Electronic Supplementary Information

Enantiodivergent Asymmetric Catalysis with Tropos BIPHEP Ligand and a Proline Derivative as Chiral Selector

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Experimental Section

General:

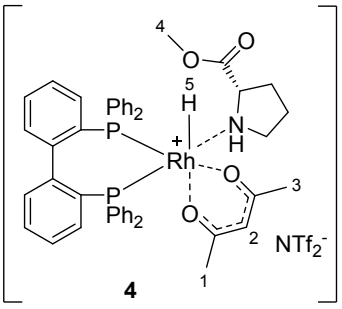
All reactions were carried out under a dry argon atmosphere either with Schlenk technique or in a glovebox. Multinuclear NMR spectra were recorded with a Bruker AV III 400 or AV 600 spectrometer. The operation frequencies for the spectrometers are 400.2 MHz for ^{1}H, 100.6 MHz for ^{13}C, 376.4 MHz for ^{19}F and 162.0 MHz for ^{31}P with the AV III 400 spectrometer and 600.1 MHz for ^{1}H, 150.9 MHz for ^{13}C, 564.6 MHz for ^{19}F and 242.9 MHz for ^{31}P with the AV 600 spectrometer. Various temperature NMR experiments were exclusively recorded with the AV 600 spectrometer. Chemical shifts (δ) of ^{1}H and ^{13}C{^{1}H} NMR-spectroscopy are given in ppm using the residual solvent signal as internal standards. For ^{31}P{^{1}H} NMR spectroscopy chemical shifts are given relative to 85 % phosphoric acid as external standard. Coupling constants *J* are given in Hertz (Hz) and for the characterization of the multiplicity the following symbols are used: s = singlet, d = doublet, t = triplet, dd = doublet of a doublet, m = multiplet, br = broad . The assignment of the signals was made on the basis of 2D-NMR spectroscopy (^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{1}H COSY, ^{1}H-^{31}P HMBC). HR-MS-ESI data was recorded with a Thermo Fisher Scientific LTQ Orbitrap XL (ESI) and ESI-MS measurements were performed with a 500-MS from Varian. The mass of the molecular ion is given. Reagents were purchased from ABCR, Aldrich, Heraeus, io-li-tec and were used without further purification. Anhydrous solvents were obtained from a solvent drying system of Innovative Technologies. Methanol was delivered from Acros in anhydrous grade and was purified and degased by freeze-pump-thaw cycles as well as stored under argon atmosphere. Water was degassed by purging argon through a frit for 2 h. Deuterated solvents (1,2-Dichloroethane-d_4, methylene chloride-d_2) were purchased from Euriso-top and were degassed with freeze-pump-thaw cycles. (S_c)-Prolinium-methylester-bis[(trifluoromethyl)sulfonyl]-amide (**2**) was prepared following a literature procedure,[1,2] degassed, and dried under high vacuum (1×10^{-3} mbar) at 60 °C overnight prior to use. NMR-spectra of air-sensitive species were recorded using screw-cap NMR-tubes filled under argon. Hydrogenation reactions were performed in 10 mL (experiments in Table 1) or 20 mL stainless steel reactors build at the ITMC and equipped with a 6 mL glass liner (10 mL reactor) or a 12 mL glass liner (20 mL reactor).

Synthesis of complexes and catalyst precursors

Synthesis of [Rh(BIPHEP)(acac)] (3):

[Rh(CO)$_2$(acac)] (206 mg, 800 µmol) and 2,2'-bis(diphenylphosphanyl)-1,1'-biphenyl **1** (BIPHEP, 418 mg, 800 µmol, 1.00 eq.) were placed in a Schlenk tube and dissolved in CH_2Cl_2 (20 mL). The red reaction mixture was allowed to stir for 1 h at room temperature. All volatiles were removed *in vacuo* resulting in a red to orange solid (580 mg, quant.). ^{1}H-NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.98-6.79 (m, 26H, H_{Ar}), 6.59-6.48 (m, 2H, H_{Ar}), 5.25 (s, 1H, C*H*), 1.44 (s, 6H, CH_3). ^{31}P{^{1}H }-NMR (161 MHz, CD_2Cl_2, 25 °C): δ = 51.49 (d, $J_{P\text{-}Rh}$ = 189.2 Hz). HR-MS (ESI)(+): *m/z* = 724.11841 (7) [M]$^+$ calculated for $C_{41}H_{35}O_2P_2Rh$: 724.11618.

Preparation of [(H)Rh(κ^2-BIPHEP)(η^2-acac)(κ^1-ProlOMe)][NTf$_2$] (4):



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(S_c)-Prolinium-methylester-bis(trifluoromethyl)sulfonylamide **2** (33 mg, 80 µmol, 1.7 eq.) was added to a solution of [Rh(BIPHEP)(acac)] (29 mg, 40 µmol) in CH_2Cl_2 (0.4 mL) at -50 °C. The resulting red mixture was stirred for 10 min at -30 °C. At constant temperature of -30 °C both diastereomers [Rh{((S_a)-BIPHEP}{(S_c)-ProlOMe}][NTf$_2$] and [Rh{(R_a)-BIPHEP}{(S_c)-ProlOMe}][NTf$_2$] ({S_aS_c}/{R_aS_c}-**4**) were detected by NMR (> 93 % by ^{31}P-NMR). Diastereomer A: ^{1}H-NMR (600 MHz, CD_2Cl_2, -30 °C)[a]: δ = 8.17-5.87 (m, H_{Ar}),[b] 5.08 (s, 1H, H-2), 3.61 (s, 3H, H-4), 2.11 (s, 3H, H-1), 0.91 (s, 3H, H-3), -16.57 (dt, 1H, $^{1}J_{HRh}$ = 15.1 Hz, $^{2}J_{HP}$ = 23.4 Hz, H-5). ^{31}P{^{1}H}-NMR (243 MHz, CD_2Cl_2, -30 °C): δ = 43.06 (dd, $J_{P\text{-}Rh}$ = 130.3 Hz, $J_{P\text{-}P}$ = 38.5 Hz), 32.59 (dd, $J_{P\text{-}Rh}$ = 124.1 Hz, $J_{P\text{-}P}$ = 39.6 Hz).[c] Diastereomer B: ^{1}H-NMR (600 MHz, CD_2Cl_2, -30 °C)[a]: δ = 8.17-5.87 (m, H_{Ar}),[b] 5.03 (s, 1H, H-2), 3.54 (s, 3H, H-4), 2.10 (s, 3H, H-1), 0.90 (s, 3H, H-3), -16.88 (dt, 1H, $^{1}J_{HRh}$ = 16.4 Hz, $^{2}J_{HP}$ = 23.5 Hz, H-5). ^{31}P{^{1}H}-NMR (243 MHz, CD_2Cl_2, -30 °C): δ = 41.16 (dd, $J_{P\text{-}Rh}$ = 130.0 Hz, $J_{P\text{-}P}$ = 35.7 Hz), 33.37 (dd, $J_{P\text{-}Rh}$ = 123.8 Hz, $J_{P\text{-}P}$ = 36.5 Hz).[c]

[a] signals of coordinated ProlOMe are not listed as they overlap with the corresponding signals of **2** present in excess.

[b] signal integration is not possible due to overlapping with signals of **2** in the same region.

[c] in the spectra an additional coupling was observed because of insufficient broadband proton-decoupling of the strongly upfield shifted hydride signal.

Preparation of the diastereomeric mixture {S_aS_c}/{R_aS_c}-[Rh{BIPHEP}{(S_c)-ProlOMe}][NTf_2] ({S_aS_c}/{R_aS_c}-5):
(S_c)-Prolinium-methylester-bis(trifluoromethyl)sulfonylamide (230 mg, 561 µmol, 14 eq.) was added to a solution of [Rh(BIPHEP)(acac)] (29 mg, 40 µmol) in CH_2Cl_2 (0.4 mL) at -10 °C. The resulting dark red mixture was stirred for 10 min at 0 °C. At constant temperature of 0 °C both diastereomers [Rh{(S_a)-BIPHEP}{(S_c)-ProlOMe}][NTf_2] and [Rh{(R_a)-BIPHEP}{(S_c)-ProlOMe}][NTf_2] ({S_aS_c}/{R_aS_c}-**5**) were formed in a 1:1 ratio (NMR). (S_aS_c)-[Rh{BIPHEP}{(*S*)-ProlOMe}][NTf_2] ({S_aS_c}-**5**): ^{1}H-NMR (400 MHz, CD_2Cl_2, 25 °C)[a]: δ = 8.02-6.86 (m, H_{Ar}),[b] 6.50-6.41 (m, 2H, H_{Ar}), 6.36-6.29 (m, 2H, H_{Ar}). ^{31}P{^{1}H }-NMR (161 MHz, CD_2Cl_2, 25 °C): δ = 50.44 (dd, $J_{P\text{-}Rh}$ = 204.0 Hz, $J_{P\text{-}P}$ = 66.8 Hz), 46.33 (dd, $J_{P\text{-}Rh}$ = 173.7 Hz, $J_{P\text{-}P}$ = 67.0 Hz). (R_aS_c)-[Rh{BIPHEP}{(*S*)-ProlOMe}][NTf_2] ({R_aS_c}-**5**): ^{1}H-NMR (400 MHz, CD_2Cl_2, 25 °C)[a]: δ = 8.02-6.86 (m, H_{Ar}),[b] 6.50-6.41 (m, 2H, H_{Ar}), 6.36-6.29 (m, 2H, H_{Ar}). ^{31}P{^{1}H }-NMR (161 MHz, CD_2Cl_2, 25 °C): δ = 52.08 (dd, $J_{P\text{-}Rh}$ = 205.9 Hz, $J_{P\text{-}P}$ = 65.8), 45.84 (dd, $J_{P\text{-}Rh}$ = 170.5 Hz, $J_{P\text{-}P}$ = 65.8).

[a] signals of coordinated ProlOMe are not listed as they overlap with the corresponding signals of **2** present in excess.
[b] signal integration is not possible due to overlapping with signals of **2** in the same region.

Preparation of the diastereomeric pure [Rh{(*R*)-BIPHEP}{(*S*)-ProlOMe}][NTf_2] {R_aS_c}-5:
(S_c)-Prolinium-methylester-bis(trifluoromethyl)sulfonylamide (230 mg, 561 µmol, 14 eq.) was added to a solution of [Rh(BIPHEP)(acac)] (29.0 mg, 40 µmol) in methylene chloride (0.4 mL). The resulting dark red mixture was stirred for 10 min at r.t. and then transferred in a pressure resistant screw-cap NMR-tube via a steal needle. The solution was subsequently heated at 50 °C for 20 h. The red catalyst solution (c = 0.1 mol·L^{-1}, 0.4 mL, 40 µmol) was cooled to r.t. (> 95 % by ^{31}P-NMR). ^{1}H-NMR (400 MHz, CD_2Cl_2, 25 °C)[a]: δ = 8.02-6.86 (m, H_{Ar}),[b] 6.50-6.41 (m, 2H, H_{Ar}), 6.36-6.29 (m, 2H, H_{Ar}). ^{31}P{^{1}H }-NMR (161 MHz, CD_2Cl_2, 25 °C): δ = 52.08 (dd, $J_{P\text{-}Rh}$ = 205.9 Hz, $J_{P\text{-}P}$ = 65.8), 45.84 (dd, $J_{P\text{-}Rh}$ = 170.5 Hz, $J_{P\text{-}P}$ = 65.8).

[a] signals of coordinated ProlOMe are not listed as they overlap with the corresponding signals of **2** present in slight excess.
[b] signal integration is not possible due to overlapping with signals of **2** in the same region.

Catalytic procedures

Typical procedure for R-selective catalytic hydrogenations reported in Table 1 and figure 3:
The substrate (1.75 mmol, 175 eq.) and $HNTf_2$ (7.0 mg, 25 µmol, 2.5 eq.) were dissolved in methanol (2 mL) (substrate **12**) or methanol (1 mL) and water (1 mL) (substrates **6**, **8**, **10**, **14**) and were combined with a solution freshly prepared solution of [Rh{(*R*)-BIPHEP}{(*S*)-ProlOMe}] (R_aS_c)-**5** which was formed *in situ* as described above (c = 0.1 mol·L^{-1}, 0.1 mL, 10 µmol). After stirring for 10 min, the red solution was transferred into a 10 mL stainless steel reactor equipped with a 6 mL glass vial and a stirring bar which was tempered to 0° C through a cryostat. The reactor was pressurized with hydrogen (40 bar). The mixture was continuously stirred at 0 °C for 16 h. Then, the pressure was released carefully and the resulting homogeneous solution was diluted with methanol, filtered through a SiO_2 pad, and analyzed by GC or HPLC.

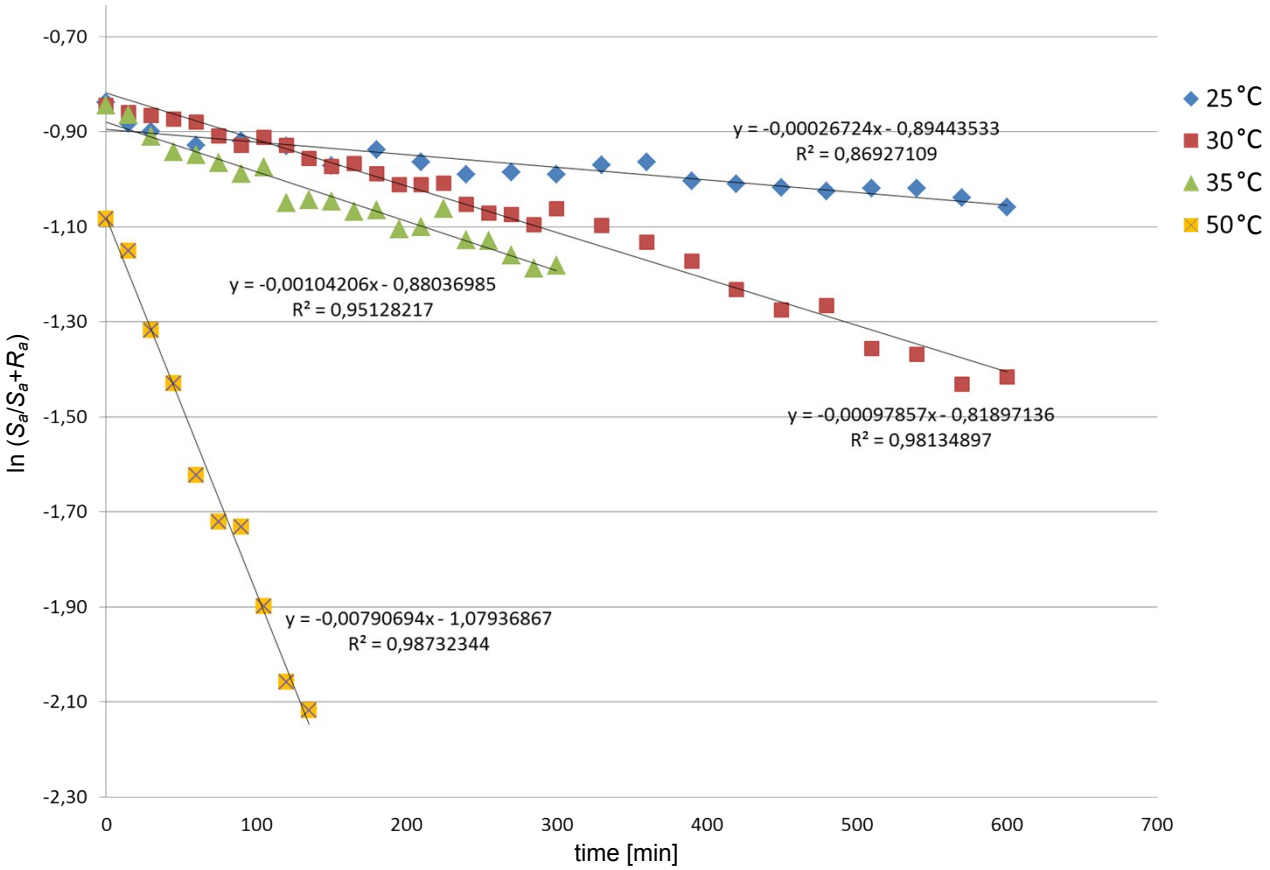
Typical procedure for *S*-selective catalytic hydrogenations reported in figure 3: The substrate (1.75 mmol, 175 eq.) and [Rh(BIPHEP)(acac)] (7.2 mg, 10 µmol) were dissolved in CH_2Cl_2 (1 mL) and stirred for 10 min. The solution was transferred into a 10 mL stirred stainless steel reactor equipped with a 6 mL glass vial and a stirring bar which was previously tempered at 0° C through a cryostat. A cold solution (0 °C) of (S_c)-prolinium-methylester-bis[(trifluoromethyl)sulfonyl]-amide (**2**) (57 mg, 140 µmol, 14 eq.) in CH_2Cl_2 (1 mL) was transferred into the reactor. After stirring for 10 min, the reactor was pressurized with hydrogen (40 bar). The mixture was continuously stirred at 0 °C for 16 h. Then, the pressure was released carefully and the resulting homogeneous solution was diluted with CH_2Cl_2 or CH_3OH, filtered through a SiO_2 pad, and analyzed by GC or HPLC.

Procedure for *R*-selective hydrogenation of 6 at 0.025 mol-% catalyst loading: Methyl 2-acetamidoacrylate (**6**) (573 mg, 4.00 mmol, 4000 eq.) was dissolved in CH_2Cl_2 (4 mL) and combined with a freshly prepared solution of [Rh{(*R*)-BIPHEP}{(*S*)-ProlOMe}] (R_aS_c)-**5** (c = 0.001 mol·L^{-1}, 1.0 mL, 1 µmol) in CH_2Cl_2 (see above). After stirring for 10 min, the slightly red solution was transferred into a 20 mL stainless steel reactor tempered at 0° C through a cryostat and equipped with a 12 mL glass liner and a stirring bar. The stirrer was switched off and the reactor pressurized with hydrogen (40 bar). Afterwards the stirrer was started with a stirring speed of 700 rpm. The pressure drop was monitored with a digital pressure transducer (±0.1 bar). After 75 minutes the pressure was constant. Then, the pressure was carefully released and the resulting homogeneous solution was diluted with CH_2Cl_2 filtered through a SiO_2 pad and analyzed by GC.

Procedure for S-selective hydrogenation of 6 at 0.025 mol-% catalyst loading: Methyl 2-acetamidoacrylate (**6**) (573 mg, 4.00 mmol, 4000 eq.) was dissolved in CH_2Cl_2 (4 mL) and cooled to -10 °C. The substrate solution was combined with a freshly prepared solution of [Rh{*rac*-BIPHEP}{(*S*)-ProlOMe}] (R_aS_c)/(S_aS_c)-**5** (c = 0.001 mol·L^{-1}, 1.0 mL, 1 µmol) in CH_2Cl_2 (see above). After stirring for 10 min, the slightly red solution was transferred into a 20 mL stainless steel reactor tempered to 0° C through a cryostat and equipped with a 12 mL glass liner and a stirring bar. The stirrer was switched off and the reactor pressurized with hydrogen (40 bar). Afterwards the stirrer was switched on with a stirring speed of 700 rpm. The pressure drop was monitored with a digital pressure transducer (±0.1 bar). After 75 minutes the pressure was constant. Then, the pressure was released carefully and the resulting homogeneous solution was diluted with CH_2Cl_2 filtered through a SiO_2 pad and analyzed by GC.

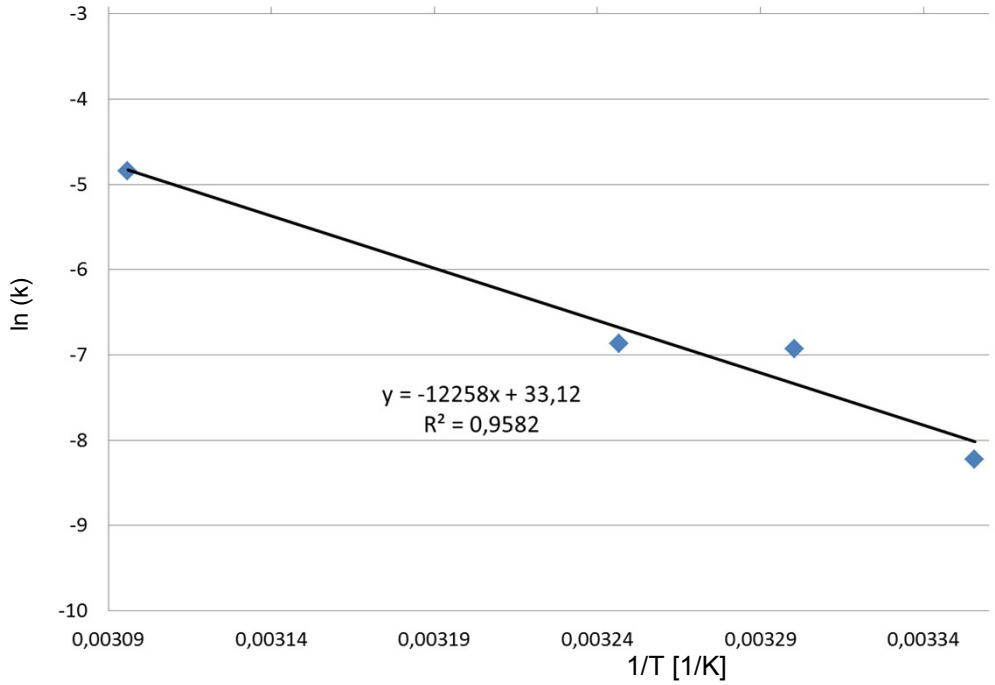
Typical procedure for the catalytic hydroboration of styrene: The solvent of a freshly prepared [Rh{(R_a)-BIPHEP}{(S_c)-ProlOMe}] (R_aS_c)-**5** (c = 0.1 mol·L^{-1}, 0.1 mL, 10 µmol) in CH_2Cl_2 (prepared by procedure A) was evaporated with a high vacuum pump. The Schlenk was introduced in a Glovebox, styrene (**16**) (170.0 µl, 1.48 mmol, 148 eq) was added and diluted with the appropriate solvent (2.0 mL). The red solution was tempered to the reaction temperature through a cryostat and catecholborane (250 µl, 2.35 mmol, 235 eq) was slowly added to the solution. The reaction mixture was kept at constant temperature during the reaction time (rt = 1 h, 0 °C = 3 h, <0 °C = 12 h). After the reaction time, ethanol (2.5 mL), hydrogen peroxide (2.5 mL, 30% aqueous solution), and sodium hydroxide (2.5 mL, 2M aqueous solution) were added to the solution. The reaction mixture was allowed to warm to room temperature and stirred for 3 h at ambient pressure. The reaction mixture was then extracted with diethylether (50 mL). The organic phase was separated and washed with sodium hydroxide (25 mL, 2M aqueous solution), deionized water (25 mL) and sodium chloride (2 x 25 mL). The organic phase was dried with sodium sulfate and volatiles were evaporated at 40 °C and 800 mbar. A part of the residue was dissolved in methylene chloride (1 mL) and 1-hexanol (app. 10 mg) as an external standard for GC-analysis was added. Selectivity and enantioselectivity were determined by GC-analysis.

Kinetic of the diastereomerisation of ({S_aS_c}/{R_aS_c}-5) to {R_aS_c}-5 at different temperatures



Rate constants (first reaction order) of the diastereomerisation of ({S_aS_c}/{R_aS_c}-**5**) to {R_aS_c}-**5** at different temperatures. Ratios ({S_aS_c}-**5**/{R_aS_c}-**5**) determined by $^{31}P\{^1H\}$-NMR spectroscopy (CD_2ClCD_2Cl).

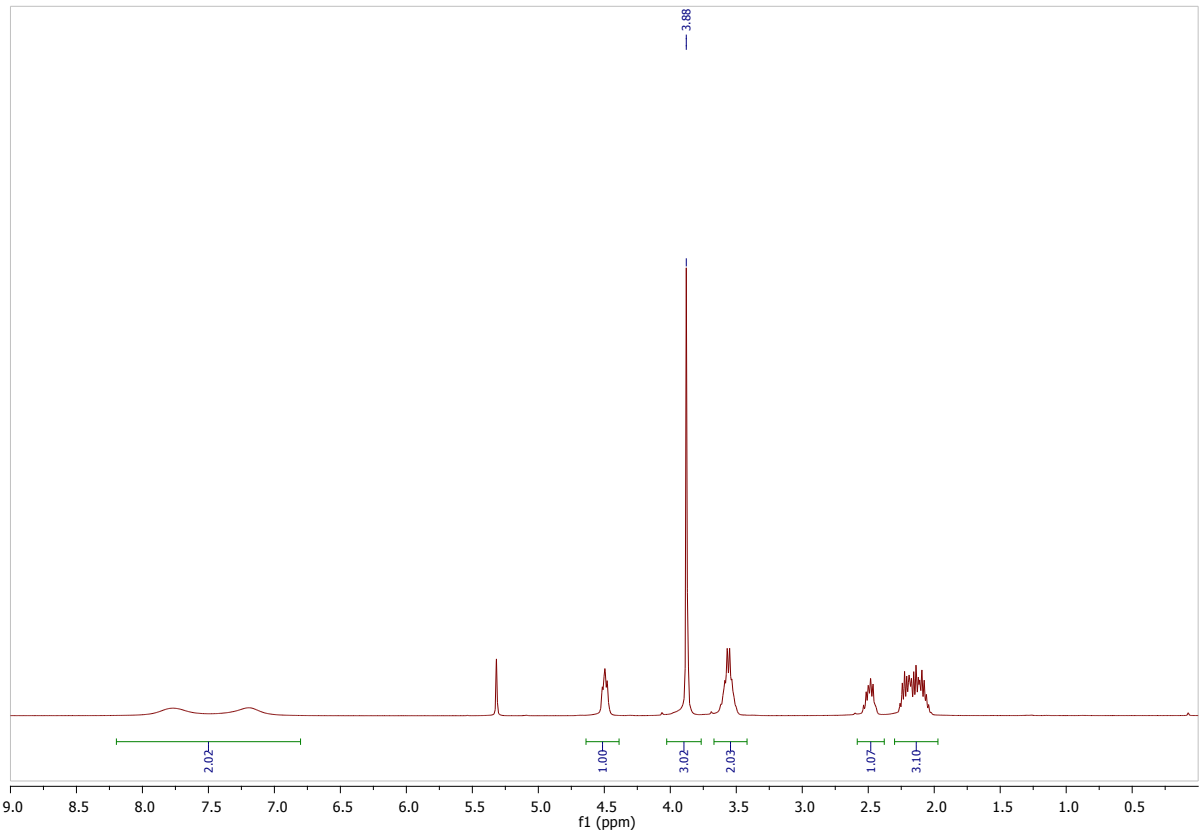
Arrhenius Plot for the diastereomerisation of ({S_aS_c}/{R_aS_c}-5) to {R_aS_c}-5 at different temperatures

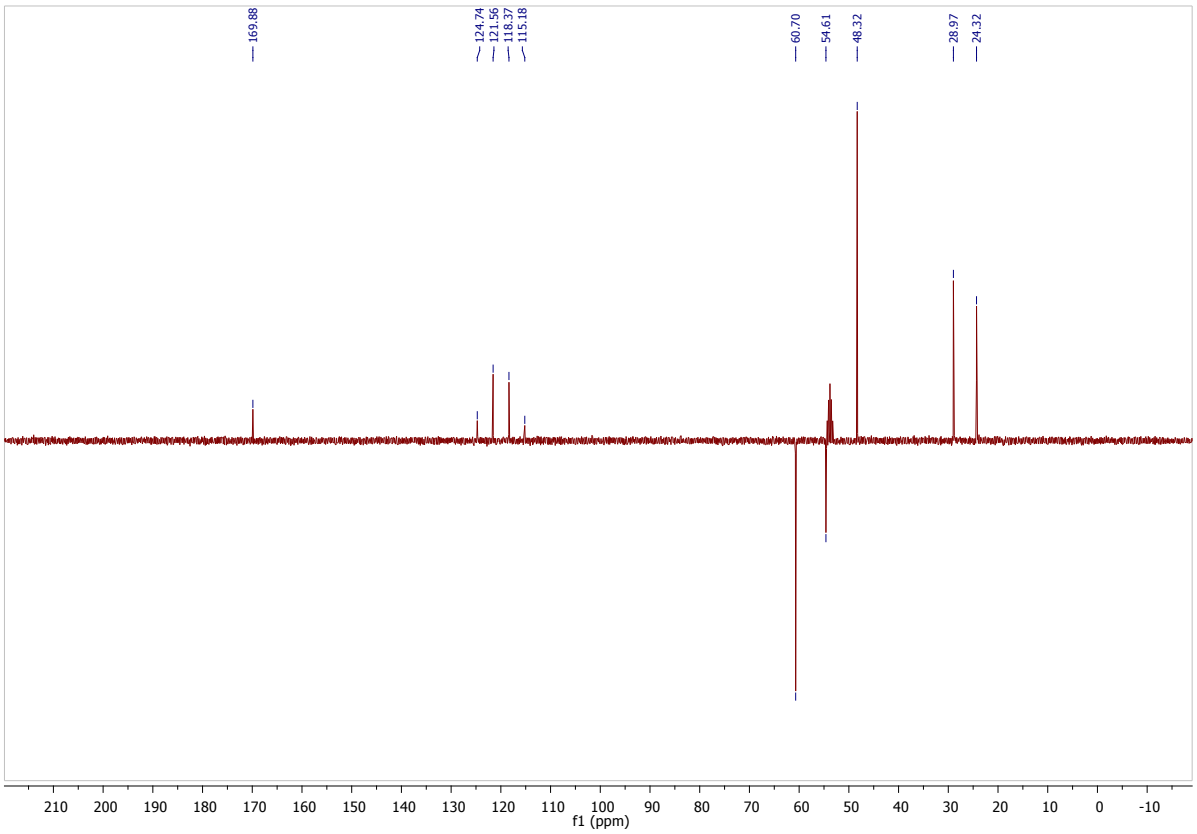


E_A = 12258 × 8.314 / 4,1868 / 1000 = 24.3 kcal/mol; σ(%) = 1-R^2 = 4.2% => EA = 24.3 ± 1.0 kcal/mol

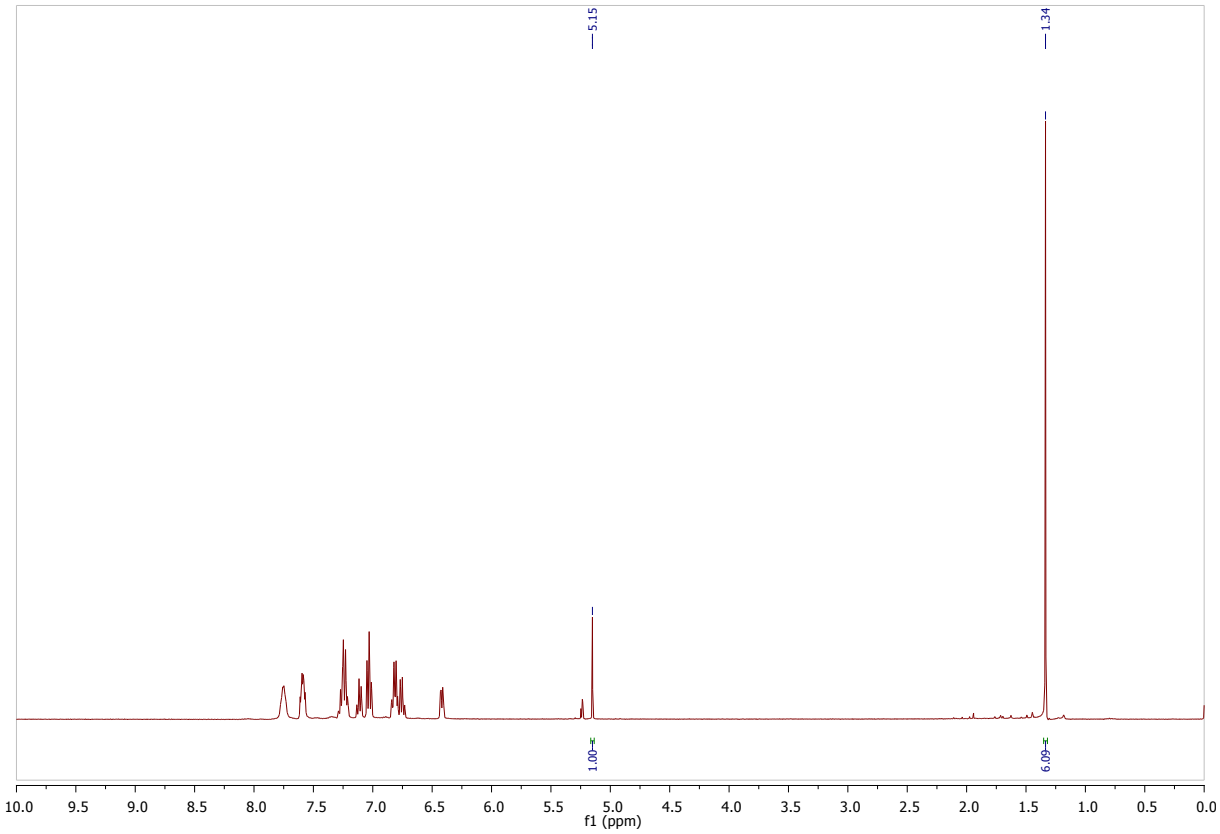
NMR-data:

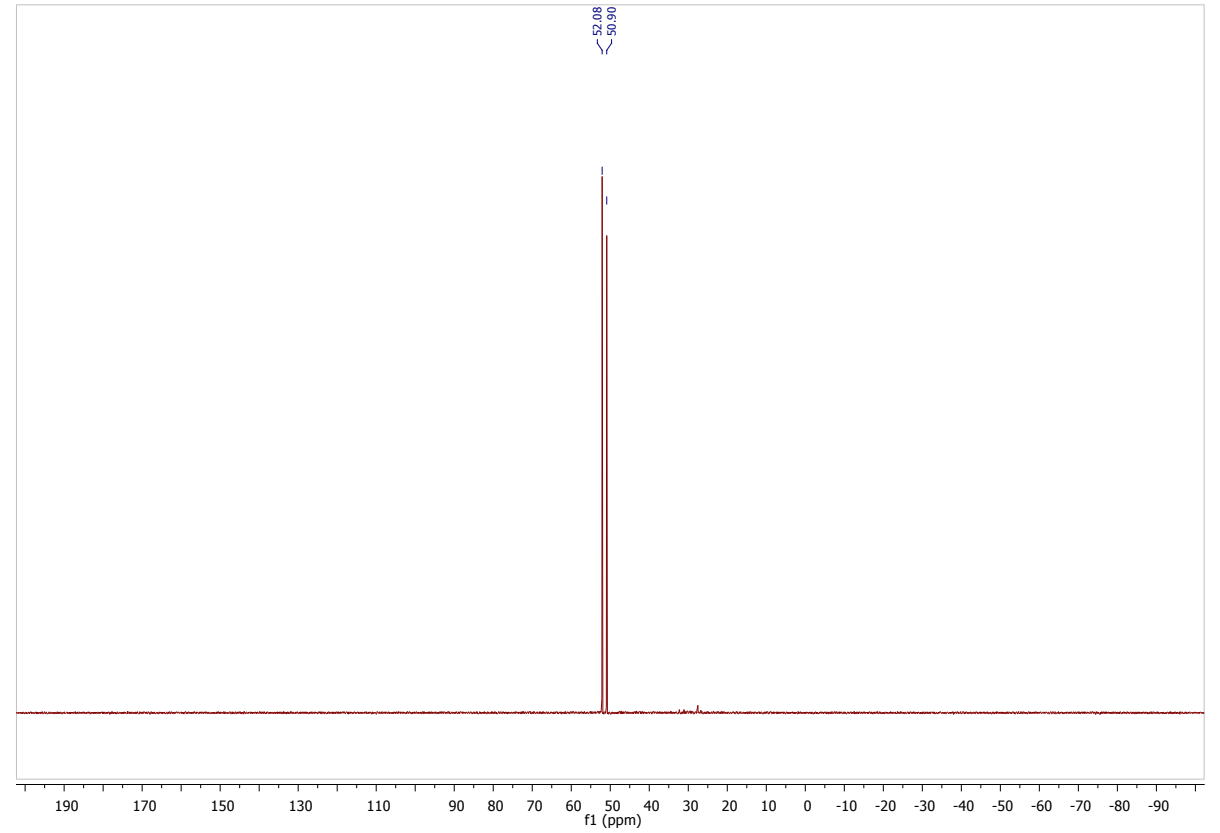
(S_c)-Prolinium-methylester-bis[(trifluoromethyl)sulfonyl]-amide (**2**):



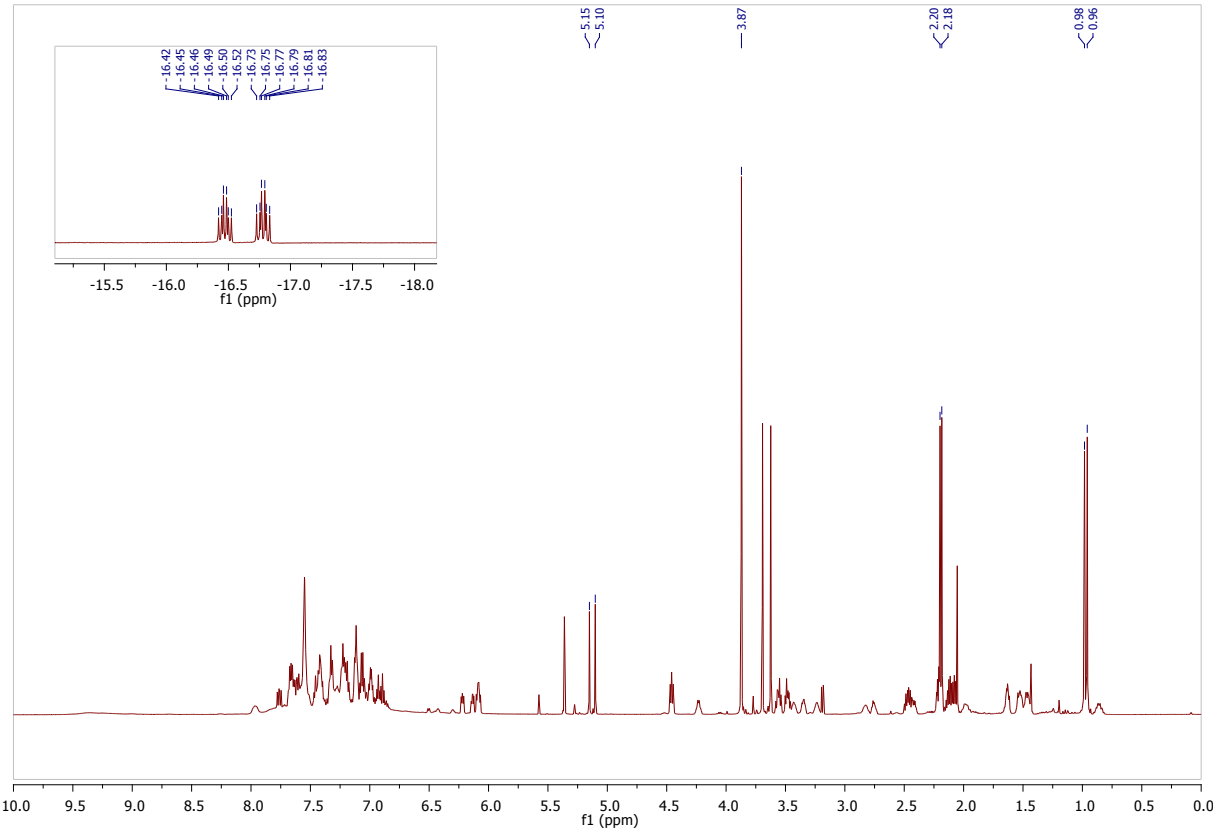


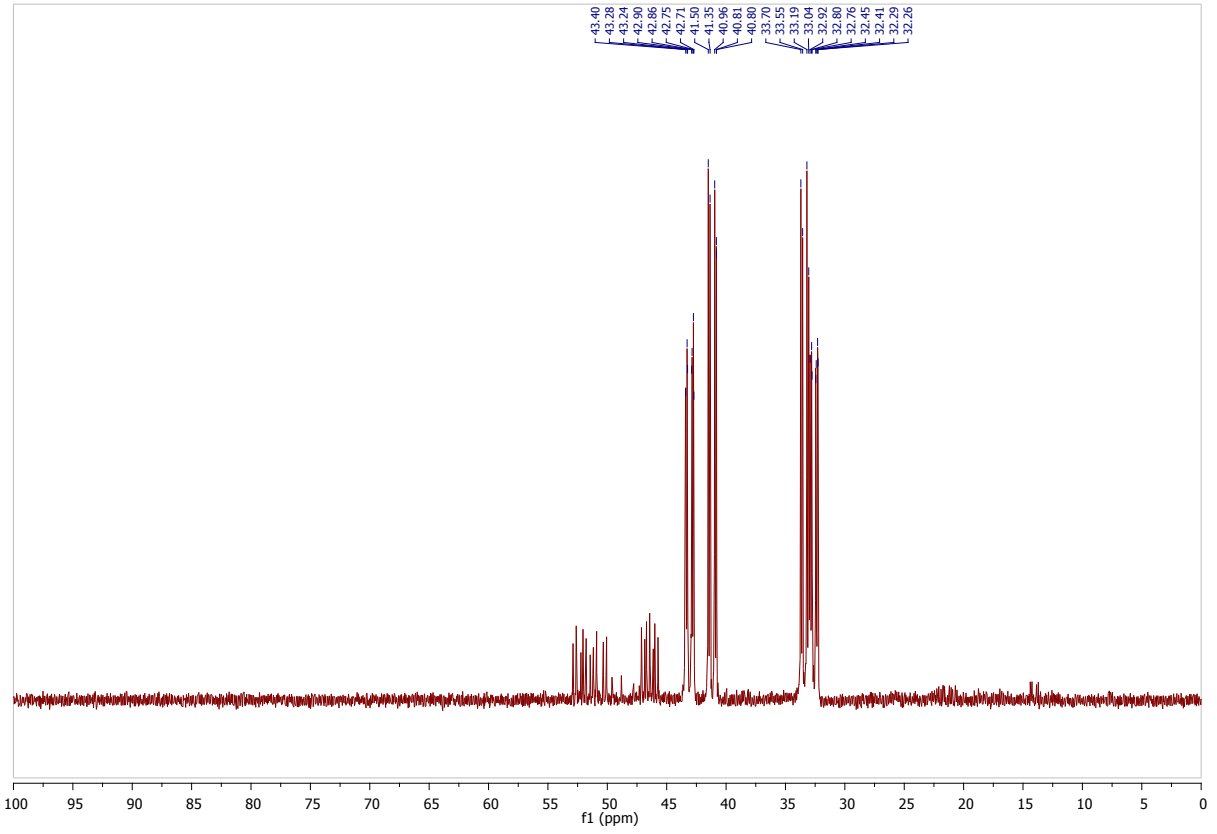
[Rh(BIPHEP)(acac)] (**3**):



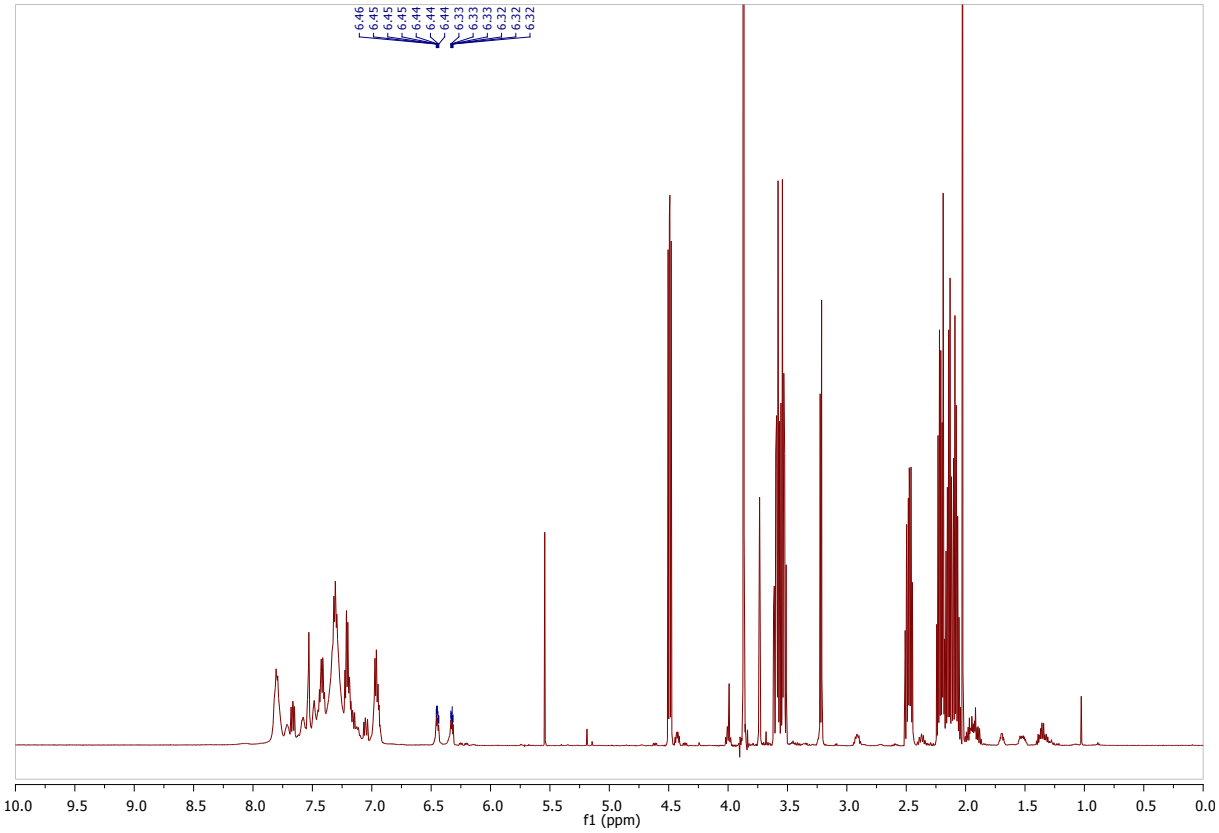


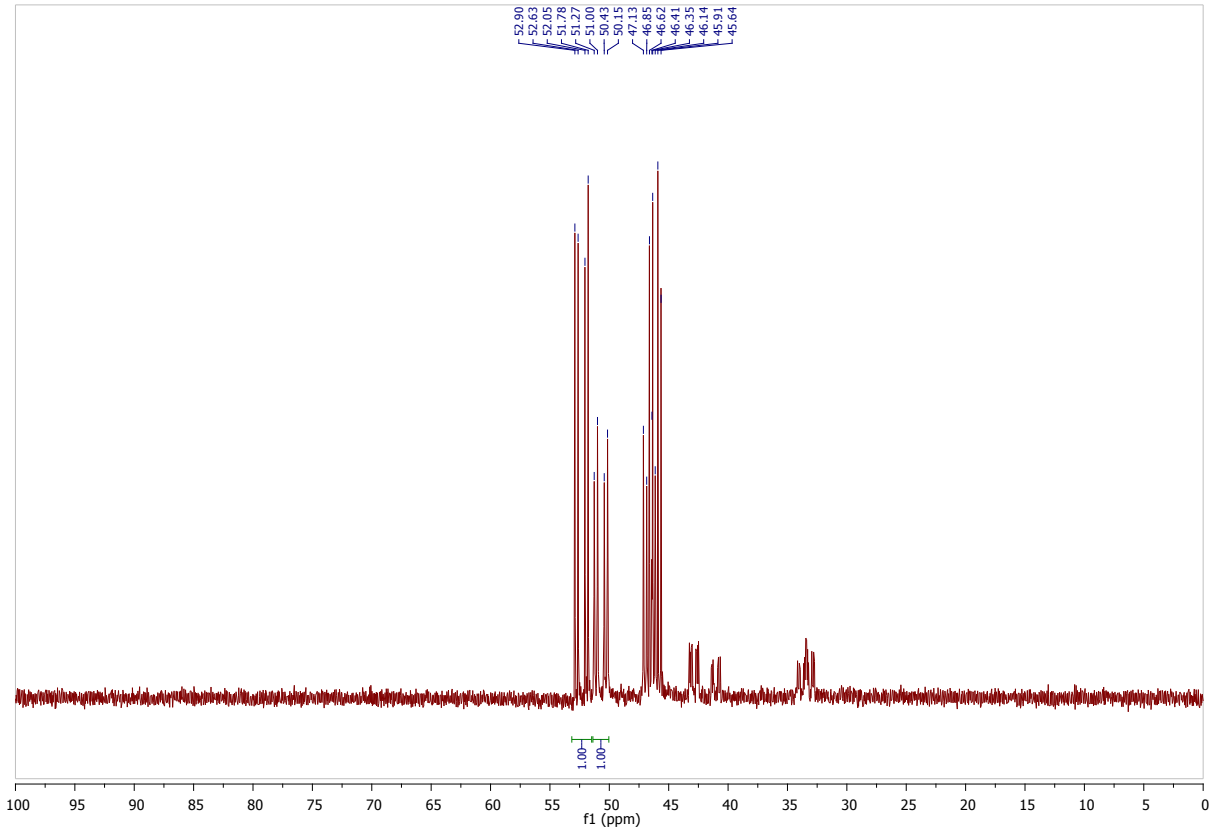
[(H)Rh(κ^2-BIPHEP)(η^2-acac)(κ^1-ProlOMe)][NTf$_2$] (**4**):



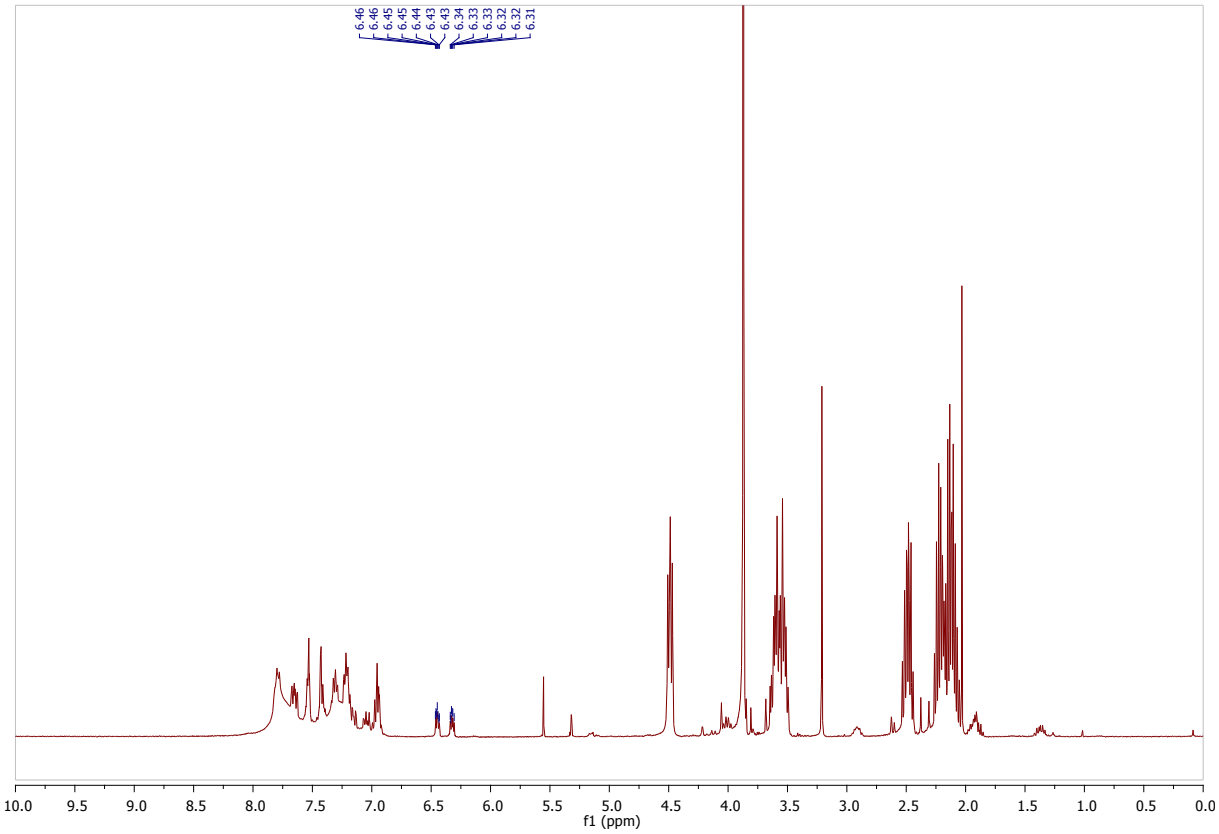


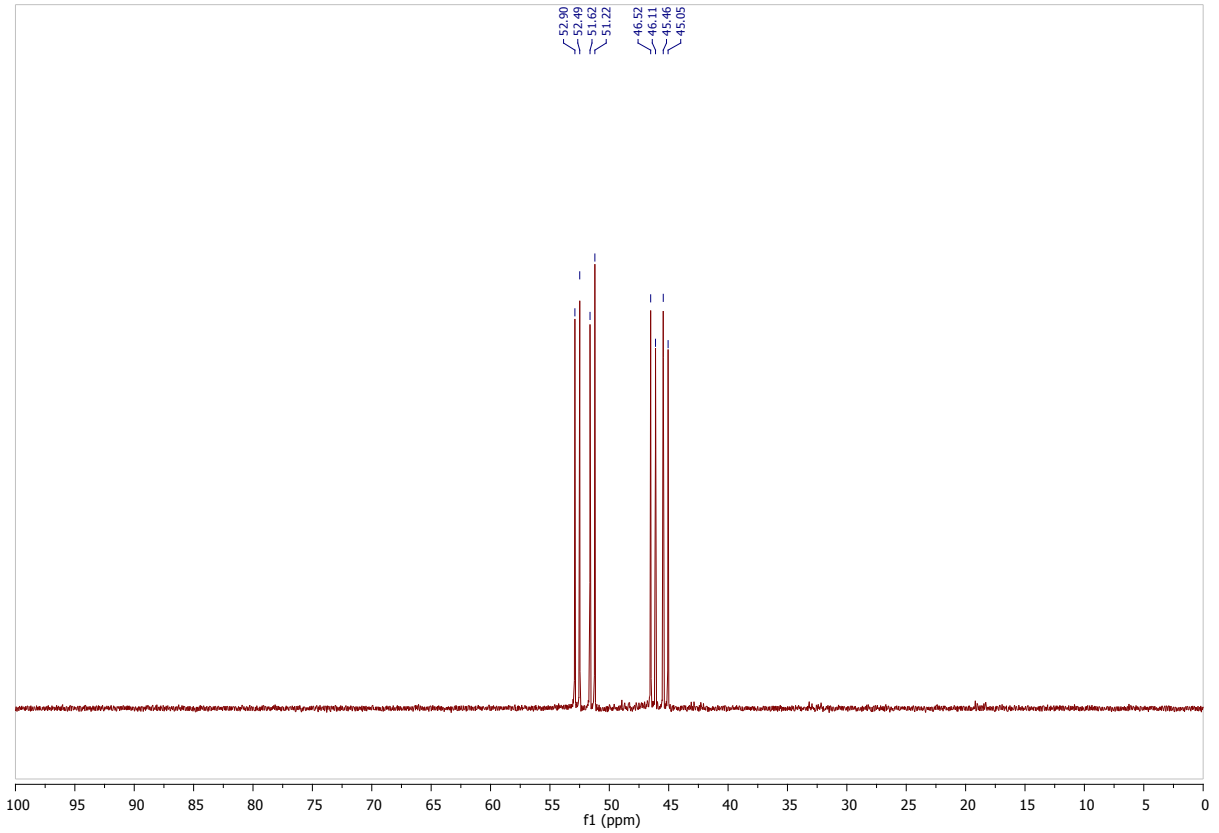
{S_aS_c}/{R_aS_c}-[Rh{BIPHEP}{(S_c)-ProlOMe}][NTf_2] ({S_aS_c}/{R_aS_c}-**5**)



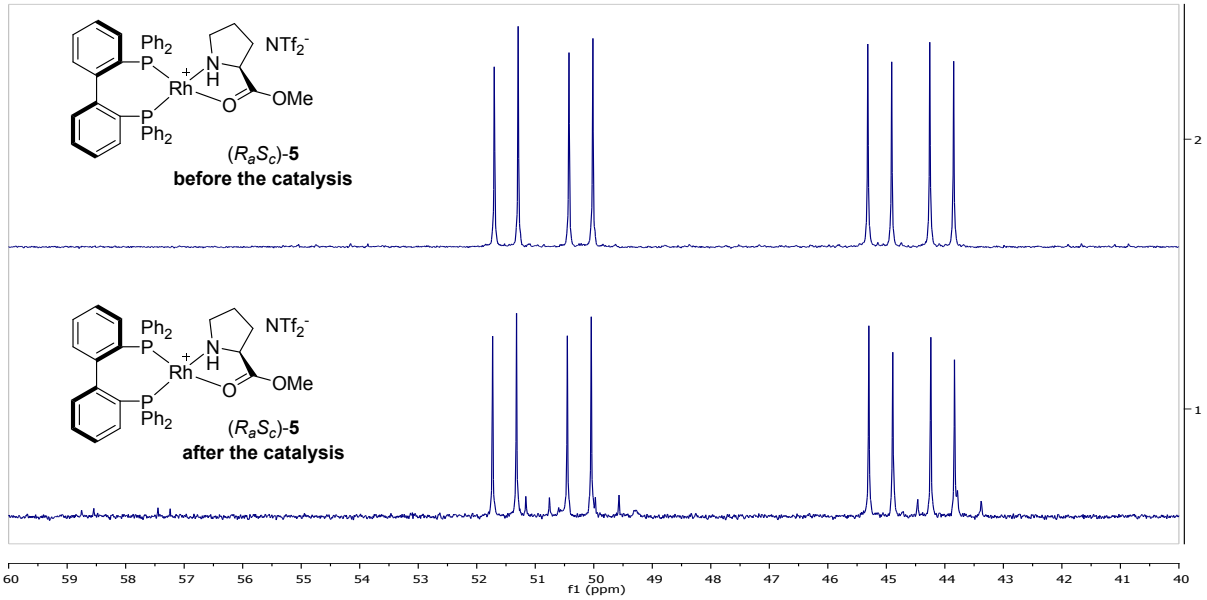


[Rh{(*R*)-BIPHEP}{(*S*)-ProlOMe}][NTf_2] {R_aS_c}-**5**



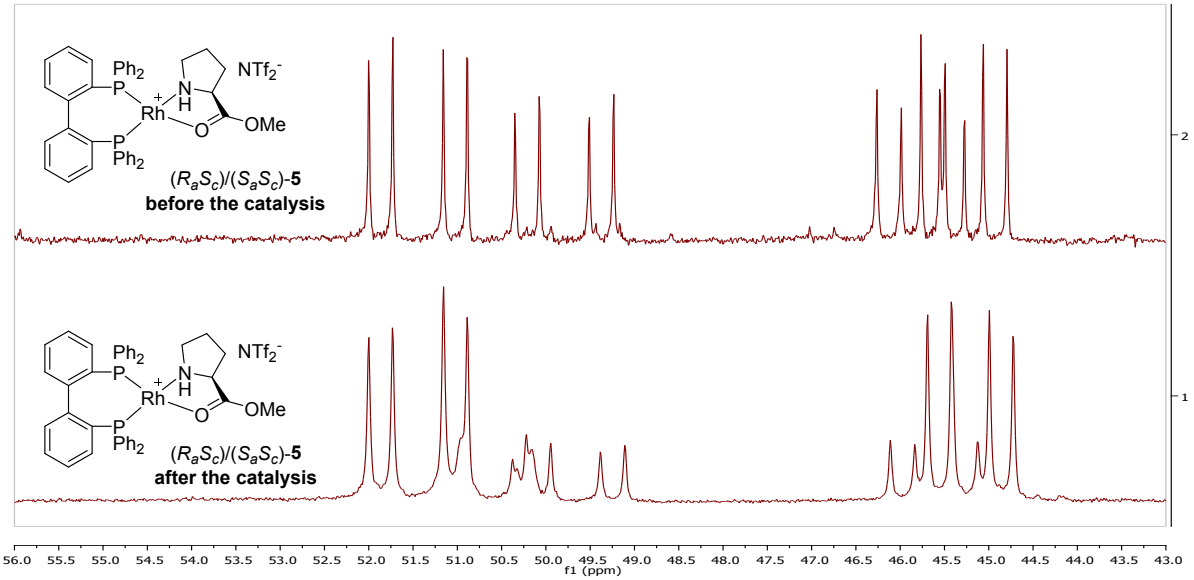


$^{31}P\{^1H\}$-NMR spectra of (R_aS_c)-5 before and after hydrogenation of methyl 2-acetamidoacrylate (6)



$^{31}P\{^1H\}$-NMR spectra of the crude reaction mixture before (CD_2Cl_2, 0 °C, 162 MHz (upper spectrum)) and after 243 MHz (lower spectrum)) hydrogenation of **6** using (R_aS_c)-**5**.

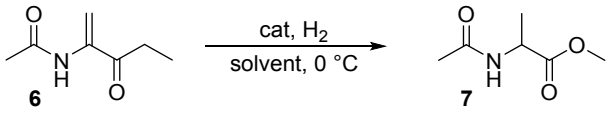
$^{31}P\{^1H\}$-NMR spectra of (R_aS_c)/(S_aS_c)-5 before and after hydrogenation of methyl 2-acetamidoacrylate (6)



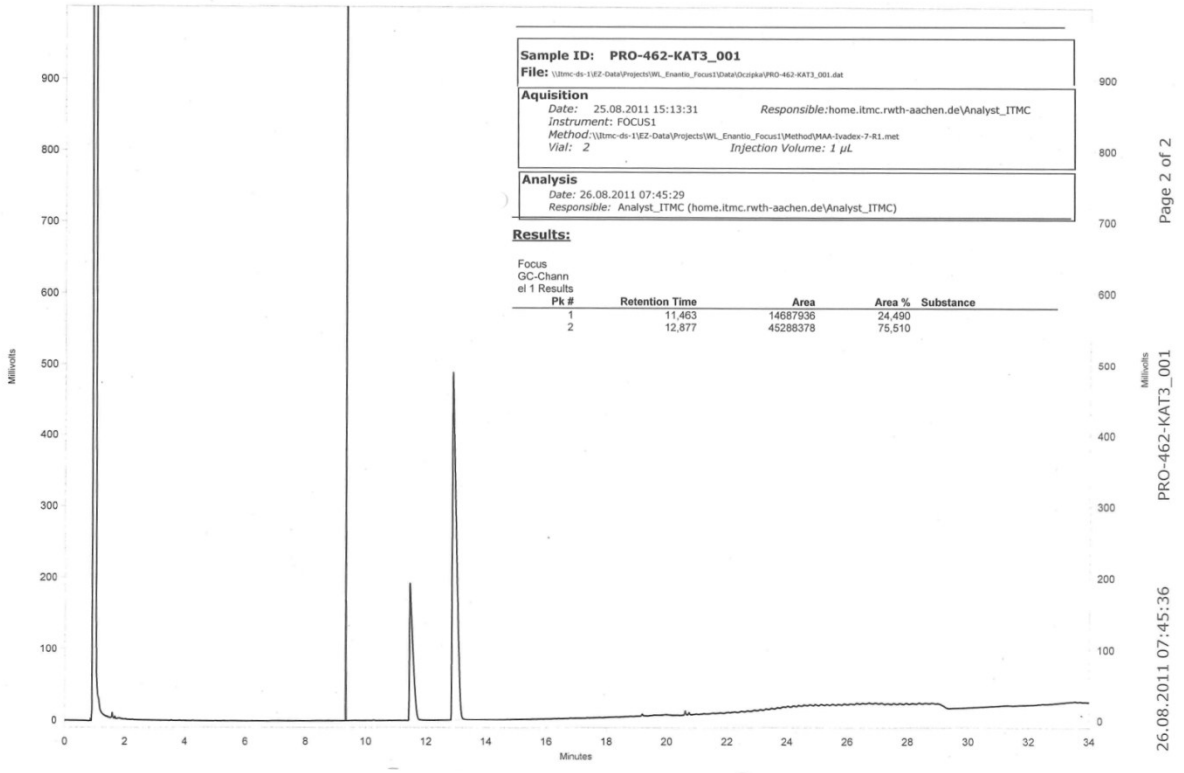
$^{31}P\{^1H\}$-NMR spectra of the crude reaction mixture before (CD_2Cl_2, 0 °C, 243 MHz (upper spectrum)) and after 243 MHz (lower spectrum)) hydrogenation of **6** using the diastereomeric mixture (S_aS_c)/(R_aS_c)-**5** as catalyst.

GC/HPLC-data of the hydrogenation products:

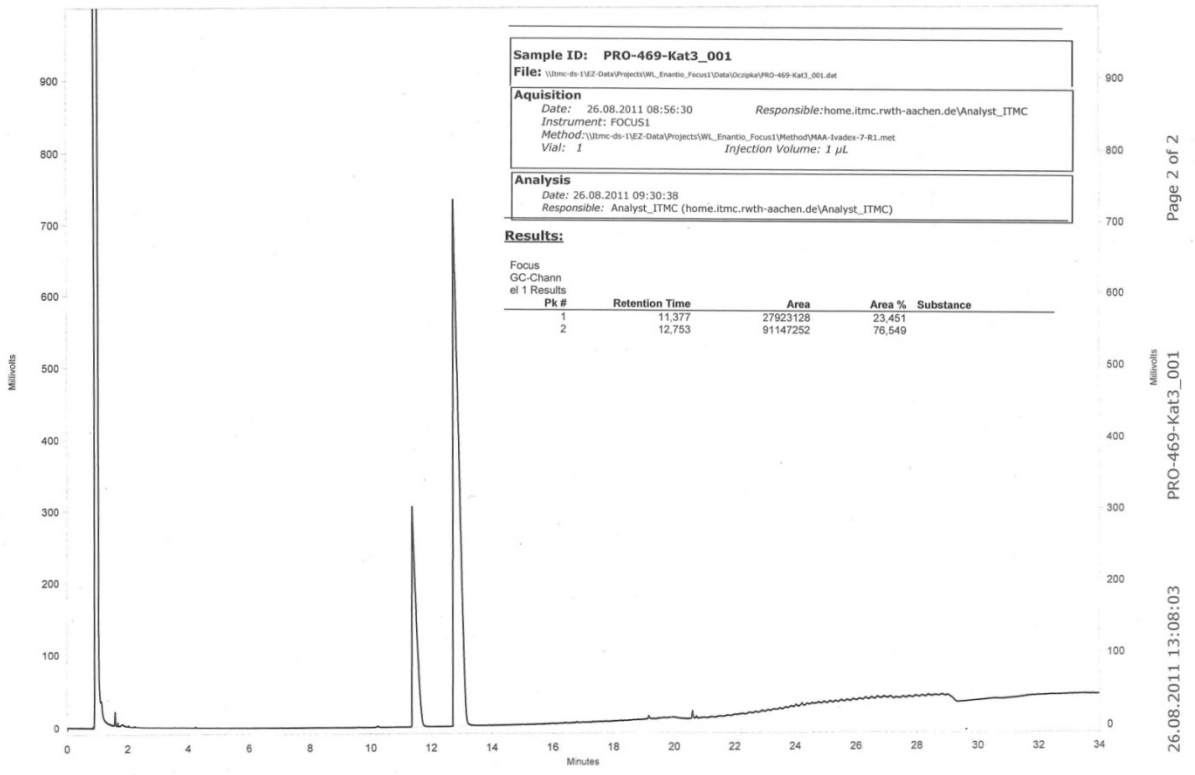
Methyl 2-acetamidoacrylate (6):



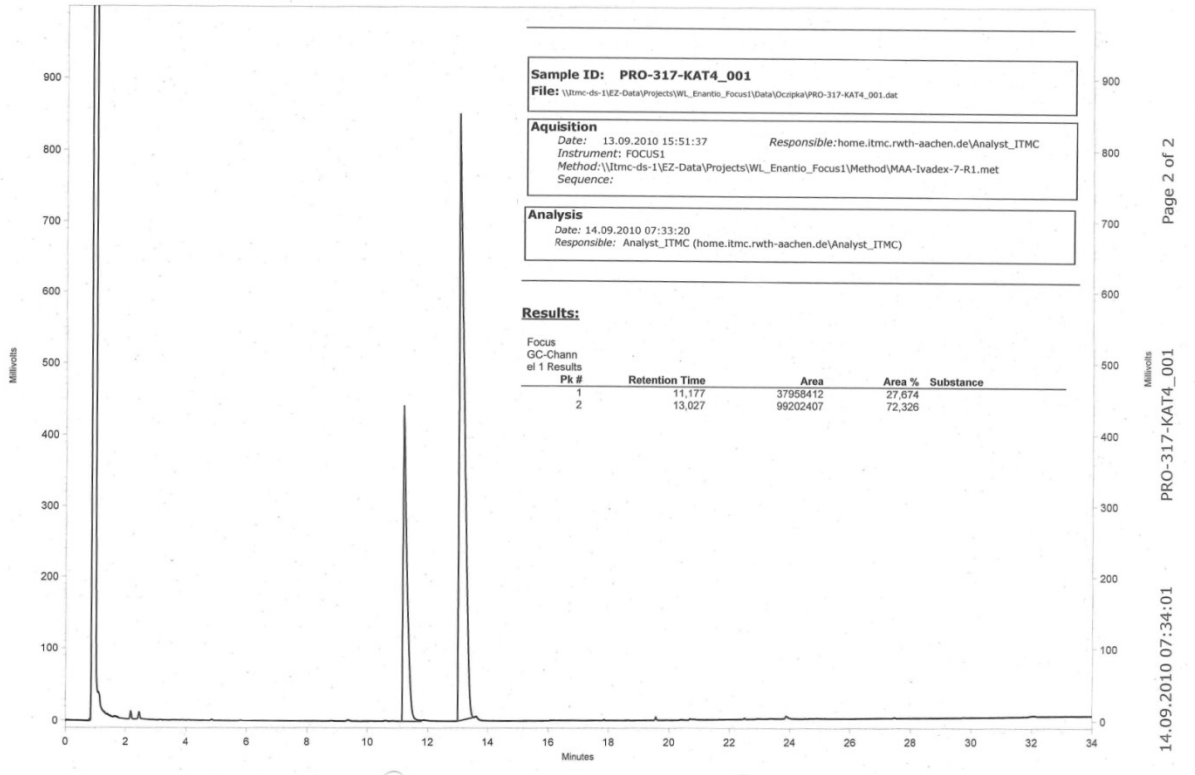
Chiral GC analysis: *Ivadex 7* (25 m), hydrogen flow (2 mL / min), film thickness (0.25 µm), inner diameter (0.25 mm), injector temperature = 250 °C, temperature program = 90 °C isotherm (10 min), 90 °C – 160 °C (5 °C / min), 160 °C isotherm (10 min), t_r = (*R*)-**7**: 12.88 min, (*S*)-**7**: 11.46 min, **6**: 9.40 min.



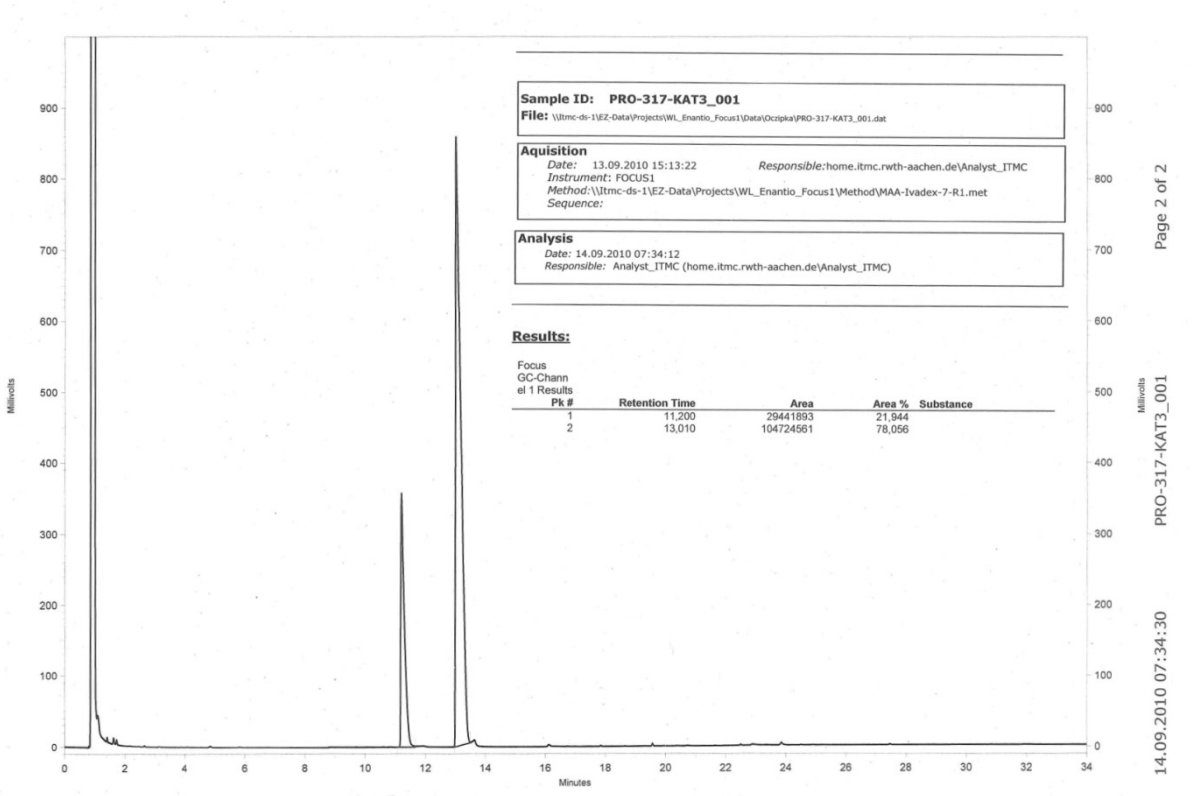
Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*R*)-selectivity (Table 1, entry 1).



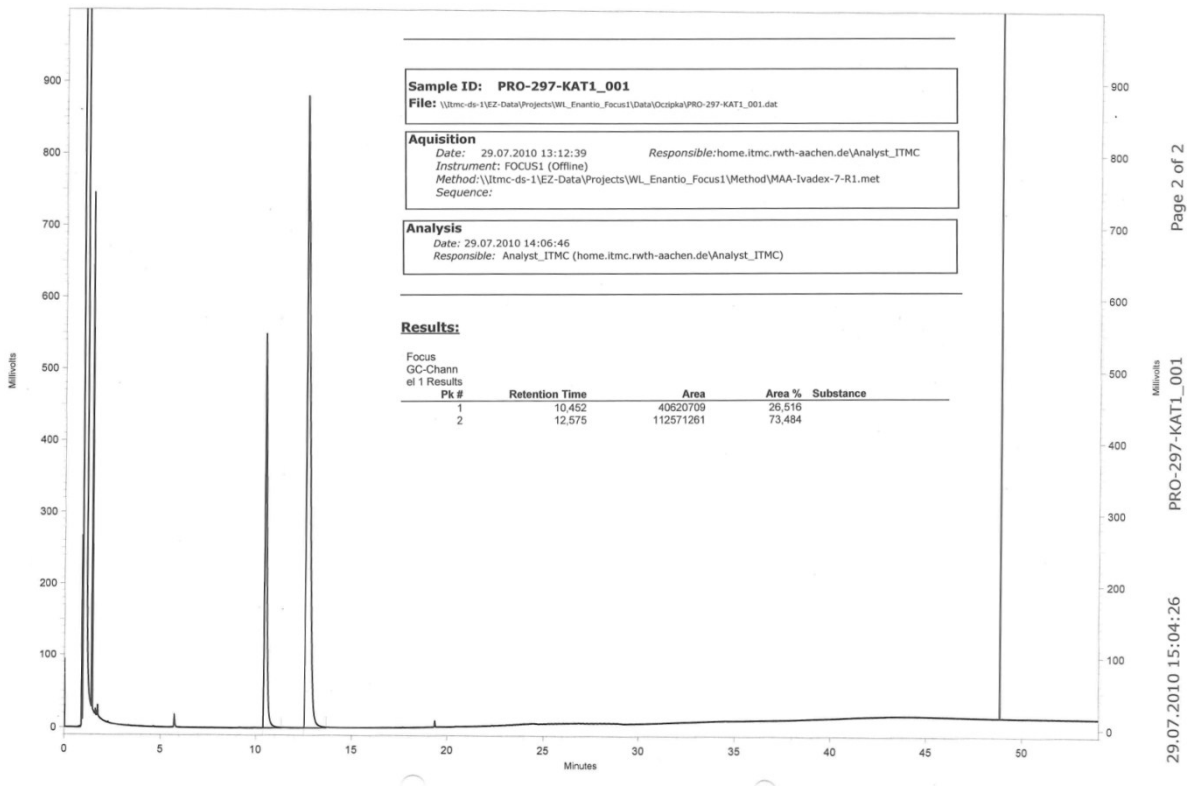
Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*R*)-selectivity (Table 1, entry 2).



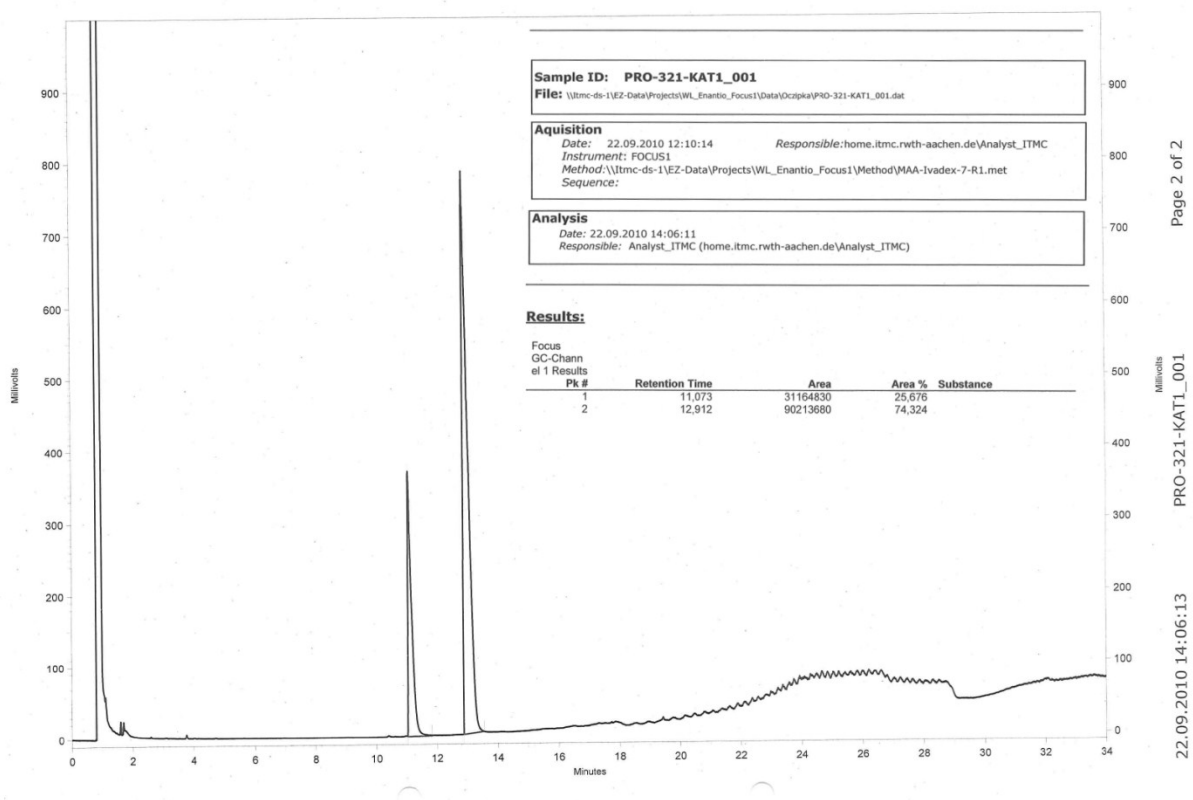
Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*R*)-selectivity (Table 1, entry 3).



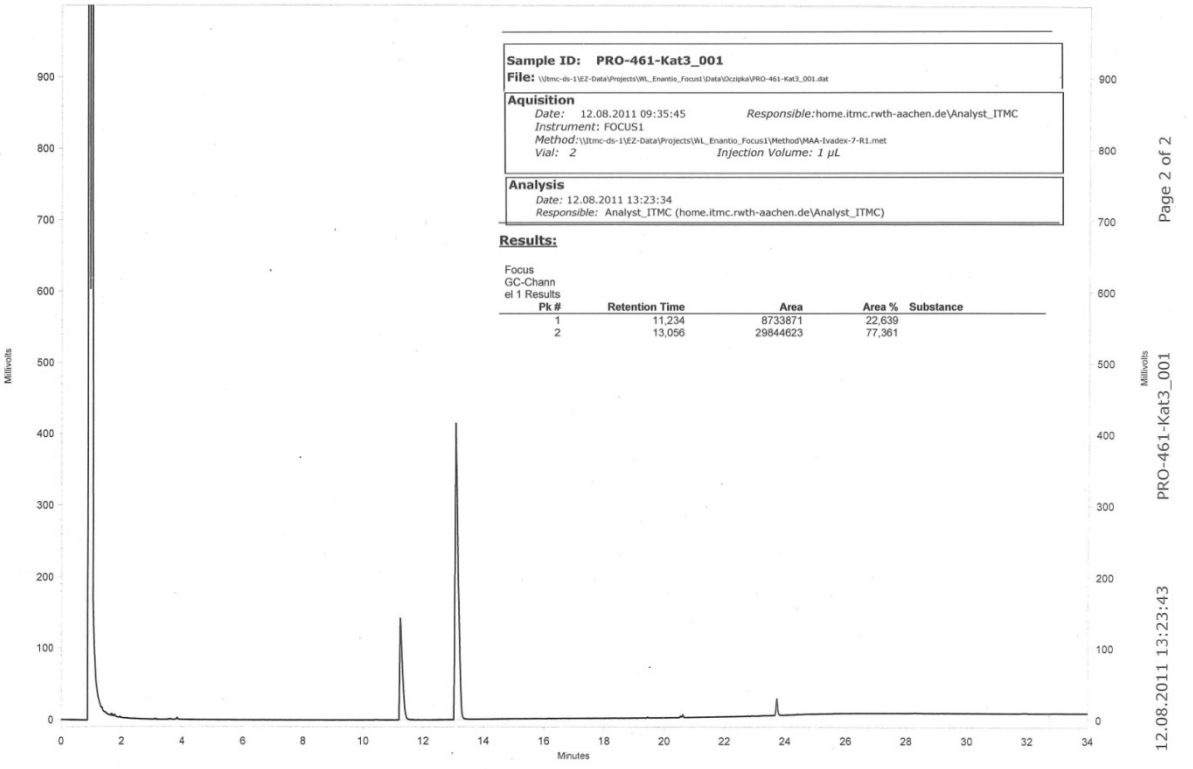
Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*R*)-selectivity (Table 1, entry 4).



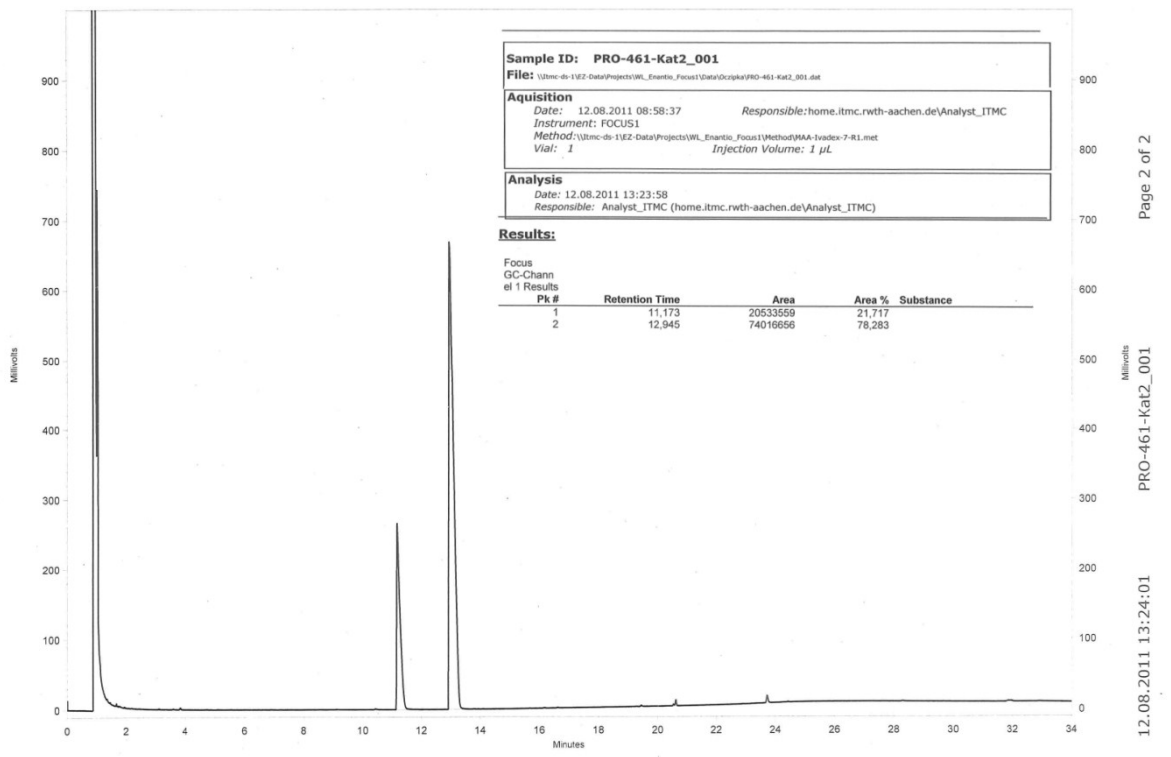
Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*R*)-selectivity (Table 1, entry 5).



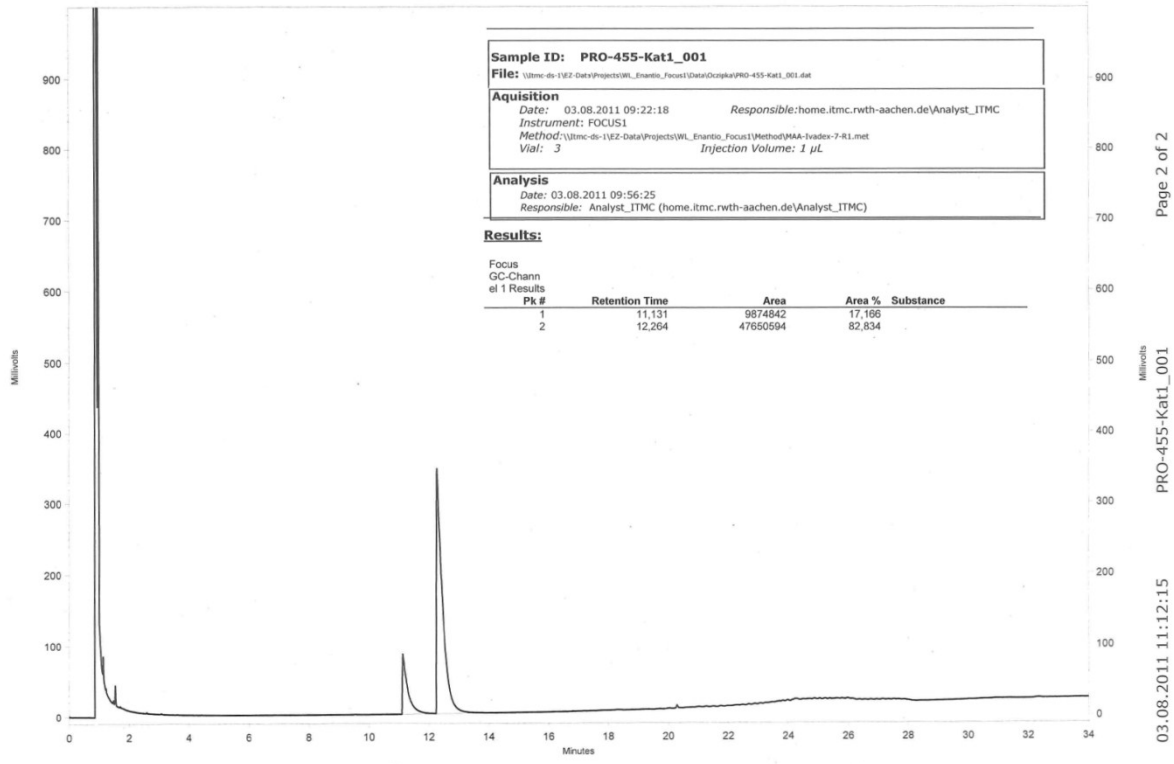
Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*R*)-selectivity (Table 1, entry 6).



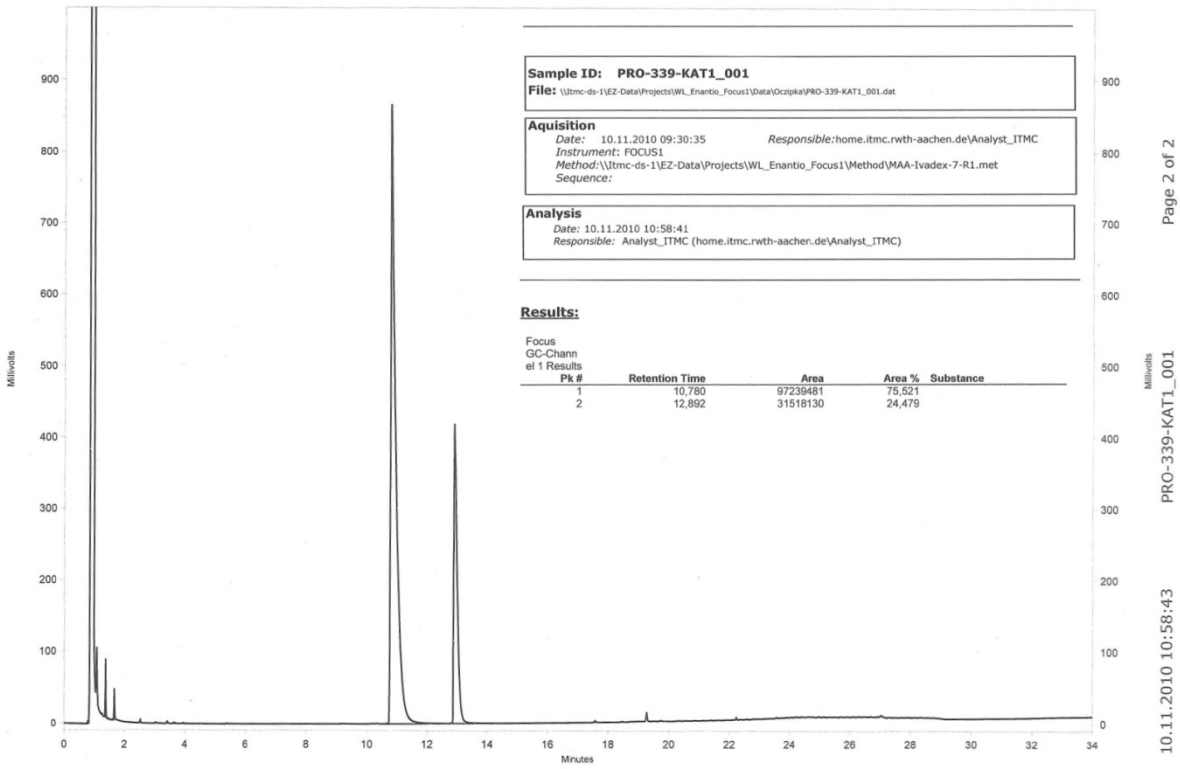
Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*R*)-selectivity (Table 1, entry 7).



Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*R*)-selectivity (Table 1, entry 8).

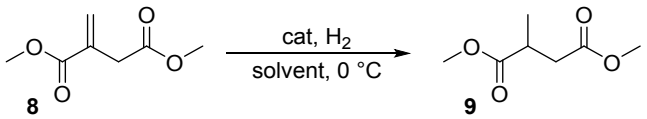


Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*R*)-selectivity (Table 1, entry 9 and Fig. 3).



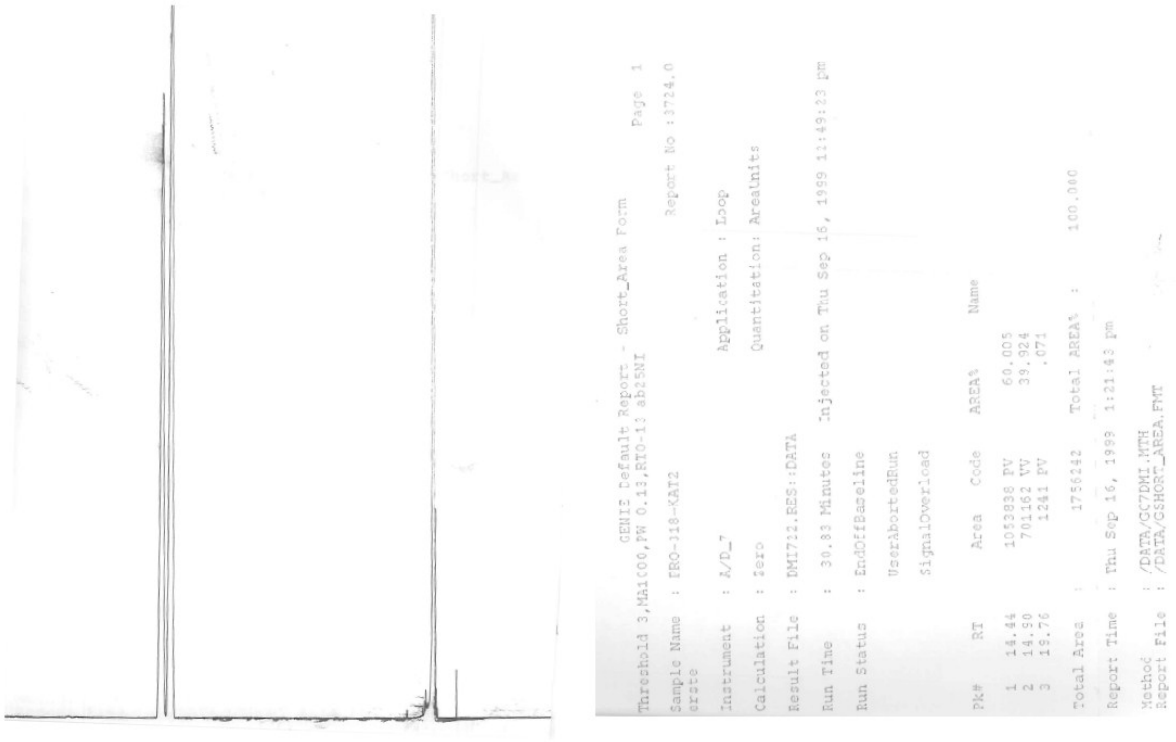
Hydrogenation of Methyl 2-acetamidoacrylate (**6**) – resulting in (*S*)-selectivity (Fig. 3).

Dimethyl itaconate (8):

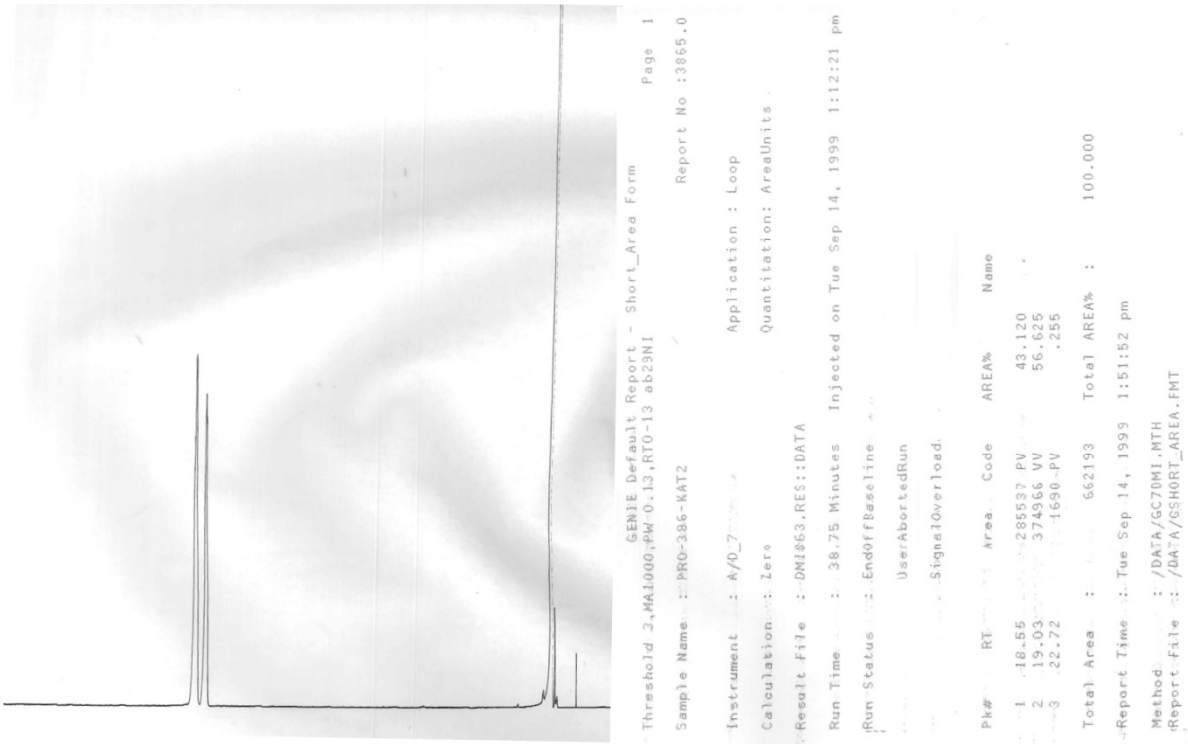


8 **9**

Chiral GC analysis: *Lipodex E* (25 m), hydrogen pressure (0.6 bar), injector temperature = 250 °C, temperature program = 80 °C isotherm, t_r = **8**: 19.76, (*S*)-**9**: 14.90, (*R*)-**9**: 14.44.

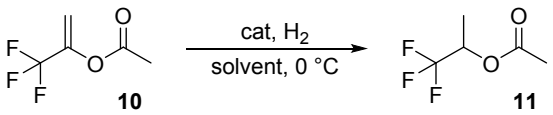


Hydrogenation of Dimethyl itaconate (**8**) resulting in (*R*)-selectivity (Fig. 3).

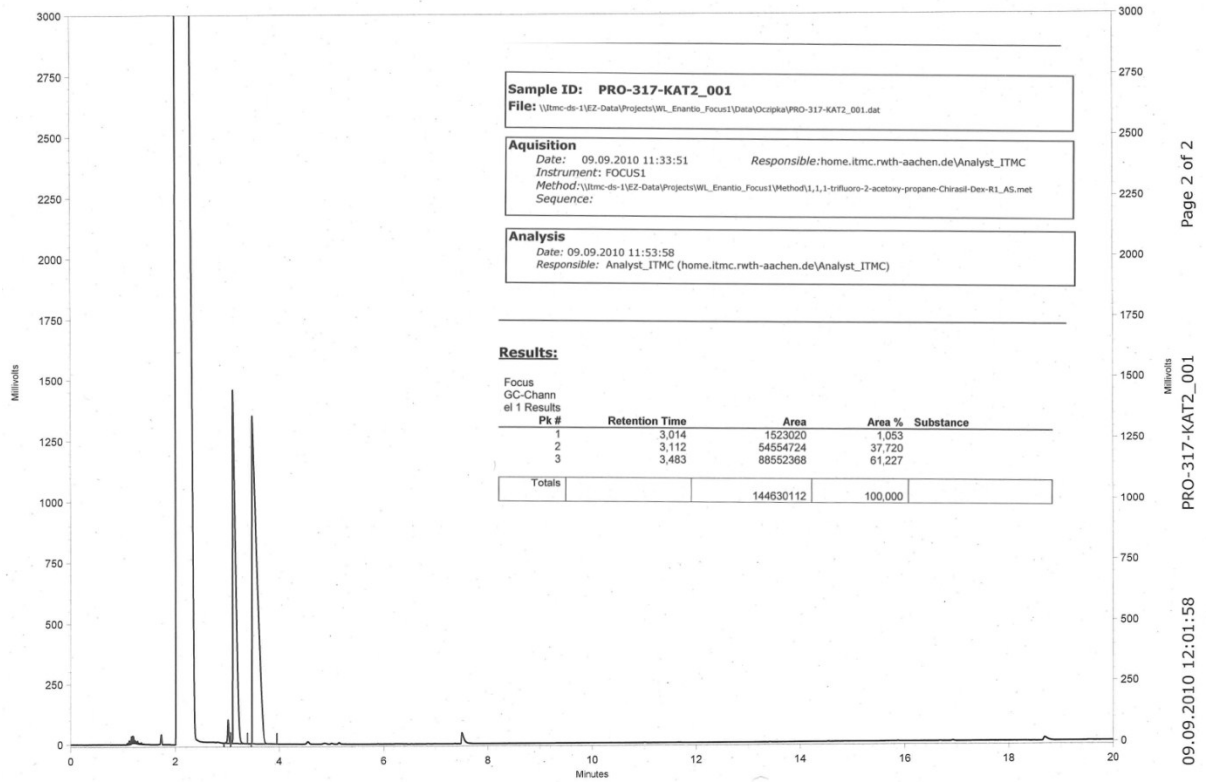


Hydrogenation of Dimethyl itaconate (**8**) resulting in (*S*)-selectivity (Fig. 3).

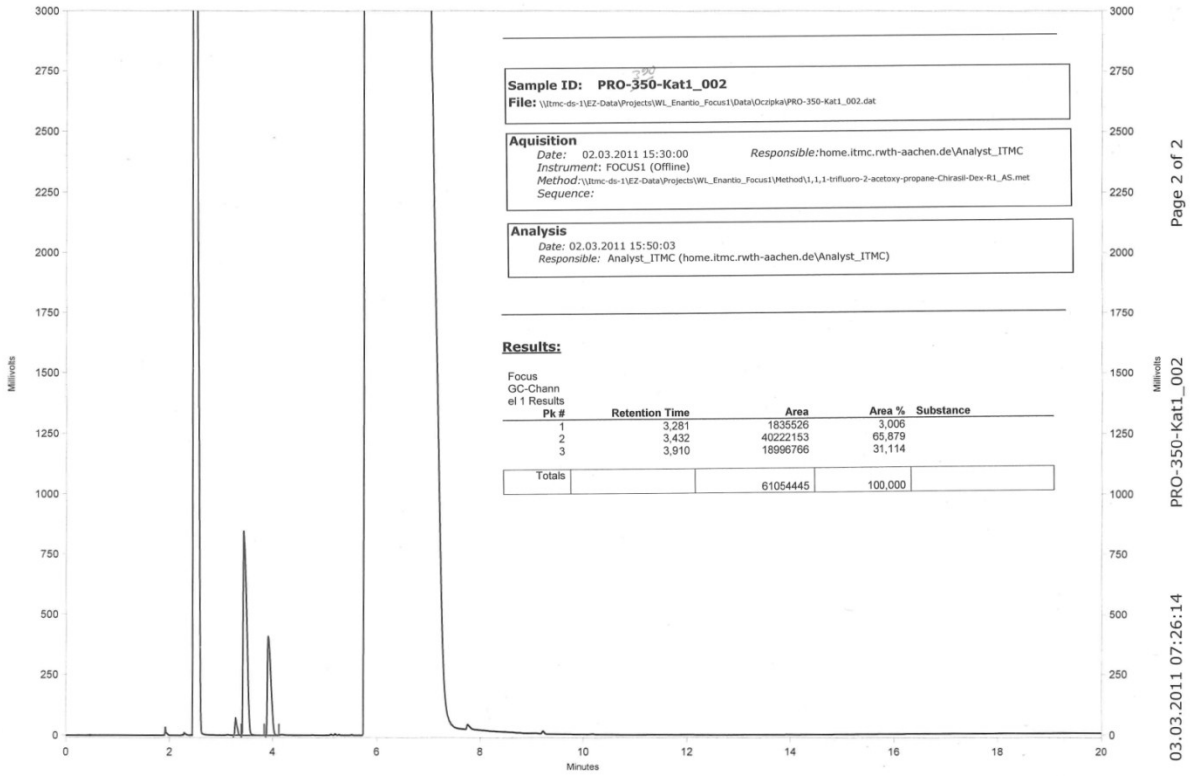
Methyl 2-(trifluoromethyl)acrylate (10):



The product solution was diluted with toluene to prevent signal overlapping of the enantiomere and substrate signals.
Chiral GC analysis: *Chiralsil-DEX* (25 m), hydrogen flow (2 mL / min), film thickness (0.25 µm), inner diameter (0.25 mm), injector temperature = 250 °C, temperature program = 50 °C isotherm (4.5 min), 50 °C – 160 °C (10 °C /min), 160 °C isotherm (4.5 min), t_r = (*R*)-**11**: 3.48, (*S*)-**11**: 3.11, **10**: 3.01 min.

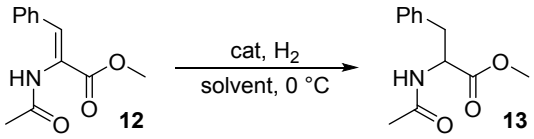


Hydrogenation of Methyl 2-(trifluoromethyl)acrylate (**10**) resulting in (*R*)-selectivity (Fig. 3).

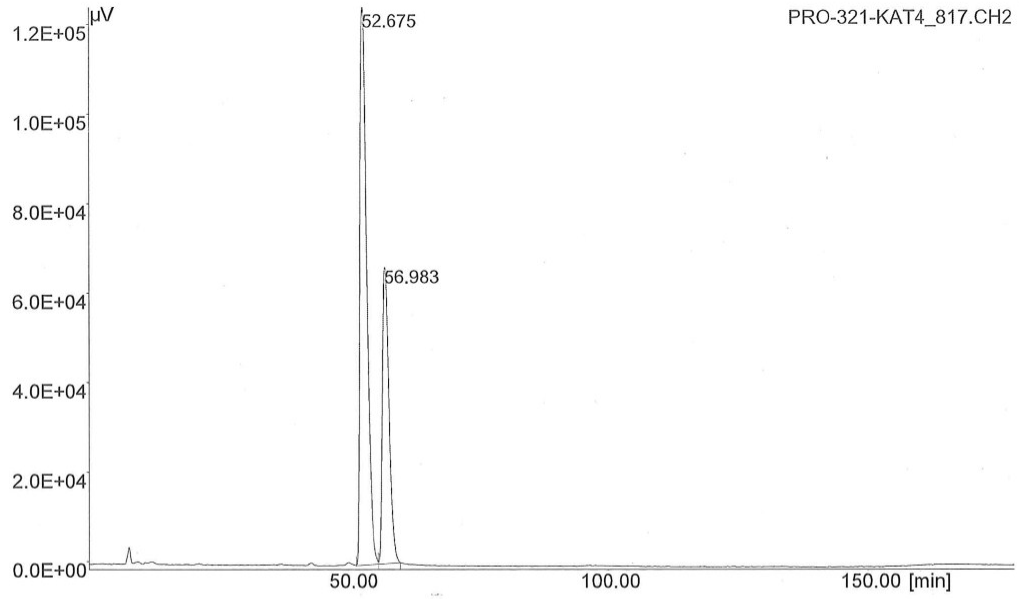


Hydrogenation of Methyl 2-(trifluoromethyl)acrylate (**10**) resulting in (*S*)-selectivity (Fig. 3).

Methyl 2-acetamido-3-phenylacrylate (12):

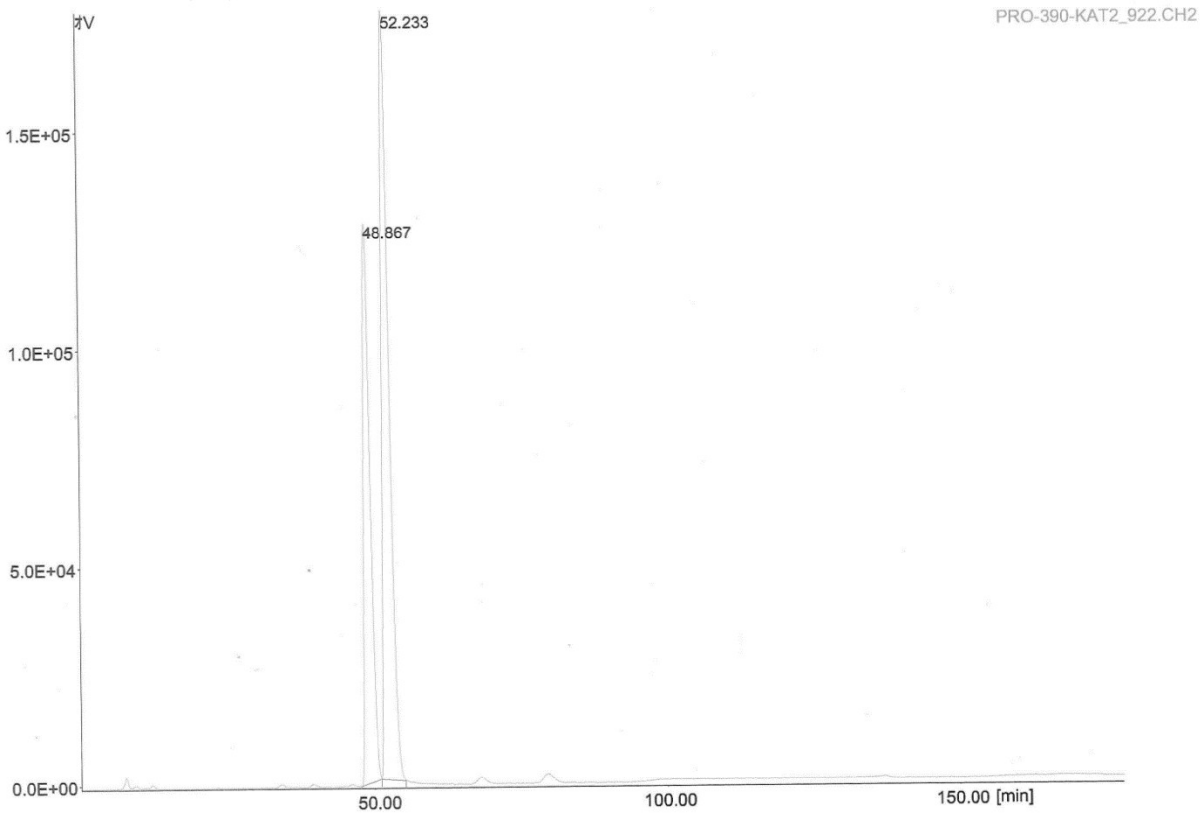


Chiral HPLC analysis: *Chiralpak IB* (250 mm), eluent flow (0.5 mL / min), particle size (5.0 µm), inner diameter (4.6 mm), eluent: *n*-heptane : 2-propanol (95:5), DAD: 220 nm, t_r = **12**: 132.23 min, (*S*)-**13**: 56.98 min, (*R*)-**13**: 52.68 min.




```
File name : PRO-321-KAT4_817.CH2

Info :
27.09.2010
PRO-321-KAT4
3,0mg in 1mL 90:10 C7:IPA
Chiralpak IB Nov.06
0,5 ml/min 95:5 C7 IPA
DAD 220nm
20°C
5 µl

Vial # = 1 Rack # = 1
Injection Date :27-Sep-2010  15:13:56
Curr. Date : 28-Sep-2010   8:06:24
User : DEFAULT
Group : DATA
Acquisition Time :178.00 [min]
Control Method :PAA_5_IPA

 #    Name          RT       Height[µV]      Area[µV.Sec]      %Area

   1                52.675       124594          10658043       65.39
   2                56.983        66287           5640173       34.61

Total Area of Peak =  16298216 [µV.Sec]
Total Area of Signal =    6258426
Injection Volume = 5.00 ul
Noise (max) : 1307 µV (Calculated between 0.00 and 1.00 min)
```

Hydrogenation of Methyl 2-acetamido-3-phenylacrylate (**12**) resulting in (*R*)-selectivity (Fig. 3).



File name : PRO-390-KAT2_922.CH2

Info :
21.02.2011
PRO-390-KAT2
ca 10mg in 3mL 90:10 C7:IPA
Chiralpak IB Nov.06
0,5 ml/min 95:5 C7 IPA
DAD 220nm
20°C
5 µl

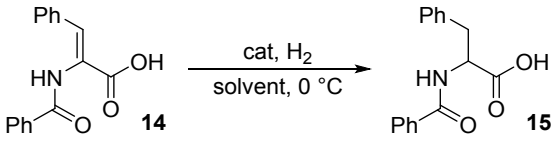
Vial # = 1 Rack # = 1
Injection Date :21-Feb-2011 15:00:56
Curr. Date : 22-Feb-2011 7:33:42
User : DEFAULT
Group : DATA
Acquisition Time :178.00 [min]
Control Method :PAA_5_IPA

#	Name	RT	Height[µV]	Area[µV.Sec]	%Area
1		48.867	128554	9581734	40.04
2		52.233	176382	14348105	59.96

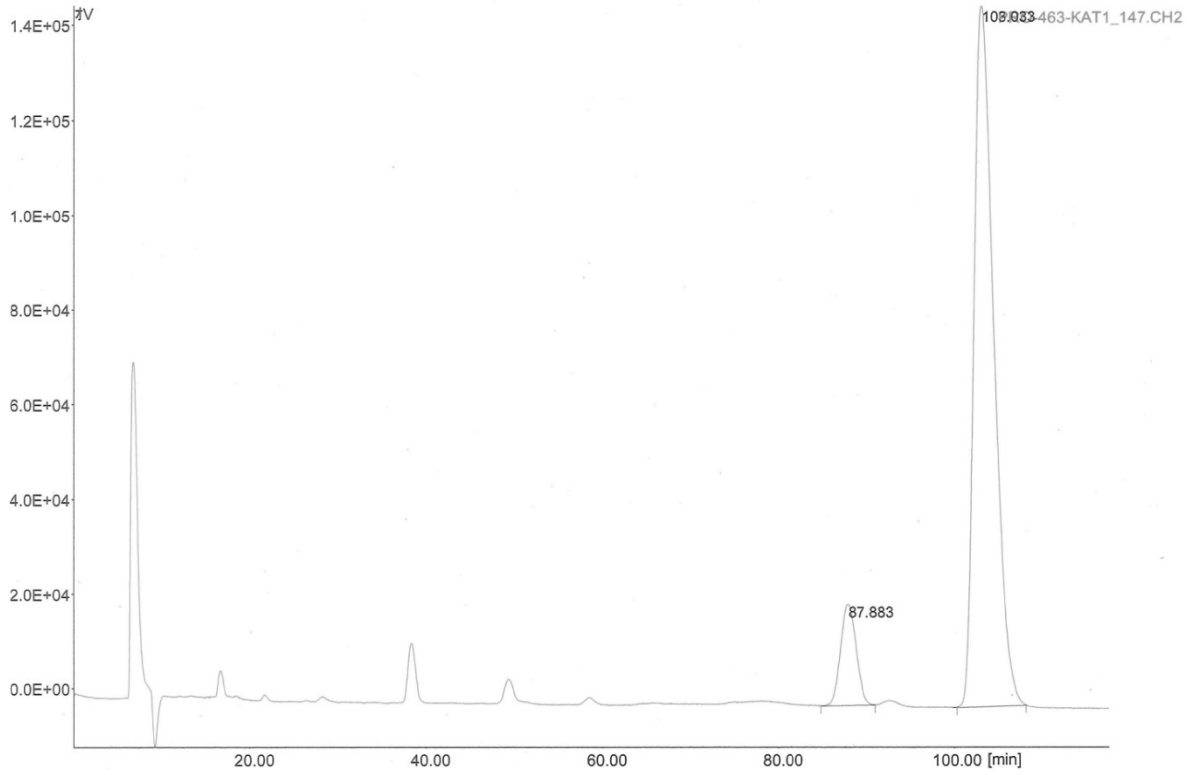
Total Area of Peak = 23929840 [µV.Sec]
Total Area of Signal = 27185161
Injection Volume = 5.00 ul
Noise (max) : 249 µV (Calculated between 0.00 and 1.00 min)

Hydrogenation of Methyl 2-acetamido-3-phenylacrylate (**12**) resulting in (*S*)-selectivity (Fig. 3).

(*Z*)-2-Benzamido-3-phenylacrylic acid (14):

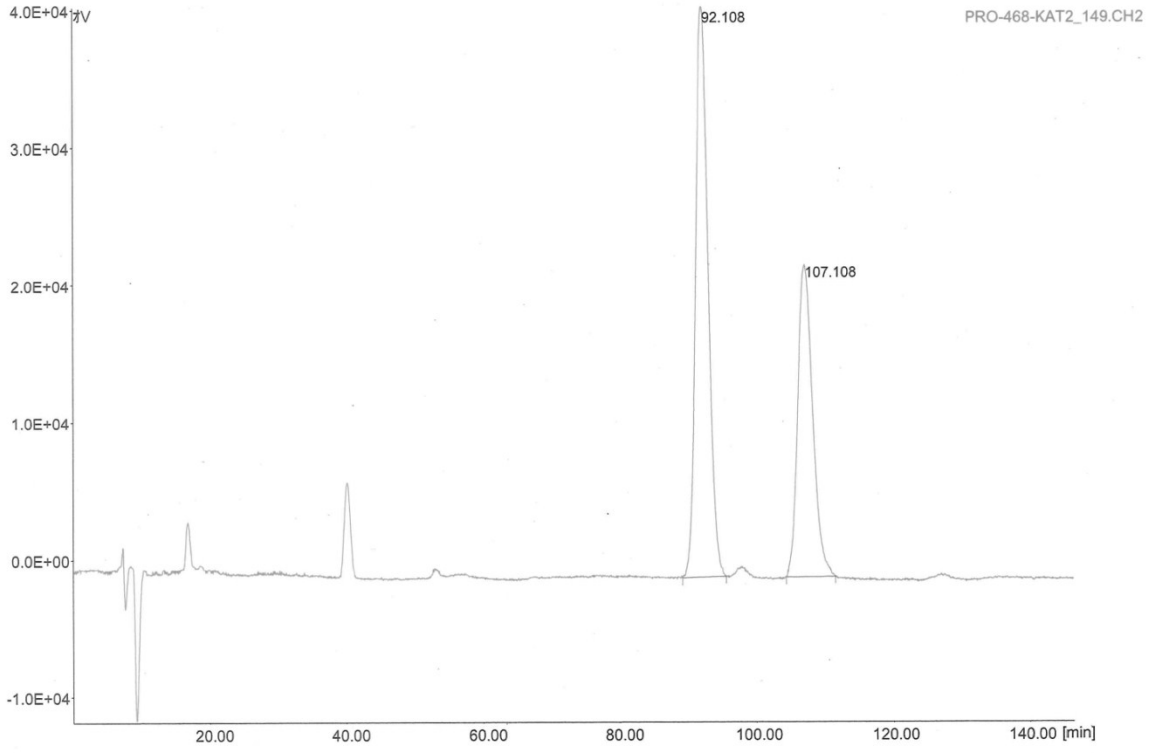


The product solution was diluted with methanol to prevent 1:25 (V:V) before HPLC analysis.
Chiral HPLC analysis: *Chiralpak-AD-H* (250 mm), eluent flow (0.5 mL / min), particle size (5.0 µm), inner diameter (4.6 mm), eluent: *n*-heptane : 2-propanol (95:5) – acidified with 0.1 % trifluoroacetic acid, DAD: 220 nm, t_r = (*R*)-**15**: 103.03 min, (*S*)-**15**: 87.88 min.




```
File name : PRO-463-KAT1_147.CH2

Info :
24.08.2011
PRO-463-KAT1
ca 5 mg / 1,5 ml 95:5 C7:IPA
Chiralpak AD-H
0,5 ml/min  95:5 C7 : IPA + 0,5mL TFA
DAD 220nm
20°C
10 µl

Vial # = 1 Rack # = 1
Injection Date :24-Aug-2011  14:07:42
Curr. Date : 24-Aug-2011  16:06:26
User : DEFAULT
Group : DATA
Acquisition Time :117.48 [min]
Control Method :OCZIPKA-3

 #    Name          RT       Height[µV]      Area[µV.Sec]      %Area

   1                87.883        21327           2569724       10.23
   2               103.033       147905          22541786       89.77

Total Area of Peak =  25111510 [µV.Sec]
Total Area of Signal =     8430544
Injection Volume = 10.00 ul
Noise (max) : 9180 µV (Calculated between 0.00 and 1.00 min)
```

Hydrogenation of (*Z*)-2-Benzamido-3-phenylacrylic acid (**14**) resulting in (*R*)-selectivity (Fig. 3).



File name : PRO-468-KAT2_149.CH2

Info :
02.09.2011
PRO-468-KAT2
ca 5 mg / 1,5 ml 95:5 C7:IPA
Chiralpak AD-H
0,5 ml/min 95:5 C7 : IPA + 0,5mL TFA
DAD 220nm
20°C
10 µl

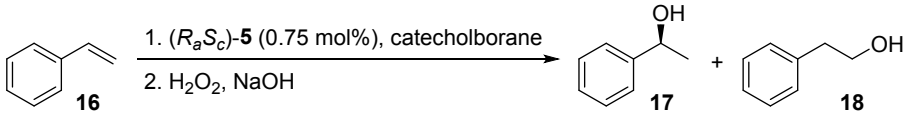
Vial # = 1 Rack # = 1
Injection Date : 2-Sep-2011 11:48:38
Curr. Date : 2-Sep-2011 14:34:48
User : DEFAULT
Group : DATA
Acquisition Time :146.42 [min]
Control Method :OCZIPKA-3

#	Name	RT	Height[µV]	Area[µV.Sec]	%Area
1		92.108	41537	5248997	60.84
2		107.108	22759	3378783	39.16

Total Area of Peak = 8627780 [µV.Sec]
Total Area of Signal = -2468076
Injection Volume = 10.00 ul
Noise (max) : 412 µV (Calculated between 0.00 and 1.00 min)

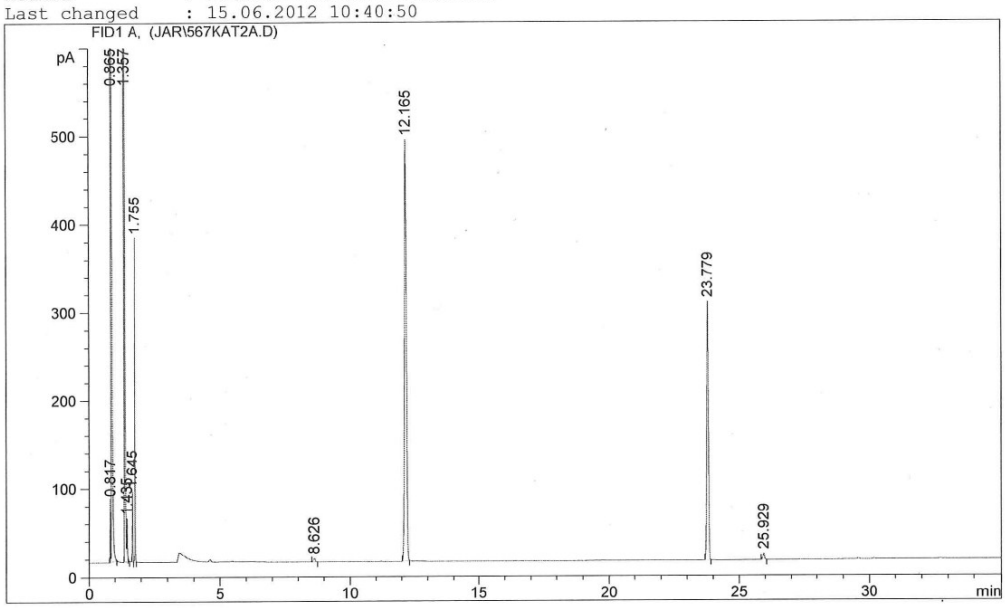
Hydrogenation of (*Z*)-2-Benzamido-3-phenylacrylic acid (**14**) resulting in (*S*)-selectivity (Fig. 3).

GC-data of the hydroboration of styrene (16):



Yield determination by GC: *Hp-Wax* (30 m), nitrogen pressure (1 bar), evaporating temperature = 250 °C, temperature program = 50 °C isotherm (5 min), 50 °C – 180 °C (8 °C / min), 180 °C isotherm (15 min), t_r = 2-Phenylethanol (**18**): 25.93 min, 1-Phenylethanol (**17**): 23.78 min, 1-Hexanol (Standard): 12.17 min, **16**: 8.63 min.

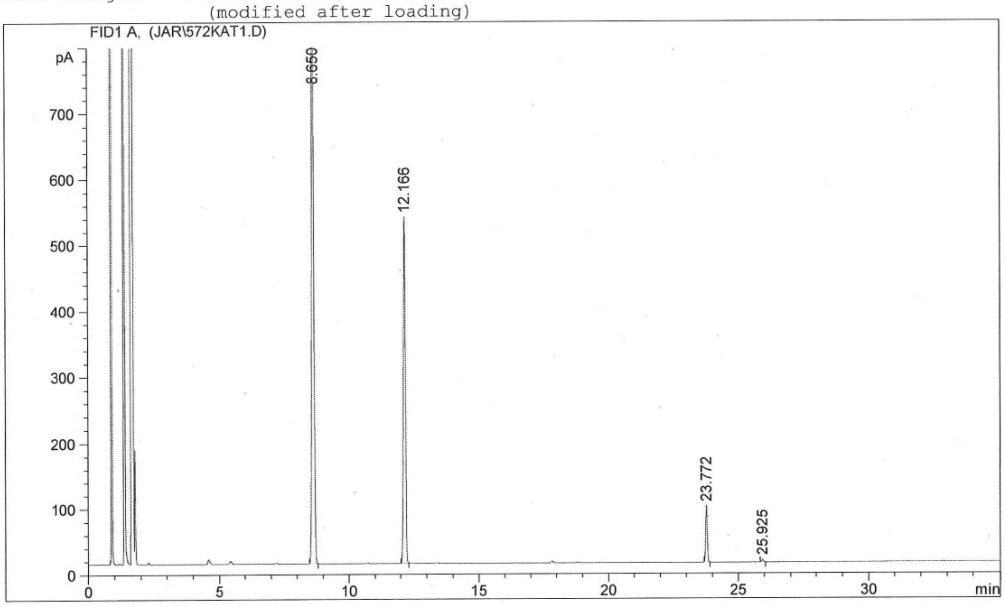
```
==========================================================================
Injection Date  : 15.06.2012 15:26:16          Seq. Line :   7
Sample Name     : PRO-567-Kat-2A               Location : Vial 3
Acq. Operator   :                                 Inj :   1
Acq. Instrument : Fix                          Inj Volume : 1 µl
Sequence File   : D:\HPCHEM1\2\SEQUENCE\JAR.S
Method          : D:\HPCHEM1\2\METHODS\JAR.M
Last changed    : 15.06.2012 10:40:50
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   0.817 PV    0.0129   53.10404   69.72542  0.03733
   2   0.865 VB S  0.0120 1.32648e5  1.71631e5  93.23745
   3   1.357 PB S  0.0226 5146.35840 3615.42554  3.61735
   4   1.435 BB X  0.0223   54.18645   38.86090  0.03809
   5   1.645 BP    0.0235  118.90597   79.10825  0.08358
   6   1.755 BB    0.0254  577.71039  366.74973  0.40607
   7   8.626 BB    0.0804   18.31955    3.47824  0.01288
   8  12.165 BB    0.0763 2343.56055  477.24570  1.64728
   9  23.779 BB    0.0639 1277.89368  292.78973  0.89823
  10  25.929 BB    0.0708   30.93761    6.84033  0.02175
```

Hydroboration of styrene (**16**) – *n*/*iso*-ratio and conversion (Table 2, entry 2).

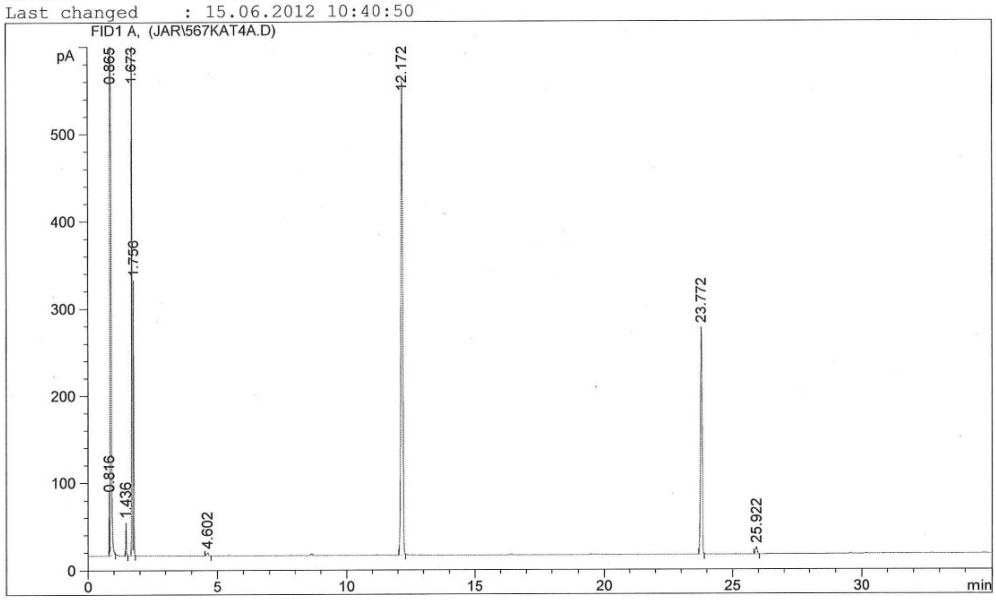
```
Injection Date  : 27.06.2012 07:51:45          Seq. Line :   1
Sample Name     : PRO-572-Kat1_01              Location : Vial 1
Acq. Operator   :                                  Inj :   1
Acq. Instrument : Fix                      Inj Volume : 1 µl
Acq. Method     : D:\HPCHEM1\2\METHODS\JAR.M
Last changed    : 26.06.2012 10:13:09
Analysis Method : D:\HPCHEM1\2\METHODS\KAY.M
Last changed    : 27.06.2012 07:48:47
                  (modified after loading)
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   8.650 BB    0.0794 5027.17578  924.36194 62.16679
   2  12.166 BB    0.0742 2664.82715  525.34808 32.95364
   3  23.772 BB    0.0698  374.18713   85.98278  4.62725
   4  25.925 BB    0.0682   20.40324    4.56105  0.25231
```

Hydroboration of styrene (**16**) – *n*/*iso*-ratio and conversion (Table 2, entry 3).

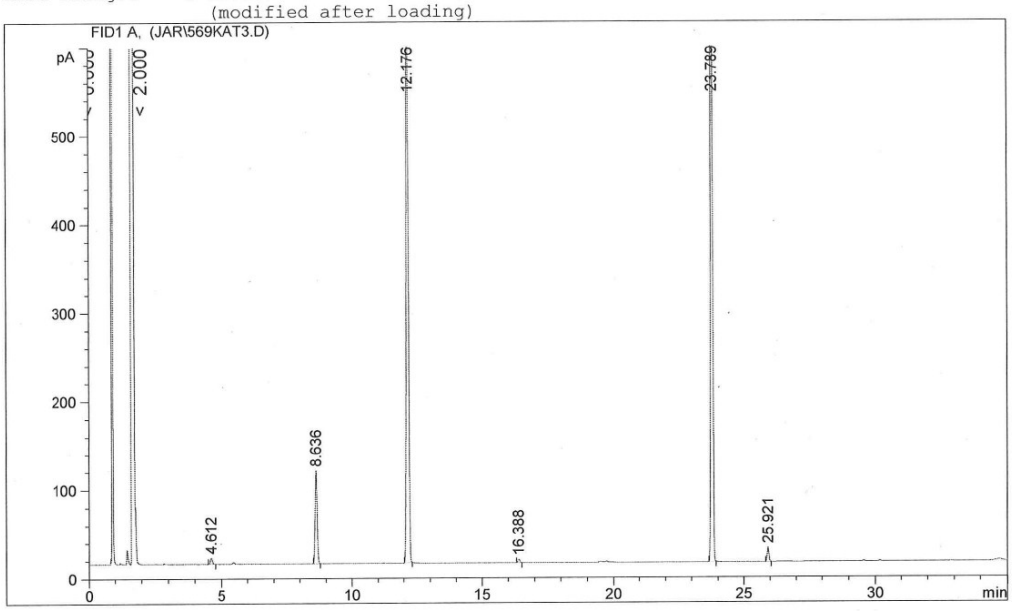
```
Injection Date  : 15.06.2012 17:41:15          Seq. Line :  10
Sample Name     : PRO-567-Kat-4A               Location : Vial 6
Acq. Operator   :                                 Inj :   1
Acq. Instrument : Fix                         Inj Volume : 1 µl
Sequence File   : D:\HPCHEM1\2\SEQUENCE\JAR.S
Method          : D:\HPCHEM1\2\METHODS\JAR.M
Last changed    : 15.06.2012 10:40:50
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   0.816 PV    0.0124   54.71035   67.89900  0.03855
   2   0.865 VB S  0.0133 1.35771e5  1.53336e5  95.66215
   3   1.436 BB    0.0251   61.71612   37.77594  0.04348
   4   1.673 BV    0.0282 1513.55762  834.08936  1.06643
   5   1.756 VB    0.0257  504.98322  315.04260  0.35580
   6   4.602 BP    0.0787   17.16370    3.41185  0.01209
   7  12.172 BB    0.0784 2786.69971  547.74280  1.96346
   8  23.772 BB    0.0661 1184.10205  260.07214  0.83430
   9  25.922 BB    0.0693   33.70065    7.52380  0.02374
```

Hydroboration of styrene (**16**) – *n*/*iso*-ratio and conversion (Table 2, entry 4).

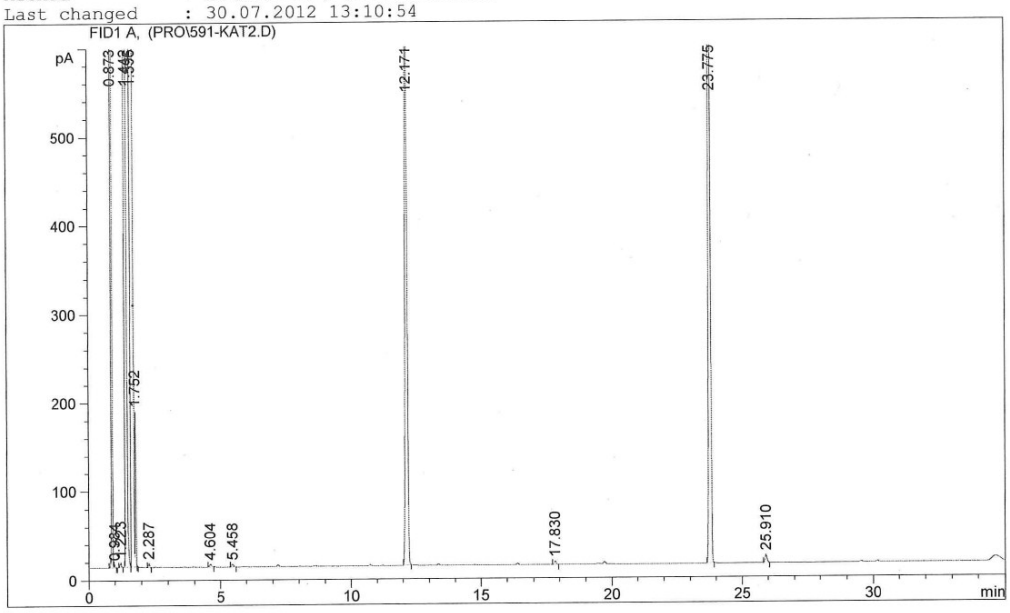
```
================================================================================
Injection Date  : 20.06.2012 16:55:56              Seq. Line :   3
Sample Name     : PRO-569-Kat-3                    Location : Vial 3
Acq. Operator   :                                     Inj :   1
Acq. Instrument : Fix                           Inj Volume : 1 µl
Sequence File   : D:\HPCHEM1\2\SEQUENCE\JAR.S
Acq. Method     : D:\HPCHEM1\2\METHODS\JAR.M
Last changed    : 20.06.2012 15:19:49
Analysis Method : D:\HPCHEM1\2\METHODS\JAR.M
Last changed    : 21.06.2012 08:15:38
                  (modified after loading)
```




```
================================================================================
                              Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   4.612 BB    0.0887   37.06781    6.68113  0.41052
   2   8.636 BB    0.0823  566.22339  104.43385  6.27079
   3  12.176 BB    0.0755 3598.81323  705.26984 39.85600
   4  16.388 BB    0.0723   17.51404    3.56849  0.19396
   5  23.789 BB    0.0687 4737.93848 1049.22168 52.47154
   6  25.921 BB    0.0663   71.98285   16.04917  0.79719
```

Hydroboration of styrene (**16**) – *n*/*iso*-ratio and conversion (Table 2, entry 5).

```
Injection Date  : 30.07.2012 14:12:18          Seq. Line :   2
Sample Name     : PRO-591-Kat2_01              Location : Vial 2
Acq. Operator   :                                 Inj :   1
Acq. Instrument : Fix                          Inj Volume : 1 µl
Method          : D:\HPCHEM1\2\METHODS\JAR.M
Last changed    : 30.07.2012 13:10:54
```

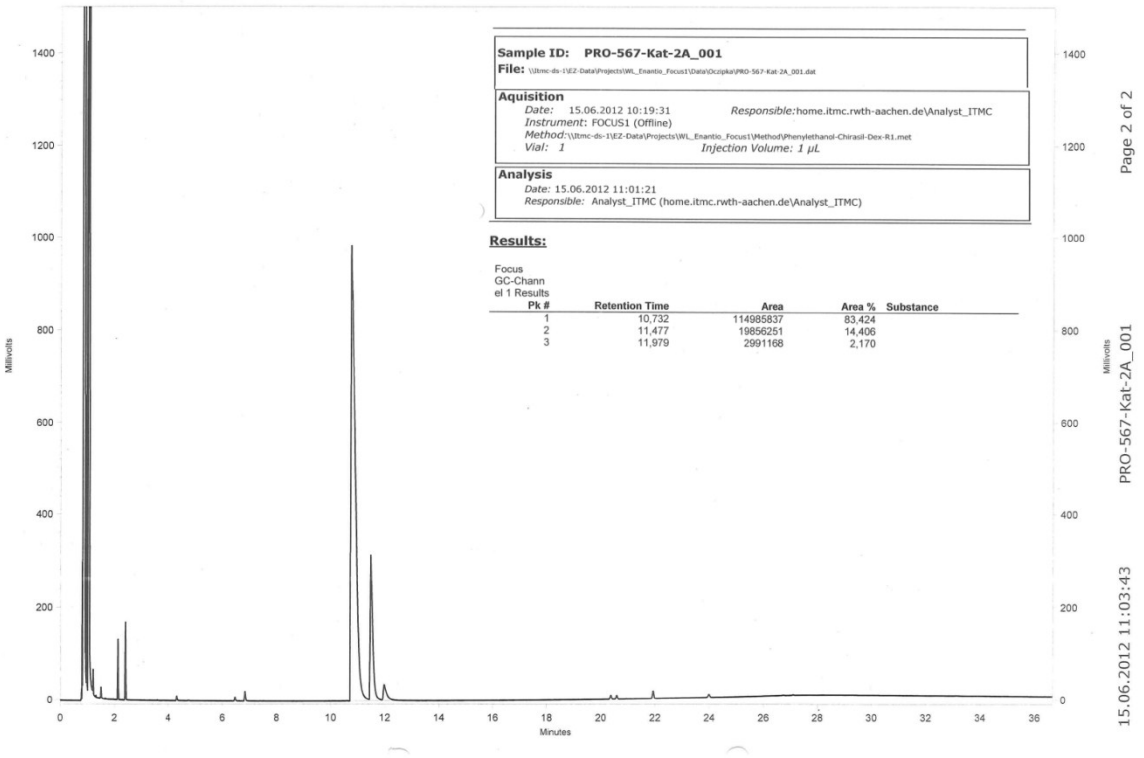



```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,
```

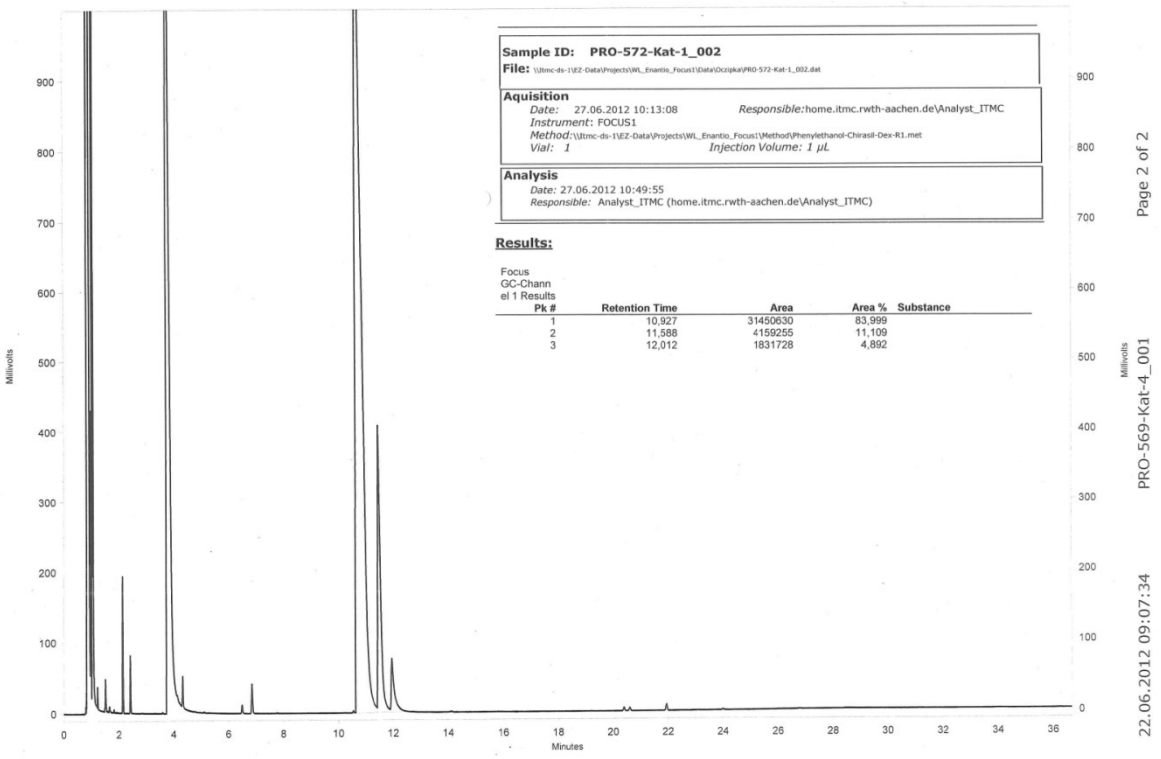
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	0.873	PB S	0.0206	1.41738e4	9370.81934	10.33677
2	0.984	BB T	0.0125	1.46533	1.95812	0.00107
3	1.223	BB	0.0419	15.64670	5.37836	0.01141
4	1.442	BP	0.0427	1.35631e4	4433.43848	9.89139
5	1.596	VB S	0.0561	9.93642e4	2.95120e4	72.46499
6	1.752	BB T	0.0368	436.72949	165.57539	0.31850
7	2.287	PB	0.0490	13.75633	4.46289	0.01003
8	4.604	PB	0.0772	14.15342	2.88723	0.01032
9	5.458	BB	0.0811	15.44831	2.94988	0.01127
10	12.171	BB	0.0757	4000.44629	769.13171	2.91747
11	17.830	PP	0.0730	18.16529	3.71980	0.01325
12	23.775	BB	0.0675	5455.21289	1235.76721	3.97842
13	25.910	BB	0.0765	48.14921	9.13800	0.03511

Hydroboration of styrene (**16**) – *n*/*iso*-ratio and conversion (Table 2, entry 6).

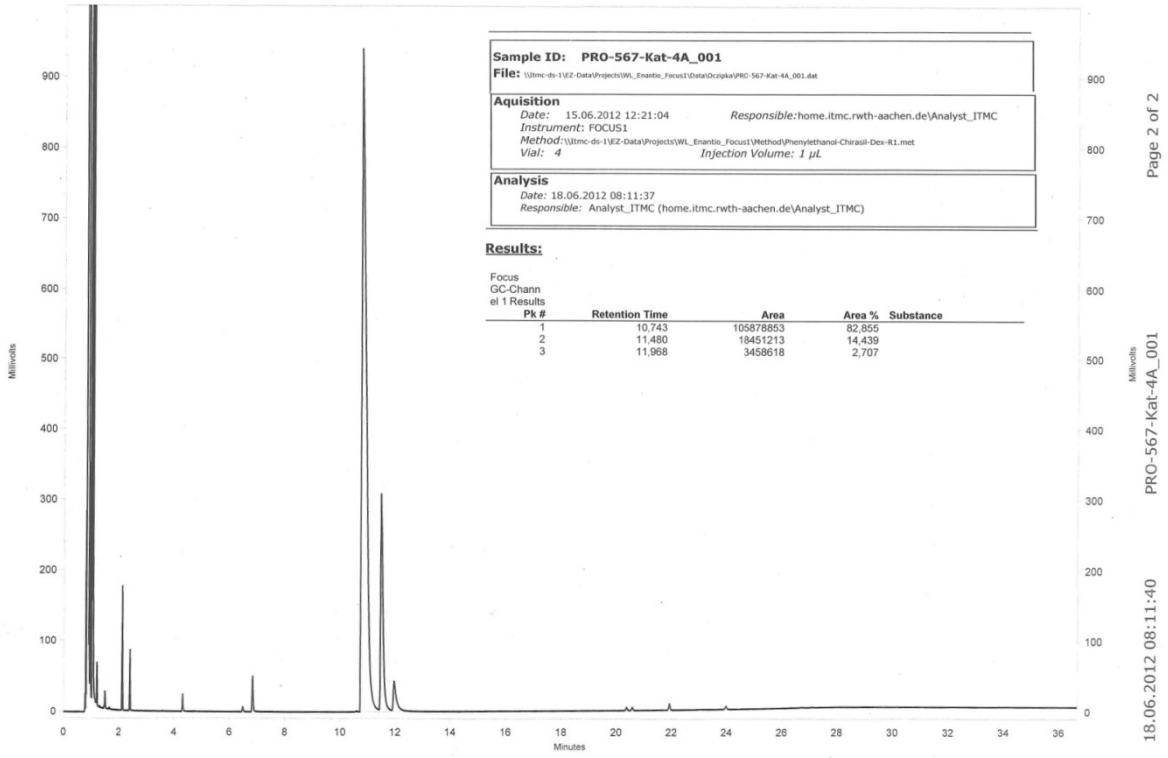
Chiral GC analysis: *Chirasil-DEX* (25 m), hydrogen flow (2 mL / min), film thickness (0.25 µm), inner diameter (0.25 mm), injector temperature = 250 °C, temperature program = 50 °C – 160 °C (3 °C /min), 160 °C isotherm (10 min), t_r = 2-Phenylethanol (**18**): 11.98 min, (*S*)-**17**: 11.48 min, (*R*)-**17**: 10.73 min.



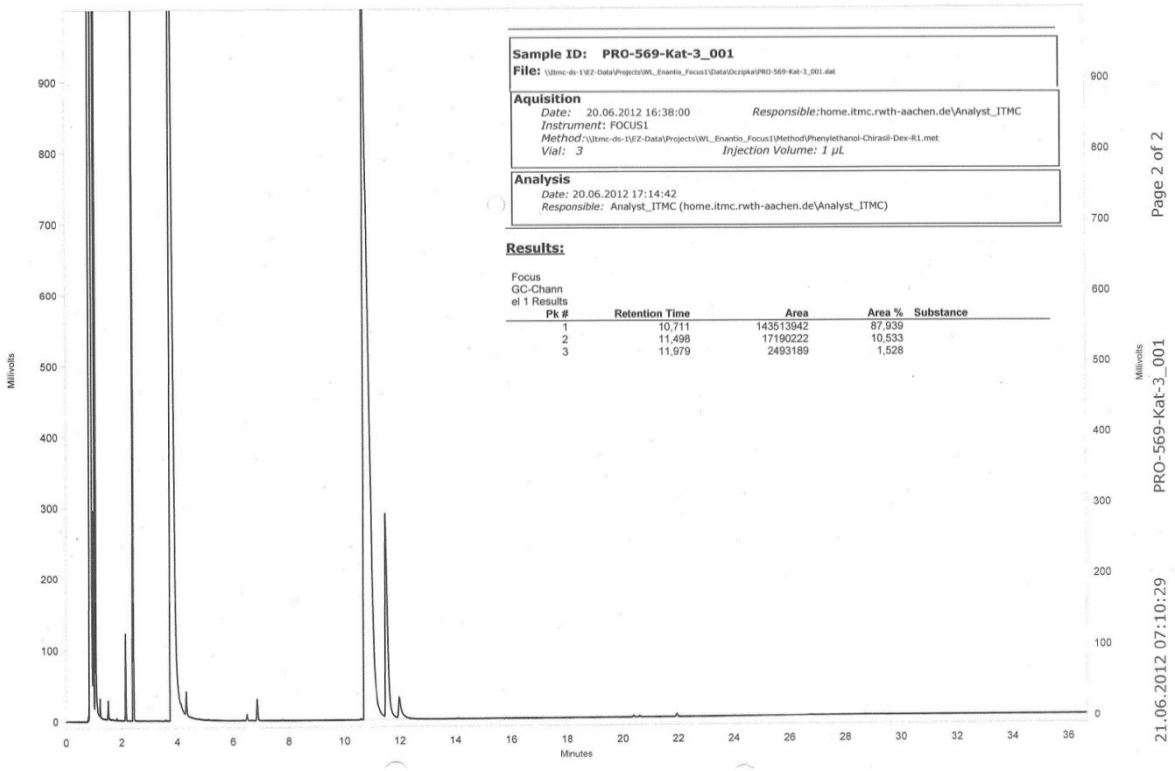
Hydroboration of styrene (**16**) – determination of enantioselectivity (Table 2, entry 2).



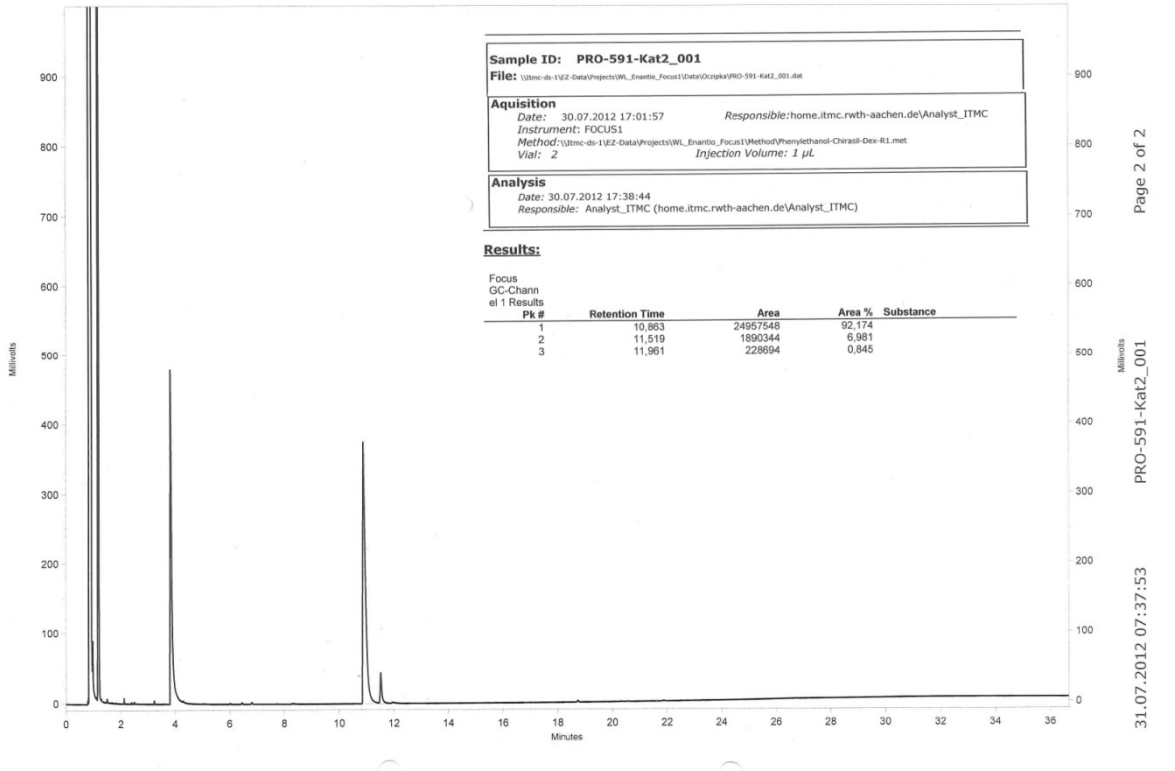
Hydroboration of styrene (**16**) – determination of enantioselectivity (Table 2, entry 3).



Hydroboration of styrene (**16**) – determination of enantioselectivity (Table 2, entry 4).

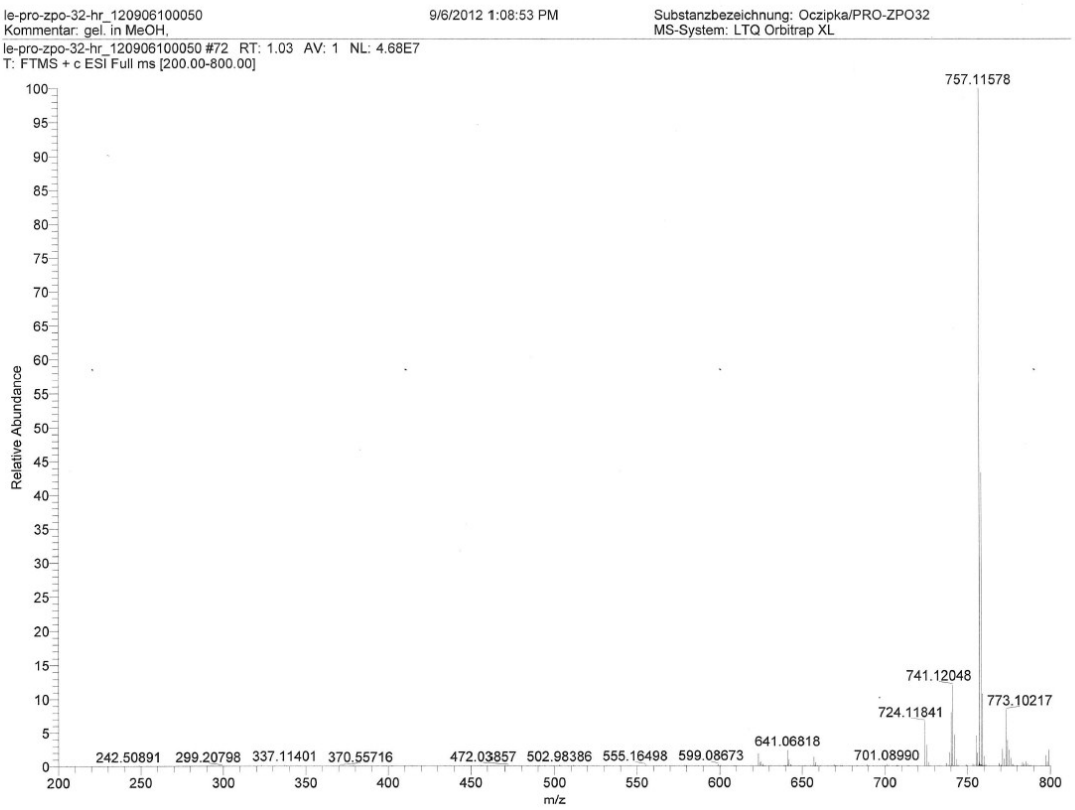


Hydroboration of styrene (**16**) – determination of enantioselectivity (Table 2, entry 5).



Hydroboration of styrene (**16**) – determination of enantioselectivity (Table 2, entry 6).

HR-MS (ESI)(+):
[Rh(BIPHEP)(acac)] (3):



References

1. M. Schmitkamp, D. Chen, W. Leitner, J. Klankermayer, G. Franciò, *Chem. Commun.* **2007**, 4012-4014.
2. G.-h. Tao, L. He, N. Sun, Y. Kou, *Chem. Commun.* **2005**, 3562-3564.