SUPPLEMENTARY INFORMATION

Development of Homogeneous and Heterogenized Rhodium(I) and Palladium(II) Complexes with Ligands Based on a Chiral Proton Sponge Building Block and their Application as Catalysts

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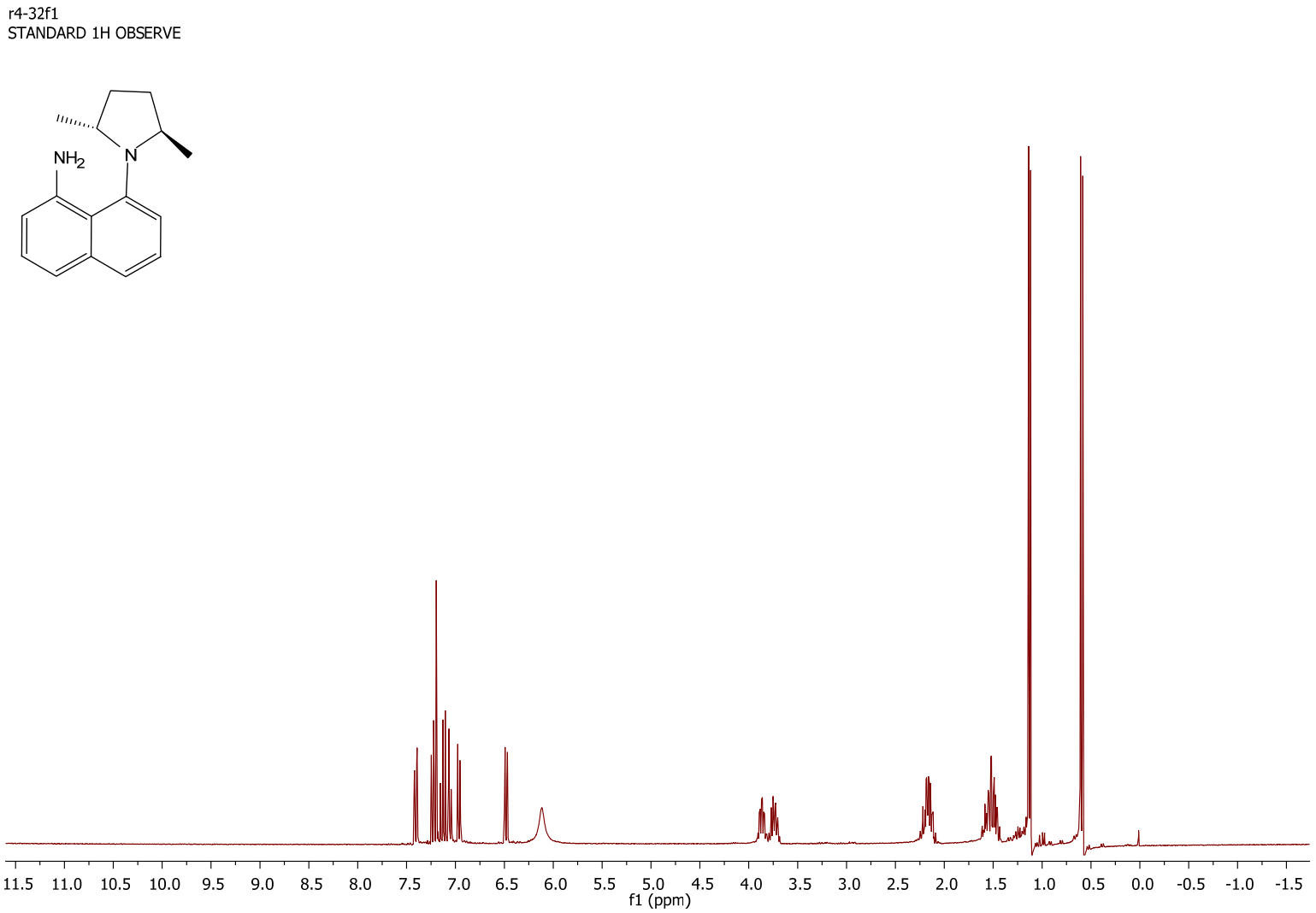
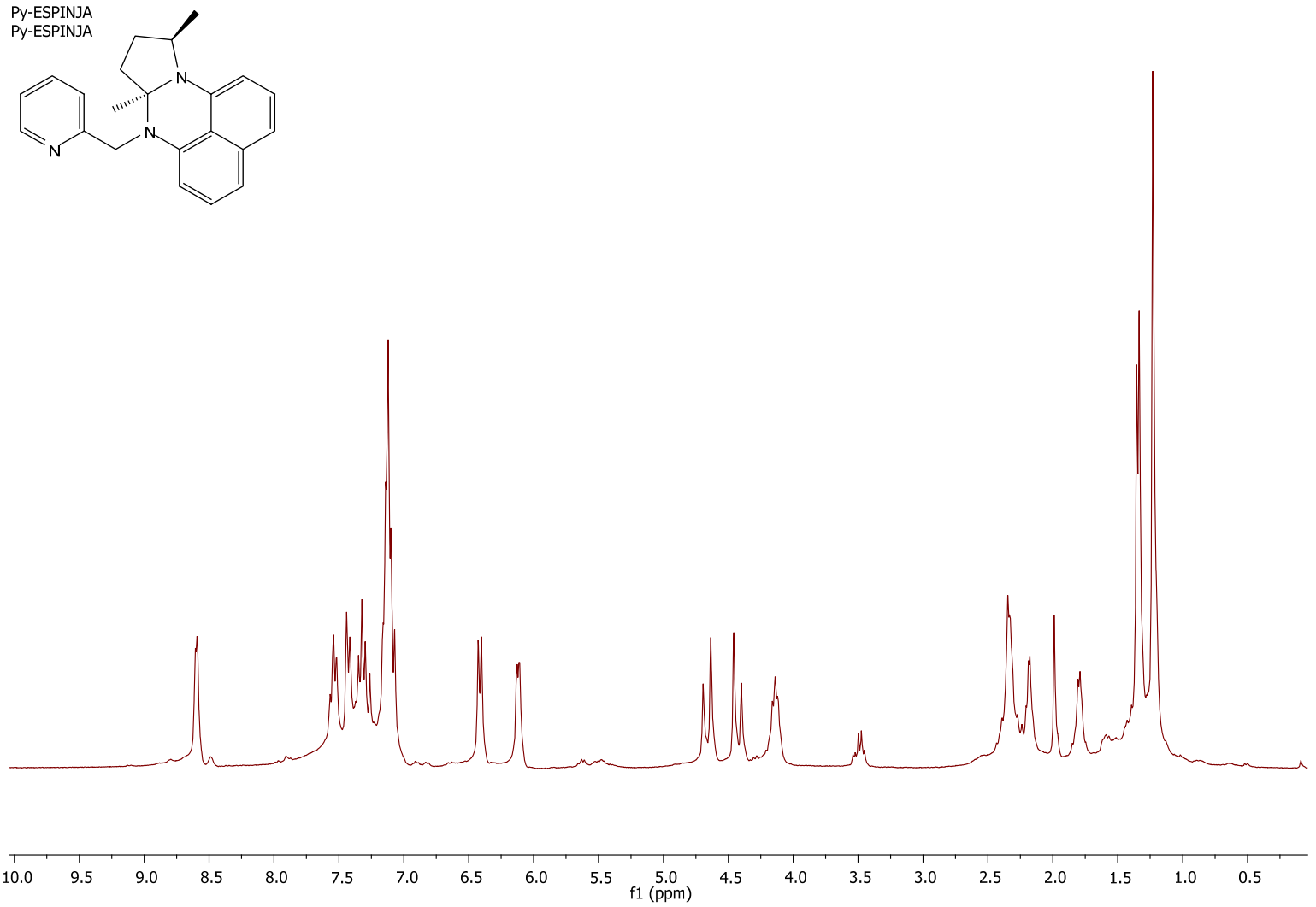
^{1}H-NMR
Starting chiral amine

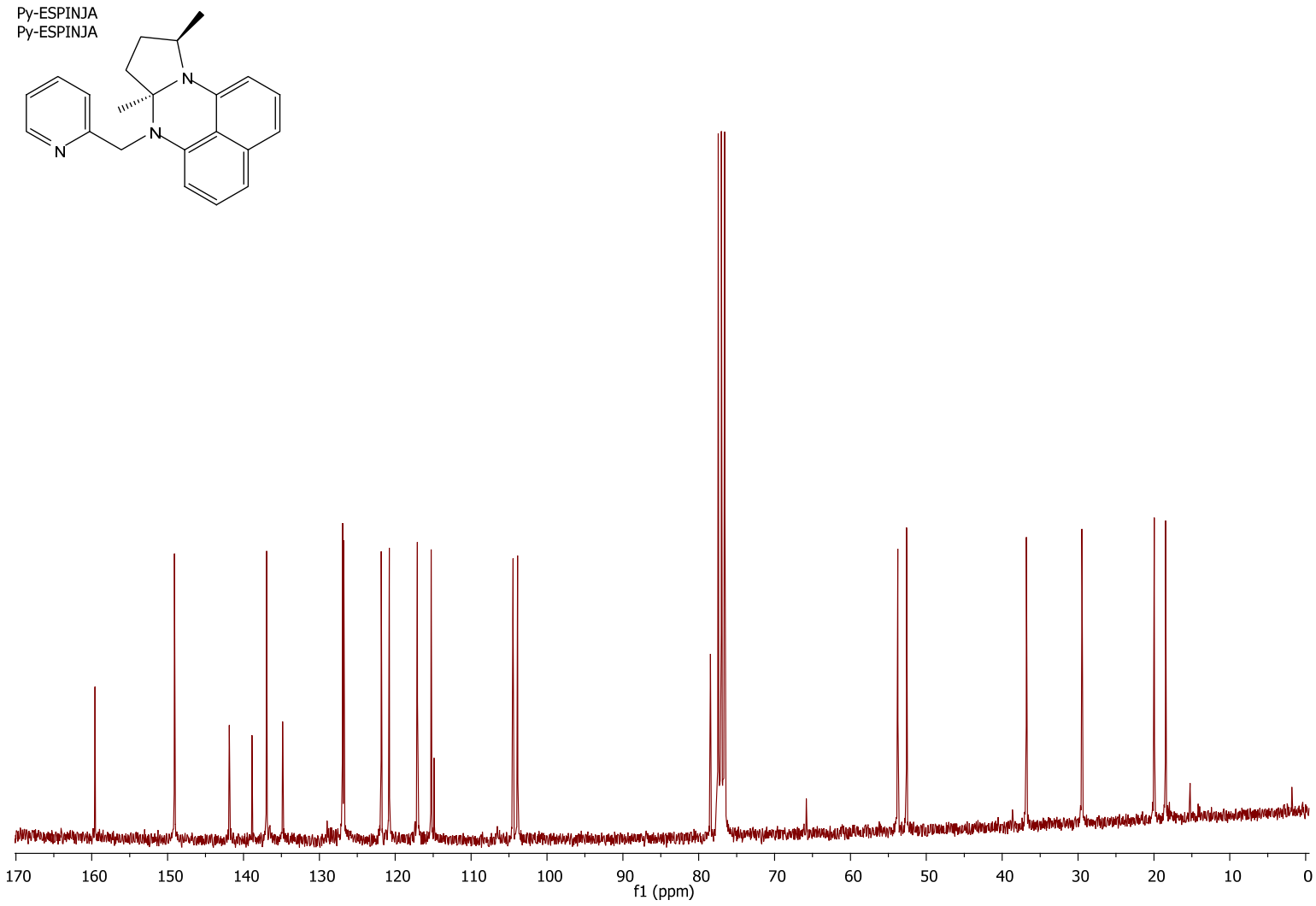


^{1}H-NMR

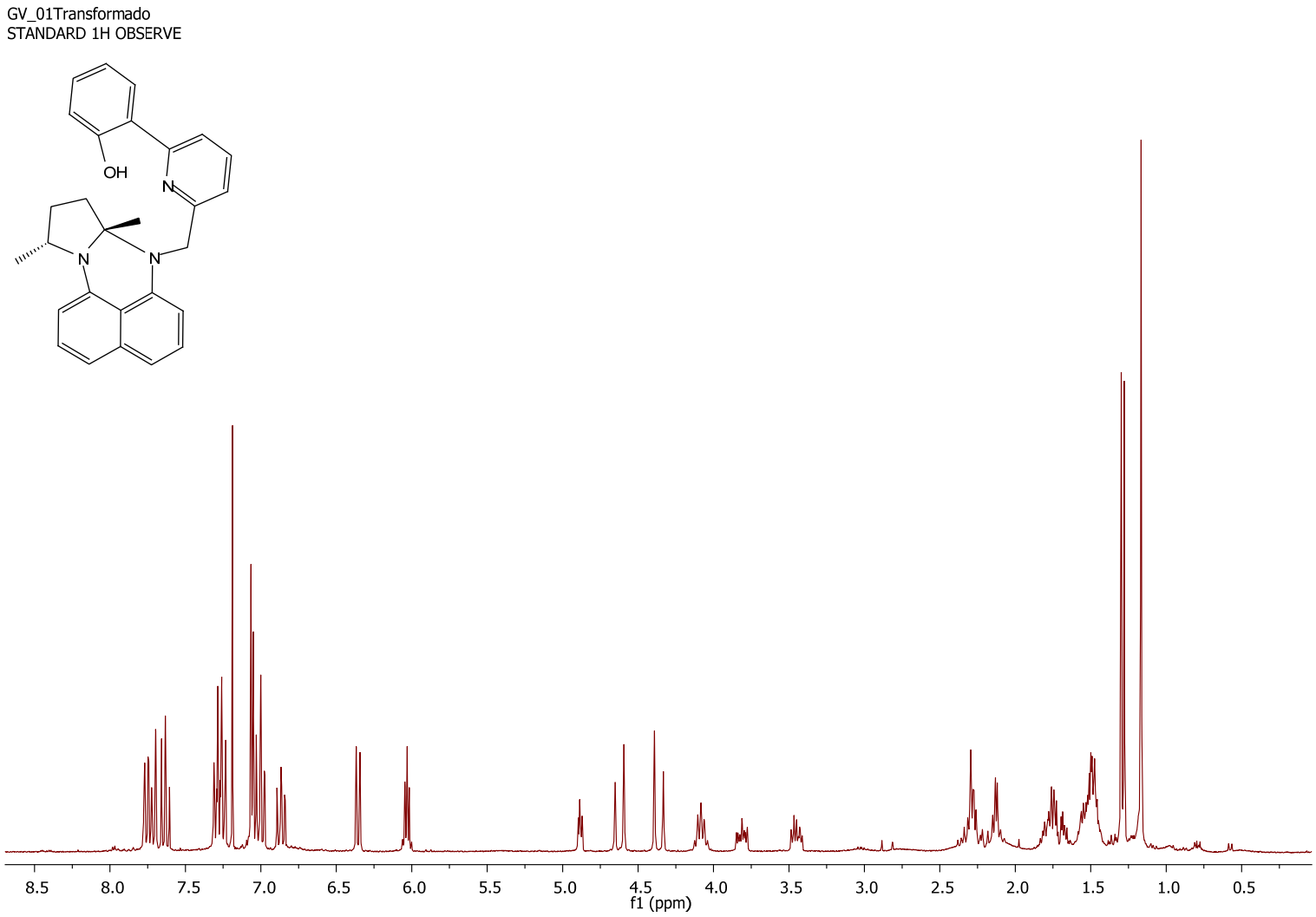
(R,R)-5



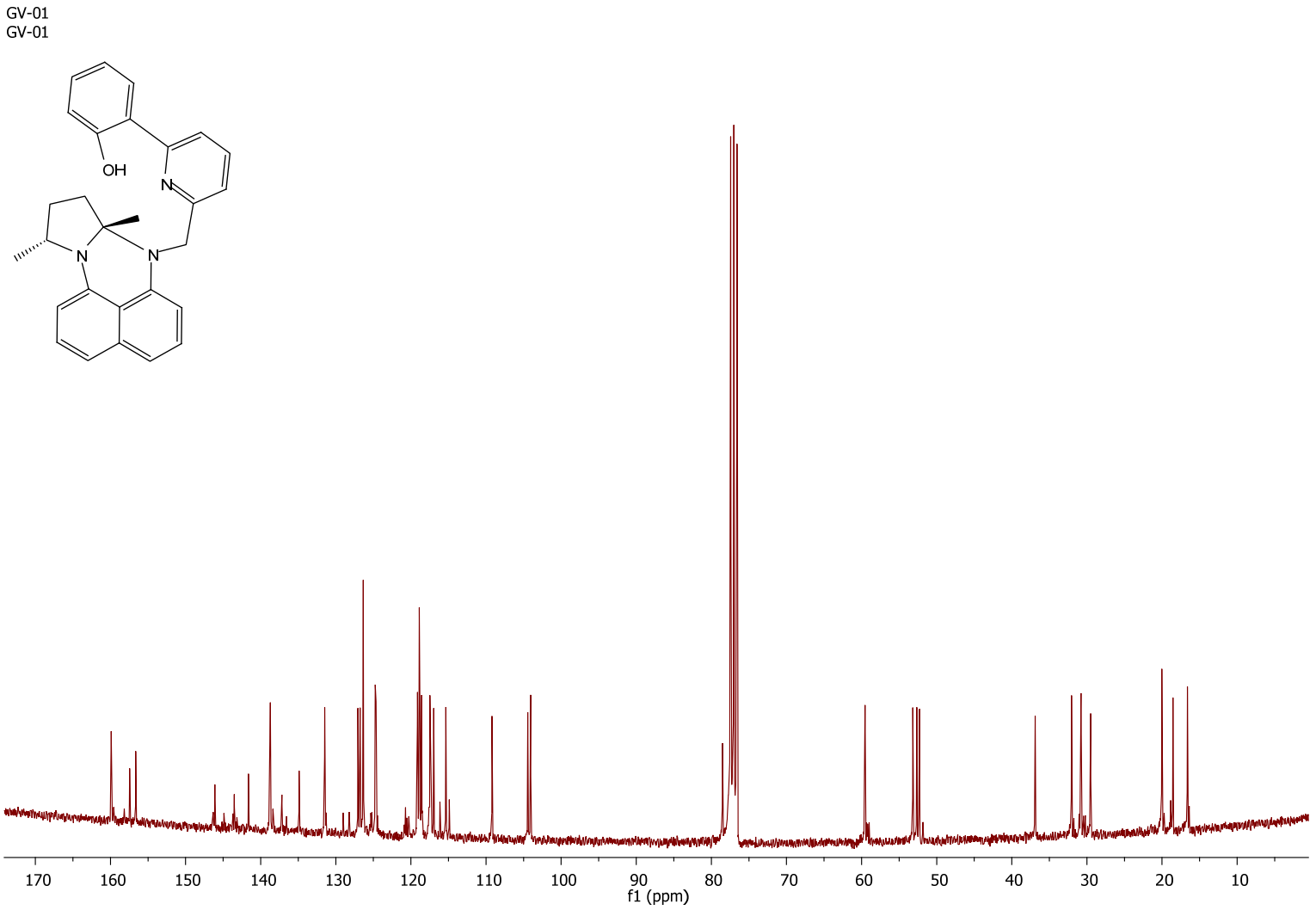
^{13}C-NMR (R,R)-5



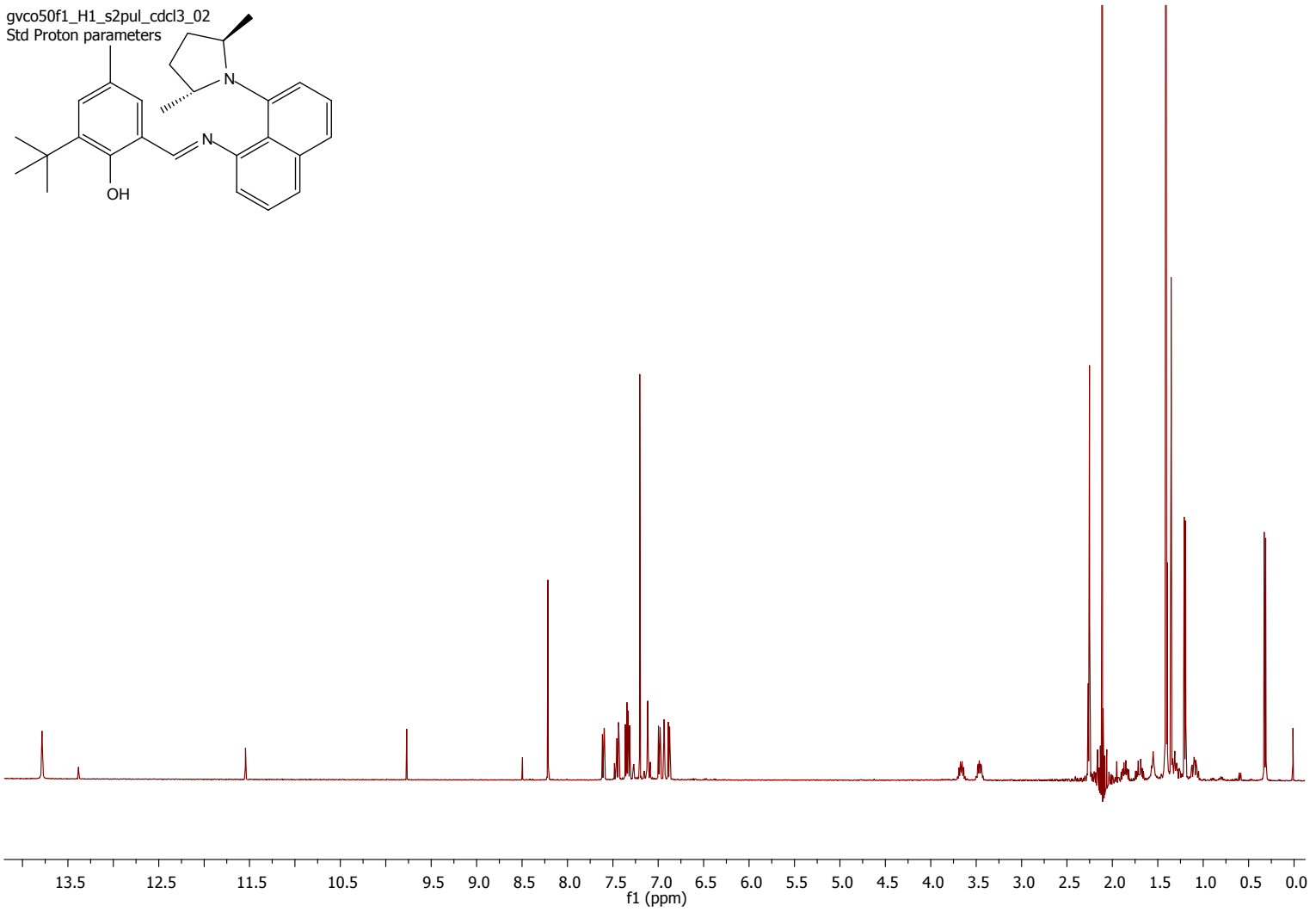
^{1}H-NMR (R,R)-6



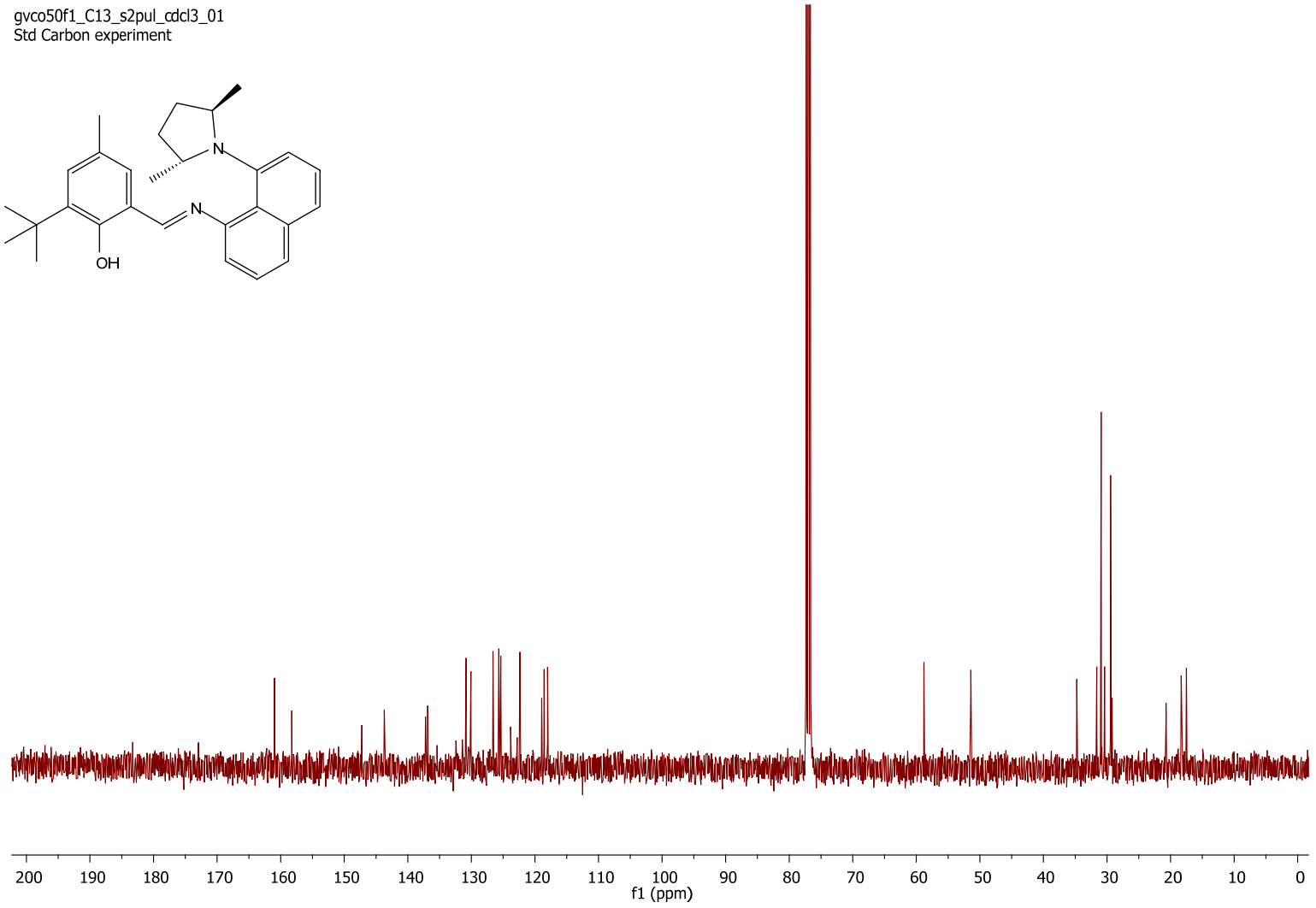
^{13}C-NMR (R,R)-6



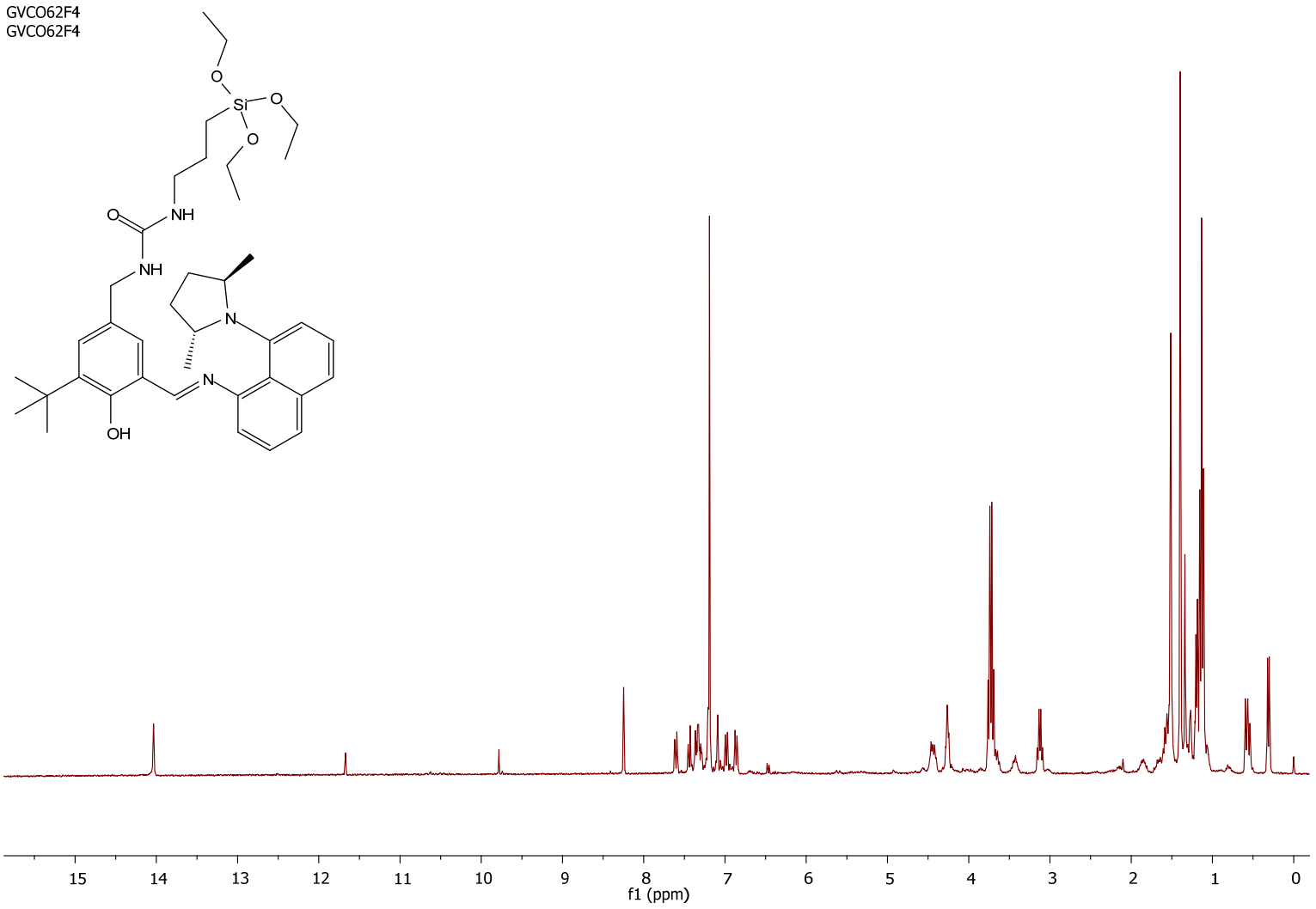
^{1}H-NMR. (R,R)-7



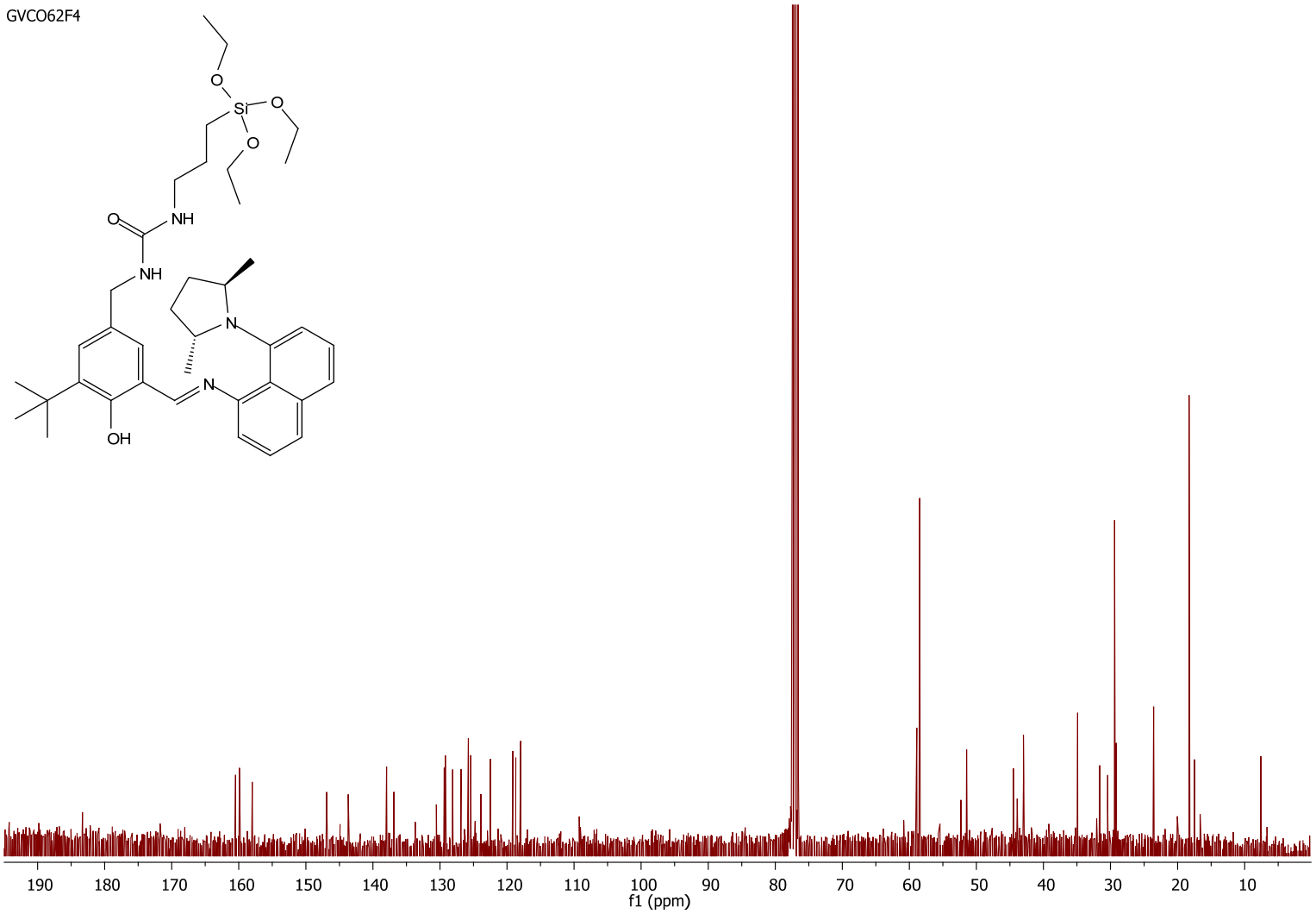
^{13}C-NMR (R,R)-7



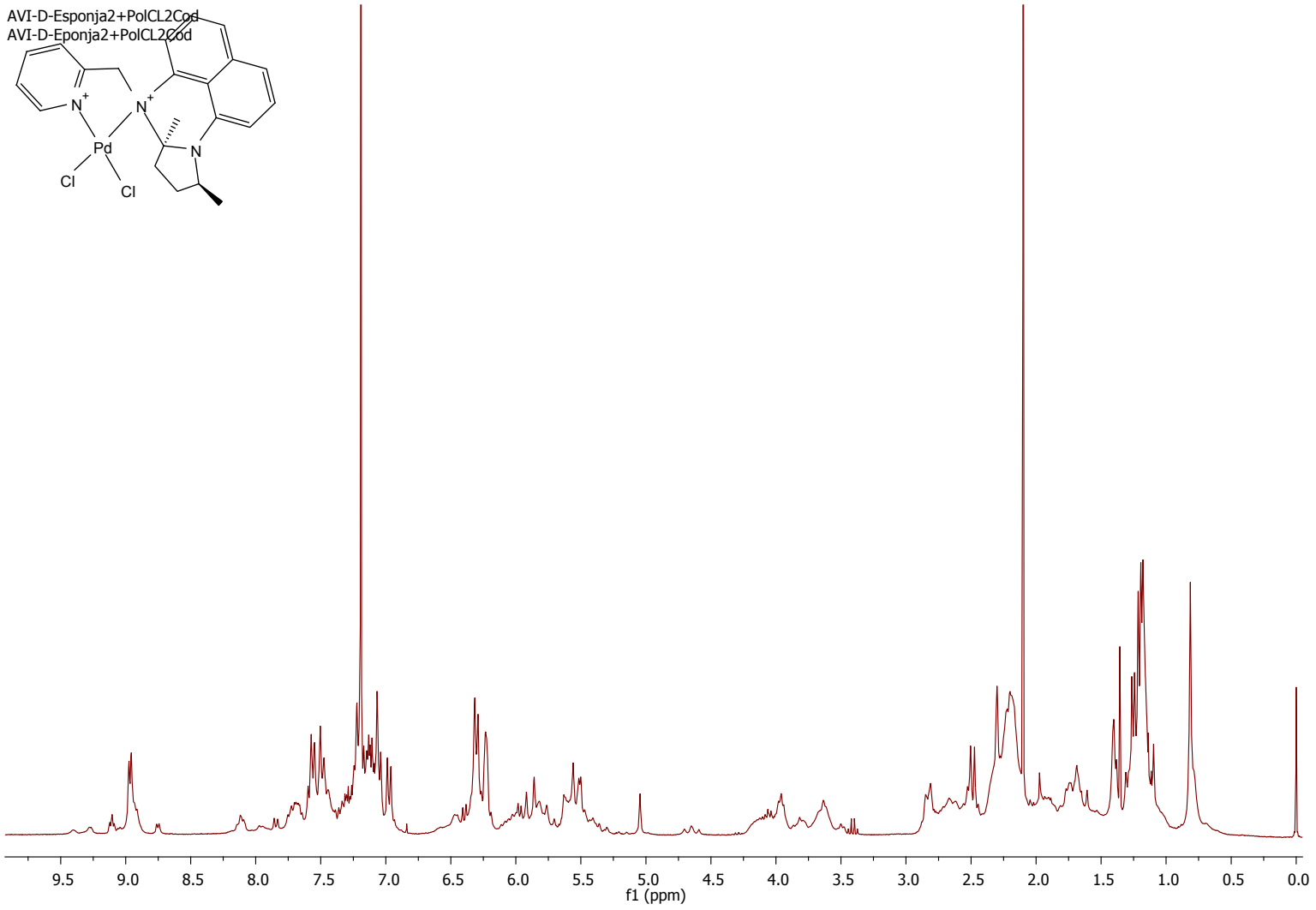
^{1}H-NMR (R,R)-8



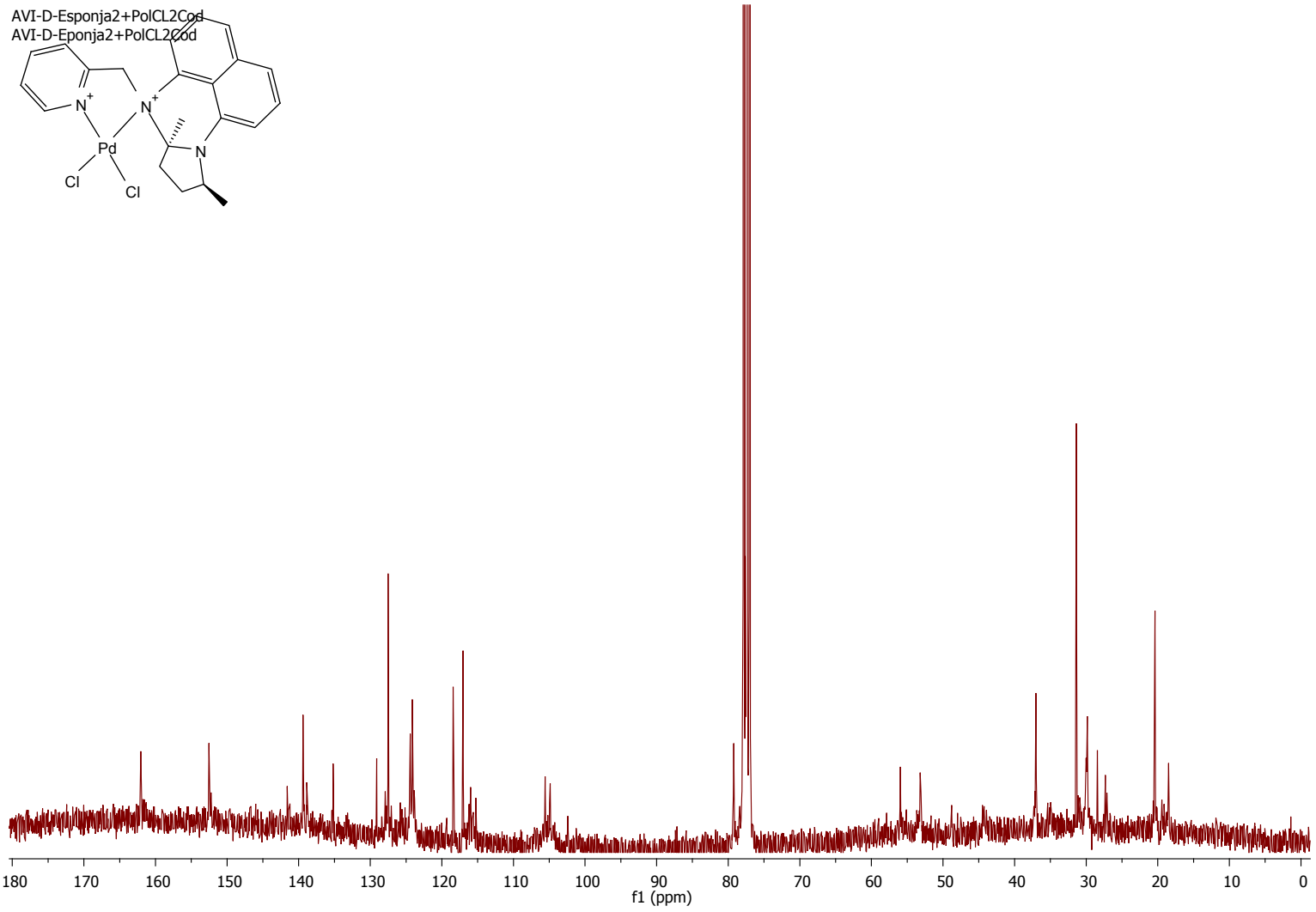
^{13}C-NMR (R,R)-8



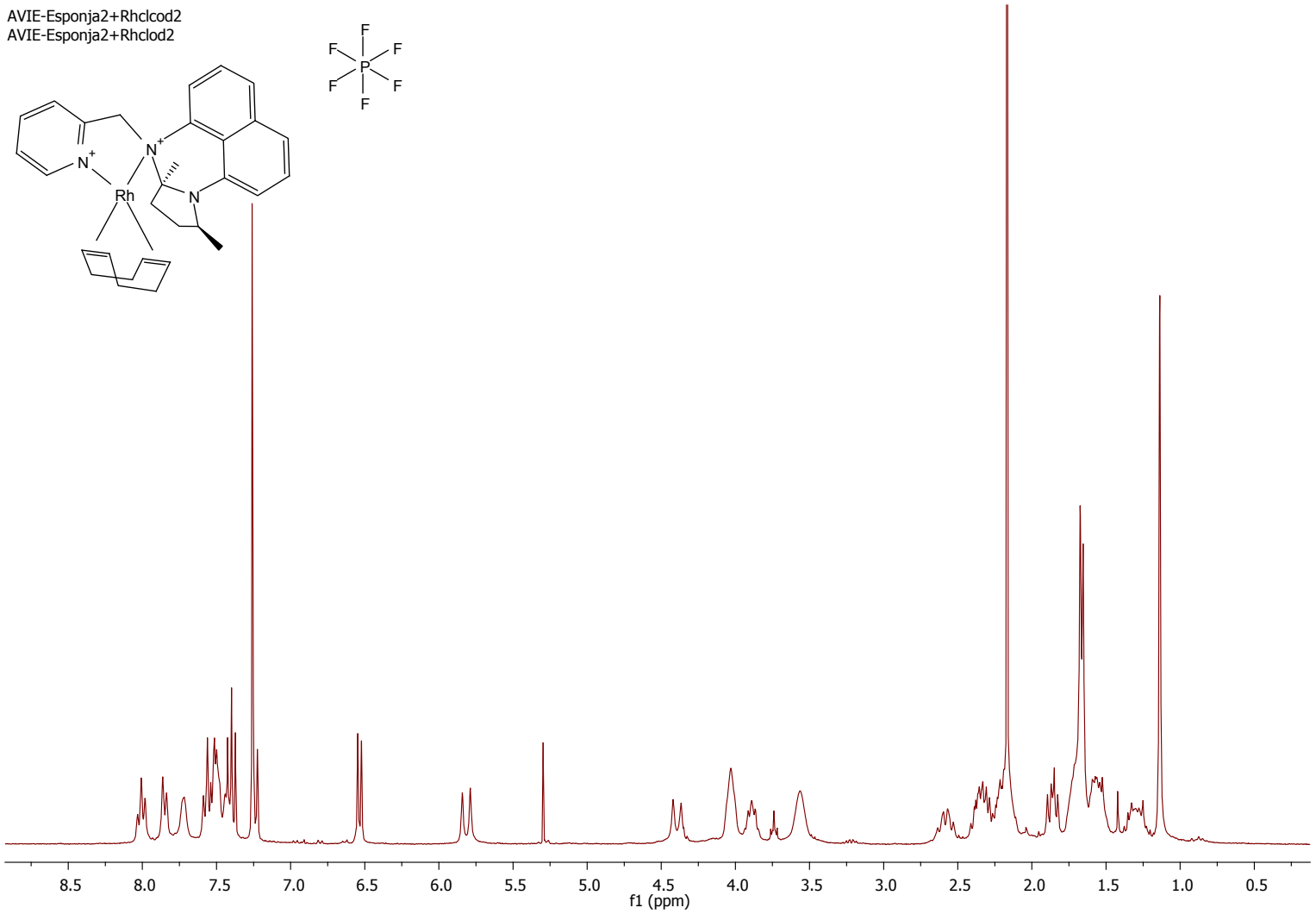
^{1}H-NMR (R,R)-5Pd



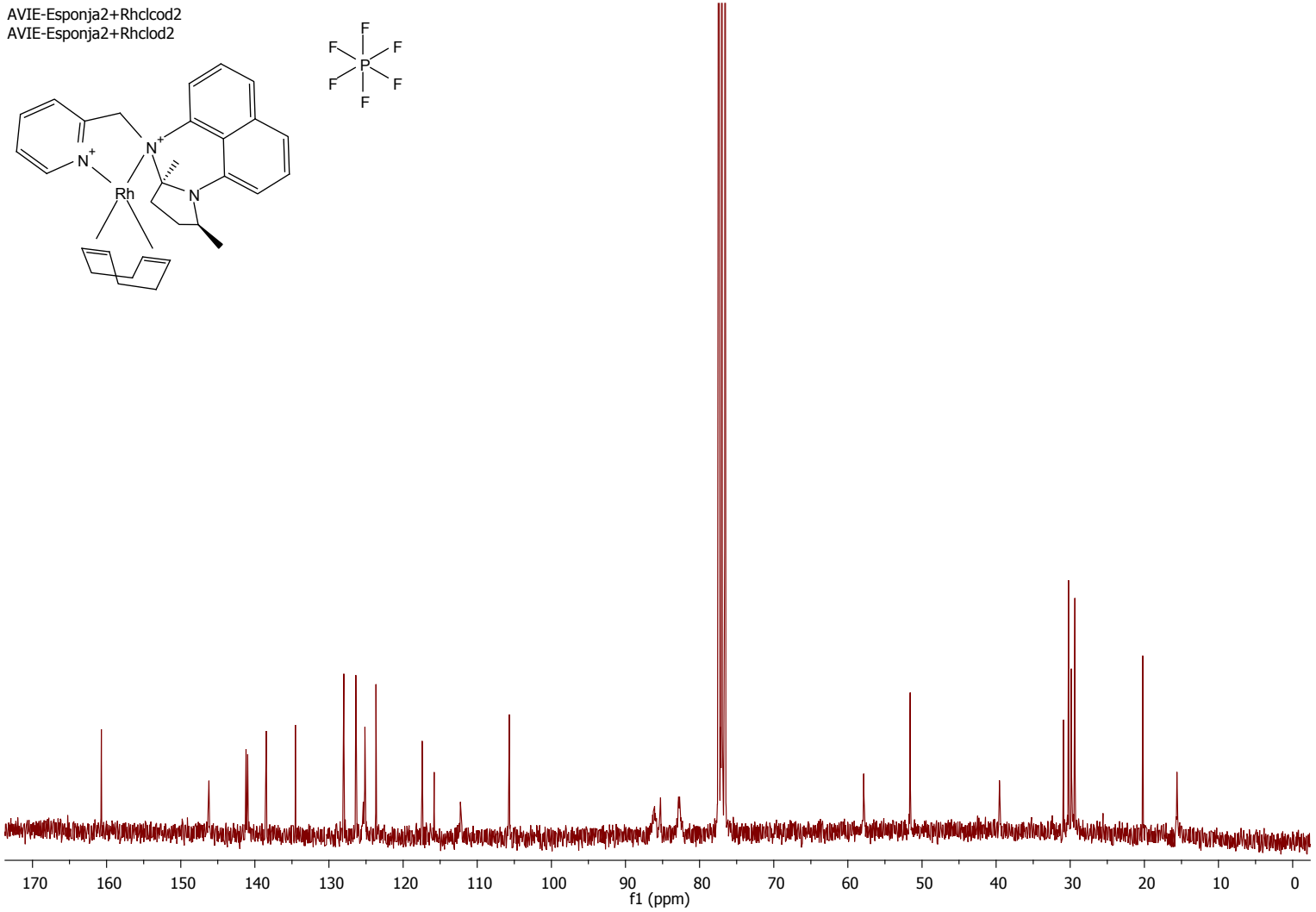
^{13}C-NMR (R,R)-5Pd



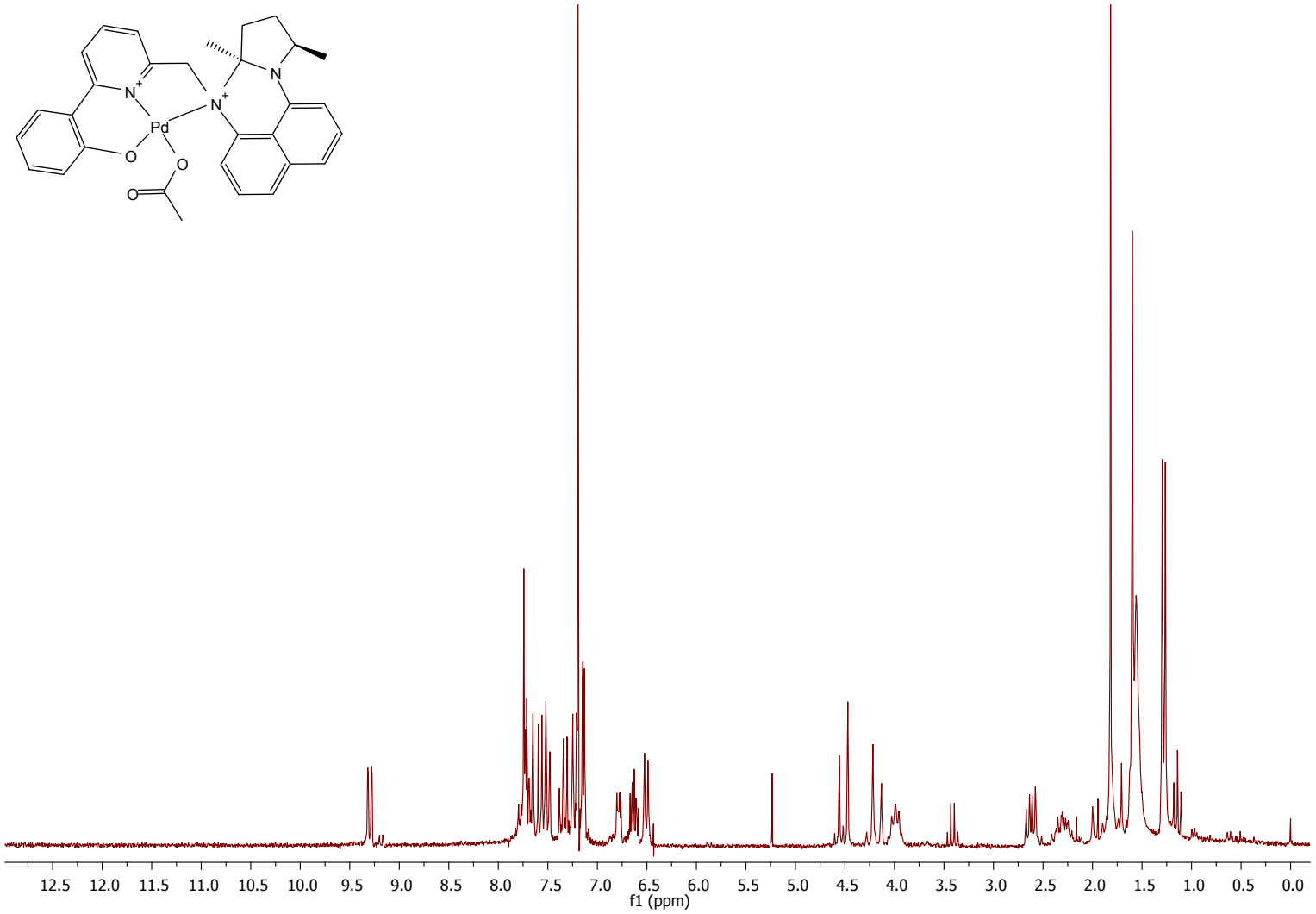
^{1}H-NMR (R,R)-5Rh



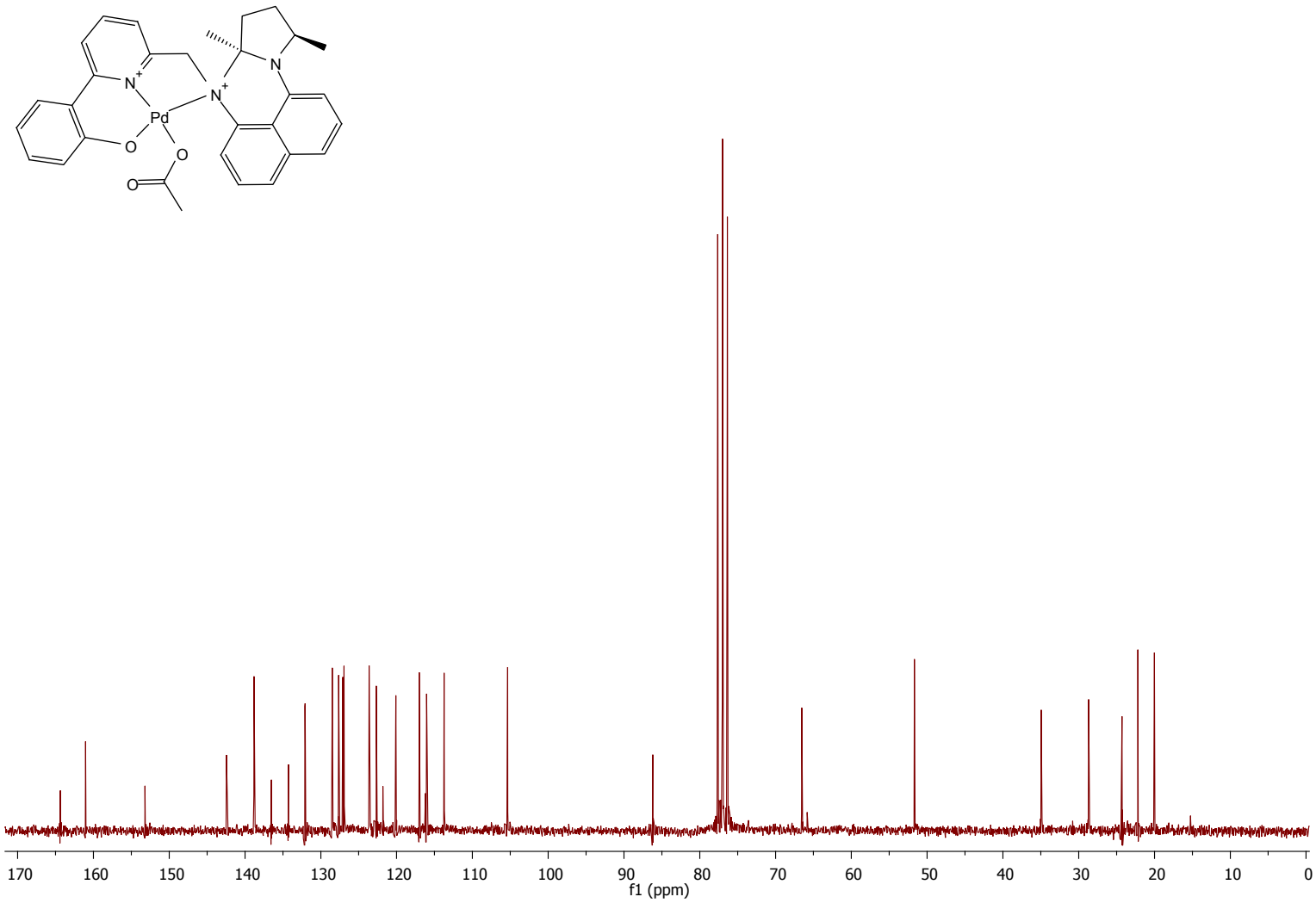
^{13}C-NMR (R,R)-5Rh



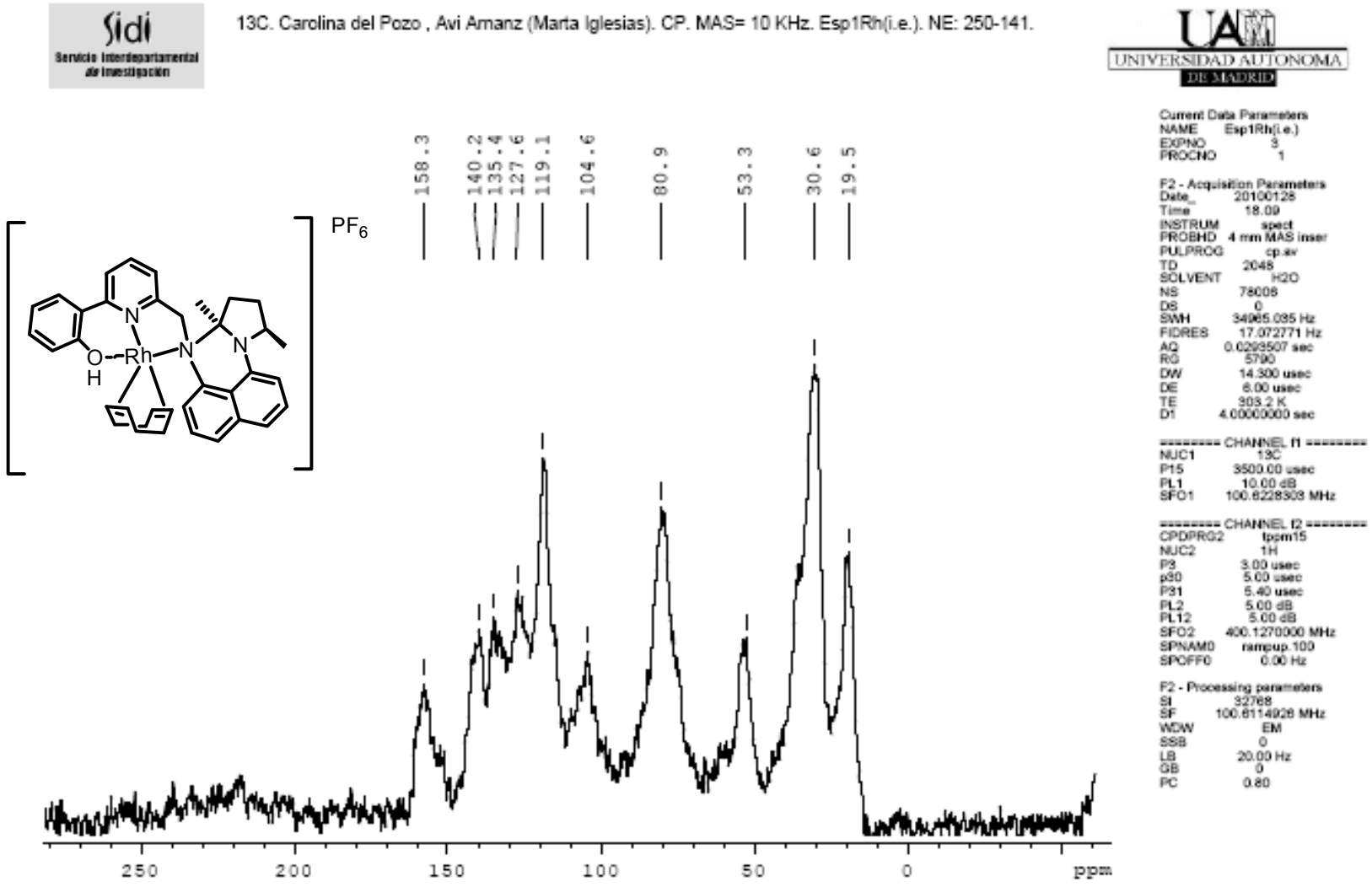
^{1}H-NMR (R,R)-6Pd



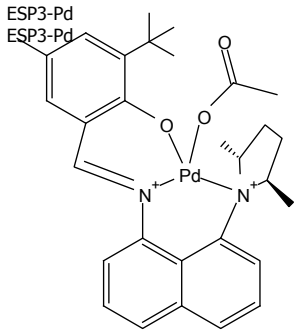
^{13}C-NMR (R,R)-6Pd



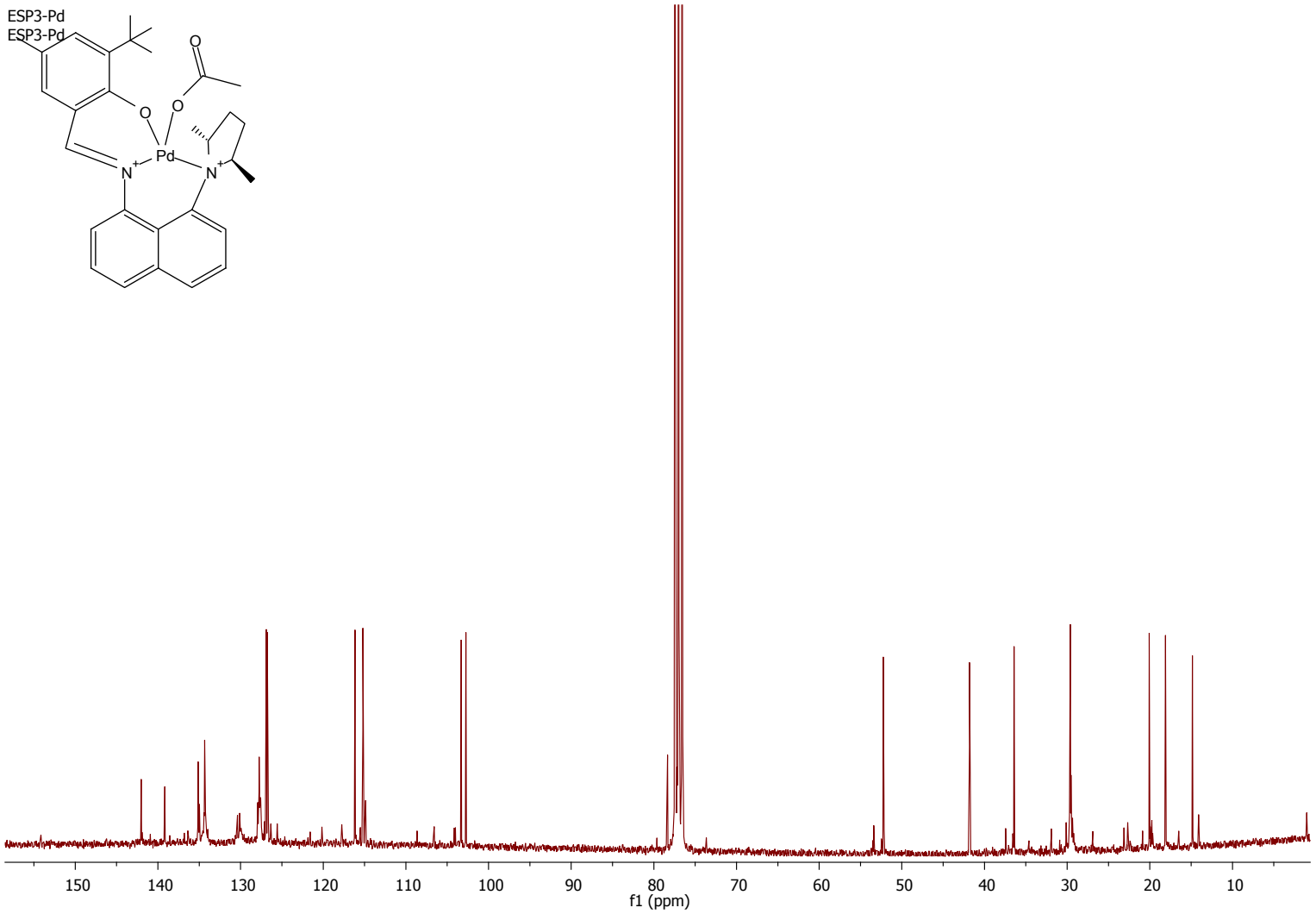
CP MAS ^{13}C-NMR (R,R)-6Rh-MCM



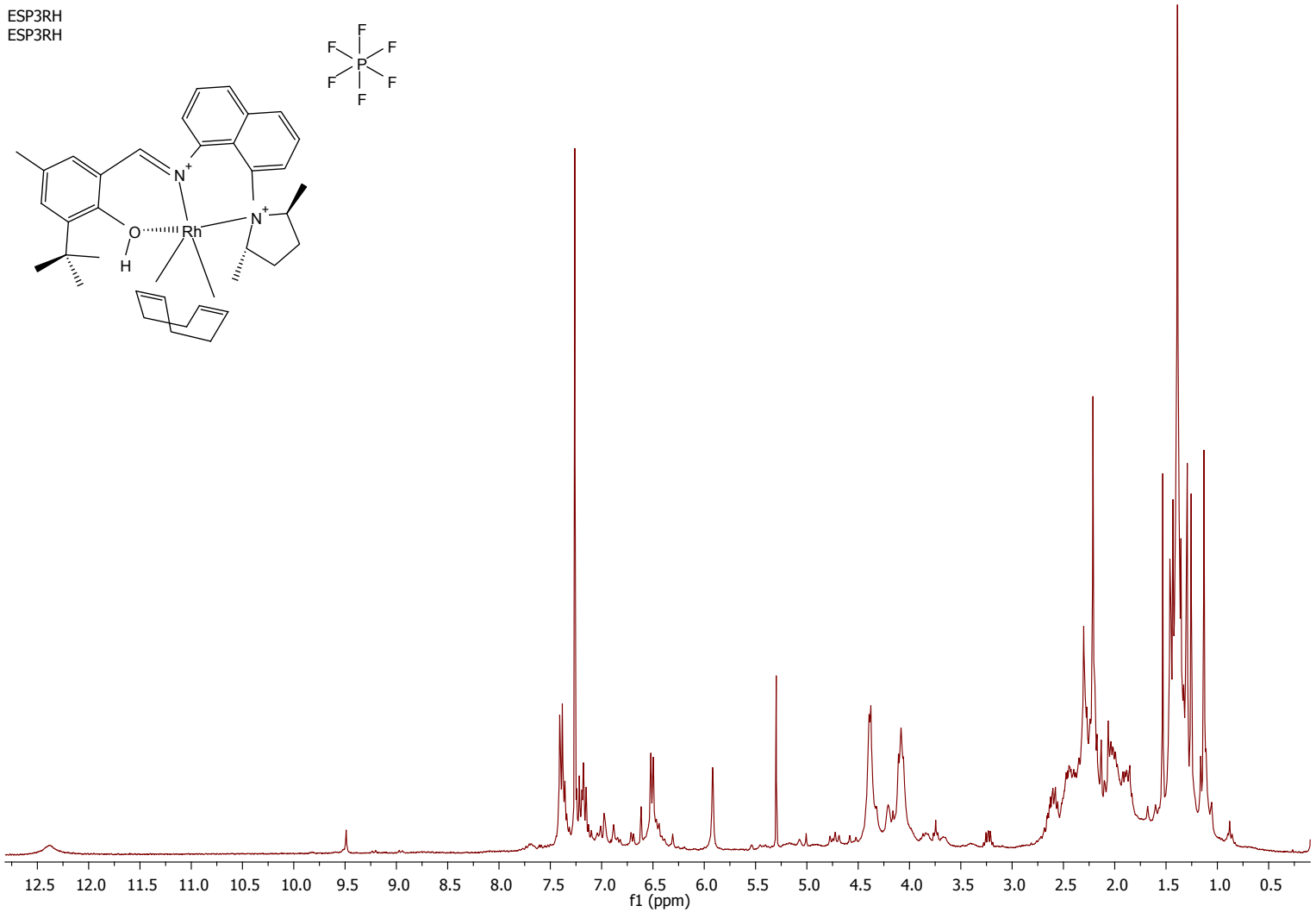
^{1}H-NMR (R,R)-7Pd



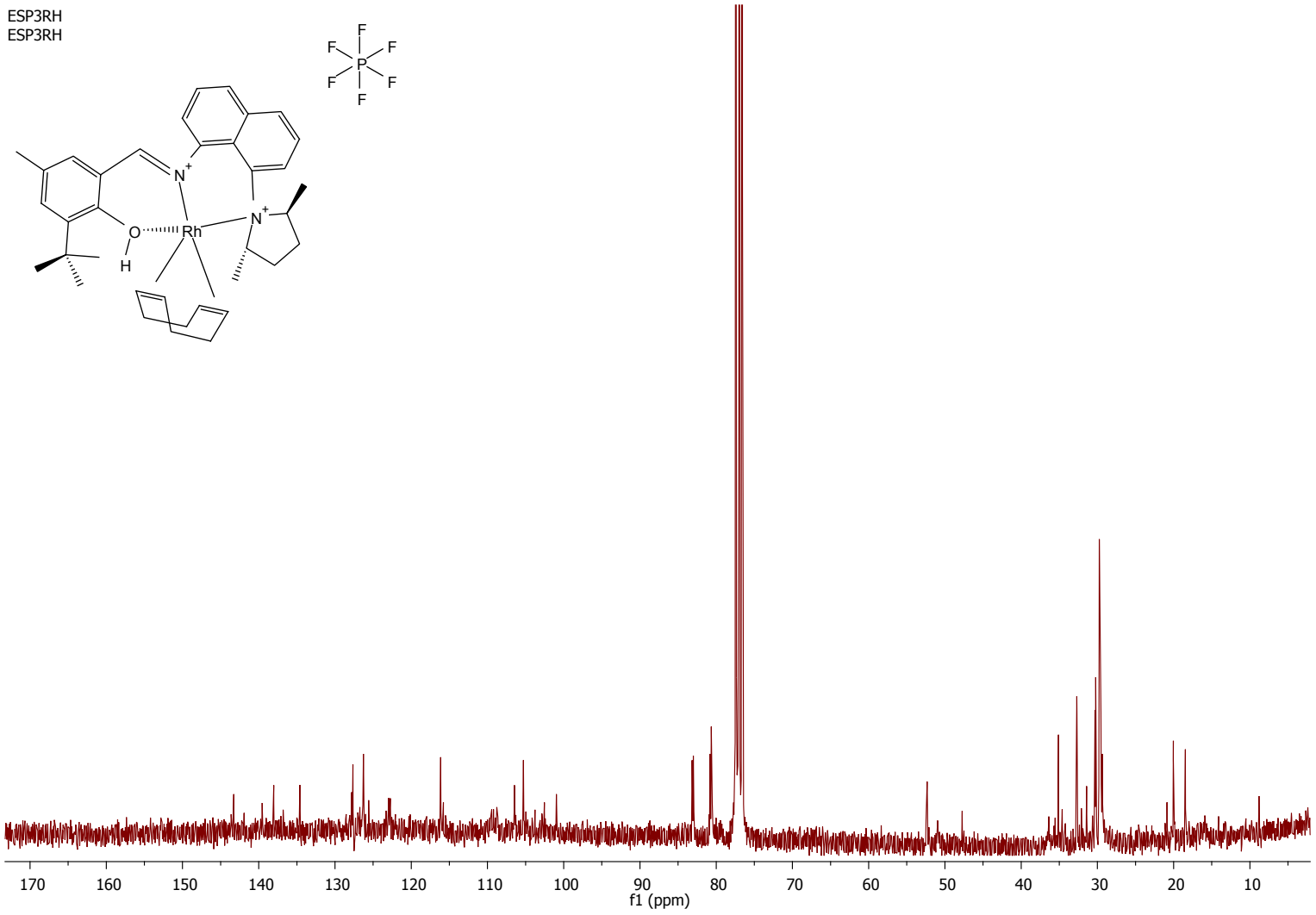
^{13}C-NMR (R,R)-7Pd



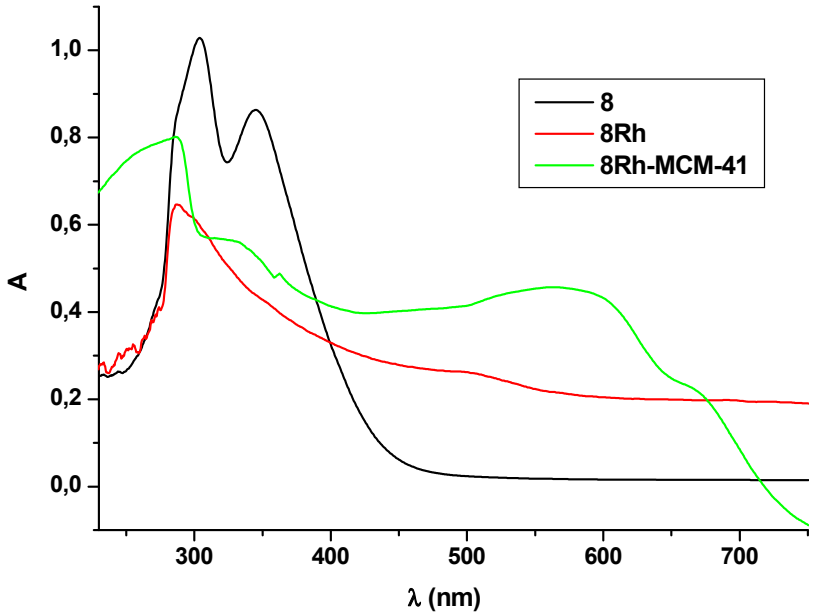
^{1}H-NMR (R,R)-8Rh

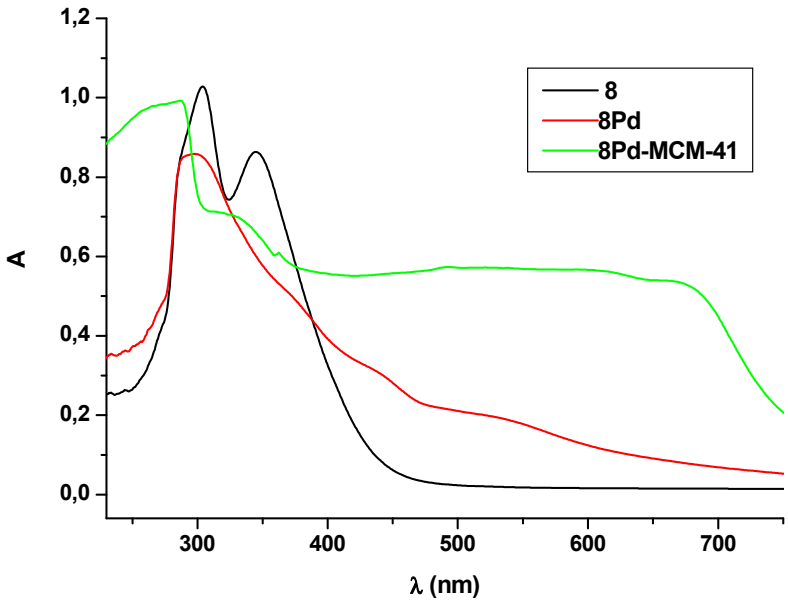

ESP3RH
ESP3RH
F
F
F
P
F
F
F
N+
N+
O
Rh
H
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

^{13}C-NMR (R,R)-8Rh

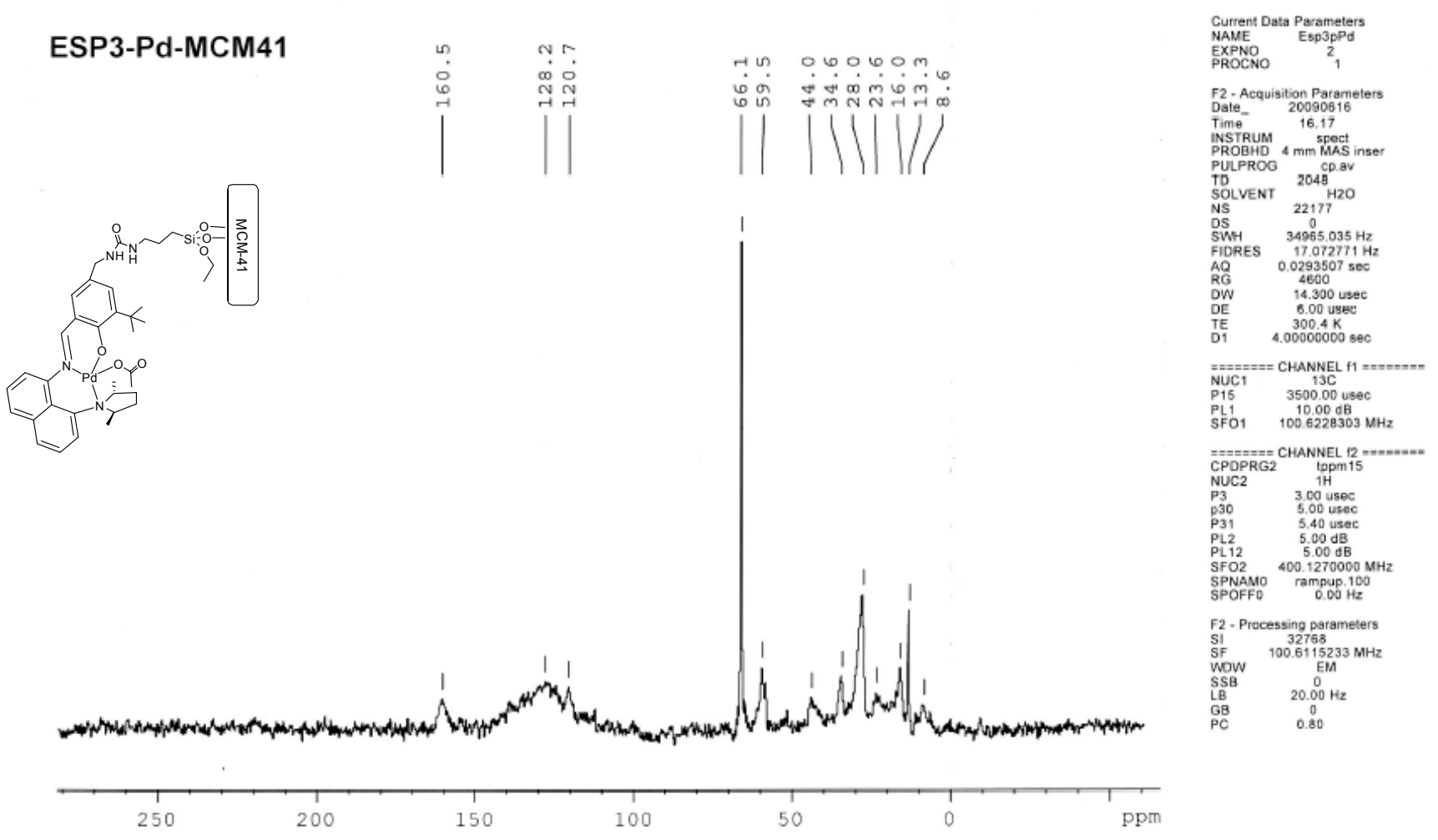


UV-Vis and DFTR





^{13}C-NMR 8Pd-MCM (CP MAS)



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PROCNO 1

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NS 22177
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FIDRES 17.072771 Hz
AQ 0.0293507 sec
RG 4600
DW 14.300 usec
DE 6.00 usec
TE 300.4 K
D1 4.00000000 sec

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P15 3500.00 usec
PL1 10.00 dB
SFO1 100.6228303 MHz

======== CHANNEL f2 ========
CPDPRG2 tppm15
NUC2 1H
P3 3.00 usec
p30 5.00 usec
P31 5.40 usec
PL2 5.00 dB
PL12 5.00 dB
SFO2 400.1270000 MHz
SPNAM0 rampup.100
SPOFF0 0.00 Hz

F2 - Processing parameters
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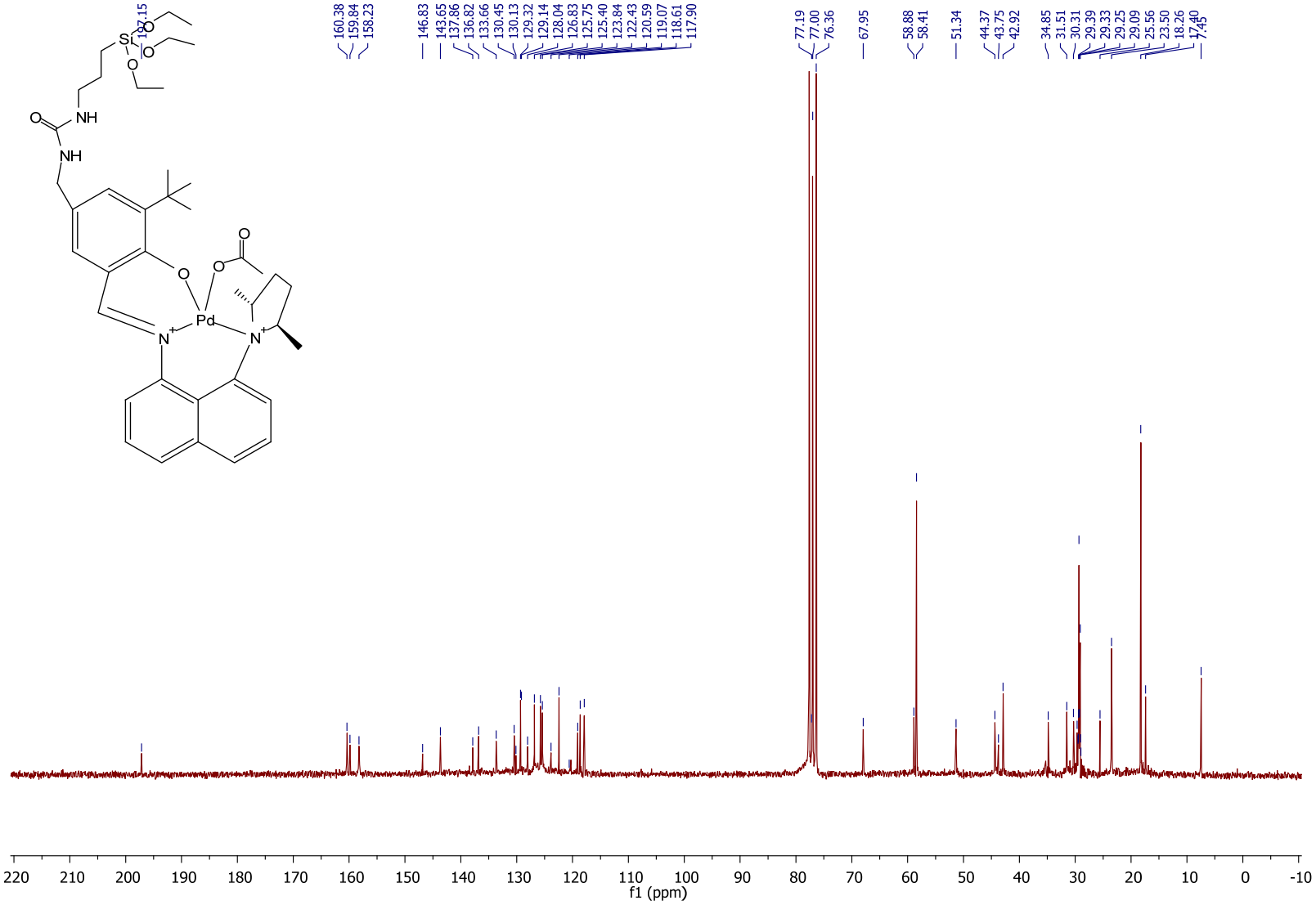
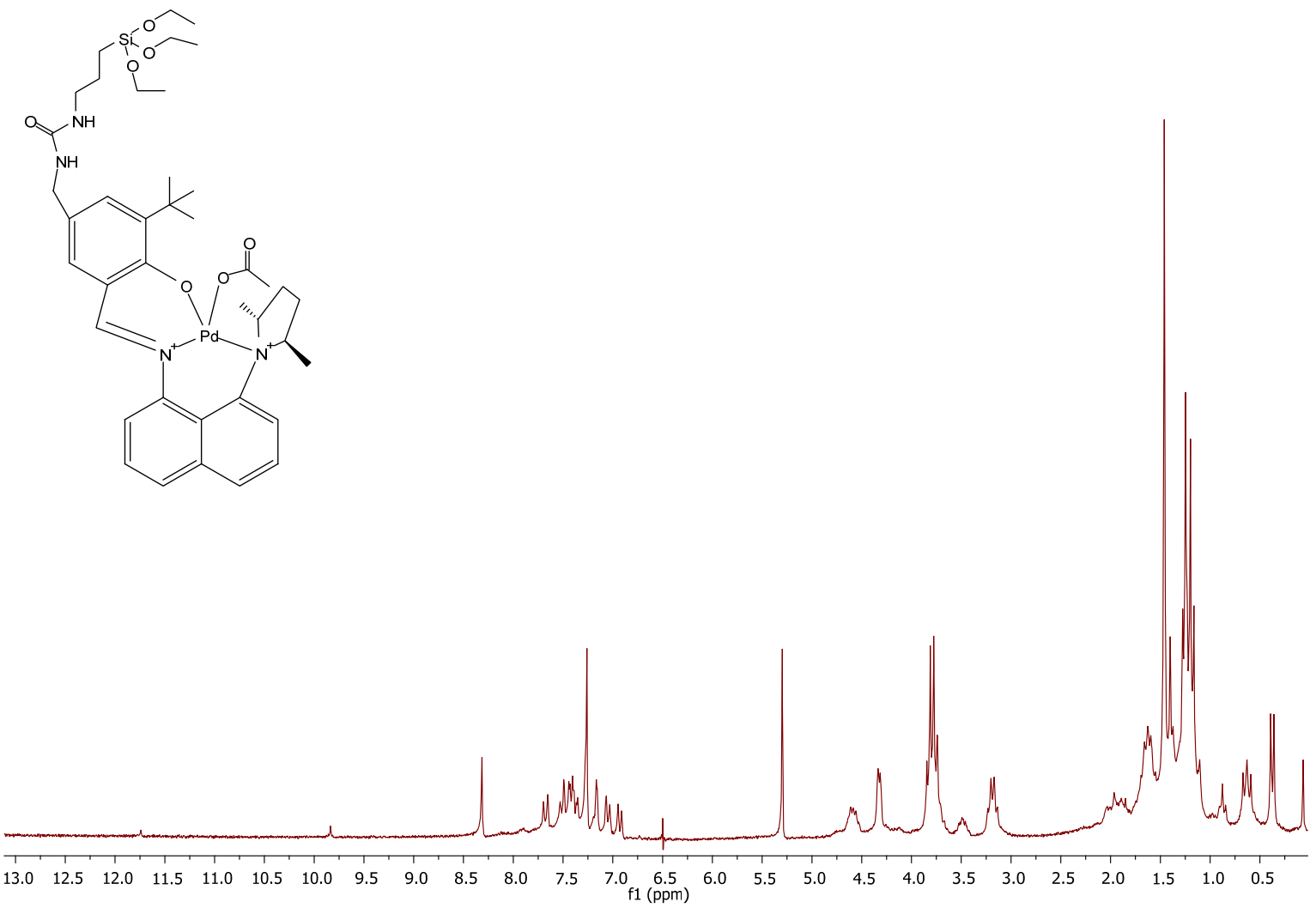
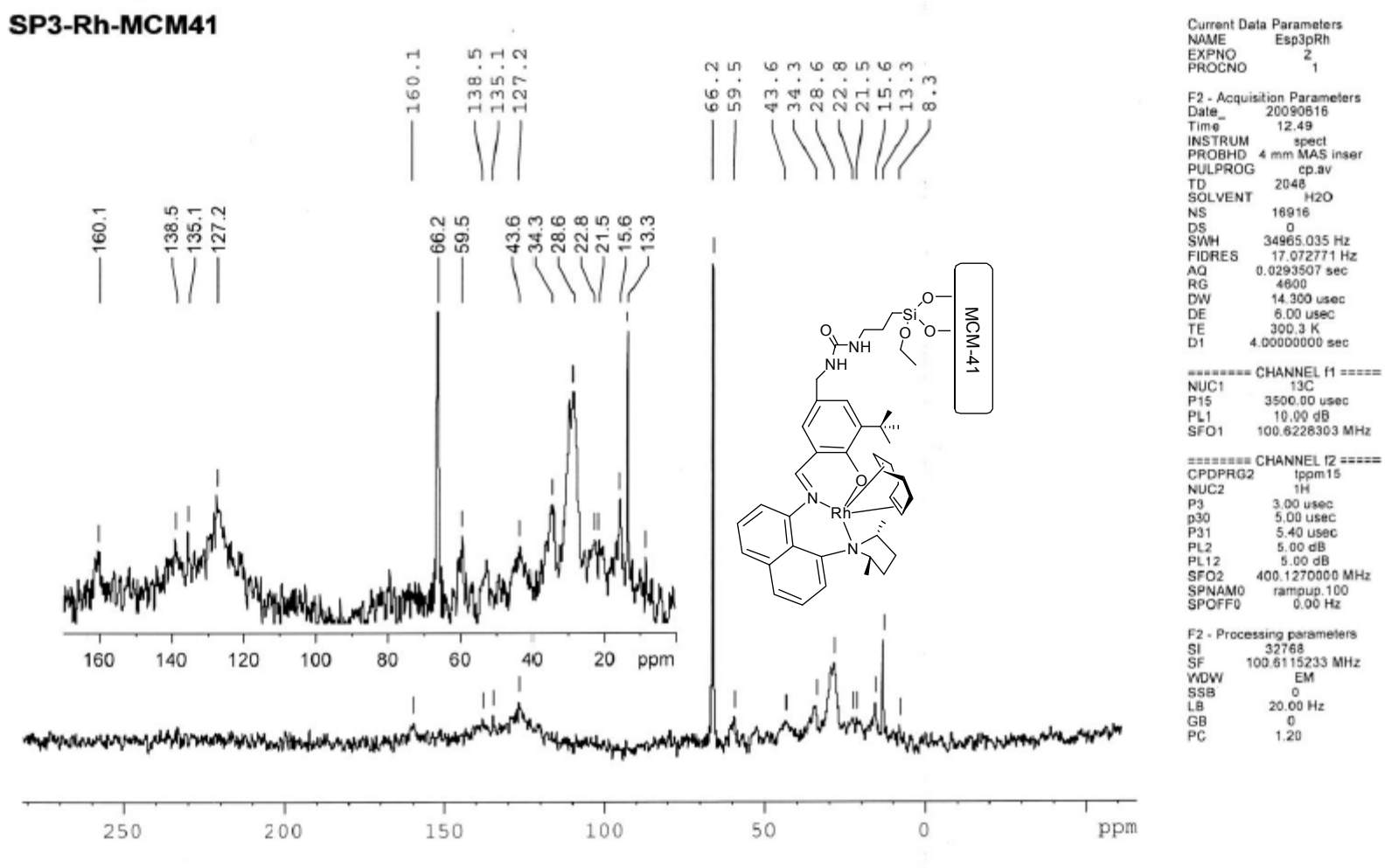
^{13}C-NMR (R,R)-8Pd



^{1}H-NMR (R,R)-8Pd



^{13}C-NMR 8Rh-MCM (solid Phase)



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EXPNO 2
PROCNO 1

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PULPROG cp.av
TD 2048
SOLVENT H2O
NS 16916
DS 0
SWH 34965.035 Hz
FIDRES 17.072771 Hz
AQ 0.0293507 sec
RG 4600
DW 14.300 usec
DE 6.00 usec
TE 300.3 K
D1 4.00000000 sec

======== CHANNEL f1 =====
NUC1 13C
P15 3500.00 usec
PL1 10.00 dB
SFO1 100.6228303 MHz

======== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
P3 3.00 usec
p30 5.00 usec
P31 5.40 usec
PL2 5.00 dB
PL12 5.00 dB
SFO2 400.1270000 MHz
SPNAM0 rampup.100
SPOFF0 0.00 Hz

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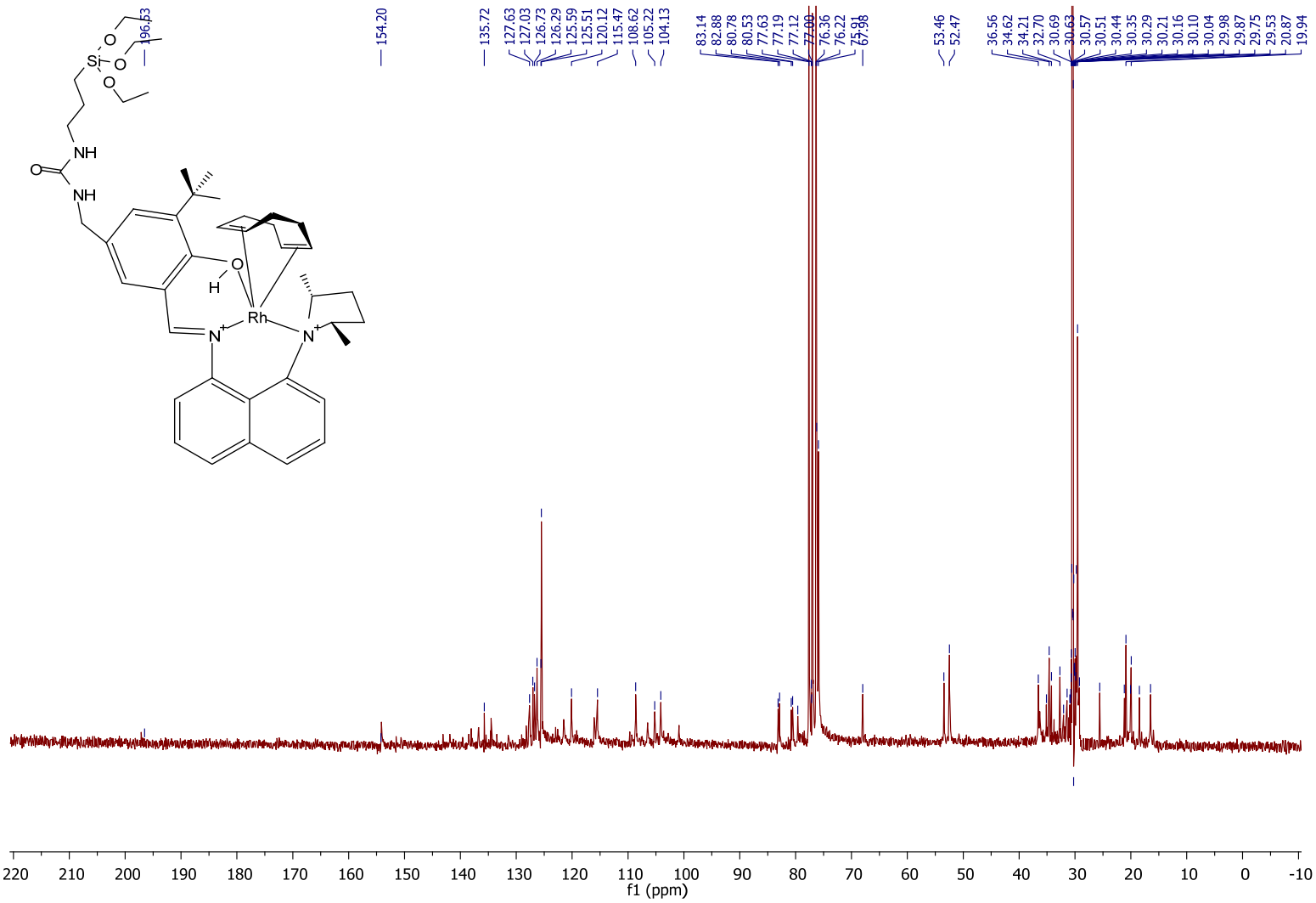
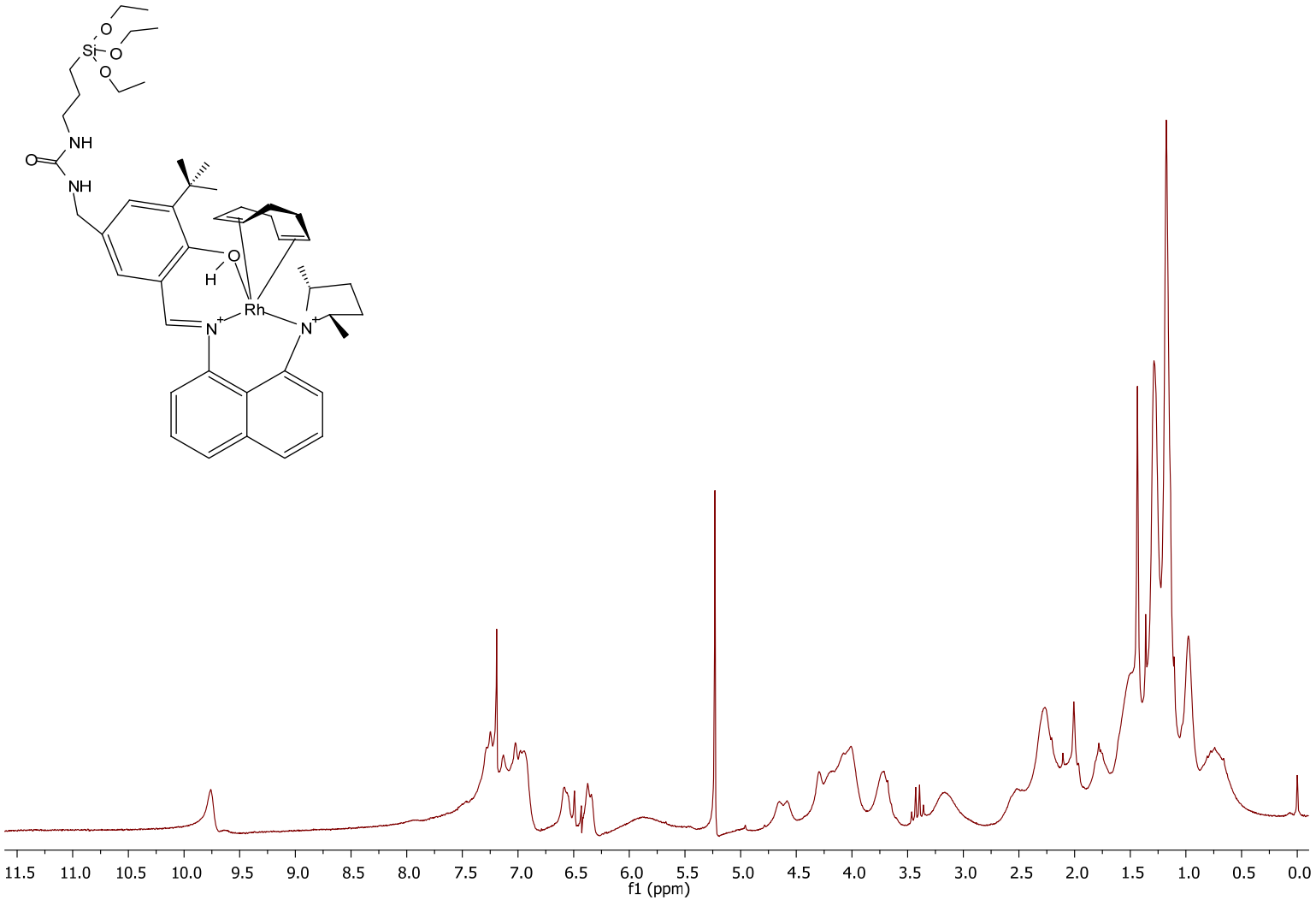
^{13}C-NMR 8Rh

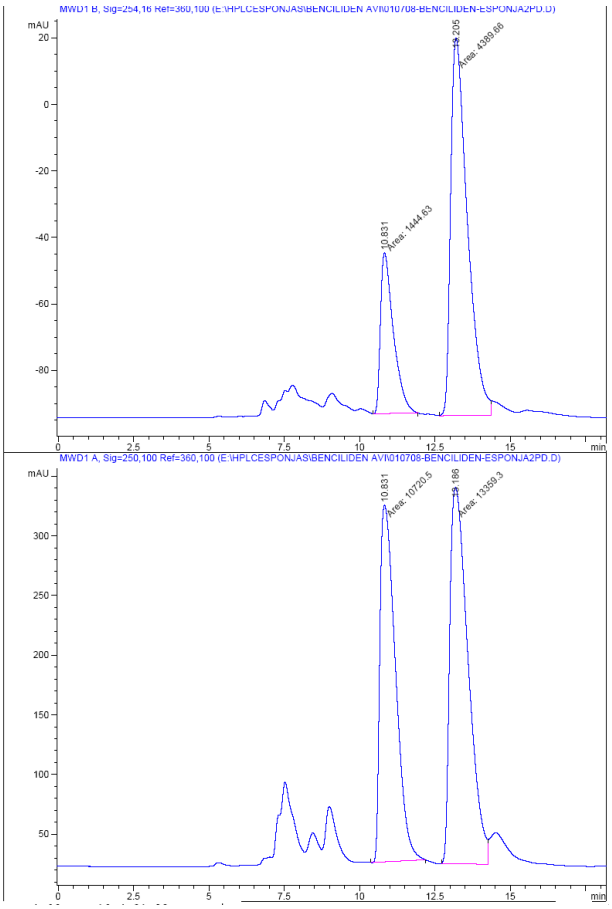


^{1}H-NMR 8Rh



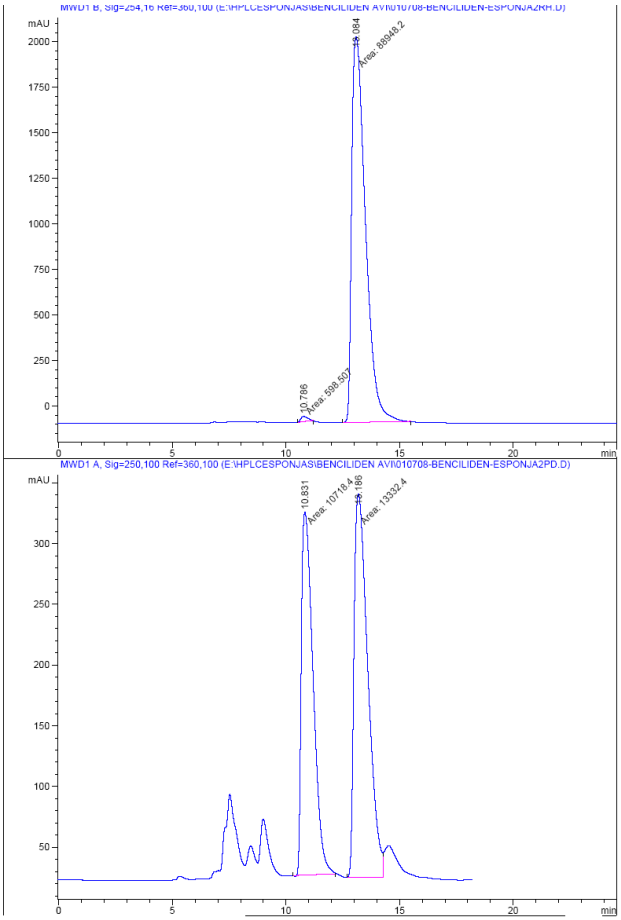
HPLC traces

5Pd



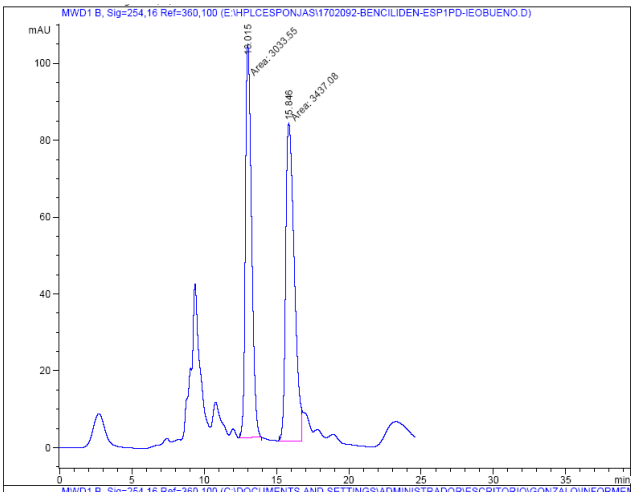
Pd/C

5Rh



Pd/C

6Pd **6Rh**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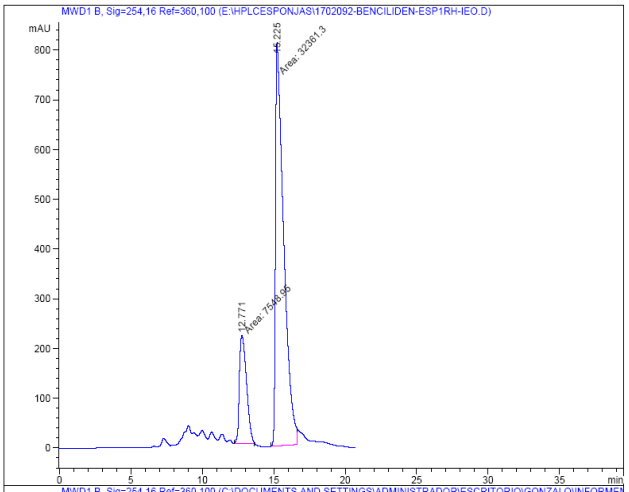
min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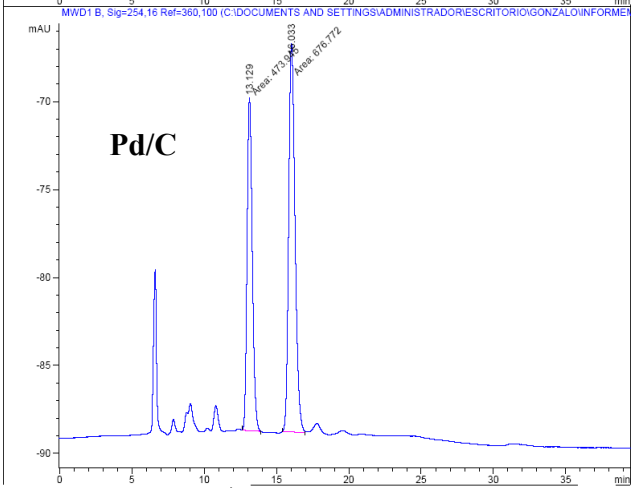
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mAU
Pd/C
13.129
Area: 473.906
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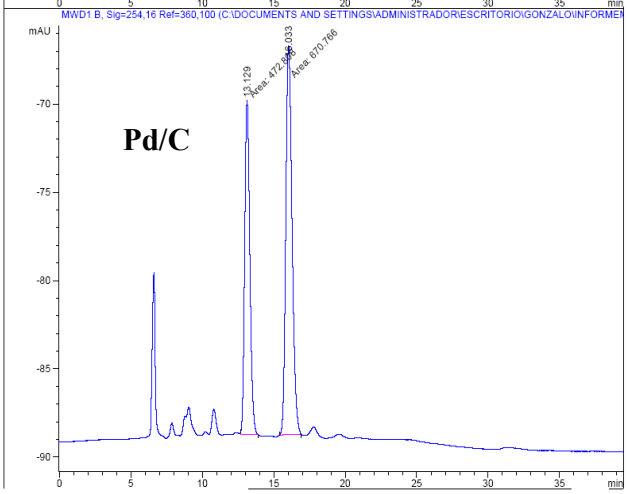
Area: 676.772
min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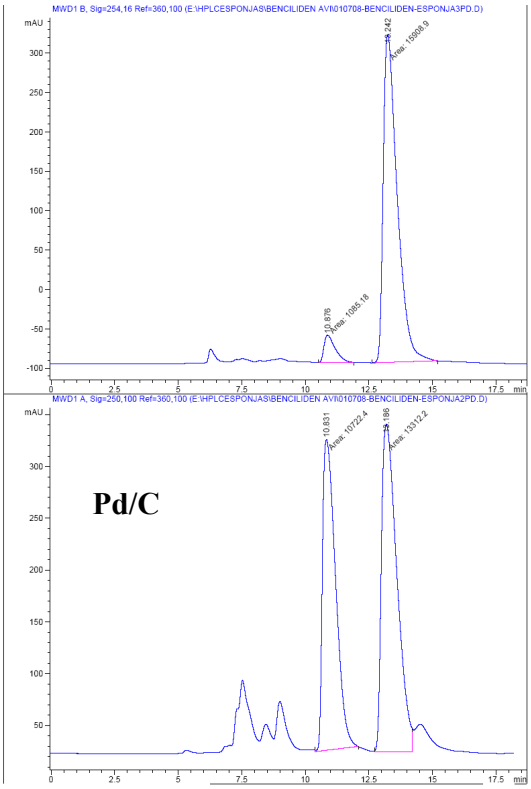
mAU
Pd/C
13.129
Area: 472.906
15.033
Area: 670.766
min

7Pd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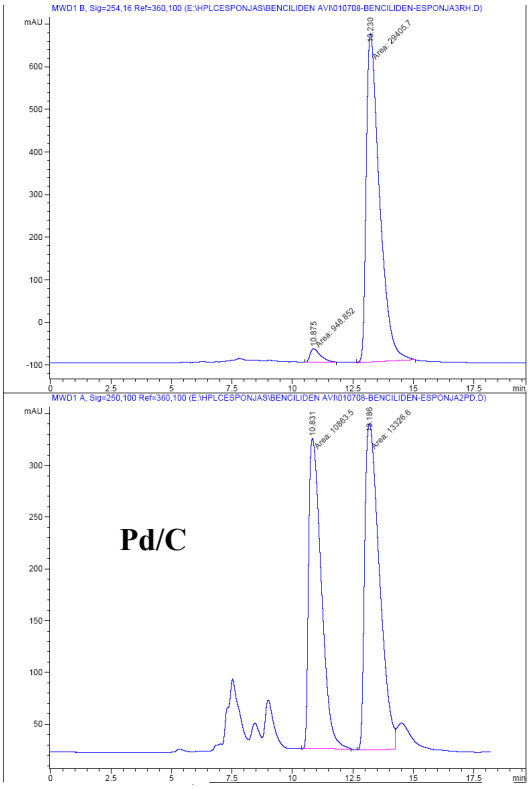
min

7Rh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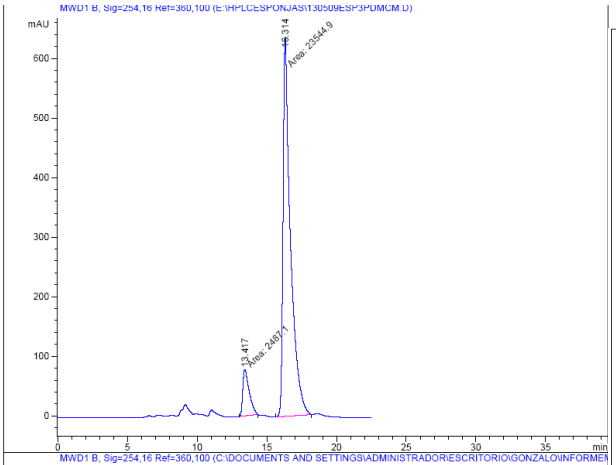
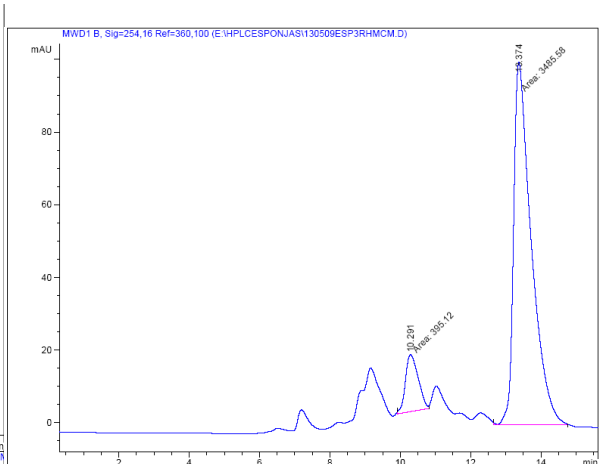
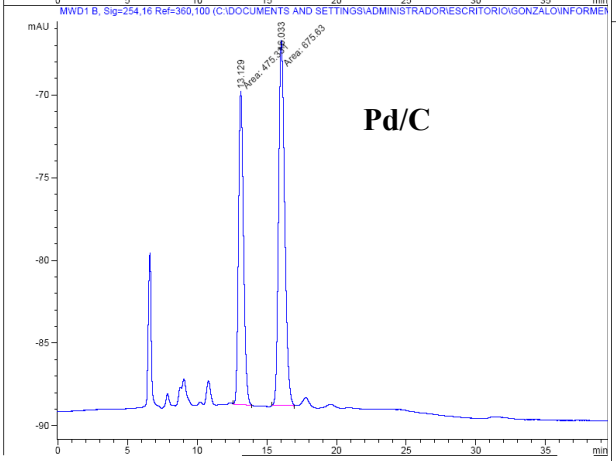
min

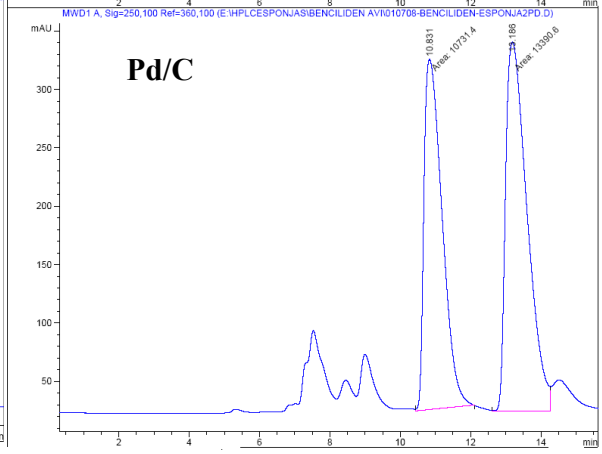
8Pd-MCM



8Rh-MCM







Single-Crystal X-ray Diffraction.

Data for **(R,R)-6** and **(R,R-8)** were collected on a Bruker Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoKα radiation, λ = 0.71073 Å) operating at 40 kV and 8 mA. Data were collected at room temperature over a hemisphere of the reciprocal space in a combination of several sets of exposures. Each exposure of 20s covered 0.5 or 0.3º in ω. Unit cell dimensions were determined by a least-squares fit of 60 reflections with I >20σ(I). The structures were solved by direct methods. The final cycles of refinement were carried out by full-matrix least-squares analyses with anisotropic thermal parameters for all non-hydrogen atoms The final cycles of refinement were carried out by full-matrix least-squares analyses using SMART software for data collection and data reduction and SHELXTL[1], and anisotropically refined (Hydrogen atoms were geometrically situated) by full-matrix least-squares methods on F2 (SHELXL- 97)

Table S1. *Crystallographic and refinement data for* **(R,R)-6**.

Identification code	**(R,R)-6**
Empirical formula	$C_{28}H_{27}N_3O$
Formula weight	421.53
Temperature	*296(2) K*
Wavelength	0.71073 Å
Crystal system, space group	*Orthorhombic, P 2_1 2_1 2_1*
Unit cell dimensions	*a = 10.414 (3) Å* *b = 13.565 (3) Å* *c = 15.401(4) Å*
Volume	*2175.6 (10) Å^3*
Z, Calculated density	*4, 1.287 Mg/m^3*
Absorption coefficient	0.079 mm^{-1}
F(000)	896.0
Crystal size	0.4 x 0.3 x 0.2
Theta range for data collection	2.36° to 25.40°
Limiting indices	-12<=h<=12 -16<=k<=16 -18<=l<=18
Reflections collected / unique	15489 / 2280
Completeness to theta = 25.00°	57 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2280 / 0 / 293
Goodness-of-fit on F^2	1.148
Final R indices [I>2σ(I)]	R1 = 0.0376, wR2 = 0.0812
R indices (all data)	R1 = 0.0475, wR2 = 0.0846
Largest diff. peak and hole	0.111 and -0.100 e·Å^{-3}

Table S2. *Crystallographic and refinement data for* **(R,R-7)**.

Identification code	**(R,R-7)**
Empirical formula	$C_{28}H_{34}N_2O$
Formula weight	414.57
Temperature	*296(2) K*
Wavelength	0.71073 Å
Crystal system, space group	*Monoclinic, P* 2_1
Unit cell dimensions	*a = 9.8047 (8) Å; α = 90°* *b = 8.8134 (8) Å; β = 91.363 (1)* *c = 14.0070 (12) Å; γ = 90 °*
Volume	*1210.04 (18)* $Å^3$
Z, Calculated density	*2, 1.138* Mg/m^3
Absorption coefficient	0.069 mm^{-1}
F(000)	448.0
Crystal size	0.45 x 0.3 x 0.2
Theta range for data collection	2.31° to 25.39°
Limiting indices	-11<=h<=11 -10<=k<=10 -16<=l<=16
Reflections collected / unique	8037 / 4000
Completeness to theta = 25.00°	90 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.986 and 0.974
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4000 / 0 / 287
Goodness-of-fit on F^2	1.074
Final R indices [I>2σ(I)]	R1 = 0.0636, wR2 = 0.1125
R indices (all data)	R1 = 0.1082, wR2 = 0.1281
Largest diff. peak and hole	0.119 and -0.194 $e \cdot Å^{-3}$

$R1 = [\Sigma(|Fo|-|Fc|)]/ \Sigma|Fo|$; $wR2 = \Sigma(w|Fo|^2-|Fc|^2)^2]/ \Sigma[w(|Fo|^2)^2]^{1/2}$ $w = 1/[\sigma^2|Fo|^2+(0.0410p)^2]$ where $p = (|Fo|^2+2|Fc|^2)/3$

[1] Siemens SHELXTL, version 5.0, Siemens Analytical X-ray Instruments, Inc., Madison, WI, **1995**.