Alkyne-Coordinating Tridentate Ligands: Structural Properties and Reactivity of Their Rhodium Complexes

Kazuhiro Okamoto,* Yusuke Omoto, Hayato Sano, and Kouichi Ohe*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

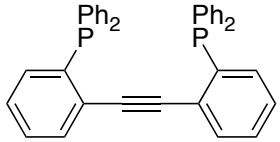
e-mail: kokamoto@scl.kyoto-u.ac.jp; ohe@scl.kyoto-u.ac.jp

Supporting Information

I. General. NMR spectra were recorded on a JEOL EX-400 spectrometer at 25 °C (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 162 MHz for ^{31}P NMR). Chemical shifts are reported in δ ppm referenced to $CDCl_3$ (δ 7.26 for ^{1}H NMR and δ 77.00 for ^{13}C NMR). IR spectra were recorded with an FT-IR spectrometer (JASCO FT/IR-460 Plus). Melting points (mp) are uncorrected. MALDI-TOF mass spectra were obtained with 1,8-Dihydroxy-9(10H)-anthracenone (DIT) as a matrix on a SHIMADZU KRATOS TOF MASS spectrometer AXIMA-CFR Plus. High-resolution mass spectra (HRMS) were recorded on a JEOL JMX-SX 102A spectrometer. Elemental analyses were not successful because of instability of a series of the rhodium complexes. CH_2Cl_2 and THF were purified by passed through a neutral alumina column under argon atmosphere. Hexane and benzene were distilled over sodium and benzophenone under nitrogen. $[RhCl(cod)]_2$ [1] and NaBArF (sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) [2] were prepared according to the literatures. All other materials were purchased and used without further purification.

II. Preparation of a ligand.

Bis(2-(diphenylphosphino)phenyl)acetylene (1) [CAS 345342-51-0][3]



1

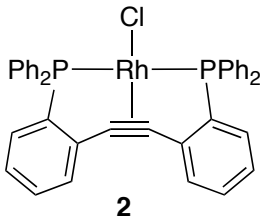
A typical procedure for the synthesis of ligands is shown below. To a stirred suspension of *t*-BuOK (6.06 g, 54.0 mmol) in hexane (66 mL) and THF (92 mL) was added *n*-BuLi (1.6 N in hexane solution, 28 mL, 44.0 mmol) dropwise at –78 °C over 15 min. After stirring for additional 15 min, diphenylacetylene (3.56 g, 20.0 mmol) dissolved in THF (20 mL) was added dropwise over 10 min. The mixture was stirred at –78 °C for 40 min, and then at –25 °C for 1.5 h. The

1 J. Chatt, *J. Chem. Soc.* 1957, 4753.
2 N. A. Yakelis and R. G. Bergman, *Organometallics* 2005, **24**, 3579.
3 J. Kowalik and L. M. Tolbert, *J. Org. Chem.* 2001, **66**, 3229.

resulting solution was cooled to –43 °C, and chlorodiphenylphosphine (8.26 mL, 46.0 mmol) was added dropwise over 10 min. The reaction mixture was warmed to room temperature over 5 h, and quenched with degassed water (10 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was recrystallized from hexane/CH_2Cl_2 to give 3.64 g of ligand **1** (6.66 mmol, 33% yield) as a white powder. Mp 142.2 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 6.79–6.81 (m, 2H), 7.12–7.15 (m, 2H), 7.16–7.24 (m, 4H), 7.32–7.37 (m, 20H). ^{13}C NMR (CD_2Cl_2): δ 95.3–95.4 (m), 127.9 (d, J = 30.1 Hz), 128.6 (d, J = 16.5 Hz), 128.899, 128.903 (d, J = 7.4 Hz), 129.2, 132.7, 132.8 (m), 134.4 (d, J = 20.7 Hz), 136.9 (d, J = 12.0 Hz), 140.7 (d, J = 13.1 Hz). ^{31}P NMR (CD_2Cl_2): δ –8.6. HRMS (FAB) calcd for $C_{38}H_{28}P_2$ $[M]^+$ 547.1745, found 547.1750.

III. Complexation with rhodium(I).

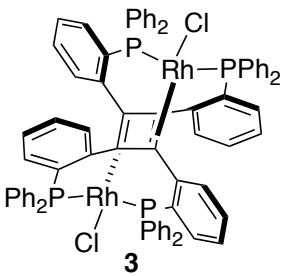
2



2

A solution of ligand **1** (109.3 mg, 0.20 mmol) and $[RhCl(cod)]_2$ (49.3 mg, 0.10 mmol) in dry CH_2Cl_2 (15 mL) was stirred at room temperature for 15 min, and then dry hexane (30 mL) was added to the reaction mixture. After the additional stirring for 1 h, the solvent was concentrated by nitrogen flow. The precipitate was filtered, washed with hexane, and dried under vacuum to give complex **2** as a red prism (119 mg, 0.17 mmol, 85%). Mp 85.0 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.33–7.43 (m, 14H), 7.56 (t, J = 7.4 Hz, 2H), 7.60-7.64 (m, 2H), 7.74-7.80 (m, 8H), 8.05 (d, J = 7.6 Hz, 2H). ^{13}C NMR (CD_2Cl_2): δ 101.7 (d, $J_{C\text{-}Rh}$ = 9.1 Hz), 128.1, 128.6 (virtual t, $J_{C–P\ sum}$ = 10.0 Hz), 130.5, 131.4 (virtual t, $J_{C–P\ sum}$ = 18.0 Hz), 131.8, 133.7, 134.0 (virtual t, $J_{C–P\ sum}$ = 6.8 Hz), 134.2 (virtual t, $J_{C–P\ sum}$ = 6.2 Hz), 138.2 (virtual t, $J_{C–P\ sum}$ = 37.8 Hz), 149.0 (virtual t, $J_{C–P\ sum}$ = 51.6 Hz). ^{31}P NMR (CD_2Cl_2): δ 46.5 (d, $J_{Rh\text{-}P}$ = 122 Hz). HRMS (FAB) calcd for $C_{38}H_{28}ClP_2Rh$ $[M]^+$ 684.0410, found 684.0415.

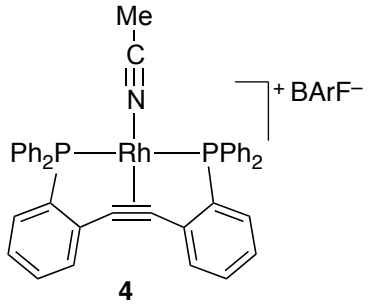
3



3

A solution of ligand **1** (10.9 mg, 20.0 μmol) and $[RhCl(cod)]_2$ (4.9 mg, 10.0 μmol) in dry benzene (1.5 mL) was stirred at 50 °C for 48 h (in the dark). The dark red crystal was filtered, washed with benzene, and dried under vacuum to give complex **3** as a dark red prism (12.0 mg, 8.6 μmol, 86%). Mp >250 °C. ^{1}H NMR ($CDCl_3$): δ 6.37–6.41 (m, 2H), 6.45–6.49 (m, 2H), 6.55–6.60 (m, 2H), 6.63–6.67 (m, 4H), 6.76–6.87 (m, 10H), 6.92–7.02 (m, 6H), 7.06–7.13 (m, 6H), 7.16–7.21 (m, 4H), 7.28–7.39 (m, 12H), 8.04–8.11 (m, 4H), 8.40–8.43 (m, 2H), 8.85–8.88 (m, 2H). ^{31}P NMR ($CDCl_3$): δ 6.24 (dd, $J_{P\text{-}Rh}$ = 146 Hz, $J_{P\text{-}P}$ = 396 Hz), 22.74 (dd, $J_{P\text{-}Rh}$ = 146 Hz, $J_{P\text{-}P}$ = 396 Hz). HRMS (FAB) calcd for $C_{76}H_{56}Cl_2P_4Rh_2$ $[M]^+$ 1368.0820, found 1368.0819.

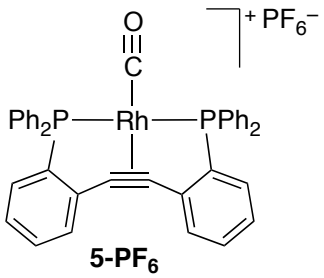
4



4

A solution of complex **2** (35.0 mg, 50.0 μmol) and NaBArF (44.3 mg, 50.0 μmol) in dry CH_3CN (3.8 mL) was stirred at room temperature for 30 min, and then the mixture was filtered through Celite, washed with hexane, and dried under vacuum to give complex **4** as an orange solid (47.2 mg, 30.0 μmol, 60%). Mp 146-148 °C. ^{1}H NMR (CD_2Cl_2): δ 1.79 (s, 3H), 7.43-7.48 (m, 8H), 7.50-7.56 (m, 8H), 7.58 (s, 4H), 7.63–7.68 (m, 10H), 7.75 (s, 8H), 8.11 (d, J = 7.6 Hz, 2H). ^{13}C NMR (CD_2Cl_2) for characteristic peaks: δ 99.2 (alkyne, d, J = 9.3 Hz). ^{31}P NMR (CD_2Cl_2): δ 53.2 (d, $J_{Rh\text{-}P}$ = 116 Hz). MALDI-TOF-MS (DIT): *m/z* 690.3 ($[M–BArF]^+$, $C_{40}H_{31}NP_2Rh$, calcd. 690.1); 863.5 ($[BArF]^-$, $C_{32}H_{12}BF_{24}$, calcd. 863.1). HRMS (FAB) calcd for $C_{40}H_{31}NP_2Rh$ $[M–BArF]^+$ 690.0987, found 690.0988.

5-PF$_6$



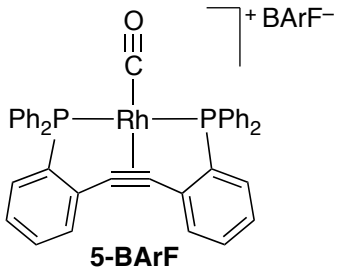
5-PF$_6$

A solution of ligand **1** (16.4 mg, 30.0 μmol) and $[RhCl(CO)_2]_2$ (5.8 mg, 15.0 μmol) in dry CH_2Cl_2 (1.0 mL) was stirred at room temperature for 15 min, and then $AgPF_6$ (7.6 mg, 30.0 μmol) was added to the reaction mixture. After the additional stirring for 1 h, the reaction mixture was filtered through Celite, and then concentrated by nitrogen flow to give 22.7 mg of complex **5-PF$_6$**

as a yellow prism (27.6 μmol, 92%).

Mp > 250 °C. ^{1}H NMR (CD_2Cl_2): δ 7.47–7.54 (m, 8H), 7.55–7.74 (m, 16H), 7.84 (t, J = 7.8 Hz, 2H), 8.22 (d, J = 7.8 Hz, 2H). ^{13}C NMR (CD_2Cl_2) for characteristic peaks: δ 106.3 (alkyne, d, J = 5.8 Hz). ^{31}P NMR (CD_2Cl_2): δ –144.2 (sept, $J_{F\text{-}P}$ = 715 Hz), 57.2 (d, $J_{Rh\text{-}P}$ = 104 Hz). IR (nujol): 2016 cm^{-1} (ν_{C-O}). MALDI-TOF-MS (DIT): m/z 677.3 ([M–PF_6]$^+$, $C_{39}H_{28}OP_2Rh$, calcd. 677.1). HRMS (FAB) calcd for $C_{39}H_{28}OP_2Rh$ [M–PF_6]$^+$ 677.0670, found 677.0666.

5-BArF



5-BArF

5-BArF was prepared according to the similar procedure for **5-PF_6**. Yellow crystal. 96% yield. Mp 71.2-71.9 °C. ^{1}H NMR (CD_2Cl_2): δ 7.48–7.51 (m, 8H), 7.57–7.71 (m, 16H), 7.77 (t, J = 7.8 Hz, 2H), 8.37 (d, J = 7.8 Hz, 2H). ^{13}C NMR (CD_2Cl_2) for characteristic peaks: δ 106.3 (alkyne, d, J = 5.8 Hz). ^{31}P NMR (CD_2Cl_2) δ 57.3 (d, $J_{Rh\text{-}P}$ = 104 Hz). IR (nujol): 2028 cm^{-1} (ν_{C-O}). MALDI-TOF-MS (DIT): m/z 677.1 ([M–BArF]$^+$, $C_{39}H_{28}OP_2Rh$, calcd. 677.1); 863.3 ([BArF]$^-$, $C_{32}H_{12}BF_{24}$, calcd. 863.1). HRMS (FAB) calcd for $C_{39}H_{28}OP_2Rh$ [M–BArF]$^+$ 677.0670, found 677.0670.

IV. X-ray crystallographic analyses.

Table S1. Crystallographic data of **2**

Empirical Formula	$C_{39.50}H_{31}Cl_4P_2Rh$
Formula Weight	812.34
Crystal Color, Habit	orange, prism
Crystal System	monoclinic
Lattice Parameters	
a (Å)	11.0023(10)
b (Å)	18.907(2)
c (Å)	17.537(2)
β (°)	105.272(5)
V (Å^3)	3519.3(6)
Space Group	$P2_1/c$ (#4)
Z value	4
D_{calc} (g cm^{-3})	1.533
F_{000}	1644.00
μ (MoKa) (cm^{-1})	9.072
Radiation	MoK (λ = 0.71070 Å) graphite monochromated
Temperature (°C)	–129.8
Max 2θ (°)	55.0
No. of Reflections Measured	Total: 27279
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
No. Observations (All reflections)	8035
No. Variables	579
Reflection/Parameter Ratio	13.88
Residuals: R_1; wR_2	0.0385; 0.0956
Goodness of Fit Indicator	1.073
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map (e Å^{-3})	1.18
Minimum peak in Final Diff. Map (e Å^{-3})	–0.63

Table S2. Crystallographic data of **3**

Empirical Formula	$C_{82}H_{68}Cl_2P_4Rh_2$
Formula Weight	1526.12
Crystal Color, Habit	red, prism
Crystal System	triclinic
Lattice Parameters	
a (Å)	11.810(4)
b (Å)	12.102(4)
c (Å)	13.653(4)
α (°)	66.667(9)
β (°)	72.108(11)
γ (°)	86.21(2)
V (Å^3)	1701.6(8)
Space Group	P-1 (#2)
Z value	1
D_{calc} (g cm^{-3})	1.489
F_{000}	780.00
μ (MoKa) (cm^{-1})	7.058
Radiation	MoK (λ = 0.71070 Å) graphite monochromated
Temperature (°C)	–149.8
Max 2θ (°)	54.9
No. of Reflections Measured	Total: 13769
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
No. Observations (All reflections)	7462
No. Variables	433
Reflection/Parameter Ratio	17.23
Residuals: R_1; wR_2	0.0938; 0.2355
Goodness of Fit Indicator	1.121
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map (e Å^{-3})	2.42
Minimum peak in Final Diff. Map (e Å^{-3})	–1.36

Table S3. Crystallographic data of **5-PF$_6$**

Empirical Formula	$C_{53}H_{44}F_6OP_3Rh$
Formula Weight	1006.75
Crystal Color, Habit	yellow, prism
Crystal System	triclinic
Lattice Parameters	
a (Å)	11.129(4)
b (Å)	14.638(5)
c (Å)	15.649(5)
α (°)	98.691(5)
β (°)	90.116(3)
γ (°)	112.174(3)
V (Å^3)	2328.9(12)
Space Group	P-1 (#2)
Z value	2
D_{calc} (g cm^{-3})	1.436
F_{000}	1028.00
μ (MoKa) (cm^{-1})	5.314
Radiation	MoK (λ = 0.71070 Å) graphite monochromated
Temperature (°C)	–129.8
Max 2θ (°)	54.9
No. of Reflections Measured	Total: 27643
Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F^2
No. Observations (All reflections)	10611
No. Variables	577
Reflection/Parameter Ratio	18.39
Residuals: R_1; wR_2	0.0691; 0.2025
Goodness of Fit Indicator	1.231
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map (e Å^{-3})	3.16
Minimum peak in Final Diff. Map (e Å^{-3})	–0.83

V. Cartesian atomic coordinates for the optimized structure of complexes 2 and 5^{+} (LanL2DZ for rhodium and B3LYP/6-31G(d,p) for other atoms).

2

Atom	X	Y	Z
Rh	-0.1218695	-0.2297227	0.0000000
Cl	2.2616784	-0.6973241	0.0000000
P	0.0379404	-0.0557087	2.3461969
C	-1.6799858	-0.0653337	3.0101535
C	-2.0797933	-0.1205368	4.3475429
C	-3.4386164	-0.1146633	4.6702832
C	-4.4011504	-0.0535814	3.6549184
C	-4.0166762	-0.0119932	2.3179628
C	-2.6489292	-0.0288209	1.9852757
C	-2.1750112	-0.0423064	0.6300000
C	0.9084326	-1.3506960	3.3181069
C	0.9887456	-2.6442002	2.7817408
C	1.5777688	-3.6738591	3.5157887
C	2.1017726	-3.4198760	4.7851190
C	2.0391600	-2.1310573	5.3188745
C	1.4473253	-1.0987050	4.5889767
C	0.7771664	1.5323969	2.9231695
C	2.1134001	1.8026731	2.5767365
C	2.7124169	2.9972957	2.9730034
C	1.9891860	3.9425593	3.7054960
C	0.6596538	3.6867628	4.0397581
C	0.0547700	2.4880205	3.6524956
H	-1.3342419	-0.1772935	5.1355822
H	-3.7487791	-0.1610881	5.7104201
H	-5.4573028	-0.0488169	3.9104785
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H	-0.9805093	2.3051504	3.9204348
H	0.0867836	4.4185009	4.6035961
H	2.4584778	4.8750194	4.0082445
H	3.7459648	3.1930859	2.6998888
H	2.6692797	1.0849081	1.9807248
H	0.6091446	-2.8287533	1.7814072
H	1.6402628	-4.6713810	3.0893096
H	2.5673997	-4.2213841	5.3526886
H	2.4567994	-1.9259871	6.3011814
H	1.4191109	-0.0950553	5.0035512
P	0.0379404	-0.0557087	-2.3461969
C	-1.6799858	-0.0653337	-3.0101535
C	-2.0797933	-0.1205368	-4.3475429
C	-3.4386164	-0.1146633	-4.6702832
C	-4.4011504	-0.0535814	-3.6549184

C	-4.0166762	-0.0119932	-2.3179628
C	-2.6489292	-0.0288209	-1.9852757
C	-2.1750112	-0.0423064	-0.6300000
C	0.9084326	-1.3506960	-3.3181069
C	0.9887456	-2.6442002	-2.7817408
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C	2.1017726	-3.4198760	-4.7851190
C	2.0391600	-2.1310573	-5.3188745
C	1.4473253	-1.0987050	-4.5889767
C	0.7771664	1.5323969	-2.9231695
C	2.1134001	1.8026731	-2.5767365
C	2.7124169	2.9972957	-2.9730034
C	1.9891860	3.9425593	-3.7054960
C	0.6596538	3.6867628	-4.0397581
C	0.0547700	2.4880205	-3.6524956
H	-1.3342419	-0.1772935	-5.1355822
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H	-0.9805093	2.3051504	-3.9204348
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H	2.4584778	4.8750194	-4.0082445
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H	2.6692797	1.0849081	-1.9807248
H	0.6091446	-2.8287533	-1.7814072
H	1.6402628	-4.6713810	-3.0893096
H	2.5673997	-4.2213841	-5.3526886
H	2.4567994	-1.9259871	-6.3011814
H	1.4191109	-0.0950553	-5.0035512

5^+

Atom	X	Y	Z
Rh	0.0412229	-0.2014839	0.0000000
P	-0.0549100	-0.0465604	2.3818488
P	-0.0549100	-0.0465604	-2.3818488
O	-2.9687920	-0.4511775	0.0000000
C	-1.8220903	-0.3385432	0.0000000
C	2.2408161	-0.2398490	0.6225216
C	2.6436163	-0.2641265	2.0010843
C	1.6605972	-0.1988074	3.0065621
C	2.0304258	-0.2561288	4.3526676
C	3.3787620	-0.3632828	4.6978591
C	4.3587041	-0.4141497	3.6998728
C	4.0018476	-0.3661617	2.3551811
C	-1.0315497	-1.3096547	3.2776309
C	-1.1410852	-2.5925957	2.7172072
C	-1.8144938	-3.6030021	3.4031202
C	-2.3891072	-3.3399608	4.6487392
C	-2.2883200	-2.0648351	5.2093367
C	-1.6118170	-1.0506320	4.5302231
C	-0.6677626	1.5878961	2.9433189
C	0.2144767	2.5927391	3.3678988
C	-0.2742641	3.8520380	3.7217722
C	-1.6417514	4.1196811	3.6545498
C	-2.5256059	3.1242756	3.2286823
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H	-0.7005797	-2.7964078	1.7445810
H	1.2803569	2.3983061	3.4282824
H	3.6664523	-0.4098861	5.7437145
H	-2.9191087	-4.1256166	5.1792718
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C	-1.0315497	-1.3096547	-3.2776309
C	-1.1410852	-2.5925957	-2.7172072
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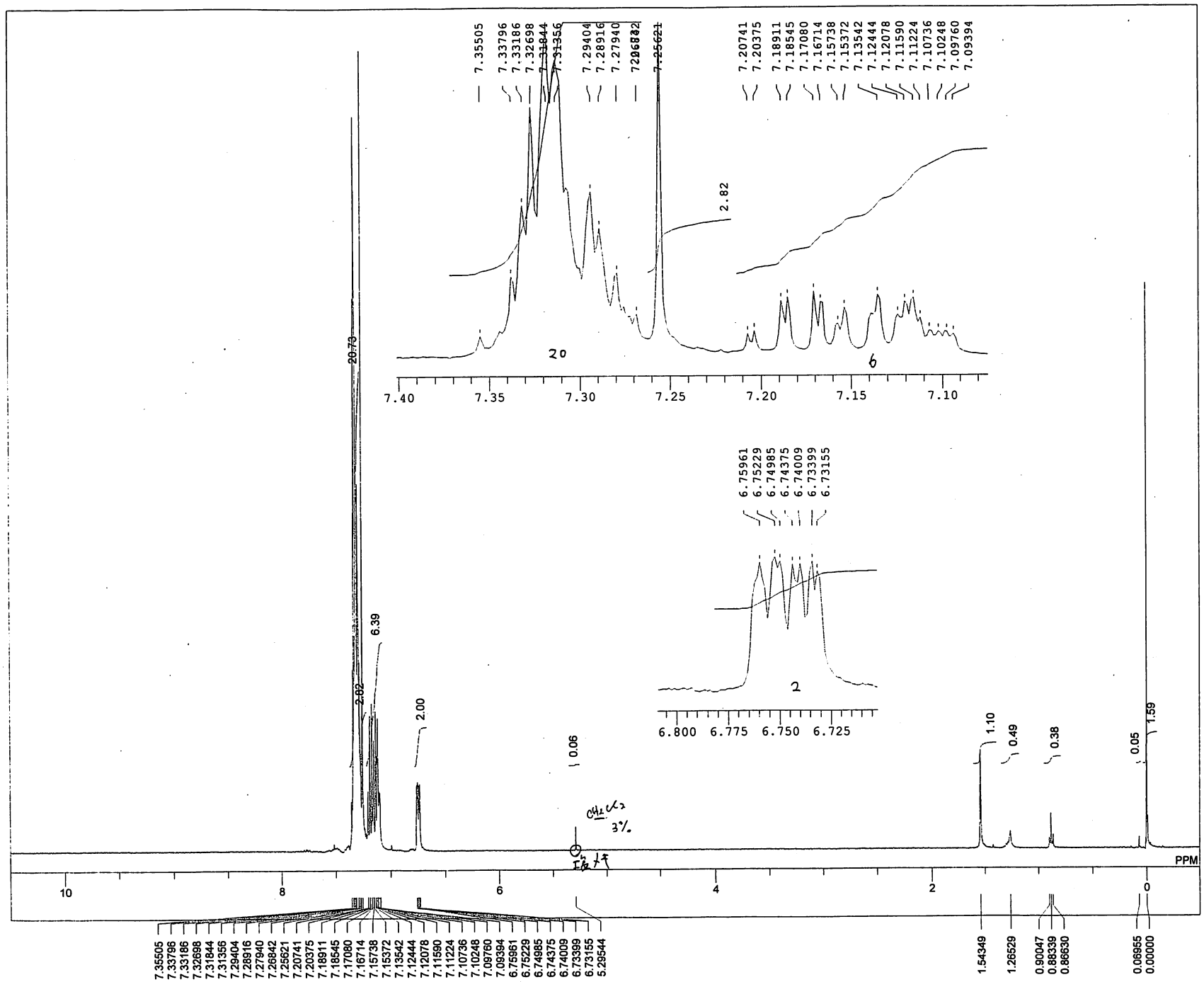
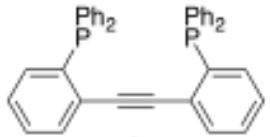
C	-0.2742641	3.8520380	-3.7217722
C	-1.6417514	4.1196811	-3.6545498
C	-2.5256059	3.1242756	-3.2286823
C	-2.0441245	1.8667653	-2.8692726
H	5.4061410	-0.4986146	-3.9732052
H	1.2719424	-0.2239742	-5.1289838
H	-1.5504882	-0.0594961	-4.9690127
H	4.7599424	-0.4148151	-1.5802358
H	-1.8961604	-4.5922863	-2.9624187
H	-0.7005797	-2.7964078	-1.7445810
H	1.2803569	2.3983061	-3.4282824
H	3.6664523	-0.4098861	-5.7437145
H	-2.9191087	-4.1256166	-5.1792718
H	-2.7441890	1.1032797	-2.5417346
H	-2.0192784	5.0992736	-3.9327513
H	-2.7394318	-1.8563912	-6.1751106
H	-3.5914664	3.3262019	-3.1760282
H	0.4172548	4.6213052	-4.0529524

88test



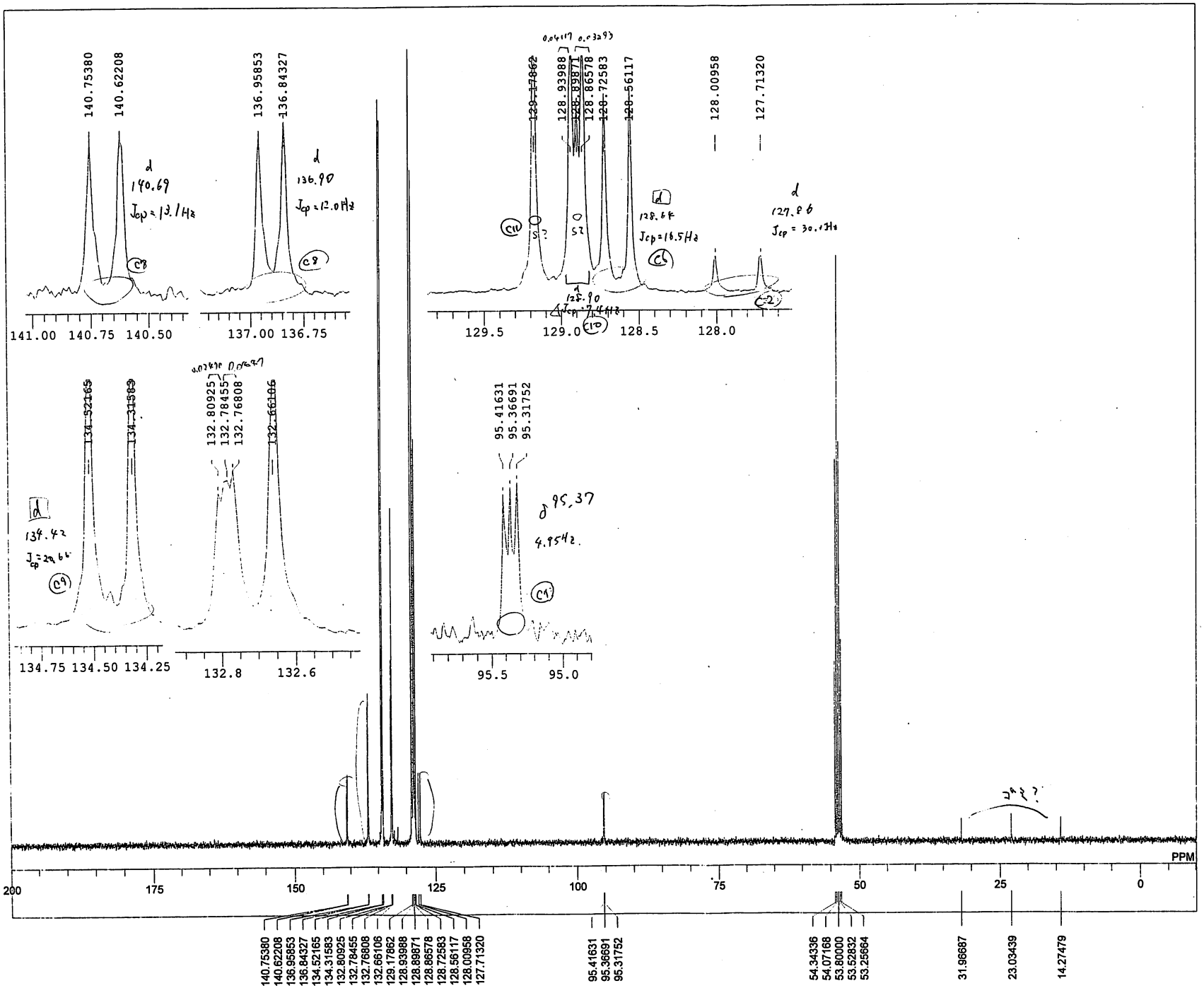
DFILE _DEFAULT.ALS
COMNT 88test
DATIM Wed Jan 19 10:32:44 2011
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 7.20 usec
IRNUC 1H
CTEMP 25.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 19

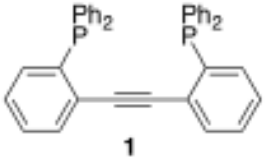


1

exp88a-CD2Cl2_13C

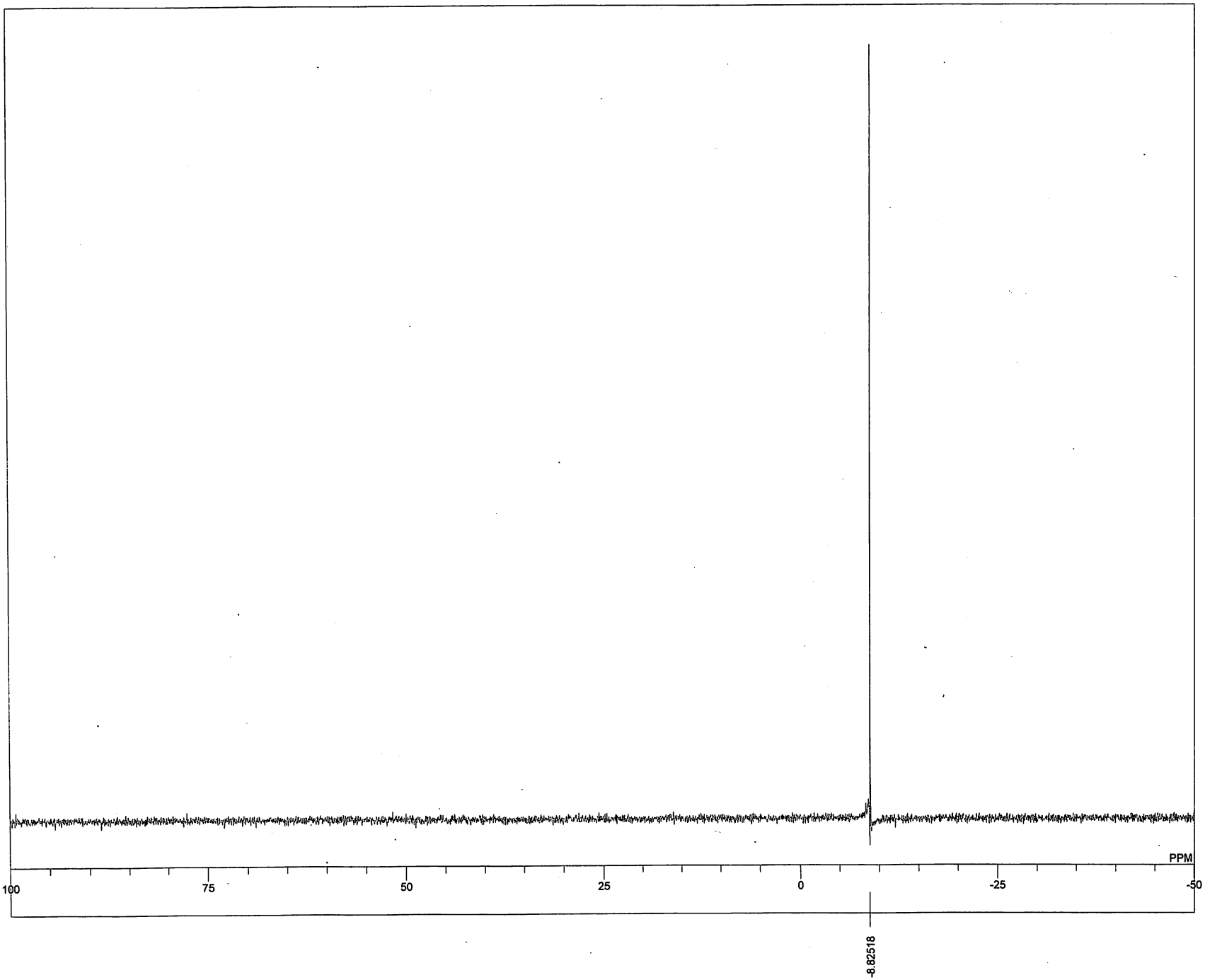
DFILE	_DEFAULT.ALS
COMNT	exp88a-CD2Cl2_13C
DATIM	Mon Nov 29 23:48:17 2010
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	1296
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	CD2CL
EXREF	53.80 ppm
BF	1.00 Hz
RGAIN	28



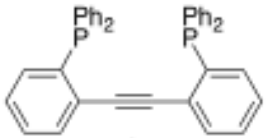


1

88test_31P

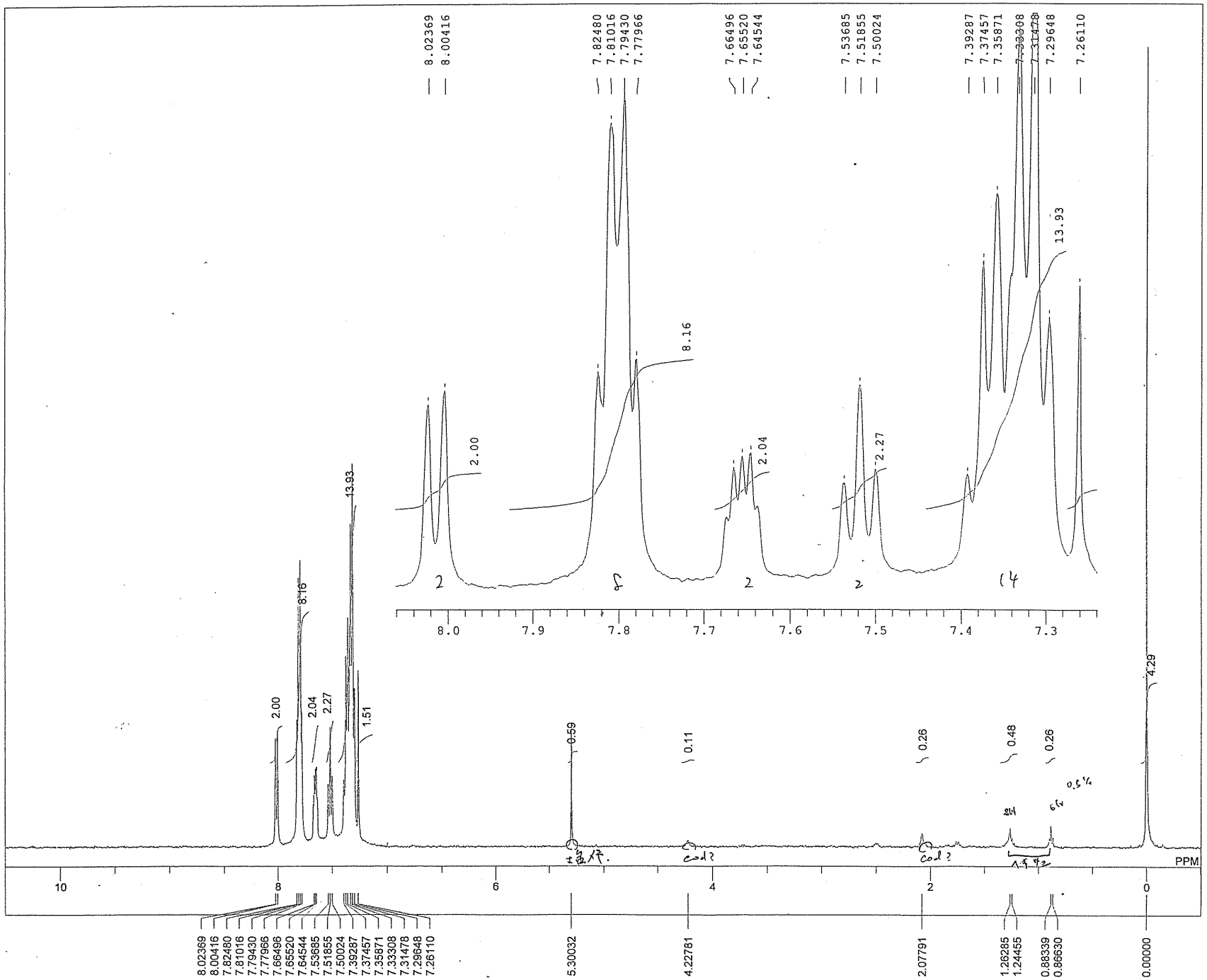


DFILE	_DEFAULT.ALS
COMNT	88test_31P
DATIM	Wed Jan 19 10:41:09 2011
OBNUC	31P
EXMOD	BCM
OBFRQ	161.70 MHz
OBSET	142.00 KHz
OBFIN	10220.00 Hz
POINT	16384
FREQU	100000.00 Hz
SCANS	128
ACQTM	0.1638 sec
PD	1.2000 sec
PW1	3.90 usec
IRNUC	1H
CTEMP	25.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.10 Hz
RGAIN	29

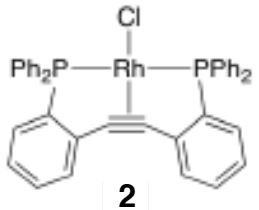


1

156

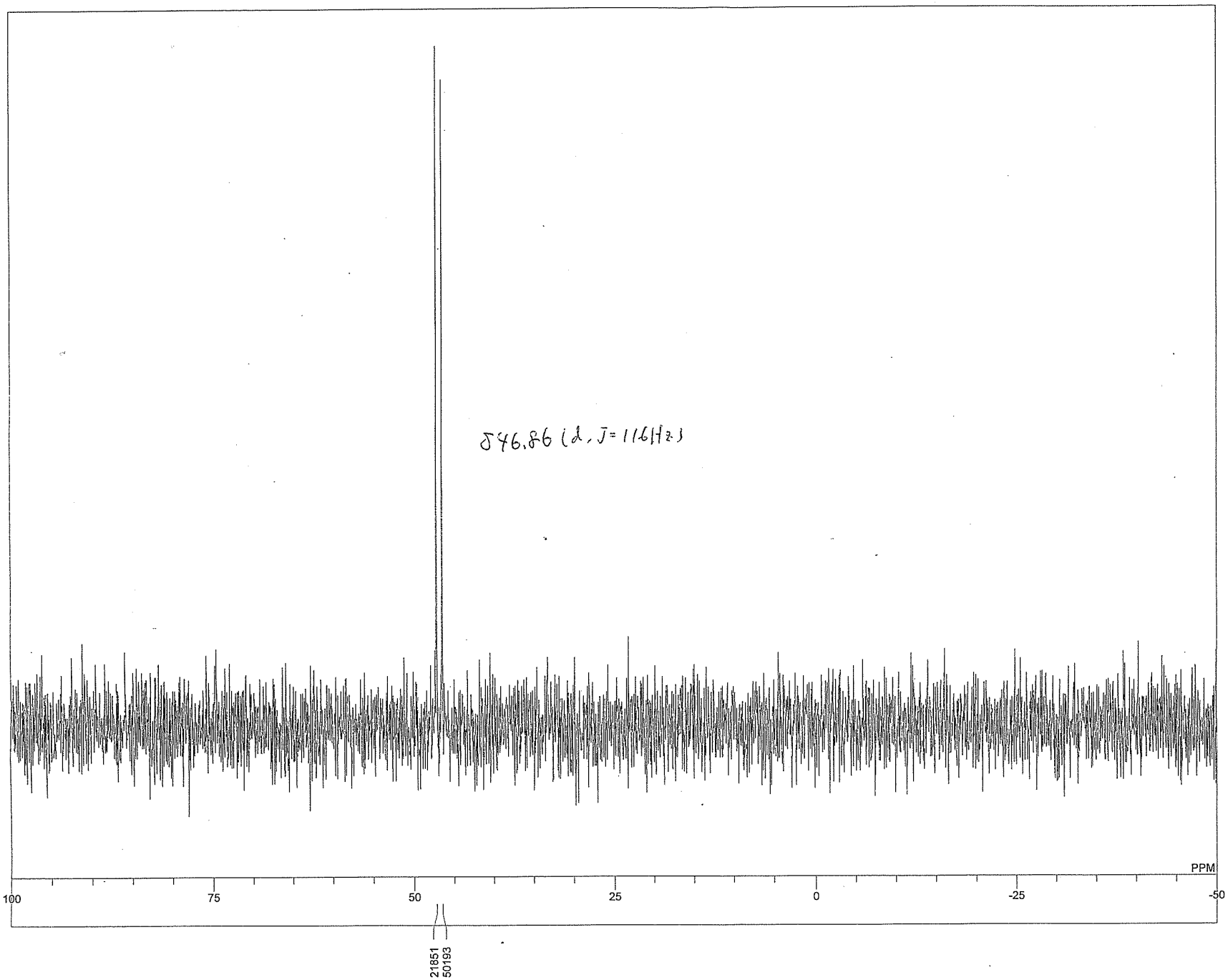


DFILE _DEFAULT.ALS
COMNT 156
DATIM Fri Jan 21 12:32:57 2011
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0501 sec
PD 2.9500 sec
PW1 7.20 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
RGAIN 25

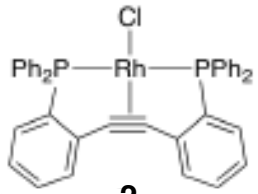


2

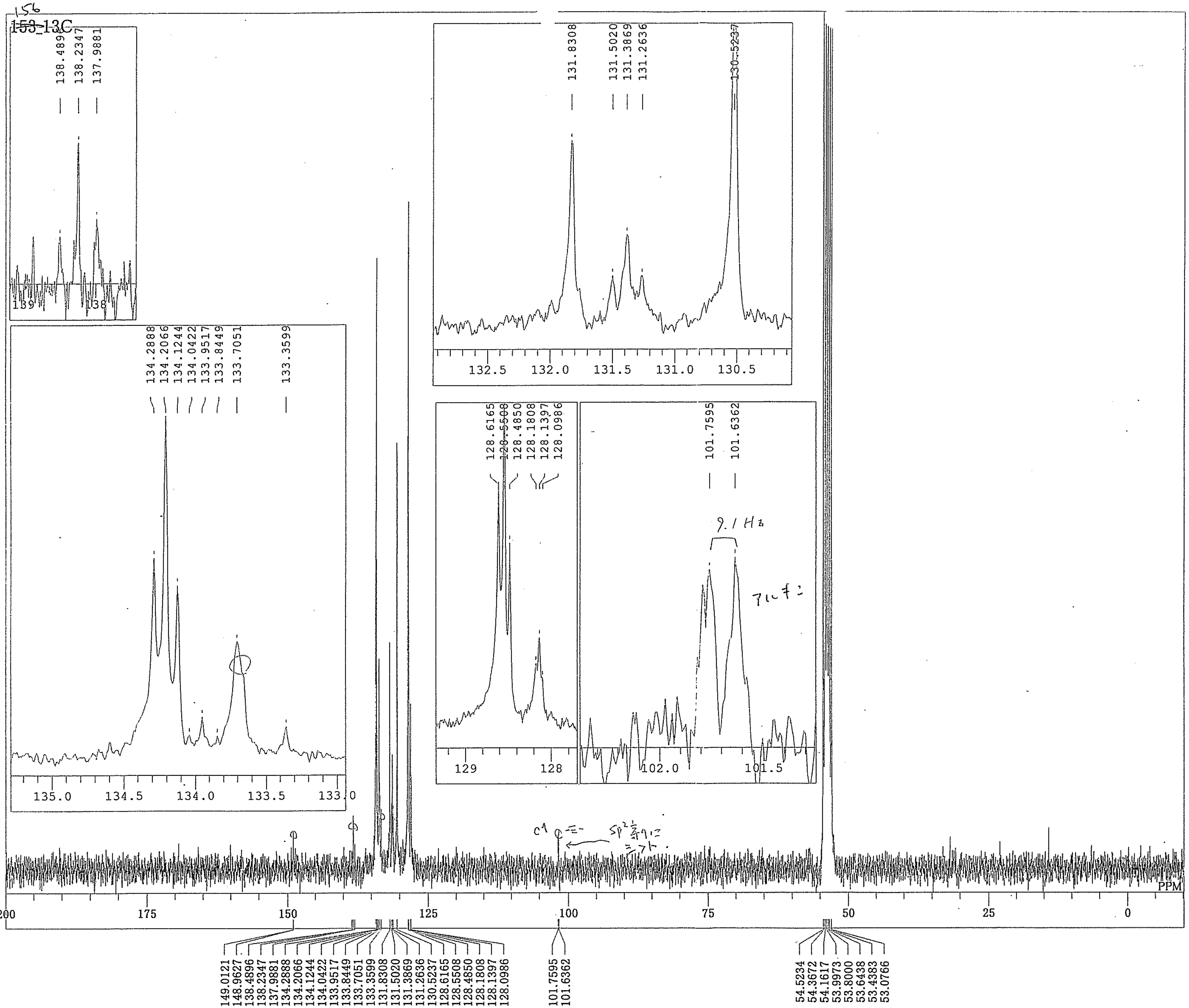
156_31P



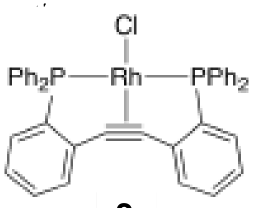
DFILE	_DEFAULT.ALS
COMNT	156_31P
DATIM	Fri Jan 21 12:39:56 2011
OBNUC	31P
EXMOD	BCM
OBFRQ	161.70 MHz
OBSET	142.00 KHz
OBFIN	10220.00 Hz
POINT	16384
FREQU	100000.00 Hz
SCANS	128
ACQTM	0.1638 sec
PD	1.2000 sec
PW1	3.90 usec
IRNUC	1H
CTEMP	24.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.00 Hz
RGAIN	29



2



DFILE	156 _DEFAULT.ALS
COMNT	~~153~~ 13C
DATIM	Sat Feb 05 09:38:49 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.00 Hz
POINT	32768
FREQU	20356.23 Hz
SCANS	13360
ACQTM	1.6097 sec
PD	1.3900 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	22.2 c
SLVNT	CD2CL2
EXREF	53.80 ppm
BF	1.00 Hz
RGAIN	27

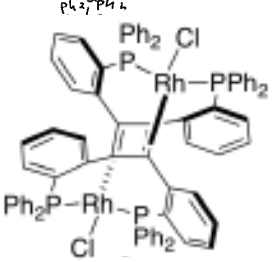


2

180-2

C:\Documents and Settings\JEOL\My Documents\alice_DEFAULT.ALS

DFILE	_DEFAULT.ALS
COMNT	180-2
DATIM	Wed Feb 09 11:41:13 2011
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	16
ACQTM	2.0501 sec
PD	2.9500 sec
PW1	7.20 usec
IRNUC	1H
CTEMP	25.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.10 Hz
RGAIN	24

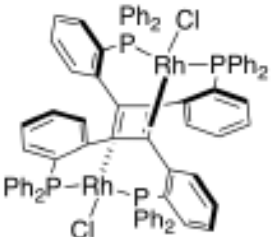


3

180-2_31P

C:\Documents and Settings\JEOL\My Documents\alice_DEFAULT.ALS

DFILE	_DEFAULT.ALS
COMNT	180-2_31P
DATIM	Wed Feb 09 12:03:09 2011
OBNUC	31P
EXMOD	BCM
OBFRQ	161.70 MHz
OBSET	142.00 KHz
OBFIN	10220.00 Hz
POINT	16384
FREQU	100000.00 Hz
SCANS	704
ACQTM	0.1638 sec
PD	1.2000 sec
PW1	3.90 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.10 Hz
RGAIN	28



3

δ22.74
dd. J = 146Hz, 396Hz)
6.24
(dd. J = 186Hz, 396Hz

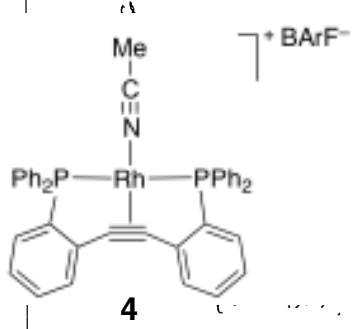
PPM

100 75 50 25 0 -25 -50

4.40126 3.53382 1.98753 1.08238 .92004 .01489 .46860 .56345

208-2

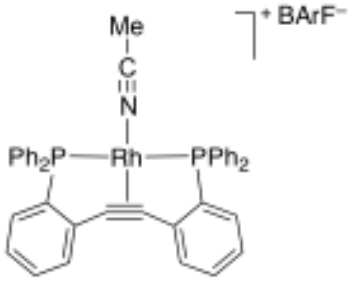
DFILE	_DEFAULT.ALS
COMNT	208-2
DATIM	Fri Feb 25 11:02:17 2011
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	16
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	7.20 usec
IRNUC	1H
CTEMP	25.7 c
SLVNT	CD2CL
EXREF	5.32 ppm
BF	0.10 Hz
RGAIN	14



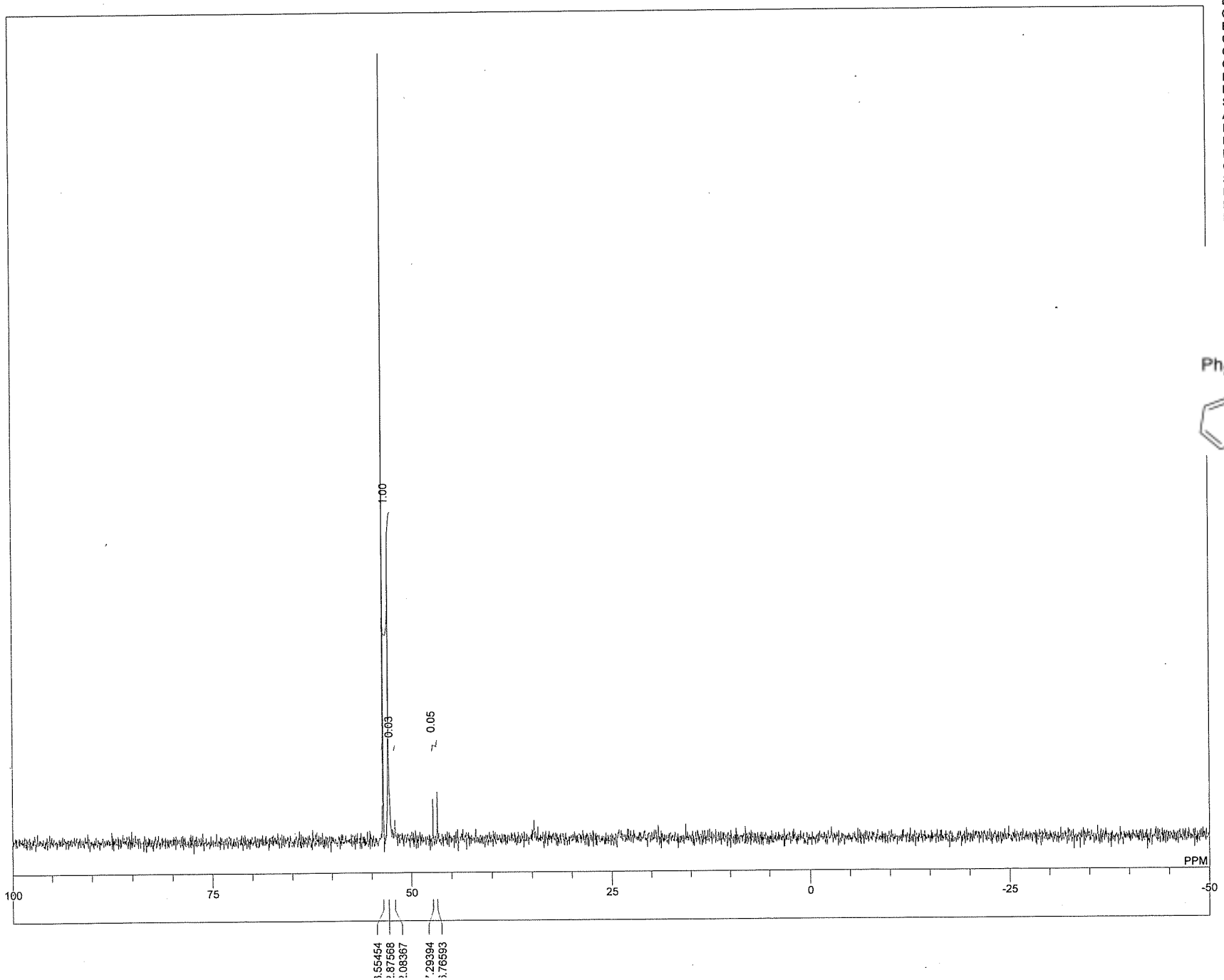
4

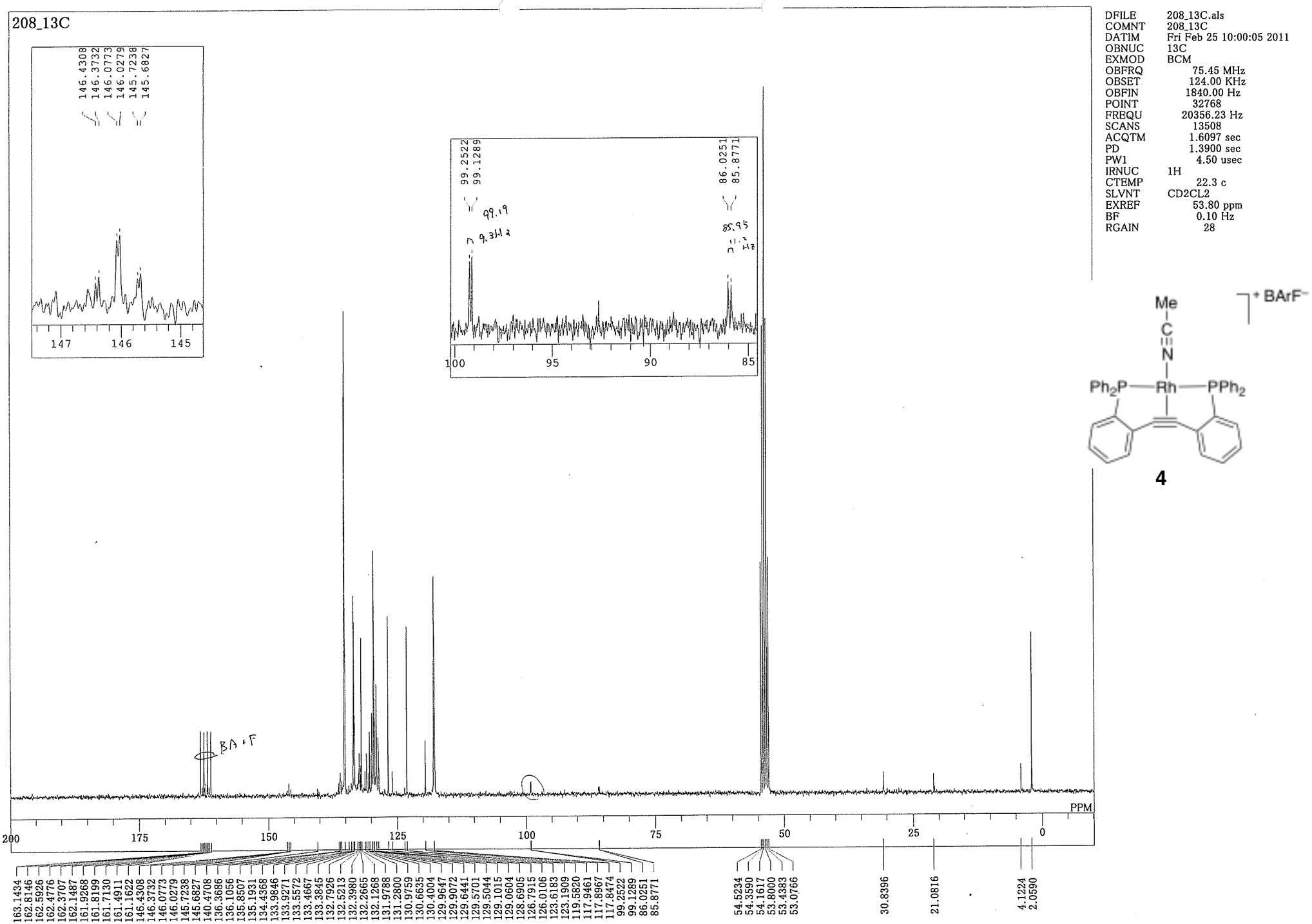
208-2_31P

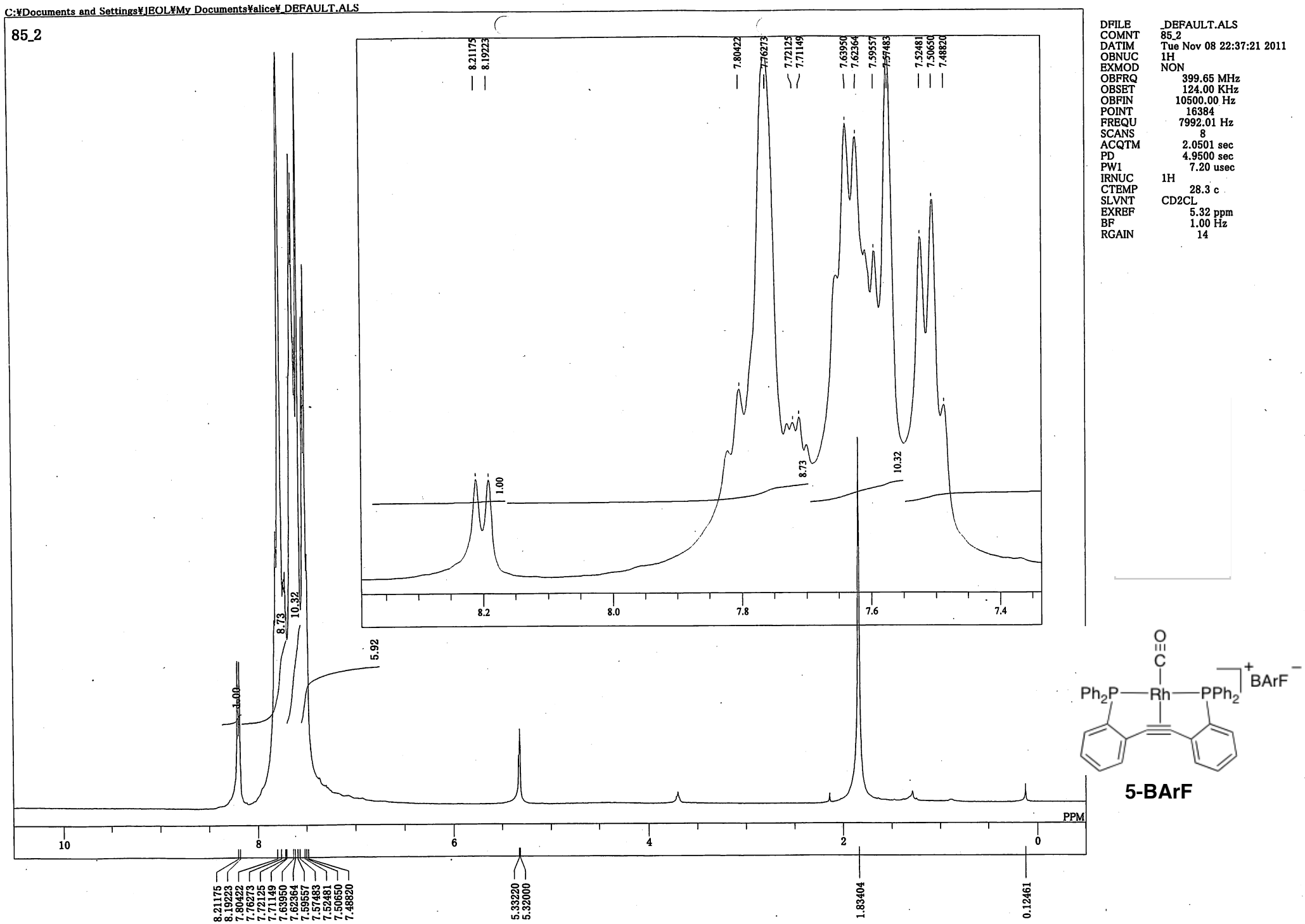
DFILE	_DEFAULT.ALS
COMNT	208-2_31P
DATIM	Fri Feb 25 11:18:16 2011
OBNUC	31P
EXMOD	BCM
OBFRQ	161.70 MHz
OBSET	142.00 KHz
OBFIN	10220.00 Hz
POINT	16384
FREQU	100000.00 Hz
SCANS	512
ACQTM	0.1638 sec
PD	1.2000 sec
PW1	3.90 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CD2CL
EXREF	0.00 ppm
BF	0.10 Hz
RGAIN	28



4





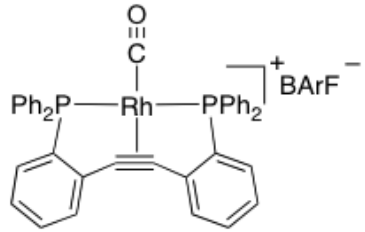


5-BArF

C:¥Documents and Settings¥JEOL¥My Documents¥alice¥_DEFAULT.ALS

85_2_13C

DFILE	_DEFAULT.ALS
COMNT	85_2_13C
DATIM	Wed Nov 09 09:51:17 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	13324
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	27.9 c
SLVNT	CD2CL
EXREF	53.80 ppm
BF	1.00 Hz
RGAIN	31



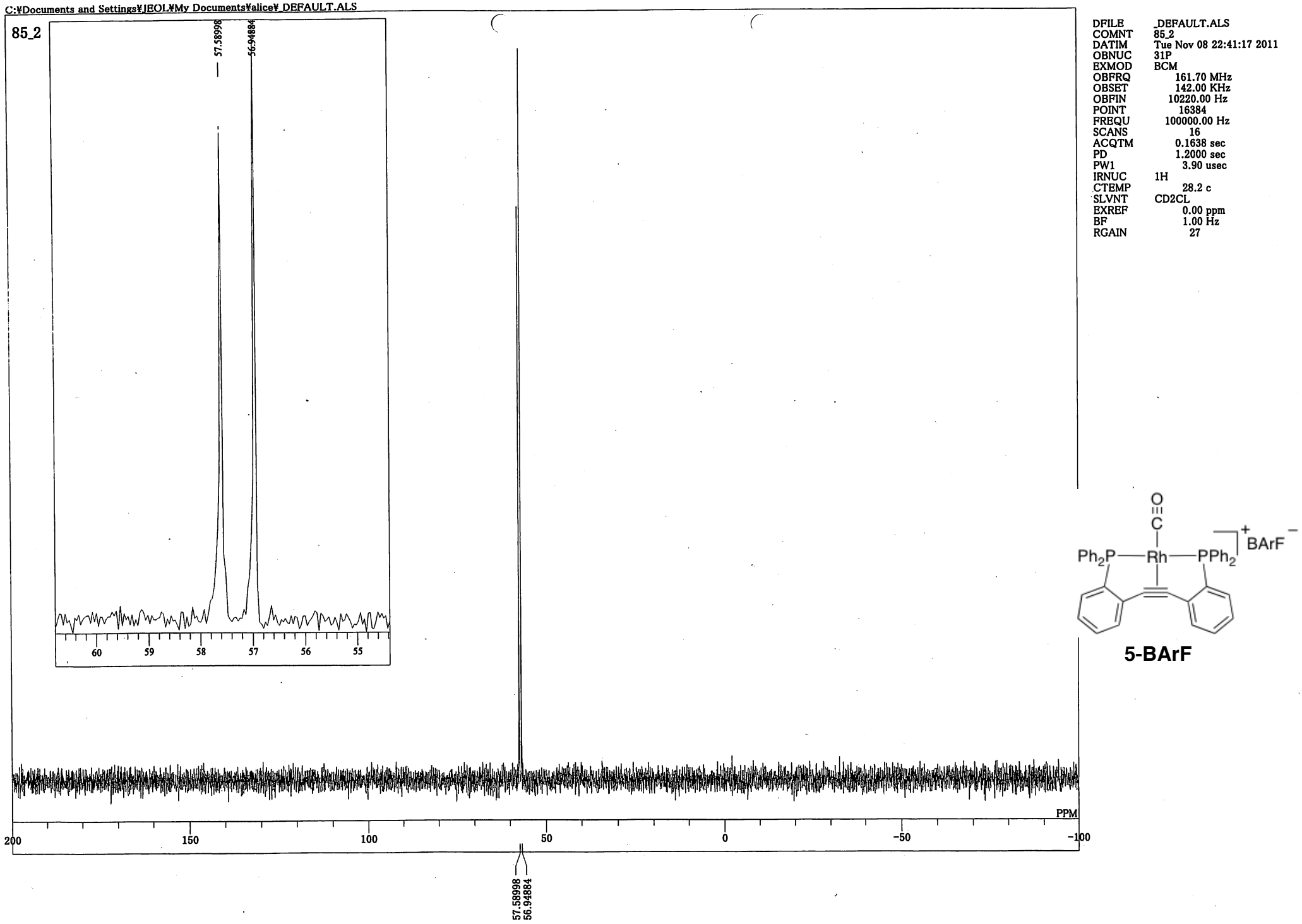
5-BArF

CO

alkyne

PPM

162.96565 162.47168 161.97772 161.48376 146.99420 146.74722 146.47554 135.26260 134.29937 133.96183 133.86304 133.76425 133.46787 133.40201 133.33615 132.94098 132.41408 132.22473 132.04361 131.48379 131.45086 131.40969 130.10069 130.04307 129.99367 129.91134 129.81255 129.64790 129.54910 129.52441 129.49147 129.37622 129.23626 129.21156 129.17863 129.15393 129.11277 128.86579 126.40421 123.68742 120.97886 117.96569 117.92453 117.88336 106.33288 106.27525 54.34336 54.07168 53.80000 53.52832 53.25664



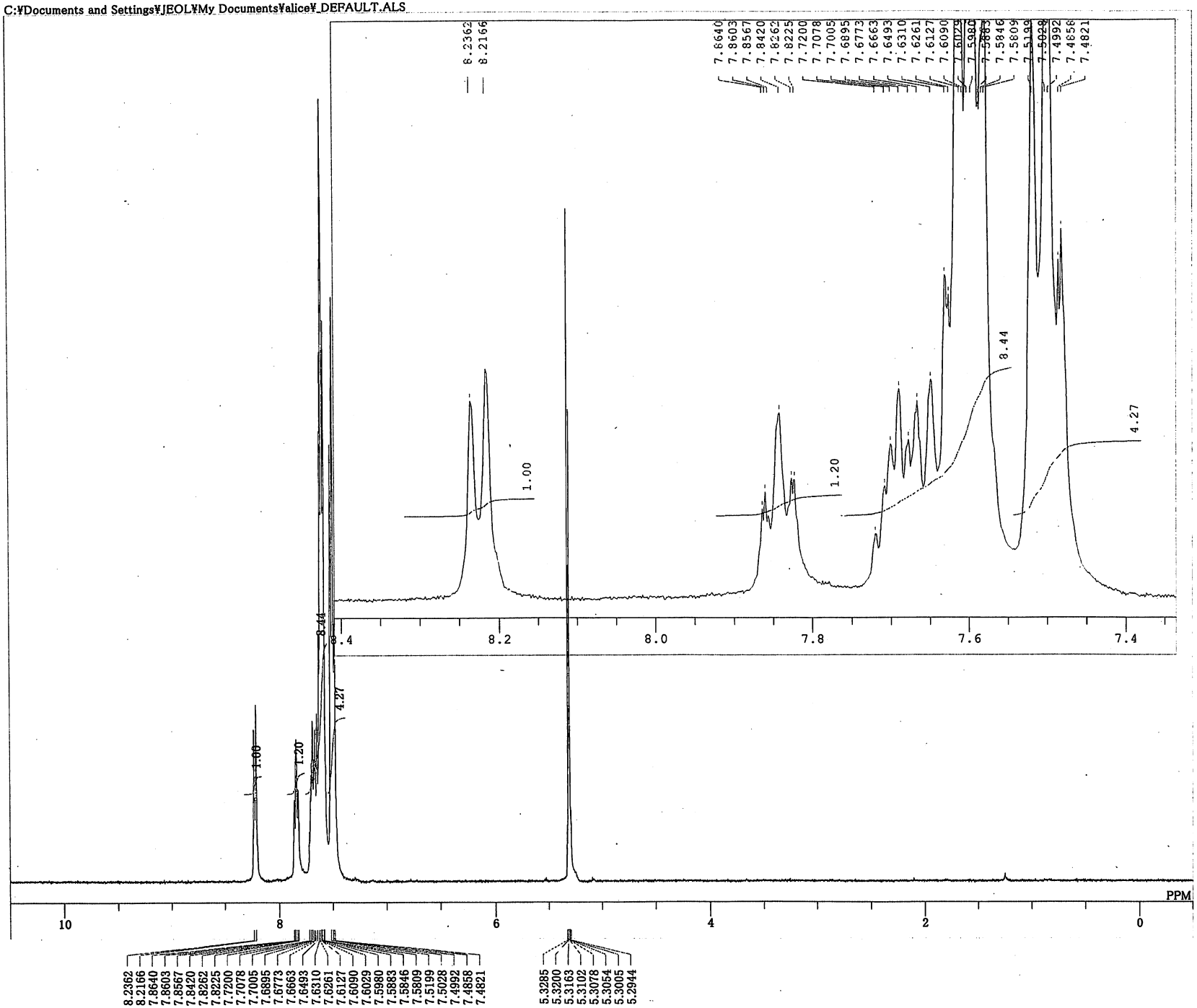
DFILE	_DEFAULT.ALS
COMNT	85_2
DATIM	Tue Nov 08 22:41:17 2011
OBNUC	31P
EXMOD	BCM
OBFRQ	161.70 MHz
OBSET	142.00 KHz
OBFIN	10220.00 Hz
POINT	16384
FREQU	100000.00 Hz
SCANS	16
ACQTM	0.1638 sec
PD	1.2000 sec
PW1	3.90 usec
IRNUC	1H
CTEMP	28.2 c
SLVNT	CD2CL
EXREF	0.00 ppm
BF	1.00 Hz
RGAIN	27

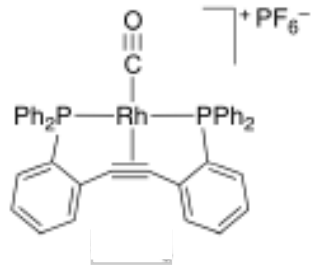
5-BArF

RhCO_PF6

C:¥Documents and Settings¥JEOL¥My Documents¥alice¥_DEFAULT.ALS

DFILE	_DEFAULT.ALS
COMNT	RhCO_PF6
DATIM	Mon Dec 12 16:30:18 2011
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	16
ACQTM	2.0501 sec
PD	4.9500 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	27.6 c
SLVNT	CD2CL
EXREF	5.32 ppm
BF	0.10 Hz
RGAIN	21



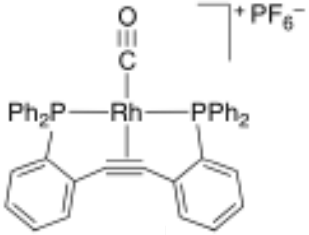


5-PF6

C:¥Documents and Settings¥JEOL¥My Documents¥alice¥_DEFAULT.ALS

99_13C

DFILE	_DEFAULT.ALS
COMNT	99_13C
DATIM	Fri Nov 25 09:25:33 2011
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	13480
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	28.0 c
SLVNT	CD2CL
EXREF	53.80 ppm
BF	0.12 Hz
RGAIN	31



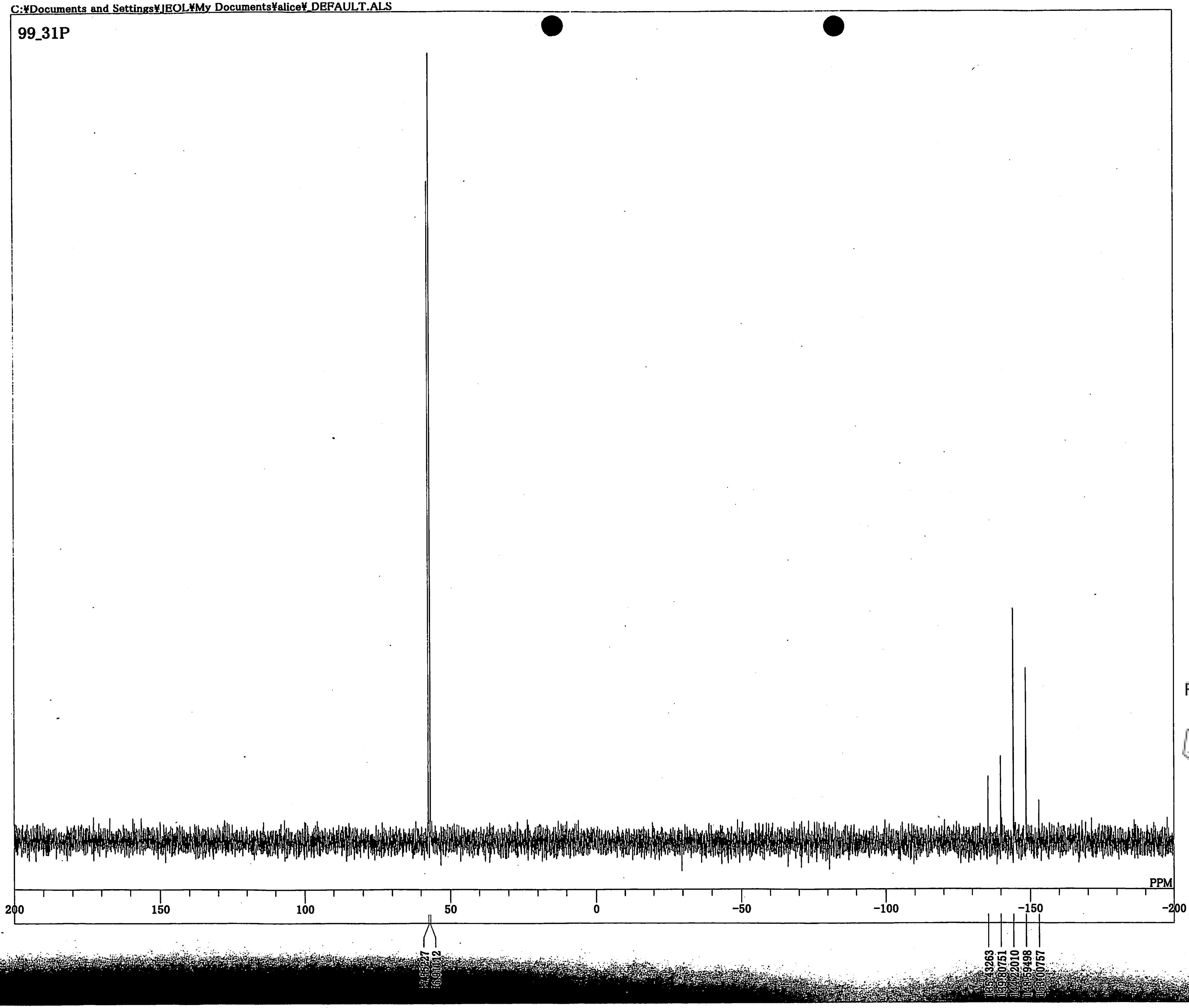
5-PF6

PPM

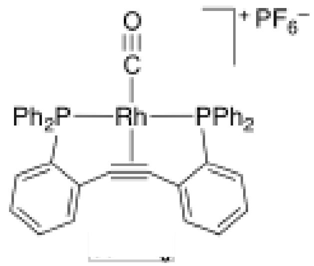
146.77191 146.52493 146.23679 134.41463 134.20881 134.13471 134.04415 133.94536 133.44317 133.37731 133.31144 132.89158 132.32352 132.14240 131.95305 131.50848 131.47555 131.43439 130.06776 130.01836 129.96073 129.64789 129.38445 106.29171 106.23408

54.34336 54.07168 53.80000 53.52832 53.25664

C:¥Documents and Settings¥JEOL¥My Documents¥alice¥_DEFAULT.ALS



DFILE	_DEFAULT.ALS
COMNT	99_31P
DATIM	Thu Nov 24 22:06:15 2011
OBNUC	31P
EXMOD	BCM
OBFRQ	161.70 MHz
OBSET	142.00 KHz
OBFIN	10220.00 Hz
POINT	16384
FREQU	100000.00 Hz
SCANS	48
ACQTM	0.1638 sec
PD	1.2000 sec
PW1	3.90 usec
IRNUC	1H
CTEMP	28.6 c
SLVNT	CD2CL
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	27



5-PF6