Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Highly active, chemo- and enantioselective Pt-SPO catalytic systems for the synthesis of aromatic carboxamides

Supporting information

Content

15. X-ray structures of the racemic [1,1’-binaphthalene]-2,2’-dicarbonitrile, the enantioenriched [1,1’-binaphthalene]-2,2’-dicarbonitrile (2), and [1,1'-binaphthalene]-2,2'-dicarboxamide (4)

1. General information on the experimental conditions, chemicals, and instrumentation

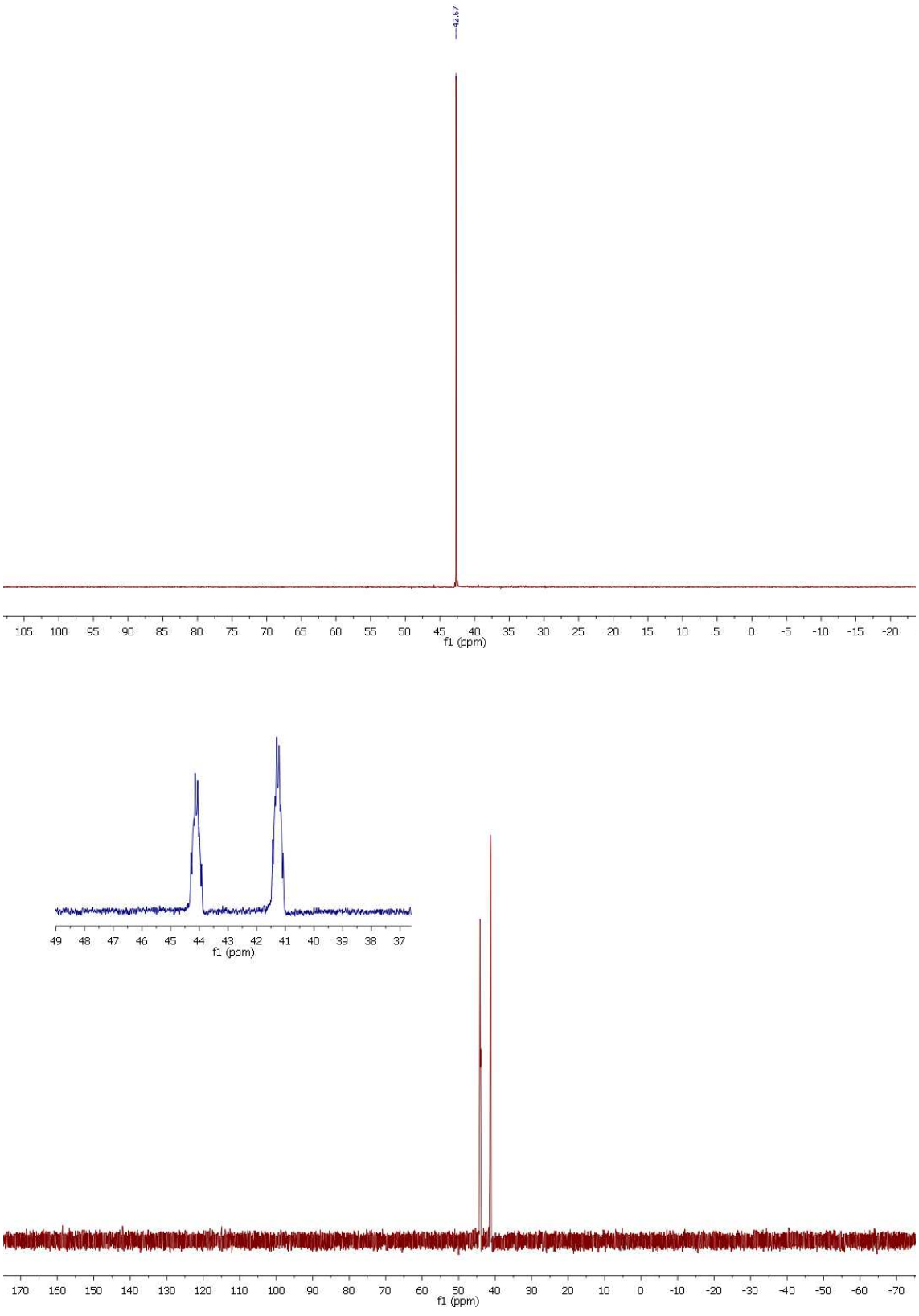
All manipulations in the course of the synthesis of the secondary phosphine-oxide **1** were carried out under argon or nitrogen using Schlenk-line techniques. Solvents were purified, dried and deoxygenated using standard methods. All the achiral nitrile substrates, as well as $Pt(COD)Cl_2$ and $Pt(PPh_3)_4$ were purchased from Aldrich, and used as received. (*rac*)-[1,1'-binaphthalene]-2,2'-dicarbonitrile was prepared according to a published method.[i] The synthesis of ligand **1** has been described by us earlier,[ii] here we publish an optimized method, which yields purer crude product, and higher isolated yields. $^{31}P\{^1H\}$-NMR, ^{31}P-NMR, ^1H-NMR, $^{13}C\{^1H\}$-NMR-spectra were recorded using Bruker ATM-400 spectrometer operating at 161.98, 161.98, 400.13, 100.61 MHz, respectively. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shift of residual solvents resonances. $^{31}P\{^1H\}$ and ^{31}P NMR chemical shifts are reported in ppm (δ) relative to H_3PO_4. Coupling constants (*J*) are given in Hz, and the multiplicity of the signals is described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Mass spectra were recorded using a Waters LCT Premier spectrometer. Gas chromatography was performed on an Agilent gas chromatograph, using an HP-5 column (30m), 50 °C initial temperature, 325 °C final temperature, 25 °C/min heating rate, 1.5 mL/min gas flow.

2. Experimental procedure of the improved synthesis of the chiral SPO 1

4-diethylamino-4,5-dihydro-3H-dinaphtho(2,1-c; 1',2'-e)phosphepine obtained from 2,2'-dimethyl-1,1'-binaphtyl-dilithium·2N,N,N',N'-tetramethylethylenediamine (8.87 g, 16.8 mmol), not purified, was dissolved in 96% EtOH (45 mL). Aqueous HCl solution (17 mL, 6N, 102 mmol) was added at 0 °C external temperature. It was stirred at room temperature overnight. $^{31}P\{^{1}H\}$- and ^{31}P-NMR spectra of the reaction mixture confirmed the formation of the product. All the volatiles were removed in vacuum. The solid residue was taken up in a 1 M HCl : DCM solvent mixture (30 mL / 30 mL). The organic phase was separated, the aqueous phase was washed with DCM (2 x 20 mL). The combined organic phase was washed with 0.1 N HCl solution (30 mL), and water (3-4 x 20 mL), until the aqueous extract was neutral. During the extraction steps the system tends to form an emulsion. The organic phase was dried over $MgSO_4$. The solvent was removed in vacuum. The off-white, foamy crude product (5.79 g) was purified by column chromatography. CH_2Cl_2 was used as eluent to separate dimethylbinaphthyl, then CH_2Cl_2:EtOH (9:1) was used to isolate the product. The column was repeated (CH_2Cl_2:EtOH = 9:1, then 95:5) to isolate the product from some mixed fractions of the first column. The product fractions were combined, and all the volatiles were removed in vacuum. Residual EtOH was removed from the product by dissolving it in DCM, removal of the solvent in vacuum, and drying the product in high vacuum. White solid. Overall yield (based on the lithiated dimethyl-binaphthyl): 3.43 g (62%). The product can be recrystallized from hot benzene yielding the title compound as large colorless crytals.[iii]

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.94-3.14 (m, 2H, CH_2, CH_2'), 3.26-3.47 (m, 2H, CH_2, CH_2'), 7.26 (dd, J_{PH} = 461 Hz, J_{HH} = 7.9 Hz, P(O)H), 7.19-7.33 (m, 4H, binaphthyl), 7.45-7.56 (pseudo q, 3H, binaphthyl), 7.66 (d, J_{HH} = 8.2 Hz, 1H, binaphthyl), 7.92-8.03 (m, 4H, binaphthyl). $^{31}P\{^{1}H\}$-NMR (162 MHz, $CDCl_3$): δ = 42.67 (s). ^{31}P-NMR (162 MHz, CDCl3): δ = 42.67 (dm, J_{PH} = 461 Hz).

3. $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra of SPO 1



4. HPLC analysis of SPO1 isolated by column chromatography

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                       (modified after loading)
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                       gradient 10% MeCN up to 100% in 20min
                       1 mL/min
                       1.5mg/mL (MeOH)
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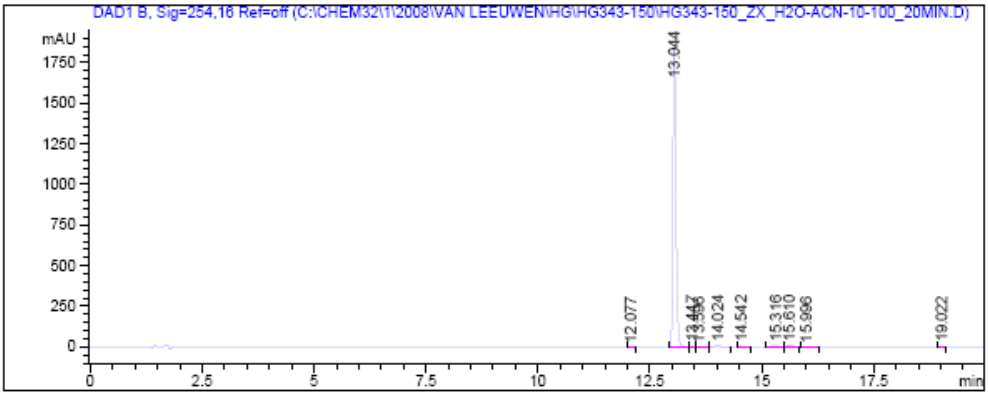


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                              Area Percent Report
    ======================================================================

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    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=254,16 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]    [mAU*s]    [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.077 VV    0.0643    5.44126    1.26108   0.0610
       2  13.044 BV    0.0726 8694.01953 1856.09387  97.4006
       3  13.447 VV    0.0792   18.01774    3.32347   0.2019
       4  13.596 VB    0.1350    9.53338    1.03989   0.1068
       5  14.024 BV    0.1754   44.04807    3.68518   0.4935
       6  14.542 VB    0.1017   19.93422    2.65118   0.2233
       7  15.316 BV    0.1396   41.08949    3.94225   0.4603
       8  15.610 VB    0.0976   76.42979   10.92734   0.8563
       9  15.996 BB    0.0986    9.46443    1.36967   0.1060
      10  19.022 BV    0.0787    8.06756    1.55173   0.0904

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HPLC-1 2/6/2008 4:04:38 PM ecm                                Page   1 of 1
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5. Single crystal X-ray analysis of the chiral SPO 1

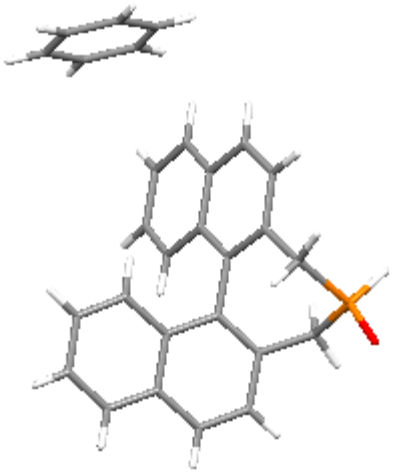

Table 1. Crystal data and structure refinement for **SPO1**.

Identification code	hg427150_0m	
Empirical formula	C28 H23 O P	
Formula weight	406.43	
Temperature	100(2)K	
Wavelength	0.71073 Ĺ	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.9622(4)Ĺ	α= 90.00°.
	b = 12.3209(7)Ĺ	β = 90.00°.
	c = 21.0198(11)Ĺ	γ = 90.00°.
Volume	2062.07(19) Ĺ^3	
Z	4	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	0.151 mm^{-1}	
F(000)	856	
Crystal size	0.10 x 0.10 x 0.03 mm^3	
Theta range for data collection	2.74 to 38.03°.	
Index ranges	-6<=h<=13,-21<=k<=7,-36<=l<=27	
Reflections collected	10895	
Independent reflections	9504[R(int) = 0.0286]	
Completeness to theta =38.03°	0.984%	
Absorption correction	Empirical	

Max. and min. transmission	0.9955 and 0.9851
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10895/ 0/ 275
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1006
R indices (all data)	R1 = 0.0500, wR2 = 0.1058
Largest diff. peak and hole	0.521 and -0.252 e.Ĺ$^{-3}$

Table 2. Bond lengths [Ĺ] and angles [°] for **SPO1**.

Bond lengths----	
C1-C2	1.5065(14)
C1-P1	1.8282(9)
C2-C11	1.3886(12)
C2-C3	1.4224(13)
C3-C4	1.3714(15)
C4-C5	1.4225(13)
C5-C6	1.4187(14)
C5-C10	1.4282(13)
C6-C7	1.3737(15)
C7-C8	1.4159(15)
C8-C9	1.3768(14)
C9-C10	1.4254(12)
C10-C11	1.436(13)
C11-C12	1.4912(12)
C12-C21	1.3854(12)
C12-C13	1.4356(12)
C13-C18	1.4224(13)
C13-C14	1.4248(13)
C14-C15	1.3767(13)
C15-C16	1.4168(15)
C16-C17	1.372(15)
C17-C18	1.4196(13)
C18-C19	1.4216(13)
C19-C20	1.3703(14)
C20-C21	1.4213(13)
C21-C22	1.5097(13)

C22-P1	1.8155(9)
O1-P1	1.4873(8)
C1A-C6A	1.3907(16)
C1A-C2A	1.3957(16)
C2A-C3A	1.3874(16)
C3A-C4A	1.3945(15)
C4A-C5A	1.3925(15)
C5A-C6A	1.3898(16)

Angles----------

C2-C1-P1	110.74(6)
C11-C2-C3	119.88(9)
C11-C2-C1	120.49(8)
C3-C2-C1	119.58(8)
C4-C3-C2	120.97(9)
C3-C4-C5	120.74(9)
C6-C5-C4	121.33(9)
C6-C5-C10	119.72(9)
C4-C5-C10	118.88(9)
C7-C6-C5	120.67(9)
C6-C7-C8	119.89(10)
C9-C8-C7	120.89(9)
C8-C9-C10	120.54(9)
C9-C10-C5	118.28(8)
C9-C10-C11	122.25(8)
C5-C10-C11	119.41(8)
C2-C11-C10	119.88(8)
C2-C11-C12	119.90(8)
C10-C11-C12	120.15(7)
C21-C12-C13	119.59(8)
C21-C12-C11	119.93(8)
C13-C12-C11	120.44(7)
C18-C13-C14	118.39(8)
C18-C13-C12	119.19(8)
C14-C13-C12	122.31(8)
C15-C14-C13	120.57(9)
C14-C15-C16	120.79(9)
C17-C16-C15	119.77(9)

C16-C17-C18	120.80(9)
C17-C18-C19	120.71(9)
C17-C18-C13	119.67(8)
C19-C18-C13	119.55(8)
C20-C19-C18	120.14(8)
C19-C20-C21	120.91(8)
C12-C21-C20	120.26(8)
C12-C21-C22	119.89(8)
C20-C21-C22	119.84(8)
C21-C22-P1	112.36(6)
O1-P1-C22	113.14(5)
O1-P1-C1	115.32(5)
C22-P1-C1	104.96(4)
C6A-C1A-C2A	120.06(10)
C3A-C2A-C1A	119.70(10)
C2A-C3A-C4A	120.21(9)
C5A-C4A-C3A	120.05(10)
C6A-C5A-C4A	119.71(10)
C5A-C6A-C1A	120.25(9)

Table 3. Torsion angles [°] for **SPO1**.

P1-C1-C2-C11	71.71(10)
P1-C1-C2-C3	-105.99(8)
C11-C2-C3-C4	-2.20(14)
C1-C2-C3-C4	175.51(9)
C2-C3-C4-C5	-1.99(14)
C3-C4-C5-C6	-174.09(9)
C3-C4-C5-C10	2.94(13)
C4-C5-C6-C7	176.82(9)
C10-C5-C6-C7	-0.18(14)
C5-C6-C7-C8	0.02(14)
C6-C7-C8-C9	0.61(15)
C7-C8-C9-C10	-1.08(14)
C8-C9-C10-C5	0.90(13)
C8-C9-C10-C11	-176.54(9)

C6-C5-C10-C9	-0.27(12)
C4-C5-C10-C9	-177.35(8)
C6-C5-C10-C11	177.24(8)
C4-C5-C10-C11	0.17(12)
C3-C2-C11-C10	5.29(13)
C1-C2-C11-C10	-172.40(8)
C3-C2-C11-C12	-177.83(8)
C1-C2-C11-C12	4.48(12)
C9-C10-C11-C2	173.14(8)
C5-C10-C11-C2	-4.27(12)
C9-C10-C11-C12	-3.73(12)
C5-C10-C11-C12	178.86(8)
C2-C11-C12-C21	-65.53(11)
C10-C11-C12-C21	111.35(10)
C2-C11-C12-C13	112.10(10)
C10-C11-C12-C13	-71.03(11)
C21-C12-C13-C18	-4.16(13)
C11-C12-C13-C18	178.21(8)
C21-C12-C13-C14	171.91(8)
C11-C12-C13-C14	-5.73(13)
C18-C13-C14-C15	1.56(14)
C12-C13-C14-C15	-174.53(9)
C13-C14-C15-C16	-1.32(15)
C14-C15-C16-C17	0.13(16)
C15-C16-C17-C18	0.78(16)
C16-C17-C18-C19	176.31(10)
C16-C17-C18-C13	-0.50(15)
C14-C13-C18-C17	-0.66(13)
C12-C13-C18-C17	175.55(9)
C14-C13-C18-C19	-177.51(8)
C12-C13-C18-C19	-1.29(13)
C17-C18-C19-C20	-171.79(9)
C13-C18-C19-C20	5.02(14)
C18-C19-C20-C21	-3.32(14)
C13-C12-C21-C20	5.95(13)
C11-C12-C21-C20	-176.41(8)
C13-C12-C21-C22	-173.02(8)
C11-C12-C21-C22	4.63(13)

C19-C20-C21-C12	-2.24(14)
C19-C20-C21-C22	176.73(9)
C12-C21-C22-P1	71.08(10)
C20-C21-C22-P1	-107.89(8)
C21-C22-P1-O1	-168.56(7)
C21-C22-P1-C1	-42.01(8)
C2-C1-P1-O1	81.62(8)
C2-C1-P1-C22	-43.58(8)
C6A-C1A-C2A-C3A	0.93(17)
C1A-C2A-C3A-C4A	-0.75(16)
C2A-C3A-C4A-C5A	-0.46(16)
C3A-C4A-C5A-C6A	1.50(15)
C4A-C5A-C6A-C1A	-1.33(15)
C2A-C1A-C6A-C5A	0.11(16)

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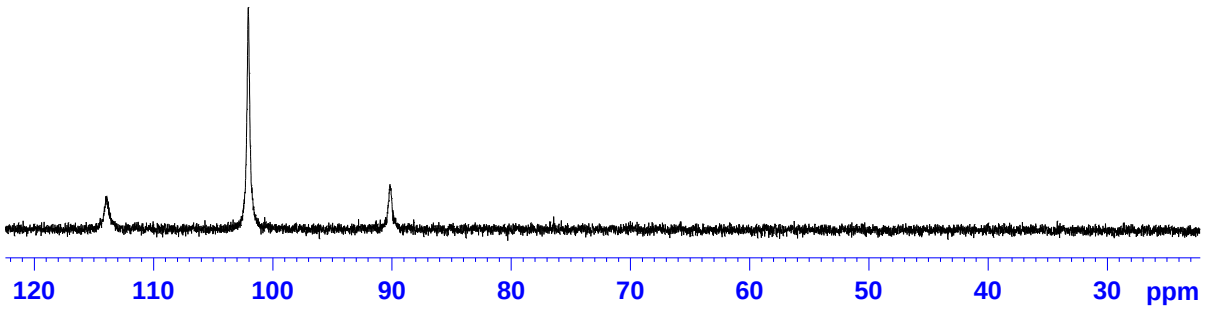
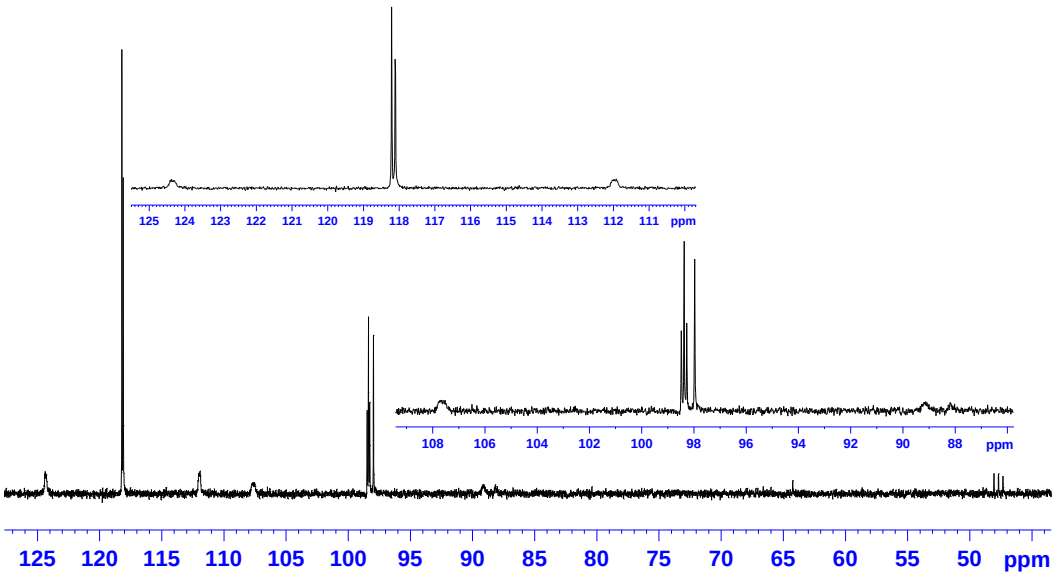
6. Formation of the *cis*-$Pt(1)_2Cl_2$ in the reaction of $Pt(COD)_2Cl_2$ with two equivalents of 1

$^{31}P\{^{1}H\}$-NMR ($CDCl_3$)



7. Formation of the $[Pt(1)_3Cl]Cl$ in the reaction of $Pt(COD)_2Cl_2$ with three equivalents of 1

$^{31}P\{^{1}H\}$-NMR (CD_3OD:$CDCl_3$ V/V = 5:2)

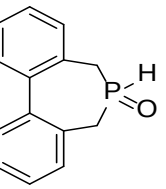


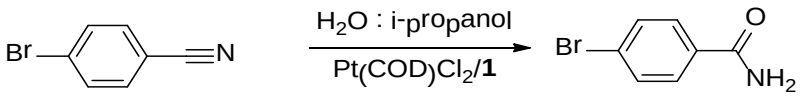
8. In situ formed $Pt(COD)Cl_2$/1 catalytic system, effect of the Pt:P ratio on the catalytic activity

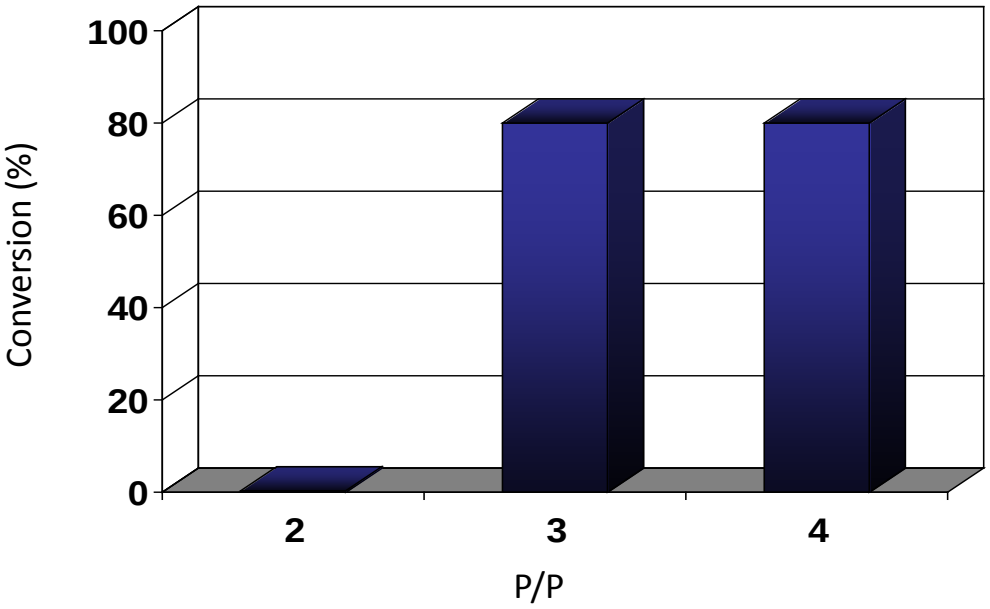
$Pt(COD)Cl_2$ (7.5 mg, 0.02 mmol), SPO **1** (13.8 mg, 0.042 mmol / 20.7 mg, 0.063 mmol / 27.6 mg / 0.084 mmol), and 4-bromo-benzonitrile (182 mg, 1 mmol) were subsequently transferred into a 14 mL screw-cap vials, supplied with magnetic stir bars. The vials were purged with argon via the septum of the cap, and then isopropanol (6 mL) was added. Each vial was placed into an oil bath heated at 80 °C. After a few minutes water (1 mL) was added, the septum of the cap was sealed with clay and parafilm, and the reaction mixtures were stirred for 10 hours.

Test reaction:

1:





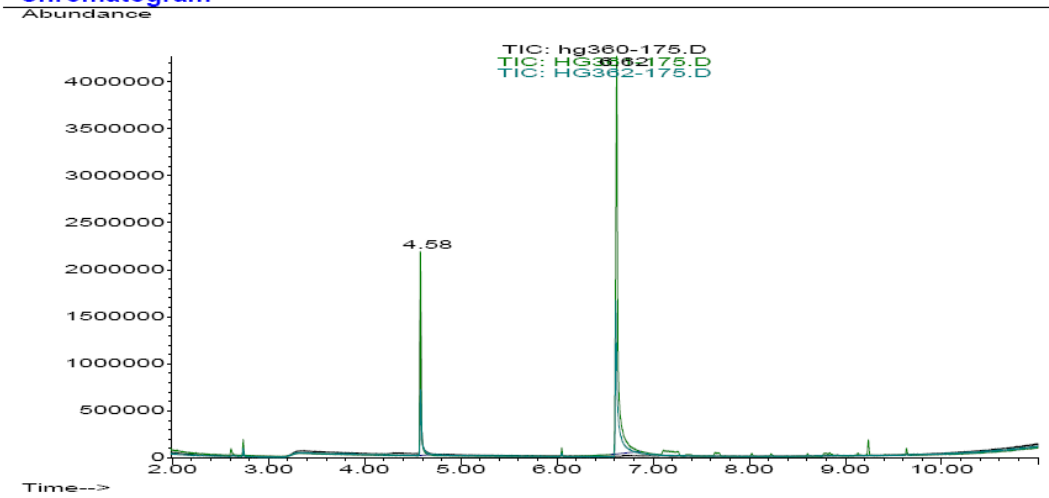


General conditions: 1 mol% $Pt(COD)Cl_2$, 2-4 P/Pt ratio,1 mmol nitrile, 6 mL of *i*-propanol, 1 mL of H_2O, 80 ^{o}C, 10 hours.

Method

Column: DB-5 30m, ID 0.25mm, 0.25µm
conc: ? mg/mL (THF)
Inj vol: 0.2µL
split 50:1
Tinj/aux: 260°C
He flow: 1.5 mL/min
oven: 50°C up to 325°C (25°C/min)

Chromatogram



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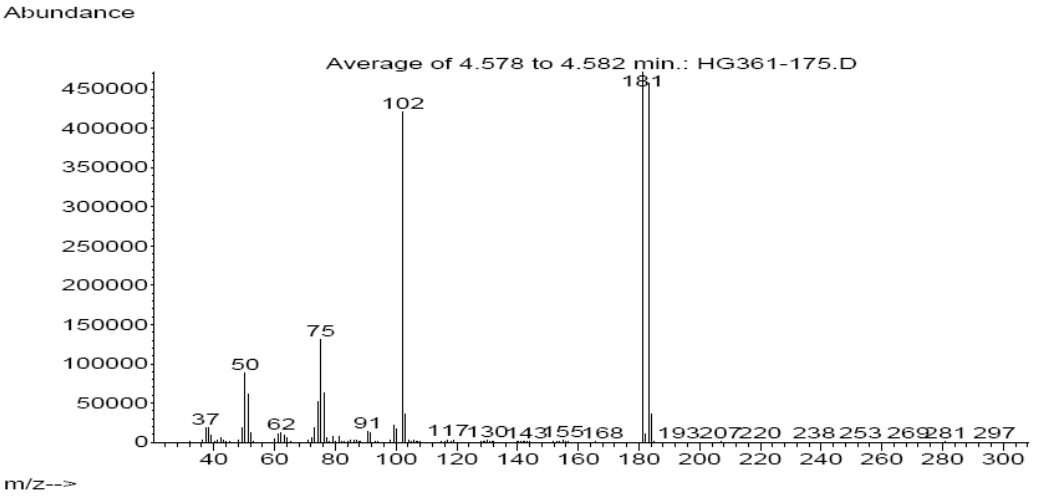

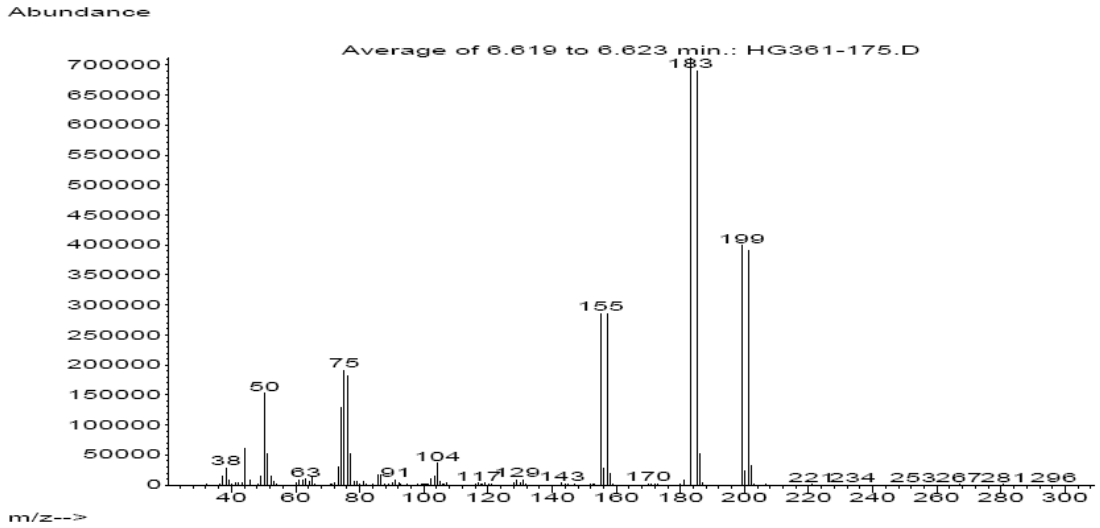

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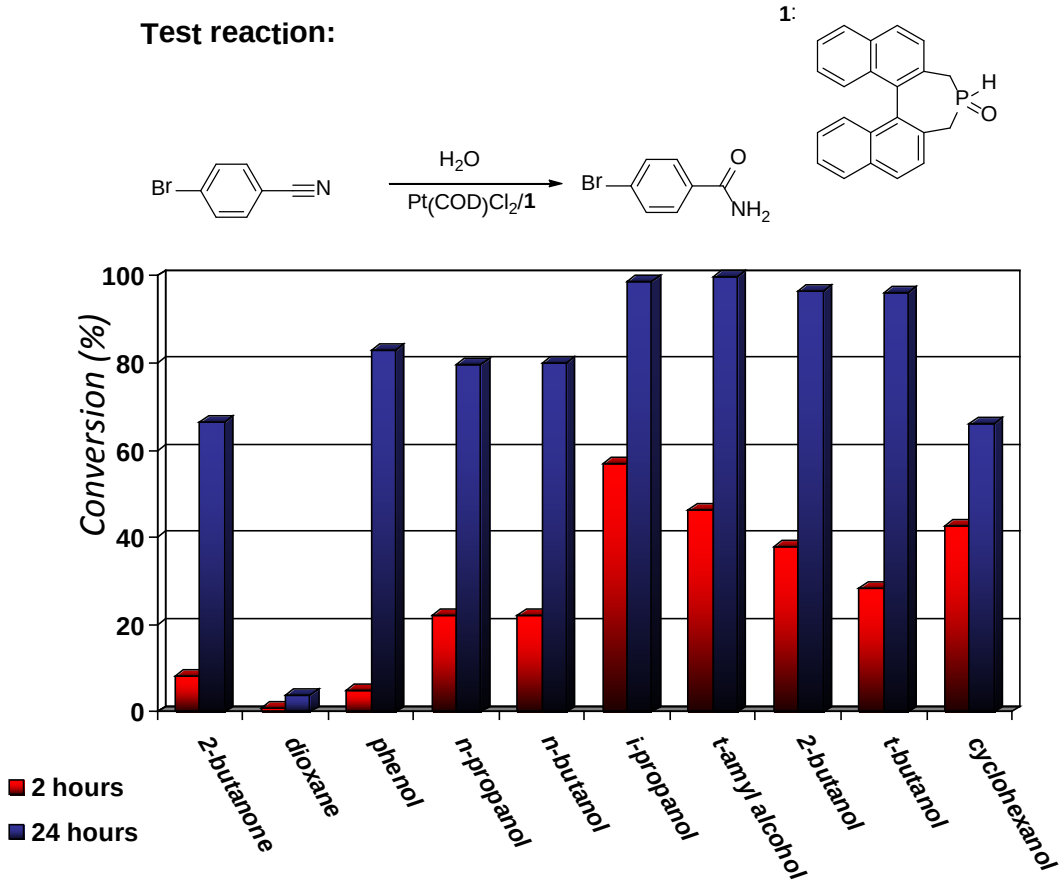
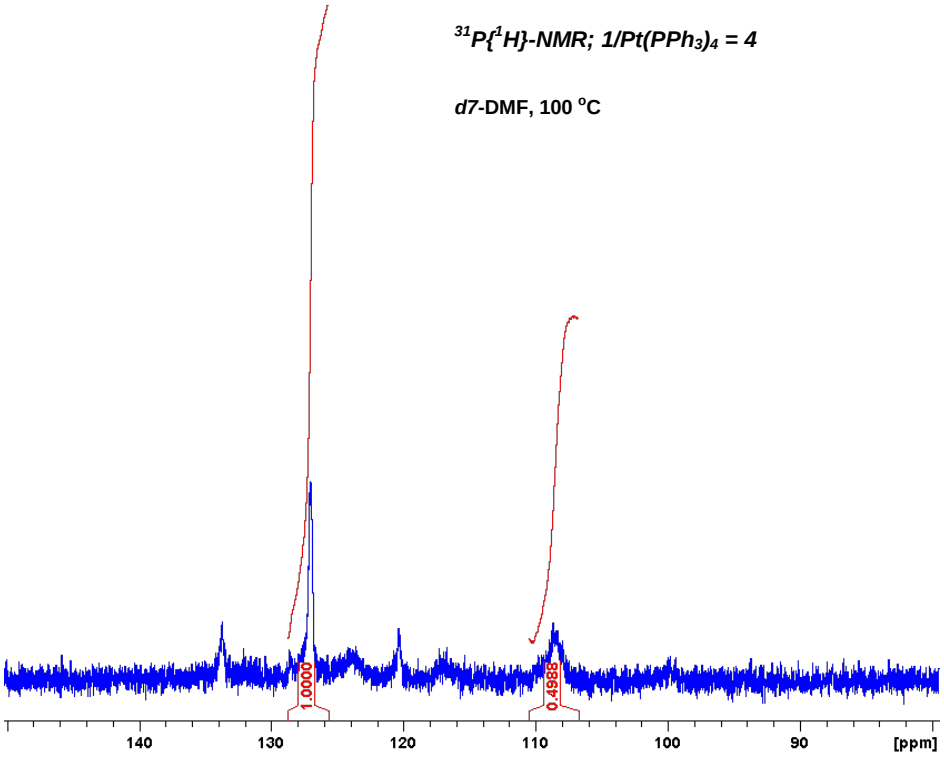
9. Solvent optimization for the synthesis of carboxamides using the in situ formed $Pt(COD)Cl_2$/1 catalytic system

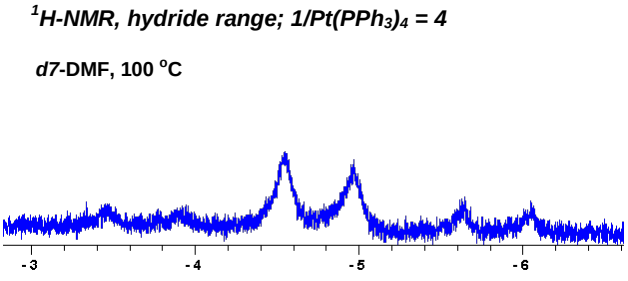
$Pt(COD)Cl_2$ (3.74 mg, 0.01 mmol), SPO **1** (11.5 mg, 0.035 mmol), and 4-bromo-benzonitrile (91 mg, 0.5 mmol) were subsequently transferred into a 14 mL screw-cap vial, supplied with magnetic stir bar. The vial was carefully purged with argon via the septum of the cap, and then the appropriate solvent (3 mL) was added. Each vial was placed into an oil bath heated at 80 °C. After a few minutes water (0.6 mL) was added, the septum of the cap was sealed with clay, and the reaction mixtures were stirred for 24 hours. Analytical samples were taken and analysed at 2 and at 24 hours.



General conditions: 2 mol% $Pt(COD)Cl_2$, 3.5 SPO:Pt ratio, 3 mL of solvent, 0.6 mL of H_2O, 80 ^{o}C. Chemoselectivity: 100% in each case.

10. Formation of $PtH(PR_2OH)(PR_2O\text{--}H\text{--}OR_2P)$ (PR_2OH = 1) in the reaction of $Pt(PPh_3)_4$ with 4 equivalents of 1*





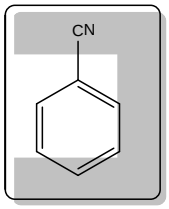
*The experiment has also been carried out at a **1**/$Pt(PPh_3)_4$ ratio 3. The formation of the same complex, $PtH(PR_2OH)(PR_2O\text{--}H\text{--}OR_2P)$ (PR_2OH = 1), as only product was observed.

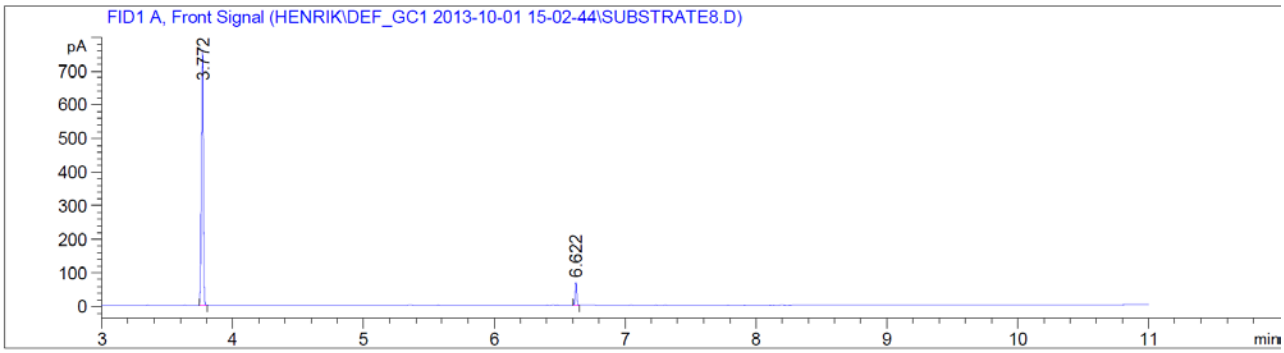
10. Selected examples of the catalytic experiments; GC and GC-MS analyses for the hydration of benzonitrile into benzamide (a), 4-bromobenzonitrile into 4-bromobenzamide (c), 2-bromobenzonitrile into 2-bromobenzamide (e), and 2-phenylacetonitrile into 2-phenylacetamide (j)

BENZONITRILE

GC analysis of the benzonitrile substrate

RT in THF: 3.772 min

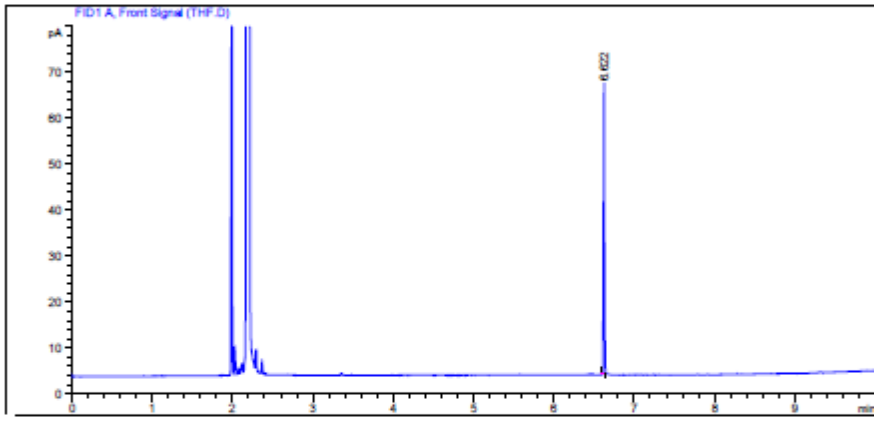




GC analysis of THF

RT of main impurity: 6.622 min

```
Data File C:\CHEM32\1\DATA\HENRIK\DEF_GC1 2013-10-01 17-33-48\THF.D
Sample Name: THF

------------------------------------------------------------------------
Acq. Operator   : SYSTEM                        Seq. Line :   3
Acq. Instrument : 7890 GC                       Location : Vial 111
Injection Date  : 01-Oct-13 6:08:36 PM               Inj :   1
                                               Inj Volume : 2 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Sequence File   : C:\CHEM32\1\DATA\HENRIK\DEF_GC1 2013-10-01 17-33-48\DEF_GC1.S
Acq. Method     : C:\CHEM32\1\DATA\HENRIK\DEF_GC1 2013-10-01 17-33-48\HENRIK1.M
Last changed    : 01-Oct-13 5:33:48 PM by SYSTEM
Analysis Method : C:\CHEM32\1\DATA\HENRIK\DEF_GC1 2013-10-01 17-33-48\HENRIK1.M (Sequence
                  Method)
Last changed    : 28-Apr-14 7:39:14 PM by SYSTEM
Method Info     : spo henrik
```

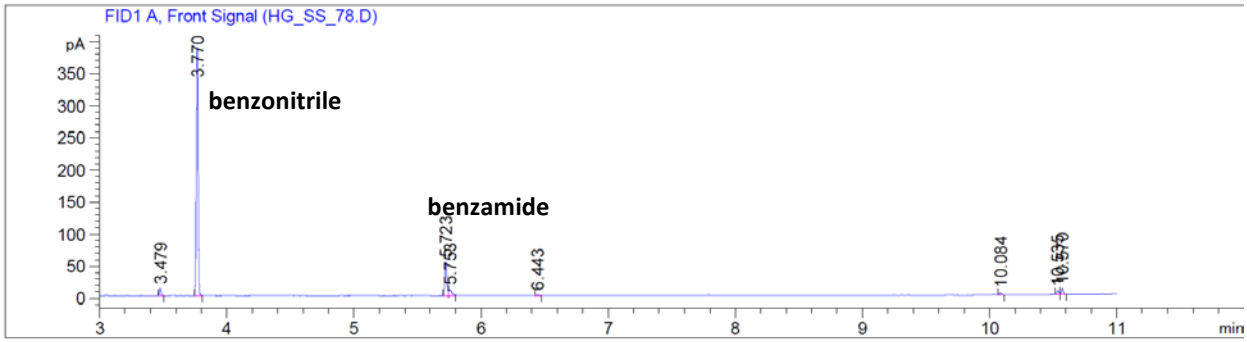



```
------------------------------------------------------------------------
                          Area Percent Report
------------------------------------------------------------------------

Sorted By             :      Signal
Calib. Data Modified  :      16-Jul-13 3:56:25 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime  Type   Width     Area      Area    Name
  #   [min]          [min]   [pA*s]       %
----|-------|------|-------|----------|--------|--------------------
   1   3.800         0.0000    0.00000  0.00000 acetophenone
   2   5.628         0.0000    0.00000  0.00000 Ciclohexanol
   3   5.803         0.0000    0.00000  0.00000 Ciclohexanona
   4   6.622 BB      0.0145   56.76570 1.000e2  ?

Totals :                      56.76570
```

GC analysis of the reaction mixtures of the catalytic reactions

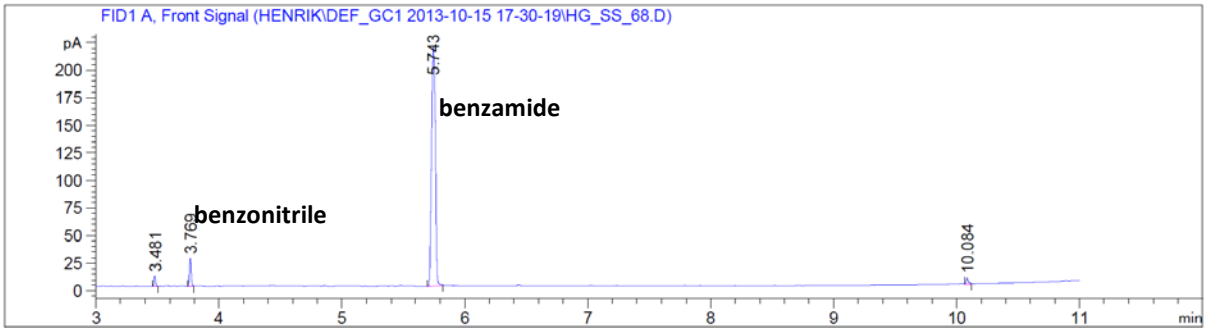
Catalytic hydration of benzonitrile into benzamide (**a**) with $Pt(COD)Cl_2$/**1**, reaction time 2h

Yield: 16%.



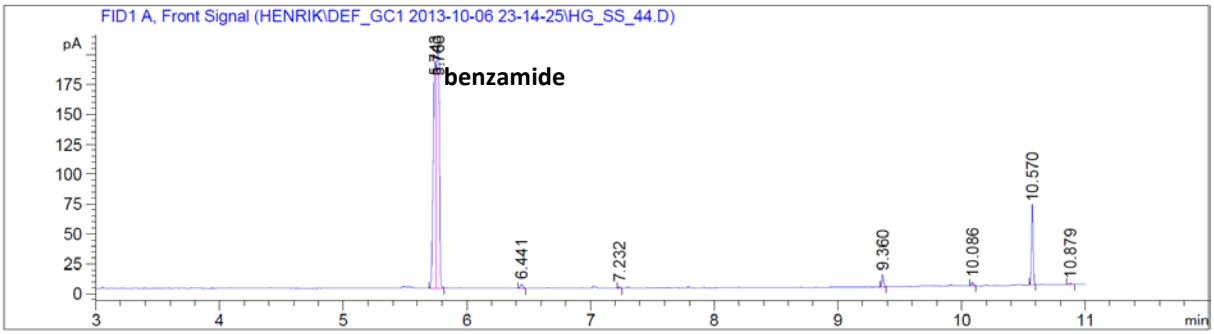
Catalytic hydration of benzonitrile into benzamide (**a**) with $Pt(COD)Cl_2$/**1**, reaction time 24h

Yield: 95%.



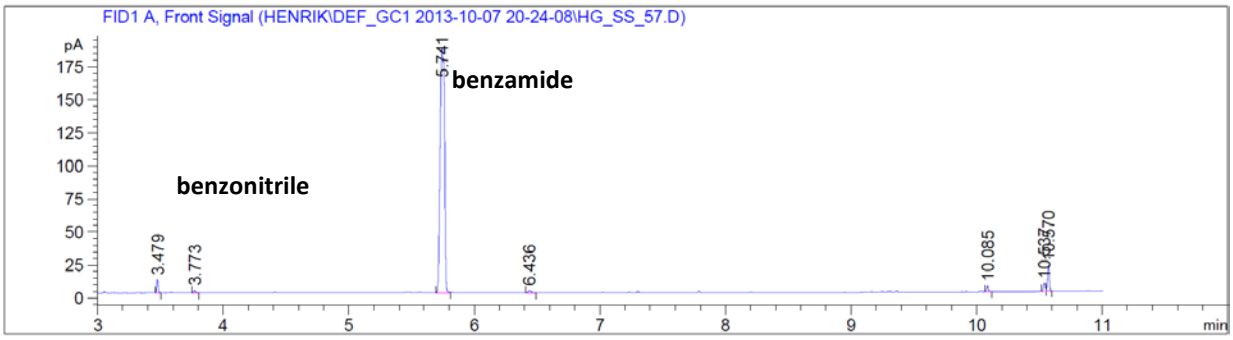
Catalytic hydration of benzonitrile into benzamide (**a**) with $Pt(PPh_3)_4$/**1**, reaction time 1h

Yield: >99%.



Catalytic hydration of benzonitrile into benzamide (**a**) with $Pt(COD)Cl_2/AgNO_3$/**1** reaction time 1h

Yield: >99%.

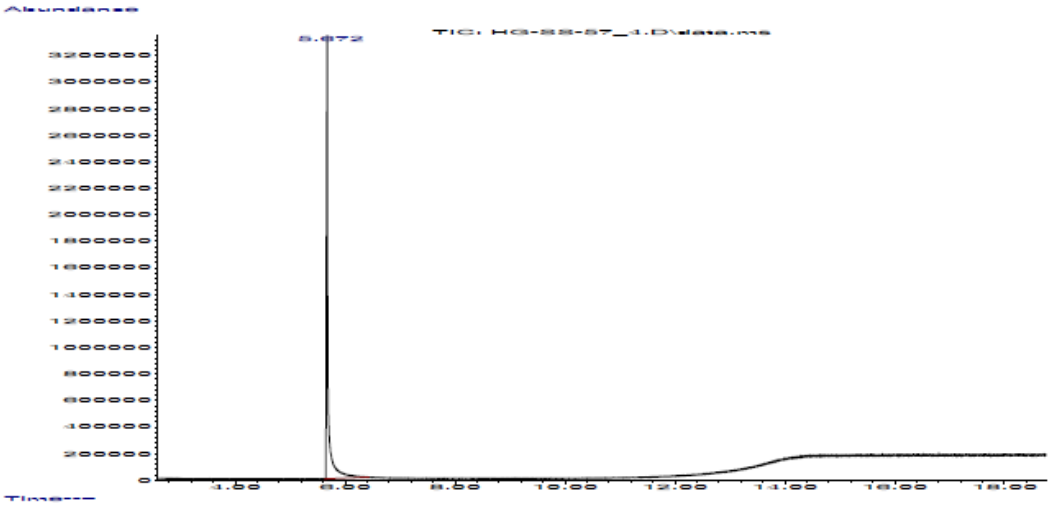


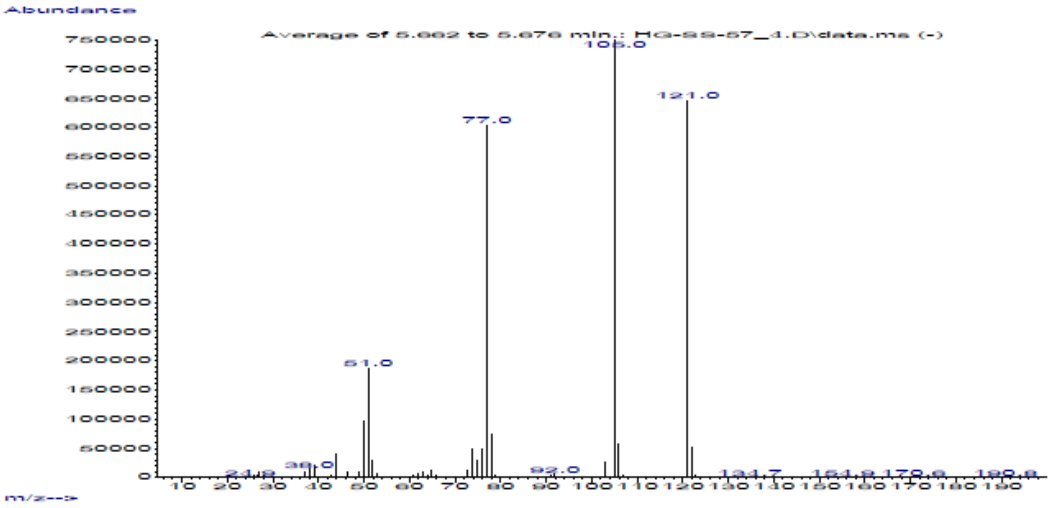
Isolation of benzamide (a) (Scheme 4, $Pt(COD)Cl_2/AgNO_3$/1 system)

The product was isolated on a chromatotron (centrifugal thin-layer chromatography) using a DCM:EtOH eluent mixture (v/v 10/1). Yield: 66 mg (quantitative). CAS: 55-21-0.

Sample HG-SS-57

HP-5MS, 30mx0.25mmx0.25µm
Tinj-aux: 280°C
1.5mL/min
Split 30:1 (1µl)
50°C-325°C(10')/20°Cmin-1
Sample as received

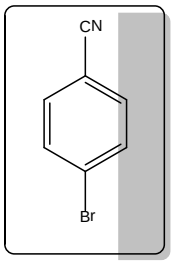


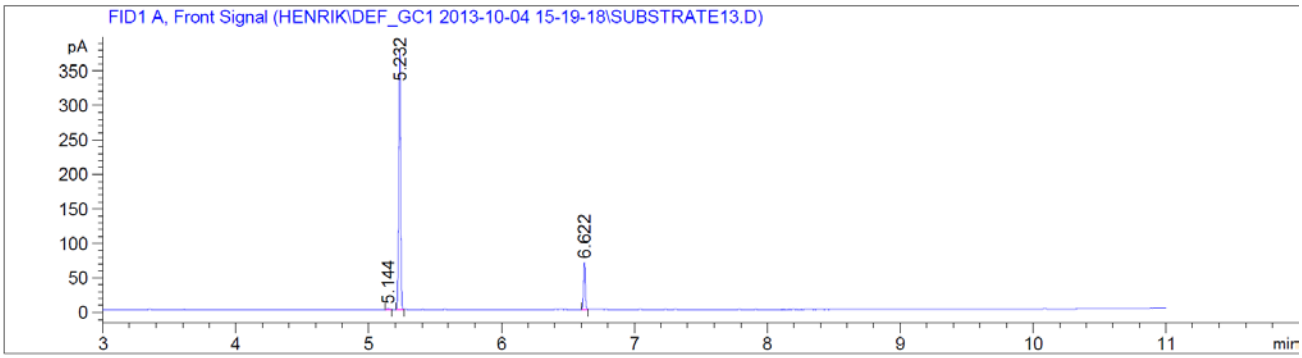


4-BROMOBENZONITRILE

GC analysis of the 4-bromobenzonitrile substrate

RT in THF: 5.232 min

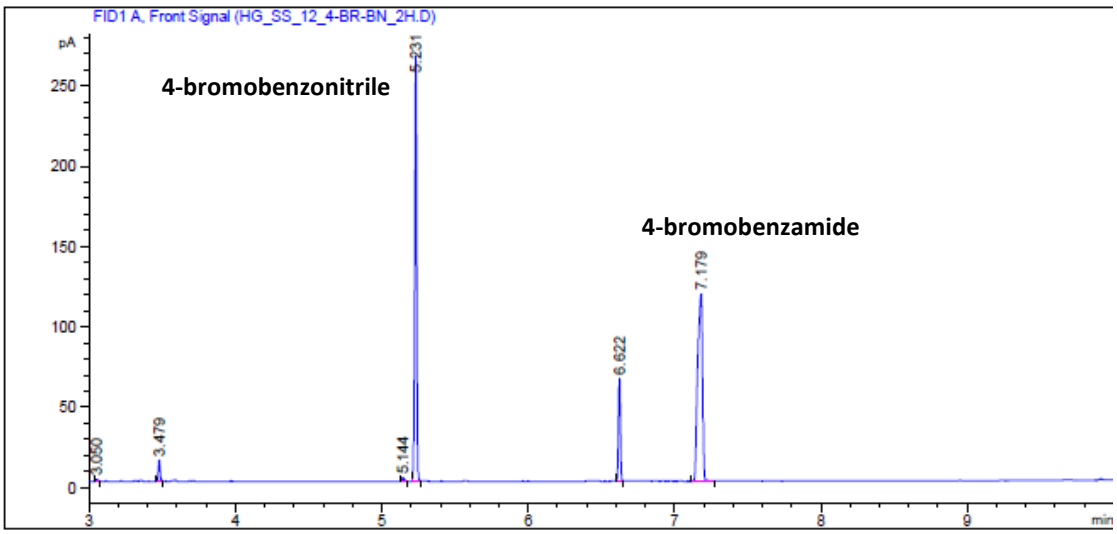




GC analysis of the reaction mixtures of the catalytic reactions

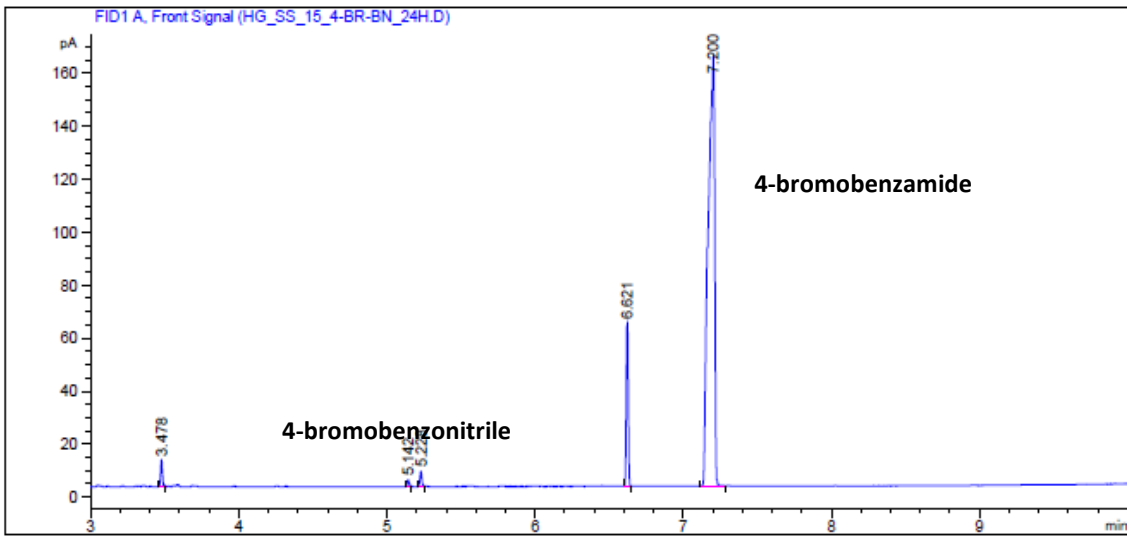
Catalytic hydration of 4-bromobenzonitrile into 4-bromobenzamide (**c**) with $Pt(COD)Cl_2$/**1**, reaction time 2h

Yield: 51%.



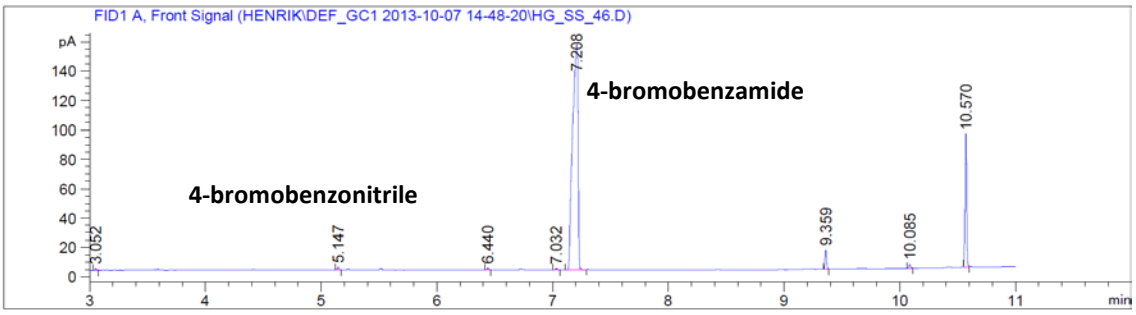
Catalytic hydration of 4-bromobenzonitrile into 4-bromobenzamide (**c**) with $Pt(COD)Cl_2$/**1**, reaction time 24h

Yield: 99%.



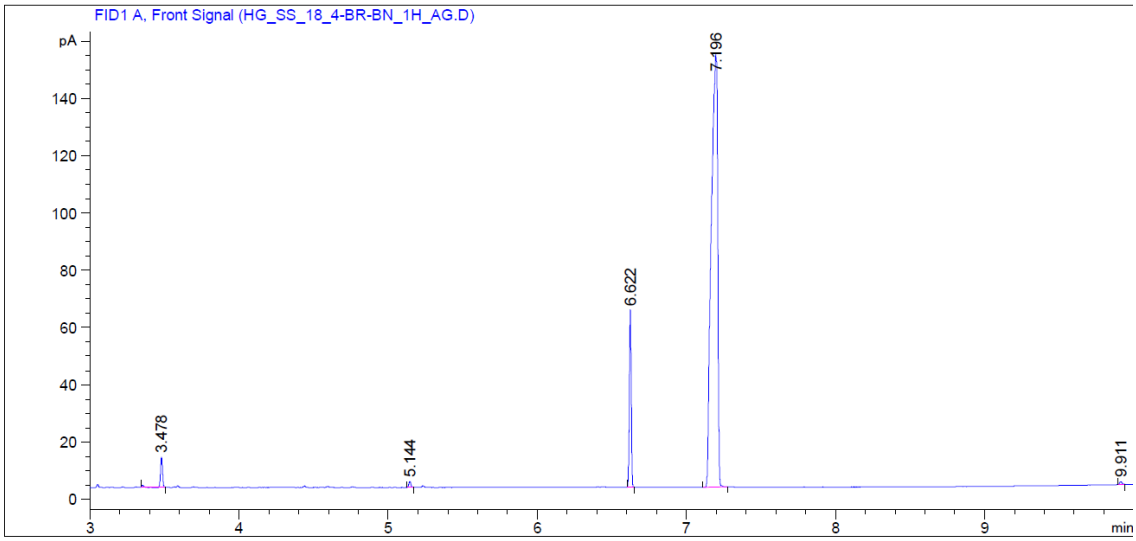
Catalytic hydration of 4-bromobenzonitrile into 4-bromobenzamide (**c**) with $Pt(PPh_3)_4$/**1**, reaction time 1h

Yield: >99%.



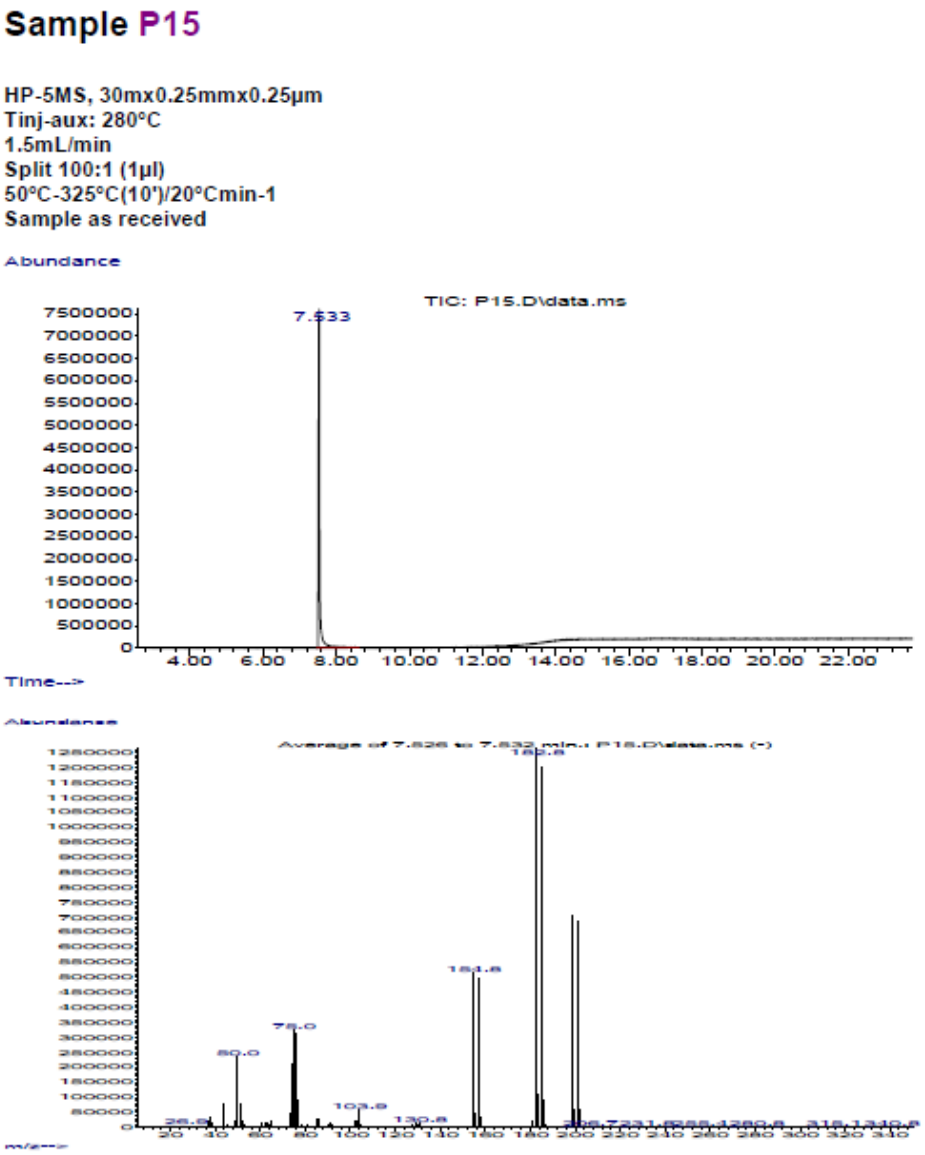
Catalytic hydration of 4-bromobenzonitrile into 4-bromobenzamide (**c**) with $Pt(COD)Cl_2/AgNO_3$/**1** reaction time 1h

Yield: >99%.



Isolation of 4-bromobenzamide (c) (Scheme 3, $Pt(COD)Cl_2$/1 system)

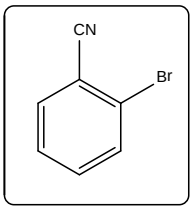
The product was isolated by column chromatography using a silica column and DCM:EtOH eluent mixture (v/v 10/1). Yield: 99 mg (99%). CAS: 698-67-9.

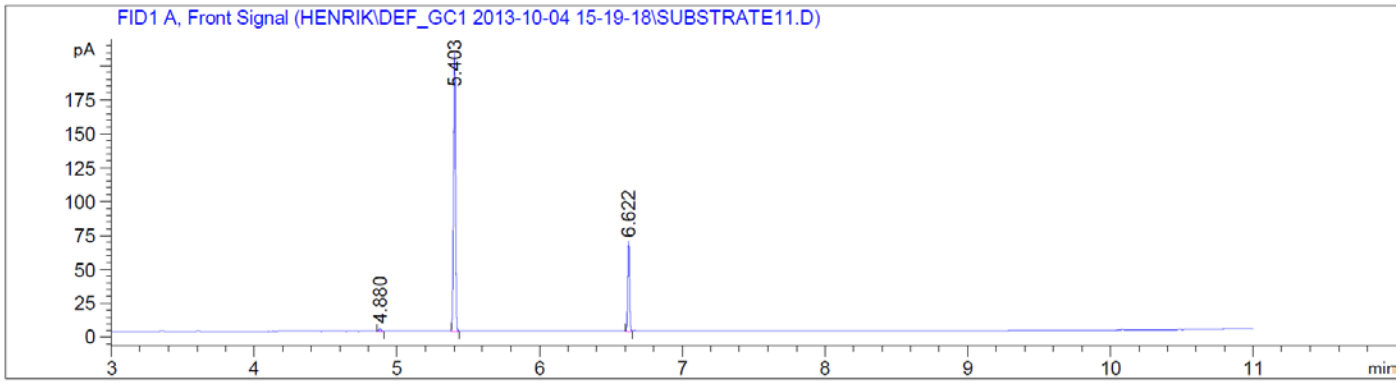


2-BROMOBENZONITRILE

GC analysis of the 2-bromobenzonitrile substrate

RT in THF: 5.403 min

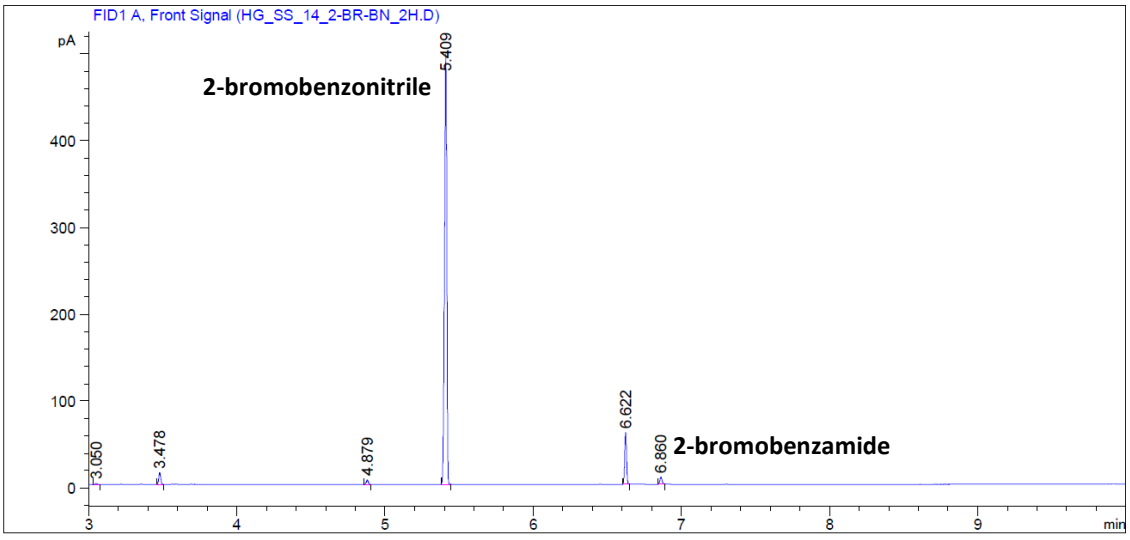




GC analysis of the reaction mixtures of the catalytic reactions

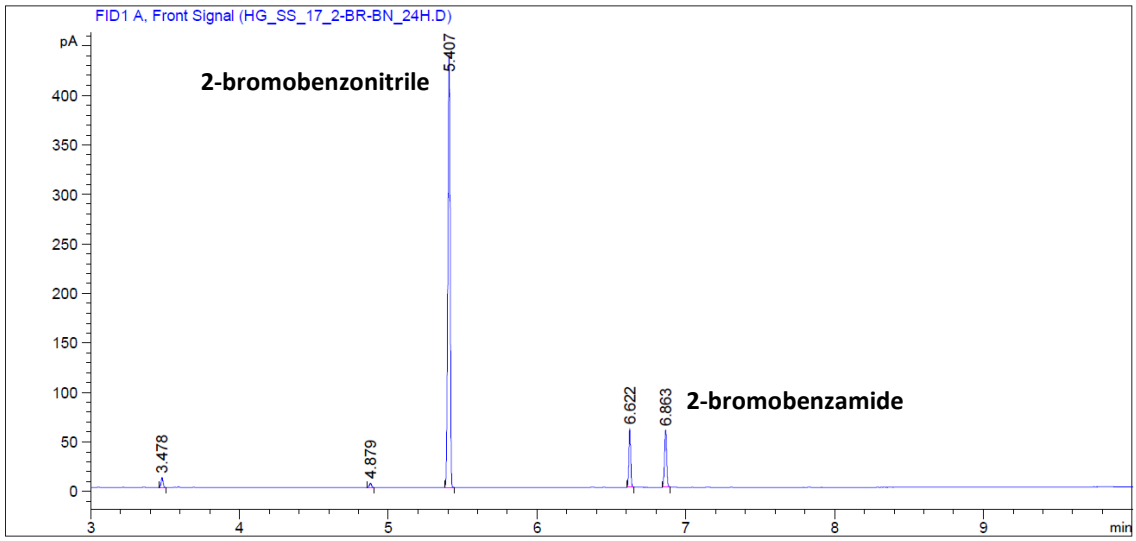
Catalytic hydration of 2-bromobenzonitrile into 2-bromobenzamide (**e**) with $Pt(COD)Cl_2$/**1**, reaction time 2h

Yield: 1.7%.



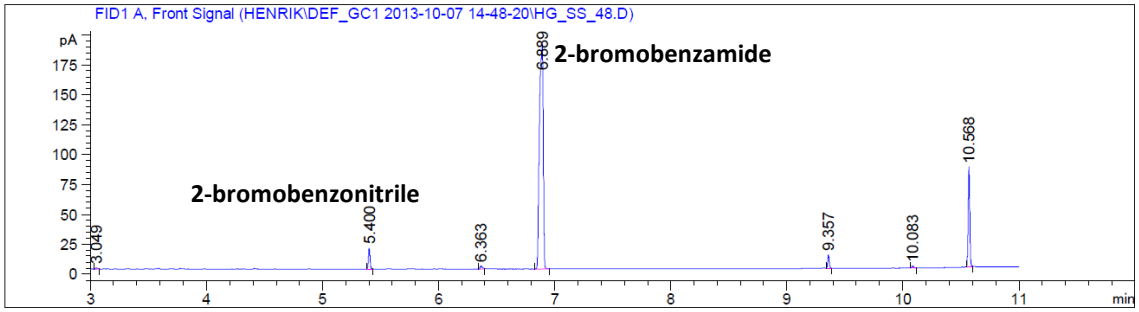
Catalytic hydration of 2-bromobenzonitrile into 2-bromobenzamide (**e**) with $Pt(COD)Cl_2$/**1**, reaction time 24h

Yield: 11%.



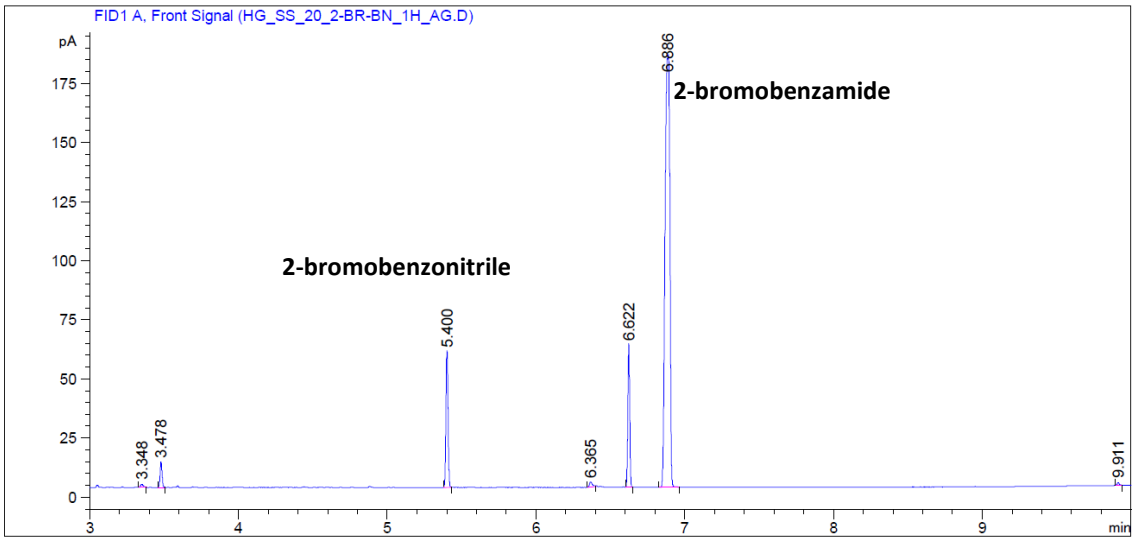
Catalytic hydration of 2-bromobenzonitrile into 2-bromobenzamide (**e**) with $Pt(PPh_3)_4$/**1**, reaction time 1h

Yield: 96%.



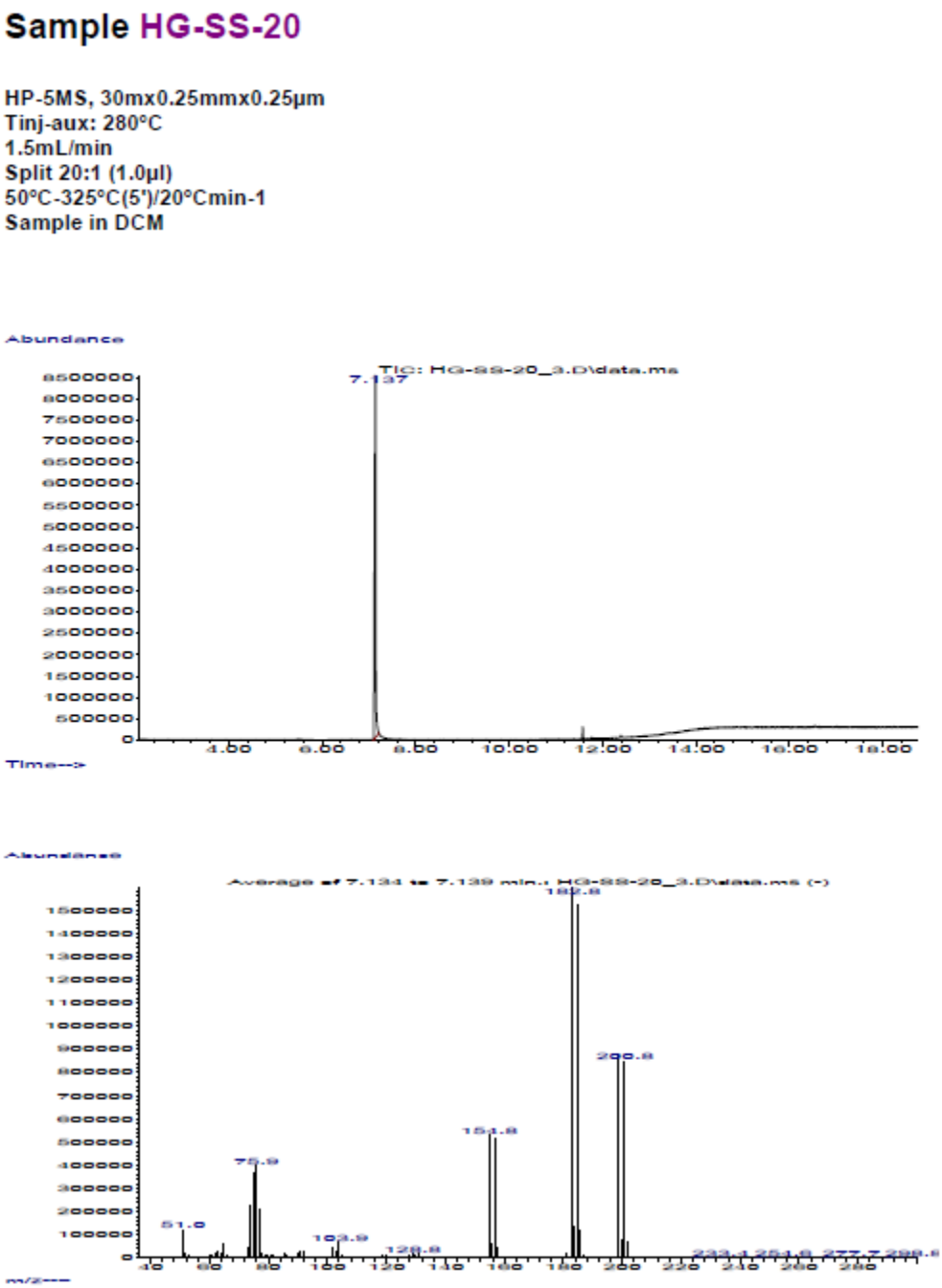
Catalytic hydration 2-bromobenzonitrile (into caboxamide **e**) with $Pt(COD)Cl_2/AgNO_3$/**1** reaction time 1h

Yield: 88%.



Isolation of 2-bromobenzamide (e) (Scheme 4, $Pt(COD)Cl_2/AgNO_3$/1 system)

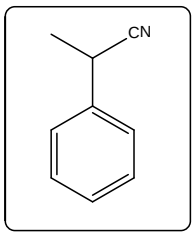
The product was isolated by column chromatography using a silica column and DCM:EtOH eluent mixture (v/v 10/1). Yield: 87 mg (87%). CAS: 4001-73-4.

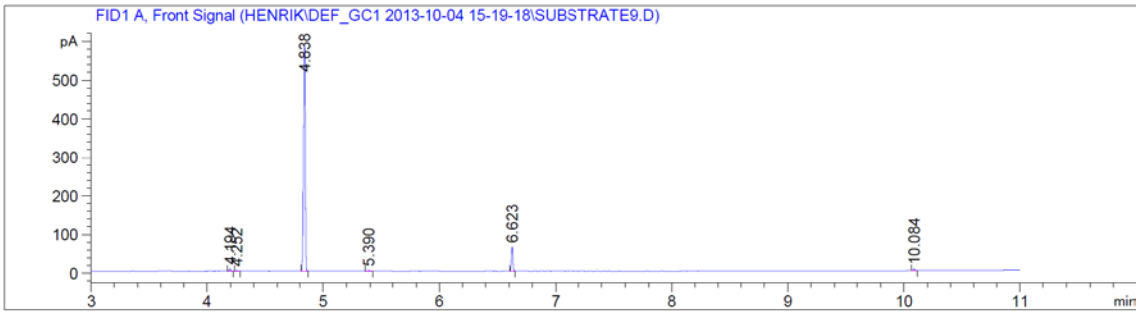


2-PHENYLPROPANENITRILE

GC analysis of the 2-phenylpropanenitrile substrate

RT in THF: 4.838 min

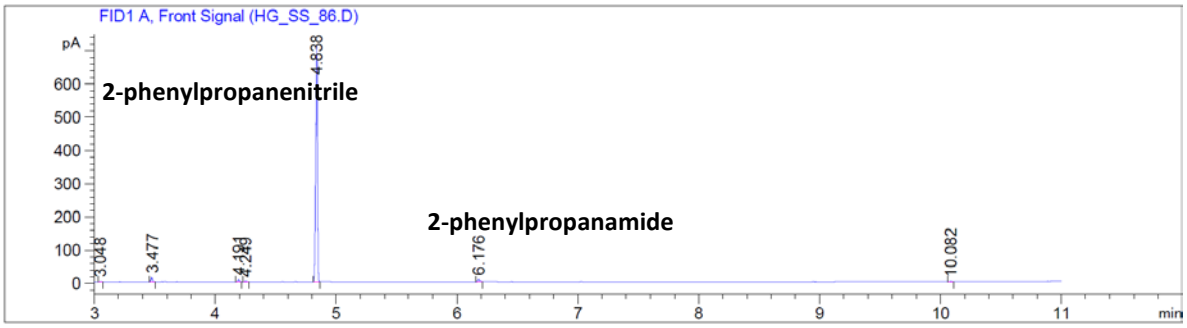




GC analysis of the reaction mixtures of the catalytic reactions

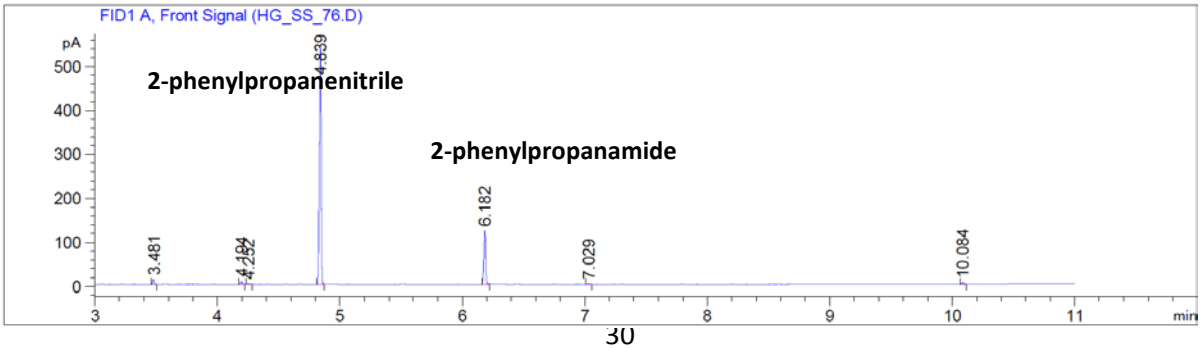
Catalytic hydration of 2-phenylpropanenitrile into 2-phenylpropanamide (**k**) with Pt(COD)Cl_2/**1**, reaction time 2h

Yield: 1.4%.



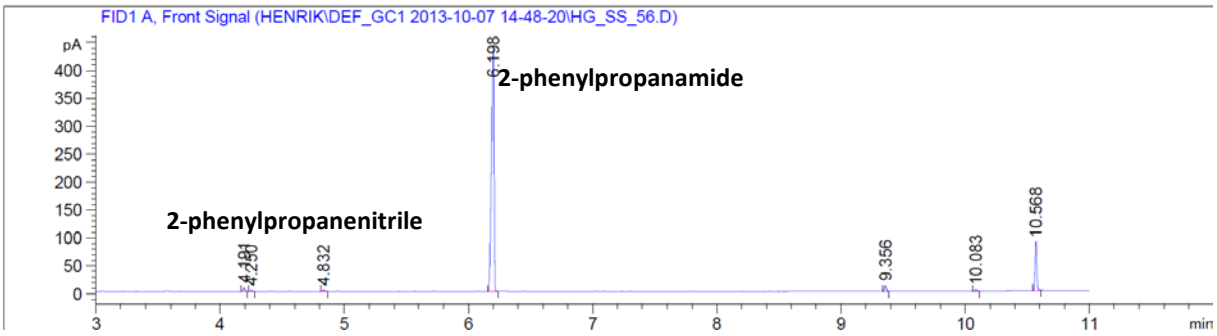
Catalytic hydration of 2-phenylpropanenitrile into 2-phenylpropanamide (**k**) with Pt(COD)Cl_2/**1**, reaction time 24h

Yield: 19%.



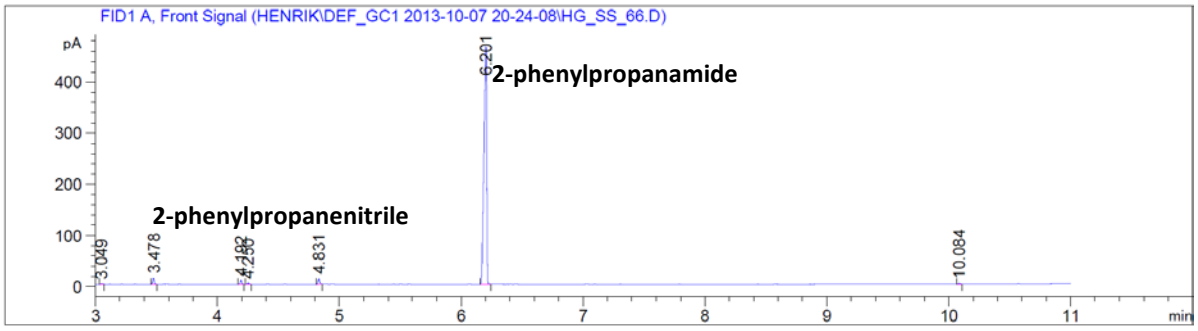
Catalytic hydration of 2-phenylpropanenitrile into 2-phenylpropanamide (**k**) with $Pt(PPh_3)_4$/**1**, reaction time 1h

Yield: >99%.



Catalytic hydration 2-phenylpropionitrile (into caboxamide **k**) with $Pt(COD)Cl_2/AgNO_3$/**1**, reaction time 1h

Yield: 99%.

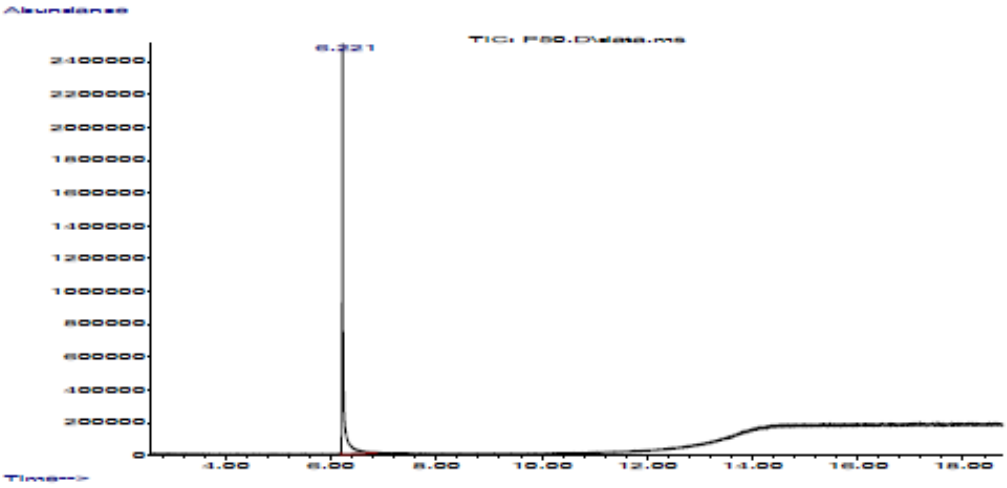


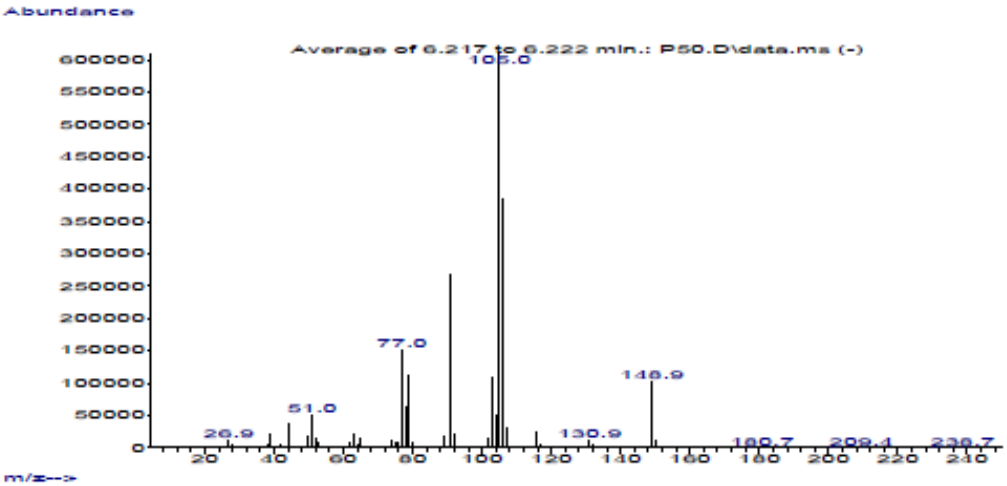
Isolation of 2-phenylpropanamide (k) (Scheme 4, $Pt(COD)Cl_2/AgNO_3$/1 system)

The product was isolated on a chromatotron (centrifugal thin-layer chromatography) using a DCM:EtOH eluent mixture (v/v 10/1). Yield: 75 mg (quantitative). CAS: 1125-70-8.

Sample P50

HP-5MS, 30mx0.25mmx0.25µm
Tinj-aux: 280°C
1.5mL/min
Split 100:1 (1µl)
50°C-325°C(10')/20°Cmin-1
Sample as received





12. X-ray structures of 4-bromobenzamide (c), 3-bromobenzamide (d) and 2-bromobenzamide (e)

X-ray structure of 4-bromobenzamide (c)

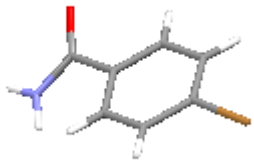


Table 1. Crystal data and structure refinement for 4-bromobenzamide (**c**)

Identification code	HG483_0m	
Empirical formula	C7 H6 Br N O	
Formula weight	200.04	
Temperature	100(2) K	
Wavelength	0.71073 Ĺ	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 4.9200(7) Ĺ	α= 90.00 °.
	b = 5.3316(8) Ĺ	β = 93.562(6) °.
	c = 27.538(5) Ĺ	γ = 90.00 °.
Volume	720.97(19) Ĺ^3	
Z	4	
Density (calculated)	1.843 Mg/m^3	
Absorption coefficient	5.624 mm^{-1}	
F(000)	392	
Crystal size	0.40 x 0.40 x 0.15 mm^3	
Theta range for data collection	1.48 to1.48 °.	
Index ranges	-7 <=h<=7 ,-8 <=k<=8 ,-43 <=l<=43	
Reflections collected	3157	
Independent reflections	2791 [R(int) = 0.0639]	
Completeness to theta =35.18 °	0.982 %	
Absorption correction	Empirical	
Max. and min. transmission	0.4859 and 0.2119	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3157 / 0 / 91	
Goodness-of-fit on F^2	1.080	

Final R indices [I>2sigma(I)]	R1 = 0.0387 , wR2 = 0.1026
R indices (all data)	R1 = 0.0439 , wR2 = 0.1057
Largest diff. peak and hole	1.820 and -1.372 e.Ĺ$^{-3}$

Table 2. Bond lengths [Ĺ] and angles [°] for 4-bromobenzamide (**c**)

Bond lengths----	
Br1-C1	1.8961(15)
C1-C2	1.384(2)
C1-C6	1.389(2)
C4-C3	1.389(2)
C4-C5	1.3986(19)
C4-C7	1.491(2)
C2-C3	1.397(2)
C5-C6	1.386(2)
C7-O1	1.2454(15)
C7-N1	1.3419(17)
Angles----------	
C2-C1-C6	121.82(14)
C2-C1-Br1	120.29(12)
C6-C1-Br1	117.88(11)
C3-C4-C5	119.09(14)
C3-C4-C7	119.61(12)
C5-C4-C7	121.31(12)
C1-C2-C3	118.91(14)
C6-C5-C4	121.16(13)
C5-C6-C1	118.45(13)
C4-C3-C2	120.54(14)
O1-C7-N1	121.99(14)
O1-C7-C4	121.44(12)
N1-C7-C4	116.57(11)

Table 3. Torsion angles [°] for 4-bromobenzamide (**c**)

C6-C1-C2-C3	0.0(2)
Br1-C1-C2-C3	178.97(12)
C3-C4-C5-C6	-0.8(2)
C7-C4-C5-C6	179.01(14)
C4-C5-C6-C1	-0.9(2)
C2-C1-C6-C5	1.3(2)
Br1-C1-C6-C5	-177.76(12)
C5-C4-C3-C2	2.0(2)
C7-C4-C3-C2	-177.75(14)
C1-C2-C3-C4	-1.6(2)
C3-C4-C7-O1	-25.9(2)
C5-C4-C7-O1	154.37(15)
C3-C4-C7-N1	154.48(15)
C5-C4-C7-N1	-25.3(2)

X-ray structure of 3-bromobenzamide (d)

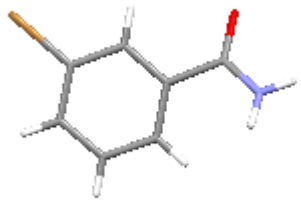


Table 1. Crystal data and structure refinement for 3-bromobenzamide (**d**)

Identification code	HG_SS16	
Empirical formula	C7 H6 Br N O	
Formula weight	200.04	
Temperature	100(2) K	
Wavelength	0.71073 Ĺ	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.189(2)Ĺ	α= 90°.
	b = 4.6448(7)Ĺ	β = 92.866(5)°.
	c = 9.8821(17)Ĺ	γ = 90°.

Volume	742.2(2) Ĺ^3
Z	4
Density (calculated)	1.790 Mg/m^3
Absorption coefficient	5.463 mm^{-1}
F(000)	392
Crystal size	0.25 x 0.25 x 0.04 mm^3
Theta range for data collection	1.259 to 30.536°.
Index ranges	-22<=h<=11,-6<=k<=2,-8<=l<=13
Reflections collected	3504
Independent reflections	1998[R(int) = 0.0448]
Completeness to theta =30.536°	87.6%
Absorption correction	Empirical
Max. and min. transmission	0.811 and 0.624
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1998/ 0/ 91
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0524, wR2 = 0.1469
R indices (all data)	R1 = 0.0660, wR2 = 0.1579
Largest diff. peak and hole	1.139 and -1.341 e.Ĺ$^{-3}$

Table 2. Bond lengths [Ĺ] and angles [°] for 3-bromobenzamide (**d**)

Bond lengths----	
Br1-C5	1.899(4)
N1-C7	1.329(5)
O1-C7	1.246(4)
C1-C2	1.392(5)
C1-C6	1.392(5)
C1-C7	1.504(5)
C2-C3	1.397(6)
C3-C4	1.379(6)
C4-C5	1.391(5)
C5-C6	1.400(5)
Angles----------	
C2-C1-C6	120.3(3)
C2-C1-C7	122.4(3)

C6-C1-C7	117.3(3)
C1-C2-C3	119.8(4)
C4-C3-C2	121.0(4)
C3-C4-C5	118.6(4)
C4-C5-C6	121.8(4)
C4-C5-Br1	119.4(3)
C6-C5-Br1	118.8(3)
C1-C6-C5	118.5(3)
O1-C7-N1	122.8(4)
O1-C7-C1	120.3(3)
N1-C7-C1	116.9(3)

Table 3. Torsion angles [°] for 3-bromobenzamide (**d**)

C6-C1-C2-C3	-0.3(5)
C7-C1-C2-C3	178.0(3)
C1-C2-C3-C4	-0.8(6)
C2-C3-C4-C5	0.6(6)
C3-C4-C5-C6	0.7(5)
C3-C4-C5-Br1	-178.7(3)
C2-C1-C6-C5	1.5(5)
C7-C1-C6-C5	-176.8(3)
C4-C5-C6-C1	-1.7(5)
Br1-C5-C6-C1	177.7(3)
C2-C1-C7-O1	153.9(3)
C6-C1-C7-O1	-27.8(5)
C2-C1-C7-N1	-27.8(5)
C6-C1-C7-N1	150.5(3)

X-ray structure of 2-bromobenzamide (e)

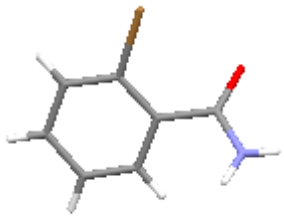


Table 1. Crystal data and structure refinement for 2-bromobenzamide (**e**)

Identification code	HG_SS20_0m	
Empirical formula	C7 H6 Br N O	
Formula weight	200.04	
Temperature	100(2) K	
Wavelength	0.71073 Ĺ	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 5.0263(6)Ĺ	α= 90°.
	b = 10.9683(15)Ĺ	β = 93.465(3)°.
	c = 13.3113(14)Ĺ	γ = 90°.
Volume	732.51(15) Ĺ^3	
Z	4	
Density (calculated)	1.814 Mg/m^3	
Absorption coefficient	5.535 mm^{-1}	
F(000)	392	
Crystal size	0.35 x 0.05 x 0.05 mm^3	
Theta range for data collection	2.408 to 31.971°.	
Index ranges	-7<=h<=2,-4<=k<=11,-17<=l<=8	
Reflections collected	1110	
Independent reflections	980[R(int) = 0.0073]	
Completeness to theta =31.971°	38.600002%	
Absorption correction	Empirical	
Max. and min. transmission	0.769 and 0.626	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	980/ 0/ 91	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0197, wR2 = 0.0499	
R indices (all data)	R1 = 0.0227, wR2 = 0.0512	
Largest diff. peak and hole	0.247 and -0.214 e.Ĺ$^{-3}$	

Table 2. Bond lengths [Ĺ] and angles [°] for 2-bromobenzamide (**e**)

Bond lengths----	
Br1-C3	1.903(3)
N1-C1	1.336(2)
O1-C1	1.238(3)
C1-C2	1.492(4)
C2-C7	1.387(4)
C2-C3	1.407(3)
C3-C4	1.387(4)
C4-C5	1.377(5)
C5-C6	1.398(4)
C6-C7	1.380(4)
Angles----------	
O1-C1-N1	121.8(3)
O1-C1-C2	122.10(18)
N1-C1-C2	116.1(2)
C7-C2-C3	117.7(3)
C7-C2-C1	119.6(2)
C3-C2-C1	122.6(2)
C4-C3-C2	121.0(3)
C4-C3-Br1	117.7(2)
C2-C3-Br1	121.2(2)
C5-C4-C3	119.7(2)
C4-C5-C6	120.4(3)
C7-C6-C5	119.2(3)
C6-C7-C2	121.8(2)

Table 3. Torsion angles [°] for 2-bromobenzamide (**e**)

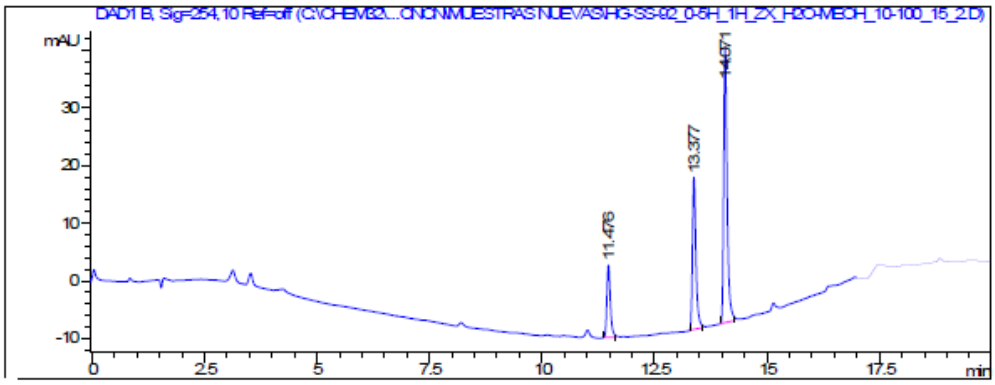
O1-C1-C2-C7	137.3(3)
N1-C1-C2-C7	-41.4(4)
O1-C1-C2-C3	-44.0(4)
N1-C1-C2-C3	137.3(3)
C7-C2-C3-C4	-3.3(4)
C1-C2-C3-C4	177.9(3)
C7-C2-C3-Br1	173.0(2)
C1-C2-C3-Br1	-5.7(4)
C2-C3-C4-C5	2.7(4)
Br1-C3-C4-C5	-173.8(2)
C3-C4-C5-C6	-1.1(5)
C4-C5-C6-C7	0.3(5)
C5-C6-C7-C2	-1.1(5)
C3-C2-C7-C6	2.6(4)
C1-C2-C7-C6	-178.7(3)

13. Kinetic resolution in the hydration of [1,1'-binaphthalene]-2,2'-dicarbonitrile using the $Pt(PPh_3)_4$/1 and $Pt(COD)Cl_2/AgNO_3$/1 catalytic systems

Catalytic hydration of [1,1'-binaphthalene]-2,2'-dicarbonitrile with $Pt(PPh_3)_4$/1, reaction time 0.5h

HPLC, reversed phase. Conversion: 45%; yield of the enantioenriched dicarbonitrile (**2**): 55%; yield of the monoamide (**3**): 30%; yield of the diamide (**4**): 15%.

```
Data File C:\CHEM32\...\ZX\CNCN\MUESTRAS NUEVAS\HG-SS-92_0-5H_1H_ZX_H2O-MEOH_10-100_15_2.D
Sample Name: HG-SS-92_0-5h

==========================================================================
Acq. Operator   : LFG                          Seq. Line :   3
Acq. Instrument : Instrument 1                  Location : Vial 14
Injection Date  : 12/11/2013 10:32:29 AM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\1\METHODS\APCI.M
Last changed    : 12/10/2013 6:53:34 PM by LFG
Analysis Method : C:\CHEM32\1\METHODS\END.M
Last changed    : 12/20/2013 4:38:19 PM by s
                  (modified after loading)
Sample Info     : Zorbax XDB C18 100x4.6mm, 5µm
                  H2O/ MeOH 90:10
                  10% up to 100% in 15', hold 5'
                  APCI +
                  Samplein 100µL DCM
```

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

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


Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.476 BB    0.0828   67.55444   12.54962  14.5712
   2  13.377 BB    0.0826  141.63557   26.41323  30.5502
   3  14.071 BB    0.0799  254.42584   47.97517  54.8786

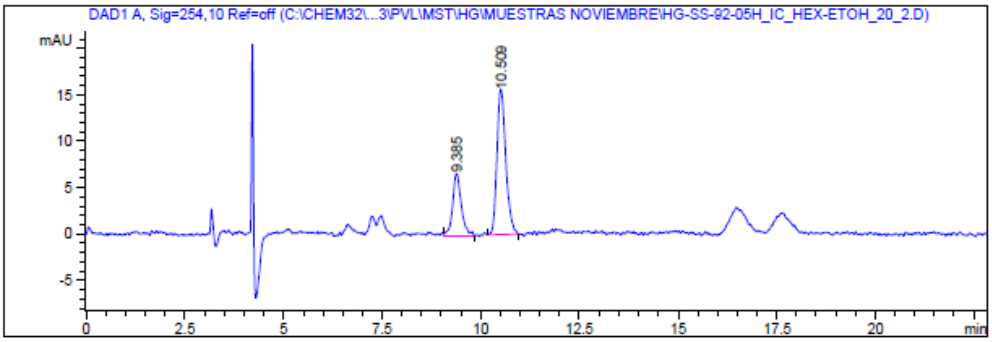
Totals :                   463.61586   86.93802

==========================================================================
                        *** End of Report ***
```

Chiral HPLC, normal phase. E.r. of the enantioenriched dicarbonitrile (**2**): 71/29.

```
Data File C:\CHEM32\...\2013\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-92-05H_IC_HEX-ETOH_20_2.D
Sample Name: HG-SS-92-05H

======================================================================
Acq. Operator   : sc                              Seq. Line :   1
Acq. Instrument : Instrument 2                    Location : Vial 1
Injection Date  : 12/20/2013 4:08:22 PM               Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC1.M
Last changed    : 12/20/2013 4:31:20 PM by sc
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC1.M
Last changed    : 12/20/2013 5:05:58 PM by sc
                  (modified after loading)
Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                  Hex / EtOH 80:20
                  1 mL/min
                  25°C
                  Sample: in 100µL DCM
```

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

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


Signal 1: DAD1 A, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.385 BB    0.2481  101.05391   6.40451  29.2756
   2  10.509 BB    0.2507  244.12706  15.25613  70.7244

Totals :                   345.18097  21.66065
```
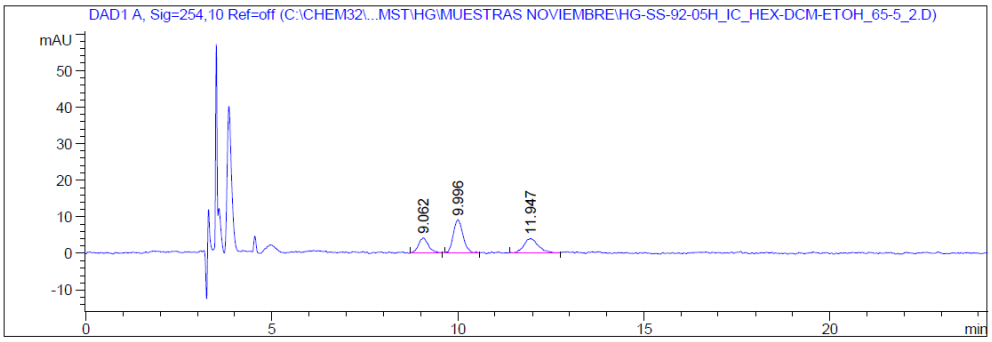

Chiral HPLC, normal phase. E.r. of the monoamide (**3**): 32/68; e.r. of the diamide (**4**): >99/1.

```
Data File C:\CHEM32\...PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-92-05H_IC_HEX-DCM-ETOH_65-5_2.D
Sample Name: HG-SS-92-05H

    ======================================================================
    Acq. Operator    : sc                          Seq. Line :   2
    Acq. Instrument : Instrument 2                  Location : Vial 1
    Injection Date  : 12/20/2013 4:42:41 PM              Inj :   1
                                                  Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC2.M
    Last changed    : 11/22/2013 4:44:10 PM by MH
    Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC1.M
    Last changed    : 12/20/2013 5:05:58 PM by sc
                      (modified after loading)
    Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                      Hex / DCM / EtOH 30:65:5
                      1 mL/min
                      25°C
                      Sample: as received
```

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

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


    Signal 1: DAD1 A, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.062 BB    0.2841   76.55771    4.05778  22.0678
       2   9.996 BB    0.2951  164.66672    8.93102  47.4652
       3  11.947 BB    0.4149  105.69659    3.86704  30.4670

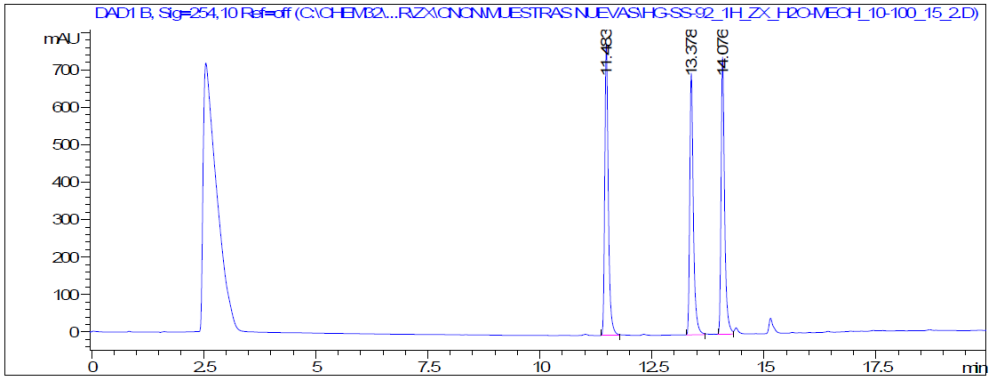
    Totals :                   346.92102   16.85584
```

Catalytic hydration of [1,1'-binaphthalene]-2,2'-dicarbonitrile with $Pt(PPh_3)_4$/1, reaction time 1h

HPLC, reversed phase. Conversion: 67%; yield of the enantioenriched dicarbonitrile (**2**): 33%; yield of the monoamide (**3**): 32%; yield of the diamide (**4**): 35%.

```
Data File C:\CHEM32\...-CNER\ZX\CNCN\MUESTRAS NUEVAS\HG-SS-92_1H_ZX_H2O-MEOH_10-100_15_2.D
Sample Name: HG-SS-92_1h

==========================================================================
Acq. Operator   : LFG                          Seq. Line :   4
Acq. Instrument : Instrument 1                  Location : Vial 15
Injection Date  : 12/11/2013 10:57:31 AM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\1\METHODS\APCI.M
Last changed    : 12/10/2013 6:53:34 PM by LFG
Analysis Method : C:\CHEM32\1\METHODS\END.M
Last changed    : 12/19/2013 11:26:23 AM by LFG
                  (modified after loading)
Sample Info     : Zorbax XDB C18 100x4.6mm, 5µm
                  H2O/ MeOH 90:10
                  10% up to 100% in 15', hold 5'
                  APCI +
                  Sample as received
```

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

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


Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  11.483 BB    0.0846 4295.11084  776.11755  35.1106
   2  13.378 BB    0.0830 3899.77026  699.96521  31.8789
   3  14.076 BV    0.0816 4038.20044  740.63208  33.0105

Totals :                  1.22331e4  2216.71484

==========================================================================
                        *** End of Report ***
```
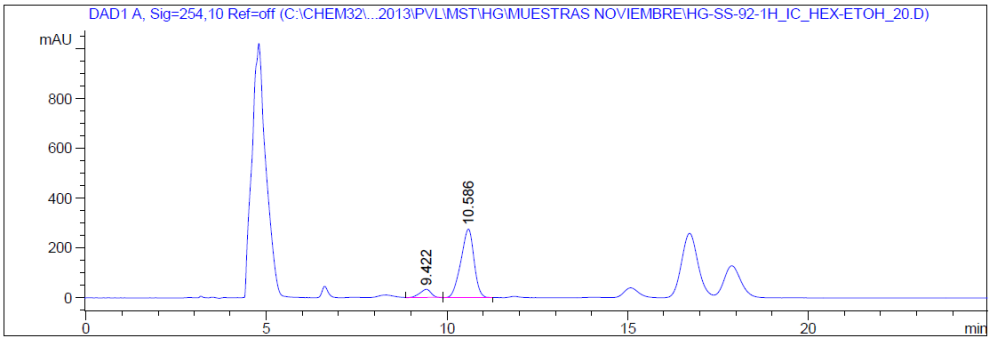

Chiral HPLC, normal phase. E.r. of the enantioenriched dicarbonitrile (**2**): 10/90.

```
Data File C:\CHEM32\...127\2013\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-92-1H_IC_HEX-ETOH_20.D
Sample Name: HG-SS-92-1H

======================================================================
Acq. Operator   : sc                          Seq. Line :   7
Acq. Instrument : Instrument 2                 Location : Vial 6
Injection Date  : 11/26/2013 2:08:39 PM             Inj :   1
                                              Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC1.M
Last changed    : 11/22/2013 4:40:02 PM by MH
Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
Last changed    : 12/19/2013 10:58:05 AM by sc
                  (modified after loading)
Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                  Hex / EtOH 80:20
                  1 mL/min
                  25°C
                  Sample: as received
```

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

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


Signal 1: DAD1 A, Sig=254,10 Ref=off

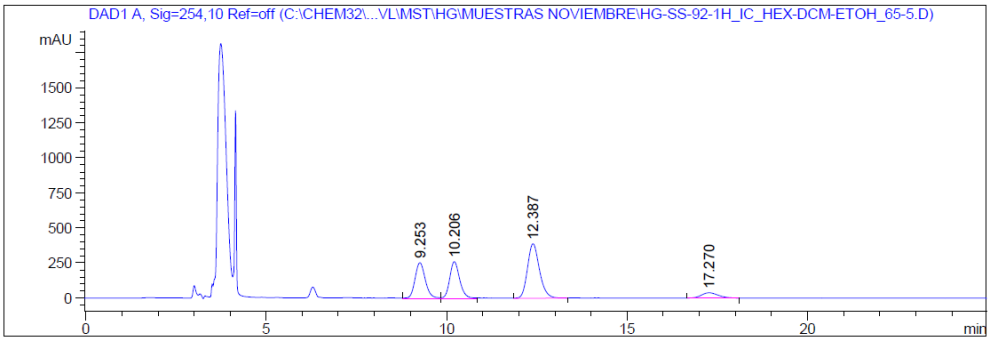
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.422 VV    0.3210  747.02631   33.64717   9.6951
   2  10.586 VB    0.3727 6958.15723  275.45242  90.3049

Totals :                  7705.18353  309.09960
```

Chiral HPLC, normal phase. E.r. of the monoamide (**3**): 50/50; e.r. of the diamide (**4**): 86/14.

```
Data File C:\CHEM32\...13\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-92-1H_IC_HEX-DCM-ETOH_65-5.D
Sample Name: HG-SS-92-1H

    ======================================================================
    Acq. Operator   : sc                          Seq. Line :  16
    Acq. Instrument : Instrument 2                 Location : Vial 6
    Injection Date  : 11/26/2013 6:05:05 PM             Inj :  1
                                                  Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC2.M
    Last changed    : 11/22/2013 4:44:10 PM by MH
    Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
    Last changed    : 12/19/2013 11:19:28 AM by sc
                      (modified after loading)
    Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                      Hex / DCM / EtOH 30:65:5
                      1 mL/min
                      25°C
                      Sample: as received
```

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

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


    Signal 1: DAD1 A, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.253 VV    0.3081 5136.05615  256.00064  24.6276
       2  10.206 VV    0.2960 5099.90234  263.21988  24.4542
       3  12.387 VV    0.3583 9192.74219  390.92609  44.0795
       4  17.270 VV    0.4710 1426.19421   40.28499   6.8387

    Totals :                  2.08549e4   950.43159
```
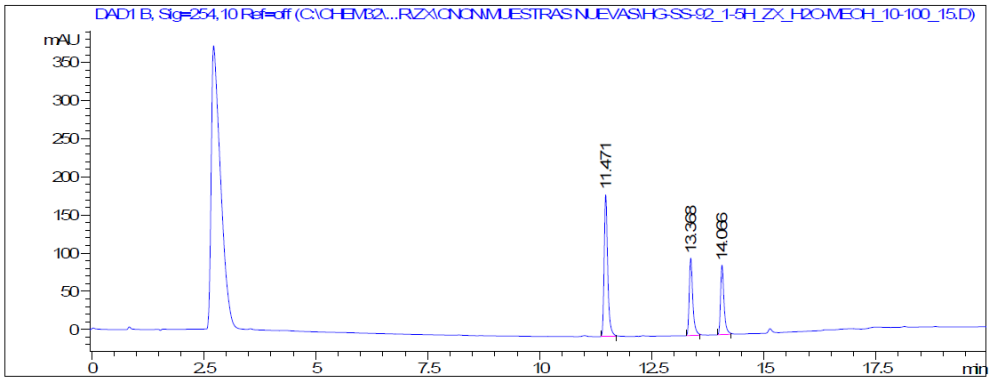

Catalytic hydration of [1,1'-binaphthalene]-2,2'-dicarbonitrile with $Pt(PPh_3)_4$/1, reaction time 1.5h

HPLC, reversed phase. Conversion: 77%; yield of the enantioenriched dicarbonitrile (**2**): 23%; yield of the monoamide (**3**): 27%; yield of the diamide (**4**): 50%.

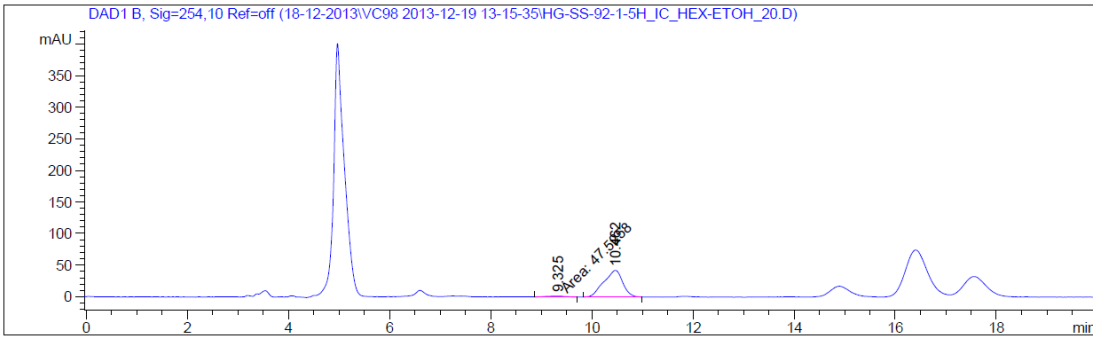
```
Data File C:\CHEM32\...-CNER\ZX\CNCN\MUESTRAS NUEVAS\HG-SS-92_1-5H_ZX_H2O-MEOH_10-100_15.D
Sample Name: HG-SS-92_1-5h

==========================================================================
Acq. Operator   : LFG                          Seq. Line :   8
Acq. Instrument : Instrument 1                  Location : Vial 23
Injection Date  : 12/11/2013 12:37:39 PM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\1\METHODS\APCI.M
Last changed    : 12/10/2013 6:53:34 PM by LFG
Analysis Method : C:\CHEM32\1\METHODS\END.M
Last changed    : 12/19/2013 11:26:23 AM by LFG
                  (modified after loading)
Sample Info     : Zorbax XDB C18 100x4.6mm, 5µm
                  H2O/ MeOH 90:10
                  10% up to 100% in 15', hold 5'
                  APCI +
                  Sample as received
```




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

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


Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  11.471 BB    0.0842 1022.19702  185.81451  49.5068
   2  13.368 BB    0.0841  557.47748  101.39591  26.9996
   3  14.066 BB    0.0801  485.08466   91.19616  23.4935

Totals :                  2064.75916  378.40659

==========================================================================
                        *** End of Report ***
```

Chiral HPLC, normal phase. E.r. of the enantioenriched dicarbonitrile (**2**): 96/4.

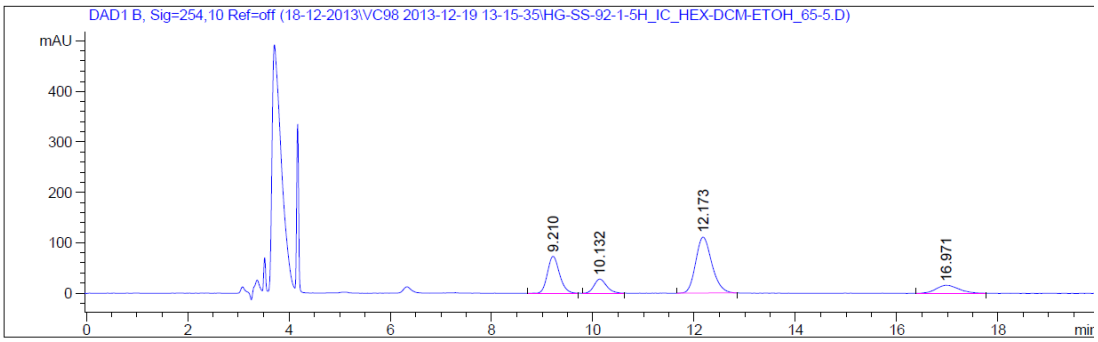
```
Data File C:\CHEM32\...\18-12-2013\VC98 2013-12-19 13-15-35\HG-SS-92-1-5H_IC_HEX-ETOH_20.D
Sample Name: HG-SS-92-1-5h

    ======================================================================
    Acq. Operator   : sc                          Seq. Line :   4
    Acq. Instrument : Instrument 1                 Location : Vial 5
    Injection Date  : 12/19/2013 2:21:02 PM             Inj :   1
                                                  Inj Volume : 5 µl
    Acq. Method     : C:\Chem32\1\DATA\18-12-2013\VC98 2013-12-19 13-15-35\CHIRAL IC.M
    Last changed    : 12/19/2013 12:56:18 PM by sc
    Analysis Method : C:\CHEM32\1\METHODS\CHIRAL IC2.M
    Last changed    : 12/19/2013 3:56:58 PM by sc
                      (modified after loading)
    Sample Info     : Chiralpak IC 250x4.6mm, 5µm
                      Hex / EtOH 80:20
                      1mL/min
                      25°C
                      sample as received
```




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

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


    Signal 1: DAD1 B, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.325 MM    0.4746   47.52580    1.66903   4.1216
       2  10.462 BV    0.3682 1105.56458   42.40327  95.8784

    Totals :                  1153.09037   44.07230
```

Chiral HPLC, normal phase. E.r. of the monoamide (**3**): 72/28; e.r. of the diamide (**4**): 83/17.

```
Data File C:\CHEM32\...-2013\VC98 2013-12-19 13-15-35\HG-SS-92-1-5H_IC_HEX-DCM-ETOH_65-5.D
Sample Name: HG-SS-92-1-5h

    ======================================================================
    Acq. Operator   : sc                              Seq. Line :  10
    Acq. Instrument : Instrument 1                     Location : Vial 5
    Injection Date  : 12/19/2013 4:28:59 PM                 Inj :   1
                                                    Inj Volume : 5 µl
    Acq. Method     : C:\Chem32\1\DATA\18-12-2013\VC98 2013-12-19 13-15-35\CHIRAL IC2.M
    Last changed    : 12/19/2013 12:57:54 PM by sc
    Analysis Method : C:\CHEM32\1\METHODS\CHIRAL IC2.M
    Last changed    : 12/19/2013 3:56:58 PM by sc
                      (modified after loading)
    Sample Info     : Chiralpak IC 250x4.6mm, 5µm
                      Hex / DCM / EtOH 30:65:5
                      1mL/min
                      25°C
                      sample as received
```



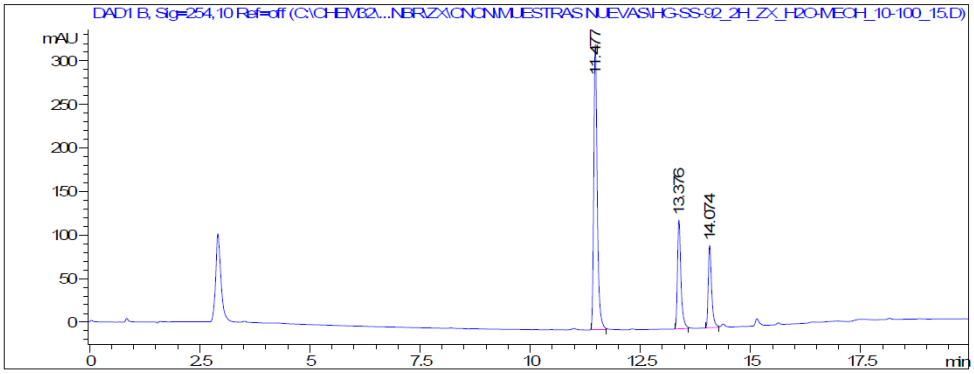

```
    ======================================================================
                              Area Percent Report
    ======================================================================

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


    Signal 1: DAD1 B, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.210 VB    0.2499 1217.86023   73.27901  25.9517
       2  10.132 BB    0.2564  488.28006   28.14875  10.4049
       3  12.173 BB    0.3379 2476.42358  111.15575  52.7708
       4  16.971 VB    0.3899  510.22571   16.18047  10.8725

    Totals :                  4692.78958  228.76398
```

Catalytic hydration of [1,1'-binaphthalene]-2,2'-dicarbonitrile with $Pt(PPh_3)_4$/1, reaction time 2h

HPLC, reversed phase. Conversion: 83%; yield of the enantioenriched dicarbonitrile (**2**): 17%; yield of the monoamide (**3**): 23%; yield of the diamide (**4**): 60%.

Data File C:\CHEM32\...CN-CNBR\ZX\CNCN\MUESTRAS NUEVAS\HG-SS-92_2H_ZX_H2O-MEOH_10-100_15.D
Sample Name: HG-SS-92_2h

Acq. Operator	: LFG	Seq. Line	: 9
Acq. Instrument	: Instrument 1	Location	: Vial 24
Injection Date	: 12/11/2013 1:02:41 PM	Inj	: 1
		Inj Volume	: 5 µl
Acq. Method	: C:\CHEM32\1\METHODS\APCI.M		
Last changed	: 12/10/2013 6:53:34 PM by LFG		
Analysis Method	: C:\CHEM32\1\METHODS\END.M		
Last changed	: 12/19/2013 11:26:23 AM by LFG (modified after loading)		
Sample Info	: Zorbax XDB C18 100x4.6mm, 5µm H2O/ MeOH 90:10 10% up to 100% in 15', hold 5' APCI + Sample as received		



Area Percent Report

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

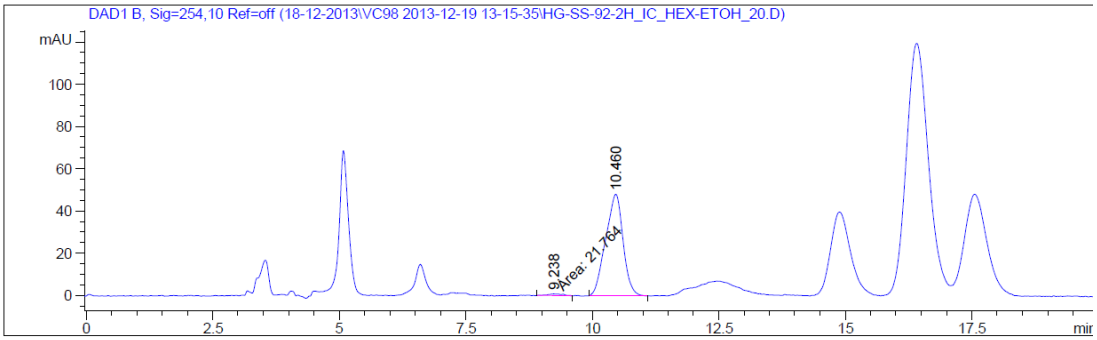
Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.477	BB	0.0841	1803.32397	328.03119	60.2039
2	13.376	BB	0.0842	689.61877	125.32379	23.0229
3	14.074	BB	0.0800	502.41931	94.59338	16.7732
Totals :				2995.36206	547.94836	

*** End of Report ***

Chiral HPLC, normal phase. E.r. of the enantioenriched dicarbonitrile (**2**): 2/98.

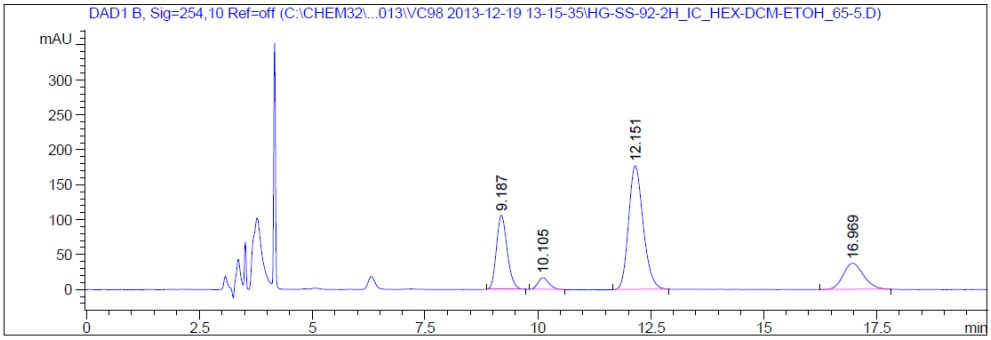
```
Data File C:\CHEM32\...TA\18-12-2013\VC98 2013-12-19 13-15-35\HG-SS-92-2H_IC_HEX-ETOH_20.D
Sample Name: HG-SS-92-2h

    ======================================================================
    Acq. Operator   : sc                          Seq. Line :   5
    Acq. Instrument : Instrument 1                 Location : Vial 6
    Injection Date  : 12/19/2013 2:42:24 PM             Inj :   1
                                                  Inj Volume : 5 µl
    Acq. Method     : C:\Chem32\1\DATA\18-12-2013\VC98 2013-12-19 13-15-35\CHIRAL IC.M
    Last changed    : 12/19/2013 12:56:18 PM by sc
    Analysis Method : C:\CHEM32\1\METHODS\CHIRAL IC2.M
    Last changed    : 12/19/2013 3:56:58 PM by sc
                      (modified after loading)
    Sample Info     : Chiralpak IC 250x4.6mm, 5µm
                      Hex / EtOH 80:20
                      1mL/min
                      25°C
                      sample as received
```




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

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


    Signal 1: DAD1 B, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.238 MM    0.3978   21.76396 9.11840e-1   1.8569
       2  10.460 BB    0.3392 1150.30652   48.07404  98.1431

    Totals :                  1172.07048   48.98588
```

Chiral HPLC, normal phase. E.r. of the monoamide (**3**): 86/14; e.r. of the diamide (**4**): 76/24.

```
Data File C:\CHEM32\...12-2013\VC98 2013-12-19 13-15-35\HG-SS-92-2H_IC_HEX-DCM-ETOH_65-5.D
Sample Name: HG-SS-92-2h

    ======================================================================
    Acq. Operator    : sc                              Seq. Line :  11
    Acq. Instrument  : Instrument 1                     Location : Vial 6
    Injection Date   : 12/19/2013 4:50:23 PM                 Inj :   1
                                                      Inj Volume : 5 µl
    Acq. Method      : C:\Chem32\1\DATA\18-12-2013\VC98 2013-12-19 13-15-35\CHIRAL IC2.M
    Last changed     : 12/19/2013 12:57:54 PM by sc
    Analysis Method  : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC1.M
    Last changed     : 12/20/2013 5:16:36 PM by sc
                       (modified after loading)
    Sample Info      : Chiralpak IC 250x4.6mm, 5µm
                       Hex / DCM / EtOH 30:65:5
                       1mL/min
                       25°C
                       sample as received
```

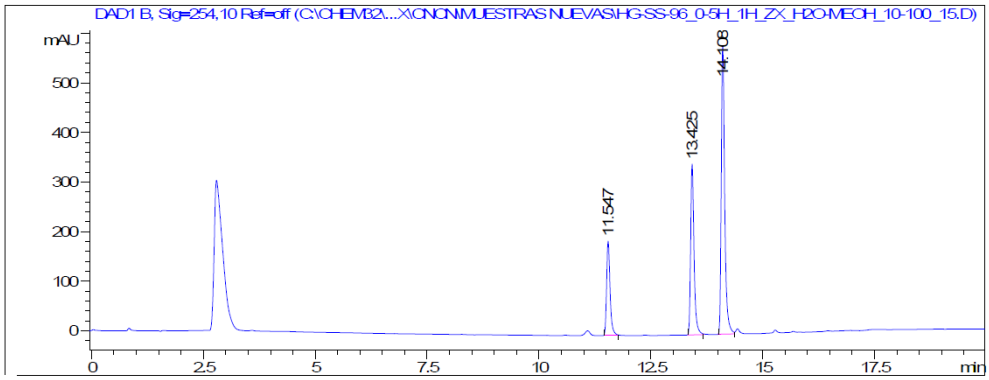



```
    ======================================================================
                              Area Percent Report
    ======================================================================

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


    Signal 1: DAD1 B, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.187 BB    0.2555 1759.92163  106.10857  24.2970
       2  10.105 BB    0.2554  291.90778   16.90764   4.0300
       3  12.151 BB    0.3429 3993.02393  177.20164  55.1265
       4  16.969 VB    0.4233 1198.52576   37.65733  16.5465

    Totals :                  7243.37909  337.87519
```

Catalytic hydration of [1,1'-binaphthalene]-2,2'-dicarbonitrile with $Pt(COD)_2Cl_2/AgNO_3$/1, reaction time 0.5h

HPLC, reversed phase. Conversion: 48%; yield of the enantioenriched dicarbonitrile (**2**): 52%; yield of the monoamide (**3**): 31%; yield of the diamide (**4**): 17%.

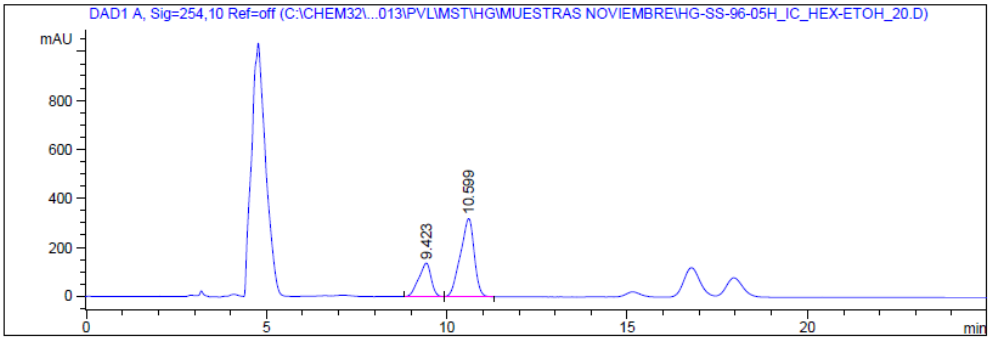
```
Data File C:\CHEM32\...BR\ZX\CNCN\MUESTRAS NUEVAS\HG-SS-96_0-5H_1H_ZX_H2O-MEOH_10-100_15.D
Sample Name: HG-SS-96_0-5h

==========================================================================
Acq. Operator   : LFG                                 Seq. Line :  10
Acq. Instrument : Instrument 1                         Location : Vial 10
Injection Date  : 12/10/2013 11:00:48 PM                    Inj :  1
                                                    Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\1\METHODS\APCI.M
Last changed    : 12/10/2013 6:53:34 PM by LFG
Analysis Method : C:\CHEM32\1\METHODS\END.M
Last changed    : 12/19/2013 11:26:23 AM by LFG
                  (modified after loading)
Sample Info     : Zorbax XDB C18 100x4.6mm, 5µm
                  H2O/ MeOH 90:10
                  10% up to 100% in 15', hold 5'
                  APCI +
                  Sample as received
```




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

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


Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  11.547 BB    0.0806 1023.40985  190.67078  17.2501
   2  13.425 BB    0.0797 1820.82080  344.44064  30.6909
   3  14.108 BV    0.0796 3088.54883  584.51880  52.0591

Totals :                  5932.77948 1119.63022

==========================================================================
                        *** End of Report ***
```

Chiral HPLC, normal phase. E.r. of the enantioenriched dicarbonitrile (**2**): 28/72.

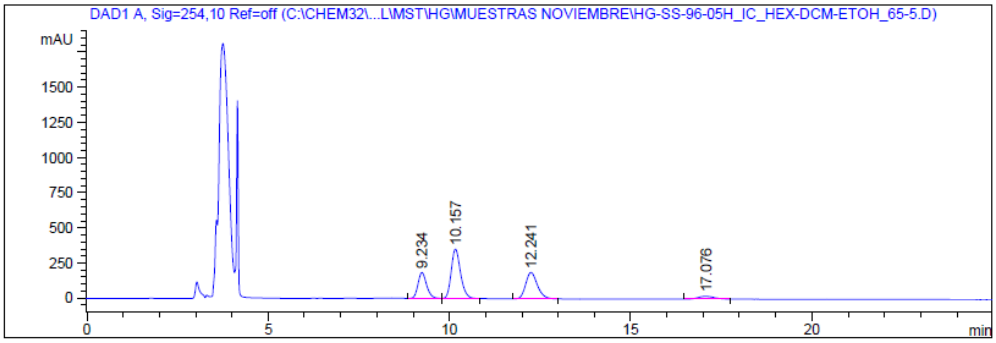
```
Data File C:\CHEM32\...27\2013\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-96-05H_IC_HEX-ETOH_20.D
Sample Name: HG-SS-96-05H

    ========================================================================
    Acq. Operator   : sc                          Seq. Line :   2
    Acq. Instrument : Instrument 2                 Location : Vial 1
    Injection Date  : 11/26/2013 11:57:03 AM            Inj :   1
                                                  Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC1.M
    Last changed    : 11/22/2013 4:40:02 PM by MH
    Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
    Last changed    : 12/19/2013 10:58:05 AM by sc
                      (modified after loading)
    Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                      Hex / EtOH 80:20
                      1 mL/min
                      25°C
                      Sample: as received
```




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

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


    Signal 1: DAD1 A, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.423 BV    0.3416 3281.65430  136.95309  27.8240
       2  10.599 VB    0.3890 8512.66602  319.36984  72.1760

    Totals :                  1.17943e4   456.32294
```

Chiral HPLC, normal phase. E.r. of the monoamide (**3**): 33/67; e.r. of the diamide (**4**): 85/15.

```
Data File C:\CHEM32\...3\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-96-05H_IC_HEX-DCM-ETOH_65-5.D
Sample Name: HG-SS-96-05H

    ======================================================================
    Acq. Operator    : sc                          Seq. Line :  11
    Acq. Instrument  : Instrument 2                 Location : Vial 1
    Injection Date   : 11/26/2013 3:53:24 PM             Inj :   1
                                                  Inj Volume : 5 µl
    Acq. Method      : C:\CHEM32\2\METHODS\CHIRAL IC2.M
    Last changed     : 11/22/2013 4:44:10 PM by MH
    Analysis Method  : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
    Last changed     : 12/19/2013 11:19:28 AM by sc
                       (modified after loading)
    Sample Info      : Chiralpack IC 250x4.6mm, 5µm
                       Hex / DCM / EtOH 30:65:5
                       1 mL/min
                       25°C
                       Sample: as received
```

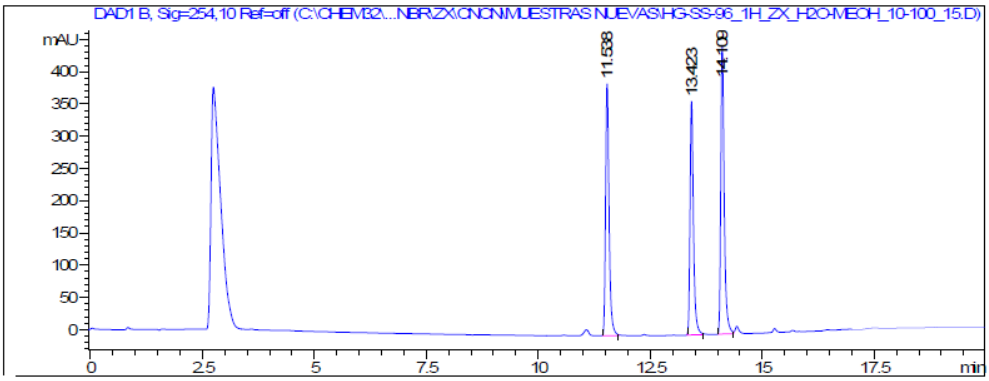



```
    ======================================================================
                            Area Percent Report
    ======================================================================

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


    Signal 1: DAD1 A, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.234 VV    0.2662 3259.55981  188.06247  22.0303
       2  10.157 VV    0.2798 6498.92090  354.57260  43.9241
       3  12.241 VV    0.3489 4331.87354  189.33440  29.2777
       4  17.076 VV    0.4091  705.43457   21.15105   4.7678

    Totals :                  1.47958e4   753.12051
```

Catalytic hydration of [1,1'-binaphthalene]-2,2'-dicarbonitrile with $Pt(COD)_2Cl_2/AgNO_3$/1, reaction time 1h

HPLC, reversed phase. Conversion: 63%; yield of the enantioenriched dicarbonitrile (**2**): 37%; yield of the monoamide (**3**): 30%; yield of the diamide (**4**): 33%.

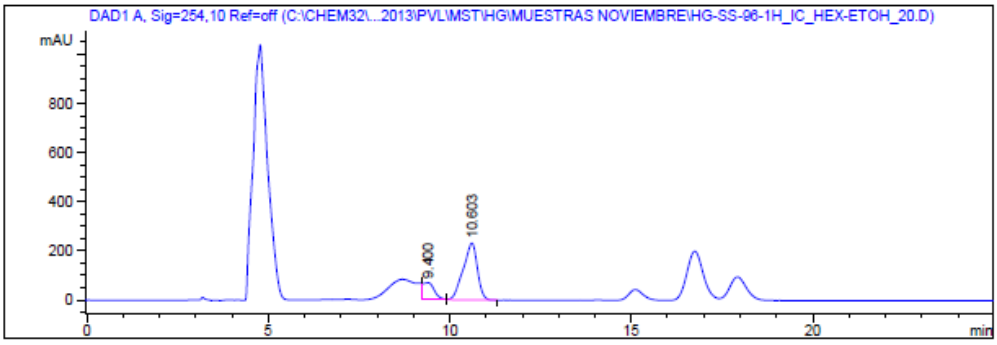
```
Data File C:\CHEM32\...CN-CNBR\ZX\CNCN\MUESTRAS NUEVAS\HG-SS-96_1H_ZX_H2O-MEOH_10-100_15.D
Sample Name: HG-SS-96_1h

==========================================================================
Acq. Operator   : LFG                                 Seq. Line :  11
Acq. Instrument : Instrument 1                         Location : Vial 11
Injection Date  : 12/10/2013 11:25:52 PM                    Inj :  1
                                                    Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\1\METHODS\APCI.M
Last changed    : 12/10/2013 6:53:34 PM by LFG
Analysis Method : C:\CHEM32\1\METHODS\END.M
Last changed    : 12/19/2013 11:26:23 AM by LFG
                  (modified after loading)
Sample Info     : Zorbax XDB C18 100x4.6mm, 5µm
                  H2O/ MeOH 90:10
                  10% up to 100% in 15', hold 5'
                  APCI +
                  Sample as received
```




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

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


Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  11.538 BB    0.0832 2118.43872  391.09674  33.0793
   2  13.423 BB    0.0817 1925.26819  363.74927  30.0629
   3  14.109 BV    0.0793 2360.41699  448.95795  36.8578

Totals :                  6404.12390 1203.80396

==========================================================================
                        *** End of Report ***
```

Chiral HPLC, normal phase. E.r. of the enantioenriched dicarbonitrile (**2**): 19/81.

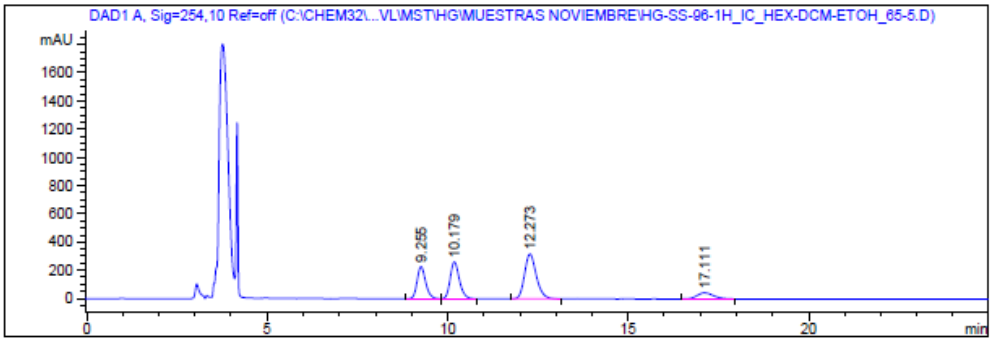
```
Data File C:\CHEM32\...127\2013\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-96-1H_IC_HEX-ETOH_20.D
Sample Name: HG-SS-96-1H

======================================================================
Acq. Operator   : sc                              Seq. Line :   3
Acq. Instrument : Instrument 2                    Location : Vial 2
Injection Date  : 11/26/2013 12:23:20 PM               Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC1.M
Last changed    : 11/22/2013 4:40:02 PM by MH
Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
Last changed    : 12/19/2013 10:58:05 AM by sc
                  (modified after loading)
Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                  Hex / EtOH 80:20
                  1 mL/min
                  25°C
                  Sample: as received
```




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

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


Signal 1: DAD1 A, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.400 VV    0.3116 1487.64771   69.54395  19.0320
   2  10.603 VB    0.4007 6328.91797  231.65947  80.9680

Totals :                  7816.56567  301.20341
```

Chiral HPLC, normal phase. E.r. of the monoamide (**3**): 45/55; e.r. of the diamide (**4**): 84/16.

```
Data File C:\CHEM32\...13\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-96-1H_IC_HEX-DCM-ETOH_65-5.D
Sample Name: HG-SS-96-1H

=====================================================================
Acq. Operator   : sc                              Seq. Line :  12
Acq. Instrument : Instrument 2                    Location : Vial 2
Injection Date  : 11/26/2013 4:19:43 PM                Inj :   1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC2.M
Last changed    : 11/22/2013 4:44:10 PM by MH
Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
Last changed    : 12/19/2013 11:19:28 AM by sc
                  (modified after loading)
Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                  Hex / DCM / EtOH 30:65:5
                  1 mL/min
                  25°C
                  Sample: as received
```

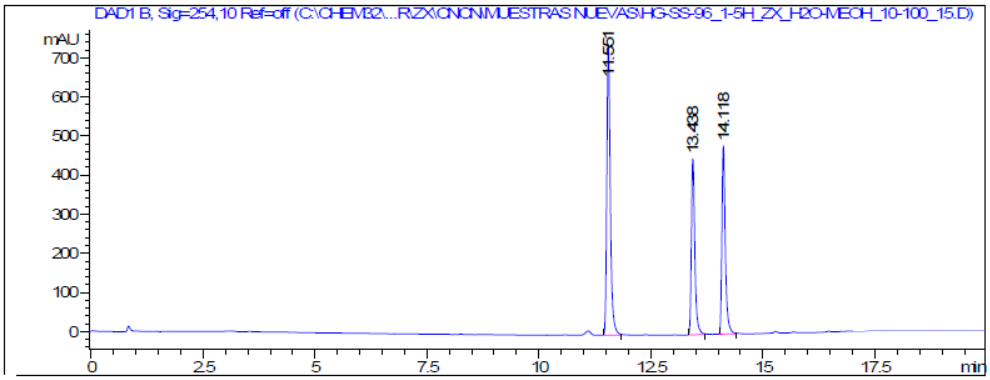



```
=====================================================================
                        Area Percent Report
=====================================================================

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


Signal 1: DAD1 A, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.255 VV    0.2551 3819.77856  228.39145  22.1614
   2  10.179 VV    0.2731 4698.25830  262.18631  27.2581
   3  12.273 VV    0.3457 7263.83691  318.91525  42.1430
   4  17.111 VV    0.4727 1454.30017   44.33474   8.4375

Totals :                 1.72362e4   853.82775
```

Catalytic hydration of [1,1'-binaphthalene]-2,2'-dicarbonitrile with $Pt(COD)_2Cl_2/AgNO_3$/1, reaction time 1.5h

HPLC, reversed phase. Conversion: 72%; yield of the enantioenriched dicarbonitrile (**2**): 28%; yield of the monoamide (**3**): 27%; yield of the diamide (**4**): 45%.

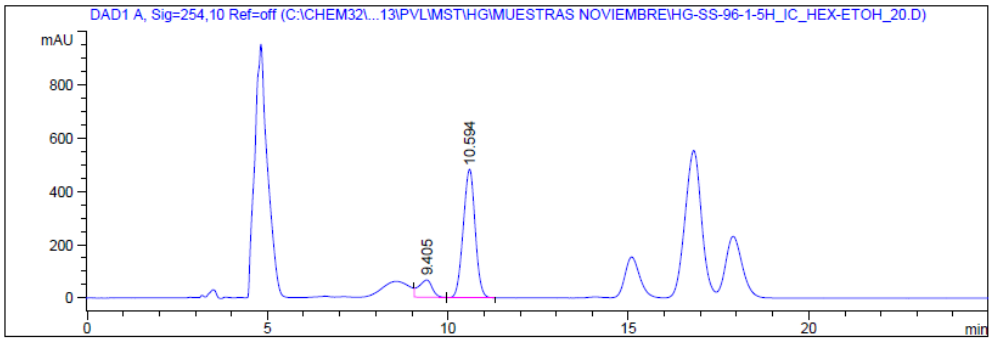
```
Data File C:\CHEM32\...-CNBR\ZX\CNCN\MUESTRAS NUEVAS\HG-SS-96_1-5H_ZX_H2O-MEOH_10-100_15.D
Sample Name: HG-SS-96_1-5h

==========================================================================
Acq. Operator   : LFG                          Seq. Line :  12
Acq. Instrument : Instrument 1                  Location : Vial 12
Injection Date  : 12/10/2013 11:50:54 PM           Inj :  1
                                               Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\1\METHODS\APCI.M
Last changed    : 12/10/2013 6:53:34 PM by LFG
Analysis Method : C:\CHEM32\1\METHODS\END.M
Last changed    : 12/19/2013 11:26:23 AM by LFG
                  (modified after loading)
Sample Info     : Zorbax XDB C18 100x4.6mm, 5µm
                  H2O/ MeOH 90:10
                  10% up to 100% in 15', hold 5'
                  APCI +
                  Sample as received
```




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

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


Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  11.551 BB    0.0819 4066.34106  742.43195  45.0288
   2  13.438 BB    0.0801 2401.93237  450.97620  26.5979
   3  14.118 BB    0.0798 2562.25586  483.50641  28.3733

Totals :                  9030.52930 1676.91455

==========================================================================
                        *** End of Report ***
```

Chiral HPLC, normal phase. E.r. of the enantioenriched dicarbonitrile (**2**): 14/86.

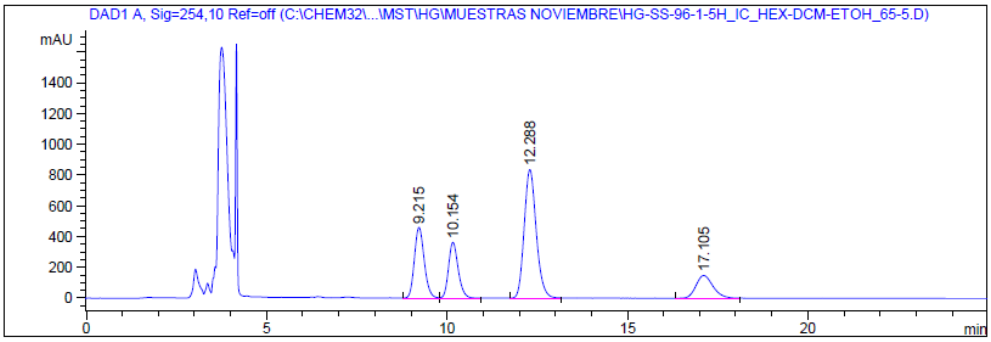
```
Data File C:\CHEM32\...7\2013\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-96-1-5H_IC_HEX-ETOH_20.D
Sample Name: HG-SS-96-1-5H

    ======================================================================
    Acq. Operator   : sc                              Seq. Line :   4
    Acq. Instrument : Instrument 2                     Location : Vial 3
    Injection Date  : 11/26/2013 12:49:41 PM                Inj :   1
                                                    Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC1.M
    Last changed    : 11/22/2013 4:40:02 PM by MH
    Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
    Last changed    : 12/19/2013 10:58:05 AM by sc
                      (modified after loading)
    Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                      Hex / EtOH 80:20
                      1 mL/min
                      25°C
                      Sample: as received
```




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

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


    Signal 1: DAD1 A, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]    [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.405 VV    0.3836 1753.39001   66.06741  13.6593
       2  10.594 VV    0.3573 1.10832e4   483.72638  86.3407

    Totals :                  1.28366e4   549.79379
```

Chiral HPLC, normal phase. E.r. of the monoamide (**3**): 56/44; e.r. of the diamide (**4**): 80/20.

```
Data File C:\CHEM32\...\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-96-1-5H_IC_HEX-DCM-ETOH_65-5.D
Sample Name: HG-SS-96-1-5H

    ======================================================================
    Acq. Operator   : sc                          Seq. Line :  13
    Acq. Instrument : Instrument 2                 Location : Vial 3
    Injection Date  : 11/26/2013 4:46:04 PM             Inj :   1
                                                  Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC2.M
    Last changed    : 11/22/2013 4:44:10 PM by MH
    Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
    Last changed    : 12/19/2013 11:19:28 AM by sc
                      (modified after loading)
    Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                      Hex / DCM / EtOH 30:65:5
                      1 mL/min
                      25°C
                      Sample: as received
```



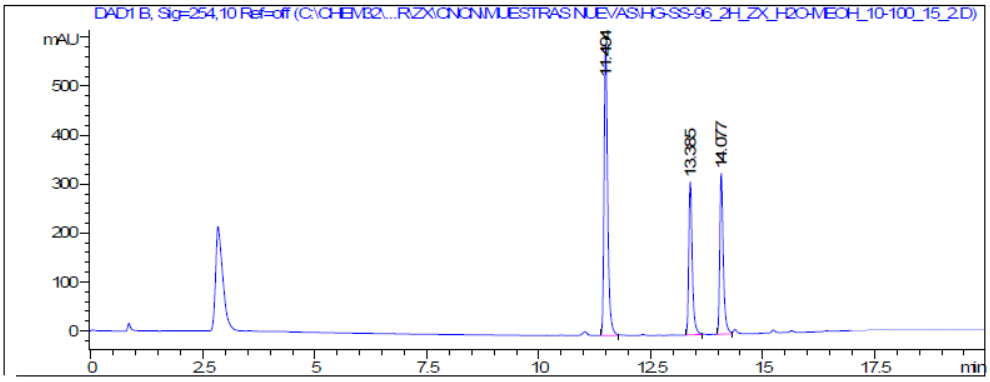

```
    ======================================================================
                            Area Percent Report
    ======================================================================

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


    Signal 1: DAD1 A, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.215 VV    0.2951 8822.46289  461.39587  21.9541
       2  10.154 VV    0.2897 6873.66309  364.93018  17.1046
       3  12.288 VV    0.3578 1.95111e4   837.55072  48.5521
       4  17.105 VV    0.5011 4978.72705  149.29800  12.3892

    Totals :                  4.01860e4  1813.17477
```

Catalytic hydration of [1,1'-binaphthalene]-2,2'-dicarbonitrile with $Pt(COD)_2Cl_2/AgNO_3$/1, reaction time 2h

HPLC, reversed phase. Conversion: 74%; yield of the enantioenriched dicarbonitrile (**2**): 26%; yield of the monoamide (**3**): 25%; yield of the diamide (**4**): 49%.

Data File C:\CHEM32\...-CNER\ZX\CNCN\MUESTRAS NUEVAS\HG-SS-96_2H_ZX_H2O-MEOH_10-100_15_2.D
Sample Name: HG-SS-96_2h

Acq. Operator	: LFG	Seq. Line	: 2
Acq. Instrument	: Instrument 1	Location	: Vial 13
Injection Date	: 12/11/2013 10:07:26 AM	Inj	: 1
		Inj Volume	: 5 µl
Acq. Method	: C:\CHEM32\1\METHODS\APCI.M		
Last changed	: 12/10/2013 6:53:34 PM by LFG		
Analysis Method	: C:\CHEM32\1\METHODS\END.M		
Last changed	: 12/19/2013 11:26:23 AM by LFG (modified after loading)		
Sample Info	: Zorbax XDB C18 100x4.6mm, 5µm H2O/ MeOH 90:10 10% up to 100% in 15', hold 5' APCI + Sample as received		



Area Percent Report

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

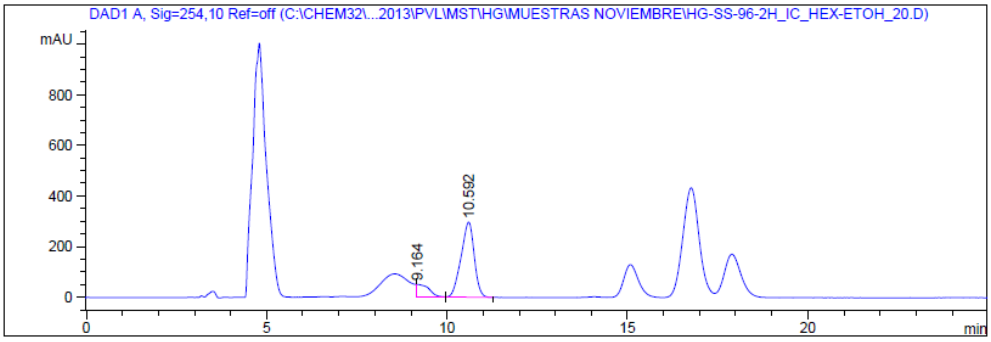
Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.494	BB	0.0849	3305.18970	594.29810	48.6904
2	13.385	BB	0.0817	1708.14355	313.02380	25.1635
3	14.077	BV	0.0811	1774.83887	328.23285	26.1460
Totals :				6788.17212	1235.55475	

*** End of Report ***

Chiral HPLC, normal phase. E.r. of the enantioenriched dicarbonitrile (**2**): 14/86.

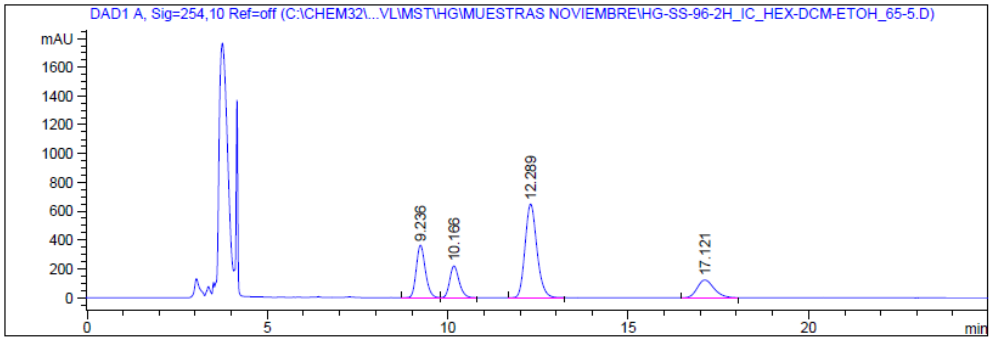
```
Data File C:\CHEM32\...127\2013\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-96-2H_IC_HEX-ETOH_20.D
Sample Name: HG-SS-96-2H

======================================================================
Acq. Operator   : sc                          Seq. Line :   5
Acq. Instrument : Instrument 2                 Location : Vial 4
Injection Date  : 11/26/2013 1:16:00 PM             Inj :   1
                                              Inj Volume : 5 µl
Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC1.M
Last changed    : 11/22/2013 4:40:02 PM by MH
Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
Last changed    : 12/19/2013 10:58:05 AM by sc
                  (modified after loading)
Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                  Hex / EtOH 80:20
                  1 mL/min
                  25°C
                  Sample: as received
```




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

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


Signal 1: DAD1 A, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.164 VV    0.2975 1232.53357   50.71912  14.0054
   2  10.592 VV    0.3887 7567.86230  297.57462  85.9946

Totals :                  8800.39587  348.29374
```

Chiral HPLC, normal phase. E.r. of the monoamide (**3**): 61/39; e.r. of the diamide (**4**): 78/22.

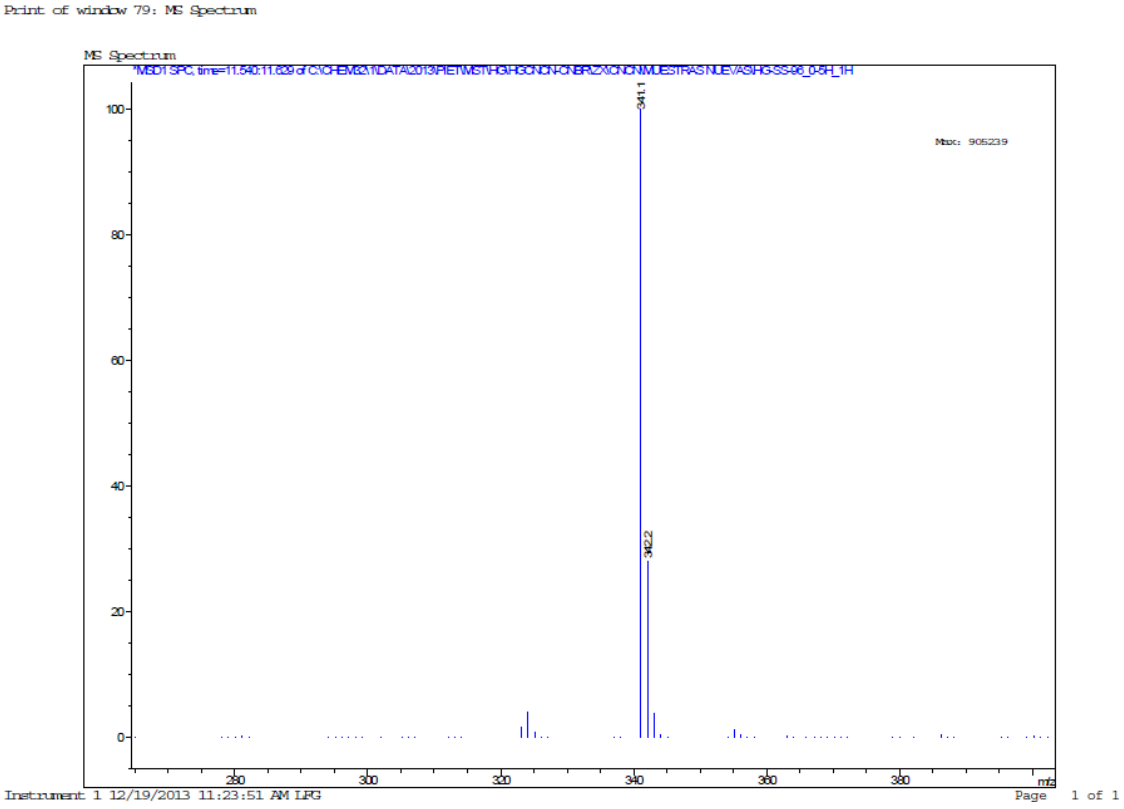
```
Data File C:\CHEM32\...13\PVL\MST\HG\MUESTRAS NOVIEMBRE\HG-SS-96-2H_IC_HEX-DCM-ETOH_65-5.D
Sample Name: HG-SS-96-2H

    ======================================================================
    Acq. Operator   : sc                          Seq. Line :  14
    Acq. Instrument : Instrument 2                 Location : Vial 4
    Injection Date  : 11/26/2013 5:12:25 PM             Inj :   1
                                                  Inj Volume : 5 µl
    Acq. Method     : C:\CHEM32\2\METHODS\CHIRAL IC2.M
    Last changed    : 11/22/2013 4:44:10 PM by MH
    Analysis Method : C:\CHEM32\2\METHODS\CHIRAL SCREENING_IC.M
    Last changed    : 12/19/2013 11:19:28 AM by sc
                      (modified after loading)
    Sample Info     : Chiralpack IC 250x4.6mm, 5µm
                      Hex / DCM / EtOH 30:65:5
                      1 mL/min
                      25°C
                      Sample: as received
```




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

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


    Signal 1: DAD1 A, Sig=254,10 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]    [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.236 VV    0.2724 6468.01416  365.65027  21.8669
       2  10.166 VV    0.2799 4067.26294  221.83714  13.7505
       3  12.289 VV    0.3545 1.49873e4   651.10242  50.6686
       4  17.121 VV    0.4940 4056.47363  123.88087  13.7140

    Totals :                  2.95790e4  1362.47070
```

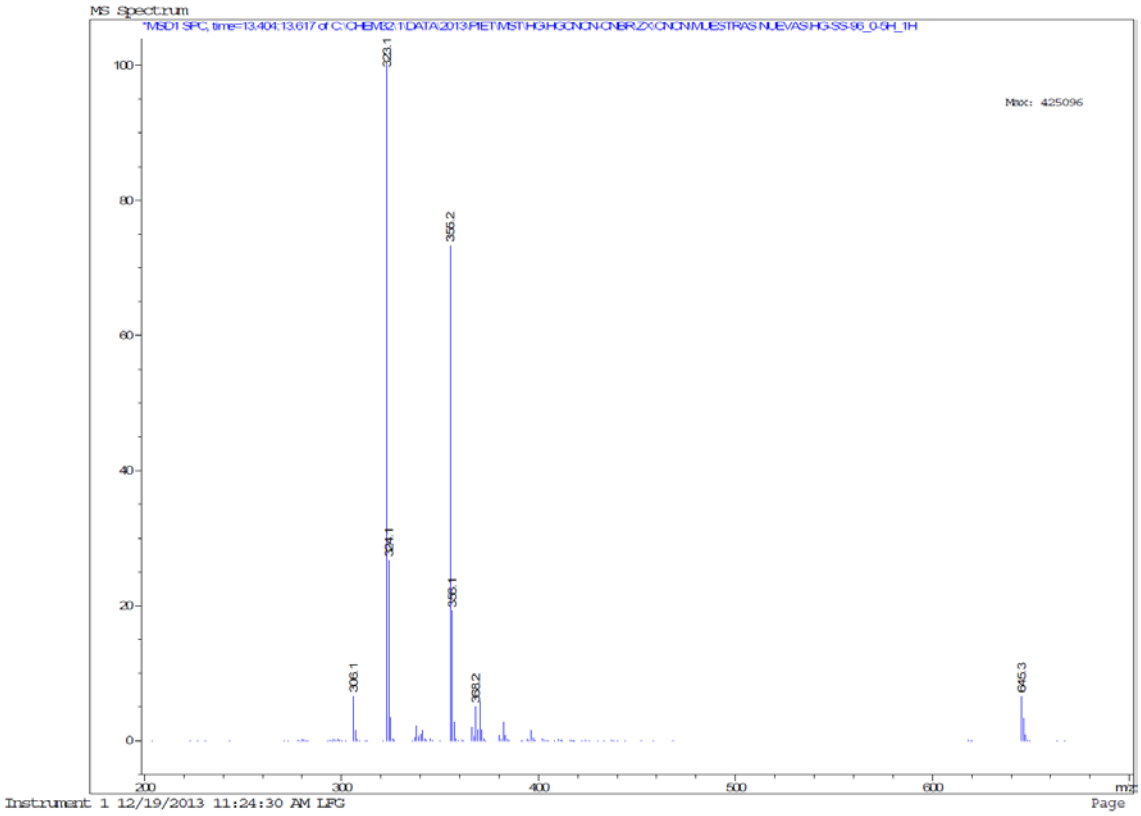
14. Mass spectra of the [1,1’-binaphthalene]-2,2’-dicarbonitrile (2), 2'-cyano-[1,1'-binaphthalene]-2-carboxamide (3) and [1,1'-binaphthalene]-2,2'-dicarboxamide (4)

Mass spectrum of [1,1'-binaphthalene]-2,2'-dicarboxamide (**4**) ($M + H^+$)



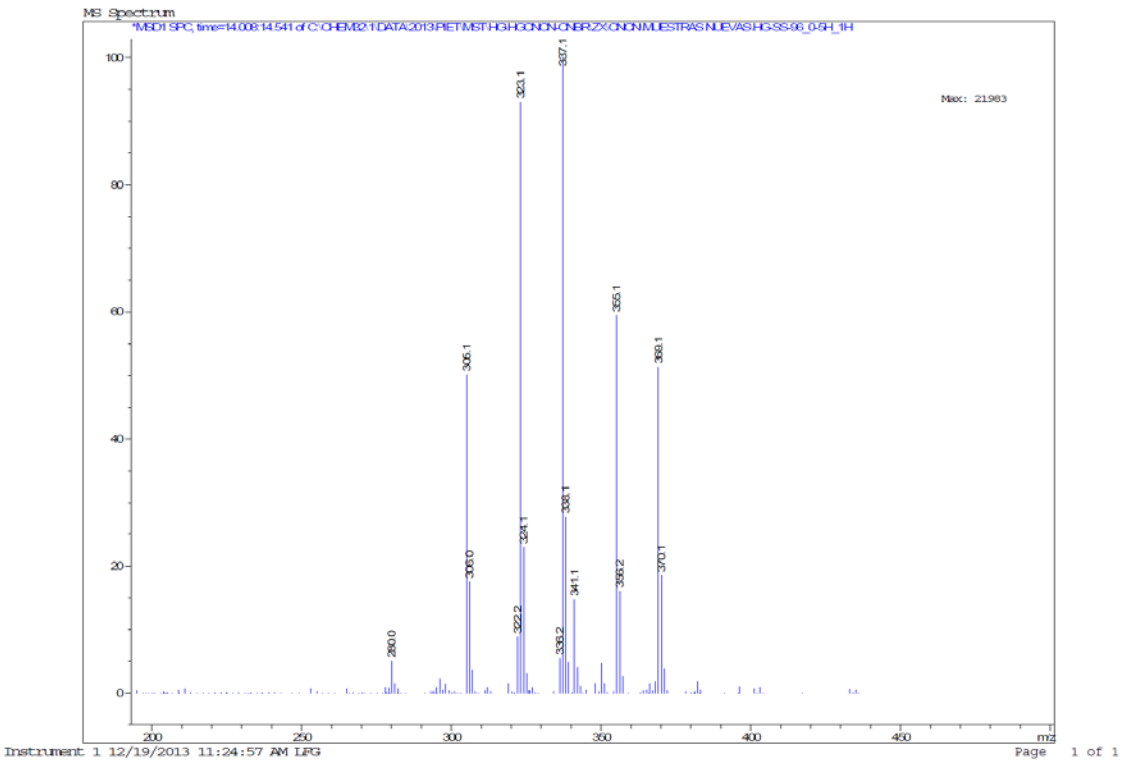
Mass spectrum of 2'-cyano-[1,1'-binaphthalene]-2-carboxamide (**3**) (M + H^+)

Print of window 79: MS Spectrum



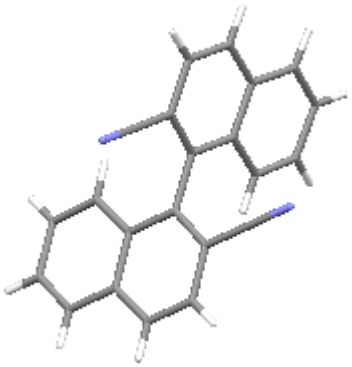
Mass spectrum of [1,1'-binaphthalene]-2,2'-dicarbonitrile (**2**) (M + H^+)

Print of window 79: MS Spectrum



15. X-ray structures of the racemic [1,1'-binaphthalene]-2,2'-dicarbonitrile, the enantioenriched [1,1'-binaphthalene]-2,2'-dicarbonitrile (2), and the [1,1'-binaphthalene]-2,2'-dicarboxamide (4)

X-ray analysis of single crystals obtained from the (rac)-[1,1'-binaphthalene]-2,2'-dicarbonitrile



Space group P21/c

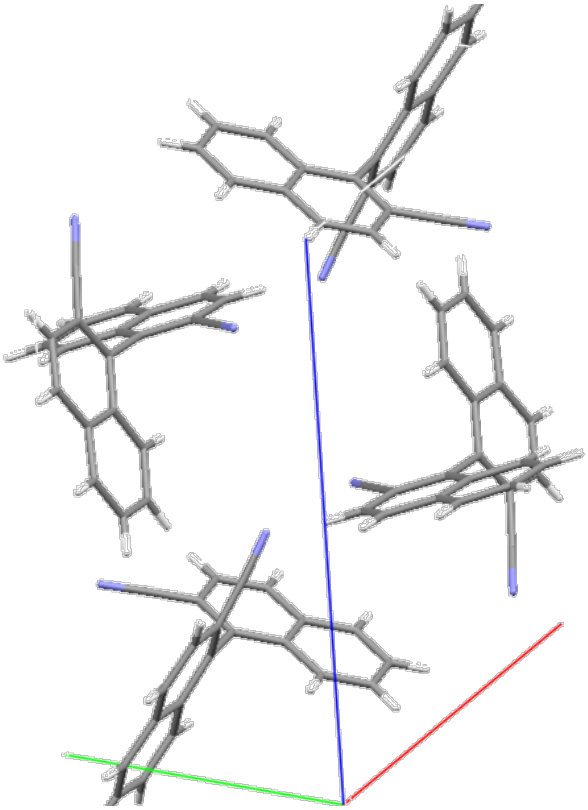


Table 1. Crystal data and structure refinement for racemic [1,1'-binaphthalene]-2,2'-dicarbonitrile

Identification code	hg492f3-4	
Empirical formula	C22 H12 N2	
Formula weight	304.34	
Temperature	100(2) K	
Wavelength	0.71073 Ĺ	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.3869(6) Ĺ	α= 90.00 °.
	b = 7.7560(4) Ĺ	β = 95.514(3) °.
	c = 16.0899(8) Ĺ	γ = 90.00 °.
Volume	1538.65(13) Ĺ^3	
Z	4	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	632	
Crystal size	0.40 x 0.30 x 0.10 mm^3	
Theta range for data collection	1.65 to1.65 °.	
Index ranges	-20 <=h<=20 ,0 <=k<=12 ,0 <=l<=26	
Reflections collected	7412	
Independent reflections	4819 [R(int) = 0.0000]	
Completeness to theta =36.38 °	0.990 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9923 and 0.9695	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7412 / 0 / 217	
Goodness-of-fit on F^2	0.971	
Final R indices [I>2sigma(I)]	R1 = 0.0610 , wR2 = 0.1588	
R indices (all data)	R1 = 0.0888 , wR2 = 0.1710	
Largest diff. peak and hole	0.737 and -0.284 e.Ĺ$^{-3}$	

Table 2. Bond lengths [Ĺ] and angles [°] for racemic [1,1'-binaphthalene]-2,2'-dicarbonitrile

Bond lengths----	
C1-C2	1.3834(12)
C1-C10	1.4226(12)
C1-C11	1.4922(11)
N1-C21	1.1491(13)
C2-C3	1.4153(12)
C2-C21	1.4408(13)
N2-C22	1.1458(14)
C3-C4	1.3642(13)
C4-C5	1.4129(13)
C5-C6	1.4164(13)
C5-C10	1.4224(11)
C6-C7	1.3674(15)
C7-C8	1.4079(14)
C8-C9	1.3666(13)
C9-C10	1.4167(13)
C11-C12	1.3834(12)
C11-C20	1.4239(12)
C12-C13	1.4204(11)
C12-C22	1.4378(13)
C13-C14	1.3618(14)
C14-C15	1.4154(13)
C15-C16	1.417(13)
C15-C20	1.4209(11)
C16-C17	1.3631(14)
C17-C18	1.4062(13)
C18-C19	1.3671(14)
C19-C20	1.4171(13)
Angles----------	
C2-C1-C10	118.99(7)
C2-C1-C11	118.88(7)
C10-C1-C11	122.13(8)
C1-C2-C3	121.90(8)
C1-C2-C21	118.61(8)
C3-C2-C21	119.49(8)

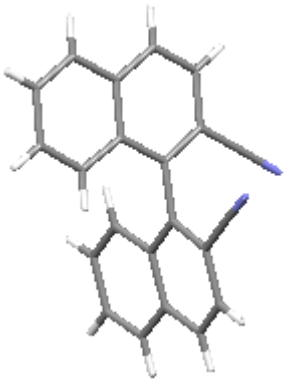
C4-C3-C2	119.34(8)
C3-C4-C5	120.95(8)
C4-C5-C6	121.38(8)
C4-C5-C10	119.75(8)
C6-C5-C10	118.87(8)
C7-C6-C5	120.93(8)
C6-C7-C8	120.03(9)
C9-C8-C7	120.68(9)
C8-C9-C10	120.63(8)
C9-C10-C5	118.84(8)
C9-C10-C1	122.09(7)
C5-C10-C1	119.07(8)
C12-C11-C20	119.13(7)
C12-C11-C1	120.37(8)
C20-C11-C1	120.36(8)
C11-C12-C13	121.70(8)
C11-C12-C22	119.97(8)
C13-C12-C22	118.17(8)
C14-C13-C12	119.37(8)
C13-C14-C15	120.92(8)
C14-C15-C16	121.08(8)
C14-C15-C20	119.86(8)
C16-C15-C20	119.06(8)
C17-C16-C15	120.79(8)
C16-C17-C18	120.02(9)
C19-C18-C17	120.99(9)
C18-C19-C20	120.29(8)
C19-C20-C15	118.81(8)
C19-C20-C11	122.23(7)
C15-C20-C11	118.95(8)
N1-C21-C2	178.89(12)
N2-C22-C12	175.93(10)

Table 3. Torsion angles [°] for racemic [1,1'-binaphthalene]-2,2'-dicarbonitrile

C10-C1-C2-C3	-0.39(14)
C11-C1-C2-C3	-179.84(9)
C10-C1-C2-C21	178.67(9)
C11-C1-C2-C21	-0.77(14)
C1-C2-C3-C4	0.04(15)
C21-C2-C3-C4	-179.01(10)
C2-C3-C4-C5	0.30(15)
C3-C4-C5-C6	179.80(10)
C3-C4-C5-C10	-0.29(15)
C4-C5-C6-C7	-178.93(10)
C10-C5-C6-C7	1.16(15)
C5-C6-C7-C8	-0.30(16)
C6-C7-C8-C9	-0.97(17)
C7-C8-C9-C10	1.34(17)
C8-C9-C10-C5	-0.46(15)
C8-C9-C10-C1	178.90(10)
C4-C5-C10-C9	179.31(9)
C6-C5-C10-C9	-0.78(13)
C4-C5-C10-C1	-0.07(13)
C6-C5-C10-C1	179.85(9)
C2-C1-C10-C9	-178.96(9)
C11-C1-C10-C9	0.47(14)
C2-C1-C10-C5	0.40(13)
C11-C1-C10-C5	179.82(8)
C2-C1-C11-C12	-92.19(11)
C10-C1-C11-C12	88.38(11)
C2-C1-C11-C20	83.39(11)
C10-C1-C11-C20	-96.03(11)
C20-C11-C12-C13	-0.62(13)
C1-C11-C12-C13	175.02(8)
C20-C11-C12-C22	-176.09(8)
C1-C11-C12-C22	-0.45(13)
C11-C12-C13-C14	-1.44(14)
C22-C12-C13-C14	174.11(9)
C12-C13-C14-C15	1.52(14)
C13-C14-C15-C16	-179.65(9)

C13-C14-C15-C20	0.42(14)
C14-C15-C16-C17	-178.36(9)
C20-C15-C16-C17	1.56(14)
C15-C16-C17-C18	-0.11(16)
C16-C17-C18-C19	-1.42(16)
C17-C18-C19-C20	1.44(16)
C18-C19-C20-C15	0.04(14)
C18-C19-C20-C11	-179.06(9)
C14-C15-C20-C19	178.41(9)
C16-C15-C20-C19	-1.52(13)
C14-C15-C20-C11	-2.46(13)
C16-C15-C20-C11	177.61(8)
C12-C11-C20-C19	-178.37(9)
C1-C11-C20-C19	5.99(13)
C12-C11-C20-C15	2.53(13)
C1-C11-C20-C15	-173.11(8)
C1-C2-C21-N1	-44(6)
C3-C2-C21-N1	135(6)
C11-C12-C22-N2	125.4(15)
C13-C12-C22-N2	-50.2(16)

X-ray analysis of single crystals obtained from the enantioenriched [1,1'-binaphthalene]-2,2'-dicarbonitrile (2)



Space group P21

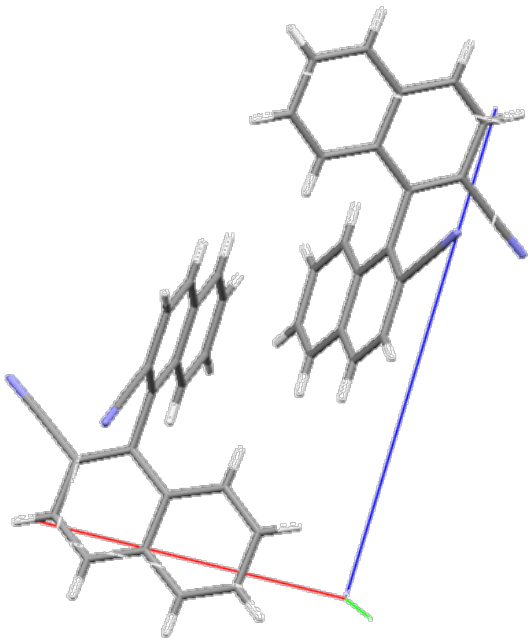


Table 1. Crystal data and structure refinement for the enantioenriched [1,1'-binaphthalene]-2,2'-dicarbonitrile (**2**)

Identification code	hg513_0m
Empirical formula	C22 H12 N2
Formula weight	304.34
Temperature	100(2)K

Wavelength	0.71073 Ĺ	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.8740(8)Ĺ	α= 90.00°.
	b = 7.9775(8)Ĺ	β = 92.715(2)°.
	c = 12.3173(11)Ĺ	γ = 90.00°.
Volume	772.84(13) Ĺ^3	
Z	2	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	316	
Crystal size	0.60 x 0.40 x 0.20 mm^3	
Theta range for data collection	3.01 to3.01°.	
Index ranges	-10<=h<=10,-9<=k<=9,-4<=l<=16	
Reflections collected	2638	
Independent reflections	2561[R(int) = 0.0241]	
Completeness to theta =28.99°	0.855%	
Absorption correction	Empirical	
Max. and min. transmission	0.9847 and 0.9549	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2638/ 1/ 217	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.1091	
R indices (all data)	R1 = 0.0414, wR2 = 0.1111	
Largest diff. peak and hole	0.393 and -0.170 e.Ĺ$^{-3}$	

Table 2. Bond lengths [Ĺ] and angles [°] for [1,1'-binaphthalene]-2,2'-dicarbonitrile (**2**)

Bond lengths----	
C1-N1	1.149(2)
C1-C2	1.446(2)
C2-C11	1.389(2)
C2-C3	1.4214(18)
C3-C4	1.367(2)
C3-H3	0.95
C4-C5	1.417(2)
C4-H4	0.95
C5-C6	1.423(2)
C5-C10	1.4247(18)
C6-C7	1.369(2)
C6-H6	0.95
C7-C8	1.413(2)
C7-H7	0.95
C8-C9	1.372(2)
C8-H8	0.95
C9-C10	1.423(2)
C9-H9	0.95
C10-C11	1.4299(19)
C11-C12	1.491(18)
C12-C21	1.382(2)
C12-C13	1.422(2)
C13-C14	1.423(3)
C13-C18	1.431(18)
C14-C15	1.371(3)
C14-H14	0.95
C15-C16	1.413(2)
C15-H15	0.95
C16-C17	1.365(3)
C16-H16	0.95
C17-C18	1.421(2)
C17-H17	0.95
C18-C19	1.417(3)
C19-C20	1.367(3)
C19-H19	0.95

C20-C21	1.4253(19)
C20-H20	0.95
C21-C22	1.445(2)
C22-N2	1.144(2)

Angles----------

N1-C1-C2	178.13(17)
C11-C2-C3	121.84(13)
C11-C2-C1	119.15(13)
C3-C2-C1	118.99(13)
C4-C3-C2	119.63(14)
C4-C3-H3	120.2
C2-C3-H3	120.2
C3-C4-C5	120.61(13)
C3-C4-H4	119.7
C5-C4-H4	119.7
C4-C5-C6	121.07(13)
C4-C5-C10	120.00(13)
C6-C5-C10	118.90(14)
C7-C6-C5	120.53(14)
C7-C6-H6	119.7
C5-C6-H6	119.7
C6-C7-C8	120.49(14)
C6-C7-H7	119.8
C8-C7-H7	119.8
C9-C8-C7	120.63(15)
C9-C8-H8	119.7
C7-C8-H8	119.7
C8-C9-C10	120.19(13)
C8-C9-H9	119.9
C10-C9-H9	119.9
C9-C10-C5	119.24(13)
C9-C10-C11	121.62(12)
C5-C10-C11	119.14(13)
C2-C11-C10	118.72(13)
C2-C11-C12	120.76(13)
C10-C11-C12	120.29(13)
C21-C12-C13	119.32(13)

C21-C12-C11	118.03(14)
C13-C12-C11	122.65(14)
C12-C13-C14	122.57(13)
C12-C13-C18	118.89(15)
C14-C13-C18	118.54(15)
C15-C14-C13	120.67(15)
C15-C14-H14	119.7
C13-C14-H14	119.7
C14-C15-C16	120.64(18)
C14-C15-H15	119.7
C16-C15-H15	119.7
C17-C16-C15	120.21(17)
C17-C16-H16	119.9
C15-C16-H16	119.9
C16-C17-C18	120.98(15)
C16-C17-H17	119.5
C18-C17-H17	119.5
C19-C18-C17	121.30(14)
C19-C18-C13	119.75(15)
C17-C18-C13	118.95(15)
C20-C19-C18	121.01(14)
C20-C19-H19	119.5
C18-C19-H19	119.5
C19-C20-C21	119.07(16)
C19-C20-H20	120.5
C21-C20-H20	120.5
C12-C21-C20	121.95(15)
C12-C21-C22	118.52(13)
C20-C21-C22	119.52(16)
N2-C22-C21	179.05(18)

Table 3. Torsion angles [°] for [1,1'-binaphthalene]-2,2'-dicarbonitrile (**2**)

N1-C1-C2-C11	-142(6)
N1-C1-C2-C3	37(6)
C11-C2-C3-C4	0.2(3)
C1-C2-C3-C4	-178.37(17)
C2-C3-C4-C5	-2.2(3)
C3-C4-C5-C6	-176.08(17)
C3-C4-C5-C10	1.8(3)
C4-C5-C6-C7	177.06(18)
C10-C5-C6-C7	-0.8(3)
C5-C6-C7-C8	1.9(3)
C6-C7-C8-C9	-1.5(3)
C7-C8-C9-C10	-0.1(3)
C8-C9-C10-C5	1.2(3)
C8-C9-C10-C11	-177.97(17)
C4-C5-C10-C9	-178.67(18)
C6-C5-C10-C9	-0.8(2)
C4-C5-C10-C11	0.6(2)
C6-C5-C10-C11	178.46(17)
C3-C2-C11-C10	2.1(3)
C1-C2-C11-C10	-179.32(16)
C3-C2-C11-C12	-172.38(16)
C1-C2-C11-C12	6.2(3)
C9-C10-C11-C2	176.78(16)
C5-C10-C11-C2	-2.4(2)
C9-C10-C11-C12	-8.7(3)
C5-C10-C11-C12	172.07(15)
C2-C11-C12-C21	89.6(2)
C10-C11-C12-C21	-84.78(19)
C2-C11-C12-C13	-91.13(19)
C10-C11-C12-C13	94.48(19)
C21-C12-C13-C14	179.21(14)
C11-C12-C13-C14	0.0(2)
C21-C12-C13-C18	-0.6(2)
C11-C12-C13-C18	-179.86(13)
C12-C13-C14-C15	-179.76(14)
C18-C13-C14-C15	0.1(2)

C13-C14-C15-C16	-1.0(3)
C14-C15-C16-C17	1.1(2)
C15-C16-C17-C18	-0.3(2)
C16-C17-C18-C19	178.96(15)
C16-C17-C18-C13	-0.6(2)
C12-C13-C18-C19	0.9(2)
C14-C13-C18-C19	-178.87(15)
C12-C13-C18-C17	-179.44(14)
C14-C13-C18-C17	0.7(2)
C17-C18-C19-C20	179.74(14)
C13-C18-C19-C20	-0.7(2)
C18-C19-C20-C21	0.0(2)
C13-C12-C21-C20	0.0(2)
C11-C12-C21-C20	179.26(14)
C13-C12-C21-C22	-179.77(13)
C11-C12-C21-C22	-0.5(2)
C19-C20-C21-C12	0.3(2)
C19-C20-C21-C22	-179.93(16)
C12-C21-C22-N2	22(12)
C20-C21-C22-N2	-158(12)

X-ray analysis of single crystals obtained from the [1,1'-binaphthalene]-2,2'-dicarboxamide (4)

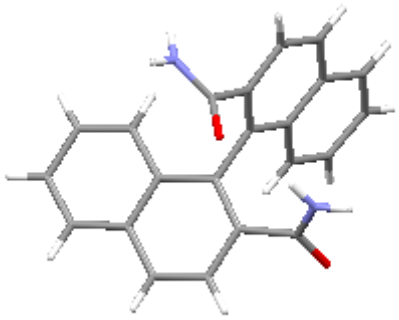


Table 1. Crystal data and structure refinement for [1,1'-binaphthalene]-2,2'-dicarboxamide (**4**)

Identification code	hg513frac3_0m	
Empirical formula	C22 H16 N2 O2	
Formula weight	340.37	
Temperature	100(2)K	
Wavelength	0.71073 Ĺ	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.3024(10)Ĺ	α= 90.00°.
	b = 8.3301(11)Ĺ	β = 94.100(5)°.
	c = 21.227(2)Ĺ	γ = 90.00°.
Volume	1640.7(3) Ĺ^3	
Z	4	
Density (calculated)	1.378 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	712	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	2.33 to2.33°.	
Index ranges	-14<=h<=15,-6<=k<=13,-34<=l<=32	
Reflections collected	7548	
Independent reflections	4222[R(int) = 0.0793]	
Completeness to theta =36.60°	0.933%	
Absorption correction	Empirical	
Max. and min. transmission	? and ?	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7548/ 0/ 235	

Goodness-of-fit on F^2	0.976
Final R indices [I>2sigma(I)]	R1 = 0.0647, wR2 = 0.1531
R indices (all data)	R1 = 0.1347, wR2 = 0.1887
Largest diff. peak and hole	0.629 and -0.401 e.Ĺ$^{-3}$

Table 2. Bond lengths [Ĺ] and angles [°] for [1,1'-binaphthalene]-2,2'-dicarboxamide (**4**)

Bond lengths----	
C1-O1	1.2307(18)
C1-N1	1.328(2)
C1-C2	1.496(19)
C2-C11	1.3773(18)
C2-C3	1.409(2)
C3-C4	1.358(2)
C3-H3	0.95
C4-C5	1.4121(19)
C4-H4	0.95
C5-C6	1.412(2)
C5-C10	1.4188(19)
C6-C7	1.364(2)
C6-H6	0.95
C7-C8	1.402(2)
C7-H7	0.95
C8-C9	1.364(2)
C8-H8	0.95
C9-C10	1.4121(19)
C9-H9	0.95
C10-C11	1.4263(19)
C11-C12	1.4896(19)
C12-C21	1.37(2)
C12-C13	1.428(19)
C13-C14	1.409(2)
C13-C18	1.418(2)
C14-C15	1.364(2)
C14-H14	0.95
C15-C16	1.406(2)
C15-H15	0.95
C16-C17	1.358(3)
C16-H16	0.95
C17-C18	1.415(2)
C17-H17	0.95
C18-C19	1.41(2)
C19-C20	1.365(2)

C19-H19	0.95
C20-C21	1.414(2)
C20-H20	0.95
C21-C22	1.4924(19)
C22-O2	1.2371(17)
C22-N2	1.3242(18)
N1-H1A	0.88
N1-H1B	0.88
N2-H2A	0.88
N2-H2B	0.88

Angles----------

O1-C1-N1	124.14(14)
O1-C1-C2	119.72(14)
N1-C1-C2	116.08(13)
C11-C2-C3	121.49(13)
C11-C2-C1	121.92(12)
C3-C2-C1	116.59(12)
C4-C3-C2	120.35(13)
C4-C3-H3	119.8
C2-C3-H3	119.8
C3-C4-C5	120.31(13)
C3-C4-H4	119.8
C5-C4-H4	119.8
C6-C5-C4	120.83(13)
C6-C5-C10	119.33(12)
C4-C5-C10	119.82(13)
C7-C6-C5	120.81(14)
C7-C6-H6	119.6
C5-C6-H6	119.6
C6-C7-C8	119.91(14)
C6-C7-H7	120.0
C8-C7-H7	120.0
C9-C8-C7	120.79(14)
C9-C8-H8	119.6
C7-C8-H8	119.6
C8-C9-C10	120.84(14)
C8-C9-H9	119.6

C10-C9-H9	119.6
C9-C10-C5	118.33(13)
C9-C10-C11	122.57(13)
C5-C10-C11	119.10(12)
C2-C11-C10	118.91(12)
C2-C11-C12	120.11(12)
C10-C11-C12	120.91(11)
C21-C12-C13	119.20(12)
C21-C12-C11	121.37(12)
C13-C12-C11	119.41(13)
C14-C13-C18	118.55(13)
C14-C13-C12	122.22(13)
C18-C13-C12	119.21(14)
C15-C14-C13	120.88(15)
C15-C14-H14	119.6
C13-C14-H14	119.6
C14-C15-C16	120.39(16)
C14-C15-H15	119.8
C16-C15-H15	119.8
C17-C16-C15	120.35(14)
C17-C16-H16	119.8
C15-C16-H16	119.8
C16-C17-C18	120.58(14)
C16-C17-H17	119.7
C18-C17-H17	119.7
C19-C18-C17	121.43(13)
C19-C18-C13	119.38(13)
C17-C18-C13	119.19(15)
C20-C19-C18	120.78(13)
C20-C19-H19	119.6
C18-C19-H19	119.6
C19-C20-C21	119.79(15)
C19-C20-H20	120.1
C21-C20-H20	120.1
C12-C21-C20	121.49(13)
C12-C21-C22	120.01(12)
C20-C21-C22	118.29(14)
O2-C22-N2	123.57(13)

O2-C22-C21	120.26(13)
N2-C22-C21	116.13(12)
C1-N1-H1A	120.0
C1-N1-H1B	120.0
H1A-N1-H1B	120.0
C22-N2-H2A	120.0
C22-N2-H2B	120.0
H2A-N2-H2B	120.0

Table 3. Torsion angles [°] for [1,1'-binaphthalene]-2,2'-dicarboxamide (**4**)

O1-C1-C2-C11	-121.96(16)
N1-C1-C2-C11	60.62(19)
O1-C1-C2-C3	58.05(18)
N1-C1-C2-C3	-119.37(15)
C11-C2-C3-C4	-1.3(2)
C1-C2-C3-C4	178.72(14)
C2-C3-C4-C5	1.2(2)
C3-C4-C5-C6	178.44(15)
C3-C4-C5-C10	0.0(2)
C4-C5-C6-C7	-178.00(15)
C10-C5-C6-C7	0.4(2)
C5-C6-C7-C8	-0.3(2)
C6-C7-C8-C9	0.0(2)
C7-C8-C9-C10	0.1(2)
C8-C9-C10-C5	0.0(2)
C8-C9-C10-C11	179.35(15)
C6-C5-C10-C9	-0.3(2)
C4-C5-C10-C9	178.14(14)
C6-C5-C10-C11	-179.64(14)
C4-C5-C10-C11	-1.2(2)
C3-C2-C11-C10	0.1(2)
C1-C2-C11-C10	-179.91(14)
C3-C2-C11-C12	-176.96(14)
C1-C2-C11-C12	3.0(2)
C9-C10-C11-C2	-178.19(14)
C5-C10-C11-C2	1.1(2)
C9-C10-C11-C12	-1.2(2)
C5-C10-C11-C12	178.16(13)
C2-C11-C12-C21	-107.16(16)
C10-C11-C12-C21	75.86(18)
C2-C11-C12-C13	71.07(18)
C10-C11-C12-C13	-105.91(16)
C21-C12-C13-C14	-177.66(13)
C11-C12-C13-C14	4.1(2)
C21-C12-C13-C18	3.6(2)
C11-C12-C13-C18	-174.66(12)

C18-C13-C14-C15	1.7(2)
C12-C13-C14-C15	-177.01(14)
C13-C14-C15-C16	0.3(2)
C14-C15-C16-C17	-1.3(2)
C15-C16-C17-C18	0.2(2)
C16-C17-C18-C19	-178.42(14)
C16-C17-C18-C13	1.8(2)
C14-C13-C18-C19	177.50(13)
C12-C13-C18-C19	-3.7(2)
C14-C13-C18-C17	-2.8(2)
C12-C13-C18-C17	176.01(13)
C17-C18-C19-C20	-178.90(14)
C13-C18-C19-C20	0.8(2)
C18-C19-C20-C21	2.2(2)
C13-C12-C21-C20	-0.6(2)
C11-C12-C21-C20	177.61(13)
C13-C12-C21-C22	-175.23(12)
C11-C12-C21-C22	3.0(2)
C19-C20-C21-C12	-2.3(2)
C19-C20-C21-C22	172.39(13)
C12-C21-C22-O2	60.1(2)
C20-C21-C22-O2	-114.69(16)
C12-C21-C22-N2	-122.11(15)
C20-C21-C22-N2	63.11(19)

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[i] T. Schareina, A. Zapf, W. Mägerlein, N. Müller, M. Beller *Chem. Eur. J.*, **2007**, *13*, 6249-6254.

[ii] P. M. Castro, H. Gulyás, J. Benet-Buchholz, C. Bo, Z. Freixa, P. W. N. M. van Leeuwen *Catal. Sci. Technol.*, **2011**,*1*, 401-407.

[iii] Carcinogenic solvent. It should only be used in a well-ventiled hood, with appropriate protection and great care.