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Diastereoselective 1,3-Dipolar Cycloaddition of Nitrilimines to γ-Oxygenated α,β-unsaturated Enones and Esters

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Abstract. The stereochemical outcome of the 1,3-dipolar cycloaddition of nitrilimines to γ-oxygenated α,β-unsaturated enones and esters was investigated. By means of X-ray and NMR analysis the main diastereomers were assigned as the *syn*-derivatives. Novel enantiomerically pure nitrilimines were included in the investigations but did not influence the stereochemical course of the cycloaddition significantly. Copyright © 1996 Elsevier Science Ltd

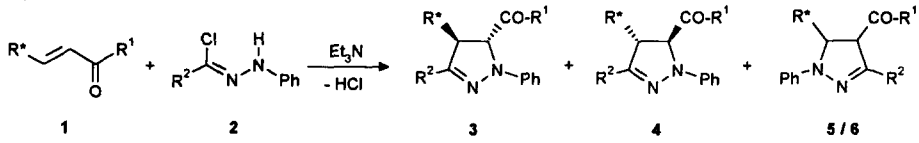
Introduction

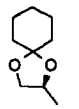
Chiral α,β-unsaturated ketones and esters oxygenated in γ-position have proved to be versatile starting materials in Diels-Alder reactions [1] and 1,3-dipolar cycloadditions.[2a-c] With regard to the stereochemical result, however, a complex picture emerges: For the cycloaddition with azomethine ylides[2a], nitrones[2b] and nitrile oxides[2c] high *anti*-selectivities ranging from >95 : 5 to 4 : 1 were observed. The first examples for a reversed stereoselection were found recently. The *syn*-adducts predominate in cycloadditions with diazo compounds and silylnitronates as dipoles.[3] Although it was predicted on the basis of quantum mechanical calculations, that the cycloaddition of nitrilimines to compounds **2** should allow a high degree of *anti*-stereoselection[2c] no experimental proof has been available for this hypothesis. Therefore we decided to investigate the cycloaddition of compounds **1** with nitrilimines in order to reveal the stereochemical outcome and to have a broad basis for theoretical considerations.[4]

Results and Discussion

The reaction of **1** with several nitrilimines generated in situ from hydrazonoyl chlorides **2** leads predominately to the formation of the 5-acetyl-pyrazolines **3** and **4**. A significant appearance of the 4-acyl isomers **5** and **6** was only observed with the diphenylnitrilimine (entry 5). [5,6] In other experiments (entry 8 and 9) only traces of regioisomers **5/6** were detected by HPLC. The differentiation of the regioisomers **3,4** and **5/6** rests on characteristic signals in the NMR spectra. In the ^{13}C-NMR spectra of the 5-acyl derivatives typical signals for C4 and C5 of the pyrazoline ring appear at 70 ppm (C5) and 53 ppm (C4), respectively, whereas the corresponding atoms of the regioisomers **5/6** show absorption about 60 - 65 ppm (C4,5). Furthermore, protons H4 and H5 exhibit characteristic coupling patterns for each isomer, due to the coupling with the residue R*.

Scheme 1



1	a	b	c
R*			
R^1	Me	Me	OEt

2	R^2
a	COOEt
b	Ph
c	COO-(-)-Menthyl
d	COO-(+)-Menthyl
e	(S)-COO-CH_2-$CH(CH_3)$-C_2H_5
f	COMe

Table 1: Synthesis of pyrazolines **3** and **4** from unsaturated carbonyl compounds **1** and hydrazonoyl chlorides **2**

entry	1	2	product	temp.	yield	ratio of diastereomers	
						3 : 4	**5/6**
1	**a**	**a**	**3a + 4a**	80°C	82 %	60 : 40	
2				25°C	76 %	70 : 30	
3				5°C	43 %	65 : 35	
4				-20°C [a]	14 %	67 : 33	
5	**a**	**b**	**3b + 4b + 5b/6b**	25°C	74 %	37 : 33	15 : 15
6	**a**	**c**	**3c + 4c + 5c/6c**	25°C	81 %	54 : 41	5 : 0
7	**a**	**d**	**3d + 4d + 5d/6d**	25°C	77 %	55 : 41	4 : 0
8	**a**	**e**	**3e + 4e**	25°C	79 %	60 : 40	
9	**a**	**f**	**3f + 4f**	25°C	15 %	60 : 40	
10	**b**	**a**	**3g + 4g**	25°C	68 %	67 : 33	
11	**c**	**a**	**3h + 4h**	25°C	71 %	61 : 59	

[a] n-BuLi instead of NEt_3 ; diethylether was used as solvent

The diastereoselectivity ranging from nearly 1 : 1 (entry 5) to 7 : 3 (entry 2) is only modest. Attempts to influence the stereoselection by means of temperature and base variation showed only marginal improvements (entry 1-4).

For the principal aim - the assignment of the absolute configuration of the major diastereomers - separation of the diastereomeric mixture was needed, which was difficult to achieve with chromatographic methods. Fortunately in the course of HPLC-investigations one pure diastereomer **3a** crystallized from the eluent spontaneously.

The X-ray analysis of compound **3a** (Figure 1) revealed that the H-atoms at C4 and R* exhibit a *syn*-relationship (e.g. considering the products **3** as depicted in scheme 1 the relative orientation of the H-atoms at the stereogenic centre R* and at the neighbouring ring C-atom is *syn*). Furthermore it is worth mentioning that

the dioxolane substituent is placed almost parallel and the phenyl substituent periplanar to the heterocyclic ring.

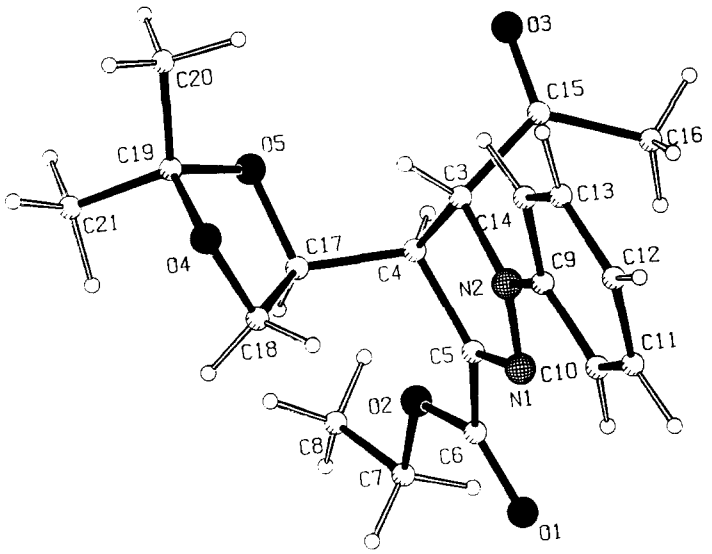
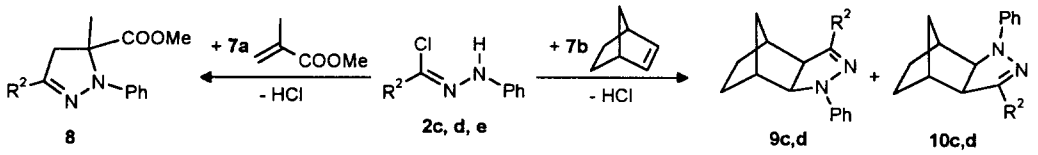


Fig. 1: X-ray structural analysis of compound **3a**

Based on the X-ray analysis of **3a** the other products can be assigned to *syn*- or *anti*-products by means of typical NMR-signals. For example the carbonyl group of the acyl residue gives a signal around 203 ppm (except for **3c** 206 ppm) for the *syn*-isomers **3**, whereas the *anti*-compounds **4** exhibit the corresponding resonance at 206 ppm (or greater). The shift difference of the two methyl groups of 2,2-dimethyldioxolane derivatives **3a-f,h** is in the range of 0.25 ppm, but for compounds **4a-f,g**, however, about 0.1 ppm.

In further attempts to improve the stereoselectivity of the cycloaddition (Scheme 1) novel enantiomerically pure hydrazonoyl chlorides **2c-e** were used possessing a chiral alkoxycarbonyl, such as menthyloxycarbonyl. To the best of our knowledge there is only one other example of enantiomerically pure nitrilimines, generated from a sugar hydrazone in the presence of $Pb(OAc)_4$. [7] Hence, we first performed reactions with simple dipolarophiles to test the suitability of compounds **2c-e** in asymmetric cycloadditions (Scheme 2). As expexted **2c,d** gave diastereospecificly the regioisomeric hexahydroindazole derivatives **9c,d** and **10c,d** in equal amounts by *exo-cis*-addition to norbornene.[8] After fractional crystallization one pure compound was separated, which however was not suitable for X-ray analysis. The cycloaddition of the chiral nitrilimines to methyl methylacrylate afforded 50 : 50 mixtures of diastereomers **8** in all cases.

Scheme 2



In agreement with this finding no significant influence on the stereochemical course of the addition of hydrazonoyl chlorides **2c-e** to enone **1a** (entry 6-8), sometimes even a slightly worse stereoselection, was found. It is worth noting that derivatives **2c** and **2d**, derived from (-) and (+)-menthyl derivatives, respectively, gave the same results. Obviously the stereocenters in the nitrilimine are placed too far from the reaction center to exert an asymmetric induction. Modelling investigations confirmed this assumption. Concerning the mechanism of the cycloaddition a transition state like in the cycloaddition of diazo compounds [3] to **1** is proposed, where the oxygen at the stereogenic centre occupies a position antiperiplanar with respect to the dipole attack ("antiperiplanar effect"[9]). Our results reported here and those published earlier [3] demonstrate that attempts to predict the stereochemical outcome of the cycloaddition of nitrilimines and diazomethane to α,β-unsaturated ketones and esters on the basis of quantum mechanical calculations [2c] have not been successful. Probably this failure was caused by the fact, that based on the known experimental data, it was assumed that all dipoles react with *anti*-preference and a reversed stereoselection was not taken into account. Theoretical calculations which also include the dependence of the facial selectivity on the nature of the dipole are currently underway in our laboratory.

Acknowledgement. We thank Dr. B. Ziemer for performing the X-ray analysis. G.G. thanks the Humboldt-Universität for a scholarship (NaFöG -Stipendium).

Experimental Part

The ^{1}H-NMR spectra were recorded on a Bruker AC-300 (300 MHz) spectrometer, the ^{13}C-NMR spectra were recorded on a Bruker AC-300 (75 MHz) spectrometer. The samples were dissolved in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad singlet. Elemental analysis were performed in a Leco CHNS-932 apparatus. Optical rotations were measured on a Perkin Elmer 241 polarimeter using a 10 cm cell (c = 1.0; $CHCl_3$). HPLC analyses were carried out on a Knauer instrument with HPLC Pump 64, variable wavelength monitor (detection at 220 and 350 nm) and Chiralyser software. Columns and parameters: a) Si-100, 5 µm, 250 • 4 (i.d.) mm, cyclohexane/2-propanol = 350:1, flow rate 1 ml/min; b) OD-H 250 • 4 (i.d.) mm, n-hexane/2-propanol = 15 : 1, flow rate 0.5 ml/min. In case of diastereomeric mixtures the analytical data of the major isomer and partly of the minor isomer were reported. Enones were prepared according to literature procedures (**1a**[10], **1b**[3]), enoate **1c** was purchased from Merck Co.

General Procedure[11] *for the Synthesis of Enantiomerically Pure Hydrazonoyl Chlorides.*

The corresponding chiral alcohol (0.1 mol) and 2,2,6-trimethyl-1,3-dioxine-4-one (0.1 mol) in xylene (20 ml) was heated to 140°C for 30 min. The 3-oxobutyrate thus formed was purified by distillation under reduced pressure. To 0.1 mol of 3-oxybutyrate was added SO_2Cl_2 (0.1 mol) so that the temperature did not exceed 40°C. After the reaction had finished, reduced pressure was used to remove gaseous HCl and SO_2 from the solution. The crude 2-chlor-3-oxo-butyrate was dissolved in ethanol (150 ml) and a solution of sodium acetate (13 g) in water (50 ml) was added. Diazonium salt (from 4.65 g of aniline, 17.5 ml of concentrated HCl, 27 ml of water, 3.4 g of $NaNO_2$) was added dropwise with stirring and cooling. After 3 hours stirring at 0-5°C the mixture was diluted with water (250 ml) and extracted with diethyl ether. Evaporation of the ether gave a red oil that was taken up with ethanol. The product was precipitated with water and recrystallized from ethanol/water.

(-)-1(*S*)-Menthyl chloro-(phenylhydrazono)-acetate 2c: *(-)-1(S)-Menthyl 3-oxo-butyrate:* 20.1 g, ^{1}H-NMR (δ/ppm, J/Hz): 4.66 (dt, 1H, H3'), 3.36 (s, 2H, H2), 2.19 (s, 3H, H4), 1.99-1.92 (m, 1H), 1.86-1.76 (m, 1H), 1.64-1.58 (m, 2H), 1.48-1.14 (m, 2H), 1.05-0.90 (m, 2H), 0.85-0.77 (m, 7H), 0.70 (d, 3H, H7'); ^{13}C-NMR (δ/ppm): 200.6 (C3), 166.7 (C1), 75.4 (C3'), 50.6 (C2), 46.8 (C4'), 40.6 (C2'), 34.1 (C6'), 31.3 (C1'), 30.0 (C4), 26.1 (C8'), 23.2 (C5'), 21.9 (C7'), 20.7 (C9'), 16.1 (C10'); $bp._{0.1\ Torr}$ 138°C (lit.: $bp._{0.1\ Torr}$ 95-102°C [12]), colourless oil; *(-)-1(S)-Menthyl 2-chlor-3-oxo-butyrate:* ^{1}H-NMR (δ/ppm, J/Hz): 4.80-4.71 (m, 1H, H3'), 4.76, 4.74 (s, 1H, H2), 2.37 (s, 3H, H4), 2.05-1.97 (m, 1H), 1.91-1.76 (m, 1H), 1.68-1.61 (m, 2H), 1.52-1.11 (m, 2H), 1.08-0.65 (m, 12H); ^{13}C-NMR (δ/ppm): 196.6, 196.5 (C1), 164.5 (C3), 77.6, 77.5 (C3'), 61.7, 61.5 (C2), 46.7 (C4'), 40.3, 40.2 (C2'), 34.0 (C6'), 31.4 (C1'), 26.1, 26.0 (C5'), 25.9 (C4'), 21.9 (C7'), 20.6 (C9'), 16.1, 15.9 (C10'); $bp._{0.05\ Torr}$ 110°C, colourless oil; *(-)-1(S)-Menthyl chloro-(phenylhydrazono)-acetate:* 12.7 g (75%); ^{1}H-NMR (δ/ppm, J/Hz): 8.35 (s, 1H, NH), 7.01-7.33 (m, 5H, ar. CH), 4.84 (dt, 1H, 5.6/10.9, H1'), 2.07-2.13 (m, 1H), 1.90-2.00 (m, 1H), 1.60-1.74 (m, 2H), 1.45-1.58 (m, 2H), 1.06-1.18 (m, 2H), 0.84-1.04 (m, 1H), 0.91 (d, 6H, 7.1, H9', H10'), 0.80 (d, 3H, 7.0, H7'); ^{13}C-NMR (δ/ppm): 159.3 (COO), 141.0 (ar. C), 129.4, 123.0, 114.4 (ar. CH), 116.2 (CNCl), 76.6 (C3'), 47.1 (C4'), 40.6 (C2'), 34.2 (C6'), 31.4 (C1'), 26.7 (C8'), 23.9 (C5'), 22.0 (C7'), 20.6 (C9'), 16.8 (C10'); $[\alpha]_{546}^{25}$= -103.0; mp. 99°C, yellow plates.

(+)-1(*R*)-Menthyl chloro-(phenylhydrazono)-acetate 2d: *(+)-1(R)-Menthyl 3-oxo-butyrate*[12] : ^{1}H-NMR (δ/ppm, J/Hz): 4.67 (dt, 1H, H3'), 3.38 (s, 2H, H2), 2.20 (s, 3H, H4), 2.00-1.75 (m, 2H), 1.70-1.58 (m, 2H), 1.54-1.27 (m, 2H), 1.05-0.88 (m, 2H), 0.85 (d, 3H, H9'), 0.83 (d, 3H, H10'), 0.70 (d, 3H, H7'); ^{13}C-NMR (δ/ppm): 200.7 (C3), 166.7 (C1), 75.4 (C3'), 50.5 (C2), 46.8 (C4'), 40.6 (C2'), 34.1 (C6'), 31.3 (C1'), 30.0 (C4), 26.0 (C8'), 23.2 (C5'), 21.9 (C7'), 20.7 (C9'), 16.1 (C10'); $[\alpha]_{589}^{25}$= +64.3 ; $bp._{0.8\ Torr}$ 122°C, colourless oil; *(+)-1(R)-Menthyl 2(RS)-2-chlor-3-oxo-butyrate:* ^{1}H-NMR (δ/ppm, J/Hz): 4.80-4.71 (m, 1H, H3'), 4.71, 4.70 (s, 1H, H2), 2.32 (s, 3H, H4), 2.01-1.93 (m, 1H), 1.91-1.76 (m, 1H), 1.68-1.61 (m, 2H), 1.52-1.11 (m, 2H), 1.08-0.65 (m, 12H); ^{13}C-NMR (δ/ppm): 196.6, 196.5 (C1), 164.5 (C3), 77.7, 77.6 (C3'), 61.7, 61.5 (C2),

46.7 (C4'), 40.3, 40.2 (C2'), 34.0 (C6'), 31.4 (C1'), 26.1, 26.0 (C5'), 25.9 (C4'), 21.9 (C7'), 20.6 (C9'), 16.1, 15.9 (C10'); $bp._{0.005\ Torr}$ 82°C, pale yellow oil; *(+)-1(R)-Menthyl chloro-(phenylhydrazono)-acetate:* 13.3 g (79%); ^{1}H-NMR (δ/ppm, J/Hz): 8.39 (s, 1H, NH), 7.00-7.34 (m, 5H, ar. CH), 4.86 (dt, 1H, 4.4/13.9, H3'), 2.45-2.08 (m, 1H), 1.92-2.02 (m, 1H), 1.69-1.75 (m, 2H), 1.46-1.62 (m, 2H), 1.07-1.19 (m, 2H), 0.84-0.98 (m, 1H), 0.94 (d, 3H, 6.0, H9'), 0.92 (d, 3H, 6.0, H10'), 0.82 (d, 3H, 7.0, H7'); ^{13}C-NMR (δ/ppm): 159.0 (COO), 141.7 (ar. C), 129.4, 123.0, 114.4 (ar. CH), 116.2 (CNCl), 77.2 (C3'), 47.0 (C4'), 40.6 (C2'), 34.2 (C6'), 31.4 (C1'), 26.6 (C8'), 23.9 (C5'), 22.0 (C7'), 20.6 (C9'), 16.8 (C10'); $[\alpha]_{589}^{25}$= +86.1; mp. 89-91°C, yellow crystals.

(-)-2(*S*)-Methylbutyl chloro-(phenylhydrazono)-acetate 2e: *(+)-2(S)-2-Methylbutyl 3-oxo-butyrate*: ^{1}H-NMR (δ/ppm, J/Hz): 3.92, 3.86 (m, 1H, H1'), 3.38 (s, H2), 2.18 (s, 3H, H4), 1.60 (m, 1H), 1.32 (m, 1H), 1.11 (m, 1H), 0.83 (d, 1H, $\underline{CH_3}$-CH), 0.82 (t, 3H, H4'); ^{13}C-NMR (δ/ppm): 200.6 (C3), 168.7 (C1), 69.9 (C1'), 50.0 (C3), 33.9 (C2'), 25.8 (C3'), 16.2 ($\underline{CH_3}$-CH), 11.1 (C4'); $[\alpha]_{589}^{25}$= +3.6; $bp._{0.2\ Torr}$ 72°C, colourless oil; *(+)-2(S)-2-Methylbutyl 2(RS)-2-chlor-3-oxo-butyrate:* ^{13}C-NMR (δ/ppm): 196.6 (C2), 165.0 (C4), 71.5 (C1'), 61.3 (C3), 34.0 (C1), 26.1 (C2'), 25.7 (C3'), 16.1 ($\underline{CH_3}$-CH), 11.1 (C4'); $[\alpha]_{589}^{25}$= +4.6; pale yellow oil; *(-)-2(S)-2-Methylbutyl chloro-(phenylhydrazono)-acetate:* 12.7 g (75%); ^{1}H-NMR (δ/ppm, J/Hz): 8.40 (s, 1H, NH), 7.02-7.36 (m, 5H, ar. CH), 4.18, 4.13 (dt, 1H, 6.0/10.7, H1'), 1.85 (m, 1H), 1.51 (m, 1H), 1.29 (m, 1H), 1.00 (d, 3H, 6.7, $\underline{CH_3}$-CH), 0.96 (t, 3H, CH_3); ^{13}C-NMR (δ/ppm): 158.8 (COO), 141.6 (ar. C), 129.5, 123.1 (ar. CH), 115.8 (CNCl), 114.4 (ar. CH), 71.2 (C1'), 34.2 (C2'), 26.0 (C3'), 16.4 ($\underline{CH_3}$-CH), 11.3 (C4'); $[\alpha]_{546}^{25}$= -6.4; MS (CI) *m/z* (relative intensity) 268 (9, M^+), 198 (38, M^+-C_5H_{10}, *McLafferty*), 91 (25), 46 (26), 45 (53), 43 (40), 31 (100), 29 (33); mp. 51°C, pale yellow plates.

General Procedure for the Cycloaddition of Nitrilimines.

To a solution of the unsaturated carbonyl compound **1** or olefin **7** (1.2 mmol) and triethylamine (3 ml) in acetone/ether (1/1, 30 ml) was added 1 mmol of the appropriate hydrazonoyl chloride. The mixture was stirred at the given temperature (see Table 1). The reaction was monitored by HPLC (48 to 72 hours). After filtering off triethylamine hydrochloride the solution was concentrated by rotary evaporation to yield an oil. Column chromatography over silica gel (eluent: ethyl acetate/hexane) was used to separate diastereomeric compounds **3-5**. In case of pyrazolines **9-10** the mixture of diastereomers was dissolved in ethanol and water was added at 40°C as long as the turbidity disappeared. After some days in the refrigerator the crystalline product **9** was filtered off and the solution was evaporated to dryness to give **9+10**.

Ethyl 4(*S*)5(*R*)-5-acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyra-zole-3-carboxylate 3a: ^{1}H-NMR (δ/ppm, J/Hz): 6.99-7.28 (m, 5H, ar. CH), 4.91 (d, 1H, 5.4, H5), 4.76 (ddd, 1H, 4.1/5.5/7.1, CH-O), 4.34 (q, 2H, 9.3, CH_3-$\underline{CH_2}$), 3.92 (ABX, 1H, 7.1/9.3, CH_2O), 3.75 (dd, 1H, 5.4/4.1, H4), 3.54 (ABX, 1H, 5.5/9.3, CH_2O), 2.19 (s, 3H, CH_3-CO), 1.56 (s, 3H, CH_3C), 1.38 (t, 3H, 9.3, $\underline{CH_3}$-CH_2), 1.35

(s, 3H, CH_3C); ^{13}C-NMR (δ/ppm): 203.1 (C=O), 162.0 (COO), 141.5 (ar. C), 136.4 (C=N), 129.4, 122.2, 114.1 (ar. CH), 109.9 (OCO), 73.5 (CH-O), 70.3 (C5), 65.2 (CH_2O), 61.5 (CH_3-$\underline{CH_2}$), 52.1 (C4), 26.1 ($\underline{CH_3}$-CO), 25.4, 24.2 (CH_3C), 14.3 ($\underline{CH_3}$-CH_2); $[\alpha]_{546}^{25}$ = +265.1; mp. 98°C; MS (CI) *m/z* (relative intensity) 360 (M^+, 6), 217 (100), 171 (72), 101 (59), 44 (57), 43 (90); Anal. Calcd. for $C_{19}H_{24}N_2O_5$ (360.41): C: 63.32%, H: 6.71%, N: 7.77%, Found: C: 62.99%, H: 6.73%, N: 7.78%; t_R = 26.32 min (a), t_R = 14.39 min (b).

Crystal data at 295 K: $C_{19}H_{24}N_2O_5$, monoclinic, $P2_1$, a = 10.8707 (15), b = 7.1337 (12), c = 12.577 (3) Å, ß = 100.55 (5)° , Z = 2, Mo-$K\alpha$ radiation, Stoe STADI-4 diffractometer, $2\Theta_{max}$ 50 °. The structure was refined on F^2 (program SHELXL-93, G. M. Sheldrick, 1993) to $wR(F^2) = 0.0776$ for all 1833 reflections (conventional $R(F) = 0.0387$). The absolute configuration could not be determined directly but was based on the known configuration of the starting material.[13]

Ethyl 4(*R*)5(*S*)-5-acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyra-zole-3-carboxylate 4a: ^{1}H-NMR (δ/ppm, J/Hz): 6.88-7.24 (m, 5H, ar. CH), 4.80 (d, 1H, 5.1, H5), 4.50 (m, 1H, CH-O), 4.23 (q, 2H, 9.3, CH_3-$\underline{CH_2}$), 3.90 (ABX, 1H, 5.5/7.1, CH_2O), 3.75 (m, 1H, H4), 3.52 (ABX, 1H, 5.5/7.1, CH_2O), 2.01 (s, 3H, CH_3-CO), 1.25 (s, 3H, CH_3C), 1.38 (t, 3H, 9.3, $\underline{CH_3}$-CH_2), 1.26 (s, 3H, CH_3C); ^{13}C-NMR (δ/ppm): 206.4 (C=O), 161.9 (COO), 141.8 (ar. C), 137.6 (C=N), 129.4, 121.9, 113.6 (ar. CH), 109.5 (OCO), 73.8 (CH-O), 70.2 (C5), 66.9 (CH_2O), 61.3 (CH_3-$\underline{CH_2}$), 53.5 (C4), 26.1 ($\underline{C}H_3$-CO), 25.6, 24.4 (CH_3C), 14.2 ($\underline{CH_3}$-CH_2); t_R = 34.02 min (a).

4(*S*)5(*R*)-5-Acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole 3b: ^{1}H-NMR (δ/ppm, J/Hz): 6.86-7.68 (m, 10H, ar. CH), 4.82 (d, 1H, 4.1, H5), 4.57-4.65 (m, 1H, CH-O), 3.98 (t, 1H, 4.2, H4), 3.78 (ABX, 1H, 6.0/9.0, CH_2O), 3.53 (ABX, 1H, 6.0/9.0, CH_2O), 2.11 (s, 3H, CH_3-CO), 1.55 (s, 3H, CH_3C), 1.29 (s, 3H, CH_3C); ^{13}C-NMR (δ/ppm): 205.9 (C=O), 146.0, 143.3 (ar. C), 131.2 (C=N), 129.5, 129.1, 128.8, 126.1, 120.0, 112.7 (ar. CH), 110.0 (OCO), 73.3 (CH-O), 69.3 (C5), 65.3 (CH_2O), 52.8 (C4), 26.3 ($\underline{CH_3}$-CO), 25.5, 24.5 (CH_3C); t_R = 7.48 min (a).

4(*R*)5(*S*)-5-Acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole 4b: ^{1}H-NMR (δ/ppm, J/Hz): 6.84-7.75 (m, 10H, ar. CH), 4.70 (d, 1H, 4.1, H5), 4.42-4.48 (m, 1H, CH-O), 3.90-4.12 (m, 2H, H4, CH_2O), 3.69 (ABX, 1H, 3.8/9.0, CH_2O), 2.06 (s, 3H, CH_3-CO), 1.17 (s, 3H, CH_3C), 1.15 (s, 3H, CH_3C); ^{13}C-NMR (δ/ppm): 209.8 (C=O), 147.3, 143.9 (ar. C), 131.4 (C=N), 129.4, 129.3, 128.7, 126.4, 119.8, 112.5 (ar. CH), 109.8 (OCO), 74.1 (CH-O), 69.9 (C5), 66.9 (CH_2O), 53.9 (C4), 27.4 ($\underline{CH_3}$-CO), 26.0, 24.6 (CH_3C); t_R = 13.55 min (a).

4(*S*)5(*R*)-4-Acetyl-5-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole 5b: ^{1}H-NMR (δ/ppm, J/Hz): 6.86-7.68 (m, 10H, ar. CH), 4.69 (t, 1H, 3.6, H5), 4.57-4.65 (m, 1H, CH-O), 4.40 (d, 1H, 3.5, H4), 3.92 (ABX, 1H, 5.7/9.7, CH_2O), 3.67 (ABX, 1H, 5.7/8.7, CH_2O), 2.00 (s, 3H, CH_3-CO), 1.57 (s, 3H, CH_3C), 1.30 (s, 3H, CH_3C); ^{13}C-NMR (δ/ppm): 203.9 (C=O), 146.4, 143.3 (ar. C), 131.0 (C=N), 129.4, 129.1, 128.9, 126.2, 120.2, 113.5 (ar. CH), 110.2 (OCO), 73.4 (CH-O), 65.1 (C4), 65.2 (CH_2O), 60.4 (C5), 27.3 ($\underline{CH_3}$-CO), 26.2, 24.3 (CH_3C); t_R = 6.45 min (a).

4(*R*)5(*S*)-4-Acetyl-5-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole 6b: ^{1}H-NMR (δ/ppm, J/Hz): 6.86-7.68 (m, 10H, ar. CH), 4.58 (t, 1H, 3.5, H5), 4.42-4.49 (m, 1H, CH-O), 4.26 (d, 1H, 3.3, H4), 3.90-4.12 (m, 1H, CH_2O), 3.82 (ABX, 1H, 5.8/8.8, CH_2O), 2.01 (s, 3H, CH_3-CO), 1.56 (s, 3H, CH_3C), 1.32 (s, 3H, CH_3C); ^{13}C-NMR (δ/ppm): 204.6 (C=O), 145.8, 143.9 (ar. C), 131.8 (C=N), 129.0, 129.0, 128.8, 126.1, 120.2, 114.1 (ar. CH), 109.9 (OCO), 75.1 (CH-O), 65.8 (CH_2O), 65.7 (C4), 60.9 (C5), 26.3 ($\underline{CH_3}$-CO), 26.0, 24.8 (CH_3C); t_R = 13.08 min (a).

(+)-Menthyl 4(*S*)5(*R*)-5-acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate 3c: (unseparable mixture with compound **4c**); ^{13}C-NMR (δ/ppm): 203.0 (C=O), 161.6 (COO), 141.6 (ar. C), 137.8 (C=N), 129.4, 122.0, 113.7 (ar. CH), 109.8 (OCO), 75.6, 74.0 (CH-O), 70.1 (C5), 67.2 (CH_2O), 51.9 (C4), 47.0, 30.9 (CH), 34.1, 23.4 (CH_2), 26.1 ($\underline{CH_3}$-CO), 25.5, 24.7 (CH_3C), 22.6, 20.6, 16.3 ($\underline{CH_3}$-CH); t_R = 12.35 min (a).

(-)-Menthyl 4(*R*)5(*S*)-5-acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate 4c: (unseparable mixture with compound **3c**); ^{13}C-NMR (δ/ppm): 206.6 (C=O), 161.6 (COO), 141.0 (ar. C), 136.4 (C=N), 129.4, 122.4, 114.1 (ar. CH), 109.4 (OCO), 75.5, 73.4 (CH-O), 70.5 (C5), 65.2 (CH_2O), 53.2 (C4), 47.0, 31.4 (CH), 40.8, 34.2, 23.4 (CH_2), 26.4 ($\underline{CH_3}$-CO), 25.7, 24.1 (CH_3C), 22.0, 20.8, 16.6 ($\underline{CH_3}$-CH); t_R = 11.58 min (a).

(-)-Menthyl 4-acetyl-5-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate 5c: ^{1}H-NMR (δ/ppm, J/Hz): 6.99-7.34 (m, 5H, ar. CH), 4.92 (dt, 1H, 10.9/4.9, H5), 4.87 (m 1H, H3'), 4.60 (m, 1H, CH-O), 4.31 (d, 1H, 4.7, H4), 4.05 (ABX, 1H, 8.9/7.2, CH_2O), 3.72 (ABX, 1H, 8.9/5.5, CH_2O), 2.28 (s, 3H, CH_3-CO), 1.45-2.16 (m, 9H), 1.37 (s, 3H, CH_3C), 1.24 (s, 3H, CH_3C), 0.93 (d, 3H, 6.4, H10'), 0.89 (d, 3H, 7.0, H9'), 0.80 (d, 3H, 7.0, H7'); ^{13}C-NMR (δ/ppm): 204.3 (C=O), 161.9 (COO), 141.5 (ar. C), 136.0 (C=N), 129.3, 122.3, 115.7 (ar. CH), 110.1 (OCO), 75.4, 73.3 (CH-O), 66.7 (C4), 65.6 (CH_2O),

57.7 (C5), 47.0, 31.5 (CH), 40.8, 34.2, 29.5 (CH_2), 26.4 ($\underline{CH_3}$-CO), 25.9, 24.4 (CH_3C), 22.0, 20.7, 16.3 ($\underline{CH_3}$-CH); t_R = 9.47 min (a).

(+)-Menthyl 4(*S*)5(*R*)-5-acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate 3d: (unseparable mixture with compound **4d**) ^{13}C-NMR (δ/ppm): 203.3 (C=O), 161.5 (COO), 141.6 (ar. C), 136.8 (C=N), 129.3, 122.0, 114.0 (ar. CH), 109.8 (OCO), 75.5, 73.7 (CH-O), 70.4 (C5), 62.2 (CH_2O), 52.0 (C4), 46.9, 31.4 (CH), 40.7, 34.1, 23.9 (CH_2), 26.1 ($\underline{CH_3}$-CO), 25.4, 24.3 (CH_3C), 22.0, 20.5, 16.7 ($\underline{CH_3}$-CH); t_R = 12.54 min (a).

(-)-Menthyl 4(*R*)5(*S*)-5-acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate 4d: ^{13}C-NMR (δ/ppm): 206.6 (C=O), 161.5 (COO), 142.0 (ar. C), 137.8 (C=N), 129.4, 121.8, 113.7 (ar. CH), 109.5 (OCO), 75.3, 73.9 (CH-O), 70.3 (C5), 66.9 (CH_2O), 53.4 (C4), 47.0, 31.4 (CH), 40.9, 34.1, 23.5 (CH_2), 26.3 ($\underline{CH_3}$-CO), 25.7, 24.4 (CH_3C), 22.0, 20.8, 16.4 ($\underline{CH_3}$-CH); t_R = 11.54 min (a).

(+)-Menthyl 4-acetyl-5-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate 5d: ^{1}H-NMR (δ/ppm, J/Hz): 7.00-7.34 (m, 5H, ar. CH), 4.92 (dt, 1H, 10.8/4.8, H5), 4.87 (m 1H, H3'), 4.62 (m, 1H, CH-O), 4.31 (d, 1H, 4.5, H4), 4.05 (ABX, 1H, 8.9/7.2, CH_2O), 3.72 (ABX, 1H, 8.9/5.3, CH_2O), 2.29 (s, 3H, CH_3-CO), 1.43-2.17 (m, 9H), 1.37 (s, 3H, CH_3C), 1.24 (s, 3H, CH_3C), 0.92 (d, 3H, 6.45 H10'), 0.89 (d, 3H, 7.0, H9'), 0.79 (d, 3H, 7.2, H7'); ^{13}C-NMR (δ/ppm): 204.4 (C=O), 161.9 (COO), 141.5 (ar. C), 136.0 (C=N), 129.2, 122.3, 115.6 (ar. CH), 110.1 (OCO), 75.4, 73.6 (CH-O), 66.6 (C4), 65.6 (CH_2O), 57.7 (C5), 47.0, 31.5 (CH), 40.8, 34.2, 29.3 (CH_2), 26.4 ($\underline{CH_3}$-CO), 25.9, 24.4 (CH_3C), 22.0, 20.7, 16.3 ($\underline{CH_3}$-CH); t_R = 9.16 min (a).

2(*S*)-2-Methyl-butyl 4(*S*)5(*R*)-5-acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihy- dro-1H-pyrazole-3-carboxylate 3e: ^{1}H-NMR (δ/ppm, J/Hz): 6.96-7.33 (m, 5H, ar. CH), 4.93 (d, 1H, 5.5, H5), 4.78 (ddd, 1H, 5.4/7.0/9.6, CH-O), 4.06-4.10 (m, 2H, CH-$\underline{CH_2}$), 3.92 (ABX, 1H, 7.1/9.0, CH_2O), 3.76 (dd, 1H, 4.1/5.3, H4), 3.55 (ABX, 1H, 5.5/9.0, CH_2O), 2.18 (s, 3H, CH_3-CO), 1.54, 1.32 (s, 3H, CH_3C), 0.80-1.00 (m, 9H, CH_3, CH_2, CH); ^{13}C-NMR (δ/ppm): 203.1 (C=O), 162.0 (COO), 141.9 (ar. C), 136.3 (C=N), 129.4, 122.1, 114.0 (ar. CH), 109.8 (OCO), 73.5 (CH-O), 70.3 (C5), 69.9 (CH-$\underline{CH_2}$), 65.2 (CH_2O), 52.0 (C4), 34.2 (CH_3-$\underline{CH}$), 26.1 ($\underline{CH_3}$-CO), 26.1 (CH_3-$\underline{CH_2}$), 25.4, 24.2 (CH_3C), 16.4 ($\underline{CH_3}$-CH), 11.2 ($\underline{CH_3}$-CH_2); t_R = 15.8 min (a).

2(*S*)-2-Methyl-butyl 4(*R*)5(*S*)-5-acetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihy-dro-1H-pyrazole-3-carboxylate 4e: ^{1}H-NMR (δ/ppm, J/Hz): 6.96-7.33 (m, 5H, ar. CH), 4.88 (d, 1H, 5.2, H5), 4.58 (ddd, 1H, 3.9/6.7/10.6, CH-O), 3.95-4.10 (m, 4H, CH-$\underline{CH_2}$, CH_2O), 3.45 (dd, 1H, 3.9/5.3, H4), 2.09 (s,

3H, CH_3-CO), 1.27, 1.26 (s, 3H, CH_3C), 0.80-1.00 (m, 8H, CH_3, CH_2); ^{13}C-NMR (δ/ppm): 206.7 (C=O), 162.0 (COO), 141.7 (ar. C), 137.5 (C=N), 129.4, 123.0, 113.7 (ar. CH), 109.6 (OCO), 73.8 (CH-O), 70.3 (C5), 69.9 (CH-$\underline{CH_2}$), 67.0 (CH_2O), 53.4 (C4), 34.2 (CH_3-$\underline{CH}$), 26.1 ($\underline{CH_3}$-CO), 26.1 (CH_3-$\underline{CH_2}$), 26.0, 24.5 (CH_3C), 16.4 ($\underline{CH_3}$-CH), 11.2 ($\underline{CH_3}$-CH_2); t_R = 18.0 min (a).

4(*S*)5(*R*)-3,5-Diacetyl-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyrazole 3f: ^{1}H-NMR (δ/ppm, J/Hz): 6.98-7.33 (m, 5H, ar. CH), 4.95 (d, 1H, 5.5, H5), 4.82 (dt, 1H, 4.3/7.2, CH-O), 3.85 (ABX, 1H, 7.2/9.0, CH_2O), 3.77 (dd, 1H, 5.5/4.3, H4), 3.43 (ABX, 1H, 5.6/9.0, CH_2O), 2.46, 2.21 (s, 3H, CH_3-CO), 1.53, 1.31 (s, 3H, CH_3C); ^{13}C-NMR (δ/ppm): 202.4 (C=O), 193.2 (C3-$\underline{C}$=O), 141.3 (ar. C), 144.5 (C=N), 129.5, 122.8, 114.2 (ar. CH), 109.7 (OCO), 73.0 (CH-O), 70.5 (C5), 65.1 (CH_2O), 50.7 (C4), 26.2, 25.7 ($\underline{CH_3}$-CO), 25.0, 24.2 (CH_3C).

Ethyl 4(*S*)5(*R*)-5-acetyl-4-(1(*S*)-1,2-O-cyclohexylidene-ethyl)-1-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate 3g: ^{1}H-NMR (δ/ppm, J/Hz): 6.89-7.37 (m, 5H, ar. CH), 4.89 (d, 1H, 5.4, H5), 4.71 (ddd, 1H, 4.3/5.4/7.0, CH-O), 4.25 (q, 2H, 9.3, CH_3-$\underline{CH_2}$), 3.85 (ABX, 1H, 7.0/9.0, CH_2O), 3.72 (dd, 1H, 4.3/5.4, H4), 3.45 (ABX, 1H, 4.3/9.0, CH_2O), 2.13 (s, 3H, CH_3-CO), 1.31-2.03 (m, 10H, CH_2C), 1.29 (t, 3H, 9.3, $\underline{CH_3}$-CH_2); ^{13}C-NMR (δ/ppm): 202.8 (C=O), 161.9 (COO), 141.5 (ar. C), 136.3 (C=N), 129.4, 122.1, 114.1 (ar. CH), 110.5 (OCO), 73.1 (CH-O), 70.2 (C5), 64.8 (CH_2O), 61.4 (CH_3-$\underline{CH_2}$), 52.0 (C4), 25.4 ($\underline{CH_3}$-CO), 36.0, 33.7, 25.1, 24.0, 23.6 (CH_2-cyclohex.), 14.3 ($\underline{CH_3}$-CH_2); $[\alpha]_{546}^{25}$ = +18.6; t_R = 16.9 min (a).

Ethyl 4(*R*),5(*S*)-5-acetyl-4-(1(*S*)-1,2-O-cyclohexylidene-ethyl)-1-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate 4g: ^{13}C-NMR (δ/ppm): 206.3 (C=O), 161.9 (COO), 141.9 (ar. C), 137.6 (C=N), 129.4, 122.0, 113.7 (ar. CH), 110.1 (OCO), 73.6 (CH-O), 70.5 (C5), 66.8 (CH_2O), 61.4 (CH_3-$\underline{CH_2}$), 53.4 (C4), 25.1 ($\underline{CH_3}$-CO), 35.9, 34.0, 25.6, 23.9, 23.7 (CH_2-cyclohex.), 14.2 ($\underline{CH_3}$-CH_2) ; t_R = 25.1 min (a).

Diethyl 4(*S*)5(*R*)-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate 3h: ^{1}H-NMR (δ/ppm, J/Hz): 6.90-7.24 (m, 5H, ar. CH), 4.87 (d, 1H, 5.4, H5), 4.68 (ddd, 1H, 4.1/5.5/7.0, CH-O), 4.26 (q, 2H, 9.3, CH_3-$\underline{CH_2}$), 4.10 (q, 2H, 9.3, CH_3-$\underline{CH_2}$), 3.86 (m, 2H, CH_2O and H4), 3.55 (ABX, 1H, 5.0/9.1, CH_2O), 1.46 (s, 3H, CH_3C), 1.29 (t, 3H, 9.3, $\underline{CH_3}$-CH_2), 1.25 (s, 3H, CH_3C), 1.10 (t, 3H, 9.3, $\underline{CH_3}$-CH_2); ^{13}C-NMR (δ/ppm): 169.5, 162.1 (COO), 141.7 (ar. C), 137.0 (C=N), 129.2, 122.1, 114.2 (ar. CH), 109.8 (OCO), 73.8 (CH-O), 65.3 (CH_2O), 64.4 (C5), 62.0, 61.4 (CH_3-$\underline{CH_2}$), 53.5 (C4), 26.0, 24.3 (CH_3C), 14.3, 13.9 ($\underline{CH_3}$-CH_2); $[\alpha]_{546}^{25}$ = +109.5; Anal. Calcd. for $C_{20}H_{26}N_2O_6$ (390.43): C: 61.53%, H: 6.71%, N: 7.18%, Found: C: 61.10%, H: 6.71%, N: 6.68%; t_R = 20.1 min (a).

Diethyl 4(*R*)5(*S*)-4-(4(*S*)-2,2-dimethyl-[1,3]-dioxolane-4-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate 4h: ^{1}H-NMR (δ/ppm, J/Hz): 6.90-7.24 (m, 5H, ar. CH), 4.96 (d, 1H, H5), 4.60 (m, 1H, CH-O), 4.30 (q, 2H, 9.3, CH_3-$\underline{CH_2}$), 4.16 (q, 2H, 9.3, CH_3-$\underline{CH_2}$), 4.12 (m, 1H, H4), 4.04, 3.62 (m, 1H, CH_2O), 1.35 (t, 3H, 9.3, $\underline{CH_3}$-CH_2), 1.25, 1.24 (s, 3H, CH_3C), 1.16 (t, 3H, 9.3, $\underline{CH_3}$-CH_2); ^{13}C-NMR (δ/ppm): 170.3, 162.0 (COO), 141.6 (ar. C), 136.2 (C=N), 129.2, 122.0, 115.4 (ar. CH), 110.3 (OCO), 73.5 (CH-O), 65.4 (CH_2O), 67.3 (C5), 62.0, 61.2 (CH_3-$\underline{CH_2}$), 50.1 (C4), 25.9, 24.4 (CH_3C), 14.3, 14.0 ($\underline{CH_3}$-CH_2); t_R = 31.2 min (a).

(-)-Menthyl 1-phenyl-3a,4,5,6,7,7a-hexahydro-1H-4,7-methano-indazole-3-carboxylate 9c: ^{1}H-NMR (δ/ppm, J/Hz): 6.90-7.31 (m, 5H, ar. CH), 4.80 (dt, 1H, H3'), 4.20 (d, 1H, 10.0, H7a), 3.41 (d, 1H, 10.0, H4a), 2.78 (s, 1H), 2.64 (s, 1H), 1.08-2.00 (m, 15H), 0.92 (d, 6H, 6.5, H9'/H10'), 0.81 (d, 3H, 7.0, H7'); ^{13}C-NMR (δ/ppm): 162.7 (COO), 142.5 (C3), 141.3 (ar. C), 129.1, 120.7, 113.8 (ar. CH), 74.8 (C3'), 69.2 (C7a), 54.2 (C4a), 47.0 (C4'), 41.4 (C4), 40.9 (C2'), 40.8 (C7), 34.3 (C6'), 33.1 (C6), 31.5 (C1'), 27.6 (C5), 26.5 (C8'), 24.6 (C8), 23.6 (C5'), 22.1 (C7'), 20.8 (C9'), 16.5 (C10'); $[\alpha]_{589}^{25}$ = -370; mp. 120°C; yellowish crystals; MS (CI) *m/z* (relative intensity) 394 (27, M^+), 256 (100, M^+-$C_{10}H_{18}$, *McLafferty*), 239 (11), 211 (10), 145 (13), 41 (12); Anal. Calcd. for $C_{25}H_{34}N_2O_2$ (394.56): C: 76.10%, H: 8.69%, N: 7.10%, Found: C: 76.25%, H: 8.41%, N: 6.88%; t_R = 2.39 min; (a), t_R = 6.05 min; (b).

(+)-Menthyl 1-phenyl-3a,4,5,6,7,7a-hexahydro-1H-4,7-methano-indazole-3-carboxylate 10c: ^{1}H-NMR (δ/ppm, J/Hz): 6.90-7.29 (m, 5H, ar. CH), 4.86 (dt, 1H, 4.4/10.9, H3'), 4.21 (d, 1H, 9.9, H7a), 3.87 (d, 1H, 9.9, H4a), 2.77 (s, 1H), 2.62 (s, 1H), 0.95-2.10 (m, 15H), 0.91 (d, 6H, 6.5, H9'/H10'), 0.80 (d, 3H, 7.0, H7'); ^{13}C-NMR (δ/ppm): 162.5 (COO), 142.4 (C3), 141.3 (ar. C), 129.0, 120.8, 113.8 (ar. CH), 74.7 (C3'), 69.1 (C7a), 54.3 (C4a), 47.1 (C4'), 41.3 (C4), 41.0 (C2'), 40.9 (C7), 34.3 (C6'), 33.1 (C6), 31.4 (C1'), 27.6 (C5), 26.7 (C8'), 24.6 (C8), 23.9 (C5'), 22.1 (C7'), 20.7 (C9'), 16.8 (C10'); mp. 119-121°C; yellowish crystals; t_R = 2.45 min; (a), t_R = 8.12 min; (b).

(+)-Menthyl 1-phenyl-3a,4,5,6,7,7a-hexahydro-1H-4,7-methano-indazole-3-carboxylate 9d: ^{1}H-NMR (δ/ppm, J/Hz): 6.92-7.31 (m, 5H, ar. CH), 4.86 (dt, 1H, H3'), 4.21 (d, 1H, 9.5, H7a), 3.41 (d, 1H, 9.5, H4a), 2.79 (s, 1H), 2.63 (s, 1H), 1.00-2.11 (m, 15H), 0.92 (d, 6H, 6.5, H9'/H10'), 0.81 (d, 3H, 7.0, H7'); ^{13}C-NMR (δ/ppm): 162.7 (COO), 142.5 (C3), 141.3 (ar. C), 129.1, 120.7, 113.8 (ar. CH), 74.8 (C3'), 69.2 (C7a), 54.2 (C4a), 47.0 (C4'), 41.4 (C4), 40.9 (C2'), 40.8 (C7), 34.2 (C6'), 33.2 (C6), 31.4 (C1'), 27.6 (C5), 26.4 (C8'), 24.6 (C8), 23.6 (C5'), 22.1 (C7'), 20.8 (C9'), 16.5 (C10'); $[\alpha]_{589}^{25}$ = +185; mp. 130-131°C; yellowish crystals; t_R = 12.55 min; (b).

(-)-Menthyl 1-phenyl-3a,4,5,6,7,7a-hexahydro-1H-4,7-methano-indazole-3-carboxylate 10d: ^{1}H-NMR (δ/ppm, J/Hz): 6.92-7.36 (m, 5H, ar. CH), 4.87 (dt, 1H, H3'), 4.20 (d, 1H, 10.0, H7a), 3.39 (d, 1H, 10.0, H4a),

2.79 (s, 1H), 2.64 (s, 1H), 1.05-2.09 (m, 15H), 0.93 (d, 3H, 6.4, H10'), 0.91 (d, 3H, 7.0, H9'), 0.81 (d, 3H, 6.9, H7'); ^{13}C-NMR (δ/ppm): 162.5 (COO), 142.3 (C3), 141.3 (ar. C), 129.1, 120.7, 113.8 (ar. CH), 74.7 (C3'), 69.1 (C7a), 54.2 (C4a), 47.1 (C4'), 41.3 (C4), 40.9 (C2'), 40.8 (C7), 34.3 (C6'), 33.1 (C6), 31.4 (C1'), 27.6 (C5), 26.7 (C8'), 24.6 (C8), 23.8 (C5'), 22.1 (C7'), 20.7 (C9'), 16.8 (C10'); mp. 118-120°C; yellow crystals; t_R = 6.17 min; (b).

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