

Electronic Supplementary Information

Ionic Liquids Are not Innocent in Pd Catalysis. C-H Arylation of Thiazolium and Imidazolium Ionic Liquids with Aryl Halides

Takahide Fukuyama,^{a*} Md. Taifur Rahman,^a Hiroshi Mashima,^a Hideo Takahashi^a and Ilhyong Ryu^{a,b*}

^aDepartment of Chemistry, Graduate School of Science, Osaka Prefecture University
Sakai, Osaka 599-8531, Japan

^bDepartment of Applied Chemistry, National Chiao Tung University
Hsinchu 30010 (Taiwan)

fukuyama@c.s.osakafu-u.ac.jp

Table of Contents.

General Information	S2
Synthesis of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (1a)	S2
Procedure for Pd-catalyzed C-H Arylation of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (1a)	S2
Typical Procedure for Pd-catalyzed C-H Arylation of Imidazolium based Ionic Liquids	S3
Typical Procedure for Isolation of Arylated Imidazolium based Ionic Liquids	S3
Competition Experiments	S4
Spectral data of 1a, 1b, and 5a-j.	S4
Copies of ¹H and ¹³C NMR Spectra	S8

General information.

^1H NMR spectra were recorded with a JEOL JMN ECP-500 (500 MHz) spectrometer in CDCl_3 or $\text{CD}_3\text{C}(\text{O})\text{CD}_3$ and are referenced at 0.0 ppm for TMS. ^{13}C NMR spectra were recorded with a JEOL JMN ECP-500 (125 MHz) spectrometer and are referenced at 77.0 ppm for CDCl_3 or at 28.8 ppm for $\text{CD}_3\text{C}(\text{O})\text{CD}_3$. ^{19}F NMR spectra were recorded with a JEOL JMN ECP-500 (470 MHz) spectrometer. ^{31}P NMR spectra were recorded with a JEOL JMN ECP-500 (202 MHz) spectrometer. Chemical shifts are reported in parts per million (δ). NMR yields were determined by using 1,1,2,2-tetrachloroethane as an internal standard. Infrared spectra were obtained on a Shimadzu FTIR 8400 spectrometer; absorptions are reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL MS700 spectrometer. The C-H arylated products **5a-5e** were separated from the corresponding iodine salts by flash chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40-50 μm), and further purified using preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) equipped with GPC columns (JAIGEL-1H + JAIGEL-2H columns) using CHCl_3 as eluent. Imiazolium-based ionic liquids **1c-1e** were prepared according to the reported procedures.¹

Synthesis of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (**1a**).

To a 100 mL round bottom flask were added 4-methyl-5-thiazoleethanol (14.3 g, 100 mmol), benzyl chloride (13.1 g, 103 mmol), acetonitrile, and the mixture was stirred at 90 °C for 24 h. The resultant solid was washed with hexane, toluene, and acetonitrile. Remaining solvents were removed at 90 °C under reduced pressure to give 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride as a white solid (22.7 g, 84.1 mmol, 84%, m.p. 141-142 °C). To a 100 mL round bottom flask were added the thiazolium chloride (14.5 g, 53.7 mmol), H_2O (45 mL), bis(trifluoromethane)sulfonimide lithium salt (15.4 g, 53.7 mmol), and the resulting mixture was stirred at 70 °C for 10 h. The ionic liquid layer was washed with H_2O (10 x 50 mL). Remaining H_2O was removed at 90 °C under reduced pressure for 10 h to give thiazolium ionic liquid **1a** as a yellow liquid (23.7 g, 46.1 mmol, 86%). Thiazolium ionic liquid (**1b**) was prepared with similar procedure.

Procedure for Pd-catalyzed C-H Arylation of 3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (**1a**).

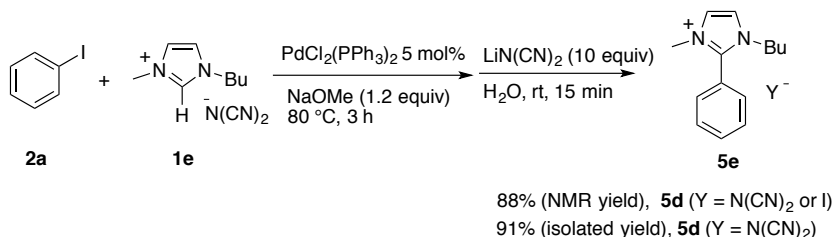
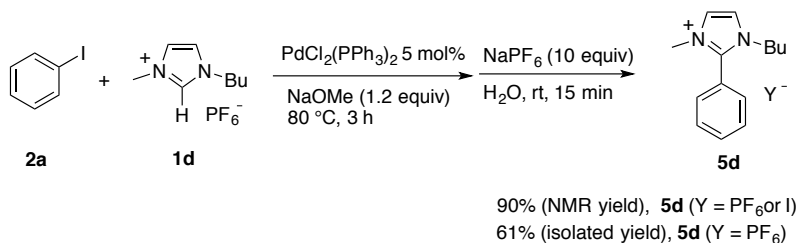
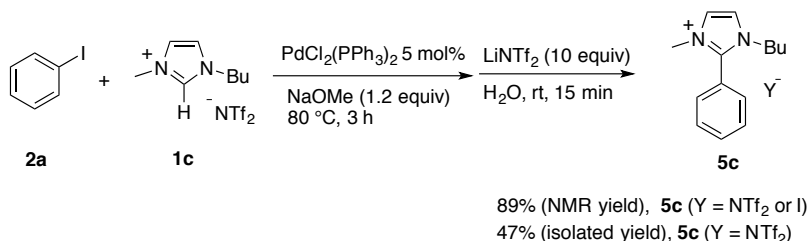
Thiazolium based ionic liquid **1a** (254.3 mg, 0.5 mmol), iodobenzene (**2a**, 121.0 mg, 0.6 mmol), *i*-Pr₂NH (200.5 mg, 1.8 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (18.0 mg, 0.025 mmol) were placed in a screw-capped test tube. The reaction mixture was stirred at 80 °C for 3 h. NMR yield was determined using 1,1,2,2-tetrachloroethane as an internal standard. The NTf_2 salt was separated from the corresponding iodine salt by flash chromatography on silica gel (gradient from hexane/EtOAc = 1/2 to EtOAc), which gave a mixture of NTf_2 salt **5a** and triphenylphosphine oxide. Further purification by preparative HPLC gave pure NTf_2 salt **5a** (117 mg 40%). The reaction of **1b** with **2a** was carried out in a similar manner.

Typical Procedure for Pd-catalyzed C-H Arylation of Imidazolium Ionic Liquids (Table 1, entry 6).

1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (**1c**, 223.3 mg, 0.5 mmol), iodobenzene (**2a**, 123.0 mg, 0.6 mmol), 28% NaOMe in MeOH (117.7 mg, NaOMe 0.6 mmol), PdCl₂(PPh₃)₂ (17.5 mg, 0.025 mmol) were placed in a screw-capped test tube. After removal of MeOH under reduced pressure, the reaction mixture was stirred at 80 °C for 3 h. NMR yield was determined by using 1,1,2,2-tetrachloroethane as an internal standard (89% yield).

Typical Procedure for Isolation of Arylated Imidazolium Ionic Liquids (Table 2, entry 1).

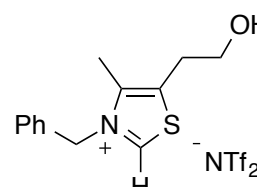
1-Butyl-3-methylimidazolium hexafluorophosphate (**1d**, 148.4 mg, 0.52 mmol), iodobenzene (**2a**, 127.1 mg, 0.62 mmol), 28% NaOMe in MeOH (116.2 mg, NaOMe 0.60 mmol), PdCl₂(PPh₃)₂ (18.6 mg, 0.026 mmol) were placed in a screw-capped test tube. After removal of MeOH under reduced pressure, the reaction mixture was stirred at 80 °C for 3 h. At this stage NMR yield was determined using 1,1,2,2-tetrachloroethane as an internal standard. The reaction mixture was poured into aqueous solution of NaPF₆ (840.1 mg 5.0 mmol) and stirred at room temperature for 15 min. The mixture was extracted with CHCl₃ (3 x 10 mL). The combined organic layers were concentrated in vacuo. The PF₆ salt was separated from the corresponding iodine salt by using flash chromatography on silica gel (gradient from hexane/EtOAc = 1/2 to EtOAc), which gave a mixture of PF₆ salt **5d** and triphenylphosphine oxide. The mixture was purified by preparative HPLC to give pure PF₆ salt **5d** (110.6 mg, 61%). **5c** and **5e** were obtained in 47% and 91% isolated yield respectively by using LiNTf₂ and LiN(CN)₂ in stead of NaPF₆.



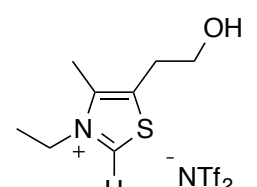
Competition Experiment: Sonogashira reaction vs. C-H Arylation.

1-Butyl-3-methylimidazolium hexafluorophosphate (**1d**, 142.2 mg, 0.5 mmol), iodobenzene (**2a**, 102.9 mg, 0.5 mmol), 1-octyne (55.2 mg, 0.5 mmol), piperidine (147.5 mg, 1.8 mmol), PdCl₂(PPh₃)₂ (17.6 mg, 0.025 mmol) were placed in a screw-capped test tube. After purge with Ar, the reaction mixture was stirred at 80 °C for 3 h. Yields were determined by NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard (**5d**: trace, **4b**: 97%). The reaction using NaOMe was conducted with same procedure (**5d**: 30%, **4b**: 50%).

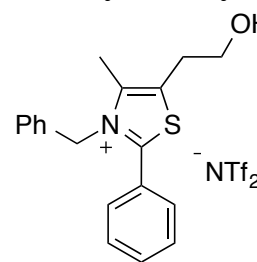
3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (**1a**)²

 ¹H NMR (500 MHz, CD₃COCD₃) δ 2.59 (s, 3H), 3.22 (t, 2H, *J* = 5.5 Hz), 3.90 (q, 1H, *J* = 5.3 Hz), 4.44 (t, 2H, *J* = 4.8 Hz), 5.92 (s, 2H), 7.53-7.46 (m, 5H), 9.97 (s, 1H); ¹³C NMR (125 MHz, CD₃COCD₃) δ 10.91, 56.43, 59.78, 119.69 (q, *J* = 321.2 Hz), 128.10, 155.39, 129.08, 131.89, 136.47, 142.03, 155.41; ¹⁹F NMR (CD₃COCD₃) δ -79.62; IR (neat) 3532, 3097, 2944, 2892, 1589, 1453, 1351, 1195, 1138, 1055 cm⁻¹; MS (FAB+) *m/z* (rel intensity), 234 ((M-NTf₂)⁺, 100), 91(33); MS (FAB-) *m/z* (rel intensity), 280 (NTf₂⁻, 100).

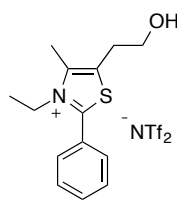
3-Ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (**1b**)²

 ¹H NMR (500 MHz, CD₃COCD₃) δ 1.65 (t, 3H, *J* = 7.3 Hz), 2.61 (s, 3H), 3.18 (t, 2H, *J* = 5.7 Hz), 3.88 (q, 2H, *J* = 5.5 Hz), 4.31 (t, 1H, *J* = 5.3 Hz), 4.61 (q, 2H, *J* = 7.2 Hz), 9.87 (s, 1H); ¹³C NMR (125 MHz, CD₃COCD₃) δ 10.93, 13.48, 49.08, 60.33, 120.08 (q, *J* = 321.5 Hz), 136.22, 142.23, 155.33; ¹⁹F NMR (CD₃COCD₃) δ -79.74; IR (neat) 3536, 1589, 1455, 1352, 1193, 1138 cm⁻¹; MS (FAB+) *m/z* (rel intensity), 172 ((M-NTf₂)⁺, 100); MS (FAB-) *m/z* (rel intensity), 280 (NTf₂⁻, 100).

3-Benzyl-5-(2-hydroxyethyl)-4-methyl-2-phenylthiazolium bis(trifluoromethanesulfonyl)amide (**5a**)

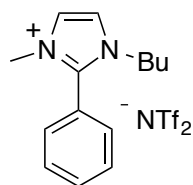
 Light yellow liquid, (R_f = 0.1, CHCl₃ : MeOH = 9 : 1). ¹H NMR (500 MHz, CDCl₃) δ 2.37 (s, 3H), 2.80 (br, 1H), 3.11 (t, 1H, *J* = 5.3 Hz), 3.93 (t, 2H, *J* = 5.3 Hz), 4.36 (q, 2H, *J* = 7.3 Hz), 6.94 (d, *J* = 6.9 Hz, 2H), 7.32-7.40 (m, 3H), 7.50-7.58 (m, 4H), 7.62-7.64 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 12.69, 29.85, 54.11, 60.33, 119.72 (q, *J* = 12.33, 14.69, 14.71, 29.75, 46.39, 60.30, 119.65 (q, *J* = 319.5 Hz), 125.07, 125.54, 125.60, 129.52, 129.72, 129.86, 132.44, 133.20, 135.00, 142.83, 169.40; ¹⁹F HMR(CDCl₃) δ -78.49; IR (neat) 3529, 1590, 1454, 1352, 1193, 1136, 1057 cm⁻¹; MS (FAB+) *m/z* (rel intensity), 310 ((M-NTf₂)⁺, 100); MS (FAB-) *m/z* (rel intensity) 280 (NTf₂⁻, 100); HRMS (FAB+) *m/z* calcd for C₁₉H₂₀N₁O₁S₁ ((M-NTf₂)⁺) 310.1260, found 310.1254; HRMS (FAB-) *m/z* calcd for C₂O₄NF₆S₂ (NTf₂⁻) 279.9173, found 279.9175.

3-Ethyl-5-(2-hydroxyethyl)-4-methyl-2-phenylthiazolium bis(trifluoromethanesulfonyl)amide (5b)



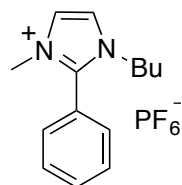
Light Yellow liquid, ($R_f = 0.09$, $\text{CHCl}_3 : \text{MeOH} = 9 : 1$). ^1H NMR (500 MHz, CDCl_3) δ 1.41 (t, $J = 7.3$ Hz), 2.61 (s, 3H), 3.06 (t, 1H, $J = 5.3$ Hz), 3.90 (t, 2H, $J = 5.3$ Hz), 4.36 (q, 2H, $J = 7.3$ Hz), 7.64-7.62 (m, 4H), 7.72-7.69 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 12.33, 14.69, 14.71, 29.75, 46.39, 60.30, 119.65 (q, $J = 318.8$ Hz), 125.10, 129.43, 129.74, 132.88, 134.87, 141.93, 167.86; ^{19}F HMR (CDCl_3) δ -78.66; IR (neat) 3533, 1589, 1448, 1352, 1193, 1136, 1055 cm^{-1} ; MS (FAB+) m/z (rel intensity), 248 ((M-NTf₂)⁺, 100), 172 (12); MS (FAB-) m/z (rel intensity), 280 (NTf₂⁻, 100); HRMS (FAB+) m/z calcd for $\text{C}_{14}\text{H}_{18}\text{N}_1\text{O}_1\text{S}_1$ ((M-NTf₂)⁺) 248.1104, found 248.1110; HRMS (FAB-) m/z calcd for $\text{C}_2\text{O}_4\text{NF}_6\text{S}_2$ (NTf₂⁻) 279.9173, found 279.9172.

1-Butyl-2-phenyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (5c)



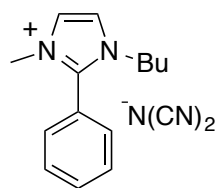
Yellow liquid, ($R_f = 0.38$, hexane : EtOAc = 1 : 3). ^1H NMR (500 MHz, CDCl_3) δ 0.83 (t, $J = 7.3$ Hz, 3H), 1.23 (sext, $J = 7.5$ Hz, 2H), 1.71 (quint, $J = 7.6$ Hz, 2H), 3.72 (s, 3H), 3.98 (t, $J = 7.3$ Hz, 2H), 7.45 (d, $J = 2.3$ Hz, 1H), 7.47 (d, $J = 2.3$ Hz, 1H), 7.54-7.56 (m, 2H), 7.66-7.69 (m, 2H), 7.71-7.75 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.08, 19.26, 31.74, 35.88, 35.91, 48.82, 118.53, 120.67, 121.09, 121.52, 121.60, 123.58, 123.65, 130.04, 132.95, 144.67; ^{19}F NMR (470 MHz, CDCl_3) δ -78.69; IR (neet) 3020, 2400, 1352, 1216, 1137, 1059, 756, 669 cm^{-1} ; MS (FAB+) m/z (rel intensity) 215 ((M-NTf₂)⁺, 100), 159 (12); MS (FAB-) m/z (rel intensity) 280 (NTf₂⁻, 100), 153 (34), 149 (34); HRMS (FAB+) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{N}_2$ ((M-NTf₂)⁺) 215.1548, found 215.1558; HRMS (FAB-) m/z calcd for $\text{C}_2\text{O}_4\text{NF}_6\text{S}_2$ (NTf₂⁻) 279.9173, found 279.9171.

1-Butyl-2-phenyl-3-methylimidazolium hexafluorophosphate (5d)



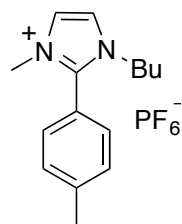
Light brown liquid, ($R_f = 0.38$, hexane : EtOAc = 1 : 4). ^1H NMR (500 MHz, CDCl_3) δ 0.82 (t, $J = 7.3$ Hz, 3H), 1.23 (sext, $J = 7.4$ Hz, 2H), 1.72 (quint, $J = 7.6$ Hz, 2H), 3.74 (s, 3H), 3.99 (t, $J = 7.3$ Hz, 2H), 7.53-7.59 (m, 4H), 7.66-7.73 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.18, 19.29, 31.83, 35.95, 48.78, 120.86, 121.67, 121.74, 123.82, 123.88, 130.01, 130.24, 132.81, 144.45; ^{19}F NMR (470 MHz, CDCl_3) δ -72.99 (d, $J = 714.0$ Hz); ^{31}P NMR (202 MHz, CDCl_3) δ -143.90 (sept; $J = 712.1$ Hz); IR (neet) 3019, 2400, 1215, 758, 669 cm^{-1} ; MS (FAB+) m/z (rel intensity) 215 ((M-PF₆)⁺, 100), 154 (65), 136 (52), 69 (39); MS (FAB-) m/z (rel intensity) 145 (PF₆⁻, 100), 127 (14); HRMS (FAB+) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{N}_2$ ((M-PF₆)⁺) 215.1548, found 215.1553; HRMS (FAB-) m/z calcd for PF_6 (PF₆⁻) 144.9642, found 144.9647.

1-Butyl-2-phenyl-3-methylimidazolium dicyanamide (5e)



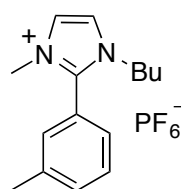
Yellow liquid, ($R_f = 0.35$, MeOH : EtOAc = 1 : 10). ^1H NMR (500 MHz, CDCl_3) δ 0.72 (t, $J = 7.3$ Hz, 3H), 1.51 (sext, $J = 7.4$ Hz, 2H), 1.65 (quint, $J = 7.6$ Hz, 2H), 3.70 (s, 3H), 3.95 (t, $J = 7.6$ Hz, 2H), 7.51-7.65 (m, 7H); ^{13}C NMR (125 MHz, CDCl_3) δ 12.91, 19.03, 31.53, 35.97, 36.00, 48.62, 120.31, 121.49, 121.55, 123.41, 123.47, 129.76, 129.95, 132.66, 144.37; IR (neet) 3020, 2400, 1216, 757, 669 cm^{-1} ; MS (FAB+) m/z (rel intensity) 215 ($(\text{M}-\text{N}(\text{CN})_2)^+$, 100), 154 (75), 136 (54), 107 (18), 78 (16); MS (FAB-) m/z (rel intensity) 66 ($\text{N}(\text{CN})_2^-$, 100); HRMS (FAB+) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{N}_2$ ($(\text{M}-\text{N}(\text{CN})_2)^+$) 215.1548, found 215.1547; HRMS (FAB-) m/z calcd for $\text{N}(\text{CN})_2$ ($\text{N}(\text{CN})_2^-$) 66.0092, found 66.0095.

1-Butyl-2-(p-methylphenyl)-3-methylimidazolium hexafluorophosphate (5f)



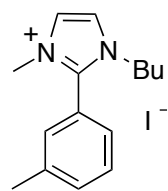
Light brown liquid, ($R_f = 0.25$, hexane : EtOAc = 1 : 2). ^1H NMR (500 MHz, CDCl_3) δ 0.82 (t, $J = 7.3$ Hz, 3H), 1.23 (sext, $J = 7.5$ Hz, 2H), 1.71 (quint, $J = 7.6$ Hz, 2H), 2.49 (s, 3H), 3.71 (s, 3H), 3.97 (t, $J = 7.6$ Hz, 2H), 7.41-7.42 (m, 2H), 7.45-7.51 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.19, 19.29, 21.60, 21.64, 31.84, 35.75, 35.78, 48.70, 117.74, 121.50, 121.58, 123.61, 123.69, 129.94, 129.98, 130.69, 143.60, 144.72; ^{19}F NMR (470 MHz, CDCl_3) δ -73.02 (d, $J = 702.5$ Hz); ^{31}P NMR (202 MHz, CDCl_3) δ -143.90 (sept; $J = 712.1$ Hz); IR (neet) 3019, 2400, 1639, 1216, 759, 669 cm^{-1} ; MS (FAB+) m/z (rel intensity) 229 ($(\text{M}-\text{PF}_6^-)^+$, 100), 154 (33), 136 (26), 69 (7); MS (FAB-) m/z (rel intensity) 145 (PF_6^- , 100); HRMS (FAB+) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{N}_2$ ($(\text{M}-\text{PF}_6^-)^+$) 229.1705, found 229.1698; HRMS (FAB-) m/z calcd for PF_6 (PF_6^-) 144.9642, found 144.9642.

1-Butyl-2-(m-methylphenyl)-3-methylimidazolium hexafluorophosphate (5g)



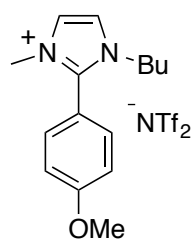
Light brown liquid, ($R_f = 0.25$, hexane : EtOAc = 1 : 2). ^1H NMR (500 MHz, CDCl_3) δ 0.82 (t, $J = 7.3$ Hz, 3H), 1.23 (sext, $J = 7.4$ Hz, 2H), 1.71 (quint, $J = 7.6$ Hz, 2H), 3.71 (s, 3H), 3.97 (t, $J = 7.6$ Hz, 2H), 7.30-7.35 (m, 2H), 7.46-7.47 (m, 1H), 7.50-7.56 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.20, 19.26, 21.25, 21.28, 31.80, 35.76, 35.78, 48.68, 120.75, 121.51, 121.58, 123.60, 123.67, 129.83, 129.85, 130.40, 130.46, 133.57, 140.35, 144.68; ^{19}F NMR (470 MHz, CDCl_3) δ -72.94 (d, $J = 714.0$ Hz); ^{31}P NMR (202 MHz, CDCl_3) δ -143.87 (sept; $J = 712.1$ Hz); IR (neet) 3019, 2400, 1215, 845, 668 cm^{-1} ; MS (FAB+) m/z (rel intensity) 229 ($(\text{M}-\text{PF}_6^-)^+$, 100), 174 (11); MS (FAB-) m/z (rel intensity) 145 (PF_6^- , 100), 121 (12); HRMS (FAB+) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{N}_2$ ($(\text{M}-\text{PF}_6^-)^+$) 229.1705, found 229.1705; HRMS (FAB-) m/z calcd for PF_6 (PF_6^-) 144.9642, found 144.9641.

1-Butyl-2-(m-methylphenyl)-3-methylimidazolium iodide (5g')



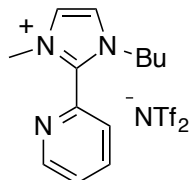
Yellow liquid, ($R_f = 0.30$, MeOH : EtOAc = 1 : 10). ^1H NMR (500 MHz, CDCl_3) δ 0.84 (t, $J = 7.3$ Hz, 3H), 1.28 (sext, $J = 7.5$ Hz, 2H), 1.78 (quint, $J = 7.4$ Hz, 2H), 2.49 (s, 3H), 3.88 (s, 3H), 4.10 (t, $J = 7.3$ Hz, 2H), 7.48-7.58 (m, 4H), 7.83 (d, $J = 2.3$ Hz, 1H), 7.99 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.18, 19.29, 21.27, 21.31, 31.92, 36.78, 48.86, 120.56, 121.86, 124.04, 129.78, 130.60, 130.66, 133.58, 140.17, 144.54; IR (neet) 3020, 2936, 2401, 1216, 757, 668 cm^{-1} ; MS (FAB+) m/z (rel intensity) 229 ((M-I) $^+$, 100), 174 (6); MS (FAB-) m/z (rel intensity) 126 (I $^-$, 100); HRMS (FAB+) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{N}_2$ ((M-I) $^+$) 229.1705 found 229.1707; HRMS (FAB-) m/z calcd for I (I $^-$) 126.9047, found 126.9045.

1-Butyl-2-(p-methoxyphenyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (5i)



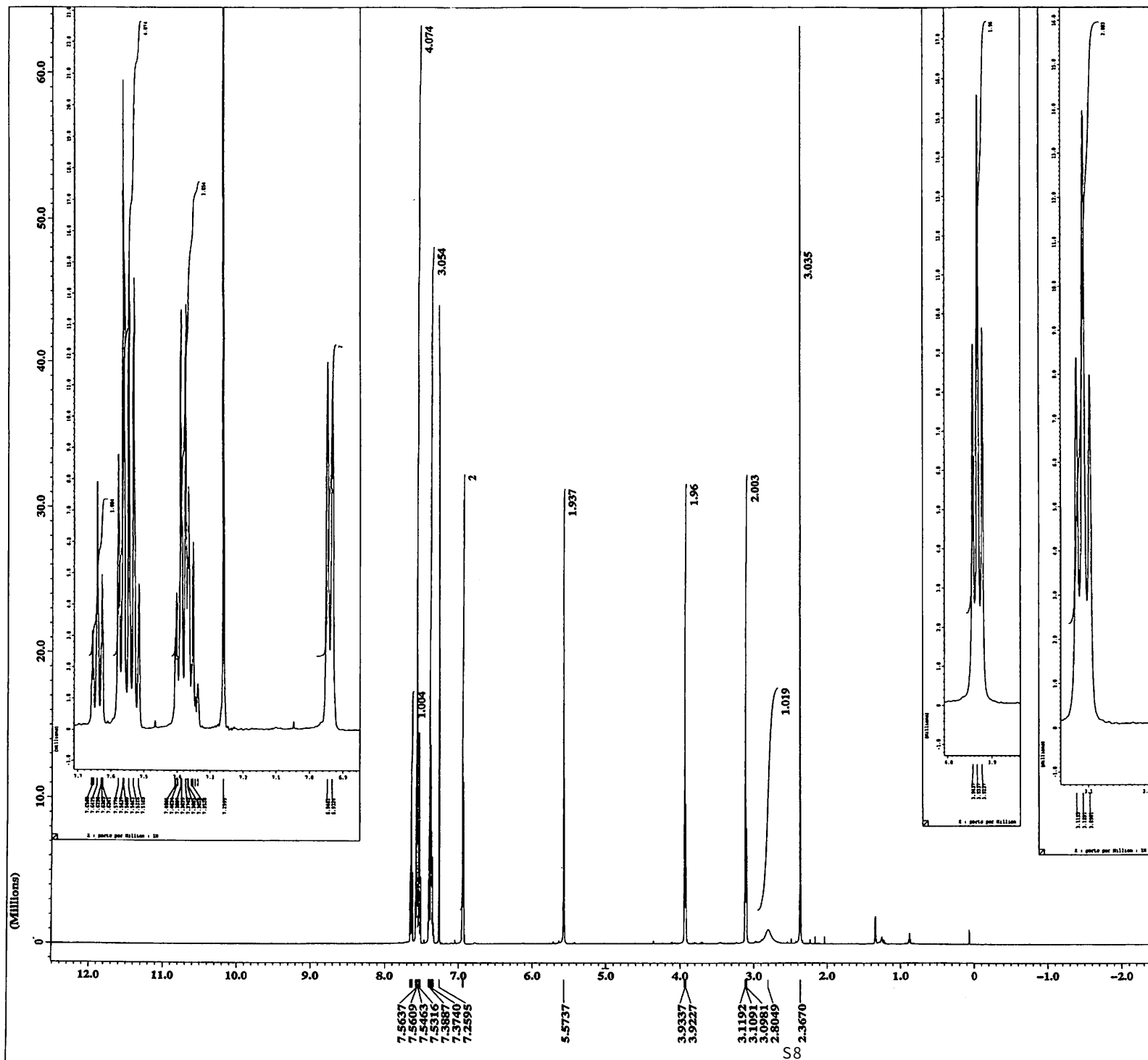
Light brown liquid, ($R_f = 0.40$, hexane : EtOAc = 1 : 2). ^1H NMR (500 MHz, CDCl_3) δ 0.84 (t, $J = 7.3$ Hz, 3H), 1.23 (sext, $J = 7.5$ Hz, 2H), 1.71 (quint, $J = 7.6$ Hz, 2H), 3.71 (s, 3H), 3.92 (s, 3H), 3.96 (t, $J = 7.6$ Hz, 2H), 7.14-7.47 (m, 2H), 7.41-7.47 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.14, 19.30, 31.76, 35.85, 48.75, 55.65, 111.97, 115.52, 115.58, 118.54, 121.09, 121.32, 121.39, 131.75, 131.79, 144.92, 162.90; ^{19}F NMR (470 MHz, CDCl_3) δ -78.69; IR (neet) 3021, 2400, 1613, 1352, 1216, 1137, 1059, 840, 758, 669 cm^{-1} ; MS (FAB+) m/z (rel intensity) 245 ((M-NTf $_2^-$) $^+$, 100), 244 (100), 215 (59), 188 (45), 135 (41), 74 (59); MS (FAB-) m/z (rel intensity) 280 (NTf $_2^-$, 100), 264 (18), 211 (18), 147 (60); HRMS (FAB+) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}$ ((M-NTf $_2^-$) $^+$) 245.1654, found 245.1655; HRMS (FAB-) m/z calcd for $\text{C}_2\text{O}_4\text{NF}_6\text{S}_2$ (NTf $_2^-$) 279.9173, found 279.9169.

1-Butyl-2-(2-pyridyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (5j)



Light brown liquid, ($R_f = 0.35$, hexane : EtOAc = 1 : 4). ^1H NMR (500 MHz, CDCl_3) δ 0.83 (t, $J = 7.3$ Hz, 3H), 1.25 (sext, $J = 7.5$ Hz, 2H), 1.71-1.77 (m, 2H), 3.85 (s, 3H), 4.14 (t, $J = 7.6$ Hz, 2H), 7.46 (d, $J = 1.8$ Hz, 1H), 7.50 (d, $J = 1.8$ Hz, 1H), 7.62-7.64 (m, 1H), 7.95 (d, $J = 7.8$ Hz, 1H), 8.06-8.09 (m, 1H), 8.84 (d, $J = 5.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.02, 13.09, 19.20, 31.72, 36.28, 36.31, 49.21, 118.48, 121.03, 122.02, 123.79, 123.90, 127.21, 138.27, 140.73, 142.38, 151.04, 151.14; ^{19}F NMR (470 MHz, CDCl_3) δ -78.76; IR (neet) 3020, 2400, 1352, 1216, 1137, 1059, 760, 669 cm^{-1} ; MS (FAB+) m/z (rel intensity) 216 ((M-NTf $_2^-$) $^+$, 100), 186 (89), 160 (100), 137 (31), 73 (54); MS (FAB-) m/z (rel intensity) 280 (NTf $_2^-$, 100), 211 (12), 143 (46); HRMS (FAB+) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{N}_3$ ((M-NTf $_2^-$) $^+$) 216.1501, found 216.1504; HRMS (FAB-) m/z calcd for $\text{C}_2\text{O}_4\text{NF}_6\text{S}_2$ (NTf $_2^-$) 279.9173, found 279.9172.

1. P. Bonhote, A. P. Dias, A. Papageorgion, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* **1996**, 35, 1168.
2. P. C. Hillesheim, S. M. Mahurin, P. F. Fulvio, J. S. Yeary, Y. Oyola, D. Jiang, S. Dai, *Ind. Eng. Chem. Res.* **2012**, 51, 11530.



X : parts per Million : 1H

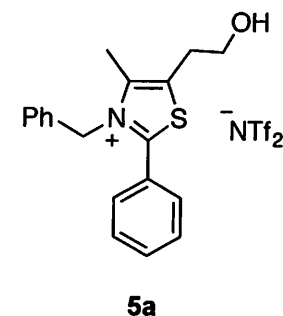
JEOL

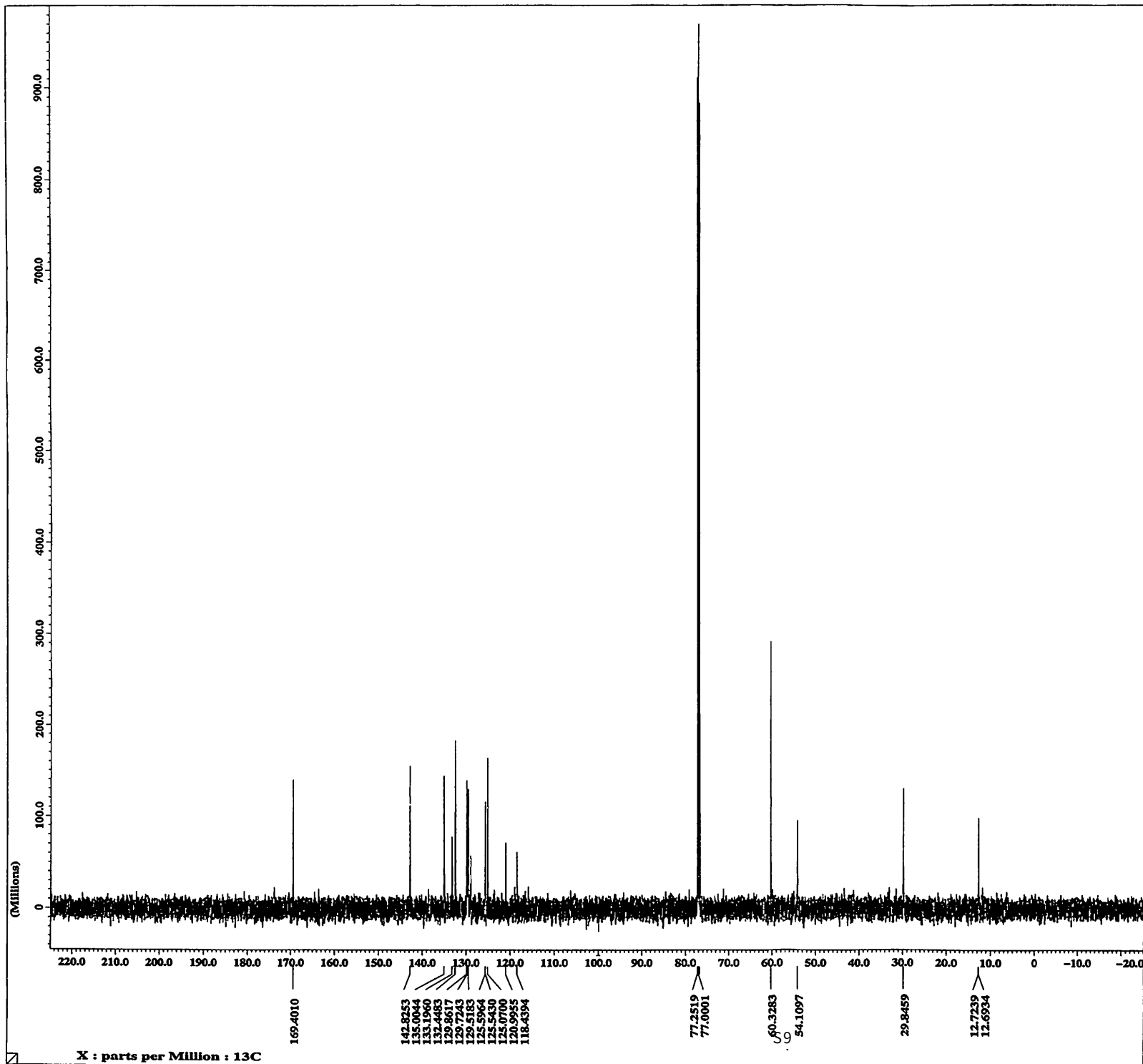
```

----- ACQUISITION PARAMETERS -----
File Name      = id_spectrum.3632
Author         =
Sample ID      = 1H
Content        = Single Pulse Experiment
Creation Date   = 5-NOV-2007 17:25:17

Revision Date   = 7-NOV-2007 12:24:12
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       = 15 [Hz]
Temp_get       = 24.9 [°C]
Recvr_gain     = 23
Field_strength = 11.7473579 [T]
Filter_mode    = BURRHOUGH
Filter_width   = 3.75119936 [kHz]
  
```



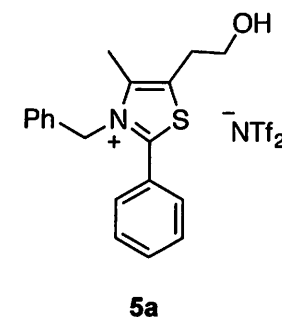


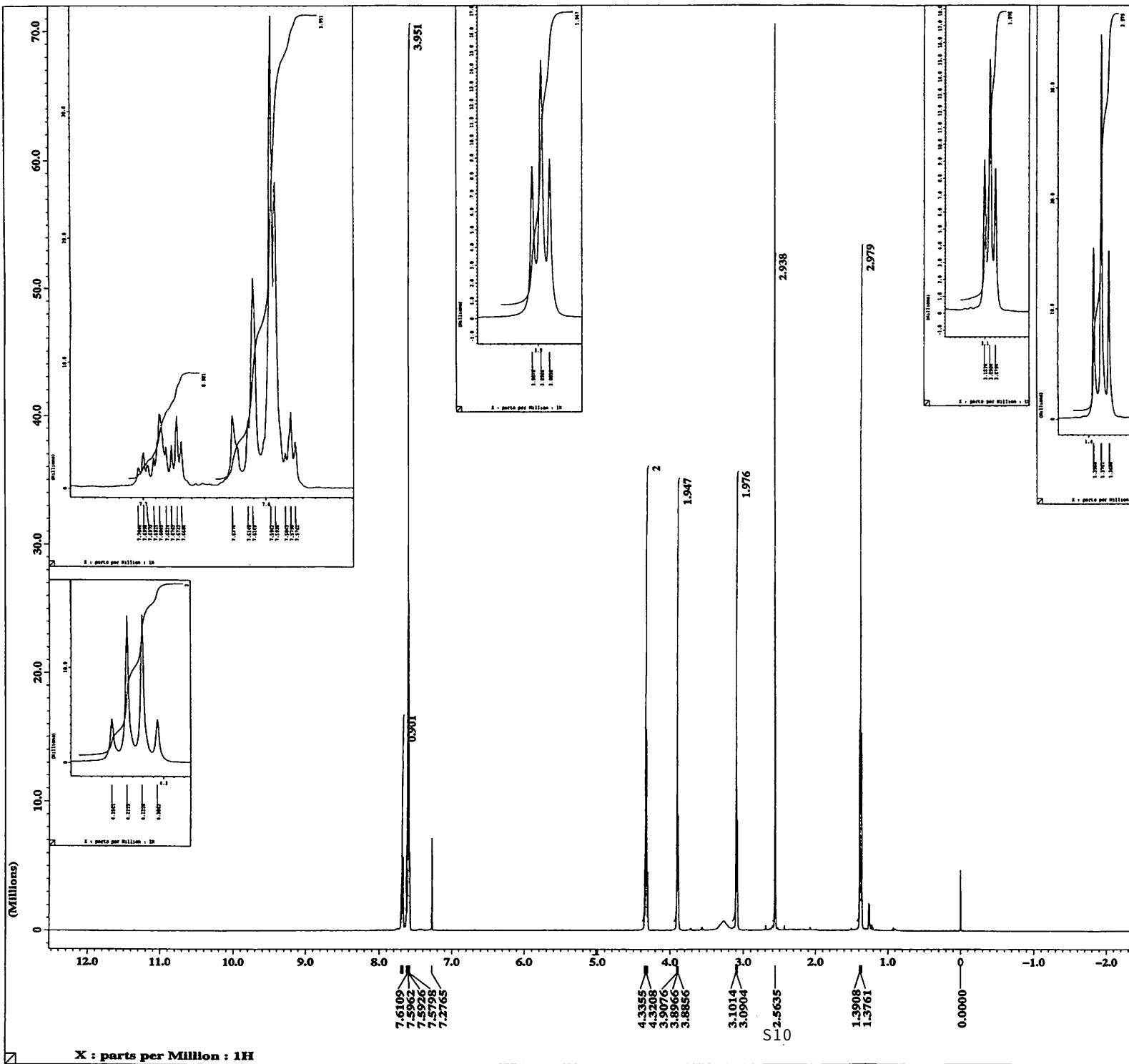
JEOL

----- ACQUISITION PARAMETERS -----
File Name = 1d_13c_spectrum.153
Author =
Sample ID = chia ph 13C
Content = Single Pulse with Broad
Creation Date = 5-NOV-2007 17:17:58

Revision Date = 7-NOV-2007 12:11:57
Spec Site = ECP500

Spec Type = DELTA HX
Data Format = 1D COMPLEX
Dimensions = 1
Dim Title = 13C
Dim Size = 32768
Dim Units = [ppm]
Scans = 400
Mod_return = 1
X_domain = 13C
X_offset = 100[ppm]
X_freq = 125.77787547[MHz]
X_sweep = 31.44654088[MHz]
Solvent = CHLOROFORM-D
Spin_get = 15[Hz]
Temp_get = 26.3[degC]
Recvr_gain = 30
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 15.72066221[kHz]





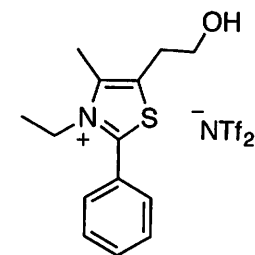
JEOL

```

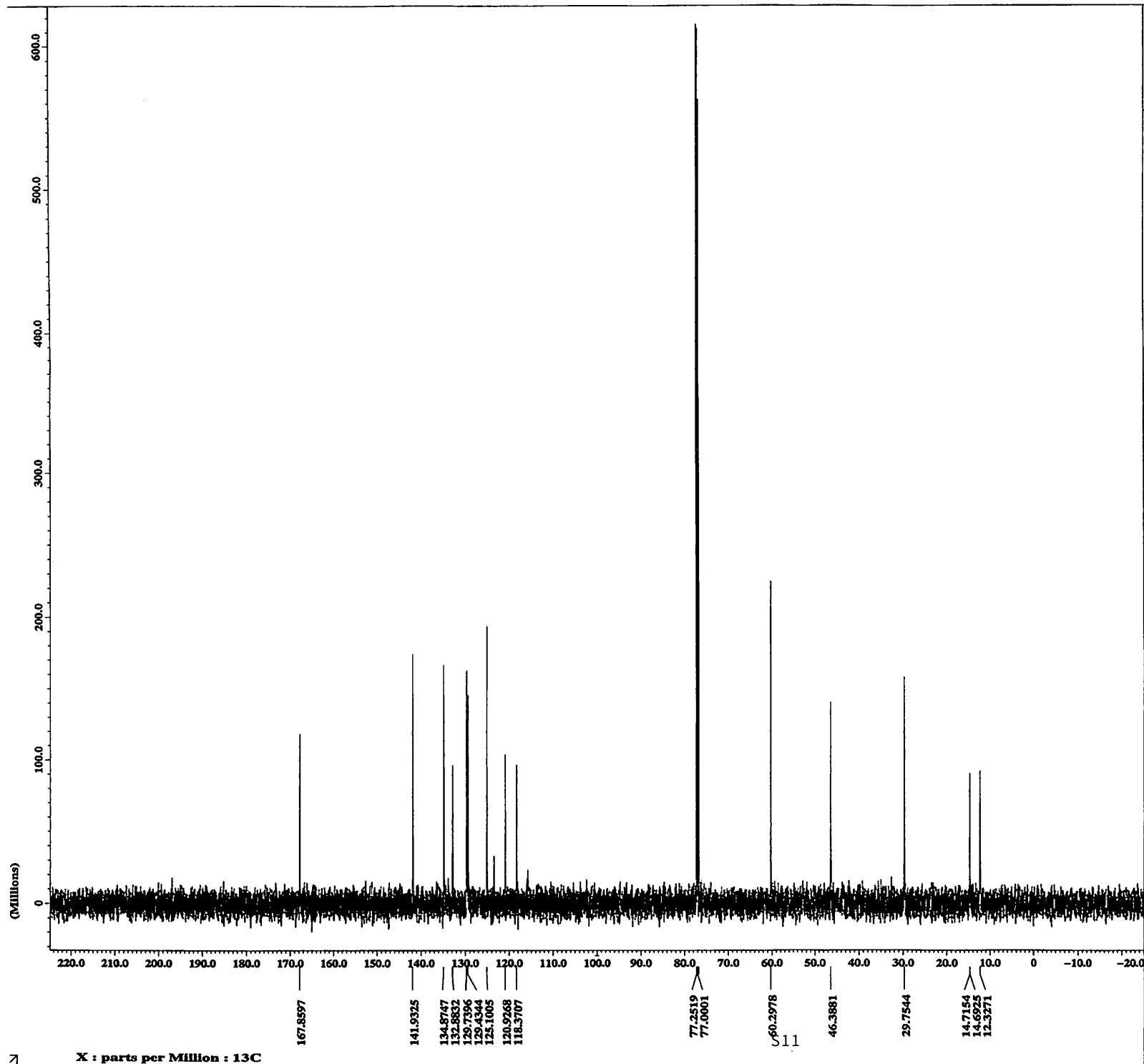
----- ACQUISITION PARAMETERS -----
File Name      = id_spectrum.448
Author         =
Sample ID      = hplc nahco3
Content        = Single Pulse Experiment
Creation Date   = 1-DEC-2007 10:24:22

Revision Date  = 3-DEC-2007 04:50:37
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[MHz]
Solvent        = CHLOROFORM-D
Spin_get       = 16[Hz]
Temp_get       = 23.6[degC]
Recvr_gain     = 21
Field_strength = 11.7473579[T]
Filter_mode    = BUTTERWORTH
Filter_width   = 3.75119936[kHz]
  
```

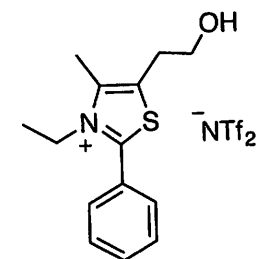


5b

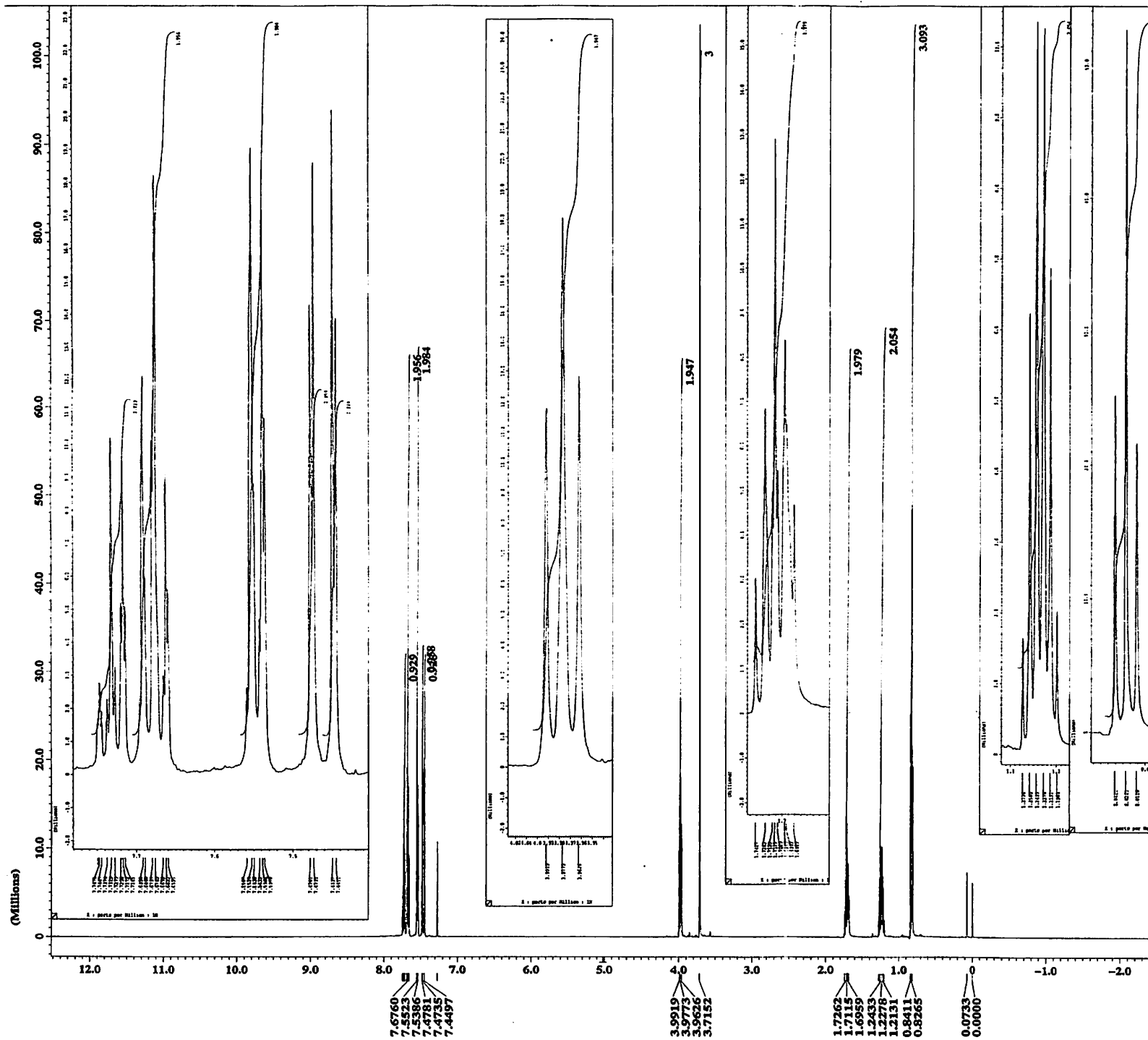


JEOL

----- ACQUISITION PARAMETERS -----
File Name = 1d_13c_spectrum.08
Author =
Sample ID = chia etyl 13c
Content = Single Pulse with Broad
Creation Date = 1-DEC-2007 10:35:33
Revision Date = 3-DEC-2007 04:56:50
Spec Site = ECP500
Spec Type = DELTA_MGR
Data Format = 1D COMPLEX
Dimensions = x
Dim Title = 13c
Dim Size = 32768
Dim Units = [ppm]
Scans = 244
Mod_return = 1
X_domain = 13c
X_offset = 100[ppm]
X_freq = 125.77787547[MHz]
X_sweep = 31.44654088[MHz]
Solvent = CHLOROFORM-D
Spin_get = 17[Hz]
Temp_get = 24[degC]
Recvr_gain = 30
Field_strength = 11.7473579[T]
Filter_mode = EXPERIMENT
Filter_width = 15.72066221[MHz]



5b

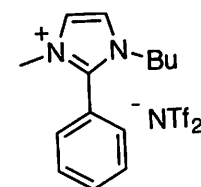


JEOL

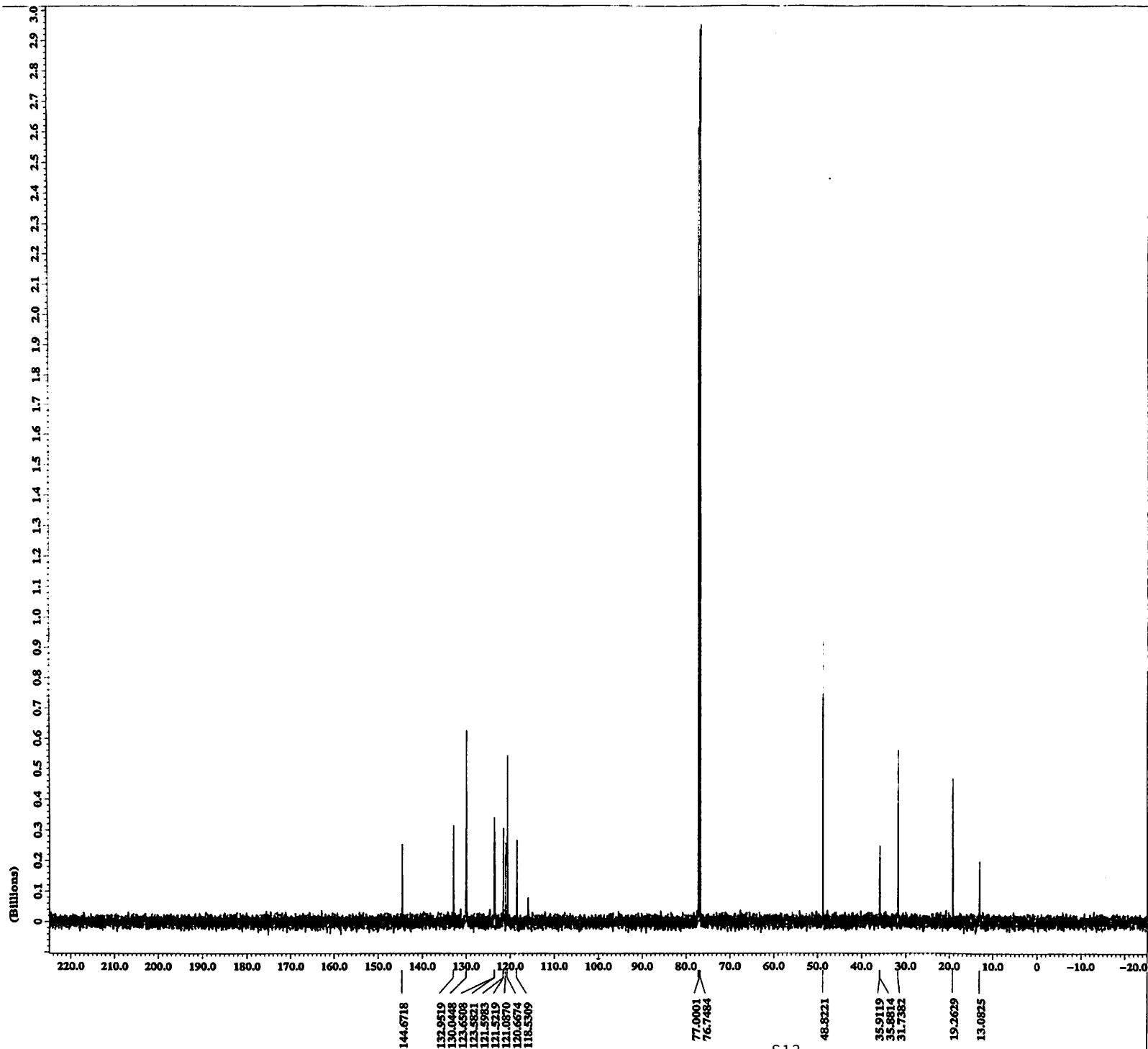
----- ACQUISITION PARAMETERS -----

File Name = id_spectrum.1692
 Author =
 Sample ID = bt-mi-029-6
 Content = Single Pulse Experiment
 Creation Date = 18-MAY-2007 20:09:26
 Revision Date = 20-MAY-2007 10:56:25
 Spec Site = MCP500

Spec Type = DELTA JNM
 Data Format = 1D COMPLEX
 Dimensions = X
 Dim Title = 1X
 Dim Size = 16384
 Dim Units = [ppm]
 Scans = 8
 Mod_return = 1
 X_domain = 1X
 X_offset = 5 [ppm]
 X_freq = 500.16241602 [MHz]
 X_sweep = 7.50750751 [kHz]
 Solvent = CHLOROFORM-D
 Spin_get = 17 [Hz]
 Temp_get = 24.6 [degC]
 Recv_gain = 23
 Field_strength = 11.7473579 [T]
 Filter_mode = BUTTERWORTH
 Filter_width = 3.75119936 [kHz]



5c



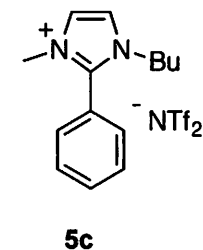
JEOL

```

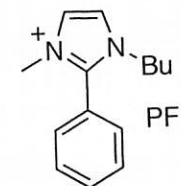
---- ACQUISITION PARAMETERS ----
File Name      = id_13c_spectrum.370
Author         =
Sample ID      = baimstf2ph 13C
Content        = Single Pulse with Broad
Creation Date   = 18-MAY-2007 21:01:37

Revision Date  = 20-MAY-2007 11:45:52
Spec Site      = ECP500

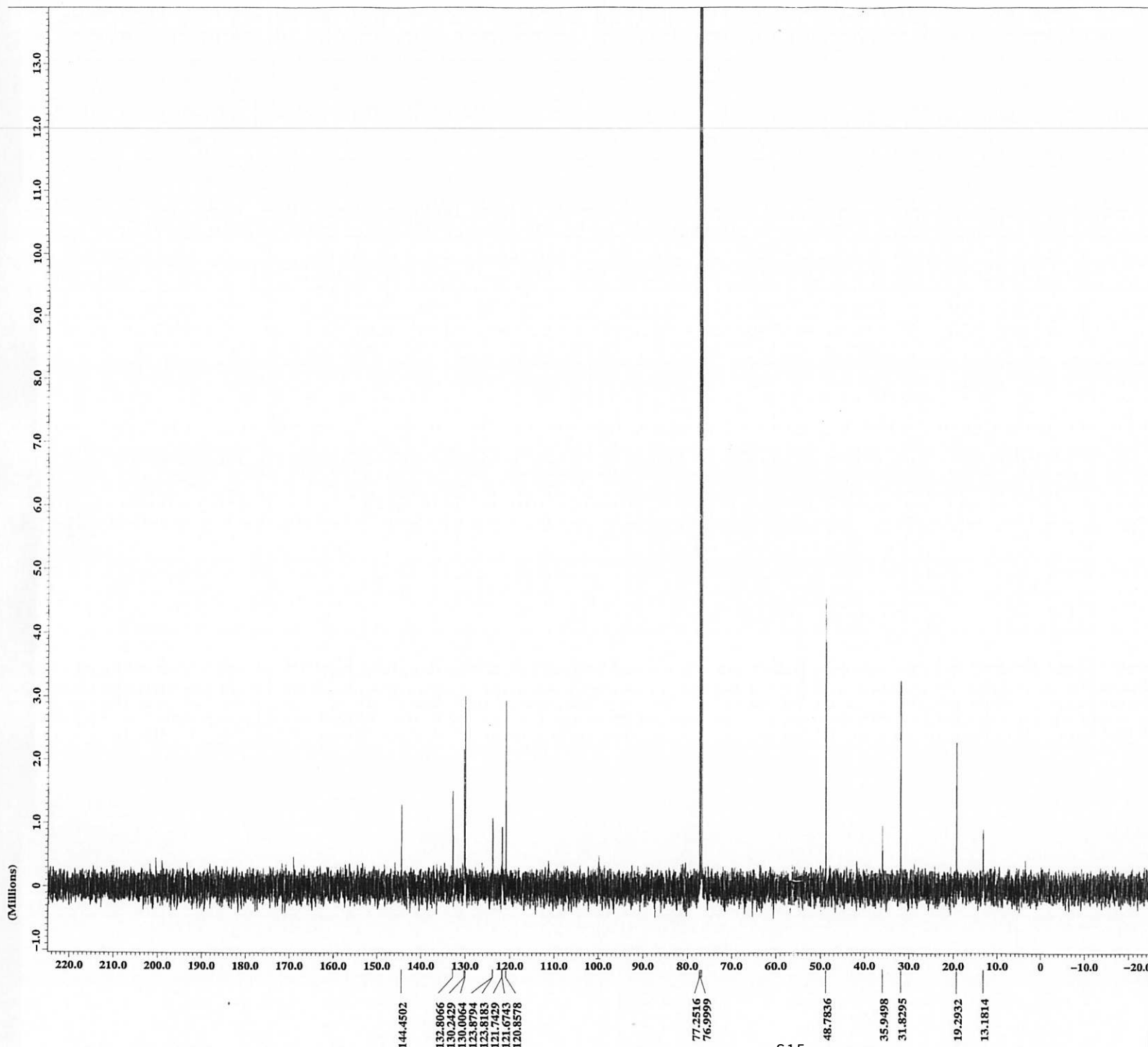
Spec Type      = DELTA RGR
Data Format     = 1D COMPLEX
Dimensions     = X
Dim Title      = 13C
Dim Size       = 32768
Dim Units      = [ppm]
Scans          = 1139
Mod_return     = 1
X_domain       = 13C
X_offset       = 100 [ppm]
X_freq         = 125.77787547 [MHz]
X_sweep        = 31.44654088 [kHz]
Solvent        = CHLOROFORM-D
Spin_get       = 16 [Hz]
Temp_get       = 26.3 [dC]
Recvr_gain     = 30
Field_strength = 11.7473579 [T]
Filter_mode    = BUTTERWORTH
Filter_width   = 15.72066221 [kHz]
  
```



----- ACQUISITION PARAMETERS -----
 File Name = id_13c_spectrum.391
 Author =
 Sample ID = lmlmPF6ph 13C
 Content = Single Pulse with Broad
 Creation Date = 22-MAY-2007 18:06:07
 Revision Date = 24-MAY-2007 08:55:58
 Spec Site = ECP500
 Spec Type = DELTA_NMR
 Data Format = 1D COMPLEX
 Dimensions = X
 Dim Title = 13C
 Dim Size = 32768
 Dim Units = [ppm]
 Scans = 640
 Mod_return = 1
 X_domain = 13C
 X_offset = 100 [ppm]
 X_freq = 125.77787547 [MHz]
 X_sweep = 31.44654088 [kHz]
 Solvent = CHLOROFORM-D
 Spin_get = 13 [Hz]
 Temp_get = 25.7 [dc]
 Recvr_gain = 15
 Field_strength = 11.7473579 [T]
 Filter_mode = BUTTERWORTH
 Filter_width = 15.72066221 [kHz]

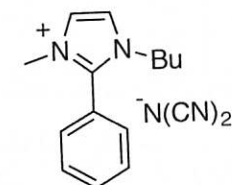


5d

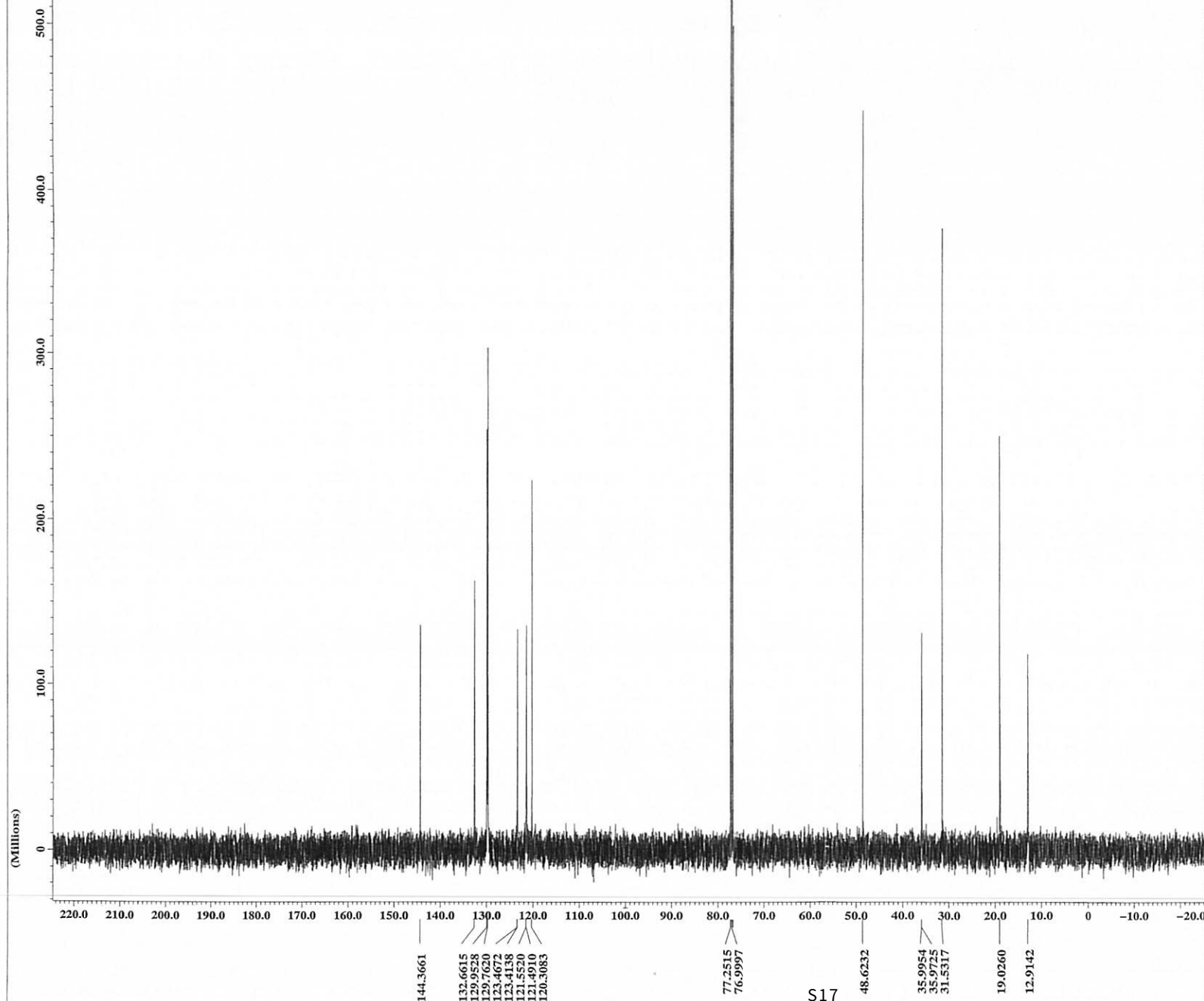


S15

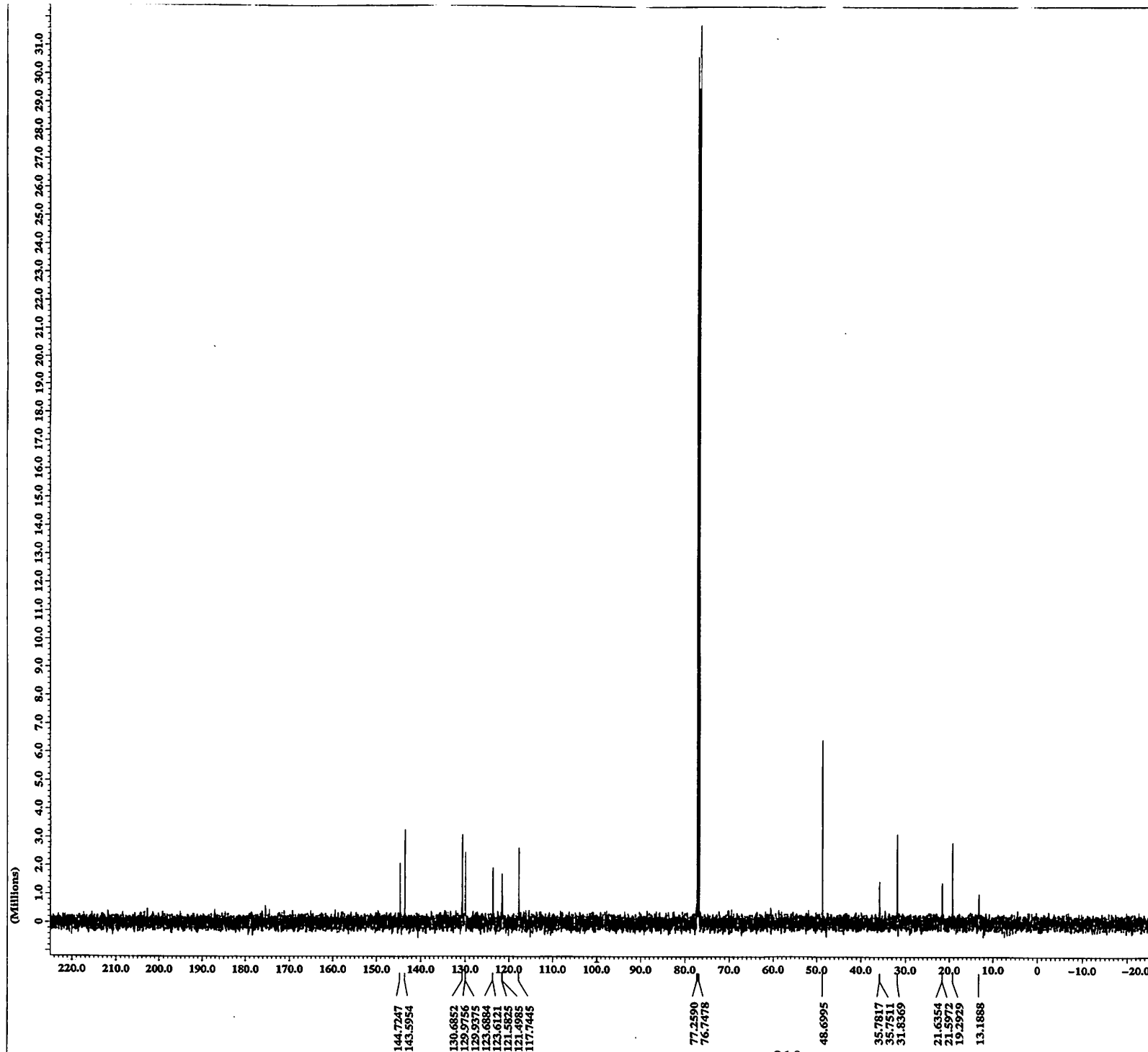
----- ACQUISITION PARAMETERS -----
 File Name = id_13c_spectrum.680
 Author =
 Sample ID = HT-M1-057-3-C
 Content = Single Pulse with Broad
 Creation Date = 3-OCT-2007 16:22:59
 Revision Date = 5-OCT-2007 10:40:12
 Spec Site = ECP500
 Spec Type = DELTA NMR
 Data Format = 1D COMPLEX
 Dimensions = X
 Dim Title = 13C
 Dim Size = 32768
 Dim Units = [ppm]
 Scans = 219
 Mod_return = 1
 X_domain = 13C
 X_offset = 100 [ppm]
 X_freq = 125.77787547 [MHz]
 X_sweep = 31.44654088 [kHz]
 Solvent = CHLOROFORM-D
 Spin_get = 15 [Hz]
 Temp_get = 26.3 [dC]
 Recvr_gain = 30
 Field_strength = 11.7473579 [T]
 Filter_mode = BUTTERWORTH
 Filter_width = 15.72066221 [kHz]



5e



X : parts per Million : 13C



X : parts per Million : 13C

S19

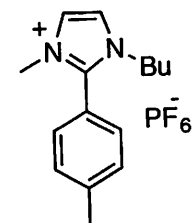
JEOL

```

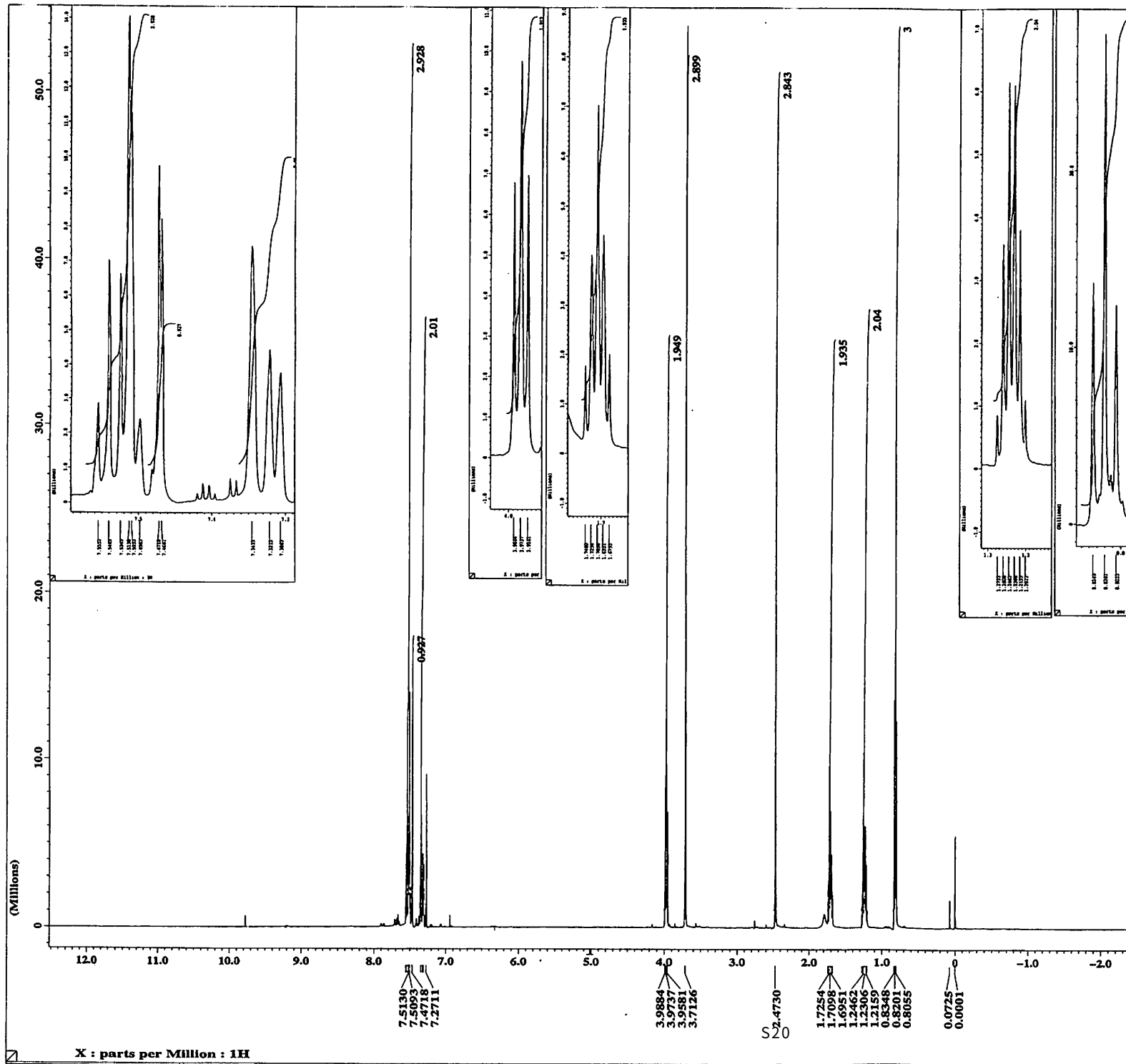
----- ACQUISITION PARAMETERS -----
File Name      = hainPF6 p-m-ph 13C.3
Author         =
Sample ID      = hainPF6 p-m-ph 13C
Content        = Single Pulse with Broad
Creation Date   = 23-MAY-2007 20:03:21

Revision Date  = 13-OCT-2007 06:06:44
Spec Site      = ECP500

Spec Type      = DELTA_RMR
Data Format     = 1D COMPLEX
Dimensions     = 1
Dim Title      = 13C
Dim Size       = 32768
Dim Units      = [ppm]
Scans          = 800
Mod_return     = 1
X_domain       = 13C
X_offset       = 100 [ppm]
X_freq         = 125.77787547 [MHz]
X_sweep        = 31.44654088 [kHz]
Solvent        = CHLOROFORM-D
Spin_get       = 15 [Hz]
Temp_get       = 25.7 [degC]
Recvr_gain     = 15
Field_strength = 11.7473579 [T]
Filter_mode    = BUTTERWORTH
Filter_width   = 15.72066221 [kHz]
  
```



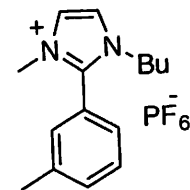
5f



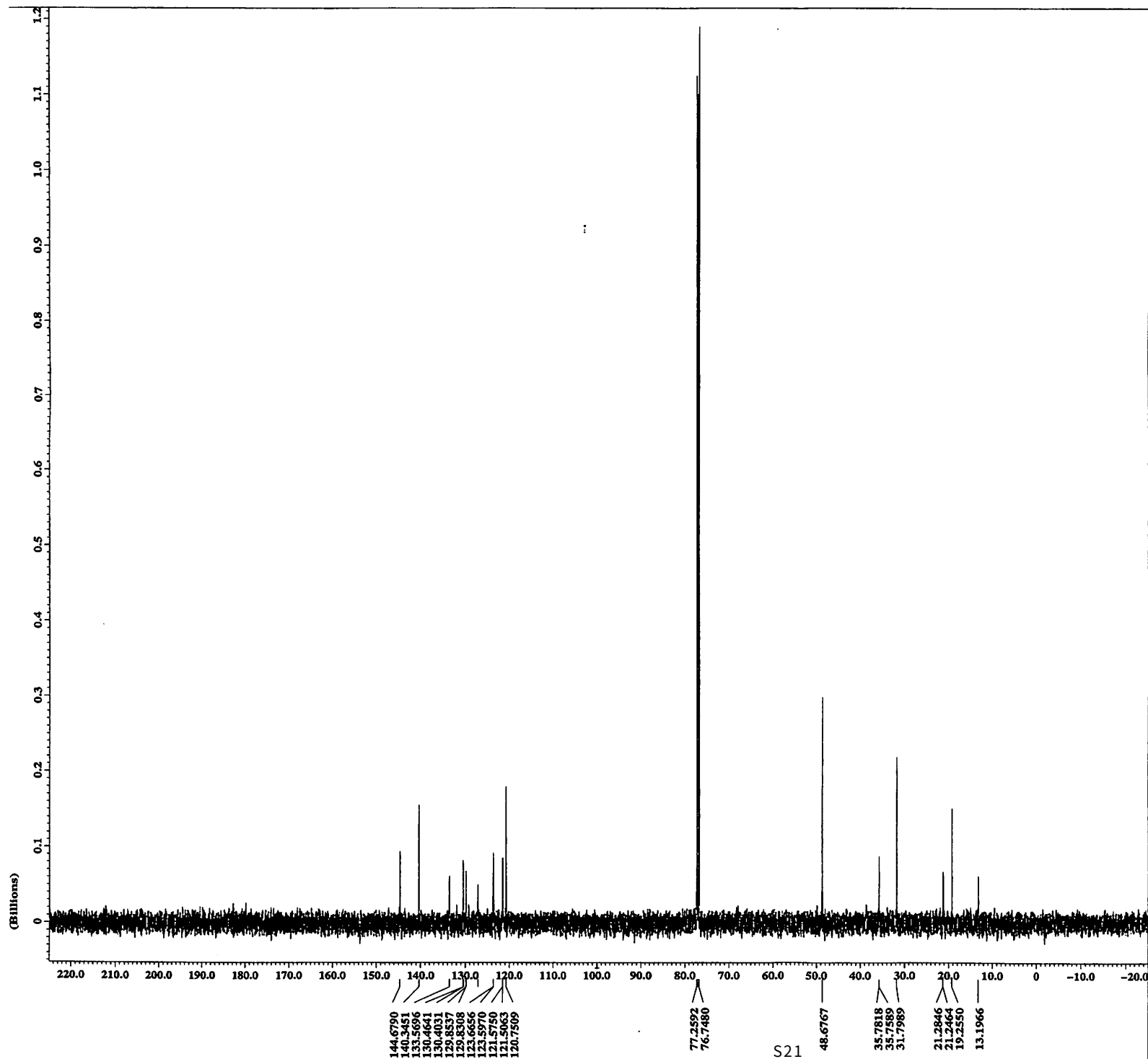
JEOL

----- ACQUISITION PARAMETERS -----

File Name = haimPF6 m-m-ph 1H true.
 Author =
 Sample ID = ht-mi-039-10
 Content = Single Pulse Experiment
 Creation Date = 27-JUN-2007 15:47:29
 Revision Date = 14-OCT-2007 05:14:46
 Spec Site = ECP500
 Spec Type = DELTA 500
 Data Format = 1D COMPLEX
 Dimensions = X
 Dim Title = 1H
 Dim Size = 16384
 Dim Units = [ppm]
 Scans = 6
 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 = 16 [Hz]
 Temp_get = 25.1 [dC]
 Recvr_gain = 23
 Field_strength = 11.7473579 [T]
 Filter_mode = BURRENORTH
 Filter_width = 3.75119936 [kHz]



5g



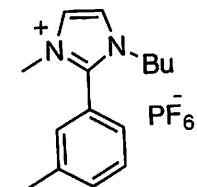
JEOL

```

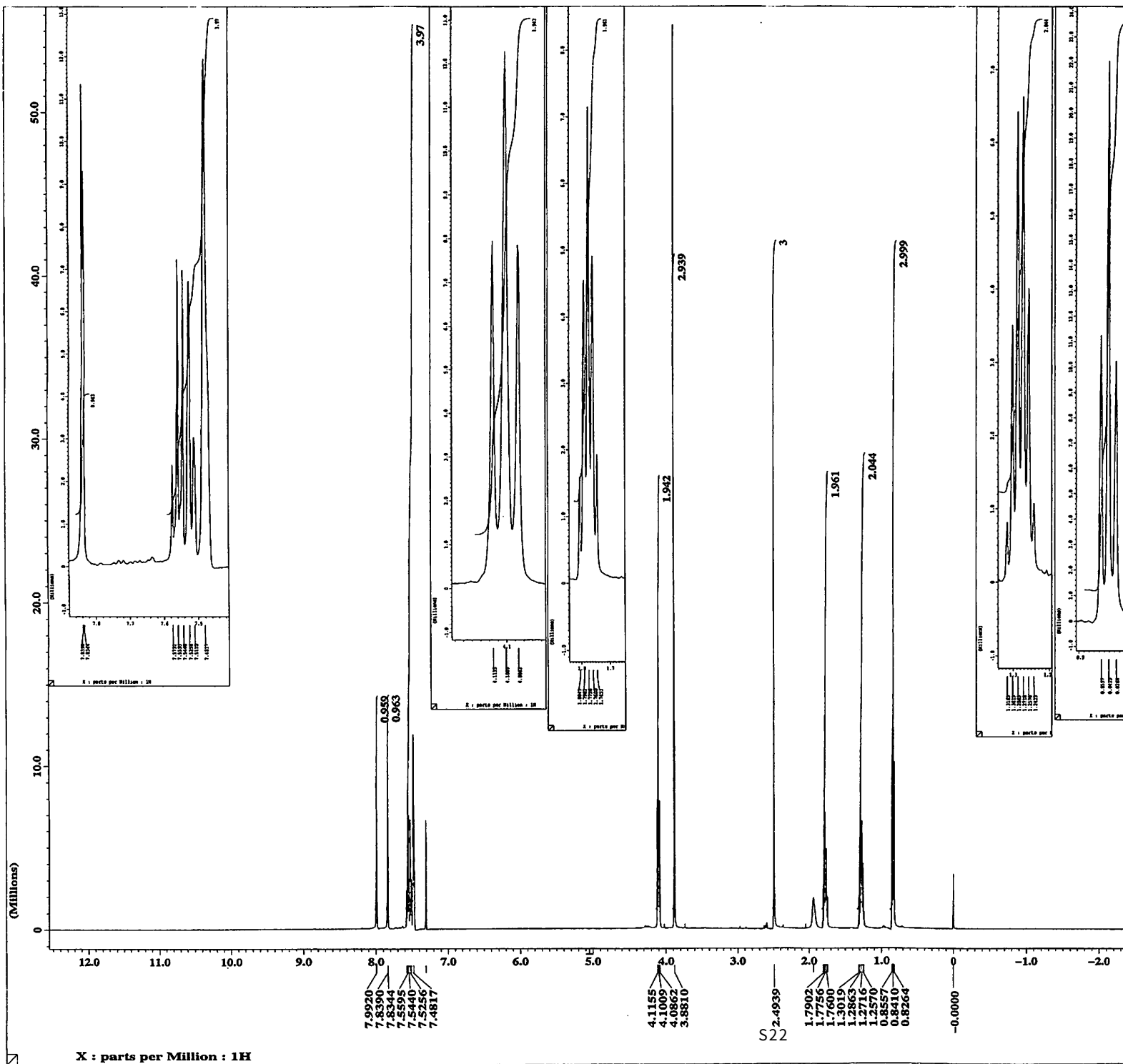
----- ACQUISITION PARAMETERS -----
File Name      = 1d_13c_spectrum.176
Author         =
Sample ID      = hmlmpf6 m-m-ph 13C
Content        = Single Pulse with Broad
Creation Date   = 27-JUN-2007 16:07:30

Revision Date  = 29-JUN-2007 07:36:14
Spec Site      = ECP500

Spec Type      = DELTA_NMR
Data Format     = 1D_COMPLEX
Dimensions     = 1
Dim Title      = 13C
Dim Size       = 32768
Dim Units      = [ppm]
Scans          = 503
Mod_return     = 1
X_domain       = 13C
X_offset       = 100 [ppm]
X_freq         = 125.77787547 [MHz]
X_sweep        = 31.44654080 [kHz]
Solvent        = CHLOROFORM-D
Spin_get       = 16 [Hz]
Temp_get       = 26.5 [dC]
Recvr_gain     = 30
Field_strength = 11.7473579 [T]
Filter_mode    = BUTTERWORTH
Filter_width   = 15.72066221 [kHz]
  
```



5g



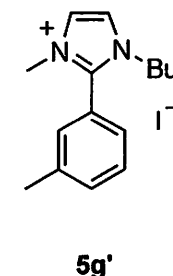
JEOL

----- ACQUISITION PARAMETERS -----

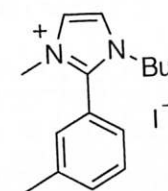
File Name = hainp76a-n-ph 1H.3
 Author =
 Sample ID = ht-m1-039-3-2
 Content = Single Pulse Experiment
 Creation Date = 19-JUN-2007 20:47:02

Revision Date = 14-OCT-2007 05:17:42
 Spec Site = ECP500

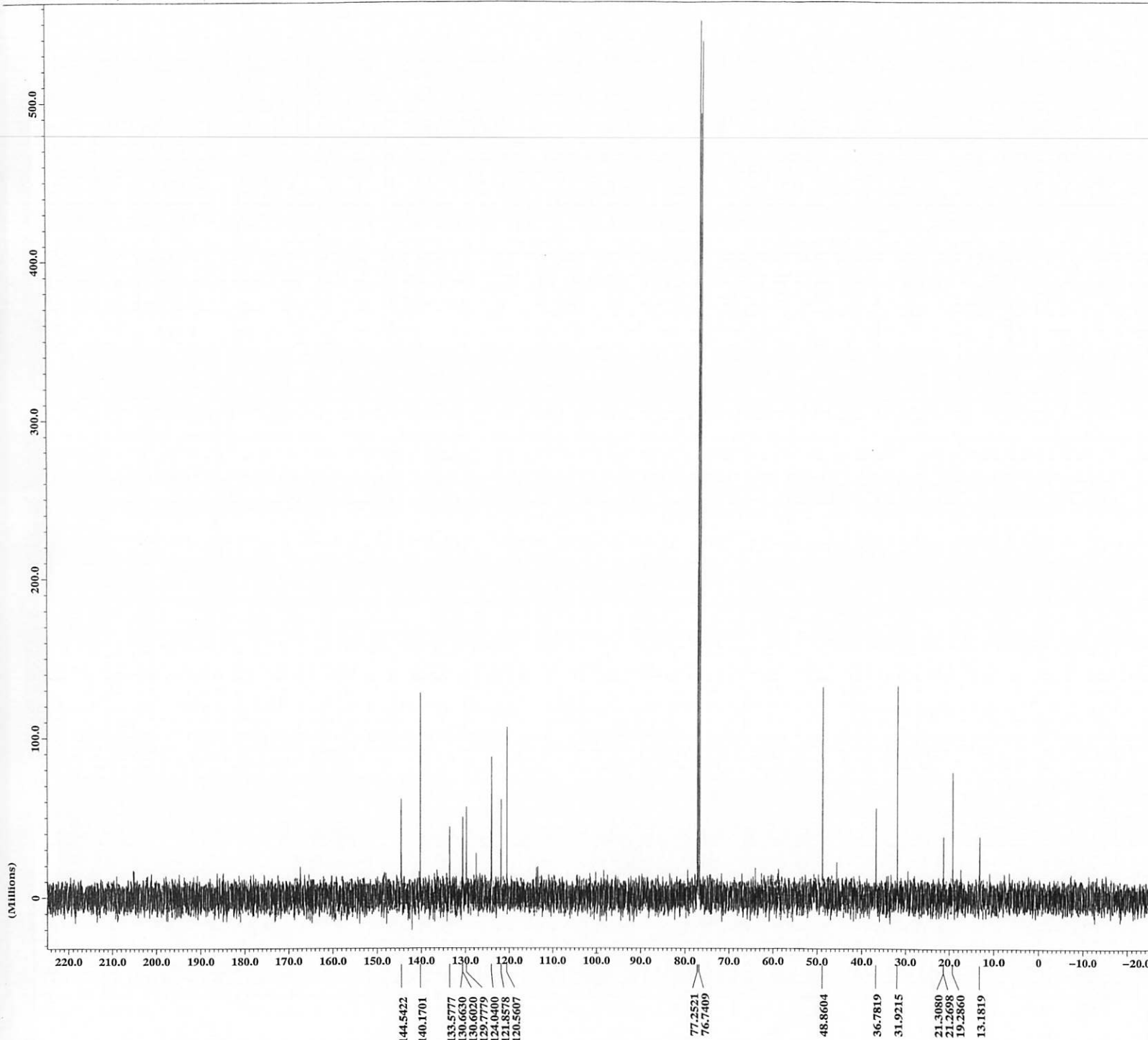
Spec Type = DELTA_RMR
 Data Format = 1D COMPLEX
 Dimensions = 1
 Dim Title = 1H
 Dim Size = 16384
 Dim Units = [ppm]
 Scans = 8
 Mod_return = 1
 X_domain = 1H
 X_offset = 5[ppm]
 X_freq = 500.16241602[MHz]
 X_sweep = 7.50750751[MHz]
 Solvent = CHLOROFORM-D
 Spin_get = 15[Hz]
 Temp_get = 25.7[degC]
 Recvr_gain = 23
 Field_strength = 11.7473579[T]
 Filter_mode = BUTTERWORTH
 Filter_width = 3.75119936[MHz]



----- ACQUISITION PARAMETERS -----
 File Name = id_13c_spectrum.122
 Author =
 Sample ID = ht-m1-039-c-1
 Content = Single Pulse with Broad
 Creation Date = 19-JUN-2007 21:06:38
 Revision Date = 21-JUN-2007 12:30:11
 Spec Site = ECP500
 Spec Type = DELTA NMR
 Data Format = 1D COMPLEX
 Dimensions = X
 Dim Title = 13C
 Dim Size = 32768
 Dim Units = [ppm]
 Scans = 246
 Mod_return = 1
 X_domain = 13C
 X_offset = 100[ppm]
 X_freq = 125.77787547[MHz]
 X_sweep = 31.44654088[kHz]
 Solvent = CHLOROFORM-D
 Spin_get = 15[Hz]
 Temp_get = 25.8[dC]
 RecvT_gain = 30
 Field_strength = 11.7473579[T]
 Filter_mode = BUTTERNORTH
 Filter_width = 15.72066221[kHz]



5g'

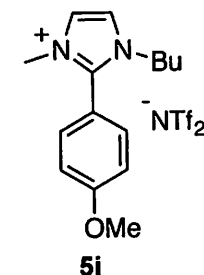


```

----- ACQUISITION PARAMETERS -----
File Name      = 1d_13c_spectrum.56
Author         =
Sample ID      = p-MeO
Content        = Single Pulse with Broad
Creation Date   = 11-JUN-2007 20:03:33

Revision Date  = 13-JUN-2007 11:13:53
Spec Site      = ECP500

Spec Type      = DELTA NMR
Data Format     = 1D COMPLEX
Dimensions     = X
Dim Title      = 13C
Dim Size       = 32768
Dim Units      = [ppm]
Scans          = 539
Mod_return     = 1
X_domain       = 13C
X_offset       = 100 [ppm]
X_freq         = 125.77787547 [MHz]
X_sweep        = 31.44654088 [kHz]
Solvent        = CHLOROFORM-D
Spin_get       = 14 [Hz]
Temp_get       = 26.3 [dC]
Recvr_gain     = 30
Field_strength = 11.7473579 [T]
Filter_mode     = BUTTERWORTH
Filter_width    = 15.72066221 [kHz]
    
```



(Billions)

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

162.8999

144.9233

131.7918

131.7460

121.3920

121.3157

121.0944

118.5383

115.5778

115.5168

111.9688

76.9999

76.7481

S24

55.6508

48.7531

35.8506

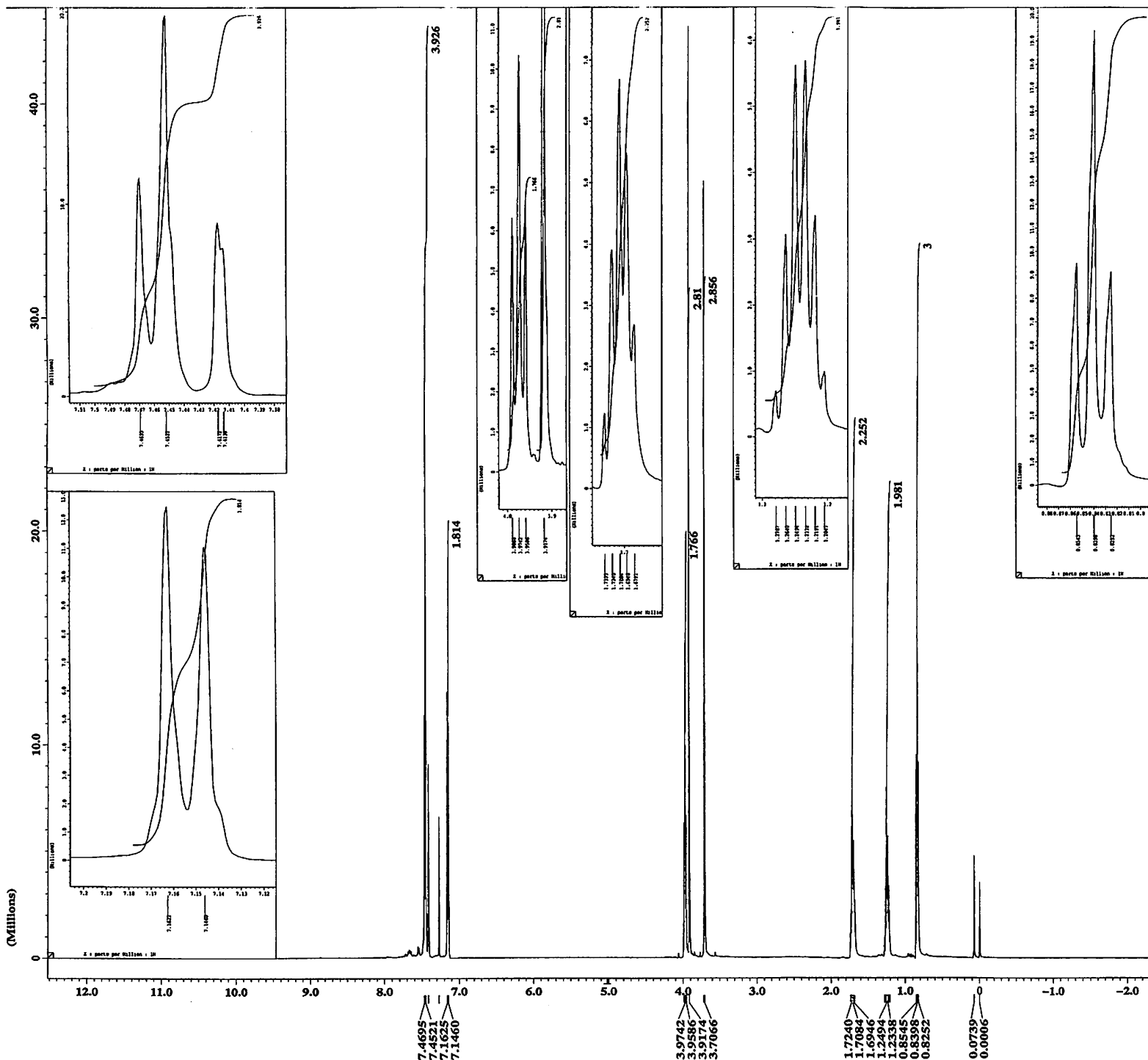
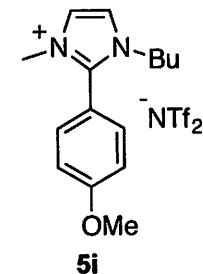
31.7608

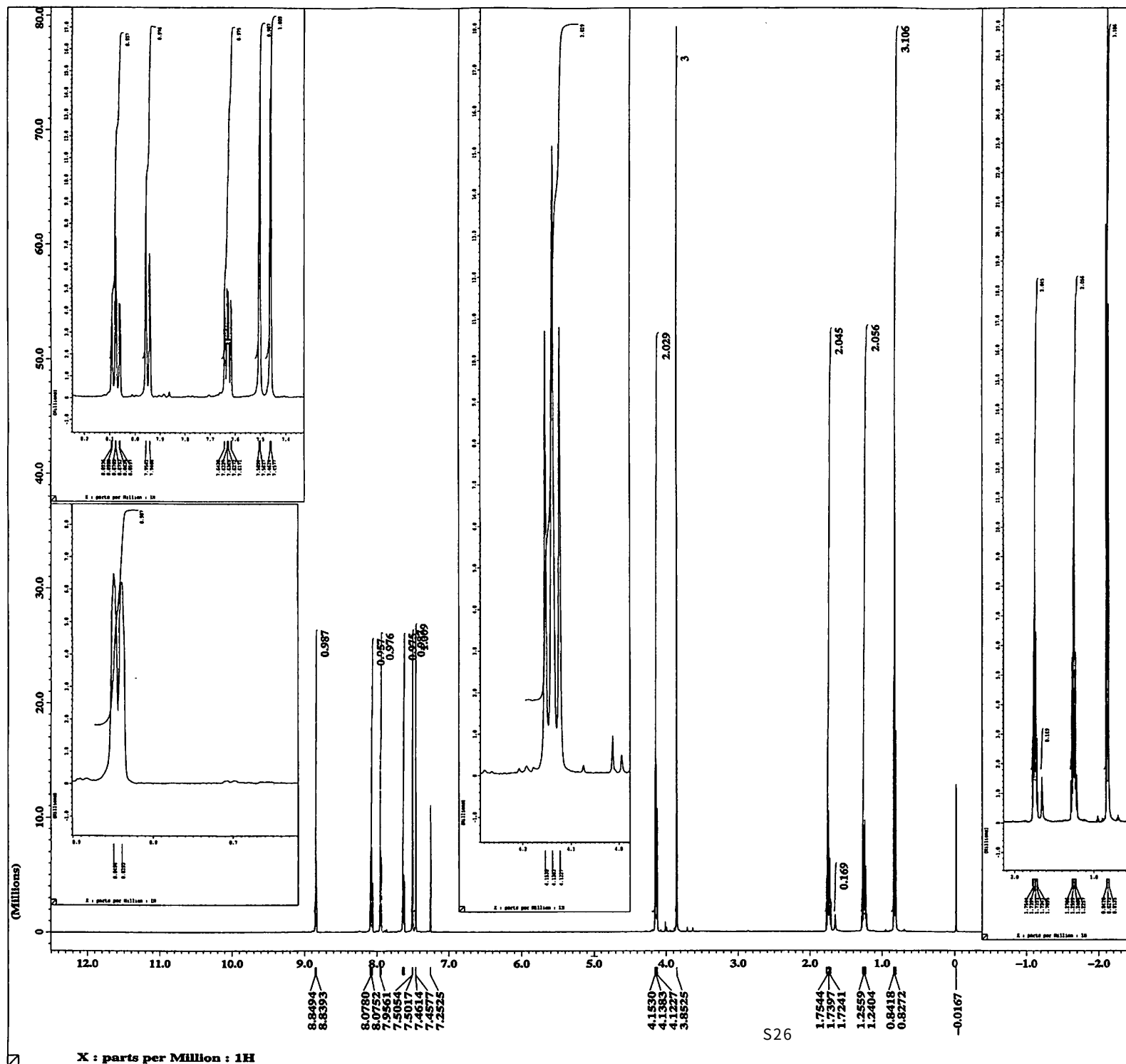
19.3008

13.1357

X : parts per Million : 13C

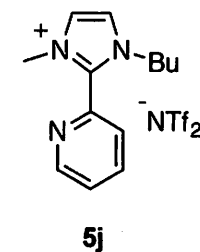
----- ACQUISITION PARAMETERS -----
 File Name = hmainwf2 p-MeO-ph 1H.5
 Author =
 Sample ID = hplc-1
 Content = Single Pulse Experiment
 Creation Date = 11-JUN-2007 19:32:50
 Revision Date = 14-OCT-2007 05:07:58
 Spec Site = ECP900
 Spec Type = DELTA_ROR
 Data Format = 1D_COMPLEX
 Dimensions = X
 Dim 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 = 15[Hz]
 Recv_gain = 24.9[dc]
 Field_strength = 11.7473579[T]
 Filter_mode = BUTTERWORTH
 Filter_width = 3.75119936[KHz]



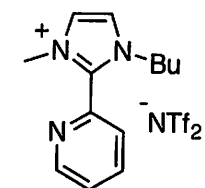


JEOL

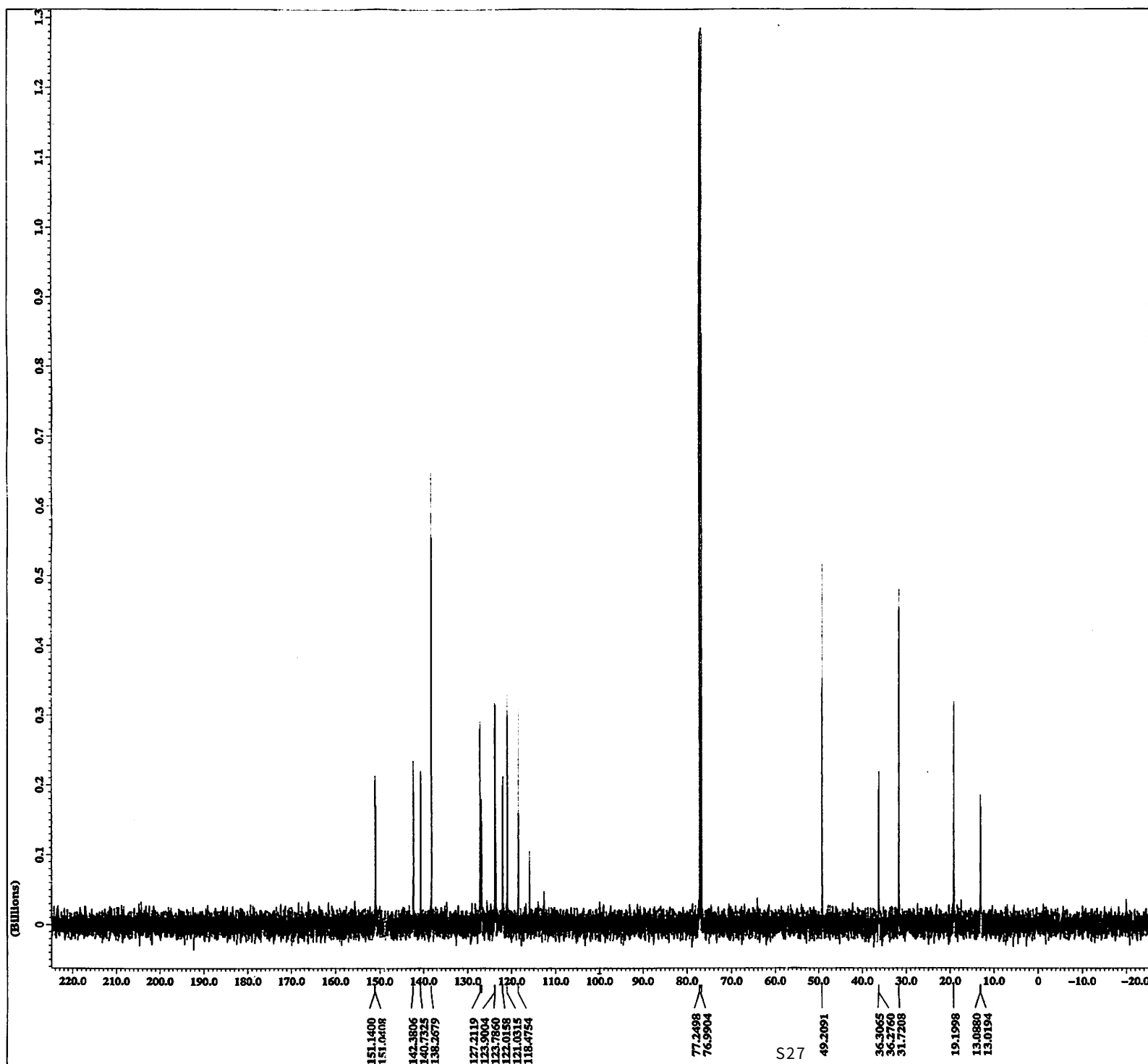
----- ACQUISITION PARAMETERS -----
 File Name = id_spectrum.5702
 Author =
 Sample ID = n-118-a-1
 Content = Single Pulse Experiment
 Creation Date = 27-FEB-2007 20:16:02
 Revision Date = 1-MAR-2007 09:30:46
 Spec Site = ECP500
 Spec Type = DELTA_500
 Data Format = 1D COMPLEX
 Dimensions = 2
 Dim Title = 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 = 16 [Hz]
 Temp_get = 24.7 [degC]
 Recvr_gain = 25
 Field_strength = 11.7473579 [T]
 Filter_mode = BUTTERWORTH
 Filter_width = 3.75119936 [kHz]



----- ACQUISITION PARAMETERS -----
 File Name = 1d_13c_spectrum.24
 Author =
 Sample ID = n-ntf2
 Content = Single Pulse with Broad
 Creation Date = 19-MAR-2007 18:03:46
 Revision Date = 21-MAR-2007 07:40:29
 Spec Site = ECP500
 Spec Type = DELTA_RMR
 Data Format = 1D COMPLEX
 Dimensions = X
 Dim Title = 13C
 Dim Size = 32768
 Dim Units = [ppm]
 Scans = 985
 Mod_return = 1
 X_domain = 13C
 X_offset = 100 [ppm]
 X_freq = 125.77767547 [MHz]
 X_sweep = 31.44654088 [kHz]
 Solvent = CHLOROFORM-D
 Spin_get = 16 [Hz]
 Temp_get = 24.9 [dC]
 Recvr_gain = 30
 Field_strength = 11.7473579 [T]
 Filter_mode = BUTTERWORTH
 Filter_width = 15.72066221 [kHz]



5j



X : parts per Million : 13C