Supporting Information

Mizoroki-Heck Arylation of α,β-Unsaturated Acids with a Hybrid Fluorous Ether, F-626: Facile Filtrative Separation of Products and Efficient Recycling of a Reaction Medium Containing a Catalyst

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General information. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3OD or DMSO-d_6. For ^{1}H NMR spectra, Chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared absorptions are are reported in reciprocal centimeters. Mass spectra were obtained with ionization voltages of 70 eV. Coupling products were purified by flash chromatography on silica gel. All products are known compounds and were identified by NMR and melting point with comparison of literature data. F-626, *1H,1H,2H,2H*-perfluorooctyl 1,3-dimethylbutyl ether, was provided from Kao Corporation.

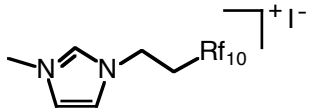
Typical Procedure for Mizoroki-Heck Reaction (Method A).

F-626 was degassed under reduced pressure at room temperature for 30 min, and then nitrogen gas was introduced. $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), fluorous ionic liquid **II** (16 mg, 0.02 mmol), PPh_3 (5.2 mg, 0.02 mmol), tripropylamine (215 mg, 1.5 mmol), iodobenzene (**1a)** (204 mg, 1 mmol), and acrylic acid (**2a)** (93 mg, 1.3 mmol) were added sequentially to F-626 (0.5 mL, 850 mg). The suspension was heated at 120 °C, upon which a homogenous solution was obtained. Coupling product and the ammonium salts were precipitated as the reaction progressed. After 2 h, the reaction mixture was cooled and precipitate consisting of cinnamic acid and the amine salt was obtained by filtration and washed with FC-72 (5 x 1 mL). F-626 was recovered 96% (820 mg, containing less than 2% of Pd catalyst) by concentration of the filtrate under reduced pressure. The precipitate was dissolved in EtOAc (30 mL), washed with HCl aqueous solution (2 M, 20 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on SiO_2 (hexane/EtOAc = 4/1) to afford the coupling product, *trans*-cinnamic acid (130 mg, 88%), as a white solid.

Procedure for the Catalyst Recycling Study.

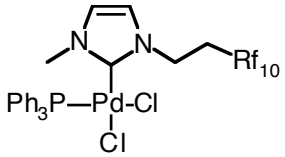
After the reaction, the resulting precipitate consisting of cinnamic acid and the amine salt was obtained by filtration and washed with FC-72 (5 x 1 mL). F-626 was recovered 96% by concentration of the filtrate under reduced pressure. To the remaining F-626, containing Pd catalyst, were added tripropylamine (140 mg, 1.4 mmol), iodobenzene (204 mg, 1 mmol), and acrylic acid (94 mg, 1.3 mmol). This solution was heated at 120 °C for 2 h, cooled and the resulting precipitate consisting of cinnamic acid and the amine salt was obtained by filtration and washed with FC-72 (5 x 1 mL). F-626 was recovered 94% by concentration of the filtrate under reduced pressure. The precipitate was dissolved in EtOAc (30 mL), washed with HCl aqueous solution (2 M, 20 mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on SiO_2 (hexane/EtOAc = 4/1) to afford *trans*-cinnamic acid (125 mg, 85%) as a white solid.

Preparation of Fluorous Ionic Liquid (II).



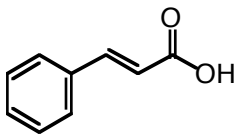
To a solution of 1-methylimidazole (0.9 g, 11 mmol) in toluene (20 mL) was added 2-(perfluorodecyl)ethyl iodide (7.6 g, 11 mmol), and the resulting mixture was heated at 120 °C for 12 h under nitrogen. The resulting precipitate was separated by filtration. The solid was washed with toluene (100 mL) to remove 1-methylimidazol. The precipitate was dissolved in $CHCl_3$, and the solution was passed through short column of activated Al_2O_3 (200 mesh). The solvent was removed under reduced pressure to give fluorous ionic liquid (3.9 g, 51%) as a white solid. mp 158-160 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) 2.94-3.35 (m, 2H), 3.87 (s, 3H), 4.56 (t, J = 7.1 Hz, 2H), 7.73 (s, 1H), 7.87 (s, 1H), 9.20 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz), (partial) 30.8 (t, $^2J_{CF}$ = 20.2), 36.7, 41.7, 123.0, 124.1, 137.9; IR (KBr) 1211, 1154 cm^{-1}. MS (FAB) *m/z* 629 (M^+-I, 100), HRMS (FAB) *m/z* calcd for $C_{16}H_{10}F_{21}N_2$ (M^+-I) 629.0509, found 629.0517.

Preparation of Fluorous Pd Carbene Complex (I).



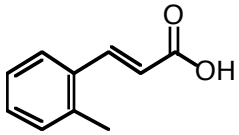
Fluorous ionic liquid **II** (752 mg, 1 mmol), PPh_3 (262 mg, 1 mmol), triethylamine (505 mg, 5 mmol), lithium chloride (424 mg, 10 mmol) were added sequentially to a stirred solution of $Pd(OAc)_2$ (224 mg, 1 mol) in THF (12 mL) under nitrogen. The resulting mixture was heated at 70 °C for 12 h under nitrogen. After 12 h, the reaction mixture was dissolved in EtOAc (20 mL), washed with water (20mL). Two layers were separated, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on SiO_2 (hexane/EtOAc = 1/1) to afford the fluorous Pd carbene complex (**I**) (350 mg, 33%) as a yellow solid. mp 173-175 °C; ^{1}H NMR (CD_3OD, 500 MHz) 2.28-2.34 (m, 1H), 2.90-3.06 (s, 1H), 3.59 (s, 3H), 3.78-3.88 (m, 1H), 4.42-4.52 (m, 1H), 6.65 (s, 1H), 6.70 (s, 1H), 7.20-7.60 (m, 15H); ^{13}C NMR (CD_3OD, 125 MHz) 30.7, 36.7, 41.7, 106.80-120.02 (C-F bond), 159.8, 165.1, ^{31}P NMR ($CDCl_3$, 202 MHz) 24.45; IR (KBr) 1213, 1155 cm^{-1}.

***trans*-Cinnamic acid (3a).**[1]



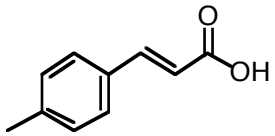
White solid, mp 133-134 °C (lit.[1] mp 132-135 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) 6.47 (d, J = 16.0 Hz, 1H), 7.41 (m, 3H), 7.50-7.60 (m, 2H), 7.81 (d, J = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 117.3, 128.3, 128.9, 130.7, 134.0, 147.1, 172.7; EIMS, *m/z* (relative intensity) 148 (M^+, 100), 102 (34); IR (KBr) 3439, 1678, 1630 cm^{-1}.

***trans-o*-Methylcinnamic acid (3b).**[2]



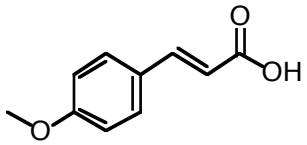
White solid, mp 175-176 °C (lit.[2] mp 175-176 °C); ^{1}H NMR (CD_3OD, 500 MHz) 2.41 (s, 3H), 6.37 (d, J = 15.6 Hz, 1H), 7.18-7.30 (m, 3H), 7.60 (d, J = 7.8 Hz 1H), 7.98 (d, J = 15.6 Hz, 1H); ^{13}C NMR (CD_3OD, 125 MHz) 19.7, 120.3, 127.4, 131.2, 131.8, 134.5, 138.7, 143.8, 170.4; EIMS, *m/z* (relative intensity) 162 (M^+, 12), 147 (45) 115 (100); IR (KBr) 2945, 1686, 1622 cm^{-1}.

***trans-p*-Methylcinnamic acid (3c)**.[3]



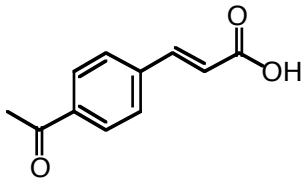
White solid, mp 199-200 °C (lit.[3] mp 200-201 °C); ^{1}H NMR (CD_3OD, 500 MHz) 2.34 (s, 3H), 6.40 (d, J = 15.6 Hz, 1H), 7.18-7.22 (m, 2H), 7.44-7.48 (m, 2H), 7.62 (d, J = 16.0 Hz, 1H); ^{13}C NMR (CD_3OD, 125 MHz) 21.4, 118.2, 129.2, 130.7, 133.1, 142.0, 146.4, 170.5; EIMS, *m/z* (relative intensity) 162 (M^+, 84), 161 (61), 147 (54), 115 (100), 91 (63); IR (KBr) 2922, 1686, 1624 cm^{-1}.

***trans-p*-Methoxycinnamic acid (3d).**[3]



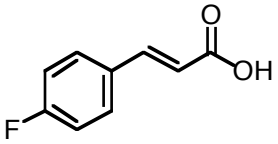
White solid, mp 175-176 °C (lit.[3] mp 172-173 °C); ^{1}H NMR (CD_3OD, 500 MHz) 3.83 (s, 3H, H-8), 6.32 (d, J = 15.8 Hz, 1H, H-2), 6.91-6.96 (m, 2H), 7.50-7.56 (m, 2H), 7.62 (d, J = 15.8 Hz, 1H); ^{13}C NMR (CD_3OD, 125 MHz) 55.9, 115.4, 116.6, 128.4, 130.9, 146.2, 163.1, 170.8; EIMS, *m/z* (relative intensity) 178 (M^+, 100), 161 (41); IR (KBr) 2935, 1686, 1600 cm^{-1}.

***trans-p*-Acetylcinnamic acid (3e).**[4]



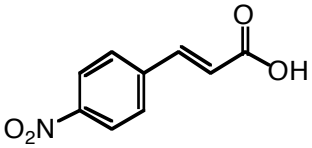
White solid, mp 224-226 °C (lit.[4] mp 224-225 °C); ^{1}H NMR (CD_3OD, 500 MHz) 2.60 (s, 3H), 6.60 (d, J = 16.0 Hz, 1H), 7.68-7.73 (m, 3H), 7.98-8.03 (m, 2H); ^{13}C NMR (CD_3OD, 125 MHz) 26.6, 121.9, 129.4, 130.0, 139.0, 140.4, 144.6, 169.7, 199.8; EIMS, *m/z* (relative intensity) 190 (M^+, 12), 175 (100); IR (KBr) 2978, 1680, 1630 cm^{-1}.

***trans-p*-Fluorocinnamic acid (3f).**[5]



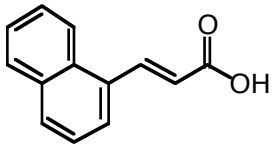
White solid, mp 205-207 °C (lit.[5b] mp 208 °C); ^{1}H NMR (CD_3OD, 500 MHz) 6.42 (d, J = 16.0 Hz, 1H), 7.10-7.16 (m, 2H), 7.60-7.70 (m, 3H); ^{13}C NMR (CD_3OD, 125 MHz), 117.0, 119.3, 131.3, 132.3, 145.0, 165.4 (d, $^{2}J_{CF}$ = 249.5 Hz), 170.2; EIMS, *m/z* (relative intensity) 166 (M^+, 54), 121 (100); IR (KBr) 2980, 1686, 1630 cm^{-1}.

***trans-p*-Nitrocinnamic acid (3g).**[3]



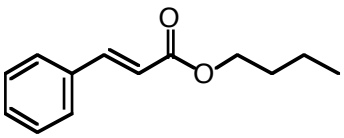
White solid, mp 286-287 °C (lit.[3] mp 286-287 °C); ^{1}H NMR (DMSO-d_6, 500 MHz) 6.75 (d, J = 16.0 Hz, 1H), 7.69 (d, J = 16.0 Hz, 1H), 7.95-8.01 (m, 2H), 8.22-8.26 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) 124.1, 124.4, 129.8, 141.3, 141.9, 148.5, 167.6; EIMS, *m/z* (relative intensity) 193 (M^+, 100), 176 (65); IR (KBr) 2976, 1681, 1631 cm^{-1}.

***trans*-1-Naphthylpropenoic acid (3h)**.[6]



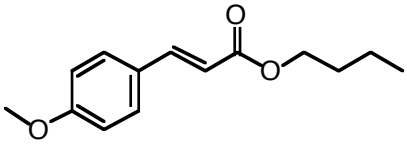
White solid, mp 213-214 °C (lit.[6] mp 213-215 °C); ^{1}H NMR (CD_3OD, 500 MHz) 6.54 (d, J = 16.0 Hz, 1H), 7.46-7.61 (m, 3H), 7.79-7.95 (m, 3H), 8.15-8.20 (m, 1H), 8.52 (d, J = 16.0 Hz, 1H); ^{13}C NMR (CD_3OD, 125 MHz) 122.0, 124.1, 126.1, 126.6, 127.4, 128.0, 129.8, 131.7, 132.7, 135.3, 143.1, 170.1; EIMS, *m/z* (relative intensity) 198 (M^+, 25), 153 (100); IR (KBr) 3049, 1680, 1616 cm^{-1}.

Butyl *trans*-cynnamate (3i).[7]



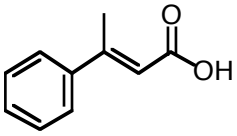
Colorless liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) 0.96 (t, *J* = 7.4 Hz, 3H), 1.43 (sext, *J* = 7.3 Hz, 2H), 1.69 (quint, *J* = 7.3 Hz, 2H), 4.20 (t, *J* = 6.7 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 7.25-7.38 (m, 3H), 7.51-7.53 (m, 2H), 7.67 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 13.3, 18.8, 30.4, 63.9, 117.9, 127.6, 128.5, 129.8, 134.0, 144.1, 166.6; EIMS, *m/z* (relative intensity) 204 (M^+, 32), 143 (100), 131 (42), 103 (37); IR (KBr) 2961, 1714, 1639 cm^{-1}.

Butyl *trans-p-Methoxycinnamate* (3j).[7]



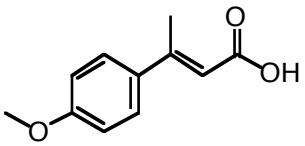
Colorless liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) 0.93 (t, *J* = 7.3 Hz, 3H), 1.40 (sext, *J* = 7.3 Hz, 2H), 1.65 (quint, *J* = 6.4 Hz, 2H), 4.16 (t, *J* = 6.4 Hz, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.84-6.86 (m, 3H), 7.42-7.44 (m, 2H), 7.60 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 13.8, 19.3, 30.9, 55.3, 64.3, 114.3, 115.8, 127.2, 129.7, 144.2, 161.4, 167.4; EIMS, *m/z* (relative intensity) 234 (M^+, 56), 178 (100), 161 (94), 133 (37); IR (KBr) 2961, 1711, 1635 cm^{-1}.

***(E)*-3-Methylcinnamic acid (3k).**[8]



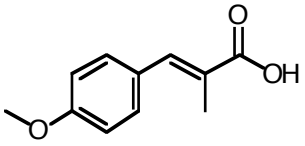
The *E*-configuration was determined by comparing with reported ^{1}H NMR spectrum (ref 8a). White solid, mp 97-99 °C (lit.[8b] mp 98-99 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) 2.62 (s, 3H), 6.20 (s, 1H), 7.35-7.44 (m, 3H), 7.45-7.56 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) 18.3, 116.5, 126.4, 128.5, 129.3, 141.9, 158.5, 172.6; EIMS, *m/z* (relative intensity) 162 (M^+, 72), 161 (82), 144 (50), 115 (78); IR (KBr) 3074, 1678, 1620 cm^{-1}.

***(E)*-3-Methyl-*p*-methoxycinnamic acid (3l).**[8]



The *E*-configuration was determined by comparing with reported ^{1}H NMR data (ref 8a). White solid, mp 155-157 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) 2.58 (s, 3H), 3.82 (s, 3H), 6.14 (s, 1H), 6.87-6.93 (m, 2H), 7.45-7.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) 17.9, 55.3, 113.9, 114.4, 127.8, 134.0, 157.9, 160.7, 172.3; EIMS, *m/z* (relative intensity) 192 (M^+, 100), 146 (33); IR (KBr) 2948, 1686, 1593 cm^{-1}.

***(E)*-2-Methyl-*p*-Methoxycinnamic acid (3m).**[9]



The *E*-configuration was determined by comparing with reported 1H NMR data (ref 9a). White solid, mp 155-157 °C (lit.[9b] mp 157-157 °C); ^{1}H NMR ($CDCl_3$, 500 MHz) 2.15 (s, 3H), 3.84 (s, 3H), 6.92-6.96 (m, 2H), 7.41-7.46 (m, 2H), 7.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 13.7, 55.3, 113.9, 125.1, 128.2, 131.8, 140.8, 160.0, 174.5; EIMS, *m/z* (relative intensity) 192 (M^+, 100), 146 (39); IR (KBr) 2955, 1670, 1602 cm^{-1}.

References

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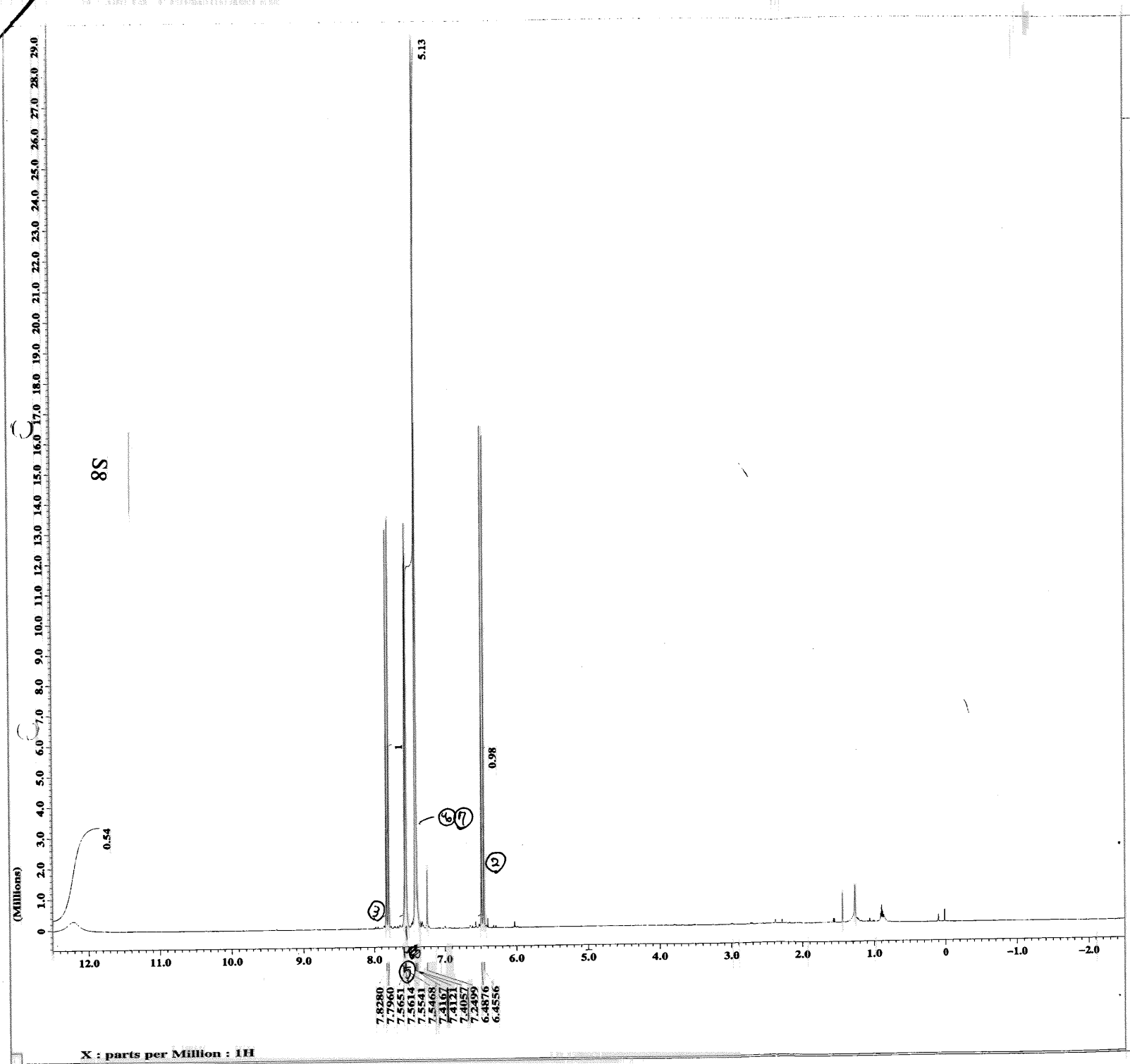

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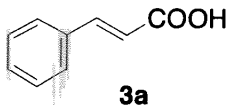

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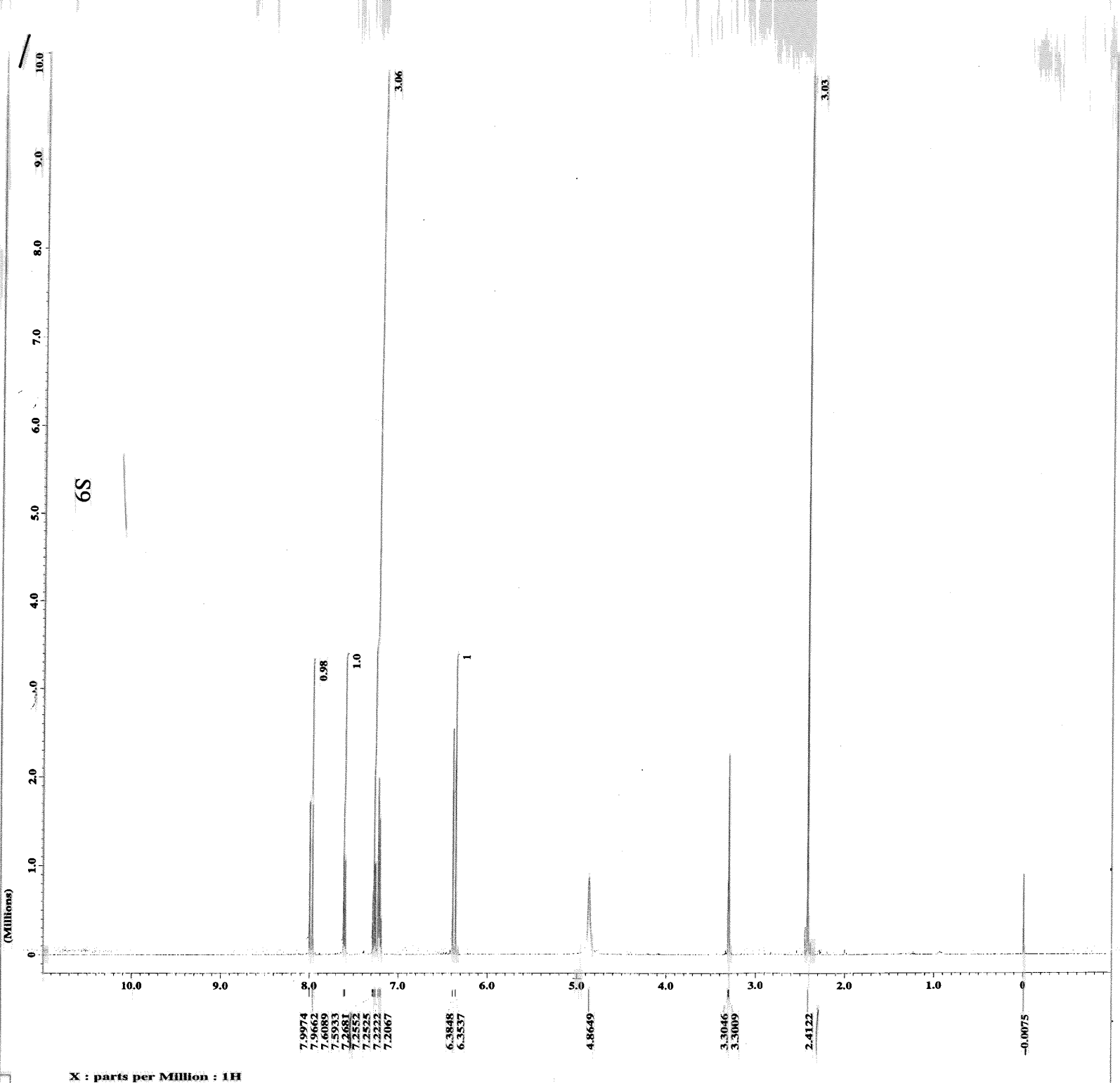

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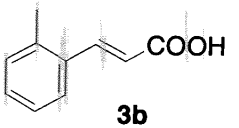
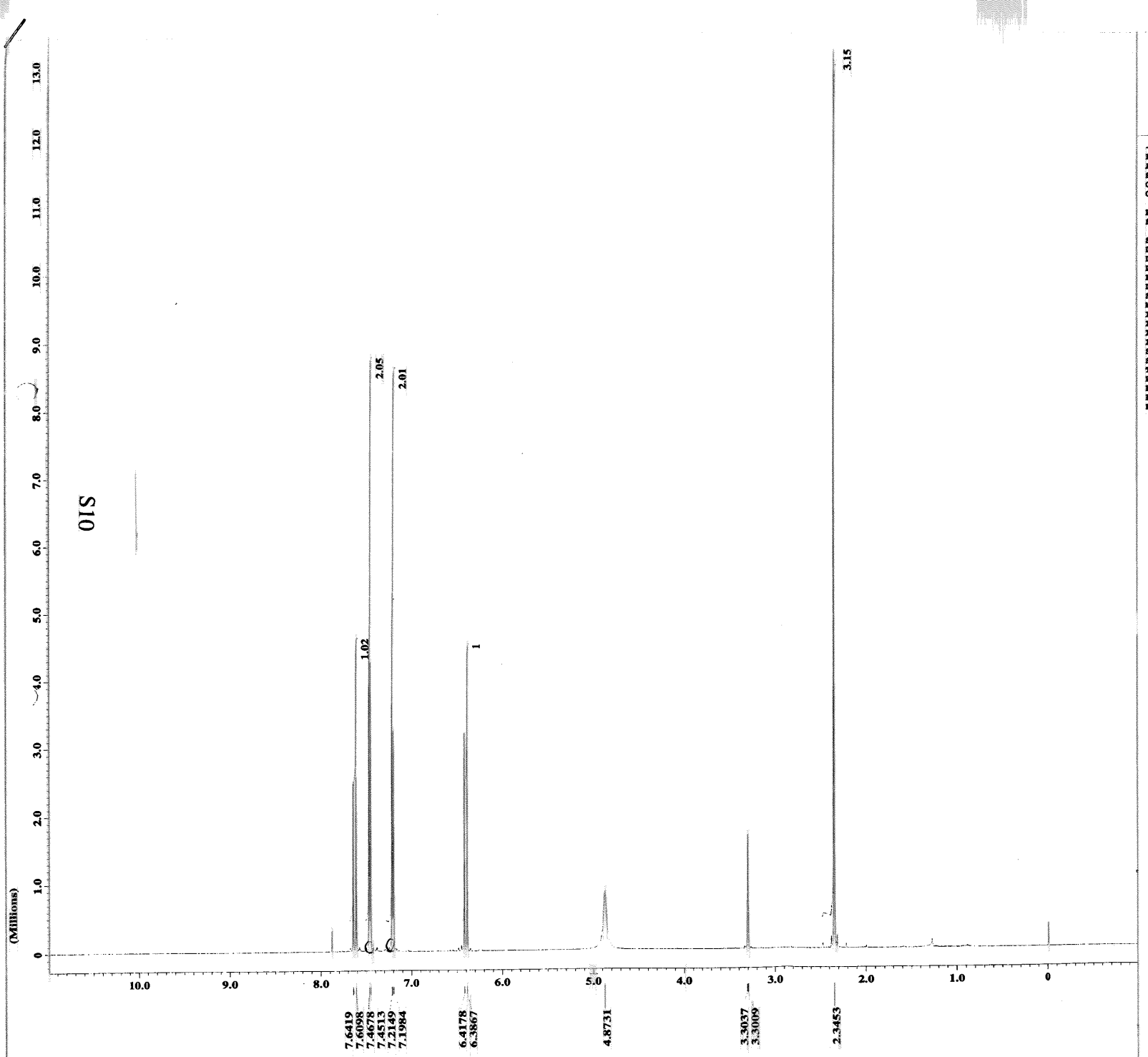


3b

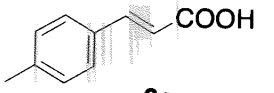


JEOL

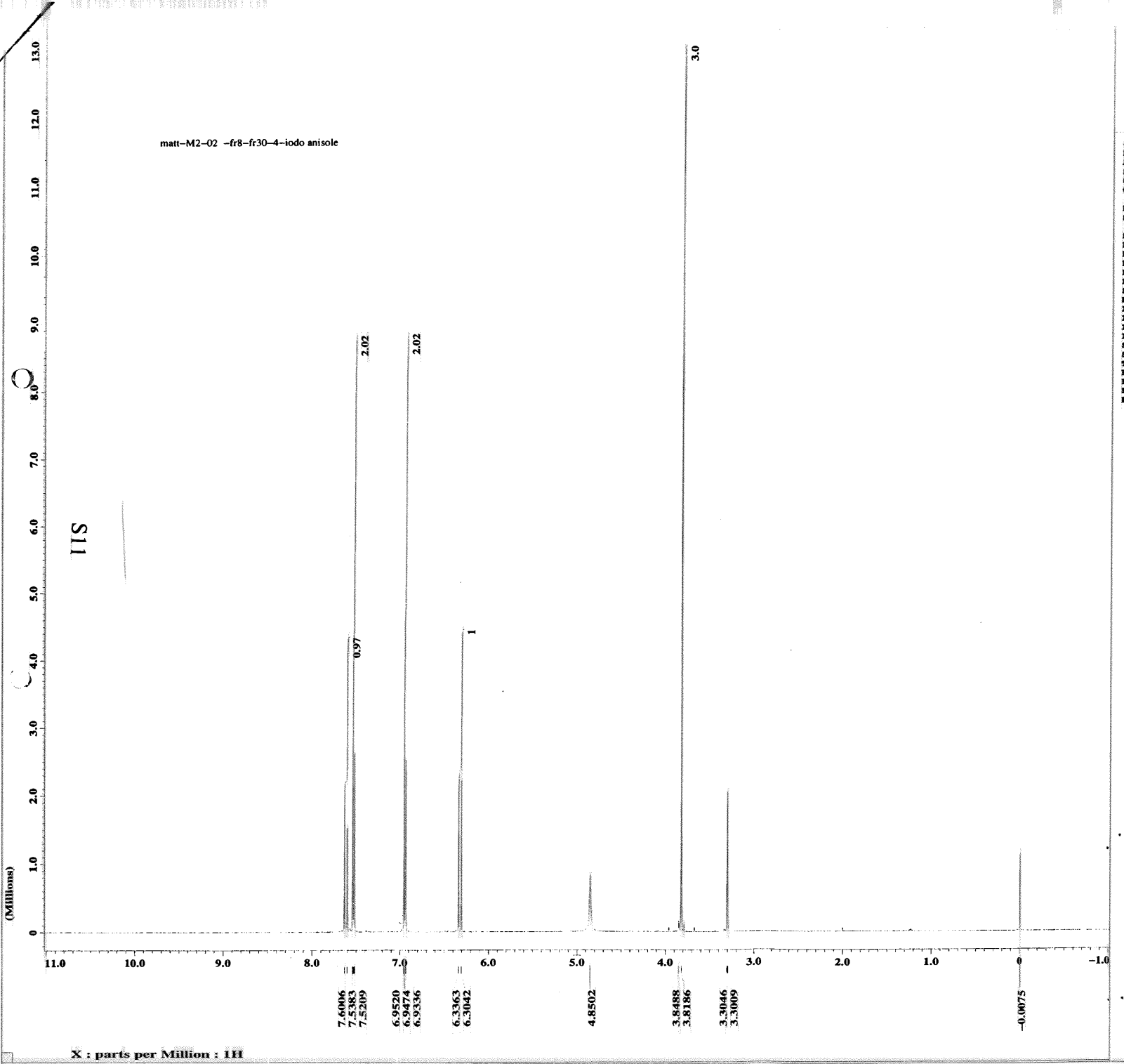
```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_spectrum.4969
Author          = JEOL LTD.
Sample ID       = matt-M2-024-fr6-fr16-4-
Content         = Single Pulse Experiment
Creation Date   = 15-MAY-2003 21:59:29

Revision Date   = 16-MAY-2003 11:04:15
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 8
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = METHANOL-D3
Spin_set        = 15[Hz]
Temp_set        = 24.7[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.7519936[kHz]
```



3c

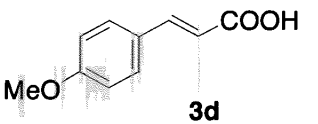


JEOL

```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_spectrum.5102
Author          = JEOL LTD.
Sample ID       = matt-M2-02    -fr8-fr30-
Content         = Single Pulse Experiment
Creation Date   = 21-MAY-2003 10:22:31

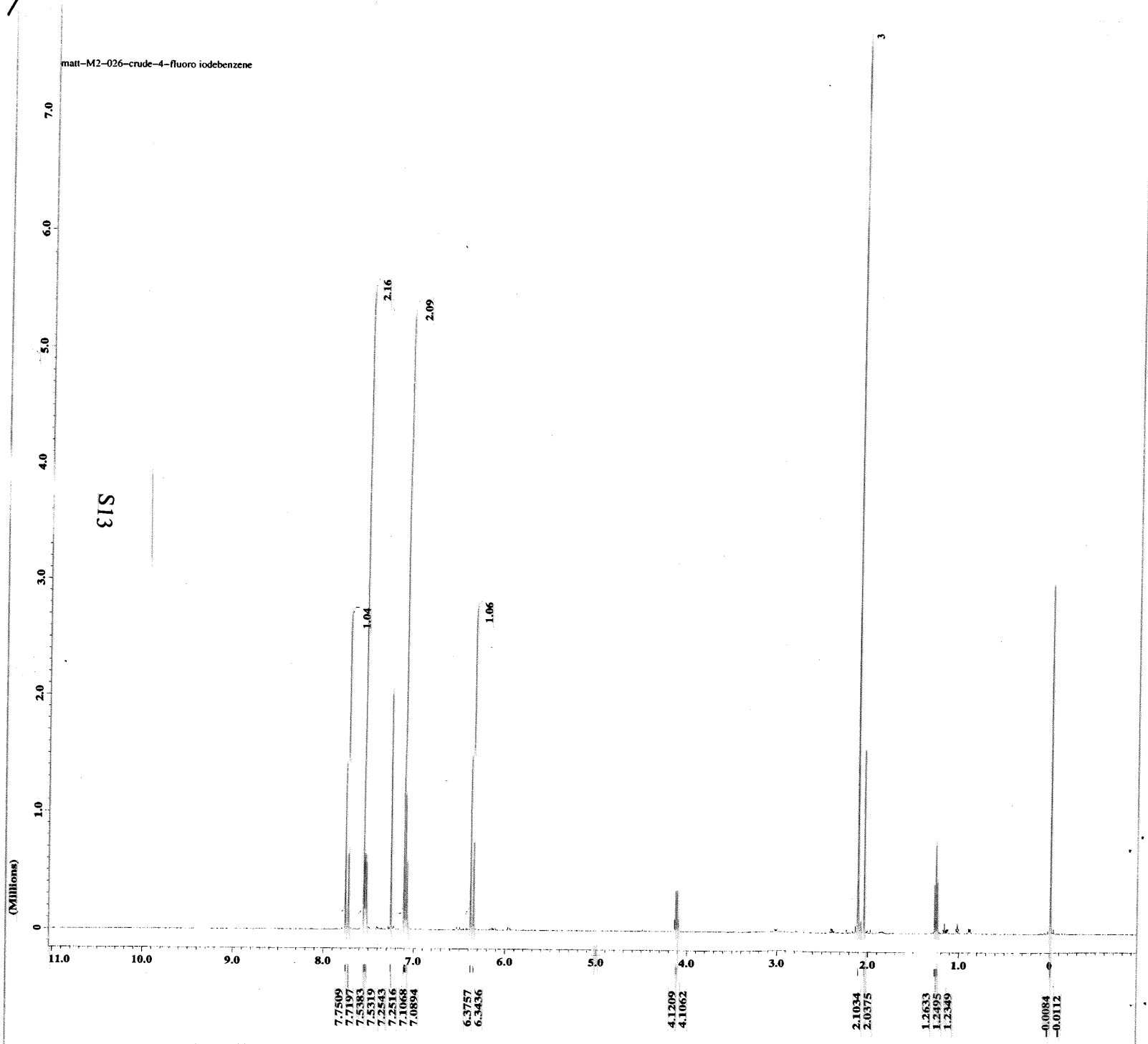
Revision Date   = 21-MAY-2003 23:32:48
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 8
Nod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = METHANOL-D3
Spin_set        = 14[Hz]
Temp_set        = 24.7[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
```



3d


JEOL
---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.5105
Author = JEOL LTD.
Sample ID = matt-M2- -fr21-fr5
Content = Single Pulse Experiment
Creation Date = 21-MAY-2003 10:44:40
Revision Date = 21-MAY-2003 23:54:09
Spec Site = ECP500
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Scans = 8
Mod_return = 1
X_domain = 1H
X_offset = 5[ppm]
X_freq = 500.16241602[MHz]
X_sweep = 7.50750751[kHz]
Solvent = METHANOL-D3
Spin_get = 15[Hz]
Temp_get = 25.2[dC]
Recvr_gain = 15
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 3.75119936[kHz]
COOH
O
3e
S12
(Millions)
3.19
2.95
2.0
1
8.0203
8.0038
7.7280
7.7152
7.7115
6.6130
6.5809
4.8429
3.3073
3.3037
3.3009
3.2972
3.2945
2.6367
2.6055
-0.0066
X : parts per Million : 1H

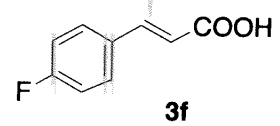


JEOL

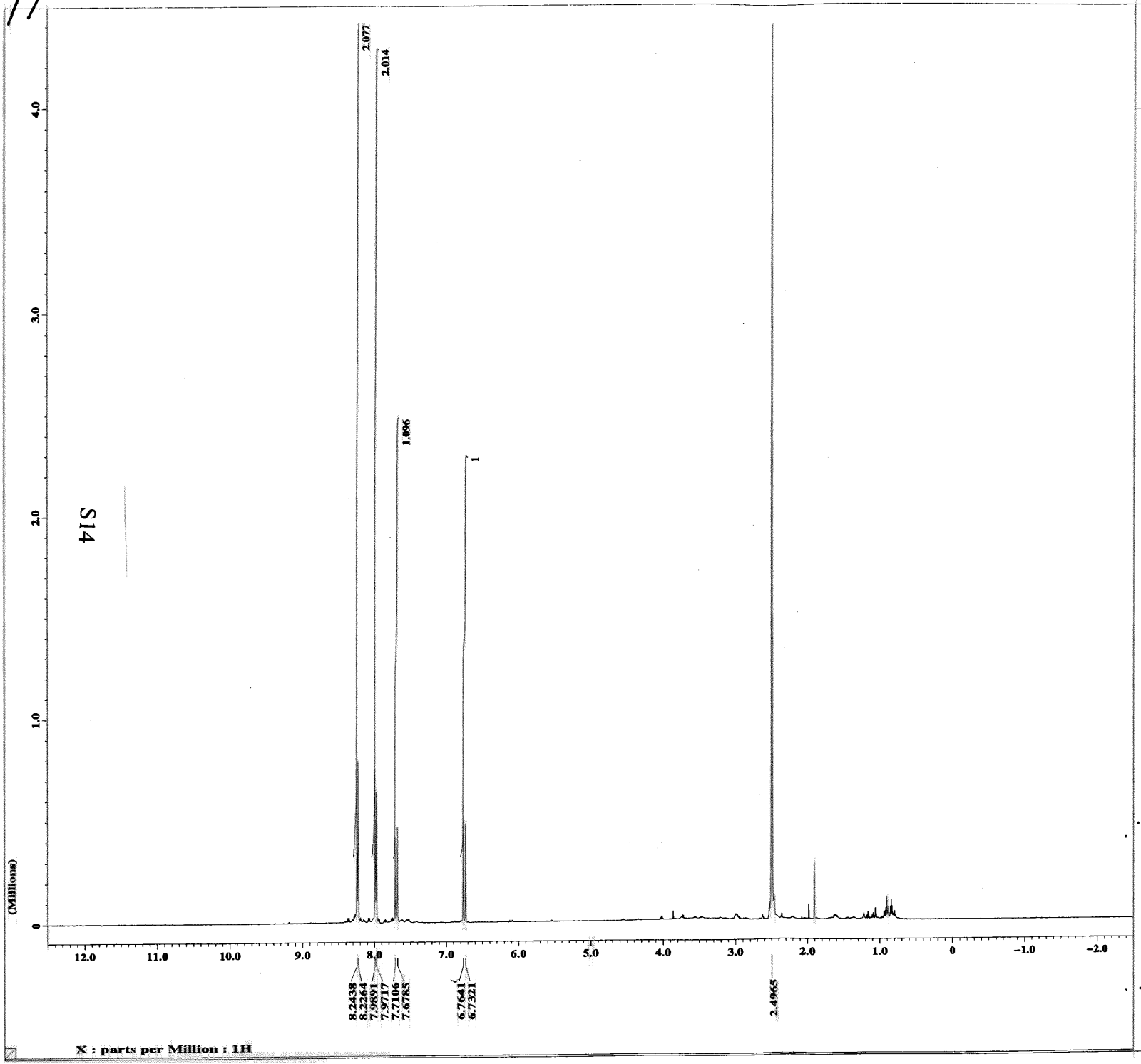
```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_spectrum.5034
Author          = JEOL LTD.
Sample ID       = matt-M2-026-crude-fluor
Content         = Single Pulse Experiment
Creation Date   = 19-MAY-2003 10:28:49

Revision Date   = 19-MAY-2003 23:37:11
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 8
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = CHLOROFORM-D
Spin_get        = 14[Hz]
Temp_get        = 24.5[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
```



3f

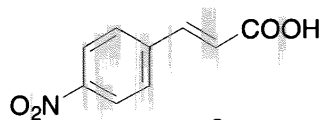


JEOL

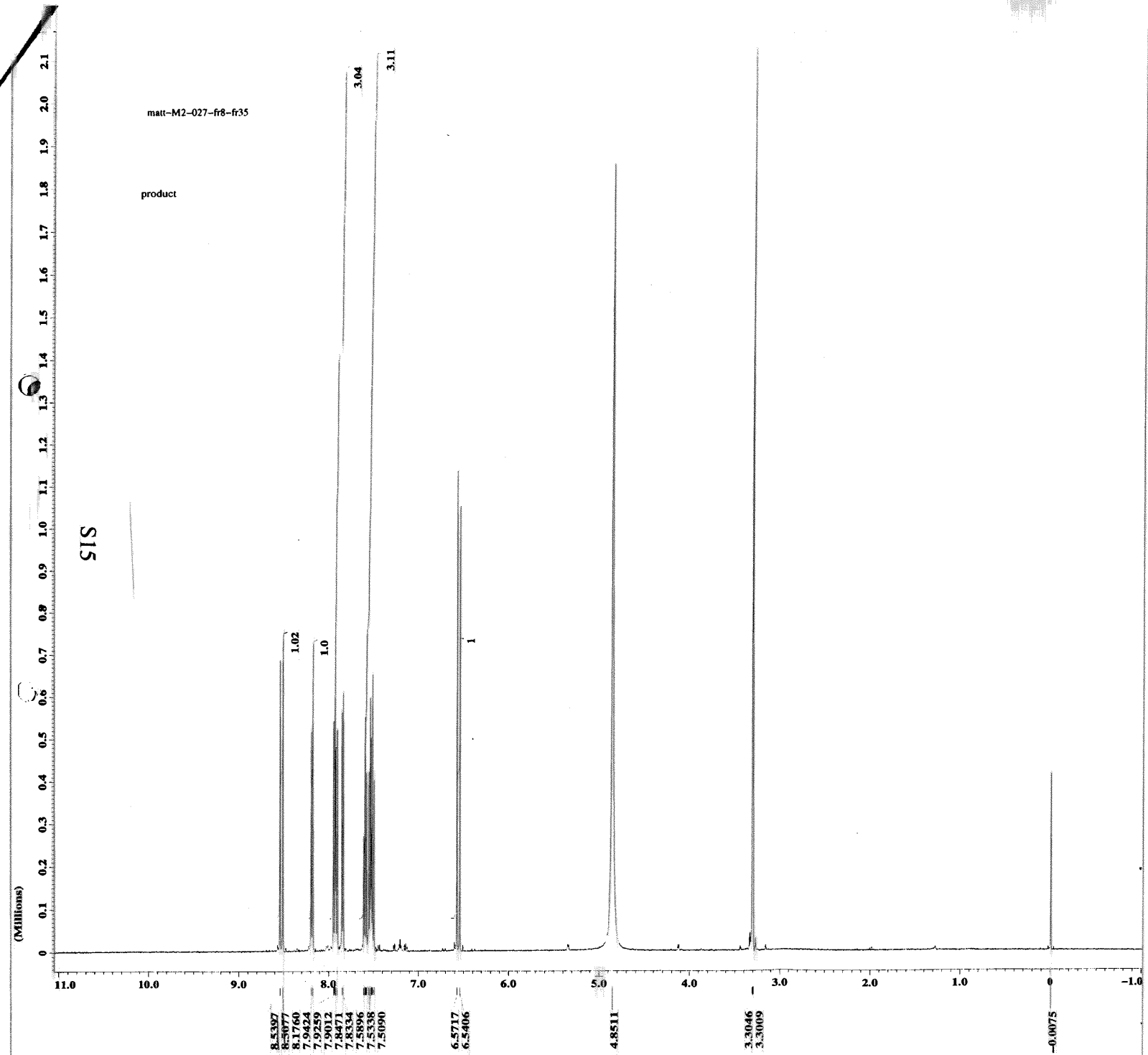
```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_spectrum.2706
Author          =
Sample ID       = S#446548
Content         = Single Pulse Experiment
Creation Date   = 16-JAN-2004 19:57:09

Revision Date   = 17-JAN-2004 12:27:31
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 8
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = DMSO-D6
Spin_get        = 17[Hz]
Temp_get        = 22.2[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
```



3g

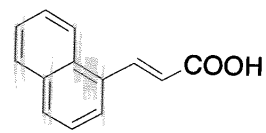


JEOL

```
---- ACQUISITION PARAMETERS ----
File Name          = 1d_spectrum.5043
Author             = JEOL LTD.
Sample ID          = matt-M2-027-fr8-fr35-na
Content            = Single Pulse Experiment
Creation Date      = 19-MAY-2003 11:08:44

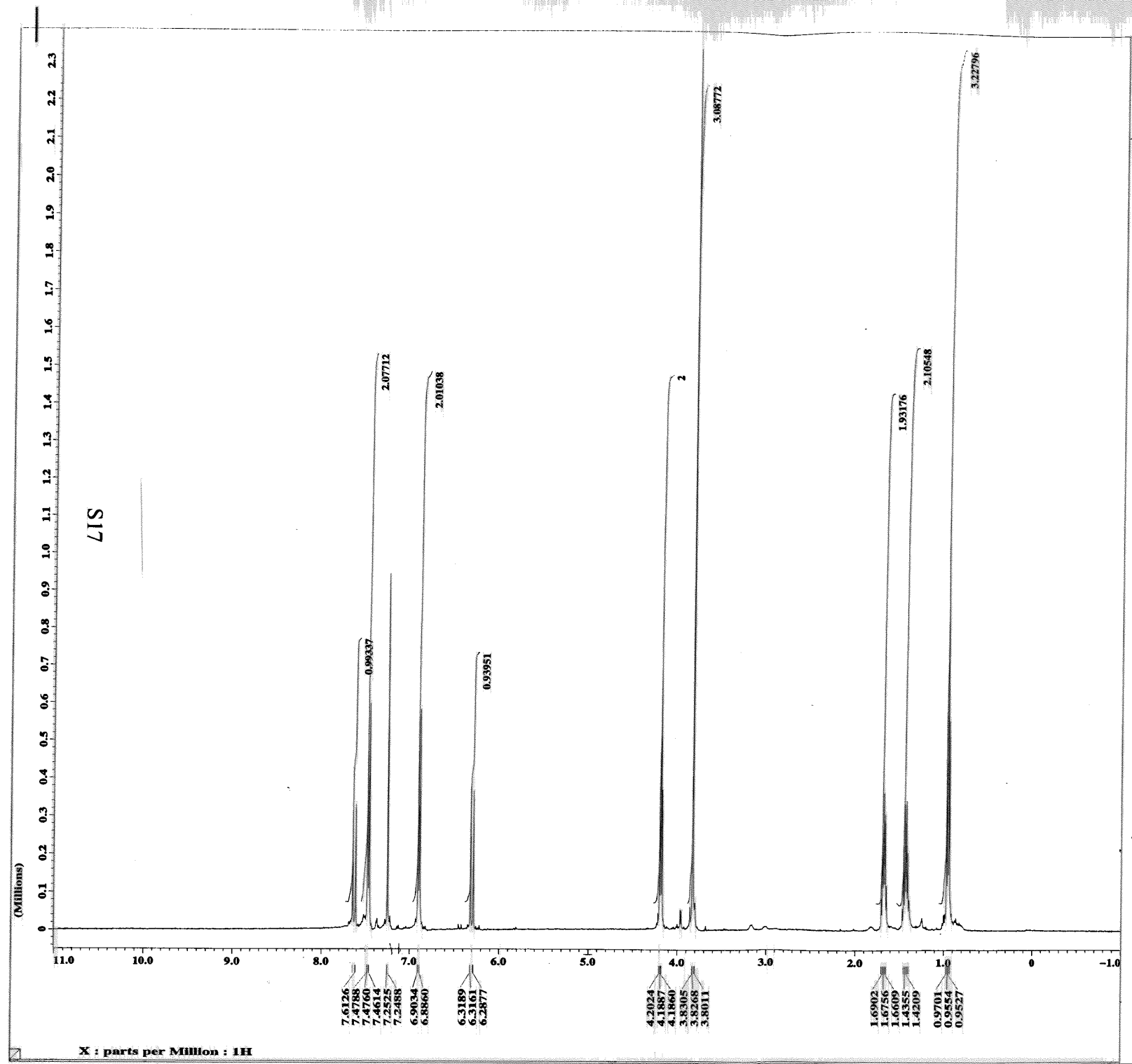
Revision Date      = 20-MAY-2003 00:17:15
Spec Site          = ECP500

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 1H
Dim Size           = 16384
Dim Units          = [ppm]
Scans              = 8
Mod_return         = 1
X_domain           = 1H
X_offset           = 5[ppm]
X_freq             = 500.16241602[MHz]
X_sweep            = 7.50750751[kHz]
Solvent            = METHANOL-D3
Spin_set           = 14[Hz]
Temp_set           = 25.1[dC]
Recvr_gain         = 15
Field_Strength     = 11.7473579[T]
Filter_Mode        = BUTTERWORTH
Filter_width       = 3.75119936[kHz]
```



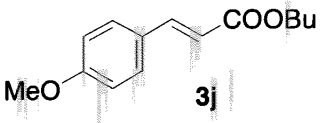
3h


S16
(Millions)
X : parts per Million : 1H
2.90658
2.99851
2.06517
2.01439
2.00691
2.0148
1.00368
1
7.5154
7.3817
7.3798
7.3734
7.3688
7.2516
6.4517
6.4197
4.2189
4.2061
4.1924
1.7012
1.6866
1.6710
1.4419
1.4273
0.9756
0.9609
0.9453
-0.0084
-0.0139
JEOL
---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.308
Author =
Sample ID = S#330352
Content = Single Pulse Experiment
Creation Date = 27-FEB-2004 15:59:49
Revision Date = 28-FEB-2004 09:13:14
Spec Site = ECP500
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Scans = 8
Mod_return = 1
X_domain = 1H
X_offset = 5[ppm]
X_freq = 500.16241602[MHz]
X_sweep = 7.50750751[kHz]
Solvent = CHLOROFORM-D
Spin_set = 14[Hz]
Temp_set = 25.2[dC]
Recvr_gain = 15
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 3.75119936[kHz]
COOBu
3i

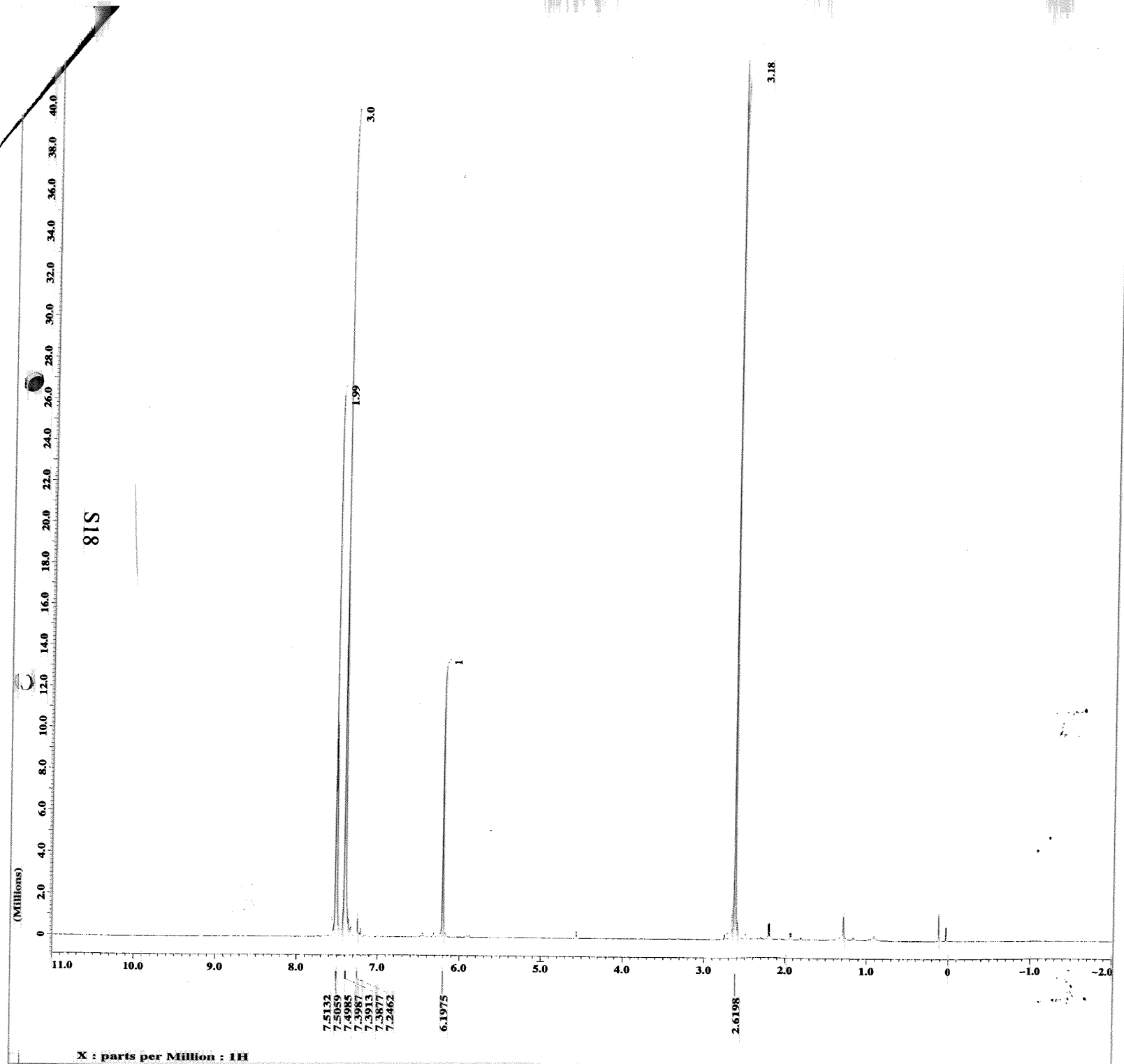


---- ACQUISITION PARAMETERS ----

File Name	= 1d_spectrum.432
Author	=
Sample ID	= methoxy crude
Content	= Single Pulse Experiment
Creation Date	= 6-MAR-2004 10:54:35
Revision Date	= 7-MAR-2004 04:16:31
Spec Site	= ECP500
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Scans	= 8
Mod_return	= 1
X_domain	= 1H
X_offset	= 5[ppm]
X_freq	= 500.16241602[MHz]
X_sweep	= 7.50750751[kHz]
Solvent	= CHLOROFORM-D
Spin_get	= 14[Hz]
Temp_get	= 23[dC]
Recvr_gain	= 15
Field_strength	= 11.7473579[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.75119936[kHz]



3j

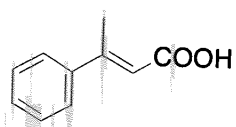


JEOL

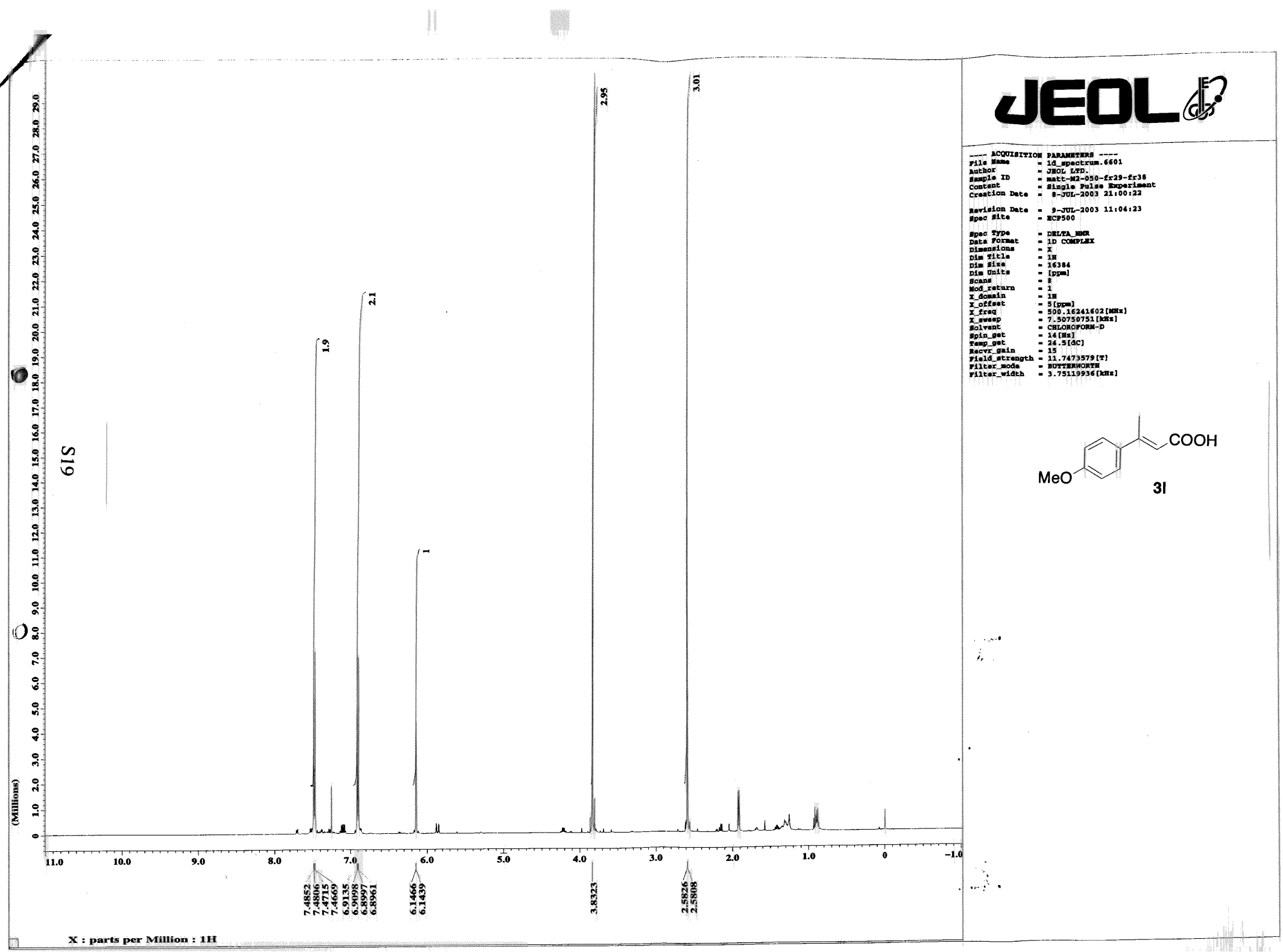
```
---- ACQUISITION PARAMETERS ----
File Name       = id_spectrum.5436
Author          = JEOL LTD.
Sample ID       = matt-M2-031-fr13-fr26
Content         = Single Pulse Experiment
Creation Date   = 29-MAY-2003 12:02:20

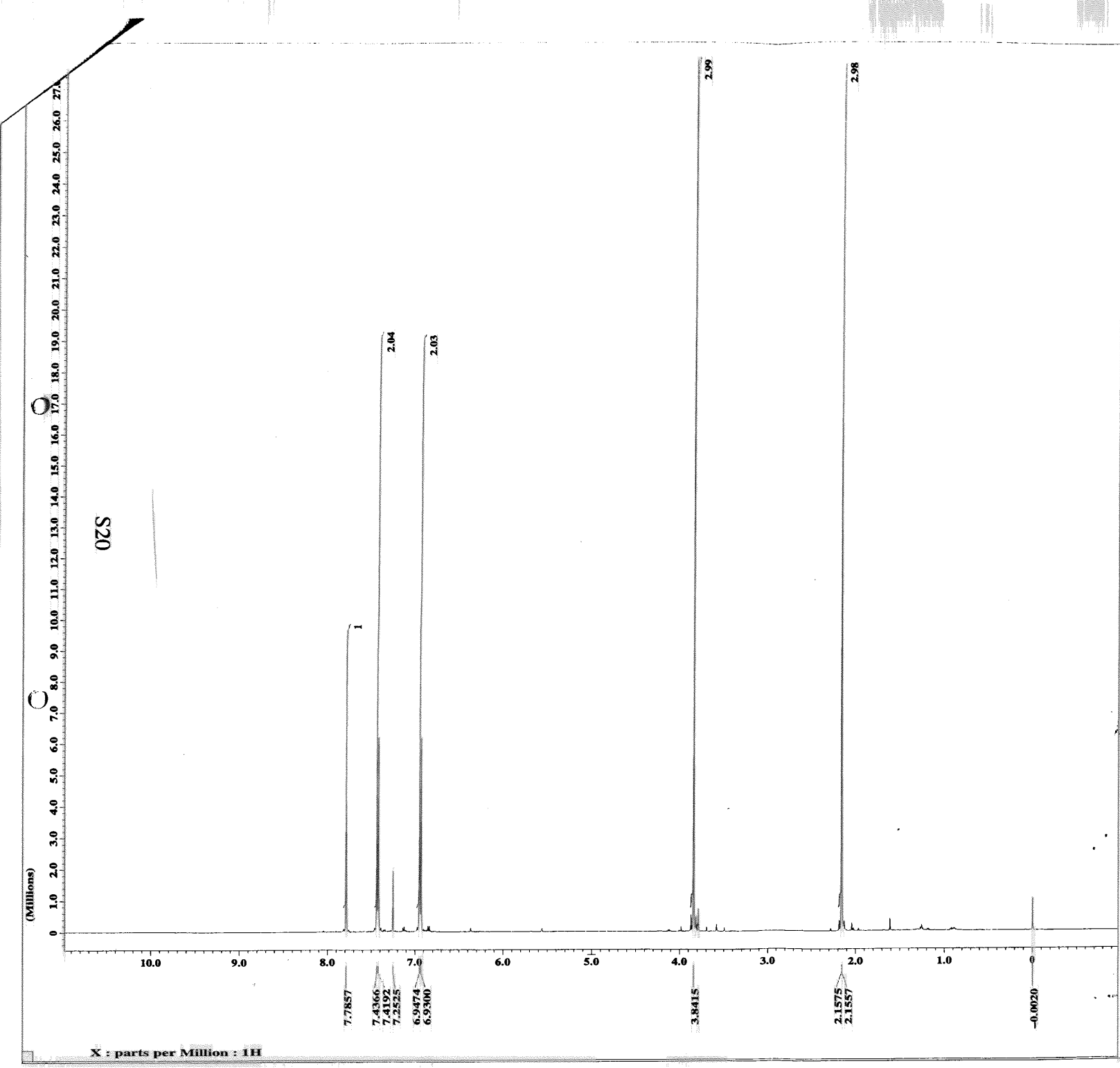
Revision Date   = 30-MAY-2003 01:22:58
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 8
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = CHLOROFORM-D
Spin_set        = 16[Hz]
Temp_set        = 24.4[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
```



3k


JEOL
---- ACQUISITION PARAMETERS ----
File Name = 1d_spectrum.6601
Author = JEOL LTD.
Sample ID = matt-M2-050-fr29-fr36
Content = Single Pulse Experiment
Creation Date = 8-JUL-2003 21:00:22
Revision Date = 9-JUL-2003 11:04:23
Spec Site = ECP500
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Scans = 8
Mod_return = 1
X_domain = 1H
X_offset = 5[ppm]
X_freq = 500.16241602[MHz]
X_sweep = 7.50750751[kHz]
Solvent = CHLOROFORM-D
Spin_get = 14[Hz]
Temp_get = 24.5[dC]
Recvr_gain = 15
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 3.75119936[kHz]
COOH
MeO
3l
S19
(Millions)
1.9
2.1
1
2.95
3.01
7.4852
7.4806
7.4715
7.4669
6.9135
6.9098
6.8997
6.8961
6.1466
6.1439
3.8323
2.5826
2.5808
X : parts per Million : 1H

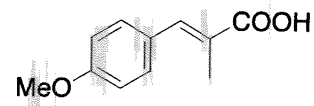


JEOL

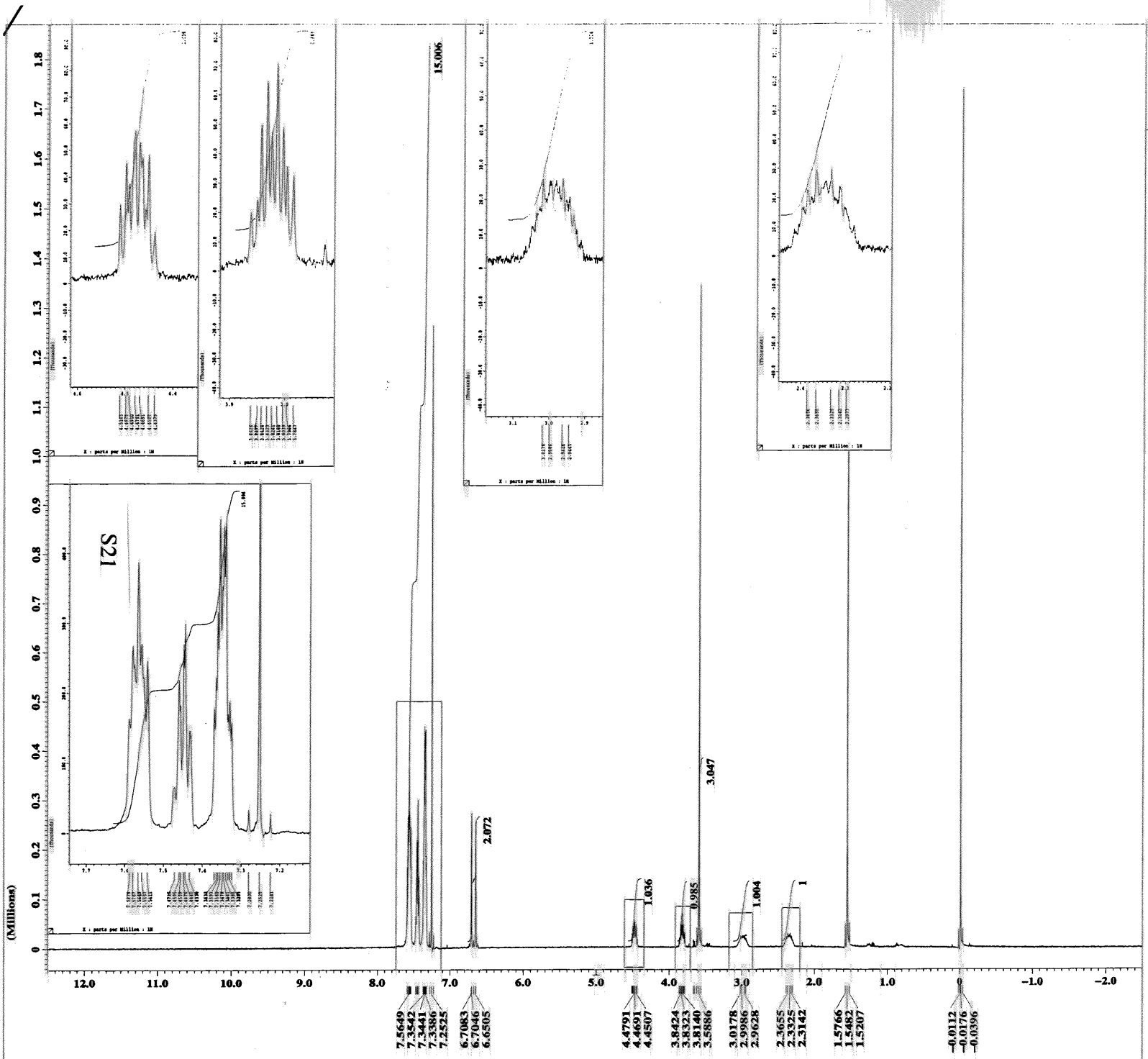
```
----- ACQUISITION PARAMETERS -----
File Name       = 1d_spectrum.6608
Author          = JEOL LTD.
Sample ID       = matt-M2-051-fr10-fr54
Content         = Single Pulse Experiment
Creation Date   =  8-JUL-2003 21:43:43

Revision Date   =  9-JUL-2003 11:51:40
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 8
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = CHLOROFORM-D
Spin_get        = 13[Hz]
Temp_get        = 24.7[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
```



3m



JEOL

```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_spectrum.2654
Author          =
Sample ID       = FLUOROUS CARBENE COMPLE
Content         = Single Pulse Experiment
Creation Date   = 16-JAN-2004 10:27:10

Revision Date   = 17-JAN-2004 02:58:32
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 8
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = CHLOROFORM-D
Spin_get        = 13[Hz]
Temp_get        = 22.3[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
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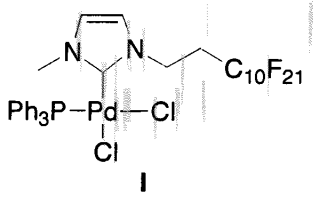
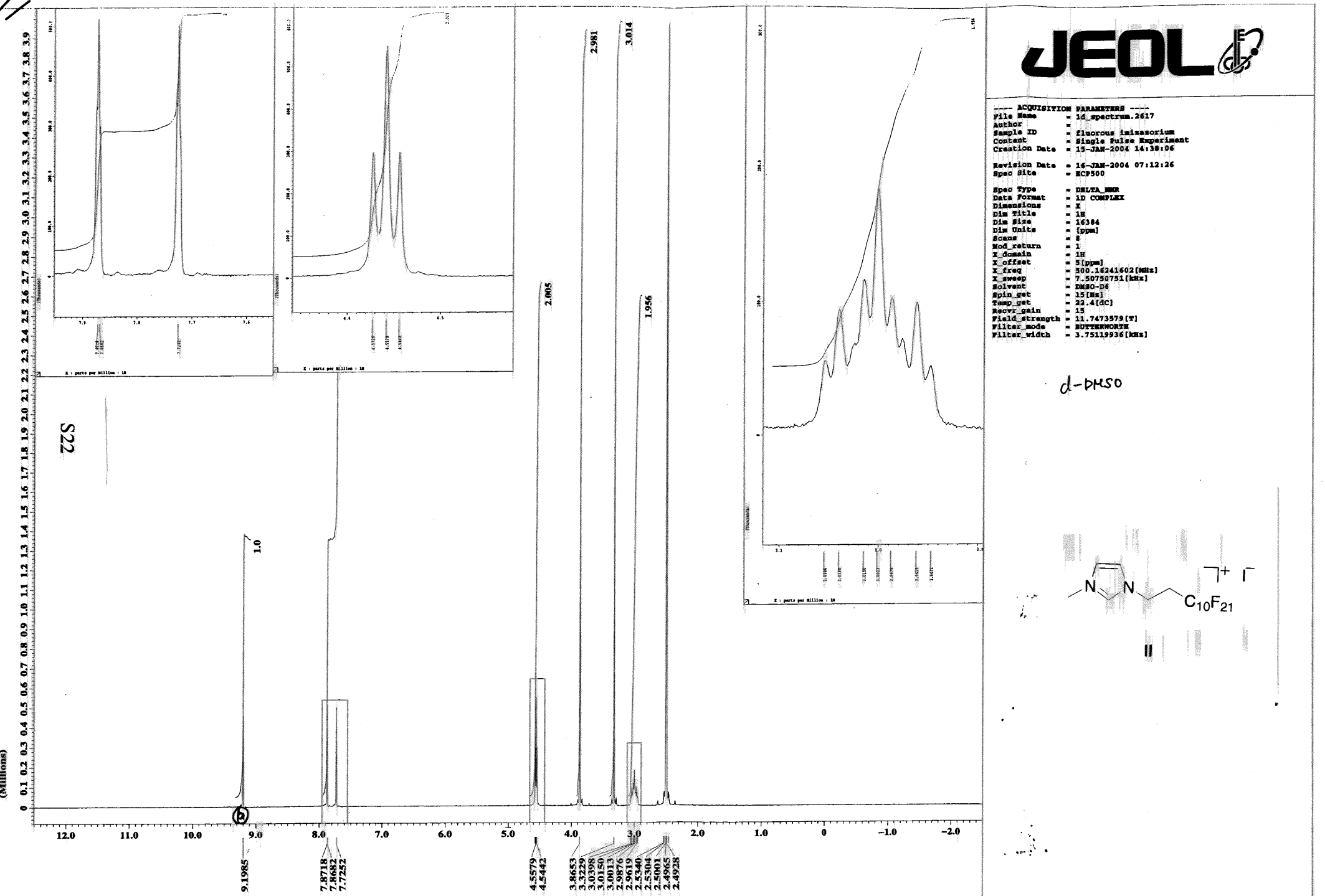


I



JEOL

```
---- ACQUISITION PARAMETERS ----
File Name       = 1d_spectrum.2617
Author          =
Sample ID       = fluorous imixazorium
Content         = Single Pulse Experiment
Creation Date   = 15-JAN-2004 14:38:06

Revision Date   = 16-JAN-2004 07:12:26
Spec Site       = ECP500

Spec Type       = DELTA_NMR
Data Format     = 1D COMPLEX
Dimensions      = X
Dim Title       = 1H
Dim Size        = 16384
Dim Units       = [ppm]
Scans           = 8
Mod_return      = 1
X_domain        = 1H
X_offset        = 5[ppm]
X_freq          = 500.16241602[MHz]
X_sweep         = 7.50750751[kHz]
Solvent         = DMSO-D6
Spin_set        = 15[Hz]
Temp_set        = 22.4[dC]
Recvr_gain      = 15
Field_strength  = 11.7473579[T]
Filter_mode     = BUTTERWORTH
Filter_width    = 3.75119936[kHz]
```

d-DMSO

II