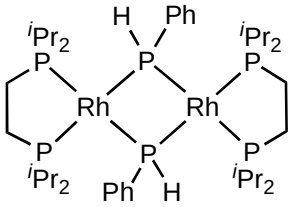
Supporting Information for

Selective Homo- and Heterodehydrocouplings of Phosphines Catalyzed by Rhodium Phosphido Complexes

Li-Biao Han and T. Don Tilley

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1460

Data for new compounds:

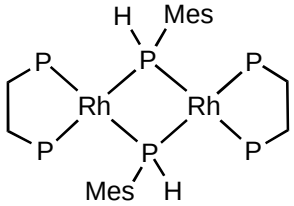


Complex **3a (See Copies of NMR Charts 1 and 2)**

The NMR spectroscopies of **3a** at room temperature in benzene are complicated and not easily assignable (NMR Charts 1 and 2). The proposed structure is consistent with the elemental analysis, and the NMR data is consistent with that of crystallographically characterized **3b**, which was unambiguously shown to be a dimer.

Brown solid, mp 238 ºC (dec). Calcd for $C_{40}H_{76}P_6Rh_2$: C, 50.64; H, 8.07. Found: C, 50.99; H, 8.26.

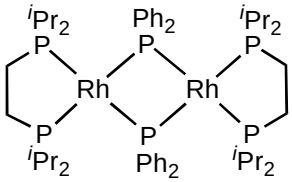
^{1}H NMR (C_6D_6, 400 MHz) δ 8.03-8.19 (m, 4 H), 7.06-7.18 (m, 6 H), 3.15-4.95 (m, 2 H, P-H), 2.21-2.32 (m, 2 H, CH_2P), 2.02-2.18 (m, 2 H, CH_2P), 1.85-1.97 (m, 4 H, CH_2P), 0.38-1.49 (m, 28 H, i-Pr). ^{31}P NMR (C_6D_6, 162 MHz) δ 82.3-86.0 (multiple sets of doublets, dppe), -120.6 - -118.3 (m, PH), -126.5 - -124.0 (m, PH).



Complex **3b (See Copies of NMR Charts 3 and 4)**

Orange solid; mp 245 ºC (dec). Calcd for $C_{46}H_{88}P_6Rh_2$: C, 53.49; H, 8.59. Found: C, 53.71; H, 8.79.

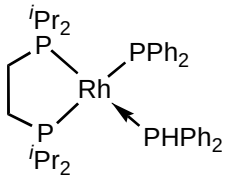
^{1}H NMR (C_6D_6, 400 MHz) δ 6.99 (s, 2 H, $C_6\underline{H}_2Me_3$), 6.84 (s, 2 H, $C_6\underline{H}_2Me_3$), 4.63 (s, 6 H, $C_6H_2\underline{Me}_3$), 3.24-3.91 (m, 2 H, PH), 2.83 (s, 6 H, $C_6H_2\underline{Me}_3$), 2.31 (s, 6 H, $C_6H_2\underline{Me}_3$), 1.71-1.88 (m, 8 H, CH_2), 1.63 (dd, 12 H, J = 7.2, 13.2 Hz, $CH\underline{Me}_2$), 1.17 (dd, 12 H, J = 6.8, 14.0 Hz, $CH\underline{Me}_2$), 0.79-0.91 (m,), 0.82 (t-like, 12 H, J = 7.6 Hz, $CH\underline{Me}_2$), 0.71-0.82 (m, 4 H, $\underline{CH}Me_2$), 0.46 (dd, 12 H, J = 7.2, 15.6 Hz, $CH\underline{Me}_2$). ^{31}P NMR (C_6D_6, 162 MHz) δ 81.3-83.6 (multiple sets of doublets, dppe), -253.8 - -251.0 (m, PH).



Complex **3c·PhMe (See Copies of NMR Charts 5 and 6)**

Red solid; mp 198 ºC (dec). Calcd for $C_{59}H_{92}P_6Rh_2$: C, 59.40; H, 7.77. Found: C, 59.29; H, 7.50.

^{1}H NMR (C_6D_6, 400 MHz) δ 8.38-8.47(m, 8 H, Ph), 6.95-7.18(m, 12 H, Ph), 1.62 (bs, 8 H, CH_2), 0.87-1.11 (m, 56 H, i-Pr). ^{31}P NMR (C_6D_6, 162 MHz) δ 71.4-75.6 (multiple sets of doublets, dppe), -112.4 - -108.1 (m, μ-PPh_2).



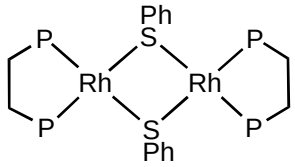
Complex **4 (See Copies of NMR Charts 7 and 8)**

Red solid; mp 151 ºC (dec). Calcd for $C_{38}H_{53}P_4Rh$: C, 61.96; H, 7.25. Found: C, 62.02; H, 7.32.

^{1}H NMR (C_6D_6, 400 MHz) δ 7.99 (bs, 4 H, Ph), 7.43 (bs, 4 H), 6.89-7.02 (m, 12 H), 6.00 (bs, 1 H, P-H), 2.77 (bs, 4 H, CH_2), 0.84-1.35 (m, 28 H, i-Pr). ^{31}P NMR (C_6D_6, 162 MHz) δ 79.8-81.5 (multiple sets of doublets, dppe), 74.3-77.5 (multiple sets of

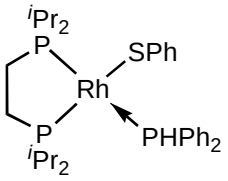
doublets, dppe), 13.7-16.7 (multiple sets of doublets, $PHPh_2$), -47.2 - -46.3 (m, PPh_2).

Complex **6 (See Copies of NMR Charts 9 and 10)**



Orange solid; mp 155 ºC (dec). Calcd for $C_{40}H_{74}P_4Rh_2S_2$: C, 50.63; H, 7.86. Found: C, 50.94; H, 7.81.
^{1}H NMR (C_6D_6, 400 MHz) δ 8.29-8.30 (m, 4 H, Ph), 6.92-7.11 (m, 6 H, Ph), 1.72-1.90 (m, 4 H, CH_2), 1.32-1.33 (m, 12 H, i-Pr), 0.94-1.03 (m, 16 H, i-Pr). ^{31}P NMR (C_6D_6, 162 MHz) δ 88.3 (d, J_{PRh} = 173.0 Hz).

Complex **7b (See Copies of NMR Charts 11 and 12)**



Yellow solid; mp 128 ºC (dec). Calcd for $C_{32}H_{48}P_3RhS$: C, 58.18; H, 7.32; S, 4.85. Found: C, 58.30; H, 7.45; S, 4.68.
^{1}H NMR (C_6D_6, 400 MHz) δ 7.80-7.91 (m, 6 H), 6.79-7.02 (m, 9 H), 5.98 (d, 1 H, J = 10.8 Hz), 2.28-2.42 (m, 2 H, CH_2), 1.61-1.80 (m, 2 H, CH_2), 0.84-1.37 (m, 28 H, i-Pr). ^{31}P NMR (C_6D_6, 162 MHz) δ 89.7 (ddd, $-CH_2\underline{P}^iPr_2$ *cis* to PPh_2H, J_{PP} = 24.7, 35.9 Hz, J_{PRh} = 152.7 Hz), 81.2 (ddd, $-CH_2\underline{P}^iPr_2$ *trans* to PPh_2H, J_{PP} = 24.7, 351.5 Hz, J_{PRh} = 145.6 Hz), 1.2 (ddd, PPh_2H, J_{PP} = 35.9, 356.5 Hz, J_{PRh} = 131.5 Hz).

Rhodium-catalyzed Dehydrocoupling of phosphines

(1) Dehydrocoupling of $PhPH_2$ was carried out under various reaction conditions as summarized below. For concentrations in the range of 0.18 M to 1.00 M, reactions proceed similarly. On the other hand, the addition of dippe gave a better yield of the coupling products. Though heating the mixture at 70 ºC gave a better conversion of $PhPH_2$, other products were also formed as confirmed by ^{31}P NMR and the selectivity to $(PPhH)_2$ was only 36%. The reaction proceeds faster in THF to give a complicated mixture of dehydrocoupling products in which $(PPhH)_2$ was formed with a selectivity of 30%. Catalysts generated *in situ*, by addition of dippe or dchpe to **1**, behaved similarly to those based on the isolated phosphine complexes. As shown below, other catalysts obtained by addition of a phosphine to **1** did not show catalytic activity (20 ºC, overnight). A typical ^{31}P NMR spectrum of a dehydrocoupling reaction mixture (5 mol% cat. **1**, 1.0 M, 20 h) is attached (**NMR Chart 13**). The product $(PPhH)_2$ was identified by comparing its spectra with those reported in the literature (Xin, S.; Woo, H. G.; Harrod, J. F.; Samuel, E.; Lebuis A.-M. *J. Am. Chem. Soc.* **1997**, *119*, 5307).

(2) Dehydrocoupling products from other phosphines.

$(2\text{-EtC}_6H_4PH)_2$: a mixture of *meso,rac* isomers; ratio (^{31}P NMR chemical shift): 53 (-76.0 ppm), 47 (-83.5 ppm); HRMS calcd for $C_{16}H_{20}P_2$, m/z 274.1040. Found: 274.1045.

$(2\text{-i-PrC}_6H_4PH)_2$: a mixture of *meso,rac* isomers; ratio (^{31}P NMR chemical shift): 57 (-72.6 ppm), 43 (-80.4 ppm); HRMS calcd for $C_{18}H_{24}P_2$, m/z 302.1353. Found: 302.1359.

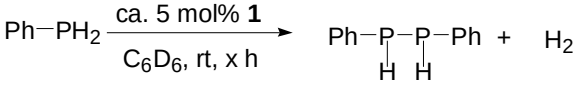
$(MesPH)_2$: a mixture of *meso,rac* isomers; ratio (^{31}P NMR chemical shift): 62 (-111.9 ppm), 38 (-119.2 ppm); HRMS calcd for $C_{18}H_{24}P_2$, m/z 302.1353. Found: 302.1348.

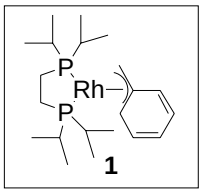
$(MesPH)_2$: a mixture of *meso,rac* isomers; ratio (^{31}P NMR chemical shift): 59 (-113.3 ppm), 41 (-118.0 ppm); HRMS calcd for $C_{30}H_{48}P_2$, m/z 470.3231. Found: 470.3238.

$(Ph_2P)_2$: This is a know compound, Bohm, V. P. W.; Brookhart, M. *Angew. Chem. Int. Ed.* **2001**, *40*, 4694.

Ph_2PSPh: ^{31}P NMR chemical shift: -41.7; HRMS calcd for $C_{18}H_{15}PS$, m/z 294.0632. Found: 294.0627. This is a know compound: (a) Peake, S.C.; Schmutzler, R. *J. Chem. Soc. A*, **1970**,1049-1054. (b) Hall, C. D.; Tweedy, B. R.; Kayhanian, R.; Lloyd, J. R. *J. Chem. Soc. Perkin Trans.2* **1992**, 775.

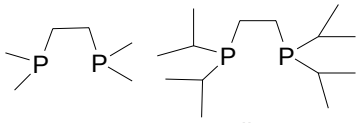
Optimization of the reaction condition



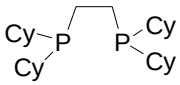


concentration	[0.18 M]	20 h, 30 %
	[0.68 M]	3h, 20% ; 20 h, 34%
	[1.00 M]	3h, 20% ; 20 h, 36% [70°C (1 h), 60% conv. of $PhPH_2$ (36% sel. to $(PPhH)_2$)]
additive →	[1.00 M] /1.0 equiv. **dippe**	20 h, 51%
solvent	[1.00 M] /1.0 equiv. dippe **THF**	20 h, 80 % conv. of $PhPH_2$ (30% sel. to $(PPhH)_2$)
	[1.00 M] /1.0 equiv. dippe **hexane**	20 h, 36 %
	[1.00 M] /1.0 equiv. dippe **CH_2Cl_2**	20 h, 20%
in situ generated cat.	Rh(cod)Bn/1.0 equiv. dippe/[1.00 M]	20 h, 31%
	Rh(cod)Bn/2.0 equiv. dippe/[1.00 M]	20 h, 52%
	Rh(cod)Bn/1.0 equiv. dchpe/[1.00 M]	20 h, 32%

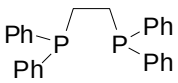
No coupling with Rh(cod)Bz, Rh(cod)Bz/ 2 or 4 equiv. PEt_3, Rh(cod)Bz/ 2 or 4 equiv. $P(t\text{-}Bu)_3$, Rh(cod)Bz/ 2 equiv. dmpe, Rh(cod)Bz/ 2 equiv. dppe, $[Rh(cod)Cl]_2$, $[Rh(cod)Cl]_2$/2equiv. dippe



dippe



dichpe



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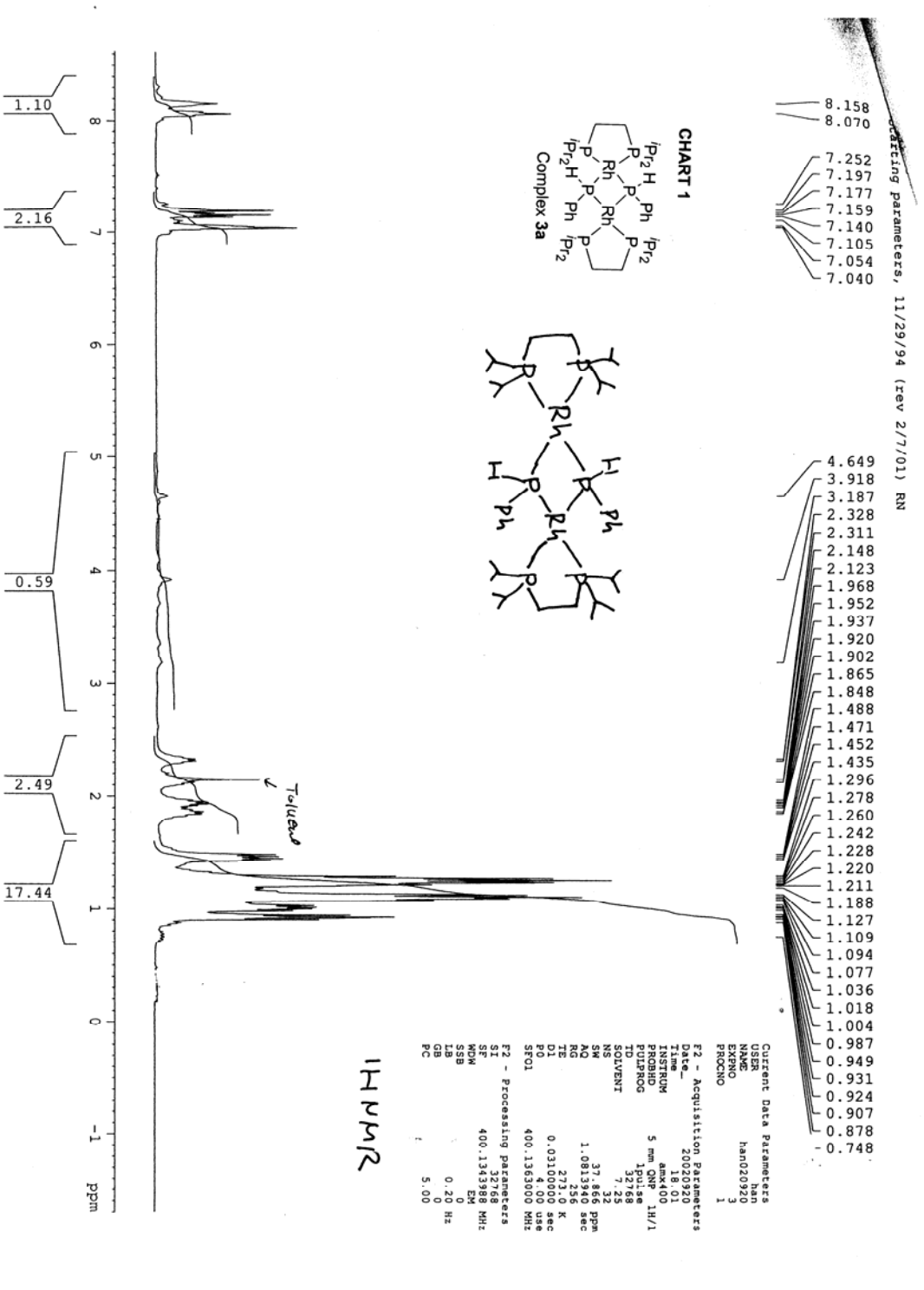
PPh_3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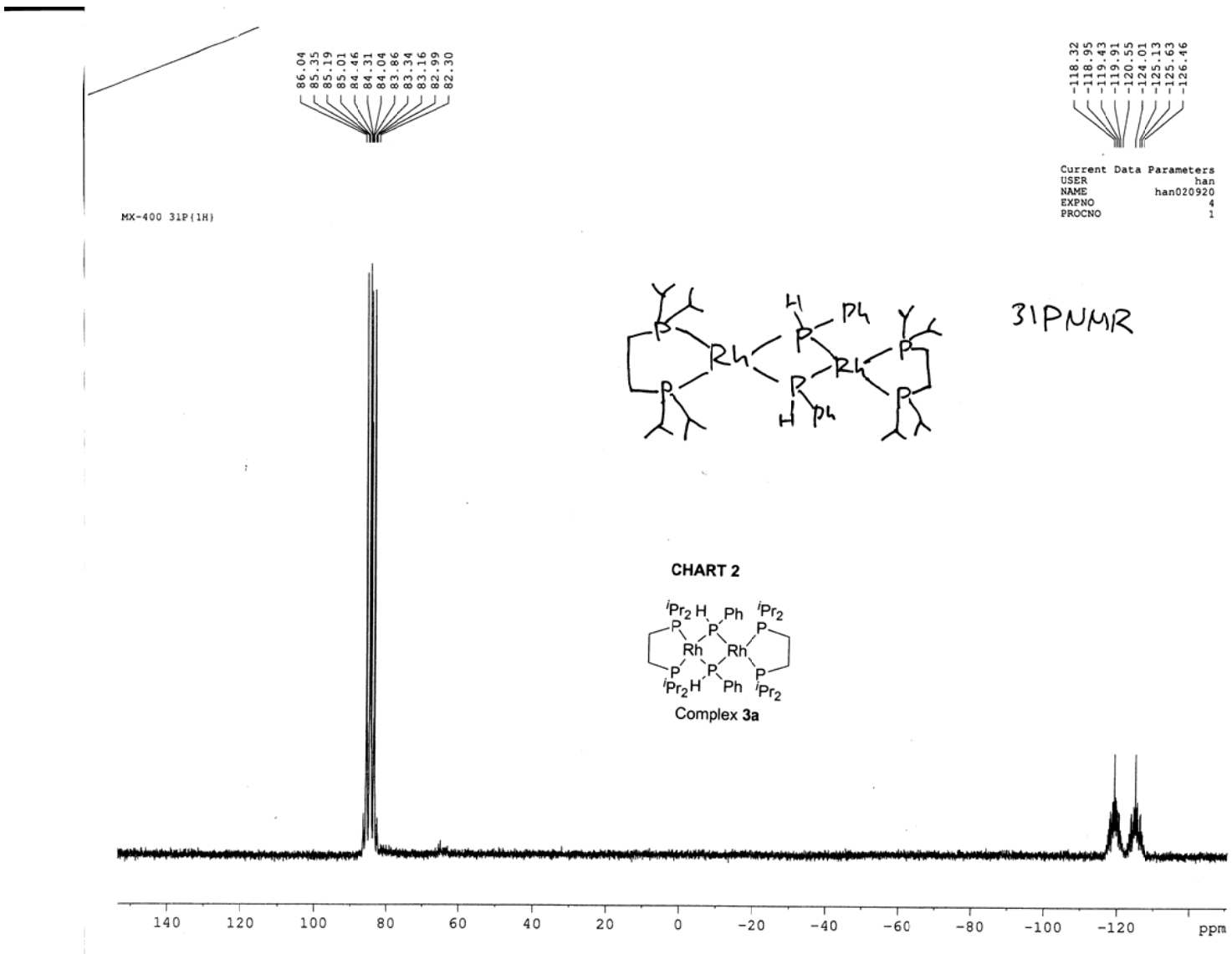
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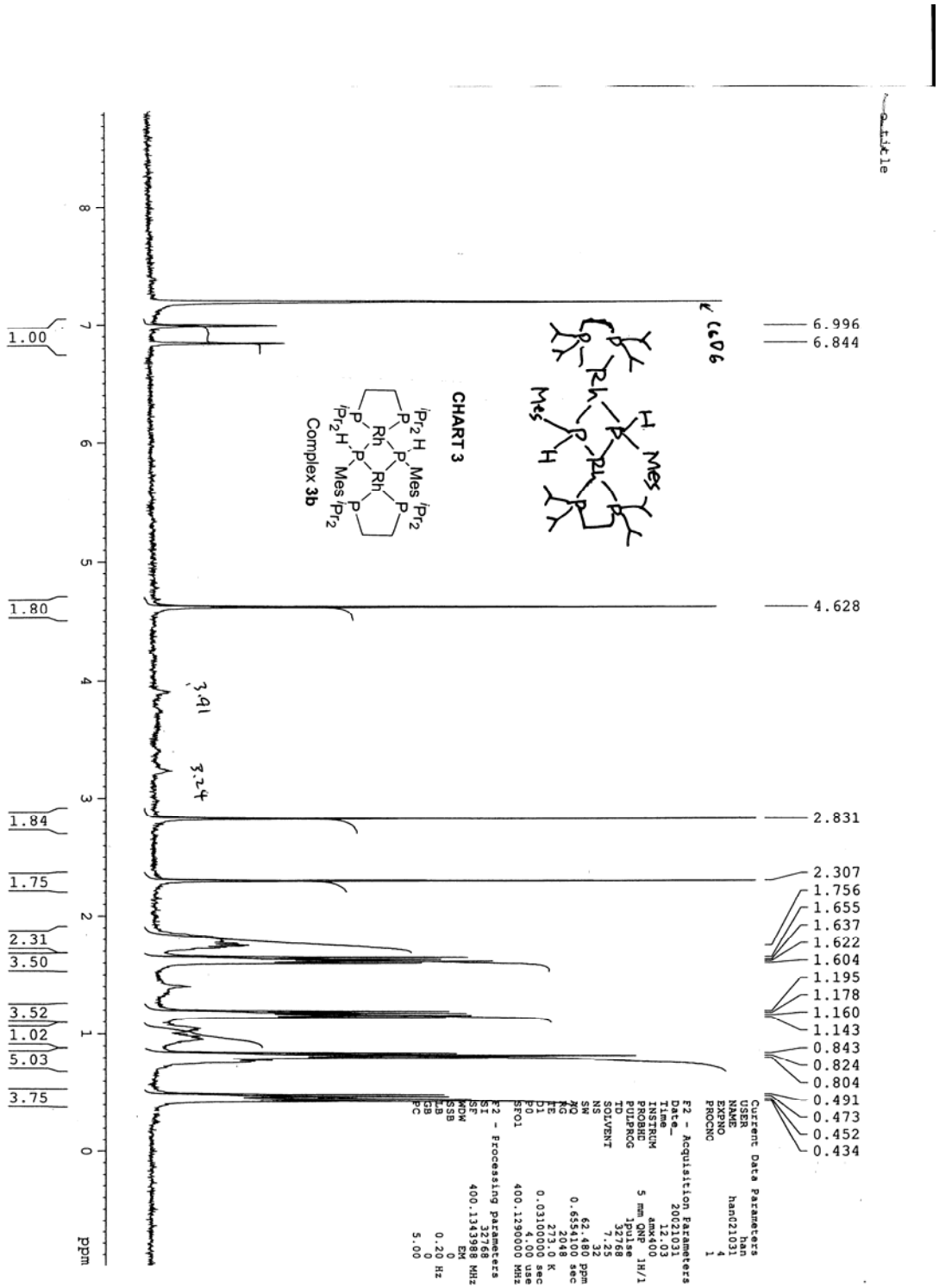
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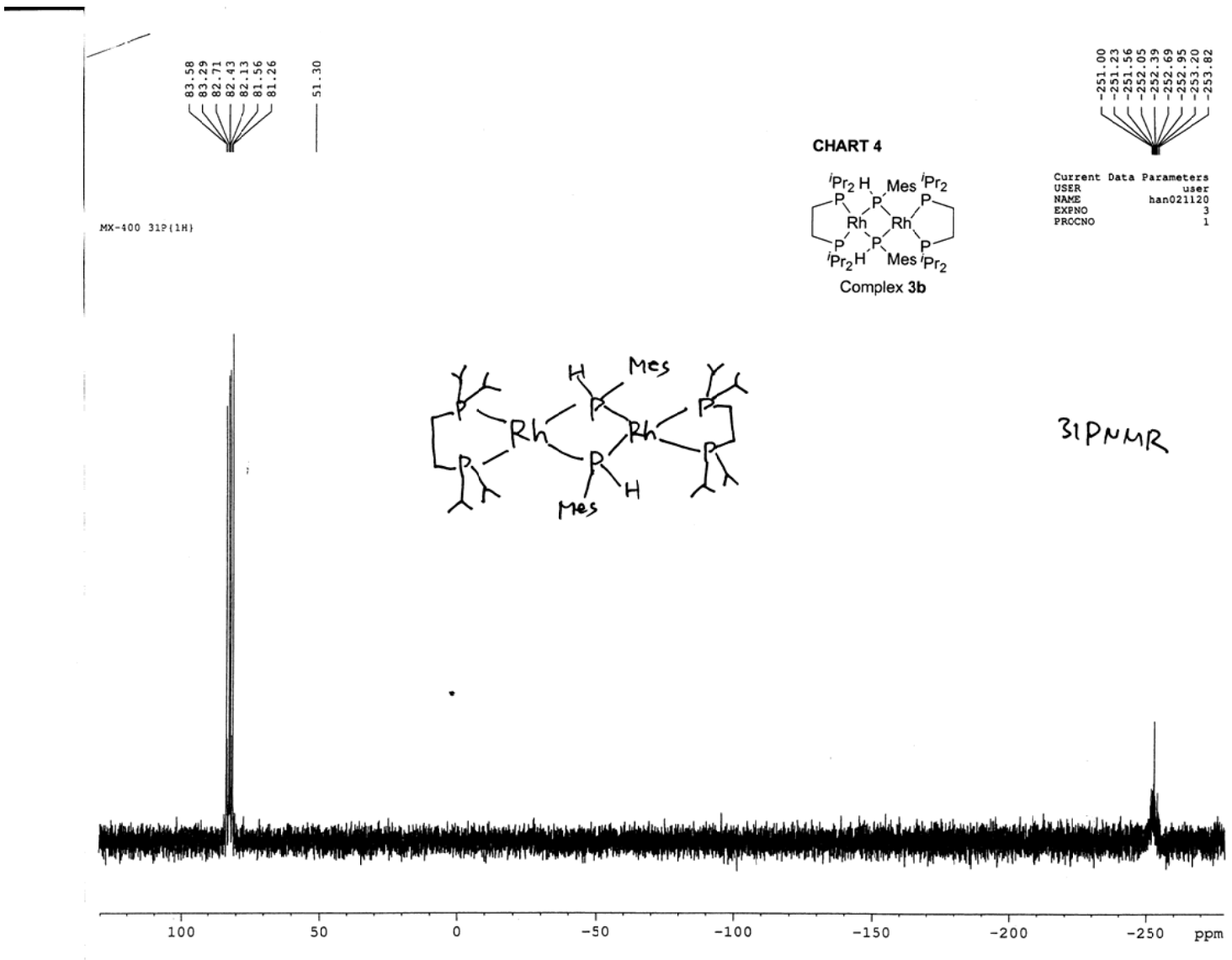
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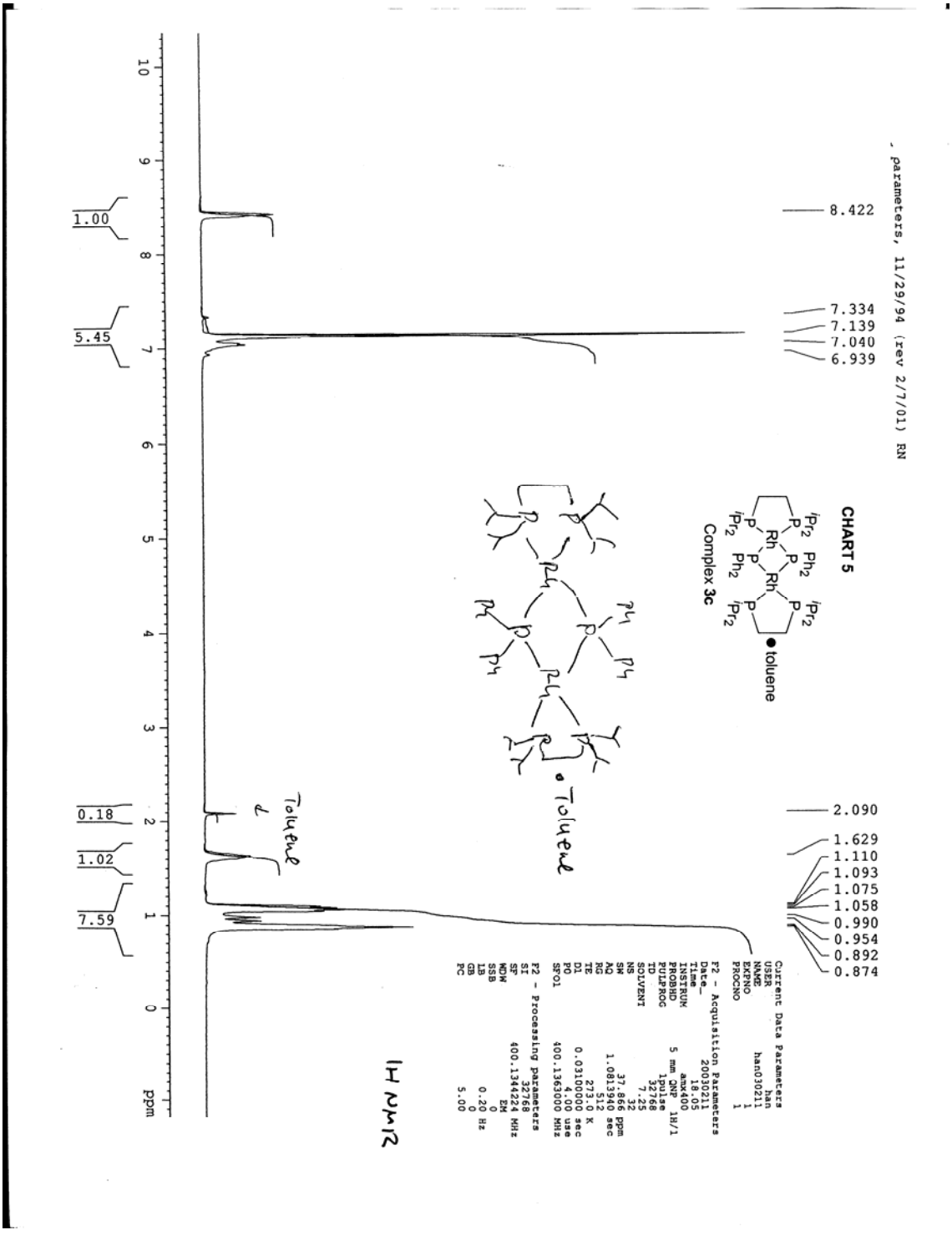
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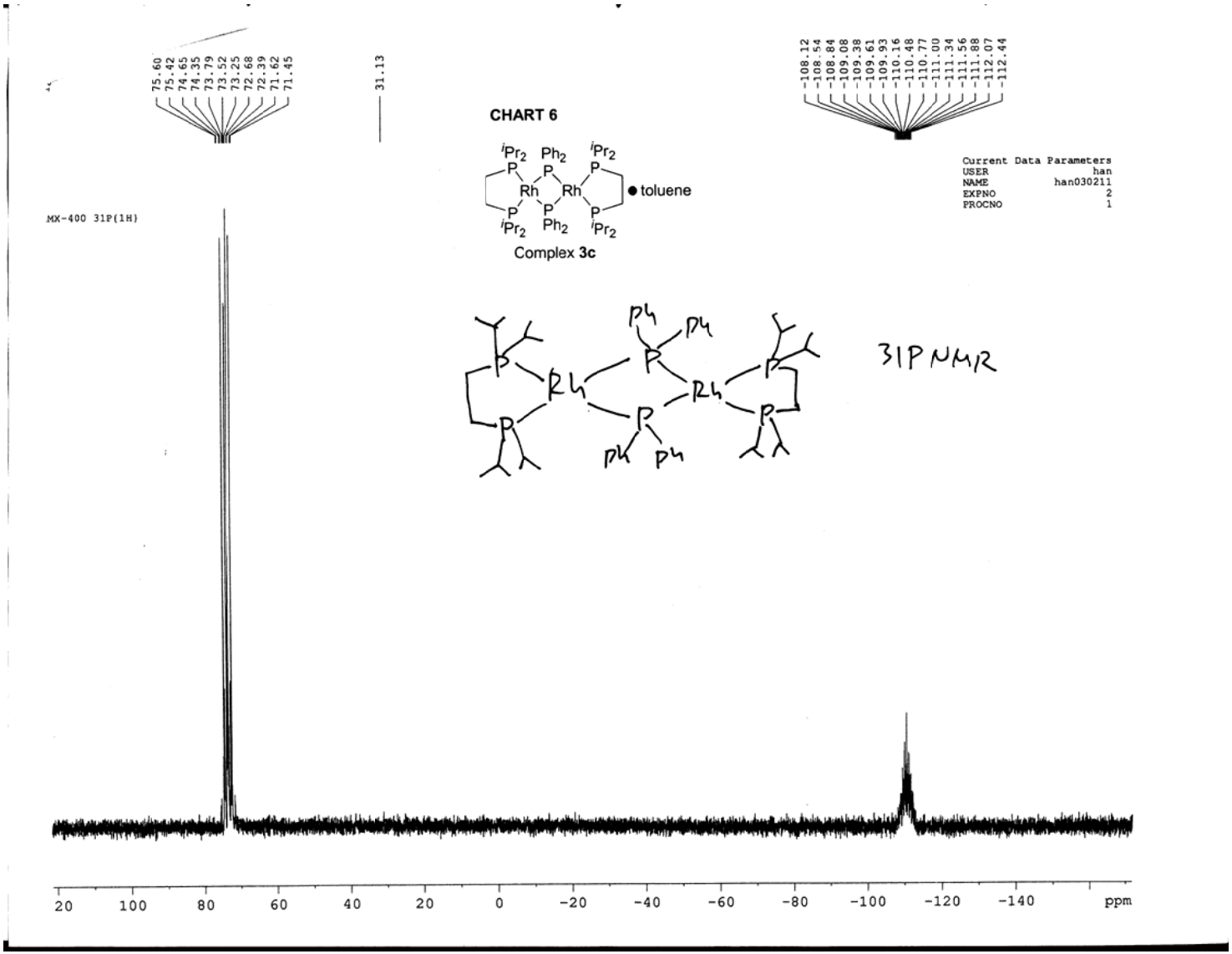
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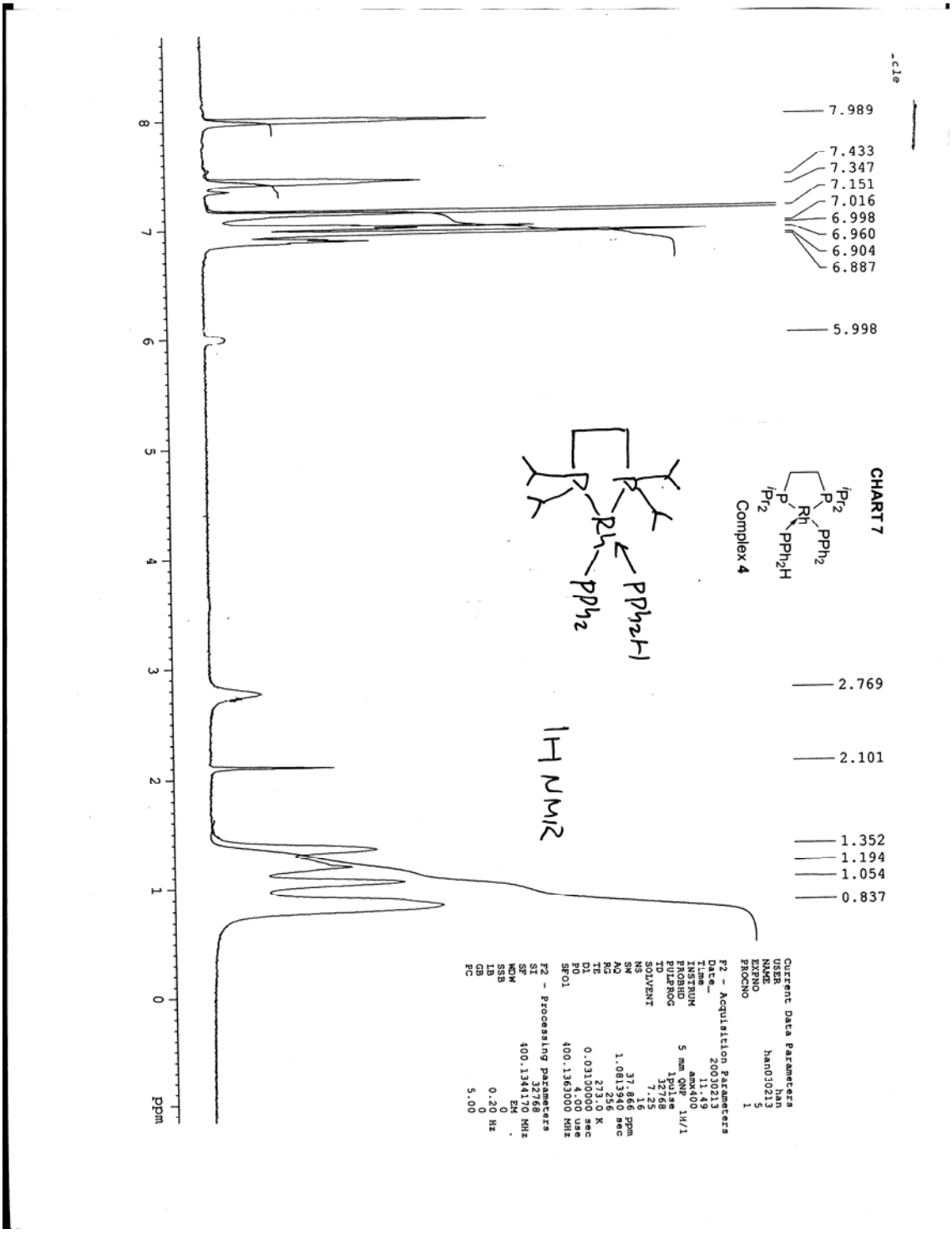
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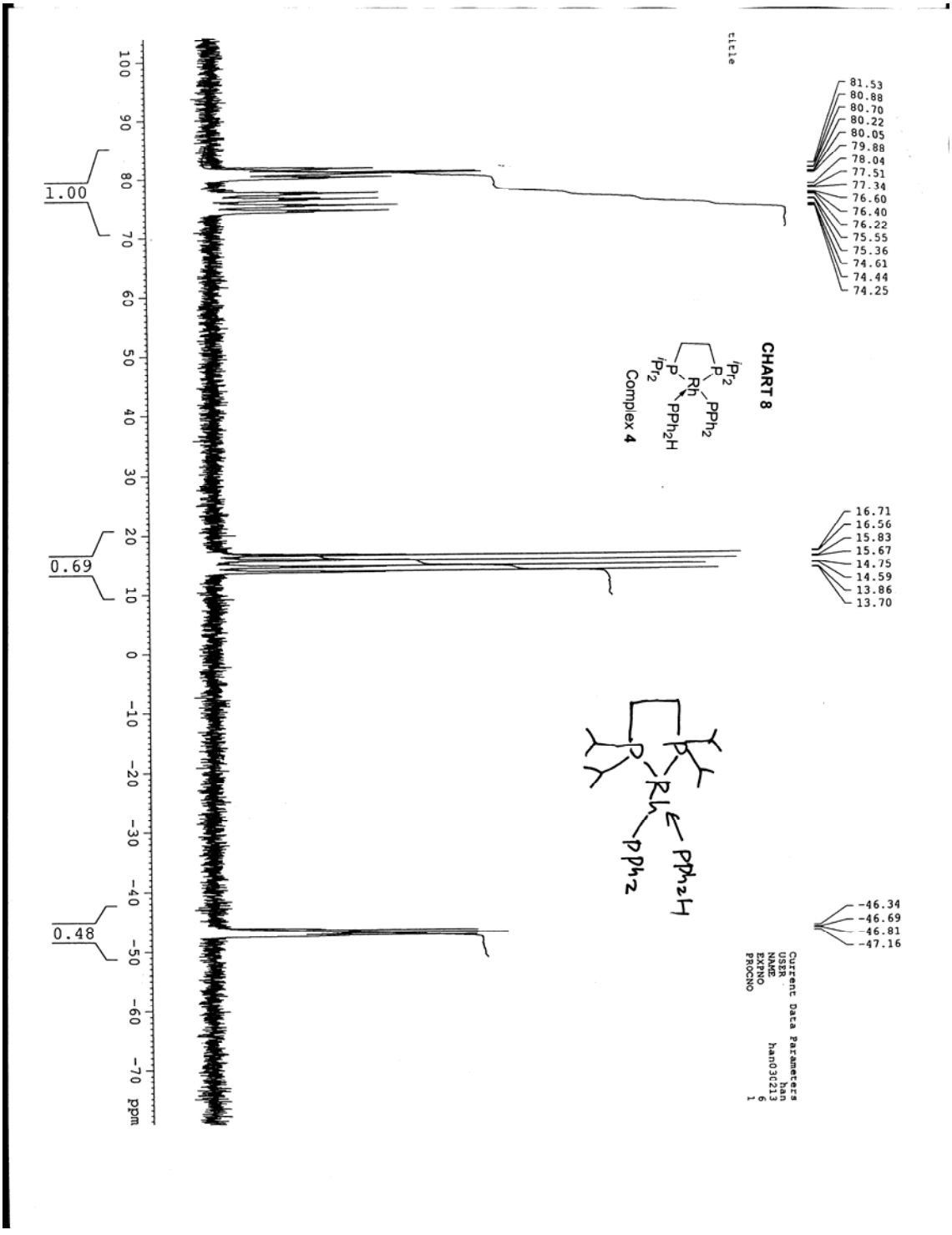
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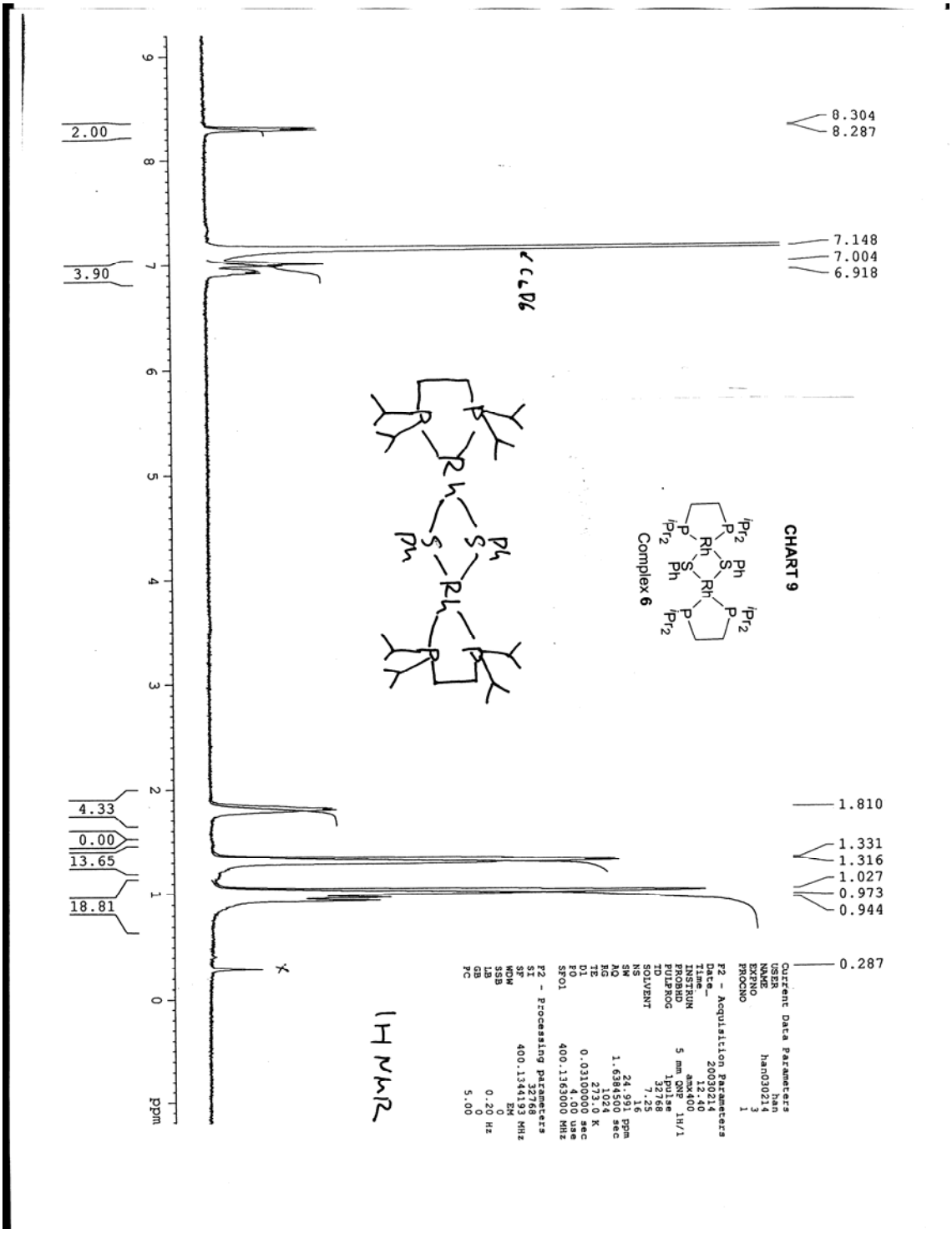
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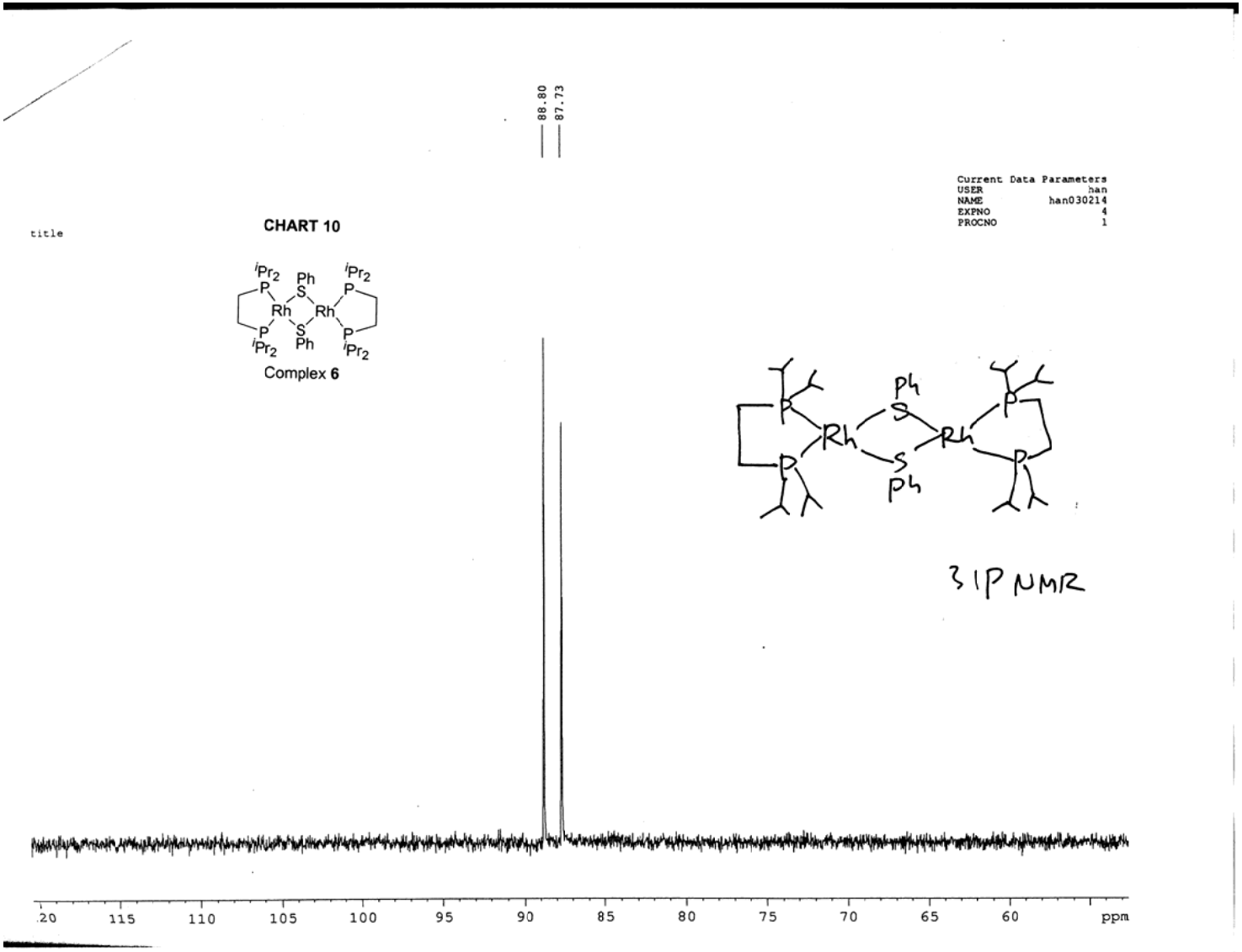
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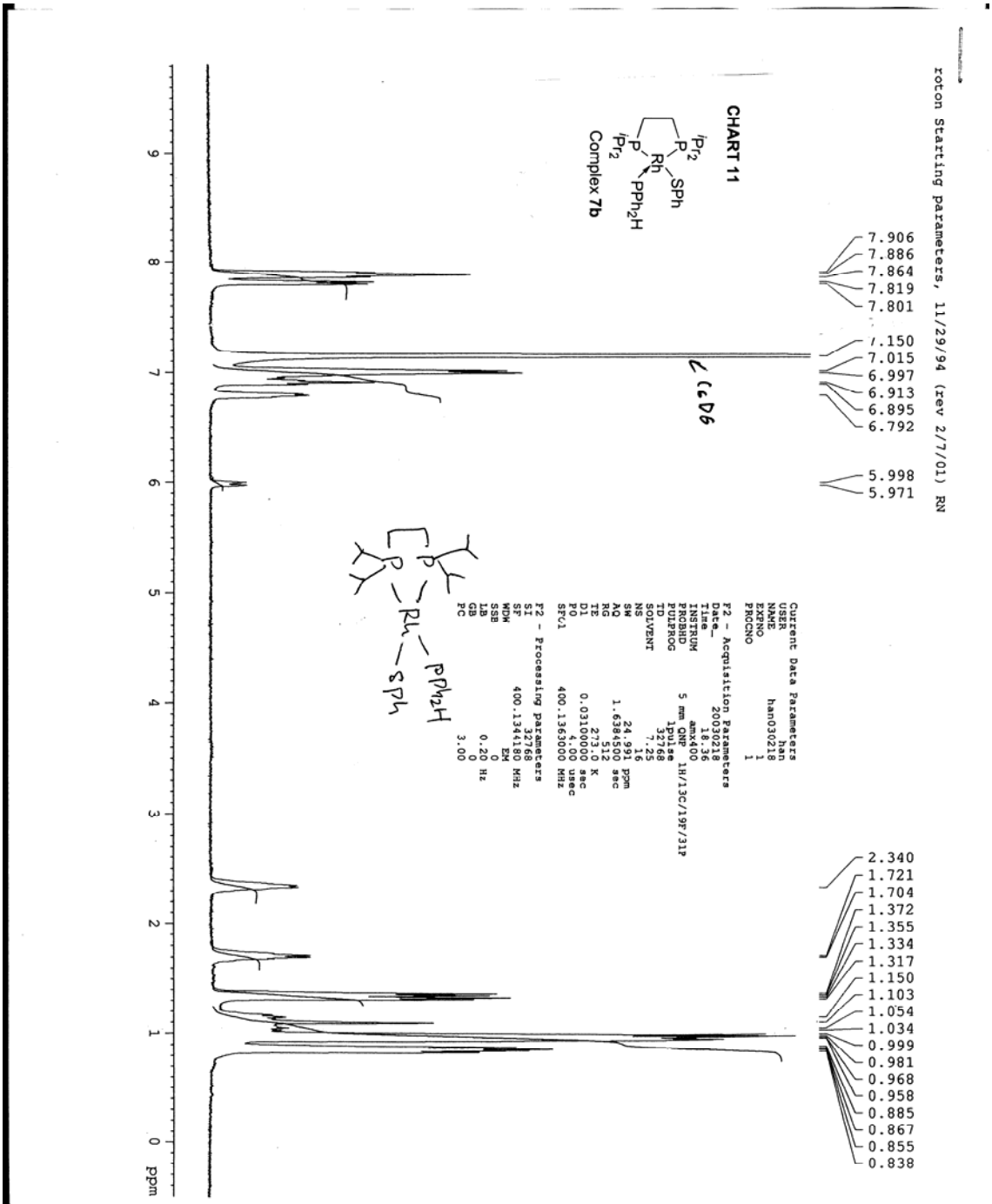
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1.704
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1.334
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1.103
1.054
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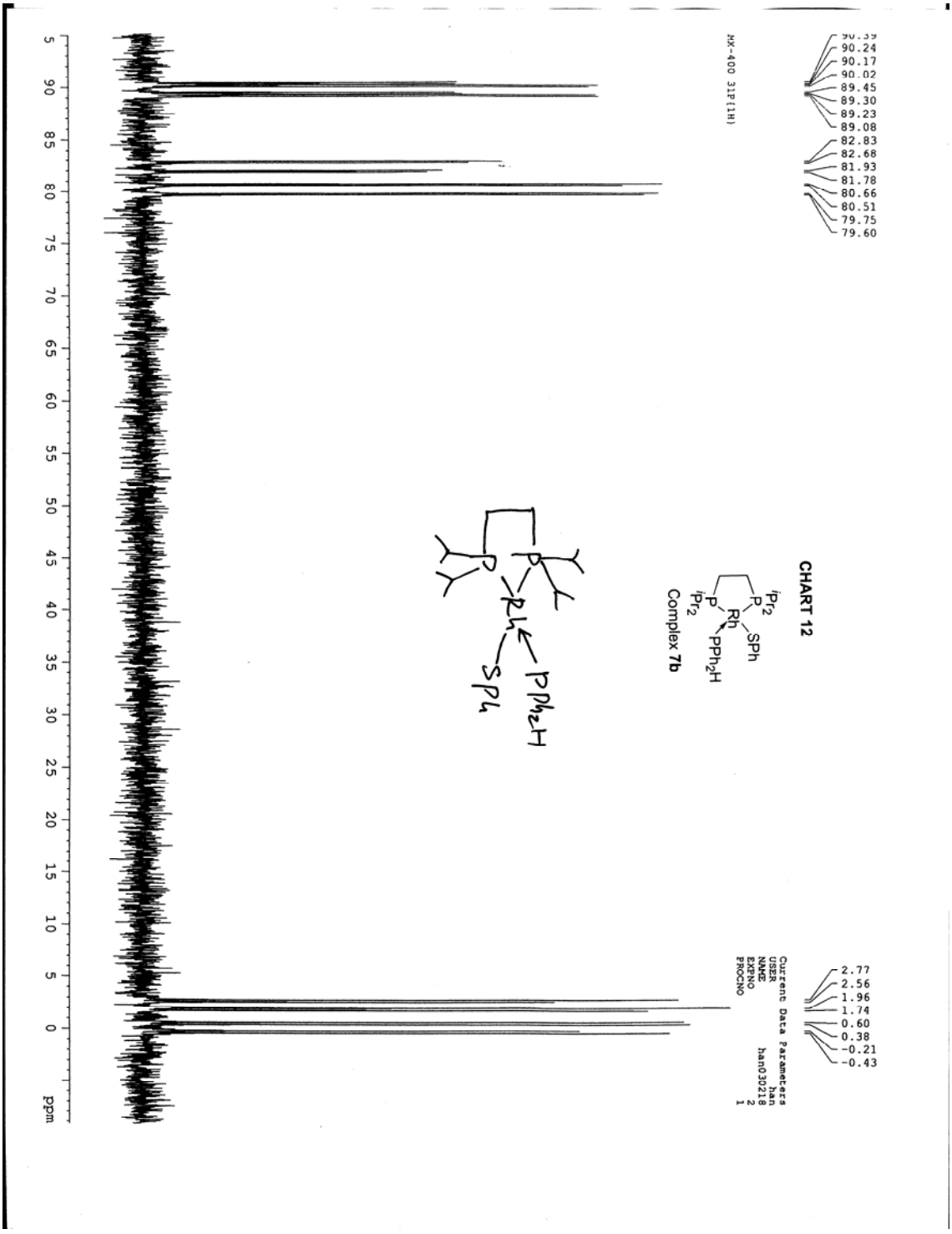
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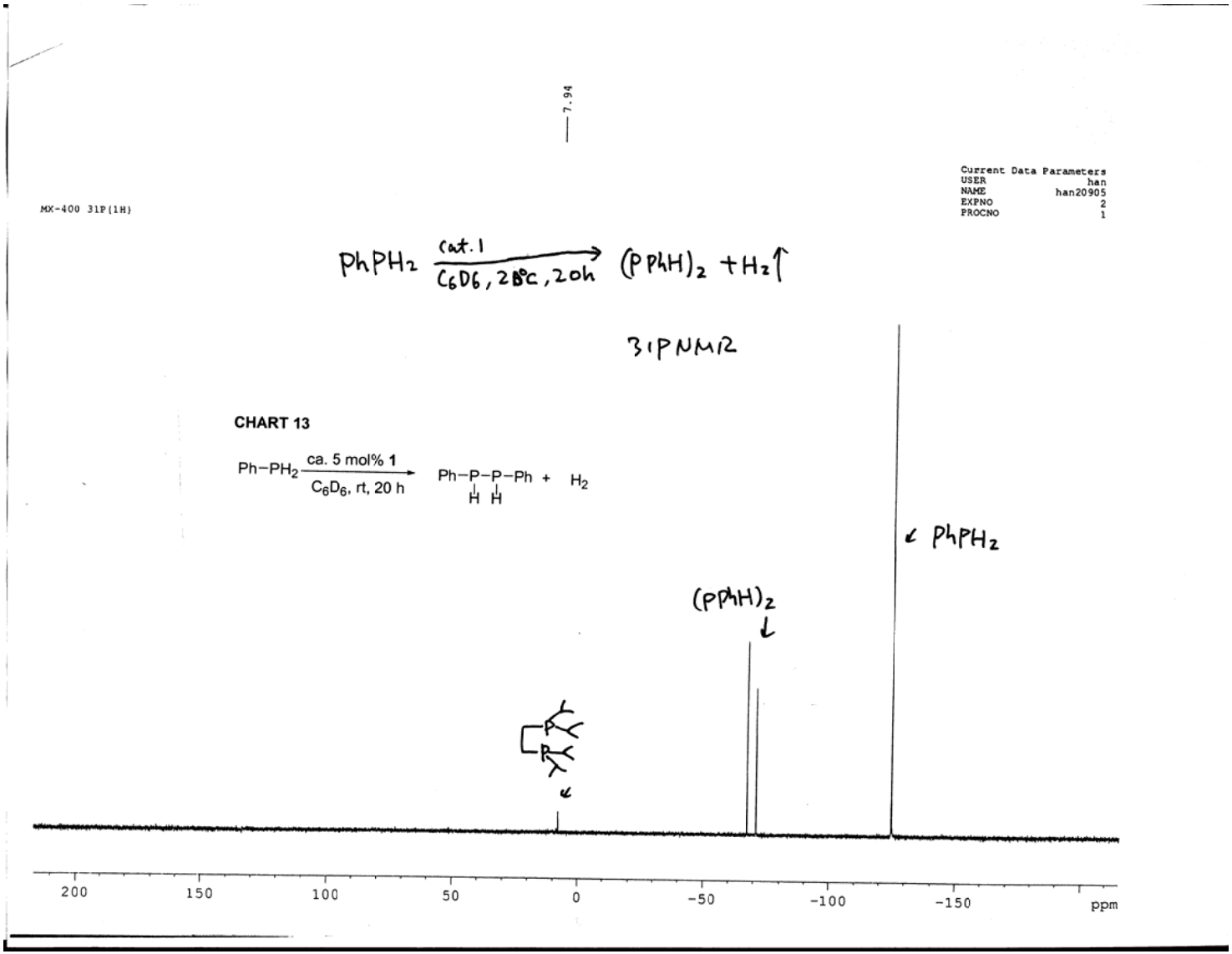
79.75
79.60
MX-400 31P{1H}
CHART 12
Complex 7b
SPh
PPh2H
2.77
2.56
1.96
1.74
0.60
0.38
-0.21
-0.43
Current Data Parameters
USER han
NAME han030218
EXPNO 2
PROCNO 1
5 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm


7.94
MX-400 31P{1H}
Current Data Parameters
USER han
NAME han20905
EXPNO 2
PROCNO 1
PhPH2 cat.1 / C6D6, 28°C, 20h (PPhH)2 + H2↑
31P NMR
CHART 13
Ph–PH2 ca. 5 mol% 1 / C6D6, rt, 20 h Ph–P–P–Ph + H2
H H
PhPH2
(PPhH)2
200
150
100
50
0
-50
-100
-150
ppm