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One-pot synthesis of cyclopentane-fused 5'-aryl-4-cycloalkylamino-2,2'-bipyridines *via* the *aza*-Diels–Alder/S_N^{ipso} reactions

Alexey P. Krinochkin, Ekaterina S. Starnovskaya, Maria I. Valieva, Dmitry S. Kopchuk, Sougata Santra, Pavel A. Slepukhin, Grigory V. Zyryanov, Adinath Majee and Oleg N. Chupakhin

Experimental Section

General Information:

All reagents were purchased from commercial sources and used without further purification. Silica gel 60 (Kieselgel 60, 230-400 mesh) was used for the column chromatography. NMR spectra were recorded on a Bruker Avance-400 spectrometer, 298 K, digital resolution ± 0.01 ppm, using TMS as internal standard. UV–Vis spectra were recorded on Lambda 45 spectrophotometer (Perkin Elmer). Luminescence spectra were recorded on a Horiba-Fluoromax-4 spectrofluorimeter equipped with integrated sphere. Mass spectrometric studies were performed on an Agilent 6545 Q-TOF LC/MS (Agilent Technologies, USA) quadrupole time-of-flight mass spectrometer with an electrospray ionization source in the positive (negative) ion mode. An Agilent 1290 Infinity II chromatographic system was used to inject the sample. Elemental analysis was performed on a PE 2400 II CHN-analyzer (Perkin Elmer).

The XRD analysis was carried out using equipment of the Center for Joint Use 'Spectroscopy and Analysis of Organic Compounds' at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Branch). The experiments were accomplished on the automated X-ray diffractometer Xcalibur 3 with CCD detector on standard procedure (MoK_α-irradiation, graphite monochromator, ω-scans with 1° step at T= 295(2) K). Empirical absorption correction was applied. The solution and refinement of the structures were accomplished with using Olex program package.[S1] The structures were solved by method of the intrinsic phases in ShelXT program and refined by ShelXL by full-matrix least-squared method for non-hydrogen atoms.[S2] The H-atoms were placed in the calculated positions and were refined in isotropic approximation in the "rider" model.

Hydrazones of isonitrosoacetophenones **2**[S3] were synthesized as described in literature.

*General procedure for the synthesis of 1,2,4-triazines **1***

The corresponding hydrazone (2.69 mmol) was dissolved in ethanol (30 ml), and a solution of 4-bromopyridine-2-carbaldehyde (0.50 g, 2.69 mmol) in ethanol (25 ml) was added. The resulting mixture was kept at room temperature for 12 h. The precipitate was filtered off, washed with ethanol and dried. Then the obtained intermediate was suspended in acetic acid (30 ml), and the mixture was heated to reflux two times. The solvent was removed under reduced pressure. Ethanol (30 ml) was added to the residue; the resulting crystals of **1** were filtered off, washed with ethanol and dried. The crude triazines were used directly in the next step without addition purification.

3-(4-Bromopyridin-2-yl)-6-(4-methoxyphenyl)-1,2,4-triazine (1a). Dark-yellow powder. M.p. 203-204 °C. Yield 460 mg (1.34 mmol, 50%). **^{1}H NMR** (DMSO-d_6, δ, ppm): 3.91 (s, 3H, OMe), 7.10-7.17 (m, 2H, $C_6\underline{H}_4$OMe), 8.81 (dd, 1H, ^{3}J 5.2 Hz, ^{4}J 2.0 Hz, H-5 (Py)), 8.26-8.32 (m, 2H, $C_6\underline{H}_4$OMe), 8.66 (d, 1H, ^{4}J 1.6 Hz, H-3 (Py)), 8.70 (d, 1H, ^{3}J 5.4 Hz, H-6 (Py)), 9.46 (s, 1H, H-5). **^{13}C NMR** (DMSO-d_6, δ, ppm): 56.0, 115.4, 125.5, 126.8, 128.9, 129.2, 133.4, 147.6, 151.8, 154.7, 155.8, 160.4, 162.5. **ESI-MS**, *m/z*: found 343.02, calculated 343.02 $(M+H)^+$.

3-(4-Bromopyridin-2-yl)-6-phenyl-1,2,4-triazine (1b). Dark-yellow powder. M.p. 188-189 °C. Yield 450 mg (1.44 mmol, 53%). **NMR ^{1}H** (DMSO-d_6, δ, ppm): 7.60-7.68 (m, 3H, Ph), 8.87 (dd, 1H, ^{3}J 5.4 Hz, ^{4}J 1.6 Hz, H-5(Py)), 8.29-8.36 (m, 2H, Ph), 8.69 (d, 1H, ^{4}J 1.6 Hz, H-3(Py)), 8.73 (d, 1H, ^{3}J 5.4 Hz, H-6(Py)), 9.55 (s, 1H, H-5). **NMR ^{13}C** ($CDCl_3$, δ, ppm): 127.1, 127.3, 128.9, 129.5, 131.5, 132.7, 134.1, 147.1, 151.1, 153.6, 156.4, 160.7. **ESI-MS**, *m/z*: found 313.00, calculated 313.01 $(M+H)^+$.

6-(3-Bromophenyl)-3-(4-bromopyridin-2-yl)-1,2,4-triazine (1c). Dark-yellow powder. M.p. 210-211 °C. Yield 580 mg (1.48 mmol, 55%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 7.51 (dd, 1H, ^{3}J 8.4, 8.4 Hz, H-5(CH_{arom})), 7.71 (dd, 1H, ^{3}J 5.0 Hz, ^{4}J 1.8 Hz, H-5(Py)), 7.74-7.78 and 8.12-8.17 (both m, 1H, H-4 and H-6(CH_{arom}), 8.39 (dd, 1H, ^{4}J 1.6, 1.6 Hz, H-2(CH_{arom})), 8.74 (d, 1H, ^{3}J 5.2 Hz, H-6(Py)), 8.70 (d, 1H, ^{4}J 1.6 Hz, H-3(Py)), 9.19 (s, 1H, H-5). **^{13}C NMR** ($CDCl_3$, δ, ppm): 123.8, 125.6, 127.5, 129.1, 130.0, 131.0, 134.2, 134.4, 134.7, 147.0, 151.1, 153.4, 155.2, 161.1. **ESI-MS**, *m/z*: found 390.92, calculated 390.92 $(M+H)^+$.

*General procedure for the synthesis of 2,2'-bipyridines **3***

A mixture of the corresponding 1,2,4-triazine **1** (0.40 mmol) and enamine (2.0 mmol) was stirred at 200 °C for 2 h under argon atmosphere. Then, an additional portion of amine (1 mmol) was added, and the resulting mixture was stirred for additional 1 h under the same conditions. The reaction mixture was cooled to room temperature. The products were separated by flash chromatography (DCM as eluent) and then were purified by recrystallization (ethanol).

4-{2-[4-(4-Methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridin-1-yl]pyridin-4-yl}-morpholine (3a). Brown gummy. Yield 109 mg (0.28 mmol, 70%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 2.09 (m, 2H, CH_2-6), 3.04 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.40-3.44 (m, 4H, H-3,5), 3.45 (t, 2H, ^3J 7.6 Hz, CH_2-5), 3.86-3.92 (m, 4H, H-2,6), 3.90 (s, 3H, OMe), 6.71 (dd, 1H, ^3J 6.0 Hz, ^4J 2.8 Hz, H-5′(Py)), 7.01-7.07 (m, 2H, $C_6\underline{H}_4$OMe), 7.43-7.48 (m, 2H, $C_6\underline{H}_4$OMe), 7.63 (d, 1H, ^4J 2.8 Hz, H-3′(Py)), 8.43 (d, 1H, ^3J 6.0 Hz, H-6′(Py)), 8.51 (s, 1H, H-3(Py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 24.5, 32.7, 33.4, 46.4 (2C), 55.3, 66.5 (2C), 107.5, 107.6, 114.1 (2C), 129.7 (2C), 130.2, 133.2, 139.3, 146.3, 149.3, 151.0, 152.9, 155.8, 158.9, 159.3. **ESI-MS**, *m/z*: found 388.20, calculated 388.20 $(M+H)^+$. Found, %: C 74.26, H 6.38, N 10.99. **$C_{24}H_{25}N_3O_2$**. Calculated, %: C 74.39, H 6.50, N 10.84.

4-[2-(4-Phenyl-6,7-dihydro-5*H*-cyclopenta[*c*]pyridin-1-yl)pyridin-4-yl]morpholine (3b). Brown powder. M.p. 160-163 °C. Yield 105 mg (0.29 mmol, 74%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 2.10 (m, 2H, CH_2-6), 3.06 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.43 (t, 4H, ^3J 5.0 Гц, H-3,5), 3.46 (t, 2H, ^3J 7.6 Hz0., CH_2-5), 3.89 (t, 4H, ^3J 5.0 Гц, H-2,6), 6.72 (dd, 1H, ^3J 5.8 Hz, ^4J 2.4 Hz, H-5′(Py)), 7.40-7.46 (m, 1H, Ph), 7.48-7.53 (m, 4H, Ph), 7.65 (d, 1H, ^4J 2.4 Hz, H-3′(Py)), 8.44 (d, 1H, ^3J 5.8 Hz, H-6′(Py)), 8.54 (s, 1H, H-3(Py)). **NMR ^{13}C** ($CDCl_3$, δ, ppm): 24.5, 31.6, 32.4, 45.4 (2C), 65.5 (2C), 106.5, 106.6, 126.6, 127.5 (2C), 127.6 (2C), 132.5, 136.9, 138.3, 145.4, 148.3, 150.5, 152.1, 154.8, 158.0. **ESI-MS**, *m/z*: found 358.19, calculated 358.19 $(M+H)^+$. Found, %: C 77.15, H 6.54, N 11.61. **$C_{23}H_{23}N_3O$**. Calculated, %: C 77.28, H 6.49, N 11.76.

4-{2-[4-(3-Bromophenyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridin-1-yl]pyridin-4-yl}-morpholine (3c). Brown powder. M.p. 177-178 °C. Yield 136 mg (0.31 mmol, 78%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 2.11 (m, 2H, CH_2-6), 3.03 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.43 (t, 4H, ^3J 4.8 Hz, H-3,5), 3.47 (t, 2H, ^3J 7.6 Hz, CH_2-5), 3.89 (t, 4H, ^3J 4.8 Hz, H-3,5), 6.72 (dd, 1H, ^3J 5.6 Hz, ^4J 2.8 Hz, H-5′(Py)), 7.37 (dd, 1H, ^3J 8.0, 8.0 Hz, H-5(CH_{arom})), 7.41-7.46 and 7.53-7.58 (both m, 1H, H-4 and H-6(CH_{arom})), 7.63-7.68 (m, 2H, H-2(CH_{arom}), H-3′(Py)), 8.44 (d, 1H, ^3J 5.8 Hz, H-6′(Py)), 8.48 (s, 1H, H-3(Py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 25.5, 32.5, 33.4, 46.4 (2C), 66.5 (2C), 107.6, 107.7, 122.7, 127.2, 130.1, 130.7, 131.5, 132.2, 139.5, 140.1, 146.2, 149.4, 152.0, 153.2, 155.9, 158.8. **ESI-MS**, *m/z*: found 436.10, calculated 436.10 $(M+H)^+$. Found, %: C 63.19, H 4.95, N 9.78. **$C_{23}H_{22}BrN_3O$**. Calculated, %: C 63.31, H 5.08, N 9.63. Crystal Data for $C_{23}H_{20}BrN_3OF$ (M = 434.33 g/mol): monoclinic, space group $P2_1/c$, a = 11.5920(15) Å, b = 5.7099(8) Å, c = 29.910(5) Å, β = 94.832(13)°, V = 1972.7(5) Å^3, Z = 4, T = 295(2) K, μ(Mo K_α) = 2.102 mm^{-1}, D_{calc} = 1.462 g/cm^3, 11946 reflections measured (7.056° ≤ 2Θ ≤ 52.738°), 3966 unique (R_{int} = 0.0886, R_{sigma} = 0.1278) which were used in all calculations. The final R_1 = 0.0681,

wR_2 = 0.1522 ($I > 2\sigma(I)$) and R_1 = 0.1837, wR_2 = 0.2120 (all data). Largest diff. peak/hole 0.34/-0.39 ēÅ^{-3}. CCDC 2117784 contains the crystallographic data for this compound.

4-(3-Bromophenyl)-1-[4-(piperidin-1-yl)pyridin-2-yl]-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (3d). Brown gummy. Yield 122 mg (0.28 mmol, 70%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 1.63-1.73 (m, 6H, piperidine), 2.03-2.12 (m, 2H, CH_2-6), 3.00 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.40-3.48 (m, 6H, piperidine, CH_2-5), 6.68 (dd, 1H, ^3J 6.0 Hz, ^4J 2.4 Hz, H-5′(Py)), 7.34 (dd, 1H, ^3J 8.0, 8.0 Hz, H-5 (C_6H_4Br)), 7.39-7.44 and 7.50-7.55 (both m, 2H, H-4 and H-6 (C_6H_4Br)), 7.64 (dd, 1H, ^4J 1.6, 1.6 Hz, H-2 (C_6H_4Br)), 8.35 (d, 1H, ^4J 6.0 Hz, H-6′(Py)), 8.49 (s, 1H, H-6 (Py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 24.4, 25.3, 25.5, 32.5, 33.4, 47.4, 107.7, 107.8, 122.7, 127.2, 130.1, 130.6, 131.5, 132.0, 139.3, 140.2, 146.2, 149.3, 152.5, 153.0, 155.6, 158.6. **ESI-MS**, *m/z*: found 434.12, calculated 434.12 $(M+H)^+$. Found, %: C 66.23, H 5.64, N 9.78. **$C_{24}H_{24}BrN_3$**. Calculated, %: C 66.36, H 5.57, N 9.67.

4-(3-Bromophenyl)-1-[4-(pyrrolidin-1-yl)pyridin-2-yl]-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (3e). Brown powder. M.p. 129-131 °C. Yield 122 mg (0.29 mmol, 72%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 2.01-2.11 (m, 6H, pyrrolidine, CH_2-6), 3.00 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.39-3.44 (m, 6H, pyrrolidine, CH_2-5), 6.41 (dd, 1H, ^3J 6.0 Hz, ^4J 2.4 Hz, H-5′(Py)), 7.22 (d, 1H, ^4J 2.4 Hz, H-3′(Py)), 7.34 (dd, 1H, ^3J 8.0, 8.0 Hz, H-5 (C_6H_4Br)), 7.40-7.43 and 7.51-7.54 (both m, 2H, H-4 and H-6 (C_6H_4Br)), 7.63 (dd, 1H, ^4J 1.6, 1.6 Hz, H-2 (C_6H_4Br)), 8.31 (d, 1H, ^4J 6.0 Hz, H-6′(Py)), 8.48 (s, 1H, H-6 (Py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 25.4, 25.5, 32.6, 33.3, 47.2, 106.3, 106.4, 122.7, 127.3, 130.1, 130.6, 131.5, 132.0, 139.3, 140.2, 146.3, 148.6, 152.5, 153.0. **ESI-MS**, *m/z*: found 420.11, calculated 420.11 $(M+H)^+$. Found, %: C 65.81, H 5.16, N 9.82. **$C_{23}H_{22}BrN_3$**. Calculated, %: C 65.72, H 5.28, N 10.00.

*General procedure for the synthesis of 2,2'-bipyridines **2***

The corresponding triazine **1a-c** (0.50 mmol) was dissolved in *o*-xylene (25 ml), 1-morpholinocyclopentene (0.16 ml, 1.0 mmol) was added, and the resulting mixture was refluxed for 2 h. Then an addition portion of 1-morpholinocyclopentene (0.08 ml, 0.5 mmol) was added, and mixture was refluxed for 1 h. The solvent was removed under reduced pressure. Then the obtained intermediate was suspended in acetic acid (30 ml), and the mixture was heated to reflux two times. The solvent was removed under reduced pressure. Ethanol (30 ml) was added to the residue; the resulting crystals of **2** were filtered off, washed with ethanol and dried. The product was recrystallized from ethanol.

1-(4-Bromopyridin-2-yl)-4-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[*c*]-pyridine (2a). Light-brown powder. M.p. 115-117 °C. Yield 130 mg (0.34 mmol, 68%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 2.05-2.12 (m, 2H, CH_2-6), 3.03 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.45 (t, 2H, ^3J 7.6 Hz, CH_2-5), 3.88 (s, 3H, OMe), 7.00-7.05 (m, 2H, $C_6\underline{H}_4$OMe), 7.41-7.46 (m, 3H, $C_6\underline{H}_4$OMe, H-5′(Py)), 8.47 (d, 1H, ^4J 2.0 Hz, H-6′(Py)), 8.50 (d, 1H, ^3J 5.4 Hz, H-3′(Py)), 8.52 (s, 1H, H-6(Py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 25.5, 32.7, 33.5, 55.4, 114.2, 125.9, 126.3, 129.7, 129.9, 133.3, 133.9, 139.9, 146.4, 148.7, 149.4, 153.4, 159.4, 159.5. **ESI-MS**, *m/z*: found 381.06, calcu-

lated 381.06 $(M+H)^+$. Found, %: C 63.19, H 4.37, N 7.22. **$C_{20}H_{17}BrN_2O$**. Calculated, %: C 63.00, H 4.49, N 7.35.

1-(4-Bromopyridin-2-yl)-4-phenyl-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (2b). Light-brown powder. M.p. 102-104 °C. Yield 130 mg (0.37 mmol, 74%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 2.06-2.16 (m, 2H, CH_2-6), 3.06 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.49 (t, 2H, ^3J 7.6 Hz, CH_2-5), 7.40-7.54 (m, 6H, H-5′(Py), Ph), 8.49-8.63 (m, 3H, H-6 (Py), H-3′,H′ (Py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 25.4, 32.6, 33.5, 125.9, 126.3, 127.9, 128.6, 128.7, 133.3, 134.2, 137.6, 139.9, 146.7, 149.2, 149.3, 153.5, 159.5. **ESI-MS**, *m/z*: found 351.05, calculated 351.05 $(M+H)^+$. Found, %: C 64.83, H 4.41, N 8.12. **$C_{19}H_{14}BrN_2$**. Calculated, %: C 64.97, H 4.30, N 7.98.

*General procedure for the synthesis of 2,2'-bipyridines **3f,g***

The mixture of corresponding bipyridine **2** (0.23 mmol) and the corresponding amine (0.70 mmol) was stirred at 200 °C for 8 h under argon atmosphere. The reaction mass was cooled to room temperature. The product was separated by flash chromatography (DCM as eluent) and then was purified by recrystallization (ethanol).

4-(4-Methoxyphenyl)-1-(4-(pyrrolidin-1-yl)pyridin-2-yl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (3f). Brown powder. M.p. 168-170 °C. Yield 59 mg (0.16 mmol, 69%). **^{13}C NMR** ($CDCl_3$, δ, ppm): 2.02-2.14 (m, 6H, pyrrolidine, CH_2-6), 3.04 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.40-3.48 (m, 6H, pyrrolidine, CH_2-5), 3.89 (s, 3H, OMe), 6.44 (dd, 1H, ^3J 6.0 Hz, ^4J 2.4 Hz, H-5′ (Py)), 7.00-7.06 (m, 2H, $C_6\underline{H}_4$OMe), 7.22 (d, 1H, ^4J 2.4 Hz, H-3′ (Py)), 7.42-7.48 (m, 2H, $C_6\underline{H}_4$OMe), 8.35 (d, 1H, ^4J 6.0 Hz, H-6′ (Py)), 8.52 (s, 1H, H-6 (Py)). **^{13}C NMR** ($CDCl_3$, δ, ppm): 25.4, 25.6, 32.8, 33.3, 47.1, 55.4, 106.2, 106.3, 114.1, 129.7, 130.4, 133.0, 139.1, 146.4, 148.7, 151.7, 152.4, 152.6, 158.2, 159.2. **ESI-MS**, *m/z*: found 372.21, calculated 372.21 $(M+H)^+$. Found, %: C 77.47, H 6.61, N 11.48. **$C_{24}H_{25}N_3O$**. Calculated, %: C 77.60, H 6.78, N 11.31.

***N*-(Furan-2-ylmethyl)-2-(4-phenyl-6,7-dihydro-5*H*-cyclopenta[*c*]pyridin-1-yl)pyridin-4-amine (3g).** Brown gummy. Yield 59 mg (0.16 mmol, 70%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 2.03-2.13 (m, 2H, CH_2-6), 3.04 (t, 2H, ^3J 7.6 Hz, CH_2-7), 3.42 (t, 2H, ^3J 7.6 Hz, CH_2-5), 4.46 (d, 1H, ^3J 5.6 Hz, NHC$\underline{H}_2$), 4.94 (m, 1H, NH), 6.28-6.31 (m, 1H, H-3(fur)), 6.34-6.37 (m, 1H, H-4(fur)), 6.56 (dd, 1H, ^3J 5.8 Hz, ^4J 2.4 Hz, H-3(fur)), 7.38-7.45 (Ph, H-3′,5′ (Py)), 7.46-7.54 (m, 4H, Ph), 8.34 (d, 1H, ^3J 5.6 Hz, H-6′ (Py)), 8.53 (s, 1H, H-6 (Py). **^{13}C NMR** ($CDCl_3$, δ, ppm): 25.5, 29.7, 32.7, 33.3, 40.2, 107.0, 107.3, 107.5, 110.5, 127.7, 128.6, 128.6, 133.7, 137.9, 139.3, 142.3, 146.5, 148.8, 151.0, 151.4, 153.2, 153.8, 158.0. **ESI-MS**, *m/z*: found 368.18, calculated 368.18 $(M+H)^+$. Found, %: C 78.32, H 5.62, N 11.61. **$C_{24}H_{21}N_3O$**. Calculated, %: C 78.45, H 5.76, N 11.44.

References

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S2. G.M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3.
S3. B.B. Dey, *J. Chem. Soc.*, 1914, **105**, 1039.

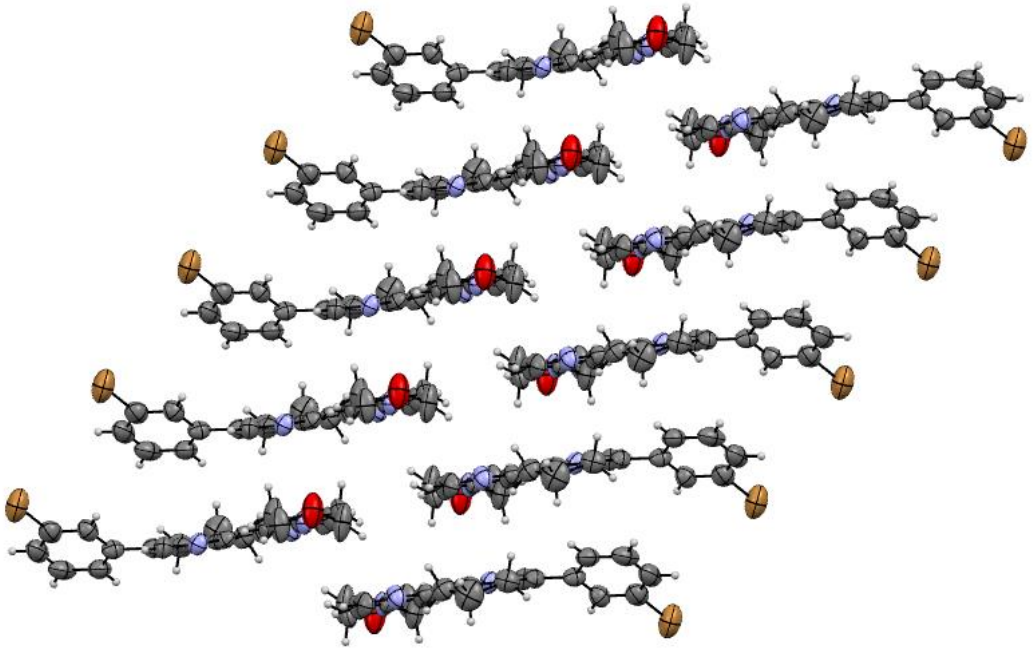
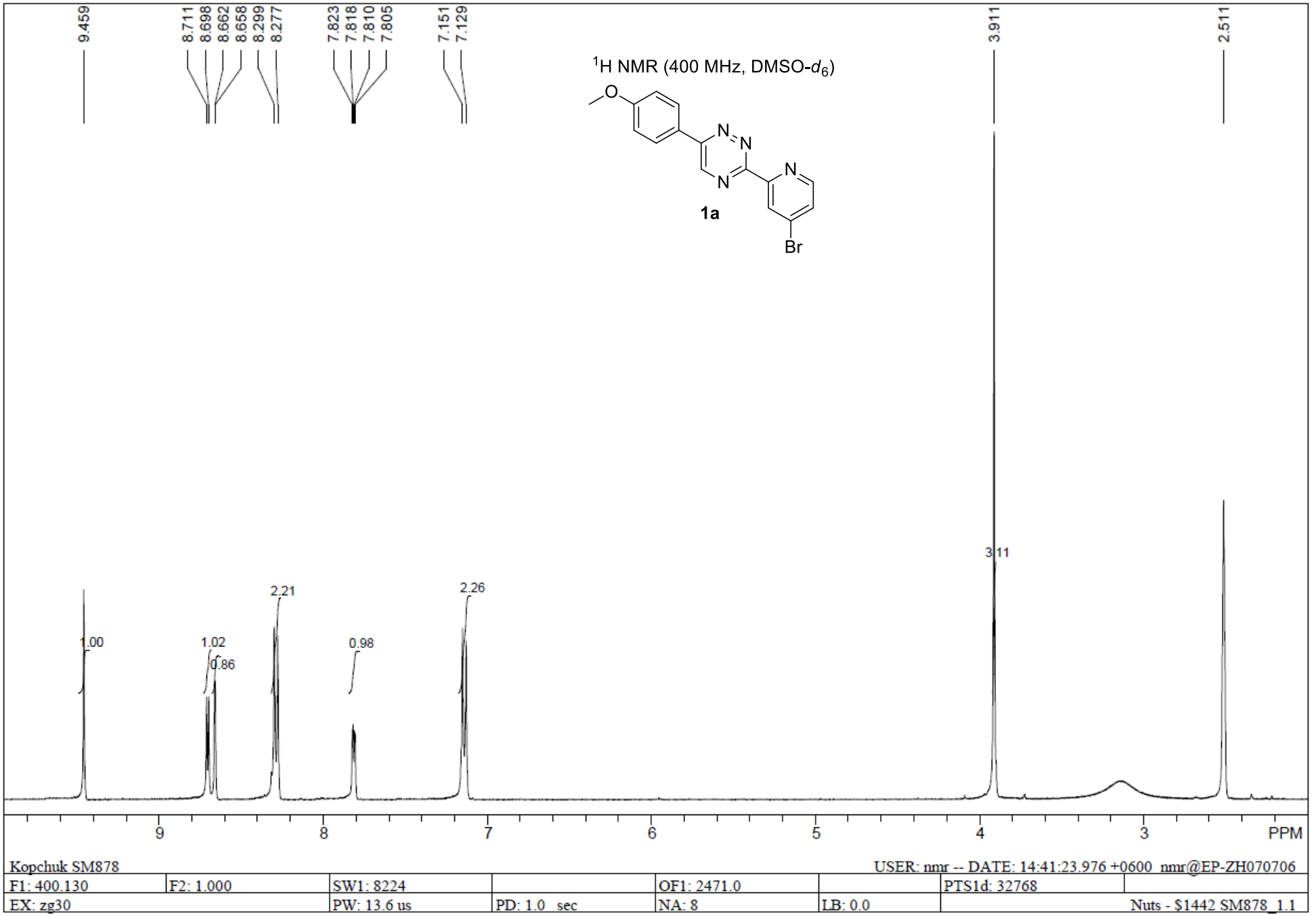


Figure S1. π-π-Stacking between molecules of **3c**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0.98
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9
8
7
6
5
4
3
PPM
Kopchuk SM878
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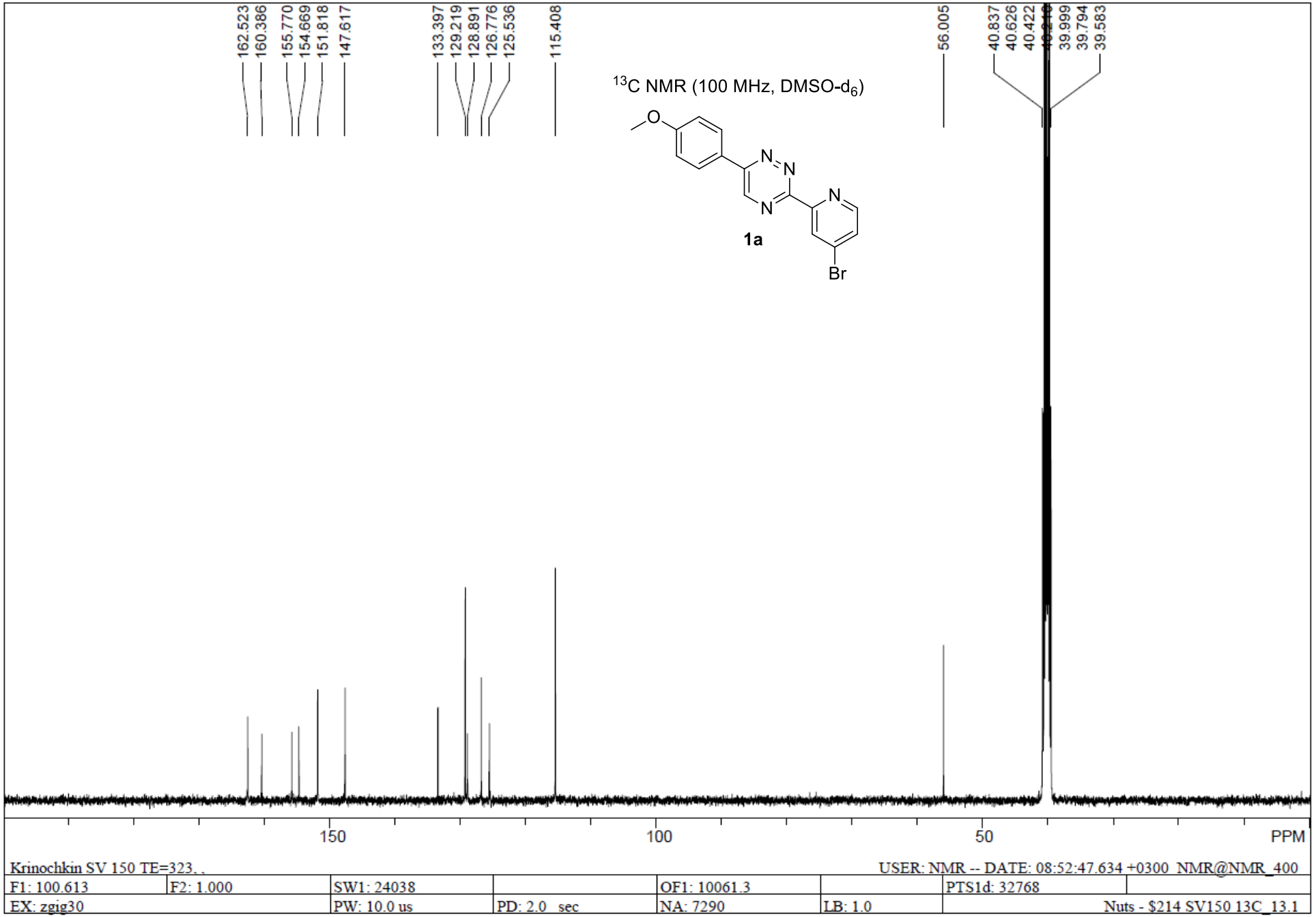
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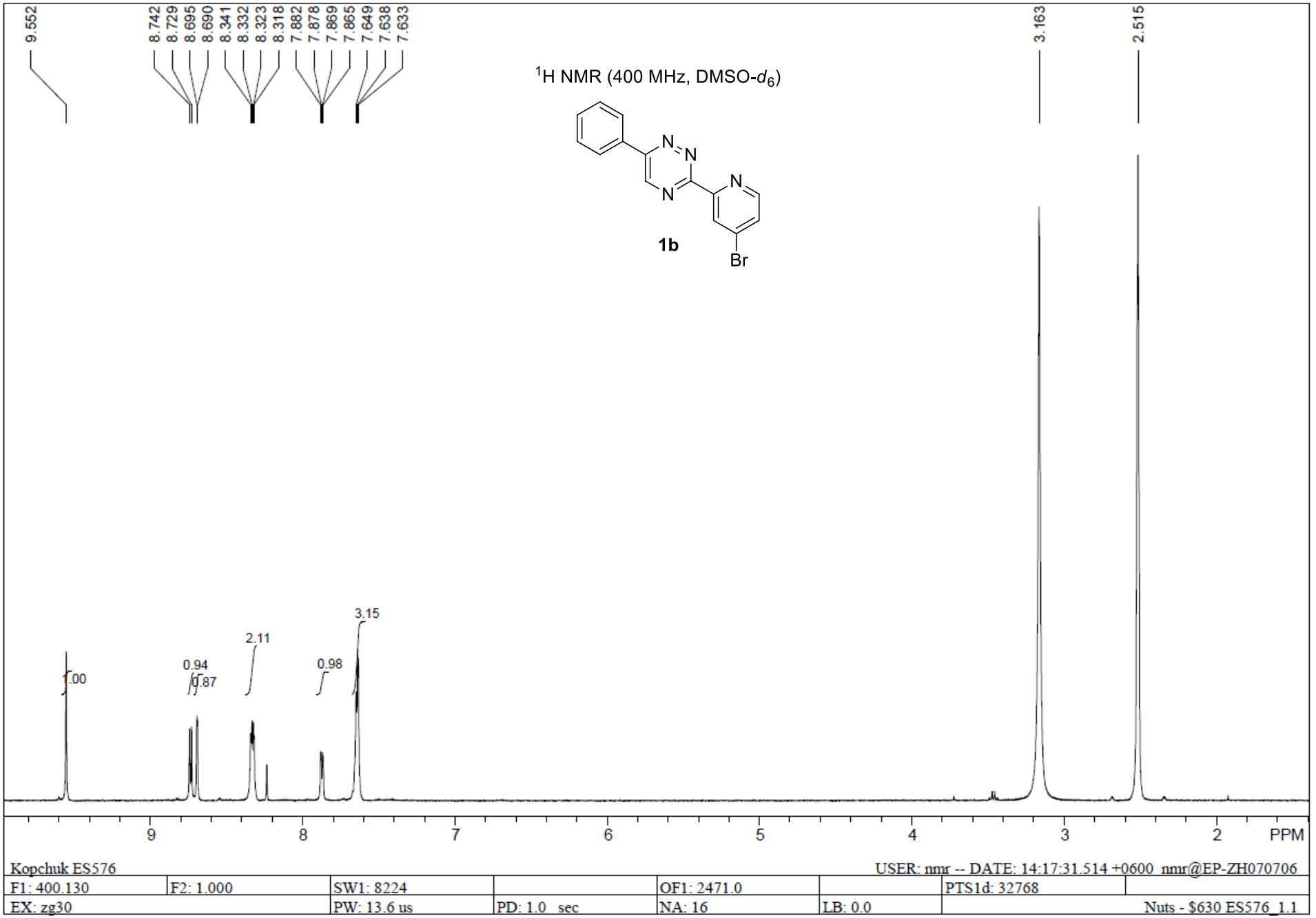
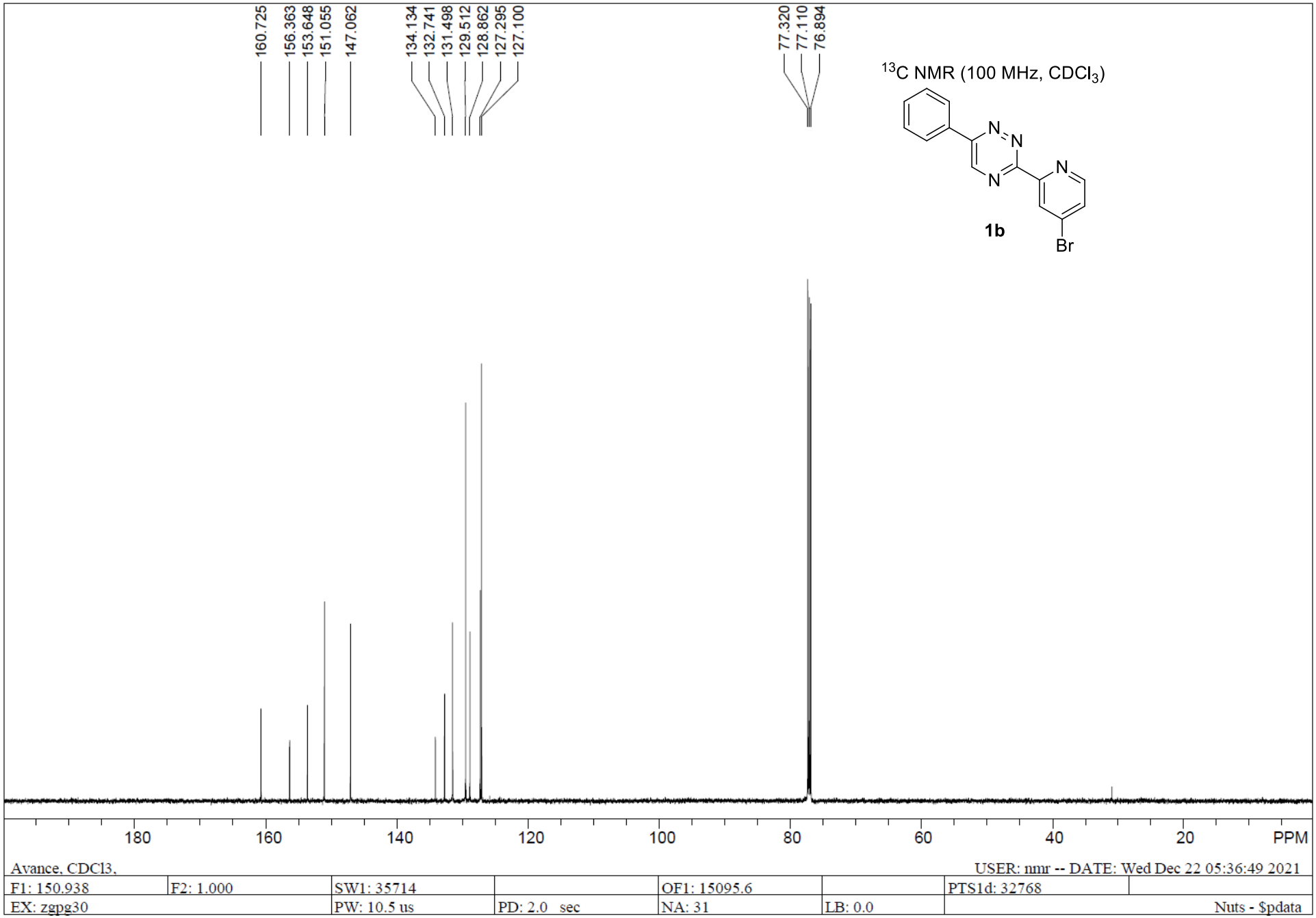
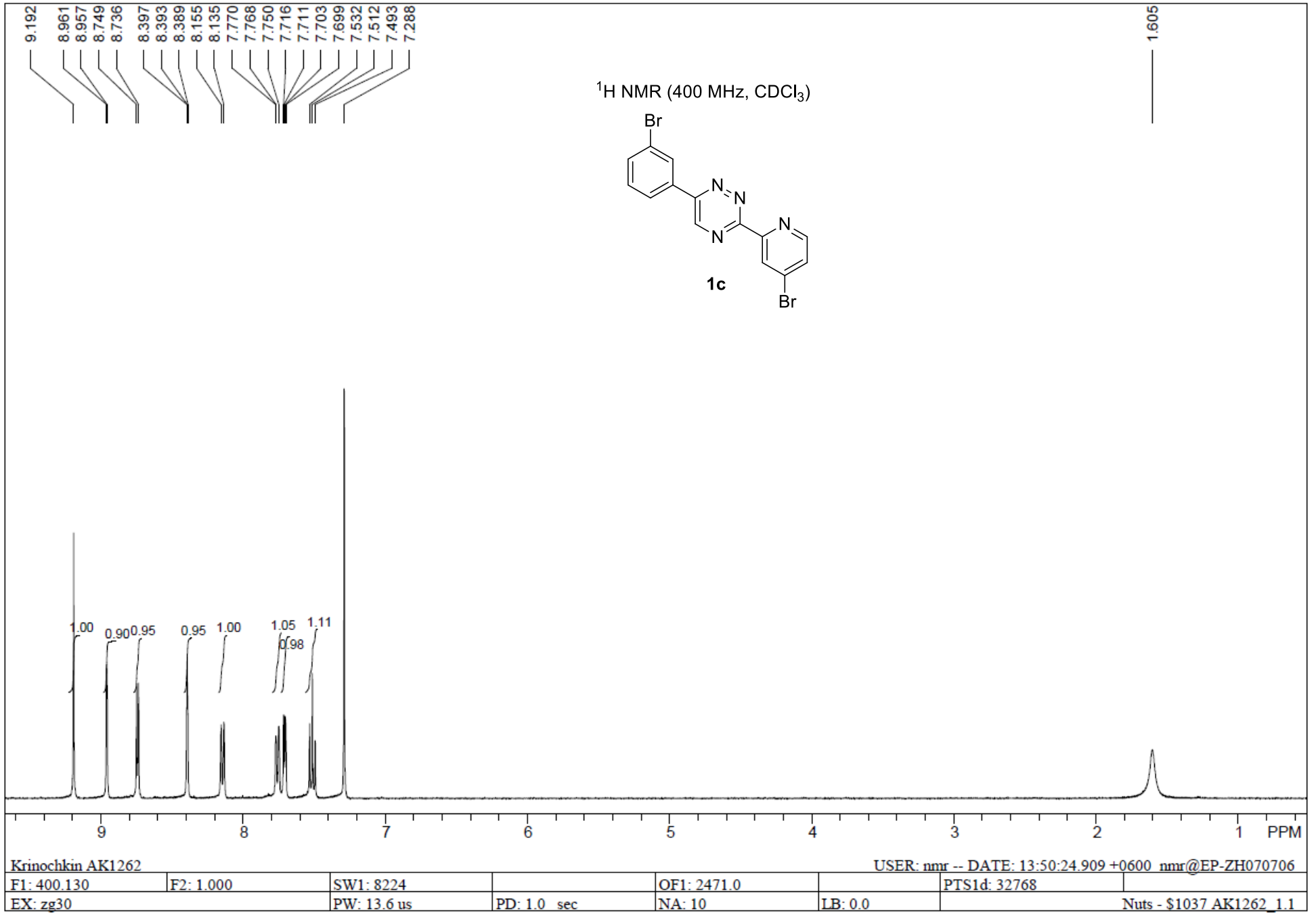
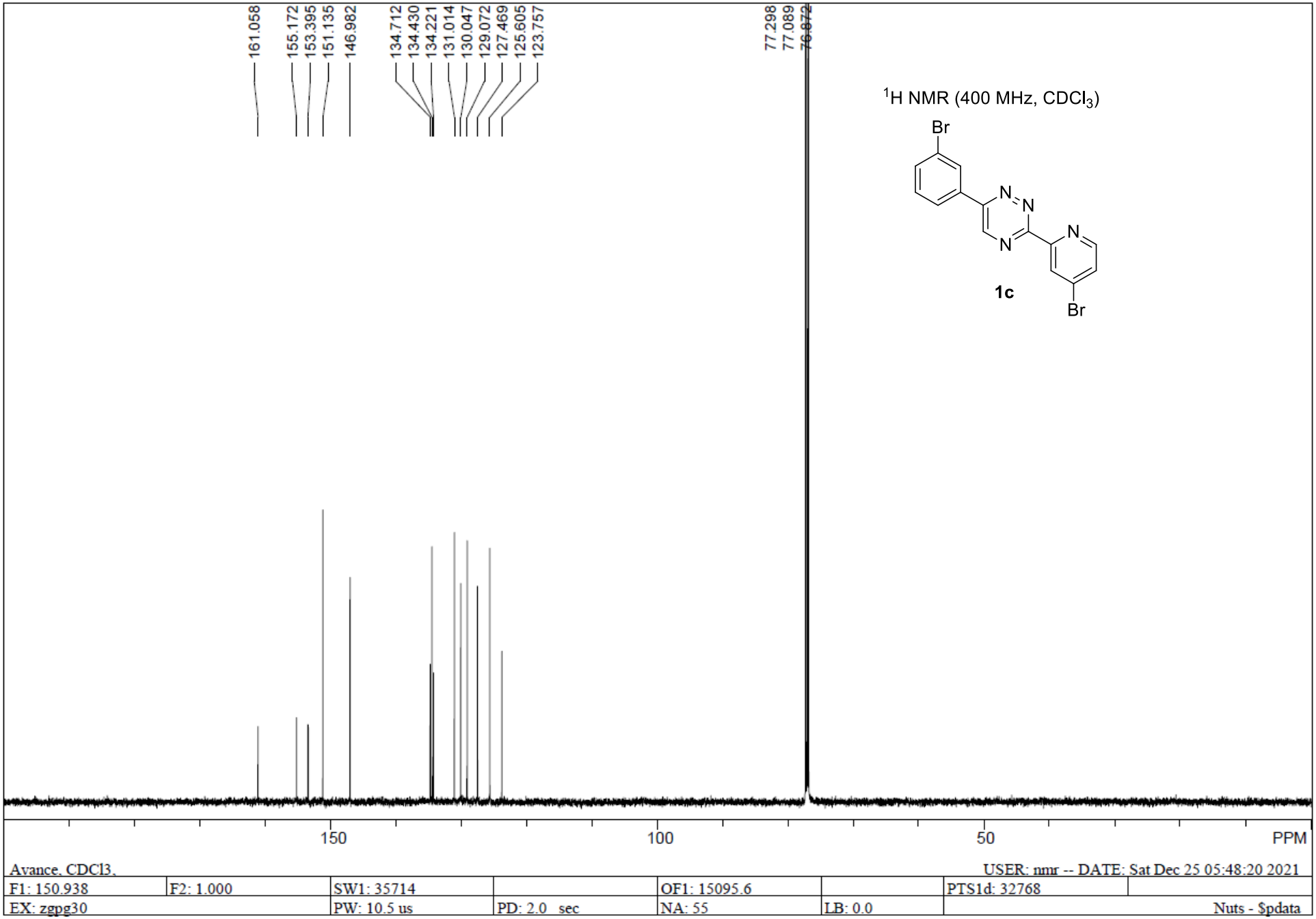
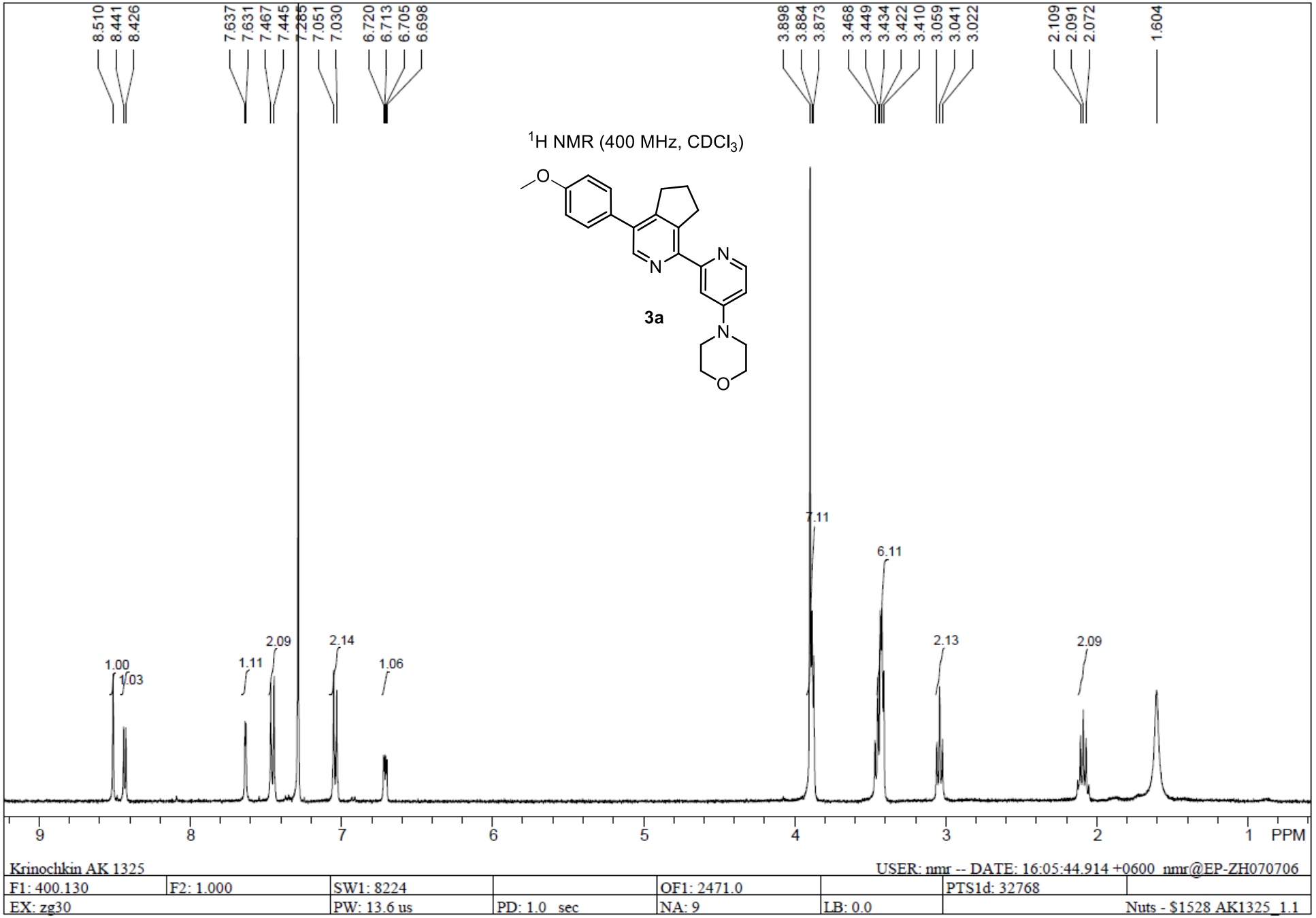
LB: 1.0
Nuts - $214 SV150 13C_13.1

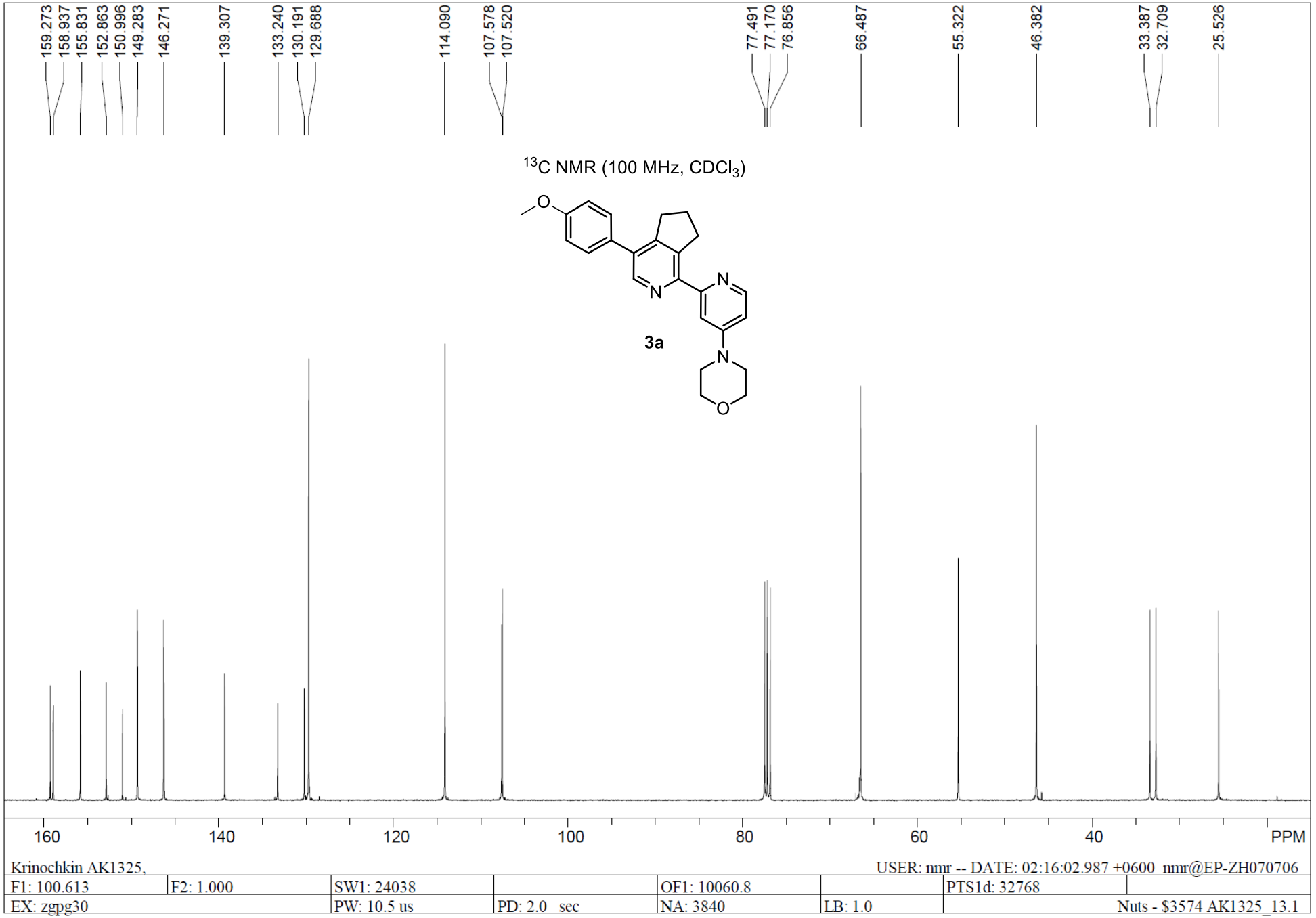

9.552
8.742
8.729
8.695
8.690
8.341
8.332
8.323
8.318
7.882
7.878
7.869
7.865
7.649
7.638
7.633
3.163
2.515
^{1}H NMR (400 MHz, DMSO-d_6)
1b
Br
1.00
0.94
0.87
2.11
0.98
3.15
9
8
7
6
5
4
3
2
PPM
Kopchuk ES576
USER: nmr -- DATE: 14:17:31.514 +0600 nmr@EP-ZH070706
F1: 400.130
F2: 1.000
SW1: 8224
OF1: 2471.0
PTS1d: 32768
EX: zg30
PW: 13.6 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $630 ES576_1.1

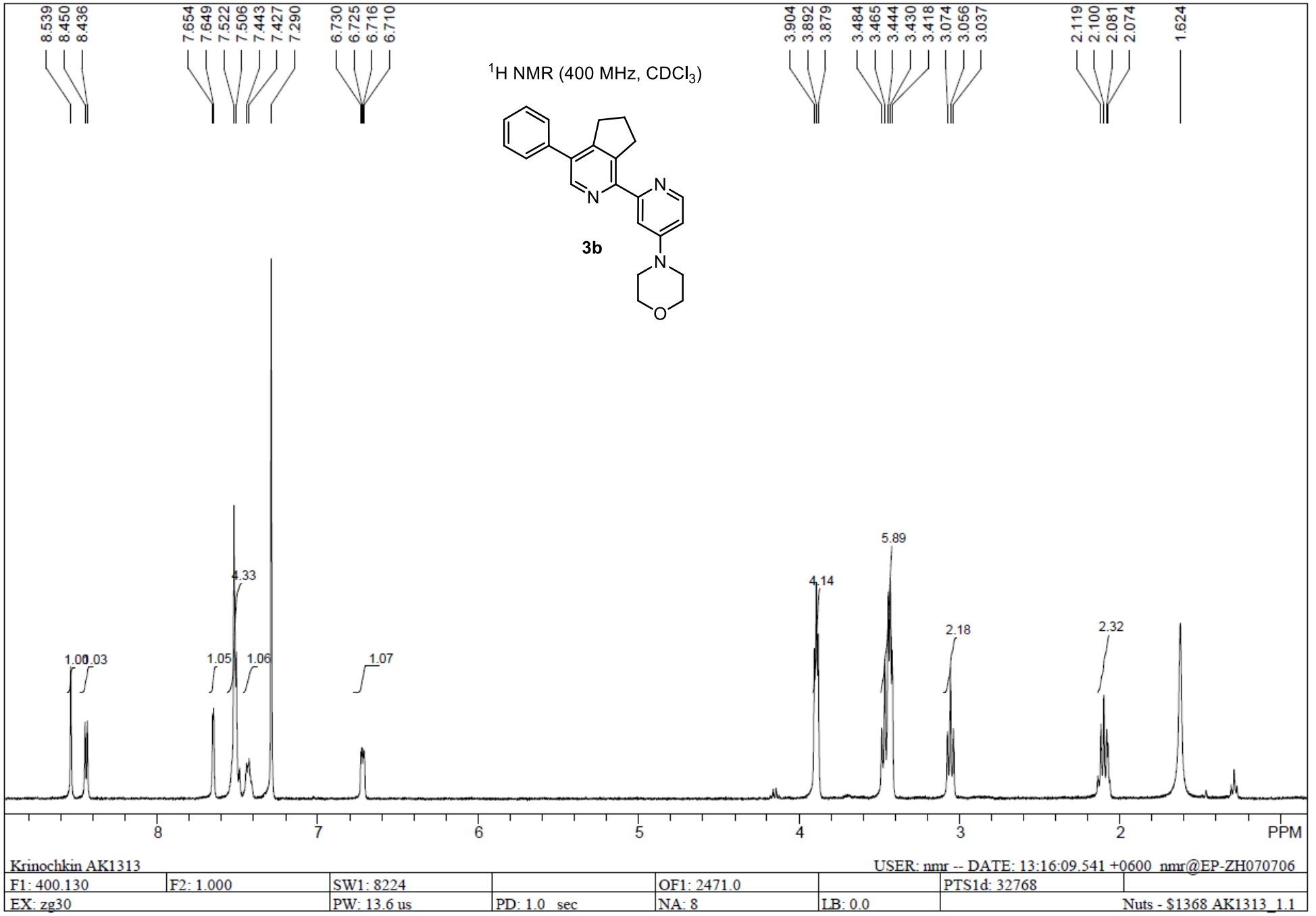

160.725
156.363
153.648
151.055
147.062
134.134
132.741
131.498
129.512
128.862
127.295
127.100
77.320
77.110
76.894
^{13}C NMR (100 MHz, $CDCl_3$)
1b
Br
180
160
140
120
100
80
60
40
20
PPM
Avance, CDCl3,
USER: nmr -- DATE: Wed Dec 22 05:36:49 2021
F1: 150.938
F2: 1.000
SW1: 35714
OF1: 15095.6
PTS1d: 32768
EX: zgpg30
PW: 10.5 us
PD: 2.0 sec
NA: 31
LB: 0.0
Nuts - $pdata

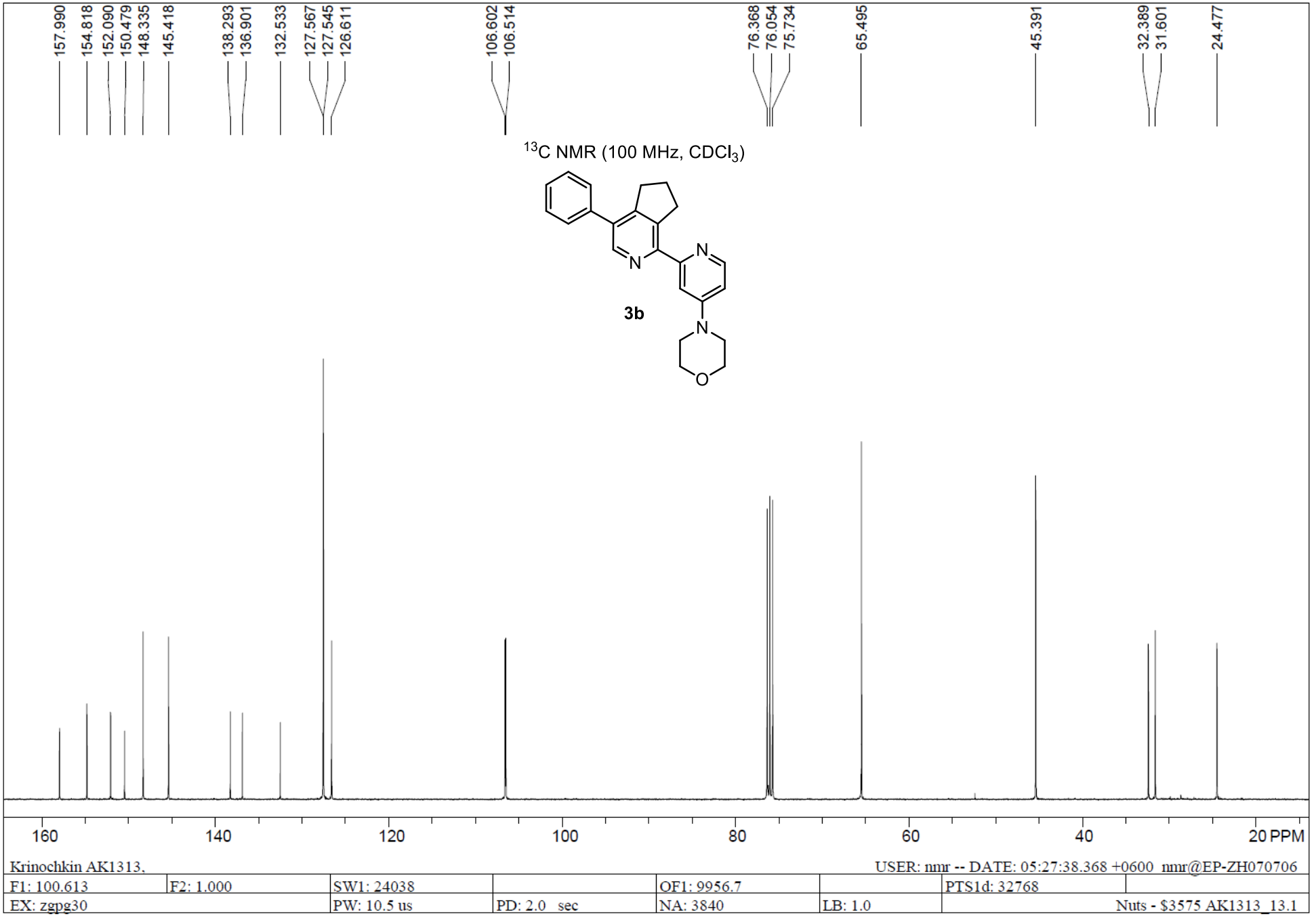

9.192
8.961
8.957
8.749
8.736
8.397
8.393
8.389
8.155
8.135
7.770
7.768
7.750
7.716
7.711
7.703
7.699
7.532
7.512
7.493
7.288
1.605
^{1}H NMR (400 MHz, CDCl$_3$)
Br
N
N
N
Br
1c
1.00
0.90
0.95
0.95
1.00
1.05
0.98
1.11
9
8
7
6
5
4
3
2
1
PPM
Krinochkin AK1262
USER: nmr -- DATE: 13:50:24.909 +0600 nmr@EP-ZH070706
F1: 400.130
F2: 1.000
SW1: 8224
OF1: 2471.0
PTS1d: 32768
EX: zg30
PW: 13.6 us
PD: 1.0 sec
NA: 10
LB: 0.0
Nuts - $1037 AK1262_1.1

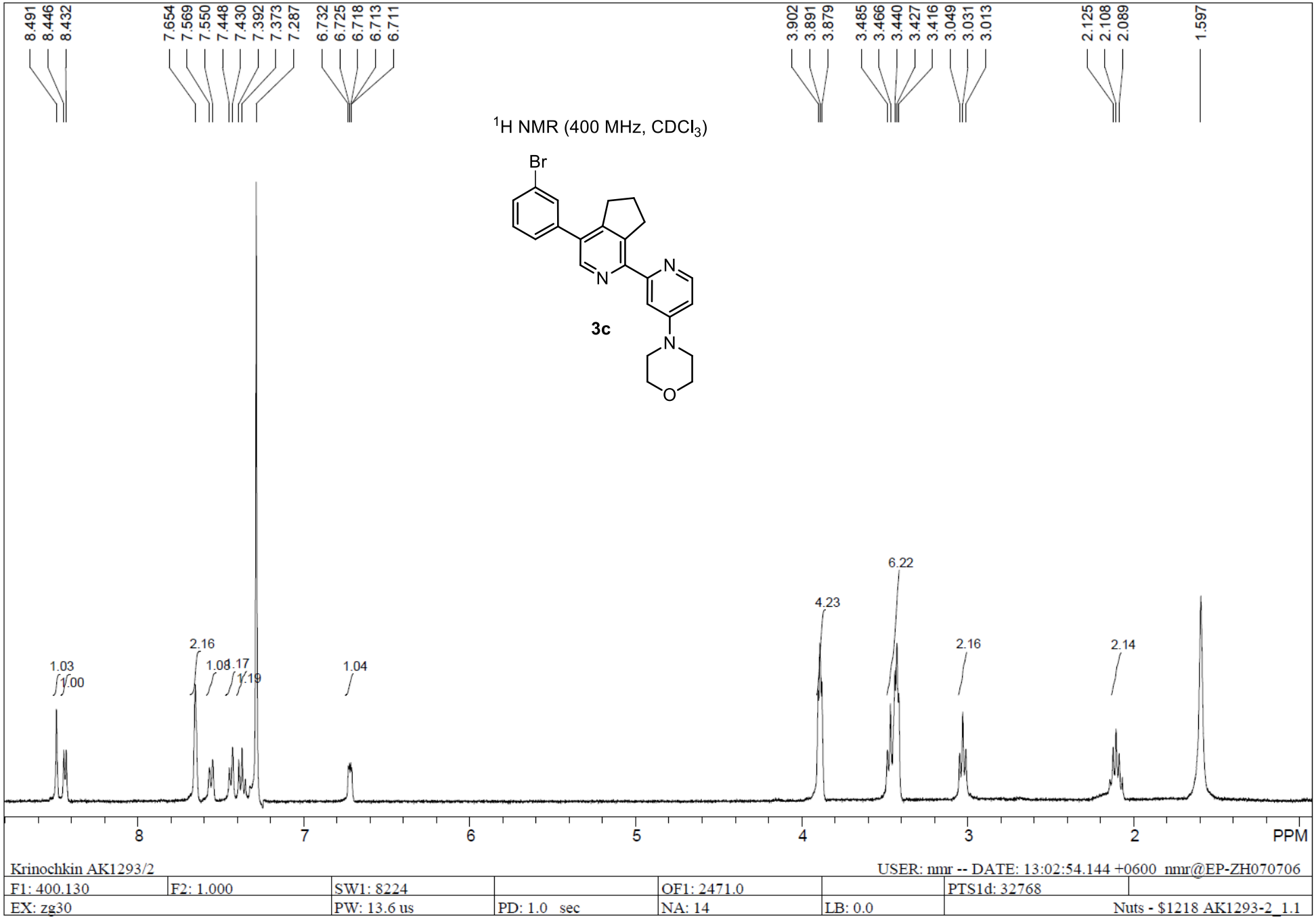

161.058
155.172
153.395
151.135
146.982
134.712
134.430
134.221
131.014
130.047
129.072
127.469
125.605
123.757
77.298
77.089
76.872
^{1}H NMR (400 MHz, CDCl$_3$)
Br
N
N
N
N
Br
1c
150
100
50
PPM
Avance, CDCl3,
USER: nmr -- DATE: Sat Dec 25 05:48:20 2021
F1: 150.938
F2: 1.000
SW1: 35714
OF1: 15095.6
PTS1d: 32768
EX: zgpg30
PW: 10.5 us
PD: 2.0 sec
NA: 55
LB: 0.0
Nuts - $pdata

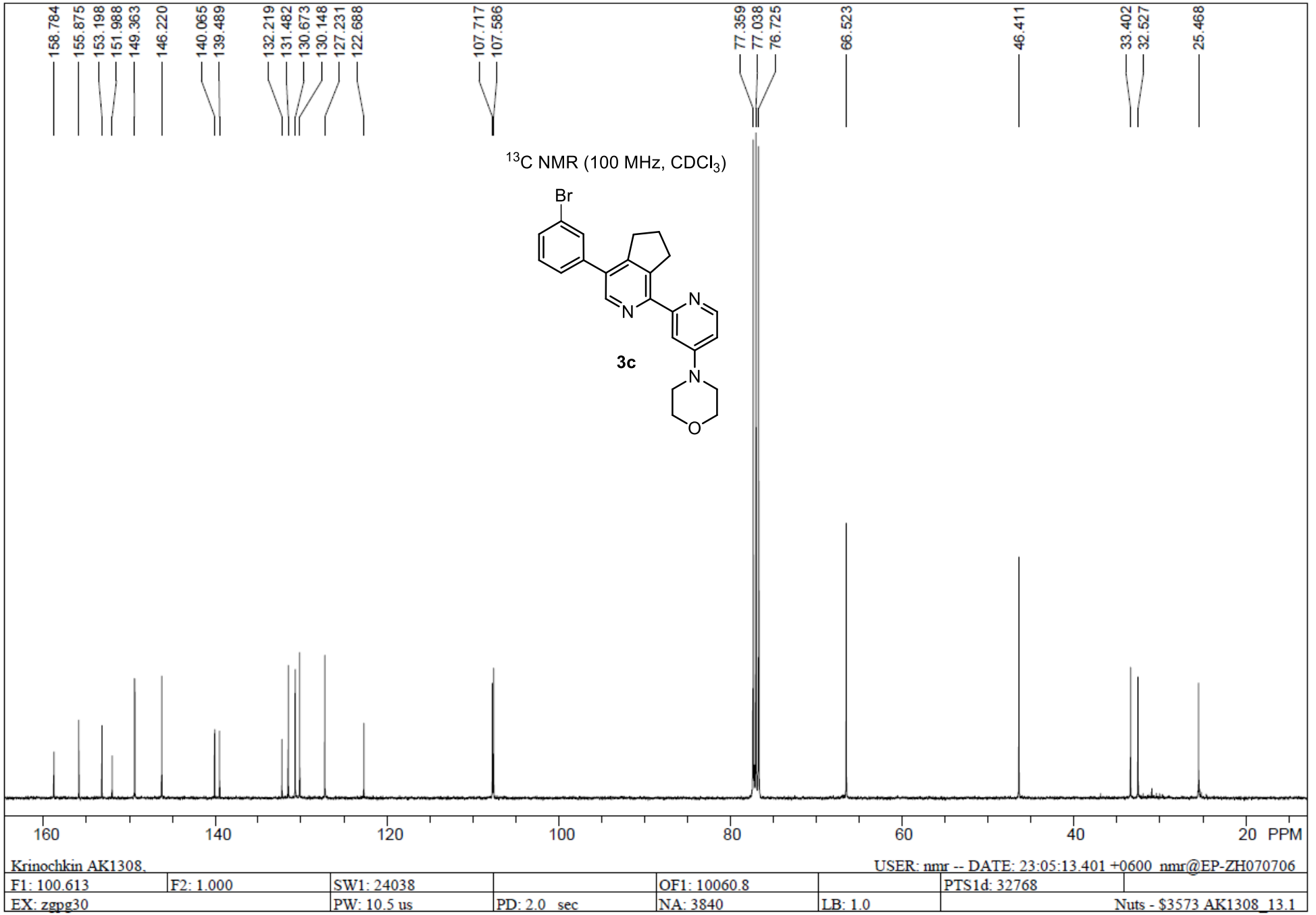

8.510
8.441
8.426
7.637
7.631
7.467
7.445
7.285
7.051
7.030
6.720
6.713
6.705
6.698
3.898
3.884
3.873
3.468
3.449
3.434
3.422
3.410
3.059
3.041
3.022
2.109
2.091
2.072
1.604
^{1}H NMR (400 MHz, CDCl$_3$)
3a
1.00
1.03
1.11
2.09
2.14
1.06
7.11
6.11
2.13
2.09
9
8
7
6
5
4
3
2
1
PPM
Krinochkin AK 1325
USER: nmr -- DATE: 16:05:44.914 +0600 nmr@EP-ZH070706
F1: 400.130
F2: 1.000
SW1: 8224
OF1: 2471.0
PTS1d: 32768
EX: zg30
PW: 13.6 us
PD: 1.0 sec
NA: 9
LB: 0.0
Nuts - $1528 AK1325_1.1

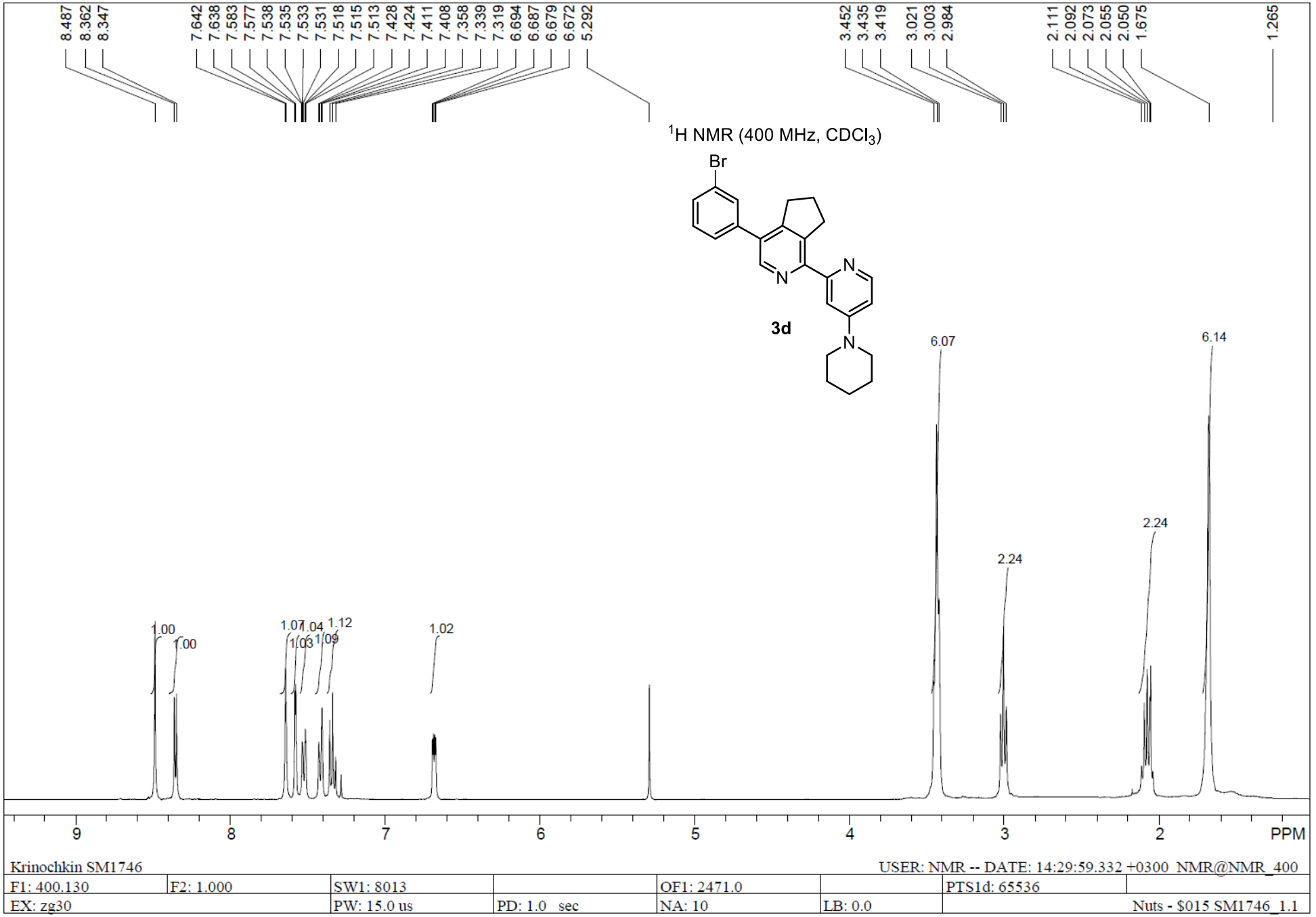

159.273
158.937
155.831
152.863
150.996
149.283
146.271
139.307
133.240
130.191
129.688
114.090
107.578
107.520
77.491
77.170
76.856
66.487
55.322
46.382
33.387
32.709
25.526
13C NMR (100 MHz, CDCl3)
O
N
N
N
O
3a
160
140
120
100
80
60
40
PPM
Krinochkin AK1325,
USER: nmr -- DATE: 02:16:02.987 +0600 nmr@EP-ZH070706
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.8
PTS1d: 32768
EX: zgpg30
PW: 10.5 us
PD: 2.0 sec
NA: 3840
LB: 1.0
Nuts - $3574 AK1325_13.1

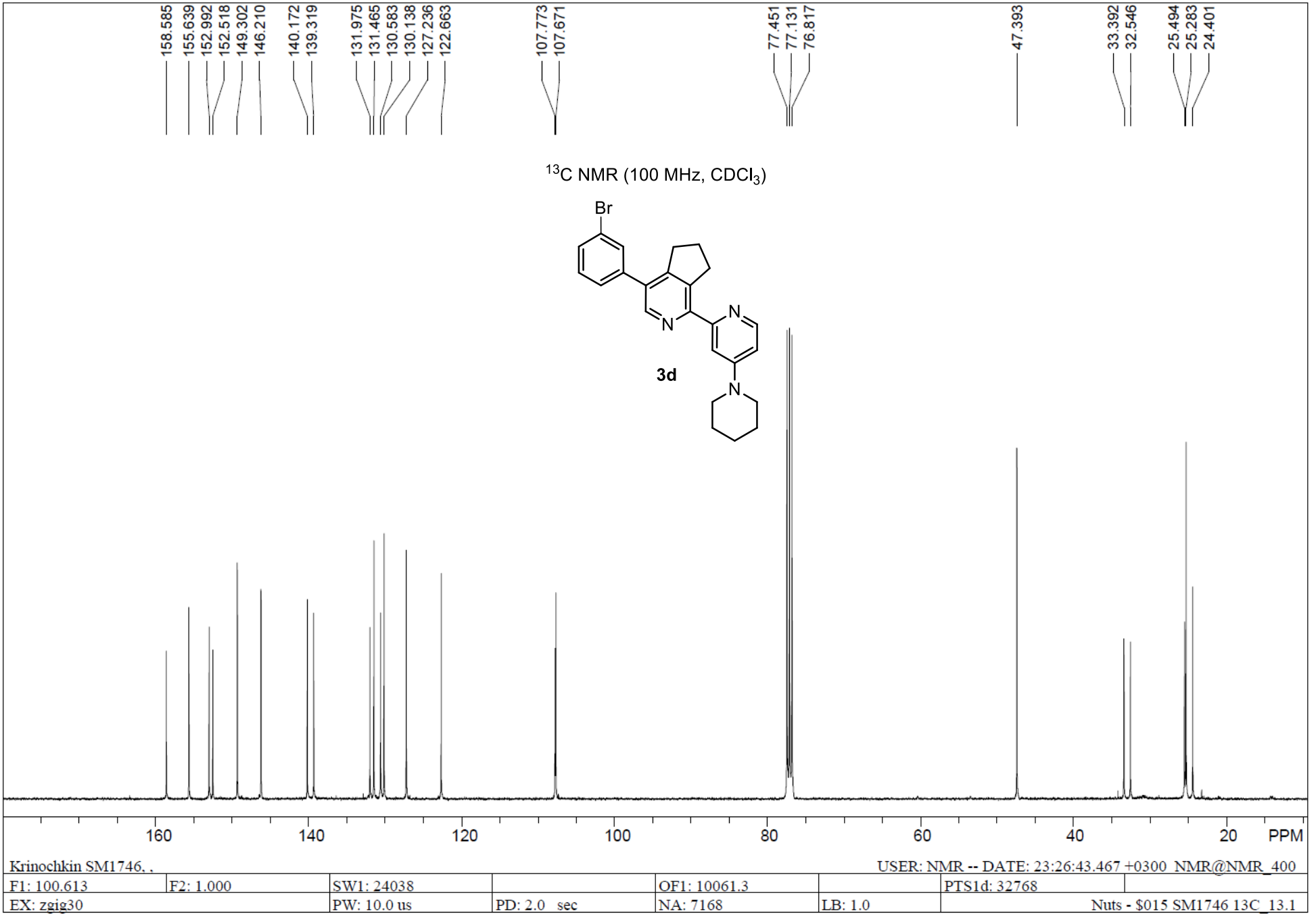

8.539
8.450
8.436
7.654
7.649
7.522
7.506
7.443
7.427
7.290
6.730
6.725
6.716
6.710
3.904
3.892
3.879
3.484
3.465
3.444
3.430
3.418
3.074
3.056
3.037
2.119
2.100
2.081
2.074
1.624
^{1}H NMR (400 MHz, $CDCl_3$)
3b
1.00
1.03
1.05
4.33
1.06
1.07
4.14
5.89
2.18
2.32
8
7
6
5
4
3
2
PPM
Krinochkin AK1313
USER: nmr -- DATE: 13:16:09.541 +0600 nmr@EP-ZH070706
F1: 400.130
F2: 1.000
SW1: 8224
OF1: 2471.0
PTS1d: 32768
EX: zg30
PW: 13.6 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $1368 AK1313_1.1

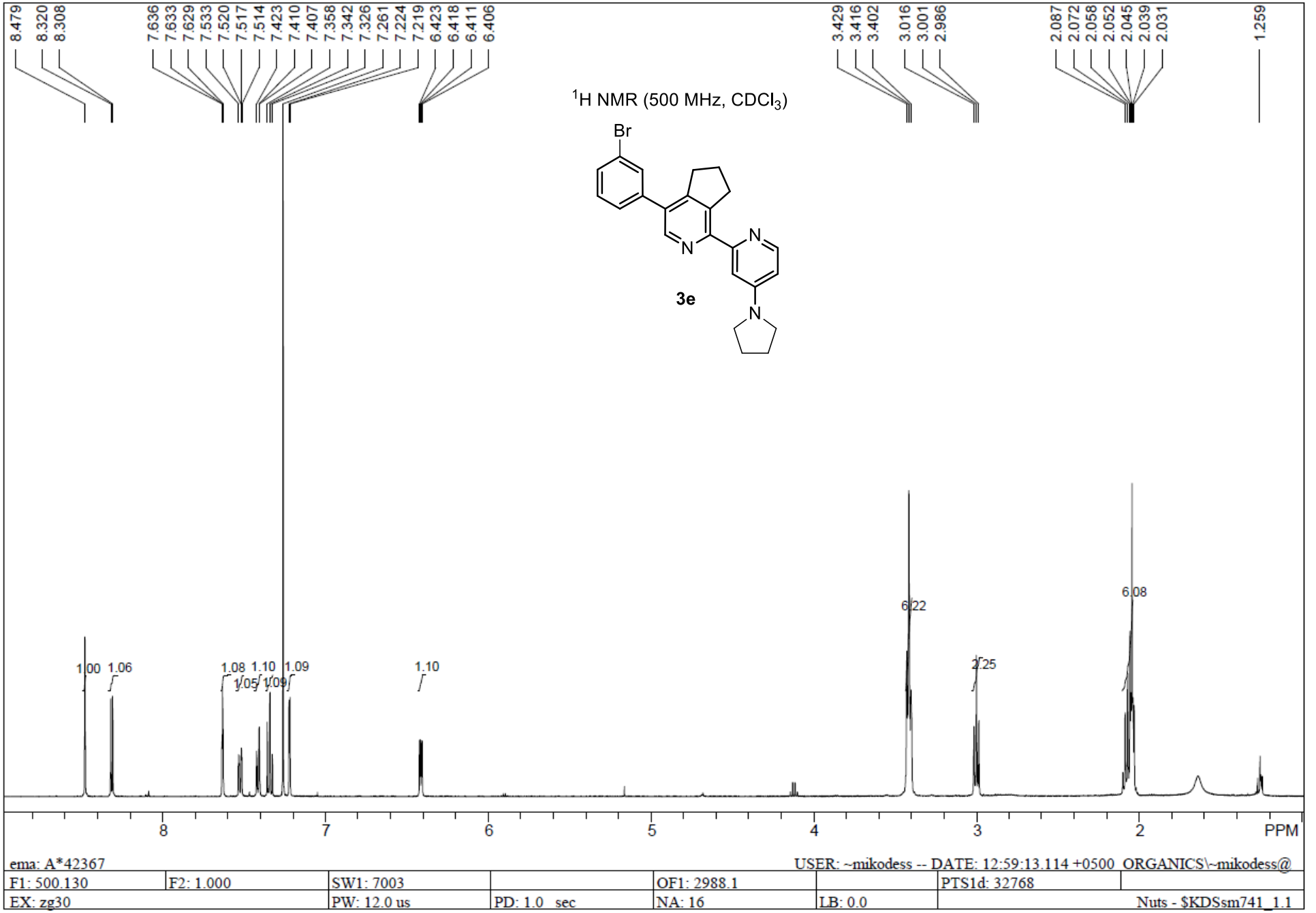

157.990
154.818
152.090
150.479
148.335
145.418
138.293
136.901
132.533
127.567
127.545
126.611
106.602
106.514
76.368
76.054
75.734
65.495
45.391
32.389
31.601
24.477
13C NMR (100 MHz, CDCl3)
N
N
N
O
3b
160
140
120
100
80
60
40
20 PPM
Krinochkin AK1313.
USER: nmr -- DATE: 05:27:38.368 +0600 nmr@EP-ZH070706
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 9956.7
PTS1d: 32768
EX: zgpg30
PW: 10.5 us
PD: 2.0 sec
NA: 3840
LB: 1.0
Nuts - $3575 AK1313_13.1

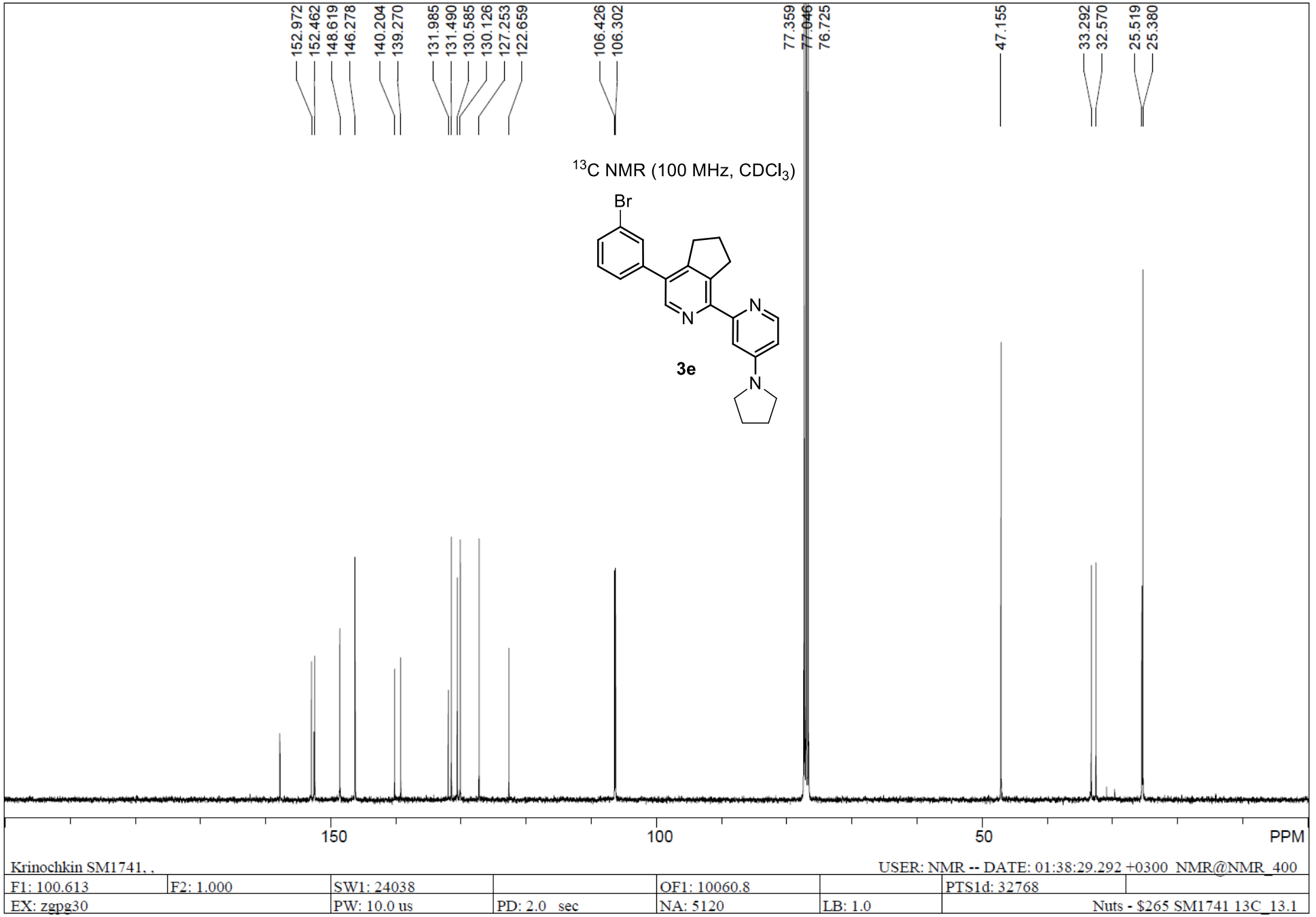

8.491
8.446
8.432
7.654
7.569
7.550
7.448
7.430
7.392
7.373
7.287
6.732
6.725
6.718
6.713
6.711
3.902
3.891
3.879
3.485
3.466
3.440
3.427
3.416
3.049
3.031
3.013
2.125
2.108
2.089
1.597
^{1}H NMR (400 MHz, $CDCl_3$)
Br
N
N
N
O
3c
1.03
1.00
2.16
1.08
1.17
1.19
1.04
4.23
6.22
2.16
2.14
8
7
6
5
4
3
2
PPM
Krinochkin AK1293/2
USER: nmr -- DATE: 13:02:54.144 +0600 nmr@EP-ZH070706
F1: 400.130
F2: 1.000
SW1: 8224
OF1: 2471.0
PTS1d: 32768
EX: zg30
PW: 13.6 us
PD: 1.0 sec
NA: 14
LB: 0.0
Nuts - $1218 AK1293-2_1.1

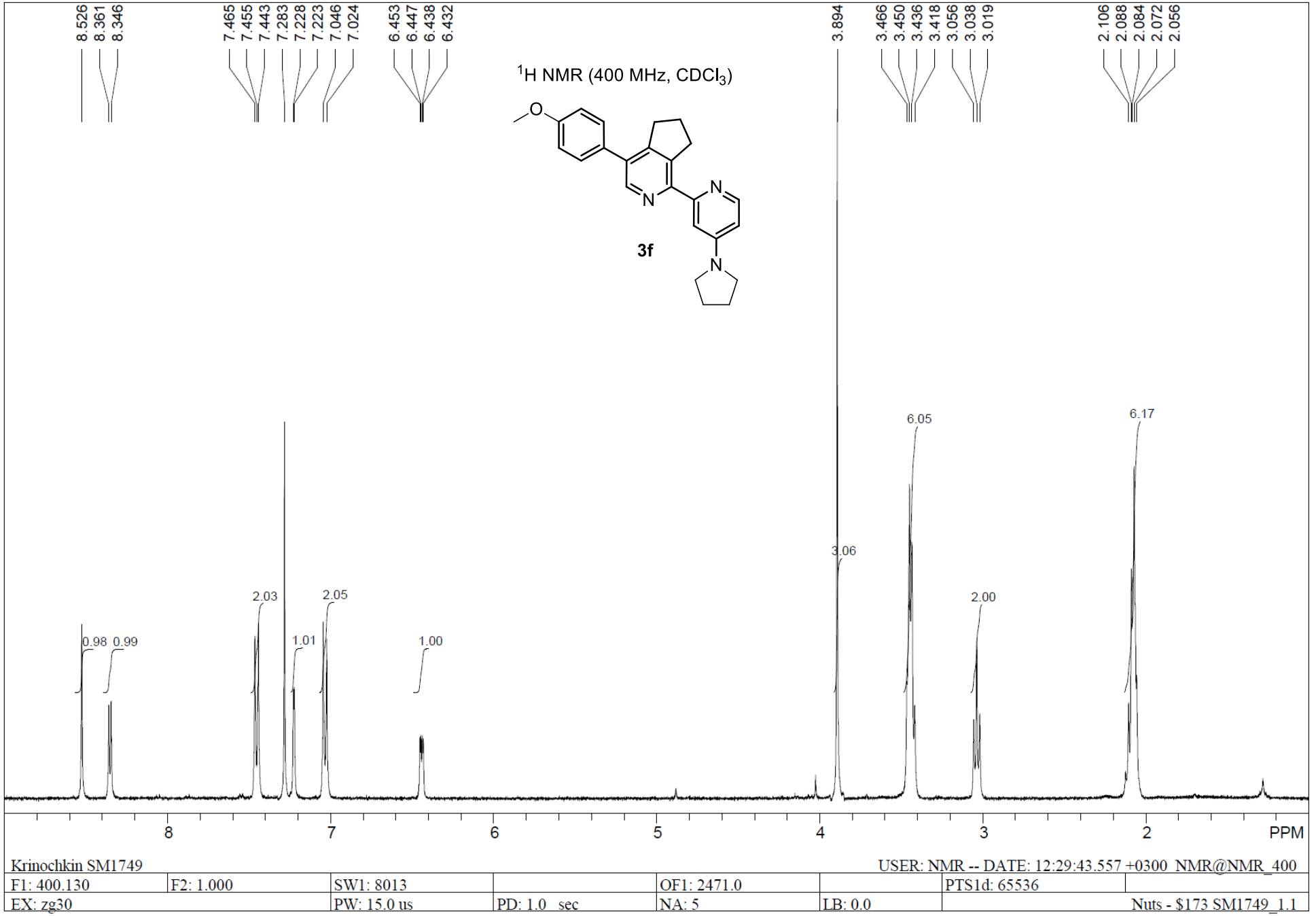

158.784
155.875
153.198
151.988
149.363
146.220
140.065
139.489
132.219
131.482
130.673
130.148
127.231
122.688
107.717
107.586
77.359
77.038
76.725
66.523
46.411
33.402
32.527
25.468
13C NMR (100 MHz, CDCl3)
Br
N
N
N
O
3c
160
140
120
100
80
60
40
20 PPM
Krinochkin AK1308.
USER: nmr -- DATE: 23:05:13.401 +0600 nmr@EP-ZH070706
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.8
PTS1d: 32768
EX: zgpg30
PW: 10.5 us
PD: 2.0 sec
NA: 3840
LB: 1.0
Nuts - $3573 AK1308_13.1

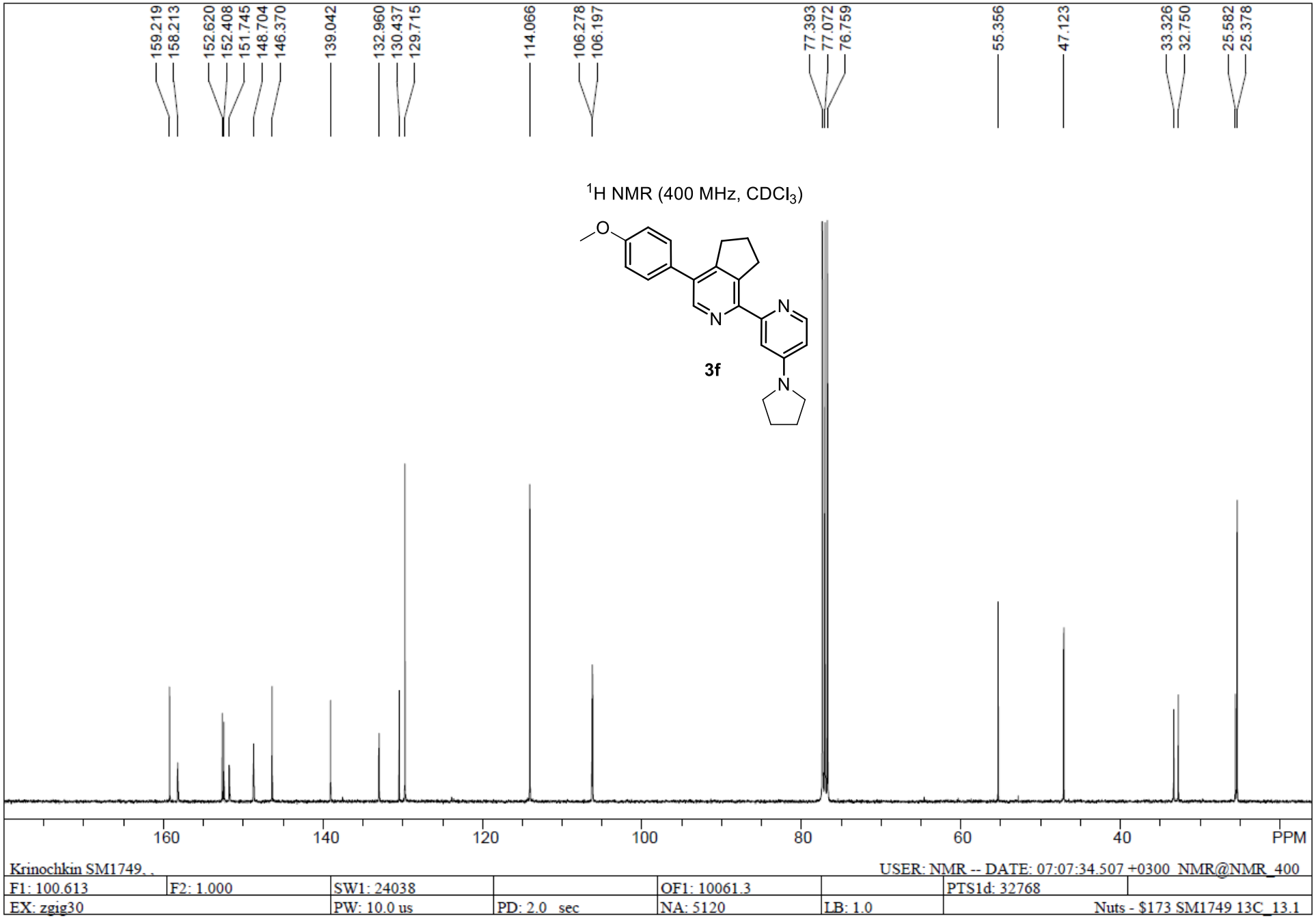

8.487
8.362
8.347
7.642
7.638
7.583
7.577
7.538
7.535
7.533
7.531
7.518
7.515
7.513
7.428
7.424
7.411
7.408
7.358
7.339
7.319
6.694
6.687
6.679
6.672
5.292
3.452
3.435
3.419
3.021
3.003
2.984
2.111
2.092
2.073
2.055
2.050
1.675
1.265
1H NMR (400 MHz, CDCl3)
Br
N
N
N
3d
6.07
6.14
2.24
2.24
1.00
1.00
1.07
1.04
1.12
1.03
1.09
1.02
9
8
7
6
5
4
3
2
PPM
Krinochkin SM1746
USER: NMR -- DATE: 14:29:59.332 +0300 NMR@NMR_400
F1: 400.130
F2: 1.000
SW1: 8013
OF1: 2471.0
PTS1d: 65536
EX: zg30
PW: 15.0 us
PD: 1.0 sec
NA: 10
LB: 0.0
Nuts - $015 SM1746_1.1

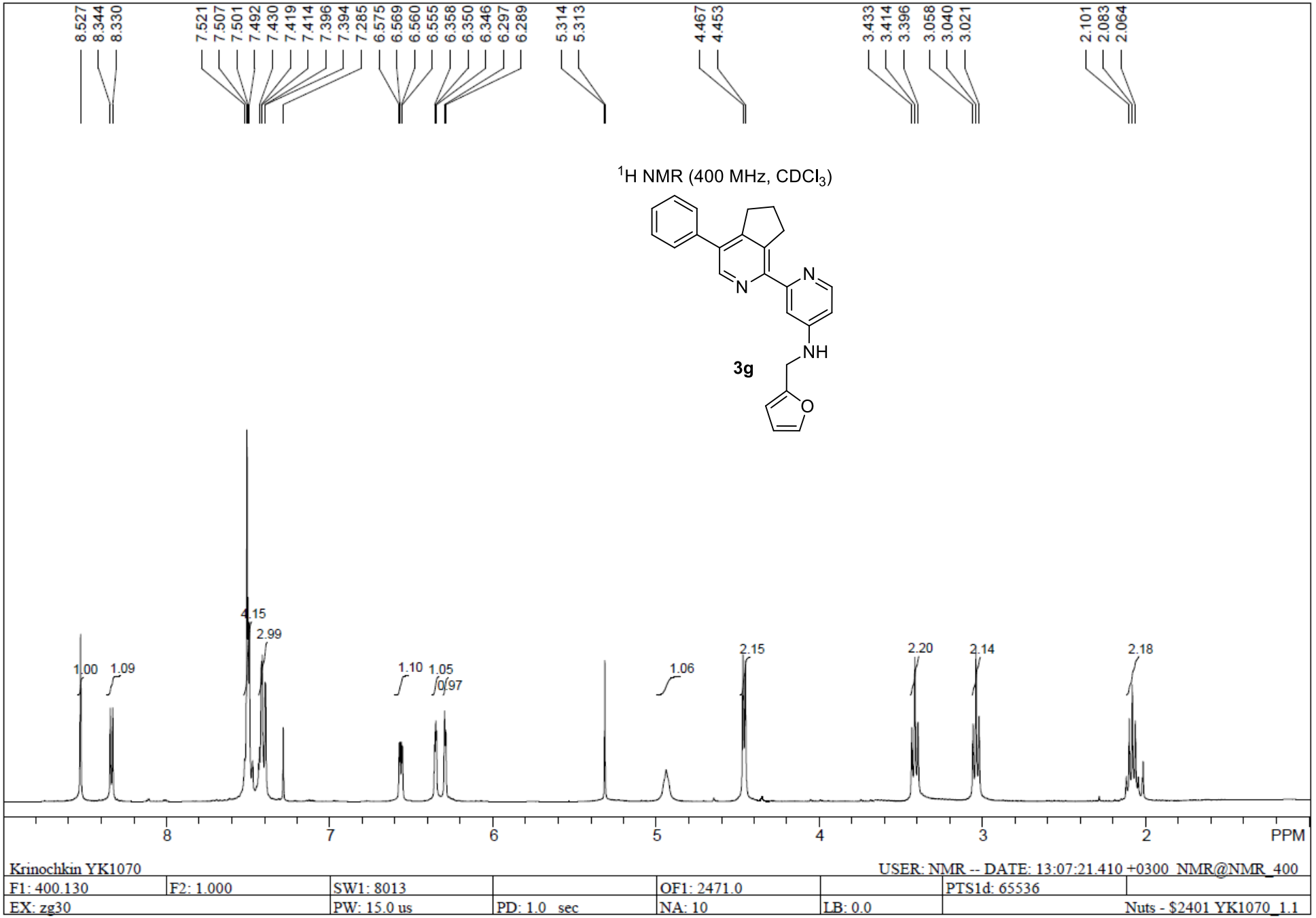

158.585
155.639
152.992
152.518
149.302
146.210
140.172
139.319
131.975
131.465
130.583
130.138
127.236
122.663
107.773
107.671
77.451
77.131
76.817
47.393
33.392
32.546
25.494
25.283
24.401
^{13}C NMR (100 MHz, CDCl$_3$)
Br
N
N
N
3d
160
140
120
100
80
60
40
20
PPM
Krinochkin SM1746, .
USER: NMR -- DATE: 23:26:43.467 +0300 NMR@NMR_400
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10061.3
PTS1d: 32768
EX: zgig30
PW: 10.0 us
PD: 2.0 sec
NA: 7168
LB: 1.0
Nuts - $015 SM1746 13C_13.1

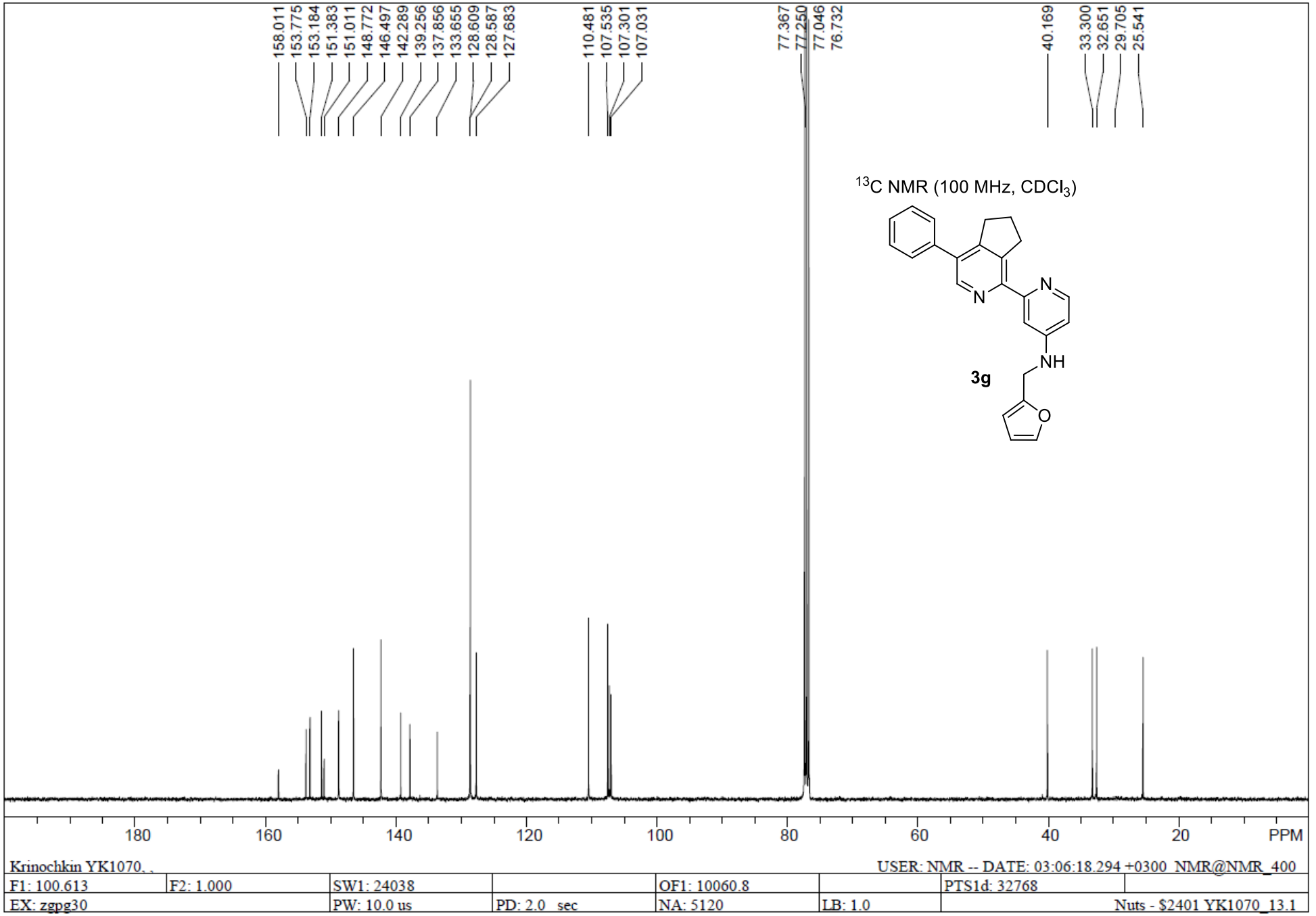

8.479
8.320
8.308
7.636
7.633
7.629
7.533
7.520
7.517
7.514
7.423
7.410
7.407
7.358
7.342
7.326
7.261
7.224
7.219
6.423
6.418
6.411
6.406
3.429
3.416
3.402
3.016
3.001
2.986
2.087
2.072
2.058
2.052
2.045
2.039
2.031
1.259
^{1}H NMR (500 MHz, $CDCl_3$)
Br
N
N
N
3e
1.00
1.06
1.08
1.05
1.10
1.09
1.10
6.22
2.25
6.08
8
7
6
5
4
3
2
PPM
ema: A*42367
USER: ~mikodess -- DATE: 12:59:13.114 +0500 ORGANICS\~mikodess@
F1: 500.130
F2: 1.000
SW1: 7003
OF1: 2988.1
PTS1d: 32768
EX: zg30
PW: 12.0 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $KDSsm741_1.1

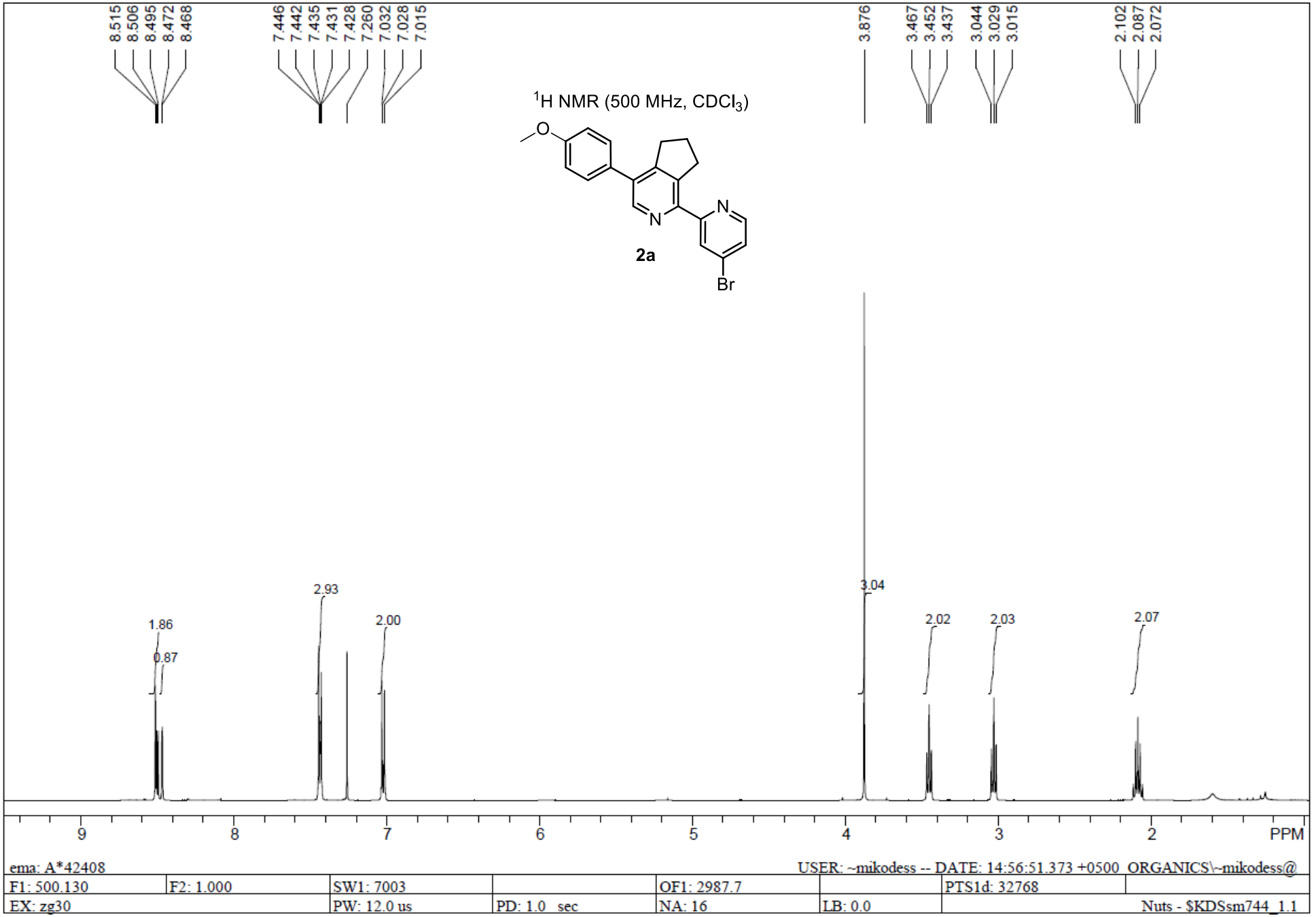

152.972
152.462
148.619
146.278
140.204
139.270
131.985
131.490
130.585
130.126
127.253
122.659
106.426
106.302
77.359
77.046
76.725
47.155
33.292
32.570
25.519
25.380
^{13}C NMR (100 MHz, $CDCl_3$)
Br
N
N
N
3e
150
100
50
PPM
Krinochkin SM1741. .
USER: NMR -- DATE: 01:38:29.292 +0300 NMR@NMR_400
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.8
PTS1d: 32768
EX: zgpg30
PW: 10.0 us
PD: 2.0 sec
NA: 5120
LB: 1.0
Nuts - $265 SM1741 13C_13.1

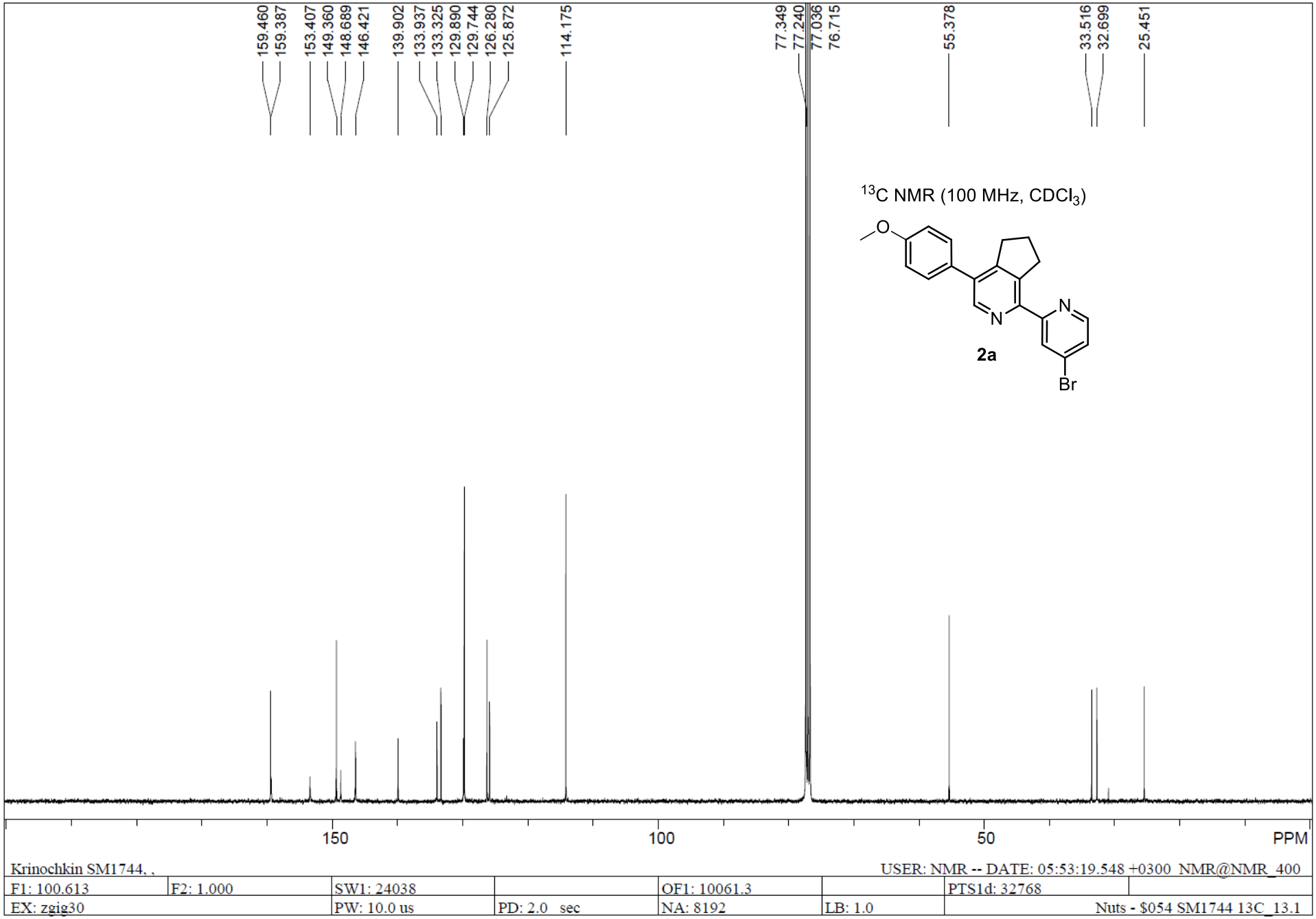

8.526
8.361
8.346
7.465
7.455
7.443
7.283
7.228
7.223
7.046
7.024
6.453
6.447
6.438
6.432
3.894
3.466
3.450
3.436
3.418
3.056
3.038
3.019
2.106
2.088
2.084
2.072
2.056
^{1}H NMR (400 MHz, $CDCl_3$)
O
N
N
N
3f
0.98
0.99
2.03
1.01
2.05
1.00
3.06
6.05
2.00
6.17
8
7
6
5
4
3
2
PPM
Krinochkin SM1749
USER: NMR -- DATE: 12:29:43.557 +0300 NMR@NMR_400
F1: 400.130
F2: 1.000
SW1: 8013
OF1: 2471.0
PTS1d: 65536
EX: zg30
PW: 15.0 us
PD: 1.0 sec
NA: 5
LB: 0.0
Nuts - $173 SM1749_1.1

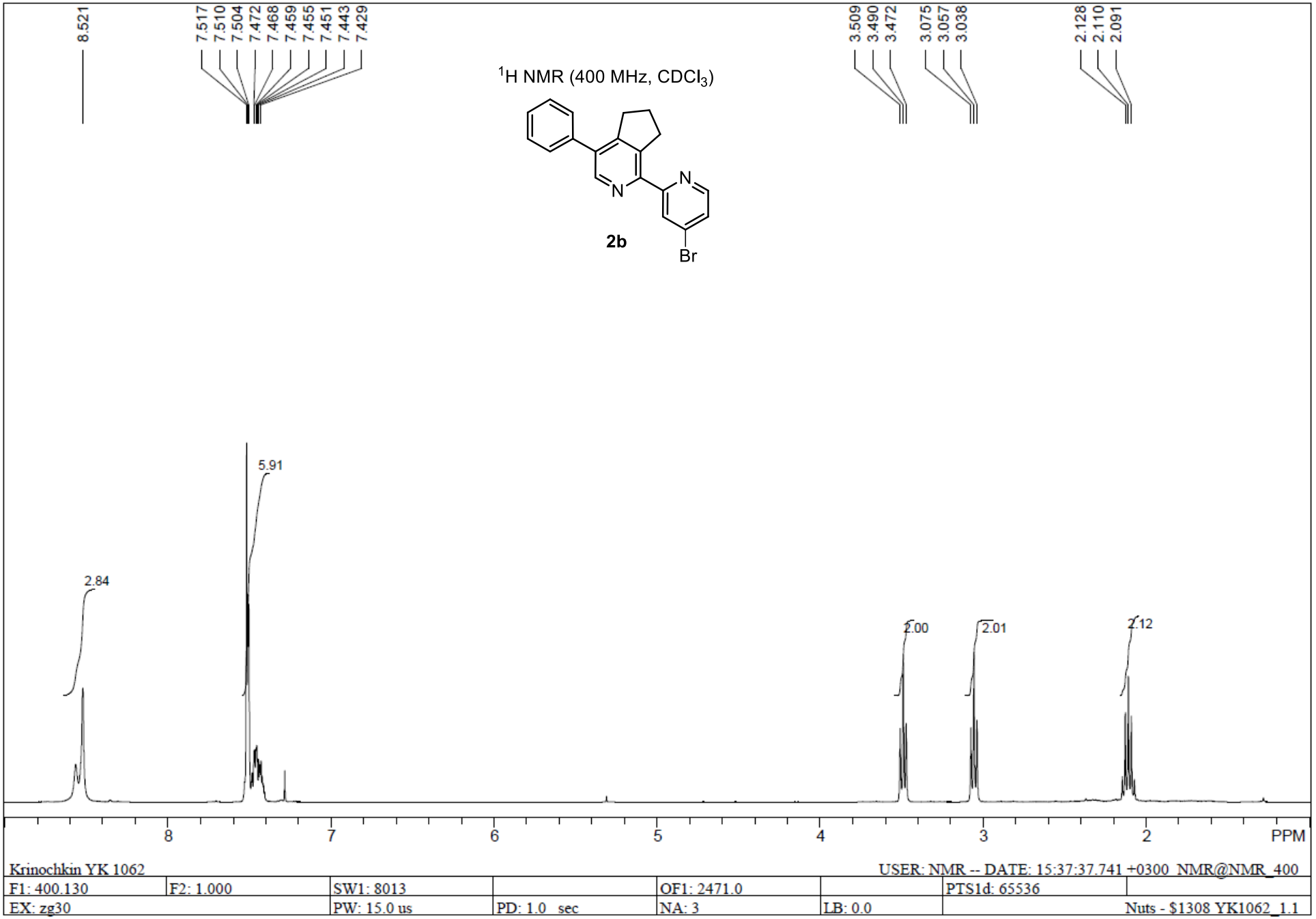

159.219
158.213
152.620
152.408
151.745
148.704
146.370
139.042
132.960
130.437
129.715
114.066
106.278
106.197
77.393
77.072
76.759
55.356
47.123
33.326
32.750
25.582
25.378
^{1}H NMR (400 MHz, CDCl$_3$)
O
N
N
N
3f
160
140
120
100
80
60
40
PPM
Krinochkin SM1749, ,
USER: NMR -- DATE: 07:07:34.507 +0300 NMR@NMR_400
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10061.3
PTS1d: 32768
EX: zgig30
PW: 10.0 us
PD: 2.0 sec
NA: 5120
LB: 1.0
Nuts - $173 SM1749 13C_13.1

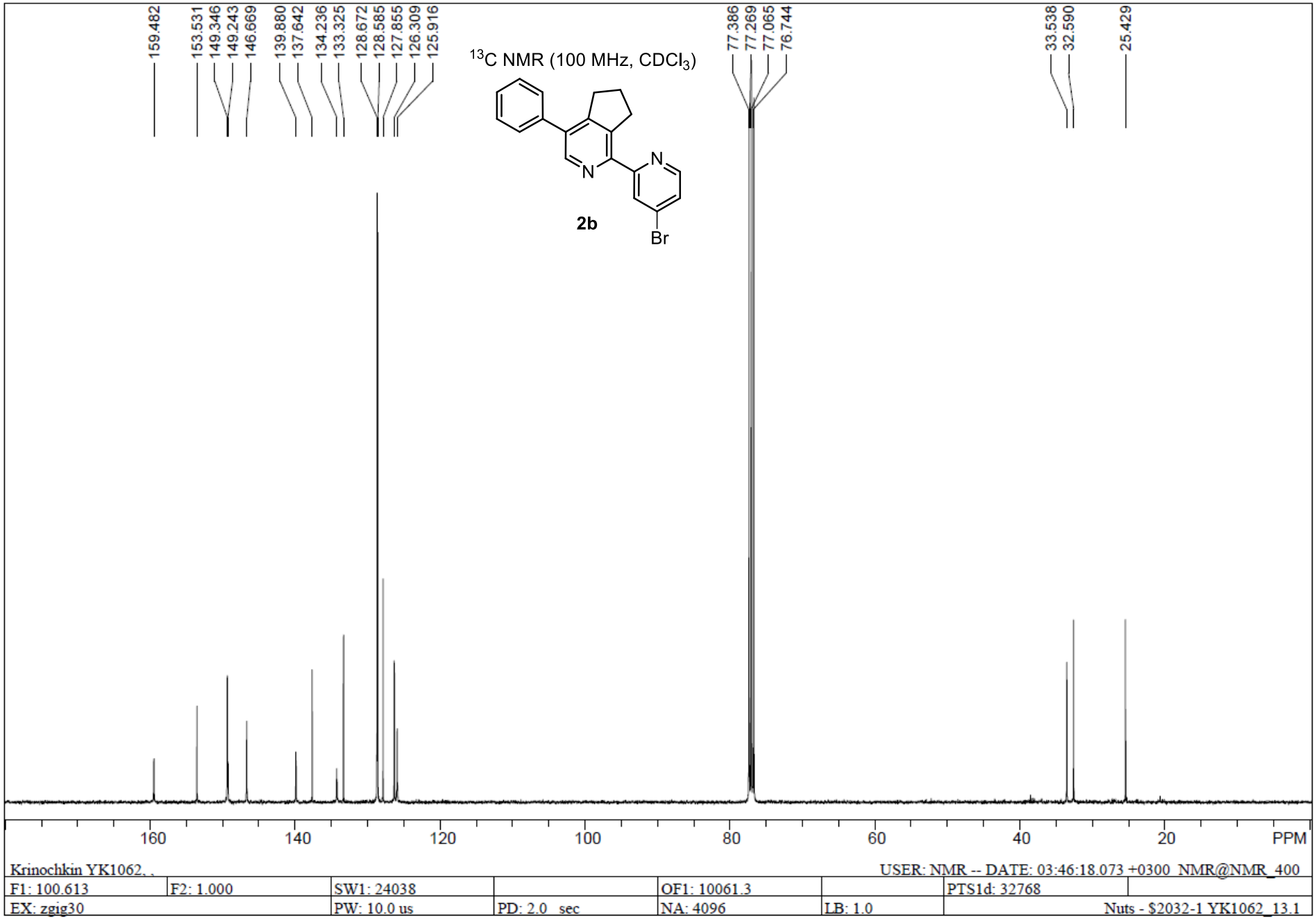

8.527
8.344
8.330
7.521
7.507
7.501
7.492
7.430
7.419
7.414
7.396
7.394
7.285
6.575
6.569
6.560
6.555
6.358
6.350
6.346
6.297
6.289
5.314
5.313
4.467
4.453
3.433
3.414
3.396
3.058
3.040
3.021
2.101
2.083
2.064
1H NMR (400 MHz, CDCl3)
N
N
NH
O
3g
4.15
2.99
1.00
1.09
1.10
1.05
0.97
1.06
2.15
2.20
2.14
2.18
8
7
6
5
4
3
2
PPM
Krinochkin YK1070
USER: NMR -- DATE: 13:07:21.410 +0300 NMR@NMR_400
F1: 400.130
F2: 1.000
SW1: 8013
OF1: 2471.0
PTS1d: 65536
EX: zg30
PW: 15.0 us
PD: 1.0 sec
NA: 10
LB: 0.0
Nuts - $2401 YK1070_1.1


158.011
153.775
153.184
151.383
151.011
148.772
146.497
142.289
139.256
137.856
133.655
128.609
128.587
127.683
110.481
107.535
107.301
107.031
77.367
77.250
77.046
76.732
40.169
33.300
32.651
29.705
25.541
13C NMR (100 MHz, CDCl3)
N
N
NH
O
3g
180
160
140
120
100
80
60
40
20
PPM
Krinochkin YK1070, .
USER: NMR -- DATE: 03:06:18.294 +0300 NMR@NMR_400
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.8
PTS1d: 32768
EX: zgpg30
PW: 10.0 us
PD: 2.0 sec
NA: 5120
LB: 1.0
Nuts - $2401 YK1070_13.1


8.515
8.506
8.495
8.472
8.468
7.446
7.442
7.435
7.431
7.428
7.260
7.032
7.028
7.015
3.876
3.467
3.452
3.437
3.044
3.029
3.015
2.102
2.087
2.072
1H NMR (500 MHz, CDCl3)
O
N
N
Br
2a
1.86
0.87
2.93
2.00
3.04
2.02
2.03
2.07
9
8
7
6
5
4
3
2
PPM
ema: A*42408
USER: ~mikodess -- DATE: 14:56:51.373 +0500 ORGANICS\~mikodess@
F1: 500.130
F2: 1.000
SW1: 7003
OF1: 2987.7
PTS1d: 32768
EX: zg30
PW: 12.0 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $KDSsm744_1.1


159.460
159.387
153.407
149.360
148.689
146.421
139.902
133.937
133.325
129.890
129.744
126.280
125.872
114.175
77.349
77.240
77.036
76.715
55.378
33.516
32.699
25.451
^{13}C NMR (100 MHz, CDCl$_3$)
O
N
N
Br
2a
150
100
50
PPM
Krinochkin SM1744, ,
USER: NMR -- DATE: 05:53:19.548 +0300 NMR@NMR_400
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10061.3
PTS1d: 32768
EX: zgig30
PW: 10.0 us
PD: 2.0 sec
NA: 8192
LB: 1.0
Nuts - $054 SM1744 13C_13.1


8.521
7.517
7.510
7.504
7.472
7.468
7.459
7.455
7.451
7.443
7.429
3.509
3.490
3.472
3.075
3.057
3.038
2.128
2.110
2.091
^{1}H NMR (400 MHz, $CDCl_3$)
N
N
Br
2b
5.91
2.84
2.00
2.01
2.12
8
7
6
5
4
3
2
PPM
Krinochkin YK 1062
USER: NMR -- DATE: 15:37:37.741 +0300 NMR@NMR_400
F1: 400.130
F2: 1.000
SW1: 8013
OF1: 2471.0
PTS1d: 65536
EX: zg30
PW: 15.0 us
PD: 1.0 sec
NA: 3
LB: 0.0
Nuts - $1308 YK1062_1.1


159.482
153.531
149.346
149.243
146.669
139.880
137.642
134.236
133.325
128.672
128.585
127.855
126.309
125.916
77.386
77.269
77.065
76.744
33.538
32.590
25.429
13C NMR (100 MHz, CDCl3)
N
N
Br
2b
160
140
120
100
80
60
40
20
PPM
Krinochkin YK1062, ,
USER: NMR -- DATE: 03:46:18.073 +0300 NMR@NMR_400
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10061.3
PTS1d: 32768
EX: zgig30
PW: 10.0 us
PD: 2.0 sec
NA: 4096
LB: 1.0
Nuts - $2032-1 YK1062_13.1