*Supporting information for*

# Phase-vanishing Method with Acetylene Evolution and Its Utilization in Several Organic Syntheses

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**Table of Contents**

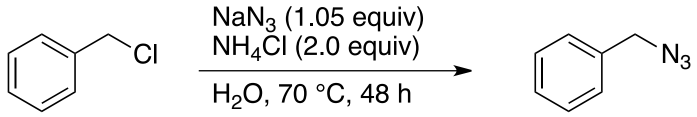
## I. General Remarks

Melting points were obtained with Yanako micro melting point apparatus and are not corrected. Products were purified by column chromatography on silica gel (Kanto Chemical Co., Inc., Silica Gel 60N (spherical, neutral), 63-210 mm). $^1$H NMR spectra were recorded with a JEOL-ECP-500 (500 MHz) and a JEOL-ECS-400 (400 MHz) spectrometer in $CDCl_3$. Chemical shifts were reported in parts per million (δ) referenced to the solvent peak at 7.26 ppm. $^{13}$C NMR spectra were recorded with a JEOL-ECP-500 (126 MHz) and a JEOL-ECS-400 (100 MHz) spectrometer in $CDCl_3$ and referenced to the solvent peak at 77.0 ppm. Coupling constants, *J*, were reported in Hertz (Hz), and splitting patterns were designated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet) and m (multiplet). IR spectra were obtained on a JASCO FT/IR-4100 spectrometer; absorptions were reported in reciprocal centimeters. Conventional mass spectra were recorded with a SHIMADZU GCMS-QP2010Plus spectrometer and high-resolution mass spectra were recorded with a JEOL MS-700 spectrometer.

## II. Materials

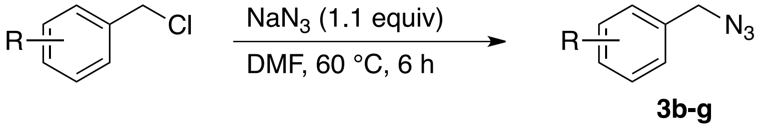
Benzyl azides (**3a**-**3h**) were prepared according to procedures (Methods A–C) in literature. The other compounds were purchased from commercially available sources and used without further purification.

## III. General Procedures for the Preparation of Azides 3a–h



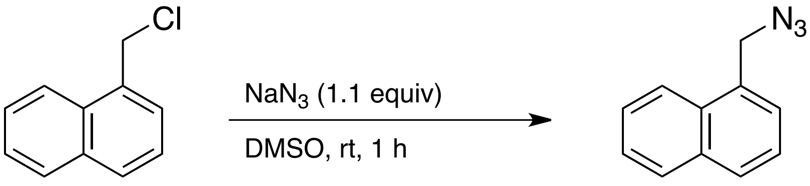

**3a**

**Method A**[S1]: Benzyl chloride (10 mmol) was suspended in water at a concentration of 1.5 M. To the suspension, sodium azide (10.6 mmol) and ammonium chloride (20 mmol) were added, and the mixture was heated at 70 °C for 48 h with vigorous stirring. After cooling, the mixture was extracted with diethyl ether, and collected organic layer was dried over sodium sulfate. After filtration, evaporation of the solvent yielded pure benzyl azide.




**3b-g**

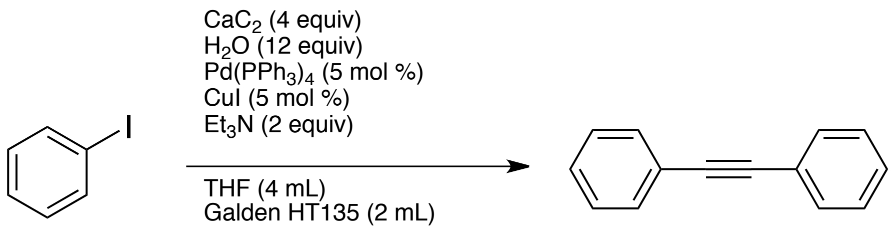
**Method B**[S2]: A mixture of substituted benzyl chloride (10 mmol) and sodium azide (11 mmol) in DMF (5 mL) was gradually heated to 60 °C and stirred for 6 h. After cooling, diethyl ether and water were added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water and brine, and dried over sodium sulfate. After filtration, evaporation of the solvent yielded the analytically pure substituted azidomethylbenzenes.




**3h**

**Method C**[S3]: To a solution of sodium azide (11 mmol) in DMSO (5 mL), 1-(chloromethyl)naphthalene (10 mmol) was added, and the mixture was stirred at room temperature for 1 h. After checking that the starting material (chloromethylnaphthalene) was consumed, the reaction was quenched with water and allowed to cool to room temperature with stirring. The mixture was then extracted with ethyl acetate. The collected organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the solvent was evaporated and the residue was purified by column chromatography on silica gel to afford 1-(azidomethyl)naphthalene.

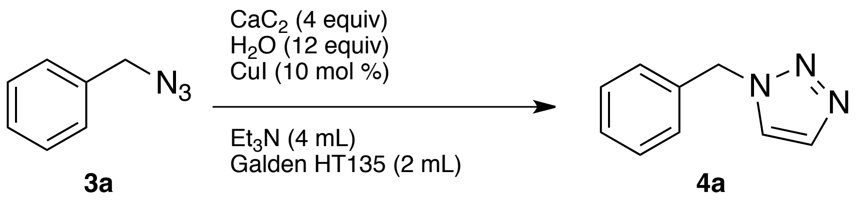
## IV. Typical Procedure for Sonogashira Coupling by the Phase-vanishing Method (Table 1, entry 1)




**1a** **2a**

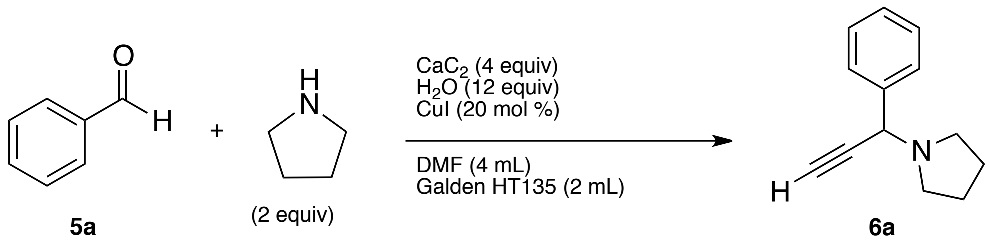
Calcium carbide (512 mg, 8.0 mmol) and a magnetic stirring bar (oval, 10 mm × 5 mm) were placed in a Pyrex test tube (15 mm ϕ × 130 mm), to which Galden HT135 (2 mL) was added slowly using a syringe. Subsequently, water (420 mg, 23.3 mmol), a solution of phenyl iodide (408 mg, 2.0 mmol) in THF (4 mL), $Pd(PPh_3)_4$ (115 mg, 0.10 mmol), CuI (24 mg, 0.13 mmol), and triethylamine (409 mg, 4.0 mmol) were added slowly in order, forming four layers. A rubber septum was fitted to the test tube, and a needle equipped with a balloon, which acted as a reservoir of acetylene gas during the reaction, was then pricked into the septum. The air in the test tube was removed by a syringe until the balloon was completely flattened. The test tube was heated in an oil bath at 55 °C for 20 h with slow stirring, taking care not to mix the layers, then allowed to cool to ambient temperature. After removal of the Galden HT135 by glass pipette, the organic layer and inorganic salts were moved to a separatory funnel using diethyl ether and water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were then dried over sodium sulfate, filtered, and concentrated. Purification by column chromatography on silica gel with hexane gave diphenylacetylene as white crystalline solid (165 mg, 94%).

## V. Typical Procedure for Copper-catalyzed Azide-Alkyne Cycloaddition (CuAAC) by the Phase-vanishing Method (Table 2, entry 1)




Calcium carbide (259 mg, 4.0 mmol) and a magnetic stirring bar (oval, 10 mm × 5 mm) were placed at bottom of a Pyrex test tube (15 mm ϕ × 130 mm), to which Galden HT135 (2 mL) was added slowly using a syringe. Subsequently, water (300 mg, 16.6 mmol), a solution of benzyl azide (132 mg, 1.0 mmol) in triethylamine (4 mL), and CuI (20 mg, 0.11 mmol) were added slowly in order, forming four layers. A rubber septum was fitted to the test tube, and a needle equipped with a balloon, which acted as a reservoir of acetylene gas during the reaction, was then pricked into the septum. The air in the test tube was removed by a syringe until the balloon was completely flattened. The test tube was heated in an oil bath at 55 °C for 20 h with slow stirring, taking care not to mix the layers, and then allowed to cool to ambient temperature. The organic layer was taken up with a glass pipette. Ethyl acetate was placed on the residual Galden HT135 layer, and then decanted. The collected organic layer was mixed with hydrochloric acid (2 M). After checking that the pH was less than 7 with pH indicator paper, the layers was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated. Purification by column chromatography on silica gel with hexane–ethyl acetate (1:1) gave 1-benzyl-1*H*-1,2,3-triazole as pale yellow crystalline solid (137 mg, 85%).

## VI. Typical Procedure for Aldehyde-Alkyne-Amine Coupling ($A^3$-coupling) by the Phase-vanishing Method (Table 3, entry 1)

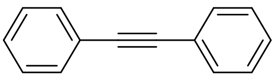



Calcium carbide (259 mg, 4.0 mmol) and a magnetic stirring bar (oval, 10 mm × 5 mm) were placed in a Pyrex test tube (15 mm ϕ x 130 mm), to which Galden HT135 (2 mL) was added slowly using a syringe. Subsequently, water (250 mg, 13.9 mmol), a solution of benzaldehyde (**1a**) (110 mg, 1.0 mmol) in DMF (4 mL), pyrrolidine (147 mg, 2.1 mmol), and CuI (40 mg, 0.21 mmol) were added slowly in order, forming four layers. A rubber septum was fitted to the test tube, and a needle equipped with a balloon, which acted as a reservoir of acetylene gas during the reaction, was then pricked into the septum. The air in the test tube was removed by a syringe until the balloon was completely flattened. The test tube was heated in an oil bath at

55 °C for 20 h with slow stirring, taking care not to mix the layers, and then allowed to cool to ambient temperature. After removal of the Galden HT135 by glass pipette, the organic layer and inorganic salts were moved to a separatory funnel using diethyl ether and water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were then dried over sodium sulfate, filtered, and concentrated. Purification by a column chromatography on silica gel with hexane-ethyl acetate (4/1) gave 1-(1-phenylprop-2-ynyl)pyrrolidine (**6a**) as reddish yellow oil (144 mg, 75%).

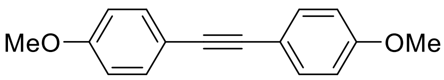
## VII. Spectroscopic Data

**Diphenyl acetylene (2a)[S4]:**



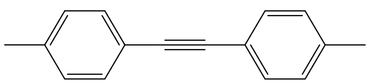
White crystalline solid (165 mg); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.56－7.53 (m, 4H), 7.38 – 7.33 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$): δ 131.50, 128.23, 128.14, 123.16, 89.26.

**1,2-Bis(4-methoxyphenyl)acetylene (2b)[S4]:**



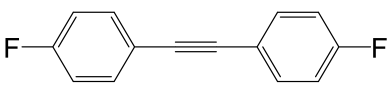

Yellow crystalline solid (186 mg); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, $J$ = 8.0 Hz, 4H), 6.87 (d, $J$ = 8.0 Hz, 4H), 3.83 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 159.32, 132.81, 115.65, 113.91, 87.90, 55.21.

**Bis(p-tolyl)acetylene (2c)[S4]:**



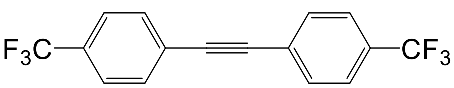
Pale yellow crystalline solid (196 mg,); $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, $J$ = 8.3 Hz, 4H), 7.15 (d, $J$ = 8.3 Hz, 4H), 2.36 (s, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$): δ 138.15, 131.41, 129.07, 120.37, 88.85, 21.48.

**1,2-Bis(4-fluorophenyl)acetylene (2d)[S4]:**




Pale yellow crystalline solid (208 mg); $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.50 (dt, $J$ = 8.7, 3.2 Hz, 4H), 7.05 (t, $J$ = 8.7 Hz, 4H); $^{13}$C NMR (126 MHz, $CDCl_3$): δ 162.33 (d, $J_{C\text{-}F}$ = 251 Hz), 133.23 (d, $J_{C\text{-}F}$ = 8.6 Hz), 119.00, 115.53 (d, $J_{C\text{-}F}$ = 22.1 Hz), 87.84.

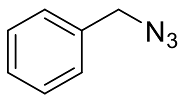
**1,2-Bis(4-(trifluoromethyl)phenyl)acetylene (2e)[S4]:**




Greenish pale yellow crystalline solid (302 mg); $^{1}$H NMR

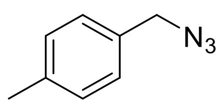
(500 MHz, $CDCl_3$): δ 7.67－7.62 (m, 8H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 131.96, 130.46 (q, $J_{C-F}$ = 32.8 Hz), 126.36, 125.37 (broad d, $J_{C-F}$ = 2.9 Hz), 123.84 (q, $J_{C-F}$ = 271.6 Hz), 90.11.

**Benzyl azide (3a)[S5]:**



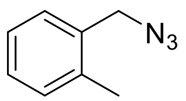

Pale yellow oil (1.15 g); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.42－7.26 (m, 5H), 4.34 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 135.23, 128.69, 128.12, 128.05, 54.56.

**1-(Azidomethyl)-4-methylbenzene (3b)[S2]:**



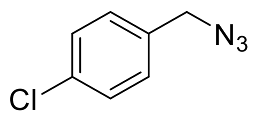

Pale yellow oil (646 mg); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.22－7.20 (m, 4H), 4.29 (s, 2H), 2.36 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 138.15, 132.26, 129.50, 128.27, 54.56, 21.18.

**1-(Azidomethyl)-2-methylbenzene (3c)[S6]:**



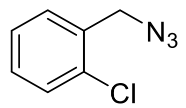

Pale yellow oil (617 mg); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.27－7.21 (m, 4H), 4.35 (s, 2H), 2.37 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 136.77, 133.37, 130.64, 129.31, 128.62, 126.20, 53.03, 18.96.

**1-(Azidomethyl)-4-chlorobenzene (3d)[S2]:**



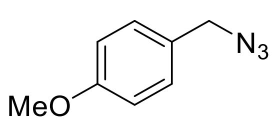

Pale yellow oil (799 mg); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.38－7.34 (m, 2H), 7.27－7.24 (m, 2H), 4.32 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 134.21, 133.84, 129.49, 129.02, 54.02.

**1-(Azidomethyl)-4-chlorobenzene (3e)[S2]:**



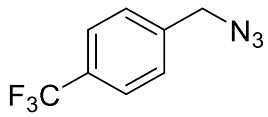

Pale yellow liquid (801 mg); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.44－7.39 (m, 2H), 7.32－7.26 (m, 2H), 4.50 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 133.77, 133.28, 130.00, 129.78, 129.64, 127.15, 52.26.

**1-(Azidomethyl)-4-methoxybenzene (3f)[S2]:**



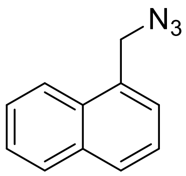

Pale red oil (791 mg); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.25 (d, $J$ = 8.0 Hz, 2H), 6.91 (d, $J$ = 8.0 Hz, 2H), 4.27 (s, 2H), 3.82 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 159.61, 129.74, 127.37, 114.16, 55.24, 54.35.

**1-(Azidomethyl)-4-trifluoromethylbenzene (3g)[S5]:**



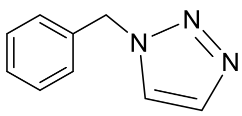
Yellow oil (976 mg); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, $J$ = 8.0 Hz, 2H), 7.45 (d, $J$ = 8.0 Hz, 2H), 4.43 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 139.41, 130.43 (q, $J_{C-F}$ = 32.4 Hz), 128.24, 125.78 (q, $J_{C-F}$ = 3.8 Hz), 123.95 (q, $J_{C-F}$ = 269 Hz), 54.04.

**1-(Azidomethyl)naphthalene (3h)[S3]:**



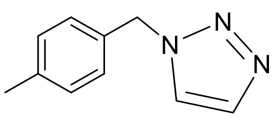
Pale yellow oil (1.75 g); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, $J$ = 8.0 Hz, 1H), 7.91－7.87 (m, 2H), 7.59－7.46 (m, 4H), 4.77 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 133.73, 131.18, 130.81, 129.25, 128.66, 127.08, 126.57, 126.00, 125.06, 123.33, 52.76.

**1-Benzyl-1H-1,2,3-triazole (4a)[S7]:**



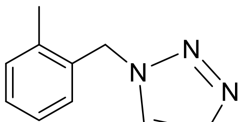
Pale yellow crystalline solid (137 mg); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.47 (s, 1H), 7.47－7.35 (m, 3H), 7.28－7.25 (m, 2H), 5.57 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 134.66, 134.23, 129.09, 128.71, 127.98, 123.26, 53.94.

**1-(4-Methylbenzyl)-1H-1,2,3-triazole (4b)[S7]:**



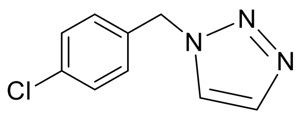
White crystalline solid (101 mg); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.47 (s, 1H), 7.17 (m, 4H), 5.52 (s, 2H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 138.15, 133.72, 131.46, 129.35, 127.68, 123.12, 53.29, 20.77.

**1-(2-Methylbenzyl)-1H-1,2,3-triazole (4c)[S7]:**



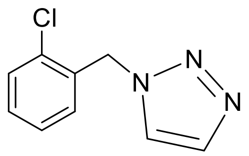
Light brown crystalline solid (100 mg); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.35 (s, 1H), 7.30－7.13 (m, 4H), 5.58 (s, 2H), 2.78 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 136.49, 133.63, 132.38, 130.64, 128.93, 128.72, 126.30, 123.08, 51.74, 18.61.

**1-(4-Chlorobenzyl)-1H-1,2,3-triazole (4d)[S7]:**



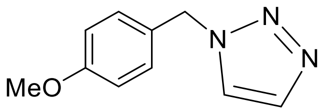
Light brown crystalline solid (170 mg); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.48 (s, 1H), 7.37－7.34 (m, 2H), 7.22－7.19 (m, 2H), 5.54 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 134.31, 134.02, 133.11, 129.08, 128.95, 123.33, 52.84.

**1-(2-Chlorobenzyl)-1H-1,2,3-triazole (4e)[S7]:**



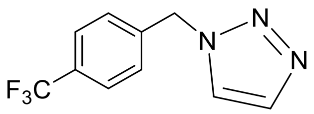

Light brown crystalline solid (162 mg); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.59 (s, 1H), 7.45－7.43 (m, 1H), 7.32－7.27 (m, 2H), 7.18－7.15 (m, 1H), 5.71 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 133.82, 133.14, 132.31, 129.97×2, 129.62, 127.34, 123.67, 50.97.

**1-(4-Methoxylbenzyl)-1H-1,2,3-triazole (4f)[S7]:**



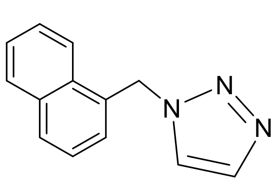

Light brown crystalline solid (157 mg); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.43 (s, 1H), 7.23 (d, $J$ = 8.4 Hz, 2H), 6.91－6.89 (m, 2H), 5.50 (s, 2H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 159.0, 133.73, 129.27, 126.46, 123.00, 114.08, 54.99, 53.08.

**1-(4-Trifluoromethylbenzyl)-1H-1,2,3-triazole (4g):**



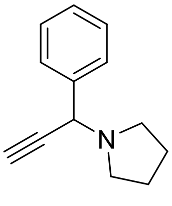

Light brown crystalline solid (168 mg); mp 52.5–53.0 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.64 (d, $J$ = 8.0 Hz, 2H), 7.52 (s, 1H), 7.36 (d, $J$ = 8.0 Hz, 2H), 5.64 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 138.68, 134.16, 130.51 (q, $J_{C\text{-}F}$ = 32.5 Hz), 127.91, 125.76 (d, $J_{C\text{-}F}$ = 4.0 Hz), 123.65, 123.60 (q, $J_{C\text{-}F}$ = 270.2 Hz), 52.93; IR (KBr): 2965, 2927, 2857, 2812, 2076, 1444, 1123 883, 747 cm$^{-1}$; GC-MS (EI): 227 (5), 198 (47), 172 (19), 159 (100), 130 (58), 109 (62), 40 (21 %); HRMS (EI) Calcd. For $C_{10}H_8N_3F_3$: 227.0670, Found: 227.0672.

**1-(1-Naphthylmethyl)-1H-1,2,3-triazole (4h)[S8]:**



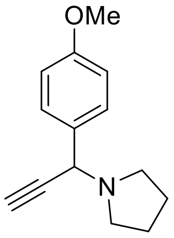

Off-white crystalline solid (185 mg); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.97－7.89 (m, 3H), 7.65 (s, 1H), 7.54－7.34 (m, 4H), 7.26 (s, 1H), 6.03 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 133.76, 133.59, 130.82, 129.66, 128.65, 127.44, 126.93, 126.10, 125.11, 123.20, 122.6, 51.72.

**1-(1-phenylprop-2-ynyl)pyrrolidine (6a)[S9]:**



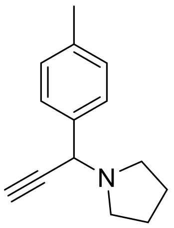

Reddish yellow oil (144 mg); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, $J$ = 3.6 Hz, 2H), 7.36－7.28 (m, 3H), 4.68 (d, $J$ = 1.2 Hz, 1H), 2.61 (t, $J$ = 6.8 Hz, 4 H), 2.48 (d, $J$ = 1.2 Hz, 1H), 1.79－1.76 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 138.95, 128.22, 128.08, 127.58, 80.76, 74.52, 58.33, 50.01, 23.38.

**1-(1-(4-Methoxyphenyl)prop-2-ynyl)pyrrolidine (6b)[S10]:**



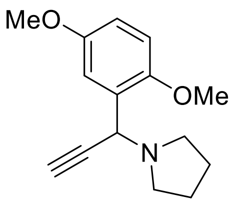

Reddish yellow oil (89 mg); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz), 4.61 (d, *J* = 2.0 Hz, 1H), 3.81 (s, 3H), 2.61-2.57 (m, 4H), 2.46 (d, *J* = 2.4 Hz, 1H), 1.77-1.75 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.93, 131.14, 129.11, 113.45, 81.03, 74.23, 57.64, 55.14, 49.91, 23.30.

**1-(1-(4-Methylphenyl)prop-2-ynyl)pyrrolidine (6d):**



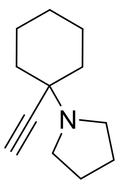

Reddish yellow oil (93 mg); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.63 (d, *J* = 2.0 Hz, 1H), 2.60 (t, *J* = 7.2 Hz, 4H), 2.46 (d, *J* = 2.4 Hz, 1H), 2.34 (s, 3H), 1.78−1.75 (m, 4H) ; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 137.20, 136.01, 128.88, 127.96, 81.03, 74.24, 58.07, 50.02, 23.35, 21.07; IR (neat): 3297, 2966, 2875, 2813, 1511, 1267 cm$^{-1}$; GC-MS (EI): 199 (29), 129 (100), 108 (79), 70 (40 %); HRMS (EI) Calcd. For $C_{14}H_{17}N$: 199.1361, Found: 199.1357.

**1-(1-(2,5-Dimethylphenyl)prop-2-ynyl)pyrrolidine (6e):**




Reddish yellow oil (95 mg); $^1$H NMR (400 MHz, $CDCl_3$): δ7.20 (d, *J* = 2.4 Hz, 1H), 6.81−6.79 (m, 2H), 5.07 (d, *J* = 2.0 Hz, 1H), 3.81−3.79 (d, *J* = 1.2 Hz, 3H×2), 2.67 (s, 4H), 2.37 (d, *J* = 2.4 Hz, 1H), 1.78−1.77 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 153.32, 150.77, 128.32, 115.32, 113.31, 112.06, 81.80, 72.96, 56.37, 55.63, 51.09, 50.32, 23.26; IR (neat): 3286, 2962, 2833, 1499, 1464, 1279, 1246, 1216 cm$^{-1}$; GC-MS (EI): 245 (23), 216 (21), 175 (100), 161 (49), 132 (44), 108 (99), 91 (43), 70 (94 %); HRMS (EI) Calcd. For $C_{15}H_{19}NO_2$: 245.1416, Found: 245.1412.

**1-(1-ethynyl-cyclohexyl)-pyrrolidine (6f):**




Light brown crystalline solid (55 mg); mp 62.5–63.5 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.73−2.70 (m, 4H), 2.28 (s, 1H), 1.94 (d, *J* = 12.4 Hz, 2H), 1.78 (quint, *J* = 3.6 Hz, 4 H), 1.67−1.46 (m, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 84.48, 72.98, 58.63, 46.78, 37.71, 25.55, 23.35, 22.74; IR (KBr): 3127, 2420, 1623, 1424, 1325, 1217, 1167, 1136, 1107, 1065, 830, 798 cm$^{-1}$; GC-MS (EI): 177 (11), 162 (18), 148 (21), 134 (100), 120 (21), 79 (10), 70 (26), 65 (10), 41 (10 %); HRMS (EI) Calcd. For $C_{12}H_{19}N$: 177.1517, Found: 177.1520.

## VIII. References


S1 Maisonial, A.; Serafin, P.; Traïkia, M.; Debiton, E.; Théry, V.; Aitken, D. J.; Lemoine, P; Viossat, B; Gautier, A. *Eur. J. Inorg. Chem.* **2008**, *2*, 298.

S2 Hédou, D.; Deau, E.; Dubouilh-Benard, C.; Sanselme, M.; Martinet, M.; Chosson, E.; Levacher, V.; Besson, T. *Eur. J. Org. Chem.* **2013**, *33*, 7533.

S3 Suzuki, T.; Ota, Y.; Ri, M.; Bando, M.; Gotoh, A.; Itoh, Y.; Tsumoto, H.; Tatum, P. R.; Mizukami, T.; Nakagawa, H.; Iida, S.; Ueda, R.; Shirahige, K.; Miyata, N. *J. Med. Chem.* **2012**, *55*, 9562.

S4 Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett*. **2002**, *4*, 3199.

S5 Stefely, J. A.; Palchaudhuri, R.; Miller, P. A.; Peterson, R. J.; Moraski, G. C.; Hergenrother, P. J.; Miller, M. J. *J. Med. Chem*. **2010**, *53*, 3389.

S6 Liu, M.; Reiser, O. *Org. Lett.* **2011**, *13*, 1102.

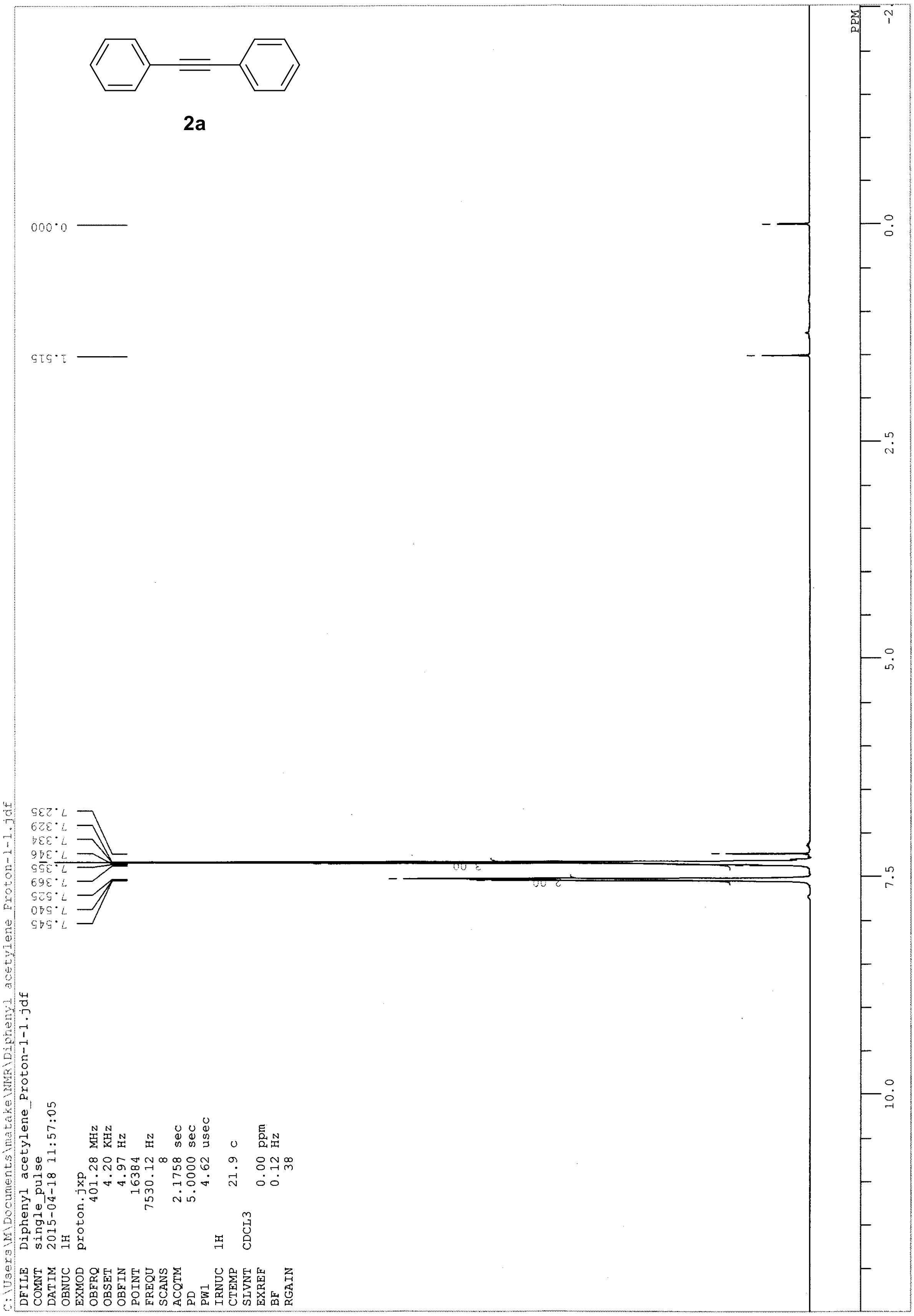
S7 Wu, L. Y.; Xie, Y. X.; Chen, Z. S.; Niu, Y. N.; Liang, Y. M. *Synlett* **2009**, 1453.

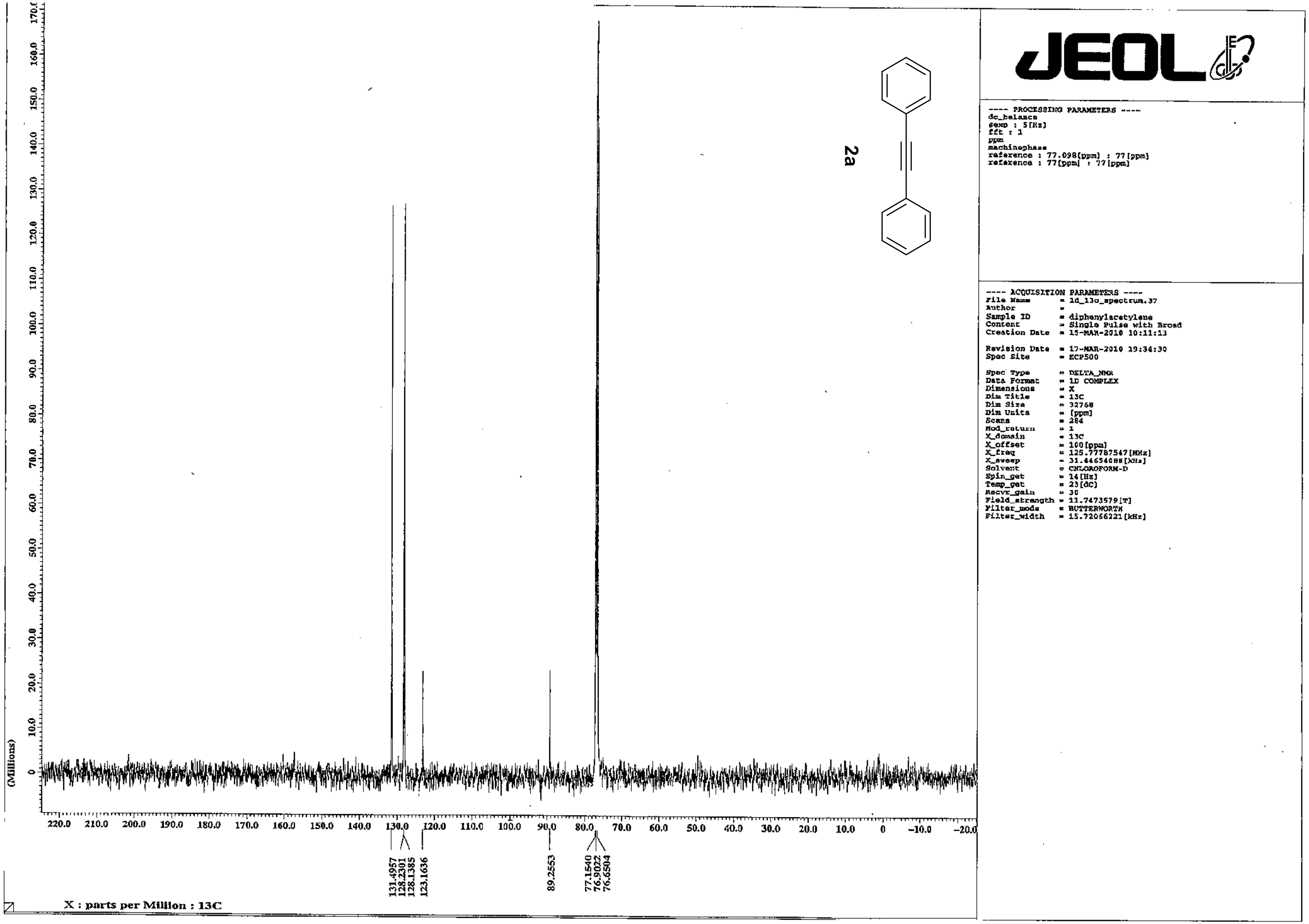
S8 Ikemoto, T.; Ito, T.; Tomimatsu, K.; Sawai, Y.; Nishiyama, H.; Isogami, Y. PCT Int. Appl. WO 2002006, 2002.

S9 Lin, Z.; Yu, D.; Sum, Y. N.; Zhang, Y. *ChemSusChem* **2012**, *5*, 625.

S10 Lee, A. S.-Y.; Chen, G.-A.; Chang, Y.-T.; Chu, S.-F. *Synlett* **2009**, 441.

# IX. NMR Spectra

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Temp_get = 23[dC]
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Filter_width = 15.72066221[kHz]
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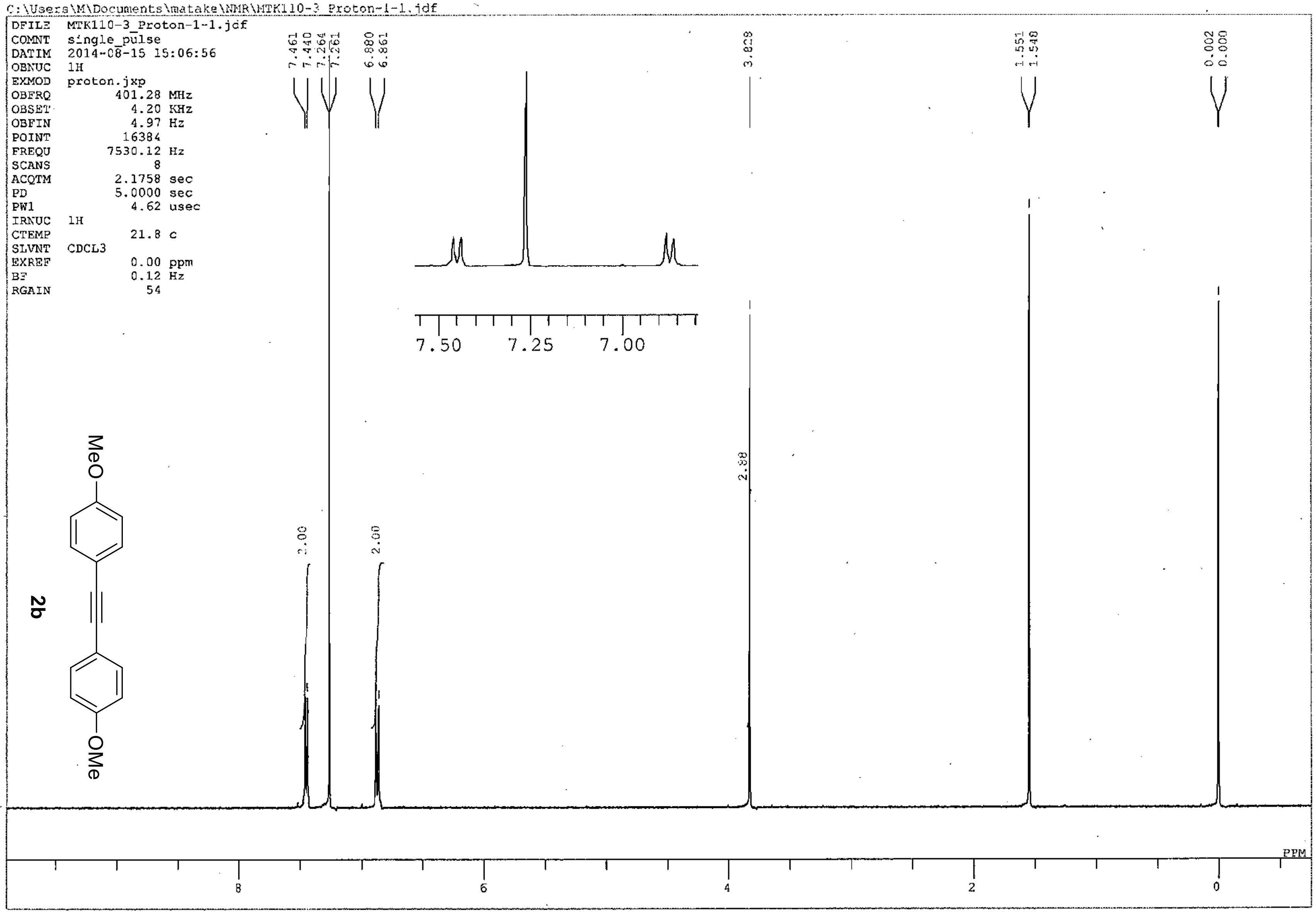
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7.00
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2.00
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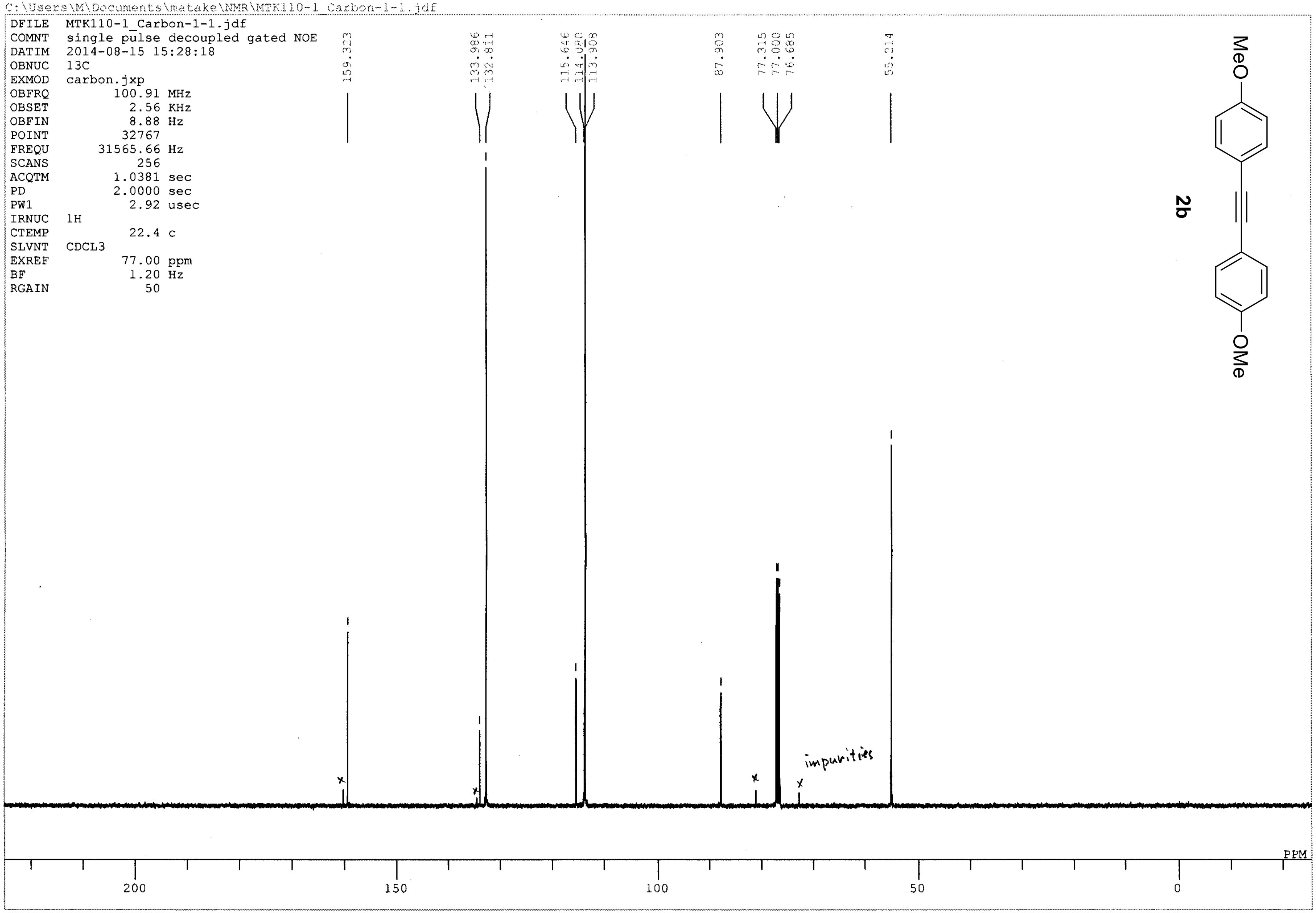

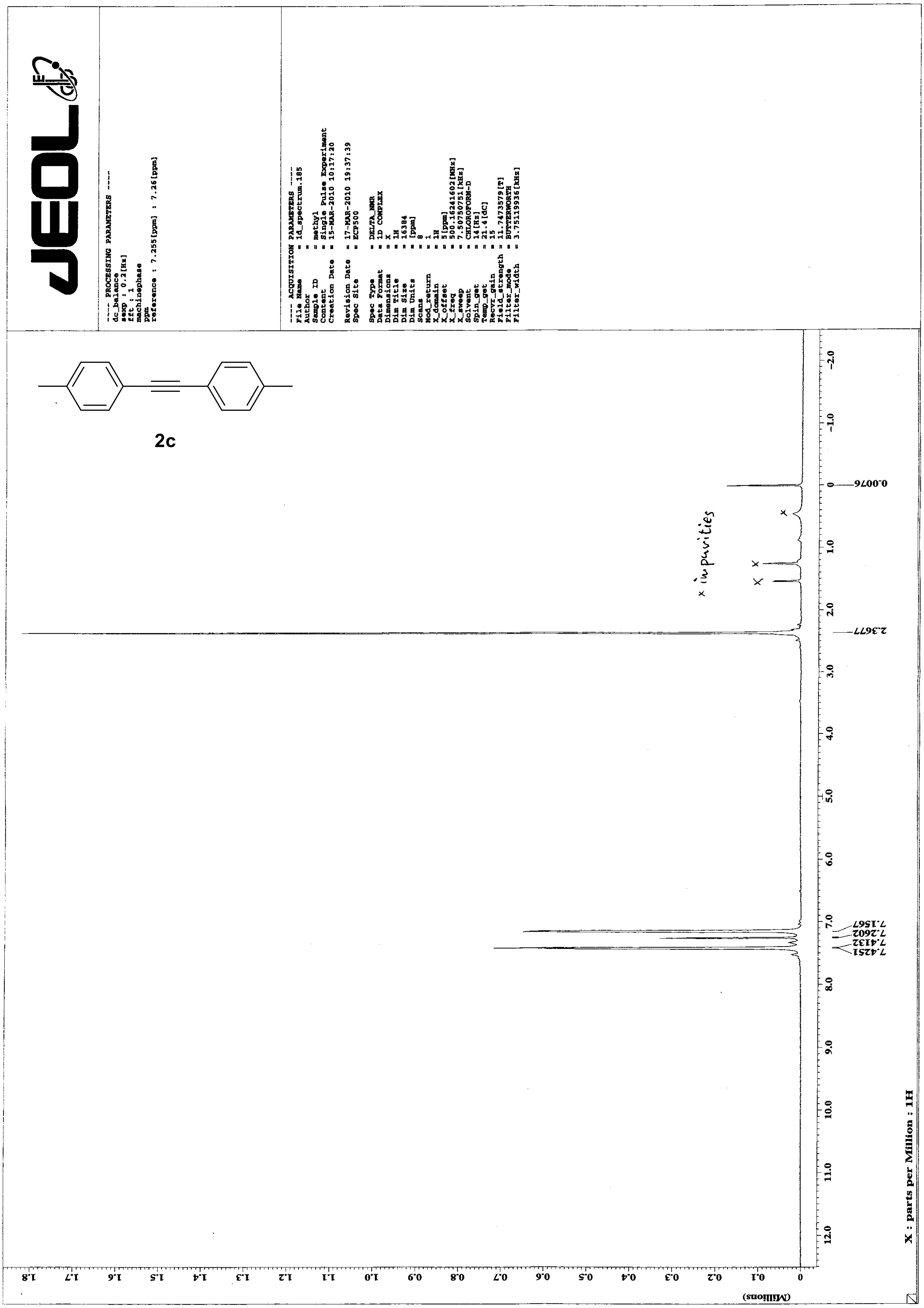
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Field_strength = 11.7473579[T]
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Filter_width = 3.75119936[kHz]
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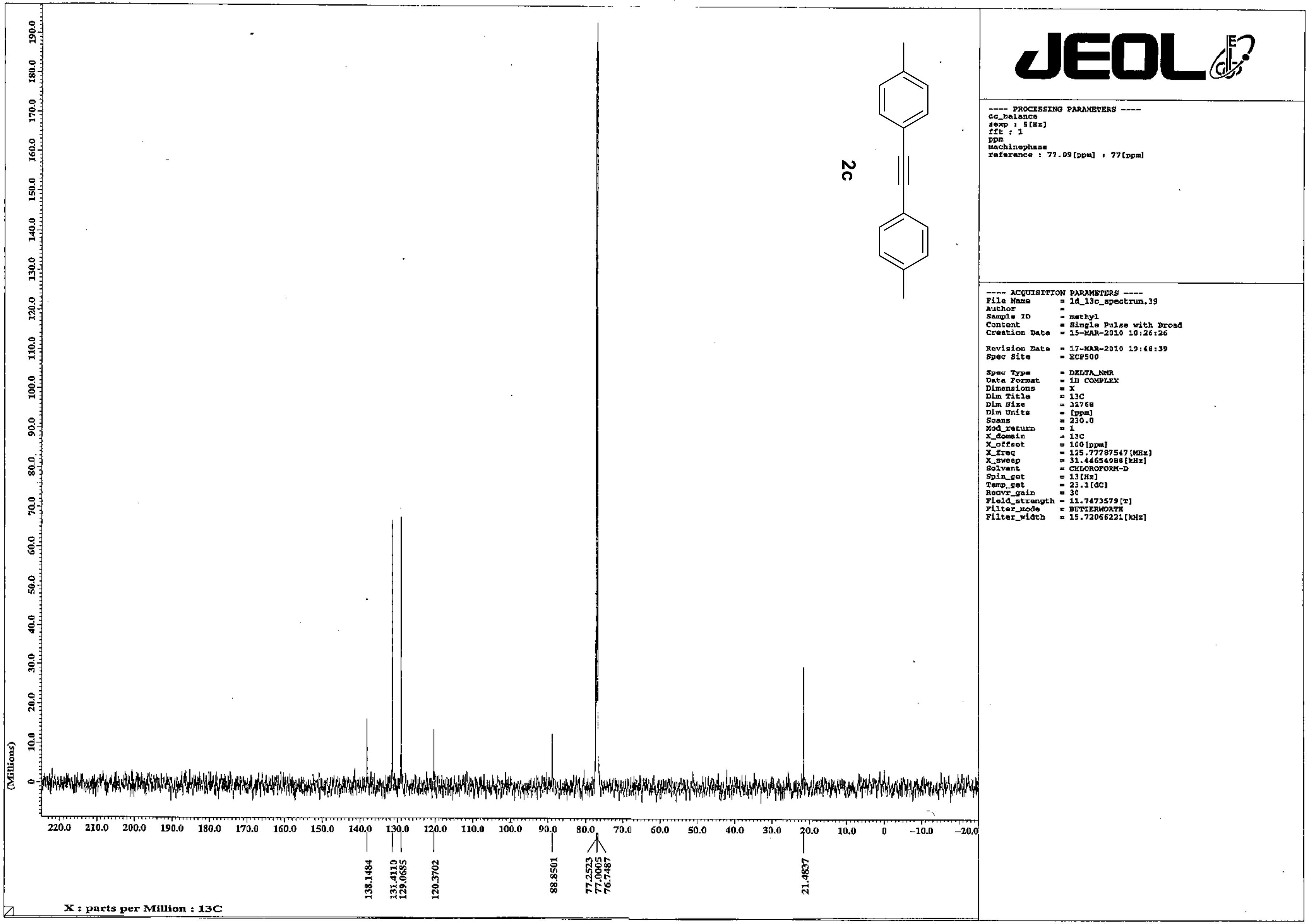
(Millions)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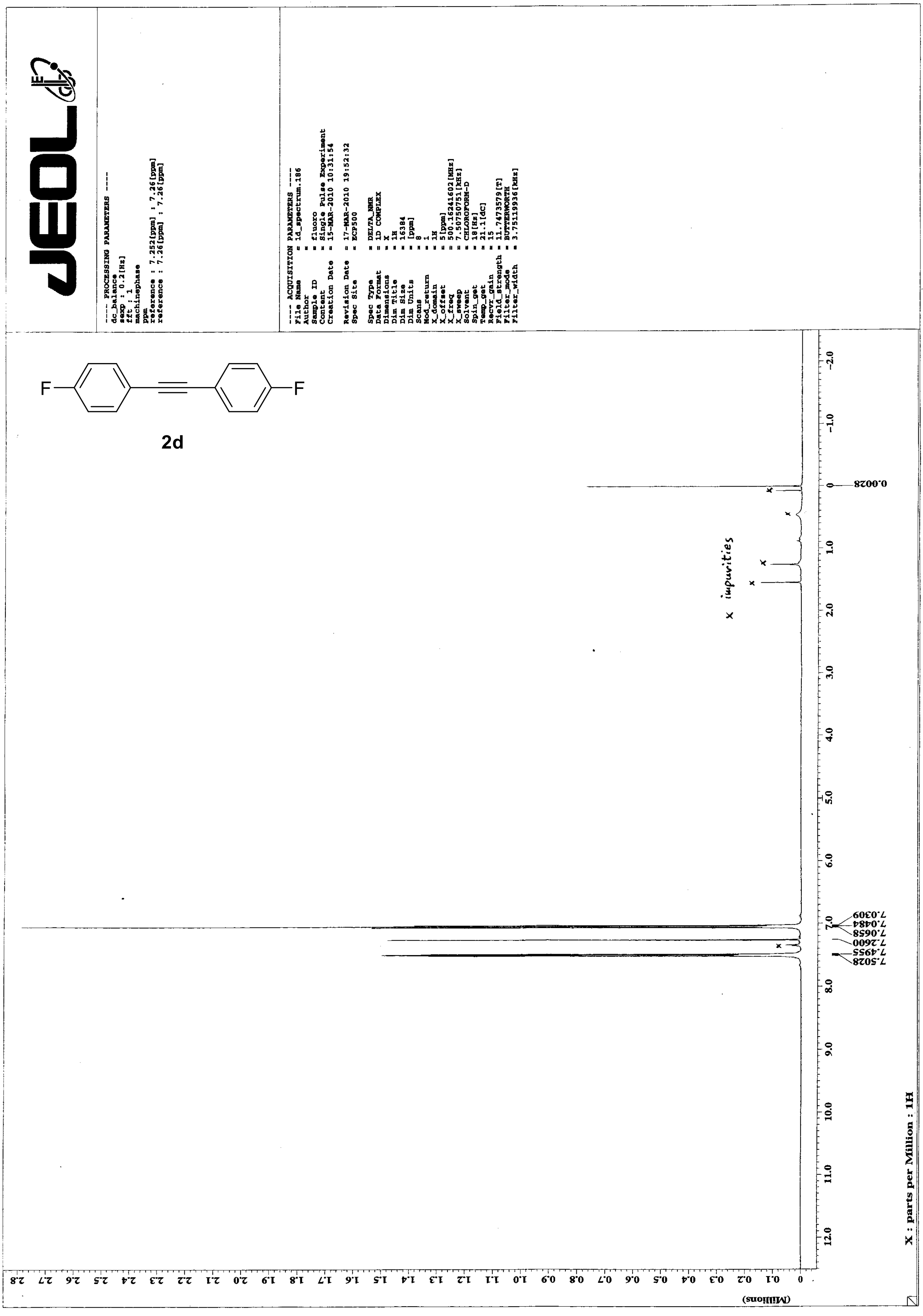
X : parts per Million : 13C



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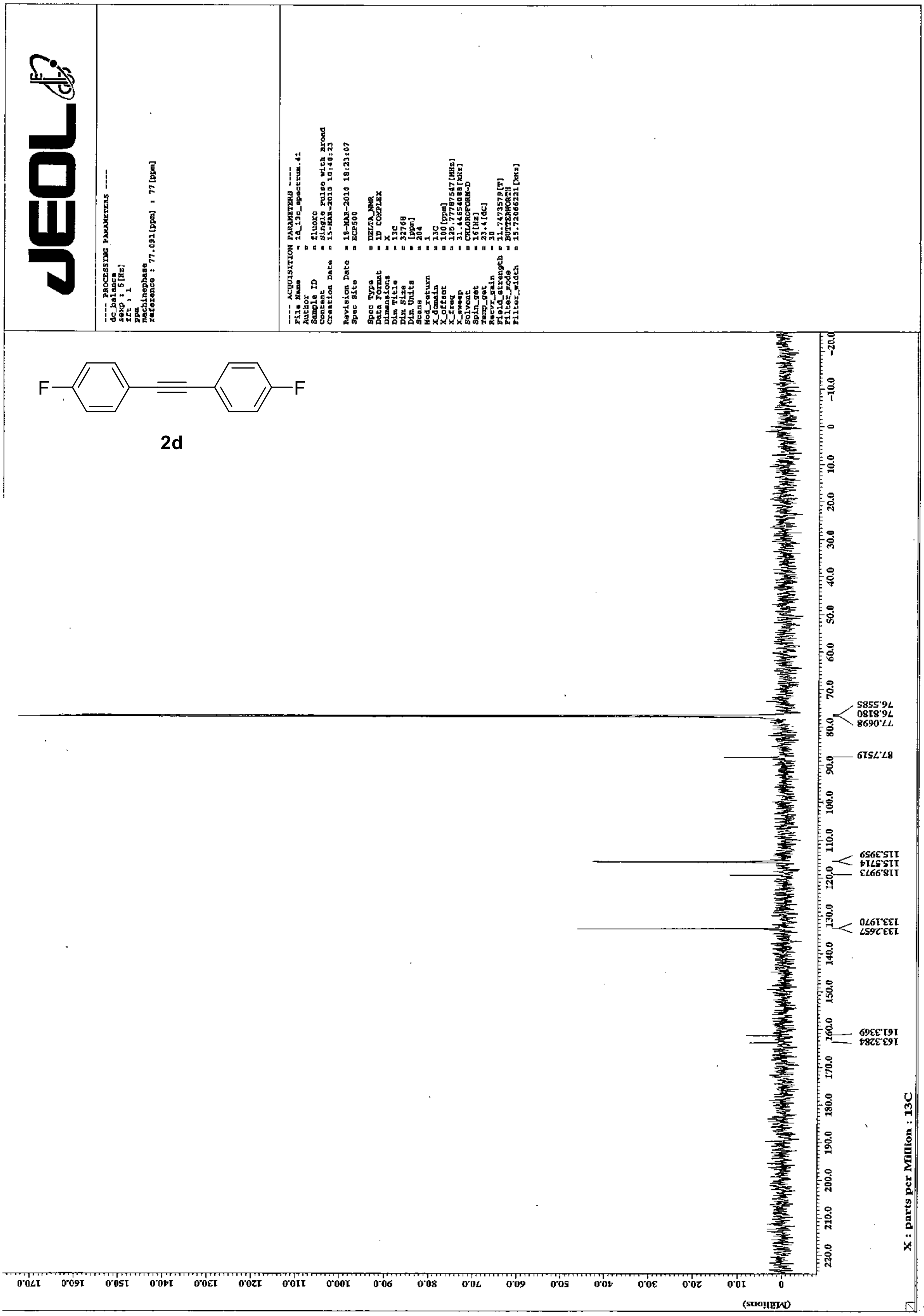
(Millions)



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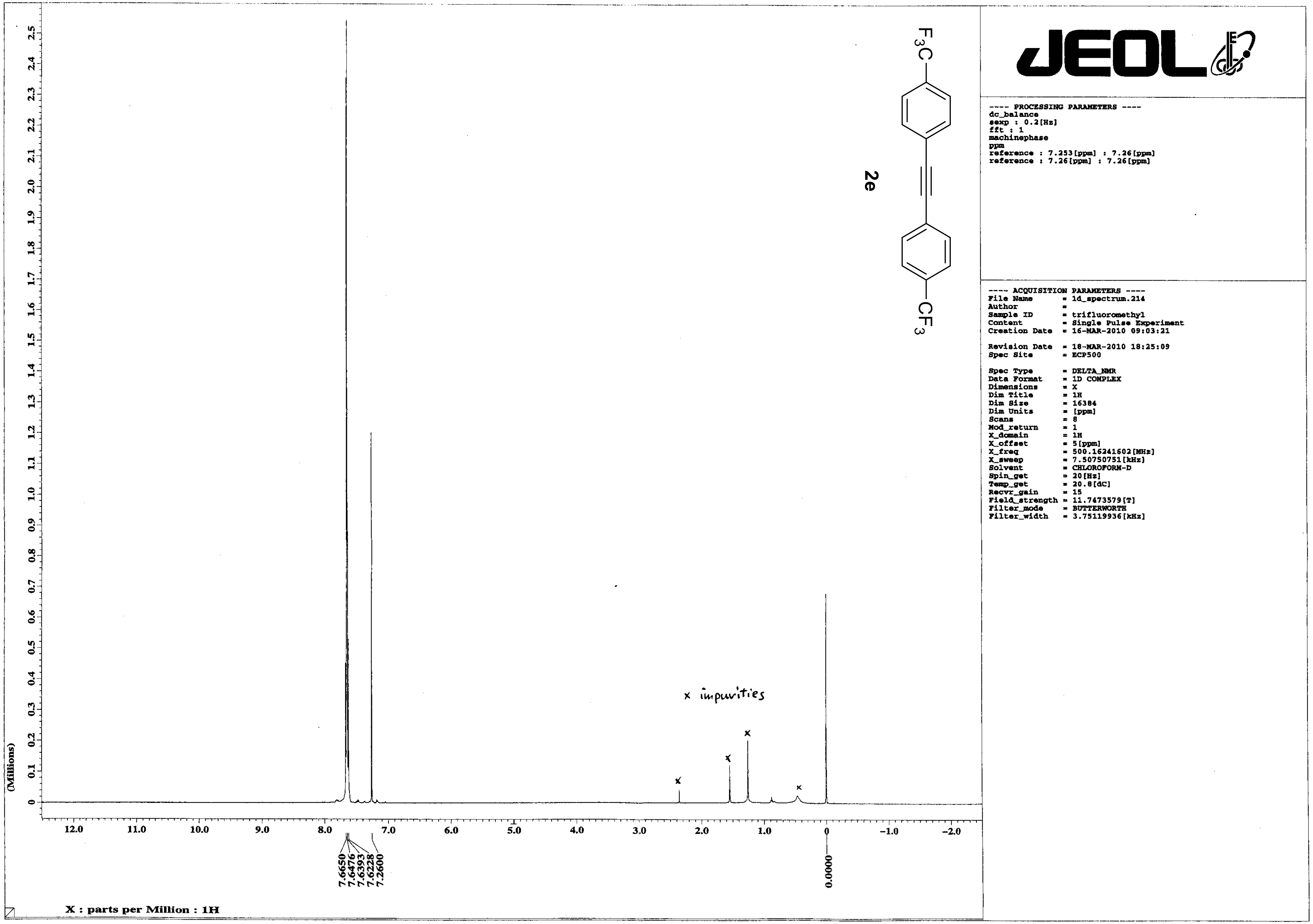
(Millions)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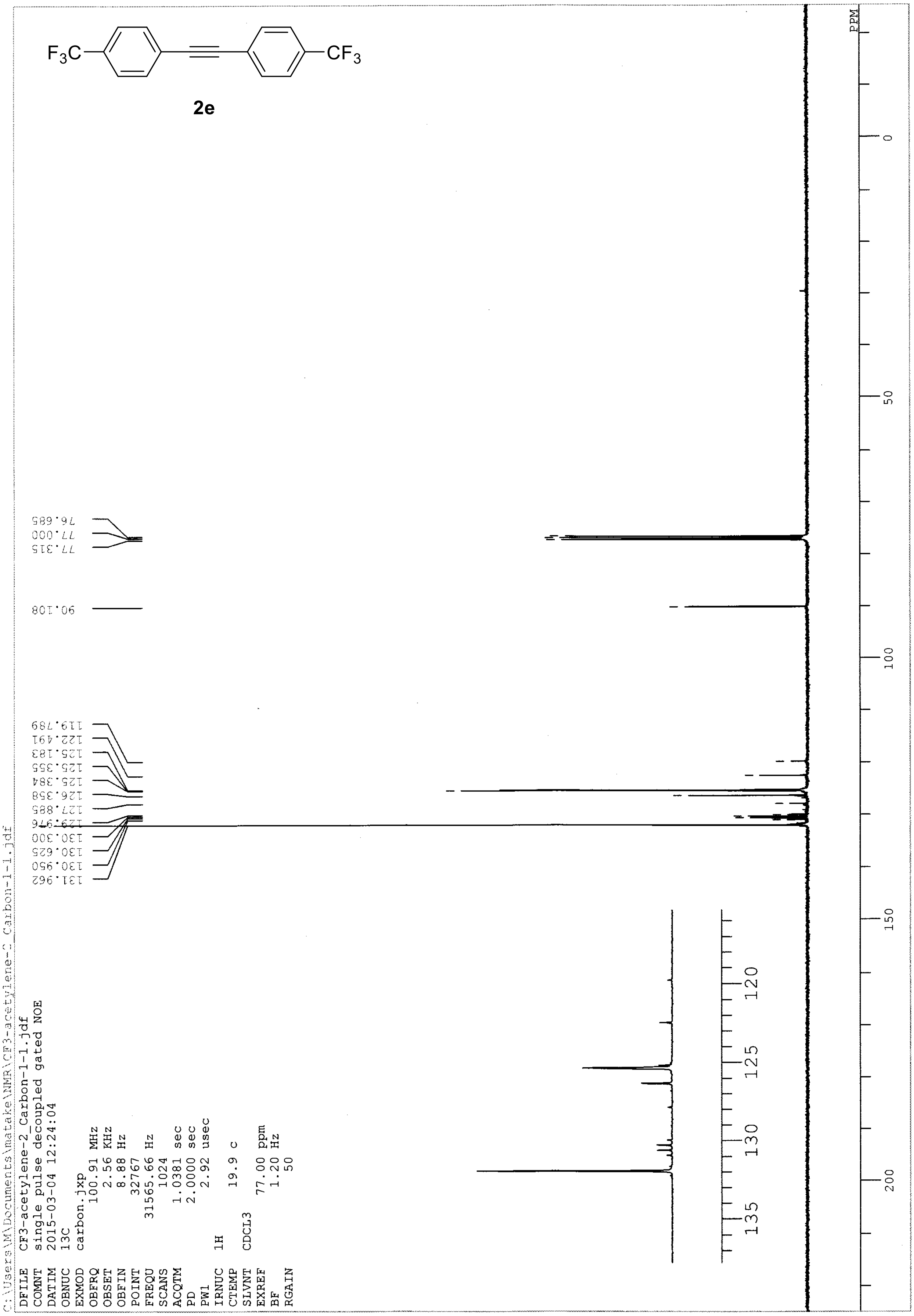
X : parts per Million : 1H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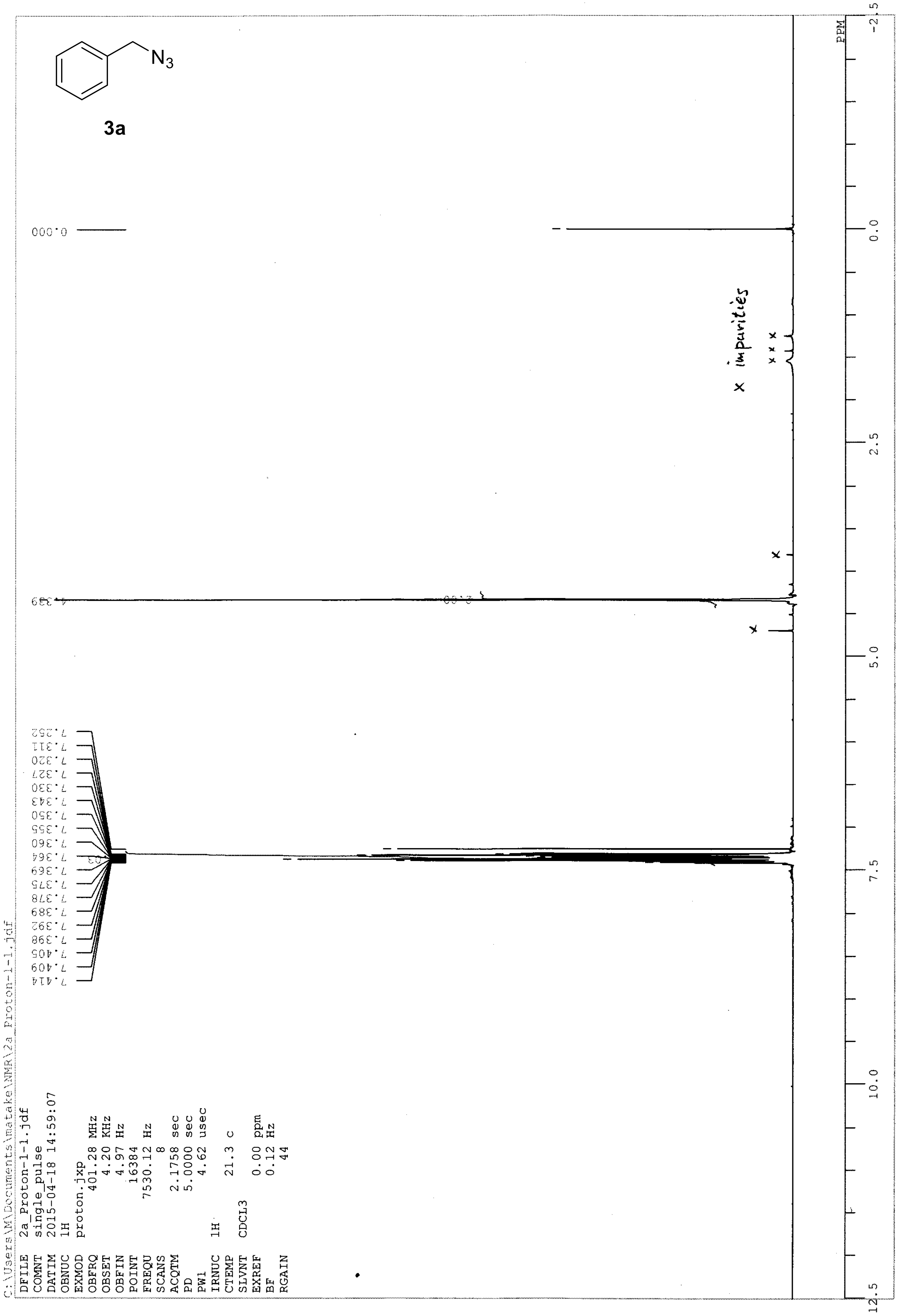
**2e**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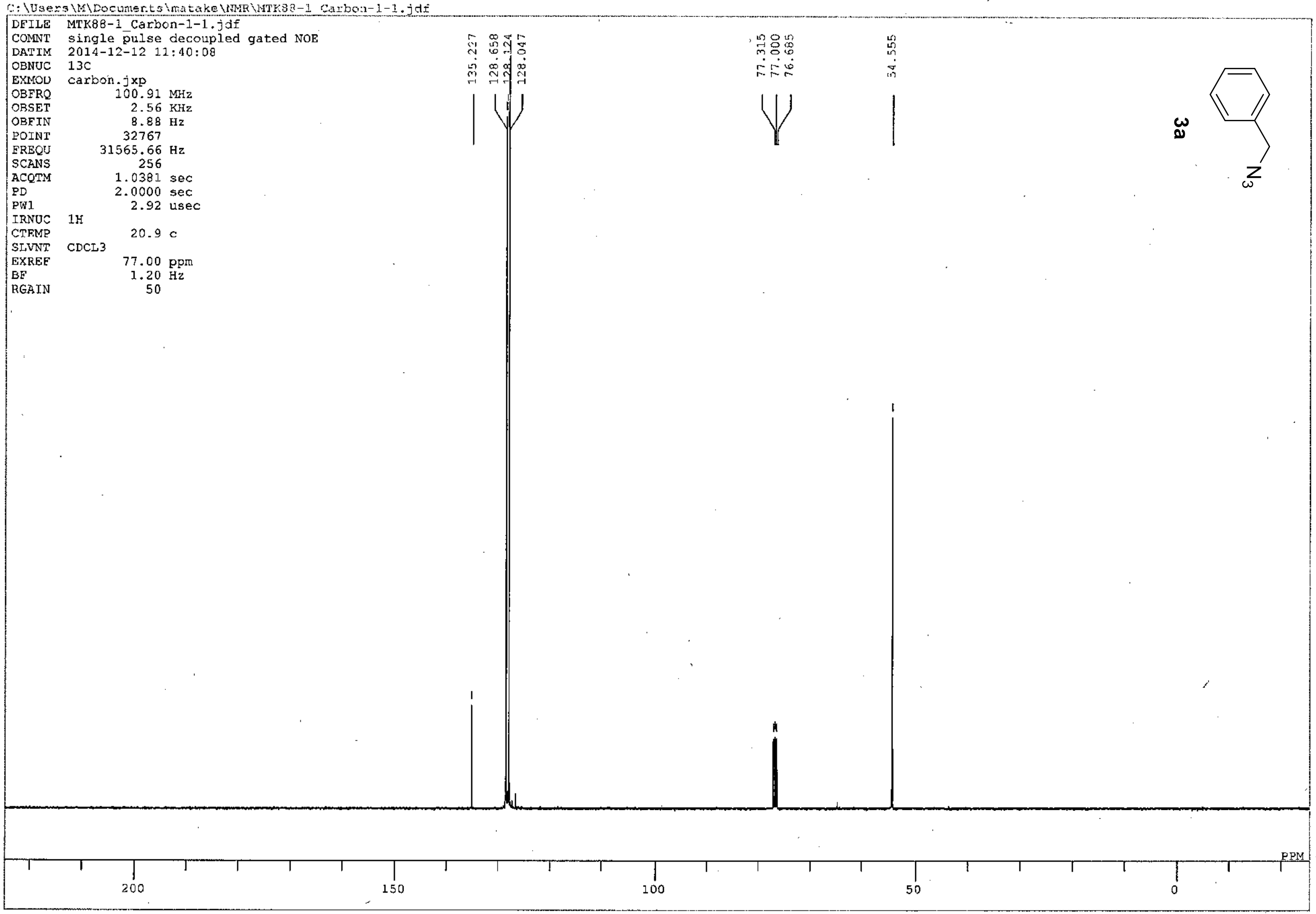
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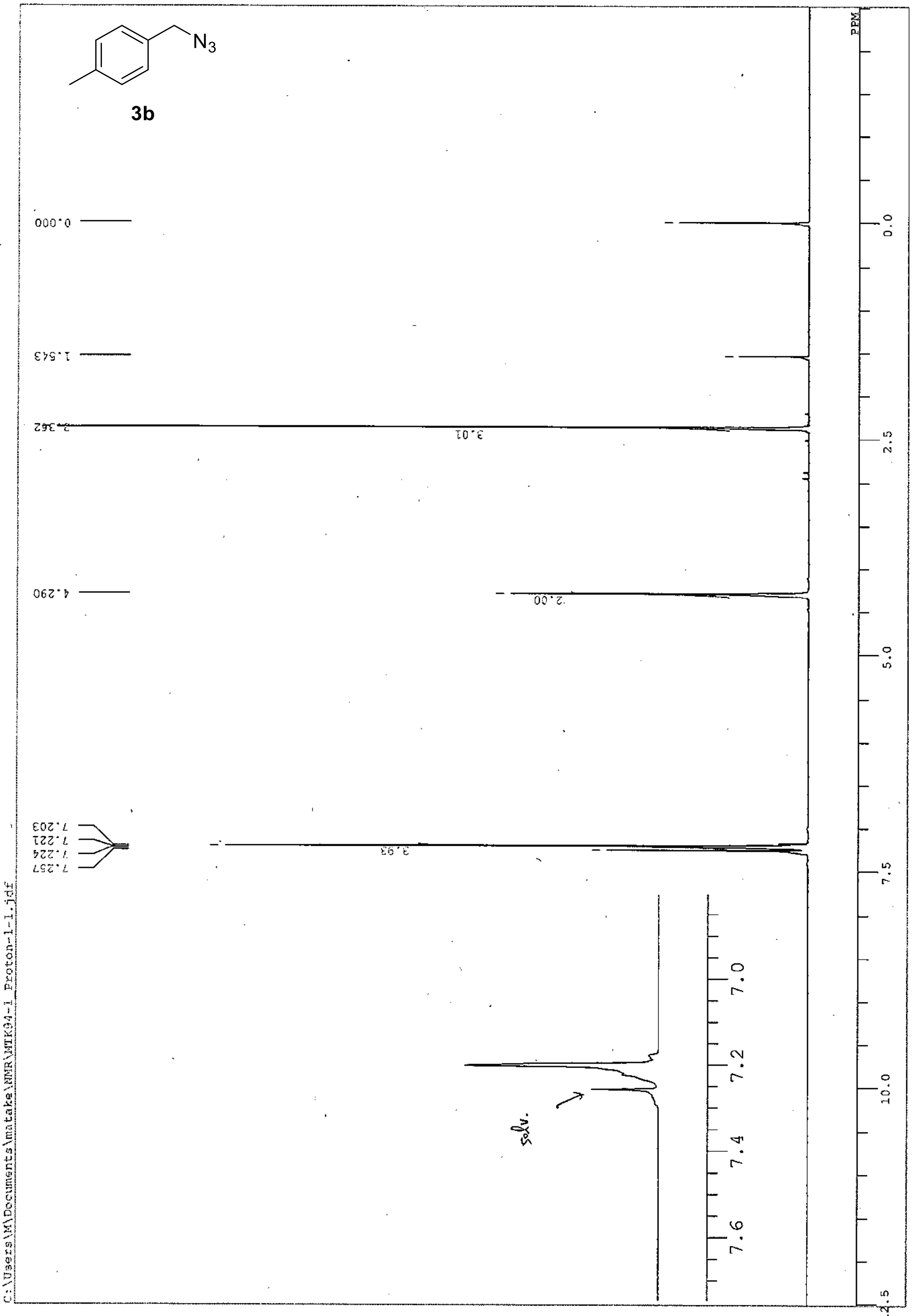
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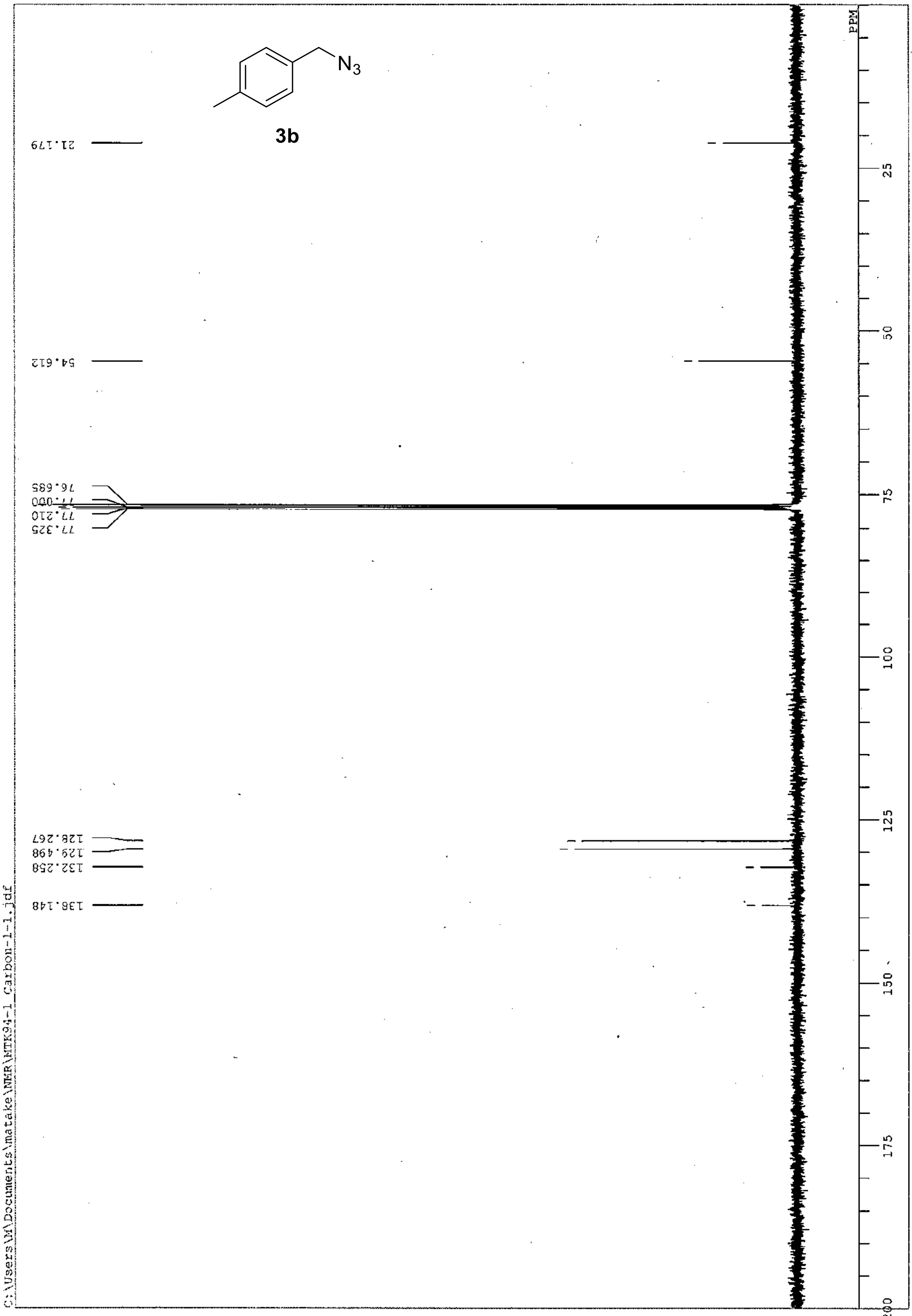
7.4
7.6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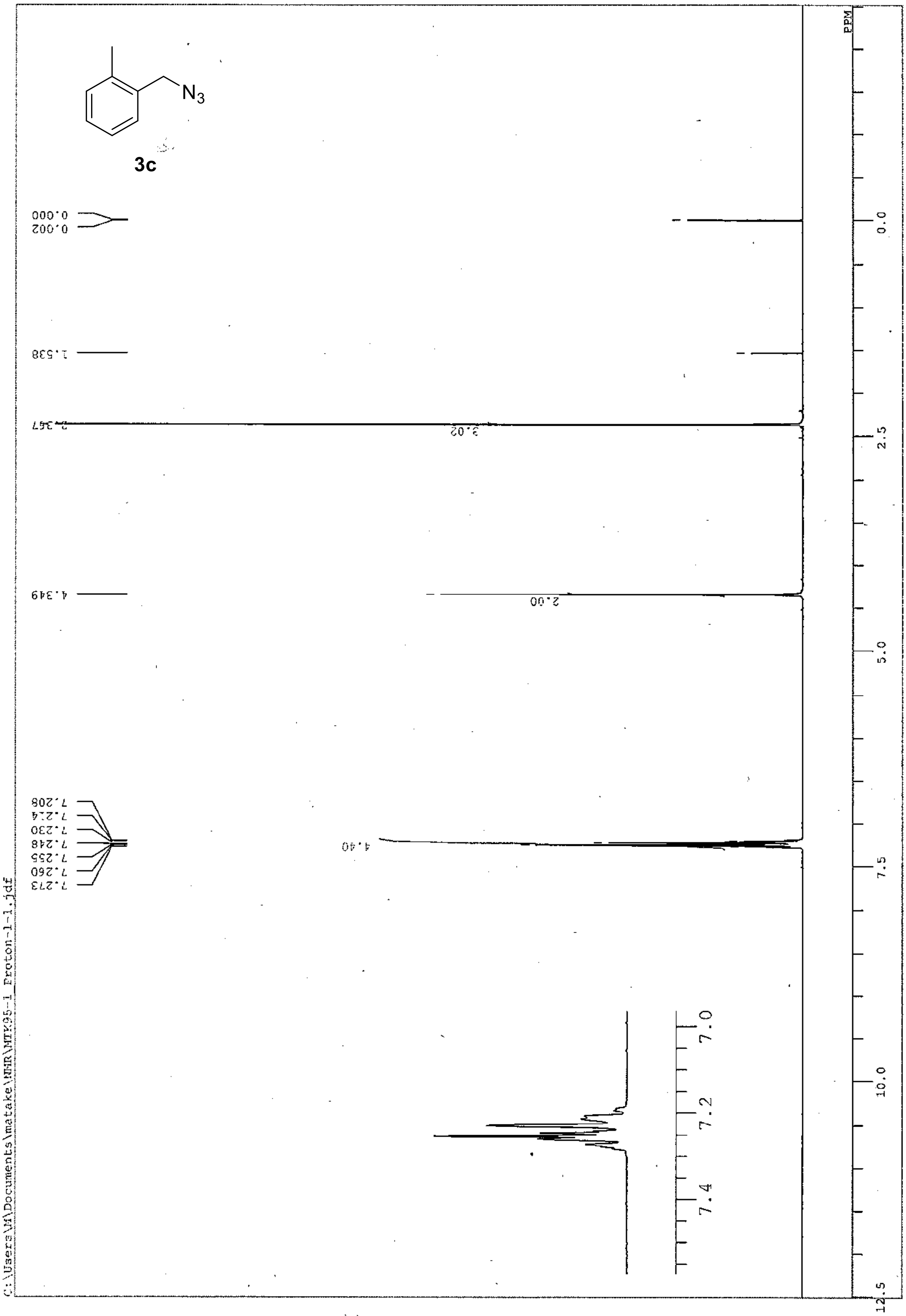
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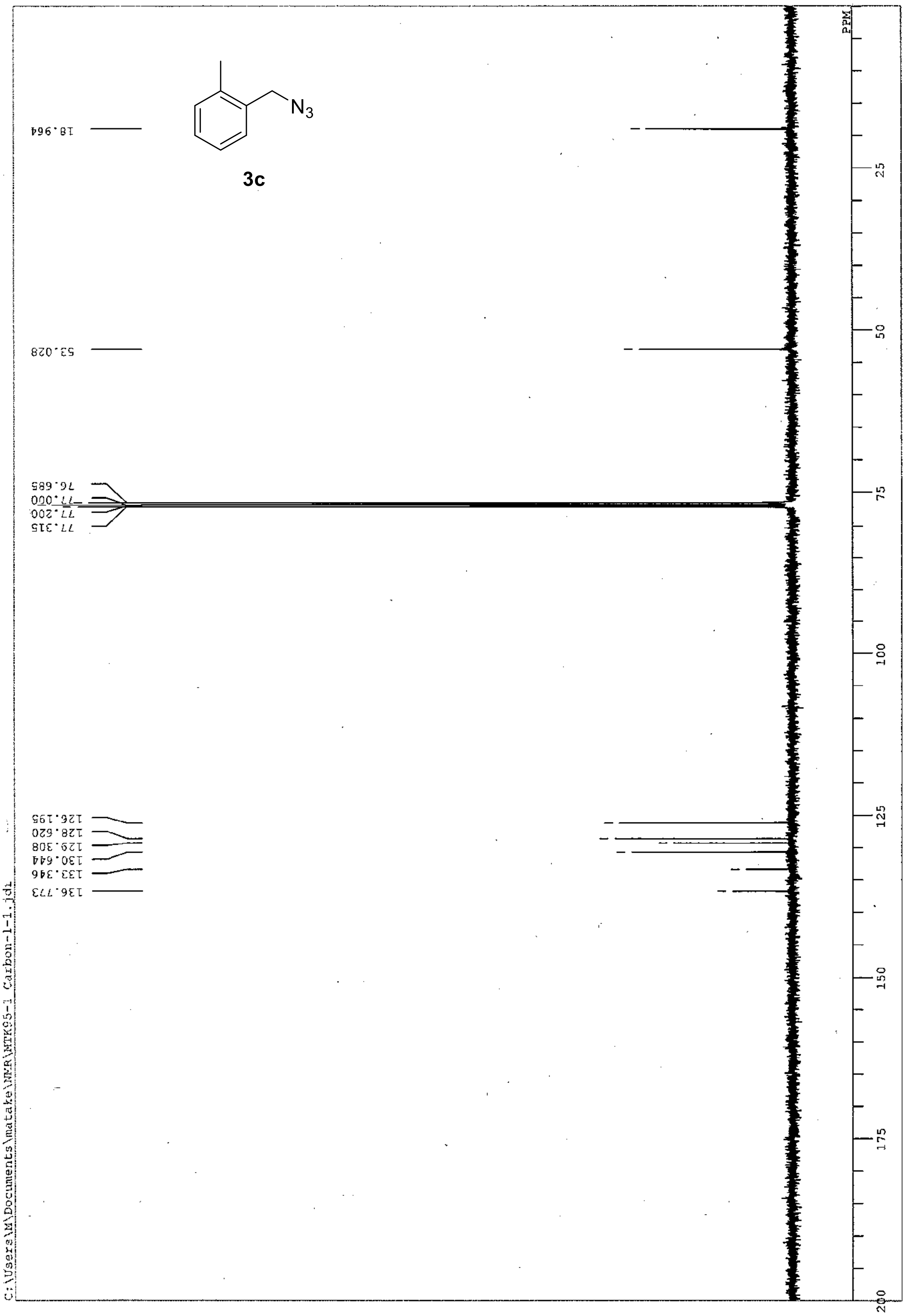
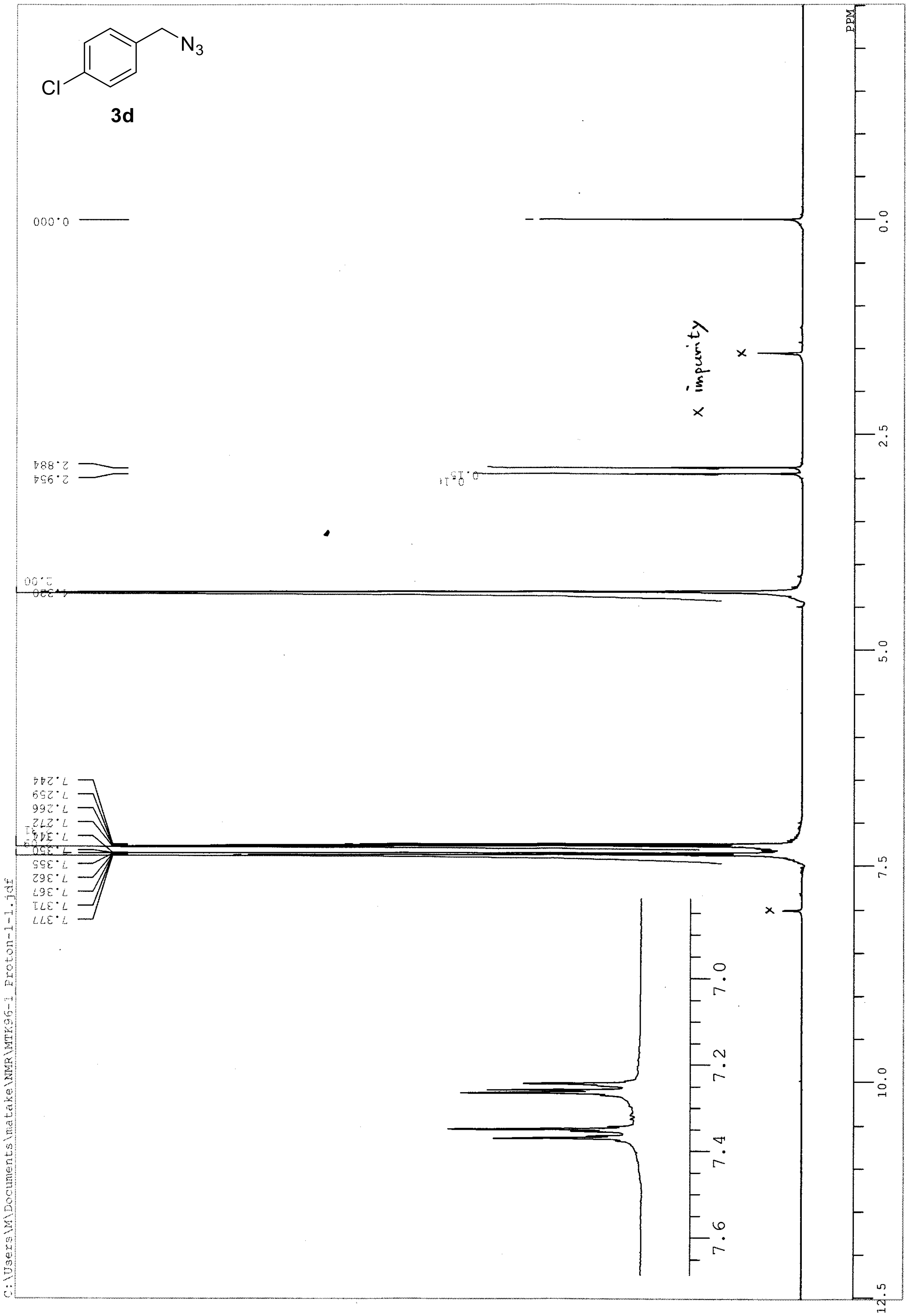
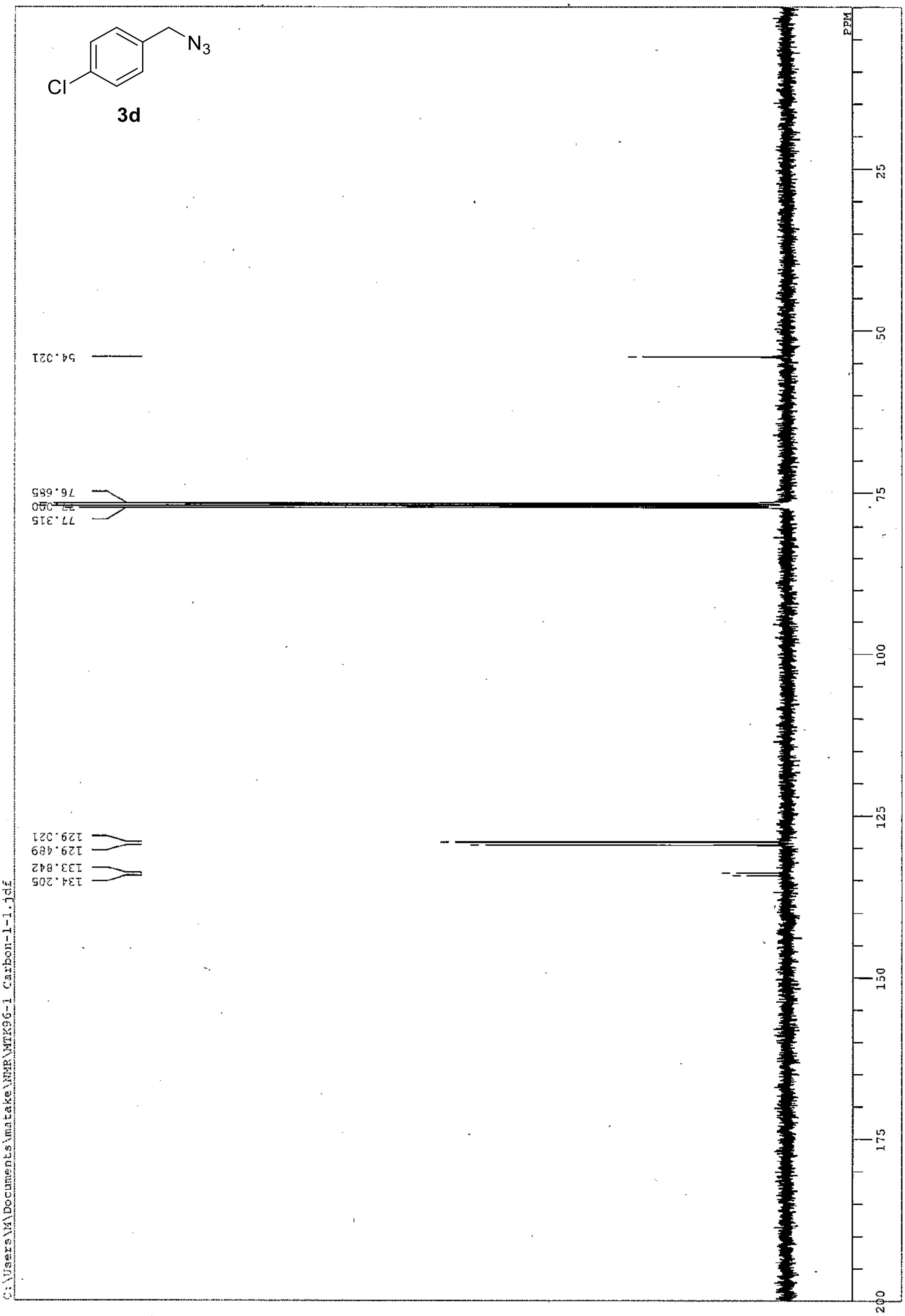
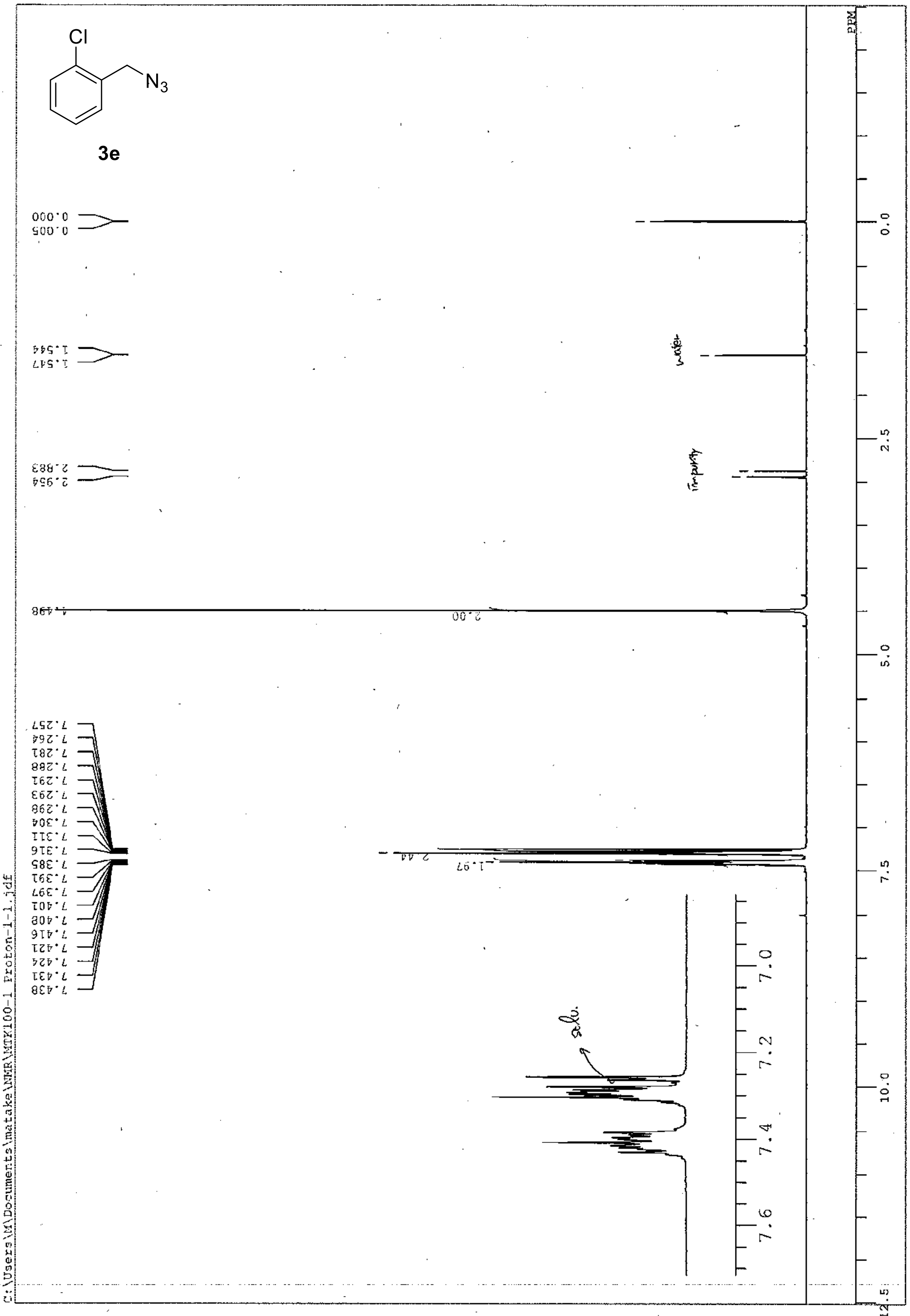
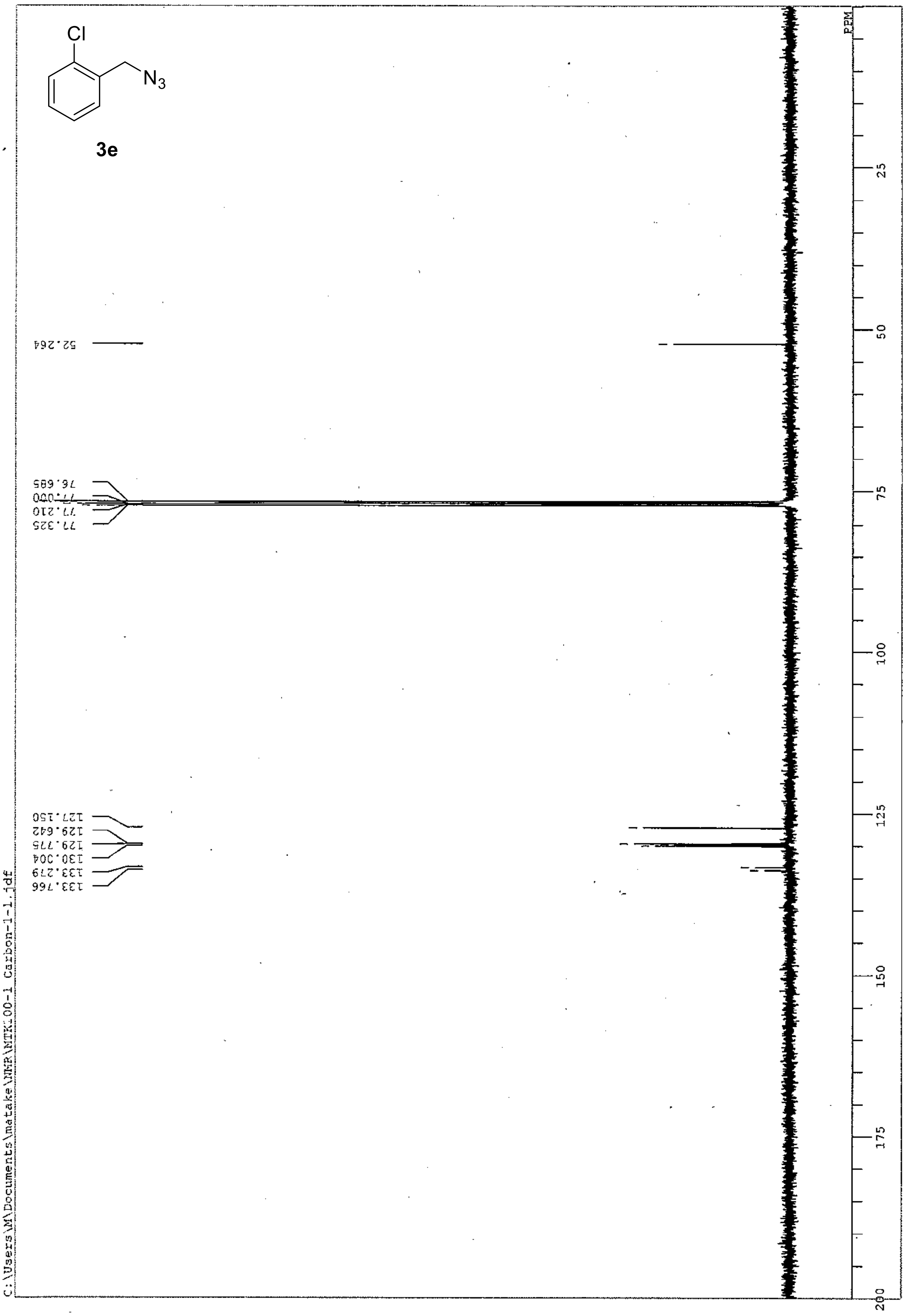
12.5
7.0
7.2
7.4
C:\Users\M\Documents\mmatake\NMR\MTK95-1 Proton-1-1.jdf

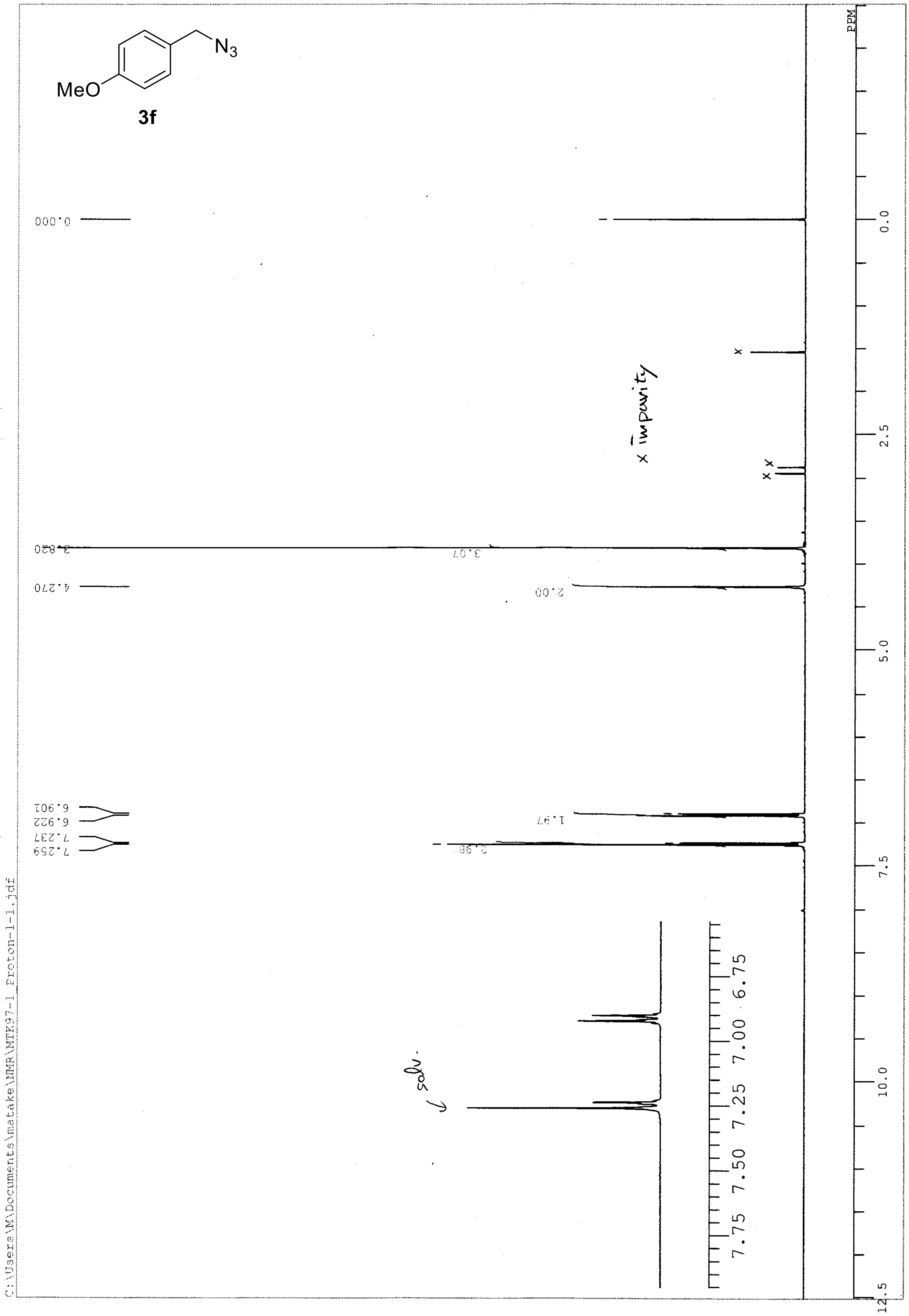

3c
N3
18.964
53.028
76.685
77.000
77.200
77.315
126.195
128.620
129.308
130.644
133.346
136.773
PPM
25
50
75
100
125
150
175
200
C:\Users\M\Documents\matake\NMR\MTK95-1 Carbon-1-1.jdf

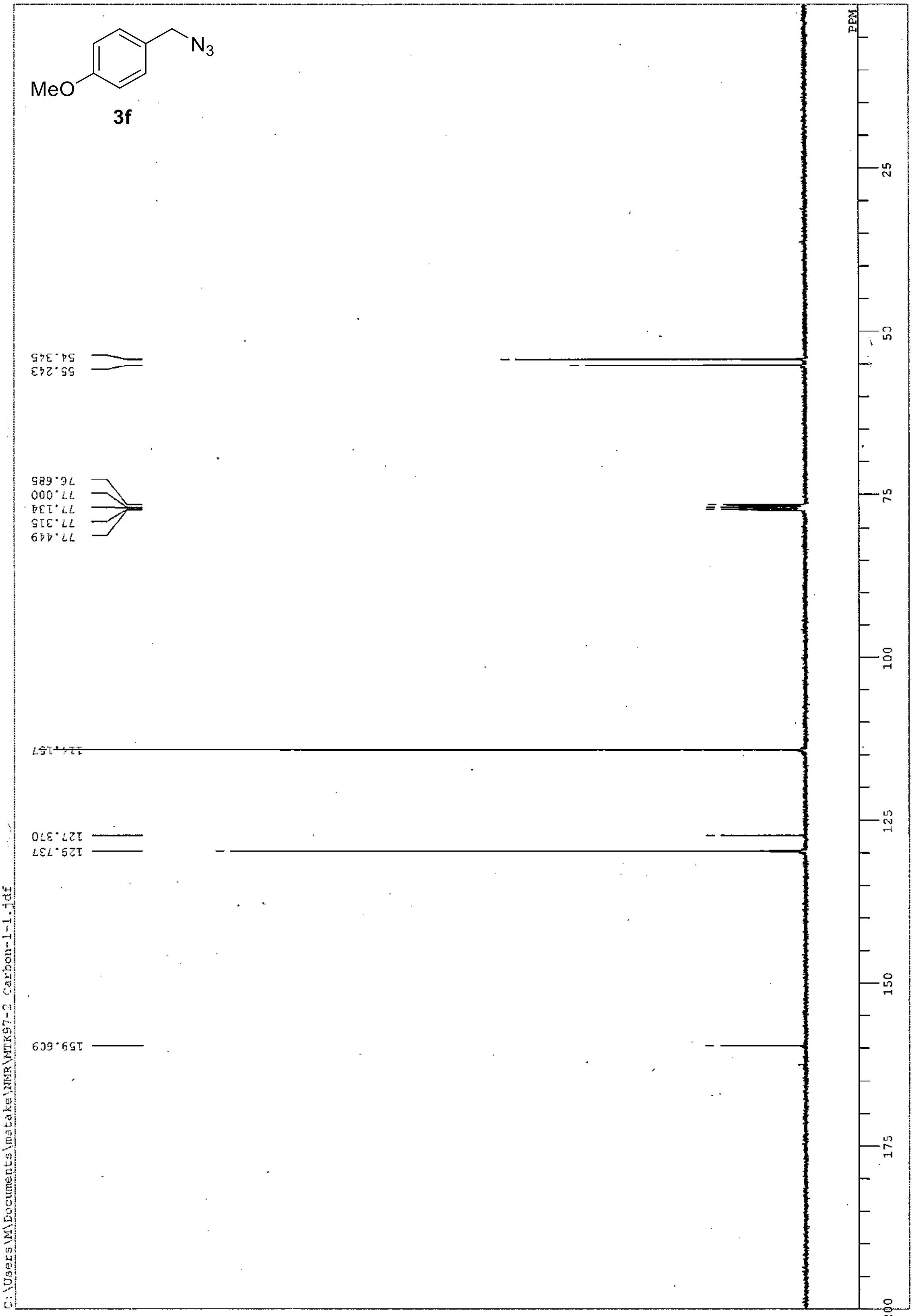

Cl
N3
3d
C:\Users\M\Documents\matake\NMR\MTK96-1_Proton-1-1.jdf
0.000
2.884
2.954
4.300
7.244
7.259
7.266
7.272
7.344
7.350
7.355
7.362
7.367
7.371
7.377
x impurity
PPM
0.0
2.5
5.0
7.5
10.0
12.5
7.0
7.2
7.4
7.6


N3
Cl
3d
54.021
76.685
77.000
77.315
129.021
129.489
133.842
134.205
PPM
25
50
75
100
125
150
175
200
C:\Users\M\Documents\matake\NMR\MTK96-1_Carbon-1-1.jdf

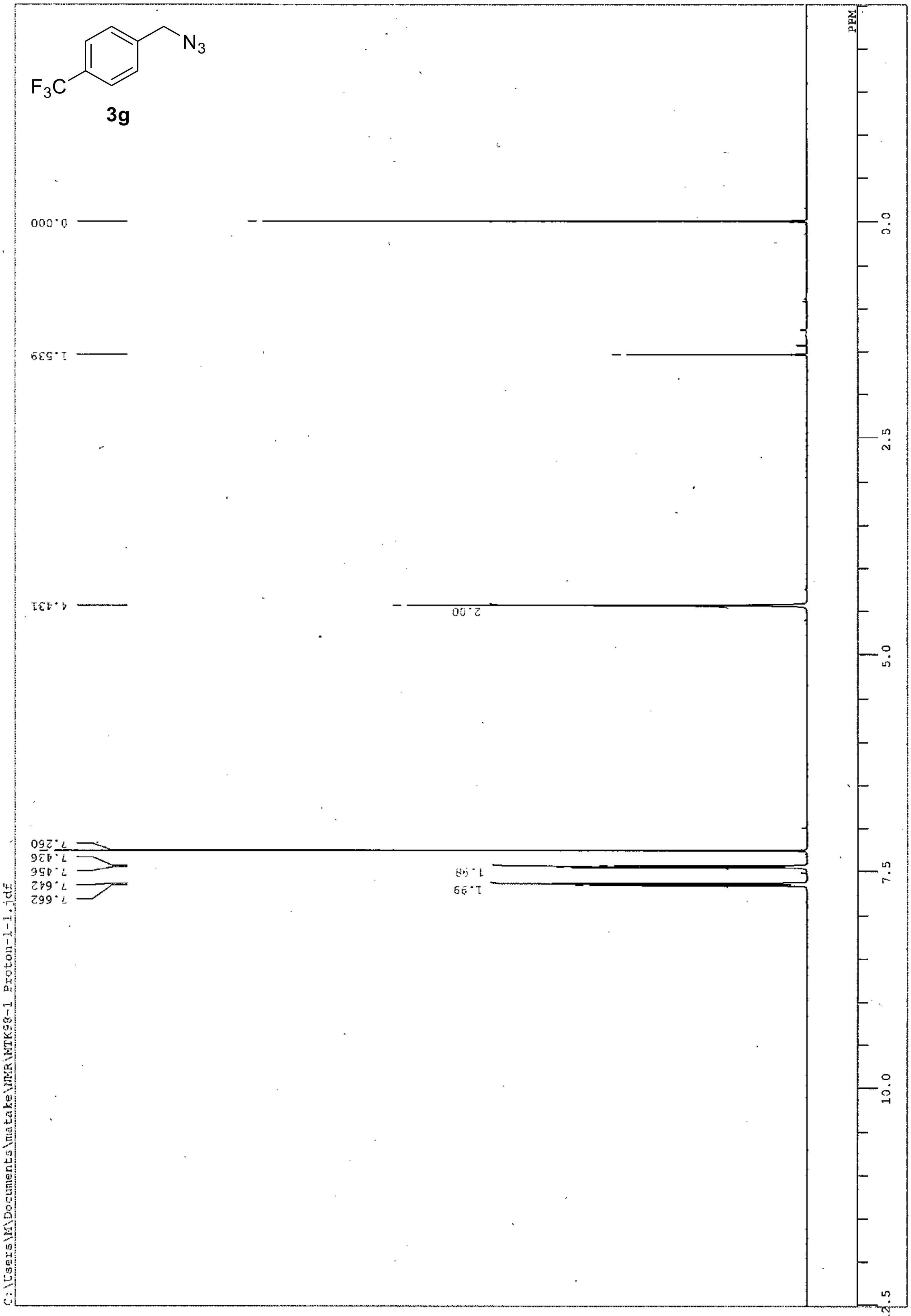

Cl
N3
3e
0.000
0.005
1.544
1.547
2.883
2.954
4.498
7.257
7.264
7.281
7.288
7.291
7.293
7.298
7.304
7.311
7.316
7.385
7.391
7.397
7.401
7.408
7.416
7.421
7.424
7.431
7.438
water
impurity
2.00
2.44
1.97
7.0
7.2
7.4
7.6
PPM
0.0
2.5
5.0
7.5
10.0
12.5

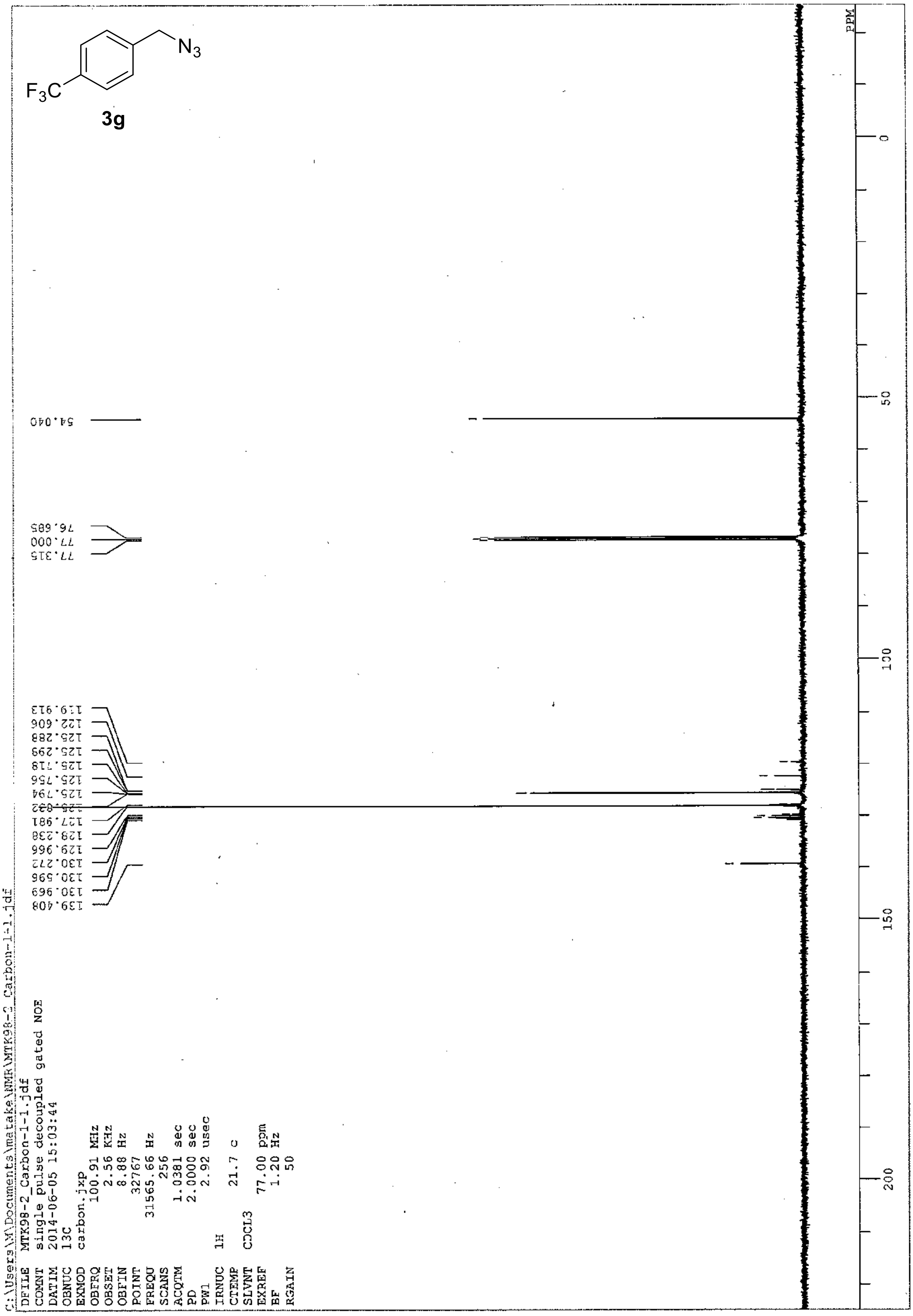

Cl
N3
3e
52.264
76.685
77.000
77.210
77.325
127.150
129.642
129.775
130.004
133.279
133.766
PPM
25
50
75
100
125
150
175
200
C:\Users\M\Documents\matake\NMR\MTK\MTK100-1 Carbon-1-1.jdf


MeO
N3
3f
C:\Users\M\Documents\matake\NMR\MTK97-1_Proton-1-1.jdf
0.000
3.820
4.270
6.901
6.922
7.237
7.259
3.07
2.00
1.97
x impurity
solv.
PPM
0.0
2.5
5.0
7.5
10.0
12.5
7.75 7.50 7.25 7.00 6.75

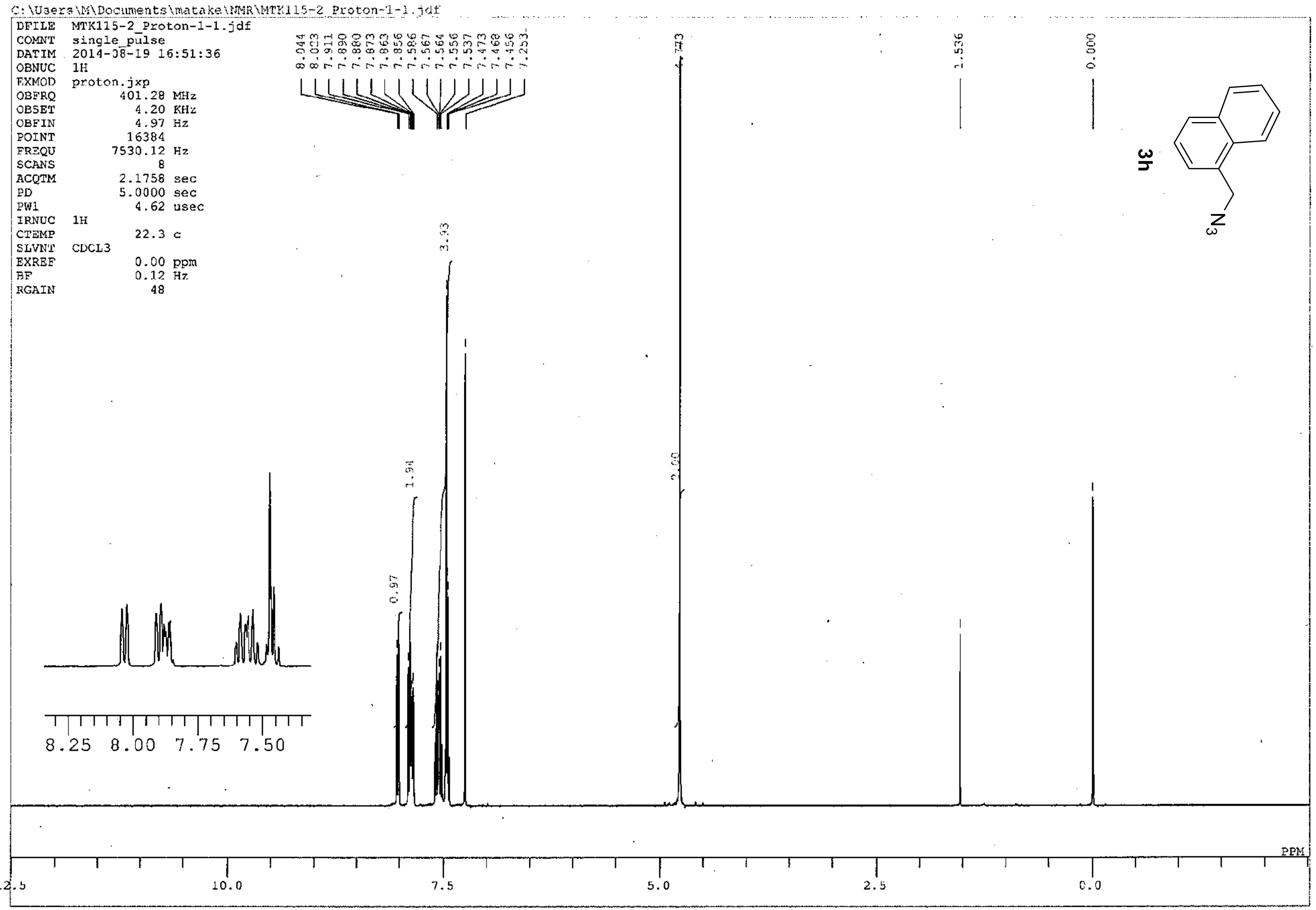


MeO
N3
3f
54.345
55.243
76.685
77.000
77.134
77.315
77.449
114.167
127.370
129.737
159.609
PPM
25
50
75
100
125
150
175
200
C:\Users\M\Documents\matake\NMR\MTK97-2 Carbon-1-1.jdf

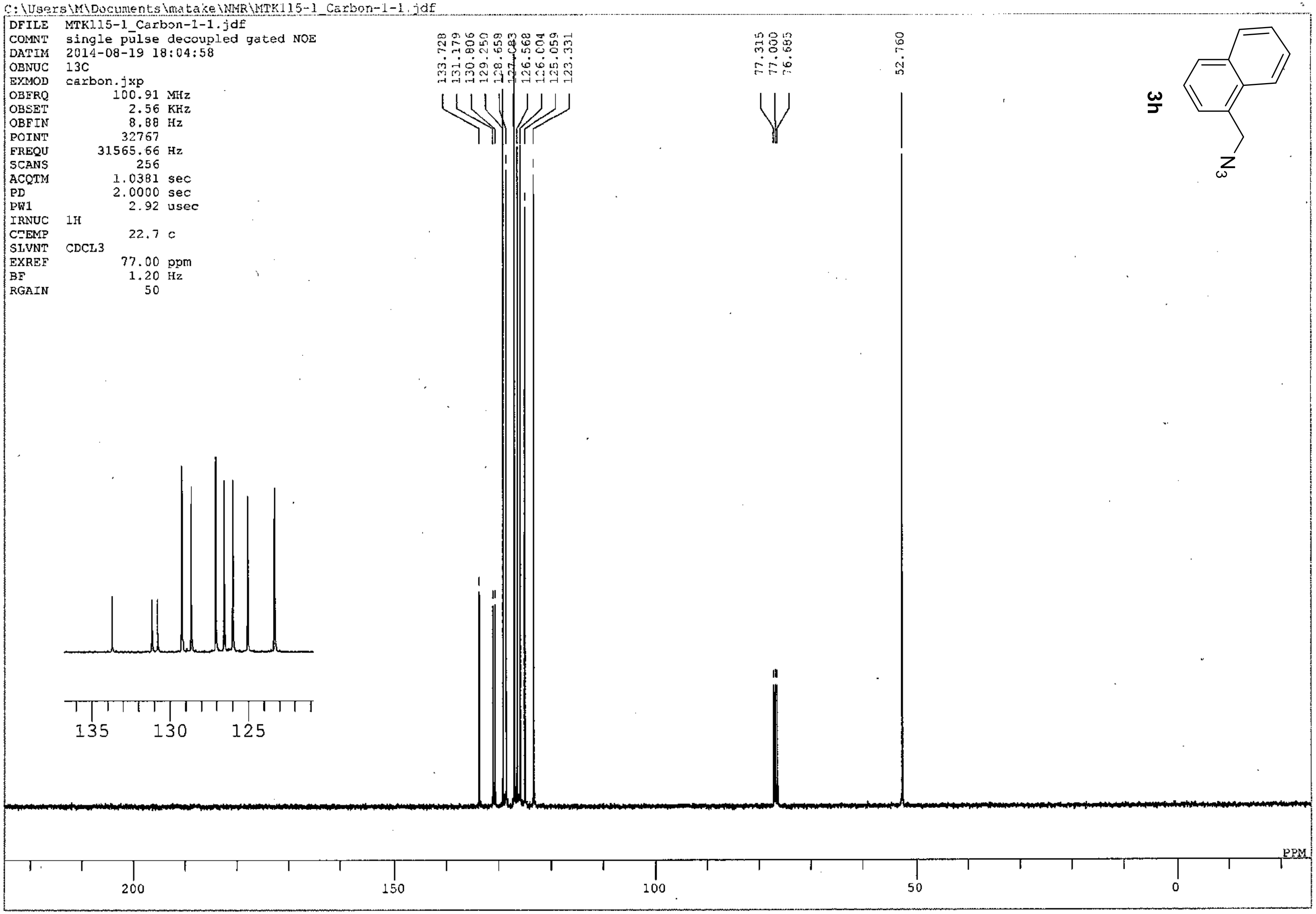

N3
F3C
3g
0.000
1.539
4.431
7.260
7.436
7.456
7.642
7.662
2.00
1.98
1.99
PPM
0.0
2.5
5.0
7.5
10.0
12.5
C:\Users\M\Documents\matake\NMR\MTK98-1 Proton-1-1.jdf

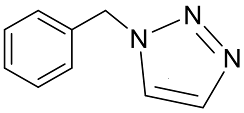


$N_3$
$F_3C$
3g
54.040
76.685
77.000
77.315
119.913
122.606
125.288
125.299
125.718
125.756
125.794
125.832
127.981
128.238
129.966
130.272
130.596
130.969
139.408
C:\Users\M\Documents\matake\NMR\MTK98\MTK98-2_Carbon-1-1.jdf
DFILE MTK98-2_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-06-05 15:03:44
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
PPM
0
50
100
150
200

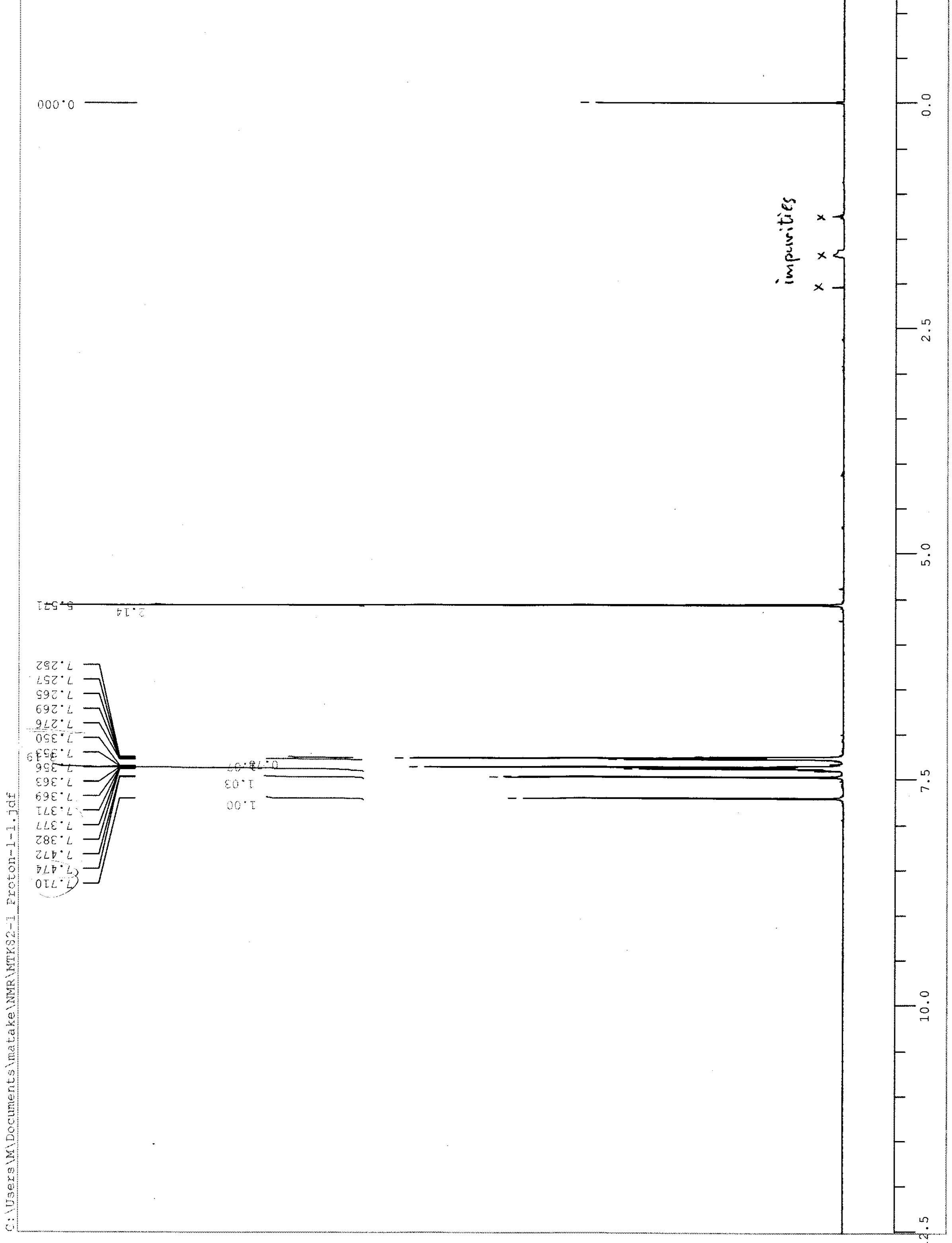


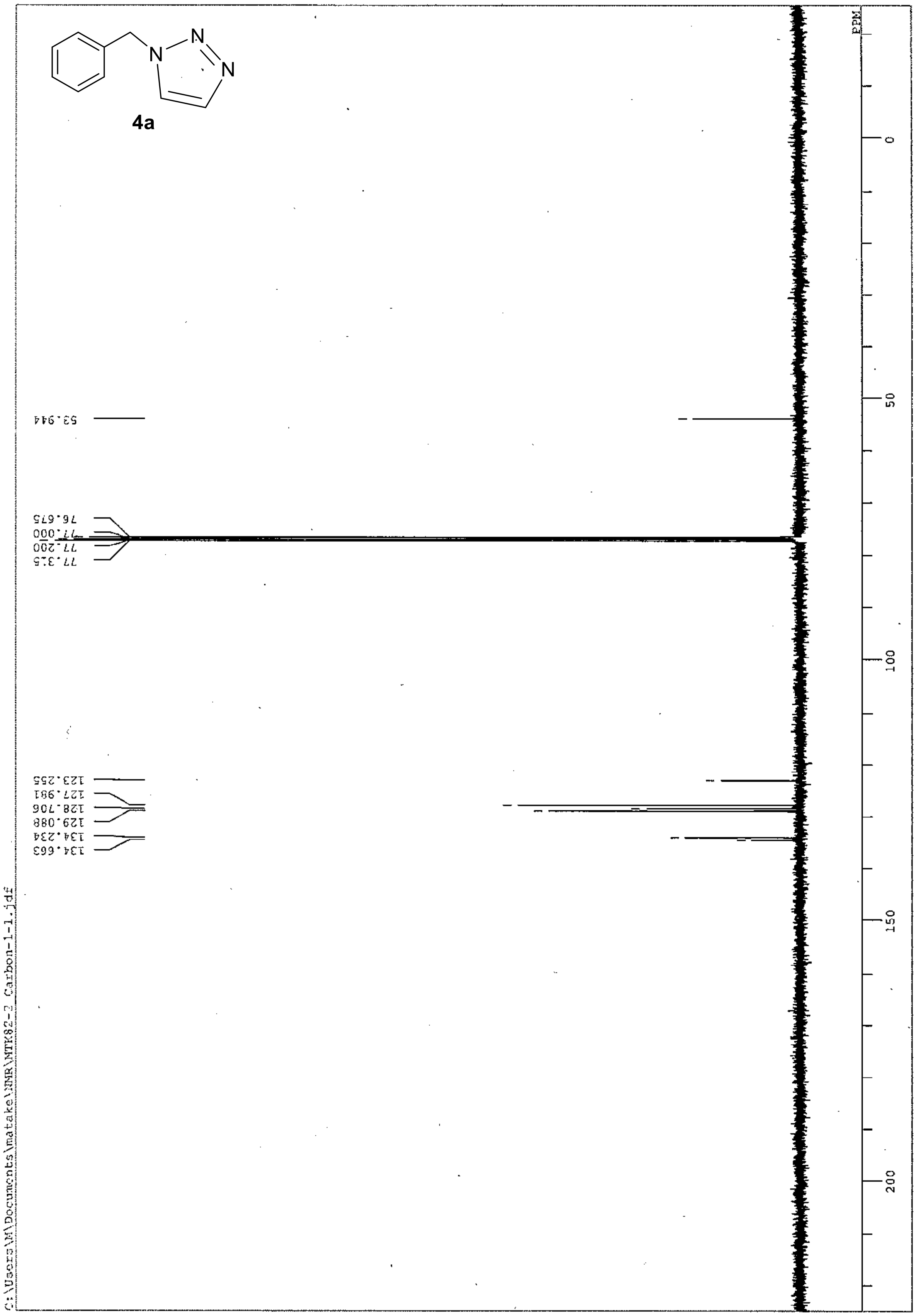
C:\Users\M\Documents\matake\NMR\MTK115-2_Proton-1-1.jdf
DFILE MTK115-2_Proton-1-1.jdf
COMNT single_pulse
DATIM 2014-08-19 16:51:36
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48
8.044
8.023
7.911
7.890
7.880
7.873
7.863
7.856
7.586
7.567
7.564
7.556
7.537
7.473
7.468
7.456
7.253
1.536
0.000
3h
$N_3$
3.93
1.94
0.97
2.00
8.25 8.00 7.75 7.50
PPM
12.5
10.0
7.5
5.0
2.5
0.0

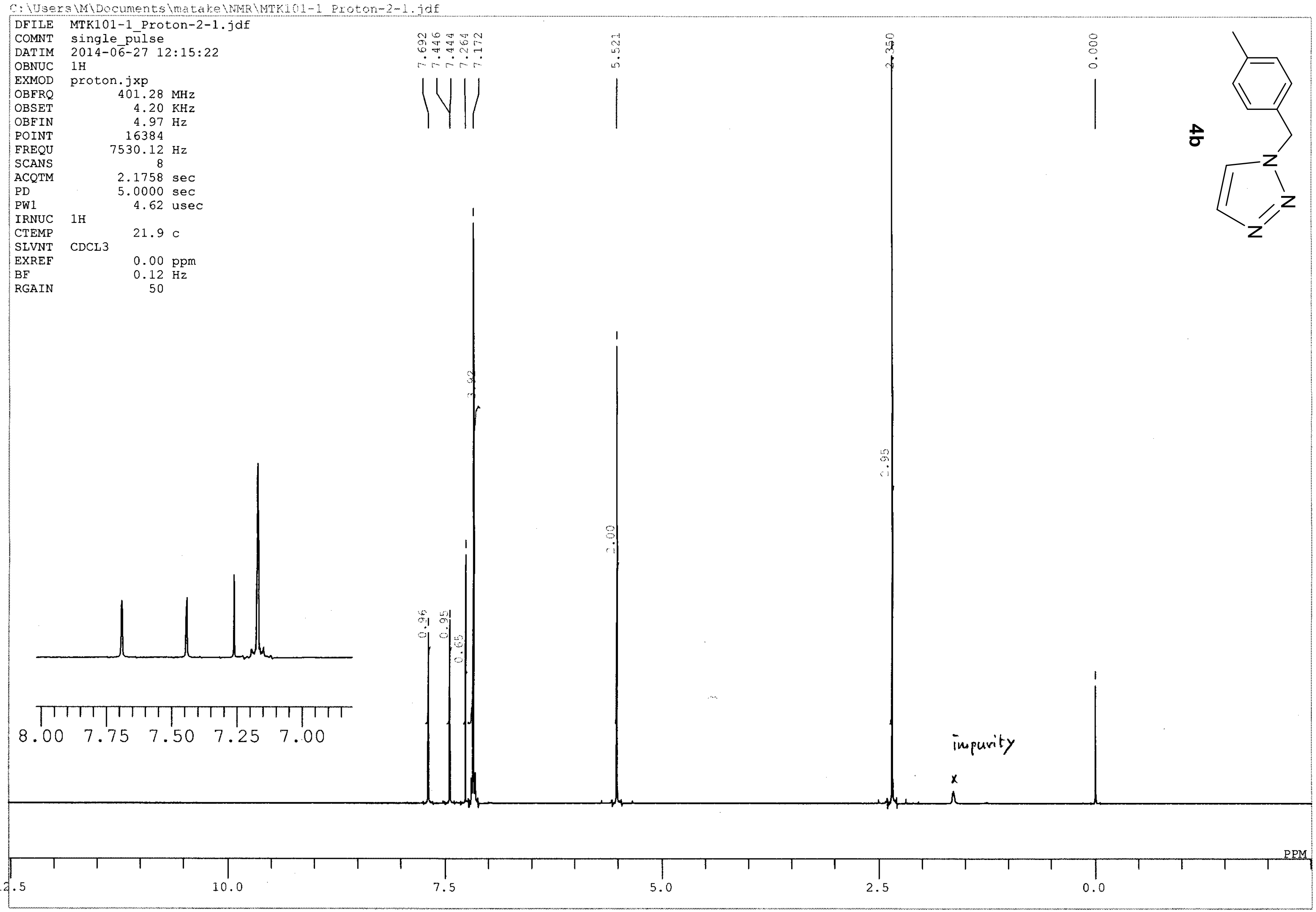

C:\Users\M\Documents\matake\NMR\MTK115-1_Carbon-1-1.jdf
DFILE MTK115-1_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-08-19 18:04:58
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
133.728
131.179
130.806
129.250
128.659
127.083
126.568
126.004
125.059
123.331
77.315
77.000
76.685
52.760
N3
3h
135
130
125
200
150
100
50
0
PPM

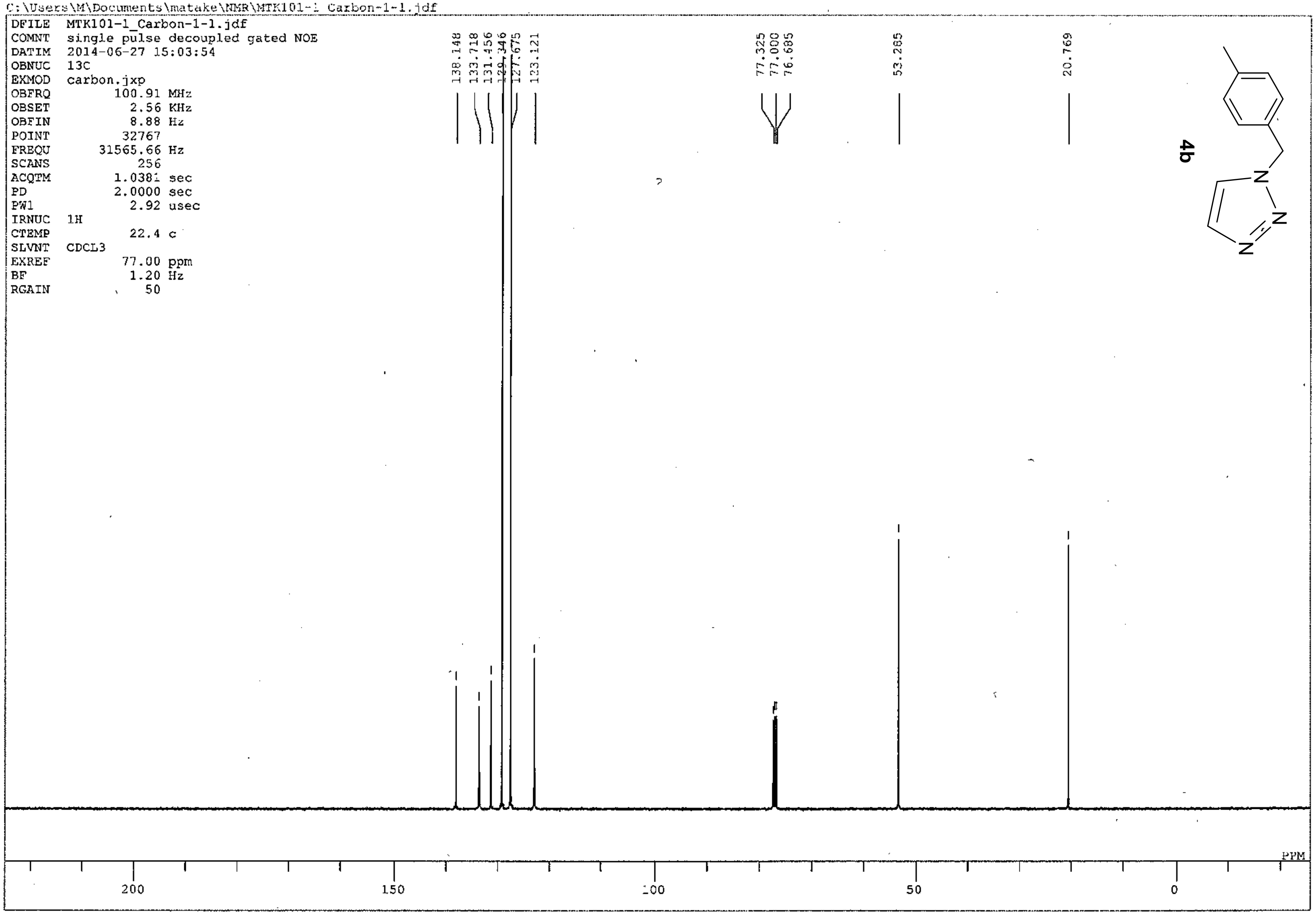


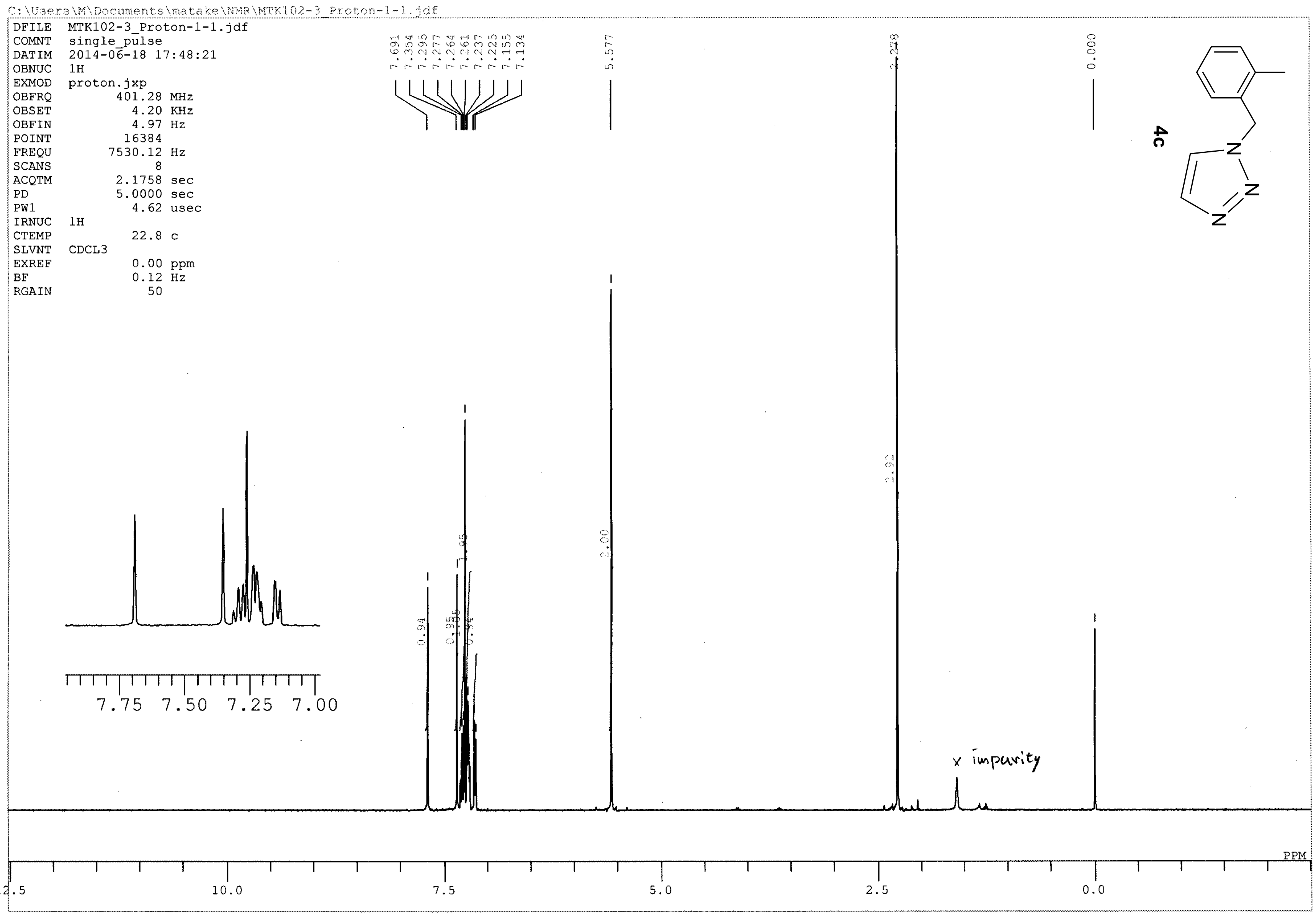
**4a**

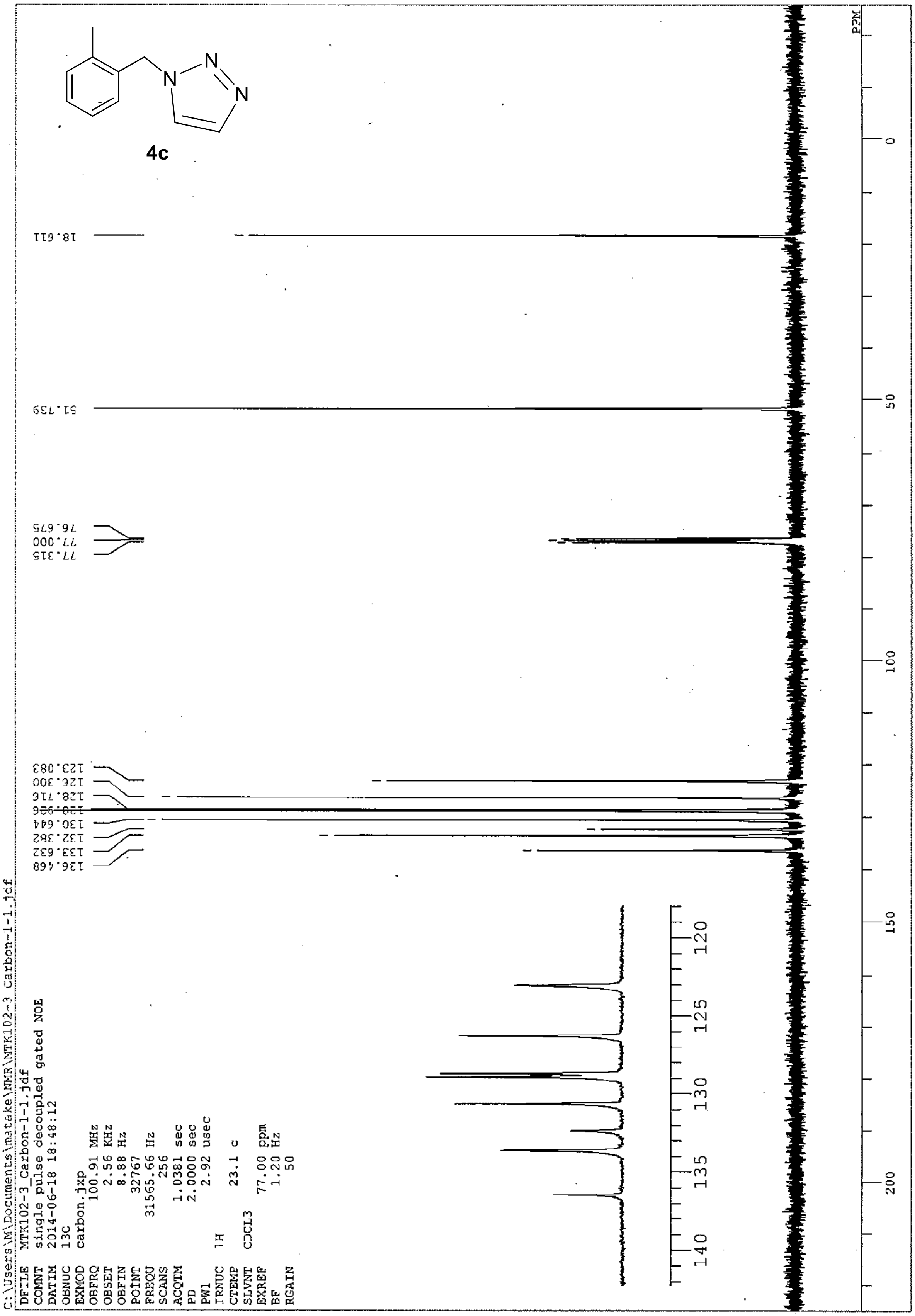

C:\Users\M\Documents\matake\NMR\MTK82-1_Proton-1-1.jdf
PPM
0.0
2.5
5.0
7.5
10.0
12.5
0.000
5.531
2.14
7.252
7.257
7.265
7.269
7.276
7.350
7.356
7.363
7.369
7.371
7.377
7.382
7.472
7.474
7.710
1.03
1.00
impurities

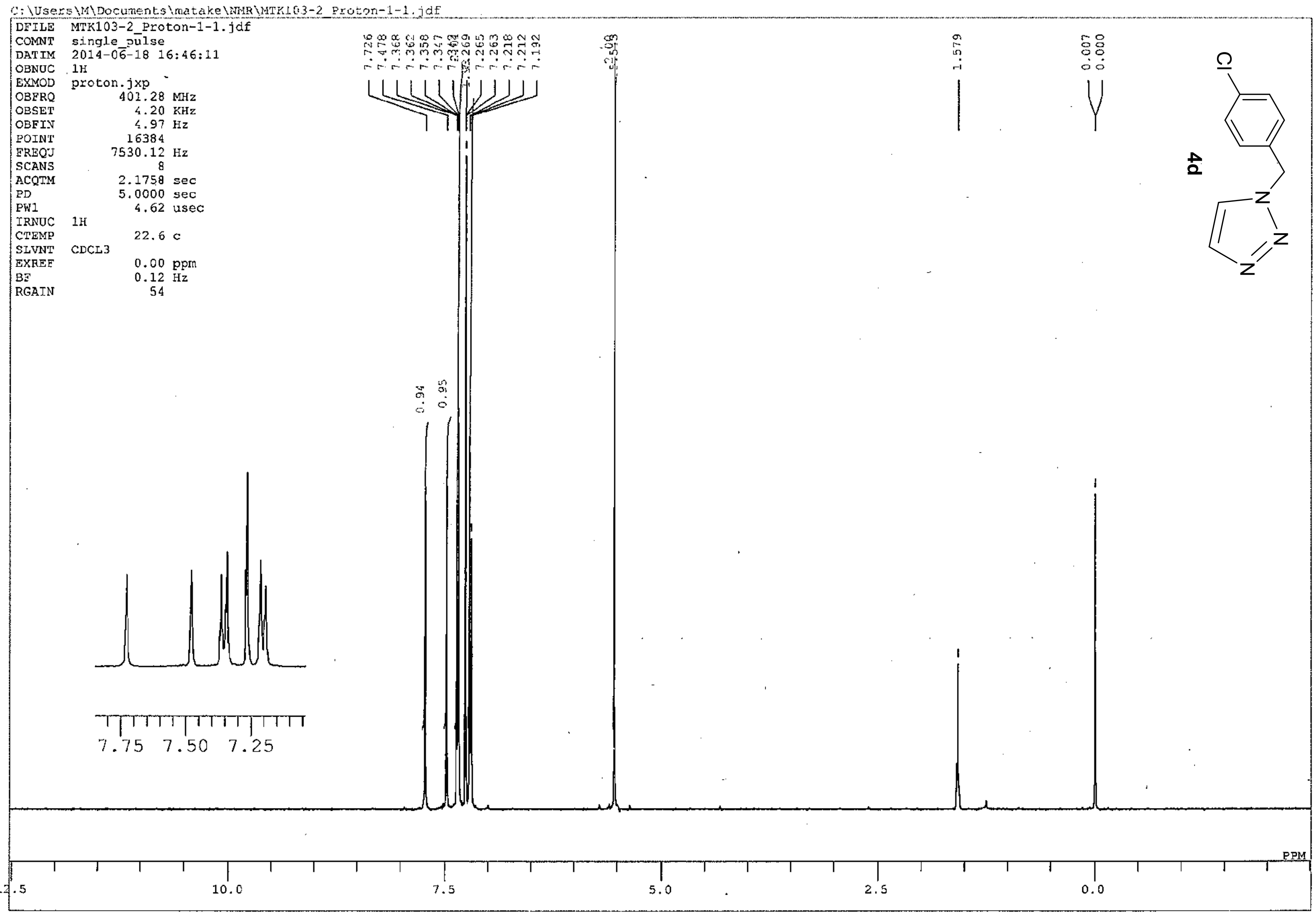

4a
53.944
76.675
77.000
77.200
77.315
123.255
127.981
128.706
129.088
134.234
134.663
PPM
0
50
100
150
200
C:\Users\M\Documents\matake\NMR\MTK82-2_Carbon-1-1.jdf

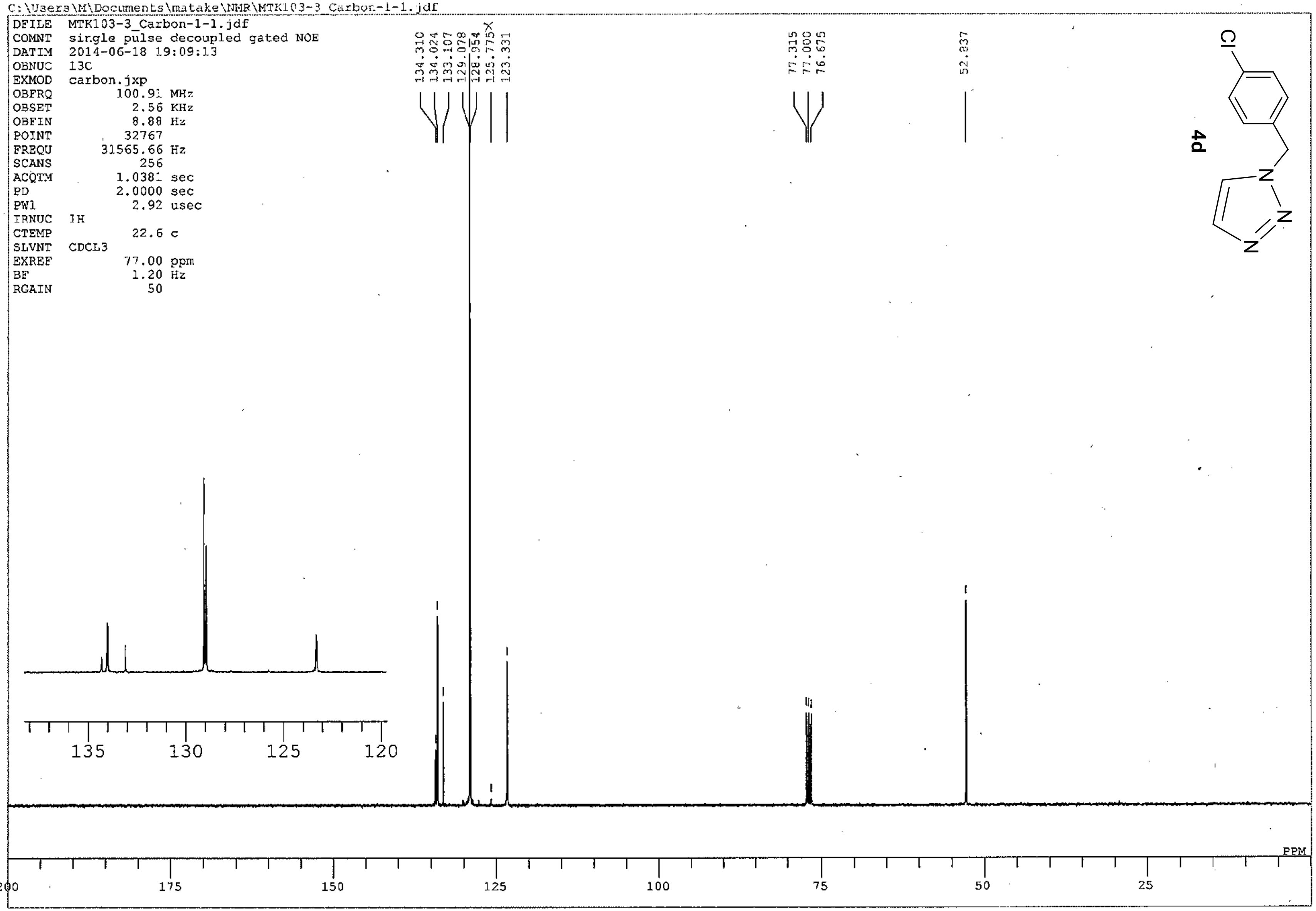

C:\Users\M\Documents\matake\NMR\MTK101-1_Proton-2-1.jdf
DFILE MTK101-1_Proton-2-1.jdf
COMNT single_pulse
DATIM 2014-06-27 12:15:22
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
7.692
7.446
7.444
7.264
7.172
5.521
2.350
0.000
4b
impurity
x
0.96
0.95
0.65
2.00
8.00 7.75 7.50 7.25 7.00
12.5
10.0
7.5
5.0
2.5
0.0
PPM


C:\Users\M\Documents\matake\NMR\MTK101-1_Carbon-1-1.jdf
DFILE MTK101-1_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-06-27 15:03:54
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
138.148
133.718
131.456
129.346
127.675
123.121
77.325
77.000
76.685
53.285
20.769
N
N
N
4b
PPM
200
150
100
50
0

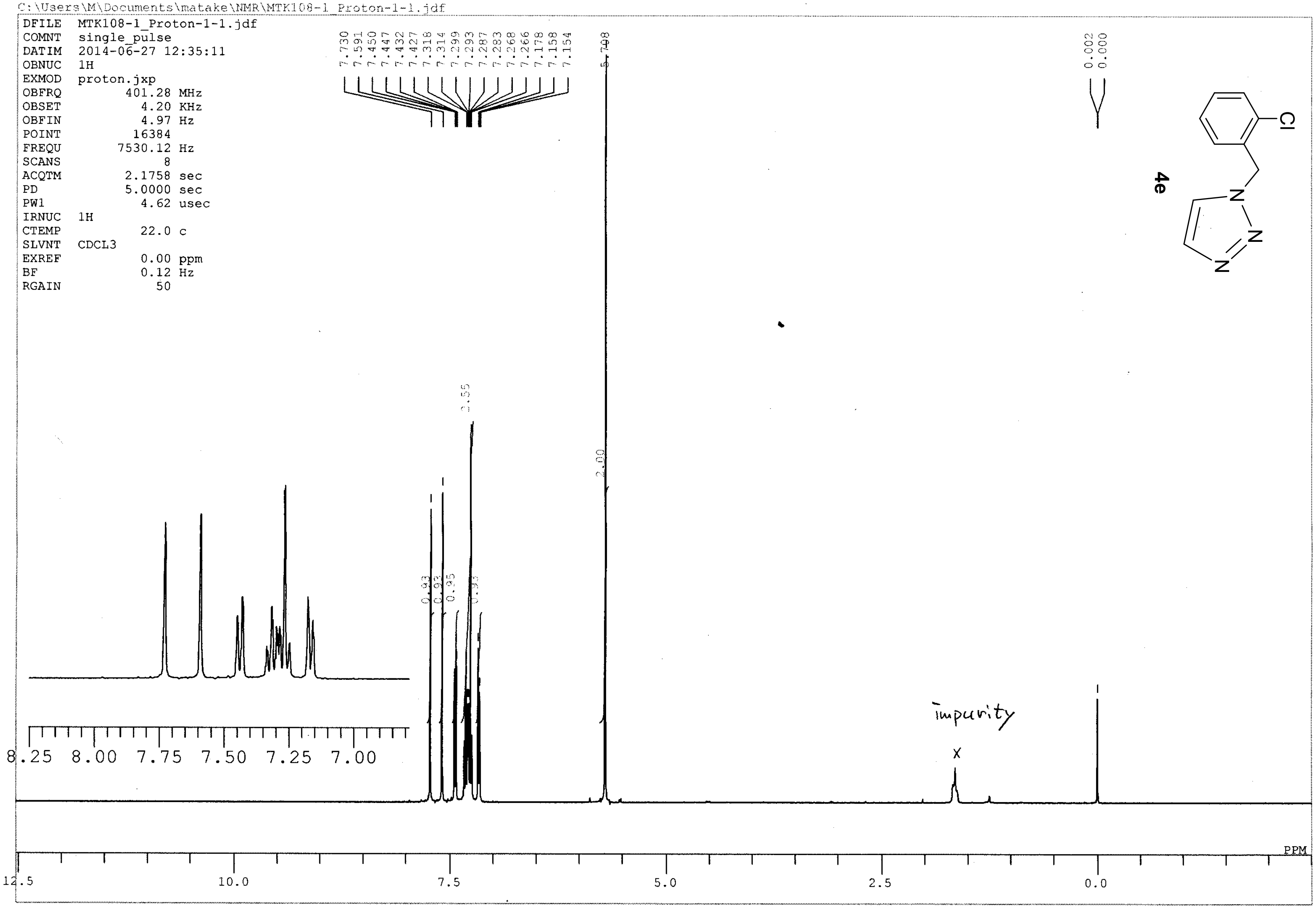

C:\Users\M\Documents\matake\NMR\MTK102-3_Proton-1-1.jdf
DFILE MTK102-3_Proton-1-1.jdf
COMNT single_pulse
DATIM 2014-06-18 17:48:21
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
7.691
7.354
7.295
7.277
7.264
7.261
7.237
7.225
7.155
7.134
5.577
2.278
0.000
4c
N
N
N
0.94
0.95
1.95
0.94
2.00
2.92
7.75 7.50 7.25 7.00
x impurity
PPM
12.5
10.0
7.5
5.0
2.5
0.0


4c
C:\Users\M\Documents\matake\NMR\MTK102-3 Carbon-1-1.jdf
DFILE MTK102-3_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-06-18 18:48:12
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
18.611
51.739
76.675
77.000
77.315
123.083
126.300
128.716
129.936
130.644
132.382
133.632
136.468
PPM
0
50
100
150
200
120
125
130
135
140

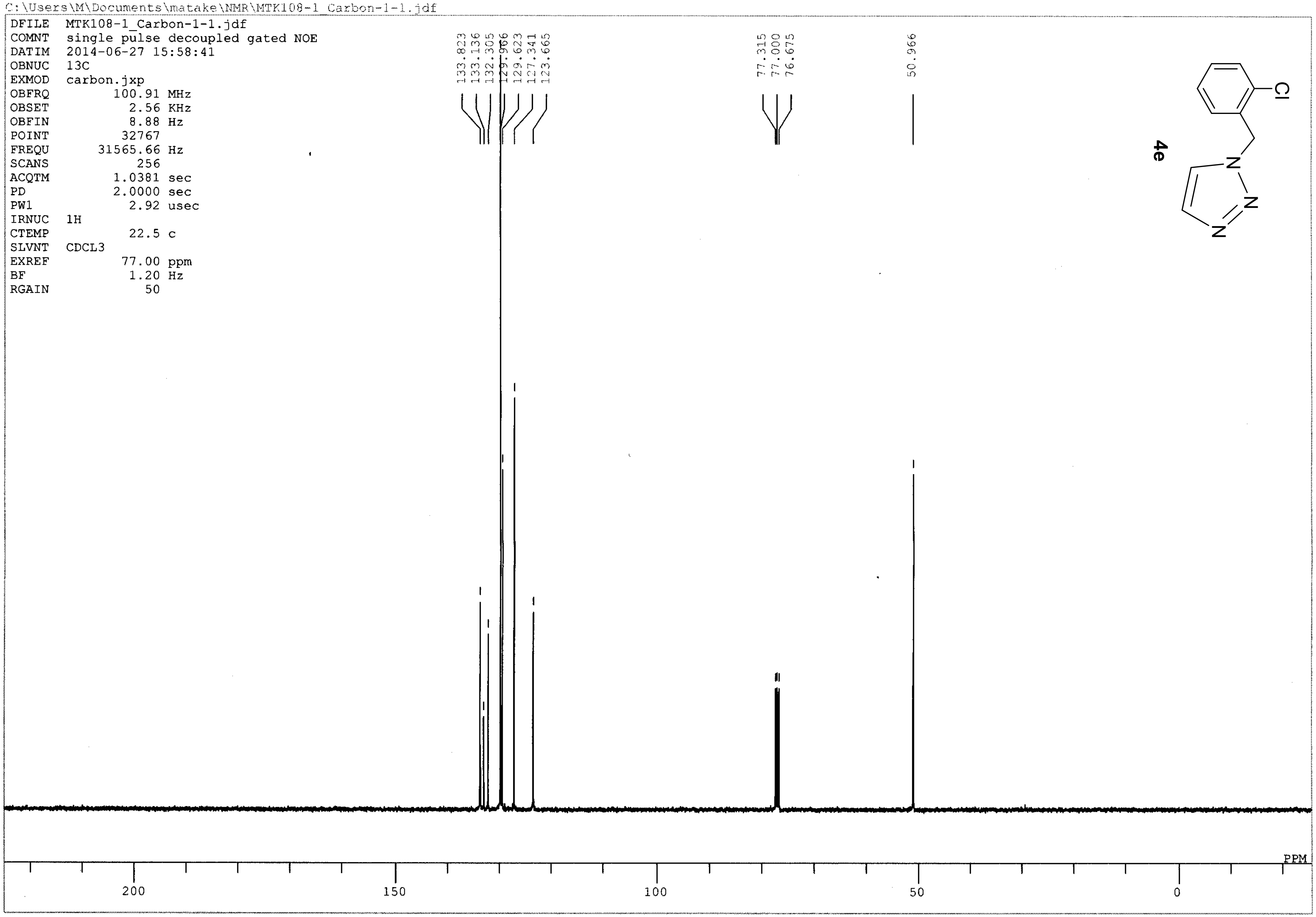

C:\Users\M\Documents\matake\NMR\MTK103-2_Proton-1-1.jdf
DFILE MTK103-2_Proton-1-1.jdf
COMNT single_pulse
DATIM 2014-06-18 16:46:11
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 54
7.726
7.478
7.368
7.362
7.358
7.347
7.269
7.265
7.263
7.218
7.212
7.192
1.579
0.007
0.000
0.94
0.95
2.00
Cl
N
N
N
4d
7.75 7.50 7.25
PPM
12.5
10.0
7.5
5.0
2.5
0.0

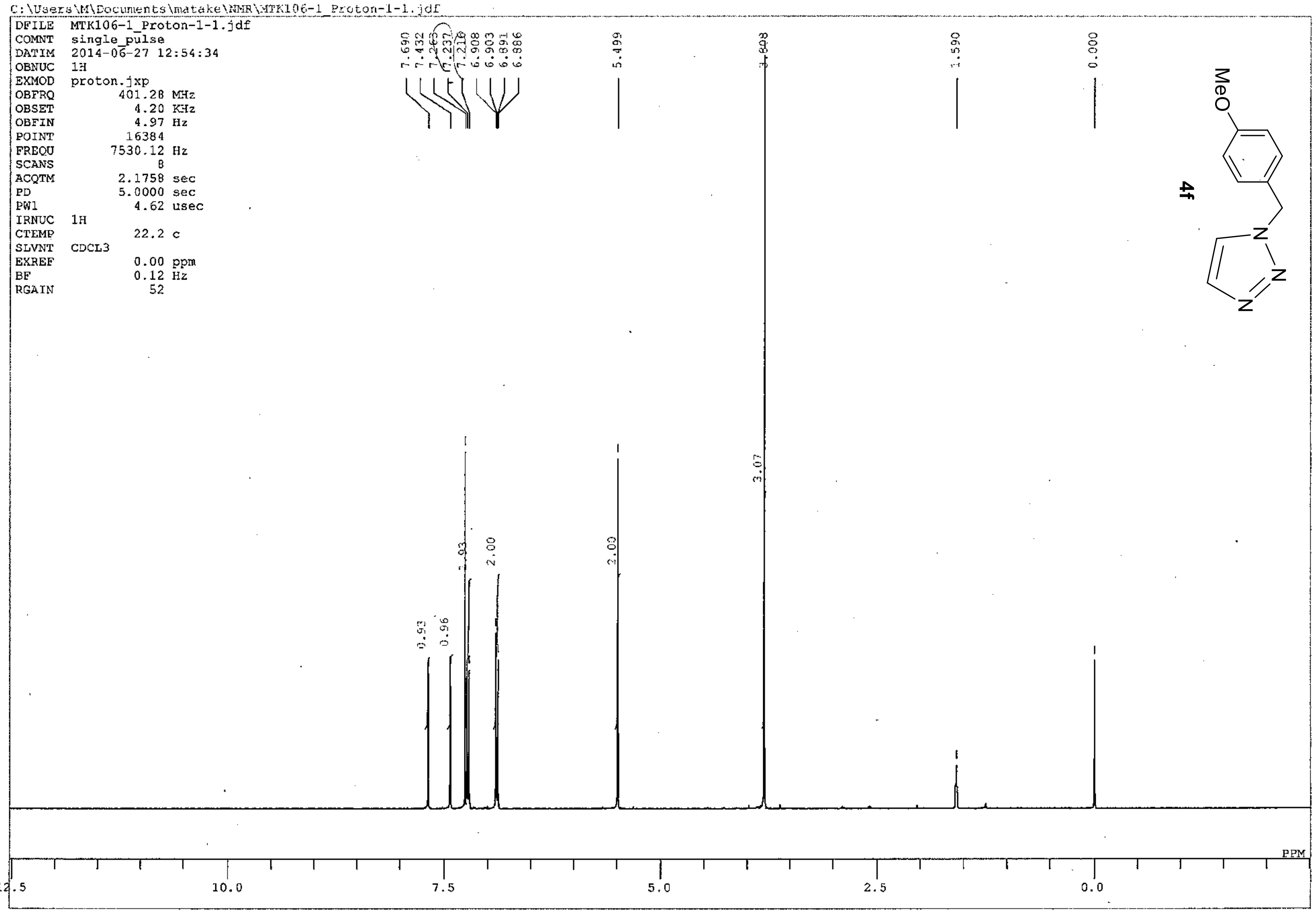

C:\Users\M\Documents\matake\NMR\MTK103-3_Carbon-1-1.jdf
DFILE MTK103-3_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-06-18 19:09:13
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
134.310
134.024
133.107
129.078
128.954
125.775
123.331
77.315
77.000
76.675
52.837
Cl
N
N
N
4d
135
130
125
120
PPM
200
175
150
125
100
75
50
25

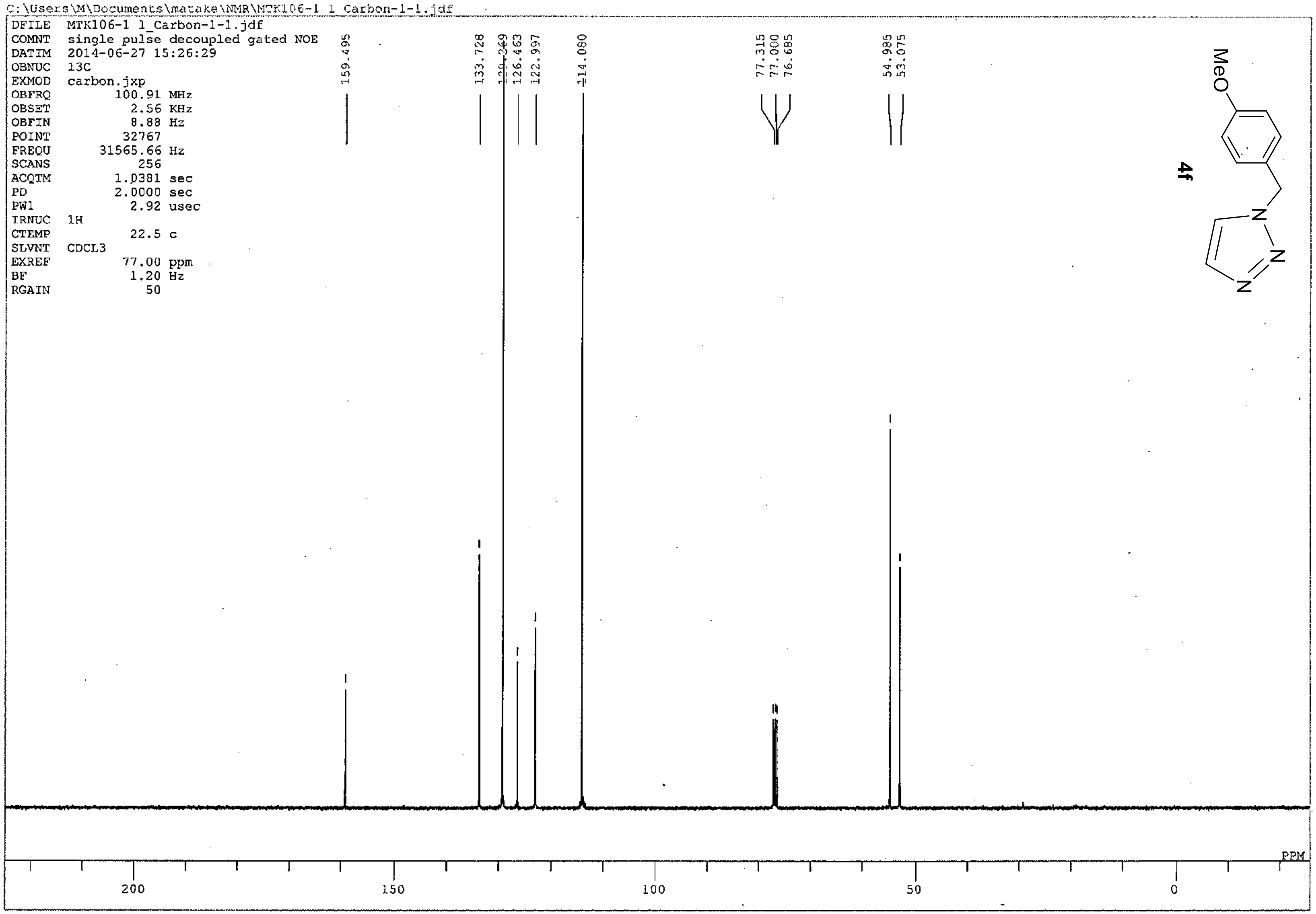
C:\Users\M\Documents\matake\NMR\MTK108-1_Proton-1-1.jdf

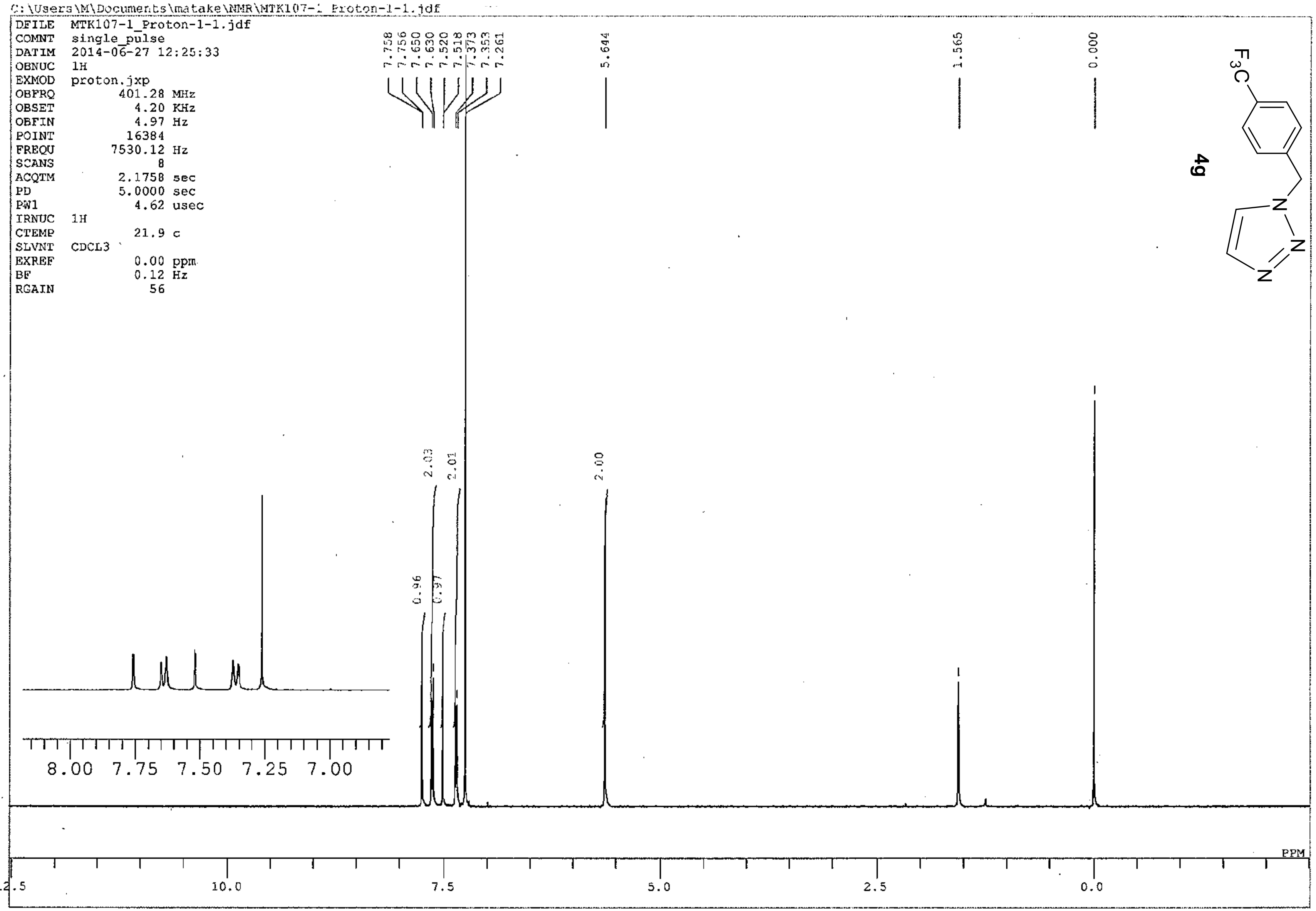


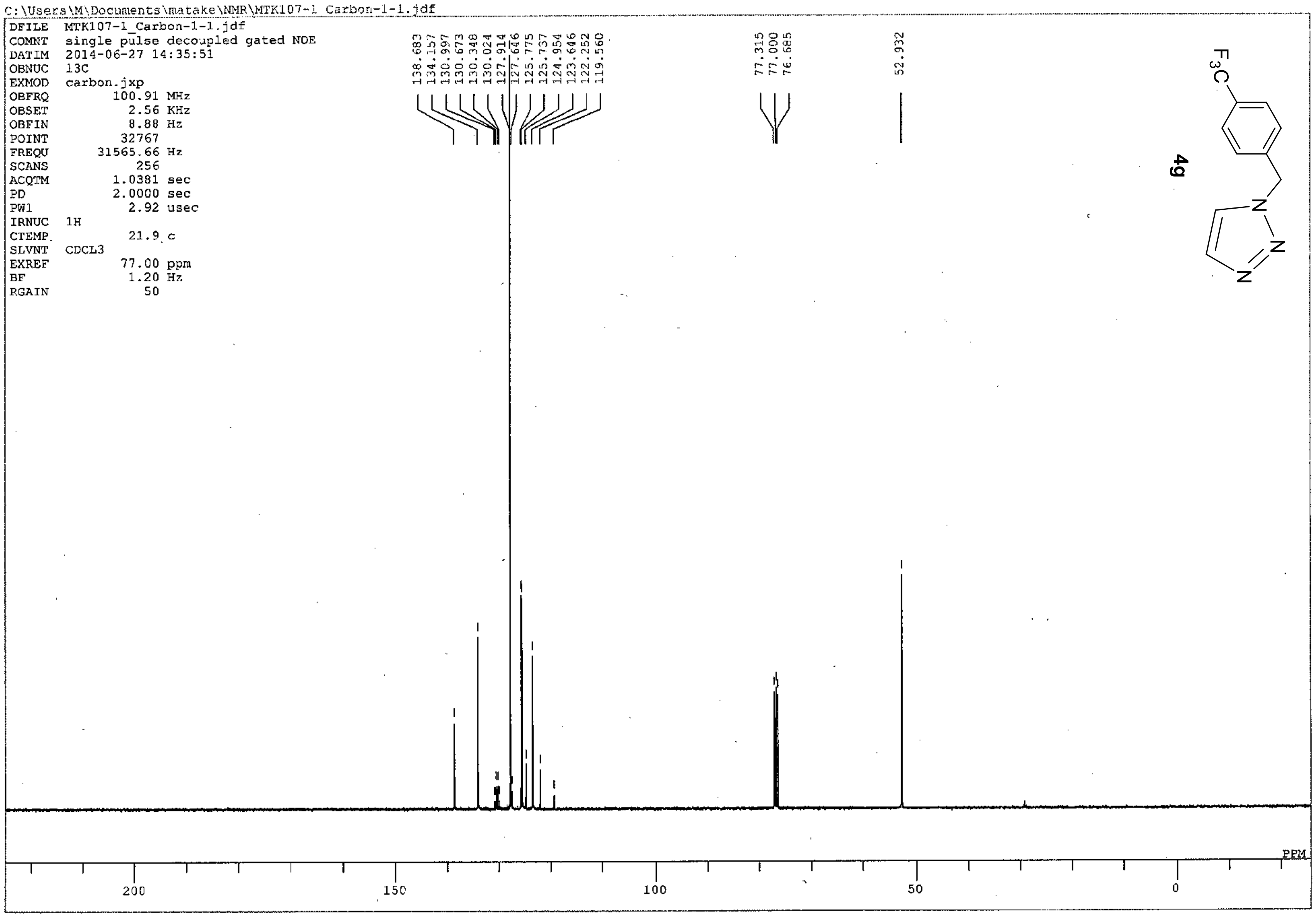

**4e**

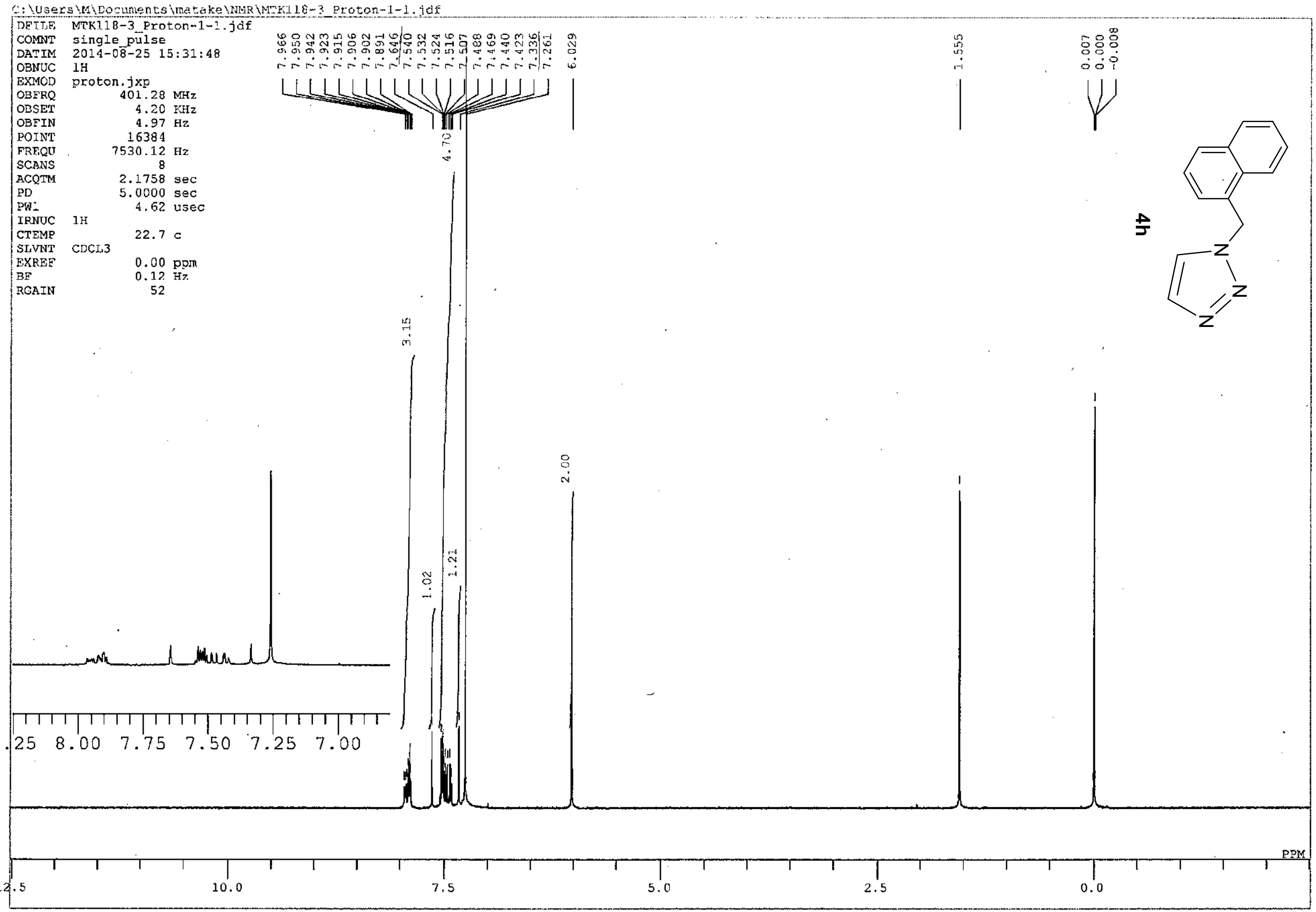

C:\Users\M\Documents\matake\NMR\MTK108-1_Carbon-1-1.jdf
DFILE MTK108-1_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-06-27 15:58:41
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 22.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
133.823
133.136
132.305
129.966
129.623
127.341
123.665
77.315
77.000
76.675
50.966
Cl
N
N
N
4e
200
150
100
50
0
PPM


C:\Users\M\Documents\matake\NMR\MTK106-1_Proton-1-1.jdf
DFILE MTK106-1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2014-06-27 12:54:34
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 52
7.690
7.432
7.263
7.237
7.216
6.908
6.903
6.891
6.886
5.499
3.808
1.590
0.000
MeO
N
N
N
4f
0.93
0.96
1.93
2.00
2.00
3.07
PPM
12.5
10.0
7.5
5.0
2.5
0.0

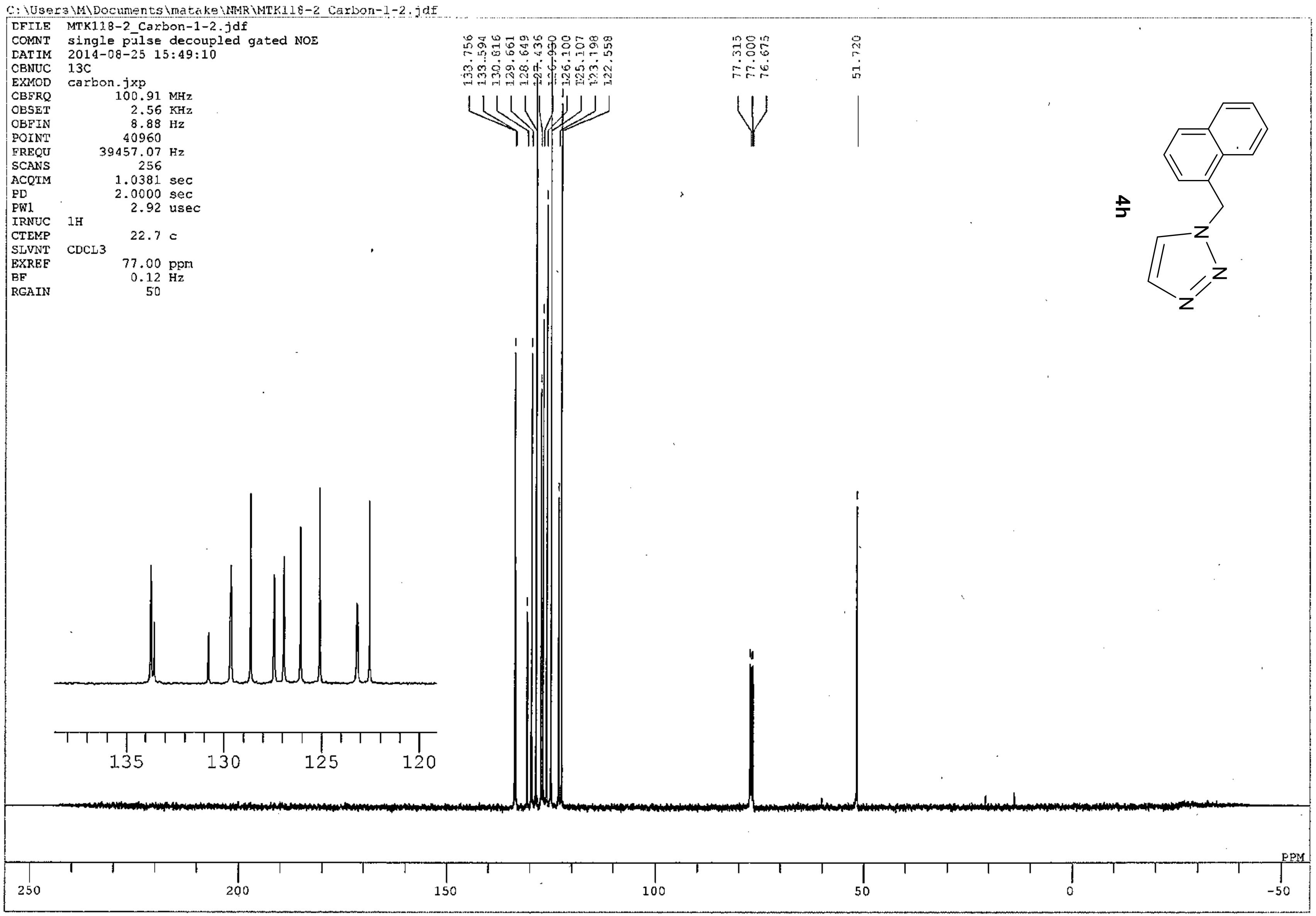

C:\Users\M\Documents\matake\NMR\MTK106-1 1 Carbon-1-1.jdf
DFILE MTK106-1 1_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-06-27 15:26:29
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 22.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
159.495
133.728
129.269
126.463
122.997
114.080
77.315
77.000
76.685
54.985
53.075
MeO
N
N
N
4f
PPM
200
150
100
50
0

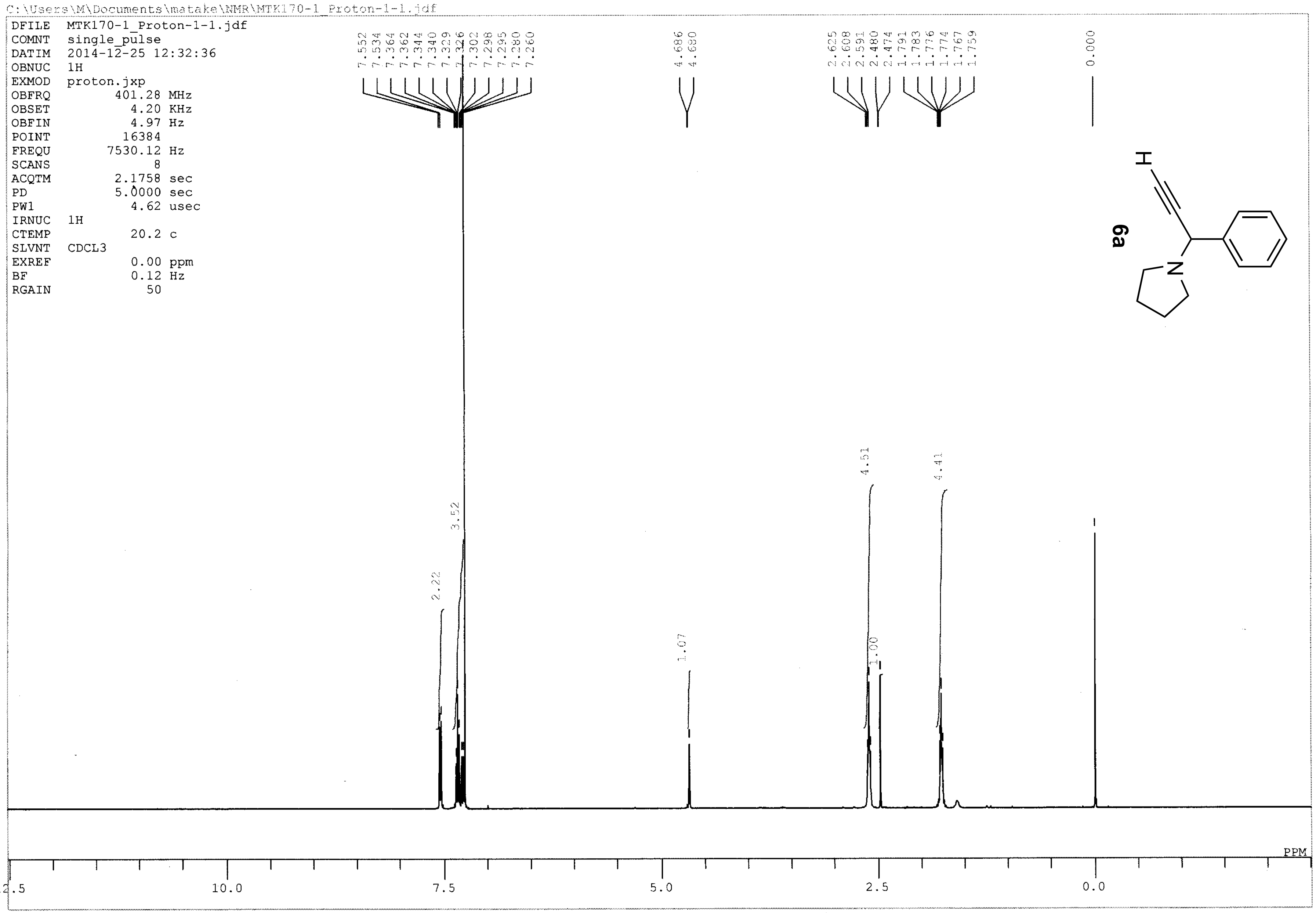

C:\Users\M\Documents\matake\NMR\MTK107-1_Proton-1-1.jdf
DFILE MTK107-1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2014-06-27 12:25:33
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 56
7.758
7.756
7.650
7.630
7.520
7.518
7.373
7.353
7.261
5.644
1.565
0.000
F3C
N
N
N
4g
0.96
2.03
0.97
2.01
2.00
8.00 7.75 7.50 7.25 7.00
PPM
12.5
10.0
7.5
5.0
2.5
0.0

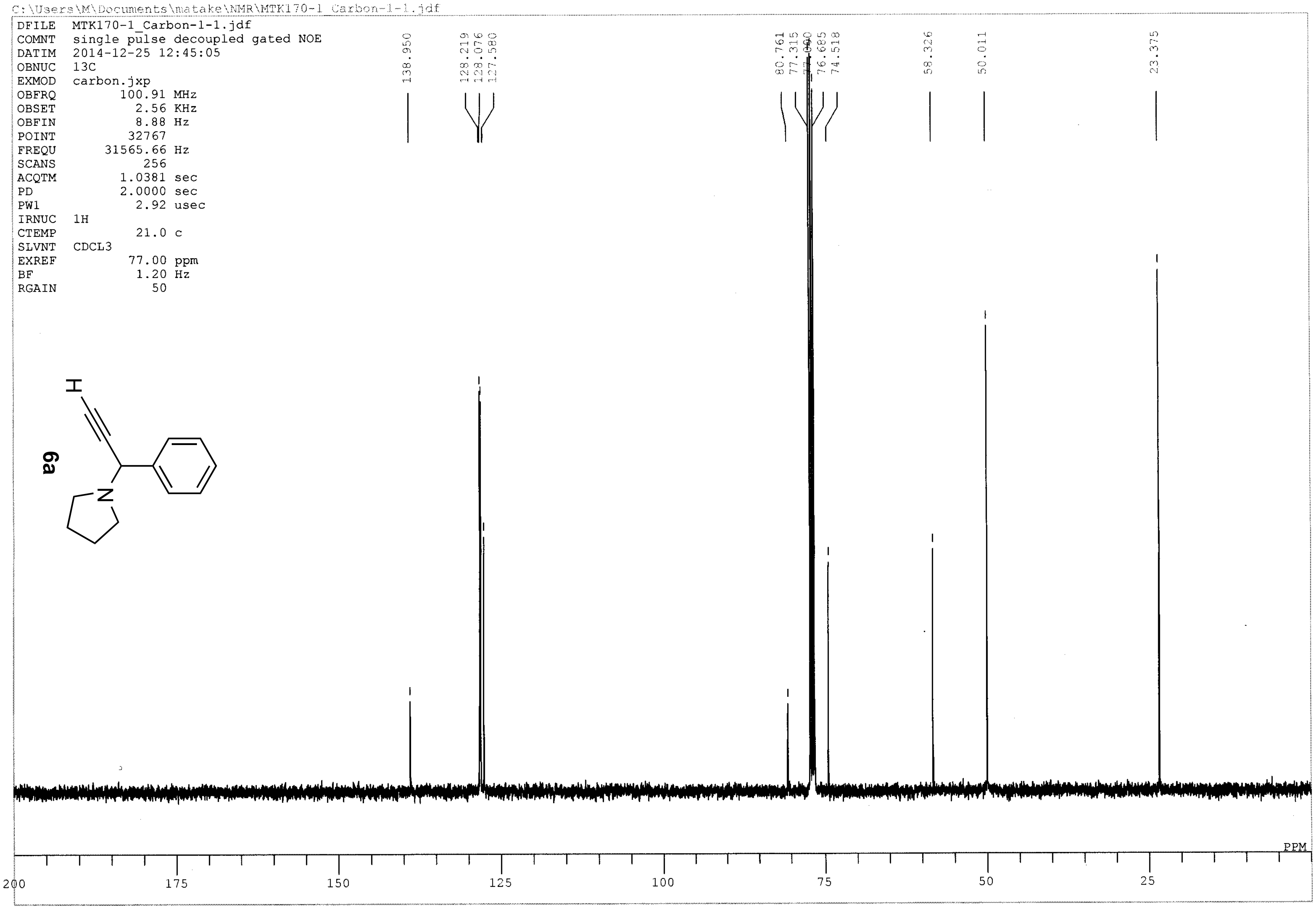

C:\Users\M\Documents\matake\NMR\MTK107-1 Carbon-1-1.jdf
DFILE MTK107-1_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-06-27 14:35:51
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
138.683
134.157
130.997
130.673
130.348
130.024
127.914
127.646
125.775
125.737
124.954
123.646
122.252
119.560
77.315
77.000
76.685
52.932
F3C
N
N
N
4g
200
150
100
50
0
PPM

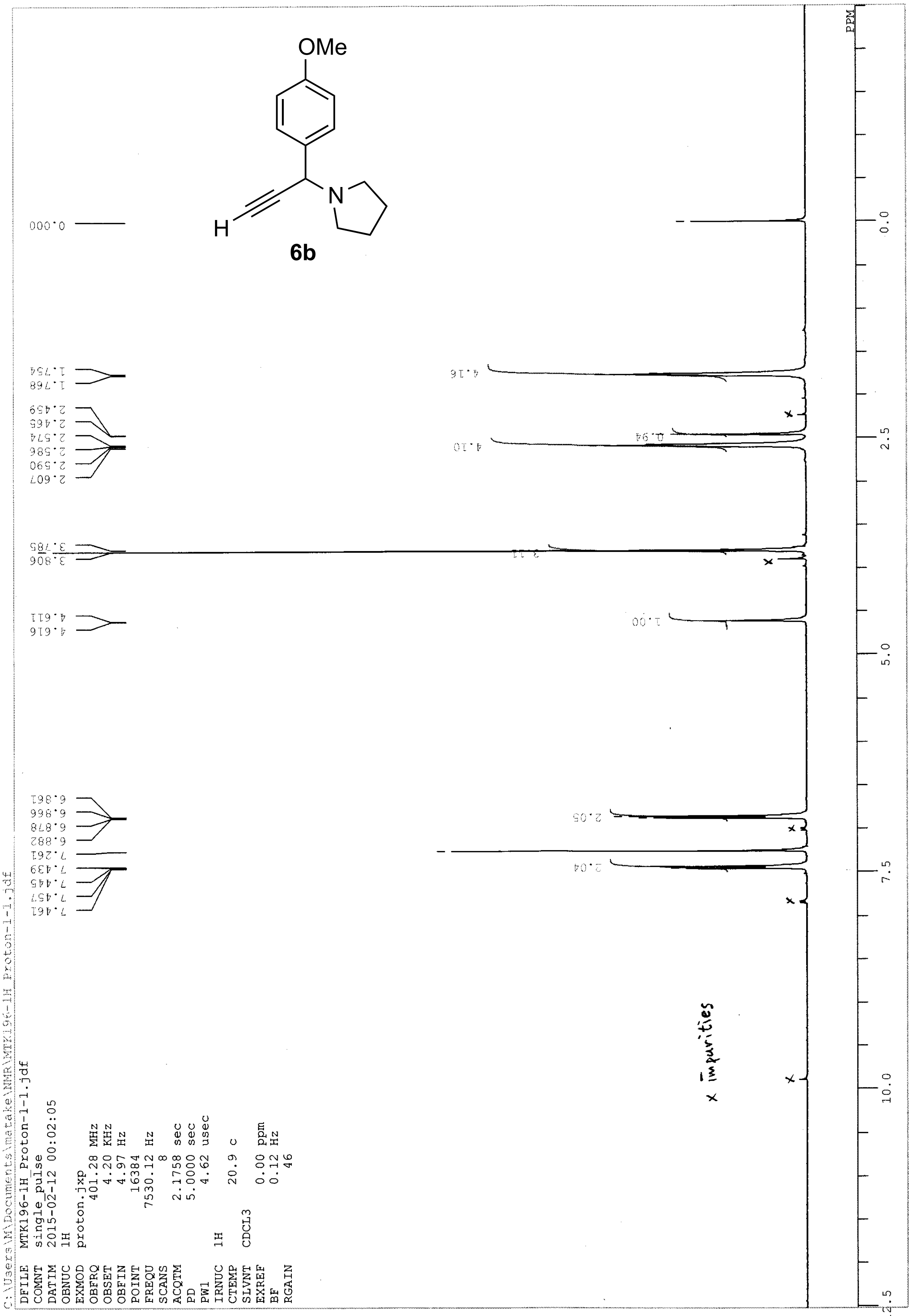


C:\Users\M\Documents\matake\NMR\MTK118-3_Proton-1-1.jdf
DFILE MTK118-3_Proton-1-1.jdf
COMNT single_pulse
DATIM 2014-08-25 15:31:48
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 52
7.966 7.950 7.942 7.923 7.915 7.906 7.902 7.891 7.646 7.540 7.532 7.524 7.516 7.507 7.488 7.469 7.440 7.423 7.336 7.261
6.029
1.555
0.007 0.000 -0.008
4h
3.15
4.70
1.02
1.21
2.00
8.25 8.00 7.75 7.50 7.25 7.00
12.5 10.0 7.5 5.0 2.5 0.0
PPM

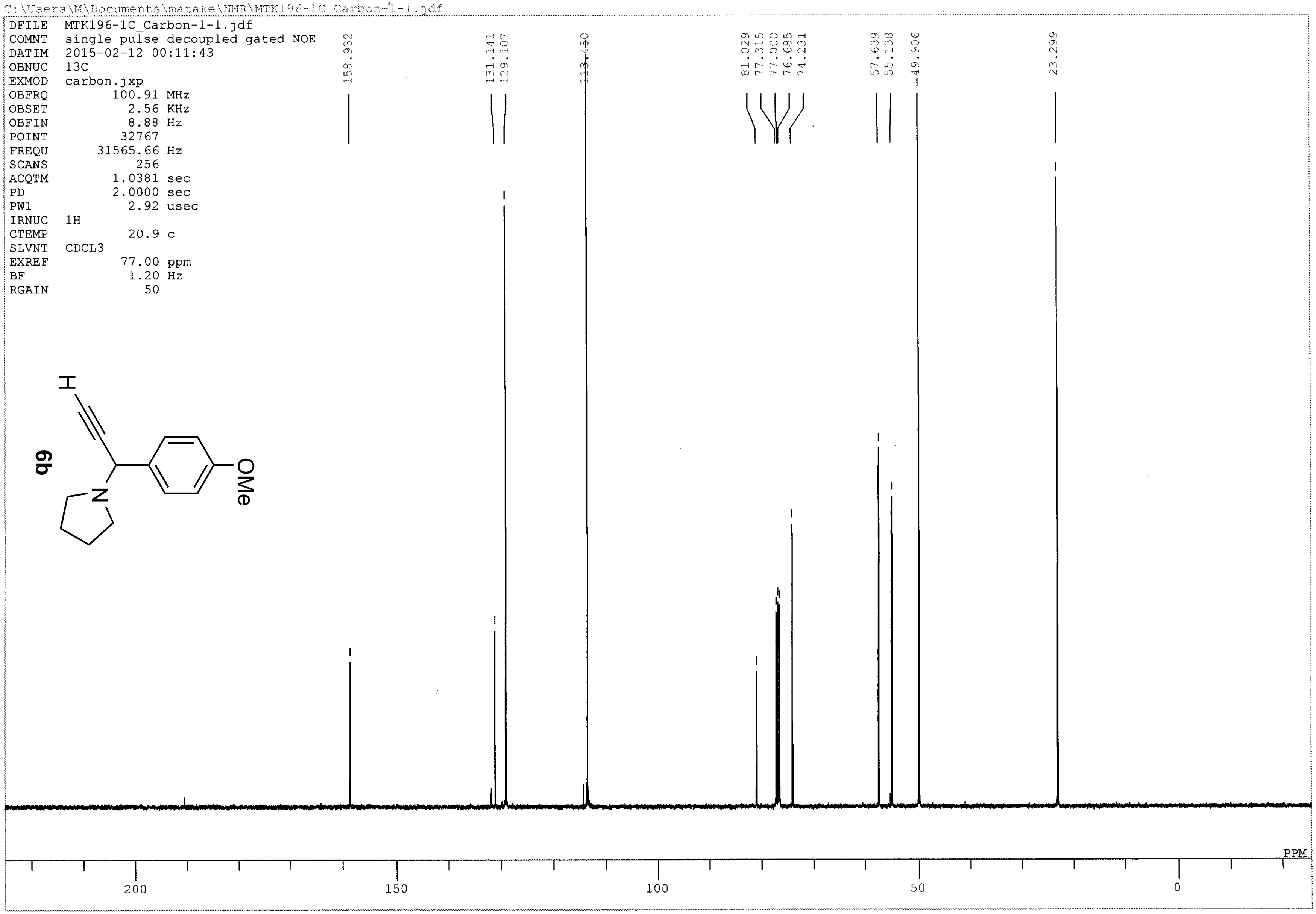

C:\Users\M\Documents\matake\NMR\MTK118-2_Carbon-1-2.jdf
DFILE MTK118-2_Carbon-1-2.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-08-25 15:49:10
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 40960
FREQU 39457.07 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50
133.756
133.594
130.816
129.661
128.649
127.436
126.930
126.100
125.107
123.198
122.558
77.315
77.000
76.675
51.720
4h
N
N
N
135
130
125
120
PPM
250
200
150
100
50
0
-50


C:\Users\M\Documents\matake\NMR\MTK170-1_Proton-1-1.jdf
DFILE MTK170-1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2014-12-25 12:32:36
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
7.552
7.534
7.364
7.362
7.344
7.340
7.329
7.326
7.302
7.298
7.295
7.280
7.260
4.686
4.680
2.625
2.608
2.591
2.480
2.474
1.791
1.783
1.776
1.774
1.767
1.759
0.000
H
N
6a
2.22
3.52
1.07
1.00
4.51
4.41
PPM
12.5
10.0
7.5
5.0
2.5
0.0


C:\Users\M\Documents\matake\NMR\MTK170-1_Carbon-1-1.jdf
DFILE MTK170-1_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2014-12-25 12:45:05
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
138.950
128.219
128.076
127.580
80.761
77.315
76.685
74.518
58.326
50.011
23.375
H
N
6a
200
175
150
125
100
75
50
25
PPM

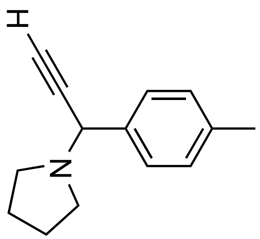


OMe
N
H
6b
C:\Users\M\Documents\matake\NMR\MTK196-1H_Proton-1-1.jdf
DFILE MTK196-1H_Proton-1-1.jdf
COMNT single_pulse
DATIM 2015-02-12 00:02:05
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46
0.000
1.754
1.768
2.459
2.465
2.574
2.586
2.590
2.607
3.785
3.806
4.611
4.616
6.861
6.866
6.878
6.882
7.261
7.439
7.445
7.457
7.461
4.16
4.10
0.94
3.11
1.00
2.05
2.04
x impurities
PPM
0.0
2.5
5.0
7.5
10.0
12.5

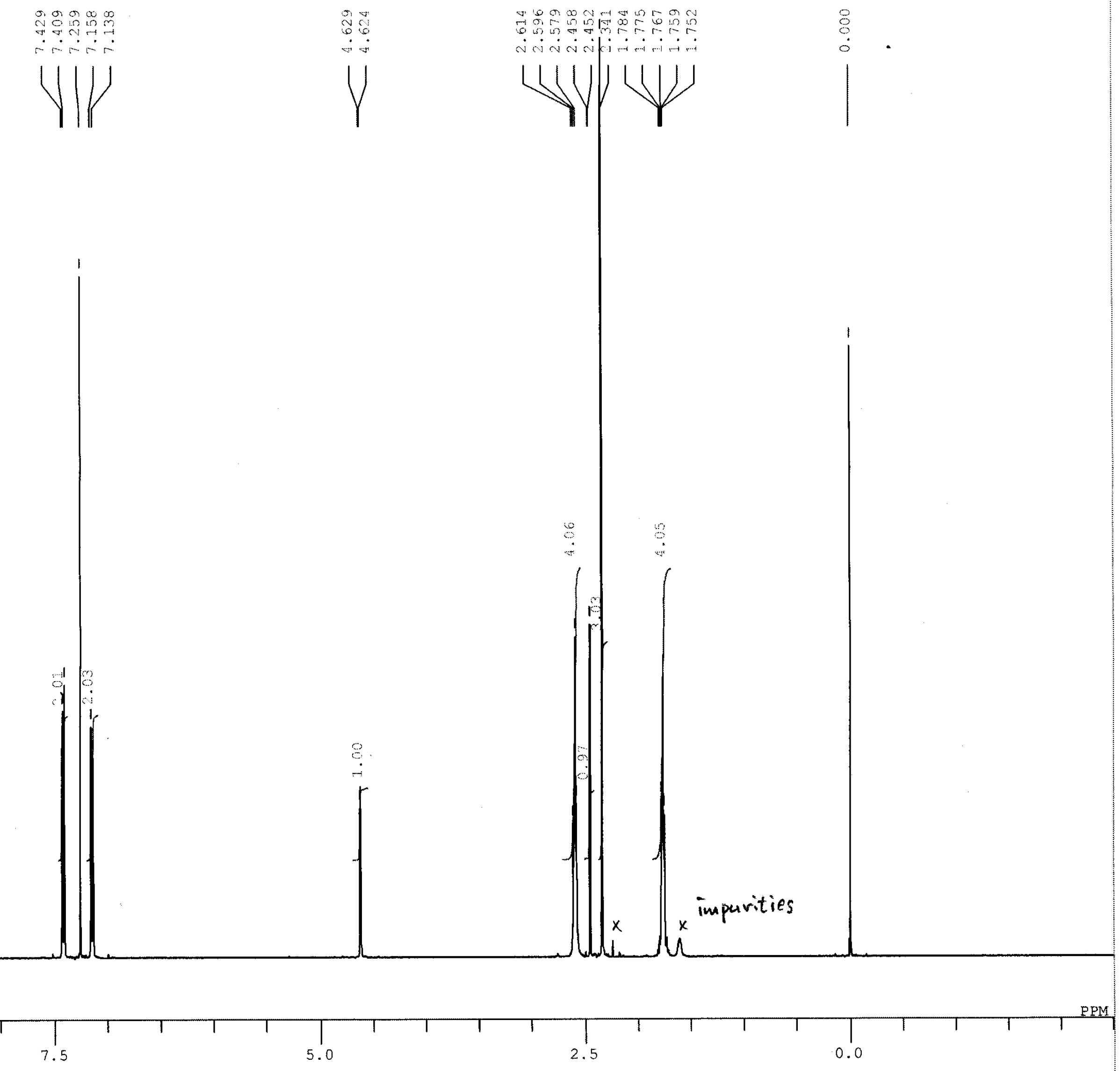

C:\Users\M\Documents\matake\NMR\MTK196-1C_Carbon-1-1.jdf
DFILE MTK196-1C_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2015-02-12 00:11:43
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
158.932
131.141
129.107
113.450
81.029
77.315
77.000
76.685
74.231
57.639
55.138
49.906
23.299
OMe
N
H
6b
PPM
200
150
100
50
0

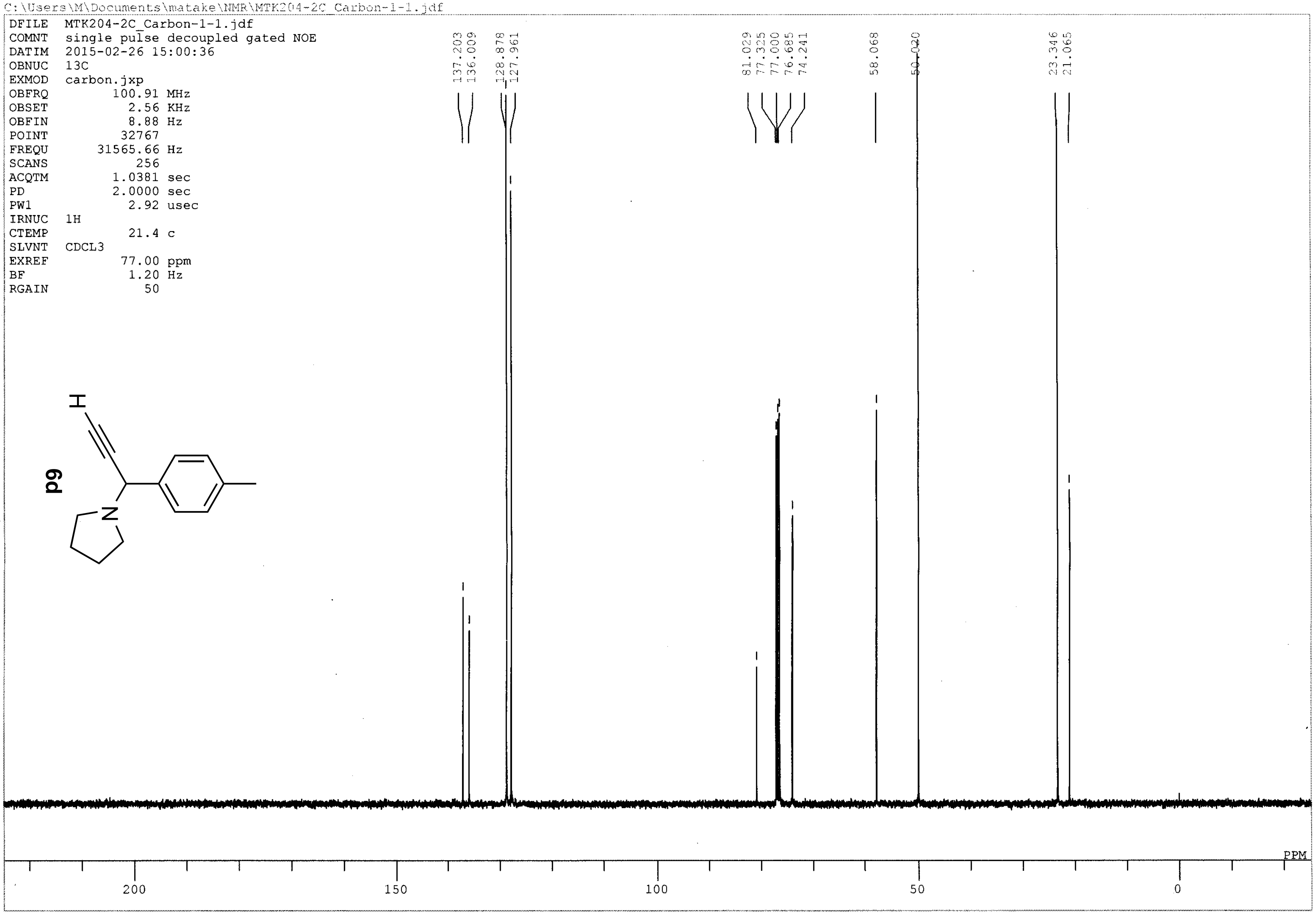
C:\Users\M\Documents\matake\NMR\MTK204-2H_Proton-1-1.jdf

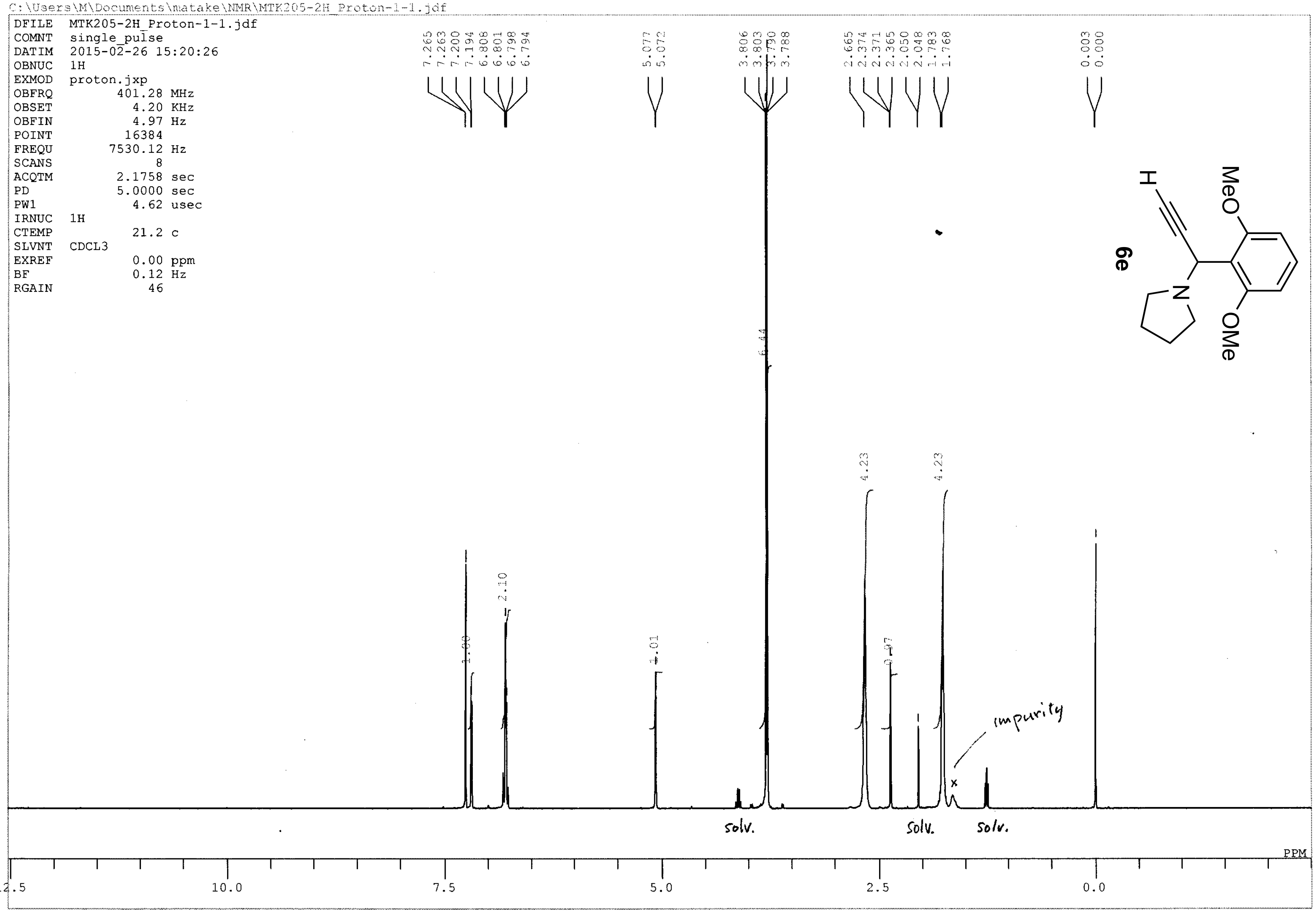
```
DFILE   MTK204-2H_Proton-1-1.jdf
COMNT   single_pulse
DATIM   2015-02-26 15:49:38
OBNUC   1H
EXMOD   proton.jxp
OBFRQ        401.28 MHz
OBSET          4.20 KHz
OBFIN          4.97 Hz
POINT         16384
FREQU       7530.12 Hz
SCANS             8
ACQTM        2.1758 sec
PD           5.0000 sec
PW1            4.62 usec
IRNUC   1H
CTEMP          21.1 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            48
```



**6d**

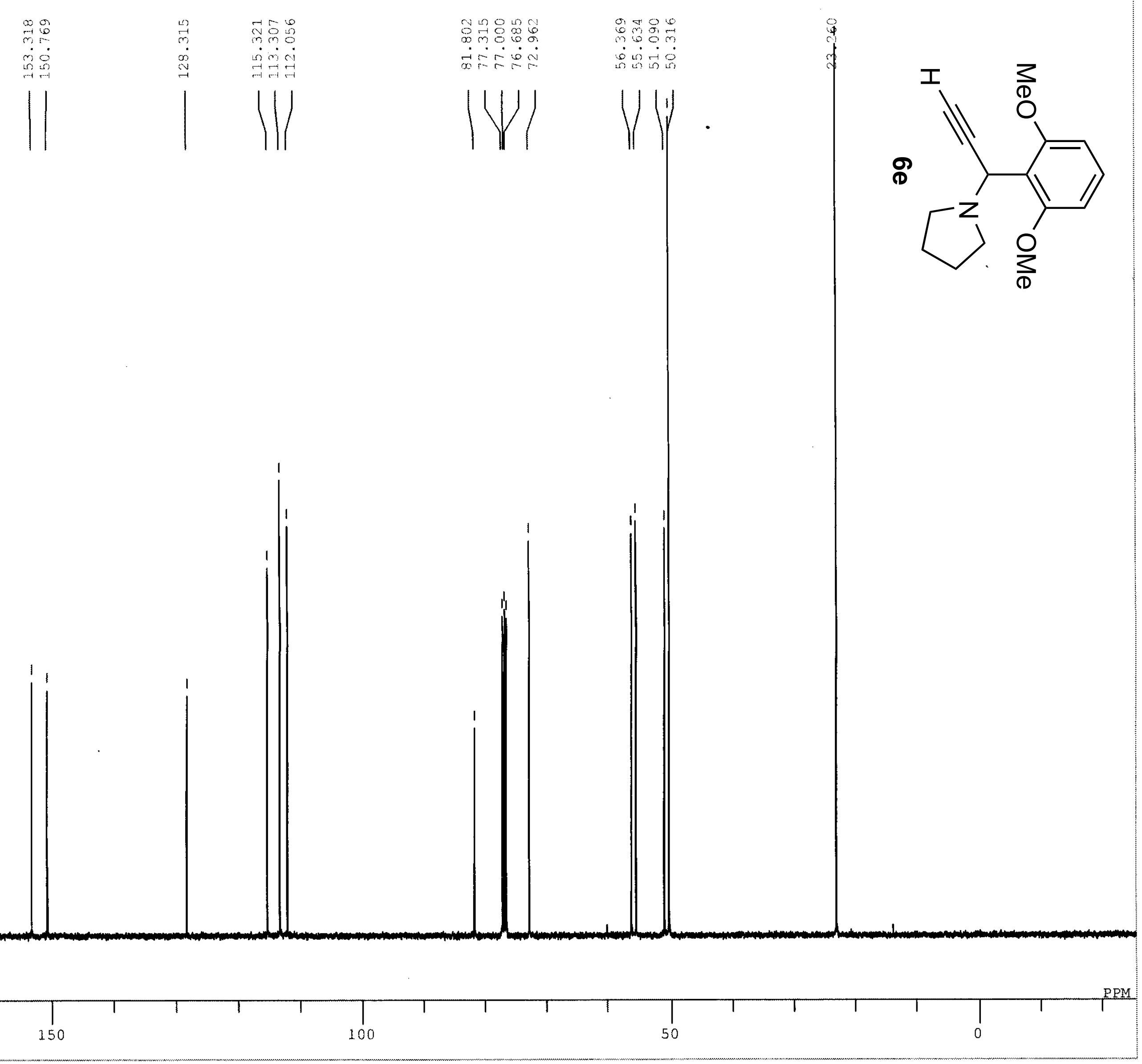



C:\Users\M\Documents\matake\NMR\MTK204-2C_Carbon-1-1.jdf
DFILE MTK204-2C_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2015-02-26 15:00:36
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
137.203
136.009
128.878
127.961
81.029
77.325
77.000
76.685
74.241
58.068
50.020
23.346
21.065
H
N
6d
200
150
100
50
0
PPM

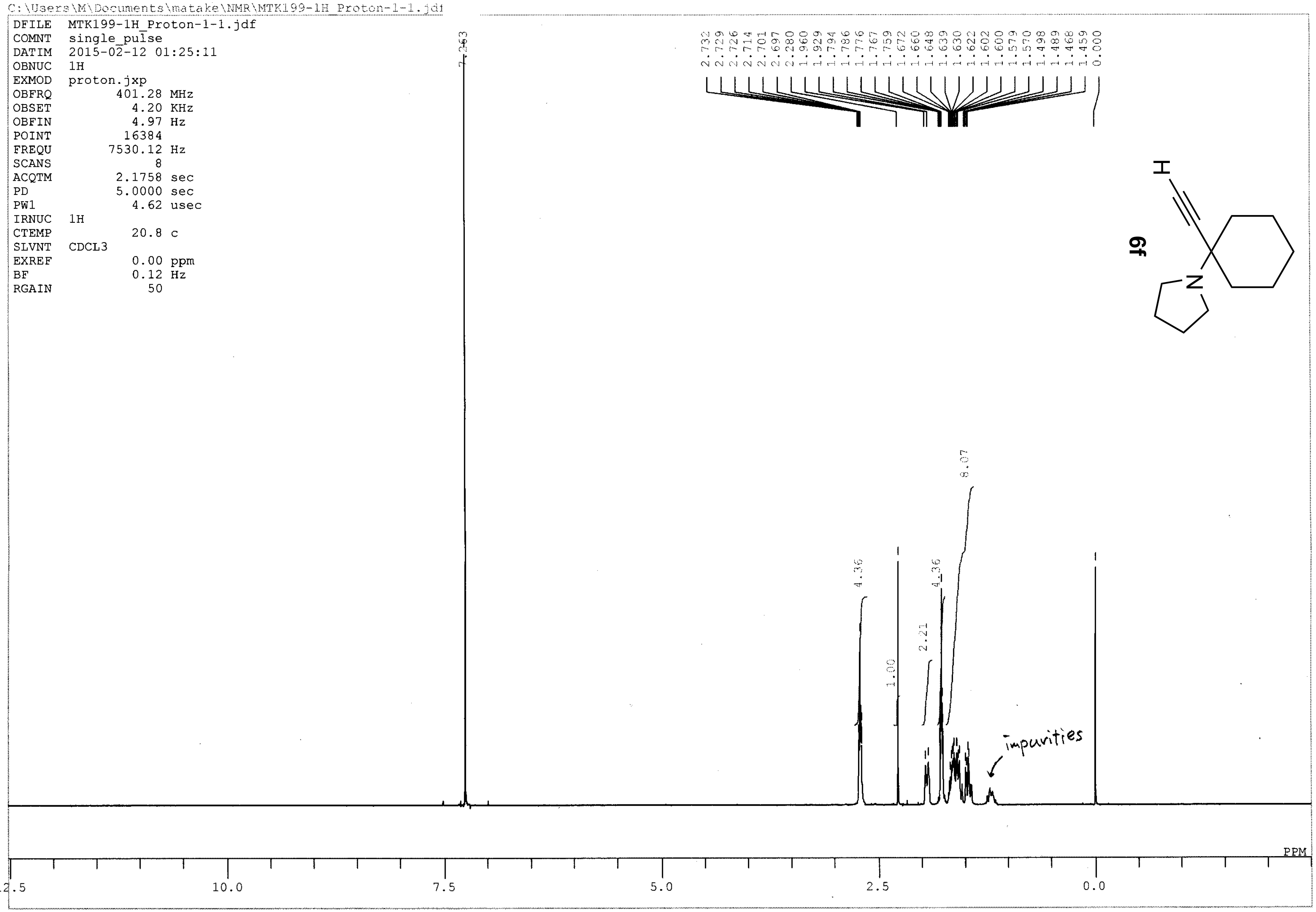

C:\Users\M\Documents\matake\NMR\MTK205-2H_Proton-1-1.jdf
DFILE MTK205-2H_Proton-1-1.jdf
COMNT single_pulse
DATIM 2015-02-26 15:20:26
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46
7.265
7.263
7.200
7.194
6.808
6.801
6.798
6.794
5.077
5.072
3.806
3.803
3.790
3.788
2.665
2.374
2.371
2.365
2.050
2.048
1.783
1.768
0.003
0.000
MeO
OMe
N
H
6e
6.44
4.23
4.23
2.10
1.00
1.01
0.97
impurity
solv.
solv.
solv.
PPM
12.5
10.0
7.5
5.0
2.5
0.0

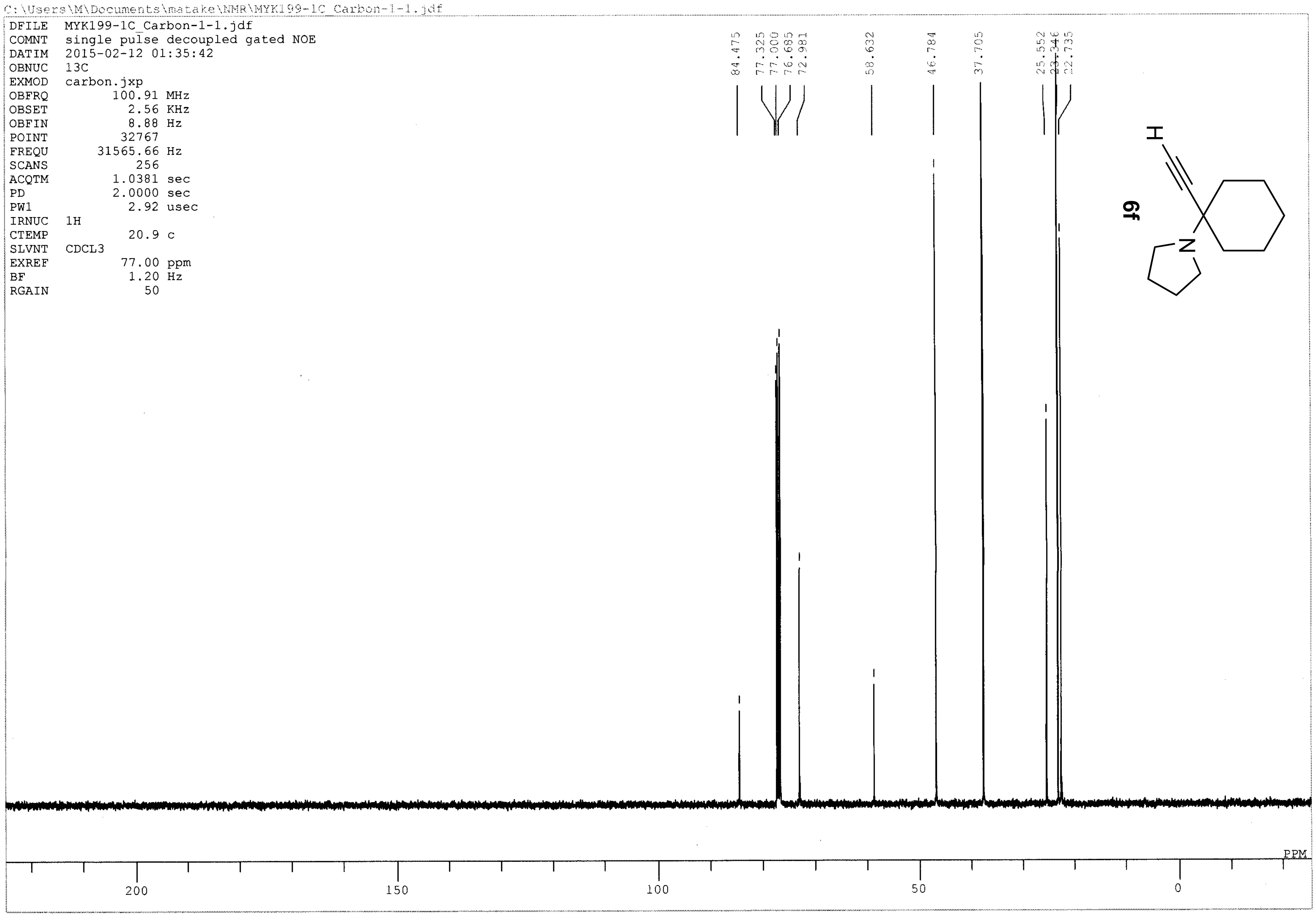
C:\Users\M\Documents\matake\NMR\MTK205-2C_Carbon-1-1.jdf

```
DFILE   MTK205-2C_Carbon-1-1.jdf
COMNT   single pulse decoupled gated NOE
DATIM   2015-02-26 15:28:41
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ        100.91 MHz
OBSET          2.56 KHz
OBFIN          8.88 Hz
POINT         32767
FREQU      31565.66 Hz
SCANS           256
ACQTM        1.0381 sec
PD           2.0000 sec
PW1            2.92 usec
IRNUC   1H
CTEMP          21.3 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            50
```




6e


C:\Users\M\Documents\matake\NMR\MTK199-1H_Proton-1-1.jdf
DFILE MTK199-1H_Proton-1-1.jdf
COMNT single_pulse
DATIM 2015-02-12 01:25:11
OBNUC 1H
EXMOD proton.jxp
OBFRQ 401.28 MHz
OBSET 4.20 KHz
OBFIN 4.97 Hz
POINT 16384
FREQU 7530.12 Hz
SCANS 8
ACQTM 2.1758 sec
PD 5.0000 sec
PW1 4.62 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
7.263
2.732
2.729
2.726
2.714
2.701
2.697
2.280
1.960
1.929
1.794
1.786
1.776
1.767
1.759
1.672
1.660
1.648
1.639
1.630
1.622
1.602
1.600
1.579
1.570
1.498
1.489
1.468
1.459
0.000
H
N
6f
4.36
1.00
2.21
4.36
8.07
impurities
12.5
10.0
7.5
5.0
2.5
0.0
PPM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DFILE MYK199-1C_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2015-02-12 01:35:42
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.91 MHz
OBSET 2.56 KHz
OBFIN 8.88 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 256
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 2.92 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 50
84.475
77.325
77.000
76.685
72.981
58.632
46.784
37.705
25.552
23.346
22.735
H
N
6f
PPM
200
150
100
50
0