*m*, 3 H,); 2.04–2.10 (*m*, 2 H); 2.13–2.14 (*m*, 1 H); 3.41 (*d*, *J* = 13.8, 1 H); 3.53 (*d*, *J* = 13.8, 1 H); 3.83–3.85 (*m*, 1 H); 4.27 (*t*, *J* = 7.5, COCH); 7.27 (*d*, *J* = 7.6, 2 arom. H); 7.39 (*d*, *J* = 7.6, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.65; 19.78; 20.56; 20.82; 26.26; 32.75; 38.13; 38.44; 44.52; 47.61; 48.15; 50.12; 53.00; 65.41; 128.19; 130.14; 132.86; 136.51; 173.05. EI-MS: 409 (M^+). Anal. calc. for $C_{21}H_{28}ClNO_3S$ (409.97): C 61.52, H 6.88, N 3.42, S 7.82; found: C 61.75, H 6.89, N 3.30, S 8.14.

(+)-N-*[(2*R*)-2-(4-Chlorophenyl)pentanoyl]bornane-10,2-sultam* (=*(2*R*)-2-(4-Chlorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]pentan-1-one*; (2′*R*)-**2a**). White solid. M.p. 182–184°. Yield 7.62 g (93%). Spectroscopic data: identical to those of (2′*S*)-**2a**.

(+)-N-*[(2*S*)-2-(4-Chlorophenyl)hexanoyl]bornane-10,2-sultam* (=*(2*S*)-2-(4-Chlorophenyl)-1-[(3a*R*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]hexan-1-one*; (2′*S*)-**2b**). White solid. M.p. 129–131°. Yield 7.97 g (94%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*t*, *J* = 7.2, 3 H); 0.98 (*s*, Me); 1.21 (*s*, Me); 1.24–1.35 (*m*, 6 H); 1.78–1.82 (*m*, 1 H); 1.84–1.90 (*m*, 3 H,); 2.05–2.13 (*m*, 3 H); 3.41 (*d*, *J* = 14.0, 1 H); 3.52 (*d*, *J* = 14.0, 1 H); 3.82–3.84 (*m*, 1 H); 4.25 (*t*, *J* = 7.2, COCH); 7.26 (*d*, *J* = 8.4, 2 arom. H); 7.39 (*d*, *J* = 8.4, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.80; 19.88; 20.87; 22.28; 26.35; 29.55; 32.90; 35.83; 38.53; 44.62; 47.71; 48.52; 50.38; 53.15; 65.54; 128.31; 130.21; 133.01; 136.55; 173.22. EI-MS: 423 (M^+). Anal. calc. for $C_{22}H_{30}ClNO_3S$ (424.0): C 62.32, H 7.13, N 3.30, S 7.56; found: C 62.43, H 6.91, N 3.09, S 7.58.

(+)-N-*[(2*R*)-2-(4-Chlorophenyl)hexanoyl]bornane-10,2-sultam* (=*(2*R*)-2-(4-Chlorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]hexan-1-one*; (2′*R*)-**2b**). White solid. M.p. 129–131°. Yield 7.97 g (94%). Spectroscopic data: identical to those of (2′*S*)-**2b**.

(+)-N-*[(2*S*)-2-(4-Chlorophenyl)-3-phenylpropanoyl]bornane-10,2-sultam* (=*(2*S*)-2-(4-Chlorophenyl)-1-[(3a*R*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]-3-phenylpropan-1-one*; (2′*S*)-**2c**). White solid. M.p. 205–206°. Yield 7.14 g (78%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.63 (*s*, Me); 0.87 (*s*, Me); 1.25–1.27 (*m*, 2 H); 1.73–1.82 (*m*, 4 H); 1.92–1.98 (*m*, 1 H); 3.04–3.08 (*m*, 1 H, PhCH_2); 3.29–3.41 (*m*, 3 H); 3.72–3.75 (*m*, 1 H); 4.60–4.64 (*m*, COCH); 7.14–7.48 (*m*, 9 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.74; 20.42; 26.30; 32.76; 38.23; 42.50; 44.53; 47.47; 48.03; 51.95; 52.97; 65.30; 126.67; 128.28; 128.38; 129.37; 130.20; 133.22; 136.08; 137.60; 171.97. EI-MS: 457 (M^+). Anal. calc. for $C_{25}H_{28}ClNO_3S$ (458.01): C 65.56, H 6.16, N 3.06, S 7.00; found: C 65.59, H 5.65, N 3.26, S 7.28.

(+)-N-*[(2*R*)-2-(4-Chlorophenyl)-3-phenylpropanoyl]bornane-10,2-sultam* (=*(2*R*)-2-(4-Chlorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]-3-phenylpropan-1-one*; (2′*R*)-**2c**). White solid. M.p. 205–206°. Yield 6.96 g (76%). Spectroscopic data: identical to those of (2′*S*)-**2c**.

(+)-N-*[(2*S*)-2-(4-Fluorophenyl)pentanoyl]bornane-10,2-sultam* (=*(2*S*)-2-(4-Fluorophenyl)-1-[(3a*R*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]pentan-1-one*; (2′*S*)-**2d**). White solid. M.p. 161–163°. Yield 7 g (89%). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.91 (*t*, *J* = 7.2,

3 H); 0.98 (*s*, Me); 1.21 (*s*, Me); 1.31–1.34 (*m*, 4 H); 1.76–1.79 (*m*, 1 H); 1.84–1.90 (*m*, 3 H,); 2.04–2.10 (*m*, 2 H); 2.13–2.14 (*m*, 1 H); 3.44 (*d*, *J* = 13.8, 1 H); 3.53 (*d*, *J* = 13.8, 1 H); 3.83–3.85 (*m*, 1 H); 4.28 (*t*, *J* = 7.2, COCH); 6.98–7.00 (*m*, 2 arom. H); 7.41–7.43 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.62; 19.74; 20.54; 20.78; 26.23; 32.70; 38.20; 38.43; 44.50; 47.57; 48.11; 49.93; 52.96; 65.36; 114.71; 114.92; 130.24; 130.32; 133.71; 161.87; 173.3. EI-MS: 393 (M^+). Anal. calc. for $C_{21}H_{28}FNO_3S$ (393.52): C 64.10, H 7.17, N 3.56, S 8.15; found: C 64.36, H 6.86, N 3.40, S 8.10.

(+)-N-*[(2*R*)-2-(4-Fluorophenyl)pentanoyl]bornane-10,2-sultam* (=*(2*R*)-2-(4-Fluorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]pentan-1-one*; (2′*R*)-**2d**). White solid. M.p. 161–163°. Yield 7.16 g (91%). Spectroscopic data: identical to those of (2′*S*)-**2d**.

(+)-N-*[(2*S*)-2-(4-Fluorophenyl)hexanoyl]bornane-10,2-sultam* (=*(2*S*)-2-(4-Fluorophenyl)-1-[(3a*R*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]hexan-1-one*; (2′*S*)-**2e**). White solid. M.p. 134–136°. Yield 7.09 g (87%). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.85 (*t*, *J* = 7.0, 3 H); 0.98 (*s*, Me); 1.21 (*s*, Me); 1.25–1.34 (*m*, 6 H); 1.78–1.82 (*m*, 1 H); 1.84–1.90 (*m*, 3 H,); 2.06–2.10 (*m*, 2 H); 2.14–2.17 (*m*, 1 H); 3.42 (*d*, *J* = 13.8, 1 H); 3.53 (*d*, *J* = 13.8, 1 H); 3.83–3.85 (*m*, 1 H); 4.24 (*t*, *J* = 7.0, COCH); 6.97–7.00 (*m*, 2 arom. H); 7.41–7.43 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.75; 19.80; 20.79; 22.22; 26.28; 29.50; 32.78; 35.88; 38.46; 44.56; 47.63; 48.17; 50.13; 53.05; 65.43; 114.99; 130.28; 130.36; 133.71; 161.87; 173.3. EI-MS: 407 (M^+). Anal. calc. for $C_{22}H_{30}FNO_3S$ (407.54): C 64.84, H 7.42, N 3.44, S 7.87; found: C 64.63, H 7.14, N 3.34, S 8.00.

(+)-N-*[(2*R*)-2-(4-Fluorophenyl)hexanoyl]bornane-10,2-sultam* (=*(2*R*)-2-(4-Fluorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]hexan-1-one*; (2′*R*)-**2e**). White solid. M.p. 134–136°. Yield 6.85g (84%). Spectroscopic data: identical to those of (2′*S*)-**2e**.

(+)-N-*[(2*S*)-2-(2,4-Dichlorophenyl) ethanoyl]bornane-10,2-sultam* (=*(2*S*)-2-(2,4-Dichlorophenyl)-1-[(3a*R*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]propan-1-one*; (2′*S*)-**2f**). White solid. M.p. 129–130°. Yield 7.66 g (92%). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.97 (*s*, Me); 1.17 (*s*, Me); 1.33–1.40 (*m*, 2 H); 1.56 (*d*, *J* = 6, 3 H); 1.88–2.06 (*m*, 3 H); 2.07 (*d*, *J* = 7.2, 2 H); 3.47 (*d*, *J* = 7.2, 2 H); 3.76 (*s*, 1 H); 4.85 (*d*, *J* = 6.6, COCH); 7.23 (*d*, *J* = 8.4, 1 arom. H); 7.39 (*s*, 1 arom. H); 7.43 (*d*, *J* = 8.4, 1 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.03; 19.73; 20.57; 25.85; 26.24; 29.17; 38.24; 44.42; 47.65; 48.34; 52.82; 65.26; 126.88; 129.13; 129.67; 133.25; 134.36; 135.73; 172.73. EI-MS: 415 (M^+). Anal. calc. for $C_{19}H_{23}Cl_2NO_3S$ (416.36): C 54.81, H 5.57, N 3.36, S 7.70; found: C 55.08, H 5.77, N 3.19, S 7.62.

(+)-N-*[(2*R*)-2-(2,4-Dichlorophenyl)ethanoyl]bornane-10,2-sultam* (=*(2*R*)-2-(2,4-Dichlorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]propan-1-one*; (2′*R*)-**2f**). White solid. M.p. 129–130°. Yield 7.58 g (91%). Spectroscopic data: identical to those of (2′*S*)-**2f**.

(+)-N-*[(2*S*)-2-(2,4-Dichlorophenyl)hexanoyl]bornane-10,2-sultam* (=*(2*S*)-2-(2,4-Dichlorophenyl)-1-[(3a*R*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]hexan-1-one*; (2′*S*)-**2g**). White solid. M.p. 149–152°. Yield 8.52 g (93%). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.86 (*t*, *J* = 7.2, 3 H); 0.98 (*s*, Me); 1.20 (*s*, Me); 1.24–1.36 (*m*, 6 H); 1.72 (br., 1 H); 1.89 (br., 3 H); 2.11 (br., 1 H); 2.12 (br., 2 H); 3.38 (*d*, *J* = 13.8, 1 H); 3.50 (*d*, *J* = 13.8, 1 H); 3.89 (br., 1 H); 4.79 (br., COCH); 7.20 (*d*, *J* = 8.4, 1 arom. H); 7.39 (*s*, 1 arom. H); 7.53 (*d*, *J* = 8.4, 1 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.77; 19.80; 20.74; 22.10; 26.31; 29.54; 32.75; 35.49; 38.47; 44.58; 46.40; 47.68; 48.29; 52.99; 65.39; 126.92; 129.27; 129.69; 133.06; 134.68; 134.89; 171.96. EI-MS: 458 ($[M+1]^+$). Anal. calc. for $C_{22}H_{29}Cl_2NO_3S$ (458.44): C 56.74, H 6.38, N 3.06, S 6.99; found: C 57.13, H 6.20, N 2.81, S 6.91.

(+)-N-*[(2*R*)-2-(2,4-Dichlorophenyl)hexanoyl]bornane-10,2-sultam* (=*(2*R*)-2-(2,4-Dichlorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]hexan-1-one*; (2′*R*)-**2g**). White solid. M.p. 149–152°. Yield 8.16 g (89%). Spectroscopic data: identical to those of (2′*S*)-**2g**.

(+)-N-*[(2*S*)-2-(2,4-Dichlorophenyl)pent-4-enoyl]bornane-10,2-sultam* (=*(2*S*)-2-(2,4-Dichlorophenyl)-1-[(3a*R*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]-pent-4-en-1-one*; (2′*S*)-**2h**). White solid. M.p. 172–174°. Yield 7.16 g (81%). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.97 (*s*, Me); 1.19 (*s*, Me); 1.35 (br., 2 H); 1.88 (br., 3 H); 2.10 (br., 2 H); 2.49–2.51 (*m*, 1 H); 2.74–2.76

(*m*, 1 H); 3.37 (*d*, *J* = 13.8, 1 H); 3.50 (*d*, *J* = 13.8, 1 H); 3.88 (br., 1 H); 4.92 (br., COCH); 5.03 (*d*, *J* = 10.2, 1 H); 5.13 (*d*, *J* = 16.8, 1 H); 5.80 (br., 1 H); 7.20 (*d*, *J* = 8.4, 1 arom. H); 7.39 (*s*, 1 arom. H); 7.55 (*d*, *J* = 8.4, 1 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.70; 20.69; 26.20; 32.60; 38.21; 39.07; 44.47; 45.83; 47.56; 48.21; 52.83; 62; 29; 117.74; 126.87; 129.24; 129.68; 133.15; 134.02; 134.48; 170.93. EI-MS: 441 (M^+). Anal. calc. for $C_{21}H_{25}Cl_2NO_3S$ (442.4): C 57.01, H 5.70, N 3.17, S 7.25; found: C 56.79, H 5.76, N 3.15, S 7.13.

*(+)-*N*-[(2*R*)-2-(2,4-Dichlorophenyl)pent-4-enoyl]bornane-10,2-sultam* (=*(2*R*)-2-(2,4-Dichlorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]-pent-4-en-1-one*; (2′*R*)-**2h**). White solid. M.p. 172–174°. Yield 7.43 g (84%). Spectroscopic data: identical to those of (2′*S*)-**2h**.

*(+)-*N*-[(2*S*)-2-(2,4-Dichlorophenyl)-3-Phenylpropanoyl]bornane-10,2-sultam* (=*(2*S*)-2-(2,4-Dichlorophenyl)-1-[(3a*R*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]-3-phenylpropan-1-one*; (2′*S*)-**2i**). White solid. M.p. 228–230°. Yield 7.98 g (81%). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.61 (*s*, Me); 0.86(*s*, Me); 1.26 (br., 2 H); 1.65–1.71 (*m*, 2 H); 1.81 (br., 2 H); 1.92–1.96 (*m*, 1 H); 3.06–3.08 (*m*, 1 H, PhCH_2); 3.16–3.25 (*m*, 1 H, PhCH_2); 3.26(*d*, *J* = 13.8, 1 H); 3.36 (*d*, *J* = 13.8, 1 H); 3.76 (br., 1 H); 5.18 (br., COCH); 7.18–7.29 (*m*, 6 arom. H); 7.41 (*s*, 1 arom. H); 7.65 (*d*, *J* = 8.4, 1 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.61; 20.20; 26.19; 32.57; 38.04; 41.29; 44.47; 47.36; 47.99; 48.26; 52.77; 65.00; 126.61; 127.03; 128.19; 129.12; 129.41; 133.27; 134.10; 134.39; 137.59; 170.61. EI-MS: 492 (M^+). Anal. calc. for $C_{25}H_{27}Cl_2NO_3S$ (492.46): C 60.97, H 5.53, N 2.84, S 6.51; found: C 60.55, H 5.61, N 2.81, S 6.78.

*(+)-*N*-[(2*R*)-2-(2,4-Dichlorophenyl)-3-Phenylpropanoyl]bornane-10,2-sultam* (=*(2*R*)-2-(2,4-Dichlorophenyl)-1-[(3a*S*)-tetrahydro-8,8-dimethyl-2,2-dioxido-3a,6-methano-2,1-benzothiazol-1(3*H*,4*H*)-yl]-3-phenylpropan-1-one*; (2′*R*)-**2i**). White solid. M.p. 228–230°. Yield 7.68 g (78%). Spectroscopic data: identical to those of (2′*S*)-**2i**.

4. *Synthesis of* **3**. A soln. of $NaBH_4$ (40 mmol; 4 equiv.) in H_2O (10 ml) was added dropwise to a cooled (ice-water) soln. of **2** (10 mmol) in THF (30 ml). The mixture was stirred at r.t., and the completion of the reaction was monitored by TLC. To the mixture was added 2M HCl at a rate to maintain the internal temp. at 20–25°. The mixture was extracted with AcOEt (2 × 50 ml). The combined org. layers were washed with brine (50 ml), concentrated, and purified by SiO_2 chromatography to afford the desired products **3**, using 10% AcOEt/petroleum ether (60–90°) as an eluent. The enatiomeric products were prepared according to the same procedure [25].

*(2*R*)-2-(4-Chlorophenyl)pentan-1-ol* ((*R*)-**3a**). Colorless oil. Yield 1.85 g (93%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.85 (*t*, *J* = 7.4, Me); 1.14–1.19 (*m*, CH_2); 1.44–1.48 (*m*, 1 H of CH_2); 1.59–1.64 (*m*, 1 H of CH_2); 2.35 (br., OH); 2.67 (br., CH); 3.54 (br., CH_2OH); 7.09 (*d*, *J* = 8.0, 2 arom. H); 7.25 (*d*, *J* = 8.0, 2 arom. H).

*(2*S*)-2-(4-Chlorophenyl)pentan-1-ol* ((*S*)-**3a**). Colorless oil. Yield 1.89 g (95%). Spectroscopic data: identical to those of (*R*)-**3a**.

*(2*R*)-2-(4-Chlorophenyl)hexan-1-ol* ((*R*)-**3b**). Colorless oil. Yield 1.91 g (90%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*t*, *J* = 7.2, Me); 1.13–1.21 (*m*, CH_2); 1.22–1.30 (*m*, CH_2, OH); 1.51–1.58 (*m*, 1 H of CH_2); 1.66–1.69 (*m*, 1 H of CH_2); 2.75 (br., CH); 3.69–3.76 (*m*, CH_2OH); 7.15 (*d*, *J* = 8.2, 2 arom. H); 7.30 (*d*, *J* = 8.2, 2 arom. H).

*(2*S*)-2-(4-Chlorophenyl)hexan-1-ol* ((*S*)-**3b**). Colorless oil. Yield 1.96 g (92%). Spectroscopic data: identical to those of (*R*)-**3b**.

*(2*R*)-2-(4-Chlorophenyl)-3-phenylpropan-1-ol* ((*R*)-**3c**). Colorless oil. Yield 2.05 g (83%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.28 (br., OH); 2.82–2.85 (*m*, 1 H of CH_2); 2.98–3.07 (*m*, 1 H of CH_2); 3.71–3.75 (*m*, CH_2OH); 7.03–7.26 (*m*, 9 arom. H).

*(2*S*)-2-(4-Chlorophenyl)-3-phenylpropan-1-ol* ((*S*)-**3c**). Colorless oil. Yield 2.12 g (86%). Spectroscopic data: identical to those of (*R*)-**3c**.

*(2*R*)-2-(4-Fluorophenyl)pentan-1-ol* ((*R*)-**3d**). Colorless oil. Yield 1.57 g (86%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 (*t*, *J* = 7.4, Me); 1.18–1.26 (*m*, OH, CH_2); 1.49–1.56 (*m*, 1 H of CH_2); 1.61–1.68 (*m*, 1 H of CH_2); 2.77–2.81 (*m*, CH); 3.66–3.74 (*m*, CH_2OH); 7.00–7.04 (*m*, 2 arom. H); 7.16–7.19 (*m*, 2 arom. H).

(2S)-2-(4-Fluorophenyl)pentan-1-ol ((*S*)-**3d**). Colorless oil. Yield 1.6 g (88%). Spectroscopic data: identical to those of (*R*)-**3d**.

(2R)-2-(4-Fluorophenyl)hexan-1-ol ((*R*)-**3e**). Colorless oil. Yield 1.63 g (83%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*t*, *J* = 7.2, Me); 1.10–1.20 (*m*, CH_2); 1.22–1.37 (*m*, CH_2); 1.39 (br., OH); 1.41–1.56 (*m*, 1 H of CH_2); 1.64–1.71 (*m*, 1 H of CH_2); 2.73–2.78 (*m*, CH); 3.64–3.76 (*m*, CH_2OH); 7.00–7.04 (*m*, 2 arom. H); 7.15–7.18 (*m*, 2 arom. H).

(2S)-2-(4-Fluorophenyl)hexan-1-ol ((*S*)-**3e**). Colorless oil. Yield 1.63 g (83%). Spectroscopic data: identical to those of (*R*)-**3e**.

(2R)-2-(2,4-Dichlorophenyl)propan-1-ol ((*R*)-**3f**). Colorless oil. Yield 1.74 g (85%). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.27 (*d*, *J* = 7.6, Me); 1.38 (*s*, OH); 3.47–3.51 (*m*, CH); 3.69–3.73 (*m*, 1 H of CH_2OH); 3.76–3.79 (*m*, 1 H of CH_2OH); 7.24 (*d*, *J* = 9.6, 2 arom. H); 7.40 (*s*, 1 arom. H).

(2S)-2-(2,4-Dichlorophenyl)propan-1-ol ((*S*)-**3f**). Colorless oil. Yield 1.66 g (81%). Spectroscopic data: identical to those of (*R*)-**3f**.

(2R)-2-(2,4-Dichlorophenyl)hexan-1-ol ((*R*)-**3g**). Colorless oil. Yield 2.3 g (93%). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.86 (*t*, *J* = 7.2, Me); 1.16 (br., OH); 1.21–1.31 (*m*, 2 CH_2); 1.56–1.59 (*m*, 1 H of CH_2); 1.76–1.77 (*m*, 1 H of CH_2); 3.40–3.42 (*m*, CH); 3.75–3.77 (*m*, CH_2OH); 7.20–7.25 (*m*, 2 arom. H); 7.40 (*s*, arom. H).

(2S)-2-(2,4-Dichlorophenyl)hexan-1-ol ((*S*)-**3g**). Colorless oil. Yield 2.32 g (94%). Spectroscopic data: identical to those of (*R*)-**3g**.

(2R)-2-(2,4-Dichlorophenyl)pent-4-en-1-ol ((*R*)-**3h**). Colorless oil. Yield 1.89 g (82%). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.36 (*s*, OH); 2.37–2.42 (*m*, 1 H of CH_2); 2.52–2.56 (*m*, 1 H of CH_2); 3.49–3.51 (*m*, CH); 3.79–3.81 (*m*, CH_2OH); 4.99–5.05 (*m*, CH_2); 5.68–5.74 (*m*, CH); 7.21–7.25 (*m*, 2 arom. H); 7.41 (*s*, 1 arom. H).

(2S)-2-(2,4-Dichlorophenyl)pent-4-en-1-ol ((*S*)-**3h**). Colorless oil. Yield 2.0 g (87%). Spectroscopic data: identical to those of (*R*)-**3h**.

(2R)-2-(2,4-Dichlorophenyl)-3-phenylpropan-1-ol ((*R*)-**3i**). Colorless oil. Yield 2.47 g (88%). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.31 (*s*, OH); 2.93–2.95 (*m*, 1 H of CH_2); 3.01–3.03 (*m*, 1 H of CH_2Ph); 3.71 (br., CH); 3.80 (br., CH_2); 7.14–7.38 (*m*, 8 arom. H).

(2S)-2-(2,4-Dichlorophenyl)-3-phenylpropan-1-ol ((*S*)-**3i**). Colorless oil. Yield 2.39 g (85%). Spectroscopic data: identical to those of (*R*)-**3i**.

5. *Synthesis of* **4**. A 100-ml round-bottom flask equipped with a stir bar was charged with 10 mmol of **3** and 30 ml (0.21 mol) of HBr. The mixture was refluxed and stirred for 10–12 h at 100–110°. After completion of the reaction, the mixture was extracted with $CHCl_3$ (40 × 3 ml). The combined org. phases were washed with H_2O, $NaHCO_3$ (aq. sat.), and brine (50 ml), dried (Na_2SO_4), and concentrated to yield a crude oil, which was purified by SiO_2 chromatography with petroleum ether (60–90°) to give pure **4** as a colorless oil. The enantiomeric products were prepared according to the same procedure.

(2R)-1-Bromo-2-(4-chlorophenyl)pentane ((*R*)-**4a**). Colorless oil. Yield 1.54 g (59%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.85 (*t*, *J* = 7.2, Me); 1.16–1.20 (*m*, MeCH_2); 1.55–1.59 (*m*, 1 H of CH_2); 1.79–1.85 (*m*, 1 H of CH_2); 2.90–2.94 (*m*, CH); 3.45–3.54 (*m*, CH_2Br); 7.10 (*d*, *J* = 8.4, 2 arom. H); 7.27 (*d*, *J* = 8.4, 2 arom. H).

(2S)-1-Bromo-2-(4-chlorophenyl)pentane ((*S*)-**4a**). Colorless oil. Yield 1.57 g (60%). Spectroscopic data: identical to those of (*R*)-**4a**.

(2R)-1-Bromo-2-(4-chlorophenyl)hexane ((*R*)-**4b**). Colorless oil. Yield 1.63 g (59%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*t*, *J* = 7.2, Me); 1.10–1.32 (*m*, 2 CH_2); 1.57–1.61 (*m*, 1 H of CH_2); 1.84–1.89 (*m*, 1 H of CH_2); 2.89–2.93 (*m*, CH); 3.47–3.57 (*m*, CH_2Br); 7.11 (*d*, *J* = 8.6, 2 arom. H); 7.30 (*d*, *J* = 8.6, 2 arom. H).

(2S)-1-Bromo-2-(4-chlorophenyl)hexane ((*S*)-**4b**). Colorless oil. Yield 1.52 g (55%). Spectroscopic data: identical to those of (*R*)-**4b**.

(2R)-1-Bromo-2-(4-chlorophenyl)-3-phenylpropane ((*R*)-**4c**). Colorless oil. Yield 1.52 g (49%). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.92–2.95 (*m*, 1 H, PhCH_2); 3.13–3.16 (*m*, 1 H, PhCH_2); 3.18–3.24 (*m*, CH_2Br); 3.53–3.60 (*m*, CH); 7.04–7.33 (*m*, 9 arom. H).

(2S)-1-Bromo-2-(4-chlorophenyl)-3-phenylpropane ((*S*)-**4c**). Colorless oil. Yield 1.61 g (52%). Spectroscopic data: identical to those of (*R*)-**4c**.

*(2*R*)-1-Bromo-2-(4-fluorophenyl)pentane* ((*R*)-**4d**). Colorless oil. Yield 1.44 g (59%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 (*t*, *J* = 7.2, Me); 1.16–1.22 (*m*, CH_2); 1.55–1.61 (*m*, 1 H of CH_2); 1.82–1.87 (*m*, 1 H of CH_2); 2.92–2.96 (*m*, CH); 3.48–3.57 (*m*, CH_2Br); 6.99–7.04 (*m*, 2 arom. H); 7.12–7.16 (*m*, 2 arom. H).

*(2*S*)-1-Bromo-2-(4-fluorophenyl)pentane* ((*S*)-**4d**). Colorless oil. Yield 1.42 g (58%). Spectroscopic data: identical to those of (*R*)-**4d**.

*(2*R*)-1-Bromo-2-(4-fluorophenyl)hexane* ((*R*)-**4e**). Colorless oil. Yield 1.37 g (53%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*t*, *J* = 7.2, Me); 1.11–1.33 (*m*, 2 CH_2); 1.56–1.61 (*m*, 1 H, CH_2); 1.85–1.91 (*m*, 1 H, CH_2); 2.90–2.94 (*m*, CH); 3.48–3.57 (*m*, CH_2Br); 7.00–7.04 (*m*, 2 arom. H); 7.12–7.16 (*m*, 2 arom. H).

*(2*S*)-1-Bromo-2-(4-fluorophenyl)hexane* ((*S*)-**4e**). Colorless oil. Yield 1.45 g (56%). Spectroscopic data: identical to those of (*R*)-**4e**.

*(2*R*)-1-Bromo-2-(2,4-dichlorophenyl)propane* ((*R*)-**4f**). Colorless oil. Yield 1.34 g (50%). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.40 (*d*, *J* = 7.2, Me); 3.48–3.50 (*m*, 1 H of CH_2); 3.60–3.61 (*m*, 1 H of CH_2); 3.64–3.68 (*m*, CH); 7.19–7.21 (*m*, 1 arom. H); 7.21–7.22 (*m*, 1 arom. H); 7.40 (*s*, 1 arom. H).

*(2*S*)-1-Bromo-2-(2,4-dichlorophenyl)propane* ((*S*)-**4f**). Colorless oil. Yield 1.31 g (49%). Spectroscopic data: identical to those of (*R*)-**4f**.

*(2*R*)-1-Bromo-2-(2,4-dichlorophenyl)hexane* ((*R*)-**4g**). Colorless oil. Yield 1.8 g (58%). ^{1}H-NMR (600 MHz, $CDCl_3$): 0.89 (*t*, *J* = 7.2, Me); 1.20–1.36 (*m*, 4 H); 1.65 (*d*, *J* = 9, 1 H); 1.84–1.86 (*m*, 1 H); 3.56–3.59 (*m*, CH_2Br, CH); 7.17 (*d*, *J* = 7.8, 1 arom. H); 7.25 (*d*, *J* = 9, 1 arom. H); 7.40 (*d*, *J* = 7.8, 1 arom. H).

*(2*S*)-1-Bromo-2-(2,4-dichlorophenyl)hexane* ((*S*)-**4g**). Colorless oil. Yield 1.86 g (60%). Spectroscopic data: identical to those of (*R*)-**4g**.

*(2*R*)-5-Bromo-4-(2,4-dichlorophenyl)pent-1-ene* ((*R*)-**4h**). Colorless oil. Yield 1.23 g (42%). ^{1}H-NMR (600 MHz, $CDCl_3$): 2.44–2.49 (*m*, 1 H, CH_2); 2.59–2.66 (*m*, 1 H, CH_2); 3.60–3.66 (*m*, CH_2Br, CH); 5.03–5.10 (*m*, CH_2=CH); 5.62–5.69 (*m*, CH_2=CH); 7.16 (*d*, *J* = 8.4, 1 arom. H); 7.25 (*d*, *J* = 8.4, 1 arom. H); 7.41 (*s*, 1 arom. H).

*(2*S*)-5-Bromo-4-(2,4-dichlorophenyl)pent-1-ene* ((*S*)-**4h**). Colorless oil. Yield 1.53 g (52%). Spectroscopic data: identical to those of (*R*)-**4h**.

*(2*R*)-1-Bromo-2-(2,4-dichlorophenyl)-3-phenylpropane* ((*R*)-**4i**). Colorless oil. Yield 1.93 g (56%). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.97–3.02 (*m*, 1 H, PhCH_2); 3.09–3.14 (*m*, 1 H, PhCH_2); 3.53–3.63 (*m*, CH_2Br); 3.84–3.87 (*m*, CH); 7.13–7.38 (*m*, 8 arom. H).

*(2*S*)-1-Bromo-2-(2,4-dichlorophenyl)-3-phenylpropane* ((*S*)-**4i**). Colorless oil. Yield 1.86 g (54%). Spectroscopic data: identical to those of (*R*)-**4i**.

6. *Synthesis of* **5**. A mixture of **4** (5 mmol), K_2CO_3 (25 mmol), and 1*H*-1,2,4 triazole (6 mmol) in MeCN (25 ml) was stirred at 60–70° for 5–7 h. After completion of the reaction, the mixture was cooled to r.t. and filtered. The filtrate was washed with H_2O (5 ml), dried (Na_2SO_4), and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by SiO_2 chromatography to give compounds **5**, with Et_2O as an eluent. The enantiomeric products were prepared according to the same procedure [26].

*1-[(2*R*)-2-(4-Chlorophenyl)pentyl]-1*H*-1,2,4-triazole* ((*R*)-**5a**). Colorless oil. Yield 0.91 g (73%). $[\alpha]_D^{25} = +83.7$ (*c* = 1.0, CH_2Cl_2). 99% ee (HPLC: t_R 16.91 (minor); 11.28 (major)). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.85 (*t*, *J* = 7.2, Me); 1.17–1.23 (*m*, CH_2Me); 1.61–1.67 (*m*, CH_2CH$_2$Me); 3.19–3.23 (*m*, CH); 4.15–4.21 (*m*, 1 H, CH_2); 4.34–4.39 (*m*, 1 H, CH_2); 6.93–7.03(*m*, 4 arom. H); 7.61 (*s*, 1 triazole H); 7.89 (*s*, 1 triazole H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.56; 19.94; 34.51; 45.20; 55.24; 128.51; 128.63; 132.51; 139.23; 143.00; 151.55. EI-MS: 250 ($[M+1]^+$). Anal. calc. for $C_{13}H_{16}ClN_3$ (249.74): C 62.52, H 6.46, N 16.83; found: C 62.33, H 6.58, N 16.38.

*1-[(2*S*)-2-(4-Chlorophenyl)pentyl]-1*H*-1,2,4-triazole* ((*S*)-**5a**). Colorless oil. Yield 0.89 g (71%). $[\alpha]_D^{25} = -82.8$ (*c* = 1.0, CH_2Cl_2). 94% ee (HPLC: t_R 11.96 (minor); 15.23 (major)). Spectroscopic data: identical to those of (*R*)-**5a**.

*1-[(2*R*)-2-(4-Chlorophenyl)hexyl]-1*H*-1,2,4-triazole* ((*R*)-**5b**). Colorless oil. Yield 0.99 g (75%). $[\alpha]_D^{25} = +67.5$ (*c* = 1.0, CH_2Cl_2). 87% ee (HPLC: t_R 13.71 (minor); 10.31 (major)). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.82(*t*, *J* = 7.2, Me); 1.13–1.31 (*m*, 2 CH_2); 1.63–1.69 (*m*, CH_2CH$_2$Me); 3.19 (*t*, *J* = 6.8, CH);

4.15–4.21 (*m*, 1 H, CH_2); 4.35–4.40 (*m*, 1 H, CH_2); 6.93–7.03 (*m*, 4 arom. H); 7.70 (*s*, 1 triazole H); 7.89 (*s*, 1 triazole H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.58; 22.18; 28.97; 33.24; 45.34; 55.51; 115.26; 115.47; 128.61; 128.68; 136.49; 143.01; 151.51; 161.45. EI-MS: 264 ($[M+1]^+$). Anal. calc. for $C_{13}H_{16}ClN_3$ (263.77): C 62.52, H 6.46, N 16.83; found: C 62.33, H 6.58, N 16.38.

*1-[(2*S*)-2-(4-Chlorophenyl)hexyl]-1*H*-1,2,4-triazole* ((*S*)-**5b**). Colorless oil. Yield 0.96 g (73%). $[\alpha]_D^{25} = -69.7$ ($c = 1.0$, CH_2Cl_2). 95% ee (HPLC: t_R 11.46 (minor); 13.96 (major)). Spectroscopic data: identical to those of (*R*)-**5b**.

*1-[(2*R*)-2-(4-Chlorophenyl)-3-phenylpropyl]-1*H*-1,2,4-triazole* ((*R*)-**5c**). Colorless oil. Yield 0.89 g (60%). $[\alpha]_D^{25} = +19.7$ ($c = 1.0$, CH_2Cl_2). 98% ee (HPLC: t_R 33.60 (minor); 21.45 (major)). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.97–3.00 (*m*, PhCH_2); 3.53 (*d*, $J = 7.2$, CH); 4.23–4.29 (*m*, 1 H, CH_2); 4.40–4.45 (*m*, 1 H, CH_2); 7.07 (*d*, $J = 8.4$, 2 arom. H); 7.16–7.26 (*m*, 5 arom. H); 7.60 (*s*, 1 triazole H); 7.90 (*s*, 1 triazole H). ^{13}C-NMR (100 MHz, $CDCl_3$): 39.41; 47.33; 54.36; 126.55; 127.47; 128.49; 128.81; 128.91; 128.94; 130.33; 133.06; 138.16; 138.80; 143.37; 151.97. EI-MS: 297 (M^+). Anal. calc. for $C_{17}H_{16}ClN_3$ (297.78): C 68.57, H 5.42, N 14.11; found: C 68.19, H 5.47, N 14.02.

*1-[(2*S*)-2-(4-Chlorophenyl)-3-phenylpropyl]-1*H*-1,2,4-triazole* ((*S*)-**5c**). Colorless oil. Yield 0.86 g (58%). $[\alpha]_D^{25} = -23.1$ ($c = 1.0$, CH_2Cl_2). 99% ee (HPLC: t_R 21.10 (minor); 34.03 (major)). Spectroscopic data: identical to those of (*R*)-**5c**.

*1-[(2*R*)-2-(4-Fluorophenyl)pentyl]-1*H*-1,2,4-triazole* ((*R*)-**5d**). Colorless oil. Yield 0.68 g (58%). $[\alpha]_D^{25} = +70.2$ ($c = 1.0$, CH_2Cl_2). 90% ee (HPLC: t_R 18.91 (minor); 17.29 (major)). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.86 (*t*, $J = 7.2$, Me); 1.17–1.24 (*m*, CH_2Me); 1.61–1.67 (*m*, CH_2CH$_2$Me); 3.19–3.23 (*m*, CH); 4.15–4.21 (*m*, 1 H, CH_2); 4.34–4.39 (*m*, 1 H, CH_2); 6.93–7.03 (*m*, 4 arom. H); 7.61 (*s*, 1 triazole H); 7.89 (*s*, 1 triazole H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.57; 19.97; 34.67; 45.08; 55.48; 115.26; 115.47; 128.26; 128.70; 136.43; 140.01; 151.54; 161.49. EI-MS: 234 ($[M+1]^+$). Anal. calc. for $C_{13}H_{16}FN_3$ (233.28): C 66.93, H 6.91, N 18.01; found: C 66.72, H 7.21, N 18.35.

*1-[(2*S*)-2-(4-Fluorophenyl)pentyl]-1*H*-1,2,4-triazole* ((*S*)-**5d**). Colorless oil. Yield 0.7 g (60%). $[\alpha]_D^{25} = -70.7$ ($c = 1.0$, CH_2Cl_2). 89% ee (HPLC: t_R 17.29 (minor); 18.99 (major)). Spectroscopic data: identical to those of (*R*)-**5d**.

*1-[(2*R*)-2-(4-Fluorophenyl)hexyl]-1*H*-1,2,4-triazole* ((*R*)-**5e**). Colorless oil. Yield 0.7 g (57%). $[\alpha]_D^{25} = +59.9$ ($c = 1.0$, CH_2Cl_2). 98% ee (HPLC: t_R 35.36 (minor); 41.33 (major)). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.81 (*d*, $J = 6.8$, Me); 1.17–1.26 (*m*, 2 CH_2); 1.66 (*d*, $J = 6.4$, CH_2CH$_2$Me); 3.19 (*s*, CH); 4.19 (*t*, $J = 8.8$, 1 H, CH_2); 4.35–4.40 (*m*, 1 H, CH_2); 6.93–7.01 (*m*, 4 arom. H); 7.63 (*s*, 1 triazole H); 7.89 (*s*, 1 triazole H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.57; 19.97; 34.67; 45.08; 54.48; 115.26; 115.47; 128.62; 128.70; 136.43; 143.01; 151.54; 161.49. EI-MS: 248 ($[M+1]^+$). Anal. calc. for $C_{13}H_{16}FN_3$ (247.31): C 67.99, H 7.34, N 16.99; found: C 67.64, H 7.58, N 17.24.

*1-[(2*S*)-2-(4-Fluorophenyl)hexyl]-1*H*-1,2,4-triazole* ((*S*)-**5e**). Colorless oil. Yield 0.73 g (59%). $[\alpha]_D^{25} = -68.8$ ($c = 1.0$, CH_2Cl_2). >99% ee (HPLC: t_R 42.17(major)). Spectroscopic data: identical to those of (*R*)-**5e**.

*1-[(2*R*)-2-(2,4-Dichlorophenyl)propyl]-1*H*-1,2,4-triazole* ((*R*)-**5f**). Colorless oil. Yield 0.69 g (54%). $[\alpha]_D^{25} = +13.5$ ($c = 1.0$, CH_2Cl_2). 99% ee (HPLC: t_R 18.46 (minor); 16.14 (major)). ^{1}H-NMR (600 MHz, $CDCl_3$): 1.31 (*d*, $J = 7.2$, Me); 3.87–3.88 (*m*, CH); 4.25–4.29 (*m*, CH_2); 4.37–4.40 (*m*, 1 H, CH_2); 7.10 (*d*, $J = 7.8$, 1 arom. H); 7.23 (*d*, $J = 7.8$, 1 arom. H); 7.39 (*s*, 1 arom. H); 7.81 (*s*, 1 triazole H); 7.92 (*s*, 1 triazole H). ^{13}C-NMR (100 MHz, $CDCl_3$): 17.41; 36.17; 54.50; 127.57; 128.34; 129.71; 133.41; 134.50; 137.92; 143.17; 151.88. EI-MS: 256 (M^+). Anal. calc. for $C_{11}H_{11}Cl_2N_3$ (256.13): C 51.58, H 4.33, N 16.41; found: C 51.3, H 4.19, N 15.71.

*1-[(2*S*)-2-(2,4-Dichlorophenyl)propyl]-1*H*-1,2,4-triazole* ((*S*)-**5f**). Colorless oil. Yield 0.72 g (56%). $[\alpha]_D^{25} = -13.2$ ($c = 1.0$, CH_2Cl_2). 97% ee (HPLC: t_R 18.86 (minor); 15.19 (major)). Spectroscopic data: identical to those of (*R*)-**5f**.

*1-[(2*R*)-2-(2,4-Dichlorophenyl)hexyl]-1*H*-1,2,4-triazole* ((*R*)-**5g**). Colorless oil. Yield 0.97 g (65%). $[\alpha]_D^{25} = +20.7$ ($c = 1.0$, CH_2Cl_2). 98% ee (HPLC: t_R 39.31 (minor); 35.83 (major)). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.83 (*t*, $J = 7.2$, Me); 1.14–1.32 (*m*, 2 CH_2); 1.68–1.74 (*m*, CH_2); 3.77 (*t*, $J = 7.2$, CH); 4.33–4.39 (*m*, CH_2); 7.05 (*d*, $J = 8.0$, 1 arom. H); 7.21–7.23 (*m*, 1 arom. H); 7.36 (*d*, $J = 2.0$, 1 arom. H); 7.71 (*s*, 1 triazole H); 7.89 (*s*, 1 triazole H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.72; 22.36; 28.87; 31.55; 41.64; 53.78;

127.46; 128.71; 129.63; 133.16; 135.13; 136.73; 143.03; 151.67. EI-MS: 298 ($[M+1]^+$). Anal. calc. for $C_{14}H_{17}Cl_2N_3$ (298.21): C 56.39, H 5.75, N 14.09; found: C 56.76, H 5.36, N 14.24.

*1-[(2*S*)-2-(2,4-Dichlorophenyl)hexyl]-1*H*-1,2,4-triazole* ((*S*)-**5g**). Colorless oil. Yield 1.03 g (69%). $[\alpha]_D^{25} = -26.9$ ($c = 1.0$, CH_2Cl_2). >99% ee (HPLC: t_R 39.60 (major)). Spectroscopic data: identical to those of (*R*)-**5g**.

*1-[(2*R*)-2-(2,4-Dichlorophenyl)pent-4-enyl]-1*H*-1,2,4-triazole* ((*R*)-**5h**). Colorless oil. Yield 0.83 g (59%). $[\alpha]_D^{25} = +27.4$ ($c = 1.0$, CH_2Cl_2). 88% ee (HPLC: t_R 15.91 (minor); 9.85 (major)). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.46–2.53 (*m*, CH_2); 3.87 (*t*, J =7.2, CH); 4.35–4.46 (*m*, CH_2); 5.03–5.09 (*m*, CH=CH_2); 5.62–5.69 (*m*, C*H*=CH_2); 7.02 (*d*, $J = 8.4$, 1 arom. H); 7.19–7.22 (*m*, 1 arom. H); 7.37 (*d*, $J = 2$, 1 arom. H); 7.74 (*s*, 1 triazole H); 7.90 (*s*, 1 triazole H). ^{13}C-NMR (100 MHz, $CDCl_3$): 35.91; 41.17; 52.57; 118.05; 127.39; 128.92; 133.40; 134.02; 134.85; 136.08; 143.19; 151.73. EI-MS: 282 ($[M+1]^+$). Anal. calc. for $C_{13}H_{13}Cl_2N_3$ (282.17): C 55.34, H 4.64, N 14.89; found: C 55.07, H 5.12, N 15.29.

*1-[(2*S*)-2-(2,4-Dichlorophenyl)pent-4-enyl]-1*H*-1,2,4-triazole* ((*S*)-**5h**). Colorless oil. Yield 0.87 g (62%). $[\alpha]_D^{25} = -28.4$ ($c = 1.0$, CH_2Cl_2). 90% ee (HPLC: t_R 9.04 (minor); 16.33 (major)). Spectroscopic data: identical to those of (*R*)-**5h**.

*1-[(2*R*)-2-(2,4-Dichlorophenyl)-3-phenylpropyl]-1*H*-1,2,4-triazole* ((*R*)-**5i**). Colorless oil. Yield 0.85g (51%). $[\alpha]_D^{25} = +8.3$ ($c = 1.0$, CH_2Cl_2). 93% ee (HPLC: t_R 22.18 (minor); 17.77 (major)). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.01–3.08 (*m*, PhCH_2); 4.11 (*t*, $J = 6.8$, CH); 4.40–4.41 (*m*, CH_2); 6.98 (*d*, $J = 8.4$, 2 arom. H); 7.12–7.32 (*m*, 7 arom. H); 7.66 (*s*, 1 triazole H); 7.88 (*s*, 1 triazole H). ^{13}C-NMR (100 MHz, $CDCl_3$): 18.10; 37.94; 43.12; 52.03; 126.56; 127.30; 128.43; 129.64; 133.37; 134.71; 135.99; 137.71; 143.20; 151.68. EI-MS: 332 ($[M+1]^+$). Anal. calc. for $C_{17}H_{15}Cl_2N_3$ (332.23): C 61.46, H 4.55, N 12.65; found: C 61.18, H 4.98, N 112.29.

*1-[(2*S*)-2-(2,4-Dichlorophenyl)-3-phenylpropyl]-1*H*-1,2,4-triazole* ((*S*)-**5i**). Colorless oil. Yield 0.96 g (58%). $[\alpha]_D^{25} = -11.3$ ($c = 1.0$, CH_2Cl_2). 99% ee (HPLC: t_R 17.75 (minor); 22.12 (major)). Spectroscopic data: identical to those of (*R*)-**5i**.

7. *Antifungal-Activity Determination*. The *in vitro* fungicidal activities against *Fusarium oxysporium*, *Rhizoctonia solani*, *Botrytis cinereapers*, *Gibberella zeae*, *Dothiorella gregaria*, and *Colletotrichum gossypii* were tested according to the method reported in [27]. The medium was amended with aliquots of each tested compound soln. to provide concentration of 50 and 12.5 mg/l. The tested compounds were dissolved in 0.3 ml of DMF and added aseptically to molten agar after autoclaving, when the agar had cooled to *ca.* 45–50°.The concentration of solvent never exceeded 0.1 mg/l. The mixed medium without sample was used as the blank control. The inocula, 5 mm in diameter, were removed from the margins of actively growing colonies of mycelium, placed in the centers of the above plates. Three replicates were conducted for each concentration, and the control plates were sealed with parafilm and incubated at 26° in darkness. The diameter of the mycelium was measured for 48 h. The inhibition percent was used to describe the efficiency of the compounds: inhibition percent [%] = (hyphal diameter in the control − hyphal diameter in the treatment)/hyphal diameter in the control.

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