## Supporting Information

## for

## Diastereoselective anodic hetero- and homo-coupling of menthol-, 8-methylmenthol- and 8-phenylmenthol-2-alkylmalonates

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${ }^{8}$ X-ray structure analysis

## Experimental part

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24. 2-((Benzyloxy)carbonyl)-3-methylbutanoic acid (5):

160 mL ( $250 \mathrm{mmol}, 1.6 \mathrm{M}$ in $n$-hexane) $n$-butyllithium were added to a solution of 35.14 mL $(25.3 \mathrm{~g}, 250 \mathrm{mmol})$ of dry diisopropylamine in 250 mL dry THF at $-70^{\circ} \mathrm{C}$. Finally, 41.2 g
( 210 mmol ) benzyl 3-methylbutanoate, dissolved in 170 mL THF, were added. After complete addition a stream of dry carbon dioxide was bubbled through the solution for about 20 min . At $-70^{\circ} \mathrm{C}$ the reaction mixture was carefully quenched with 40 mL of water and warmed up to rt . After acidification with conc. HCl the mixture was extracted with diethyl ether ( $3 \times 150 \mathrm{~mL}$ ). The combined organic layers were extracted with saturated sodium hydrogen carbonate ( $5 \times 70 \mathrm{~mL}$ ). The combined aqueous layers were washed with 70 mL of ether and then acidified with conc. HCl to pH 1 . The acidic solution was extracted with ether $(4 \times 100 \mathrm{~mL})$, and the combined extracts were dried over $\mathrm{MgSO}_{4}$. After the evaporation of the solvent 44.68 g ( $189.1 \mathrm{mmol}, 88 \%$ ) monoester 5 was obtained as an oily liquid.

FT-IR (film): $v=1732,1714 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=1.00,1.04(2 \mathrm{~d}, J=6.7$, each $\left.3 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.41\left(\mathrm{dsept}, J=6.9 \mathrm{~Hz}, J=6.7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 3.24(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.\mathrm{CHCH}\left(\mathrm{CH}_{3}\right)_{2}\right), 5.17\left(\mathrm{~d}, J=12.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{PhCH}_{a} \mathrm{H}_{\mathrm{b}}\right), 5.22\left(\mathrm{~d}, J=12.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{PhCH}_{\mathrm{a}} H_{b}\right)$, 7.30-7.40(m, 5H, phenyl). - ${ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=20.22,20.32\left(2 \mathrm{q}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 29.25(\mathrm{~d}$, $\left.C H\left(\mathrm{CH}_{3}\right)_{2}\right), 45.94\left(\mathrm{~d}, \mathrm{CHCH}\left(\mathrm{CH}_{3}\right)_{2}\right), 67.23\left(\mathrm{t}, \mathrm{PhCH}_{2} \mathrm{O}\right), 128.26,128.43,128.60(3 \mathrm{~d},=C-$ $\left.\mathrm{H}_{\text {phenyl }}\right), 135.27\left(\mathrm{~s},=C-\mathrm{C}_{\text {phenyl }}\right), 168.93\left(\mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {ester }}\right), 173.55\left(\mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {acid }}\right)$. - MS (GC/MS, 5 as methylester), $m / z$ (\%): 250 (19), 222 (14), 219 (4), 143 (14), 127 (3), 116 (86), 107 (18), 101 (52), 91 (100), 69 (17), 65 (10), 59 (18). $-\mathrm{C}_{13} \mathrm{H}_{16} \mathrm{O}_{4}$ (236.3): calcd. C 66.09, H 6.83; found C 66.10, H 6.86.
2. 2-((Benzyloxy)carbonyl)-3,3-dimethylbutanoic acid (6):
$125 \mathrm{~mL} n$-butyllithium ( $200 \mathrm{mmol}, 1.6 \mathrm{M}$ in $n$-hexane) were added to a solution of 20.2 g $(0.2 \mathrm{~mol}, 28.1 \mathrm{~mL})$ diisopropylamine in 500 mL dry THF at $-40^{\circ} \mathrm{C}$. The solution was stirred for 15 min and then $11.6 \mathrm{~g}(100 \mathrm{mmol}, 13 \mathrm{~mL})$ tert-butylacetic acid were added. The mixture was heated at $50^{\circ} \mathrm{C}$ for 1 h . After cooling to $-70^{\circ} \mathrm{C} 17.1 \mathrm{~g}(100 \mathrm{mmol}, 14.3 \mathrm{~mL})$ benzyl chloroformate were added. The solution was stirred for an additional 20 min ., then poured on
ice and the mixture was then acidified with $30 \mathrm{~mL}(0.3 \mathrm{~mol})$ conc. HCl . The aqueous layer was extracted with ether $(6 \times 150 \mathrm{~mL})$. After evaporation of the solvent a yellow oil was obtained. The oil was treated with saturated sodium hydrogen carbonate and washed with ether ( $3 \times 40 \mathrm{~mL}$ ) for purification. The aqueous layer was acidified with conc. HCl to pH 1 with cooling. Extraction with ether ( $5 \times 70 \mathrm{~mL}$ ), drying with $\mathrm{MgSO}_{4}$ and evaporation of the solvent yielded the yellow, oily product $\mathbf{6}(18.27 \mathrm{~g}, 73.0 \mathrm{mmol}, 73 \%)$.

FT-IR (film): $v=1737,1713 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=1.12\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 3.32(\mathrm{~s}$, $1 \mathrm{H}, \mathrm{CHtBu}), 5.15,5.20\left(2 \mathrm{~d}, J=12.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{PhCH}_{a} H_{b}\right), 7.25-7.40\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta=28.0\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 34.2\left(\mathrm{~s}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 61.1(\mathrm{~d}, \mathrm{CH} t \mathrm{Bu}), 70.1\left(\mathrm{t}, \mathrm{OCH}_{2} \mathrm{Ph}\right)$, 128.3, 128.4, $128.6\left(\mathrm{~d},=C-\mathrm{H}_{\text {phenyl }}\right), 135.2\left(\mathrm{~s},=C-\mathrm{C}_{\text {phenyl }}\right), 168.8\left(\mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {ester }}\right), 173.3$ ( s , $\mathrm{C}=\mathrm{O}_{\text {acid }}$ ). - MS (GC/MS, ion trap, $\mathbf{6}$ as methylester), $m / z$ (\%): 264 (3), 157 (1), 130 (35), 115 (45), 101 (28), 91 (100), 65 (16), 57 (12). - HR MS (EI): $\mathrm{C}_{14} \mathrm{H}_{18} \mathrm{O}_{4}$ : calcd. 250.1205; found 250.1208.

## 3. 1-Benzyl 3-[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl] ( $\left.2^{\prime} R / S\right)-2^{\prime}$-isopropylmalonate

( $\mathbf{7 a} / \mathbf{b}$ ): $1.41 \mathrm{~g}(9.0 \mathrm{mmol})(-)-$ menthol and $4.25 \mathrm{~g}(18 \mathrm{mmol})$ monobenzyl ester $\mathbf{5}$ were converted according to the general procedure for the preparation of the menthol esters to afford $1.91 \mathrm{~g}(5.10 \mathrm{mmol}, 57 \%)$ of carboxylic acid $\mathbf{7 a} / \mathbf{b}$ as a diastereomeric mixture after flash chromatography (petroleum ether/diethyl ether, 10:1).

FT-IR (film): $v=1753,1731 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.68,0.71(2 \mathrm{~d}, J=6.9 \mathrm{~Hz}$, in total $3 \mathrm{H}, 10-\mathrm{H}), 0.80-2.00(\mathrm{~m}, 9 \mathrm{H}, 2-\mathrm{H}$ to $7-\mathrm{H}), 0.99,1.00(2 \mathrm{~d}, J=6.7 \mathrm{~Hz}$, in total 6 H , $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.83,0.87,0.88(3 \mathrm{~d}, J=7.3 \mathrm{~Hz}$ or $J=6.4 \mathrm{~Hz}$, in total $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 2.42$ (dsept, $\left.1 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 3.151,3.154\left(2 \mathrm{~d}\right.$, each $\left.J=8.8 \mathrm{~Hz}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right), 4.69(\mathrm{ddd}, J=4.5 \mathrm{~Hz}, J=10.9$ $\mathrm{Hz}, J=10.9 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}), 5.10,5.20\left(2 \mathrm{~d}, J=12.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{a} H_{b} \mathrm{Ph}, 7 \mathbf{a}\right), 5.12,5.18(2 \mathrm{~d}, J=$ $\left.12.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{a} H_{b} \mathrm{Ph}, 7 \mathbf{7}\right), 7.25-7.40\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=15.91(\mathrm{q}, \mathrm{C}-$
10), 20.32, 20.49 ( $2 \mathrm{q}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}$ ), 20.66, 21.94 (2q, C-8, C-9), 23.18 (t, C-3), 25.91, 26.02 (2d, C-5), 28.54, $28.68\left(2 \mathrm{~d}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 31.31$ (d, C-7), 34.17 (t, C-4), 40.37, 40.61 (2t, C-6), 46.71, 46.81 (2d, C-2), 59.34, 59.38 (2d, C-2'), 66.76 (t, $\mathrm{OCH}_{2} \mathrm{Ph}$ ), 75.32 (d, C-1), 128.19, 128.25, 128.49 ( $3 \mathrm{~d},=C-\mathrm{H}_{\text {phenyl }}$ ), 135.53 ( $\left.\mathrm{s},=C-\mathrm{C}_{\text {phenyl }}\right), 168.12,168.25,168.69(3 \mathrm{~s}, \mathrm{C}=\mathrm{O}) .-$ MS (GC/MS), $m / z(\%): 374$ (0.5), 359 (0.1), 236 (36), 208 (14), 138 (20), 107 (27), 95 (24), 91 (100), 83 (45). - $\mathrm{C}_{23} \mathrm{H}_{34} \mathrm{O}_{4}$ (374.5): calcd. C 73.76, H 9.15; found C 73.86, H 9.45.

## 4. 1-Benzyl 3-[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl] ( $\left.2^{\top} R / S\right)-2^{\prime}$-(tert-butyl)malonate

( $\mathbf{8 a} / \mathbf{b}$ ): $1.25 \mathrm{~g}(8.0 \mathrm{mmol})(-)$-menthol and $3.00 \mathrm{~g}(12 \mathrm{mmol})$ monobenzyl ester $\mathbf{6}$ were converted according to the general procedure for the preparation of the menthol esters to afford $2.16 \mathrm{~g}(5.56 \mathrm{mmol}, 69 \%) \mathbf{8 a} / \mathrm{b}$ as a diastereomeric mixture after flash chromatography (petroleum ether/diethyl ether, 20:1).

FT-IR (film): $v=1753,1730 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.66,0.71(2 \mathrm{~d}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}$, $10-\mathrm{H}), 0.80-2.00(\mathrm{~m}, 9 \mathrm{H}, 2-\mathrm{H}$ to $7-\mathrm{H}), 1.13\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.81,0.83,0.85,0.88(4 \mathrm{~d}, J=$ 6.9 Hz , in total $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 3.26,3.27\left(2 \mathrm{~s}, 1 \mathrm{H}, \mathrm{CHC}\left(\mathrm{CH}_{3}\right)_{3}\right), 4.68,4.69(2 \mathrm{ddd}, J=4.3 \mathrm{~Hz}$, $J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}), 5.08-5.18\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{a} H_{b} \mathrm{Ph}\right), 7.25-7.38\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{5}\right)$. $-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=15.91(\mathrm{q}, \mathrm{C}-10), 20.69,21.94(2 \mathrm{q}, \mathrm{C}-8, \mathrm{C}-9), 23.18(\mathrm{t}, \mathrm{C}-3), 26.02$ (d, C-5), $28.04\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.94(\mathrm{~d}, \mathrm{C}-7), 33.53,33.66\left(2 \mathrm{~s}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 34.17(\mathrm{t}, \mathrm{C}-4), 40.40$, 40.71 (2t, C-6), 46.71, 46.84 (2d, C-2), 61.47, 61.63 (2d, $\mathrm{CH} t \mathrm{Bu}$ ), 66.52 (t, $\mathrm{OCH}_{2} \mathrm{Ph}$ ), 75.11 (d, C-1), 128.19, 128.29, 128.46 ( $3 \mathrm{~d},=C-\mathrm{H}_{\text {phenyl }}$ ), 135.69 ( $\left.\mathrm{s},=C-\mathrm{C}_{\text {phenyl }}\right), 167.75,168.25(2 \mathrm{~s}$, C=O). — MS (GC/MS), $m / z(\%): 388$ (0.5), 373 (0.2), 250 (40), 193 (1), 138 (27), 107 (22), 95 (20), 91 (100), 83 (55), 57 (29). - $\mathrm{C}_{24} \mathrm{H}_{36} \mathrm{O}_{4}$ (388.6): calcd. C 74.19, H 9.34; found C 73.88, H 9.53.
5. 1-Benzyl 3-[(lR,2S,5R)-2-(tert-butyl)-5-methylcyclohexyl] ( $\left.2^{\prime} R / S\right)-2^{\prime}-(t e r t-b u t y l) m a l o n a t e$ (9a/b): $1.00 \mathrm{~g}(5.87 \mathrm{mmol})(-)-8$-methylmenthol $\mathbf{2}$ and $1.78 \mathrm{~g}(7.11 \mathrm{mmol})$ monobenzyl ester 6 were converted according to the general procedure for the preparation of the menthol esters
to afford $1.62 \mathrm{~g}(4.02 \mathrm{mmol}, 68 \%) \mathbf{9 a} / \mathrm{b}$ as a diastereomeric mixture after flash chromatography (petroleum ether/diethyl ether, 10:1).

FT-IR (film): $v=1751,1730 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.74(\mathrm{~d}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}, 11-\mathrm{H})$, $0.60-1.90(\mathrm{~m}, 8 \mathrm{H}, 2-\mathrm{H}$ to $6-\mathrm{H}), 0.79(\mathrm{~s}, 9 \mathrm{H}, 8-\mathrm{H}$ to $10-\mathrm{H}), 1.05,1.06\left(2 \mathrm{~s}, 9 \mathrm{H}, \mathrm{COC}\left(\mathrm{CH}_{3}\right)_{3}\right)$, $3.13,3.16\left(2 \mathrm{~s}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right), 4.67(\mathrm{ddd}, J=4.3 \mathrm{~Hz}, J=10.5 \mathrm{~Hz}, J=10.5 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}), 5.01$, 5.09, ( $2 \mathrm{~d}, J=12.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{a} H_{b} \mathrm{Ph}, 9 \mathrm{mb}$, superposed by 9 a$), 5.01,5.11(2 \mathrm{~d}, J=12.2 \mathrm{~Hz}, 2 \mathrm{H}$, $\left.\mathrm{CH}_{a} \mathrm{H}_{b} \mathrm{Ph}, 9 \mathbf{9}\right), 7.21-7.32\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=21.77(\mathrm{q}, \mathrm{C}-11), 26.45(\mathrm{t}$, $\mathrm{C}-3), 28.10\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 28.98$ (q, C-8 to C-10), 31.17 (d, C-5), 32.52 (s, C-7), 33.70 (s, $\left.C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.57$ (t, C-4), 41.01, 41.65 (2t, C-6), 49.60, 49.81 (2d, C-2), 61.57, 61.94 (2d, C-
 $=C-\mathrm{C}_{\text {phenyl }}$ ), 167.21, $168.32(2 \mathrm{~s}, \mathrm{C}=\mathrm{O}) .-\mathrm{MS}(\mathrm{GC} / \mathrm{MS}), m / z(\%): 387(0.2), 345(0.3), 250$ (10), 152 (5), 107 (6), 91 (100), 83 (9), 57 (37). $-\mathrm{C}_{25} \mathrm{H}_{38} \mathrm{O}_{4}$ (402.6): calcd. C 74.59, H 9.51; found C 74.36, H 9.57.
6. 1-Benzyl 3-[(1R,2S,5R)-2-(2-phenylpropan-2-yl)-5-methylcyclohexyl] ( $\left.2^{\top} R / S\right)-2^{\prime}-($ tertbutyl)malonate ( $\mathbf{1 0 a} / \mathbf{b}$ ): $654 \mathrm{mg}(2.81 \mathrm{mmol})(-)-8$-phenylmenthol $\mathbf{3}$ and $1.08 \mathrm{~g}(4.31 \mathrm{mmol})$ monobenzyl ester $\mathbf{6}$ were converted according to the general procedure for the preparation of the menthol esters to afford $901 \mathrm{mg}(1.94 \mathrm{mmol}, 69 \%) \mathbf{1 0 a} / \mathrm{b}$ as a diastereomeric mixture after flash chromatography (petroleum ether/diethyl ether, 10:1). An analytical sample of each diastereomer was separated by flash chromatography.

FT-IR (film): $v=1748,1729 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{1 0 a}: \delta=0.60-2.00(\mathrm{~m}, 8 \mathrm{H}, 2-\mathrm{H}$ to $6-\mathrm{H}), 0.72(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}), 1.09\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.19,1.27(2 \mathrm{~s}$, each $3 \mathrm{H}, 8-\mathrm{H}, 9-$ H), $2.58\left(\mathrm{~s}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right), 4.75(\mathrm{ddd}, J=4.3 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}), 5.08(\mathrm{~s}, 2 \mathrm{H}$, $\left.\mathrm{OCH}_{2} \mathrm{Ph}\right), 7.10-7.40\left(\mathrm{~m}, 10 \mathrm{H}, 2 \mathrm{C}_{6} H_{5}\right) ; \mathbf{1 0 b}: \delta=0.60-2.10(\mathrm{~m}, 8 \mathrm{H}, 2-\mathrm{H}$ to $6-\mathrm{H}), 0.85(\mathrm{~d}, J=$ $6.4 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}), 1.00\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.14,1.21(2 \mathrm{~s}$, each $3 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 2.71\left(\mathrm{~s}, 1 \mathrm{H}, 2^{\prime}-\right.$ H), 4.77 (ddd, $J=4.3 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}), 5.11,5.18(2 \mathrm{~d}, J=12.4 \mathrm{~Hz}$,
each $\left.1 \mathrm{H}, \mathrm{OCH}_{\mathrm{a}} \mathrm{H}_{\mathrm{b}} \mathrm{Ph}\right), 7.00-7.40\left(\mathrm{~m}, 10 \mathrm{H}, 2 \mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): 10 \mathrm{a}: \delta=21.74(\mathrm{q}$, C-10), 26.12, 26.86 (2q, C-8, C-9), 26.66 (t, C-3), $27.97\left(q, C\left(\mathrm{CH}_{3}\right)_{3}\right), 31.17(\mathrm{~d}, \mathrm{C}-5), 33.23$ (s, $\left.C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.47(\mathrm{t}, \mathrm{C}-4), 39.73$ ( $\mathrm{s}, \mathrm{C}-7$ ), 40.71 ( $\mathrm{t}, \mathrm{C}-6$ ), 49.94 (d, C-2), $60.79(\mathrm{~d}, \mathrm{C}-2$ ) , $66.52\left(\mathrm{t}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 74.88(\mathrm{~d}, \mathrm{C}-1), 125.09,125.42,127.98,128.25,128.46\left(5 \mathrm{~d},=C-\mathrm{H}_{\text {phenyl }}\right)$, $135.53\left(\mathrm{~s},=C-\mathrm{C}_{\text {benzy }}\right), 151.30\left(\mathrm{~s},=C-\mathrm{C}_{\text {phenyl }}\right), 167.04,168.52(2 \mathrm{~s}, \mathrm{C}=\mathrm{O}) ; 10 \mathrm{~b}: \delta=21.74(\mathrm{q}, \mathrm{C}-$ 10), 26.31 ( $\mathrm{q}, \mathrm{C}-8, \mathrm{C}-9$ ), 26.76 (t, C-3), $28.07\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.27(\mathrm{~d}, \mathrm{C}-5), 33.77$ ( s , $\left.C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.54(\mathrm{t}, \mathrm{C}-4), 39.73(\mathrm{~s}, \mathrm{C}-7), 41.52(\mathrm{t}, \mathrm{C}-6), 50.44(\mathrm{~d}, \mathrm{C}-2), 60.89\left(\mathrm{~d}, \mathrm{C}-2^{\prime}\right), 66.49$ (t, $\left.\mathrm{OCH}_{2} \mathrm{Ph}\right), 75.92(\mathrm{~d}, \mathrm{C}-1), 124.95,125.42,127.88,128.19,128.46\left(5 \mathrm{~d},=C-\mathrm{H}_{\text {phenyl }}\right), 135.67$ $\left(\mathrm{s},=C-\mathrm{C}_{\text {benzyl }}\right), 151.34\left(\mathrm{~s},=C-\mathrm{C}_{\text {phenyl }}\right), 167.82,168.02(2 \mathrm{~s}, \mathrm{C}=\mathrm{O}) .-\mathrm{MS}(\mathrm{GC} / \mathrm{MS}$, ion trap) , $m / z$ (\%): 345 (4), 214 (15), 206 (9), 199 (8), 119 (61), 91 (100). - $\mathrm{C}_{30} \mathrm{H}_{40} \mathrm{O}_{4}$ (464.7): calcd. C 77.55, H 8.68; found C 77.68, H 8.89.
7. 1-Benzyl 3-[(1R,2S,5R)-2-(2-phenylpropan-2yl)-5-methylcyclohexyl] ( $\left.2^{\prime} R / S\right)-2^{\prime}-$ isopropylmalonate (11a/b): $681.7 \mathrm{~g}(2.93 \mathrm{mmol})(-)-8$-phenylmenthol $\mathbf{3}$ and 1.06 g ( 4.31 mmol ) monobenzyl ester $\mathbf{5}$ were converted according to the general procedure for the preparation of the menthol esters to afford $1.31 \mathrm{~g}(2.91 \mathrm{mmol}, 99 \%) \mathbf{1 1 a} / \mathrm{b}$ as a diastereomeric mixture after flash chromatography (petroleum ether/diethyl ether, 5:1).

FT-IR (film): $v=1751,1724 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.60-2.00(\mathrm{~m}, 8 \mathrm{H}, 2-\mathrm{H}$ to $6-\mathrm{H})$, $0.78(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}, 11 \mathrm{a}), 0.84(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}, 11 \mathrm{~b}), 0.89(\mathrm{~d}, J=6.7 \mathrm{~Hz}$, in total $6 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}, \mathbf{1 1 a}$, superposed by 11b), $0.90,0.91(2 \mathrm{~d}, J=6.7 \mathrm{~Hz}$, in total 6 H , $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}, 11 \mathrm{~b}\right), 1.17,1.25(2 \mathrm{~s}$, in total $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}, 11 \mathrm{~b}), 1.20,1.28$ ( 2 s , in total $6 \mathrm{H}, 8-\mathrm{H}$, 9-H, 11a), 2.20 (dsept, $\left.J=6.7 \mathrm{~Hz}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CHCH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.51\left(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}, 2^{\prime}-\right.$ H, 11a), 2.74 (d, $\left.J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}, \mathbf{1 1 b}\right), 4.79$ (ddd, $J=4.3 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}$, $1 \mathrm{H}, 1-\mathrm{H}), 5.08\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}, 11 \mathrm{a}\right) 5.15,5.18\left(2 \mathrm{~d}, J=12.2 \mathrm{~Hz}\right.$, each $\left.1 \mathrm{H}, \mathrm{OCH}_{\mathrm{a}} \mathrm{H}_{\mathrm{b}} \mathrm{Ph}, 11 \mathrm{~b}\right)$, 7.10-7.40 (m, 10H, $\left.2 \mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=19.75,20.02$, 20.39, $20.96(4 \mathrm{q}$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 21.70(\mathrm{q}, \mathrm{C}-10), 25.88,26.05(2 \mathrm{q}, \mathrm{C}-8), 26.66,26.82(2 \mathrm{t}, \mathrm{C}-3), 26.92(\mathrm{q}, \mathrm{C}-9)$,
28.10, 28.71 (2d, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 31.14,31.24$ (2d, C-5), 34.47 (t, C-4), 39.73, 39.83 (2s, C-7), $40.84,41.45$ (2t, C-6), 50.04, 50.35 (2d, C-2), 58.47 (d, C-2'), 66.55, 66.69 ( $2 \mathrm{t}, \mathrm{OCH}_{2} \mathrm{Ph}$ ), $75.21,76.09(2 \mathrm{~d}, \mathrm{C}-1), 125.02,125.49,127.85,128.22,128.45\left(5 \mathrm{~d},=C-\mathrm{H}_{\mathrm{pheny}}\right), 135.60(\mathrm{~s}$, $\left.=C-\mathrm{C}_{\text {benzyl }}\right), 151.14\left(\mathrm{~s},=C-\mathrm{C}_{\text {phenyl }}\right), 168.19,168.52(2 \mathrm{~s}, \mathrm{C}=\mathrm{O}) .-\mathrm{MS}(\mathrm{GC} / \mathrm{MS}$, ion trap) $\mathrm{m} / \mathrm{z}$ (\%): 450 (0.5), 359 (0.5), 331 (8), 214 (15), 199 (8), 119 (61), 91 (100). $-\mathrm{C}_{29} \mathrm{H}_{38} \mathrm{O}_{4}$ (450.6): calcd. C 77.30, H 8.50; found C 77.38, H 8.63.
8. 1-Benzyl 3-\{(1R,2S,5R)-2-[2-(4-methoxyphenyl)propan-2-yl)]-5-methylcyclohexyl\} ( $\left.2^{\wedge} R / S\right)$ -$2^{\prime}$-(tert-butyl)malonate (12a/b): $3.16 \mathrm{~g}(12.0 \mathrm{mmol})(-)-8$-anisylmenthol $\mathbf{4}$ and 3.00 g ( 12.0 mmol ) monobenzyl ester $\mathbf{6}$ were converted according to the general procedure for the preparation of the menthol esters to afford $3.61 \mathrm{~g}(7.30 \mathrm{mmol}, 61 \%) \mathbf{1 2 a} / \mathrm{b}$ as a diastereomeric mixture after flash chromatography (petroleum ether/diethyl ether, 5:1). An analytical sample of each diastereomer was separated by flash chromatography.

FT-IR (film): $v=1748,1728 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{1 2 a}: \delta=0.65-1.90(\mathrm{~m}, 8 \mathrm{H}, 2-\mathrm{H}$ to $6-\mathrm{H}), 0.78(\mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}), 1.08\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.18,1.25(2 \mathrm{~s}$, each $3 \mathrm{H}, 8-\mathrm{H}, 9-$ H), $2.72\left(\mathrm{~s}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right), 3.76\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 4.74(\mathrm{ddd}, J=4.3 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}$, $1 \mathrm{H}, 1-\mathrm{H}), 5.10\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 6.77-6.83,7.10-7.17\left(2 \mathrm{~m}, 4 \mathrm{H},=\mathrm{C}-\mathrm{H}_{\text {anisy }}\right), 7.30-7.40(\mathrm{~m}$, $\left.5 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{5}\right) ;$ 12b: $\delta=0.75-1.60(\mathrm{~m}, 8 \mathrm{H}, 2-\mathrm{H}$ to $6-\mathrm{H}), 0.85(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}), 1.03(\mathrm{~s}$, $\left.9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.13,1.21(2 \mathrm{~s}$, each $3 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 2.81\left(\mathrm{~s}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right), 3.71\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right)$, $4.74(\mathrm{ddd}, J=4.3 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}), 5.13,5.17(2 \mathrm{~d}, J=12.4 \mathrm{~Hz}$, each $\left.1 \mathrm{H}, \mathrm{OCH}_{\mathrm{a}} \mathrm{H}_{\mathrm{b}} \mathrm{Ph}\right), 6.70-6.81,7.08-7.15\left(2 \mathrm{~m}, 4 \mathrm{H},=\mathrm{C}-H_{\text {anisyl }}\right), 7.30-7.40\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-$ NMR $\left(\mathrm{CDCl}_{3}\right): 12 \mathrm{a}: \delta=21.67(\mathrm{q}, \mathrm{C}-10), 26.60(\mathrm{q}, \mathrm{C}-8), 26.79(\mathrm{t}, \mathrm{C}-3), 26.90(\mathrm{q}, \mathrm{C}-9), 28.01$ (q, C( $\left.\mathrm{CH}_{3}\right)_{3}$ ), $31.18(\mathrm{~d}, \mathrm{C}-5), 33.26\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.51$ (t, C-4), 39.20 (s, C-7), $40.85(\mathrm{t}, \mathrm{C}-6)$, 50.18 (d, C-2), $55.17\left(\mathrm{q}, \mathrm{OCH}_{3}\right), 61.03\left(\mathrm{~d}, \mathrm{C}-2^{\prime}\right), 66.52\left(\mathrm{t}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 75.05(\mathrm{~d}, \mathrm{C}-1), 113.33$, $126.44\left(2 \mathrm{~d},=C-\mathrm{H}_{\text {anisyl }}\right), 128.23,128.46\left(2 \mathrm{~d},=C-\mathrm{H}_{\text {benzy }}\right), 135.61\left(\mathrm{~s},=C-\mathrm{C}_{\text {benzy }}\right), 143.26(\mathrm{~s},=C-$ $\left.\mathrm{C}_{\text {anisy }}\right), 157.08\left(\mathrm{~s},=C-\mathrm{O}_{\text {anisy }}\right), 167.03,168.51(2 \mathrm{~s}, \mathrm{C}=\mathrm{O}) ; \mathbf{1 2 b}: \delta=21.74(\mathrm{q}, \mathrm{C}-10), 26.15(\mathrm{q}$,
$\mathrm{C}-8), 26.82(\mathrm{t}, \mathrm{C}-3), 26.96(\mathrm{q}, \mathrm{C}-9), 28.07\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.27(\mathrm{~d}, \mathrm{C}-5), 33.84\left(\mathrm{~s}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, 34.54 ( $\mathrm{t}, \mathrm{C}-4$ ), 39.19 ( $\mathrm{s}, \mathrm{C}-7$ ), 41.55 (t, C-6), 50.62 (d, C-2), $55.10\left(\mathrm{q}, \mathrm{OCH}_{3}\right), 61.03\left(\mathrm{~d}, \mathrm{C}-2^{\prime}\right)$, $66.52\left(\mathrm{t}, \mathrm{OCH}_{2} \mathrm{Ph}\right), 75.99(\mathrm{~d}, \mathrm{C}-1), 113.19,126.40\left(2 \mathrm{~d},=C-\mathrm{H}_{\text {anisy }}\right), 128.22,128.46(2 \mathrm{~d},=C-$ $\left.\mathrm{H}_{\text {benzyl }}\right), 135.64\left(\mathrm{~s},=C-\mathrm{C}_{\text {benzy }}\right), 143.35\left(\mathrm{~s},=C-\mathrm{C}_{\text {anisyl }}\right), 156.97\left(\mathrm{~s},=C-\mathrm{O}_{\text {anisyl }}\right), 167.78,168.02$ (2s, C=O). — MS (GC/MS), $m / z$ (\%): 494 (4), 345 (0.5), 245 (1), 149 (100), 91 (17), 84 (17). - $\mathrm{C}_{31} \mathrm{H}_{42} \mathrm{O}_{5}$ (494.7): calcd. C 75.27, H 8.56; found C 75.16, H 8.60.
9. $2^{\prime}-[(1 R, 2 S, 5 R)-2-I s o p r o p y l-5-m e t h y l c y c l o h e x y l o x y c a r b o n y l]\left(2^{\prime} R / S\right)-3^{\prime}$-methylbutanoic acid (13a/b):
$785.9 \mathrm{mg}(2.10 \mathrm{mmol})$ benzyl ester $\mathbf{7 a} / \mathbf{b}$ were converted according to the general procedure for the hydrogenation of the benzyl esters to afford $590.7 \mathrm{mg}(2.08 \mathrm{mmol}, 99 \%)$ of the free carboxylic acid 13a/b as a diastereomeric mixture.

FT-IR (film): $v=3600-2600,1737,1713 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.75(\mathrm{~d}, J=6.9 \mathrm{~Hz}$, $3 \mathrm{H}, 10-\mathrm{H}), 0.80-2.10(\mathrm{~m}, 9 \mathrm{H}, 2-\mathrm{H}$ to $7-\mathrm{H}), 1.02-1.06\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.88,0.90(2 \mathrm{~d}, J=$ 7.2 Hz , in total $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 2.39$ (dsept, $\left.1 \mathrm{H}, \mathrm{CHCH}\left(\mathrm{CH}_{3}\right)_{2}\right), 3.15\left(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right)$, $4.72,4.74(2 \mathrm{ddd}, J=4.8 \mathrm{~Hz}, J=10.9 \mathrm{~Hz}, J=10.9 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=$ 15.94, 16.07 (2q, C-10), 20.25, $20.35\left(2 \mathrm{q}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 20.69,21.94$ (2q, C-8, C-9), 23.18, 23.29 (2t, C-3), 26.08 (d, C-5), 29.05, $29.28\left(2 \mathrm{~d}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 31.41$ (d, C-7), 34.17 (t, C-4), 40.40, 40.64 (2t, C-6), 46.81, 46.91 (2d, C-2), 58.57, 58.94 (2d, C-2'), 75.92, 75.99 (d, C-1), $168.79,169.20\left(2 \mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {ester }}\right), 173.27,173.44\left(2 \mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {acid }}\right) .-\mathrm{MS}(\mathrm{GC} / \mathrm{MS}, 13$ as methylester), $m / z$ (\%): 283 (0.1), 267 (0.4), 255 (0.2), 223 (0.3), 161 (25), 143 (55), 138 (100), 123 (36), 95 (88), 83 (55), 81 (66). IR and ${ }^{1} \mathrm{H}-\mathrm{NMR}$ are identical with those reported for the compound by Fukumoto[SI-1].
10. $2^{\prime}-\left[(1 R, 2 S, 5 R)-2-\right.$ Isopropyl-5-methylcyclohexyloxycarbonyl)-( $\left.2^{\prime} R / S\right)-3^{\prime}, 3^{\prime}-$ dimethylbutanoic acid (14a/b): $1.62 \mathrm{~g}(4.17 \mathrm{mmol}$ benzyl ester $\mathbf{8 a} / \mathbf{b}$ were converted
according to the general procedure for the hydrogenation of the benzyl esters to afford 1.20 g ( $4.02 \mathrm{mmol}, 96 \%$ ) of the free carboxylic acid $\mathbf{1 4} \mathbf{a} / \mathbf{b}$ as a diastereomeric mixture.

FT-IR (film): $v=3600-2600,1753,1712 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.74(\mathrm{~d}, J=6.9 \mathrm{~Hz}$, $3 \mathrm{H}, 10-\mathrm{H}), 0.80-2.10(\mathrm{~m}, 9 \mathrm{H}, 2-\mathrm{H}$ to $7-\mathrm{H}), 1.14\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.85-0.92(\mathrm{~m}$, in total 6 H , $8-\mathrm{H}, 9-\mathrm{H}), 3.24\left(\mathrm{~s}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right), 4.72,4.77(2 \mathrm{ddd}, J=4.5 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-$ H). $-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=15.80,16.07(2 \mathrm{q}, \mathrm{C}-10), 20.76,21.94(2 \mathrm{q}, \mathrm{C}-8, \mathrm{C}-9), 23.08$, 23.32 ( $2 \mathrm{t}, \mathrm{C}-3$ ), 25.98, 26.12 (2d, C-5), $28.14\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.41(\mathrm{~d}, \mathrm{C}-7), 33.93,34.34$ (2s, $\left.C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.17$ (t, C-4), 40.44, 40.71 (2t, C-6), 46.74, 46.94 (2d, C-2), $61.09,61.60$ (2d, C$2^{\prime}$ ), 76.09, 76.19 (2d, C-1), 169.06, 170.15 ( $2 \mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {ester }}$ ), 171.89, 172.63 (2s, $\mathrm{C}=\mathrm{O}_{\text {acid }}$ ). - MS (GC/MS, 14 as methylester), $m / z(\%): 297$ (0.5), 281 (0.6), 256 (1), 175 (24), 157 (20), 138 (100), 123 (18), 118 (10), 101 (42), 95 (37), 83 (36), 69 (14), 57 (29). - $\mathrm{C}_{17} \mathrm{H}_{30} \mathrm{O}_{4}$ (298.4): calcd. C 68.42, H 10.13; found C 68.23, H 10.32.
11. $2^{\prime}-[(1 R, 2 S, 5 R)-2$-(tert-Butyl)-5-methylcyclohexyloxycarbonyl $]\left(2^{\prime} R / S\right)-3^{\prime}, 3^{\prime}-$ dimethylbutanoic acid (15a/b): $841 \mathrm{mg}(2.11 \mathrm{mmol})$ benzyl ester $\mathbf{9 a} / \mathbf{b}$ were converted according to the general procedure for the hydrogenation of the benzyl esters to afford 653 mg ( $2.09 \mathrm{mmol}, 99 \%$ ) of the free carboxylic acid $\mathbf{1 5 a} / \mathbf{b}$ as a diastereomeric mixture.

FT-IR (film): $v=3600-2800,1749,1711 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.87(\mathrm{~d}, J=5.1 \mathrm{~Hz}$, $3 \mathrm{H}, 11-\mathrm{H}), 0.8-2.05(\mathrm{~m}, 8 \mathrm{H}, 2-\mathrm{H}$ to $6-\mathrm{H}), 0.89(\mathrm{~s}, 9 \mathrm{H}, 8-\mathrm{H}$ to $10-\mathrm{H}), 1.14,1.16(2 \mathrm{~s}, 9 \mathrm{H}$, $\left.\operatorname{COCHC}\left(\mathrm{CH}_{3}\right)_{3}\right), 3.20\left(\mathrm{~s}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right), 4.79(\mathrm{ddd}, J=4.3 \mathrm{~Hz}, J=10.5 \mathrm{~Hz}, J=10.5 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}$, 15a), 4.84 (ddd, $J=4.3 \mathrm{~Hz}, J=10.5 \mathrm{~Hz}, J=10.5 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}, \mathbf{1 5 b}$, superposed by $\mathbf{1 5 a}$ ). ${ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=21.80(\mathrm{q}, \mathrm{C}-11), 26.55,26.51(2 \mathrm{t}, \mathrm{C}-3), 28.17\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 28.98(\mathrm{q}$, C-8 to C-10), 31.31 (d, C-5), 32.55 (s, C-7), $33.80\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.54,34.64$ (2t, C-4), 41.01, 41.65 (2t, C-6), 49.70, 49.87 (2d, C-2), 61.97 (d, C-2'), 76.63, 77.24 (2d, C-1), 167.38, 168.32 (2s, C=O). — MS (GC/MS, 15 as methylester), $m / z$ (\%): 311 (1), 271 (2), 269 (1), 175 (100),

157 (77), 152 (14), 119 (18), 101 (50), 57 (52). - HR MS ( $\mathrm{NH}_{3}$-DCI): $\mathrm{C}_{18} \mathrm{H}_{32} \mathrm{O}_{4}:$ calcd. 330.2644 ; found $330.2632\left\{\mathrm{M}+\mathrm{NH}_{4}{ }^{+}\right\}$.
12. 3',3'-Dimethyl-2'-[(1R,2S,5R)-5-methyl-2-(2-phenylpropan-2-yl)cyclohexyloxycarbonyl] ( 2 R/S)-butanoic acid ( $\mathbf{1 6 a / b}$ ): $631 \mathrm{mg}(1.36 \mathrm{mmol})$ benzyl ester $\mathbf{1 0 a} / \mathbf{b}$ were converted according to the general procedure for the hydrogenation of the benzyl esters to afford $441.5 \mathrm{mg}(1.18 \mathrm{mmol}, 87 \%)$ of the free carboxylic acid $\mathbf{1 6 a} / \mathbf{b}$ as a diastereomeric mixture. An analytical sample of 16a was separated by flash chromatography (petroleum ether/diethyl ether, 1:1).

FT-IR (film): $v=3600-2800,1740,1711 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{1 6 a}: \delta=0.70-2.00(\mathrm{~m}$, $8 \mathrm{H}, 2-\mathrm{H}$ to $6-\mathrm{H}), 0.85(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}), 1.07\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.20,1.30(2 \mathrm{~s}$, each $3 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 2.59\left(\mathrm{~s}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right), 4.79(\mathrm{ddd}, J=4.3 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H})$, 7.10-7.40 (m, 5H, $\left.\mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{1 6 a}: \delta=21.70(\mathrm{q}, \mathrm{C}-10), 26.25,26.75(2 \mathrm{q}$, C-8, C-9), $26.79(\mathrm{t}, \mathrm{C}-3), 28.00\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.27(\mathrm{~d}, \mathrm{C}-5), 33.29\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.51(\mathrm{t}, \mathrm{C}-$ 4), 39.73 ( $\mathrm{s}, \mathrm{C}-7$ ), 40.74 (t, C-6), 50.01 (d, C-2), 60.83 (d, C-2'), 75.62 (d, C-1), 125.12, 125.42, $128.02\left(3 \mathrm{~d},=C-\mathrm{H}_{\text {phenyl }}\right), 151.24\left(\mathrm{~s},=C-\mathrm{C}_{\text {pheny }}\right), 166.94\left(\mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {ester }}\right), 174.49(\mathrm{~s}$, $\mathrm{C}=\mathrm{O}_{\text {acid }}$ ). — MS (GC/MS, 16 as methylester), $m / z(\%): 388$ (0.3), 269 (5), 214 (15), 199 (3), 175 (4), 119 (61), 105 (14), 91 (100), 57 (10). - HR MS ( $\left.\mathrm{NH}_{3}-\mathrm{DCI}\right): \mathrm{C}_{23} \mathrm{H}_{34} \mathrm{O}_{4}$ : calcd. 392.28008 ; found $392.2793\left\{\mathrm{M}+\mathrm{NH}_{4}{ }^{+}\right\}$.
13. 3'-Methyl-2'-[(1R,2S,5R)-2-(1-Methyl-1-phenylethyl)-5-methylcyclohexyloxycarbonyl)] ( $\left.2^{\prime} R / S\right)$-butanoic acid $(\mathbf{1 7 a} / \mathbf{b})$ : $1.135 \mathrm{~g}(2.52 \mathrm{mmol})$ benzyl ester $\mathbf{1 1 a} / \mathbf{b}$ was converted according to the general procedure for the hydrogenation of the benzyl esters to afford 904 mg ( $2.51 \mathrm{mmol}, 99 \%$ ) of the free carboxylic acid $\mathbf{1 7 a} / \mathbf{b}$ as a diastereomeric mixture.

FT-IR (film): $v=3600-2800,1735,1711 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.70-2.00(\mathrm{~m}, 8 \mathrm{H}$, $2-\mathrm{H}$ to $6-\mathrm{H}), 0.85(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}, \mathbf{1 7 a}), 0.87(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}, \mathbf{1 7 b}), 0.88$,
$0.90\left(2 \mathrm{~d}, J=6.7 \mathrm{~Hz}\right.$, in total $\left.6 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}, \mathbf{1 7 b}\right), 0.97,1.00(2 \mathrm{~d}, J=6.7 \mathrm{~Hz}$, in total 6 H , $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}, \mathbf{1 7 a}\right), 1.20,1.21,1.30(3 \mathrm{~s}$, in total $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 2.34\left(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right.$, 17b), 2.47 (d, $\left.J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}, 17 \mathrm{a}\right), 4.84(\mathrm{ddd}, J=4.3 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, 1 \mathrm{H}$, $1-\mathrm{H}, \mathbf{1 7 a}$, superposed by 17b), $4.88(\mathrm{ddd}, J=4.3 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}, \mathbf{1 7 b})$, 7.10-7.30 (m, 5H, C $\left.\mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=19.68,19.85,20.19,20.86(4 \mathrm{q}$,
$\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 21.74(\mathrm{q}, \mathrm{C}-10), 25.81,27.13(2 \mathrm{q}, \mathrm{C}-8, \mathrm{C}-9), 26.42,26.69(2 \mathrm{t}, \mathrm{C}-3), 28.21,28.41$ (2d, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 30.19,31.27$ (2d, C-5), 34.41 (t, C-4), 39.52, 39.81 (2s, C-7), 40.81, 41.48 (2t, C-6), 49.97, 50.31 (2d, C-2), 56.55, 58.03 (2d, C-2'), 75.69, 76.39 (2d, C-1), 125.12 125.36, 125.42, 127.95, $128.05\left(5 \mathrm{~d},=C-\mathrm{H}_{\text {phenyl }}\right), 151.24\left(\mathrm{~s},=C-\mathrm{C}_{\text {phenyl }}\right), 167.68\left(\mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {ester }}\right)$, 170.98, 171.69 (s, $\mathrm{C}=\mathrm{O}_{\text {acid }}$ ). — MS (GC/MS, 17 as methylester), $m / z(\%): 374$ (1), 343 (0.5), 255 (10), 214 (44), 199 (4), 143 (21), 119 (96), 118 (100), 105 (15), 91 (26). IR and ${ }^{1} \mathrm{H}-\mathrm{NMR}$ are identical with those reported for the compound by Fukumoto[SI-1].
14. 2'-(1R,2S,5R)-2-[2-(4-Methoxyphenyl)propan-2-yl)-5-methylcyclohexyloxycarbonyl] ( $\left.2^{\top} R / S\right)-3^{\prime}, 3^{\prime}$-dimethylbutanoic acid (18a/b): $2.56 \mathrm{~g}(5.12 \mathrm{mmol})$ benzyl ester $\mathbf{1 2 a} / \mathbf{b}$ were converted according to the general procedure for the hydrogenation of the benzyl esters to afford $2.02 \mathrm{~g}(5.00 \mathrm{mmol}, 98 \%)$ of the free carboxylic acid $\mathbf{1 8 a} / \mathbf{b}$ as a diastereomeric mixture. FT-IR (film): $v=3600-2600,1747,1709 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.65-1.90(\mathrm{~m}, 8 \mathrm{H}$, $2-\mathrm{H}$ to $6-\mathrm{H}), 0.85,0.90(2 \mathrm{~d}, J=6.4 \mathrm{~Hz}$, in total $3 \mathrm{H}, 10-\mathrm{H}), 0.97,1.12(2 \mathrm{~s}$, in total 9 H , $\left.\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.20,1.21,1.26,1.29(4 \mathrm{~s}$, in total $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 2.31,2.72\left(2 \mathrm{~s}\right.$, in total $\left.1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right)$, $3.79,3.81\left(2 \mathrm{~s}\right.$, in total $\left.3 \mathrm{H}, \mathrm{OCH}_{3}\right), 4.78,4.85(2 \mathrm{ddd}, J=4.3 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}$, in total $1 \mathrm{H}, 1-\mathrm{H}), 6.77-6.88,7.10-7.20\left(2 \mathrm{~m}, 4 \mathrm{H},=\mathrm{C}-H_{\text {anisyl }}\right) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=21.74$, 23.89 (2q, C-10), 26.55, 26.96 (2q, C-8, C-9), 26.89 (t, C-3), 28.07, $28.31\left(2 q, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, 29.18, 31.31 (2d, C-5), 33.39 (s, $C\left(\mathrm{CH}_{3}\right)_{3}$ ), 34.54 (t, C-4), 39.22 ( s, C-7), 40.84, 41.48 (2t, C6), $50.18,50.45(2 \mathrm{~d}, \mathrm{C}-2), 55.23\left(\mathrm{q}, \mathrm{OCH}_{3}\right), 60.25,60.96(2 \mathrm{~d}, \mathrm{C}-2$ ) $, 75.82,77.00(2 \mathrm{~d}, \mathrm{C}-1)$,
$113.39,113.56,125.93,126.47\left(4 \mathrm{~d},=C-\mathrm{H}_{\text {anisyl }}\right), 143.28\left(\mathrm{~s},=C-\mathrm{C}_{\text {anisy }}\right), 157.13\left(\mathrm{~s},=C-\mathrm{O}_{\text {anisyl }}\right)$, $167.11\left(\mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {ester }}\right), 173.85\left(\mathrm{~s}, \mathrm{C}=\mathrm{O}_{\text {acid }}\right) .-\mathrm{MS}(\mathrm{GC} / \mathrm{MS}, 18$ as methylester), $m / z(\%): 418$ (8), 269 (1), 245 (6), 229 (3), 173 (2), 149 (100), 135 (18), 121 (17), 109 (8), 91 (17), 84 (17), 57 (10). - HR MS (GC-EI, 18a/b as trimethylsilylester): $\mathrm{C}_{24} \mathrm{H}_{35} \mathrm{O}_{5} \mathrm{SiMe}_{3}$ : calcd. 476.2958; found 476.2924.
15. (1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl ( $\left.2^{\prime} R / S\right)-2^{\prime}$-isopropyl-4,4-dimethylpentanoate ( $\mathbf{2 1 a} \mathbf{a} / \mathbf{b}$ ): $74.5 \mathrm{mg}(0.262 \mathrm{mmol})$ of $\mathbf{1 4 a} / \mathbf{b}$ and $364.5 \mathrm{mg}(3.14 \mathrm{mmol})$ tert-butylacetic acid were electrolyzed according to the general procedure for the Kolbe electrolysis to afford 41.8 mg ( $0.135 \mathrm{mmol}, 51 \%$ ) $\mathbf{2 1} \mathbf{2} / \mathbf{b}$ as a diastereomeric mixture after flash chromatography and HPLC (petroleum ether/diethyl ether, 20:1). The diasteromers 21a and 21b have not been separated. The diasteromeric ratio was determined by inverse gated coupling ${ }^{13} \mathrm{C}$-NMR to be $52.5: 47.5$ (5\% de).

FT-IR (film): $v=1730 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.71,0.73(2 \mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H})$, $0.85,0.86\left(2 \mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.80-2.20\left(\mathrm{~m}, 13 \mathrm{H}, 2-\mathrm{H}\right.$ to $\left.7-\mathrm{H}, 2^{\prime}-\mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 4.62,4.64$ (2ddd, $J=10.7 \mathrm{~Hz}, J=10.7 \mathrm{~Hz}, J=4.3 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=15.60$, $15.67(2 \mathrm{q}, \mathrm{C}-8), 19.55,19.88,20.19,20.35\left(4 \mathrm{q}, \mathrm{COCHCH}\left(\mathrm{CH}_{3}\right)_{2}\right), 20.96(\mathrm{q}, \mathrm{C}-9), 22.07(\mathrm{q}$, $\mathrm{C}-10), 22.84,22.98$ (2t, C-3), $25.68(\mathrm{~d}, \mathrm{C}-7), 29.32,29.42\left(2 \mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 30.50,30.56(2 \mathrm{~s}$, $\left.C\left(\mathrm{CH}_{3}\right)_{3}\right), 31.41(\mathrm{~d}, \mathrm{C}-5), 31.84,32.15\left(2 \mathrm{~d}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 34.34(\mathrm{t}, \mathrm{C}-4), 40.51,40.88(2 \mathrm{t}, \mathrm{C}-6)$, 41.92, 42.16 ( $2 \mathrm{t}, \mathrm{CH}_{2} \mathrm{tBu}$ ), 47.01 (d, C-2), 47.99, 48.46 (2d, C-2'), 74.00, 74.07 (2d, C-1), 176.11, 176.34 (2s, C=O). — MS (GC/MS), $m / z(\%): 309$ (0.2), 295 (0.4), 268 (0.6), 173 (14), 157 (26), 155 (12), 138 (100), 127 (10), 95 (41), 83 (54), 71 (45), 57 (56). $-\mathrm{C}_{20} \mathrm{H}_{38} \mathrm{O}_{2}$ (310.5): calcd. C 77.36, H 12.33; found C 77.42, H 12.40.
16. (1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl ( $\left.2^{\prime} R / S\right)-2^{\prime}-\left(\right.$ tert-butyl) $-4^{\prime}, 4^{\prime}-$
dimethylpentanoate (22a/b): $98.0 \mathrm{mg}(0.262 \mathrm{mmol})$ of $\mathbf{1 3 a} / \mathbf{b}$ and $384.0 \mathrm{mg}(3.31 \mathrm{mmol})$ tertbutylacetic acid were electrolyzed according to the general procedure for the Kolbe electrolysis to afford $62.0 \mathrm{mg}(0.191 \mathrm{mmol}, 58 \%) \mathbf{2 2 a} / \mathbf{b}$ as a diastereomeric mixture after
flash chromatography and HPLC (petroleum ether/diethyl ether, 50:1). The diasteromers 22a and 22b have not been separated. The diasteromeric ratio was determined by GLC to be 55 : 45 ( $10 \% \mathrm{de}$ ).

FT-IR (film): $v=1726 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.68,0.72(2 \mathrm{~d}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H})$, $0.86\left(\mathrm{~d}, J=3.6 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.94\left(\mathrm{~s}, 18 \mathrm{H}, 2 \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.80-2.20(\mathrm{~m}, 12 \mathrm{H}, 2-\mathrm{H}$ to $7-$ $\mathrm{H}, t \mathrm{BuCHCH} 2), 4.57,4.61(2 \mathrm{ddd}, J=10.9 \mathrm{~Hz}, J=10.8 \mathrm{~Hz}, J=4.3 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}) .-{ }^{13} \mathrm{C}-$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta=15.47(\mathrm{q}, \mathrm{C}-10), 21.03,22.07(2 \mathrm{q}, \mathrm{C}-8, \mathrm{C}-9), 22.71(\mathrm{t}, \mathrm{C}-3), 25.41(\mathrm{~d}, \mathrm{C}-$ 7), 27.67, $27.80\left(2 \mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 29.28$, $29.42\left(2 \mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 30.46,30.63\left(2 \mathrm{~s}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.37$, 31.44 (2d, C-5), 33.46, 33.73 (2s, $C\left(\mathrm{CH}_{3}\right)_{3}$ ), 34.34 (t, C-4), 40.34, 40.88 (2t, C-6), 41.38, $42.02\left(2 \mathrm{t}, \mathrm{t} \mathrm{BuCHCH}_{2}\right), 46.94,47.01$ (d, C-2), 51.42, 52.10 (2d, C-2'), 74.44 (d, C-1), 176.11, 176.34 (2s, C=O). — MS (GC/MS), $m / z(\%): 309$ (0.5), 268 (3), 187 (10), 171 (22), 169 (10), 138 (100), 127 (18), 95 (24), 85 (16), 83 (45), 57 (51). $-\mathrm{C}_{21} \mathrm{H}_{40} \mathrm{O}_{2}$ (324.6): calcd. C 77.72, H 12.42; found C 77.54, H 12.50 .
17. (1R,2S,5R)-2-(tert-Butyl)-5-methylcyclohexyl ( $2^{\prime} R$ )- $2^{\prime}$-(tert-butyl)-4', $4^{\prime}$-dimethylpentanoate (23a) and ( $1 R, 2 S, 5 R$ )-2-(tert-butyl)-5-methylcyclohexyl ( $\left.2^{\prime} S\right)-2^{\prime}$-(tert-butyl)-4' $4^{\prime}$ ' dimethylpentanoate (23b): $128.2 \mathrm{mg}(0.410 \mathrm{mmol})$ of $\mathbf{1 5 a} / \mathbf{b}$ and $473.0 \mathrm{mg}(4.072 \mathrm{mmol})$ tertbutylacetic acid were electrolyzed according to the general procedure for the Kolbe electrolysis to afford $59.7 \mathrm{mg}(0.176 \mathrm{mmol}, 43 \%) \mathbf{2 3 a}$ and $36.7 \mathrm{mg}(0.108 \mathrm{mmol}, 26 \%)$ 23b after flash chromatography and HPLC (methylene chloride/petroleum ether, 1:3). The diastereomeric ratio was determined by GLC to be 23a:23b $=63.5: 36.5(27 \% ~ d e)$. m.p. $49-53^{\circ} \mathrm{C}(\mathbf{2 3 b}) .-[\alpha]_{\mathrm{D}}{ }^{20}=-101.6^{\circ}(\mathbf{2 3 a}, c=0.6$ in trichloromethane $) ;-18.5^{\circ}(\mathbf{2 3 b}, c=$ 1.0 in trichloromethane). - FT-IR (film): $v=1723 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{2 3 a}: \delta=0.86$ (d, $J=6.4 \mathrm{~Hz}, 3 \mathrm{H}, 11-\mathrm{H}), 0.88,0.95,0.96(3 \mathrm{~s}$, each $9 \mathrm{H}, \mathrm{tBu}), 0.80-1.70(\mathrm{~m}, 6 \mathrm{H}), 1.37(\mathrm{dd}$, $\left.J=1 \mathrm{~Hz}, J=14.3 \mathrm{~Hz}, 1 \mathrm{H}, t \mathrm{BuCHCH}_{a} \mathrm{H}_{\mathrm{b}}\right), 1.70(\mathrm{dd}, J=14.3 \mathrm{~Hz}, J=9.3 \mathrm{~Hz}, 1 \mathrm{H}$,
$\left.t \mathrm{BuCHCH}_{\mathrm{a}} H_{b}\right), 1.86\left(\mathrm{~m}_{\mathrm{c}}, 1 \mathrm{H}\right), 2.13\left(\mathrm{dd}, J=1 \mathrm{~Hz}, J=9.3 \mathrm{~Hz}, 1 \mathrm{H}, 2^{\prime}-\mathrm{C}\right), 2.19\left(\mathrm{~m}_{\mathrm{c}}, 1 \mathrm{H}\right), 4.61$ (ddd, $J=10.5 \mathrm{~Hz}, J=10.4 \mathrm{~Hz}, J=3.8 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}) ; \mathbf{2 3 b}: \delta=0.88(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 3 \mathrm{H}, 11-\mathrm{H})$, $0.86,0.93,0.94\left(3 \mathrm{~s}\right.$, each $\left.9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.80-1.60(\mathrm{~m}, 5 \mathrm{H}), 1.29(\mathrm{dd}, J=0.7 \mathrm{~Hz}, J=14.1 \mathrm{~Hz}$, $\left.1 \mathrm{H}, t \mathrm{BuCHCH} \mathrm{H}_{\mathrm{b}}\right), 1.66,1.86\left(2 \mathrm{~m}_{\mathrm{c}}\right.$, each 1 H$), 1.89(\mathrm{dd}, J=14.1 \mathrm{~Hz}, J=9.8 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.t \mathrm{BuCHCH}_{\mathrm{a}} H_{b}\right), 2.06\left(\mathrm{dd}, J=0.7 \mathrm{~Hz}, J=9.8 \mathrm{~Hz}, 1 \mathrm{H}, 2^{\prime}-\mathrm{H}\right), 2.22\left(\mathrm{~m}_{\mathrm{c}}, 1 \mathrm{H}\right), 4.58(\mathrm{ddd}, J=10.5$ $\mathrm{Hz}, J=10.4 \mathrm{~Hz}, J=3.8 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{2 3 a}: \delta=21.90(\mathrm{q}, \mathrm{C}-11), 27.79$ (t, C-3), 27.87, 29.18, $29.59\left(3 \mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 30.80\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 31.31(\mathrm{~d}, \mathrm{C}-5), 32.55(\mathrm{~s}, \mathrm{C}-7)$, $33.93\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.88(\mathrm{t}, \mathrm{C}-4), 41.08(\mathrm{t}, \mathrm{C}-6), 41.82\left(\mathrm{t}, t \mathrm{BuCHCH}_{2}\right), 50.11(\mathrm{~d}, \mathrm{C}-2), 52.37$ (d, C-2'), 77.03 (d, C-1), 176.48 ( $\mathrm{s}, \mathrm{C}=\mathrm{O}$ ); 23b: $\delta=21.94$ (q, C-11), 26.62 (t, C-3), 28.24, 29.05, $29.62\left(3 \mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 30.33\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 31.34(\mathrm{~d}, \mathrm{C}-5), 32.69(\mathrm{~s}, \mathrm{C}-7), 33.97$ (s, $\left.C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.91(\mathrm{t}, \mathrm{C}-4), 40.94(\mathrm{t}, \mathrm{C}-6), 41.45(\mathrm{t}, t \mathrm{BuCHCH} 2), 50.24(\mathrm{~d}, \mathrm{C}-2), 51.46$ (d, C-2'), 77.10 (d, C-1), 175.09 (s, C=O). — MS (GC/MS), $m / z(\%): 323$ (2), 282 (0.5), 187 (61), 169 (12), 153 (36), 152 (34), 131 (10), 97 (40), 94 (28), 57 (100). $-\mathrm{C}_{22} \mathrm{H}_{42} \mathrm{O}_{2}$ (338.6): calcd. C 78.05, H 12.50; found C 78.11, H 12.74 .
18.(1R,2S,5R)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (2'R)-2'-isopropyl-4', $4^{\prime}$ dimethylpentanoate (24a) and (1R,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl ( $2^{\prime}$ S)- $\mathbf{2}^{\prime}$-isopropyl-4', $4^{\prime}$-dimethylpentanoate ( $\mathbf{2 4 b}$ ): $142.2 \mathrm{mg}(0.394 \mathrm{mmol})$ of $\mathbf{1 7 a} / \mathbf{b}$ and 384.0 mg ( 3.31 mmol ) tert-butylacetic acid were electrolyzed according to the general procedure for the Kolbe electrolysis to afford $32.9 \mathrm{mg}(0.085 \mathrm{mmol}, 22 \%) \mathbf{2 4 a} / \mathbf{b}$ as a diastereomeric mixture after flash chromatography (petroleum ether/diethyl ether, 20:1). The diasteromers 24a and 24b have not been separated. The diasteromeric ratio was determined by GLC to be 24a:24b = 69:31(38\% de).

FT-IR (film): $v=1725 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=0.65,0.77\left(2 \mathrm{~d}, 6 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.81$, $0.83(2 \mathrm{~d}, J=5.5 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}), 0.76,0.75\left(2 \mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.80-2.05(\mathrm{~m}, 12 \mathrm{H}), 1.13$,
$1.16,1.27,1.31(4 \mathrm{~s}, 6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 4.60,4.64(2 \mathrm{ddd}, J=9.1 \mathrm{~Hz}, J=8.7 \mathrm{~Hz}, J=3.6 \mathrm{~Hz}, 1 \mathrm{H}$, 1-H), 7.02-7.30 (m, 5H, C $\left.\mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta=18.12$, 18.66, 20.12, $21.10(4 \mathrm{q}$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 21.82,21.85(2 \mathrm{q}, \mathrm{C}-10), 25.15,26.28,26.72,28.49(4 \mathrm{q}, \mathrm{C}-8, \mathrm{C}-9), 26.95,27.31$ (t, C-3), 29.43 (q, C(CH3 $\left.)_{3}\right), 30.24\left(\mathrm{~d}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 30.31,30.49\left(2 \mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 31.30,31.54$ (2d, C-5), 34.68, 34.78 (2t, C-4), 39.85, 40.11 (2s, C-7), 40.50 (t, C-6), 41.15, 41.35 (2t, $t \mathrm{BuCH}_{2}$ ), 46.51 (d, C-2', 24b), 47.33 (d, C-2', 24a), 50.09, 50.28 (2d, C-2), 75.32, 75.55 (2d, C-1), 124.96, 125.12, 125.41, 125.58, 127.90, 127.93 ( $6 \mathrm{~d},=C-\mathrm{H}_{\text {phenyl }}$ ), 151.83, $151.29(2 \mathrm{~s}$, $\left.=C-\mathrm{C}_{\text {phenyl }}\right), 175.11(\mathrm{~s}, \mathrm{C}=\mathrm{O}, \mathbf{2 4 b}), 176.40(\mathrm{~s}, \mathrm{C}=\mathrm{O}, \mathbf{2 4 a}) .-\mathrm{MS}(\mathrm{GC} / \mathrm{MS}), m / z(\%): 386$ (0.5), 267 (14), 215 (7), 214 (17), 199 (4), 173 (12), 119 (100), 118 (64), 105 (14), 91 (10), 57
(8). - HR MS ( $\left.\mathrm{NH}_{3}-\mathrm{DCI}\right): \mathrm{C}_{26} \mathrm{H}_{42} \mathrm{O}_{2}$ : calcd. 404.3529 ; found $404.3520\left\{\mathrm{M}+\mathrm{NH}_{4}{ }^{+}\right\}$.
19. (1R,2S,5R)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl ( $\left.2^{\prime} R\right)-2^{\prime}-\left(\right.$ tert-butyl)-4', $4^{\prime}-$ dimethylpentanoate (25a) and (1R,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl ( $2^{\prime}$ S)- $2^{\prime}$ '(tert-butyl)-4', $4^{\prime}$-dimethylpentanoate ( $\mathbf{2 5 b}$ ): $148.3 \mathrm{mg}(0.396 \mathrm{mmol})$ of $\mathbf{1 6 a} / \mathbf{b}$ and 463.9 mg ( 3.99 mmol ) tert-butylacetic acid were electrolyzed according to the general procedure for the Kolbe electrolysis to afford $49.1 \mathrm{mg}(0.123 \mathrm{mmol}, 31 \%) \mathbf{2 5 a}$ and 14.1 mg ( $0.035 \mathrm{mmol}, 8.9 \%$ ) $\mathbf{2 5 b}$ after flash chromatography and HPLC (methylene chloride/petroleum ether, 1:4). The diastereomeric ratio was determined by GLC to be 25a : $\mathbf{2 5 b}=82.5: 17.5(65 \% d e)$.
$[\alpha]_{\mathrm{D}}{ }^{20}=-34.1^{\circ}(\mathbf{2 5 a}, c=0.8$ in trichloromethane $) ;-6.8^{\circ}(\mathbf{2 5 b}, c=1.8$ in trichloromethane $)$. — FT-IR (film): $v=1720 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{2 5 a}: \delta=0.86(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 3 \mathrm{H}, 10-$ H), $0.85,0.94\left(2 \mathrm{~s}\right.$, each $\left.9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.24,1.46(2 \mathrm{~s}$, each $3 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 0.80-1.65(\mathrm{~m}, 8 \mathrm{H})$, $2.00-2.10(\mathrm{~m}, 1 \mathrm{H}), 1.90,2.29\left(2 \mathrm{~m}_{\mathrm{c}}\right.$, each 1 H$), 4.65(\mathrm{ddd}, J=10.5 \mathrm{~Hz}, J=10.4 \mathrm{~Hz}, J=3.6$ $\mathrm{Hz}, 1 \mathrm{H}, 1-\mathrm{H}), 7.12-7.71\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{5}\right) ; \mathbf{2 5 b}: \delta=0.88(\mathrm{~d}, J=5.5 \mathrm{~Hz}, 3 \mathrm{H}, 10-\mathrm{H}), 0.84(\mathrm{~s}$, $\left.18 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.19,1.41(2 \mathrm{~s}$, each $3 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 0.80-1.65(\mathrm{~m}, 6 \mathrm{H}), 1.80-2.40(\mathrm{~m}, 5 \mathrm{H})$,
$4.57(\mathrm{ddd}, J=10.5 \mathrm{~Hz}, J=10.4 \mathrm{~Hz}, J=3.6 \mathrm{~Hz}, 1 \mathrm{H}, 1-\mathrm{H}), 7.12-7.35\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-$ NMR ( $\mathrm{CDCl}_{3}$ ): 25a: $\delta=21.84(\mathrm{q}, \mathrm{C}-10), 24.47,28.95(2 \mathrm{q}, \mathrm{C}-8, \mathrm{C}-9), 27.57(\mathrm{t}, \mathrm{C}-3), 27.73$, $29.62\left(2 \mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 30.80\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 31.44(\mathrm{~d}, \mathrm{C}-5), 33.87\left(\mathrm{~s}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 34.81(\mathrm{t}, \mathrm{C}-4)$, 40.17 ( $\mathrm{s}, \mathrm{C}-7$ ), 41.01 (t, C-6), 41.95 (t, $t \mathrm{BuCHCH}_{2}$ ), 50.48 (d, C-2), 51.69 (d, C-2'), 76.80 (d, $\mathrm{C}-1$ ), 125.12, $125.63,127.98$ (3d, C-2' to $\mathrm{C}-4^{\prime}$ ), $151.51\left(\mathrm{~s}, \mathrm{C}-1^{\prime}\right), 176.68(\mathrm{~s}, \mathrm{C}=\mathrm{O}) ; \mathbf{2 5 b}: \delta=$ 21.87 (q, C-10), 25.37, 27.57 (2q, C-8, C-9), 27.46 (t, C-3), 28.24, $29.52\left(2 q, C\left(\mathrm{CH}_{3}\right)_{3}\right), 30.33$ ( $\left.\mathrm{s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 31.47(\mathrm{~d}, \mathrm{C}-5), 33.70\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 34.95(\mathrm{t}, \mathrm{C}-4), 40.03(\mathrm{~s}, \mathrm{C}-7), 40.61(\mathrm{t}, \mathrm{C}-6)$, $41.35\left(\mathrm{t}, \mathrm{tBuCHCH}_{2}\right), 50.65(\mathrm{~d}, \mathrm{C}-2), 50.85\left(\mathrm{~d}, \mathrm{C}-2^{\prime}\right), 77.00(\mathrm{~d}, \mathrm{C}-1), 124.95,125.46,127.95$ (3d, $\left.=C-\mathrm{H}_{\text {phenyl }}\right), 151.94$ ( $\left.\mathrm{s},=C-\mathrm{C}_{\text {pheny }}\right)$, 175.06 ( $\mathrm{s}, \mathrm{C}=\mathrm{O}$ ). $-\mathrm{MS}(\mathrm{GC} / \mathrm{MS}), m / z(\%): 400$ (0.1), 281 (15), 215 (16), 214 (22), 199 (6), 187 (12), 171 (11), 119 (98), 118 (100), 105 (46), 91 (29), 57 (59). — HR MS ( $\mathrm{NH}_{3}$-DCI): $\mathrm{C}_{27} \mathrm{H}_{44} \mathrm{O}_{2}$ : calcd. 418.3685; found 418.3687 \{ M $\left.+\mathrm{NH}_{4}{ }^{+}\right\}$.
20. Di[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl] $\left(2^{\prime} R^{*}, 3^{\prime} R^{*}\right)-2^{\prime}, 3^{\prime}$-diisopropylsuccinate (26a), di[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl] ( $\left.2^{\prime} R, 3^{\prime} S\right)-2^{\prime}, 3^{\prime}$-diisopropylsuccinate (26b) and di[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl] (2'S*, $\left.3^{\prime} S^{*}\right)$-2', $3^{\prime}$-diisopropylsuccinate ( $\mathbf{2 6 c}$ ): $469.0 \mathrm{mg}(1.89 \mathrm{mmol})$ of $\mathbf{1 4 a} / \mathbf{b}$ were electrolyzed according to the general procedure for the Kolbe electrolysis to afford $51.7 \mathrm{mg}(0.108 \mathrm{mmol}, 13 \%) \mathbf{2 6 a}, 88.9 \mathrm{mg}$ ( $0.186 \mathrm{mmol}, 23 \%$ ) 26b and $35.9 \mathrm{mg}(0.075 \mathrm{mmol}, 9 \%) \mathbf{2 6 c}$ after flash chromatography and HPLC (petroleum ether/diethyl ether, 40:1). The diastereomeric ratio was determined by GLC to be 26a : 26b : 26c $=1.17: 2.00: 0.81$. m.p. $136-137^{\circ} \mathrm{C}$ (26a); $145-146^{\circ} \mathrm{C}$ (26b); 108-109 ${ }^{\circ} \mathrm{C}(\mathbf{2 6 c}) .-[\alpha]_{\mathrm{D}}{ }^{20}=-43.5^{\circ}(\mathbf{2 6 a}, c=$ 0.8 in trichloromethane); $-65.2^{\circ}(\mathbf{2 6 b}, c=1.2$ in trichloromethane $) ;-102.8^{\circ}(\mathbf{2 6 c}, c=1.0$ in trichloromethane). - FT-IR (KBr): $v=1725 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{2 6 a}: \delta=0.73(\mathrm{~d}$, $J=6.9 \mathrm{~Hz}, 6 \mathrm{H}, 2 \times 10-\mathrm{H}$ ), $0.87-0.91,1.04$ (superposing doublets, $24 \mathrm{H}, 2 \times 8-\mathrm{H}, 2 \times 9-\mathrm{H}$,
$\left.2 \times \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.80-1.10(\mathrm{~m}, 6 \mathrm{H}), 1.30-1.55(\mathrm{~m}, 4 \mathrm{H}), 1.66\left(\mathrm{~m}_{\mathrm{c}}, 4 \mathrm{H}\right), 1.90-2.10(\mathrm{~m}, 6 \mathrm{H}), 2.53$ $\left(\mathrm{m}_{\mathrm{c}}, 2 \mathrm{H}, 2^{\prime}-\mathrm{H}, 3^{\prime}-\mathrm{H}\right), 4.66(\mathrm{ddd}, J=10.9 \mathrm{~Hz}, J=10.8 \mathrm{~Hz}, J=4.3 \mathrm{~Hz}, 2 \mathrm{H}, 2 \times 1-\mathrm{H}) ; \mathbf{2 6 b}: \delta=$ $0.73,0.74(2 \mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}, 2 \times 10-\mathrm{H}), 0.87-0.99$ (superposing doublets, $24 \mathrm{H}, 2 \times 8-\mathrm{H}$, $\left.2 \times 9-\mathrm{H}, 2 \times \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.80-1.10(\mathrm{~m}, 6 \mathrm{H}), 1.30-2.10(\mathrm{~m}, 14 \mathrm{H}), 2.81\left(\mathrm{~m}_{\mathrm{c}}, 2 \mathrm{H}, 2^{\prime}-\mathrm{H}, 3^{\prime}-\mathrm{H}\right)$, 4.64, 4.70 (2ddd, $J=10.9 \mathrm{~Hz}, J=10.8 \mathrm{~Hz}, J=4.3 \mathrm{~Hz}, 2 \mathrm{H}, 2 \times 1-\mathrm{H}) ; \mathbf{2 6 c}: \delta=0.73(\mathrm{~d}, J=6.9$ $\mathrm{Hz}, 6 \mathrm{H}, 2 \times 10-\mathrm{H}), 0.86\left(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}, 1 \times \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.89,0.90(2 \mathrm{~d}, J=7.0 \mathrm{~Hz}$, each $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 1.08\left(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}, 1 \times \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 0.8-1.1(\mathrm{~m}, 6 \mathrm{H}), 1.30-1.55(\mathrm{~m}, 4 \mathrm{H})$, $1.66\left(\mathrm{~m}_{\mathrm{c}}, 4 \mathrm{H}\right), 1.90-2.10(\mathrm{~m}, 6 \mathrm{H}), 2.67\left(\mathrm{~m}_{\mathrm{c}}, 2 \mathrm{H}, 2^{\prime}-\mathrm{H}, 3^{\prime}-\mathrm{H}\right), 4.60(\mathrm{ddd}, J=10.9 \mathrm{~Hz}, J=10.8$ $\mathrm{Hz}, J=4.3 \mathrm{~Hz}, 2 \mathrm{H}, 2 \times 1-\mathrm{H}) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{2 6 a}: \delta=15.74(\mathrm{q}, \mathrm{C}-10), 19.51,20.86$ (2q, C-8, C-9), 21.33, 22.11 (2q, CH( $\left.\mathrm{CH}_{3}\right)_{2}$ ), 22.98 (t, C-3), 25.81 (d, C-7), 27.23 (d, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 31.47$ (d, C-5), 34.37 (t, C-4), 40.74 (t, C-6), 46.81 (d, C-2), 51.83 (d, C-2', C-3'), 74.47 (d, C-1), 173.11 (s, C=O); 26b: $\delta=15.47,15.57$ ( $2 \mathrm{q}, \mathrm{C}-10$ ), 16.85, 17.05, 20.86, 20.93 (4q, C-8, C-9), 21.90, $22.04\left(2 \mathrm{q}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 22.75,22.88$ (2t, C-3), 25.64, 25.78 (2d, C-7), 28.88, 29.22 (2d, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right)$, 31.40, 31.47 (2d, C-5), 34.27 (t, C-4), 40.74, 41.15 (2t, C-6), 46.81, 46.87 (2d, C-2), 51.35, 51.56 (2d, C-2', C-3'), 74.44, 74.61 (2d, C-1), 172.40, 172.70 ( $\mathrm{s}, \mathrm{C}=\mathrm{O}$ ); 26c: $\delta=16.11(\mathrm{q}, \mathrm{C}-10), 18.00,20.86(2 \mathrm{q}, \mathrm{C}-8, \mathrm{C}-9), 22.07\left(\mathrm{q}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 23.25(\mathrm{t}$, C-3), 25.68 (d, C-7), $26.68\left(\mathrm{~d}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 31.44$ (d, C-5), 34.34 (t, C-4), 41.18 (t, C-6), 46.94 (d, C-2), 50.45 (d, C-2', C-3'), 74.34 (d, C-1), 173.21 (s, C=O). — MS (GC/MS), m/z (\%): 478 (1.5), 393 (1), 341 (4), 325 (1), 239 (18), 203 (24), 185 (52), 157 (6), 139 (100), 101 (46), 83 (57). - $\mathrm{C}_{30} \mathrm{H}_{54} \mathrm{O}_{4}$ (478.8): calcd. C 75.26, H 11.37; found C 75.23, H 11.27.
21. Di[(lR,2S,5R)-2-isopropyl-5-methylcyclohexyl] ( $\left.2^{\prime} R^{*}, 3^{\prime} R^{*}\right)-2^{\prime}, 3^{\prime}-$ di(tert-butyl)succinate (27a), di[(lR,2S,5R)-2-isopropyl-5-methylcyclohexyl] ( $\left.2^{\prime} R, 3^{\prime} S\right)-2^{\prime}, 3^{\prime}-$ di(tert-butyl)succinate (27b) and di[(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl] ( $\left.2^{\prime} S^{*}, 3^{\prime} S^{*}\right)-2^{\prime}, 3^{\prime}-$ di(tert-butyl)succinate ( $\mathbf{2 7} \mathbf{c}$ ): $546.9 \mathrm{mg}(1.83 \mathrm{mmol})$ of $\mathbf{1 3 a} / \mathbf{b}$ were electrolyzed according to the general
procedure for the Kolbe electrolysis to afford $80.1 \mathrm{mg}(0.158 \mathrm{mmol}, 17 \%) \mathbf{2 7 a}, 118.1 \mathrm{mg}$ ( $0.233 \mathrm{mmol}, \mathbf{2 6 \%}$ ) 27b and $31.7 \mathrm{mg}(0.063 \mathrm{mmol}, 7 \%) \mathbf{2 7} \mathbf{c}$ after flash chromatography and HPLC (methylene chloride/petroleum ether, 1:2). The diastereomeric ratio was determined by GLC to be 27a : 27b $: \mathbf{2 7} \mathbf{c}=1.39: 2.00: 0.67$. m.p. $40-45^{\circ} \mathrm{C}(\mathbf{2 7 a}) ; 177-182{ }^{\circ} \mathrm{C}(\mathbf{2 7 b}) ; 145-150{ }^{\circ} \mathrm{C}(\mathbf{2 7} \mathbf{c}) .-[\alpha]_{\mathrm{D}}{ }^{20}=-89.8^{\circ}(\mathbf{2 7 a}, c=0.9$ in trichloromethane); $-39.7^{\circ}(\mathbf{2 7 b}, c=1.0$ in trichloromethane $) ;-75.4^{\circ}(\mathbf{2 7} \mathbf{c}, c=1.0$ in trichloromethane). - FT-IR (KBr): $v=1727 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{2 7 a}: \delta=0.72(\mathrm{~d}$, $J=6.9 \mathrm{~Hz}, 6 \mathrm{H}, 10-\mathrm{H}), 0.89,0.91(2 \mathrm{~d}, J=4.8 \mathrm{~Hz}$, each $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 1.02(\mathrm{~s}, 18 \mathrm{H}, 2 \mathrm{x}$ $\left.\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.80-1.10(\mathrm{~m}, 4 \mathrm{H}), 1.20-1.70(\mathrm{~m}, 10 \mathrm{H}), 2.18,1.98\left(2 \mathrm{~m}_{\mathrm{c}}\right.$, each 2 H$), 2.42\left(\mathrm{~s}, 2 \mathrm{H}, 2^{\prime}-\right.$ $\left.\mathrm{H}, 3^{\prime}-\mathrm{H}\right), 4.66(\mathrm{ddd}, J=10.9 \mathrm{~Hz}, J=10.8 \mathrm{~Hz}, J=4.3 \mathrm{~Hz}, 2 \mathrm{H}, 1-\mathrm{H}) ; \mathbf{2 7 b}: \delta=0.68,0.70(2 \mathrm{~d}$, $J=6.9 \mathrm{~Hz}$, each $3 \mathrm{H}, 2 \mathrm{x} 10-\mathrm{H}), 0.88,0.90,0.92,0.93(4 \mathrm{~d}, J=6.7 \mathrm{~Hz}$, each $3 \mathrm{H}, 2 \mathrm{x} 8-\mathrm{H}, 2 \mathrm{x} 9-$ H), 0.99, 1.02 (2s, each 9H, 2x C( $\left.\mathrm{CH}_{3}\right)_{3}$ ), 0.80-1.10 (m, 4H), 1.30-1.80 (m, 10H), 2.05-2.35 (m, 4H), 2.65, $2.70\left(2 \mathrm{~d}, J=10.7 \mathrm{~Hz}\right.$, each $\left.1 \mathrm{H}, 2^{\prime}-\mathrm{H}, 3^{\prime}-\mathrm{H}\right), 4.49,4.51(2 \mathrm{ddd}, J=10.9 \mathrm{~Hz}, J=$ $10.8 \mathrm{~Hz}, J=4.3 \mathrm{~Hz}, 2 \mathrm{H}, 2 \mathrm{x} 1-\mathrm{H}) ; \mathbf{2 7} \mathbf{c}: \delta=0.78(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}, 2 \mathrm{x} 10-\mathrm{H}), 0.87,0.89(2 \mathrm{~d}$, $J=6.7 \mathrm{~Hz}$, each $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 1.02\left(\mathrm{~s}, 18 \mathrm{H}, 2 \mathrm{x} \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.80-1.10(\mathrm{~m}, 4 \mathrm{H}), 1.20-1.70(\mathrm{~m}$, $10 \mathrm{H}), 2.05-2.25(\mathrm{~m}, 4 \mathrm{H}), 2.41\left(\mathrm{~s}, 2 \mathrm{H}, 2^{\prime}-\mathrm{H}, 3^{\prime}-\mathrm{H}\right), 4.64(\mathrm{ddd}, J=10.9 \mathrm{~Hz}, J=10.8 \mathrm{~Hz}, J=$ $4.3 \mathrm{~Hz}, 2 \mathrm{H}, 1-\mathrm{H}) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): 27 \mathrm{a}: \delta=15.70(\mathrm{q}, \mathrm{C}-10), 20.96,22.14(2 \mathrm{q}, \mathrm{C}-8, \mathrm{C}-$ 9), 22.88 (t, C-3), 25.68 (d, C-7), $28.04\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.41$ (d, C-5), $34.51(\mathrm{t}, \mathrm{C}-4), 34.64$ ( s , $\left.C\left(\mathrm{CH}_{3}\right)_{3}\right), 40.27$ (t, C-6), 47.08 (d, C-2), 53.98 (d, C-2', C-3'), 73.70 (d, C-1), 172.29 (s, $\mathrm{C}=\mathrm{O}$ ); 27b: $\delta=15.47,15.64(2 \mathrm{q}, \mathrm{C}-10), 21.16,21.23,22.07(3 \mathrm{q}, \mathrm{C}-8, \mathrm{C}-9), 22.68(\mathrm{t}, \mathrm{C}-3)$, 24.90, 25.17 (2d, C-7), 28.88, $28.98\left(2 \mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.41$ (d, C-5), 34.07, 34.20 (2t, C-4), $34.64\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 40.37$ (t, C-6), 47.11 (d, C-2), 53.65, 54.46 (2d, C-2', C-3'), 75.08, 75.48 (2d, C-1), 174.25, 174.42 ( $2 \mathrm{~s}, \mathrm{C}=\mathrm{O}$ ); 27c: $\delta=15.59$ (q, C-10), 21.06, 22.14 (2q, C-8, C-9), 22.71 (t, C-3), 25.07 (d, C-7), $27.97\left(\mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.44(\mathrm{~d}, \mathrm{C}-5), 34.62(\mathrm{t}, \mathrm{C}-4), 35.10(\mathrm{~s}$, $\left.C\left(\mathrm{CH}_{3}\right)_{3}\right), 40.86$ (t, C-6), 47.09 (d, C-2), 53.73 (d, C-2', C-3'), 74.40 (d, C-1), 172.29 (s,
$\mathrm{C}=\mathrm{O}) .-\mathrm{MS}(\mathrm{GC} / \mathrm{MS}), m / z(\%): 506$ (0.4), 491 (0.4), 450 (1), 393 (20), 369 (25), 231 (95), 213 (100), 139 (36), 117 (26), 83 (43), 57 (27). $-\mathrm{C}_{32} \mathrm{H}_{58} \mathrm{O}_{4}$ (506.8): calcd. C 75.84, H 11.53; found C 75.83, H 11.73.
22. Di[(lR,2S,5R)-2-(tert.-butyl)-5-methylcyclohexyl] ( $\left.2^{\prime} R, 3^{\prime} R\right)^{\prime} 2^{\prime}, 3^{\prime}$-di(tert.-butyl)succinate (28a) and di[(lR,2S,5R)-2-(tert.-butyl)-5-methylcyclohexyl] ( $\left.2^{\prime} R, 3^{\prime} S\right)-2^{\prime}, 3^{\prime}-d i(t e r t .-$ butyl)succinate (28b): $511.3 \mathrm{mg}(1.64 \mathrm{mmol})$ of $\mathbf{1 5 a} / \mathbf{b}$ were electrolyzed according to the general procedure for the Kolbe electrolysis to afford $152.1 \mathrm{mg}(0.284 \mathrm{mmol}, 35 \%)$ 28a and $66.2 \mathrm{mg}(0.124 \mathrm{mmol}, 15 \%) \mathbf{2 8 b}$ after flash chromatography and HPLC (methylene chloride: petroleum ether, 1:3). The diastereomeric ratio was determined by GLC to be 28a : 28b : 28c $=5.14: 2.00: 0.21$. The very small amount of 28c could not be isolated.
m.p. $95-99^{\circ} \mathrm{C}(\mathbf{2 8 a}) .-[\alpha]_{\mathrm{D}}{ }^{20}=-90.8^{\circ}(\mathbf{2 8 a}, c=1.0$ in trichloromethane $) ;-98.0^{\circ}(\mathbf{2 8 b}, c=$ 0.4 in trichloromethane). - FT-IR $(\mathrm{KBr}): v=1726 \mathrm{~cm}^{-1} .-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \mathbf{2 8 a}: \delta=0.92$ (d, $J=6.7 \mathrm{~Hz}, 6 \mathrm{H}, 11-\mathrm{H}), 0.94,1.06\left(2 \mathrm{~s}\right.$, each $\left.18 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.80-1.60(\mathrm{~m}, 10 \mathrm{H}), 1.65,1.84$, $2.32\left(3 \mathrm{~m}_{\mathrm{c}}\right.$, each 2 H ), $2.40\left(\mathrm{~s}, 2 \mathrm{H}, 2^{\prime}-\mathrm{H}, 3^{\prime}-\mathrm{H}\right), 4.56(\mathrm{ddd}, J=10.8 \mathrm{~Hz}, J=10.6 \mathrm{~Hz}, J=3.8 \mathrm{~Hz}$, $2 \mathrm{H}, 1-\mathrm{H}) ; \mathbf{2 8 b}: \delta=0.88(\mathrm{~d}, J=6.7 \mathrm{~Hz}, 6 \mathrm{H}, 11-\mathrm{H}), 0.96,0.97,1.04,1.08(4 \mathrm{~s}$, each 9 H , $\left.\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.80-1.60(\mathrm{~m}, 10 \mathrm{H}), 1.66,1.87,2.33\left(3 \mathrm{~m}_{\mathrm{c}}\right.$, each 2 H$), 2.57,2.76(2 \mathrm{~d}, J=6.9 \mathrm{~Hz}$, each $\left.1 \mathrm{H}, 2^{\prime}-\mathrm{H}, 3^{\prime}-\mathrm{H}\right), 4.55,4.59(2 \mathrm{ddd}, J=10.8 \mathrm{~Hz}, J=10.5 \mathrm{~Hz}, J=3.8 \mathrm{~Hz}$, each $1 \mathrm{H}, 1-\mathrm{H})$. — ${ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): 28 \mathrm{a}: \delta=22.17(\mathrm{q}, \mathrm{C}-11), 26.76(\mathrm{t}, \mathrm{C}-3), 28.61,29.15\left(2 \mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, 31.44 (d, C-5), $32.59\left(\mathrm{~s}, C\left(\mathrm{CH}_{3}\right)_{3}\right), 35.08$ (t, C-4), 35.15 (s, C-7), 40.57 (t, C-6), 50.11 (d, C2), 54.05 (d, C-2', C-3'), $76.60(\mathrm{~d}, \mathrm{C}-1), 172.90(\mathrm{~s}, \mathrm{C}=\mathrm{O}) ; \mathbf{2 8 b}: \delta=22.01(\mathrm{q}, \mathrm{C}-11), 26.59(\mathrm{t}$, $\mathrm{C}-3)$, 29.12, 29.18, 29.35, $29.52\left(4 \mathrm{q}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.27(\mathrm{~d}, \mathrm{C}-5), 32.69,32.79\left(2 \mathrm{~s}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, 34.74 (t, C-4), 34.61, 34.95 (2s, C-7), 40.74 (t, C-6), 50.18, 50.55 (2d, C-2), 54.69, 54.76 (2d, C-2', C-3'), 77.10, 78.21 (2d, C-1), 173.68, 174.29 (2s, C=O). - MS (GC/MS), $m / z(\%): 519$ (1), 478 (1), 421 (6), 383 (2), 367 (2), 269 (14), 231 (100), 213 (82), 174 (18), 153 (46), 117
(23), 97 (66), 83 (30), 57 (93). $-\mathrm{C}_{34} \mathrm{H}_{62} \mathrm{O}_{4}$ (534.9): calcd. C 76.35, H 11.68; found C 76.24, H 11.88.
23. Di[(1R,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl] ( $\left.2^{\prime} R, 3^{\prime} R\right)-2^{\prime}, 3^{\prime}-d i(t e r t-$ butyl)succinate (29a) and di[(1R,2S,5R)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl] ( $\left.2^{\prime} R, 3^{\prime} S\right)-2^{\prime}, 3^{\prime}-$ di(tert-butyl)succinate (29b): $613.9 \mathrm{mg}(1.64 \mathrm{mmol})$ of $\mathbf{1 6 a} / \mathbf{b}$ were electrolyzed according to the general procedure for the Kolbe electrolysis to afford 91.3 mg $(0.138 \mathrm{mmol}, 17 \%) \mathbf{2 9 a}$ and $22.8 \mathrm{mg}(0.035 \mathrm{mmol}, 4 \%) \mathbf{2 9 b}$ after flash chromatography and HPLC (petroleum ether(diethyl ether, 20:1). The diastereomeric ratio was determined by GLC to be 29a: 29b : 29c = $7.03: 2.00:$ n.d.. The very small amount of $\mathbf{2 9 c}$ could not be isolated nor determined.
m.p. $144-148{ }^{\circ} \mathrm{C}(\mathbf{2 9 a}) ; 84-88^{\circ} \mathrm{C}(\mathbf{2 9 b}) .-[\alpha]_{\mathrm{D}}{ }^{20}=-50.0^{\circ}(\mathbf{2 9} \mathbf{a}, c=1.0$ in trichloromethane); $-33.8^{\circ}(\mathbf{2 9 b}, c=1.0$ in trichloromethane $) .-$ FT-IR $(\mathrm{KBr}): v=1720 \mathrm{~cm}^{-1}$. $-{ }^{1} \mathrm{H}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right):$ 29a: $\delta=0.89(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 6 \mathrm{H}, 10-\mathrm{H}), 0.84\left(\mathrm{~s}, 18 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.15$, 1.33 (2s, each $6 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 0.80-1.70(\mathrm{~m}, 12 \mathrm{H}), 1.75\left(\mathrm{~s}, 2 \mathrm{H}, 2^{\prime}-\mathrm{H}, 3^{\prime}-\mathrm{H}\right), 2.08,2.29\left(2 \mathrm{~m}_{\mathrm{c}}\right.$, each 2 H ), 4.48 (ddd, $J=10.5 \mathrm{~Hz}, J=10.4 \mathrm{~Hz}, J=3.6 \mathrm{~Hz}, 2 \mathrm{H}, 1-\mathrm{H}), 7.10-7.35(\mathrm{~m}, 10 \mathrm{H}$, $\left.\mathrm{C}_{6} \mathrm{H}_{5}\right) ; \mathbf{2 9 b}: \delta=0.86(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 6 \mathrm{H}, 10-\mathrm{H}), 0.99,1.08\left(2 \mathrm{~s}\right.$, each $\left.9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.24,1.27$, $1.47,1.52(4 \mathrm{~s}$, each $3 \mathrm{H}, 8-\mathrm{H}, 9-\mathrm{H}), 0.70-1.60(\mathrm{~m}, 12 \mathrm{H}), 2.40,2.53\left(2 \mathrm{~d}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}, 2^{\prime}-\mathrm{H}\right.$, $\left.3^{\prime}-\mathrm{H}\right), 1.90-2.60(\mathrm{~m}, 4 \mathrm{H}), 4.62,4.63(2 \mathrm{ddd}, J=10.5 \mathrm{~Hz}, J=10.4 \mathrm{~Hz}, J=3.6 \mathrm{~Hz}$, each $1 \mathrm{H}, 1-$ H), 7.10-7.35 (m, 10H, C $\left.\mathrm{C}_{6} \mathrm{H}_{5}\right) .-{ }^{13} \mathrm{C}-\mathrm{NMR}\left(\mathrm{CDCl}_{3}\right):$ 29a: $\delta=22.14(\mathrm{q}, \mathrm{C}-10), 25.71,27.26$ (2q, C-8, C-9), 27.13 (t, C-3), 28.27 (q, C( $\left.\left(\mathrm{CH}_{3}\right)_{3}\right), 31.54(\mathrm{~d}, \mathrm{C}-5), 34.81\left(\mathrm{~s}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 35.01(\mathrm{t}$, C-4), 39.66 (s, C-7), 40.40 (t, C-6), 50.11 (d, C-2), 52.80 (d, C-2', C-3'), 76.43 (d, C-1), 124.99, 125.66, $127.88\left(3 \mathrm{~d},=C-\mathrm{H}_{\text {phenyl }}\right), 152.18\left(\mathrm{~s},=C-\mathrm{C}_{\text {phenyl }}\right), 173.17(\mathrm{~s}, \mathrm{C}=\mathrm{O}) ; 29 \mathrm{~b}: \delta=$ 21.87 (q, C-10), 22.37, 23.98, 28.85, 30.51 (4q, C-8, C-9), 27.40, 27.58 (2t, C-3), 29.01, 29.40 (2q, $\left.\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 31.41(\mathrm{~d}, \mathrm{C}-5), 34.47,34.92\left(2 \mathrm{~s}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 34.59(\mathrm{t}, \mathrm{C}-4), 40.18,40.50(2 \mathrm{~s}, \mathrm{C}-$

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7), }40.80\mathrm{ (t, C-6), 50.51, 51.01 (2d, C-2), 53.99, 54.43 (2d, C-2', C-3'), 77.17, 78.17 (2d, C-
1), 125.14, 125.20, 125.52, 125.58, 127.96, 127.99 (6d, =C-H H
C Chenyl), 173.54, 174.38 (2s, C=O). — MS (DEI), m/z (%): 540 (12), 445 (3), 422 (5), 325
(17), 231 (25), 214 (19), 127 (16), 119 (60), }118\mathrm{ (30), }85\mathrm{ (58), 71 (79), 57 (100). - HR MS
(NH3-DCI): C}\mp@subsup{\textrm{C}}{44}{}\mp@subsup{\textrm{H}}{66}{}\mp@subsup{\textrm{O}}{4}{}:\mathrm{ : calcd. 659.5039; found 659.5057{M +H+
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24. (1R,2S,5R)-5-methyl-2-(2-phenylpropan-2-yl) cyclohexyl (2-R)-4,4-dimethyl-2phenylpentanoate ( $R$-30c) [SI-2]

Ester 30c was prepared by esterification of 2-phenyl-4,4-dimethylpentanoic acid (32) with the auxiliary $\mathbf{3}$. Acid $\mathbf{3 2}$ was prepared in $94 \%$ yield by addition of tert-butyl lithium to styrene and carboxylation of the intermediate benzyl lithium compound with carbon dioxide [SI-2].

In a two-necked flask with reflux condenser annealed to $80^{\circ} \mathrm{C}$ under argon acid $\mathbf{3 2}(464 \mathrm{mg}$, $2.25 \mathrm{mmol})$ and thionyl chloride $(0.3 \mathrm{~mL})$ dissolved in absolute dichloromethane were refluxed for 3 h . After stirring for further 2 h at rt excess thionylchloride was distilled off under reduced pressure and the colourless residue was dissolved at $-10^{\circ} \mathrm{C}$ in dichloromethane ( 10 mL ). Thereafter a solution of 4-dimethylaminopyridine ( $25 \mathrm{mg}, 0.2$ mmol, triethylamine ( $0.3 \mathrm{~g}, 3.00 \mathrm{mmol}$ ) and 8-phenylmenthol ( $\mathbf{3}, 472 \mathrm{mg}, 2.04 \mathrm{mmol}$ ) in abs. dichloromethane ( 10 mL ) were added slowly and then the solution was stirred for 3 h at $-10^{\circ} \mathrm{C}$. After stirring for further 16 h at rt , a sat. sodium hydrogen carbonate solution ( 10 mL ) was slowly added dropwise and then the organic phase was separated. The aqueous phase was extracted with dichloromethane $(2 \times 10 \mathrm{~mL})$ and the combined organic phases were dried $\left(\mathrm{MgSO}_{4}\right)$. Finally the solvent was rotaevaporated and the crude product purified by flash chromatography (PE/E 15:1). From the combined fractions, which contained both diastereomers the solvent was rotaevaporated to yield 410 mg and the residue was dissolved in ethanol ( 1 mL ). After 24 h the $R$-isomer precipitated in white needles. The filtered crystals
were recrystallized twice from ethanol. The ( $S$ )-isomer could be isolated by way of middle pressure chromatography (PE/E 30:1).

Yield: $95 \mathrm{mg}(0.23 \mathrm{mmol}, 11 \%) R$ - 30c; for the configuration of $R$-30c see [SI-2]; 149 mg ( $0.35 \mathrm{mmol}, 17 \%$ ) (S)-30c;
$\mathrm{R}_{\mathrm{f}}$-value: $0.49(R-\mathbf{3 0 c}), 0.51((S)-\mathbf{3 0 c})(\mathrm{PE}: \mathrm{E}=30: 1)$.
( $R-30 \mathrm{c}$ ):
$[\alpha]^{20}{ }_{\mathrm{D}}:-41.7^{\circ}\left(\mathrm{c}=0.9, \mathrm{CHCl}_{3}\right)$

FT-IR (film): $v=3084,3009,2949,2921,2854(\mathrm{~s}), 1719(\mathrm{~s}), 1599,1492(\mathrm{~m}), 1387,1366(\mathrm{~m})$, 1206, 1152 (s)765, 730, 701(s).
${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right): \delta(\mathrm{ppm})=0.84\left(\mathrm{~d},{ }^{3} J=6.4 \mathrm{~Hz}, 3 \mathrm{H}\right), 0.86(\mathrm{~s}, 9 \mathrm{H}), 0.97,1.01(2 \mathrm{~s}$, each 3 H$)$, $0.65-0.94,1.18-1.51(2 \mathrm{~m}, 6 \mathrm{H}), 1.55\left(\mathrm{dd},{ }^{3} J=4.5 \mathrm{~Hz},{ }^{2} J=14.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 1.79-1.88(\mathrm{~m}, 1 \mathrm{H})$, 1.93-2.03 (m, 1H), $2.22\left(\mathrm{dd},{ }^{3} J=8.1 \mathrm{~Hz},{ }^{2} J=14.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 3.41\left(\mathrm{dd},{ }^{3} J=4.5 \mathrm{~Hz},{ }^{3} J=8.1 \mathrm{~Hz}\right.$, 1H) $4.66\left(\mathrm{ddd},{ }^{3} J=4.5 \mathrm{~Hz},{ }^{3} J=8.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 4.66\left(\mathrm{ddd},{ }^{3} J=4.5 \mathrm{~Hz},{ }^{3} J=10.5 \mathrm{~Hz},{ }^{3} J=10.5\right.$ Hz,1H), 7.04-7.21 (m, 10H).
${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta(\mathrm{ppm})=21.8(\mathrm{q}), 24.3,29.3(2 \mathrm{q}), 27.3(\mathrm{t}), 29.6(\mathrm{q}), 31.1(\mathrm{~s}), 31.3()$, 34.6 (t), 40.1 ( s$), 41.4$ (t), 48.1 ( t , 48.7 (d), 50.6 (d), 75.7 (d), 125.2, 125.7, 126.9, 127.9, 128.3, 128.4 (6d), 140.6 (s), 1740 (s).

MS (GC/MS-coupling) $m / z(\%)=420(1), 301(10), 214(38), 119(100), 105(24), 91$ (19) 57 (19).
$\mathrm{C}_{24} \mathrm{H}_{40} \mathrm{O}_{2}$ (420.64) calc. C 82.81, H 9.58; found C 82.89, H 9.68.

Cleavage of the auxiliary from ( $R$-30c) [SI-2]
(2-R)-4,4_Dimethyl-2-phenylpentanol ( $R$-31c): In an annealed two neck flask under argon to a suspension of lithium aluminium hydride ( $11.3 \mathrm{mg}, 0.310 \mathrm{mmol}$ ) in THF ( 2 mL ) was added dropwise at $0^{\circ} \mathrm{C}$ to a solution of ester $R \mathbf{- 3 0 c}(82.3 \mathrm{mg}, 0.196 \mathrm{mmol})$ in 3 mL THF and the mixture was then stirred for 60 h at rt . Then a sat. ammonium chloride solution $(0.5 \mathrm{~mL})$ and a sat. sodium chloride solution $(5 \mathrm{~mL})$ were added. After separating the org. phase, the aqueous phase was extracted with diethyl ether $(4 \times 5 \mathrm{~mL})$ and then the combined org. phases were dried $\left(\mathrm{MgSO}_{4}\right)$. After rotaevaporating the solvent the crude oily product was purified by flash chromatography (PE/E 4:1) to obtain alcohol $R$-31c ( $35.1 \mathrm{mg}, 0.182 \mathrm{mmol}, 93 \%$ ) and 8phenyl menthol (3) ( $37.7 \mathrm{mg}, 0.163 \mathrm{mmol}, 83 \%$ ).
(2R)-4,4-Dimethyl-2-phenylpentanol ( $R$-31c)
$\mathrm{R}_{\mathrm{f}}$-value: 0.13 (PE: $\mathrm{E}=4: 1$ ); mp. $49-50{ }^{\circ} \mathrm{C} ;[\alpha]^{20}{ }_{\mathrm{D}}:-4.2^{\circ}\left(\mathrm{c}=1.02, \mathrm{CHCl}_{3}\right)$.

FT-IR (KBr): $v\left(\mathrm{~cm}^{-1}\right)=3246(\mathrm{br}), 3085,3027(\mathrm{~m}), 2956,2935,2868(\mathrm{~s}), 618,494(\mathrm{w}), 1384$, 1365 (m), 760, 702 (s).
${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right): \delta(\mathrm{ppm})=0.82(\mathrm{~s}, 9 \mathrm{H}), 1.52\left(\mathrm{~d},{ }^{3} J=3.6 \mathrm{~Hz},{ }^{2} J=14.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 1.66\left(\mathrm{dd},{ }^{3} J\right.$ $\left.=8.3 \mathrm{~Hz},{ }^{2} J=14.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 2.87(\mathrm{~m}, 1 \mathrm{H}), 3.58\left(\mathrm{dd},{ }^{3} J=8.3 \mathrm{~Hz},{ }^{2} J=10.7 \mathrm{~Hz}, 1 \mathrm{H}\right), 3.66\left(\mathrm{dd},{ }^{3} J\right.$ $\left.=6.0 \mathrm{~Hz},{ }^{2} J=10.7 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.18-7.35(\mathrm{~m})$.
${ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm})=28.0(\mathrm{q}), 31.1(\mathrm{~s}), 45.4(\mathrm{~d}), 45.8(\mathrm{t}), 69.0(\mathrm{t}), 126.5,128.25$, 128.6 (3d), 144.2 (s).

MS (GC/MS-coupling): $m / z(\%)=192(18), 162(26), 121(7), 105(42), 91(23), 57(100)$.
$\mathrm{C}_{13} \mathrm{H}_{20} \mathrm{O}$ (192.30) calc. C 81.19, H 10.49; found: C81.24, H 10.51 .
25. $X$-ray crystal structure analysis of 23b: formula $\mathrm{C}_{22} \mathrm{H}_{42} \mathrm{O}_{2}, M=338.56,0.50 \times 0.25 \times 0.20$ $\mathrm{mm}, a=9.634(1), b=10.240(2), c=11.754(2) \AA, \beta=102.74(1)^{\circ}, V=1131.0(3) \AA^{3}, \rho_{\text {calc }}=$
$0.994 \mathrm{~g} \cdot \mathrm{~cm}^{-3}, \mu=4.62 \mathrm{~cm}^{-1}$, empirical absorption correction via $\varphi$ scan data $(0.895 \leq C \leq$ 0.998 ), $Z=2$, monoclinic, space group $\mathrm{P} 2_{1}$ (No. 4), $\lambda=1.54178 \AA, T=223 \mathrm{~K}, \omega / 2 \theta$ scans, 2580 reflections collected $(+h,+k, \pm l),[(\sin \theta) / \lambda]=0.62 \AA^{-1}, 2436$ independent and 1738 observed reflections $[I \geq 2 \sigma(I)]$, 227 refined parameters, $R=0.050, w R^{2}=0.122$, max. residual electron density $0.17(-0.18)$ e $\AA^{-3}$, Flack parameter $0.0(4)$, hydrogens calculated and refined as riding atoms.
$X$-ray crystal structure analysis of $\mathbf{2 8 a}$ : formula $\mathrm{C}_{34} \mathrm{H}_{62} \mathrm{O}_{4}, M=534.84,0.50 \times 0.25 \times 0.15$ $\mathrm{mm}, a=11.751(1), b=11.222(1), c=27.374(4) \AA, \beta=95.93(1)^{\circ}, V=3590.5(7) \AA^{3}, \rho_{\text {calc }}=$ $0.989 \mathrm{~g} \cdot \mathrm{~cm}^{-3}, \mu=4.81 \mathrm{~cm}^{-1}$, empirical absorption correction via $\varphi$ scan data $(0.971 \leq C \leq$ 0.998 ), $Z=4$, monoclinic, space group $\mathrm{P} 2_{1}$ (No. 4), $\lambda=1.54178 \AA, T=223 \mathrm{~K}, \omega / 2 \theta$ scans, 7861 reflections collected $( \pm h,-k,-l),[(\sin \theta) / \lambda]=0.62 \AA^{-1}, 7701$ independent and 6165 observed reflections $[I \geq 2 \sigma(I)], 714$ refined parameters, $R=0.043, w R^{2}=0.115$, max. residual electron density $0.18(-0.17) \mathrm{e} \cdot \AA^{-3}$, Flack parameter $0.1(2)$, hydrogens calculated and refined as riding atoms.
$X$-ray crystal structure analysis of 29a: formula $\mathrm{C}_{44} \mathrm{H}_{66} \mathrm{O}_{4}, M=658.97,0.40 \times 0.30 \times 0.20$ $\mathrm{mm}, a=10.860(1), b=16.786(1), c=22.380(2) \AA, V=4079.8(6) \AA^{3}, \rho_{\text {calc }}=1.073 \mathrm{~g} \cdot \mathrm{~cm}^{-3}, \mu$ $=5.11 \mathrm{~cm}^{-1}$, empirical absorption correction via $\varphi$ scan data $(0.976 \leq C \leq 0.999), Z=4$, orthorhombic, space group $\mathrm{P} 2_{1} 2_{1} 2_{1}($ No. 19$), \lambda=1.54178 \AA, T=223 \mathrm{~K}, \omega / 2 \theta$ scans, 4626 reflections collected $(-h,-k,-l),[(\sin \theta) / \lambda]=0.62 \AA^{-1}, 4626$ independent and 4206 observed reflections $[I \geq 2 \sigma(I)], 446$ refined parameters, $R=0.037, w R^{2}=0.104$, max. residual electron density $0.15(-0.12) \mathrm{e} \cdot \AA^{-3}$, Flack parameter $0.1(2)$, hydrogens calculated and refined as riding atoms.

## References

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