DIASTEREO- AND ENANTIOSELECTIVE SYNTHESIS OF Δ^2-1,2,4-OXADIAZOLINES BY 1,3-DIPOLAR CYCLOADDITION OF NITRILE OXIDES WITH CHIRAL HYDRAZONES

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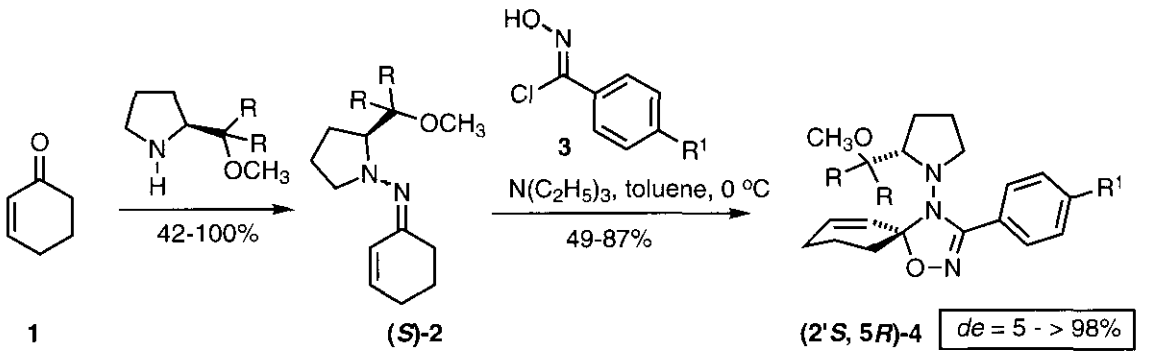
Abstract - Diastereo- and enantioselective 1,3-dipolar cycloadditions of nitrile oxides (**3**) with α,β-unsaturated hydrazones (**2**) gave spiro oxadiazolines (**4**) in good yields and low to excellent diastereomeric excesses (*de* = 5 - ≥98%). Open chain hydrazones (**6**) afforded 5,5-disubstituted Δ^2-1,2,4-oxadiazolines (**7**). A subsequent N-N bond cleavage to remove the chiral auxiliary was achieved with formic acid and gave the oxadiazolines (**8**) (*ee* = 0 - 91%).

Intermolecular 1,3-dipolar cycloaddition reactions of chiral nitrile oxides usually proceed with moderate control of stereoselectivity.[1] Possible causes for moderate ratios of diastereomers (usually < 75:25) are the linear dipole, the lack of orientation by complexation and the relatively long distance between the auxiliary and center of reaction.[2] However, intramolecular stereoselective 1,3-dipolar cycloadditions *via* nitrile oxides have been successfully carried out, for instance by Takahashi and Iwamoto, generating two key building blocks for the synthesis of taxol derivatives.[3] Further examples of intramolecular diastereo- and enantioselective nitrile oxide cycloadditions leading to functionalized *cis*-decalins [4] or the stereoselective total synthesis of (+)-pumiliotoxin C by Fukumoto *et al.*[5] have recently been reported. Chiral dipolarophiles have also been used for diastereo- and enantioselective 1,3-dipolar cycloadditions with nitrile oxides.[6] For example, Carretero *et al.* successfully utilized *α,β*-unsaturated sulfones as enantiopure dipolarophiles and opened an efficient entry to functionalized isoxazolines.[7] Some of the observed diastereoselectivities can be explained with the "inside alkoxy-model" by Houk *et al.*[8] Isoxazolines may also be prepared by a catalytic 1,3-dipolar cycloaddition of nitrile oxides as was reported by Ukaji *et al.*[9] Using equimolar amounts of (*R,R*)-diisopropyl tartrate in the presence of diethylzinc as catalyst furnished the heterocycles in good yields and *ee*-values of 84 - 93%.

We wish now to report our results on diastereo- and enantioselective 1,3-dipolar cycloaddition reactions of nitrile oxides utilizing proline derived hydrazones as enantiopure dipolarophiles.

The cyclohexenone hydrazones ((*S*)-**2**) were readily prepared by condensation of a variety of hydrazines (SAMP, SADP, SAEP and SAPP)[10] with cyclohexenone (**1**) in 42-100% yield, following our standard protocol.[11] The hydrazones were isolated as mixtures of *E*/*Z*-isomers which were separated by column chromatography. Although several methods for the generation of nitrile oxides are known,[12] the method starting from hydroxamoyl chlorides (**3**), readily available from the corresponding oximes and *N*-chlorosuccinimide (NCS), turned out to be the preferable method.[13] Thus, a variety of aromatic hydroxamoyl chlorides (**3**) were prepared *in situ* by reacting the corresponding oximes with NCS. Triethylamine was added at 0° C and the nitrile oxides were trapped with the SAMP-hydrazones ((*S*)-**2**) present in the reaction mixture. The 1,3-dipolar cycloadditions took place instantaneously and the spiro oxadiazolines (**4**) were isolated after column chromatography in moderate to good yields (Scheme 1, Table 1). The diastereomeric excesses were determined by analytical HPLC of the crude reaction mixtures. The cycloadditions took place under complete control of regio- and chemoselectivity. No addition to the C=C double bond or the formation of furazanes was observed. (*E*)- as well as (*Z*)-isomers were employed in the reaction sequence. Interestingly, a correlation between diastereoselectivity and the configuration of the starting hydrazone is evident. In general, stereoselectivity was remarkably higher, when the (*E*)-isomer was used (*de* = 32-58%). The (*Z*)-isomers gave lower diastereoselectivities (*de* = 5-20%) (Table 1) with the major isomer in both cases having the (2'*S*,5*R*)-configuration (Figure 1).



Scheme 1. Diastereoselective 1,3-Dipolar Cycloadditions of Nitrile Oxides with Hydrazones

In order to increase the diastereofacial selectivity during the cycloadditions, the sterically more demanding SADP, SAEP and SAPP hydrazones were employed as dipolarophiles. It turned out that the protocol had to be modified to obtain good yields. Hence the hydrazones (**2**) and triethylamine were dissolved in $CHCl_3$ at 0 °C. Then the hydroxamoyl chlorides (**3**), isolated from the reaction of the corresponding oxime and NCS,[14] were slowly added over a period of 6-8 h utilizing a syringe pump. The nitrile oxides were generated and the cycloaddition to the α,β-unsaturated six-membered hydrazones took

place, giving rise to the corresponding spiro oxadiazolines (**4**) in good to excellent yields. Again the (*E*)- and (*Z*)-isomers of the hydrazones showed a different selectivity. The heterocycles derived from the (*E*)-isomer were isolated with diastereomeric excesses of 28-86% with the (2'*S*,5*R*) diastereomer being the major one. Interestingly, the corresponding diastereomer (2'*S*,5*S*) was favored (*de* = 90 - ≥98%), when the (*Z*)-hydrazone was used. Consequently, both diastereomers are directly available by utilizing the (*E*)- or (*Z*)-isomer as dipolarophile, respectively. In addition, all mixtures of diastereomers could be separated by HPLC.

Table 1. Spiro oxadiazolines (**4**) derived from cyclohexenone hydrazones (**2**)

4		R	R[1]	*de*[a] [%]	yield [%]	(2'*S*,5*R*)[b] [α]	(2'*S*,5*S*)[c] [α]
a	*Z*	H	H	20	79	–136.0	–321.8
a	*E*	H	H	58	67	–136.0	–321.8
b	*Z*	H	F	14	49	–108.2	–303.8
b	*E*	H	F	59	54	–108.2	–303.8
c	*Z*	H	OCH_3	5	69	–130.5	–325.5
c	*E*	H	OCH_3	32	69	–130.5	–325.5
d	*E*	CH_3	H	81	87	–257.0	-
d	*Z*	CH_3	H	≥98	87	-	–321.5
e	*E*	CH_2CH_3	H	86	91	–226.6	-
e	*Z*	CH_2CH_3	H	≥98	70	-	–314.2
f	*E*	C_6H_5	H	28	88	-	-
f	*Z*	C_6H_5	H	90	73	-	–184.4

[a] Determined by analytical HPLC of the crude product. - [b] Major isomer. - [c] Minor isomer.

The assignment of the configurations is based on extensive ^{1}H NMR spectroscopic investigations (e.g. NOE) on the minor isomer of **4b**. Due to the rotation barrier of the pyrrolidine system along the N-N bond, the signals in the NMR spectra appear broadened and therefore the experiments were carried out at 80 °C.

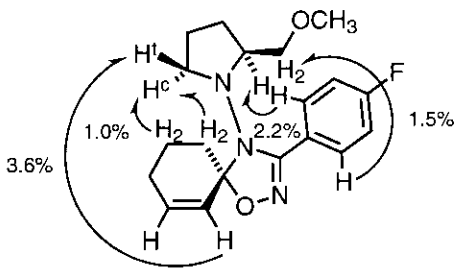


Figure 1. Determination of absolute and relative configuration by NOE-experiments of (2′*S*,5*S*)-**4b**

A signal enhancement of 3.6% of H^t upon irradiation of the =CH proton and a NOE effect (1.0%) between H^c and the methylene protons of the ring were observed. Similar effects were acquired between the NC***H*** proton (2.2%) and the CH_2OCH_3 moiety (1.5%) upon saturation of the *ortho* proton of the aromatic ring. These effects can only be explained by the configuration depicted in Figure 1. Thus, the absolute configuration of the newly generated stereogenic center of the minor isomer of **4b** was assigned as (*S*). The relative configurations of the SAEP, SADP and SAPP hydrazone adducts were deduced from the NMR data and the NOE experiments on **4b** assuming a uniform reaction mechanism.

The stereochemical outcome of the cycloaddition reactions may be explained by the following transition state models.

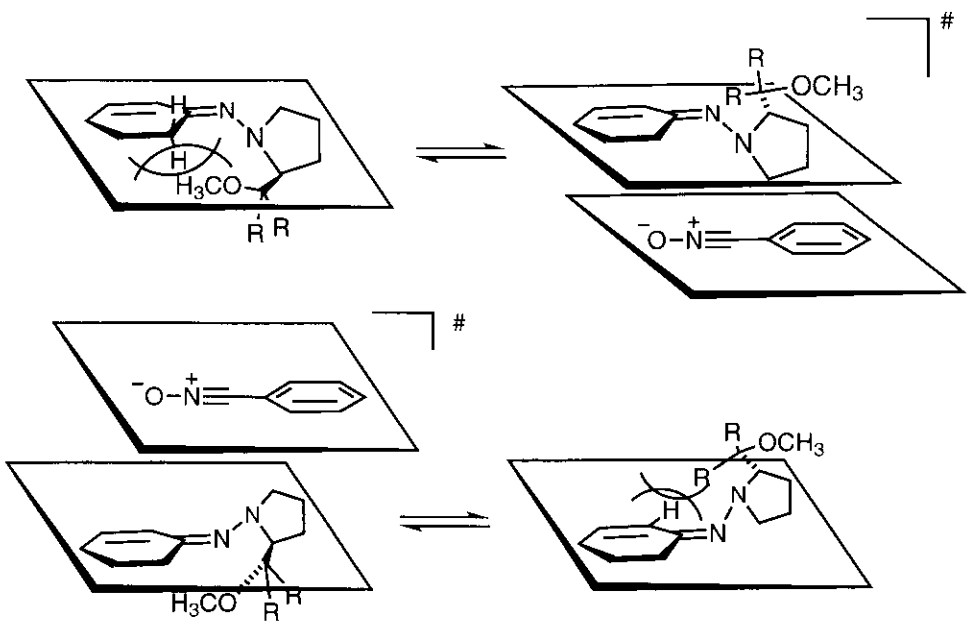
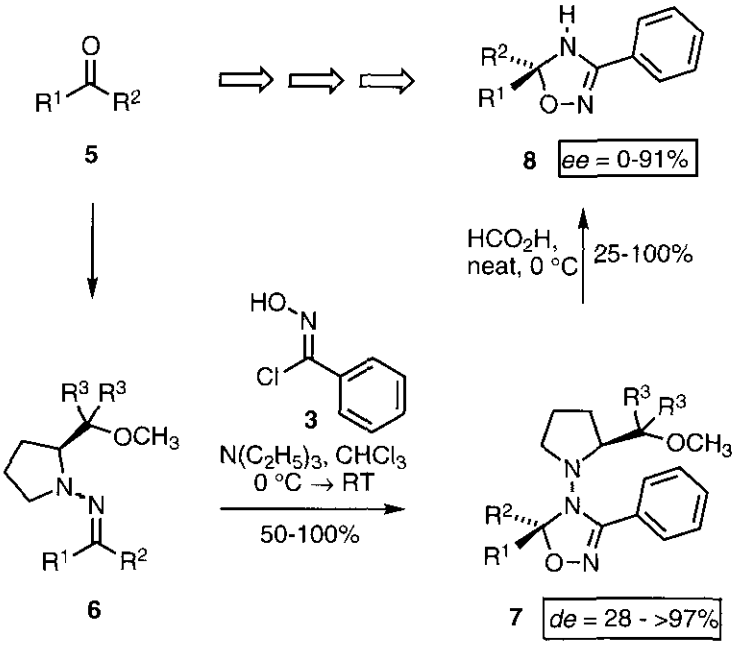


Figure 2. Transition state models for 1,3-dipolar cycloaddition reactions of nitrile oxides with cyclohexenone hydrazones

The pyrrolidine ring is orientated perpendicular to a plane defined by the C=C-C=N system. Due to the steric repulsions between the side chain of the auxiliary (CR_2OCH_3) and the α-methylene group of the cyclohexene moiety, the hydrazone (*E*)-isomer prefers the conformation shown on the right side of Figure 2 (top), whereas the (*Z*)-isomer is forced to the conformation depicted on the left side (bottom, Figure 2). Thus, attack to the (*Z*)-isomer will take place from the *si* face and to the *re* face of the (*E*)-isomer, giving rise to the major diastereomers observed. The occupations of the preferred conformations are sensitive to the substituent R. Thus, in the case of the SAMP hydrazone differences in steric demand are assumed to be smaller than in the SAEP-, SADP- and SAPP-hydrazones, explaining the modest diastereofacial discrimination in this case.

The same reaction sequence was applied to hydrazones of unsymmetrically substituted ketones. They were prepared by condensation of a variety of ketones (**5**) with different hydrazines in 24-86% yield. In this series, separation of the (*E*/*Z*)-isomers was not possible. Therefore, generation of the nitrile oxide was carried out by addition of the hydroxamoyl chloride (**3**) to a solution of a (*E*/*Z*)-mixture of the phenylhydrazones (**6**) and triethylamine in $CHCl_3$ over a period of 6-8 h. After work up and purification the 3,4,5,5-tetrasubstituted Δ^2-1,2,4-oxadiazolines (**7**) were isolated in moderate to quantitative yields (*Scheme 2*).



Scheme 2. 1,3-Dipolar cycloaddition of benzonitrile oxide with acyclic unsymmetric ketone hydrazones

The diastereomeric excesses of **7** were determined by NMR spectroscopy or analytical HPLC to 28 - ≥97% *de* (Table 2). The employment of SAMP hydrazones gave cycloadducts with 28 -57% *de*. Far better diastereofacial selectivity was observed when SADP or SAEP hydrazones were utilized as dipolarophiles (59 - ≥ 96% *de* and 77 - ≥97% *de*, respectively). The corresponding SAPP hydrazones gave moderate *de*-values of 55 - 66%. A second tendency was deduced from the experimental data. In general, better diastereomeric excesses were observed when the distinction in steric demand of R^1 and R^2 was large.

Table 2. Synthesized 5,5-disubstituted Δ^2-1,2,4-oxadiazolines (**7**)

7	R^1	R^2	R^3	*de*[a] [%]	yield [%]	(2'*S*,5*S*)[b] [α]	(2'*S*,5*R*)[c] [α]
a	$(CH_2)_3CH_3$	CH_3	H	28	92	–320.4	–92.7
b	$(CH_2)_2C_6H_5$	CH_3	H	37	86	–322.6	–54.1
c	C_6H_5	CH_2CH_3	H	57	86	–333.8	–112.4
d	$(CH_2)_2CH_3$	CH_3	CH_3	63	96	–276.7	-
e	$(CH_2)_3CH_3$	CH_3	CH_3	59	71	–217.9	–214.2
f	$(CH_2)_2C_6H_5$	CH_3	CH_3	70	74	–175.6	–173.9
g	C_6H_5	CH_2CH_3	CH_3	≥96[d]	53	–345.8	-
h	$(CH_2)_2CH_3$	CH_3	CH_2CH_3	77[d]	81	–288.7	-
i	$(CH_2)_3CH_3$	CH_3	CH_2CH_3	77[d]	100	–257.0	–187.1
j	$(CH_2)_2C_6H_5$	CH_3	CH_2CH_3	82	73	–257.2	-
k	C_6H_5	CH_2CH_3	CH_2CH_3	≥97[e]	50	–266.2	-
l	$(CH_2)_2CH_3$	CH_3	C_6H_5	55	74	–216.9	–167.4
m	$(CH_2)_3CH_3$	CH_3	C_6H_5	57	60	–186.9	–133.9
n	$(CH_2)_2C_6H_5$	CH_3	C_6H_5	66	52	–227.3	-

[a] Determined by analytical HPLC. All diastereomers were separated by HPLC. - [b] Major isomer. - [c] Minor isomer. - [d] Determined by ^{13}C NMR spectroscopy. - [e] Determined by ^1H NMR spectroscopy.

The absolute configuration of the newly created stereogenic center was determined by extensive NOE experiments and an X-Ray structure analysis on **7k** (Figure 3).[15, 27]

The stereochemical outcome of the cycloaddition reactions leading to **7** can be explained by a similar transition state model as is depicted in Figure **2**. Finally, the N-N bond was cleaved and the auxiliary removed in this way. Reagents like $LiAlH_4$ are known to cleave the N-O bond of isoxazolines to give 1,3-amino alcohols,[16] and β-hydroxy ketones are formed by catalytic hydrogenolysis.[17] Thus, a new chemoselective N,N-bond cleavage method had to be developed.

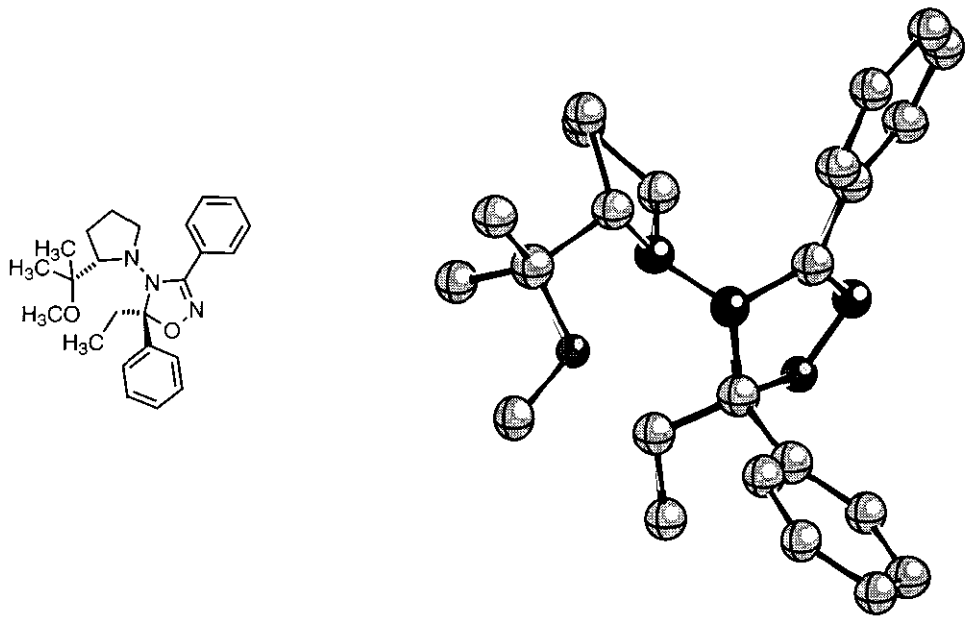


Figure 3. Structure of (*S*, *S*)-**7g** in the crystal

When reacting the oxadiazolines (**7**) at 0 °C with formic acid, an immediate reaction occurred and the N-N bond was chemoselectively cleaved. After purification by column chromatography, the N-unsubstituted oxadiazolines (**8**) were isolated in moderate to excellent yields (Table 3).

From the experimental data it is evident that the cleavage of the N-N bond proceeded with partial racemization. The degree of racemization was higher when longer reaction times were necessary. Thus, the cleavage reaction of the 5,5-disubstituted oxadiazolines (**7**) was terminated after a short time and uncompleted conversion yielding **8** with marginal loss of optical purity. Zinc/acetic acid is also an applicable system for the chemoselective N-N bond cleavage, however, under the conditions applied racemization was always complete.[18]

In summary, we have provided a new access to spiro oxadiazolines (**4**) in good yields and good to excellent diastereomeric excesses by 1,3-dipolar cycloaddition of nitrile oxides to chiral hydrazones. By using the (*E*)- or the (*Z*)-isomers of the hydrazone dipolarophiles (**2**) both possible diastereomers can be prepared alternatively, utilizing the same chiral auxiliary. Open chain unsymmetrical ketone hydrazones (**6**) lead to 5,5-disubstituted oxadiazolines (**7**) in moderate to quantitative yields. Subsequent N-N bond cleavage with formic acid affords the parent N-unsubstituted oxadiazolines (**8**) with low to high enantiomeric excesses.

Table 3: N-unsubstituted oxadiazolines (**8**)

8	7	R^1	R^2	config.	time [min.]	yield [%]	*ee*[a] [%]
a	**d**	$(CH_2)_2CH_3$	CH_3	(2′*S*,5*S*)	40	67	74
a	**h**	$(CH_2)_2CH_3$	CH_3	(2′*S*,5*S*)	10	(80) [b,c]	83
a	**l**	$(CH_2)_2CH_3$	CH_3	(2′*S*,5*S*)	15	100	43
a	**l**	CH_3	$(CH_2)_2CH_3$	(2′*S*,5*R*)	10	-[c]	36
b	**a**	$(CH_2)_3CH_3$	CH_3	(2′*S*,5*S*)	120	25	5
b	**a**	CH_3	$(CH_2)_3CH_3$	(2′*S*,5*R*)	30	25	17
b	**e**	$(CH_2)_3CH_3$	CH_3	(2′*S*,5*S*)	80	38	2
b	**e**	CH_3	$(CH_2)_3CH_3$	(2′*S*,5*R*)	10	100	26
b	**i**	$(CH_2)_3CH_3$	CH_3	(2′*S*,5*S*)	10	30	35
b	**i**	CH_3	$(CH_2)_3CH_3$	(2′*S*,5*R*)	10	-[c]	63
b	**m**	$(CH_2)_3CH_3$	CH_3	(2′*S*,5*S*)	20	100	55
c	**b**	$(CH_2)_2C_6H_5$	CH_3	(2′*S*,5*S*)	300	17	17
c	**b**	CH_3	$(CH_2)_2C_6H_5$	(2′*S*,5*R*)	20	(10)[b,c]	91
c	**f**	$(CH_2)_2C_6H_5$	CH_3	(2′*S*,5*S*)	8	(20)[b,c]	81
c	**f**[d]	CH_3	$(CH_2)_2C_6H_5$	(2′*S*,5*R*)[e]	8	100	75
c	**j**	$(CH_2)_2C_6H_5$	CH_3	(2′*S*,5*S*)	10	20	81
c	***n***	$(CH_2)_2C_6H_5$	CH_3	(2′*S*,5*S*)	5	29	65
c	**n**[f]	CH_3	$(CH_2)_2C_6H_5$	(2′*S*,5*R*)	10	-[c]	28
d	**c**	CH_2CH_3	C_6H_5	(2′*S*,5*R*)	30	100	0
d	**g**	C_6H_5	CH_2CH_3	(2′*S*,5*S*)	5	91	56
d	**k**	C_6H_5	CH_2CH_3	(2′*S*,5*S*)	5	100	59

[a] Determined by analytical HPLC. - [b] Value in brackets () refers to conversion which is given in %. [c] Yields were not determined. - [d] *de* = 84%. - [e] Starting material with 84% *de* was used. - [f] *de* = 64%.

EXPERIMENTAL SECTION

General. All reactions were carried out using standard Schlenk techniques. Solvents were dried and purified by conventional methods prior to use. Reagents were purchased from common commercial suppliers and were used from freshly opened containers unless otherwise stated. The chiral hydrazones (**2,6**) were prepared following standard literature procedures.[12,19] The oximes[20] of aromatic aldehydes and the hydroxamoyl chlorides[14] were prepared according to published procedures. *Apparatus*. Melting points are uncorrected and were measured on a Dr. Tottoli apparatus (Büchi 510). Optical rotations: Perkin-Elmer P 241 polarimeter; solvents of Merck UVASOL quality. - IR spectra: Perkin-Elmer FT 1750 or Perkin-Elmer PE 1760. - ^{1}H NMR spectra (300 MHz, 500 MHz) and ^{13}C NMR spectra (75 MHz, 125 MHz): Varian VXR 300, Varian Unity 500, Gemini 300 (δ in ppm, solvent: $CDCl_3$, TMS as internal standard). - MS spectra: Varian MAT 212 (EI 70 eV), Finnigan SSQ 7000 (EI 70 eV). - Microanalyses: Heraeus CHN-O-RAPID. - Analytical HPLC: Hewlett-Packard HPLC 1050, UV detection, ChiralcelOD, (*S,S*)-

Whelk-O1 ; Preparative HPLC: Gilson Abimed; Merck. LiCrosorb®-column (25 cm x 25 mm, silica 60, particle size 0.007 mm), UV detection.

General procedure 1 for the preparation of Δ^2-1,2,4-oxadiazolines (4) by 1,3-dipolar cycloadditions. A Schlenk flask was charged with 2 eq oxime, 2 eq. *N*-chlorosuccinimide (NCS) and toluene (10 mL/ mmol), the reaction mixture was stirred at ambient temperature until the NCS was completely dissolved and was then cooled to 0 °C. Then, 1 eq. of the hydrazone and 2 eq. triethylamine were added dropwise. The mixture was allowed to warm to rt and stirred until the completion of the reaction was detected by TLC. The solvent was removed under reduced pressure and the remaining residue dissolved in ether. The organic phase was washed with water, dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude cycloadduct was purified by column chromatography (SiO_2; petroleum ether: ether).

General procedure 2 for the preparation of Δ^2-1,2,4-oxadiazolines (4) by 1,3-dipolar cycloadditions. A Schlenk flask was charged with 1 eq. of the hydrazone and $CHCl_3$ (10 mL/mmol). Then, 2 eq. triethylamine were added, and the mixture was cooled to 0 °C. 2 eq. hydroxamoyl chloride (**3**), dissolved in $CHCl_3$ (5 mL/mmol), were added by a syringe pump over a period of 6-8 h. Stirring was continued until the completion of the reaction was detected by TLC. The solvent was removed under reduced pressure and the remaining residue dissolved in ether. The organic phase was washed with water, dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude cycloadduct was purified by column chromatography (SiO_2; petroleum ether: ether).

General procedure 3 for the formic acid mediated N-N bond cleavage. The neat cycloadduct (**7**) was cooled to 0 °C. Then, 40 eq. formic acid were added dropwise under stirring. Stirring was continued until the completion of the reaction was detected by TLC (10-90 min). The reaction mixture was poured into water, and the aqueous phase extracted with ether. The organic phase was washed with water, dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude cycloadduct was purified by column chromatography (SiO_2; petroleum ether: ether).

(2′*S*,5*R*/*S*)-(–)-4-[2-(Methoxymethyl)tetrahydro-1*H*-1-pyrrolyl]-3-phenyl-1-oxa-2,4-diazaspiro[4.5]-deca-2,6-diene [4a]. a) NCS (0.27 g, 2 mmol), 0.24 g (2 mmol) of benzaldehyde oxime, 0.21 g (1 mmol) of (*Z*)-cyclohexenone SAMP hydrazone and 0.28 mL (2 mmol) triethylamine reacted for 24 h at –78 °C according to the general procedure 1, yielding 0.26 g of (2′*S*,5*R*/*S*)-**4a**[21] (79%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 3:2); *de* = 20%. - b) The (*E*)-hydrazone gave 0.22 g of (2′*S*,5*R*/*S*)-**4a**[21] (67%) as a colorless oil after column chromatography; *de* = 58%. - (2′*S*,5*R*)-**4a**: *de* = ≥ 98%; $[\alpha]_D^{25}$ = –136.0 °(c = 1.05; $CHCl_3$). - (2′*S*,5*S*)-**4a**: *de* = ≥ 98%; $[\alpha]_D^{25}$ = –321.8 ° (c = 0.97; $CHCl_3$). - IR ($CHCl_3$): $\tilde{\nu}$ = 3057 cm^{-1} (m), 3028 (m), 2939 (s), 2872 (s), 2831 (s), 1648 (m), 1592 (m), 1563 (m, ν(C=N)), 1495 (m), 1446 (s), 1394 (m), 1356 (s), 1308 (m), 1287 (m), 1267 (m), 1234 (m), 1196 (m), 1174 (m), 1111 (s, ν(COC)), 1047 (m, ν(CO)), 1026 (m), 1001 (w), 972 (m), 947 (s), 924 (m),

867 (m), 838 (m), 769 (s), 722 (m), 698 (s), 679 (m), 667 (m), 628 (w), 587 (m). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*R*): δ = 1.45 (m, 4H, NCH_2CH_2, $NCHCH_2$), 1.90 (m, 4H, CCH_2CH_2), 2.10 (br m, 2H, $CH{=}CHCH_2$), 2.83 (br m, 1H, NCHH′), 3.02 (m, 1H, NCHH′), 3.18 (m, 1H, CHH′O), 3.34 (s, 4H, NCH, OCH_3), 3.53 (dd, 1H, *J* = 9.1 Hz, 3.6 Hz, CHH′O), 5.87 (br m, 1H, $CH{=}CHCH_2$), 6.08 (br m, 1H, $CH{=}CHCH_2$), 7.41 (m, 3H, $CH_{arom.}$), 7.78 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*S*): δ = 1.50 (br m, 4H, NCH_2CH_2, $NCHCH_2$), 1.85 (br m, 3H, CCH_2CHH'), 1.93 (br m, 1H, CCH_2CHH'), 2.13 (br m, 2H, $CH{=}CHCH_2$), 2.78 (br m, 1H, NCHH′), 3.02 (br m, 1H, NCHH′), 3.18 (br m, 1H, CHH′O), 3.37 (br m, 4H, NCH, OCH_3), 3.58 (br m, 1H, CHH′O), 5.80 (br m, 1H, $CH{=}CHCH_2$), 6.16 (dt, 1H, *J* = 10.1 Hz, 3.7 Hz, $CH{=}CHCH_2$), 7.43 (m, 3H, $CH_{arom.}$), 7.75 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*R*): δ= 19.4 br (CCH_2CH_2), 22.2 ($NCHCH_2$), 24.9 ($CCH{=}CHCH_2$), 27.2 br (NCH_2CH_2), 29.6 br (CCH_2), 52.5 br (NCH_2), 59.0 (OCH_3), 62.3 br (NCH), 75.1 (CH_2O), 98.2 br (C), 127.5 br ($CCH{=}CH$), 128.6, 130.4 br (C arom., CH arom.), 132.5 br ($CCH{=}CH$), 157.9 br (C=N) ppm; (2′*S*,5*S*): δ = 19.4 br (CCH_2CH_2), 21.9 ($NCHCH_2$), 25.2 ($CCH{=}CHCH_2$), 27.1 br (NCH_2CH_2), 33.7 (CCH_2), 51.0 br (NCH_2), 59.1 (OCH_3), 62.5, br (NCH), 75.8 br (CH_2O), 98.4 br (C), 123.2 br ($CCH{=}CH$), 128.6, 130.6 br (C arom., CH arom.), 135.6 br ($CCH{=}CH$), 158.6 br (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 186 (72) [M^+–CH_2OCH_3, –C_6H_8O], 183 (13), 163 (40), 145 (26), 119 (6) [$C_6H_5C{\equiv}N\text{-}O^+$], 117 (23) [$M^+$–SMP, –$C_6H_8O$], 104 (12), 103 (12) [$C_6H_5C{\equiv}N^+$], 97 (41), 96 (7) [$C_6H_8O^+$], 79 (37), 77 (23), 72 (36), 71 (100), 68 (69), 67 (34), 59 (21), 58 (45), 57 (22), 55 (14), 45 (43). - Anal. Calcd for $C_{19}H_{25}N_3O_2$: C, 69.70; H, 7.70; N, 12.83. Found: C, 69.93; H, 7.84; N, 12.65.

(2′*S*,5*R/S*)-(–)-3-(4-Fluorophenyl)-4-[2-(methoxymethyl)tetrahydro-1*H*-1-pyrrolyl]-1-oxa-2,4-diaza-spiro[4.5]deca-2,6-diene [4b]. a) NCS (0.27 g, 2 mmol), 0.28 g (2 mmol) of *p*-fluorobenzaldehyde oxime, 0.21 g (1 mmol) of (*Z*)-cyclohexenone SAMP hydrazone and 0.28 mL (2 mmol) of triethylamine reacted for 24 h at –78 °C according to the general procedure 1 yielding 0.17 g of (2′*S*,5*R/S*)-**4b**[21] (49%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 3:1); *de* = 14%. - b) The (*E*)-hydrazone yielded 0.19 g of (2′*S*,5*R/S*)-**4b**[21] (54%) as a colorless oil after column chromatography; *de* = 59%. - (2′*S*,5*R*)-**4b**: *de* = 97%; $[\alpha]_D^{25}$ = –108.2 ° (c = 0.97; $CHCl_3$). - (2′*S*,5*S*)-**4b**: *de* = ≥ 98%; $[\alpha]_D^{25}$ = –303.8 ° (c = 0.98; $CHCl_3$). - IR ($CHCl_3$): $\tilde{\nu}$ = 3045 cm^{-1} (w), 2942 (s), 2874 (s), 2832 (m), 1649 (w), 1602 (s, ν(C=C)), 1569 (m, ν(C=N)), 1508 (s), 1451 (m), 1440 (m), 1428 (m), 1411 (m), 1399 (m), 1344 (s), 1289 (m), 1227 (s), 1040 (m, ν(CO)), 1014 (w), 973 (m), 950 (s), 869 (m), 845 (s), 819 (m), 756 (s), 595 (m). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*R*): δ = 1.58 (br m, 4H, NCH_2CH_2, $NCHCH_2$), 1.89 (br m, 4H, CCH_2CH_2), 2.12 (br m, 2H, $CH{=}CHCH_2$), 2.80 (br m, 1H, NCHH′), 3.02 (br m, 1H, NCHH′), 3.19 (m, 1H, CHH′O), 3.34 (s, 4H, NCH, OCH_3), 3.50 (dd, 1H, *J* = 9.1 Hz, 3.0 Hz, CHH′O), 5.84 (br m, 1H, $CH{=}CHCH_2$), 6.12 (br m, 1H, $CH{=}CHCH_2$), 7.10 (m, 2H, $CH_{arom.}$), 7.78 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*S*): δ = 1.39 (br m, 2H, NCH_2CH_2), 1.54 (br m, 2H, $NCHCH_2$), 1.74 (m, 1H, CCH_2CHH'), 1.81 (m, 1H, CCH_2CHH'), 1.84 (m, 2H, CCH_2), 2.10 (m, 2H, $CH{=}CHCH_2$), 2.85 (br s, 1H, NCHH′), 2.98 (br

m, 1H, NCH***H***′), 3.07 (br t, 1H, *J* = 7.6 Hz, C***H***H′O), 3.20 (s, 3H, OCH_3), 3.26 (br m, 1H, CHN), 3.35 (br s, CHH′O), 5.79 (br d, 1H, *J* = 10.1 Hz, C***H***=$CHCH_2$), 6.14 (dt, 1H, *J* = 10.4 Hz, 3.7 Hz, CH=C***H***CH_2), 7.28 (m, 2H, $CH_{arom.}$), 7.77 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C-NMR ($CDCl_3$): δ = 19.5 br (CCH_2***C***H_2), 22.2 (NCH***C***H_2), 24.9 (CCH=CH***C***H_2), 27.1 br (NCH_2***C***H_2), 29.6 br (C***C***H_2), 52.4 br (NCH_2), 59.0 (OCH_3), 62.6 br (NCH), 75.0 (CH_2O), 98.5 br (C), 115.6 br (CH arom.), 124.4 br (C***C***H=CH), 130.6 br (C arom., CH arom.), 135.7 br (CCH=***C***H), 158.0 br (C=N), 164.0 (C-F) [d, *J* = 250.9 Hz] ppm; (2′*S*,5*S*): δ = 18.7 (CCH_2***C***H_2), 21.2 (NCH***C***H_2), 24.3 (CCH=CH***C***H_2), 26.5 (NCH_2***C***H_2), 33.1 (C***C***H_2), 51.2 br (NCH_2), 58.0 (OCH_3), 61.5 br (NCH), 74.6 (CH_2O), 97.0 br (C), 115.4 (CH arom.) [d, *J* = 22.0 Hz], 123.7 br (C***C***H=CH), 130.3 (CH arom.) [d, *J* = 8.8 Hz], 135.1 (CCH=***C***H), 156.1 br (C=N), 163.2 (C-F) [d, *J* = 249.0 Hz] ppm. - MS (70 eV); *m/z* (% b.p.) = 204 (41) [M^+–CH_2OCH_3, –C_6H_8O], 163 (35), 135 (32) [M^+–SMP, –C_6H_8O], 121 (6) [$FC_6H_4C{\equiv}N^+$], 99 (11), 97 (45), 96 (8) [$C_6H_8O^+$], 94 (14), 79 (40), 77 (16), 72 (38), 71 (100), 68 (54), 67 (29), 59 (24), 58 (44), 57 (14). - Anal. Calcd for $C_{19}H_{24}N_3O_2F$: C, 66.07; H, 7.00; N, 12.17. Found: C, 66.58; H, 7.20; N, 11.80.

(2′*S*,5*R*/*S*)-(–)-3-(4-Methoxyphenyl)-4-[2-(methoxymethyl)tetrahydro-1*H*-1-pyrrolyl]-1-oxa-2,4-diazaspiro[4.5]deca-2,6-diene [4c]. a) NCS (0.27 g, 2 mmol), 0.30 g (2 mmol) of *p*-methoxy-benzaldehyde oxime, 0.21 g (1 mmol) of (*Z*)-cyclohexenone SAMP hydrazone and 0.28 mL (2 mmol) of triethylamine reacted for 24 h at –78 °C according to the general procedure 1 yielding 0.25 g of (2′*S*,5*R*/*S*)-**4c**[21] (69%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 2:1); *de* = 5%. - b) The (*E*)-hydrazone gave 0.25 g of (2′*S*,5*R*/*S*)-**4c**[21] (69%) as a colorless oil after column chromatography; *de* = 32%. - (2′*S*,5*R*)-**4c**: *de* = ≥ 98%; $[\alpha]_D^{25}$ = –130.5 ° (c = 0.94; $CHCl_3$). - (2′*S*,5*S*)-**4c**: *de* = ≥ 97%; $[\alpha]_D^{25}$ = –325.5 ° (c = 1.06; $CHCl_3$). - IR (Et_2O): $\tilde{\nu}$ = 3043 cm^{-1} (w), 2937 (s), 2872 (m), 2836 (m), 1650 (w), 1611 (s, ν(C=C)), 1590 (m, ν(C=N)), 1564 (w), 1511 (s), 1459 (m), 1420 (m), 1399 (m), 1345 (m), 1303 (m), 1254 (s), 1172 (s), 1109 (s), 1074 (m, ν(COC)), 1029 (m, ν(CO)), 972 (w), 949 (m), 869 (m), 869 (m), 838 (m), 732 (w), 637 (w), 600 (w). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*R*): δ = 1.54 (m, 4H, NCH_2C***H***$_2$, NCHC***H***$_2$), 1.89 (br m, 4H, CC***H***$_2C$***H***$_2$), 2.10 (br m, 2H, CH=CHC***H***$_2$), 2.82 (br m, 1H, NC***H***H′), 3.02 (m, 1H, NCH***H***′), 3.19 (m, 1H, C***H***H′O), 3.33 (m, 1H, NCH), 3.35 (s, 3H, CH_2OCH_3), 3.53 (m, 1H, CH***H***′O), 3.84 (s, 3H, OCH_3), 5.84 (br m, 1H, C***H***=$CHCH_2$), 6.06 (br m, 1H, CH=C***H***CH_2), 6.94 (m, 2H, $CH_{arom.}$), 7.64 (br m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*S*): δ = 1.52 (m, 4H, NCH_2C***H***$_2$, NCHC***H***$_2$), 1.88 (m, 4H, CC***H***$_2C$***H***$_2$), 2.13 (m, 2H, CH=CHC***H***$_2$), 2.77 (br m, 1H, NC***H***H′), 2.96 (br m, 1H, NCH***H***′), 3.18 (br m, 1H, C***H***H′O), 3.31 (br m, 1H, NCH), 3.35 (s, 3H, CH_2OCH_3), 3.56 (br m, 1H, CH***H***′O), 3.84 (s, 3H, OCH_3), 5.78 (br m, 1H, C***H***=$CHCH_2$), 6.14 (dt, *J* = 10.4 Hz, 3.6 Hz, 1H, CH=C***H***CH_2), 6.94 (m, 2H, $CH_{arom.}$), 7.69 (br m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$): δ = 19.5 br (CCH_2***C***H_2), 22.1 (NCH***C***H_2), 24.9 (CCH=CH***C***H_2), 26.9 br (NCH_2***C***H_2), 29.7 br (C***C***H_2), 52.4 br (NCH_2), 55.3 (OCH_3), 59.1 (CH_2O***C***H_3), 62.4 br (NCH), 75.2 (CH_2O), 98.4 (C), 114.0 br (CH arom.), 120.3, br (C***C***H=CH), 130.1 br (CH arom.), 132.2 br (C arom.), 135.4 (CCH=***C***H), 158.2 (C=N), 161.3

(***C***-OCH_3) ppm; (2′*S*,5*S*): δ = 19.5 br ($CCH_2\boldsymbol{C}H_2$), 21.8 ($NCH\boldsymbol{C}H_2$), 25.2 ($CCH{=}CH\boldsymbol{C}H_2$), 27.1 br ($NCH_2\boldsymbol{C}H_2$), 33.6 ($C\boldsymbol{C}H_2$), 50.7 br ($NCH_2$), 55.3 ($OCH_3$), 59.1 ($CH_2O\boldsymbol{C}H_3$), 62.5 br (NCH), 75.9 br (CH_2O), 98.2 br (C), 114.1 br (CH arom.), 123.2 br ($C\boldsymbol{C}H{=}CH$), 130.1 br (C arom., CH arom.), 135.4 ($CCH{=}\boldsymbol{C}H$), 158.2 br (C=N), 161.5 br (***C***-OCH_3) ppm. - MS (70 eV); *m/z* (% b.p.) = 261 (9) [M^+–C_6H_8O], 216 (35) [M^+–CH_2COCH_3, –C_6H_8O], 163 (73), 149 (10) [$H_3COC_6H_4C{\equiv}N\text{-}O^+$], 148 (15), 147 (100) [$M^+$–SMP, –$C_6H_8O$], 134 (12), 133 (29) [$H_3COC_6H_4C{\equiv}N^+$], 103 (6) [$C_6H_5C{\equiv}N^+$], 97 (16), 96 (8) [$C_6H_8O^+$], 94 (23), 83 (14), 79 (18), 77 (13), 71 (34), 70 (11), 68 (28), 67 (28), 58 (14), 57 (13), 55 (11), 45 (11). - Anal. Calcd for $C_{20}H_{27}N_3O_3$: C, 67.20; H, 7.61; N, 11.76. Found: C, 67.62; H, 7.92; N, 11.70.

(2′*S*,5*R*/*S*)-(–)-4-[2-(1-Methoxy-1-methylethyl)tetrahydro-1*H*-1-pyrrolyl]-3-phenyl-1-oxa-2,4-diaza-spiro[4.5]deca-2,6-diene [4d]. a) 0.20 g (0.86 mmol) of (*Z*)-cyclohexenone SADP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.27 g of (2′*S*,5*S*)-**4d** (87%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 5:1). - *de* = ≥98%. - b) 0.20 g (0.86 mmol) of (*E*)-cyclohexenone SADP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.27 g of (2′*S*,5*R*)-**4d** (87%) as a yellow oil after column chromatography (silica gel; petroleum ether: ether 5:1). - *de* = 81%. - (2′*S*,5*S*)-**4d**: $[\alpha]_D^{24}$ = –321.5 ° (c = 0.98; $CHCl_3$); mp 108-110 °C. - (2′*S*,5*R*)-**4d**: $[\alpha]_D^{27}$ = –257.0 ° (c = 1.23; $CHCl_3$). - IR (neat): $\tilde{\nu}$ = 3046 cm^{-1} (m), 2969 (s), 2940 (s), 2874 (s), 2829 (m), 1649 (m), 1607 (w), 1589 (w), 1564 (m, ν(C=N)),1494 (m), 1446 (s), 1400 (m), 1380 (m), 1363 (m), 1342 (s), 1308 (m), 1279 (m), 1234 (m), 1175 (s), 1151 (s), 1134 (s), 1075 (s, ν(COC)), 1026 (m, ν(CO)), 950 (m), 936 (s), 915 (m), 868 (m), 839 (m), 809 (m), 772 (s), 732 (m), 698 (s), 678 (m), 626 (w), 614 (w), 594 (m). - ^1H NMR ($CDCl_3$) (2′*S*,5*R*): δ = 1.01 (s, 3H, CH_3), 1.11 (m, 1H, $NCH_2C\boldsymbol{H}H'$), 1.21 (m, 1H, $NCH_2CH\boldsymbol{H}'$), 1.23 (s, 3H, CH_3'), 1.48 (m, 2H, $NCHC\boldsymbol{H}H'$, $CCH_2C\boldsymbol{H}H'$), 1.75 (m, 2H, $NCHCH\boldsymbol{H}'$, $CCH_2CH\boldsymbol{H}'$), 1.89 (m, 1H, $CH{=}CHC\boldsymbol{H}H'$), 2.03 (m, 1H, $CH{=}CHCH\boldsymbol{H}'$), 2.14 (m, 2H, CCH_2), 2.98 (m, 2H, NCH_2), 3.17 (s, 3H, OCH_3), 3.40 (br m, 1H, NCH), 5.96 (br d, 1H, *J* = 10.4 Hz, $C\boldsymbol{H}{=}CHCH_2$), 6.22 (ddd, 1H, *J* = 10.2 Hz, 4.1 Hz, 2.7 Hz, $CH{=}C\boldsymbol{H}CH_2$), 7.43 (m, 3H, $CH_{arom.}$), 7.78 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*S*): δ = 0.86 (m, 1H, $NCH_2C\boldsymbol{H}H'$), 1.00 (m, 1H, $NCHC\boldsymbol{H}H'$), 1.05 (s, 3H, CH_3), 1.18 (s, 3H, CH_3'), 1.38 (m, 1H, $NCH_2CH\boldsymbol{H}'$), 1.68 (m, 1H, $NCHCH\boldsymbol{H}'$), 1.84 (m, 2H, $CCH_2C\boldsymbol{H}_2$), 2.08 (m, 3H, CCH_2, $CH{=}CHC\boldsymbol{H}H'$), 1.89 (m, 1H, $CH{=}CHC\boldsymbol{H}H'$), 2.40 (m, 1H, $NC\boldsymbol{H}H'$), 2.94 (m, 1H, $CH{=}CHCH\boldsymbol{H}'$), 3.03 (m, 1H, $NCH\boldsymbol{H}'$), 3.17 (s, 3H, OCH_3), 3.48 (br m, 1H, NCH), 5.84 (br m, 2H, $C\boldsymbol{H}{=}C\boldsymbol{H}CH_2$), 7.42 (m, 3H, $CH_{arom.}$), 7.78 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*R*): δ = 19.5 ($CCH_2\boldsymbol{C}H_2$), 20.3, 22.8 (CH_3), 24.1 ($NCH_2\boldsymbol{C}H_2$), 25.3 ($CCH{=}CH\boldsymbol{C}H_2$), 25.4 ($NCH\boldsymbol{C}H_2$), 33.5 ($C\boldsymbol{C}H_2$), 49.1 ($O\boldsymbol{C}H_3$), 52.7 ($NCH_2$), 71.1 (NCH), 78.1 ($CH_2O$), 98.2 (C), 122.7 ($C\boldsymbol{C}H{=}CH$), 128.5 (C arom.), 128.6, 129.0, 130.7 (CH arom.), 136.6 ($CCH{=}\boldsymbol{C}H$), 159.0 (C=N) ppm; (2′*S*,5*S*): δ = 19.9 ($CCH_2\boldsymbol{C}H_2$), 20.8, 22.3 (CH_3), 24.1 ($NCH_2\boldsymbol{C}H_2$), 24.7 ($CCH{=}CH\boldsymbol{C}H_2$), 25.8 ($NCH\boldsymbol{C}H_2$), 29.1 ($C\boldsymbol{C}H_2$),

49.0 (OCH_3), 54.4 (NCH_2), 70.4 (NCH), 78.0 (C), 98.5 (OCN), 128.0 (C*C*H=CH), 128.6 (C arom.), 128.6, 129.2, 129.9 (CH arom.), 130.6 (CCH=*C*H), 158.1 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 355 (1) [M^+], 186 (49) [M^+–C_6H_8O, –$C(CH_3)_2OCH_3$], 183 (32), 163 (29), 145 (28), 117 (18) [M^+–SDP, –C_6H_8O], 113 (13), 103 (10) [$C_6H_5C{\equiv}N^+$], 99 (19), 97 (15), 96 (26) [$C_6H_8O^+$], 94 (18), 86 (29), 85 (100), 81 (24), 80 (15), 79 (46), 77 (21), 73 (67) [$C(CH_3)_2OCH_3^+$], 72 (40), 71 (13), 70 (16), 69 (14), 68 (19), 67 (23), 65 (11), 59 (10), 55 (18). - Anal. Calcd for $C_{21}H_{29}N_3O_2$: C, 70.97; H, 8.22; N, 11.82. Found: C, 70.47; H, 8.21; N, 11.69.

(2′*S*,5*R*/*S*)-(–)-4-[2-(1-Ethyl-1-methoxylpropyl)tetrahydro-1*H*-1-pyrrolyl]-3-phenyl-1-oxa-2,4-diaza-spiro[4.5]deca-2,6-diene [**4e**]. a) 0.23 g (0.86 mmol) of (*Z*)-cyclohexenone SAEP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.23 g of (2′*S*,5*S*)-**4e** (70%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 3:1). - *de* = ≥98%[22]. - b) 0.23 g (0.86 mmol) of (*E*)-cyclohexenone SAEP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.30 g of (2′*S*,5*R*)-**4e** (91%) as a yellow oil after column chromatography (silica gel; petroleum ether: ether 3:1). - *de* = 86%. - (2′*S*,5*S*)-**4e**: $[\alpha]_D^{24}$ = –314.2 ° (c = 0.88; $CHCl_3$). - (2′*S*,5*R*)-**4e**: $[\alpha]_D^{27}$ = –226.6 ° (c = 0.99; $CHCl_3$). - IR (neat): $\tilde{\nu}$ = 3047 cm^{-1} (m), 2966 (s), 2879 (s), 2830 (s), 1650 (m), 1607 (w), 1589 (m), 1564 (m, ν(C=N)), 1494 (m), 1458 (s), 1446 (s), 1400 (m), 1379 (m), 1333 (s), 1308 (m), 1284 (m), 1248 (m), 1234 (m), 1169 (m), 1078 (s, ν(COC)), 1027 (m, ν(CO)), 1002 (w), 970 (m), 935 (s), 881 (s), 869 (s), 855 (m), 833 (m), 772 (s), 732 (s), 698 (s), 647 (w), 614 (w), 596 (m). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*S*): δ = 0.83 (t, 3H, *J* = 7.4 Hz, C***H***$_3$), 0.90 (t, 3H, *J* = 7.4 Hz, C***H***$_3$′), 1.00 (m, 1H, NCH_2C***H***H′), 1.26 (m, 2H, NCH_2CH***H***′, NCHC***H***H′), 1.34 (dq, 1H, *J* = 15.1 Hz, 7.4 Hz, C***H***H′), 1.52 (m, 2H, NCHCH***H***′, C***H***H′), 1.64 [dq, 1H, *J* = 15.3 Hz, 7.7 Hz, (C***H***H′)′], 1.83 [m, 4H, (CH***H***′)′, CCH_2C***H***$_2$, CH=CHC***H***H′], 2.03 (m, 1H, CC***H***H′), 2.16 (m, 2H, CCH***H***′, CH=CHCH***H***′), 2.95 (m, 2H, NCH_2), 3.25 (s, 3H, OCH_3), 3.47 (dd, 1H, *J* = 8.8 Hz, 4.4 Hz, NCH), 5.88 (br d, 1H, *J* = 10.4 Hz, C***H***=$CHCH_2$), 6.23 (ddd, 1H, *J* = 10.2 Hz, 4.4 Hz, 3.0 Hz, CH=C***H***CH_2), 7.42 (m, 3H, $CH_{arom.}$), 7.75 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*R*): δ = 0.85 (br t, 3H, *J* = 7.7 Hz, C***H***$_3$), 0.90 (br t, 3H, *J* = 7.7 Hz, C***H***$_3$′), 1.00 (m, 1H, NCH_2C***H***H′), 1.18 (m, 1H, NCHC***H***H′), 1.48 (m, 4H, NCH_2CH***H***′, NCHCH***H***′, CH_2), 1.62 (m, 2H, CH_2), 1.90 (br m, 2H, CCH_2C***H***$_2$), 2.04 (br m, 1H, CC***H***H′), 2.10 (br m, 2H, CCHH′, CH=CHC***H***H′), 2.42 (br m, 1H, NC***H***H′), 2.97 (br m, 1H, CH=CHCH***H***′), 3.05 (br m, 1H, NCH***H***′), 3.25 (s, 3H, OCH_3), 3.58 (br m, 1H, NCH), 5.85 (br m, 2H, C***H***=C***H***CH_2), 7.41 (m, 3H, $CH_{arom.}$), 7.78 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*S*): δ = 8.8 (CH_2***C***H_3), 20.1 (CCH_2***C***H_2), 24.0 (NCH_2***C***H_2), 25.1 (CCH=CH***C***H_2), 25.5, 25.9 (***C***H_2CH_3), 27.4 (NCH***C***H_2), 34.2 br (C***C***H_2), 51.3 br (OCH_3), 53.1 (NCH_2), 70.3 (NCH), 80.9 (C), 99.1 (OCN), 123.4 (C***C***H=CH), 128.9, 129.5, 131.2 (CH arom.), 129.1 (C arom.), 136.9 (CCH=***C***H), 159.5 (C=N) ppm; (2′*S*,5*R*): δ = 8.4, 8.5 (CH_2***C***H_3), 20.0 (CCH_2***C***H_2), 24.1 (NCH_2***C***H_2), 14.6, 24.7

($\boldsymbol{C}H_2CH_3$), 25.1 (CCH=CH$\boldsymbol{C}H_2$), 26.4 (NCH$\boldsymbol{C}H_2$), 29.4 (C$\boldsymbol{C}H_2$), 50.3 (OCH_3), 54.7 (NCH_2), 69.6 (NCH), 80.4 (C), 98.7 (OCN), 128.1 (C$\boldsymbol{C}$H=CH), 128.5, 129.3, 130.6 (CH arom.), 129.2 (C arom.), 130.1 (CCH=$\boldsymbol{C}$H), 158.2 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 383 (2) [M^+], 282 (13) [M^+–$C(CH_2CH_3)_2OCH_3$], 213 (15), 187 (14), 186 (100) [M^+–C_6H_8O, –$C(CH_2CH_3)_2OCH_3$], 184 (14), 183 (88), 163 (35), 145 (40), 127 (43), 124 (14), 119 (6) [$C_6H_5C{\equiv}N\text{-}O^+$], 117 (22) [$M^+$–SEP, –$C_9H_{10}O$], 103 (8) [$C_6H_5C{\equiv}N^+$], 101 (41) [$C(CH_2CH_3)_2OCH_3^+$], 99 (69), 97 (11), 95 (26), 94 (15), 86 (33), 80 (16), 79 (46), 77 (18), 71 (13), 70 (26), 69 (21), 68 (23), 67 (22), 65 (11), 59 (19), 55 (13). - Anal. Calcd for $C_{23}H_{33}N_3O_2$: C, 72.03; H, 8.67; N, 10.96. Found: C, 72.17; H, 9.08; N, 10.83.

(2′*S*,5*R*/*S*)-(–)-4-{2-[Methoxy(diphenyl)methyl]tetrahydro-1*H*-1-pyrrolyl}-3-phenyl-1-oxa-2,4-diazaspiro[4.5]deca-2,6-diene [4f]. a) 0.31 g (0.86 mmol) of (*E*)-cyclohexenone SAPP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.36 g of (2′*S*,5*R*/*S*)-**4f**[21] (88%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 6:1). - *de* = 28%.[22] - b) 0.31 g (0.86 mmol) of (*Z*)-cyclohexenone SAPP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 3 yielding 0.30 g of (2′*S*,5*S*)-**4f** (73%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 6:1). - *de* = 90%.[22] - (2′*S*,5*R*)-**4f**: mp 123-125 °C. - (2′*S*,5*S*)-**4f**: $[\alpha]_D^{25}$ = –184.4 ° (c = 0.99; $CHCl_3$); mp 58-59 °C. - IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (m), 3030 (m), 2933 (s), 2876 (s), 2827 (m), 1649 (w), 1590 (w), 1566 (w, ν(C=N)), 1494 (m), 1446 (s), 1394 (m), 1334 (s), 1277 (w), 1236 (m), 1174 (m), 1142 (m), 1074 (s, ν(COC)), 1031 (m, ν(CO)), 965 (m), 946 (m), 925 (m), 868 (m), 824 (m), 760 (s), 700 (s), 611 (m). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*R*): δ = 0.61 (m, 1H, $NCH_2C\boldsymbol{H}H'$), 1.37 (m, 1H, $NCH_2CH\boldsymbol{H}'$), 1.40 (m, 1H, $CCH_2C\boldsymbol{H}H'$), 1.80 (m, 2H, $CCH_2CH\boldsymbol{H}'$, CH=CHC$\boldsymbol{H}$H′), 2.02 (m, 3H, C$\boldsymbol{C}H_2$, CH=CHCH$\boldsymbol{H}'$), 2.27 (m, 1H, NC$\boldsymbol{H}$H′), 2.64 (m, 1H, NCH$\boldsymbol{H}'$), 2.94 (s, 3H, OCH_3), 4.65 (d, 1H, *J* = 9.4 Hz, NCH), 5.69 (d, 1H, *J* = 10.1 Hz, C$\boldsymbol{H}$=CHCH_2), 6.31 (dt, 1H, *J* = 10.1 Hz, 3.7 Hz, CH=C$\boldsymbol{H}CH_2$), 7.31 (m, 9H, $CH_{arom.}$), 7.49 (m, 4H, $CH_{arom.}$), 7.82 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*S*): δ = 0.88 (m, 4H, $NCH_2C\boldsymbol{H}_2$, NCHC$\boldsymbol{H}_2$), 1.27 (m, 1H, $CCH_2C\boldsymbol{H}H'$), 1.49 (m, 1H, $CCH_2CH\boldsymbol{H}'$), 1.72 (m, 1H, CH=CHC$\boldsymbol{H}$H′), 1.87 (m, 2H, C$\boldsymbol{C}H_2$), 2.04 (m, 1H, CH=CHCH$\boldsymbol{H}'$), 2.48 (ddd, 1H, *J* = 10.2 Hz, 8.2 Hz, 2.8 Hz, NC$\boldsymbol{H}$H′), 2.76 (dt, 1H, *J* = 10.2 Hz, 8.0 Hz, NCH$\boldsymbol{H}'$), 2.88 (s, 3H, OCH_3), 4.57 (dd, 1H, *J* = 9.3 Hz, 1.7 Hz, NCH), 5.88 (br d, 1H, *J* = 9.9 Hz, C$\boldsymbol{H}$=$CHCH_2$), 6.19 (ddd, 1H, *J* = 10.2 Hz, 5.0 Hz, 1.9 Hz, CH=C$\boldsymbol{H}CH_2$), 7.28 (m, 7H, $CH_{arom.}$), 7.47 (m, 4H, $CH_{arom.}$), 7.59 (m, 2H, $CH_{arom.}$), 7.82 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*R*): δ = 19.8 ($CCH_2\boldsymbol{C}H_2$), 23.8 (NCH$\boldsymbol{C}H_2$), 24.7 (CCH=CH$\boldsymbol{C}H_2$), 25.9 ($NCH_2\boldsymbol{C}H_2$), 28.7 (C$\boldsymbol{C}H_2$), 51.3 (OCH_3), 53.8 (NCH_2), 71.8 (NCH), 86.2 (C), 96.2 (OCN), 121.9 (CCH=$\boldsymbol{C}$H), 127.2, 127.3, 127.6, 128.7, 129.0, 129.4, 129.7, 129.9, 130.1 (CH arom.), 137.9 (C$\boldsymbol{C}$H=CH), 128.4, 141.0, 141.8 (C arom.), 158.2 (C=N) ppm; (2′*S*,5*S*): δ = 19.5 ($CCH_2\boldsymbol{C}H_2$), 23.4 (NCH$\boldsymbol{C}H_2$), 25.1 (CCH=CH$\boldsymbol{C}H_2$), 26.1 ($NCH_2\boldsymbol{C}H_2$), 33.2 (C$\boldsymbol{C}H_2$), 51.5 (OCH_3), 53.5 (NCH_2), 72.0 br (NCH), 86.3 (C), 98.5 (OCN), 123.2

(C*C*H=CH), 127.0, 127.2, 130.8, 127.1, 127.3, 129.1, 130.0, 130.5 (CH arom.), 128.6, 139.3, 141.0 (C arom.), 136.2 (CCH=*C*H), 158.9 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 198 (18), 197 (87) [$C(C_6H_5)_2OCH_3^+$], 187 (12), 186 (87) [M^+–C_6H_8O, –$C(C_6H_5)_2OCH_3$], 183 (14), 119 (8) [$C_6H_5C{\equiv}N$-O^+], 118 (14), 117 (5) [M^+–SPP, –C_6H_8O], 105 (38), 104 (10), 96 (35) [$C_6H_8O^+$], 77 (39), 70 (23), 69 (11), 68 (100). - Anal. Calcd for $C_{31}H_{33}N_3O_2$: C, 77.63; H, 6.94; N, 8.76. Found: C, 77.25; H, 7.09; N, 8.37.

(2′*S*,5*S*/*R*)-(–)-5-Butyl-4-[2-(methoxymethyl)tetrahydro-1*H*-1-pyrrolyl]-5-methyl-3-phenyl-4,5-dihydro-1,2,4-oxadiazole [**7a**]. 0.16 g (0.74 mmol) of 2-hexanone SAMP hydrazone, 0.21 mL (1.48 mmol) of triethylamine and 0.23 g (1.48 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.23 g of (2′*S*,5*S*/*R*)-**7a**[23] (92%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 5:1). - *de* = 28%. - (2′*S*,5*S*)-**7a**: $[\alpha]_D^{25}$ = –320.4 ° (c = 1.03; $CHCl_3$). - (2′*S*,5*R*)-**7a**: $[\alpha]_D^{25}$ = –92.7 ° (c = 0.91; $CHCl_3$). - IR (neat): $\tilde{\nu}$ = 3060 cm^{-1} (w), 2956 (s), 2871 (s), 1591 (w, ν(C=C)), 1563 (m, ν(C=N)), 1494 (m), 1458 (s), 1446 (s), 1382 (s), 1344 (s), 1311 (m), 1250 (m), 1196 (m), 1177 (m), 1117 (s), 1071 (m, ν(COC)), 1026 (m, ν(CO)), 970 (w), 919 (m), 897 (s), 840 (w), 768 (s), 733 (m), 699 (s), 664 (w). - ^1H NMR ($CDCl_3$) (2′*S*,5*S*): δ = 0.92 (t, 3H, *J* = 7.1 Hz, CH_2CH_3), 1.34 (m, 3H, NCH_2CH_2, NCHC*H*H′), 1.46 (m, 2H, NCHCH*H*′, C*H*H′CH_3), 1.51 (s, 3H, CH_3), 1.54 (m, 3H, CH*H*′CH_3, CCH_2CH_2), 1.67 (m, 2H, CCH_2), 2.73 (q, 1H, *J* = 8.1 Hz, NC*H*H′), 2.97 (m, 1H, NCH*H*′), 3.25 (m, 1H, C*H*H′O), 3.33 (m, 1H, NCH), 3.39 (s, 3H, OCH_3), 3.55 (dd, 1H, *J* = 8.4 Hz, 3.0 Hz, CH*H*′O), 7.43 (m, 3H, $CH_{arom.}$), 7.71 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*R*): δ = 0.94 (t, 3H, *J* = 7.4 Hz, CH_2CH_3), 1.34 (m, 4H, NCH_2CH_2, $NCHCH_2$), 1.44 (s, 3H, CH_3), 1.50 (m, 4H, CCH_2CH_2, CH_2CH_3), 1.79 (m, 2H, CCH_2), 2.84 (m, 1H, NC*H*H′), 3.04 (m, 1H, NCH*H*′), 3.23 (m, 2H, NCH, C*H*H′O), 3.37 (s, 3H, OCH_3), 3.54 (dd, 1H, *J* = 10.4 Hz, 5.4 Hz, CH*H*′O), 7.37 (m, 3H, $CH_{arom.}$), 7.73 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*S*): δ = 14.1 (CH_2CH_3), 19.3 (CH_3), 22.0 (NCH_2CH_2), 23.0 (CH_2CH_3), 26.0 (CCH_2CH_2), 26.9 ($NCHCH_2$), 39.6 (CCH_2), 51.5 (NCH_2), 59.1 (OCH_3), 62.9 (NCH), 75.7 (CH_2O), 102.4 (C), 128.4 (C arom.), 128.6, 128.7 , 130.6 (CH arom.), 158.5 (C=N) ppm; (2′*S*,5*R*): δ = 14.1 (CH_2CH_3), 21.9 (NCH_2CH_2), 22.7 (CH_3), 23.3 (CH_2CH_3), 26.3 (CCH_2CH_2), 27.1 ($NCHCH_2$), 35.4 (CCH_2), 53.1 (NCH_2), 59.1 (OCH_3), 62.2 (NCH), 75.5 (CH_2O), 101.6 (C), 128.7, 130.6 (CH arom.), 128.8 (C arom.), 158.6 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 187 (21), 186 (100) [M^+–$C_6H_{12}O$, -CH_2OCH_3], 167 (25), 145 (29), 117 (23) [M^+–SMP, –$C_6H_{12}O$], 104 (37), 103 (8) [$C_6H_5C{\equiv}N^+$], 72 (24), 71 (63), 68 (28), 58 (24), 57 (13), 45 (15). - Anal. Calcd for $C_{19}H_{29}N_3O_2$: C, 68.85; H, 8.82; N, 12.68. Found: C, 68.59; H, 8.95; N, 12.98.

(2′*S*,5*S*/*R*)-(–)-4-[2-(Methoxymethyl)tetrahydro-1*H*-1-pyrrolyl]-5-methyl-3-phenyl-5-phenetyl-4,5-dihydro-1,2,4-oxadiazole [**7b**]. 0.25 g (0.96 mmol) of benzylacetone SAMP hydrazone, 0.28 mL (2 mmol) of triethylamine and 0.31 g (2 mmol) of phenylhydroxamoyl chloride reacted for 24 h according

to the general procedure 2, yielding 0.31 g of (2′*S*,5*S*/*R*)-**7b**[23] (86%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 4:1). - *de* = 37%. - (2′*S*,5*S*)-**7b**: $[\alpha]_D^{25}$ = –322.6 ° (c = 1.04; $CHCl_3$). - (2′*S*,5*R*)-**7b**: $[\alpha]_D^{25}$ = –54.1 ° (c = 1.12; $CHCl_3$). - IR ($CHCl_3$): $\tilde{\nu}$ = 3084 cm^{-1} (w), 3061 (m), 3025 (m), 2974 (s), 2937 (s), 2873 (s), 2829 (m), 1603 (m), 1592 (m), 1563 (w, ν(C=N)), 1496 (m), 1454 (s), 1447 (s), 1382 (m), 1347 (m), 1310 (m), 1194 (m), 1156 (m), 1113 (s), 1071 (m, ν(COC)), 1028 (m, ν(CO)), 972 (w), 896 (m), 844 (w), 756 (s), 700 (s), 667 (w). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*S*): δ = 1.31 (m, 1H, NCH_2CHH'), 1.47 (m, 3H, NCH_2CHH', $NCHCH_2$), 1.58 (s, 3H, CH_3), 2.00 (m, 2H, CCH_2), 2.76 (q, 1H, *J* = 8.1 Hz, $NCHH'$), 2.85 (m, 2H, $CH_2C_6H_5$), 3.00 (m, 1H, $NCHH'$), 3.28 (m, 1H, $CHH'O$), 3.37 (s, 3H, OCH_3), 3.38 (m, 1H, NCH), 3.53 (dd, 1H, *J* = 8.4 Hz, 3.4 Hz, $CHH'O$), 7.23 (m, 5H, $CH_{arom.}$), 7.44 (m, 3H, $CH_{arom.}$), 7.71 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*R*): δ = 1.25 (br m, 2H, NCH_2CH_2)), 1.45 (m, 2H, $NCHCH_2$), 1.55 (s, 3H, CH_3), 2.10 (m, 2H, CCH_2), 2.86 (m, 3H, $NCHH'$, $CH_2C_6H_5$), 3.05 (br m, 1H, $NCHH'$), 3.24 (m, 2H, NCH, $CHH'O$), 3.35 (s, 3H, OCH_3), 3.52 (m, 1H, $CHH'O$), 7.25 (m, 5H, $CH_{arom.}$), 7.42 (m, 3H, $CH_{arom.}$), 7.72 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C-NMR ($CDCl_3$) (2′*S*,5*S*): δ = 19.5 (CH_3), 22.0 (NCH_2CH_2), 26.9 ($NCHCH_2$), 30.2 (CH_2Ph), 41.9 (CCH_2), 51.7 (NCH_2), 59.1 (OCH_3), 62.9 (NCH), 75.7 (CH_2O), 101.9 (C), 125.8, 130.7, 128.3, 128.4, 128.7 (CH arom.), 128.2, 142.1 (C arom.), 158.6 (C=N) ppm; (2′*S*,5*R*): δ = 21.9 (NCH_2CH_2), 22.8 (CH_3), 27.0 ($NCHCH_2$), 30.6 (CH_2Ph), 38.0 (CCH_2), 53.3 (NCH_2), 59.0 (OCH_3), 62.3 (NCH), 75.3 (CH_2O), 101.1 (C), 125.9, 130.6, 128.4, 128.5, 128.7, 129.4 (CH arom.), 128.5, 142.2 (C arom.), 158.1 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 379 (5) [M^+], 187 (11), 186 (87) [M^+–$C_{10}H_{12}O$, -CH_2OCH_3], 148 (43) [$C_{10}H_{12}O^+$], 145 (24), 119 (8) [$C_6H_5C{\equiv}N\text{-}O^+$], 117 (22) [$M^+$–SMP, –$C_{10}H_{12}O$], 105 (44), 104 (35), 91 (25), 77 (10), 72 (35), 71 (100), 70 (19), 68 (48), 67 (11), 59 (23), 58 (39). - Anal. Calcd for $C_{23}H_{29}N_3O_2$: C, 72.79; H, 7.70; N, 11.07. Found: C, 72.70; H, 7.71; N, 11.20.

(2′*S*,5*S*/*R*)-(–)-5-Ethyl-4-[2-(methoxymethyl)tetrahydro-1*H*-1-pyrrolyl]-3,5-diphenyl-4,5-dihydro-1,2,4-oxadiazole [7c]. 0.25 g (1 mmol) of propiophenone SAMP hydrazone, 0.28 mL (2 mmol) of triethylamine and 0.31 g (2 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.31 g of (2′*S*,5*S*/*R*)-**7c**[23] (86%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 5:1). - *de* = 57%. - (2′*S*,5*S*)-**7c**: $[\alpha]_D^{24}$ = –333.8 ° (c = 1.20; $CHCl_3$). - (2′*S*,5*R*)-**7c**: $[\alpha]_D^{24}$ = –112.4 ° (c = 0.98; $CHCl_3$); mp 39-41 °C. - IR ($CHCl_3$): $\tilde{\nu}$ = 3060 cm^{-1} (m), 3026 (m), 2974 (s), 2938 (s), 2876 (s), 2829 (m), 1590 (m), 1563 (m, ν(C=N)), 1493 (m), 1460 (s), 1447 (s), 1383 (m), 1340 (m), 1286 (m), 1219 (m), 1195 (m), 1174 (m), 1157 (m), 1112 (s), 1071 (m, ν(COC)), 1026 (m, ν(CO)), 1000 (m), 951 (m), 926 (m), 884 (m), 847 (m), 758 (s), 699 (s), 667 (m), 620 (w). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*S*): δ = 0.86 (t, 3H, *J* = 7.4 Hz, CH_3), 1.42 (m, 3H, NCH_2CH_2, $NCHCHH'$), 1.61 (m, 1H, $NCHCHH'$), 2.16 (q, 2H, *J* = 7.4 Hz, CCH_2), 2.82 (q, 1H, *J* = 8.4 Hz, $NCHH'$), 3.09 (dt, 1H, *J* = 8.4 Hz, 3.7 Hz, $NCHH'$), 3.33 (m, 2H, NCH, $CHH'O$), 3.40 (s, 3H, OCH_3), 3.59 (dd, 1H, *J* = 12.1 Hz, 7.5 Hz, $CHH'O$), 7.34 (m, 6H, $CH_{arom.}$), 7.70 (m, 4H, $CH_{arom.}$) ppm;

(2′*S*,5*R*): δ = 0.97 (t, 3H, *J* = 7.4 Hz, CH_3), 1.33 (m, 2H, NCH_2CHH', $NCHCHH'$), 2.16 (m, 2H, NCH_2CHH', $NCHCHH'$), 2.29 (pen, 2H, *J* = 7.4 Hz, $CCHH'$), 2.46 (q, 1H, *J* = 7.7 Hz, $NCHH'$), 3.00 (br m, 1H, $NCHH'$), 3.23 (m, 1H, $NCHH'$), 3.30 (br m, 2H, NCH, $OCHH'$), 3.42 (s, 3H, OCH_3), 3.57 (m, 1H, $OCHH'$), 7.36 (m, 6H, $CH_{arom.}$), 7.64 (m, 4H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*S*): δ = 8.6 (CH_3), 21.9 (NCH_2CH_2), 26.7 ($NCHCH_2$), 27.5 (CCH_2), 51.3 (NCH_2), 59.1 (OCH_3), 62.8 (NCH), 75.8 (CH_2O), 103.9 (C), 126.7, 127.6, 128.5, 128.9, 127.8, 130.8 (CH arom.), 128.1, 142.4 (C arom.), 158.7 (C=N) ppm; (2′*S*,5*R*): δ = 8.0 (CH_3), 21.8 (NCH_2CH_2), 27.2 ($NCHCH_2$), 30.7 (CCH_2), 52.5 (NCH_2), 59.1 (OCH_3), 62.1 (NCH), 75.5 (CH_2O), 103.2 (C), 127.3, 127.5, 127.9, 128.6, 129.0, 130.5 (CH arom.), 127.8, 139.2 (C arom.), 158.6 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 365 (4) [M^+], 187 (12), 186 (93) [M^+–$C_9H_{10}O$, -CH_2OCH_3], 145 (27), 135 (34), 119 (7) [$C_6H_5C{\equiv}N\text{-}O^+$], 117 (51) [$M^+$–SMP, –$C_9H_{10}O$], 105 (72), 104 (13), 103 (19) [$C_6H_5C{\equiv}N^+$], 77 (34), 76 (5), 72 (35), 71 (100), 68 (44), 67 (13), 59 (18), 58 (35), 57 (20), 45 (21) [$CH_2OCH_3^+$]. - Anal. Calcd for $C_{22}H_{27}N_3O_2$: C, 72.30; H, 7.45; N, 11.50. Found: C, 72.66; H, 7.62; N, 11.26.

(2′*S*,5*S*)-(–)-4-[2-(1-Methoxy-1-methylethyl)tetrahydro-1*H*-1-pyrrolyl]-5-methyl-3-phenyl-5-propyl-4,5-dihydro-1,2,4-oxadiazole [7d]. 0.20 g (0.79 mmol) of 2-pentanone SADP hydrazone, 0.22 mL (1.58 mmol) of triethylamine and 0.25 g (1.58 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.26 g of (2′*S*,5*S*/*R*)-**7d**[23] (96%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 5:1). - *de* = 63%. - (2′*S*,5*S*)-**7d**: $[\alpha]_D^{24}$ = –276.7 ° (c = 0.89; $CHCl_3$; *de* = ≥96%). - IR (neat): $\tilde{\nu}$ = 2963 cm^{-1} (s), 2878 (s), 2825 (m), 1631 (w), 1459 (m), 1377 (m), 1360 (m), 1281 (w), 1244 (w), 1212 (w), 1185 (w), 1119 (m), 1084 (s, ν(COC)), 1053 (m), 1024 (m, ν(CO)), 923 (m), 882 (w), 792 (w), 773 (w). - ^{1}H NMR ($CDCl_3$) δ = 0.90 (t, 3H, *J* = 7.0 Hz, CH_2CH_3), 1.06 (s, 3H, CH_3), 1.14 (m, 2H, NCH_2CHH', $NCHCHH'$), 1.24 (s, 3H, CH_3'), 1.48 (m, 5H, NCH_2CHH', $NCHCHH'$, $CCHH'CH_2$), 1.62 (s, 3H, CCH_3), 1.74 (m, 1H, $CCHH'$), 2.89 (m, 1H, $NCHH'$), 2.98 (ddd, 1H, *J* = 10.4 Hz, 6.4 Hz, 4.6 Hz, $NCHH'$), 3.23 (s, 3H, OCH_3), 3.50 (dd, 1H, *J* = 9.5 Hz, 4.6 Hz, NCH), 7.43 (m, 3H, $CH_{arom.}$), 7.76 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) δ = 14.4 (CH_2CH_3), 17.3 (CH_2CH_3), 19.2 (CCH_3), 20.9, 22.0 (CH_3), 24.3 (NCH_2CH_2), 25.9 ($NCHCH_2$), 42.2 (CCH_2), 49.1 (OCH_3), 53.4 (NCH_2), 70.9 (NCH), 78.2 (C), 102.7 (OCN), 128.5, 128.9, 130.5 (CH arom.), 128.6 (C arom.), 158.9 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 365 (8) [M^+], 187 (10), 186 (76) [M^+–$C_5H_{10}O$, -$C(CH_3)_2OCH_3$], 173 (43), 161 (31), 153 (24), 145 (32), 132 (16), 131 (18), 119 (10) [$C_6H_5C{\equiv}N\text{-}O^+$], 117 (26) [$M^+$–SDP, –$C_5H_{10}O$], 113 (12), 104 (37), 103 (11) [$C_6H_5C{\equiv}N^+$], 99 (22), 96 (18), 86 (30), 85 (100), 81 (21), 73 (74) [$C(CH_3)_2OCH_3^+$], 72 (39), 71 (13), 70 (20), 69 (18), 68 (14), 57 (13), 55 (25). - Anl. Calcd for $C_{22}H_{27}N_3O_2$: C, 72.30; H, 7.45; N, 11.50. Found: C, 72.66; H, 7.62; N, 11.26.

(2′*S*,5*S*/*R*)-(–)-5-Butyl-4-[2-(1-methoxy-1-methylethyl)tetrahydro-1*H*-1-pyrrolyl]-5-methyl-3-

phenyl-4,5-dihydro-1,2,4-oxadiazole [7e]. 0.21 g (0.86 mmol) of 2-hexanone SADP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.22 g of (2′*S*,5*S*/*R*)-**7e**[23] (71%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 6:1). - *de* = 59%. - (2′*S*,5*S*)-**7e**: $[\alpha]_D^{25}$ = – 217.9 ° (c = 1.00; $CHCl_3$; *de* = ≥96%). - (2′*S*,5*R*)-**7e**: $[\alpha]_D^{25}$ = –214.2 ° (c = 0.28; $CHCl_3$); mp 45-47 °C. - IR (neat): $\tilde{\nu}$ = 3061 cm^{-1} (m), 2959 (s), 2872 (s), 2826 (m), 1591 (m), 1564 (m, ν(C=N)), 1494 (m), 1467 (s), 1446 (s), 1382 (s), 1363 (s), 1341 (s), 1308 (m), 1266 (m), 1242 (m), 1230 (m), 1208 (m), 1178 (s), 1117 (s), 1140 (s), 1071 (s, ν(COC)), 1026 (m, ν(CO)), 993 (w), 955 (m), 899 (s), 843 (m), 768 (s), 733 (m), 700 (s), 665 (w), 647 (w). - ^{1}H-NMR ($CDCl_3$) (2′*S*,5*S*): δ = 0.89 (t, 3H, *J* = 7.1 Hz, CH_2CH_3), 1.05 (s, 3H, CH_3), 1.14 (m, 2H, NCH_2CHH', $NCHCHH'$)), 1.21 (s, 3H, CH_3'), 1.42 (m, 7H, NCH_2CHH', $NCHCHH'$, CCH_2CH_2, CH_2CH_3, $CCHH'$), 1.62 (s, 3H, CCH_3), 1.74 (m, 1H, $CCHH'$), 2.88 (ddd, 1H, *J* = 12.4 Hz, 7.4 Hz, 1.9 Hz, $NCHH'$), 2.98 (m, 1H, $NCHH'$), 3.22 (s, 3H, OCH_3), 3.49 (dd, 1H, *J* = 9.1 Hz, 4.1 Hz, NCH), 7.44 (m, 3H, $CH_{arom.}$), 7.76 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*R*): δ = 0.96 (t, 3H, *J* = 7.1 Hz, CH_2CH_3), 1.06 (s, 3H, CH_3), 1.14 (m, 2H, NCH_2CHH', $NCHCHH'$), 1.21 (s, 3H, CH_3'), 1.39 (s, 3H, CCH_3), 1.42 (m, 3H, NCH_2CHH', $NCHCHH'$, $CHH'CH_3$), 1.56 (m, 2H, CCH_2CHH', $CHH'CH_3$) 1.72 (br m, 1H, CCH_2CHH'), 1.90 (m, 1H, $CCHH'$), 2.09 (m, 1H, $CCHH'$), 2.88 (dt, 1H, *J* = 9.9 Hz, 6.9 Hz, $NCHH'$), 2.97 (ddd, 1H, *J* = 10.8 Hz, 9.9 Hz, 5.5 Hz, $NCHH'$), 3.23 (s, 3H, OCH_3), 3.47 (dd, 1H, *J* = 9.1 Hz, 4.7 Hz, NCH), 7.44 (m, 3H, $CH_{arom.}$), 7.77 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*S*): δ = 14.1 (CH_2CH_3), 19.2 (CCH_3), 20.9, 22.0 (CH_3), 23.1 (NCH_2CH_2), 24.3 (CH_2CH_3), 25.9 (CH_2), 26.1 ($NCHCH_2$), 39.6 (CCH_2), 49.1 (OCH_3), 53.4 (NCH_2), 71.0 (NCH), 78.2 (CH_2O), 102.9 (C), 128.6, 129.0, 130.6 (CH arom.), 128.8 (C arom.), 159.0 (C=N) ppm; - (2′*S*,5*R*): δ = 14.0 (CH_2CH_3), 21.0, 22.0 (CH_3), 23.3 (CCH_3), 23.5 (NCH_2CH_2), 24.2 (CH_2CH_3), 26.0 (CH_2), 26.5 ($NCHCH_2$), 34.4 (CCH_2), 49.1 (OCH_3), 54.1 (NCH_2), 70.4 (NCH), 78.2 (C), 102.1 (OCN), 128.6, 129.1, 130.6 (CH arom.), 128.8 (C arom.), 158.4 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 359 (4) [M^+], 187 (61), 186 (100) [M^+–$C_6H_{12}O$, -$C(CH_3)_2OCH_3$], 167 (24), 161 (24), 146 (10), 145 (32), 144 (12), 131 (16), 119 (11) [$C_6H_5C{\equiv}N$-O^+], 117 (22) [M^+–SDP, –$C_6H_{12}O$], 113 (12), 104 (44), 103 (6) [$C_6H_5C{\equiv}N^+$], 99 (18), 96 (15), 86 (22), 85 (73), 73 (55) [$C(CH_3)_2OCH_3^+$], 72 (16), 55 (13). - Anal. Calcd for $C_{21}H_{33}N_3O_2$: C, 70.16; H, 9.25; N, 11.69. Found: C, 70.16; H, 9.33; N, 11.79.

(2′*S*,5*S*/*R*)-(–)-4-[2-(1-Methoxy-1-methylethyl)tetrahydro-1*H*-1-pyrrolyl]-5-methyl-5-phenethyl-3-phenyl-4,5-dihydro-1,2,4-oxadiazole [7f]. 0.25 g (0.86 mmol) of benzylacetone SADP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.26 g of (2′*S*,5*S*/*R*)-**7f**[23] (74%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 5:1). - *de* = 70%. - (2′*S*,5*S*)-**7f**: $[\alpha]_D^{25}$ = –175.6 ° (c = 1.13; $CHCl_3$; *de* = ≥96%). - (2′*S*,5*R*)-**7f**: $[\alpha]_D^{25}$ = –173.9 ° (c = 0.11; $CHCl_3$; *de* = 84%). - IR ($CHCl_3$): $\tilde{\nu}$ = 3084 cm^{-1} (s), 3061 (s), 3025 (m), 2971 (s), 2940 (s), 2874 (m), 2825 (m), 1603 (m), 1591

(m), 1564 (m, ν(C=N)),1496 (m), 1454 (s), 1446 (s), 1382 (s), 1362 (m), 1341 (s), 1309 (m), 1276 (m), 1241 (m), 1189 (w), 1153 (s), 1137 (s), 1070 (s, ν(COC)), 1027 (m, ν(CO)), 981 (w), 946 (w), 926 (m), 897 (m), 843 (m), 815 (w), 754 (s), 700 (s), 666 (w). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*S*): δ = 1.06 (s, 3H, CH_3), 1.15 (m, 2H, NCH_2CHH', $NCHCHH'$), 1.21 (s, 3H, CH_3'), 1.38 (m, 1H, $NCHCHH'$), 1.44 (m, 1H, NCH_2CHH'), 1.70 (s, 3H, CCH_3), 1.92 (ddd, 1H, *J* = 13.7 Hz, 12.5 Hz, 4.9 Hz, $CCHH'$), 2.09 (ddd, 1H, *J* = 13.7 Hz, 12.8 Hz, 4.9 Hz, $CCHH'$), 2.80 (td, 1H, *J* = 13.4 Hz, 4.9 Hz, C_6H_5CHH'), 2.86 (td, 1H, *J* = 12.8 Hz, 4.9 Hz, C_6H_5CHH'), 2.92 (dt, 1H, *J* = 10.1 Hz, 7.3 Hz, $NCHH'$), 3.01 (ddd, 1H, *J* = 10.4 Hz, 7.0 Hz, 5.5 Hz, $NCHH'$), 3.21 (s, 3H, OCH_3), 3.53 (dd, 1H, *J* = 8.9 Hz, 4.6 Hz, NCH), 7.16 (m, 3H, $CH_{arom.}$), 7.24 (m, 2H, $CH_{arom.}$), 7.42 (m, 3H, $CH_{arom.}$), 7.77 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*R*): δ = 1.03 (s, 3H, CH_3), 1.08 (m, 1H, NCH_2CHH'), 1.17 (s, 3H, CH_3'), 1.20 (m, 1H, $NCHCHH'$), 1.36 (m, 1H, NCH_2CHH', $NCHCHH'$), 1.50 (s, 3H, CCH_3), 2.25 (ddd, 1H, *J* = 14.0 Hz, 9.8 Hz, 7.6 Hz, $CCHH'$), 2.39 (ddd, 1H, *J* = 14.0 Hz, 10.7 Hz, 7.6 Hz, $CCHH'$), 2.91 (m, 3H, $NCHH'$, $C_6H_5CH_2$), 2.98 (dt, 1H, *J* = 10.1 Hz, 6.1 Hz, $NCHH'$), 3.24 (s, 3H, OCH_3), 3.51 (dd, 1H, *J* = 9.2 Hz, 4.9 Hz, NCH), 7.27 (m, 5H, $CH_{arom.}$), 7.45 (m, 3H, $CH_{arom.}$), 7.78 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*S*): δ = 19.4 (CCH_3), 20.9, 21.8 (CH_3), 24.2 (NCH_2CH_2), 26.0 ($NCHCH_2$), 30.4 ($CH_2C_6H_5$), 42.0 (CCH_2), 49.1 (OCH_3), 53.6 (NCH_2), 71.2 (NCH), 78.2 (C), 102.3 (OCN), 125.6, 128.3, 128.6, 128.9, 130.6 (CH arom.), 128.3, 142.2 (C arom.), 158.9 (C=N) ppm; (2′*S*,5*R*): δ = 21.2, 21.7 (CH_3), 23.5 (CCH_3), 24.2 (NCH_2CH_2), 26.1 ($NCHCH_2$), 30.7 ($CH_2C_6H_5$), 36.5 (CCH_2), 49.1 (OCH_3), 54.3 (NCH_2), 70.6 (NCH), 78.1 (CH_2O), 101.5 (C), 125.8, 128.3, 128.4, 128.6, 129.0), 130.6 (CH arom.), 128.5, 142.3 (C arom.), 158.5 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 407 (7) [M^+], 265 (10), 235 (22), 215 (17), 187 (14), 186 (100) [M^+–$C_{10}H_{12}O$, –$C(CH_3)_2OCH_3$], 148 (17) [$C_{10}H_{12}O^+$], 145 (30), 144 (40), 132 (13), 131 (15), 119 (14) [$C_6H_5C{\equiv}N\text{-}O^+$], 117 (33) [$M^+$–SDP, –$C_{10}H_{12}O$], 113 (15), 105 (54), 104 (64), 103 (14) [$C_6H_5C{\equiv}N^+$], 99 (22), 96 (21), 91 (24), 86 (27), 85 (85), 81 (16), 77 (11), 73 (77) [$C(CH_3)_2OCH_3^+$], 72 (23), 71 (11), 70 (18), 69 (1055 (13). - Anal. Calcd for $C_{25}H_{33}N_3O_2$: C, 73.68; H, 8.16; N, 10.31. Found: C, 73.56; H, 8.38; N, 10.29.

(2′*S*,5*S*)-(-)-5-Ethyl-4-[2-(1-methoxy-1-methylethyl)tetrahydro-1*H*-1-pyrrolyl]-3,5-diphenyl-4,5-dihydro-1,2,4-oxadiazole [**7g**]. 0.24 g (0.86 mmol) of propiophenone SADP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.18 g of (2′*S*,5*S*)-**7g** (53%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 10:1). - *de* = ≥ 96%[24]- (2′*S*,5*S*)-**7g**: $[\alpha]_D^{25}$ = – 345.8 ° (c = 1.02; $CHCl_3$); mp 100-102 °C. - IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} (m), 3025 (m), 2974 (s), 2934 (s), 2875 (s), 2827 (s), 1587 (w), 1559 (m, ν(C=N)),1493 (m), 1465 (s), 1447 (s), 1381 (s), 1339 (s), 1306 (m), 1283 (s), 1244 (w), 1224 (m), 1169 (s), 1129 (s), 1093 (s), 1067 (s, ν(COC)), 1027 (m, ν(CO)), 1003 (m), 945 (m), 927 (s), 907 (m), 884 (s), 843 (m), 816 (m), 799 (w), 774 (s), 760 (s), 723 (s), 701 (s), 668 (m), 605 (w). - ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, 3H, *J* = 7.4 Hz, CH_2CH_3), 1.09 (s, 3H, CH_3), 1.15 (m, 1H,

$NCH_2C\boldsymbol{H}H'$), 1.27 (s, 3H, CH_3'), 1.33 (m, 2H, $NCH_2CH\boldsymbol{H}'$, $NCHC\boldsymbol{H}H'$), 1.49 (ddd, 1H, J = 14.1 Hz, 7.1 Hz, 4.0 Hz, $NCHCH\boldsymbol{H}'$), 2.22 (dq, 1H, J = 15.1 Hz, 7.4 Hz, $CC\boldsymbol{H}H'CH_3$), 2.32 (dq, 1H, J = 15.1 Hz, 7.4 Hz, $CCH\boldsymbol{H}'CH_3$), 3.02 (m, 2H, NCH_2), 3.26 (s, 3H, OCH_3), 3.59 (dd, 1H, J = 9.1 Hz, 4.4 Hz, NCH), 7.32 (m, 6H, $CH_{arom.}$), 7.71 (m, 2H, $CH_{arom.}$), 7.84 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$): δ = 8.7 ($CH_2\boldsymbol{C}H_3$), 20.3, 21.5 (CH_3), 24.6 ($NCH_2\boldsymbol{C}H_2$), 26.3 ($NCH\boldsymbol{C}H_2$), 27.8 ($\boldsymbol{C}H_2CH_3$), 48.9 (OCH_3), 52.9 (NCH_2), 72.6 (NCH), 78.8 (C), 104.6 (OCN), 127.1, 127.3, 127.5, 128.4, 129.0, 130.7 (CH arom.), 128.2, 142.8 (C arom.), 159.2 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 393 (2) [M^+], 320 (7) [M^+–$C(CH_3)_2OCH_3$], 221 (32), 206 (19), 201 (13), 187 (13), 186 (99) [M^+–$C_9H_{10}O$, –$C(CH_3)_2OCH_3$], 145 (30), 132 (16), 117 (54) [M^+–SDP, –$C_9H_{10}O$], 115 (10), 113 (18), 105 (20), 104 (11), 103 (14) [$C_6H_5C{\equiv}N^+$], 99 (26), 96 (22), 86 (28), 85 (100), 81 (15), 77 (21), 73 (59) [$C(CH_3)_2OCH_3^+$], 72 (26), 55 (10). - Anal. Calcd for $C_{24}H_{31}N_3O_2$: C, 73.25; H, 7.94; N, 10.72. Found: C, 73.05; H, 7.71; N, 10.63.

(2′*S*,5*S*)-(–)-4-[2-(1-Ethyl-1-methoxylpropyl)tetrahydro-1*H*-1-pyrrolyl]-5-methyl-3-phenyl-5-propyl-4,5-dihydro-1,2,4-oxadiazole [7h]. 0.20 g (0.86 mmol) of 2-pentanone SAEP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.26 g of (2′*S*,5*S*)-**7h** (81%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 8:1). - *de* = 77%.[24] - (2′*S*,5*S*)-**7h**: $[\alpha]_D^{23}$ = –288.7 ° (c = 1.02; $CHCl_3$); mp 38-40 °C. - IR (KBr): $\tilde{\nu}$ = 3084 cm^{-1} (m), 3063 (m), 2969 (s), 2937 (s), 2874 (s), 2827 (m), 1775 (m), 1701 (m), 1618 (m), 1589 (m), 1567 (m, ν(C=N)),1491 (m), 1446 (s), 1383 (s), 1334 (s), 1251 (m), 1218 (m), 1176 (s), 1156 (s), 1121 (s), 1087 (s, ν(COC)), 1026 (m, ν(CO)), 992 (m), 952 (m), 919 (s), 897 (s), 880 (s), 854 (m), 827 (m), 771 (s), 720 (m), 700 (s), 665 (m), 609 (m). - ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, 3H, J = 7.4 Hz, $CH_2C\boldsymbol{H}_3$), 0.91 (t, 3H, J = 7.3 Hz, $CCH_2C\boldsymbol{H}_3$), 0.94 (t, 3H, J = 7.3 Hz, $CCH_2C\boldsymbol{H}_3'$), 1.00 (m, 1H, $NCH_2C\boldsymbol{H}H'$), 1.22 (m, 1H, $NCH_2CH\boldsymbol{H}'$), 1.42 (dq, 1H, J = 14.7 Hz, 7.3 Hz, $CC\boldsymbol{H}H'CH_3$), 1.54 (m, 5H, $NCHC\boldsymbol{H}_2$, $C\boldsymbol{H}_2CH_3$, $CC\boldsymbol{H}H'$), 1.56 (dq, 1H, J = 14.9 Hz, 7.6 Hz, $CCH\boldsymbol{H}'CH_3$), 1.63 (s, 3H, CH_3), 1.65 (dq, 1H, J = 14.9 Hz, 7.3 Hz, $[CC\boldsymbol{H}H'CH_3]'$), 1.75 (m, 1H, $CCH\boldsymbol{H}'$), 1.76 (dq, 1H, J = 14.7 Hz, 7.6 Hz, $[CCH\boldsymbol{H}'CH_3]'$), 2.87 (ddd, 1H, J = 10.7 Hz, 7.0 Hz, 6.4 Hz, $NC\boldsymbol{H}H'$), 2.98 (dt, 1H, J = 10.4 Hz, 6.7 Hz, $NCH\boldsymbol{H}'$), 3.27 (s, 3H, OCH_3), 3.58 (dd, 1H, J = 9.2 Hz, 4.9 Hz, NCH), 7.42 (m, 3H, $CH_{arom.}$), 7.74 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C-NMR ($CDCl_3$): δ = 8.4 ($CCH_2\boldsymbol{C}H_3$), 14.4 ($CH_2\boldsymbol{C}H_3$), 17.3 ($\boldsymbol{C}H_2CH_3$), 19.4 ($C\boldsymbol{C}H_3$), 23.9 ($NCH_2\boldsymbol{C}H_2$), 24.6, 25.0 ($C\boldsymbol{C}H_2CH_3$), 26.6 ($NCH\boldsymbol{C}H_2$), 42.4 ($C\boldsymbol{C}H_2$), 50.3 (OCH_3), 53.4 (NCH_2), 69.7 (NCH), 80.3 (C), 102.8 (OCN), 128.4, 129.1, 130.6 (CH arom.), 128.6 (C arom.), 158.9 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 373 (3) [M^+], 272 (29) [M^+–$C(CH_2CH_3)_2OCH_3$], 203 (19), 186 (64) [M^+–$C_5H_{10}O$, –$C(CH_2CH_3)_2OCH_3$], 174 (10), 173 (100), 161 (82), 153 (21), 145 (45), 132 (14), 131 (36), 127 (26), 124 (10), 119 (21) [$C_6H_5C{\equiv}N{-}O^+$], 117 (21) [M^+–SDP, –$C_9H_{10}O$], 104 (43), 101 (35) [$C(CH_2CH_3)_2OCH_3^+$], 99 (43), 95 (16), 85 (23), 71 (10), 70 (16), 69 (19), 59 (13), 57 (15), 55 (16). - Anal. Calcd for $C_{22}H_{35}N_3O_2$: C, 70.74; H, 9.44; N, 11.25. Found: C, 70.65; H, 9.61; N, 11.31.

(2′*S*,5*S*/*R*)-(–)-5-Butyl-4-[2-(1-ethyl-1-methoxylpropyl)tetrahydro-1*H*-1-pyrrolyl]-5-methyl-3-phenyl-4,5-dihydro-1,2,4-oxadiazole [7i]. 0.20 g (0.86 mmol) of 2-hexanone SAEP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.33 g of (2′*S*,5*S*/*R*)-**7i**[23] (100%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 10:1). - *de* = 77%.[24] - (2′*S*,5*S*)-**7i**: $[\alpha]_D^{23}$ = –257.0 ° (c = 1.02; $CHCl_3$); mp 38-40 °C. - (2′*S*,5*R*)-**7i**: $[\alpha]_D^{23}$ = –187.1 ° (c = 0.07; $CHCl_3$). - IR (neat): $\tilde{\nu}$ = 3060 cm^{-1} (w), 2962 (s), 2875 (s), 2827 (m), 1590 (w), 1564 (w, ν(C=N)), 1493 (m), 1459 (s), 1446 (s), 1382 (s), 1337 (s), 1309 (m), 1285 (w), 1249 (w), 1228 (w), 1210 (m), 1176 (m), 1126 (m), 1080 (s, ν(COC)), 1026 (m, ν(CO)), 901 (m), 849 (w), 833 (w), 768 (s), 733 (s), 700 (s), 664 (w). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*S*): δ = 0.86 (t, 3H, *J* = 7.4 Hz, CH_2CH_3), 0.89 (t, 3H, *J* = 7.4 Hz, CCH_2CH_3), 0.93 (t, 3H, *J* = 7.4 Hz, CCH_2CH_3'), 1.28 (m, 3H, NCH_2CH_2, NCHCHH′), 1.48 (m, 9H, NCHCHH′, CCH_2CH_2, CH_2CH_3, CCH_2CH_3, CCH_2CH_3'), 1.63 (s, 3H, CH_3), 1.74 (m, 2H, CCH_2), 2.88 (dt, 1H, *J* = 10.8 Hz, 7.1 Hz, NCHH′), 2.98 (ddd, 1H, *J* = 10.8 Hz, 6.7 Hz, 3.7 Hz, NCHH′), 3.27 (s, 3H, OCH_3), 3.56 (dd, 1H, *J* = 9.4 Hz, 5.0 Hz, NCH), 7.42 (m, 3H, $CH_{arom.}$), 7.73 (m, 2H, $CH_{arom.}$) ppm; - (2′*S*,5*R*): δ = 0.87 (t, 3H, *J* = 7.4 Hz, CH_2CH_3), 0.93 (t, 3H, *J* = 7.4 Hz, CCH_2CH_3), 0.95 (t, 3H, *J* = 7.4 Hz, CCH_2CH_3'), 1.18 (m, 1H, NCH_2CHH'), 1.40 (s, 3H, CH_3), 1.56 (m, 11H, NCH_2CHH', $NCHCH_2$, CCH_2CH_2, CH_2CH_3, CCH_2CH_3, CCH_2CH_3'), 1.87 (m, 1H, CCHH′), 2.08 (m, 1H, CCHH′), 2.87 (m, 1H, NCHH′), 2.98 (m, 1H, NCHH′), 3.27 (s, 3H, OCH_3), 3.54 (dd, 1H, *J* = 9.1 Hz, 5.0 Hz, NCH), 7.42 (m, 3H, $CH_{arom.}$), 7.73 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*S*): δ = 8.4 (CCH_2CH_3), 14.1 (CH_2CH_3), 19.4 (CCH_3), 23.1 (NCH_2CH_2), 23.9 (CH_2CH_3), 24.6, 26.2 (CCH_2CH_3), 25.0 (CH_2), 26.7 ($NCHCH_2$), 39.8 (CCH_2), 50.3 (OCH_3), 53.4 (NCH_2), 69.7 (NCH), 80.3 (C), 103.0 (OCN), 128.5, 129.1, 130.7 (CH arom.), 128.7 (C arom.), 158.9 (C=N) ppm; (2′*S*,5*R*): δ = 8.4, 8.5 (CCH_2CH_3), 14.0 (CH_2CH_3), 23.5 (NCH_2CH_2), 23.5 (CCH_3), 24.0 (CH_2CH_3), 24.6, 26.5 (CCH_2CH_3), 25.1 (CH_2), 26.6 ($NCHCH_2$), 34.6 (CCH_2), 50.2 (OCH_3), 53.9 (NCH_2), 69.5 (NCH), 80.4 (C), 102.1 (OCN), 128.5, 129.2, 130.6 (CH arom.), 128.8 (C arom.), 158.5 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 387 (5) [M^+], 286 (26) [M^+–$C(CH_2CH_3)_2OCH_3$], 217 (19), 188 (14), 187 (98), 186 (84) [M^+–$C_6H_{12}O$, –$C(CH_2CH_3)_2OCH_3$], 175 (28), 167 (19), 162 (10), 161 (100), 146 (23), 145 (43), 131 (21), 127 (30), 119 (17) [$C_6H_5C{\equiv}N$-O^+], 117 (24) [M^+–SEP, –$C_6H_{12}O$], 106 (20), 104 (40), 101 (40) [$C(CH_2CH_3)_2OCH_3^+$], 100 (9) [$C_6H_{12}O^+$], 99 (58), 97 (10), 95 (23), 86 (24), 85 (13), 71 (14), 70 (27), 69 (25), 68 (11), 59 (17), 58 (10), 57 (29), 55 (23). - Anal. Calcd for $C_{23}H_{37}N_3O_2$: C, 71.28; H, 9.62; N, 10.84. Found: C, 71.23; H, 9.93; N, 11.00.

(2′S,5S)-(–)-4-[2-(1-Ethyl-1-methoxylpropyl)tetrahydro-1H-1-pyrrolyl]-5-methyl-5-phenylethyl-3-phenyl-4,5-dihydro-1,2,4-oxadiazole [7j]. 0.27 g (0.86 mmol) of benzylacetone SAEP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.27 g of (2′*S*,5*S*)-**7j** (73%) as a colorless oil after

column chromatography (silica gel; petroleum ether: ether 5:1). - *de* = 82%. - (2′*S*,5*S*)-**7j**: $[\alpha]_D^{25}$ = –257.2 ° c = 0.99; $CHCl_3$). - IR ($CHCl_3$): $\tilde{\nu}$ = 3061 cm^{-1} (m), 3021 (m), 2966 (s), 2941 (s), 2879 (m), 2826 (m), 1603 (m), 1564 (w, ν(C=N)), 1496 (s), 1453 (s), 1382 (m), 1356 (m), 1337 (m), 1310 (m), 1283 (m), 1186 (m), 1161 (m), 1124 (m), 1080 (s, ν(COC)), 1030 (m, ν(CO)), 944 (w), 897 (m), 834 (w), 751 (s), 700 (s), 643 (w), 610 (w). - ^{1}H NMR ($CDCl_3$) δ = 0.87 (t, 3H, *J* = 7.7 Hz, C***H***$_3$), 0.94 (t, 3H, *J* = 7.7 Hz, C***H***$_3$′), 1.02 (m, 1H, NCH_2CHH'), 1.22 (m, 1H, NCH_2CHH'), 1.48 (m, 1H, NCHC***H***H′), 1.56 (m, 4H, C***H***$_2CH_3$) 1.71 (s, 3H, CCH_3), 1.73 (m, 1H, NCHCH***H***′), 1.92 (dt, 1H, *J* = 12.4 Hz, 5.5 Hz, CC***H***H′), 2.06 (dt, 1H, *J* = 12.4 Hz, 5.0 Hz, CCH***H***′), 2.85 (m, 3H, $C_6H_5CH_2$, NC***H***H′), 3.02 (m, 1H, NCH***H***′), 3.27 (s, 3H, OCH_3), 3.61 (dd, 1H, *J* = 9.1 Hz, 4.9 Hz, NCH), 7.22 (m, 5H, $CH_{arom.}$), 7.42 (m, 3H, $CH_{arom.}$), 7.74 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C-NMR ($CDCl_3$): δ = 8.4, 8.5 (CCH_2CH_3), 19.6 (CCH_3), 24.0 (NCH_2CH_2), 24.6, 25.1 (CCH_2CH_3), 26.6 ($NCHCH_2$), 30.5 ($CH_2C_6H_5$), 42.2 (CCH_2), 50.2 (OCH_3), 53.6 (NCH_2), 69.8 (NCH), 80.3 (C), 102.5 (OCN), 125.8, 128.4, 128.5, 128.6, 129.2, 130.8 (CH arom.), 128.4, 142.2 (C arom.), 159.0 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 435 (2) [M^+], 335 (10), 334 (41) [M^+–$C(CH_2CH_3)_2OCH_3$], 266 (10), 265 (40), 236 (11), 235 (56), 215 (15), 187 (14), 186 (93) [M^+–$C_{10}H_{12}O$, -$C(CH_2CH_3)_2OCH_3$], 185 (7), 161 (28), 148 (18) [$C_{10}H_{12}O^+$], 145 (30), 144 (56), 133 (7), 132 (24), 131 (23), 128 (5), 127 (37), 124 (10), 119 (35) [$C_6H_5C{\equiv}N\text{-}O^+$], 118 (6), 117 (36) [$M^+$–SEP, –$C_{10}H_{12}O$], 106 (10), 105 (100), 104 (75), 103 (17) [$C_6H_5C{\equiv}N^+$], 102 (6), 101 (65) [$C(CH_2CH_3)_2OCH_3^+$], 99 (52), 95 (16), 91 (35), 86 (18), 77 (18), 71 (10), 70 (31), 69 (18), 59 (22), 55 (12), 45 (15). - Anal. Calcd for $C_{27}H_{37}N_3O_2$: C, 74.45; H, 8.56; N, 9.65. Found: C, 74.04; H, 8.56; N, 9.52.

(2′*S*,5*S*)-(–)-5-Ethyl-4-[2-(1-ethyl-1-methoxylpropyl)tetrahydro-1*H*-1-pyrrolyl]-3,5-diphenyl-4,5-dihydro-1,2,4-oxadiazole [7k]. 0.26 g (0.86 mmol) of propiophenone SAEP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.18 g of (2′*S*,5*S*)-**7k** (50%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 10:1). - *de* = ≥97%.[22]. - (2′*S*,5*S*)-**7k**: $[\alpha]_D^{24}$ = –266.2 ° (0.68; $CHCl_3$); mp 117-119 °C. - IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (m), 3025 (w), 2970 (s), 2941 (s), 2882 (s), 2824 (m), 1602 (w), 1584 (w), 1557 (m, ν(C=N)), 1493 (m), 1464 (s), 1448 (s), 1374 (m), 1336 (s), 1310 (m), 1283 (s), 1222 (m), 1168 (s), 1093 (s), 1071 (s, ν(COC)), 1028 (m, ν(CO)), 1003 (m), 947 (m), 926 (s), 882 (s), 835 (m), 780 (s), 761 (s), 724 (s), 703 (s), 667 (m), 620 (w), 555 (m). - ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 6H, *J* = 7.4 Hz, CH_2CH_3, C***H***$_3$), 0.97 (t, 3H, *J* = 7.4 Hz, CH_2CH_3'), 1.46 (m, 5H, NCH_2CH_2, $NCHCH_2$, C***H***H′CH_3), 1.66 (dq, 1H, *J* = 15.1 Hz, 7.4 Hz, CH***H***′CH_3), 1.76 [dq, 1H, *J* = 15.1 Hz, 7.4 Hz, (C***H***H′CH_3)′], 1.84 [dq, 1H, *J* = 14.8 Hz, 7.4 Hz, (CH***H***′CH_3)′], 2.27 (qd, 2H, *J* = 7.4 Hz, 1.7 Hz, CH_2), 2.96 (dt, 1H, *J* = 11.0 Hz, 7.1 Hz, NC***H***H′), 3.06 (ddd, 1H, *J* = 12.4 Hz, 11.2 Hz, 6.3 Hz, NCH***H***′), 3.30 (s, 3H, OCH_3), 3.65 (dd, 1H, *J* = 9.3 Hz, 4.7 Hz, NCH), 7.31 (m, 6H, $CH_{arom.}$), 7.65 (m, 2H, $CH_{arom.}$), 7.78 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$): δ = 8.1 (CH_2CH_3), 8.7, 8.8 (CCH_2CH_3), 24.5 (NCH_2CH_2), 24.9, 25.2 (CCH_2CH_3), 26.5 ($NCHCH_2$), 27.9 (CH_2CH_3), 50.0 (OCH_3),

52.9 (NCH_2), 70.2 (NCH), 80.6 (C), 105.0 (OCN), 127.0, 127.5, 127.6, 128.3, 129.2, 130.8 (CH arom.), 128.3, 142.5 (C arom.), 159.1 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 421 (2) [M^+], 320 (43) [M^+–$C(CH_2CH_3)_2OCH_3$], 222 (12), 221 (66), 206 (27), 186 (80) [M^+–$C_9H_{10}O$, -$C(CH_2CH_3)_2OCH_3$], 145 (28), 134 (9) [$C_9H_{10}O^+$], 132 (15), 127 (55), 124 (12), 119 (11) [$C_6H_5C{\equiv}N\text{-}O^+$], 118 (12), 117 (78) [$M^+$–SEP, –$C_9H_{10}O$], 115 (15), 105 (75), 104 (19), 103 (30) [$C_6H_5C{\equiv}N^+$], 101 (89) [$C(CH_2CH_3)_2OCH_3^+$], 100 (14), 99 (100), 95 (29), 91 (17), 86 (28), 85 (13), 77 (51), 71 (15), 70 (27), 69 (27), 68 (11), 67 (12), 59 (34), 57 (18), 55 (19), 51 (14), 45 (22). - Anal. Calcd for $C_{26}H_{35}N_3O_2$: C, 74.08; H, 8.37; N, 9.97. Found: C, 73.88; H, 8.27; N, 9.89.

Crystal data and experimental details:[15,25] Data were collected on an ENRAF-NONIUS CAD4 diffractometer at ambient temperature (25°C) employing monochromated CuK_α radiation (λ=1.54179 Å). The structure was solved by direct methods. Orthorhombic space group $P2_12_12_1$ (No. 19), a = 8.264 (2), b = 10.4678 (5), c = 25.988 (2) Å, Z = 4, $D_{calc.}$ = 1.163 gcm^{-1}, μ=5.56 cm^{-1}. Measured reflections 5494 (Friedel pairs collected), unique refl. 4490, obs. refl. 1935, no. of parameters 263, R = 0.076, (R_W = 0.062). Further crystal data, anisotropic displacement parameters, final atomic positional coordinates, bond lengths and bond angles have been deposited in the Cambridge Crystallografic Data Centre as supplementary publication CCDC - 102776. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, [fax: 44-1223-336-033, e-mail: deposit@chemcrys.cam.ac.uk].

(2′*S*,5*S*/*R*)-(–)-4-{2-[Methoxy(diphenyl)methyl]tetrahydro-1*H*-1-pyrrolyl}-5-methyl-3-phenyl-5-propyl-4,5-dihydro-1,2,4-oxadiazole [7l]. 0.23 g (0.66 mmol) of 2-pentanone SAPP hydrazone, 0.18 mL (1.32 mmol) of triethylamine and 0.21 g (1.32 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.23 g of (2′*S*,5*S*/*R*)-**7l**[23] (74%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 8:1). - *de* = 55%. - (2′*S*,5*S*)-**7l**: $[\alpha]_D^{22}$ = –216.9 ° (c = 2.44; $CHCl_3$); mp 47-49 °C. - (2′*S*,5*R*)-**7l**: $[\alpha]_D^{22}$ = –167.4 ° (c = 0.80; $CHCl_3$; *de* = 76%); mp 44-46 °C. - IR (KBr): $\tilde{\nu}$ = 3088 cm^{-1} (m), 3059 (s), 3034 (s), 3024 (s), 2959 (s), 2932 (s), 2874 (s), 2852 (s), 2826 (s), 1716 (m), 1664 (m), 1623 (m), 1601 (m), 1567 (m, ν(C=N)), 1494 (s), 1447 (s), 1381 (s), 1338 (s), 1317 (m), 1290 (m), 1245 (m), 1220 (s), 1179 (s), 1157 (s), 1131 (m), 1075 (s, ν(COC)), 1033 (s, ν(CO)), 1002 (m), 962 (m), 918 (s), 902 (s), 830 (m), 761 (s), 700 (s), 671 (m), 639 (m), 623 (m). - ^1H NMR ($CDCl_3$) (2′*S*,5*S*): δ = 0.62 (m, 1H, NCH_2CHH'), 0.88 (t, 3H, *J* = 6.7 Hz, CH_2CH_3), 0.99 (m, 1H, NCH_2CHH'), 1.34 (m, 5H, $NCHCH_2$, $CCHH'$, CH_2CH_3), 1.39 (s, 3H, CH_3), 1.53 (m, 1H, $CCHH'$), 2.47 (ddd, 1H, *J* = 10.7 Hz, 8.6 Hz, 3.4 Hz, $NCHH'$), 2.65 (dt, 1H, *J* = 10.4 Hz, 9.1 Hz, $NCHH'$), 2.91 (s, 3H, OCH_3), 4.65 (br d, 1H, *J* = 8.7 Hz, NCH), 7.37 (m, 11H, $CH_{arom.}$), 7.60 (m, 2H, $CH_{arom.}$), 7.83 (m, 2H, $CH_{arom.}$) ppm; (2′*S*,5*R*): δ = 0.62 (m, 1H, NCH_2CHH'), 0.99 (t, 3H, *J* = 7.4 Hz, CH_2CH_3), 1.00 (m, 2H, NCH_2CHH', $NCHCHH'$), 1.25 (s, 3H, CH_3), 1.45 (m, 3H, $NCHCHH'$, CH_2CH_3), 1.80 (m, 2H, CCH_2), 2.46 (ddd, 1H, *J* = 10.7 Hz, 9.1 Hz, 3.4 Hz, $NCHH'$), 2.63 (dt, 1H, *J* = 10.7 Hz, 8.7 Hz, $NCHH'$),

2.95 (s, 3H, OCH_3), 4.65 (dd, 1H, J = 9.7 Hz, 1.3 Hz, NCH), 7.36 (m, 9H, $CH_{arom.}$), 7.48 (m, 2H, $CH_{arom.}$), 7.56 (m, 2H, $CH_{arom.}$), 7.80 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*S*): δ = 14.4 ($CH_2\boldsymbol{C}H_3$), 17.3 ($\boldsymbol{C}H_2CH_3$), 19.5 ($C\boldsymbol{C}H_3$), 23.8 ($NCH_2\boldsymbol{C}H_2$), 25.9 ($NCH\boldsymbol{C}H_2$), 41.8 ($C\boldsymbol{C}H_2$), 51.6 (OCH_3), 53.3 (NCH_2), 73.0 (NCH), 86.3 (C), 102.8 (OCN), 127.1, 127.3, 127.5, 128.7, 129.6, 130.3, 130.8 (CH arom.), 128.6, 140.0, 141.4 (C arom.), 158.9 (C=N) ppm; (2′*S*,5*R*): δ = 14.9 ($CH_2\boldsymbol{C}H_3$), 17.6 ($\boldsymbol{C}H_2CH_3$), 22.8 ($C\boldsymbol{C}H_3$), 23.7 ($NCH_2\boldsymbol{C}H_2$), 26.0 ($NCH\boldsymbol{C}H_2$), 37.0 ($C\boldsymbol{C}H_2$), 51.5 (OCH_3), 53.4 (NCH_2), 72.2 (NCH), 86.3 (C), 102.1 (OCN), 127.1, 127.4, 128.3, 128.7, 128.9, 129.6, 130.3, 130.8 (CH arom.), 127.8, 140.3, 141.6 (C arom.), 158.4 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 272 (39) [M^+–$C(C_6H_5)_2OCH_3$], 203 (22), 198 (16), 197 (100) [$C(C_6H_5)_2OCH_3^+$], 186 (51) [M^+–$C_5H_{10}O$, –$C(C_6H_5)_2OCH_3$], 173 (80), 161 (69), 153 (8), 145 (17), 144 (17), 132 (11), 131 (23), 119 (32) [$C_6H_5C{\equiv}N\text{-}O^+$], 117 (18) [$M^+$–SPP, –$C_5H_{10}O$], 105 (49), 104 (4077 (35), 70 (11). - Anal. Calcd for $C_{30}H_{35}N_3O_2$: C, 76.73; H, 7.51; N, 8.95. Found: C, 76.67; H, 7.67; N, 8.84.

(2′*S*,5*S*/*R*)-(–)-5-Butyl-4-{2-[methoxy(diphenyl)methyl]tetrahydro-1*H*-1-pyrrolyl}-5-methyl-3-phenyl-4,5-dihydro-1,2,4-oxadiazole [7m]. 0.23 g (0.63 mmol) of 2-hexanone SAPP hydrazone, 0.18 mL (1.26 mmol) of triethylamine and 0.20 g (1.26 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.18 g of (2′*S*,5*S*/*R*)-**7m**[23] (60%) as a colorless oil after column chromatography (silica gel; petroleum ether: ether 8:1). - *de* = 57%. - (2′*S*,5*S*)- **7m**: $[\alpha]_D^{25}$ = –186.9 ° (c = 0.34; $CHCl_3$); mp 47-49 °C. - (2′*S*,5*R*)-**7m**: $[\alpha]_D^{25}$ = –133.9 ° (c = 0.23; $CHCl_3$; *de* = 89%). - IR (neat): $\tilde{\nu}$ = 3087 cm^{-1} (m), 3059 (s), 3033 (m), 2955 (s), 2872 (s), 2825 (s), 1686 (w), 1657 (m), 1600 (m), 1564 (m, ν(C=N)), 1494 (s), 1446 (s), 1383 (s), 1337 (s), 1245 (m), 1209 (m), 1177 (s), 1156 (s), 1127 (s), 1073 (s, ν(COC)), 1030 (s, ν(CO)), 964 (m), 897 (s), 830 (m), 761 (s), 700 (s). - ^{1}H NMR ($CDCl_3$) (2′*S*,5*S*): δ = 0.62 (m, 1H, $NCH_2C\boldsymbol{H}H'$), 0.89 (t, 3H, J = 7.1 Hz, $CH_2C\boldsymbol{H}_3$), 0.94 (m, 2H, $NCH_2CH\boldsymbol{H}'$, $NCHC\boldsymbol{H}H'$), 1.27 (m, 5H, $NCHCH\boldsymbol{H}'$, $CCH_2C\boldsymbol{H}_2$, $C\boldsymbol{H}_2CH_3$), 1.39 (s, 3H, CH_3), 1.44 (m, 1H, $CC\boldsymbol{H}H'$), 1.57 (m, 1H, $CCH\boldsymbol{H}'$), 2.47 (ddd, 1H, J = 10.7 Hz, 8.7 Hz, 3.4 Hz, $NC\boldsymbol{H}H'$), 2.65 (dt, 1H, J = 10.7 Hz, 8.7 Hz, $NCH\boldsymbol{H}'$), 2.92 (s, 3H, OCH_3), 4.64 (dd, 1H, J = 8.3 Hz, 0.8 Hz, NCH), 7.37 (m, 9H, $CH_{arom.}$), 7.59 (m, 3H, $CH_{arom.}$), 7.80 (m, 3H, $CH_{arom.}$) ppm; (2′*S*,5*R*): δ = 0.62 (m, 1H, $NCH_2C\boldsymbol{H}H'$), 0.90 (m, 2H, $NCH_2CH\boldsymbol{H}'$, $NCHC\boldsymbol{H}H'$), 0.94 (t, 3H, J = 7.1 Hz, $CH_2C\boldsymbol{H}_3$), 1.23 (s, 3H, CH_3), 1.45 (m, 6H, $NCHCH\boldsymbol{H}'$, $CC\boldsymbol{H}H'$, $CCH_2C\boldsymbol{H}_2$, $C\boldsymbol{H}_2CH_3$), 1.80 (m, 1H, $CC\boldsymbol{H}H'$), 2.48 (m, 1H, $NC\boldsymbol{H}H'$), 2.62 (m, 1H, $NCH\boldsymbol{H}'$), 2.94 (s, 3H, OCH_3), 4.62 (dd, 1H, J = 9.3 Hz, 1.4 Hz, NCH), 7.39 (m, 11H, $CH_{arom.}$), 7.57 (m, 2H, $CH_{arom.}$), 7.80 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$) (2′*S*,5*S*): δ = 14.1 ($CH_2\boldsymbol{C}H_3$), 19.3 ($C\boldsymbol{C}H_3$), 23.0 ($NCH_2\boldsymbol{C}H_2$), 23.8 ($\boldsymbol{C}H_2CH_3$), 25.9 (CH_2), 26.2 ($NCH\boldsymbol{C}H_2$), 39.2 ($C\boldsymbol{C}H_2$), 51.6 (OCH_3), 53.2 (NCH_2), 72.9 (NCH), 86.4 (C), 102.9 (OCN), 127.1, 127.3, 127.5, 128.3, 128.8, 128.9, 129.6, 130.3, 130.8 (CH arom.), 128.3, 141.2, 141.9 (C arom.), 159.0 (C=N) ppm; (2′*S*,5*R*): δ = 13.8 ($CH_2\boldsymbol{C}H_3$), 22.9 ($C\boldsymbol{C}H_3$), 23.4 ($NCH_2\boldsymbol{C}H_2$), 23.7 ($\boldsymbol{C}H_2CH_3$), 25.9 (CH_2), 26.3 ($NCH\boldsymbol{C}H_2$), 34.4 ($C\boldsymbol{C}H_2$), 51.5 (OCH_3), 53.4 (NCH_2), 72.3 (NCH), 86.3 (C), 102.3 (OCN), 127.1, 128.3, 128.6, 129.2, 129.8, 130.8 (CH arom.),

128.6, 140.1, 141.4 (C arom.), 158.5 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 198 (21), 197 (100) [$C(C_6H_5)_2OCH_3$], 187 (15), 186 (14) [M^+–$C_6H_{12}O$, -$C(C_6H_5)_2OCH_3$], 161 (38), 119 (45) [$C_6H_5C{\equiv}N$-O^+], 105 (26), 100 (16) [$C_6H_{12}O^+$], 77 (20), 70 (20), 69 (10), 58 (48), 57 (17). - Anal. Calcd for $C_{31}H_{37}N_3O_2$: C, 76.99; H, 7.71; N, 8.69. Found: C, 77.10; H, 7.58; N, 8.67.

(2′*S*,5*S*)-(–)-4-{2-[Methoxy(diphenyl)methyl]tetrahydro-1*H*-1-pyrrolyl}-5-methyl-5-phenylethyl-3-phenyl-4,5-dihydro-1,2,4-oxadiazole [7n]. 0.35 g (0.86 mmol) of benzylacetone SAPP hydrazone, 0.24 mL (1.72 mmol) of triethylamine and 0.27 g (1.72 mmol) of phenylhydroxamoyl chloride reacted for 24 h according to the general procedure 2, yielding 0.17 g of (2′*S*,5*S*)-**7n** (52%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 7:1). - *de* = 66%. - (2′*S*,5*S*)- **7n**: $[\alpha]_D^{25}$ = –227.3 ° (c = 1.12; $CHCl_3$); mp 55-58 °C. - IR ($CHCl_3$): $\tilde{\nu}$ = 3085 cm^{-1} (w), 3059 (m), 3025 (m), 2938 (m), 2879 (m), 2824 (w), 1602 (m), 1562 (w, ν(C=N)), 1495 (m), 1447 (s), 1381 (m), 1355 (m), 1337 (m), 1312 (w), 1283 (w), 1244 (w), 1219 (m), 1188 (m), 1160 (m), 1125 (m), 1073 (s, ν(COC)), 1031 (m, ν(CO)), 1002 (w), 965 (w), 897 (m), 832 (w), 759 (s), 700 (s), 669 (w), 622 (w). - ^1H NMR ($CDCl_3$) δ= 0.63 (m, 1H, NCH_2CHH'), 0.86 (m, 1H, NCH_2CHH'), 0.97 (m, 1H, $NCHCHH'$), 1.39 (m, 1H, $NCHCHH'$), 1.45 (s, 3H, CH_3), 1.67 (td, 1H, *J* = 13.4 Hz, 4.9 Hz, $CCHH'$), 1.94 (td, 1H, *J* = 13.7 Hz, 4.6 Hz, $CCHH'$), 2.50 (ddd, 1H, *J* = 10.7 Hz, 8.9 Hz, 3.4 Hz, $NCHH'$), 2.66 (td, 1H, *J* = 12.9 Hz, 4.9 Hz, C_6H_5CHH'), 2.67 (dt, 1H, *J* = 10.7 Hz, 8.6 Hz, $NCHH'$), 2.78 (td, 1H, *J* = 13.1 Hz, 4.6 Hz, C_6H_5CHH'), 2.91 (s, 3H, OCH_3), 4.67 (dd, 1H, *J* = 9.5 Hz, 1.2 Hz, NCH), 7.30 (m, 12H, $CH_{arom.}$), 7.48 (m, 4H, $CH_{arom.}$), 7.59 (m, 2H, $CH_{arom.}$), 7.82 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C NMR ($CDCl_3$): δ= 19.2 (CCH_3), 23.8 (NCH_2CH_2), 25.9 ($NCHCH_2$), 30.6 ($CH_2C_6H_5$), 41.3 (CCH_2), 51.6 (OCH_3), 53.3 (NCH_2), 73.2 (NCH), 86.4 (C), 102.3 (OCN), 125.7, 127.1, 127.3, 127.4, 127.5, 128.4, 128.7, 128.9, 129.6, 130.3, 130.8 (CH arom.), 128.3, 139.8, 141.1, 142.2 (C arom.), 159.0 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 198 (21), 197 (100) [$C(C_6H_5)_2OCH_3$], 186 (22) [M^+–$C_{10}H_{12}O$, -$C(C_6H_5)_2OCH_3$], 161 (18), 148 (56) [$C_{10}H_{12}O^+$], 119 (22) [$C_6H_5C{\equiv}N$-O^+], [M^+–SPP, –$C_{10}H_{12}O$], 105 (79), 104 (16), 103 (10) [$C_6H_5C{\equiv}N^+$], 91 (43), 79 (11), 77 (28), 70 (16), 69 (22), 68 (12), 57 (11). - Anal. Calcd for $C_{35}H_{37}N_3O_2$: C, 79.06; H, 7.01; N, 7.90. Found: C, 79.07; H, 7.50; N, 7.42.

(5*S*)-(–)-5-Methyl-3-phenyl-5-propyl-4,5-dihydro-1,2,4-oxadiazole [8a]. a) 0.05 g (0.14 mmol) of (2′*S*,5*S*) -**7d** and 0.1 g (20 mmol) of formic acid reacted for 40 min according to the general procedure 3, yielding 0.02 g of **8a** (67%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*S*)-**8a**: *ee* = 74%.[26]- b) 0.05 g (0.13 mmol) of (2′*S*,5*S*)-**7h** and 0.1 g (20 mmol) of formic acid reacted for 10 min according to the general procedure 3 and 80% conversion, yielding **8a** and 0.01g of **7h** after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*S*)-**8a**: *ee* = 83%.[26] - c) 0.03 g (0.06 mmol) of (2′*S*,5*S*)-**7l** and 0.1 g (20 mmol) of formic acid reacted for 15 min according to the general procedure 3, yielding 0.02 g **8a** (100%) as a colorless solid after column chromatography (silica

gel; petroleum ether: ether 3:1). - (5*S*)-**8a**: *ee* = 43%.[26] - d) 0.02 g (0.04 mmol) of *(2´S,5R)*-**7l** and 0.1 g (20 mmol) of formic acid reacted for 10 min according to the general procedure 3, yielding **8a** as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*R*)-**8a**: *ee* = 36%.[26] - (5*S*)-**8a**: $[\alpha]_D^{21}$ = –30.9 ° (c = 1.71; $CHCl_3$; *ee* = 83%). - (5*R*)-**8a**: $[\alpha]_D^{21}$ = +11.6 ° (c = 0.50; $CHCl_3$; *ee* = 36%). - mp 123-125 °C. - IR (KBr): $\tilde{\nu}$ = 3202 cm^{-1} (s, ν(NH)), 3061 (m), 2957 (s), 2932 (s), 2874 (s), 1715 (m), 1600 (s), 1569 (m, ν(C=N)), 1511 (s), 1468 (s), 1437 (s), 1367 (s), 1347 (m), 1293 (m), 1259 (s), 1228 (m), 1178 (m), 1144 (m), 1121 (m), 1073 (m), 1032 (m, ν(CO)), 985 (w), 958 (w), 908 (m), 870 (s), 831 (s), 764 (s), 691 (s), 675 (s), 630 (m), 513 (m). - ^{1}H NMR ($CDCl_3$) δ= 0.96 (t, 3H, *J* = 7.4 Hz, CH_2CH_3), 1.49 (m, 2H, CH_2CH_3), 1.54 (s, 3H, CH_3), 1.78 (m, 2H, CCH_2), 2.20 (m, 2H, CCH*H´*), 4.44 (br s, 1H, NH), 7.41 (m, 3H, $CH_{arom.}$), 7.68 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C-NMR ($CDCl_3$): δ = 14.2 (CH_2CH_3), 17.0 (CH_2CH_3), 26.1 (CH_3), 42.8 (CCH_2), 98.8 (C), 126.1 (C_{arom}), 126.3, 128.7, 130.6 (CH_{arom}), 155.1 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 204 (9) [M^+], 161 (35) [M^+–C_3H_7], 119 (100) [$C_6H_5C{\equiv}N\text{-}O^+$], 104 (14), 77 (22), 71 (11). - HRMS $C_{12}H_{16}N_2O$: Calcd 204.1263; found 204.1268.

(5*S*)-5-Butyl-5-methyl-3-phenyl-4,5-dihydro-1,2,4-oxadiazole [**8b**]. a) 0.18 g (0.54 mmol) of (2´*S*,5*S*)-**7a** and 4.9 g (100 mmol) of formic acid reacted for 120 min according to the general procedure 3, yielding 0.03 g of **8b** (25%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*S*)-**8b**: *ee* = 5%.[26] - b) 0.12 g (0.54 mmol) of *(2´S,5R)*-**7a** and 3.5 g (72 mmol) of formic acid reacted for 30 min according to the general procedure 3, yielding 0.02 g of **8b** (25%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*R*)-**8b**: *ee* = 17%.[26] - c) 0.13 g (0.36 mmol) of (2´*S*,5*S*)-**7e** and 3.5 g (72 mmol) of formic acid reacted for 80 min according to the general procedure 3, yielding 0.03 g of **8b** (38%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*S*)-**8b**: *ee* = 2%.[26] - d) 0.04 g (0.11 mmol) of *(2´S,5R)*-**7e** and 1.1 g (22 mmol) of formic acid reacted for 10 min according to the general procedure 3, yielding 0.02 g of **8b** (100%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*R*)-**8b**: *ee* = 26%.[26] - e) 0.17 g (0.44 mmol) of (2´*S*,5*S*)-**7i** and 4.3 g (88 mmol) of formic acid reacted for 10 min according to the general procedure 3, yielding 0.03 g of **8b** (30%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*S*)-**8b**: *ee* = 35%.[26] - f) 0.01 g (0.03 mmol) of *(2´S,5R)*-**7j** and 0.3 g (6 mmol) of formic acid reacted for 10 min according to the general procedure 3, yielding **8b** as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*R*)-**8b**: *ee* = 63%.[26] - g) 0.04 g (0.08 mmol) of (2´*S*,5*S*)-**7m** and 0.8 g (16 mmol) of formic acid reacted for 20 min according to the general procedure 3, yielding 0.05 g of **8b** (100%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*S*)-**8b**: *ee* = 55%.[26] - (5*S*)-**8b**: $[\alpha]_D^{23}$ = –32.9 ° (c = 0.73; $CHCl_3$; *ee* = 55%). - (5*R*)-**8b** $[\alpha]_D^{23}$ = +16.4 ° (c = 0.63; $CHCl_3$; *ee* = 63%). - mp 108-110 °C. - IR (KBr): $\tilde{\nu}$ = 3216 cm^{-1} (s, ν(NH)), 3062 (m), 2950 (s), 2933 (s), 2862 (s), 1601 (m), 1569

(m, ν(C=N)), 1511 (s), 1469 (s), 1436 (s), 1371 (m), 1340 (m), 1303 (m), 1291 (m), 1260 (m), 1246 (s), 1216 (m), 1178 (m), 1142 (m), 1120 (m), 1073 (s), 1027 (w, ν(CO)), 1001 (w), 984 (w), 939 (w), 920 (m), 884 (m), 869 (m), 839 (s), 786 (w). - ^{1}H NMR ($CDCl_3$) δ = 0.91 (t, 3H, J = 7.1 Hz, CH_2CH_3), 1.41 (m, 4H, CCH_2CH_2, CH_2CH_3), 1.54 (s, 3H, CH_3), 1.78 (m, 2H, CCH_2), 4.45 (br s, 1H, NH), 7.41 (m, 3H, $CH_{arom.}$), 7.66 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C-NMR ($CDCl_3$): δ = 14.0 (CH_2CH_3), 22.8 (CH_2CH_3), 25.8 (CH_2), 26.2 (CH_3), 40.3 (CCH_2), 98.9 (C), 126.2 (C arom.), 126.3, 128.7, 130.6 (CH arom.), 155.1 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 218 (6) [M^+], 161 (41) [M^+–C_4H_9], 119 (100) [$C_6H_5C{\equiv}N\text{-}O^+$], 104 (13), 77 (19). - HRMS $C_{13}H_{18}N_2O$: Calcd. 218.1419; found 218.1416.

(5S)-5-Methyl-5-phenylethyl-3-phenyl-4,5-dihydro-1,2,4-oxadiazole [8c]. a) 0.35 g (0.9 mmol) of (2′*S*,5*S*)-**7b** and 9.0 g (184 mmol) of formic acid reacted for 300 min according to the general procedure 3, yielding 0.04 g of **8c** (17%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 2:1). - (5*S*)-**8c**: *ee* = 17%.[26] - b) 0.13 g (0.34 mmol) of *(2′S,5R)*-**7b** and 9.0 g (184 mmol) of formic acid reacted for 20 min according to the general procedure 3 and 10% conversion, yielding **8c** and 0.12 g (0.31 mmol) of **7b** after column chromatography (silica gel; petroleum ether: ether 2:1). - (5*R*)-**8c**: *ee* = 91%.[26] - c) 0.15 g (0.37 mmol) of (2′*S*,5*S*)-**7f** and 3.6 g (74 mmol) of formic acid reacted for 8 min according to the general procedure 3 and 20% conversion, yielding **8c** and 0.12 g (0.30 mmol) of **7f** after column chromatography (silica gel; petroleum ether: ether 2:1). - (5*S*)-**8c**: *ee* = 81%.[26] - d) 0.05 g (0.12 mmol) of *(2′S,5R)*-**7f** (*de* = 84%) and 1.2 g (24 mmol) of formic acid reacted for 8 min according to the general procedure 3, yielding 0.03 g of **8c** (100%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 2:1). - (5*R*)-**8c**: *ee* = 75%.[26] - e) 0.09 g (0.21 mmol) of (2′*S*,5*S*)-**7j** and 2.1 g (42 mmol) of formic acid reacted for 8 min according to the general procedure 3, yielding 0.01 g of **8c** (20%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 2:1). - (5*S*)-**8c**: *ee* = 81%.[26] - f) 0.07 g (0.13 mmol) of (2′*S*,5*S*)**7n** and 1.3 g (26 mmol) of formic acid reacted for 5 min according to the general procedure 3 and 29% conversion, yielding **8c** and 0.05 g (0.09 mmol) of **7n** after column chromatography (silica gel; petroleum ether: ether 2:1). - (5*S*)-**8c**: *ee* = 65%.[26] - g) 0.04 g (0.21 mmol) of *(2′S,5R)*-**7n** (*de* = 65%) and 0.4 g (8 mmol) of formic acid reacted for 10 min according to the general procedure 3, yielding **8c** as a colorless solid after column chromatography (silica gel; petroleum ether: ether 2:1). - (5*R*)-**8c**: *ee* = 28%.[26] - (5*S*)-**8c**: $[\alpha]_D^{23}$ = –42.3 ° (c = 0.39; $CHCl_3$; *ee* = 81%). - (5*R*)-**8c**: $[\alpha]_D^{23}$ = +29.5 ° (c = 0.73; $CHCl_3$; *ee* = 91%). - mp 158-159 °C. - IR (KBr): $\tilde{\nu}$ = 3197 cm^{-1} (s, ν(NH)), 3084 (m), 3059 (m), 3025 (m), 2978 (m), 2947 (m), 2924 (s), 2856 (m), 1618 (w), 1600 (s), 1566 (m, ν(C=N)), 1513 (s), 1497 (m), 1469 (s), 1437 (s), 1376 (m), 1331 (w), 1320 (w), 1292 (m), 1272 (m), 1238 (s), 1220 (m), 1157 (m), 1124 (m), 1071 (m), 1028 (m, ν(CO)), 985 (m), 931 (m), 939 (w), 920 (m), 870 (m), 849 (s), 772 (s), 743 (m), 698 (s), 668 (m). - ^{1}H NMR ($CDCl_3$) δ = 1.60 (s, 3H, CH_3), 2.09 (dt, 1H, J = 14.0 Hz, 8.0 Hz, $CCHH'$), 2.16 (ddd, 1H, J = 14.0 Hz, 8.2 Hz, 7.4 Hz, $CCHH'$), 2.84 (t, 2H, J = 8.2 Hz, $C_6H_5CH_2$), 4.42 (br s, 1H, NH), 7.40 (m, 3H, $CH_{arom.}$), 7.63 (m, 2H, $CH_{arom.}$)

ppm. - ^{13}C-NMR ($CDCl_3$): δ = 26.5 (CH_3), 29.9 ($\mathbf{C}H_2C_6H_5$), 42.1 (C$\mathbf{C}H_2$), 98.5 (C), 125.9 (C arom.), 126.0, 126.3, 128.4, 128.5, 128.7, 130.7 (CH arom.), 141.6 (C arom.), 155.2 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 266 (7) [M^+], 161 (68) [M^+–C_8H_9], 120 (10), 119 (100) [$C_6H_5C{\equiv}N$-O^+], 105 (14) [$C_8H_9^+$], 104 (11), 91 (19), 77 (18). - Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.13; H, 6.87; N, 10.33.

(5S)-5-Ethyl-3,5-diphenyl-4,5-dihydro-1,2,4-oxadiazole [8d]. a) 0.10 g (0.27 mmol) of *(2´S,5R)*-**7c** and 2.6 g (54 mmol) of formic acid reacted for 30 min according to the general procedure 3, yielding 0.07 g of **8d** (100%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*R*)-**8d**: *ee* = 0%.[26] - b) 0.17 g (0.43 mmol) of (2´*S*,5*S*)-**7g** and 4.2 g (86 mmol) of formic acid reacted for 5 min according to the general procedure 3, yielding 0.10 g of **8d** (91%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*S*)-**8d**: *ee* = 56%.[26] - c) 0.02 g (0.05 mmol) of (2´*S*,5*S*)-**7k** and 0.5 g (10 mmol) of formic acid reacted for 5 min according to the general procedure 3, yielding 0.01 g of **8d** (100%) as a colorless solid after column chromatography (silica gel; petroleum ether: ether 3:1). - (5*S*)-**8d**: *ee* = 59%.[26] - (5*S*)-**8d**: $[\alpha]_D^{21}$ = –39.6 ° (c = 0.39; $CHCl_3$; *ee* = 56%). - mp 136-137 °C. - IR (KBr): $\tilde{\nu}$ = 3248 cm^{-1} (s, ν(NH)), 3081 (m), 3060 (m), 3027 (m), 2972 (s), 2929 (s), 2877 (m), 1655 (w), 1598 (m), 1565 (s, ν(C=N)), 1509 (s), 1460 (s), 1437 (s), 1384 (m), 1337 (m), 1290 (m), 1224 (s), 1175 (m), 1133 (m), 1074 (m), 1028 (m, ν(CO)), 997 (m), 977 (m), 956 (m), 900 (s), 868 (m). - ^{1}H NMR ($CDCl_3$) δ = 1.00 (t, 3H, *J* = 7.4 Hz, CH_3), 2.16 (q, 2H, *J* = 7.4 Hz, CH_2), 5.01 (br s, 1H, NH), 7.36 (m, 6H, $CH_{arom.}$), 7.55 (m, 2H, $CH_{arom.}$), 7.69 (m, 2H, $CH_{arom.}$) ppm. - ^{13}C-NMR ($CDCl_3$): δ = 7.9 (CH_3), 33.5 (C$\mathbf{C}H_2$), 100.6 (C), 124.9, 126.5, 128.5, 128.7 (CH arom.), 125.8 (C arom.), 128.2, 130.7 (CH arom), 143.2 (C arom.), 155.1 (C=N) ppm. - MS (70 eV); *m/z* (% b.p.) = 252 (6) [M^+], 223 (53) [M^+–C_2H_5], 105 (100), 77 (25). - Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 75.93; H, 6.33; N, 11.00.

ACKNOWLEDGMENTS

This work was supported by the *Fonds der Chemischen Industrie* and by the *Deutsche Forschungsgemeinschaft* (Leibniz prize). We thank the companies *BASF* AG, *Bayer AG*, *Degussa AG*, *Höchst AG* and *Boehringer Mannheim AG* for their donation of chemicals.

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Received, 4th September, 1998