Kinetic Resolution of *trans*-Cycloalkane-1,2-Diols *via* Steglich Esterification

*Radim Hrdina, Christian E. Müller, and Peter R. Schreiner**

Supporting Information

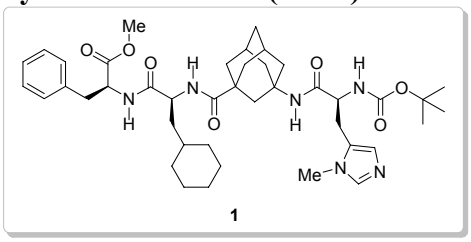
Contents

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 was distilled from appropriate drying agents prior to use and stored under argon atmosphere. The carboxylic acids were used without further purifications. All catalytic reactions were carried out under an argon atmosphere employing oven- and flame-dried glassware. Column chromatography and filtration 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. ^{1}H 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/acetic acid solutions of the respective compounds. High resolution ESI mass spectrometry was performed on a Thermo Scientific LTQ FT Ultra hybrid mass spectrometer using methanol/water solutions of the respective compounds. Optical rotation was measured by using a Jasco P-2000 polarimeter. Elemental analyses were measured using a Carlo Erba 1106 CHN analyzer. GC analyses were performed by using Hewlett Packard 5890 and Carlo Erba 2900 gas chromatographs. The analytical HPLC was accomplished by using a Spectra SP 8700 system and the preparative HPLC by using a Knauer system (Knauer Differential-Refractometer, Knauer HPLC Pump 64, Knauer 2151 Variable Wavelength Monitor).

2. Synthesis of peptide 1 via solid phase peptide synthesis

Synthesis of Boc-L-(π-Me)-His-^{A}Gly-L-Cha-L-Phe-OMe (1):



1

Tetramer **1** was synthesized on solid support using commercially available Wang polystyrene resin endcapped and preloaded with Fmoc-protected L-phenylalanine (0.405 g, 0.74 mmol/g, 0.3 mmol). Fmoc cleavage was performed by shaking the resin twice in 25% piperidine in DMF (v/v). The resin was washed 5 times each with DMF, dichloromethane, and DMF. Chain elongation with Fmoc-L-Cha-OH was performed by a double coupling procedure (1 h shaking per coupling step) using Fmoc-L-Cha-OH (0.237 g, 0.6 mmol), HBTU (0.228 g, 0.6 mmol), HOBt·H_2O (0.092 g, 0.6 mmol), and DIPEA (0.155 g, 204.1 µL, 1.2 mmol) per coupling step (2:2:2:4 equiv., respectively). After washing and cleavage of the Fmoc-protective group as described above, the peptide was elongated using Fmoc-^{A}Gly-OH (0.250 g, 0.6 mmol), HBTU, HOBt, and DIPEA in the same stoichiometric ratio as given above. After washing and cleavage of the Fmoc-protective group as described above, the peptide was elongated using again a double coupling strategy (2h shaking per coupling) Boc-L-(π-Me)-His-OH (0.121 g, 0.45 mmol) , HBTU (0.228 g, 0.6 mmol), HOBt·H_2O (0.092 g, 0.6 mmol), and DIPEA (0.155 g, 204.1 µL, 1.2 mmol) per coupling step (1.5:2:2:4 equiv., respectively). After washing (5 times each with DMF, dichloromethane, and diethylether), the tetramer was cleaved from the resin by shaking two times for 2 days with methanol, triethylamine and THF

(9:1:1, v/v). The resin was filtered off and washed several times with THF. The collected solutions were concentrated and the residue was purified by HPLC (eluent: TBME/CH_3OH 85:15, 6 ml/min.; UV-detector λ = 254 nm, E_{max} = 2.56; refractometer; column l = 250 mm, d = 8 mm, LiChrosorb Diol (7 µm, Merck); retention time (**1**) = 10.43 minutes. The peptide was characterized by ESI-MS, HR-ESI-MS, NMR, IR and EA.

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm = 7.35 [s, 1 H, C*H*-Imidazole (His)]; 7.24 – 7.15 [m, 3 H, H_{Ar} (Phe)]; 7.05 – 7.01 [m, 2 H, H_{Ar} (Phe)]; 6.79 [s, 1 H, C*H*-Imidazole (His)]; 6.44 [d, J = 7.8 Hz, 1 H, N*H* (Phe)]; 5.91 [d, J = 7.9 Hz, 1 H, N*H* (Cha)]; 5.68 [s, 1 H, N*H* (^{A}Gly)]; 5.09 [d, J = 8.3 Hz, 1 H, N*H* (His)]; 4.78 – 4.70 [m, 1 H, H_α (Phe)]; 4.41 – 4.30 [m, 1 H, H_α (Cha)]; 4.13 – 4.03 [m, 1 H, H_α (His)]; 3.64 (s, 3 H, OCH_3); 3.54 (s, 3 H, NCH_3); 3.09 – 2.98 [m, 2 H, H_β (Phe)]; 2.98 – 2.88 [m, 2 H, H_β (His)]; 2.13 (m, 2 H, adamantane); 1.93 – 1.80 (m, 6 H, adamantane + Cha); 1.71 – 1.51 (m, 12 H, adamantane + Cha); 1.40 – 1.36 (m, 1 H, Cha); 1.37 [s, 9 H, C(CH_3)$_3$]; 1.23 – 1.00 (m, 4 H, Cha); 0.92 – 0.69 (m, 2 H, Cha).
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm = 176.3 (C=O); 171.9 (C=O); 171.6 (C=O); 169.7 (C=O); 155.4 (C=O); 138.3; 135.7; 129.2; 128.6; 128.2; 127.2; 127.2; 80.5; 54.4; 53.2; 52.3; 50.7; 42.5; 42.1; 40.3; 40.3; 39.5; 38.2; 38.0; 37.8; 35.1; 34.2; 33.5; 32.7; 31.5; 29.1; 29.1; 28.3; 26.8; 26.3; 26.1; 26.1;
IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3427; 2921; 2853; 2912; 1746; 1661; 1510; 1518; 1450; 1366; 1280 1249; 1169.
MS:
ESI: m/z = 761.5 $[M+H]^+$ (calc. m/z = 761.5); m/z = 783.4 $[M+Na]^+$ (calc. m/z = 783.4); m/z = 1521.3 $[2M+H]^+$ (calc. m/z = 1521.9); m/z = 1543.3 $[2M+Na]^+$ (calc. m/z = 1543.9).
HR-ESI: m/z = 761.45963 $[M+H]^+$ (calc. m/z = 761.45963).
Elem. Anal.: $C_{32}H_{43}N_5O_6$ calc. C 66.29; H 7.95; N 11.04; found C 64.45; H 7.75; N 10.33.

3. Availability of the acids and racemic starting materials: *Trans*-cyclopentane-1,2-diol ((±)-**5**), *trans*-cyclohexane-1,2-diol ((±)-**2**), *trans*-cycloheptane-1,2-diol ((±)-**6**), *trans*-cyclooctane-1,2-diol ((±)-**7**)

The racemic acids were commercially purchased and used without further purification. Racemic *trans*-cyclopentane-1,2-diol ((±)-**5**) was purchased from Aldrich (97% purity) and used without further purification. Racemic *trans*-cyclohexane-1,2-diol ((±)-**2**) was purchased from Acros Organics (98% purity). *Trans*-cycloheptane-1,2-diol ((±)-**6**) was synthesized according to the method of the *Organikum*[1] using freshly distilled cycloheptene (purchased from Aldrich, 92% purity), formic acid, H_2O_2 followed by a saponification with aq. NaOH. *Trans*-cyclooctane-1,2-diol ((±)-**7**) was synthesized via epoxide opening of cyclooctaneoxide (purchased from Alfa Aesar, 99% purity) in water with p-toluenesulfonic acid.

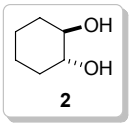
[1] Autorenkollektiv. *Organikum*: *Organisch-chemisches Grundpraktikum*, 19th ed.; Deutscher Verlag der Wissenschaften: Leipzig, **1993**.

4. Description of the catalytic experiments for the variation of the carbodiimide source (Table 1)

Exemplary Description of Standard Conditions for Catalytic Runs in Table 1:

Catalyst **1** (1.9 mg, 0.0025 mmol) was dissolved in 500 µL of dry toluene (or DCM). 100 µL of this catalyst solution (0.0005 mmol, 2 mol%) were added to a clear solution of *trans*-cyclohexane-1,2-diol ((±)-**2**) (2.9 mg, 0.025 mmol) in 4.5 mL dry toluene (or DCM). 1.0 equiv. of carbodiimide (0.025 mmol) [for EDC*HCl we additionally added 1 equiv. of DiPEA (4.2 µL, 0.025 mmol) for deprotonation] were added via Eppendorf Pipette. The reaction mixture was cooled to 0 °C and 1 equiv. of acetic acid **3b** (1.5 µL, 0.025 mmol) was then added with an Eppendorf Pipette and allowed to stir at 0 °C. After the reaction the reaction mixture was quenched with methanol and directly analyzed by chiral GC-analysis.

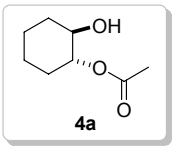
Data for diol (2):



2

See chapter 7.

Data for monoacetate (4a):



4a

See chapter 7.

5. Comparison of the acetylation of 2 with 1 and DMAP

Description of Standard Conditions for Catalytic Runs:

DMAP (1.0 mg, 0.0082 mmol) was dissolved in 500 µL of dry toluene (or DCM). 30.5 µL of this catalyst solution (0.0005 mmol, 2 mol%) were added to a clear solution of *trans*-cyclohexane-1,2-diol ((±)-**2**) (2.9 mg, 0.025 mmol) in 4.5 mL dry toluene (or DCM). 1.2 equiv. of DIC (0.03 mmol were added via Eppendorf Pipette). The reaction mixture was cooled to 0 °C and 2 equiv. of acetic acid **3b** (2.9 µL, 0.05 mmol) was then added with an Eppendorf Pipette and allowed to stir at 0 °C. After the reaction the reaction mixture was quenched with methanol and directly analyzed by chiral GC-analysis.

Solvent	*t* (h)	GC-Yield of remaining **2** (%)	GC-Yield of **4b** (%)	GC-Yield of diacylated product (%)
Toluene	24	44	54	2
DCM	24	72	27	1

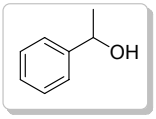
6. Acylation of 1-phenyl ethanol with catalyst 1

Condition for the Catalytic Run:

Catalyst **1** (1.9 mg, 0.0025 mmol) was dissolved in 500 µL of dry toluene. 100 µL of this catalyst solution (0.0005 mmol, 2 mol%) were added to a clear solution of 1-phenyl ethanol (3.06 µL, 0.025 mmol) in 4.5 mL dry toluene. 1.2 equiv. of DIC (0.03 mmol) were added via Eppendorf Pipette. The reaction mixture was cooled to 0 °C and 2 equiv. of acetic acid **3b** (2.9 µL, 0.05 mmol) was then added with an Eppendorf Pipette and allowed to stir at 0 °C. After the reaction the reaction mixture was quenched with methanol and directly analyzed by chiral GC-analysis.

Solvent	*t* (h)	C (%)	*ee* (%) of **4b**	*ee* (%) of **2**
Toluene	40	11	6	0

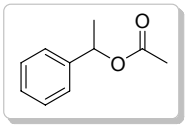
Data for 1-phenyl ethanol:



1-phenyl ethanol was purchased from Aldrich at the highest purity grade available and was used without further purifications.

Assay of enantiomeric purity.
Enantiomers of 1-phenyl ethanol were separated by chiral GC employing a FS-Hydrodex β-6TBDM column (Macherey Nagel).
T (Injector + Detector) = 250 °C
Splitflow = 80 mL/min
Precolumn pressure = 0.8 bar
Conditions: 100 °C – 130 °C, 1 °C/min
Retention Times: R_1 = 18.6 min; R_2 = 19.5 min

Data for acetate of 1-phenyl ethanol:



Assay of enantiomeric purity.
Enantiomers of the acetate of 1-phenyl ethanol were separated by chiral GC employing a FS-Hydrodex β-6TBDM column (Macherey Nagel).
T (Injector + Detector) = 250 °C
Splitflow = 80 mL/min
Precolumn pressure = 0.8 bar
Conditions: 100 °C – 130 °C, 1 °C/min
Retention Times: R_1 = 13.1 min; R_2 = 14.7 min

Proof of GC retention times of acylated 1-phenyl ethanol:

Acylated 1-phenyl ethanol is commercially available from Aldrich and was used to prove the GC retention times.

Analytical data of the acylated product 1-phenyl ethanol are also reported in literature:

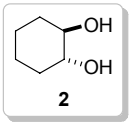
N. Sakai, T. Moriya, T. Konakahara, *J. Org. Chem.* **2007**, 72, 5920-5922.
S. Magens, M. Ertelt, A. Jatsch, B. Plietker, *Org. Lett.* **2008**, 10, 53-56.

7. Description of the catalytic experiments of Tables 2 and 3 with *trans*-cyclopentane-1,2-diol ((±)-**5**), *trans*-cyclohexane-1,2-diol ((±)-**2**), *trans*-cycloheptane-1,2-diol ((±)-**6**) and *trans*-cyclooctane-1,2-diol ((±)-**7**) [Table 2 and 3]

Description of Standard Conditions for Catalytic Runs

The conditions for the kinetic resolutions of *trans*-cyclopentane-1,2-diol ((±)-**5**), *trans*-cyclohexane-1,2-diol ((±)-**2**), *trans*-cycloheptane-1,2-diol ((±)-**6**) and *trans*-cyclooctane-1,2-diol ((±)-**7**) with the various acids **3a**–**3j** are given exemplary by the following experimental protocol. Catalyst **1** (1.9 mg, 0.0025 mmol) was dissolved in 500 µL of dry toluene. 100 µL of this catalyst solution (0.0005 mmol, 2 mol%) were added to a clear solution of *trans*-cyclohexane-1,2-diol ((±)-**2**) (2.9 mg, 0.025 mmol) in 4.5 mL dry toluene. Then 1.2 equiv. or 2 equiv. (4.65 µL, 0.03 mmol) DIC were added via Eppendorf Pipette. The reaction mixture was cooled to 0 °C and 2 equiv. of the corresponding acid **3a**–**3j** (0.05 mmol) were added with an Eppendorf Pipette and allowed to stir at 0 °C. After the reaction the reaction mixture was quenched with methanol and directly analyzed by chiral GC-analysis.

Data for diol 2:



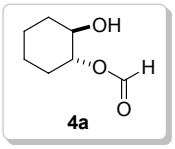
2

Diol (±)-**2** was purchased from Acros Organics at the highest purity grade available and was used without further purifications.

Assay of enantiomeric purity.
Enantiomers of diol **2** 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*) = 9.0 min; R_2 (*R*,*R*) = 9.5 min

Assay of enantiomeric purity (only in the case of formic acid because of signal overlay).
Enantiomers of diol **2** were separated by chiral GC employing a 30 m FS-Hydrodex γ-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*) = 18.6 min; R_2 (*S*,*S*) = 18.8 min

Data for monoformate 4a:



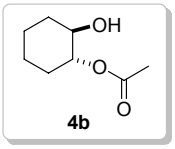
Assay of enantiomeric purity.
Enantiomers of monoacetate **4a** were separated by chiral GC employing a 30 m FS-Hydrodex γ-TBDAc column (Macherey Nagel).
T (Injector + Detector) = 250 °C
Splitflow = 80 mL/min
Precolumn pressure = 0.8 bar
Conditions: 100 °C – 160 °C, 2 °C/min
Retention Times: R_1 (*S*,*S*) = 21.4 min; R_2 (*R*,*R*) = 22.1 min

Proof of GC retention times:

4a was synthesized analog to **4c**.
Chromatography: Merck silica gel 60 (0.040 – 0.063 mm), EtOAc:hexane 1:1 (R_f (**4a**) = 0.27).
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:
J. Barluenga, P. J. Campos, E. Gonzalez-Nuñez, G. Asensio, *Synthesis* **1985**, 14, 426-428.

Data for monoformate 4b:



Assay of enantiomeric purity.
Enantiomers of monoacetate **4b** 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*) = 8.0 min; R_2 (*R*,*R*) = 8.2 min

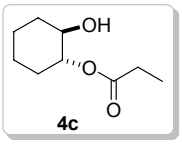
Proof of GC retention times:

Racemic *trans*-cyclohexane-1,2-diol ((±)-**2**) (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 ((±)-**4b**) was purified by silica flash gel chromatography (EtOAc, R_f (**4b**) = 0.42). 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 with those reported in literature:

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

Data for monopropionate 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: 140 °C isothermal
Retention Times: R_1 (*S*,*S*) = 11.2 min; R_2 (*R*,*R*) = 11.5 min

Proof of GC retention times for 4c:

Racemic trans-cyclohexane-1,2-diol ((±)-**2**) (0.232 g, 2.0 mmol) was treated with EDC (420 mg, 2.2 mmol), triethylamine (310 µL, 2.2 mmol and propionic acid (186 µL, 2 mmol) in the presence of N,N-dimethylaminopyridine (0.012 g, 0.01 mmol, 0.5 mol%) in 10 mL dichloromethane and the resulting solution was stirred for 18 h at room temperature. Dichloromethane was then removed in vacuo, and the monoacylated product ((±)-**4c)** was purified by silica flash gel chromatography (EtOAc:hexane 1:1, R_f (**4c**) = 0.28). Isolated racemic ((±)-**4c**) was characterized and then subjected to the GC assay described above to proof the origin of the GC signals.

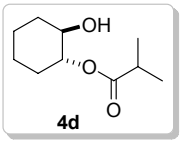
Analytical data:

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 4.69 – 4.50 (m, 1 H); 3.64 – 3.46 (m, 1 H); 2.49 – 1.94 (m, 5 H); 1.81 – 1.59 (m, 2 H); 1.44 – 1.05 (m, 7 H).
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm = 174.8; 78.0; 72.7; 33.1; 30.0; 27.9; 23.9; 23.8; 9.2.
IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3455; 2941; 2864; 1735; 1453; 1352; 1277; 1194; 1082; 1026.
HR-MS(EI): m/z = 173.11777 $[M+H]^+$ (calc. m/z = 173.11774).

Analytical data of the monoacylated product ((±)-**4c**) were identical with those reported in literature:

N. Iranpoor, H. Firouzabadi, A. Safavi, M. Shekarriz, *Synth. Commun.* **2002**, *32*, 2287-2293.

Data for monoisobutyrate 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: 140 °C isothermal
Retention Times: R_1 (*S*,*S*) = 12.8 min; R_2 (*R*,*R*) = 13.0 min

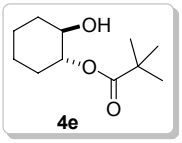
Proof of GC retention times for 4d:

4d was synthesized analog to **4b**.
Chromatography: Merck silica gel 60 (0.040 – 0.063 mm), EtOAc:hexane 1:1 (R_f (**4d**) = 0.26). Isolated racemic ((±)-**4d**) 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 ((±)-**4d**) were identical with those reported in literature:

T. Kawabata, M. Nagato, K. Takasu, K. Fuji, *J. Am. Chem. Soc.* **1997**, *119*, 3169-3170.

Data for monopivalate 4e:



Assay of enantiomeric purity.
Enantiomers of monoacetate **4e** 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*) = 13.0 min; R_2 (*R*,*R*) = 13.2 min

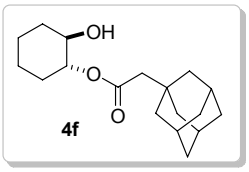
Proof of GC retention times for 4e:

4e was synthesized analog to **4b**.
Chromatography: Merck silica gel 60 (0.040 – 0.063 mm), EtOAc:hexane 1:3 (R_f (**4e**) = 0.28). Isolated racemic ((±)-**4e**) was characterized and then subjected to the GC assay described above to proof the origin of the GC signals.

Analytical data:

^{1}H NMR (400 MHz, $CDCl_3$): 4.57 – 4.42 (m, 1 H); 3.58 – 3.47 (m, 1 H); 2.11 (bs, 1H); 2.05 – 1.87 (m, 2 H); 1.72 – 1.55 (m, 2 H); 1.35 – 1.14 (m, 13 H).
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm = 178.9; 77.7; 72.8; 38.9; 32.9; 29.7; 27.2; 23.8; 23.7.
IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3455; 2938; 2865; 1728; 1481;1454;1397; 1285; 1169; 1076; 1038; 1012.
HR-MS(EI): m/z = 201.15046 $[M+H]^+$ (calc. m/z = 201.14907).

Data for mono-1-adamantylacetate 4f:



Assay of enantiomeric purity.
Enantiomers of monoacetate **4f** were separated by chiral HPLC employing a Chiralpak IB column (Daicel)
Eluent: Hexane/2-Propanol 95:5
Flow: 0.7 ml/min.
UV-detector λ = 220 nm and refractometer
Retention Times: R_1 (*R*,*R*) = 8.9 min; R_2 (*S*,*S*) = 9.3 min

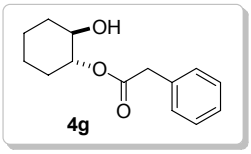
Proof of HPLC retention times for 4f:

4f was synthesized analog to **4c**.
Chromatography: Merck silica gel 60 (0.040 – 0.063 mm), EtOAc:hexane 1:1 (R_f (**4f**) = 0.38).
Isolated racemic ((±)**-4f**) was characterized and then subjected to the HPLC assay described above to proof the origin of the HPLC signals.

Analytical data:

^{1}H NMR (400 MHz, $CDCl_3$): 4.63 – 4.52 (m, 1 H); 3.62 – 3.51 (m, 1 H); 2.29 – 1.93 (m, 8 H); 1.78 – 1.53 (m, 14 H); 1.41 – 1.19 (m, 4 H).
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm = 172.1; 78.0; 72.8; 49.2; 42.4; 36.7; 33.0; 32.9; 30.1; 28.6; 23.9; 23.8.
IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3438; 2903; 2848; 1728; 1451; 1260; 1199; 1139; 1163; 1023.
HR-MS(EI): m/z = 292.20779 $[M]^+$ (calc. m/z = 292.20384).

Data for mono-2-phenylacetate 4g:



Assay of enantiomeric purity.
Enantiomers of monoacetate **4g** were separated by chiral HPLC employing a Chiralpak IB column (Daicel)
Eluent: Hexane/2-Propanol 90:10
Flow: 0.7 ml/min.;
UV-detector λ = 220 nm and refractometer

Retention Times: R_1 (*R*,*R*) = 10.8 min; R_2 (*S*,*S*) = 13.1 min

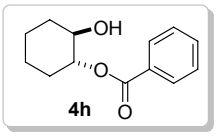
Proof of HPLC retention times for 4g:

4g was synthesized analog to **4c**.
Chromatography: Merck silica gel 60 (0.040 – 0.063 mm), EtOAc:hexane 1:1 (R_f (**4g**) = 0.28). Isolated racemic ((±)-**4g**) was characterized and then subjected to the HPLC assay described above to proof the origin of the HPLC signals.

Analytical data:

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.35 – 7.22 (m, 5 H); 4.63 – 4.50 (m, 1 H); 3.70 – 3.60 (m, 2 H); 3.58 – 3.46 (m, 1 H); 2.20 (bs, 1H), 2.05 – 1.94 (m, 2 H); 1.75 – 1.62 (m, 2 H); 1.38 – 1.16 (m, 4 H).
^{13}C NMR (150 MHz, $CDCl_3$): δ/ppm = 171.8; 134.2; 129.1; 128.6; 127.1; 78.6; 72.6; 41,7; 32.8; 29.8; 23.8; 23.7.
IR (KBr): $\tilde{\nu}$ /cm^{-1} = 3448; 2939; 2863; 1732; 1454; 1348; 1259; 1277; 1163; 1076; 1020; 724; 709; 696.
HR-MS(EI): m/z = 234.12569 $[M]^+$ (calc. m/z = 234.12559).

Data for monobenzoate 4h:



Assay of enantiomeric purity.
Enantiomers of monoacetate **4h** 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: 160 °C isothermal
Retention Times: R_1 (*R*,*R*) = 70.3 min; R_2 (*S*,*S*) = 72.4 min

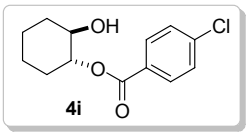
Proof of GC retention times for 4h:

4h was synthesized analog to **4c**.
Chromatography: Merck silica gel 60 (0.040 – 0.063 mm), EtOAc:hexane 1:1 (R_f (**4h**) = 0.35). Isolated racemic ((±)-**4h**) 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 ((±)-**4h**) were identical with those reported in literature:

Y. Matsumura, T. Maki, S. Murakami, O. Onomura, *J. Am. Chem. Soc.* **2003**, *125*, 2052-2053.

Data for mono-4-chlorobenzoate 4i:



Assay of enantiomeric purity.
Enantiomers of monoacetate **4i** were separated by chiral GC employing a 30 m FS-Hydrodex γ-TBDAc column (Macherey Nagel).
T (Injector + Detector) = 250 °C
Splitflow = 80 mL/min
Precolumn pressure = 0.8 bar
Conditions: 180 °C isothermal
Retention Times: R_1 (*R*,*R*) = 52.1 min; R_2 (*S*,*S*) = 53.2 min

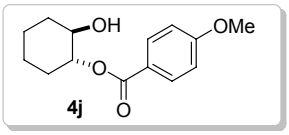
Proof of GC retention times for 4i:

4i was synthesized analog to **4c**.
Chromatography: Merck silica gel 60 (0.040 – 0.063 mm), EtOAc:hexane 1:1 (R_f (**4i**) = 0.35).
Isolated racemic ((±)-**4i**) 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 ((±)-**4i**) were identical with those reported in literature:

S. Mizuta, Y. Ohtsubo, T. Tsuzuki, T. Fujimoto, I. Yamamoto, *Tetrahedron Lett.* **2006**, *47*, 8227-8229.
E. A. Jaseer, A. B. Naidu, S. S. Kumar, R. Koteshwar Rao, K. G. Thakur, G. Sekar, *Chem. Comm.* **2007**, 867-869.

Data for mono-4-methoxybenzoate 4j:



Assay of enantiomeric purity.
Enantiomers of monoacetate **4j** were separated by chiral HPLC employing a Chiralpak IB column (Daicel)
Eluent: Hexane/2-Propanol 90:10
Flow: 0.7 ml/min.
UV-detector λ = 220 nm and refractometer
Retention Times: R_1 = 12.8 min; R_2 = 15.8 min

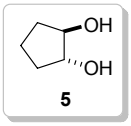
Proof of HPLC retention times for 4j:

4j was synthesized analog to **4c**.
Chromatography: Merck silica gel 60 (0.040 – 0.063 mm), EtOAc:hexane 1:1 (R_f (**4j**) = 0.28).
Isolated racemic ((±)-**4j**) was characterized and then subjected to the HPLC assay described above to proof the origin of the HPLC signals.

Analytical data of the monoacylated product ((±)-**4j**) were identical with those reported in literature:

E. A. Jaseer, A. B. Naidu, S. S. Kumar, R. Koteshwar Rao, K. G. Thakur, G. Sekar *Chem. Comm.* **2007**, 867-869.

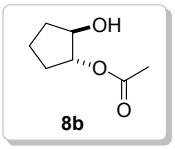
Data for diol 3:



Diol (±)**-5** was purchased from Aldrich at the highest purity grade available and was used without further purifications.

Assay of enantiomeric purity.
Enantiomers of diol **5** 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 8b:



Assay of enantiomeric purity.
Enantiomers of monoacetate **8b** 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

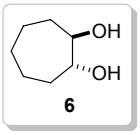
Proof of GC retention times:

Racemic *trans*-cyclopentane-1,2-diol ((±)**-5**) (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 ((±)**-8b** was purified by silica flash gel chromatography (EtOAc, R_f ((±)**-8b**) = 0.53). Isolated racemic (±)**-8b** 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 (±)**-8b** were identical to those reported in literature:

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

Data for diol (6):



Diol (±)-**6** was synthesized according to the method of the *Organikum* (see chapter 3).

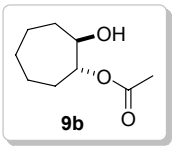
Analytical data of the diol (±)-**6** were identical with those reported in literature:

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

^{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.

Assay of enantiomeric purity.
Enantiomers of diol **6** 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 (9b):



Assay of enantiomeric purity.
Enantiomers of monoacetate **9b** 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

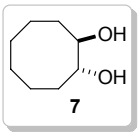
Proof of GC retention times:

Racemic *trans*-cycloheptane-1,2-diol ((±)-**6**) (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 (±)-**9b** was purified by silica flash gel chromatography (EtOAc, R_f ((±)-**9b**) = 0.49). Isolated racemic (±)-**9b** 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 ((±)-**9b**) were identical to those reported in literature:

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

Data for diol (7):



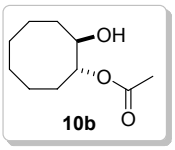
Diol ((±)-**7**) was synthesized according to the method mentioned in chapter 3. Analytical data of the diol ((±)-**7**) were identical to those reported in literature:

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

^{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.

Assay of enantiomeric purity.
Enantiomers of diol **7** 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*) = 12.2 min; R_2 (*R,R*) = 12.4 min

Data for monoacetate (10b):



Assay of enantiomeric purity.
Enantiomers of monoacetate **10b** 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*) = 25.4 min; R_2 (*S,S*) = 26.0

Proof of GC retention times:

Racemic *trans*-cyclooctane-1,2-diol ((±)-**7**) (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 ((±)-**10b**) was purified by silica flash gel chromatography (EtOAc, R_f ((±)-**10b**) =

0.50). Isolated racemic ((±)-**10b**) 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 ((±)-**10b**) were identical to those reported in literature:

V. Bódai, O. Orovecz, G. Szakács, L. Novák and L. Poppe, *Tetrahedron*: *Asymmetry* **2003**, *14*, 2605-2612.
G. H. Posner, D. Z. Rogers, *J. Am. Chem. Soc*. **1977**, *99*, 8208-8214.

8. Description of the preparative experiments with *trans*-cyclohexane-1,2-diol ((±)-2) using the acids 3b, 3c, 3d and 3g

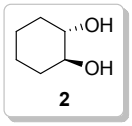
The conditions for the preparative kinetic resolution of **2** with **3b**, **3c**, **3d** and **3g** are given exemplary by the following experimental protocol. Catalyst **1** (7.6 mg, 0.01 mmol, 1 mol%) and diol (±)-**2** (116.2 mg, 1 mmol) were dissolved in 180 mL (185 mL) of dry toluene to produce a clear solution. Then 1.2 equiv. DIC (0.186 mL, 1.2 mmol) were added. The reaction mixture was cooled to 0 °C and 2 equiv. of the corresponding acid (2 mmol) were added and the reaction was allowed to stir for 15 h min at 0 °C. The reaction mixture was quenched with 10 mL methanol and then filtered using 30 g silica gel suspended with EtOAc to remove the catalyst (the silica gel was washed with EtOAc). Purification methods were different for each synthesis and can be found in the corresponding paragraph (see below).

Data for the preparative kinetic resolution of racemic 2 with 3b:

Purification:

After the filtration the solvents were removed under reduced pressure. The crude product was directly purified by silica gel column chromatography. Eluting with EtOAc afforded 80.3 mg (0.508 mmol, 50.8%) of monoacetate **4b** (R_f = 0.42) and 44.9 mg (0.387 mmol, 38.7%) of diol **2** (R_f = 0.20). The products were then directly characterized by chiral GC analysis and NMR.

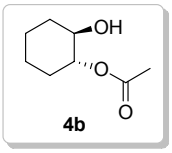
Data for diol (*S*,*S*)-2:



2

$[\alpha]_D^{24} = +40.0\ ^\circ$ (0.75 g/100 mL; $CHCl_3$); (98% *ee*)

Data for monoacetate (*R*,*R*)-4b:



4b

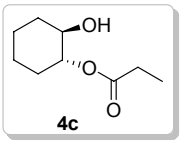
$[\alpha]_D^{24} = -38.0\ ^\circ$ (1.35 g/100 mL; $CHCl_3$); (82% *ee*)

Data for the preparative kinetic resolution of racemic 2 with 3c:

Purification:

After the filtration the solvents were removed under reduced pressure. The crude product was directly purified by silica gel column chromatography. Eluting with EtOAc afforded 82.3 mg (0.478 mmol, 47.8%) of monoacetate **4c** (R_f = 0.46) and 49.9 mg (0.430 mmol, 43.0%) of diol **2** (R_f = 0.20). Diol **2** was then directly characterized by chiral GC analysis and NMR. Monoacetate **4c** was further purified by HPLC (eluent: TBME/methanol/hexane 19:1:80, 6 ml/min.; UV-detector λ = 254 nm, refractometer; column l = 250 mm, d = 8 mm, LiChrosorb Diol (7 µm, Merck); retention time (**4c**) = 7.4 minutes) and then directly characterized by GC analysis and NMR.

Data for monopropionate (*R,R*)-4c:



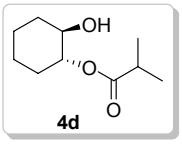
$[\alpha]_D^{24} = -31.5\ °$ (1.01 g/100 mL; $CHCl_3$); (90% *ee*)

Data for the preparative kinetic resolution of racemic 2 with 3d:

Purification:

After the filtration the solvents were removed under reduced pressure. The crude product was directly purified by silica gel column chromatography. Eluting with EtOAc afforded 91.1 mg (0.489 mmol, 48.9%) of monoacetate **4d** (R_f = 0.52) and 47.7 mg (0.411 mmol, 41.1%) of diol 2 (R_f = 0.20). Diol **2** was then directly characterized by chiral GC analysis and NMR. Monoacetate **4d** was further purified by HPLC (eluent: TBME/hexane 10:90, 6 ml/min.; UV-detector λ = 254 nm, refractometer; column l = 250 mm, d = 8 mm, LiChrosorb Diol (7 µm, Merck); retention time (**4d**) = 12.33 minutes) and then directly characterized by GC analysis and NMR.

Data for monoisobutyrate (*R,R*)-4d:



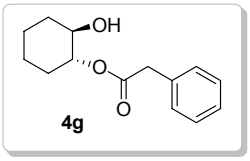
$[\alpha]_D^{25} = -76.0\ °$ (0.24 g/100 mL; $CHCl_3$); (90% *ee*)

Data for the preparative kinetic resolution of racemic 2 with 3g:

Purification:

After the filtration the solvents were removed under reduced pressure. The crude product was directly purified by silica gel column chromatography. Eluting with EtOAc:NEt_3 99:1 afforded 127.0 mg (0.542 mmol, 54.2%) of monoacetate **4g** (R_f = 0.50) and 47.1 mg (0.405 mmol, 40.5%) of diol **2** (R_f = 0.20). The products were then directly characterized by chiral GC analysis and NMR.

Data for mono-2-phenylacetate (*R,R*)-4g:

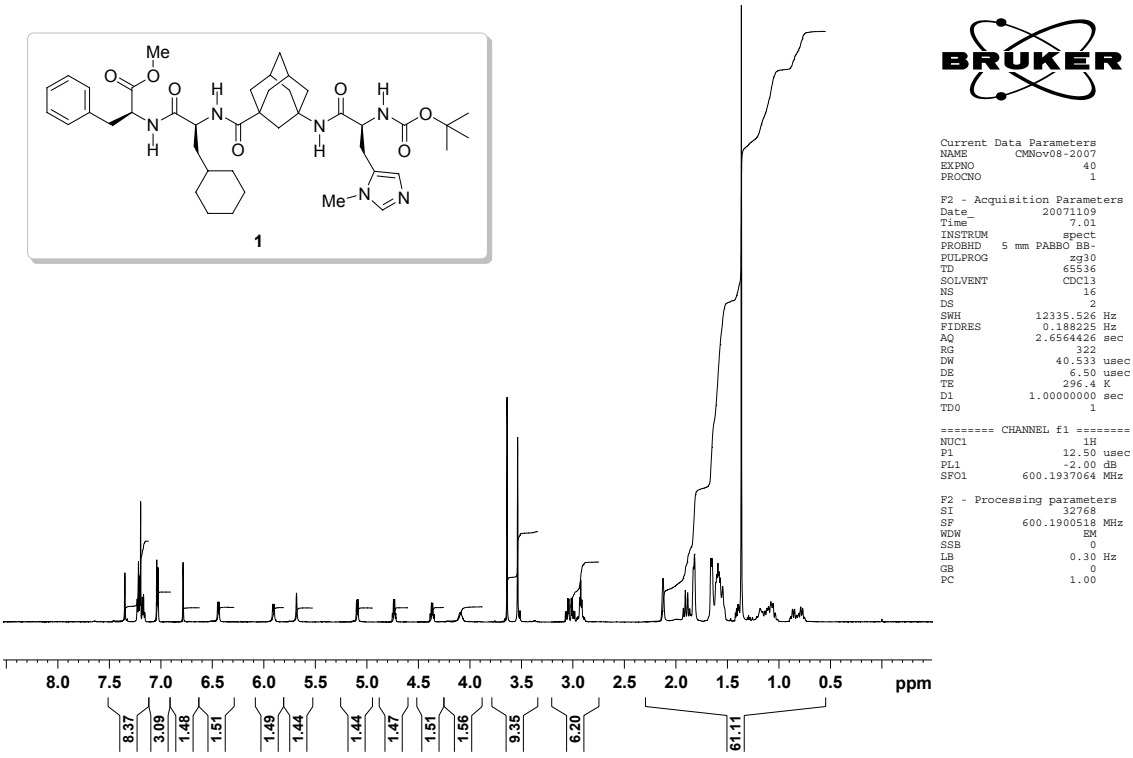


4g

$[\alpha]_D^{24} = -37.3\ ^\circ$ (1.46 g/100 mL; $CHCl_3$); (82% *ee*)

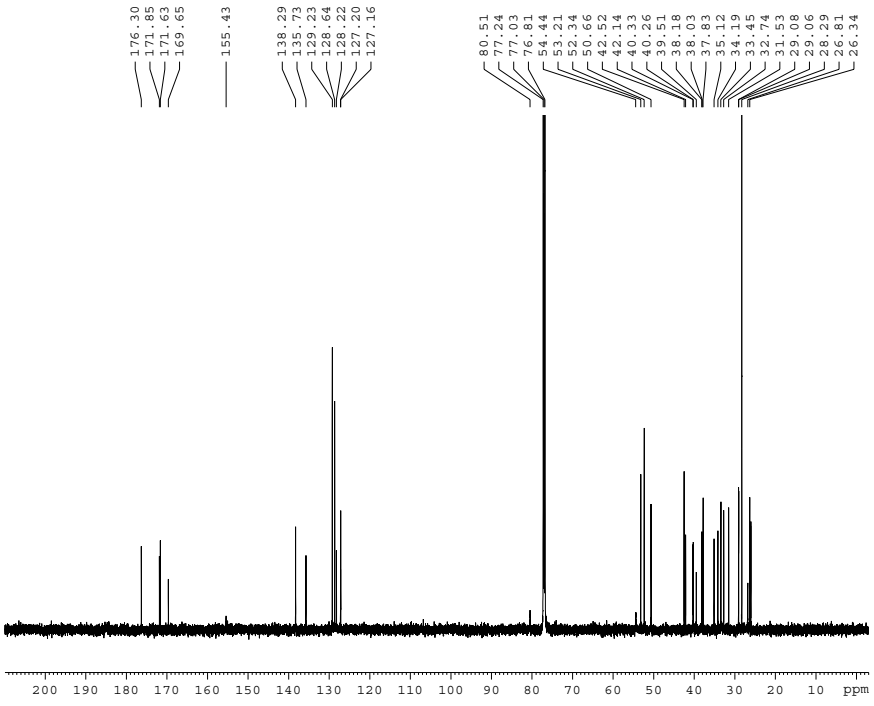
9. Spectra

Boc-L-(π-Me)-His-^{A}Gly-L-Cha-L-Phe-OMe (1):



BRUKER

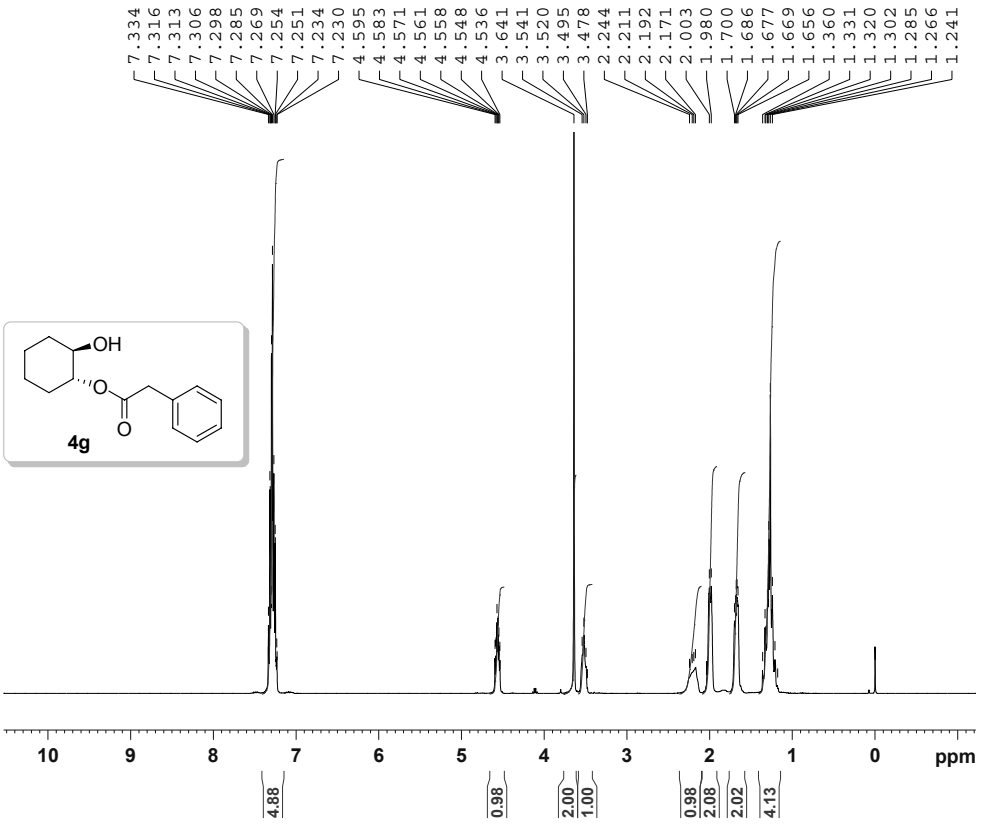
```
Current Data Parameters
NAME         CMNov08-2007
EXPNO                  40
PROCNO                  1

F2 - Acquisition Parameters
Date_           20071109
Time                7.01
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12335.526 Hz
FIDRES         0.188225 Hz
AQ             2.6564426 sec
RG                   322
DW              40.533 usec
DE               6.50 usec
TE               296.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.50 usec
PL1               -2.00 dB
SFO1        600.1937064 MHz

F2 - Processing parameters
SI                 32768
SP          600.1900518 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```



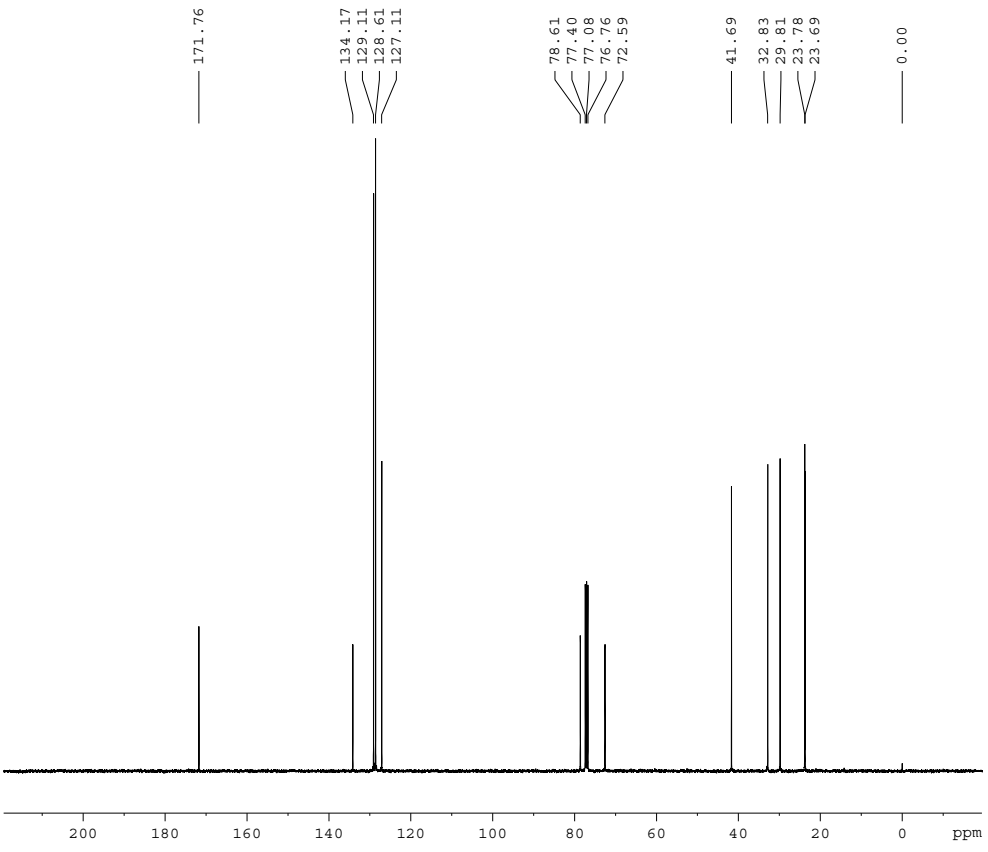
BRUKER

```
Current Data Parameters
NAME         CMNov08-2007
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_           20071109
Time               10.15
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH            36057.691 Hz
FIDRES         0.550197 Hz
AQ             0.9088159 sec
RG                  2050
DW              13.867 usec
DE               6.50 usec
TE               296.9 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                9.50 usec
PL1               2.00 dB
SFO1        150.9329873 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            77.00 usec
PL12             14.00 dB
PL13             20.00 dB
PL2              -2.00 dB
SFO2        600.1924008 MHz

F2 - Processing parameters
SI                 32768
SF          150.9178960 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

Mono-2-phenylacetate 4g:

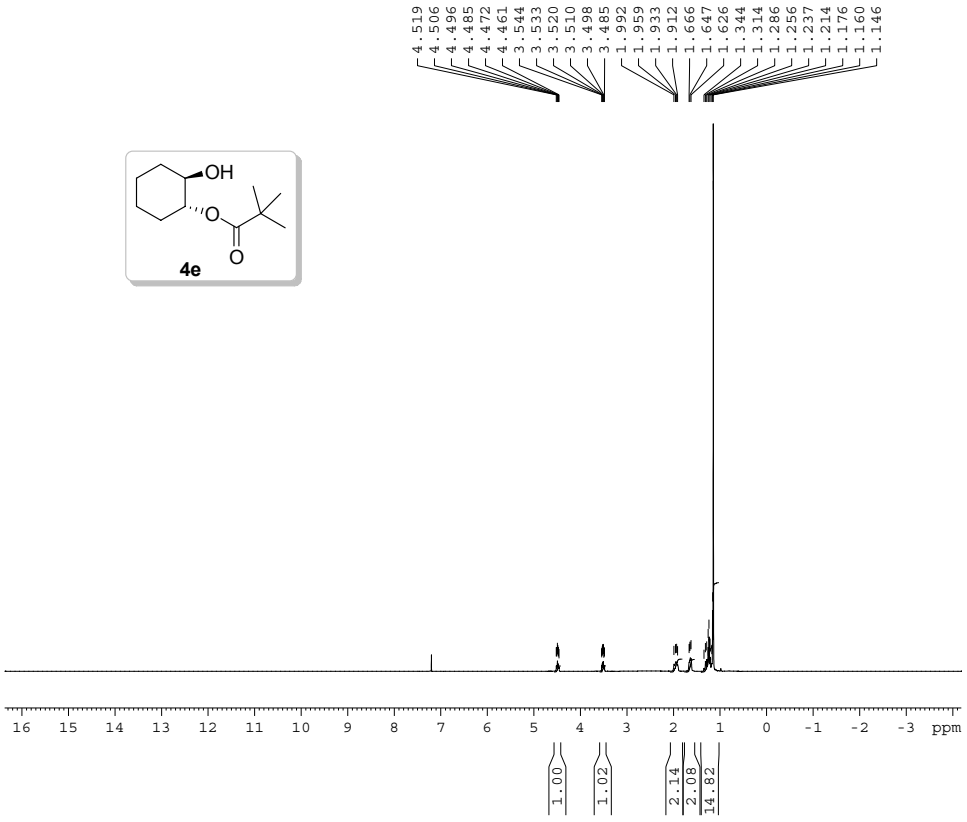



```
Current Data Parameters
NAME        RHSep22-2009
EXPNO                130
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090922
Time                17.56
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                    36
DW                60.800 usec
DE                 6.00 usec
TE                296.6 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.00 usec
PL1                -2.50 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300109 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

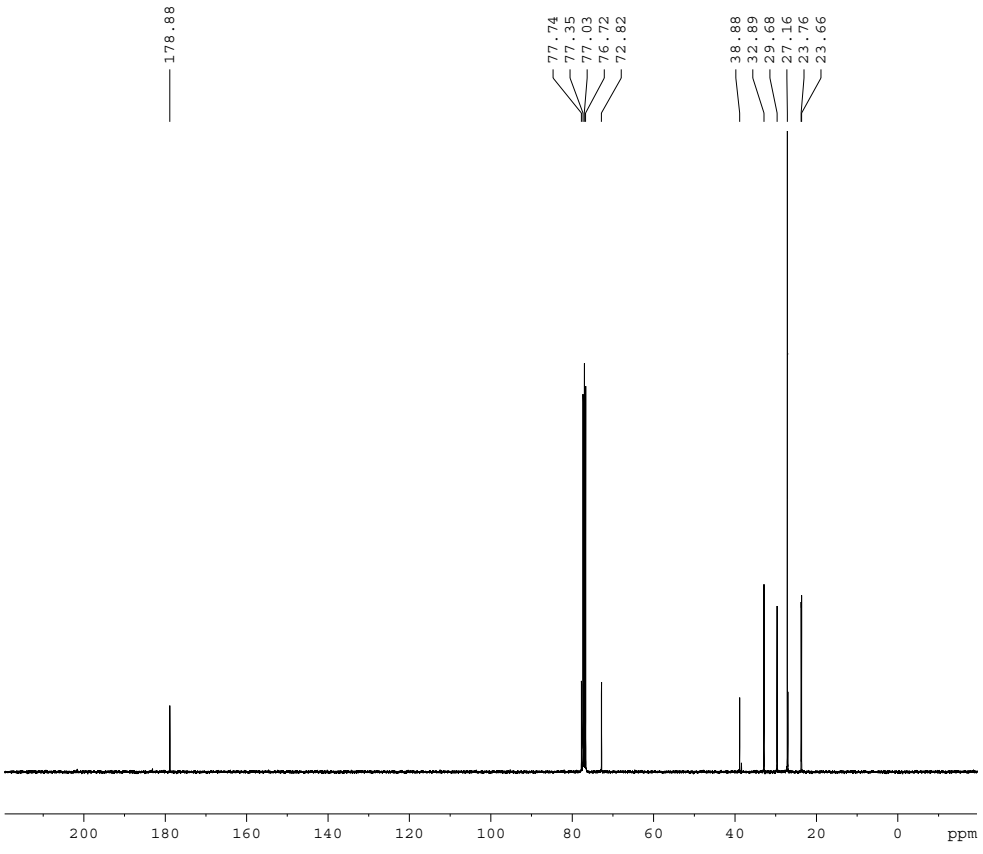



```
Current Data Parameters
NAME        RHSep22-2009
EXPNO                131
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090922
Time                18.57
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                297.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.80 usec
PL1                -2.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.80 dB
PL12               13.30 dB
PL13               25.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127715 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Monopivalate 4e:

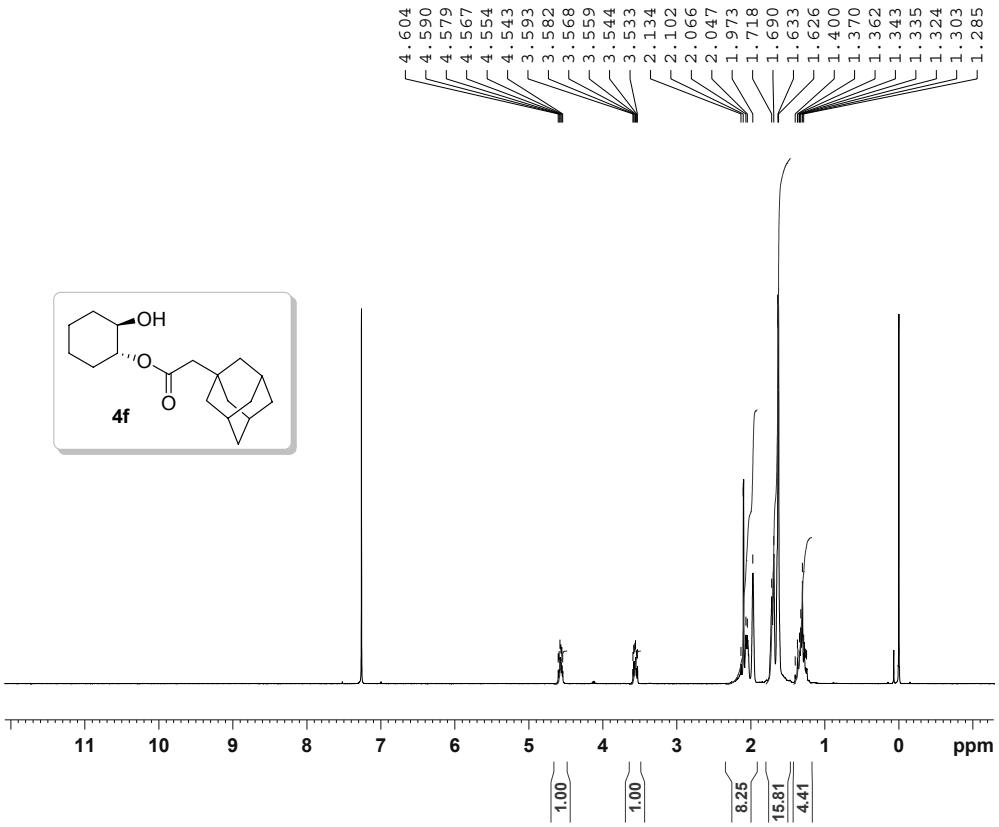



```
Current Data Parameters
NAME        CMSep28-2007
EXPNO                100
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070930
Time              20.07
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                   64
DW               60.800 usec
DE                6.00 usec
TE               296.1 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.00 usec
PL1               -2.50 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                32768
SF           400.1300327 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

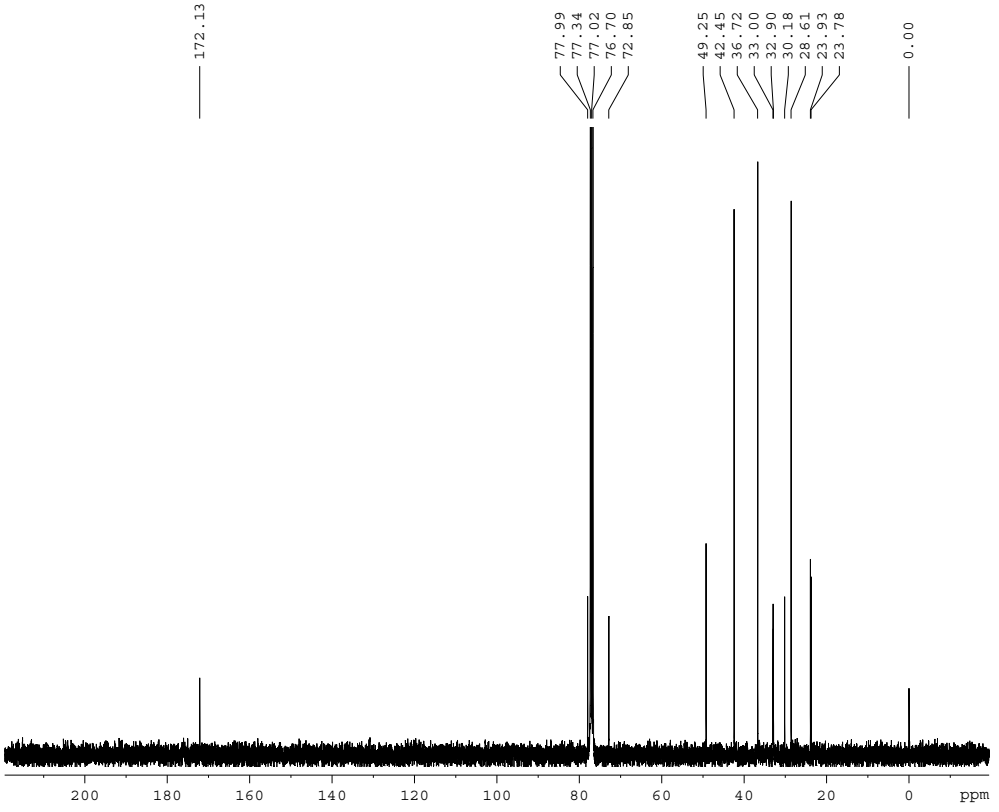



```
Current Data Parameters
NAME        CMSep28-2007
EXPNO                104
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070930
Time              23.04
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
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                 8.80 usec
PL1               -2.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.80 dB
PL12              13.30 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
```

Mono-1-adamantylacetate 4f:




```
Current Data Parameters
NAME        RHSep22-2009
EXPNO                140
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090922
Time               19.06
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                   228
DW                60.800 usec
DE                 6.00 usec
TE                296.5 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.00 usec
PL1               -2.50 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300078 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME        RHSep22-2009
EXPNO                141
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090922
Time               20.07
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                297.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.80 usec
PL1               -2.60 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2               -1.80 dB
PL12              13.30 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
```