Supplementary Information for

Selective Dimerization of 1,6-Diynes Catalyzed by Ionic Liquid-Supported Nickel Complexes in An Ionic Liquid/Toluene Biphasic System

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Experimental Section

General: NMR spectra were recorded in $CDCl_3$ at 600, 500, 270 and 90 MHz for ^1H and 150, 125, 67.5 and 22.5 MHz for ^{13}C on JEOL JNM-ECA600, -ECA500, –EX270 and HITACHI R-1900 spectrometers, respectively. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si (δ 0.00) or residual $CHCl_3$ (δ 7.26 for ^1H NMR) and $CDCl_3$ (δ 77.0 for ^{13}C NMR). IR spectra were recorded on JASCO IR FT/IR 4100 spectrometer. UV-vis. absorption and fluorescence spectra were measured on SHIMADZU UV-2450 and RF-5300PC spectrometers, respectively. High-resolution mass spectra (HR-MS) were measured on JEOL Accu TOF T-100 equipped with ESI ionization. The *M*n and *M*w/*M*n of polymers were measured with a TOSOH HLC-8020 gel-permeation chromatography (GPC) unit (eluent: THF; calibration: polystyrene standards) using two TSK-gel columns (2 x Multipore H_{XL}-M). MALDI-TOF mass spectra were recorded on a SHIMADZU Biotech Axima CFRplus curved field reflection (CFR) in the reflection ion mode by use of a laser (λ = 337 nm).

All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere. Dry solvents [tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), dichloromethane (CH_2Cl_2), toluene and diethyl ether (ether)] were purchased from Kanto Chemicals. (DME)$NiBr_2$ (DME = 1,2-dimethoxyethane)) and 3-butyl-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate (BMI) were purchased from Aldrich. 2-(2,6-Diisopropylphenyliminomethyl)pyridine (DIPIMP) was prepared from pyridine 2-carboxaldehyde and 2,6-diisopropylaniline by the reported procedure.[1] All of the other commercially chemicals were used as received, unless otherwise indicated.

Procedure for Synthesizing Annulated Cyclooctateraene 2a and Polymeric Material(s) from 1,6-Diyne 1a in THF (Mono-phasic Reaction: Table 1, Entry 1).

To a stirred mixture of Zn powder (6.5 mg, 0.10 mmol) and diyne **1a** (236 mg, 1.0 mmol) in THF (2 mL) was added a solution of $NiCl_2$-$6H_2O$ (6 mg, 0.05 mmol) and DIPIMP (8 mg, 0.06 mmol) in THF (2 mL) at room temperature. The reaction progress was checked by TLC analysis. After complete consumption of diyne **1a**, 2 mL of Et_2O was added and the mixture was passed through a pad of Celite with ether. The filtrate was concentrated to dryness and the resulting colored residue was chromatographed on silica gel using hexane/EtOAc (3:1) to give a mixture of COT **2a** and dimer **3a** and trimer **4a**. Pure **2a** (40 mg) was obtained after the resulting yellow solids of a mixture of **2a** and **3a** was washed with hexane /EtOAc (5:1) to remove the residual dimer **3a**. More polar materials (polymeric compounds) were obtained by further eluting of the column using EtOAc (*vide infra*).

Typical Procedure for the Preparation of 1-Methoxyethoxyethyl-3-butyl-1*H*- imidazol- 3-ium Bromide (MEEBI) and 1-Methoxyethoxyethyl-3-methyl-1*H*-imidazol-3-ium Bromide (MEEMI).

A mixture of *N*-alkyl imidazole (10 mmol) and 1-bromo-2-(2-methoxyethoxy)ethane (10 mmol) was heated at 80 °C for overnight. The brown crude reaction mixture was cooled and washed several times with diehtylether and hexane.

1-Methoxyethoxyethyl-3-butyl-1*H*- imidazol- 3-ium Bromide (MEEBI): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 10.38 (br s, 1H, NC*H*N), 7.67 and 7.37 (2 br s, each 1H, HC=CH), 4.67 (t, *J* = 4.8 Hz, 2H, NCH_2CH_2O), 4.32 (t, *J* = 7.2 Hz, 2H, $NCH_2CH_2CH_2$), 3.92 (t, *J* = 4.8 Hz, 2H, NCH_2CH_3O), 3.67 (t, *J* = 4.8 Hz, 2H, OCH_2CH_2OMe), 3.53 (t, *J* = 4.8 Hz, 2H, OCH_2CH_2OMe), 3.37 (s, 3H, OCH_3), 1.92 (t, *J* = 7.2 Hz, 2H, $NCH_2CH_2CH_2$), 1.40 (q, *J* = 7.2 Hz, 2H, CH_2CH_3), 0.98 (t, *J* = 7.2 Hz, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 136.2, 123.0, 121.5, 71.2, 69.8, 68.5, 58.5, 49.4, 49.2, 31.7, 19.0, 13.0; IR (Neat) 2933, 2874, 1638, 1563, 1459, 1383, 1165, 1097, 848 cm^{-1}. HR-MS: *m*/*z*= calcd For $(C_{12}H_{23}N_2O_2)^+$: 227.1760; found 227.1748.

1-Methoxyethoxyethyl-3-methyl-1*H*-imidazol-3-ium Bromide (MEEMI): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 10.38 (br s, 1H, NC*H*N), 7.60 and 7.32 (2 br s, each 1H, HC=CH), 4.63 (t, *J* = 4.8 Hz, 2H, NCH_2), 4.08 (s, 3H, NCH_3), 3.91 (t, *J* = 4.8 Hz, 2H, NCH_2CH_2), 3.67 (t, *J* = 4.8 Hz, 2H, OCH_2CH_2OMe), 3.54 (t, *J* = 4.8 Hz, 2H, OCH_2CH_2OMe), 3.37 (s, 3H, CH_2OCH_3); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 137.0, 123.1, 122.9, 71.3, 70.1, 68.7, 58.7, 49.4, 36.5; IR (Neat) 2931, 1638, 1572, 1451, 1353, 1170, 1096, 750 cm^{-1}. HR-MS: *m*/*z*= calcd For $(C_9H_{17}N_2O_2)^+$ 185.1290, found 185.1282.

Typical Procedure for Cyclodimerization of 1,6-Diynes 1 to Annulated Cyclooctateraenes 2.

To a mixture of Zn powder (6.5 mg, 0.10 mmol), $NiBr_2$-$3H_2O$ (13.6 mg, 0.05 mmol) and MEEBI (18.4 mg, 0.06 mmol) was added a solution of diyne **1** (1.0 mmol) in toluene (4 mL). 0.2 ml of 3-butyl-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate (BMI) was added in a portion. The resulting heterogeneous reaction mixture was placed into a 60 °C oil bath. The mixture slowly turned from colorless to deep red over the course of 5 min. After complete consumption of the starting diyne, the reaction mixture was allowed to cool to ambient temperature. The supernatant was decanted and filtered through a pad of Celite with ether. The solvents were removed under reduce pressure and the residue was chromatographed on silica gel to give the corresponding annulated cyclooctatetraene **2**.

Compound 2a: M.p. 136-137 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.58 (s, 4H, olefinic protons), 4.20 (q, *J* = 7.2 Hz, 8H, OCH_2CH_3), 2.93 (s, 8H, CCH_2), 1.25 (t, *J* = 7.2 Hz, 12H, OCH_2CH_3); ^{13}C

NMR ($CDCl_3$, 150 MHz) δ 171.7, 137.0, 130.2, 61.6, 58.7, 44.6, 14.0; IR (KBr) 2980, 2832, 2848, 1726, 1262, 1186, 1074, 859 cm^{-1}. HR-MS: *m/z*= calcd For $C_{26}H_{32}O_8Na$ [M+Na]: 495.1995, found 495.1955.

Compound 2b: ^1H NMR ($CDCl_3$, 600 MHz) δ 5.59 (s, 4H, olefinic protons), 3.75 (s, 12H, OCH_3), 2.94 (s, 8H, CH_2); ^{13}C NMR ($CDCl_3$, 150 MHz) δ ; 172.2, 136.9, 130.1, 58.5, 52.9, 44.6; IR (KBr) 3001, 2954, 2845, 1735, 1435, 1258, 1199, 1168, 1053, 867 cm^{-1}. These spectroscopic data and crystallographic data were identical to those reported.[2] HR-MS: *m/z*= calcd For $C_{22}H_{24}O_8Na$ [M+Na]: 439.1369, found 439.1338.

Compound 2c: ^1H NMR ($CDCl_3$, 600 MHz) δ 5.54 (s, 4H, olefinic protons), 5.00 (heptet, *J* = 6.0 Hz, 4H, $OCHCH_3$), 2.85 (s, 8H, CH_2) 1.98 (d, *J* = 6.0 Hz, 24H, $CHCH_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ ; 171.1, 136.9, 130.1, 68.8, 58.7, 44.4, 21.4; IR (Neat) 2980, 2934, 1726, 1454, 1266, 1102 cm^{-1}. HR-MS: *m/z*= calcd For $C_{30}H_{40}O_8Na$ [M+Na]: 551.2621, found 551.2588.

Compound 2d: ^1H NMR ($CDCl_3$, 600 MHz) δ 5.62 (s, 4H, olefinic protons), 2.82 (s, 8H, CH_2), 2.15 (s, 12H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz) δ ; 204.7, 137.2, 130.2, 72.5, 41.6, 26.3; IR (Neat) 3004, 2917, 2853, 1715, 1694, 1423, 1356, 1216, 774 cm^{-1}. HR-MS: *m/z*= calcd For $C_{22}H_{24}O_4Na$ [M+Na]: 375.1572, found 375.1555.

Compound 2e: M.p. 246-247 °C; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.71 (d, *J* = 8.4 Hz, 4H, Ar), 7.35 (d, *J* = 8.4 Hz, 4H, Ar), 5.51 (s, 4H, olefinic protons), 3.92 (s, 8H, CH_2), 2.47 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 143.9, 134.9, 134.0, 129.9, 128.9, 127.5, 57.48, 21.63; IR (Neat) 2953, 2922, 2827, 1597, 1348, 1164,1108,671, 575 cm^{-1}. These spectroscopic data and crystallographic data were identical to those reported.[2] HR-MS: *m/z*= calcd For $C_{26}H_{26}N_2O_4S_2Na$ [M+Na]: 517.1231, found 517.1218.

Compound 2f: ^1H NMR ($CDCl_3$, 600 MHz) δ 5.78 (s, 4H, olefinic protones), 3.69 (s, 8H, OCH_2), 2.19 (s, 8H, CCH_2C) 1.42 (s, 12H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz) δ ; 138.0, 130.5, 97.7, 69.1, 44.5, 40.4, 23.8; IR (Neat) 2988, 2939, 2904, 2859, 1447, 1381, 1200, 1156, cm^{-1}. HR-MS: *m/z*= calcd For $C_{24}H_{32}O_4Na$ [M+Na]: 407.2198, found 407.2182.

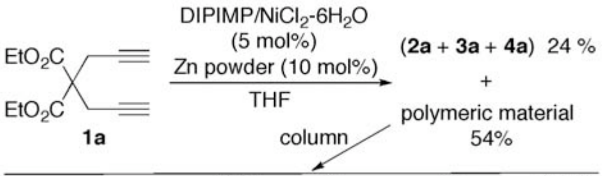
Isolation and Characterization of Polymeric Materials Derived from Diyne 1a by the Reaction with a DIPIMP/$NiCl_2$-$6H_2O$/Zn Catalyst.

Polar colored fractions were obtained by column chromatography of the residue, obtained by the reaction of **1a** (236 mg, 1.0 mmol) with Zn powder (6.5 mg, 0.10 mmol), $NiCl_2$-$6H_2O$ (12 mg, 0.05 mmol) and DIPIMP (16 mg, 0.06 mmol) in THF (4 ml), on silica gel with hexane/EtOAc (1/1 to

0/1). A less polar yellow solid (61.5 mg, 26%) and a more polar orange solid (66.9 mg, 28%) were separated. The resulting yellow and orange solid materials were subjected to ^{1}H NMR, IR, UV-vis absorption, GPC and TOF-MS analyses.

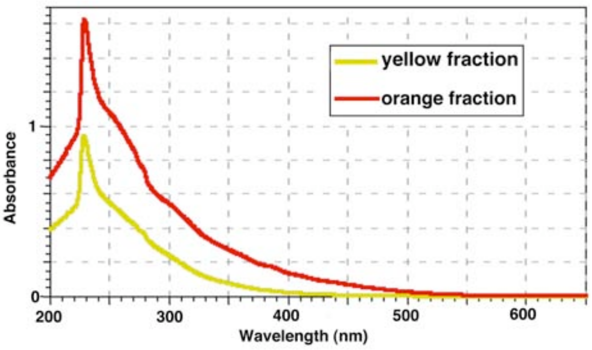
From GPC (THF) analyses [Figure 1, (d) and (e)], *M*w of these fractions were calculated to be 1.2 x 10^3 and 5.1 x 10^3 for yellow- and deep orange-materials, respectively. The polar material had higher molecular weight and it was assumed that the color-change might have originated from the difference in the length of the conjugated segment. TOF-MS spectra [Figure 1, (c)] of the yellow-colored fraction indicated that the material was a mixture of oligomeric molecules comprising a unit of *m/z* 236, which is identical to the molecular weight of **1a** (Exact Mass: 236.104). In addition, each major peak could be calculated as the formula [2H + *n***1a** + Na^+], which indicates a linear polymeric structure and not a cyclic one. Figure 1 (a) shows the UV-vis spectra of these fractions in CH_2Cl_2 with a smooth absorption profile extended to 500 nm. The more polar material exhibited stronger absorption for a wider wavelength range, probably due to its higher conjugation. ^{1}H NMR spectra of these fractions in $CDCl_3$ [Figure 2 (b)] shows olefinic protons in the range δ = 6.8-7.2 ppm, which are characteristically shifted downfield due to their highly conjugated segment.

(a)



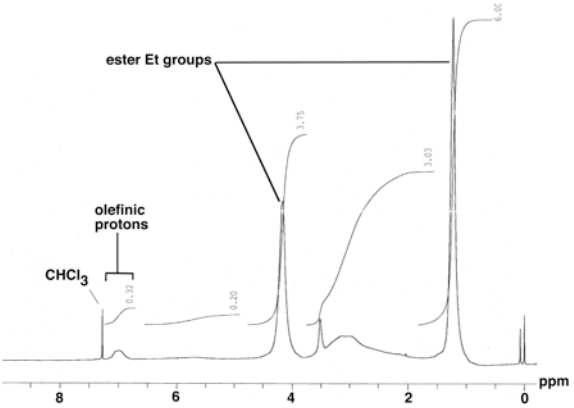
	yield	*Mw*	*Mn*	*Mw/Mn*
yellow material (*less polar*)	26%	1.2 x 10^3 †	0.95 x 10^3 †	1.28
orange material (*polar*)	28%	5.1 x 10^3 †	2.25 x 10^3 †	2.27

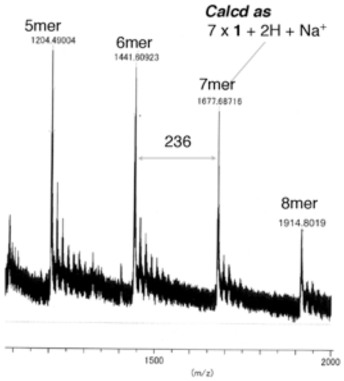
†GPC (THF), polystyrene standards.



(b)

(c)





(d)

(e)

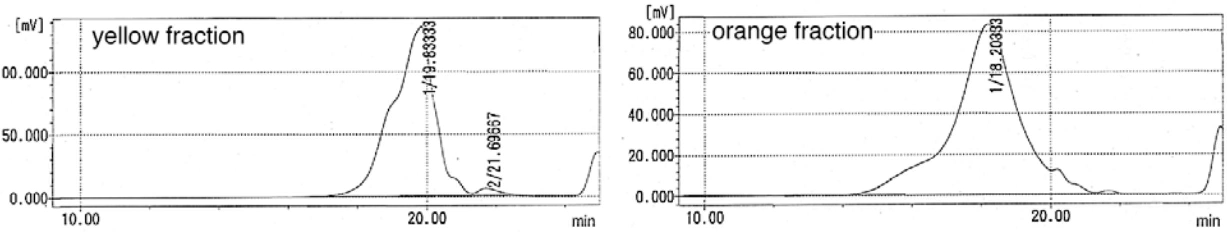


Figure 1. Spectral Data of Polymeric Product. (a) UV-vis absorption spectra / CH_2Cl_2 solution (1.0 mg/L). Yellow line: less polar part, orange line: polar part, brown line: most polar part. (b) 270 MHz ^1H NMR spectra of orange-colored material ($CDCl_3$). (c) Accu TOF-MS spectra with ESI. (d) GPC chart for yelow fraction. (e) GPC chart for orange fraction.

Based on these results, it may be postulated that the colored material might have a polymeric structure of **6a** [Figure 3]. However, since IR spectra of these colored materials showed small peaks corresponding to an alkyne moiety, this suggests that alkyne residues unreacted in the reaction were partially incorporated at the internal positions such as **7a** and/or at the terminal position(s) such as the polymer **6a** having a ***T***^{2}-structure. Alternatively, the corresponding isomeric structures **6a'** and **7a'** can not be ruled out.

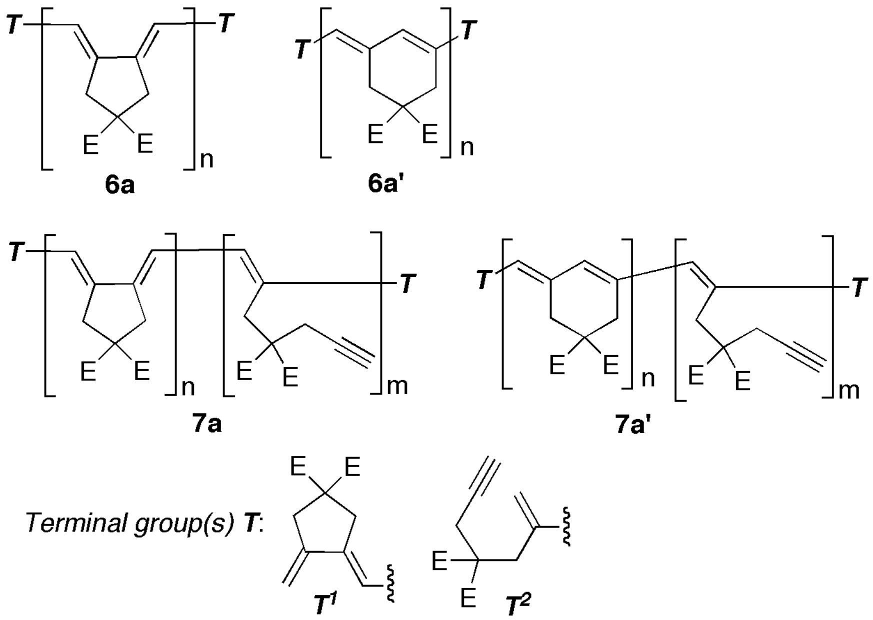


Figure 2. Proposed Polymer Structure. (E = CO_2Et)

References

(1) Cámpora, J.; del Mar Conejo, M.; Mereiter, K.; Palma, P.; Pérez, C.; Reyes, M. L.; Ruiz, C. *J. Organomet. Chem.* **2003**, *683*, 220. Saino, N.; Kogure, D.; Kase, K.; Okamoto, S. *J. Organomet. Chem.* **2006**, *691*, 3129.

(2) Wender, P. A.; Christy, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 13402.

Q

MEEBI Br+

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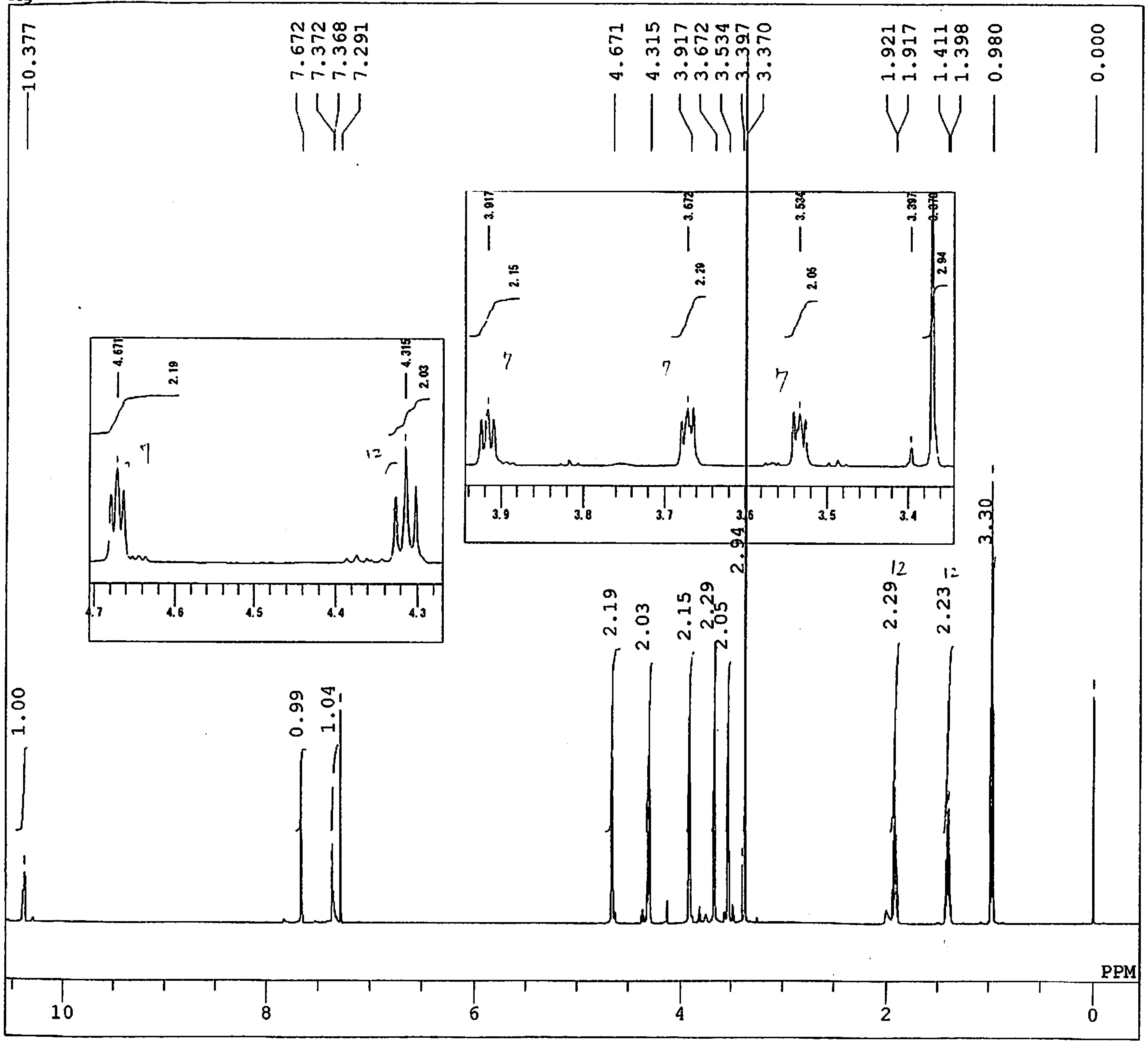

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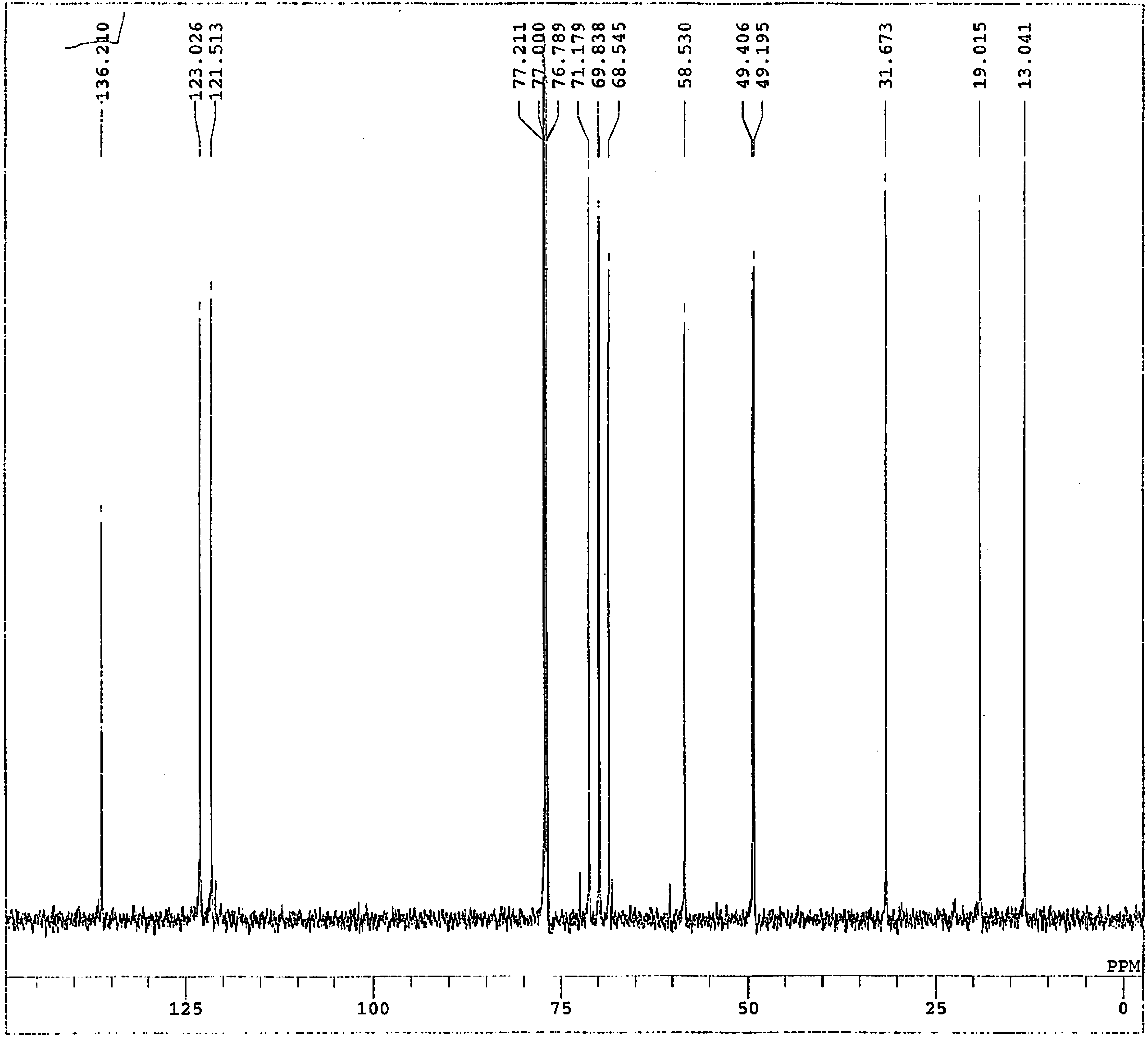

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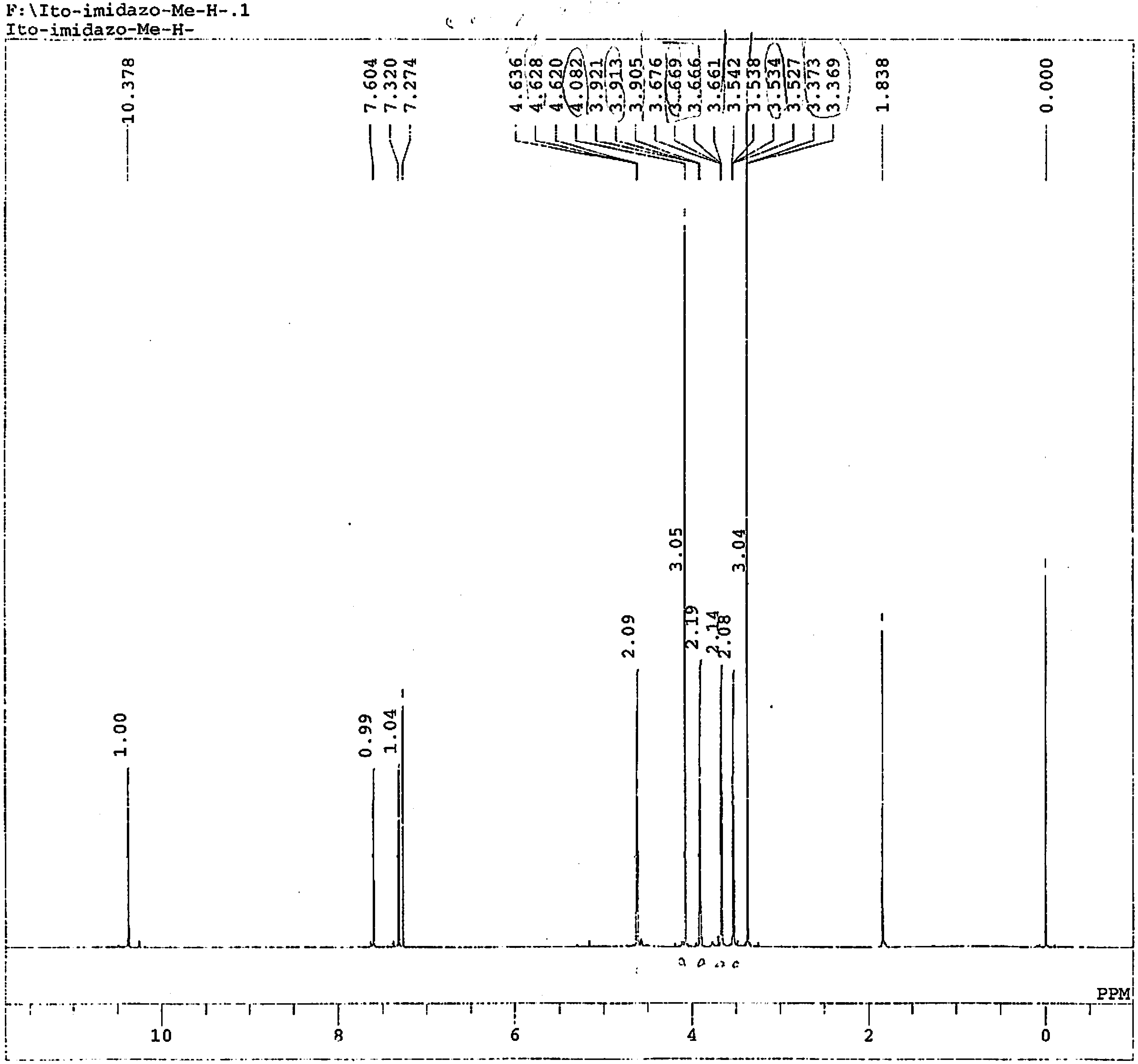

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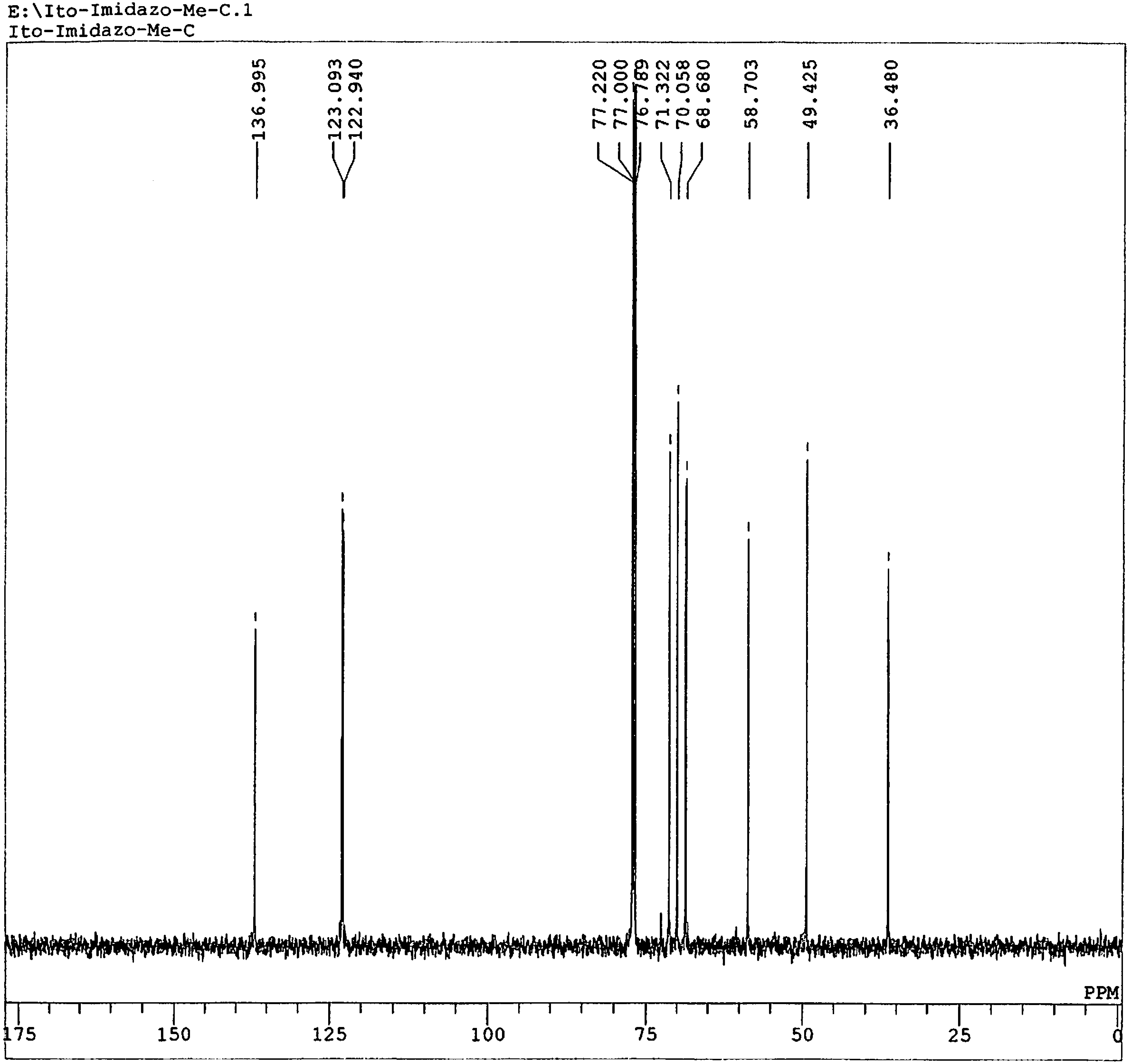

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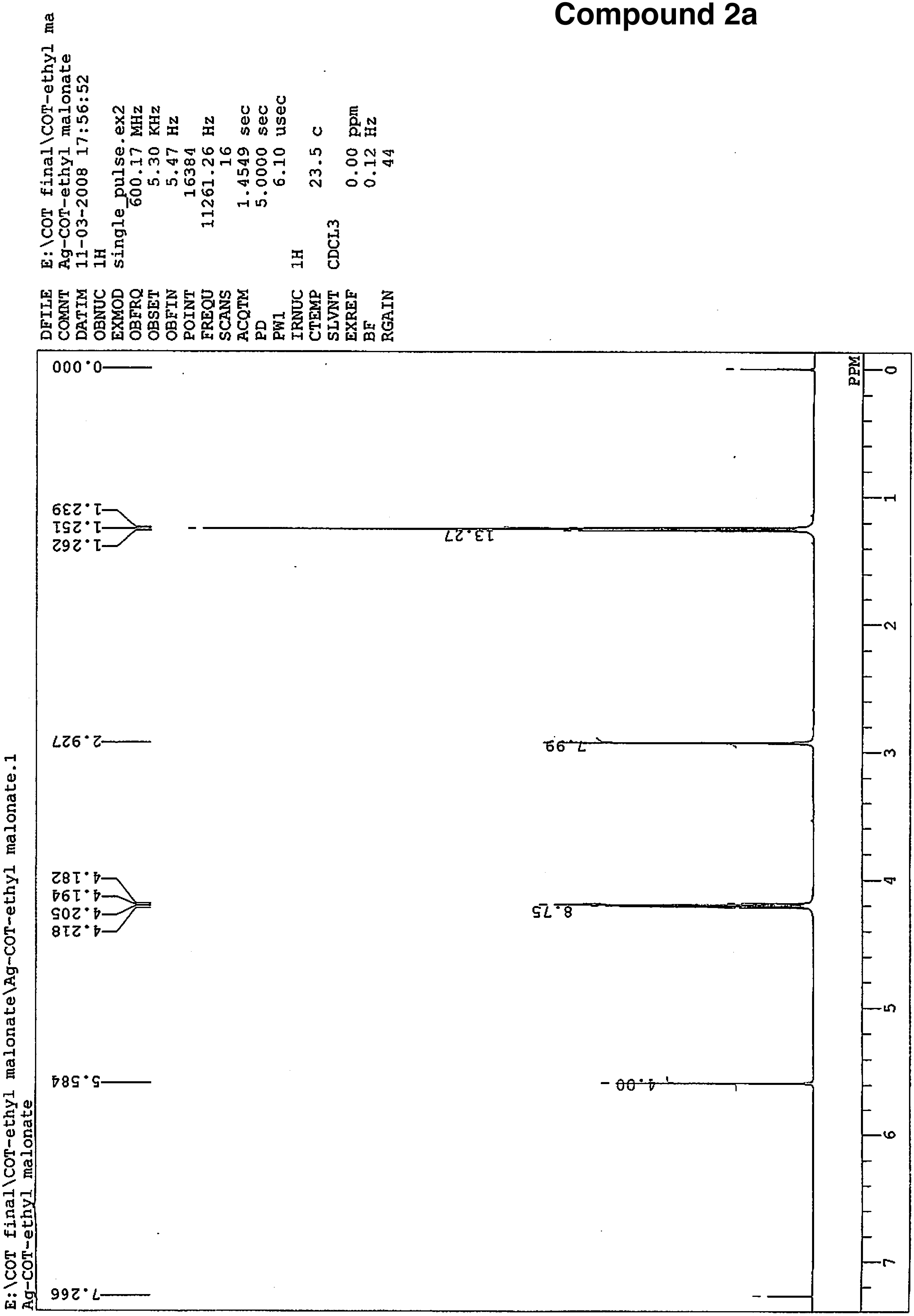
Compound 2a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Compound 2a

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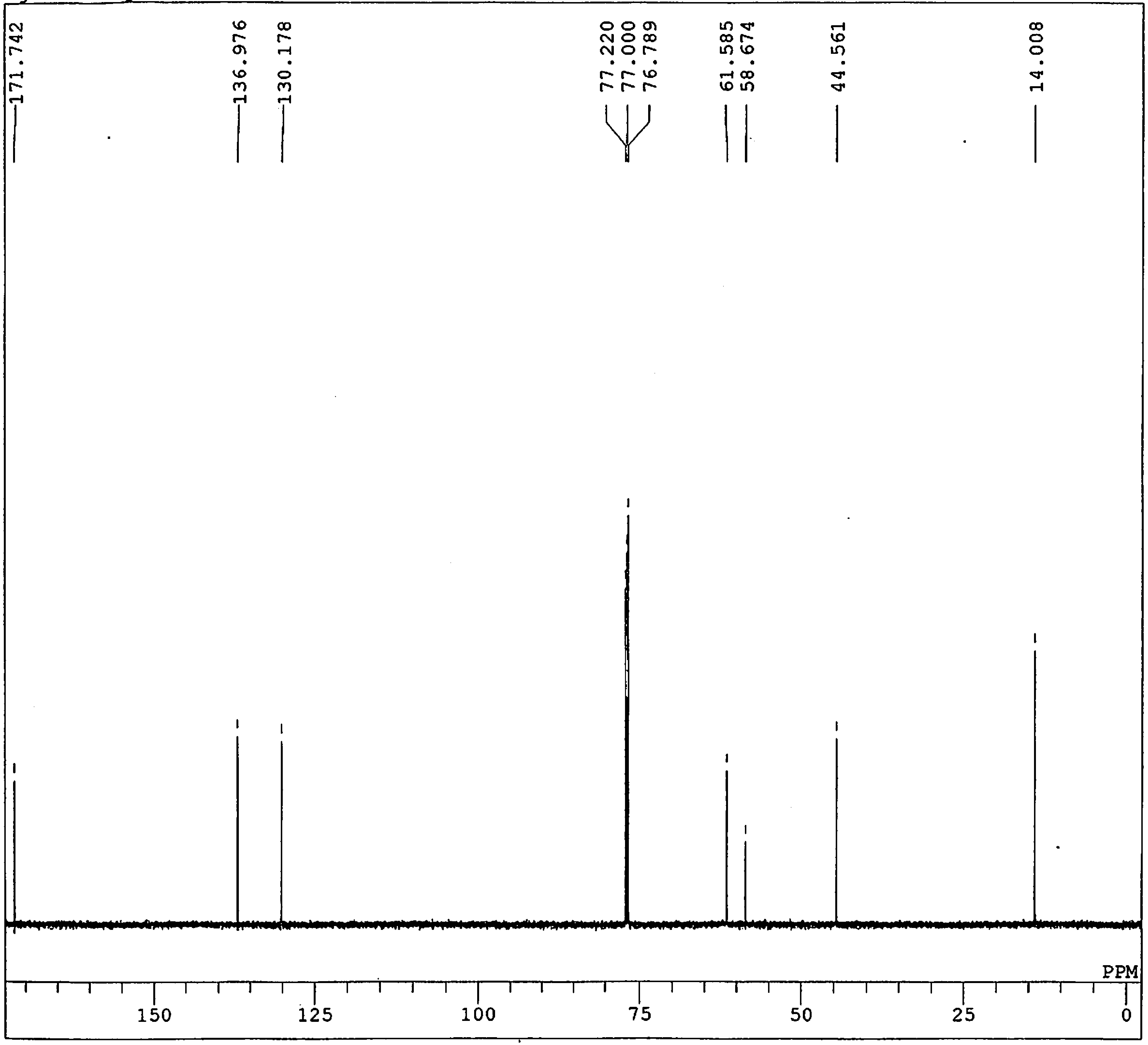

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Supplementary Material (ESI) for Chemical Communications
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Compound 2b

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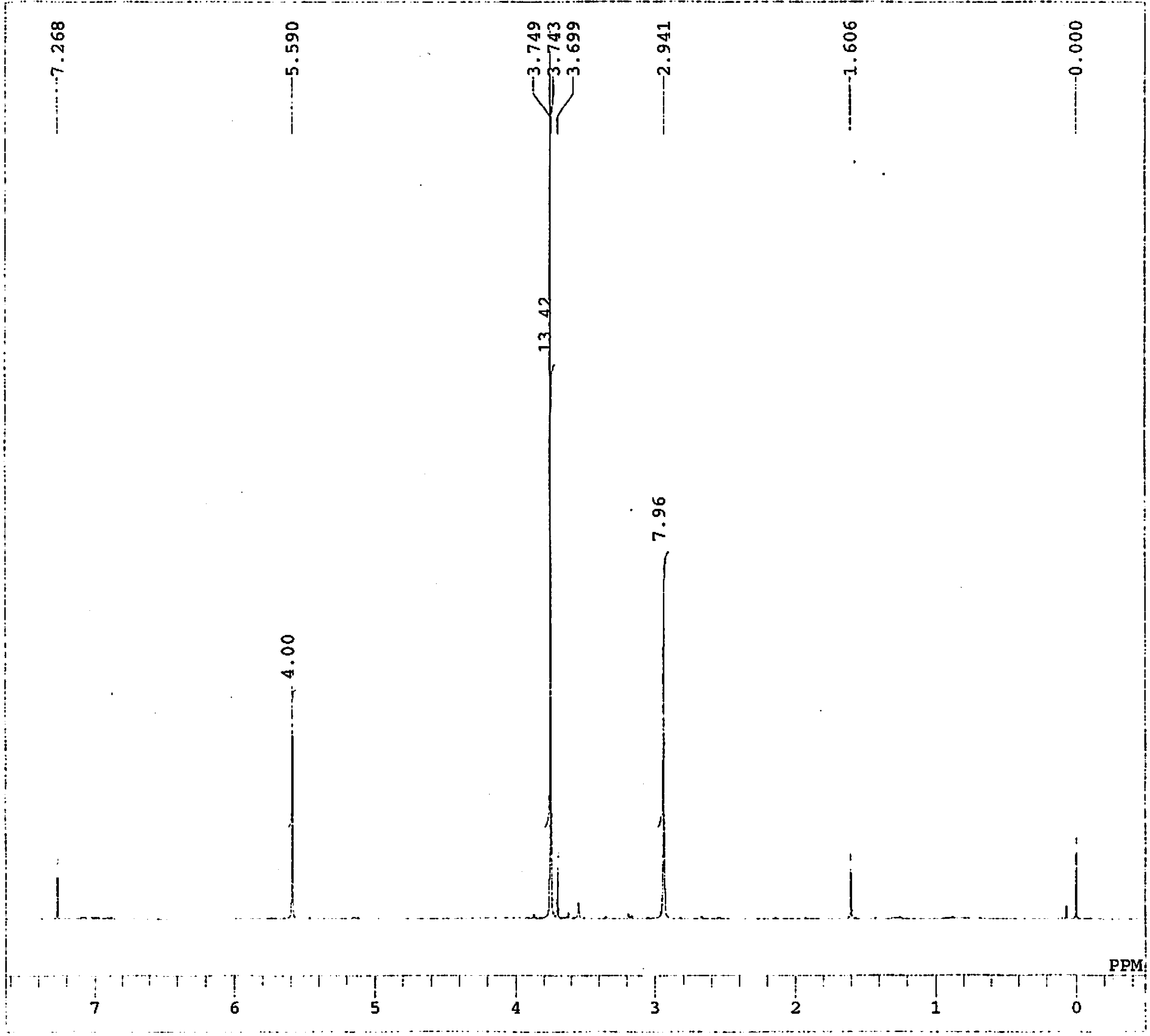

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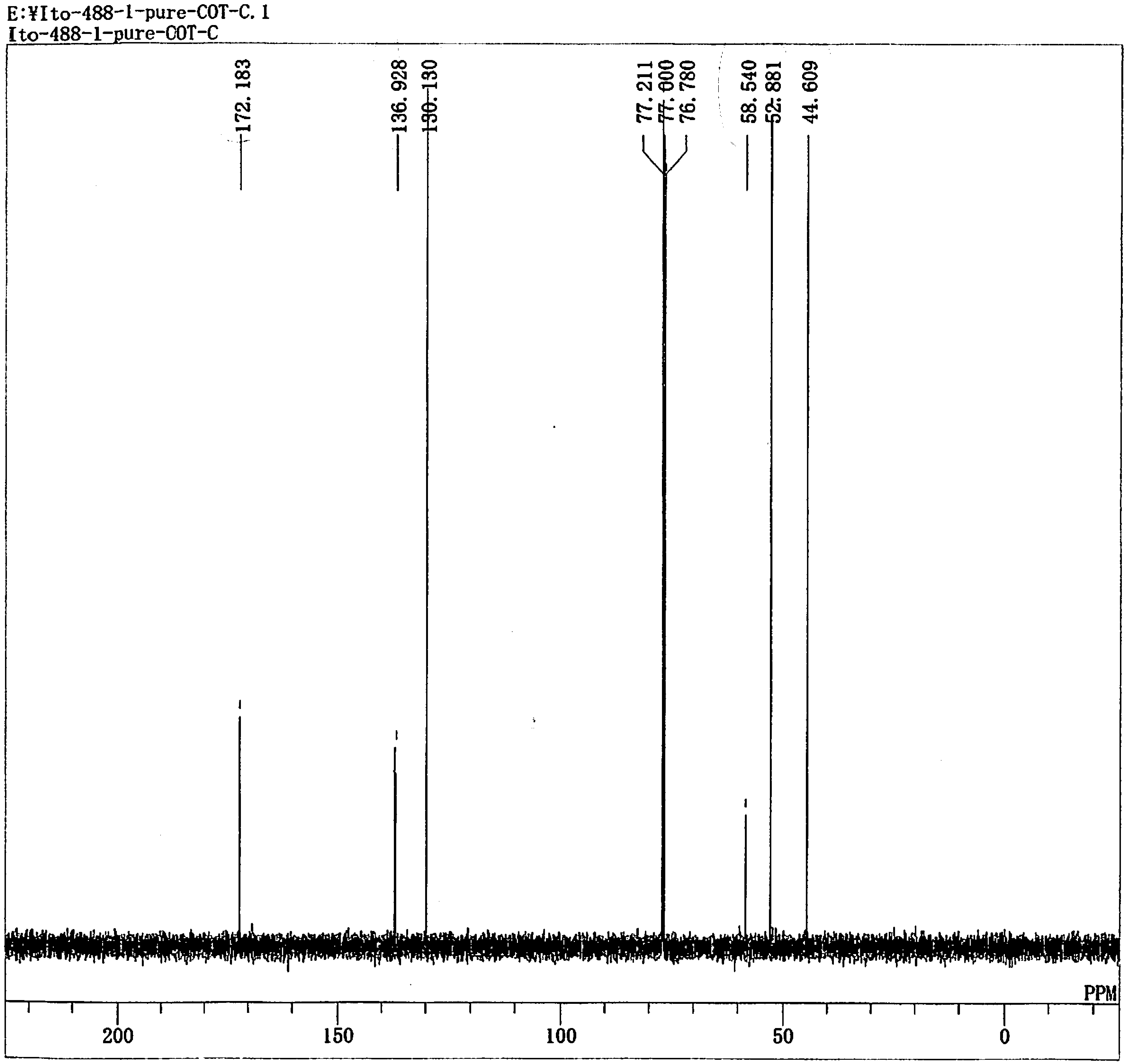
Compound 2b



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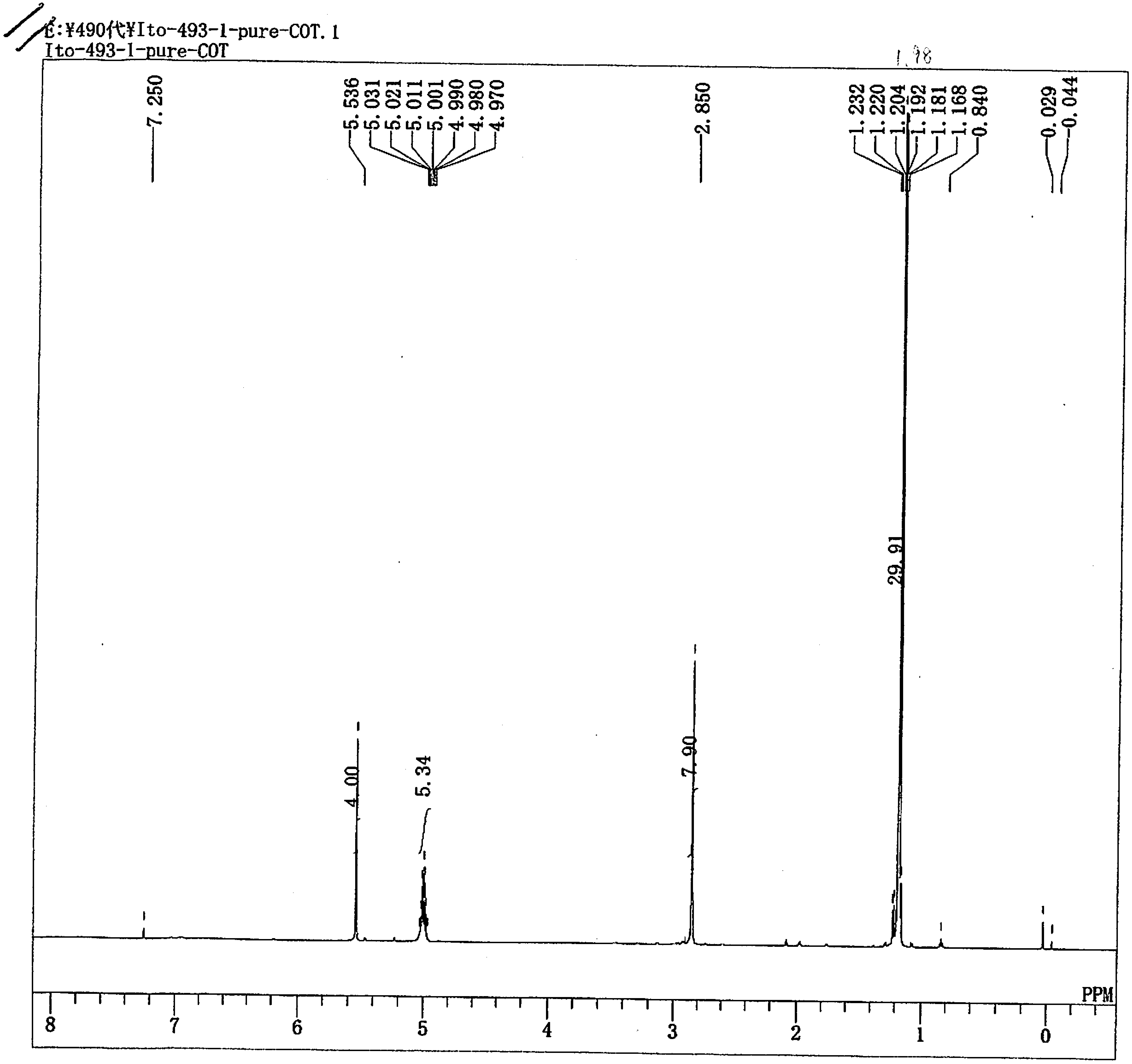

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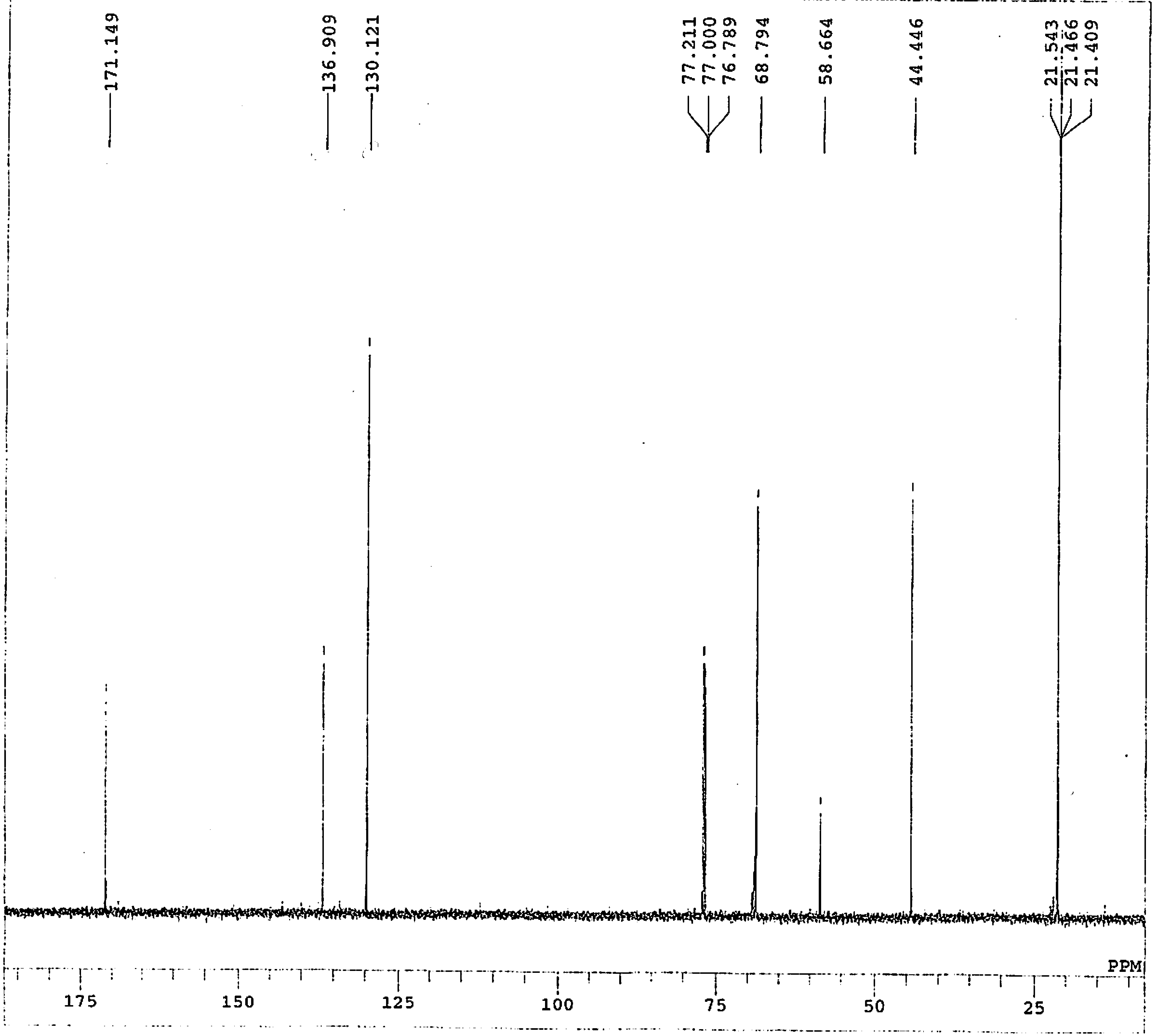
DATIM   17-05-2008 20:30:60
OBNUC   1H
EXMOD   single_pulse.ex2
OBFRQ          600.17 MHz
OBSET            5.30 KHz
OBFIN            5.47 Hz
POINT           16384
FREQU        11261.26 Hz
SCANS              16
ACQTM          1.4549 sec
PD             5.0000 sec
PW1              6.00 usec
IRNUC   1H
CTEMP            23.7 c
SLVNT   CDCL3
EXREF            7.25 ppm
BF               0.12 Hz
RGAIN              30
```

Compound 2c

Compound 2c

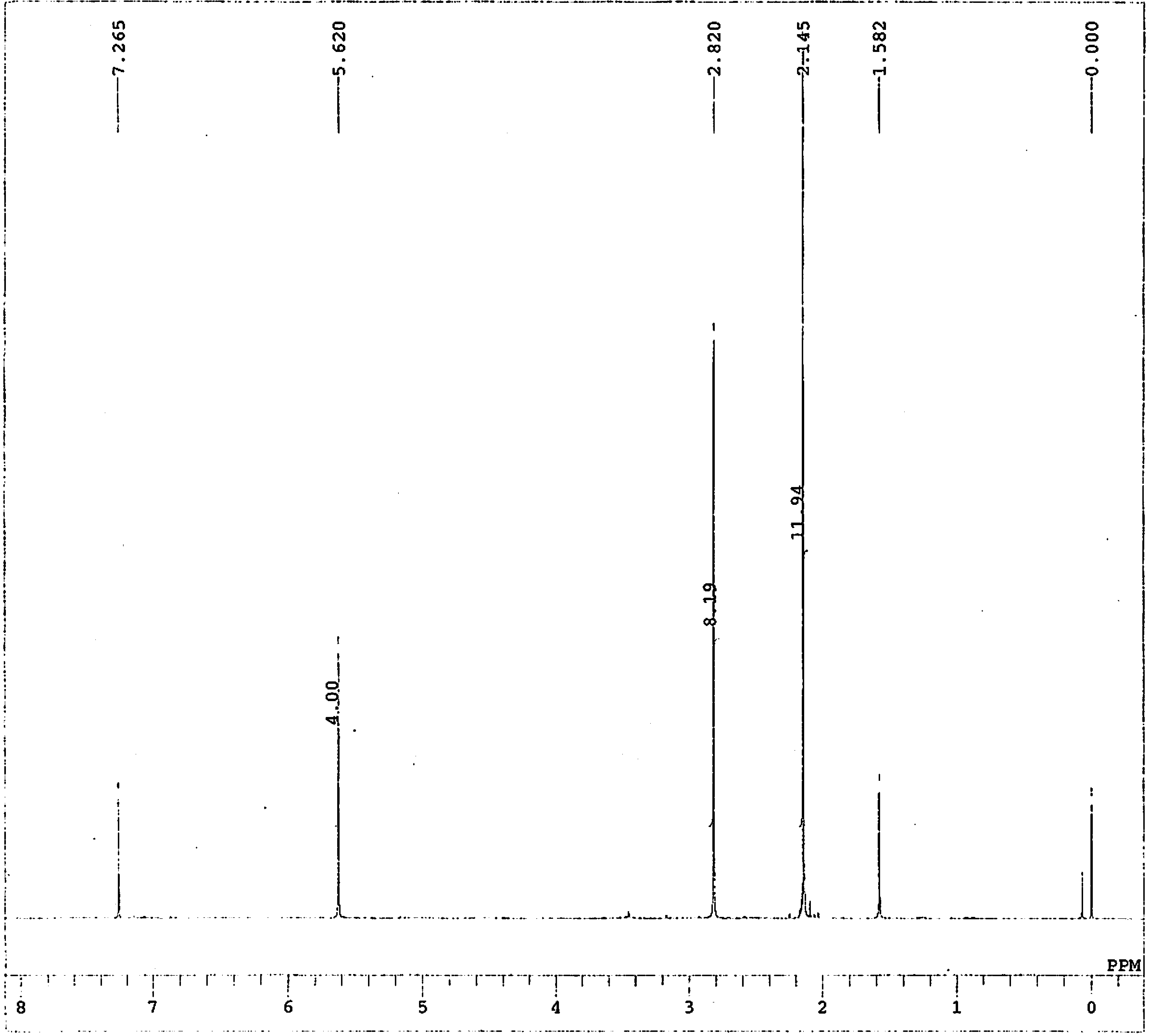
F:\490'ã\Ito-493-1-pure-COT-C.1
Ito-493-1-pure-COT-C



```
DFILE   F:\490'ã\Ito-493-1-pur
COMNT   Ito-493-1-pure-COT-C
DATIM   17-05-2008 20:33:47
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ          150.92 MHz
OBSET            8.52 KHz
OBFIN            1.74 Hz
POINT           32768
FREQU        47348.49 Hz
SCANS              53
ACQTM          0.6921 sec
PD             2.0000 sec
PW1              4.00 usec
IRNUC   1H
CTEMP            24.4 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              50
```

Compound 2d

F:\470'ã\Ito-479-2-pure.1
Ito-479-2-pure

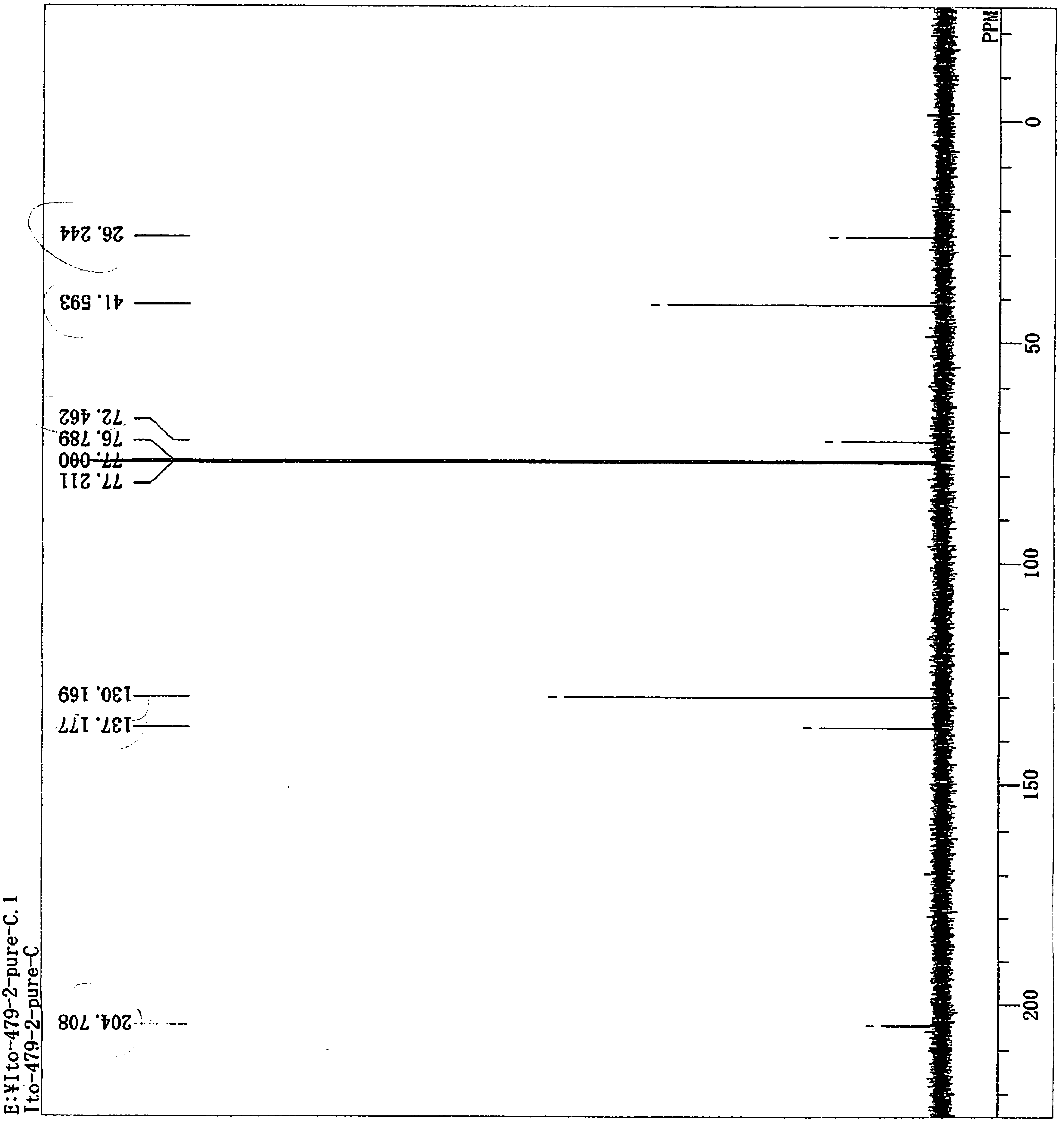


```
DFILE   F:\470'ã\Ito-479-2-pur·
COMNT   Ito-479-2-pure
DATIM   15-05-2008 14:50:08
OBNUC   1H
EXMOD   single_pulse.ex2
OBFRQ          600.17 MHz
OBSET            5.30 KHz
OBFIN            5.47 Hz
POINT           13106
FREQU         9008.87 Hz
SCANS              10
ACQTM          1.4549 sec
PD             5.0000 sec
PW1              6.00 usec
IRNUC   1H
CTEMP            23.7 c
SLVNT   CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              50
```

Q

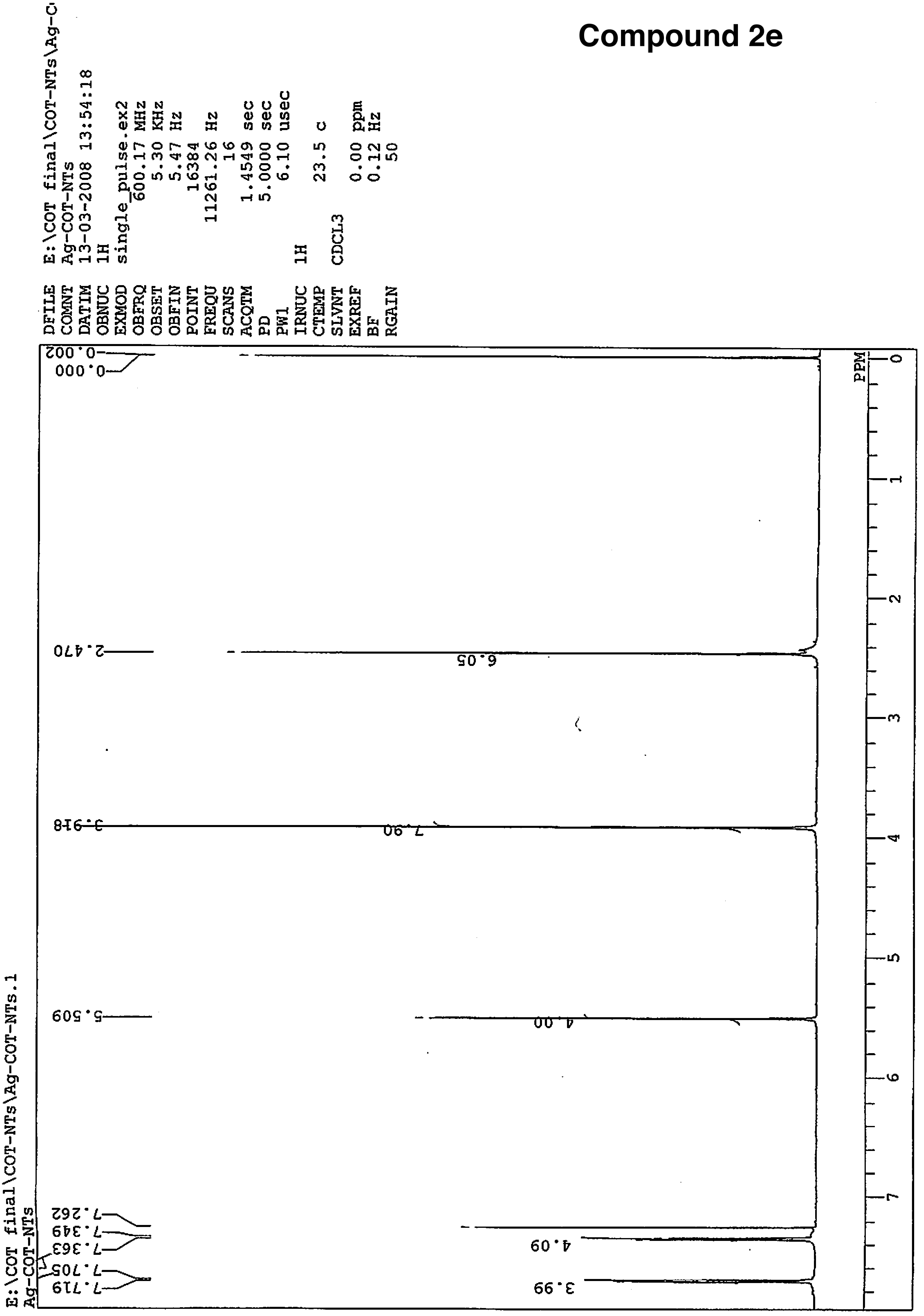
Compound 2d

```
DFILE  E:¥Ito-479-2-pure-C.1
COMNT  Ito-479-2-pure-C
DATIM  15-05-2008 15:02:19
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ     150.92 MHz
OBSET       8.52 KHz
OBFIN       1.74 Hz
POINT      32768
FREQU   47348.49 Hz
SCANS        253
ACQTM     0.6921 sec
PD        2.0000 sec
PW1         4.00 usec
IRNUC  1H
CTEMP       24.3 c
SLVNT  CDCL3
EXREF      77.00 ppm
BF          0.12 Hz
RGAIN         50
```



0

Compound 2e



Supplementary Material (ESI) for Chemical Communications
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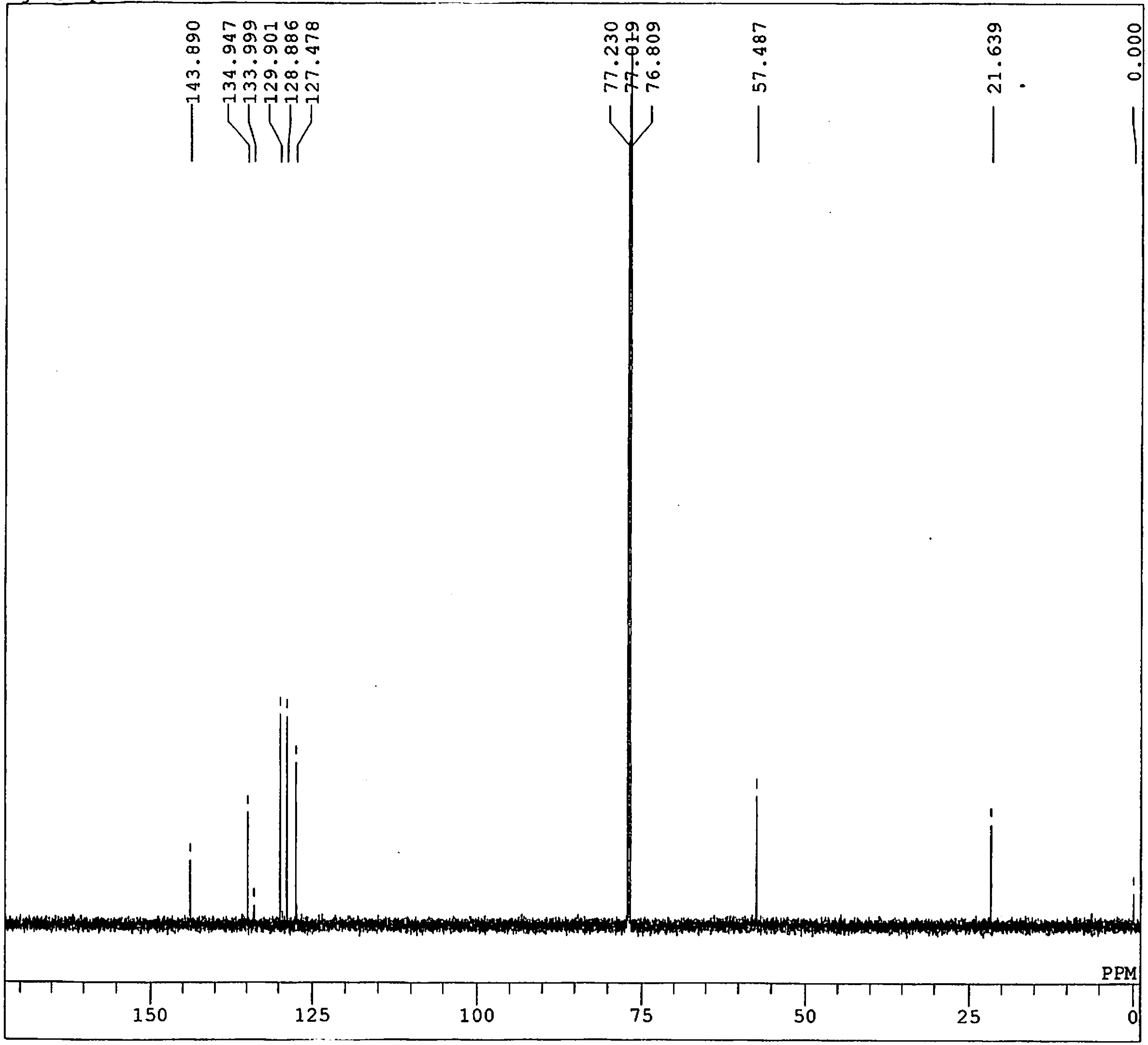
Compound 2e

```
C:\DOCUME~1\NMR\LOCALS~1\Temp\~FTP6CF7.1
Ag-COT-pure-NTs-carbon
```

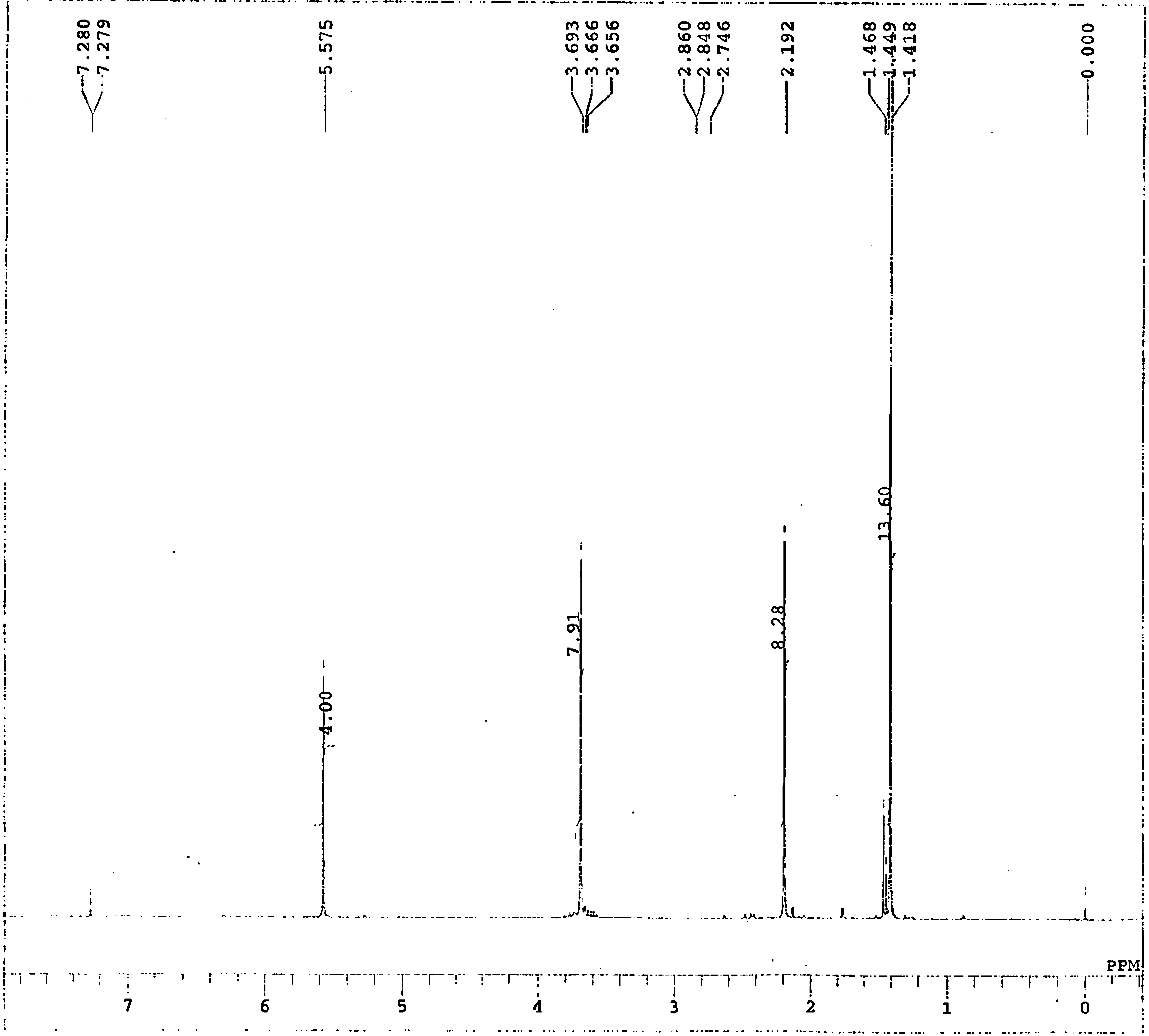


```
DFILE   C:\DOCUME~1\NMR\LOCALS~1\'
COMNT   Ag-COT-pure-NTs-carbon
DATIM   13-03-2008 14:18:57
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ          150.92 MHz
OBSET            8.52 KHz
OBFIN            1.74 Hz
POINT           32768
FREQU        47348.49 Hz
SCANS             500
ACQTM          0.6921 sec
PD             2.0000 sec
PW1              3.67 usec
IRNUC   1H
CTEMP            24.1 c
SLVNT   CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              60
```

9

Compound 2f

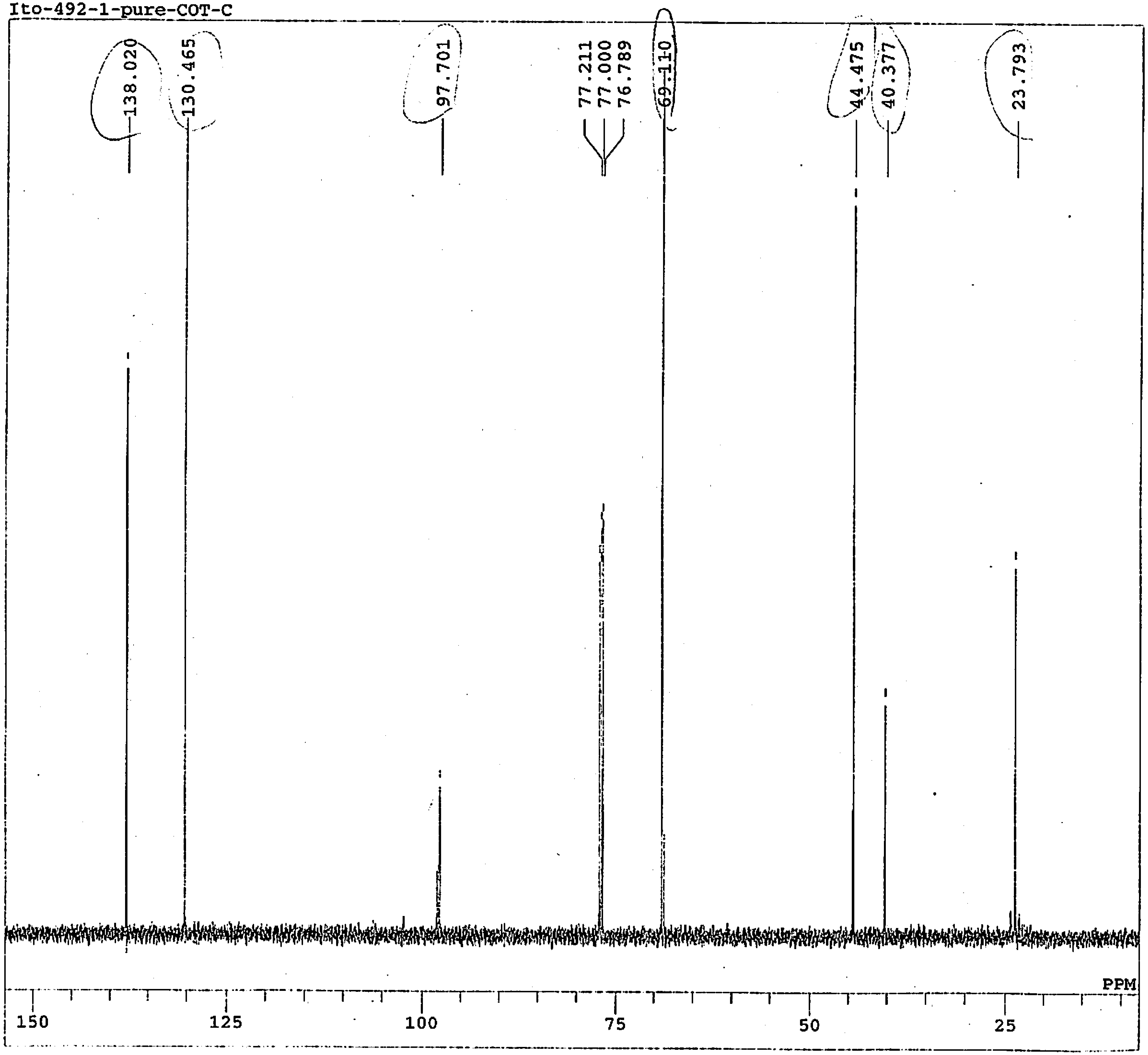
F:\490'ă\Ito-492-1-pure-COT.als
Ito-492-1-pure-COT



```
DFILE   F:\490'ă\Ito-492-1-pur
COMNT   Ito-492-1-pure-COT
DATIM   17-05-2008 20:49:52
OBNUC   1H
EXMOD   single_pulse.ex2
OBFRQ         600.17 MHz
OBSET           5.30 KHz
OBFIN           5.47 Hz
POINT          13107
FREQU        9008.87 Hz
SCANS              8
ACQTM         1.4549 sec
PD            5.0000 sec
PW1             6.00 usec
IRNUC   1H
CTEMP           23.5 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             30
```

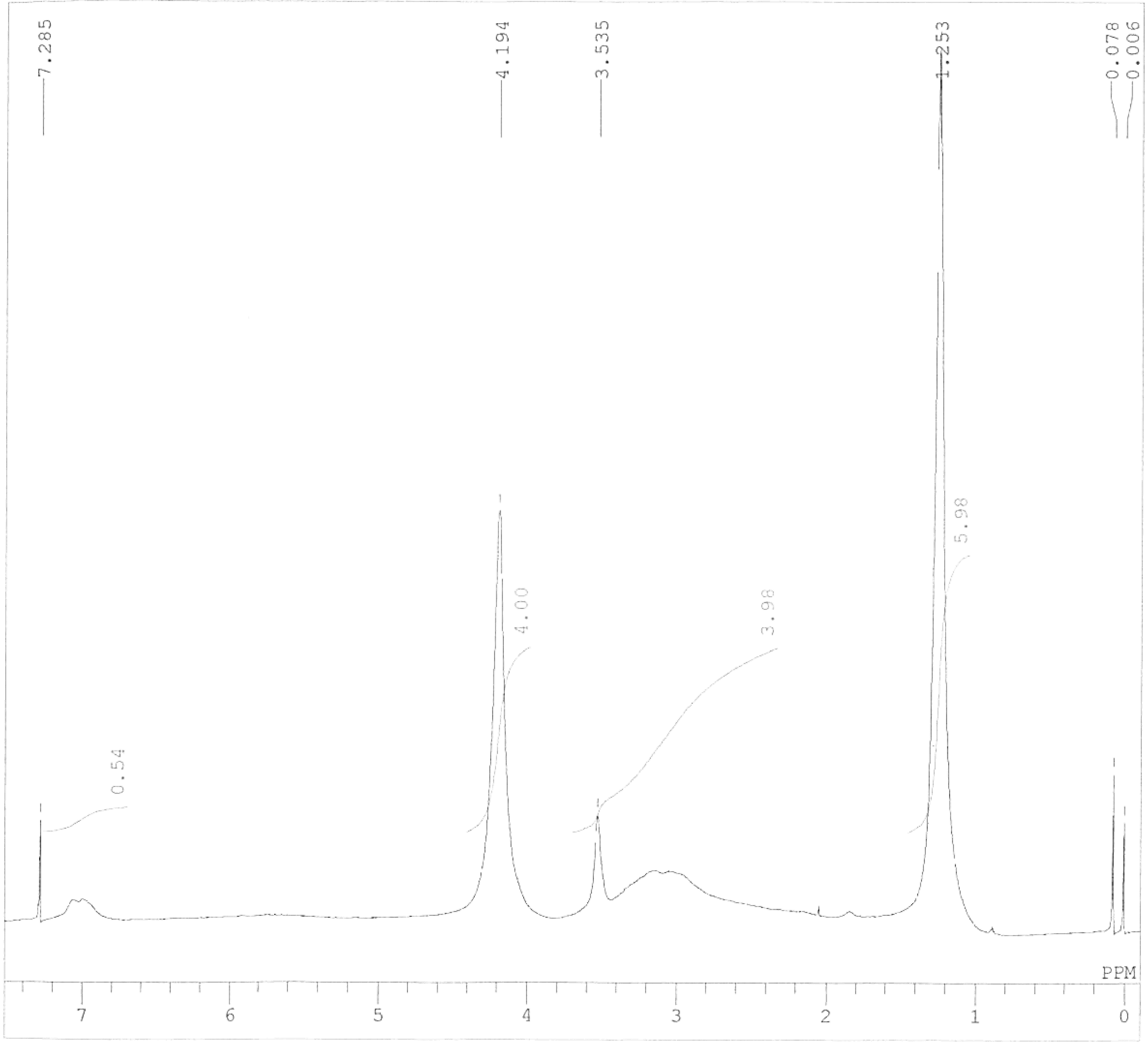
Compound 2f

F:\490'ã\Ito-492-1-pure-COT-C.1
Ito-492-1-pure-COT-C



DFILE	F:\490'ã\Ito-492-1-pur	
COMNT	Ito-492-1-pure-COT-C	
DATIM	17-05-2008 20:17:56	
OBNUC	13C	
EXMOD	single_pulse_dec	
OBFRQ	150.92	MHz
OBSET	8.52	KHz
OBFIN	1.74	Hz
POINT	32768	
FREQU	47348.49	Hz
SCANS	54	
ACQTM	0.6921	sec
PD	2.0000	sec
PW1	4.00	usec
IRNUC	1H	
CTEMP	24.2	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	0.12	Hz
RGAIN	50	

C:\DOCUME~1\NMR\LOCALS~1\Temp\~FTP68ED.1
AG-polymerization-1st fraction-16-17

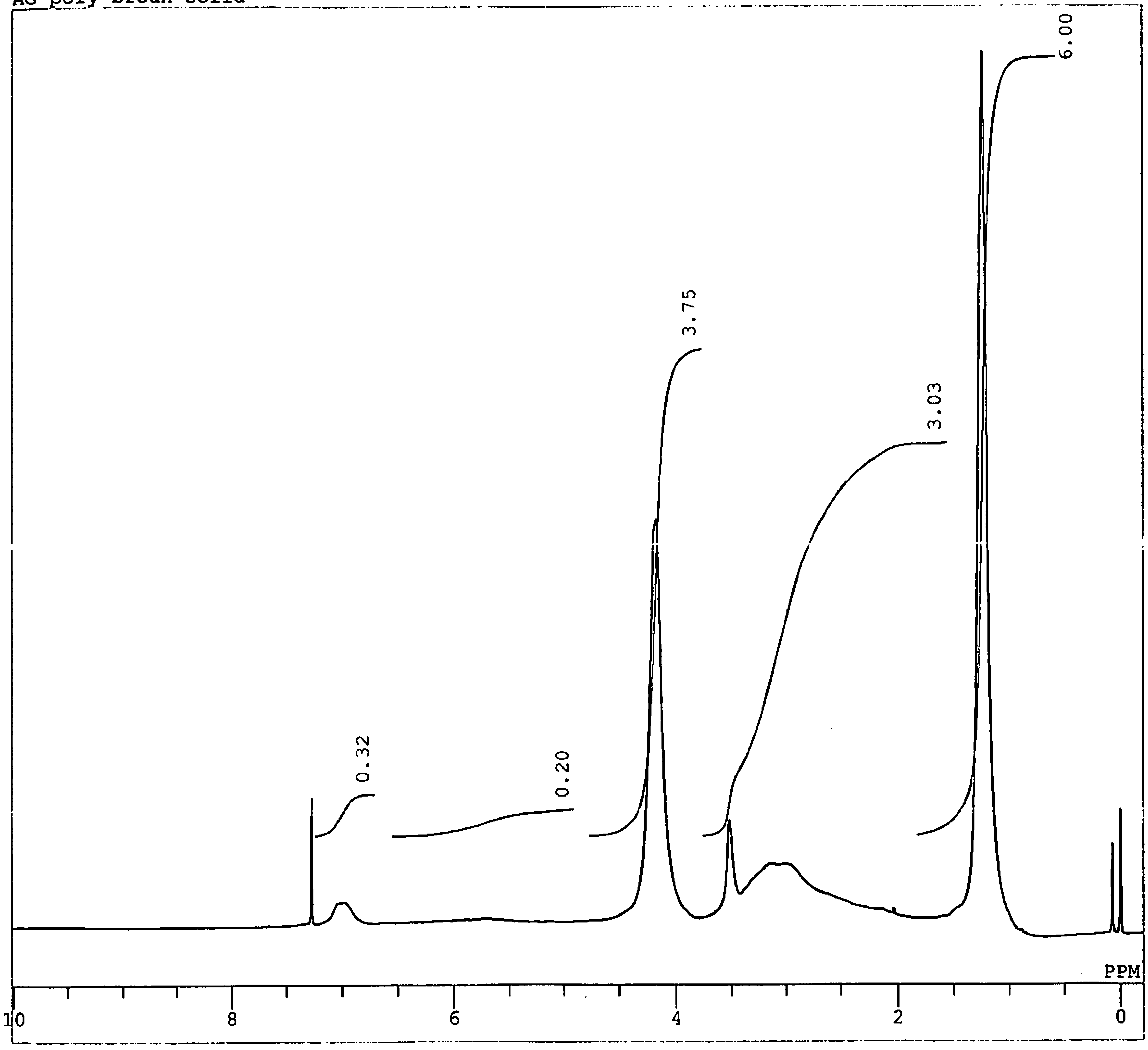


```
DFILE  C:\DOCUME~1\NMR\LOCALS~1\
COMNT  AG-polymerization-1st fra
DATIM  09-02-2008 14:44:39
OBNUC  1H
EXMOD  single_pulse.ex2
OBFRQ         600.17 MHz
OBSET           5.30 KHz
OBFIN           5.47 Hz
POINT          16384
FREQU       11261.26 Hz
SCANS             16
ACQTM         1.4549 sec
PD            5.0000 sec
PW1             6.10 usec
IRNUC  1H
CTEMP           23.5 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             34
```

yellow fraction
1st fraction

Polymer
Yellow fraction
(less polar)

```
C:\WINNMR98\COMMON\_DEFAULT.ALS
AG-poly-broun-solid
```



```
DFILE   C:\WINNMR98\COMMON\_DEFAULT
COMNT   AG-poly-broun-solid
DATIM   Thu Feb 14 15:11:35 2008
OBNUC   1H
EXMOD   NON
OBFRQ        270.05 MHz
OBSET        112.00 KHz
OBFIN        5800.0 Hz
POINT         32768
FREQU        5402.4 Hz
SCANS             8
ACQTM         6.065 sec
PD            0.935 sec
PW1             5.2 us
IRNUC   1H
CTEMP          25.1 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             1.00 Hz
RGAIN            15
```

Orange fraction
2nd fraction

Polymer
Orange fraction
(polar)