General experimental details

All reactions were carried out under argon atmosphere using standard Schlenk technique. Catalytic reactions at atmospheric pressure were carried out in a three-necked flask. Catalytic reactions at higher pressure were carried out in an isolated stainless steel autoclave (100 mL internal volume) equipped with glass test tube and manometer. $^{31}P\{1H\}$-, $^{13}C\{1H\}$- and ^{1}H-NMR spectra were recorded on either a VARIAN UNITY 300, on a Bruker Avance 400, or on a Bruker DRX-500 spectrometer.

Preparation of PTA/$Al_2O_3^{140}$

$Al_2O_3^{150}$ (54 g, Strem, activated, neutral, 60 mesh, 250 μm, Cat. No: 93-1338) was suspended in 450 mL ethanol. PTA (11.4 g, 3.96 mmol, Merck B311282 641, cryst. extra pure) in 150 mL ethanol was added to the suspension of $Al_2O_3^{140}$ and stirred for 4.5 hours. After that the mixture was filtered. The solid was dried under vacuum at 50 °C, to obtain 68.2 g of solid carrier. The PTA/$Al_2O_3^{140}$ was wet sieved to obtain the carrier with diameter between 32 μm-250 μm.[1]

Immobilization of the catalyst on PTA/$Al_2O_3^{140}$

Ligand **4** (106.6 mg, 0.17 mmol) in 5 mL of abs. CH_2Cl_2 was added to the solution of $[Rh(COD)_2]BF_4$ (69.0 mg, 0.17 mmol) in 5 mL of abs. CH_2Cl_2. The homogeneous mixture was stirred for 20 min at RT, when the color of the mixture changed from red to orange. The *in situ* formed complex was then added to the stirred suspension of PTA/$Al_2O_3^{140}$ (3.0 g) in 40 mL of abs. CH_2Cl_2. The formed suspension was stirred for 4 h at RT, filtered and washed with 4 x 5 mL of CH_2Cl_2 and dried to give 2.86 g of the orange colored immobilized catalyst ([Rh(COD)(**4**)]/PTA/$Al_2O_3^{140}$).

Table 1. Textural characterization of support, the support modified by PTA, and the immobilized complex

	S_{BET} [m^2/g]	S_{BJH} [m^2/g]	S_{micro} [m^2/g]	$V_{1,7\text{-}300}$ [cm^3/g]	$D_{avg.}$ [nm]
$Al_2O_3^{140}$	140.2	210.8	2.49	0.46	12.9
PTA/$Al_2O_3^{140}$	134.4	173.5	0	0.32	9.4
[Rh(COD)(**4**)]/PTA/$Al_2O_3^{140}$	119.1	156.2	0	0.28	9.4

Figure 1. Nitrogen adsorption–desorption isotherms of supports and catalysts (Rh-PTA/$Al_2O_3^{140}$: [Rh(COD)(4)]/PTA/$Al_2O_3^{140}$, dotted line: desorption isotherm, continuous line: adsorption isotherm)

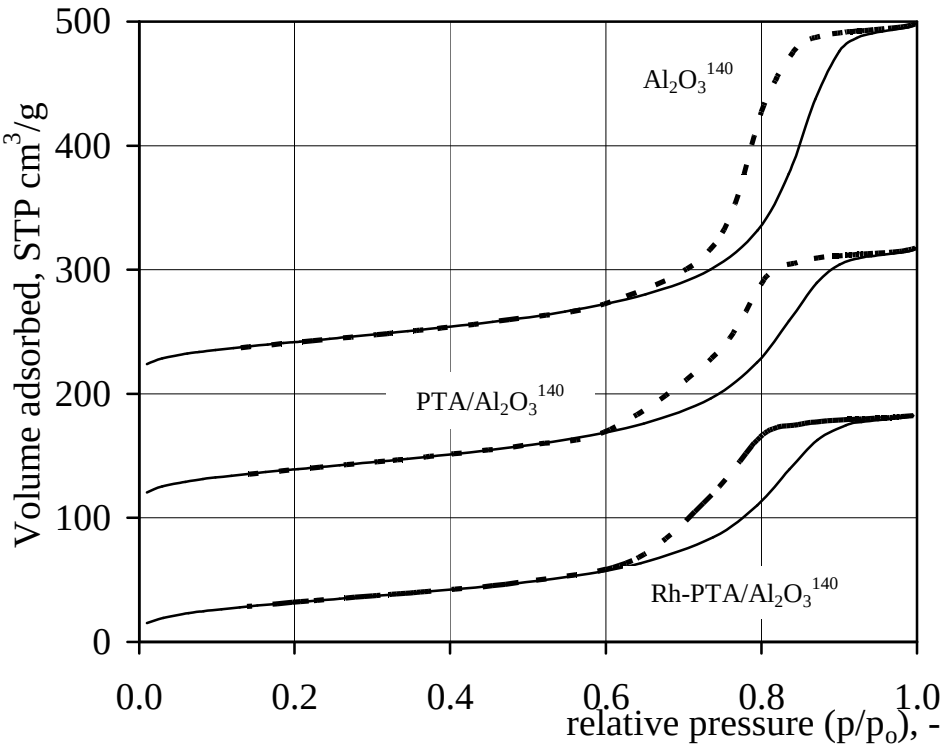
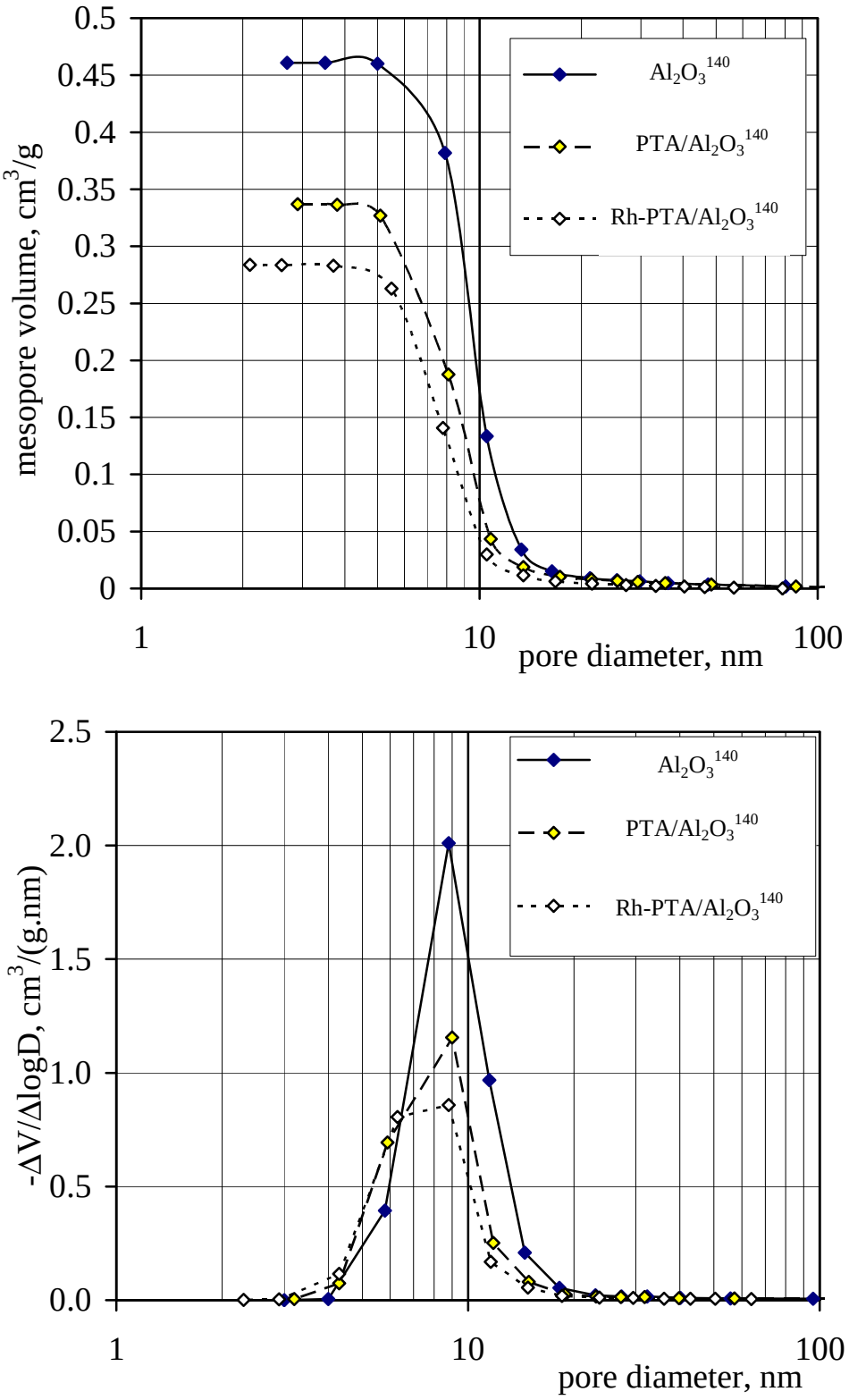


Figure 2. Pore volume frequency of supports and catalysts estimated by BJH method (Rh-PTA/$Al_2O_3^{140}$: [Rh(COD)(4)]/PTA/$Al_2O_3^{140}$)



Preparation of PTA/$Al_2O_3^{431}$

$Al_2O_3^{431}$ was prepared as described in the literature.[2] $Al_2O_3^{431}$ (2.67 g, S_{BET} = 431m^2/g; $D_{avg.}$ = 8.5 nm) was suspended in 56 mL 2-propanol. PTA (0.54 g, 0.19 mmol, Merck B311282 641, cryst. extra pure) in 28 mL 2-propanol was added to the suspension of $Al_2O_3^{431}$ and stirred for 2 hours.

Immobilization of the catalyst on PTA/$Al_2O_3^{431}$

Compound **4** (125.5 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of $[Rh(COD)_2]BF_4$ (81.2 mg, 0.2 mmol) in CH_2Cl_2 (5 mL). The resulting orange solution was stirred for 20 min and then added to the suspension of PTA/$Al_2O_3^{431}$. The suspension was stirred for 3 hours and then filtered. The orange colored immobilized catalyst was washed with 2 x 10 mL of 2-propanol and dried to give 3.23 g of [Rh(COD)(**4**)]/PTA/$Al_2O_3^{431}$.

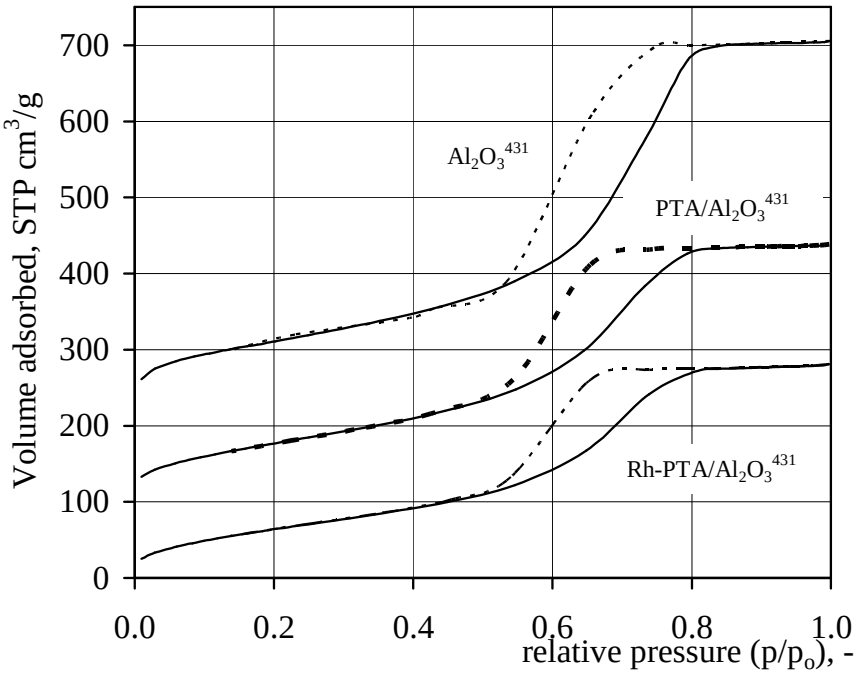
Table 2. ICP-AES data of supported catalysts

	Rh	W	Al	P	Rh	W	Al	P
	mg/kg	mg/kg	mg/kg	mg/kg	m/m%	m/m%	m/m%	m/m%
[Rh(COD)(**4**)]/PTA/$Al_2O_3^{140}$	4466	128058	370805	3880	0.45	12.81	37.1	0.41
[Rh(COD)(**4**)]/PTA/$Al_2O_3^{431}$	3132	93829	346978	2617	0.31	9.38	34.7	0.28

Table 3. Textural characterization of support, the support modified by PTA, and the immobilized complex

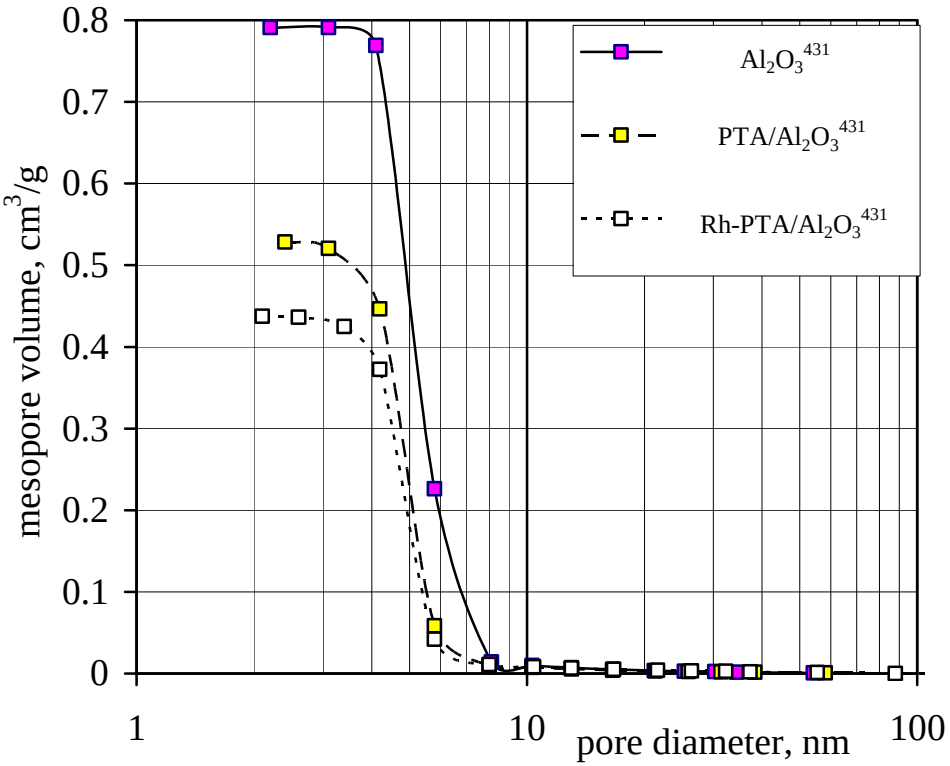
	S_{BET} [m^2/g]	S_{BJH} [m^2/g]	S_{micro} [m^2/g]	$V_{1,7\text{-}300}$ [cm^3/g]	$D_{avg.}$ [nm]
$Al_2O_3^{431}$	431.0	634.2	18.3	0.92	8.5
PTA/$Al_2O_3^{431}$	277.3	441.6	0	0.62	8.8
[Rh(COD)(**4**)]/PTA/$Al_2O_3^{431}$	251.6	377.0	0	0.44	8.7

Figure 3. Nitrogen adsorption–desorption isotherms of supports and catalysts (Rh-PTA/$Al_2O_3^{431}$: [Rh(COD)(4)]/PTA/$Al_2O_3^{431}$, dotted line: desorption isotherm, continuous line: adsorption isotherm)



The supports used in this work were commercially available neutral gamma-alumina ($Al_2O_3^{140}$) and alumina ($Al_2O_3^{431}$) prepared by the method described in the literature.[2] The overall mesoporosity of Al_2O_3, PTA/Al_2O_3, and [Rh(COD)(**4**)]/PTA/Al_2O_3 was examined by nitrogen gas porosimetry, and the results are shown in Table 1 and 3 and Figure 1-4. It is important to note that for the clarity of the hysteresis curves (Figure 1 and 3), the measured adsorbed volumes of nitrogen were increased by values of 200 cm^3/g in the case of the samples of Al_2O_3, and by values of 100 cm^3/g in the case of the samples of PTA/$Al_2O_3^{140}$ and PTA/$Al_2O_3^{431}$, respectively. The narrow pore-size distribution of the tested samples implies that the pores within the Al_2O_3 support and PTA/Al_2O_3 composites are uniform. It can be seen that Brunauer-Emmett-Teller (BET) surface areas and pore volumes of the parent Al_2O_3 decreased with the PTA and catalyst loading. The pore diameter decreases suggesting a partial blockage of the smaller pores of Al_2O_3 matrix by active species. It can be inferred from the structural parameters shown in Table 1 and 3 that the incorporation of organometallic complexes onto both PTA/Al_2O_3 caused a small decrease in mesopore size, surface area, and pore volume, obviously because of the coverage of pore surface with the organometallic complexes leading to an increase in the original wall thickness and even partial blockage of the mesoporous channels.

Figure 4. Pore volume frequency of supports and catalysts estimated by BJH method (Rh-PTA/$Al_2O_3^{431}$: [Rh(COD)(4)]/PTA/$Al_2O_3^{431}$)



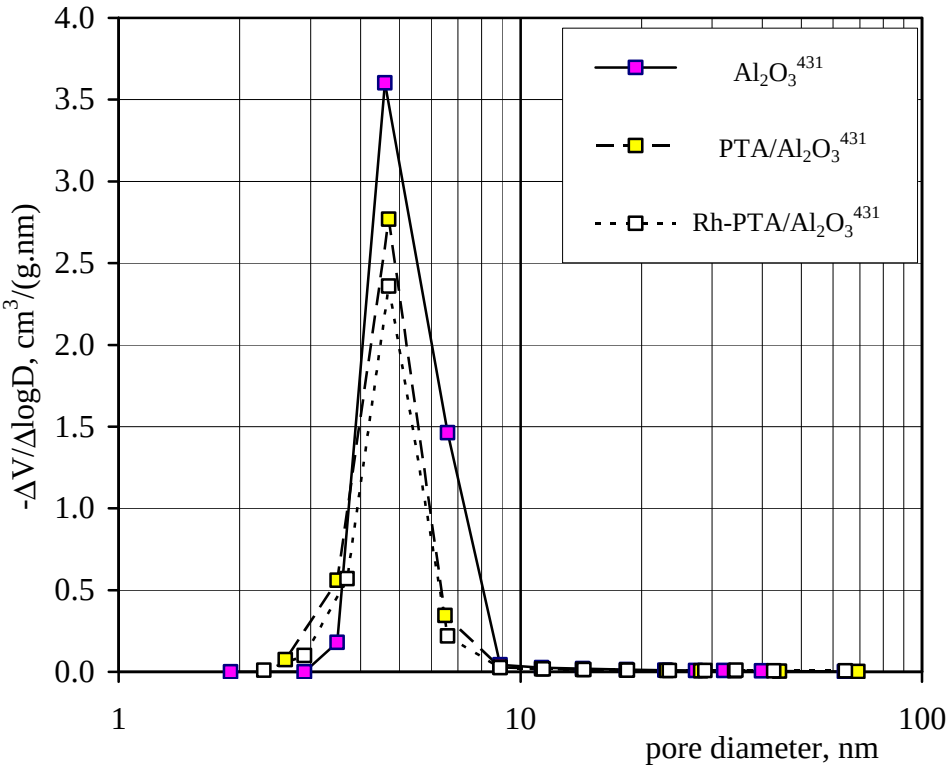


Figure 5. ^{31}P NMR spectrum of compound 4

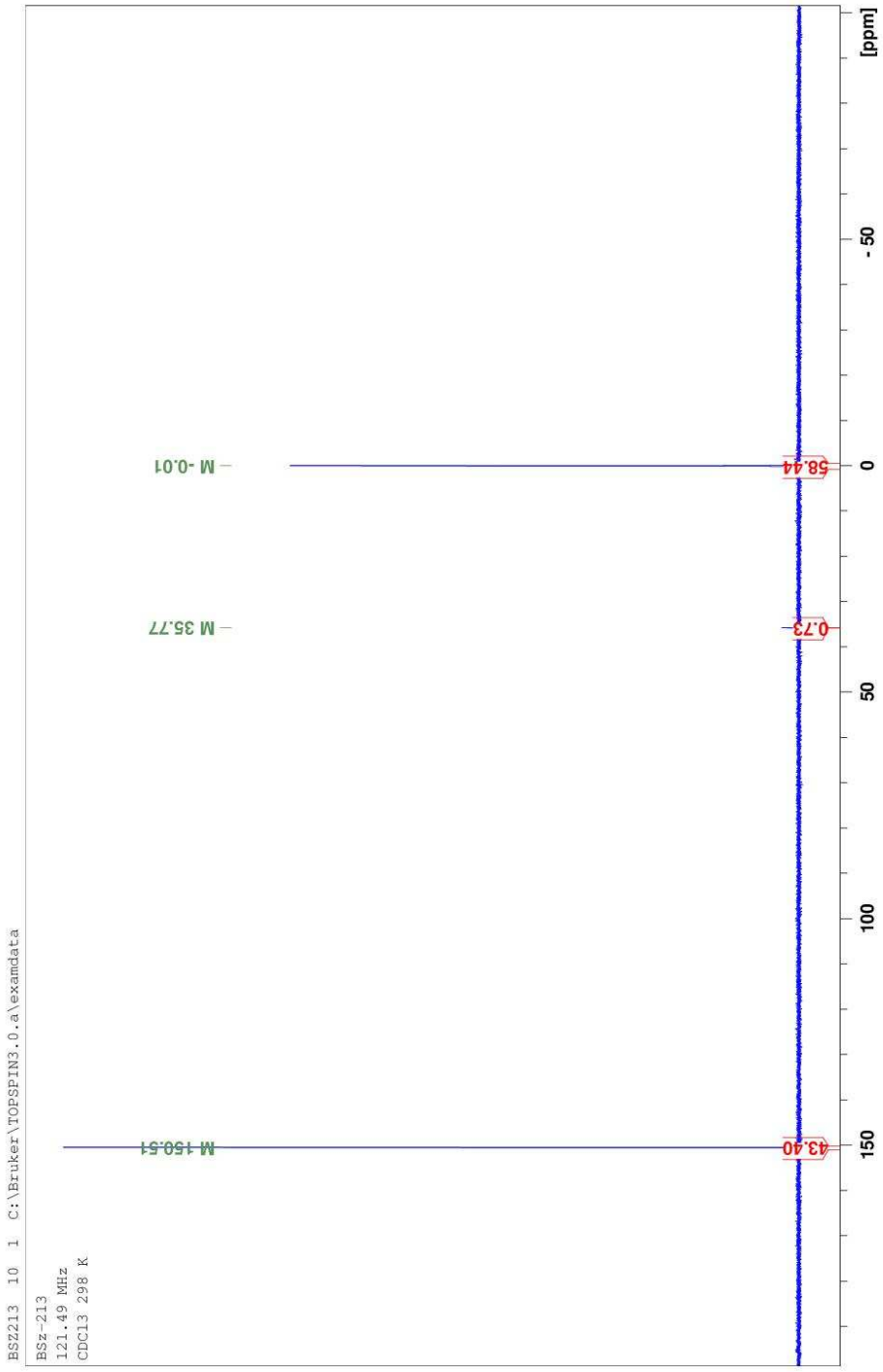


Figure 6. ^{1}H NMR spectrum of compound 4

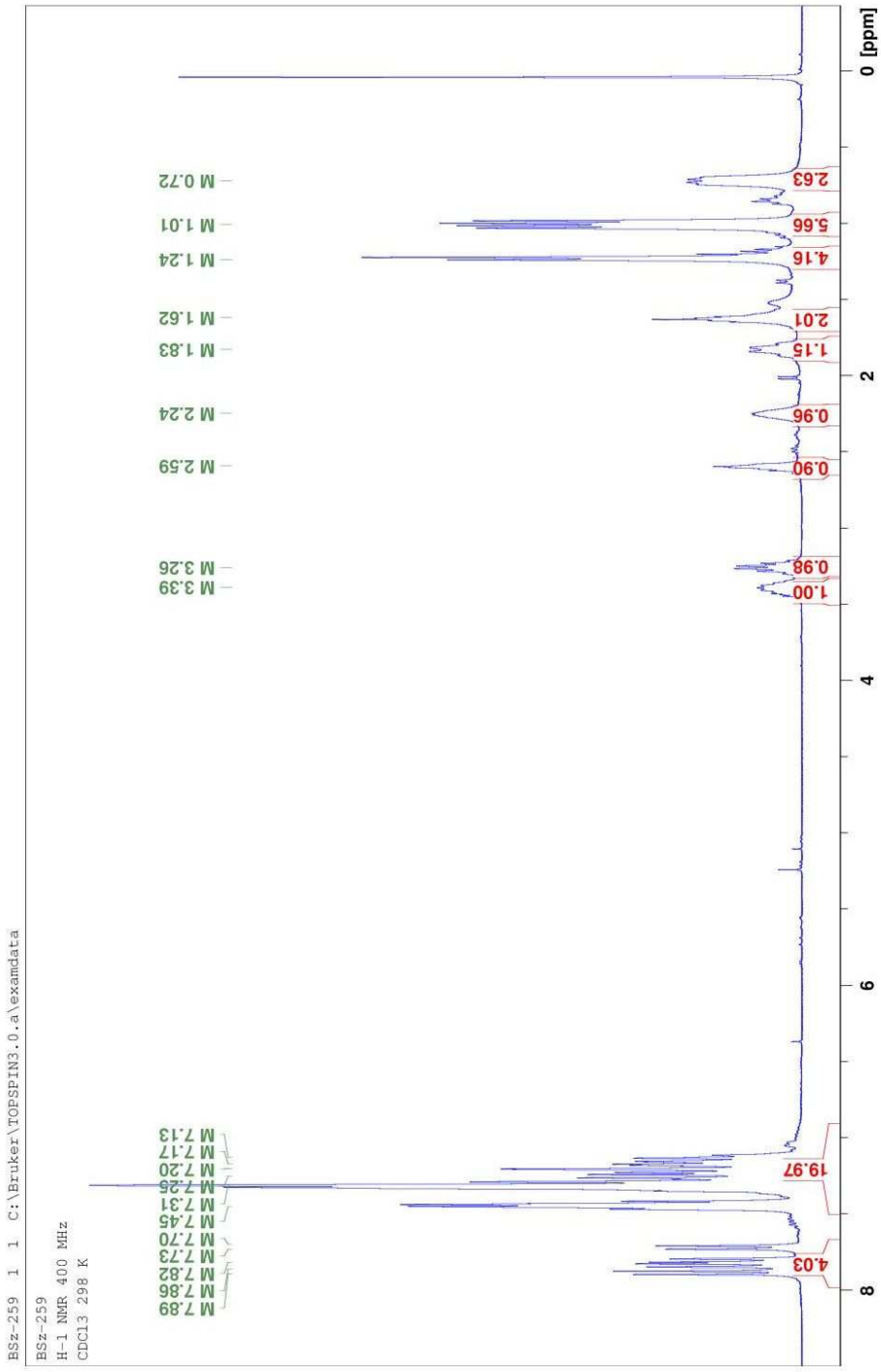
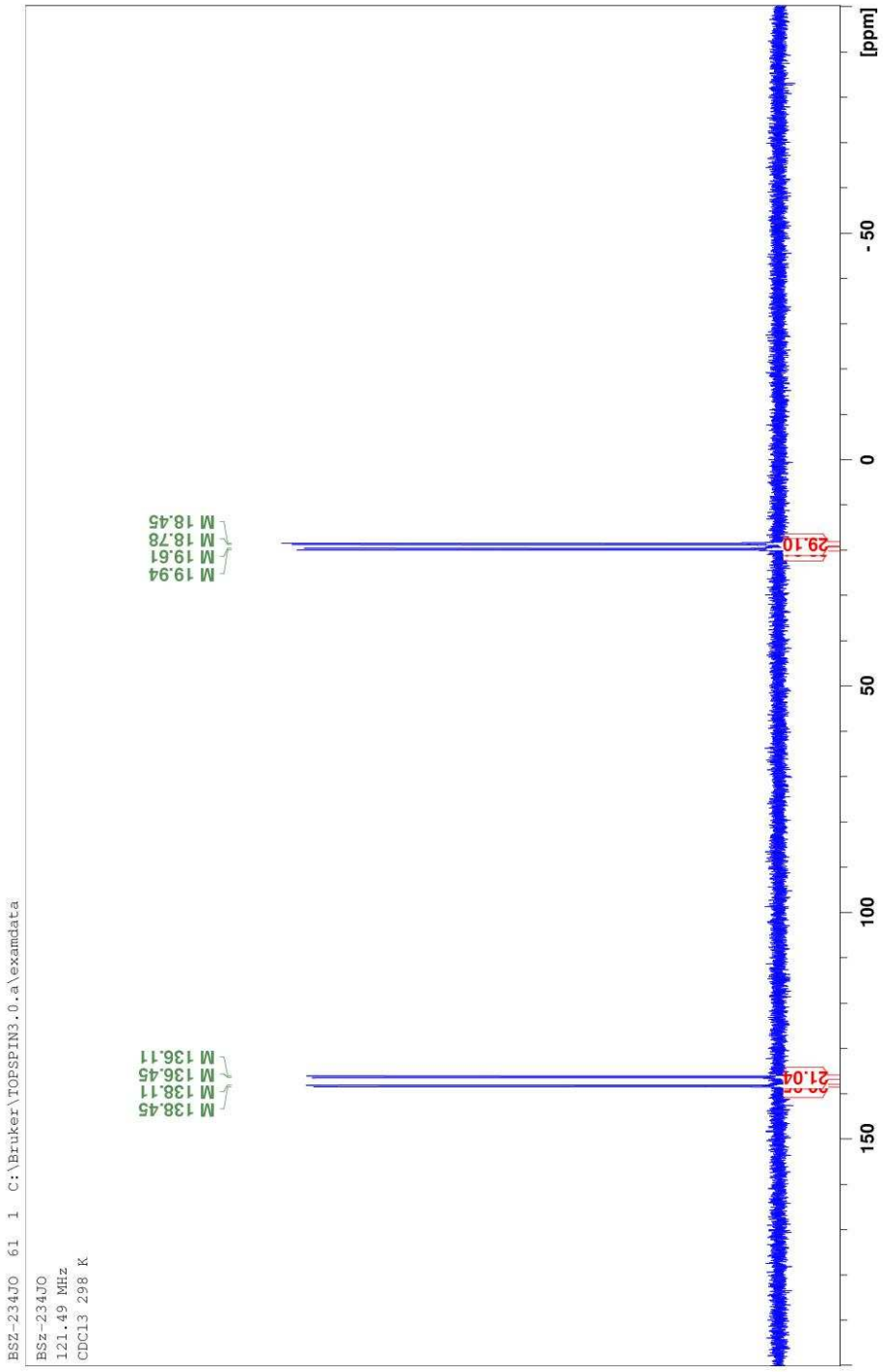
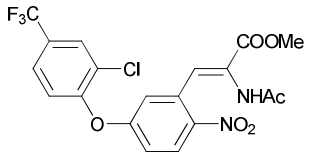


Figure 7. ^{31}P NMR spectrum of $[Rh(COD)(4)]BF_4$



Hydrogenation of 5-(2-chloro-4-trifluoromethyl)-phenoxy-2-nitro-(*Z*)-α-acetamido-cinnamic acid methyl ester



Synthesis of a racemic sample

The catalyst was prepared „*in situ*" by mixing $[Rh(COD)_2]BF_4$ (4.1 mg, 0.01 mmol) with PPh_3 (5.8 mg, 0.022 mmol) in 5 mL MeOH and the reaction mixture was stirred for 10 minutes. 1.25 mmol substrate was added and the mixture was pressurized to 5 bar with H_2.

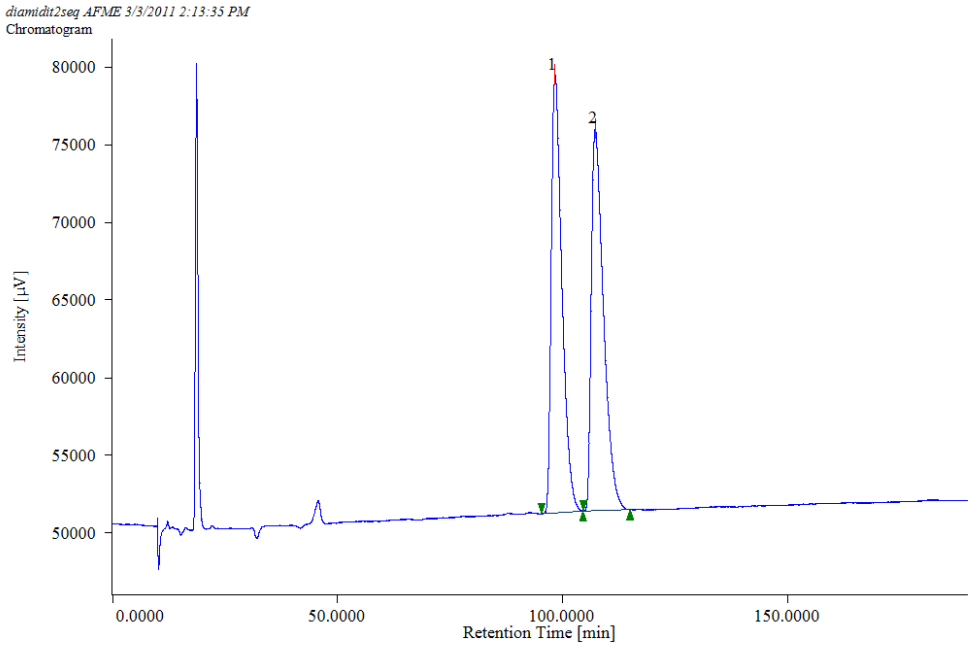
Preparation of the sample for analysis

1 mL of the homogenous reaction mixture was evaporated and the remaining yellow solid was filtered through a short pad of silica with ethyl acetate eluent to remove the catalyst. The filtrate was evaporated and the remaining white solid was dissolved in 10 mL of 2-propanol.

HPLC analysis

Conditions: Kromasil 3-CelluCoat, 4.6x150 mm, 20 ^{o}C, *n*-hexane/2-propanol = 95/5, flow rate = 0.3 $mLmin^{-1}$, pressure = 43 bar, detection wavelength = 275 nm.

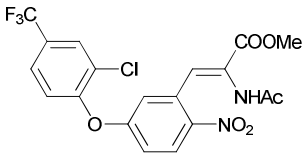
Figure 8. HPLC chromatogram of the racemic sample



Peak Information

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	98.291	4641732	28212	50.184	53.411
2	107.209	4607745	24609	49.816	46.589

Asymmetric hydrogenation of 5-(2-chloro-4-trifluoromethyl)-phenoxy-2-nitro-(*Z*)-α-acetamidocinnamic acid methyl ester (Table 2, Entry 12)



The catalyst was prepared „*in situ*" by mixing $[Rh(COD)_2]BF_4$ (4.1 mg, 0.01 mmol) with compound **4** (6.9 mg, 0.011 mmol) in 5 mL MeOH and the reaction mixture was stirred for 10 minutes. 1.25 mmol substrate was added and the mixture was pressurized to 5 bar with H_2.

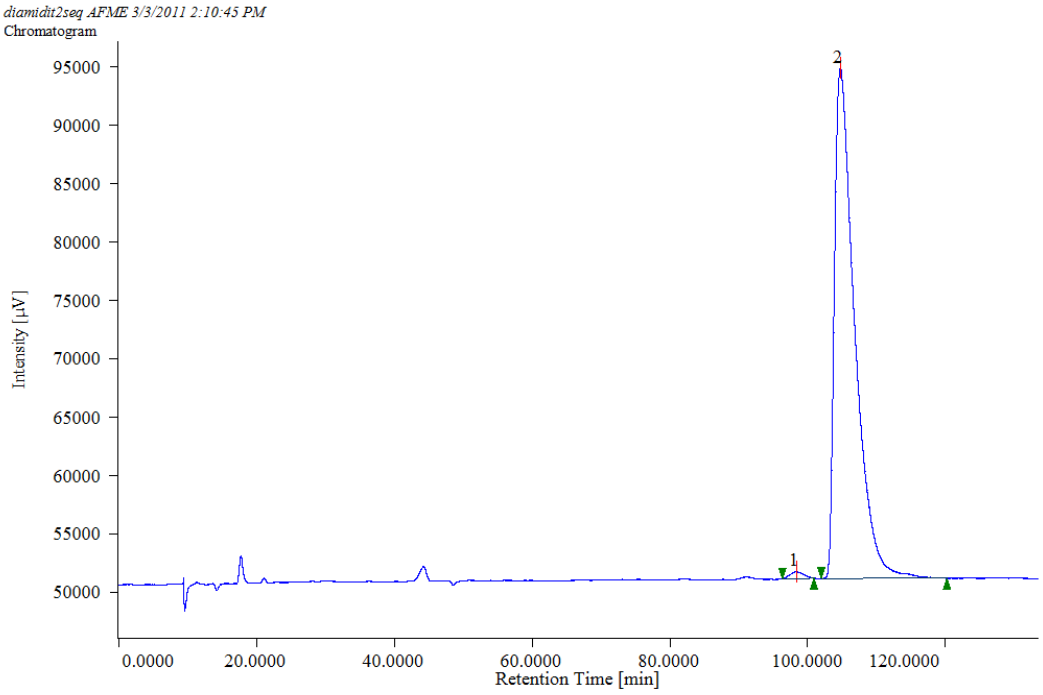
Preparation of the sample for analysis

1 mL of the homogenous reaction mixture was evaporated and the remaining yellow solid was filtered through a short pad of silica with ethyl acetate eluent to remove the catalyst. The filtrate was evaporated and the remaining white solid was dissolved in 10 mL of 2-propanol.

HPLC analysis

Conditions: Kromasil 3-CelluCoat, 4.6x150 mm, 20 ^{o}C, *n*-hexane/2-propanol = 95/5, flow rate = 0.3 mLmin^{-1}, pressure = 43 bar, detection wavelength = 275 nm.

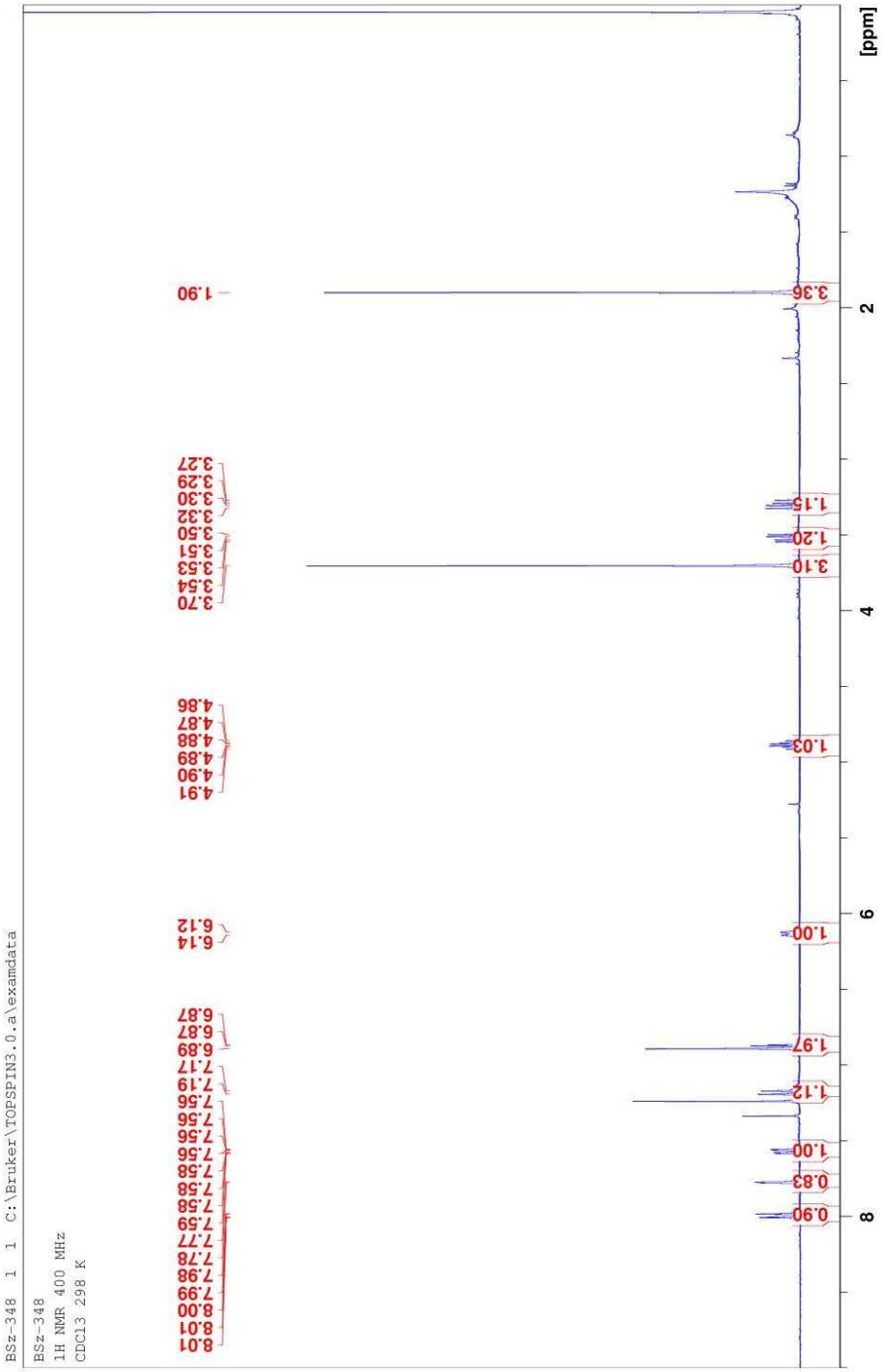
Figure 9. HPLC chromatogram of the product



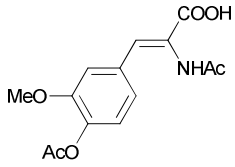
Peak Information

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	98.305	79990	594	0.893	1.341
2	104.723	8881881	43684	99.107	98.659

Figure 10. ^{1}H NMR spectrum of methyl 2-acetamido-3-(5-(2-chloro-4-(trifluoromethyl)phenoxy)-2-nitrophenyl)propanoate



Hydrogenation of 3-metoxy-4-acetoxy-(Z)-α-acetamidocinnamic acid



Synthesis of a racemic sample

The catalyst was prepared „*in situ*" by mixing $[Rh(COD)_2]BF_4$ (4.1 mg, 0.01 mmol) with PPh_3 (5.8 mg, 0.022 mmol) in 5 mL MeOH and the reaction mixture was stirred for 10 minutes. 1.25 mmol substrate was added and the mixture was pressurized to 5 bar with H_2.

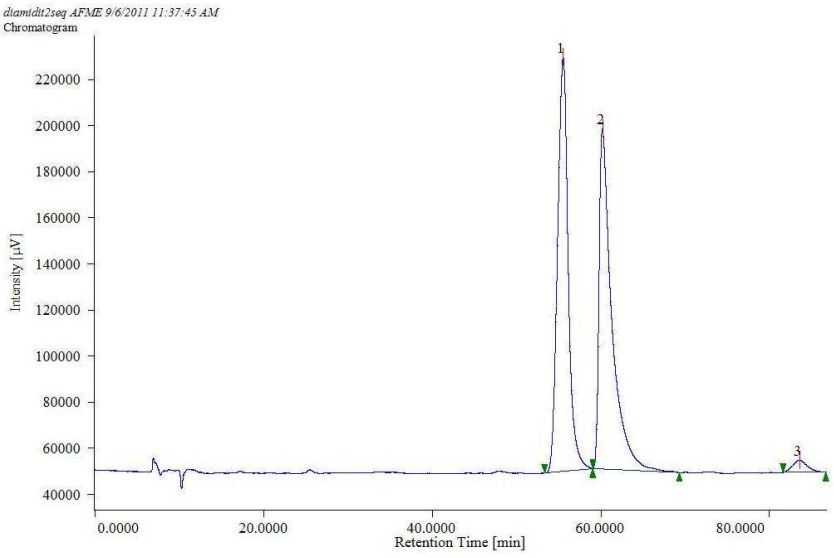
Preparation of the sample for analysis

1 mL of the homogenous reaction mixture was transferred into a test tube and diazomethane in diethyl-ether was added and stirred for 1 h at -20 ^oC. After evaporation of the solvents the remaining yellow solid was filtered through a short pad of silica with ethyl acetate eluent to remove the catalyst. The filtrate was evaporated and the remaining white solid was dissolved in 10 mL of *n*-hexane/2-propanol = 90/10.

HPLC analysis

Conditions: Kromasil 3-AmyCoat, 4.6x150 mm, 20 ^oC, *n*-hexane/2-propanol = 90/10, flow rate = 0.25 $mLmin^{-1}$, pressure = 18 bar, detection wavelength = 275 nm.

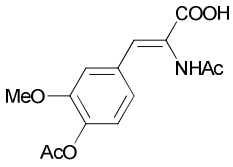
Figure 11. HPLC chromatogram of the racemic sample



Peak Information

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	55.519	15698137	179660	49.374	54.018
2	60.174	15455400	147723	48.611	44.416
3	83.571	640739	5210	2.015	1.566

Asymmetric hydrogenation of 3-metoxy-4-acetoxy-(Z)-α-acetamidocinnamic acid (Table 2, Entry 9)

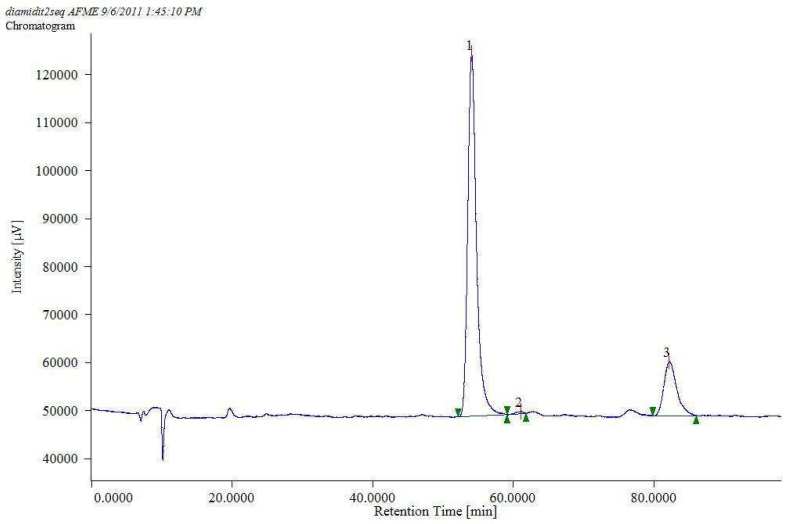


The catalyst was prepared „*in situ*" by mixing $[Rh(COD)_2]BF_4$ (4.1 mg, 0.01 mmol) with compound **4** (6.9 mg, 0.011 mmol) in 5 mL of propylene carbonate and the reaction mixture was stirred for 10 minutes. 1.25 mmol substrate was added and the mixture was pressurized to 5 bar H_2.

Preparation of the sample for analysis

The conversion was determined by ^1H NMR spectroscopy. Since propylene carbonate hinders HPLC measurement, the suspension of the reaction mixture was filtered through a short pad of silica and washed with diethyl ether to remove the reaction solvent. The product was washed with methanol from the column. 1 mL of the homogenous solution was transferred into a test tube and diazomethane in diethyl ether was added and stirred for 1 h at -20 ^oC. After evaporation of the solvents the remaining yellow solid was filtered through a short pad of silica with ethyl acetate eluent to remove the catalyst. The filtrate was evaporated and the remaining white solid was dissolved in 10 mL of *n*-hexane/2-propanol = 90/10.

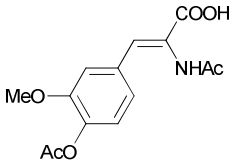
Figure 12. HPLC chromatogram of the product



Peak Information

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	54.037	6539091	75467	81.801	86.454
2	61.019	34837	511	0.436	0.585
3	82.108	1420001	11313	17.763	12.960

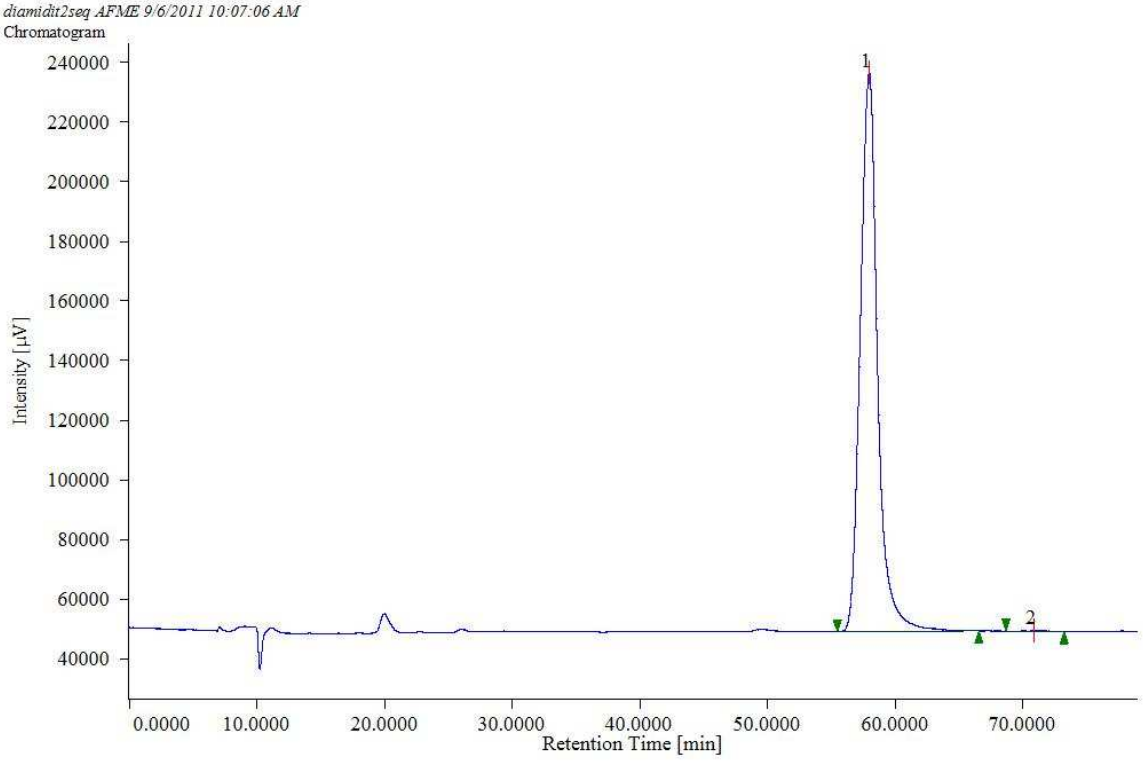
Asymmetric hydrogenation of 3-metoxy-4-acetoxy-(Z)-α-acetamidocinnamic acid (Table 2, Entry 9)



Preparation of the sample for analysis

The conversion was determined by ^{1}H NMR spectroscopy. The reaction mixture was filtered. The solid was washed with diethyl ether and let dry. The resulting white solid was dissolved in MeOH. Small amount of this homogenous solution was transferred into a test tube and diazomethane in diethyl ether was added and stirred for 1 h at -20 ^{o}C. After evaporation of the solvents, the remaining white solid was dissolved in 10 mL of *n*-hexane/2-propanol = 90/10.

Figure 13. HPLC chromatogram of the product



Peak Information

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	57.949	17687836	187388	99.804	99.858
2	70.873	34820	267	0.196	0.142

Figure 14. ^{1}H NMR spectrum of filtered L-DOPA precursor (Table 2, Entry 9)

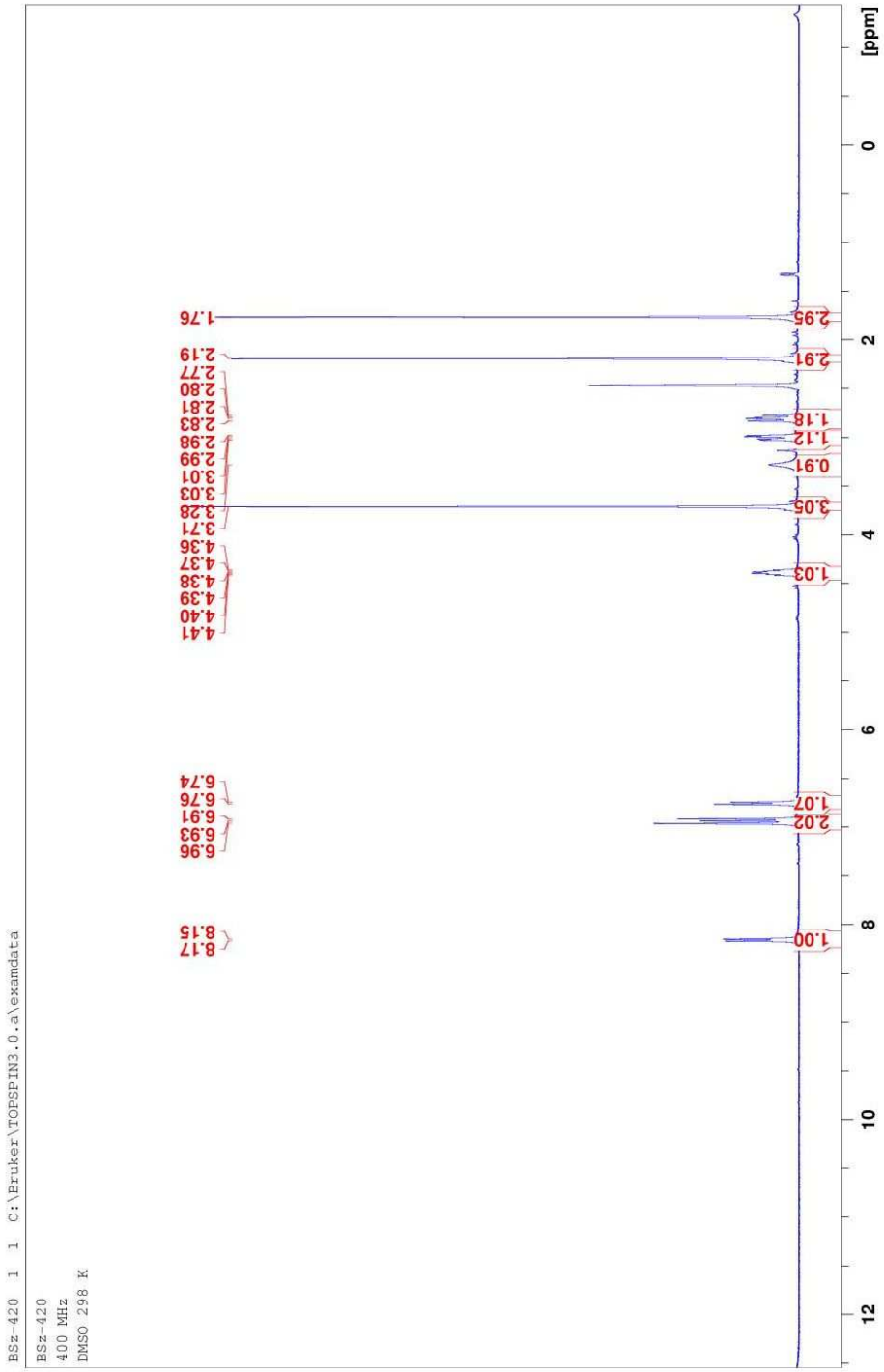
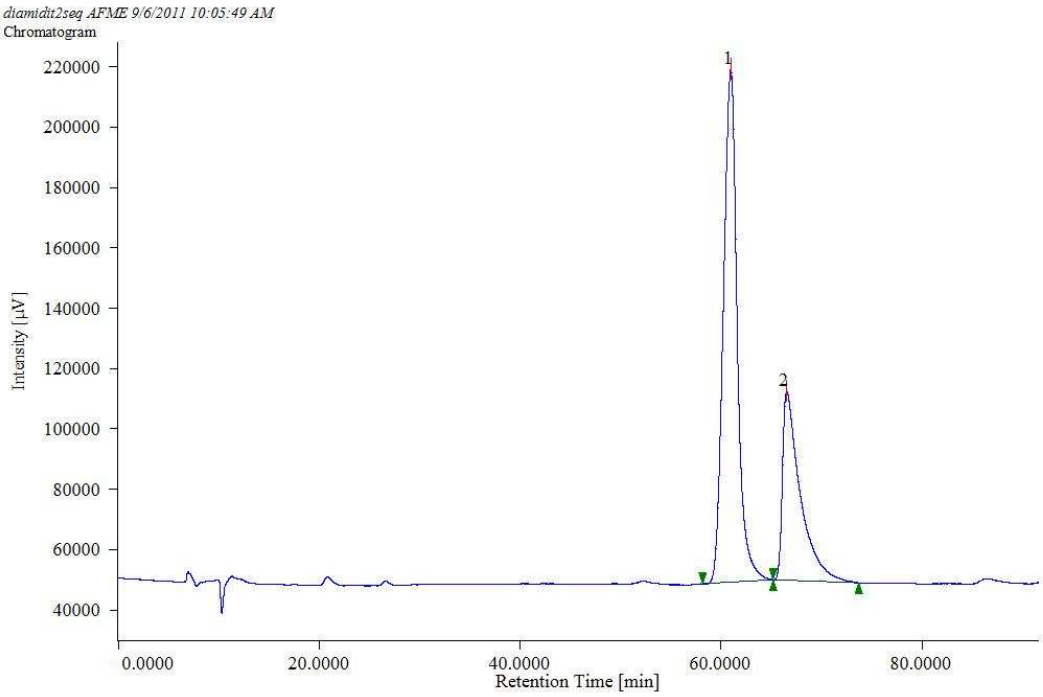


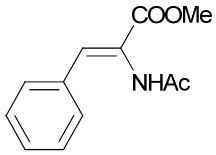
Figure 15. Racemic sample mixed with the filtered product of Entry 9



Peak Information

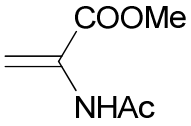
#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	60.957	16261249	169944	67.943	73.056
2	66.512	7672353	62676	32.057	26.944

Asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid methyl ester



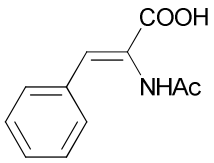
The conversions of the hydrogenation reactions of (*Z*)-α-acetamidocinnamic acid methyl ester and the enantiomeric excesses of the product were determined by chiral GC using a Hewlett Packard HP 4890 D, equipped with CHIRASIL-L-VAL column (25 m x 0.25 mm, df = 0.12 μm), N_2 as carrier gas, a split/split less injector at 250 °C, and a FID at 250 °C. Temperature program: 2 min at 140 °C; 2 °C/min from 140 °C to 180 °C; 40 min at 180 °C. Retention times were 12.3 min for (*R*), 13.2 min for (*S*)-product, and 22.1 min for (*Z*)-α-acetamidocinnamic acid methyl ester.

Asymmetric hydrogenation of acetamidoacrilyc acid methyl ester



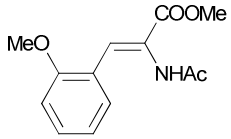
The conversions of the hydrogenation reactions of acetamidoacrilyc acid methyl ester and the enantiomeric excesses of the product were determined by chiral GC using a Hewlett Packard HP 4890 D, equipped with β-Dex 255 column (30 m x 0.25 mm, df = 0.25 μm), N_2 as carrier gas, a split/splitless injector at 250 °C, and a FID at 250 °C. Retention times at 140 °C isotherm were 6.7 min for (*S*), 7.4 min for (*R*) -product, and 5.9 min for acetamidoacrilyc acid methyl ester.

Asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid



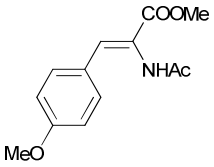
1 mL homogenous sample of the reaction mixture of asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid were methylated with CH_2N_2 after the reaction. The conversions of the reaction and the enantiomeric excesses of the product were determined by chiral GC using a Hewlett Packard HP 4890 D, equipped with CHIRASIL-L-VAL column (25 m x 0.25 mm, df = 0.12 μm), N_2 as carrier gas, a split/split less injector at 250 °C, and a FID at 250 °C. Temperature program: 2 min at 140 °C; 2 °C/min from 140 °C to 180 °C; 40 min at 180 °C. Retention times were 12.3 min for (*R*), 13.2 min for (*S*)-product, and 22.1 min for (*Z*)-α-acetamidocinnamic acid methyl ester.

Asymmetric hydrogenation of 2-methoxy-(*Z*)-α-acetamidocinnamic acid



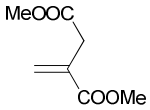
The conversions of the hydrogenation reactions of 2-methoxy-(*Z*)-α-acetamidocinnamic acid methyl ester and the enantiomeric excesses of the product were determined by chiral GC using a Hewlett Packard HP 4890 D, equipped with CHIRASIL-L-VAL column (25 m x 0.25 mm, df = 0.12 μm), N_2 as carrier gas, a split/split less injector at 250 °C, and a FID at 250 °C. Temperature program: 2 min at 140 °C; 2 °C/min from 140 °C to 180 °C; 40 min at 180 °C. Retention times were 21.9 min for (*R*), 22.6 min for (*S*)-product, and 34.9 min for 2-methoxy-(*Z*)-α-acetamidocinnamic acid methyl ester.

Asymmetric hydrogenation of 4-methoxy-(*Z*)-α-acetamidocinnamic acid



The conversions of the hydrogenation reactions of 4-methoxy-(*Z*)-α-acetamidocinnamic acid methyl ester and the enantiomeric excesses of the product were determined by chiral GC using a Hewlett Packard HP 4890 D, equipped with CHIRASIL-L-VAL column (25 m x 0.25 mm, df = 0.12 μm), N_2 as carrier gas, a split/split less injector at 250 °C, and a FID at 250 °C. Temperature program: 2 min at 140 °C; 2 °C/min from 140 °C to 180 °C; 40 min at 180 °C. Retention times were 25.7 min for (*R*), 26.3 min for (*S*)-product, and 53.6 min for 4-methoxy-(*Z*)-α-acetamidocinnamic acid methyl ester.

Asymmetric hydrogenation of dimethyl itaconate



The conversions of the hydrogenation reactions of dimethyl itaconate and the enantiomeric excesses of the product were determined by chiral GC using a Hewlett Packard HP 4890 D, equipped with β-Dex 255 column (30 m x 0.25 mm, df = 0.25 μm), N_2 as carrier gas, a split/split less injector at 250 °C, and a FID at 250 °C. Retention times at 85 °C isotherm were 18.8 min for (*R*), 20.0 min for (*S*)-product, and 27.6 min for dimethyl itaconate.

1 R. L. Augustine, S. K. Tanielyan, N. Mahata, Y. Gao, Á. Zsigmond, H. Yang *Applied Catalysis A: General*, 2003, **256**, 69.
2 Z. Shan, J. C. Jansen, W. Zhou, T. Maschmeyer *Appl. Catal. A*, 2003, **254**, 339–343.