

## Supporting Information

# Valorisation of Biobased Olefins via Rh-Catalyzed Transfer Hydroformylation and Isomerization using Formaldehyde as CO/H<sub>2</sub> Surrogate

Matias Concha-Puelles,<sup>a</sup> Antonio Cortínez,<sup>a</sup> Nicolás Lezana,<sup>a</sup> Marcelo Vilches-Herrera\*,<sup>a</sup>,  
Susan Lühr.\*,<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Sciences, University of Chile, Las Palmeras 3425, Ñuñoa, Santiago, Chile  
[susanluhr@uchile.cl](mailto:susanluhr@uchile.cl)  
[luis.vilches@u.uchile.cl](mailto:luis.vilches@u.uchile.cl)

General	S2
General procedure for the syngas-free hydroformylation of <b>1 a-d</b>	S2
General procedure for the isomerization of <b>1 a-d</b>	S2
Generation of syngas for hydroformylation of safrole under isomerization conditions	S3
<sup>1</sup> H- and <sup>31</sup> P-NMR Experiments	S3
<sup>1</sup> H-NMR spectrum of the crude <b>4 a-d</b>	S3
<sup>1</sup> H- and <sup>31</sup> P-NMR spectrum	S11
References	S?

## General

All reagents were used as received without further purification. Anaerobic reactions were run under an argon atmosphere using Schlenk techniques.  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR were recorded at room temperature on a Bruker 400.13 MHz with  $\text{CHCl}_3$  (7.26 ppm) as an internal standard in deuterated chloroform or in toluene- $d_8$  with phosphoric acid (0 ppm) as an external standard. Gas chromatography measurements were performed on a Shimadzu GC-2014 Plus with a HP-5 column (30 mm x 0.25 mm x 0.25  $\mu\text{m}$ ). The corresponding  $^1\text{H}$ -NMR of the products **2a** and **3a** are in agreement with the literature.<sup>1</sup>

General procedure for the syngas-free hydroformylation of **1 a-d**.

In a 10 mL Schlenk tube with a stir bar were placed the metal precursor [Rh] (1.0 or 2.0 mol%), decarbonylation ligand *rac*-BINAP (2.0 mol%) and the hydroformylation ligand (4.0 mol%). After the tube was purged three times with argon, toluene or tetrahydrofuran (5.0 mL) and a solution of the substrate in toluene or tetrahydrofuran (1.0 mL, 1.0 mmol) were added into the tube under argon flow. Once formaldehyde (375  $\mu\text{L}$ , 5.0 mmol) was added an argon flow was maintained for some seconds. The reaction mixture was stirred at 90 °C for 20 hours. A sample was taken for GC-FID analysis. The reaction mixture was concentrated under pressure and the crude was analyzed by  $^1\text{H}$  NMR. Conversions, yield and ratios were determined by GC.

General procedure for the isomerization of **1 a-d**.

In a 10 mL Schlenk tube with a stir bar were placed the metal precursor [Rh(acac)(CO)<sub>2</sub>] (5.2 mg, 0.2 mmol),  $\text{PPh}_3$  (10.5 mg, 0.4 mmol). After the tube was purged three times with argon, toluene (5.0 mL) and a solution of the substrate in toluene (1.0 mL, 1.0 mmol) were added into the tube under argon flow. Once formaldehyde (375  $\mu\text{L}$ , 5.0 mmol) was added an argon flow was maintained for some seconds. The reaction mixture was stirred at 90 °C for 20 hours. A sample was taken for GC-FID analysis. The reaction mixture was concentrated under pressure and the crude was analyzed by  $^1\text{H}$  NMR. Conversions, yield and ratios were determined by GC. E/Z stereoselectivity was determined by  $^1\text{H}$  NMR.

### <sup>31</sup>P-NMR Experiments

[Rh(acac)(CO)<sub>2</sub>] (1.3 mg, 0.005 mmol) and/or PPh<sub>3</sub> (10.4 mg, 0.04 mmol) and/or (*S*)-BINAP (25 mg, 0.04 mmol), were placed into a NMR tube under argon atmosphere. After 5 minutes, the spectrum was immediately recorded. After the addition of formaldehyde (0.019 mL, 0.25 mmol) a new spectrum was measured.

### Generation of syngas for hydroformylation of safrole under isomerization conditions

In two broad vials (A and B) with screw caps and linked by a glass apparatus was performed the hydroformylations (Figure S2). In vial A was generated syngas *in situ* with the catalytic system [Rh(COD)Cl]<sub>2</sub>/*rac*-BINAP and formaldehyde.



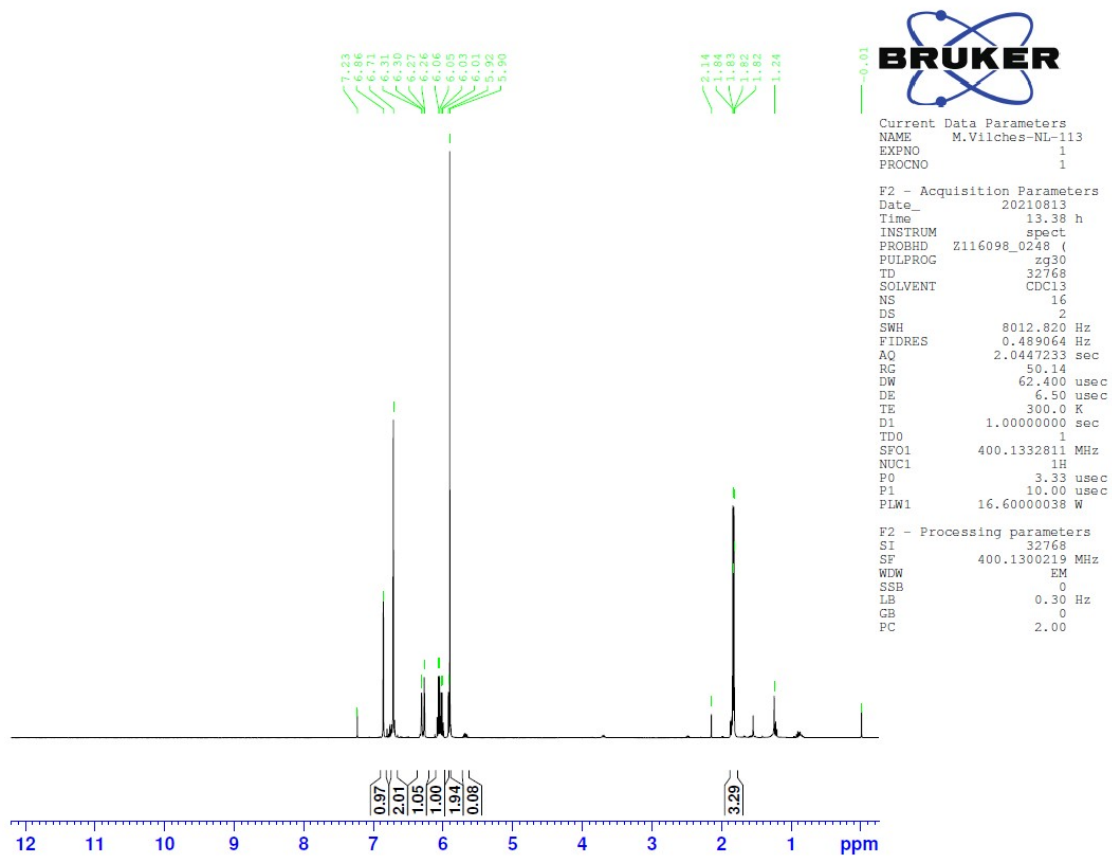
Figure S1. Glass apparatus used for the hydroformylation of safrole under isomerization conditions.

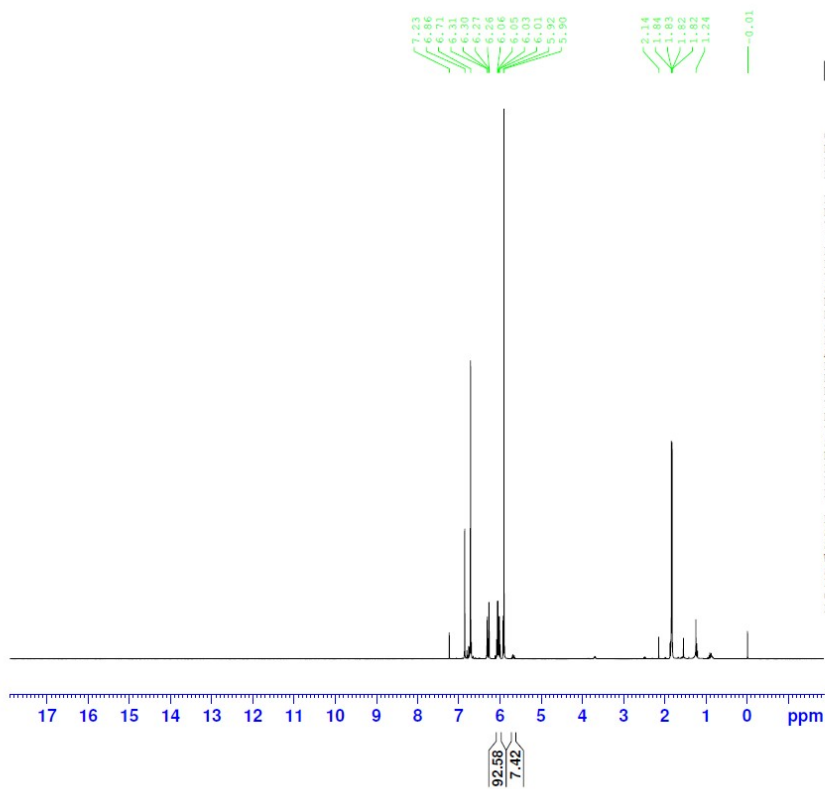
[Rh(COD)Cl]<sub>2</sub> (9.9 mg, 0.02 mmol), *rac*-BINAP (25 mg, 0.04 mmol), formaldehyde (0.75 mL, mol) were added into the vial A, which was purged with argon three times and toluene (6 mL) was added to the vial through an argon flow. The reaction mixture was stirred at 90 °C. After 40 minutes the solution C\* was added into the vial B through an argon flow and both mixture was stirred at 90 °C for 5 hours. A sample was analyzed by gas chromatography.

\*Preparation of solution C:

[Rh(acac)(CO)<sub>2</sub>] (5.2 mg, 0.02 mmol), PPh<sub>3</sub> (10.4 mg, 0.04 mmol), safrole (1.0 mmol), toluene (6.0 mL) and formaldehyde (0.36 mL) were added into a Schlenk tube through an argon flow.

<sup>1</sup>H-NMR spectrum of the crude **4a**





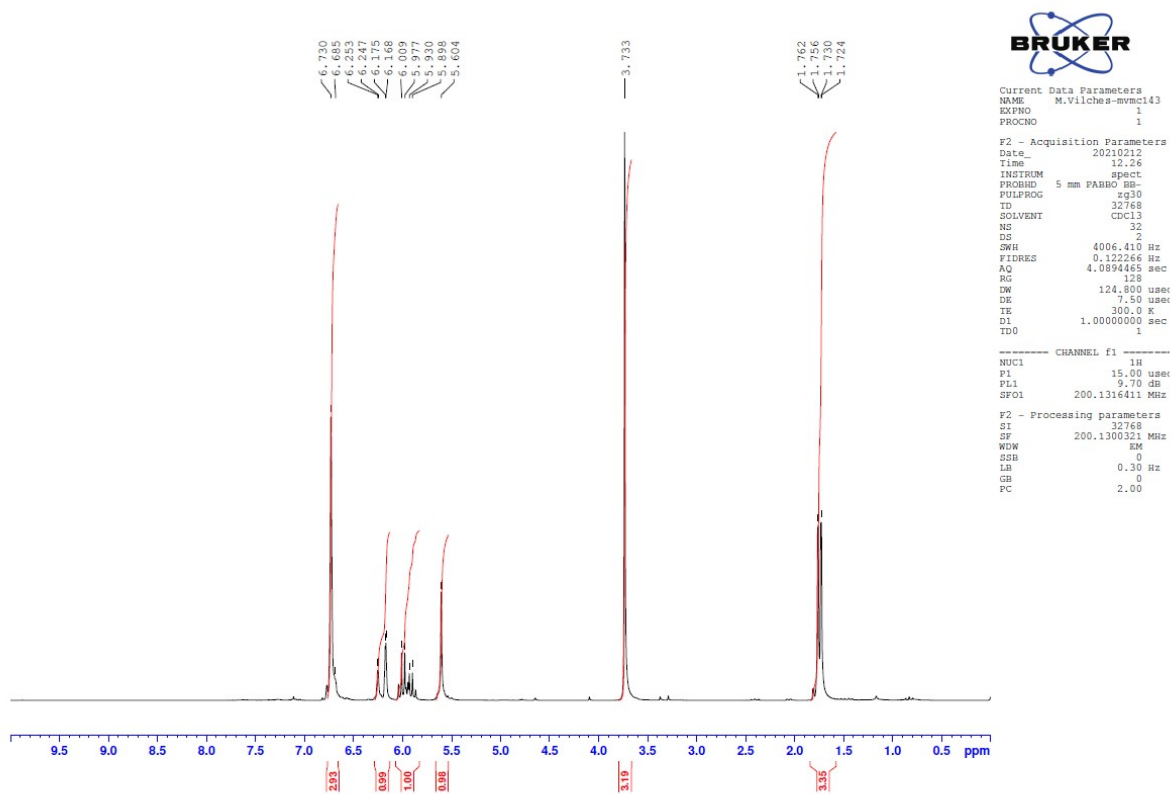
Current Data Parameters  
 NAME M.Vilches-NL-113  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20210813  
 Time 13.38 h  
 INSTRUM spect  
 PROBRD Z116098\_0248 (  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 8012.820 Hz  
 FIDRES 0.489064 Hz  
 AQ 2.0447233 sec  
 RG 50.14  
 DW 62.400 usec  
 DE 6.50 usec  
 TE 300.0 K  
 D1 1.00000000 sec  
 TDO 1  
 SFO1 400.1332811 MHz  
 NUC1 1H  
 P0 3.33 usec  
 P1 10.00 usec  
 PLW1 16.60000038 W

F2 - Processing parameters  
 SI 32768  
 SF 400.1300219 MHz  
 WFW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 2.00

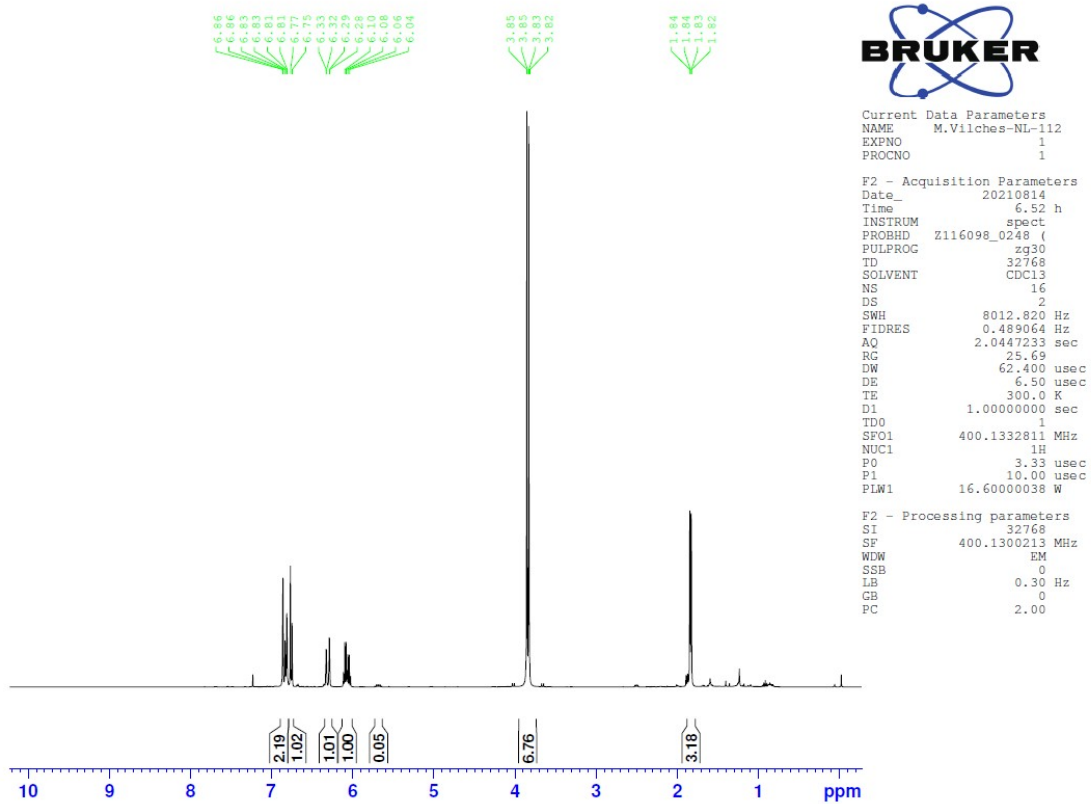
E/Z ratio of **4a** (93:7).

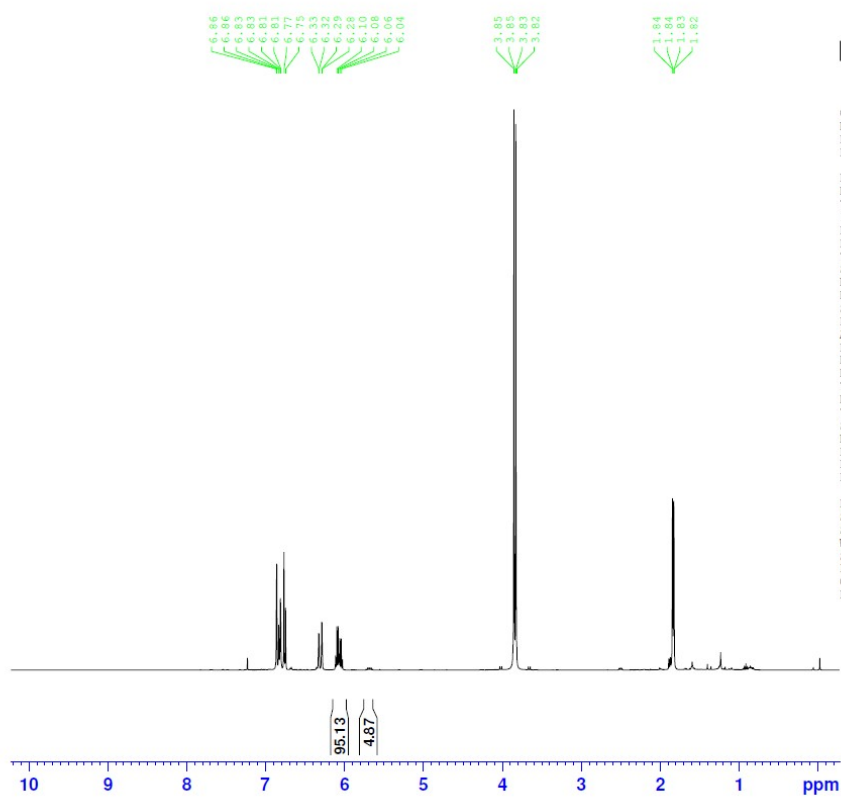
<sup>1</sup>H-NMR spectrum of the crude **4b**



E/Z ratio of **4b** (100:0).

<sup>1</sup>H-NMR spectrum of the crude **4c**





```

Current Data Parameters
NAME      M.Vilches-NL-112
EXPNO    1
PROCNO   1

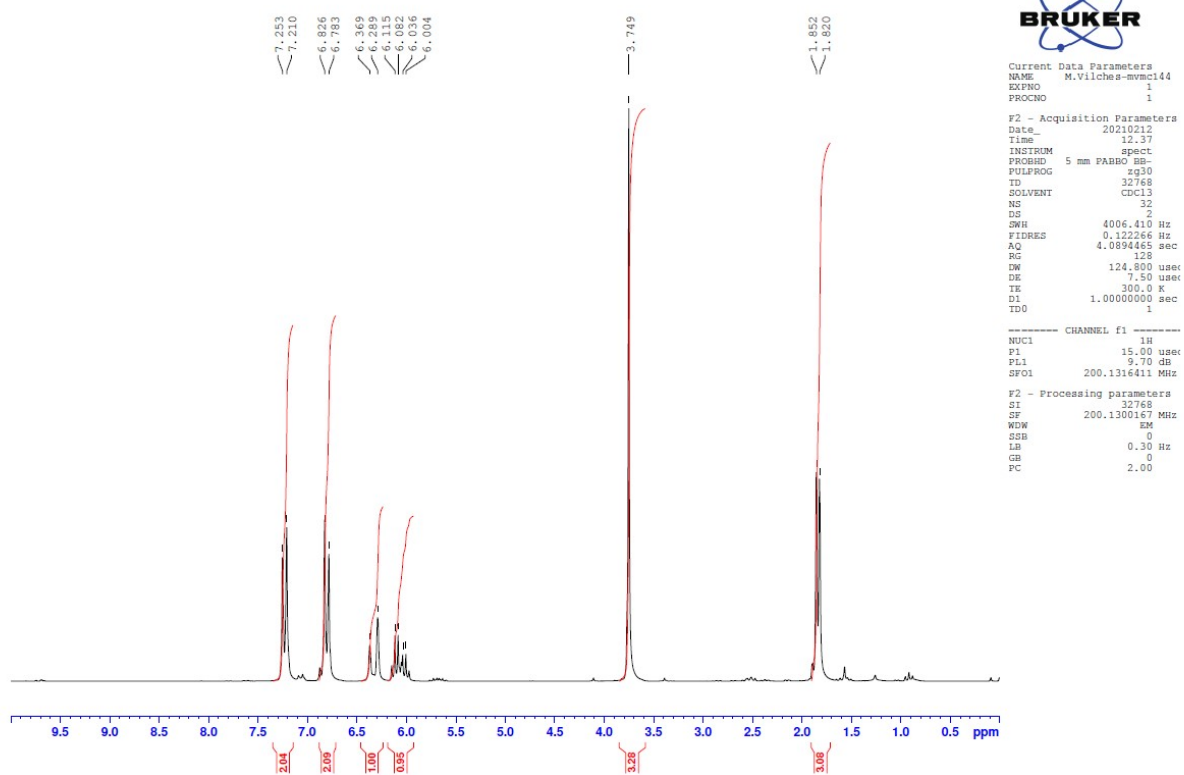
F2 - Acquisition Parameters
Date_    20210814
Time     6.52 h
INSTRUM  spect
PROBHD   Z116098_0248 (
PULPROG  zg30
TD        32768
SOLVENT  CDCl3
NS        16
DS        2
SWH       8012.820 Hz
FIDRES    0.489064 Hz
AQ         2.0447233 sec
RG         25.69
DW         62.400 usec
DE         6.50 usec
TE         300.0 K
D1         1.00000000 sec
TD0        1
SFO1      400.1332811 MHz
NUC1       1H
P0         3.33 usec
P1         10.00 usec
PLW1      16.60000038 W

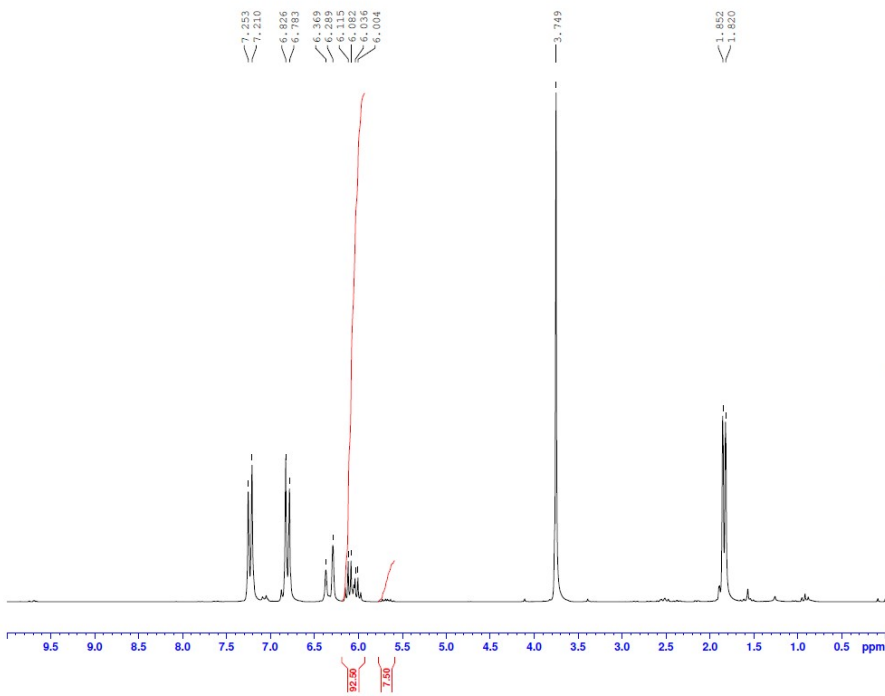
F2 - Processing parameters
SI         32768
SF         400.1300213 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         2.00
  
```

E/Z ratio of 4c (95:5).



<sup>1</sup>H-NMR spectrum of the crude **4d**





**BRUKER**

```

Current data Parameters
NAME      M.Vilchez-mvnc144
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20210212
Time     12.37
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD       32768
SOLVENT  CDCl3
NS       2
DS       2
SFO      4006.410 Hz
FIDRES   0.122266 Hz
AQ       4.8894465 sec
RG       128
DM       124.800 usec
DE       7.50 usec
TE       300.0 K
D1       1.00000000 sec
TD0      1

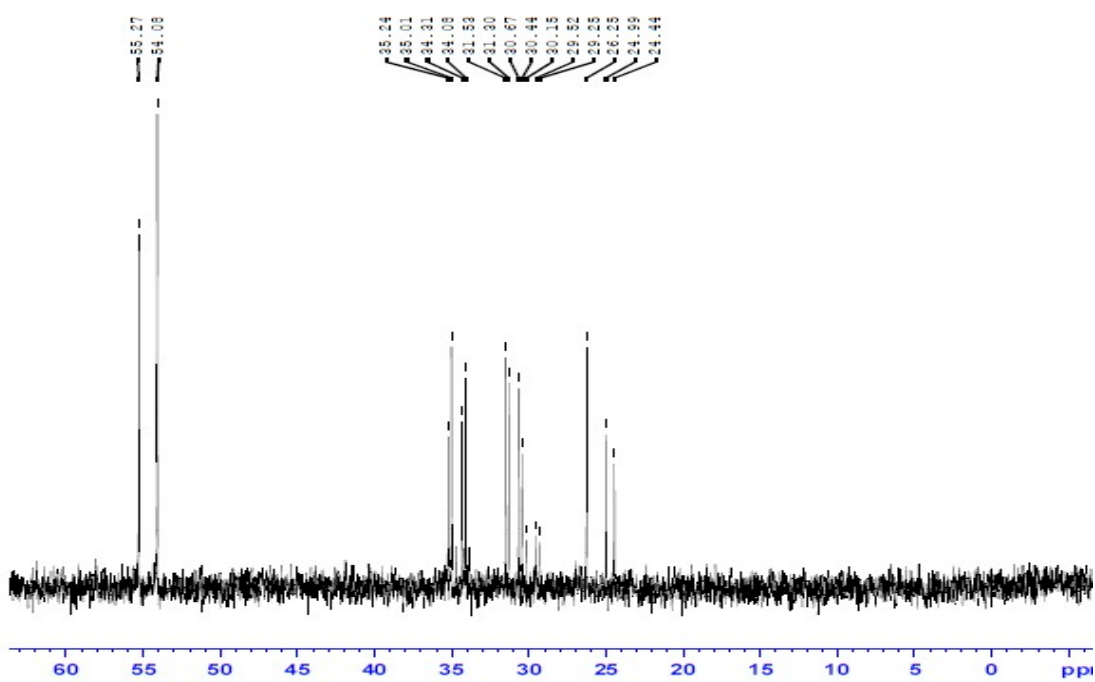
----- CHANNEL f1 -----
NUC1     1H
P1       15.00 usec
PL1      9.70 dB
SFO1     200.1316411 MHz

F2 - Processing parameters
SI       32768
SF       200.1300167 MHz
RG       64
SFO      400.1300167 MHz
SSB      0
LB       0.30 Hz
GB       0
PC       2.00

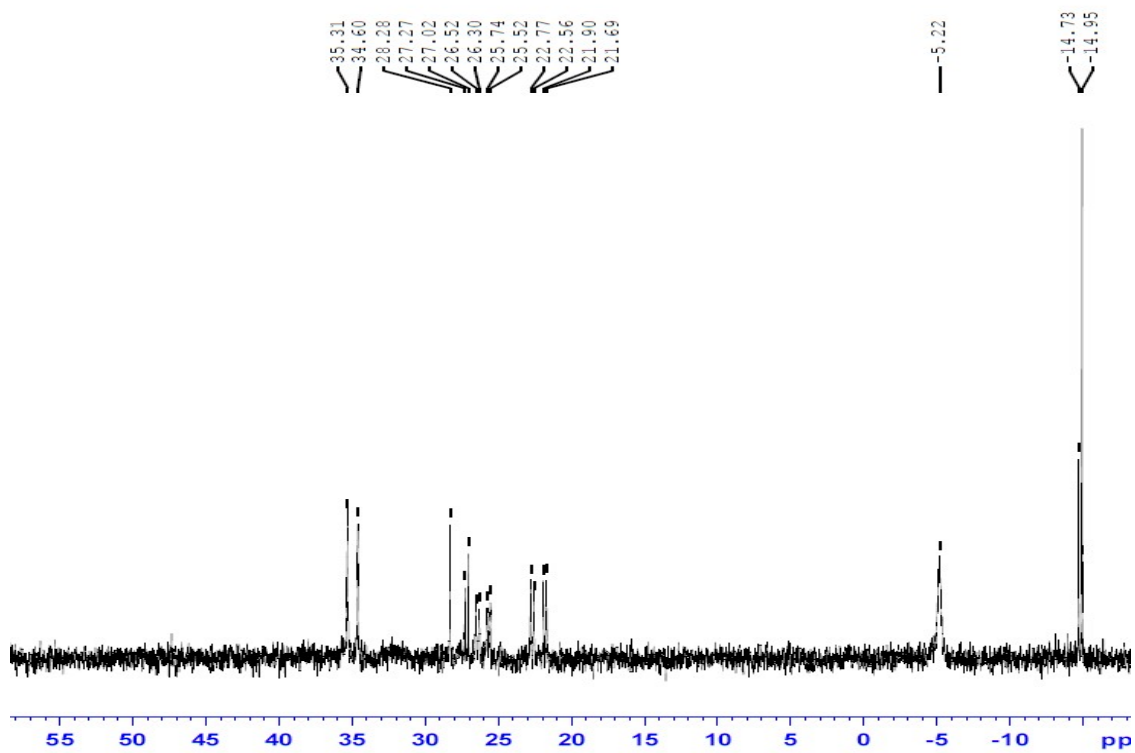
```

E/Z ratio of **4d** (93:7).

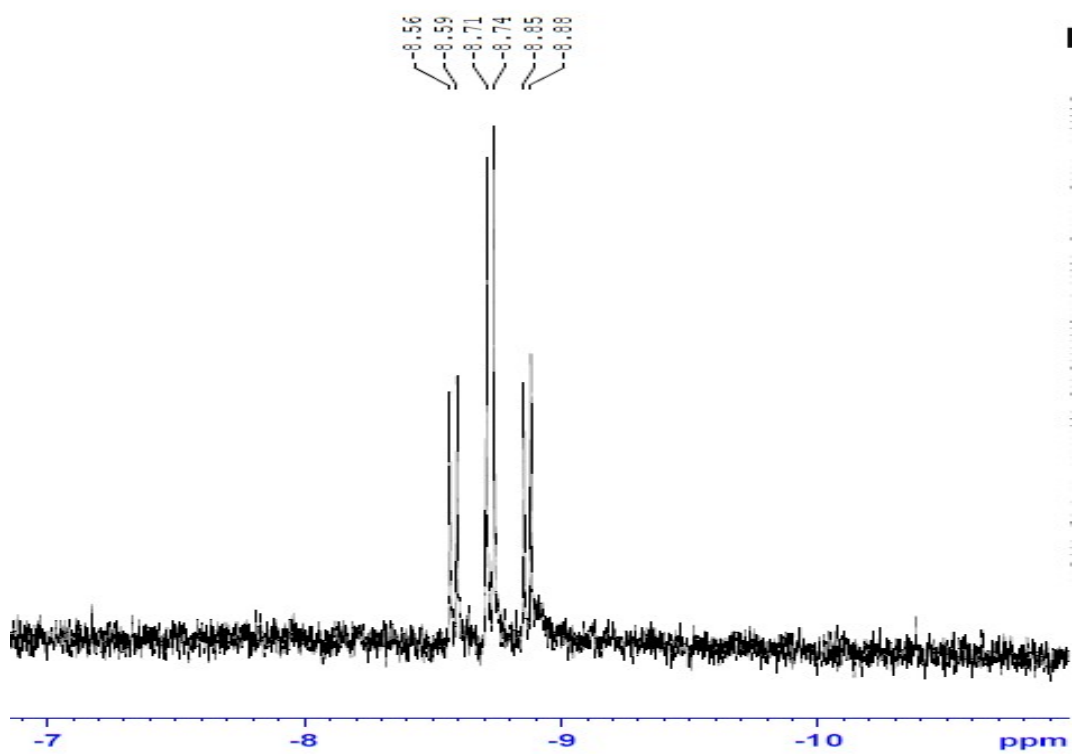
$^{31}\text{P}$ -NMR spectrum of the mixture  $[\text{Rh}(\text{acac})(\text{CO})_2]/(S)\text{-BINAP}/\text{PPh}_3$



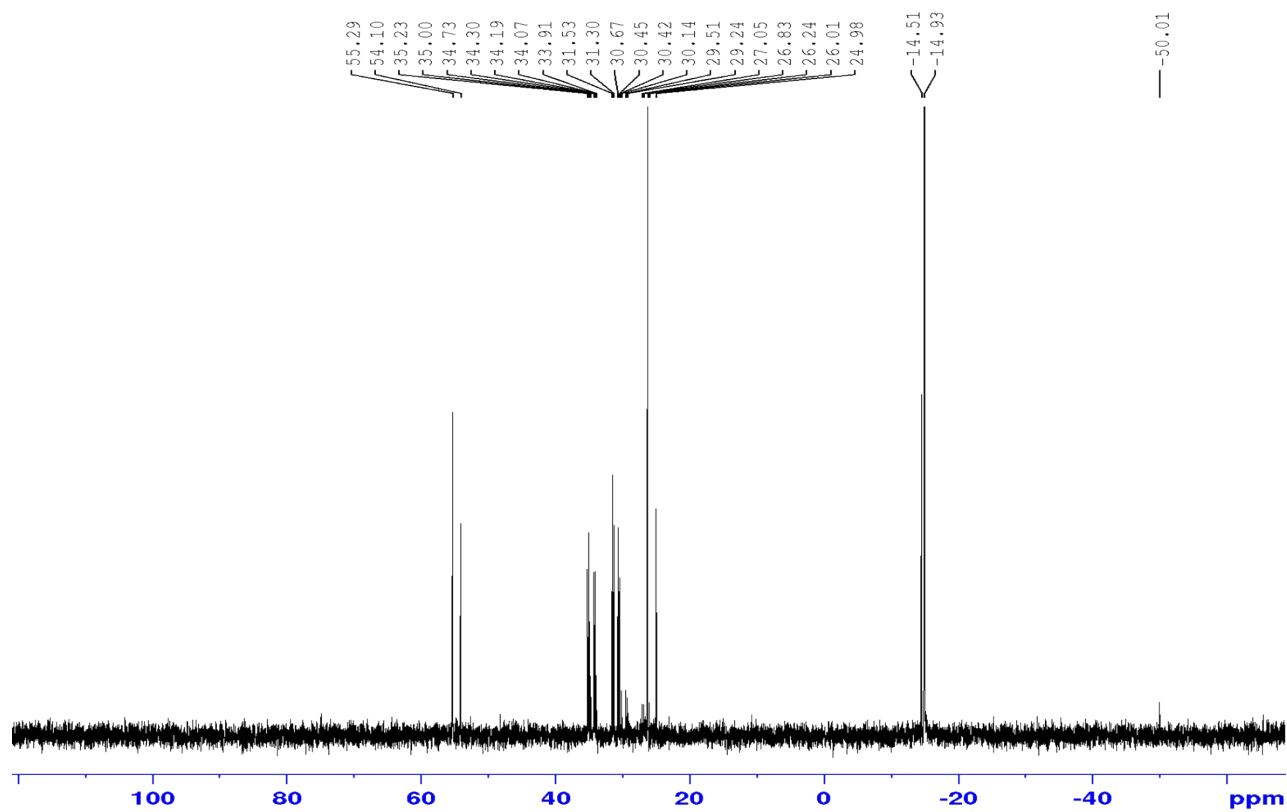
$^{31}\text{P}$ -NMR spectrum of the mixture  $[\text{Rh}(\text{acac})(\text{CO})_2]/(S)\text{-BINAP}/\text{PPh}_3/\text{HCHO}$



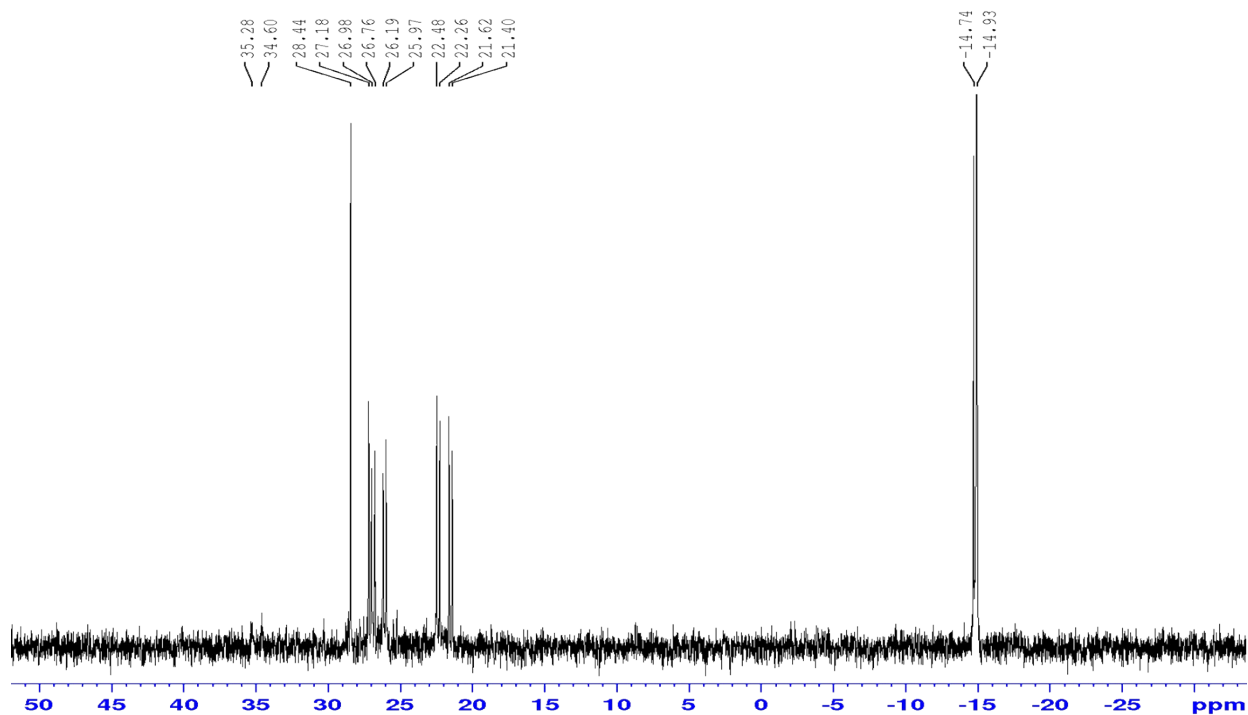
<sup>1</sup>H-NMR spectrum of the mixture  $[\text{Rh}(\text{acac})(\text{CO})_2]/(S)\text{-BINAP}/\text{PPh}_3/\text{HCHO}$



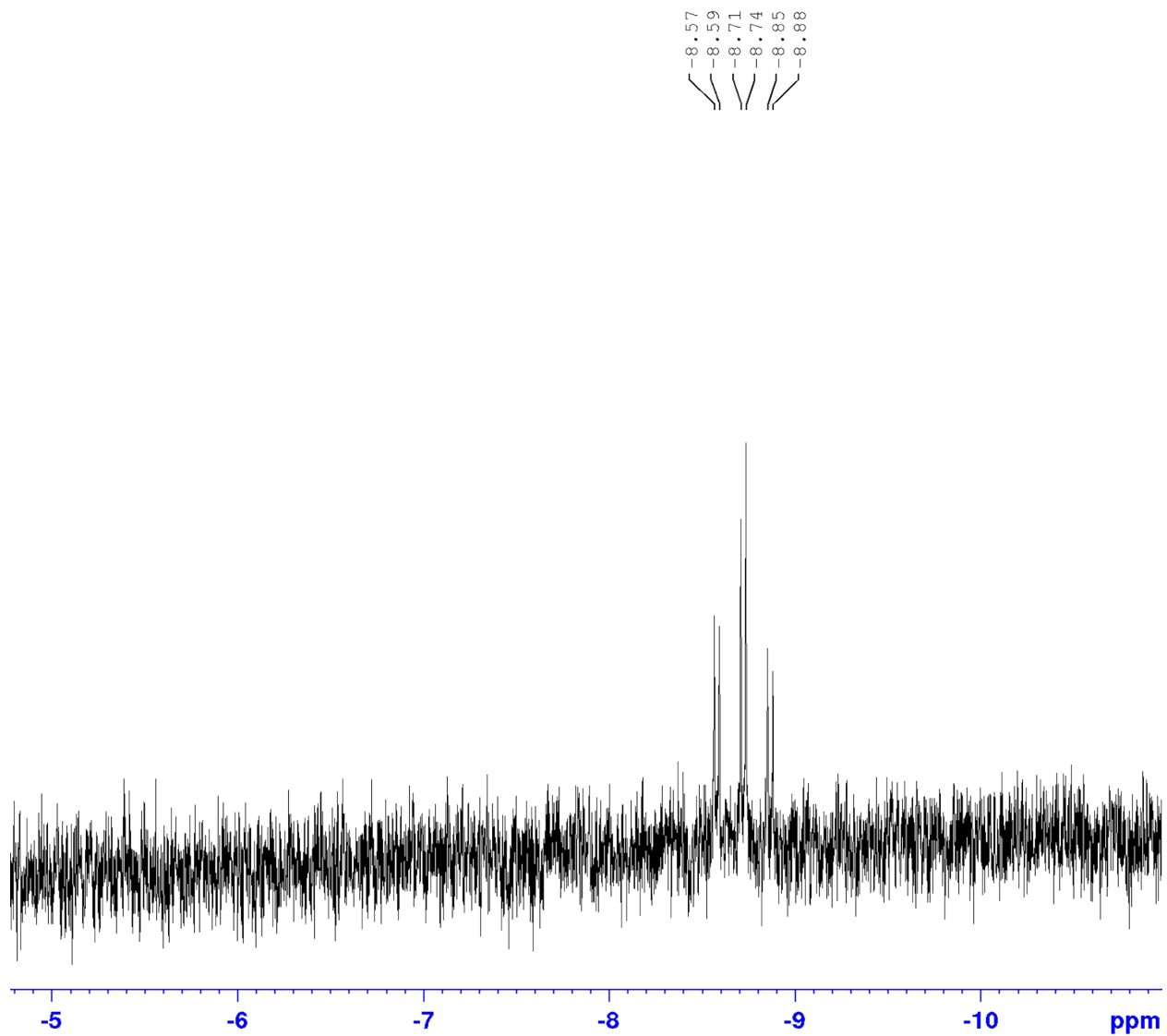
$^{31}\text{P}$ -NMR spectrum of the mixture  $[\text{Rh}(\text{acac})(\text{CO})_2]/(S)\text{-BINAP}$



$^{31}\text{P}$ -NMR spectrum of the mixture  $[\text{Rh}(\text{acac})(\text{CO})_2]/(S)\text{-BINAP}/\text{HCHO}$

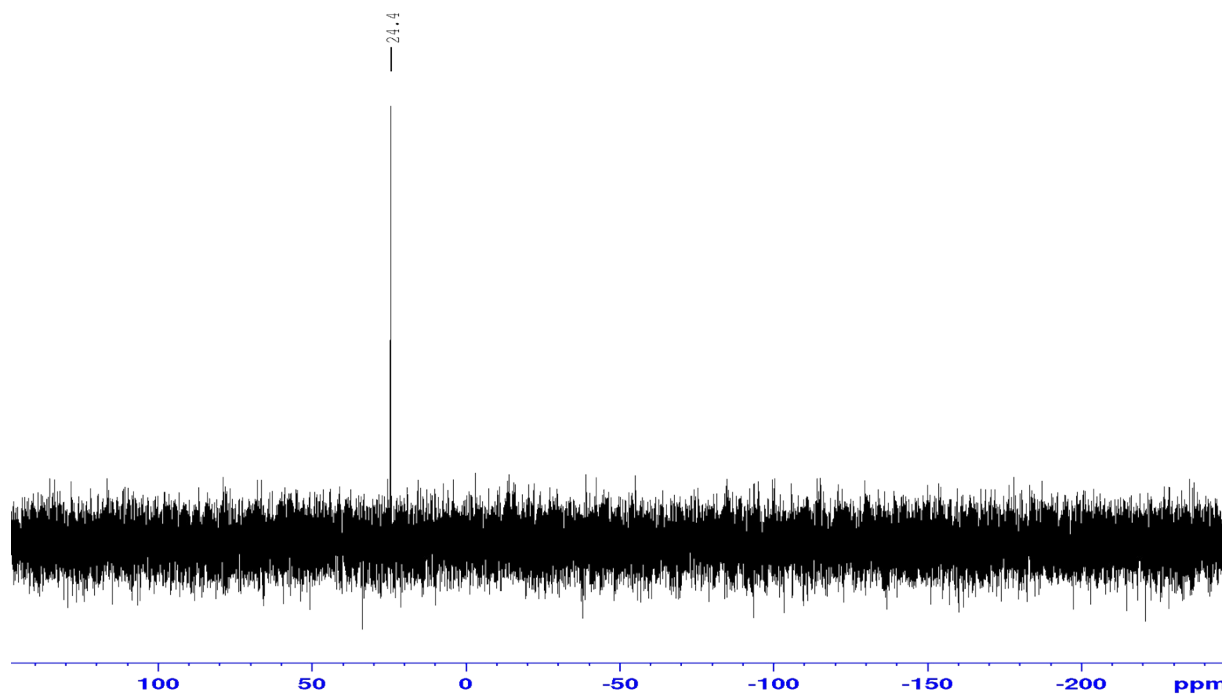


$^1\text{H-NMR}$  spectrum of the mixture  $[\text{Rh}(\text{acac})(\text{CO})_2]/(S)\text{-BINAP/HCHO}$



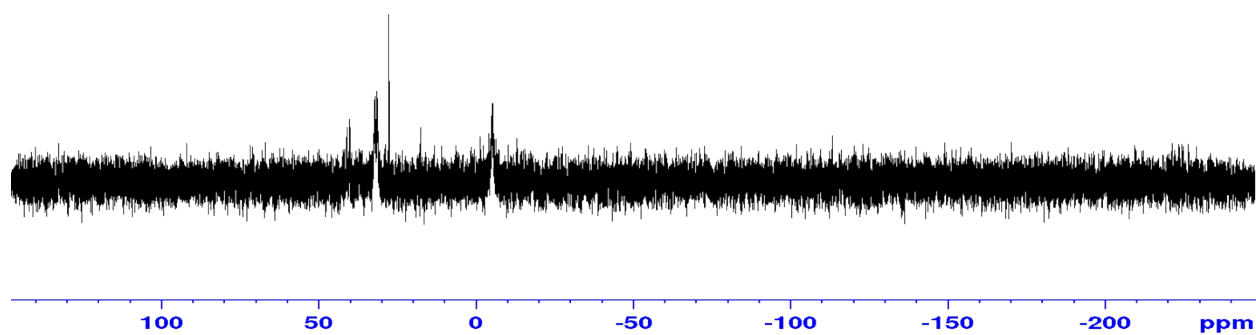
$^{31}\text{P}$ -NMR spectrum of the mixture  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_3$



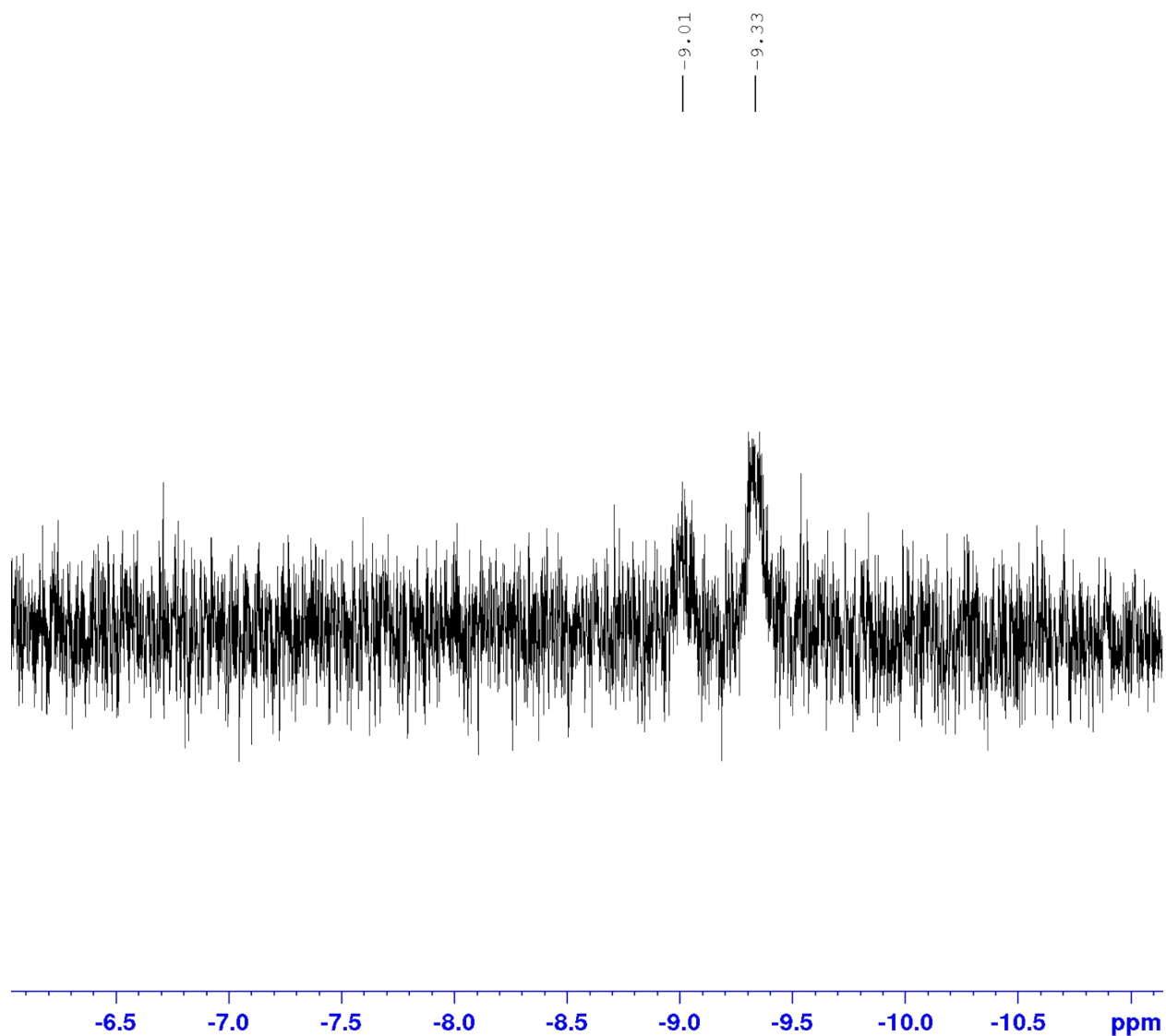


$^{31}\text{P}$ -NMR spectrum of the mixture  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_3/\text{HCHO}$

40.1  
32.1  
31.5  
27.6  
-5.2



$^1\text{H}$ -NMR spectrum of the mixture  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_3/\text{HCHO}$



## References

- 1 M. Vilches-Herrera, M. Concha-Puelles, N. Carvajal, J. Molina, R. Santander, M. Caroli Rezende, S. Lühr, Influence of the bite natural angle of bidentate diphosphine ligands in the syngas-free branched hydroformylation of  $\beta$ -functionalized olefins. *Catal. Comm.* 2018, 116, 61-66.