Enantiomerically Enriched *trans*-Diols from Alkenes in One Pot: A Multicatalyst Approach

*Radim Hrdina, Christian E. Müller, Raffael C. Wende, Lukas Wanka, and Peter R. Schreiner**

Justus-Liebig-Universität, Institut für Organische Chemie, Heinrich Buff-Ring 58, D-35392, Germany

prs@org.chemie.uni-giessen.de

Electronic Supporting Information

Contents

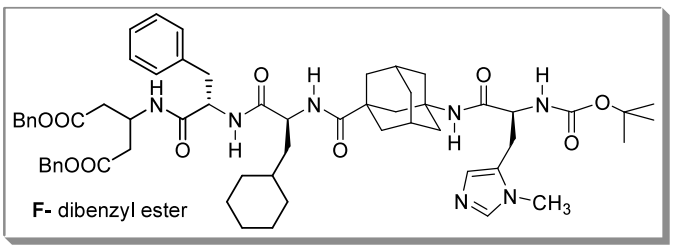
1. General remarks

Unless otherwise noted, chemicals were purchased from Acros Organics, Alfa Aesar, Aldrich, Lancaster, Merck, Novabiochem or Fluka at the highest purity grade available and were used without further purifications. All solvents were distilled prior to use. Toluene and $CHCl_3$ were distilled from appropriate drying agents prior to use and stored under argon atmosphere. Acetic anhydride was distilled prior to use and stored in a Schlenk tube. All catalytic reactions were carried out under an argon atmosphere employing oven- and flame-dried glassware. Column chromatography was conducted using J.T. Baker silica gel (0.063 – 0.200 mm) or, for flash column chromatography, Merck silica gel 60 (0.040 – 0.063 mm), respectively. TLC R_f values are reported. ^1H and ^{13}C NMR spectra were recorded on Bruker AV600, AV400 or AV200 spectrometers, respectively, using TMS as the internal standard with chemical shifts given in ppm relative to TMS or the respective solvent residual peaks. Infrared spectra were recorded on a Bruker IFS25 spectrometer. MS / HRMS were recorded on a Finnigan MAT95 sectorfield spectrometer; ESI mass spectra on a Finnigan LCQDuo spectrometer using methanol solutions of the respective compounds. High resolution ESI mass spectrometry was performed on a Thermo Scientific LTQ FT Ultra hybrid mass spectrometer using methanol solutions of the respective compounds. Optical rotation was measured by using a Jasco P-2000 polarimeter. GC analyses were performed by using Hewlett Packard 5890 and Carlo Erba 2900 gas chromatographs.

2. Synthesis of the peptide catalysts

Peptides **A**–**G** were synthesized in solution using Boc-strategy and EDC/HOBt mediated couplings. The general peptide synthesis is exemplarily given for **F**.

Synthesis of Boc-L-(π-Me)-His-^{A}Gly-L-Cha-L-Phe-$^{\beta}$Asp-(OBzl)$_2$:



Procedure for the EDC/HOBt peptide coupling in solution: An equimolar ratio of the *N*-Boc-protected amino acid (4 mmol) and the peptide fragment (4 mmol), 1.1 eq of EDC (4.4 mmol) and 1.1 eq of HOBt (4.4 mmol) were dissolved in dry dichloromethane. Then 1.1 eq of triethyl amine (4.4 mmol) were added and the solution was stirred overnight. The reaction mixture was added to 300 mL ethyl acetate and extracted with a 0.5 M citric acid solution (100 mL) and a saturated $NaHCO_3$ solution (100 mL). The organic phase was dried over $MgSO_4$ and the evaporation of the solvent gave the product. The same strategy was used for the esterification of Boc-$^{\beta}$Asp-OBzl with benzylalcohol to prepare the starting material Boc-$^{\beta}$Asp-$(OBzl)_2$. All peptide fragments were used for the next coupling step without further purification. The last coupling step with the peptide and *N*-Boc-π-Me-His was realized with a twofold excess of coupling reagents 2.2 eq of EDC (8.8 mmol), 2.2 eq of HOBt (8.8 mmol) and 2.2 eq of triethyl amine (8.8 mmol).

Procedure for the cleavage of the Boc-protecting group: The peptide (4 mmol) was dissolved in a solution of 4 M HCl in 1,4-dioxane (4 mL) and stirred for 30 min. The excessive HCl was removed by flushing the reaction mixture with argon for 30 min. After evaporation of the solvent under reduced pressure the deprotected peptides were used for further peptide coupling steps without purification.

After the last coupling step the crude peptide was purified by silica gel column chromatography. Eluting with $CHCl_3$/MeOH 9:1 afforded 2.3 g (2.18 mmol, 54 %) of colorless pentapeptide Boc-L-(π-Me)-His-^{A}Gly-L-Cha-L-Phe-$^{\beta}$Asp-$(OBzl)_2$.

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 0.75 – 1.00 (m, 2H), 1.05 – 1.30 (m, 6H), 1.42 (s, 9H), 1.43 – 1.57 (m, 1H), 1.57 – 1.75 (m, 12H), 1.80 – 2.00 (m, 6H), 2.15 – 2.20 (m, 2H), 2.38 v 2.48 (m, 1H), 2.52 – 2.70 (m, 3H), 2.90 – 3.10 (m, 5H), 3.58 (s, 3H), 4.20 – 4.30 (m, 1H), 4.36 – 4.44 (m, 1H), 4.48 – 4.64 (m, 2H), 5. 01 – 5.13 (m, 4H), 5.35 – 5.45 (m, 1H), 6.80 – 6.95 (m, 3H), 7.10 – 7.20 (m, 3H), 7.20 – 7.28 (m, 2H), 7.29 – 7.38 (m, 8H), 7.39 – 7.42 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 27.0, 28.3, 29.1, 31.5, 32.4, 33.6, 34.2, 35.1, 37.5, 37.7, 37.9, 38.1, 39.3, 40.1, 40.2, 42.2, 42.5, 43.0, 51.2, 52.2, 54.4, 66.5, 66.6, 76.8, 77.1, 77.4, 80.3, 126.9, 127.3, 128.0, 128.2, 128.2, 128.3, 128.6, 128.7, 129.3, 135.5, 135.5, 136.5, 138.0, 155.4, 169.8, 169.9, 170.7, 170.7, 172.1, 176.9;

IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3304, 3064, 3032, 2922, 2852, 1738, 1654, 1509, 1455, 1391, 1366, 1247, 1168, 1111, 1057, 1028, 910, 735, 698, 662, 498.

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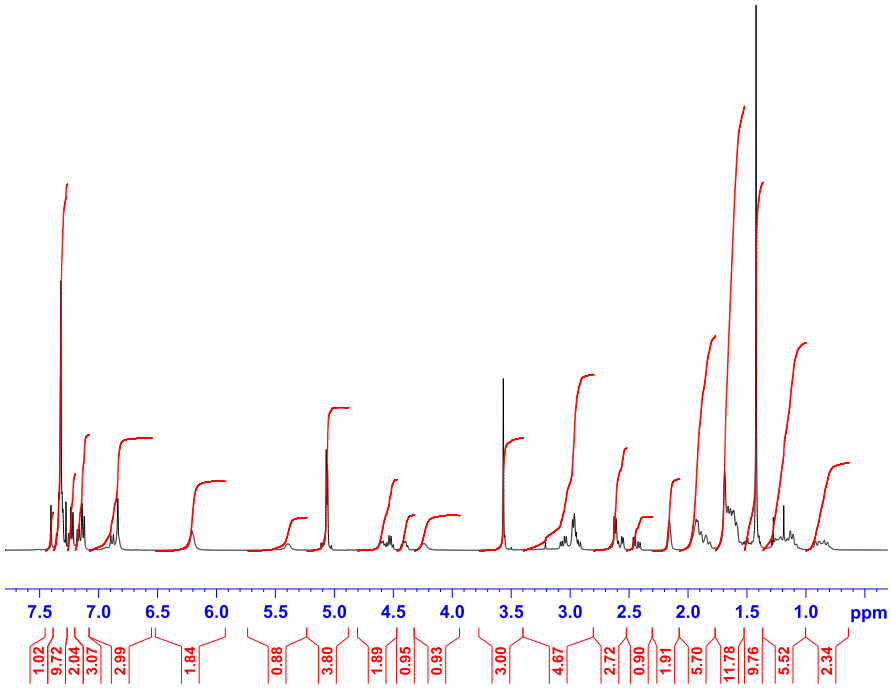
HR-ESI: m/z = 1056.5805 $[M+H]^+$ (calc. m/z =1056.5805).

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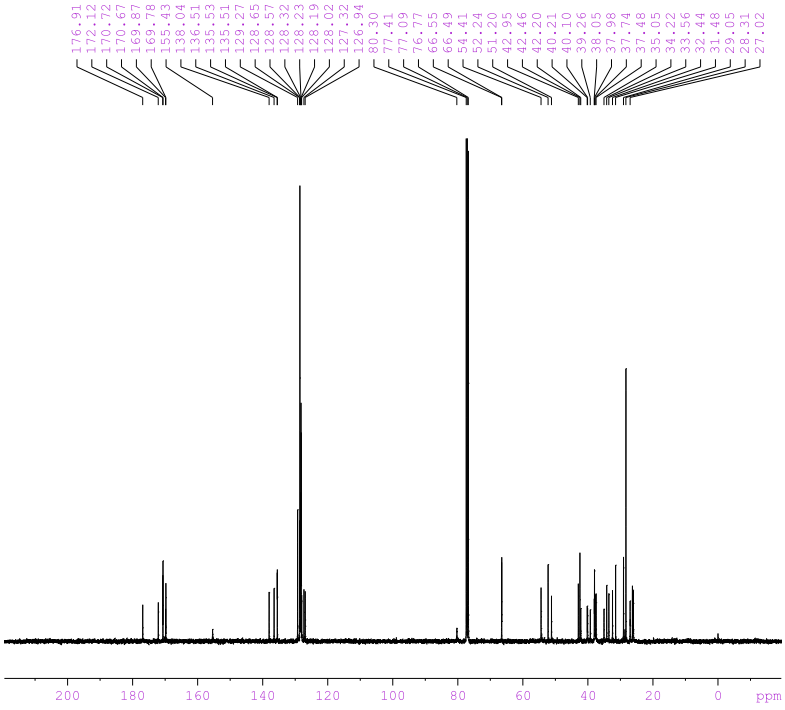


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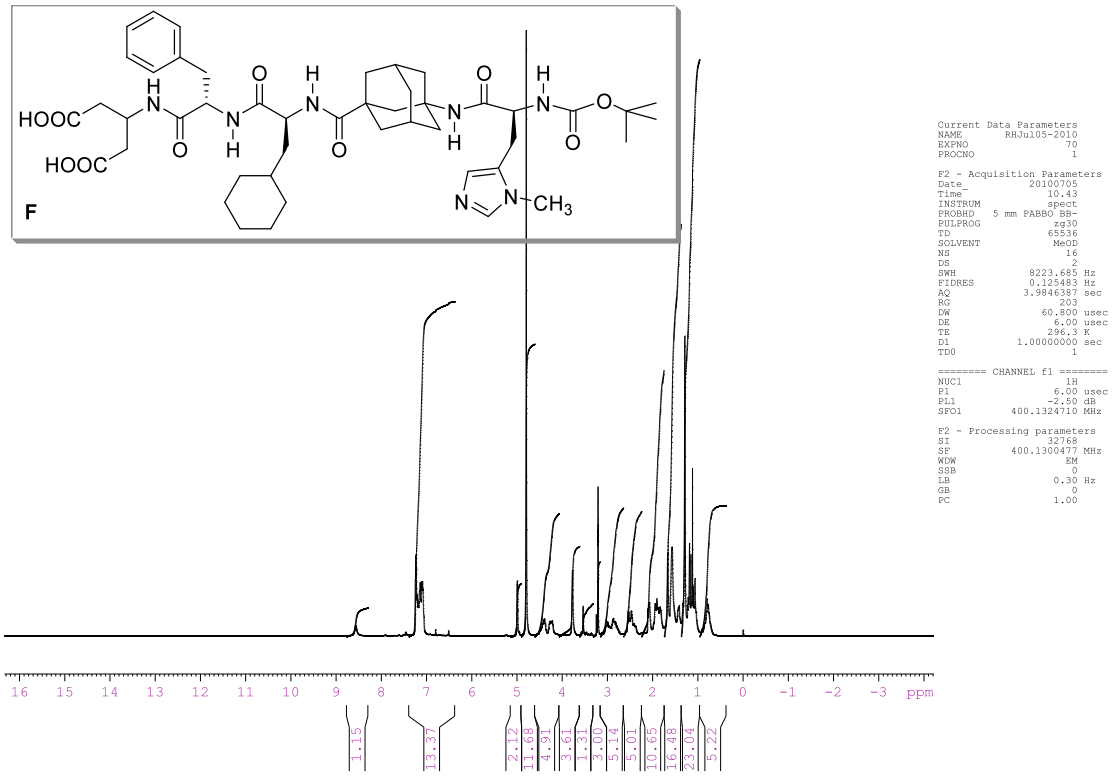
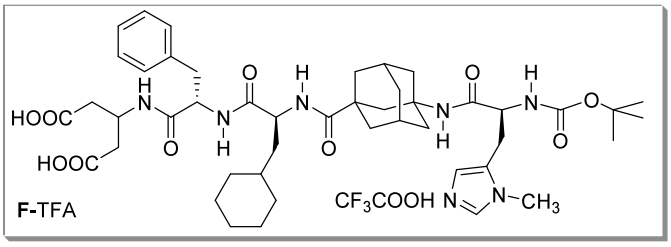
General procedure for the acetyl-protection of the *N*-terminus of the peptides: Prior to the acetyl introduction, the Boc protecting group of the peptide (1 mmol) was removed as described above, using 4 M HCl in 1,4-dioxane (2 mL). The excessive HCl was removed by flushing the reaction mixture with argon for 30 min. After evaporation of the solvent the deprotected peptide was dissolved in dry DCM (10 mL) by addition of Et_3N (20 mmol, 2.8 mL, 20 eq). The resulting solution was cooled to 0 °C and acetic anhydride (10 mmol, 945 µL, 10 eq) was added. The reaction mixture was allowed to warm to room temperature, while stirring for 1.5 h. The reaction mixture was then added to 300 mL ethyl acetate and extracted with 0.5 M citric acid solution (100 mL), saturated $NaHCO_3$ solution (100 mL). The organic phase was dried over $MgSO_4$ and the evaporation of the solvent gave the product. The crude product was purified by silica gel column chromatography eluting with $CHCl_3$/MeOH 9/1.

Procedure for the reductive benzylester-deprotection: The deprotection of the benzyl ester groups was performed by using 0.8 mmol of Boc-L-(π-Me)-His-^{A}Gly-L-Cha-L-Phe-$^{\beta}$Asp-$(OBzl)_2$ (844 mg) in 50 mL flask and 10% Pd/C (115 mg) in ^{t}BuOH (6 mL) under hydrogen atmosphere for 48 h. The reaction mixture was then filtrated through a frit and two times through filtration paper. The solvent was evaporated under reduced pressure and peptide **F** was used for catalysis without additional purification (purity of the corresponding peptides were controlled by NMR and ESI).



For entire characterizations the peptides **D**, **E**, **F** were purified by HPLC (HP/Agilent 1050 equipment and a Restek Viva C18 column (21.2 × 250 mm, 5 µM, 300 Å) employing a gradient elution at 3.5 mL/min flow using gradients of eluent E1 (0.1% TFA in water) and eluent E2 (0.1% TFA in acetonitrile): 27-37% E2 in E1 for 20 min, to 52% E2 in E1 65 min., then to 90% E2 in 70 min and at 90% E2 until 75 min.



^{1}H NMR (400 MHz, d_6-DMSO): δ/ppm = 0.69 – 0.92 (m, 2H), 0.98 – 1.22 (m, 5H), 1.33 (s, 9H), 1.38 – 1.51 (m, 2H), 1.53 – 1.69 (m, 10H), 1.69 – 1.78 (m, 2H), 1.80 – 2.05 (m, 6H), 2.05 – 2.21 (m, 2H), 2.90 – 3.00 (m, 5H), 3.83 (s, 3H), 4.20 – 4.35 (m, 3H), 4.38 – 4.50 (m, 1H), 6.80 – 7.00 (m, 1H), 7.15 – 7.30 (m, 6H), 7.30 – 7.50 (m, 2H), 7.55 – 7.75 (m, 2H), 8.05 – 8.15 (m, 1H), 8.95 (s, 1H), 12.30 (bm, 1H), 14.40 (bs, 1H).

^{13}C NMR (100 MHz, d_6-DMSO): δ/ppm = 25.6, 25.8, 26.0, 26.4, 28.0, 28.7, 31.6, 33.1, 33.6, 34.9, 37.4, 37.5, 37.8, 38.0, 38.4, 41.8, 42.0, 43.1, 50.3, 51.5, 52.5, 53,4, 78.4, 118.0, 126.2, 127.9, 129.2, 130.9, 135.3, 137.4, 155.0, 169.2, 170.0, 171.9, 172.1, 172.1, 175.9.

IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3407, 3067, 2925, 2855, 1666, 1526, 1451, 1393, 1368, 1280, 1252, 1202, 1139, 1057, 888, 836, 800, 748, 722, 703, 627.

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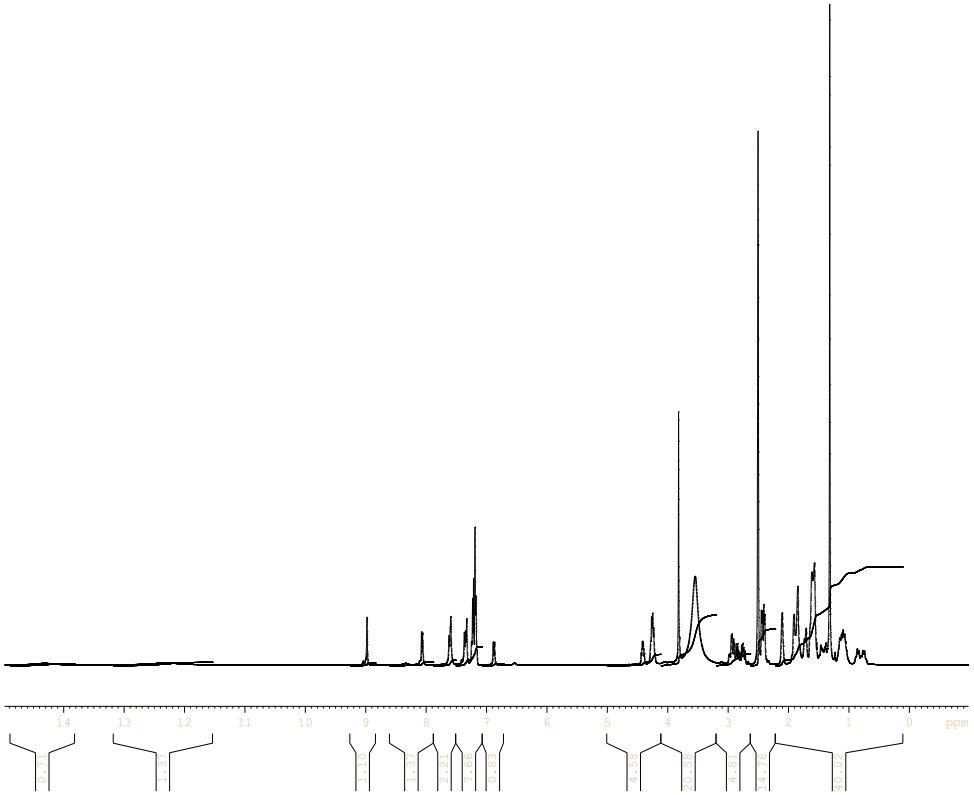
HR-ESI: m/z = 876.4860 $[M+H]^+$ (calc. m/z = 876.4866).



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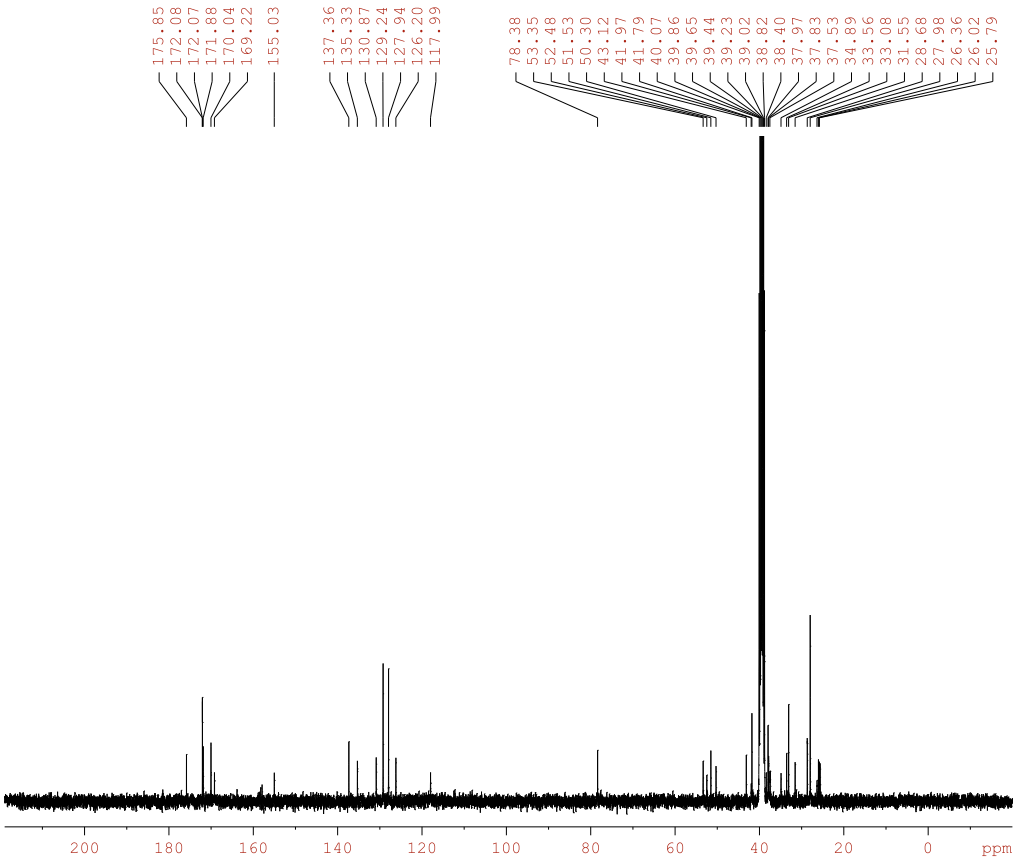


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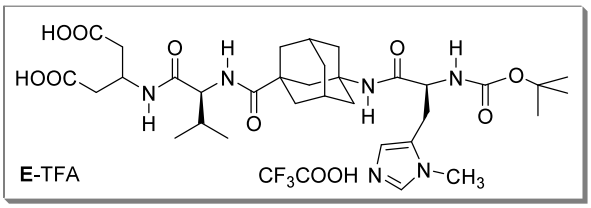

^{1}H NMR (400 MHz, d_6-DMSO): δ/ppm = 0.48 – 0.58 (m, 6H), 1.13 (s, 9H), 1.23 – 1.72 (m, 10H), 1.82 – 1.90 (m, 2H), 2.18 – 2.30 (m, 10H), 3.8 – 4.10 (m, 4H), 6.64 – 6.83 (m 2H), 7.08 (s, 1H), 7.36 (s, 1H), 7.76 – 7.80 (m, 2H), 8.74 (s, 1H), 12.30 (bm, 1H), 14.40 (bs, 1H).

^{13}C NMR (100 MHz, d_6-DMSO): δ/ppm = 18.1, 19.2, 26.3, 28.0, 28.7, 30.7, 33.1, 34.8, 37.6, 38.0, 42.1, 43.1, 51.5, 52.5, 57.4, 78.4, 118.0, 130.9, 155.0, 169.3, 170.4, 172.0, 172.1, 175.4.

IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3305, 3140, 3074, 2917, 1667, 1523, 1455, 1394, 1369, 1252, 1202, 1057, 1024, 888, 836, 799, 722, 671, 627.

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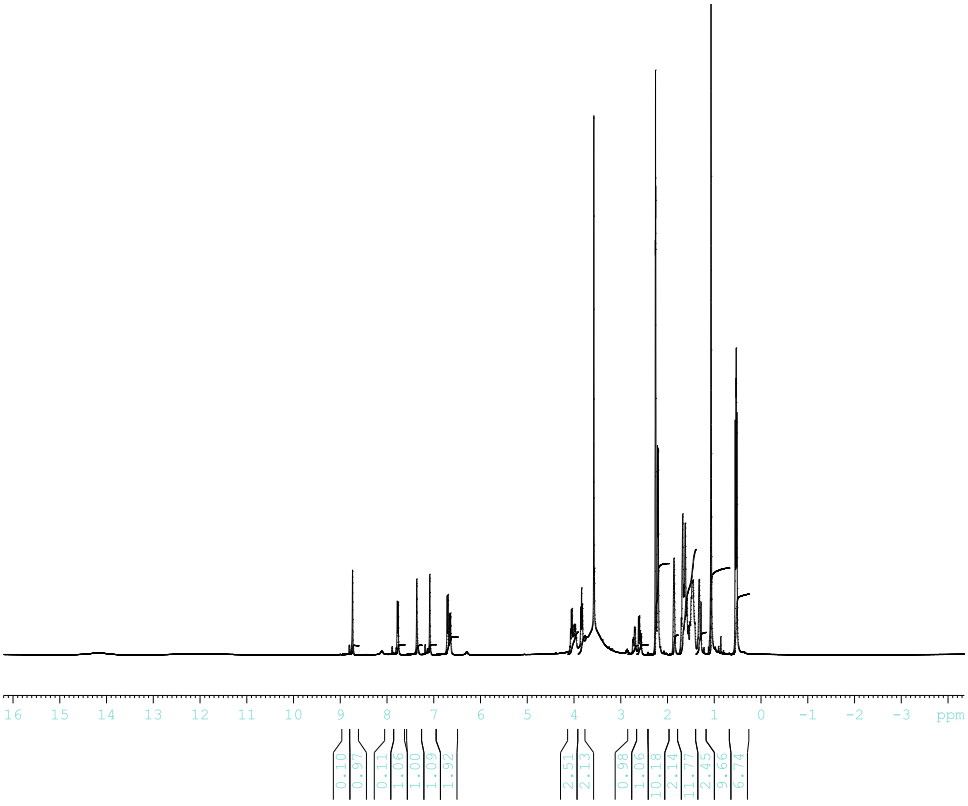
HR-ESI: m/z = 675.3697 $[M+H]^+$ (calc. m/z = 675.3712).

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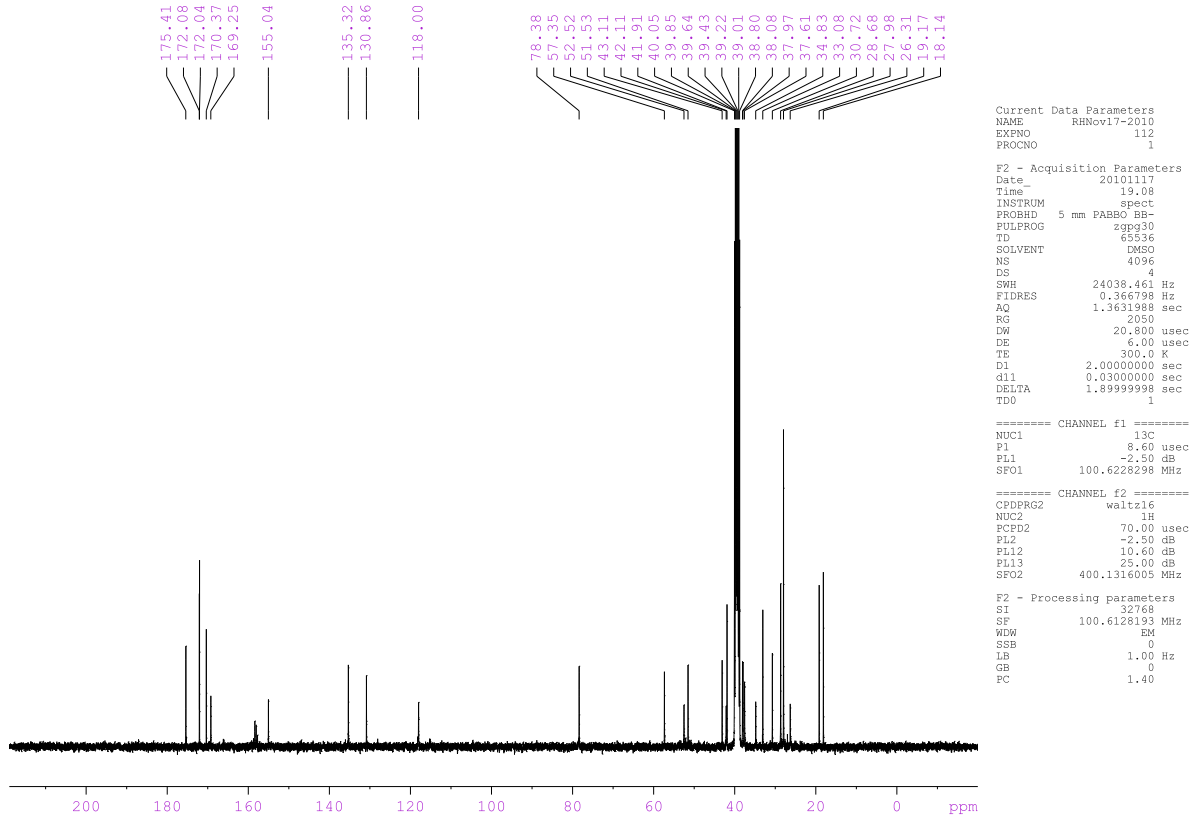

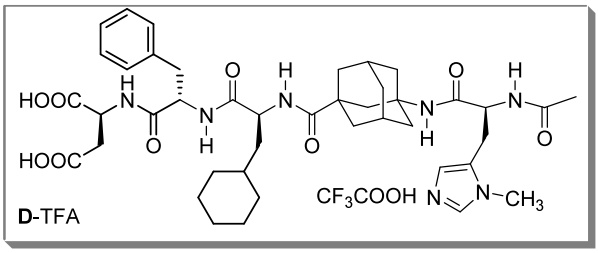

^{1}H NMR (400 MHz, d_6-DMSO): δ/ppm = 0.48 – 0.70 (m, 2H), 0.75 – 1.00 (m, 4H), 1.09 – 1.80 (m, 22H), 1.85 – 1.93 (m, 2H), 2.20 – 2.42 (m, 8H), 2.44 – 2.80 (m, 5H), 4.03 – 4.09 (m, 1H), 4.25 – 4.45 (m, 3H), 6.90 – 7.21 (m, 7H), 7.46 – 7.52 (m, 2H), 7.94 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 8.77 (s, 1H), 12.30 (bs, 1H), 14.40 (bs, 1H).

^{13}C NMR (100 MHz, d_6-DMSO): δ/ppm = 25.8, 26.0, 26.4, 28.7, 31.5, 33.1, 33.6, 34.9, 35.9, 37.4, 37.5, 37.7, 38.5, 40.3, 41.8, 41.9, 48.6, 50.2, 51.0, 51.6, 53.1, 117.8, 126.2, 127.2, 127.9, 129.3, 130.7, 135.4, 137.4, 169.0, 169.2, 170.7, 171.6, 172.0, 172.2, 175.8.

IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3417, 3069, 2925, 2855, 1724, 1658, 1532, 1450, 1380, 1344, 1285, 1202, 1139, 1030, 900, 836, 800, 722, 702, 625.

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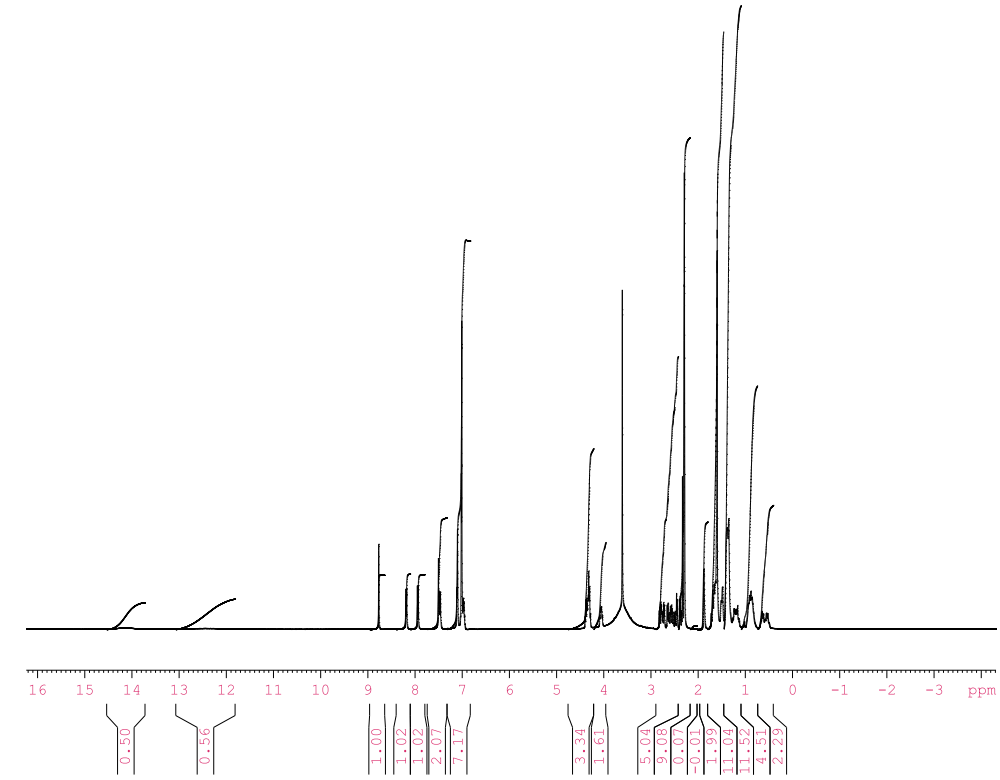
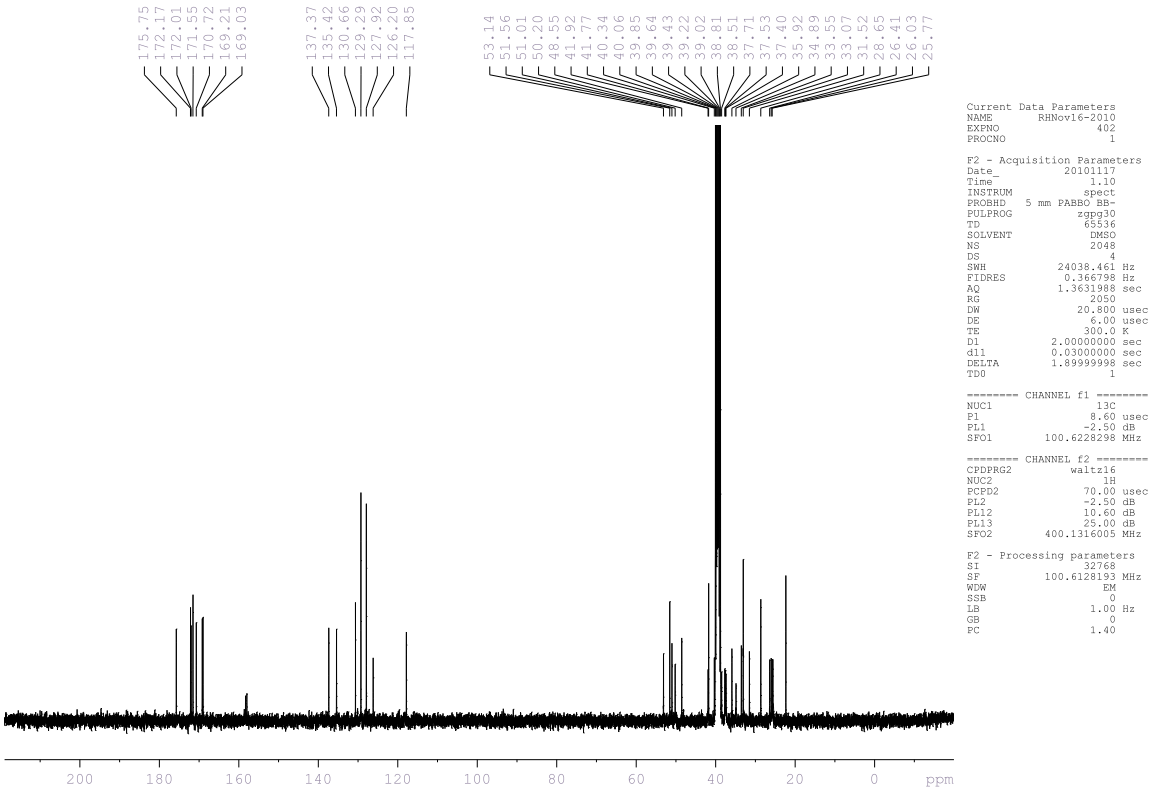
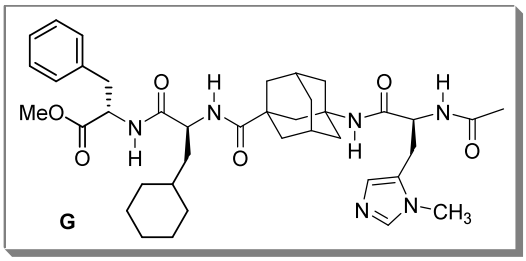
HR-ESI: m/z = 804.4291 $[M+H]^+$ (calc. m/z = 804.4291).







^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.34 (s, 1 H), 7.25 – 7.15 (m, 3 H), 7.08 – 7.03 (m, 2 H), 6.79 (s, 1 H), 6.75 (d, *J* = 7.8 Hz, 1 H), 6.57 (d, *J* = 7.9 Hz, 1 H), 6.10 (d, *J* = 7.9 Hz, 1 H), 6.00 (s, 1 H), 4.78 – 4.71 (m, 1 H), 4.48 – 4.39 (m, 2 H), 3.64 (s, 3 H), 3.56 (s, 3 H), 3.10 – 2.98 (m, 2 H), 2.98 – 2.84 (m, 2 H), 2.13 (m, 2 H), 1.96 – 1.81 (m, 6 H), 1.93 (s, 3 H), 1.71 – 1.51 (m, 12 H), 1.46 – 1.37 (m, 1 H), 1.23 – 0.99 (m, 4 H), 0.92 – 0.72 (m, 2 H).

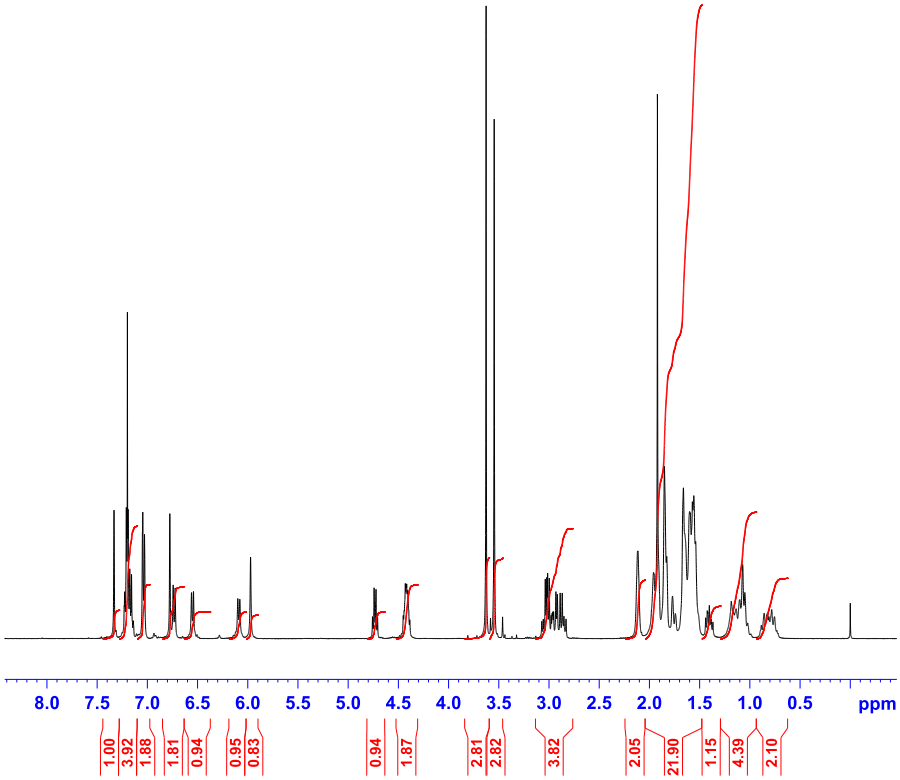
^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 176.3, 172.1, 171.7, 170.1, 169.5, 138.2, 135.8, 129.2, 128.6, 128.4, 127.1, 127.1, 53.3, 53.2, 52.5, 52.3, 50.7, 42.5, 42.2, 40.4, 40.2, 39.7, 38.2, 38.0, 37.9, 35.1, 34.2, 33.5, 32.8, 31.5, 29.1, 29.1, 27.1, 26.3, 26.2, 26.1, 23.2.

IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3295, 3063, 3030, 2921, 2852, 1745, 1653, 1510, 1449, 1371, 1342, 1283, 1217, 1176, 1110.

ESI: m/z = 703.2 $[M+H]^+$ (calc. m/z = 703.4 $[M+H]^+$); m/z = 725.7 $[M+Na]^+$ (calc. m/z = 725.4 $[M+Na]^+$); m/z = 1405.3 $[2M+H]^+$ (calc. m/z = 1405.8 $[2M+H]^+$); m/z = 1427.2 $[2M+Na]^+$
(calc. m/z = 1427.8 $[2M+Na]^+$).

HR-ESI: m/z = 703.4180 $[M+H]^+$ (calc. m/z = 703.4178 $[M+H]^+$).

Specific optical rotation: $[\alpha]_{589}^{26}$ = - 3,4 ° (*c* 0.5, $CHCl_3$)

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AQ              3.9846387 sec
RG                   256
DW                60.800 usec
DE                 6.00 usec
TE                296.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.60 usec
PL1                -2.50 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300337 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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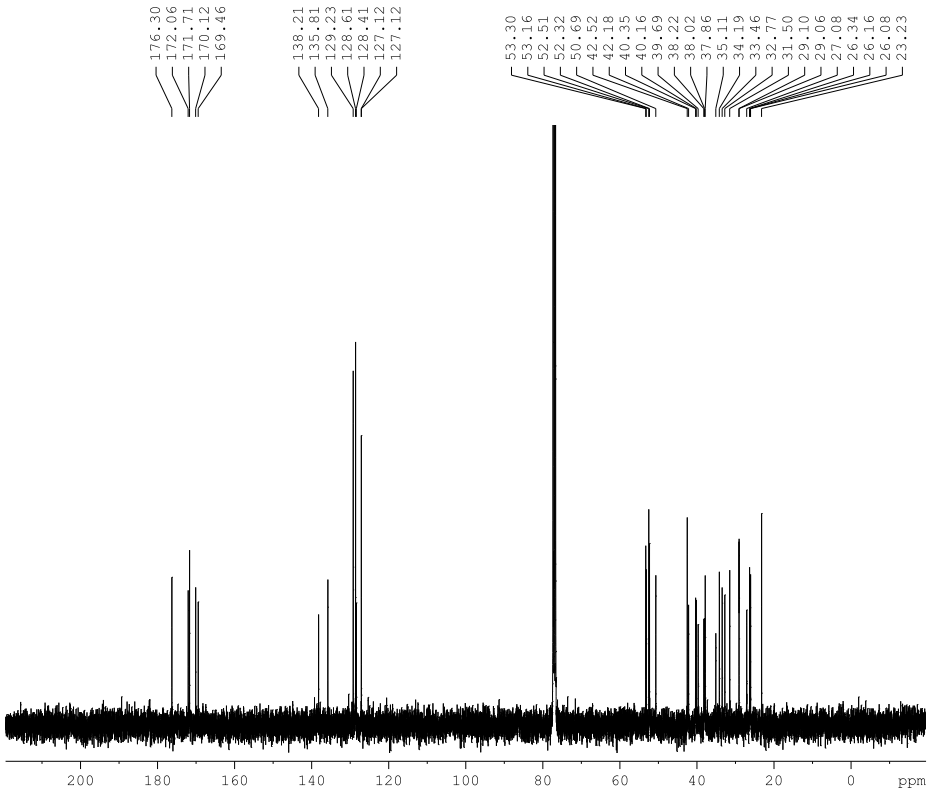


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Current Data Parameters
NAME          Aug25-2010
EXPNO                221
PROCNO                 1

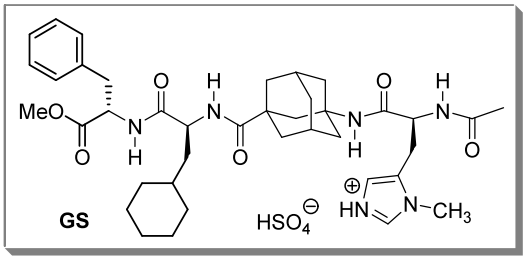
F2 - Acquisition Parameters
Date_           20100825
Time               16.35
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.00 usec
TE                297.3 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.60 usec
PL1                -2.50 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                -2.50 dB
PL12               10.60 dB
PL13               25.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Procedure for the formation of the bisulphate salt of peptide G: Acetyl-protected pentapeptide **G** (0.15 mmol, 105.5 mg) was dissolved in dry DCM (6 mL). Then concentrated sulfuric acid (0.15 mmol, 8.4 µL, 1 eq) was added. After stirring for 1 h the solvent was evaporated and the peptide bisulfate salt was dried in vacuo.



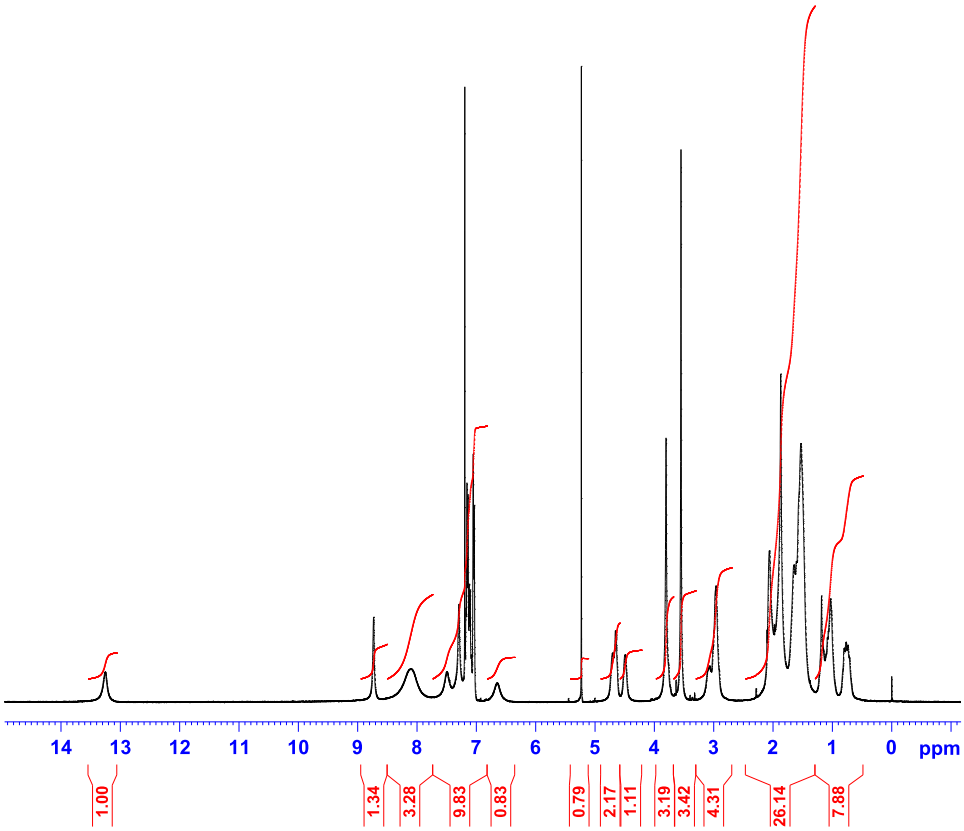
^{1}H NMR (400 MHz, $CDCl_3$/MeOD): δ/ppm = 8.64 (s, 1 H), 7.24 – 7.13 (m, 3 H), 7.10 (s, 1 H), 7.10 – 7.05 (m, 2 H), 4.67 – 4.61 (m, 1 H), 4.55 – 4.48 (m, 1 H), 4.40 – 4.34 (m, 1 H), 3.81 (s, 3 H), 3.62 (s, 3 H), 3.10 – 3.00 (m, 2 H), 3.00 – 2.90 (m, 2 H), 2.13 (m, 2 H), 1.98 – 1.81 (m, 6 H), 1.91 (s, 3 H), 1.72 – 1.51 (m, 12 H), 1.51 – 1.40 (m, 1 H), 1.23 – 0.99 (m, 4 H), 0.91 – 0.71 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$/MeOD): δ/ppm = 177.9, 173.6, 172.4, 172.2, 169.7, 136.7, 136.0, 131.2, 129.7, 129.0, 127.4, 118.8, 54.1, 53.9, 53.0, 52.7, 52.4 51.2, 42.9, 42.2, 40.3, 40.2, 39.7, 38.4, 38.1, 38.0, 35.6, 34.6, 33.8, 32.9, 29.6, 29.5, 26.8, 26.7, 26.6, 26.5, 22.8.

IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3289; 3136; 3064; 2921; 2853; 1746; 1652; 1542; 1449; 1371; 1342; 1283; 1222; 1081; 1048.

Specific optical rotation: $[\alpha]_{589}^{26}$ = - 19.2 ° (*c* 0.5, $CHCl_3$)

In $CDCl_3$:

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Current Data Parameters
NAME          Aug31-2010
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100831
Time               7.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                  203
DW               60.800 usec
DE                6.00 usec
TE               295.3 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.60 usec
PL1               -2.50 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300341 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```
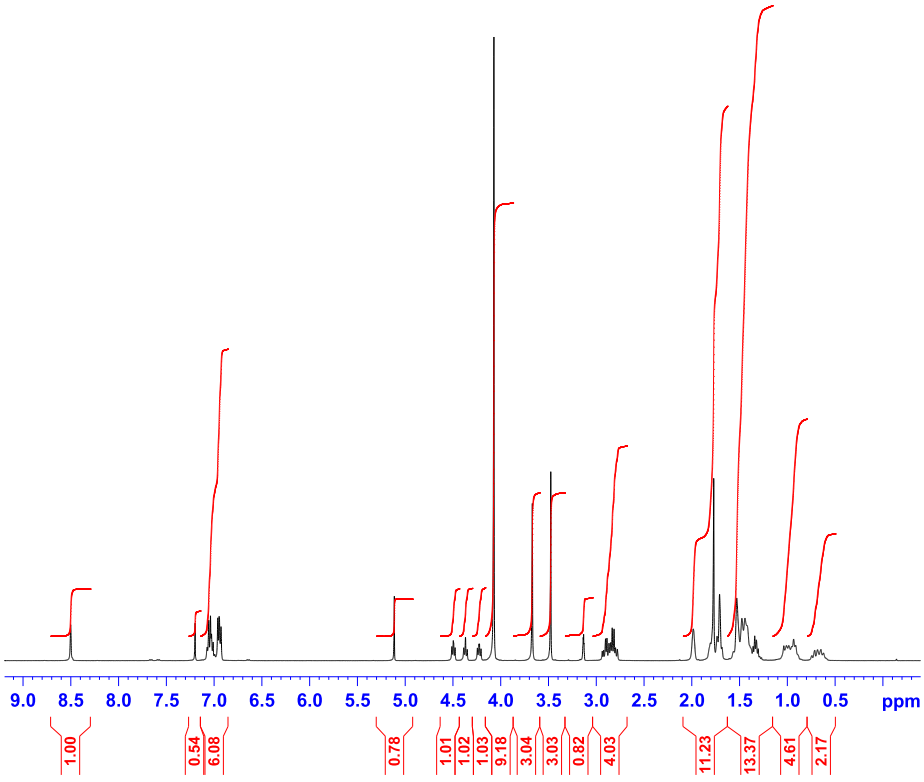

In $CDCl_3$/MeOD:

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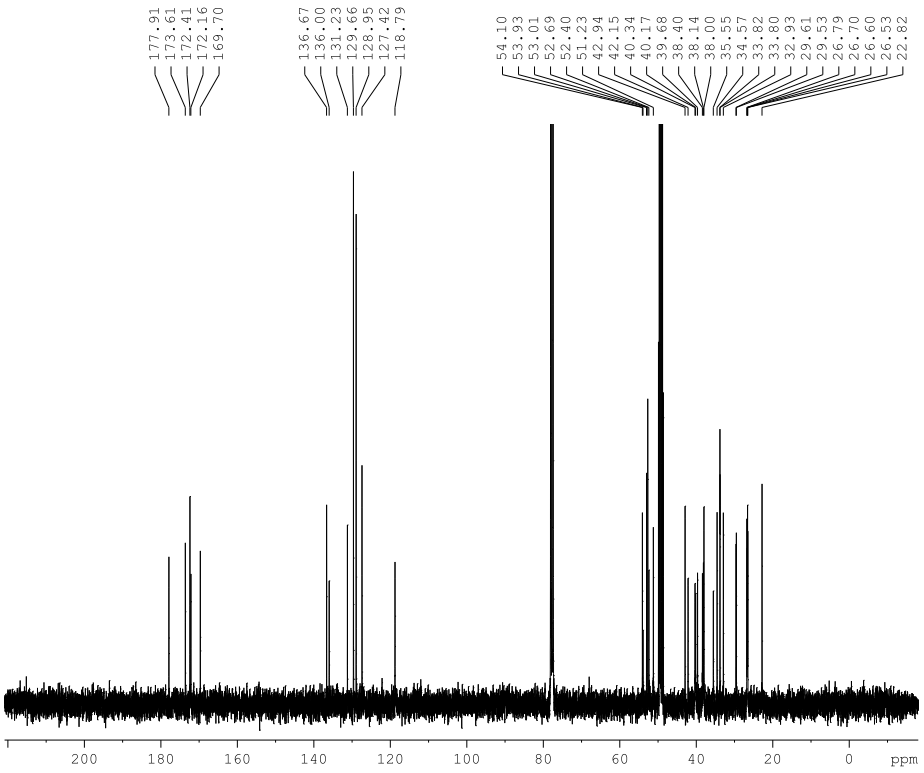
Current Data Parameters
NAME          Aug31-2010
EXPNO                 50
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100831
Time              10.20
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT           MeOD
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9846387 sec
RG                  161
DW               60.800 usec
DE                6.00 usec
TE               295.7 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                13.60 usec
PL1               -2.50 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1297057 MHz
WDW                  EM
SSB                   0
LB                0.30 Hz
GB                    0
PC                1.00
```

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Current Data Parameters
NAME          Aug31-2010
EXPNO                 51
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100831
Time              10.34
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT           MeOD
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.00 usec
TE               296.5 K
D1          2.00000000 sec
d11         0.03000000 sec
DELTA       1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.60 usec
PL1               -2.50 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             70.00 usec
PL2               -2.50 dB
PL12              10.60 dB
PL13              25.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6126261 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40
```
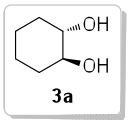

3. Catalysis

Scheme 2. *General procedure for sequence of reactions catalyzed by peptide* ***F*** *leading to chiral trans-alkane-1,2-diols:*

Catalyst **F** (0.05 mmol, 21.9 mg, 5%), alkene (1 mmol, 1 eq) and DIC (1.2 mmol, 185 µL, 1.2 eq) were dissolved in 2 mL DCM. To this mixture H_2O_2/H_2O water peroxide (130 µL, 1.2 eq) was added and the resulting reaction mixture was allowed to stir at room temperature for 24 h. After this time the addition of DIC (1.2 mmol, 185 µL, 1.2 eq) and 30% H_2O_2/H_2O water peroxide (130 µL, 1.2 eq) was repeated and the reaction was stirred under the same conditions for additional 24h. Then toluene (6 mL) was added, followed by the addition of H_2O (10 mmol, 180 µL, 10 eq) and hydrazine sulphate (0.1 mmol, 13 mg, 0.1 eq) and the reaction was stirred at room temperature for 18h. In the next step toluene (180 mL) and $^{i}Pr_2EtN$ (5.3 mmol, 876 µL, 5.3 eq) was added and the reaction was cooled to 0 °C. Ac_2O (5.3 mmol, 540.6 µL, 5.3 eq) was then added to start the acylation and the kinetic resolution was monitored by chiral GC. After 17 hours the reaction was quenched by methanol (10 mL), the solvents were evaporated under reduced pressure and the column chromatography on silicagel in hexane/ EtOAc 1/1 followed and afforded compounds (*S*,*S*)-**3** and (*R*,*R*)-**4** in summarized yields and optical purities.

Data for diol 3a:



3a

Assay of enantiomeric purity.

Enantiomers of diol **3a** were separated by chiral GC employing a 30 m FS-Hydrodex β-6TBDM column (Macherey Nagel).

T (Injector + Detector) = 250°C

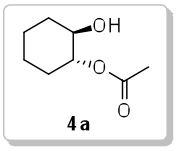
Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 140 °C isothermal

Retention Times: R_1 (*S*,*S*) = 10.9 min; R_2 (*R*,*R*) = 11.5 min

Data for monoacetate 4a:



Assay of enantiomeric purity.

Enantiomers of monoacetate **4a** were separated by chiral GC employing a 30 m FS-Hydrodex β-6TBDM column (Macherey Nagel).

T (Injector + Detector) = 250°C

Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 140 °C isothermal

Retention Times: R_1 (*S*,*S*) = 9.3 min; R_2 (*R*,*R*) = 9.6 min

Proof of GC retention times:

Racemic *trans*-cyclohexane-1,2-diol ((±)-**3a**) (0.345 g, 3.0 mmol) was treated with acetic anhydride (371 µL, 4 mmol) in the presence of *N,N*-dimethylaminopyridine (0.073 g, 0.6 mmol) in 20 mL dichloromethane and the resulting solution was stirred for 3 h at room temperature (25 °C). Dichloromethane was then removed *in vacuo*, and the monoacylated product ((±)-**4a)** was purified by silica flash gel chromatography (EtOAc, R_f (**4a**) = 0.42). Isolated racemic ((±)-**4a)** was characterized and then subjected to the chiral GC assay described above to proof the origin of the GC signals.

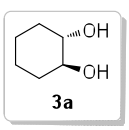
Analytical data of the monoacylated product ((±)-**4a**) were identical with those reported in literature.[1-3]

[1] C. Fang, T. Ogawa, H. Suemune, K. Sakai, *Tetrahedron*: *Asymmetry* **1991**, *2*, 389-398.

[2] A. Sevin, J.-M. Cense, *Bull. Chem. Soc. Fr*. **1974**, 918.

[3] V. Bódai, O. Orovecz, G. Szakács, L. Novák, L. Poppe, *Tetrahedron*: *Asymmetry* **2003**, *14*, 2605-2612.

Data for diol 3a:



Assay of enantiomeric purity.

Enantiomers of diol **3a** were separated by chiral GC employing a 30 m FS-Hydrodex β-6TBDM column (Macherey Nagel).

T (Injector + Detector) = 250°C

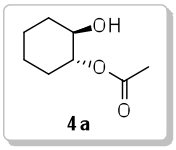
Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 140 °C isothermal

Retention Times: R_1 (*S*,*S*) = 10.9 min; R_2 (*R*,*R*) = 11.5 min

Data for monoacetate 4a:



Assay of enantiomeric purity.

Enantiomers of monoacetate **4a** were separated by chiral GC employing a 30 m FS-Hydrodex β-6TBDM column (Macherey Nagel).

T (Injector + Detector) = 250°C

Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 140 °C isothermal

Retention Times: R_1 (*S*,*S*) = 9.3 min; R_2 (*R*,*R*) = 9.6 min

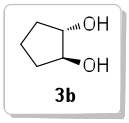
Proof of GC retention times:

Racemic *trans*-cyclohexane-1,2-diol ((±)-**3a**) (0.345 g, 3.0 mmol) was treated with acetic anhydride (371 µL, 4 mmol) in the presence of *N,N*-dimethylaminopyridine (0.073 g, 0.6 mmol) in 20 mL dichloromethane and the resulting solution was stirred for 3 h at room temperature (25 °C). Dichloromethane was then removed *in vacuo*, and the monoacylated product ((±)-**4a)** was purified by silica flash gel chromatography (EtOAc, R_f (**4a**) = 0.42). Isolated racemic ((±)-**4a)** was characterized and then subjected to the GC assay described above to proof the origin of the GC signals.

Analytical data of the monoacylated product ((±)-**4a**) were identical with those reported in literature.[1-3]

[1] C. Fang, T. Ogawa, H. Suemune, K. Sakai, *Tetrahedron*: *Asymmetry* **1991**, *2*, 389-398.
[2] A. Sevin, J.-M. Cense, *Bull. Chem. Soc. Fr*. **1974**, 918.
[3] V. Bódai, O. Orovecz, G. Szakács, L. Novák, L. Poppe, *Tetrahedron*: *Asymmetry* **2003**, *14*, 2605-2612.

Data for diol 3b:



3b

Diol (±)-**3b** was purchased from Aldrich at the highest purity grade available and was used without further purifications.

Assay of enantiomeric purity.

Enantiomers of diol **3b** were separated by chiral GC employing a 30 m FS-Hydrodex β-TBDAc column (Macherey Nagel).

T (Injector + Detector) = 250 °C

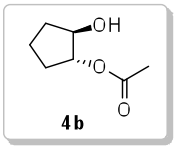
Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 100 °C – 180 °C, 2 °C/min

Retention Times: R_1 (*S*,*S*) = 26.1 min; R_2 (*R*,*R*) = 26.5 min

Data for monoacetate 4b:



4b

Assay of enantiomeric purity.

Enantiomers of monoacetate **4b** were separated by chiral GC employing a 30 m FS-Hydrodex β-TBDAc column (Macherey Nagel).

T (Injector + Detector) = 250°C

Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 100 °C – 180 °C, 2 °C/min

Retention Times: R_1 (*R*,*R*) = 14.7 min; R_2 (*S*,*S*) = 15.5 min

Proof of GC retention times:

Racemic *trans*-cyclopentane-1,2-diol ((±)-**3b**) (0.306 g, 3.0 mmol) was treated with acetic anhydride (371 µL, 4 mmol) in the presence of *N,N*-dimethylaminopyridine (0.073 g, 0.6 mmol) in 20 mL dichloromethane and the resulting solution was stirred for 3 h at room temperature (25 °C). Dichloromethane was then removed *in vacuo*, and the monoacylated product (±)-**4b** was purified by silica flash gel chromatography (EtOAc, R_f ((±)-**4b**) = 0.53). Isolated racemic (±)-**4b** was characterized and then subjected to the GC assay described above to proof the origin of the GC signals.

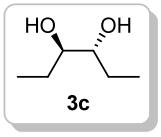
Analytical data of the monoacylated product (±)-**4b** were identical to those reported in literature.[1-3]

[1] C. Fang, T. Ogawa, H. Suemune, K. Sakai, *Tetrahedron*: *Asymmetry* **1991**, *2*, 389-398.

[2] A. Sevin, J.-M. Cense, *Bull. Chem. Soc. Fr*. **1974**, 918.

[3] V. Bódai, O. Orovecz, G. Szakács, L. Novák, L. Poppe, *Tetrahedron*: *Asymmetry* **2003**, *14*, 2605-2612.

Data for diol 3c:



Analytical data of the diol (±)-**3d** were identical with those reported in literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 3.40 – 3.33 (m, 2 H); 1.99 (bs, 2 H, OH); 1.65 – 1.39 (m, 4 H); 1.00 (t, *J* = 7.5 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 75.5; 26.5; 10.0.

[4] O. Bartolini, G. Fantin, M. Fogagnolo, P. P. Giovannini, A. Guerrini, A. Medici, *J. Org. Chem.* **1997**, *62*, 1854-1856.

Assay of enantiomeric purity.

Enantiomers of diol **3c** were separated by chiral GC employing a 30 m FS-Hydrodex β-6TBDM column (Macherey Nagel).

T (Injector + Detector) = 250°C

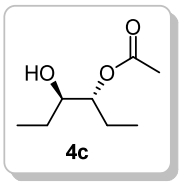
Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 80 °C – 120 °C, 1 °C/min

Retention Times: R_1 (*S*,*S*) = 21.2 min; R_2 (*R*,*R*) = 23.7 min

Data for monoacetate 4c:



4c

Assay of enantiomeric purity.

Enantiomers of monoacetate **4c** were separated by chiral GC employing a 30 m FS-Hydrodex β-6TBDM column (Macherey Nagel).

T (Injector + Detector) = 250°C

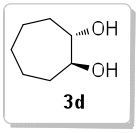
Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 80 °C – 120 °C, 1 °C/min

Retention Times: R_1 (*S*,*S*) = 21.7 min; R_2 (*R*,*R*) = 30.9 min

Data for diol (3d):



3d

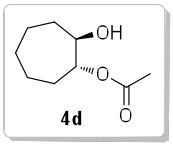
Diol (±)**-3d** was synthesized according to the method of the *Organikum*[6] (see chapter 3). Analytical data of the diol (±)**-3d** were identical with those reported in literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 3.37 – 3.36 (m, 2 H); 2.67 (bs, 2 H, OH); 1.87 – 1.77 (m, 2 H); 1.59 – 1.57 (m, 2 H); 1.49 – 1.39 (m, 6 H).
^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 77.9; 32.4; 26.4; 22.1.

[6] Autorenkollektiv. *Organikum*: *Organisch-chemisches Grundpraktikum*, 19th ed.; Deutscher Verlag der Wissenschaften: Leipzig, **1993**.
[7] L. N. Owen, G. S. Saharia, *J. Chem. Soc.* **1953**, 2582.

Assay of enantiomeric purity.
Enantiomers of diol **3d** were separated by chiral GC employing a 30 m FS-Hydrodex β-6TBDM column (Macherey Nagel).
T (Injector + Detector) = 250°C
Splitflow = 80 mL/min
Precolumn pressure = 0.8 bar
Conditions: 100 °C – 180 °C, 2 °C/min
Retention Times: R_1 (*S*,*S*) = 27.24 min; R_2 (*R*,*R*) = 27.73 min

Data for monoacetate (4d):



Assay of enantiomeric purity.
Enantiomers of monoacetate **4d** were separated by chiral GC employing a 30 m FS-Hydrodex β-6TBDM column (Macherey Nagel).
T (Injector + Detector) = 250°C
Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 100 °C – 180 °C, 2 °C/min

Retention Times: R_1(*S*,*S*) = 23.97 min; R_2 (*R*,*R*) = 24.20 min

Proof of GC retention times:

Racemic *trans*-cycloheptane-1,2-diol ((±)-**3d**) (0.391 g, 3.0 mmol) was treated with acetic anhydride (371 µL, 4 mmol) in the presence of *N,N*-dimethylaminopyridine (0.073 g, 0.6 mmol) in 20 mL dichloromethane and the resulting solution was stirred for 3 h at room temperature (25 °C). Dichloromethane was then removed *in vacuo*, and the monoacylated product (±)-**4d** was purified by silica flash gel chromatography (EtOAc, R_f ((±)-**4d**) = 0.49). Isolated racemic (±)-**4d** analytically characterized and then subjected to the GC assay described above to proof the origin of the GC signals.

Analytical data of the monoacylated product ((±)-**4d**) were identical to those reported in literature.[3]

[3] V. Bódai, O. Orovecz, G. Szakács, L. Novák and L. Poppe, *Tetrahedron*: *Asymmetry* **2003**, *14*, 2605-2612.

Scheme 3. *General procedure for kinetic resolution of trans-cyclohexane-1,2-diol with the bi-functional catalysts:*

Catalyst **X** (0.0005 mmol, 2 mol%) was dissolved in 4.5 mL of toluene and the resulting solution was cooled to 0 °C. $^{i}Pr_2EtN$ (21.9 µL, 0.1325 mmol, 5.3 eq) and Ac_2O (12.5 µL, 0.1325 mmol, 5.3 eq) were added *via* syringe and subsequently the reaction was started by the addition of *trans*-cyclohexane-1,2-diol (2.9 mg, 0.025 mmol). After 3 h the reaction was quenched with 0.5 mL MeOH and the sample was directly subjected to the chiral GC assay.

Table 1. *Epoxidation of cyclohexene using phthalic and terephthalic acid as catalyst:*

To a mixture of (tere)pthalic acid (3.32 mg, 2 mol%), cyclohexene (101 µL, 1 mmol), 30% H_2O_2/H_2O (132 µL, 1.2 mmol) and dodecane (22.7 µL, 0.1 mmol) as internal standard in DCM (1 mL), diisopropylcarbodiimide DIC (185 µL, 1.2 mmol) was added and the reaction mixture was stirred at r.t. and monitored by GC-MS.

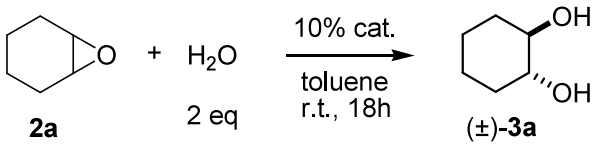
Table 1. *Epoxidation of cyclohexene using cat.* ***D–F****:*

To a mixture of cat. (0.01 mmol, 5 mol%), cyclohexene (20 µL, 0.2 mmol), 30% H_2O_2/H_2O (26 µL, 0.24 mmol) and dodecane (4.7 µL, 0.02 mmol) as internal standard in DCM (400 µL), diisopropylcarbodiimide DIC (37 µL, 0.24 mmol) was added and the reaction mixture was stirred at r.t. for 24 h. Then again 30% H_2O_2/H_2O (26 µL, 0.24 mmol) and diisopropylcarbodiimide DIC (37 µL, 0.24 mmol) were added and the reaction mixture was stirred at r.t. for additional 24 h. After this time the reaction yield was determined by GC-MS.

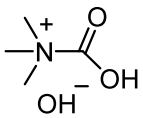
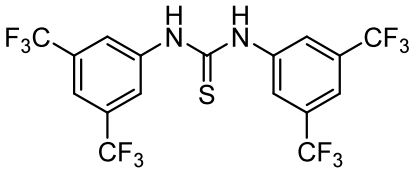
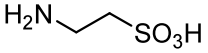
Scheme 4. *General procedure for the organocatalytic opening of epoxides using hydrazine sulfate as catalyst:*

To the mixture of hydrazine sulfate (13.7 mg, 0.1 mmol), epoxide **2** (1 mmol) and dodecane (22.7 µL, 0.1 mmol) as internal standard in 1 mL of toluene, water (180 µL, 10 mmol) was added and the reaction mixture was stirred at r.t. for 18 h. The reaction yield was determined using GC-MS.

For the ***epoxide opening*** with small amounts of water in an organic solvent (toluene) we screened a large variety of small organocatalysts using cyclohexene epoxide as model compound.



2a (±)-**3a**

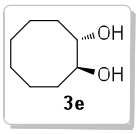
catalyst	yield of **3a**	catalyst	yield of **3a**
DMAP	0 %		0 %
$NaHCO_3$	0 %		
NaOH	0 %		
NH_4Cl	0 %		0 %
$CH_3COOCOCH_3$	0 %		
CH_3COOH	traces		
p-tolSO$_3$H	traces	$H_3N^+–NH_2\ HSO_4^-$	20 %
	0 %	[b] $H_3N^+–NH_2\ HSO_4^-$	100%

b: 20% hydrazinium sulphate, 20 eq H_2O

Scheme 5. *Values in brackets indicate a preparative experiment at a 1.0 mmol scale:*
Cat. **GS** (0.005 mmol, 4.0 mg, 5 mol %) [0.05 mmol, 40.0 mg, 5 mol%] and cyclohexene oxide (0.1 mmol, 10.1 µL, 1eq) [1.0 mmol, 98.1 mg, 101 µL] were dissolved in toluene (100 µL) [1 mL] with dodecane as internal standard (0.01 mmol, 2.27 µL, 0.1 eq) and water (2 mmol, 36 µL, 20 eq) [20 mmol, 360 µL, 20 eq] was added. The reaction mixture was stirred at room temperature for 18h. In the next step toluene (18 mL) [180 mL] and $^{i}Pr_2EtN$ (0.53 mmol, 90.1 µL, 5.3 eq) [5.3 mmol, 901 µL, 5.3 eq] were added and the reaction was cooled to 0 °C. Ac_2O (0.53 mmol, 50.1 µL, 5.3 eq) [5.3 mmol, 501 µL, 5.3 eq] was then added to start the acylation and the kinetic resolution was monitored by chiral GC.
The reaction mixture was then quenched with 10 mL of methanol, filtered through silicagel (30 g) suspended with ethyl acetate, and washed with ethyl acetate to remove the catalyst. After evaporation of the solvent *in vacuo* the products were purified by column chromatography. Eluting with ethyl acetate afforded 85.5 mg (0.54 mmol; 54%; 65% *ee*) of the acetylated diol (R_f = 0.46) and 28.3 mg (0.24 mmol; 24%; > 99% *ee*) of the diol (R_f = 0.22).

Protocol with TFA as reactant for opening of epoxide
To a mixture of cat. **G** (0.005 mmol, 3.5 mg, 5 mol%), cyclooctene oxide (0.1 mmol, 12.6 mg) and dodecane as internal standard (0.01 mmol, 2.27 µL, 0.1 eq) in toluene (100 µL) was added trifluoroacetic acid (0.1 mmol, 7.7 µL). After stirring for 3 d at room temperature water (0.2 mmol, 3.6 µL, 2.0 eq) and $^{i}Pr_2EtN$ (0.53 mmol, 90.1 µL, 5.3 eq) were added and the reaction mixture was stirred for 24 h. In the next step toluene (16 mL) was added and the reaction was cooled to 0 °C. Ac_2O (0.53 mmol, 50.1 µL, 5.3 eq) was then added to start the acylation and the kinetic resolution was monitored by chiral GC.

Data for diol (3e):



3e

Analytical data of the diol ((±)-**3e**) were identical to those reported in literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 3.55 – 3.49 (m, 2 H); 2.64 (bs, 2 H, OH); 1.83 – 1.76 (m, 2 H); 1.67 – 1.58 (m, 4 H); 1.55 – 1.40 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 76.2; 31.9; 26.2; 23.7.

[8] A. C. Cope, S. W. Fenton, C. F. Spencer, *J. Am. Chem. Soc.* **1952**, *74*, 5884.

Assay of enantiomeric purity.

Enantiomers of diol **3e** were separated by chiral GC employing a 30 m FS-Hydrodex β-6TBDM column (Macherey Nagel).

T (Injector + Detector) = 250°C

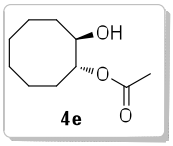
Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 160 °C isothermal

Retention Times: R_1 (*S*,*S*) = 13.24 min; R_2 (*R*,*R*) = 13.50 min

Data for monoacetate (4e):



Assay of enantiomeric purity.

Enantiomers of monoacetate **4e** were separated by chiral GC employing a 30 m Chiraldex G-TA column (Astech).

T (Injector + Detector) = 250°C

Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 100 °C – 180 °C, 2 °C/min

Retention Times: R_1 (*R*,*R*) = 25.63 min; R_2 (*S*,*S*) = 26.31

Proof of GC retention times:

Racemic *trans*-cyclooctane-1,2-diol ((±)-**3e**) (0.433 g, 3.0 mmol) was treated with acetic anhydride (371 µL, 4 mmol) in the presence of *N,N*-dimethylaminopyridine (0.073 g, 0.6 mmol) in 20 mL dichloromethane and the resulting solution was stirred for 3 h at room temperature (25 °C). Dichloromethane was then removed *in vacuo*, and the monoacylated product ((±)-**4e**) was purified by silica flash gel chromatography (EtOAc, R_f ((±)-**4e**) = 0.50).

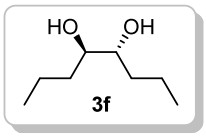
Isolated racemic ((±)-**4e**) was characterized and then subjected to the GC assay described above to proof the origin of the GC signals.

Analytical data of the monoacylated product ((±)-**4e**) were identical to those reported in literature.[3,9]

[3] V. Bódai, O. Orovecz, G. Szakács, L. Novák and L. Poppe, *Tetrahedron*: *Asymmetry* **2003**, *14*, 2605-2612.

[9] G. H. Posner, D. Z. Rogers, *J. Am. Chem. Soc*. **1977**, *99*, 8208-8214.

Data for diol 3f:



Analytical data of the diol ((±)-**3f**) were identical to those reported in literature.[10]

^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 3.46 – 3.33 (m, 2 H); 2.94 (bs, 2 H, OH); 1.62 – 1.30 (m, 8 H); 1.05 – 0.85 (m, 6 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 74.2; 35.6; 18.8; 14.0.

[10] A. Nelson, S. Warren, *J. Chem. Soc., Perkin Trans. 1* **1999**, 3425-3433.

Assay of enantiomeric purity.

Enantiomers of diol **3f** were separated by chiral GC employing a 30 m FS-Hydrodex β-TBDAc column (Macherey Nagel).

T (Injector + Detector) = 250°C

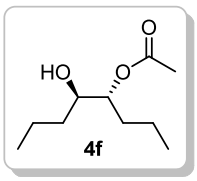
Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 100 °C – 160 °C, 2 °C/min

Retention Times: R_1 (*R*,*R*) = 21.1 min; R_2 (*S*,*S*) = 21.4 min

Data for monoacetate 4f:



Assay of enantiomeric purity

Enantiomers of monoacetate **4f** were separated by chiral GC employing a 30 m Chiraldex G-TA column (Astech).

T (Injector + Detector) = 250 °C

Splitflow = 80 mL/min

Precolumn pressure = 0.8 bar

Conditions: 100 °C – 150 °C, 2 °C/min

Retention Times: R_1 (*S*,*S*) = 15.3 min; R_2 (*R*,*R*) = 15.9 min

Analytical data of the monoacylated product ((±)-**4f**) were identical to those reported in literature.[11]

[11] A. Lethbridge, R. O. C. Norman, C. B. Thomas, W. J. E. Parr, *J. Chem. Soc. Perkin Trans 1* **1975**, 231-241.

Scheme 6. *One pot epoxidation of cyclohexene catalyzed by phthalic acid, subsequent opening with water catalyzed by* ***GS*** *and acetylation catalyzed by the N-π-methyl histidine moiety of* ***G****. Values in brackets indicate a preparative experiment at a 1.0 mmol scale:*

To a mixture of phthalic acid (1.66 mg, 0.01 mmol, 5 mol%) [8.3 mg, 0.05 mmol, 5 mol%], **GS** (8.01 mg, 5 mol%) [40.0 mg, 0.05 mmol, 5 mol%], cyclohexene (0.2 mmol, 20.3 µL) [1.0 mmol, 82.2 mg, 101 µL], 30% H_2O_2/H_2O (24.5 µL, 0.24 mmol, 1.2 eq. H_2O_2) [130 µL, 1.2 mmol, 1.2 eq. H_2O_2], and dodecane (0.02 mmol, 4.54 µL, 0.1 eq) as internal standard in toluene (200 µL) [1 mL], diisopropylcarbodiimide DIC (0.24 mmol, 37.2 µL, 1.2 eq) [1.2 mmol, 185 µL, 1.2 eq] was added and the reaction mixture was stirred at r.t. for 24 h. After this time the addition of DIC (0.24 mmol, 37.2 µL, 1.2 eq) [1.2 mmol, 185 µL, 1.2 eq] and 30% H_2O_2/H_2O (24.5 µL, 0.24 mmol, 1.2 eq. H_2O_2) [130 µL, 1.2 mmol, 1.2 eq. H_2O_2] was repeated and the reaction was stirred under the same conditions for additional 24 h. This was followed by the addition of H_2O (4.0 mmol, 72 µL, 20 eq) [20 mmol, 360 µL, 20 eq] and the reaction was stirred for 24 h. The yield of the diol was determined by GC-MS. In the next step

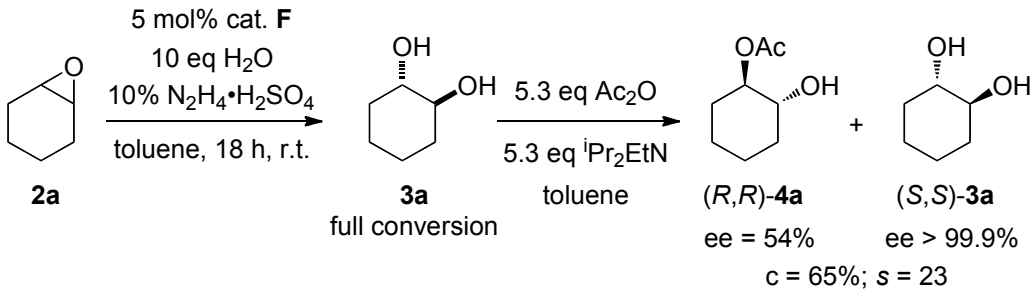
toluene (36 mL) [180 mL] and $^{i}Pr_2EtN$ (1.06 mmol, 180.2 µL, 5.3 eq) [5.3 mmol, 901 µL, 5.3 eq] was added and the reaction was cooled to 0 °C. Ac_2O (1.06 mmol, 100.2 µL, 5.3 eq) [5.3 mmol, 501 µ L, 5.3 eq] was added to start the acylation and the kinetic resolution was monitored by chiral GC. After 3 hours [4 h] the reaction was quenched by methanol (2 mL) [20 mL], the *s*-value, the conversion and the *ee* of the product and the diol were determined by chiral GC.

The reaction mixture was quenched with 10 mL methanol, filtered through silicagel (30 g) suspended with ethyl acetate, and washed with ethyl acetate to remove the catalyst. After evaporation of the solvent *in vacuo* the products were purified by column chromatography. Eluting with ethyl acetate afforded 70.5 mg (0.45 mmol; 45%; 59% *ee*) of the acetylated diol (R_f = 0.46) and 41.2 mg (0.36 mmol; 36%; > 99% *ee*) of the diol (R_f = 0.22).

Additional Scheme:

Scheme S1. *Control of the selectivity with cat F:*

Cat. **F** (0.005 mmol, 4.4 mg, 5 mol%), hydrazine sulphate (0.01 mmol, 1.3 mg, 10 mol%), and cyclohexene oxide (0.1 mmol, 10.1 µ L, 1eq), were dissolved in toluene (100 µ L) with dodecane as internal standard (0.01 mmol, 2.27 µL, 0.1 eq) and water (1 mmol, 18 µL, 10 eq) was added. The reaction mixture was stirred at room temperature for 18h. In the next step toluene (18 mL) and $^{i}Pr_2EtN$ (0.53 mmol, 90.1 µL, 5.3 eq) were added and the reaction was cooled to 0 °C. Ac_2O (0.53 mmol, 50.1 µL, 5.3 eq) was then added to start the acylation and the kinetic resolution was monitored by chiral GC.



Scheme S1. One-pot epoxide opening with hydrazine sulfate and subsequent peptide **F** catalyzed enantioselective acylation.