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CHIRAL INDUCTION IN PHOTOCHEMICAL REACTIONS - V. REGIO- AND DIASTEREOSELECTIVITY IN THE PHOTOCHEMICAL [2+2] CYCLOADDITION OF CHIRAL CYCLENONE-3-CARBOXYLATES WITH 1,1'-DIETHOXYETHENE

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Abstract - The chiral cyclenone-3-carboxylates 5-12 induce high regio - but only fair diastereoselectivities in the photochemical [2+2] cycloaddition with 1,1'-diethoxyethene 23. Cyclohex-2-ene-1-one-3-carboxylates gain higher diastereoselectivites compared to the ringhomologous cyclopent-2-ene-1-one-3-carboxylates. The face-differentiating effect of the chiral 3-estergroup is not only sterically caused but also indicates an electronic component which is demonstrated by comparison of 5 with 7 and 6 with 8, respectively.

Photochemical [2+2] cycloadditions of cyclic enone-systems are well-established synthetic methods for cyclobutane derivatives in natural product synthesis.[2-4] Concerning the chiral induction in such reactions, there are only a few reports available.[5] We now present a system capable of demonstrating facts which are responsible for regio- and diastereoselectivity on forming four-membered rings in the systems: cyclenone/1.1'diethoxyethene/light.

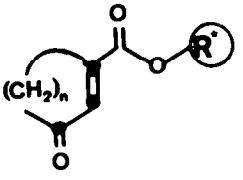
A: Synthesis of the chiral cyclenone-carboxylates.

The esters 1 and 2 are prepared as described in the literature.[3,6,7] Experience has shown us that esterifications of the carboxylates 3 and 4 succeed in better yields applying the method of Stadler[8] (Table 1).

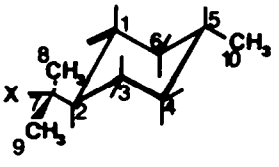
Table 1: Chemical yields of the enone carboxylates

R*	n	comp.	yields %
CH_3	2	1	--
	3	2	95*
H	2	3	--
	3	4	--
a	2	5	65
	3	6	75
b	2	7	56
	3	8	76
c	2	9	32
	3	10	46
d	2	11	50
	3	12	60

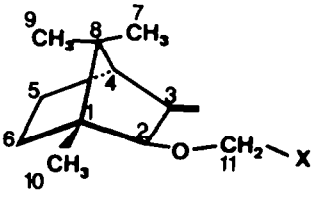
*Compound 2 is not crystalline and must be purified as 4.



R* = a (x=H)
b (x=Ph)



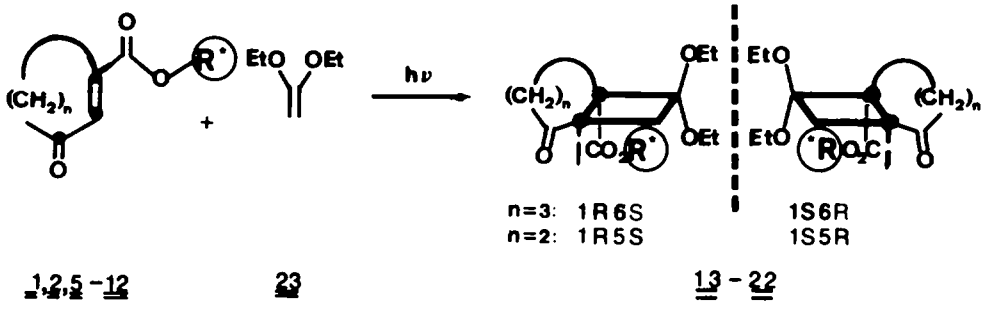
R* = c (x=t-Bu)
d (x=Ph)



Scheme 1: Structure of the enone carboxylates

B: [2+2] cycloaddition of the chiral cyclenone-carboxylates 5 to 12 with 1,1'-diethoxyethene 23

The photochemical cycloaddition of the cyclenonecarboxylates (Scheme 2) leads to the cyclobutane derivatives 13-22 (Table 2) and besides to oxetanes by adding 23 to the carbonylgroup. The reaction was processed up to 95 percent conversion. The diastereomeric excess (% d.e.) of the resulting cyclobutane derivatives was examined by HPLC and ^{13}C nmr.



1,2,5-12 23 13-22

Scheme 2: Cycloaddition of the cyclenones

No regioisomers were found.[9] In a few cases (see compounds 16, 18, 19, 20 and 22) each of the diastereomeric compounds was isolated (Table 2) and used as standards for HPLC-analysis.

Table 2: Results of the [2+2]-cycloaddition.

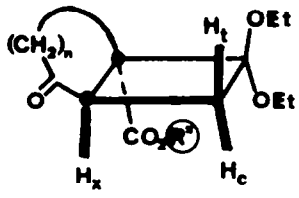
					chem.yield/%			de/%**	
R*	n*	comp.	solvent	Tem./C°	1S 6R***	total	1R6S	HPLC	13 C nmr
CH_3	2	13	benzene	23	--	41	--	--	--
	3	14	"	23	--	40	--	--	--
a	2	15	"	23	--	39	--	5-10	8
	3	16	"	23	24	42	18	16	14
b	2	17	"	23	--	35	--	15-18	22
	3	18	toluene	-40	58	75	17	56	56
	3	18	benzene	23	35	45	10	56	56
	3	18	cyclohexane	23	33	44	11	52	52
	3	18	CH_2Cl_2	23	23	38	15	22	22
c	2	19	benzene	23	19	36	17	5	--
	3	20	"	"	23	44	20	7	6
d	2	21	"	"	--	41	--	6-8	8
	3	22	"	"	26	46	20	11	11

*Compare to Table 1; **Tolerance of error: ± 1%, if not mentioned otherwise; n=2 leads to 1S 5R and 1R 5S.

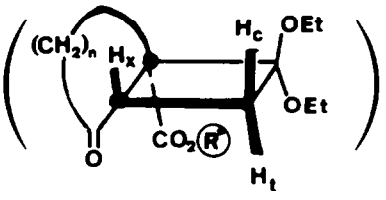
The chemical yields of the cyclobutane derivatives in Table 2 decrease with increasing temperature but without changing their diastereoselectivity (see compound 18). The diastereoselectivity and the chemical yield (proved by compound 18) decrease rapidly if polar solvents are used.

Generally, the cyclohexenone carboxylates (n-3) generate higher de-values than the cyclopentenone systems (n=2).

C: Regiochemistry and structure of the cyclobutane derivatives 13-22.
Regioselectivity[9] of the [2+2] cycloaddition of the cyclenone carboxylates with 1,1'-diethoxyethene should reveal in general compounds A (cis-fused) or B (trans-fused), respectively (Scheme 3).



A



B

Scheme 3: Structure of the cyclobutane derivatives on the basis of the analysis of coupling constants (Table 3) $J_{ct}J_{cx}J_{tx}$ for the protons Hx, Hc and Ht.

Table 3: ^{1}H nmr data of the protons H_x, H_c, H_t (see Scheme 2).

Comp.	δ/ppm			J/Hz		
	Hx	Hc	Ht	HcHt	HcHx	HtHx
15	3.03	2.79	2.07	-12.2	10.9	5.7
17	2.79	2.53	2.11	-12.2	10.9	5.7
16	3.24	2.58	2.09	-12.2	9.8	9.0
18(1S,6R)	2.96	2.51	2.15	-12.2	9.8	9.0
18(1R,6S)	3.12	2.55	2.12	-12.2	9.8	9.0

It turns out that the ring fusion is always cis (compound A, Scheme 3).
This result is based on a comparison of compound 15 to 17 and 16 to 18, respectively (Table 3) as follows: The proton Hx (Scheme 3) in 17 and 18 (both with (R*) = (-)8-phenylmenthol) endures a remarkably high field shift (aromatic ring) compared to the compounds 15 and 16 (both with (R*) = (-)menthol). This shift is only possible in compound A (cis-fused) in Scheme 3.
For the $\Delta\delta_{Hx}$-data see Table 4.

Table 4: Relations between ^{1}H and ^{13}C nmr of 17 and 18.

compound	$^1H^*$ Δδ Hx/ppm	$^{13}C^{2*}$ Δδ 8/9/ppm	PA^{3*}	ΔδHx / PA	configuration
17	-0.25	--	--	--	--
18 (major)	-0.28	4.94	0.14	-2.0	1S 6R
18 (minor)	-0.12	3.40	0.22	-0.5	1R 6S

*) compared to menthol system 15 and 16.

2*) 8/9 are the two methylgroups in the fragment $-C(Me)_2Ph$.

3*) P_A = (7.5-Δδ8/9)/7.57+11.25) = population of rotamers.[1a]

The value $\Delta\delta Hx/P_A$=-2.0 of the main isomer indicates that Hx is close to the aromatic ring and leads to 1S,6R configuration.[1a]

D.: Diastereoselectivity

The highest attainable diastereoselectivity (Table 2) is 56 % (compound 18). Obviously, the chiral auxiliaries ((-)8-phenylmenthol[10] or the bornyl derivatives[11]), which usually generate high de-values[1,2], are not sufficiently face-differentiating in our systems.

Nmr analysis of conformations[1a] explains these results.

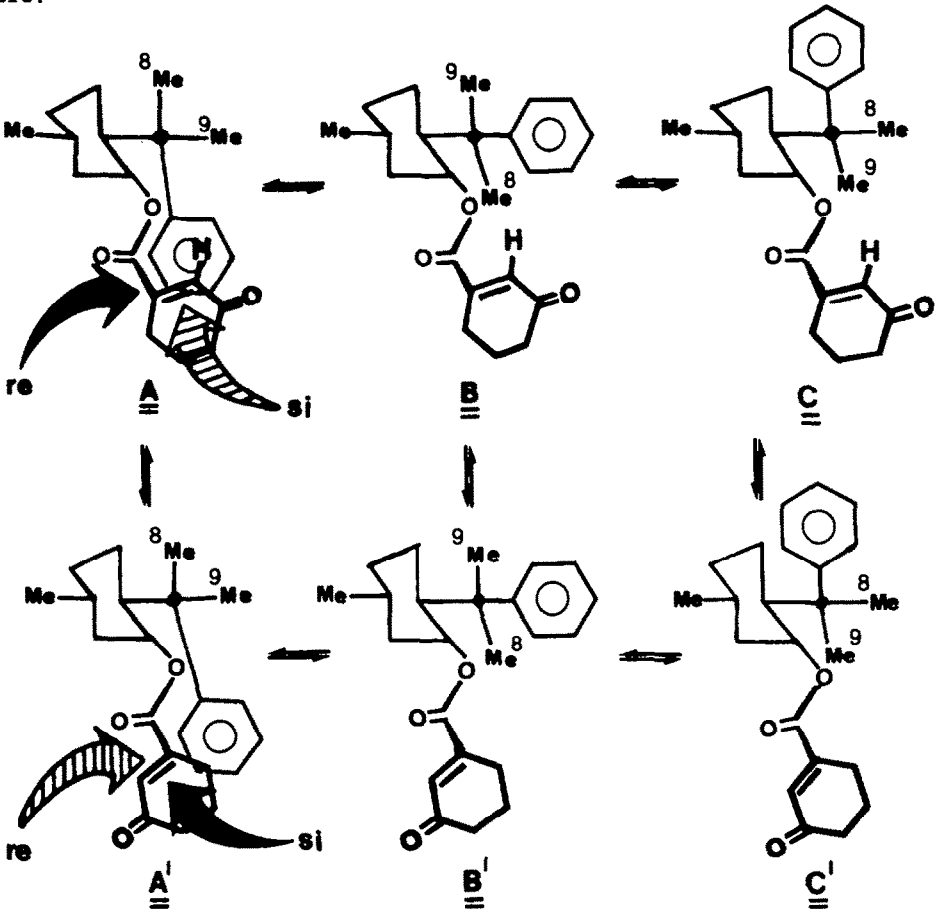
Table 5: ^{1}H and ^{13}C nmr data of the cyclenone-carboxylates 7 and 8:

comp.	1 H nmr/ppm* $\Delta\delta_H$	$\Delta\delta_{CH_2}$**	$\Delta\delta$ 8/9	P_A	$\frac{\Delta\delta 8/9}{P_A}$	$\frac{\Delta\delta CH_2}{P_A}$
7	-0.61	-0.57	6.52	0.75	-0.81	-0.76
8	-0.56	-0.49	6.51	0.75	-0.75	-0.65

*) Comparison to the menthol carboxylates 5 and 6.

**) Both protons do not show any diastereotopic splitting.

In the enone esters 7 and 8 (Table 5) ((R*) =8-phenylmenthol) both the olefinic and the ringmethylenic protons endure high field shifts compared to their analoga 5 and 6 ((R*)=menthol). This fact indicates an equilibrium between the conformers A and A' (Scheme 4), with roughly equal amounts of each, as we have demonstrated elsewhere.[1a]



Scheme 4: Equilibrium of the ester conformers of compound 8.
Population: (A+A')=75%; (B+B'+C+C')=25%;A:A'=1:1)[1a]

Furthermore the rotamer population P_A[1a] can be determined by coordination of the ^1H nmr to the ^{13}C nmr data (Table 5). The amount of species A and A' together is 75 percent. This fact demonstrates a "concave system".[11a]
Conformation A alone might lead to high diastereoselectivity in the reaction with 2, since the alternative si-face-attack[12] in Scheme 4 is strongly sterically hindered. The situation for the conformer A' is exactly the reverse. If we take into consideration that species A forms the minor isomer, A' forms the major one and that the ratio of A/A' is about 1, there is no doubt, that the diastereomeric excess is low. This deduction coud be applied in particular to the cyclopentenone system because of its planarity, while in the case of the cyclohexenone system there is an additional sterical differentiation caused by its chair-conformation, which discriminates the formation of the minor diastereomer.
Consequently the cyclohexenone system leads to higher diastereomeric excess (Table 2) than its cyclopentenone-analogue.

EXPERIMENTAL

Ir spectra were run on a Perkin Elmer 377. Uv spectra (λ=200 to 400 nm): Perkin Elmer 320. ^1H nmr: Varian EM-390. ^{13}C nmr: Varian CFT 20. Internal reference: TMS. HPLC: Abimed-Gilson pumps 304, module 803, uv-detector: Spectrochrome and Holochrome, ri-detector: Bischoff LCD 202, columns: Bischoff 7µ LiChrosorb Si 60 2.2x26cm (prep.) and 7µ LiChrosorb Si 60 0.8x26 cm (anal.).- Eluent: Mixture 10 % ethyl acetate in n-hexane, if not mentioned otherwise.- Melting points: Büchi (Dr. Tottoli), uncorrected.- Specific rotation: Perkin-Elmer 241.- The solvents were purified by general methods. The chiral alcohols were synthesized as described.[10,11] 1.1'-diethoxyethene is also prepared according.[13] Chemical yields refer to isolated, analytically pure materials.

Synthesis of cyclopentene-(2)-1-one-3-methylcarboxylate (1)

The enonecarboxylate 1 was prepared according[3,7] and is analytically pure after distillation and recrystallisation. yield: (4 steps) 8-9 g (10-14%).- bp.: 103-106°C/4.5 torr.- mp.: 43-44°C (pentane/ether 70:30), $C_7H_8O_3$ (140.1): calc. C, 60.00; H, 5.71; found C, 60.27; H, 5.91.- Ir ($CDCl_3$): 1714 (C=O), 1606 (C=C) cm^{-1}.- Uv (hexane). $\lambda max_{\pi\pi^*}$ (lg ε)= 238 nm (3.96), $\lambda max_{n\pi^*}$ (lg ε)= 346 nm (1.30).- ^1H nmr ($CDCl_3$): δ = 6.73 (t, 1.5 Hz, 1H, olefin-H), 3.85 (s,3H,CH_3); 3.1-2.4 (m,4H,CH_2)ppm.- ^{13}C nmr ($CDCl_3$): δ = 208.69 (CO), 164.76 (C=), 164.00 (CO_2), 138.09 (=CH), 52.47 (CH_3), 35.58 (CH_2), 27.61 (CH_2)ppm.

Cyclohexene (2)-1-one-3 methylcarboxylate (2)

The first three steps were synthesized according to the methylcarboxylate 1.
The oxidation has been described in the literature.[6] After distillation the product 2 was 94 % pure (GC).[6] Transforming into the free carboxylate 4, recrystallisation and esterification led to analytically pure methylcarboxylate 2. Yield: (4 steps) 12.5g(33%) (GC: 94%), (6 steps) 8.9g(24%) (GC: 100%).- bp.: 118-120°C/11 torr.- $C_8H_{10}O_3$ (154.1): calc. C, 62.33; H, 6.55; found C, 62.47; H, 6.63%.- Ir ($CDCl_3$): 1724 (CO-keto), 1695 (CO-carboxyl), 1620 (C=C) cm^{-1}.- Uv (hexane): $\lambda max_{\pi\pi}$* (lg ε)= 232 nm (4.65), $\lambda max_{n\pi}$* (lg ε)= 360 nm (1.89).- ^1H nmr ($CDCl_3$): δ = 6.69 (t, 1Hz, 1H, olefin-H), 3.81 (s,3H,CH_3), 2.32-2.70 (m,4H,CH_2), 2.20-1.85 (m,2H,CH_2) ppm.- ^{13}C nmr ($CDCl_3$): δ = 199.99 (CO), 167.00 (CO_2), 148.91 (C=), 133.01 (=CH), 52.62 (CH_3), 37.71 (CH_2), 24.90 (CH_2), 22.21 (CH_2) ppm.

Cyclopentene (2)-1-one-3 carboxylate (3)

8 g (57 mmol) 1 were stirred with 70mmol Na_2CO_3 in 80 ml water for 100 min, and were

evacuated from time to time. After extraction with 20 ml ether the aqueous layer was acidified (ph = 2 to 3) at 0°C. The precipitating carboxylate 3 was recrystallized from isopropanol and dried at 60°C/0.05 torr. Yield: 3.2-3.6 g (45-50%).- mp. 193-194°C (isopropanol).- $C_6H_6O_3$ (126.1): calc.C, 57.14; H, 4.76; found C,57.54; H, 4.91; Ir (KBr): 3090 (=CH), 2930 (OH max.), 1725 (CO-keto), 1670 (CO-carboxyl) 1609 (C=C) cm^{-1}.

Cyclohexene (2-)-1-one-3 carboxylate (4)

12.5 g (81 mmol) enonecarboxylate 2 were stirred with 0.1 mol of Na_2CO_3 in 100 ml water for 7 h at 23°C. The solution was acidified with HCl (10 %) to ph=2 and immediately extracted twice with methylene chloride. After evaporation the residue was solved in 20 ml methylene chloride and precipitated by 100 ml pentane. After filtration the product was dried at 40°C/0.05 torr. Yield: 8.5 g (75 %). mp.: 123°C.[14] $C_7H_8O_3$ (140.1): calc. C, 59.99; H, 5.77; found C, 59.76; H, 5.78.- Ir 3420-2560 (OH), 1750 (CO-keto), 1645 (CO-carboxyl), 1618 (C=C) cm^{-1}.- ^1H nmr δ = 10.86 (s,1H,COOH), 6.85 (t,1.5 Hz,1H,olefin-H), 2.80-2.33 (m,4H,CH_2), 2.33-1.78 (m,2H,CH_2)ppm.

General procedure for preparing the chiral enone carboxylates[8]: 6.1 ml (78 mmol) DMF and 15 ml acetonitrile are cooled under nitrogen to -20°C. 2.7 mol (19 mmol) of oxalyl chloride, dissolved in 10 ml acetonitrile, are added. After 15 min 39 mmol carboxylate 3 or 4 are added. When the white precipitate has dissolved, 39 mmol alcohol, dissolved in 6.2 ml (39 mmol) pyridine and 15 ml acetonitrile, are added. Usually the reaction mixture is allowed to stand overnight at room temp. The mixture is diluted with 150 ml of methylene chloride, washed with cold (1M) Na_2CO_3-solution and twice with water. After extraction with methylene chloride the mixture is dried over $MgSO_4$, filtered, evaporated and distilled or chromatographied. Cyclohexene (2)-1-one-3-methylcarboxylate (2). yield 5.7 g (95 %).

Cyclopentene (2)-1-one-3 [(-)(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl]-carboxylate (5)

Procedure: distillation.- Yield: 6.7 g (65 %). bp. (bulb to bulb): 185°C/0.08 torr.- mp.: 31°C (pentane at -10°C). -$C_{16}H_{24}O_3$ (264.4): calc. C, 72.69; H, 9.15; found C, 72.73; H, 9.26.- $[\alpha]_D^{22}$=-82.2° (c=1.07 in $CHCl_3$).- Ir ($CDCl_3$): 1710 (CO), 1605(C=C) cm^{-1}. Uv ($CHCl_3$): $\lambda max_{\pi\pi^*}$ (lg ε)= 242 nm (3.63); (benzene): $\lambda max_{n\pi^*}$ (lg ε)= 346 nm (1.42).- ^1H nmr ($CDCl_3$): δ = 6.66 (t,1Hz,1H,olefin-H), 4.84 (dt,4.5/10.4 Hz,1H, CHO), 2.86 (m,4H,CH_2-enone), 1.96-0.85 (m,9H,cyclohexane ring), 0.95, 0.92, 0.82 (3d,CH_3,9H)ppm.- ^{13}C nmr ($CDCl_3$): δ = 208.60 (CO), 164.80 (C=CH), 163.93 (CO_2), 137.90 (C=CH) 75.94 (C-1), 47.06 (C-2), 40.76 (C-6), 35.58 (CH_2-CO), 33.52 (C-4), 31.41 (C-5), 27.55 (CH_2-C=), 26.60 (C-7), 23.64 (C-3), 22.00 (C-10),20.73 (C-9), 16.54 (C-8) ppm.

Cyclohexene (2)-1-one-3[(-)(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl]-carboxylate (6)

Procedure: distillation.- Yield 8.1 g (75 %). bp. (bulb to bulb): 198°C/0.05 torr.- m.p.: 47°C (pentane/ether 70:30).- $C_{17}H_{25}O_3$ (278.4): calc. C, 73.33; H, 9.43; found C, 73.50; H, 9.37.- $[\alpha]_D^{22}$=-74.5° (c=1.39 in $CHCl_3$).- Ir ($CDCl_3$): 1710 (CO-keto), 1682 (CO-carboxyl), 1620 (C=C) cm^{-1}.- Uv (hexane): $\lambda max_{\pi\pi^*}$ (lg ε)= 232 nm (3.99), $max_{n\pi^*}$ (lg ε)= 360 nm (1.42).- ^1H nmr ($CDCl_3$): δ = 6.69 (t,1.5 Hz,1H,olefin-H), 4.76 (dt, 4.5/10.5 Hz,1H,CHO), 2.54 (m,6H,CH_2-enone), 1.90-0.80 (m,9H,cyclohexane ring), 0.90. 0.76, 0.67 (3d,9H,CH_3) ppm.- ^{13}C nmr ($CDCl_3$): δ = 199.50 (CO), 163.74 (CO_2), 149.35 (C=CH), 132.58, (C=CH), 75.44 (C-1), 47.02 (C-2), 40.71 (C-6), 37.63 (CH_2-CO), 34.19 (C-4), 31.39 (C-5), 26.35 (C-7), 24.86 (CH_2-enone), 23.44 (C-3), 22.21 (CH_2-enone), 22.00 (C-10), 20.73 (C-9), 16.34 (C-8) ppm.

Cyclopentene (2)-1-one-3[(-) (1R,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)-cyclohexyl]-carboxylate (7) and (+) (1S,2R,5R)-isomer (7a)

Procedure: A: distillation, B. filtration through a short (10 cm) column (silica) in ethyl acetate/hexane (10:50).- If the minor isomer of 8-phenylmenthol[10] is not separated, carboxylate 7a is formed. Purification succeeds by column chromatography (silica 100/200) from ethyl acetate/hexane (10:50) or by HPLC (ethyl acetate/hexane=10:90). In order to give complete data, both carboxylates 7 and 7a are characterized now: yield 7 : 7.2g (56%); 7a : 1.2g(9%).- b.p. (bulb to bulb): 220°C/0.01 torr.- mp.: 7a: 98°C.- $C_{21}H_{28}O_3$ (328.5). calc. C, 76.79; H, 8.59; found 7: C, 76.89 H, 8.41.- 7a: C, 76.18; H, 8.32.- $[\alpha]_D^{22}$ (7)=-26.9° (c-1.00 in ethanol); (7a)=+12.6° (c=0.99 in ethanol). Ir ($CDCl_3$) 7 u. 7a: 1715 (CO), 1610 (C=C) cm^{-1}. ^1H nmr ($CDCl_3$) 7 [7a]: δ = 7.27 [7.30] (m,5H,Ph), 6.04 [6.20] (t,1.5 Hz,1H,olefin H), 4.97[5.23] (d.t, 4.5/10.4 Hz; 1H, CHO), 2.29 [2.40](m,4H,CH_2-enone), 1.86-0.70 1.91-0-75 (m, 8H, cyclohexane ring), 1.32, 1.17, (2S,6H,2CH_3(9/8)); 0.88 (d,3H,CH_3,10) ppm.- ^{13}C nmr ($CDCl_3$) 7 [7a]: δ = 209.07 [209.12](CO); 164.11 [164.26] (CO_2); 163.28 [163.21] (C=CH); 151.80 [151.29](Ph-1); 128.03 [128.02] (meta); 125.25 [125.37] (ortho); 125.00 [125.06] (para); 137.55 [137.48] (C=CH); 75.25 [72.32](C-1); 50.20 [50.77] (C-2); 41.63 [38.34] (C-6); 39.45 [39.72] (C-7); 35.40 [35.41] (CH_2-CO); 34.45 [34.15] (C-4); 31.30 [31.07](C-5); 29.70 [29.24] (C-9); 26.85 [26.89] (CH_2-C=); 26.22 [23.20](C-3); 22.99 [23.53] (C-8); 21.76 [18.37](C-10) ppm.

Cyclohexene (2)-1-one-3 [(-)(1R,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)-cyclohexyl]-carboxylate (8) and (+)(1S,2R,5R)-isomer (8a)

Preparation: see compounds 7 and 7a.- Yield: 8 : 10.2g(76%); 8a 1.7g(13%); HPLC: rt= 12.0 min (8), 13.8 min (8a) , Flow=12ml/min.- bp. (bulb to bulb): 170°C/0.01 torr.- mp. (8a): 110°C.- $C_{22}H_{30}O_3$ (342.5): calc. C, 77.15; H, 8.85; found 8: C, 77.34; H, 8.76; 8a: C, 77.14; H, 8.86.- $[\alpha]_D^{22}$(8)=-30.7°C (c=0.19 in $CHCl_3$); 8a=+20.5° (c=0.21 in $CHCl_3$).- Ir ($CDCl_3$) 8 [8a]: 1706 [1709](CO-keto), 1679 [1679] (CO-carboxyl), 1618 [1620], 1597 [1596] (C=C) cm^{-1}.- Uv (hexane) 8 [8a]: $\lambda max_{\pi\pi^*}$ (lg ε) = 233 nm (4.09) [=233 (4.09)] ; $\lambda max_{n\pi^*}$ (lg ε)= 356 nm (1.39) [=355 nm (1.42)]; $\lambda max_{aromat.}$ (lg ε)= 209 nm (4.19) [=209nm (4.14)] .- ^1H nmr ($CDCl_3$) 8 [8a] : δ = 7.25 [7.22](m,5H,Ph); 6.15 [6.22] (t,1Hz,1H,olefin-H); 5.01 [5.21] (d.t, 4.5/10.5 Hz [6.0/9.0 Hz] ; 1H, CHO); 2.05 (m,6H,CH_2-enone); 1.80-0.60 [1.85-0.80] (m,8H,cyclohexane ring); 1.30, 1.15 [1.30, 1.20](2s,6H,2CH_3(8/9)); 0.9 [1.12] (d,3H,CH_3(10)). ^{13}C nmr ($CDCl_3$) 8 [8a] : δ = 199.78 [200.06] (CO); 165.29 [165.35] (CO_2); 151.66 [151.16] (Ph-1), 148.64 [148.97] (C=CH); 132.41 [132.48] (C=CH); 128.02 [120.08] (meta);125.21 [125.51] (ortho); 125.00 [125.25] (para); 75.09 [72.44] (C-1); 50.29 [50.81] (C-2); 41.69 [38.32] (C-6); 39.42 [39.86] (C-7); 37.55 [37.65] (CH_2-CO); 34.47 [31.12] (C-4); 31.29 [27.36] (C-5); 29.61 [28.84] (C-9); 26.33 [22.08] (C-3); 24.20 [24.41] (CH_2-enone), 23.10 [24.13] (C-8); 21.99 [21.28] (CH_2-C=C); 21.76 [18.67] (C-10) ppm.

Cyclopentene (2)-1-one-3- [(1R,2S,3R,4S)-2-neopentyloxy-3-bornyl] carboxylate (9)

Preparation: filtration through a short silica column (10 cm) and HPLC-separation from ethyl acetate/hexane (10:90) - Yield: 4.3 g (32 %).- $C_{21}H_{32}O_4$ (348.5): calc. C, 72.37; H, 9.27; found C, 72.69; H, 9.18.- Ir ($CDCl_3$): 1710 (CO), 16.06 (C=C) cm^{-1}. ^1H nmr ($CDCl_3$): δ = 208.86 (CO); 164.88 (CO_2); 163.50 (C=CH); 138.04 (C=CH), 87.48 (C-3); 83.49 (C-11); 79.26 (C-2); 49.94 (C-1); 49.34 (C-4); 47.03 (C-8); 35.59 (CH_2-CO); 33.17 (C-5); 32.21 (C-(CH_3)$_3$] 27.40 (CH_2-C=C); 26.77 (C-(CH_3)$_3$] 23.98 (C-6); 20.86 (C-10); 20.58 (C-7); 11.39 (C-9) ppm.

Cyclohexene (2)-1-one-3-[(+)(1R,2S,3R,4S)-2-neopentyloxy-3-bornyl]-carboxylate (10)

Preparation: see compound 9. Yield: 6.5 g (46 %) HPLC:rt=13.4 min, Flow=12,5 ml/min.

$C_{22}H_{32}O_4$ (362.5): calc. C, 72.88; H, 9.49; found C, 73.84; H, 9.52. $[\alpha]_D^{22}$=+14.4°C (c=0.55 in $CHCl_3$). Ir ($CDCl_3$): 1710 (CO-keto), 1680 (CO-carboxyl):1617 (C=C) cm^{-1}. Uv (hexane): $\lambda max_{\pi\pi^*}$ (lg ε)= 233 nm (4.15); $\lambda max_{\eta\pi^*}$ (lg ε)= 360 nm (1.39). ^1H nmr ($CDCl_3$): δ = 6.73 (t,1Hz,olefin H); 4.82 (d,7Hz,1H,CHOCO); 3.34 (d,7Hz,1H,CHOR); 3.07 (s,2H,OCH_2); 2.7-2.3 (m,4H,CH_2-enone); 2.20-1.90 (m,2H,CH_2-enone); 1.90-0.70 (m,5H, bornane); 1.20, 0.94, 0.89 (3S,9H,$3CH_3$); 0.78 (S,9H$(CH_3)_3$) ppm. ^{13}C nmr ($CDCl_3$): δ = 200.16 (CO); 165.80 (CO_2); 149.57 (C=CH); 133.08 (C=CH); 87.54 (C-3); 83.53 (C-11); 79.46 (C-2); 49.99 (C-1); 49.38 (C-4); 47.07 (C-8); 37.82 (CH_2-CO); 33.21 (C-5); 32.28 (C-$(CH_3)_3$); 26.72 (C-$(CH_3)_3$) 24.95 (CH_2-enone); 24.13 (C-6); 22.27 (CH_2-c=); 20.78 (C-7); 20.89 (C-10); 11.43 (C-9) ppm.

Cyclopentene (2)-1-one-3-[1R,2S,3R,4S)-2-benzyloxy-3-bornyl] carboxylate (11)
Preparation: filtration through a short silica column and recrystallisation.- Yield: 6.5g (45 %).- mp.: 86-87°C (from ether/pentane (50:50) refrigerated at -50°C). $C_{23}H_{28}O_4$ (368.5): calc. C, 74.96; H, 7.67; found C, 74.54; H, 7.81.- Ir ($CDCl_3$): 1710 (CO), 1605 (C=C) cm. ^1H nmr ($CDCl_3$): δ = 7.23 (S,5H,Ph), 6.61 (t,2Hz,1H,=CH); 4.94 (d,7.2 Hz,1H,CHO-CO); 4.64 a. 4.35 (d,11Hz,1H,CH_2O); 3.54 (d,7.2Hz,1H,CHOR); 2.44 (m,4H,CH_2-enone); 2.05-1.50 (m,5H,bornane); 1.21, 1.02, 0.88 (3S,9H,$3CH_3$)ppm.- ^{13}C nmr ($CDCl_3$): δ = 209.20 (CO); 164.80 (C=CH); 163.87 (CO_2); 138.63 (C=CH); 137.75 (Ph-1); 128.02 (ortho); 127.30 (meta); 127.09 (para); 87.88 (C-3), 79.46 (C-2);75.00 (C-11); 49.70 (C-1); 49.05 (C-4); 47.23 (C-8); 35.47 (CH_2-CO); 33.15 (C-5); 27.21 (CH_2-C=); 23.98 (C-6); 20.96 (C-10); 20.82 (C-7); 11.34 (C-9) ppm.

Cyclohexene (2)-1-one-3 [(-)(1R,2S,3R,4S)-benzyloxy-3-bornyl] -carboxylate (12)

Preparation: see compound 11.- Yield: 9 g (60 %).- mp.: 62-63°C (from ether/pentane (50:50).- $C_{24}H_{30}O_4$ (382.5): calc. C, 75.36; H, 7.92; found C, 75.00; H, 8.01.- $[\alpha]_D^{20}$=-24.9°C (c=0.25, $CHCl_3$).- Uv (hexane): $\lambda_{max\,\eta\pi^*}$(lg ε)= 355 nm (1.45), $\lambda_{max\,\pi\pi^*}$ (lg ε)= 232 nm (4.09), $\lambda_{max\ aromat}$ (lg ε)= 206 nm (4.13).- ^1H nmr ($CDCl_3$): δ =7.16 (s,5H,Ph); 6.59 (t,1Hz,=CH); 4.84 (d,6Hz,1H,CHO-CO); 4.52 u. 4.29 (d,10.8Hz,2H,OCH_2); 3.48 (d,6.7Hz,1H,CHOR); 2.40-2.20 (m,4H,CH_2-enone); 2.05-1.80 (m,2H,CH_2-enone); 1.90-0.70 (m,5H,bornane); 1.18, 0.97, 0.83 (3S,9H,$3CH_3$) ppm.- ^{13}C nmr ($CDCl_3$): δ = 200.00 (CO); 166.11 (CO_2); 149.41 (C=CH); 138.68 (C=CH); 132.74 (Ph-1); 128.03 (meta);127.21 (para); 127.15 (ortho); 87.84 (C-3); 79.46 (C-2); 74.95 (C-11); 49.65 (C-1); 49.08 (C-4); 47.16 (C-8); 37.61 (CH_2-CO); 33.14 (C-5); 24.67 (CH_2-enone); 24.07 (C-6);21.98 (CH_2-C=); 20.96 (C-7/10); 11.34 (C-9) ppm.

Preparation of the photo-products 13 to 22
A 250 ml solution of 5.0 mmol enone carboxylate (C=0.02), 1.32 (10 mmol) 1.1'-diethoxyethene[13] 23 (C=0.04)in benzene is flushed with nitrogen and irradiated (HPK 125 W, Philips, Pyrex) until 95 % of the enone carboxylates have reacted (control HPLC). The cyclopentenone carboxylates need 290 min, the cyclohexenone carboxylates 390 min under these conditions. After evaporation,the residue is filtered through a short silica column (100/200) from ethyl acetate/hexane (10:50) in order to destroy the rest of 23 and resulting polymers. After evaporation, the mixture is dissolved in ethyl acetate/hexane (10:90, 2 ml for 300 mg mixture) and separated by HPLC. The fractions are evaporated and evacuated (1h, 10^{-2} torr). Half of the crude product is carefully separated by preparative HPLC into single compounds,which are identified by nmr. With this information the other half is then analysed by ^1H and ^{13}C nmr resp. analytic HPLC to determine the de-values. About 5 % of the enone-carboxylates 5-12 can be recovered. Oxetane (by)-products are hydrolysed by silica gel.

6.6-Diethoxy-bicyclo[3.2.0] heptane-2-one-5-methylcarboxylate (13)
Yield: 0.52 g (41%), HPLC: rt = 20.8 min, Flow = 18 ml/min.- $C_{13}H_{18}O_5$ (254.3): calc. C, 60.99; H, 7.88, found C, 61.03; H, 8.02.- ^{1}H nmr ($CDCl_3$): δ =3.70 (s,3H,OCH_3); 3.57, 3.45 (2q,7.2Hz,4H,OCH_2CH_3) 2.92 (dd, 10.8/5.7 Hz,1H,CH-CH_2); 2.58 (dd,-12.3/10:8Hz,1H,CH-CHH,cis); 2.03 (dd,-12.2/5.7Hz,CH-CHH,trans); 2.46-2.19 (m,4H,CH_2-CH_2); 1.18, 1.10 (2t,7Hz,6H,$2CH_3$)ppm.- ^{13}C nmr ($CDCl_3$): δ =217.43 (CO), 172.39 (CO_2), 101.11 (O-CO); 61.54 (C); 57.96, 57.35 (CH_2O); 51.92 (OCH_3); 40.09 (CH); 38.26 (CH_2-CH); 33.98 (CH_2CO); 24.69 (CH_2); 15.06, 14.96 (CH_3) ppm.

7.7-Diethoxy-bicyclo[4.2.0]octane-2-one-6-methylcarboxylate (14)
Yield: 0.54 g (40 %); HPLC: rt = 28.7 min, Flow=12.5 ml/min.- $C_{14}H_{20}O_5$ (268.3): calc. C, 62.67; H, 8.20; found C, 62.33; H, 8.01.- Ir ($CDCl_3$): 1722 (CO-keto), 1705 (CO-carboxyl) cm^{-1}.- ^{1}H nmr ($CDCl_3$): δ = 3.73 (s,3H,OCH_3); 3.64 (qd,7.2/10.0 Hz,1H, OCHHCH$_3$); 3.62 (qd, 7.2/10.0 Hz,1H,OCHHCH$_3$); 3.42 (q, 7.2 Hz,2H,OCH_2CH_3); 3.21 (dd,10.2/9.8 Hz,1H,CH-CH_2); 2.58 (dd,-12.3/10.2 Hz, 1H,CH-CHH,cis); 2.19 (dd,-12.3/9.8Hz,CH-CHH,trans); 2.40-1.80 (m,6H,CH_2-CH_2-CH_2); 1.22 (t,7.2 Hz,3H,CH_3); 1.17 (t,7.2 Hz,3H,CH_3)ppm. ^{13}C nmr ($CDCl_3$): δ = 211.14 (CO); 172.99 (CO_2); 101.73 (OCO); 61.35 (C); 58.56, 57.57 (CH_2O); 52.12 (OCH_3); 38.76 (CH); 38.37 (CH_2-CO); 33.35 (CH-CH_2); 25.73, 21.44 (CH_2-CH_2); 15.09 (CH_3)ppm.

6,6-Diethoxy-bicyclo[3.2.0]heptane-2-one-5[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl]-carboxylate (15)
Yield: 0.74 (39%); HPLC:rt = 11.8 min, Flow=14.5 ml/min.- $C_{22}H_{36}O_5$ (380.5): calc. C, 69.96; H, 9.56; found C, 70.17; H, 9.39.- ^{1}H nmr ($CDCl_3$): δ =4.75 (td, 10.5/4.5 Hz,1H,CHO); 3.80-3.20 (m,4H,OCH_2); 3.03 (dd,10.8/5.7 Hz,1H,CH-CH_2); 2.79 (dd,-12.2/10.8 Hz,1H,CH-CHH,cis); 2.40-1.90 (m,4H,CH_2-CH_2); 2.07 (dd,-12.2/5.7Hz,CH-CHH,trans); 1.80-1.30 (m,9H,cyclohexane); 1.30-1.08 (m,6H,CH_3CH_2O); 0.95, 0.90 (d,6H,CH_3(8/9)); 0.64 (d,3H,$CH_3$10)ppm.- ^{13}C nmr ($CDCl_3$): δ = 218.03 (CO); 171.50 [171.20] (CO_2,de=8%); 101.05 (COC); 74.98 [74.79] (C-1,de=6%); 61.54, 61.42 (C); 58.18, 57.20 (OCH_2); 47.06 (C-2); 40.76 (C-6); 40.09 (CH); 39.86 [38.30] (CH-CH_2,de=8%), 34.24 (C-4); 33.52 (CH_2-CO); 31.41 (C-5); 26.60 (C-7); 25.11 (CH_2); 23.15 (C-3); 22.00 (C-10); 20.93, 20.85 (C-8/9); 16.38, 16.11 (C-8/9); 15.01, 14.90 (CH_2-CH_3)ppm.

7.7-Diethoxy-bicyclo [4.2.0] octane-2-one-6[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl] -carboxylate (16)
Yield: 0.83 g (42 %), HPLC:rt=18.2min (58%), 20.6 min (42%), (de=16%), Flow=12.5 ml/min.- $C_{23}H_{38}O_5$ (394.6): calc. C, 70.00; H, 9.73; found C, 70.01; H, 9.58.- Ir ($CDCl_3$): 1722 (CO-keto), 1712 (CO-carboxyl)cm^{-1}.- ^{1}H nmr ($CDCl_3$): δ = 4.76 (td,10.5/4.5 Hz,1H,CHO); 3.76 (qd,7.5/10.0 Hz,1H,OCHHCH$_3$); 3.70 (qd,7.5/10.0 Hz,1H,OCHHCH$_3$); 3.45 (q,7.5Hz,2H,OCH_2CH_3); 3.24 (dd,9.8/9.0 Hz,1H,CH-CH_2); 2.58 (dd,-12.2/9.8 Hz, 1H,CH-CHH,cis); 2.09 (dd,-12.2/9.0Hz,CH-CHH,trans); 2.42-1.80 (m,6H,CH_2-CH_2-CH_2); 1.80-0.60 (m,9H,cyclohexane); 1.16(t,7.5Hz,3H,OCH_2CH_3); 1.12 (t,7.5Hz,3H,OCH_2CH_3); 0.97-0.71 (m,9H,$3CH_3$)ppm.- ^{13}C nmr ($CDCl_3$): δ =211.41 (CO), 171.80 [171.56] (CO_2, de=14%), 101.79 [101.69] (O-C-O,de=14%); 74.91 [74.86] (C-1,de=13%); 61.30 [61.41] (C,de=15%); 58.76 [57.40](OCH$_2$); 46.86 [47.02] (C-2,de=14%); 40.87 (C-6); 38.45 [38.28] (CH,de=14%); 38.17 (CH_2CO); 34.27 (C-4); 32.90 (CH-CH_2); 31.40 (C-5); 26.13 (C-7); 25.72 (CH_2-cyclohexanone); 23.14 (C-3); 22.02 (C-10); 20.88 (C-8/9); 21.12 (CH_2-cyclohexanone); 16.27, 16.06 (C-8/9); 15.10, 14.93 (CH_2-CH_3)ppm.

6.6-Diethoxy-bicyclo[3.2.0] heptane-2-one-5 [(1R,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)-cyclohexyl] -carboxylate (17)
Yield: 0.80 g (35 %); HPLC:rt=12 min, Flow=15 ml/min (de=15-18%).- $C_{28}H_{40}O_5$ (456.6): calc. C, 73.65 ; H, 8.85; found C, 72.97; H, 8.94.- ^{1}H nmr ($CDCl_3$): δ = 7.25 (m,5H,Ph);

4.93 (td,10.5/4.5 Hz,1H,CHO); 3.79 - 3.20 (m,4H,O$\underline{CH_2}CH_3$), 2.79 (dd,10.9/5.7Hz,1H, $\underline{CH}$-CH_2); 2.53 (dd,-12.2/10.9Hz,1H,CH-C$\underline{HH}$, cis); 2.40 - 2.19 (m,4H,CH_2-cyclopentanone); 2.11 (dd,-12.2/5.7 Hz,1H,CH-CH$\underline{H}$,trans); 1.95 - 0.70 (m,8H,cyclohexane); 1.39-1.08 (m,6H,$OCH_2\underline{CH_3}$); 1.07-0.82 (m,9H,$3CH_3$) ppm.- ^{13}C nmr ($CDCl_3$): δ = 218.64 [217.75] (CO,de=23%); 171.37 [171.13] (CO_2de=18%); 151.38 [151.26] (Ph-1,de=18%); 128.03 (meta), 125.44 (ortho); 125.28 (para); 101.35 [101.21](CO_2,de=24%); 76.01 [75.09] (C-1, de=24%); 62.09 [61.10](C-bicyclus, de=24%); 58.24 [57.30] (OCH_2 de=24%); 57.30 [57.08] (OCH_2, de=24%); 50.08 [49.79] (C-2), de=18%); 41.84 [41.75] (C-6); 40.01 [39.21] ($\underline{CH}$-CH_2); 39.66 (C-7); 38.26 ($\underline{CH_2}$-CO); 34.74 (C-4); 33.00 (CH-$\underline{CH_2}$); 31.33 (C-5); 28.04 (C-8/9), 27.50 (C-3); 24.42 (C-8/9); 24.16 (CH_2-cyclopentanone); 21.75 (C-10); 14.92 ($OCH_2\underline{CH_3}$)ppm.

7.7-Diethoxy-bicyclo[4.2.0]octane-2-one-6[(1R,2S,5R)-5-methyl-2-(1-methyl-1-phenyl-ethyl cyclohexyl]-carboxylate (18)

Yield: 1.06 g (45%) at 23°C in benzene, 1.75 g (75%) at -40°C in toluene: HPLC; rt= 19.2 min (1S,6R:78%); 27.4 min (1R,6S:22%), de=56% Flow= 12ml/min.- $C_{29}H_{42}O_5$ (470.7): calc. C, 74.00; H, 9.01; found C, 73.56; H, 8.88.- Ir ($CDCl_3$): 1726 (CO-keto);1705 (CO-carboxyl), 1592 (C=C, aromat) cm^{-1}.- ^{1}H nmr ($CDCl_3$) 18 (1S,6R)[18a] (1R,6S): δ = 7.28 [7.30] (m,5,ph); 5.00 [4.97] (td, 10.5/4.5 Hz, 1H,CHO); 3.64 [3.63] (qd, 7.2/10.0 Hz,1H,OCH$\underline{H}$$CH_3$); 3.58 [3.58] (qd,7.2/10.0 Hz,1H,OC$\underline{H}$$HCH_3$); 3.45 [3.43](q,7.2 Hz,2H,O$\underline{CH_2}CH_3$); 2.96 [3.12] (dd,9.8/8.0 Hz,1H,$\underline{CH}$-CH_2); 2.51 [2.55](dd,-12.2/9.8Hz, 1H,CH-C$\underline{HH}$, cis); 2.15 [2.12] (dd,-12-2/9.0 Hz,1H,CH-CH$\underline{H}$,trans); 2.31-1.82 (m,6H,CH_2-cyclohexanone); 1.80-0.65 (m,8H,cyclohexane); 1.29 [1.40] (S,3H,CH_3-8/9); 1.22 [1.24] (s,3H,CH_3-8/9); 1.19 [1.20] (t,7.2Hz,3H,$OCH_2\underline{CH_3}$) 1.12 [1.18] (t,7.2Hz,3H,$OCH_2\underline{CH_3}$); 0.75 [0.86] (d,6Hz,3H,CH_3-10).- ^{13}C nmr ($CDCl_3$) 18 (1S,6R) [18a](1R,6S); δ =210.88 [211.48] (CO,de=57%); 172.01 [171.94] (CO_2,de=56%); 150.61 [150.57] (Ph-1, de=55%) 128.07 [128.11] (meta); 125.54 [125.82] (ortho); 125.34 (para); 101.28 [101.94] (OCO, de=56%); 76.21 [76.54] (C-1, de56%); 61.26 [61.08] (C-bicyclus, de=55%); 58.49 [58.88] (OCH_2,de=54%); 57.46 [57.39] (O$\underline{CH_2}$, de=54%); 50.12 [49.92] (C-2, de=56%); 41.85 [46.96] (C-6); 40.30 [40.18] (C-7); 38.31 [38.37] ($\underline{CH_2}$CO); 38.30 [38.22] ($\underline{CH}$-CH_2); 34.50 [34.58] (C-4); 33.65 [32.87] (CH-$\underline{CH_2}$); 31.36 [31.44] (C-5); 29.38 [28.52] (C-8/9); 25.57 [25.78] (CH_2); 25.30 (C-8/9); 21.72 [21.22] (CH_2); 21.73 [21.76] (C-10); 14.95 [15.11] ($\underline{CH_3}$-CH_2O); 14.95 [14.96] ($\underline{CH_3}CH_2O$) ppm.

6.6-Diethoxy-bicyclo[3.2.0] heptane-2-one-5 [(1R,2S,3R,4S)-2-neopentyloxy-3-bornyl]-carboxylate (19)

Yield: 0.91 g (36%); HPLC:rt=12.6 min (47.6%); 13.4 min (52.4%), de=5%, Flow= min.- $C_{27}H_{44}O_6$ (464.7): calc. C, 69.77; H, 9.56; found C, 70.02; H, 9.49.- ^{1}H nmr ($CDCl_3$): δ = 4.81 (d,7Hz,1H,C$\underline{H}$OCO); 3.51 (q,7.5Hz,4H,O$\underline{CH_2}CH_3$); 3.29 3.08 and 2.95 (d,7Hz,1H,OC$\underline{H}$$\underline{H}$tBu); 2.88 (dd,10.5/5.5Hz,1H,$\underline{CH}$-CHH); 2.40 (dd,-12.5/ 10.5Hz,1H,CH-C$\underline{HH}$,cis); 2.20 (dd.-12.5,5Hz,1H,CH-CH$\underline{H}$,trans); 2.40-2.12 (m,4H,CH_2); 1.88-0.70 (m,5H,bornane); 1.21 (t,7Hz,3H,$OCH_2\underline{CH_3}$); 1.11 (t,7Hz,3H,$OCH_2\underline{CH_3}$); 0.90 (S,3H,CH_3); 0.80 (S,9H,tBu); 0.78, 0.79 (2S,6H,$2CH_3$)ppm.

7.7-Diethoxy-bicyclo[4.2.0]octane-2-one-6[(1R,2S,3R,4S)-2-neopentyloxy-3-bornyl]-carboxylate (20)

Yield: 1.05 g (44%); HPLC:rt=19.8 min (53%), 20.4 min (47%), de=6%, Flow=12.5ml/ min.- $C_{20}H_{46}O_6$ (478.7): calc. C, 70.25; H, 9.71, found C, 7018; H, 9.75.- ^{1}H nmr ($CDCl_3$): δ =4.88 (d,7Hz,1H,CHOCO); 3.62 (dq,J= 3/7 Hz,2H,OCHHCH$_3$); 3.46 (q,7Hz,2H, O$\underline{CH_2}CH_3$); 3.20 (dq,3.0/8.7 Hz,2H,OC$\underline{H}$$\underline{H}$tBu), 3.19 (d,7Hz,1H,C$\underline{H}$$OCH_2$); 2.98 (dd,10.5/ 8.4 Hz,1H-C$\underline{H}$-CHH); 2.64 (dd,-12.3/10.5Hz,1H,CH-C$\underline{H}$$\underline{H}$,cis); 2.24 (dd,-12.2/8.4 Hz, 1H,CH-CH$\underline{H}$,trans); 2.45-1.82 (m,6H,CH_2); 1.81-0.66 (m,5H,bornane); 1.20 (dt,3.0/ 7.0 Hz,6H,$OCH_2\underline{CH_3}$); 0.95 (s,3H,CH_3); 0.84 (S,9H,tBu); 0.83, 0.82 (2S,6H,$2CH_3$)ppm.-

^{13}C nmr ($CDCl_3$): δ = 211.21 [211.23] (CO); 172.28 [172.44] (CO_2de= 7%); 102.17 [102.06] (OCO, de=6%), 89.35 [89.26] (C-3); 83.54 [83.62] (C-11, de=5%); 79.57 (C-2); 61.29 [61.45] (C-bicyclus, de =6%); 58.54 [58.79] ($CH_3\underline{C}H_2O$, de=6%); 57.57 [57.37] ($CH_3\underline{C}H_2O$, de=4%); 50.37 [50.58] (C-1); 50.25 [50.12] (C-4); 46.75 (C-8); 38.63 [38.49] ($\underline{C}H$-CH_2); 38.36 (CH_2CO); 33.95 [33.35] (C-5); 32.63 (C-$(CH_3)_3$); 27.00 [26.82] (C-$(CH_3)_3$), de=6%), 25.65 [26.01] (CH_2); 24.00 [24.08] (C-6); 21.57 (CH_2); 21.08 (C-10); 20.86 [20.94] (C-7); 14.99 [15.11] ($\underline{C}H_3CH_2O$); 14.99 [15.22] ($\underline{C}H_3CH_2O$); 11.75 (C-9) ppm.

6.6-Diethoxy-bicyclo[3.2.0]heptan-4-one-5[(1R,2S,3R,4S)-2-benzyloxy-3-bornyl]-carboxylate (21)

Yield: 1.0 g (41%); HPLC:rt=12.0-15.2 min (de=6-8%), Flow= 16.5 ml/min.- $C_{29}H_{40}O_6$ (484.7): calc. C, 71.86, H, 8.34; found C, 71.94; H, 8.26.- ^1H nmr ($CDCl_3$): δ =7.12 (m,5H,Ph); 4.89 (d,7Hz,1H,$\underline{C}$HOCO); 4.49 (d,11.5 Hz,1H,$\underline{C}$HHOBn); 4.31 (d,11.5 Hz,1H, CHHOBn); 3.58 (dq,3/7Hz,2H,OCHHCH$_3$) 3.29 (d,7Hz,1H,CHOR); 3.25 (q,7Hz,2H,O$\underline{C}H_2CH_3$); 3.10 (dd,10.5/6.3Hz,1H,$\underline{C}$H-CH_2); 2.49 (dd,-12.5/10.5Hz,1H,CH-C$\underline{H}$H,cis); 2.02 (dd,-12.5/ 6.3 Hz,1H,CH-CH$\underline{H}$,trans); 2.40-2.10 (m,4H,CH_2); 1.80-0.65 (m,5H,bornane); 1.24 (t,7Hz, O$CH_2\underline{C}H_3$); 1.01 (t,7Hz,O$CH_2\underline{C}H_3$); 0.93 [0.91] (2S,6H,CH_3); 0.67 (s,3H,CH_3)ppm.- ^{13}C nmr ($CDCl_3$): δ =218.52 (CO), 171.89 (CO_2); 138.90 (Ph-1); 128.29 (meta); 127.37 (ortho); 126.86 (para); 101.29 [101.28](OCO, de=8%); 87.85 (C-3); 78.69 (C-2); 74.67 (C-11); 61.57 (C-bicyclus); 57.96 (O$\underline{C}H_2CH_3$); 57.46 (O$\underline{C}H_2CH_3$); 49.82 (C-1); 49.54 (C-4); 47.12 (C-8); 40.47 ($\underline{C}$H-CH_2); 38.21 (CH-$\underline{C}H_2$); 34.36 (C-5); 33.40 (CH_2); 24.64 (CH_2); 24.12 (C-6); 20.97 (C-7); 20.96 (C-10); 15.22 ($\underline{C}H_3CH_2O$); 14.89 ($\underline{C}H_3CH_2O$); 11.48 (C-9)ppm.

7.7-Diethoxy-bicyclo[4.2.0]octane-2-one-6 [(1R,2S,3R,4S)-2-benzyloxy-3-bornyl]-carboxylate (22)

Yield: 1.15 g (46%); HPLC:rt=17.4 min 44.5%, 20.7 min(55.5 %) de=11%, Flow=15.5 ml/min.- $C_{30}H_{42}O_6$ (498.7): calc. C, 72.25; H, 8.51; found C, 73.10; H, 8.46.- ^1H nmr ($CDCl_3$): δ = 7.22 (S,5H,Ph); 4.80 (d,7Hz,1H,CHOCO); 4.52 (d,11.8Hz,1H,C$\underline{H}$HOBn); 4.39 (d,11.8Hz,1H,CH$\underline{H}$OBn); 3.56 (dq,3.0/7.0 Hz,2H,OCHHCH$_3$); 3.47 (d,7Hz,1H,$\underline{C}$HOR); 3.36 (q,7Hz,2H,O$\underline{C}H_2CH_3$); 3.16 (dd,10.0/9.2 Hz,1H,$\underline{C}$H-CH_2); 2.52 (dd,-12.2/10.0 Hz, 1H,CH-C$\underline{H}$H,cis); 2.09 (dd,-12.2/9.2 Hz,1H,CH-CH$\underline{H}$,trans); 2.30-1.86 (m,6H,CH_2); 1.85-0.65 (m,5H,bornane); 1.12 (t,7Hz,3H,O$CH_2\underline{C}H_3$); 1.09 (t,7Hz,3H,O$CH_2\underline{C}H_3$); 0.80 (S,3H,CH_3)ppm.- ^{13}C nmr ($CDCl_3$): δ =211.00 [211.11] (CO); 171.92 [172.06] (CO_2de= 11%); 138.85 [138.85] (Ph-1); 128.18 [128.16] (meta); 127.19 [127.25] (ortho); 127.05 (para); 101.79 [101.95] (OCO,de=12%); 87.78 [87.68] (C-3); 78.75 [78.86] (C-2); 74.51 [74.30] (C-11,de=9%); 61.25 [61.09](C-bicyclo, de=11%); 58.46 [58.56] (O$\underline{C}H_2CH_3$); 57.35 [57.25] (O$\underline{C}H_2CH_3$); 49.83 [49.68] (C-4); 49.75 [49.62] (C-1); 47.00 [46.96](C-8); 38.85 [38.59] ($\underline{C}$H-CH_2); 38.22[38.11](CH-$\underline{C}H_2$); 33.46 [33.19](C-5); 33.35 [33.40] ($\underline{C}H_2$-CO); 25.71 [25.28] (CH_2); 24.14 [23.99] (C-6); 21.17 [21.00] (CH_2); 20.93 [21.06] (C-7); 20.87 [20.92] (C-10); 15.11 [15.23] (O$CH_2\underline{C}H_3$); 14.96 [15.11] (O$CH_2\underline{C}H_3$); 11.50 (C-9) ppm.

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