Synthetic Procedures

All solvents were dried before use. All chemicals were purchased from Acros, Fluka, Janssen, Lancaster, Merck, Roth or Sigma-Aldrich. The products were purified by flash chromatography on silica gel (silica gel 60, Merck) with the stated solvent mixture as mobile phase unless otherwise noted. Thin layer chromatography was performed on Merck silica gel 60 F-254 TLC plates with the stated solvent mixtures as mobile phase. 1H and 13C NMR were obtained with a Bruker DRX-500 NMR spectrometer at room temperature with the stated solvents as internal standards. Chemical shifts are given in parts per million (δ) coupling constants are given in Hertz (Hz). High-resolution mass spectra were obtained with a 7 T APEX II mass spectrometer or a Finnegan MAT MS 70. Melting points were determined in open capillaries using a Büchi Melting Point B-540 apparatus and are uncorrected.

General Procedures:

a) Benzylation

1.5eq NaH (60% suspension in mineral oil) were added at 0°C in small portions to a solution of the desired alcohol, tetrabutyl-ammoniumiodide (0.01eq.) and benzyl bromide (1.5eq) in DMF. After stirring for additional 4 h excess sodium hydride was quenched by addition of brine and the reaction mixture was extracted three times with ethyl ether. The combined organic layers were washed twice with brine and dried over sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified on silica (hexane/ethyl acetate 2:1) to yield the desired benzyl ether.

b) Selective glycol deprotection

A solution of the desired ketal and toluene sulfonic acid (0.05eq) in ethylene glycole/DMF 1:1 was stirred for 2h at 65°C. After cooling to room temperature water was added and the reaction mixture was extracted three times with ether. The combined organic layers were washed with brine and dried over sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified on silica (hexane/ethyl acetate 1:10).

c) Saponification

3eq 1N NaOH were added to a solution of the desired ester in methanol. Saturated $NaHCO_3$–solution was added after stirring for 24h at room temperature. The aqueous layer was extracted three times with DCM. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure to yield the desired alcohol.

d) Chloroacetyl carbamate

2eq chloroacetyl isocyanate were added at 0°C to a solution of the desired alcohol in DCM. The reaction mixture was stirred for 1h and the solvent was removed under reduced pressure. The remaining oil was directly applied on silica and eluted with hexane/ethyl acetate 1:1 to yield the desired carbamate.

e) Diazomethane methylation

A solution of diazomethane (2.6eq, prepared from Diazald) in DCM was carefully added in three portions over 2 minutes at -78°C to a solution of the desired alcohol in DCM (Caution! use glassware that is specifically designed for the use of diazomethane). After addition of the individual portions of diazo methane, BF_3Et_2O (8.5µl/mmol alcohol, 10% in DCM) were added. After complete decolouration of the solvent mixture it was warmed to room temperature and water was added. The organic layer was separated and the aqueous layer was extracted two more times with DCM. The combined organic layers were dried over sodium sulfate. After removal of the solvent under reduced pressure the desired ether was obtained without any further purification.

f) Spiroketal deprotection I

A solution of cerium ammonium nitrate (0.15eq) in borate buffer (pH8) was added to a solution of the desired spiroketal in acetonitrile and stirred for 10h at 65°C. After cooling to room temperature water was added and the aqueous layer was extracted three times with DCM. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude ketone was further purified on silica (hexane/ethyl acetate 1:2!, crucial for high yields is to minimize the contact time with silica, the purification process should not last longer than 5min!) to yield the desired product.

g) Selective benzoylation

Bu_2SnO (1.14eq) was added to a solution of the desired diol in methanol. The reaction mixture was refluxed for 5h in a round bottom flask that had been equipped with a Soxlett-extractor (filled with molecular sieves 4Å). After cooling to room temperature the solvent was removed under reduced pressure and the remaining syrup was dissolved in dry THF and cooled to -30°C. After addition of benzoyl chloride (1.5eq) the reaction mixture was stirred for 2h at –30°C - –20°C and then warmed to room temperature. Subsequently, $NaHCO_3$–solution was added and the aqueous layer was extracted three times with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered through celite and the solvent was removed under reduced pressure. After purification on silica (hexane/ethyl acetate 2:1) the desired ester was yielded as a white solid.

h) Nysted reaction

To a solution of the desired ketone in THF Nysted's reagent (3 mL/mmol ketone of a 20% suspension in THF, Sigma-Aldrich) were added at –78°C. After 5 minutes titanium tetrachloride solution (1.2mL/mmol ketone, 10% in cyclohexane) were added dropwise. Now the reaction mixture was first stirred for additional 10 min at -78°C and then 3h at room temperature. Water was added and the reaction mixture was extracted three times with DCM. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product is purified on silica (hexane/ethyl acetate 5:1) to yield the desired alkene.

i) Spiroketal deprotection II

A solution of 0.2eq cerium ammonium nitrate in 5% $KHSO_4$ (17mL/mmol spiroketal) was added to a solution of the desired spiroketal in acetonitrile and refluxed for 16h. After cooling to room temperature water was added and the aqueous layer was extracted three times with DCM. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude ketone was further purified on silica (hexane/ methyl *tert.*-butyl ether 1:3!, crucial for high yields is to minimize the contact time with silica, the purification process should not last longer than 5min!) to yield the desired product.

j) Epoxidation

To a solution of 220mg (1mmol) trimethylsulfoxonium iodide in 10mL DMSO/THF 1:1 were added 38mg NaH (0.95mmol, 60% suspension in mineral oil) and the mixture was stirred over night.
Above solution (19mL/mmol ketone) was added to a solution of the desired ketone in DMSO and stirred at room temperature. After 5 min water was added and the aqueous layer was extracted three times with ether. The combined organic layers were dried over sodium sulfate. After removal of the solvent under reduced pressure the desired product was obtained without further purification.

2-Methoxybenzoic acid ethyl ester 4

178ml oxalyl chloride (266.5g; 2.10mol = 1.05eq) were added over 1h to a solution of 304.3 g (2mol) 2-methoxybenzoic acid in 1500 mL DCM at 0°C. The solution was stirred for additional 2h at 0°C and 16h at

room temperature. The solvent was removed under reduced pressure to yield a yellow oil which was redissolved in 1500 mL DCM and cooled in an ice bath to 0°C. After sequential addition of 600mL (10mol) ethanol and 195mL pyridine (2.5mol) the reaction mixture was stirred additional 2h at 0°C and 16h at room temperature. The clear solution was washed twice with 500mL sulfuric acid (5% in water), followed by 500mL water and 500mL saturated $NaHCO_3$-solution. The organic layer was dried over sodium sulfate. The desired product was obtained after removal of the solvent under reduced pressure as colourless yellow oil in excellent purity.
Yield: 358.95g, 1.99mol, 99.6%, colourless oil
R_F-Value: 0.25 (hexane/ethyl acetate 10:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.77 (dd, J = 1.8, 7.8, 1H, Ar), 7.43 (ddd, J = 1.8, 7.4, 8.5, 1H, Ar), 7.95 (m, 2H, Ar), 4.34 (q, J = 7.3, 2H, C**H**$_2$Me), 3.87 (s, 3H, OC**H**$_3$), 1.36 (t, J = 7.2, 3H, CH_2C**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.1(q); 159.0(q); 133.3(t); 131.4(t); 120.4(q); 120.0(t); 112.0(t); 60.7(s); 55.9(p); 14.2(p).
HRMS (EI, 70 eV): calc. $C_{10}H_{12}O_3$ $[M]^+$: 180.0786, found: 180.0790

All compounds described in the following section are synthesized as the racemic mixture. For clarity purpose only one of both enantiomers is shown.

(1*S)-2-Methoxy-cyclohexa-2,5-diene carboxylic acid ethyl ester 5**

To a cooled (-78°C) solution of 71.58g (0.40mol) 2-methoxybenzoic acid ethyl ester **4** in 700mL THF and 7.5mL water (0.41mol) in a 3-neck round bottom flask that had been equipped with a mechanic stirrer and a dry ice condenser were added 700mL ammonia (liquid). After slow addition of diced sodium (23g, 1mol) under vigorous stirring, the dry ice bath is removed and the greenish/brown mixture is refluxed (-30°C!) for 2h. In order to quench unreacted sodium the reaction mixture is cooled again to -78°C and solid ammonium chloride is added in small portions until complete decolouration is achieved. The cold reaction mixture is poured into a vigorously stirred solution of saturated ammonium chloride (Caution! This can only be done in a well working fume hood set to maximum ventilation capacity to avoid inhaling of ammonia). The aqueous layer is then extracted three times with hexane. The combined organic layers were washed with water and dried over sodium sulfate. The crude product was used for the next step without further purification.
Yield: 61.2g, 0.34mol, 84%, pale yellow oil
R_F-value: 0.55 (hexane/ethyl acetate 5:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.88 (m, 1H, C**H**=CH), 5.66 (m, 1H, CH=C**H**), 4.83 (m, 1H, C**H**=COMe), 4.16 (m, 2H, C**H**$_2$Me), 3.76 (m, 1H, C**H**COOEt), 3.56 (s, 3H, OC**H**$_3$), 3.74-3.96 (m, 2H, CHC**H**$_2$CH), 1.25 (t, J = 7.2, 3H, CH_2C**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 171.7(q); 150.5(q); 127.1(t); 121.5(t); 93.1(t); 61.0(s); 54.2(p); 46.1(t); 26.2(s); 14.1(p);
HRMS (EI, 70 eV): calc. $C_{10}H_{14}O_3$ $[M]^+$: 182.0943, found: 182.0950

(6*S)-1,4-Dioxa-spiro[4.5]dec-7-ene-6-carboxylic acid ethyl ester 6**

A solution of 51.34g (282mmol) diene **5** and 2g *p*-toluene sulfonic acid in 250mL ethylene glycol and 70mL DMF was heated to 80°C for 1h. After cooling to room temperature, the reaction mixture was poured into water and extracted three times with ether. The combined organic layers were washed twice with brine and dried over sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified on silica (hexane/ ethyl acetate 5:1) to yield 43.1g of the desired ketal as pale yellow oil.
Yield: 43.1g, 203mmol, 70%, pale yellow oil
R_F-value: 0.4 (hexane/ethyl acetate 5:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.91 (m, 1H, C8**H**=CH), 5.60 (m, 1H, CH=C7**H**), 4.16 (dq, J = 2.3, 7.1, 2H, C**H**$_2$Me), 3.94-4.06 (m, 4H, OC**H**$_2$C**H**$_2$O), 3.27 (m, 1H, C**H**COOEt), 2.20-2.32 and 1.67 (m, 4H, CC**H**$_2$C**H**$_2$C), 1.26 (t, J = 7.1, 3H, CH_2C**H**$_3$).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 170.9(q); 129.5(t); 122.4(t); 107.6(q); 64.9(s); 64.4(s); 60.8(s); 50.7(t); 28.9(s); 24.2(s); 14.1(p);
HRMS (EI, 70 eV): calc. $C_{11}H_{16}O_4$ $[M]^+$: 212.1049, found: 212.1054

(6*S,7*S**,8*R**)-7,8-Dihydroxy-1,4-dioxaspiro[4.5]-decane-6-carboxylic acid ethyl ester 39**

A solution of 39g (288mmol) *N*-methylmorpholine-*N*-oxide monohydrate and 1010mg K_2OsO_4 dihydrate (2.7mmol) in 500mL water was added to a solution of 58.30g (275mmol) alkene **6** in 500mL acetone. After stirring over night at room temperature 32g $NaHS_2O_5$ (168mmol) and 32g Florisil were added and stirred for 30min. The reaction mixture was filtered to remove the Florisil and concentrated under reduced pressure to yield a yellowish grey syrup which was extracted 5 times with ethyl acetate. The combined organic layers were dried over sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified on silica (hexane/ethyl acetate 1:10) to yield the desired diol as a colourless oil.
Yield: 66.1g, 269 mmol, 98%, colourless oil
R_F-value: 0.3 (hexane/ethyl acetate 1:10)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.18 (dq, J = 0.5, 7.1, 2H, C**H**$_2$Me), 4.13 (m, 1H, C7-**H**), 4.02 (1H, m, C8-**H**), 3.80-3.96 (m, 4H, OC**H**$_2$C**H**$_2$O), 3.35 (br, 1H, OH), 3.19 (d, J = 10.1, 1H, C**H**COOEt), 2.90 (br, 1H, O**H**), 1.57, 1.70 and 1.83 (m, 4H, CC**H**$_2$C**H**$_2$C), 1.28 (t, J = 7.1, 3H, CH_2C**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 171.3(q); 109.2(q);71.3(t); 67.8(t); 64.9(s); 64.5(s); 60.9(s); 52.8(t); 29.2(s); 26.2(s); 14.1(p);
HRMS (EI, 70 eV): calc. $C_{11}H_{18}O_6$ $[M]^+$: 246.1103, found: 246.1104

(6*S,7*S**,8*R**)-7,8-*O*-(1-Methylethylidene)-1,4-dioxaspiro[4.5]-decane-6-carboxylic acid ethyl ester 7**

2g p-toluenesulfonic acid were added to a solution of 70.9g (288mmol) ethyl ester **39** and 300mL (2.4mol) 2,2-dimethoxypropane in 300mL DMF and stirred for 1h at 65°C. After cooling to room temperature 1L water was added and the reaction mixture was extracted three times with ethyl ether. The combined organic layers were washed twice with brine and dried with sodium sulfate. After removal of the solvent under reduced pressure, the product was obtained sufficiently pure for the next reaction.
Yield: 69.9g, 244mmol, 85%, pale yellow oil
R_F-value: 0.55 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500MHz, $CDCl_3$): δ(ppm): 4.57 (dd, J = 4.8, 9.4, 1H, C7-**H**), 4.26 (m, 1H, C8-**H**), 4.21 (q, J = 7.2, 2H, C**H**$_2$Me); 3.85 (m, 4H, OC**H**$_2$C**H**$_2$O); 2.89 (d, J=9.4 Hz, 1H, C**H**COOEt); 2.11 (ddt, J = 2.6, 2.9, 15.4, 1H, C9-**H**$_{eq}$), 2.0 (m, 1H, C9-**H**$_{ax}$), 1.80 (dt, J = 4.9, 13.2, 1H, C10-**H**$_{ax}$), 1.57 (ddd, J = 3.1, 4.9, 13.2, 1H, C10-**H**$_{eq}$), 1.50(s, 3H, C**H$_3$**); 1.35(s, 3H, C**H$_3$**); 1.30(t, J = 7.2, 3H, C**H$_3$**).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 170.8(q); 109.1(q); 108.6(q); 76.6(t); 72.1(t); 65.2(S); 64.6(S); 60.8(S); 53.9(t); 30.1(S); 28.3(p); 26.2(p); 23.2(S); 14.28(p).
HRMS (EI, 70 eV): calc. $C_{14}H_{22}O_6$ $[M]^+$: 286.1416, found: 286.1411

(6*S,7*S**,8*R**)-6-Hydroxymethyl-7,8-*O*-(1-methylethylidene)-1,4-dioxa-spiro[4.5]decane 8**

42mL (147mmol) lithium aluminium hydride (3.5M in toluene) were carefully added to a solution of 42.0g (147mmol) ester **7** in 700mL THF at 0°C. The reaction mixture was stirred for additional 30 min at 0°C and 2h at room temperature. Excess lithium aluminium hydride was quenched by the addition of sat. ammonium chloride solution until gas evolution had ceased. Subsequently saturated ammonium chloride solution was slowly added with vigorous stirring until the suspension suddenly forms a solid gel that collapses after addition of little more ammonium chloride solution to form a compact white solid. The THF layer was decanted and the solid precipitate was washed twice with ethyl acetate. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure to yield the desired alcohol as a pale yellow to colourless oil, which crystallizes after several days.
Yield: 34.1g, 140mmol, 95%, white solid
R_F-value: 0.5 (hexane/ethyl acetate 1:10); 0.15 (hexane/ethyl acetate 2:1)
T_M: 35°C

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.20 (m, 1H, C8-**H**). 4.02 (dd, J = 4.9; 9.7, 1H, C7-**H**); 3.95 (m, 4H, OCH_2CH_2O); 3.81 (m, 2H, CH_2OH); 2.85 (br, 1H, O**H**); 2.07 (m, 2H, C**H**CH_2OBn, C**H**aHbC$(OCH_2)_2$); 1.88 (m, 1H, C**H**aHbCHOR); 1.72 (dt, J = 4.7; 13.3, 1H, CHa**H**bCHOR); 1.59 (s, 3H, CH_3); 1.58 (ddd, J = 2.9; 5.0; 13.4, 1H, CHa**H**bC$(OCH_2)_2$); 1.34 (s, 3H, CH_3);
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 110.9(q); 108.5(q); 76.3(t); 72.3(t); 64.8(s); 64.0(s); 60.4(s); 48.0(t); 28.5(s); 28.4(p); 26.3(p); 23.1(s).
HRMS (EI, 70 eV): calc. $C_{12}H_{20}O_5$ $[M]^+$: 244.1311, found: 244.1302

(6*S,7*S**,8*R**)-7,8-O-(1-Methylethylidene-1,4-dioxa-spiro[4.5]decane 6-carbaldehyde 9**

6.1g (21.9mmol) IBX were added to a solution of 3.79g (15.5mmol) alcohol **8** in 50mL acetone. The suspension was refluxed for 2h and cooled to 0°C. The precipitate was filtered off and rinsed with ice-cold acetone. After removal of the solvent under reduced pressure the aldehyde was yielded as pale yellow oil that crystallizes over time.
Yield: 3.72g, 15.4mmol, 99%, pale yellow solid
R_F-value: 0.70 (hexane/ethyl acetate 1:2)
T_M: 103°C
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.87 (d, J = 1.8, 1H, C**H**O) 4.58 (dd, J = 4.8, 8.7, 1H, C7-**H**); 4.28 (m, 1H, C8-**H**); 3.87-4.01 (m, 4H, OCH_2CH_2O); 2.84 (dd, J = 1.6, 8.7, 1H, C**H**CHO); 2.11 (m, 1H, C9-H_{eq}); 1.92 (ddt, J = 4.1, 13.4, 15, 1H, C9-H_{ax}); 1.81 (dt, J = 4.4, 13.3, 1H, C10-H_{ax}); 1.58 (ddd, J = 3.2, 4.37, 13.3, 1H, C10-H_{eq}); 1.46 (s, 3H, CCH_3Me); 1.34 (s, 3H, $CMeCH_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 200.9 (t); 109.8(q); 108.8(q); 73.1(t); 71.9(t); 65.1(s); 64.5(s); 59.5(t); 28.3(p); 28.8(s); 26.1(p); 23.0(s).
HRMS (EI, 70 eV): calc. $C_{12}H_{18}O_5$ $[M]^+$: 242.1154, found: 242.1159

(6*S,7*S**,8*R**)-6-((*S**)-1-Hydroxyethyl)-7,8-*O*-(1-Methylethylidene)-1,4-dioxa-spiro[4.5]decane 10**

20mL (60 mmol) methyl magnesium bromide (3M in Et_2O) were added dropwise to a solution of 12.11g (50mmol) of aldehyde **9** in 300mL THF at -78°C. The reaction mixture was stirred 30min at -78°C and slowly warmed to room temperature. After 3h 100mL water were added and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. After purification on silica gel, the desired alcohol is obtained as white solid.
Yield: 12.22g, 47.3 mmol, 96%, white solid
R_F-value: 0.55 (hexane/ethyl acetate 2:1)
T_M: 45°C
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.52 (dd, J = 5.2, 8.9, 1H, C7-**H**), 4.32 (tq, J = 1.6, 6.7, 1H, C**H**Me), 4.22 (m, 1H, C8-**H**), 3.82-4.05 (m, 4H, OCH_2CH_2O), 3.09 (s, 1H, O**H**), 2.01 (ddd, 3.2, 6.8, 14.7, 1H, C10-**H**a), 1.85 (dd, J = 1.2, 8.8, 1H, C**H**CHOH), 1.73-1.85 (m, 1H, C9-**H**), 1.66 (dt, J = 4.3, 13.5, 1H, C9-**H**), 1.56 (ddd, J = 3.2, 4.4, 13.5, 1H, C10-**H**b), 1.44 (s, 3H, $CMeCH_3$), 1.31 (s, 3H, CCH_3Me), 1.24 (d, J = 6.8, 3H, $CHCH_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 111.6(q); 108.1(q); 73.6(t); 72.6(t); 64.8(t); 64.2(s); 64.0(s); 50.4(t); 28.3(p); 27.7(s); 26.4(p); 23.1(s); 21.6(p).
HRMS (EI, 70 eV): calc. $C_{13}H_{22}O_5$ $[M]^+$: 258.1467, found: 258.1476

(6*S,7*S**,8*R**)-6-Benzyloxymethyl-7,8-*O*-(1-methylethylidene)-1,4-dioxa-spiro[4.5]decane 11a**

See general procedure a)
Starting material: alcohol **8** (19.6g, 80mmol)
Yield: 26.31g, 79mmol, 98%, colourless oil
R_F-value: 0.55 (hexane/ethyl acetate 2:1)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.23-7.36 (m, 5H, Ar), 4.55 (d, J = 12.3, 1H, C**H**aHbPh); 4.51 (d, J = 12.3, 1H, CHa**H**bPh); 4.22 (m, 1H, C8-**H**); 4.10 (dd, J = 4.8, 9.2, 1H, C7-**H**); 3.85 (m, 4H, OC**H**$_2$C**H**$_2$O); 3.67 (dd, J = 5.5, 9.9, 1H, C**H**aHbOBn); 3.63 (dd, J = 3.5, 9.9, 1H, CHa**H**bOBn); 2.09 (m, 2H, C**H**CH$_2$OBn, C**H**aHbC(OCH$_2$)$_2$); 1.92 (m, 1H, C**H**aHbCHOR); 1.77 (dt, J = 4.6, 13.1, 1H, CHa**H**bCHOR); 1.58 (ddd, J = 3.9, 4.6, 13.4, 1H, CHa**H**bC(OCH$_2$)$_2$); 1.51 (s, 3H, C**H**$_3$); 1.36 (s, 3H, C**H**$_3$);
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 138.7(q); 128.2(t); 127.7(t); 127.3(t); 109.6(q); 108.1(q); 76.4(t); 73.1(s); 72.6(t); 66.7(s); 65.0(s); 64.4(s); 47.2(t); 29.7(s); 28.5(p); 26.4(p); 23.5(s).
HRMS (EI, 70 eV): calc. $C_{19}H_{26}O_5$ $[M]^+$: 334.1780, found: 334.1776

(6*S,7*S**,8*R**)-6-Benzyloxymethyl-7, 8-dihydroxy-1.4-dioxa-spiro[4, 5]decane 12a**

See general procedure b)
Starting material: ketal **11a** (24.0g, 71.7mmol)
Yield: 20.27g, 68.9mmol, 100%, (based on converted starting material), colourless oil. 890mg, 2.67 mmol starting material reisolated.
R_F-value: 0.65 (hexane/ethyl acetate 1:10)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.30-7.36 (m, 5H, Ar), 4.55 (d, J = 11.7, 1H, C**H**aHbPh), 4.51 (d, J = 11.7, 1H, CHa**H**bPh), 4.48 (br, 1H, OH), 3.78-3.98 (m, 8H, OC**H**$_2$C**H**$_2$O, O**H**, C**H**aHbOBn, CH$_2$C**H**OH, C7-**H**), 3.71 (dd, J = 9.0, 9.9, 1H, CHa**H**bOBn), 2.72 (br, 1H, O**H**), 2.46 (ddd, 1H, J = 3.2, 9.5, 10.0, C**H**CH$_2$OBn), 1.87 (m, 1H, C**H**aHbCHOH), 1.81 (dd, J = 4.2, 13.1, 1H, C**H**aHbC(OCH$_2$)$_2$), 1.62 (m, 1H, CHa**H**bCHOH), 1.52 (m, 1H, CHa**H**bC(OCH$_2$)$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 137.3(q); 128.5(t); 127.9(t); 127.6(t); 109.7(q); 75.7(t); 73.7(s); 70.5(s); 67.4(t); 64.6(s); 64.4(s); 44.4(t); 28.0(s); 25.6(s).
HRMS (EI, 70 eV): calc. $C_{16}H_{22}O_5$ $[M]^+$:294.1467, found: 294.1444

(6*S,7*S**,8*R**)-Benzoic acid-6-benzyloxymethyl-7-hydroxy-1,4-dioxa-spiro[4.5]dec-8-yl-ester 13a**

See general procedure g)
Starting material: ketal **12a** (4.1g, 14mmol)
Yield: 5.08g, 12.7mmol, 92%, white solid
R_F-value: 0.65(hexane/ethyl acetate 1:1)
T_M: 98°C
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.10 (m, 2H, Ar), 7.26-7.59 (m, 8H, Ar), 5.47 (m, 1H, C**H**OBz), 4.58 (d, J = 11.8, 1H, C**H**aHbPh), 4.55 (d, J = 11.8, 1H, CHa**H**bPh), 4.14 (dt, J = 2.4, 10.2, 1H, C**H**OH), 3.85-4.04 (m, 6H, C**H**aHbOBn, OC**H**$_2$C**H**$_2$O, O**H**), 3.78 (t, J = 8.9, 1H, CHa**H**bOBn), 2.63 (dt, J = 3.2, 10.1, 1H, C**H**CH$_2$OBn), 2.05 (m, 1H, C10-**H**a), 1.65-1.86 (m, 3H, C10-**H**b, C9-**H**a, C9-**H**b).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.0(q); 137.4(q); 132.8(t); 130.6(q); 129.7(t); 128.4(t); 128.3(t); 127.8(t); 127.7(t); 109.5(q); 73.7(s); 73.7(t); 71.2(t); 69.6(s); 64.7(s); 64.6(s); 46.1(t); 29.2(s); 24.5(s).
HRMS (EI, 70 eV): calc. $C_{23}H_{26}O_6$ $[M]^+$: 398.1729, found: 398.1722

As side product (6*S**,7*S**,8*R**)-benzoic acid-6-benzyloxymethyl-8-hydroxy-1.4-dioxa-spiro[4.5]dec-7-yl-ester is isolated.

(6*S,7*S**,8*R**)-Benzoic acid-6-benzyloxymethyl-8-hydroxy-1,4-dioxa-spiro[4.5]dec-7-yl-ester**

Yield: 220mg, 0.55mmol, 4%, colourless oil
R_F-value: 0.55 (hexane/ethyl acetate 1:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.03 (m, 2H, Ar), 7.15-7.59 (m, 8H, Ar), 5.39 (dd, J = 2.8, 11.0, 1H, C**H**OBz), 4.38 (s, 2H, CH_2Ph), 4.22 (m, 1H, C**H**OH), 3.87-4.04 (m, 4H, OC**H**$_2$C**H**$_2$O), 3.71 (dd, J = 3.8, 9.8, 1H, C**H**aHbOBn), 3.58 (dd, J = 4.9, 9.8, 1H, CHa**H**bOBn), 2.75 (dt, J = 4.3, 10.9, 1H, C**H**CH$_2$OBn), 2.15 (br, 1H, O**H**), 1.60-2.0 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 165.7(q); 138.1(q); 132.9(t); 130.1(q); 129.7(t); 128.3(t); 128.0(t); 127.6(t); 127.2(t); 109.9(q); 75.9(t); 73.2(s); 67.0(t); 67.0(s); 64.8(s); 64.7(s); 44.0(t); 28.7(s); 26.3(s);

HRMS (EI, 70 eV): calc. $C_{23}H_{26}O_6$ $[M]^+$: 398.1729, found: 398.1612

(6*S,7*S**,8*R**)-Benzoic acid-6-benzyloxymethyl-7-methoxy-1,4-dioxa-spiro[4.5]dec-8-yl ester 14a**

See general procedure e)
Starting material: alcohol **13a** (4.69g, 11.7mmol)
Yield: 4.77g, 11.6mmol, 99%, colourless oil
R_F-value: 0.6 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.08 (m, 2H, Ar), 7.56 (m, 1H, Ar), 7.26-7.46 (m, 7H, Ar), 5.76 (m, 1H, C**H**OBz), 4.58 (d, J = 12.4, 1H, C**H**aHbPh), 4.53 (d, J = 12.4, 1H, CHa**H**bPh), 3.88-4.02 (m, 4H, OC**H**$_2$C**H**$_2$O), 3.71 (dd, J = 2.1, 9.8, 1H, C**H**aHbOBn), 3.64 (dd, J = 4.9, 9.8, 1H, CHa**H**bOBn), 3.55 (dd, J = 2.9, 11.4, 1H, C**H**OMe), 3.42 (s, 3H, OC**H**$_3$), 2.46 (ddd, J = 2.1, 4.8, 11.4, 1H, C**H**CH$_2$OBn), 2.02 (dq, J = 3.6, 13.9, 1H, C10-**H**$_{eq}$), 1.65-1.93 (m, 3H, C10-**H**$_{ax}$, C9-**H**a, C9-**H**b).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 165.9(q); 138.6(q); 132.9(t); 130.4(q); 129.7(t); 128.3(t); 128.2(t); 127.8(t); 127.4(t); 109.9(q); 78.9(t); 73.3(s); 66.9(t); 65.4(s); 64.9(s); 64.8(s); 57.5(p); 46.3(t); 30.0(s); 24.8(s).
HRMS (EI, 70 eV): calc. $C_{24}H_{28}O_6$ $[M]^+$: 412.1886, found: 412.1881

(1*R,2*S**,3*S**)-Benzoic acid-3-benzyloxymethyl-2-methoxy-4-oxo-cyclohexyl ester 15a**

See general procedure f)
Starting material: spiroketal **14a** (2.14g, 5.2mmol)
Yield: 1.85g, 5mmol, 96%, colourless oil
R_F-value: 0.6 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.04 (m, 2H, Ar), 7.58 (m, 1H, Ar), 7.45 (m, 2H, Ar), 7.25-7.35 (m, 5H, Ar), 5.78 (m, 1H, C**H**OBz), 4.62 (d, J = 11.9, 1H, C**H**aHbPh), 4.57 (d, J = 11.9, 1H, CHa**H**bPh), 4.03 (dd, J = 2.1, 8.9, 1H, C**H**aHbOBn), 3.75 (dd, J = 2.7, 10.6, 1H, C**H**OMe), 3.70 (dd, J = 4.1, 8.9, 1H CHa**H**bOBn), 3.40 (s, 3H, OC**H**$_3$), 2.88 (ddd, J = 2.1, 4.1, 10.5, 1H, C**H**CH$_2$OBn), 2.64 (ddd, J = 6.7, 13.0, 15.8, 1H, C6-**H**$_{ax}$), 2.44 (ddd, J = 3.1, 5.5, 15.8, 1H, C6-**H**$_{eq}$), 2.32 (m, 1H, C5-**H**$_{eq}$), 1.90 (m, 1H, C5-**H**$_{ax}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 207.0;(q) 165.7;(q) 138.3;(q) 133.2;(t) 130.0;(q) 129.6;(t) 128.4;(t) 128.2;(t) 127.6;(t) 127.5;(t) 78.8;(t) 73.4;(s) 66.8;(t) 64.2;(s) 57.6;(p) 53.2;(t) 35.7;(s) 24.5;(s).
HRMS (EI, 70 eV): calc. $C_{22}H_{24}O_5$ $[M]^+$: 368.1624, found: 368.1620

(1*R,2*S**,3*S**)-Benzoic acid-3-benzyloxymethyl-2-methoxy-4-methylene-cyclohexyl-ester 16a**

See general procedure h)
Starting material: ketone **15a** (206mg, 0.5mmol)
Yield: 120mg, 0.33mmol, 65%, colourless oil
R_F-value: 0.7 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.08 (m, 2H, Ar), 7.56 (m, 1H, Ar), 7.44 (m, 2H, Ar), 7.27-7.38 (m, 5H, Ar), 5.65 (m, 1H, C**H**OBz), 4.98 (s, 2H, C=C**H**$_2$), 4.59 (d, J = 12.1, 1H, C**H**aHbPh), 4.54 (d, J = 12.1, 1H, CHa**H**bPh), 4.03 (dd, J = 3.8, 9.4, 1H, C**H**aHbOBn), 3.70 (dd, J = 6.1, 9.4, 1H CHa**H**bOBn), 3.46 (dd, J = 2.7, 8.8, 1H, C**H**OMe), 3.41 (s, 3H, OC**H**$_3$), 2.86 (m, 1H, C**H**CH$_2$OBn), 2.44 (m, 1H, C6-H$_{ax}$), 2.25 (dt, J = 5.2, 13.8, 1H, C6-H$_{eq}$), 2.10 (m, 1H, C5-H$_{eq}$), 1.70 (m, 1H, C5-H$_{ax}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 165.9(q); 145.0(q); 138.3(q); 132.9(t); 130.5(q); 129.7(t); 2x 128.3(2x t); 127.8(t); 127.6(t); 110.6(s); 79.9(t); 73.4(s); 69.0(t); 68.1(s); 57.6(p); 45.6(t); 30.3(s); 28.3(s).
HRMS (EI, 70 eV): calc. $C_{23}H_{26}O_4$ $[M]^+$: 366.1831, found: 366.1827

(3*R,4*S**,5*S**,6*R**)-Benzoic acid-4-benzyloxymethyl-5-methoxy-1-oxa-spiro[2.5]oct-6-yl ester 17a**

24mg NaH were added to 176mg (0.8mmol) trimethylsulfoxonium iodide in 2ml DMSO/THF 1:1 and stirred over night. After addition of 55mg (0.42mmol) anhydrous LiI the solution is stirred for 1h and added dropwise at -10°C to a solution of 80mg (0.21mmol) of ketone **15a**. The reaction mixture was quenched by addition of 20mL $NaHCO_3$-solution. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The epoxide is obtained after purification on silica as colourless oil.

Yield: 35mg, 0.092mmol, 22%, colourless oil

Alternative procedure:

A solution of 135mg (0.55mmol) 3-chloroperbenzoic acid in 3mL DCM was added to a solution of 170mg (0.46mmol) alkene **16a** in 5mL DCM. The reaction mixture was stirred for one hour at room temperature and 20mL $NaHCO_3$-solution were added. The aqueous layer was extracted twice with DCM. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The epoxide was yielded without any further purification.

Yield: 168mg, 0.44mmol, 96%, colourless oil
R_F-value: 0.65 (hexane/ethyl acetate 3:1)
^{1}H-NMR (500 MHz, [D_6]DMSO, assignment supported by NOESY): δ = 7.98 (m, 2H, Ar), 7.58 (m, 1H, Ar), 7.47 (m, 2H, Ar), 7.20-7.31 (m, 5H, Ar), 5.61 (m, 1H, C**H**OBz); 4.39 (d, J = 11.8, 1H, C**H**aHbPh), 4.34 (d, J = 11.8, 1H, CHa**H**bPh), 3.53 (dd, J = 3.4, 9.5, 1H, C**H**aHbOBn), 3.30 (dd, J = 2.5, 9.7, 1H, C**H**OMe), 3.26 (s, 3H, OCH_3), 3.22 (dd, J = 8.1, 9.4, 1H, CHa**H**bOBn), 2.87 (d, J = 5.0, 1H, epoxide-**H**(*S*)), 2.57 (d, J = 5.0, 1H, epoxide-**H**(*R*)), 2.39 (m, 1H, C**H**CH_2OBn), 1.95 (m, 2H, CH_{ax}**H**$_{eq}$CHOBz and C8-**H**$_{ax}$), 1.81 (m, 1H, C**H**$_{ax}$H$_{eq}$CHOBz), 1.29 (m, 1H, C8-**H**$_{eq}$).
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.09 (m, 2H, Ar), 7.56 (m, 1H, Ar), 7.44 (m, 2H, Ar), 7.27-7.39 (m, 5H, Ar), 5.75 (m, 1H, C**H**OBz); 4.50 (d, J = 11.6, 1H, C**H**aHbPh), 4.43 (d, J = 11.6, 1H, CHa**H**bPh), 3.68 (dd, J = 3.2, 9.5, 1H, C**H**OMe), 3.39 (s, 3H, OC**H**$_3$), 3.32-3.38 (m, 2H, C**H**$_2$OBn), 3.11 (d, J = 4.8, 1H, epoxide-**H**(*S*)), 2.66 (d, J = 4.8, 1H, epoxide-**H**(*R*)), 2.65 (m, 1H, C**H**CH_2OBn), 2.07-2.20 (m, 2H, CH_{ax}**H**$_{eq}$CHOBz and C8-**H**$_{ax}$), 1.94 (m, 1H, C**H**$_{ax}$H$_{eq}$CHOBz), 1.33 (m, 1H, C8-**H**$_{eq}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 165.9(q); 138.0(q); 133.0(t); 130.3(q); 129.7(t); 128.4(t); 128.3(t); 127.9(t); 127.7(t); 78.8(t); 73.3(s); 67.6(t); 65.8(s); 57.8(q); 57.5(p); 53.4(s); 42.2(t); 28.6(s); 25.6(s).
HRMS (EI, 70 eV): calc. $C_{23}H_{26}O_5$ $[M]^+$: 382.1780, found: 382.1786

(3*R,4*S**,5*S**,6*R**)-4-Benzyloxymethyl-5-methoxy-1-oxa-spiro[2.5]octan-6-ol 41**

See general procedure c)
Starting material: ester **17a** (148mg, 0.39mmol)
Yield: 109mg, 0.39mmol, 100%, colourless oil
R_F-value: 0.65 (hexane/ethyl acetate 1:2)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.27-7.38 (m, 5H, Ar), 4.47 (d, J = 11.7, 1H, C**H**aHbPh), 4.43 (d, J = 11.7, 1H, CHa**H**bPh), 4.17 (m, 1H, C**H**OH); 3.54 (dd, J = 3.5, 9.5, 1H, C**H**aHbOBn), 3.37 (s, 3H, OC**H**$_3$), 3.34 (dd, J = 8.0, 9.5, 1H, CHa**H**bOBn), 3.19 (dd, J = 2.9, 9.5, 1H, C**H**OMe), 2.96 (d, J = 4.7, 1H, epoxide-**H**(*S*)), 2.58 (d, J = 4.7, 1H, epoxide-**H**(*R*)), 2.42 (ddd, J = 3.5, 8.1, 9.5, 1H, C**H**CH_2OBn), 2.37 (m, 1H, O**H**), 2.03 (m, 1H, CH_{ax}**H**$_{eq}$CHOH), 1.95 (ddd, J = 4.9, 9.6, 13.8, 1H, C8-**H**$_{ax}$), 1.75 (m, 1H, C**H**$_{ax}$H$_{eq}$CHOH); 1.22 (dt, J = 4.6, 13.5, 1H, C8-**H**$_{eq}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 138.1(q); 128.3(t); 127.7(t); 127.6(t); 80.5(t);b73.0(s); 66.0(s); 64.7(t); 57.9(q); 57.1(p); 53.2(s); 40.8(t); 27.7(s); 27.0(s).
HRMS (EI, 70 eV): calc. $C_{16}H_{22}O_4$ $[M]^+$: 278.1518, found: 278.1521

(3*S,4*S**,5*S**,6*R**)-(2-Chloroacetyl)-carbamic acid-4-[(benzyloxy)methyl]-5-methoxy-1-oxaspiro[2.5]oct-6-yl ester 18a**

See general procedure d)

Starting material: alcohol **41** (30mg, 0.11mmol)
Yield: 41mg, 0.103mmol, 94%, colourless oil
R_F-value: 0.5 (hexane/ethyl acetate 1:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.26 (br, 1H, N**H**), 7.27-7.38 (m, 5H, Ar), 5.47 (m, 1H, C**H**OC(O)N), 4.49 (d, J = 11.6, 1H, C**H**aHbPh), 4.48 (s, 2H, C**H**$_2$Cl), 4.43 (d, J = 11.6, 1H, CHa**H**bPh), 3.60 (dd, J = 3.1, 9.6, 1H, C**H**aHbOBn), 3.38 (s, 3H, OCH_3), 3.31 (m, 2H, C**H**OMe,CHa**H**bOBn), 3.04 (d, J = 4.6, 1H, epoxide-**H**(*S*)), 2.64 (d, J = 4.6, 1H, epoxide-**H**(*R*)), 2.45 (ddd, J = 3.0, 8.5, 10.6, 1H, C**H**CH$_2$OBn), 1.85-2.07 (m, 2H, C7-**H**$_{eq}$ and C8-**H**$_{ax}$), 1.88 (m, 1H, C7-**H**$_{ax}$), 1.33 (m, 1H, C8-**H**$_{eq}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.5(q); 150.7(q); 137.9(q); 128.4(t); 128.3(t); 127.8(t); 78.6(t); 73.2(s); 70.4(t); 65.5(s); 57.6(p); 57.5(q); 53.3(s); 43.6(s); 41.8(t); 28.2(s); 25.2(s).
HRMS (EI, 70 eV): calc. $C_{19}H_{24}ClNO_6$ $[M]^+$: 397.1292, found: 397.1297

(1*R,2*S**,3*S**)-3-[(Benzyloxy)methyl]-2-methoxy-4-methylene cyclohexanol 42**

See general procedure c)
Starting material: ester **16a** (124mg, 0.34mmol)
Yield: 90mg, 0.34mmol, 100%, colourless oil
R_F-value: 0.6 (hexane/ethyl acetate 1:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.27-7.38 (m, 5H, Ar), 4.88 (s, 1H, C=C**H**aHb), 4.86 (s, 1H, C=CHa**H**b), 4.55 (d, J = 12.1, 1H, C**H**aHbPh), 4.51(d, J = 12.1, 1H, CHa**H**bPh), 4.05 (dt, J = 3.3, 6.5, 1H, C**H**OH), 3.69 (dd, J = 4.3, 9.4, 1H, C**H**aHbOBn), 3.63 (dd, J = 5.9, 9.4, 1H CHa**H**bOBn), 3.38 (s, 3H, OC**H**$_3$), 3.32 (dd, J = 3.1, 7.9, 1H, C**H**OMe), 2.72 (m, 1H, C**H**CH$_2$OBn), 2.35 (ddd, J = 4.7, 9.9, 13.5, 1H, C5-H$_{ax}$), 2.20 (br, 1H, OH), 2.08 (m, 1H, C5-H$_{eq}$), 2.10 (m, 1H, C6-H$_{eq}$), 1.70 (m, 1H, C6-H$_{ax}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 145.7(q); 138.3(q); 128.3(t); 127.7(t); 127.5(t); 110.1(s); 81.5(t); 73.2(s); 68.4(s); 65.9(t); 57.0(p); 44.1(t); 30.4(s); 29.7(s).
HRMS (EI, 70 eV): calc. $C_{16}H_{22}O_3$ $[M]^+$: 262.1569, found: 262.1576

(1*R,2*S**,3*S**)-(2-Chloroacetyl)-carbamic acid-3-[(benzyloxy)methyl]-2-methoxy-4-methylene-cyclohexylester 19a**

See general procedure d)
Starting material: alcohol **42** (0.15mmol, 38mg)
Yield: 48mg, 0.125mmol, 86%, colourless oil
R_F-value: 0.55 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.15 (br, 1H, N**H**), 7.26-7.38 (m, 5H, Ar), 5.44 (dt, J = 3.0, 6.3, 1H, C**H**OC=O), 4.92 (s, 2H, C=C**H**$_2$), 4.55 (d, J = 12.0, 1H, C**H**aHbPh), 4.53 (d, J = 12.0, 1H, CHa**H**bPh), 4.46 (s, 2H, C**H**$_2$Cl), 3.72 (dd, J = 3.9, 9.4, 1H, C**H**aHbOBn), 3.36 (dd, J = 5.6, 9.4, 1H CHa**H**bOBn), 3.41 (dd, J = 2.8, 8.7, 1H, C**H**OMe), 3.36 (s, 3H, OC**H**$_3$), 2.67 (m, 1H, C**H**CH$_2$OBn), 2.28 (ddd, J = 4.5, 10.4, 13.9, 1H, C5-**H**$_{ax}$), 2.19 (dt, J = 5.4, 13.9, 1H, C5-**H**$_{eq}$), 2.01 (m, 1H, C6-**H**$_{eq}$), 1.63 (m, 1H, C6-**H**$_{ax}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.6(q); 150.8(q); 144.2(q); 138.2(q); 128.3(t); 127.7(t); 127.6(t); 111.0(s); 79.4(t); 73.4(s); 71.9(t); 67.9(s); 57.6(p); 45.0(t); 43.6(s); 30.0(s); 28.0(s).
HRMS (EI, 70 eV): calc. $C_{19}H_{24}ClNO_5$ $[M]^+$: 381.1343, found: 381.1329

(6*S,7*S**,8*R**)-6-Benzyloxymethyl-8-hydroxy-7-methoxy-1,4-dioxa-spiro[4.5]decan 20**

870mg (3.5mmol) Bu_2SnO were added to a solution of 940mg (3.2mmol) diol **12a** in 20mL methanol. The reaction mixture was refluxed for 5h in a round bottom flask that had been equipped with a Soxlett-extractor (filled with molecular sieves 4Å). The solvent was removed under reduced pressure and the remaining syrup was dissolved in dry DMF. 2mL (4.5g, 32mmol, 10 eq) methyl iodide were added and the reaction mixture was stirred for 16h at room temperature. Subsequently, 200mL $NaHCO_3$–solution were added and the aqueous layer was extracted three times with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered through celite and the solvent was removed under reduced pressure.

After purification on silica (hexane/methyl-*tert*.-butyl ether 5:1) the desired ester was yielded as a white solid.
Yield: 520mg, 1.7mmol, 53%, white crystals
R_F-value: 0.45 (hexane/methyl-*tert*.-butylether 1:5)
T_M: 93°C
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23-7.37 (m, 5H, Ar), 4.53 (d, J = 12.4, 1H, C**H**aHbPh), 4.47 (d, J = 12.4, 1H, CHa**H**bPh), 4.13 (m, 1H, C**H**OH), 3.80-3.98 (m, 4H, OC$\mathbf{H}_2$C$\mathbf{H}_2$O), 3.59 (m, 2H, C**H**aHbOBn, C**H**OMe), 3.38 (s, 3H, OC$\mathbf{H}_3$), 3.37 (m, 1H, CHa**H**bOBn), 2.37 (br, 1H, O**H**), 2.75 (dt, J = 3.5, 11.0, 1H, C**H**CH_2OBn), 1.45-1.94 (m, 4H, CC$\mathbf{H}_2$C$\mathbf{H}_2$C).
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 138.6(q); 128.1(t); 127.8(t); 127.3(t); 110.0(q); 80.9(t);73.1(s); 65.8(s); 2x 64.6(s); 63.9(t); 57.2(p); 44.8(t); 28.7(s); 25.6(s).
HRMS (EI, 70 eV): calc. $C_{17}H_{24}O_5$ $[M]^+$: 308.1624, found: 308.1617

(6*S,7*S**,8*R**)-(2-Chloroacetyl)-carbamic acid-6-[(benzyloxy)methyl]-7-methoxy-1.4-dioxaspiro[4.5]dec-8-yl ester 43**

See general procedure d)
Starting material: alcohol **20** (46mg, 0.15mmol)
Yield: 60mg, 0.14mmol, 94%, colourless oil
R_F-value: 0.5 (hexane/ethyl acetate 1:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.29 (br, 1H, N**H**), 7.23-7.35 (m, 5H, Ar), 5.40 (m, 1H, C**H**OC=O), 4.50 (s, 2H, C$\mathbf{H}_2$Ph), 4.43 (s, 2H, C$\mathbf{H}_2$Cl), 3.82-3.95 (m, 4H, OC$\mathbf{H}_2$C$\mathbf{H}_2$O), 3.61 (dd, J = 2.5, 9.8, 1H, C**H**aHbOBn), 3.58 (dd, J =4.4, 9.8, 1H, CHa**H**bOBn), 3.45 (dd, J = 2.9, 11.4, 1H, C**H**OMe), 3.37 (s, 3H, OC$\mathbf{H}_3$), 2.21 (ddd, J= 2.5, 4.3, 11.4, 1H, C**H**CH_2OBn), 1.58-1.98 (m, 4H, CC$\mathbf{H}_2$C$\mathbf{H}_2$C).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 167.3(q); 150.8(q); 138.4(q); 128.2(t); 127.8(t); 127.4(t); 109.5(q); 78.9(t); 73.2(s); 69.7(t); 65.3(s); 64.8(s); 57.7(p); 46.0(t); 43.6(s); 29.6(s); 24.4(s); 21.0(s).
HRMS (EI, 70 eV): calc. $C_{20}H_{26}ClNO_7$ $[M]^+$: 427.1398, found: 427.1393

(1*R,2*S**,3*S**)-(2-Chloroacetyl)-carbamic acid-3-[(benzyloxy)methyl]-2-methoxy-4-oxo cyclohexyl ester 21**

A solution of 10mg (0.018mmol) cerium ammonium nitrate in 2mL borate buffer (pH8) was added to a solution of 33mg (0.077 mmol) spiroketal **43** in 2mL acetonitrile and stirred for 2h at 65°C. After cooling to room temperature 100mL water were added and the aqueous layer was extracted three times with DCM. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude ketone was further purified on silica (hexane/ethyl acetate 1:1!, crucial for high yields is to minimize the contact time with silica, the purification process should not last longer than 5min!) to yield the desired product as colourless oil.
Yield: 14mg; 0.034mmol, 44%, colourless oil
R_F-value: 0.6 (hexane/ethyl acetate 2:1)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.24 (br, 1H, N**H**), 7.25-7.36 (m, 5H, Ar), 5.62 (m, 1H, C**H**OC(O)N), 4.58 (d, J = 12.1, 1H, C**H**aHbPh), 4.48 (d, J = 12.1, 1H, CHa**H**bPh), 4.43 (s, 2H, C$\mathbf{H}_2$Cl), 3.99 (dd, J = 2.0, 9.0, 1H, C**H**aHbOBn), 3.68 (dd, J = 2.4, 10.5, 1H, CHa**H**bOBn), 3.31 (dd, J = 3.9, 9.0, 1H, C**H**OMe), 3.38 (s, 3H, OC$\mathbf{H}_3$), 2.72 (m, 1H, C**H**CH_2OBn), 2.52 (ddd, J = 6.3, 12.9, 15.6, 1H, C$\mathbf{H}_{ax}$C=O), 2.39 (ddd, J = 3.2, 5.4, 15.6, 1H, C$\mathbf{H}_{eq}$C=O), 2.25 (m, 1H, C$\mathbf{H}_{eq}$CHOC), 1.85 (m, 1H, C$\mathbf{H}_{ax}$CHOC).
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 206.2(q); 166.1(q); 150.5(q); 138.2(q); 128.3(t); 127.6(t); 127.5(t); 78.6(t); 73.4(s); 69.5(t); 64.0(s); 57.8(p); 52.8(t); 43.4(s); 35.3(s); 24.2(s).
HRMS (EI, 70 eV): calc. $C_{18}H_{22}ClNO_6$ $[M]^+$: 383.1136, found: 383.1138

(*E*)-3, 4, 5-Trimethoxy cinnamic acid chloride 44

2.38g (10mmol) (E)-3,4,5-trimethoxy cinnamic acid were dissolved in 10mL (140mmol) thionyl chloride under nitrogen and stirred over night (pressure release!). After removal of excess thionyl chloride under reduced pressure, the acid chloride was obtained as reddish solid.
Yield: 2.56g, 10mmol, 100%, reddish solid
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 15.4, 1H, ArC**H**=CH), 6.78 (s, 2H, Ar), 6.54 (d, J = 15.4, 1H, ArCH=C**H**), 3.90 (s, 3H, OC**H**$_3$), 3.89 (s, 6H, 2x OC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 165.9(q); 153.5(q); 150.7(t); 141.6(q); 128.3(q); 121.2(t); 106.3(t); 61.0(p); 56.2(p).

(6*S,7*S**,8*R**)-(E-3,4,5-Trimethoxy cinnamic acid)-6-benzyloxymethyl-7-methoxy-1,4-dioxa-spiro[4.5]dec-8-yl ester 45**

453mg (2mmol) (*E*)-3,4,5-trimethoxy cinnamic acid **44** and 360mg (3mmol) DMAP were added to a solution of alcohol **20** (306mg, 1mmol) in 20mL DCM. The reaction mixture was stirred for 5h at room temperature, hydrolyzed with water and extracted three times with DCM. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product was further purified on silica (hexane/ethyl acetate 2:1) to yield the ester as colourless oil.
Yield: 290mg, 0.55mmol, 55%, colourless oil
R_F-value: 0.6 (hexane/ethyl acetate 1:1)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 15.9, 1H, ArC**H**=CH), 7.22-7.36 (m, 5H, Ph), 6.73 (s, 2H, Ar), 6.37 (d, J = 15.9, 1H, ArCH=C**H**), 5.56 (br, 1H, C**H**OC=O), 4.54 (d, J = 12.5, 1H, C**H**aHbPh), 4.49 (d, J = 12.5, 1H, CHa**H**bPh), 3.87-3.97 (m, 4H, OC**H**$_2$C**H**$_2$O), 3.87 (s, 6H, 2x OC**H**$_3$), 3.86 (s, 3H, OC**H**$_3$), 3.66 (dd, J = 2.4, 9.5, 1H, C**H**aHbOBn), 3.62 (dd, J = 4.6, 9.5, 1H, CHa**H**bOBn), 3.46 (dd, J = 2.9, 11.2, 1H, C**H**OMe), 3.38 (s, 3H, OC**H**$_3$), 2.39 (ddd, J = 2.4, 4.6, 11.4, 1H, C**H**CH$_2$OBn), 1.58-1.98 (m, 4H, CH$_2$C**H**$_2$).
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 166.3(q); 153.3(q); 144.5(t); 139.8(q); 138.5(q); 129.8(q); 128.1(t); 127.8(t); 127.3(t); 117.7(t); 109.8(q); 105.1(t); 78.9(t); 73.3(s); 66.5(t); 65.4(s); 64.8(s); 64.8(s); 60.8(p); 57.4(p); 56.0(p); 46.2(t); 29.7(s); 24.6(s).
HRMS (EI, 70 eV): calc. $C_{29}H_{36}O_9$ $[M]^+$: 528.2359, found: 528.2344

(1*R,2*S**,3*S**)-(E-3,4,5-Trimethoxy cinnamic acid)-3-benzyloxymethyl-2-methoxy-4-oxo-cyclohexylester 22**

See general procedure f)
Starting material: spiroketal **45** (264mg, 0.5mmol)
Yield: 205mg, 0.42mmol, 84%, colourless oil
R_F-value: 0.6 (hexane/ethyl acetate 1:1)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 15.9, 1H, ArC**H**=CH), 7.24-7.35 (m, 5H, Ph), 6.74 (s, 2H, Ar), 6.38 (d, J = 15.9, 1H, ArCH=C**H**), 5.74 (br, 1H, C**H**OC=O), 4.59 (d, J = 12.1, 1H, C**H**aHbPh), 4.50 (d, J = 12.1, 1H, CHa**H**bPh), 3.99 (dd, J = 2.1, 8.9, 1H, C**H**aHbOBn), 3.87 (s, 6H, 2x OC**H**$_3$), 3.87 (s, 3H, OC**H**$_3$), 3.66 (m, 2H, CHa**H**bOBn, C**H**OMe), 3.39 (s, 3H, OC**H**$_3$), 2.39 (ddd, J = 2.0, 3.7, 10.5, 1H, C**H**CH$_2$OBn), 2.59 (ddd, J = 6.3, 12.9, 15.4, 1H, C(O)C**H**$_{ax}$), 2.39 (ddd, J = 3.2, 5.4 15.6, 1H, C(O)C**H**$_{eq}$), 2.27 (m, 1H, C5-**H**$_{eq}$), 1.83 (m, 1H, C5-**H**$_{ax}$).
^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 207.0(q); 166.1(q); 153.3(q); 145.3(t); 140.1(q); 138.2(q); 129.6(q); 128.2(t); 127.6(t); 127.5(t); 116.9(t); 105.2(t); 78.8(t); 73.4(s); 66.3(t); 64.2(s); 60.9(p); 57.5(p); 56.1(p); 53.0(t); 35.6(s); 24.4(s).
HRMS (EI, 70 eV): calc. $C_{27}H_{32}O_8$ $[M]^+$: 484.2097, found: 484.2108

(6*S,7*S**,8*R**)-6-((*S**)-1-Benzyloxy-ethyl)-7,8-*O*-(1-methylethyliden)-1,4-dioxa-spiro[4.5]decan 11b**

See general procedure a)
Starting material: alcohol **10** (2.42g, 9.37mmol)

Yield: 3.1g, 8.9 mmol, 95%, white solid
R_F-value: 0.5 (hexane/ethyl acetate 3:1)
T_M: 53°C
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.2-7.38 (m, 5H, Ar), 4.63 (d, J = 12.0, 1H, C**H**aHbPh), 4.62 (m, 1H, C7-**H**), 4.48 (d, J = 12.0, 1H, CHa**H**bPh), 4.23 (q, J = 4.3, 1H, C8-**H**), 3.95 (dq, J = 1.1, 6.6, 1H, C**H**Me), 3.70-3.91 (m, 4H, OC**H**$_2$C**H**$_2$O), 2.02 (dq, J = 4.0, 14.7, 1H, C9-**H**$_{eq}$), 1.98 (d, J = 8.4, 1H, C**H**CHOBn), 1.85-1.93 (m, 1H, C9-**H**$_{ax}$), 1.56-1.69 (m, 2H, C10-**H**$_2$), 1.51 (s, 3H, CMeC**H**$_3$), 1.36 (s, 3H, CC**H**$_3$Me), 1.34 (d, J = 6.6, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 139.1(q); 127.9(t); 127.5(t); 127.0(t); 109.8(q); 107.7(q); 75.1(t); 72.8(t); 70.8(t); 70.7(s); 64.3(s); 64.0(s); 51.1(t); 28.7(s); 28.4(p); 26.4(p); 23.6(s); 20.7(p).
HRMS (EI, 70 eV): calc. $C_{20}H_{28}O_5$ $[M]^+$: 348.1937, found: 348.1930

(6*R,7*S**,8*R**)-6-[(1*S**)-1-(Benzyloxy)ethyl]-1,4-dioxaspiro[4.5]decane-7,8-diol 12b**

See general procedure b)
Starting material: ketal **11b** (2.99g, 8.57mmol)
Yield: 2.60g, 8.4mmol, 98%, colourless oil.
R_F-value: 0.65 (hexane/ethyl acetate 1:10)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.25-7.38 (m, 5H, Ar), 4.64 (d, J = 11.6, 1H, C**H**aHbPh), 4.52 (d, J = 11.6, 1H, CHa**H**bPh), 4.18 (br, 1H, OH), 3.79-4.05 (m, 7H, C7-**H**, C8-**H**, OC**H**$_2$C**H**$_2$O, C**H**Me), 2.62 (br, 1H, O**H**), 2.21 (dd, J = 4.8, 8.9, 1H, C**H**CHOBn), 1.58-1.85 (m, 4H, CC**H**$_2$C**H**$_2$C), 1.35 (d, J = 6.4, 3H, C**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 138.1(q); 128.3(t); 127.6(t); 127.6(t); 110.2(q); 73.9(t); 72.3(t); 71.5(s); 68.1(t); 64.4(s); 63.8(s); 51.4(t); 28.0(s); 25.8(s); 22.7(p).
HRMS (EI, 70 eV): calc. $C_{17}H_{24}O_5$ $[M]^+$: 308.1624, found: 308.1619

(6*S,7*S**,8*R**)-Benzoic acid-6-((1*S**)-1-benzyloxy-ethyl)-7-hydroxy-1,4-dioxa-spiro[4.5]dec-8-yl ester 13b**

See general procedure g)
Starting material: ketal **12b** (3.1g, 10mmol)
Yield: 3.74g; 9.1mmol, 91%, white solid
R_F-value: 0.55 (hexane/ethyl acetate 2:1)
T_M: 101°C
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.08 (m, 2H, Ar), 7.54 (m, 1H, Ar), 7.44 (m, 1H, Ar), 7.25-7.38 (m, 6H, Ar), 5.53 (m, 1H, C**H**OBz), 4.67 (d, J = 11.7, 1H, C**H**aHbPh), 4.55 (d, J = 11.7, 1H, CHa**H**bPh), 4.30 (m, 1H, C**H**OH), 3.83-4.01 (m, 5H, OC**H**$_2$C**H**$_2$O and C**H**Me), 3.79 (d, J = 4.2, 1H, O**H**), 2.35 (dd, J = 3.6, 9.6, 1H, C**H**CHMe), 2.02 (m, 1H, C**H**aHbC(OCH$_2$)$_2$), 1.65-1.85 (m, 3H, CHa**H**bC(OCH$_2$)$_2$, and C**H**a**H**bCOBz), 1.39 (d, J = 6.5, 3H, C**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.0(q); 138.2(q); 132.7(t); 130.7(q); 129.6(t); 128.3(t); 128.2(t); 127.6(t); 127.5(t); 110.0(q); 73.2(t); 71.8(t); 71.5(s); 70.6(t); 64.5(s); 64.1(s); 52.8(t); 29.0(s); 24.5(s); 22.7(p).
HRMS (EI, 70 eV): calc. $C_{24}H_{28}O_6$ $[M]^+$: 412.1886, found: 412.1897

(6*S,7*S**,8*R**)-Benzoic acid-6-((1*S**)-1-benzyloxy-ethyl)-7-methoxy-1,4-dioxa-spiro[4.5]dec-8-ylester 14b**

See general procedure e)
Starting material: alcohol **13b** (2.14g, 5.2mmol)
Yield: 2.02g, 4.89mmol, 94%, colourless oil
R_F-value: 0.6 (hexane/ethyl acetate 2:1)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.07 (m, 2H, Ar), 7.25-7.57 (m, 8H, Ar), 5.70 (m, 1H, C8-**H**), 4.64 (d, J = 11.8, 1H, C**H**aHbPh), 4.53 (d, J = 11.8, 1H, CHa**H**bPh), 3.88-4.02 (m, 5H, C**H**Me and OC**H**$_2$C**H**$_2$O), 3.86 (dd, J = 3.1, 10.7, 1H, C7-**H**), 3.38 (s, 3H, OC**H**$_3$), 2.30 (dd, J = 0.5, 10.7, 1H, C6-**H**), 1.97 (m, 1H, C10-**H**a), 1.70-1.79 (m, 3H, C10-**H**b, C9-**H**a, C9-**H**b), 1.36 (d, J = 6.6, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.0 (q); 139.7 (q); 132.7 (t); 130.7 (q); 129.6 (t); 128.2 (t); 128.0 (t); 127.4(t); 127.0(t); 110.4 (q); 79.0 (t); 71.8 (t); 71.1 (s); 68.2(t); 64.5 (s); 64.4 (s); 57.0 (p); 50.4 (t); 29.0 (s); 24.6(s); 21.3 (p).
HRMS (EI, 70 eV): calc. $C_{25}H_{30}O_6$ $[M]^+$: 426.2042, found: 426.2035

(1*R,2*S**,3*S**)-Benzoic acid-3-((1S)-1-benzyloxy-ethyl)-2-methoxy-4-oxo-cyclohexyl ester 15b**

See general procedure f)
Starting material: spiroketal **14b** (496mg, 1.20mmol)
Yield: 458mg, 1.20mmol, 100%, colourless oil
R_F-value: 0.7 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.04 (m, 2H, Ar), 7.58 (m, 1H, Ar), 7.45 (m, 2H, Ar), 7.25-7.35 (m, 5H, Ar), 5.78 (dt, J = 2.9, 7.7, 1H, C**H**OBz), 4.64 (d, J = 11.5, 1H, C**H**aHbPh), 4.44 (d, J = 11.5, 1H, CHa**H**bPh), 4.21 (dq, J = 4.8, 6.4, 1H, C**H**Me), 4.03 (dd, J = 2.5, 6.4, 1H, C**H**OMe), 3.43 (s, 3H, OC**H**$_3$), 2.70 (ddd, J = 1.2, 4.8, 6.1, 1H, C**H**CHMeOBn), 2.29-2.55 (m, 2H, C**H**aHbCO and C**H**aHbCHOBz), 2.32 (m, 1H, CHa**H**bCHOBz), 1.99 (m, 1H, CHa**H**bCO), 1.30 (d, J = 6.4, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 209.5 (q); 165.8 (q); 138.4 (q); 133.1 (t); 130.1 (q); 129.6 (t); 128.4 (t); 128.3 (t); 127.6 (t); 127.6 (t); 78.7 (t); 73.4 (t); 71.2 (s); 68.9 (t); 59.4 (t); 57.3 (p); 36.2 (s); 23.8 (s); 17.9 (p).
HRMS (EI, 70 eV): calc. $C_{23}H_{26}O_5$ $[M]^+$: 382.1780, found: 382.1760

(1*R,2*S**,3*S**)-Benzoic acid-3-[(1*S**)-1-(benzyloxy)ethyl]-2-methoxy-4-methylen-cyclohexyl ester 16b**

See general procedure h)
Starting material: ketone **15b** (358mg, 0.94mmol)
Yield: 230mg, 0.61mmol, 65%, colourless oil
R_F-value: 0.4 (hexanes/ethyl acetate 5:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.11 (m, 2H, Ar), 7.59 (m, 1H, Ar), 7.48 (m, 2H, Ar), 7.42 (m, 2H, Ar), 7.33 (m, 2H, Ar), 7.26 (m, 1H, Ar), 5.33 (ddd, J = 2.6, 4.7, 11.7, 1H, C**H**OBz), 4.96 (t, J = 1.9, 1H, C=C**H**aHb), 4.87 (t, J = 1.6, 1H, C=CHa**H**b), 4.70 (d, J = 11.3, 1H, C**H**aHbPh), 4.56 (d, J = 11.3, 1H, CHa**H**bPh), 4.07 (m, 1H, C**H**OMe), 3.74 (dq, J = 6.0, 9.9, 1H, C**H**Me), 3.51 (s, 3H, OC**H**$_3$), 2.66 (dd, J = 2.8, 10.0, 1H, C**H**CHMeOBn), 2.34 (m, 1H, C**H**$_{eq}$H$_{ax}$C=CH$_2$), 2.17 (m, 1H, C**H**aHbCHOBz), 2.05 (m, 1H, CH$_{eq}$**H**$_{ax}$C=CH$_2$), 1.94 (m, 1H, CHa**H**bCHOBz), 1.30 (d, J = 6.0, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.0(q); 143.7(q); 138.3(q); 132.8(t); 130.6(q); 129.6(t); 128.4(t); 128.3(t); 128.0(t); 127.6(t); 114.2(s); 78.3(t); 73.4(t); 72.4(t); 71.3(s); 58.6(p); 55.3(t); 30.1(s); 26.5(s); 17.9(p).
HRMS (EI, 70 eV): calc. $C_{24}H_{28}O_4$ $[M]^+$: 380.1988, found: 380.1978

(3*R,4*S**,5*S**,6*R**)-Benzoic acid-4-[(1*S**)-1-(benzyloxy)ethyl]-5-methoxy-1-oxaspiro[2.5]oct-6-ylester 17b**

A solution of 124mg (0.5mmol) 3-chloroperbenzoic acid in 4mL DCM was added to a solution of 145mg (0.38mmol) alkene **16b** in 2mL DCM. The reaction mixture was stirred for 3h at room temperature and 20mL $NaHCO_3$-solution were added. The aqueous layer was extracted twice with DCM. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The product is obtained as a diastereomeric mixture (ratio 13:1) of both epoxides, that could easily be seperated by chromatography on silica (hexane/ethyl acetate 3:1)
R_F-value (hexane/ethyl acetate 3:1) = 0.5

Yield: 9mg, 0.023mmol, 6%, colourless oil
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.07 (m, 2H, Ar), 7.57 (m, 1H, Ar), 7.46 (m, 2H, Ar), 7.37 (m, 2H, Ar), 7.32 (m, 2H, Ar), 7.25 (m, 1H, Ar), 5.43 (dt, J = 3.3, 10.2, 1H, C**H**OBz), 4.77 (d, J = 11.4 , 1H, C**H**aHbPh), 4.51 (d, J = 11.4, 1H, CHa**H**bPh), 4.01 (m, 1H, C**H**OMe), 3.94 (dq, J = 6.2, 7.6, 1H, C**H**Me), 3.43 (s, 3H, OC**H**$_3$), 2.81 (d, J = 4.8, 1H, epoxide-**H**a), 2.61 (d, J = 5.0, 1H, epoxide-**H**b), 1.82-2.20 (m, 4H, C**H**CHMeOBn, C**H**$_2$C**H**aHb), 1.37 (m, 1H, CH_2CHa**H**b), 1.34 (d, J = 6.2, 3H, CHC**H**$_3$). Supported by NOESY
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 165.7(q); 138.3(q); 132.7(t); 130.3(q); 129.6(t); 128.2(t); 128.2(t); 127.7(t); 127.4(t); 78.8(t); 73.4(t); 71.0(t); 70.8(s); 58.3(p); 57.4(q); 54.8(s); 49.5(t); 28.9(s); 24.8(s); 17.6(p).
HRMS (EI, 70 eV): calc. $C_{24}H_{28}O_5$ $[M]^+$: 396.1937, found: 396.1927

(3*S,4*S**,5*S**,6*R**)-Benzoic acid-4-[(1*S**)-1-(benzyloxy)ethyl]-5-methoxy-1-oxaspiro[2.5]oct-6-yl ester**

R_F-value (hexane/ethyl acetate 3:1) = 0.3
Yield: 115mg, 0.290mmol, 76%, colourless oil
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.01 (m, 2H, Ar), 7.58 (m, 1H, Ar), 7.46 (m, 2H, Ar), 7.24-7.37 (m, 5H, Ar), 5.22 (dt, J = 3.1, 9.2, 1H, C**H**OBz), 4.69 (d, J = 11.5, 1H, C**H**aHbPh), 4.33(d, J = 11.5, 1H, CHa**H**bPh), 3.97 (dd, J = 2.8, 5.7, 1H, C**H**OMe), 3.70 (quint, J = 6.2, 1H, C**H**MeOBn), 3.45 (s, 3H, OC**H**$_3$), 2.73 (d, J = 4.7, 1H, epoxide-**H**a), 2.55 (d, J = 4.7, 1H, epoxide-**H**b), 2.29 (m, 1H, C5-**H**a), 1.87 (t, J= 5.6, 1H, C**H**CHMeOBn), 1.60-1.83 (m, 3H, C5-**H**b, C6-**H**$_2$), 1.34 (d, J = 6.3, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.0(q); 138.4(q); 132.9(t); 130.5(q); 129.7(t); 128.3(t); 128.3(t); 127.6(t); 127.5(t); 78.6(t); 72.3(t); 70.7(t); 70.6(s); 58.1(p); 57.0(q); 50.9(s); 49.8(t); 29.5(s); 24.2(s); 18.8(p).
HRMS (EI, 70 eV): calc. $C_{24}H_{28}O_5$ $[M]^+$: 396.1937, found: 396.1946

(3*R,4*S**,5*S**,6*R**)-4-[(1*S**)-1-(Benzyloxy)ethyl]-5-methoxy-1-oxaspiro[2.5]octan-6-ol 47**

See general procedure c)
Starting material: ester **17b** (8.9mg, 0.0228mmol)
Yield: 8.5mg, 0.0214mmol, 94%, colourless oil
R_F-value: 0.5 (hexane/ethyl acetate 1:2)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.25-7.37 (m, 5H, Ar), 4.63 (d, J = 11.5, 1H, C**H**aHbPh), 4.42 (d, J = 11.5, 1H, CHa**H**bPh), 3.80-3.90 (m, 3H, C**H**OH, C**H**OMe, C**H**MeOBn), 3.37 (s, 3H, OC**H**$_3$), 2.67 (dd, J = 1.0, 5.0, 1H, epoxide-**H**a), 2.55 (d, J = 5.0, 1H, epoxide-**H**b), 2.50 (br, 1H, O**H**), 1.70-1.95 (m, 4H, C**H**$_2$C**H**aHb, C**H**CHMeOBn), 1.32 (d, J = 6.3, 3H, CHC**H**$_3$), 1.20 (m, 1H, CH_2CHa**H**b).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 138.3(q); 128.3(t); 127.7(t); 127.6(t); 80.8(t); 73.3(t); 70.6(s); 67.3(t); 57.8(q); 57.3(p); 54.6(s); 47.3(t); 28.8(s); 28.7(s); 17.7(p).
HRMS (EI, 70 eV): calc. $C_{17}H_{24}O_4$ $[M]^+$: 292.1675, found: 292.1682

(3*R,4*S**,5*S**,6*R**)-(2-Chloroacetyl)-carbamic acid-4-[(1*S**)-1-(benzyloxy)ethyl]-5-methoxy-1-oxaspiro[2.5]oct-6-yl ester 18b**

See general procedure d)
Starting material: alcohol **47** (9.1mg, 0.023mmol)
Yield: 8mg, 0.0194mmol, 86%, colourless oil
R_F-value: 0.55 (hexane/ethyl acetate 1:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.95 (br, 1H, N**H**), 7.27-7.40 (m, 5H, Ar), 5.20 (m, 1H, C**H**OC(O)N), 4.66 (d, J = 11.5, 1H, C**H**aHbPh), 4.49 (s, 2H, C**H**$_2$Cl), 4.46 (d, J = 11.5, 1H, CHa**H**bPh), 3.94 (m, 1H, C**H**OMe), 3.90 (quint, J = 6.2, 1H, C**H**MeOBn), 3.36 (s, 3H, OC**H**$_3$), 2.75 (br d, J = 5.1, 1H, epoxide-**H(*S*)**), 2.60 (d, J = 4.9, 1H, epoxide-**H(*R*)**), 1.86-2.04 (m, 2H, C**H**CHMeOBn, C7-**H$_2$**), 1.85-1.80 (m, 1H, C8-**Ha**), 1.78 (m, 1H, C7-**Hb**), 1.33 (d, J = 6.1, 3H, CHC**H**$_3$), 1.33 (m, 1H, C8-**H**$_b$).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.4(q); 150.5(q); 138.3(q); 128.3(t); 127.7(t); 127.6(t); 78.2(t);73.6(t); 73.3(t); 70.9(s); 57.8(p); 57.3(q); 55.1(s); 48.7(t); 43.5(s); 28.8(s); 24.6(s); 17.7(p).
HRMS (EI, 70 eV): calc. $C_{20}H_{26}ClNO_6$ $[M]^+$: 411.1449, found: 411.1438

(1*R,2*S**,3*S**)-3-[(1*S**)-1-(Benzyloxy)ethyl]-2-methoxy-4-methylene cyclohexanol 48**

See general procedure c)
Starting material: ester **16b** (52.8mg, 0.14mmol)
Yield: 38mg, 0.14mmol, 100%, colourless oil
R_F-value: 0.65 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.26-7.40 (m, 5H, Ar), 4.88 (m, 1H, C=C**H**aHb), 4.78 (m, 1H, C=CHa**H**b), 4.66 (d, J = 11.6 , 1H, C**H**aHbPh), 4.39 (d, J = 11.6, 1H, CHa**H**bPh), 3.88 (m, 1H, C**H**OMe), 3.69 (m, 1H, C**H**OH), 3.58 (dq, J = 6.0, 9.8, 1H, C**H**Me), 3.39 (s, 3H, OC**H**$_3$), 2.62 (dm, J = 9.5, 1H, C**H**CHMe), 2.25 (br, 1H, O**H**), 2.17 (m, 1H, C5-**H**a), 1.95 (m, 1H, C5-**H**b), 1.80 (m, 1H, C6-**H**a), 1.58 (m, 1H, C6-**H**b), 1.17 (d, J = 5.9, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 144.2(q); 138.3 (q), 128.4(t); 127.8(t); 127.7(t); 113.7(s); 80.4(t); 72.9(t), 70.8(s); 67.8(t); 56.9(p); 52.5(t); 30.9(s); 30.0(s); 17.7(p).
HRMS (EI, 70 eV): calc. $C_{17}H_{24}O_3$ $[M]^+$: 276.1725, found: 276.1737

(1*R,2*S**,3*S**)-2-Chloroacetyl)-carbamic acid-3-[(1*S**)-1-(benzyloxy)ethyl]-2-methoxy-4-methylencyclohexyl ester 19b**

See general procedure d)
Starting material: alcohol **48** (20.1mg, 0.074mmol)
Yield: 27mg, 0.068mmol, 92%, colourless oil
R_F-value: 0.4 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.00 (br, 1H, N**H**), 7.26-7.38 (m, 5H, Ar), 5.00 (ddd, J = 2.6, 4.7, 11.7, 1H, C**H**OC=O), 4.92 (m, 1H, C=C**H**aHb), 4.82 (m, 1H, C=CHa**H**b), 4.66 (d, J = 11.4, 1H, C**H**aHbPh), 4.49 (s, 2H, C**H**$_2$Cl), 4.45(d, J = 11.4, 1H, CHa**H**bPh), 3.97 (m, 1H, C**H**OMe), 3.63 (dq, J = 6.0, 9.7, 1H, C**H**MeOBn), 3.37 (s, 3H, OC**H**$_3$), 2.62 (dd, J= 2.8, 9.7, 1H, C**H**CHMeOBn), 2.28 (m, 1H, C5-**H**a), 2.09 (dt, J = 5.4, 13.9, 1H, C5-**H**b), 1.92 (m, 1H, C6-**H**a), 1.81 (m, 1H, C6-**H**b), 1.18 (d, J = 6.0, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.6(q); 150.6(q); 143.0(q); 138.2(q); 128.4(t); 127.9(t); 127.6(t); 114.7(s); 77.5(t); 74.5(t); 73.2(t); 71.1(s); 57.4(p); 53.8(t); 43.6(s); 29.8(s); 26.2(s); 17.9(p).
HRMS (EI, 70 eV): calc. $C_{20}H_{26}O_5$ $[M]^+$: 395.1500, found: 395.1516

Assignment of relative conformation of compound **10**:

(6*R,7*S**,8*R**)-6-[(1*S**)-1-(Benzyloxy)ethyl]-7,8-dimethoxy-1,4-dioxaspiro[4.5] decane 49**

20mg NaH (60% suspension in mineral oil, 0.5mm) were added at 0°C to a solution of 80mg (0.26mmol) diol **12b** in DMF, followed by 200µL methyl iodide. The reaction mixture was stirred for 2h at room temperature and hydrolyzed by addition of 50mL water. The aqueous layer was extracted twice with ether and the combined organic layers were washed twice with water and dried over sodium sulfate. The desired product is obtained after purification on silica (hexane/ethyl acetate 2:1) as white solid.
Yield: 70mg, 0.21mmol, 80% white solid.
R_F-value: 0.65 (hexane/ethyl acetate 1:10)
T_M: 63°C
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.22-7.40 (m, 5H, Ar), 4.61 (d, J = 11.8, 1H, C**H**aHbPh), 4.49 (d, J = 11.8, 1H, CHa**H**bPh), 3.80-3.98 (m, 5H, OC**H**$_2$C**H**$_2$O, C**H**Me), 4.71 (m, 1H, C8-**H**), 4.68 (dd, J = 2.8, 10.6, 1H, C7-**H**), 3.38 (s, 6H, 2 OC**H**$_3$), 2.21 (d, J = 10.5, 1H, C**H**CHMe), 1.95 (dq, J = 4.2, 14.1, 1H C9-**H**$_{eq}$), 1.62 (dd, J = 3.8, 13.2, 1H, C10-**H**a), 1.53 (dt, J = 3.8, 13.4, 1H, C10-**H**b), 1.43 (m, 1H, , C9-**H**$_{ax}$), 1.35 (d, J = 6.6, 3H, CHC**H**$_3$).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 139.8(q); 128.0(t); 127.4(t); 126.9(t); 110.7(q); 80.3(t); 74.2(t); 72.1(t); 71.0(s); 64.3(s); 64.3(s); 56.8(p); 56.5(p); 49.4(t); 28.1(s); 22.2(s); 21.3(p).
HRMS (EI, 70 eV): calc. $C_{19}H_{28}O_5$ $[M]^+$: 336.1937, found: 336.1932

(2*S,3*S**,4*R**)-2-[(1*S**)-1-(Benzyloxy)ethyl]-3,4-dimethoxycyclohexanone 34**

See general procedure f)
Starting material: spiroketal **49** (1.67g, 5mmol)
Yield: 1.20g, 4.1mmol, 82%, colourless oil
R_F-value: 0.55 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.25-7.35 (m, 5H, Ar), 4.61 (d, J = 11.7, 1H, C**H**aHbPh), 4.34 (d, J = 11.7, 1H, CHa**H**bPh), 4.14 (dq, 2H, J = 4.8, 6.4, 1H, C**H**Me), 3.88 (dd, J = 2.4, 6.7, 1H, C7-**H**), 3.81 (dt, J = 2.7, 7.6, 1H, C8-**H**), 3.41 (s, 3H, OC**H**$_3$), 3.39 (s, 3H, OC**H**$_3$), 2.67 (m, 1H, C**H**CHMe), 2.42 (m, 1H, C10-**H**a), 2.13-2.28 (m, C9-**H**a, C10-**H**b), 1.74 (m, 1H C9-**H**b), 1.27 (d, J = 6.4, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 209.9(q); 138.5(q); 128.3(t); 127.5(t); 127.5(t); 79.2(t); 74.7(t); 72.8(t); 70.8(s); 58.3(t); 56.9(p); 56.7(p); 35.8(s); 22.9(s); 18.0(p).
HRMS (EI, 70 eV): calc. $C_{17}H_{24}O_4$ $[M]^+$: 292.1675, found: 292.1668

(1*S,2*S**,3*S**,4*R**)-2-[(1*S**)-1-(Benzyloxy)ethyl]-3, 4-dimethoxycyclohexanol 50**

1.5mL (3.5mmol) lithium aluminum hydride solution (2.3M in ether) were slowly added at -78°C to a solution of 885mg (3mmol) ketone **34** in 20mL dry THF. The reaction mixture was stirred for 30min at -78°C and 1h at room temperature. The reaction mixture was diluted with 50mL ethyl acetate after addition of 100µL saturated ammonium chloride solution and dried over sodium sulfate. The solvent was removed under reduced pressure and the crude alcohol was purified on silica (hexane/ethyl acetate 1:1) to yield the desired product as colourless oil.
Yield: 690mg, 2.35mmol, 78%, colourless oil
R_F-value: 0.5 (hexane/ethyl acetate 1:2)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.23-7.34 (m, 5H, Ar), 4.69 (s, 1H, OH), 4.59 (d, J = 11.5, 1H, C**H**aHbPh), 4.55 (d, J = 11.5, 1H, CHa**H**bPh), 4.17 (m, 1H, C**H**Me), 3.76 (dt, J = 4.7, 9.9, 1H, C**H**OH), 3.67 (m, 1H, CH_2C**H**OMe), 3.40 (s, 3H, OC**H**$_3$), 3.34 (s, 3H, OC**H**$_3$), 2.90 (dd, J = 2.2, 10.7, 1H, CHC**H**OMe), 2.46 (ddd, J = 3.8, 9.9, 10.5, 1H, C**H**CHMe), 2.06 (dq, J = 3.9, 14.6, 1H, C**H**$_{eq}$HCOMe), 1.60-1.75 (m, 2H, CHOHC**H**$_2$).1.28 (d,J = 6.5, 3H, CHC**H**$_3$), 1.17(ddt, J = 2.0, 4.2, 13.9, 1H, C**H**$_{ax}$HCOMe).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 138.0(q); 128.3(t); 127.5(t); 127.5(t); 80.5(t); 76.0(t); 72.7(t); 71.2(s); 69.0(t); 56.6(p); 56.3(p); 45.3(t); 27.6(s); 22.6(s); 14.0(p);
HRMS (EI, 70 eV): calc. $C_{17}H_{26}O_4$ $[M]^+$: 294.1831, found: 294.1842

(1*S,2*R**,3*S**,4*R**)-2-[(1*S**)-1-Hydroxyethyl]-3,4-dimethoxycyclohexanol 35**

600mg (2mmol) of alcohol **50** were dissolved in 10mL methanol and flushed with nitrogen. After addition of 100mg Pd/C the atmosphere was replaced by hydrogen and the reaction mixture was stirred for 1h at room temperature. The reaction mixture was filtered through a plug of silica and the solvent was removed under reduced pressure to yield the diol as colourless oil.
Yield: 362mg, 1.77mmol, 88%, colourless oil
R_F-value: 0.3 (hexane/ethyl acetate 1:5)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.40 (m, 1H, C**H**Me), 4.12 (br, 1H, OH), 3.75 (dt, J = 5.0, 9.9, 1H, C**H**OH), 3.67 (m, 1H, CH_2C**H**OMe), 3.39 (s, 3H, OC**H**$_3$), 3.34 (s, 3H, OC**H**$_3$), 2.88 (dd, J = 2.5, 10.6, 1H, CHC**H**OMe), 2.24 (dt, J = 3.7, 10.2, 1H, C**H**CHMe), 2.06 (dq, J = 4.0, 14.6, 1H, C**H**$_{eq}$HCOMe), 1.60-1.75 (m, 3H, CHOHC**H**$_2$, O**H**).1.26 (d, J = 6.5, 3H, CHC**H**$_3$), 1.17 (dddd, J = 2.0, 4.7, 12.8, 15.5, 1H, C**H**$_{ax}$HCOMe).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 80.8(t); 72.8(t); 69.6(t); 67.9(t); 56.7(p); 56.4(p); 48.1(t); 28.1(s); 22.8(s); 17.3(p).

HRMS (EI, 70 eV): calc. $C_{10}H_{20}O_4$ $[M]^+$: 204.1362, found: 204.1377

(4*S,4a*R**,5*S**,6*R**,8a*S**)-5,6-Dimethoxy-2,2,4-trimethylhexahydro-4H-1,3-benzodioxine 36**

A solution of diol **35**, 20µL (26mg, 0.4mmol) 3,3-dimethoxypropane and catalytic amounts of *p*-toluene sulfonic acid in 1mL DMF was stirred 1h at 0°C, before 20mL of water were added. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure to yield the desired compound as colourless oil.
Yield: 10mg, 0.041mmol, 83%, colourless oil
R_F-value: 0.75 (hexane/ethyl acetate 1:5)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.31 (quintett, J = 6.8, 1H, C**H**Me), 3.75 (m, 1H, CH_2C**H**OMe), 3.68 (m, 1H, C**H**OCMe_2), 3.40 (s, 3H, OC**H**$_3$), 3.31 (s, 3H, OC**H**$_3$), 2.88 (dd, J = 2.8, 11.6, 1H, CHC**H**OMe), 2.37 (ddd, J = 6.6, 11.0, 11.2, 1H, C**H**CHMe), 2.11 (dq, J = 3.5, 14.7, 1H, C**H**$_{eq}$HCOMe), 1.59-1.67 (m, 2H, CHOHC**H**$_2$), 1.43 (s, 3H, CC**H**$_3$Me), 1.37 (s, 3H, CMeC**H**$_3$), 1.30 (d, J = 6.9, 3H, CHC**H**$_3$), 1.17 (m, J = 2.0, 4.7, 12.8, 15.5, 1H, C**H**$_{ax}$HCOMe).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 98.0(q); 79.9(t); 72.4(t); 67.6(t); 65.8(t); 56.6(p); 55.8(p); 41.2(t); 29.9(p); 26.4(p); 25.2(s); 23.0(s); 17.0(p).
HRMS (EI, 70 eV): calc. $C_{13}H_{24}O_4$ $[M]^+$: 244.1675, found: 244.1668

(6*S,7*S**,8*R**)-6-(3-Methyl-but-2-enyloxymethyl)-7,8-O-(1-methylethylidene)-1,4-dioxa-spiro[4.5]decane 51**

3.1g NaH (60% suspension in mineral oil, 78mmol) were added at 0°C in small portions to a solution of 11.2g (46 mmol) alcohol **8** and 14g allylbromide (94mmol). After stirring for 16h excess sodium hydride was quenched by addition of 200mL brine and the reaction mixture was extracted three times with ethyl ether. The combined organic layers were washed twice with brine and dried over sodium sulfate. After removal of the solvent under reduced pressure the crude product was purified on silica (hexane/ethyl acetate 2:1) to yield the desired allyl ether as colourless oil.
Yield: 11.9g, 38mmol, 82%, colourless oil
R_F-value: 0.6 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.34 (m, 1H, C**H**=CMe_2), 4.21 (m, 1H, C8-**H**), 4.05 (dd, J= 4.9, 9.2, 1H, C**H**aHbCH= CMe_2), 3.85-4.00 (m, 6H, OC**H**$_2$C**H**$_2$O, CHa**H**bCH= CMe_2, C7-**H**), 3.61 (dd, J = 3.3, 10.0, 1H, C**H**aHbOCH=CMe_2), 3.57 (dd, J = 5.8, 10.0, 1H, CHa**H**bOCH=CMe_2), 2.02-2.09 (m, 2H, C**H**CH_2OCH and C**H**aHbCOBz), 1.88-1.97 (m, 1H, CHa**H**bCOBz), 1.77 (td, J = 4.7, 13.2, 1H, C**H**$_{ax}$H$_{eq}$C$(OCH_2)_2$), 1.72 and 1.65 (2 s, 6H, CH=C(C**H$_3$**)$_2$), 1.55 (ddd, J = 3.8, 4.6, 13.2, 1H, CH_{ax}**H**$_{eq}$C$(OCH_2)_2$), 1.50 (1 s, 3H, CC**H**$_3$Me), 1.36 (s, 3H, CMeC**H**$_3$),
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 136.0(q); 121.5(t); 109.6(q); 108.1(q); 76.4(t); 72.5(t); 67.5(s); 66.4(s); 65.0(s); 64.5(s); 47.2(t); 29.8(s); 28.4(p); 26.4(p); 25.7(p); 23.5(s); 18.0(p).
HRMS (EI, 70 eV): calc. $C_{17}H_{28}O_5$ $[M]^+$: 312.1937, found: 312.1932

(6*S,7*S**,8*R**)-6-(3-Methyl-but-2-enyloxymethyl)-1,4-dioxa-spiro[4.5]decane-7,8-diol 52**

See general procedure b)
Starting material: ketal **51** (11.9g, 38mmol)
Yield: 9.2g, 34mmol, 89%, colourless oil.
R_F-value: 0.65 (hexane/ethyl acetate 1:10)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.30 (m, 1H, C**H**=CMe_2), 4.63 (br, 1H, O**H**), 3.77-3.98 (m, 8H, OC**H**$_2$C**H**$_2$O, CH_2CH=CMe_2, C7-**H**, C8-**H**), 3.60 (d, J = 9.0, 1H, C**H**aHbOCH=CMe_2), 3.58 (d, J = 9.0, 1H, CHa**H**bOCH=CMe_2), 2.75 (br, 1H, OH), 2.37 (dt, J = 3.1, 9.9, 1H, C**H**CH_2OCH), 1.85 (m, 1H, C**H**aHbCHOH), 1.73 (dd, 4.2, 13.4, 1H, CHa**H**bCHOH), 1.72 and 1.64 (2 s, 6H, CH=C(C**H$_3$**)$_2$), 1.59 (m, 1H, C**H**$_{ax}$H$_{eq}$C$(OCH_2)_2$).1.49 (m, 1H, CH_{ax}**H**$_{eq}$C$(OCH_2)_2$),

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 137.8(q); 120.2(t); 109.7(q); 75.9(t); 70.1(s); 67.9(s); 67.3(t); 64.6(s); 64.4(s); 44.1(t); 28.0(s); 25.7(p); 25.5(s); 17.9(p).
HRMS (EI, 70 eV): calc. $C_{14}H_{24}O_5$ $[M]^+$: 272.1624, found: 272.1629

(6*S,7*S**,8*R**)-Benzoic acid-6-(3-methyl-but-2-enyloxymethyl)-7-hydroxy-1,4-dioxaspiro[4.5]dec-8-yl ester 53**

See general procedure g)
Starting material: ketal **52** (5.5g, 20mmol)
Yield: 5.2g; 13.8mmol, 68%, colourless oil
R_F-value: 0.5 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = δ= 8.07 (m, 2H, Ar), 7.54 (m, 1H, Ar), 7.42 (m, 2H, Ar), 5.43 (m, 1H, C**H**OBz), 5.30 (m, 1H, C**H**=CMe_2), 4.18 (br, 1H, O**H**), 4.09 (dd, J = 3.1, 10.5, 1H, C**H**OH), 3.87-4.03 (m, 7H, C**H_2**CH=CMe_2, OC**H_2**C**H_2**O, C**H**aHbOCH_2CH=CMe_2), 3.66 (t, J = 9.6, 1H, CHa**H**bOCH_2CH=CMe_2), 2.58 (dt, J = 3.2, 9.6, 1H, C6-**H**), 1.60-2.02 (m, 4H, C**H_2**C**H_2**), 1.72 and 1.64 (2x s, 6H, CH=C(C**H_3**)$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.0(q); 137.7(q); 132.8(t); 130.6(q); 129.7(t); 128.2(t); 120.3(t); 109.5(q); 74.1(t); 71.1(t); 69.5(s); 67.9(s); 64.7(s); 64.7(s); 45.8(t); 29.1(s); 25.7(p); 24.5(s); 18.0(p).
HRMS (EI, 70 eV): calc. $C_{21}H_{28}O_6$ $[M]^+$: 376.1886, found: 376.1891

(6*S,7*S**,8*R**)-Benzoic acid-6-(3-methyl-but-2-enyloxymethyl)-7-methoxy-1,4-dioxaspiro[4.5]dec-8-yl ester 54**

520mg NaH (60% suspension in mineral oil, 13mmol) were added at 20°C in small portions to a solution of 3.76g (10 mmol) alcohol **53**, 6.1mL methyl iodide (100mmol). After stirring for 2h excess sodium hydride was quenched by addition of 200mL brine and the reaction mixture was extracted three times with ethyl ether. The combined organic layers were washed twice with brine and dried over sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified on silica (hexane/ethyl acetate 2:1) to yield the desired methyl ether as colourless oil.
Yield: 3.4g, 8.7mmol, 87%, colourless oil
R_F-value: 0.65 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.03 (m, 2H, Ar), 7.52 (m, 1H, Ar), 7.40 (m, 2H, Ar), 5.70 (m, 1H, C**H**OBz), 5.34 (m, 1H, C**H**=CMe_2), 3.88-4.06 (m, 6H, C**H_2**CH=CMe_2, OC**H_2**C**H_2**O), 3.65 (dd, J = 3.1, 9.8, 1H, C**H**aHbOCH_2CH=CMe_2), 3.59 (dd, J = 5.1, 9.8, 1H, CHa**H**bOCH_2CH=CMe_2), 3.47 (dd, J = 2.9, 11.5, 1H, C**H**OMe), 3.40 (s, 3H, OC**H_3**), 2.37 (ddd, J = 2.2, 5.1, 11.5, 1H, C**H**CH_2O), 1.60-2.02 (m, 4H, C**H_2**C**H_2**), 1.72 and 1.64 (2x s, 6H, CH=C(C**H_3**)$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 165.9(q); 136.0(q); 132.9(t); 130.4(q); 129.7(t); 128.2(t); 121.6(t); 109.9(q); 78.9(t); 67.6(s); 67.1(t); 65.1(s); 65.0(s); 64.9(s); 57.6(p); 46.4(t); 30.2(s); 25.8(p); 24.8(s); 19.9(p).
HRMS (EI, 70 eV): calc. $C_{22}H_{30}O_6$ $[M]^+$: 390.2042, found: 390.2047

(1*R,2*S**,3*S**)-Benzoic acid-3-(3-methyl-but-2-enyloxymethyl)-2-methoxy-4-oxo cyclohexyl ester 55**

See general procedure f)
Starting material: spiroketal **54** (3.4g, 8.7mmol)
Yield: 2.80g, 8.1mmol, 93%, colourless oil
R_F-value: 0.65 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.04 (m, 2H, Ar), 7.57 (m, 1H, Ar), 7.45 (m, 2H, Ar), 5.87 (m, 1H, C**H**OBz); 5.34 (m, 1H,C**H**=CMe_2); 4.03 (dd; J= 6.8, 11.5, 1H, C**H**aHbCH= CMe_2); 3.98 (dd, J = 7.2, 11.5, 1H, CHa**H**bCH= CMe_2), 3.94 (dd, J = 2.2, 9.0, 1H, C**H**aHbOCH=CMe_2), 3.71 (dd, J = 10.5, 2.6, 1H, C7-**H**), 3.62 (dd, J = 4.4, 9.0, 1H, CHa**H**bOCH=CMe_2), 3.45 (s, 3H, OC**H_3**), 2.87 (ddd, J = 2.1, 4.2, 10.5, 1H, C**H**CH_2OCH), 2.64 (ddd, J = 6.5, 12.8, 15.6, 1H, C**H_{ax}**H_{eq}C=O); 2.42 (ddd, J = 3.2, 5.4, 15.5, 1H,

$CH_{ax}\mathbf{H}_{eq}C{=}O$); 2.30 (m, 1H, $CH_{ax}\mathbf{H}_{eq}CHOBz$), 1.89 (m, 1H, $C\mathbf{H}_{ax}H_{eq}CHOBz$); 1.73 and 1.67 (2 s, 6H, $CH{=}C(C\mathbf{H_3})_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 207.1(q); 165.8(q); 136.7(q); 133.2(t); 130.0(q); 129.6(t); 128.4(t); 121.2(t); 78.9(t); 67.8(s); 66.9(t); 63.8(s); 57.6(p); 53.3(t); 35.7(s); 25.7(p); 24.6(s); 18.0(p).
HRMS (EI, 70 eV): calc. $C_{20}H_{26}O_5$ $[M]^+$: 346.1780, found: 346.1784

(3*R,4*S**,5*S**,6*R**)-Benzoic acid-4-(3-methyl-but-2-enyloxymethyl)-5-methoxy-1-oxa-spiro[2.5]oct-6-yl ester 56**

24 mg NaH were added to 176 mg (0.8 mmol) trimethylsulfoxonium iodide in 2 ml DMSO/THF 1:1 and stirred for 16h followed by the addition of 139mg (0.40 mmol) of ketone **55**. The reaction mixture was quenched after 10min by addition of 20mL $NaHCO_3$-solution. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The epoxide **56** was obtained after purification on silica as colourless oil.
Yield: 32 mg, 0.09mmol, 22%, colourless oil
R_F-value: 0.7 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.07 (m, 2H, Ar), 7.56 (m, 1H, Ar), 7.43 (m, 2H, Ar), 5.74 (m, 1H, C**H**OBz), 5.34 (m, 1H, C**H**=CMe_2), 3.92 (dd, J = 7.2, 11.2, 1H, C**H**aHbCH=CMe_2), 3.88 (dd, J = 7.2, 11.2, 1H, CHa**H**bCH=CMe_2), 3.58 (dd, J = 2.9, 9.3, 1H, CHC**H**aCHbO), 3.38 (s, 3H, OC**H**$_3$), 3.29 (dd, J = 2.7, 10.4, 1H, C**H**OMe), 3.22 (t, J = 9.0, 1H, CHCHaC**H**bO), 3.10 (d, J = 4.7, 1H, epoxide-**H**a), 2.65 (d, J = 4.7, 1H, epoxide-**H**b), 2.62 (m, 1H, C4-**H**), 2.17 (dt, J = 4.0, 13.1, 1H, C8-$\mathbf{H}_{ax}$), 2.07 (ddd, J = 4.0, 4.3, 14.3, 1H, C8-$\mathbf{H}_{eq}$), 1.92 (m, 1H, C7-$\mathbf{H}_{ax}$), 1.73 and 1.66 (2xs, 6H, 2x $C(C\mathbf{H}_3)_2$), 1.29 (dt, J = 4.0, 13.6, 1H, C7-$\mathbf{H}_{eq}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 165.9(q); 137.4(q); 133.0(t); 130.3(q); 129.7(t); 128.3(t); 120.7(t); 78.8(t); 67.4(t); 67.3(s); 65.1(s); 57.8(q); 57.4(p); 53.3(s); 42.2(t); 28.6(s); 25.8(p); 25.6(s); 17.9(p).
HRMS (EI, 70 eV): calc. $C_{21}H_{28}O_5$ $[M]^+$: 360.1937, found: 360.1941

(3*R,4*S**,5*S**,6*R**)-5-Methoxy-4-(3-Methyl-but-2-enyloxymethyl)-1-oxaspiro[2.5]octan-6-ol 57**

See general procedure c)
Starting material: ester **56** (32mg, 0.09mmol)
Yield: 23mg, 0.09mmol, 100%, colourless oil
R_F-value: 0.4 (hexane/ethyl acetate 1:2)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.31 (m, 1H, C**H**=$C(Me)_2$); 4.18 (m, 1H, C**H**OH); 3.88 (m, 2H, C$\mathbf{H}_2$CH=C); 3.46 (dd, J = 3.3; 9.4, 1H, CHC**H**aHbOCH_2); 3.38 (s, 3H, OC**H**$_3$); 3.22 (dd, J = 8.6, 9.2, 1H, CHCHa**H**bOCH_2); 3.15 (dd, J = 2.9; 9.7, 1H, C**H**OMe); 2.96 (d, J = 4.7, 1H, epoxide-**H**a); 2.59 (d, J = 4.7, 1H, epoxide-**H**b); 2.37 (m, 2H, C4-**H**, O**H**), 2.05 (m, 1H, C8-$\mathbf{H}_{ax}$); 1.95 (ddd, J = 4.6; 4.8; 13.9, 1H, C8-$\mathbf{H}_{eq}$); 1.75 (m, 1H, C7-$\mathbf{H}_{ax}$); 1.66 and 1.73 (2x s, 6H, 2x C**H**$_3$); 1.19 (dt, J = 4.4; 13.6, 1H, C7-$\mathbf{H}_{eq}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 137.1(q); 120.8(t); 80.4(t); 67.2(s); 65.5(s); 64.6(t); 58.0(q); 57.1(p); 53.2(s); 40.7(t); 27.6(s); 26.9(s); 25.8(p); 17.9(p).
HRMS (EI, 70 eV): calc. $C_{14}H_{24}O_4$ $[M]^+$: 256.1675, found: 256.1779

(3*R,4*S**,5*S**,6*R**)-(2-Chloroacetyl)-carbamic acid-5-methoxy-4-{[(3-methylbut-2-enyl)oxy]methyl}-1-oxaspiro[2.5]oct-6-yl ester 22a**

See general procedure d)
Starting material: alcohol **57** (19.8mg, 0.078mmol)
Yield: 22mg, 0.059mmol, 76%, colourless oil
R_F-value: 0.55 (hexane/ethyl acetate 1:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.07 (br, 1H, N**H**), 5.45 (m, 1H, C**H**OC(O)NH), 5.31 (m, 1H, C**H**=$C(Me)_2$), 4.45 (s, 2H, C$\mathbf{H}_2$Cl), 3.90 (dd, J = 7.0, 11.4, 1H, C**H**aHbCH=C), 3.87 (dd, J = 7.1, 11.4, 1H, CHa**H**bCH=C), 3.50 (dd, J = 3.0, 9.4, 1H, CHC**H**aHbOCH_2), 3.36 (s, 3H, OC**H**$_3$), 3.23 (dd, J = 2.7, 10.3,

1H, C**H**OMe), 3.18 (t, J = 9.0, 1H, CHCHa**H**bOCH$_2$), 3.02 (d, J = 4.7, 1H, epoxide-**H**a), 2.62 (d, J = 4.6, 1H, epoxide-**H**b), 2.39 (ddd, J = 3.0, 8.7, 10.7, 1H, C4-**H**), 1.82-2.05 (m, 3H, C8-**H**$_2$ CH, C7-**H**$_{ax}$), 1.66 and 1.73 (2x s, 6H, 2x C**H**$_3$), 1.29 (m, 1H, C7-**H**$_{eq}$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.2(q); 150.6(q); 137.2(q); 120.7(t); 78.6(t); 70.3(t); 67.3(s); 64.9(s); 57.6(p); 57.5(q); 53.3(s); 43.5(s); 41.8(t); 28.2(s); 25.7(p); 25.3(s); 17.9(p).
HRMS (EI, 70 eV): calc. $C_{17}H_{26}ClNO_6$ $[M]^+$: 375.1449, found: 375.1458

(6*S,7*S**,8*R**)-6-[1(*S**)-(3-Methyl-but-2-enyloxy)-ethyl]-7,8-*O*-(1-methylethylidene)-1,4-dioxa-spiro[4.5]decane 58**

620mg NaH (60% suspension in mineral oil, 14.5mmol) were added at 0°C in small portions to a solution of 2g (7.7mmol) alcohol **10**, 100mg (0.27mmol) tetrabutyl-ammoniumiodide and 3mL allylbromide (20.8g, 120mmol). After stirring for additional 24 h excess sodium hydride was quenched by addition of 200mL brine and the reaction mixture was extracted three times with ethyl ether. The combined organic layers were washed twice with brine and dried over sodium sulfate. After removal of the solvent under reduced pressure the crude product was purified on silica (hexane/ethyl acetate 3:1) to yield the desired allylether as colourless oil.
Yield: 1.94g, 5.96 mmol, 77%, colourless oil
R$_F$-value: 0.6 (hexane/ethyl acetate 3:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.32 (m, 1H, C**H**=CMe$_2$), 4.53 (dd, J = 5.0; 8.1, 1H, C7-**H**), 4.20 (q, J = 4.20, 1H, C8-**H**), 4.05 (dd, J = 6.4, 12.1, 1H, C**H**aHbCH= CMe$_2$), 3.85-4.00 (m, 6H, C**H$_2$**C**H$_2$**, C**H**Me**,** CHa**H**bCH= CMe$_2$), 2.00 (m, 1H, C10-Ha), 1.92 (d, J = 8.2, 1H, C**H**CHMe), 1.89 (m, 1H, C9-**H**a), 1.70 and 1.64 (2 s, 6H, C=C(C**H**$_3$)$_2$), 1.56-1.68 (m, 2H, C10-**H**b, C9-**H**b), 1.49 and 1.34 (2 s, 6H, OC(C**H**$_3$)$_2$), 1.28 (d, J = 6.6, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 134.9(q); 122.4(t); 110.0(q); 107.8(q); 75.1(t); 72.9(t); 70.4(t); 65.4(s); 64.4(s); 64.1(s); 51.0(t); 28.8(s); 28.5(p); 26.5(p); 25.8(p); 23.8(s); 20.6(p); 18.0(p).
HRMS (EI, 70 eV): calc. $C_{18}H_{30}O_5$ $[M]^+$: 326.2093, found: 326.1098

(6*S,7*S**,8*R**)-6-[1(*S**)-(3-Methyl-but-2-enyloxy)-ethyl]-1,4-dioxa-spiro[4.5]decane-7,8-diol 59**

See general procedure b)
Starting material: ketal **58** (1.73g, 5.3mmol)
Yield: 1.48g, 5.2mmol, 98%, colourless oil
R$_F$-value: 0.4 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.30 (m, 1H, C**H**=CMe$_2$), 4.46 (br, 1H, O**H**), 4.53 (dd, J = 6.8, 11.2, 1H, C7-**H**), 3.82-3.98 (m, 7H, C8-**H, CH_2**CH=CMe$_2$, **CH_2CH_2),** 3.72 (quint., J = 6.0, 1H, C**H**Me), 2.66 (br, 1H, O**H**), 2.12 (dd, J =5.5, 9.4, 1H, C**H**CHMe), 1.52-1.82 (m, 4H, C10-**H**$_2$, C9-**H**$_2$), 1.71 and 1.64 (2 s, 6H, C=C(C**H**$_3$)$_2$), 1.28 (d, J = 6.3, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 136.7(q); 121.0(t); 110.3(q); 73.9(t); 72.5(t); 68.1(t); 65.9(s); 64.4(s); 63.8(s); 51.3(t), 28.1(s), 25.8(s), 25.7(p), 22.8(p), 18.0(p).
HRMS (EI, 70 eV): calc. $C_{15}H_{26}O_5$ $[M]^+$: 286.1780, found: 286.1772

(6*S,7*S**,8*R**)-Benzoic acid-7-hydroxy-6-[(1*S**)-1-(3-methyl-but-2-enyloxy)-ethyl]-1,4-dioxa-spiro[4.5]dec-8-yl ester 60**

See general procedure g)
Starting material: ketal **59** (2.5g, 8.7mmol)
Yield: 2.44g, 6.24mmol, 72%, colourless oil
R$_F$-value: 0.6 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = δ= 8.07 (m, 2H, Ar), 7.54 (m, 1H, Ar), 7.43 (m, 2H, Ar), 5.49 (m, 1H, C**H**OBz), 5.33 (m, 1H, C**H**=CMe$_2$), 4.20 (dt, J = 3.4, 9.5, 1H, C**H**OH), 4.11 (dd, J = 6.8, 11.4, 1H, CH**H**CH= CMe$_2$), 3.94-4.05 (m, 6H, C**H$_2$**CH=CMe$_2$, C**H$_2$**C**H$_2$**), 3.82 (dq, J = 4.3, 6.4, 1H, C**H**Me), 2.30

(dd, J = 4.3, 9.5, 1H, C**H**(CO)(CHOH)), 2.0 and 1.62-1.84 (m, 4H, C**H$_2$**C**H$_2$**), 1.72 and 1.66 (2x s, 6H, CH=C(C**H$_3$**)$_2$), 1.34 (d, J = 6.4, 3H, CHC**H$_3$**).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.1(q); 136.5(q); 132.7(t); 130.7(q); 129.6(t); 128.2(t); 121.2(t); 110.0(q); 73.1(t); 71.8(t); 70.9(t); 65.9(s); 64.6(s); 64.0(s); 52.6(t); 29.0(s); 25.7(p); 24.5(s); 22.9 (p); 18.0(p).
HRMS (EI, 70 eV): calc. $C_{22}H_{30}O_6$ $[M]^+$: 390.2042, found: 390.2047

(6*S,7*S**,8*R**)-Benzoic acid-7-methoxy-6-[(1*S**)-1-(3-methyl-but-2-enyloxy)-ethyl]-1,4-dioxa-spiro[4.5]dec-8-ylester 61**

See general procedure e)
Starting material: alcohol **60** (268mg, 0.68mmol)
Yield: 160mg, 0.39mmol, 57%, colourless oil
R$_F$-value: 0.4 (hexane/ethyl acetate 3:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = δ= 8.05 (m, 2H, Ar), 7.54 (m, 1H, Ar), 7.44 (m, 2H, Ar), 5.66 (m, 1H, C**H**OBz), 5.36 (m, 1H, C**H**=CMe_2), 3.92-4.09 (m, 6H, OC**H$_2$**C**H$_2$**O and C**H$_2$**CH= CMe_2), 3.83 (dq, J = 1.2, 6.6, 1H, C**H**Me), 3.75 (dd, J = 3.1, 10.5, 1H, C**H**OMe), 3.37 (s, 3H, OC**H$_3$**), 2.23 (dd, J = 0.9, 10.5, 1H, C**H**CHMe), 1.95 (m, 1H, C**H**aHbC$(OCH_2)_2$), 1.61-1.79 (m, 3H, CHa**H**bC$(OCH_2)_2$ and C**H$_2$**COBz), 1.72 and 1.66 (2x s, 6H, CH=C(C**H$_3$**)$_2$), 1.34 (d, J = 6.6, 3H, CHC**H$_3$**).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.0(q); 134.8(q); 132.7(t); 130.7(q); 129.6(t); 128.2(t); 122.6(t); 110.4(q); 78.9(t); 70.9(t); 68.3(t); 65.5(s); 64.4(s); 64.4(s); 57.1(p); 50.3(t); 29.1(s); 25.7(p); 24.6(s); 21.4(p); 18.0(p).
HRMS (EI, 70 eV): calc. $C_{23}H_{32}O_6$ $[M]^+$: 404.2199, found: 404.2206

(1*R,2*S**,3*S**)-Benzoic acid-2-methoxy-3-((1*S**)-1-[(3-methylbut-2-enyl)oxy]ethyl)-4-oxo-cyclohexyl ester 62**

See general procedure f)
Starting material: spiroketal **61** (155mg, 0.38mmol)
Yield: 106mg, 0.29mmol, 77%, colourless oil
R$_F$-value: 0.75 (hexane/ethyl acetate 2:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.03 (m, 2H, Ar), 7.57 (m, 1H, Ar), 7.44 (m, 2H, Ar), 5.78 (ddd, J = 2.7, 3.4, 8.4, 1H, C**H**OBz), 5.30 (m, 1H, C**H**=CMe_2), 4.08 (dd, J = 6.7, 11.6, 1H, C**H**aHbCH= CMe_2), 4.02 (m, 2H, C**H**OMe and C**H**Me), 3.89 (dd, J = 6.7, 11.6, 1H, CHa**H**bCH= CMe_2), 3.43 (s, 3H, OC**H$_3$**), 2.65 (dt, J = 1.4, 5.7, 1H, C**H**CHMe), 2.42 – 2.54 (m, 2H, C**H**aHbCO and C**H**aHbCHOBz), 2.32 (m, 1H, CHa**H**bCHOBz), 2.05 (m, 1H, CHa**H**bCO), 1.73 (s, 3H, CMeC**H$_3$**), 1.65 (s, 3H, CC**H$_3$**Me), 1.30 (d, J = 6.4, 3H, CHC**H$_3$**).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 209.7(q); 165.9(q); 136.7(q); 133.1(t); 130.1(q); 129.6(t); 128.4(t); 121.1(t); 78.7(t); 72.7(t); 69.2(t); 65.5(s); 59.8(t); 57.4(p); 36.4(s); 25.7(p); 23.8(s); 18.0(p).
HRMS (EI, 70 eV): calc. $C_{21}H_{28}O_5$ $[M]^+$: 360.1937, found: 360.1943

(3*R,4*S**,5*S**,6*R**)-Benzoic acid-4-{(1*S**)-1-[(3-methylbut-2-enyl)oxy]ethyl}-5-methoxy-1-oxaspiro[2.5]oct-6-yl ester 63**

At -78°C 213µL of a 1.5M MeLi/LiBr-solution were added to a solution of 23mg of compound **62** and 24µL chloroiodomethane (0.32mmol) in 1mL THF. The reaction mixture was slowly warmed to room temperature and stirred for 1h. Then 20mL semisaturated brine was added and the aqueous layer was extracted three times with ethyl acetate. The combined organic layers were dried over sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified on silica (hexane/ethyl acetate 3:1) to yield the desired epoxide as colourless oil.
Yield: 5mg, 0.013mmol, 20%, colourless oil
R$_F$-value: 0.45 (hexane/ethyl acetate 3:1)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.03 (m, 2H, Ar), 7.53 (m, 1H, Ar), 7.42 (m, 2H, Ar), 5.40 (m, 1H, C**H**OBz).5.35 (m, 1H, C**H**=CMe_2), 4.09 (dd, J = 6.8, 11.3 .1H, C=C**H**aHb), 3.90-3.98 (m, 2H, C=CHa**H**b, C**H**Me), 3.79 (m, 1H, C**H**Me), 3.40 (s, 3H, OC**H**$_3$), 2.74 (d, J = 4.9, 1H, epoxide-Ha), 2.58 (d, J = 4.9, 1H, epoxide-Hb), 1.90-2.18 (m, 4H, C**H**CHMe, C7-**H**$_2$, C-8**H**aHb), 1.70 and 1.64 (2x s, 6H, C(C**H**$_3$)$_2$), 1.28 (m, 1H, C-7HaHbC-8Ha**H**b), 1.25 (d, J = 6.1, 3H, CHC**H**$_3$).
HRMS (EI, 70 eV): calc. $C_{22}H_{30}O_5$ $[M]^+$: 374.2093, found: 374.2078

(3*R,4*S**,5*S**,6*R**)-5-Methoxy-4-{(1*S**)-1-[(3-methylbut-2-enyl)oxy]ethyl}-1-oxaspiro[2.5]octan-6-ol 64**

See general procedure c)
Starting material: ester **63** (4.1mg, 0.0107mmol)
Yield: 2.9mg, 0.0107mmol, 100%, colourless oil
R_F-value: 0.45 (hexane/ethyl acetate 1:2)
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.33 (m, 1H, C**H**=CMe_2), 4.09 (dd, J = 6.7, 11.3 .1H, C=C**H**aHb), 3.68-4.02 (m, 4H, C**H**OH, C**H**OMe, C=CHa**H**b, C**H**Me), 3.37 (s, 3H, OC**H**$_3$), 2.65 (d, J = 4.9, 1H, epoxide-**H**a), 2.55 (d, J = 4.9, 1H, epoxide-**H**b), 2.30 (br, 1H, O**H**), 1.65-2.04 (m, 4H, C**H**C**H**Me, C7-**H**$_2$C-8**H**aHb), 1.67 and 1.75 (2x s, 6H, C(C**H**$_3$)$_2$), 1.28 (m, 1H, C-8Ha**H**b), 1.25 (d, J = 6.1, 3H, CHC**H**$_3$).
HRMS (EI, 70 eV): calc. $C_{15}H_{26}O_4$ $[M]^+$: 270.1831, found: 270.1840

(3*R,4*S**,5*S**,6*R**)-(2-Chloroacetyl)-carbamic acid-5-methoxy-4-{(1*S**)-1-[(3-methylbut-2-enyl)oxy]ethyl}-1-oxaspiro[2.5]oct-6-yl ester 23b**

See general procedure d)
Starting material: alcohol **64** (2.9mg, 0.0107mmol)
Yield: 2.4mg, 0.0062mmol, 55%, colourless oil.
R_F-value: 0.6 (hexane/ethyl acetate 1:1)
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.91 (br, 1H, N**H**), 5.35 (m, 1H, C**H**=C), 5.22 (m, 1H, C**H**OC=O), 4.42 (s, 2H, C**H**$_2$Cl), 4.10 (dd, J = 6.4, 11.3 .1H, C=C**H**aHb), 3.92 (m, 2H, C=CHa**H**b, C**H**OMe), 3.75 (quint, J = 6.3, 1H, C**H**Me), 3.56 (s, 3H, OC**H**$_3$), 2.71 (d, J = 5.2, 1H, epoxide-**H**a), 2.58 (d, J = 5.2, 1H, epoxide-Hb), 1.90-2.05 (m, 3H, C**H**CHMe, C-7**H**aHbC-8**H**aHb), 1.67 and 1.75 (2x s, 6H, C(C**H**$_3$)$_2$), 1.71 (m, 1H, C-7Ha**H**bC-8**H**aHb), 1.30 (m, 1H, C-8Ha**H**b), 1.25 (d, J = 6.2, 3H, CHC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 166.4(q); 150.5(q); 136.7(q); 121.1(t); 78.3(t); 73.7(t); 72.5(t); 65.1(s); 57.8(p); 57.2(q); 55.0(s); 48.9(t); 43.5(s); 28.8(s); 25.7(p); 24.7(s); 18.0(p); 17.9(p).
HRMS (EI, 70 eV): calc. $C_{18}H_{28}ClNO_6$ $[M]^+$: 389.1605, found: 389.1612

(6*S,7*S**,8*R**)-6-Methansulfonyloxymethyl-7,8-*O*-(1-methylethylidene)-1,4-dioxa-spiro[4.5]decane 65**

To a solution of 8.05g (33mmol) of alcohol **8** and 6.89mL (49mmol) triethylamine in 100mL DCM were added 2.82mL (36mmol, 4.16g) mesyl chloride at 0°C. The reaction mixture was stirred 1h at 0°C then 2h at room temperature. After hydrolysis with 2M sulfuric acid the aqueous layer was extracted twice with 100mL DCM. The combined organic layers were dried over sodium sulfate. After removal of the solvent under reduced pressure the product was isolated as colourless oil and used for the next step without further purification.
Yield: 10.63g, 33mmol; 100%, colourless oil.
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.47-4.37 (m, 2H, C**H**$_2$OS); 4.23 (m, 1H, C_6-**H**); 4.06-3.85 (m, 4H, OC**H**$_2$C**H**$_2$O); 3.00 (s, 3H, SC**H**$_3$); 2.20-2.14 (m, 1H, C**H**); 2.13-2.04 (m, 1H, C**H**); 1.72 (td, 2**H**, J= 13.3, 4.7 C_9-**H**$_2$); 1.63-1.54 (m, 2H, C_{10}-**H**$_2$); 1.47 (s, 3H, CC**H**$_3$); 1.34 (s, 3H, CC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 108.8 (q); 108.7 (q); 75.5 (t); 72.4 (t); 66.1 (s); 64.9 (s); 64.4 (s); 46.7 (t); 23.0 (s); 37.3 (p); 29.0 (s); 28.5 (p); 26.3 (p).
HRMS (EI): calc. $C_{13}H_{22}O_6S$ $[M]^+$: 322.1086, found: 322.1083.

(7*S,8*R**)-Methylene-7,8-*O*-(1-methylethylidene)-1,4-dioxa-spiro[4.5]decane 23**

Potassium -*tert*.-butoxide (7.4g, 66mmol) was added in small portions to a solution of 10.63g (33mmol) mesylate **65** in 200mL DMF. The reaction mixture was stirred for 10min at 0°C then 10min at room temperature. Within this time, the reaction mixture formed a highly viscous pulp. After completion (monitored by TLC), 200mL ice water are added and the aqueous layer was extracted three times with ethyl ether. The combined ether layers were washed twice with water and dried over sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified on silica (hexane/ethyl acetate 1:1) to yield the desired epoxide as colourless oil.
Yield: 6.37g, 28mmol, 85%, colourless oil.
R_F-value: 0.5 (hexane/ethyl acetate 1:1)
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 5.31-5.27 (m, 2H, C=C**H**$_2$); 4.52 (m, 1H, C**H**); 4.17 (m, 1H, C**H**); 3.96-3.74 (m, 4H, OC**H**$_2$C**H**$_2$O); 2.09-1.89 and 1.61 (m, 4H, C**H**$_2$C**H**$_2$); 1.40 (s, 3H, CC**H**$_3$); 1.30 (s, 3H, CC**H**$_3$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 144.9 (q); 111.8 (s); 108.8 (q); 107.7 (q); 76.5 (t); 73.9 (t); 65.1 (s); 63.4 (s); 30.7 (s); 27.8 (p); 26.3 (p); 23.5 (s).
HRMS (EI): calc. $C_{12}H_{18}O_4[M]^+$: 226.1205, found: 226.1220.

(7*S,8*R**)-Methylene-1,4-dioxa-spiro[4.5]decan-7,8-diol 24**

See general procedure b)
Starting material: ketal **23** (8.34g, 37mmol)
Yield: 6.15g, 33mmol, 90%, white solid (**T_M**: 122°C).
(**R_F-value**: 0.4 hexane/ethyl acetate 1:10).
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 5.37-5.23 (m, 2H, C=C**H**$_2$); 4.34 (sbr, 1H, C**H**OH); 4.03-3.96 (m, 4H, OC**H**$_2$C**H**$_2$O); 3.80 (sbr, 1H, C**H**OH); 2.97 (sbr, 1H, O**H**); 2.30 (sbr, 1H, O**H**); 1.94-1.86 and 1.70 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 144.2 (q); 111.8 (s); 108.0 (q); 74.7 (t); 71.1 (t); 64.7 (s); 64.4 (s); 32.4 (s); 26.9 (s).
HRMS (EI): calc. $C_9H_{14}O_4[M]^+$: 186.0892, found: 186.0898.

(±)-(3*R,11*R**,12*R**)-1,5,8-Trioxa-dispiro[2.0.4.4]dodecan-11,12-diol 25**

7.2mL (40mmol) of a 5.5M *tert*.-butylhydroperoxide solution were added dropwise to a solution of 3.69g (19.8mmol) alkene **24** and 790mg (3mmol) vanadium(IV)-oxyacetylacetonate in 250mL DCM at 0°C. The reaction mixture was stirred for additional 16h at 0°C. The solvent was removed under reduced pressure (water bath temperature < 30°C) and the crude product was purified on silica to yield 2.68g of the desired product as a colourless oil and 922mg of unreacted starting material.
Yield: 2.68g, 13.3mmol, 67%, colourless oil. 922mg, 5.0mmol, 25%, starting material **24**
R_F-value: 0.25 (hexane/ethyl acetate 1:10).
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 4.10 and 4.04-3.93 (m, 4H, OC**H**$_2$C**H**$_2$O); 3.83 (m, 1H, C**H**); 3.67 (m, 1H, C**H**); 3.41 (m, 1H, O**H**); 2.96 (d, 1H, J = 5.6 epoxide-**H**$_a$); 2.71 (d, 1H, J = 5.6 epoxide-**H**$_b$); 2.67 (sbr, 1H, O**H**); 1.95-1.86 and 1.64 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 107.1 (q); 74.0 (t); 70.4 (t); 66.0 (s); 65.7 (s); 60.2 (q); 47.8 (s); 30.6 (s); 26.6 (s).
HRMS (EI): calc. $C_9H_{14}O_5[M]^+$: 202.0841 found: 202.0834.

(6*R,7*R**,8*R**)-Benzoic acid-6,7-dihydroxy-6-allyloxymethyl-1,4-dioxa-spiro[4.5]dec-8-yl-ester 26**

To a solution of 315mg (1.56mmol) epoxy diol **25** in 20mL allyl alcohol were added 408mg (1.64mmol) dibutyl tin oxide. The reaction mixture was refluxed for 16h in a round bottom flask that had been equipped with a Soxlett-extractor (filled with molecular sieves 4Å). The solvent was removed under reduced pressure, after cooling to room temperature and the remaining syrup was dissolved in dry 1.4-dioxane.

After addition of 190 µL (241mg, 1.72mmol) benzoyl chloride the reaction mixture was stirred for 16h at room temperature. Subsequently, 50mL $NaHCO_3$–solution were added and the aqueous layer was extracted three times with ethyl acetate. The combined organic layer were dried over sodium sulfate, filtered through celite and the solvent was removed under reduced pressure. After purification on silica (hexane/ethyl acetate 1:2) the desired ester was yielded as a white solid. As side product the bisbenzoate(**R_F-value**: 0.75 hexane/ethyl acetate 1:2) was isolated.
Yield: 300mg, 0.82mmol, 53%, colourless oil.
(**R_F-value**: 0.45 hexane/ethyl acetate 1:2)
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.11-8.09 (m, 2H, Ar); 7.56 (m, 1H, Ar); 7.45-7.42 (m, 2H, Ar); 5.91 (m, 1H, All); 5.40 (m, 1H, C8-**H**); 5.30 (m, 1H, All); 5.21 (m, 1H, All); 4.15-3.96 (m, 7H, OC**H**$_2$C**H**$_2$O, OC**H**$_2$CH, C7-**H**); 3.78 (d, 1H, J = 10.1 OC**H**$_a$H$_b$C); 3.71 (d, 1H, J = 10.1 OCH$_a$**H**$_b$C); 3.49 (sbr, 1H, O**H**); 3.42 (sbr, 1H, O**H**); 2.06-1.99, 1.91 and 1.64 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 165.9 (q); 134.1 (t); 133.0 (t); 130.3 (q); 129.8 (t); 128.4 (t); 117.6 (s); 110.0 (q); 76.5 (q); 73.0 (s); 72.6 (t); 71.7 (s); 71.2 (t); 65.5 (2 s); 27.5 (s); 23.3 (s).
HRMS (FAB in 3-NBA): calc. $C_{19}H_{25}O_7[M-H]^+$: 365.1600, found: 365.1617.

(6*R,7*R**,8*R**)-Benzoic acid-6-allyloxymethyl-6-hydroxy-7-methoxy-1,4-dioxa-spiro[4.5]dec-8-yl-ester 27**

See general procedure e)
Starting material: alcohol **26** (1.69g, 4.6mmol)
Yield: 785mg, 2.08mmol, 45%, colourless oil.
(**R_F-value**: 0.5 hexane/ methyl *tert.*-butyl ether 1:3).
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.08-8.06 (m, 2H, Ar); 7.55 (m, 1H, Ar); 7.45-7.42 (m, 2H, Ar); 5.94 (m, 1H, All); 5.43 (m, 1H, C8-H); 5.30 (m, 1H, All); 5.20 (m, 1H, All); 4.14-3.93 (m, 6H, OC**H**$_2$C**H**$_2$O, OC**H**$_2$CH); 3.86 (d, 1H, J = 1.7 C7-**H**); 3.68-3.58 (m, 5H, OC**H**$_3$, OC**H**$_2$C); 3.31 (s, 1H, O**H**); 2.07, 1.95-1.83, 1.68 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 165.8 (q); 134.6 (t); 133.0 (t); 130.3 (q); 129.7 (t); 128.4 (t); 117.4 (s); 109.5 (q); 81.5 (t); 76.6 (q); 72.8 (s); 71.1 (t); 70.7 (s); 65.8 (s); 65.4 (s); 61.5 (p); 29.4 (s); 23.2 (s).
HRMS (EI): calc. $C_{20}H_{26}O_7[M]^+$: 378.1678, found: 378.1684.

(6*R,7*R**,8*R**)-Benzoic acid-6-allyloxymethyl-6,7-dimethoxy-1,4-dioxa-spiro[4.5]dec-8-yl-ester 28**

Yield: 422mg, 1.08mmol, 23%, colourless oil.
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.13-8.12 (m, 2H, Ar); 7.53 (m, 1H, Ar); 7.43-7.40 (m, 2H, Ar); 5.93 (m, 1H, All); 5.64 (m, 1H, C8-**H**); 5.29 (m, 1H, All); 5.18 (m, 1H, All); 4.12-3.90 (m, 6H, OC**H**$_2$C**H**$_2$O, OC**H**$_2$CH); 3.81-3.74 (m, 3H, C7-**H**, OC**H**$_2$C); 3.49 (s, 3H, OC**H**$_3$); 3.46 (s, 3H, OC**H**$_3$); 2.28, 1.97, 1.83, and 1.48 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 166.3 (q); 134.7 (t); 132.8 (t); 130.7 (q); 129.9 (t); 128.3 (t); 117.2 (s); 110.6 (q); 81.1 (q); 80.3 (t); 72.7 (s); 68.0 (t); 66.5 (s); 65.4 (s); 65.0 (s); 59.1 (p); 53.5 (p); 27.7 (s); 24.6 (s).
HRMS (EI): calc. $C_{21}H_{28}O_7[M]^+$: 392.1835, found: 392.1828.

(1*R,2*R**,3*R**)-Benzoic acid-3-allyloxymethyl-2,3-dimethoxy-4-oxo-cyclohexyl-ester 66**

See general procedure i)
Starting material: spiroketal **28** (20mg, 0.036mmol)
Yield: 60mg, 0.17mmol, 97%, colourless oil.
R_F-value: 0.8 hexane/ methyl *tert.*-butyl ether 1:3
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.10-8.08 (m, 2H, Ar); 7.57 (m, 1H, Ar); 7.47-7.43 (m, 2H, Ar); 5.91 (m, 1H, All); 5.77 (m, 1H, C1-**H**); 5.29 (m, 1H, All); 5.22 (m, 1H, All); 4.07-4.04 (m, 2H, OC**H**$_2$CH); 3.97 (m, 1H, C2-**H**); 3.91 (d, 1H, J = 9.7 OC**H**$_a$H$_b$C); 3.72 (d, 1H, J = 9.7 OCH$_a$**H**$_b$C); 3.56 (s, 3H, OC**H**$_3$); 3.42 (s, 3H, OC**H**$_3$); 2.76, 2.42, 2.34 and 2.01 (m, 4H, C**H**$_2$C**H**$_2$).

^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 205.8 (q); 166.1 (q); 134.1 (t); 133.2 (t); 130.1 (q); 129.8 (t); 128.4 (t); 117.8 (s); 84.9 (q); 80.9 (t); 72.7 (s); 69.1 (t); 67.1 (s); 60.2 (p); 52.8 (p); 34.7 (s); 24.8 (s).
HRMS (EI): calc. $C_{19}H_{24}O_6[M]^+$: 348.1572, found: 348.1568.

(3*S,4*R**,5*R**,6*R**)-Benzoic acid-4-allyloxymethyl-4,5-dimethoxy-1-oxa-spiro[2.5]oct-6-yl-ester 67**

See general procedure j)
Starting material: ketone **66** (18mg, 0.052mmol)
Yield: 16mg, 0.044mmol, 85%, colourless oil.
R_F-value: 0.8 hexane/ methyl *tert.*-butyl ether 1:3; 0.4 hexane/ methyl *tert.*-butyl ether 2:1
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.11-8.08 (m, 2H, Ar); 7.57 (m, 1H, Ar); 7.47-7.43 (m, 2H, Ar); 5.95 (m, 1H, All); 5.42 (m, 1H, C_6-**H**); 5.31 (m, 1H, All); 5.23 (m, 1H, All); 4.05-4.03 (m, 2H, OC**H**$_2$CH); 3.91 (m, 1H, C_5-**H**); 3.88 (d, 1H, J = 11.2 OC**H**$_A$H$_B$C); 3.69 (d, 1H, J = 11.2 OCH$_A$**H**$_B$C); 3.57 (s, 3H, OC**H**$_3$); 3.45 (s, 3H, OC**H**$_3$); 3.31 (d, 1H, J = 5.5, epoxide-**H**$_a$); 2.55 (d, 1H, J = 5.5, epoxide-**H**$_b$); 2.13, 1.97, 1.80 and 1.71 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 166.0 (q); 134.3 (t); 133.0 (t); 130.3 (q); 129.7 (t); 128.4 (t); 117.9 (s); 79.7 (t); 77.9 (q); 72.5 (s); 71.3 (t); 68.1 (s); 60.6 (q); 60.1 (p); 52.4 (p); 52.1 (s); 28.0 (s); 24.4 (s).
HRMS (EI): calc. $C_{20}H_{26}O_6[M]^+$: 362.1729, found: 362.1732.

(3*S,4*R**,5*R**,6*R**)-4-Allyloxymethyl-4.5-dimethoxy-1-oxa-spiro[2.5]octan-6-ol 68**

See general procedure c)
Starting material: ester **67** (16mg, 0.045mmol)
Yield: 11mg, 0.043mmol, 96%, colourless oil.
R_F-value: 0.3 hexane/ methyl *tert.*-butyl ether 1:3
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 5.89 (m, 1H, All); 5.25 (m, 1H, All); 5.18 (m, 1H, All); 4.67 (m, 1H, C_6-H); 3.96-3.94 (m, 2H, OC**H**$_2$CH); 3.82 (d, 1H, J = 10.8 OC**H**$_a$H$_b$C); 3.55 (d, 1H, J = 10.8 OCH$_a$**H**$_b$C); 3.53 (s, 3H, OC**H**$_3$); 3.47 (s, 3H, OC**H**$_3$); 3.46 (d, 1H, J = 5.8 epoxide-**H**$_a$); 3.35 (d, 1H, J = 3.0 C5-**H**); 2.63 (d, 1H, J = 5.2 epoxide-**H**$_b$); 2.14, 1.94, 1.65 and 1.24 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 134.3 (t); 117.3 (s); 81.0 (q); 80.8 (t); 72.4 (s); 68.2 (s); 66.6 (t); 58.9 (p); 58.4 (q); 53.2 (p); 52.9 (s); 28.4 (s); 25.8 (s).
HRMS (FAB in 3-NBA): calc. $C_{13}H_{23}O_5[M-H]^+$: 259.1545, found: 259.1533.

(3*S,4*R**,5*R**,6*R**)-(2-Chloro-acetyl)-carbamic acid-4-allyloxymethyl-4,5-dimethoxy-1-oxa-spiro[2.5]oct-6-yl-ester 30**

See general procedure d)
Starting material: alcohol **68** (11mg, 0.426mmol)
Yield: 9mg, 0.029mmol, 68%, colourless oil.
R_F-value: 0.5 hexane/ methyl *tert.*-butyl ether 1:3
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.03 (sbr, 1H, NH); 5.92 (m, 1H, All); 5.29 (m, 1H, All); 5.22 (m, 1H, All); 5.18 (m, 1H, C6-**H**); 5.50 (m, 2H, C**H**$_2$Cl); 4.04-3.97 (m, 2H, OC**H**$_2$CH); 3.81-3.72 (m, 2H, C5-H, OC**H**$_a$H$_b$C); 3.62 (d, 1H, J = 11.2 OCH$_a$**H**$_b$C); 3.49 (s, 3H, OC**H**$_3$); 3.44 (s, 3H, OC**H**$_3$); 3.30 (d, 1H, J = 5.3 epoxide- **H**$_a$); 2.56 (d, 1H, J = 5.4 epoxide- **H**$_b$); 2.05, 1.90 and 1.74-1.59 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 166.6 (q); 150.7 (q); 134.1 (t); 118.0 (s); 79.5 (t); 78.1 (q); 73.1 (t); 72.5 (s); 67.7 (s); 60.5 (q); 59.7 (p); 52.4 (p); 52.2 (s); 43.6 (s); 27.3 (s); 24.3 (s).
HRMS (EI): calc. $C_{16}H_{24}NO_6Cl$ $[M]^+$: 377.1241, found: 377.1236.

(3*S,4*R**,5*S**)-4-Allyloxymethyl-4,5-dimethoxy-1-oxa-spiro[2.5]octan-6-one 29**

A solution of 9mg (0.035mmol) epoxy alcohol **68** and 20mg IBX (0.07mmol) in 2mL DMSO was stirred for 2h at room temperature. After addition of 10mL water the reaction mixture was extracted three times

with ether. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure to yield the desired ketone without further purification as colourless oil.
Yield: 9mg, 0.035mmol, 100%, colourless oil.
R_F-value: 0.6 hexane/ methyl *tert.*-butyl ether 1:3
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 5.92 (m, 1H, All); 5.29 (m, 1H, All); 5.23 (m, 1H, All); 4.02-3.98 (m, 3H, OC**H**$_2$CH, C_5-H); 3.85 (d, 1H, J = 10.8 OC**H**$_a$H$_b$C); 3.56 (d, 1H, J = 4.8 epoxide- **H**$_a$); 3.47 (d, 1H, J = 10.8 OCH$_a$**H**$_b$C); 3.45 (s, 3H, OC**H**$_3$); 3.43 (s, 3H, OC**H**$_3$); 2.83 (d, 1H, J = 4.8 epoxide- **H**$_b$); 2.64-2.52 and 1.50 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 206.4 (q); 134.1 (t); 117.9 (s); 87.1 (t); 82.8 (q); 72.5 (s); 64.5 (s); 59.7 (p); 59.1 (q); 53.8 (s); 53.3 (p); 36.8 (s); 29.4 (s).
HRMS (EI): calc. $C_{13}H_{20}O_5$ $[M]^+$: 256.1310, found: 256.1306.

(1*R,2*R**,3*R**)-2-Allyloxymethyl-4-hydroxy-2,3-dimethoxy-cyclohexanone 69**

See general procedure c)
Starting material: ester **66** (20mg, 0.058mmol)
Yield: 11mg, 0.045mmol, 78%, colourless oil.
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 5.91 (m, 1H, All); 5.29 (m, 1H, All); 5.20 (m, 1H, All); 4.41 (m, 1H, C4-**H**); 4.11-4.02 (m, 2H, OC**H**$_2$CH); 3.96 (d, 1H, J = 8.6 OC**H**$_a$H$_b$C); 3.65 (d, 1H, J = 8.6 OCH$_a$**H**$_b$C); 3.60 (d, 1H, J = 3.5 C3-**H**); 3.56 (s, 3H, OC**H**$_3$); 3.24 (s, 3H, OC**H**$_3$); 2.92, 2.34-2.23 and 1.68 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 206.2 (q); 134.5 (t); 117.2 (s); 86.0 (q); 79.9 (t); 72.3 (s); 65.6 (t); 64.5 (s); 58.4 (p); 52.6 (p); 32.9 (s); 28.1 (s).
HRMS (EI): calc. $C_{12}H_{20}O_5[M]^+$: 244.1310, found: 244.1319.

(1*R,2*R**,3*R**)-(2-Chloro-acetyl)-carbamic acid-3-allyloxymethyl-2,3-dimethoxy-4-oxo-cyclohexyl-ester 31**

See general procedure d)
Starting material: alcohol **69** (6mg, 0.025mmol)
Yield: 9mg, 0.025mmol, 100%, colourless oil.
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.18 (sbr, 1H, N**H**); 5.91 (m, 1H, All); 5.56 (m, 1H, C_1-H); 5.29 (m, 1H, All); 5.23 (m, 1H, All); 4.51 (sbr, 2H, C**H**$_2$Cl); 4.10-4.01 (m, 2H, OC**H**$_2$CH); 3.92 (d, 1H, J = 9.2 OC**H**$_a$H$_b$C); 3.86 (d, 1H, J = 3.1 C2-**H**); 3.63 (d, 1H, J = 9.2 OCH$_a$**H**$_b$C); 3.54 (s, 3H, OC**H**$_3$); 3.31 (s, 3H, OC**H**$_3$); 2.78, 2.40-2.25 and 1.94 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 205.3 (q); 166.5 (q); 150.8 (q); 134.1 (t); 117.8 (s); 84.5 (q); 80.0 (t); 72.7 (s); 70.3 (t); 65.9 (s); 60.0 (p); 52.6 (p); 43.6 (s); 33.8 (s); 24.6 (s).
HRMS (EI): calc. $C_{15}H_{22}NO_7Cl[M]^+$: 363.1084, found: 363.1080.

(1*R,2*R**,3*R**)-Benzoic acid-3-allyloxymethyl-3-hydroxy-2-methoxy-4-oxo-cyclohexyl-ester 70**

See general procedure i)
Starting material: spiroketal **27** (290mg, 0.77mmol)
Yield: 199mg, 0.60mmol, 78%, colourless oil.
R_F-value: 0.75 hexane/ methyl *tert.*-butyl ether 1:3
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.10-8.05 (m, 2H, Ar); 7.59 (m, 1H, Ar); 7.48-7.43 (m, 2H, Ar); 5.88 (m, 1H, All); 5.70 (m, 1H, C1-**H**); 5.29 (m, 1H, All); 5.23 (m, 1H, All); 4.07-4.05 (m, 2H, OC**H**$_2$CH); 3.91 (m, 1H, C2-**H**); 3.85 (s, 1H, O**H**); 3.80 (d, 1H, J = 10.2 OC**H**$_a$H$_b$C); 3.66 (d, 1H, J = 10.2 OCH$_a$**H**$_b$C); 3.60 (s, 3H, OC**H**$_3$); 2.66, 2.57, 2.32 and 2.22 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 208.4 (q); 165.9 (q); 133.8 (t); 133.3 (t); 129.8 (q); 129.7 (t); 128.5 (t); 118.1 (s); 84.5 (t); 81.6 (q); 72.9 (s); 72.5 (s); 71.4 (t); 62.1 (p); 34.8 (s); 25.1 (s).
HRMS (EI): calc. $C_{18}H_{22}O_6[M]^+$: 334.1416, found: 334.1412.

(3*S,4*R**,5*R**,6*R**)-Benzoic acid-4-allyloxymethyl-4-hydroxy-5-methoxy-1-oxa-spiro[2.5]oct-6-yl-ester 71**

See general procedure j)
Starting material: ketone **70** (22mg, 0.07mmol)
Yield:13mg, 0.037mmol, 57%, colourless oil.
R_F-value: 0.1 hexane/ methyl *tert.*-butyl ether 2:1
diastereomer epoxide **72** (**R_F-value**: 0.2 hexane/ methyl *tert.*-butyl ether 2:1).
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.08-8.07 (m, 2H, Ar); 7.58 (m, 1H, Ar); 7.47-7.44 (m, 2H, Ar); 5.93 (m, 1H, All); 5.43 (m, 1H, C_6-H); 5.31 (m, 1H, All); 5.23 (m, 1H, All); 4.14-4.04 (m, 2H, OC**H**$_2$CH); 3.84 (d, 1H, J = 0.7 C5-**H**); 3.73 (d, 1H, J = 10.3 OC**H**$_a$H$_b$C); 3.62 (s, 3H, OC**H**$_3$); 3.59 (d, 1H, J = 10.3 OCH$_a$**H**$_b$C); 3.16 (d, 1H, J = 5.2 epoxide-**H**); 2.88 (s, 1H, O**H**); 2.55 (d, 1H, J = 5.2 epoxide-**H**); 2.13, 2.02-1.89 and 1.62 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 165.8 (q); 134.2 (t); 133.2 (t); 130.1 (q); 129.7 (t); 128.5 (t); 117.8 (s); 81.8 (t); 73.8 (q); 72.8 (s); 71.9 (t); 70.1 (s); 61.3 (p); 59.7 (q); 51.4 (s); 27.6 (s); 24.2 (s).
HRMS (FAB in 3-NBA): calc. $C_{19}H_{25}O_6[M\text{-}H]^+$: 349.1651, found: 349.1686.

(3*R,4*R**,5*R**,6*R**)-Benzoic acid-4-allyloxymethyl-4-hydroxy-5-methoxy-1-oxa-spiro[2.5]oct-6-yl-ester 72**

Yield: 3mg, 0.009mmol, 13%, colourless oil.
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.09-8.07 (m, 2H, Ar); 7.58 (m, 1H, Ar); 7.48-7.45 (m, 2H, Ar); 5.93 (m, 1H, All); 5.38 (m, 1H, C6-**H**); 5.32 (m, 1H, All); 5.23 (m, 1H, All); 4.12-4.03 (m, 2H, OC**H**$_2$CH); 3.82 (m, 1H, C5-**H**); 3.65 (s, 3H, OC**H**$_3$); 3.61 (m, 1H, OC**H**$_a$H$_b$C); 3.54 (d, 1H, J = 10.3 OCH$_a$**H**$_b$C); 3.13 (s, 1H, O**H**); 2.92 (d, 1H, J = 5.2 epoxide-**H**); 2.46 (d, 1H, J = 5.2 epoxide-**H**); 2.26, 2.08, 1.88 and 1.52 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 165.8 (q); 134.3 (t); 133.1 (t); 130.1 (q); 129.7 (t); 128.5 (t); 117.6 (s); 82.1 (t); 77.5 (q); 72.8 (t); 72.8 (s); 71.6 (s); 62.0 (q); 58.0 (p); 46.9 (s); 28.0 (s); 22.8 (s).
HRMS (FAB in 3-NBA): calc. $C_{19}H_{25}O_6[M\text{-}H]^+$: 349.1651, found: 349.1646.

(3*S,4*R**,5*R**,6*R**)-4-Allyloxymethyl-5-methoxy-1-oxa-spiro[2.5]octane-4,6-diol 73**

A solution of 15mg (0.043mmol) ester **71** and 2.8mg (0.043mmol) potassium cyanide in 1mL was stirred 24h at room temperature. After addition of 10mL water, the aqueous layer was extracted five times with ethyl acetate. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified on silica to yield the alcohol as colourless oil.
Yield: 10mg, 0.041mmol, 95%, colourless oil.
R_F-value: 0.5 hexane/ethyl acetate 1:10
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 5.88 (m, 1H, All); 5.26 (m, 1H, All); 5.20 (m, 1H, All); 4.17 (m, 1H, C6-**H**); 4.04-3.98 (m, 2H, OC**H**$_2$CH); 3.60 (d, 1H, J = 9.8 C**H**$_a$H$_b$O); 3.53 (s, 3H, OC**H**$_3$); 3.41 (d, 1H, J = 9.7 CH$_a$**H**$_b$O); 3.29 (d, 1H, J = 3.1, C5-**H**); 3.21-3.15 (m, 2H, O**H**, epoxide-**H**$_a$); 3.01 (d, 1H, J = 8.3 O**H**); 2.57 (d, 1H, J = 4.9 epoxide-**H**$_b$); 2.13, 1.95, 1.81 and 1.35 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 134.0 (t); 117.8 (s); 80.8 (t); 75.7 (q); 72.6 (s); 67.9 (s); 67.1 (t); 59.6 (q); 59.1 (p); 51.8 (s); 28.1 (s); 25.3 (s).
HRMS (FAB in 3-NBA): calc. $C_{12}H_{21}O_5[M\text{-}H]^+$: 245.1388, found: 245.1368.

(3*S,4*R**,5*R**,6*R**)-(2-Chloro-acetyl)-carbamic acid-4-allyloxymethyl-4-hydroxy-5-methoxy-1-oxa-spiro[2.5]oct-6-yl-ester 74**

See general procedure d)
Starting material: alcohol **73** (5mg, 0.021mmol)
Yield: 6mg, 0.017mmol, 81%, colourless oil.

R_F-value: 0.6 hexane/ethyl acetate 1:10
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.24 (sbr, 1H, N**H**); 5.92 (m, 1H, All); 5.32-5.23 (m, 3H, All, C6-**H**); 4.49 (s, 2H, C$\mathbf{H}_2$Cl); 4.14-4.03 (m, 2H, OC$\mathbf{H}_2$CH); 3.65-3.58 (m, 2H, C$\mathbf{H}_a\mathbf{H}_b$O, C5-**H**); 3.56 (s, 3H, OC$\mathbf{H}_3$); 3.52 (d, 1H, J = 10.4 C$\mathrm{H}_a\mathbf{H}_b$O); 3.18 (d, 1H, J = 5.0 epoxide-$\mathbf{H}_a$); 3.06 (sbr, 1H, O**H**); 2.57 (d, 1H, J = 5.0 epoxide-$\mathbf{H}_b$); 2.07, 1.95, 1.79 and 1.71 (m, 4H, C$\mathbf{H}_2$C$\mathbf{H}_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 166.4 (q); 150.6 (q); 134.1 (t); 117.9 (s); 80.7 (t); 74.1 (t); 73.2 (q); 72.7 (s); 69.4 (s); 60.8 (p); 59.5 (q); 51.7 (s); 43.6 (s); 26.7 (s); 24.3 (s).
HRMS (FAB in 3-NBA): calc. $C_{15}H_{23}NO_7Cl[M-H]^+$: 364.1163, found: 364.1155.

(3*S*,4R*,5S)-4-Allyloxymethyl-4-hydroxy-5-methoxy-1-oxa-spiro[2.5]octan-6-one 32**

A suspension of 9mg (0.037mmol) epoxide **73** and 21mg IBX (2eq; 0.074mmol) in 10mL acetone was refluxed over night. After cooling to -40°C the reaction mixture was filtered and the solvent was evaporated under reduced pressure. The crude product was purified on silica to yield the pure ketone as colourless oil.
Yield: 3mg, 0.013mmol, 35%, colourless oil.
R_F-value: 0.5 hexane/ methyl *tert.*-butyl ether 1:3
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 5.89 (m, 1H, All); 5.30-5.21 (m, 2H, All); 4.07-3.98 (m, 2H, OC$\mathbf{H}_2$CH); 3.80 (s, 1H, C5-**H**); 3.58-3.48 (m, 5H, OC$\mathbf{H}_3$, OC$\mathbf{H}_2$C); 3.31 (d, 1H, J = 4.7 epoxide-$\mathbf{H}_a$); 2.96 (sbr, 1H, O**H**); 2.77 (d, 1H, J = 4.7 epoxide-$\mathbf{H}_b$); 2.63-2.60, 2.45 and 1.71 (m, 4H, C$\mathbf{H}_2$C$\mathbf{H}_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 206.2 (q); 133.9 (t); 117.9 (s); 85.2 (t); 77.5 (q); 72.7 (s); 67.6 (s); 59.3 (q); 59.2 (p); 52.7 (s); 36.4 (s); 28.8 (s).
HRMS (EI): calc. $C_{12}H_{18}O_5$ $[M]^+$: 242.1154, found: 242.1005.

(6*R*,7R*,8R)-Benzoic acid-6-hydroxy-6-hydroxymethyl-7-methoxy-1,4-dioxa-spiro[4.5]dec-8-yl-ester 75**

5mg palladium (10%) on charcoal were added to a solution of 50mg (0.132mmol) compound **27** and 50mg p-toluene sulfonic acid (0.265mmol) in 10 mL water/methanol 1:1 and stirred over night at room temperature. 20mL $NaHCO_3$-solution were added and the aqueous layer was extracted five times with ethyl acetate. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude alcohol was purified on silica to yield the desired product as a colourless oil.
Yield: 35mg, 0.104mmol, 78%, colourless oil.
R_F-value: 0.3 hexane/ethyl acetate 1:10
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.09-8.07 (m, 2H, Ar); 7.55 (m, 1H, Ar); 7.44-7.41 (m, 2H, Ar); 5.61 (m, 1H, C8-**H**); 4.10-3.97 (m, 4H, OC$\mathbf{H}_2$C$\mathbf{H}_2$O); 3.82-3.75 (m, 3H, C$\mathbf{H}_2$OH, C7-**H**); 3.54 (s, 3H, OC$\mathbf{H}_3$); 3.18 (sbr, 1H, O**H**); 2.63 (sbr, 1H, O**H**); 2.16, 2.04, 1.82 and 1.58 (m, 4H, C$\mathbf{H}_2$C$\mathbf{H}_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 165.9 (q); 133.1 (t); 130.1 (q); 129.8 (t); 128.5 (t); 110.7 (q); 79.8 (t); 76.4 (q); 68.5 (t); 65.3 (s); 65.1 (s); 63.4 (s); 59.5 (p); 26.6 (s); 23.9 (s).
HRMS (EI): calc. $C_{17}H_{22}O_7$ $[M]^+$: 338.1365, found: 338.1356.

(6*R*,7R*,8R)-Benzoic acid-6-benzyloxymethyl-6-hydroxy-7-methoxy-1,4-dioxa-spiro[4.5]dec-8-yl-ester 76**

See general procedure a)
Starting material: alcohol **75** (84mg, 0.25mmol)
Yield: 52mg, 0.12mmol, 48%, colourless oil.
R_F-value: 0.55 hexane/ethyl acetate 1:2
^{1}H-NMR (400 MHz, $CDCl_3$): □ = 8.10-8.08 (m, 2H, Ar); 7.59-7.28 (m, 8H, Ar); 5.41 (m, 1H, C8-**H**); 4.62 (dd, 2H, J = 46.1; 12.3 OC$\mathbf{H}_2$Ph); 4.09-3.86 (m, 5H, OC$\mathbf{H}_2$C$\mathbf{H}_2$O, C7-**H**); 3.67 (s, 2H, OC$\mathbf{H}_2$C) 3.62 (s, 3H, OC$\mathbf{H}_3$); 3.33 (sbr, 1H, O**H**); 2.08-1.60 (m, 4H, C$\mathbf{H}_2$C$\mathbf{H}_2$).
^{13}C-NMR (100.6 MHz, $CDCl_3$): □ = 165.8 (q); 138.0 (q); 133.0 (t); 130.3 (q); 129.7 (t); 128.4 (t); 128.3 (t); 127.8 (t); 127.6 (t); 127.4 (q); 109.5 (q); 81.3 (t); 76.7 (t); 73.9 (s); 70.7 (s); 65.7 (s); 65.4 (s); 61.3 (p); 29.2 (s); 23.2 (s).

HRMS (EI): calc. $C_{24}H_{28}O_7$ $[M]^+$: 428.1835, found: 428.1842.

(1*R*,2R*,3R)-Benzoic acid-3-benzyloxymethyl-3-hydroxy-2-methoxy-4-oxo-cyclohexyl-ester 77**

See general procedure i)
Starting material: spiroketal **76** (45mg, 0.11mmol)
Yield: 23mg, 0.06mmol, 57%, colourless oil.
R_F-value: 0.9 hexane/ methyl *tert.*-butyl ether 1:3
^{1}H-NMR (400 MHz, $CDCl_3$): □ = 8.07-8.05 (m, 2H, Ar); 7.62-7.28 (m, 8H, Ar); 5.64 (m, 1H, C1-**H**); 4.60 (dd, 2H, J = 23.7, 12.2 OC**H**$_2$Ph); 3.91-3.89 (m, 2H, OH, C2-**H**); 3.75 (dd, 2H, J = 48.7, 10.2 OC**H**$_2$C) 3.59 (s, 3H, OC**H**$_3$); 2.54, 2.36-2.26 and 2.18 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (100.6 MHz, $CDCl_3$): □ = 208.4 (q); 165.9 (q); 137.2 (q); 133.4 (t); 129.7 (t); 128.5 (q, t); 128.0 (t); 127.8 (t); 84.4 (t); 81.7 (q); 73.9 (s); 72.4 (s); 71.4 (t); 62.1 (p); 34.7 (s); 25.1 (s).
HRMS (EI): calc. $C_{22}H_{24}O_6$ $[M]^+$: 384.1572, found: 384.1579.

(1*R*,2R*,3R)-2-Benzyloxymethyl-2,4-dihydroxy-3-methoxy-cyclohexanone 78**

See general procedure c)
Starting material: ester **77** (15mg, 0.04mmol)
Yield: 9mg, 0.032mmol, 80%, colourless oil.
R_F-value: 0.5 hexane/ethyl acetate 1:10
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 7.38-7.29 (m, 5H, Ar); 4.57 (dd, 2H, J = 35.9, 12.1, OC**H**$_2$Ph); 4.24-4.18 (m, 2H, C3-**H**, C2-**H**); 3.87-3.58 (m, 5H, OC**H**$_2$C, OCH$_3$); 2.50-2.41, 2.06 and 1.93 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 209.2 (q); 137.2 (q); 128.5 (t); 128.0 (t); 127.8 (t); 86.3 (t); 82.2 (q); 73.9 (s); 72.6 (s); 68.2 (t); 62.6 (p); 34.3 (s); 29.2 (s).
HRMS (EI): calc. $C_{15}H_{20}O_5$ $[M]^+$: 280.1310, found: 280.1317.

(1*R*,2R*,3R)-2-Chloro-acetyl)-carbamic acid-3-benzyloxymethyl-3-hydroxy-2-methoxy-4-oxo-cyclohexyl-ester 33**

See general procedure d)
Starting material: alcohol **78** (9mg, 0.033mmol)
Yield: 9mg, 0.023mmol, 70%, colourless oil.
R_F-value: 0.85 hexane/ethyl acetate 1:10
^{1}H-NMR (500 MHz, $CDCl_3$): □ = 8.29 (sbr, 1H, N**H**); 7.39-7.32 (m, 5H, Ar); 5.47 (m, 1H, C1-**H**); 4.61-4.56 (m, 2H, OC**H**$_2$Ph); 4.49 (sbr, 2H, C**H**$_2$Cl); 3.95 (s, 1H, O**H**); 3.87 (d, 1H, J = 1.9 C2-**H**); 3.67 (dd, 2H, J = 42.7; 10.1 OC**H**$_2$C); 3.56 (s, 3H, OC**H**$_3$); 2.56-2.53, 2.24 and 2.11 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C-NMR (125.8 MHz, $CDCl_3$): □ = 208.1 (q); 166.8 (q); 150.6 (q); 137.0 (q); 128.6 (t); 128.1 (t); 127.9 (t); 83.9 (t); 81.4 (q); 73.9 (s); 73.3 (t); 72.4 (s); 62.2 (p); 43.5 (s); 34.4 (s); 24.8 (s).
HRMS (EI): calc. $C_{18}H_{22}NO_7Cl$ $[M]^+$: 399.1084, found: 399.1092.

HUVEC Proliferation-Assay

HUVE-cells (PromoCell, Heidelberg, Germany) were added in 100µL medium (Endothelial Cell Growth Medium, PromoCell, Heidelberg, Germany) at a density of 3000-4000 cells/well to gelatine coated 96-well microtiter plates. After 24h the medium was aspirated and replaced by 90µL fresh medium. Serial dilutions of the fumagillin analogs were prepared in medium (+5% DMSO) and added (10µL/well). Controls received pure medium supplemented with 5% DMSO.
The cells were incubated for 72h. Cell proliferation was quantified by BrdU incorporation according to the manufacturer's protocol (Cell Proliferation ELISA-Kit (chemoluminecence), Roche, Germany). The incubation time after addition of BrdU was 4-6h. All data points were determined at least in triplicate.