SUPPORTING INFORMATION

Synthesis, reaction and recycle of light fluorous Grubbs-Hoveyda catalysts for alkene metathesis

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Contains procedures for reactions and spe purifications along with spectroscopic data for products and copies of NMR spectra of typical products after spe (34 pages).

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General: All melting points are uncorrected. Anhydrous CH_2Cl_2 was passed through a column of activated aluminum oxide. Anhydrous THF was distilled from sodium/benzophenone under nitrogen. ^1H and ^{19}F NMR spectra were measured in $CDCl_3$ with TMS or $CHCl_3$ as the internal standard. Non-fluorous catalyst **1** was prepared according to Hoveyda's procedure.[1] *N*,*N*-diallyl-4-methylbenzenesulfonamide and *N*,*N*-diallyl-2-methylbenzenesulfonamide were prepared by known procedures.[2,3] Acrylic acid 1-pentadecylbut-3-enyl ester was prepared by condensation of cinnamoyl chloride and corresponding alcohol. Allylpent-4-enylcarbamic acid *tert*-butyl ester is a known compound.[4] 1-Allyl-2-allyloxybenzene was prepared by the known procedure.[5] RCM products 1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (**11**),[2] 1-(toluene-2-sulfonyl)-2,5-dihydro-1*H*-pyrrole,[3] cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester,[6] 2,3,4,7-tetrahydroazepine-1-carboxylic acid *tert*-butyl ester,[4] 2,5-dihydrobenzo[*b*]oxepine[7] and 5-phenylpent-2-enoic acid benzyl ester (**13**)[8] are known products.

1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-3-iodoundecyl)-4-methoxybenzene: Under argon atmosphere, 4-allyl-1-methoxybenzene **6** (1.24 g, 8.38 mmol), $C_8F_{17}I$ (10.0 g, 18.3 mmol) and $Pd(PPh_3)_4$ (484 mg, 0.42 mmol) were dissolved CH_2Cl_2 (20 mL). Then to this solution, Me_3Al (2M hexane solution of 4.2 mL, 8.38 mmol) was slowly added at room temperature. This reaction mixture was stirred at room temperature for 24 h and then poured into dilute HCl. The organic layer was separated and evaporated. The residue was purified by column chromatography on silica gel using pure pentane - pentane/AcOEt (4:1) to give an almost pure product. Further purification by recrystallization gave desired pure product as a colorless solid (3.72 g, 64.0%); mp 54.0-55.0 °C: ^1H NMR (300 MHz, $CDCl_3$) δ 2.86 (m, 2H), 3.19 (m, 2H), 3.82 (s, 3H), 4.43 (m, 1H), 6.87 (dd, 2H, J = 6.7, 1.9 Hz), 7.13 (dd, 2H, J = 6.9, 1.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –124.9 (2F),

–122.4 (2F), –121.5 (2F), –120.7 (4F), –120.4 (2F), –111.7 (2F), –79.5 (3F); HRMS (EI) Calcd for $C_{18}H_{12}F_{17}IO$ (M^+) 693.9678. Found: 693.9661.

1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-4-methoxybenzene (7): To a solution of 1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-3-iodoundecyl)-4-methoxybenzene (2.28 g, 3.29 mmol) and tributyltin hydride (1.33 mL, 4.95 mmol) in benzene (50 mL) under argon was added AIBN (110 mg, 0.67 mmol) at room temperature. After reflux for 12 h, the reaction mixture was cooled to room temperature. Aqueous KF solution was added and the mixture was stirred vigorously for 12 h. The organic layer was separated and concentrated. The residue was purified by column chromatography on silica gel using pure pentane - pentane/AcOEt (8:1) to give the product **3** as a colorless solid (1.51g, 80.8%); mp 38.5-39.5 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (m, 2H), 2.07 (m, 2H), 2.66 (t, 2H, *J* = 7.5 Hz), 3.81 (s, 3H), 6.86 (dd, 2H, *J* = 6.6, 2.0 Hz), 7.10 (dd, 2H, *J* = 6.6, 2.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –124.9 (2F), –122.2 (2F), –121.5 (2F), –120.7 (6F), –112.9 (2F), –79.5 (3F); HRMS (EI) Calcd for $C_{18}H_{13}F_{17}O$ (M^+) 568.0697. Found: 568.0695.

4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)phenol: To a solution of 1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-4-methoxybenzene (1.39 g, 2.45 mmol) in 1,2-dichloroethane (40 mL) under argon was added boron tribromide-methyl sulfide complex (3.06 g, 9.79 mmol) at room temperature. After reflux for 12 h, the reaction mixture was hydrolyzed by adding water (30 mL). The organic layer was separated and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane/AcOEt (8:1) - hexane/AcOEt (5:1) to give the desired product as a

colorless solid (1.19 g, 87.7%); mp 92.0-93.0 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.86-1.98 (m, 2H), 2.01-2.68 (m, 2H), 2.65 (t, 2H, *J* = 7.2 Hz), 4.59 (s, 1H), 6.78 (dd, 2H, *J* = 8.5, 1.9 Hz), 7.06 (dd, 2H, *J* = 8.3, 1.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –124.9 (2F), –122.2 (2F), –121.5 (2F), –120.7 (6F), –112.9 (2F), –79.5 (3F); HRMS (EI) Calcd for $C_{17}H_{11}F_{17}O$ (M^+) 554.0531. Found: 554.0538.

1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-4-isopropoxybenzene (8): To a suspension of sodium hydride (186 mg, 4.65 mmol) in dry tetrahydrofuran (20 mL) under argon was added at 0 °C a solution of 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)phenol (1.17 g, 2.11 mmol) in dry tetrahydrofuran (20 mL). After gas evolution, dry dimethylformamide (30 mL) and isopropyl bromide (232 µl, 4.64 mmol) were syringed into the reaction mixture. The resulting mixture was stirred at room temperature for 16 h. The reaction mixture was concentrated *in vacuo* and ethyl acetate (50 mL) was added. The organic layer was washed 3 times with a saturated solution of sodium hydrogencarbonate and one time with brine and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane/AcOEt (8:1) to give **4** as a colorless oil (1.19 g, 93.8%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (d, 6H, *J* = 6.1 Hz), 1.94 (m, 2H), 2.05-2.11 (m, 2H), 2.65 (t, 2H, *J* = 7.2 Hz), 4.53 (m, 1H), 6.84 (d, 2H, *J* = 8.5 Hz), 7.09 (d, 2H, *J* = 8.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –124.9 (2F), –122.2 (2F), –121.5 (2F), –120.7 (6F), –113.0 (2F), –79.5 (3F); HRMS (EI) Calcd for $C_{20}H_{17}F_{17}O$ (M^+) 596.0987. Found: 596.1008.

2-Bromo-4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-1-isopropoxybenzene: To a solution of 1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-4-isopropoxybenzene (1.18 g, 1.98 mmol) and acetic acid (7 µl, catalytic amount) in dichloromethane (15 mL) under argon was added

bromine (116 μl, 2.18 mmol) at 0 °C. The mixture was stirred for 2 h at room temperature. The reaction mixture was then quenched with saturated sodium thiosulfate solution (5 mL). After dilution with water, the organic layer was separated and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using pure hexane-hexane/AcOEt (8:1) to give the desired product as a pale yellow solid (1.26 g, 94.4%); mp 66.0-67.0 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (d, 6H, *J* = 6.1 Hz), 1.88-1.96 (m, 2H), 2.05-2.66 (m, 2H), 2.63 (t, 2H, *J* = 7.5 Hz), 4.52 (m, 1H), 6.87 (d, 1H, *J* = 8.4 Hz), 7.04 (dd, 1H, *J* = 8.5, 2.1 Hz), 7.37 (d, 1H, *J* = 2.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –124.9 (2F), –122.2 (2F), –121.5 (2F), –120.7 (6F), –112.9 (2F), –79.5 (3F); HRMS (EI) Calcd for $C_{20}H_{16}BrF_{17}O$ (M^+) 674.0120. Found: 674.0113.

4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-1-isopropoxy-2-vinylbenzene (9a): To a solution of 2-bromo-4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-1-isopropoxybenzene (1.11 g, 1.65 mmol), and $Pd(PPh_3)_4$ (952 mg, 0.82 mmol) in dry toluene (15 mL) under argon was added tributylvinylstannane (1.44 mL, 4.94 mmol) at room temperature. After reflux for 96 h, the reaction mixture was filtrated through a plug of celite and the cake was washed with diethyl ether. The solvent was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using pure pentane - pentane/AcOEt (10:1), then by reverse fluorous solid phase extraction[8] on fluorous silica gel using FC-72/diethyl ether (2:1) to give **9a** as a colorless solid (655 mg g, 63.8%); mp 30.5-31.0 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (d, 6H, *J* = 6.0 Hz), 1.90-1.95 (m, 2H), 1.98-2.12 (m, 2H), 2.66 (t, 2H, *J* = 7.3 Hz), 4.52 (m, 1H), 5.26 (dd, 1H, *J* = 11.1, 1.2 Hz), 5.74 (dd, 1H, *J* = 17.8, 1.2 Hz), 6.84 (d, 1H, *J* = 8.4 Hz), 7.04 (m, 2H), 7.28 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –124.9 (2F), –122.2 (2F), –121.5 (2F), –120.7 (6F), –112.9 (2F), –79.5 (3F); HRMS (EI) Calcd for $C_{22}H_{19}F_{17}O$ (M^+) 622.1180. Found: 622.1164.

Fluorous catalyst 1st generation propylene spacer (f–GH 4a): To a solution of 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-1-isopropoxy-2-vinylbenzene 104 mg, 0.167 mmol), and Grubbs 1st generation catalyst (133 mg, 0.166 mmol) in dry dichloromethane (3 mL) under argon was added copper (I) chloride (21 mg, 0.208 mmol) at room temperature. After stirring for 3 h, the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel using pure dichloromethane, then the obtained product was recrystalized from a mixture of pentane and dichloromethane to give **4** as brown crystals (126 mg, 71.2%); mp 159.0-160.0 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.81 (d, 6H, *J* = 6.1 Hz), 1.29-2.12 (m, 35H), 2.72-2.35 (m, 2H), 2.83 (t, 2H, *J* = 7.5 Hz), 5.26 (m, 1H), 7.02 (d, 1H, *J* = 8.5 Hz), 7.45 (d, 1H, *J* = 8.5 Hz), 7.51 (s, 1H), 17.42 (d, 1H, *J* = 4.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –124.9 (2F), –122.1 (2F), –121.5 (2F), –120.7 (6F), –112.8 (2F), –79.5 (3F); IR: 2933, 2854, 1597, 1484, 1448, 1263, 1217, 1151, 1103 cm^{-1}; X-ray data is attached at the end of this Supporting Information.

Fluorous catalyst 1st generation ethylene spacer (f–GH 4b): To a solution of 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-1-isopropoxy-2-vinylbenzene (256 mg, 0.421 mmol), and Grubbs 1st generation catalyst (333 mg, 0.416 mmol) in dry dichloromethane (10 ml) under Ar was added copper (I) chloride (52 mg, 0.525 mmol) at room temperature. After stirring for 6 h, the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel by using a mixture of dichloromethane and hexane (3/1) then pure dichloromethane to provide C2 spacer catalyst as a brown solid (228 mg, 52.3%); mp 154.5-155.5 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (d, 6H, *J* = 6.1 Hz), 1.29-2.43 (m, 35H), 3.02 (m, 2H), 5.25 (m, 1H), 7.03 (d, 1H, *J* = 8.5 Hz), 7.48 (d, 1H, *J* = 8.5 Hz), 7.55 (s, 1H),

17.42 (d, 1H, J = 4.5 Hz); ^{19}F NMR (272 MHz, $CDCl_3$) ppm –124.9 (2F), –122.2 (2F), –121.5 (2F), –120.4 (6F), –113.4 (2F), –79.5 (3F).

Fluorous catalyst 2nd generation ethylene spacer (f–GH **5**)**:** To a solution of 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-1-isopropoxy-2-vinylbenzene (374 mg, 0.615 mmol) and Grubbs 2nd generation catalyst (497 mg, 0.585 mmol) in dry dichloromethane (10 mL) under argon was added copper (I) chloride (70 mg, 0.707 mmol) at room temperature. After stirring for 3 h, the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane (3/1) then pure dichloromethane to provide almost pure f-GH **5**, 583 mg (88.3%). Recrystallization of this product from a mixture of hexane and dichloromethane provided f-GH **5** as green crystals (368 mg, 55.7%); mp 136.5-137.5 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (d, 6H, J = 6.0 Hz), 2.27-2.30 (m, 2H), 2.41-2.48 (m, 18H), 2.87-2.92 (m, 2H), 4.19 (s, 4H), 4.87 (m, 1H), 6.72-6.74 (m, 2H), 7.09 (s, 4H), 7.34 (d, 1H, J = 8.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –124.9 (2F), –122.3 (2F), –121.5 (2F), –120.6 (4F), –120.5 (2F), –113.4 (2F), –79.6 (3F); IR: 1606, 1485, 1274, 1242, 1217, 1151, 752, 713, 505 cm^{-1}.

Non-fluorous catalyst (Grubbs-Hoveyda catalyst **1**)[1]: Brown solid; mp 193.0-194.0 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (d, 6H, J = 6.0 Hz), 1.29-2.35 (m, 33H), 2.83 (t, 2H, J = 7.5 Hz), 5.29 (m, 1H), 7.07 (m, 2H), 7.59-7.69 (m, 2H), 17.43 (d, 1H, J = 4.3 Hz).

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (11)[2]: Pale brown solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ

2.43 (s, 3H), 4.12 (s, 4H), 5.64 (s, 2H), 7.32 (d, 2H, *J* = 8.0 Hz), 7.72 (d, 2H, *J* = 8.0 Hz).

1-(Toluene-2-sulfonyl)-2,5-dihydro-1*H*-pyrrole[3]: Pale brown solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (s, 4H), 4.29 (s, 3H), 5.69 (s, 2H), 7.35 (bs, 4H).

Cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester[6]: Pale brown solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (t, 6H, *J* = 2.6 Hz), 3.02 (s, 4H), 4.18 (q, 4H, *J* = 2.6 Hz), 5.61 (s, 2H).

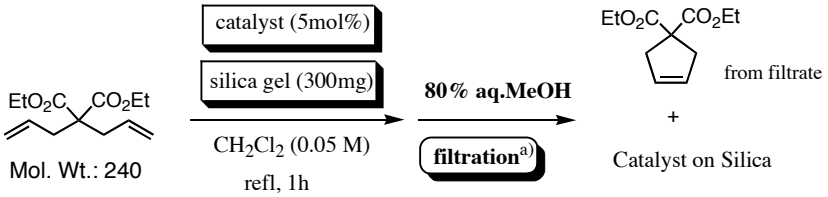
6-Pentadecyl-5,6-dihydropyran-2-one: Pale brown oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (bs, 31H), 2.30 (m, 2H), 4.38 (m, 1H), 5.96 (d, 1H, *J* = 9.6 Hz), 6.86 (m, 1H).

2,3,4,7-Tetrahydroazepine-1-carboxylic acid *tert*-butyl ester[4]: Pale brown oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.46 (s, 9H), 1.79 (m, 2H), 2.20 (m, 2H), 3.55 (m, 2H), 3.90 (m, 2H), 5.75 (m, 2H).

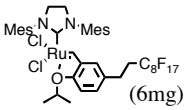
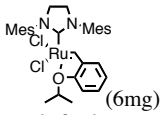
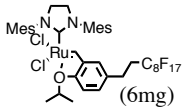
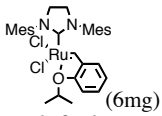
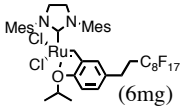
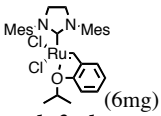
2,5-Dihydrobenzo[*b*]oxepine[7]: Pale brown oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.53 (bs, 2H), 4.63 (bs, 2H), 5.52 (d, 1H, *J* = 11.5Hz), 5.91 (m, 1H), 7.06-7.20 (m, 4H).

5-Phenylpent-2-enoic acid benzyl ester (13)[8]: Pale brown oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (m, 2H), 2.79 (t, 2H, *J* = 7.3 Hz), 5.92 (dt, 1H, *J* = 15.7, 1.1 Hz), 7.07 (dt, 1H, *J* = 15.7, 6.9 Hz), 7.18-7.39 (m, 10H).

Control experiments for supported fluorous catalyst: See Eq 2 in text and procedure above.



a)F-silica *10 vol (3 ml) and 5 ml for further washing

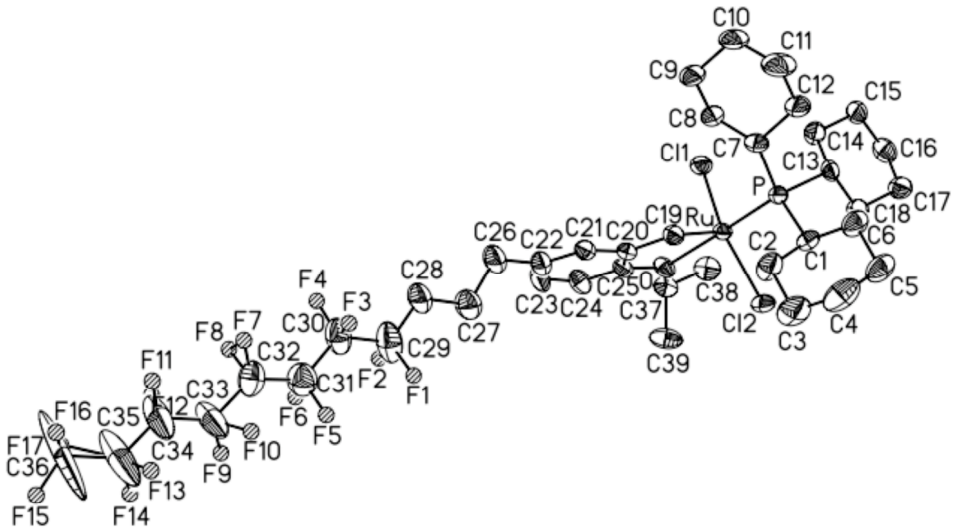
entry (SM)	catalyst (5mol%)	silica gel (300mg)	result	
			filtrate	catalyst on Silica
1 (26.8 mg)	 (6mg) Mol. Wt.: 1073	***standard*** silica gel (50w*catalyst)	23.7 mg (100%) dark green product (filtrate was **slightly green**) ^{1}H NMR: **ca. 2%** of decomposed catalyst ^{19}F NMR: **ca. 0.5%** fluorine peak*	**pale green silica gel** was recovered
2 (46.0 mg)	 (6mg) ***Hoveyda 2nd gen.*** Mol. Wt.: 627	***fluorous*** silica gel (50w*catalyst)	38.8 mg (96%) dark green product (filtrate was **green**) ^{1}H NMR:**ca. 5%** of catalyst	**almost colorless F-silica** was recovered
3 (26.8 mg)	 (6mg) Mol. Wt.: 1073	***reverse phase C18*** silica gel (50w*catalyst)	22.2 mg (94%) pale brown product (filtrate was **alomost colorless**) ^{19}F NMR: **ca. 0.3%** of fluorine peak*	**green C18 silica gel** was recovered
4 (46.0mg)	 (6mg) ***Hoveyda 2nd gen.*** Mol. Wt.: 627	***reverse phase C18*** silica gel (50w*catalyst)	42.5 mg (quant) dark green product (filtrate was **green**) ^{1}H NMR: **ca. 5%** of catalyst	**almost colorless C18 silica gel** was recovered
5 (26.8 mg)	 (6mg) Mol. Wt.: 1073	***No-silica gel***	22.1 mg (89%) pale brown product (filtrate was **slightly yellow**) ^{19}F NMR: **ca. 0.4%** of fluorine peak*	7.3 mg (89%) was rec overed from green residue in the flask and stir bar (**catalyst/RCM =74/26** catalyst: 90% RCM: 8%)
6 (46.0 mg)	 (6mg) ***Hoveyda 2nd gen.*** Mol. Wt.: 627	***No-silica gel***	40.4 mg (quant) dark green product (filtrate was **green**) ^{1}H NMR: **ca. 6%** of catalyst	**none**

*by ^{19}F NMR using 0.3 mol% BTF $CDCl_3$ solution

X-ray Crystal data of f-GH 4 and structure refinement:

Selected bond distance [Å] and angles [deg]: Ru-C(19) 1.836(6), Ru-P 2.2706(16), Ru-O 2.294(4), Ru-Cl(1) 2.3151(16), Ru-Cl(2) 2.3179(16); C(19)-Ru-P 95.3(2), C(19)-Ru-O 79.1(2), P-Ru-O 174.28(11), C(19)-Ru-Cl(1) 101.83(19), C(19)-Ru-Cl(2) 108.04(19), Cl(1)-Ru-Cl(2) 147.00(7), P-Ru-Cl(1) 97.93(6), P-Ru-Cl(2) 93.01(6), O-Ru-Cl(1) 84.26(12), O-Ru-Cl(2) 87.90(12).

An ORTEP diagram is provided below; see the cif file for full details



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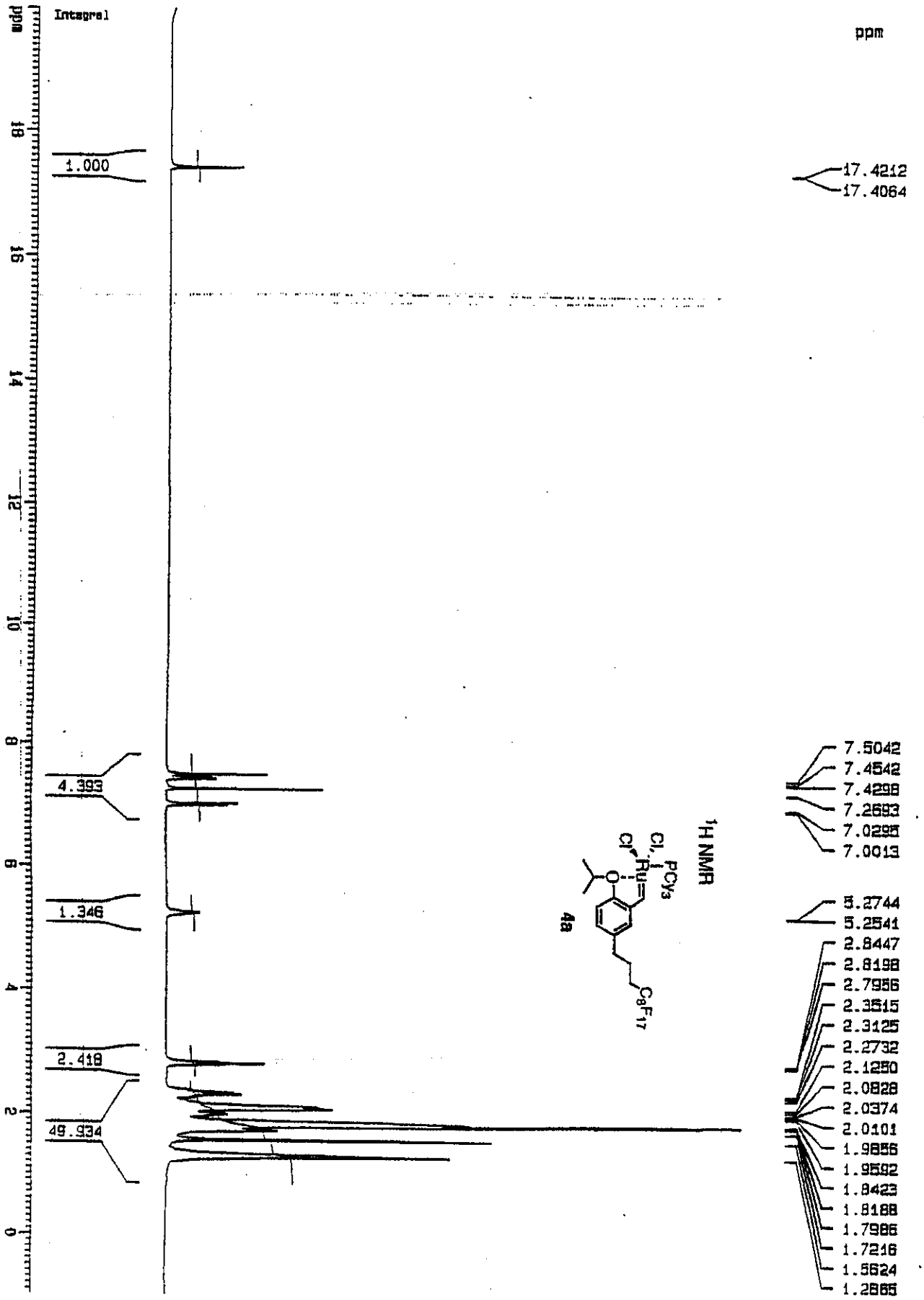
Integral
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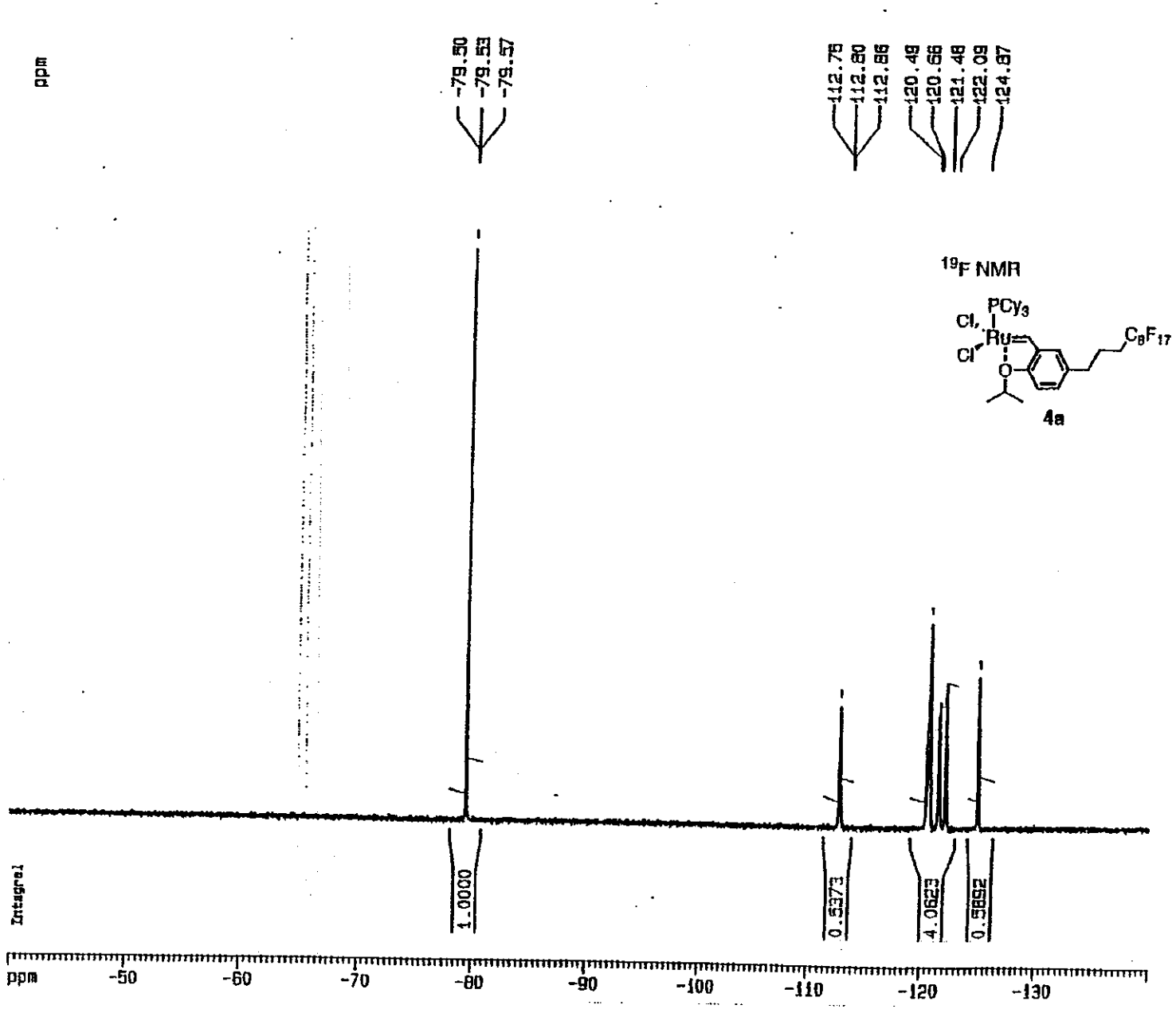
4.393
1.346
2.418
49.934
17.4212
17.4064
7.5042
7.4542
7.4298
7.2693
7.0295
7.0013
5.2744
5.2541
2.8447
2.8198
2.7956
2.3515
2.3125
2.2732
2.1250
2.0828
2.0374
2.0101
1.9856
1.9592
1.8423
1.8188
1.7986
1.7216
1.5624
1.2865
^{1}H NMR
4a



Current Data Parameters

NAME	1st
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20040616
Time	13.00
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	c13vonoe
TD	32768
SOLVENT	Aceton
NS	14
DS	0
SWH	70422.539 Hz
FIDRES	2.149125 Hz
AQ	0.2327028 sec
RG	2048
DW	7.100 usec
DE	5.04 usec
TE	300.0 K
D1	6.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 =======

NUC1	19F
P1	8.00 usec
PL1	-6.00 dB
SFO1	282.3033007 MHz

========== CHANNEL f2 =======

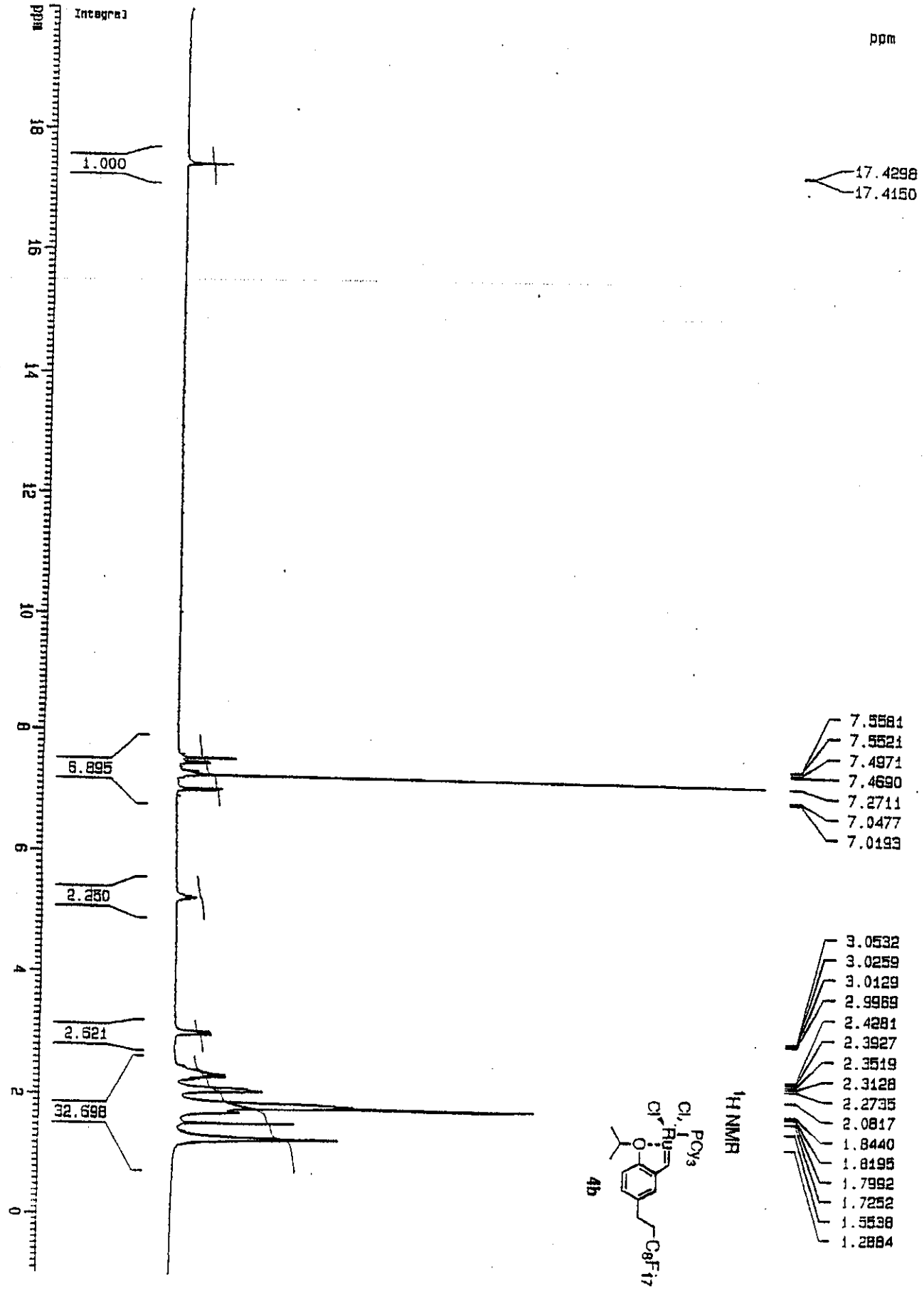
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	21.00 dB
PL12	70.00 dB
SFO2	300.1318008 MHz

F2 - Processing parameters

SI	65536
SF	282.4040236 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	-40.000 ppm
F1	-11296.16 Hz
F2P	-140.000 ppm
F2	-39536.56 Hz
PPMCM	5.00000 ppm/cm
HZCM	1412.02014 Hz/cm


Integral
ppm
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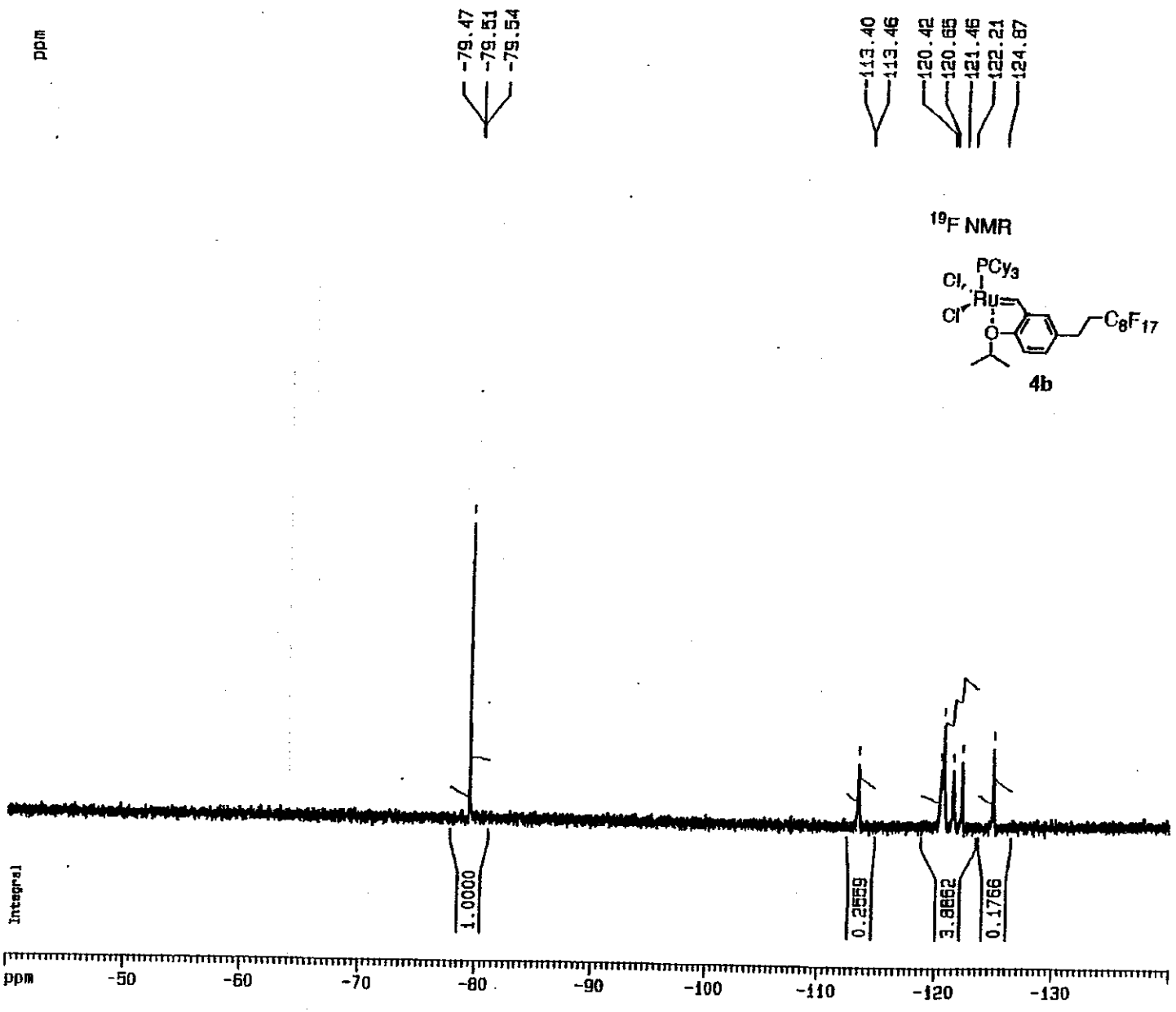
2.250
2.621
32.698
ppm
17.4298
17.4150
7.5581
7.5521
7.4971
7.4690
7.2711
7.0477
7.0193
3.0532
3.0259
3.0129
2.9969
2.4281
2.3927
2.3519
2.3128
2.2735
2.0817
1.8440
1.8195
1.7992
1.7252
1.5538
1.2884
^{1}H NMR
4b
Cl
Cl
Ru
POCy$_3$
O
C$_8$F$_{17}$



Current Data Parameters

NAME	1stgeneration
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20040225
Time	9.59
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	c13vonoe
TD	32768
SOLVENT	Aceton
NS	19
DS	0
SWH	70422.539 Hz
FIDRES	2.149125 Hz
AQ	0.2327028 sec
RG	11585.2
DW	7.100 usec
DE	5.04 usec
TE	300.0 K
D1	6.00000000 sec
D3	0.00100000 sec

======== CHANNEL f1 ========

NUC1	19F
P1	8.00 usec
PL1	-6.00 dB
SFO1	282.3833007 MHz

======== CHANNEL f2 ========

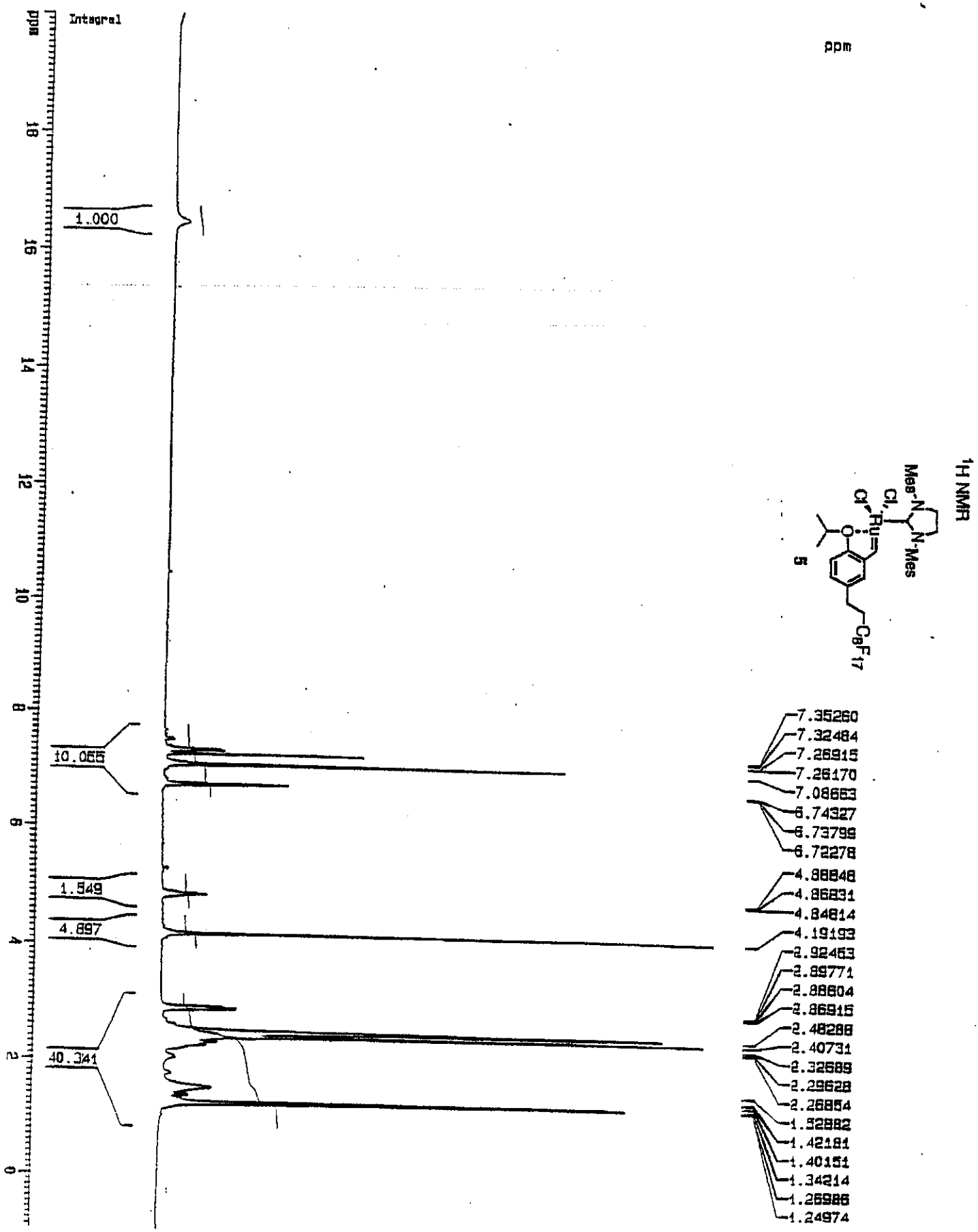
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	21.00 dB
PL12	20.00 dB
SFO2	300.1318008 MHz

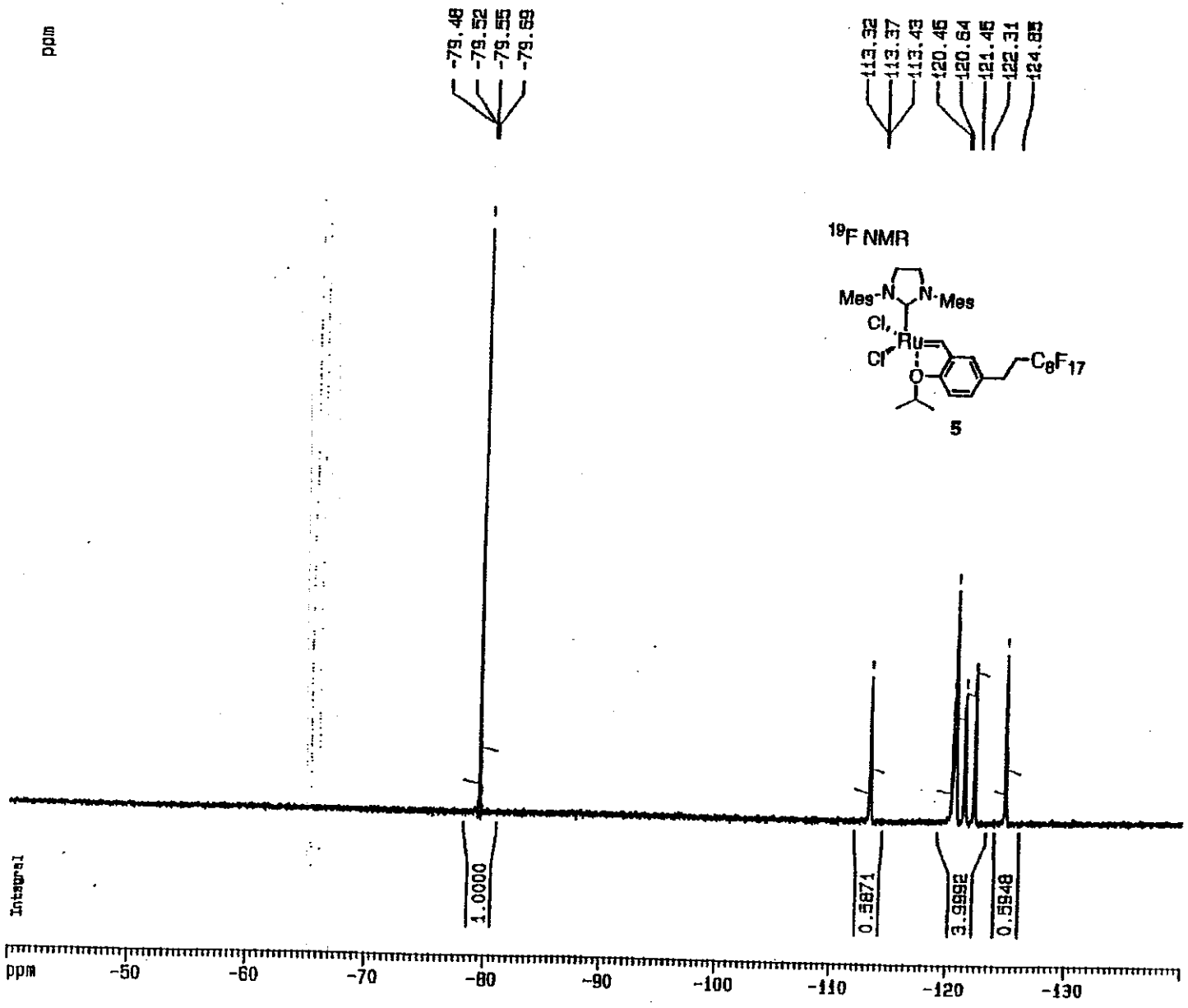
F2 - Processing parameters

SI	65536
SF	282.4040236 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	-40.000 ppm
F1	-11296.16 Hz
F2P	-140.000 ppm
F2	-39536.56 Hz
PPMCM	5.00000 ppm/cm
HZCM	1412.02014 Hz/cm


Integral
ppm
18
16
14
12
10
8
6
4
2
0
1.000
10.065
1.549
4.897
40.341
ppm
7.35260
7.32484
7.26915
7.26170
7.08663
6.74327
6.73799
6.72278
4.88848
4.86831
4.84814
4.19193
2.92463
2.89771
2.88604
2.86915
2.48288
2.40731
2.32689
2.29628
2.26854
1.52882
1.42181
1.40151
1.34214
1.26986
1.24974
Mes-N
N-Mes
Cl
Cl
Ru
O
C8F17
5
1H NMR

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Current Data Parameters
NAME                  2nd
EXPNO                   3
PROCNO                  1

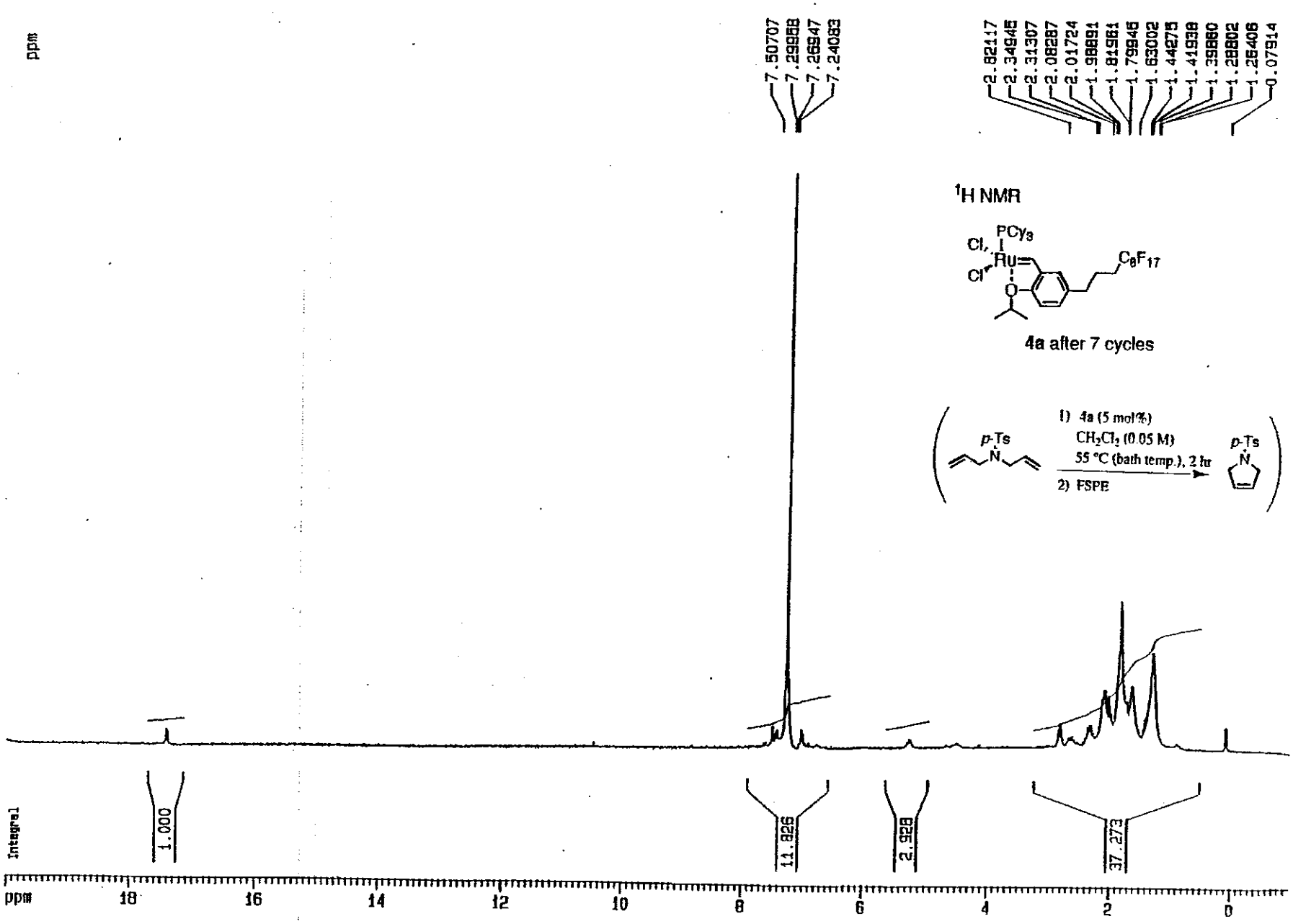
F2 - Acquisition Parameters
Date_              20040616
Time                  13.03
INSTRUM               spect
PROBHD     5 mm QNP  1H
PULPROG          c13nonoe
TD                    32768
SOLVENT               Aceton
NS                        9
DS                        0
SWH               70422.539 Hz
FIDRES             2.149125 Hz
AQ                 0.2327028 sec
RG                     2048
DW                  7.100 usec
DE                  5.04 usec
TE                  300.0 K
D1                 6.00000000 sec
D3                 0.00100000 sec

================ CHANNEL f1 =======
NUC1                    19F
P1                   8.00 usec
PL1                  -8.00 dB
SFO1            282.3833007 MHz

================ CHANNEL f2 =======
CPDPRG2             waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  21.00 dB
PL12                 20.00 dB
SFO2            300.1318008 MHz

F2 - Processing parameters
SI                     65536
SF              282.4040236 MHz
WDW                    EM
SSB                       0
LB                   0.20 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                -40.000 ppm
F1                 -11296.16 Hz
F2P                -140.000 ppm
F2                 -39536.56 Hz
PPMCM                5.00000 ppm/cm
HZCM              1412.02014 Hz/cm
```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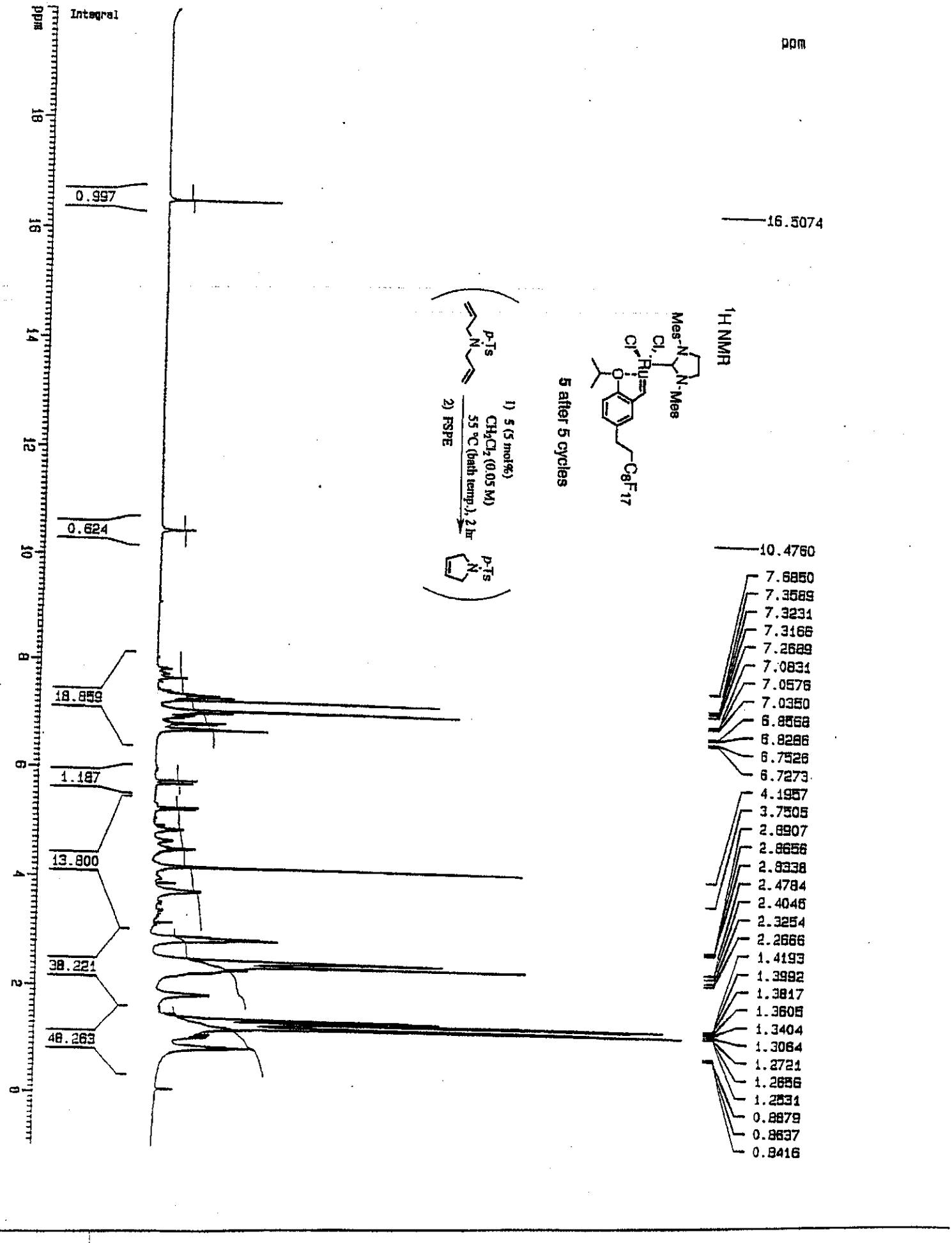
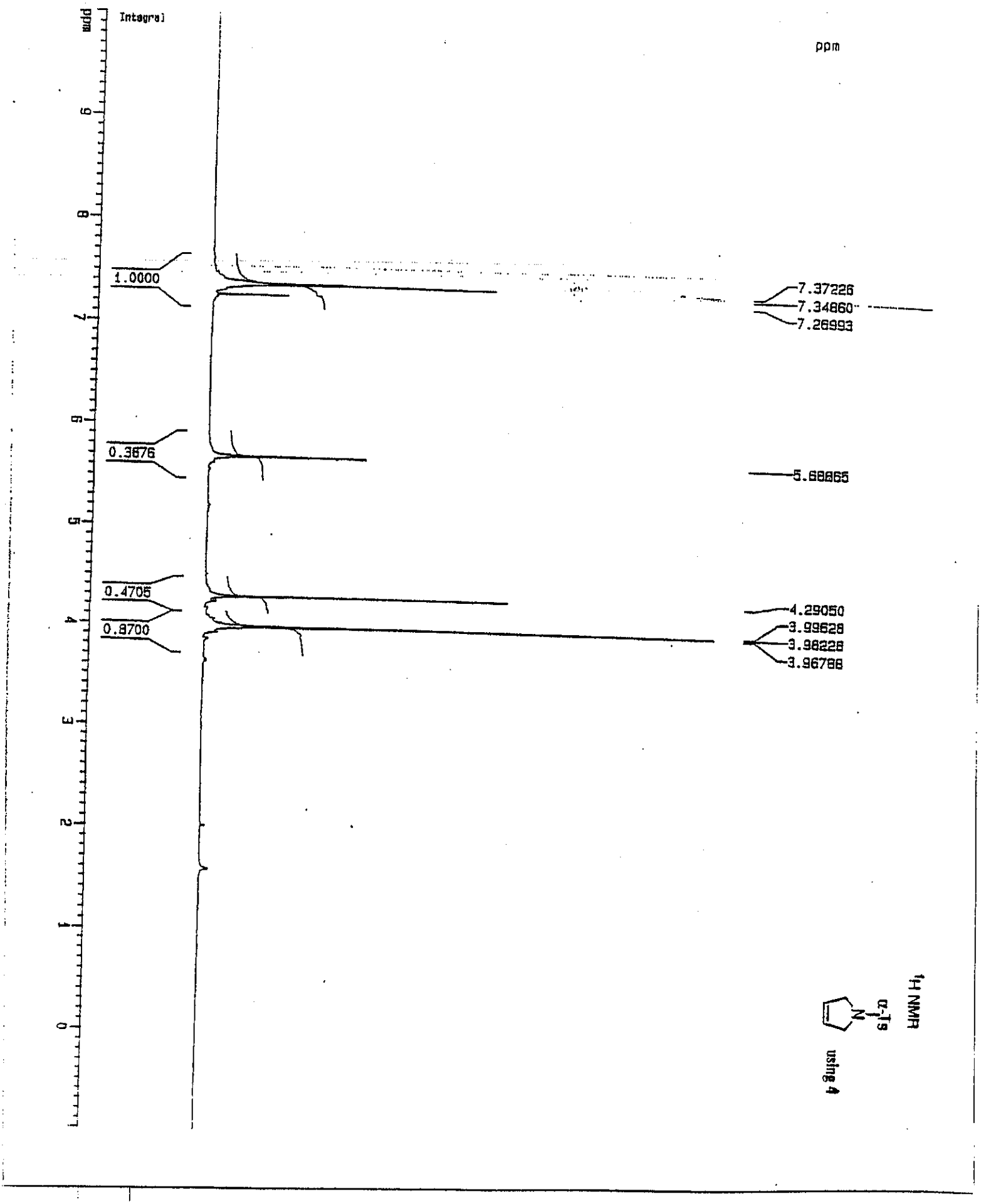
7.29988
7.26947
7.24083
2.82117
2.34945
2.31307
2.08287
2.01724
1.98691
1.81981
1.79945
1.63002
1.44275
1.41938
1.39880
1.28802
1.26406
0.07914
1H NMR
PCy3
Cl
Ru
Cl
O
C8F17
4a after 7 cycles
p-Ts
N
1) 4a (5 mol%)
CH2Cl2 (0.05 M)
55 °C (bath temp.), 2 hr
2) FSPE
p-Ts
N
Integral
1.000
11.926
2.928
37.273
ppm
18
16
14
12
10
8
6
4
2
0


Integral
ppm
0.997
0.624
18.859
1.187
13.800
38.221
48.263
16.5074
10.4760
7.6850
7.3589
7.3231
7.3166
7.2689
7.0831
7.0576
7.0350
6.8568
6.8286
6.7526
6.7273
4.1957
3.7505
2.8907
2.8656
2.8338
2.4784
2.4046
2.3254
2.2666
1.4193
1.3992
1.3817
1.3605
1.3404
1.3064
1.2721
1.2656
1.2531
0.8879
0.8637
0.8416
1H NMR
5 after 5 cycles
1) 5 (5 mol%)
CH2Cl2 (0.05 M)
55 °C (bath temp.), 2 hr
2) FSPE
p-Ts
Mes-N
N-Mes
Cl
Ru
C8F17


Integral
ppm
1.0000
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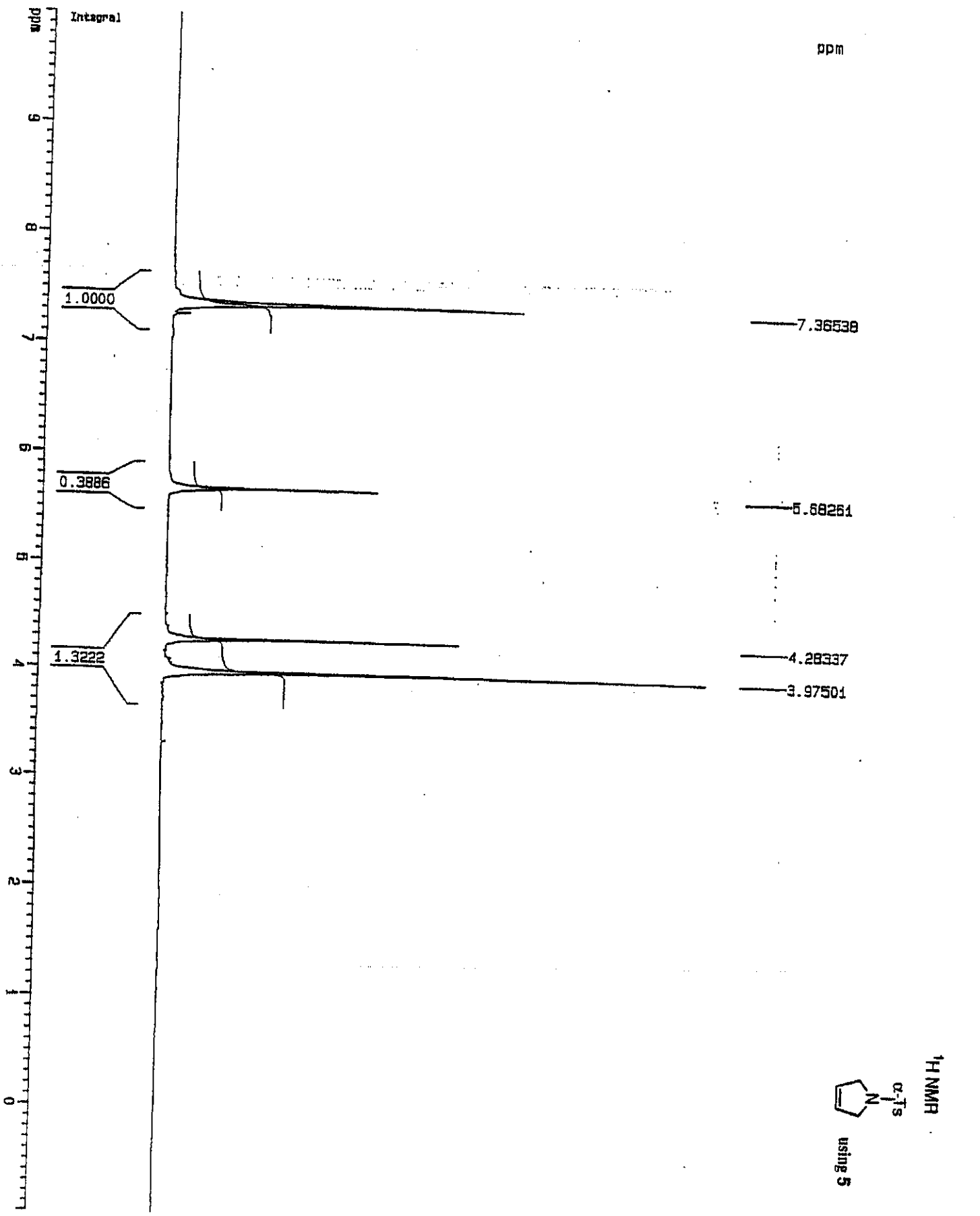
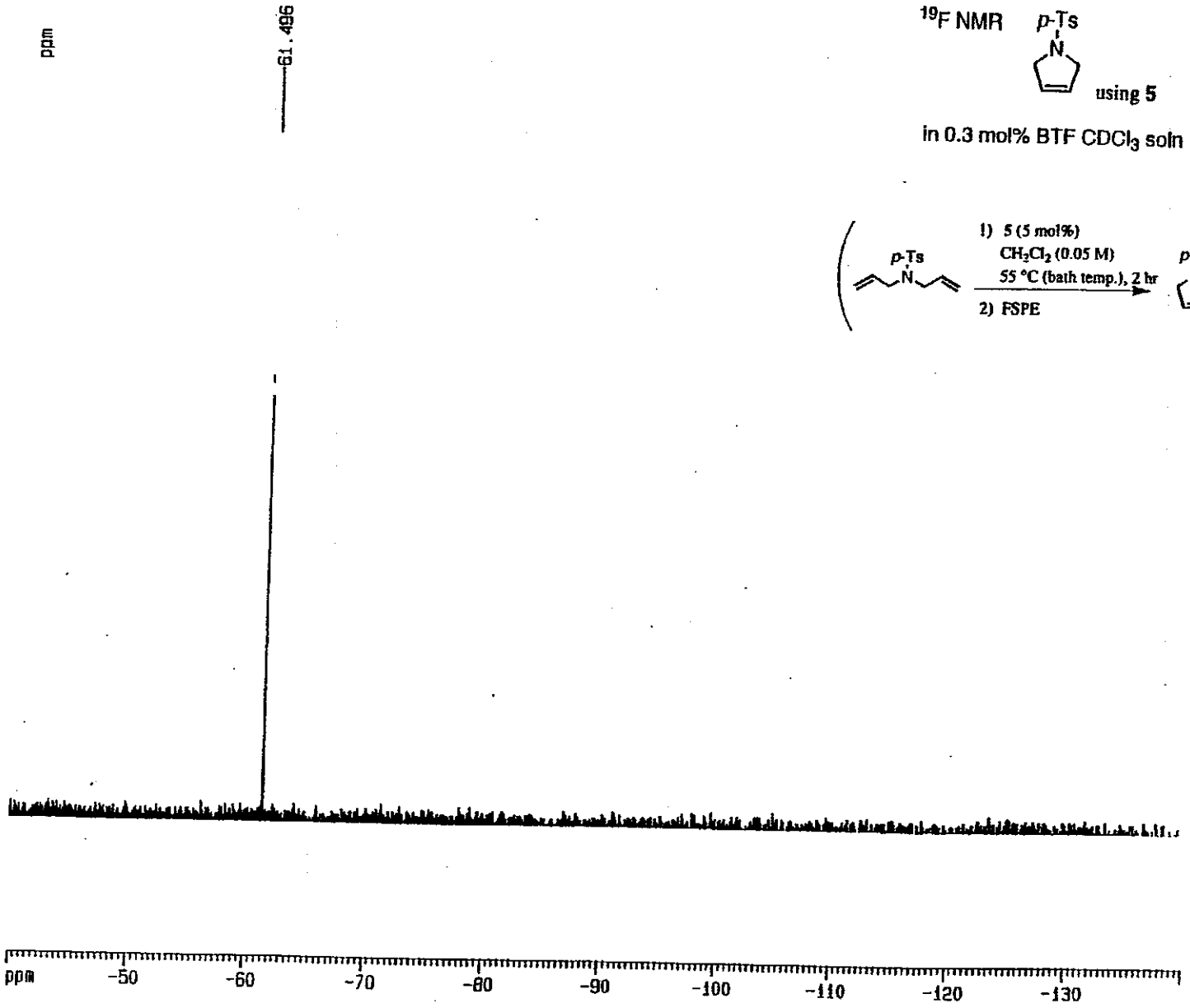
0.4705
0.8700
7.37226
7.34860
7.26993
5.68865
4.29050
3.99628
3.98228
3.96788
^{1}H NMR
α-Ts
using 4


Integral
ppm
1.0000
0.3886
1.3222
7.36538
5.68261
4.28337
3.97501
^{1}H NMR
α-Ts
using 5



^{19}F NMR *p*-Ts N using **5**

in 0.3 mol% BTF $CDCl_3$ soln


```
Current Data Parameters
NAME                  hoveyda
EXPNO                       1
PROCNO                      1

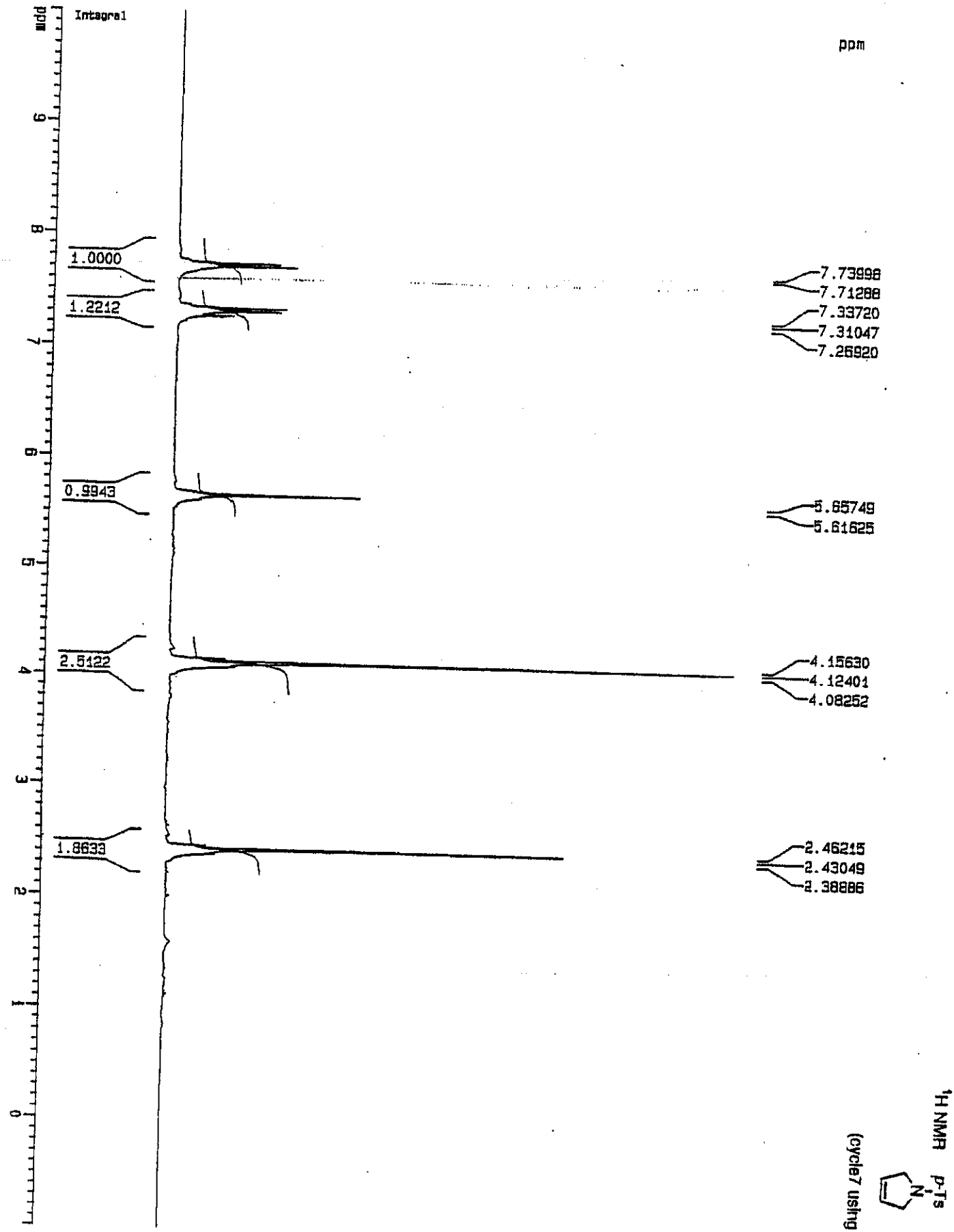
F2 - Acquisition Parameters
Date_              20040812
Time                   15.57
INSTRUM                spect
PROBHD     5 mm QNP  1H
PULPROG             c13wonoe
TD                     32768
SOLVENT                Aceton
NS                         44
DS                          0
SWH              70422.539 Hz
FIDRES           2.149125 Hz
AQ               0.2327028 sec
RG                       2048
DW                   7.100 usec
DE                   5.04 usec
TE                   300.0 K
D1              6.00000000 sec
D3              0.00100000 sec

============ CHANNEL f1 =======
NUC1                    19F
P1                   8.00 usec
PL1                 -6.00 dB
SFO1          282.3833007 MHz

============ CHANNEL f2 =======
CPDPRG2              waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  21.00 dB
PL12                 70.00 dB
SFO2          300.1318008 MHz

F2 - Processing parameters
SI                      65536
SF            282.4040236 MHz
WDW                        EM
SSB                         0
LB                   0.20 Hz
GB                          0
PC                   1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                -40.000 ppm
F1                -11296.16 Hz
F2P                -140.000 ppm
F2                -39536.56 Hz
PPMCM              5.00000 ppm/cm
HZCM           1412.02014 Hz/cm
```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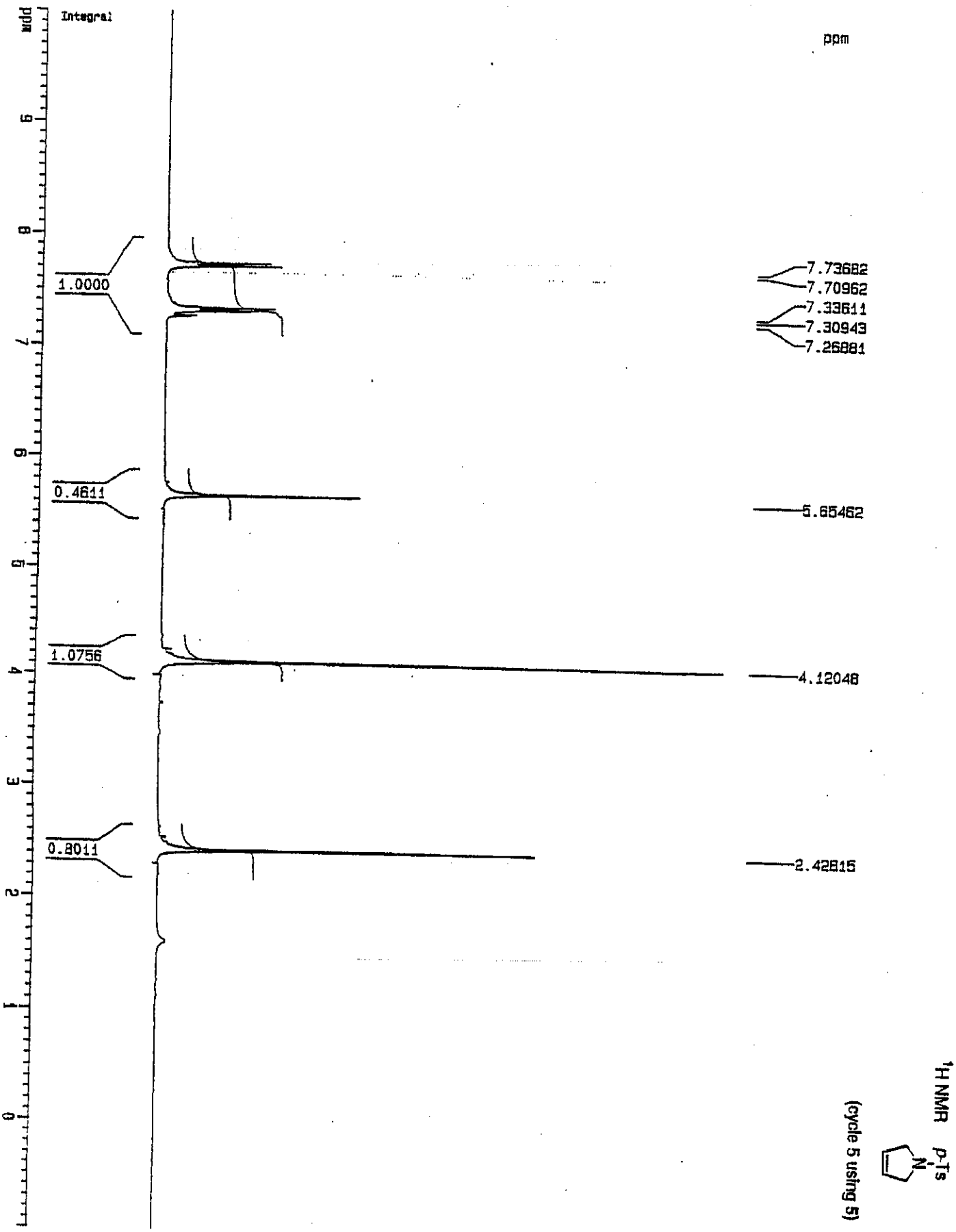
7.73998
7.71288
7.33720
7.31047
7.26920
5.65749
5.61625
4.15630
4.12401
4.08252
2.46215
2.43049
2.38886
^{1}H NMR p-Ts
(cycle7 using 4)


Integral
ppm
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0.8011
7.73682
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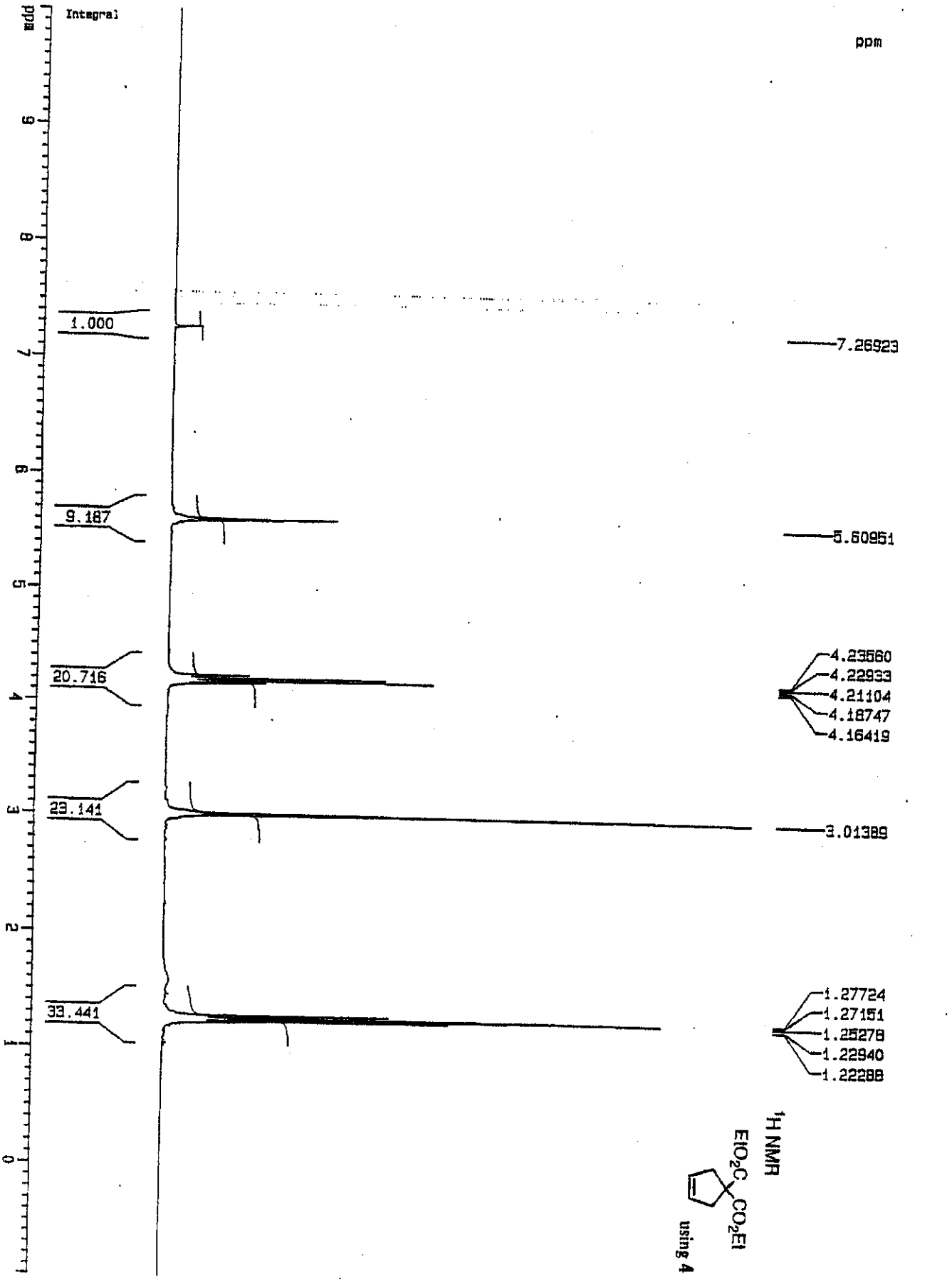
7.33611
7.30943
7.26881
5.65462
4.12048
2.42815
^{1}H NMR p-Ts
(cycle 5 using 5)


Integral
ppm
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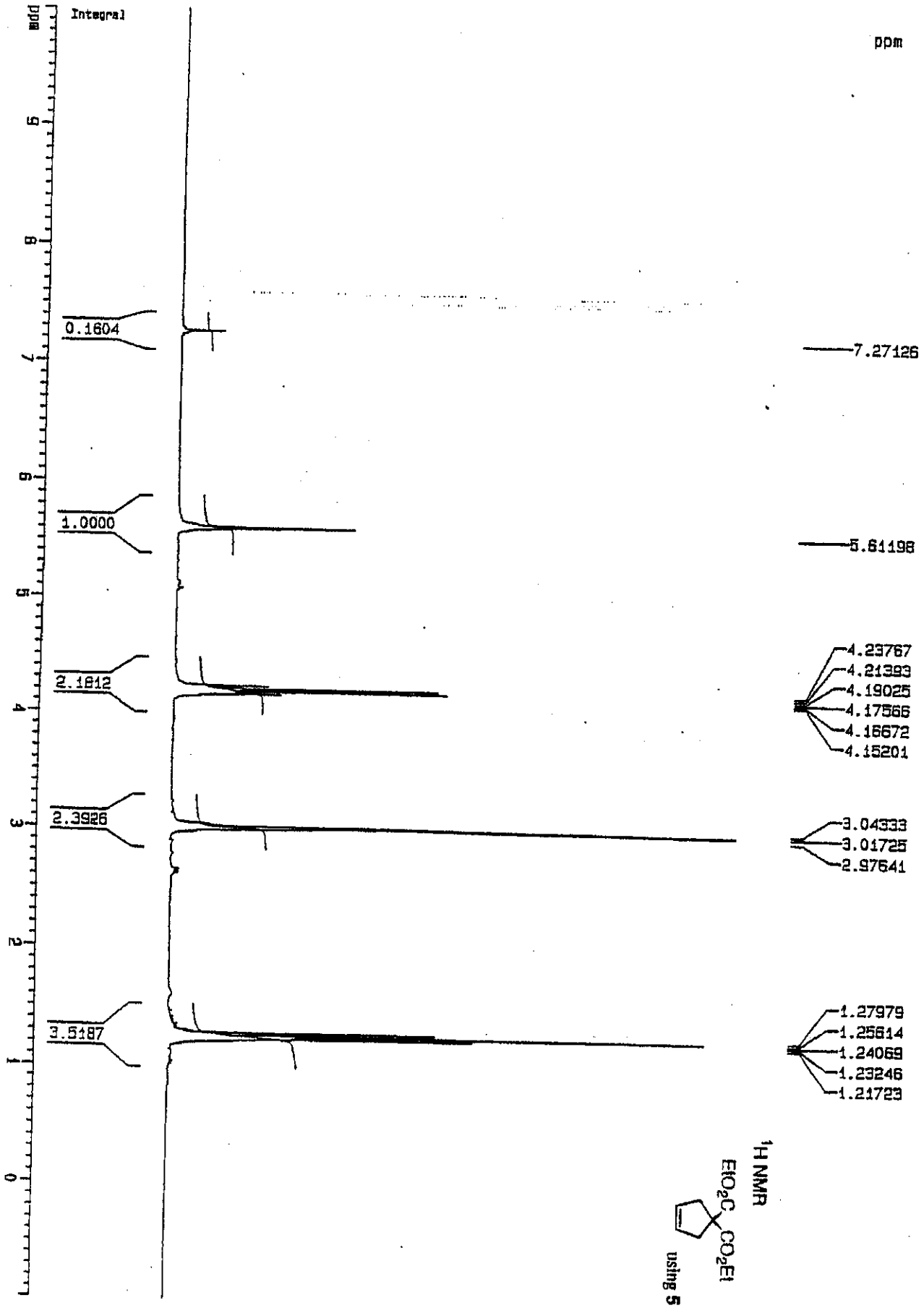
20.716
23.141
33.441
7.26923
5.60951
4.23560
4.22933
4.21104
4.18747
4.16419
3.01389
1.27724
1.27151
1.25278
1.22940
1.22288
^{1}H NMR
EtO_2C CO_2Et
using 4


Integral
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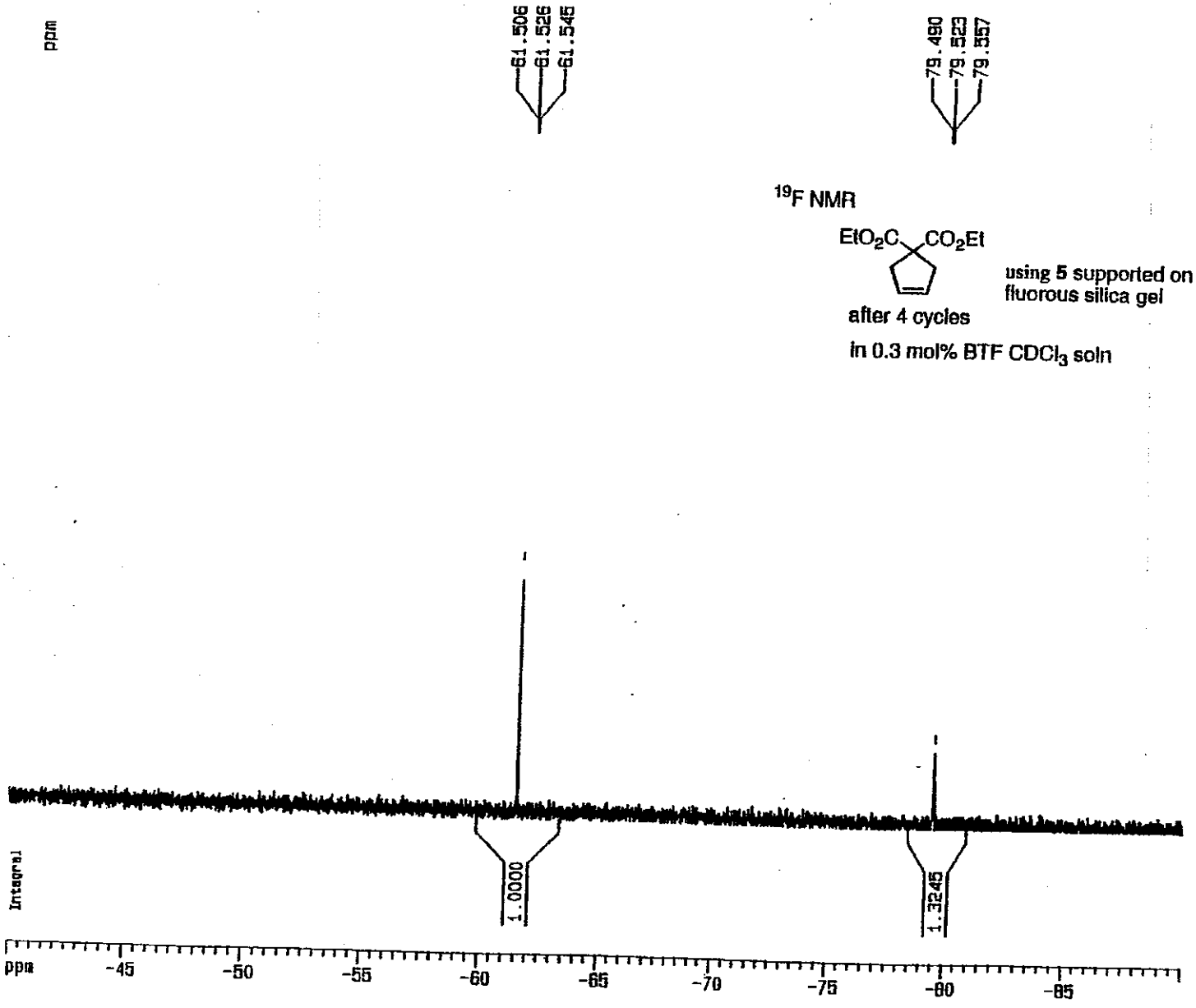
2.1812
2.3926
3.5187
7.27126
5.61198
4.23767
4.21383
4.19025
4.17566
4.16672
4.15201
3.04333
3.01725
2.97641
1.27979
1.25614
1.24069
1.23246
1.21723
^{1}H NMR
EtO_2C CO_2Et
using 5




```
Current Data Parameters
NAME                  2
EXPNO                 1
PROCNO                1

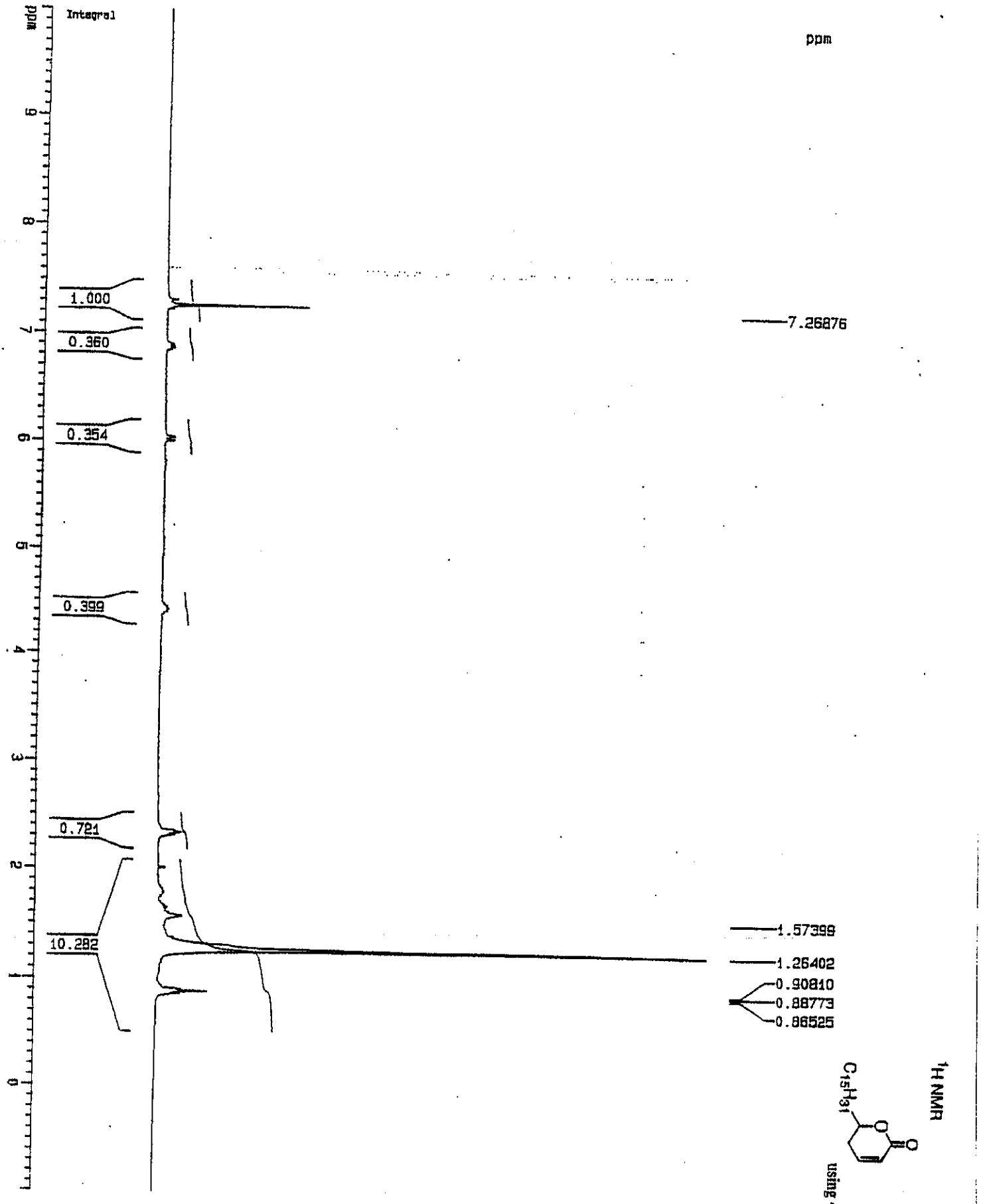
F2 - Acquisition Parameters
Date_          20040816
Time               15.25
INSTRUM            spect
PROBHD  5 mm BNP  1H
PULPROG          c13wonoe
TD                32768
SOLVENT           Aceton
NS                   27
DS                    0
SWH           70422.539 Hz
FIDRES        2.149125 Hz
AQ            0.2327028 sec
RG                 2048
DW               7.100 usec
DE               5.04 usec
TE              300.0 K
D1           6.00000000 sec
D3           0.00100000 sec

================ CHANNEL f1 ========
NUC1                 19F
P1                 8.00 usec
PL1               -6.00 dB
SFO1        282.3833007 MHz

================ CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                21.00 dB
PL12               20.00 dB
SFO2        300.1318008 MHz

F2 - Processing parameters
SI                 65536
SF          282.4040236 MHz
WDW                  EM
SSB                   0
LB                 0.20 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P             -40.000 ppm
F1            -11296.16 Hz
F2P             -90.000 ppm
F2            -25416.36 Hz
PPMCM          2.50000 ppm/cm
HZCM          706.01007 Hz/cm
```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ppm
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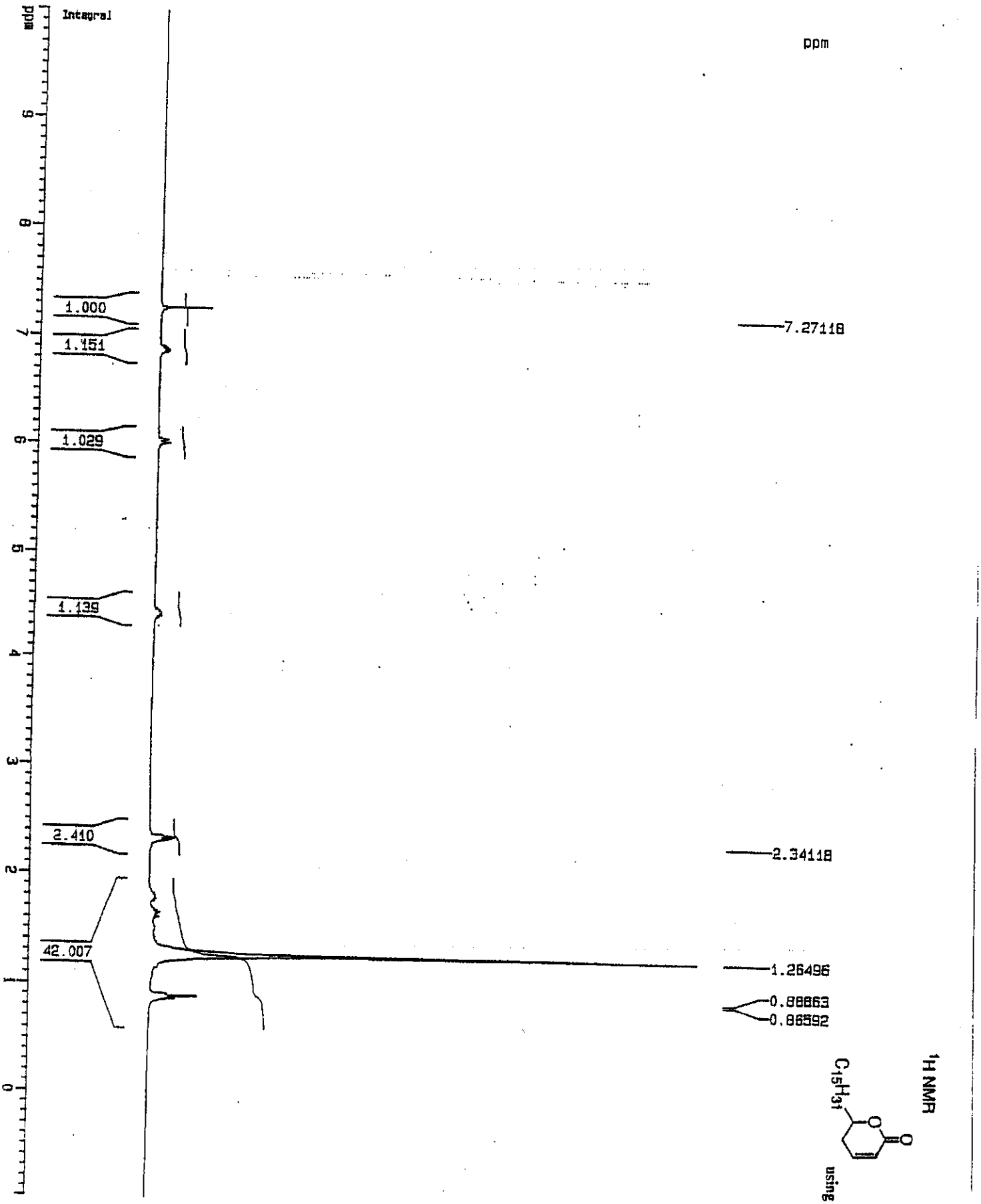
0.360
0.354
0.399
0.721
10.282
7.26876
1.57399
1.26402
0.90810
0.88773
0.86525
^{1}H NMR
$C_{15}H_{31}$
using 4


Integral
ppm
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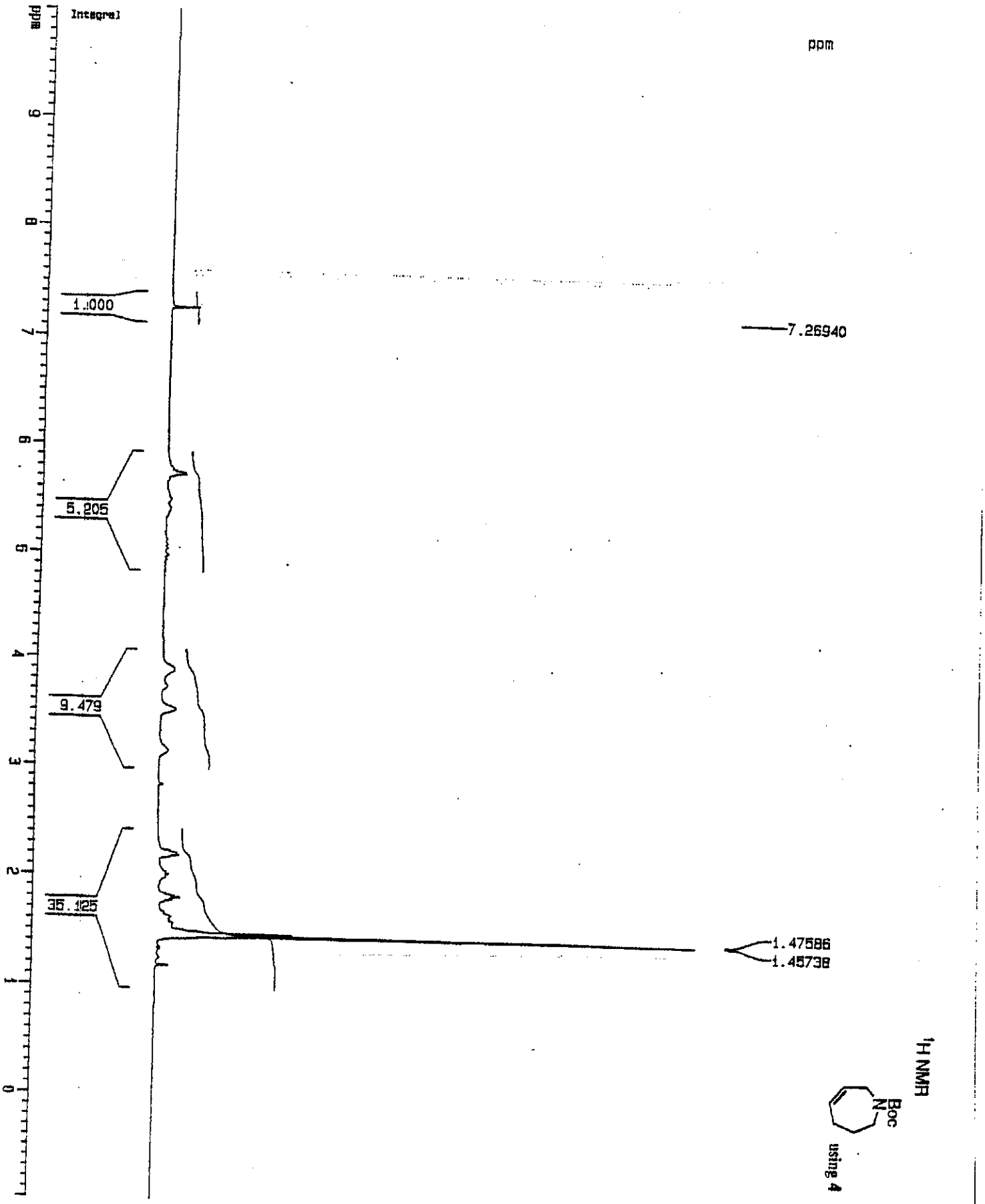
1.151
1.029
1.139
2.410
42.007
7.27118
2.34118
1.26496
0.88863
0.86592
^{1}H NMR
$C_{15}H_{31}$
using 5


Integral
ppm
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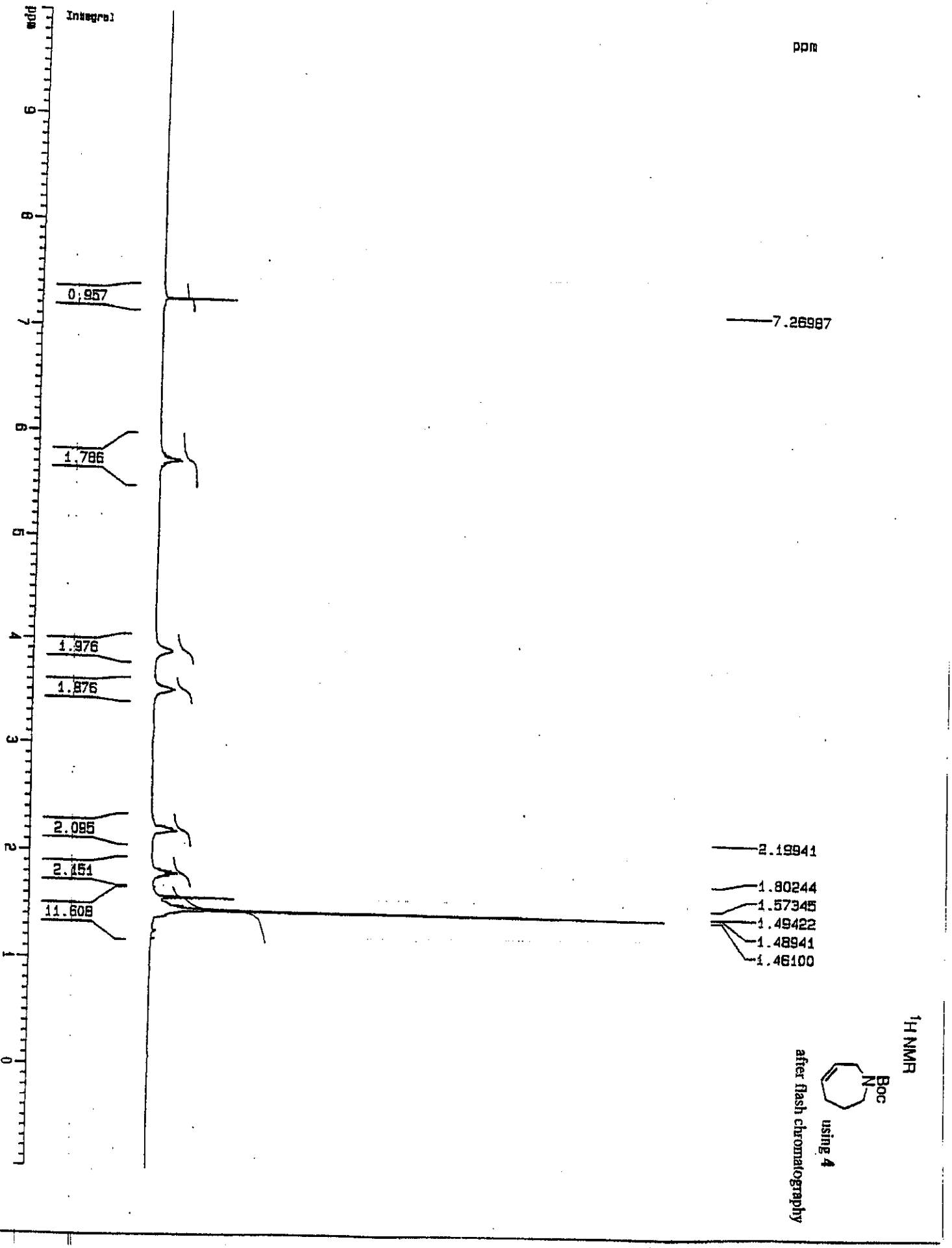
9.479
35.125
7.26940
1.47586
1.45738
^{1}H NMR
Boc
N
usina 4


Integral
ppm
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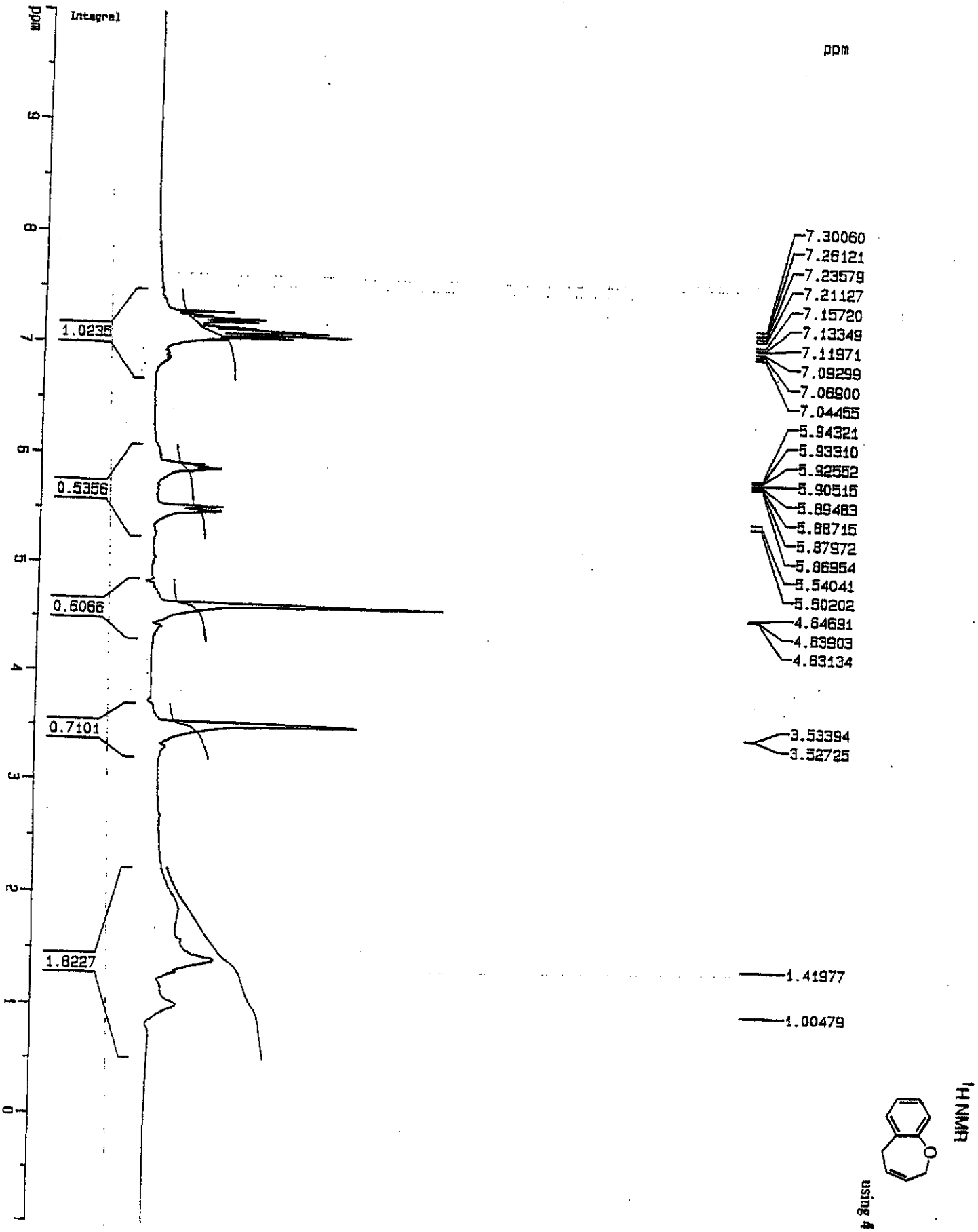
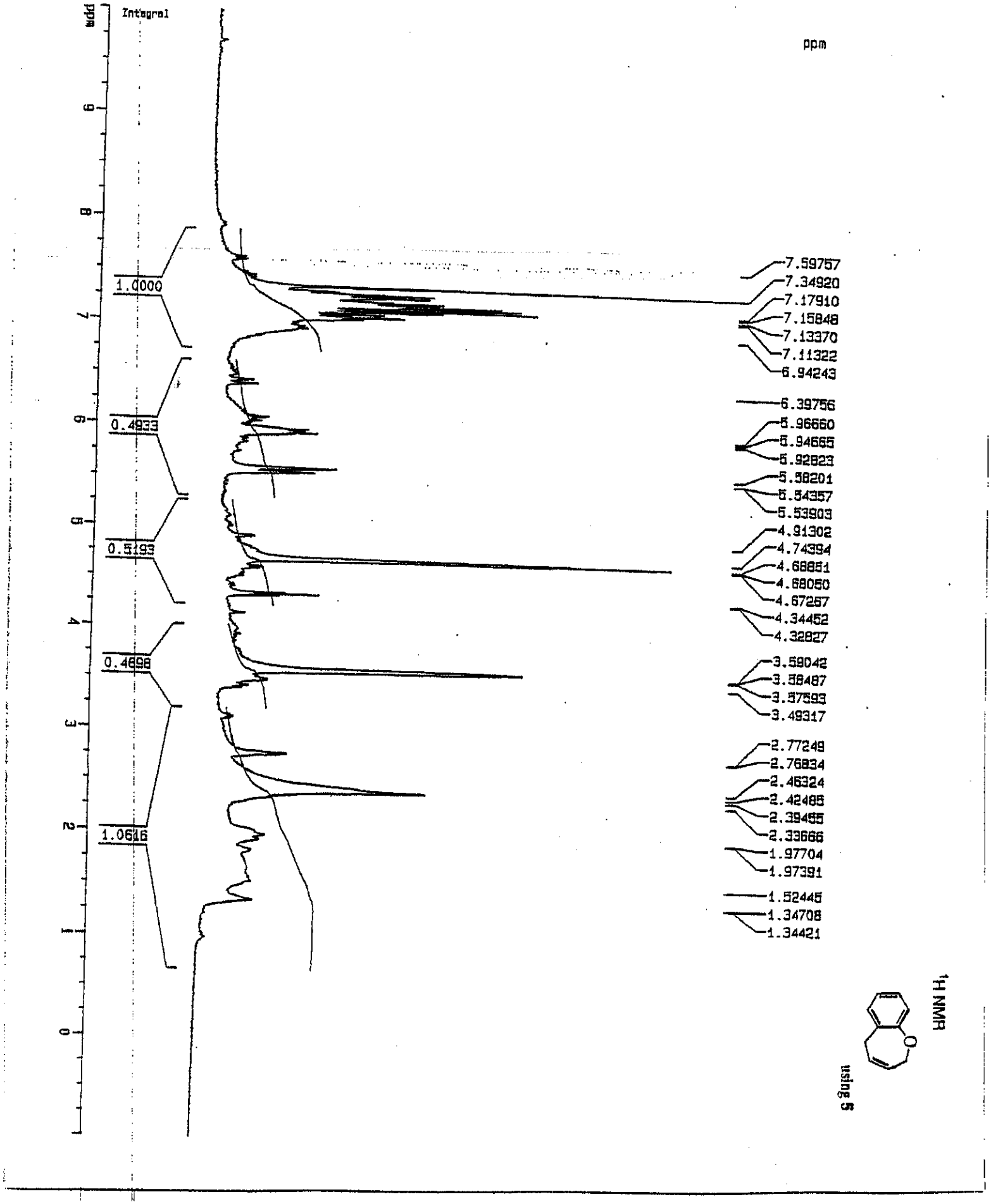
1.786
1.976
1.876
2.095
2.151
11.608
7.26987
2.19941
1.80244
1.57345
1.49422
1.48941
1.46100
Boc
N
using 4
after flash chromatography
^{1}H NMR

Integral
ppm
1.000
1.985
3.933
18.298
7.26869
3.13720
2.27555
1.62801
1.54661
1.50355
1.48616
1.48087
1.46536
1.45671
1.45270
1.27571
^{1}H NMR
Boc
N
using 5


Integral
ppm
1.0235
0.5356
0.6066
0.7101
1.8227
7.30060
7.26121
7.23579
7.21127
7.15720
7.13349
7.11971
7.09299
7.06900
7.04455
5.94321
5.93310
5.92552
5.90515
5.89483
5.88715
5.87972
5.86954
5.54041
5.50202
4.64691
4.63903
4.63134
3.53394
3.52725
1.41977
1.00479
^{1}H NMR
using 4


Integral
ppm
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0.5193
0.4698
1.0616
7.59757
7.34920
7.17910
7.15848
7.13370
7.11322
6.94243
6.39756
5.96660
5.94665
5.92823
5.58201
5.54357
5.53903
4.91302
4.74394
4.68851
4.68050
4.67267
4.34452
4.32827
3.59042
3.58487
3.57593
3.49317
2.77249
2.76834
2.46324
2.42485
2.39485
2.33666
1.97704
1.97391
1.52445
1.34708
1.34421
using S
^{1}H NMR