

SUPPLEMENTARY INFORMATION

Rapid heteroatom-transfer to arylmetals utilizing multifunctional reagent scaffolds

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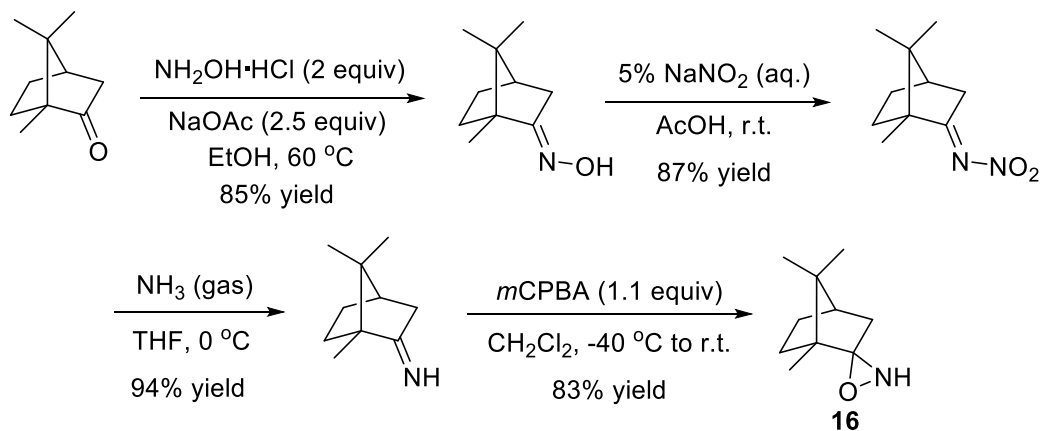
General Remarks

Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. All halogen-substituted arene reagents were purchased from Sigma-Aldrich Co. and used without further purification. All reactions were carried out in flame-dried glassware under an atmosphere of argon with magnetic stirring. All Grignard reagents were freshly prepared and the concentration of the Grignard reagents was titrated by literature reported method.¹ All reactions were monitored by thin-layer chromatography (TLC) with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032 - 0.063 mm) purchased from SiliCycle was used for flash chromatography.

Proton (¹H) and carbon (¹³C) NMR spectra were recorded on a Bruker AV-400 or a Bruker DRX-600 spectrometer operating at 400 MHz (or 600 MHz) for proton and 100 MHz (or 151 MHz) for carbon nuclei using CDCl₃ as solvent, respectively. Chemical shifts are expressed as parts per million (δ , ppm) and are referenced to 7.26 (CDCl₃) for ¹H NMR and 77.00 (CDCl₃) for ¹³C NMR. Proton signal data uses the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and *J* = coupling constant. High Resolution Mass Spectrometry was performed on a Shimadzu LCMS-IT-TOF under the conditions of electrospray ionization (ESI) in both positive and negative mode.

Synthesis of oxaziridines

Synthesis of Camphoryl N-H Oxaziridine 16 [Adapted from literature procedure ²]



Supplementary Figure 1. Synthesis of Camphoryl N-H Oxaziridine 16

(±)-Camphor oxime

To a 1 L round flask charged with a stirring bar, hydroxylamine hydrochloride (79 g, 1.0 mol), (±)-camphor (79.2 g, 0.5 mol) and ethanol (0.6 L) were added. Sodium acetate (103 g, 1.25 mol) was added into the reaction mixture and stirred at $60\text{ }^\circ\text{C}$ for 24 hours. After cooling, most of the ethanol in the reaction mixture was removed *in vacuo*. Water was then added, causing the crude oxime to precipitate from the solution as colorless crystals, which were isolated by filtration and washed with distilled water. The crystalline material was collected, dried under vacuum and recrystallized from absolute ethanol to afford (±)-camphor oxime (71.2 g, 85%); $R_f = 0.30$ (Hexanes:EtOAc = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.41 (br s, 1 H), 2.53 (dt, $J = 18.0, 4.0$ Hz, 1H), 2.03 (d, $J = 18.0$ Hz, 1H), 1.89 (t, $J = 4.8$ Hz, 1H), 1.87-1.75 (m, 1H), 1.74-1.63 (m, 1H), 1.48-1.38 (m, 1H), 1.26-1.16 (m, 1H), 0.98 (s, 3H), 0.89 (s, 3H), 0.77 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.8, 51.8, 48.3, 43.6, 33.1, 32.5, 27.2, 19.4, 18.5, 11.0.

(±)-Camphor nitrimine

(±)-Camphor oxime (33 g, 0.2 mol) in glacial acetic acid (900 mL) was treated with 5% aqueous sodium nitrite (500 mL). A bright yellow color developed and dispersed over 30 minutes. After a further 1.5 hours, the crude product was precipitated as a colorless solid by the addition of water and isolated by filtration. After drying under high vacuum, the crude product (34.2 g, 87%) was directly used for the next step reaction without further purification. $R_f = 0.40$ (Hexanes:EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 2.74-2.64 (m, 1H), 2.13 (d, $J = 18.4$, 1H), 2.03 (t, $J = 4.4$ Hz, 1H), 1.97-1.79 (m, 2H), 1.65-1.50 (m, 1H), 1.38-1.28 (m, 1 H), 1.04 (s, 3H), 0.98 (s, 3H), 0.88 (s, 3H).

(±)-Camphor N–H imine

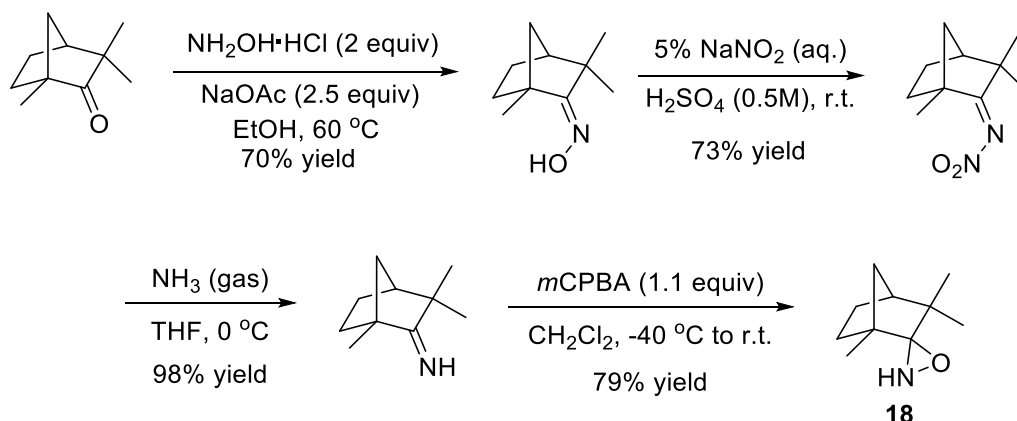
A solution of (±)-camphor nitrimine (11.8 g, 60 mmol) in dry tetrahydrofuran (100 mL) was treated at 0 °C with a slow stream of ammonia gas for 6 hours. The solvent was removed *in vacuo* (keeping the water bath below 30 °C) to give the (±)-camphor imine as a pale yellow solid (8.6 g, 94%). $R_f = 0.30$ (Hexanes:EtOAc = 3:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.18 (br s, 1H), 2.46-2.35 (m, 1H), 1.93 (d, $J = 17.2$ Hz, 1H), 1.89-1.75 (m, 2H), 1.66-1.56 (m, 1H), 1.36-1.18 (m, 2H), 0.89 (s, 3H), 0.88 (s, 3H), 0.75 (s, 3H); $^{13}\text{C NMR}$ (100.6 MHz, CDCl_3): δ 193.8, 54.6, 47.2, 43.6, 40.3, 32.0, 27.3, 19.5, 18.9, 10.3. The unpurified imine is homogeneous by spectroscopic analysis and is identical to that previously described. It was used immediately for the next step reaction without further purification.

(±)-Camphoryl N–H oxaziridine 16

A solution of purified *m*-CPBA (10.4 g, 60 mmol) in dry dichloromethane (250 mL) was cooled to -40 °C, causing some of the peracid to crystallize from the solution. On addition of a solution of the (±)-camphor imine (8.32 g, 55 mmol) in dry dichloromethane (50 mL) to this solution over a period of 10 minutes, this solution became homogeneous. This reaction mixture was then stirred overnight at between -30 °C and -40 °C and allowed to reach room temperature. The reaction mixture was stirred at room temperature for a further 2 hours until all of the peracid had reacted (TLC), by which time much of the *m*-chlorobenzoic acid by-product had crystallized from the solution. The solution was concentrated *in vacuo* until approximately 25% of the original volume remained. Hexanes (200 mL) was added and the solution again concentrated *in vacuo* until approximately 25% of the original volume remained. This process was repeated once more and finally hexanes (300 mL) was added to the mixture. The precipitated *m*-chlorobenzoic acid was removed by filtration, and the rest of this by-product washed out of the resulting solution with aqueous sodium hydroxide (1.0 M, 3 x 100 mL). The organic solution was dried (Na_2SO_4) and the solvent was removed *in vacuo* to give the crude oxaziridine, which can be further purified by column chromatography (Hexanes:EtOAc = 20:1) over silica gel to give (±)-camphoryl N–H oxaziridine **16** as a colorless solid (7.63 g, 83%).

(±)-Camphoryl N–H oxaziridine **16** was found by NMR spectroscopy to exist as a pair of diastereoisomers (A and B) at N–H in a 60:40 ratio (the major isomer is represented by A); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 4.21 (br s, 1H_A), 3.74 (br s, 1H_B), 2.33-2.21 (m, 1H_{A+B}), 1.87-1.26 (m, 6H_{A+B}), 0.93 (s, 3H_B), 0.91 (s, 3H_A), 0.88 (s, 6H_{A+B}), 0.63 (s, 3H_B), 0.62 (s, 3H_A); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 89.7, 89.4, 48.1, 47.8, 47.7, 47.5, 44.3, 44.2, 37.7, 36.5, 30.4, 29.5, 27.2, 27.0, 19.6, 19.5, 19.4, 19.3, 8.7, 8.4.

Synthesis of Fenchyl N–H Oxaziridine 18 [Adapted from literature procedure ²]



Supplementary Figure 2. Synthesis of Fenchyl N–H Oxaziridine 18

(-)-Fenchone oxime

To a 1 L round flask charged with a stirring bar, hydroxylamine hydrochloride (79 g, 1.0 mol), (-)-fenchone (77.7 g, 0.5 mol) and ethanol (0.6 L) were added. Sodium acetate (103 g, 1.25 mol) was added into the reaction mixture and stirred at 60 °C for 24 hours. After cooling, most of the ethanol in the reaction mixture was removed *in vacuo*. Water was then added, causing the crude oxime to precipitate from the solution as colorless crystals, which were isolated by filtration and washed with distilled water. The crystalline material was collected, dried under vacuum and recrystallized from absolute ethanol to afford (-)-fenchone oxime (58.2 g, 70%); $R_f = 0.30$ (Hexanes:EtOAc = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.82 (br s, 1H), 1.86-1.69 (m, 3H), 1.64-1.40 (m, 3H), 1.36-1.33 (m, 1H), 1.32 (s, 3H), 1.29 (s, 3H), 1.22 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.5, 50.1, 48.5, 44.2, 43.2, 34.1, 25.2, 22.8, 22.1, 17.1.

(-)-Fenchone nitrimine

A solution of sodium nitrite (23.5 g, 0.34 mol, 1.7 equiv) in water (150 mL) was added to a solution of (-)-fenchone oxime (33.5 g, 0.2 mol) in diethyl ether (300 mL) in a 1 L flask. A solution of 0.5 M sulfuric acid (330 mL) was added with occasional vigorous swirling over 2 hours at r.t. The mixture was allowed to stand for a further 3 hours, and the ether layer was separated, washed with saturated aqueous sodium hydrogen carbonate (2x100 mL), dried (Na_2SO_4) and the solvent removed *in vacuo*. After drying under high vacuum, the crude product (28.5 g, 73%) was directly used for the next step reaction without further purification. $R_f = 0.30$ (Hexanes:EtOAc = 10:1); The (-)-fenchone nitrimine was shown by NMR spectroscopy to be a mixture of *syn* and *anti* diastereoisomers (A and B) present in an approximately 2:1 ratio (the major isomer is represented by A): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 2.03-1.52 (m, $6\text{H}_{\text{A+B}}$), 1.47 (d, $J = 10.4$ Hz, 1H_A), 1.36 (d, $J = 10.4$ Hz, 1H_B), 1.28 (s, $3\text{H}_{\text{A+B}}$), 1.24 (s, 3H_A), 1.21 (s, 3H_B), 1.18 (s, 3H_A), 1.16 (s, 3H_B); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 189.9, 189.8, 53.6, 52.3, 49.7, 47.3, 46.7, 45.5, 45.0, 42.1, 34.0, 33.6, 26.0, 25.1, 24.6, 24.4, 23.7, 22.6, 16.1, 15.1.

(-)-Fenchone N–H imine

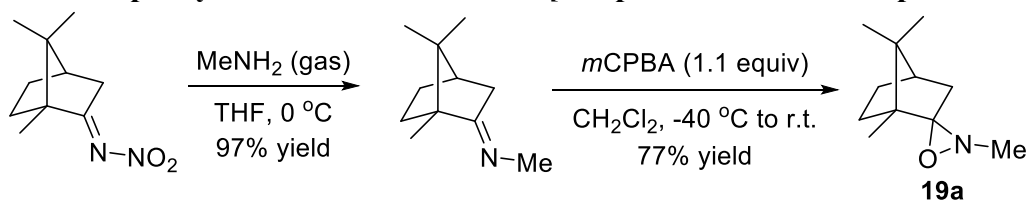
A solution of (-)-fenchone nitrimine (10.2 g, 52 mmol) in dry tetrahydrofuran (100 mL) was treated at 0 °C with a slow stream of ammonia gas for 6 hours. The solvent was removed in *vacuo* (keeping the water bath below 30 °C) to give the (-)-fenchone imine as an unstable pale yellow liquid (7.7 g, 98%). $R_f = 0.30$ (Hexanes:EtOAc = 3:1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.20 (br s, 1H), 2.01-1.95 (m, 1H), 1.75-1.69 (m, 1H), 1.68-1.55 (m, 2H), 1.49 (td, $J = 12.0, 3.6$ Hz, 1H), 1.38 (dd, $J = 10.4, 1.6$ Hz, 1H), 1.34-1.23 (m, 1H), 1.18 (s, 3H), 1.08 (s, 3H), 1.05 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 199.9, 51.9, 46.1, 44.8, 42.6, 33.3, 26.0, 25.0, 23.6, 16.0. The unpurified imine is homogeneous by spectroscopic analysis and is identical to that previously described. It was used immediately for the next step reaction without further purification.

(-)-Fenchyl N–H oxaziridine 18

A solution of purified *m*-CPBA (9.7 g, 56 mmol) in dry dichloromethane (250 mL) was cooled to -40 °C, causing some of the peracid to crystallize from the solution. On addition of a solution of the (-)-fenchone imine (7.7 g, 51 mmol) in dry dichloromethane (50 mL) to this solution over a period of 10 minutes, this solution became homogeneous. This reaction mixture was then stirred overnight at between -30 °C and -40 °C and allowed to reach room temperature. The reaction mixture was stirred at room temperature for a further 2 hours until all of the peracid had reacted (TLC), by which time much of the *m*-chlorobenzoic acid by-product had crystallized from the solution. The solution was concentrated in *vacuo* until approximately 25% of the original volume remained. Hexanes (200 mL) was added and the solution again concentrated in *vacuo* until approximately 25% of the original volume remained. This process was repeated once more and finally hexanes (300 mL) was added to the mixture. The precipitated *m*-chlorobenzoic acid was removed by filtration, and the rest of this by-product washed out of the resulting solution with aqueous sodium hydroxide (1.0 M, 3 x 100 mL). The organic solution was dried (Na_2SO_4) and the solvent was removed in *vacuo* to give the crude oxaziridine, which can be further purified by column chromatography (Hexanes:EtOAc = 20:1) over silica gel to give (-)-fenchyl N–H oxaziridine **18** as a colorless oil (6.9 g, 79%).

(-)-Fenchyl N–H oxaziridine was found by NMR spectroscopy to exist as a pair of diastereoisomers (A and B) at N–H in a 60:40 ratio (the major isomer is represented by A); $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 3.82 (br s, 1H_B), 3.70 (br s, 1H_A), 1.98-1.90 (m, 1H_{A+B}), 1.88-1.68 (m, $2\text{H}_{A/B}$), 1.62-1.26 (m, 4H_{A+B}), 0.96 (s, $3\text{H}_{A/B}$), 0.94 (s, 3H_{A+B}), 0.88 (s, $3\text{H}_{A/B}$), 0.87 (s, 3H_{A+B}); $^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 93.4, 92.9, 47.3, 47.2, 46.60, 41.8, 41.1, 39.8, 31.7, 31.1, 25.2, 23.3, 23.2, 22.6, 22.4, 14.0, 13.0.

Synthesis of Camphoryl N-Me Oxaziridine 19a [Adapted from literature procedure ²]



Supplementary Figure 3. Synthesis of Camphoryl N-Me Oxaziridine 19a

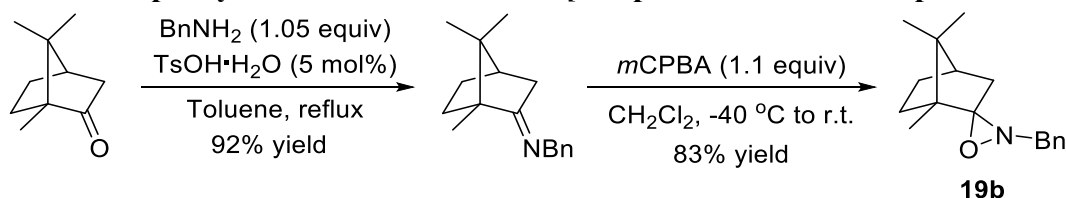
(±)-Camphor N-Me imine

A solution of (±)-camphor nitrimine (9.5 g, 48 mmol) in dry tetrahydrofuran (100 mL) was treated at 0 °C with a slow stream of methanamine gas for 5 hours. The solvent was removed *in vacuo* (keeping the water bath below 30 °C) to give the (±)-camphor N-Me imine as a pale yellow liquid (7.7 g, 97%). $R_f = 0.30$ (Hexanes:EtOAc = 3:1); ¹H NMR (400 MHz, CDCl₃): δ 3.00 (s, 3H), 2.35-2.25 (m, 1H), 1.92 (t, $J = 4.0$ Hz, 1H), 1.89-1.75 (m, 2H), 1.62 (td, $J = 12.4, 4.4$ Hz, 1H), 1.36-1.24 (m, 1H), 1.20-1.10 (m, 1H), 0.93 (s, 3H), 0.88 (s, 3H), 0.70 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 184.7, 53.7, 47.2, 43.7, 38.9, 35.2, 31.9, 27.3, 19.4, 18.8, 11.2.

(±)-Camphoryl N-Me Oxaziridine 19a

A solution of purified *m*-CPBA (5.7 g, 33 mmol) in dry dichloromethane (120 mL) was cooled to -40 °C, causing some of the peracid to crystallize from the solution. On addition of a solution of the (±)-camphor N-Me imine (4.96 g, 30 mmol) in dry dichloromethane (30 mL) to this solution over a period of 10 minutes, this solution became homogeneous. This reaction mixture was then stirred overnight at between -30 °C and -40 °C and allowed to reach room temperature. The reaction mixture was stirred at room temperature for a further 2 hours until all of the peracid had reacted (TLC), by which time much of the *m*-chlorobenzoic acid by-product had crystallized from the solution. The solution was concentrated *in vacuo* until approximately 25% of the original volume remained. Hexanes (100 mL) was added and the solution again concentrated *in vacuo* until approximately 25% of the original volume remained. This process was repeated once more and finally hexanes (150 mL) was added to the mixture. The precipitated *m*-chlorobenzoic acid was removed by filtration, and the rest of this by-product washed out of the resulting solution with aqueous sodium hydroxide (1.0 M, 3 x 50 mL). The organic solution was dried (Na₂SO₄) and the solvent was removed *in vacuo* to give the crude oxaziridine, which can be further purified by column chromatography (Hexanes:EtOAc = 20:1) over silica gel to give (±)-camphoryl N-Me oxaziridine 19a as a colorless solid (4.2 g, 77%). ¹H NMR (400 MHz, CDCl₃): δ 2.58 (s, 3H), 2.28-2.20 (m, 1H), 1.90-1.75 (m, 2H), 1.63-1.50 (m, 1H), 1.48-1.25 (m, 3H), 0.89 (s, 3H), 0.81 (s, 3H), 0.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 94.1, 49.2, 46.7, 44.3, 42.1, 32.3, 29.3, 27.2, 19.4, 19.3, 9.2.

Synthesis of Camphoryl N–Bn Oxaziridine **19b** [Adapted from literature procedure ²]



Supplementary Figure 4. Synthesis of Camphoryl N–Bn Oxaziridine **19b**

(±)-Camphor N–Bn imine

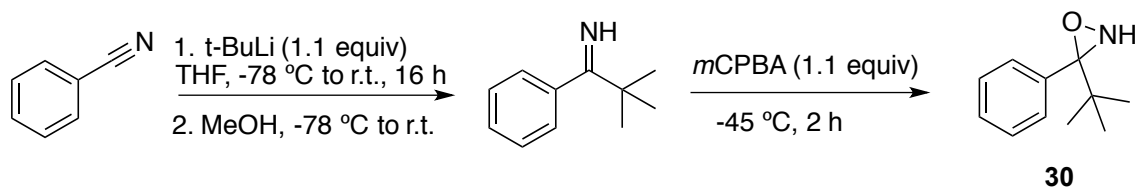
A solution of (±)-camphor (7.6 g, 50 mmol), benzylamine (5.6g, 52.5 mmol, 1.05 equiv) and *p*-toluenesulfonic acid monohydrate (0.48g, 2.5 mmol, 0.05 equiv) in toluene (100 mL) was treated at 130 °C with a Dean-Stark for 12 hours. After cooling, most of the toluene in the reaction mixture was removed *in vacuo*. The precipitates from the solution were removed by filtration. The organic solution was washed by saturated NaHCO₃ solution (2 x 100 mL) and brine (100 mL), dried over Na₂SO₄. The solvent was removed *in vacuo* to give the (±)-camphor N–Bn imine as a colorless liquid (11.1 g, 92%). R_f = 0.30 (Hexanes:EtOAc = 5:1); ¹H NMR (400 MHz, CDCl₃): δ 7.38-7.26 (m, 4H), 7.25-7.18 (m, 1H), 4.51 (d, *J* = 14.8 Hz, 1H), 4.44 (d, *J* = 14.8 Hz, 1H), 2.48-2.35 (m, 1H), 2.00-1.80 (m, 3H), 1.71 (td, *J* = 12.4, 4.0 Hz, 1H), 1.48-1.35 (m, 1H), 1.30-1.15 (m, 1H), 1.05 (s, 3H), 0.95 (s, 3H), 0.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 183.6, 140.4, 128.2, 127.4, 126.3, 55.5, 53.9, 47.1, 43.8, 35.8, 32.2, 27.4, 19.6, 19.0, 11.4.

(±)-Camphoryl N–Bn Oxaziridine **19b**

A solution of purified *m*-CPBA (7.9 g, 46 mmol) in dry dichloromethane (150 mL) was cooled to -40 °C, causing some of the peracid to crystallize from the solution. On addition of a solution of the (±)-camphor N–Bn imine (10.5 g, 44 mmol) in dry dichloromethane (50 mL) to this solution over a period of 15 minutes, this solution became homogeneous. This reaction mixture was then stirred overnight at between -30 °C and -40 °C and allowed to reach room temperature. The reaction mixture was stirred at room temperature for a further 2 hours until all of the peracid had reacted (TLC), by which time much of the *m*-chlorobenzoic acid by-product had crystallized from the solution. The solution was concentrated *in vacuo* until approximately 25% of the original volume remained. Hexanes (150 mL) was added and the solution again concentrated *in vacuo* until approximately 25% of the original volume remained. This process was repeated once more and finally hexanes (200 mL) was added to the mixture. The precipitated *m*-chlorobenzoic acid was removed by filtration, and the rest of this by-product washed out of the resulting solution with aqueous sodium hydroxide (1.0 M, 3 x 100 mL). The organic solution was dried (Na₂SO₄) and the solvent was removed *in vacuo* to give the crude oxaziridine, which can be further purified by column chromatography (Hexanes:EtOAc = 20:1) over silica gel to give (±)-camphoryl N–Bn oxaziridine **19b** as a colorless solid (9.4 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 3.86 (d, *J* = 14.8 Hz, 1H), 3.64 (d, *J* = 14.0 Hz, 1H), 2.48-2.37 (m, 1H), 1.91 (t, *J* = 4.8 Hz, 1H), 1.88-1.78 (m, 1H),

1.68-1.54 (m, 2H), 1.52-1.32 (m, 2H), 0.91 (s, 3H), 0.76 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 136.6, 128.52, 128.45, 127.4, 94.2, 59.4, 49.3, 46.9, 44.4, 33.2, 29.4, 27.1, 19.4, 19.3, 9.3.

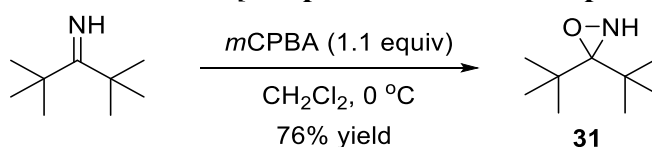
Synthesis of oxaziridine **30** [Adapted from literature procedure³]



Supplementary Figure 5. Synthesis of oxaziridine **30**

tert-Butyllithium (1.7 M, 16.4 mL, 28 mmol, 1.1 eq.) was slowly added to a solution of benzonitrile (2.58 g, 25 mmol, 1.0 eq.) in 50 mL THF at -78 °C. The reaction was allowed to reach room temperature. After 16 h, the reaction mixture was cooled back to -78 °C and 5 mL of anhydrous MeOH was added. After reaching room temperature, the reaction mixture was diluted with 50 mL hexanes and filtered through a pad of celite. The filtrate was concentrated under reduced pressure. The crude imine was re-dissolved in 25 mL of anhydrous DCM and slowly added to a suspension of *m*-CPBA (4.75 g, 27.5 mmol, 1.1 eq.) in 125 mL anhydrous DCM at -45 °C. After 2 h at -45 °C, the reaction mixture was allowed to reach room temperature. The solvent was carefully evaporated under reduced temperature, and 50 mL hexanes was added to the residue. The suspension was filtered and the solid was washed with additional hexanes (2 x 50 mL) before being discarded. The combined filtrate was washed once with 100 mL saturated aqueous NaHCO_3 and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (Hexanes:EtOAc = 25:1) to give **31** as a colorless oil (2.6 g, 58% over 2 steps). The product exists as a single pair of diastereomers (A and B). ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.30 (m, 5H, A & B), 4.40 (s, 1H, A), 3.85 (s, 1H, B), 1.07 (s, 9H, A), 1.03 (s, 9H, B); ^{13}C NMR (151 MHz, CDCl_3) δ 138.0, 132.7, 132.1, 129.1, 128.5, 128.0, 127.6, 127.6, 127.4, 86.2, 35.0, 25.5, 25.5.

Synthesis of Di-*t*-Butyl Oxaziridine **31** [Adapted from literature procedure⁴]



Supplementary Figure 6. Synthesis of Di-*t*-Butyl Oxaziridine **31**

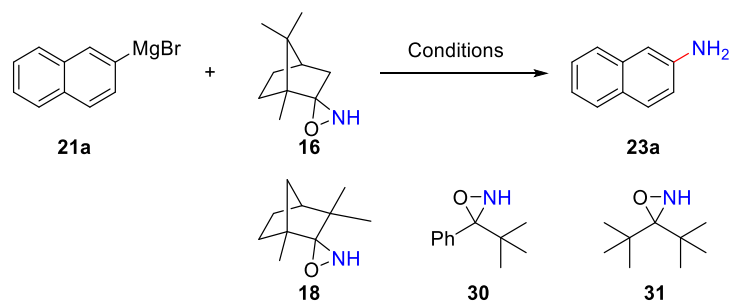
To a solution of 2,2,4,4-tetramethylpentan-3-imine (5 g, 35 mmol) in 20 mL of CH_2Cl_2 was added dropwise a solution of *m*-CPBA (7.1 g, 39 mmol, 1.1 equiv) in 80 mL of CH_2Cl_2 at 0 °C. The reaction mixture was stirred at 0 °C for 3 hours, and then concentrated in *vacuo* to remove

half of the solvent and filtered the *m*-chlorobenzoic acid by-product from the mixture. Hexanes (50 mL) was added and the solution again concentrated in *vacuo* until approximately 25% of the original volume remained. This process was repeated once more and finally hexanes (50 mL) was added to the mixture. The precipitated *m*-chlorobenzoic acid was removed by filtration, and the rest of this by-product washed out of the resulting solution with aqueous sodium hydroxide (1.0 M, 3 x 50 mL). The organic solution was dried (Na₂SO₄) and the solvent was removed in *vacuo* to give the crude oxaziridine, which can be further purified by column chromatography (Hexanes:EtOAc = 40:1) over silica gel to give di-*t*-butyl oxaziridine **31** as a colorless oil (4.2 g, 76%). ¹H NMR (600 MHz, CDCl₃): δ 3.78 (br s, 1H), 1.13 (s, 9H), 1.09 (s, 9H); ¹³C NMR (151 MHz, CDCl₃): δ 85.2, 37.5, 28.1, 27.9.

Safety Warning:

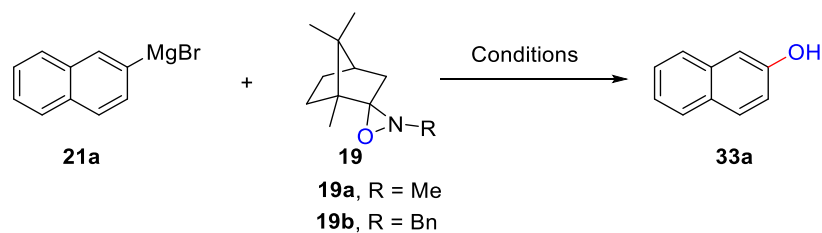
While we have experienced no ill effects of using these above mentioned oxaziridine reagents, this does not excuse carelessness in their handling.

Optimization of the reaction conditions



Entry	Equiv of 21a	Equiv of NH	Additives 1.2 equiv	Solvent	Temperature	Time	Yield of 23a
1	2.0	16 , 1.0	-	THF	-45 °C	1 h	59%
2	2.0	16 , 1.0	-	THF	-78 °C	5 h	58%
3	2.0	16 , 1.0	-	THF	-78 °C	1 h	43%
4	2.0	16 , 1.0	-	THF	0 °C	1 h	25%
5	1.5	16 , 1.0	-	THF	-45 °C	1 h	54%
6	1.0	16 , 1.5	-	THF	-45 °C	1 h	65%
7	1.0	16 , 1.5	-	THF	-45 °C	2 h	57%
8	1.0	16 , 1.2	-	THF	-78 °C	2 h	50%
9	1.0	16 , 1.2	-	THF	-45 °C	2 h	63%
10	1.0	16 , 1.2	TMEDA	THF	-45 °C	2 h	42%
11	1.0	16 , 1.2	DMPU	THF	-45 °C	2 h	45%
12	1.0	16 , 1.2	HMPA	THF	-45 °C	2 h	46%
13	1.0	16 , 1.5	-	Et ₂ O	-45 °C	2 h	43%
14	1.0	16 , 1.5	-	Toluene	-45 °C	2 h	41%
15	1.0	16 , 1.5	-	CH ₂ Cl ₂	-45 °C	2 h	33%
16	1.0	18 , 1.2	-	THF	-45 °C	2 h	77%
17	1.0	18 , 1.2	-	THF	-78 °C	2 h	81%
18	1.0	18 , 1.2	-	THF	-0 °C	2 h	68%
19	1.0	18 , 1.5	-	THF	-45 °C	2 h	69%
20	1.0	18 , 1.5	-	THF	-78 °C	2 h	68%
21	1.0	18 , 1.2	-	Et ₂ O	-78 °C	2 h	76%
22	1.0	18 , 1.2	-	Toluene	-78 °C	2 h	89%
23	1.0	18 , 1.2	-	CH ₂ Cl ₂	-78 °C	2 h	83%
24	1.0	30 , 1.2	-	Toluene	-78 °C	2 h	83%
25	1.0	31 , 1.2	-	Toluene	-78 °C	2 h	46%

Supplementary Table 1. Optimization of the amination conditions



Entry	Equiv of 21a	Equiv of 19	Solvent	Temperature	Time	Yield of 3a
1	1.5	19a , 1.0	THF	-78 °C	4 h	N.R.
2	1.5	19a , 1.0	THF	0 °C	7 h	56%
3	1.5	19a , 1.0	THF	r.t.	7 h	78%
4	1.0	-	THF	r.t.	7 h	< 5%
5	1.0	-	THF	r.t. (Air)	7 h	32%
6	1.5	19a , 1.0	THF	r.t.	2 h	64%
7	1.0	19a , 1.5	THF	r.t.	2 h	83%
8	1.0	19a , 1.5	THF	r.t. (Air)	2 h	84%
9	1.0	19a , 1.2	THF	r.t.	2 h	71%
10	1.0	19b , 1.5	THF	r.t.	2 h	86%
11	1.0	19b , 1.2	THF	r.t.	2 h	77%
12	1.0	19b , 1.5	DCM	r.t.	2 h	75%
13	1.0	19b , 1.5	Et ₂ O	r.t.	2 h	79%
14	1.0	19b , 1.5	Toluene	r.t.	2 h	85%

Supplementary Table 2. Optimization of the oxidation conditions

Experimental procedures

Amination of arylmetals:

Method A: To a flame-dried 25 mL round bottom flask was charged activated Mg (7.5 mmol, 1.5 eq.) and 5 mL anhydrous THF. To this suspension was added 2 drops of 1,2-dibromoethane. After 5 min, a solution of Aryl bromide (5 mmol, 1.0 eq.) in 5 mL anhydrous THF was slowly added to the suspension of Mg at room temperature. The reaction was mildly exothermic. The Grignard reagent was titrated and 1 mmol of this reagent was added to a flame-dried reaction vial. The solution was diluted with 3 mL anhydrous toluene and after cooling to the target temperature T , a solution of oxaziridine (1.2 mmol, 1.2 eq.) in 1 mL anhydrous toluene was added. The reaction was maintained at the targeted temperature T for time t before being quenched with saturated aqueous NH_4Cl . (The actual temperature/reaction time is listed for each substrate.)

Method B: To a flame-dried reaction vial was added $i\text{PrMgCl}\cdot\text{LiCl}$ (1.1 mmol, 1.1 eq., commercially-available THF solution from Aldrich). A solution of aryl iodide (1.0 mmol, 1.0 eq.) in 2 mL THF was added at $-45\text{ }^\circ\text{C}$. After 2 h, 3 mL of anhydrous toluene was added at $-45\text{ }^\circ\text{C}$, followed by a solution of oxaziridine (1.2 mmol, 1.2 eq.) in 1 mL anhydrous toluene. The reaction temperature was maintained at $-45\text{ }^\circ\text{C}$ for 2 h before being quenched with saturated aqueous NH_4Cl .

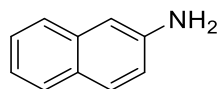
Method C: To a flame-dried reaction vial was added $\text{TMPMgCl}\cdot\text{LiCl}$ (1.1 mmol, 1.1 eq., commercially-available THF solution from Aldrich). A solution of aromatic or hetero-aromatic substrate (1.0 mmol, 1.0 eq.) in 2 mL THF was added at the temperature T_1 . After target time t_1 , the solution was cooled to temperature T_2 and 3 mL anhydrous toluene was added, followed by a solution of oxaziridine (1.2 mmol, 1.2 eq.) in 1 mL anhydrous toluene. The reaction was maintained at the targeted temperature T_2 for t_2 before being quenched with saturated aqueous NH_4Cl . (The actual temperature/reaction time is listed for each substrate.)

Method D: To a flame-dried reaction vial was added a solution of aryl bromide (1.0 mmol, 1.0 eq.) in 2 mL anhydrous THF. A solution of $n\text{-BuLi}$ in hexanes (1.1 mmol, 1.1 eq.) was slowly added at $-78\text{ }^\circ\text{C}$ and the temperature was maintained. After 30 min, a solution of oxaziridine (1.2 mmol, 1.2 eq.) in 4 mL anhydrous toluene was added at $-78\text{ }^\circ\text{C}$. The reaction was allowed to proceed at $-78\text{ }^\circ\text{C}$ for 2 h before being quenched with saturated aqueous NH_4Cl .

Method E: To a flame-dried reaction vial was added a solution of aryl bromide (1.0 mmol, 1.0 eq.) in 2 mL anhydrous THF. A solution of n-BuLi in hexanes (1.1 mmol, 1.1 eq.) was slowly added at -78 °C and the temperature was maintained at -78 °C. After 30 min, this aryl lithium solution was transferred to a suspension of MgBr₂ (1.0 mmol, 1.0 eq., freshly prepared from Mg and BrCH₂CH₂Br) at -78 °C. The reaction mixture was allowed to reach room temperature over 30 min before being cooled to the target temperature *T*. A solution of oxaziridine (1.2 mmol, 1.2 eq.) in 4 mL anhydrous toluene was added to the reaction mixture at *T*. The reaction was maintained at the targeted temperature *T* for 2 h before being quenched with saturated aqueous NH₄Cl. (The actual temperature/reaction time is listed for each substrate.)

Workup and Purification: After quenching, the reaction was diluted with 20 mL saturated aqueous NaCl and 20 mL EtOAc. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 20mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified with flash chromatography.

1. Naphthalen-2-amine (23a)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

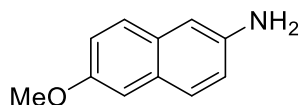
Yield = 89%; $R_f = 0.25$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.75 (d, $J = 8.0\text{ Hz}$, 1H), 7.70 (d, $J = 8.4\text{ Hz}$, 1H), 7.64 (d, $J = 8.4\text{ Hz}$, 1H), 7.43 (t, $J = 7.2\text{ Hz}$, 1H), 7.29 (t, $J = 7.2\text{ Hz}$, 1H), 7.02-6.94 (m, 2H), 3.82 (br s, 2 H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 144.0, 134.8, 129.1, 127.9, 127.6, 126.3, 125.7, 122.4, 118.2, 108.5.

Spectral data is in accordance with the literature report.⁵

2. 6-Methoxynaphthalen-2-amine (23b)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

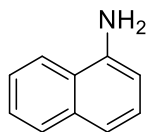
Yield = 78%; $R_f = 0.30$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.58 (d, $J = 8.8\text{ Hz}$, 1H), 7.52 (d, $J = 8.8\text{ Hz}$, 1H), 7.11-7.03 (m, 2H), 6.98-6.90 (m, 2H), 3.89 (s, 3H), 3.73 (br s, 2 H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.3, 142.3, 130.2, 128.6, 127.9, 127.3, 118.9, 118.7, 109.2, 106.0, 55.2.

Spectral data is in accordance with the literature report.⁵

3. Naphthalen-1-amine (23c)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

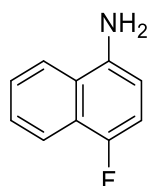
Yield = 63%; $R_f = 0.25$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.89-7.80 (m, 2H), 7.55-7.46 (m, 2H), 7.41-7.31 (m, 2H), 6.81 (dd, $J = 6.8, 1.2\text{ Hz}$, 1H), 4.12 (br s, 2 H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 142.0, 134.3, 128.5, 126.3, 125.8, 124.8, 123.5, 120.7, 118.8, 109.6.

Spectral data is in accordance with the literature report.⁶

4. 4-Fluoronaphthalen-1-amine (23d)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

Yield = 31%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

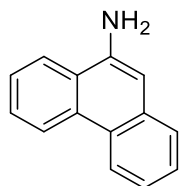
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.09 (dd, $J = 7.2, 2.4\text{ Hz}$, 1H), 7.85-7.80 (m, 1H), 7.58-7.50 (m, 2H), 6.98 (dd, $J = 10.4, 8.0\text{ Hz}$, 1H), 6.66 (dd, $J = 8.4, 4.4\text{ Hz}$, 1H), 3.99 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 152.6 (d, $J = 240.9\text{ Hz}$), 138.1 (d, $J = 2.9\text{ Hz}$), 126.1 (d, $J = 2.2\text{ Hz}$), 125.8, 124.5 (d, $J = 16.8\text{ Hz}$), 124.1 (d, $J = 16.8\text{ Hz}$), 121.1, 121.0, 109.4 (d, $J = 20.5\text{ Hz}$), 108.6 (d, $J = 8.0\text{ Hz}$);

$^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -134.6 (m).

Spectral data is in accordance with the literature report.⁷

5. Phenanthren-9-amine (23e)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 3\text{ h}$;

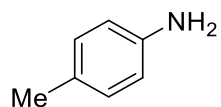
Yield = 52%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.73 (dd, $J = 8.4, 1.2\text{ Hz}$, 1H), 8.59 (d, $J = 8.0\text{ Hz}$, 1H), 7.93 (dd, $J = 8.0, 1.2\text{ Hz}$, 1H), 7.73-7.61 (m, 3H), 7.56-7.50 (m, 1H), 7.49-7.42 (m, 1H), 6.99 (s, 1H), 4.14 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 139.8, 133.2, 131.1, 126.8, 126.6, 126.3, 126.2, 126.1, 125.4, 123.4, 123.3, 122.4, 121.2, 107.4.

Spectral data is in accordance with the literature report.⁶

6. *p*-Toluidine (23f)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

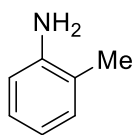
Yield = 61%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.97 (d, $J = 8.0\text{ Hz}$, 2H), 6.62 (d, $J = 8.8\text{ Hz}$, 2H), 3.53 (br s, 2H), 2.25 (s, 3H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 143.8, 129.7, 127.8, 115.2, 20.4.

Spectral data is in accordance with the literature report.⁵

7. *o*-Toluidine (23g)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

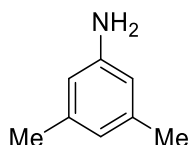
Yield = 47%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.11-7.04 (m, 2H), 6.79-6.68 (m, 2H), 3.61 (br s, 2H), 2.20 (s, 3H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 144.5, 130.4, 126.9, 122.2, 118.5, 114.9, 17.3.

Spectral data is in accordance with the literature report.⁸

8. 3,5-Dimethylaniline (23h)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

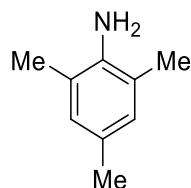
Yield = 74%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.50 (s, 1H), 6.39 (s, 2H), 3.63 (br s, 2H), 2.31 (s, 6H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 146.1, 138.8, 120.4, 113.0, 21.2.

Spectral data is in accordance with the literature report.⁸

9. 2,4,6-Trimethylaniline (23i)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 3\text{ h}$;

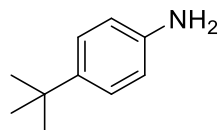
Yield = 26%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.81 (s, 2H), 3.48 (br s, 2H), 2.25 (s, 3H), 2.19 (s, 6H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 140.1, 128.8, 127.1, 121.8, 20.3, 17.5.

Spectral data is in accordance with the literature report.⁶

10. 4-(Tert-butyl)aniline (23j)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

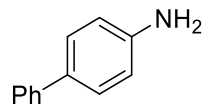
Yield = 70%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.21 (d, $J = 8.4\text{ Hz}$, 2H), 6.67 (d, $J = 8.4\text{ Hz}$, 2H), 3.52 (br s, 2H), 1.31 (s, 9H);

$^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 143.7, 141.4, 126.0, 114.9, 33.9, 31.5.

Spectral data is in accordance with the literature report.⁵

11. [1,1'-Biphenyl]-4-amine (23k)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

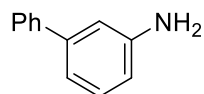
Yield = 92%; $R_f = 0.25$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.57 (d, $J = 7.6\text{ Hz}$, 2H), 7.48-7.40 (m, 4H), 7.30 (t, $J = 7.6\text{ Hz}$, 1H), 6.78 (d, $J = 8.4\text{ Hz}$, 2H), 3.73 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 145.8, 141.1, 131.5, 128.6, 128.0, 126.3, 126.2, 115.3.

Spectral data is in accordance with the literature report.⁵

12. [1,1'-Biphenyl]-3-amine (23l)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

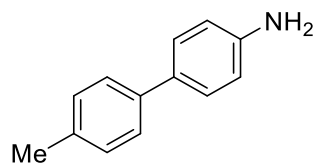
Yield = 82%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.60-7.55 (m, 2H), 7.43 (t, $J = 7.2\text{ Hz}$, 2H), 7.37-7.33 (m, 1H), 7.24 (t, $J = 8.4\text{ Hz}$, 1H), 7.03-6.98 (m, 1H), 6.92 (t, $J = 2.0\text{ Hz}$, 1H), 6.72-6.66 (m, 1H), 3.74 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 146.7, 142.4, 141.4, 129.6, 128.6, 127.2, 127.1, 117.7, 114.1, 113.9.

Spectral data is in accordance with the literature report.⁹

13. 4'-Methyl-[1,1'-biphenyl]-4-amine (23m)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

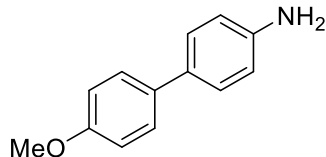
Yield = 85%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.55 (d, $J = 8.4\text{ Hz}$, 2H), 7.50 (d, $J = 8.4\text{ Hz}$, 2H), 7.32 (d, $J = 8.0\text{ Hz}$, 2H), 6.81 (d, $J = 8.8\text{ Hz}$, 2H), 3.71 (br s, 2H), 2.48 (s, 3H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 145.5, 138.2, 135.7, 131.3, 129.3, 127.7, 126.1, 115.3, 20.9.

Spectral data is in accordance with the literature report.¹⁰

14. 4'-Methoxy-[1,1'-biphenyl]-4-amine (23n)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

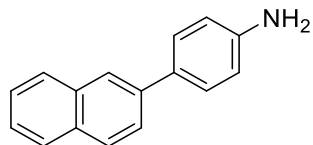
Yield = 83%; $R_f = 0.35$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.58 (d, $J = 7.2\text{ Hz}$, 2H), 7.48 (d, $J = 7.2\text{ Hz}$, 2H), 7.06 (d, $J = 7.8\text{ Hz}$, 2H), 6.86 (d, $J = 7.2\text{ Hz}$, 2H), 3.96 (s, 3H), 3.81 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 158.4, 145.3, 133.9, 131.3, 127.6, 127.4, 115.4, 114.1, 55.3.

Spectral data is in accordance with the literature report.¹⁰

15. 4-(Naphthalen-2-yl)aniline (23o)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

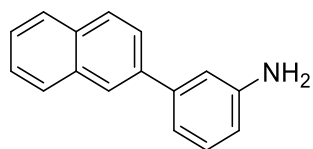
Yield = 62%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.98 (s, 1H), 7.91-7.83 (m, 3H), 7.73 (dd, $J = 8.8, 2.0\text{ Hz}$, 1H), 7.57 (dd, $J = 6.4, 2.0\text{ Hz}$, 2H), 7.51-7.44 (m, 2H), 6.81 (dd, $J = 6.8, 2.4\text{ Hz}$, 2H), 3.76 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 145.9, 138.5, 133.8, 132.1, 131.3, 128.3, 128.2, 127.9, 127.6, 126.1, 125.4, 125.3, 124.4, 115.4.

Spectral data is in accordance with the literature report.¹¹

16. 3-(Naphthalen-2-yl)aniline (23p)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

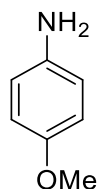
Yield = 79%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.05 (s, 1H), 7.94-7.86 (m, 3H), 7.75 (dd, $J = 8.4, 1.6\text{ Hz}$, 1H), 7.54-7.48 (m, 2H), 7.30 (t, $J = 8.0\text{ Hz}$, 1H), 7.15 (d, $J = 8.0\text{ Hz}$, 1H), 7.05 (t, $J = 2.0\text{ Hz}$, 1H), 6.76-6.70 (m, 1H), 3.73 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 146.8, 142.3, 138.7, 133.6, 132.6, 129.7, 128.2, 128.1, 127.6, 126.2, 125.8, 125.64, 125.60, 117.9, 114.2, 114.1.

Spectral data is in accordance with the literature report.¹²

17. 4-Methoxyaniline (23q)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

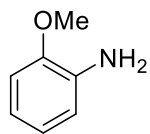
Yield = 63%; $R_f = 0.32$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.79-6.72 (m, 2H), 6.68-6.61 (m, 2H), 3.75 (s, 3 H), 3.43 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 152.6, 139.8, 116.3, 114.6, 55.6.

Spectral data is in accordance with the literature report.⁵

18. 2-Methoxyaniline (23r)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

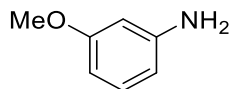
Yield = 61%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.87-6.81 (m, 2H), 6.80-6.73 (m, 1H), 3.88 (s, 3H), 3.82 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 147.2, 136.1, 120.0, 118.3, 114.9, 110.3, 55.3.

Spectral data is in accordance with the literature report.¹³

19. 3-Methoxyaniline (23s)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

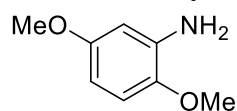
Yield = 67%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.09 (t, $J = 8.4\text{ Hz}$, 1H), 6.39-6.29 (m, 2H), 6.27 (t, $J = 2.4\text{ Hz}$, 1H), 3.78 (s, 3H), 3.71 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 160.6, 147.6, 129.9, 107.8, 103.8, 100.9, 54.9.

Spectral data is in accordance with the literature report.⁵

20. 2,5-Dimethoxyaniline (23t)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

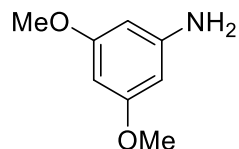
Yield = 58%; $R_f = 0.35$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.70 (d, $J = 8.8\text{ Hz}$, 1H), 6.34 (d, $J = 2.8\text{ Hz}$, 1H), 6.25 (dd, $J = 8.4, 2.8\text{ Hz}$, 1H), 3.84 (br s, 2H), 3.81 (s, 3H), 3.73 (s, 3H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 154.3, 141.8, 137.2, 111.2, 101.9, 101.8, 56.0, 55.4.

Spectral data is in accordance with the literature report.¹⁴

21. 3,5-Dimethoxyaniline (23u)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

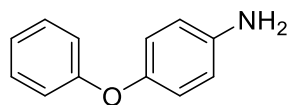
Yield = 78%; $R_f = 0.25$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 5.93 (t, $J = 2.0\text{ Hz}$, 1H), 5.87 (d, $J = 2.4\text{ Hz}$, 2H), 3.73 (s, 6H), 3.67 (s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 161.5, 148.4, 93.6, 90.7, 55.0.

Spectral data is in accordance with the literature report.¹⁵

22. 4-Phenoxyaniline (23v)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

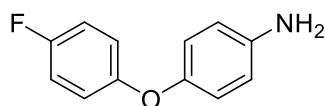
Yield = 81%; $R_f = 0.50$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.35-7.28 (m, 2H), 7.04 (t, $J = 7.4\text{ Hz}$, 1H), 6.96 (d, $J = 8.0\text{ Hz}$, 2H), 6.90 (d, $J = 8.7\text{ Hz}$, 2H), 6.69 (d, $J = 8.7\text{ Hz}$, 2H), 3.59 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 158.8, 148.5, 142.6, 129.5, 122.0, 121.0, 117.2, 116.2.

Spectral data is in accordance with the literature report.⁵

23. 3-(4-Fluorophenoxy)aniline (23w)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

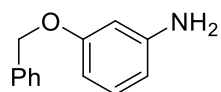
Yield = 70%; $R_f = 0.6$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.09 (t, $J = 8.4\text{ Hz}$, 1H), 7.07-6.95 (m, 4H), 6.43 (dd, $J = 8.0, 1.8\text{ Hz}$, 1H), 6.36 (dd, $J = 8.4, 1.8\text{ Hz}$, 1H), 6.31 (d, $J = 2.4\text{ Hz}$, 1H), 3.76 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 158.4 (d, $J = 133.2\text{ Hz}$), 152.7, 147.6, 130.4, 120.7, 120.6, 116.1 (d, $J = 24.3\text{ Hz}$), 110.1, 108.4, 105.0.

Spectral data is in accordance with the literature report.¹⁶

24. 3-(Benzyloxy)aniline (23x)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

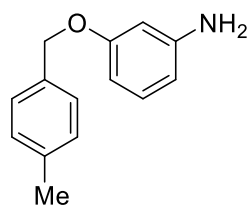
Yield = 86%; $R_f = 0.40$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.45 (d, $J = 6.6\text{ Hz}$, 2H), 7.40 (t, $J = 7.8\text{ Hz}$, 2H), 7.34 (t, $J = 7.2\text{ Hz}$, 1H), 7.09 (t, $J = 7.8\text{ Hz}$, 1H), 6.43 (dd, $J = 7.8, 2.4\text{ Hz}$, 1H), 6.38-6.30 (m, 2H), 5.04 (s, 2H), 3.72 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 160.0, 147.6, 137.2, 130.1, 128.5, 127.8, 127.4, 108.2, 104.9, 102.0, 69.8.

Spectral data is in accordance with the literature report.¹⁷

25. 3-((4-Methylbenzyl)oxy)aniline (23y)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

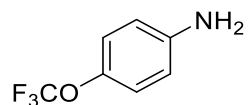
Yield = 65%; $R_f = 0.55$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.33 (d, $J = 6.6\text{ Hz}$, 2H), 7.20 (d, $J = 7.8\text{ Hz}$, 2H), 7.08 (t, $J = 8.4\text{ Hz}$, 1H), 6.45-6.40 (m, 1H), 6.37-6.29 (m, 2H), 4.99 (s, 2H), 3.73 (br s, 2H), 2.38 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 160.0, 147.5, 137.6, 134.1, 130.1, 129.2, 127.5, 108.2, 105.0, 102.1, 69.7, 21.2.

Spectral data is in accordance with the literature report.¹⁸

26. 4-(Trifluoromethoxy)aniline (23z)



Method A, $T = -20\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

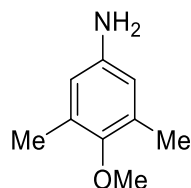
Yield = 62%; $R_f = 0.70$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.01 (d, $J = 8.4\text{ Hz}$, 2H), 6.67-6.60 (m, 2H), 3.68 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 145.2, 141.3, 122.4, 120.64 (q, $J = 255.3\text{ Hz}$), 115.4.

Spectral data is in accordance with the literature report.¹⁹

27. 4-Methoxy-3,5-dimethylaniline (24a)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

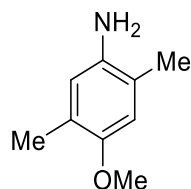
Yield = 77%; $R_f = 0.25$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.37 (s, 2H), 3.68 (s, 3H), 3.51 (br s, 2H), 2.23 (s, 6H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 149.5, 141.9, 131.3, 115.2, 59.8, 15.9.

Spectral data is in accordance with the literature report.²⁰

28. 4-Methoxy-2,5-dimethylaniline (24b)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

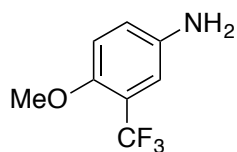
Yield = 46%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.61 (s, 1H), 6.52 (s, 1H), 3.78 (s, 3H), 3.29 (br s, 2H), 2.17 (s, 6H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 150.7, 137.6, 124.9, 120.3, 118.1, 113.3, 56.0, 17.3, 15.7.

Spectral data is in accordance with the literature report.²¹

29. 4-methoxy-3-(trifluoromethyl)aniline (24c)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

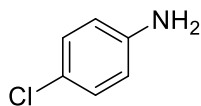
Yield = 65%; $R_f = 0.35$ (Hexanes:EtOAc = 2:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.89 (d, $J = 3.0\text{ Hz}$, 1H), 6.84 (d, $J = 9.0\text{ Hz}$, 1H), 6.81-6.76 (m, 1H), 3.81 (s, 3H), 3.50 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 150.2, 139.6, 123.6 (q, $J = 270.2\text{ Hz}$), 119.3, 119.2 (q, $J = 30.6\text{ Hz}$), 114.0, 113.8 (q, $J = 4.4\text{ Hz}$), 56.5.

Spectral data is in accordance with the literature report.²²

30. 4-Chloroaniline (24d)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

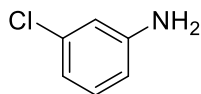
Yield = 43%; $R_f = 0.40$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.10 (d, $J = 8.8\text{ Hz}$, 2H), 6.60 (d, $J = 8.8\text{ Hz}$, 2H), 3.58 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 144.9, 129.0, 123.0, 116.2.

Spectral data is in accordance with the literature report.¹⁴

31. 3-Chloroaniline (24e)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

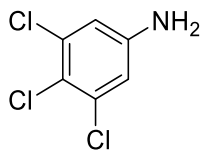
Yield = 63%; $R_f = 0.40$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.07 (t, $J = 8.0\text{ Hz}$, 1H), 6.77-6.71 (m, 1H), 6.67 (t, $J = 2.0\text{ Hz}$, 1H), 6.57-6.51 (m, 1H), 3.72 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 147.6, 134.7, 130.2, 118.3, 114.8, 113.1.

Spectral data is in accordance with the literature report.⁸

32. 3,4,5-Trichloroaniline (24f)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

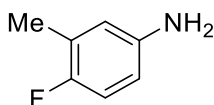
Yield = 47%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.67 (s, 2H), 3.78 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 145.6, 134.1, 119.7, 115.0.

Spectral data is in accordance with the literature report.²³

33. 4-Fluoro-3-methylaniline (24g)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

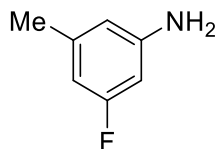
Yield = 48%; $R_f = 0.40$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.80 (t, $J = 8.8\text{ Hz}$, 1H), 6.52-6.40 (m, 2H), 3.44 (br s, 2H), 2.20 (d, $J = 1.6\text{ Hz}$, 3H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.0 (d, $J = 233.6\text{ Hz}$), 142.0 (d, $J = 1.5\text{ Hz}$), 125.2 (d, $J = 18.2\text{ Hz}$), 117.7, 115.2 (d, $J = 23.3\text{ Hz}$), 113.3 (d, $J = 7.3\text{ Hz}$), 14.6 (d, $J = 2.9\text{ Hz}$).

Spectral data is in accordance with the literature report.²⁴

34. 3-Fluoro-5-methylaniline (24h)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

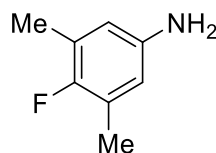
Yield = 62%; $R_f = 0.35$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.32 – 6.25 (m, 2H), 6.20 (d, $J = 10.2\text{ Hz}$, 1H), 3.68 (br s, 2H), 2.25 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 163.8 (d, $J = 242.2\text{ Hz}$), 147.8 (d, $J = 11.0\text{ Hz}$), 141.0 (d, $J = 10.0\text{ Hz}$), 111.3, 105.9 (d, $J = 19.8\text{ Hz}$), 99.2 (d, $J = 24.3\text{ Hz}$), 21.4.

HRMS (ESI) m/z calcd for $[\text{C}_7\text{H}_9\text{FN}]^+$ $[\text{M}+\text{H}]^+$: 126.0714, found 126.0716.

35. 4-Fluoro-3,5-dimethylaniline (24i)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

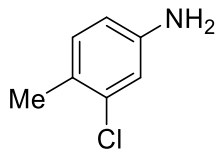
Yield = 69%; $R_f = 0.25$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.33 (s, 1H), 6.32 (s, 1H), 3.34 (br s, 2H), 2.19 (s, 3H), 2.18 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 153.6 (d, $J = 233.3\text{ Hz}$), 141.5 (d, $J = 3.3\text{ Hz}$), 124.8 (d, $J = 18.7\text{ Hz}$), 115.1 (d, $J = 3.3\text{ Hz}$), 14.62, 14.59.

HRMS (ESI) m/z calcd for $[\text{C}_8\text{H}_{11}\text{FN}]^+$ $[\text{M}+\text{H}]^+$: 140.0870, found 140.0874.

36. 3-Chloro-4-methylaniline (24j)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

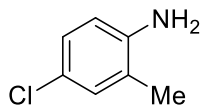
Yield = 67%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.99 (d, $J = 7.8\text{ Hz}$, 1H), 6.71 (d, $J = 2.4\text{ Hz}$, 1H), 6.49 (dd, $J = 7.8, 2.4\text{ Hz}$, 1H), 3.59 (br s, 2H), 2.26 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 145.3, 134.6, 131.3, 125.4, 115.5, 113.6, 18.9.

Spectral data is in accordance with the literature report.²⁵

37. 4-Chloro-2-methylaniline (24k)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

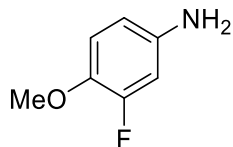
Yield = 46%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.03 (d, $J = 2.4\text{ Hz}$, 1H), 6.99 (dd, $J = 8.4, 2.4\text{ Hz}$, 1H), 6.58 (d, $J = 8.4\text{ Hz}$, 1H), 3.56 (br s, 2H), 2.13 (s, 3H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 143.1, 129.9, 126.5, 123.9, 122.7, 115.8, 17.2.

Spectral data is in accordance with the literature report.⁶

38. 3-Fluoro-4-methoxyaniline (24l)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

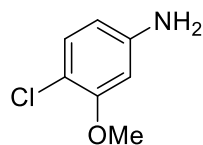
Yield = 68%; $R_f = 0.35$ (Hexanes:EtOAc = 2:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.78 (t, $J = 9.0\text{ Hz}$, 1H), 6.45 (dd, $J = 13.2, 3.0\text{ Hz}$, 1H), 6.39-6.34 (m, 1H), 3.79 (s, 3H), 3.49 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 153.1 (d, $J = 244.5\text{ Hz}$), 141.0 (d, $J = 8.9\text{ Hz}$), 140.1 (d, $J = 12.1\text{ Hz}$), 115.7 (d, $J = 3.3\text{ Hz}$), 110.2 (d, $J = 3.3\text{ Hz}$), 104.1 (d, $J = 20.8\text{ Hz}$), 57.3.

Spectral data is in accordance with the literature report.²⁶

39. 4-Chloro-3-methoxyaniline (24m)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 3\text{ h}$;

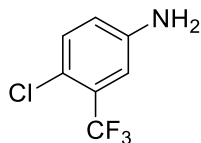
Yield = 62%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.08 (d, $J = 8.4\text{ Hz}$, 1H), 6.25 (d, $J = 2.4\text{ Hz}$, 1H), 6.23-6.17 (m, 1H), 3.81 (s, 3H), 3.69 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.4, 146.4, 130.3, 111.2, 107.7, 99.6, 55.8.

Spectral data is in accordance with the literature report.²⁷

40. 4-Chloro-3-(trifluoromethyl)aniline (24n)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

Yield = 61%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

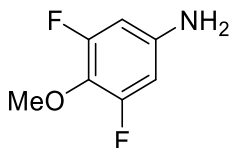
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.22 (d, $J = 8.8\text{ Hz}$, 1H), 6.95 (d, $J = 2.8\text{ Hz}$, 1H), 6.74-6.69 (m, 1H), 3.84 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 145.1, 132.0, 128.6 (q, $J = 30.6\text{ Hz}$), 122.8 (q, $J = 271.6\text{ Hz}$), 120.1, 118.6, 113.6 (q, $J = 5.1\text{ Hz}$);

$^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -62.8.

Spectral data is in accordance with the literature report.¹⁵

41. 3,5-Difluoro-4-methoxyaniline (24o)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

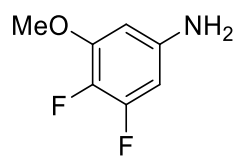
Yield = 61%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.24-6.14 (m, 2H), 3.85 (s, 3H), 3.68 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 155.6 (dd, $J = 245.5, 8.8\text{ Hz}$), 142.6 (t, $J = 12.1\text{ Hz}$), 128.3 (t, $J = 15.4\text{ Hz}$), (98.79, 98.77, 98.74, 98.64, 98.61, 98.59), 62.2 (t, $J = 3.3\text{ Hz}$).

Spectral data is in accordance with the literature report.²⁸

42. 3,4-Difluoro-5-methoxyaniline (24p)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

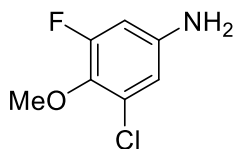
Yield = 77%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.10-6.01 (m, 2H), 3.83 (s, 3H), 3.60 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 151.6 (dd, $J = 243.4, 11.0$ Hz), 149.5 (dd, $J = 8.9, 5.6$ Hz), 142.3 (dd, $J = 11.0, 3.3$ Hz), 134.7 (dd, $J = 236.8, 14.3$ Hz), 95.8 (d, $J = 2.3$ Hz), 95.4 (d, $J = 22.0$ Hz), 56.5.

Spectral data is in accordance with the literature report.²⁹

43. 3-Chloro-5-fluoro-4-methoxyaniline (24q)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

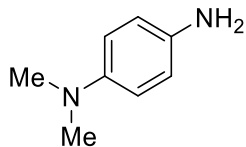
Yield = 60%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.45 (t, $J = 2.3$ Hz, 1H), 6.33 (dd, $J = 12.0, 2.7$ Hz, 1H), 3.83 (s, 3H), 3.64 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 156.8 (d, $J = 247.8$ Hz), 143.0 (d, $J = 11.0$ Hz), 136.4 (d, $J = 14.2$ Hz), 129.0 (d, $J = 5.4$ Hz), 111.3 (d, $J = 3.3$ Hz), 102.3 (d, $J = 22.0$ Hz), 61.7 (d, $J = 3.3$ Hz).

HRMS (ESI) m/z calcd for $[\text{C}_7\text{H}_8\text{ClFNO}]^+ [\text{M}+\text{H}]^+$: 176.0273, found 176.0279.

44. *N,N'*-dimethylbenzene-1,4-diamine (24r)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

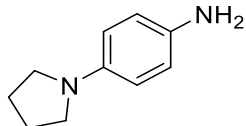
Yield = 79%; $R_f = 0.20$ (Hexanes:EtOAc = 1:1);

$^1\text{H NMR}$ (600 MHz, Acetone- d_6): δ 6.68-6.62 (m, 2H), 6.61-6.55 (m, 2H), 4.02 (br s, 2H), 2.76 (s, 6H);

$^{13}\text{C NMR}$ (151 MHz, Acetone- d_6): δ 143.9, 140.0, 115.6, 115.5, 41.5.

Spectral data is in accordance with the literature report.¹³

45. 4-(Pyrrolidin-1-yl)aniline (24s)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

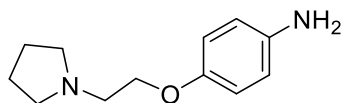
Yield = 57%; $R_f = 0.25$ (Hexanes:EtOAc = 1:1);

$^1\text{H NMR}$ (600 MHz, Acetone- d_6): δ 6.64-6.53 (m, 2H), 6.45-6.38 (m, 2H), 3.87 (br s, 2H), 3.26-3.11 (m, 4H), 2.03-1.90 (m, 4H);

$^{13}\text{C NMR}$ (151 MHz, Acetone- d_6): δ 141.6, 138.3, 116.1, 113.0, 48.1, 24.9.

Spectral data is in accordance with the literature report.³⁰

46. 4-(2-(Pyrrolidin-1-yl)ethoxy)aniline (24t)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

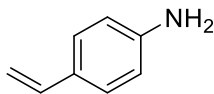
Yield = 83%; $R_f = 0.2$ (5% MeOH in DCM);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.78-6.68 (m, 2H), 6.67-6.55 (m, 2H), 4.18-3.92 (m, 2H), 3.43 (br s, 2H), 2.98-2.77 (m, 2H), 2.75-2.53 (m, 4H), 1.88-1.71 (m, 4H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 152.0, 140.0, 116.3, 115.8, 67.6, 55.2, 54.7, 23.5.

Spectral data is in accordance with the literature report.³¹

47. 4-Vinylaniline (28a)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

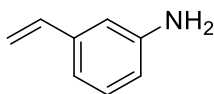
Yield = 75%; $R_f = 0.20$ (Hexanes:EtOAc = 5:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.30-7.26 (m, 2H), 6.72-6.63 (m, 3H), 5.61 (dd, $J = 17.6, 1.2\text{ Hz}$, 1H), 5.10 (dd, $J = 10.8, 1.2\text{ Hz}$, 1H), 3.70 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 146.1, 136.5, 128.2, 127.2, 114.9, 109.9.

Spectral data is in accordance with the literature report.³²

48. 3-Vinylaniline (28b)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

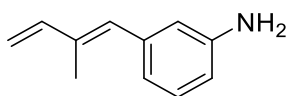
Yield = 72%; $R_f = 0.20$ (Hexanes:EtOAc = 5:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.16 (t, $J = 8.0\text{ Hz}$, 1H), 6.87 (d, $J = 7.6\text{ Hz}$, 1H), 6.76 (t, $J = 2.0\text{ Hz}$, 1H), 6.73-6.59 (m, 2H), 5.74 (dd, $J = 17.6, 1.2\text{ Hz}$, 1H), 5.25 (dd, $J = 11.2, 0.8\text{ Hz}$, 1H), 3.63 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 146.5, 138.5, 136.9, 129.3, 116.8, 114.7, 113.5, 112.6.

Spectral data is in accordance with the literature report.³³

49. (E)-3-(2-Methylbuta-1,3-dien-1-yl)aniline (28c)



Method A, $T = -45\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

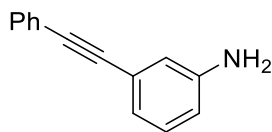
Yield = 75%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.16 (t, $J = 7.8\text{ Hz}$, 1H), 6.75 (d, $J = 7.4\text{ Hz}$, 1H), 6.65 (t, $J = 2.0\text{ Hz}$, 1H), 6.62 – 6.51 (m, 2H), 6.47 (s, 1H), 5.32 (d, $J = 17.3\text{ Hz}$, 1H), 5.15 (d, $J = 10.6\text{ Hz}$, 1H), 3.65 (br s, 2H), 2.02 (d, $J = 1.3\text{ Hz}$, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 146.0, 141.9, 138.7, 135.8, 131.8, 128.9, 119.8, 115.8, 113.6, 112.7, 13.2.

HRMS (ESI) m/z calcd for $[\text{C}_{11}\text{H}_{14}\text{N}]^+$ $[\text{M}+\text{H}]^+$: 160.1121, found 160.1120.

50. 3-(Phenylethynyl)aniline (28d)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

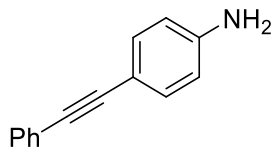
Yield = 60%; $R_f = 0.20$ (Hexanes:EtOAc = 5:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.59-7.54 (m, 2H), 7.41-7.32 (m, 3H), 7.16 (t, $J = 8.0\text{ Hz}$, 1H), 6.99 (d, $J = 8.0\text{ Hz}$, 1H), 6.88 (s, 1H), 6.67 (dd, $J = 8.0, 1.6\text{ Hz}$, 1H), 3.63 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 146.2, 131.5, 129.2, 128.3, 128.1, 123.8, 123.3, 122.0, 117.7, 115.3, 89.6, 88.7.

Spectral data is in accordance with the literature report.³⁴

51. 4-(Phenylethynyl)aniline (28e)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

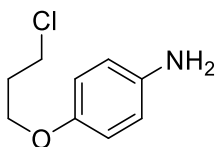
Yield = 74%; $R_f = 0.20$ (Hexanes:EtOAc = 5:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.51 (d, $J = 6.8\text{ Hz}$, 2H), 7.38-7.27 (m, 5H), 6.64 (d, $J = 8.0\text{ Hz}$, 2H), 3.81 (br s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 146.6, 132.9, 131.3, 128.2, 127.6, 123.9, 114.7, 112.6, 90.1, 87.3.

Spectral data is in accordance with the literature report.³⁵

52. 4-(3-Chloropropoxy)aniline (28f)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

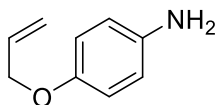
Yield = 51%; $R_f = 0.20$ (Hexanes:EtOAc = 2:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.80-6.71 (m, 2H), 6.69-6.62 (m, 2H), 4.04 (t, $J = 6.0\text{ Hz}$, 2H), 3.74 (t, $J = 6.0\text{ Hz}$, 2H), 3.47 (br s, 2H), 2.19 (p, $J = 6.0\text{ Hz}$, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 152.0, 139.9, 116.5, 115.7, 65.0, 41.6, 32.4.

Spectral data is in accordance with the literature report.³⁶

53. 4-(Allyloxy)aniline (28g)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

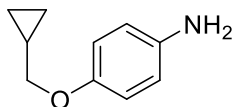
Yield = 50%; $R_f = 0.30$ (Hexanes:EtOAc = 2:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.80-6.70 (m, 2H), 6.66-6.60 (m, 2H), 6.12-5.98 (m, 1H), 5.44-5.35 (m, 1H), 5.30-5.20 (m, 1H), 4.50-4.40 (m, 2H), 3.32 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 151.7, 140.1, 133.8, 117.3, 116.3, 115.9, 69.6.

Spectral data is in accordance with the literature report.²⁵

54. 4-(Cyclopropylmethoxy)aniline (28h)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

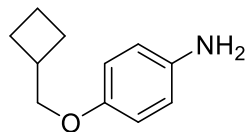
Yield = 51%; $R_f = 0.20$ (Hexanes:EtOAc = 2:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.75 (dd, $J = 6.6, 1.8\text{ Hz}$, 2H), 6.63 (dd, $J = 6.6, 2.4\text{ Hz}$, 2H), 3.72 (d, $J = 6.6\text{ Hz}$, 2H), 3.38 (br s, 2H), 1.27-1.17 (m, 1H), 0.67-0.56 (m, 2H), 0.40-0.24 (m, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 152.2, 139.8, 116.4, 115.8, 73.5, 10.4, 3.1.

Spectral data is in accordance with the literature report.³⁷

55. 4-(Cyclobutylmethoxy)aniline (28i)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

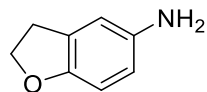
Yield = 58%; $R_f = 0.25$ (Hexanes:EtOAc = 2:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.75 (d, $J = 8.4\text{ Hz}$, 2H), 6.64 (d, $J = 8.4\text{ Hz}$, 2H), 3.86 (d, $J = 6.6\text{ Hz}$, 2H), 3.37 (br s, 2H), 2.73 (p, $J = 7.2\text{ Hz}$, 1H), 2.13 (dtd, $J = 12.6, 8.4, 4.2\text{ Hz}$, 2H), 2.04-1.76 (m, 4H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 152.5, 139.6, 116.4, 116.4, 115.8, 73.0, 34.8, 24.9, 18.6.

Spectral data is in accordance with the literature report.³⁸

56. 2,3-Dihydrobenzofuran-5-amine (28j)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

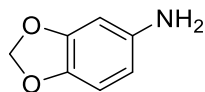
Yield = 45%; $R_f = 0.35$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.65-6.56 (m, 2H), 6.46 (dd, $J = 8.4, 2.4\text{ Hz}$, 1H), 4.49 (t, $J = 8.4\text{ Hz}$, 2H), 3.37 (br s, 2H), 3.12 (t, $J = 8.4\text{ Hz}$, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 153.1, 139.8, 127.7, 114.6, 112.6, 109.2, 70.8, 30.2.

Spectral data is in accordance with the literature report.³⁹

57. Benzo[d][1,3]dioxol-5-amine (28k)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

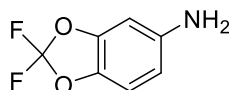
Yield = 66%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 6.62 (d, $J = 8.4\text{ Hz}$, 1H), 6.28 (d, $J = 2.4\text{ Hz}$, 1H), 6.11 (dd, $J = 8.0, 2.0\text{ Hz}$, 1H), 5.84 (s, 2H), 3.46 (br s, 2H);

¹³C NMR (100 MHz, CDCl₃): δ 148.0, 141.3, 140.1, 108.4, 106.7, 100.5, 97.9.

Spectral data is in accordance with the literature report.¹⁵

58. 2,2-Difluorobenzo[d][1,3]dioxol-5-amine (28l)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

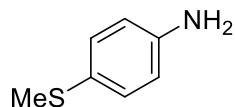
Yield = 27%; $R_f = 0.40$ (Hexanes:EtOAc = 3:1);

¹H NMR (600 MHz, CDCl₃): δ 6.81 (d, $J = 8.4\text{ Hz}$, 1H), 6.43 (d, $J = 2.4\text{ Hz}$, 1H), 6.32 (dd, $J = 8.4, 2.4\text{ Hz}$, 1H), 3.58 (br s, 2H);

¹³C NMR (151 MHz, CDCl₃): δ 144.5, 143.0, 133.4 (t, $J = 487.8\text{ Hz}$), 131.7, 109.7, 108.8, 97.7.

Spectral data is in accordance with the literature report.⁴⁰

59. 4-(Methylthio)aniline (28m)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

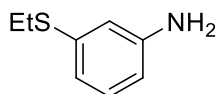
Yield = 54%; $R_f = 0.35$ (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 7.21-7.15 (m, 2H), 6.66-6.60 (m, 2H), 3.67 (br s, 2H), 2.41 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 145.0, 130.9, 125.6, 115.6, 18.7.

Spectral data is in accordance with the literature report.¹⁵

60. 3-(Ethylthio)aniline (28n)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

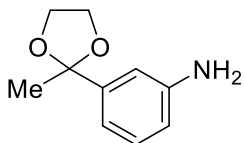
Yield = 61%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.06 (t, $J = 7.8\text{ Hz}$, 1H), 6.82-6.68 (m, 1H), 6.66 (t, $J = 2.4\text{ Hz}$, 1H), 6.49 (ddd, $J = 7.8, 2.4, 0.6\text{ Hz}$, 1H), 3.56 (br s, 2H), 2.92 (q, $J = 7.8\text{ Hz}$, 2H), 1.31 (t, $J = 7.4\text{ Hz}$, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 146.7, 137.5, 129.6, 118.9, 115.2, 112.7, 27.3, 14.4.

Spectral data is in accordance with the literature report.⁴¹

61. 3-(2-Methyl-1,3-dioxolan-2-yl)aniline (28o)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

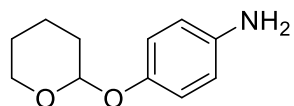
Yield = 80%; $R_f = 0.30$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.12 (t, $J = 7.8\text{ Hz}$, 1H), 6.92-6.85 (m, 1H), 6.82 (t, $J = 2.4\text{ Hz}$, 1H), 6.61 (dd, $J = 7.8, 2.4\text{ Hz}$, 1H), 4.06-3.96 (m, 2H), 3.83-3.74 (m, 2H), 3.69 (br s, 2H), 1.64 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 146.2, 144.5, 129.1, 115.5, 114.4, 112.0, 108.7, 64.3, 27.5.

Spectral data is in accordance with the literature report.⁴²

62. 4-((Tetrahydro-2H-pyran-2-yl)oxy)aniline (28p)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

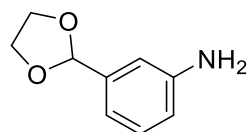
Yield = 67%; $R_f = 0.25$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.89 (d, $J = 9.0\text{ Hz}$, 2H), 6.62 (d, $J = 9.0\text{ Hz}$, 2H), 5.24 (t, $J = 3.0\text{ Hz}$, 1H), 4.00-3.90 (m, 1H), 3.62-3.55 (m, 1H), 3.54 (br s, 2H), 2.02-1.95 (m, 1H), 1.91-1.80 (m, 2H), 1.70-1.50 (m, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 150.0, 140.6, 117.9, 116.2, 97.4, 62.0, 30.4, 25.2, 18.9.

Spectral data is in accordance with the literature report.⁴³

63. 3-(1,3-Dioxolan-2-yl)aniline (28q)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

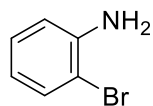
Yield = 79%; $R_f = 0.30$ (Hexanes:EtOAc = 1:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.16 (t, $J = 7.8\text{ Hz}$, 1H), 6.87 (d, $J = 7.2\text{ Hz}$, 1H), 6.81 (t, $J = 1.8\text{ Hz}$, 1H), 6.70-6.60 (m, 1H), 5.74 (s, 1H), 4.18-4.06 (m, 2H), 4.05-3.95 (m, 2H), 3.57 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 146.4, 139.0, 129.3, 116.6, 115.9, 112.8, 103.6, 65.2.

Spectral data is in accordance with the literature report.⁵

64. 2-Bromoaniline (28r)



Method B.

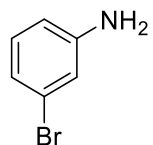
Yield = 29%; R_f = 0.40 (Hexanes:EtOAc = 5:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.41 (dd, J = 7.8, 1.2 Hz, 1H), 7.20-7.04 (m, 1H), 6.77 (d, J = 8.4 Hz, 1H), 6.63 (td, J = 7.2, 1.2 Hz, 1H), 4.01 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 144.0, 132.5, 128.3, 119.4, 115.7, 109.3.

Spectral data is in accordance with the literature report.⁶

65. 3-Bromoaniline (28s)



Method B.

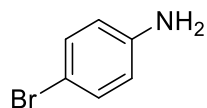
Yield = 76%; R_f = 0.35 (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.00 (t, J = 7.8 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.83 (s, 1H), 6.59 (dd, J = 7.8, 1.2 Hz, 1H), 3.69 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 147.8, 130.6, 123.0, 121.3, 117.8, 113.6.

Spectral data is in accordance with the literature report.⁵

66. 4-Bromoaniline (28t)



Method B.

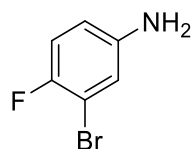
Yield = 77%; R_f = 0.35 (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.23 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 9.0 Hz, 2H), 3.59 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 145.4, 131.9, 116.6, 110.1.

Spectral data is in accordance with the literature report.⁵

67. 3-Bromo-4-fluoroaniline (28u)



Method B.

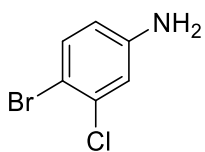
Yield = 63%; R_f = 0.30 (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.89 (t, J = 8.4 Hz, 1H), 6.86-6.81 (m, 1H), 6.59-6.50 (m, 1H), 3.58 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 152.5 (d, J = 236.6 Hz), 143.4, 119.1, 116.6 (d, J = 23.1 Hz), 115.0 (d, J = 6.6 Hz), 108.9 (d, J = 22.0 Hz).

Spectral data is in accordance with the literature report.⁴⁴

68. 4-Bromo-3-chloroaniline (28v)



Method B

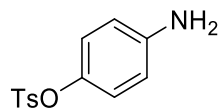
Yield = 77%; R_f = 0.30 (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.30 (d, J = 8.4 Hz, 1H), 6.76 (d, J = 3.0 Hz, 1H), 6.43 (dd, J = 8.4, 2.4 Hz, 1H), 3.74 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 146.6, 134.5, 133.8, 116.3, 114.9, 109.6.

Spectral data is in accordance with the literature report.⁴⁵

69. 4-Aminophenyl 4-methylbenzenesulfonate (28w)



Method A, T = -30 °C, t = 2 h;

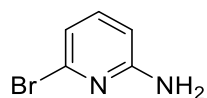
Yield = 48%; R_f = 0.25 (Hexanes:EtOAc = 2:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.67 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 6.71 (dd, J = 6.6, 1.8 Hz, 2H), 6.54-6.47 (m, 2H), 3.68 (br s, 2H), 2.43 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 145.4, 145.0, 141.5, 132.4, 129.6, 128.5, 123.1, 115.3, 21.6.

Spectral data is in accordance with the literature report.⁴⁶

70. 6-Bromopyridin-2-amine (28x)



Method D.

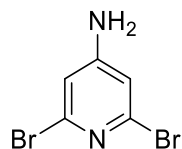
Yield = 32%; **R_f** = 0.35 (Hexanes:EtOAc = 2:1);

¹H NMR (600 MHz, DMSO-*d*₆) δ 7.26 (d, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 8.1 Hz, 1H), 6.37 (s, 2H);

¹³C NMR (151 MHz, DMSO-*d*₆) δ 160.7, 140.3, 139.9, 114.5, 107.1.

Spectral data is in accordance with the literature report.⁴⁷

71. 2,6-Dibromopyridin-4-amine (28y)



Method C, *T*₁ = 25 °C, *t*₁ = 6 min., *T*₂ = -25 °C, *t*₂ = 2 h;

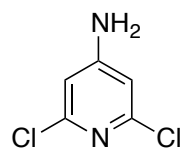
Yield = 58%; **R_f** = 0.30 (Hexanes:EtOAc = 2:1);

¹H NMR (600 MHz, CDCl₃): δ 6.67 (s, 2H), 4.33 (br s, 2H);

¹³C NMR (151 MHz, CDCl₃): δ 155.4, 140.9, 112.0.

Spectral data is in accordance with the literature report.⁴⁸

72. 2,6-Dichloropyridin-4-amine (28z)



Method C, *T*₁ = 25 °C, *t*₁ = 6 min., *T*₂ = -25 °C, *t*₂ = 2 h;

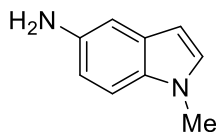
Yield = 64%; **R_f** = 0.2 (Hexanes:EtOAc = 3:1);

¹H NMR (600 MHz, DMSO-*d*₆) δ 6.76 (br s, 2H), 6.50 (s, 2H);

¹³C NMR (151 MHz, DMSO-*d*₆) δ 159.1, 149.7, 107.0.

Spectral data is in accordance with the literature report.⁴⁹

73. 1-Methyl-1H-indol-5-amine (29a)



Method B.

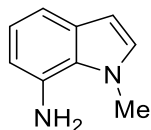
Yield = 55%; **R_f** = 0.30 (Hexanes:EtOAc = 2:1);

¹H NMR (400 MHz, CDCl₃): δ 7.18 (d, *J* = 8.8 Hz, 1H), 7.03-6.96 (m, 2H), 6.74 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.37 (d, *J* = 3.2 Hz, 1H), 3.74 (s, 3H), 3.47 (s, 2H);

¹³C NMR (100 MHz, CDCl₃): δ 139.1, 131.7, 129.2, 129.0, 112.3, 109.6, 105.5, 99.3, 32.6.

Spectral data is in accordance with the literature report.⁵⁰

74. 1-Methyl-1H-indol-7-amine (29b)



Method B.

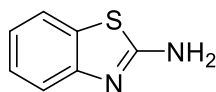
Yield = 22%; **R_f** = 0.30 (Hexanes:EtOAc = 2:1);

¹H NMR (400 MHz, CDCl₃): δ 7.18-7.14 (m, 1H), 6.95-6.88 (m, 2H), 6.49 (dd, *J* = 7.2, 0.8 Hz, 1H), 6.42 (d, *J* = 3.2 Hz, 1H), 4.10 (s, 3H), 3.66 (s, 2H);

¹³C NMR (100 MHz, CDCl₃): δ 132.6, 130.9, 130.2, 127.3, 120.2, 113.1, 109.7, 101.1, 36.2.

HRMS (ESI) *m/z* calcd for [C₉H₁₁N₂]⁺ [M+H]⁺: 147.0917, found 147.0919.

75. Benzo[*d*]thiazol-2-amine (29c)



Method C, *T*₁ = 0° C, *t*₁ = 6 min., *T*₂ = -30 °C, *t*₂ = 2 h;

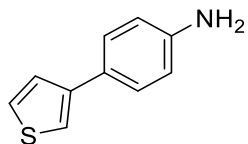
Yield = 26%; **R_f** = 0.30 (Hexanes:EtOAc = 1:1);

¹H NMR (600 MHz, CDCl₃): δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 8.4 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 5.55 (br s, 2H);

¹³C NMR (151 MHz, CDCl₃): δ 166.0, 151.8, 131.5, 126.0, 122.3, 120.9, 119.1.

Spectral data is in accordance with the literature report.³²

76. 4-(Thiophen-3-yl)aniline (29d)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$;

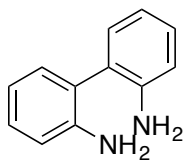
Yield = 42%; $R_f = 0.30$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.46-7.41 (m, 2H), 7.38-7.34 (m, 2H), 7.33-7.30 (m, 1H), 6.72 (dd, $J = 6.4, 2.4\text{ Hz}$, 2H), 3.70 (s, 2H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 145.5, 142.3, 127.4, 126.6, 126.1, 125.8, 118.0, 115.3.

Spectral data is in accordance with the literature report.⁵¹

77. [1,1'-biphenyl]-2,2'-diamine (29e)



Method A, $T = -78\text{ }^{\circ}\text{C}$, $t = 3\text{ h}$;

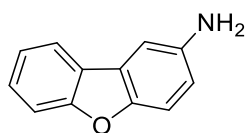
Yield = 56%; $R_f = 0.30$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.21 (t, $J = 7.7\text{ Hz}$, 2H), 7.15 (d, $J = 7.5\text{ Hz}$, 2H), 6.87 (t, $J = 7.4\text{ Hz}$, 2H), 6.80 (d, $J = 7.9\text{ Hz}$, 2H), 3.80 (s, 4H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 143.9, 130.9, 128.7, 124.6, 118.8, 115.6.

Spectral data is in accordance with the literature report.⁵²

78. Dibenzo[b,d]furan-2-amine (29f)



Method E, $T = -45\text{ }^{\circ}\text{C}$;

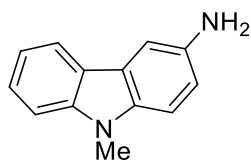
Yield = 36%; $R_f = 0.30$ (Hexanes:EtOAc = 2:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.86 (d, $J = 7.2$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.43 (td, $J = 7.2, 1.2$ Hz, 1H), 7.37 (d, $J = 8.4$ Hz, 1H), 7.30 (td, $J = 7.2, 0.6$ Hz, 1H), 7.22 (d, $J = 2.4$ Hz, 1H), 6.82 (dd, $J = 8.4, 2.4$ Hz, 1H), 3.57 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 156.7, 150.3, 142.0, 126.9, 124.8, 124.2, 122.2, 120.5, 115.7, 111.8, 111.6, 105.9.

HRMS (ESI) m/z calcd for $[\text{C}_{12}\text{H}_{10}\text{NO}]^+ [\text{M}+\text{H}]^+$: 184.0757, found 184.0762.

79. 9-Methyl-9H-carbazol-3-amine (29g)



Method D.

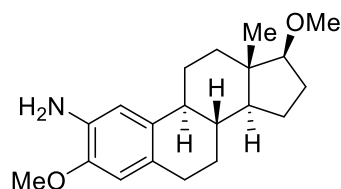
Yield = 18%; $R_f = 0.30$ (Hexanes:EtOAc = 2:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 8.00 (d, $J = 7.8$ Hz, 1H), 7.49-7.49 (m, 2H), 7.34 (d, $J = 8.4$ Hz, 1H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.17 (t, $J = 7.2$ Hz, 1H), 6.93 (dd, $J = 8.4, 1.8$ Hz, 1H), 3.79 (s, 3H), 3.31 (br s, 2H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 141.4, 138.9, 135.7, 125.5, 123.5, 122.3, 120.2, 118.1, 115.6, 108.9, 108.3, 106.2, 29.1.

Spectral data is in accordance with the literature report.⁵³

80. (8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-Dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-2-amine (29h)



Method E, $T = -45\text{ }^{\circ}\text{C}$;

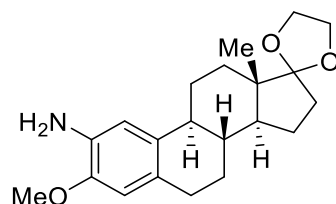
Yield = 25%; $R_f = 0.25$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.69 (s, 1H), 6.51 (s, 1H), 3.82 (s, 3H), 3.54 (br s, 2H), 3.38 (s, 3H), 3.31 (t, $J = 8.4$ Hz, 1H), 2.85-2.70 (m, 2H), 2.27-2.16 (m, 1H), 2.15-2.11 (m, 1H), 2.10-2.00 (m, 2H), 1.93-1.82 (m, 1H), 1.74-1.65 (m, 1H), 1.60-1.25 (m, 6H), 1.24-1.15 (m, 1H), 0.79 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 145.6, 133.6, 132.5, 126.5, 112.4, 111.0, 90.8, 57.9, 55.5, 50.3, 44.0, 43.2, 38.7, 38.1, 29.2, 27.8, 27.5, 26.5, 23.0, 11.5.

Spectral data is in accordance with the literature report.⁵⁴

81. (8*R*,9*S*,13*S*,14*S*)-3-Methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-2-amine (29i)



Method E, $T = -45\text{ }^{\circ}\text{C}$;

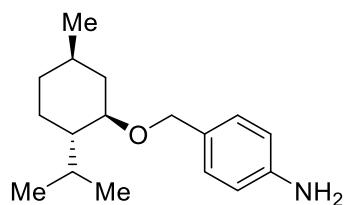
Yield = 32%; $R_f = 0.50$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.69 (s, 1H), 6.51 (s, 1H), 4.01-3.86 (m, 4H), 3.82 (s, 3H), 3.42 (br s, 2H), 2.85-2.72 (m, 2H), 2.29-2.16 (m, 2H), 2.08-1.98 (m, 1H), 1.92-1.81 (m, 2H), 1.80-1.71 (m, 2H), 1.68-1.59 (m, 1H), 1.57-1.50 (m, 1H), 1.50-1.29 (m, 4H), 0.89 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 145.6, 133.6, 132.5, 126.6, 119.4, 112.4, 111.0, 65.2, 64.5, 55.5, 49.3, 46.1, 43.7, 39.1, 34.2, 30.8, 29.2, 27.2, 26.2, 22.3, 14.3;

HRMS (ESI) m/z calcd for $[\text{C}_{21}\text{H}_{30}\text{NO}_3]^+$ $[\text{M}+\text{H}]^+$: 344.2220, found 344.2217.

82. 4-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)aniline (29j)



Method A, $T = -78\text{ }^{\circ}\text{C}$;

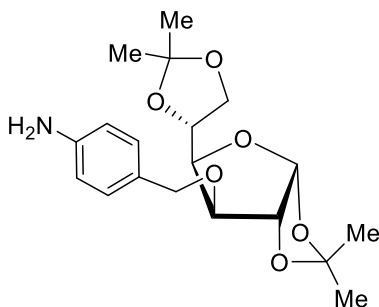
Yield = 73%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.15 (d, $J = 7.8$ Hz, 2H), 6.65 (d, $J = 7.8$ Hz, 2H), 4.55 (d, $J = 10.8$ Hz, 1H), 4.30 (d, $J = 10.2$ Hz, 1H), 3.65 (br s, 2H), 3.17-3.14 (m, 1H), 2.35-2.25 (m, 1H), 2.24-2.16 (m, 1H), 1.72-1.60 (m, 2H), 1.45-1.33 (m, 1H), 1.32-1.25 (m, 1H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.91 (d, $J = 7.2$ Hz, 3H), 1.05-0.85 (m, 3H), 0.72 (d, $J = 7.2$ Hz, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 145.6, 129.3, 129.0, 114.9, 78.0, 70.2, 48.2, 40.2, 34.5, 31.4, 25.3, 23.2, 22.3, 20.9, 15.9;

HRMS (ESI) m/z calcd for $[\text{C}_{17}\text{H}_{28}\text{NO}]^+ [\text{M}+\text{H}]^+$: 262.2165, found 262.2160.

83. 4-((((3aR,5R,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)methyl)aniline (29k)



Method A, $T = -78\text{ }^{\circ}\text{C}$;

Yield = 54%; $R_f = 0.25$ (Hexanes:EtOAc = 3:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.12 (d, $J = 8.1$ Hz, 2H), 6.65 (d, $J = 8.2$ Hz, 2H), 5.87 (d, $J = 3.7$ Hz, 1H), 4.55-4.48 (m, 3H), 4.33 (q, $J = 6.4$ Hz, 1H), 4.18-4.12 (m, 1H), 4.12-4.06 (m, 1H), 4.00-3.96 (m, 2H), 3.68 (br s, 2H), 1.48 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H);

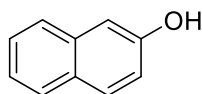
$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 146.2, 129.4, 127.4, 114.9, 111.7, 108.8, 105.3, 82.8, 81.3, 81.1, 72.6, 72.4, 67.3, 26.8, 26.7, 26.2, 25.4;

HRMS (ESI) m/z calcd for $[\text{C}_{19}\text{H}_{27}\text{NO}_6\text{Na}]^+ [\text{M}+\text{Na}]^+$: 388.1736, found 388.1726.

Hydroxylation of arylmetals:

To a flame-dried 25 mL round bottom flask was charged Activated Mg (7.5 mmol, 1.5 eq.) and 5 mL anhydrous THF. To this suspension was added 2 drops of 1,2-dibromoethane. After 5 min, a solution of Aryl bromide (5 mmol, 1.0 eq.) in 5 mL anhydrous THF was slowly added to the suspension of Mg at room temperature. The reaction was mildly exothermic. The Grignard reagent was titrated and 1 mmol of this reagent was added to a flame-dried reaction vial. The solution was diluted with 3 mL anhydrous THF and after cooling to 0 °C in an ice bath, a solution of oxaziridine (1.5 mmol, 1.5 eq.) in 1 mL anhydrous THF was added. The ice bath was removed and the reaction was allowed to reach room temperature. After time t , the reaction was quenched with saturated aqueous NH_4Cl . The reaction mixture was diluted with 20 mL saturated aqueous NaCl and 20 mL EtOAc. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 20mL). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified with flash chromatography.

84. Naphthalen-2-ol (33a)



$t = 2$ h.

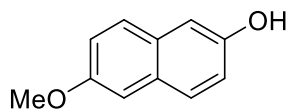
Yield = 86%; **R_f** = 0.40 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl_3): δ 7.85-7.72 (m, 2H), 7.68 (d, $J = 8.4$, 1H), 7.45 (td, $J = 8.4$, 1.2 Hz, 1H), 7.35 (td, $J = 8.4$, 1.2 Hz, 1H), 7.20-7.10 (m, 2H), 5.74 (br s, 1H);

¹³C NMR (100 MHz, CDCl_3): δ 153.3, 134.5, 129.8, 128.9, 127.7, 126.5, 126.3, 123.6, 117.7, 109.5.

Spectral data is in accordance with the literature report.⁵⁵

85. 6-Methoxynaphthalen-2-ol (33b)



$t = 4$ h.

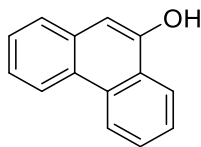
Yield = 75%; **R_f** = 0.30 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl_3): δ 7.65 (d, $J = 8.4$ Hz, 1H), 7.59 (d, $J = 8.8$ Hz, 1H), 7.15-7.05 (m, 4H), 3.90 (s, 3H);

¹³C NMR (100 MHz, CDCl_3): δ 156.1, 151.7, 129.8, 129.7, 128.5, 127.8, 119.3, 118.0, 109.7, 106.0, 55.3.

Spectral data is in accordance with the literature report.⁵⁶

86. Phenanthren-9-ol (33c)



$t = 4$ h.

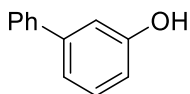
Yield = 57%; **R_f** = 0.30 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 8.71-8.67 (m, 1H), 8.63-8.59 (m, 1H), 8.35-8.30 (m, 1H), 7.74-7.63 (m, 3H), 7.57-7.49 (m, 2H), 7.01 (s, 1H), 5.33 (br s, 1H);

¹³C NMR (100 MHz, CDCl₃): δ 149.4, 132.6, 131.5, 127.2, 126.9, 126.7, 126.4, 125.5, 124.3, 122.7, 122.6, 122.3, 106.11, 106.08.

Spectral data is in accordance with the literature report.⁵⁷

87. [1,1'-Biphenyl]-3-ol (33d)



$t = 2$ h.

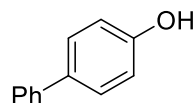
Yield = 78%; **R_f** = 0.35 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 7.62-7.58 (m, 2H), 7.49-7.43 (m, 2H), 7.42-7.31 (m, 2H), 7.25-7.20 (m, 1H), 7.13 (t, $J = 2.0$ Hz, 1H), 6.91-6.86 (m, 1H), 5.41 (br s, 1H);

¹³C NMR (100 MHz, CDCl₃): δ 155.8, 143.0, 140.7, 130.1, 128.8, 127.5, 127.2, 119.8, 114.4, 114.2.

Spectral data is in accordance with the literature report.⁵⁸

88. [1,1'-Biphenyl]-4-ol (33e)



$t = 2$ h.

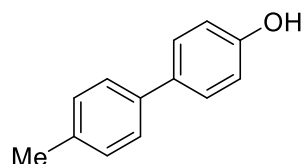
Yield = 79%; **R_f** = 0.40 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 7.57-7.53 (m, 2H), 7.49 (dd, $J = 6.8, 2.4$ Hz, 2H), 7.45-7.40 (m, 2H), 7.35-7.28 (m, 1H), 6.92 (dd, $J = 6.4, 2.0$ Hz, 2H);

¹³C NMR (100 MHz, CDCl₃): δ 155.0, 140.7, 134.0, 128.7, 128.4, 126.7 (2C), 115.6.

Spectral data is in accordance with the literature report.⁵⁵

89. 4'-Methyl-[1,1'-biphenyl]-4-ol (33f)



$t = 2$ h.

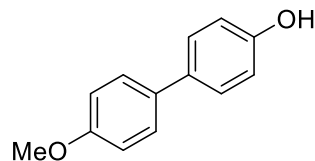
Yield = 61%; **R_f** = 0.35 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 7.49-7.43 (m, 4H), 7.23 (d, $J = 8.8$ Hz, 2H), 6.89 (dd, $J = 6.8, 2.0$ Hz, 2H), 2.39 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 154.8, 137.9, 136.4, 134.0, 129.4, 128.2, 126.5, 115.6, 21.0.

Spectral data is in accordance with the literature report.⁵⁹

90. 4'-Methoxy-[1,1'-biphenyl]-4-ol (33g)



$t = 2$ h.

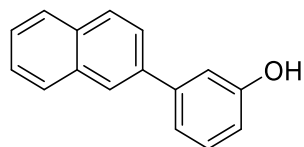
Yield = 66%; **R_f** = 0.40 (Hexanes:EtOAc = 3:1);

¹H NMR (600 MHz, CDCl₃): δ 7.47 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 6.96 (d, $J = 8.4$ Hz, 2H), 6.88 (d, $J = 8.4$ Hz, 2H), 3.85 (s, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 158.7, 154.6, 133.8, 133.4, 128.0, 127.7, 115.6, 114.2, 55.3.

Spectral data is in accordance with the literature report.⁵⁸

91. 3-(Naphthalen-2-yl)phenol (33h)



$t = 2$ h.

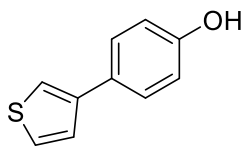
Yield = 64%; **R_f** = 0.35 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 8.03 (d, $J = 1.2$ Hz, 1H), 7.93-7.85 (m, 3H), 7.72 (dd, $J = 8.8$, 2.0 Hz, 1H), 7.56-7.48 (m, 2H), 7.41-7.30 (m, 2H), 7.21 (t, $J = 2.0$ Hz, 1H), 6.91-6.85 (m, 1H), 5.24 (br s, 1H);

¹³C NMR (100 MHz, CDCl₃): δ 155.8, 142.9, 138.0, 133.6, 132.7, 130.1, 128.4, 128.2, 127.6, 126.3, 126.0, 125.8, 125.4, 120.0, 114.32, 114.30.

Spectral data is in accordance with the literature report.⁶⁰

92. 4-(Thiophen-3-yl)phenol (33i)



$t = 2$ h.

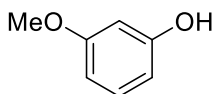
Yield = 31%; **R_f** = 0.30 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 7.48 (dd, $J = 6.8, 2.0$ Hz, 2H), 7.39-7.31 (m, 3H), 6.86 (dd, $J = 6.4, 2.0$ Hz, 2H), 4.87 (br s, 1H);

¹³C NMR (100 MHz, CDCl₃): δ 154.8, 141.9, 129.0, 127.8, 126.2, 126.1, 119.0, 115.6.

Spectral data is in accordance with the literature report.⁶¹

93. 3-Methoxyphenol (33j)



$t = 3$ h.

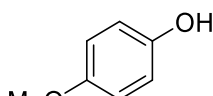
Yield = 75%; **R_f** = 0.35 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 7.14 (t, $J = 8.0$ Hz, 1H), 6.54-6.43 (m, 3H), 5.84 (br s, 1H), 3.78 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 160.7, 156.7, 130.2, 107.9, 106.4, 101.5, 55.3.

Spectral data is in accordance with the literature report.⁵⁵

94. 4-Methoxyphenol (33k)



$t = 2$ h.

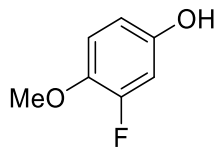
Yield = 65%; **R_f** = 0.35 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 6.82-6.75 (m, 4H), 5.46 (br s, 1H), 3.77 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 153.5, 149.5, 116.1, 114.9, 55.9.

Spectral data is in accordance with the literature report.⁵⁵

95. 3-Fluoro-4-methoxyphenol (33l)



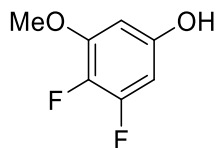
Yield = 46%; **R_f** = 0.40 (Hexanes:EtOAc = 2:1);

¹H NMR (600 MHz, CDCl₃): δ 6.83 (t, *J* = 9.0 Hz, 1H), 6.64 (dd, *J* = 12.6, 3.0 Hz, 1H), 6.58-6.50 (m, 1H), 5.68 (br s, 1H), 3.83 (s, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 152.8 (d, *J* = 245.7 Hz), 149.9 (d, *J* = 10.0 Hz), 141.5 (d, *J* = 11.0 Hz), 115.2 (d, *J* = 3.3 Hz), 110.4 (d, *J* = 3.3 Hz), 104.7 (d, *J* = 20.8 Hz), 57.3.

Spectral data is in accordance with the literature report.⁶²

96. 3,4-Difluoro-5-methoxyphenol (33m)



t = 2 h.

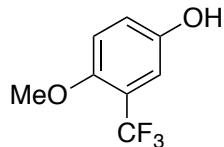
Yield = 35%; **R_f** = 0.25 (Hexanes:EtOAc = 1:1);

¹H NMR (600 MHz, CDCl₃): δ 6.30-6.18 (m, 2H), 5.23 (br s, 1H), 3.85 (s, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 151.2 (dd, *J* = 244.5, 11.0 Hz), 151.1 (dd, *J* = 12.2, 3.3 Hz), 149.4 (dd, *J* = 8.9, 5.6 Hz), 136.2 (dd, *J* = 238.9, 14.2 Hz), 96.7 (d, *J* = 2.1 Hz), 96.3 (d, *J* = 21.0 Hz), 56.6.

HRMS (ESI) *m/z* calcd for [C₇H₅F₂O₂]⁻ [M-H]⁻: 159.0263, found 159.0267.

97. 4-methoxy-3-(trifluoromethyl)phenol (33n)



$t = 2$ h.

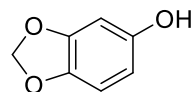
Yield = 37%; **R_f** = 0.35 (Hexanes:EtOAc = 3:1);

¹H NMR (600 MHz, CDCl₃): δ 7.06 (d, $J = 3.0$ Hz, 1H), 6.96 (dd, $J = 9.0, 3.0$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 3.84 (s, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 151.6 (q, $J = 2.3$ Hz), 148.7, 123.2 (q, $J = 272.0$ Hz), 119.6, 119.5 (q, $J = 28.5$ Hz), 114.3 (q, $J = 5.4$ Hz), 113.9, 56.6.

HRMS (ESI) m/z calcd for [C₈H₆F₃O₂]⁻ [M-H]⁻: 191.0325, found 191.0333.

98. Benzo[d][1,3]dioxol-5-ol (33o)



$t = 2$ h.

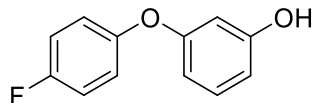
Yield = 63%; **R_f** = 0.30 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 6.65 (d, $J = 8.4$ Hz, 1H), 6.43 (d, $J = 2.8$ Hz, 1H), 6.26 (dd, $J = 8.0, 2.8$ Hz, 1H), 5.90 (s, 2H), 5.56 (br s, 1H);

¹³C NMR (100 MHz, CDCl₃): δ 150.4, 148.1, 141.5, 108.2, 106.7, 101.1, 98.3.

Spectral data is in accordance with the literature report.⁶³

99. 3-(4-Fluorophenoxy)phenol (33p)



$t = 2$ h.

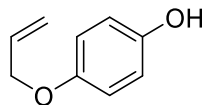
Yield = 65%; **R_f** = 0.35 (Hexanes:EtOAc = 5:1);

¹H NMR (600 MHz, CDCl₃): δ 7.16 (t, $J = 8.4$ Hz, 1H), 7.08-6.94 (m, 4H), 6.56 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.53 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.46 (t, $J = 2.4$ Hz, 1H), 5.19 (br s, 1H);

¹³C NMR (151 MHz, CDCl₃): δ 159.4 (d, $J = 101.9$ Hz), 158.2, 156.9, 152.4 (d, $J = 3.2$ Hz), 130.4, 120.9 (d, $J = 7.7$ Hz), 116.3 (d, $J = 23.1$ Hz), 110.3, 110.1, 105.4.

Spectral data is in accordance with the literature report.⁶⁴

100. 4-(Allyloxy)phenol (33q)



$t = 2$ h.

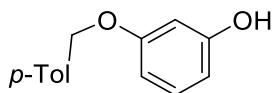
Yield = 63%; **R_f** = 0.30 (Hexanes:EtOAc = 4:1);

¹H NMR (600 MHz, CDCl₃): δ 6.86-6.78 (m, 2H), 6.77-6.71 (m, 2H), 6.10-6.00 (m, 1H), 5.40 (dq, $J = 17.4, 1.8$ Hz, 1H), 5.27 (dq, $J = 10.2, 1.8$ Hz, 1H), 4.48 (dt, $J = 6.0, 1.8$ Hz, 2H);

¹³C NMR (151 MHz, CDCl₃): δ 152.6, 149.7, 133.4, 117.6, 116.0, 116.0, 69.7.

Spectral data is in accordance with the literature report.⁶⁵

101. 3-((4-Methylbenzyl)oxy)phenol (33r)



$t = 2$ h.

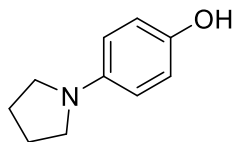
Yield = 51%; **R_f** = 0.40 (Hexanes:EtOAc = 4:1);

¹H NMR (600 MHz, CDCl₃): δ 7.32 (d, $J = 7.8$ Hz, 2H), 7.21 (d, $J = 7.8$ Hz, 2H), 7.14 (t, $J = 8.4$ Hz, 1H), 6.61-6.56 (m, 1H), 6.49 (t, $J = 2.4$ Hz, 1H), 6.46-6.41 (m, 1H), 5.04 (br s, 1H), 4.99 (s, 2H), 2.38 (s, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 160.1, 156.6, 137.7, 133.8, 130.1, 129.2, 127.6, 108.0, 107.4, 102.5, 70.0, 21.2.

Spectral data is in accordance with the literature report.⁶⁶

102. 4-(Pyrrolidin-1-yl)phenol (33s)



$t = 2$ h.

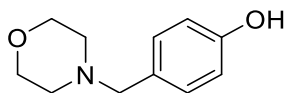
Yield = 54%; **R_f** = 0.35 (Hexanes:EtOAc = 3:1);

¹H NMR (600 MHz, Acetone-d₆) δ 7.41 (s, 1H), 6.73 (d, $J = 6.6$ Hz, 2H), 6.46 (d, $J = 8.4$ Hz, 2H), 3.39-3.09 (m, 4H), 2.02-1.86 (m, 4H);

¹³C NMR (151 MHz, Acetone-d₆) δ 148.1, 142.6, 115.8, 112.8, 48.0, 25.0.

Spectral data is in accordance with the literature report.⁶⁷

103. 4-(Morpholinomethyl)phenol (33t)



$t = 2$ h.

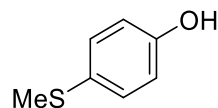
Yield = 76%; **R_f** = 0.20 (100% EtOAc);

¹H NMR (600 MHz, Acetone-d₆) δ 8.28 (s, 1H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H), 3.61 (t, $J = 4.8$ Hz, 4H), 3.38 (s, 2H), 2.51-2.23 (m, 4H);

¹³C NMR (151 MHz, Acetone-d₆) δ 156.5, 130.3, 128.8, 115.0, 66.6, 62.6, 53.5.

Spectral data is in accordance with the literature report.⁶⁸

104. 4-(Methylthio)phenol (33u)



t = 2 h.

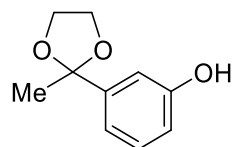
Yield = 63%; **R_f** = 0.35 (Hexanes:EtOAc = 4:1);

¹H NMR (400 MHz, CDCl₃): δ 7.21 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.42 (s, 1H), 2.44 (s, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 153.9, 130.3, 128.7, 116.1, 17.9.

Spectral data is in accordance with the literature report.⁶⁹

105. 3-(2-Methyl-1,3-dioxolan-2-yl)phenol (33v)



t = 2 h.

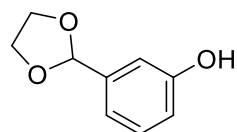
Yield = 64%; **R_f** = 0.45 (Hexanes:EtOAc = 3:1);

¹H NMR (600 MHz, CDCl₃): δ 7.22 (t, *J* = 7.8 Hz, 1H), 7.08-7.00 (m, 2H), 6.83-6.75 (m, 1H), 6.21 (s, 1H), 4.11-3.99 (m, 2H), 3.85-3.75 (m, 2H), 1.67 (s, 3H);

¹³C NMR (151 MHz, CDCl₃): δ 155.8, 144.8, 129.7, 117.4, 114.9, 112.3, 108.9, 64.4, 27.4.

Spectral data is in accordance with the literature report.⁷⁰

106. 3-(1,3-Dioxolan-2-yl)phenol (33w)



t = 2 h.

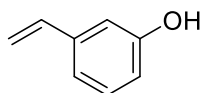
Yield = 73%; **R_f** = 0.45 (Hexanes:EtOAc = 3:1);

¹H NMR (600 MHz, CDCl₃): δ 7.20 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.91 (s, 1H), 6.77 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.40 (br s, 1H), 5.77 (s, 1H), 4.17-4.06 (m, 2H), 4.05-3.92 (m, 2H);

¹³C NMR (151 MHz, CDCl₃): δ 155.8, 139.2, 129.7, 118.7, 116.4, 113.2, 103.4, 65.2.

Spectral data is in accordance with the literature report.⁷¹

107. 3-Vinylphenol (33x)



$t = 2$ h.

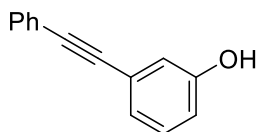
Yield = 39%; $R_f = 0.25$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.22 (t, $J = 8.0$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.92 (d, $J = 1.2$ Hz, 1H), 6.78 (dd, $J = 8.0, 0.8$ Hz, 1H), 6.67 (dd, $J = 17.6, 11.2$ Hz, 1H), 5.73 (d, $J = 17.6$ Hz, 1H), 5.32 (br s, 1H), 5.27 (d, $J = 11.2$ Hz, 1H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.5, 139.3, 136.4, 129.7, 119.1, 114.9, 114.3, 112.8.

Spectral data is in accordance with the literature report.⁷²

108. 3-(Phenylethynyl)phenol (33y)



$t = 2$ h.

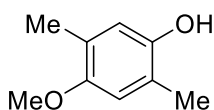
Yield = 39%; $R_f = 0.25$ (Hexanes:EtOAc = 5:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.60-7.52 (m, 2H), 7.41-7.34 (m, 3H), 7.24 (t, $J = 8.0$ Hz, 1H), 7.15 (d, $J = 7.2$ Hz, 1H), 7.08-7.00 (m, 1H), 6.85 (dd, $J = 8.0, 2.0$ Hz, 1H), 5.28 (br s, 1H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 155.2, 131.6, 129.7, 128.3(2C), 124.43, 124.37, 123.0, 118.2, 115.8, 89.4, 88.9.

Spectral data is in accordance with the literature report.⁷³

109. 4-Methoxy-2,5-dimethylphenol (33z)



$t = 2$ h.

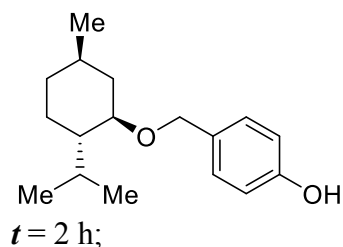
Yield = 40%; $R_f = 0.30$ (Hexanes:EtOAc = 4:1);

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.61 (s, 1H), 6.59 (s, 1H), 4.41 (br s, 1H), 3.78 (s, 3H), 2.23 (s, 3H), 2.16 (s, 3H);

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ 151.7, 147.1, 125.1, 121.1, 117.6, 113.4, 56.1, 15.8, 15.7.

Spectral data is in accordance with the literature report.²¹

110. 4-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methylphenol (34a)



Yield = 79%; **R_f** = 0.40 (Hexanes:EtOAc = 4:1);

¹H NMR (600 MHz, CDCl₃): δ 7.17 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 4.59 (d, *J* = 11.4 Hz, 1H), 4.35 (d, *J* = 11.4 Hz, 1H), 3.25-3.15 (m, 1H), 2.35-2.25 (m, 1H), 2.24-2.16 (m, 1H), 1.72-1.58 (m, 2H), 1.45-1.33 (m, 1H), 1.32-1.25 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H), 1.02-0.80 (m, 3H), 0.70 (d, *J* = 6.6 Hz, 3H);

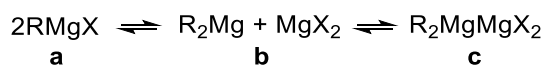
¹³C NMR (151 MHz, CDCl₃): δ 155.6, 130.1, 129.8, 115.4, 78.6, 70.3, 48.0, 40.2, 34.4, 31.5, 25.4, 23.1, 22.3, 20.9, 15.9;

HRMS (ESI) *m/z* calcd for [C₁₇H₂₅O₂]⁻ [M-H]⁻: 261.1860, found 261.1868.

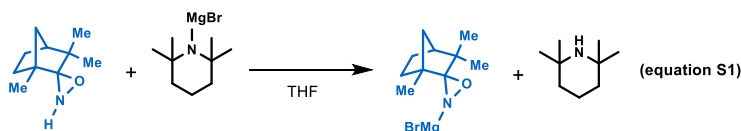
Computational Details

All ground-state and transition-state geometries were optimized in Gaussian 09 using the M06-2X density functional with an ultrafine integration grid. Stationary points were confirmed to be either minima or transition-state structures by calculation and visualization of vibrational frequencies. Intrinsic reaction coordinate (IRC) calculations were used to verify transition states. For geometries, the 6-31+G(d,p) basis set was used for all atoms, including Mg, except for Br that used the LANL2DZ pseudopotential and basis set. All optimizations were carried out in the SMD continuum model for THF. M06-2X/def2-TZVP and ω B97X-D/def2-TZVP electronic energies were calculated in THF solvent using the M06-2X/6-31+G(d,p)[LANL2DZ] geometries.⁷⁴ Free energies and enthalpies reported refer to M06-2X/def2-TZVP//M06-2X/6-31+G(d,p)[LANL2DZ] or ω B97X-D/def2-TZVP//M06-2X/6-31+G(d,p)[LANL2DZ] where zero-point energy, thermal, and entropy corrections are used from the M06-2X/6-31+G(d,p)[LANL2DZ] geometries. 3D structures were generated using CYLview.⁷⁵

The exact solution structure of phenylmagnesium bromide is dictated by solvent, temperature, and reaction conditions. It is generally assumed at low temperatures in THF there is an equilibrium between solvent-coordinated mononuclear species (**a**), solvent-coordinated Schlenk species (**b**), and several potential dinuclear bridging species (**c**).^{76–82} Under the assumption of fast equilibrium (Curtin–Hammett) the lowest energy transition states identified for amination results from bridging species where phenyl groups bridge between two Mg centers – a dinuclear phenylmagnesium bromide model was adopted in all reported calculations. Calculation of amination, proton transfer, and hydroxylation transition states with a monomeric phenylmagnesium bromide model (xyz coordinates also given below) does not reproduce experiment. With PhMgBr the proton transfer is significantly favored over amination. This is likely due to the inability of a monomeric model to replicate coordination stabilization of the N and O atoms simultaneously.



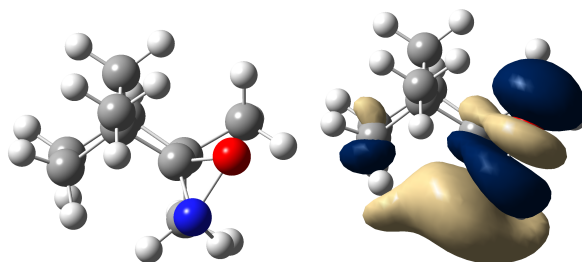
To estimate the pK_a of **18**, we used the known pK_a value for 2,2,6,6-tetramethylpiperidine (TMP) in THF as a reference.⁸³ Equation S1 was used to calculate the pK_a of **18** with relative stabilities of MgBr-coordinated anions. Without the use of MgBr, the pK_a estimate of **18** drops to ~26.



Supplementary Figure 7. Estimate the pK_a of **18**

To estimate the N–O bond energy in **18**, the N–O bond was constrained at increasing increments until intramolecular rearrangement to the amide occurred. The bond energy was taken at the point prior to this rearrangement where the N–O bond has a length of 2.21 Å. The S^2 value for this structure is 0.85, indicating a nearly complete open-shell singlet and broken bond. Spin-projection lowers the bond energy by 3.9 kcal/mol.⁸⁴

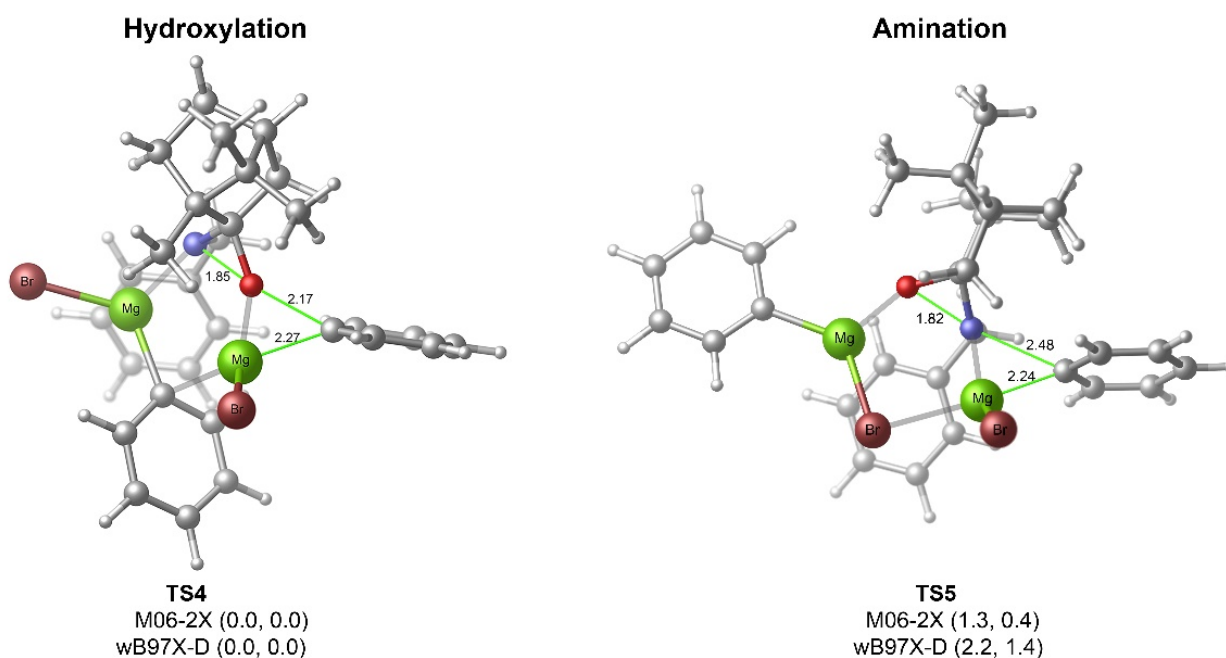
Below is a picture of the LUMO of **18** showing the σ^* orbital for M06-2X/3-21G//M06-2X//6-31+G(d,p). The 3-21G basis set is used to eliminate diffuse functions.



Supplementary Figure 8. LUMO of **18**

Previous studies have shown that transition states of nucleophilic addition to oxaziridines can exhibit radical character,^{85–87} therefore we tested the wavefunction stability (stable=opt in Gaussian) of reported transition-state structures. **TS1** and **TS2** have stable wavefunctions and have no radical character. **TS3** showed a UHF instability with $S^2 = \sim 0.2$ and has a minor amount of radical character. However, re-calculation of the UM06-2X **TS3** wavefunction as an open-shell singlet by mixing the HOMO and LUMO in the initial guess did not lead to a lower energy wavefunction.

The figure below shows the hydroxylation and amination transition states for oxaziridine **19b**. Without the NBn group amination is favored by > 10 kcal/mol. But for **19b**, the M06-2X/def2-TZVP free energy barrier for hydroxylation is favored by 1.3 kcal/mol over the amination transition state. With wB97X-D/def2-TZVP the hydroxylation transition state is predicted to be favored by 2.2 kcal/mol.



Supplementary Figure 9. 3-D illustration of **TS4** (hydroxylation) and **TS5** (amination).

XYZ coordinates and thermochemistry (in Hartree and Å)

18

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -521.09950107

Electronic and Zero-Point Energy = -520.844542

Enthalpy = -520.831948

Free Energy = -520.88063700

M06-2X/def2-TZVP

Electronic Energy = -521.1745433

C	-1.33133700	1.10302600	-0.95981400
C	-1.26491600	0.00748000	0.13518500
C	0.45545500	1.41002800	0.63340200
C	-0.23829700	2.12490500	-0.54042900
H	-1.15946600	0.67594700	-1.95466300
H	-2.32748500	1.55680600	-0.96573500
H	0.44117900	2.39147600	-1.35294600
H	-0.69455100	3.05231200	-0.18073200
C	-0.76973300	0.81279200	1.35279700
H	-0.52631200	0.17595000	2.20970600
H	-1.48984200	1.57524000	1.66900000
C	-0.00054100	-0.79166000	-0.15875300
C	1.20387200	0.13795700	0.13073900
H	1.10429200	2.05725000	1.23080300
C	-2.51992900	-0.82543100	0.28644900
H	-3.37735100	-0.17876100	0.50041600
H	-2.73228300	-1.37914500	-0.63476700
H	-2.42110700	-1.54979000	1.10010900
C	2.08942000	-0.44238600	1.23740500
H	2.49695000	-1.41341500	0.94045300
H	2.92766100	0.23701300	1.42740300
H	1.54373800	-0.58192500	2.17511800
C	2.06154700	0.37897100	-1.11525600
H	2.74086200	1.22254800	-0.94797000
H	2.67977100	-0.49816700	-1.33725400
H	1.46074500	0.59717600	-2.00354400
N	-0.02207700	-1.78286900	-1.18924700
O	0.05472200	-2.12958100	0.24565300
H	0.93672700	-1.91787300	-1.52624000

(PhMgBr)₂

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -889.66743563

Electronic and Zero-Point Energy = -889.484122

Enthalpy = -889.465265

Free Energy = -889.536643

M06-2X/def2-TZVP

Electronic Energy = -6011.99159

Mg	1.80327900	-0.01194500	-0.35822200
C	3.89456000	-0.00080700	-0.35622300
C	4.63984300	-0.01064700	-1.55189100
C	4.63888900	0.01881900	0.83990900
C	6.03770000	-0.00082900	-1.55979400
H	4.12831900	-0.02653900	-2.51320300
C	6.03673700	0.02821300	0.84869600
H	4.12657500	0.02778500	1.80088700
C	6.74133900	0.01852100	-0.35532600
H	6.57680400	-0.00861400	-2.50383100
H	6.57507500	0.04340400	1.79308300
H	7.82785800	0.02596900	-0.35497800
Br	0.00726600	-1.90029800	-0.43860400
Br	-0.00744500	1.86290200	-0.29172900
Mg	-1.80345500	-0.02545000	-0.37211200
C	-3.89473700	-0.03658700	-0.37411100
C	-4.63906300	-0.05625500	-1.57024400
C	-4.64002200	-0.02669800	0.82155500
C	-6.03691100	-0.06564300	-1.57903400
H	-4.12674600	-0.06526100	-2.53122100
C	-6.03787900	-0.03651000	0.82945600
H	-4.12849900	-0.01077100	1.78286800
C	-6.74151600	-0.05590200	-0.37501300
H	-6.57524800	-0.08086800	-2.52342100
H	-6.57698500	-0.02868700	1.77349100
H	-7.82803400	-0.06334500	-0.37536200

TS1

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1410.704861

Electronic and Zero-Point Energy = -1410.259729

Enthalpy = -1410.229557

Free Energy = -1410.321653

M06-2X/def2-TZVP

Electronic Energy = -6533.189692

C	-3.60640700	-0.87393200	-1.28979600
C	-2.19538000	-1.25777800	-1.80772600
C	-2.78294800	-2.95978800	-0.42475400
C	-4.06621900	-2.11536000	-0.48076300
H	-3.57858300	0.04077600	-0.68599100
H	-4.26132100	-0.67974600	-2.14498300
H	-4.47440100	-1.86612000	0.50068000
H	-4.83847900	-2.66805800	-1.02455200

C	-2.28471800	-2.79555900	-1.87263000
C	-1.21955800	-1.15225000	-0.62699800
C	-1.67706400	-2.22845500	0.40268700
C	-0.54100200	-3.20441000	0.72421500
C	-2.20188900	-1.61975300	1.70180300
H	-2.93457900	-3.98544600	-0.07710000
H	-3.01398600	-3.13533000	-2.61514800
H	-1.31788900	-3.26616700	-2.07894500
O	0.12303700	-1.16070400	-1.00614800
N	-0.75359000	0.17076700	-0.20823400
H	-0.82473900	0.75839700	-1.04782800
C	-1.76745600	-0.52050400	-3.06185400
H	-0.74611800	-0.77942600	-3.35437000
H	-2.43935700	-0.78062800	-3.88575900
H	-1.83304400	0.56859900	-2.93571300
C	-4.52606500	3.17445000	0.25799900
C	-4.26579500	2.41582200	1.40169200
H	-3.73380800	3.91470600	-1.60630000
C	-3.53801300	3.32332000	-0.71596000
C	-3.02662000	1.79102600	1.55851200
C	-2.01282300	1.92272300	0.59281700
C	-2.30054800	2.69838300	-0.54417100
H	-2.85598600	1.19909900	2.45616600
H	-1.54705400	2.82499000	-1.32435500
Mg	0.09267000	1.57854500	1.15093400
Mg	1.71956900	-0.47785800	-0.00272700
H	-0.13991400	-3.68802500	-0.17087800
H	0.28593900	-2.70762700	1.24180100
H	-0.92155000	-3.98200300	1.39470800
H	-2.93366400	-0.83109800	1.52032000
H	-2.68110300	-2.39904800	2.30533500
H	-1.38207500	-1.19736100	2.28978600
H	-5.03034600	2.30730500	2.16647100
H	-5.49495900	3.64789500	0.12779400
Br	3.69907700	-1.81687200	-0.55095800
Br	1.28176200	-0.22356300	2.62143500
C	3.99385500	2.94499200	-0.41593700
C	3.76426200	3.18855300	-1.77062100
C	2.58676100	2.73691600	-2.36614400
C	1.64391700	2.05117500	-1.59665300
C	1.82747100	1.78433800	-0.22016700
C	3.04280200	2.24981200	0.33284200
H	4.91450600	3.28619400	0.04922100
H	4.50477100	3.71975600	-2.36195200
H	2.40800700	2.91320200	-3.42319300
H	0.74220400	1.70656800	-2.10667200

H 3.26277900 2.05352500 1.38272700

TS2

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1410.692132

Electronic and Zero-Point Energy = -1410.252156

Enthalpy = -1410.221358

Free Energy = -1410.316087

M06-2X/def2-TZVP

Electronic Energy = -6533.176585

C	3.32574100	2.59745300	0.15621500
C	2.13777800	2.31366100	-0.79971800
C	1.40740700	4.00426500	0.53793300
C	2.88147000	3.85369800	0.95339300
H	3.53338800	1.73268300	0.79830200
H	4.22770800	2.78688800	-0.43357600
H	3.02695700	3.75855700	2.03145500
H	3.44054600	4.73508200	0.62505200
C	1.52065600	3.71756200	-0.97220400
C	1.03756600	1.70024300	0.06001500
C	0.57608000	2.78763300	1.05544500
C	-0.92558500	3.05222600	0.93640600
C	0.90489000	2.39046400	2.49701000
H	0.95604900	4.95948400	0.81992100
H	2.19662100	4.40847600	-1.48618800
H	0.56275700	3.69401100	-1.50326500
O	0.06321000	0.97366800	-0.68572400
N	0.96732500	0.31578800	0.33208500
H	1.80213200	-0.57739100	-0.06967300
C	2.49536000	1.52111900	-2.03916200
H	1.62036400	1.34760600	-2.67150100
H	3.24493400	2.06473200	-2.62307800
H	2.92191800	0.54614800	-1.77387500
C	4.96241200	-3.27128600	0.42369400
C	4.53623500	-2.42938400	1.45173500
H	4.53066600	-4.04623100	-1.54020100
C	4.19516800	-3.39573600	-0.73695300
C	3.34235000	-1.71934900	1.30725100
C	2.53780200	-1.82439800	0.15388200
C	3.00114000	-2.68332400	-0.86245700
H	3.03722500	-1.04940800	2.11302500
H	2.41958500	-2.79345200	-1.77645700
Mg	0.31456200	-1.76270700	0.59580800
Mg	-1.69349800	-0.05587900	-0.58771500
Br	-0.53738800	-1.96946800	-1.95502900
H	-1.21998300	3.36368400	-0.07008000

H	-1.50566800	2.15903100	1.20144400
H	-1.21373100	3.84210400	1.63814900
H	1.90882100	1.96659200	2.59680100
H	0.83609900	3.26565300	3.15234000
H	0.19304300	1.64514900	2.86022100
H	5.13271000	-2.32575000	2.35416000
H	5.89154000	-3.82546800	0.52378000
C	-1.75894200	-1.34319300	1.25032000
C	-2.76311300	-2.29923600	0.96972900
C	-1.89680400	-0.65153200	2.47559600
C	-3.82803800	-2.54748600	1.83870700
H	-2.71892800	-2.86605600	0.03923400
C	-2.95259900	-0.88619300	3.35761800
H	-1.15523700	0.09637400	2.75097700
C	-3.92238400	-1.83714900	3.03518800
H	-4.58165000	-3.28714300	1.58345700
H	-3.02380800	-0.33067200	4.28864200
H	-4.75026500	-2.02171300	3.71402400
Br	-3.66064200	1.12014900	-1.42716700

TS3

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1410.687124

Electronic and Zero-Point Energy = -1410.243017

Enthalpy = -1410.212713

Free Energy = -1410.305154

M06-2X/def2-TZVP

Electronic Energy = -6533.171957

C	1.85367600	-2.82130500	-2.30211900
C	2.19725000	-1.42566700	-1.71382700
C	2.85423000	-2.89049200	-0.11356700
C	2.38854200	-3.82241300	-1.24381400
H	0.78069500	-2.93333700	-2.49266800
H	2.36985900	-2.93560800	-3.26049800
H	1.64127500	-4.55121100	-0.92277400
H	3.24337800	-4.38197700	-1.63530100
C	3.47783800	-1.73965700	-0.92413400
C	1.20034900	-1.20347100	-0.56051100
C	1.64022700	-2.18758900	0.56966500
C	2.15228400	-1.49030800	1.83278400
C	0.50547700	-3.14027900	0.95331600
H	3.50177800	-3.37260700	0.62452400
H	4.29151800	-2.07030500	-1.57834400
H	3.82380700	-0.89009900	-0.32583500
O	0.95696800	0.19988700	-0.22737500
N	-0.16511400	-1.09771300	-0.89890200

H	-0.23997800	-0.83616800	-1.88774000
C	2.26064200	-0.31829400	-2.74580400
H	2.58009400	0.62421900	-2.29691900
H	2.97738900	-0.58986800	-3.52748700
H	1.29291500	-0.15673800	-3.23840100
C	4.64612100	3.25524800	0.25339900
C	3.68604300	3.32233800	-0.75743300
H	5.16183800	2.41324800	2.17005800
C	4.41967100	2.45797500	1.37726200
C	2.51095100	2.57493800	-0.64581800
C	2.26486400	1.77182200	0.47721600
C	3.23941000	1.71682700	1.48490100
H	1.77995900	2.62019900	-1.45274800
H	3.08347700	1.11222100	2.37516500
Mg	0.09890500	1.58363200	0.93548200
Mg	-1.84449500	-0.38470600	0.12860100
H	3.07898900	-0.94487400	1.64917600
H	1.41599400	-0.79999100	2.24862500
H	2.35499900	-2.25382900	2.59193600
H	-0.00959900	-3.55504600	0.08270100
H	0.90518800	-3.96892600	1.54835500
H	-0.24071800	-2.62434500	1.56787200
H	3.85757400	3.94283500	-1.63297000
H	5.56907500	3.82124200	0.16580100
Br	-3.91357000	-1.61806700	-0.32625000
C	-1.66576200	1.84458800	-0.34415300
C	-2.86866000	2.43098600	0.11060500
C	-1.41180500	1.96432700	-1.73067600
C	-3.75415700	3.09014100	-0.74497700
H	-3.13188300	2.36347200	1.16687000
C	-2.28318200	2.62098200	-2.60249200
H	-0.50087800	1.52870200	-2.14534000
C	-3.45944200	3.18406000	-2.10551400
H	-4.67259400	3.52158500	-0.35666100
H	-2.05212100	2.69056400	-3.66205100
H	-4.14717200	3.68938500	-2.77781100
Br	-1.21200500	0.04853900	2.64621900

TS4

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1680.949186

Electronic and Zero-Point Energy = -1680.395721

Enthalpy = -1680.359321

Free Energy = -1680.4657

M06-2X/def2-TZVP

Electronic Energy = -6803.516027

C	0.22487700	3.76407700	-0.44939300
C	-0.69725500	2.52720600	-0.62373200
C	-1.78184800	3.80581200	0.90554400
C	-0.52021700	4.64009500	0.59844900
H	1.22920100	3.47090700	-0.13091800
H	0.33054200	4.27862900	-1.40813000
H	0.07552200	4.80793600	1.50115400
H	-0.77638300	5.62071800	0.18902900
C	-2.11208800	3.16907100	-0.46815000
C	-0.51834400	1.77137400	0.71660000
C	-1.32214100	2.59525200	1.73956100
H	-2.59921000	4.36737400	1.36648700
C	-0.45307600	1.73303700	-1.88795200
H	-1.19373300	0.93812900	-2.03487600
H	-0.53068400	2.38909300	-2.76143000
H	0.55372700	1.29848300	-1.93619800
C	-4.45371300	-1.82337700	2.95285400
C	-4.79861800	-1.50578400	1.63819300
H	-2.86012700	-1.90940400	4.40445100
C	-3.13261300	-1.67457000	3.37871600
C	-3.82470000	-1.04367800	0.74623700
C	-2.49182200	-0.90825900	1.16019200
C	-2.16736300	-1.20389700	2.48473900
H	-4.11667200	-0.81050000	-0.27585800
H	-1.14543900	-1.05124300	2.83620500
Mg	-1.01644000	-1.16670200	-0.54561000
Br	-2.22773200	-1.78227200	-2.61211900
Mg	2.06355600	0.12252200	-0.19087700
H	-5.82649600	-1.61786400	1.30271600
H	-5.21298000	-2.17664400	3.64464100
O	-0.74576200	0.32135500	0.77158100
N	0.78966400	1.32312600	0.99269700
H	-2.15598400	1.99512600	2.11291400
H	-0.71558600	2.89718500	2.59686900
C	-3.25670500	2.15779900	-0.42682200
H	-3.36013700	1.65153500	-1.39452700
H	-3.12499000	1.39008200	0.33373400
H	-4.20357800	2.67180300	-0.22410700
C	-2.44802000	4.19128300	-1.55831500
H	-2.62246600	3.68486500	-2.51423700
H	-3.37393500	4.71461100	-1.29345100
H	-1.67523500	4.94581600	-1.71718300
C	1.15166500	1.16807500	2.40336100
H	1.45950100	2.15141500	2.78892100
H	0.29374700	0.82444000	2.99430200
C	2.28760800	0.17683700	2.49224600

C	2.09696500	-1.10401100	3.01860500
C	3.53005100	0.50563000	1.92575500
C	3.12414000	-2.04548800	2.96841500
H	1.13683600	-1.36404900	3.45750200
C	4.55266600	-0.44561800	1.85789800
H	3.70256900	1.51560200	1.55496900
C	4.34668500	-1.72331400	2.37726700
H	2.96354700	-3.03964400	3.37449100
H	5.50295800	-0.18278400	1.40362200
H	5.13728900	-2.46511500	2.32455600
C	1.24869500	-1.82200800	-0.65612400
C	0.66964300	-2.72101300	0.27664700
C	1.52575200	-2.37383000	-1.92939900
C	0.37222300	-4.05648000	-0.03476300
H	0.44404400	-2.37744200	1.28906200
C	1.26486100	-3.70623700	-2.24601000
H	1.95782900	-1.73962400	-2.70272300
C	0.67847900	-4.54999500	-1.29963300
H	-0.08847100	-4.70005500	0.70966200
H	1.49790700	-4.08531600	-3.23725400
H	0.45437100	-5.58215400	-1.55228500
Br	3.60318500	1.24506000	-1.77793000

TS5

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -1680.947235

Electronic and Zero-Point Energy = -1680.391789

Enthalpy = -1680.355885

Free Energy = -1680.46083

M06-2X/def2-TZVP

Electronic Energy = -6803.516806

C	-2.33554800	2.92308500	0.85058400
C	-0.78999900	2.86031000	0.74684800
C	-1.50466800	3.08960100	-1.40957200
C	-2.81721500	3.15754900	-0.60827800
H	-2.73813700	2.00224000	1.28611100
H	-2.62520100	3.74477900	1.51164000
H	-3.53481700	2.40377900	-0.93989900
H	-3.29473100	4.13494900	-0.71727700
C	-0.50625300	3.81160600	-0.47379000
C	-0.46911800	1.49912000	0.08506000
C	-1.01451300	1.63037200	-1.35231000
H	-1.56639800	3.48964400	-2.42499400
O	0.84226000	1.05885300	0.20140400
N	-0.67156200	0.17455300	0.68829600
C	-0.05688500	3.23191900	2.02568300

H	0.99690400	2.93646100	1.99461200
H	-0.09756700	4.31810700	2.15896600
H	-0.52124100	2.78990500	2.91208300
C	-5.69610400	-0.38713500	1.67311300
C	-5.33983100	0.02447400	0.38991500
H	-4.98973000	-1.28369900	3.50315100
C	-4.72488500	-0.94195100	2.50610100
C	-4.01928300	-0.11126800	-0.04780600
C	-3.01398400	-0.64357400	0.77855300
C	-3.40499200	-1.05533100	2.06008600
H	-3.79753800	0.19051800	-1.06850300
H	-2.68855600	-1.48507900	2.75930700
Mg	-1.37620600	-1.42861900	-0.53751200
Br	-2.41438500	-1.90230700	-2.75083700
Mg	2.21238100	-0.28785100	-0.16662200
Br	1.04481000	-2.31123200	-1.17515700
C	6.95709400	1.08698900	-0.55685200
C	5.99812700	1.96379500	-0.04843100
H	7.30535900	-0.88041100	-1.36513100
C	6.56707200	-0.18904500	-0.96588300
C	4.66319400	1.55733600	0.04642100
C	4.22641300	0.27826900	-0.35653300
C	5.22708800	-0.57565700	-0.86365600
H	3.94437000	2.27285400	0.44801400
H	4.96337700	-1.58020000	-1.19572200
H	-6.08666200	0.44909000	-0.27600400
H	-6.72032300	-0.28211400	2.01922600
H	6.28977000	2.96127500	0.27183700
H	7.99627500	1.39486100	-0.63504200
H	-0.21017600	1.41462000	-2.06184400
H	-1.83482900	0.93385200	-1.55358200
C	0.94235100	3.81071500	-0.97639500
H	1.61916300	4.15179300	-0.18459600
H	1.29977800	2.83761700	-1.31906800
H	1.03657800	4.51197400	-1.81324200
C	-0.88256700	5.27165100	-0.19668100
H	-0.09306500	5.77133000	0.37424500
H	-0.98517900	5.80650200	-1.14796500
H	-1.81707200	5.39061700	0.35566800
C	-0.37575300	0.02201400	2.13669600
H	-1.31849400	-0.08751100	2.66922600
H	0.11619700	0.91942300	2.49827800
C	0.52936000	-1.17148900	2.32397500
C	1.91399400	-0.96569800	2.40849600
C	0.03538200	-2.47888400	2.33160000
C	2.79203500	-2.05125900	2.47506300

H	2.30454200	0.05156500	2.46457300
C	0.91137500	-3.56168600	2.40898200
H	-1.03577500	-2.65877300	2.27074700
C	2.28838300	-3.35181700	2.47111700
H	3.86208700	-1.87506600	2.53387000
H	0.51628200	-4.57285000	2.40911000
H	2.96706500	-4.19730000	2.51965000

[(MgPh₂)(MgBr₂)]

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -889.678901

Electronic and Zero-Point Energy = -889.494880

Enthalpy = -889.477362

Free Energy = -889.543089

M06-2X/def2-TZVP

Electronic Energy = -6012.000342

Mg	1.86228700	0.06717100	-0.11591500
Br	0.11792600	-1.76679300	-0.84069200
Mg	-1.33655400	0.34350700	-0.32385900
C	-3.43633900	0.39880600	-0.32671500
C	-4.20114300	-0.68300900	-0.80814100
C	-4.17000200	1.52179100	0.10840600
C	-5.59845200	-0.65220200	-0.85932700
H	-3.70362600	-1.58655800	-1.16064800
C	-5.56650800	1.57035500	0.06574700
H	-3.64613800	2.39545800	0.49544200
C	-6.28694400	0.47936600	-0.42168000
H	-6.14856200	-1.50901300	-1.24061600
H	-6.09163500	2.45758400	0.41131700
H	-7.37242900	0.51064700	-0.45906400
Br	4.04790100	-0.84407400	0.48629500
C	0.49003700	1.72380900	-0.14945400
C	0.06563800	2.21193300	-1.41420400
C	0.01288500	2.44214200	0.97482400
C	-0.75398800	3.33925900	-1.55060600
H	0.38546300	1.70457300	-2.32522600
C	-0.80629600	3.56825000	0.85107200
H	0.28731800	2.11533300	1.97590800
C	-1.19002800	4.01751400	-0.41358900
H	-1.05221400	3.67943800	-2.53796200
H	-1.15060400	4.08934000	1.73992700
H	-1.83474000	4.88583300	-0.51061100

[(PhMgBr)₂]⁺

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -889.44246866

Electronic and Zero-Point Energy = -889.258479

Enthalpy = -889.240210

Free Energy = -889.308364

M06-2X/def2-TZVP

Electronic Energy = -6011.767231

Mg	2.17811000	-1.09368900	-0.16046700
C	4.39506300	-1.56217400	-0.41094900
C	4.44938100	-0.84261600	-1.59734200
C	4.65053900	-1.05656400	0.85798200
C	4.79234100	0.51594800	-1.48744200
H	4.25964700	-1.30446300	-2.56279900
C	4.98773100	0.30674700	0.92966500
H	4.61654700	-1.67933300	1.74740000
C	5.06610300	1.07362500	-0.23545800
H	4.84924200	1.12301700	-2.38526200
H	5.19465500	0.75235300	1.89755500
H	5.34102900	2.12086400	-0.16645200
Br	0.51758200	-1.43072600	-2.06066000
Br	0.64441300	0.50850600	1.14602900
Mg	-1.23925100	-0.07141400	-0.60787200
C	-3.31238400	0.07617800	-0.48240800
C	-4.14289400	-0.40858100	-1.51175800
C	-3.95867000	0.66605600	0.62098300
C	-5.53567400	-0.31048400	-1.45010100
H	-3.70194100	-0.87700000	-2.39115100
C	-5.35057900	0.76985500	0.69642200
H	-3.37325200	1.05899600	1.45152800
C	-6.14342200	0.28117700	-0.34236800
H	-6.14542200	-0.69427700	-2.26407300
H	-5.81560600	1.23148300	1.56375300
H	-7.22558500	0.36047300	-0.28913000

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M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -521.09950107

Electronic and Zero-Point Energy = -520.844542

Enthalpy = -520.831948

Free Energy = -520.880637

M06-2X/def2-TZVP

Electronic Energy = -521.2647118

C	1.29461100	1.18964400	0.85735500
C	1.25505400	-0.00862400	-0.11931000
C	-0.49928900	1.28775800	-0.74158400
C	0.18271000	2.14163700	0.34075500
H	1.12128300	0.85406900	1.88551500
H	2.27884300	1.67436400	0.83044600

H	-0.50001800	2.48144300	1.12432500
H	0.61815200	3.03697200	-0.11841200
C	0.73725200	0.65387300	-1.40604000
H	0.50178500	-0.08630000	-2.17772900
H	1.42709600	1.40292700	-1.81778300
C	0.02558700	-0.92234900	0.22850600
C	-1.20884500	0.05715100	-0.10980100
H	-1.16342400	1.86224100	-1.40030500
C	2.56096900	-0.76890400	-0.21027300
H	3.36692000	-0.12894700	-0.59322500
H	2.86383700	-1.13724900	0.77748800
H	2.44717200	-1.63427600	-0.86900200
C	-2.13774600	-0.58257500	-1.14225600
H	-2.53112400	-1.53476200	-0.77363800
H	-2.98380700	0.08625800	-1.35338000
H	-1.61938200	-0.79474800	-2.08135100
C	-2.04824300	0.41476800	1.12025700
H	-2.74962200	1.22996700	0.89395600
H	-2.64533200	-0.44789800	1.44092800
H	-1.43682600	0.71953400	1.97497400
N	0.10467700	-1.40022700	1.60258400
O	0.01296900	-2.08872400	-0.45454800
H	-0.80440300	-1.84649000	1.76983600

TS1 (Monomeric Grignard)

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -965.8101842

Electronic and Zero-Point Energy = -965.458353

Enthalpy = -965.437604

Free Energy = -965.506598

M06-2X/def2-TZVP

Electronic Energy = -3527.137326

C	0.91979200	-1.08881300	1.64906300
C	1.39068100	-1.76375000	0.34656200
C	3.19924100	-0.56652300	1.03062500
C	2.16589600	-0.30315900	2.14396500
H	0.04964200	-0.44664100	1.49014400
H	0.62107700	-1.85913600	2.36818200
H	1.96726800	0.75839400	2.31113300
H	2.52994300	-0.71640900	3.08970000
C	2.87049400	-2.03040100	0.68334900
C	2.80968600	0.17343500	-0.27967400
H	4.23141600	-0.35903400	1.32980000
C	0.57127700	-2.96221100	-0.08524800
H	0.58138100	-3.72802600	0.69771700
H	-0.48504000	-2.71060400	-0.25912600

H	0.96267200	-3.39275800	-1.01009600
C	1.57036500	-0.68092000	-0.74748600
Mg	-1.64752500	-0.33530700	-0.80832500
Br	-3.53845300	-1.61543800	0.06102300
C	-1.13526300	4.33378700	0.52603600
C	-0.94026700	1.99842300	1.13265800
C	-0.81104700	1.63208400	-0.21668100
C	-0.85625700	2.64951700	-1.18060100
C	-1.01734200	3.98960200	-0.82084700
H	-0.75022500	2.40983900	-2.24005800
H	-1.04259200	4.76080800	-1.58595300
C	-1.10480500	3.33598400	1.50152700
H	-0.91774000	1.25018500	1.92223800
H	3.43363200	-2.43601600	-0.16212900
H	2.97607200	-2.70697300	1.53898000
C	3.94077400	0.04704500	-1.30885800
H	3.63585200	0.46493800	-2.27229500
H	4.81665000	0.60162400	-0.95322100
H	4.24041200	-0.98921700	-1.48348100
C	2.52521900	1.66379500	-0.08986300
H	3.41380300	2.15718400	0.32217600
H	2.30381500	2.14165800	-1.05243900
H	1.68469600	1.86385000	0.57536700
O	1.55789500	-1.10881000	-2.01957900
N	0.31123800	0.00971400	-1.16876200
H	0.58560000	0.76244000	-1.79770800
H	-1.24880700	5.37466200	0.81474100
H	-1.20585700	3.59837300	2.55122000

TS2 (Monomeric Grignard)

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -965.8157966

Electronic and Zero-Point Energy = -965.468876

Enthalpy = -965.447457

Free Energy = -965.520094

M06-2X/def2-TZVP

Electronic Energy = -3527.143669

C	2.90382300	-2.08369100	0.84144100
C	2.19409800	-1.58668800	-0.44674800
C	3.92805100	-0.13989500	-0.15521300
C	4.15848600	-1.17550300	0.96028200
H	2.24009700	-2.01386200	1.71130000
H	3.17551000	-3.13694100	0.72128800
H	4.27880700	-0.73046800	1.95021800
H	5.06789600	-1.74521200	0.74634800
C	3.38270900	-1.05437400	-1.27048900

C	1.54946000	-0.26486000	-0.04769100
C	2.69432700	0.75178000	0.17919000
H	4.81125100	0.45558500	-0.40329700
O	0.41632400	0.15716400	-0.80148200
N	0.35169100	-0.22710600	0.69720500
H	-0.64651100	-1.00536000	0.57427600
C	1.25825200	-2.58878000	-1.08730400
H	0.81004300	-2.18883400	-2.00150800
H	1.80669000	-3.50097600	-1.34342100
H	0.44819700	-2.86548500	-0.40227900
C	-4.36560000	-2.89278800	-0.00029100
C	-3.59429200	-2.56722600	-1.11749200
H	-4.60869600	-2.65708600	2.12844300
C	-4.01025900	-2.40291900	1.25774800
C	-2.47046600	-1.75211500	-0.96914700
C	-2.07847500	-1.24028600	0.28591700
C	-2.88463400	-1.58760200	1.38900900
H	-1.87661900	-1.52015000	-1.85280800
H	-2.62077200	-1.22425000	2.38200400
Mg	-1.32672200	0.89047900	0.18017900
Br	-1.83134300	3.24996200	-0.15441400
H	4.08205900	-1.85075700	-1.54609300
H	3.06754000	-0.52854500	-2.17742900
C	2.59010300	1.92257900	-0.80395100
H	1.65826700	2.47672500	-0.65333500
H	3.42532200	2.61051500	-0.63419700
H	2.62165100	1.59823000	-1.84802100
C	2.67556800	1.30249000	1.60598600
H	3.60536500	1.84393000	1.81328900
H	1.84159000	2.00104800	1.73046500
H	2.56044100	0.51602700	2.35760000
H	-5.24029300	-3.52785100	-0.10965700
H	-3.86951000	-2.94900600	-2.09694100

TS3 (Monomeric Grignard)

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -965.7905112

Electronic and Zero-Point Energy = -965.440158

Enthalpy = -965.419276

Free Energy = -965.488625

M06-2X/def2-TZVP

Electronic Energy = -3527.118129

C	-2.03896800	-2.71519700	0.91664300
C	-1.16112300	-1.43500000	0.95443000
C	-3.24112100	-0.66681200	0.47620600
C	-3.47645600	-2.17473300	0.67798200

H	-1.70850000	-3.40971000	0.13697500
H	-1.96251400	-3.23548500	1.87680700
H	-3.98259000	-2.65264100	-0.16321900
H	-4.09852200	-2.33237300	1.56449100
C	-2.15230500	-0.40913000	1.53102700
C	-1.06332400	-0.96007000	-0.50955200
C	-2.47920400	-0.39580300	-0.85578500
H	-4.14792000	-0.05980000	0.55864400
C	0.16350700	-1.61369400	1.66907900
H	0.64971700	-0.64818700	1.86721400
H	0.01240400	-2.07940100	2.64810700
H	0.85323800	-2.26447900	1.11458800
C	-0.17448200	4.56991000	0.48212000
C	-0.15047700	3.66911500	1.54803400
H	0.12259000	4.83620600	-1.63796300
C	0.14728400	4.13661800	-0.80682700
C	0.19170300	2.33200100	1.32496600
C	0.52463400	1.89012900	0.03788900
C	0.48087400	2.79986600	-1.02644900
H	0.19634100	1.64421000	2.16872000
H	0.69058200	2.46270300	-2.03995500
Mg	1.90503800	0.18411500	-0.14272800
Br	3.84861700	-1.28190100	-0.14012300
H	-1.76105400	0.61100600	1.52386800
H	-2.47087900	-0.66650600	2.54757700
C	-2.47379400	1.10636400	-1.15720000
H	-2.15545500	1.70863000	-0.30211200
H	-1.80312100	1.33074500	-1.99131800
H	-3.48748400	1.41556800	-1.43676100
C	-3.08495200	-1.11579800	-2.06333400
H	-4.14910100	-0.86562000	-2.14805800
H	-2.58541400	-0.79921400	-2.98399800
H	-2.98755400	-2.20230400	-1.99920800
N	-0.41392700	-1.69176300	-1.47473900
O	0.07484300	0.03401900	-0.71800600
H	0.29094100	-2.28416800	-1.02006900
H	-0.44957300	5.60650900	0.65369500
H	-0.40023000	4.00505200	2.55088200

PhMgBr

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -444.8188564

Electronic and Zero-Point Energy = -444.727594

Enthalpy = -444.718739

Free Energy = -444.762486

M06-2X/def2-TZVP

Electronic Energy = -3005.979748

C	2.13940800	-1.19527300	-0.00000600
C	3.53746200	-1.20408900	0.00000300
C	4.24192000	0.00001000	0.00000700
C	3.53744700	1.20410100	0.00000300
C	2.13939300	1.19526800	-0.00000600
C	1.39316100	-0.00000800	-0.00001000
H	1.62797200	-2.15685700	-0.00000900
H	4.07597400	-2.14854100	0.00000700
H	5.32847600	0.00001700	0.00001500
H	4.07594700	2.14856000	0.00000600
H	1.62794500	2.15684500	-0.00000800
Mg	-0.70382600	-0.00001400	-0.00000300
Br	-3.14923300	0.00000300	0.00000200

[18]-MgBr

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -733.6939559

Electronic and Zero-Point Energy =

Enthalpy = -733.429585

Free Energy = -733.486234

M06-2X/def2-TZVP

Electronic Energy = -3294.949949

C	2.81844500	0.21715000	-1.47882500
C	2.53102200	0.80426600	-0.07177800
C	2.47203800	-1.44902600	0.23129200
C	2.88734500	-1.31684200	-1.24410700
H	2.04012400	0.50542900	-2.19350000
H	3.77038000	0.60875800	-1.85262700
H	2.25560800	-1.89004300	-1.92655000
H	3.91143100	-1.68286200	-1.36661400
C	3.20793100	-0.23799700	0.83654700
C	1.05707200	0.49149600	0.22335800
C	0.97797700	-1.05394100	0.41838000
H	2.69654300	-2.42520000	0.67169900
O	0.13170000	1.13763700	-0.64491600
N	0.24541200	1.41133000	0.92397400
C	2.91843500	2.25653300	0.10024100
H	2.78224100	2.58581200	1.13440900
H	3.96877700	2.40283400	-0.17441900
H	2.30362500	2.89986500	-0.53939500
H	3.00865900	-0.06923500	1.89990500
H	4.29169900	-0.28069300	0.68110200
C	0.52085200	-1.41128400	1.83758600
H	-0.52214200	-1.12164400	2.01354600
H	0.58300200	-2.49573800	1.98157200

H	1.13120200	-0.92944400	2.60717500
C	0.03030600	-1.71047600	-0.58581800
H	0.15533700	-2.79922300	-0.56773800
H	-1.02058600	-1.51891300	-0.33048700
H	0.18591700	-1.35922200	-1.60914700
Mg	-1.64141100	0.97681900	0.39237200
Br	-3.74699700	-0.07634300	-0.22991800

2,2,6,6-tetramethylpiperidine (TMP)

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -408.994149

Electronic and Zero-Point Energy = -408.722750

Enthalpy = -408.710873

Free Energy = -408.757270

M06-2X/def2-TZVP

Electronic Energy = -409.1198062

C	-1.25247400	1.23979800	-0.41748300
C	-1.28007700	-0.25426800	-0.06328200
C	1.28005500	-0.25427700	-0.06330700
C	1.25249000	1.23979700	-0.41746300
C	0.00000300	1.94334200	0.10549100
H	-0.00001100	-1.84247700	-0.25328900
H	-1.27925800	1.33403400	-1.51173900
H	-2.16033100	1.71467500	-0.02586400
H	2.16033500	1.71463000	-0.02575800
H	1.27934800	1.33410700	-1.51171000
H	-0.00000500	1.95700600	1.20262100
H	0.00000800	2.99049200	-0.21675200
C	1.61409200	-0.45287100	1.42861500
H	1.45375400	-1.49817500	1.71829800
H	2.66679800	-0.21014100	1.61313700
H	1.01230500	0.17623900	2.08737700
C	2.36983000	-0.95347700	-0.88090200
H	3.35217000	-0.51500800	-0.67449000
H	2.41690000	-2.02052500	-0.62952000
H	2.16205300	-0.86257000	-1.95143500
C	-1.61404100	-0.45287900	1.42863100
H	-2.66667300	-0.20990600	1.61327900
H	-1.45398100	-1.49826100	1.71819800
H	-1.01202500	0.17600800	2.08738200
C	-2.36987600	-0.95344200	-0.88085700
H	-2.41691000	-2.02050700	-0.62954900
H	-3.35221400	-0.51500300	-0.67436600
H	-2.16217000	-0.86246100	-1.95139900
N	-0.00001400	-0.85035600	-0.48872700

[TMP]-MgBr

M06-2X/6-31+G(d,p)[LANL2DZ]

Electronic Energy = -408.4313431

Electronic and Zero-Point Energy = -408.176426

Enthalpy = -408.164359

Free Energy = -408.211583

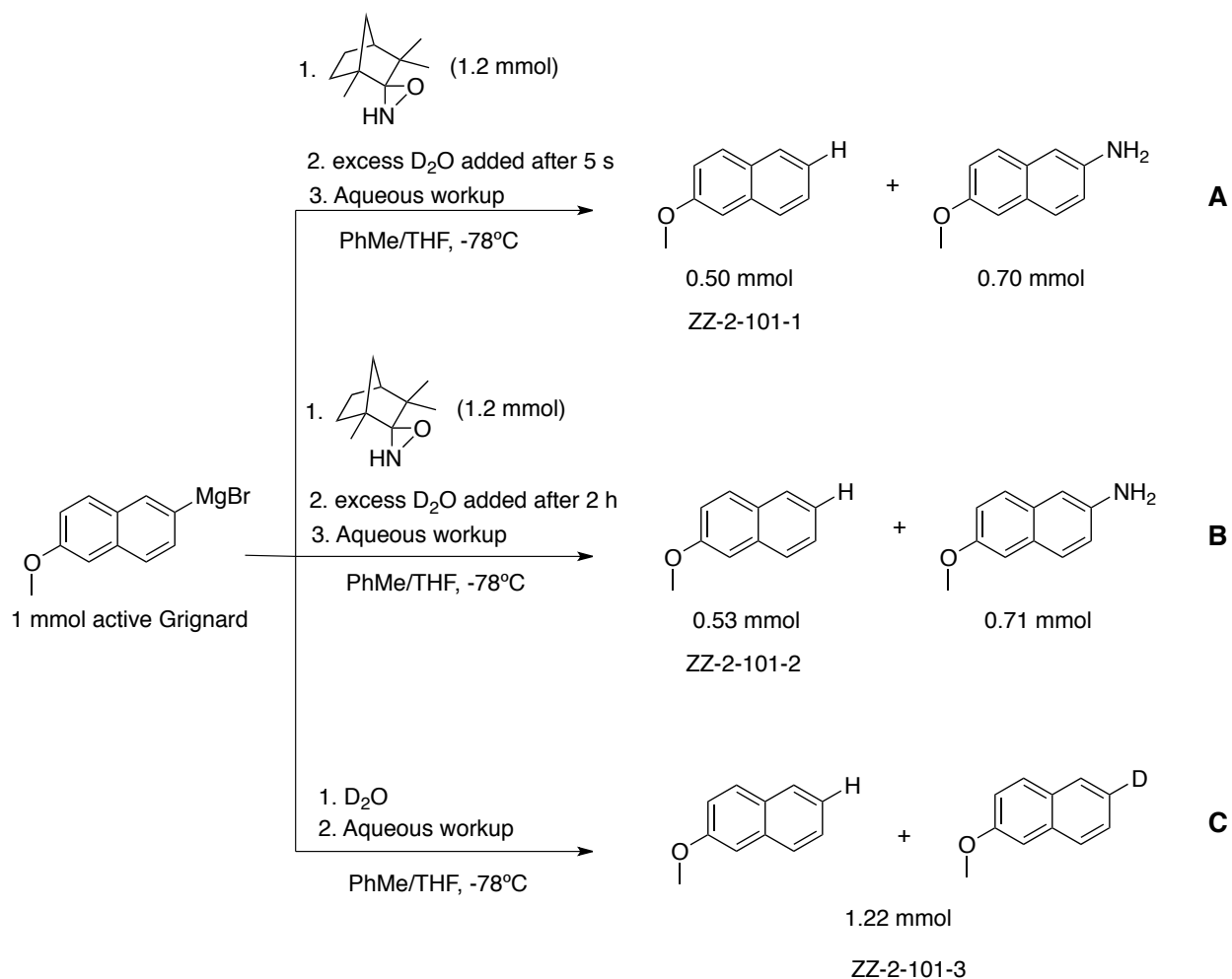
M06-2X/def2-TZVP

Electronic Energy = -408.5542895

C	2.40777200	1.40642700	-0.96904000
C	1.33138700	1.27917100	0.12919100
C	1.64164800	-1.23304100	0.10300200
C	2.71132200	-1.07634200	-0.99630200
C	3.42725300	0.27045900	-0.91162200
H	1.90572700	1.37864500	-1.94700400
H	2.90656200	2.38063800	-0.88559700
H	3.43033600	-1.90352000	-0.93286300
H	2.21332600	-1.15002200	-1.97391400
H	4.01063000	0.33089000	0.01614500
H	4.14470000	0.36710900	-1.73444300
C	2.32541600	-1.54123200	1.45358800
H	1.57955900	-1.55040500	2.25640000
H	2.81216000	-2.52360800	1.42311800
H	3.09108600	-0.80700200	1.71287500
C	0.76869600	-2.44586600	-0.24022900
H	1.35400000	-3.36890500	-0.30447300
H	0.00882500	-2.60989500	0.54046400
H	0.26739400	-2.30212500	-1.20714200
C	1.92225400	1.71418300	1.48887000
H	2.14587100	2.78786700	1.48494600
H	1.20033100	1.51755000	2.28967800
H	2.84908300	1.19089200	1.73423800
C	0.19433400	2.25659500	-0.19100900
H	-0.57594100	2.23503000	0.59602800
H	0.55312900	3.28963300	-0.24826200
H	-0.26931000	2.01415000	-1.15728500
N	0.75337700	-0.06773500	0.14063400
Mg	-1.16008100	-0.32317500	0.05404800
Br	-3.58173200	-0.02019400	-0.07127500

D₂O trapping experiments

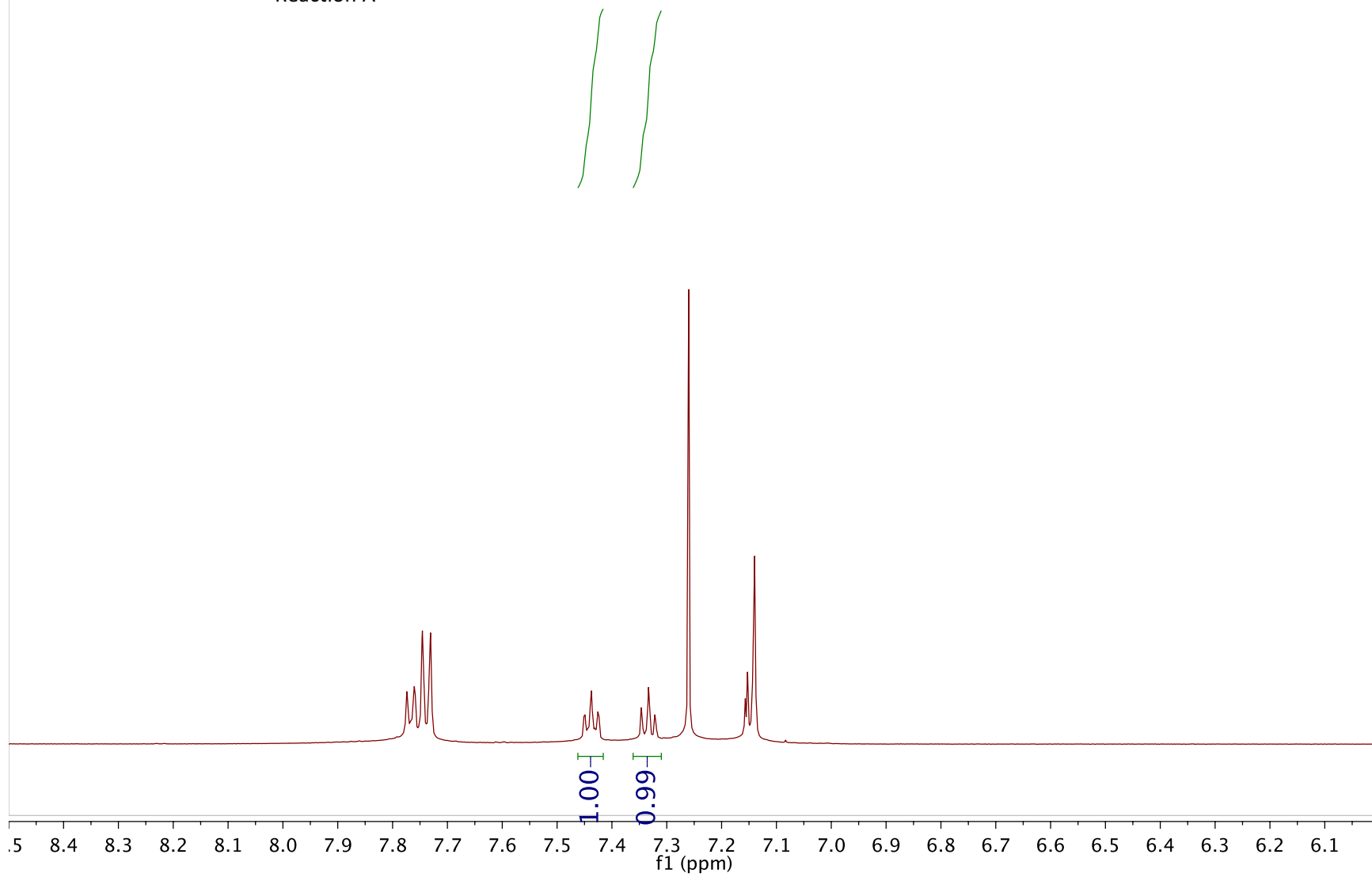
D₂O trapping experiments are conducted as illustrated below. The 2-methoxynaphthalene product from each reaction was isolated and NMR was obtained, along with a standard NMR taken with commercially available 2-methoxynaphthalene. It is clear from the spectral data that in reactions A and B, deuterium was not incorporated.



Supplementary Figure 10. Trapping experiments

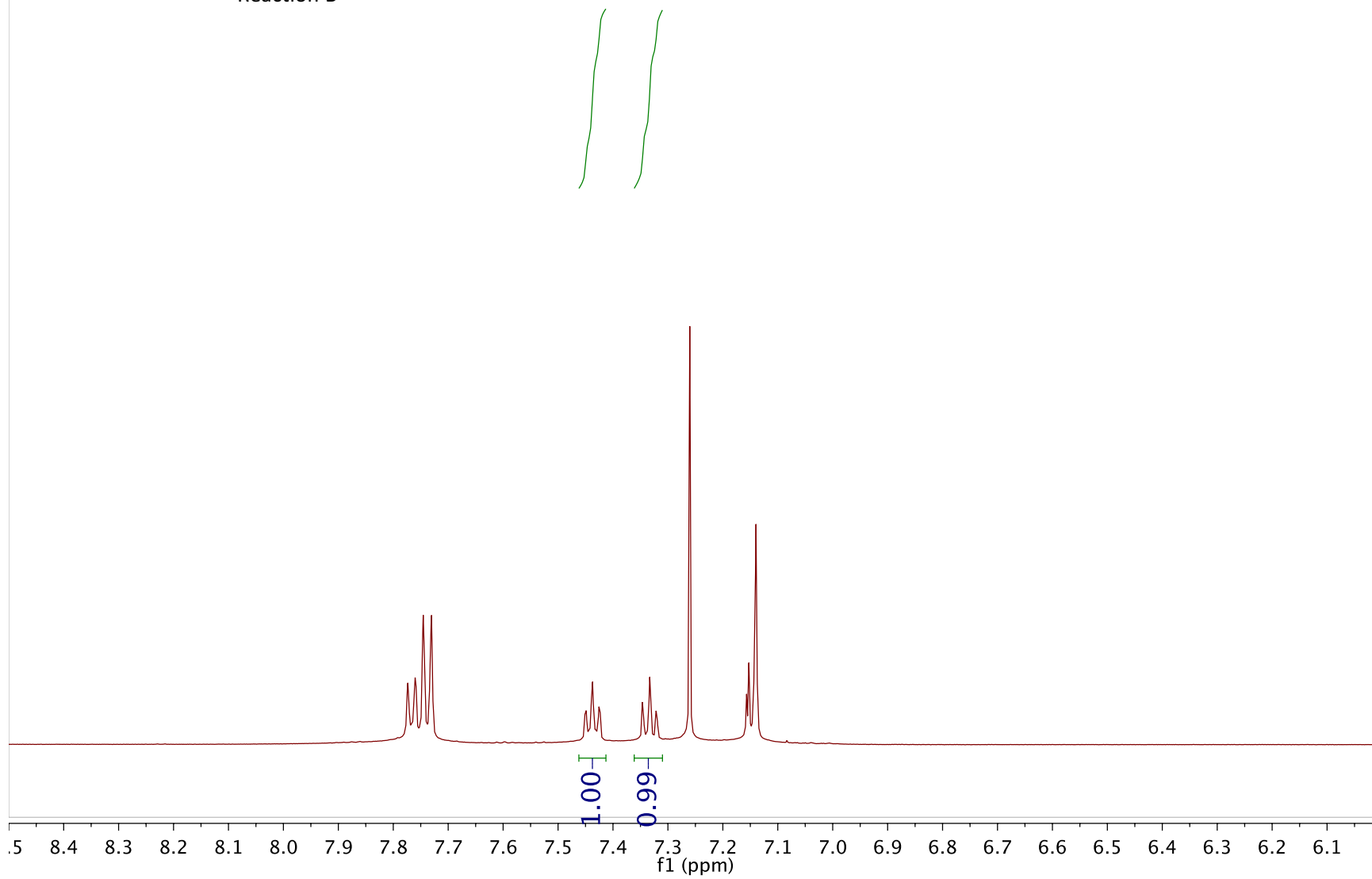
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PROTON CDCl3 {C:\DATA_Kurti} Zhe 15

Reaction A



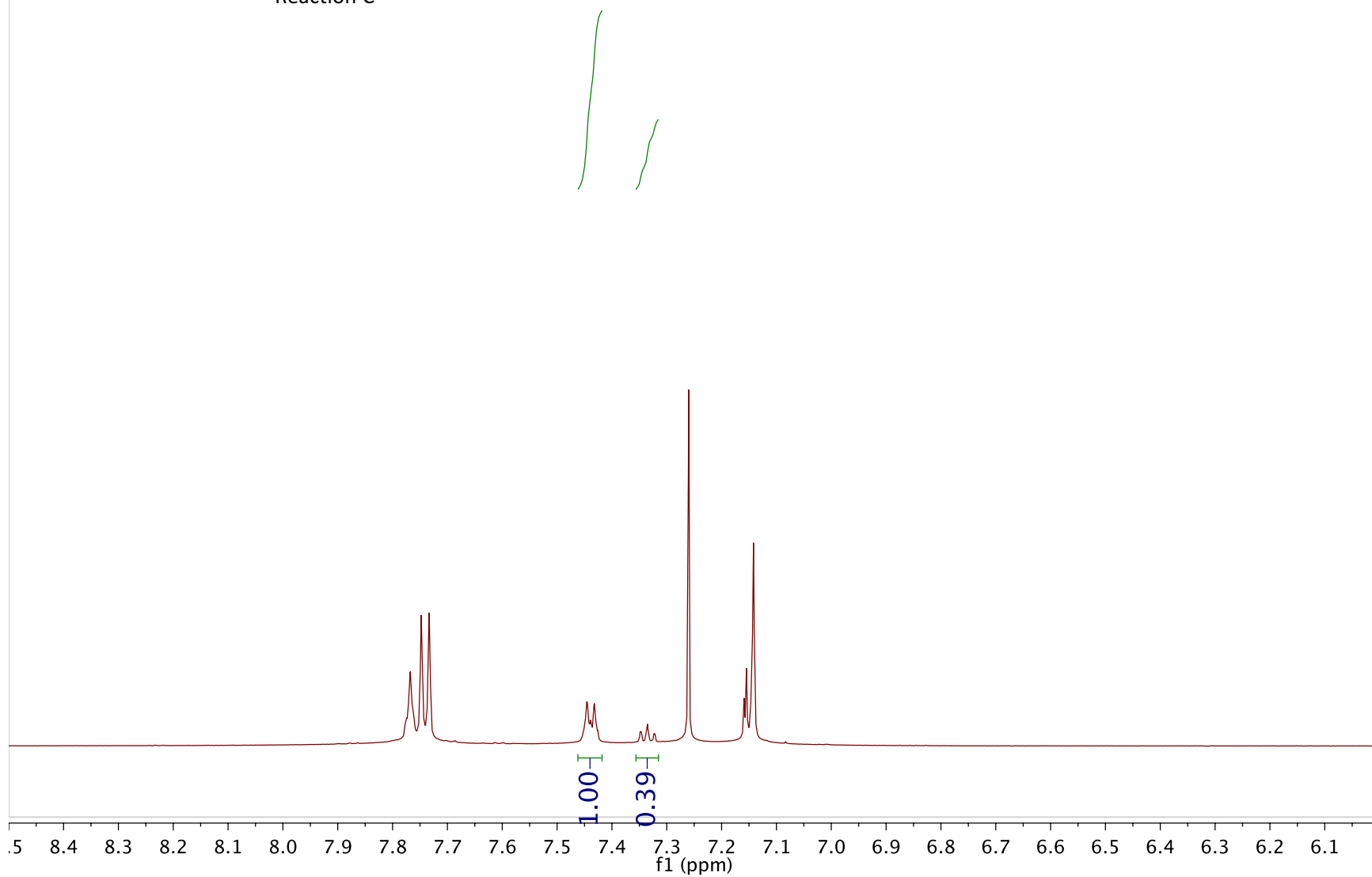
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Reaction B



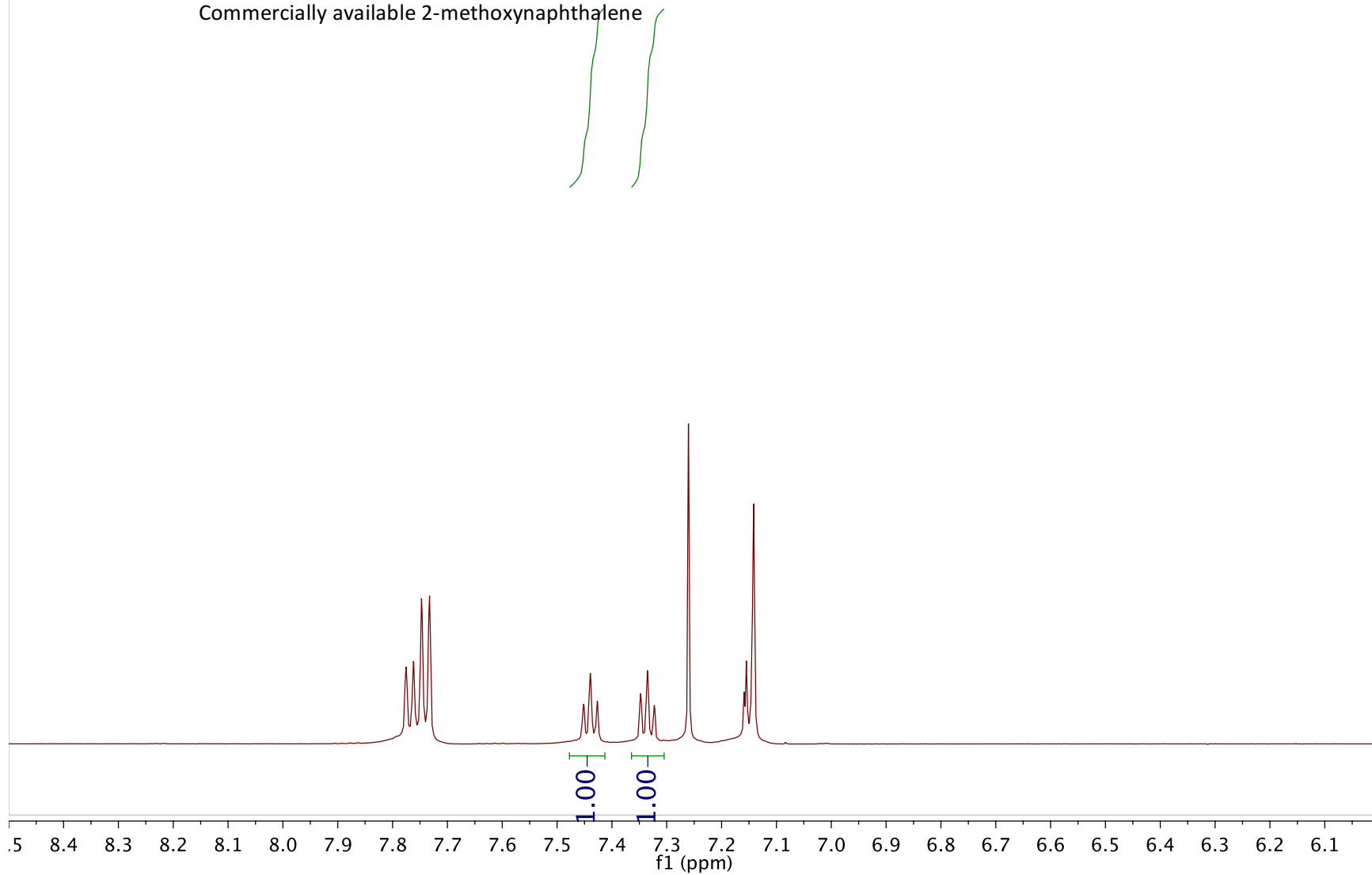
ZZ-2-101-3.1.fid
PROTON CDCl3 {C:\DATA_Kurti} Zhe 17

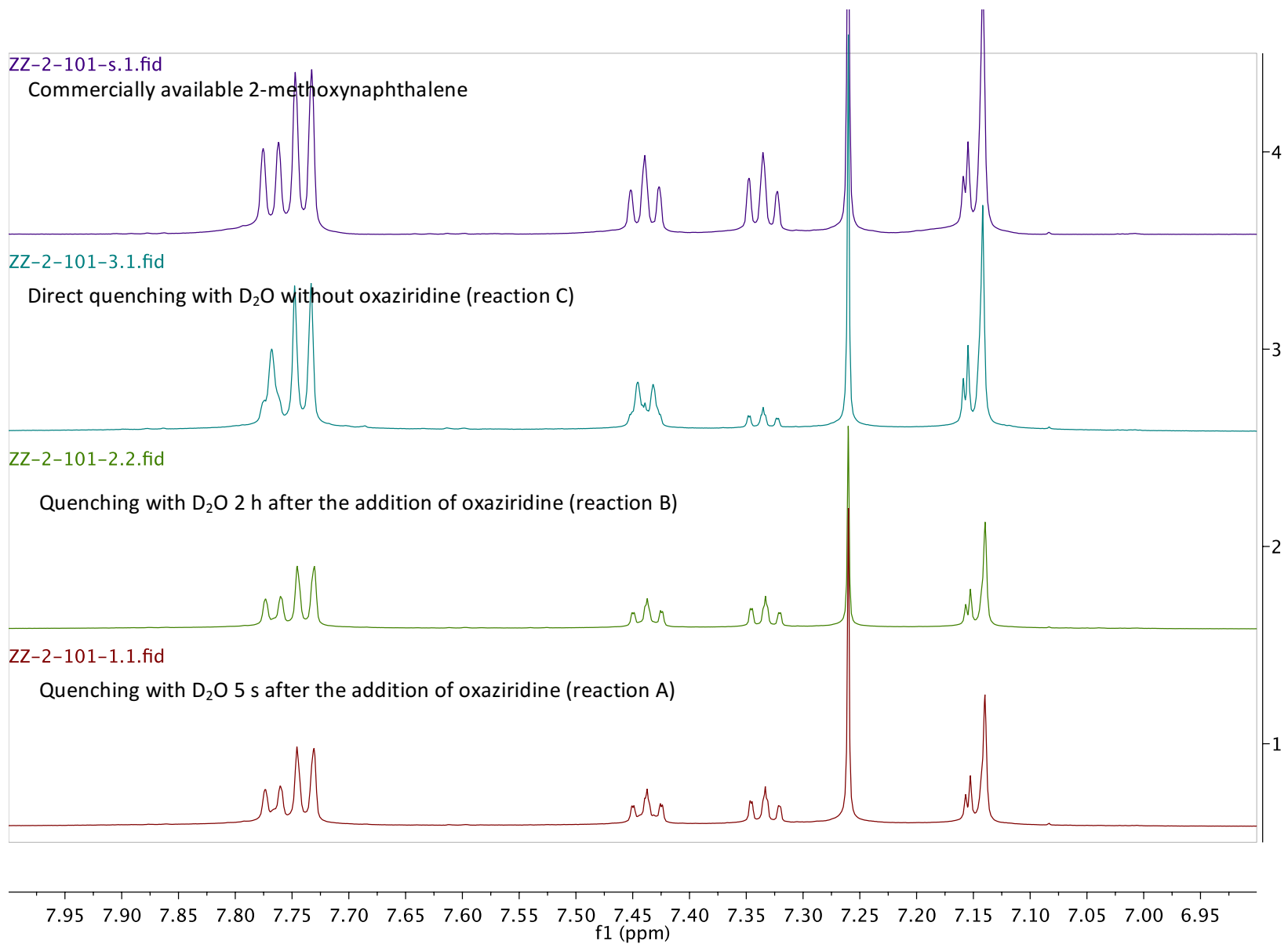
Reaction C



ZZ-2-101-s.1.fid
PROTON CDCl3 {C:\DATA_Kurti} Zhe 18

Commercially available 2-methoxynaphthalene





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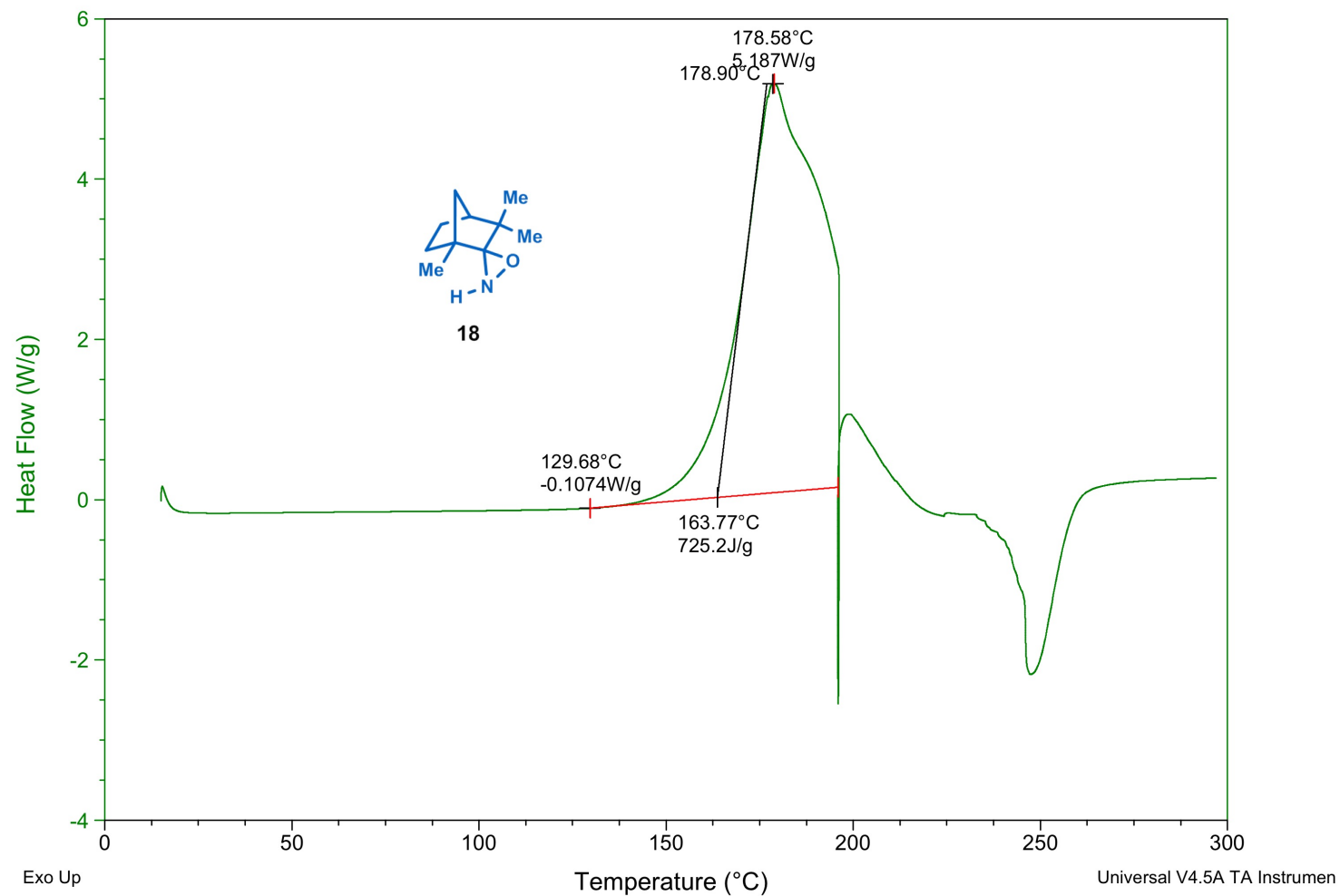
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DSC (Differential Scanning Calorimetry) Analysis Data for Oxaziridines

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Size: 6.5030 mg
Method: Ramp

DSC

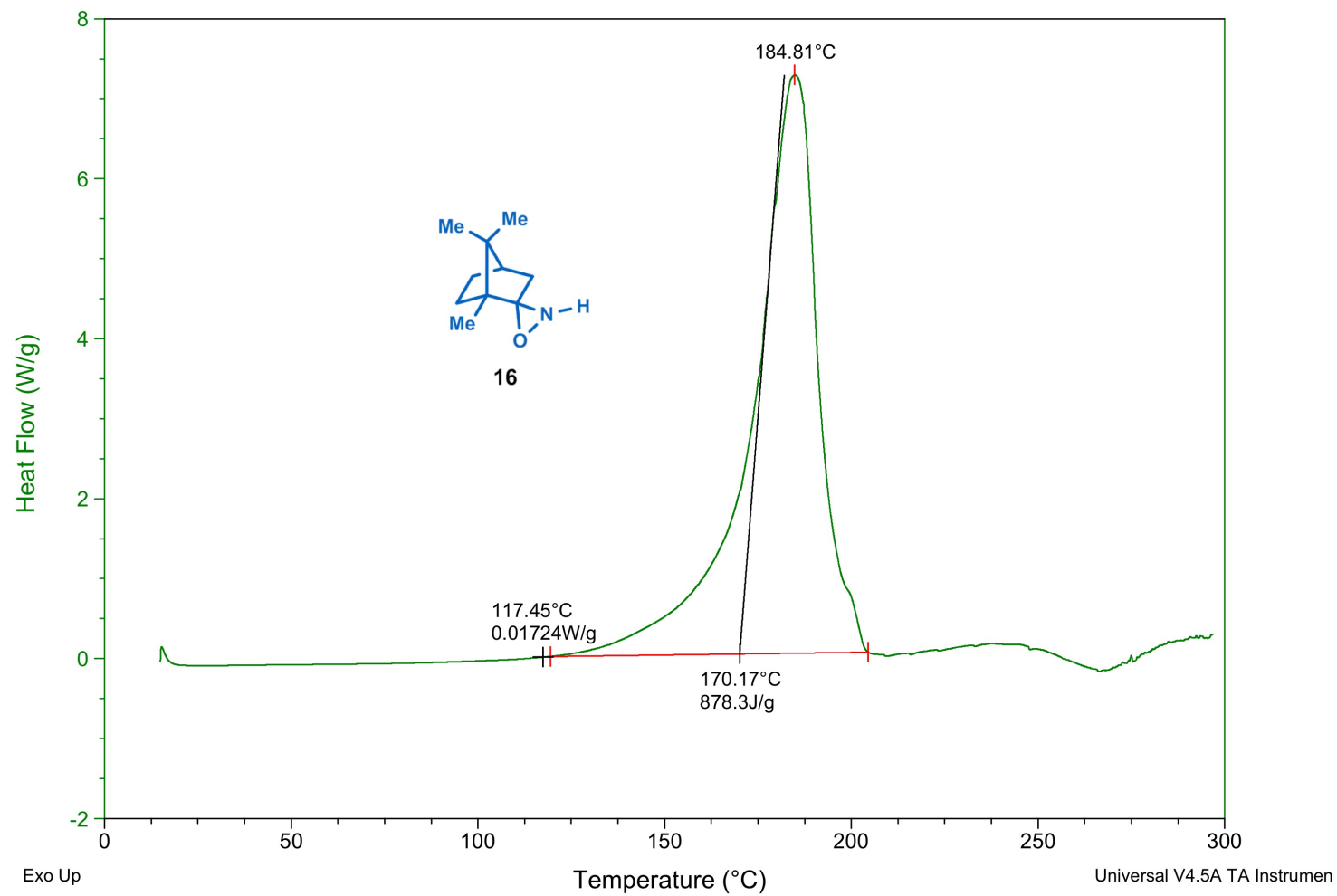
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Sample: LKNH2
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Method: Ramp

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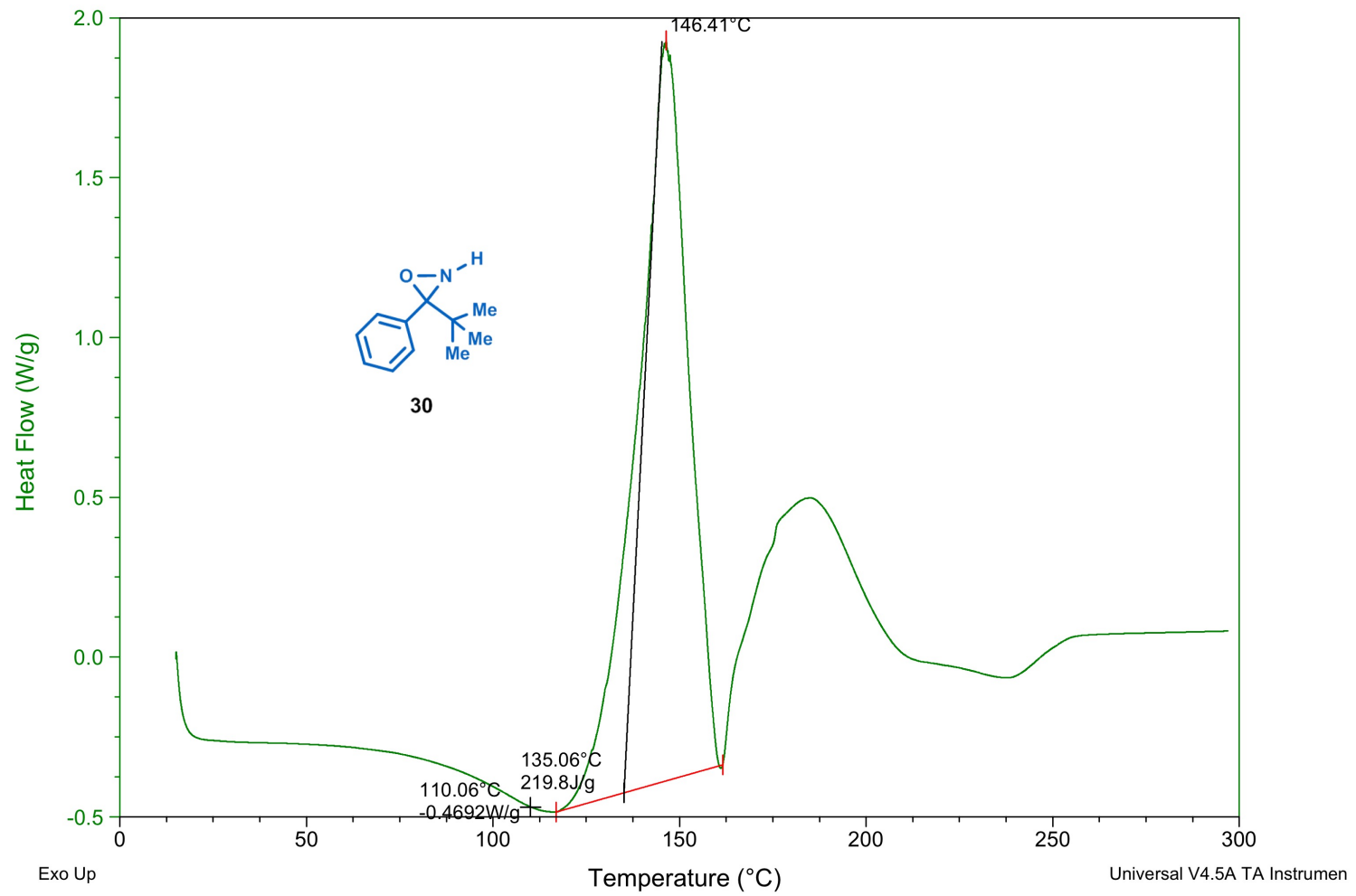
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Sample: LKNH3
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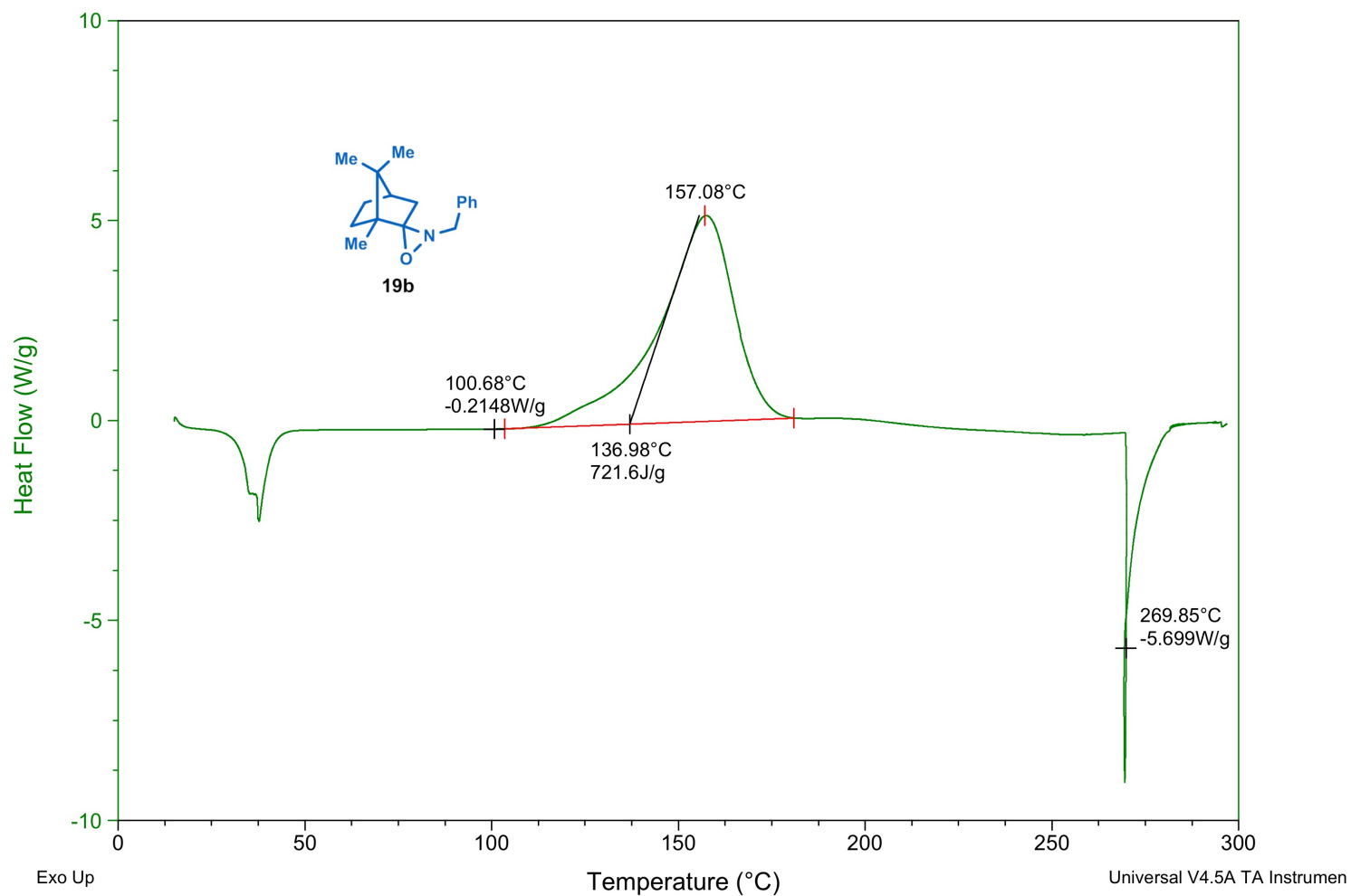
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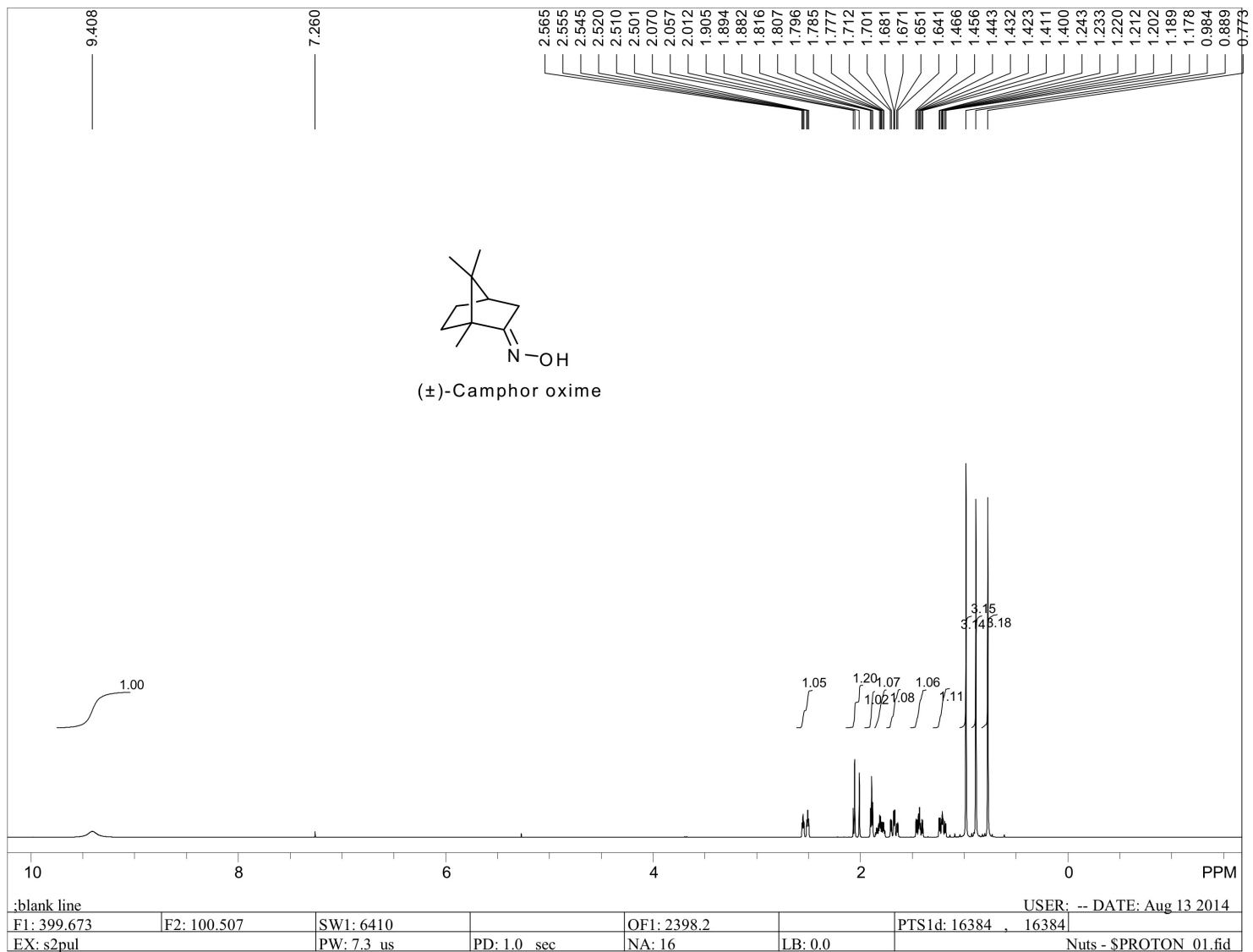
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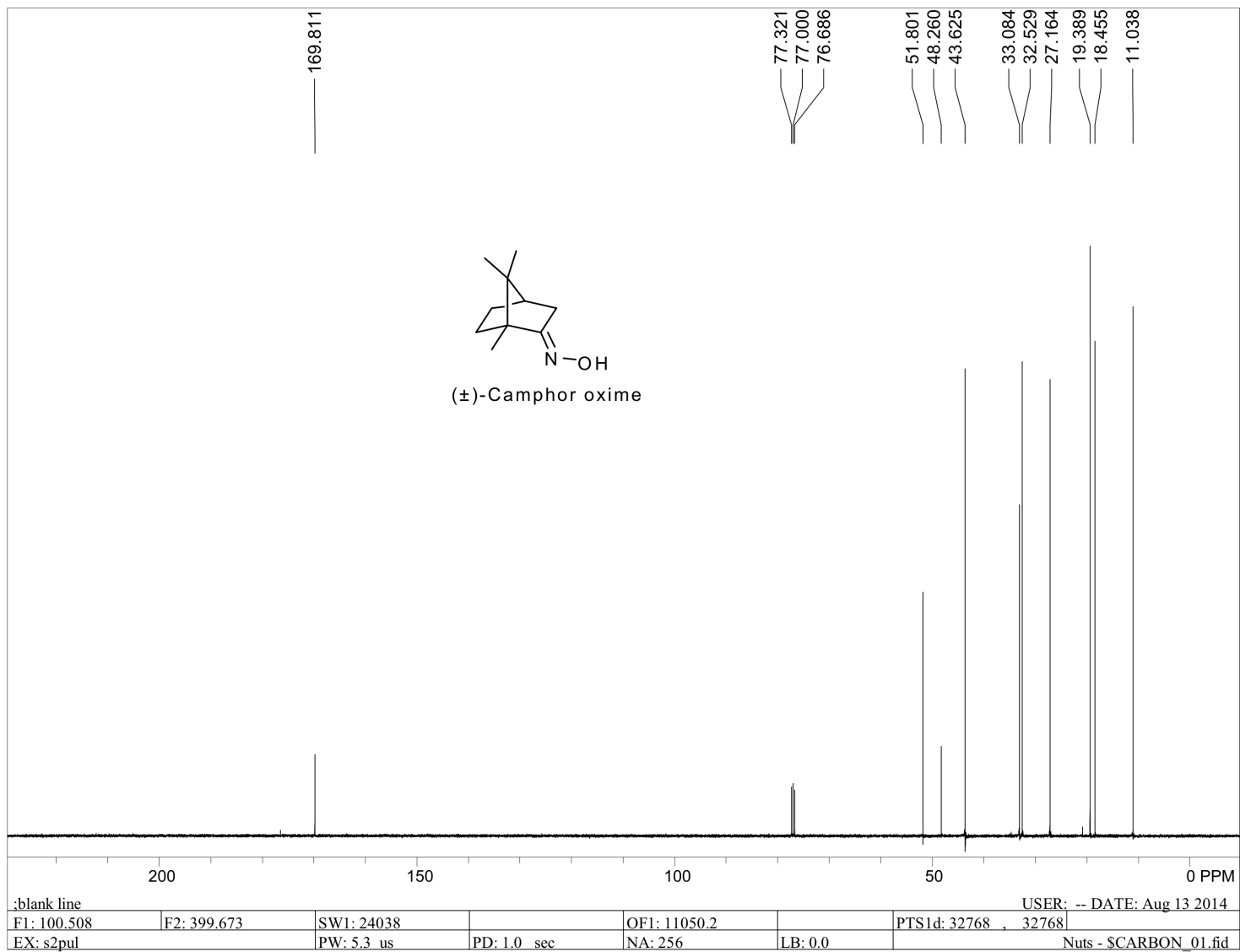
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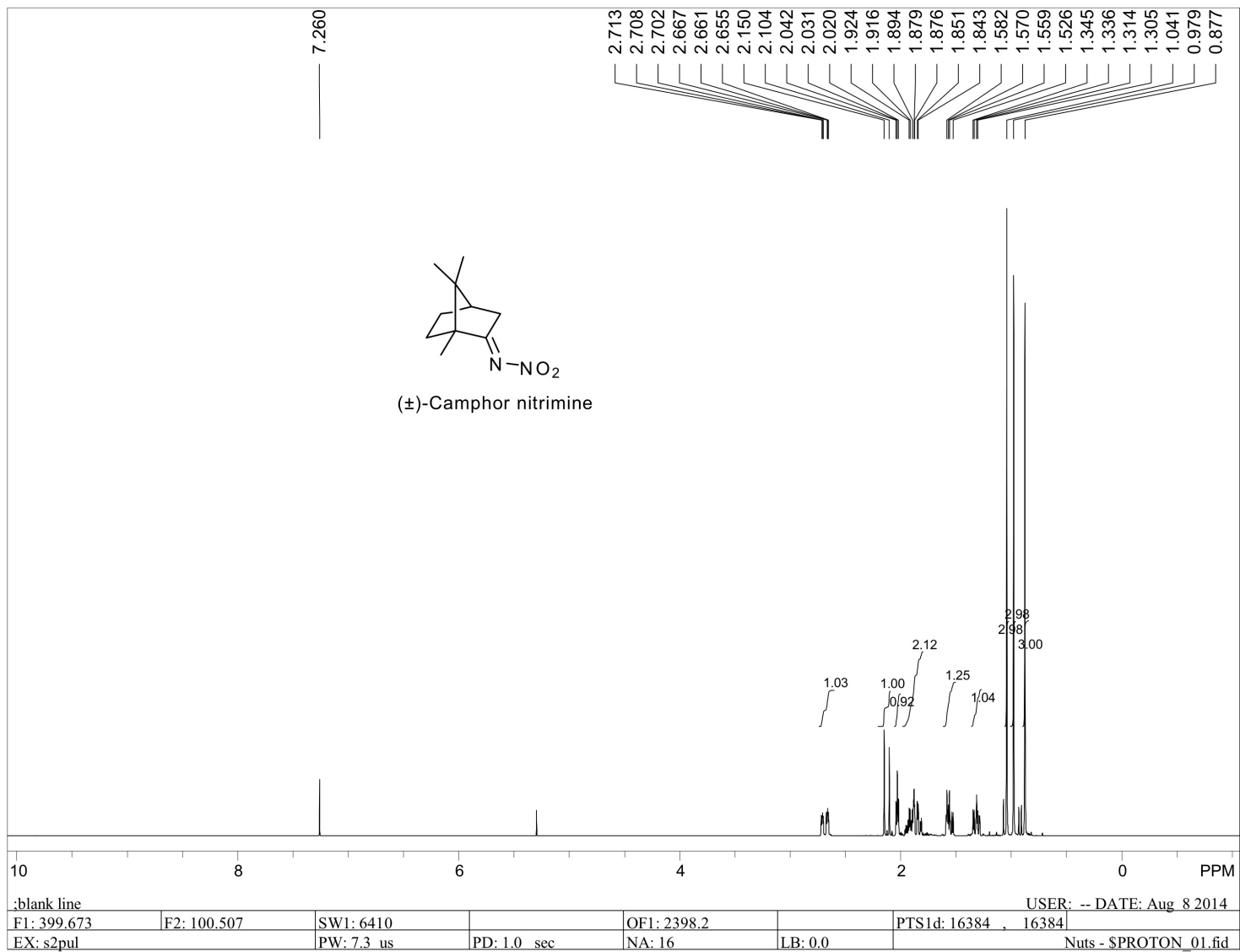
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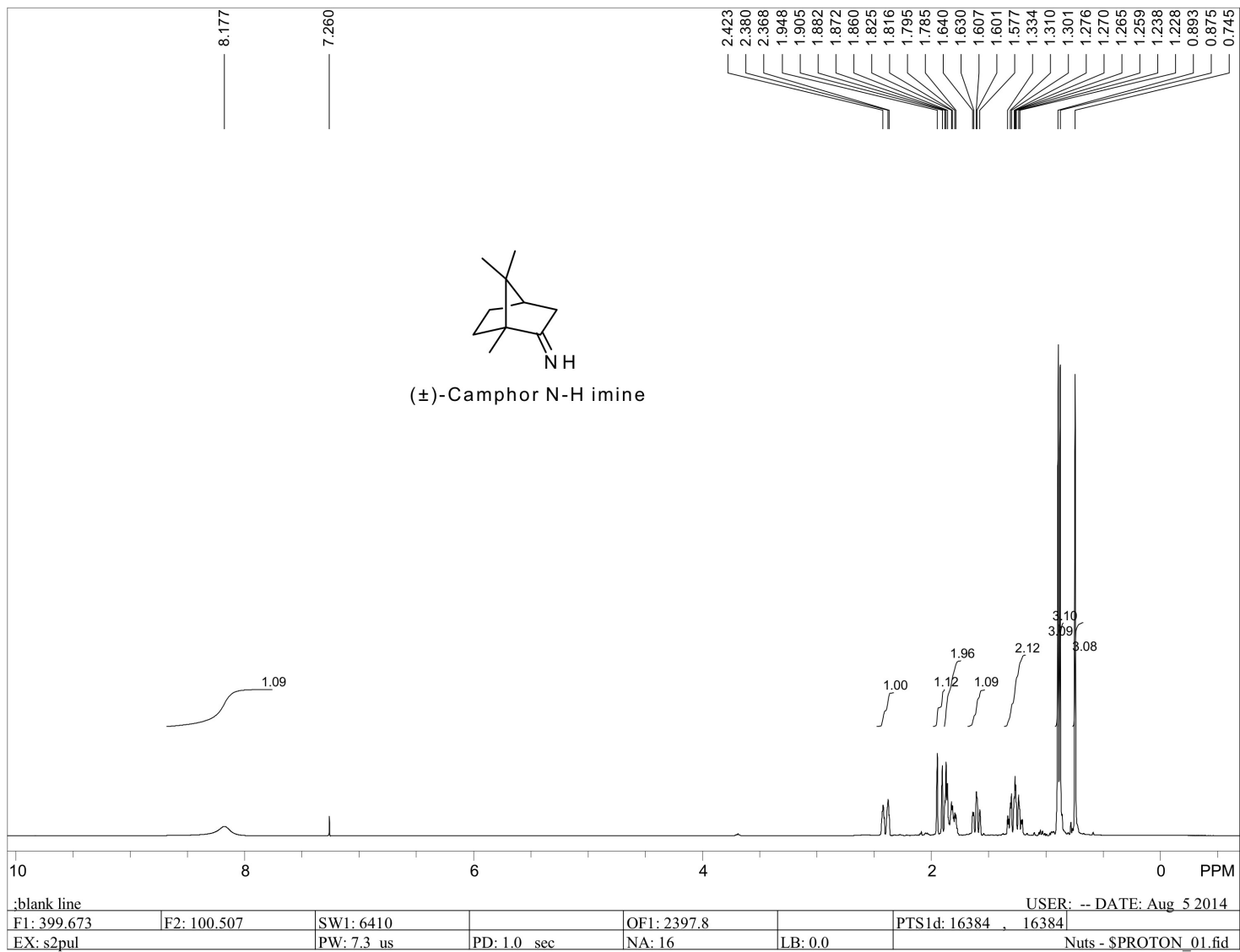


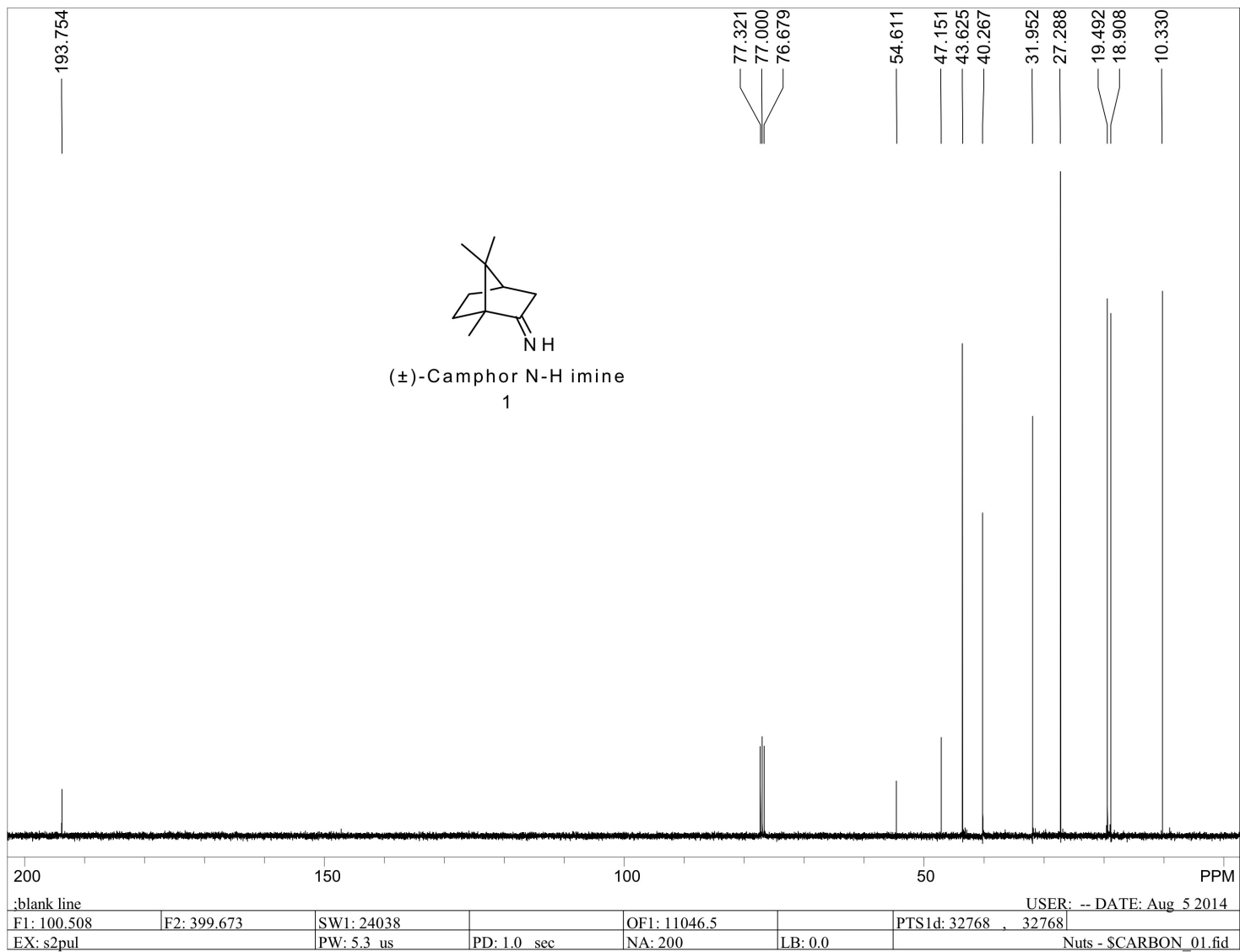
NMR Spectra of Oxaziridines

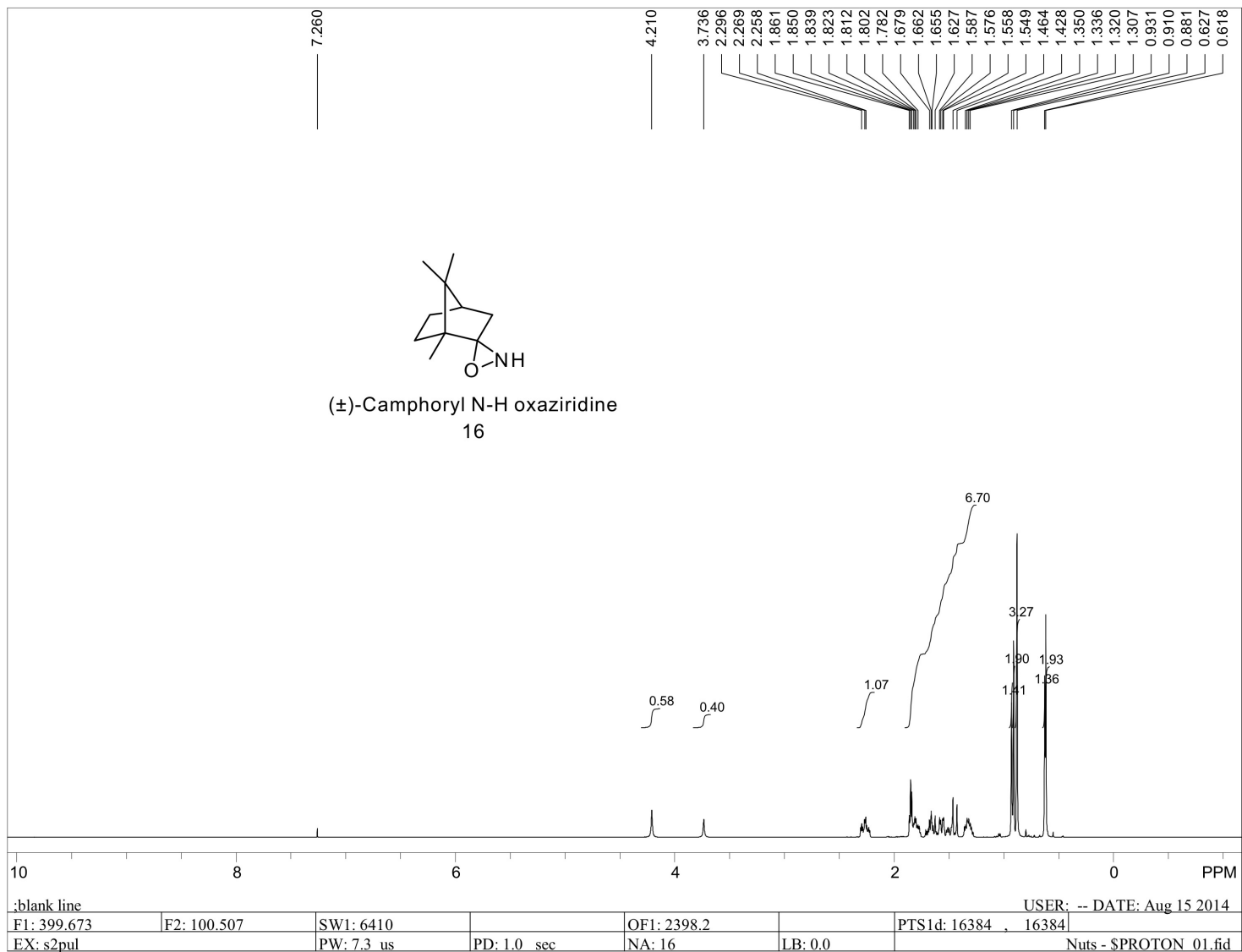


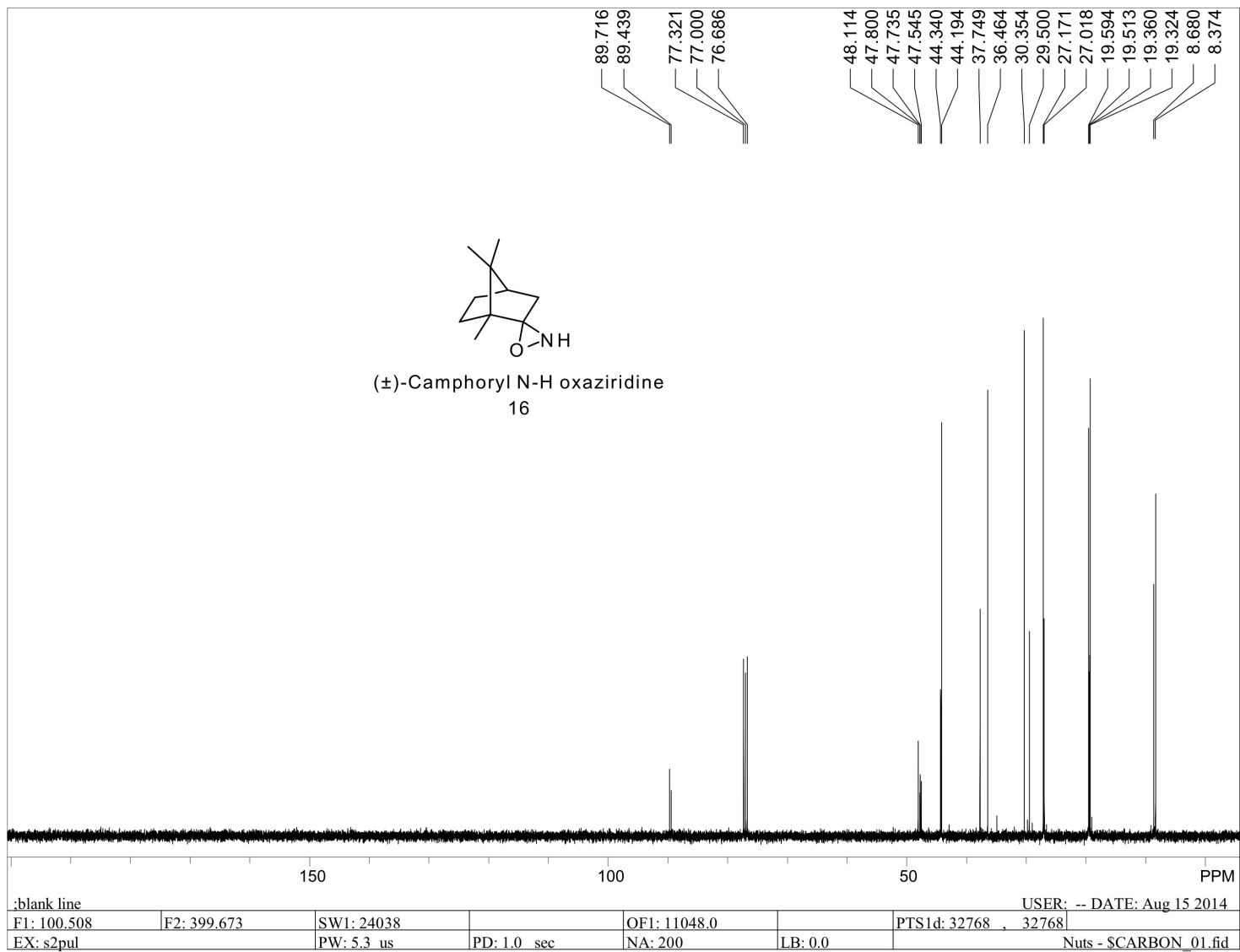


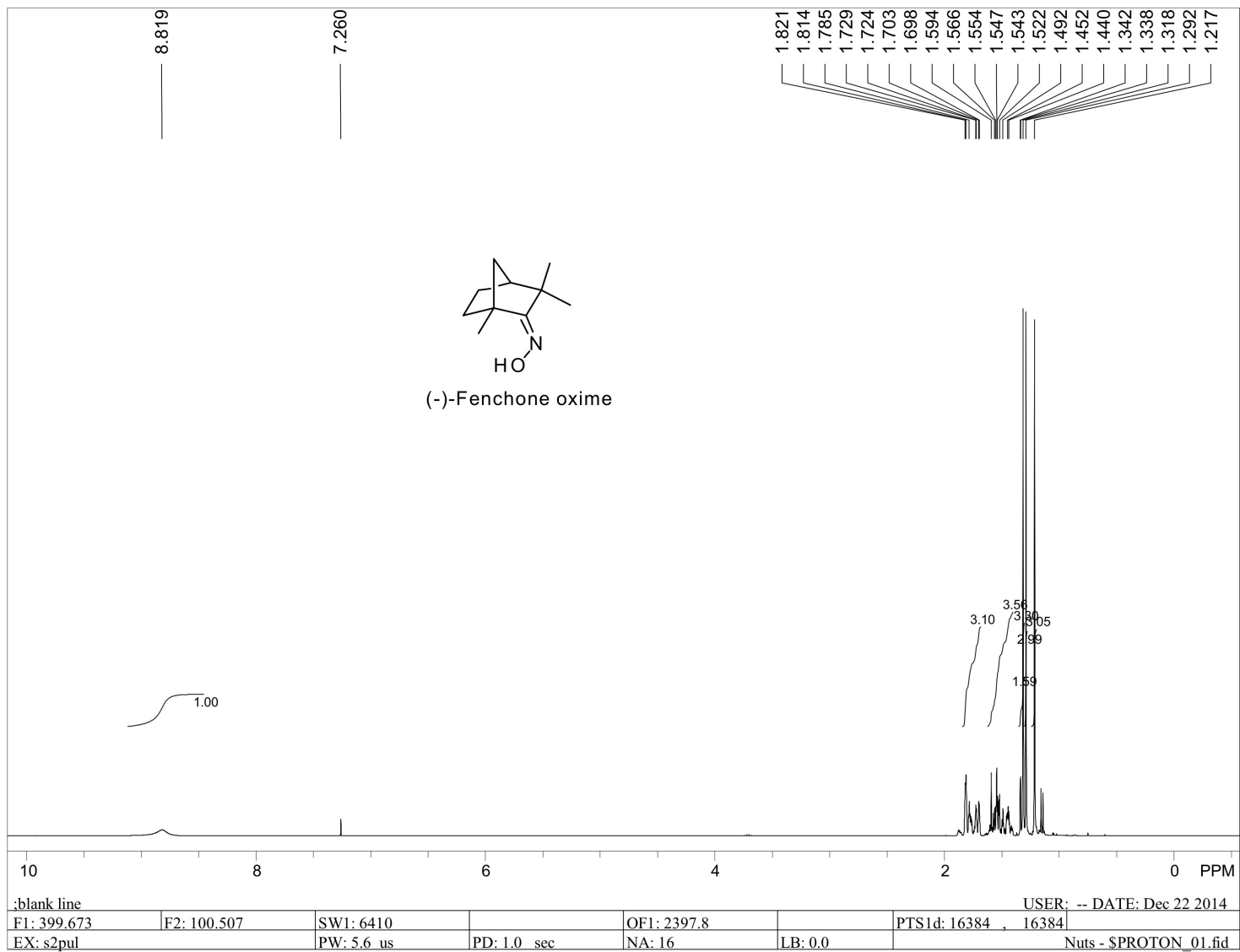


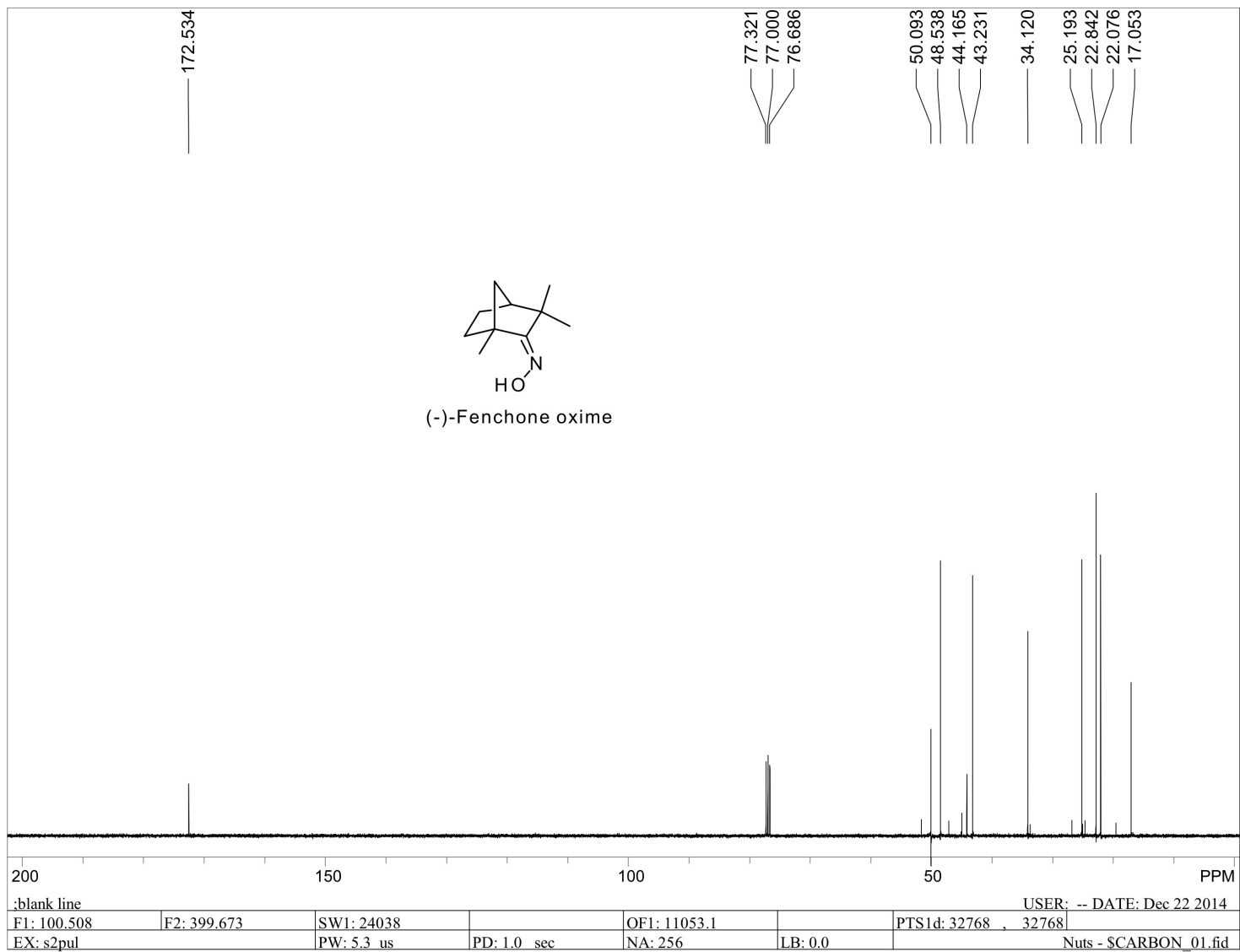


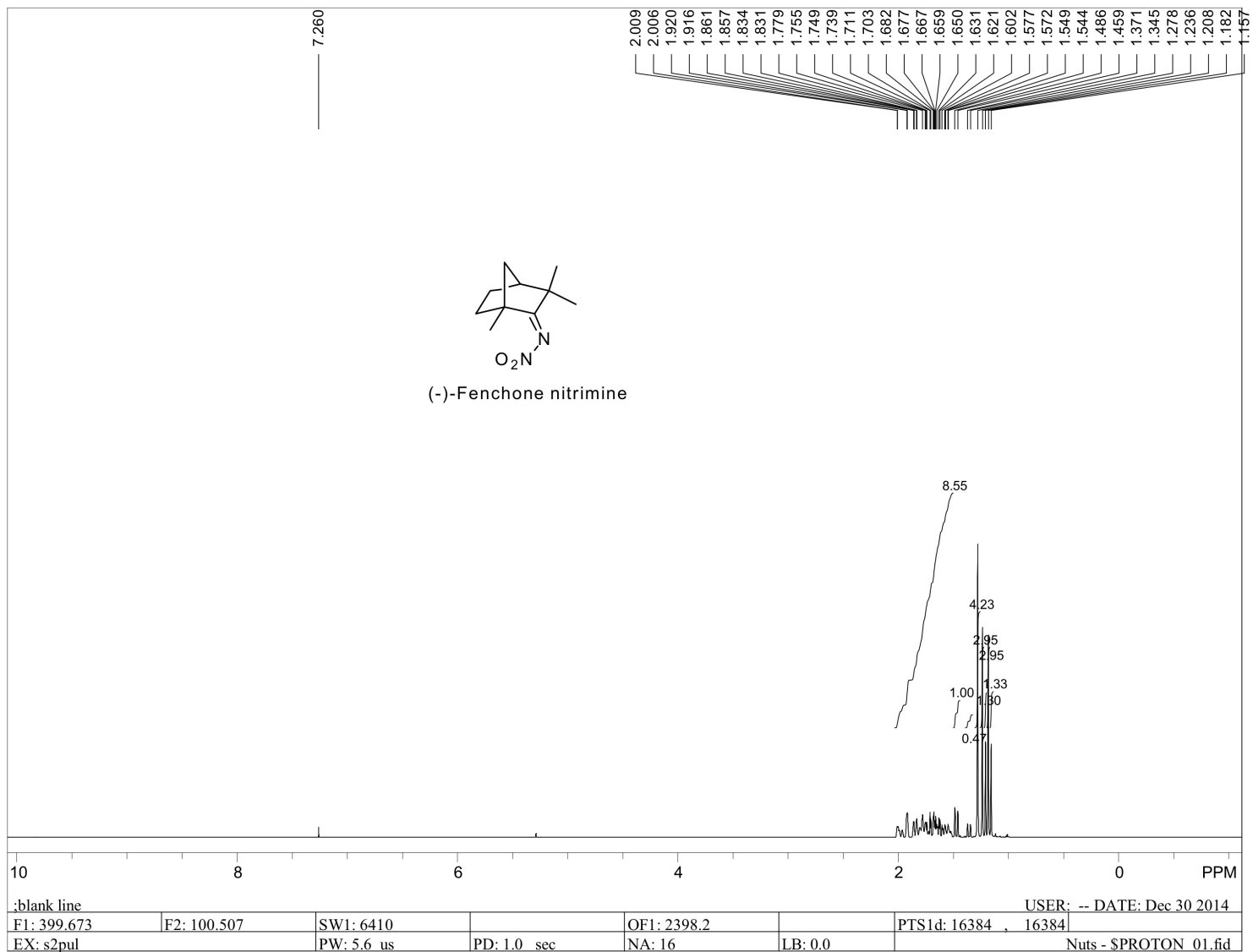


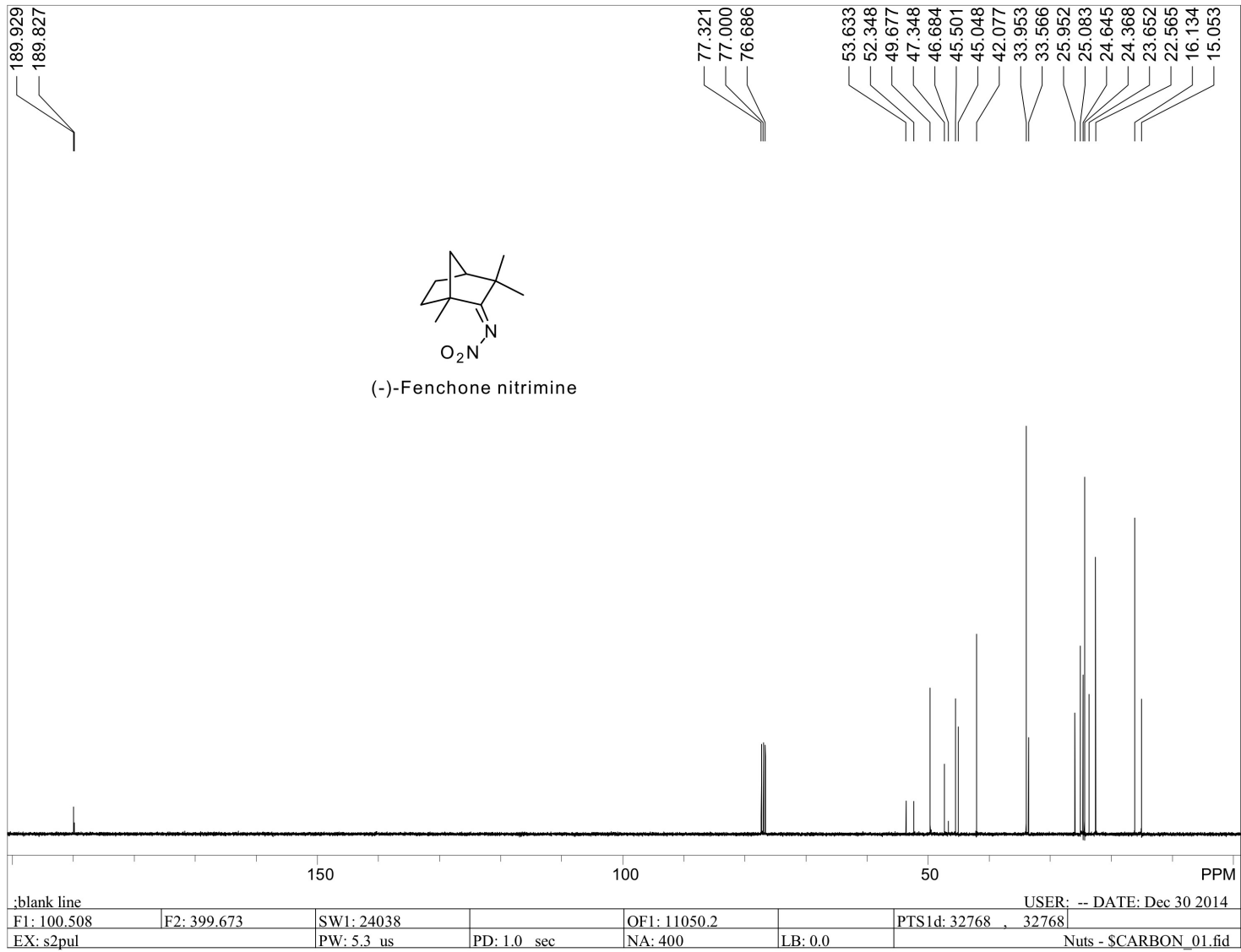


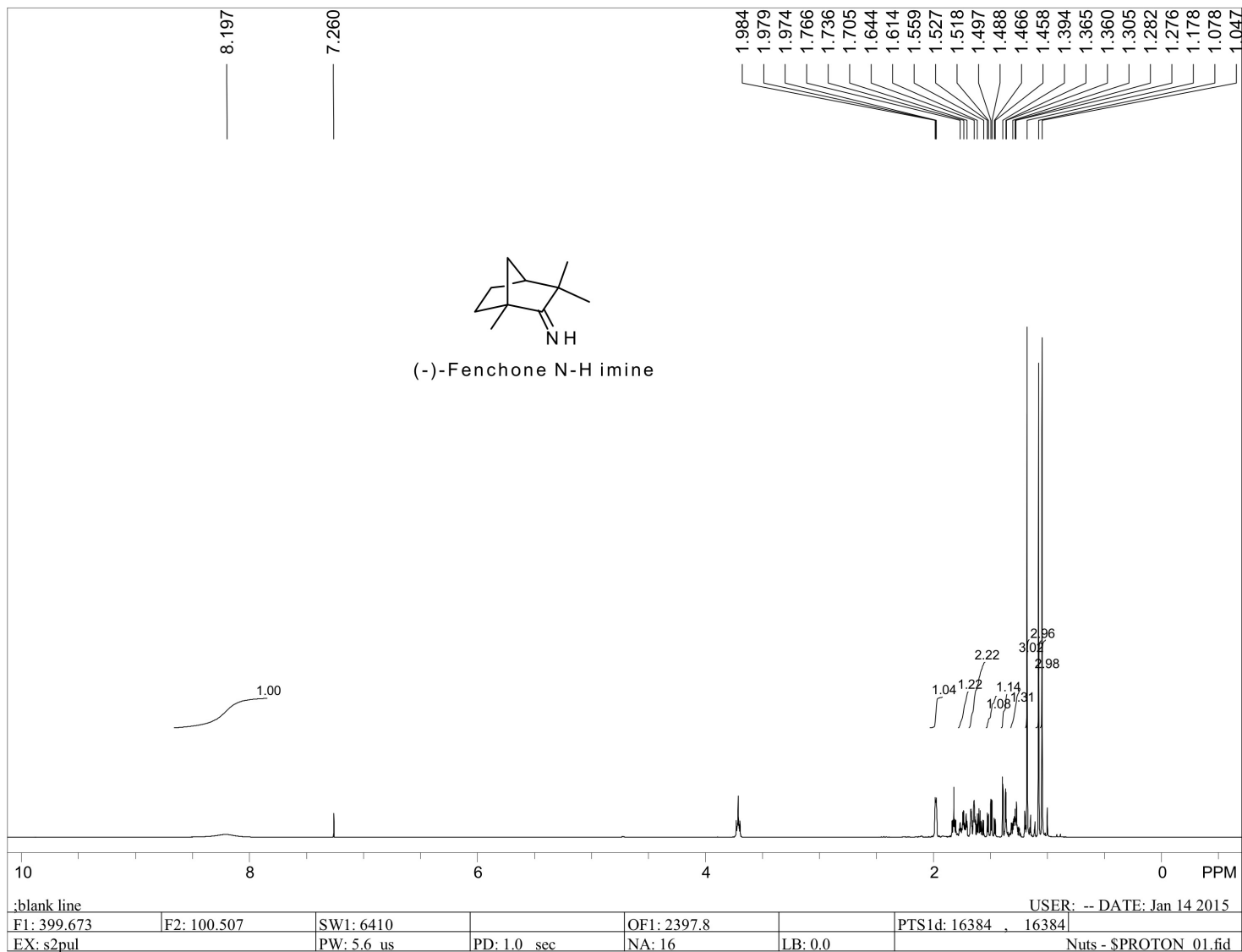


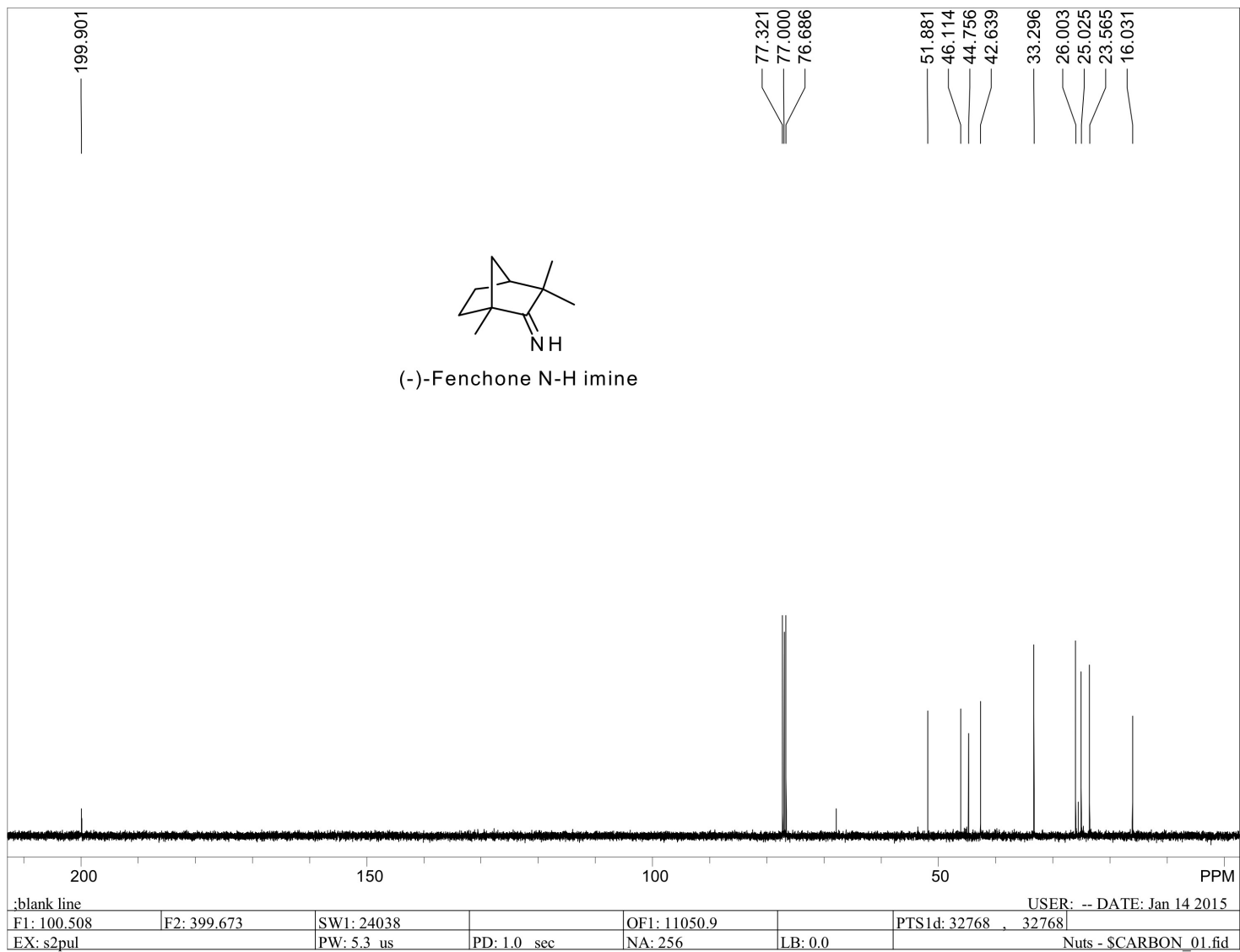


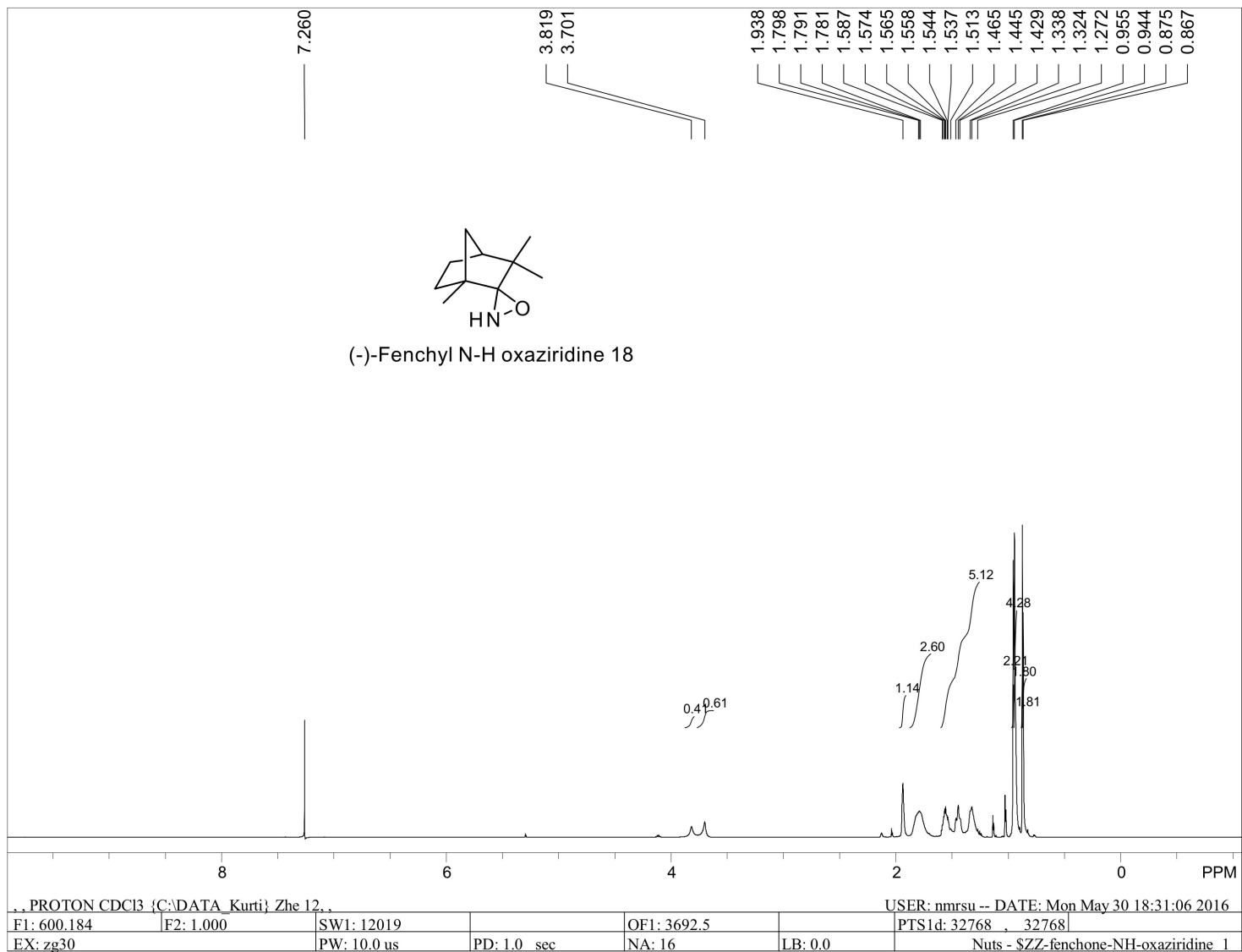


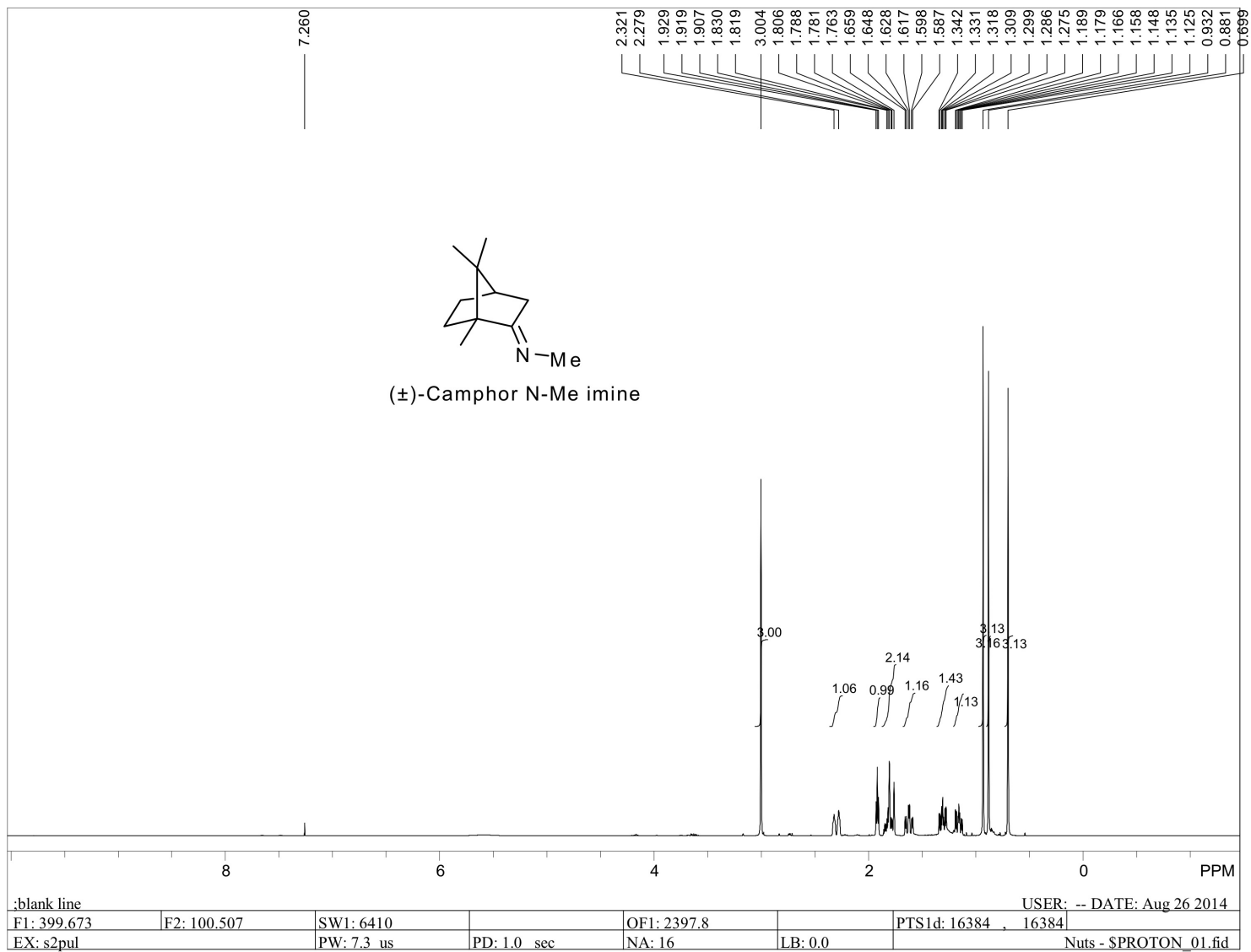


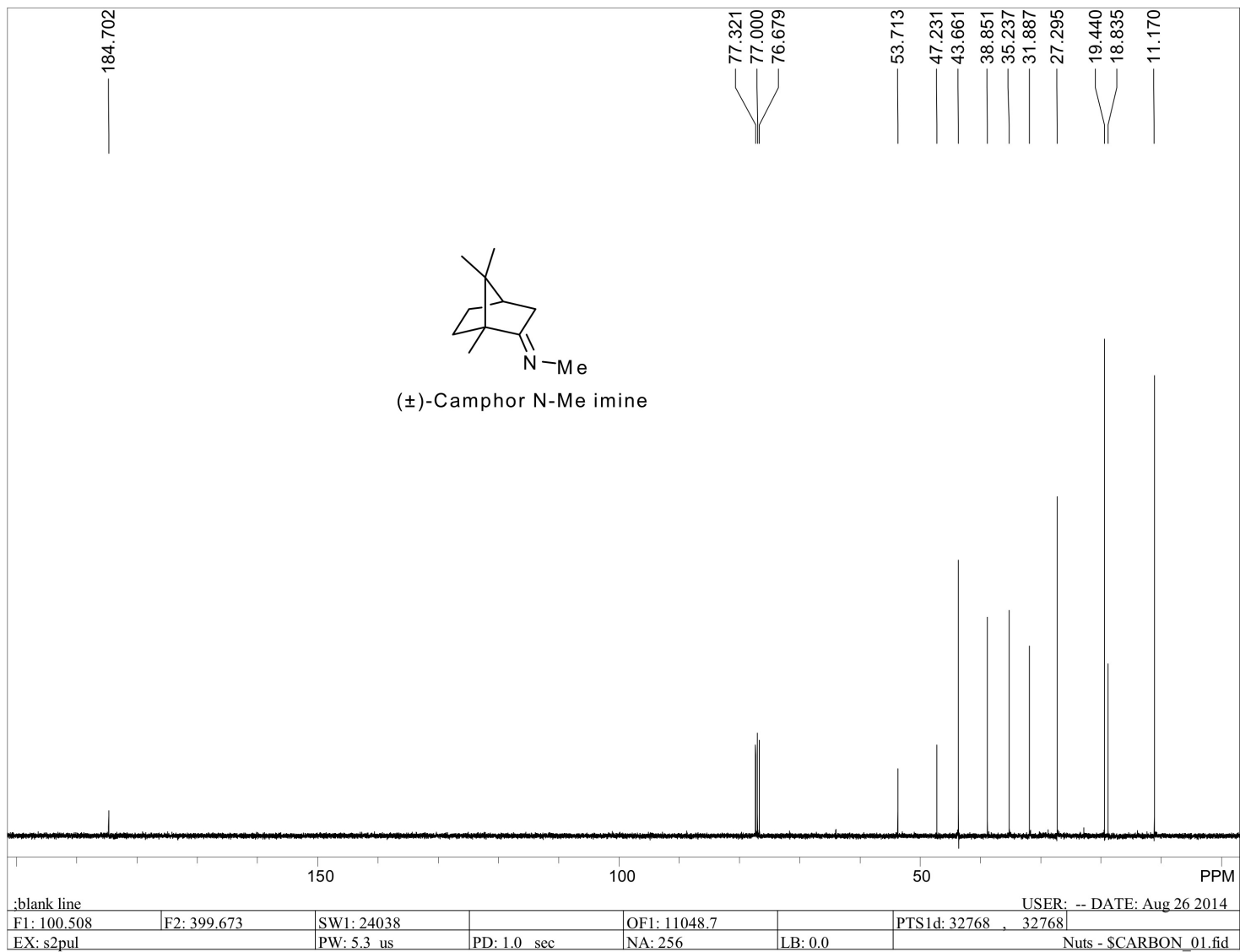


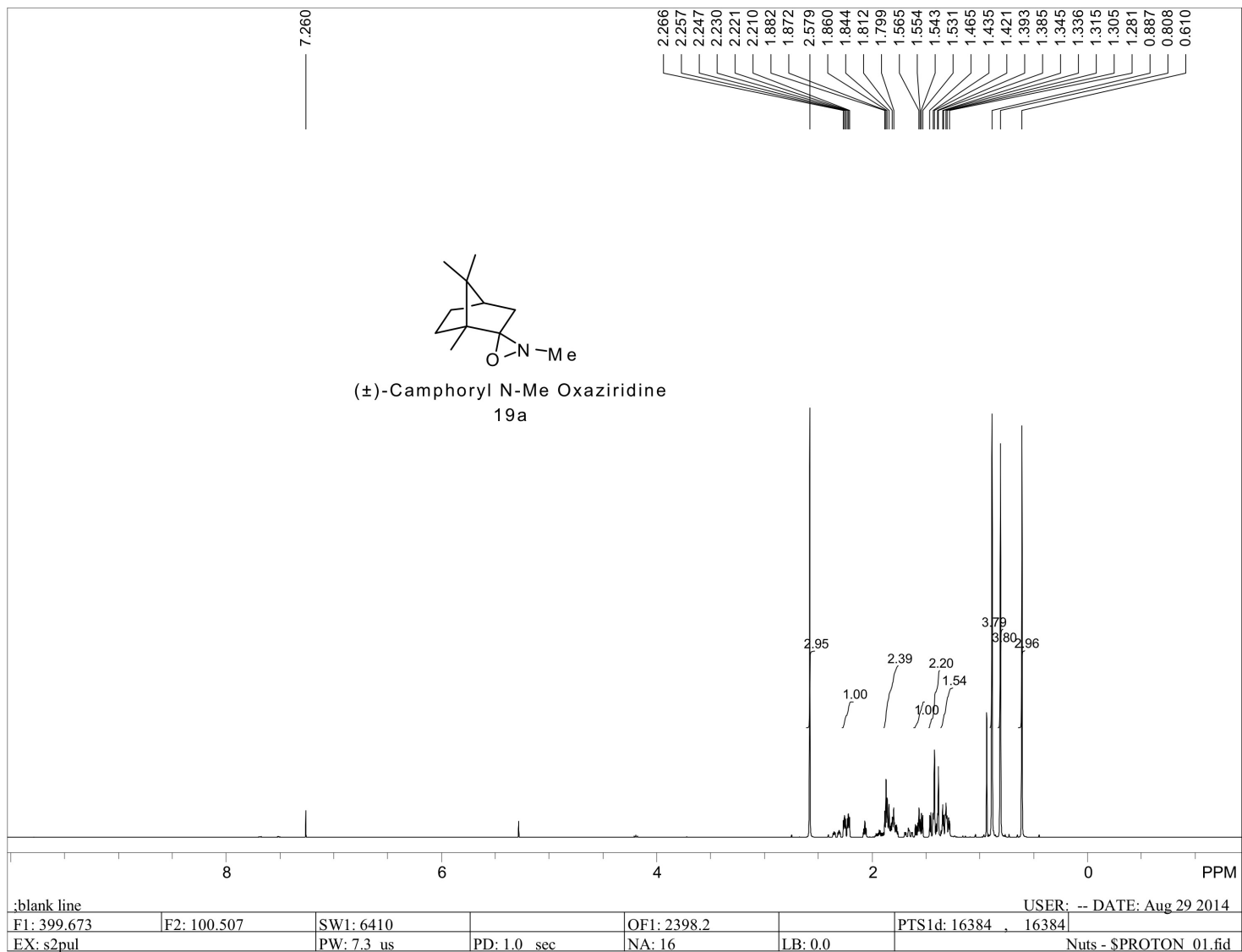


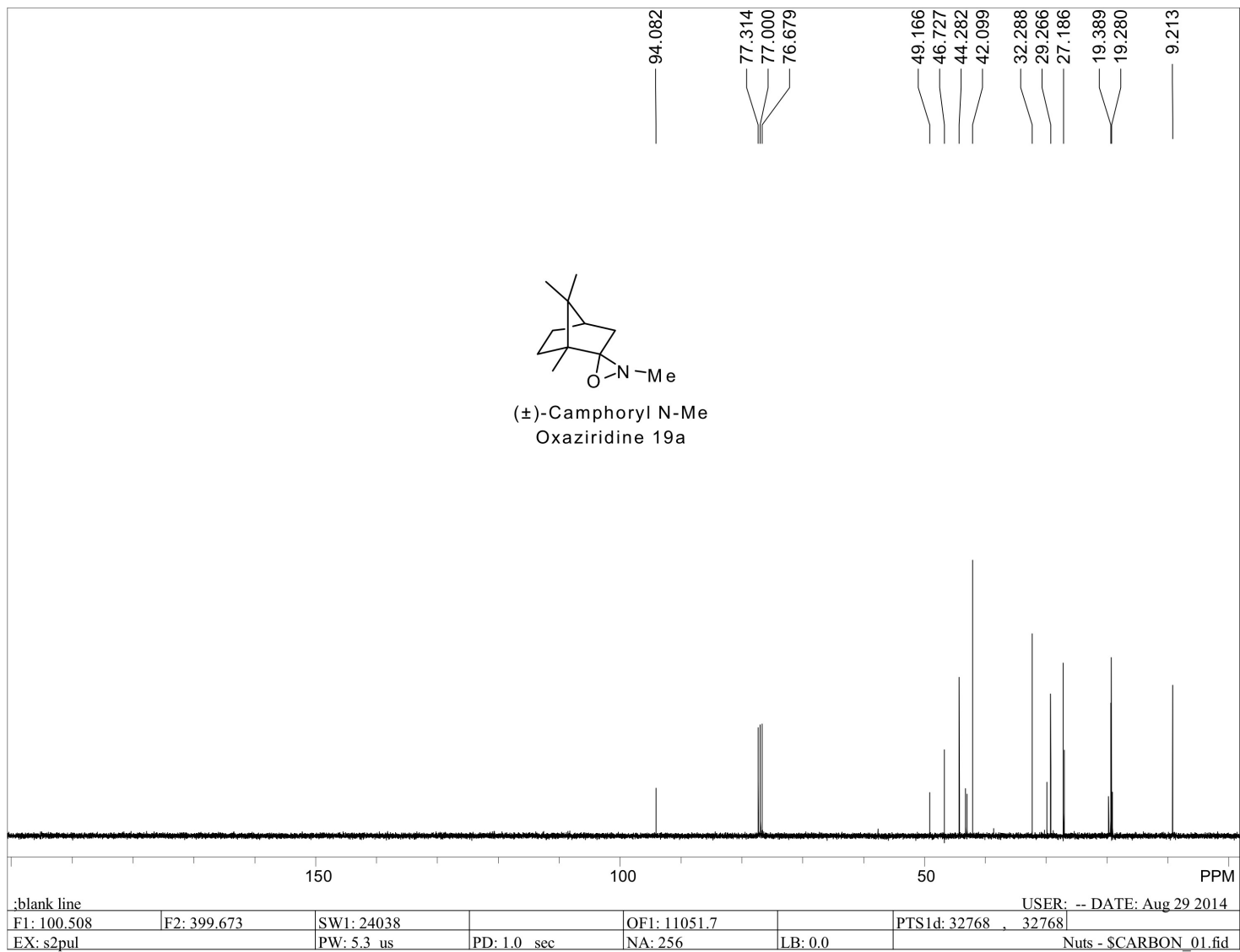


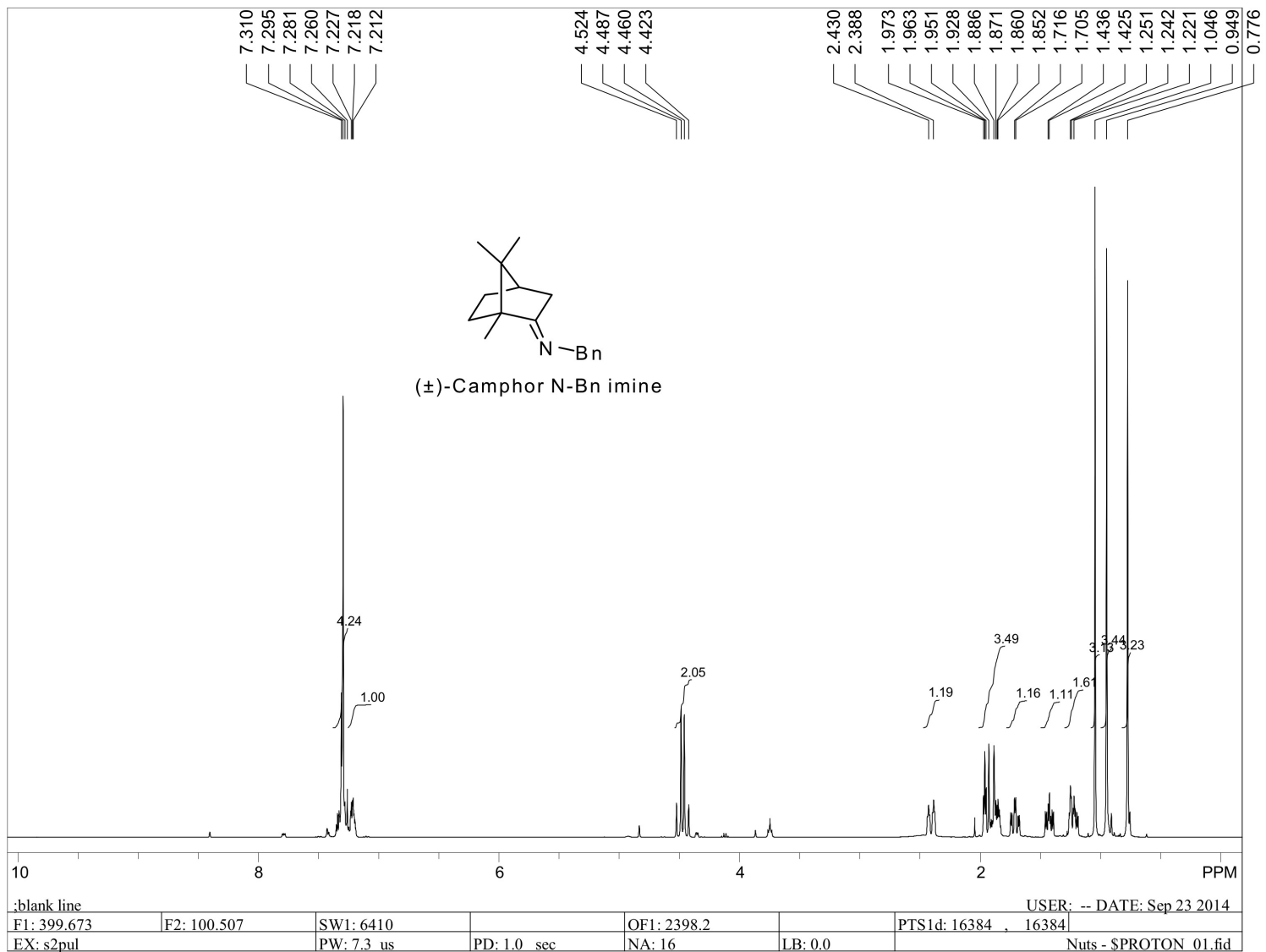


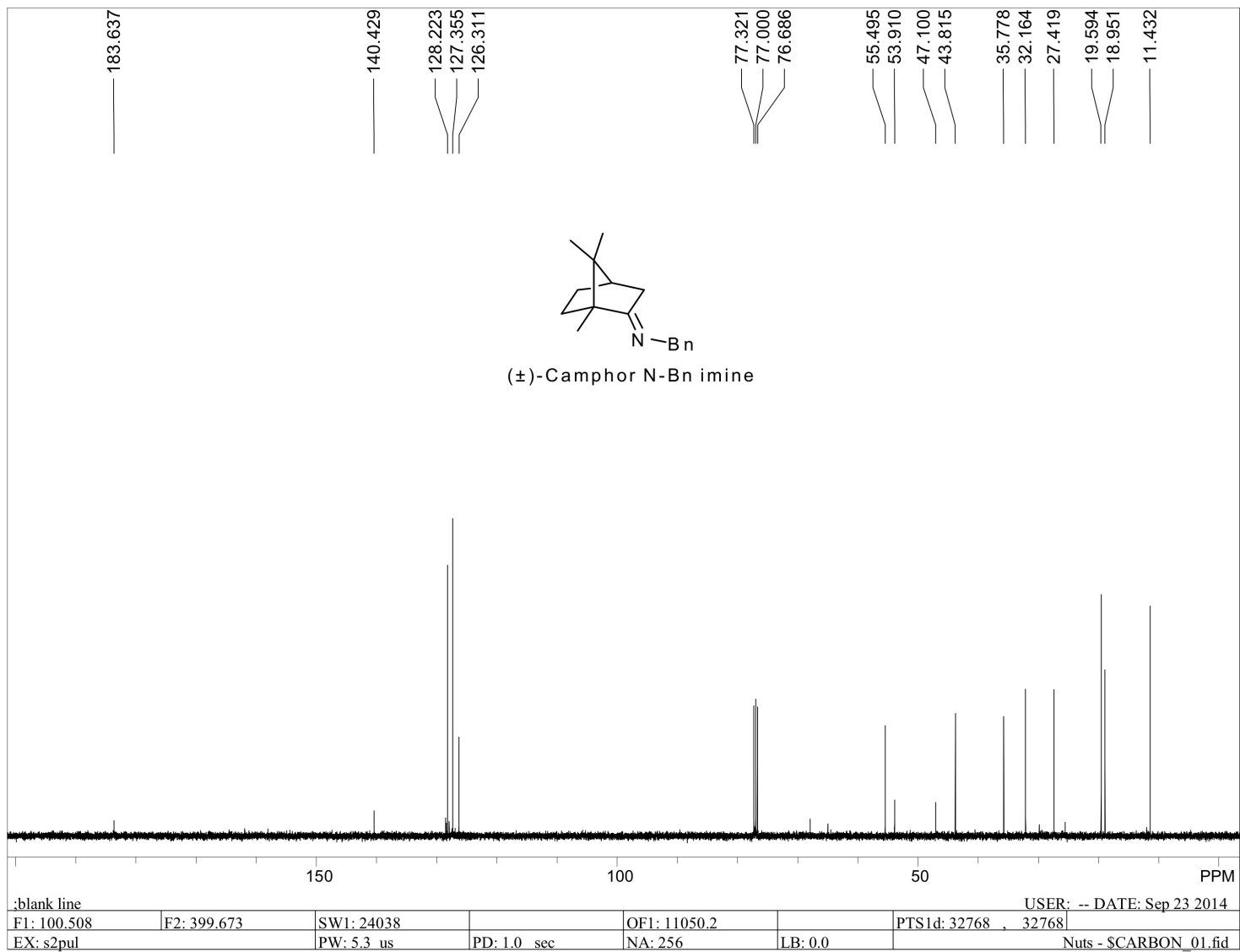


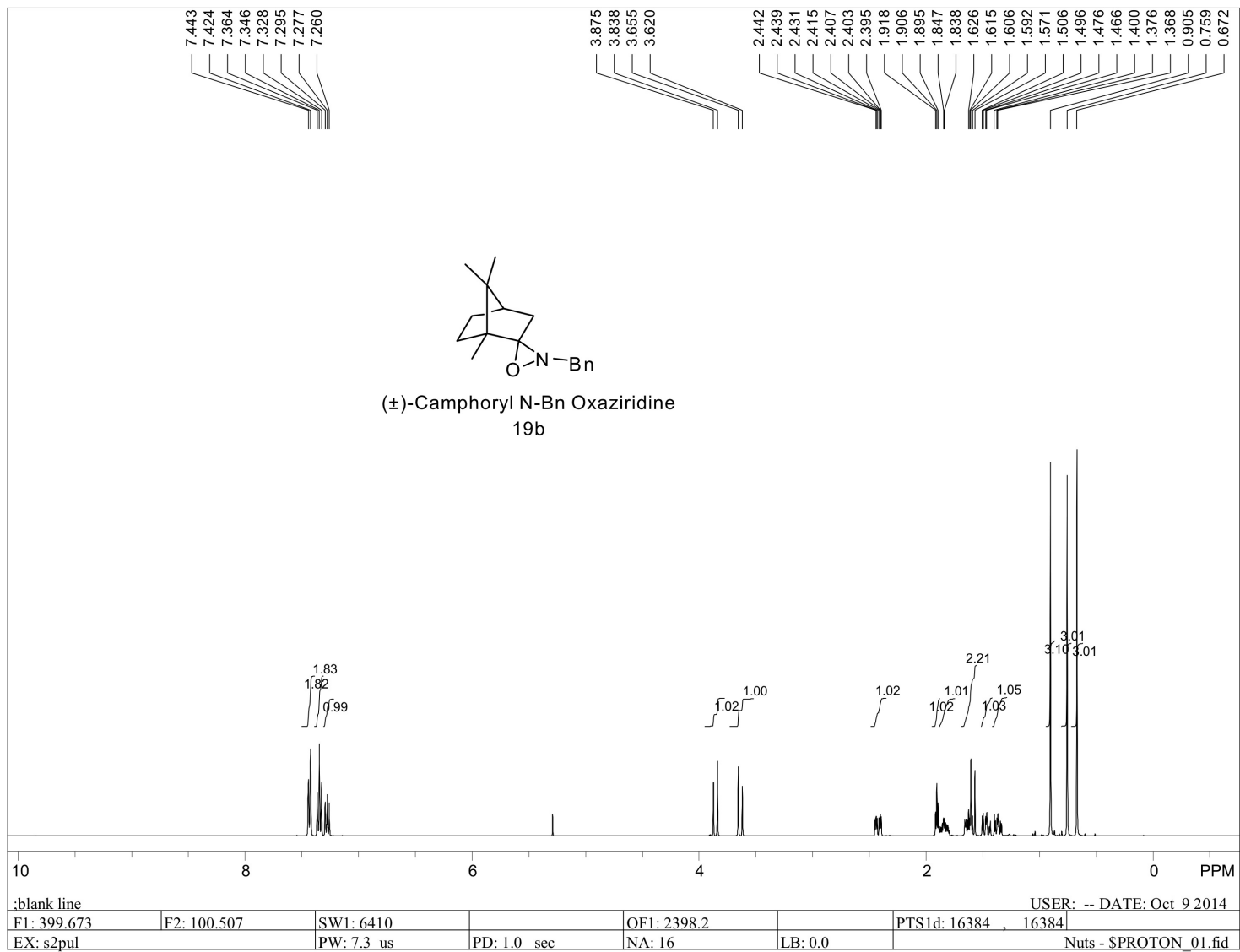


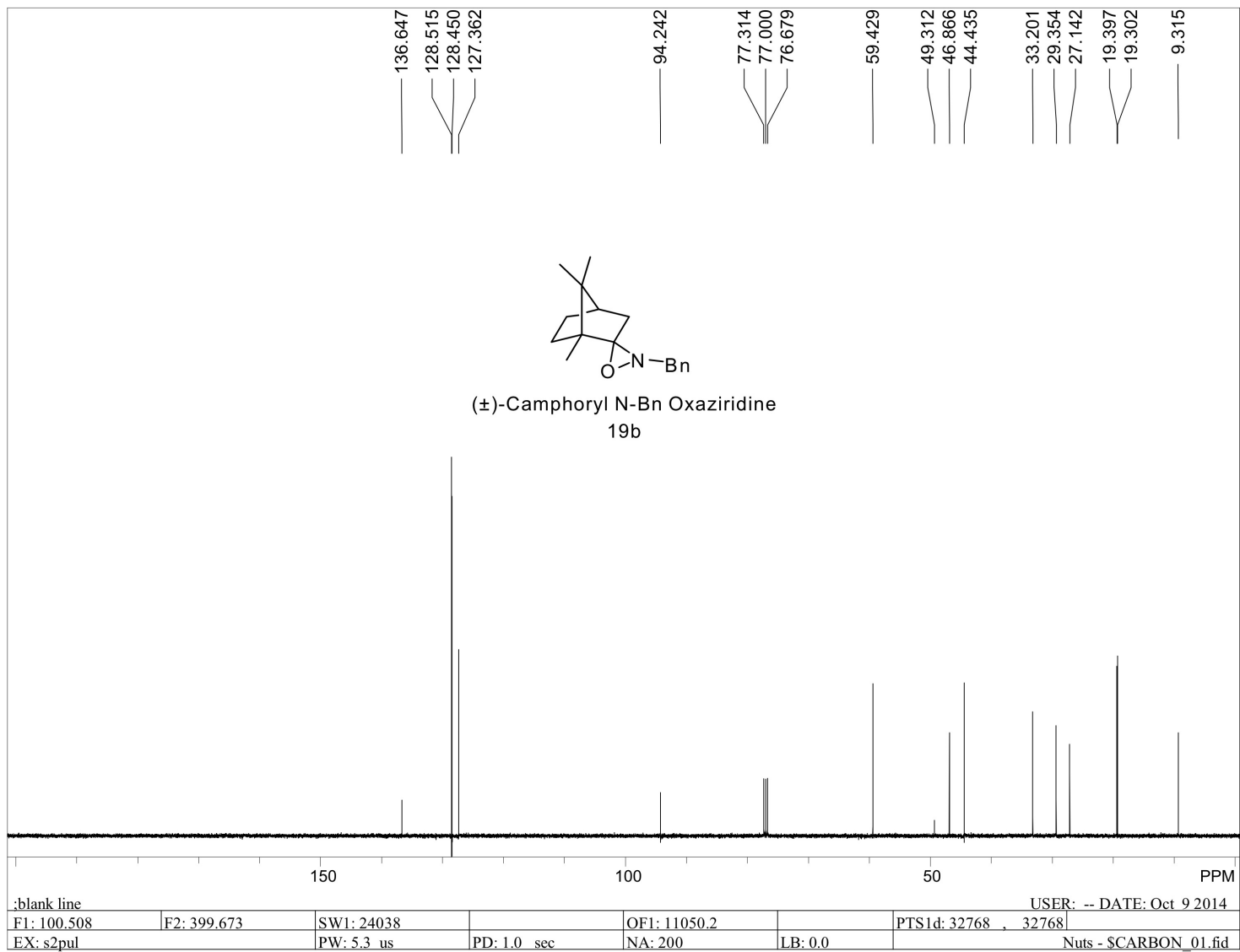


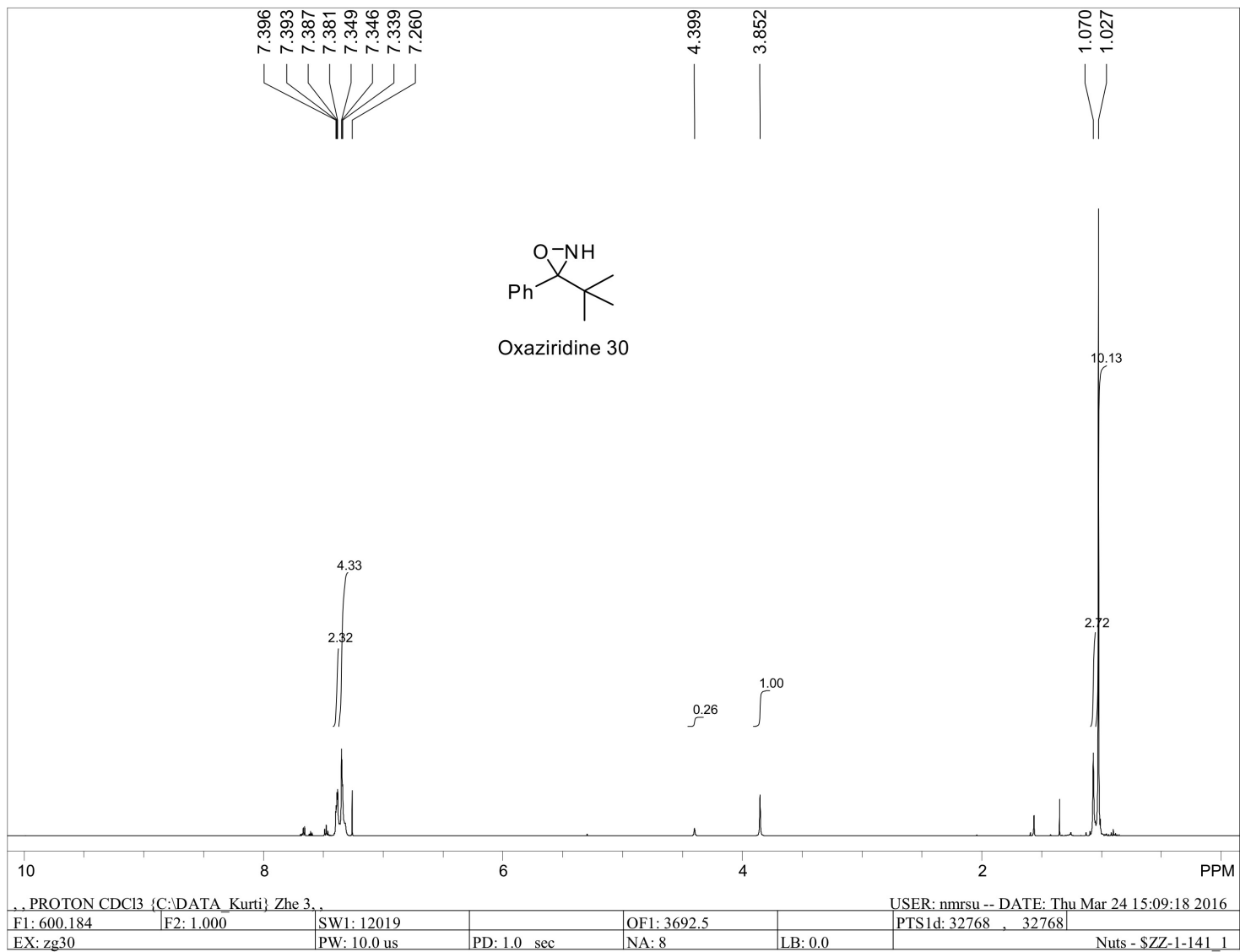


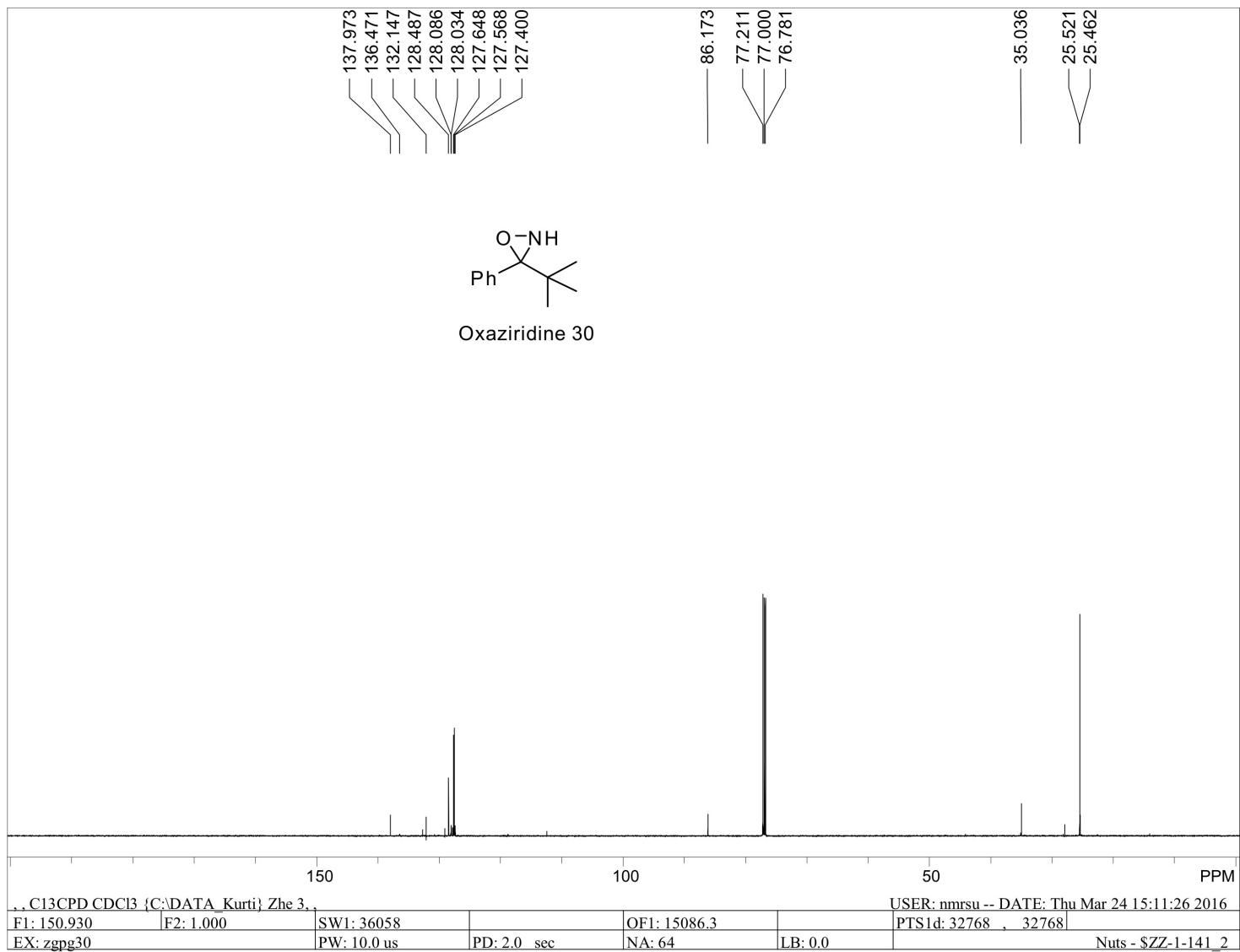


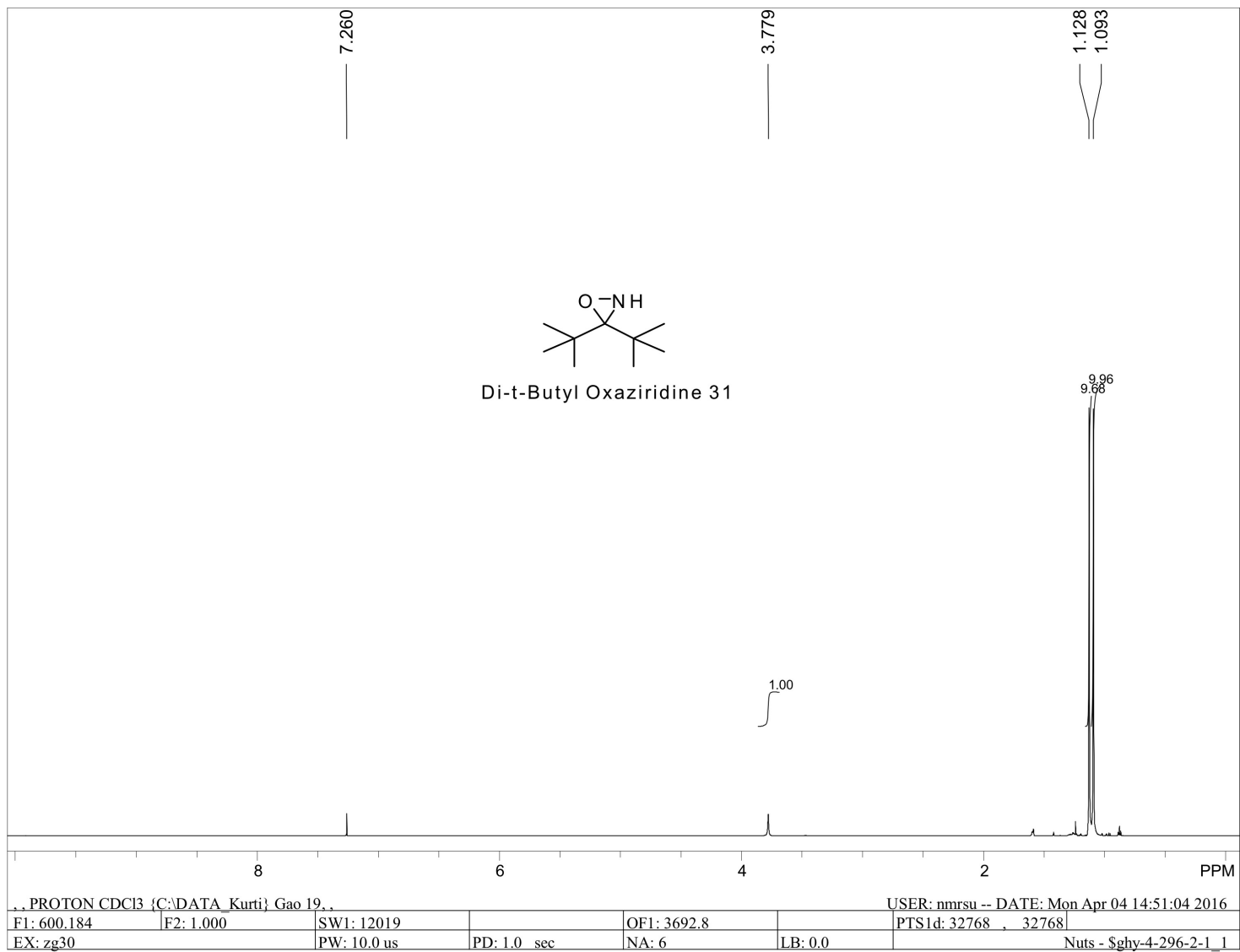


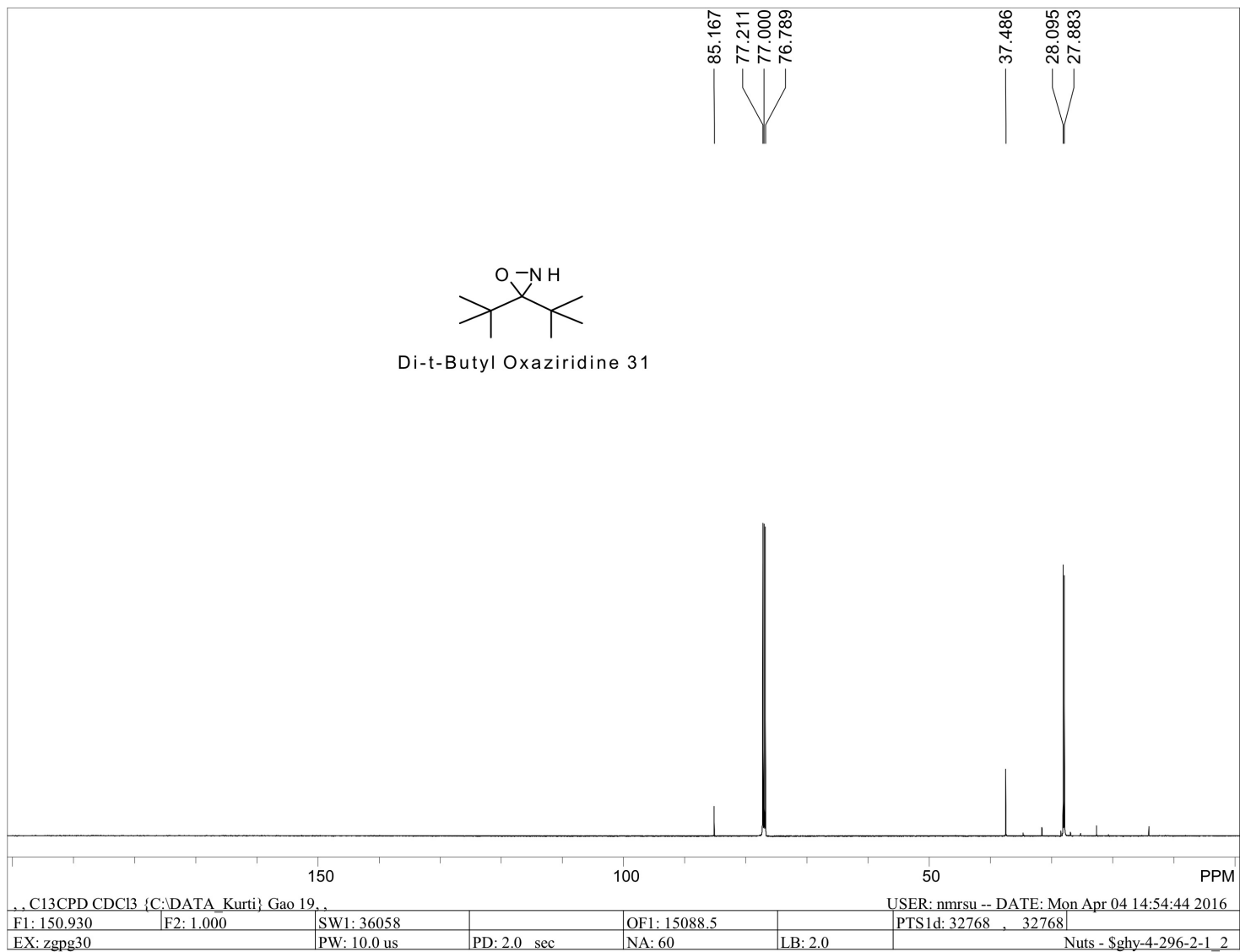




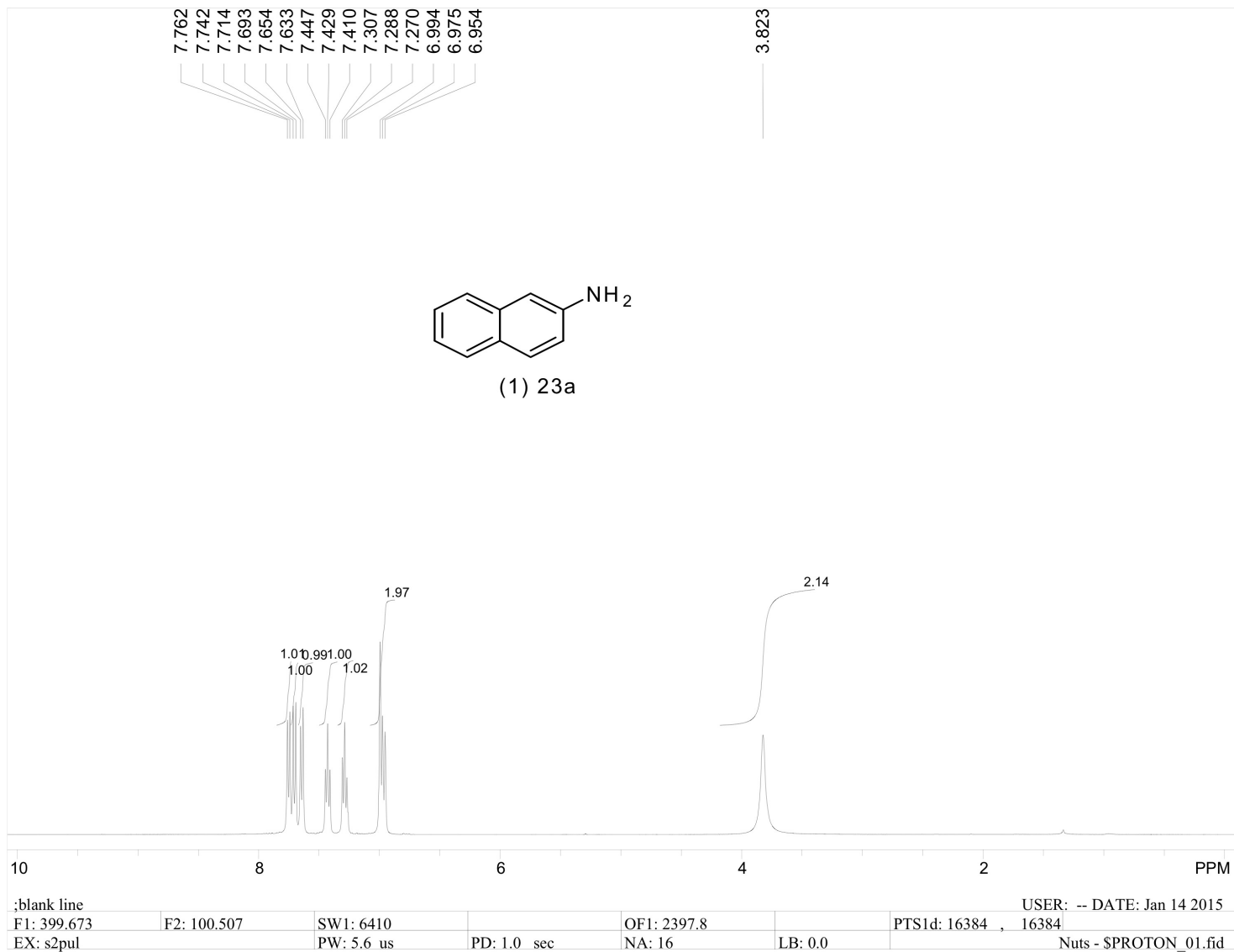


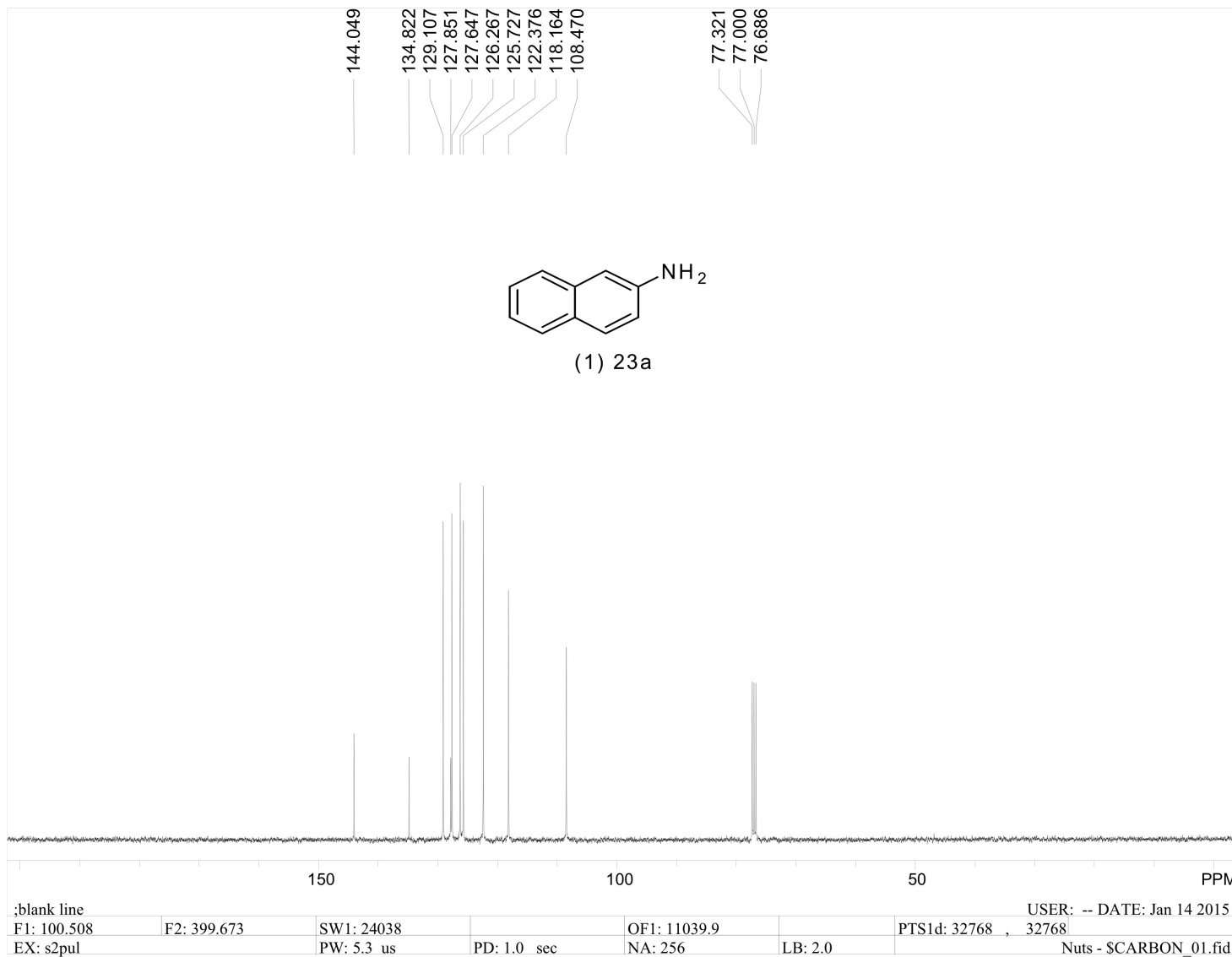


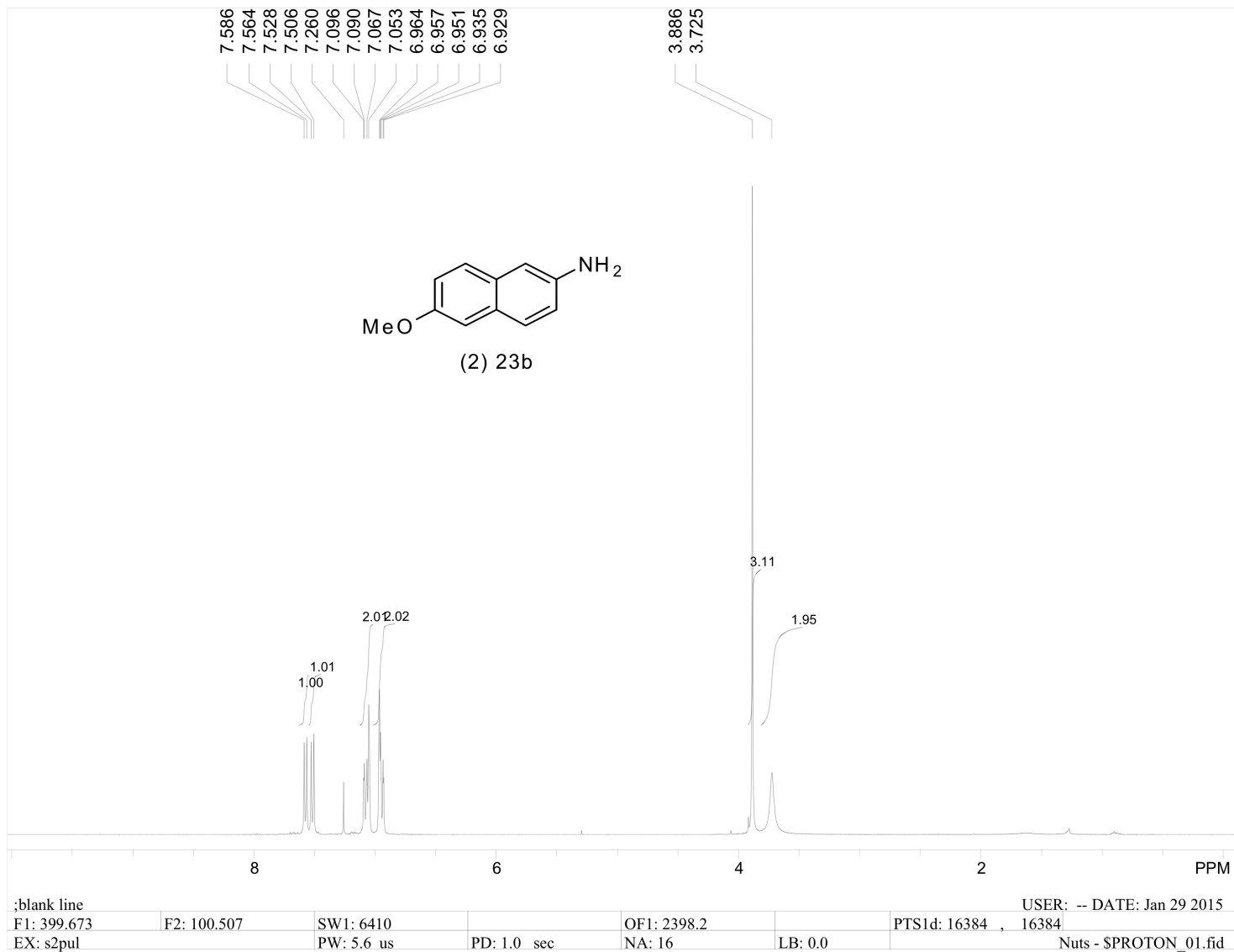


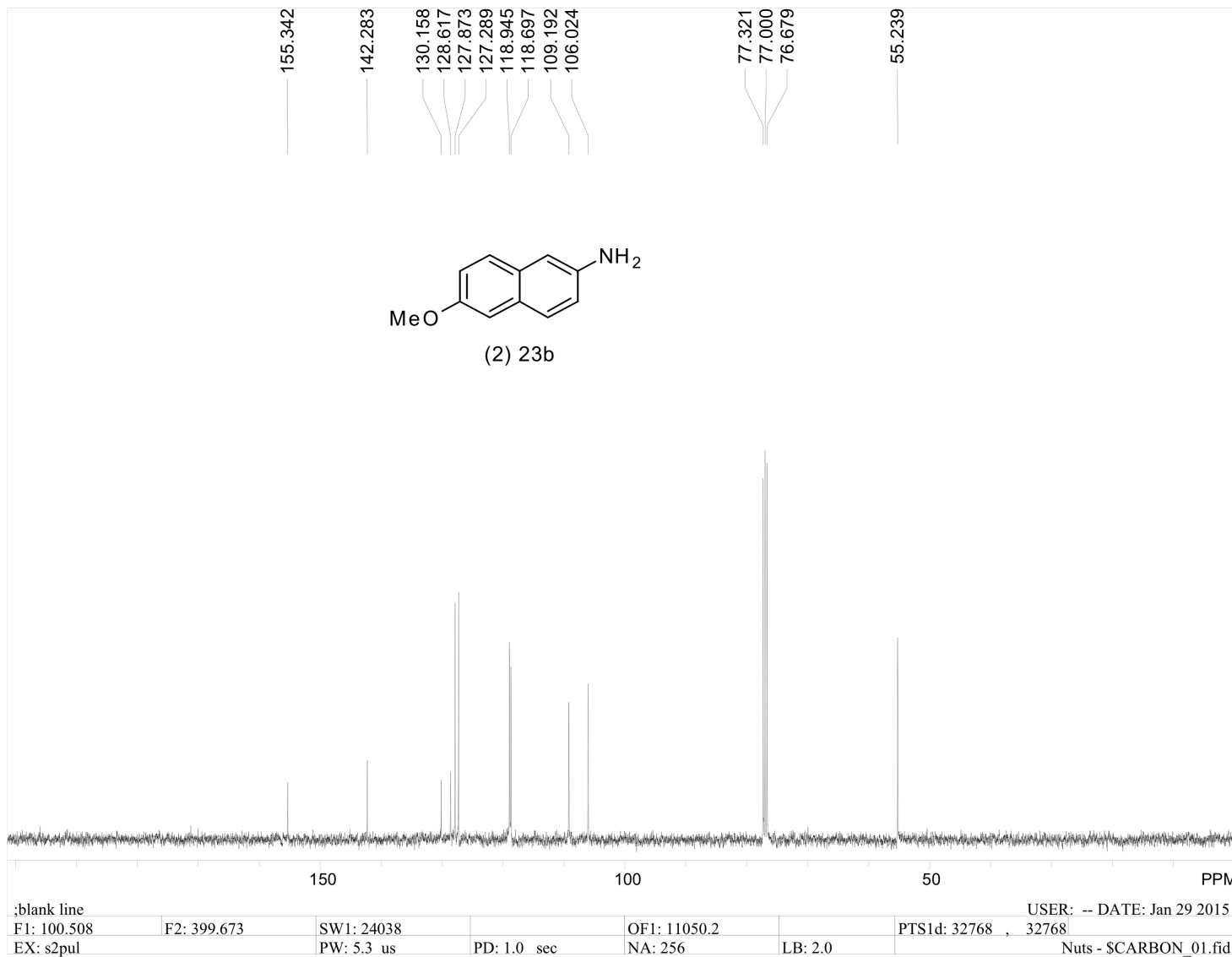


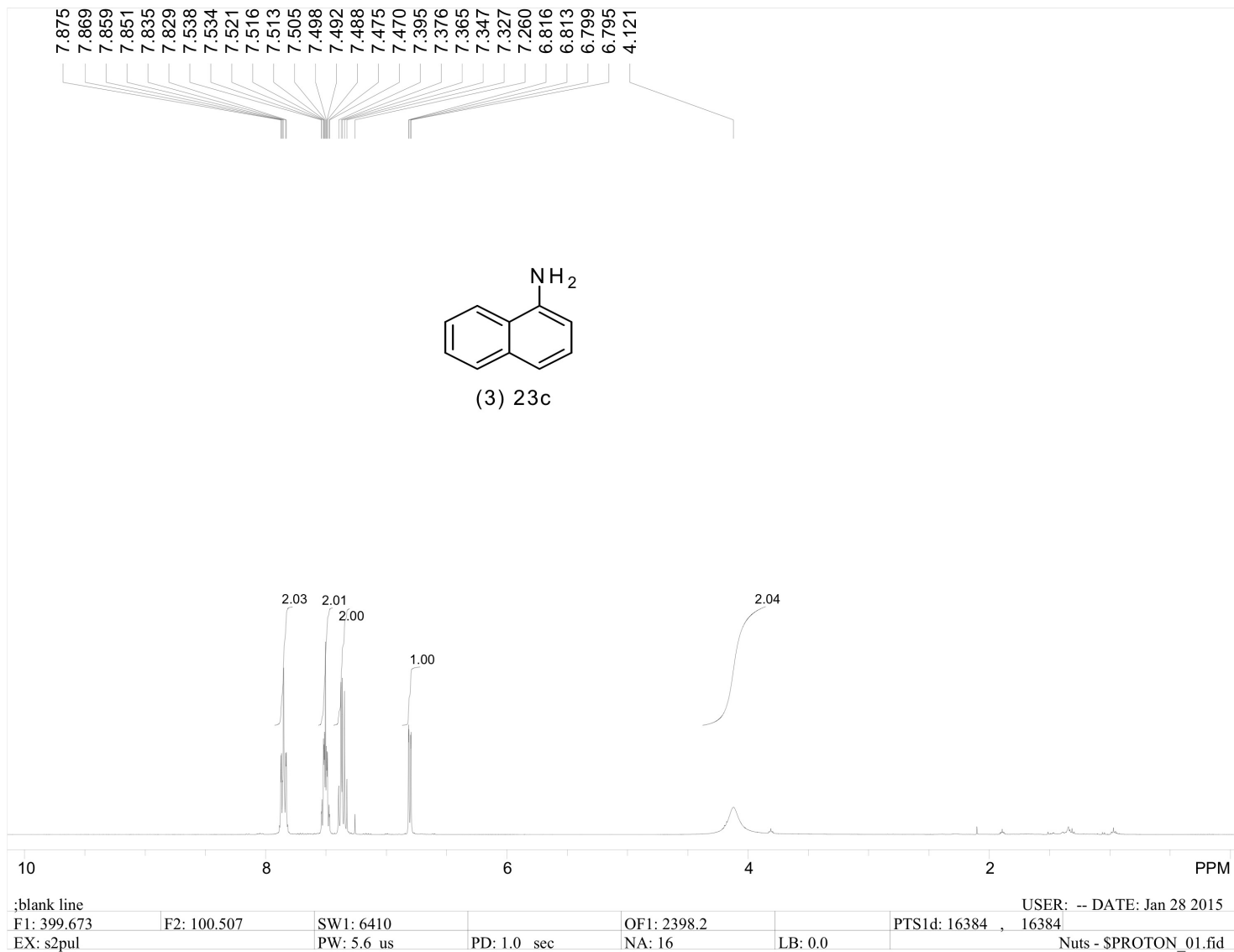
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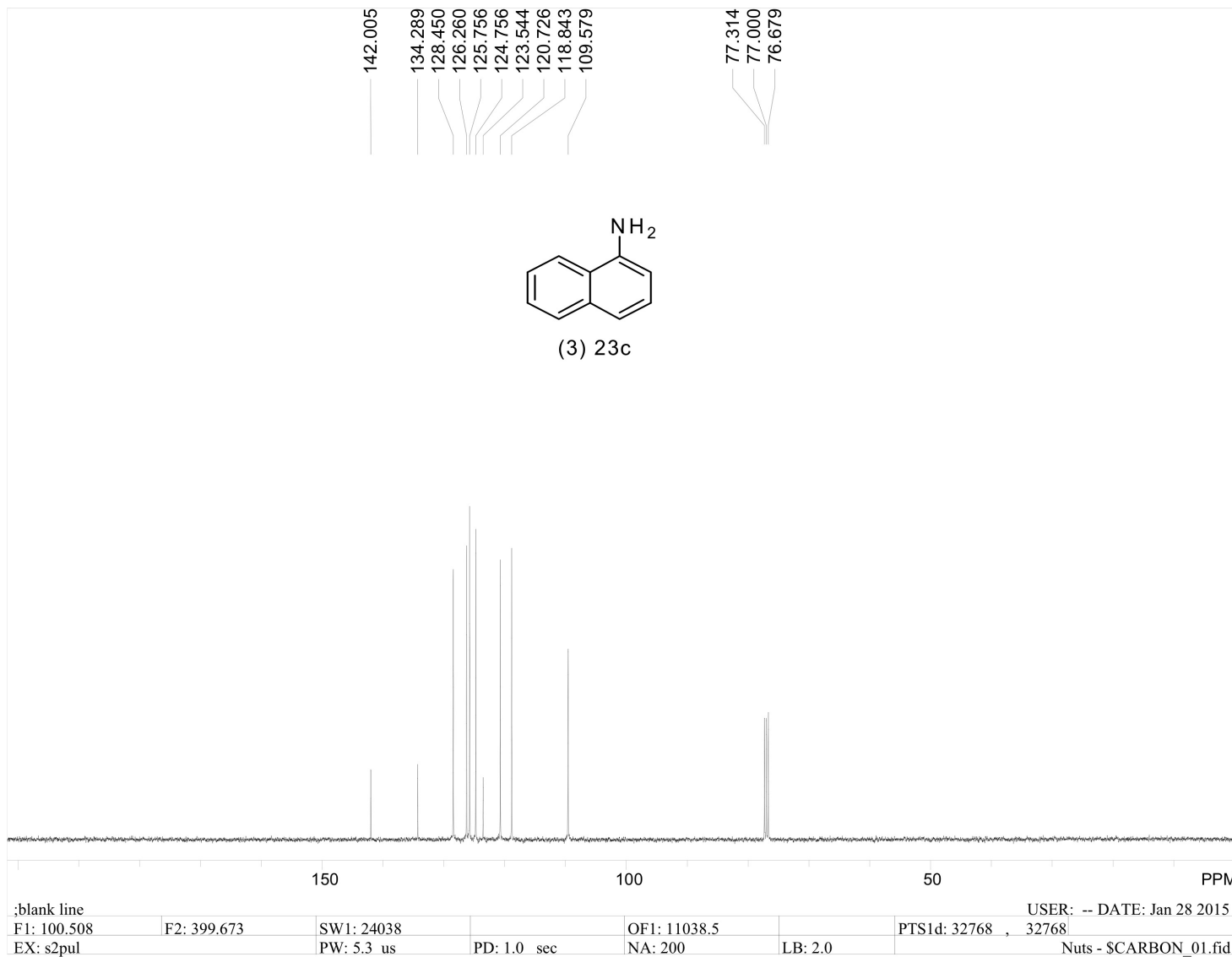


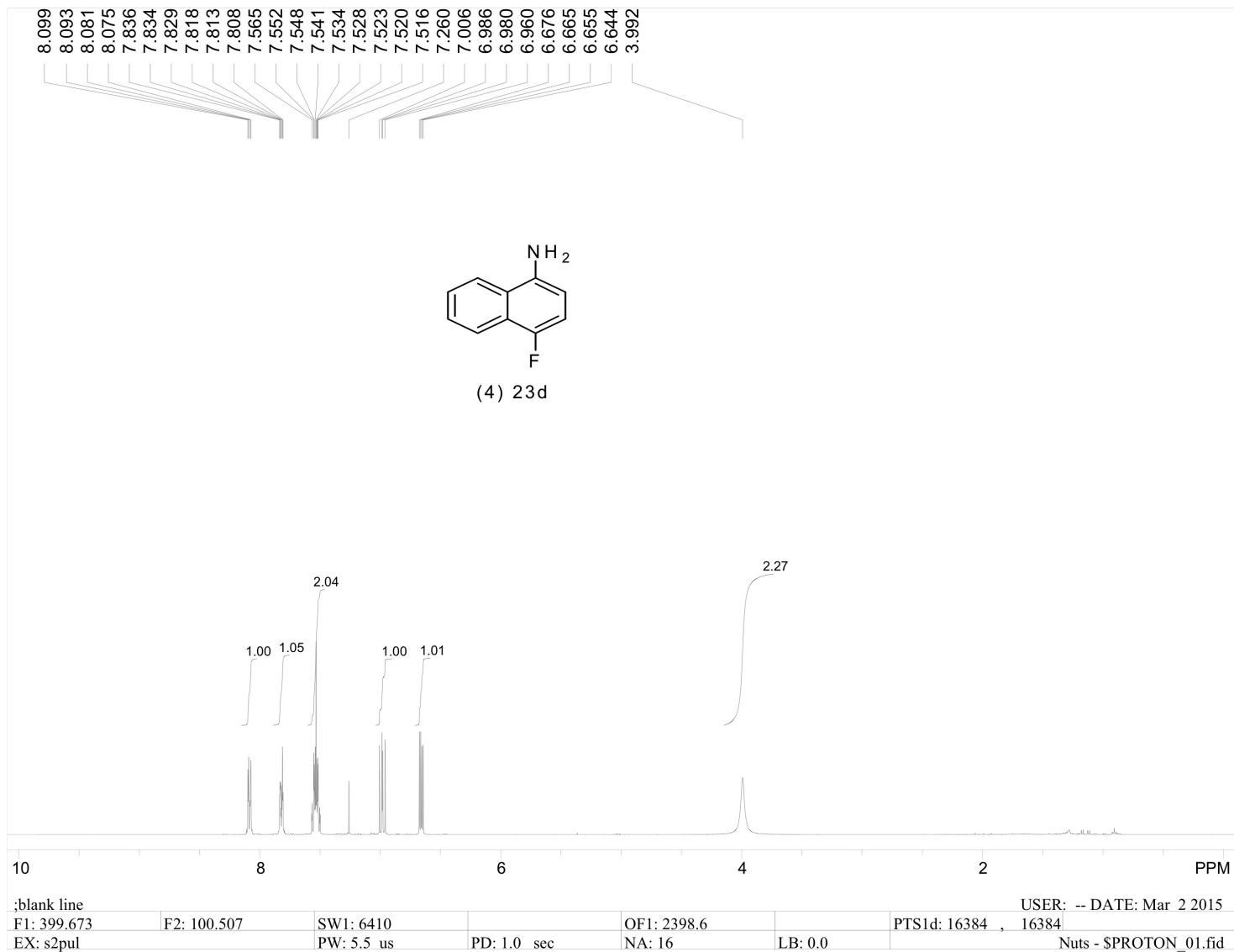


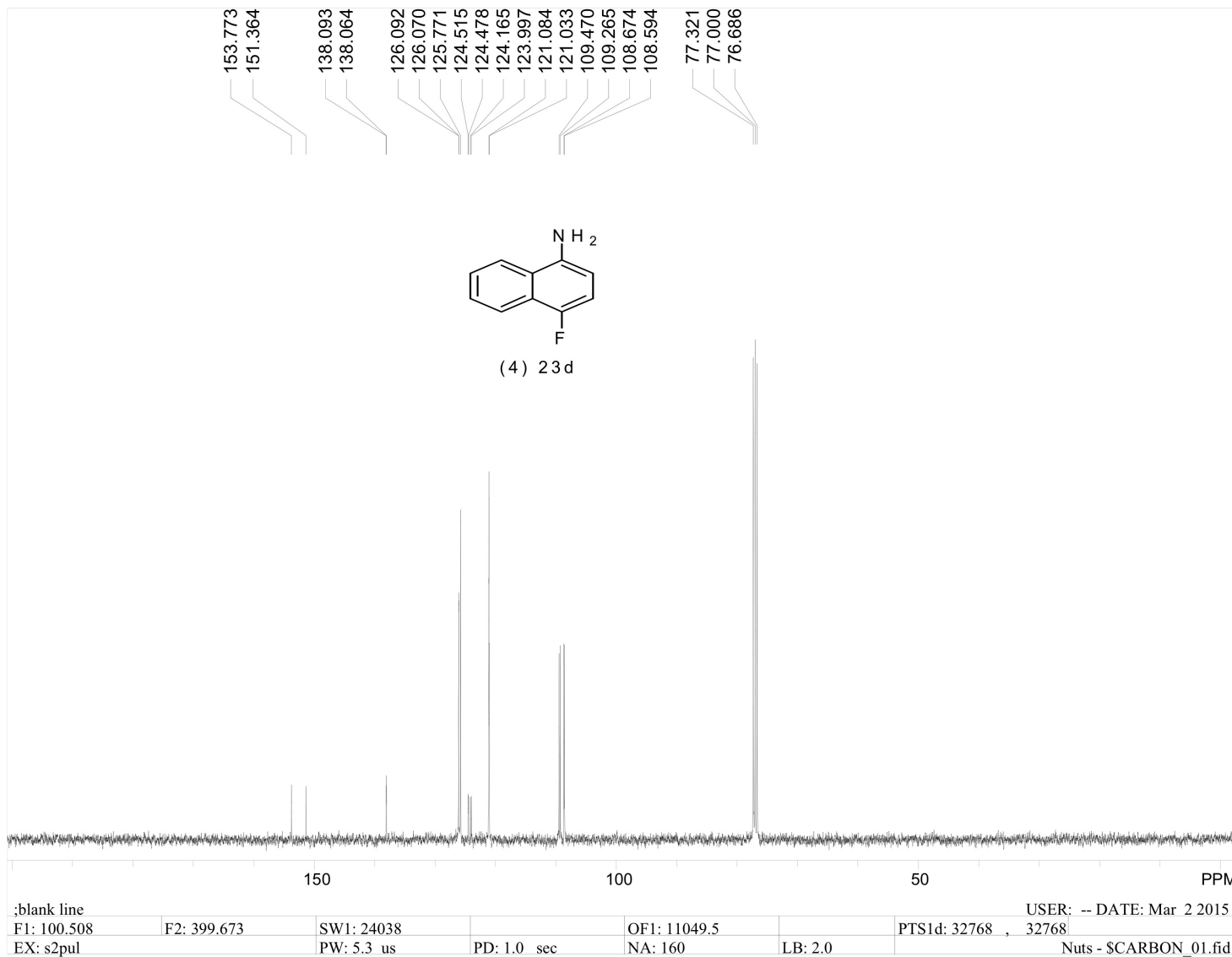


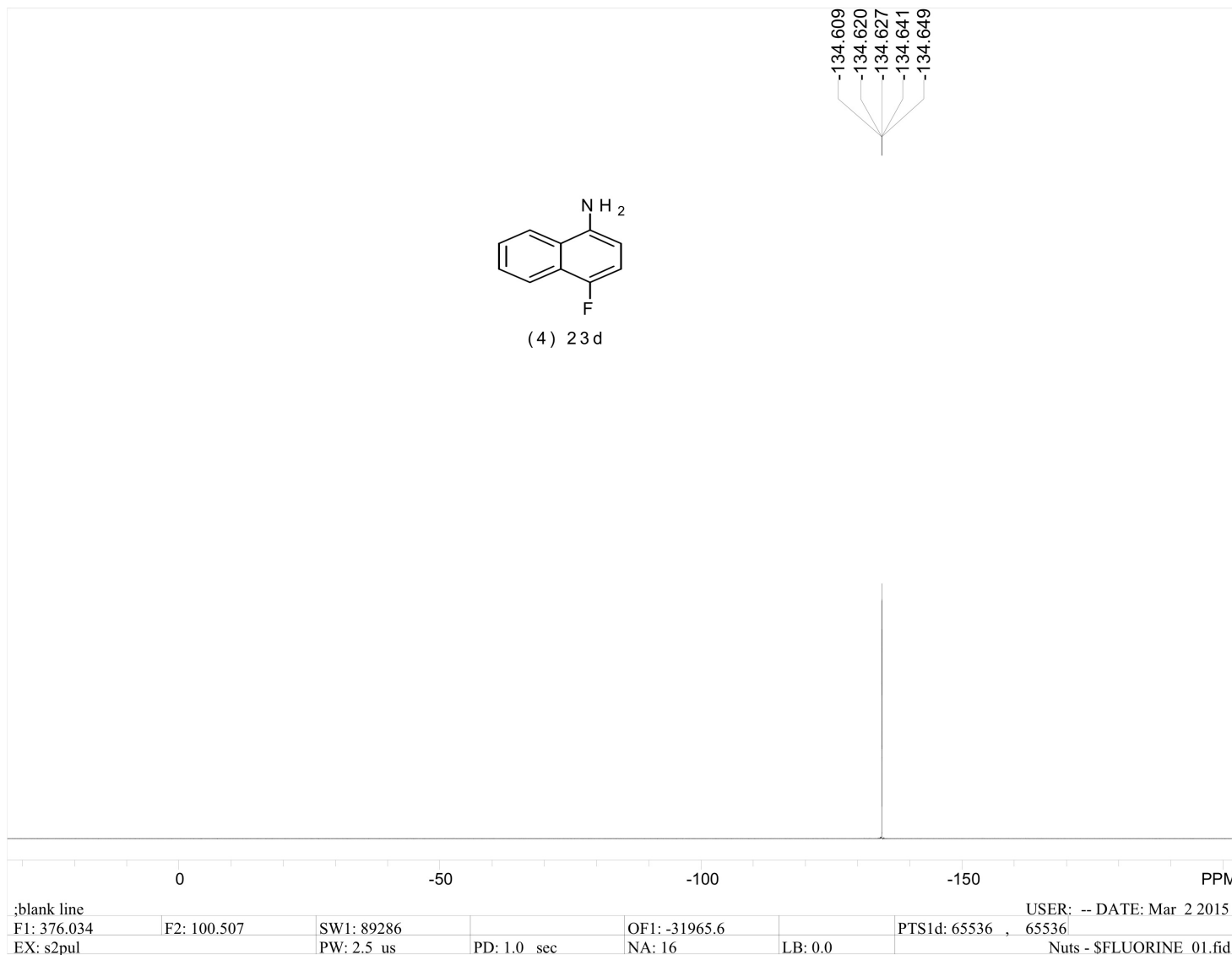


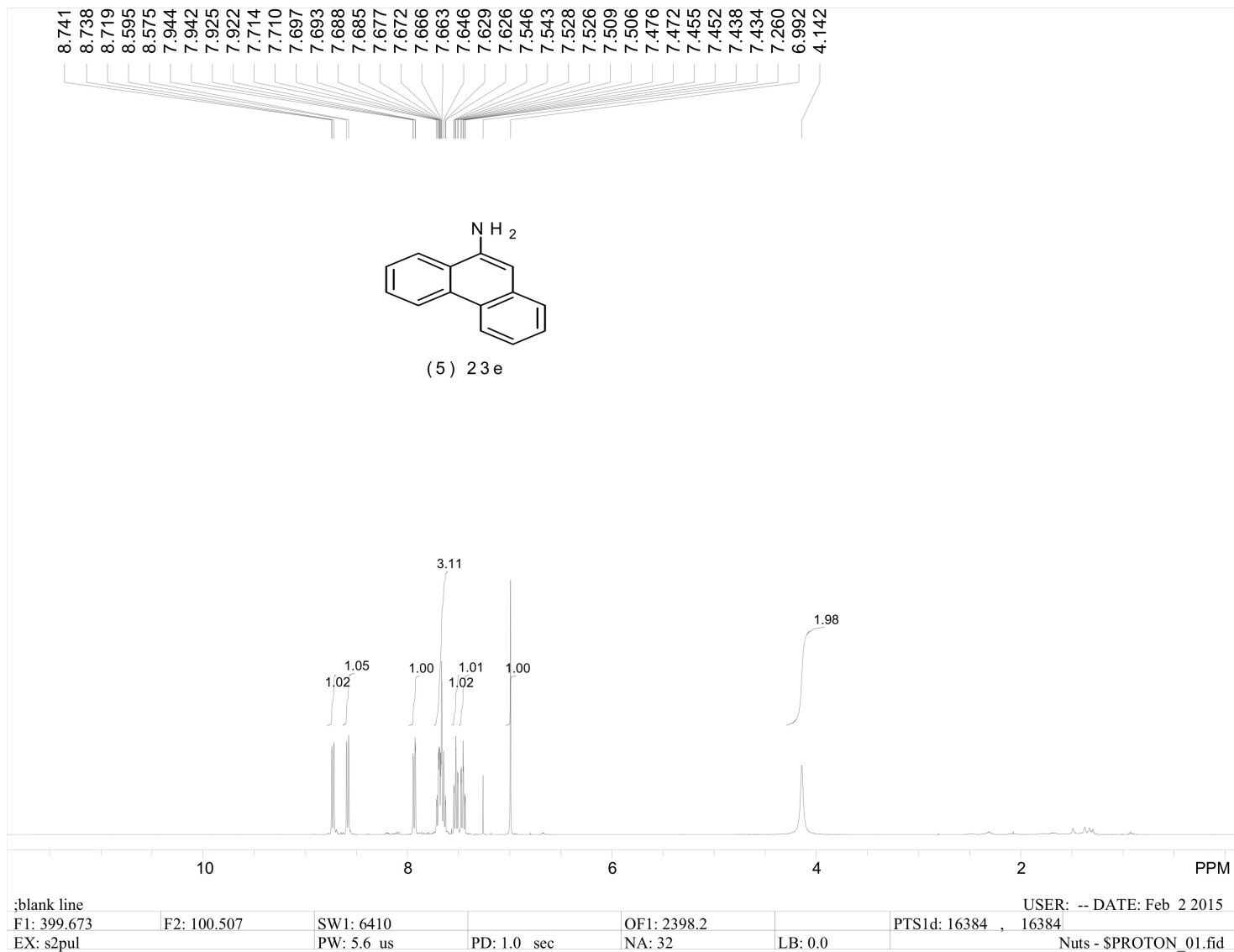


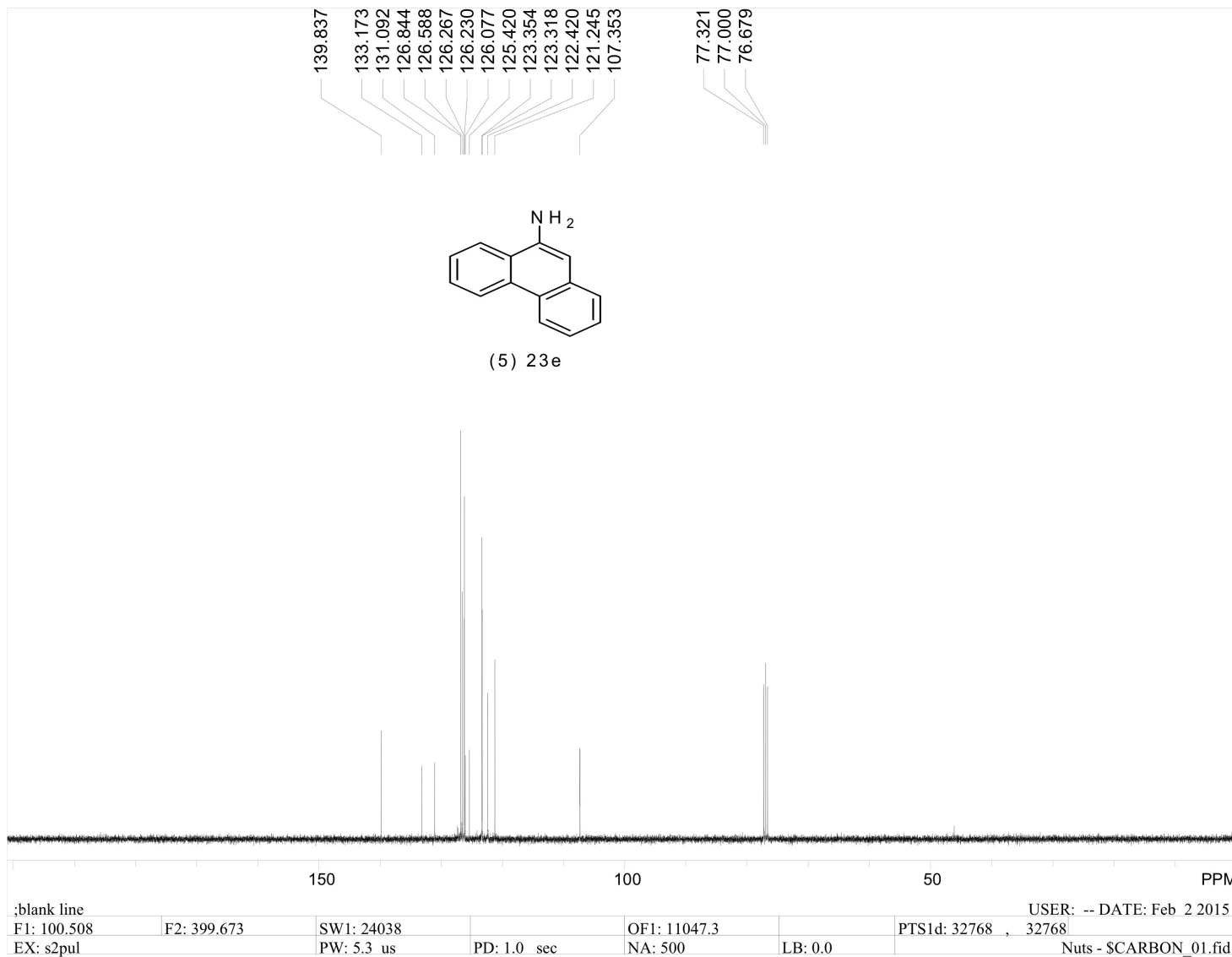


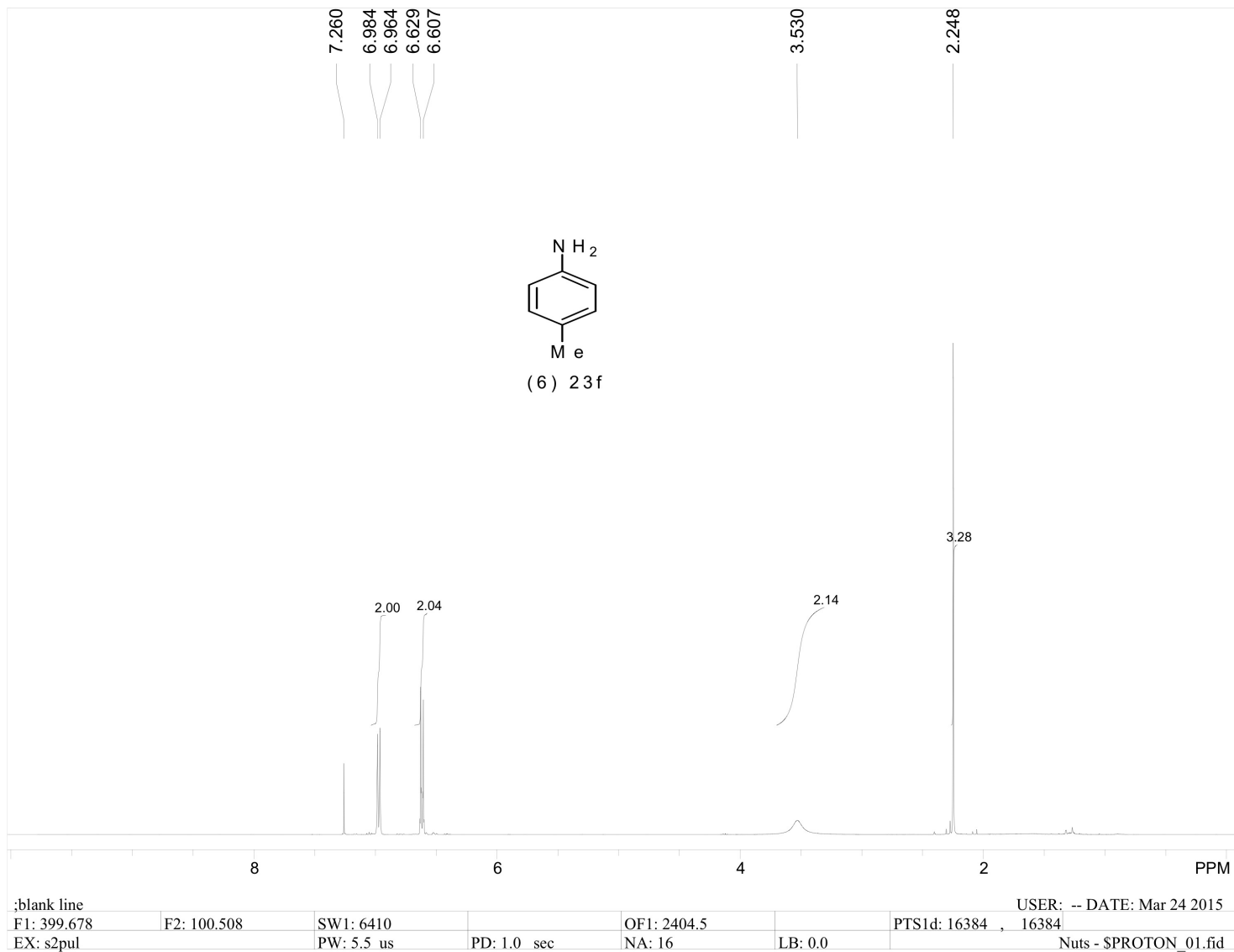


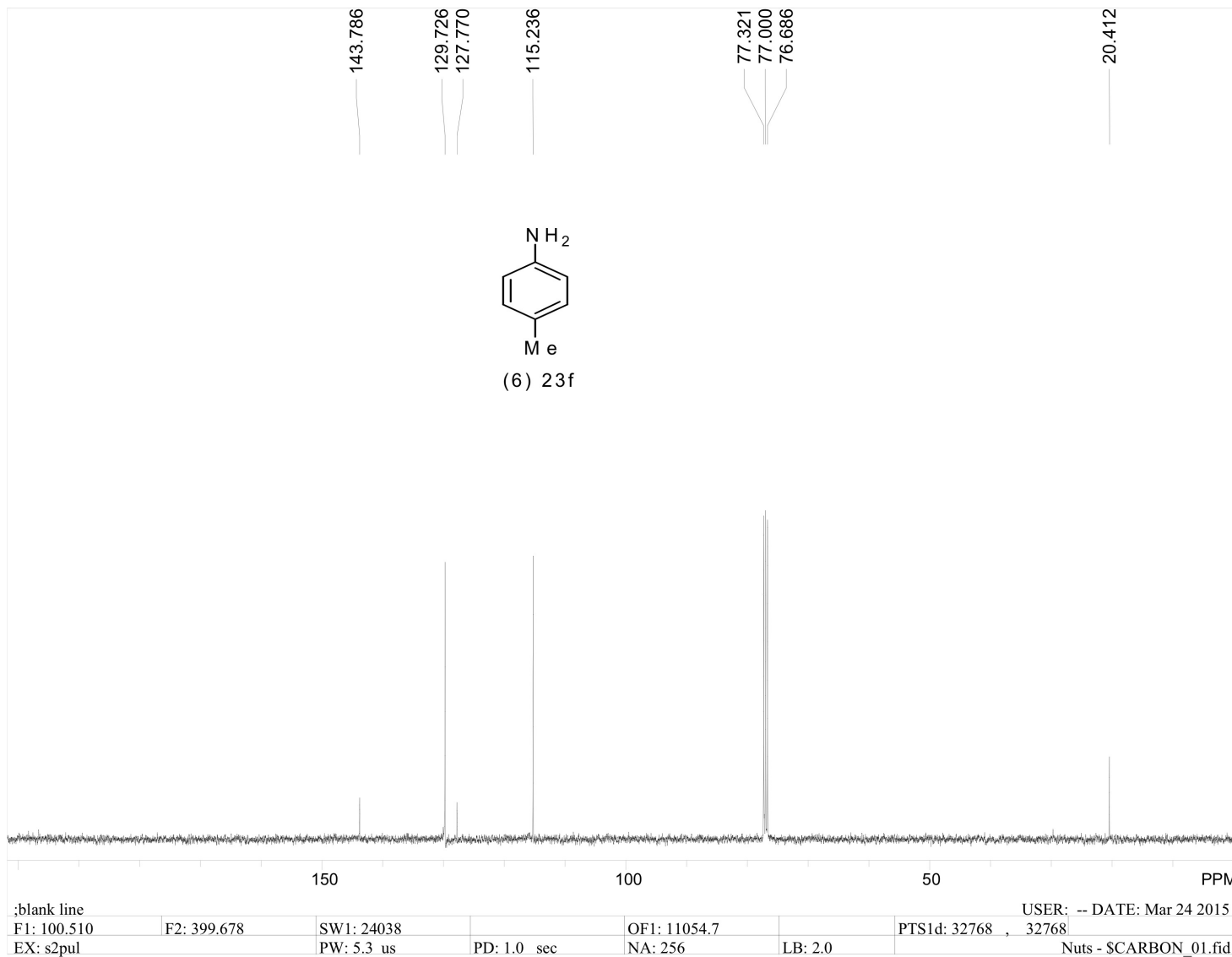


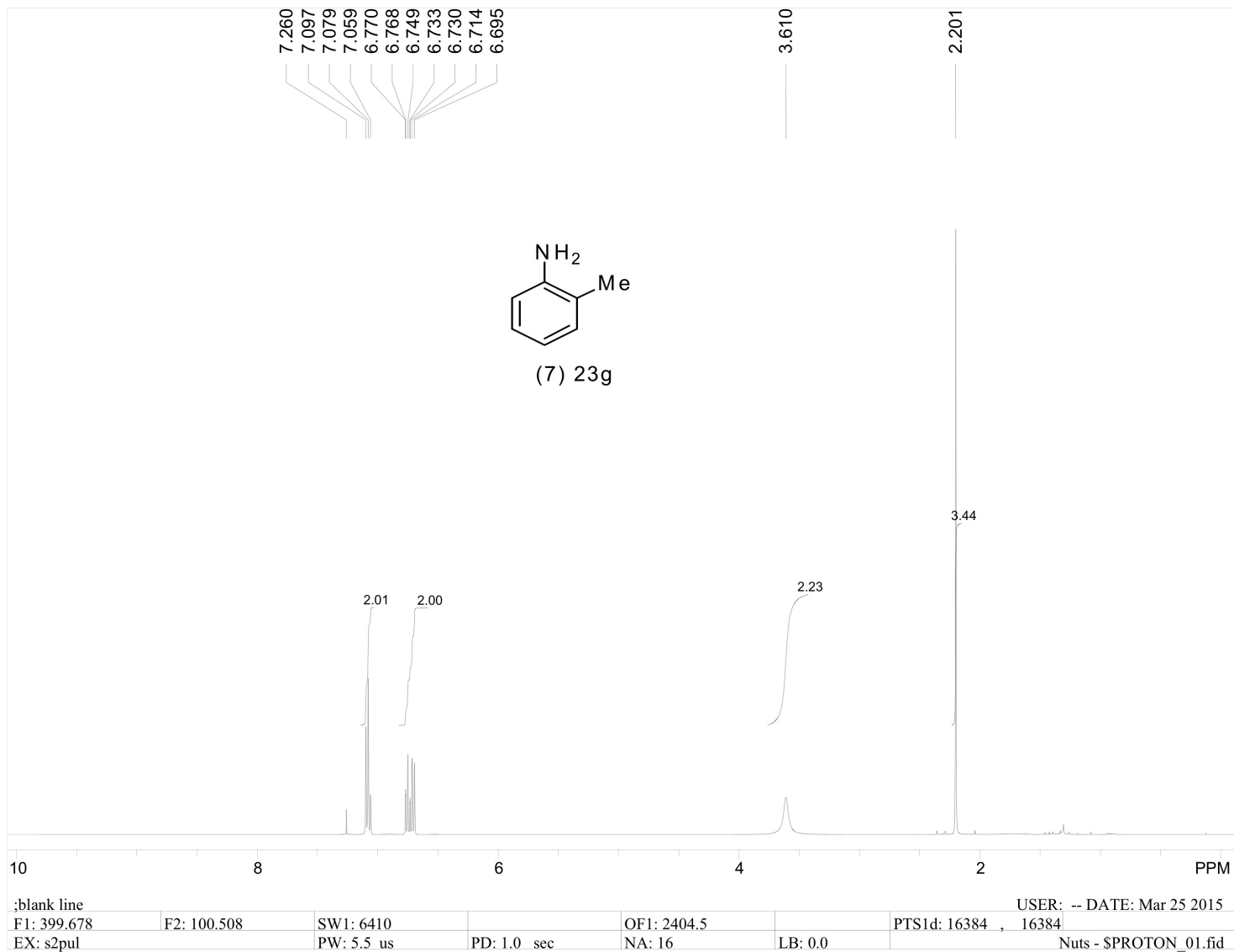


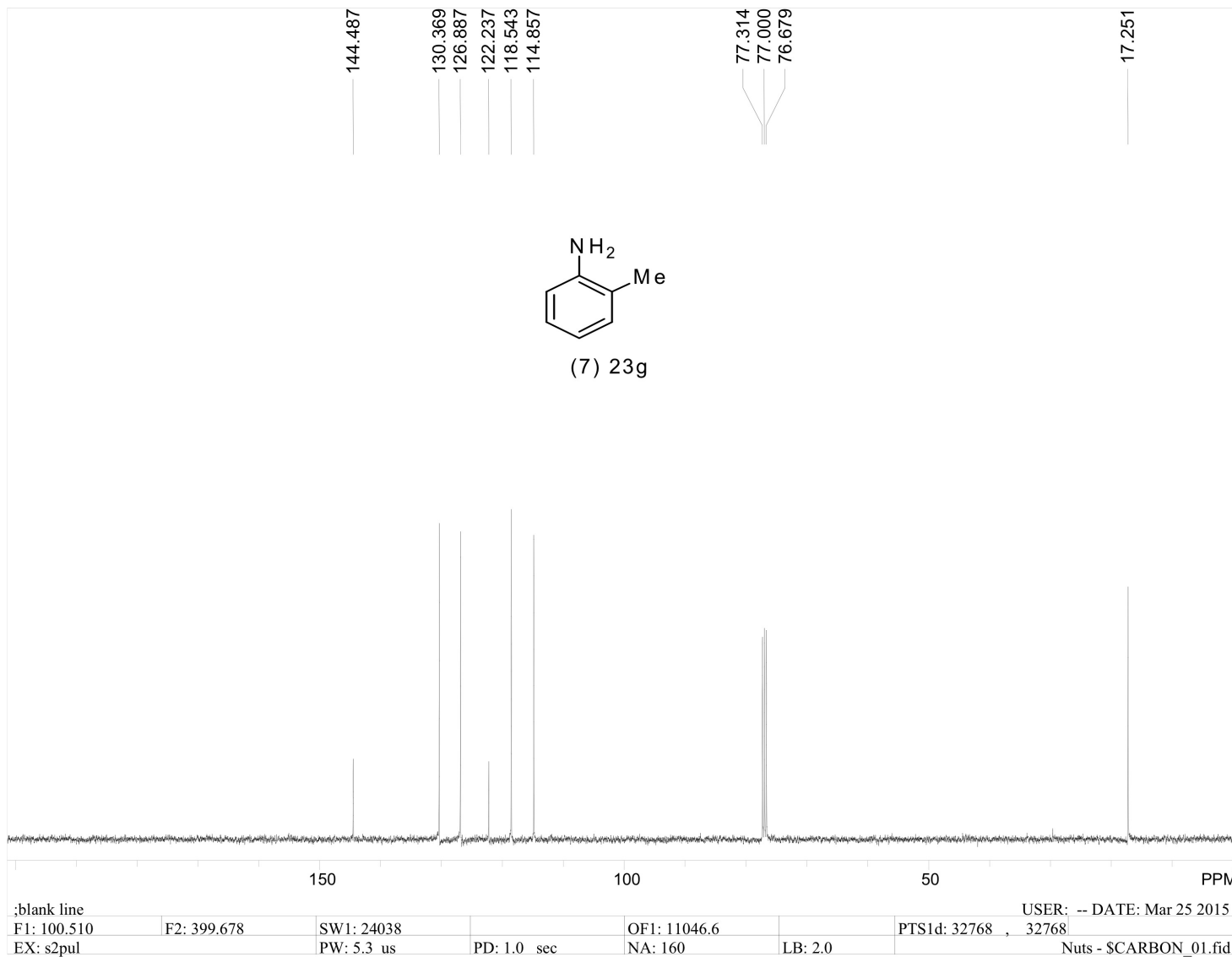


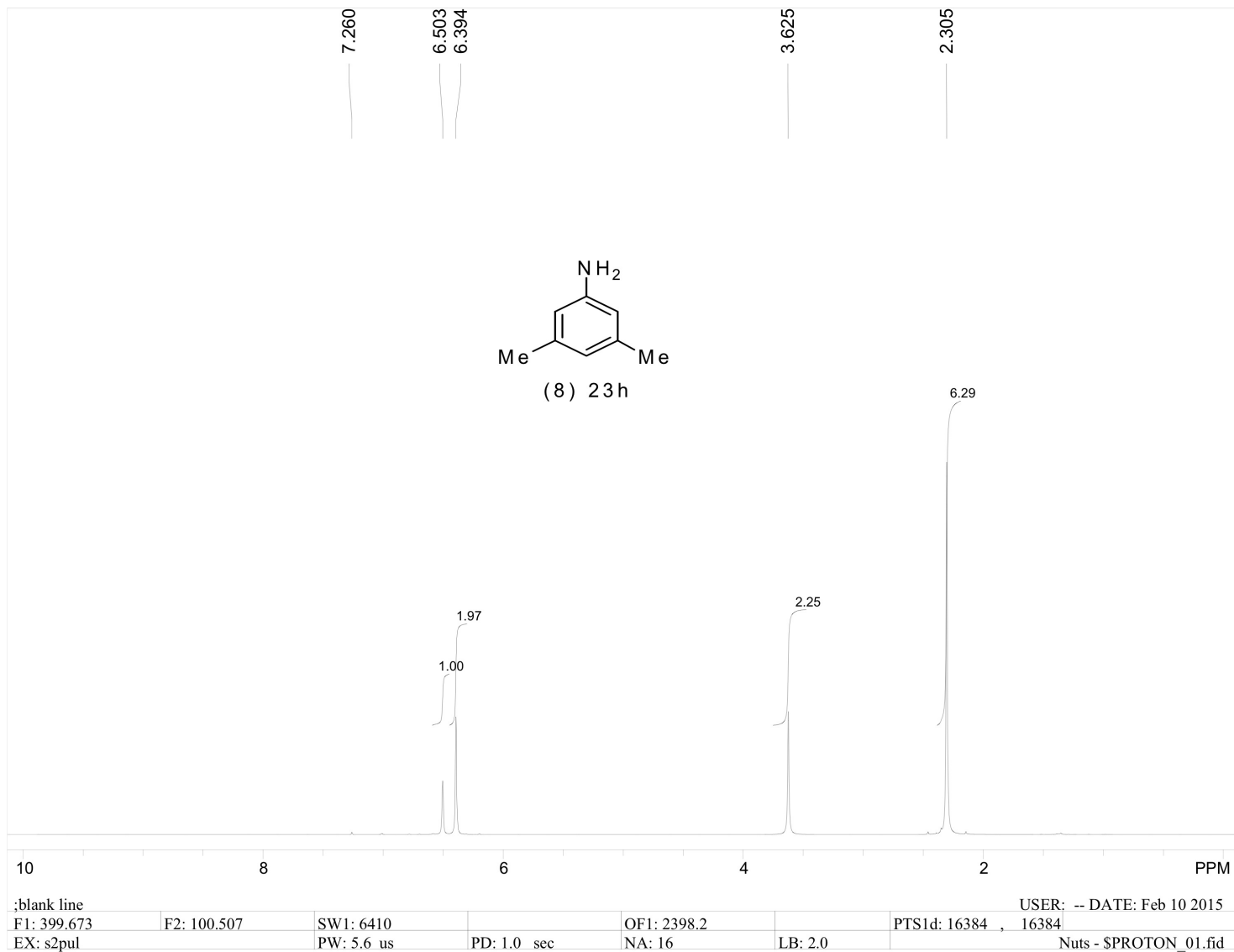


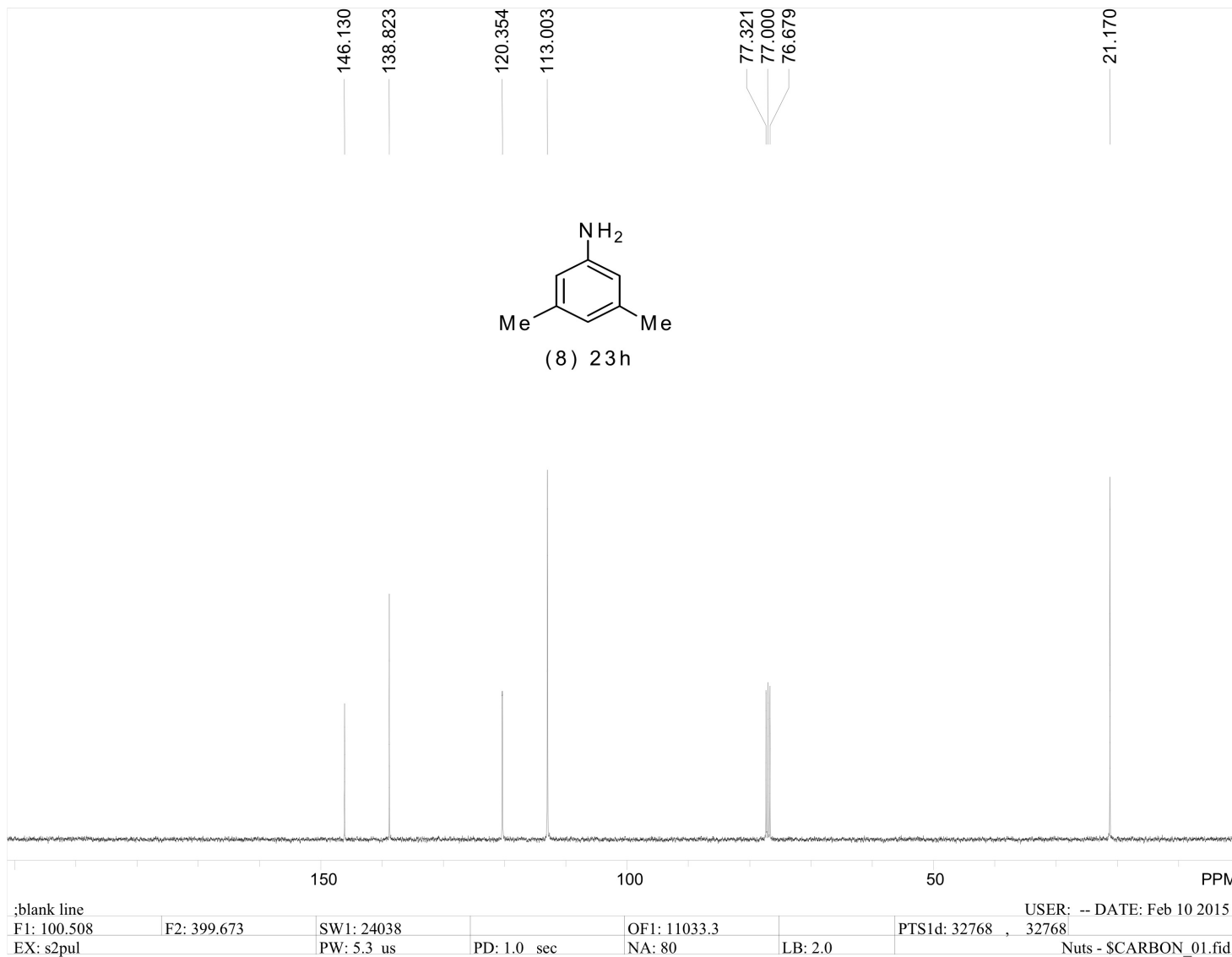


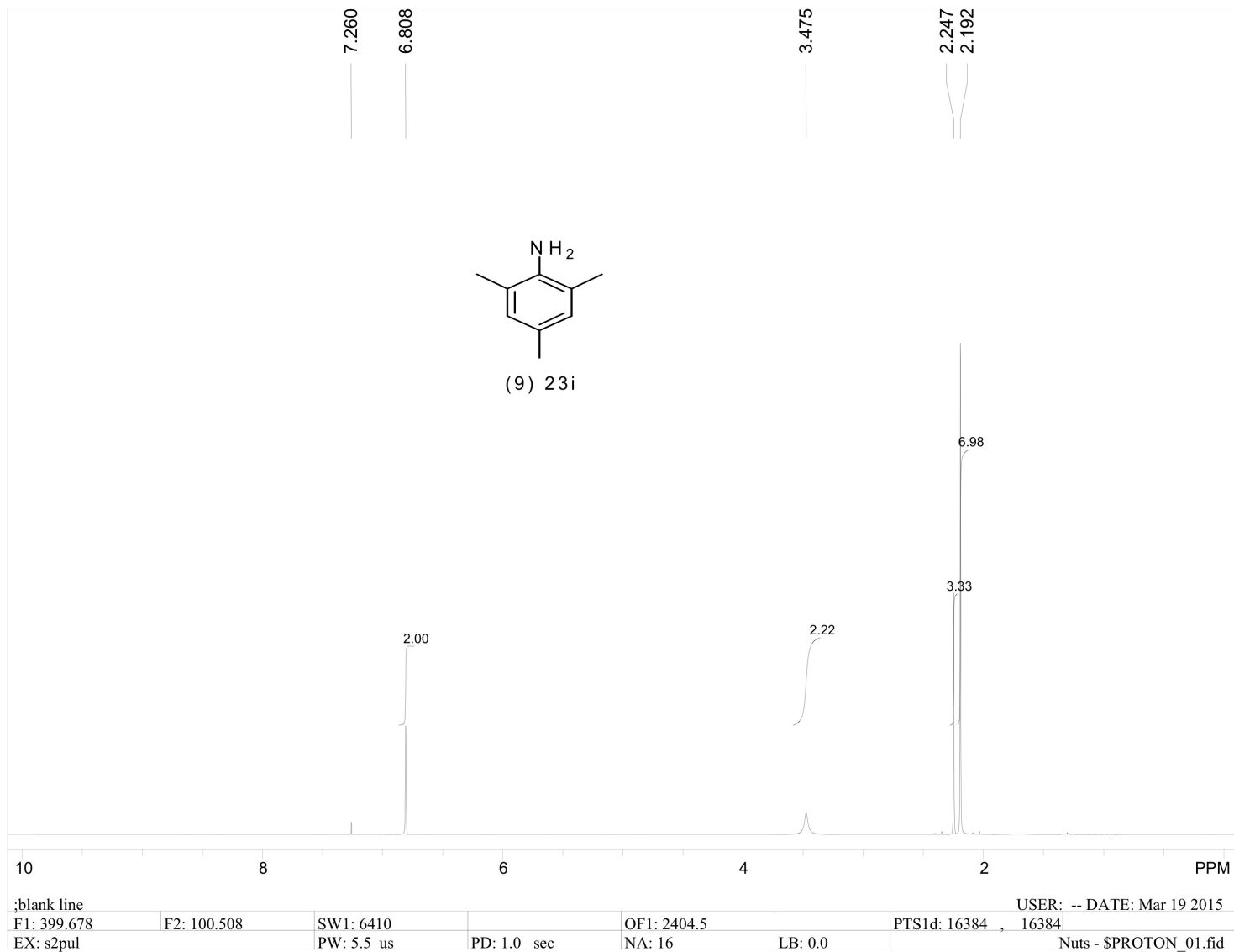


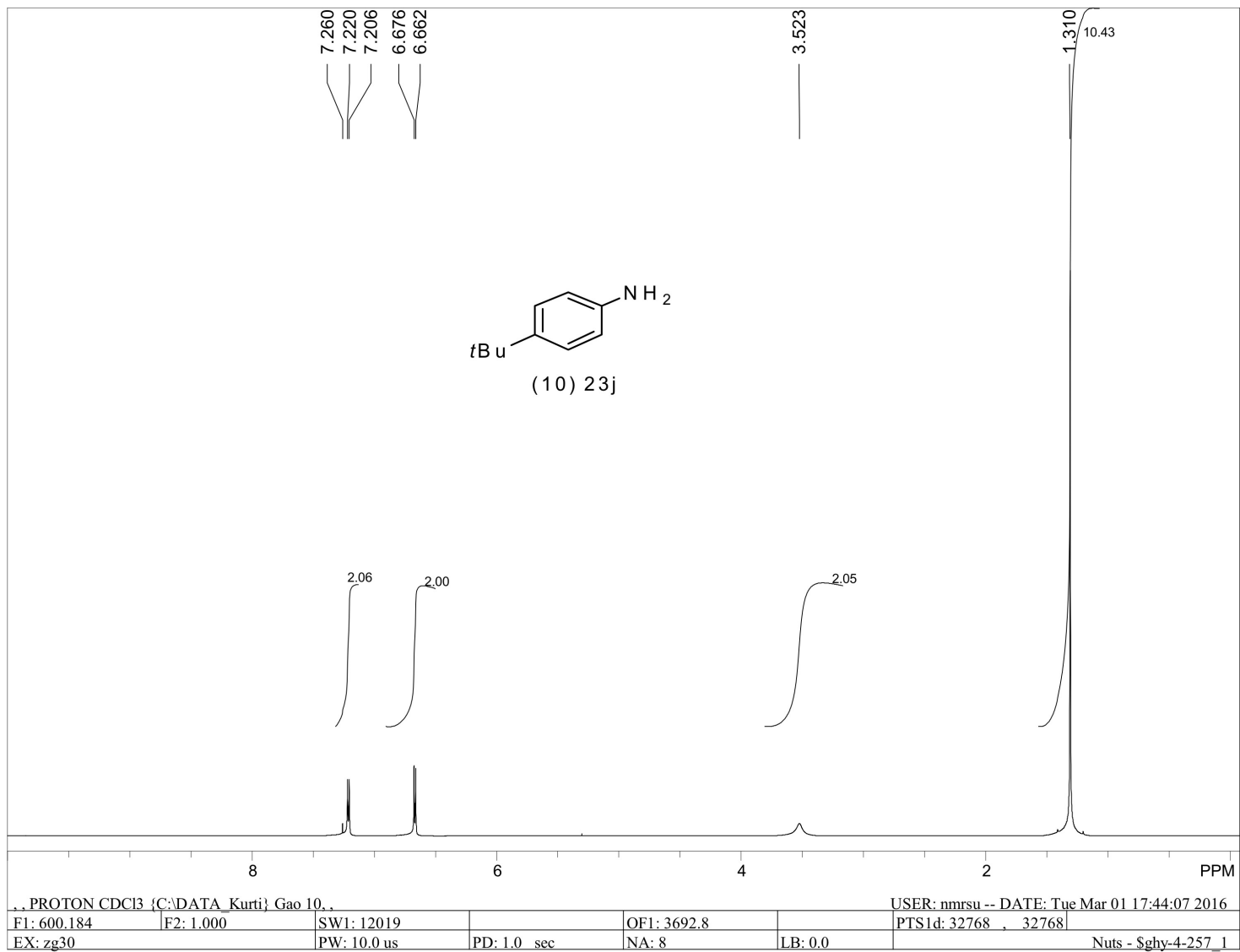


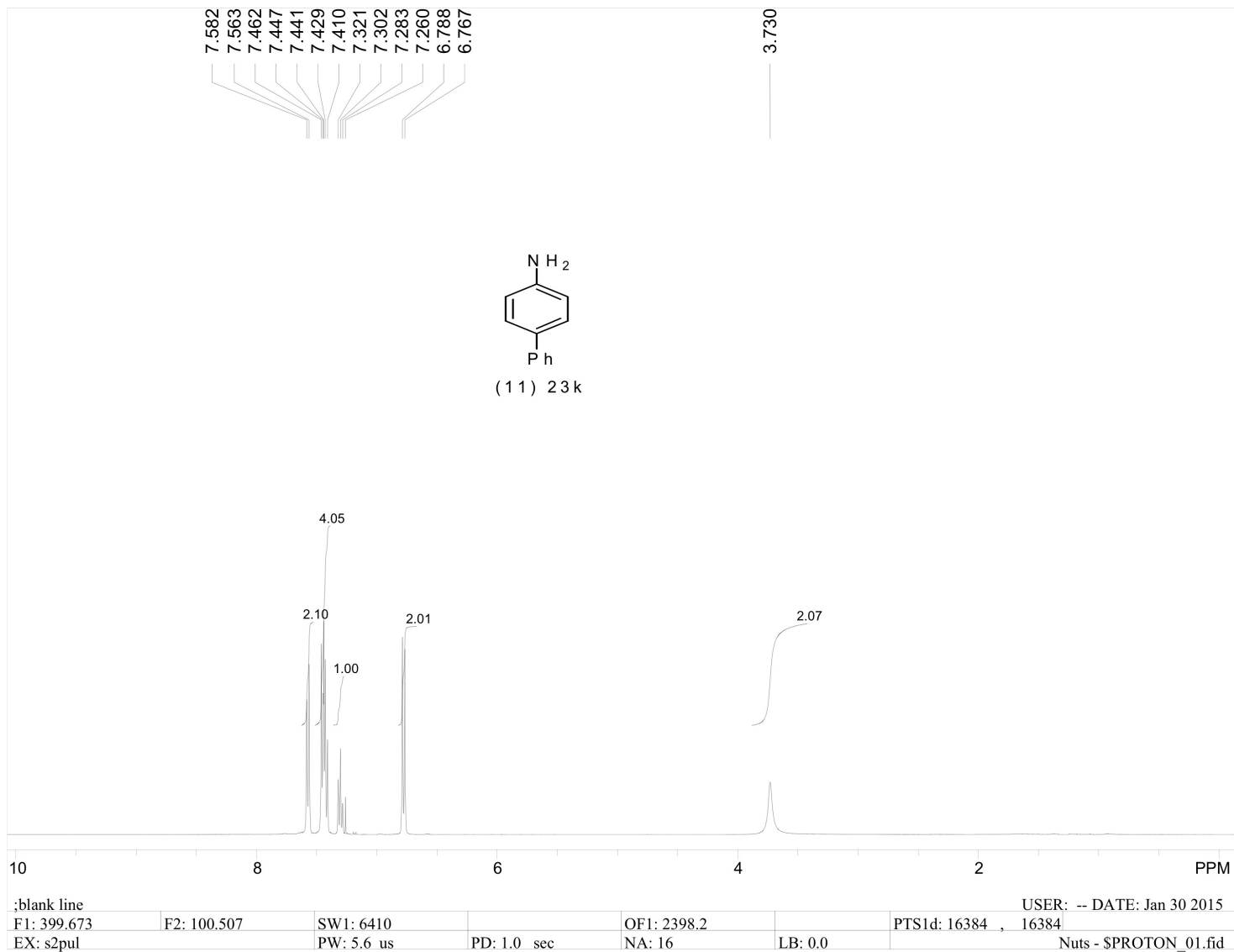


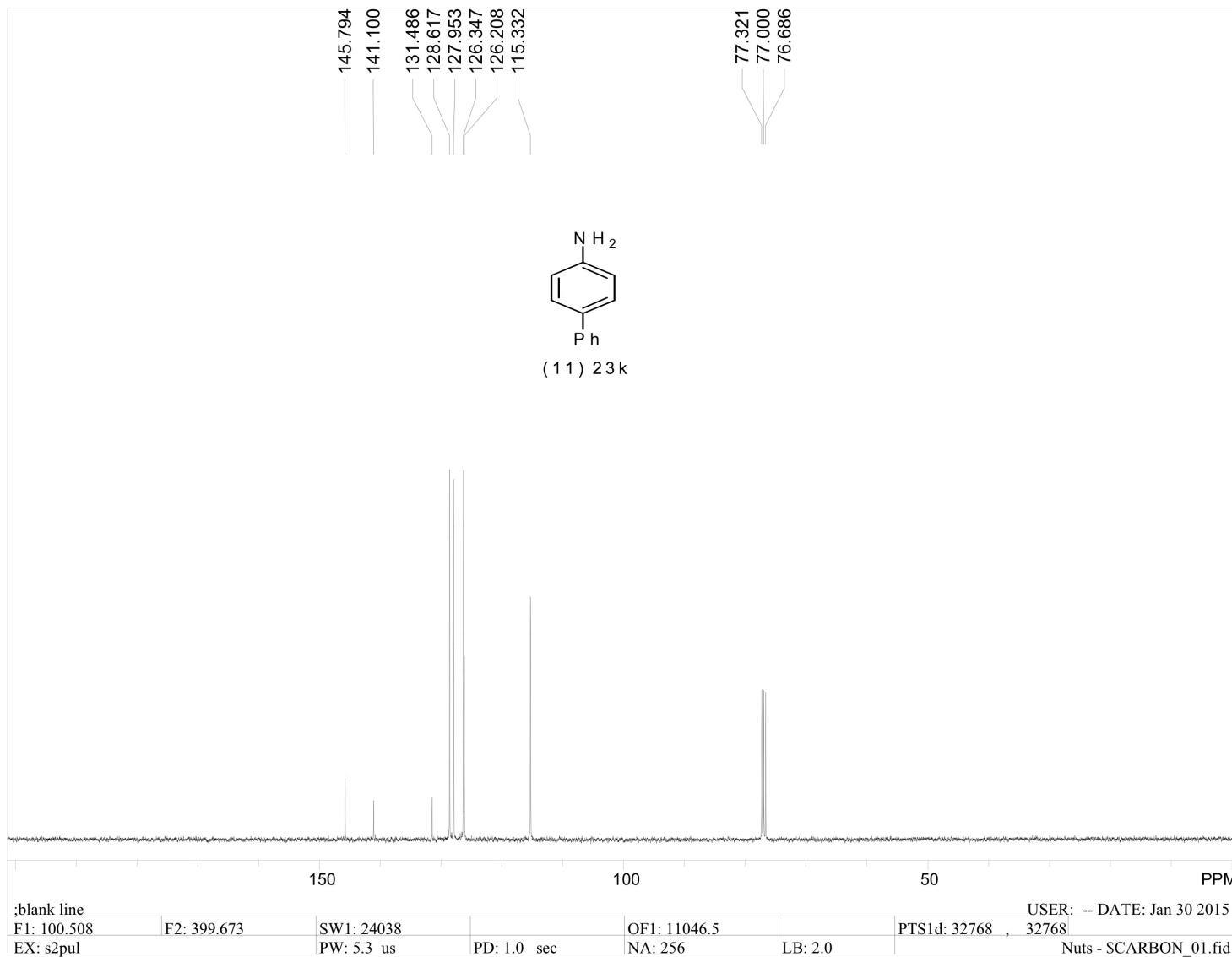


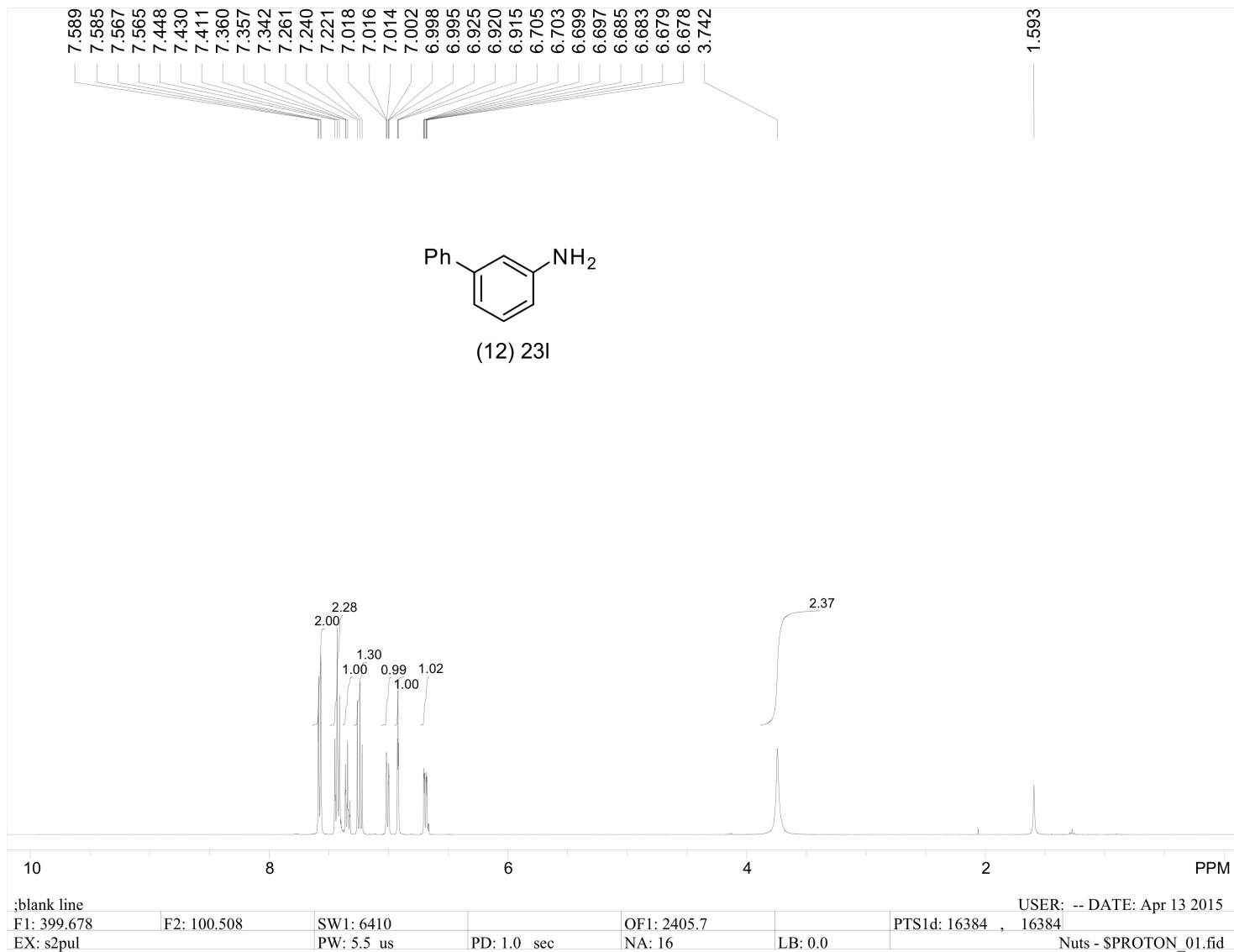


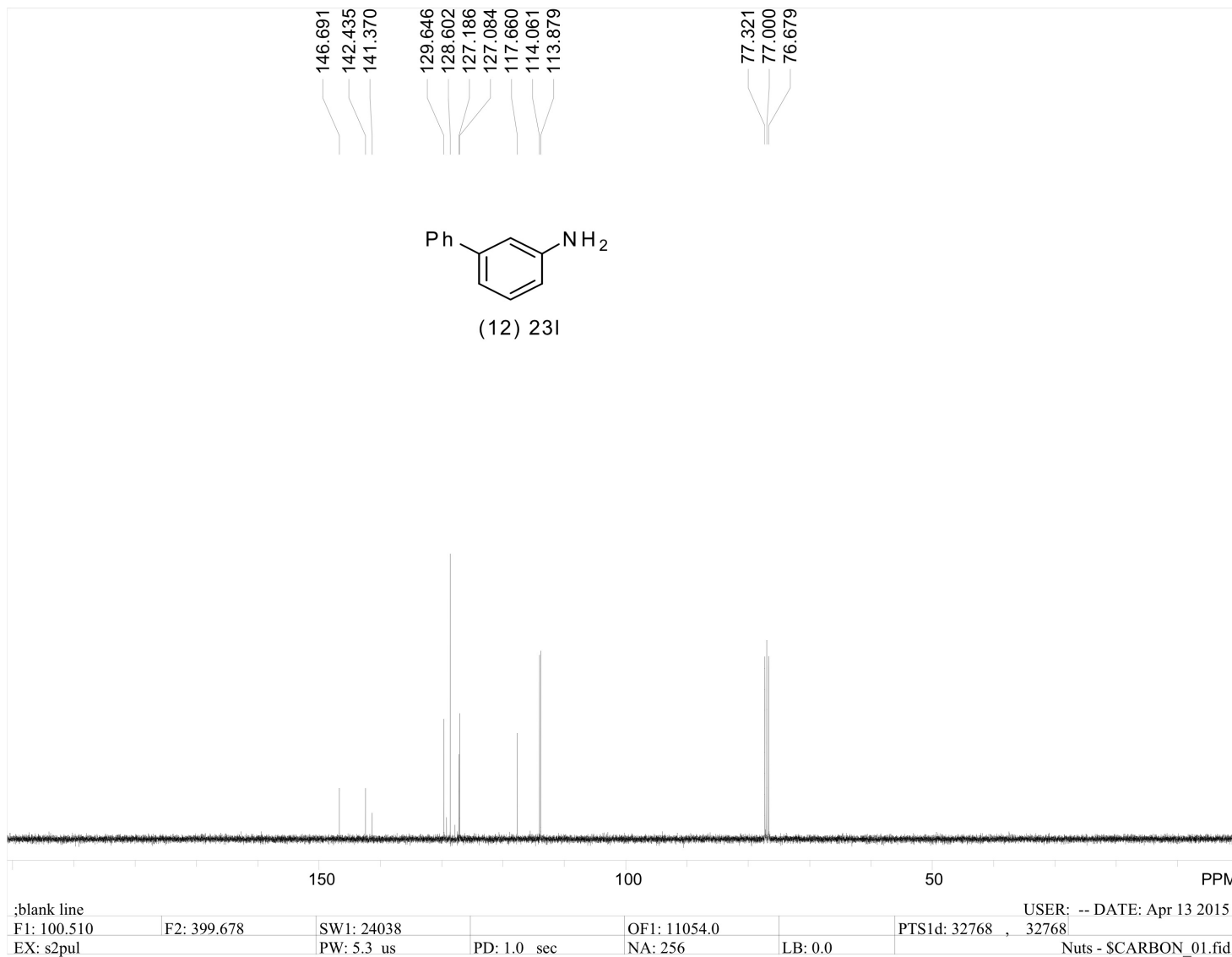


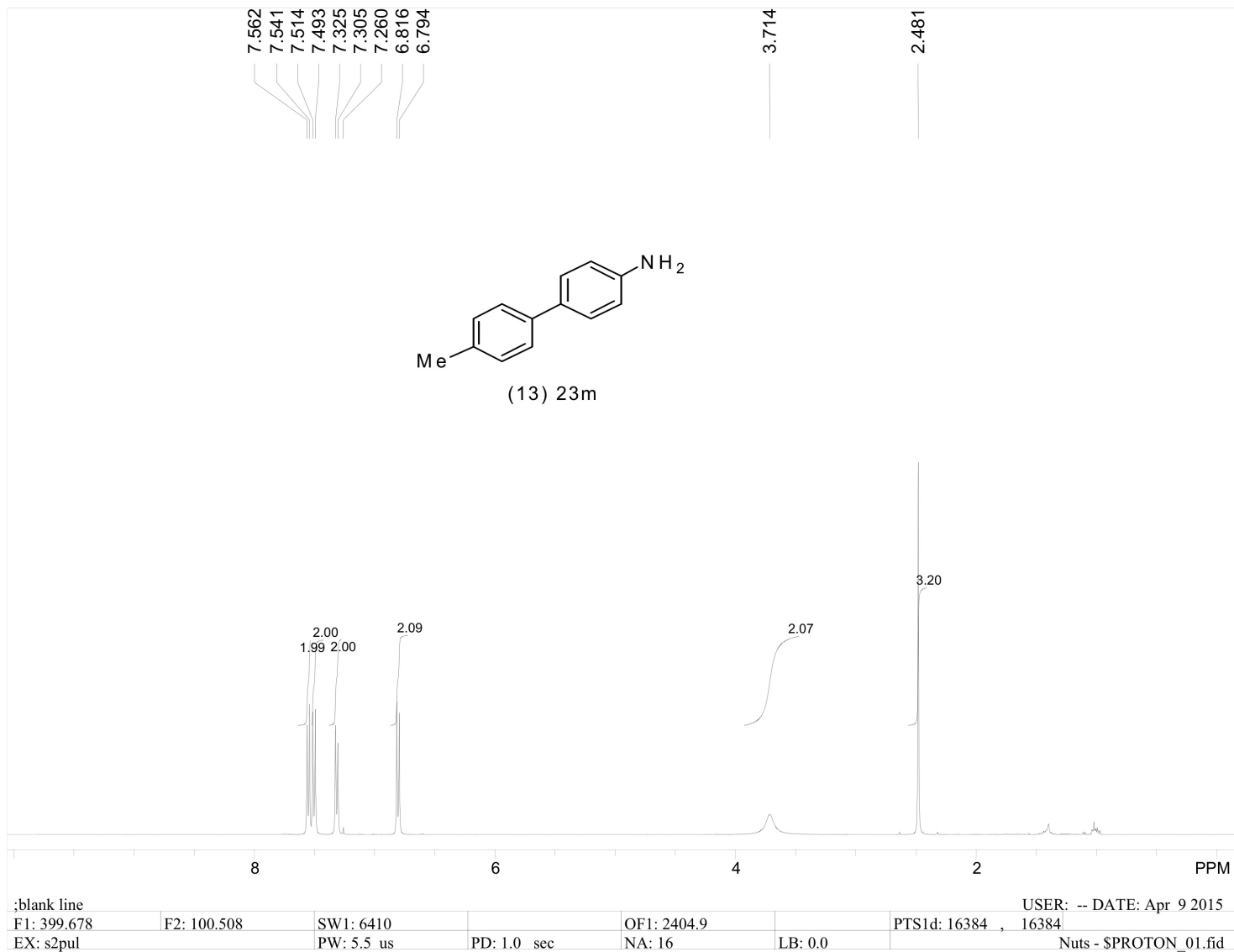


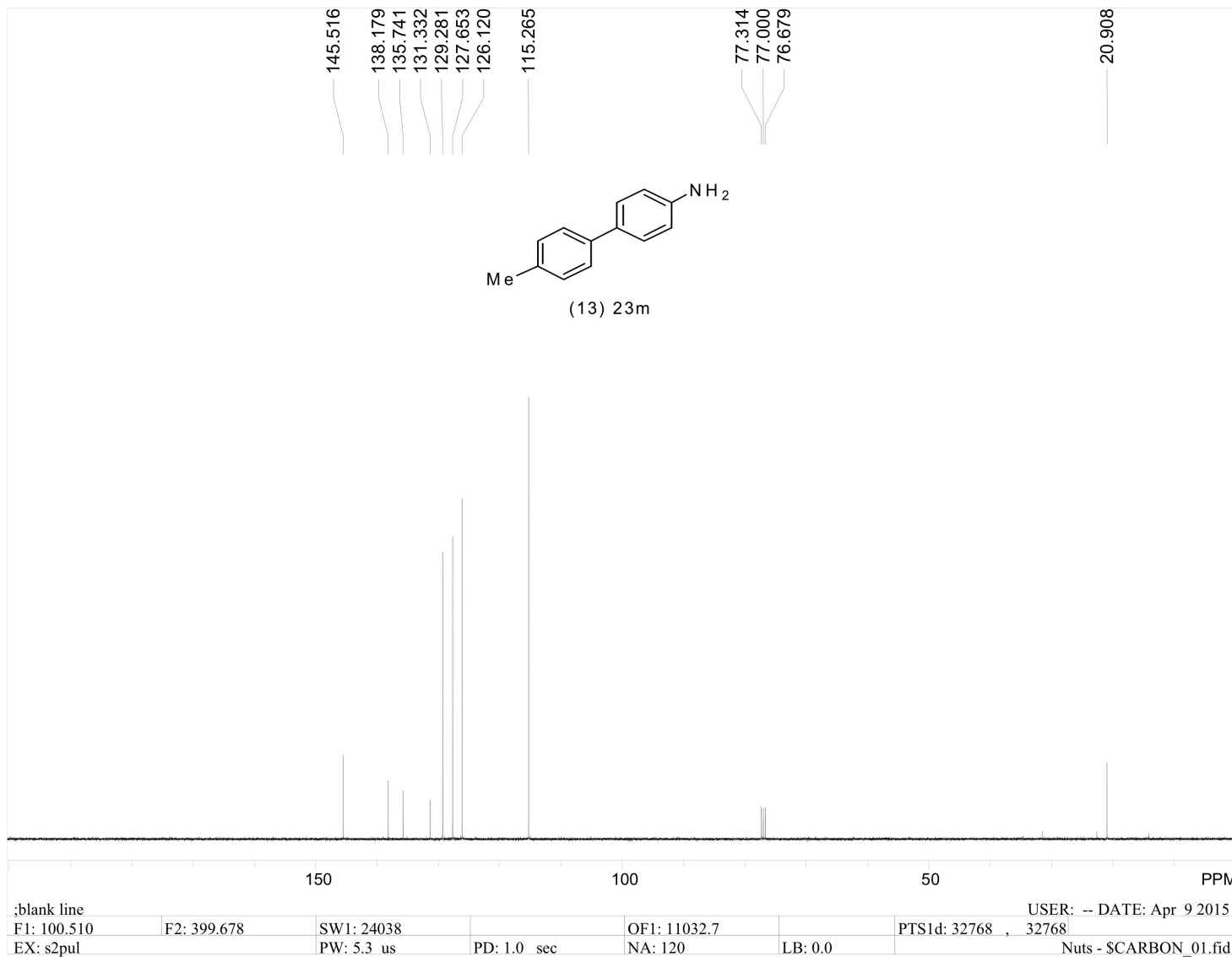


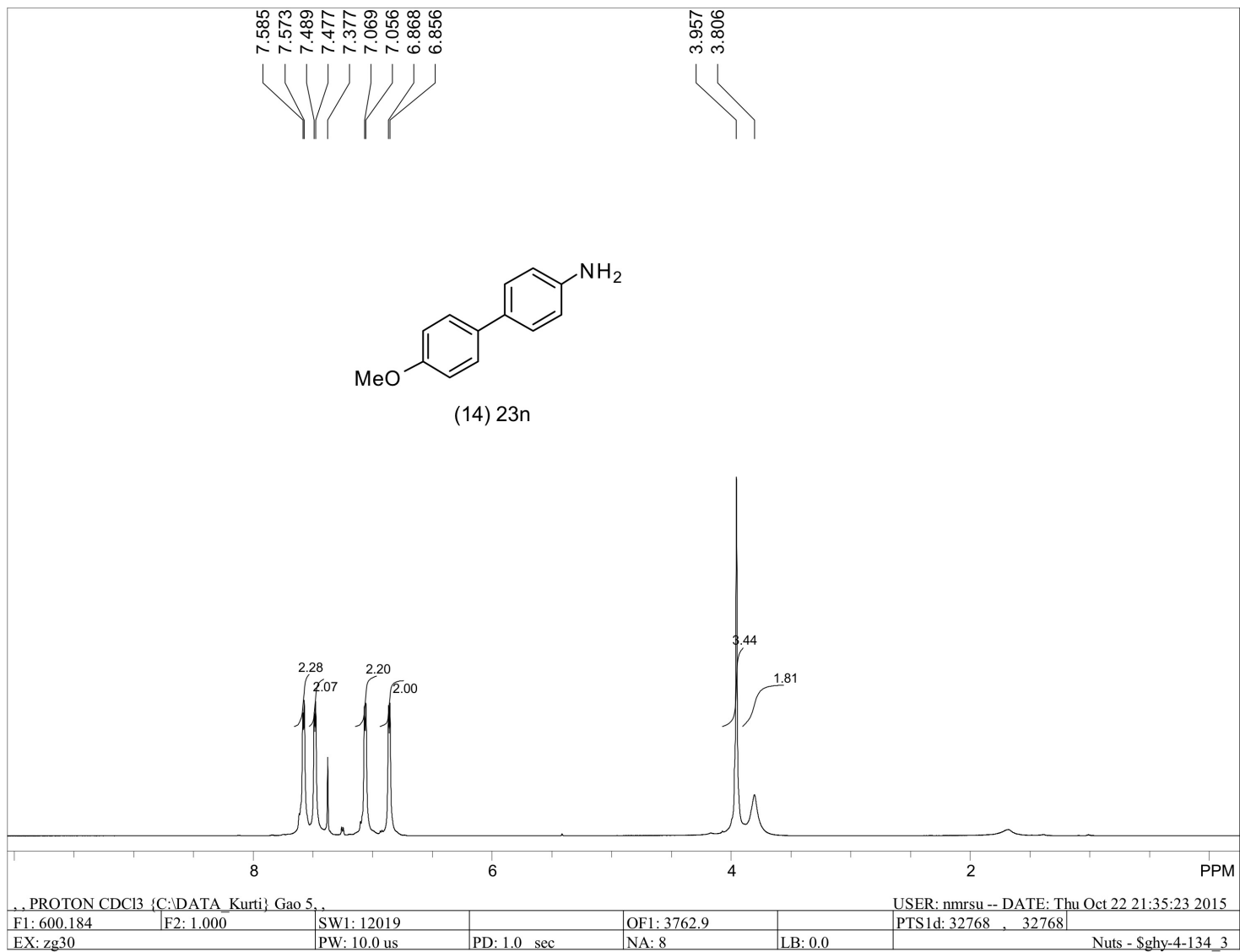


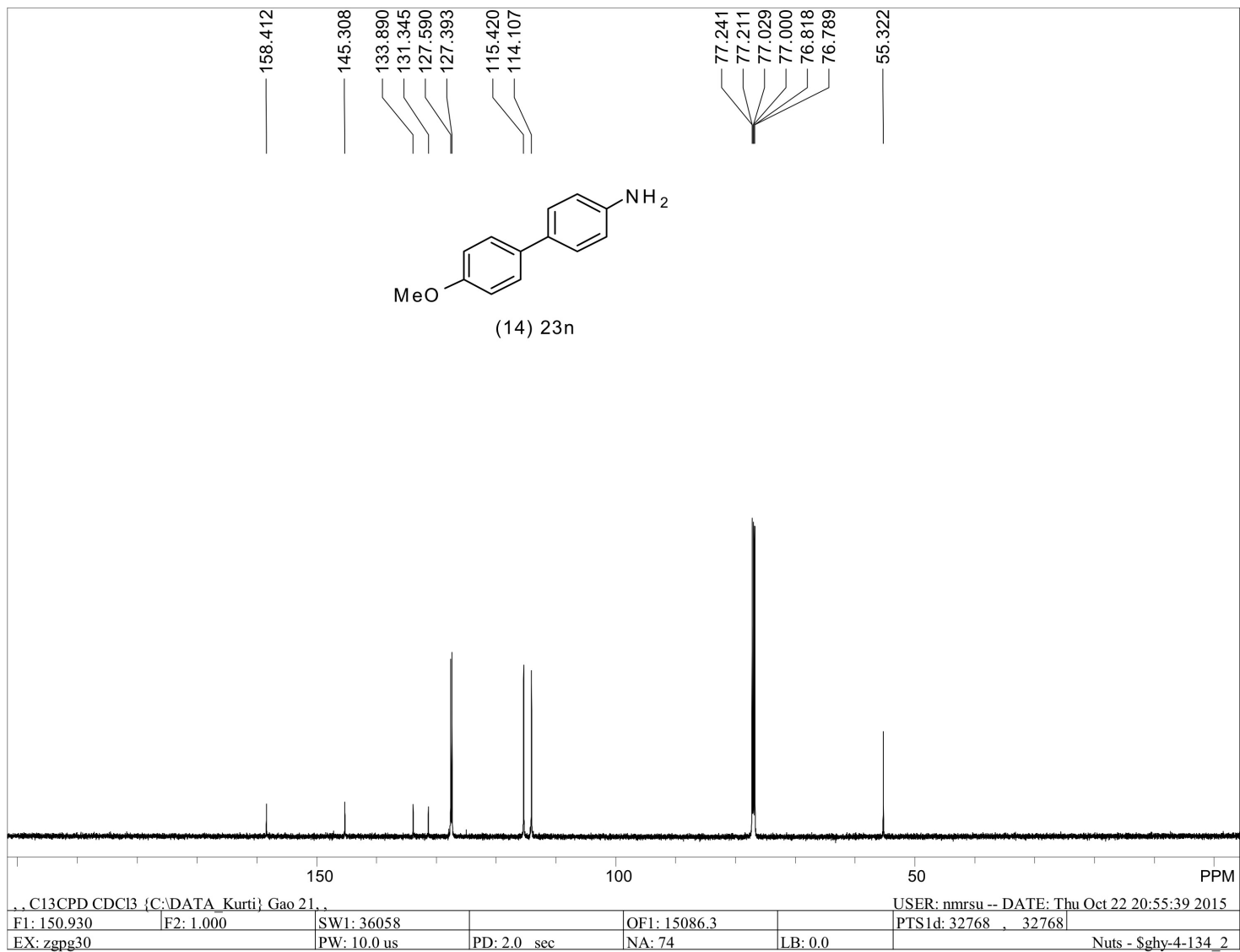


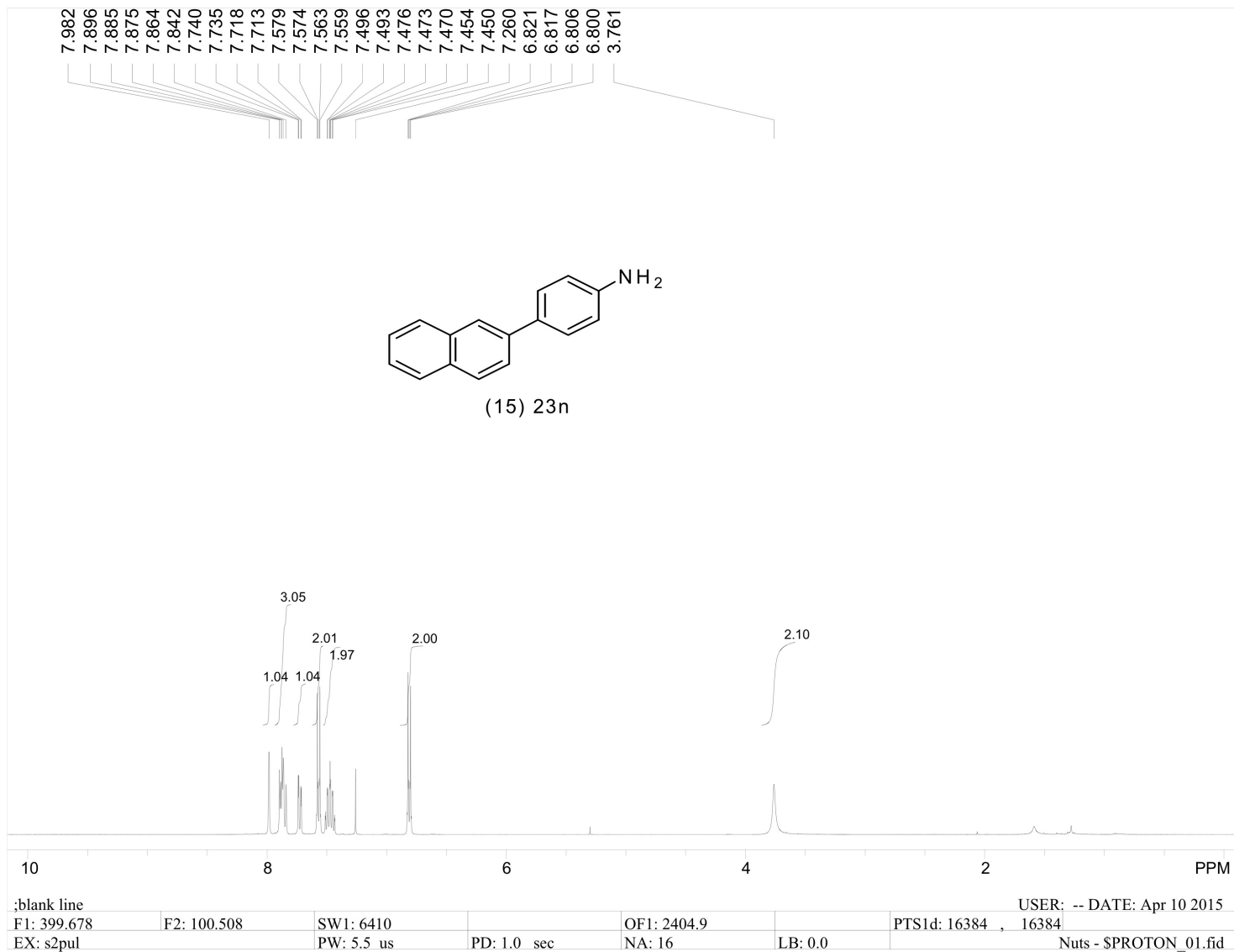


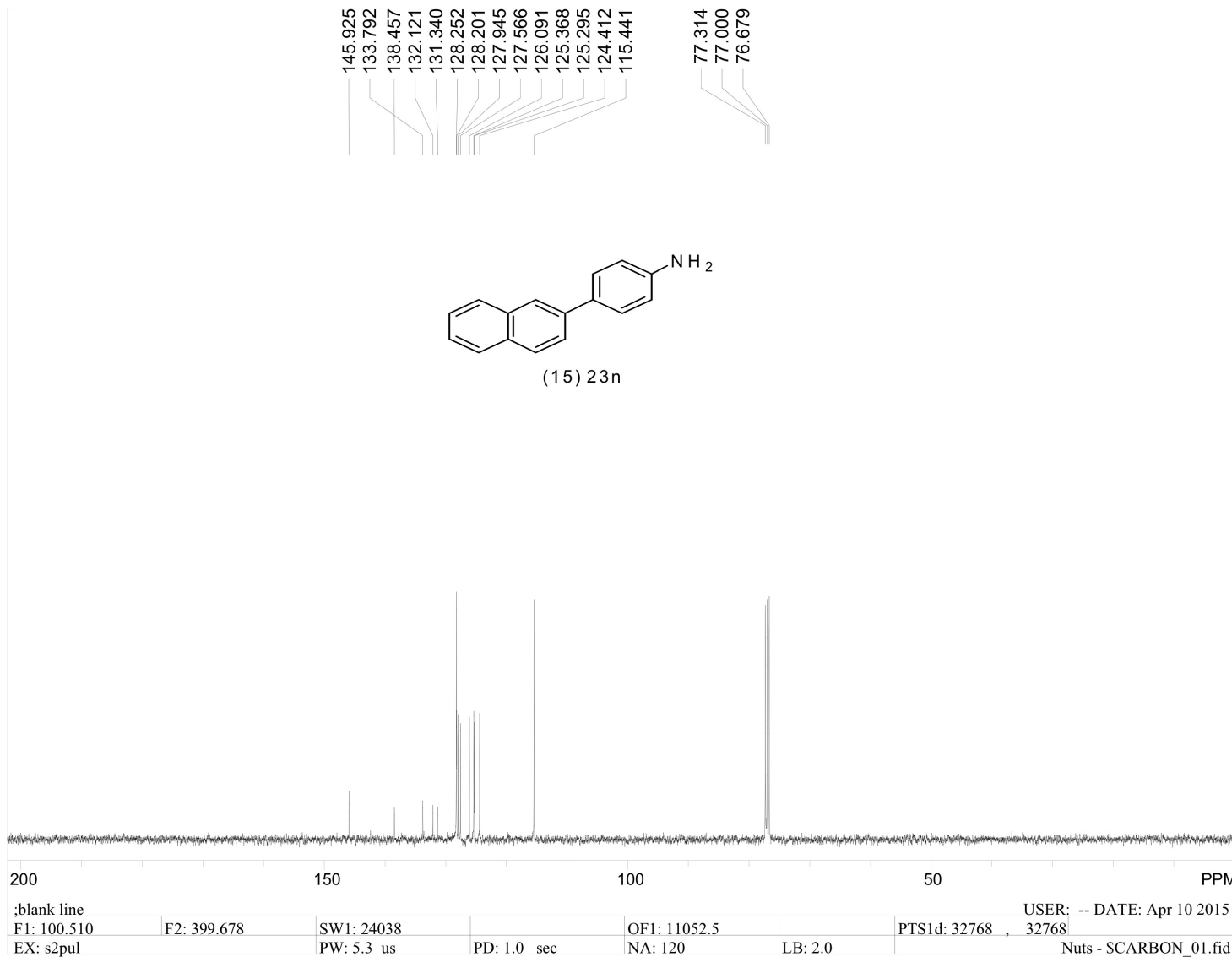


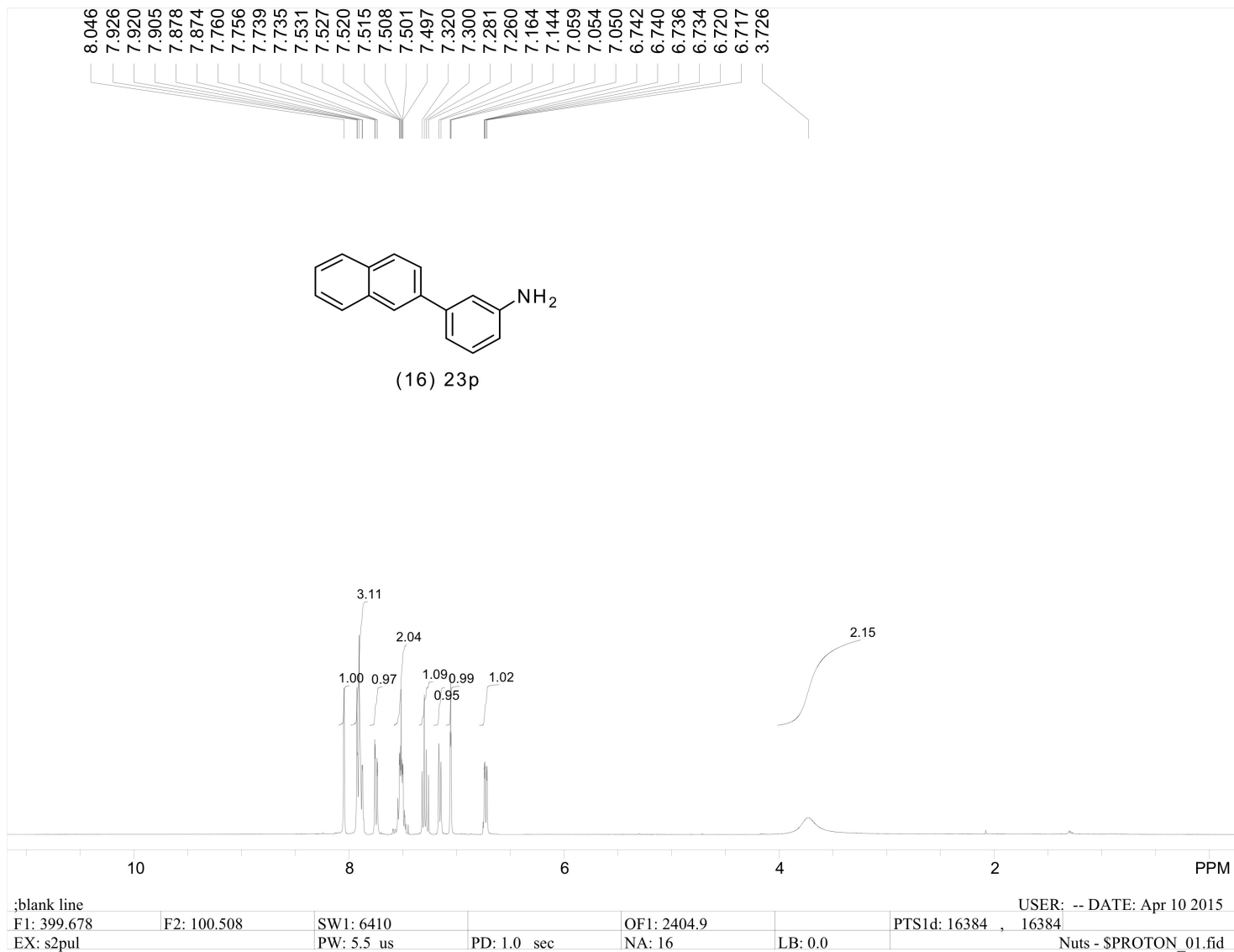


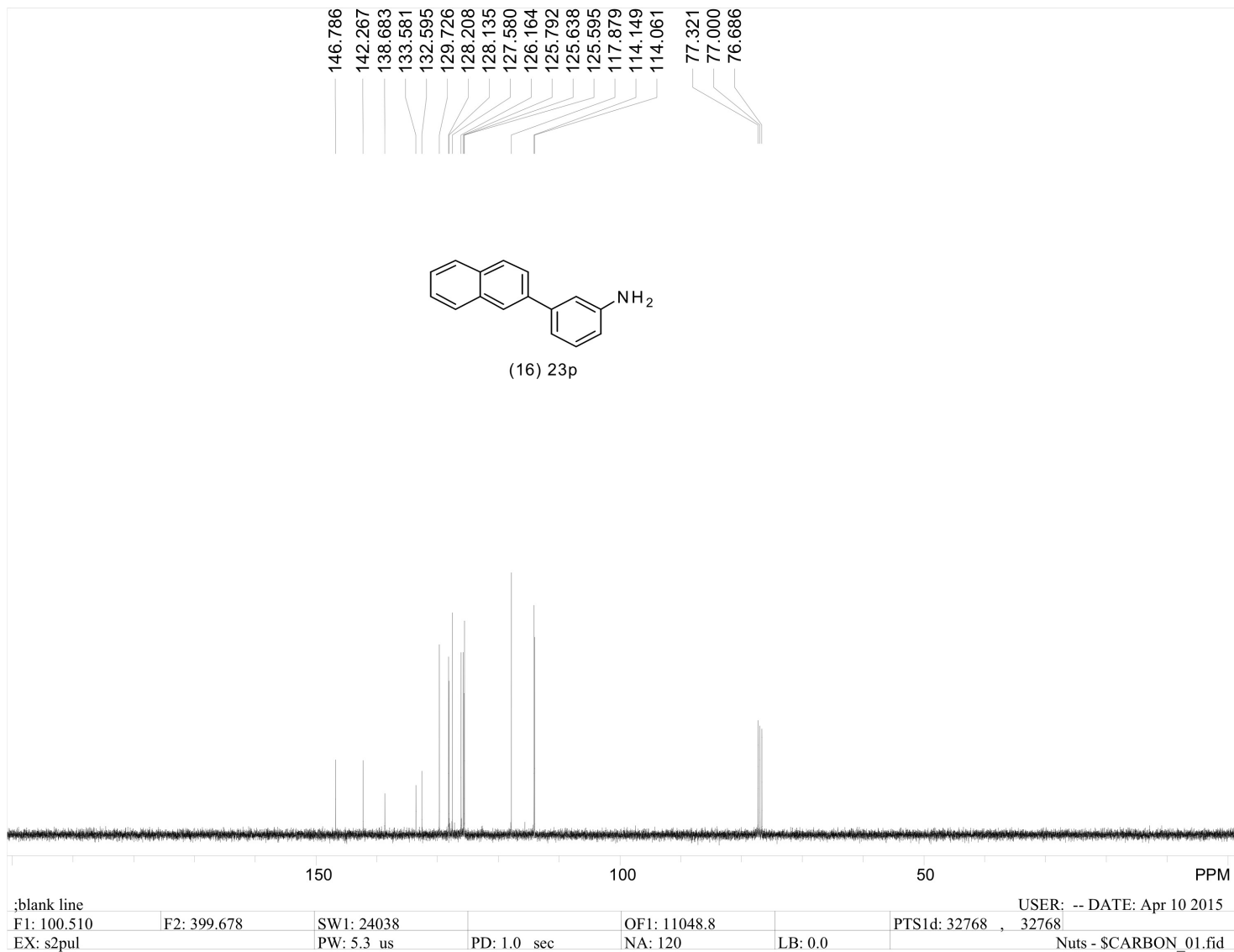


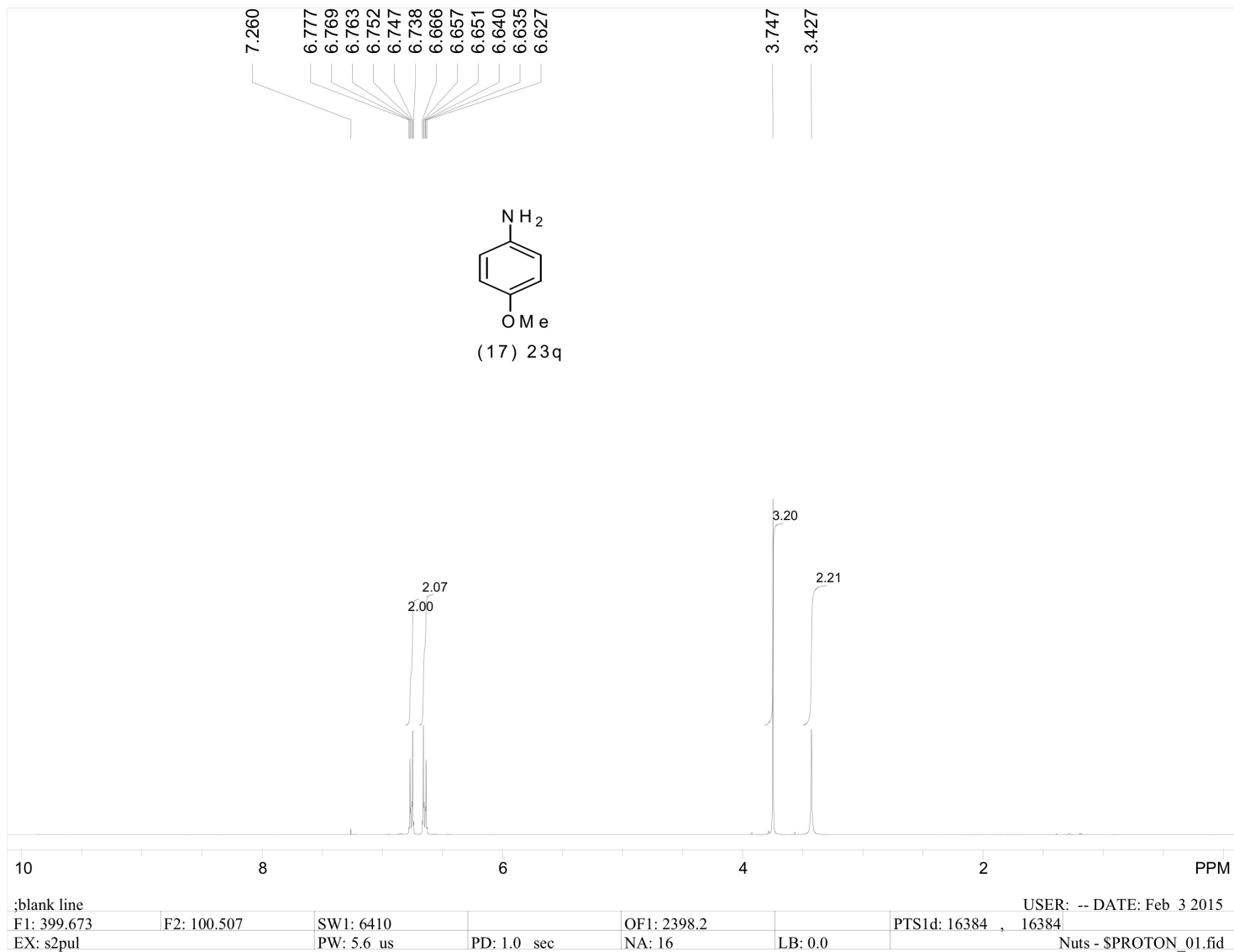


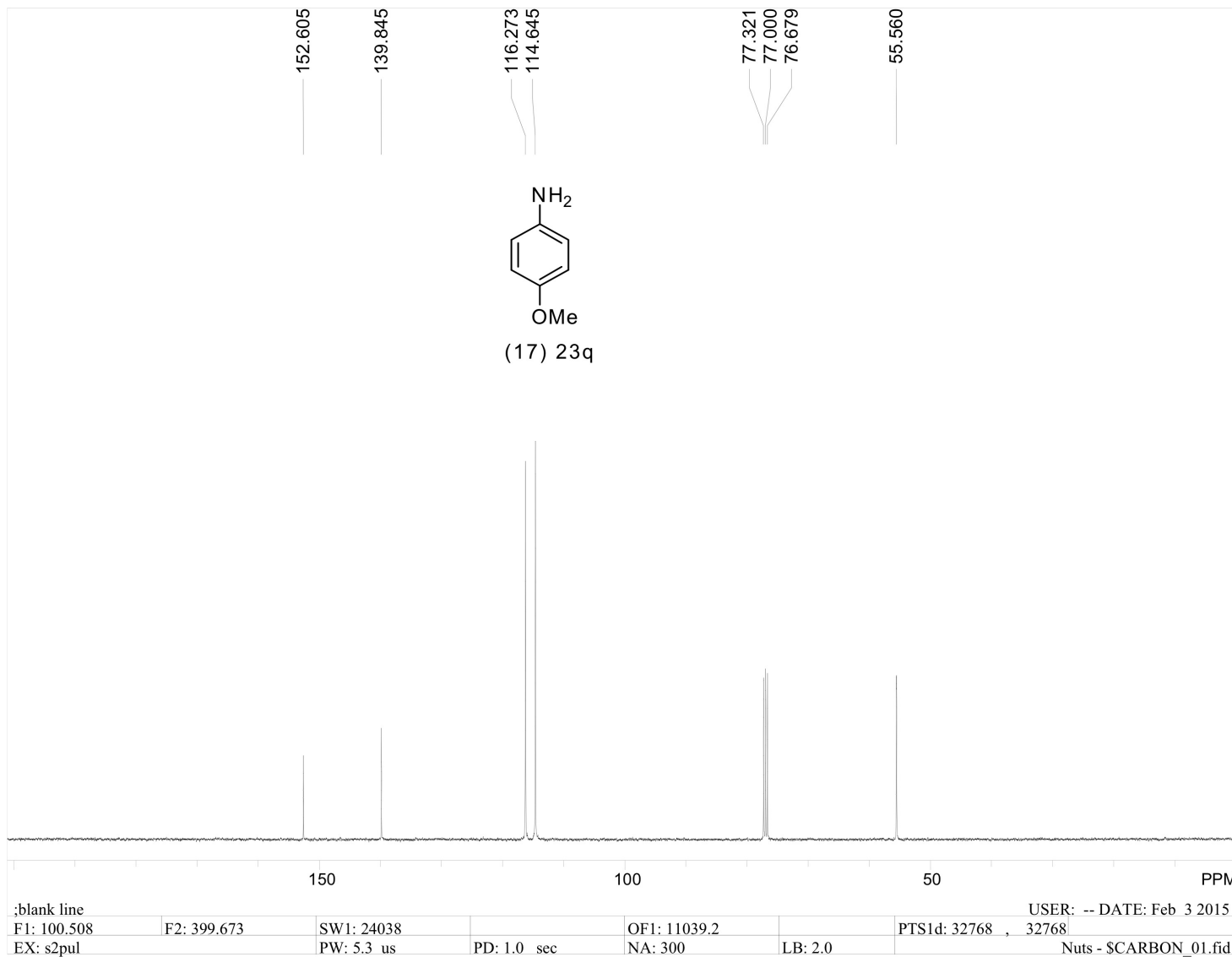


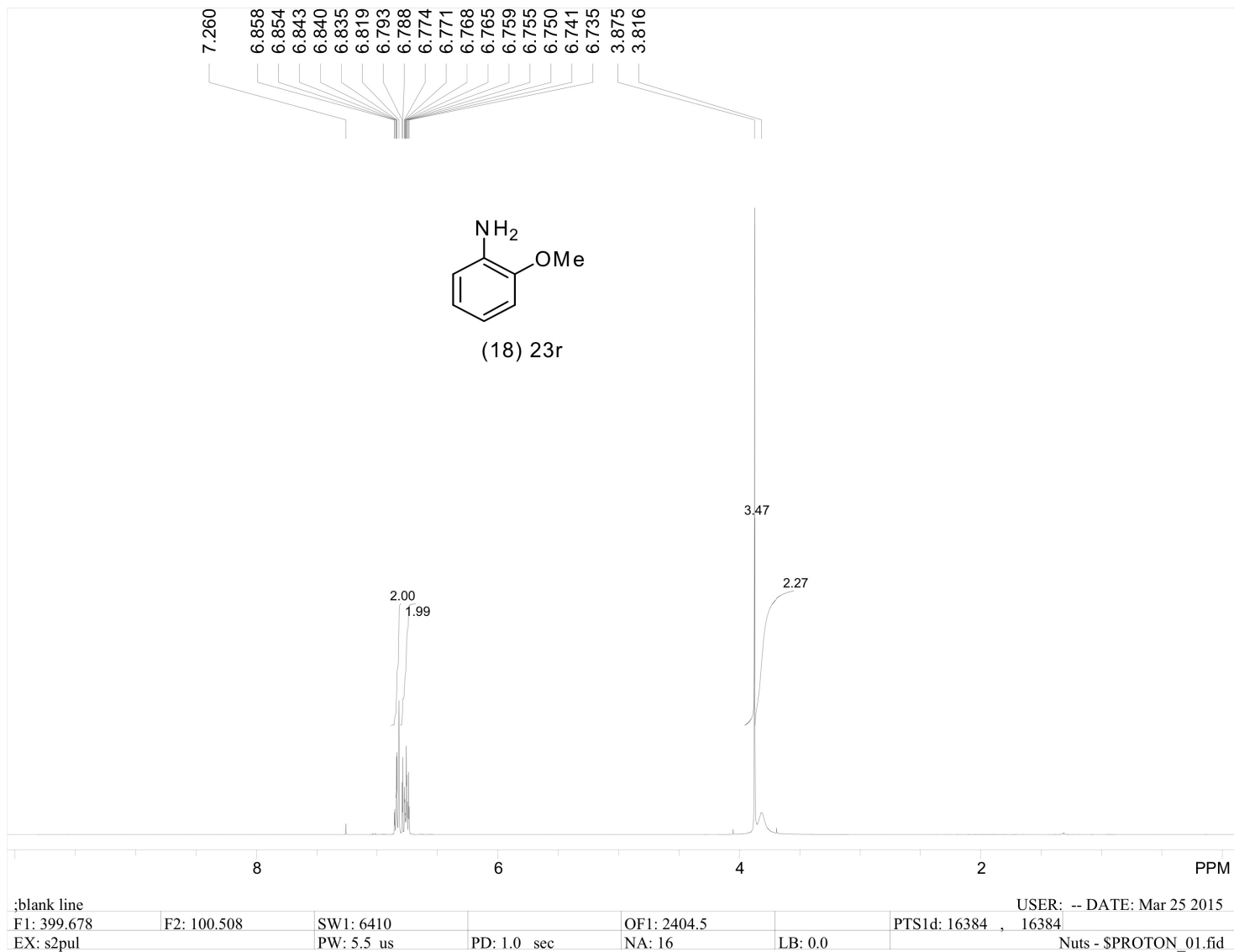


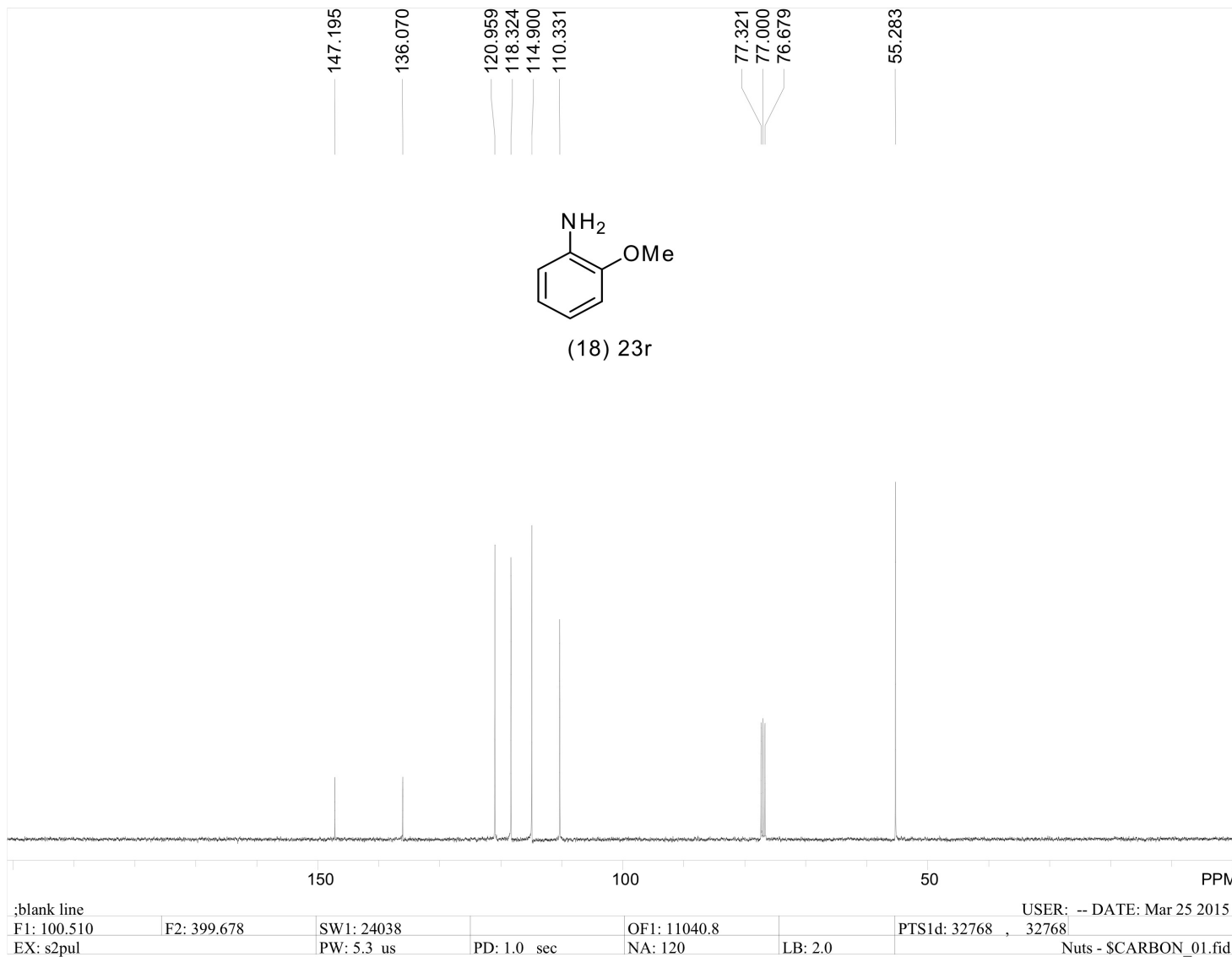


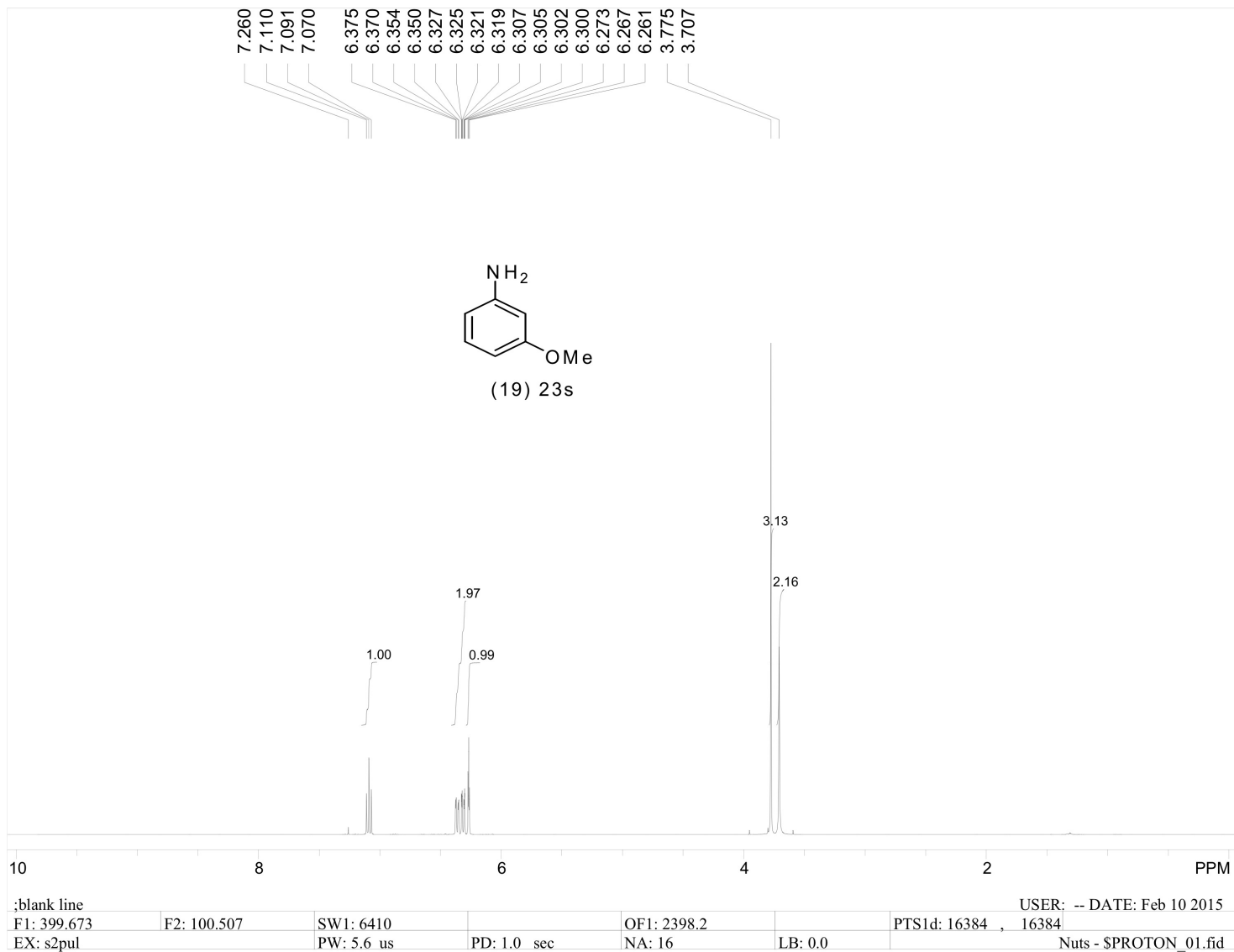


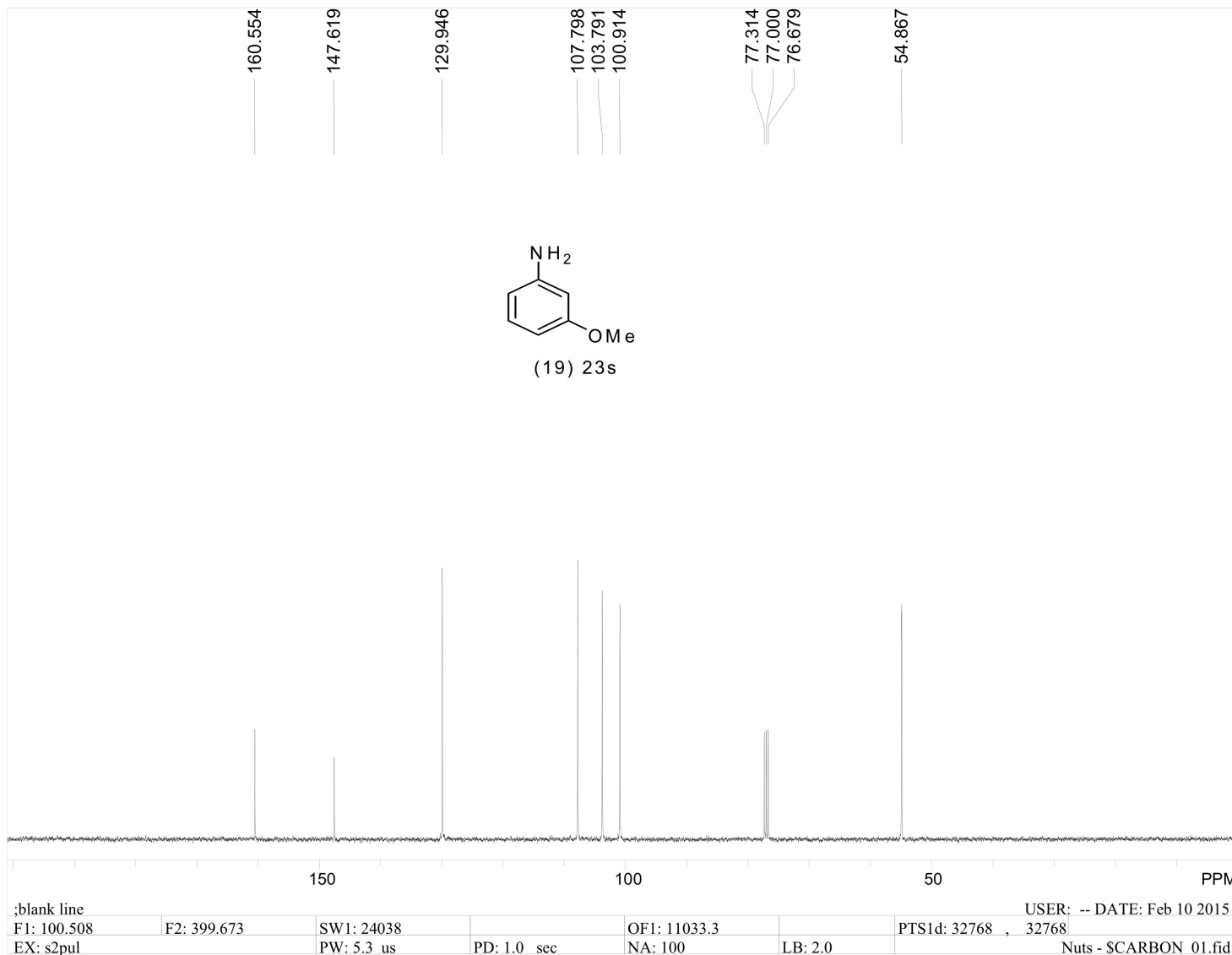


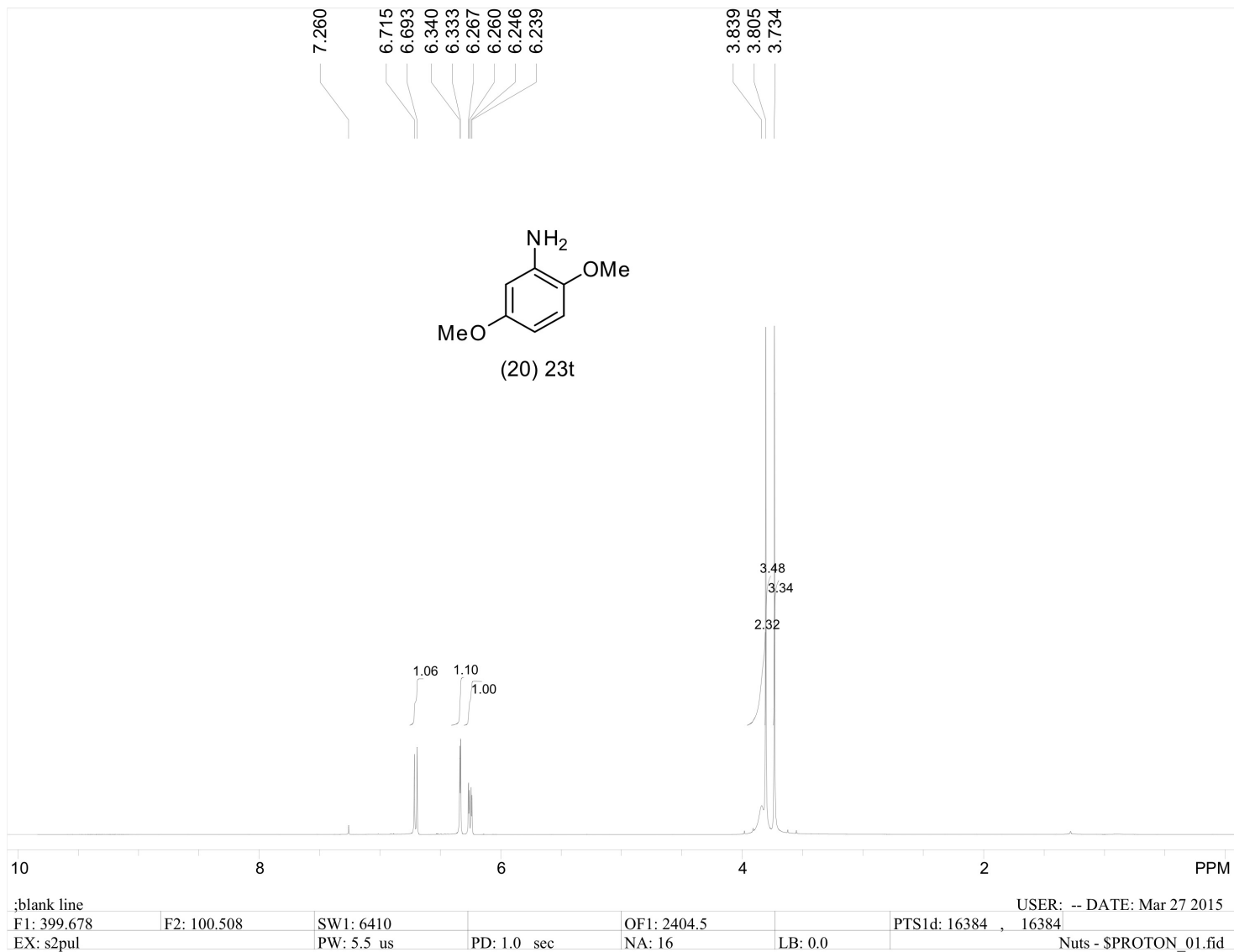


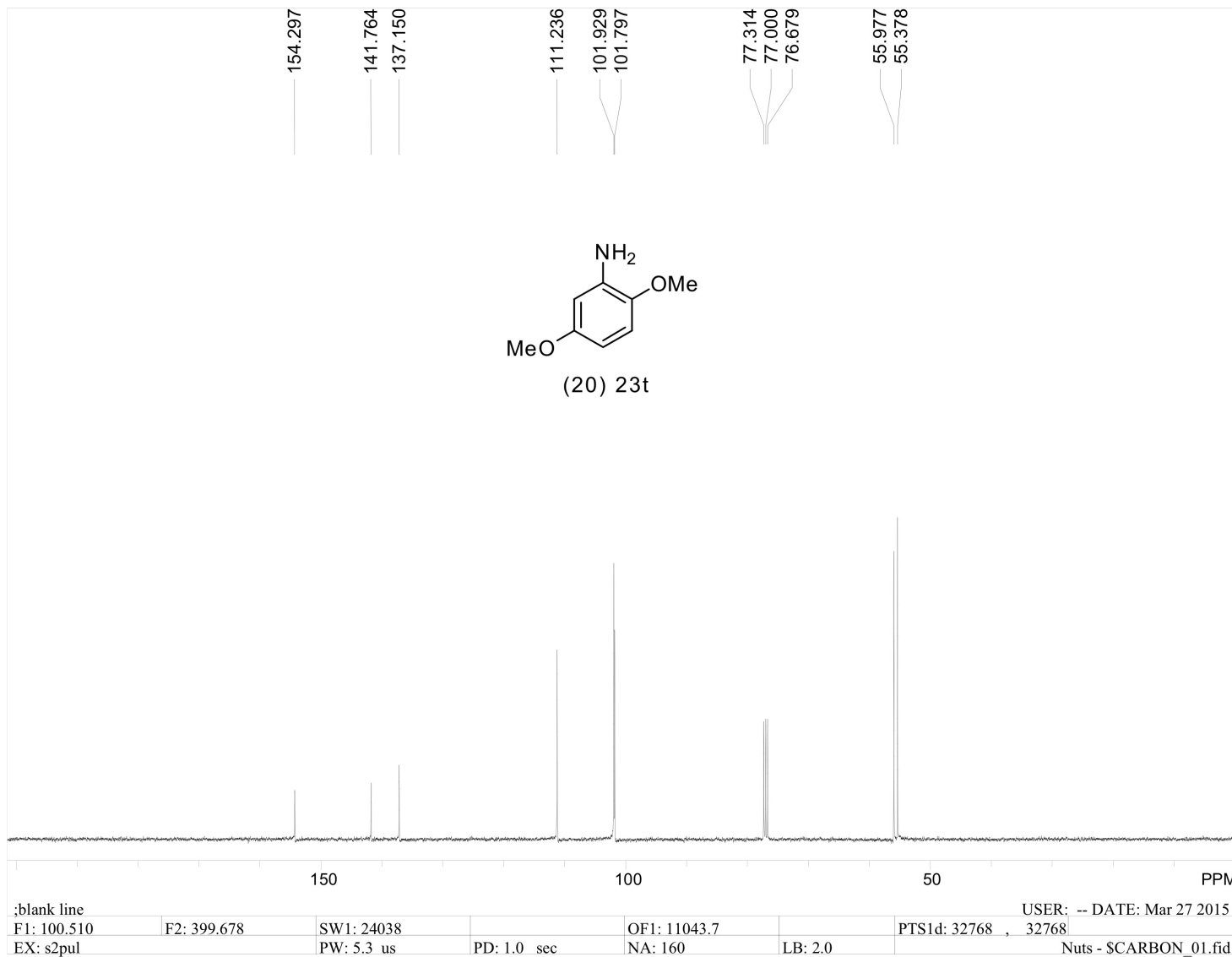


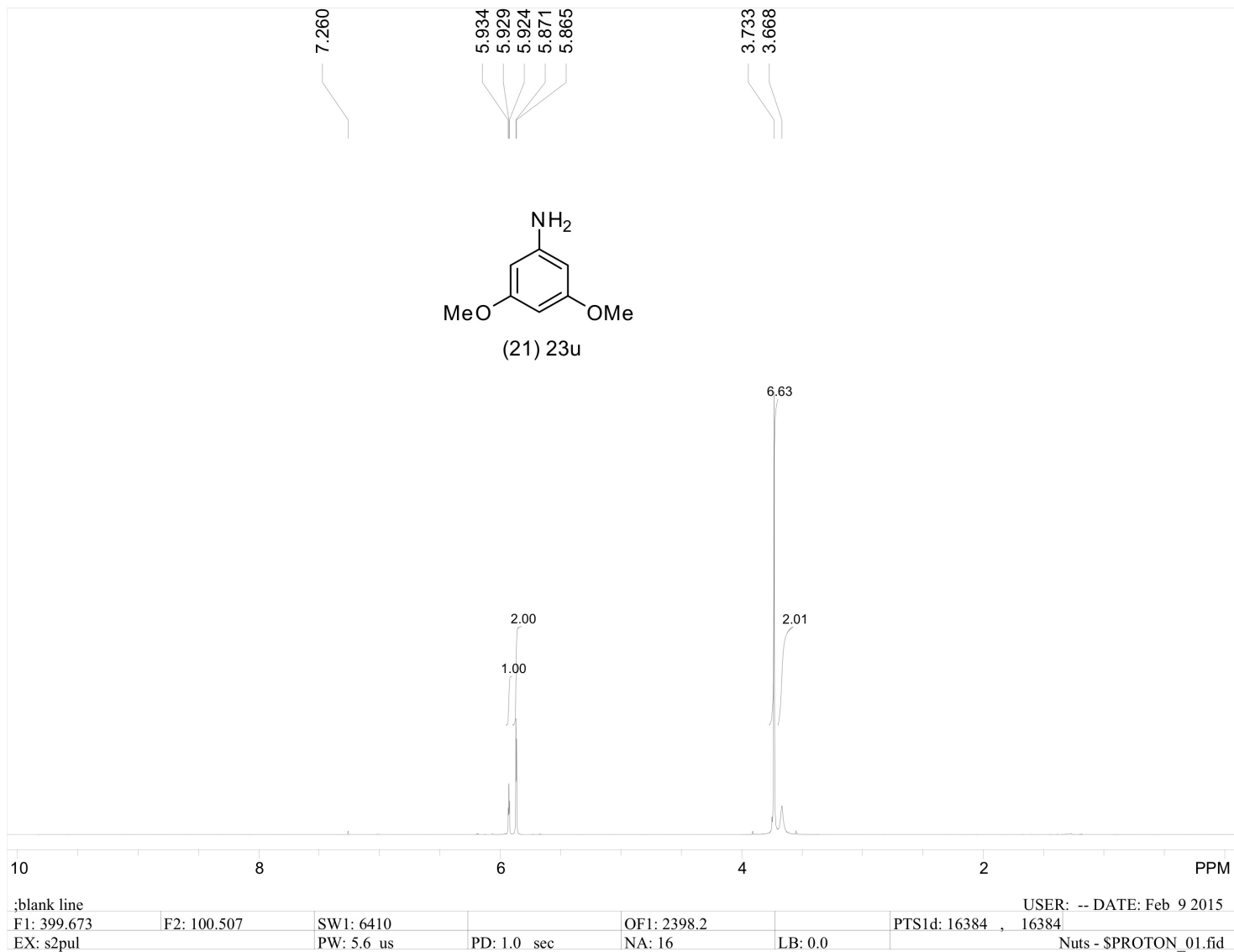


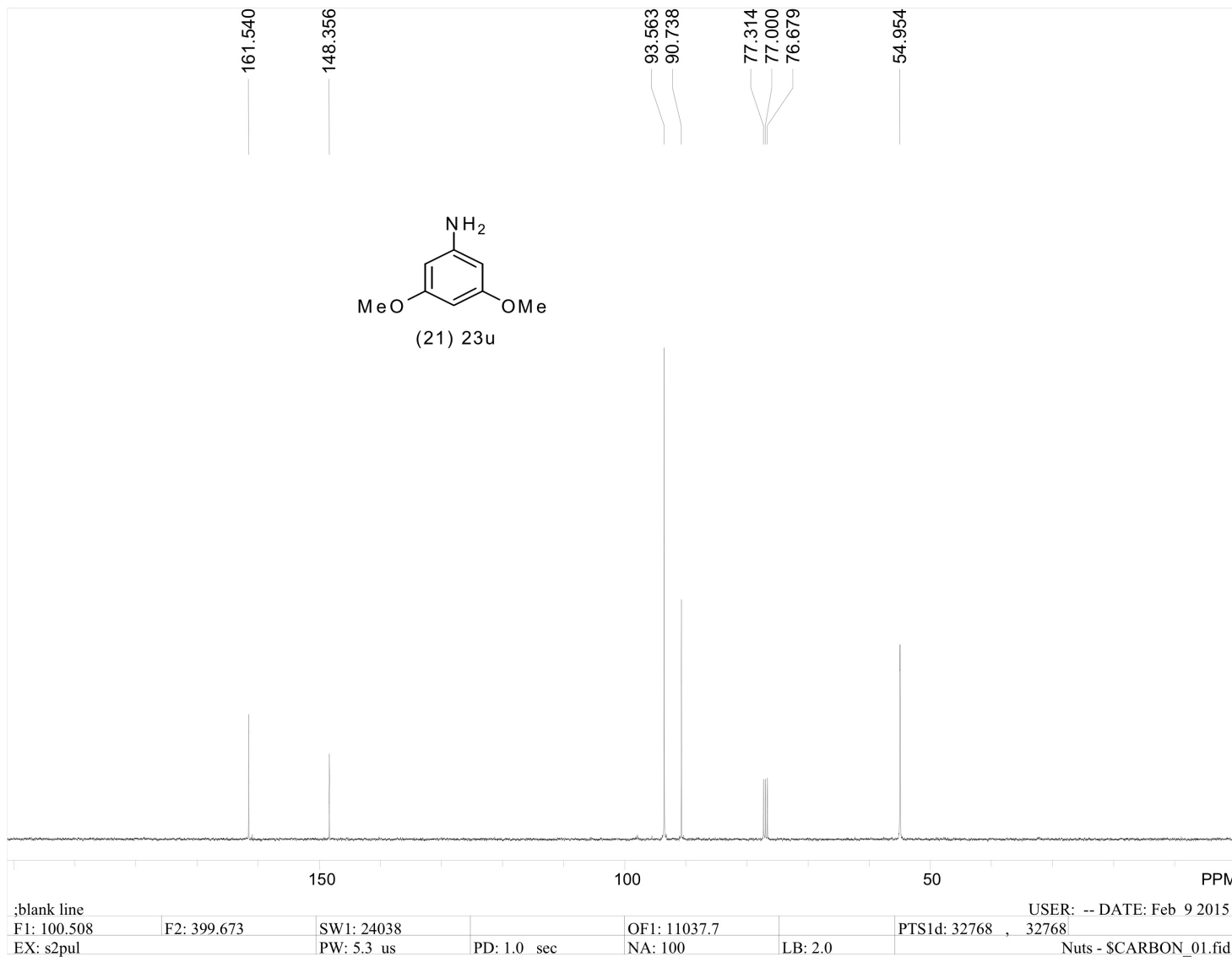


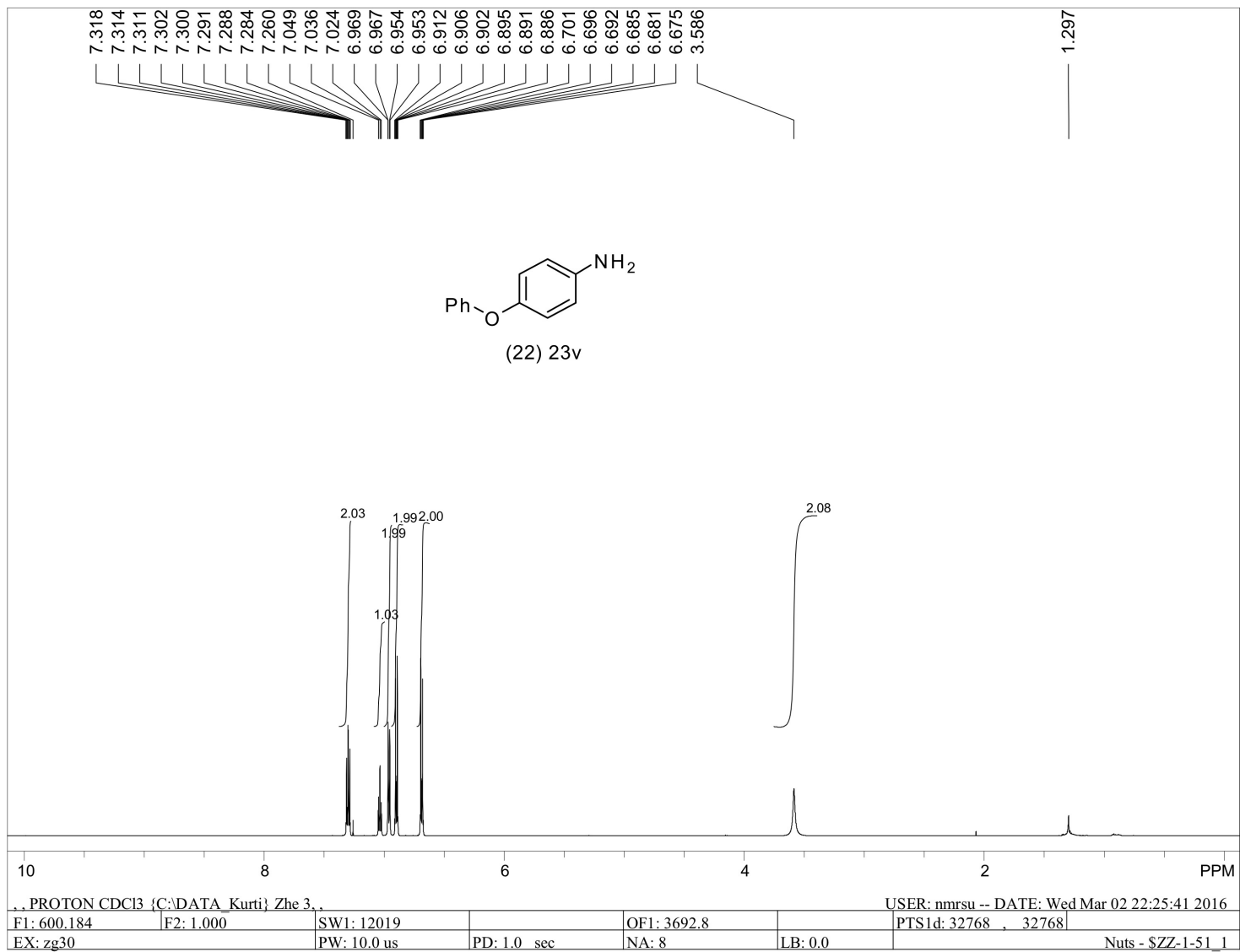


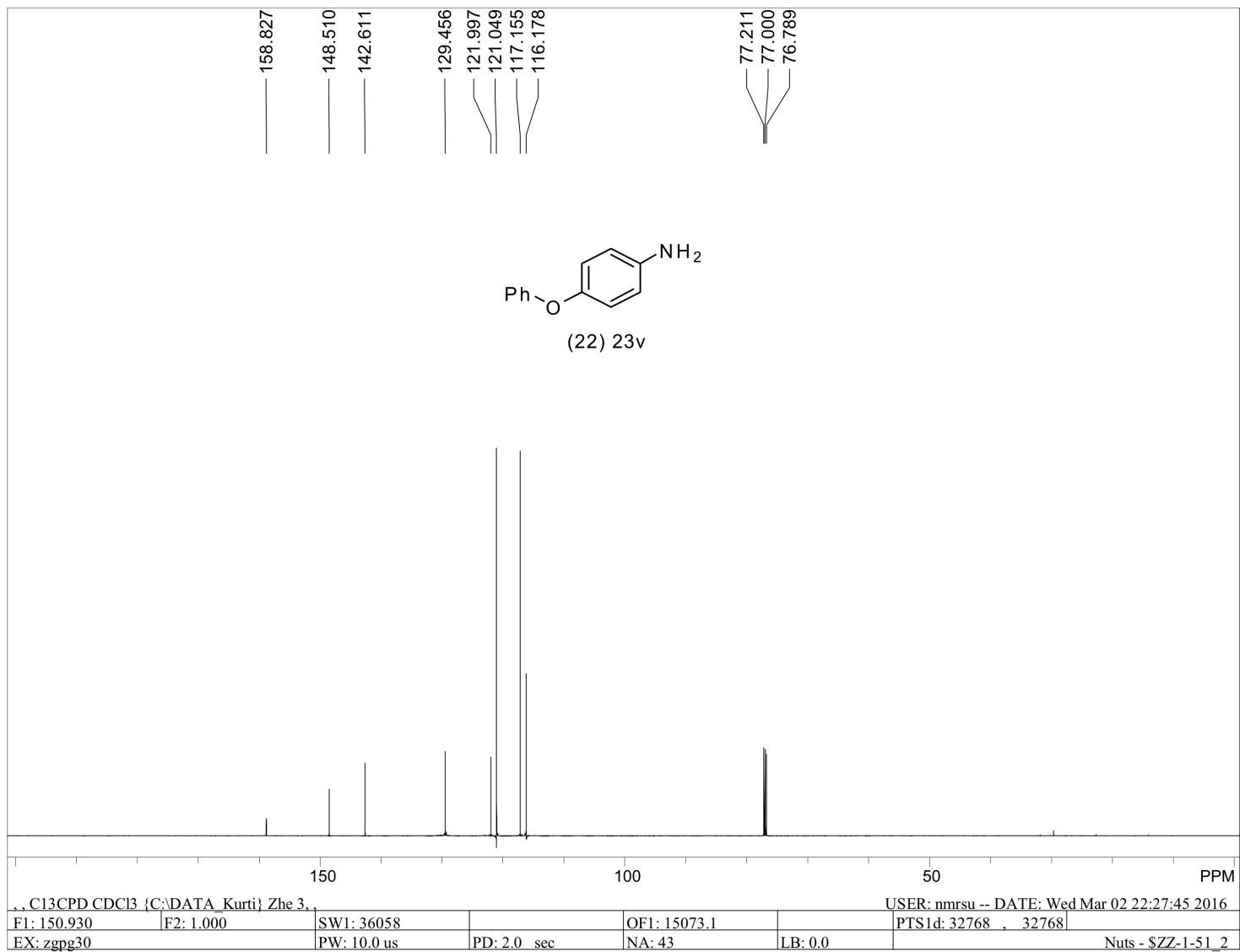


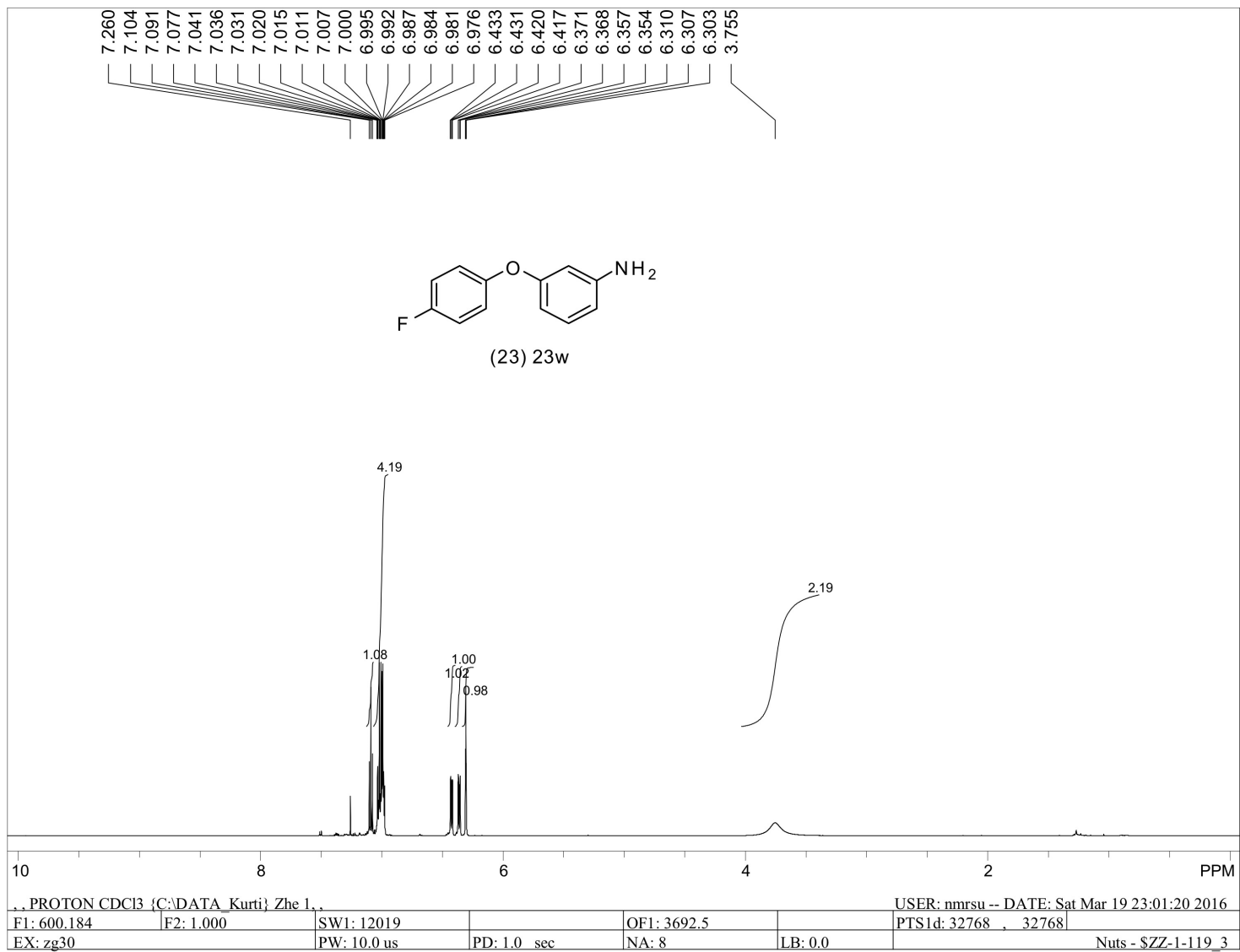


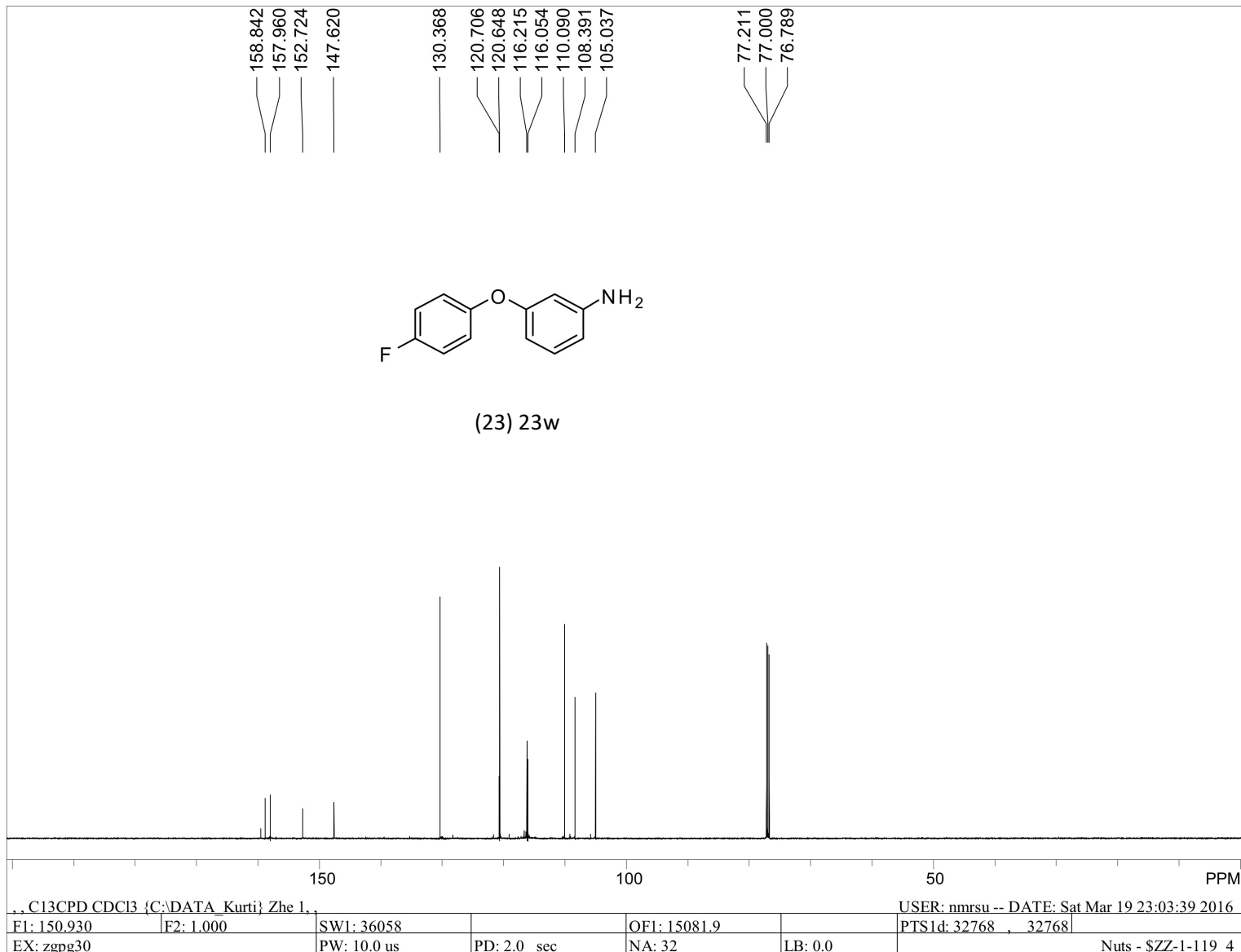


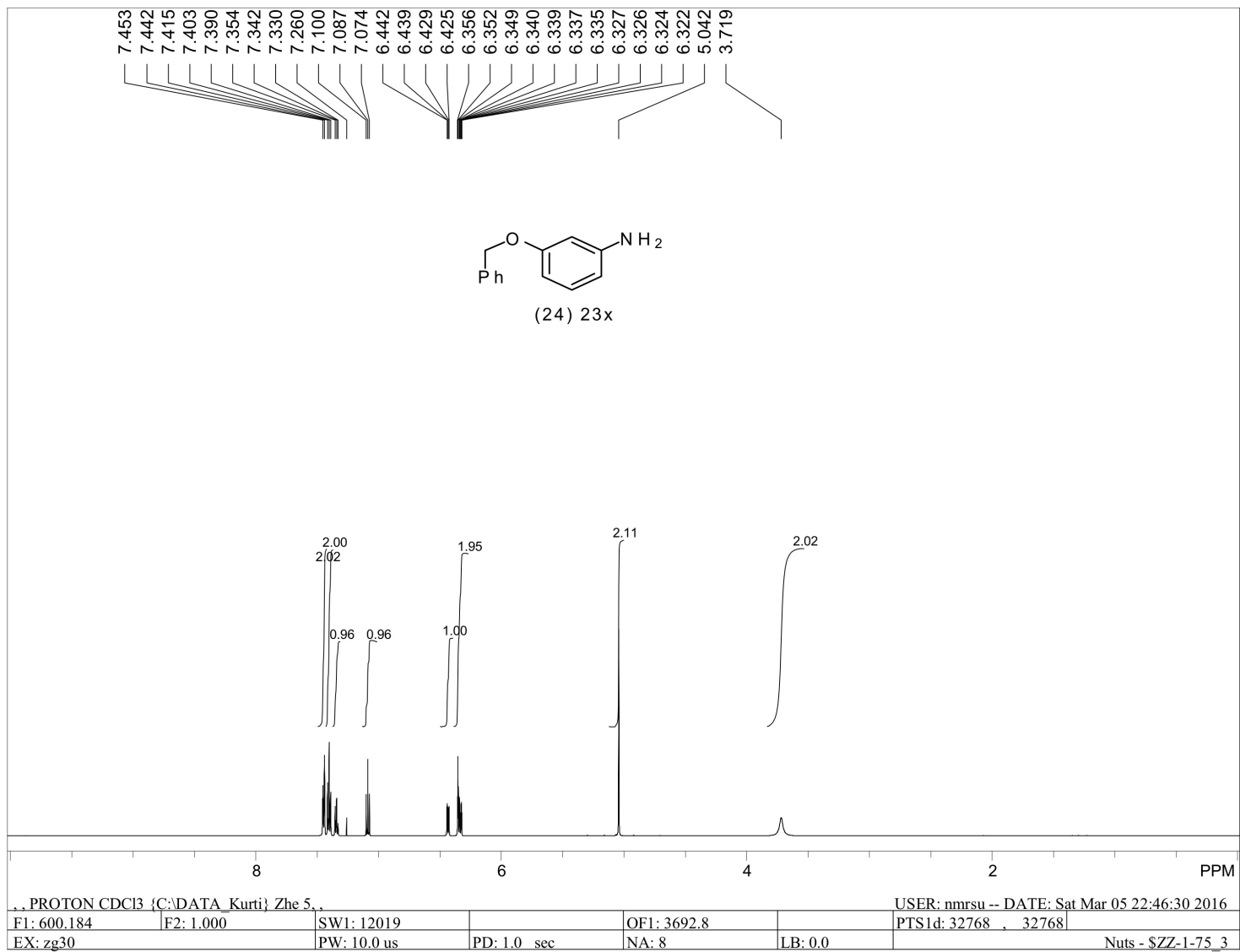


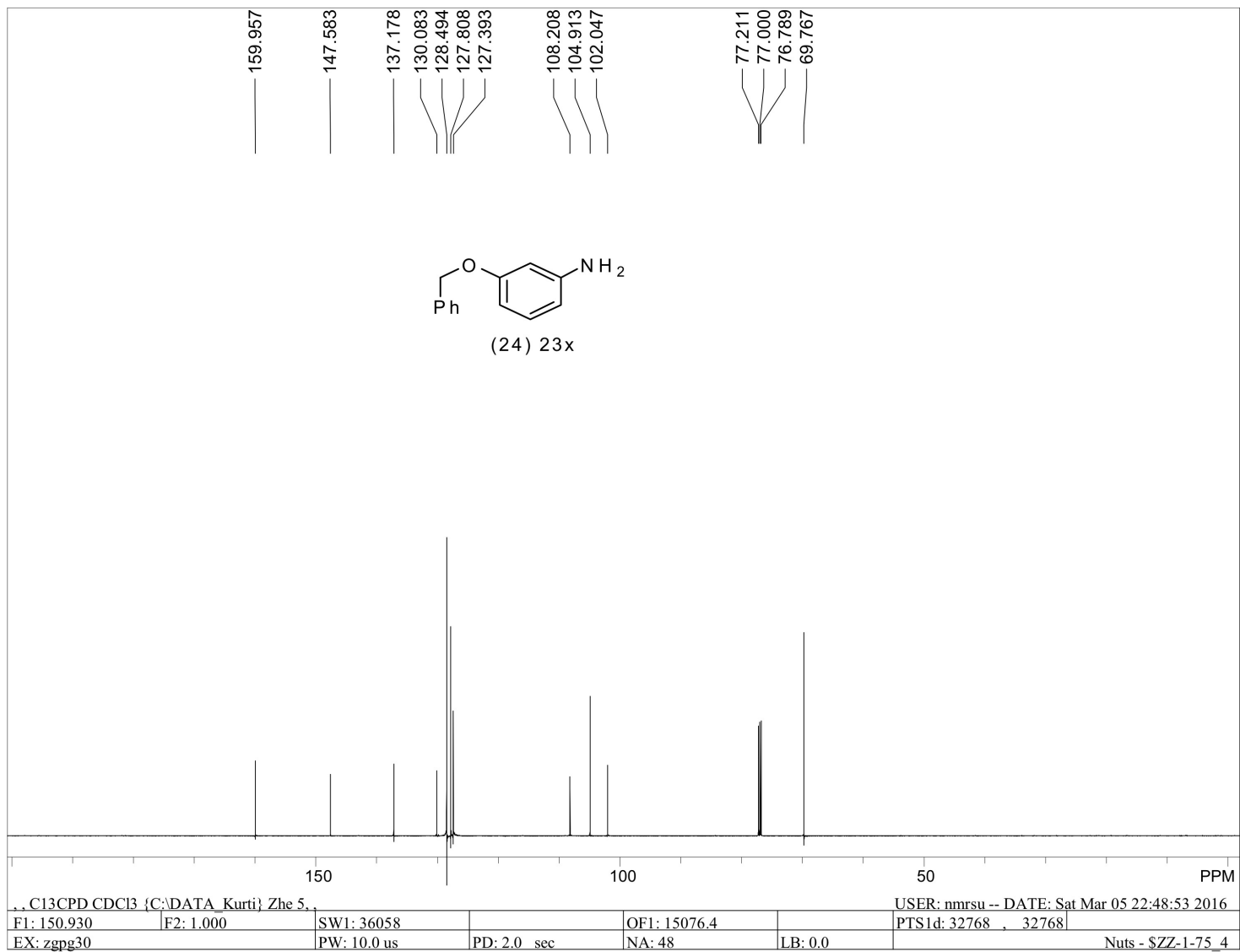


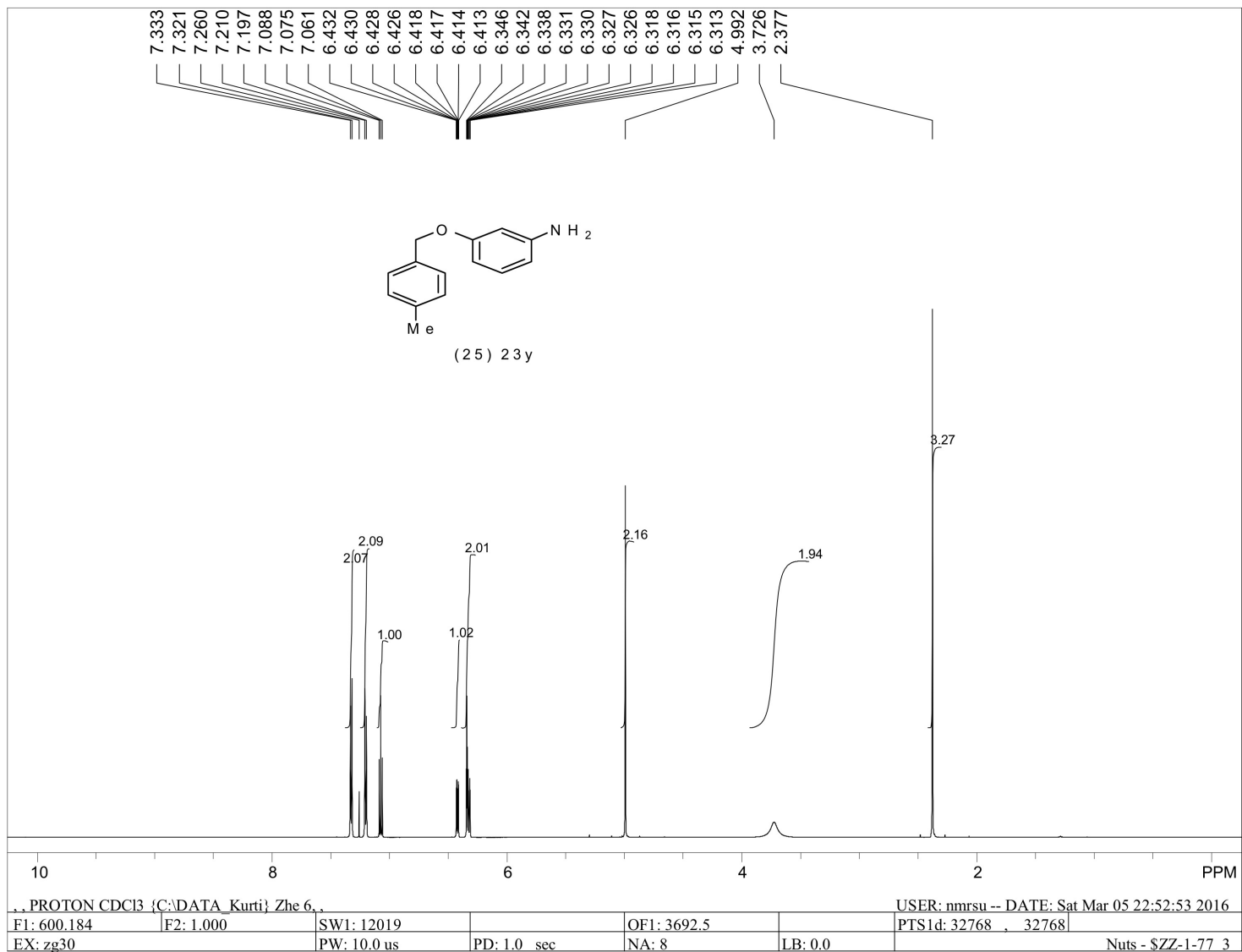


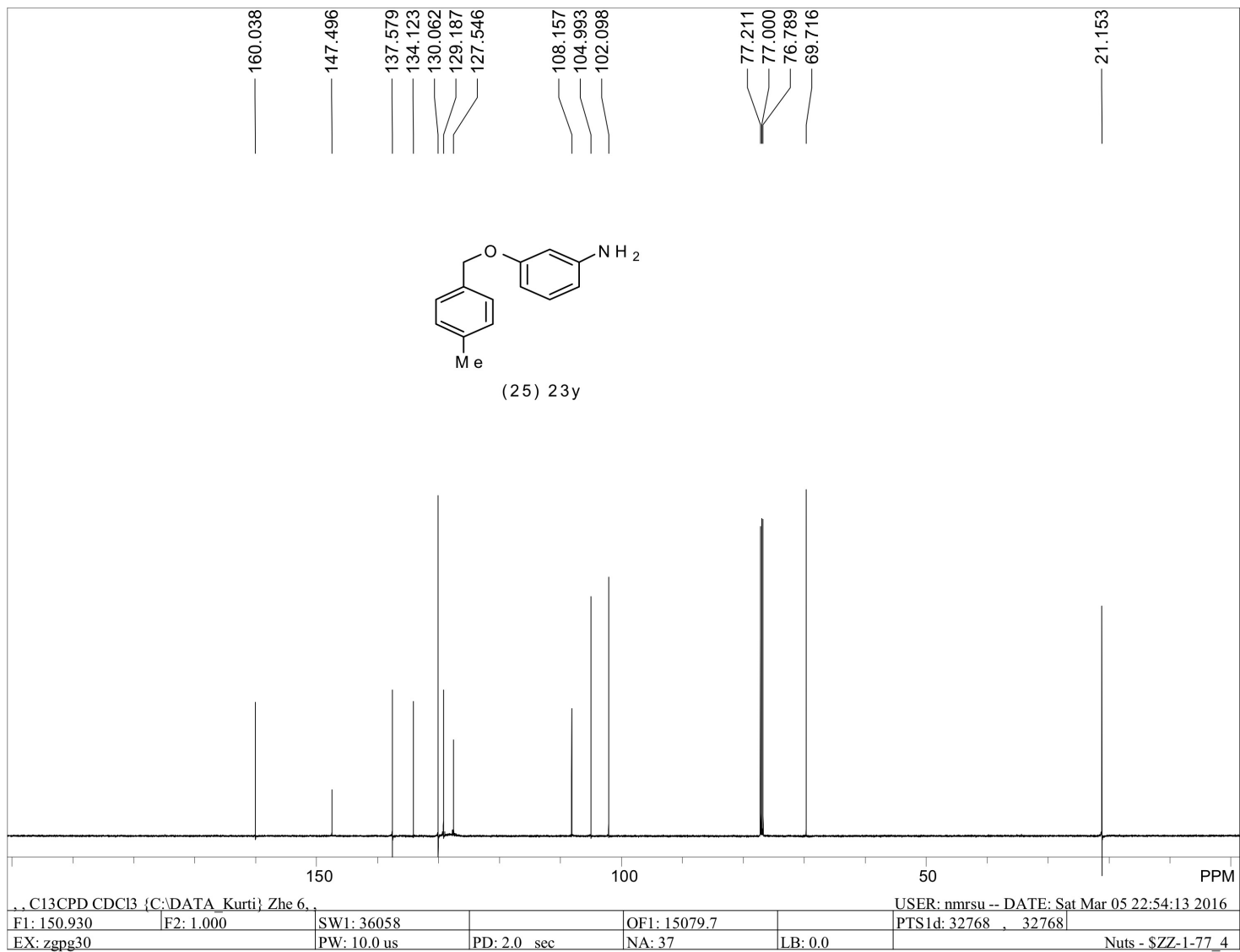


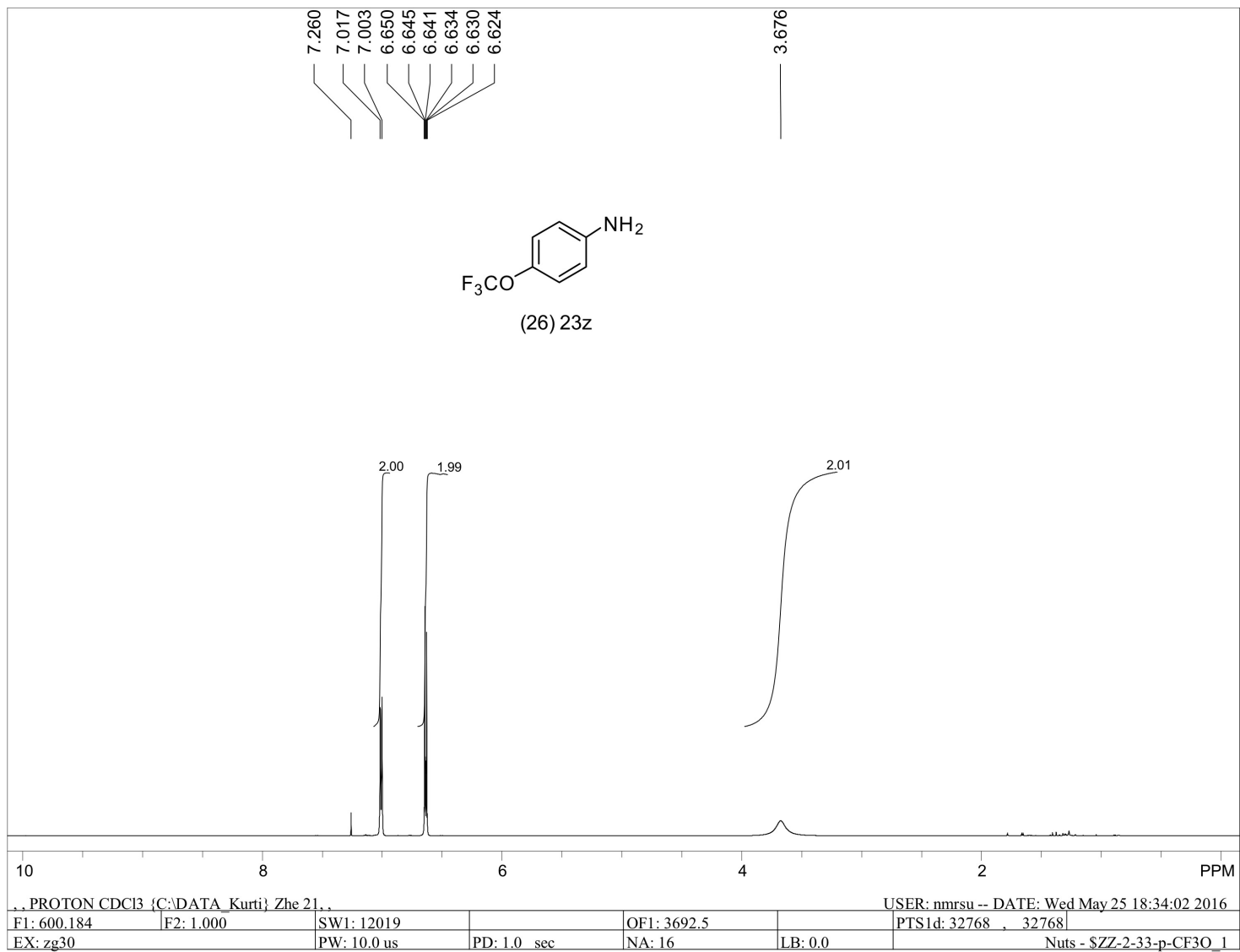


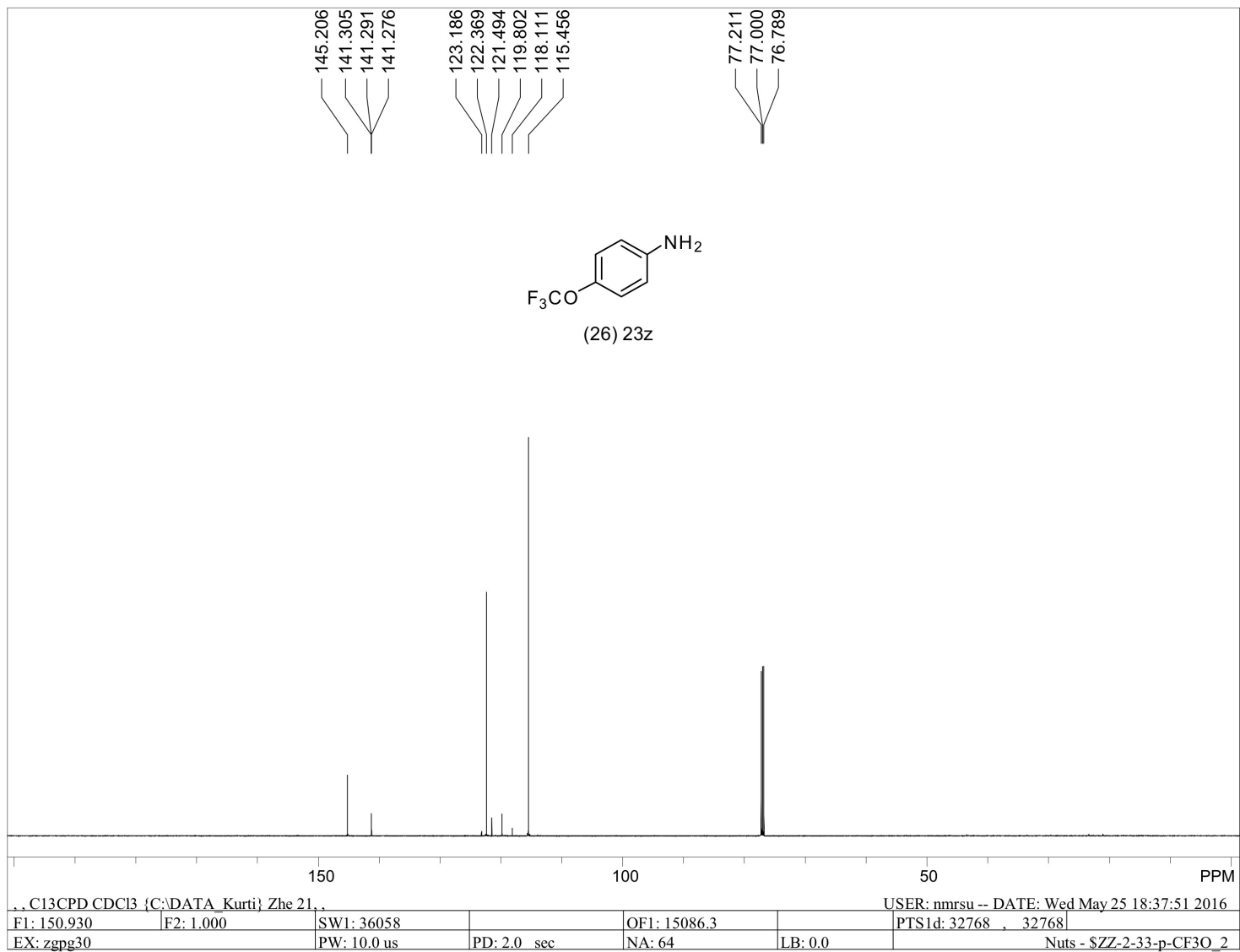


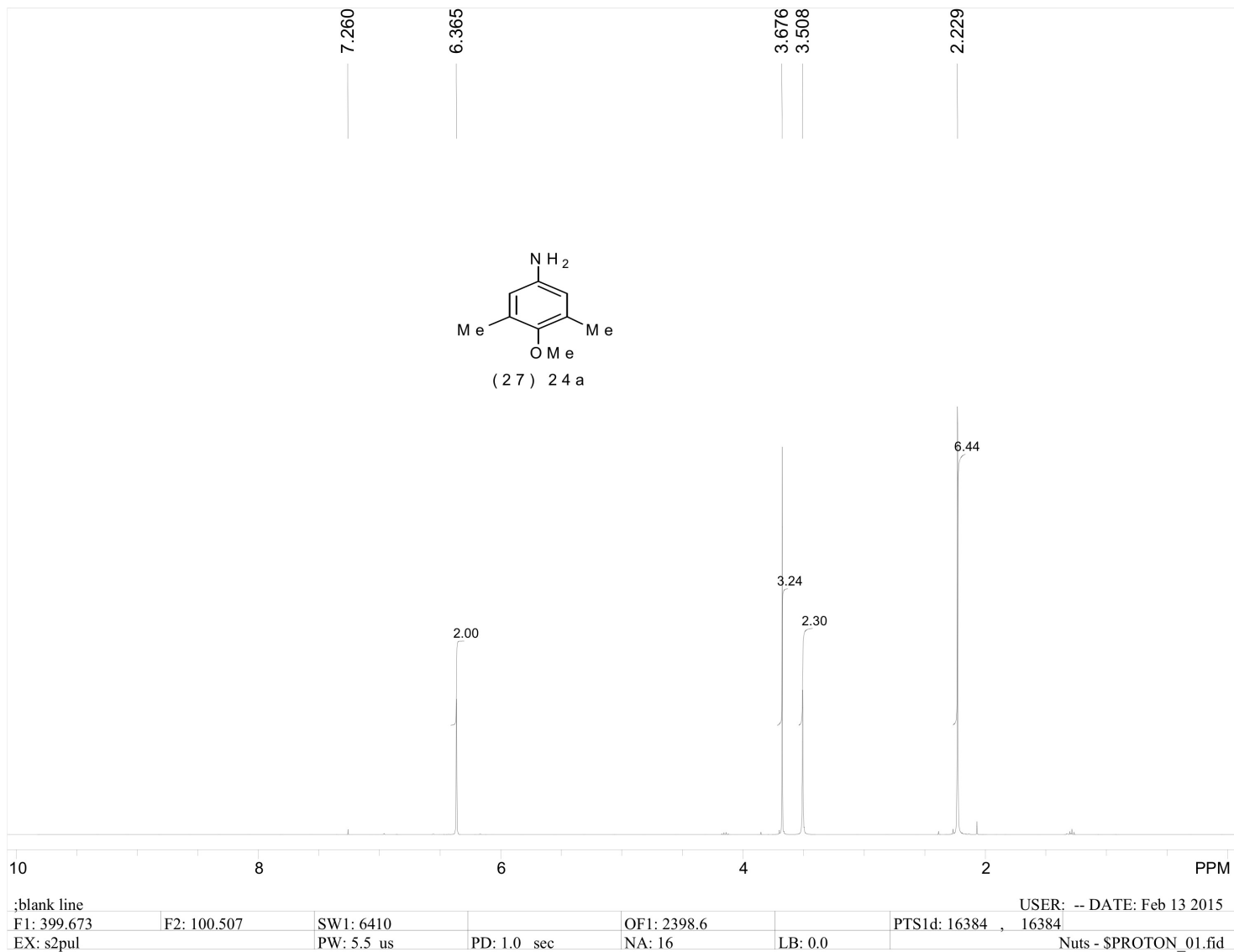


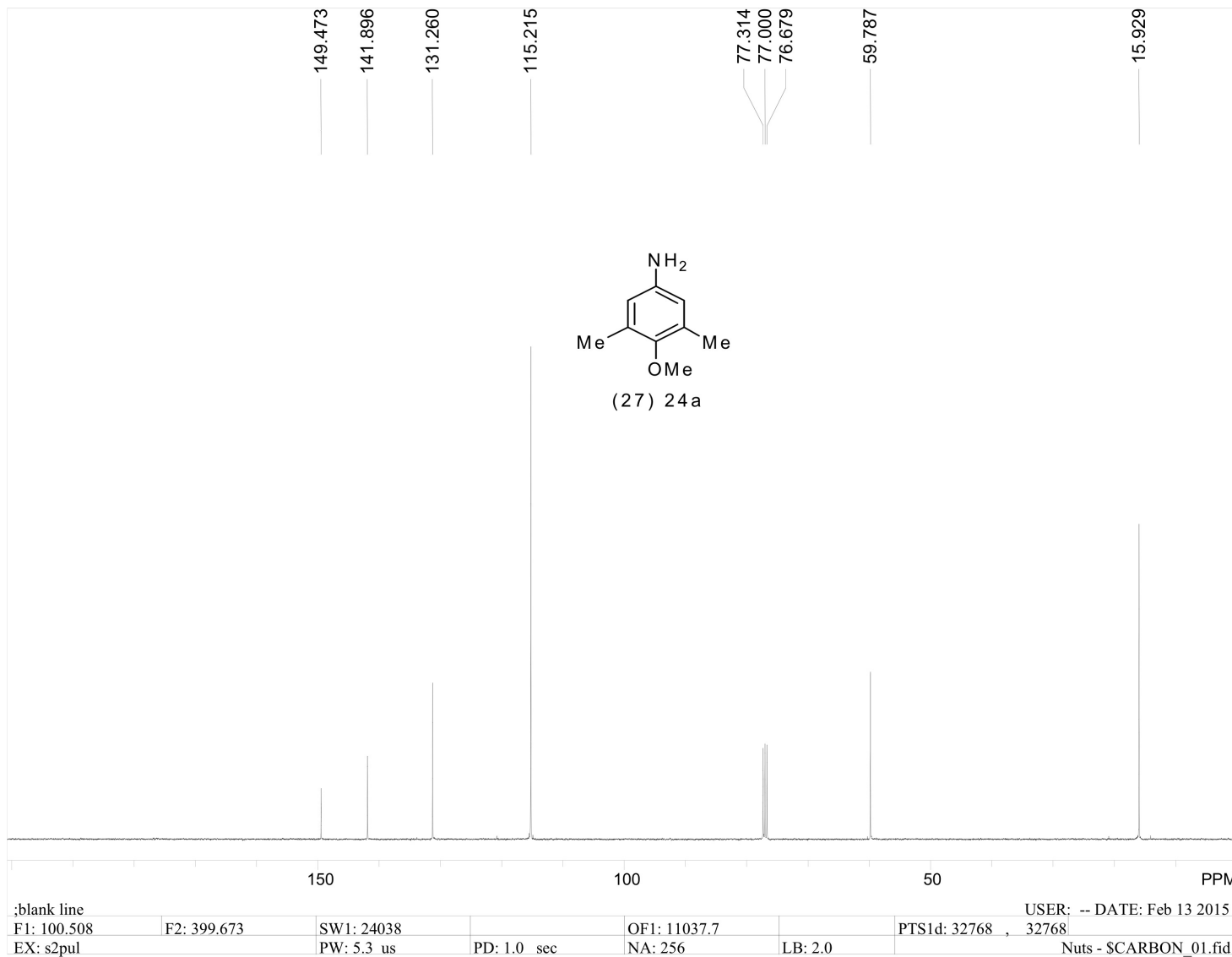


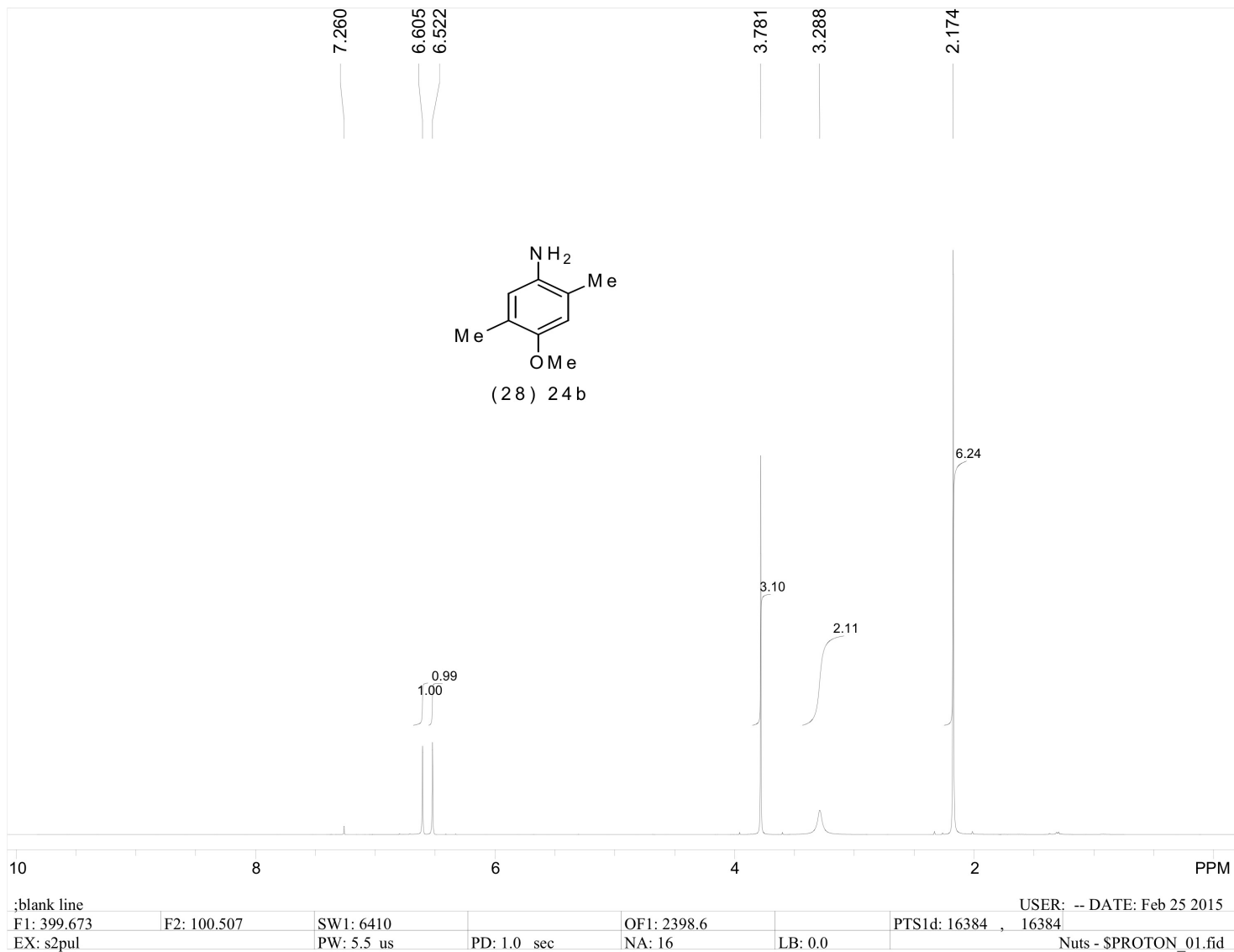


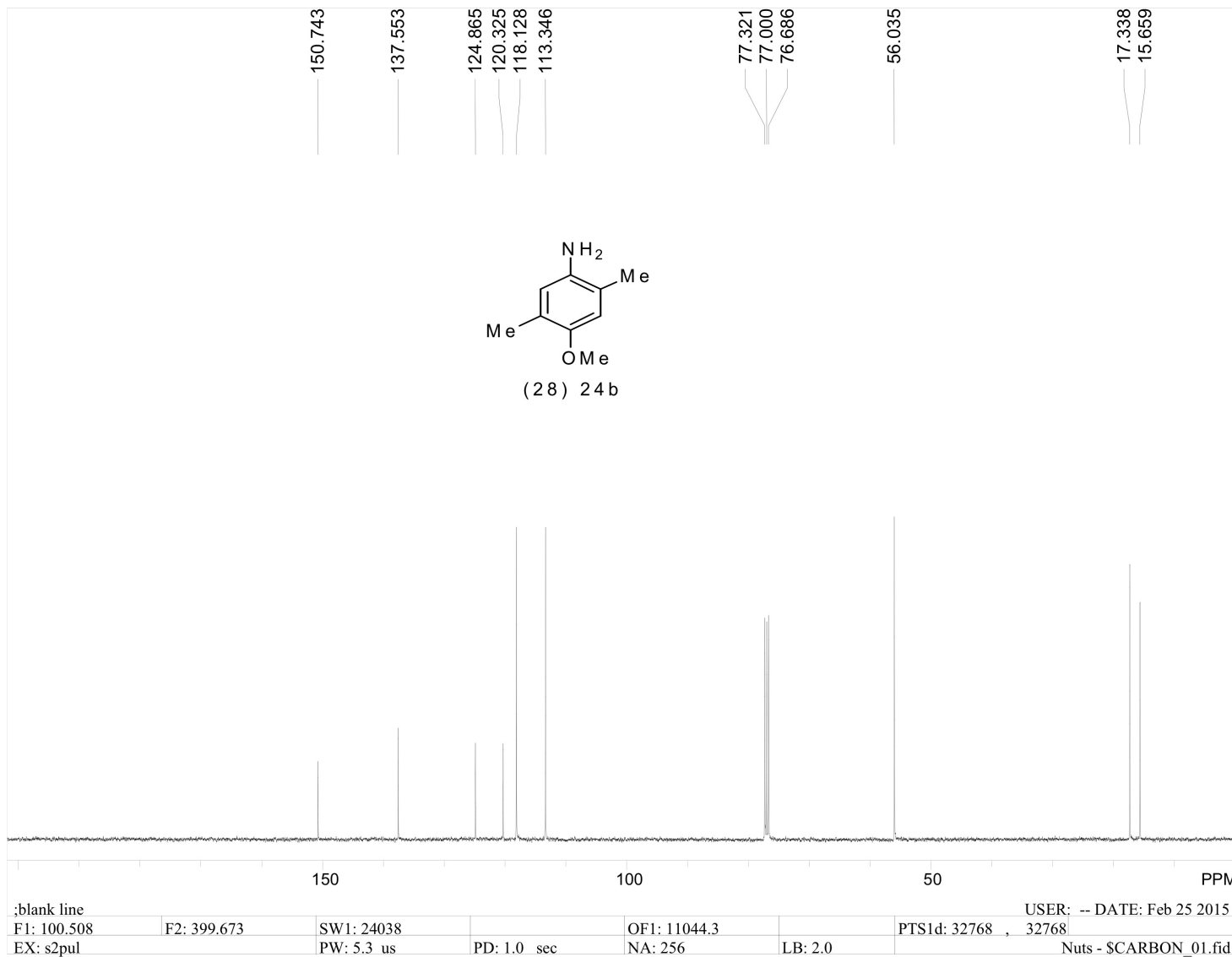


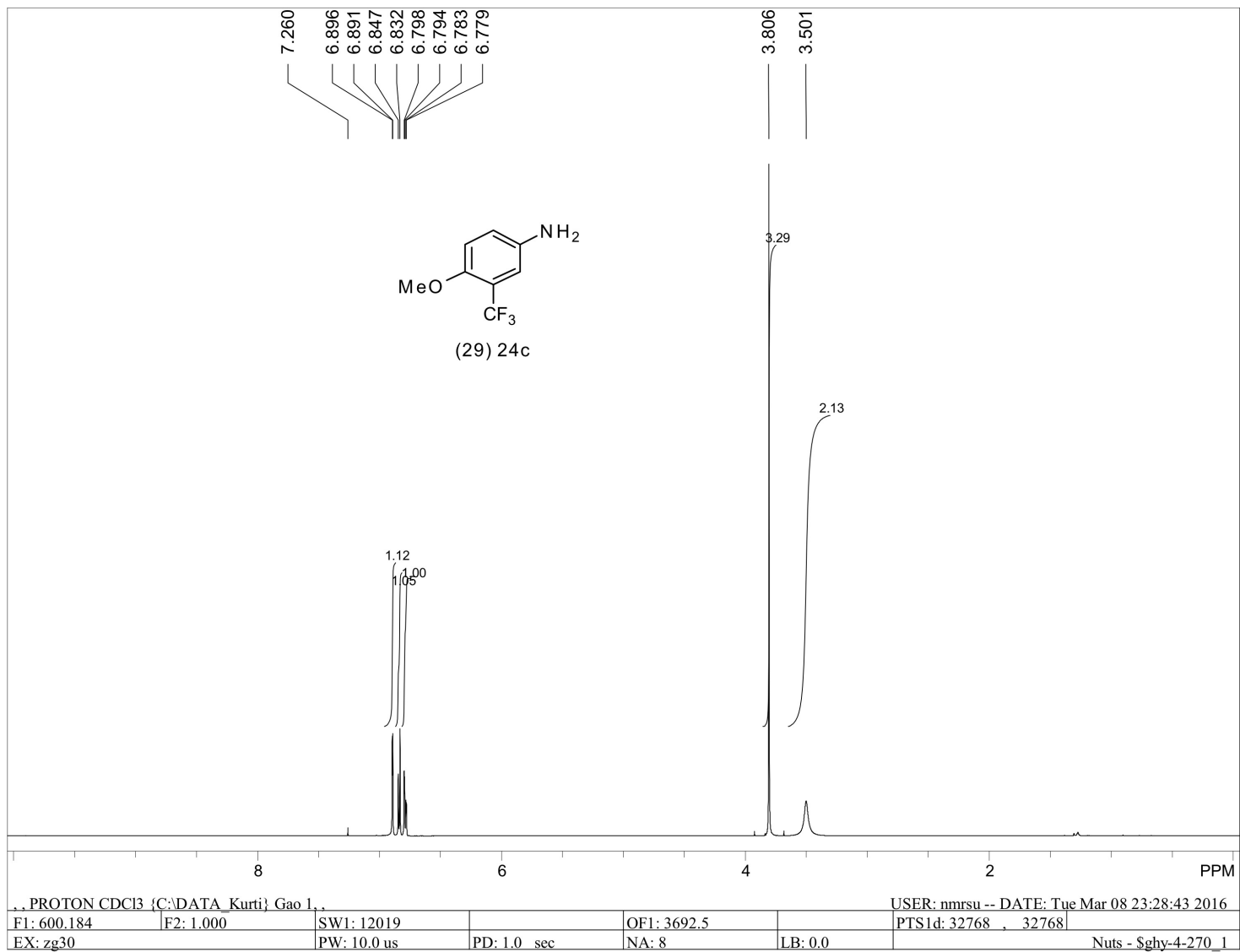


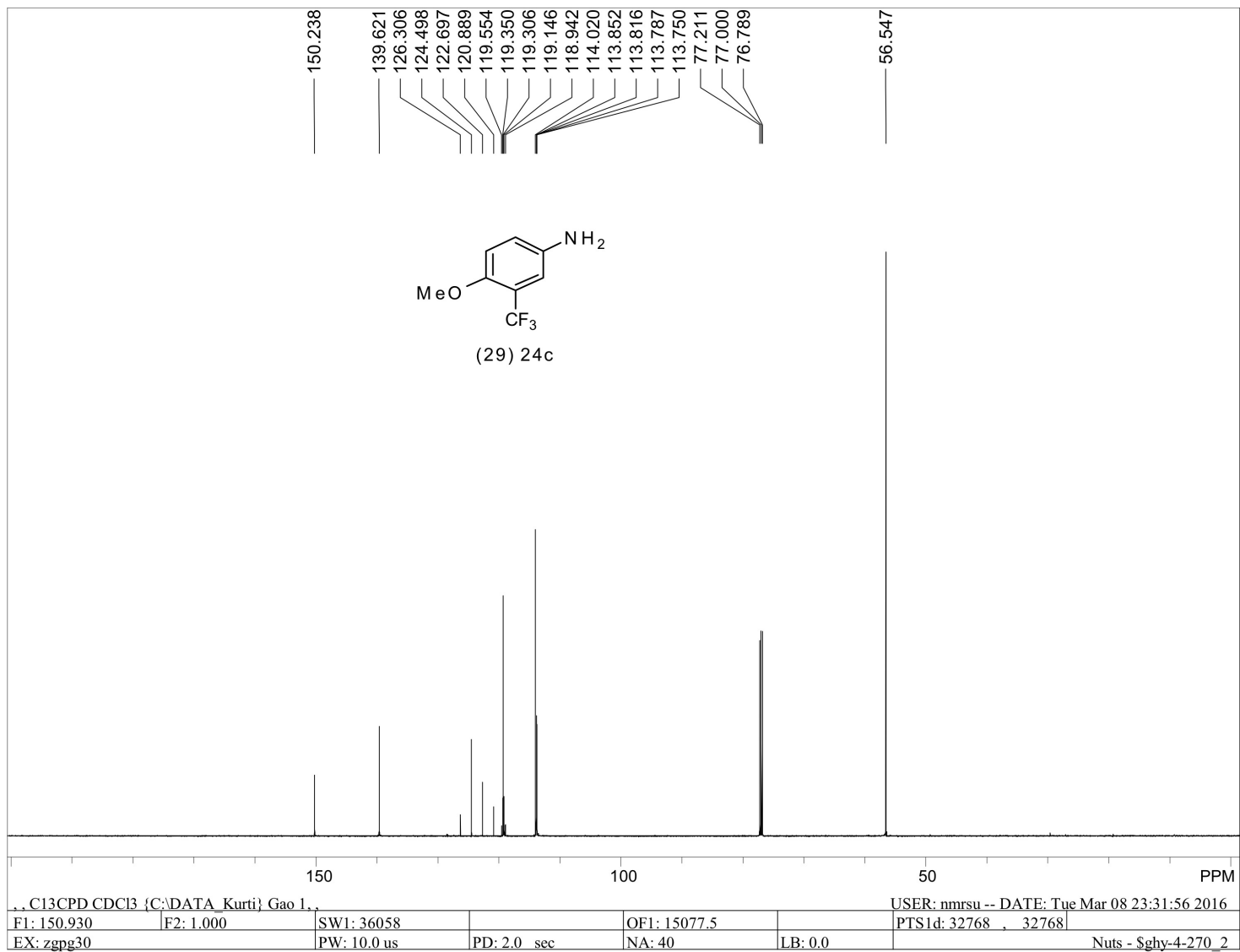


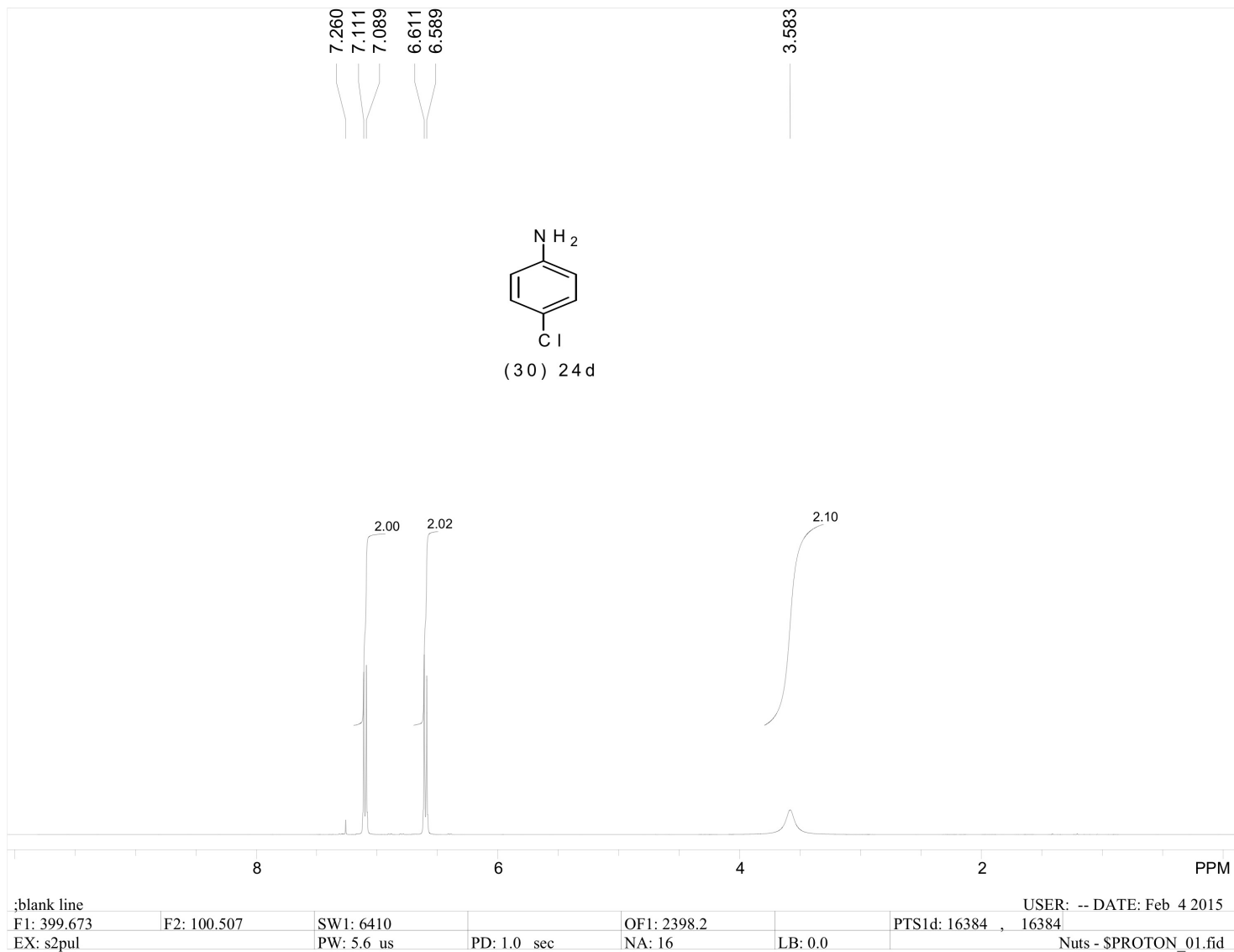


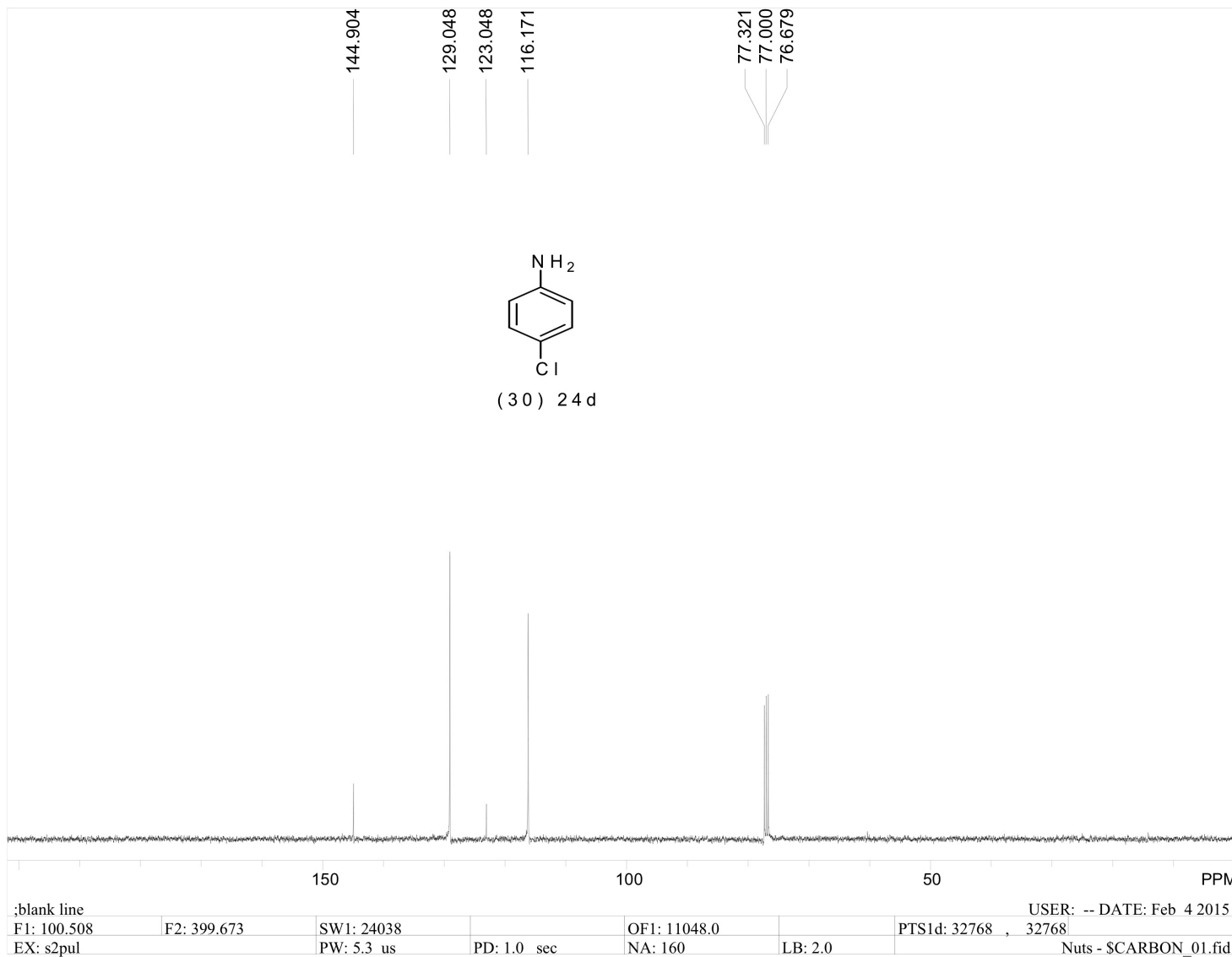


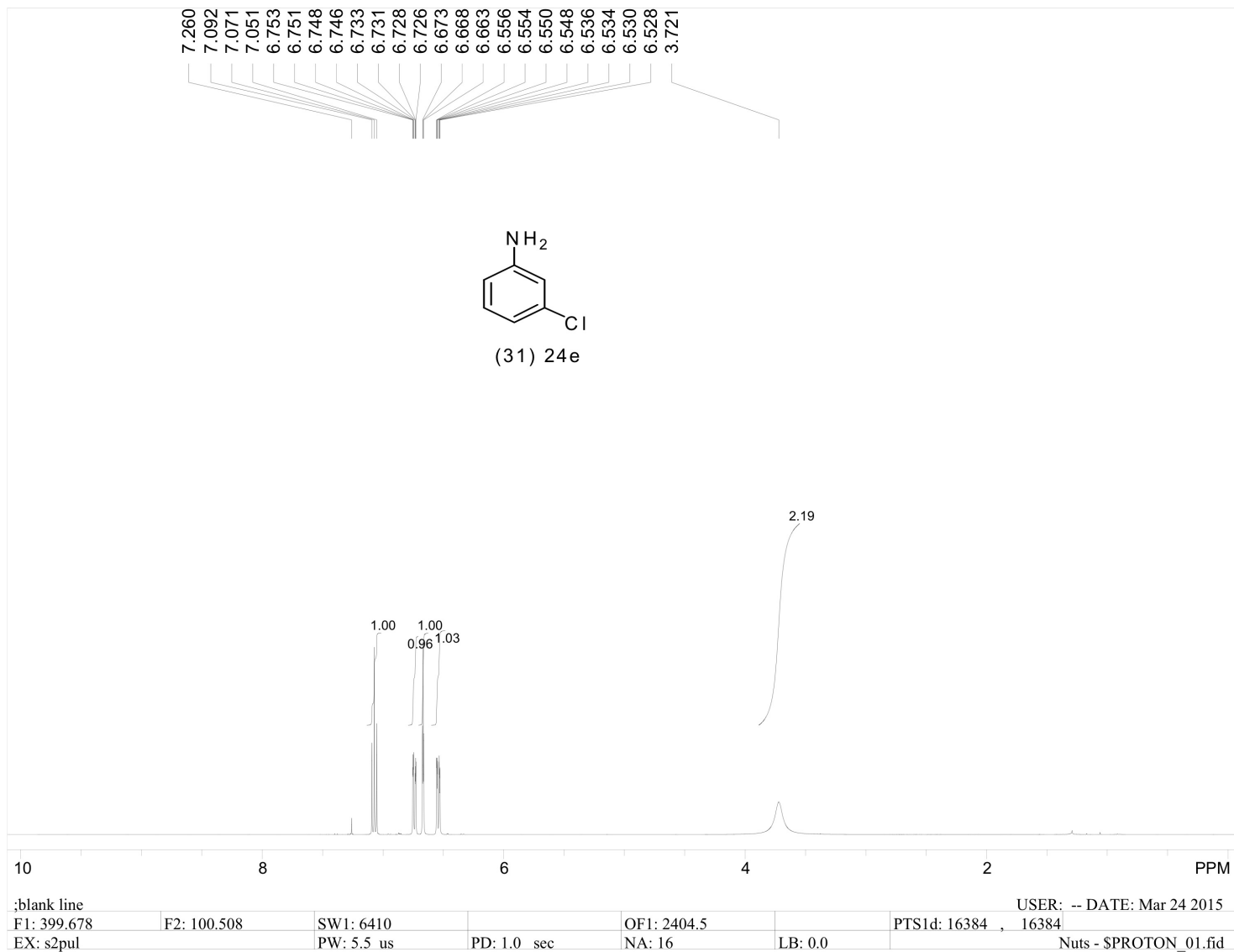


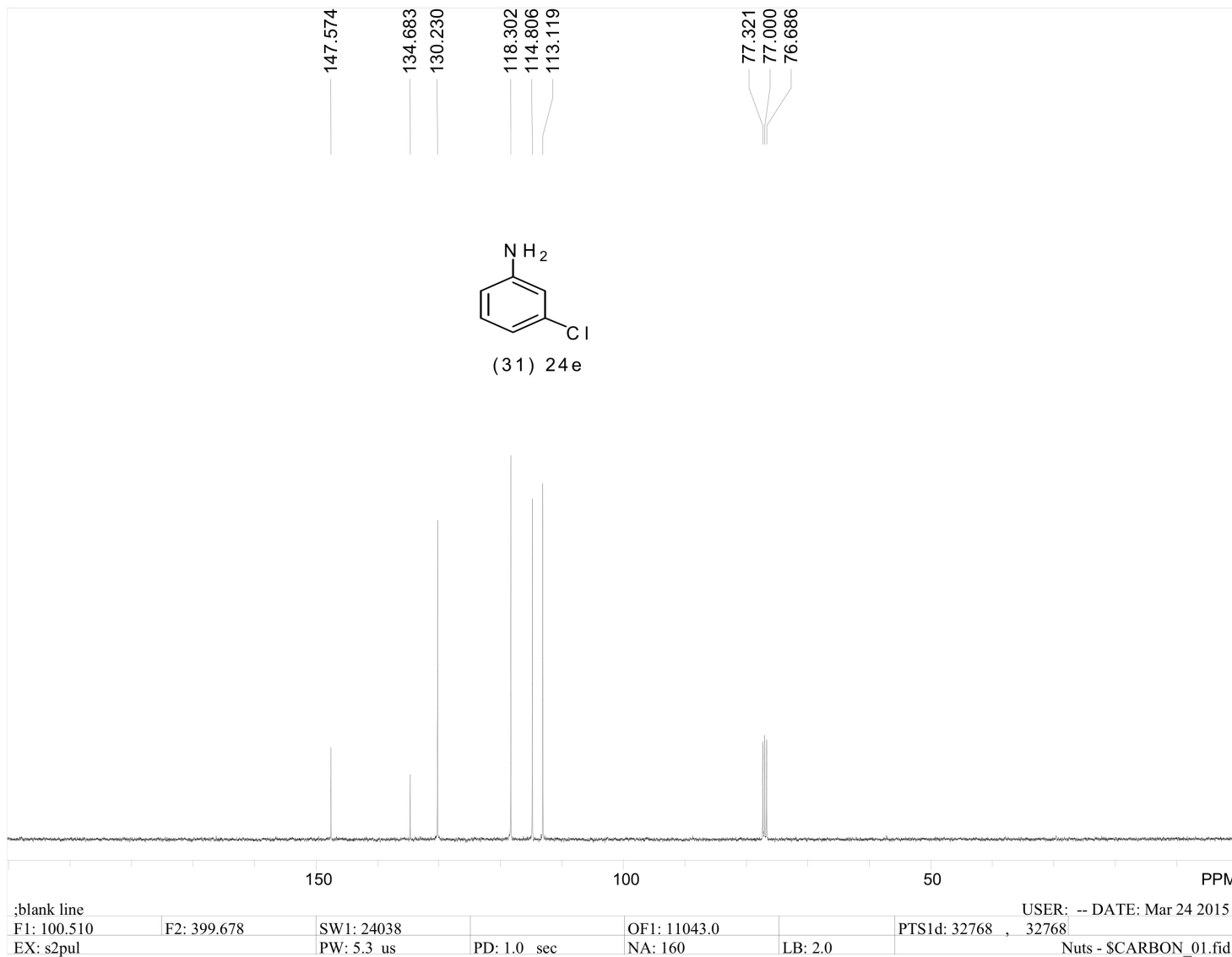


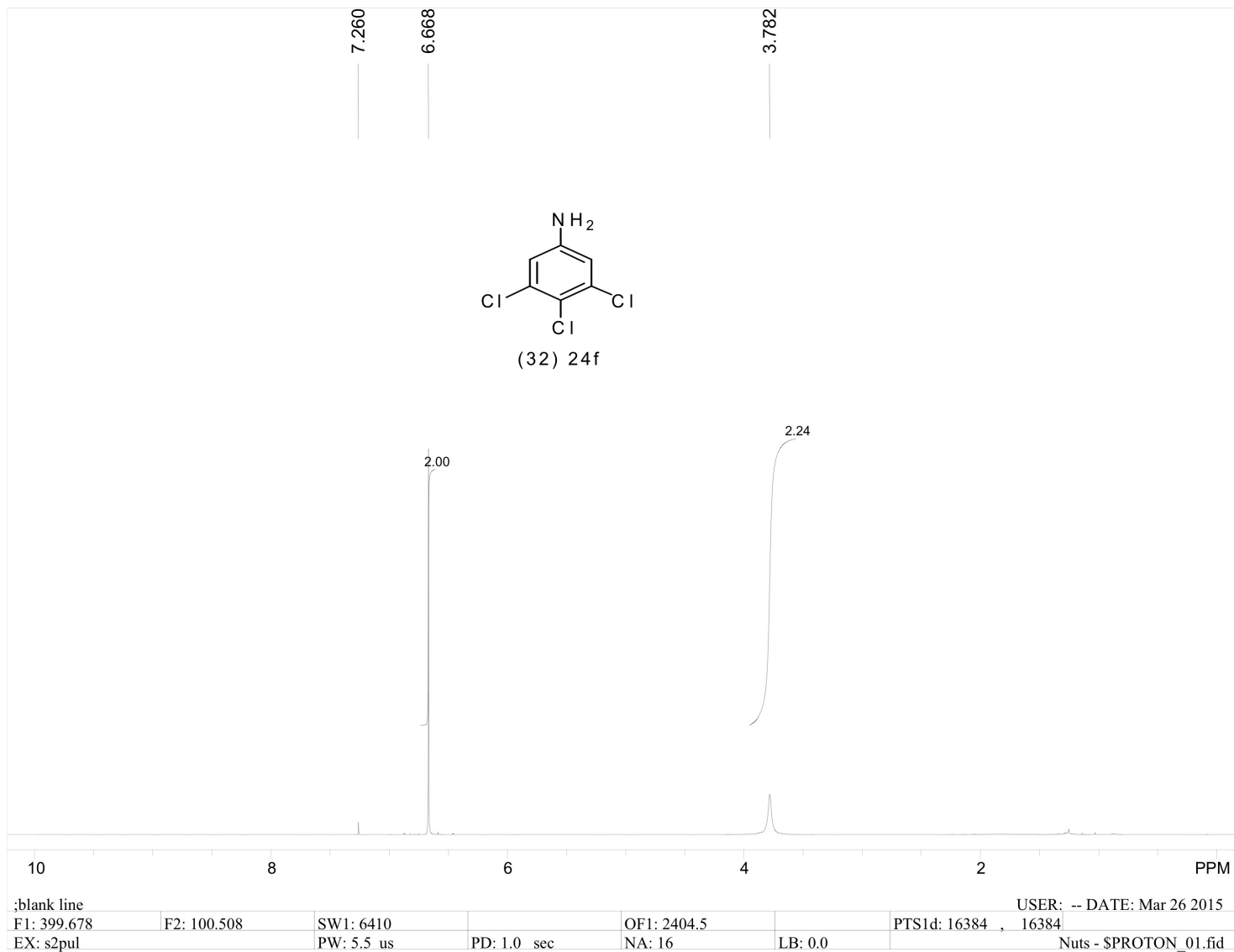


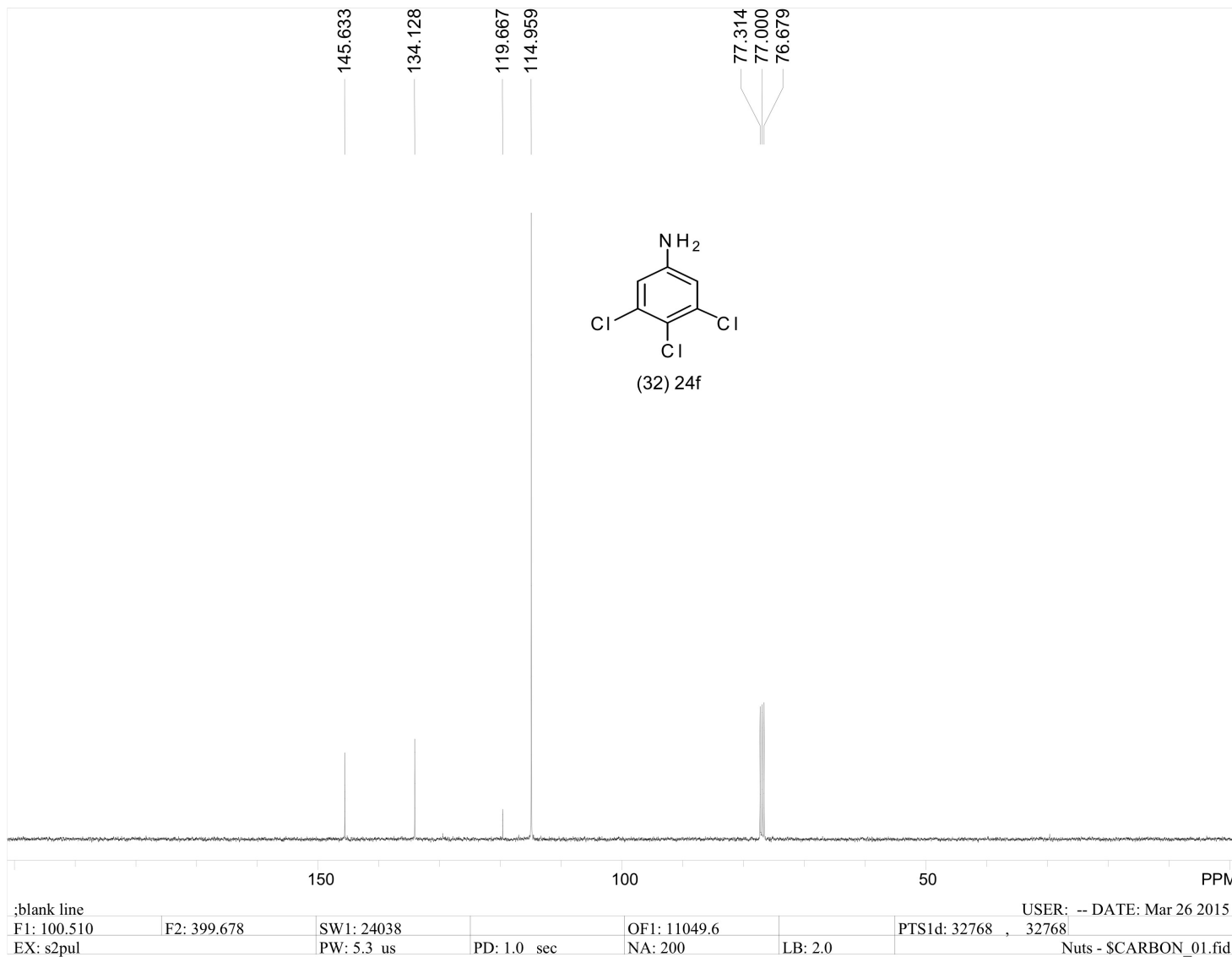


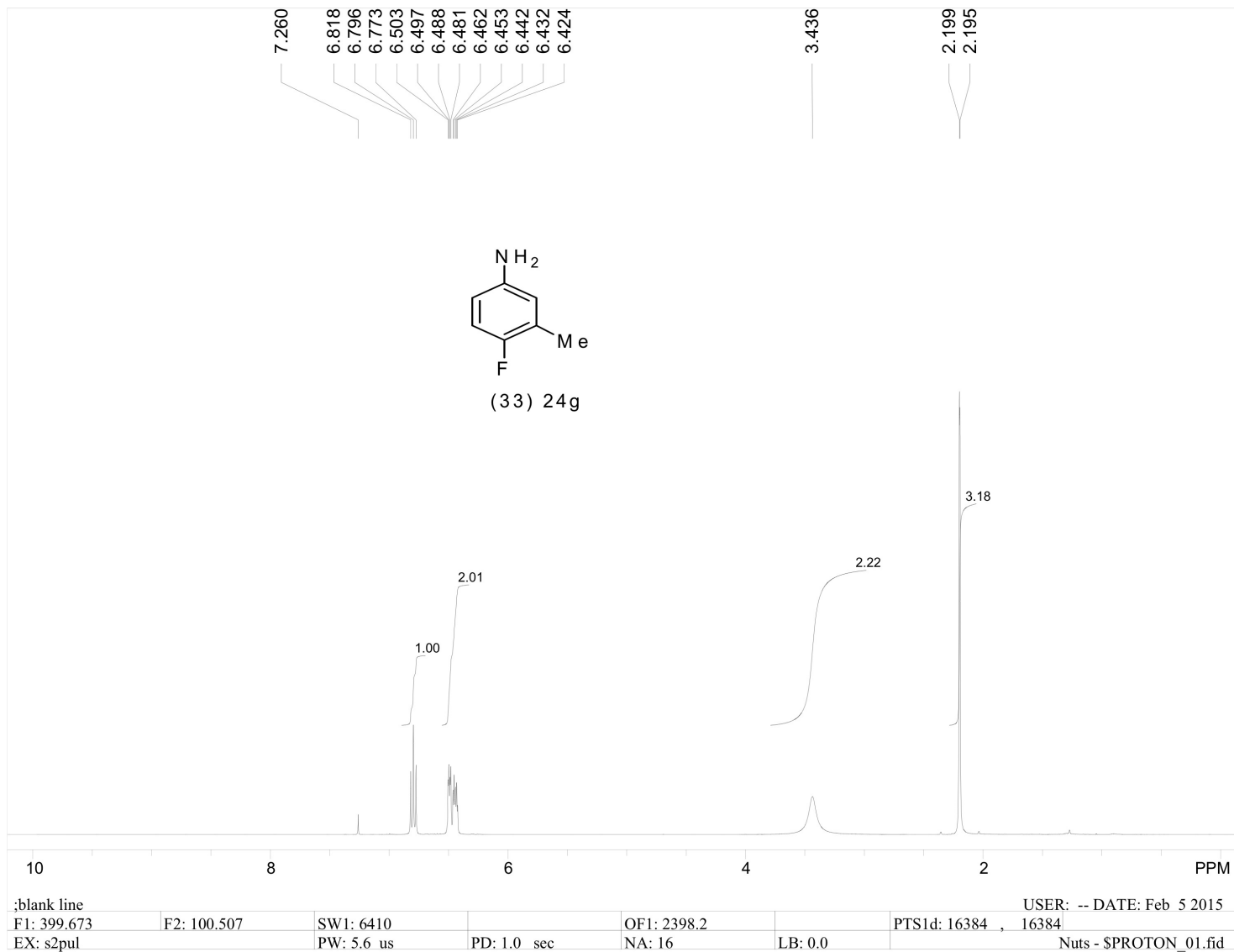


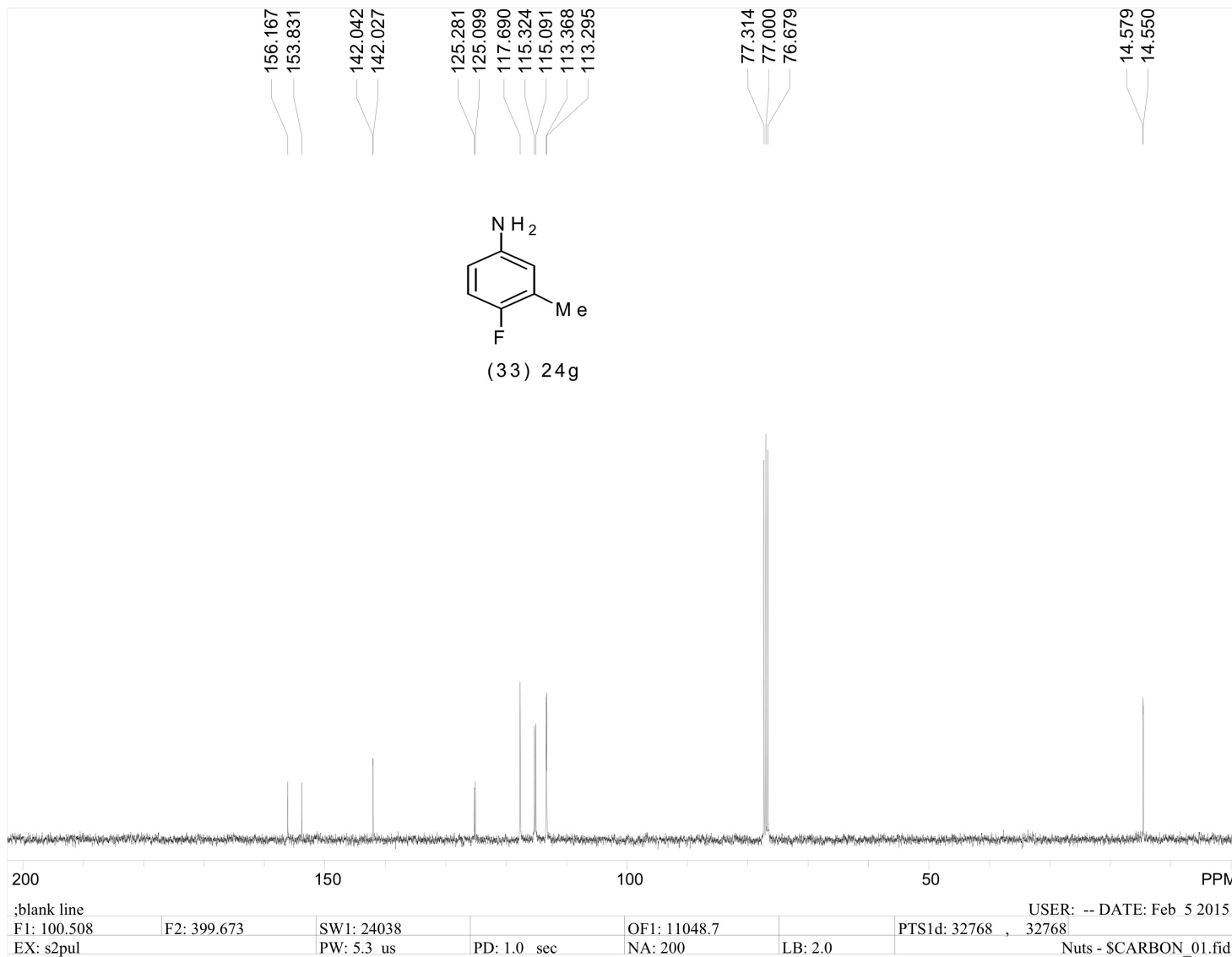


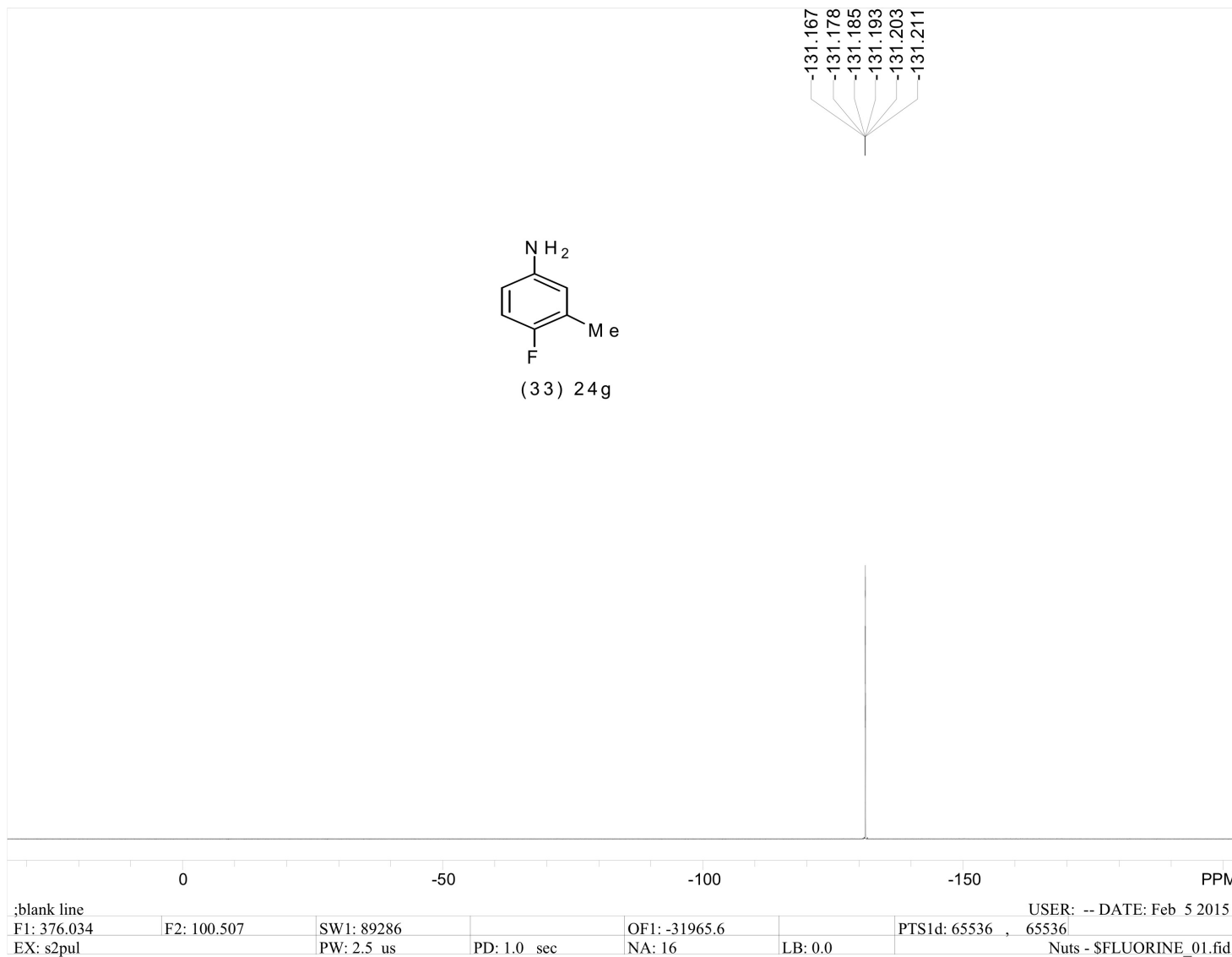


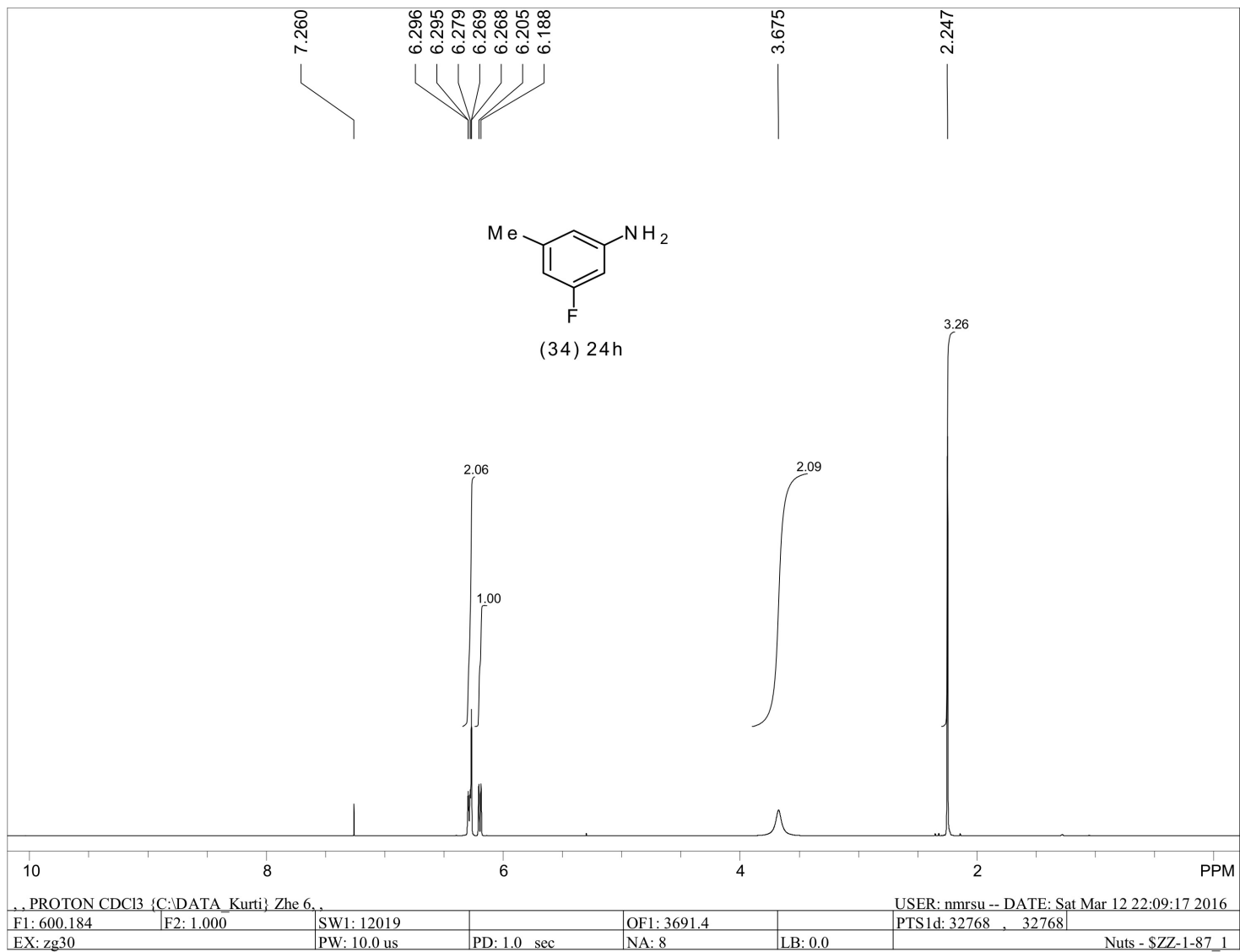


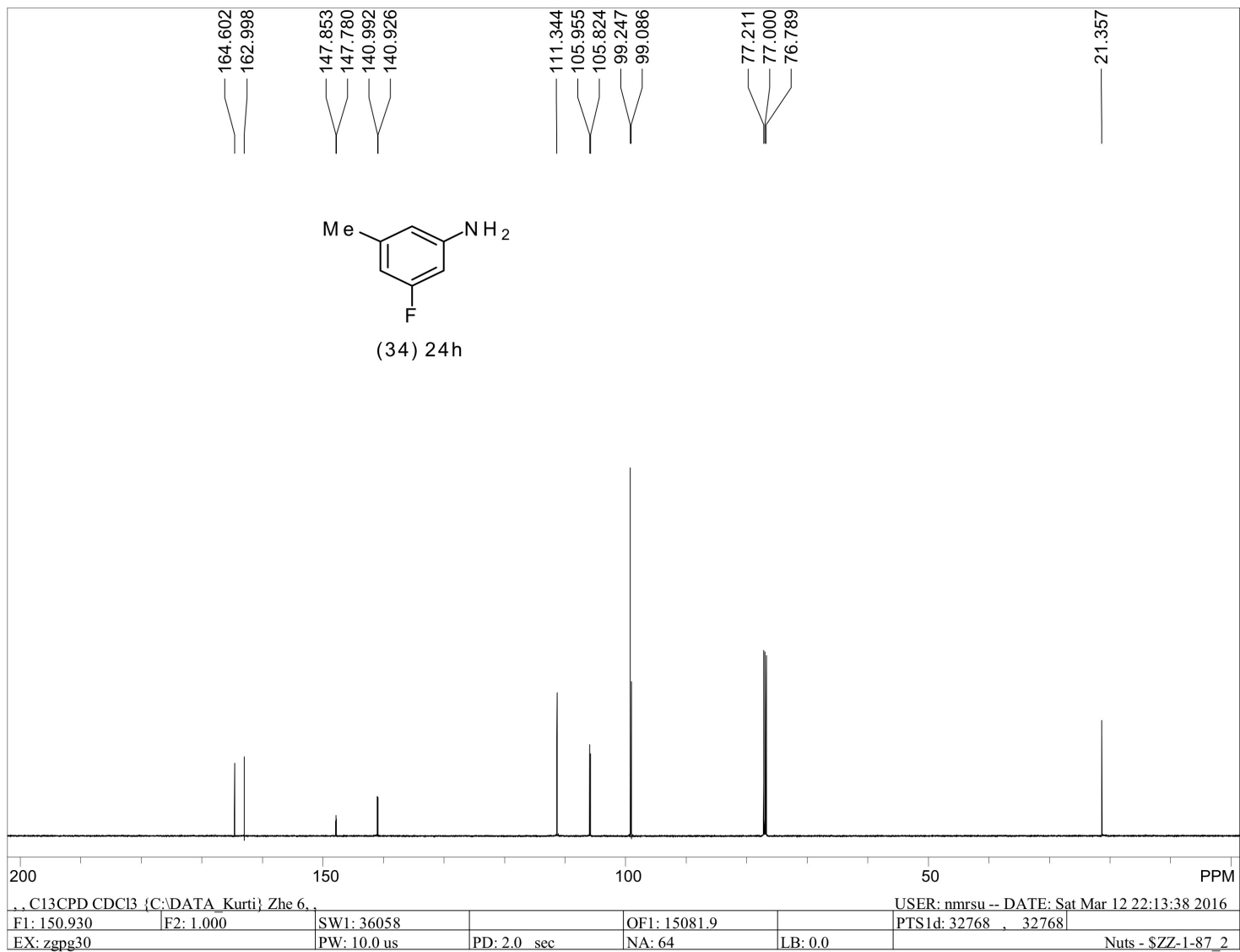


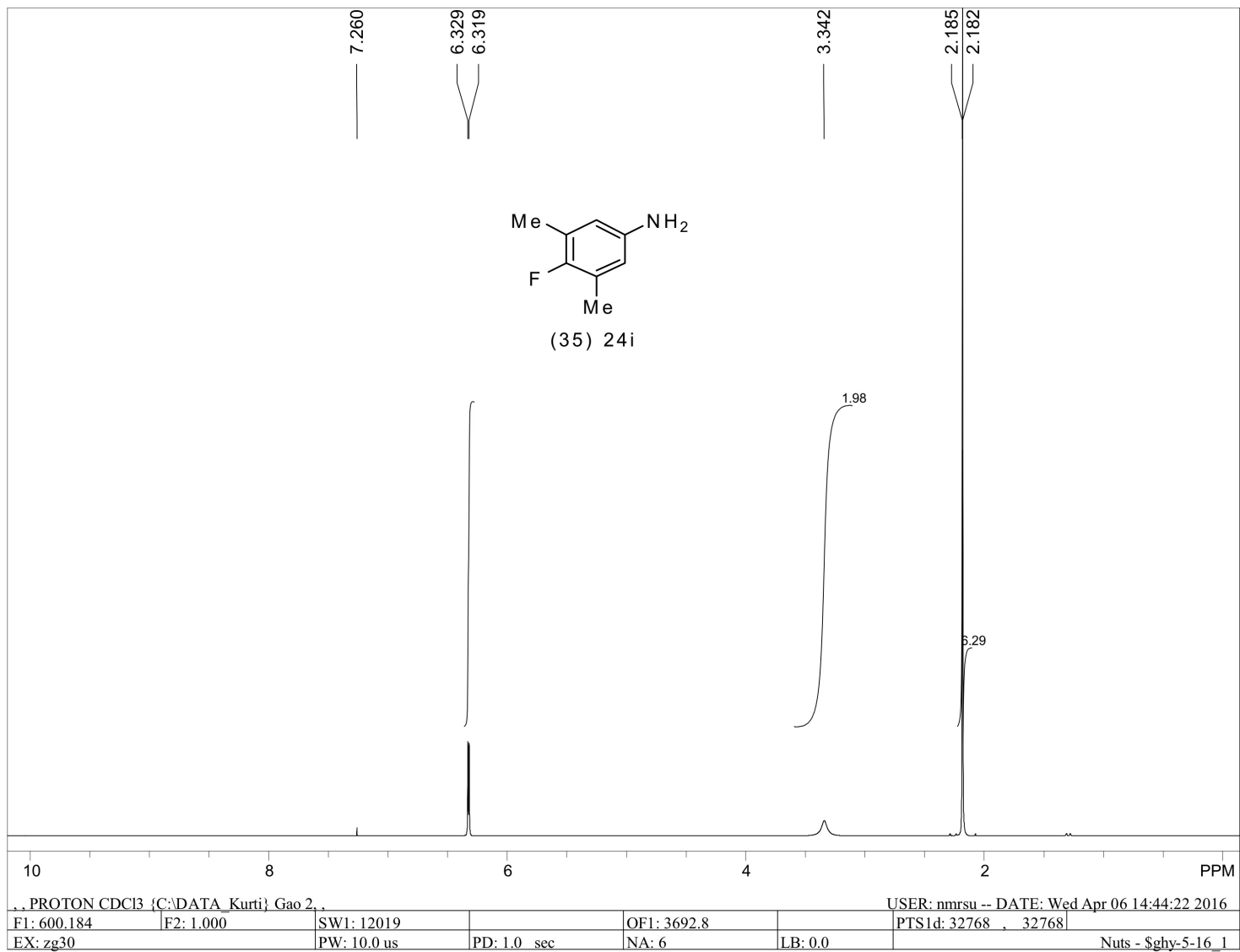


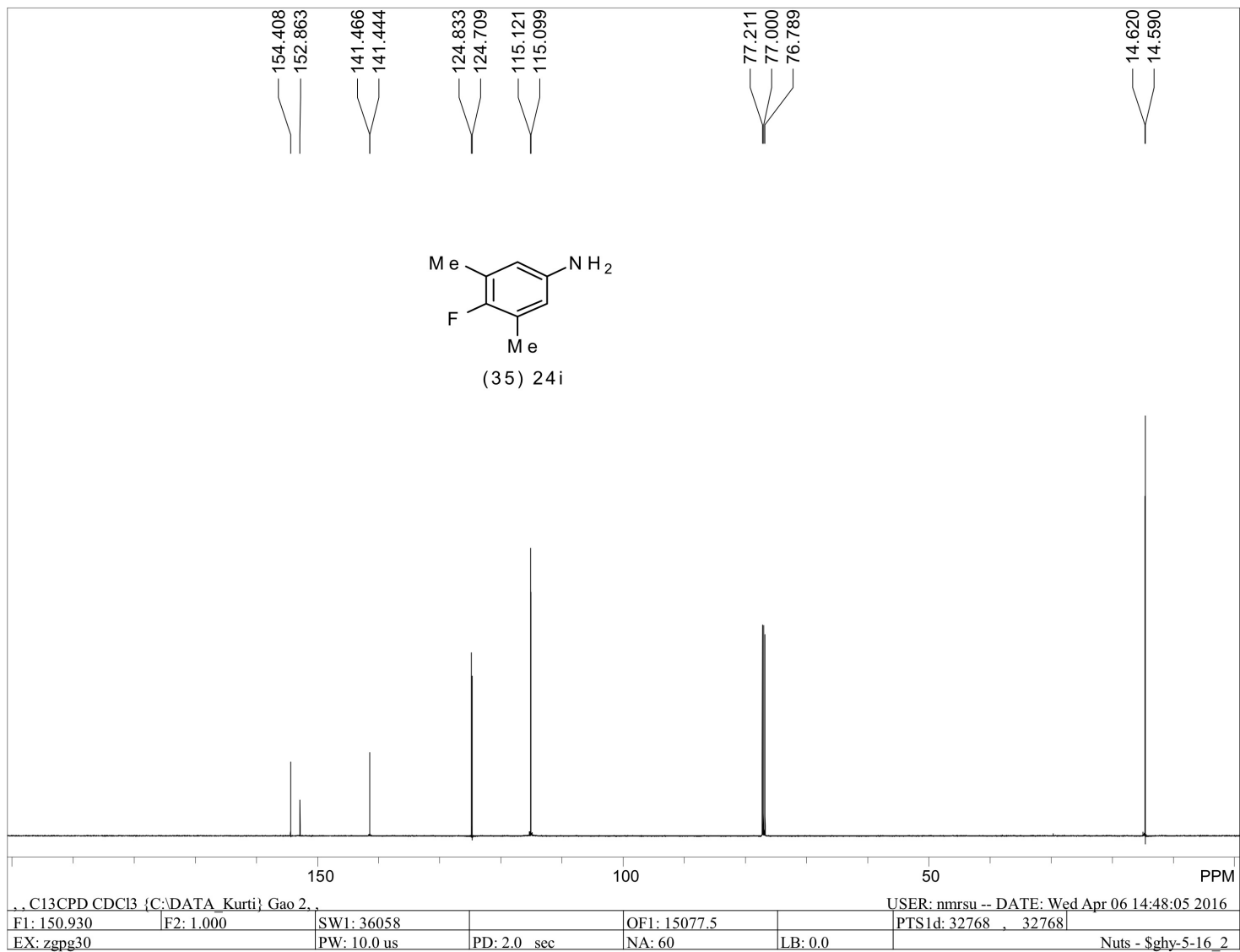


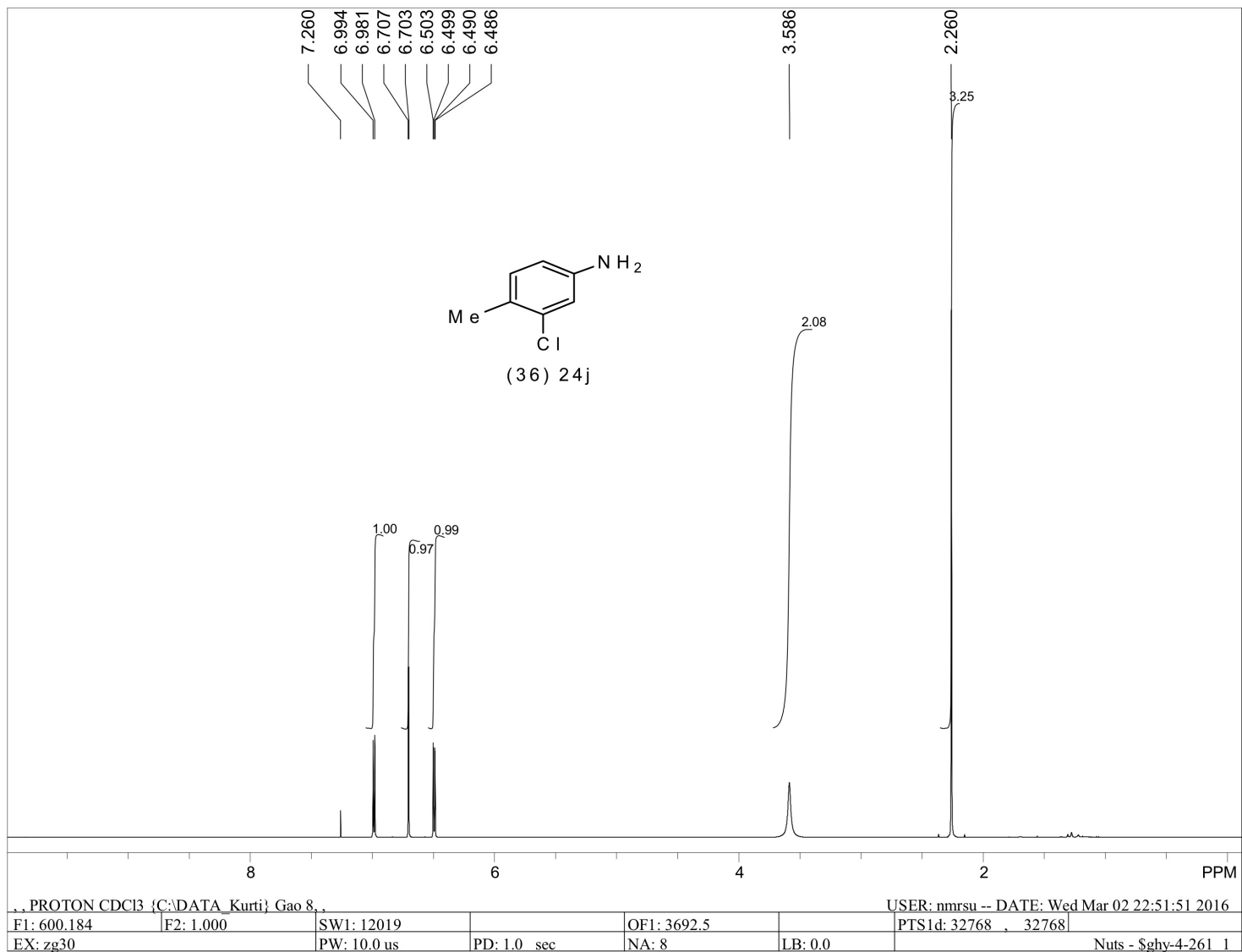


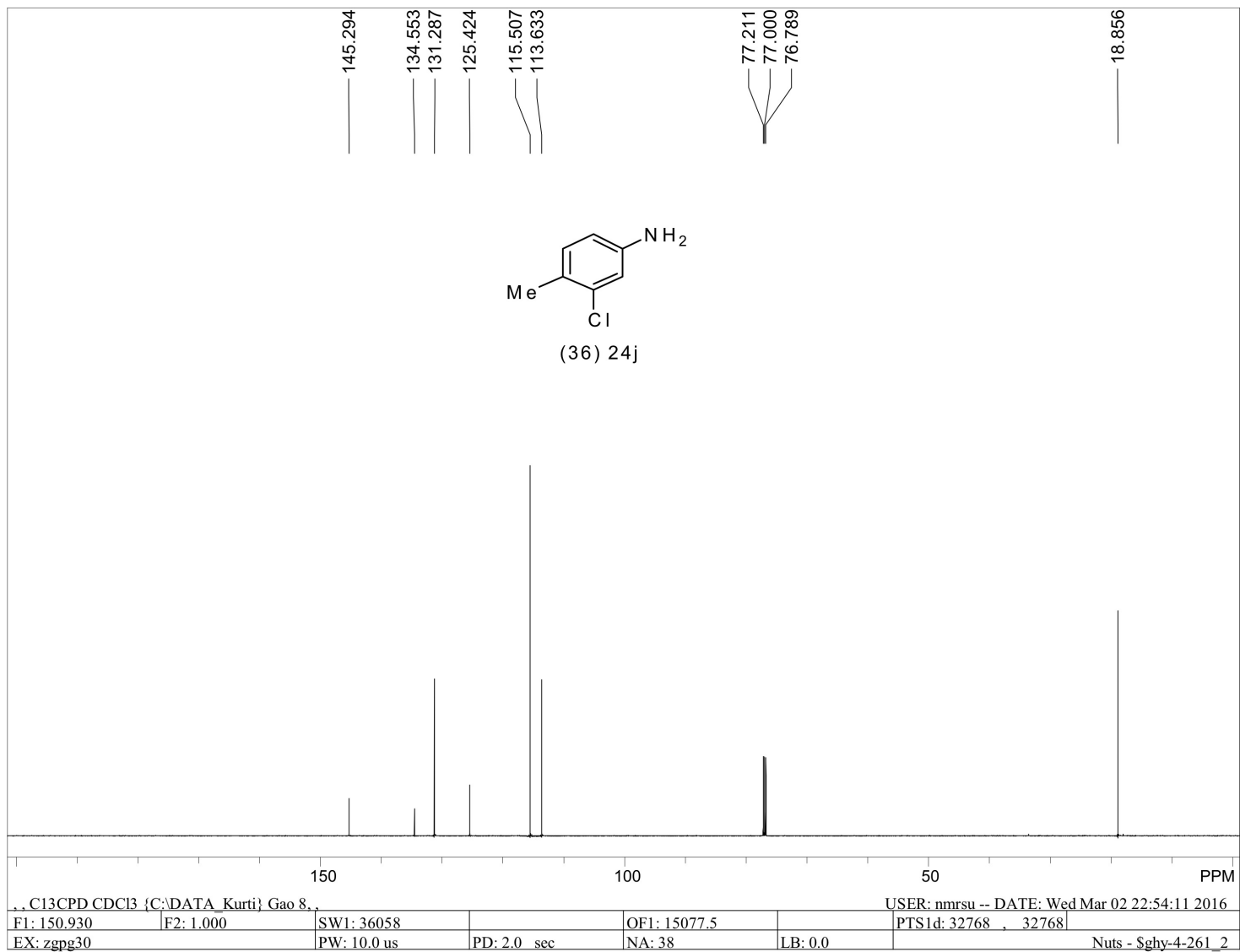


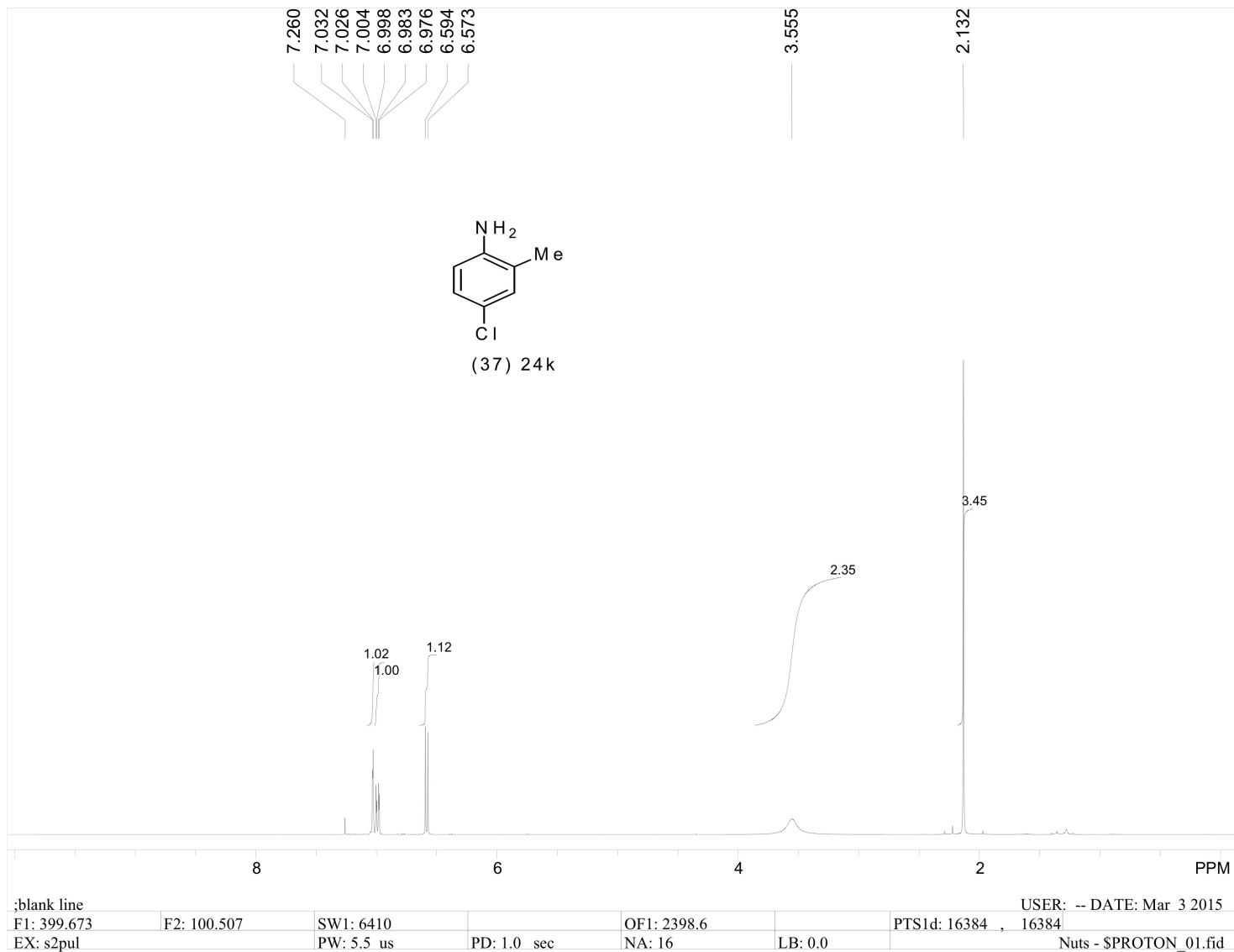


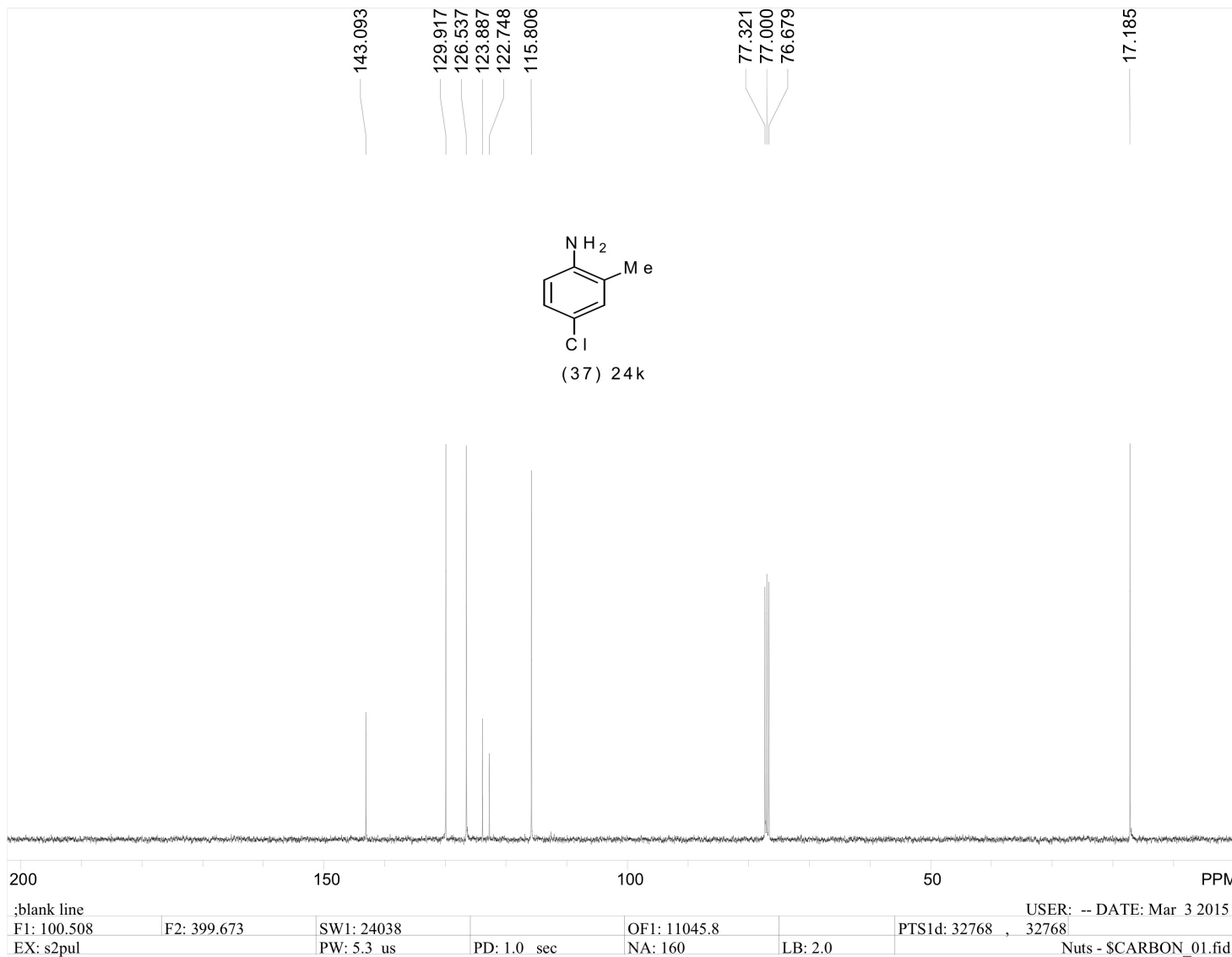


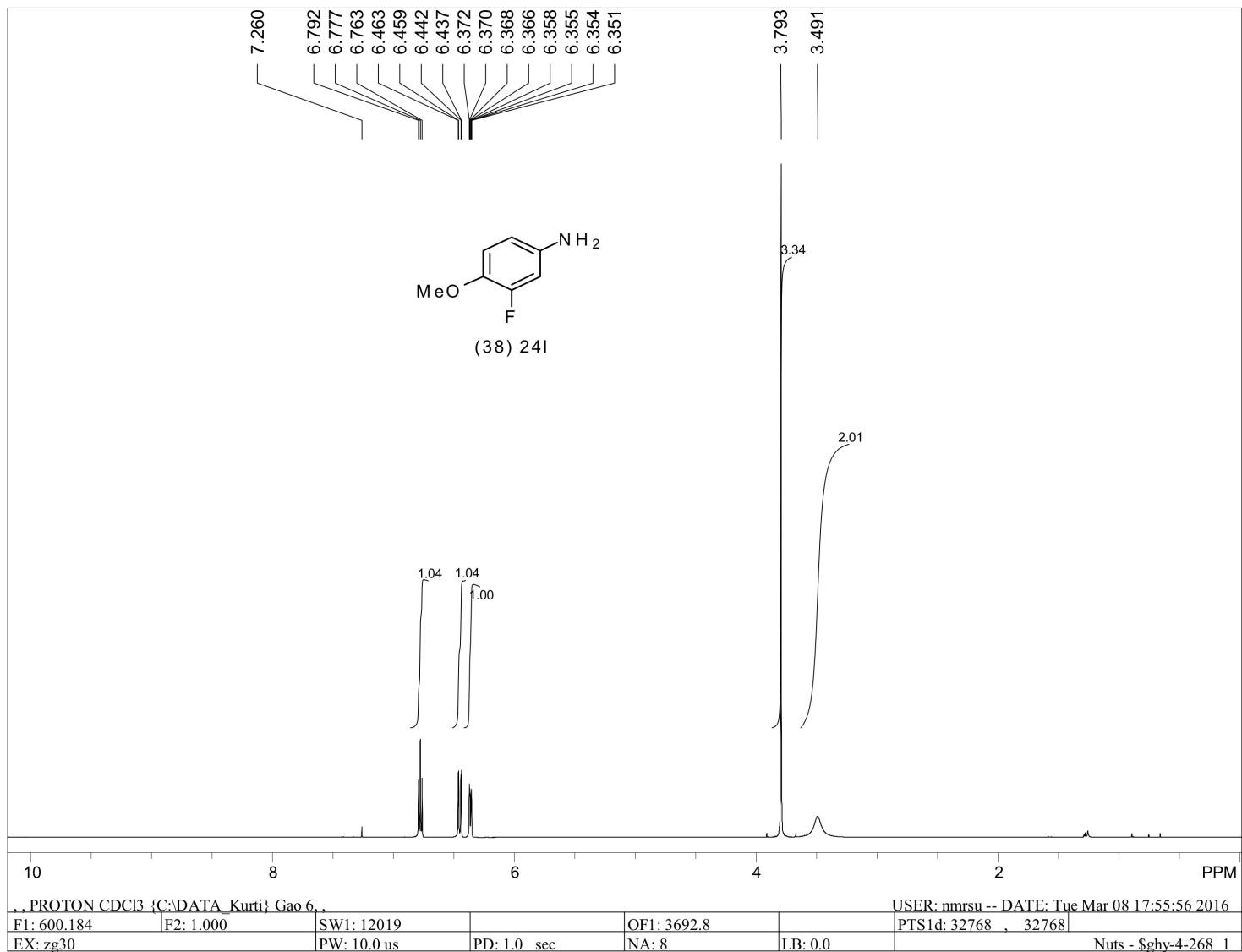


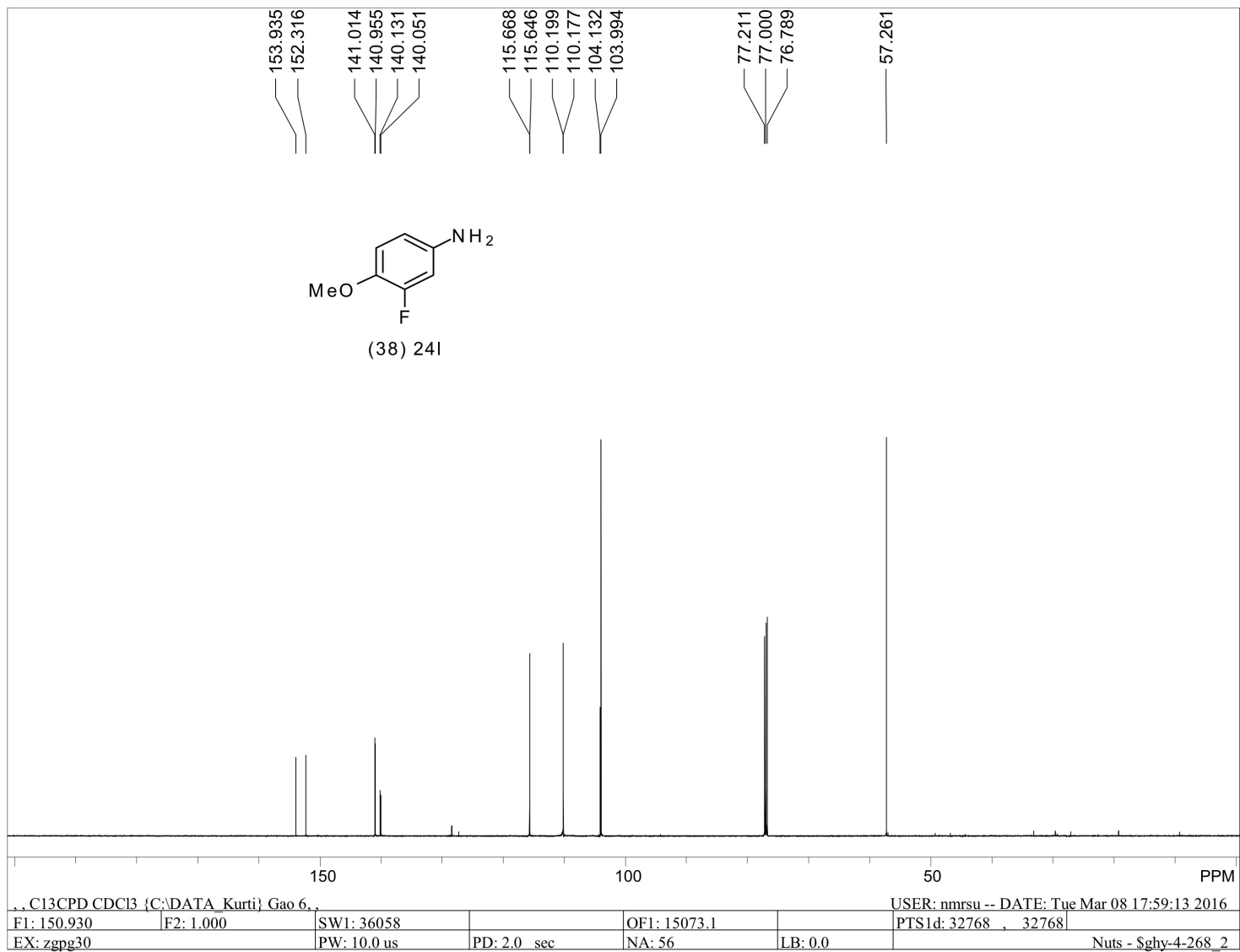


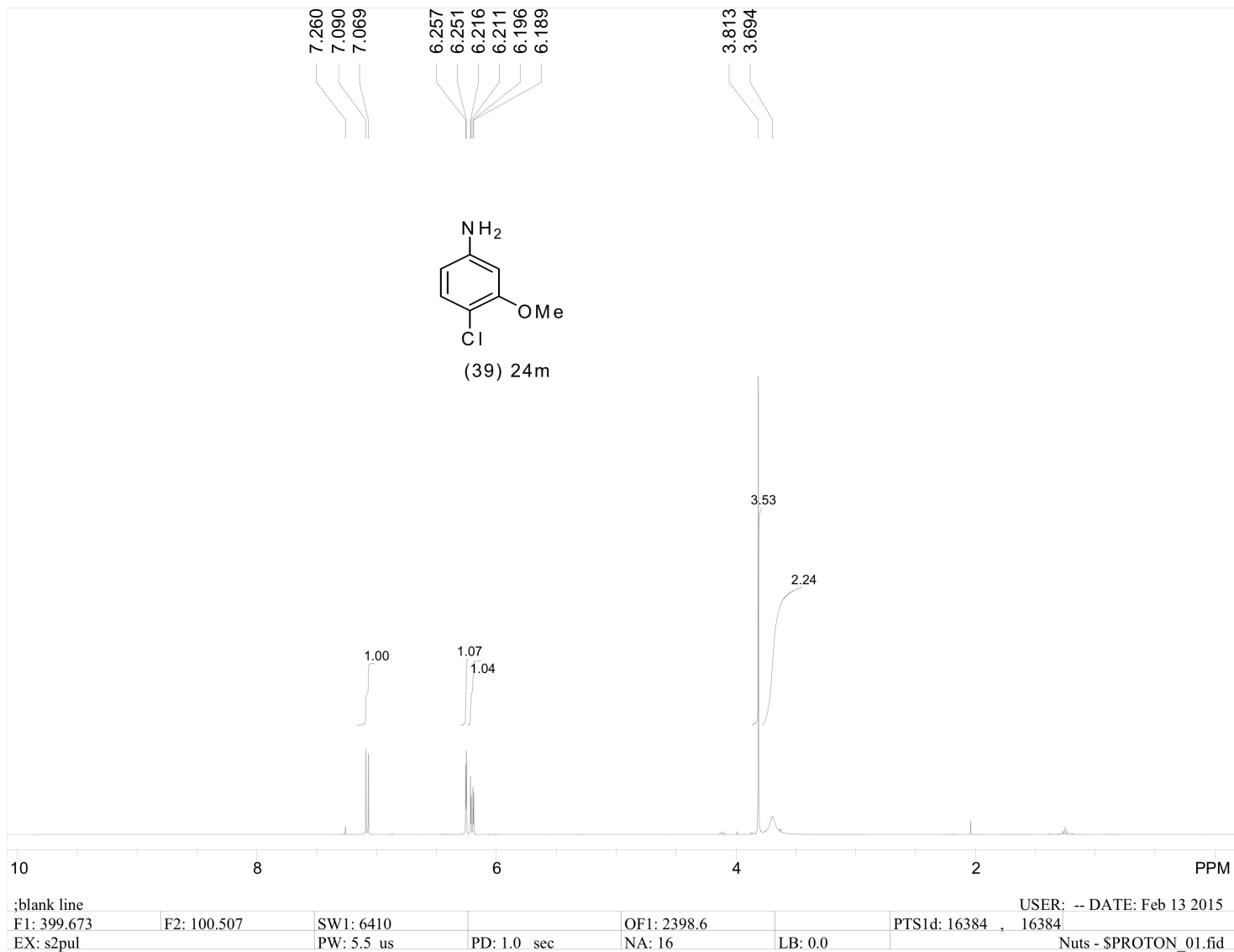


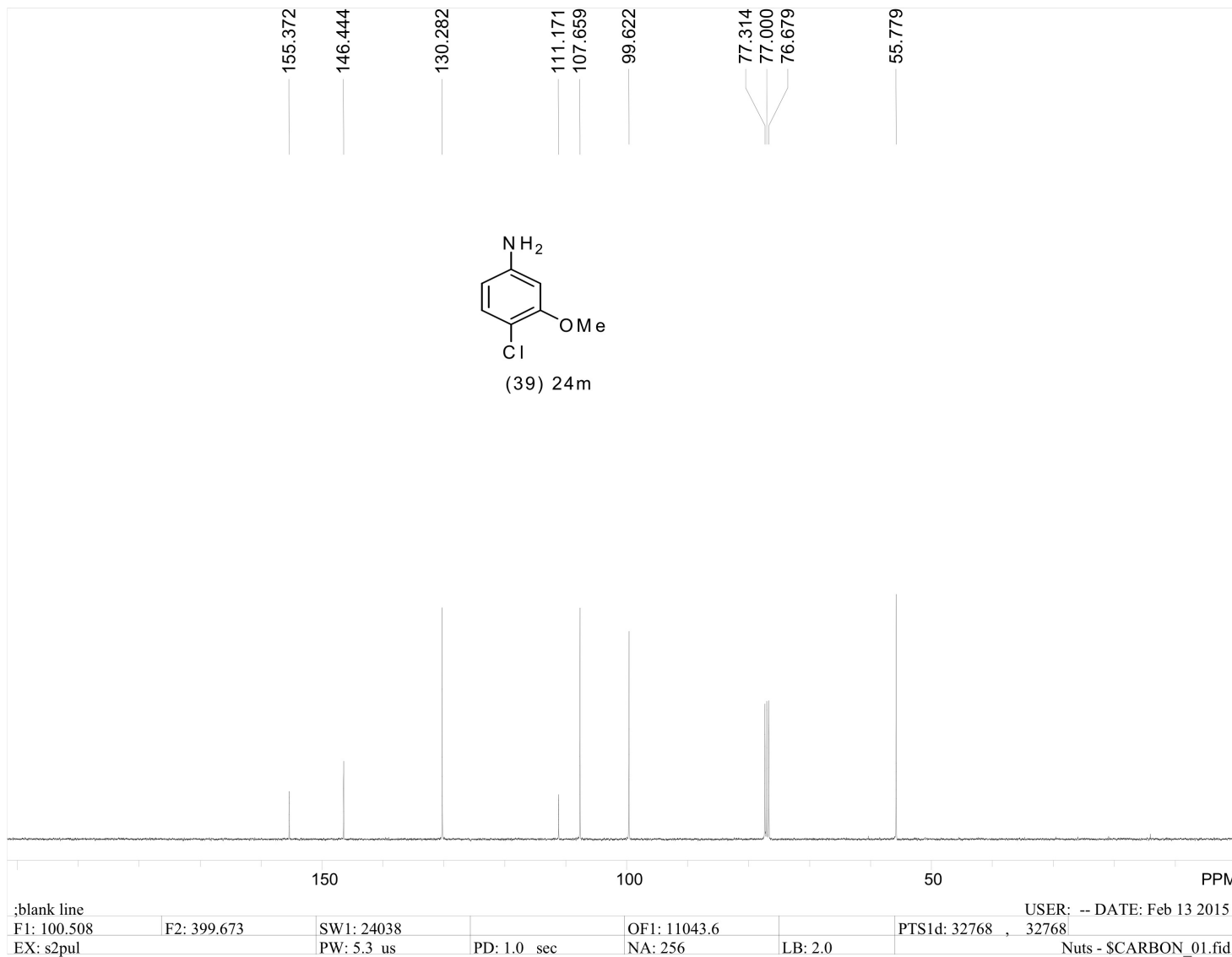


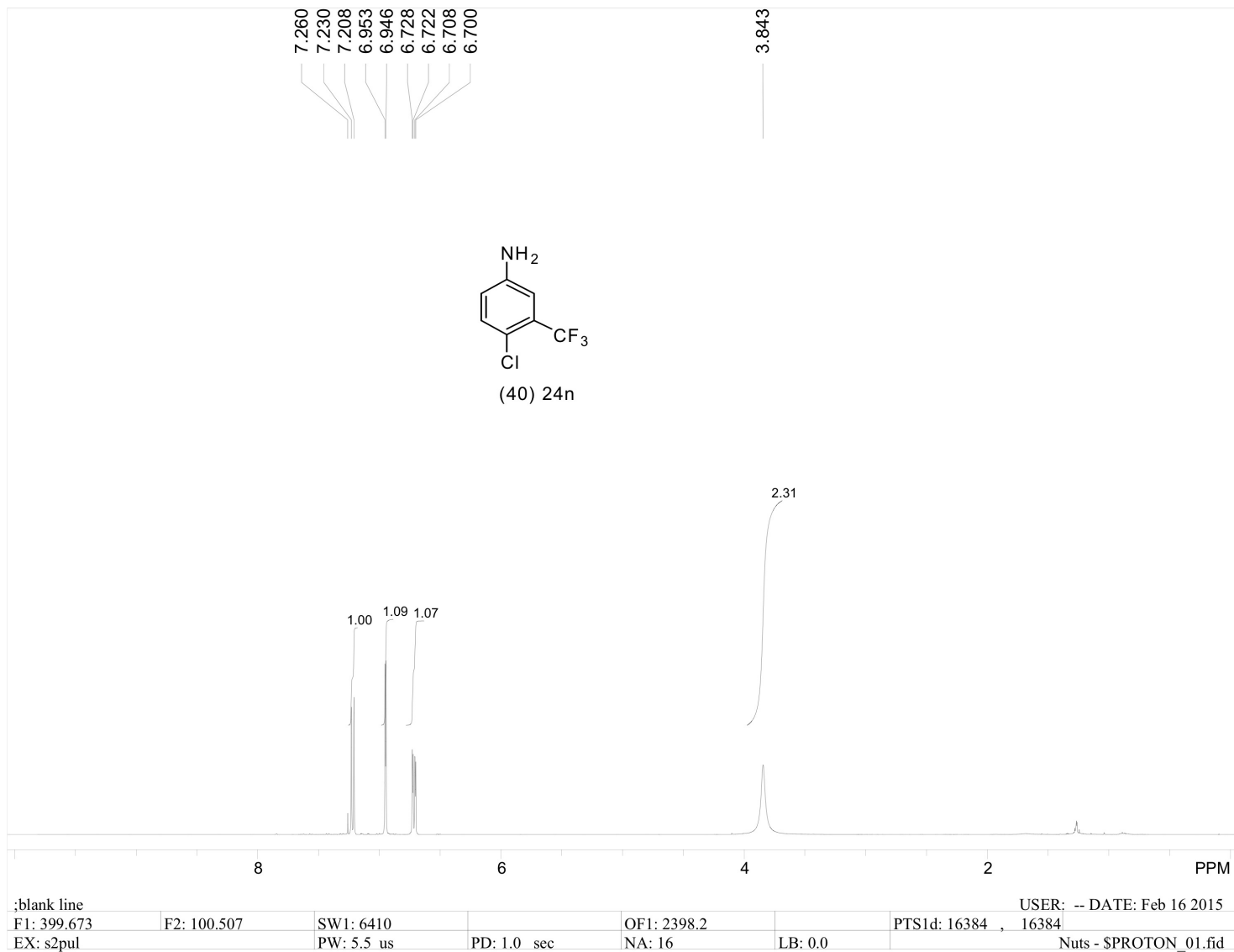


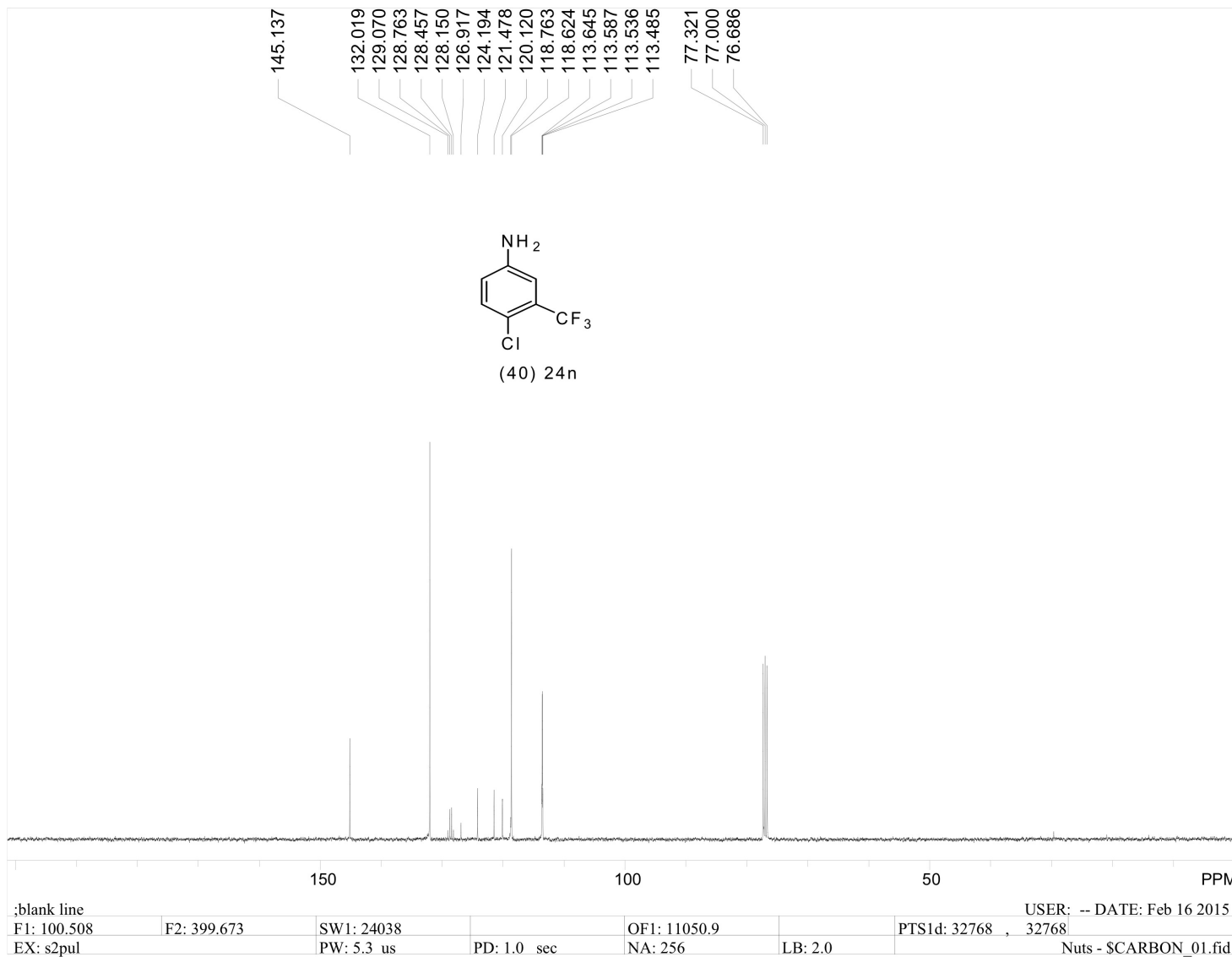


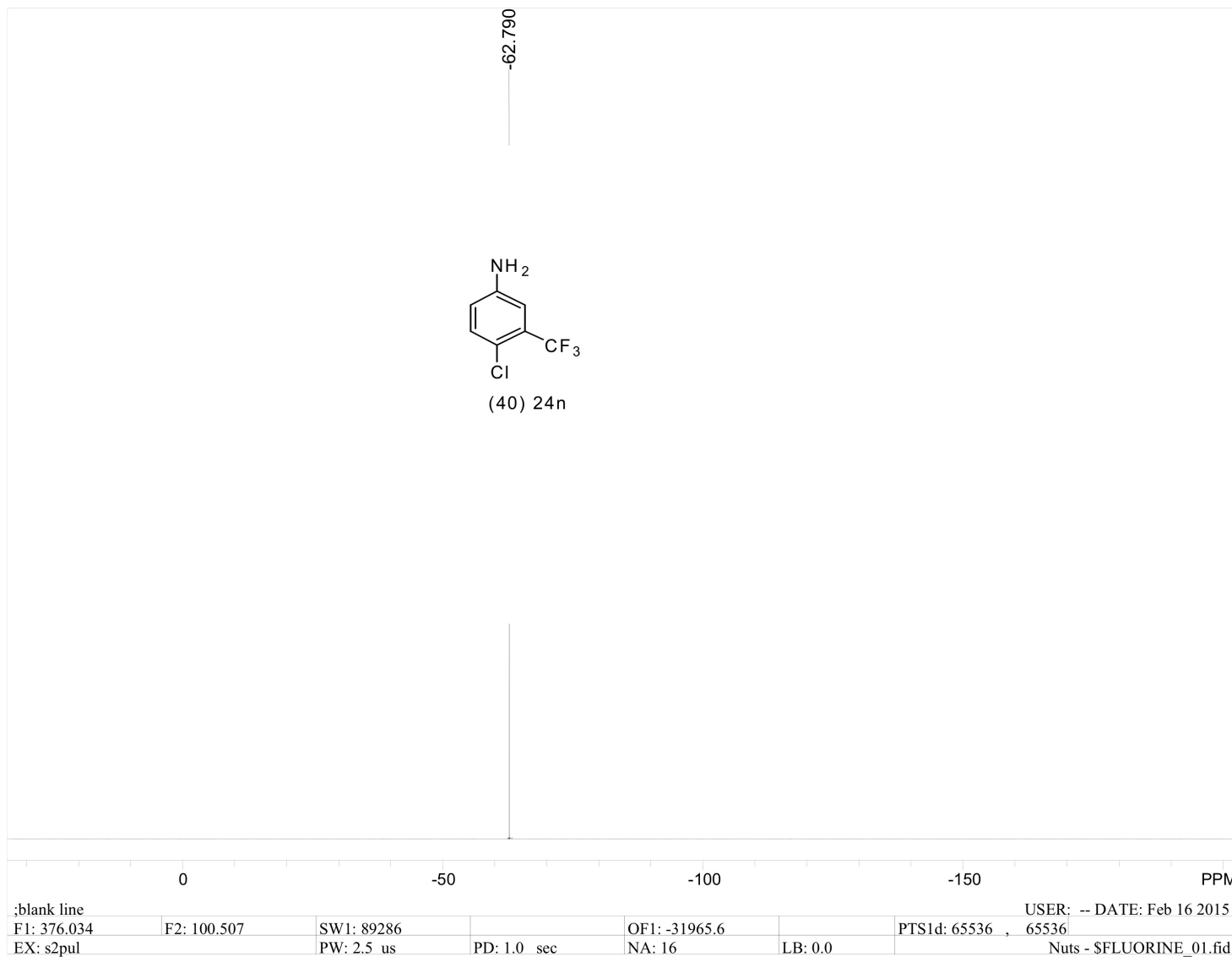


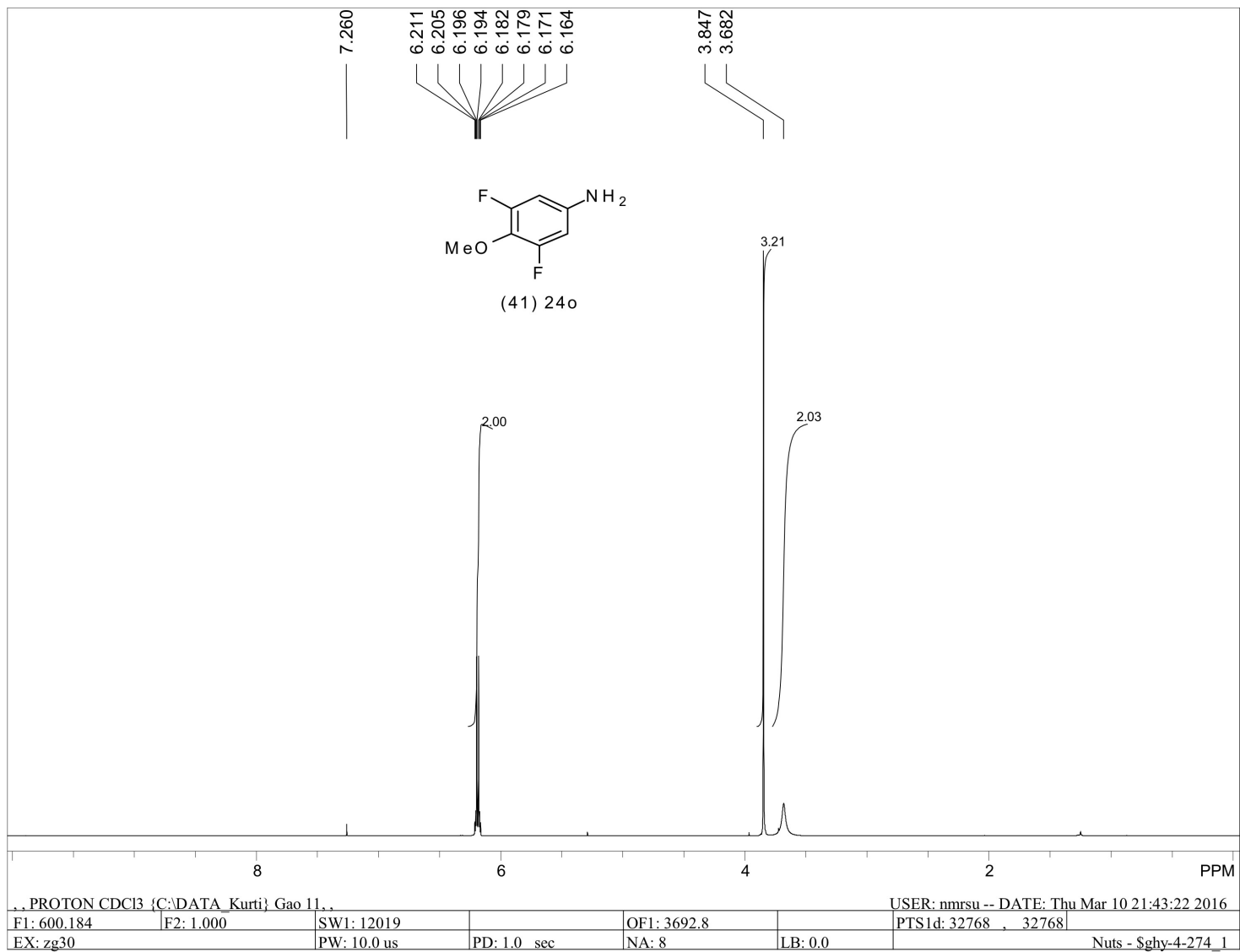


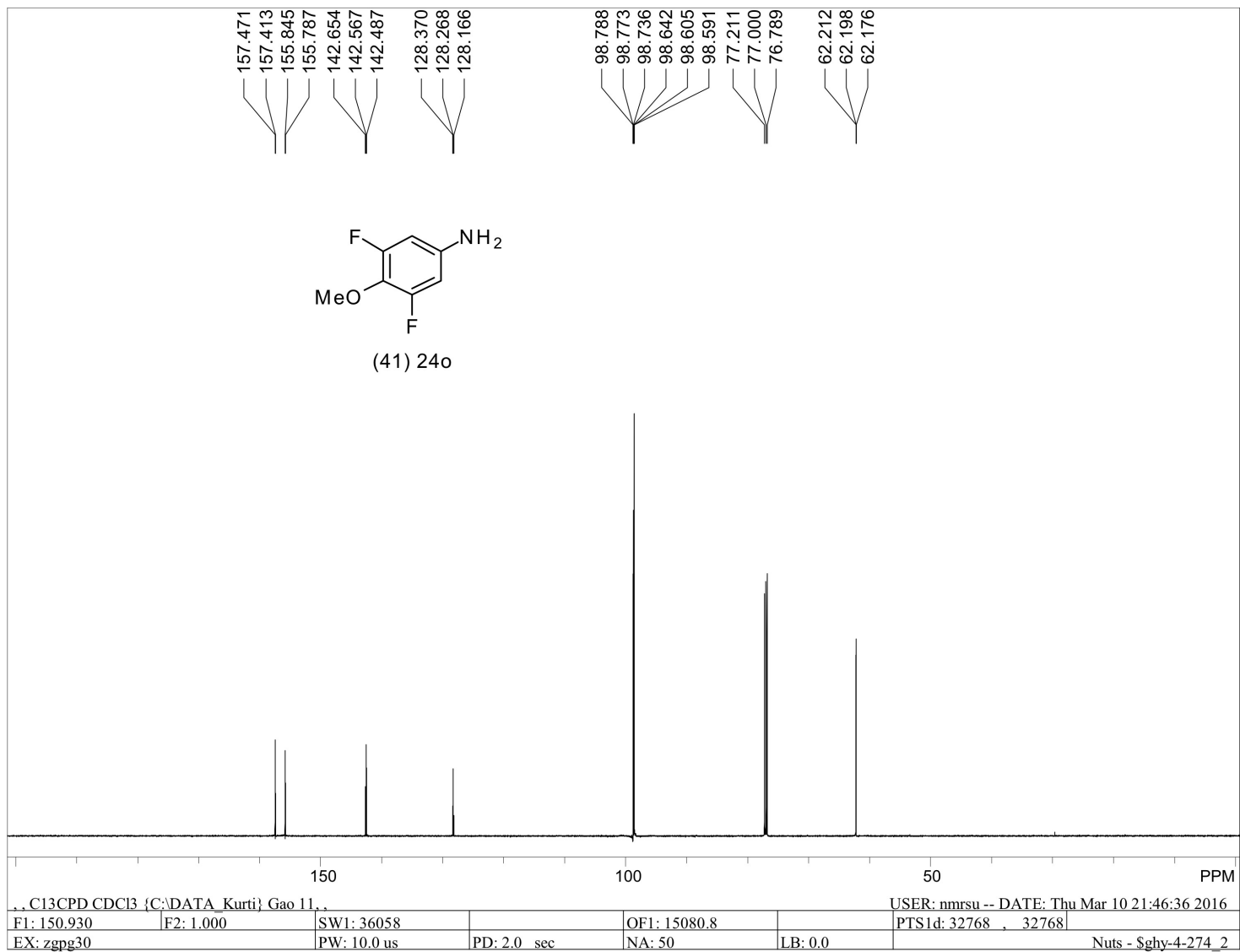


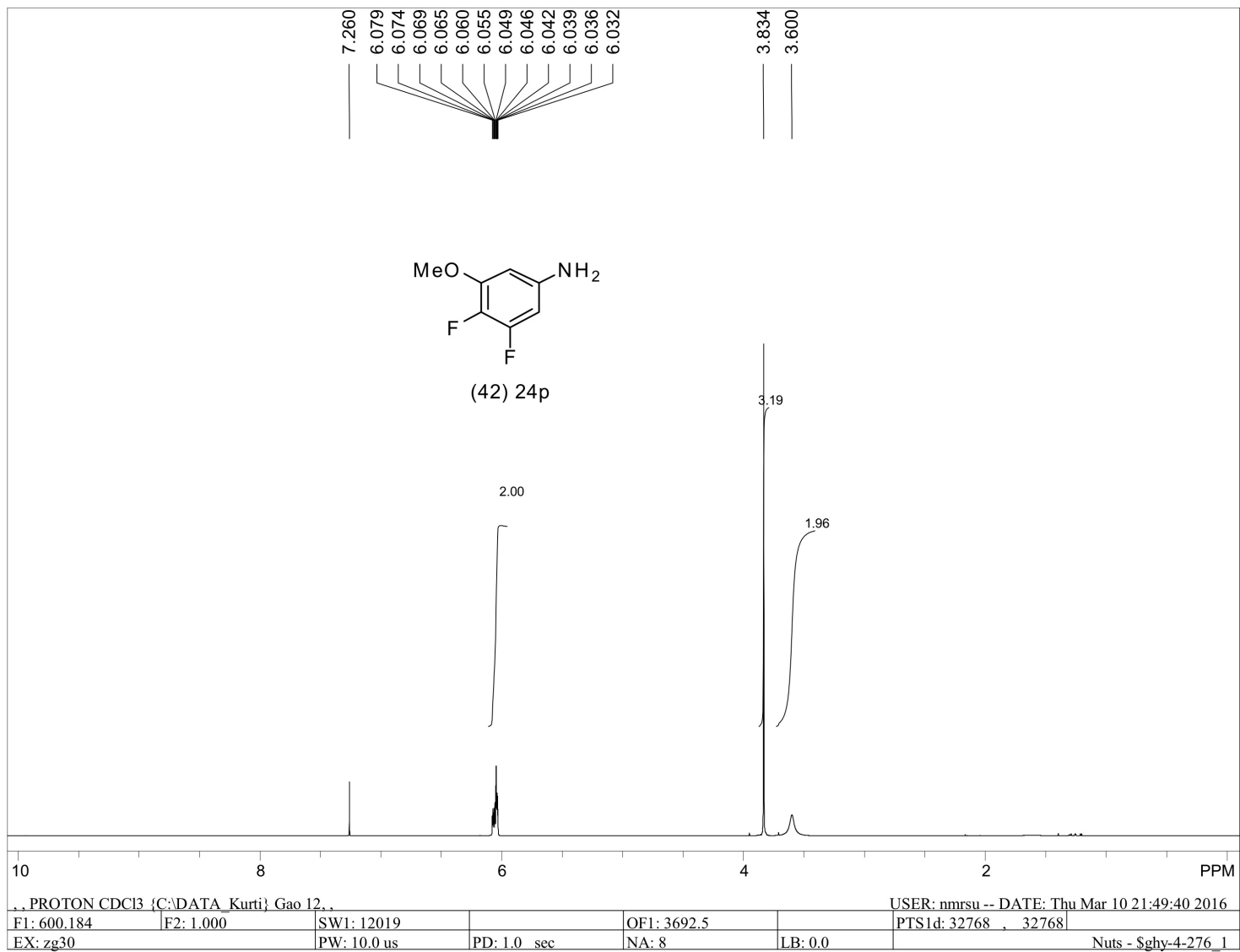


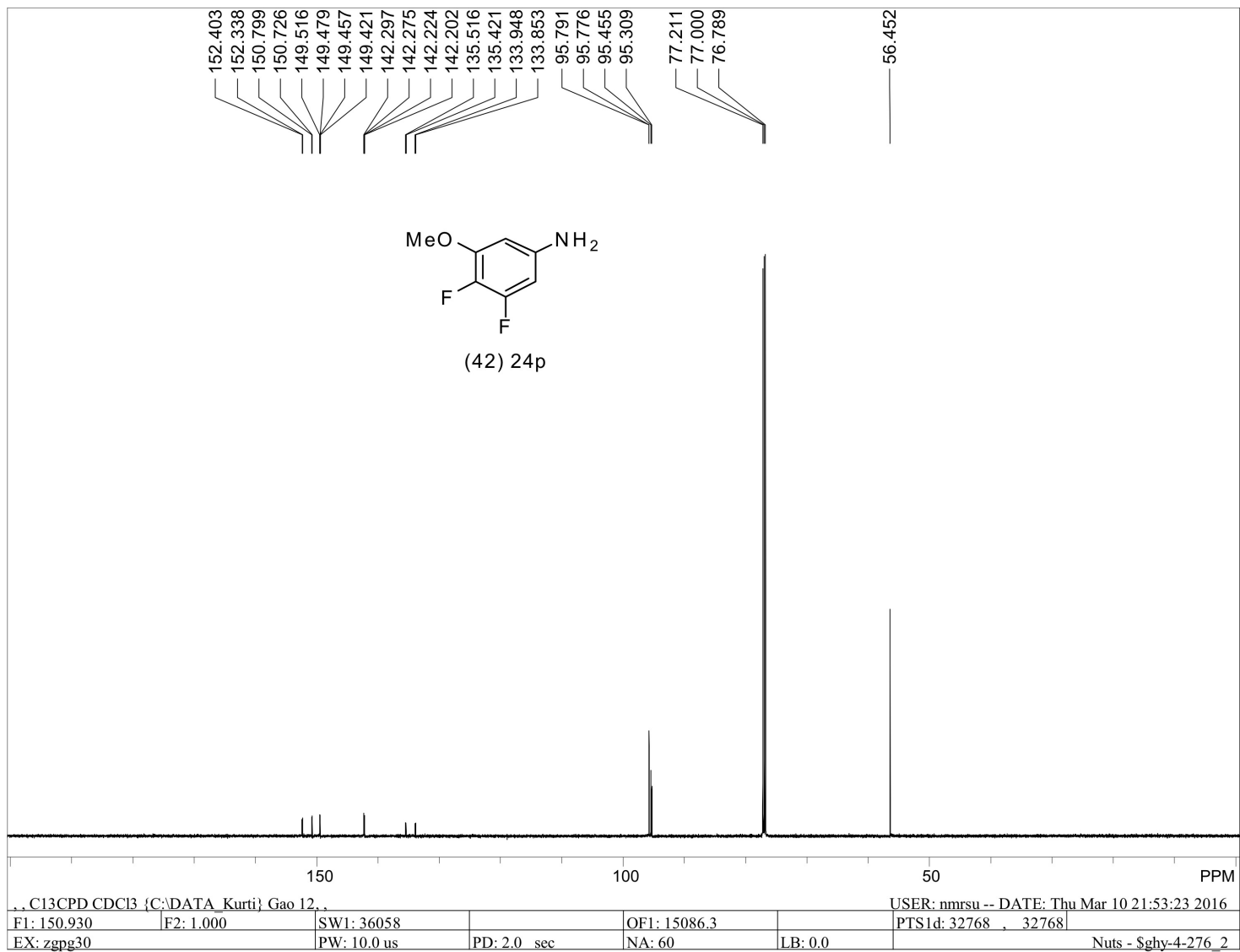


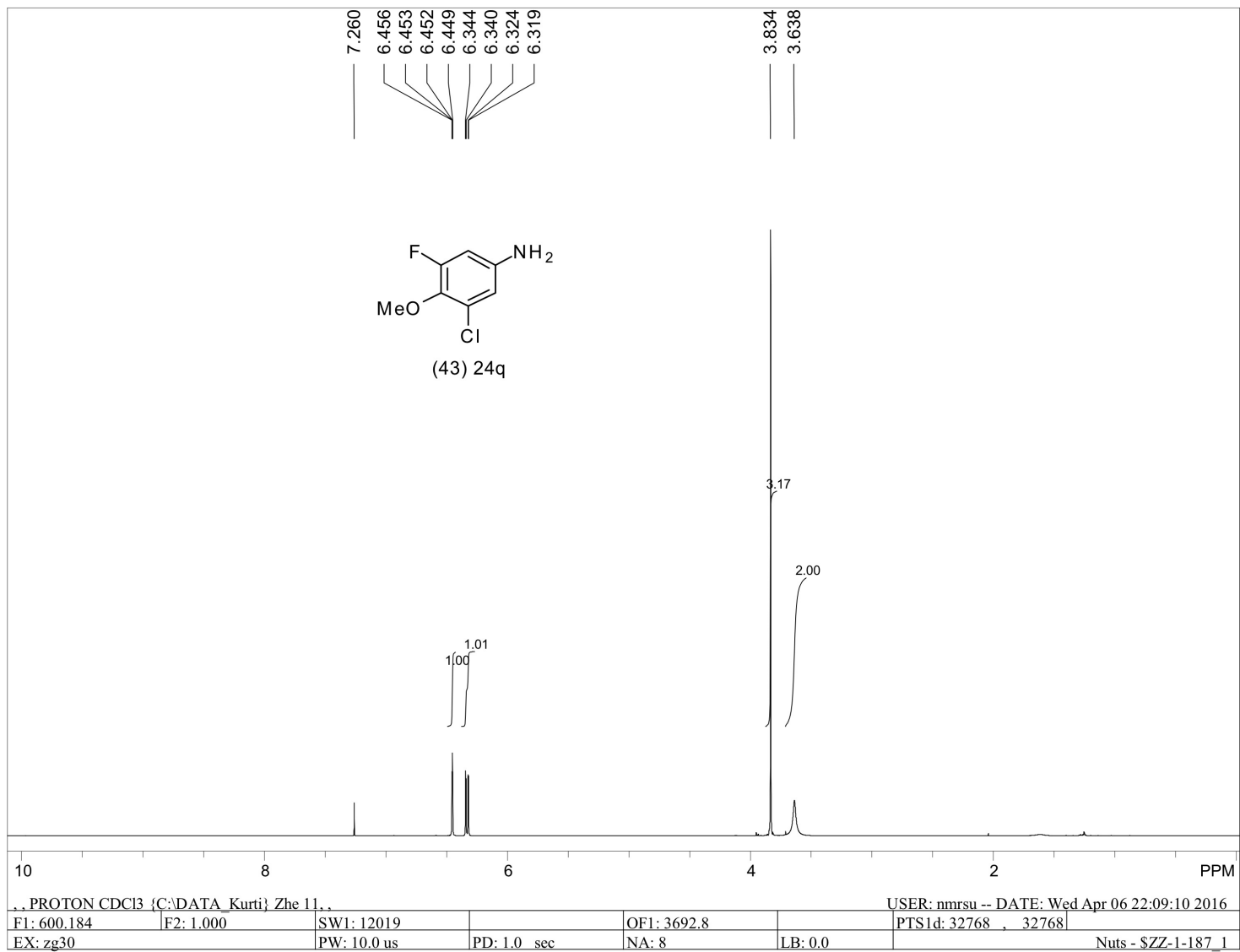


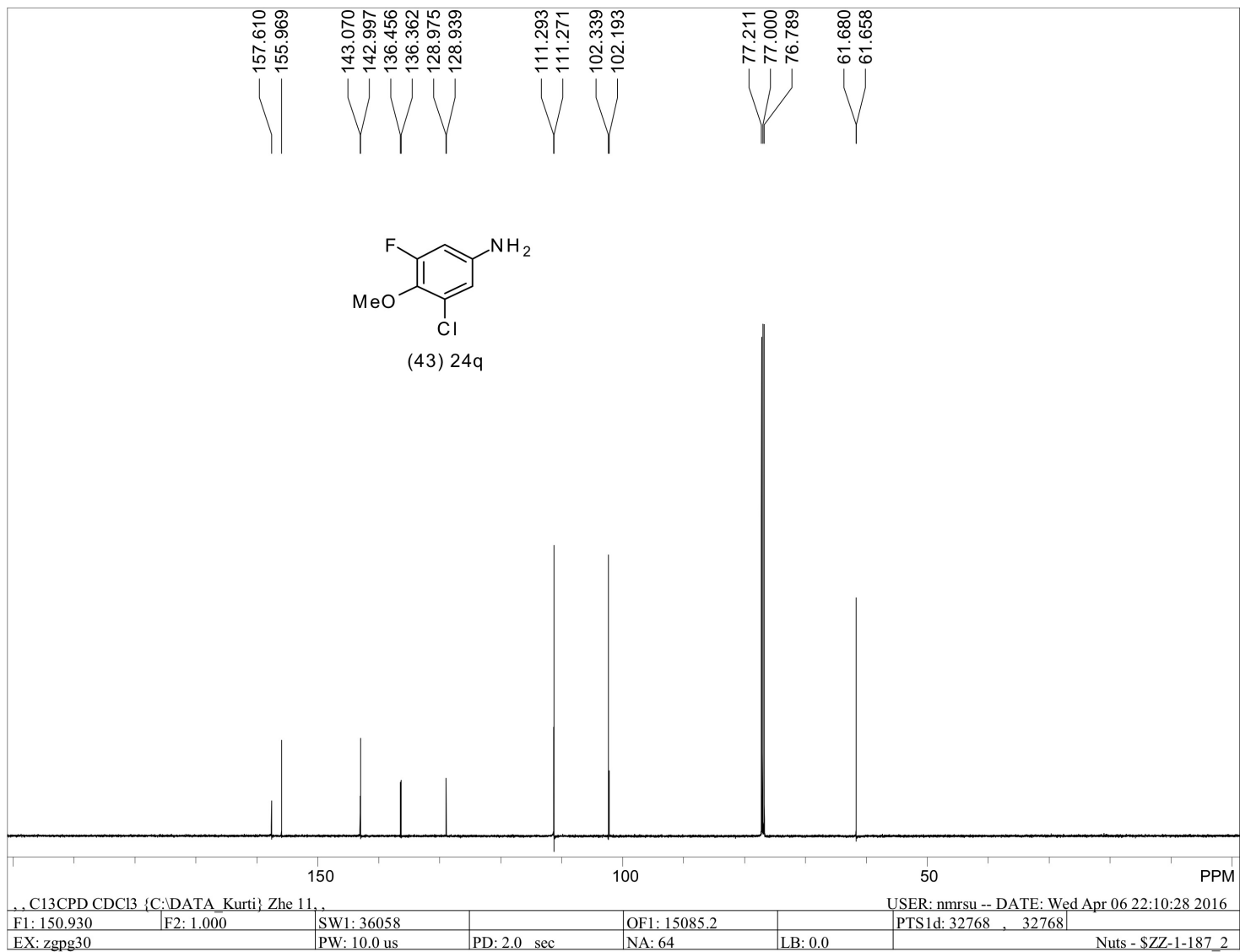


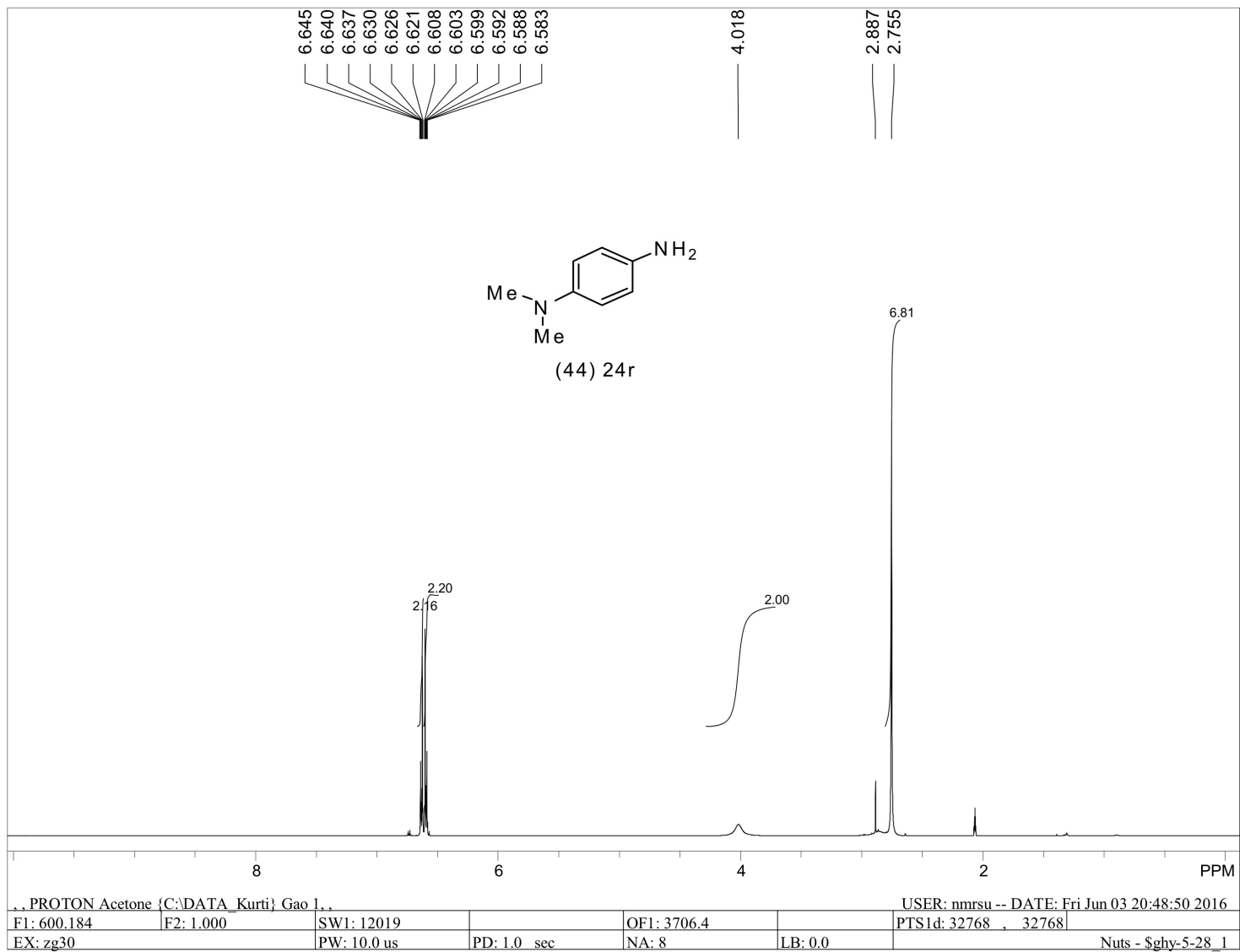


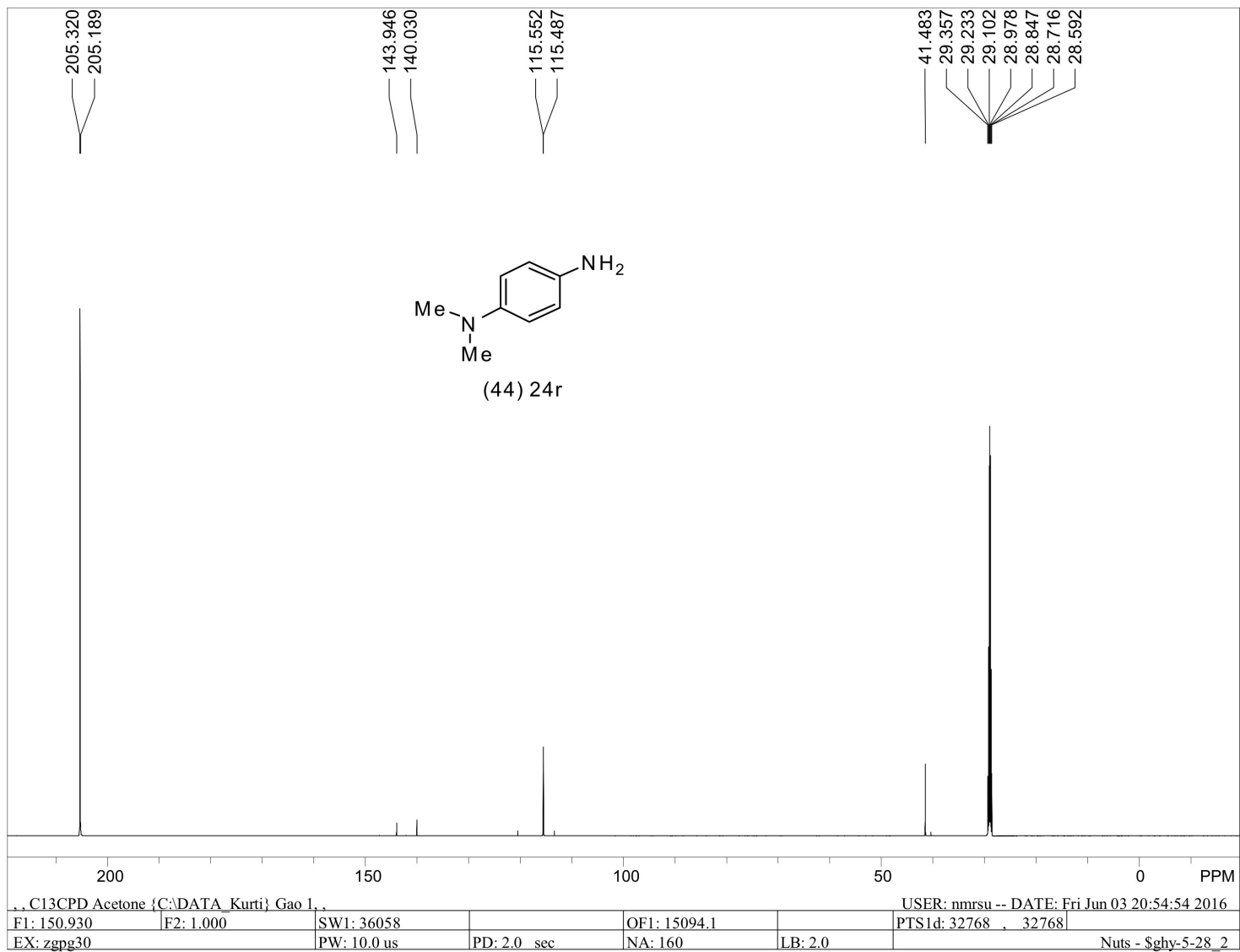


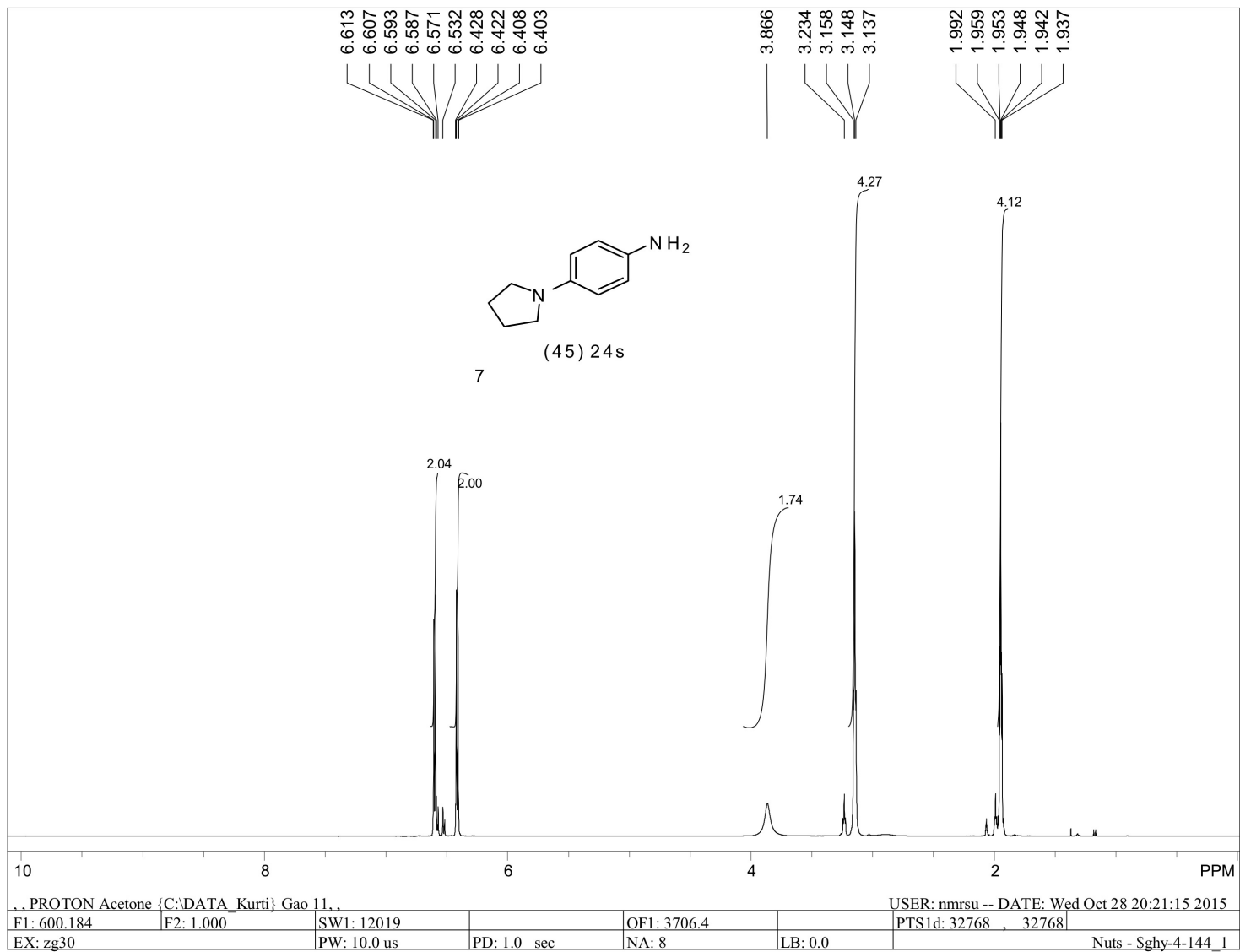


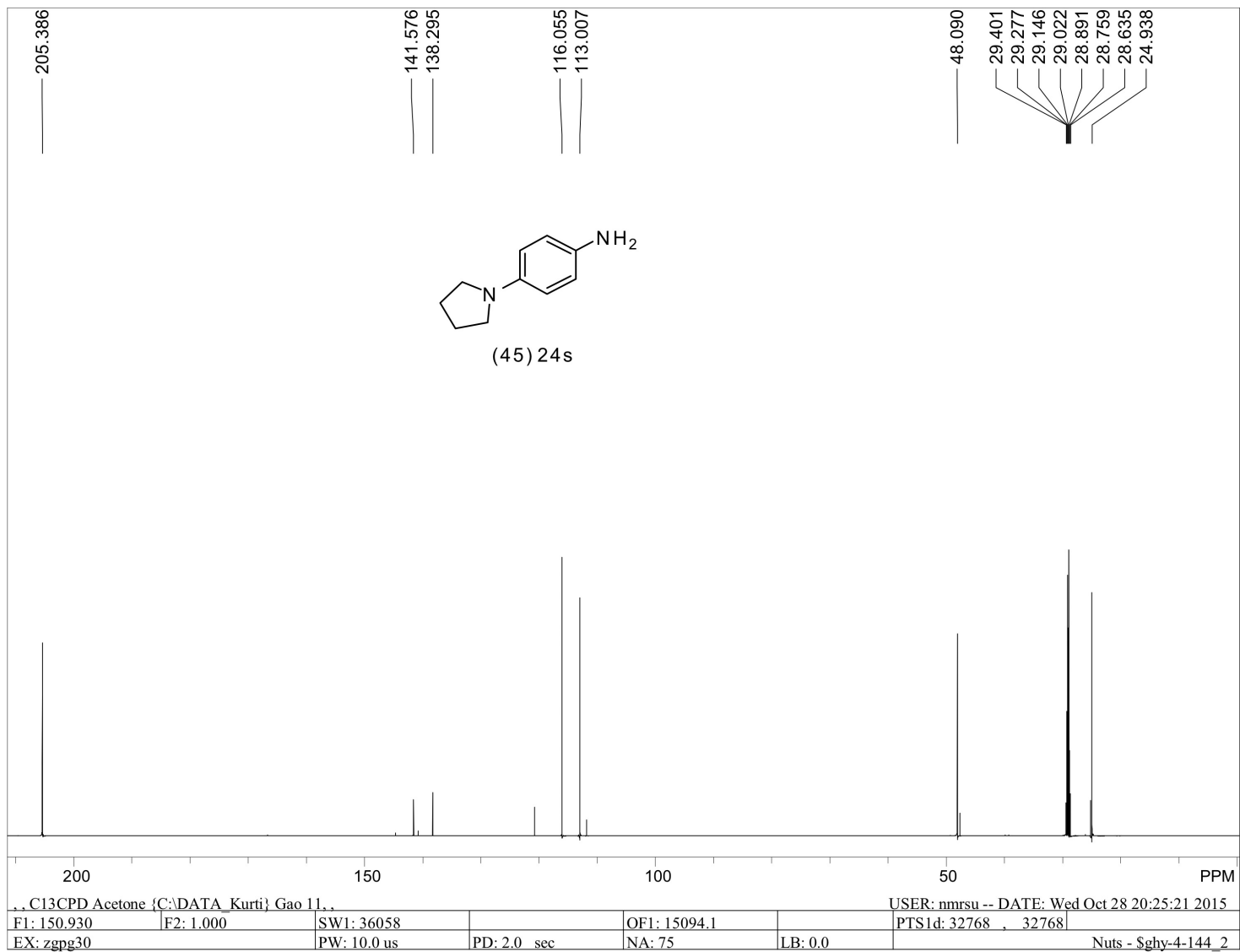


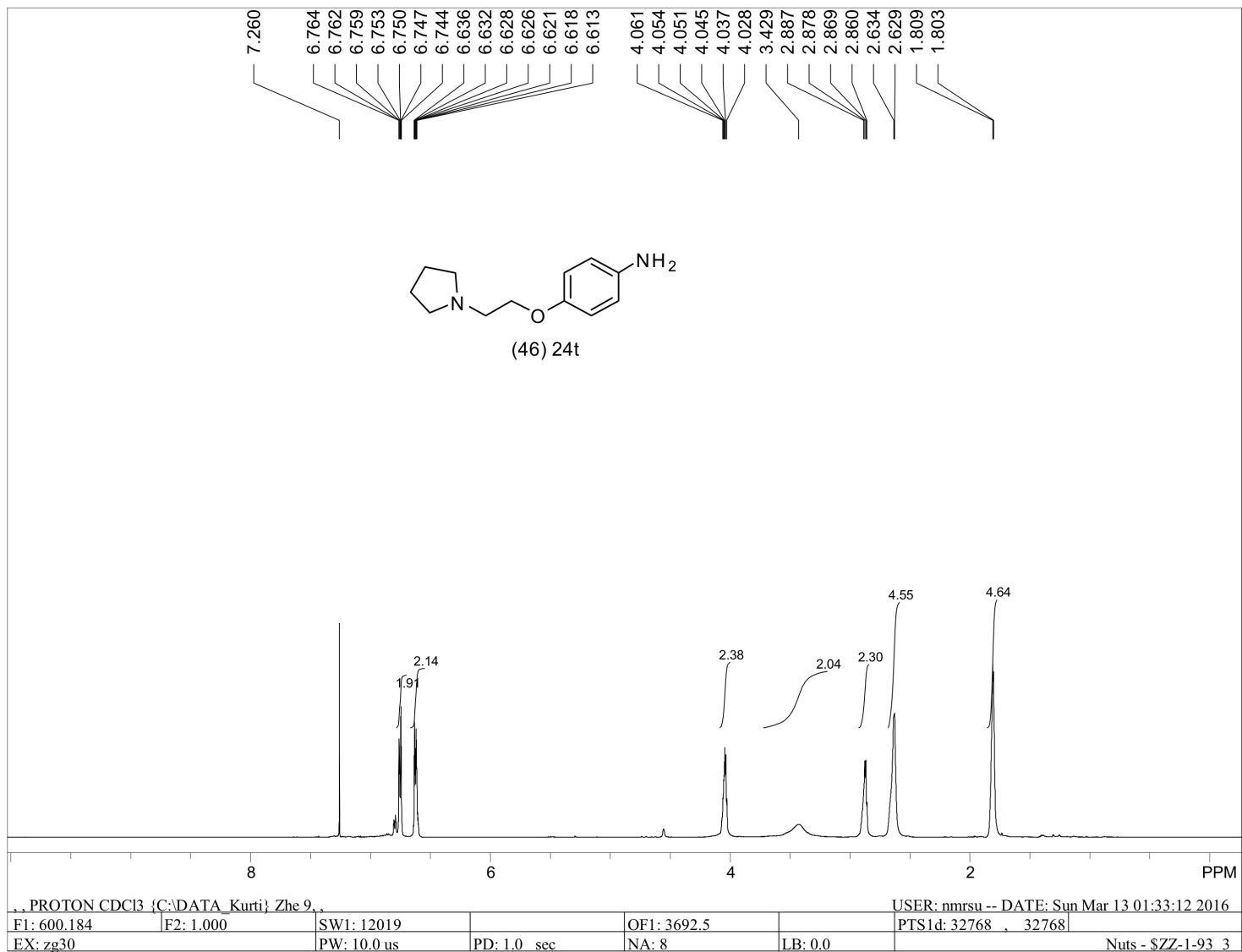


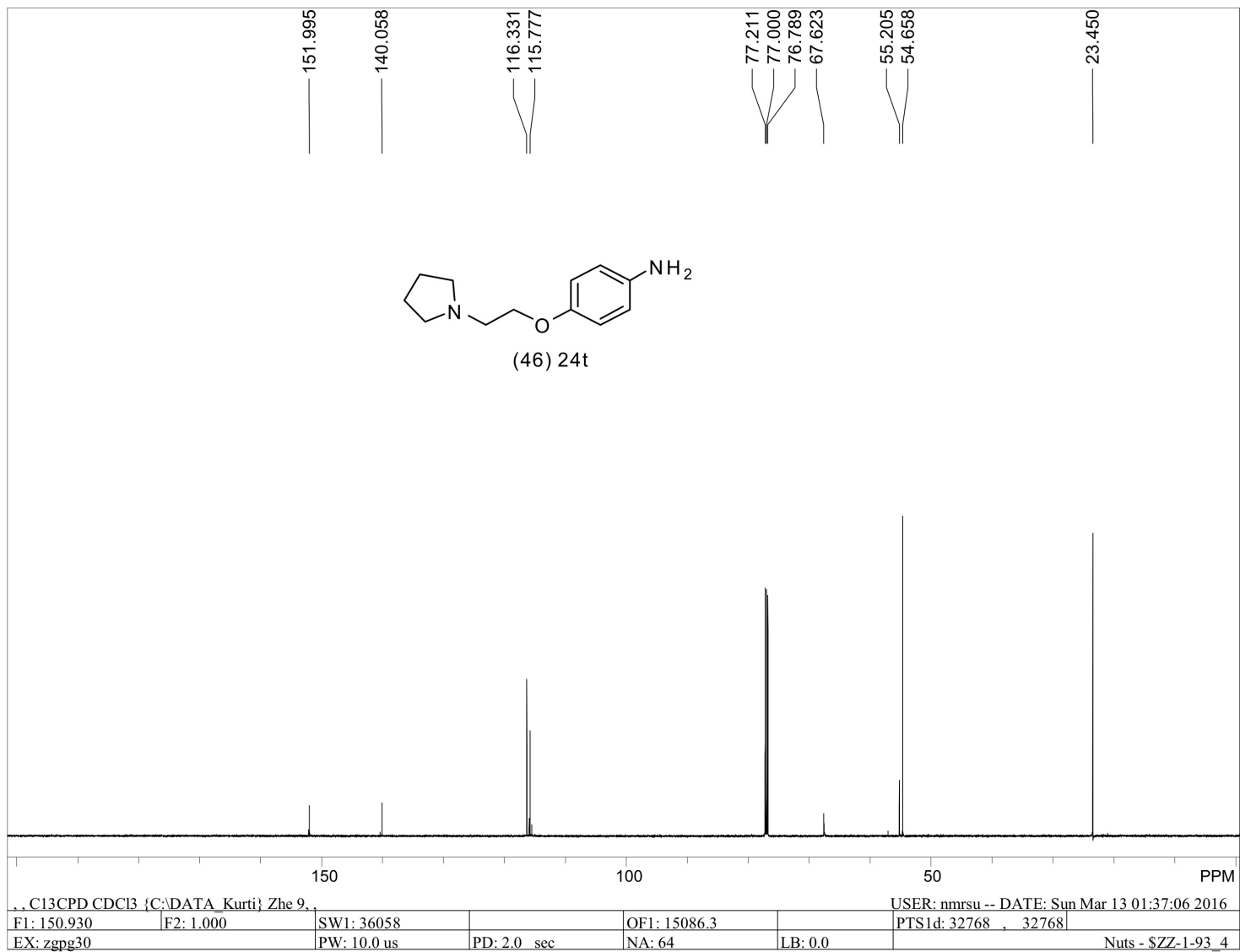


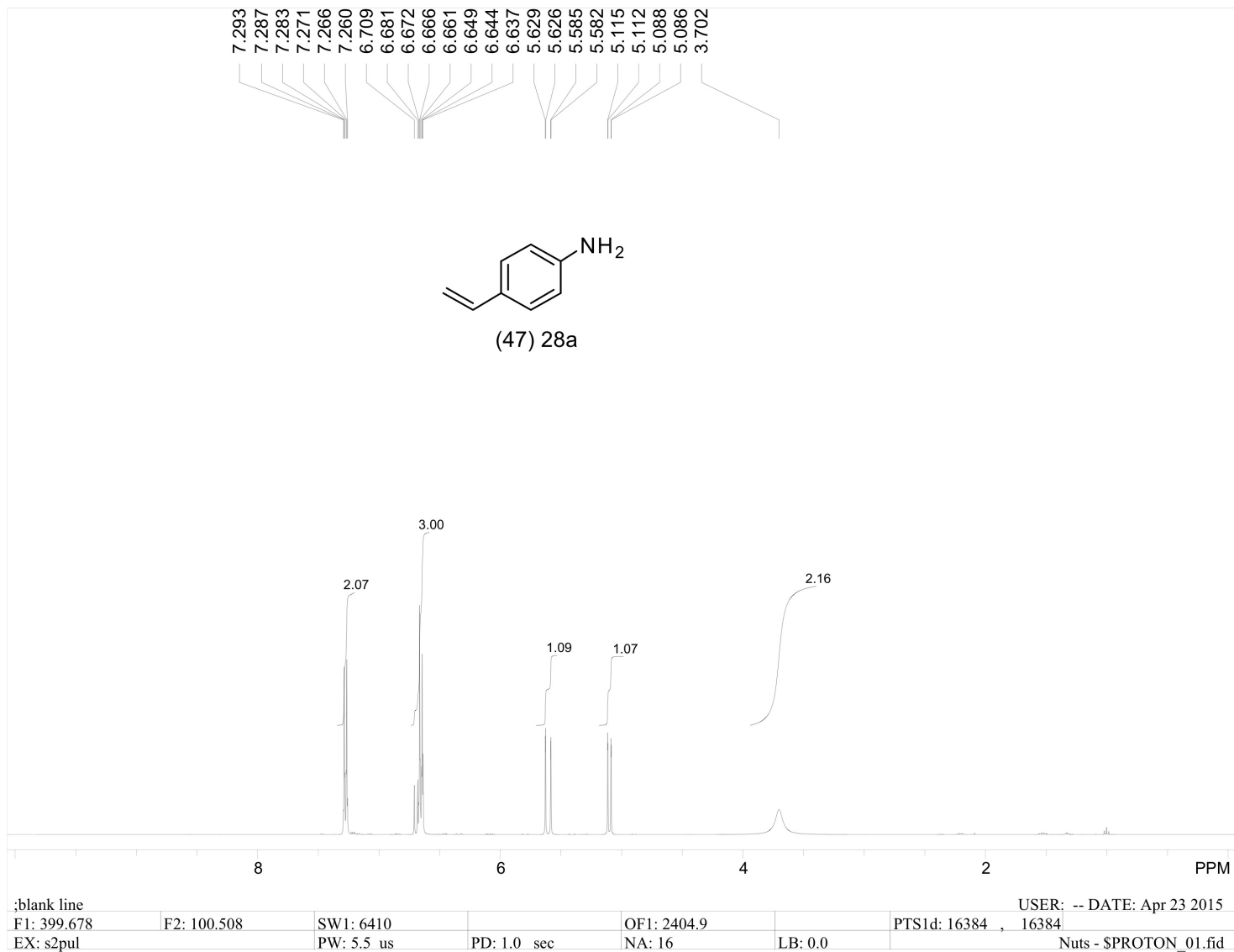


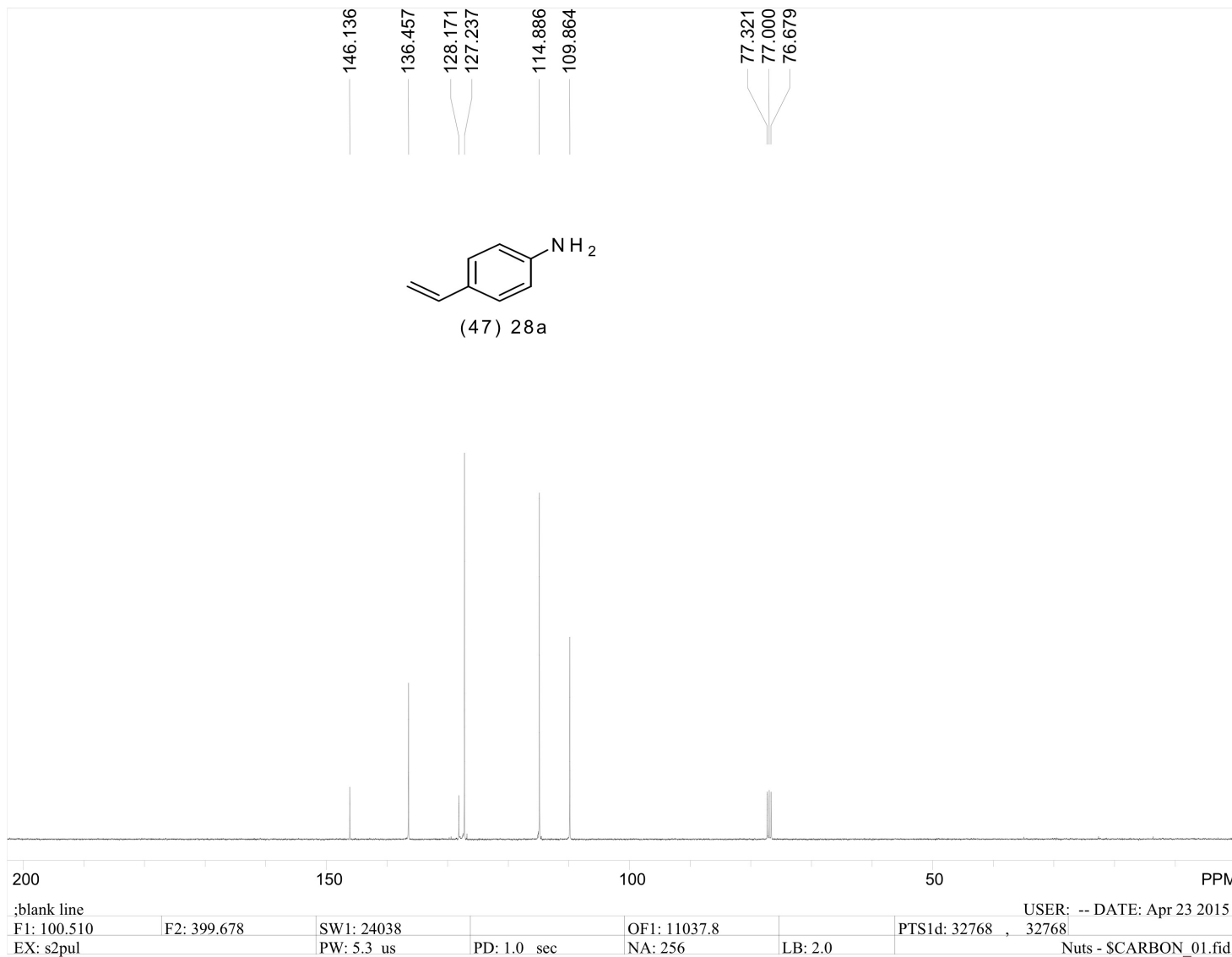


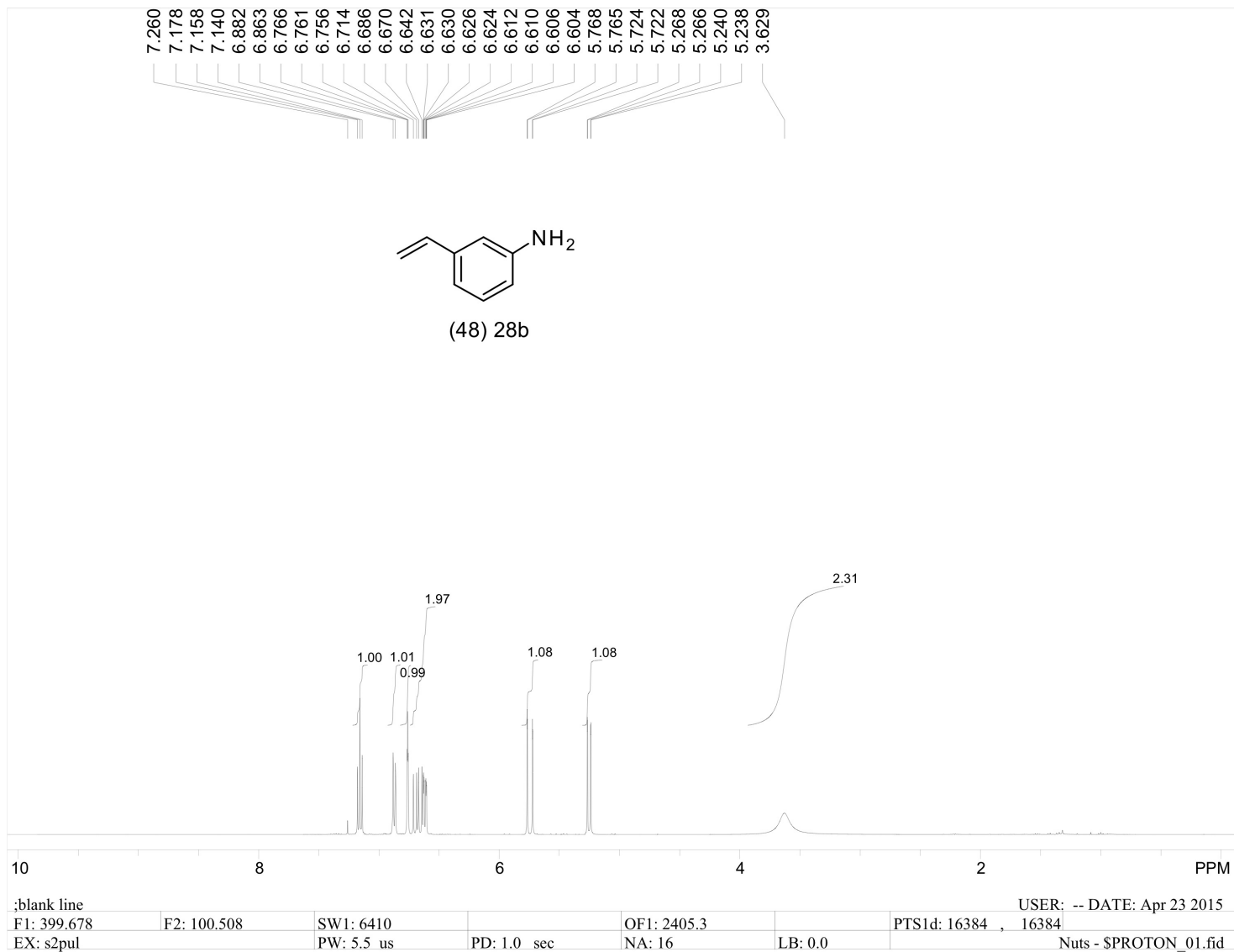


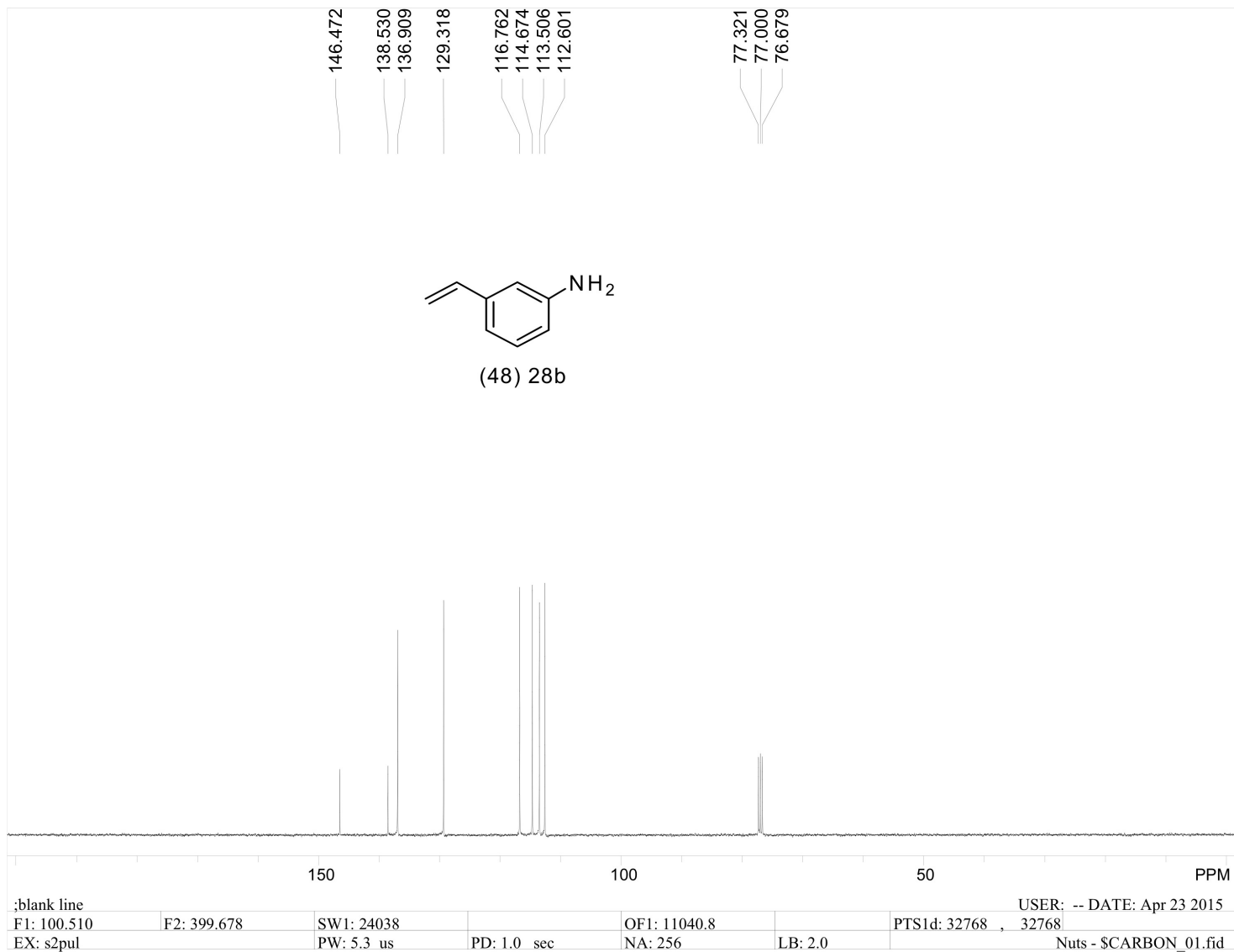


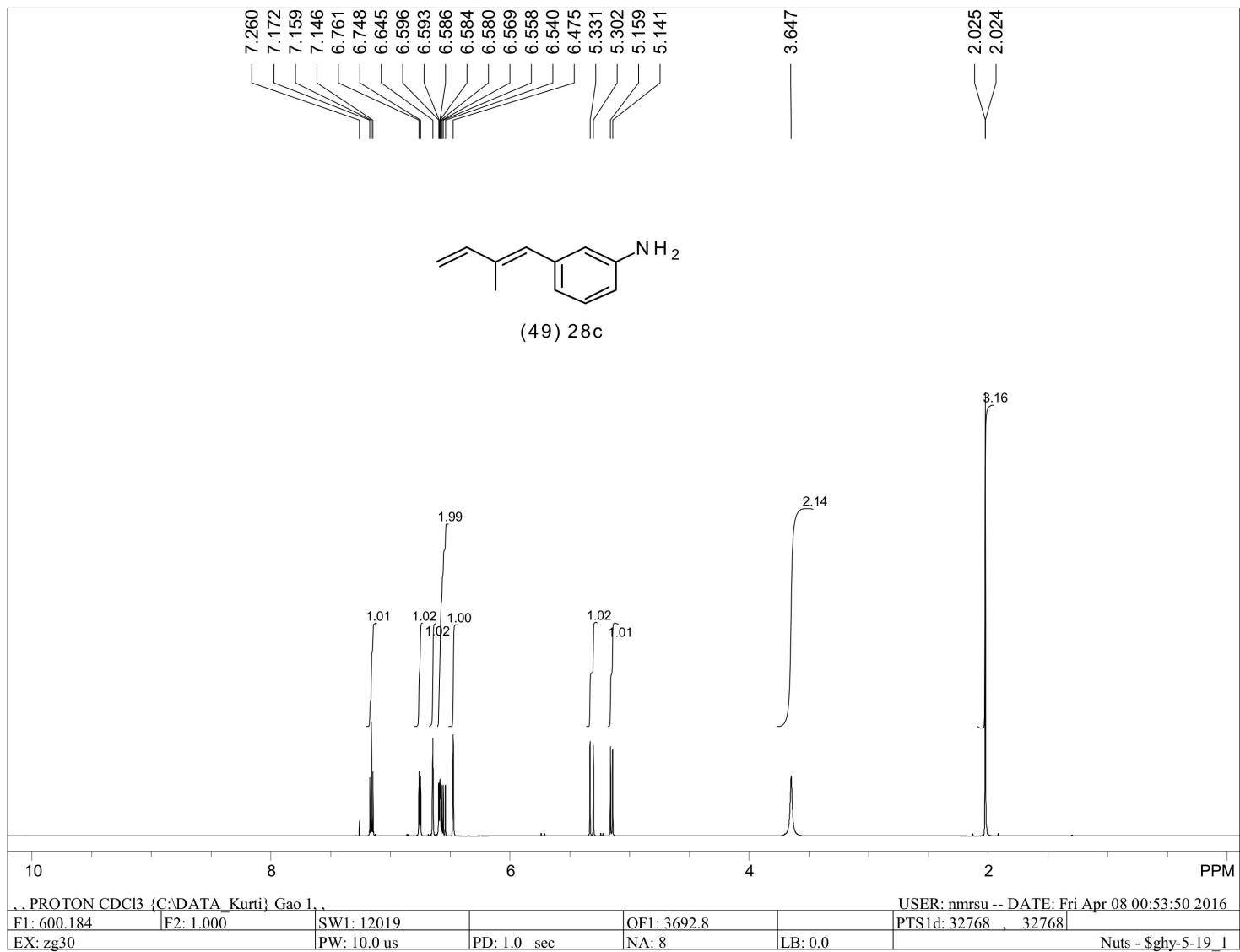


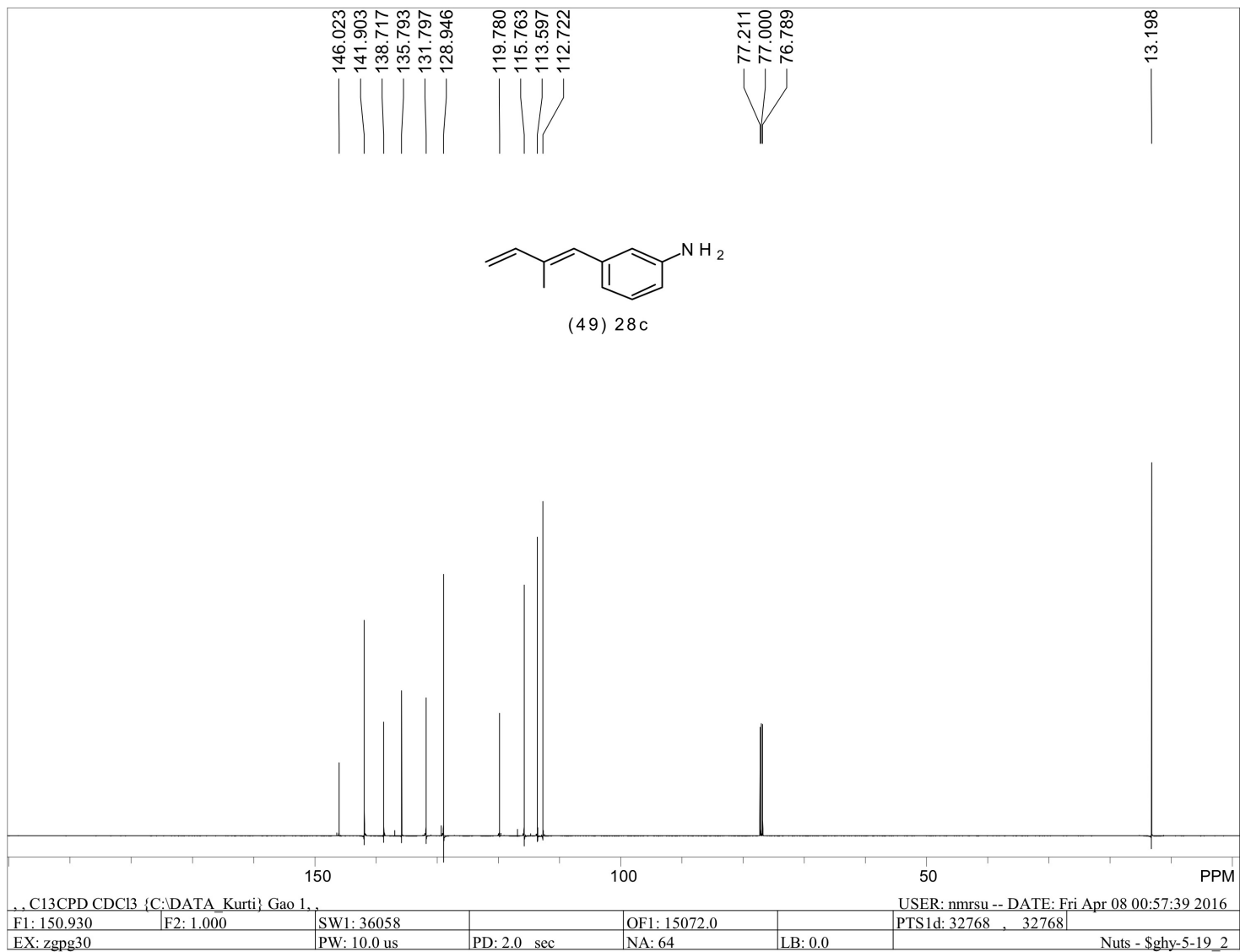


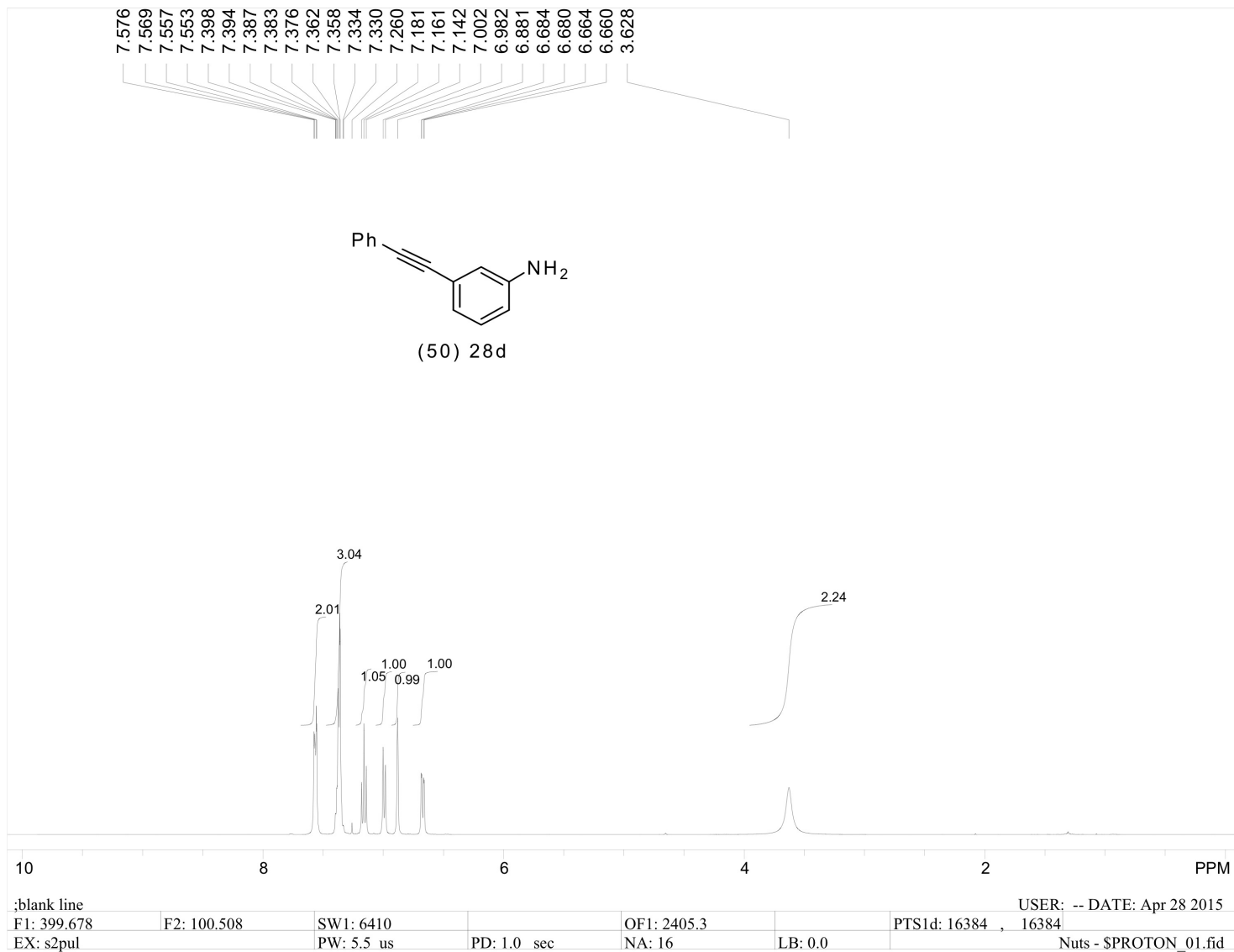


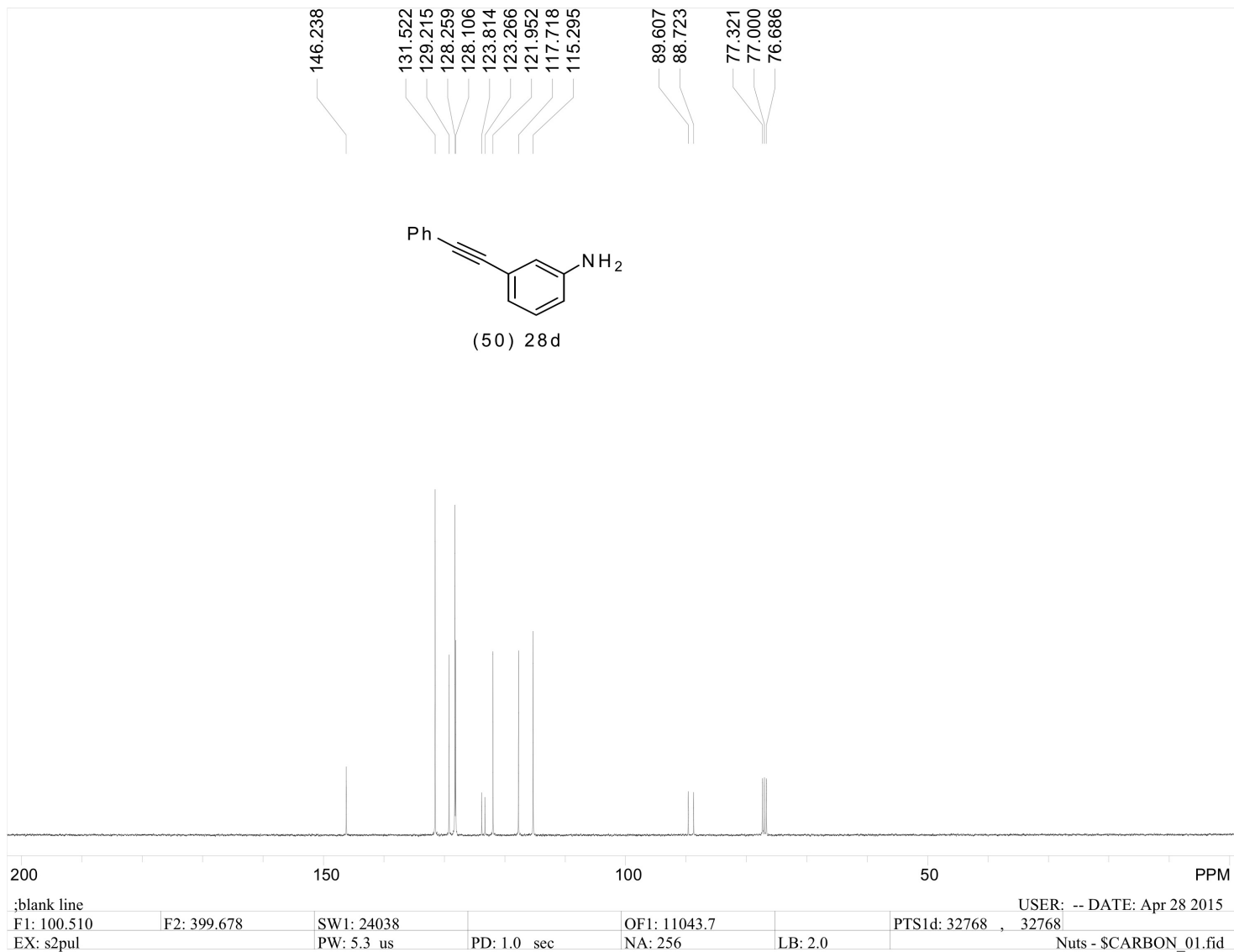


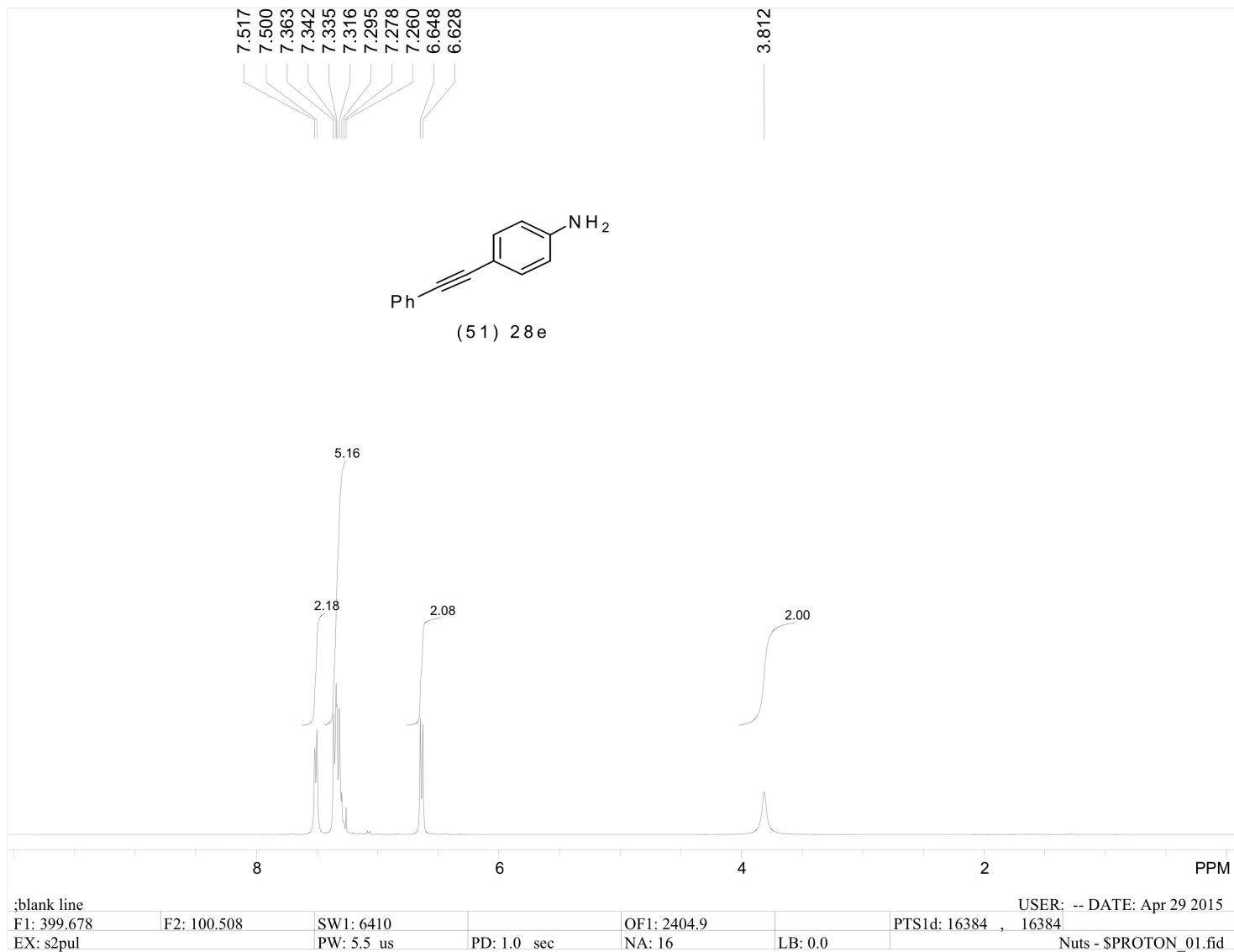


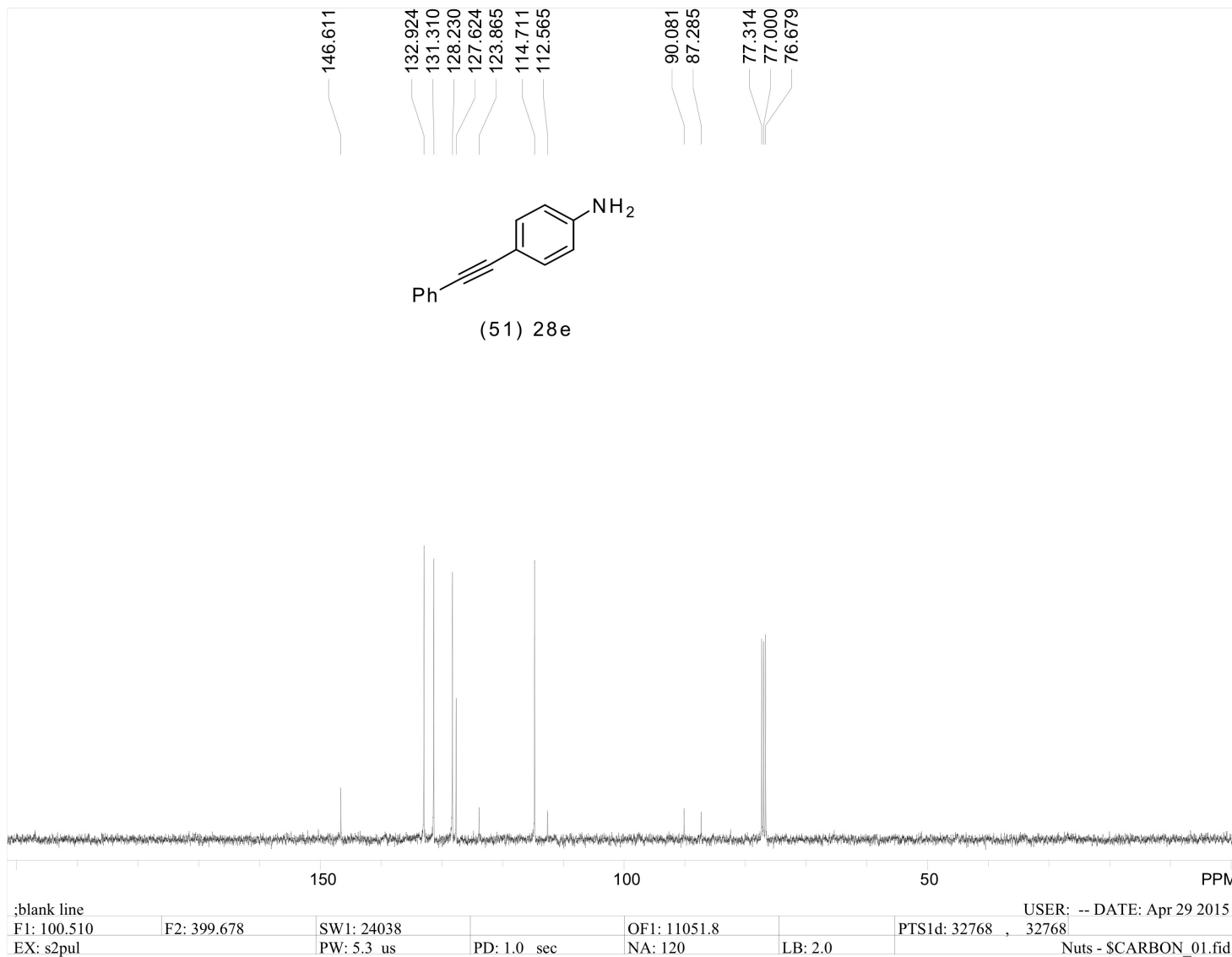


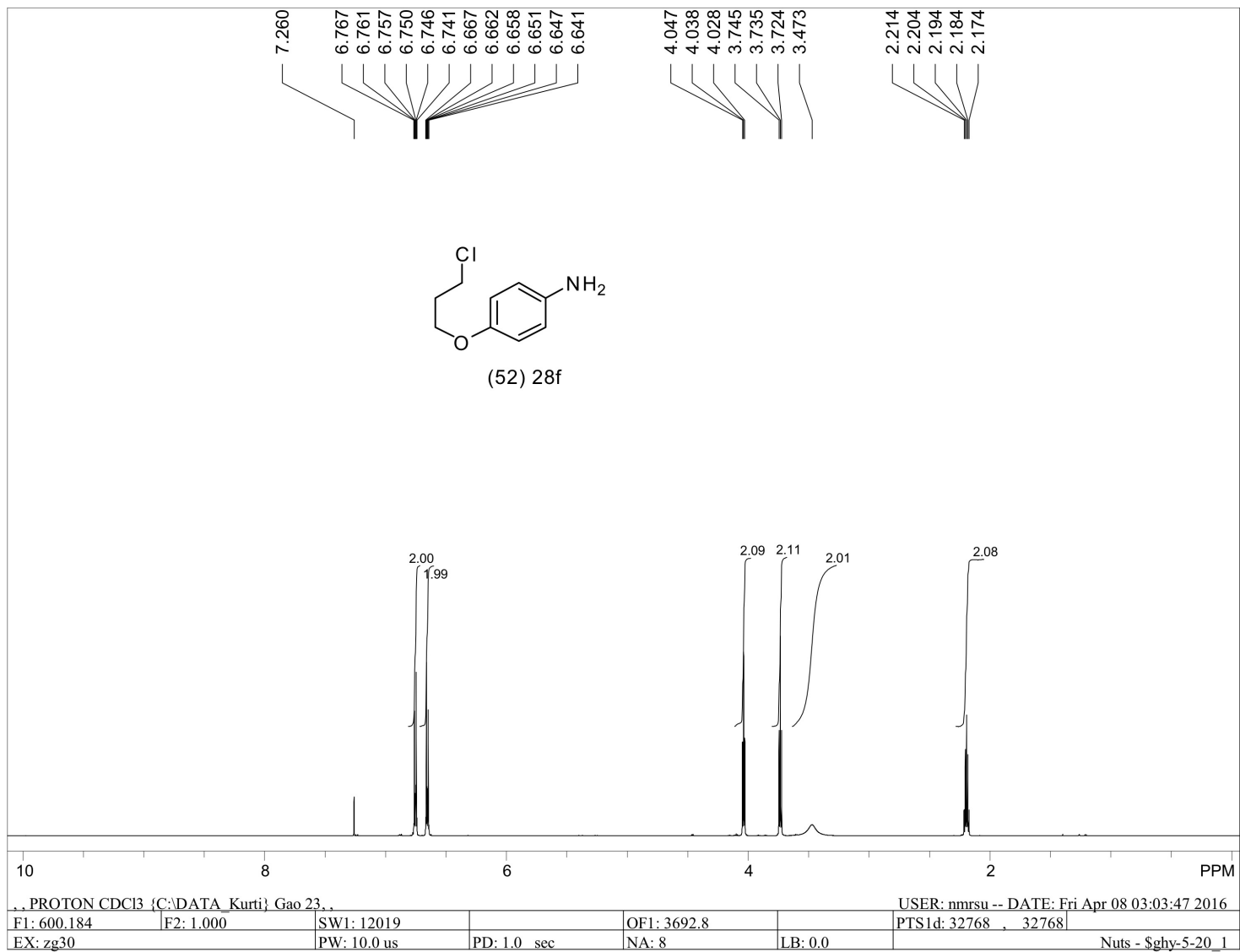


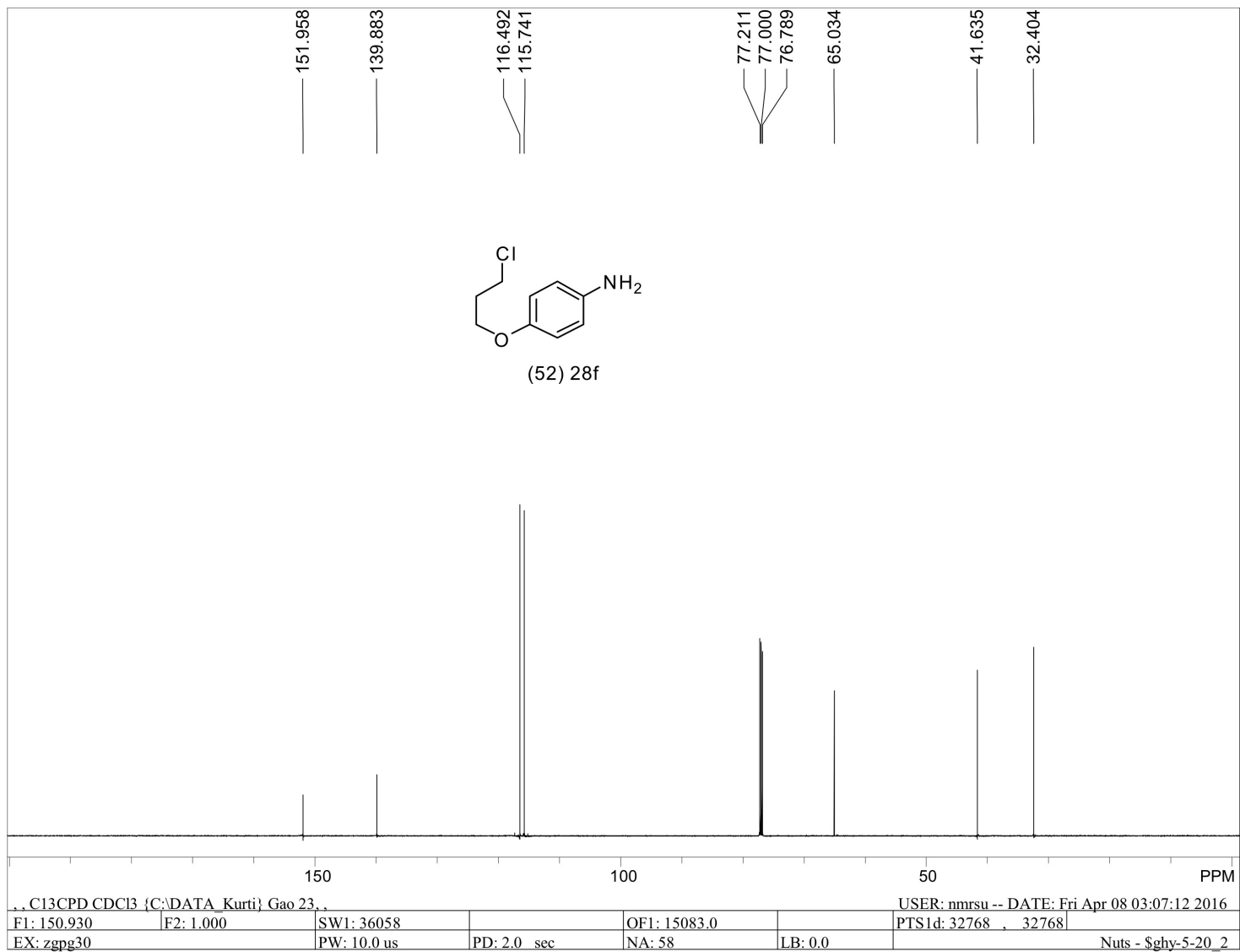


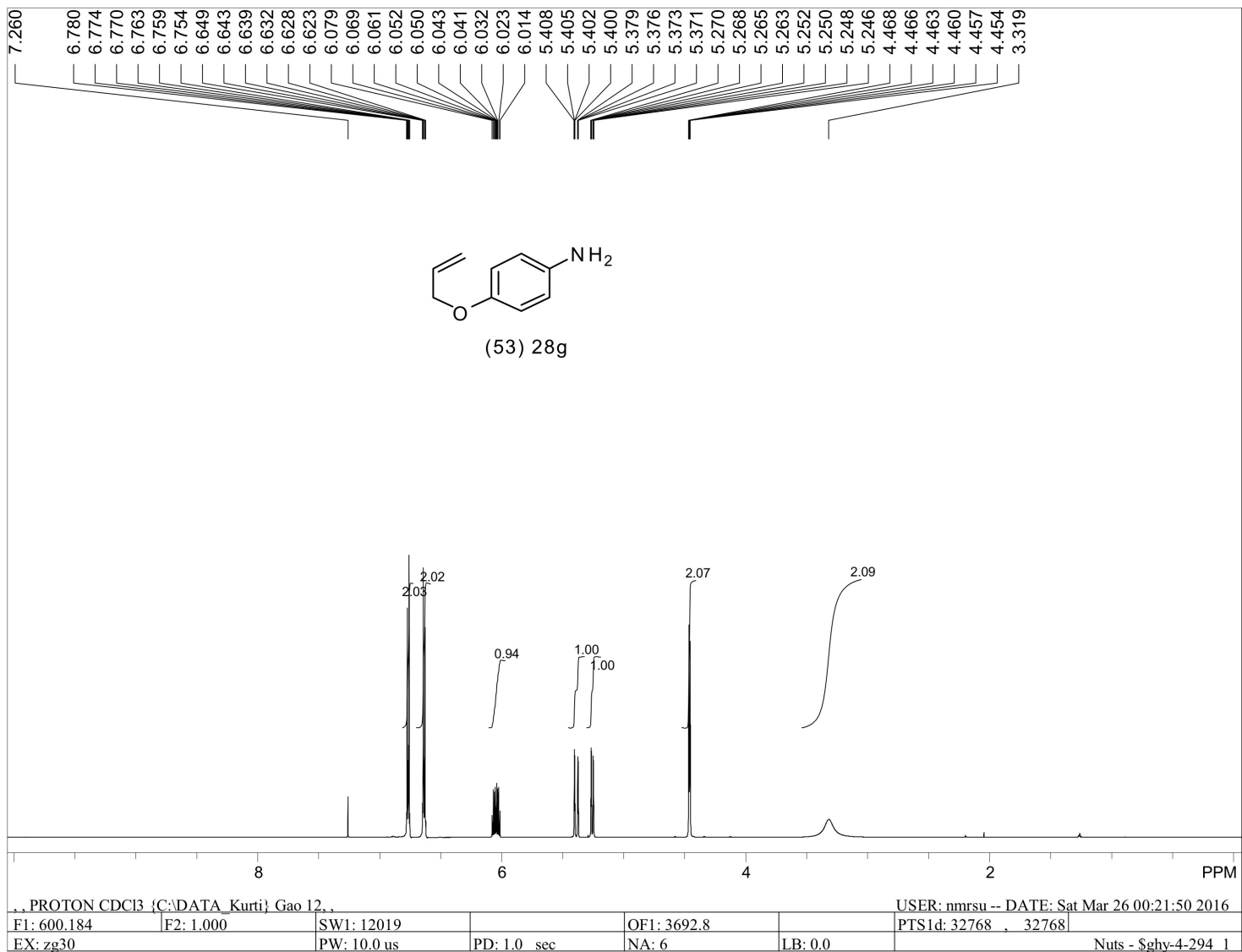


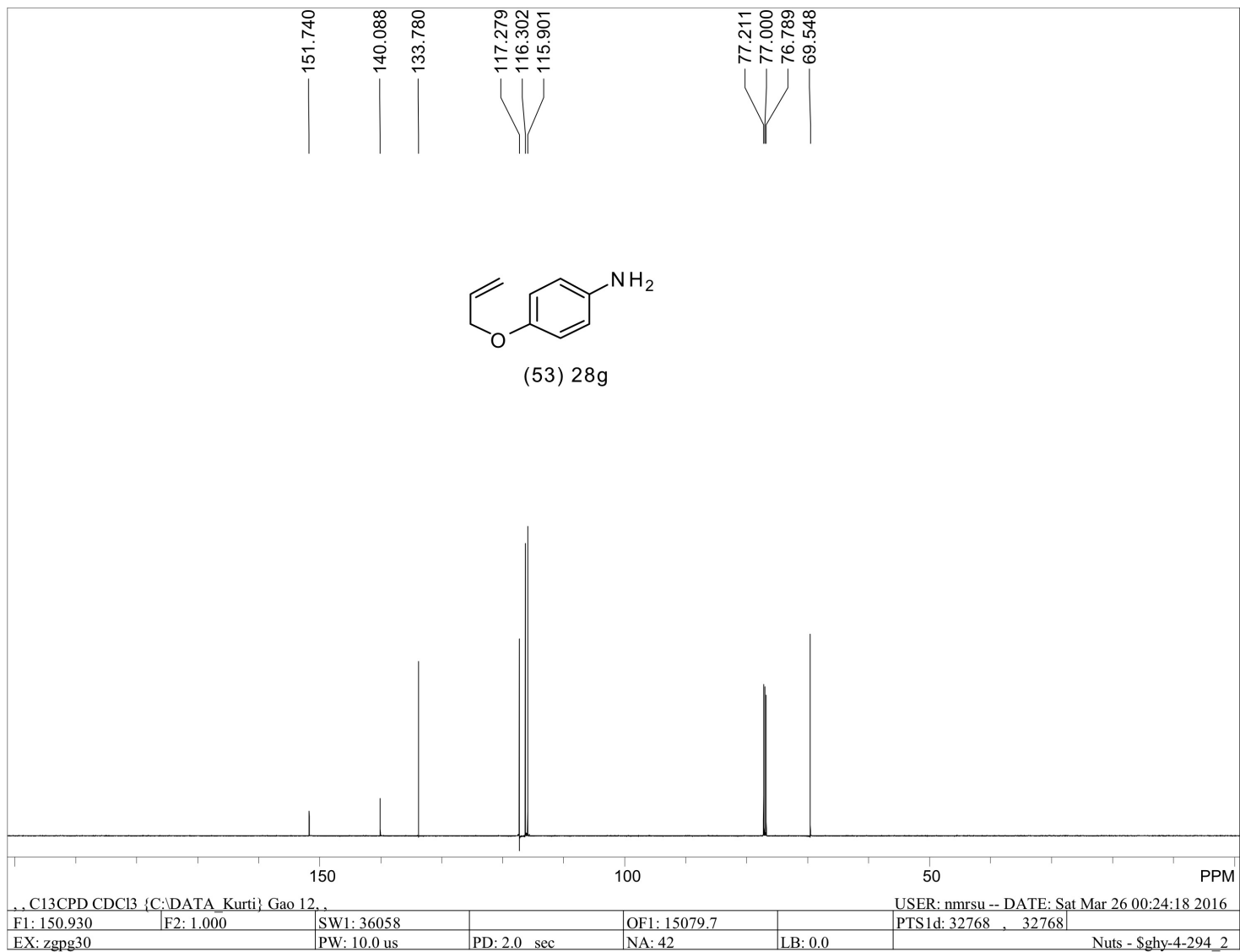


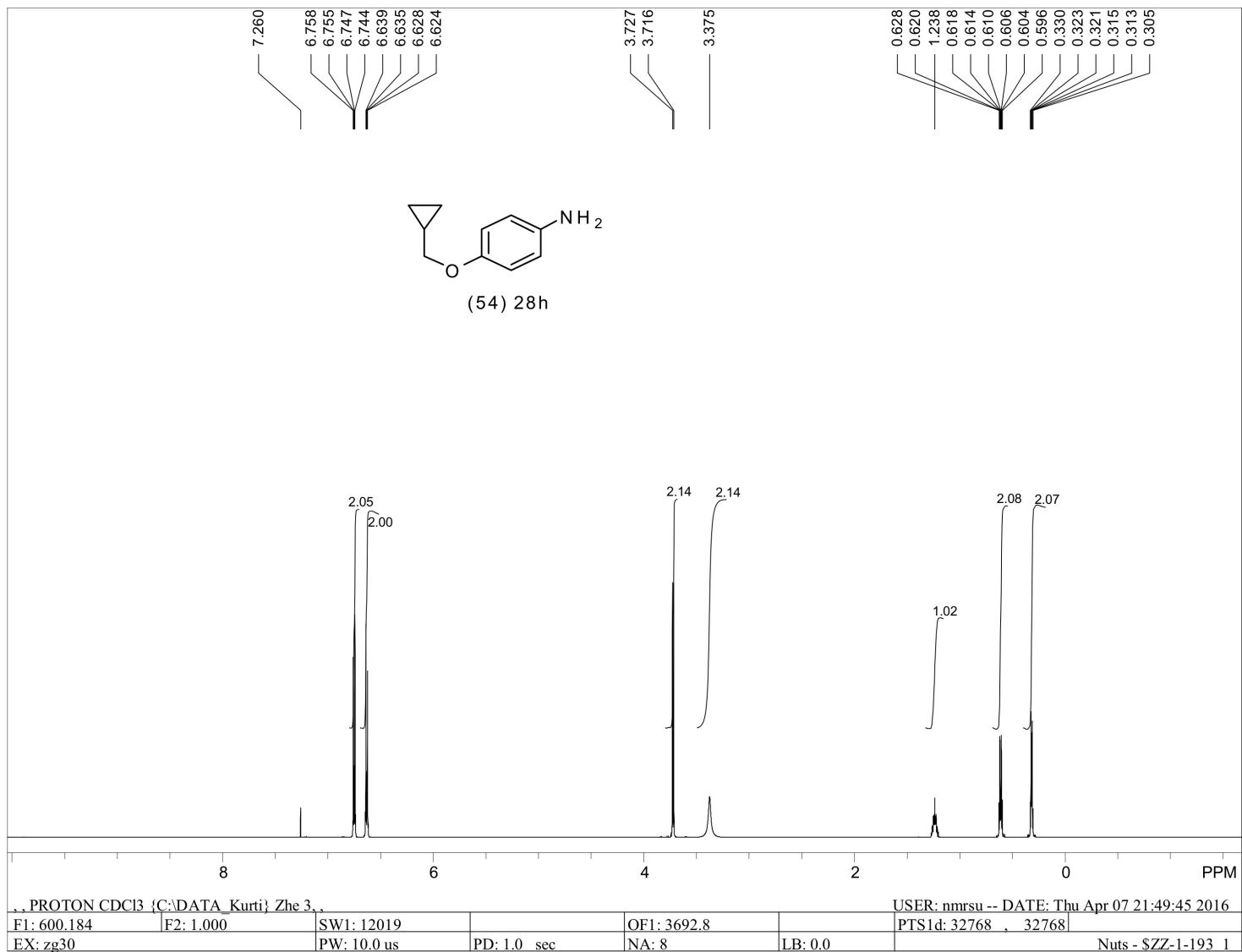


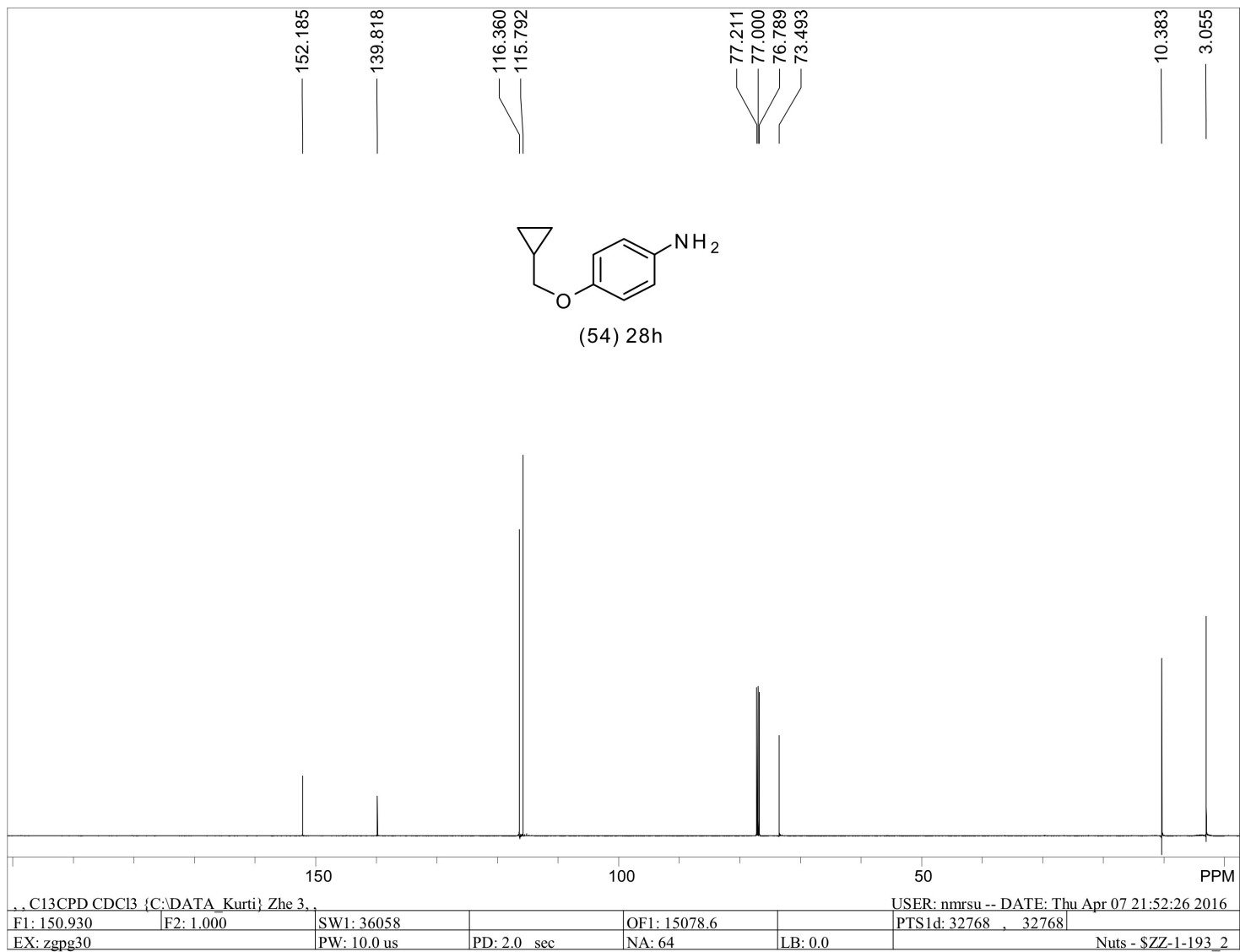


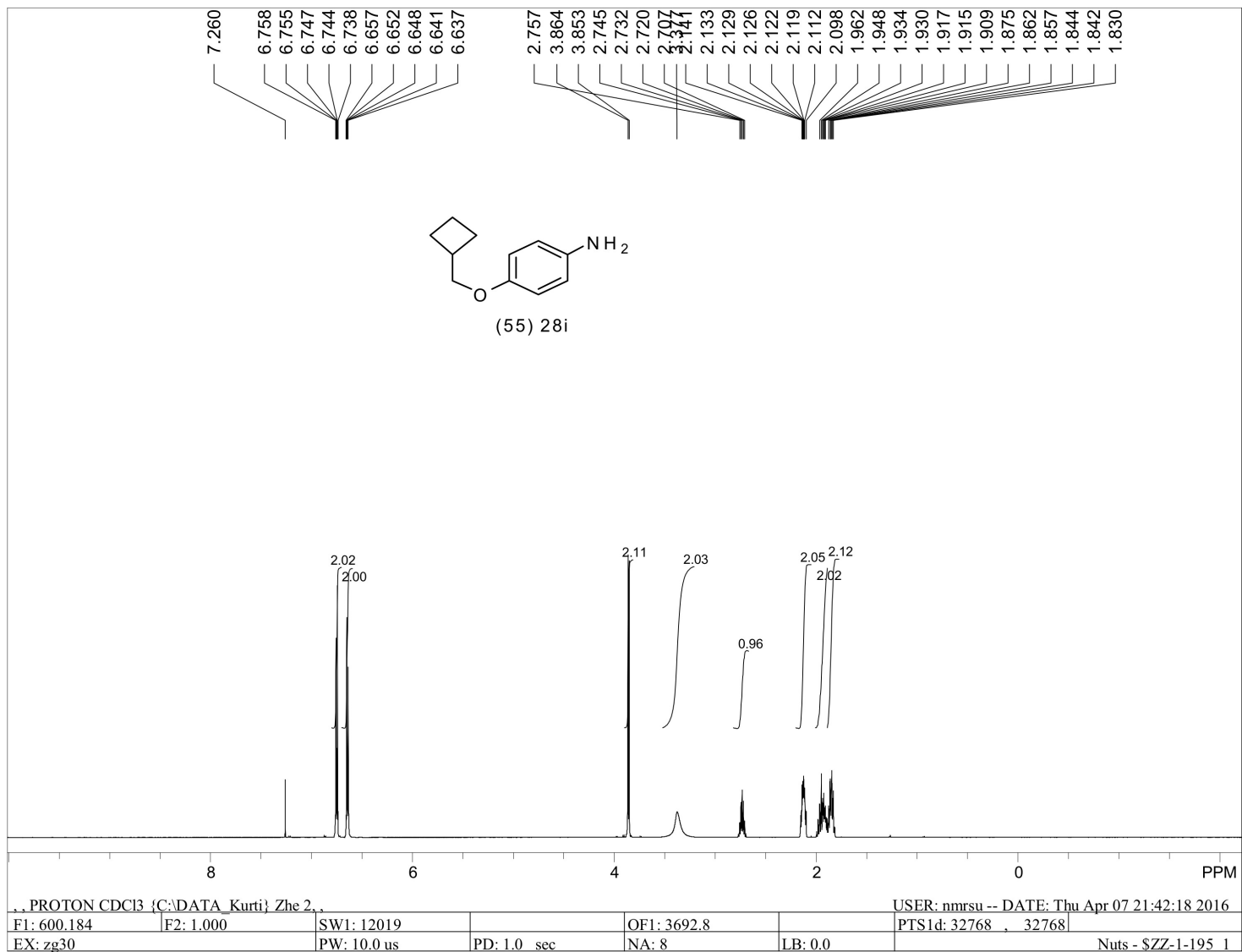


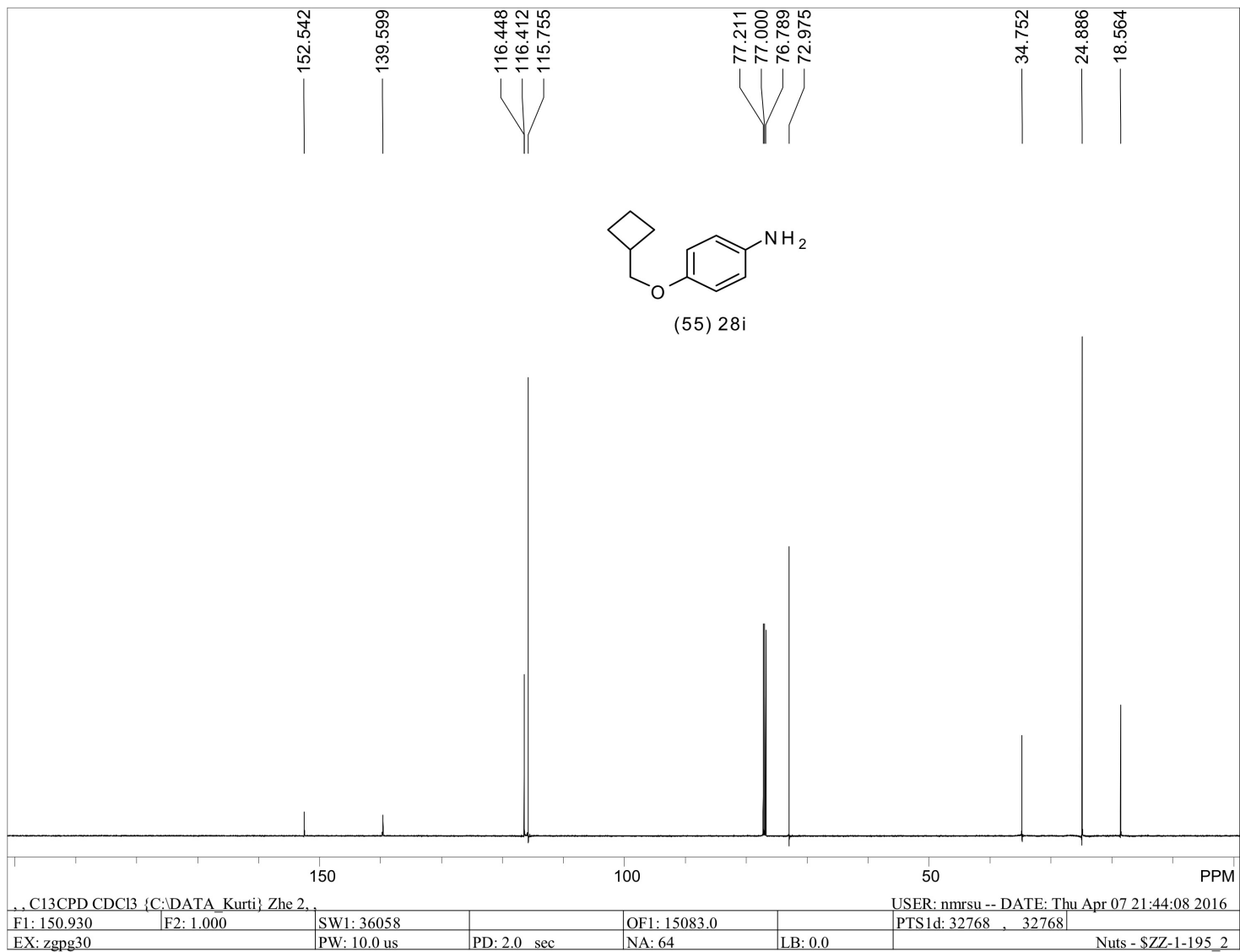


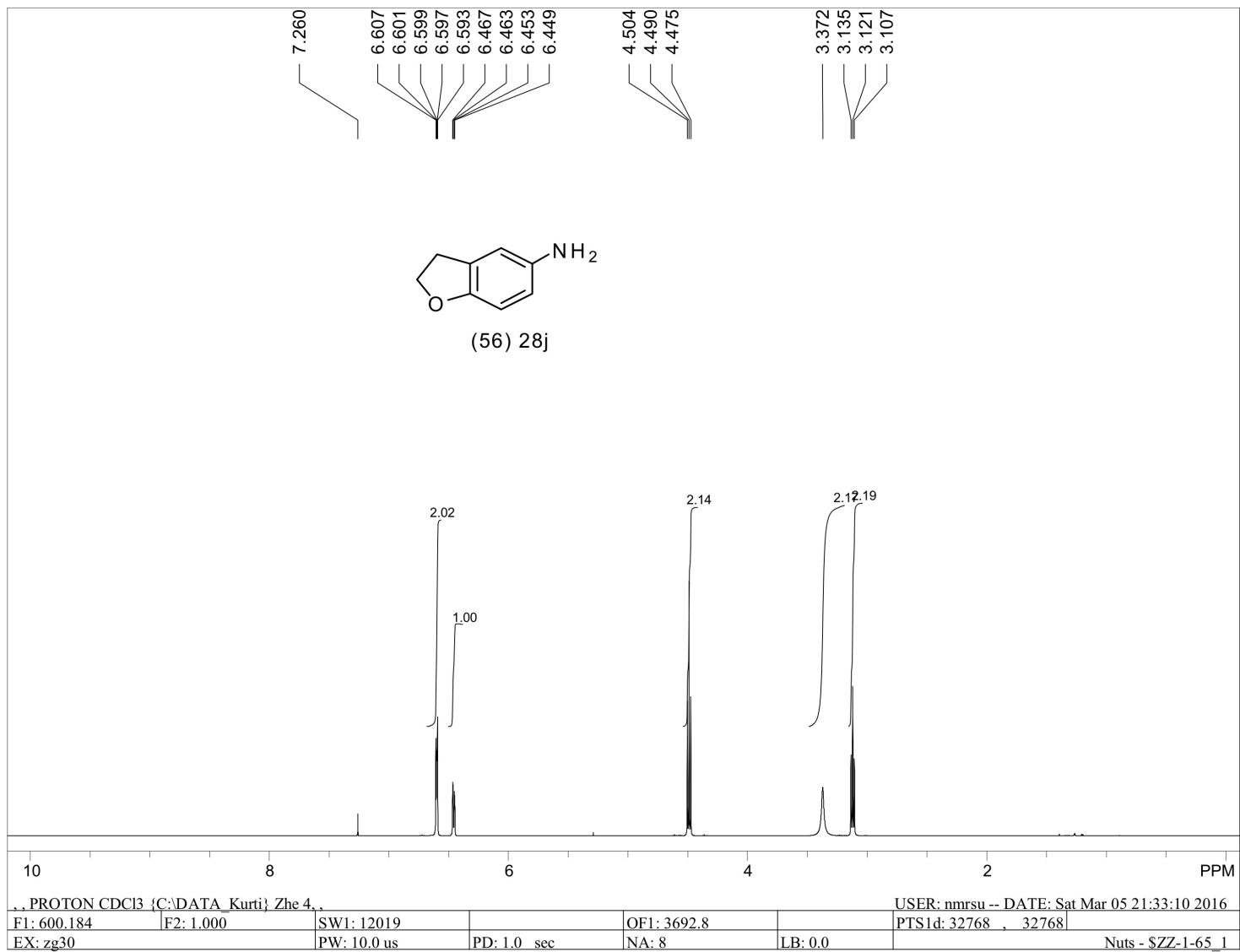


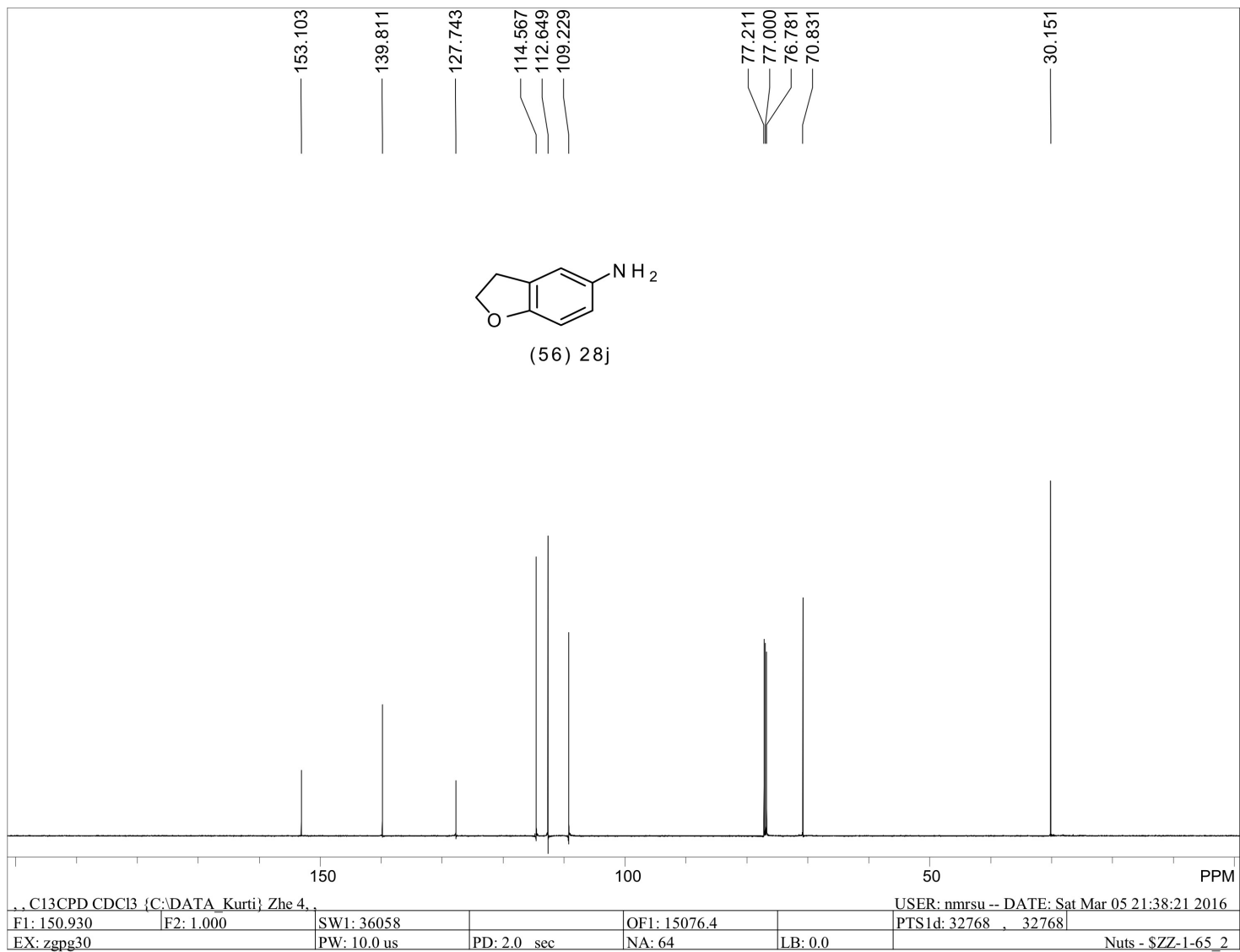


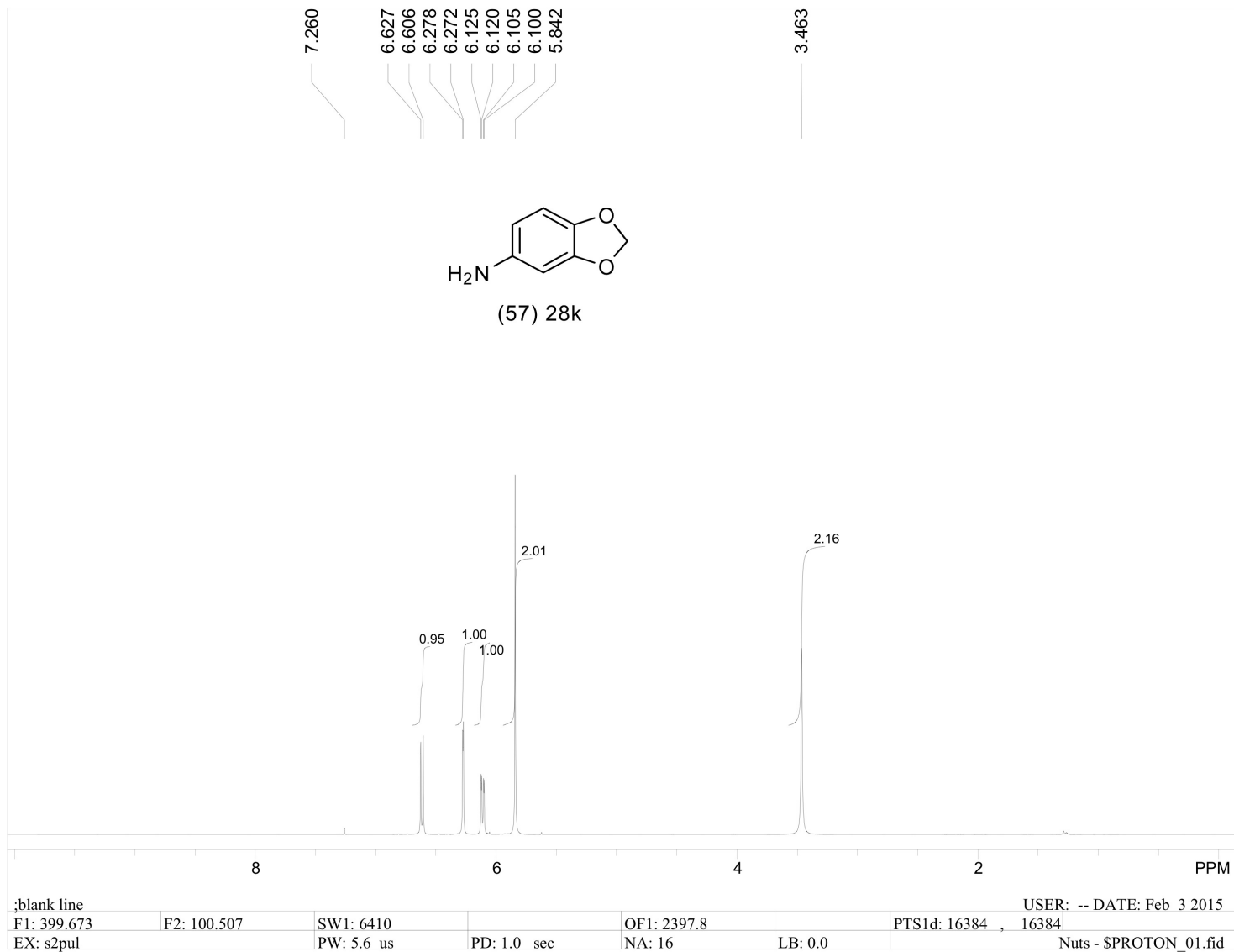


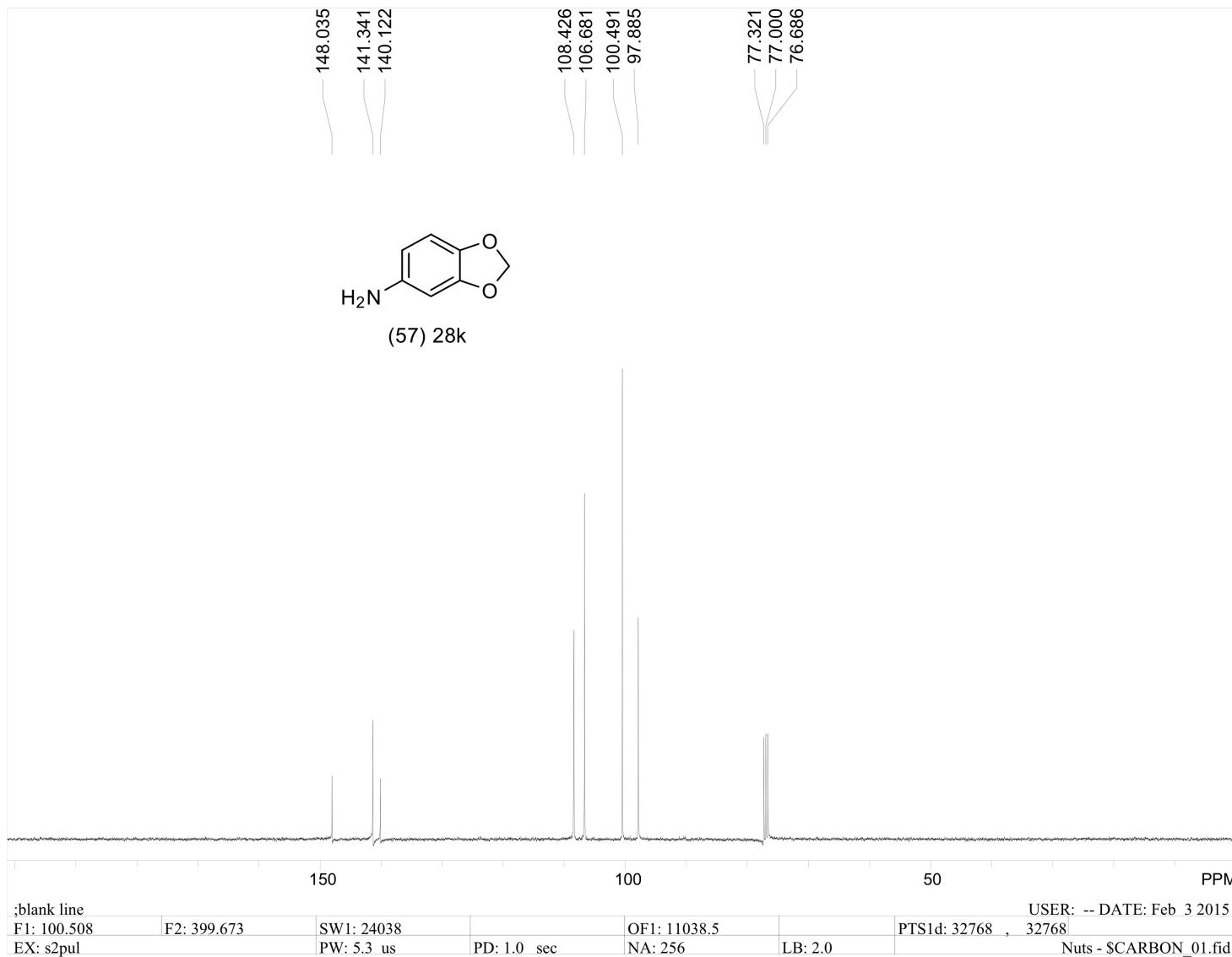


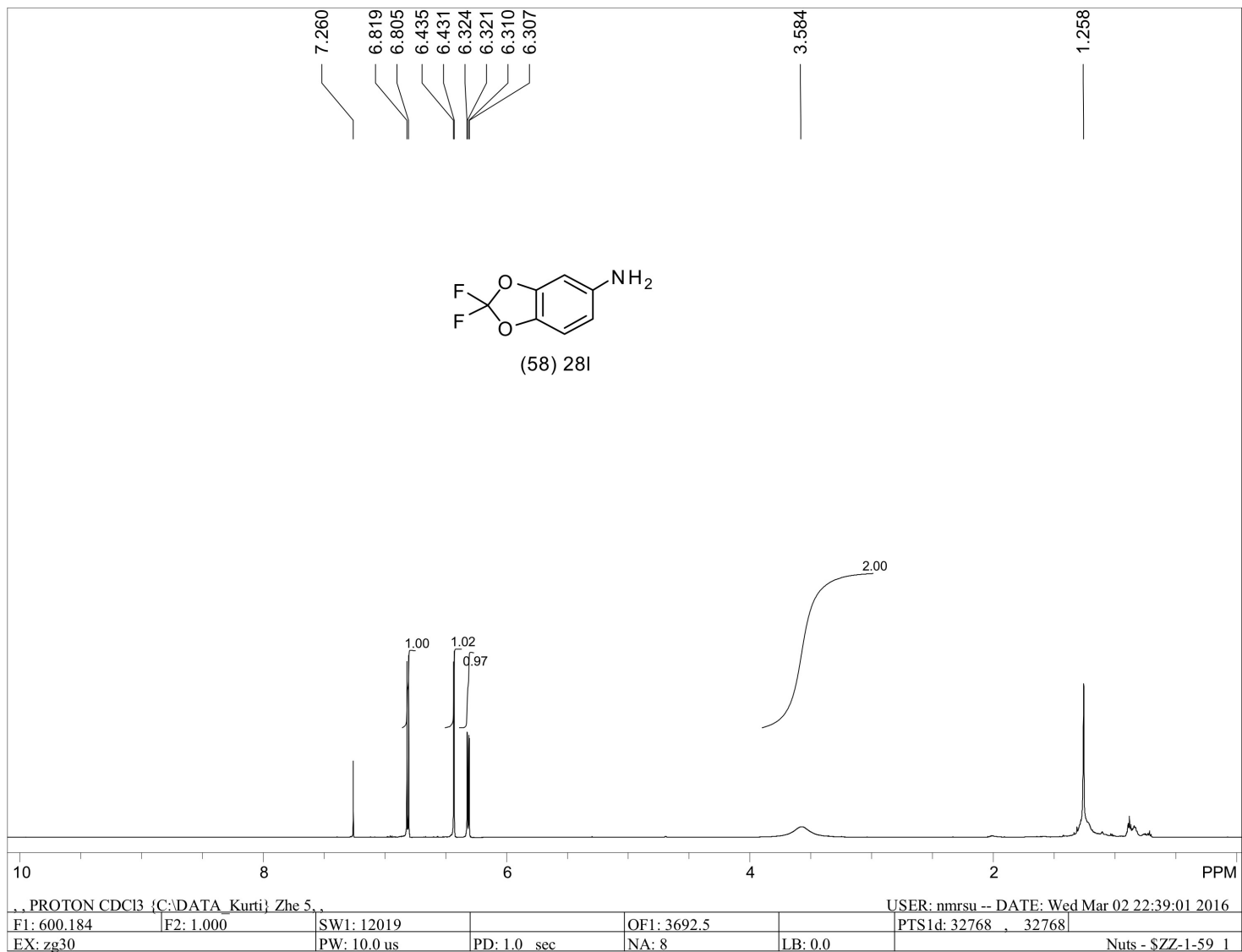


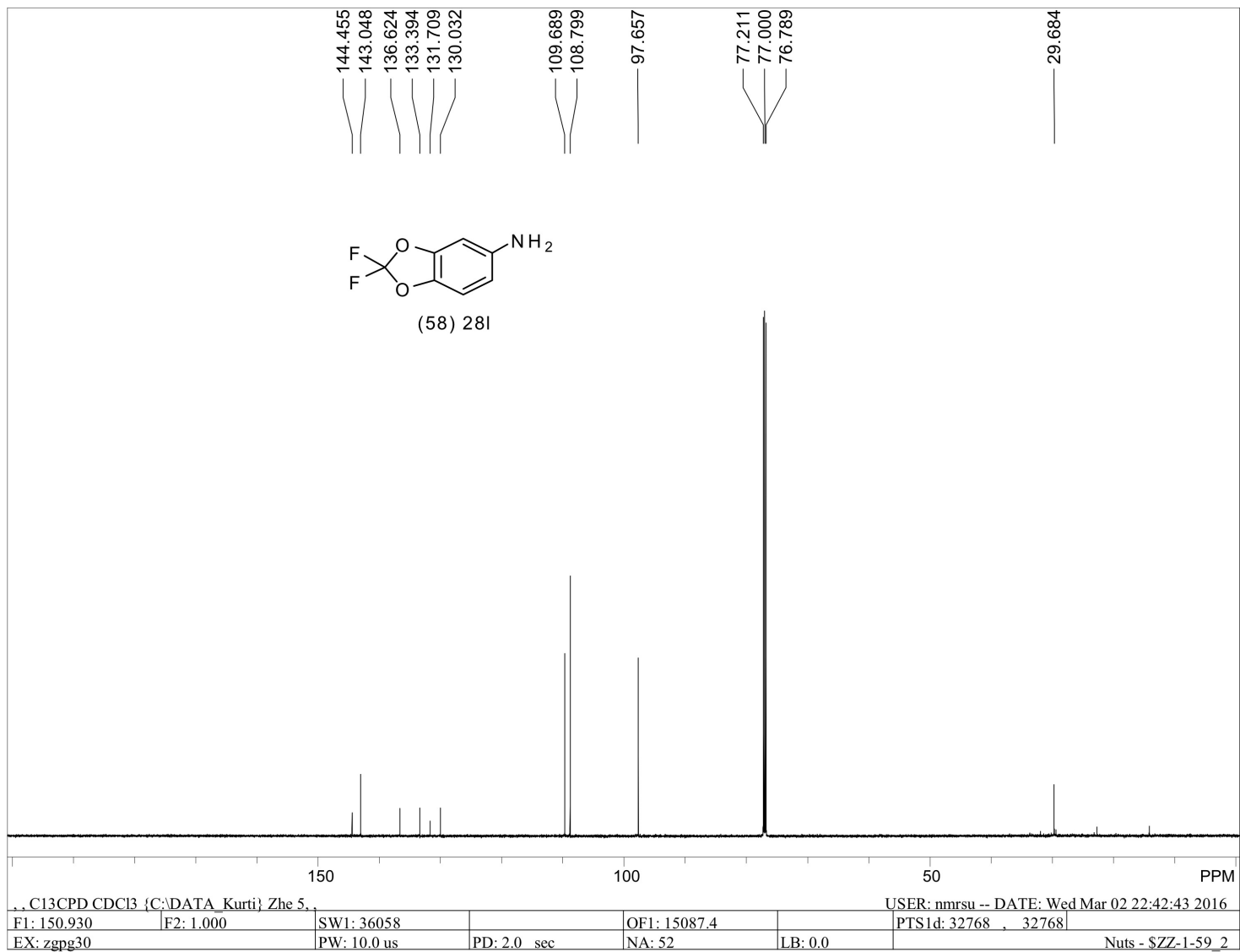


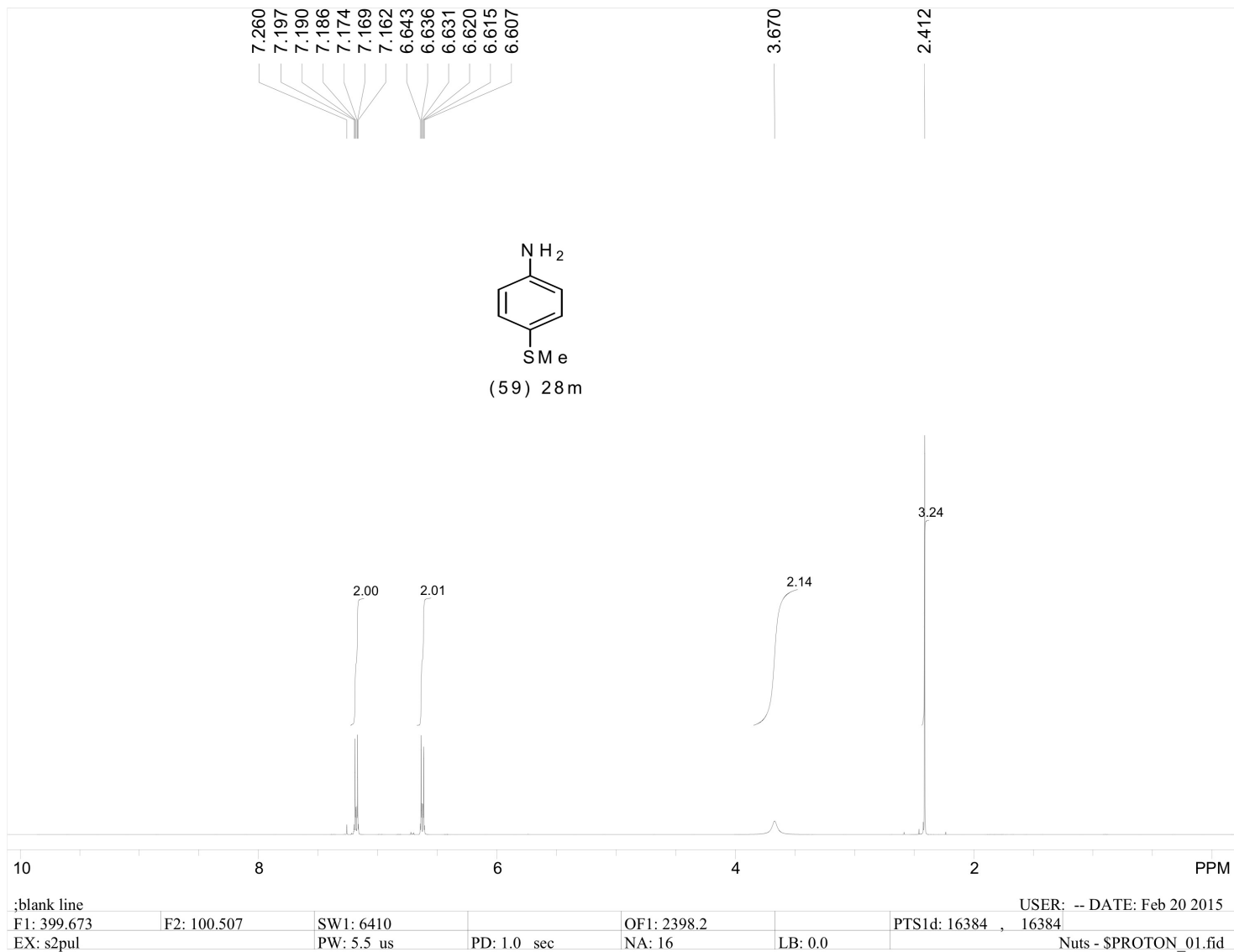


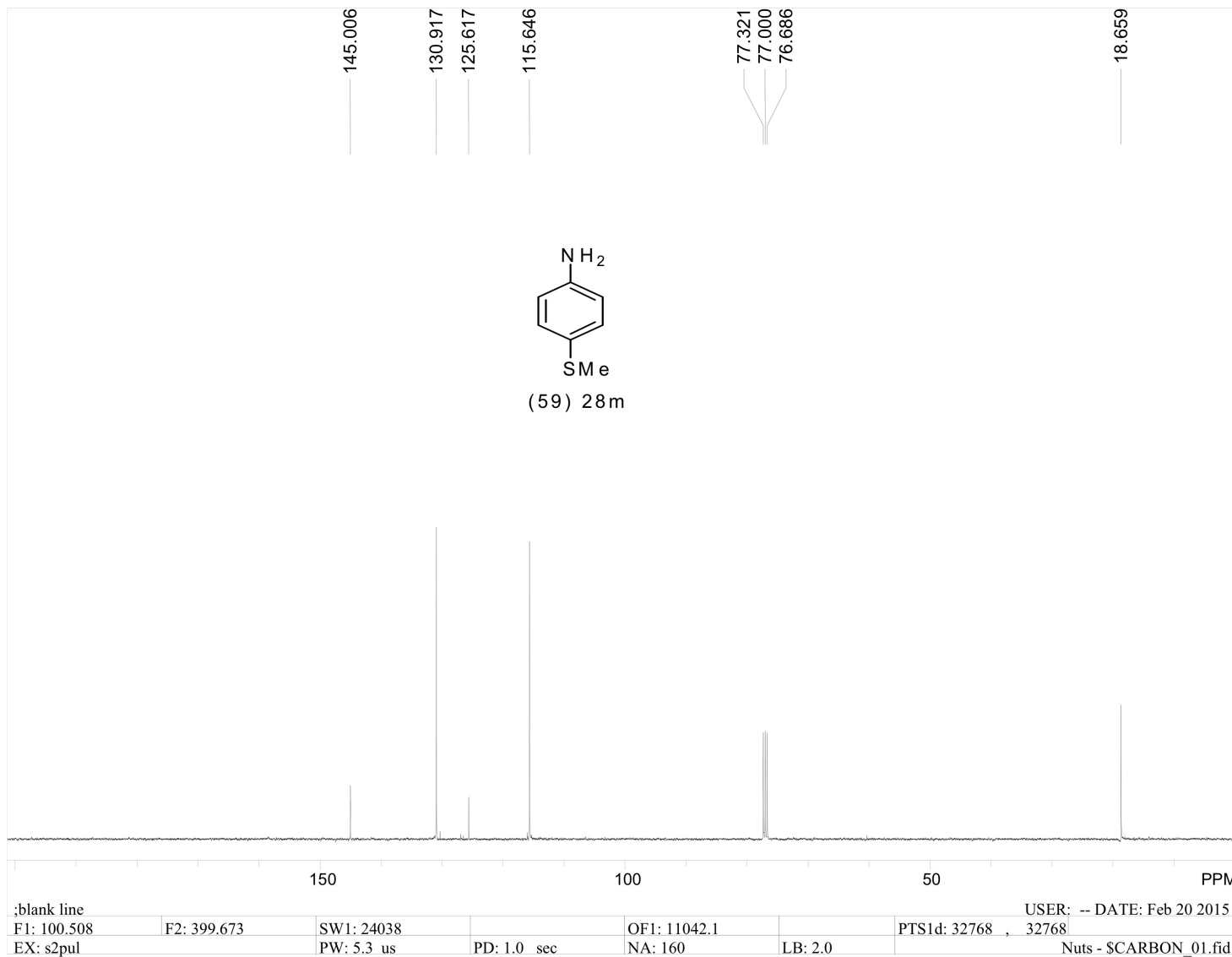


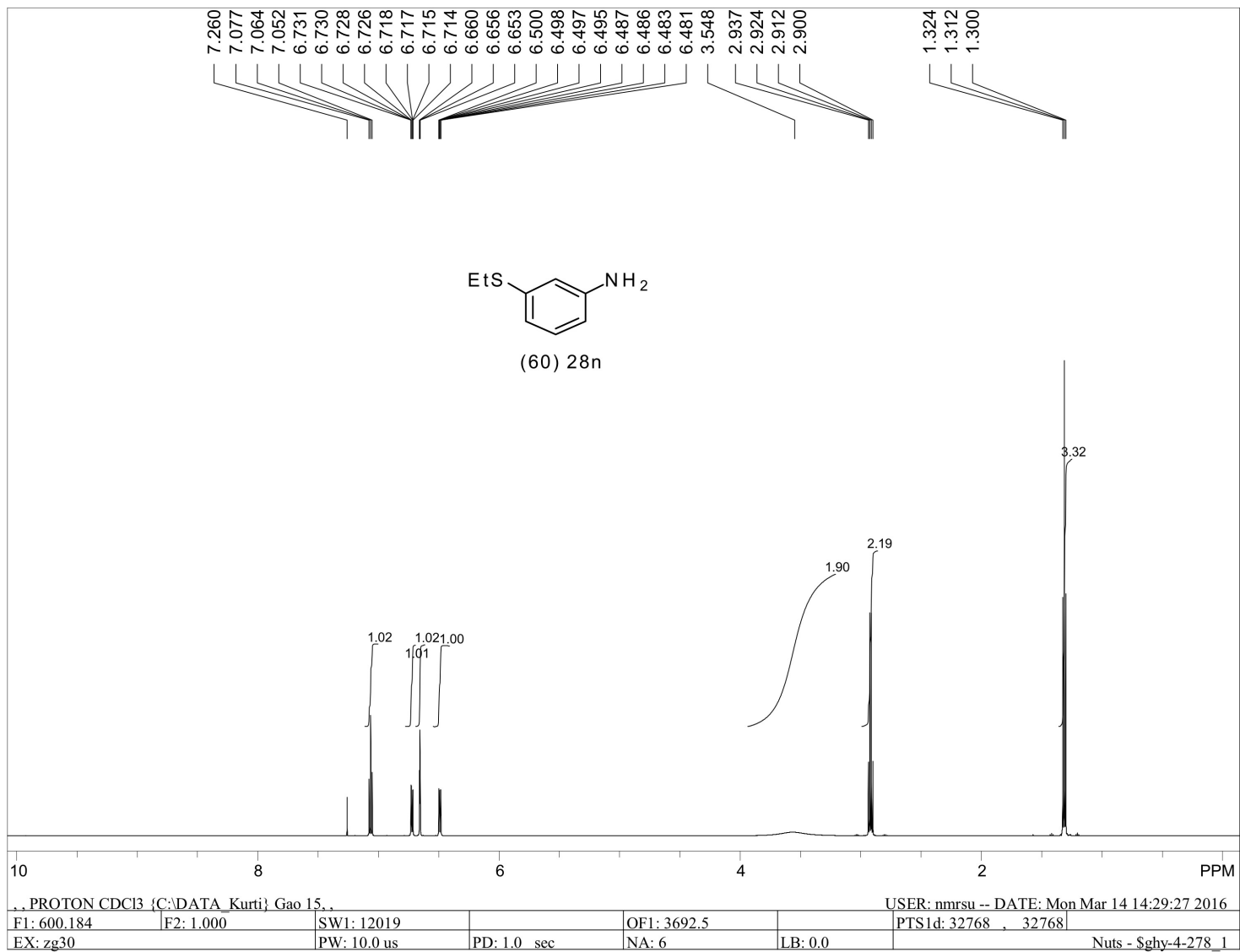


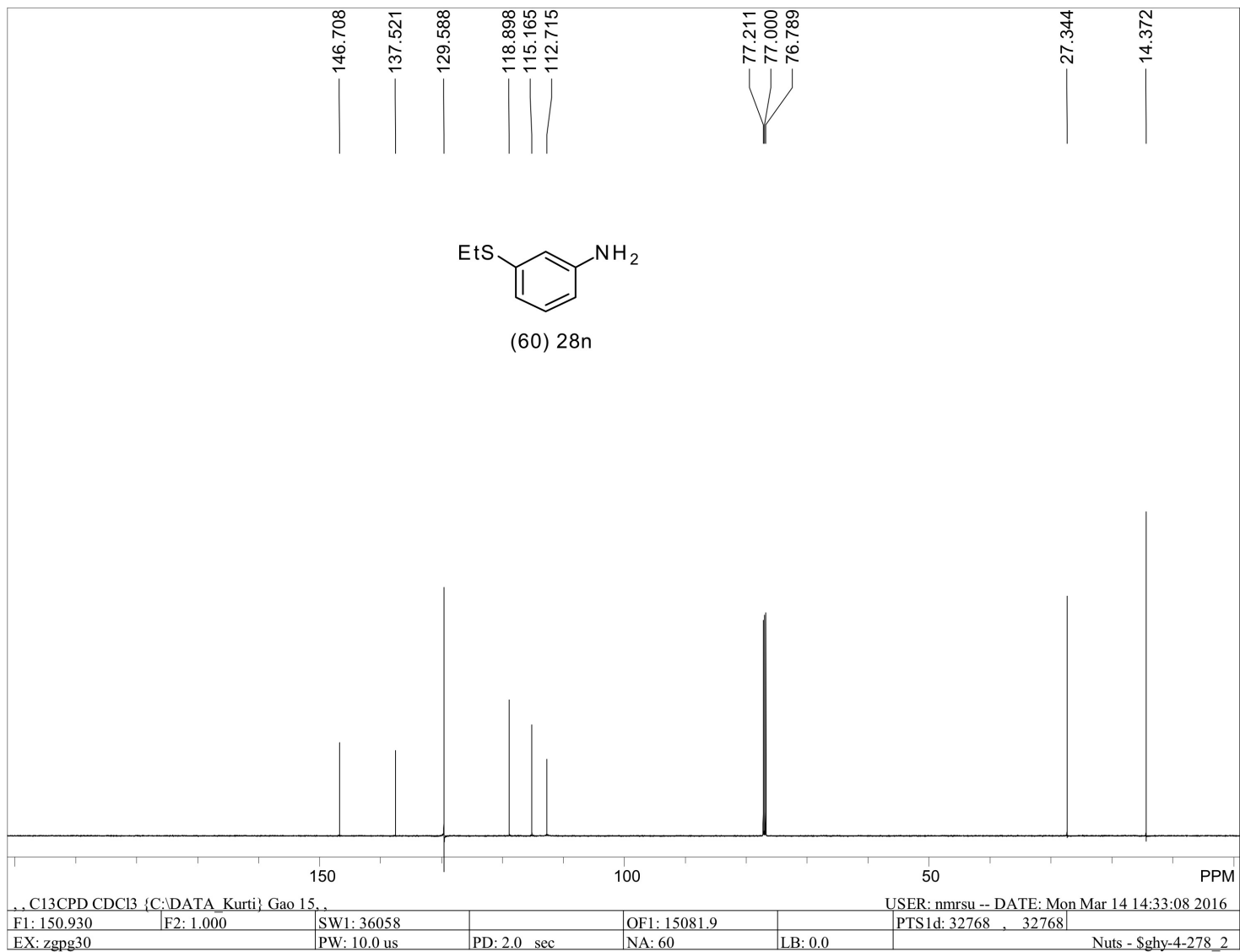


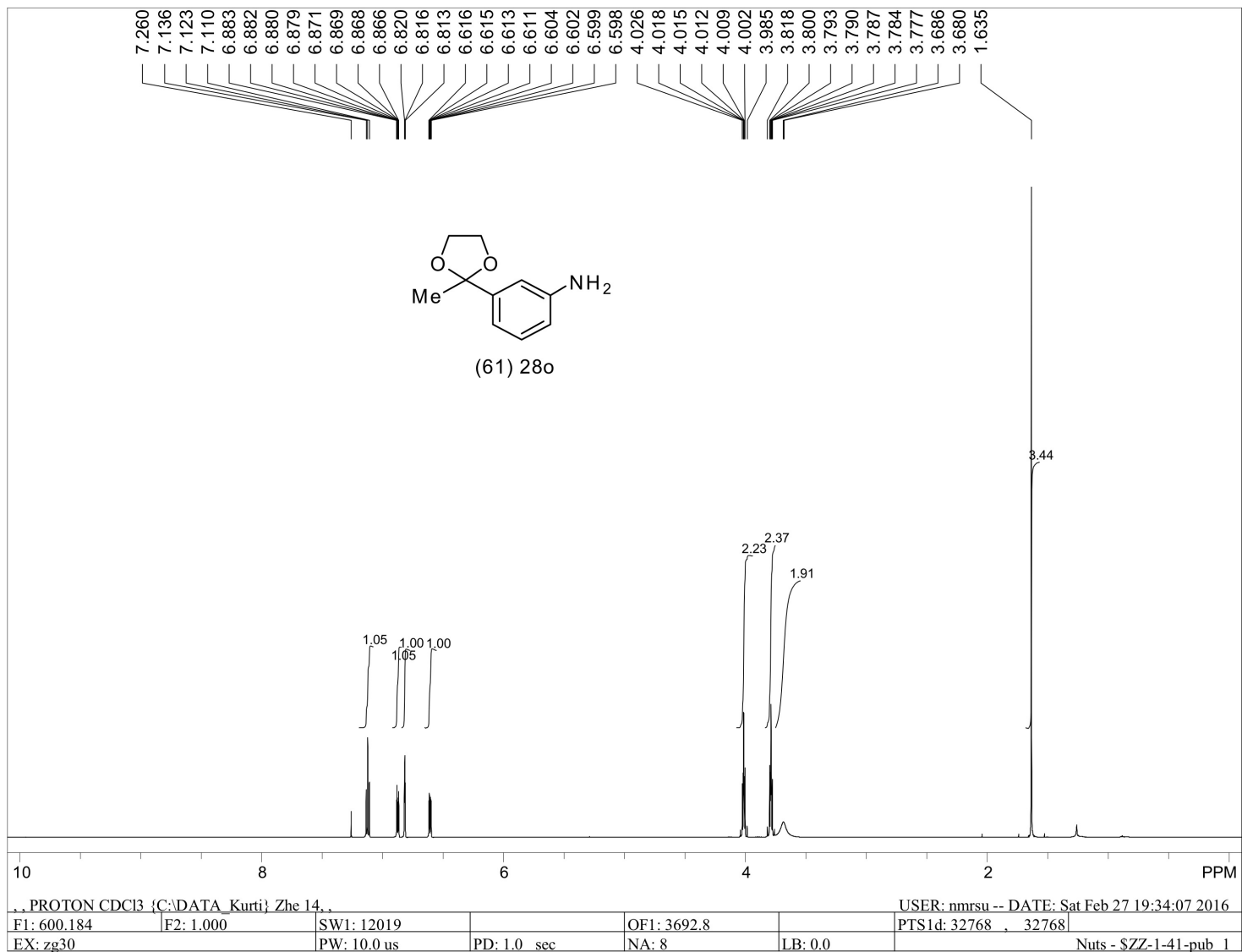


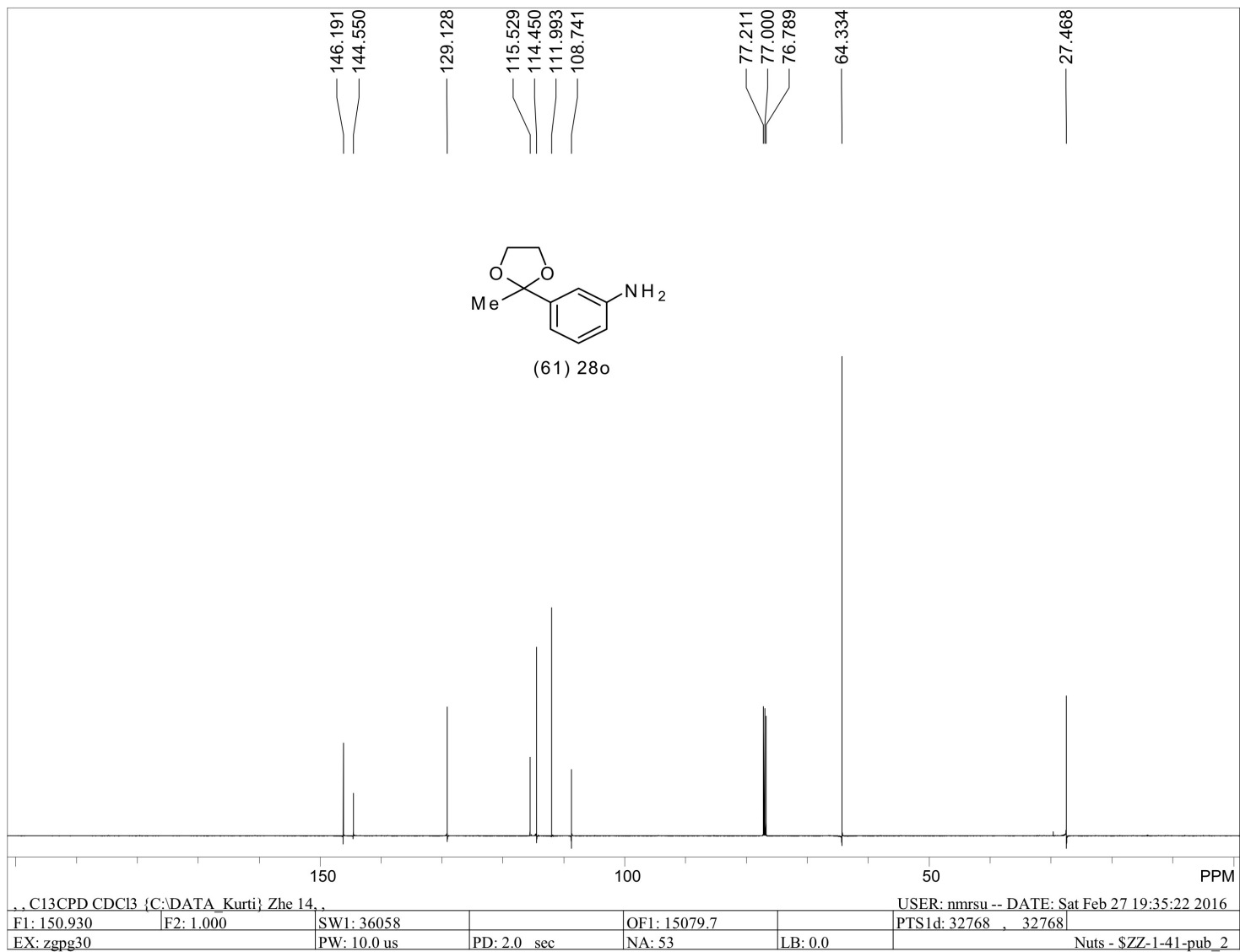


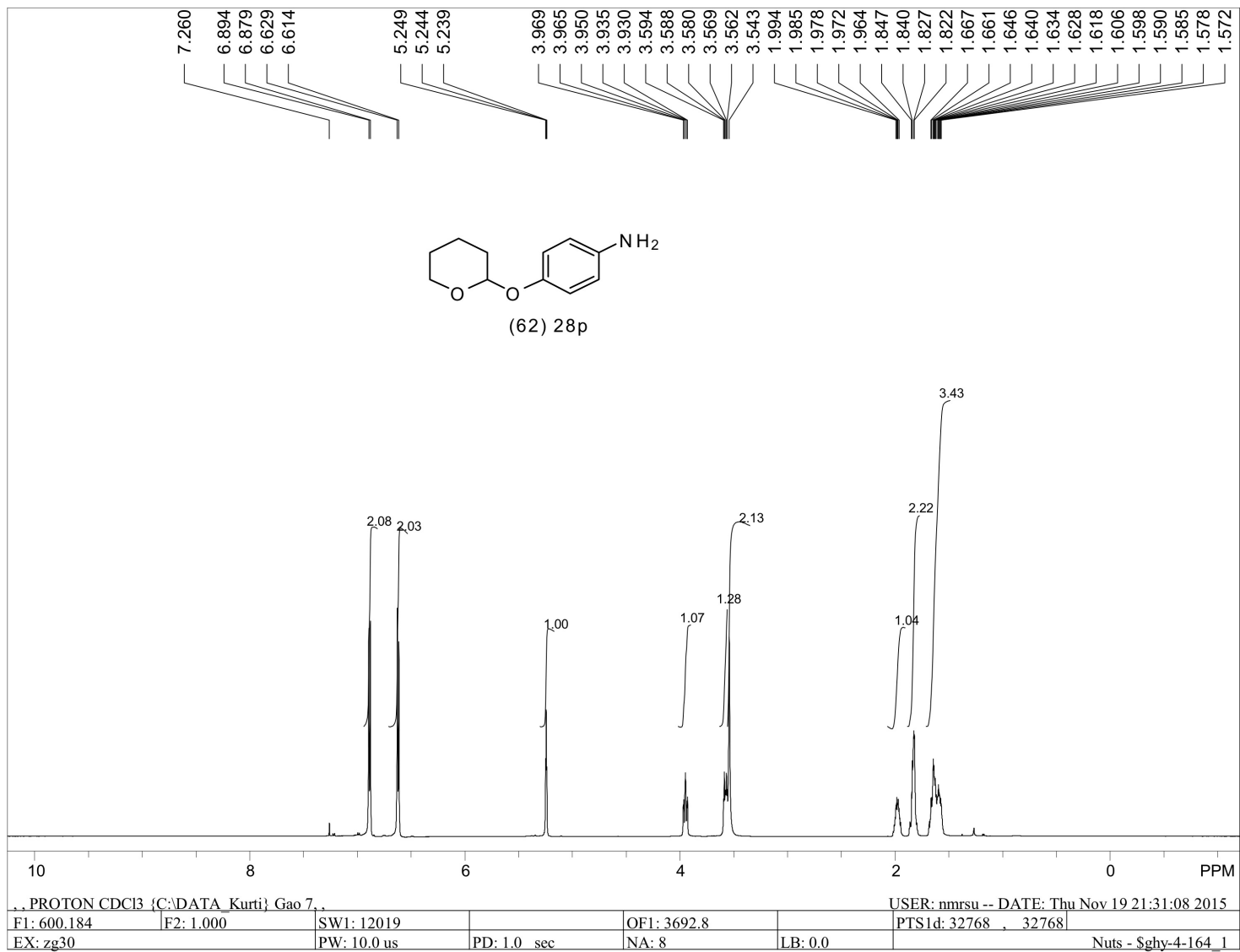


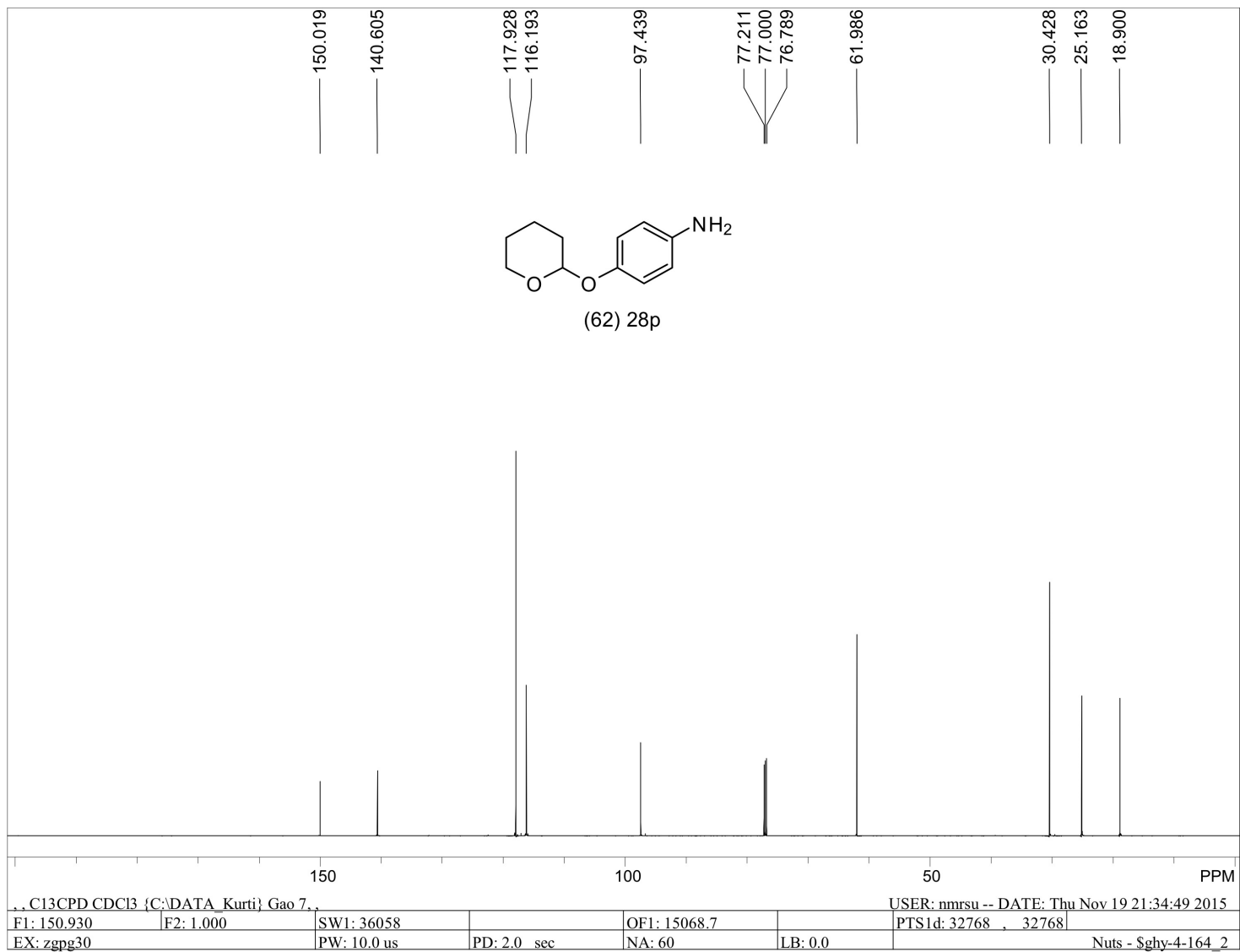


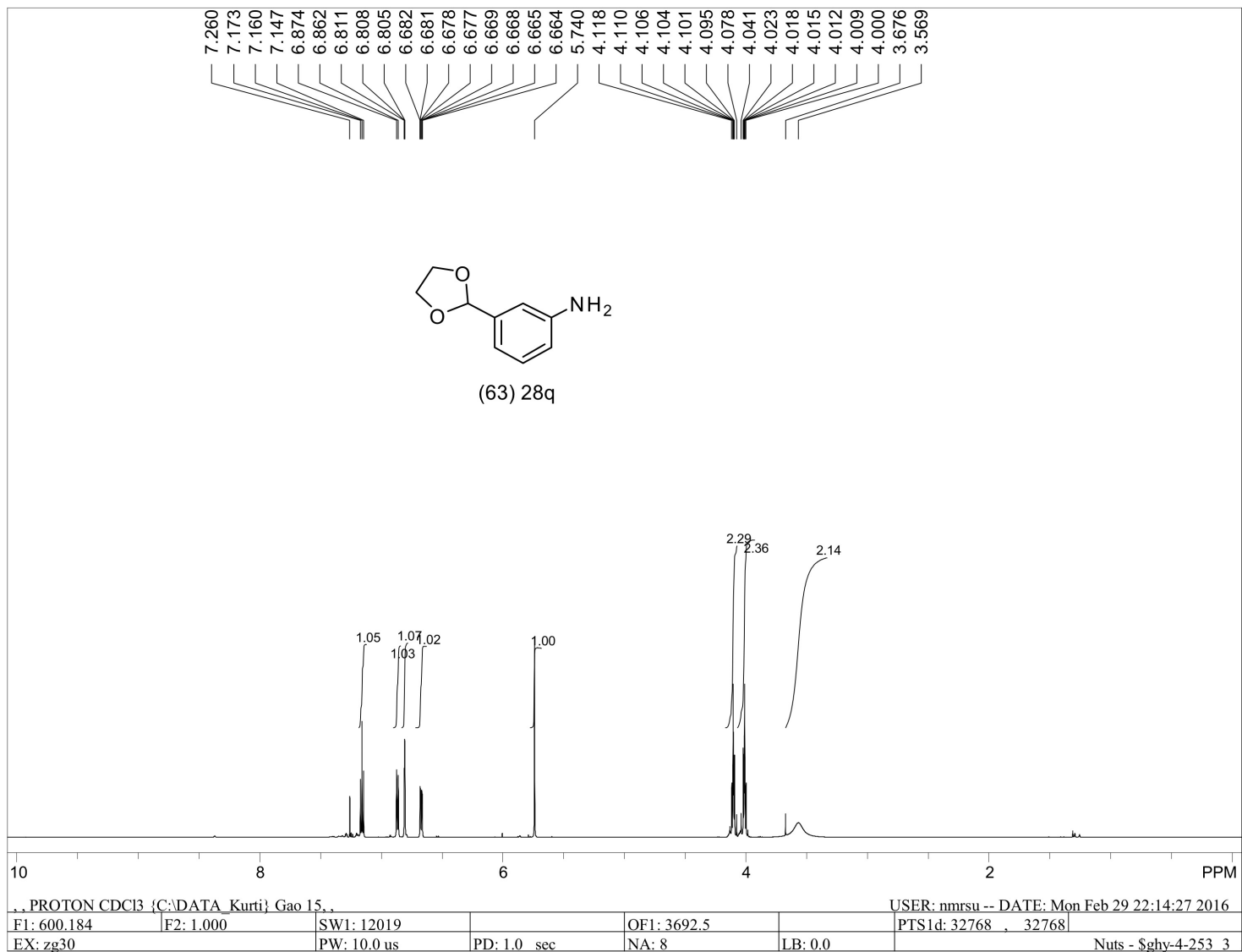


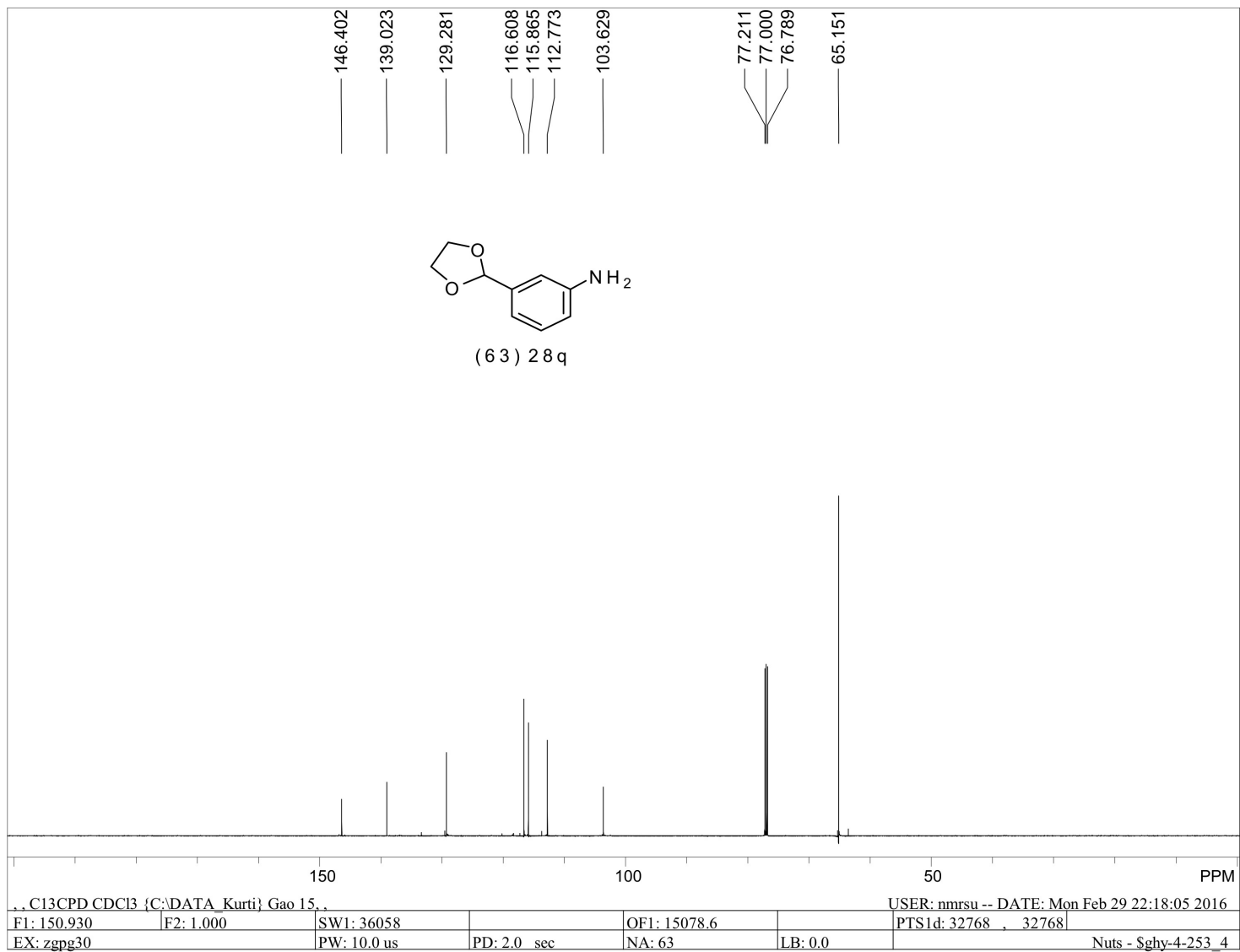


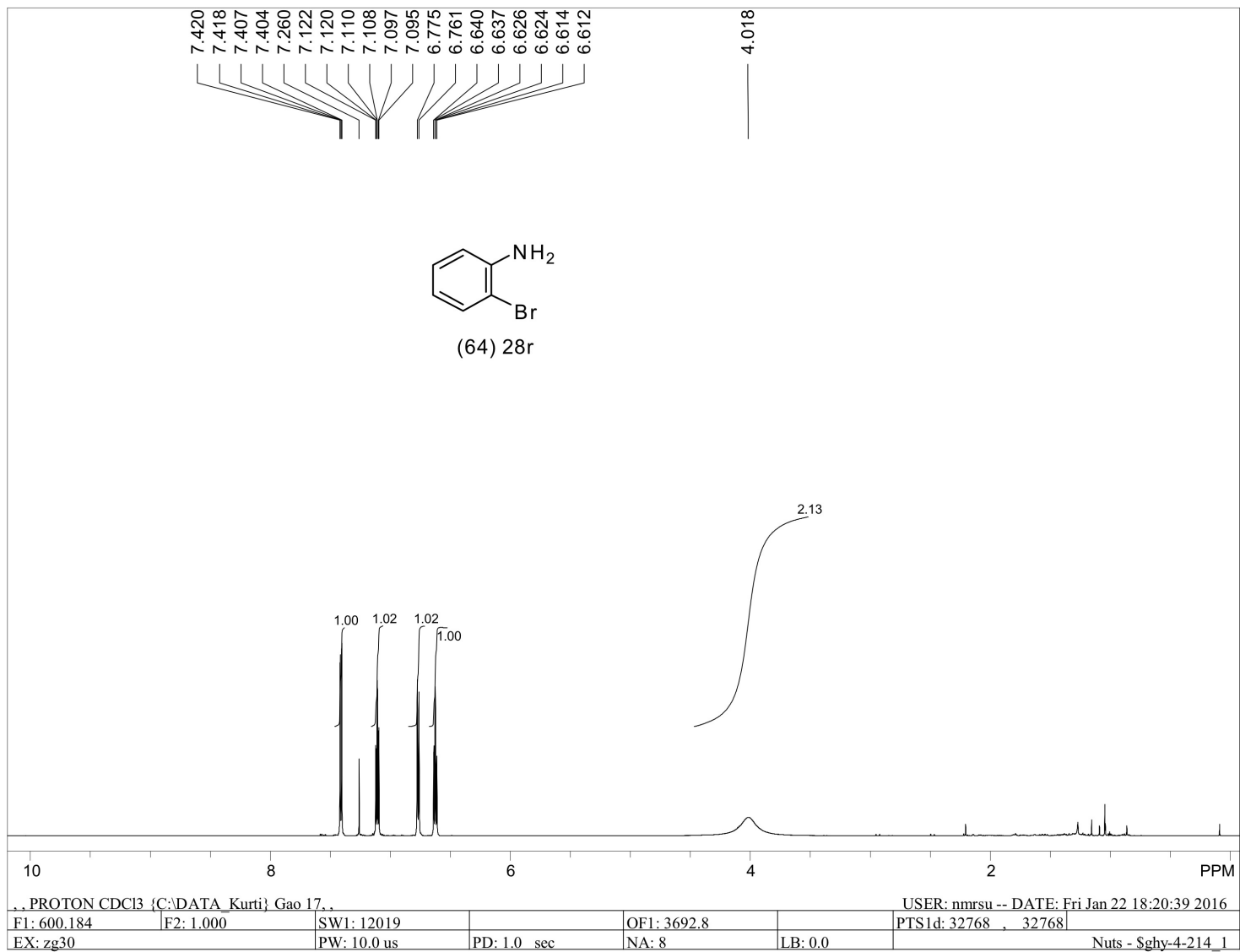


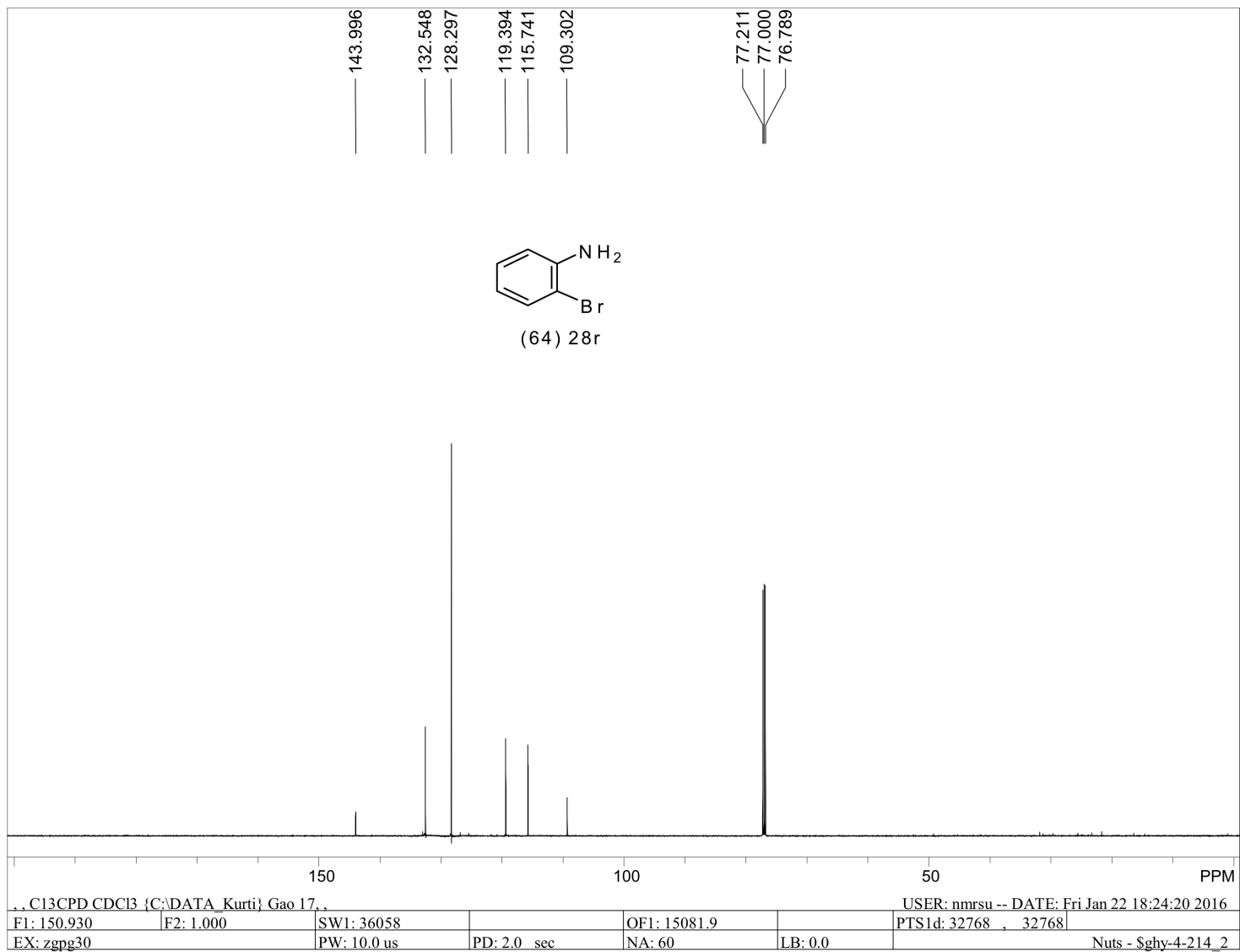


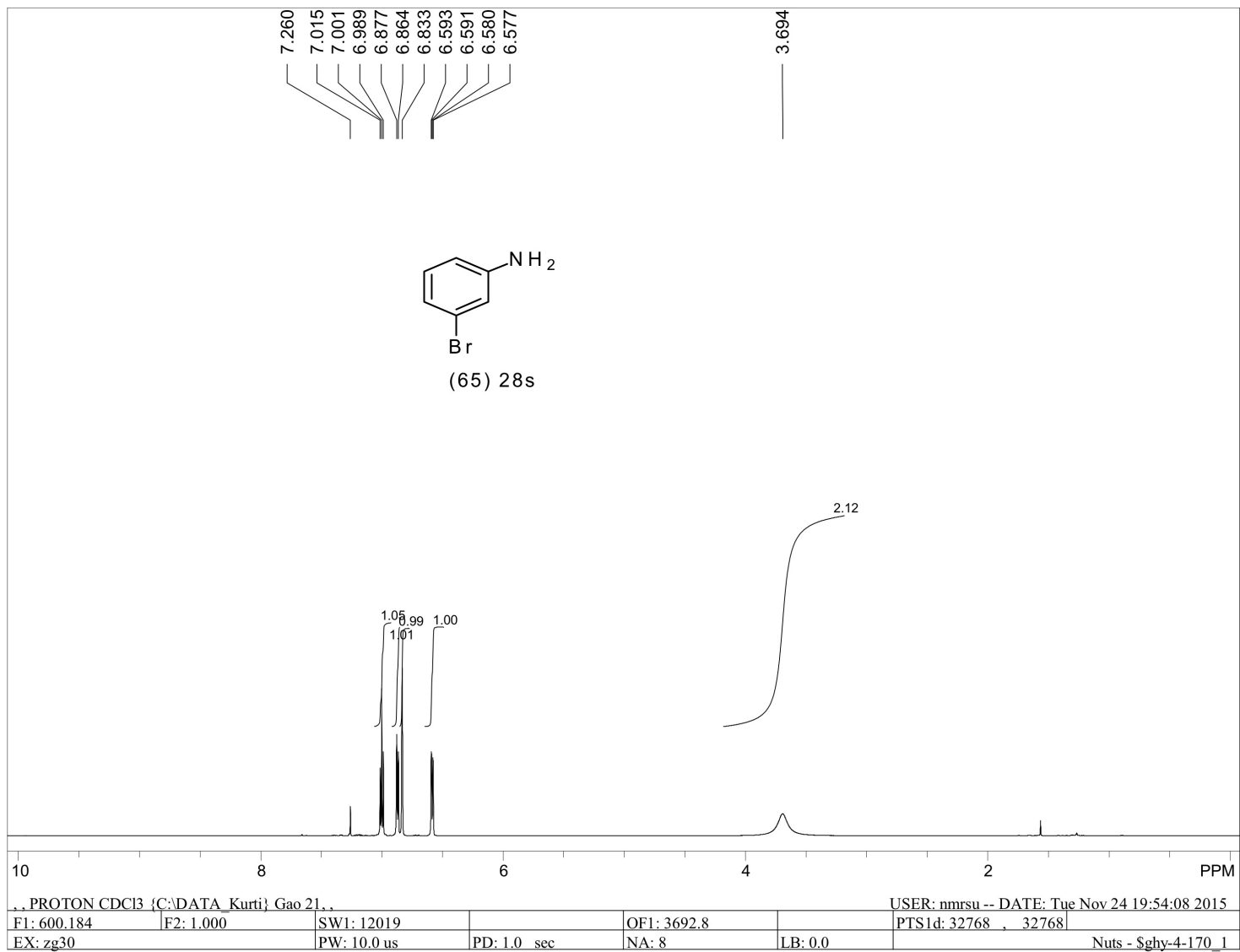


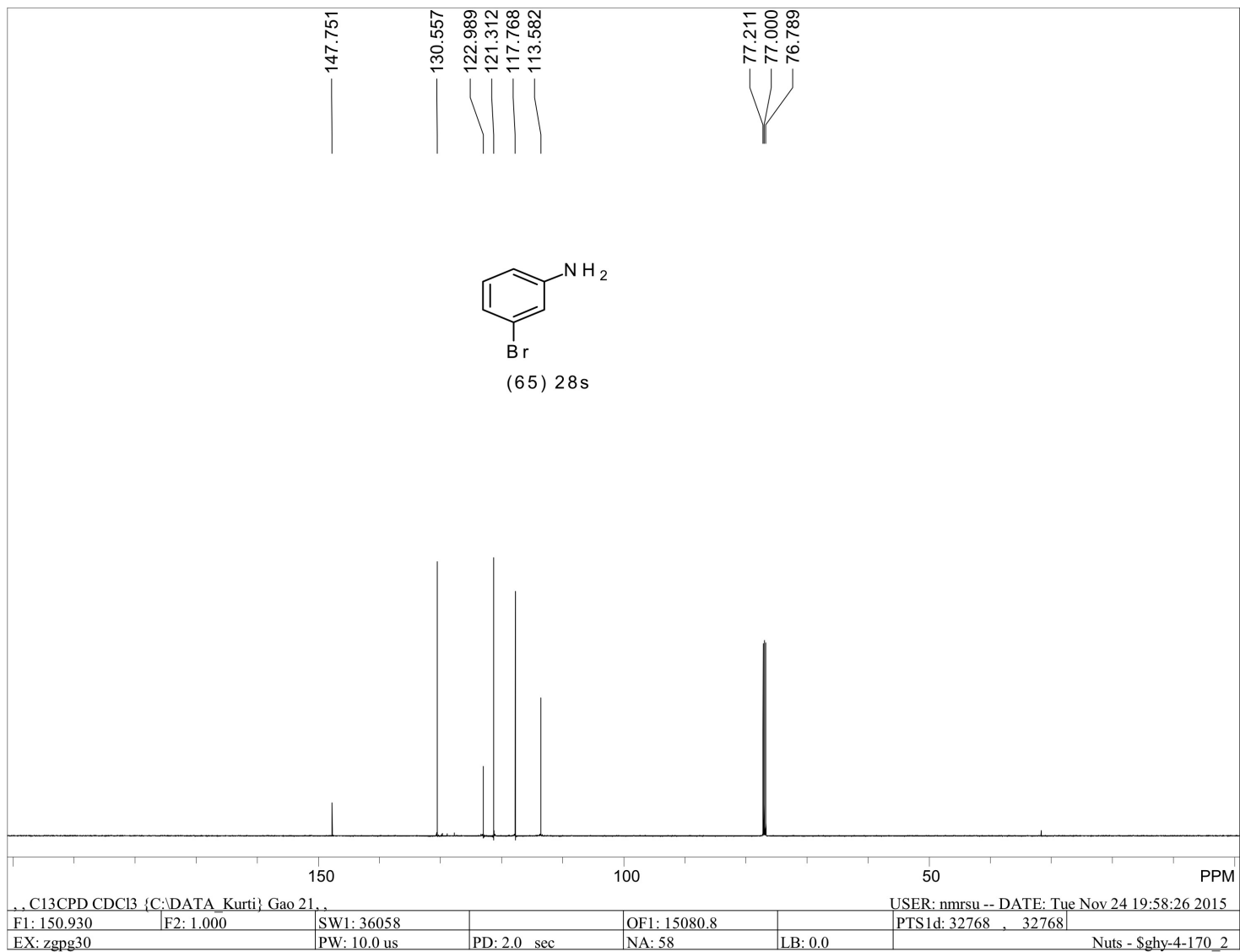


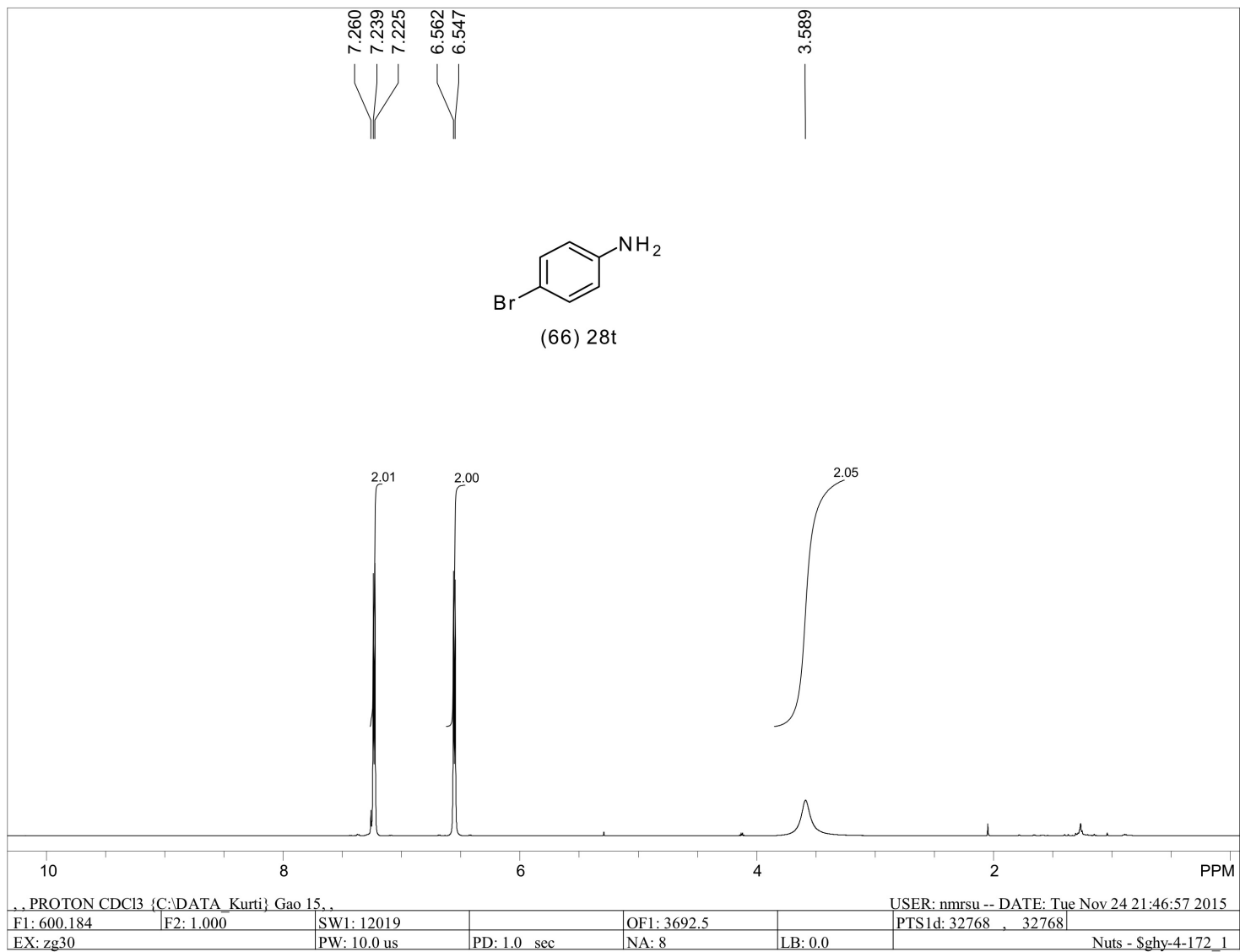


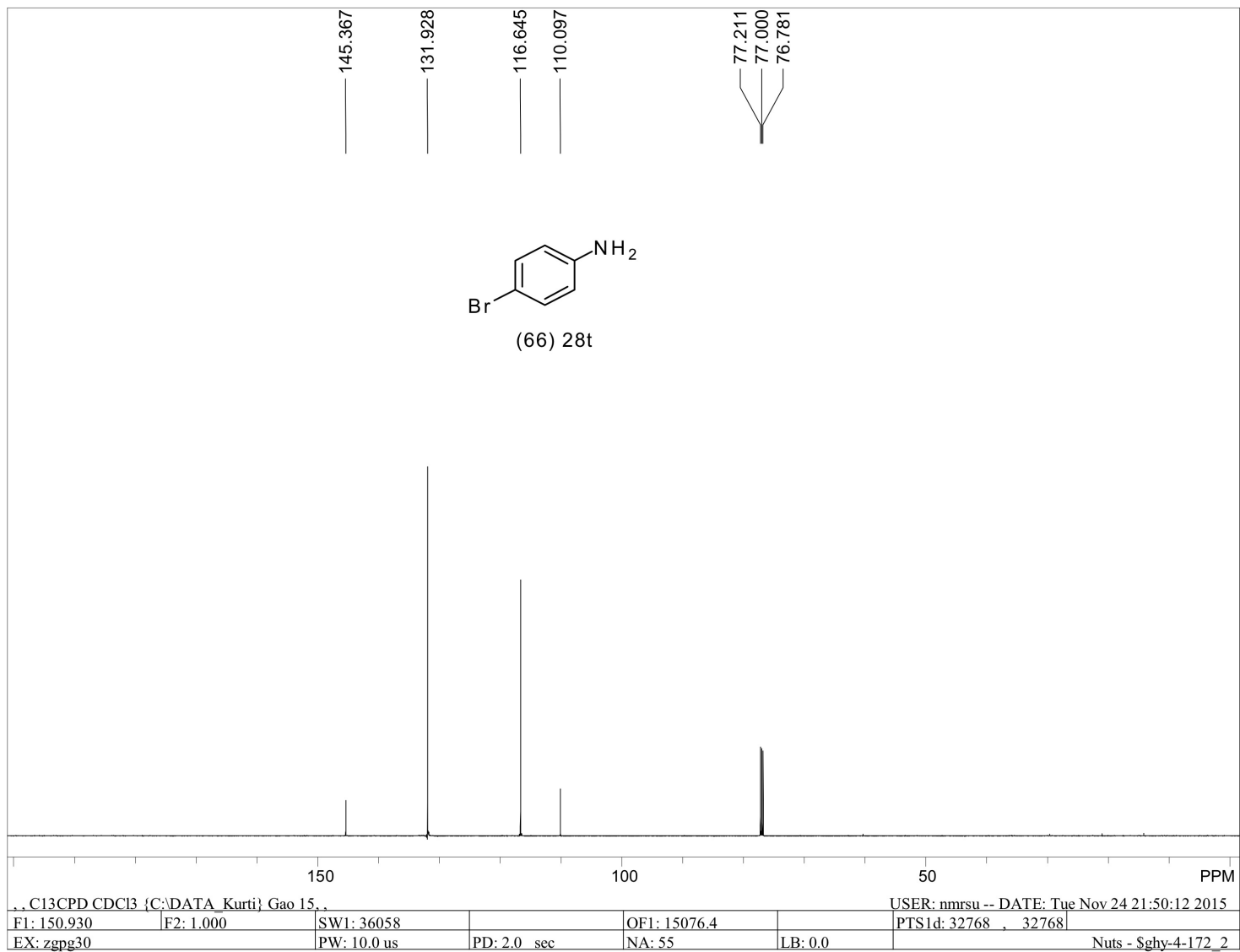


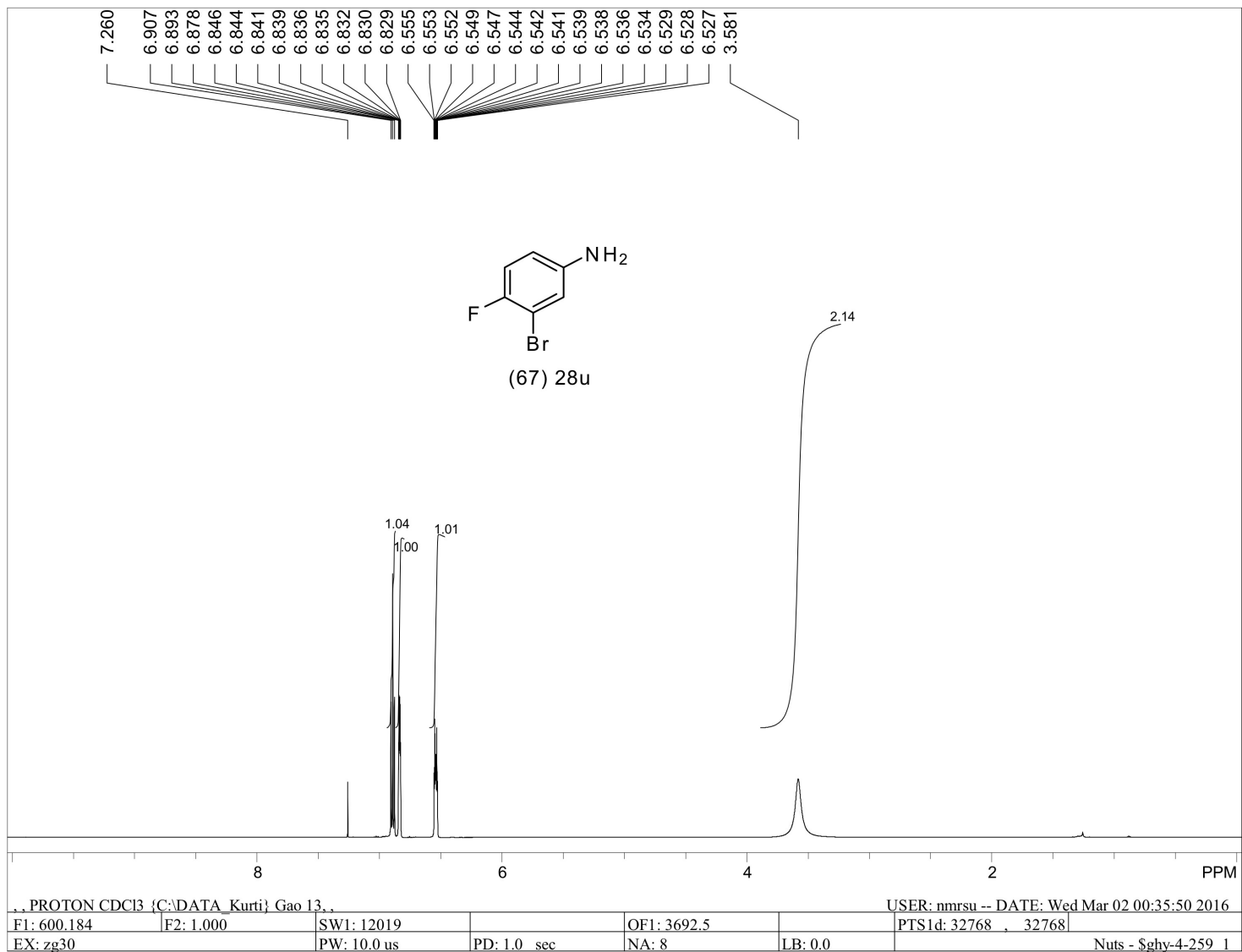


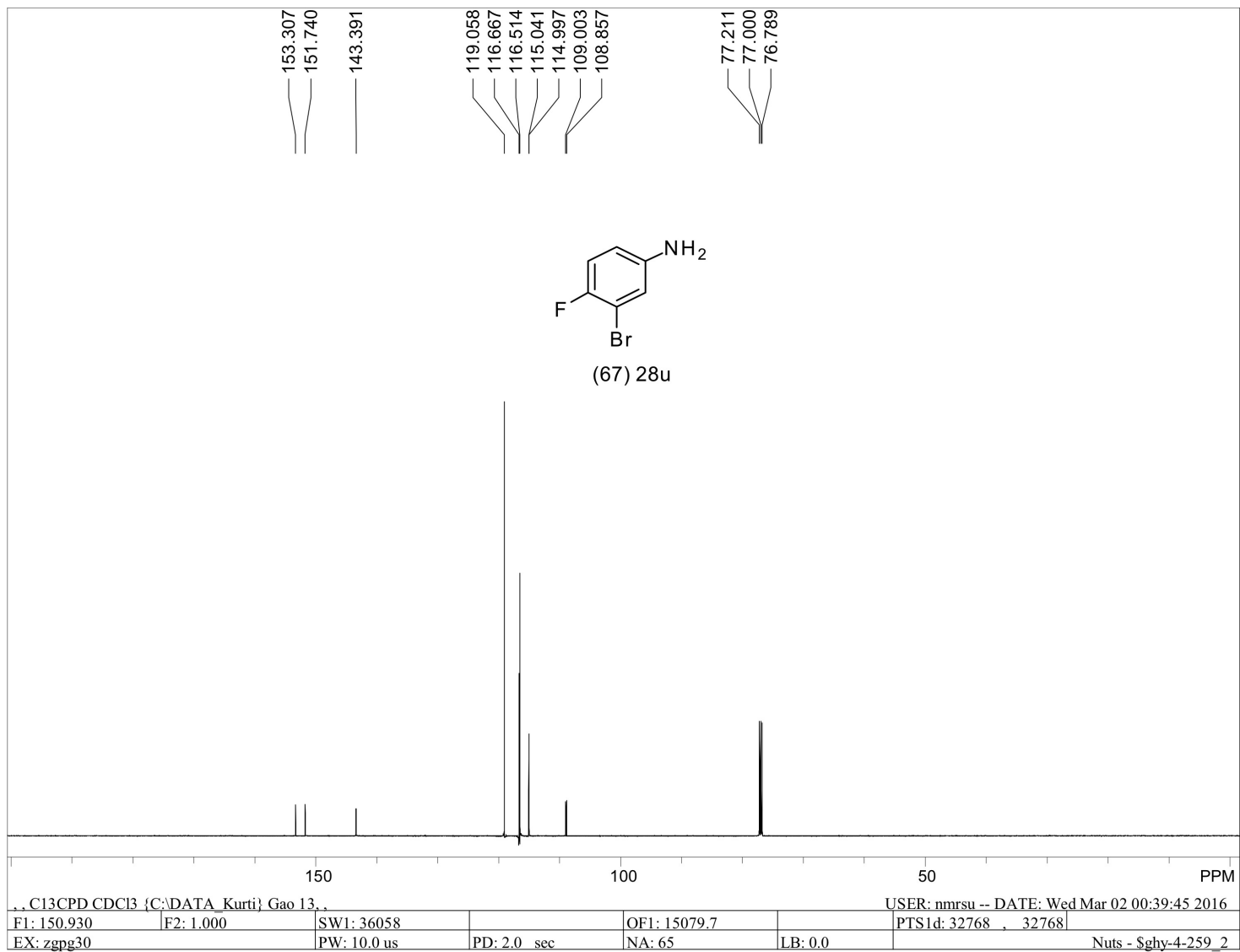


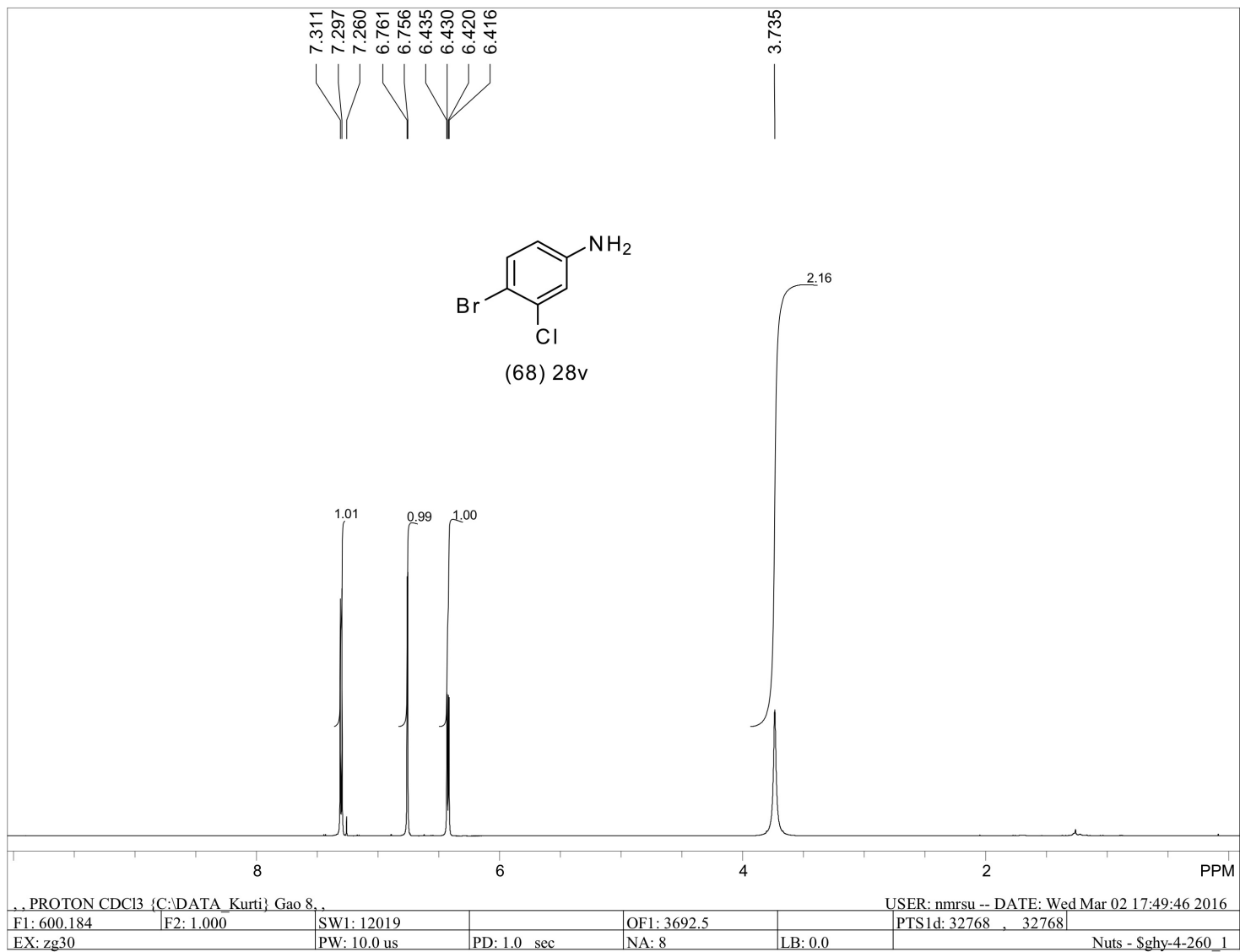


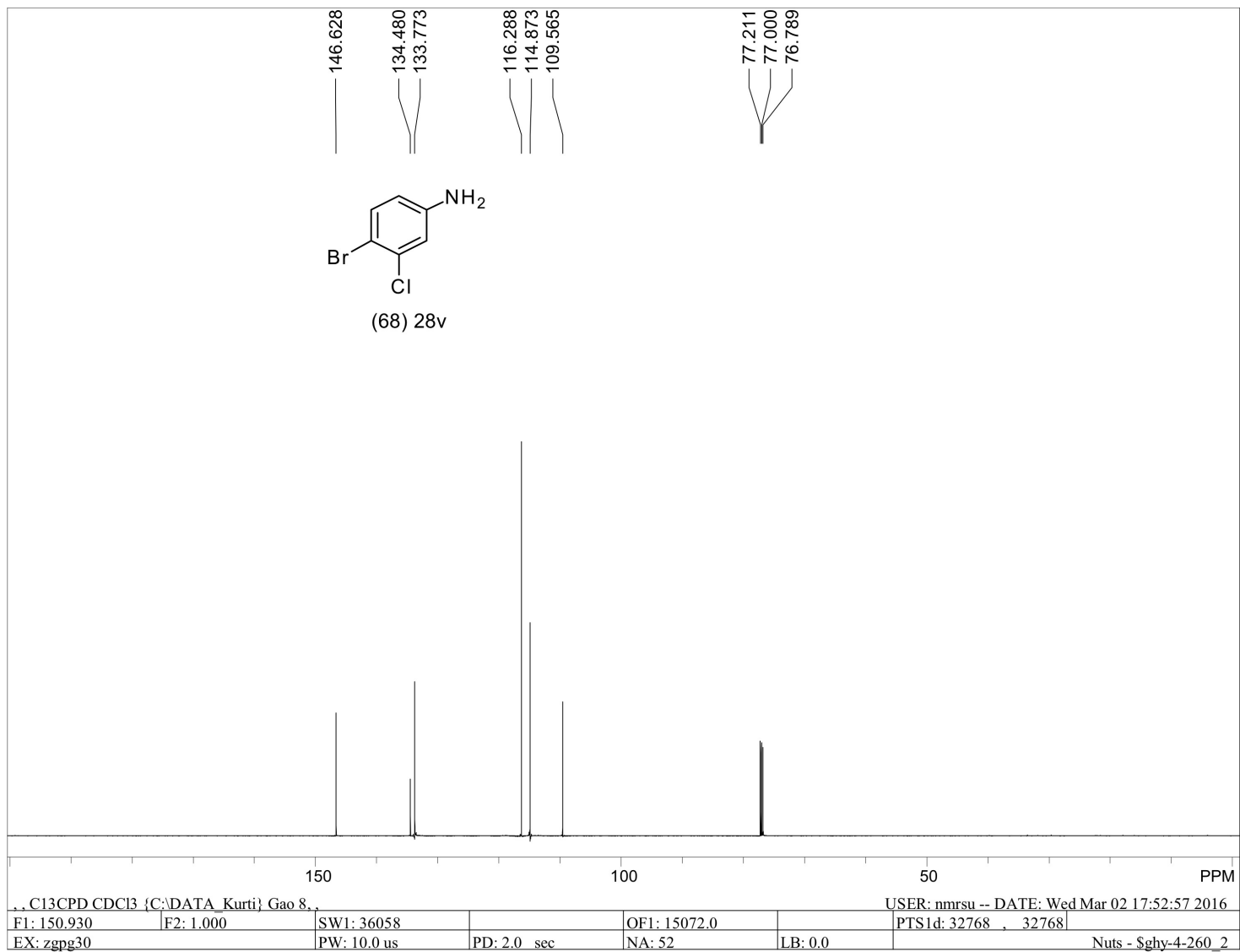


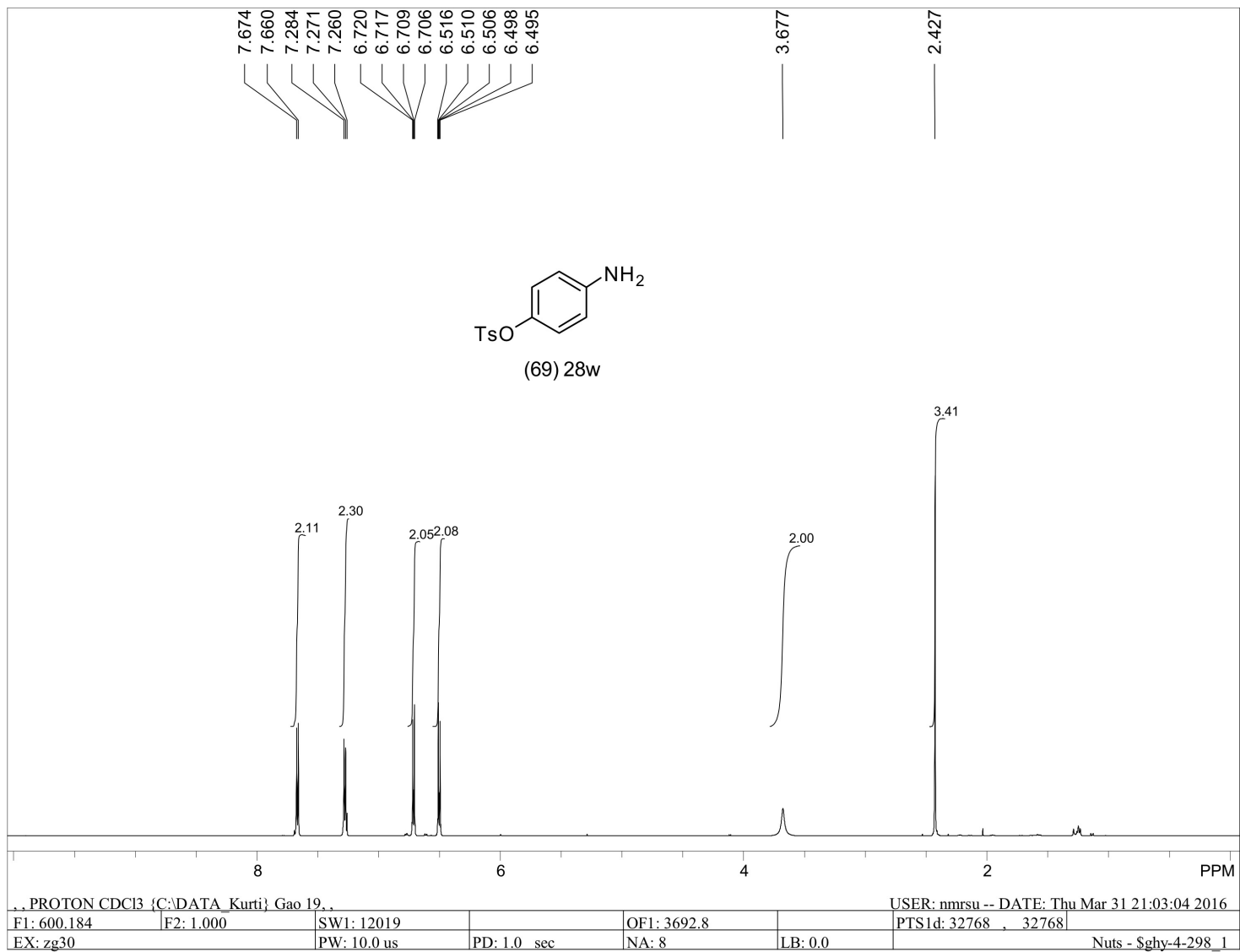


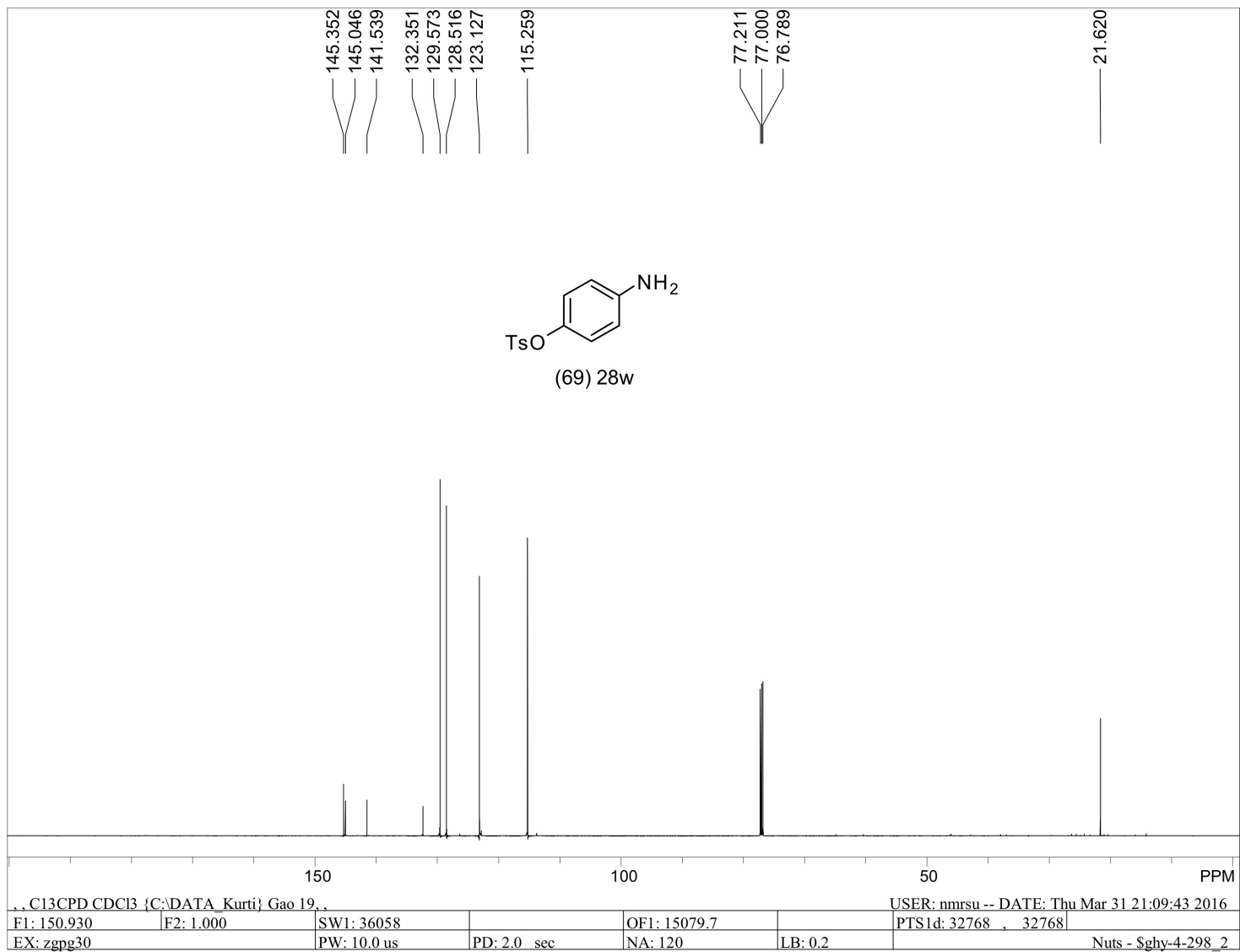


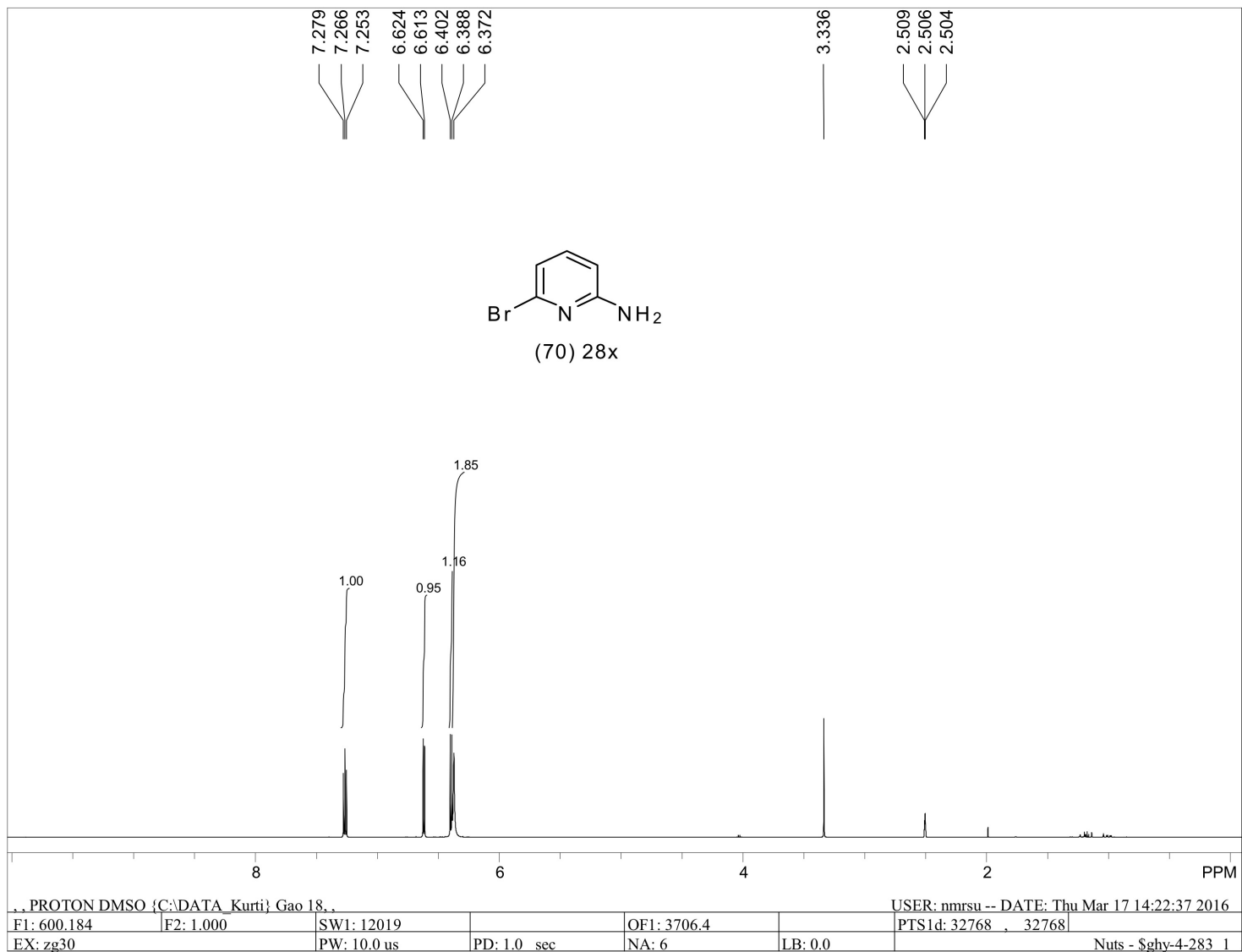


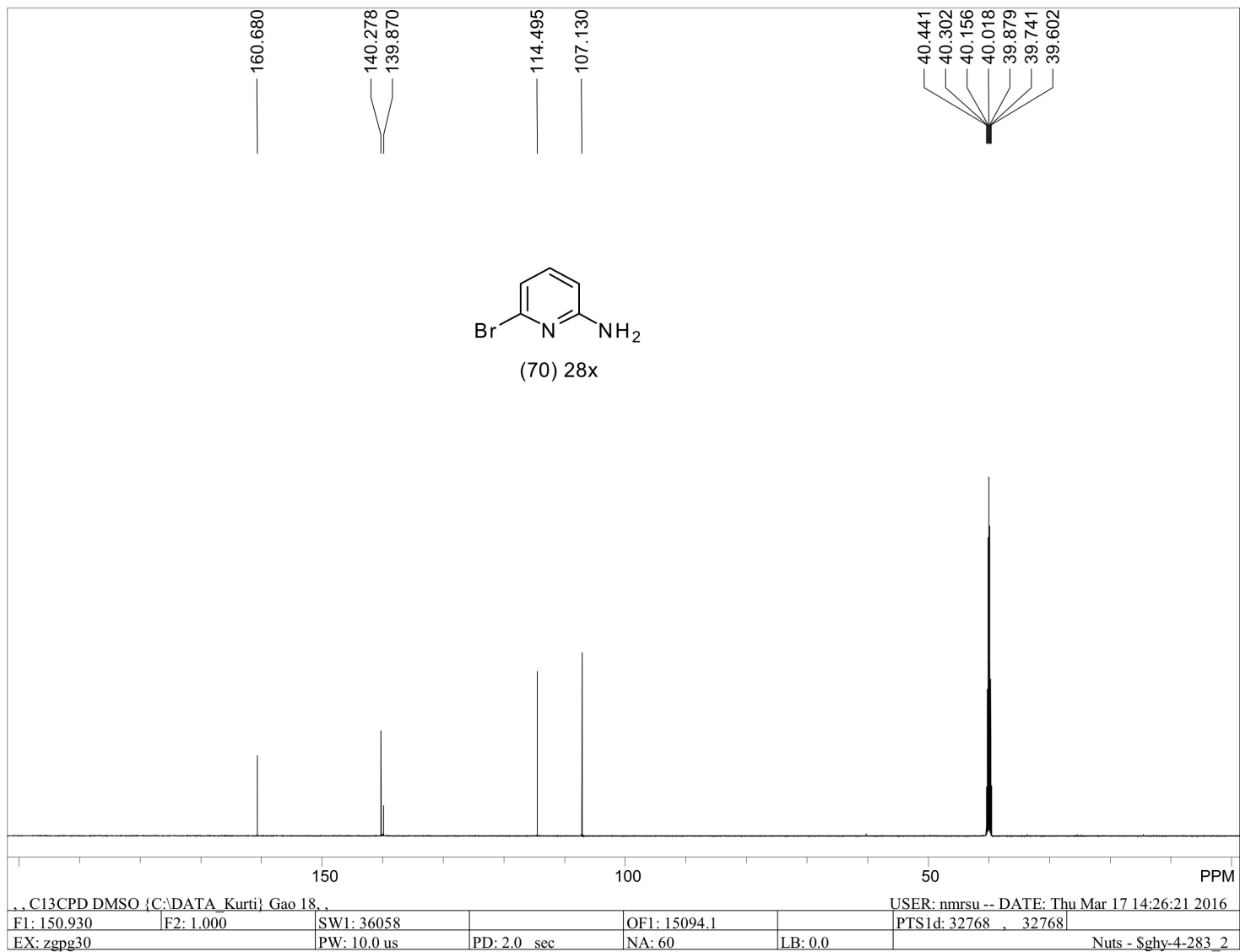


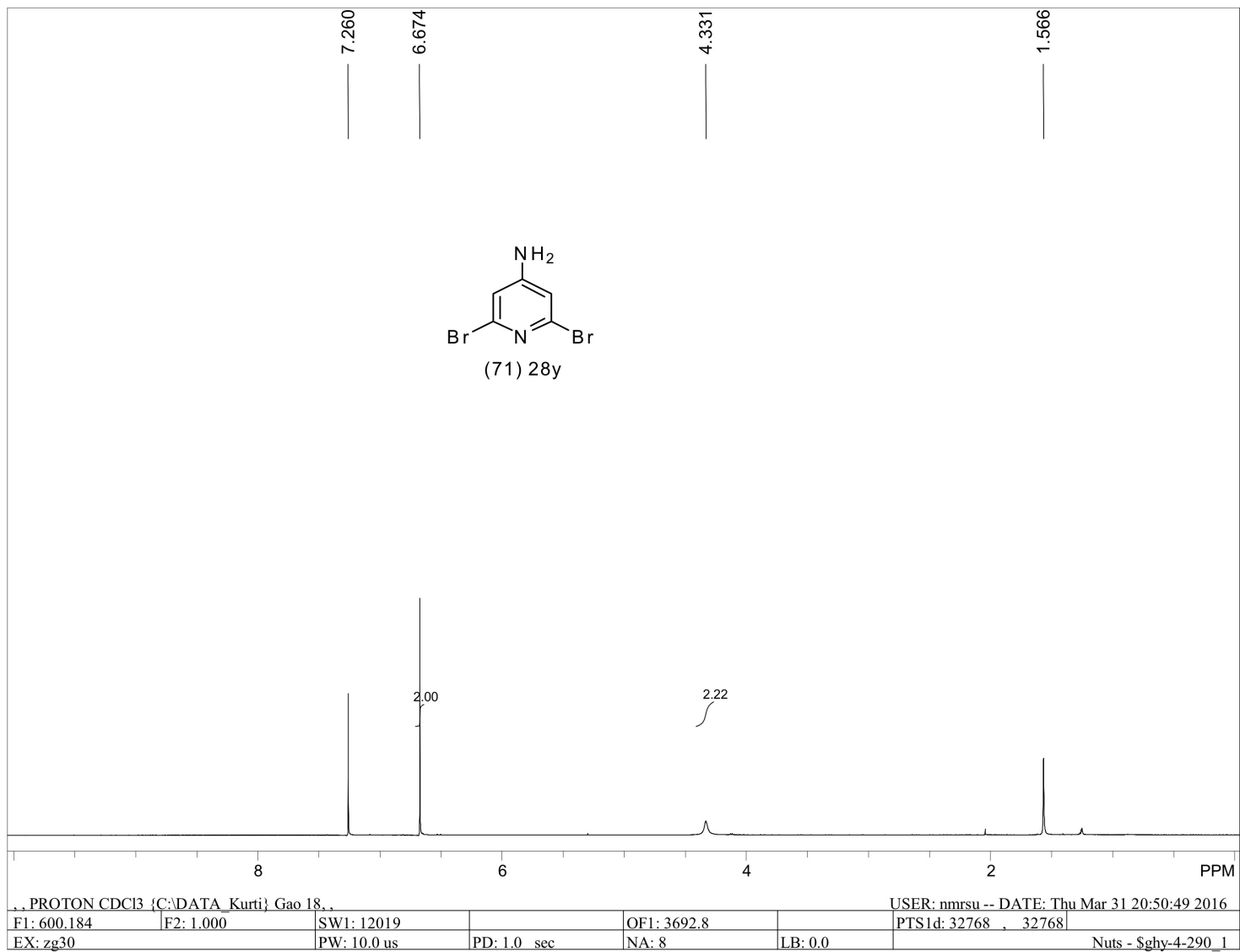


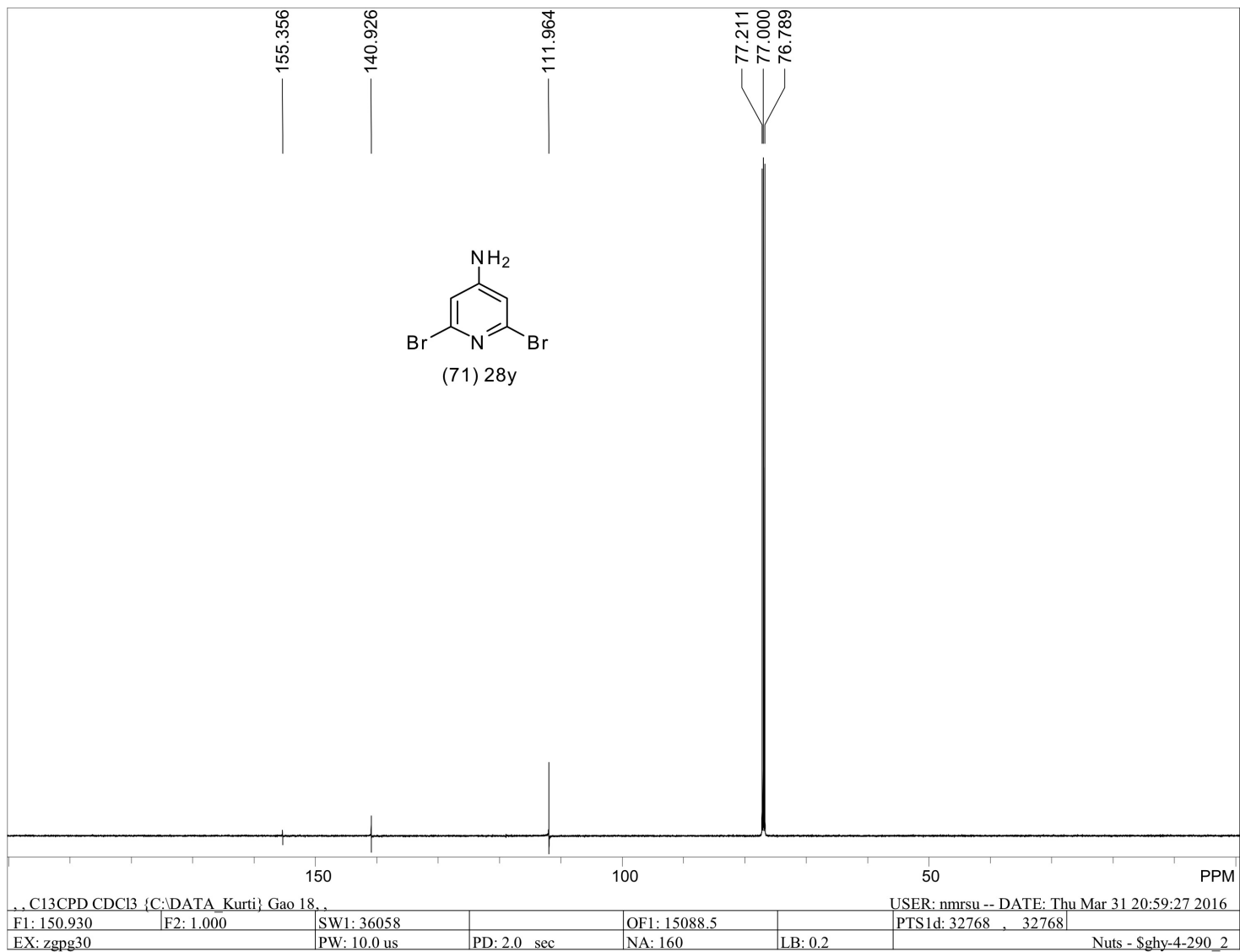


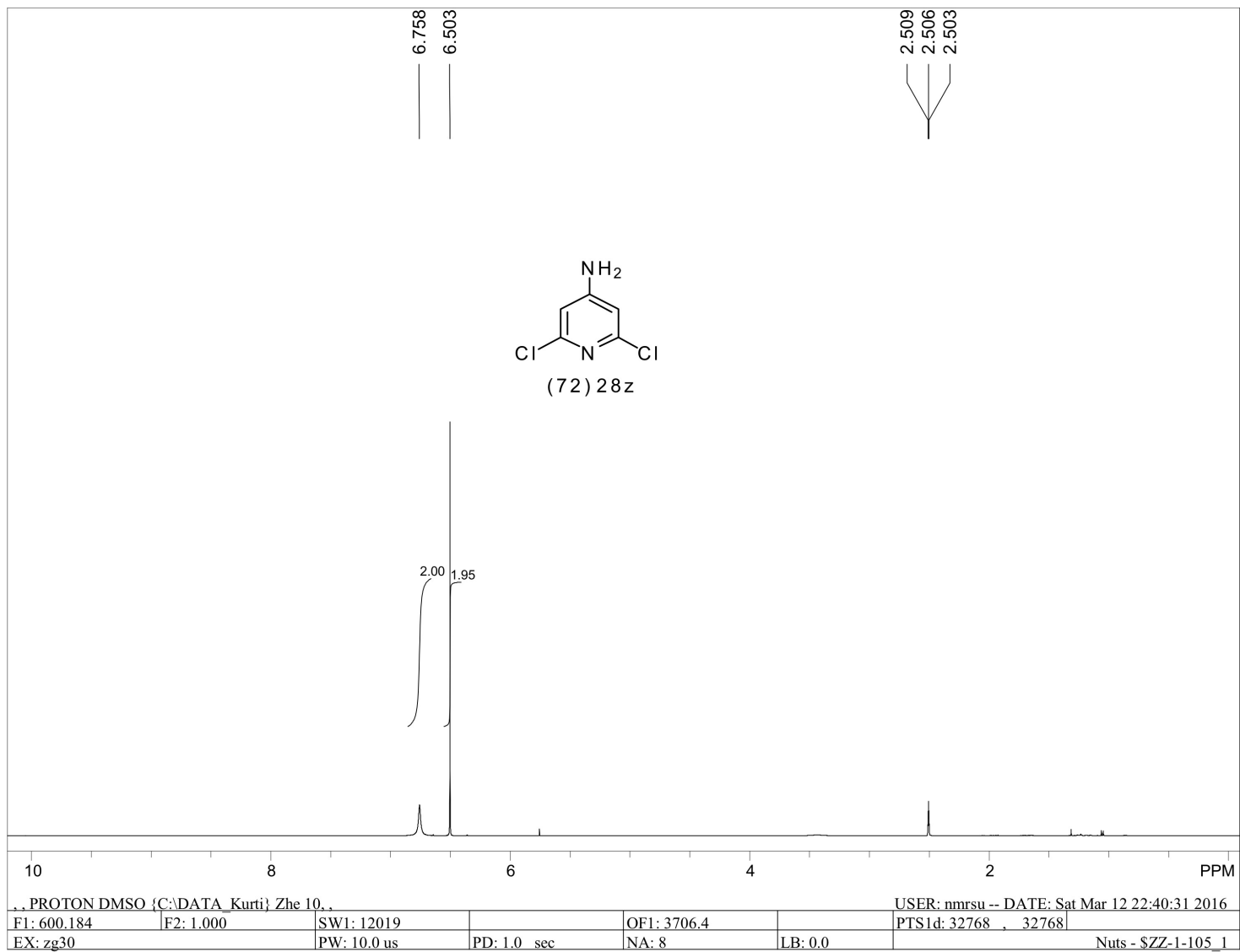


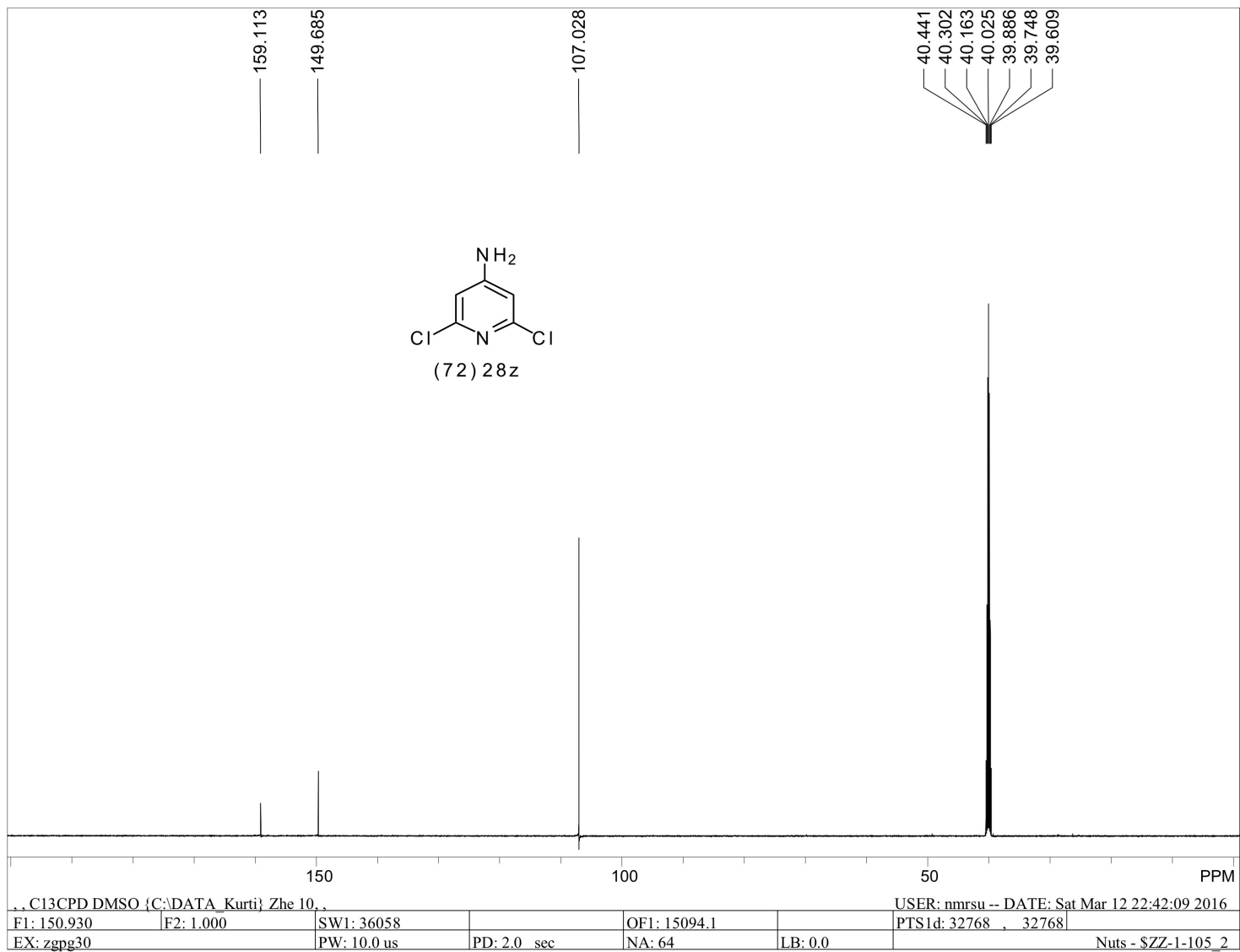


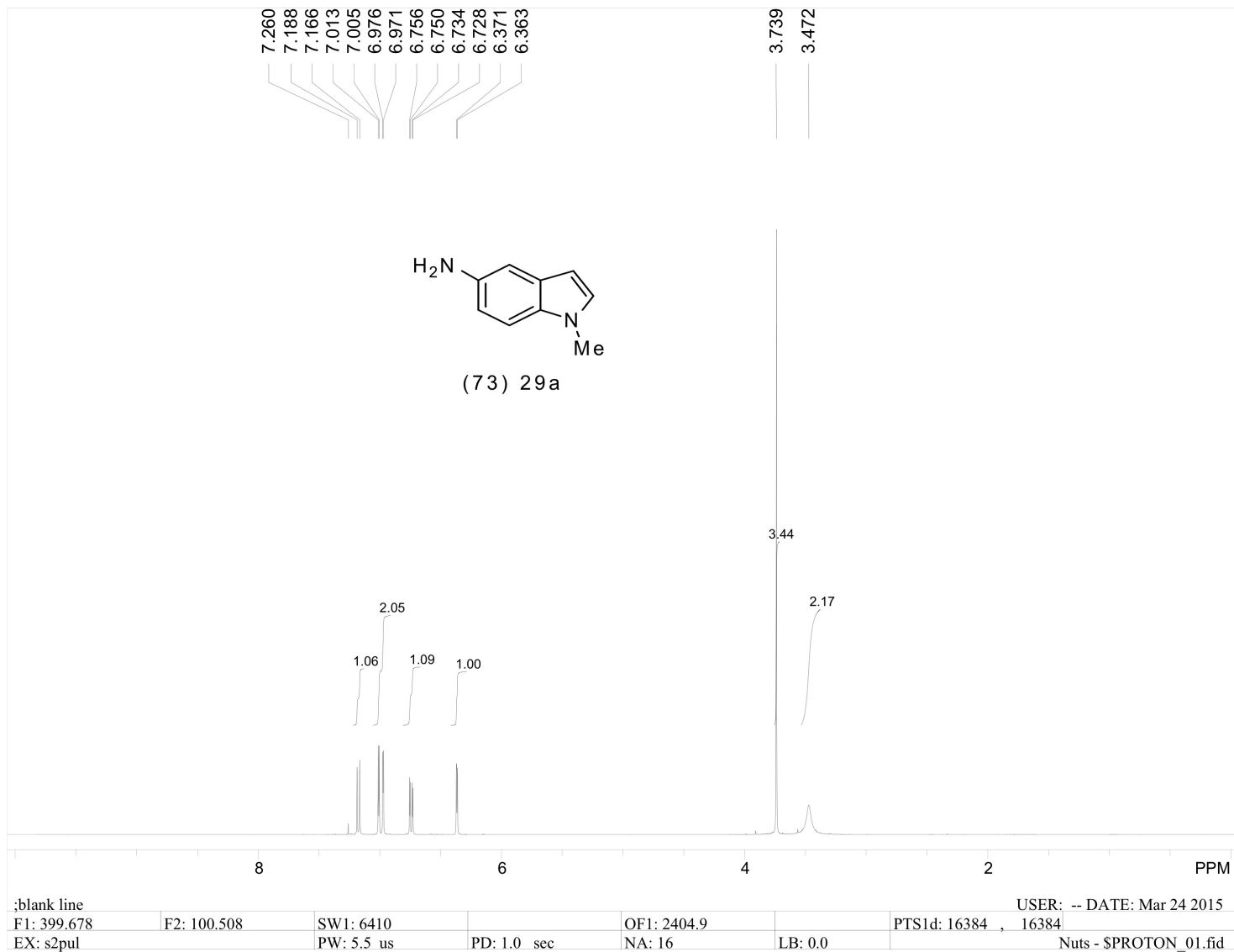


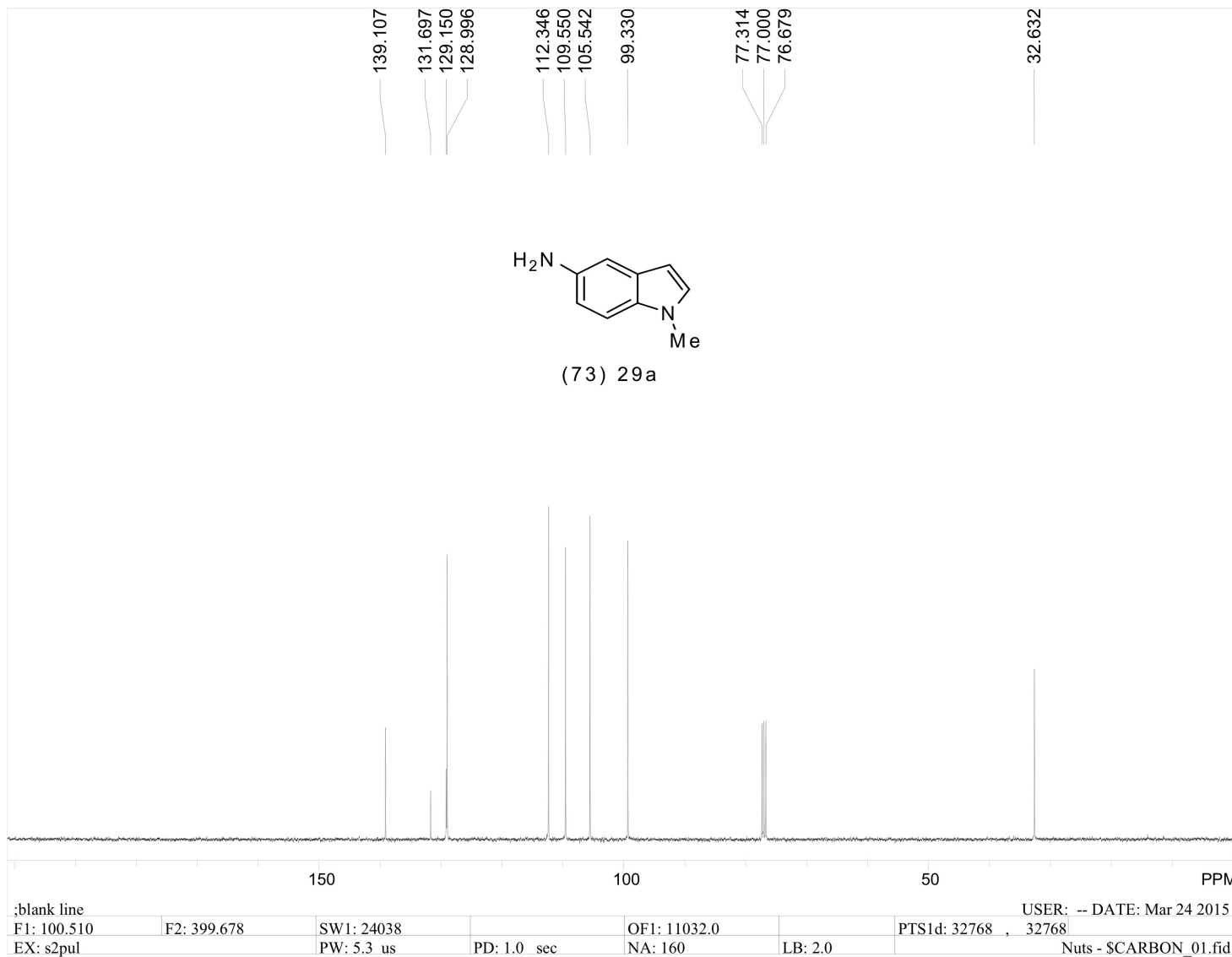


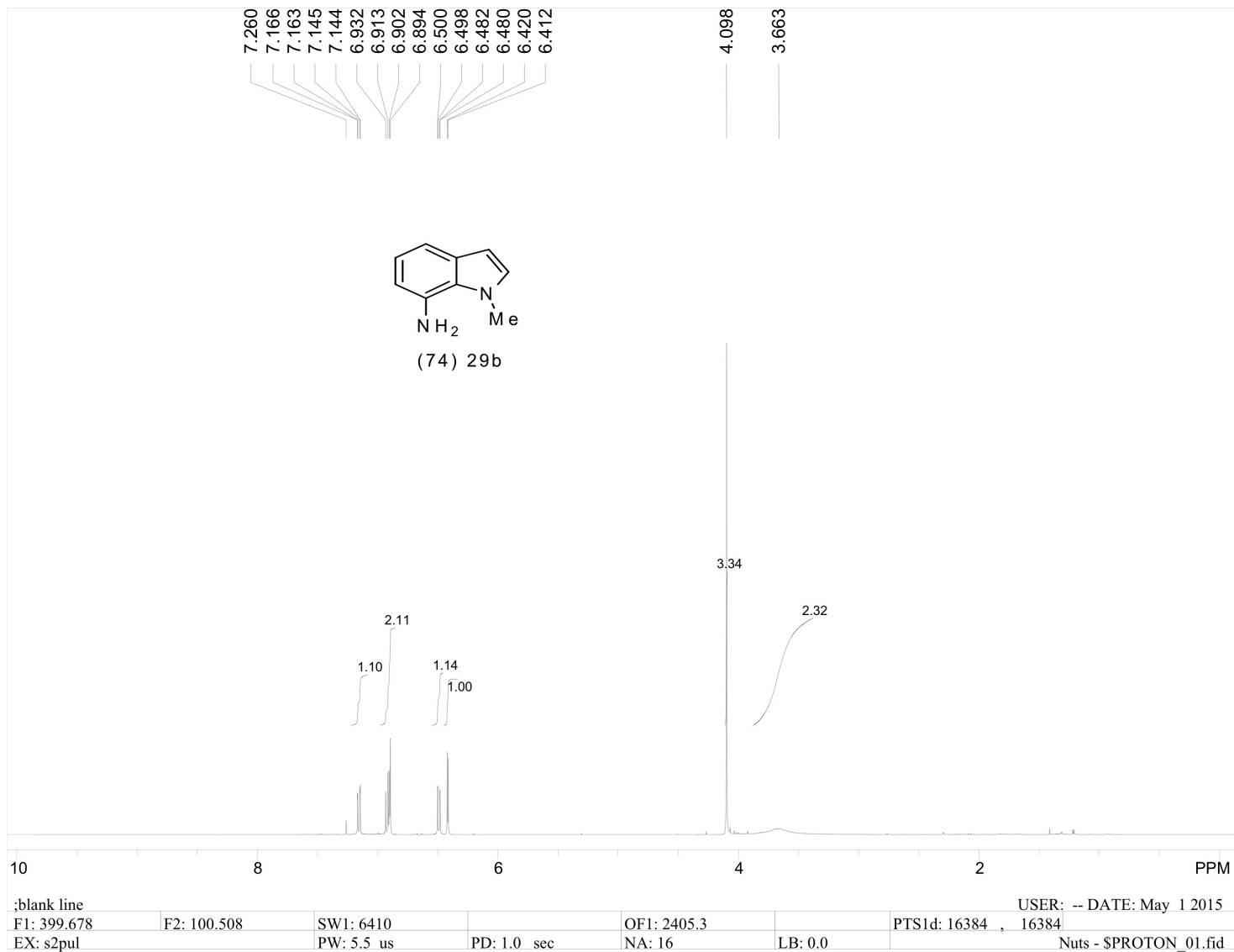


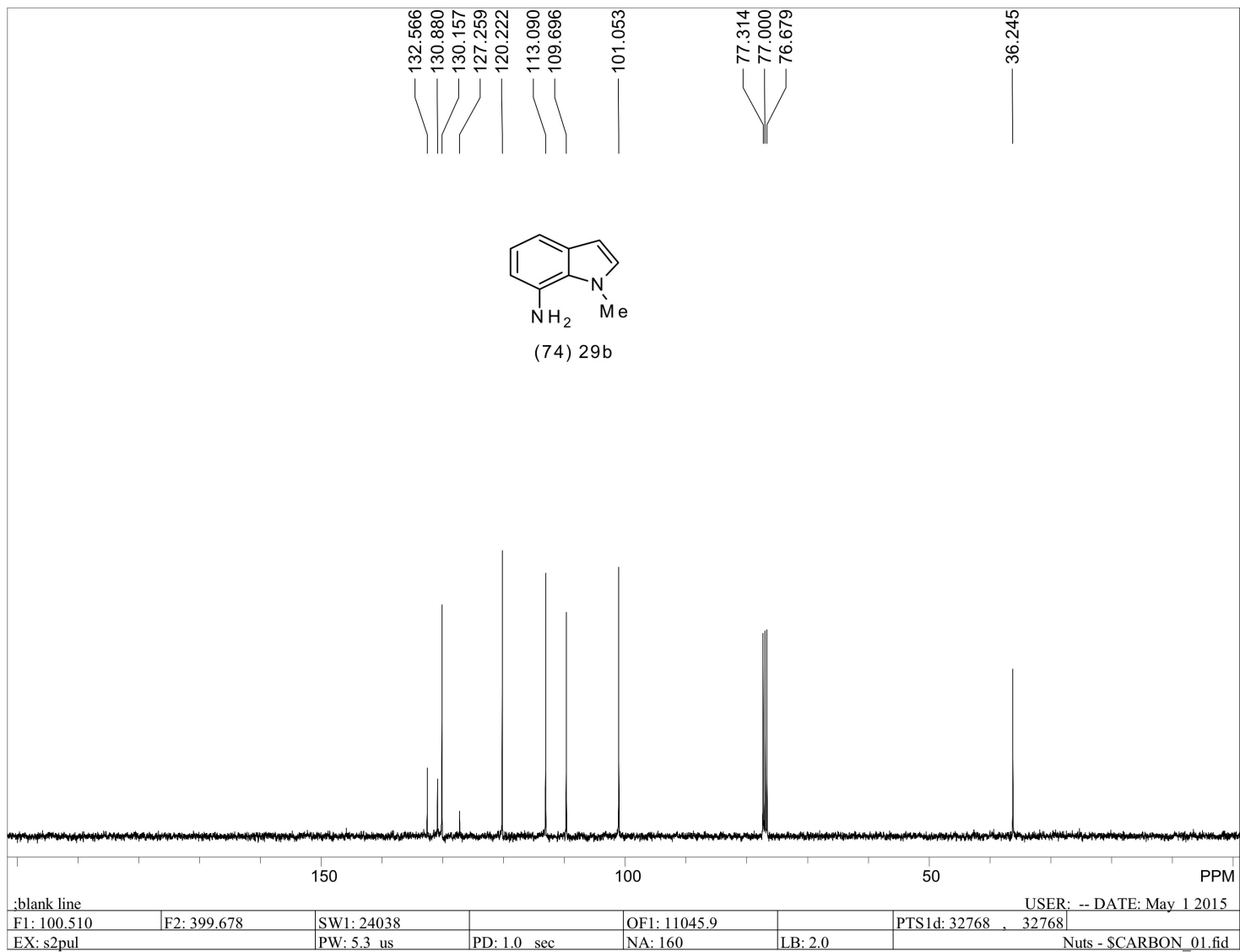


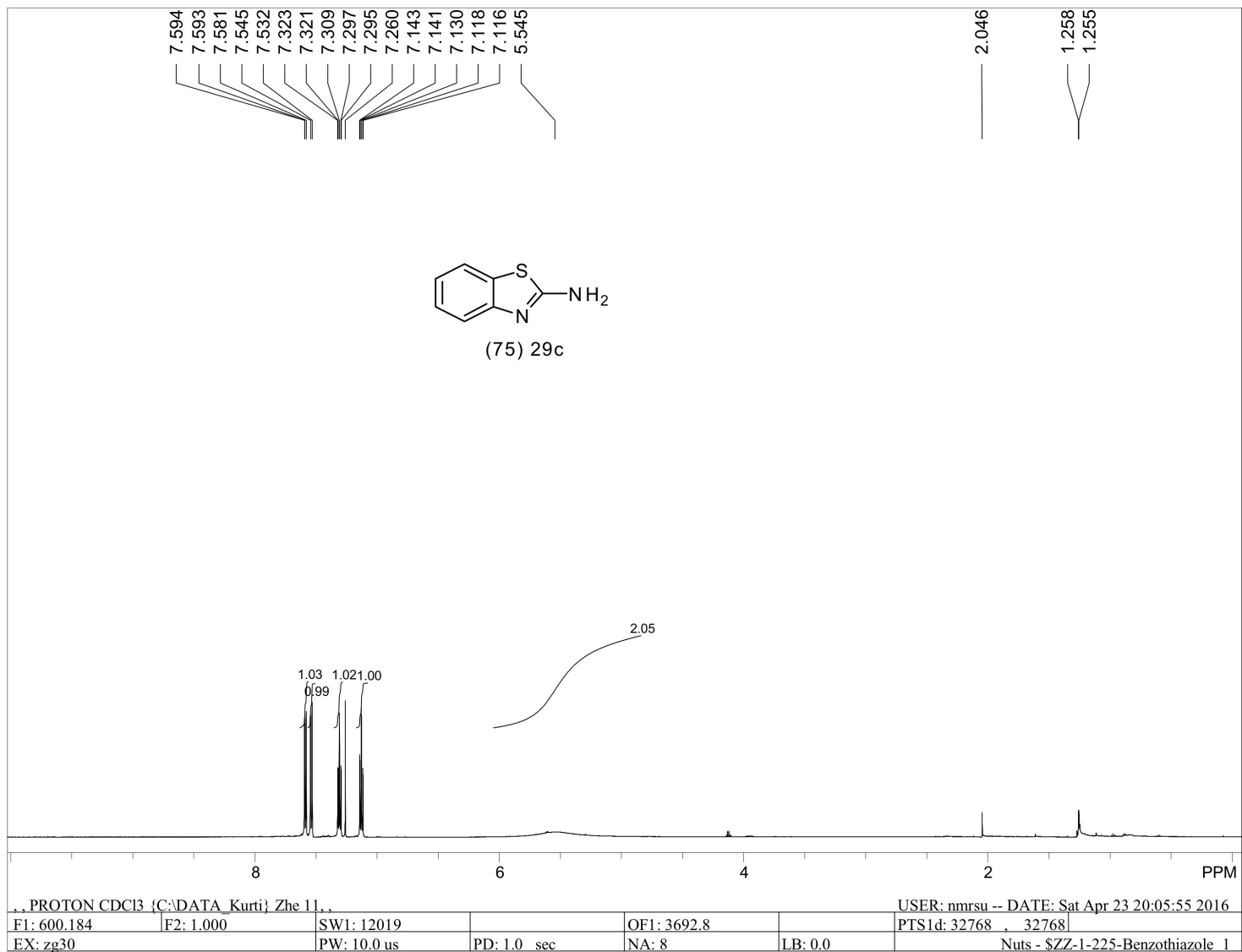


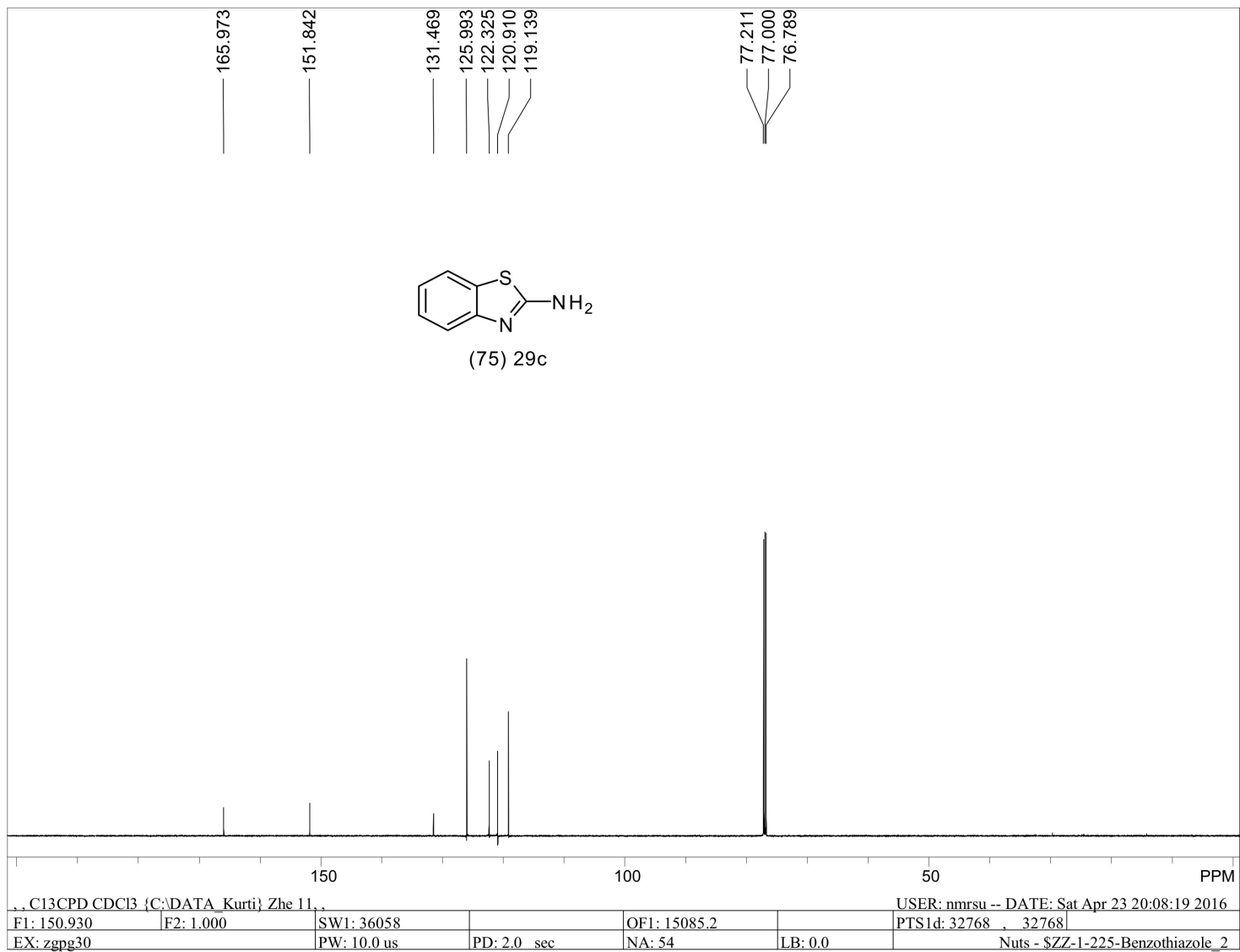


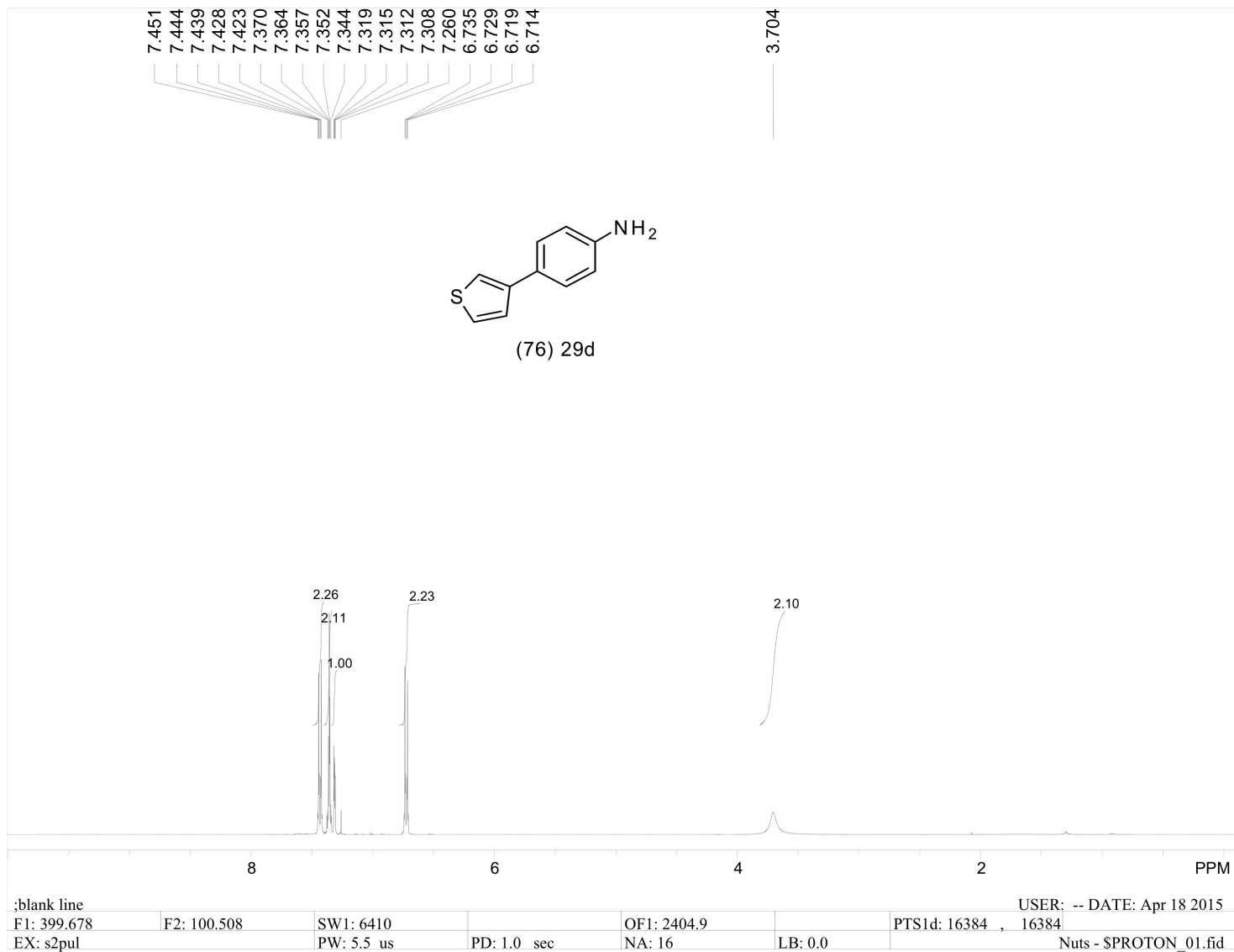


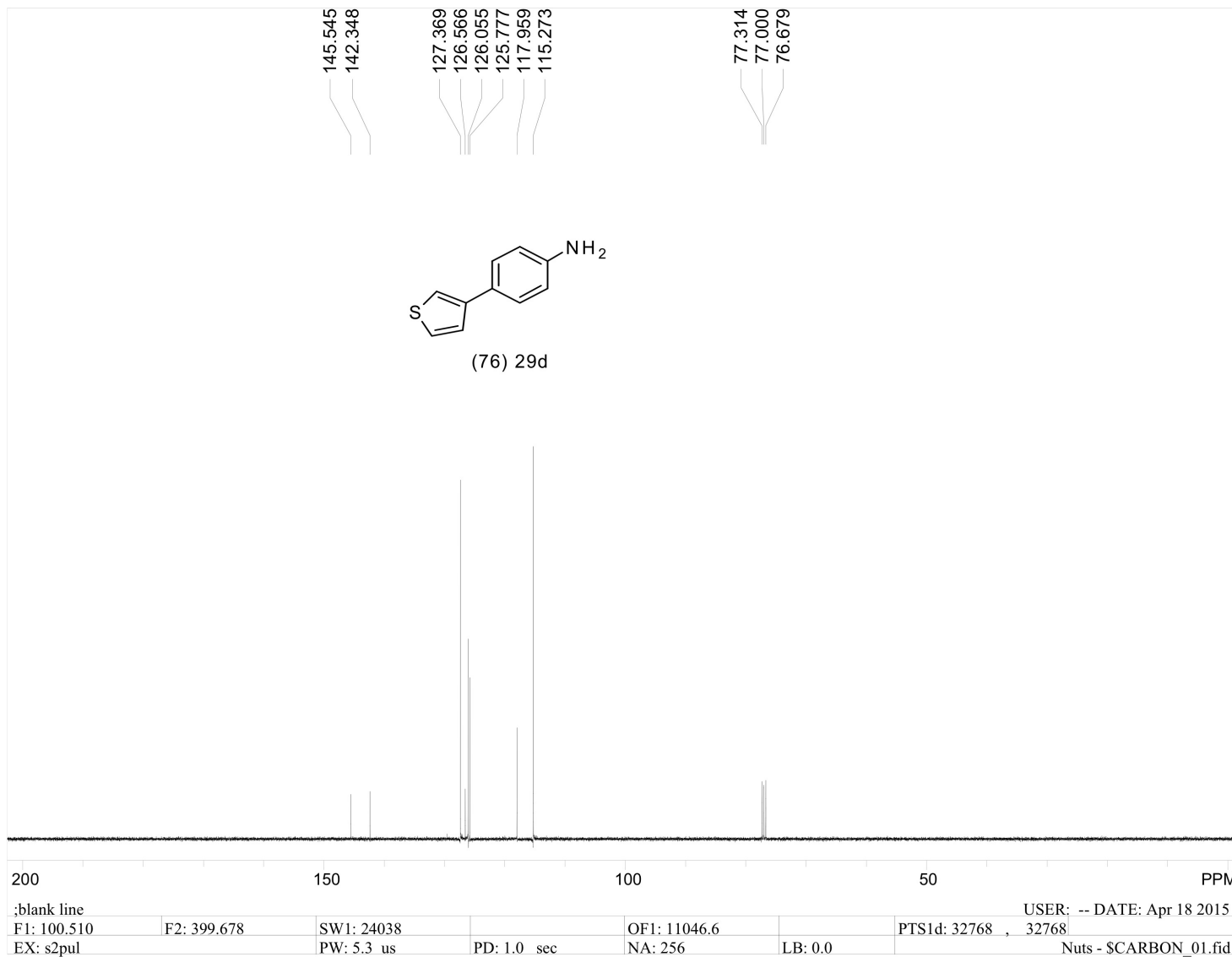


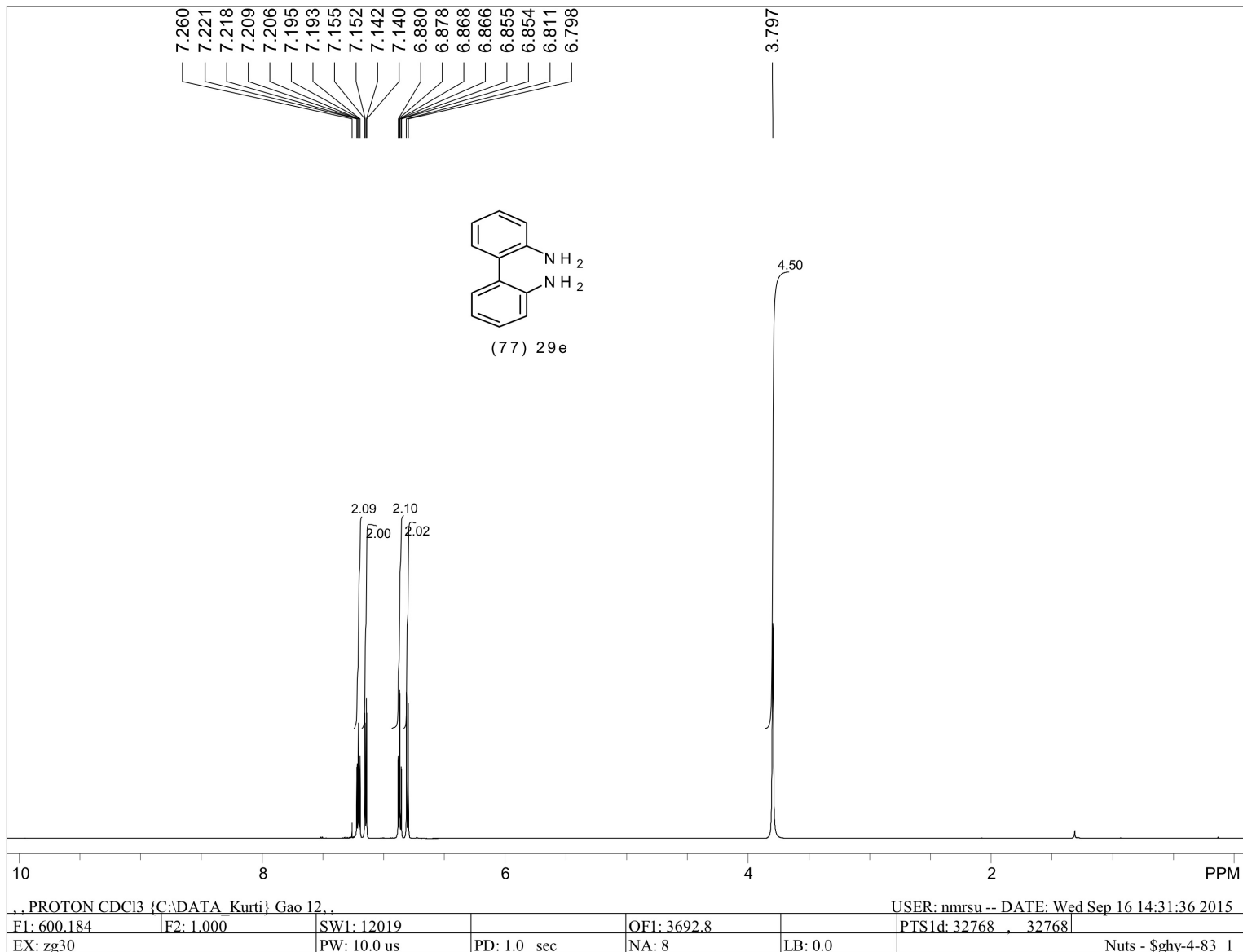


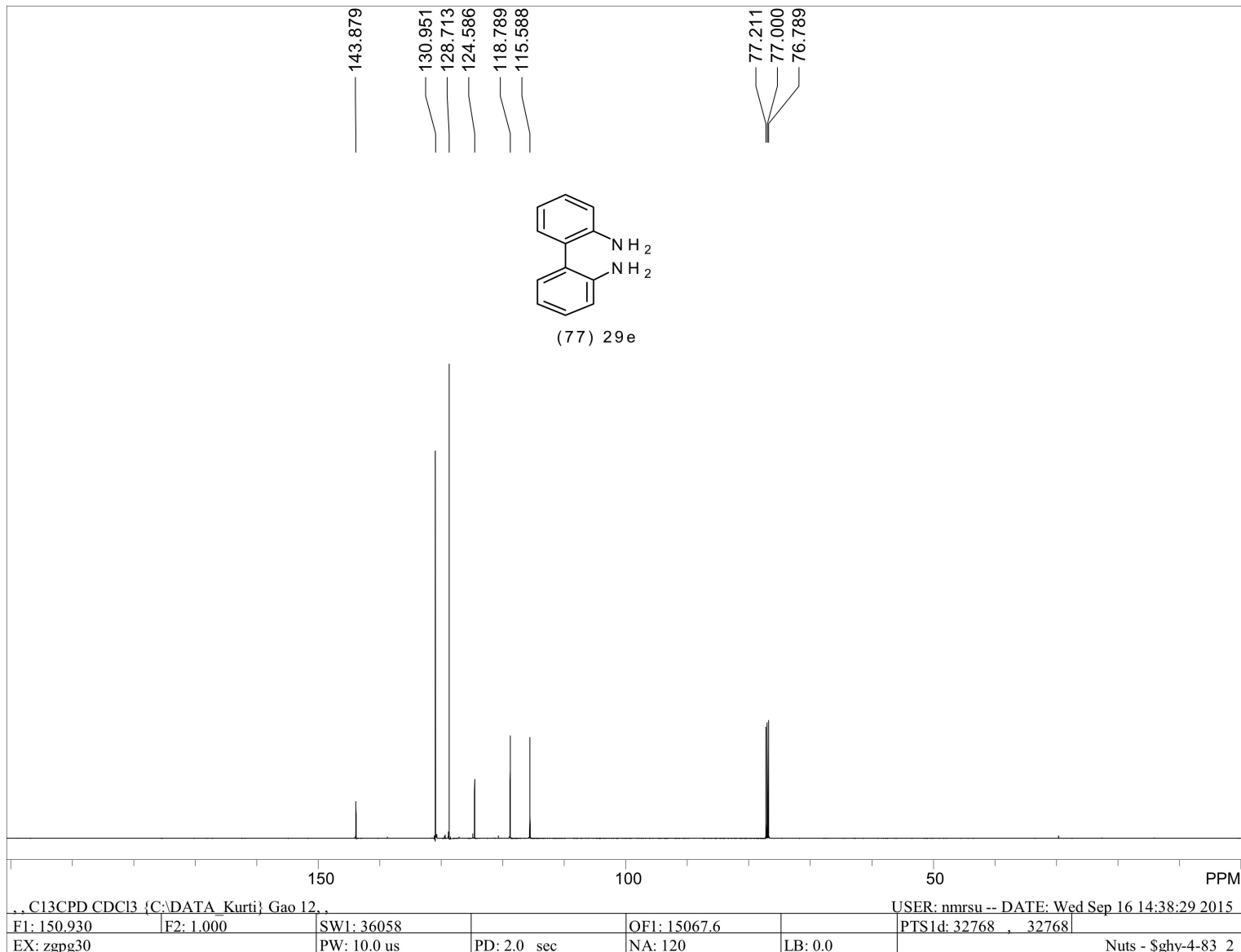


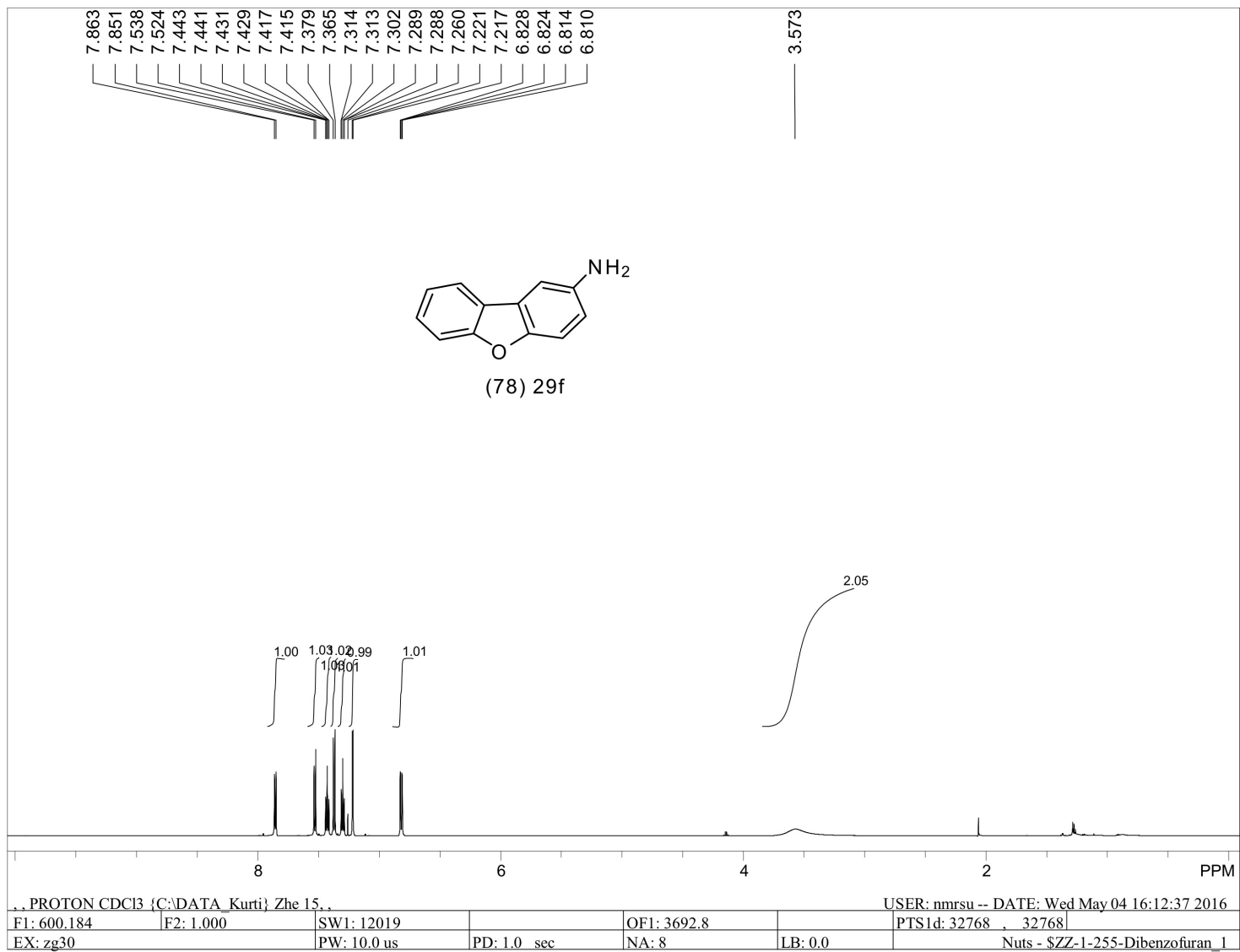




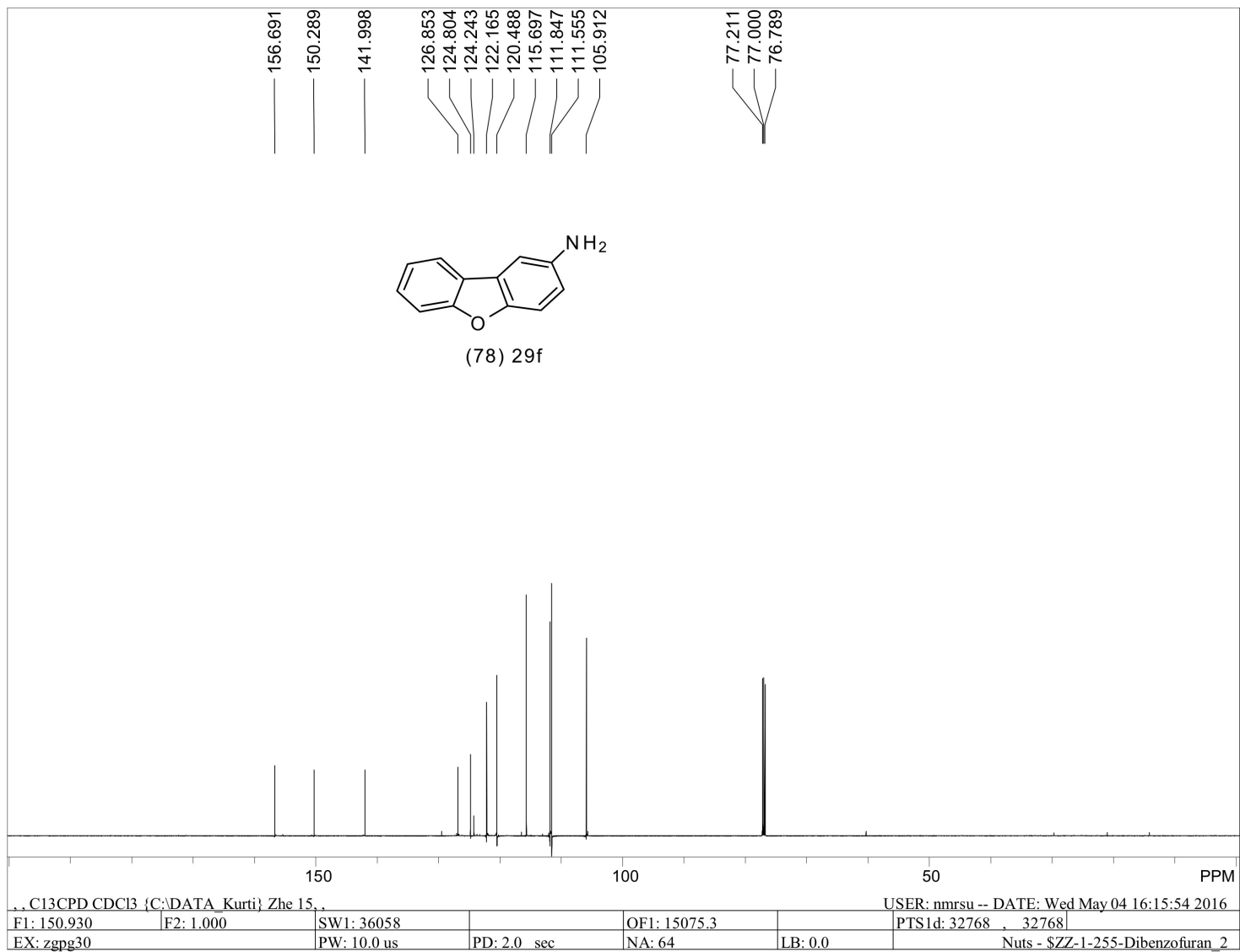




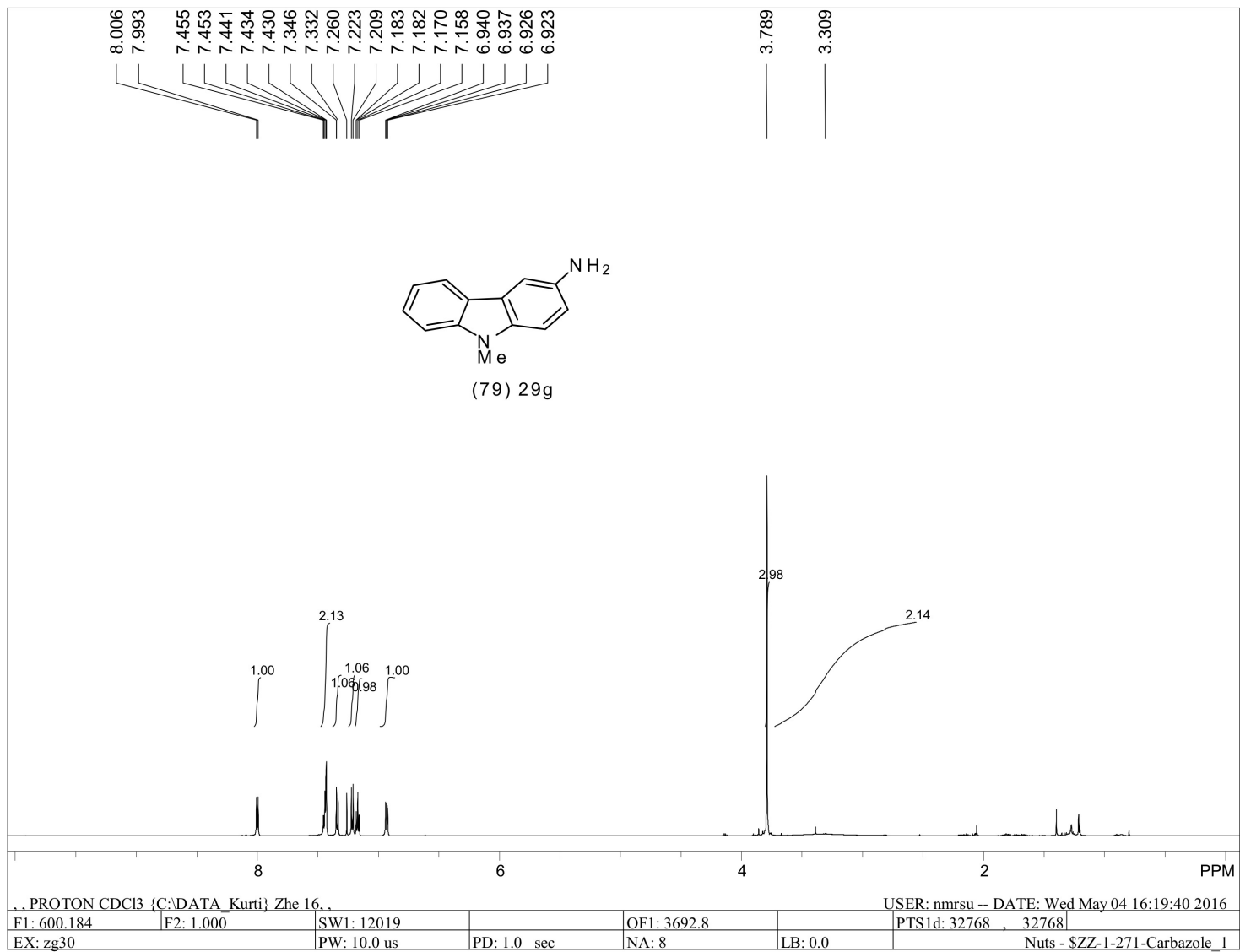




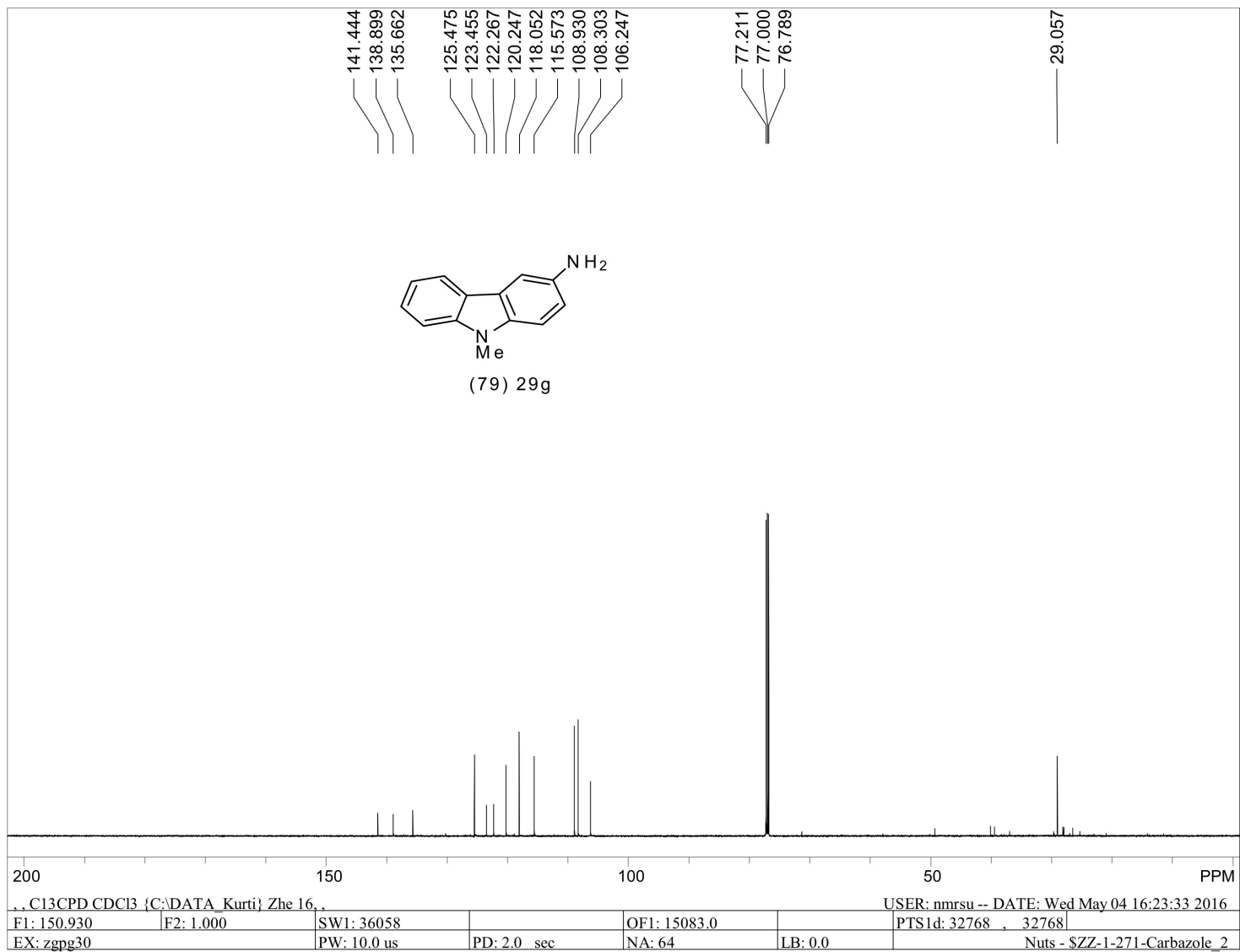
S278



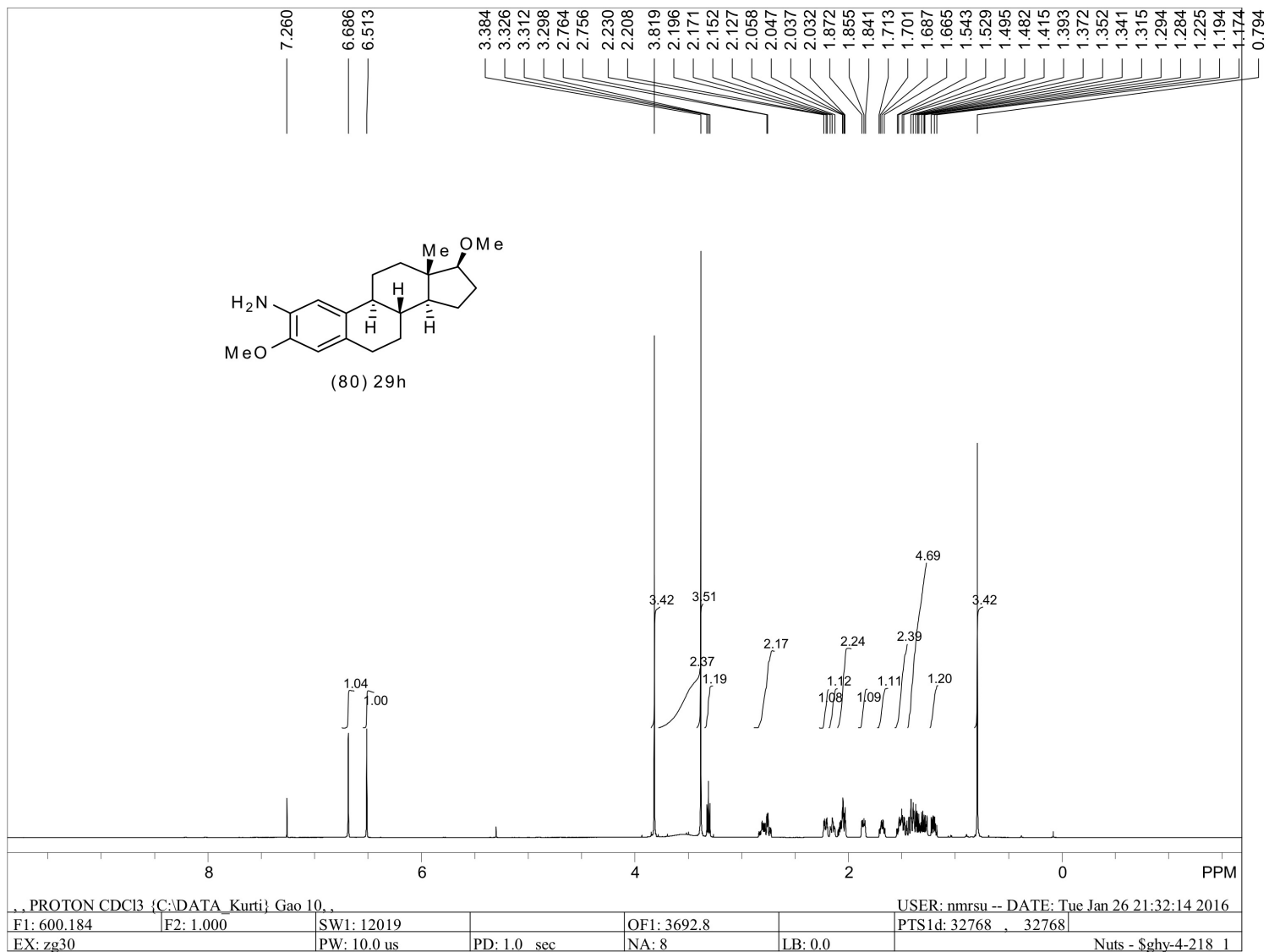
S279



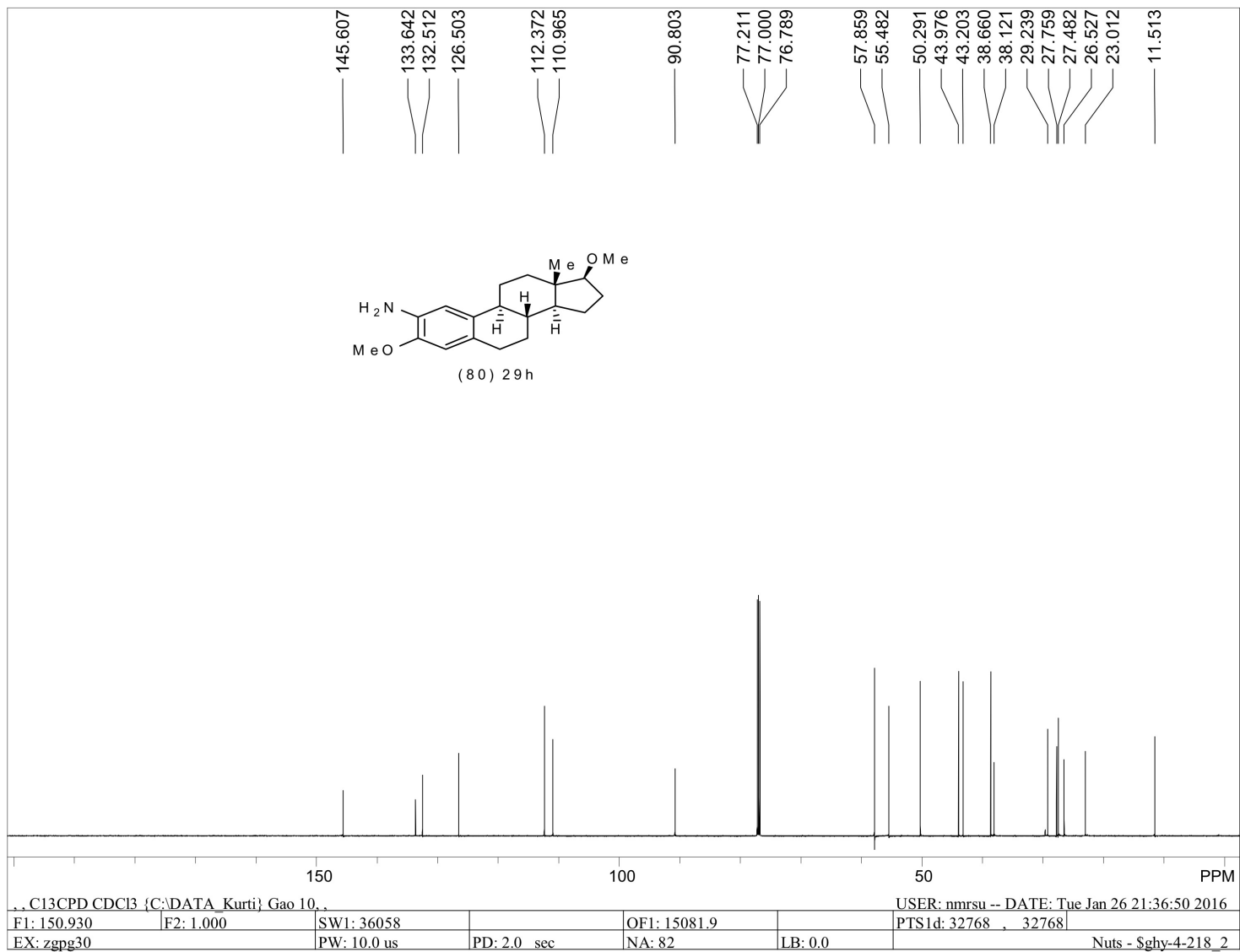
S280



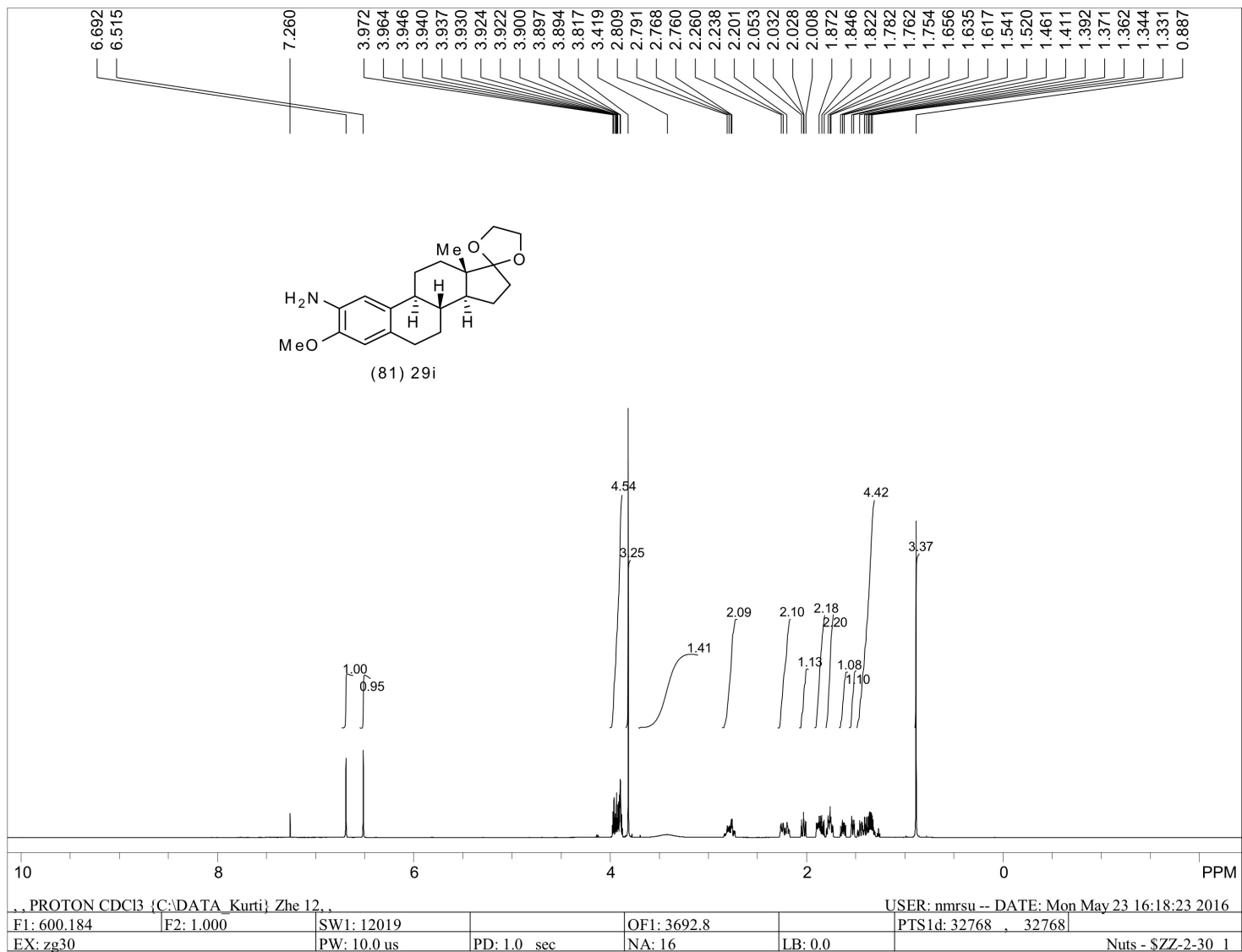
S281



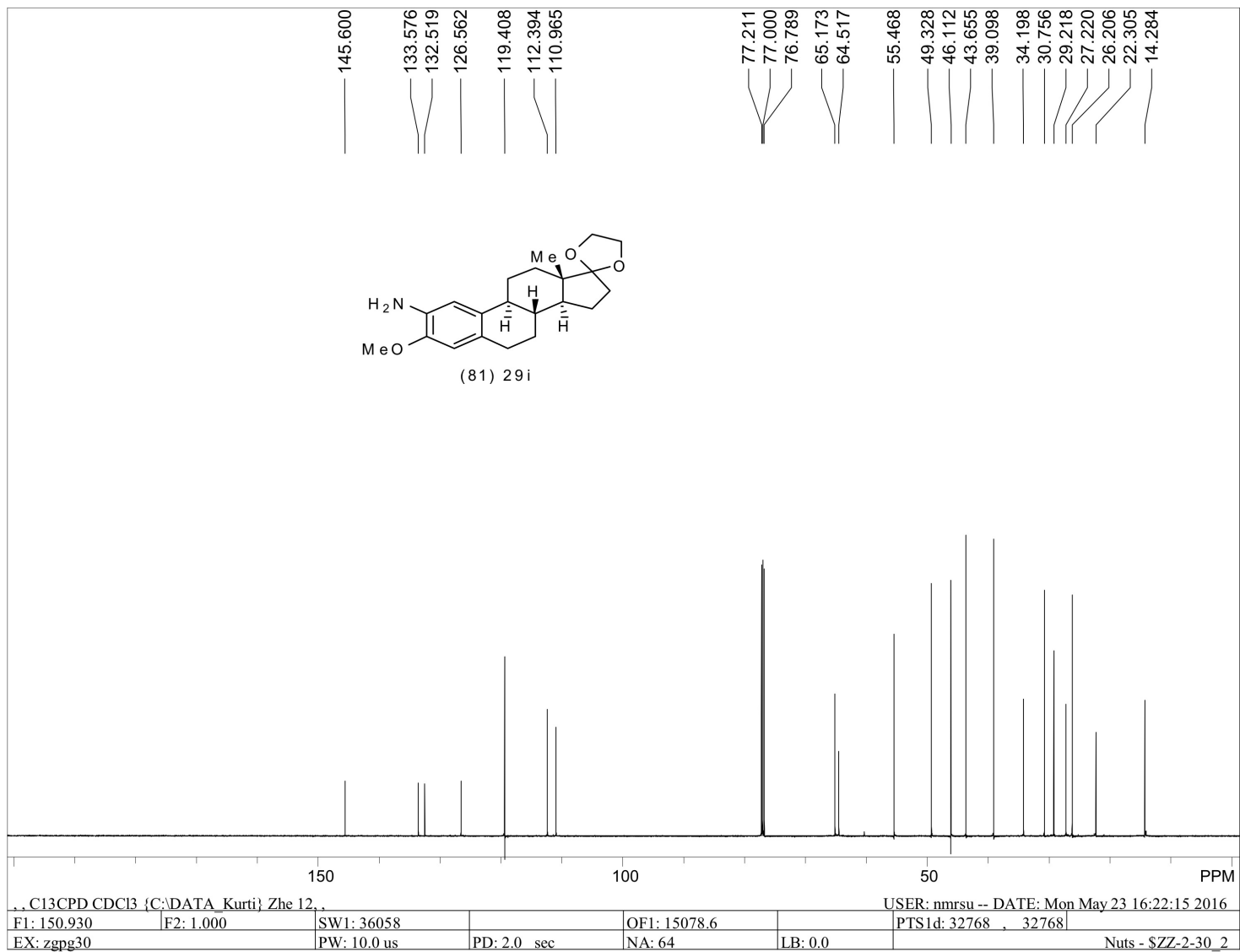
S282



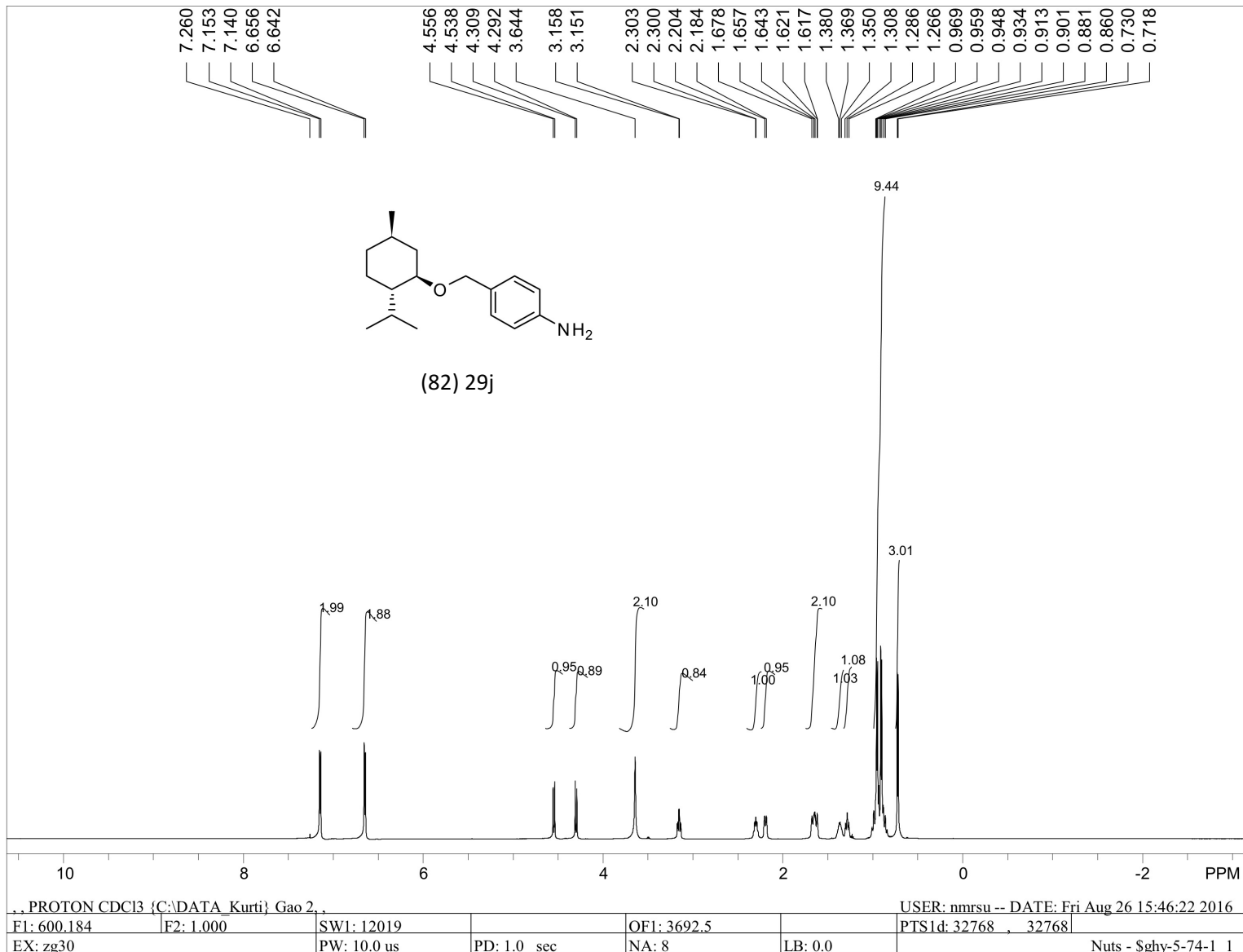
S283

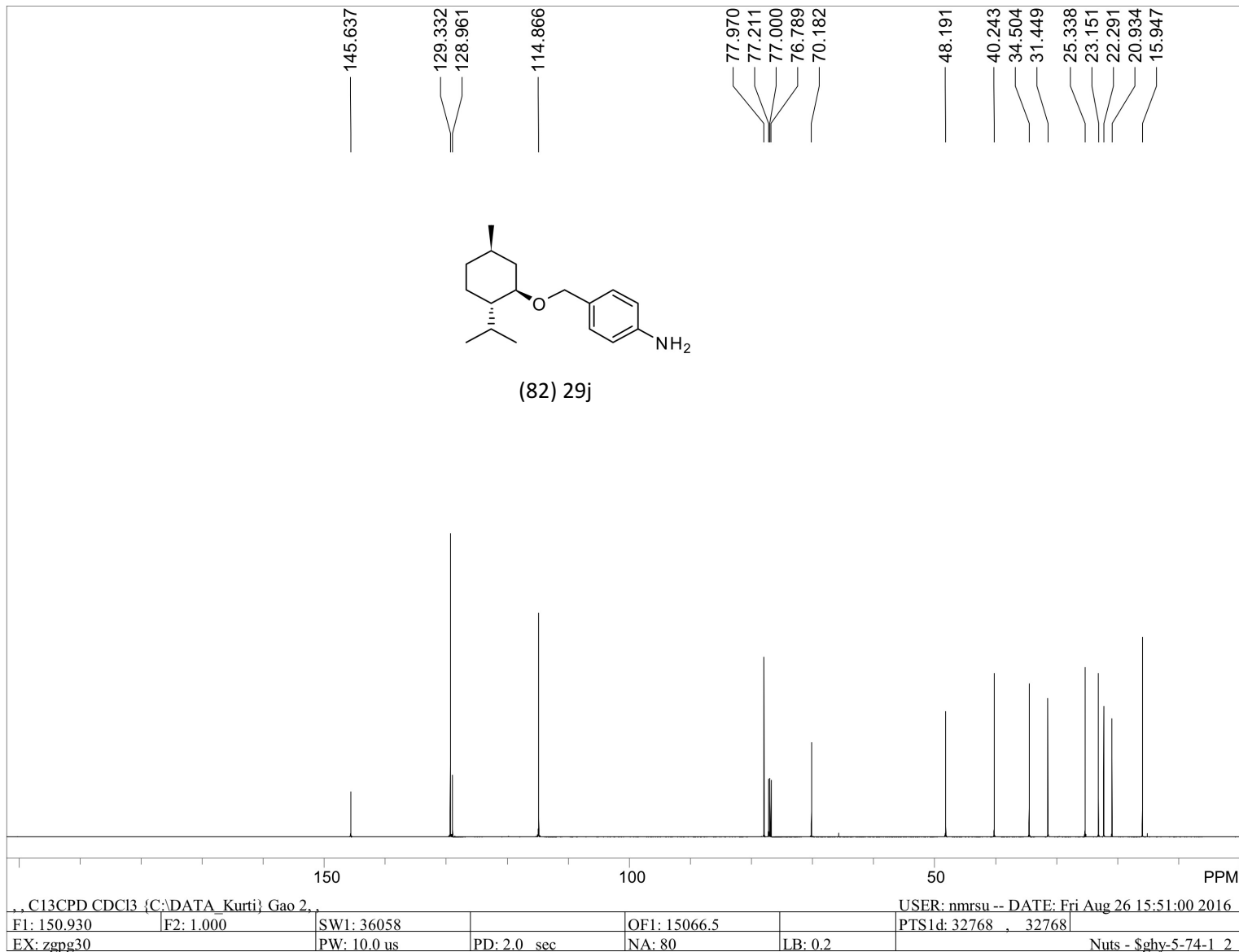


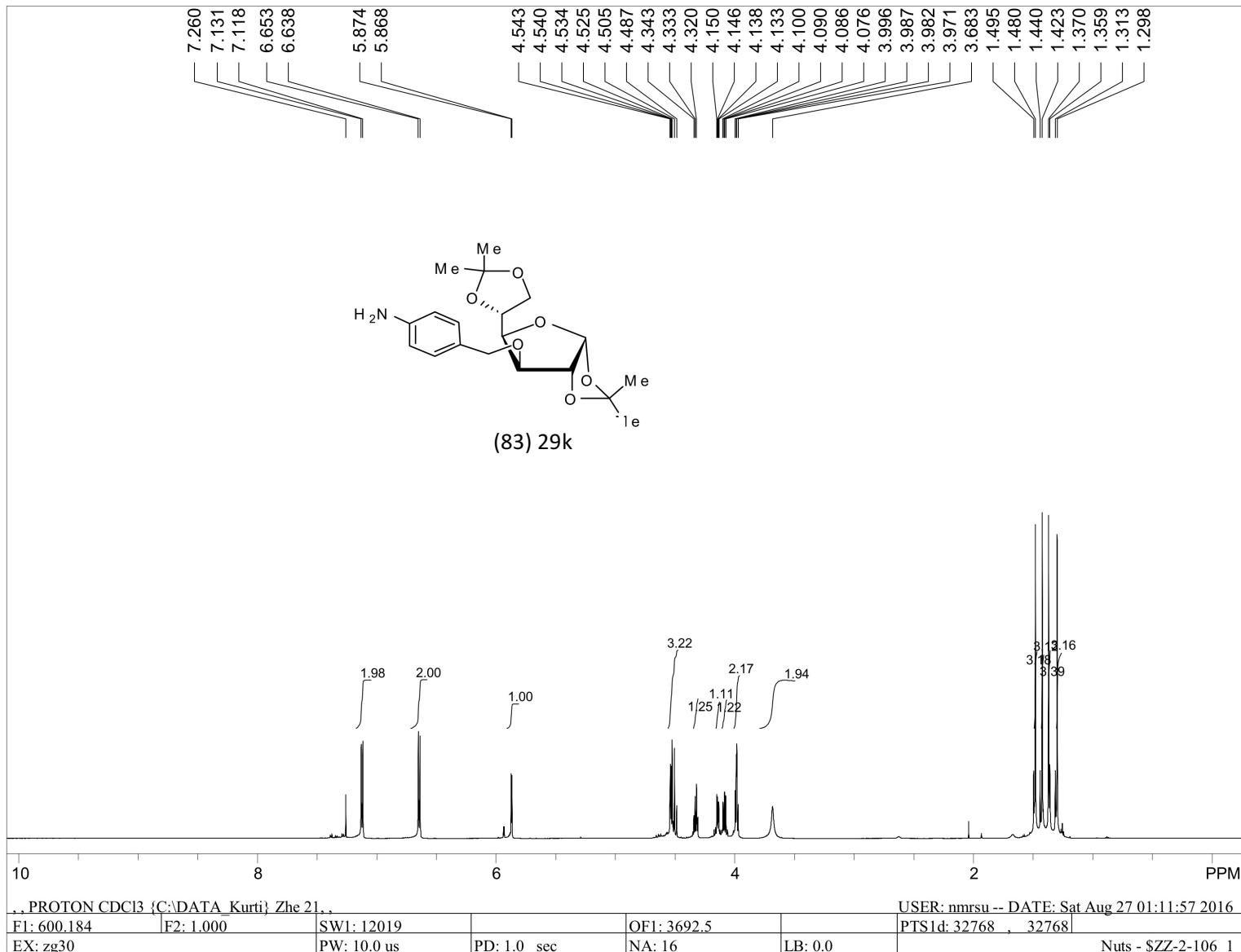
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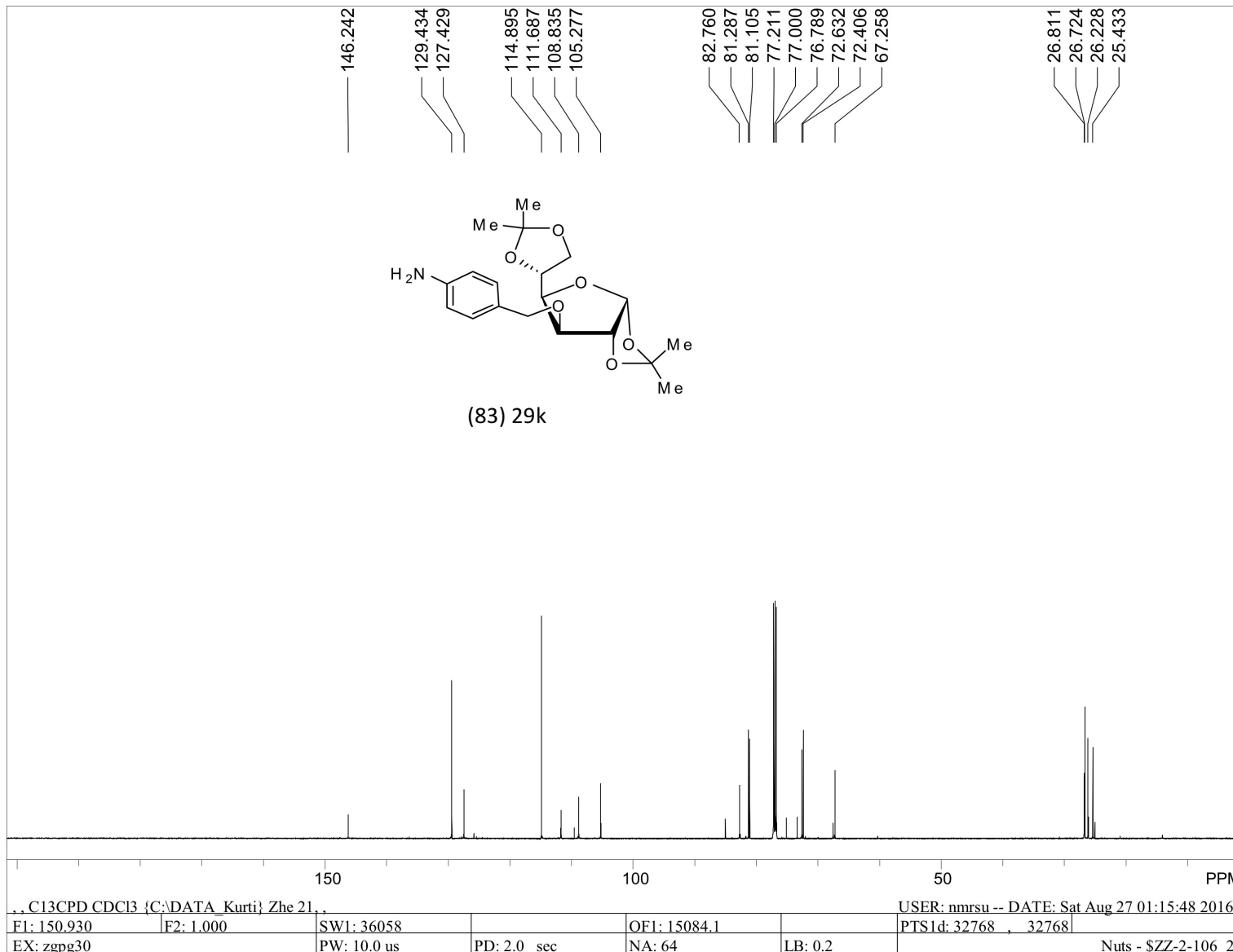


S285









NMR Spectra of Phenols

