SUPPORTING INFORMATION

Singlet oxygen-induced rearrangement of furan derivatives

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Table of Contents

General methods

All reactions were carried out under nitrogen or argon using flame dried glassware. Solvents were dried by filtration, under argon atmosphere, through a purification system similar to the one proposed by Grubbs *et al.*[1] Analytical thin layer chromatography was performed on Kieselgel F-254 pre-coated on aluminum sheet (TLC) plates by Merck. Visualization was performed with, either a 254 nm UV lamp, or a $KMnO_4$ solution. Unless specified otherwise: Flash column chromatography (FC) was carried out using Brunschwig silica gel 60 Å (32-63 mesh) following the general recommendation of Still.[2] Commercially available solid products were used without further purification and liquids were freshly distilled before use, unless specified otherwise.

NMR spectra were recorded with Bruker Avance DRX 500 (^{1}H: 500 and ^{13}C: 125.77 MHz) or Bruker Avance DPX 360 (^{1}H: 360 and ^{13}C: 90.55 MHz) or Bruker Ultrashield 300 (^{1}H: 300 and ^{13}C: 75.45 MHz) spectrometers using $CDCl_3$, CD_2Cl_2, CD_3CN, acetone-d6, THF-d8 or CD_3OD as solvents. Chemical shifts are given in ppm, calibrated on the residual solvent peak (7.27 and 77.16 ppm for $CDCl_3$, 1.94 and 1.30 ppm for CD_3CN respectively for ^{1}H and ^{13}C), coupling constants "J" are expressed in Hertz (multiplicity: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quadruplet, quint = quintet, sext = sextet, m = multiplet). IR spectroscopy was performed with a Brucker Tensor 27 equipped with a Golden Gate single reflection ATR system as a neat or with a Mattson Galaxy Series 500 FT-IR as a film. Elementary analysis was done on a CHNS EA1110 by CE Instrument. Electrospray ionization (ESI) high resolution mass spectra (HRMS) were obtained with a FT/ICR mass spectrometer Bruker 4.7T BioApex II, relative intensities are given in parenthesis. Electrospray ionization (LRMS-ESI) mass spectra (MS) were performed on Brucker Esquire HCT (ion trap) by direct infusion.

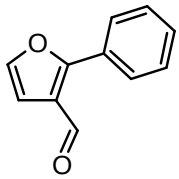
S[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
S[2] Still, W. C.; Kahn, M.; Mitra, A., *J. Org. Chem.* **1978,** *43*(14), 2923-2925.

General procedure A : Oxidation with $^1O_2$ followed by the rearrangement of 3-(1-hydroxysubstituted)furan derivatives.

A 25 mL, two-necked, quartz, cylindrical flask equipped with magnetic stirring bar, was charged with the corresponding 3-(1-hydroxyalkyl)furan (1.15 mmol), methylene blue (5.6 mg, 0.013 mmol) and MeCN (10 mL). The solution was cooled to -40 °C and oxygen was bubbled gently through the solution while it was irradiated (Osram Ultra-Vitalux®, 300 W) The consumption of 3-hydroxymethylfuran was followed by TLC. After 1h30, dimethyl sulfide (1 mL, 13.6 mmol) was added at -40 °C, rapidly followed by p-toluene sulfonic acid (218 mg, 1.15 mmol). The reaction mixture was allowed to warm to room temperature then stirred during 2 h. Saturated solution of sodium carbonate (30 mL) and methylene chloride (50 mL) were added. The layers were separated, the organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the desired aldehyde.

Procedure followed in order to obtain the ^{1}H-NMR yield using internal standard

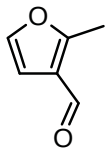
After 2h at *r.t.* the reaction mixture was diluted to 25 mL with DCM in a measuring flask. 1 mL was placed in a 10 mL round bottomed flask with 1 mL of a 0.046 M solution of 2,4-dinitro-1-fluorobenzene (Internal Standard = IS) in $CHCl_3$. The solution was concentrated under vacuum (100 mbar) and the residue was put in $CDCl_3$. The yield was calculated knowing that the number of mole of IS is the same as the number of mole of SM. The ^{1}H-NMR signals used for the IS calculation are 8.96 ppm (m, 1H), 8.52 ppm (m, 1H) and for the furanone (e.g. **7a**) 6.61 (d, J = 3.6 Hz, 1H).



3a

2-(phenyl)-3-furaldehyde (3a)

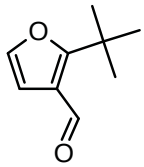
Following the general procedure A from of 3-furyl(phenyl)methanol **2a** (200 mg) yielded the desired aldehyde as a yellow solid (146 mg, 68%) after flash chromatography (SiO_2, DCM/Hex, 50/50). R_f = 0.68 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 10.11 (s, 1H), 7.72 (m, 2H), 7.48 (m, 4H), 6.90 (s, 1H). ^{13}C NMR (90 MHz, CDCl3, δ): 185.8, 161.7, 145.9, 130.3, 129.1, 129.0, 128.2, 123.1, 109.5. IR (film): 3128, 3058, 2926, 2853, 2751, 1679, 1566, 1520, 1489, 1448, 1417, 1395, 1269, 1145, 1068, 1042, 890, 770, 693. Anal. calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.47; H, 5.03.



3b

2-methyl-3-furaldehyde (3b)

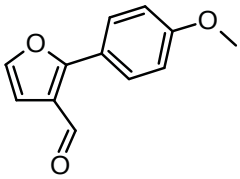
Following the general procedure A from 1-(3-furyl)ethanol **2b** (129 mg) yielded a yellow liquid as the desired aldehyde (51 mg, 40%) after flash chromatography (SiO_2, DCM/Hex, 60/40). R_f = 0.47 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 9.92 (s, 1H), 7.28 (s, 1H), 6.66 (s, 1H), 2.57 (s, 3H). ^{13}C NMR (90 MHz, $CDCl_3$, δ): 185.0, 162.1, 142.1, 122.7, 108.1, 12.7. IR (film): 3155, 3128, 2926, 2840, 2744, 1687, 1579, 1526, 1426, 1397, 1235, 1124, 1040, 948, 895, 786, 754. Anal. calcd for $C_6H_6O_2$: C, 65.45; H, 5.49. Found: C, 65.10; H, 5.76.



3c

2-*tert*-butyl-3-furaldehyde (3c)

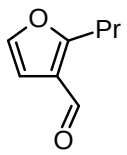
Following the general procedure A from 1-(3-furyl)-2,2-dimethylpropan-1-ol **2c** (177 mg) yielded the desired aldehyde as a yellow liquid (45 mg, 26%) after flash chromatography (SiO_2, DCM/Hex, 50/50). R_f = 0.49 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 10.26 (s, 1H), 7.25 (s, 1H), 6.73 (s, 1H), 1.46 (s, 9H). ^{13}C NMR (90 MHz, CDCl3, δ): 186.2, 171.4, 141.0, 122.6, 109.3, 35.9, 30.5. IR (film): 3130, 2974, 2935, 2910, 2874, 1674, 1567, 1523, 1479, 1464, 1407, 1367, 1266, 1159, 1064, 894, 758. Anal. calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.94. Found: C, 70.90; H, 8.18.



3d

2-(4-methoxyphenyl)-3-furaldehyde (3d)

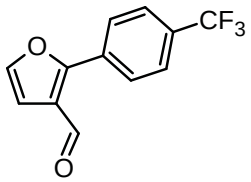
Following the general procedure A from 3-furyl(4-methoxyphenyl)methanol **2d** (235 mg) yielded the desired aldehyde as a yellow solid (68 mg, 29%) after flash chromatography (SiO_2, DCM/Hex, 50/50). R_f = 0.33 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 10.07 (s, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.42 (s, 1H), 7.01 (d, J = 8.2 Hz, 2H), 6.87 (s, 1H). ^{13}C NMR (90 MHz, CDCl3, δ): 185.8, 161.9, 161.3, 142.3, 129.7, 122.1, 121.7, 114.6, 109.5, 55.6. IR (film): 2840, 2672, 1610, 1528, 1498, 1664, 2423, 1395, 1305, 1297, 1179, 1143, 1031, 836, 759, 690. Anal. calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.36; H, 5.20.



3e

2-propyl-3-furaldehyde (3e)

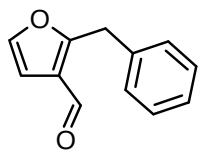
Following the general procedure A from 1-(3-furyl)butan-1-ol **2e** (161 mg) yielded the desired aldehyde as a colourless liquid (60 mg, 38%) after flash chromatography (SiO_2, DCM/Hex, 50/50). R_f = 0.47 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 9.93 (s, 1H), 7.30 (s, 1H), 6.68 (s, 1H), 2.92 (t, J = 7.5 Hz, 2H), 1.75 (tq, J = 7.5, 7.5 Hz, 2H), 1.75 (t, J = 7.3 Hz, 3H). ^{13}C NMR (90 MHz, CDCl3, δ): 184.9, 166.1, 142.2, 122.8, 107.9, 28.8, 24.8, 19.7. IR (film): 3153, 3126, 2966, 2935, 2876, 1682, 1584, 1524, 1424, 1396, 1248, 1206, 1125, 1018, 899, 754. Anal. calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.17; H, 7.40.



3f

2-[4-(trifluoromethyl)phenyl]-3-furaldehyde (3f)

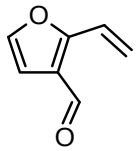
Following the general procedure A from of 3-furyl[4-(trifluoromethyl)phenyl]methanol **2f** (279 mg) yielded the desired aldehyde as a colourless solid (196 mg, 71%) after flash chromatography (SiO_2, Hex/EtOAc, 99/1). R_f = 0.51 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 10.14 (s, 1H), 7.92 (d, J = 8.17, 2H), 7.77 (d, J = 8.17, 2H), 7.54 (s, 1H), 6.95 (s, 1H). ^{13}C NMR (90 MHz, CDCl3, δ185.2, 158.9, 143.6, 132.3, 128.3, 126.2, 125.4, 124.1, 122.4, 110.4. IR (film): 3129, 2858, 1679, 1620, 1500, 1422, 1327, 1267, 1170, 1126, 1069, 1017, 891, 847, 759, 688. Anal. calcd for $C_{12}H_7F_3O_2$: C, 60.01; H, 2.94. Found: C, 60.20; H, 3.04.



3g

2-benzyl-3-furaldehyde (3g)

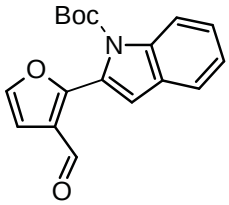
Following the general procedure A from 1-(3-furyl)-2-phenylethanol **2g** (216 mg) yielded the desired aldehyde as a yellow liquid (156 mg, 73%) after flash chromatography (SiO_2, DCM/Hex, 50/50). R_f = 0.53 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 9.97 (s, 1H), 7.28 (3, 6H), 6.71 (s, 1H), 4.29 (s, 2H). ^{13}C NMR (90 MHz, CDCl3, δ185.0, 163.1, 142.7, 136.3, 128.9, 128.7, 127.2 122.9, 108.4, 33.2. IR (film): 3125, 3067, 3031, 2836, 2748, 1681, 1582, 1521, 1495, 1455, 1423, 1243, 1179, 1124, 1079, 1030, 888, 802. Anal. calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.01; H, 5.59.



3h

2-vinyl-3-furaldehyde (3h)

Following the general procedure A from THF/Et_2O solution of 1-(3-furyl)-2-phenylethanol **2h** (140 mg pure) yielded the desired aldehyde as a slightly yellow oil (116 mg, 83%) after flash chromatography (SiO_2, DCM). R_f = 0.28 (DCM). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 5.59 (d, *J*=11.37 Hz, 1 H) 6.07 (d, *J*=17.43 Hz, 1 H) 6.76 (d, *J*=2.02 Hz, 1 H) 7.00 (dd, *J*=17.31, 11.24 Hz, 1 H) 7.36 (d, *J*=1.77 Hz, 1 H) 10.05 (s, 1 H). ^{13}C NMR (91 MHz, CHLOROFORM-*d*) δ ppm 109.26, 119.86, 122.32, 122.84, 143.02, 158.82, 184.55. IR (neat): 3127, 2918, 2849, 1678, 1554, 1505, 1405, 1257, 1129, 893, 734, 631.

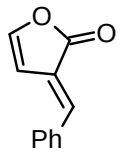


3i

***tert*-butyl 2-(3-formyl-2-furyl)-1*H*-indole-1-carboxylate (3i)**

Following the general procedure A from *tert*-butyl 2-[3-furyl(hydroxy)methyl]-1*H*-indole-1-carboxylate **2i** (81 mg) yielded the desired aldehyde as a yellow solid (43 mg, 53 %) after flash chromatography (SiO_2, DCM/Hex, 80/20. R_f = 0.40 (DCM). ^{1}H NMR (360 MHz, CHLOROFORM-*d*) δ ppm 1.46 (s, 9 H) 6.91 (d, *J*=8.63 Hz, 2 H) 7.32 (t, *J*=7.49 Hz, 1 H) 7.45 (t, *J*=7.95 Hz, 1 H) 7.54 (s, 1 H) 7.64 (d, *J*=7.72 Hz, 1 H) 8.27 (d, *J*=8.17 Hz, 1 H) 9.94 (s, 1 H). ^{13}C NMR (91 MHz, CHLOROFORM-*d*) δ ppm 27.89, 84.44, 108.34, 115.71, 116.16, 121.58, 123.63, 125.37, 125.39, 126.50, 128.23, 137.84, 143.45, 149.32, 155.98, 185.51. IR (neat): 3105, 2975, 2835, 1742, 1675, 1617, 1454, 1367, 1317, 1231, 1137, 1071, 1013, 847, 745, 708. HRMS-ESI (m/z): Calcd for $C_{18}H_{17}NO_4Na$, 334.1050; found, 334.1057.

Formation of alkylidenefurane-2-one

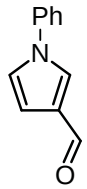


7a

3-benzylidenefuran-2(3*H*)-one (7a)

A 25 mL, two-necked, quartz, cylindrical flask equipped with magnetic stirring bar, was loaded with the 3-furyl(phenyl)methanol **2a** (200 mg, 1.15 mmol), methylene blue (5.6 mg, 0.013 mmol) and MeCN (10 mL). The solution was cooled to -40 °C and oxygen was bubbled gently through the solution while irradiated (OSRAM ULTRA-VITALUX©, 300 W) Consumption of 3-furyl(phenyl)methanol **2a** was followed by TLC (DCM/MeOH, 98/2). After 1h30, dimethyl sulfide (1 mL, 13.6mmol), rapidly followed by *para*-toluenesulfonyl chloride (218 mg, 1.15 mmol) were added at -40°C. The reaction mixture was allowed to warm to room temperature then stirred for 2 h. A saturated solution of sodium carbonate (30 mL) and DCM (50 mL) were added. The layers were separated. The organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Crude product was purified using flash chromatography (DCM/Hex, 50/50) to obtain the desired product (53mg, 27%) as a yellow liquid. R_f = 0.53 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 7.58 (m, 2H), 7.46 (m, 4H), 7.16 (s, 1H), 6.61 (d, J = 3.6 Hz, 1H). ^{13}C NMR (90 MHz, $CDCl_3$, δ): 169.5, 147.4, 137.8, 134.7, 130.7, 130.3, 129.2, 123.2, 106.3. IR (film): 3127, 2922, 2854, 1764, 1624, 1597, 1563, 1451, 1346, 1291, 1224, 1174, 1138, 1057, 980, 756, 690.

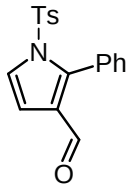
Formation of pyrrole derivative



9a

1-phenyl-1*H*-pyrrole-3-carbaldehyde (9a)

Following the general procedure A from 1-(3-furyl)-1-phenylmethanamine **8a** (199 mg) yielded a mixture of desired aldehyde as a yellow oil (125 mg, 64 %) and starting material (35 mg, 18 %) after flash chromatography (SiO_2, DCM). R_f = 0.17 (DCM). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 6.81 (dd, *J*=3.02, 1.70 Hz, 1 H) 7.09 (t, *J*=2.36 Hz, 1 H) 7.34 - 7.52 (m, 5 H) 7.67 (d, *J*=1.70 Hz, 1 H) 9.86 (s, 1 H). ^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 109.76, 121.30, 122.47, 127.29, 127.50, 128.30, 130.02, 139.71, 185.65. IR (neat): 3120, 2920, 2851, 1671, 1599, 1537, 1510, 1461, 1355, 1272, 1208, 1082, 1050, 806, 750, 690. HRMS-ESI (*m/z*): Calcd for $C_{11}H_9NONa$, 194.0576; found, 194.0582. LC-MS: 3.50 min.



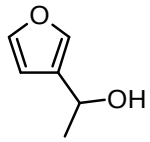
9b

1-[(4-methylphenyl)sulfonyl]-2-phenyl-1*H*-pyrrole-3-carbaldehyde (9b)

Following the general procedure A from *N*-[3-furyl(phenyl)methyl]-4-methylbenzenesulfonamide **8b** (377 mg) yielded the desired aldehyde as a colourless liquid (309 mg, 92 %) after flash chromatography (SiO_2, DCM). R_f = 0.19 (DCM). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 2.38 (s, 3 H) 6.77 (d, *J*=3.59 Hz, 1 H) 7.10 - 7.24 (m, 6 H) 7.36 (t, *J*=7.55 Hz, 2 H) 7.44 - 7.52 (m, 2 H) 9.34 (s, 1 H). ^{13}C NMR (91 MHz, CHLOROFORM-*d*) δ ppm 21.82, 108.52, 123.77, 127.19, 127.73, 127.75, 128.17, 129.83, 129.99, 132.31, 134.90, 143.22, 145.88, 186.87. IR (neat): 3151, 3064, 2830, 2746, 1674, 1596, 1472, 1424, 1376, 1303, 1176, 1127, 956, 763, 682. HRMS-ESI (*m/z*): Calcd for $C_{18}H_{16}N_1O_3SNa$, 326.0845; found, 326.0848. LC-MS: 4.34 min.

General procedure B for reaction of 3-furaldehyde derivative with Grignard reagent

A 100 mL, three-necked, flam dried round-bottom flask equipped with magnetic stirring bar, was loaded with 3-furaldehyde (**1**) (50 mmol) and dried diethylether (25 mL) under argon. The solution was cooled to -15 °C and a solution of the corresponding Grignard reagent (55 mmol) in THF was added gently. The reaction mixture was allowed to warm to room temperature then stirred during 15 minutes. Consumption of 3-furaldehyde was followed by TLC (DCM/MeOH, 95/5). After 15 minutes, NH_4Cl sat. (15 mL) was added and the reaction mixture was transferred in a separating funnel. The resulting emulsion was suppressed with small amount of HCl 1M (Never get to acidic conditions). The aqueous phase was extracted with dichloromethane (3 x 50 mL). Organic phases were combined, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Crude product was purified using flash chromatography to abtain the desired product. Grignard reaction procedure is in accordande with procedure published by Pawlicki.[3]

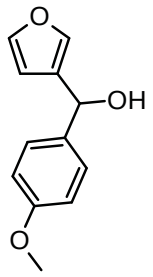


2b

1-(3-furyl)ethanol (2b)

Following the general procedure B from 3-furaldehyde and methyl magnesium bromide yielded the desired alcohol as a colourless liquid after flash chromatography (SiO_2, DCM). R_f = 0.22 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 7.36 (s, 2H), 6.41 (s, 1H), 4.83 (q, J = 6.36 Hz, 1H), 2.09 (bs, 1H), 1.46 (d, J = 6.36 Hz, 3H). ^{13}C NMR (90 MHz, $CDCl_3$, δ): 143.4, 128.6, 130.4, 108.6, 63.0, 24.0. IR (film): 3359, 2977, 2931, 2876, 1596, 1503, 1449, 1371, 1331, 1293, 1161, 1100, 1065, 1025, 961, 874, 794.

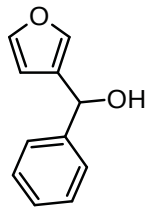
S[3] Pawlicki, M.; Grazynski, L. L.; Szterenberg, L., *J. Org. Chem.* **2002**, *67*, 5644-5653.



2d

3-furyl(4-methoxyphenyl)methanol (2d)

Following the general procedure B from 3-furaldehyde (2.29 g, 23.8 mmol) and 4-methoxyphenyl magnesium bromide (0.5 M in THF, 50 mL, 25 mmol) yielded the desired alcohol (3.01g, 62%) as a yellow liquid after flash chromatography (SiO_2, DCM/MeOH, 99/1 + trace of Net_3). Alcohol (**2d**) was not stable; when transferred, the product was filtered through basic aluminium oxide. It was quickly analysed and used for the next step. R_f = 0.43 (DCM/MeOH, 98/2). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 7.37 (s, 1H), 7.29 (m, 3H), 6.88 (d, J = 8.63 Hz, 2H), 6.31 (s, 1H), 5.69 (s, 1H), 3.80 (s,3H), 2.52 (bs, 1H). ^{13}C NMR (90 MHz, $CDCl_3$, δ): 159.3, 143.5, 135.5, 129.3, 113.9, 109.4, 69.3, 55.4. IR (film): 3371, 2990, 2935, 2874, 1595, 1502, 1467, 1380, 1291, 1160, 1101, 1065, 1022.

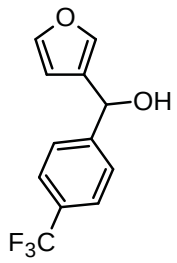


2a

3-furyl(phenyl)methanol (2a)

Following the general procedure B from 3-furaldehyde (4.8 g) and phenyl magnesium bromide (1 M in THF, 55 mL) yielded the desired alcohol (5.07g, 58%) as an off white powder after flash chromatography (SiO_2, DCM/MeOH, 99/1). R_f = 0.27 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 7.37 (m, 7H), 6.34 (s, 1H), 5.78 (s, 1H), 2.16 (s, 1H). ^{13}C NMR (90 MHz, $CDCl_3$, δ): 143.6,

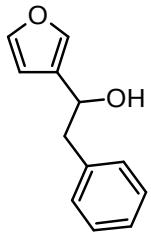
143.1, 139.9, 129.0, 128.7, 128.0, 126.5, 109.3, 69.6. IR (film): 3365, 3031, 2874, 1602, 1502, 1454, 1197, 1157, 1024. Anal. calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.84; H, 5.87.



2f

3-furyl[4-(trifluoromethyl)phenyl]methanol (2f)

Following the general procedure B from 3-furaldehyde and 4-trifluoromethylphenyl magnesium bromide yielded the desired alcohol as a slightly yellow liquid after flash chromatography (SiO_2, DCM/Hex, 90/10). R_f = 0.33 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 7.62 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H), 7.39 (s, 1H), 7.32 (s, 1H), 6.31 (s, 1H), 5.83 (s, 1H), 2.31 (bs, 1H). ^{13}C NMR (90 MHz, $CDCl_3$, δ): 146.9, 144.0, 140.1, 130.1 (q, J = 32.4 Hz), 128.5, 126.7, 125.6 (q, J = 3.3 Hz), 122.7, 109.1, 68.8. IR (film): 3339, 2891, 1927, 1621, 1504, 1418, 1328, 1161, 1126, 1068, 1029, 1016, 965, 876, 806, 771, 733.

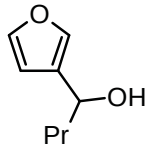


2g

1-(3-furyl)-2-phenylethanol (2g)

Following the general procedure B from 3-furaldehyde and benzyl magnesium bromide yielded the desired alcohol as an orange liquid after flash chromatography. R_f = 0.53 (DCM/MeOH 98/2). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 7.37 (s, 1H), 7.25 (m, 6H), 6.39 (s, 1H), 4.83 (m, 1H), 2.99 (m, 2H), 2.03 (bs, 1H). ^{13}C NMR (90 MHz, $CDCl_3$, δ): 134.3, 139.21, 137.8, 129.6, 128.6, 126.8,

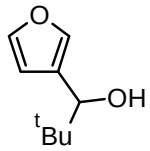
108.7, 68.0, 44.7. IR (film): 3549, 3386, 3029, 2922, 1951, 1882, 1814, 1604, 1496, 1454, 1159, 1078, 1027, 875, 793, 731, 700.



2e

1-(3-furyl)butan-1-ol (2e)

1-furan-3-ylbutan-1-one (0.478g, 34.6mmol) was reduced using an excess of $NaBH_4$ in MeOH. The reaction was quenched with water. After extraction with DCM and concentration a slightly yellow oil was obtained in quantitative yield. (SiO_2, DCM). R_f = 0.17 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 7.37 (s, 2H), 6.40 (s, 1H), 4.65 (t, J = 6.58 Hz, 1H), 1.73 (m, 3H), 1.39 (m, 2H), 0.94 (t, J = 7.49 Hz, 3H). ^{13}C NMR (90 MHz, $CDCl_3$, δ): 143.4, 139.1, 129.4, 108.6, 66.8, 40.0, 19.0, 14.0. IR (film): 3371, 2990, 2935, 2874, 1595, 1502, 1467, 1380, 1291, 1160, 1101, 1065, 1022.

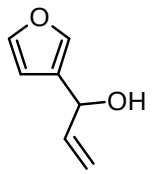


2c

1-(3-furyl)-2,2-dimethylpropan-1-ol (2c)

A 50 mL, three-necked, flamdried roundbottomed flask equipped with magnetic stirring bar, was loaded with 3-furaldehyde (0.8 g, 8.3 mmol) and dried THF (20 mL) under Argon. The solution was cooled to -80 °C and a solution of tert-butyllithium (20 mL, 1.7M in Hexane, 12.5 mmol) was added gently. Consumption of 3-furaldehyde was followed by TLC (DCM). After 5 min, a saturated solution of NH_4Cl (20 mL) was added slowly. The reaction mixture was allowed to warm to room temperature. DCM was added. Organic phase was separated and washed with water (50 mL) dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Crude product was purified by reduces pressure distillation to yielded the desired alcohol (0.94g, 74%) as a colourless liquid. R_f = 0.27 (DCM). ^{1}H NMR (360 MHz, $CDCl_3$, δ): 7.33 (s, 1H), 7.30 (s,

1H), 6.35 (s, 1H), 4.30 (s, 1H), 2.09 (bs, 1H), 0.91 (s, 9H). ^{13}C NMR (90 MHz, $CDCl_3$, δ): 142.4, 140.0, 126.7, 110.1, 75.6, 35.3, 25.8. IR (film): 3441, 2956, 2908, 2871, 1501, 1480, 1465, 1365, 1215, 1159, 1047, 1022, 1007.

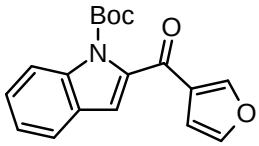


2h

1-(3-furyl)prop-2-en-1-ol (2h)

A 100 mL, three-necked, flam-dried round bottom flask equipped with magnetic stirring bar, was laoded with 3-furaldehyde (874 mg, 9.1 mmol) and dried diethylether (10 mL) under argon. The solution was cooled to 0 °C and a solution of the vinyl Grignard 1 M in THF (10 mL; 10 mmol) was added gently. The reaction mixture was allowed to warm to room temperature and then stirred for 5 minutes. The progress was monitored by LC-MS. After 5 minutes, the reaction was quenched by addition of water (15 mL). The amount of the resulting emulsion was decrease with HCl 1M without reaching into acidic conditions. The reaction mixture was transferred in a separating funnel. The aqueous phase was extracted with diethyl ether (1 x 50 mL). Organic phases were combined, dried over anhydrous $MgSO_4$, and partially concentrated under reduced pressure in order to obtain a solution of **15** in a THF and diethyl ether mixture. This solution is used as crude for the next step.

Data from a solution of 55% (^{1}H NMR estimation) of **2h** in THF and diethyl ether mixture. *Rf* = 0.90 (DCM). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 1.95 (br. s., 1 H) 5.17 (t, *J*=5.18 Hz, 1 H) 5.21 (dt, *J*=10.11, 1.26 Hz, 1 H) 5.36 (dt, *J*=17.18, 1.26 Hz, 1 H) 5.95 - 6.18 (m, 1 H) 6.40 (s, 1 H) 7.28 - 7.56 (m, 2 H). ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ ppm 68.21, 109.08, 115.56, 127.72, 139.47, 139.53, 143.59. LC-MS: 2.58 min.

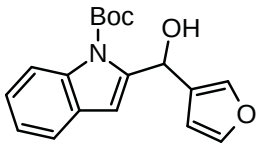


10

***tert*-butyl 2-(3-furoyl)-1*H*-indole-1-carboxylate (10)**

To a dry 100 mL round-bottomed flask was added 8 mL of THF and 0.68 mL (4 mmol) of 2,2,6,6-tetramethylpiperidine. The mixture was cooled to -80 °C, and 4 mmol of n-butyllithium was added. The mixture was stirred 5 min at -80 °C and 5 min at -10 °C and then cooled to -80 °C. To this mixture was added 0.67 mL (4 mmol) of *N*-Boc-indole, and the mixture was stirred a further 45 min at -80 °C. Ethyl 3-furoate. (0.54 mL, 4.0 mmol) was added dropwise.

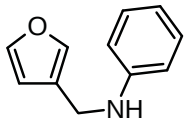
The mixture was stirred at -80 °C. The consumption of ethyl 3-furoate was monitored by LC -MS and after 2.3 h, water was added to the mixture at -80 °C. The solution was immediately allowed to warm to room temperature, the organic layer separated, and 20 mL of ether was added. The organic layer was washed twice with NH_4Cl sat. Removal of the solvent on the rotary evaporator yielded an oil which was chromatographied (SiO_2, Gradient: DCM/Hex 50/50 → DCM) to obtain 0.139 mg (0.446 mmol, 11 %) of brown oil. R_f = 0.40 (DCM). ^{1}H NMR (360 MHz, CHLOROFORM-*d*) δ ppm 1.49 (s, 9 H) 6.94 (s, 1 H) 7.00 (s, 1 H) 7.28 - 7.35 (m, 1 H) 7.45 (t, *J*=7.72 Hz, 1 H) 7.52 (s, 1 H) 7.63 (d, *J*=8.17 Hz, 1 H) 7.98 (s, 1 H) 8.17 (d, *J*=8.63 Hz, 1 H). ^{13}C NMR (91 MHz, CHLOROFORM-*d*) δ ppm 27.69, 84.96, 109.35, 114.18, 115.14, 122.31, 123.56, 126.97, 127.73, 128.09, 137.68, 137.85, 144.53, 148.95, 149.27, 180.74. IR (neat): 3132, 2980, 1737, 1651, 1394, 1368, 1324, 1257, 1219, 1154, 1103, 1020, 872, 789, 746. HRMS-ESI (m/z): Calcd for $C_{18}H_{17}NO_4Na$, 334.1050; found, 334.1055. LC-MS: 4.61 min.



2i

***tert*-butyl 2-[3-furyl(hydroxy)methyl]-1*H*-indole-1-carboxylate (2i)**

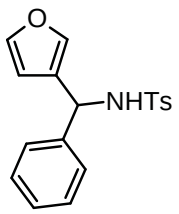
tert-butyl 2-(3-furoyl)-1*H*-indole-1-carboxylate (**10**) (0.135 g, 0.434 mmol) was reduced using an exess of $NaBH_4$ in MeOH. The reaction was quenched with water. After extraction with DCM and concentration, a brown oil (114 mg, 0.364 mmol, 84 %) was characterized as the desired compound and used without purification for further reaction. R_f = 0.33 (DCM). ^{1}H NMR (360 MHz, CHLOROFORM-*d*) δ ppm 1.70 (s, 9 H) 4.69 (d, *J*=5.00 Hz, 1 H) 6.17 (d, *J*=4.54 Hz, 1 H) 6.47 (d, *J*=9.54 Hz, 2 H) 7.18 - 7.24 (m, 1 H) 7.31 (t, *J*=7.72 Hz, 1 H) 7.43 - 7.51 (m, 3 H) 8.00 (d, *J*=8.17 Hz, 1 H). ^{13}C NMR (91 MHz, CHLOROFORM-*d*) δ ppm 28.58, 64.25, 85.80, 110.18, 110.51, 116.08, 121.51, 123.55, 125.04, 126.84, 129.10, 136.90, 140.44, 142.90, 143.32, 151.99. IR (film): 3435, 2979, 1730, 1711, 1453, 1370, 1328, 1157, 1118, 1026, 874, 745. HRMS-ESI (m/z): Calcd for $C_{18}H_{19}NO_4Na$, 336.1206; found, 336.1207. LC-MS: 4.41 min.



8a

***N*-(3-furylmethyl)aniline (8a)**

A 100 mL three-necked flam-dried round-bottom flask equipped with magnetic stirring bar, was loaded with 3-furaldehyde **(1)** (2 g, 20.8 mmol), aniline (2.09 g, 22.9 mmol) and dried ethanol (50 mL) under argon. The reaction mixture was warmed up to reflux. The progress was monitored using NMR. After 4h, $NaBH_4$ (787 mg, 20.8 mmol) was added in portion while stirring at 0°C. The reaction mixture was warmed up to reflux for 30 min. The reaction mixture was carefully quenched by addition of water and then extracted with ether, dried and concentrated under vacuum to yield a brown liquid (3.377 g, 94%). The product is pure enough for further use without purification. *Rf* = 0.50 (DCM). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 3.84 (br. s., 1 H) 4.18 (s, 2 H) 6.43 (d, *J*=1.51 Hz, 1 H) 6.68 (dd, *J*=8.59, 1.04 Hz, 2 H) 6.75 (dt, *J*=14.64, 0.99 Hz, 1 H) 7.21 (dd, *J*=8.50, 7.36 Hz, 2 H) 7.39 - 7.44 (m, 2 H). ^{13}C NMR (91 MHz, CHLOROFORM-*d*) δ ppm 39.51, 110.31, 113.11, 117.94, 123.46, 129.40, 140.11, 143.45, 148.11. IR (neat): 3410, 3050, 2847, 1602, 1503, 1432, 1316, 1247, 1157, 1063, 1020, 873, 751, 693. HRMS-ESI (*m/z*): Calcd for $C_{11}H_{12}N_1O_1Na$, 174.0913; found, 174.0914. LC-MS: 3.43 min.

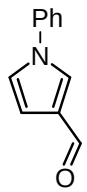


8b

***N*-[3-furyl(phenyl)methyl]-4-methylbenzenesulfonamide (8b)**

To a stirred mixture of 3-furaldehyde (**1)** (960 mg, 10 mmol) and *p*-tosylamide (1884 mg, 11 mmol) in methylene chloride (50 mL) was added trifluoroacetic anhydride (2.31 g, 11 mmol) and heated to reflux for 12 h. The reaction mixture was poured into cold water and extracted with DCM. The organic layers were dried ($MgSO_4$) and evaporated to obtain the tosylimine witch was used as crude for the next step.

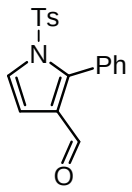
Following the general procedure B from the crude tosylimine and phenyl Grignard (11 mmol) yielded the desired tosylamine **8b** (2.69 g, 74 %) as a white solid after flash chromatography (SiO_2, DCM). *Rf* = 0.22 (DCM). ^{1}H NMR (360 MHz, CHLOROFORM-*d*) δ ppm 2.43 (s, 3 H) 5.34 (d, *J*=7.72 Hz, 1 H) 5.53 (d, *J*=7.72 Hz, 1 H) 6.17 (s, 1 H) 7.06 (s, 1 H) 7.12 - 7.39 (m, 8 H) 7.63 (d, *J*=8.17 Hz, 2 H), ^{13}C NMR (91 MHz, CHLOROFORM-*d*) δ ppm 21.62, 54.24, 109.60, 126.38, 127.16, 127.24, 127.89,128.64, 129.51, 137.54, 139.83, 140.64, 143.39, 143.72. IR (neat): 3244, 3032, 2922, 2868, 1598, 1497, 1434, 1316, 1153, 1095, 1049, 1018, 931. 874, 835, 811, 681. HRMS-ESI (*m/z*): Calcd for $C_{18}H_{17}N_1O_3SNa$, 350.0821; found, 350.0816. LC-MS: 4.16 min.



9a

1-phenyl-1*H*-pyrrole-3-carbaldehyde (9a)

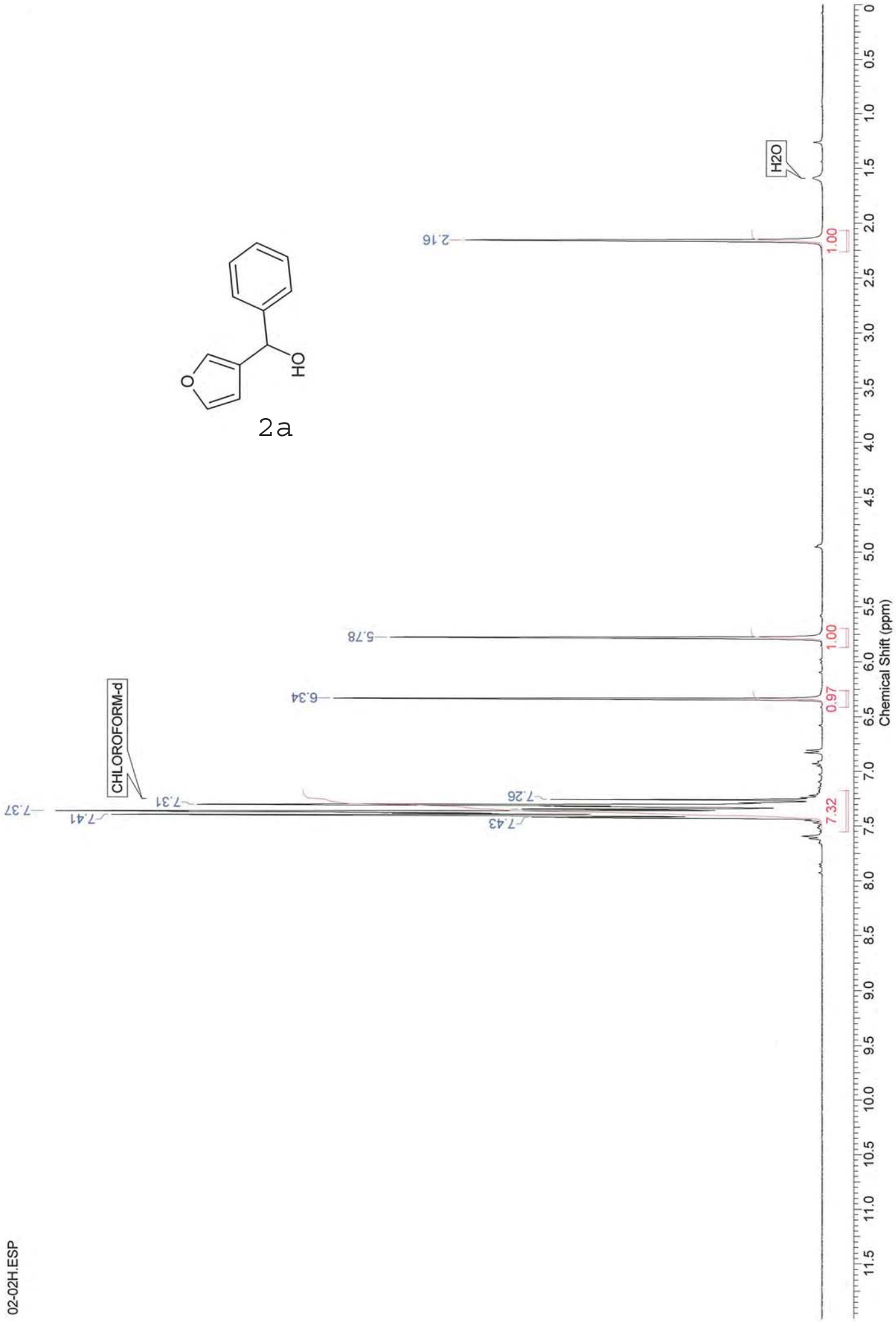
Following the general procedure A from 1-(3-furyl)-1-phenylmethanamine **8a** (199 mg) yielded a mixture of desired aldehyde as a yellow oil (125 mg, 64 %) and starting material (35 mg, 18 %) after flash chromatography (SiO_2, DCM). R_f = 0.17 (DCM). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 6.81 (dd, *J*=3.02, 1.70 Hz, 1 H) 7.09 (t, *J*=2.36 Hz, 1 H) 7.34 - 7.52 (m, 5 H) 7.67 (d, *J*=1.70 Hz, 1 H) 9.86 (s, 1 H). ^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 109.76, 121.30, 122.47, 127.29, 127.50, 128.30, 130.02, 139.71, 185.65. IR (neat): 3120, 2920, 2851, 1671, 1599, 1537, 1510, 1461, 1355, 1272, 1208, 1082, 1050, 806, 750, 690. HRMS-ESI (*m/z*): Calcd for $C_{11}H_9NONa$, 194.0576; found, 194.0582. LC-MS: 3.50 min.



9b

1-[(4-methylphenyl)sulfonyl]-2-phenyl-1*H*-pyrrole-3-carbaldehyde (9b)

Following the general procedure A from *N*-[3-furyl(phenyl)methyl]-4-methylbenzenesulfonamide **8b** (377 mg) yielded the desired aldehyde as a colourless liquid (309 mg, 92 %) after flash chromatography (SiO_2, DCM). R_f = 0.19 (DCM). ^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ ppm 2.38 (s, 3 H) 6.77 (d, *J*=3.59 Hz, 1 H) 7.10 - 7.24 (m, 6 H) 7.36 (t, *J*=7.55 Hz, 2 H) 7.44 - 7.52 (m, 2 H) 9.34 (s, 1 H). ^{13}C NMR (91 MHz, CHLOROFORM-*d*) δ ppm 21.82, 108.52, 123.77, 127.19, 127.73, 127.75, 128.17, 129.83, 129.99, 132.31, 134.90, 143.22, 145.88, 186.87. IR (neat): 3151, 3064, 2830, 2746, 1674, 1596, 1472, 1424, 1376, 1303, 1176, 1127, 956, 763, 682. HRMS-ESI (*m/z*): Calcd for $C_{18}H_{16}N_1O_3SNa$, 326.0845; found, 326.0848. LC-MS: 4.34 min.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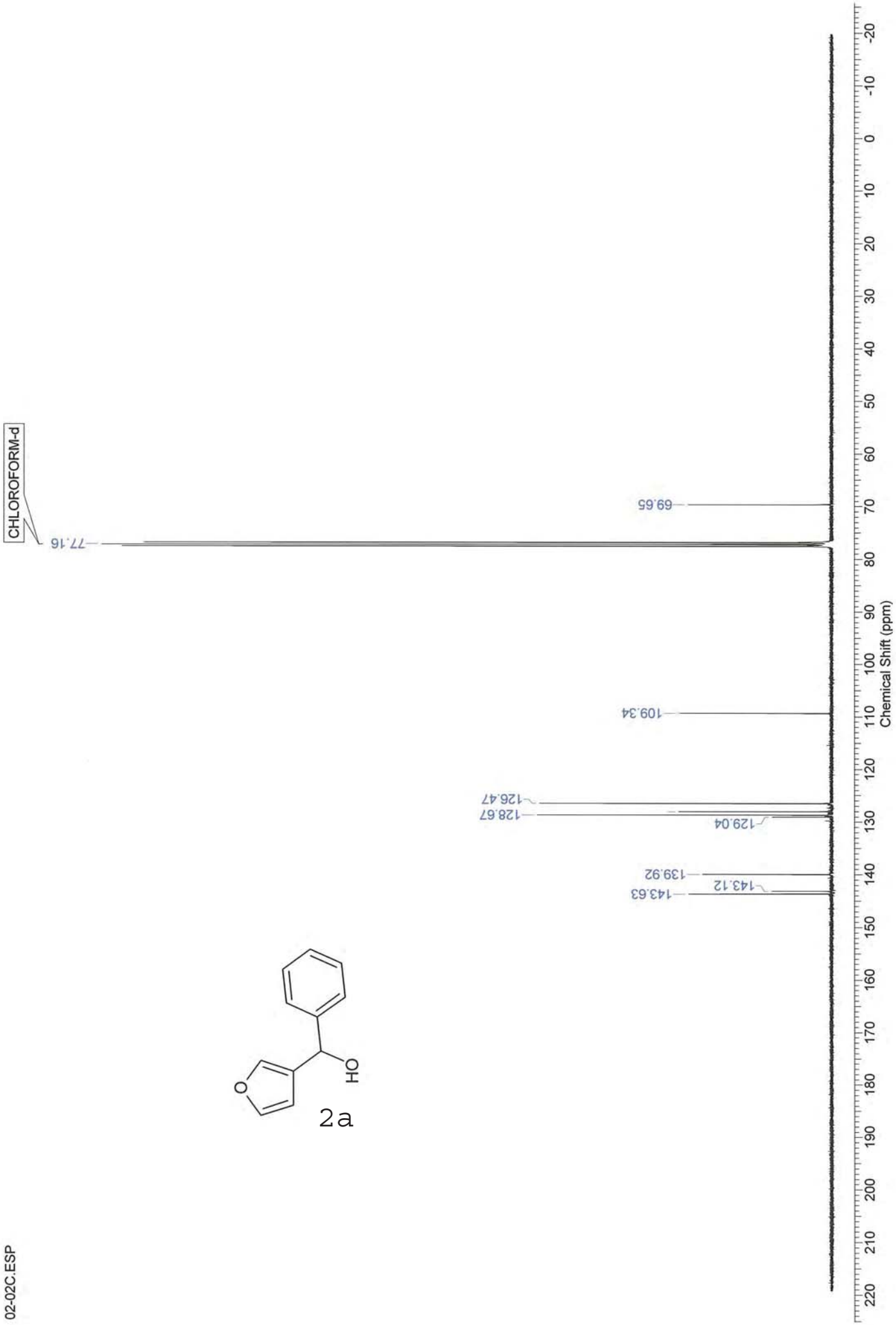
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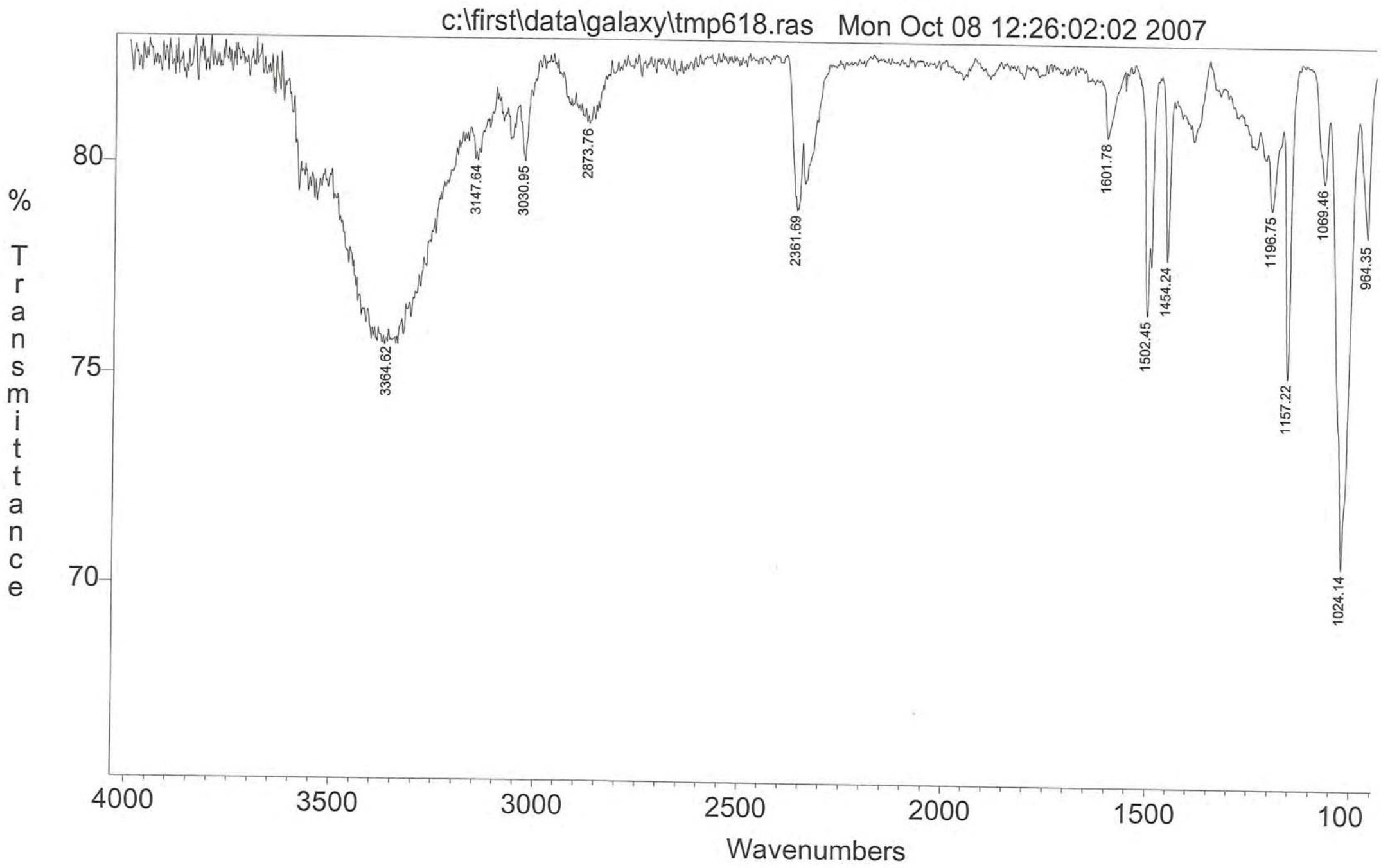
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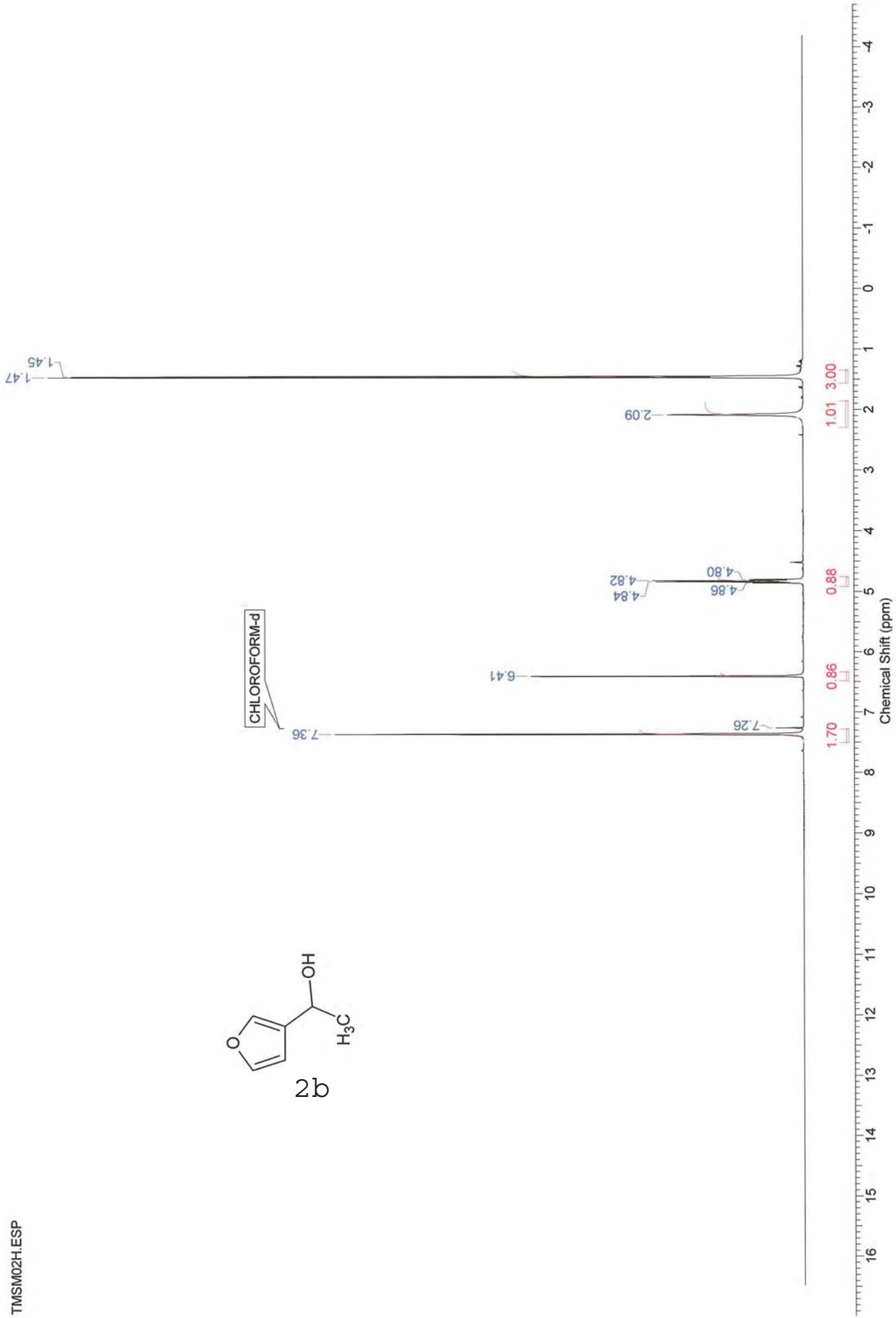
Wavenumbers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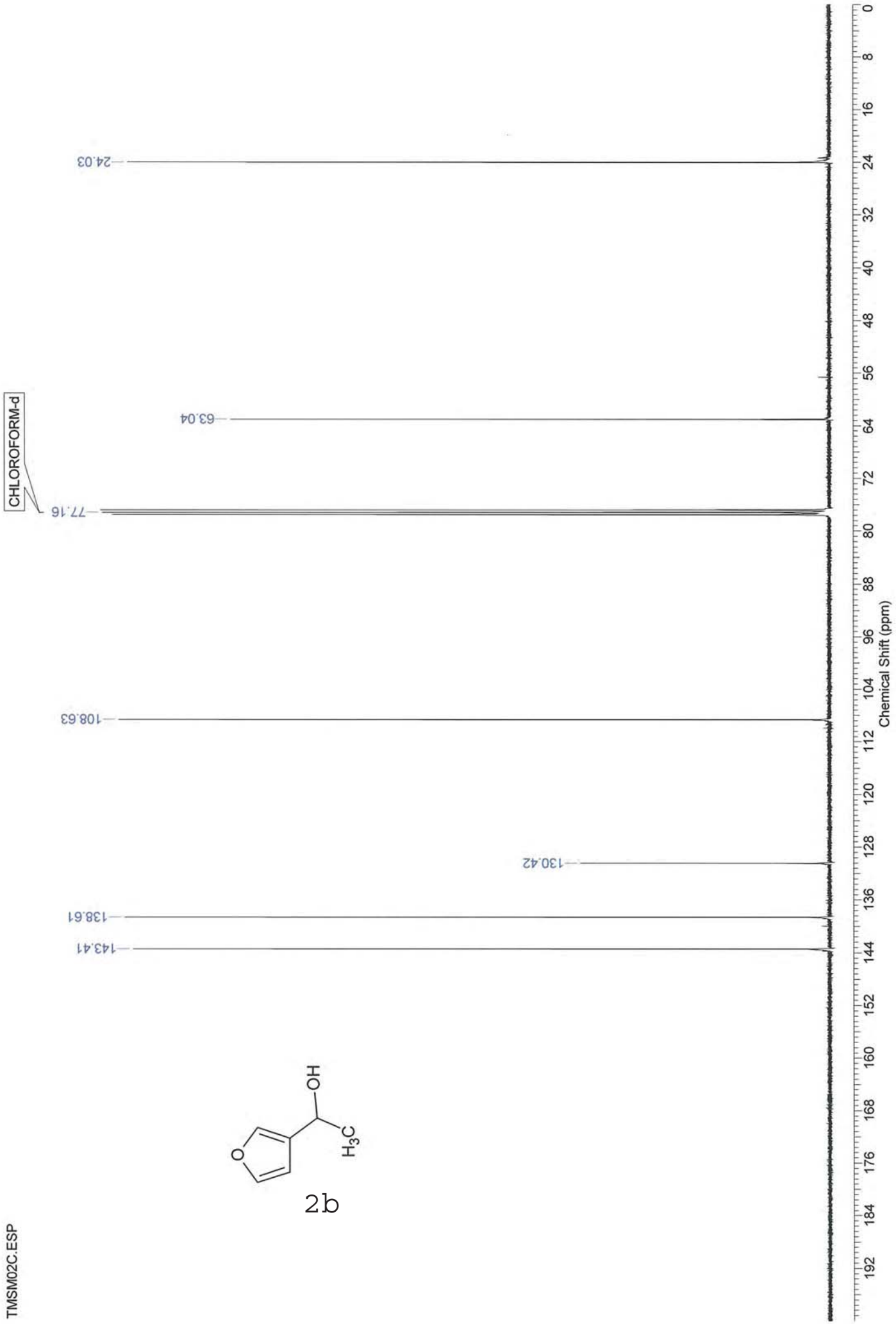
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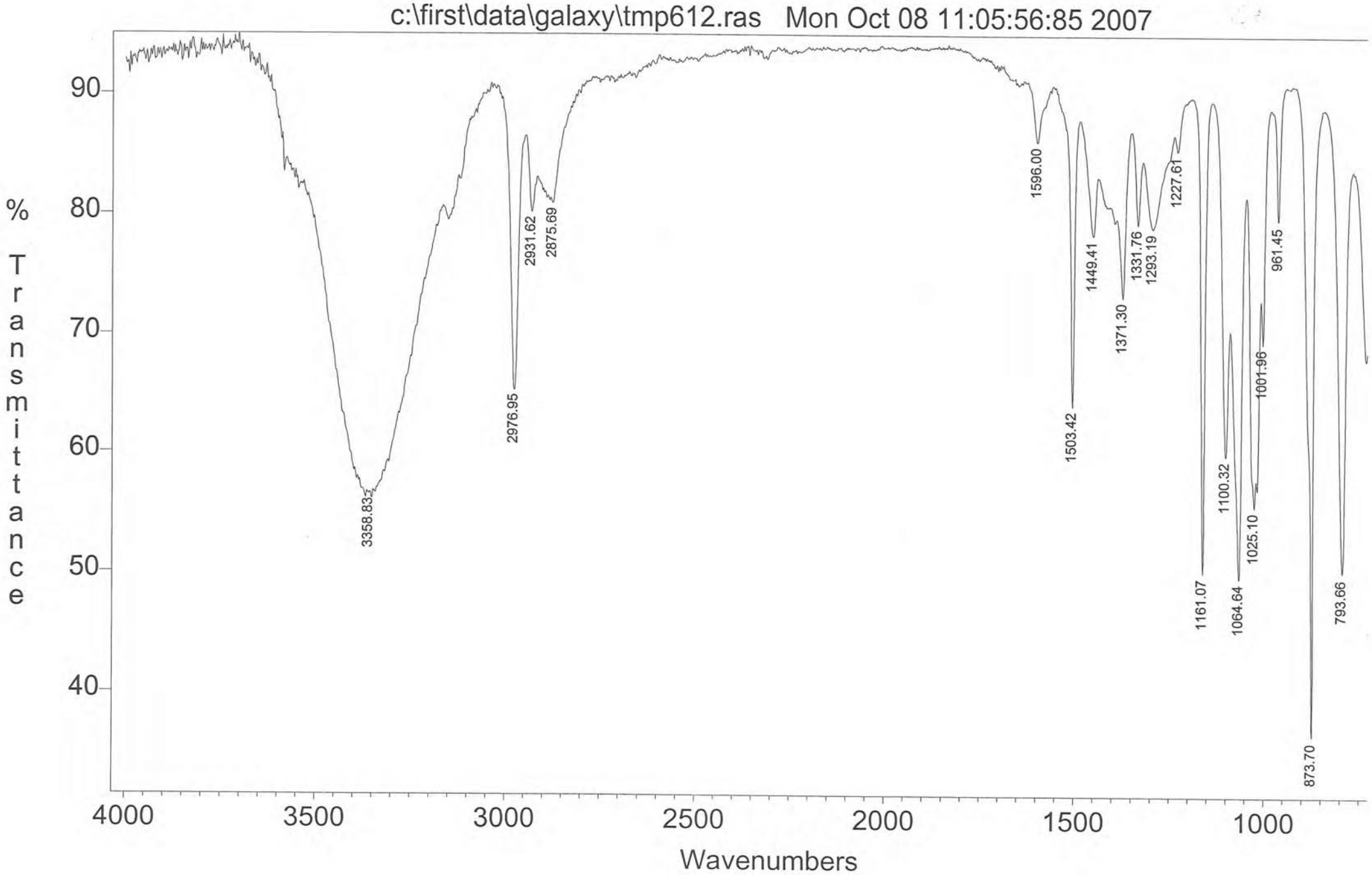
2b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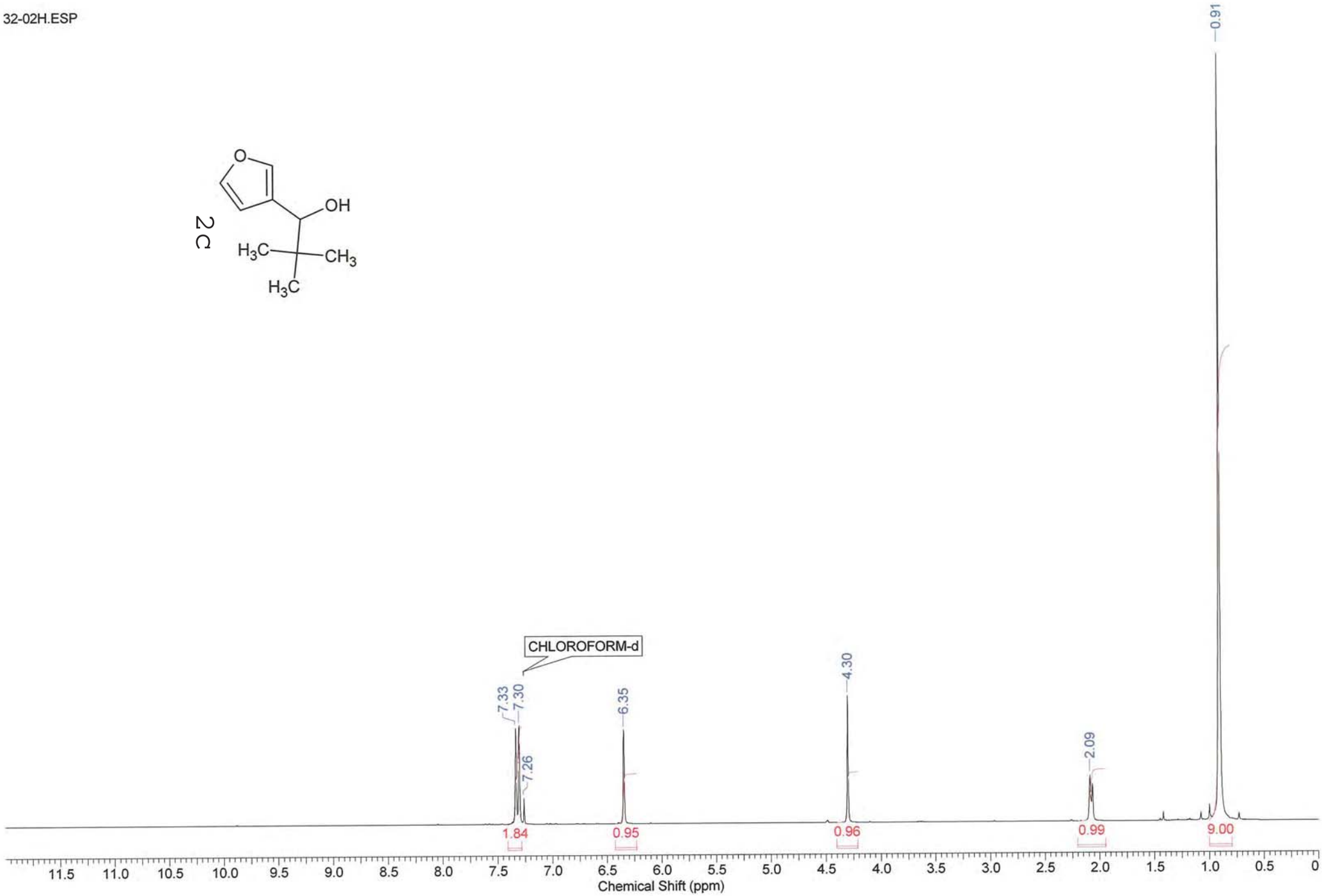
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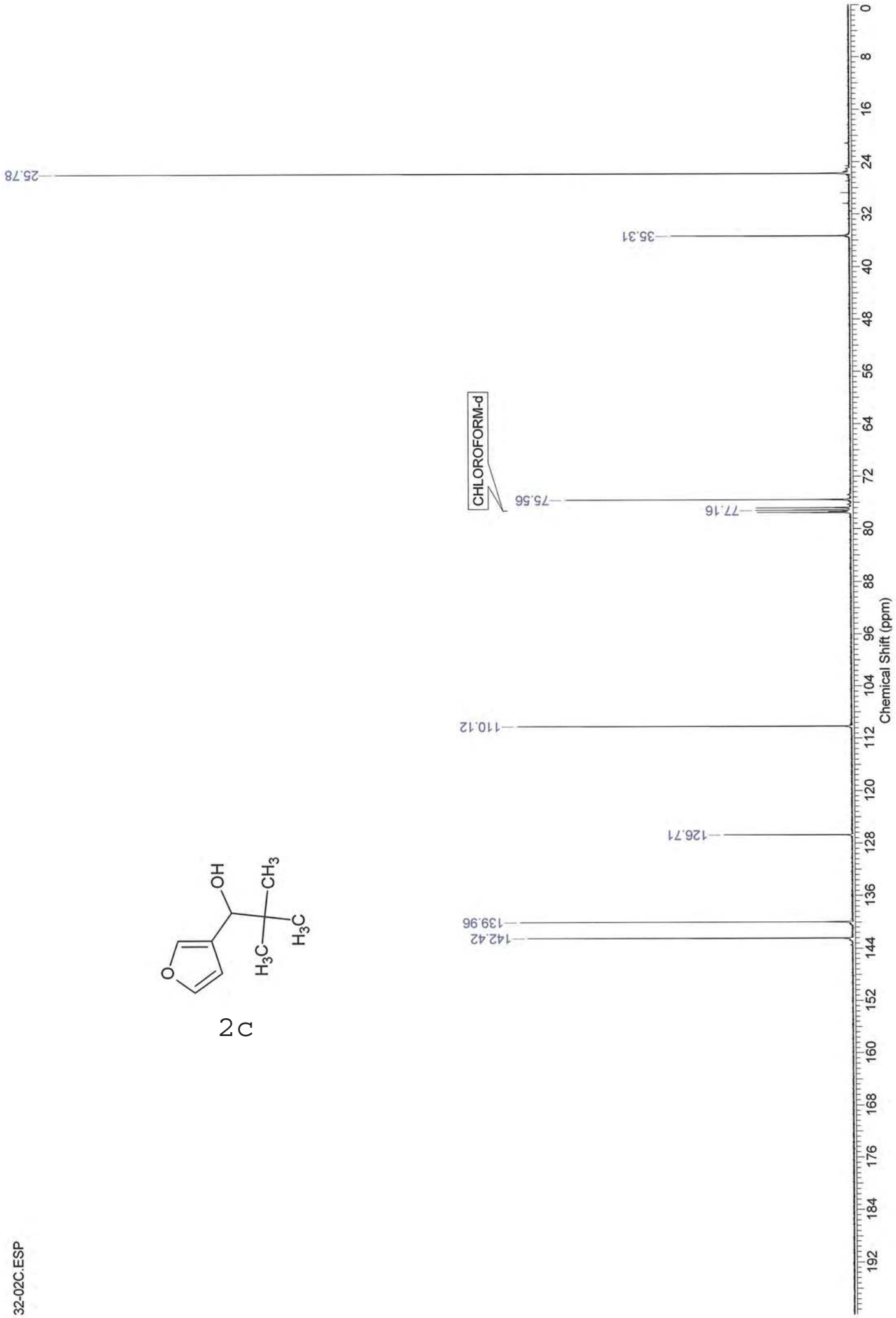
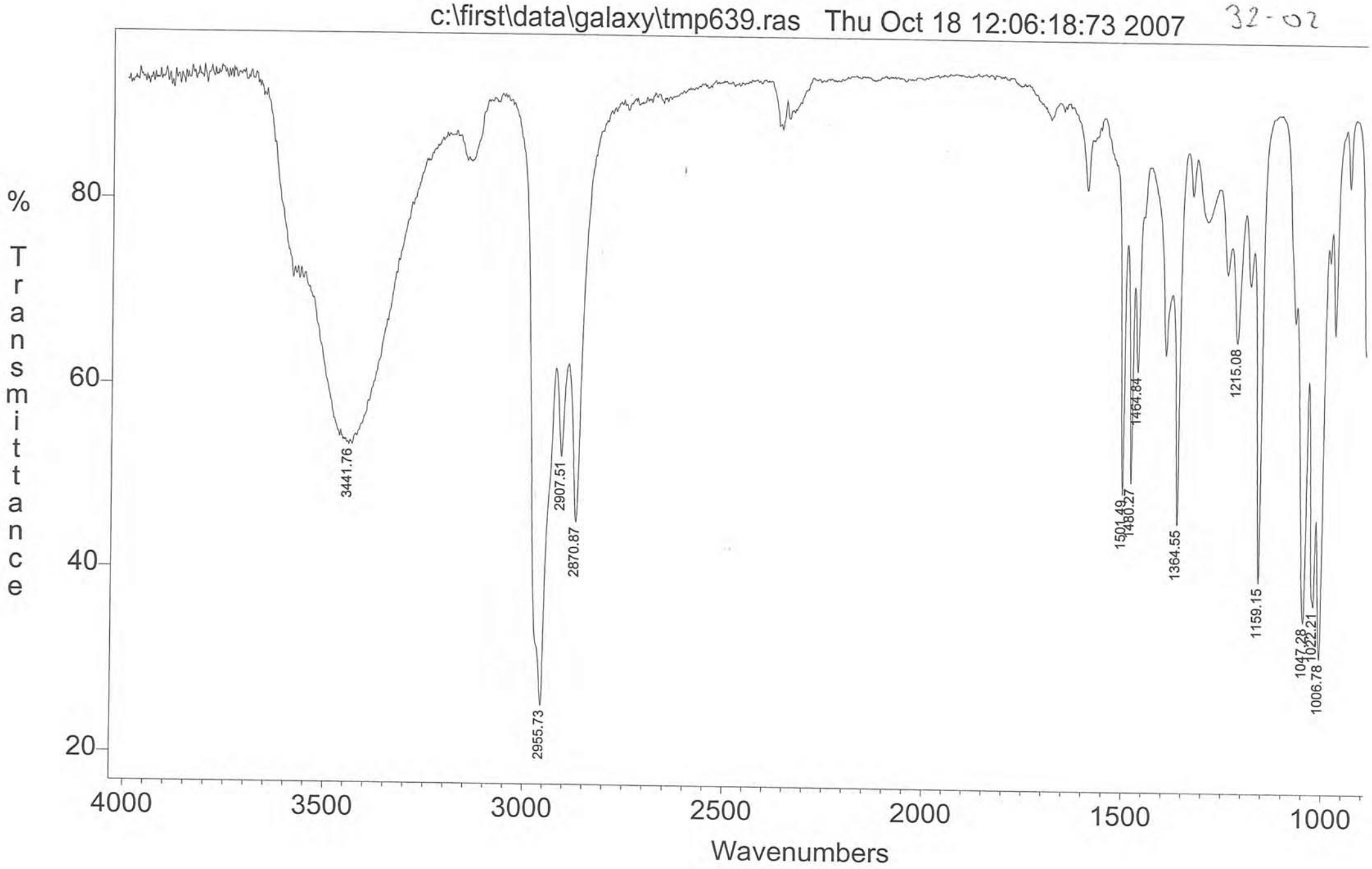
0
Chemical Shift (ppm)

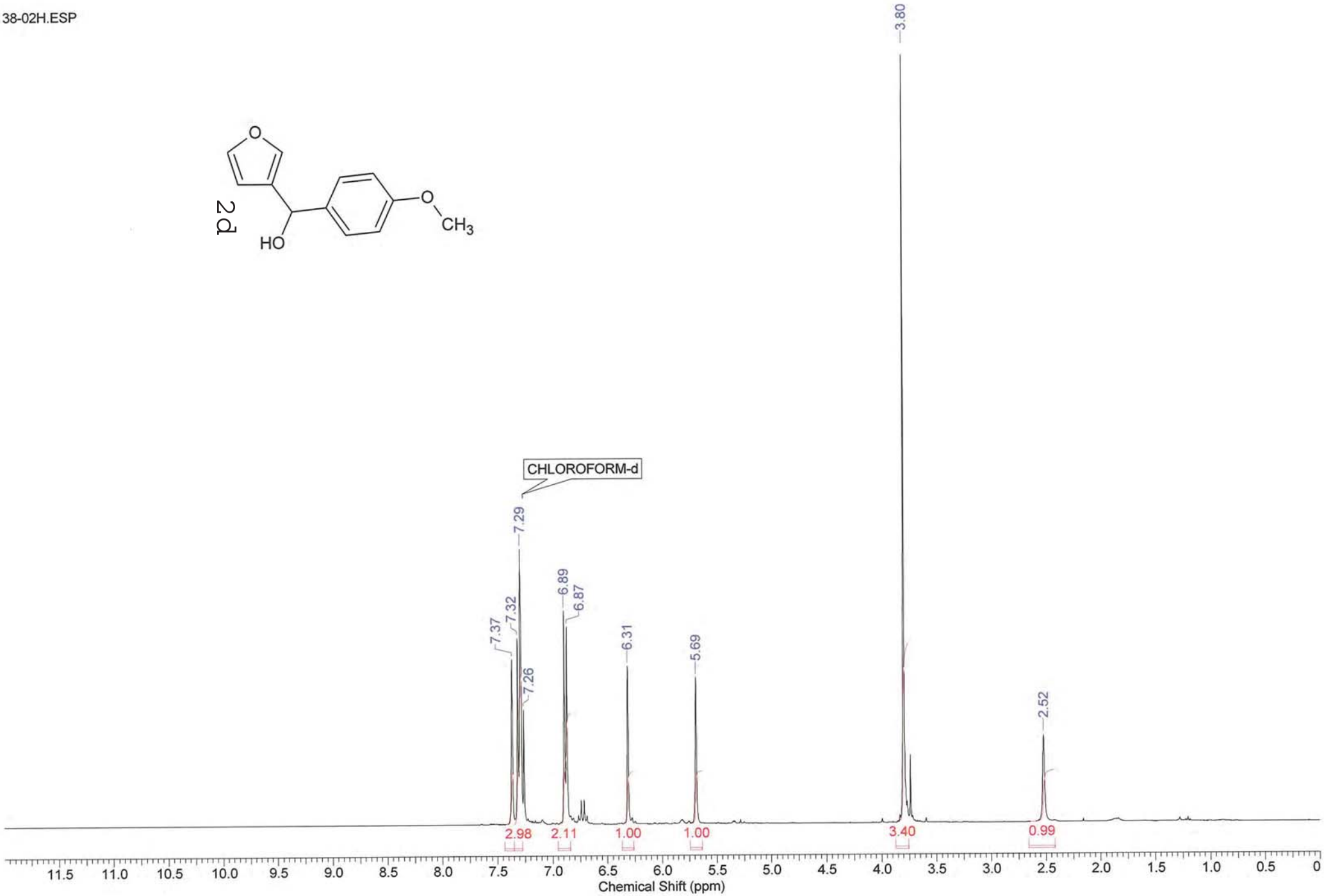

25.78
35.31
CHLOROFORM-d
75.56
77.16
110.12
126.71
139.96
142.42
Chemical Shift (ppm)
0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
128
136
144
152
160
168
176
184
192
OH
CH3
H3C
H3C
O
2c
32-02C.ESP

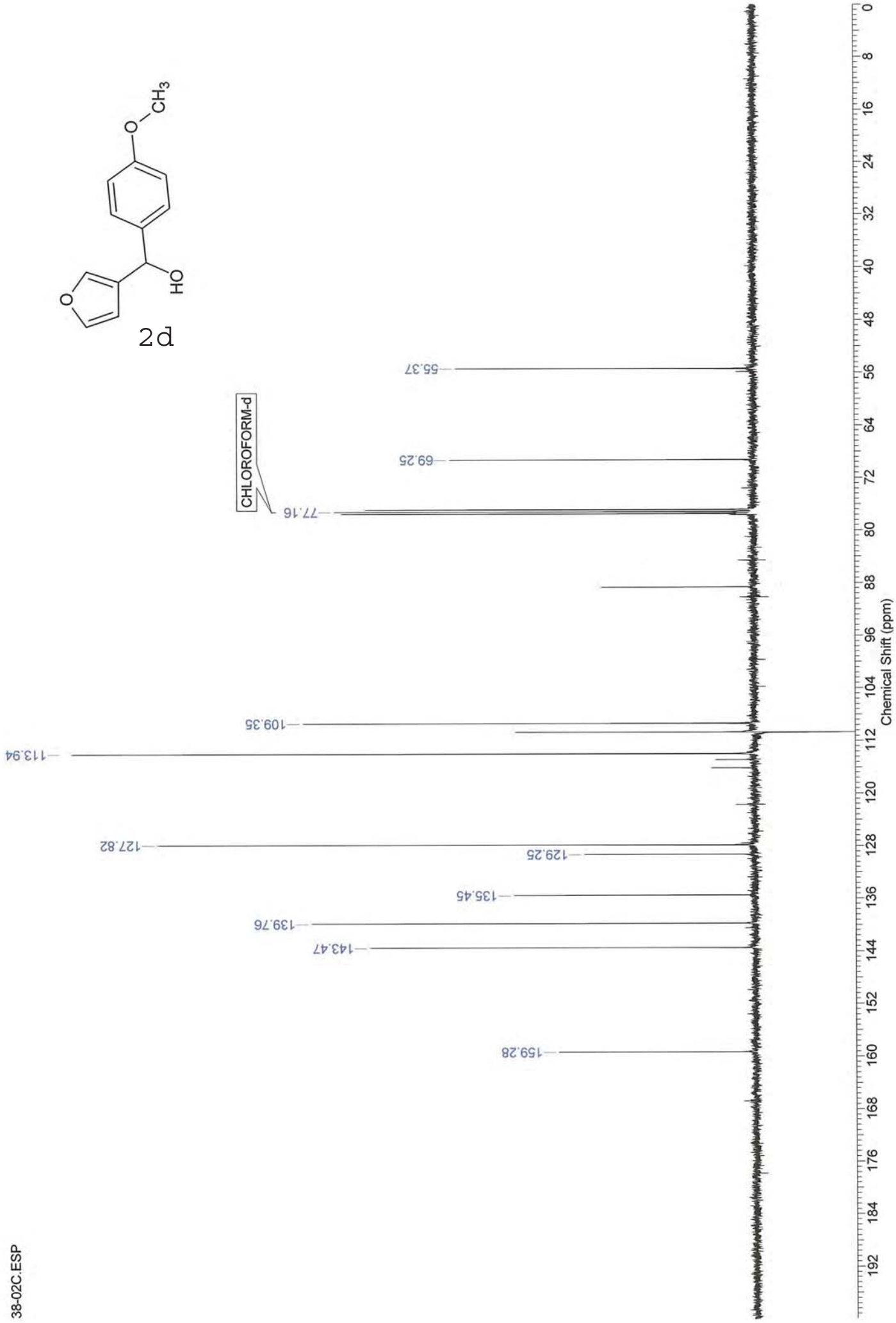

c:\first\data\galaxy\tmp639.ras Thu Oct 18 12:06:18:73 2007
32-02
% Transmittance
80
60
40
20
3441.76
2955.73
2907.51
2870.87
1501.49
1480.27
1464.84
1364.55
1215.08
1159.15
1047.28
1022.21
1006.78
4000
3500
3000
2500
2000
1500
1000
Wavenumbers

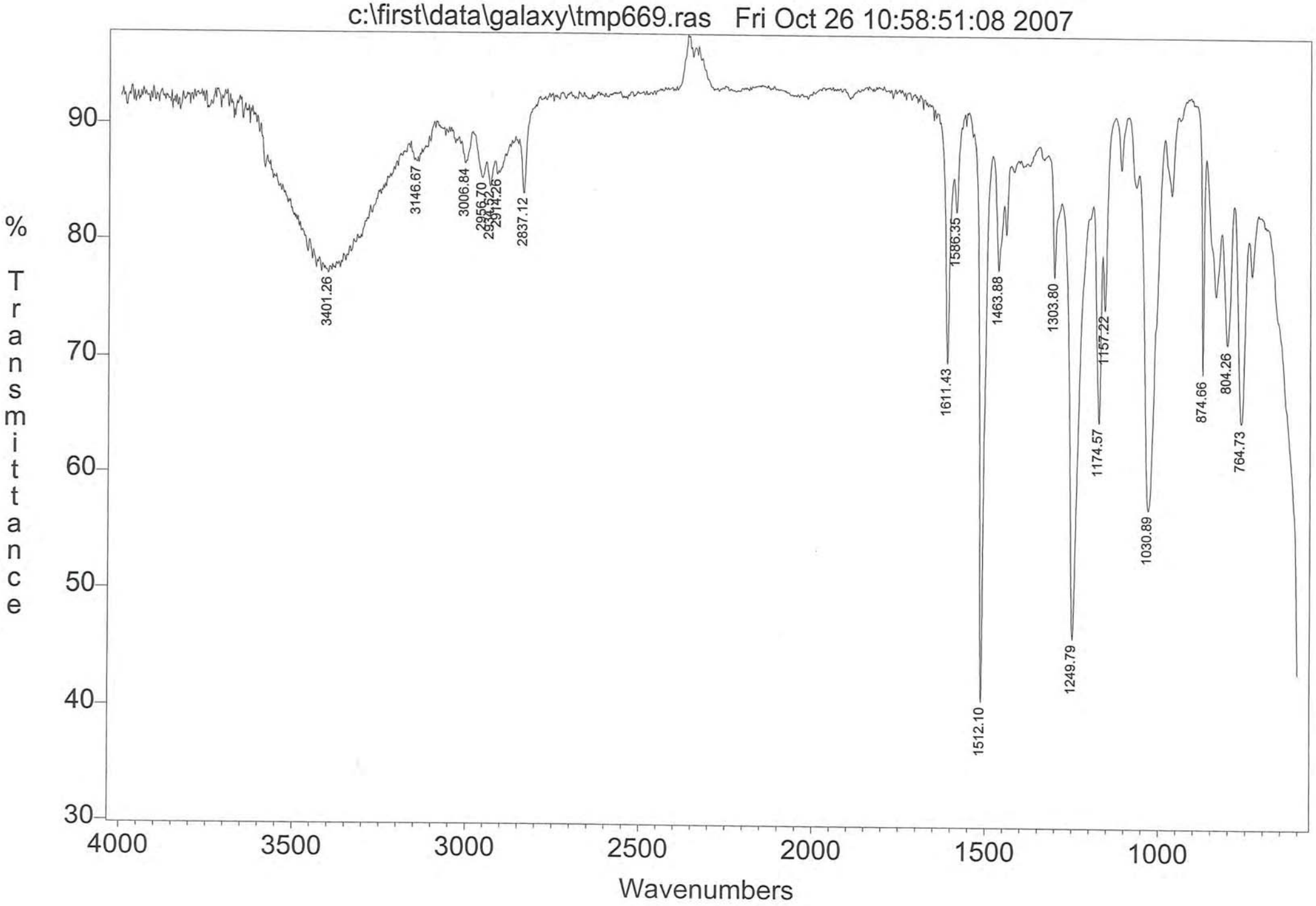
38-02H.ESP

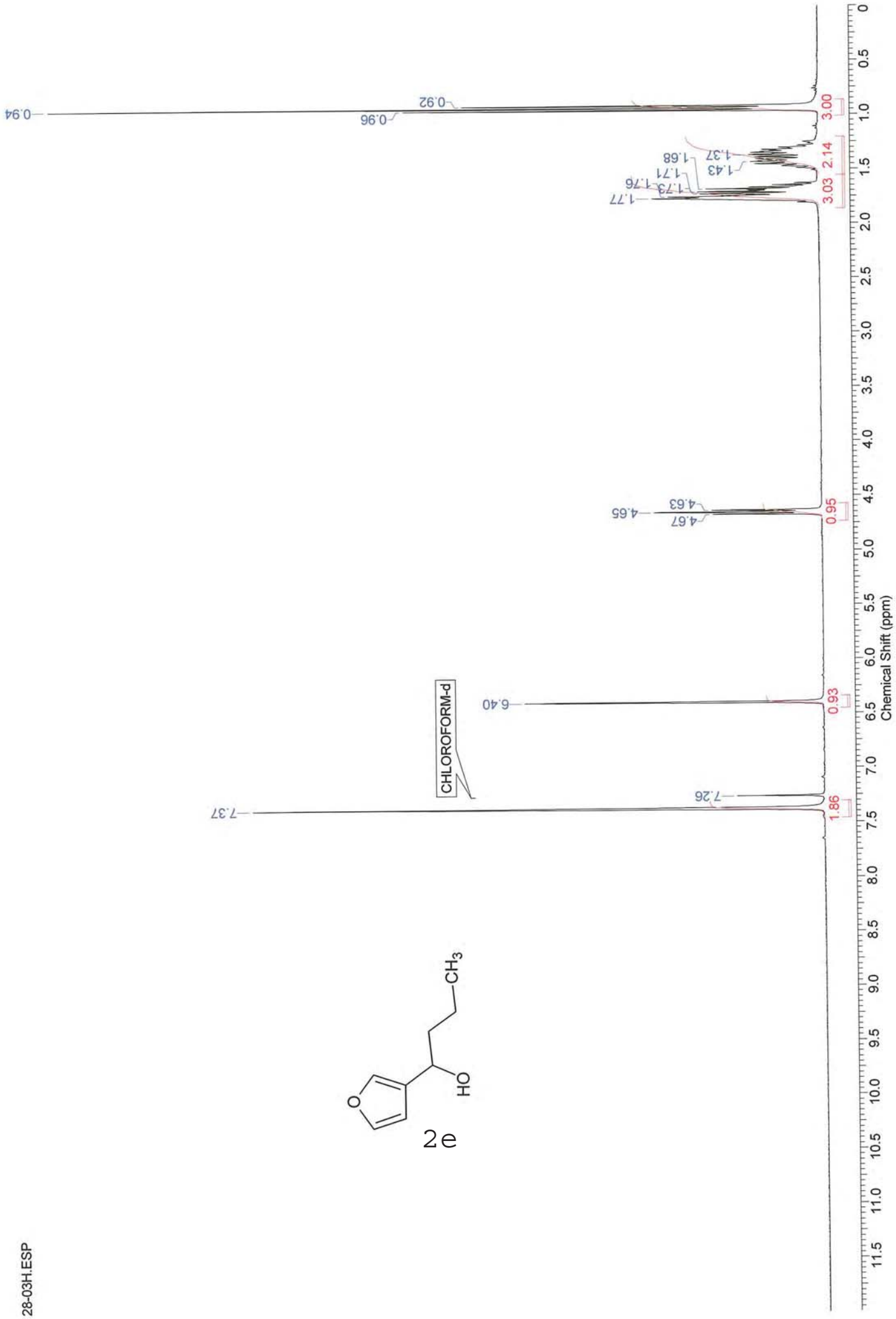
O
O
CH3
HO

2d


3.80
CHLOROFORM-d
7.29
7.37
7.32
7.26
6.89
6.87
6.31
5.69
2.52
2.98
2.11
1.00
1.00
3.40
0.99
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


2d
CHLOROFORM-d
55.37
69.25
77.16
109.35
113.94
127.82
129.25
135.45
139.76
143.47
159.28
38-02C.ESP
Chemical Shift (ppm)

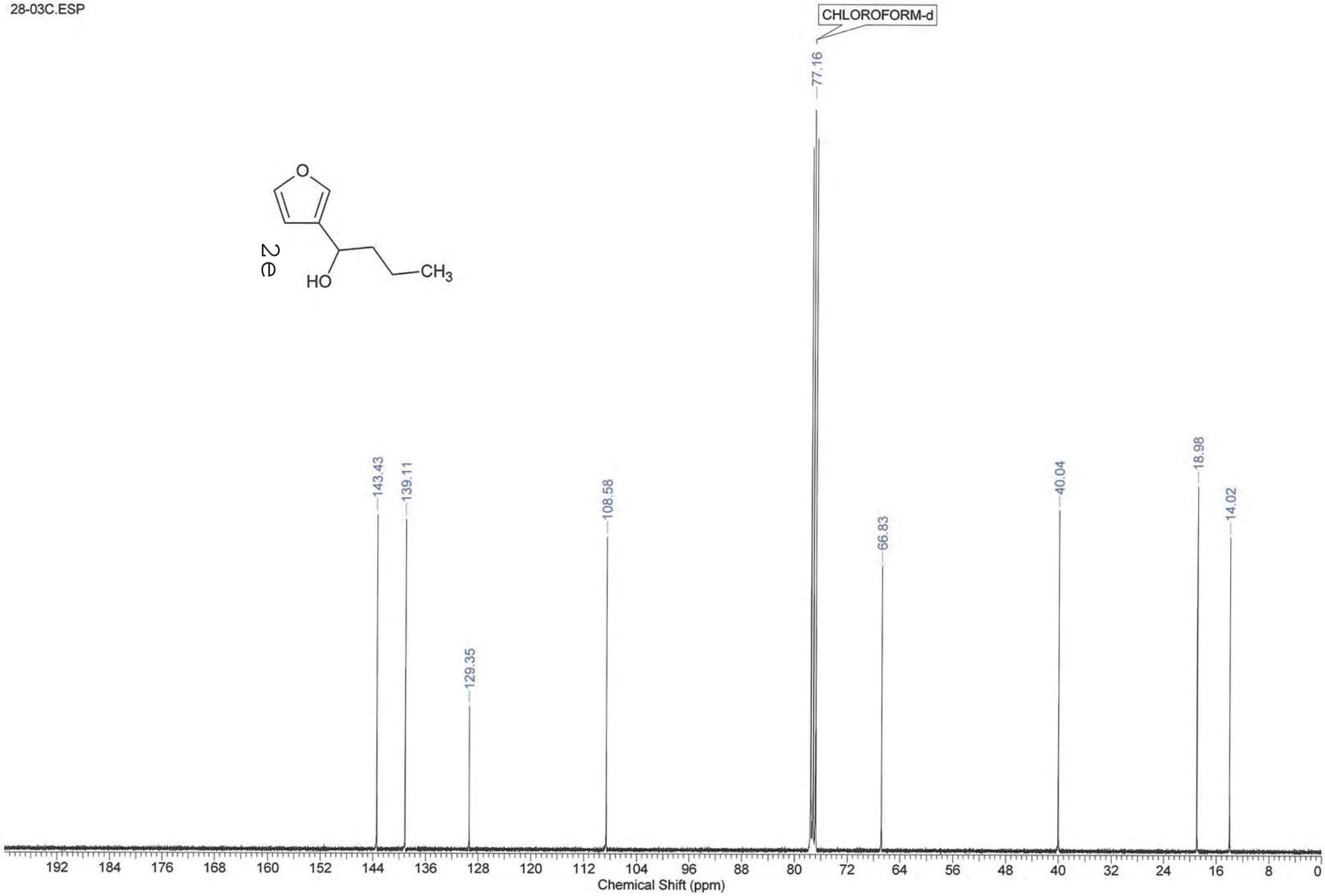

c:\first\data\galaxy\tmp669.ras Fri Oct 26 10:58:51:08 2007
% Transmittance
90
80
70
60
50
40
30
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3401.26
3146.67
3006.84
2956.70
2914.26
2837.12
1611.43
1586.35
1512.10
1463.88
1303.80
1249.79
1174.57
1157.22
1030.89
874.66
804.26
764.73

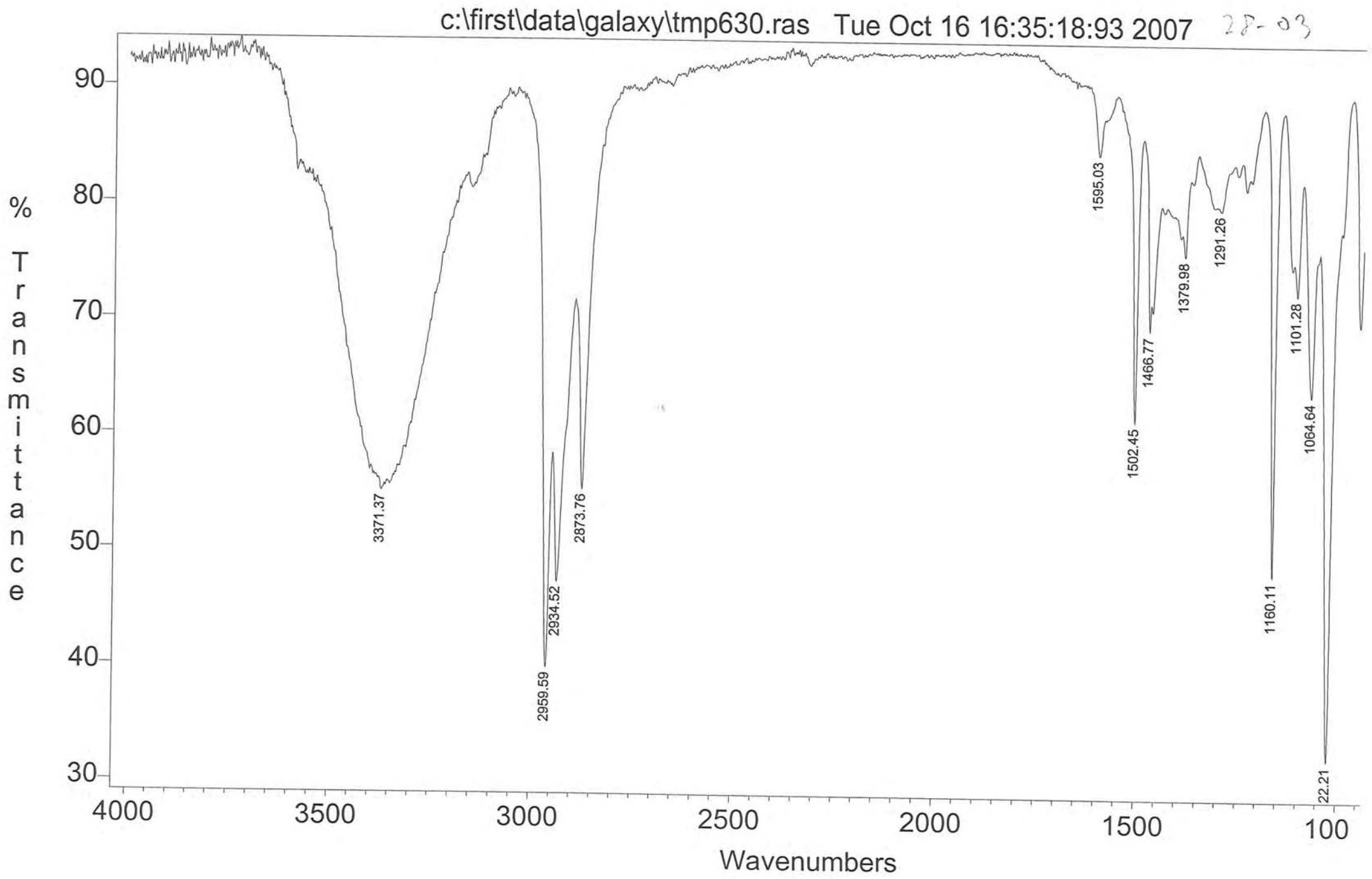

Chemical Shift (ppm)
0.94
0.96
0.92
3.00
1.77
1.73
1.76
1.71
1.68
1.43
1.37
3.03
2.14
4.65
4.67
4.63
0.95
6.40
0.93
CHLOROFORM-d
7.37
7.26
1.86
O
OH
CH3
2e
28-03H.ESP

28-03C.ESP

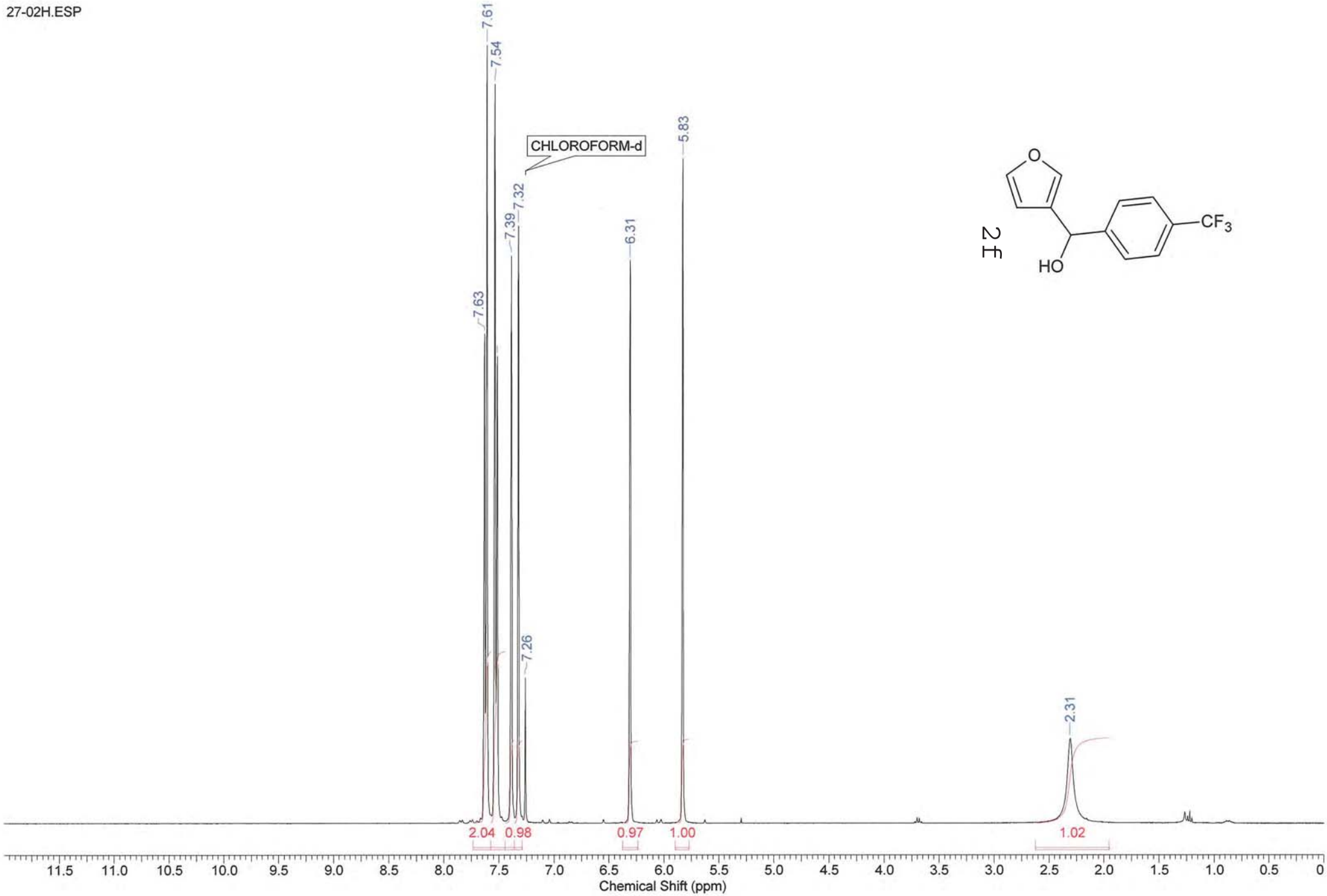
O
HO
CH3

2e


CHLOROFORM-d
77.16
143.43
139.11
129.35
108.58
66.83
40.04
18.98
14.02
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

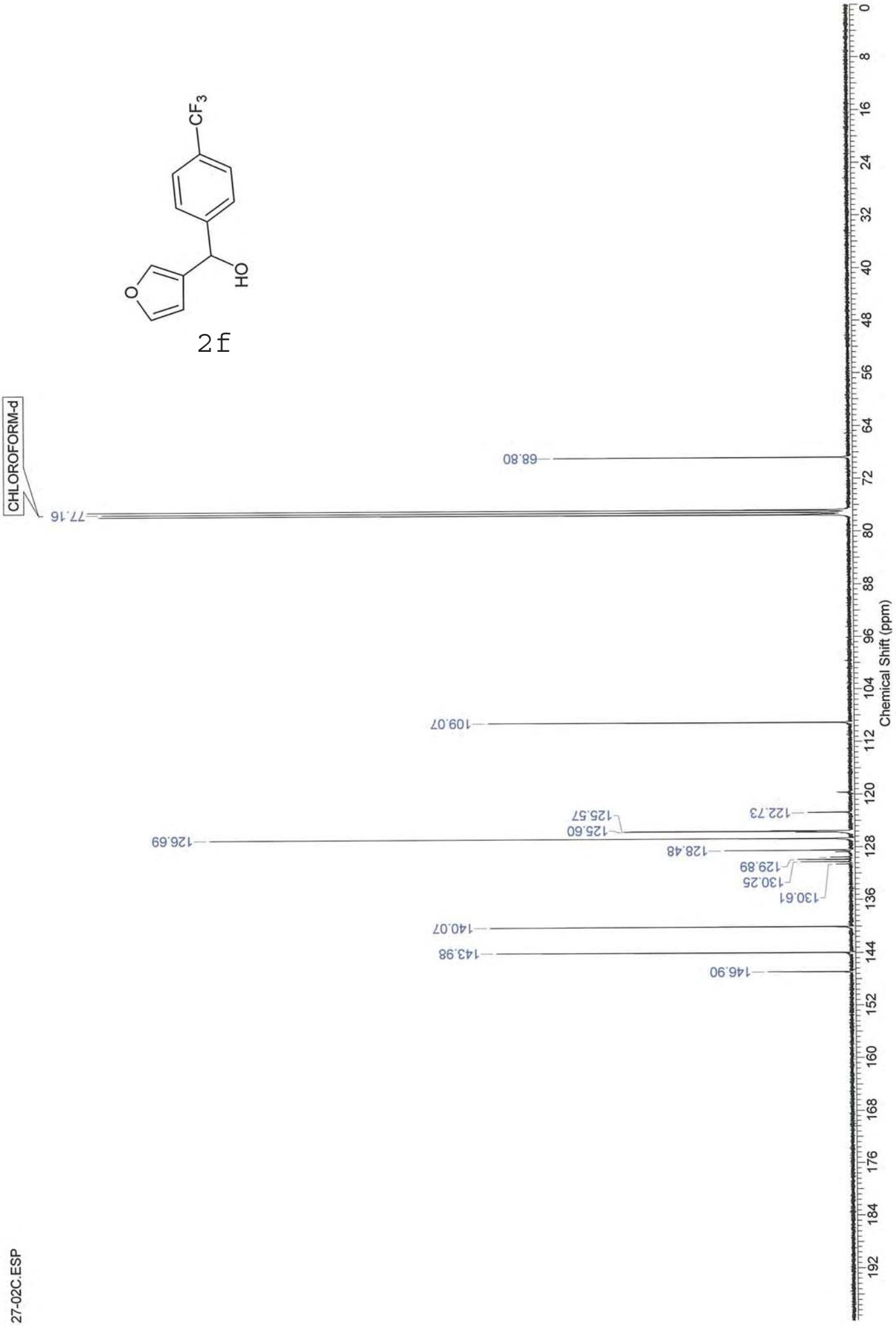

c:\first\data\galaxy\tmp630.ras Tue Oct 16 16:35:18:93 2007
28-03
% Transmittance
90
80
70
60
50
40
30
4000
3500
3000
2500
2000
1500
100
Wavenumbers
3371.37
2959.59
2934.52
2873.76
1595.03
1502.45
1466.77
1379.98
1291.26
1160.11
1101.28
1064.64
22.21

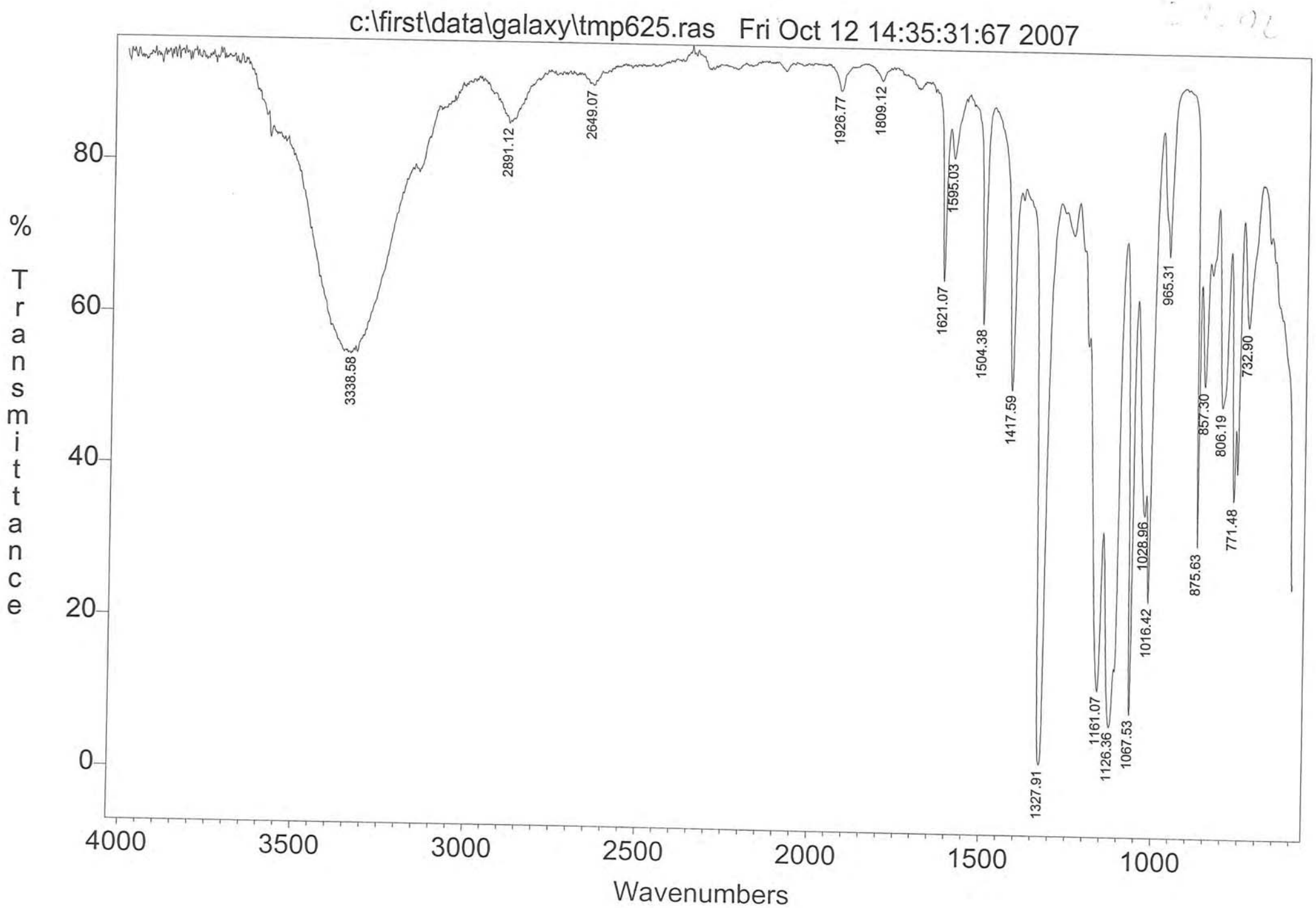
27-02H.ESP

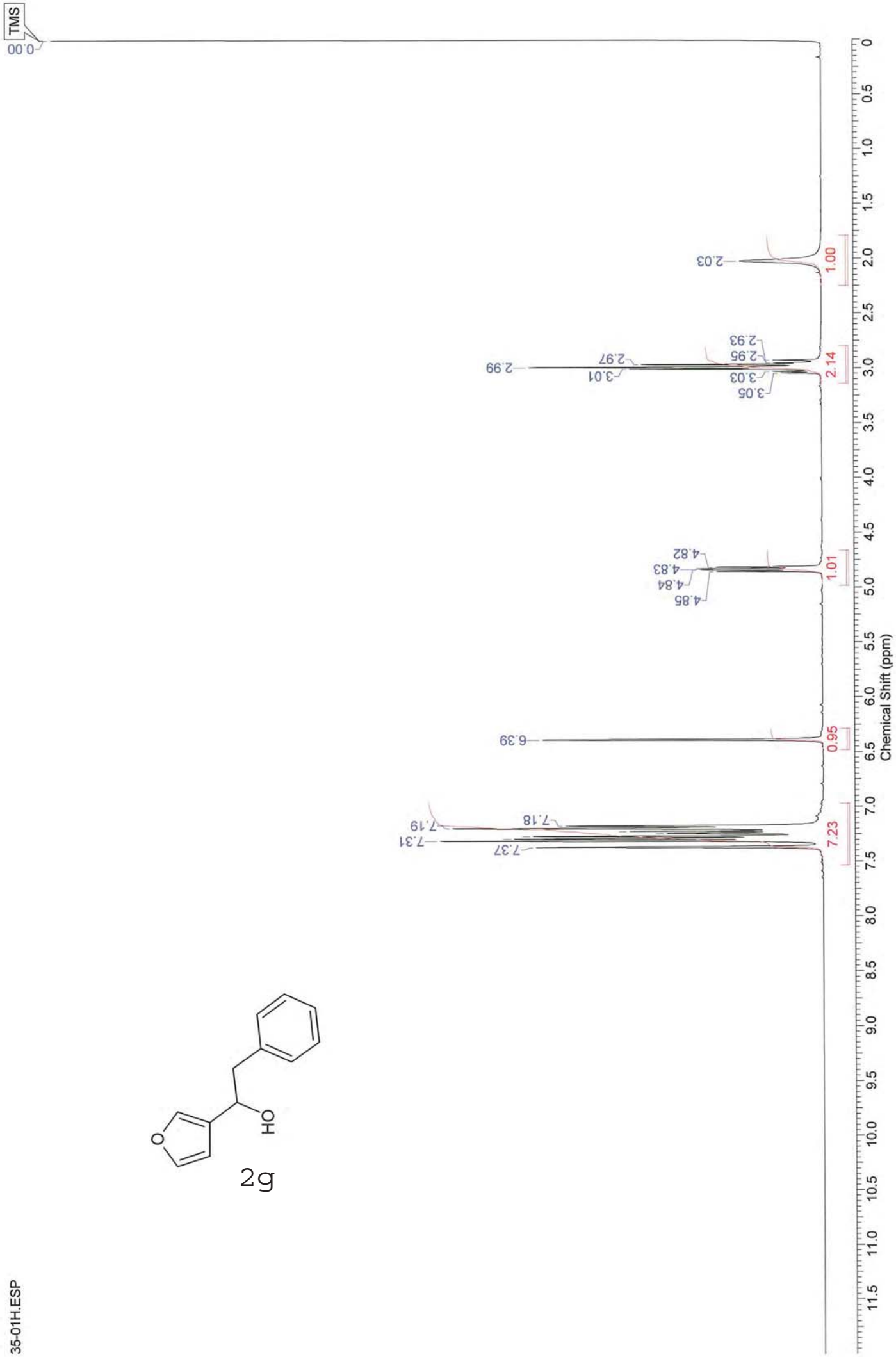

7.61
7.54
7.63
7.39
7.32
7.26
CHLOROFORM-d
6.31
5.83
2.31
2.04
0.98
0.97
1.00
1.02
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

O
CF3
HO

2f


CF3
OH
O
2f
CHLOROFORM-d
77.16
68.80
109.07
122.73
125.57
125.60
126.69
128.48
129.89
130.25
130.61
140.07
143.98
146.90
Chemical Shift (ppm)
27-02C.ESP

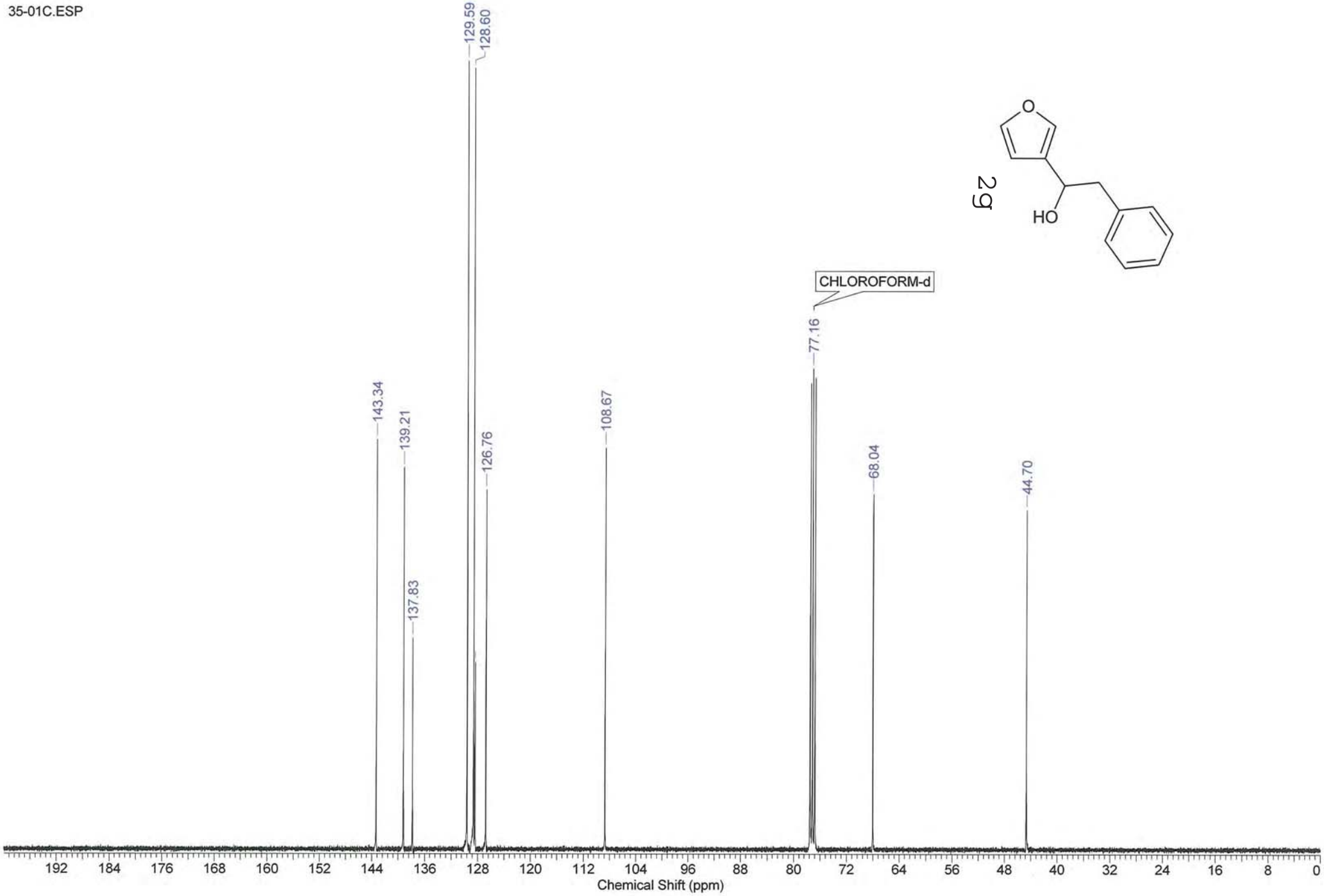

c:\first\data\galaxy\tmp625.ras Fri Oct 12 14:35:31:67 2007
% Transmittance
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3338.58
2891.12
2649.07
1926.77
1809.12
1621.07
1595.03
1504.38
1417.59
1327.91
1161.07
1126.36
1067.53
1028.96
1016.42
965.31
875.63
857.30
806.19
771.48
732.90


TMS
0.00
2.03
1.00
2.93
2.95
2.97
2.99
3.01
3.03
3.05
2.14
4.82
4.83
4.84
4.85
1.01
6.39
0.95
7.18
7.19
7.31
7.37
7.23
Chemical Shift (ppm)
35-01H.ESP

O
OH

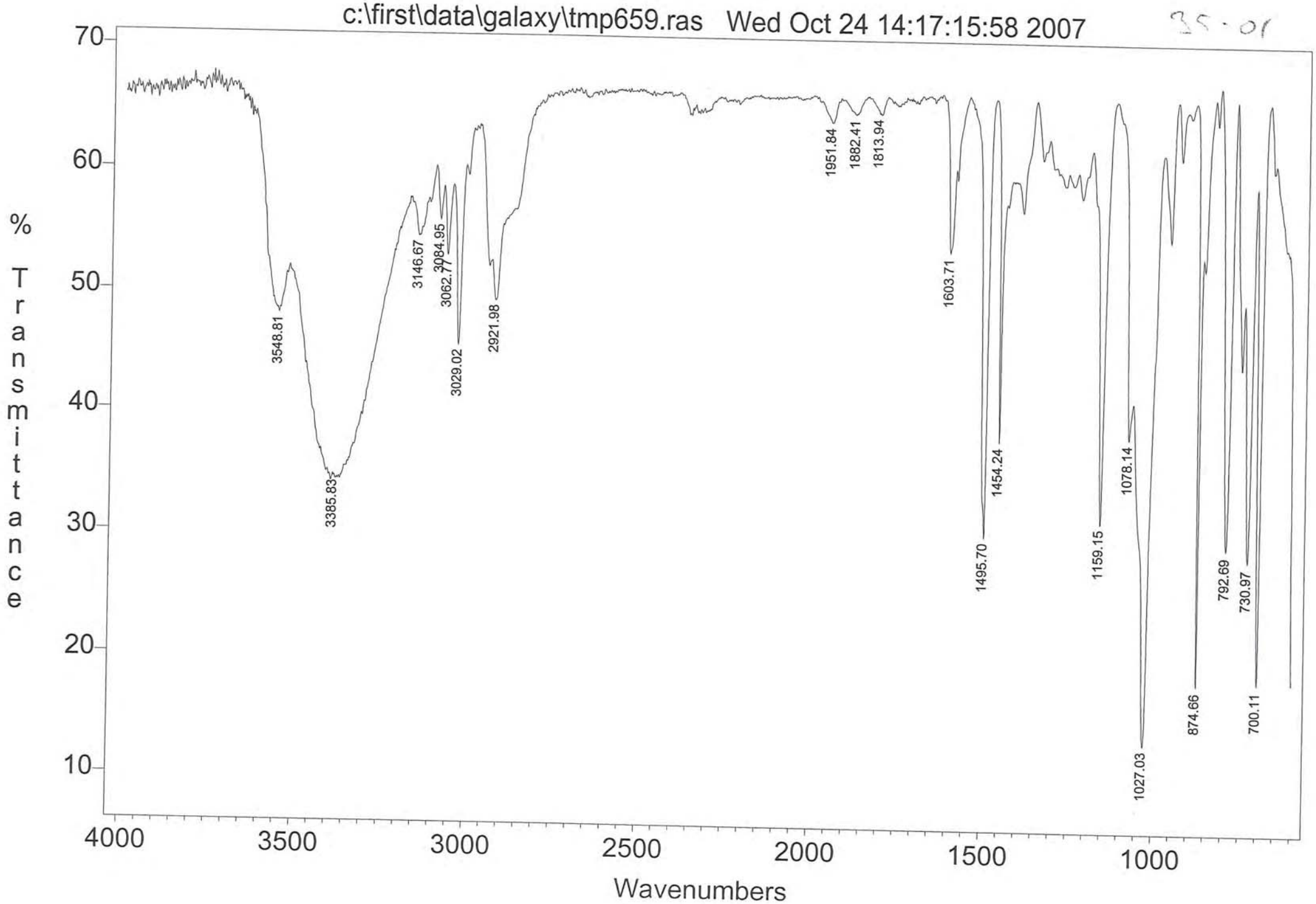
2g

35-01C.ESP

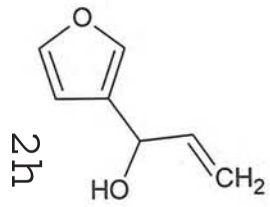

129.59
128.60
143.34
139.21
137.83
126.76
108.67
77.16
CHLOROFORM-d
68.04
44.70
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

O
HO

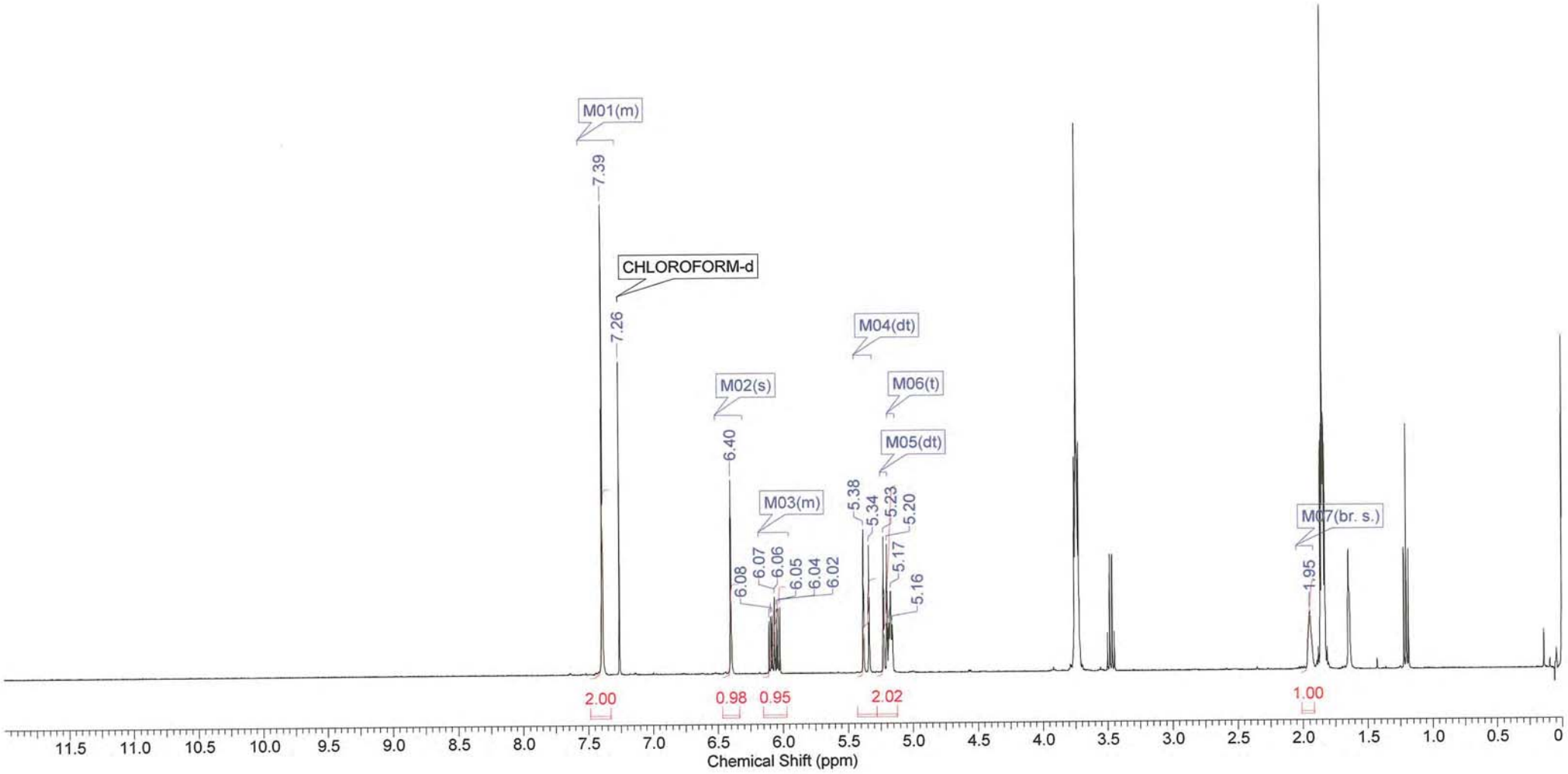
2g


c:\first\data\galaxy\tmp659.ras Wed Oct 24 14:17:15:58 2007
35-01
% Transmittance
70
60
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3548.81
3385.83
3146.67
3084.95
3062.77
3029.02
2921.98
1951.84
1882.41
1813.94
1603.71
1495.70
1454.24
1159.15
1078.14
1027.03
874.66
792.69
730.97
700.11

NC060-03_H.ESP

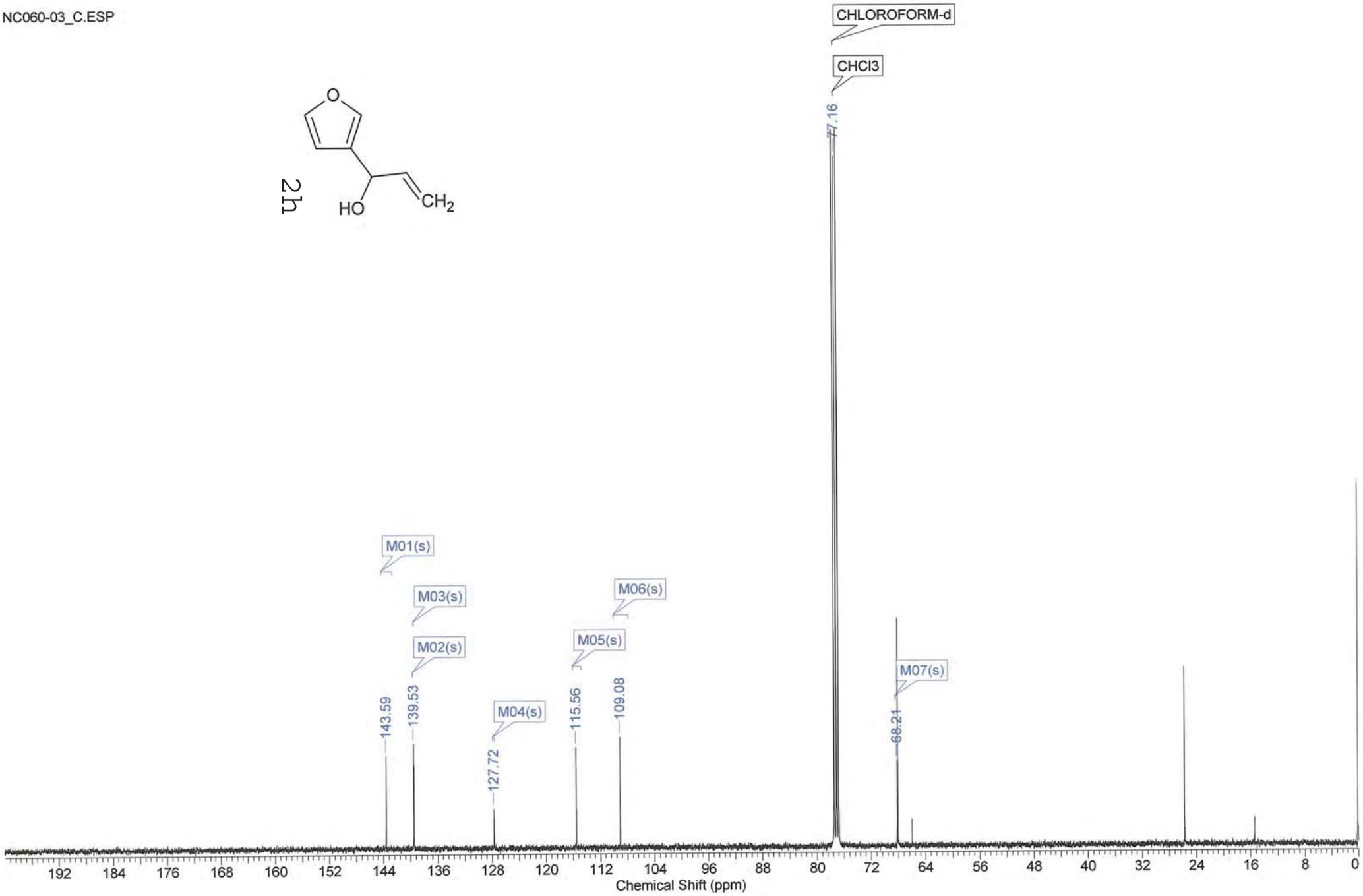


2h



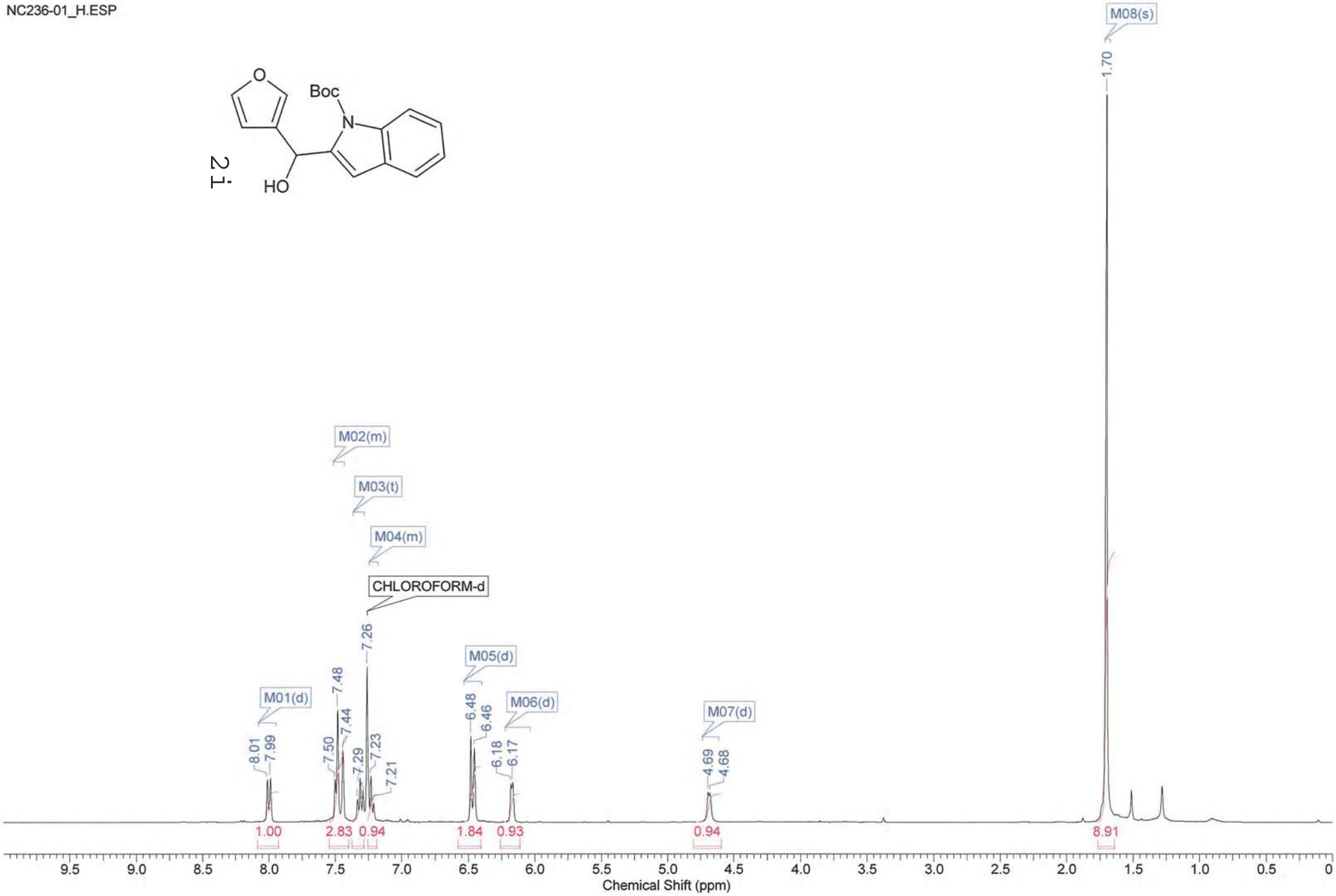
NC060-03_C.ESP

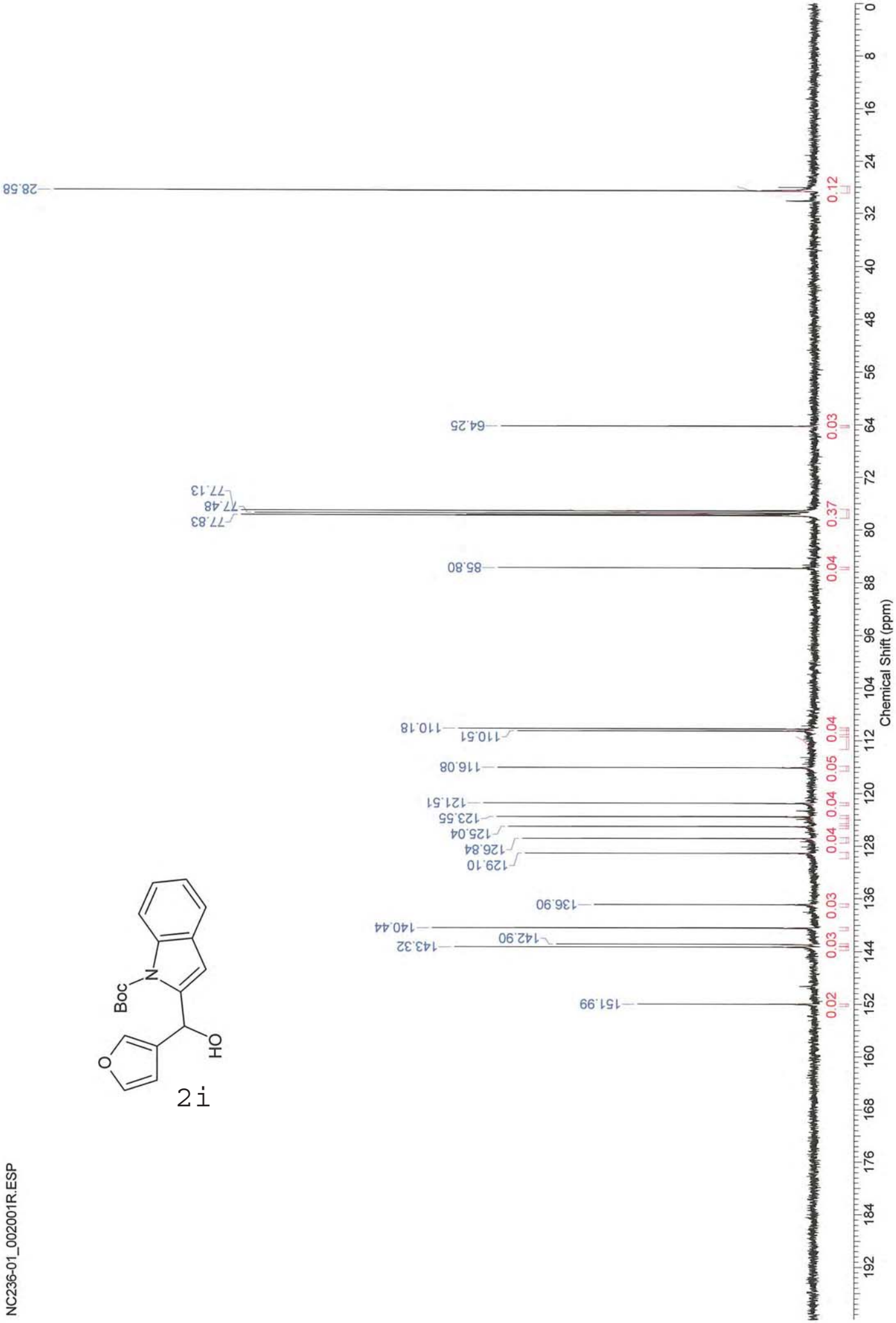
2h



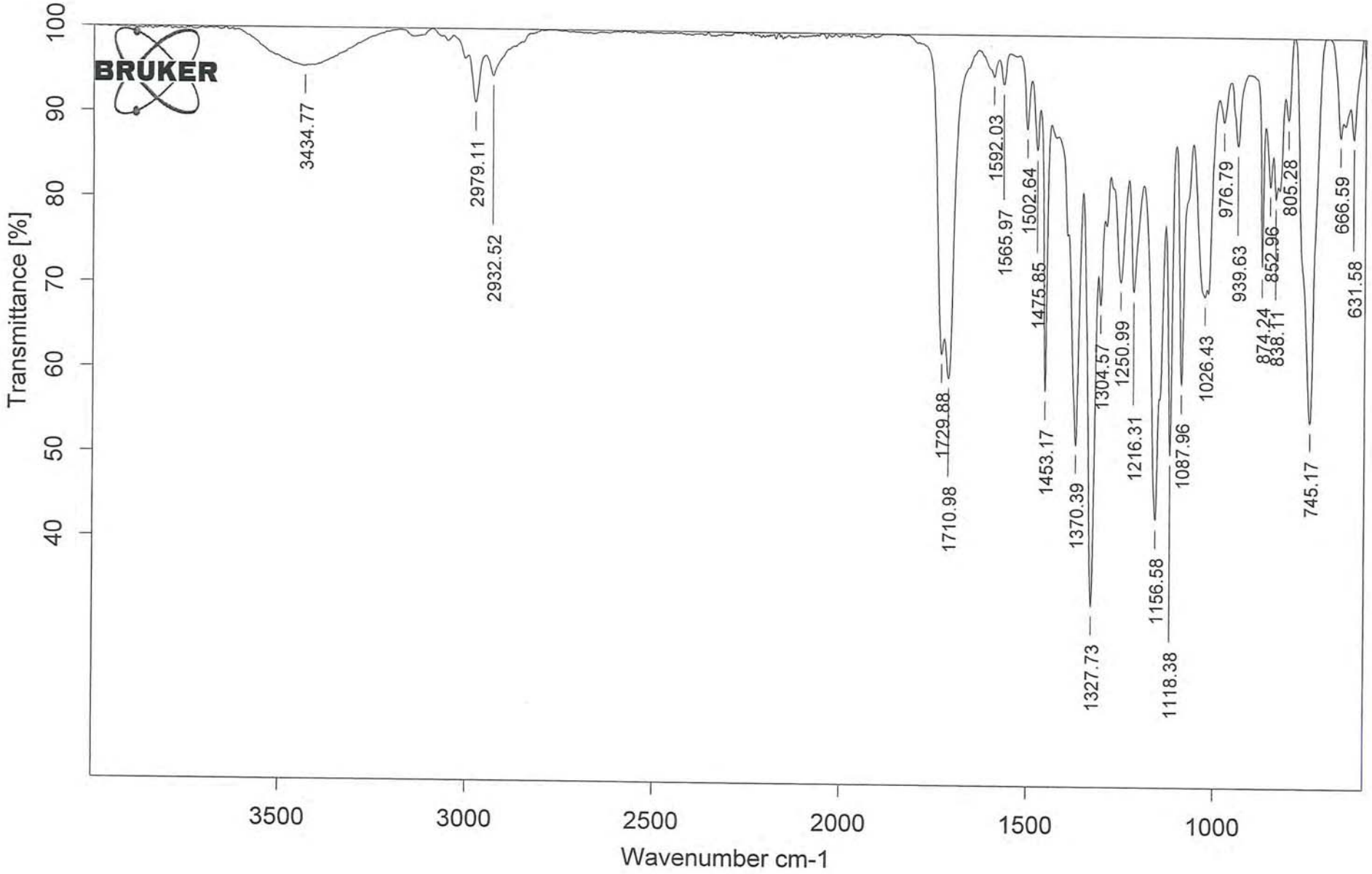
NC236-01_H.ESP

21





NC236-01_002001R.ESP



C:\Program Files\OPUS\Data\Chn\nc236-01.0	nc236-01	brown oil	05/08/2010

Page 1/1

ESI-MS: NC236-01

XMASS Mass Analysis for /Data/UNI_FR/CHAR5029_ESI/2/pdata/1/massanal.res:
XMASS Mass Analysis Constraints

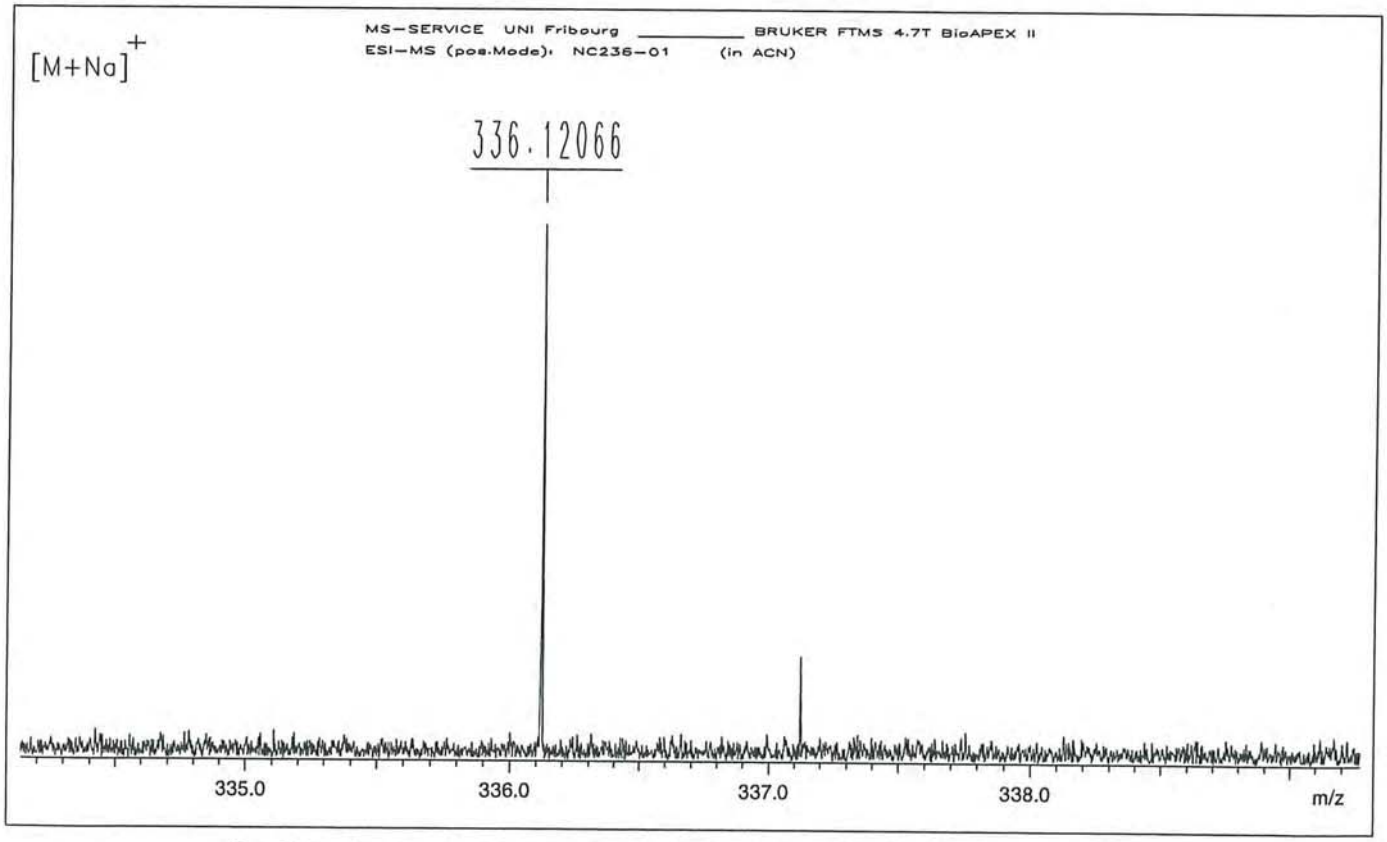
Ion mass = 336.1206630

Charge = +1

#	C	H	N	O	Na	mass	DBE	error

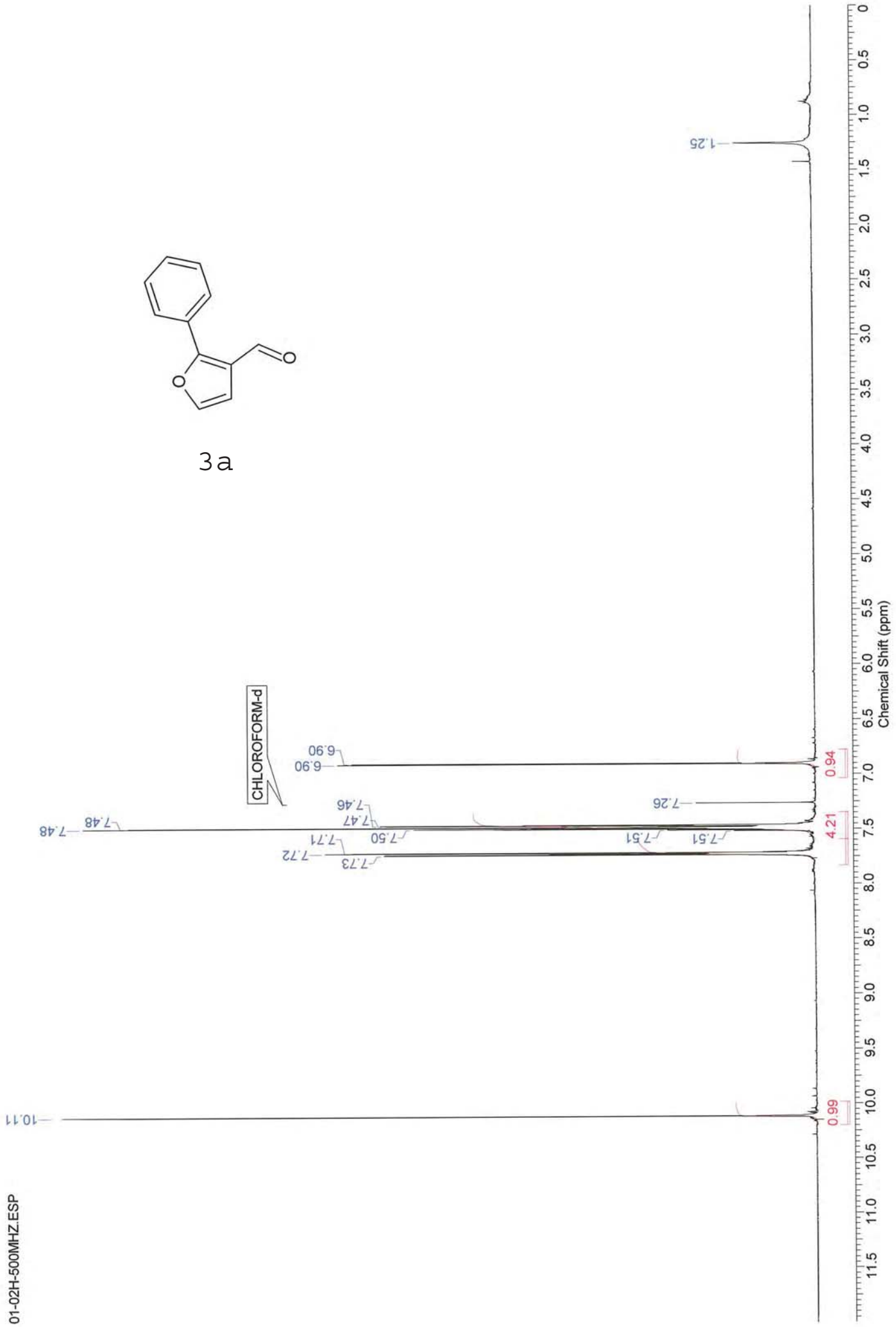
*** Mass Analysis for mass 336.1206630

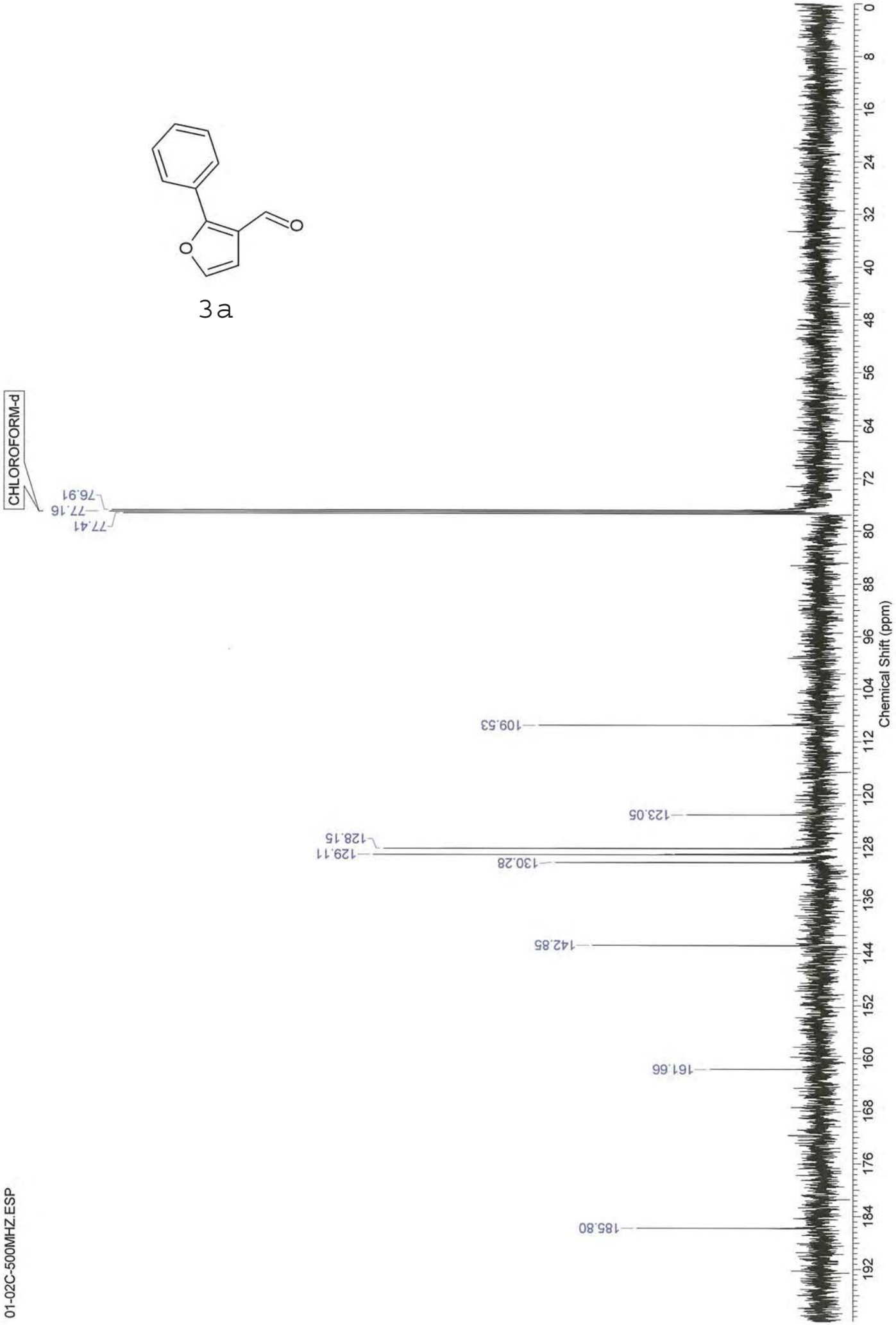
#	C	H	N	O	Na	mass	DBE	error
1	18	19	1	4	1	336.1206292	9.5	3.381e-05
2	18	16	4	3	0	336.1216918	13.0	1.029e-03
3	16	17	4	3	1	336.1192865	10.0	1.376e-03
4	20	18	1	4	0	336.1230345	12.5	2.371e-03
5	21	17	2	1	1	336.1233093	14.0	2.646e-03
6	23	16	2	1	0	336.1257146	17.0	5.052e-03
7	22	14	3	1	0	336.1131385	17.5	7.524e-03
8	20	15	3	1	1	336.1107332	14.5	9.930e-03
9	19	16	2	4	0	336.1104584	13.0	1.020e-02
10	17	19	3	3	1	336.1318626	9.5	1.120e-02

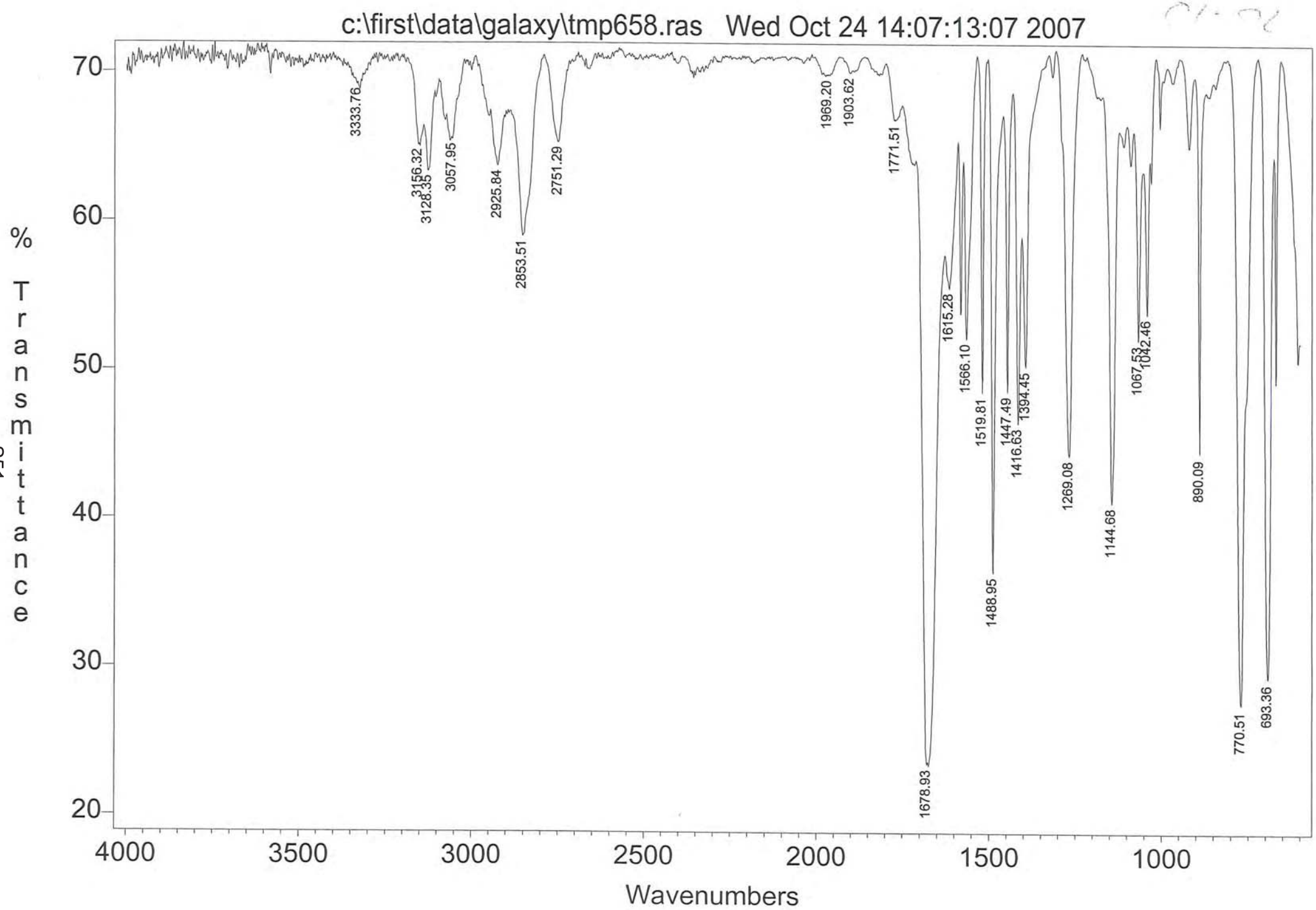


/Data/UNI_FR/CHAR5029_ESI/2/pdata/1 FTMS USER Wed Aug 11 15:17:42 2010

3a


01-02H-500MHZ.ESP
10.11
7.48
7.46
7.47
7.50
7.71
7.72
7.73
7.51
7.51
7.26
6.90
6.90
1.25
CHLOROFORM-d
0.99
4.21
0.94
Chemical Shift (ppm)

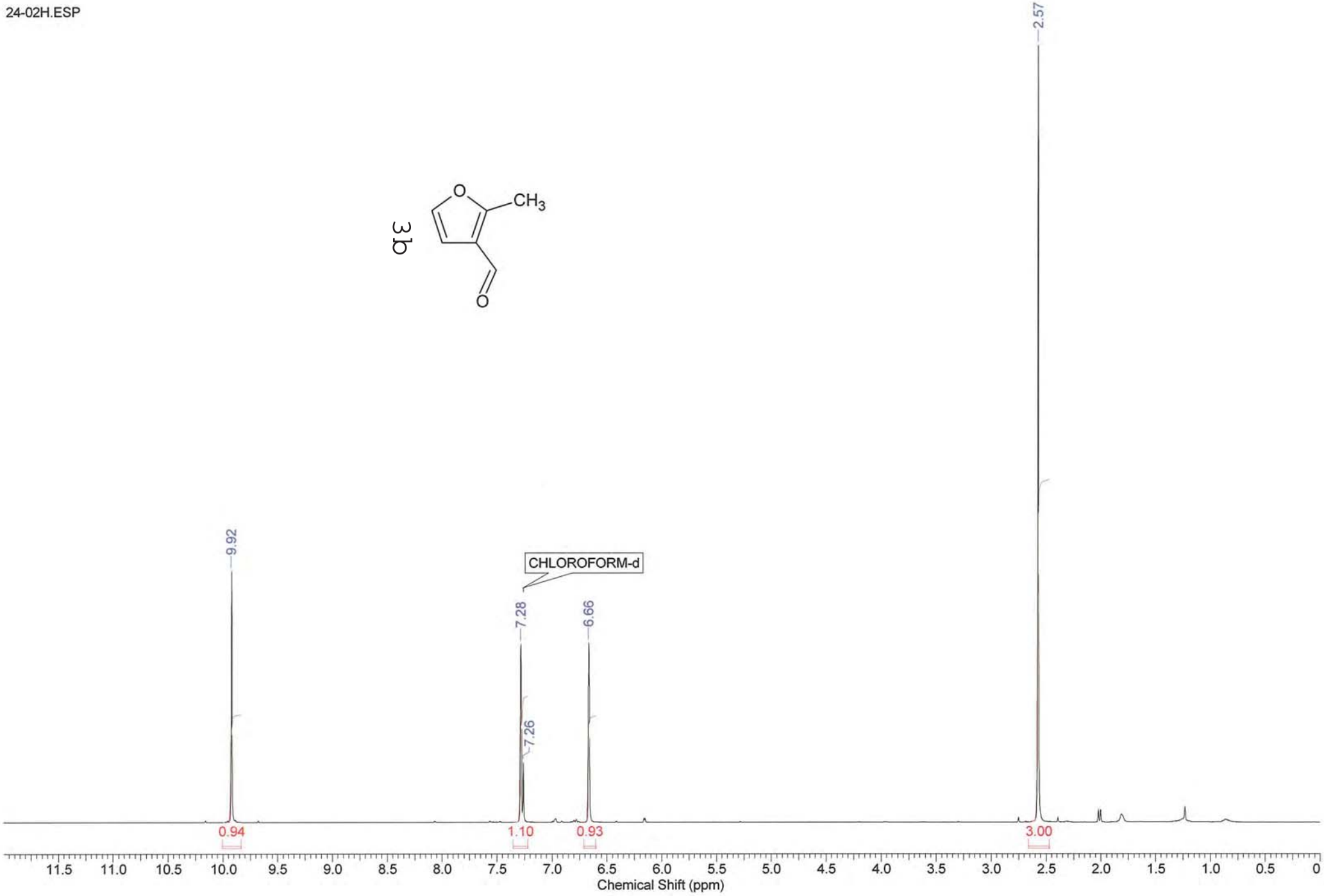

3a
CHLOROFORM-d
77.41
77.16
76.91
109.53
123.05
128.15
129.11
130.28
142.85
161.66
185.80
Chemical Shift (ppm)
01-02C-500MHZ.ESP

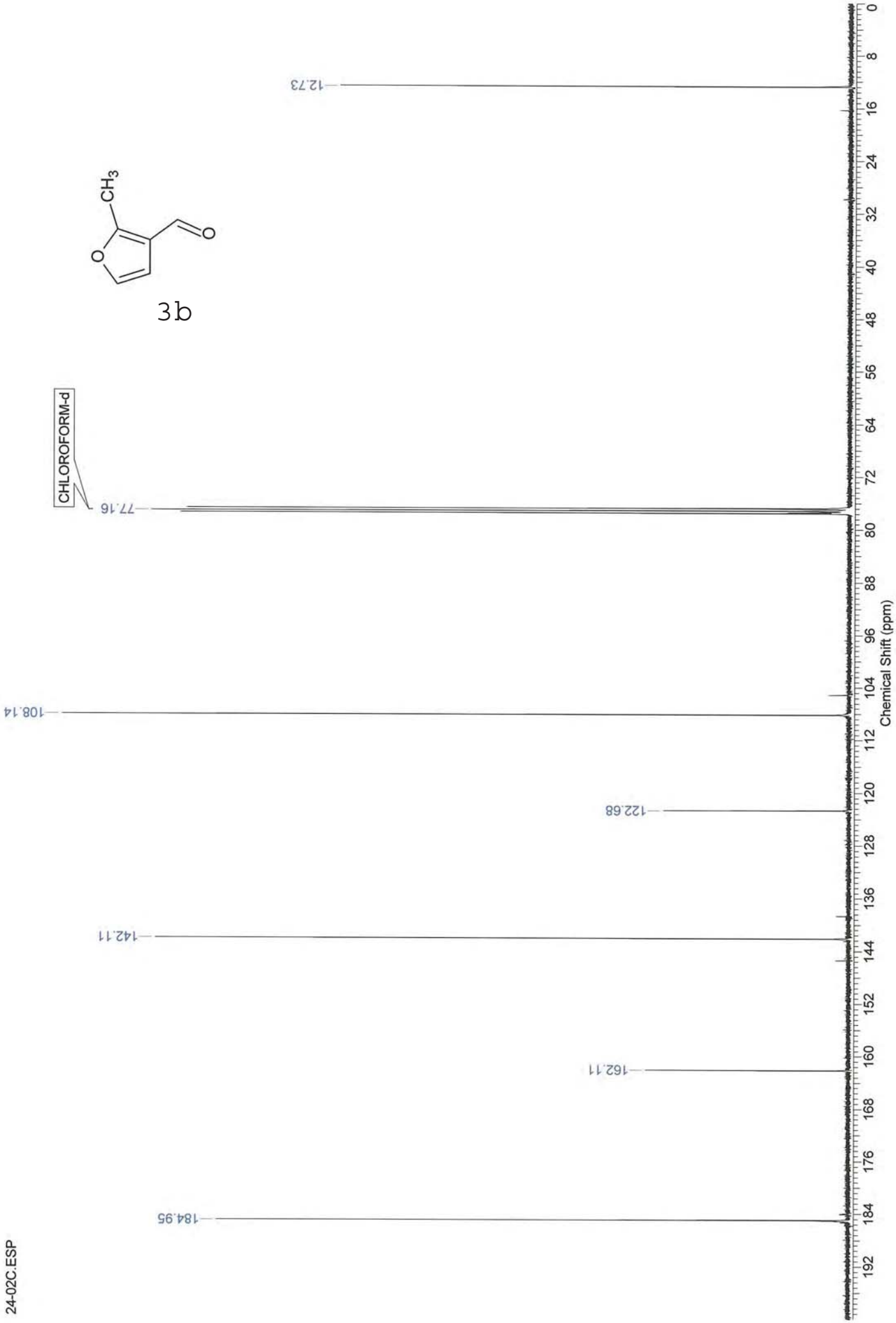

c:\first\data\galaxy\tmp658.ras Wed Oct 24 14:07:13:07 2007
% Transmittance
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3333.76
3156.32
3128.35
3057.95
2925.84
2853.51
2751.29
1969.20
1903.62
1771.51
1678.93
1615.28
1566.10
1519.81
1488.95
1447.49
1416.63
1394.45
1269.08
1144.68
1067.53
1042.46
890.09
770.51
693.36

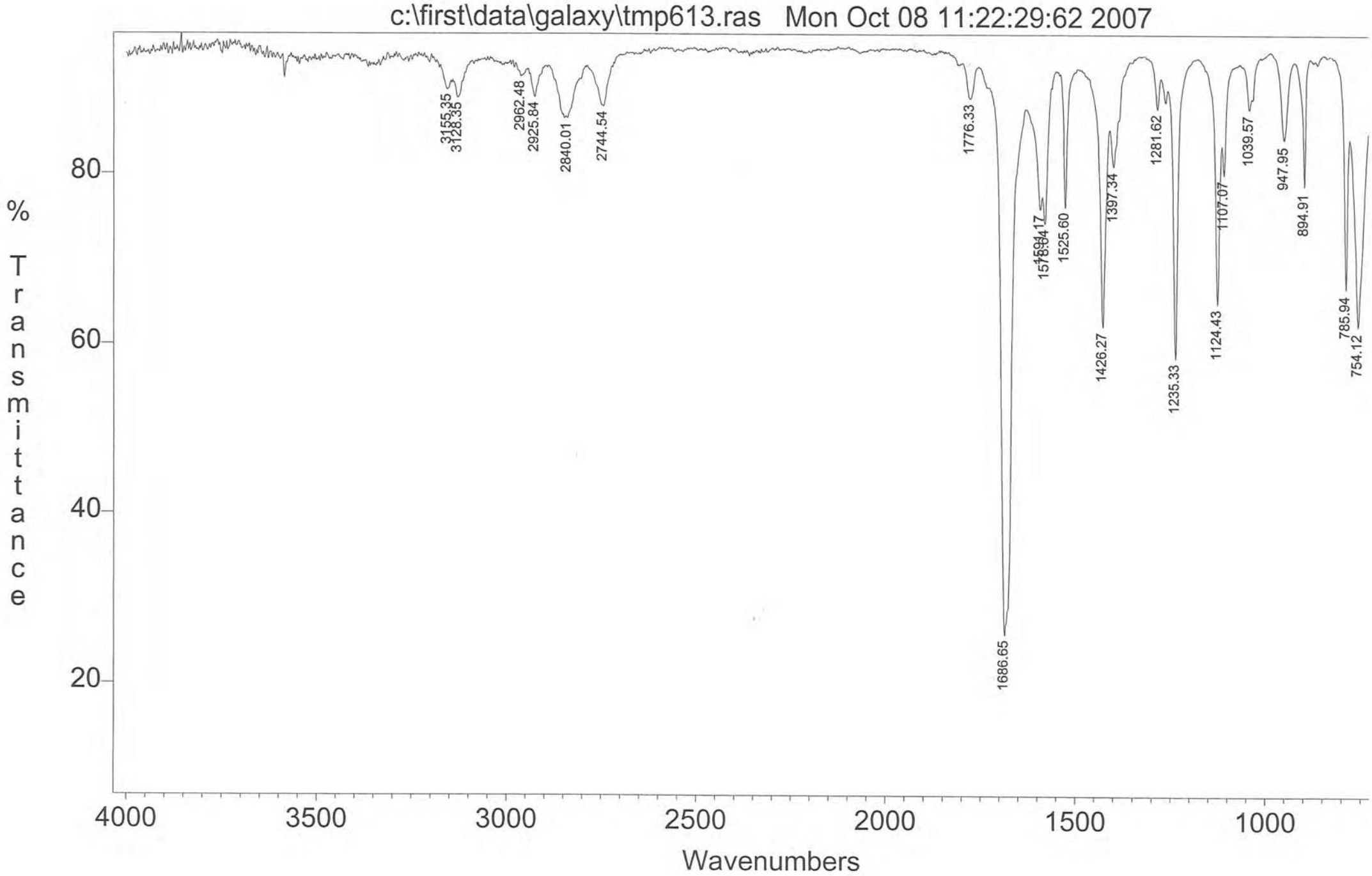
24-02H.ESP

O
CH3
O

3b


2.57
9.92
CHLOROFORM-d
7.28
6.66
7.26
0.94
1.10
0.93
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

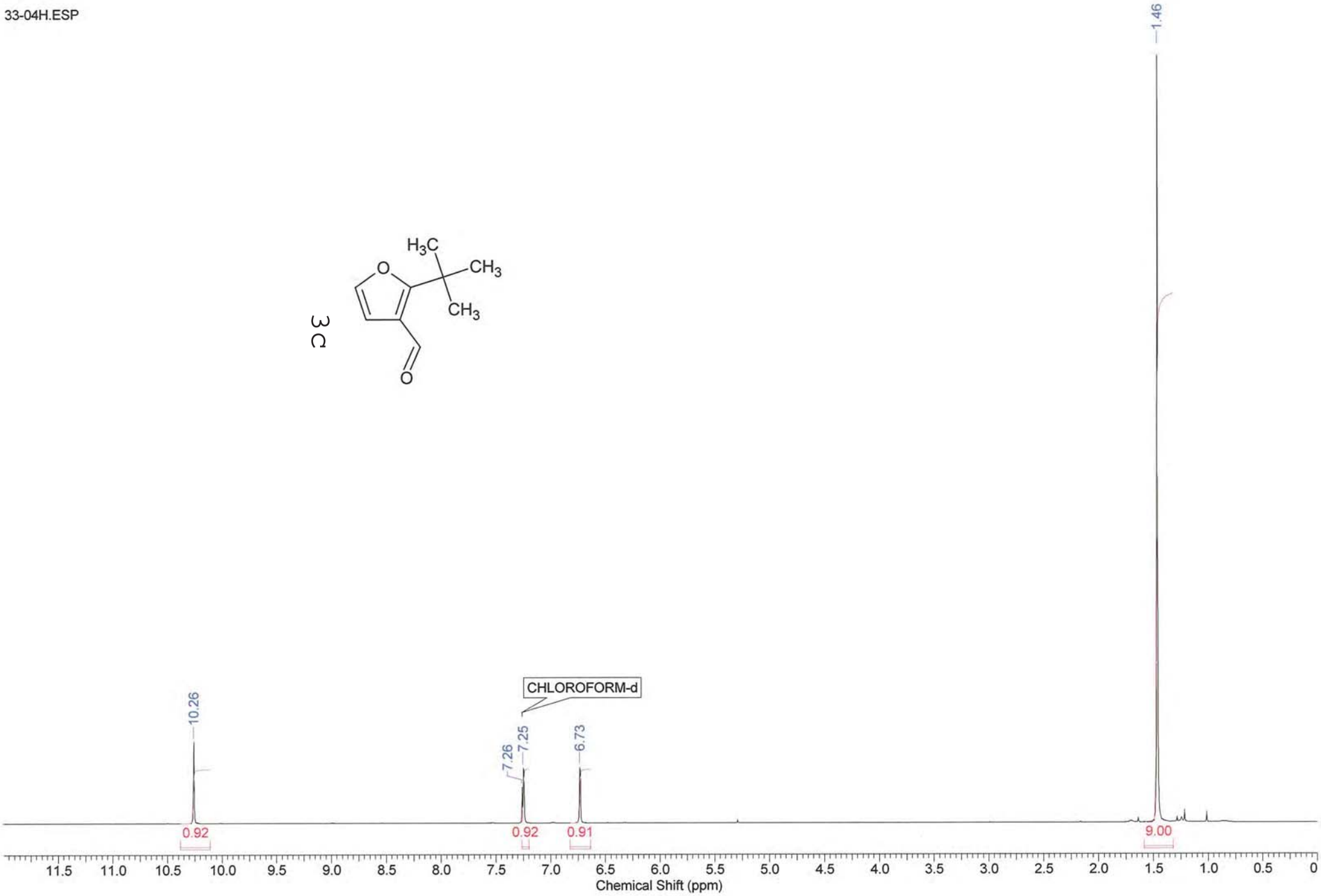

12.73
CH3
O
O
3b
CHLOROFORM-d
77.16
108.14
122.68
142.11
162.11
184.95
Chemical Shift (ppm)
24-02C.ESP

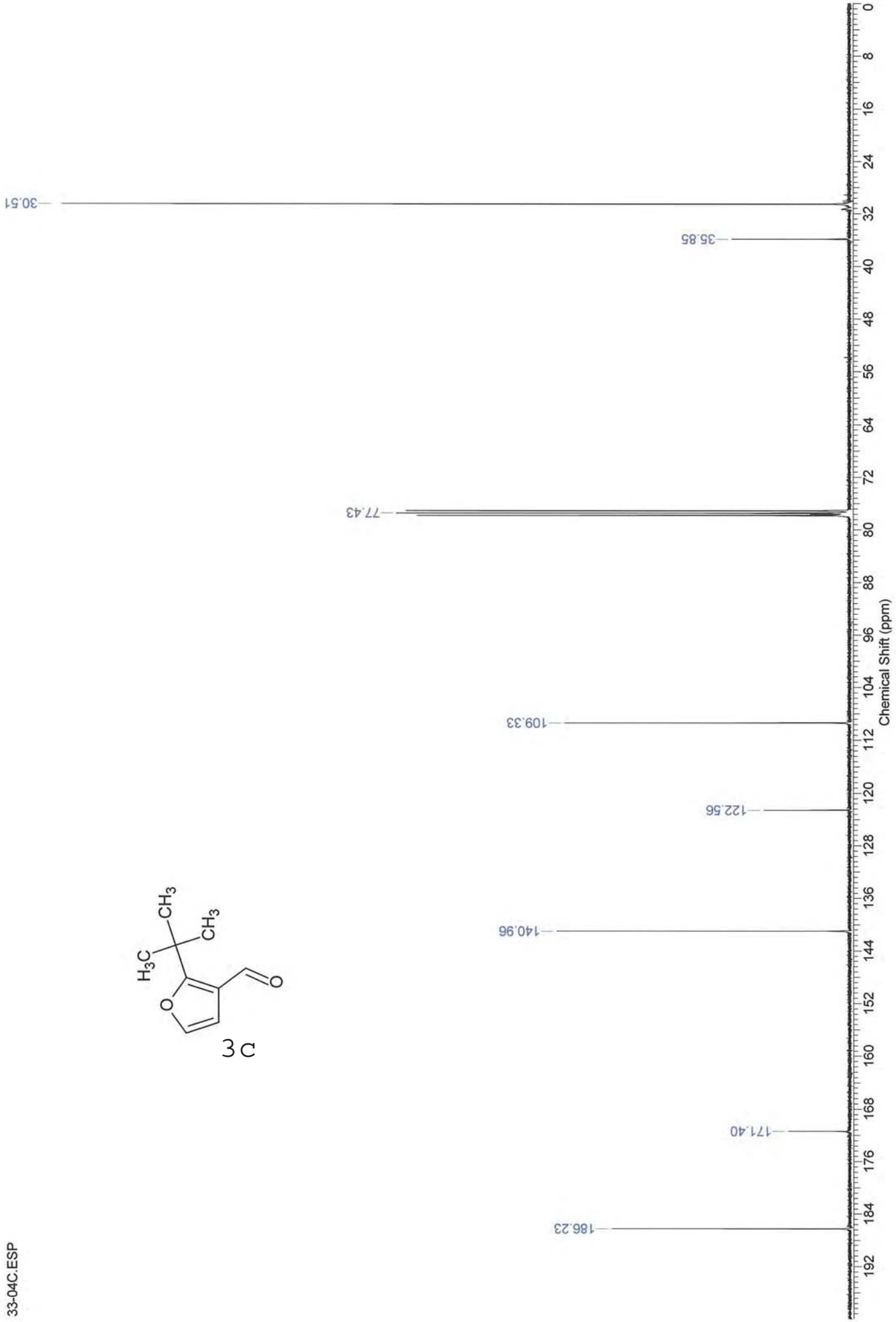

c:\first\data\galaxy\tmp613.ras Mon Oct 08 11:22:29:62 2007
% Transmittance
80
60
40
20
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3155.35
3128.35
2962.48
2925.84
2840.01
2744.54
1776.33
1686.65
1594.17
1578.94
1525.60
1426.27
1397.34
1281.62
1235.33
1124.43
1107.07
1039.57
947.95
894.91
785.94
754.12

33-04H.ESP

H3C
CH3
CH3
O
O

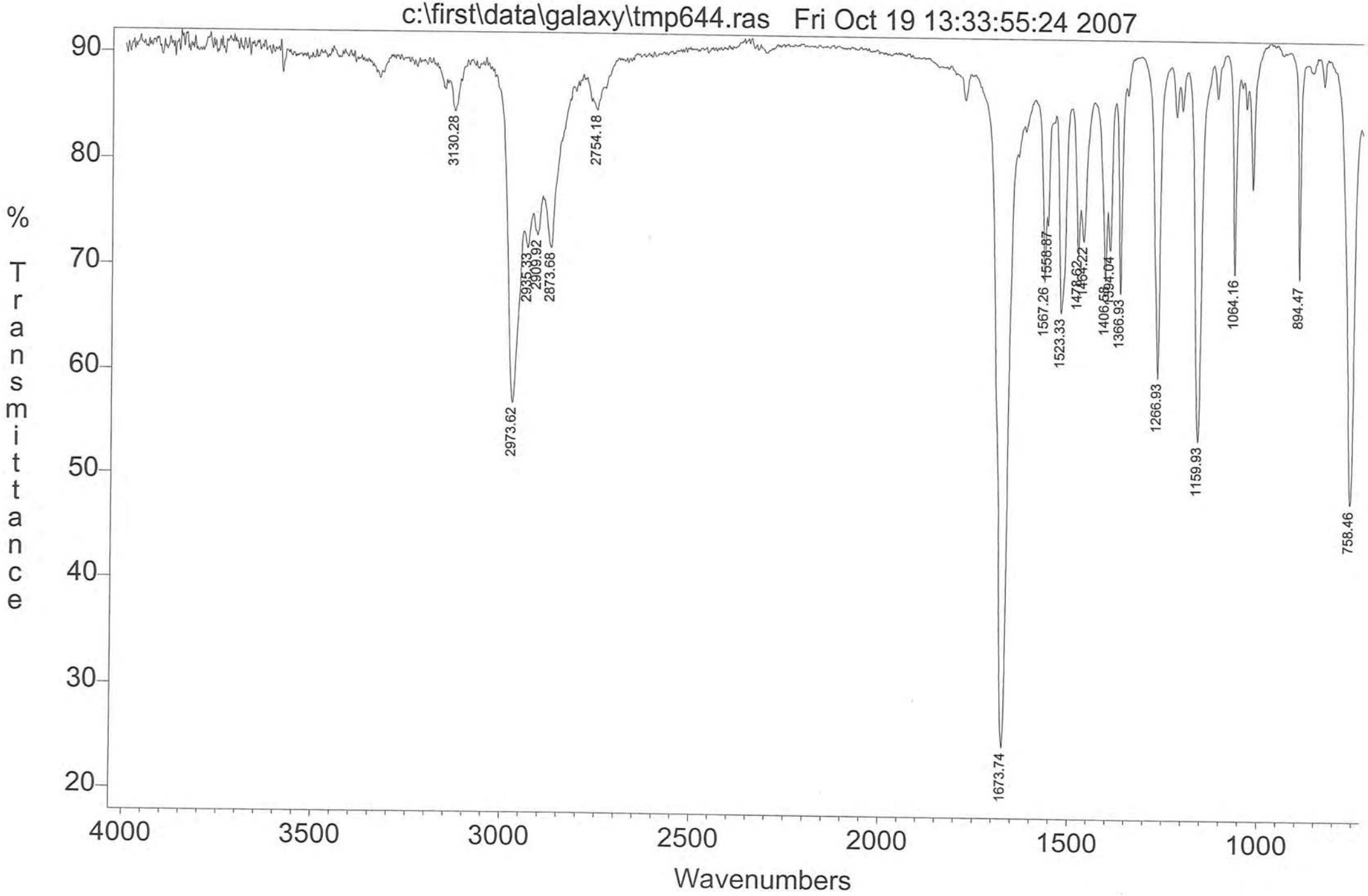
3c


1.46
10.26
CHLOROFORM-d
7.26
7.25
6.73
0.92
0.92
0.91
9.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

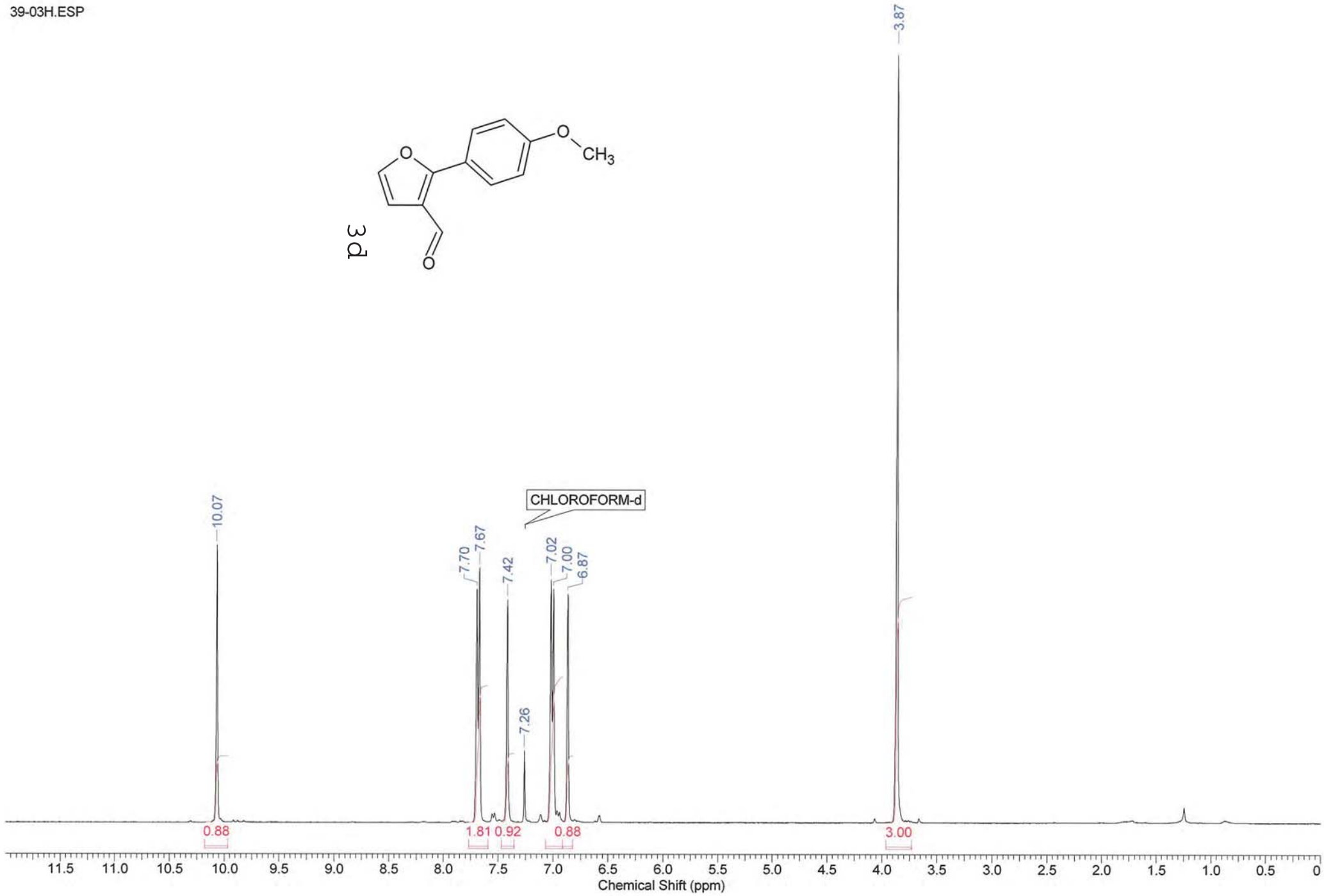

30.51
35.85
77.43
109.33
122.56
140.96
171.40
186.23
Chemical Shift (ppm)
0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
128
136
144
152
160
168
176
184
192
33-04C.ESP

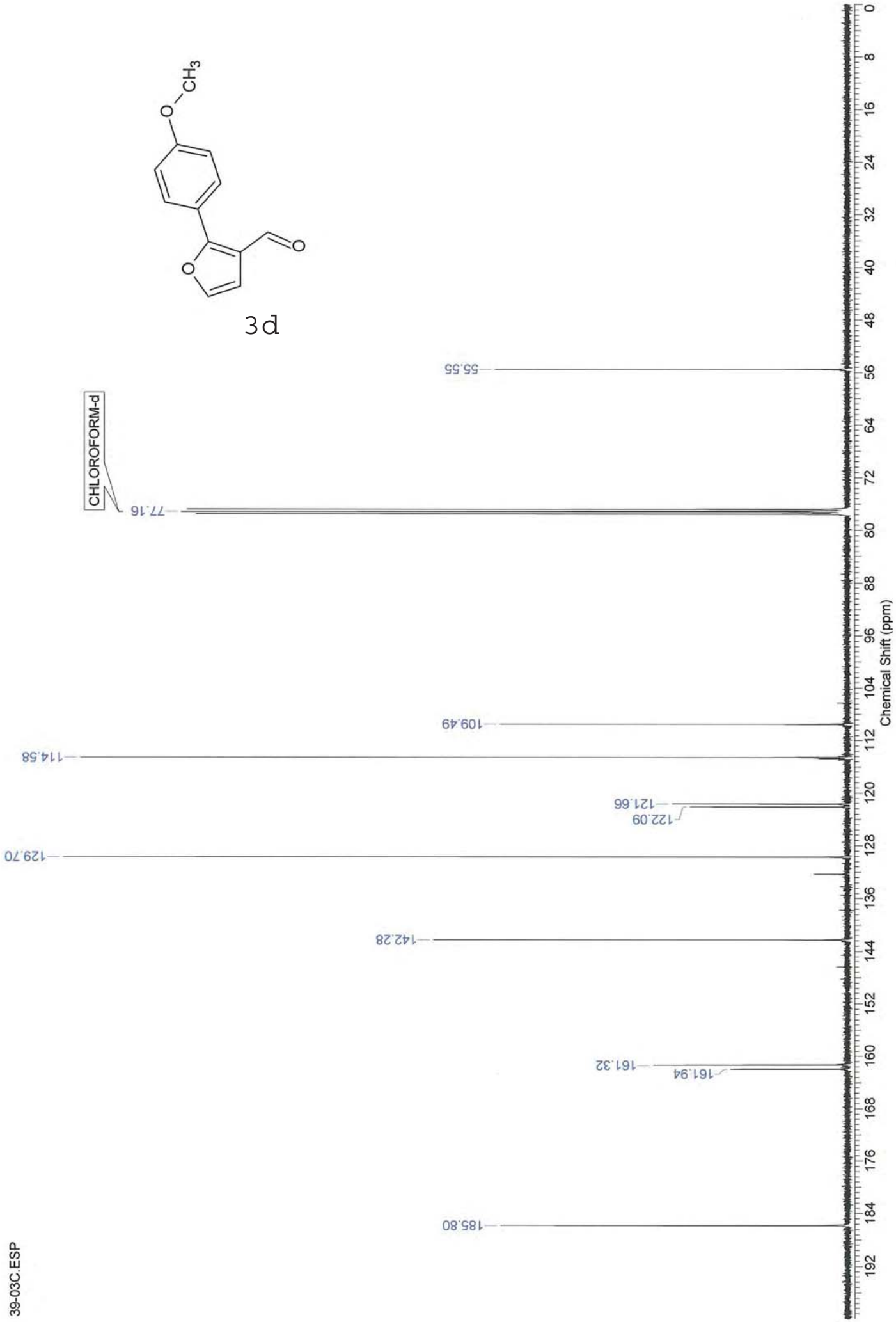
H_3C
CH_3
CH_3
O
O

3c


c:\first\data\galaxy\tmp644.ras Fri Oct 19 13:33:55:24 2007
% Transmittance
Wavenumbers
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
3130.28
2973.62
2935.33
2909.92
2873.68
2754.18
1673.74
1567.26
1558.87
1523.33
1478.62
1464.22
1406.58
1394.04
1366.93
1266.93
1159.93
1064.16
894.47
758.46

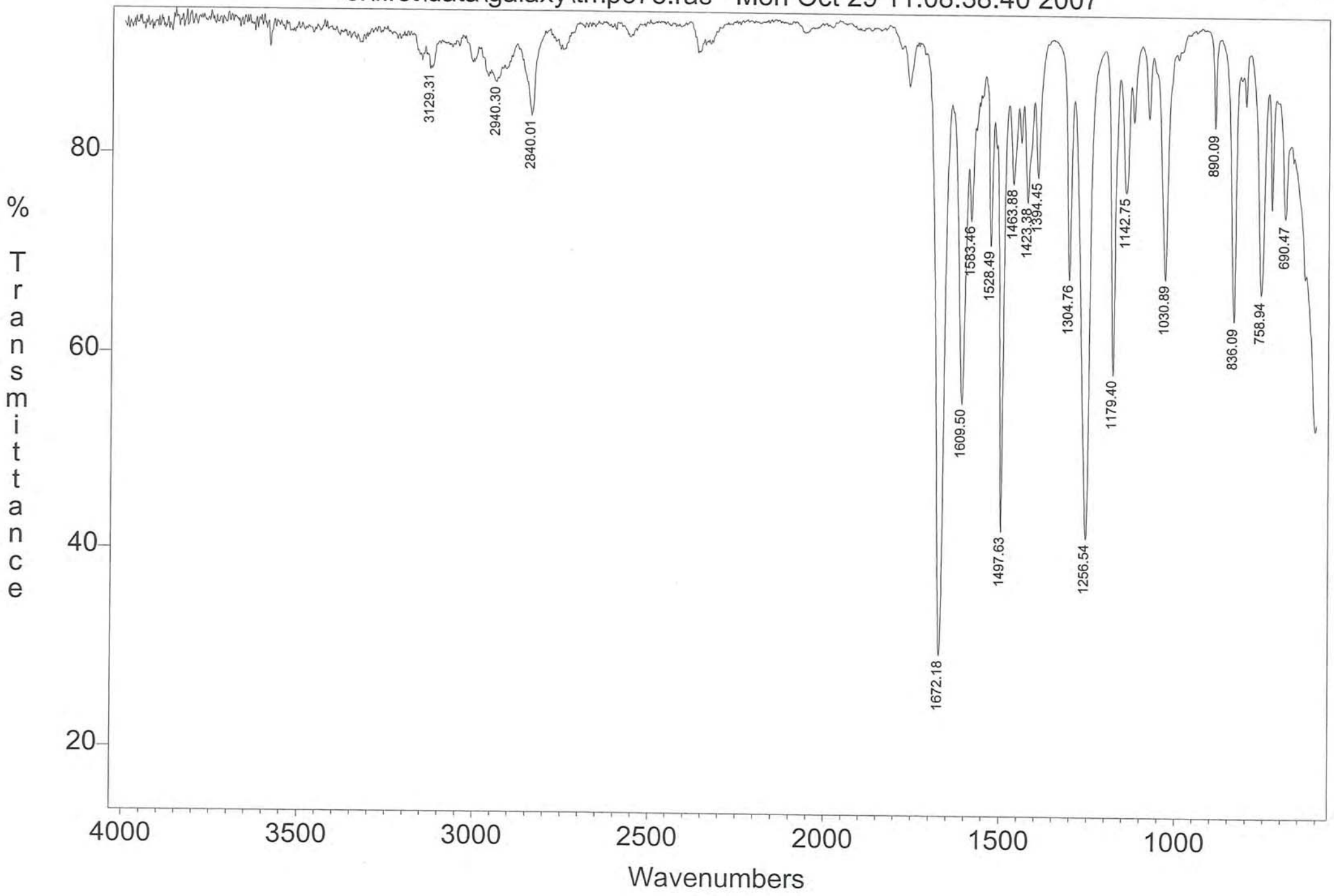
39-03H.ESP


3d
CHLOROFORM-d
10.07
7.70
7.67
7.42
7.26
7.02
7.00
6.87
3.87
0.88
1.81
0.92
0.88
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

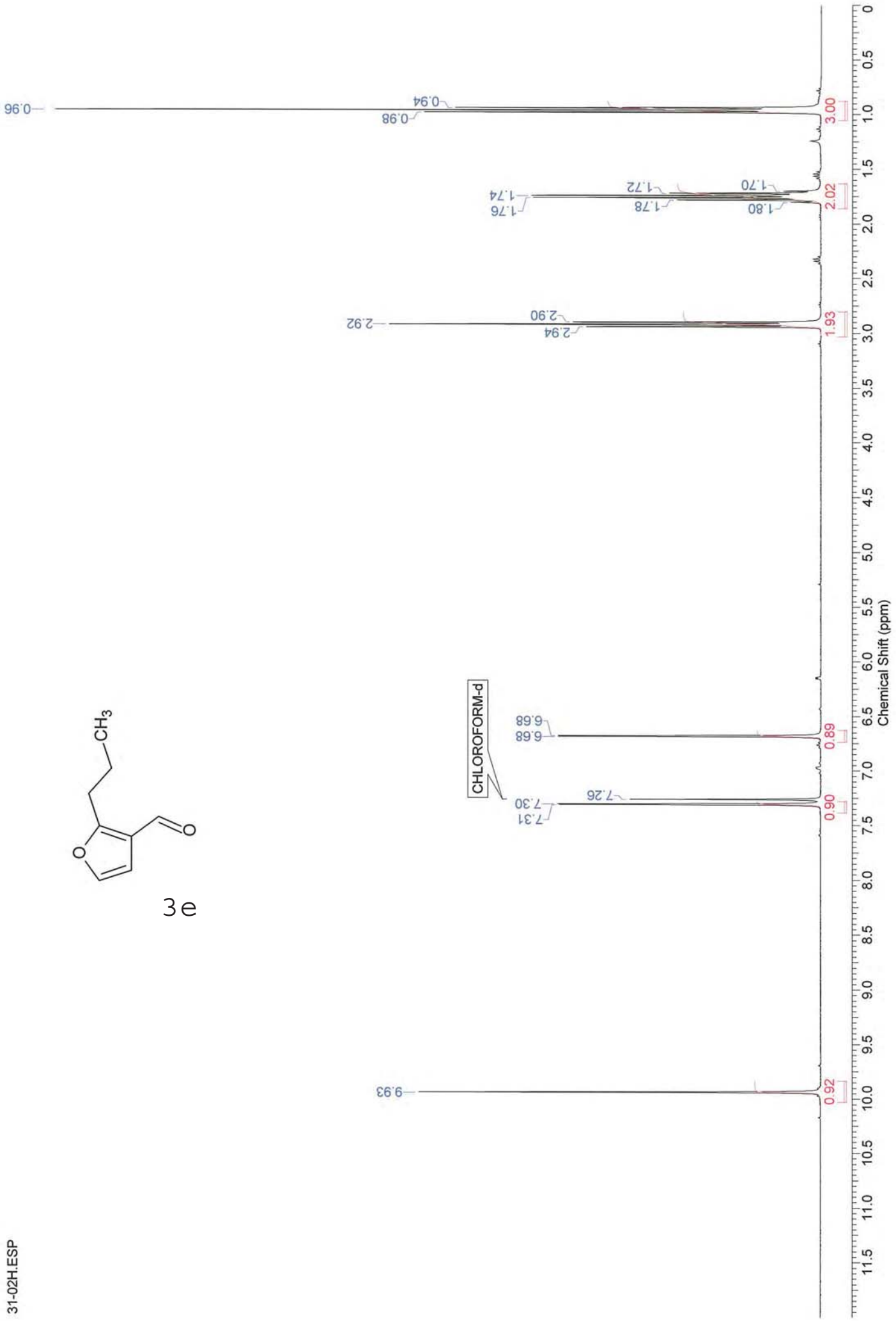

3d
CHLOROFORM-d
77.16
55.55
109.49
114.58
121.66
122.09
129.70
142.28
161.32
161.94
185.80
Chemical Shift (ppm)
39-03C.ESP

39-03

c:\first\data\galaxy\tmp675.ras Mon Oct 29 11:08:38:40 2007



S60

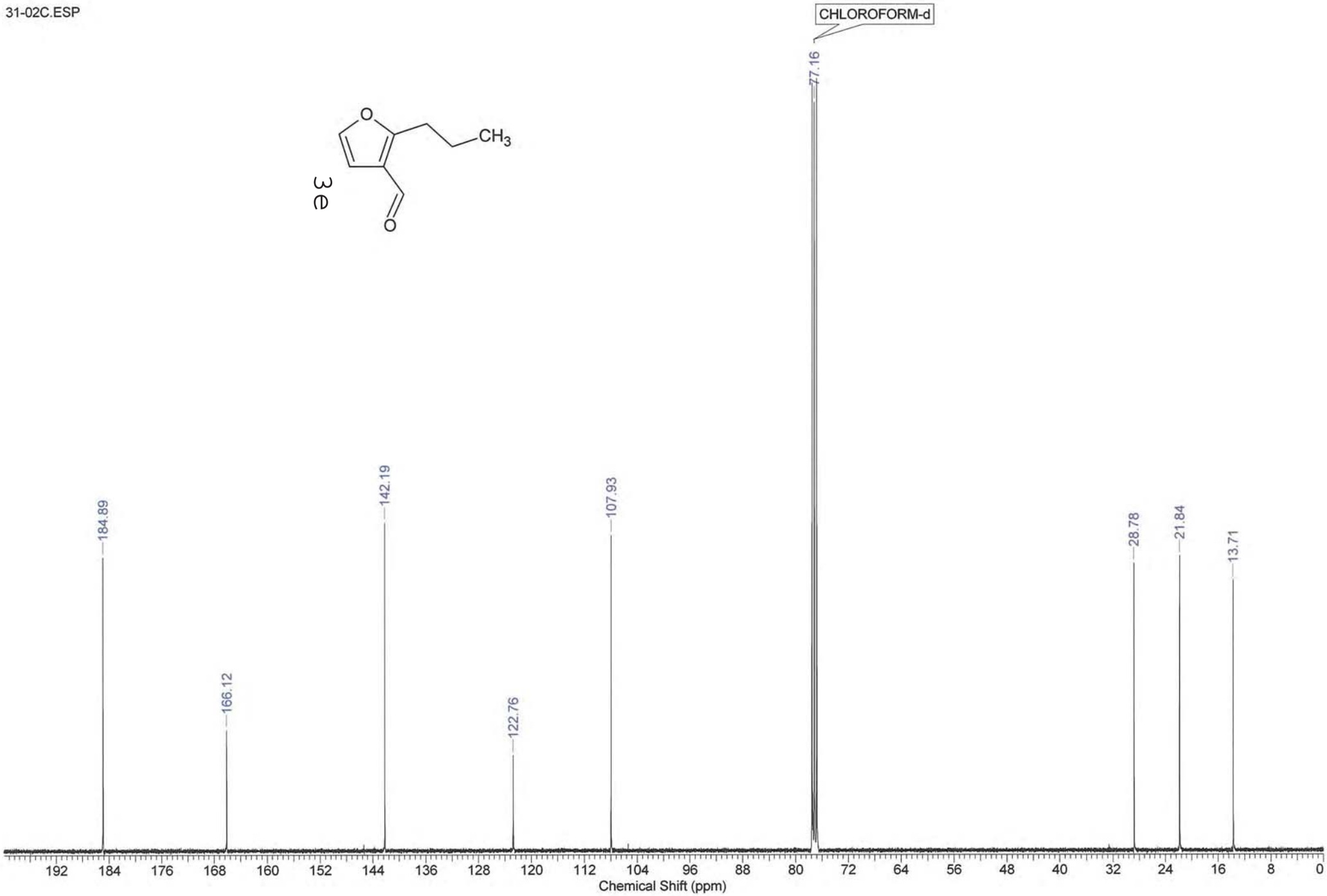

0.96
0.94
0.98
3.00
1.70
1.72
1.74
1.76
1.78
1.80
2.02
2.92
2.90
2.94
1.93
6.68
6.68
0.89
CHLOROFORM-d
7.26
7.31
7.30
0.90
9.93
0.92
Chemical Shift (ppm)
31-02H.ESP

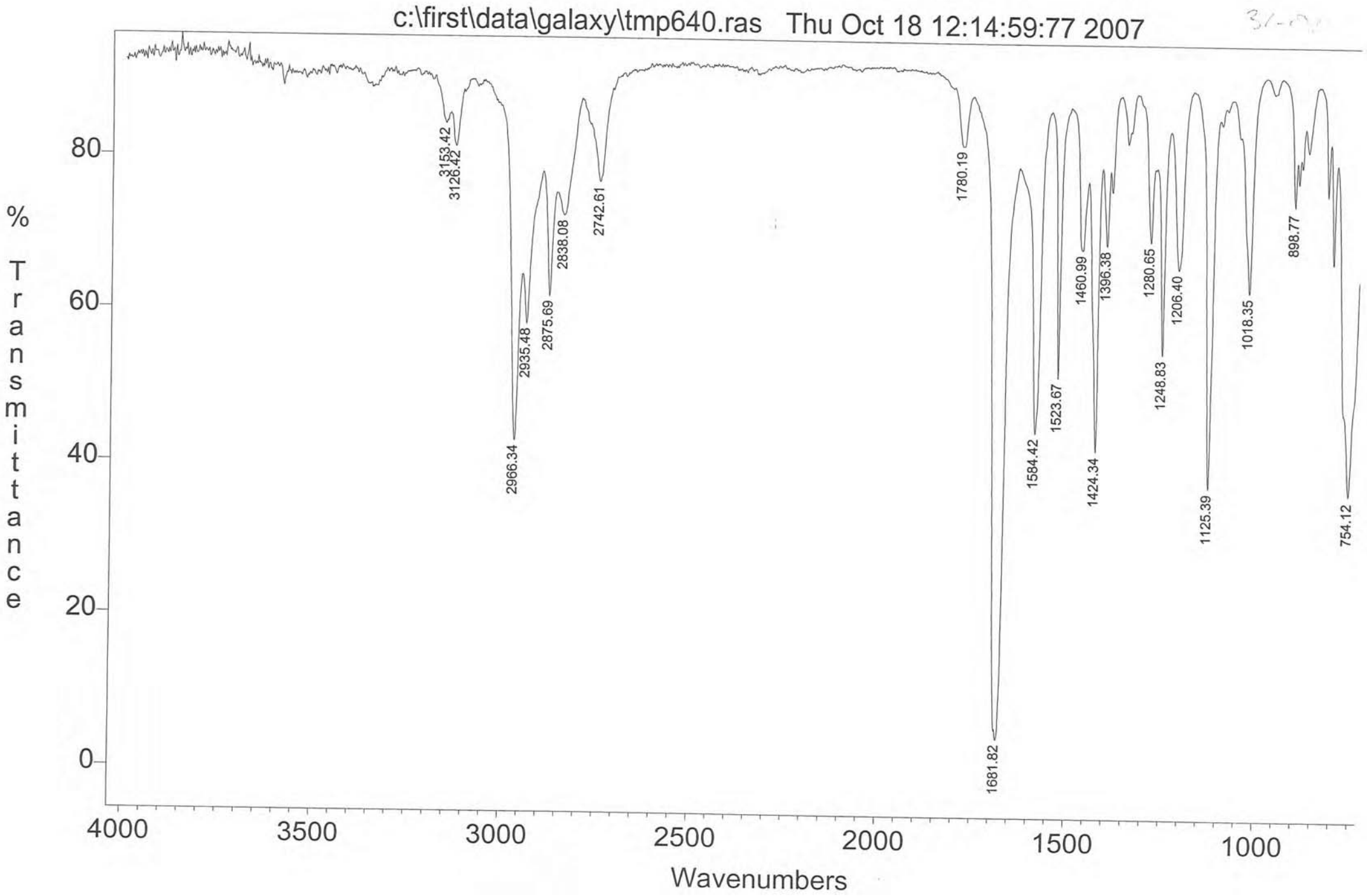
3e

31-02C.ESP

O
CH3
O

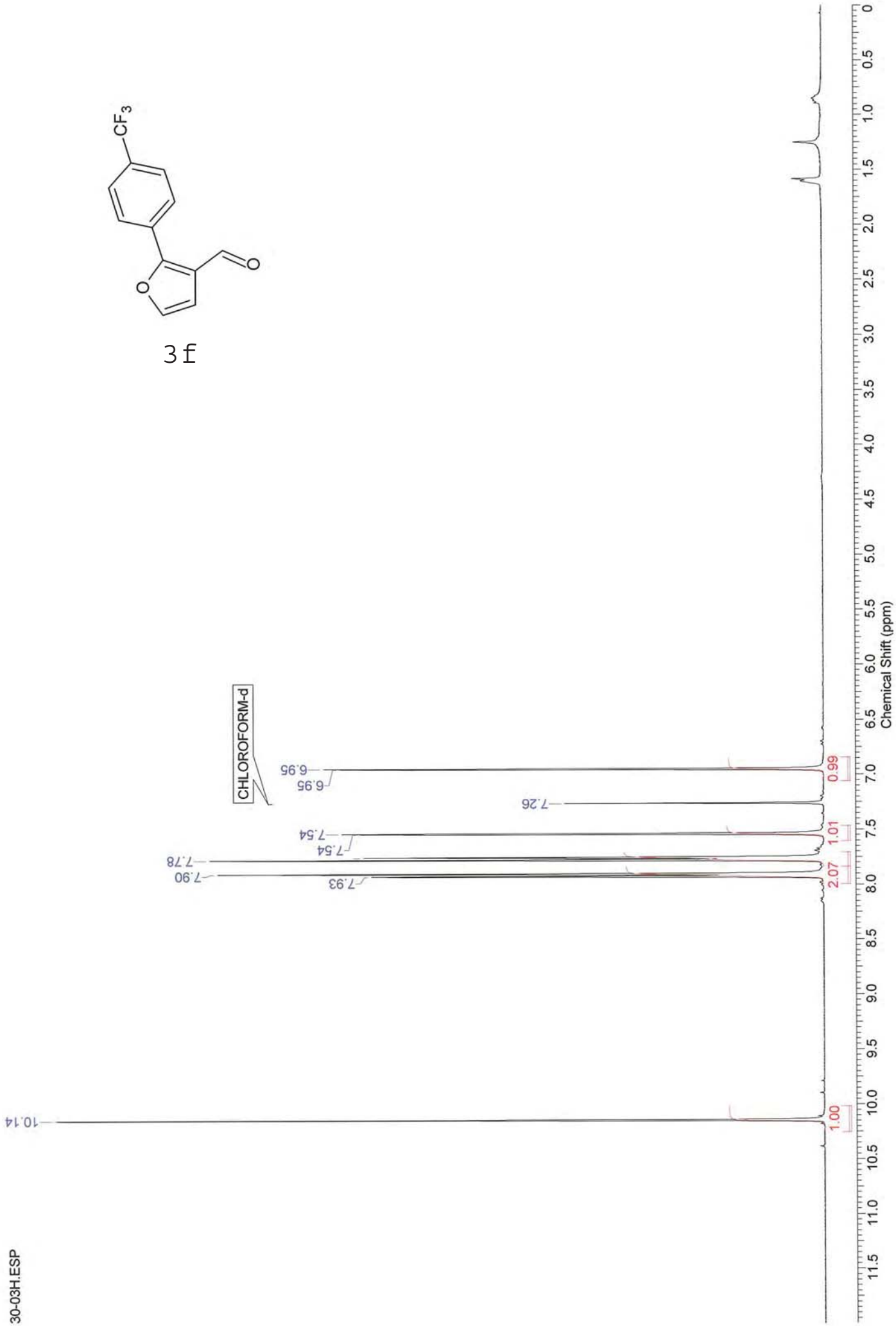
3e


CHLOROFORM-d
77.16
184.89
166.12
142.19
122.76
107.93
28.78
21.84
13.71
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


c:\first\data\galaxy\tmp640.ras Thu Oct 18 12:14:59:77 2007
% Transmittance
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3153.42
3126.42
2966.34
2935.48
2875.69
2838.08
2742.61
1780.19
1681.82
1584.42
1523.67
1460.99
1424.34
1396.38
1280.65
1248.83
1206.40
1125.39
1018.35
898.77
754.12

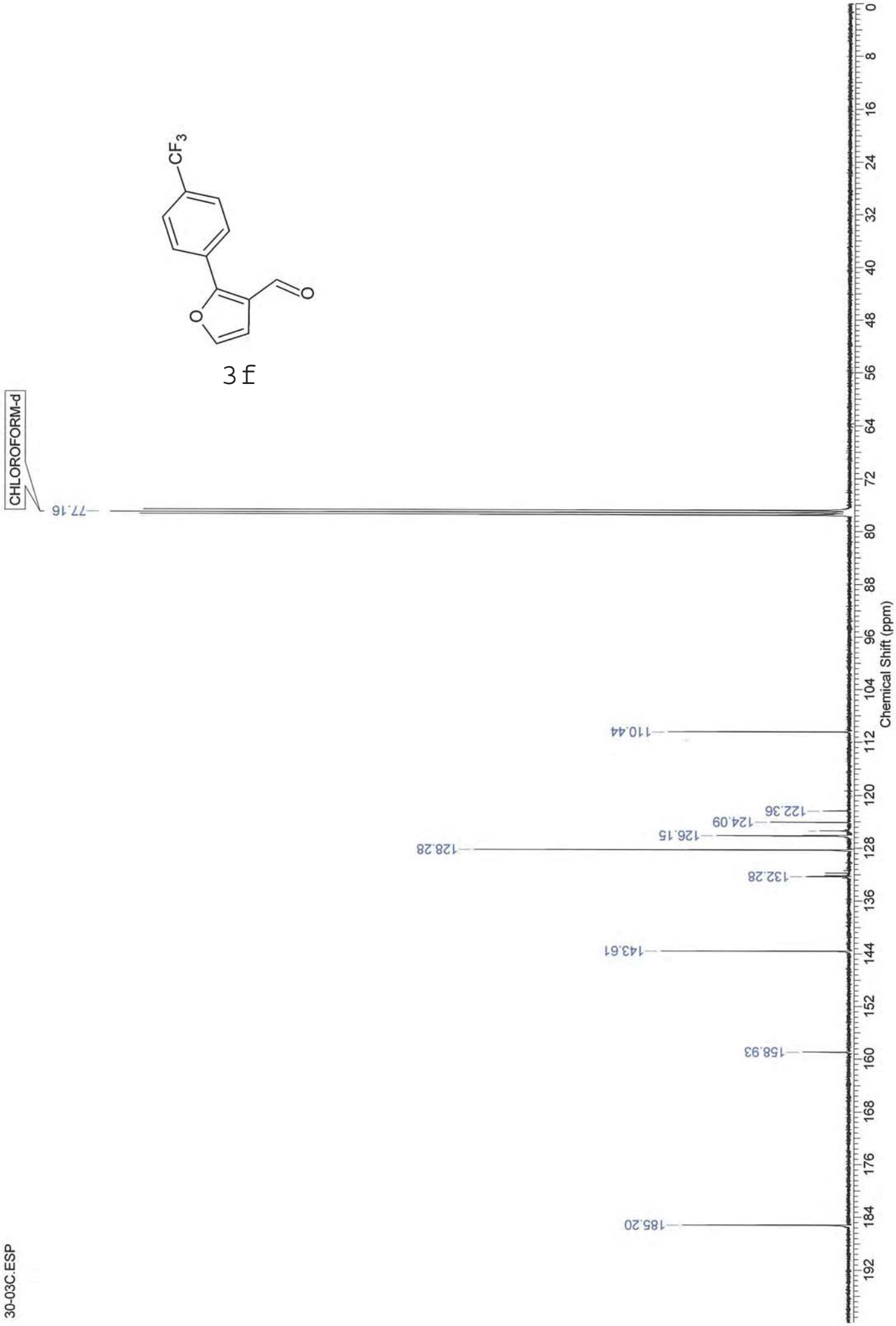
CF3
O
O

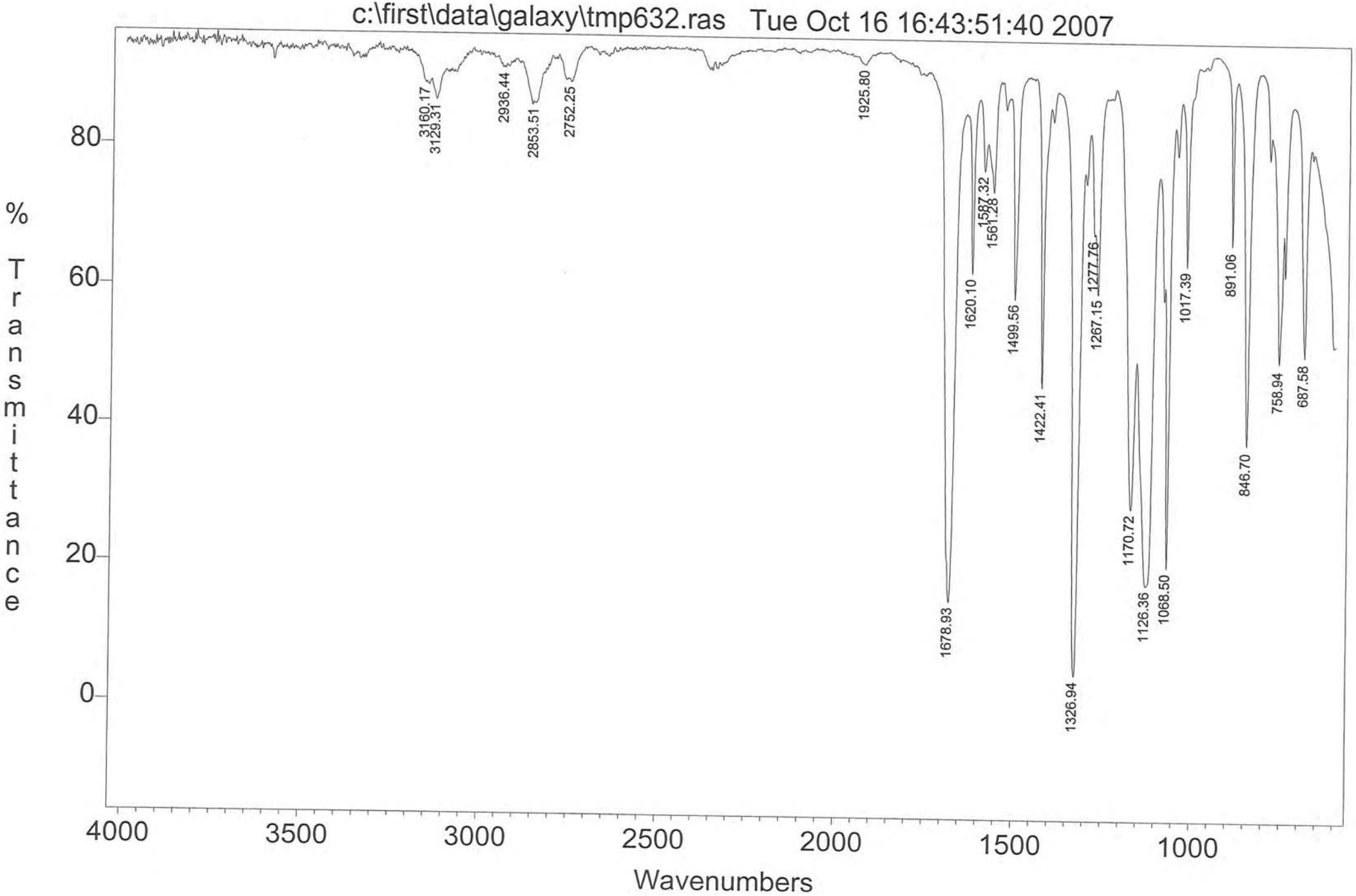
3f

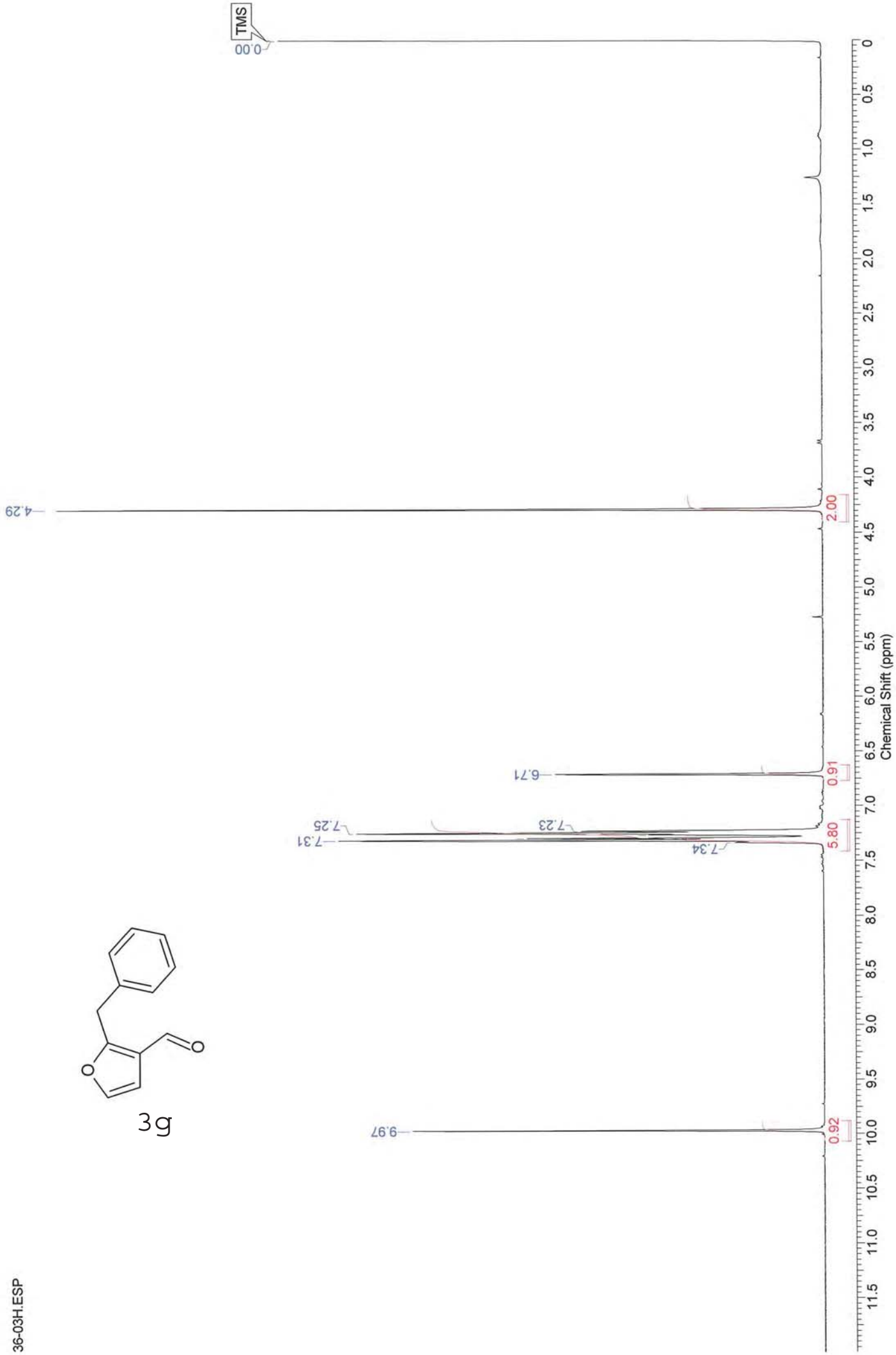

CHLOROFORM-d
10.14
7.78
7.90
7.93
7.54
7.54
7.26
6.95
6.95
1.00
2.07
1.01
0.99
Chemical Shift (ppm)
30-03H.ESP

CF3
O
O

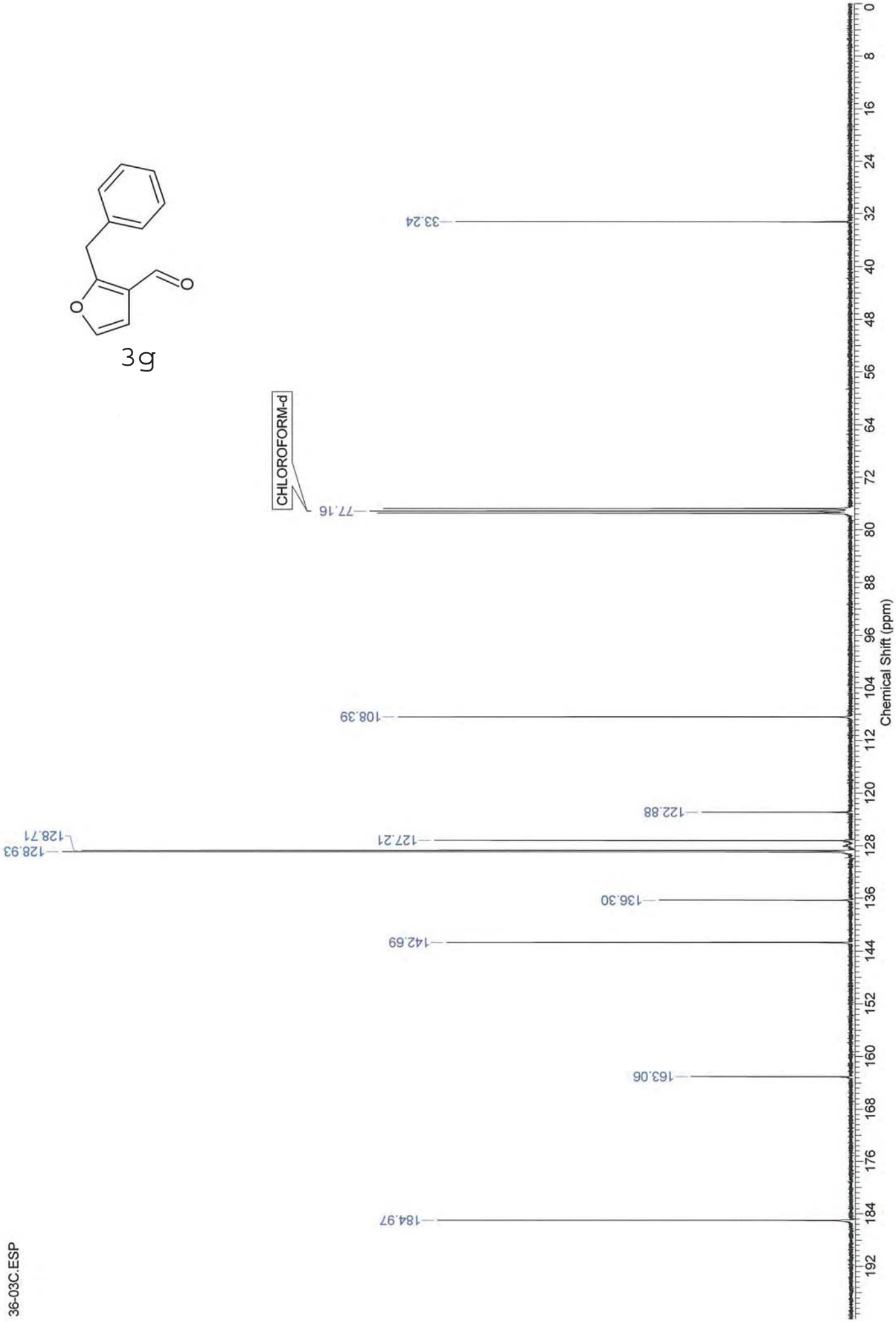
3f

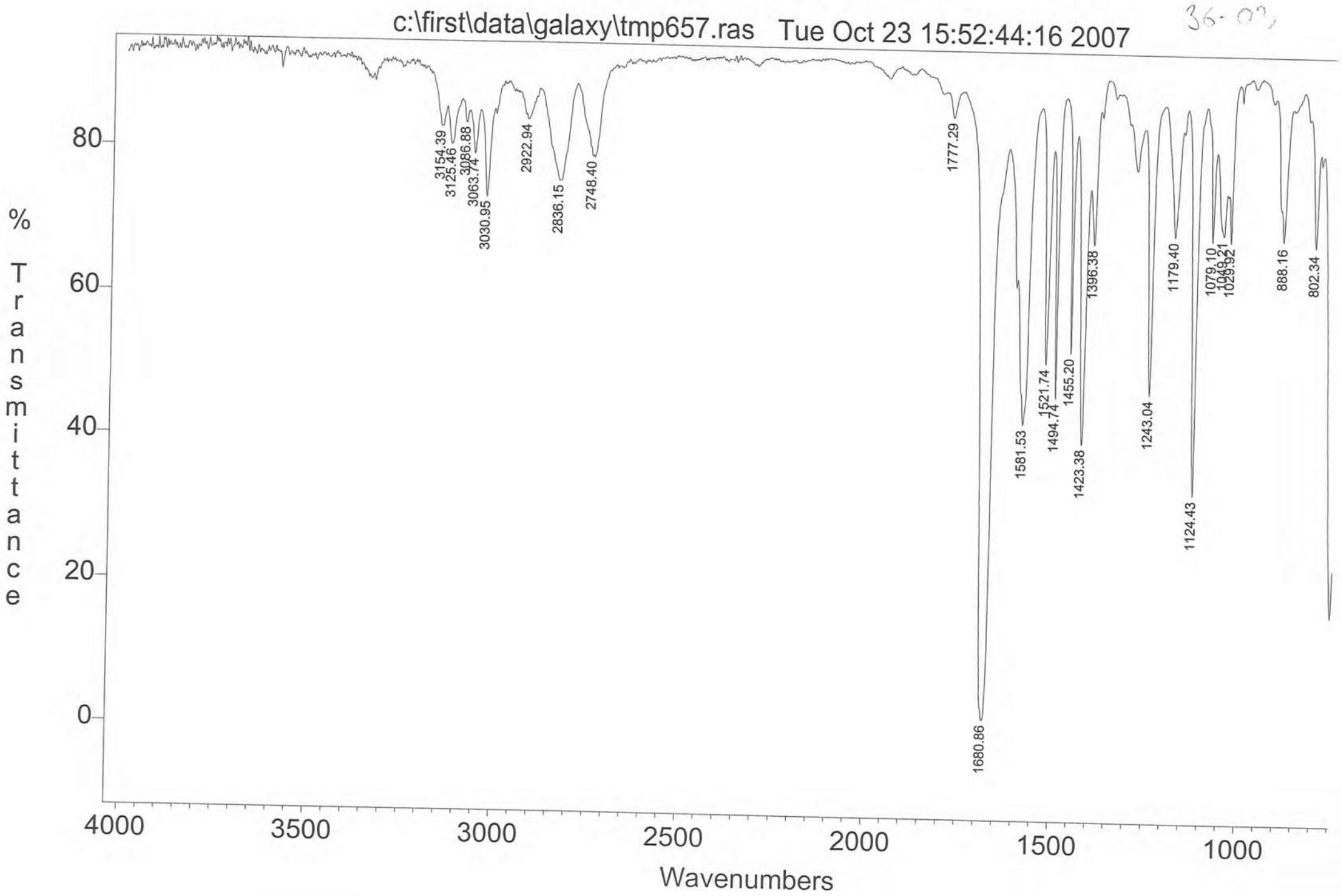

CHLOROFORM-d
77.16
110.44
122.36
124.09
126.15
128.28
132.28
143.61
158.93
185.20
Chemical Shift (ppm)
30-03C.ESP

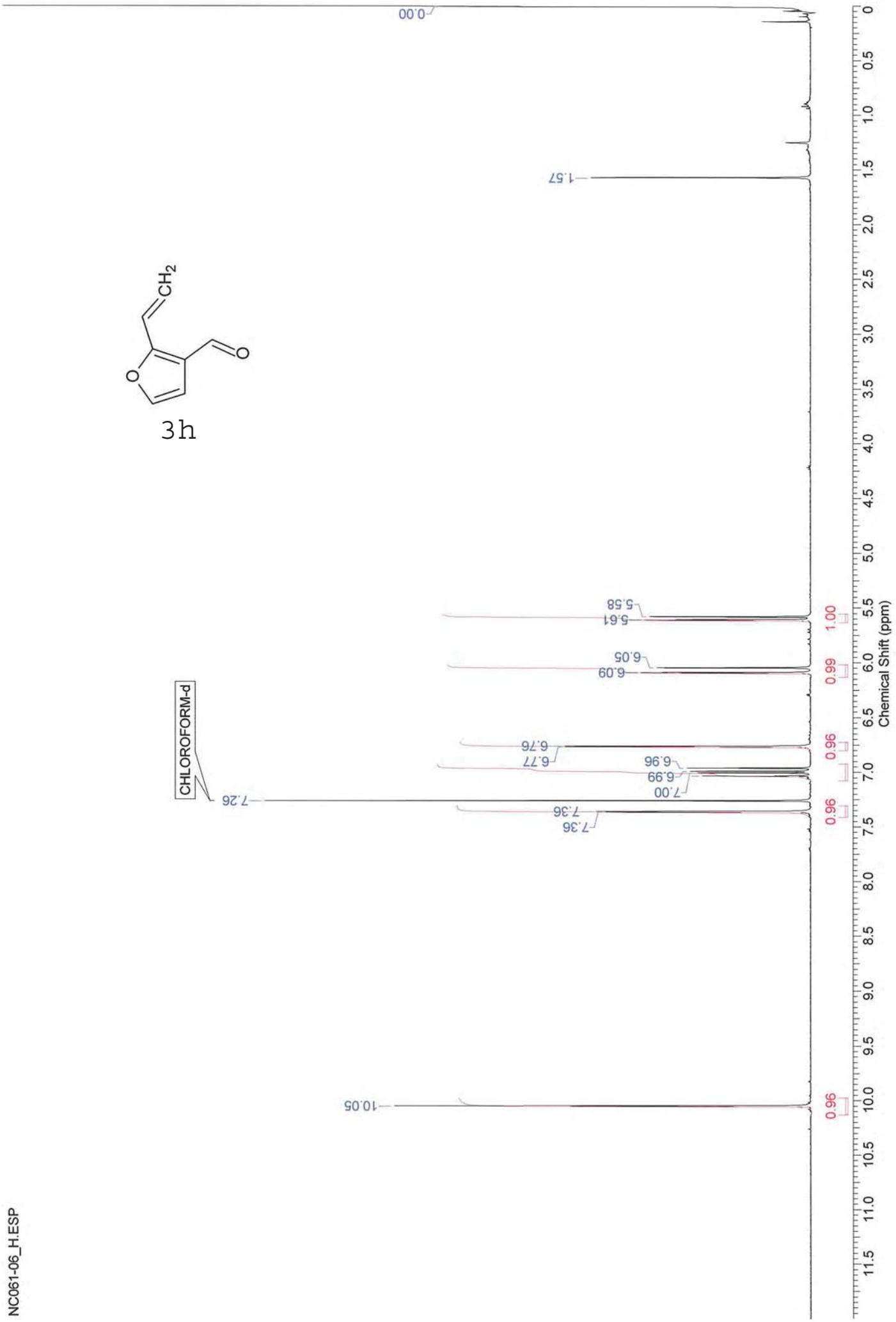

c:\first\data\galaxy\tmp632.ras Tue Oct 16 16:43:51:40 2007
% Transmittance
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3160.17
3129.31
2936.44
2853.51
2752.25
1925.80
1678.93
1620.10
1587.32
1561.28
1499.56
1422.41
1326.94
1277.76
1267.15
1170.72
1126.36
1068.50
1017.39
891.06
846.70
758.94
687.58

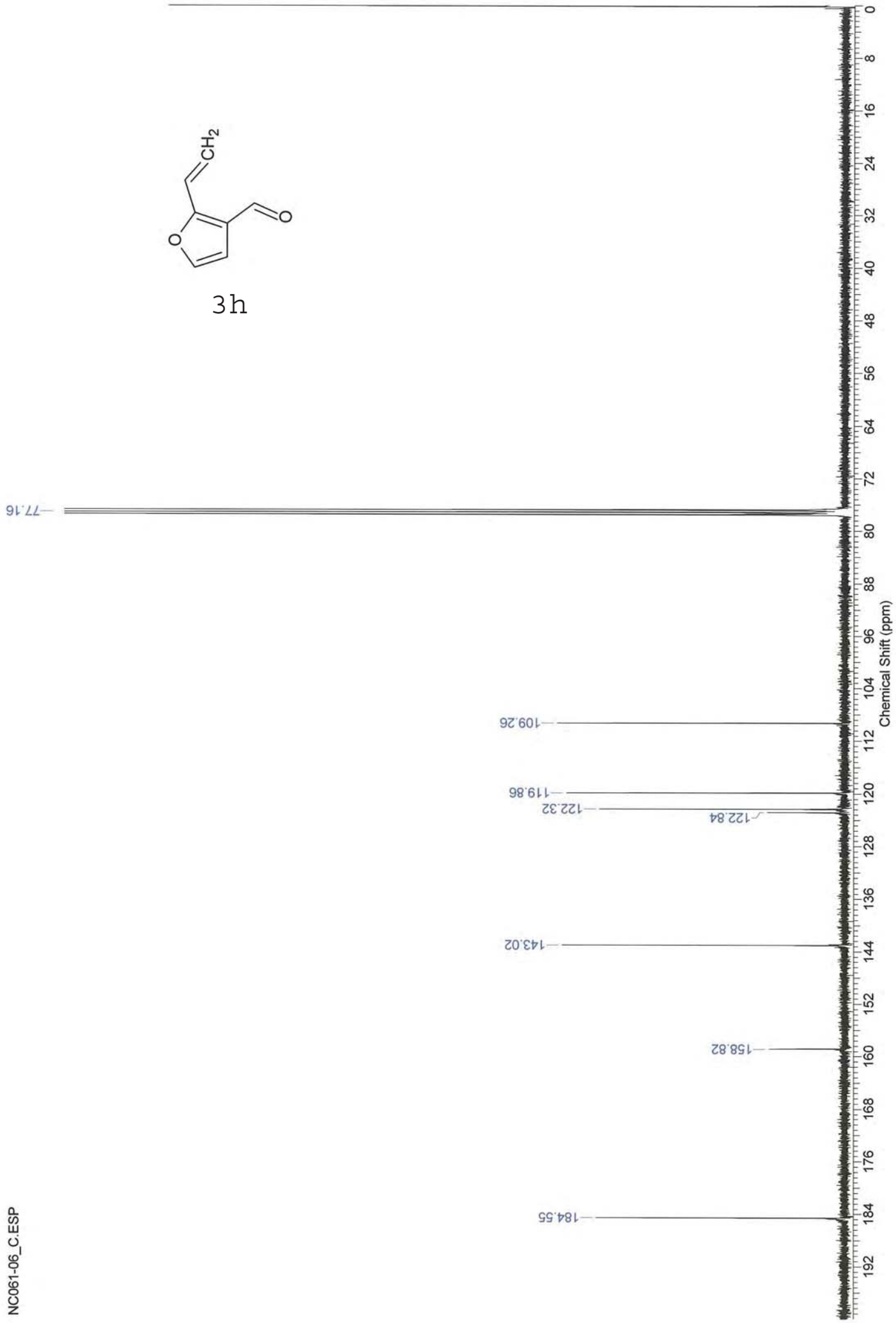

TMS
0.00
4.29
2.00
6.71
0.91
7.25
7.23
7.31
7.34
5.80
9.97
0.92
Chemical Shift (ppm)
36-03H.ESP

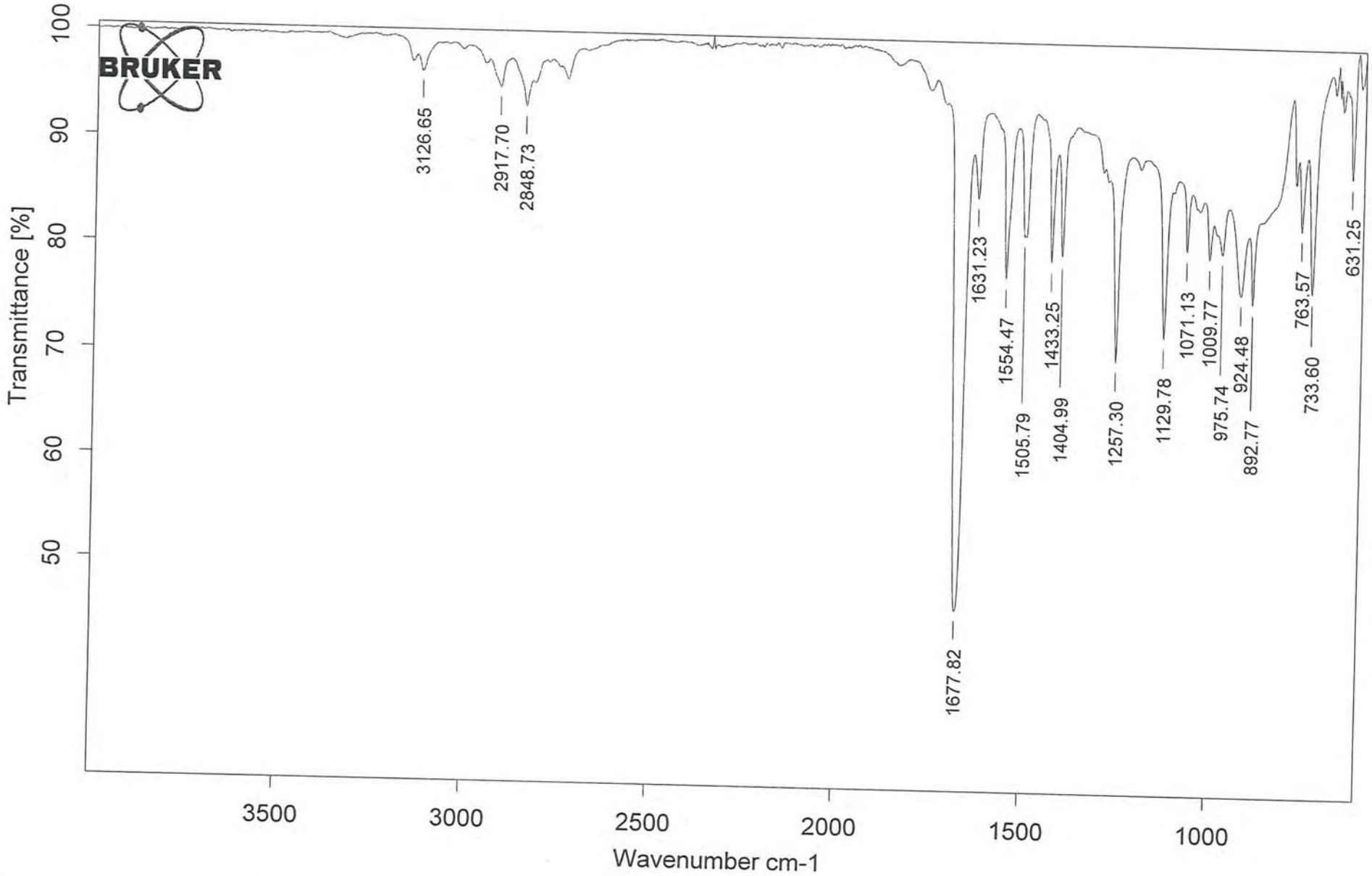
3g


3g
CHLOROFORM-d
33.24
77.16
108.39
122.88
127.21
128.71
128.93
136.30
142.69
163.06
184.97
Chemical Shift (ppm)
36-03C.ESP


c:\first\data\galaxy\tmp657.ras Tue Oct 23 15:52:44:16 2007
36-02
% Transmittance
80
60
40
20
0
3154.39
3125.46
3086.88
3063.74
3030.95
2922.94
2836.15
2748.40
1777.29
1680.86
1581.53
1521.74
1494.74
1455.20
1423.38
1396.38
1243.04
1179.40
1124.43
1079.10
1049.21
1029.92
888.16
802.34
4000
3500
3000
2500
2000
1500
1000
Wavenumbers


0.00
1.57
CH2
O
O
3h
5.61
5.58
1.00
6.09
6.05
0.99
6.76
6.77
6.96
6.99
7.00
0.96
CHLOROFORM-d
7.26
7.36
7.36
0.96
10.05
0.96
Chemical Shift (ppm)
NC061-06_H.ESP


CH2
O
O
3h
77.16
109.26
119.86
122.32
122.84
143.02
158.82
184.55
Chemical Shift (ppm)
NC061-06_C.ESP

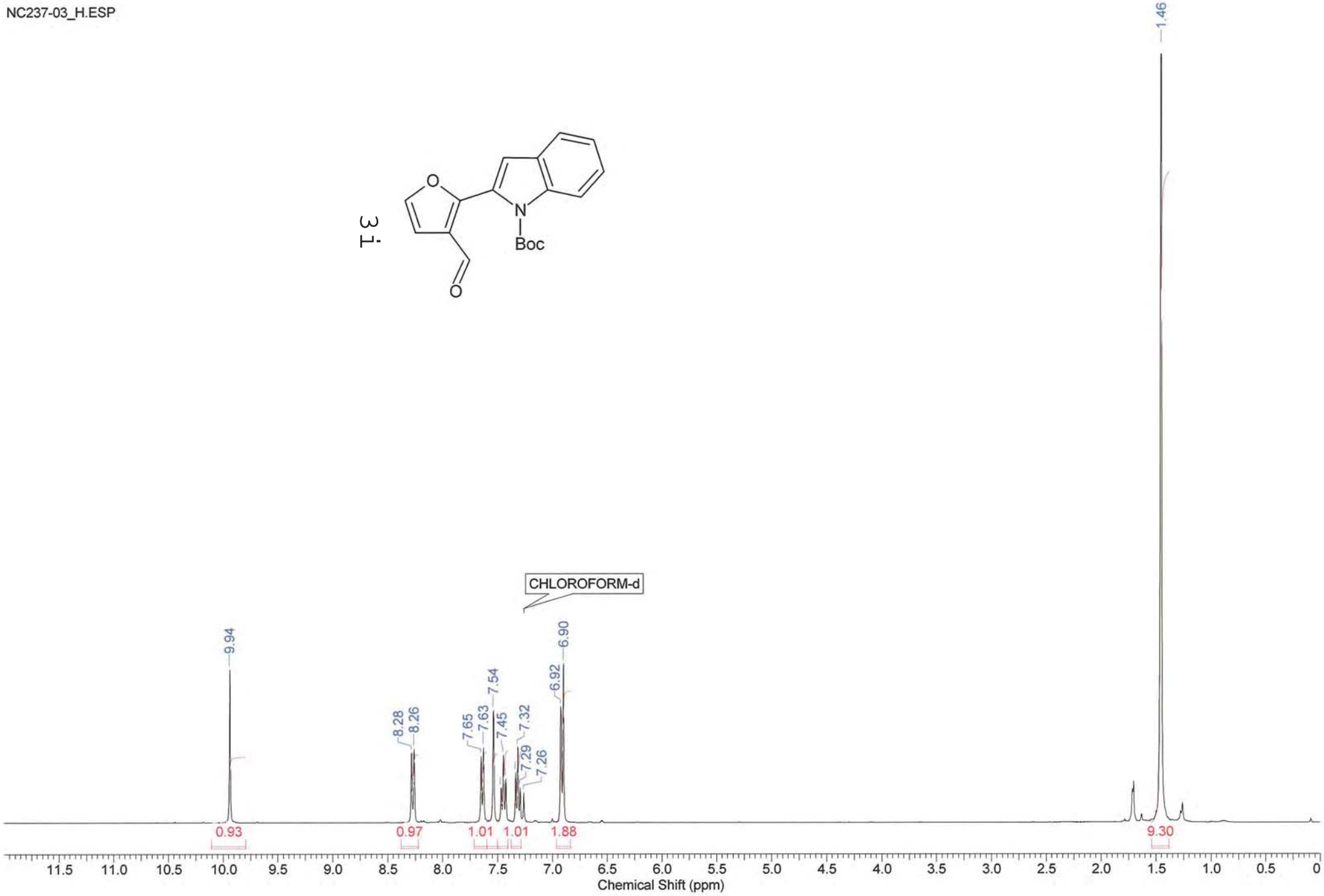


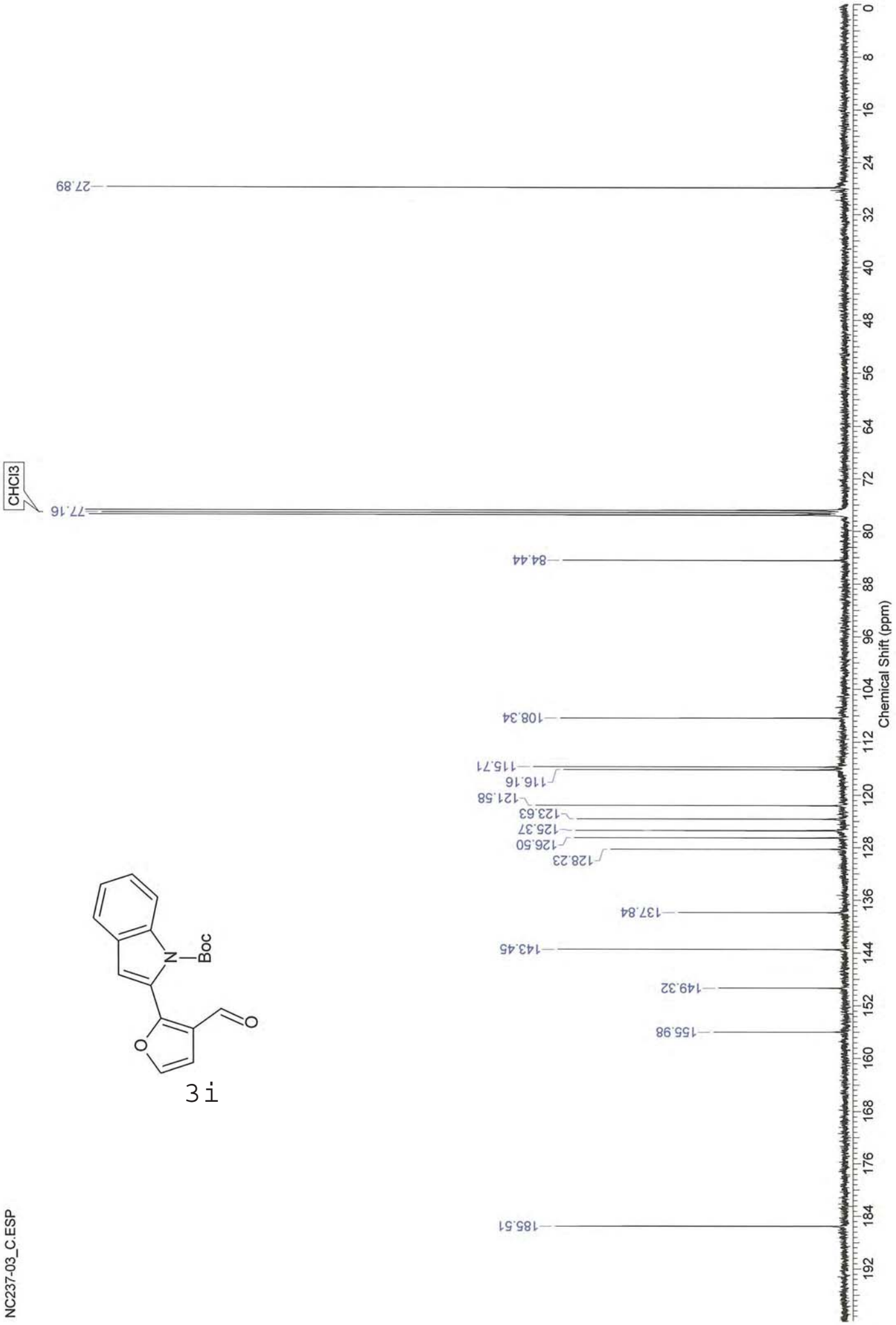
C:\Program Files\OPUS\meas\Chn\nc061-06.0	nc061-06	Instrument type and / or accessory	11/12/2008

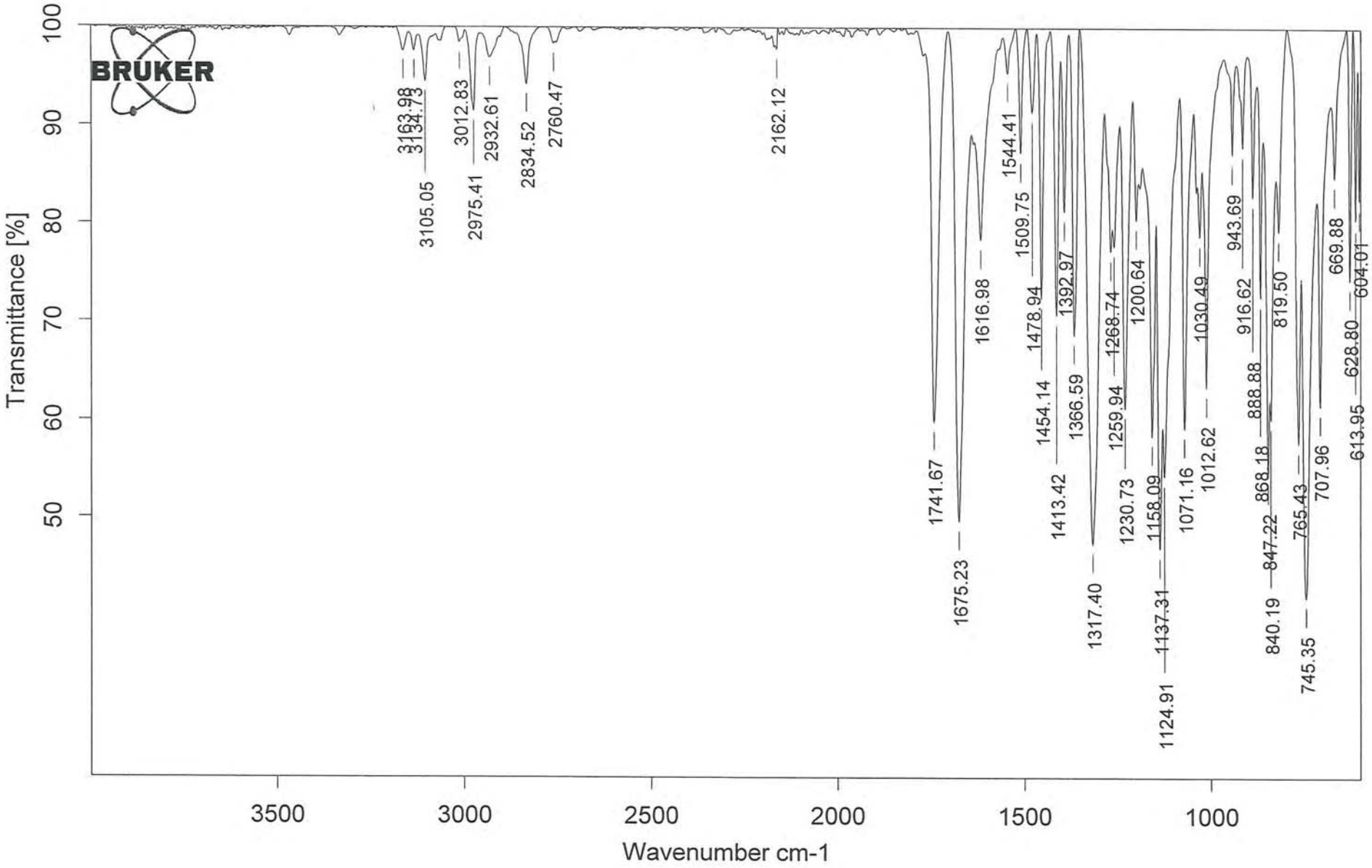
Page 1/1

NC237-03_H.ESP

3 1




27.89
CHCl3
77.16
84.44
108.34
115.71
116.16
121.58
123.63
125.37
126.50
128.23
137.84
143.45
149.32
155.98
185.51
Chemical Shift (ppm)
0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
128
136
144
152
160
168
176
184
192
N
Boc
O
O
3i
NC237-03_C.ESP



C:\Program Files\OPUS\Data\Chn\nc237-03.0	nc237-03	yellow solid	05/08/2010

Page 1/1

ESI-MS: NC237-03

XMASS Mass Analysis for /Data/UNI_FR/CHAR5028_ESI/5/pdata/1/massanal.res:
XMASS Mass Analysis Constraints

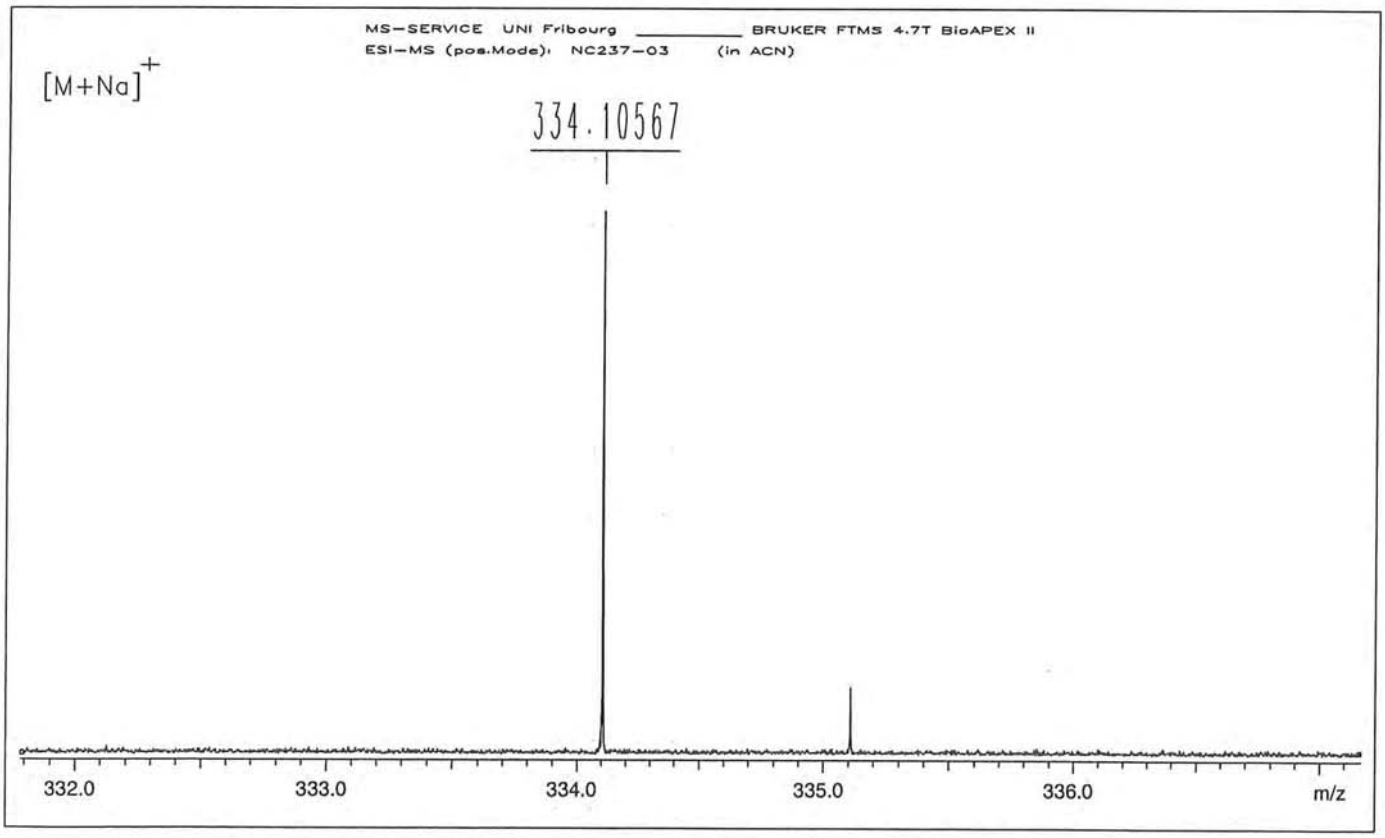
Ion mass = 334.1056670

Charge = +1

#	C	H	N	O	Na	mass	DBE	error

*** Mass Analysis for mass 334.1056670

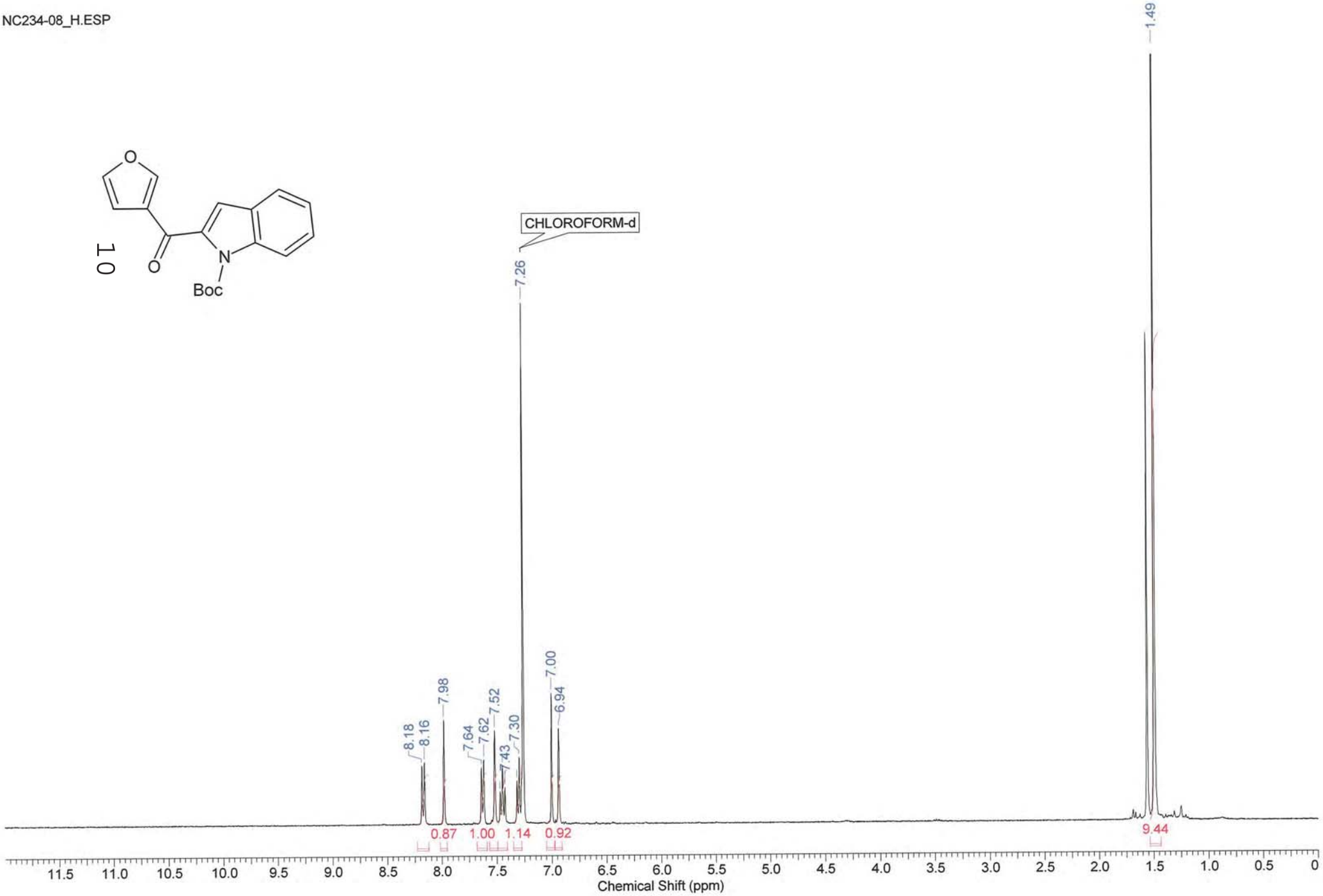
1	18	17	1	4	1	334.1049791	10.5	6.879e-04
2	20	16	1	4	0	334.1073844	13.5	1.717e-03
3	21	15	2	1	1	334.1076592	15.0	1.992e-03
4	23	14	2	1	0	334.1100645	18.0	4.398e-03
5	22	12	3	1	0	334.0974884	18.5	8.179e-03
6	17	17	3	3	1	334.1162125	10.5	1.055e-02
7	20	13	3	1	1	334.0950831	15.5	1.058e-02
8	19	14	2	4	0	334.0948084	14.0	1.086e-02
9	19	16	3	3	0	334.1186178	13.5	1.295e-02
10	17	15	2	4	1	334.0924031	11.0	1.326e-02



/Data/UNI_FR/CHAR5028_ESI/5/pdata/1 FTMS USER Wed Aug 11 15:23:45 2010

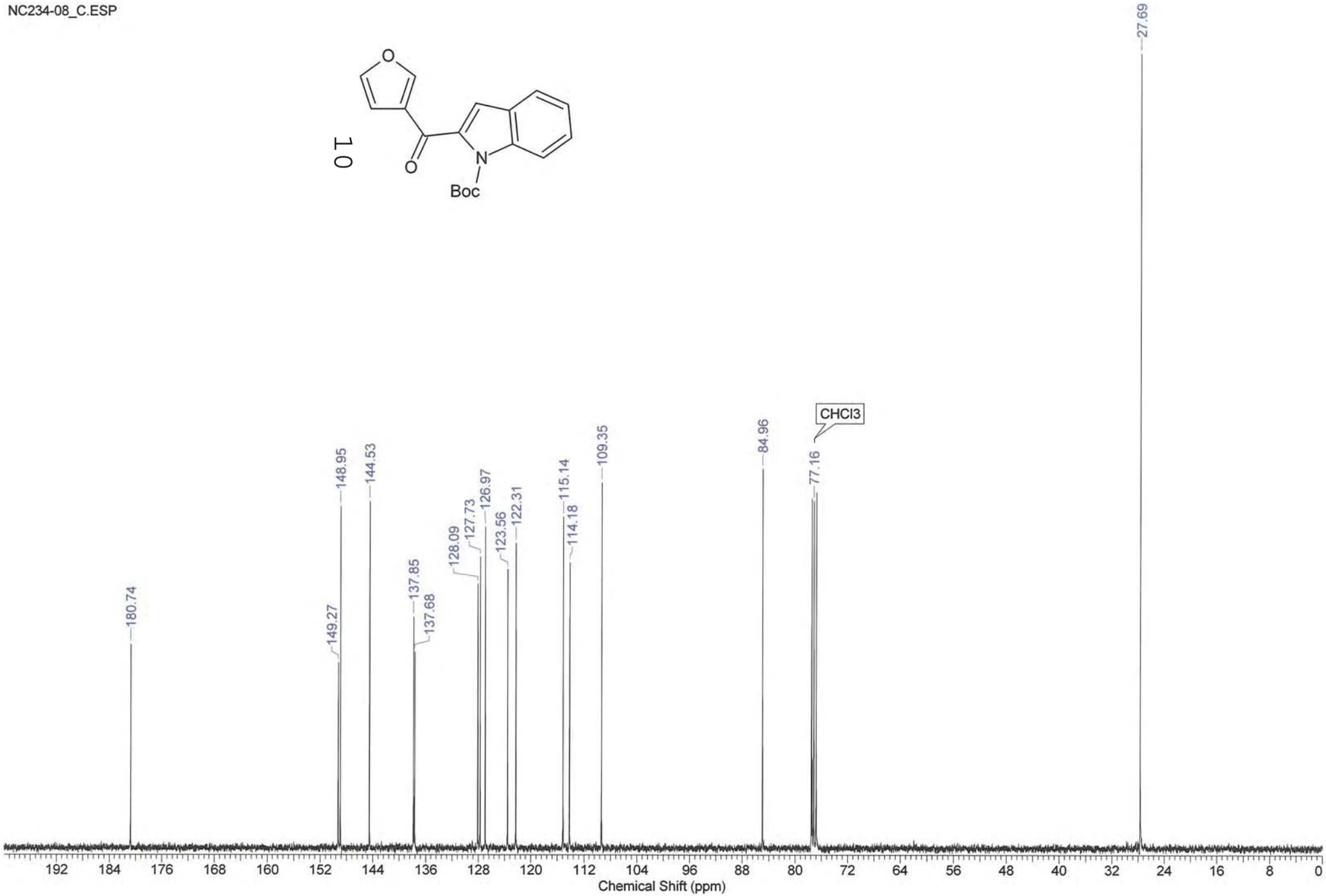
NC234-08_H.ESP

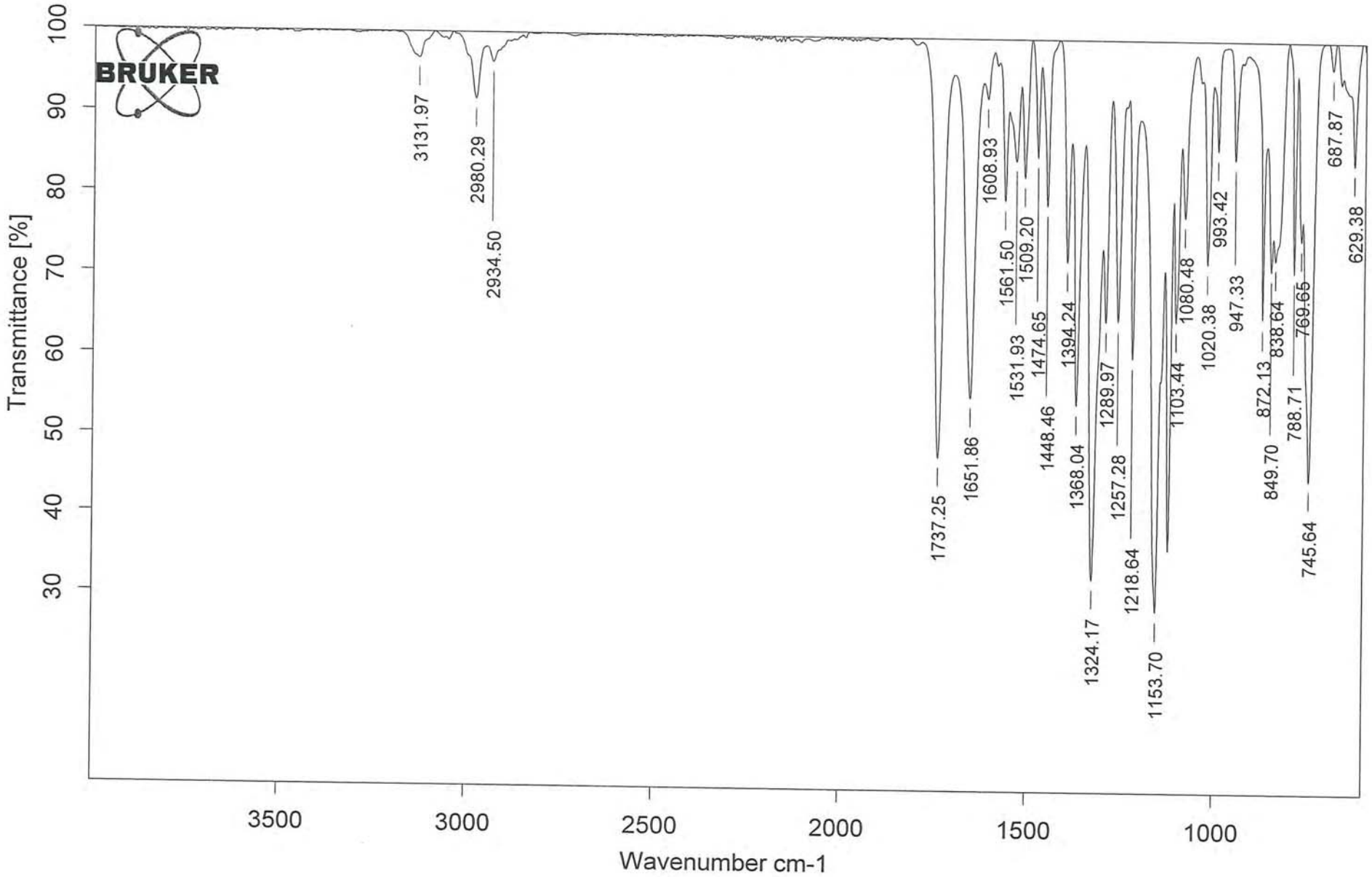
10



NC234-08_C.ESP

10





C:\Program Files\OPUS\Data\Chn\nc234-08.0	nc234-08	brown oil	03/08/2010

Page 1/1

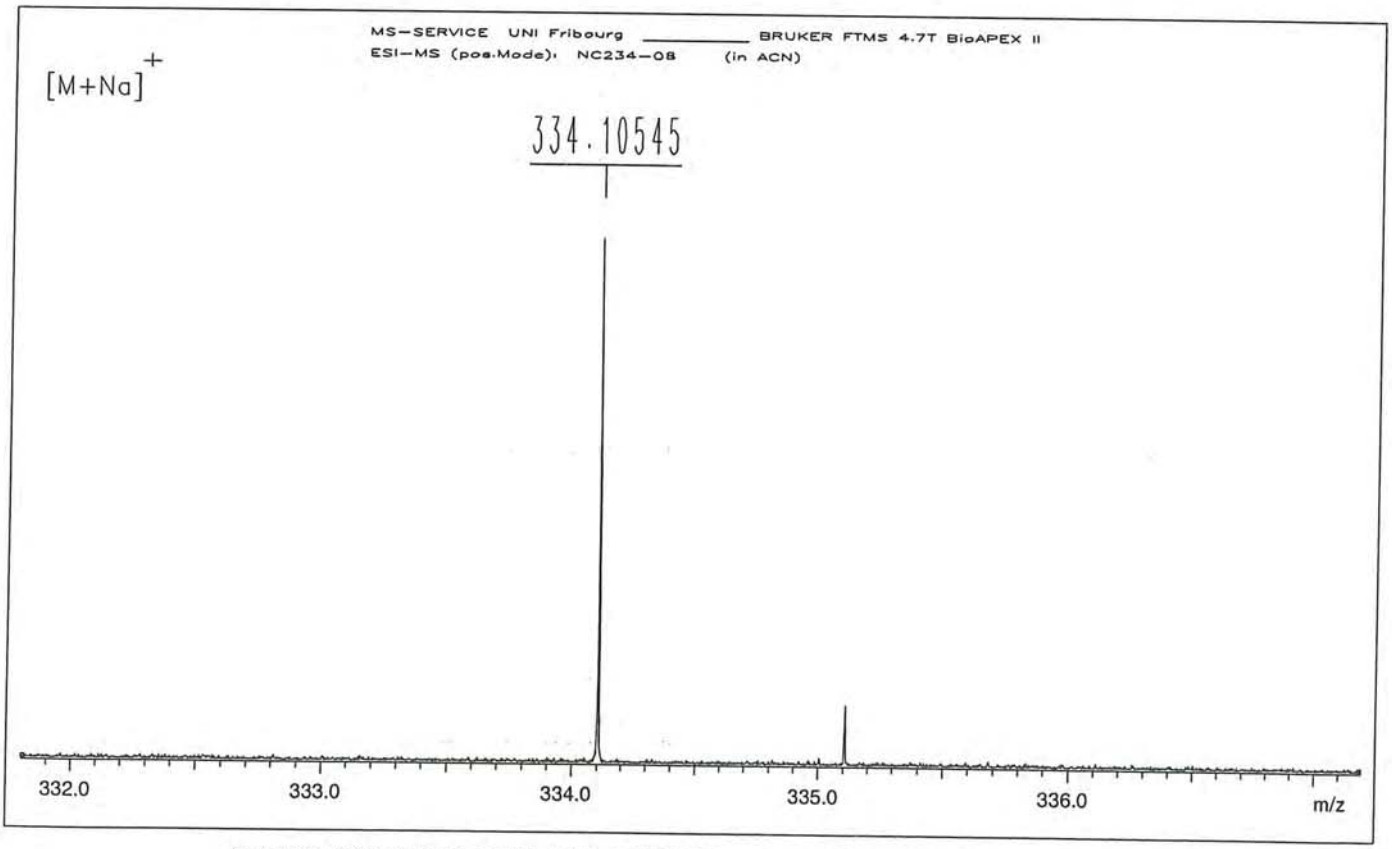
ESI-MS: NC234-08

XMASS Mass Analysis for /Data/UNI_FR/CHAR5030_ESI/2/pdata/1/massanal.res:
XMASS Mass Analysis Constraints

Ion mass = 334.1054530

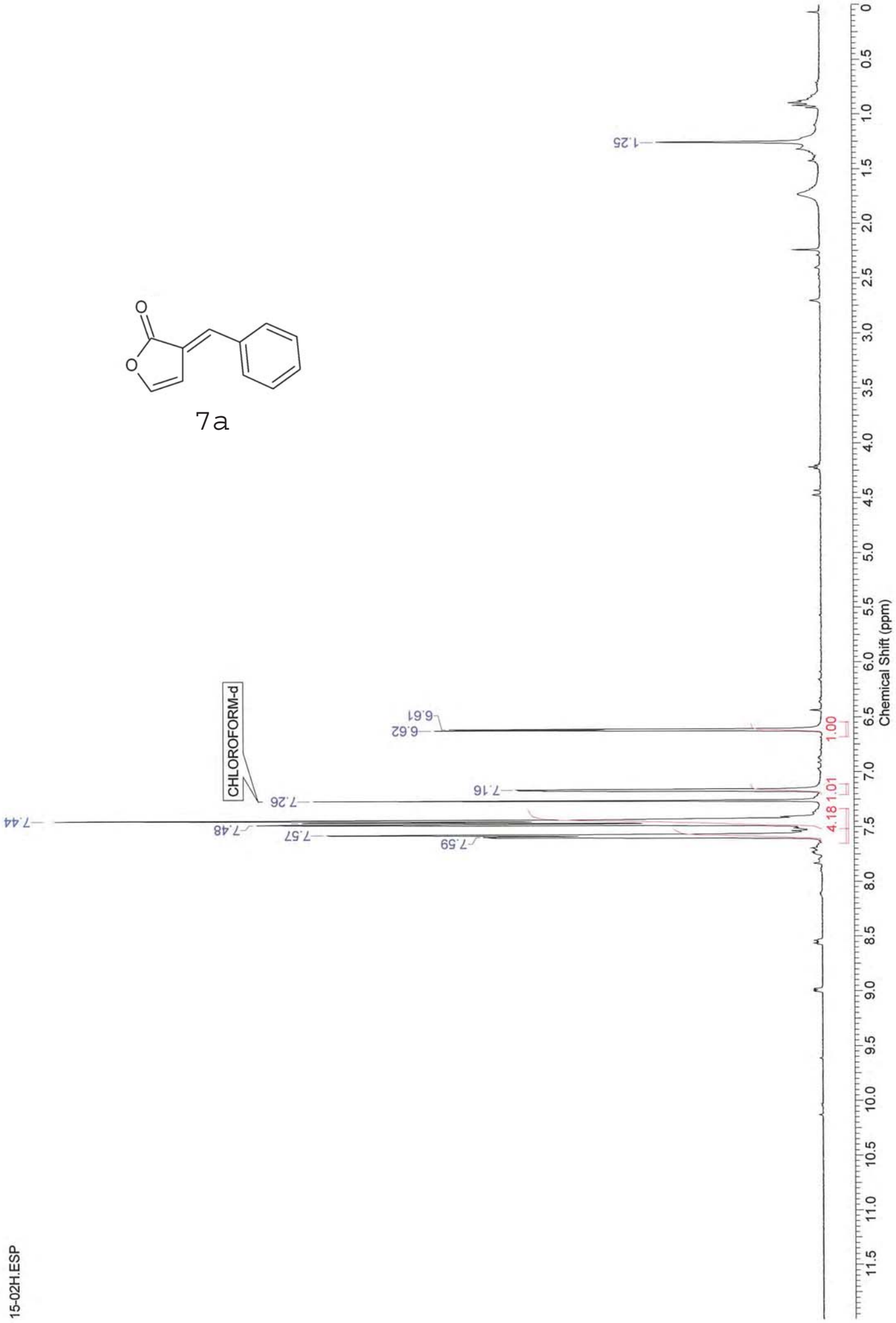
Charge = +1

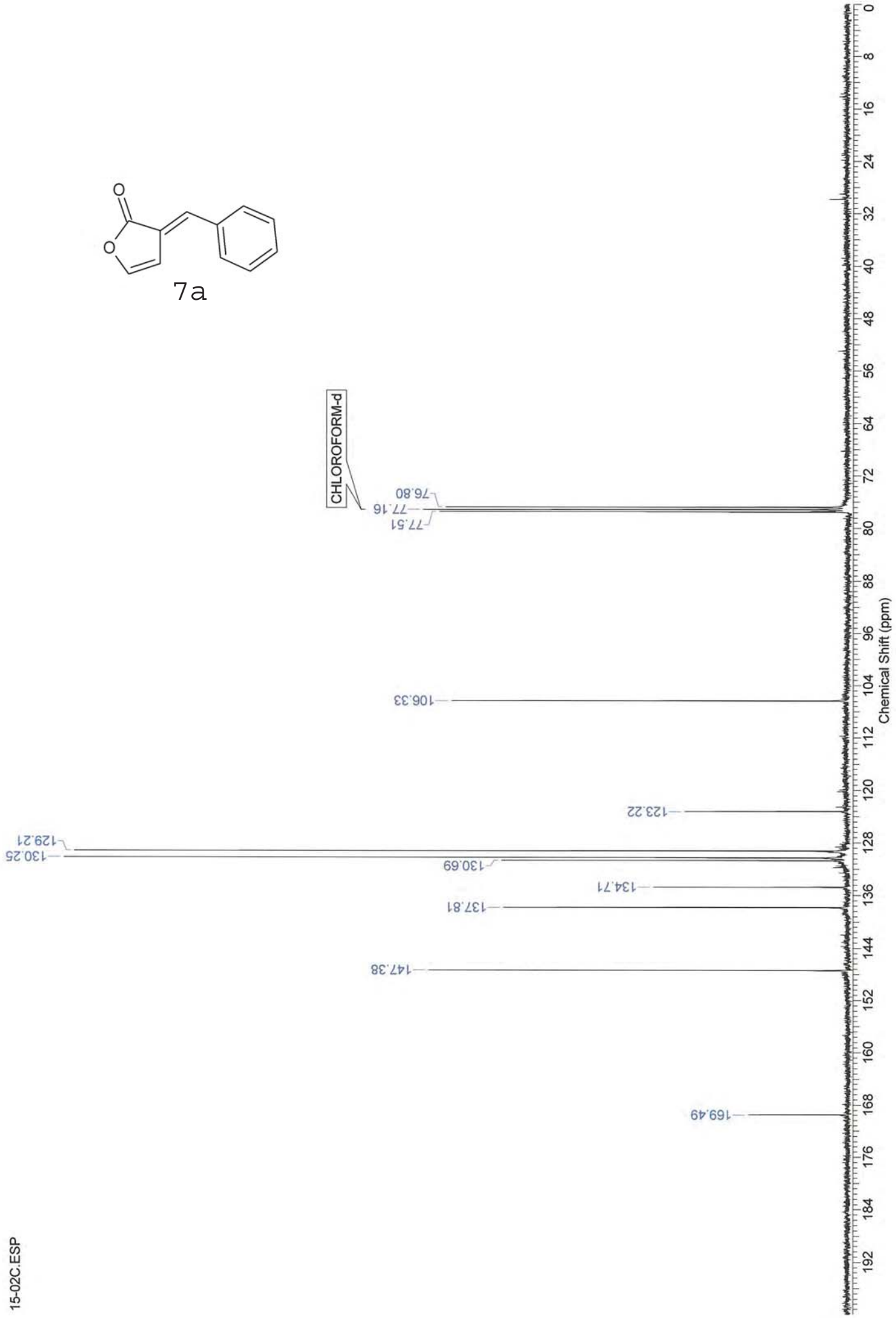
#	C	H	N	O	Na	mass	DBE	error
*** Mass Analysis for mass 334.1054530								
1	18	17	1	4	1	334.1049791	10.5	4.739e-04
2	18	14	4	3	0	334.1060418	14.0	5.888e-04
3	16	15	4	3	1	334.1036365	11.0	1.817e-03
4	20	16	1	4	0	334.1073844	13.5	1.931e-03
5	21	15	2	1	1	334.1076592	15.0	2.206e-03
6	23	14	2	1	0	334.1100645	18.0	4.612e-03
7	22	12	3	1	0	334.0974884	18.5	7.965e-03
8	20	13	3	1	1	334.0950831	15.5	1.037e-02
9	19	14	2	4	0	334.0948084	14.0	1.064e-02
10	17	17	3	3	1	334.1162125	10.5	1.076e-02

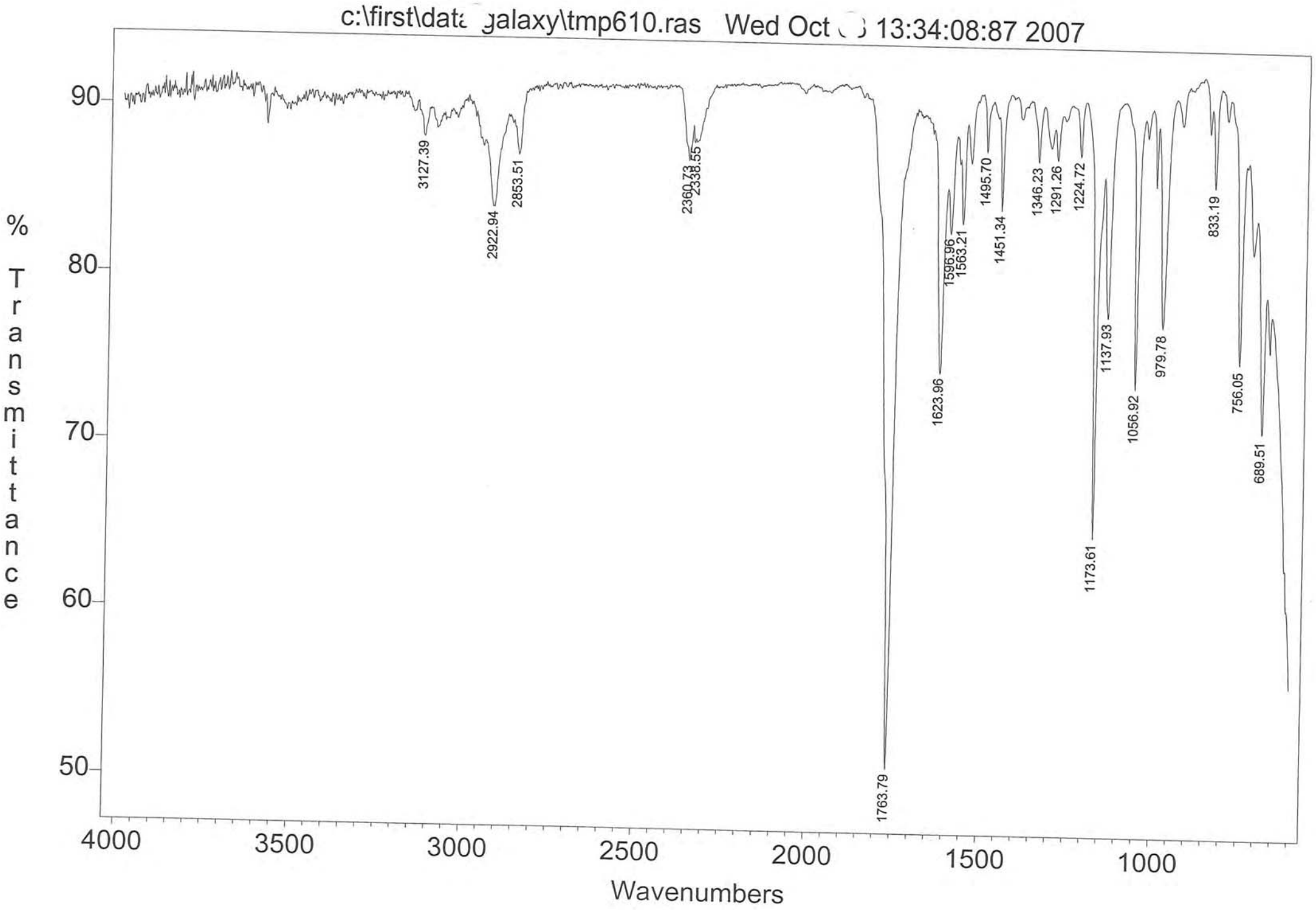


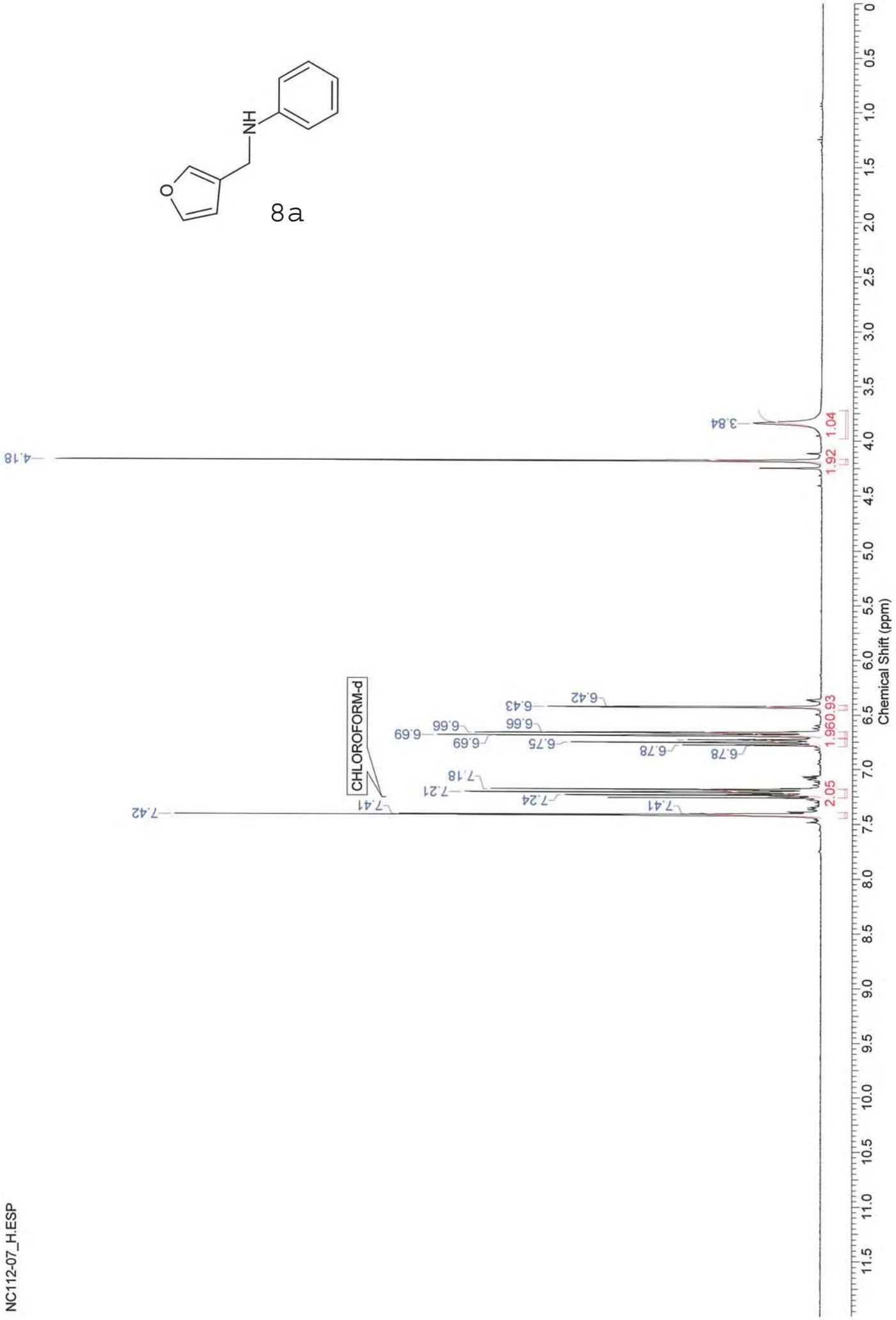
/Data/UNI_FR/CHAR5030_ESI/2/pdata/1 FTMS USER Wed Aug 11 15:20:20 2010

7a


1.25
6.62
6.61
7.26
CHLOROFORM-d
7.16
7.44
7.48
7.57
7.59
1.00
1.01
4.18
Chemical Shift (ppm)
15-02H.ESP

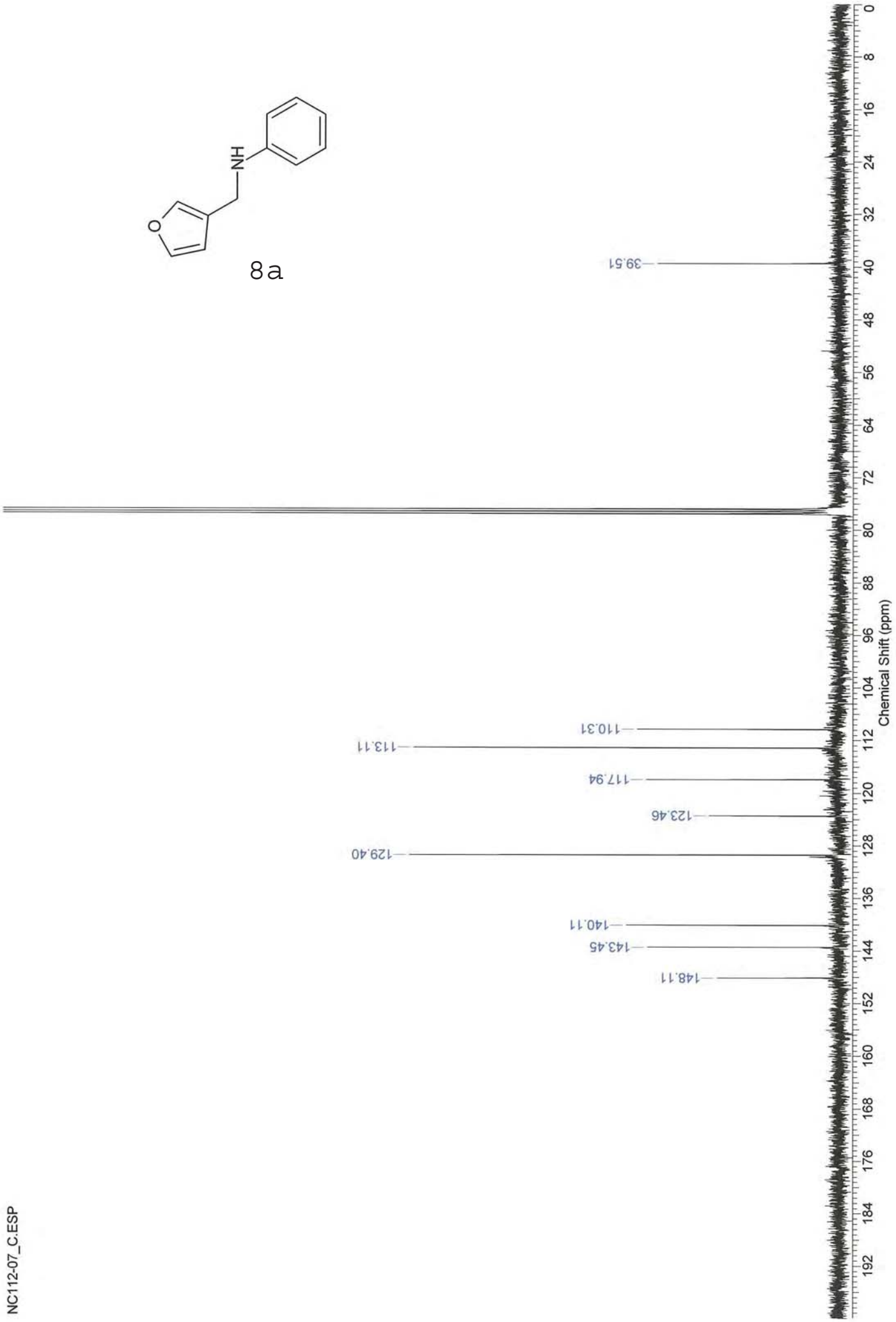

7a
CHLOROFORM-d
76.80
77.16
77.51
106.33
123.22
129.21
130.25
130.69
134.71
137.81
147.38
169.49
Chemical Shift (ppm)
15-02C.ESP

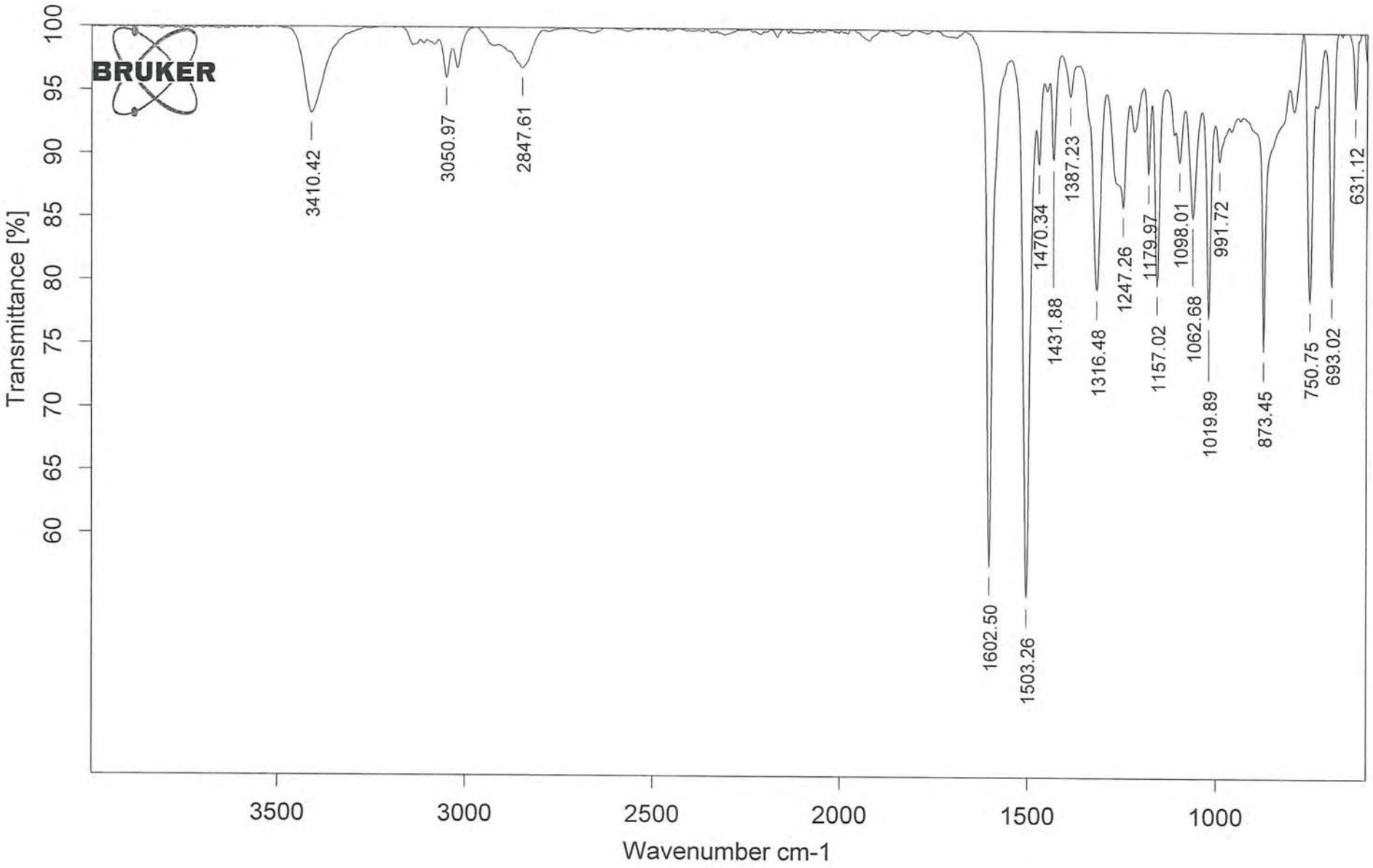

c:\first\data galaxy\tmp610.ras Wed Oct 13:34:08:87 2007
% Transmittance
90
80
70
60
50
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
3127.39
2922.94
2853.51
2360.73
2338.55
1763.79
1623.96
1596.96
1563.21
1495.70
1451.34
1346.23
1291.26
1224.72
1173.61
1137.93
1056.92
979.78
833.19
756.05
689.51


NC112-07_H.ESP
Chemical Shift (ppm)
CHLOROFORM-d
4.18
7.42
3.84
1.04
1.92
1.96
0.93
2.05
6.42
6.43
6.66
6.66
6.69
6.69
6.75
6.78
6.78
7.18
7.21
7.24
7.41
7.41
HN
O
8a

NH
O

8a


39.51
110.31
113.11
117.94
123.46
129.40
140.11
143.45
148.11
Chemical Shift (ppm)
NC112-07_C.ESP



C:\Program Files\OPUS\Data\Chn\nc112-07.0	nc112-07	nc112-07	15/04/2009

Page 1/1

ESI-MS: NC112-07

XMASS Mass Analysis for /Data/UNI_FR/CHAR4117_ESI/1/pdata/1/massanal.res:
XMASS Mass Analysis Constraints

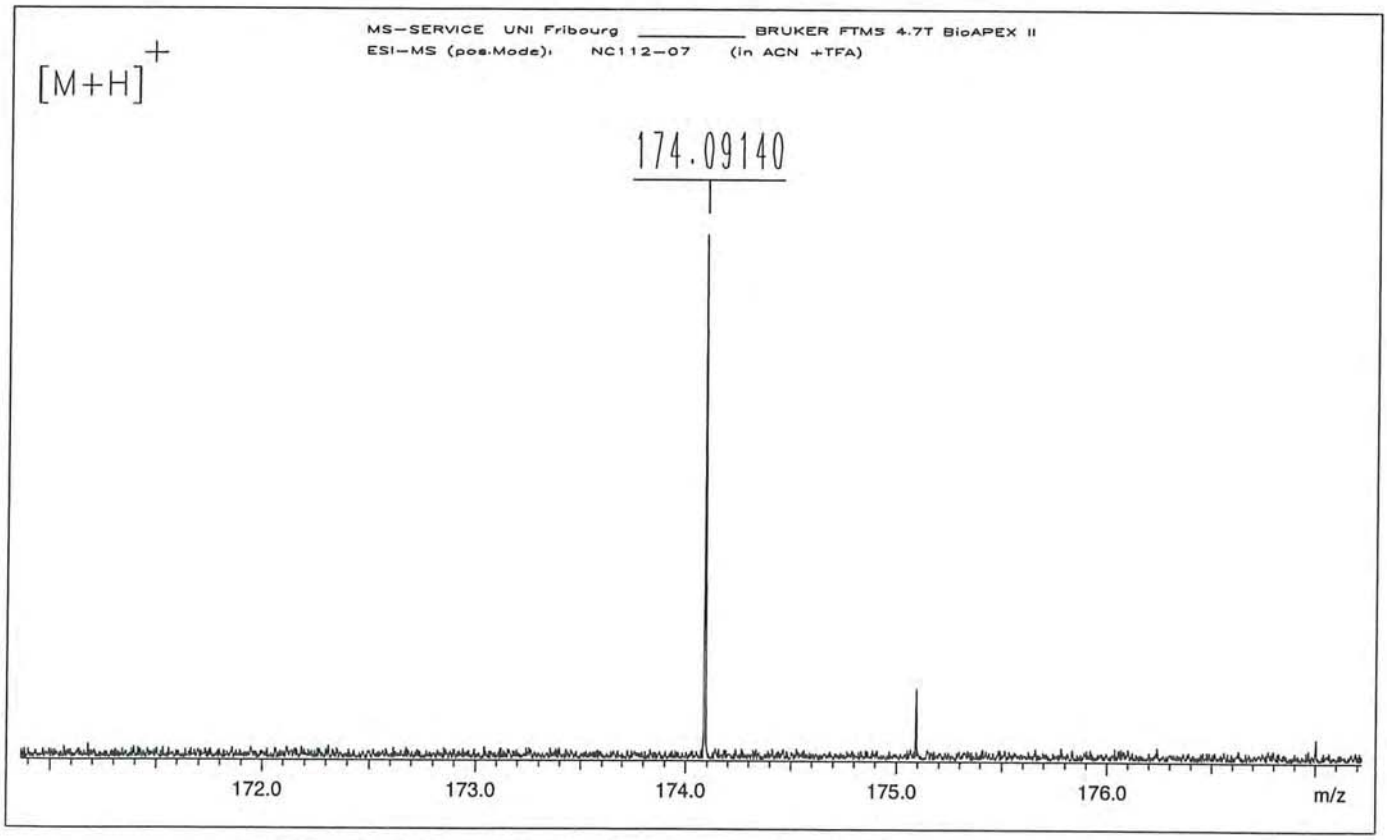
Ion mass = 174.0914000

Charge = +1

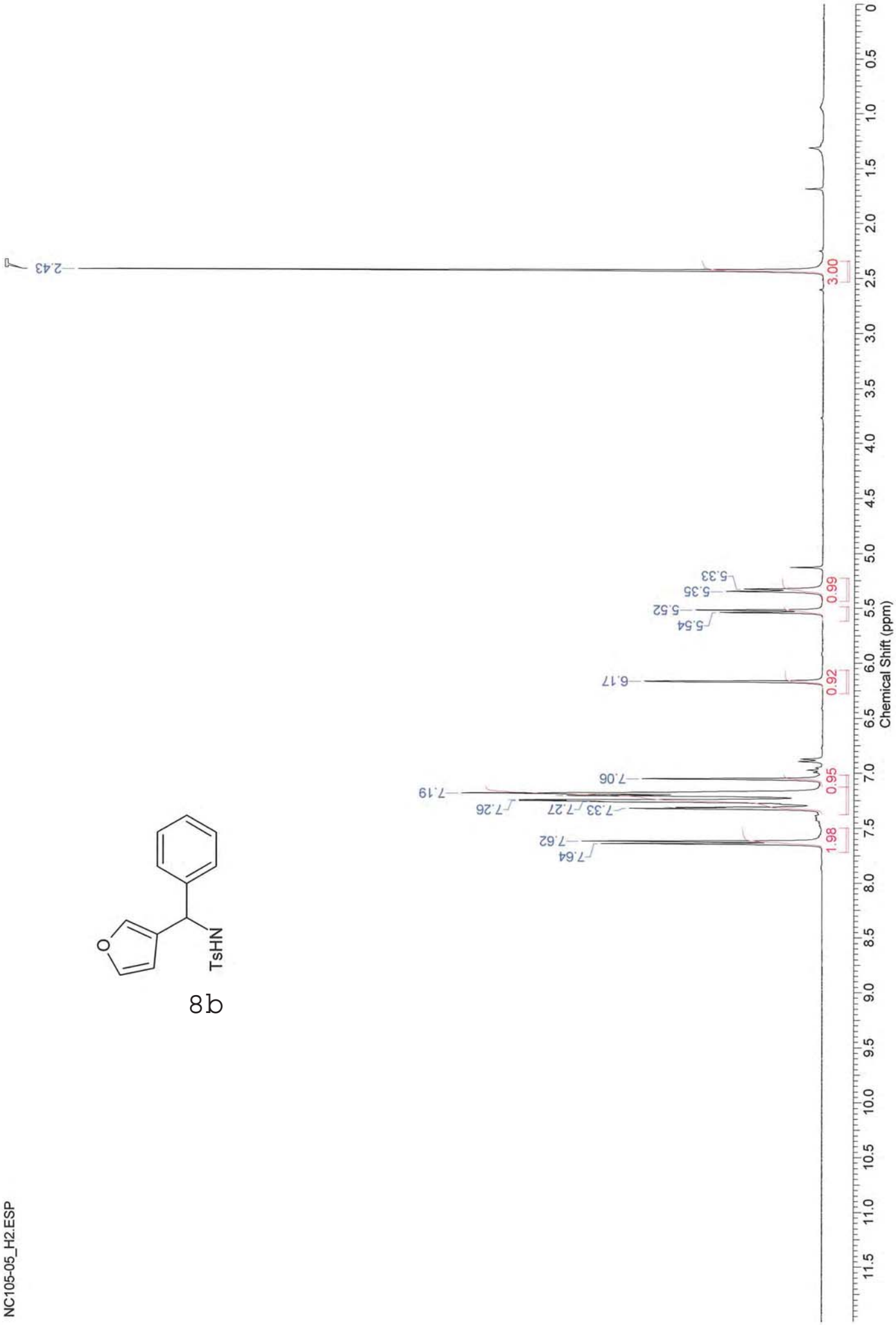
#	C	H	N	O	mass	DBE	error

*** Mass Analysis for mass 174.0914000

1	11	12	1	1	174.0913404	6.5	5.957e-05
2	6	12	3	3	174.0873177	2.5	4.082e-03
3	5	12	5	2	174.0985511	2.5	7.151e-03
4	7	14	2	3	174.0998937	2.0	8.494e-03
5	10	10	2	1	174.0787644	7.0	1.264e-02
6	7	12	1	4	174.0760843	2.5	1.532e-02
7	5	10	4	3	174.0747416	3.0	1.666e-02
8	6	14	4	2	174.1111271	2.0	1.973e-02
9	8	16	1	3	174.1124698	1.5	2.107e-02
10	9	8	3	1	174.0661883	7.5	2.521e-02



/Data/UNI_FR/CHAR4117_ESI/1/pdata/1 FTMS USER Wed Apr 15 13:35:29 2009


2.43
3.00
5.33
5.35
5.52
5.54
0.99
6.17
0.92
7.06
7.19
7.26
7.27
7.33
0.95
7.62
7.64
1.98
Chemical Shift (ppm)
NC105-05_H2.ESP

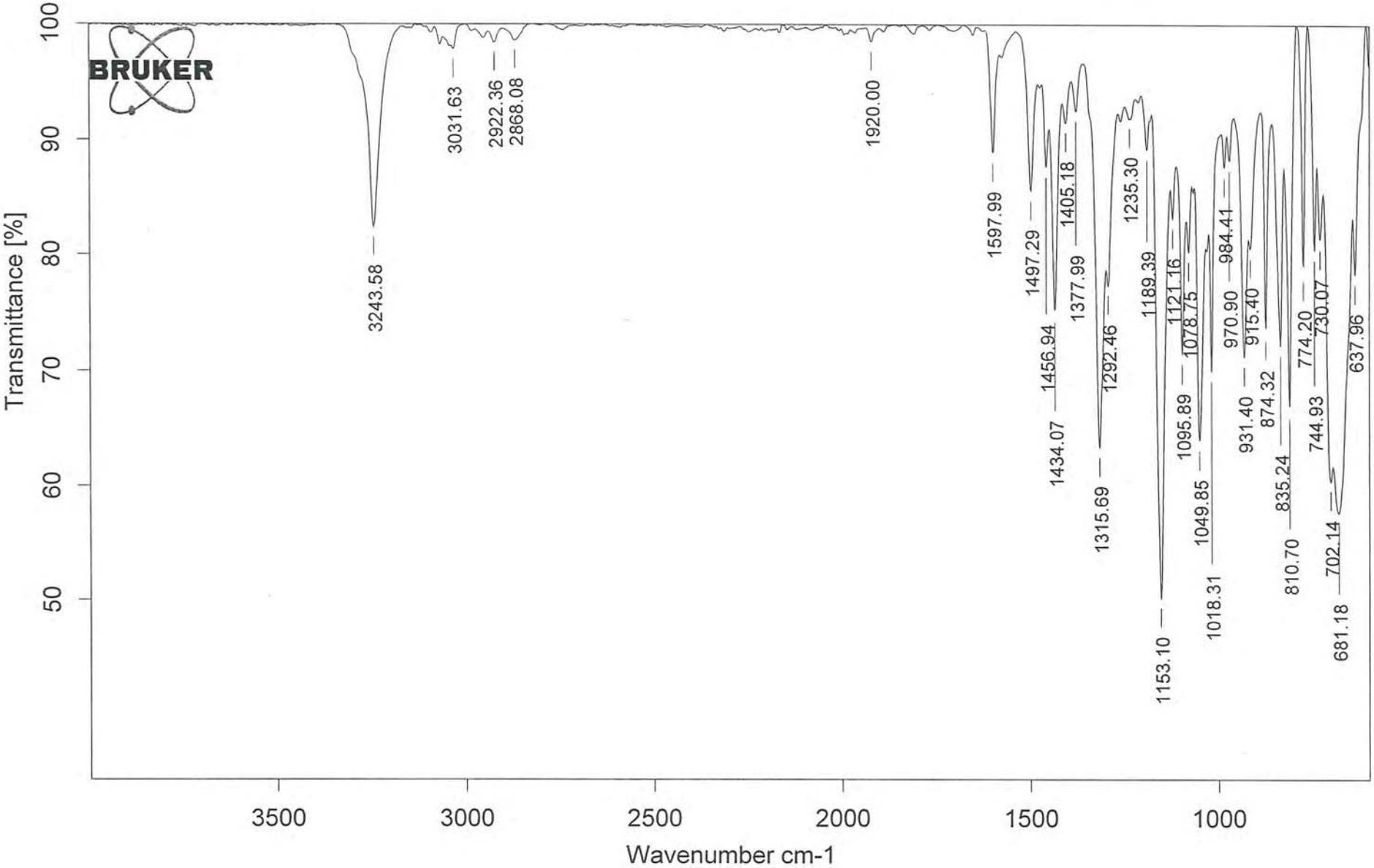
O
TsHN

8b

TsHN
O

8b


21.62
54.24
109.60
126.38
127.16
128.64
129.51
137.54
139.83
140.64
143.39
143.72
Chemical Shift (ppm)
NC105-05_C.ESP



C:\Program Files\OPUS\Data\Chn\nc105-05.0	nc105-05	nc105-05	08/04/2009

Page 1/1

S90

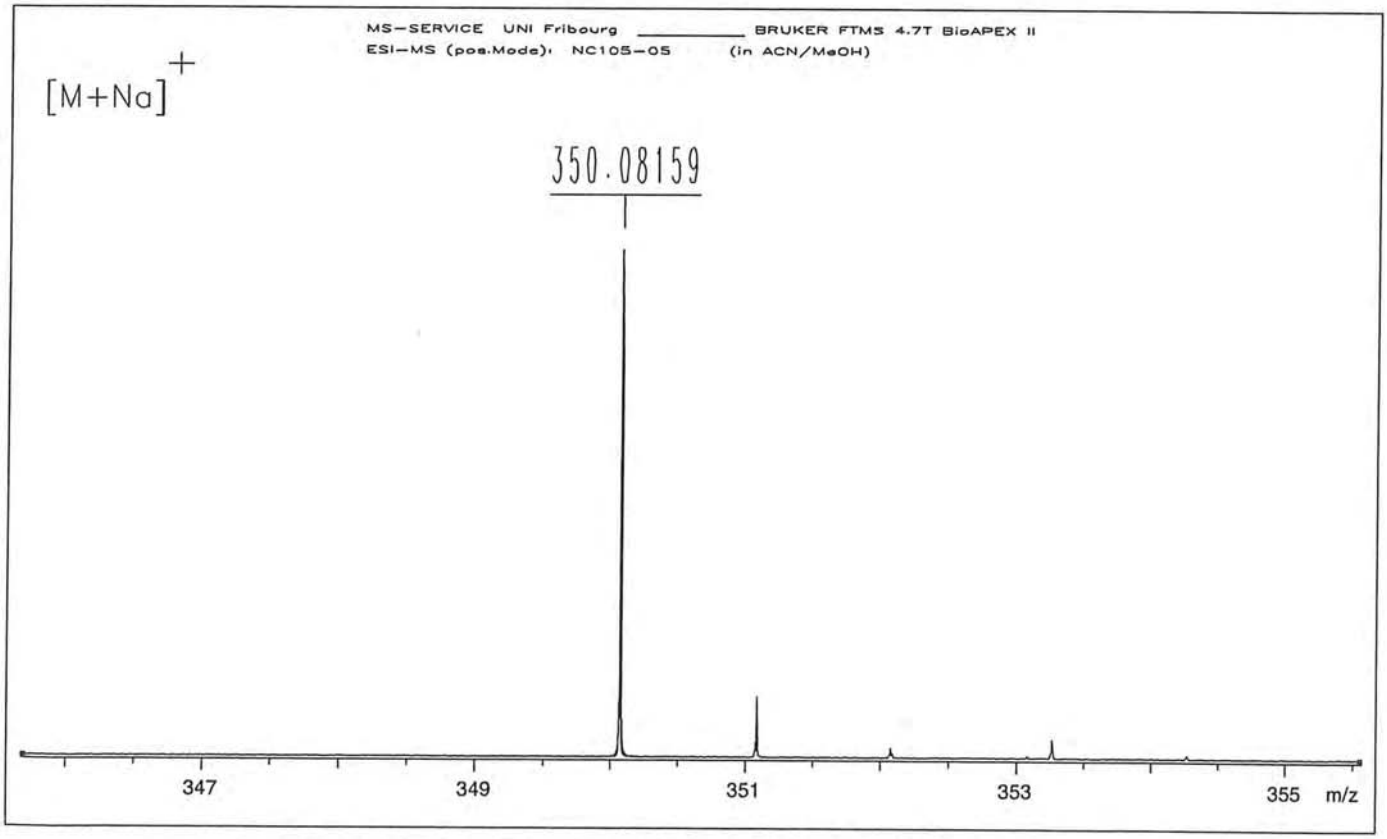
ESI-MS: NC105-05

XMASS Mass Analysis for /Data/UNI_FR/CHAR4108_ESI/5/pdata/1/massanal.res:
XMASS Mass Analysis Constraints

Ion mass = 350.0815930

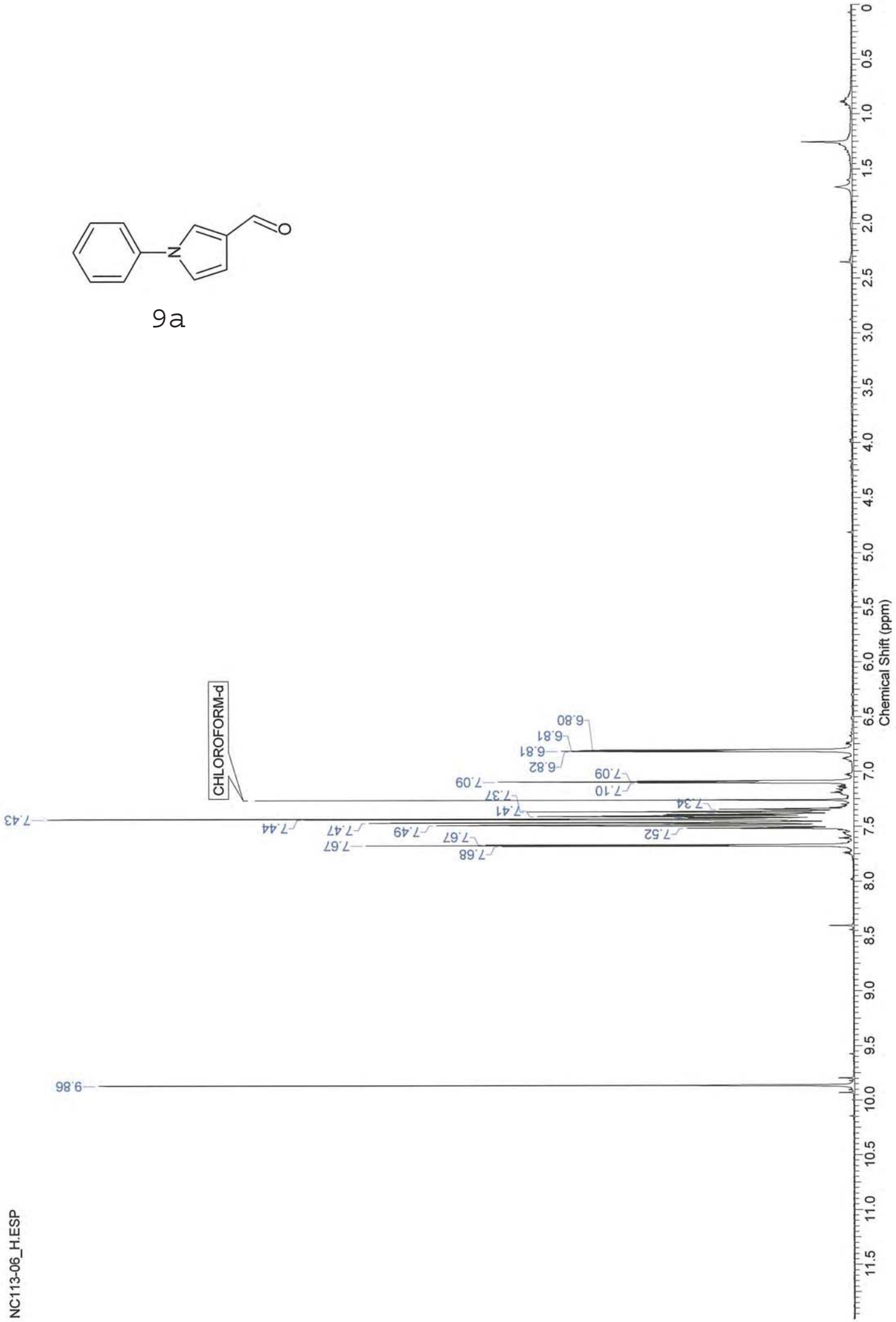
Charge = +1

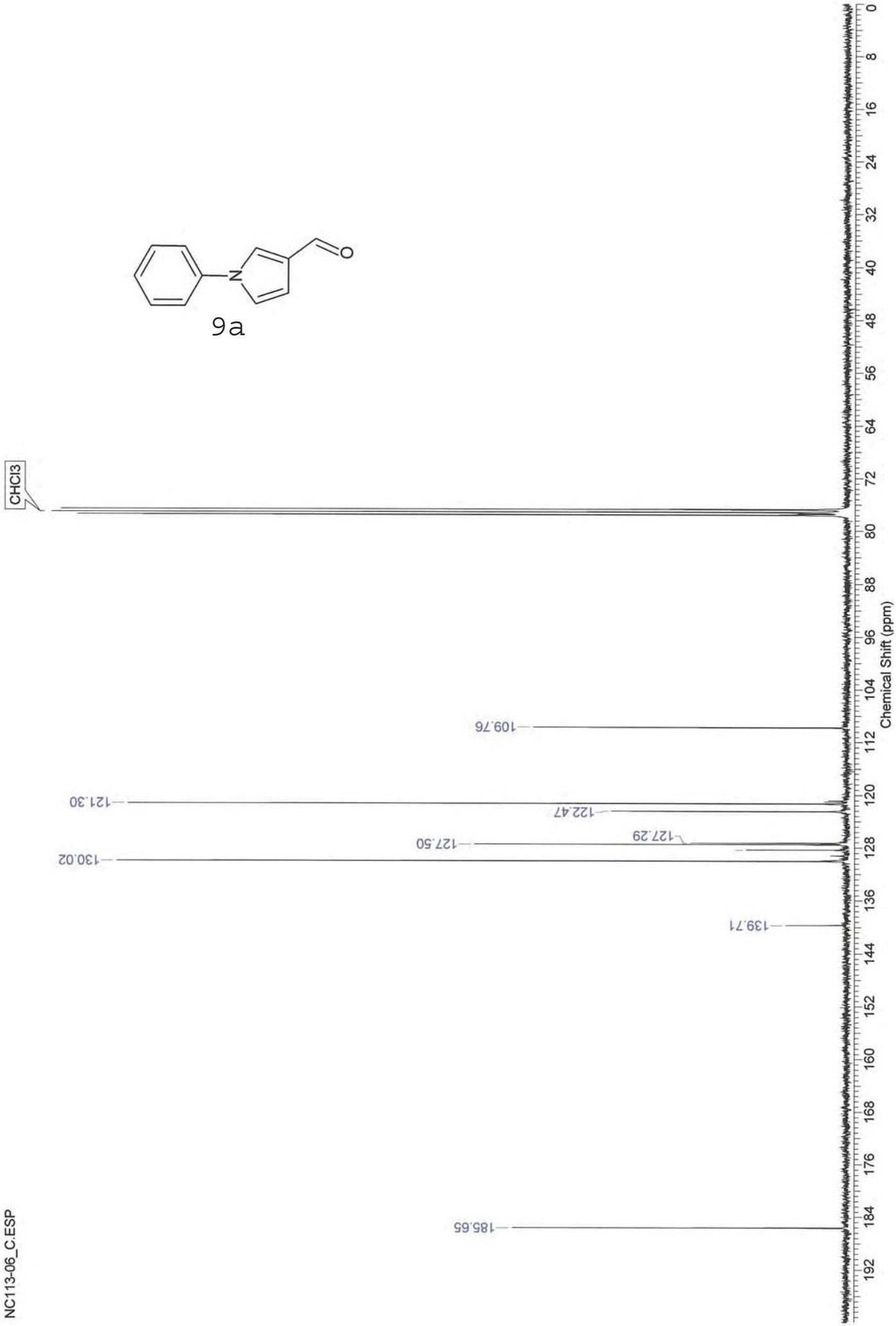
#	C	H	N	O	S	Na	mass	DBE	error
*** Mass Analysis for mass 350.0815930									
1	18	17	1	3	1	1	350.0821352	10.5	5.422e-04
2	20	16	1	3	1	0	350.0845405	13.5	2.947e-03
3	15	21	1	3	2	1	350.0855060	5.5	3.913e-03
4	16	18	2	3	2	0	350.0753353	9.0	6.258e-03
5	17	20	1	3	2	0	350.0879113	8.5	6.318e-03
6	14	19	2	3	2	1	350.0729300	6.0	8.663e-03
7	14	19	2	5	1	1	350.0906885	6.0	9.096e-03
8	19	14	2	3	1	0	350.0719644	14.0	9.629e-03
9	16	18	2	5	1	0	350.0930938	9.0	1.150e-02
10	17	15	2	3	1	1	350.0695591	11.0	1.203e-02

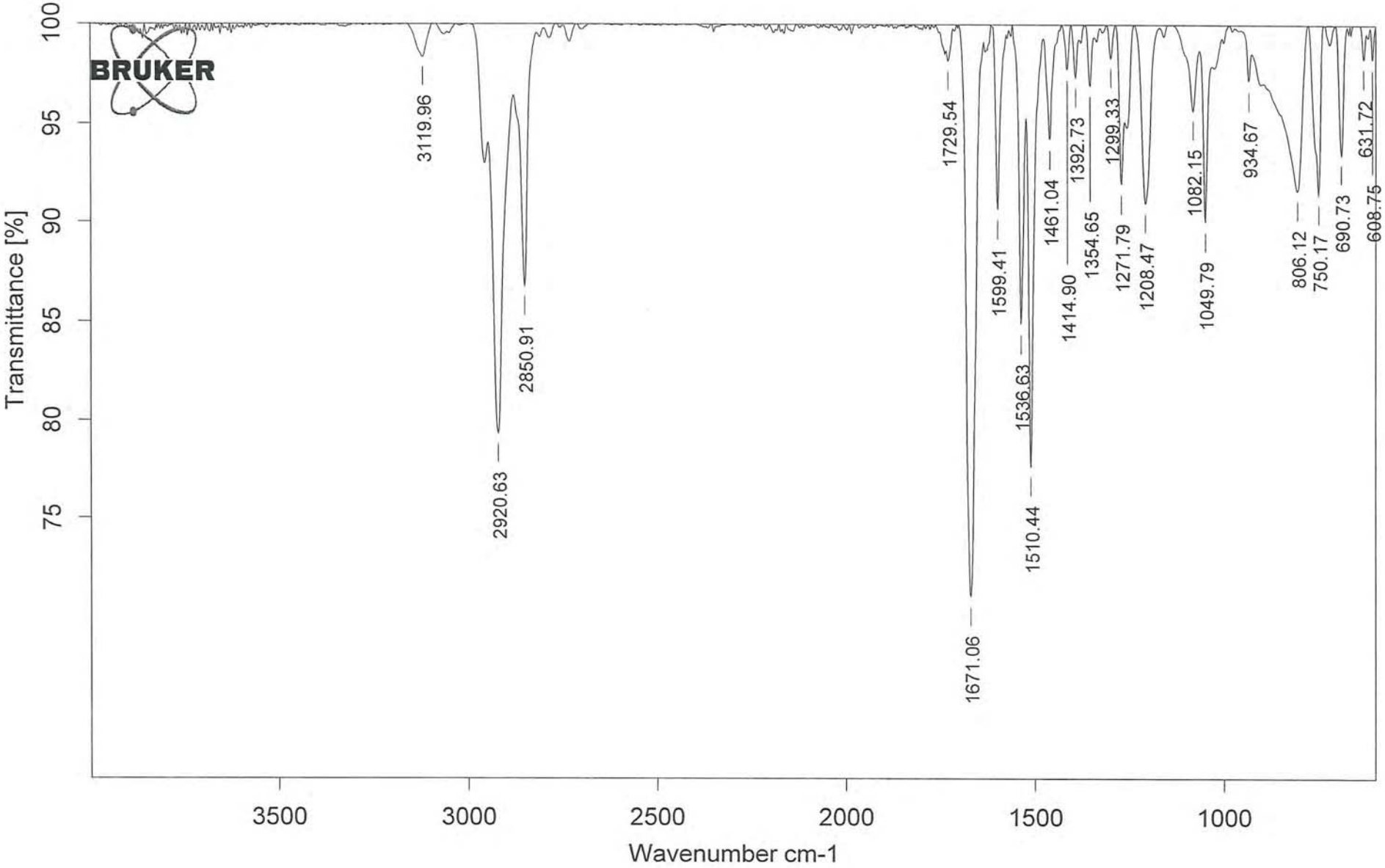


/Data/UNI_FR/CHAR4108_ESI/5/pdata/1 FTMS USER Wed Apr 8 11:23:11 2009

9a


CHLOROFORM-d
9.86
7.43
7.44
7.47
7.49
7.67
7.67
7.68
7.52
7.34
7.41
7.37
7.09
7.10
7.09
6.82
6.81
6.81
6.80
Chemical Shift (ppm)
NC113-06_H.ESP


9a
CHCl3
109.76
121.30
122.47
127.29
127.50
130.02
139.71
185.65
Chemical Shift (ppm)
NC113-06_C.ESP



C:\Program Files\OPUS\Data\Chn\nc113-06.0	nc113-06	nc113-06	16/04/2009

Page 1/1

ESI-MS: NC113-06

XMASS Mass Analysis for /Data/UNI_FR/CHAR4119_ESI/1/pdata/1/massanal.res:
XMASS Mass Analysis Constraints

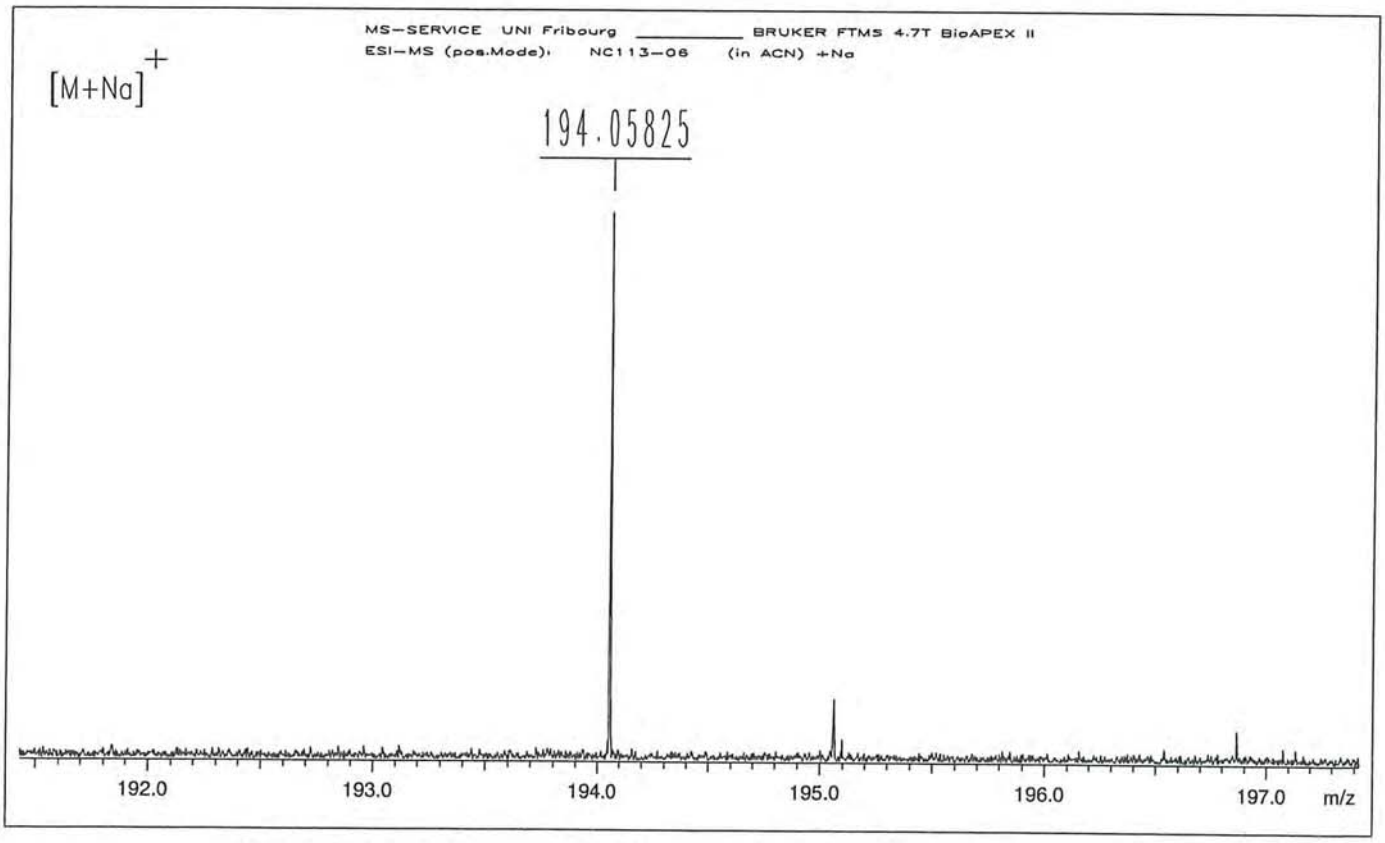
Ion mass = 194.0582450

Charge = +1

#	C	H	N	O	Na	mass	DBE	error

*** Mass Analysis for mass 194.0582450

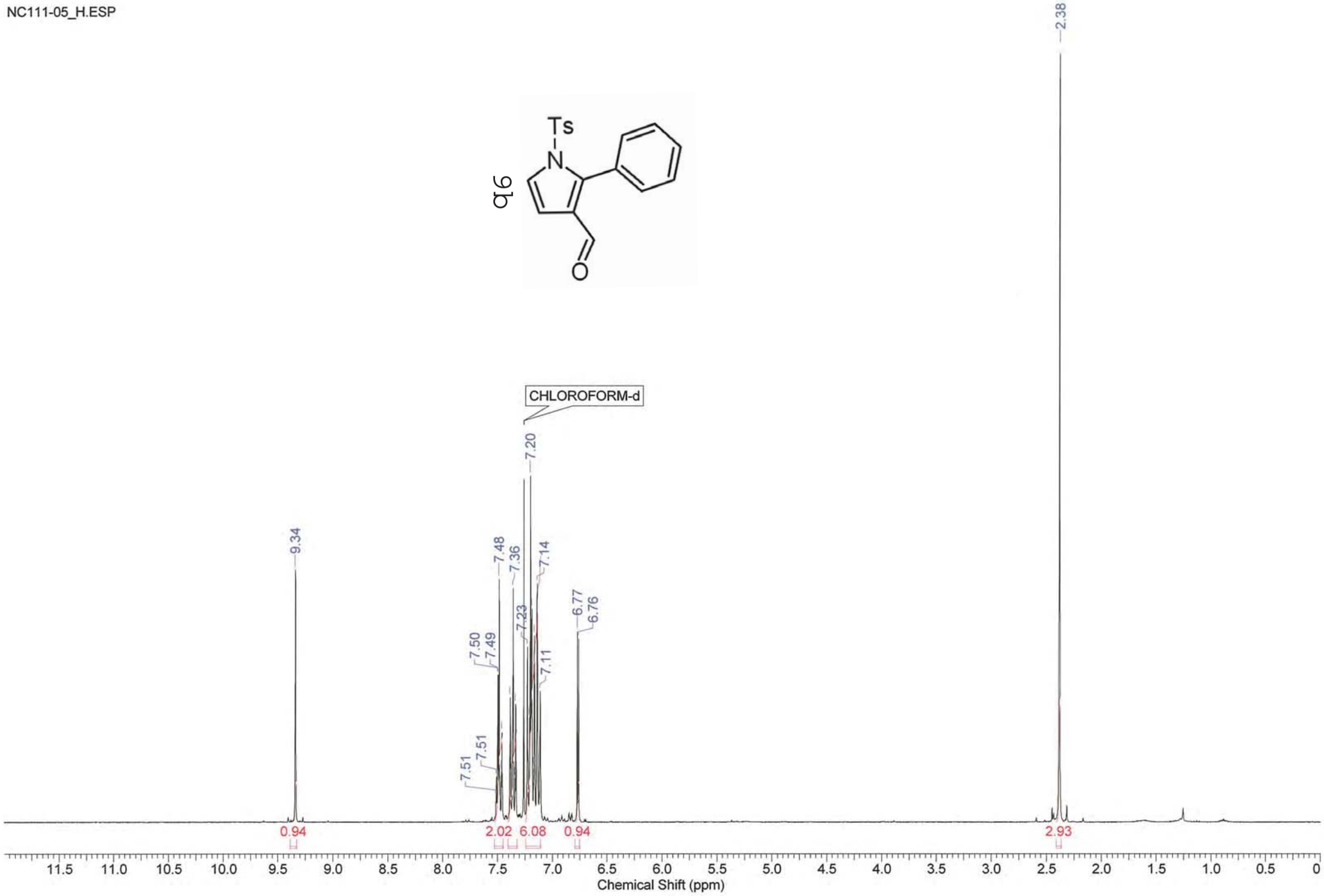
1	11	9	1	1	1	194.0576350	7.5	6.100e-04
2	13	8	1	1	0	194.0600403	10.5	1.795e-03
3	8	8	3	3	0	194.0560176	6.5	2.227e-03
4	6	6	6	2	0	194.0546749	7.0	3.570e-03
5	6	9	3	3	1	194.0536123	3.5	4.633e-03
6	5	10	2	6	0	194.0533375	2.0	4.908e-03
7	5	9	5	2	1	194.0648456	3.5	6.601e-03
8	5	6	8	1	0	194.0659083	7.0	7.663e-03
9	6	12	1	6	0	194.0659135	1.5	7.669e-03
10	7	11	2	3	1	194.0661883	3.0	7.943e-03



/Data/UNI_FR/CHAR4119_ESI/1/pdata/1 FTMS USER Thu Apr 16 15:31:48 2009

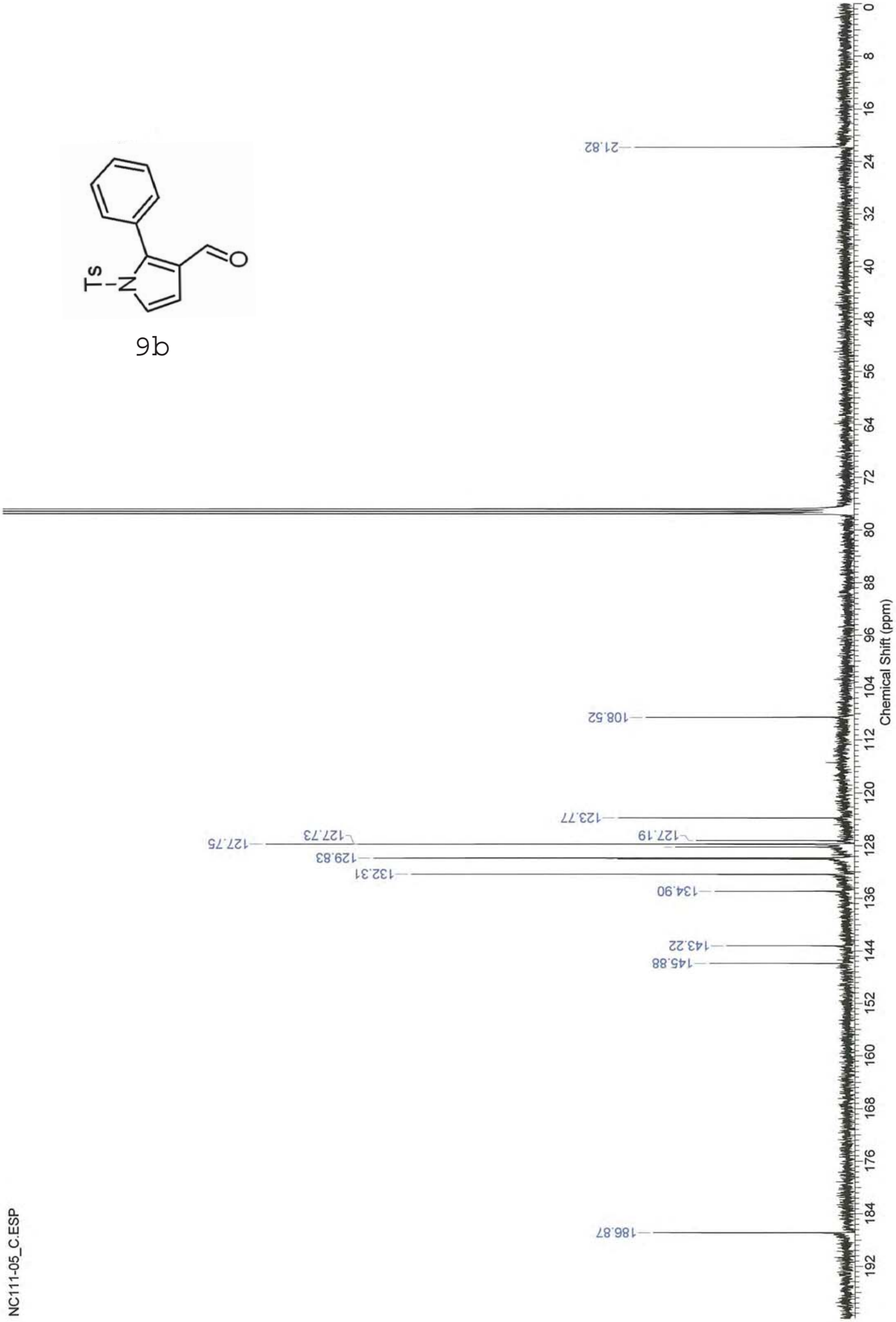
NC111-05_H.ESP

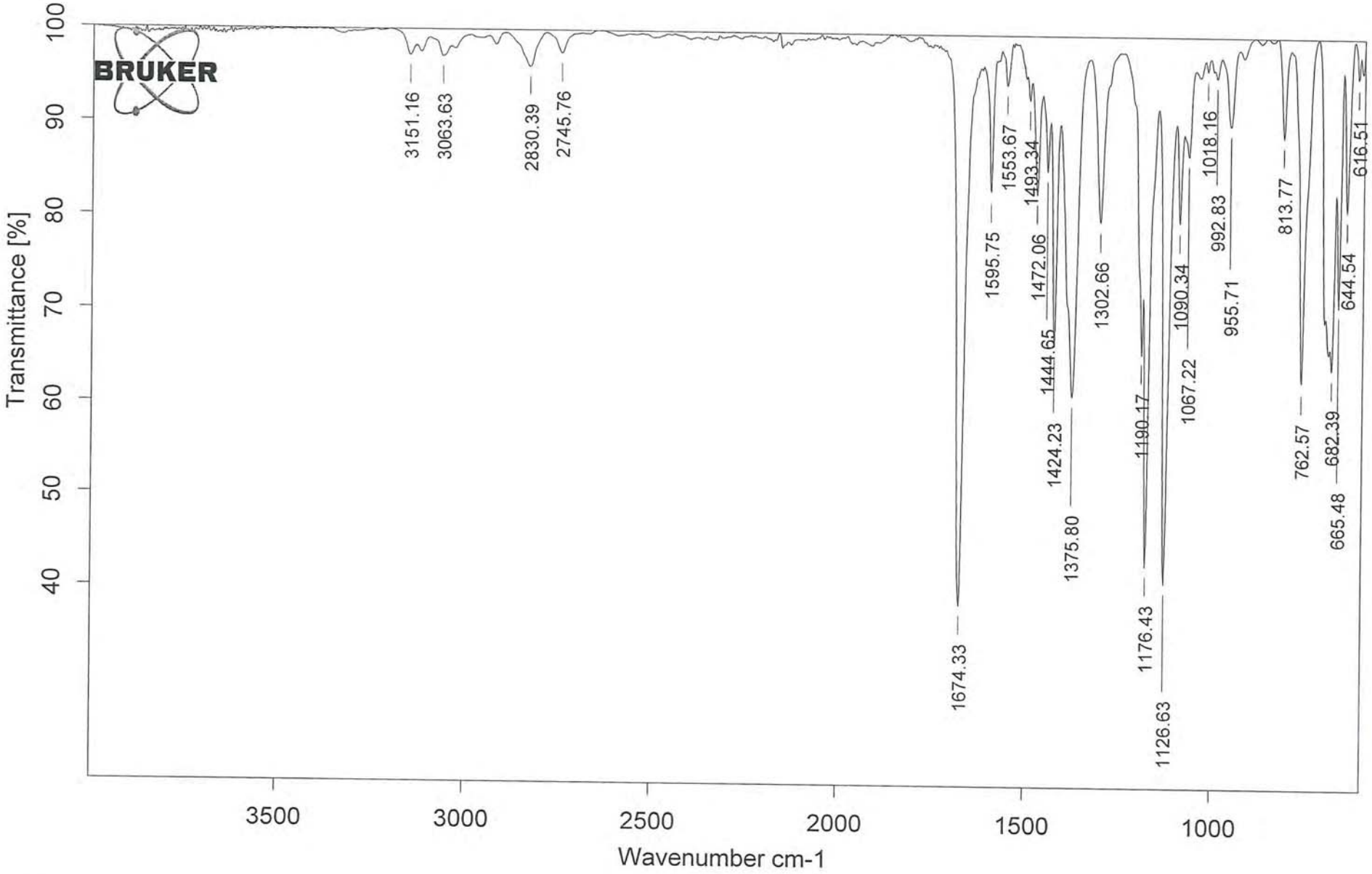
9b



Ts
N
O

9b


21.82
108.52
123.77
127.19
127.73
127.75
129.83
132.31
134.90
143.22
145.88
186.87
Chemical Shift (ppm)
NC111-05_C.ESP



C:\Program Files\OPUS\Data\Chn\nc111-05.0	nc111-05	nc111-05	09/04/2009

Page 1/1

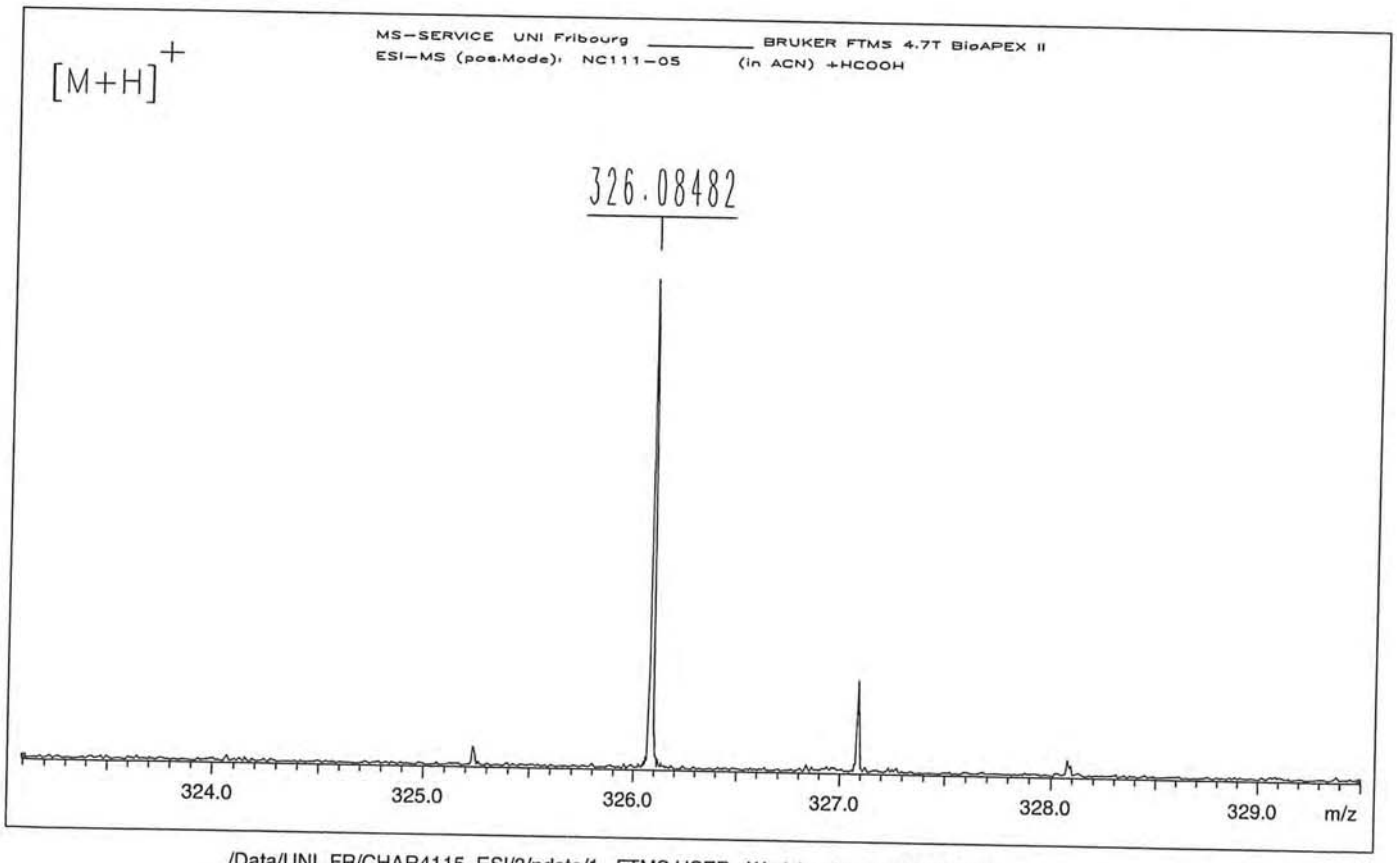
ESI-MS: NC111-05

XMASS Mass Analysis for /Data/UNI_FR/CHAR4115_ESI/3/pdata/1/massanal.res:
XMASS Mass Analysis Constraints

Ion mass = 326.0848180

Charge = +1

#	C	H	N	O	S	mass	DBE	error
*** Mass Analysis for mass 326.0848180								
1	18	16	1	3	1	326.0845405	11.5	2.775e-04
2	10	20	3	5	2	326.0838886	2.5	9.294e-04
3	16	14	4	2	1	326.0831978	12.0	1.620e-03
4	13	18	4	2	2	326.0865686	7.0	1.751e-03
5	15	20	1	3	2	326.0879113	6.5	3.093e-03
6	13	16	3	5	1	326.0805177	7.5	4.300e-03
7	12	16	5	4	1	326.0917511	7.5	6.933e-03
8	14	18	2	5	1	326.0930938	7.0	8.276e-03
9	14	18	2	3	2	326.0753353	7.0	9.483e-03
10	9	20	5	4	2	326.0951220	2.5	1.030e-02



/Data/UNI_FR/CHAR4115_ESI/3/pdata/1 FTMS USER Wed Apr 15 13:28:00 2009