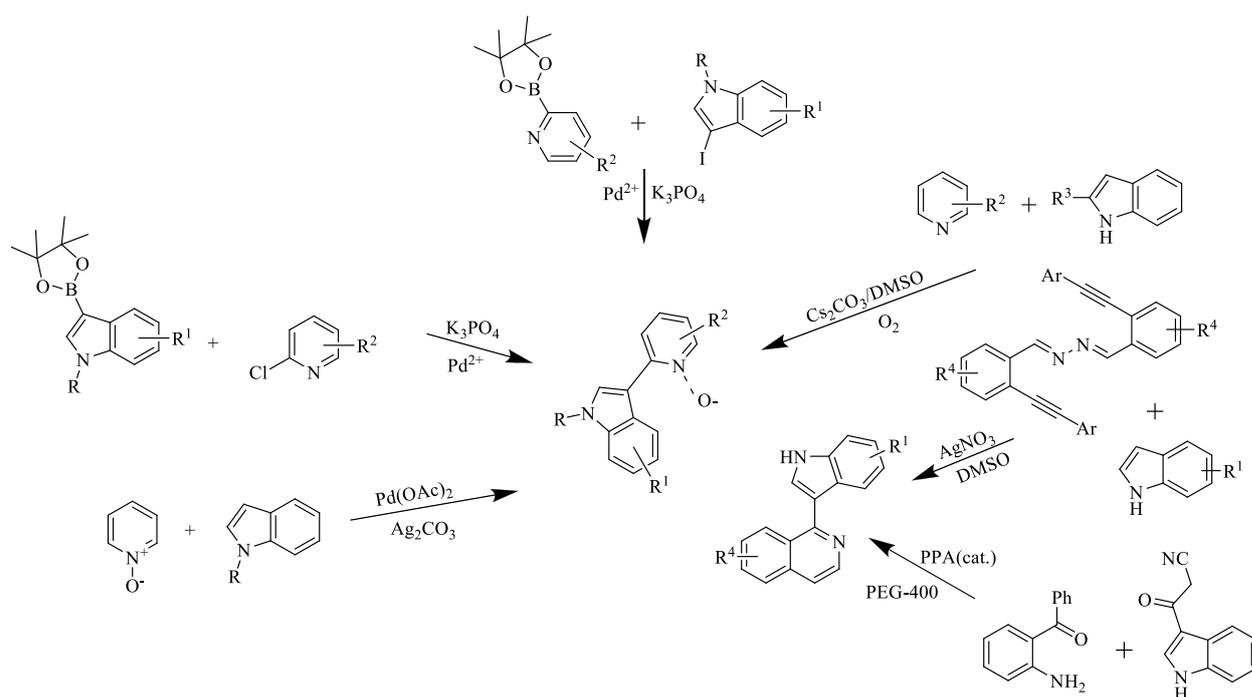


Rapid metal free construction of 3-positioned 2-pyridyl substituent in indoles

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Scheme S1 Previously reported synthetic approaches to 3-(2-pyridyl)indoles
(see Refs. 8-23 of the main text).

General All common reagents and solvents were used as purchased. Melting points were measured on the instrument Boetius. NMR spectra were acquired on a Bruker Avance-400 spectrometer, 298 K, digital resolution ± 0.01 ppm, using TMS as internal standard. Mass-spectra were recorded on MicroTOF-Q II (Bruker Daltonics), electrospray as a method of ionization. Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 elemental analyzer. The starting 1,2,4-triazine-4-oxides **1** were synthesized as described.^{S1, S2} Compounds **3** were synthesized with accordance with the described method^{S3} for similar compounds. The compound **3a** was described previously.^{S3}

3-[3,6-Bis(4-fluorophenyl)-1,2,4-triazin-5-yl]-1H-indole (3b) was obtained from triazine oxide **1b** and indole **2a**. Yield 75%. NMR ¹H (DMSO-d₆, δ, ppm): 7.02-7.03 (d, 1H, ³J 2.8 Hz, Ind), 7.22-7.25 (m, 2H, 4-FC₆H₄), 7.32-7.42 (m, 4H, 4-FC₆H₄), 7.46-7.48 (m, 1H, Ind), 7.72-7.76 (m, 2H, 4-FC₆H₄), 8.45-8.47 (m, 1H, Ind), 8.62-8.66 (m, 2H, 4-FC₆H₄), 11.74 (s, 1H, NH). NMR ¹⁹F (DMSO-d₆, δ, ppm): -111.46 (s, 1F), -109.34 (s, 1F). ESI-MS, m/z: 385.13 (M+H)⁺. Calcd for C₂₃H₁₄F₂N₄: C 71.87, H 3.67, N 14.58. Found: C 71.81, H 3.79, N 14.51.

3-[6-(4-Methoxyphenyl)-3-methyl-1,2,4-triazin-5-yl]-1H-indole (3c) was obtained from triazine oxide **1c** and indole **2a**. Yield 77%. NMR ¹H (DMSO-d₆, δ, ppm): 2.91 (s, 3H, CH₃), 3.91 (s, 3H, CH₃), 7.09-7.11 (d, 1H, ³J 3.6 Hz, Ind), 7.11-7.16 (m, 2H, 4-MeOC₆H₄), 7.23-7.30 (m, 2H, Ind), 7.48-7.54 (m, 1H, Ind), 8.52-8.58 (m, 1H, Ind), 12.44 (s, 1H, NH). ESI-MS, m/z: 317.14 (M+H)⁺. Calcd for C₁₉H₁₆N₄O: C 72.14, H 5.10, N 17.71. Found: C 72.05, H 5.01, N 17.65.

3-[6-(4-Chlorophenyl)-3-phenyl-1,2,4-triazin-5-yl]-2-methyl-1H-indole (3d) was obtained from triazine oxide **1d** and indole **2b**. Yield 70%. NMR ¹H (DMSO-d₆, δ, ppm): 2.33 (s, 3H, CH₃), 6.92 (m, 1H, Ind), 7.06 (m, 1H, Ind), 7.31-7.38 (m, 4H, CH_{arom}), 7.60 (m, 3H, CH_{arom}), 7.71-7.73 (m, 2H, CH_{arom}), 8.56 (m, 2H, Ind), 11.63 (s, 1H, NH). ESI-MS, m/z: 397.12 (M+H)⁺. Calcd for C₂₄H₁₇ClN₄: C 72.63, H 4.32, N 14.12. Found: C 72.55, H 4.28, N 14.06.

3-[6-(4-Methoxyphenyl)-3-methyl-1,2,4-triazin-5-yl]-2-methyl-1H-indole (3e) was obtained from triazine oxide **1c** and indole **2b**. Yield 80%. NMR ¹H (DMSO-d₆, δ, ppm): 2.11 (s, 3H, CH₃), 2.82 (s, 3H, CH₃), 3.78 (s, 3H, CH₃), 6.82-6.87 (m, 2H, 4-MeOC₆H₄), 6.87-6.93 (m, 1H, Ind), 7.00-7.07 (m, 1H, Ind), 7.30 (m, 1H, Ind), 7.36 (m, 1H, Ind), 7.51-7.57 (m, 2H, 4-MeOC₆H₄), 11.41 (s, 1H, NH). ESI-MS, m/z: 331.16 (M+H)⁺. Calcd for C₂₀H₁₈N₄O: C 72.71, H 5.49, N 16.96. Found: C 72.64, H 5.42, N 16.86.

3-[3,6-Bis-(4-fluorophenyl)-1,2,4-triazin-5-yl]-2-methyl-1H-indole (3f) was obtained from triazine oxide **1b** and indole **2b**. Yield 69%. NMR ¹H (DMSO-d₆, δ, ppm): 2.31 (s, 3H, CH₃), 6.91 (m, 1H, Ind), 7.05 (m, 1H, Ind), 7.12 (m, 2H, 4-FC₆H₄), 7.26-7.30 (m, 1H, Ind), 7.31-7.39 (m, 3H, 4-FC₆H₄, Ind), 7.72-7.76 (m, 2H, 4-FC₆H₄), 8.58-8.61 (m, 2H, 4-FC₆H₄), 11.61 (s, 1H, NH). NMR ¹⁹F (DMSO-d₆, δ, ppm): -111.51 (s, 1F), -109.23 (s, 1F). ESI-MS, m/z: 399.14 (M+H)⁺. Calcd for C₂₄H₁₆F₂N₄: C 72.35, H 4.05, N 14.06. Found: C 72.26, H 3.98, N 13.99.

3-[6-(4-Fluorophenyl)-3-(furan-2-yl)-1,2,4-triazin-5-yl]-2-methyl-1H-indole (3g) was obtained from triazine oxide **1e** and indole **2b**. Yield 70%. NMR ¹H (DMSO-d₆, δ, ppm): 2.29 (s, 3H, CH₃), 6.73-6.76 (dd, 1H, ³J 3.2, 1.6 Hz, Fur (H-4)), 6.86 (m, 1H, Ind), 7.01-7.06 (m, 1H, Ind), 7.07-7.13 (m, 2H, 4-FC₆H₄), 7.26 (m, 1H, Ind), 7.33 (m, 1H, Ind), 7.46 (d, 1H, ³J 3.2 Hz, Fur (H-3)), 7.67-7.74 (m, 2H, 4-FC₆H₄), 7.96 (d, 1H, ³J 1.6 Hz, Fur (H-5)), 11.66 (s, 1H, NH).

NMR ^{19}F (DMSO- d_6 , δ , ppm): -111.54 (s, 1F). ESI-MS, m/z : 371.13 ($\text{M}+\text{H}$) $^+$. Calcd for $\text{C}_{22}\text{H}_{15}\text{FN}_4\text{O}$: C 71.34, H 4.08, N 15.13. Found: C 71.29, H 4.01, N 15.04.

2-Methyl-3-(3-(thiophen-2-yl)-6-*p*-tolyl-1,2,4-triazin-5-yl)-1*H*-indole (3h) was obtained from triazine oxide **1f** and indole **2b**. Yield 69%. NMR ^1H (DMSO- d_6 , δ , ppm): 2.21 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 6.86-6.93 (m, 1H, Ind), 7.02-7.08 (m, 1H, Ind), 7.12-7.17 (m, 2H, Tol), 7.25-7.29 (dd, 1H, 3J 3.6, 4.4 Hz, Thiophene (H-4)), 7.33 (m, 1H, Ind), 7.38 (m, 1H, Ind), 7.53-7.58 (m, 2H, Tol), 7.76-7.79 (dd, 1H, 3J 4.4, 0.8 Hz, Thiophene (H-5)), 8.10-8.13 (m, 1H, Thiophene (H-3)), 11.59 (s, 1H, NH). ESI-MS, m/z : 383.13 ($\text{M}+\text{H}$) $^+$. Calcd for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{S}$: C 72.23, H 4.74, N 14.65. Found: C 72.15, H 4.66, N 14.57.

3-[6-(4-Methoxyphenyl)-3-methyl-1,2,4-triazin-5-yl]-1-methyl-1*H*-indole (3i) was obtained from triazine oxide **1c** and indole **2c**. Yield 70%. NMR ^1H (DMSO- d_6 , δ , ppm): 2.89 (s, 3H, CH_3), 3.75 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 7.07-7.13 (m, 3H, Ind, 4-MeOC $_6\text{H}_4$), 7.25-7.30 (m, 2H, Ind), 7.30-7.36 (m, 2H, Ind), 7.50-7.54 (m, 1H, Ind), 7.57-7.61 (m, 2H, 4-MeOC $_6\text{H}_4$), 8.46 (m, 1H, Ind). ESI-MS, m/z : 331.16 ($\text{M}+\text{H}$) $^+$. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}$: C 72.71, H 5.49, N 16.96. Found: C 72.65, H 5.40, N 16.89.

3-(3-Ethyl-6-*p*-tolyl-1,2,4-triazin-5-yl)-1-methyl-1*H*-indole (3j) was obtained from triazine oxide **1g** and indole **2c**. Yield 65%. NMR ^1H (DMSO- d_6 , δ , ppm): 1.56 (t, 3H, 3J 7.6 Hz, CH_2CH_3), 2.50 (s, 3H, CH_3 (Tol)), 3.19-3.25 (q, 2H, 3J 7.6 Hz, CH_2CH_3), 3.73 (s, 3H, CH_3), 7.04 (s, 1H, Ind), 7.27-7.32 (m, 1H, Ind), 7.32-7.37 (m, 1H, Ind), 7.37-7.42 (m, 2H, Tol), 7.50-7.58 (m, 3H, Ind, Tol), 8.52 (m, 1H, Ind). ESI-MS, m/z : 329.18 ($\text{M}+\text{H}$) $^+$. Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_4$: C 76.80, H 6.14, N 17.06. Found: C 76.71, H 6.06, N 16.99.

1-Methyl-3-(3-methyl-6-*p*-tolyl-1,2,4-triazin-5-yl)-1*H*-indole (3k) was obtained from triazine oxide **1h** and indole **2c**. Yield 77%. NMR ^1H (DMSO- d_6 , δ , ppm): 2.49 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 3.72 (s, 3H, CH_3), 6.96 (s, 1H, Ind), 7.20-7.26 (m, 1H, Ind), 7.26-7.33 (m, 2H, Ind), 7.34-7.38 (m, 2H, Tol), 7.45-7.54 (m, 3H, Tol, Ind), 8.42 (m, 1H, Ind). ESI-MS, m/z : 315.16 ($\text{M}+\text{H}$) $^+$. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_4$: C 76.41, H 5.77, N 17.82. Found: C 76.35, H 5.71, N 17.80.

3-[3,6-Bis-(4-fluorophenyl)-1,2,4-triazin-5-yl]-1-methyl-1*H*-indole (3l) was obtained from triazine oxide **1b** and indole **2c**. Yield 74%. NMR ^1H (DMSO- d_6 , δ , ppm): 3.77 (s, 3H, CH_3), 7.13 (s, 1H, Ind), 7.24-7.35 (m, 4H, Ind, 4-FC $_6\text{H}_4$), 7.36-7.43 (m, 2H, 4-FC $_6\text{H}_4$), 7.50 (m, 1H, Ind), 7.72-7.78 (m, 2H, 4-FC $_6\text{H}_4$), 8.36 (m, 1H, Ind), 8.60-8.66 (m, 2H, 4-FC $_6\text{H}_4$). NMR ^{19}F (DMSO- d_6 , δ , ppm): -111.08 (s, 1F), -109.17 (s, 1F). ESI-MS, m/z : 399.14 ($\text{M}+\text{H}$) $^+$. Calcd for $\text{C}_{24}\text{H}_{16}\text{F}_2\text{N}_4$: C 72.35, H 4.05, N 14.06. Found: C 72.30, H 3.95, N 13.97.

General procedure for the synthesis of pyridines 4 The corresponding 1,2,4-triazine **3** (1 mmol) was suspended in 1,2-dichlorobenzene (10 ml), 2,5-norbornadiene (0.81 ml, 8 mmol) was added and the resulting mixture was stirred at 215 °C in argon atmosphere for 20 h in autoclave. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (chloroform as eluent). The analytical samples were obtained by recrystallization (acetonitrile).

3-(3,6-Diphenylpyridin-2-yl)-1H-indole (4a). M.p. 215 °C. Yield 78%. NMR ¹H (DMSO-d₆, δ, ppm): 6.61 (d, 1H, ³J 2.8 Hz, Ind), 7.00-7.06 (m, 1H, Ind), 7.06-7.10 (m, 1H, Ind), 7.28-7.36 (m, 5H, Ph), 7.37-7.42 (m, 1H, Ind), 7.48-7.52 (m, 3H, Ph), 7.68 (d, 1H, ³J 8.0 Hz, H-3 (py)), 7.72 (d, 1H, ³J 8.0 Hz, H-4 (py)), 8.17-8.19 (m, 2H, Ph), 8.21-8.23 (m, 1H, Ind), 10.91 (s, 1H, NH). NMR ¹³C (CDCl₃, δ, ppm): 110.9, 116.2, 116.7, 120.6, 122.1, 122.4, 126.6, 126.9, 127.0, 127.2, 128.5, 128.8, 128.9, 129.5, 134.1, 135.9, 139.1, 139.5, 141.1, 152.6, 155.5. ESI-MS, m/z: 347.15 (M+H)⁺. Calcd for C₂₅H₁₈N₂: C 86.68, H 5.24, N 8.09. Found: C 86.60, H 5.16, N 8.01.

3-[3,6-Bis-(4-fluorophenyl)pyridin-2-yl]-1H-indole (4b). M.p. 238 °C. Yield 71%. NMR ¹H (DMSO-d₆, δ, ppm): 6.69 (d, 1H, ³J 2.8 Hz, Ind), 7.03-7.05 (m, 1H, Ind), 7.08-7.17 (m, 3H, Ind, 4-FC₆H₄), 7.26-7.29 (m, 2H, 4-FC₆H₄), 7.35-7.39 (m, 3H, 4-FC₆H₄, Ind), 7.72 (d, 1H, ³J 8.0 Hz, (H-3 (py))), 7.78 (d, 1H, ³J 8.0 Hz, H-4 (py)), 8.10-8.12 (m, 1H, Ind), 8.20-8.27 (m, 2H, Ind), 11.05 (s, 1H, NH). NMR ¹³C (CDCl₃, δ, ppm): 111.0, 115.5 (d, J 21.2 Hz), 115.6 (d, J 21.2 Hz), 116.1, 116.4, 120.8, 121.9, 122.5, 126.4, 127.7, 128.7 (d, J 8.1 Hz), 131.1 (d, J 8.0 Hz), 133.0, 135.5 (d, J 2.9 Hz), 135.9, 136.8 (d, J 2.9 Hz), 139.1, 152.7, 154.6, 162.3 (d, 245.8 Hz), 163.5 (d, J 246.5 Hz). NMR ¹⁹F (CDCl₃, δ, ppm): -114.88 (s, 1F), -113.25 (s, 1F). ESI-MS, m/z: 383.14 (M+H)⁺. Calcd for C₂₅H₁₆N₂F₂: C 78.52, H 4.22, N 7.33. Found: C 78.43, H 4.14, N 7.25.

3-[3-(4-Methoxyphenyl)-6-methylpyridin-2-yl]-1H-indole (4c). M.p. 234 °C. Yield 75 %. NMR ¹H (DMSO-d₆, δ, ppm): 2.60 (s, 3H, CH₃), 3.79 (s, 3H, CH₃), 6.57 (d, 1H, ³J 2.4 Hz, Ind), 6.87-6.89 (m, 2H, 4-CH₃OC₆H₄), 6.97-6.99 (m, 1H, Ind), 7.04-7.07 (m, 2H, Ind), 7.16-7.19 (m, 2H, 4-CH₃OC₆H₄), 7.29 (d, 1H, ³J 7.6 Hz, H-3 (py)), 7.45 (d, 1H, ³J 7.6 Hz, H-4 (py)), 8.14-8.18 (m, 1H, Ind), 10.89 (br. s, 1H, NH). NMR ¹³C (CDCl₃, δ, ppm): 24.4, 55.3, 110.8, 113.8, 116.2, 119.9, 120.5, 121.8, 122.2, 125.9, 126.8, 130.5, 132.5, 133.5, 135.9, 138.5, 152.2, 156.5, 158.7. ESI-MS, m/z: 315.15 (M+H)⁺. Calcd for C₂₁H₁₈N₂O: C 80.23, H 5.77, N 8.91. Found: C 80.15, H 5.71, N 8.85.

3-[3-(4-Chlorophenyl)-6-phenylpyridin-2-yl]-2-methyl-1H-indole (4d). M.p. 220 °C. Yield 71%. NMR ¹H (DMSO-d₆, δ, ppm): 2.02 (s, 3H, CH₃), 6.86-6.88 (m, 1H, Ind), 6.97-7.00 (m, 1H, Ind), 7.21-7.28 (m, 5H, CH_{arom}), 7.31-7.33 (m, 1H, Ind), 7.41-7.43 (m, 1H, Ind), 7.47-7.50 (m, 3H, CH_{arom}), 8.14-8.19 (m, 2H, H-3 (py), H-4 (py)), 10.89 (s, 1H, NH). NMR ¹³C (CDCl₃, δ, ppm): 12.5, 110.2, 113.1, 117.9, 119.5, 119.9, 121.4, 126.9, 128.4, 128.5, 128.7,

128.9, 130.2, 132.8, 133.5, 134.2, 135.6, 138.7, 138.8, 138.9, 152.7, 155.7. ESI-MS, m/z: 395.13 (M+H)⁺. Calcd for C₂₆H₁₉N₂Cl: C 79.08, H 4.85, N 7.09. Found: C 79.01, H 4.76, N 7.02.

3-[3-(4-Methoxyphenyl)-6-methylpyridin-2-yl]-2-methyl-1H-indole (4e). M.p. 224 °C. Yield 69 %. NMR ¹H (DMSO-d₆, δ, ppm): 1.88 (s, 3H, CH₃), 2.57 (s, 3H, CH₃), 3.71 (s, 3H, CH₃), 6.70-6.72 (m, 2H, 4-CH₃OC₆H₄), 6.84-6.86 (m, 1H, Ind), 6.94-6.98 (m, 1H, Ind), 7.05-7.07 (m, 2H, 4-CH₃OC₆H₄), 7.16-7.18 (m, 1H, Ind), 7.22 (d, 1H, ³J 8.0 Hz, H-3 (py)), 7.30 (d, 1H, ³J 8.0 Hz, H-4 (py)), 7.63-7.65 (m, 1H, Ind), 10.69 (s, 1H, NH). NMR ¹³C (CDCl₃, δ, ppm): 12.4, 24.3, 55.2, 109.9, 113.4, 113.6, 119.5, 119.8, 121.1, 121.2, 128.9, 129.9, 132.9, 133.1, 134.1, 135.6, 138.1, 152.1, 156.5, 158.3. ESI-MS, m/z: 329.17 (M+H)⁺. Calcd for C₂₂H₂₀N₂O: C 80.46, H 6.14, N 8.53. Found: C 80.38, H 6.06, N 8.49.

3-[3,6-Bis(4-(fluorophenyl)pyridin-2-yl)-2-methyl-1H-indole (4f). M.p. 228 °C. Yield 77 %. NMR ¹H (DMSO-d₆, δ, ppm): 2.00 (s, 3H, CH₃), 6.84 (m, 1H, Ind), 6.96-6.99 (m, 3H, 4-FC₆H₄, Ind), 7.21-7.30 (m, 7H, 4-FC₆H₄, H-3 (py), H-4 (py), Ind), 7.18-7.22 (m, 2H, 4-FC₆H₄), 10.88 (s, 1H, NH). NMR ¹³C (CDCl₃, δ, ppm): 12.5, 110.2, 113.2, 115.2 (d, J 21.1 Hz), 115.6 (d, J 21.1 Hz), 117.6, 119.5, 120.0, 121.5, 127.7, 128.5, 128.7 (d, J 8.7 Hz), 130.5 (d, J 8.4 Hz), 133.5, 135.2 (d, J 2.9 Hz), 135.5, 136.1 (d, J 2.6 Hz), 138.9, 152.7, 154.5, 161.8 (d, J 245.8), 163.6 (d, J 246.5 Hz). NMR ¹⁹F (CDCl₃, δ, ppm): -115.26 (s, 1F), -113.17 (s, 1F). ESI-MS, m/z: 397.15 (M+H)⁺. Calcd for C₂₆H₁₈N₂F₂: C 78.77, H 4.58, N 7.07. Found: C 78.69, H 4.51, N 6.99.

3-[3-(4-Fluorophenyl)-6-(furan-2-yl)pyridin-2-yl]-2-methyl-1H-indole (4g). M.p. 233 °C. Yield 71 %. NMR ¹H (DMSO-d₆, δ, ppm): 2.00 (s, 3H, CH₃), 6.57-6.60 (m, 1H, Fur (H-4)), 6.80-6.84 (m, 1H, Ind), 6.93-6.98 (m, 3H, 4-FC₆H₄, Ind), 7.03-7.05 (d, 1H, ³J 3.2 Hz, Fur (H-3)), 7.22-7.26 (m, 4H), 7.68-7.71 (m, 2H, Ind, H-3 (py)), 7.85 (d, 1H, ³J 8.0 Hz, H-4 (py)), 10.86 (s, 1H, NH). NMR ¹³C (CDCl₃, δ, ppm): 12.4, 108.9, 110.1, 112.1, 115.1 (d, J 21.2 Hz), 116.2, 119.5, 119.9, 121.3, 127.7, 128.5, 130.5 (d, J 8.0 Hz), 130.6, 134.3, 135.5, 136.1, 136.3 (d, J 3.8 Hz), 143.2, 148.0, 152.8, 153.9, 161.8 (d, J 245 Hz). NMR ¹⁹F (CDCl₃, δ, ppm): -115.41 (s, 1F). ESI-MS, m/z: 369.14 (M+H)⁺. Calcd for C₂₄H₁₇N₂FO: C 78.25, H 4.65, N 7.60. Found: C 78.16, H 4.59, N 7.52.

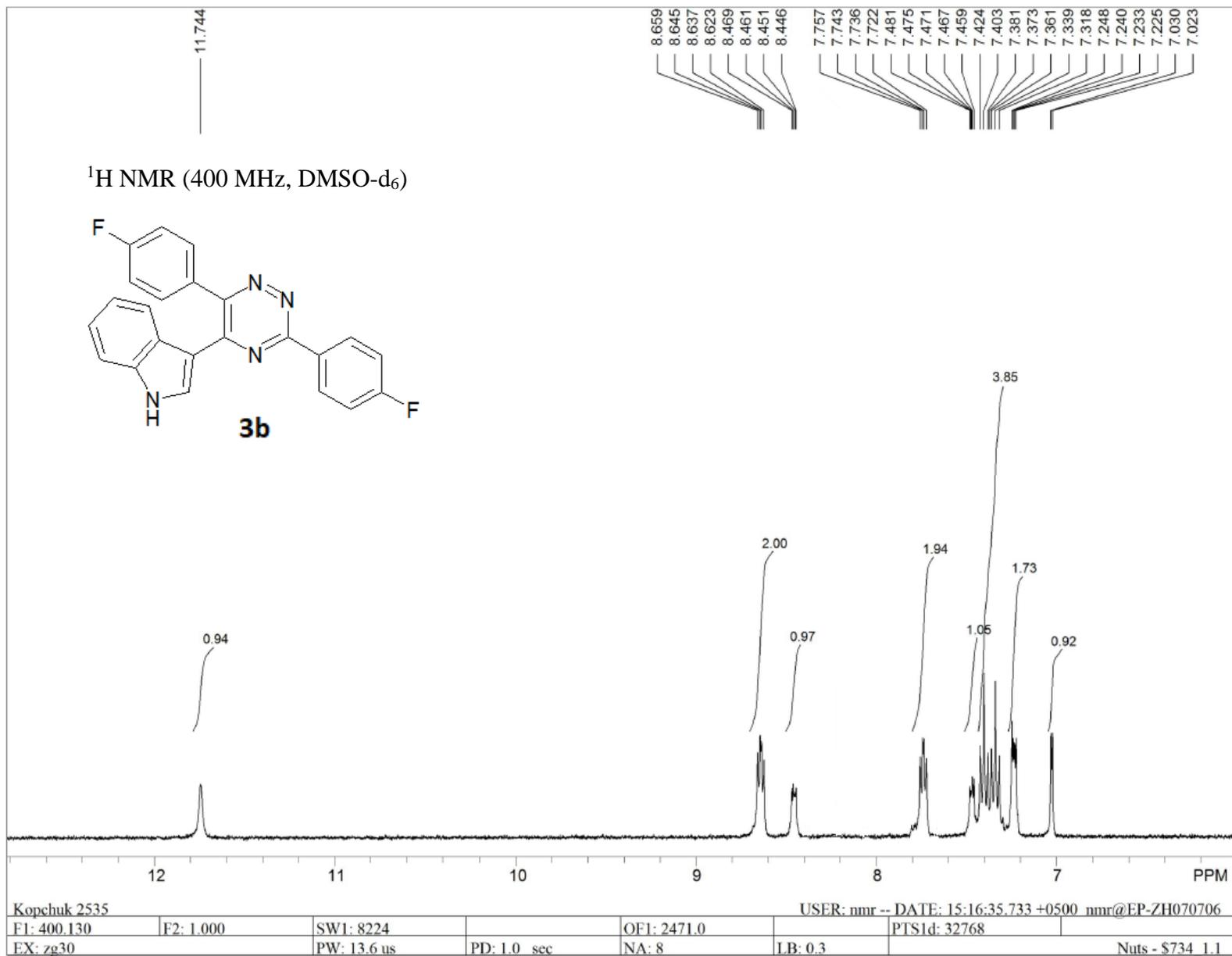
2-Methyl-3-[6-(thiophen-2-yl)-3-p-tolylpyridin-2-yl]-1H-indole (4h). M.p. 216 °C. Yield 78 %. NMR ¹H (DMSO-d₆, δ, ppm): 1.96 (s, 3H, CH₃), 2.28 (s, 3H, CH₃), 6.81-6.87 (m, 1H, Ind), 6.93-7.03 (m, 3H, Ind, Tol), 7.09-7.16 (m, 3H, Tol, Thiophene (H-4)), 7.22-7.27 (m, 1H, Ind), 7.34-7.38 (m, 1H, Ind), 7.46-7.50 (d, 1H, ³J 4.0 Hz, Thiophene (H-5)), 7.72-7.75 (d, 1H, ³J 2.8 Hz, Thiophene (H-3)), 7.77 (d, 1H, ³J 8.0 Hz, H-3 (py)), 7.81 (d, 1H, ³J 8.0 Hz, H-4 (py)), 10.80 (s, 1H, NH). NMR ¹³C (CDCl₃, δ, ppm): 12.8, 21.1, 109.9, 113.3, 116.3, 119.9, 120.1, 121.3, 124.3, 127.3, 127.9, 128.6, 128.7, 128.9, 133.8, 135.1, 135.5, 136.4, 137.4, 138.8, 145.4, 150.6, 152.2. ESI-MS, m/z: 381.14 (M+H)⁺. Calcd for C₂₅H₂₀N₂S: C 78.91, H 5.30, N 7.36. Found: C 78.82, H 5.23, N 7.28.

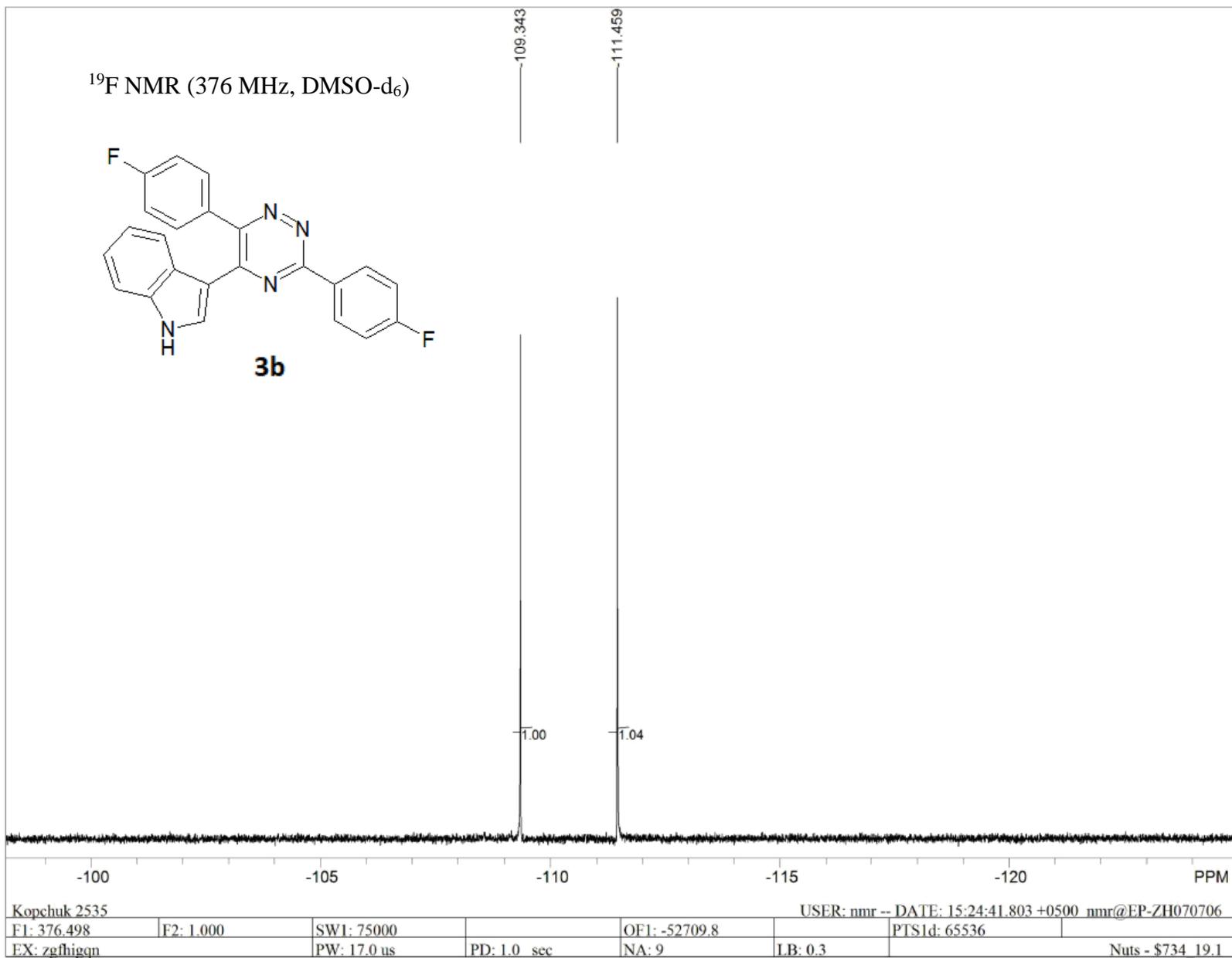
3-[3-(4-Methoxyphenyl)-6-methylpyridin-2-yl]-1-methyl-1*H*-indole (4i). M.p. 240 °C. Yield 79 %. NMR ¹H (DMSO-*d*₆, δ, ppm): 2.60 (s, 3H, CH₃), 3.67 (s, 3H, CH₃), 3.80 (s, 3H, CH₃), 6.63 (s, 1H, Ind), 6.87-6.89 (m, 2H, 4-CH₃OC₆H₄), 6.98-7.02 (m, 1H, Ind), 7.07 (d, 1H, ³*J* 8.0 Hz, H-3 (py)), 7.11-7.15 (m, 1H, Ind), 7.18-7.19 (m, 2H, 4-CH₃OC₆H₄), 7.31 (d, 1H, ³*J* 8.0 Hz, H-4 (py)), 7.47-7.49 (m, 1H, Ind), 8.03-8.05 (m, 1H, Ind). NMR ¹³C (CDCl₃, δ, ppm): 24.4, 32.9, 55.3, 108.9, 113.8, 115.0, 119.6, 120.1, 121.8, 122.1, 127.3, 130.4, 130.5, 132.1, 133.6, 138.9, 138.4, 152.2, 158.4, 158.8. ESI-MS, *m/z*: 329.17 (M+H)⁺. Calcd for C₂₂H₂₀N₂O: C 80.46, H 6.14, N 8.53. Found: C 80.40, H 6.09, N 8.44.

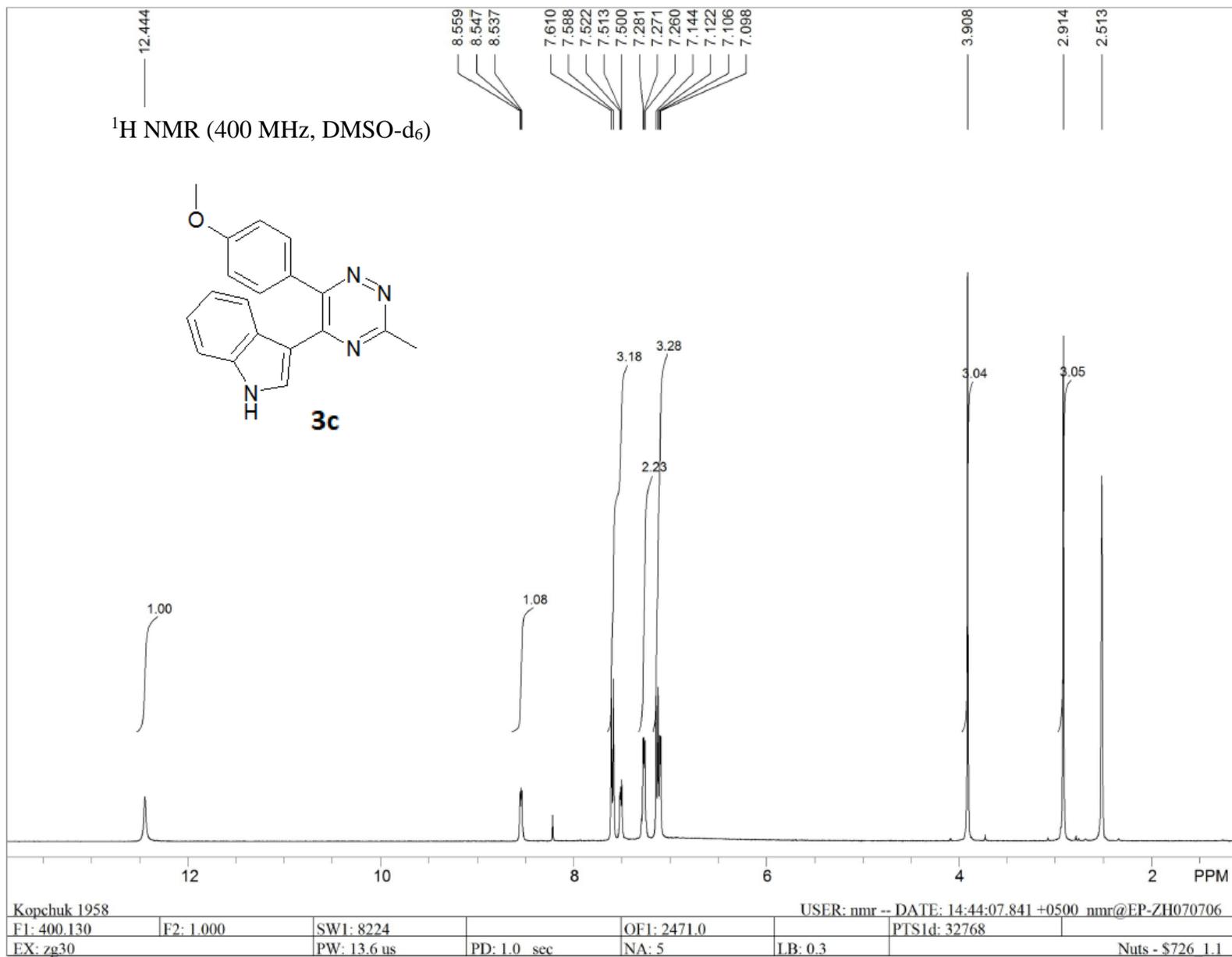
3-(6-Ethyl-3-*p*-tolylpyridin-2-yl)-1-methyl-1*H*-indole (4j). M.p. 223 °C. Yield 76 %. NMR ¹H (DMSO-*d*₆, δ, ppm): 1.41 (t, 3H, ³*J* 7.2 Hz, CH₂CH₃), 2.38 (s, 3H, CH₃), 2.85-2.89 (q, 2H, ³*J* 7.6 Hz, CH₂CH₃), 3.64 (s, 3H, CH₃), 6.56 (s, 1H, Ind), 6.98-7.04 (m, 1H, Ind), 7.05-7.09 (d, 1H, ³*J* 7.6 Hz, H-3 (py)), 7.14-7.19 (m, 5H, 4-CH₃OC₆H₄, Ind), 7.31 (m, 1H, Ind), 7.46-7.51 (d, 1H, ³*J* 7.6 Hz, H-4 (py)), 8.09-8.14 (m, 1H, Ind). NMR ¹³C (CDCl₃, δ, ppm): 13.9, 21.2, 31.3, 32.8, 108.9, 115.01, 118.2, 120.1, 121.8, 122.4, 127.5, 129.1, 129.3, 130.7, 132.5, 136.6, 136.9, 138.4, 138.5, 152.1, 161.6. ESI-MS, *m/z*: 327.19 (M+H)⁺. Calcd for C₂₃H₂₂N₂: C 84.63, H 6.79, N 8.58. Found: C 84.55, H 6.70, N 8.49.

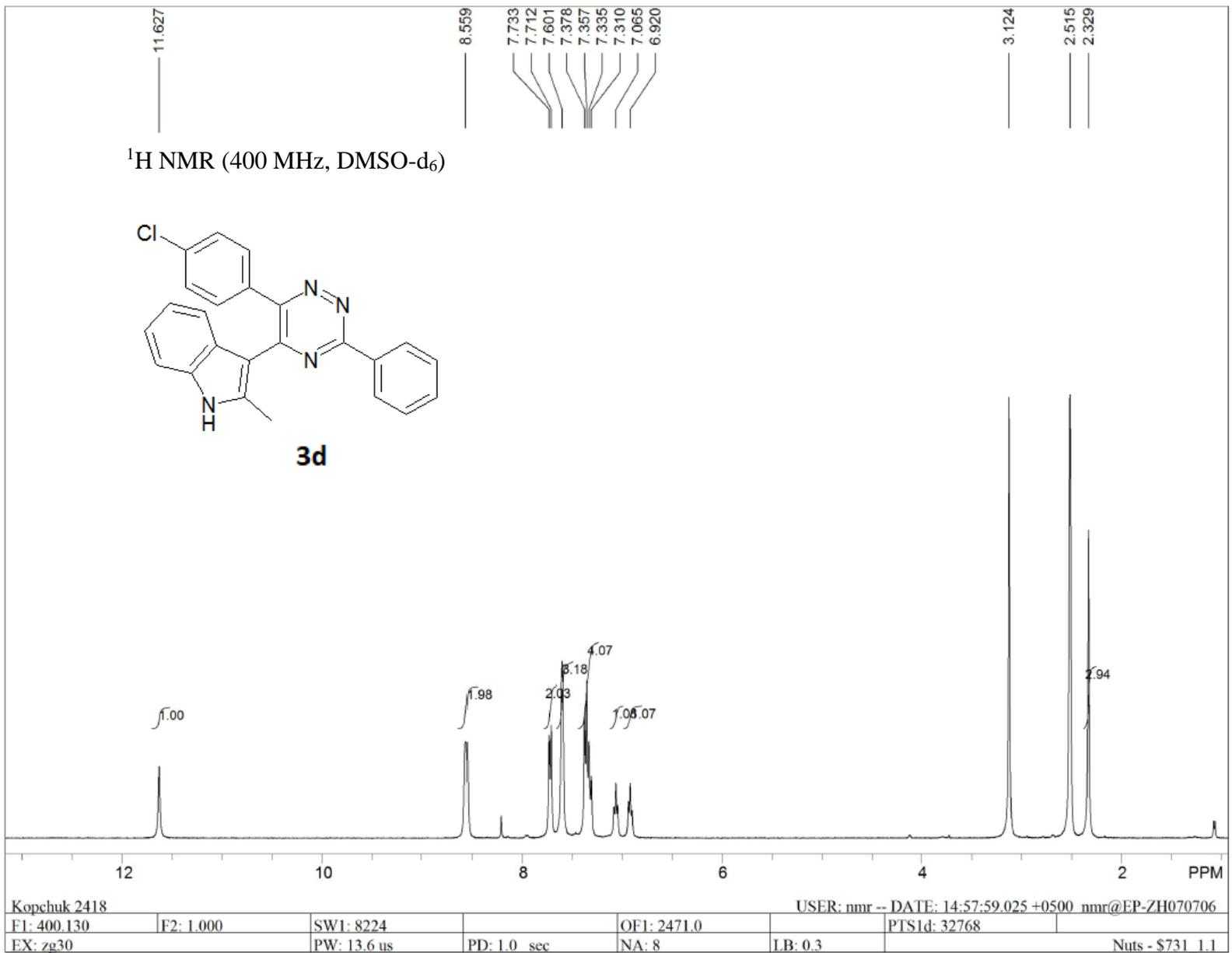
1-Methyl-3-(6-methyl-3-*p*-tolylpyridin-2-yl)-1*H*-indole (4k). M.p. 221 °C. Yield 72 %. NMR ¹H (DMSO-*d*₆, δ, ppm): 2.38 (s, 3H, CH₃), 2.61 (s, 3H, CH₃), 3.66 (s, 3H, CH₃), 6.60 (s, 1H, Ind), 6.97-7.03 (m, 1H, Ind), 7.06-7.12 (m, 1H, Ind), 7.12-7.20 (m, 5H, Tol, H-3 (py)), 7.31 (m, 1H, Ind), 7.47-7.49 (d, 1H, ³*J* 8.0 Hz, H-4 (py)), 8.04-8.06 (m, 1H, Ind). NMR ¹³C (CDCl₃, δ, ppm): 21.2, 24.4, 32.8, 108.9, 114.9, 119.6, 120.1, 121.7, 122.1, 127.4, 129.1, 129.2, 130.6, 132.4, 136.6, 136.9, 138.2, 138.5, 152.1, 156.5. ESI-MS, *m/z*: 313.17 (M+H)⁺. Calcd for C₂₂H₂₀N₂: C 84.58, H 6.45, N 8.97. Found: C 84.51, H 6.38, N 8.90.

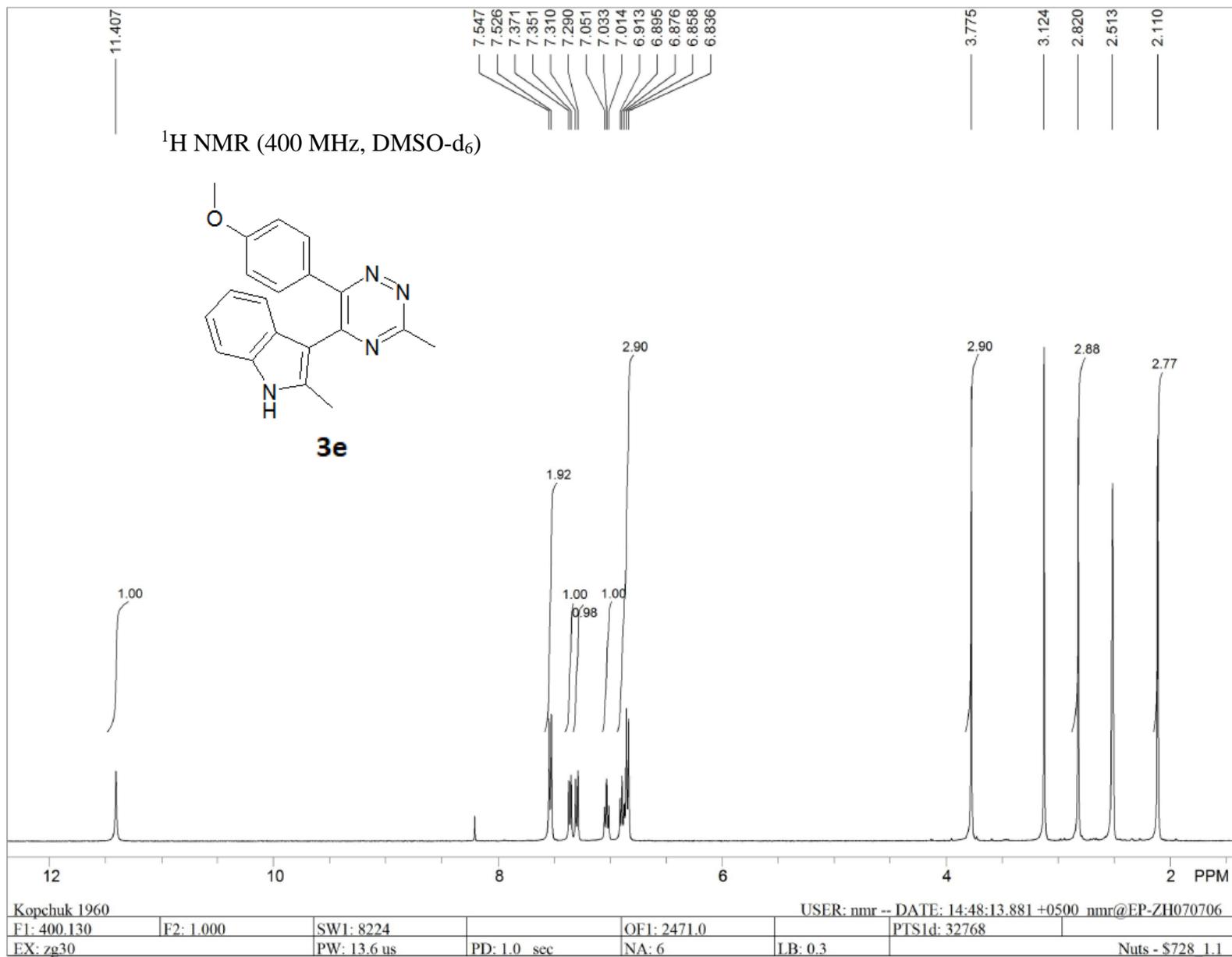
3-[3,6-Bis-(4-fluorophenyl)pyridin-2-yl]-1-methyl-1*H*-indole (4l). M.p. 226 °C. Yield 80 %. NMR ¹H (DMSO-*d*₆, δ, ppm): 3.72 (s, 3H, CH₃), 6.77 (s, 1H, Ind), 7.02-7.07 (m, 1H, Ind), 7.10-7.20 (m, 3H, 4-FC₆H₄, Ind), 7.24-7.30 (m, 2H, 4-FC₆H₄), 7.35-7.41 (m, 3H, 4-FC₆H₄, Ind), 7.74 (d, 1H, ³*J* 8.0 Hz, H-3 (py)), 7.79 (d, 1H, ³*J* 8.0 Hz, H-4 (py)), 7.96-8.01 (m, 1H, Ind), 8.21-8.28 (m, 2H, CH_{arom}). NMR ¹³C (CDCl₃, δ, ppm): 32.9, 109.2, 114.7, 115.5 (d, *J* 21.2 Hz), 115.6 (d, *J* 21.1 Hz), 116.1, 120.4, 122.1, 122.1, 127.3, 128.7 (d, *J* 8.8 Hz), 130.9, 131.0 (d, *J* 7.2 Hz), 132.6, 135.6 (d, *J* 3.6 Hz), 136.9, 136.9 (d, *J* 3.6 Hz), 139.0, 152.7, 154.6, 162.3 (d, *J* 245.7), 163.5 (d, *J* 246.7 Hz). NMR ¹⁹F (CDCl₃, δ, ppm): -114.89 (s, 1F), -113.39 (s, 1F). ESI-MS, *m/z*: 397.15 (M+H)⁺. Calcd for C₂₆H₁₈N₂F₂: C 78.77, H 4.58, N 7.07. Found: C 78.68, H 4.49, N 7.01.

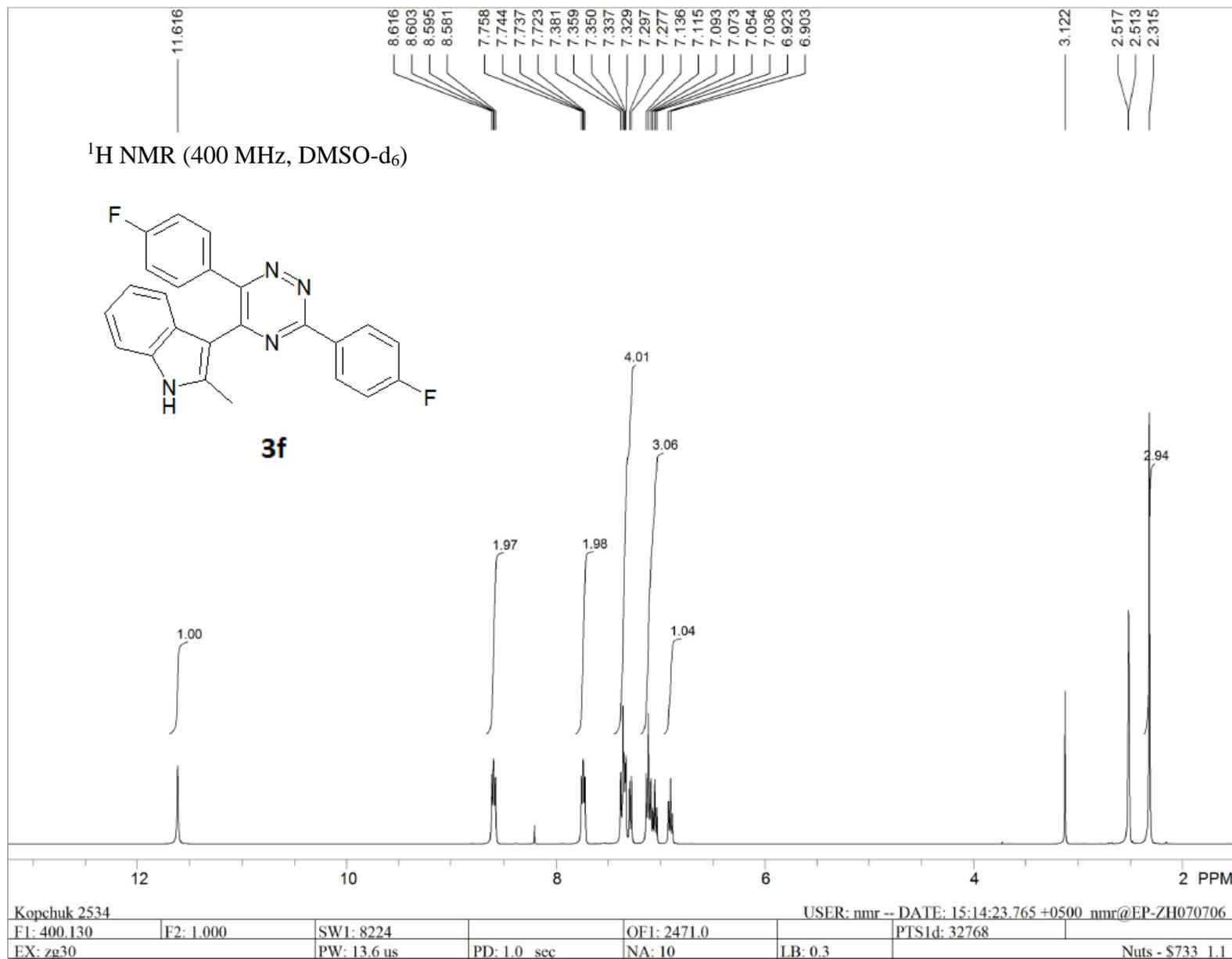


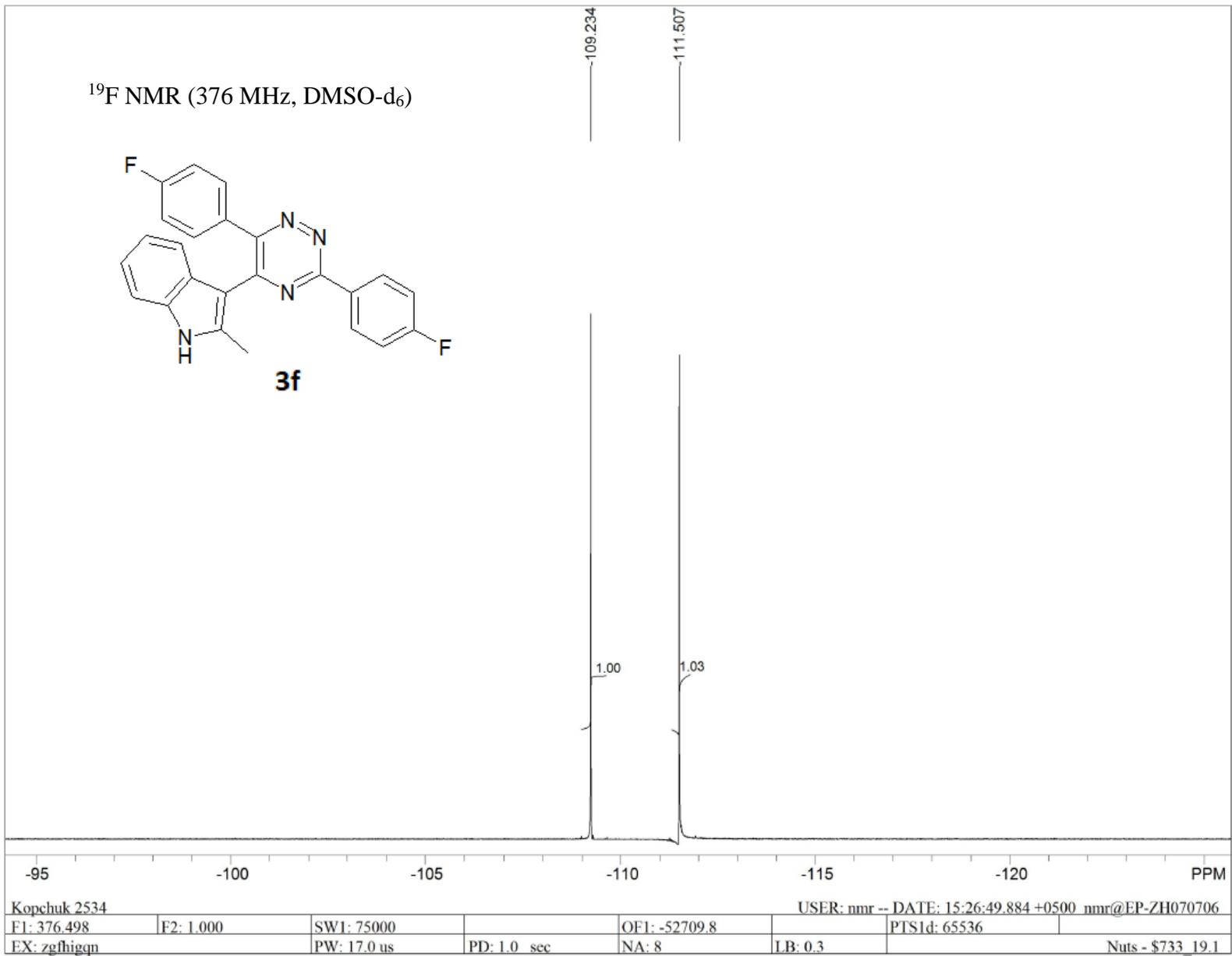


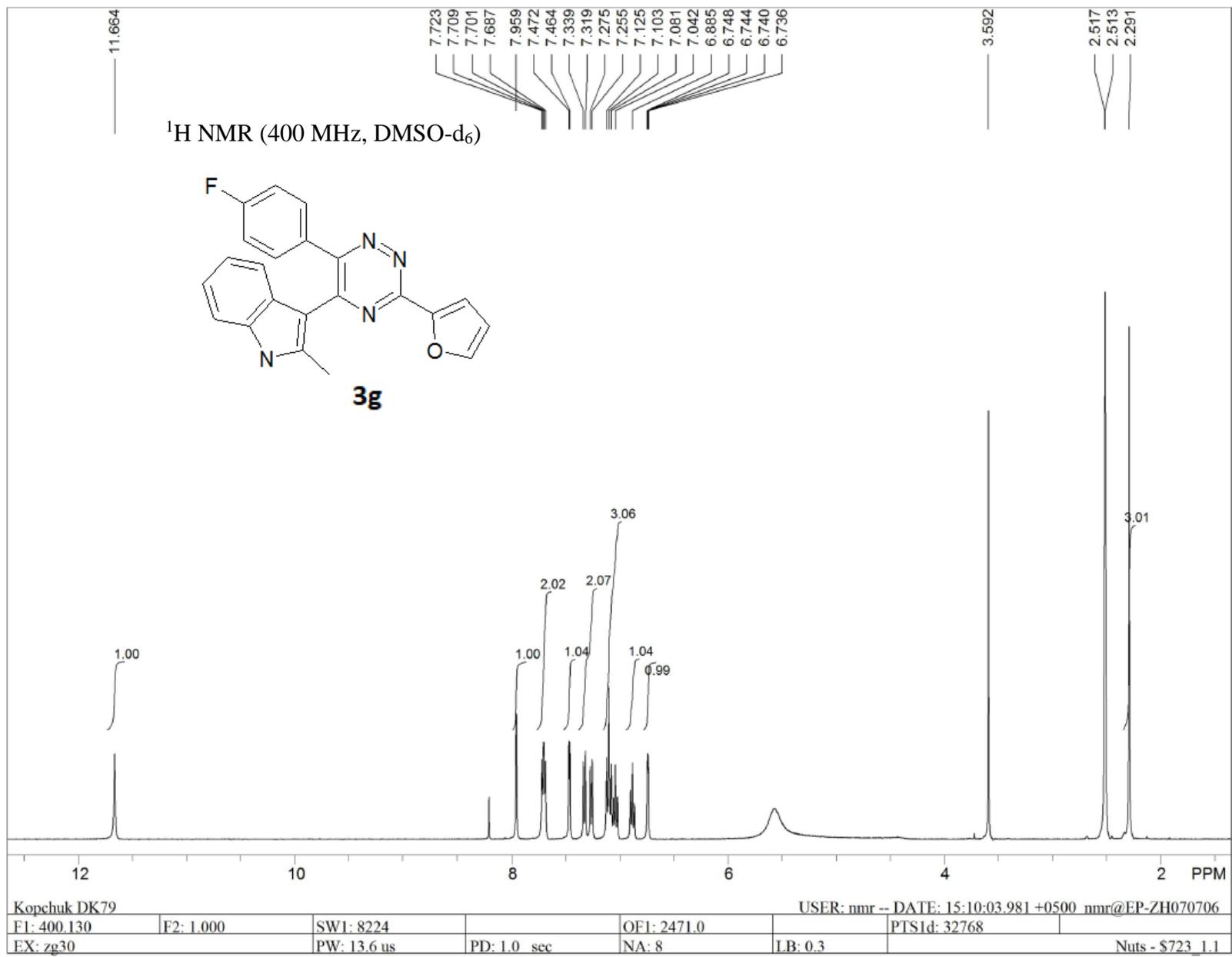




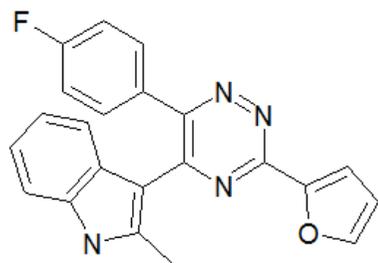








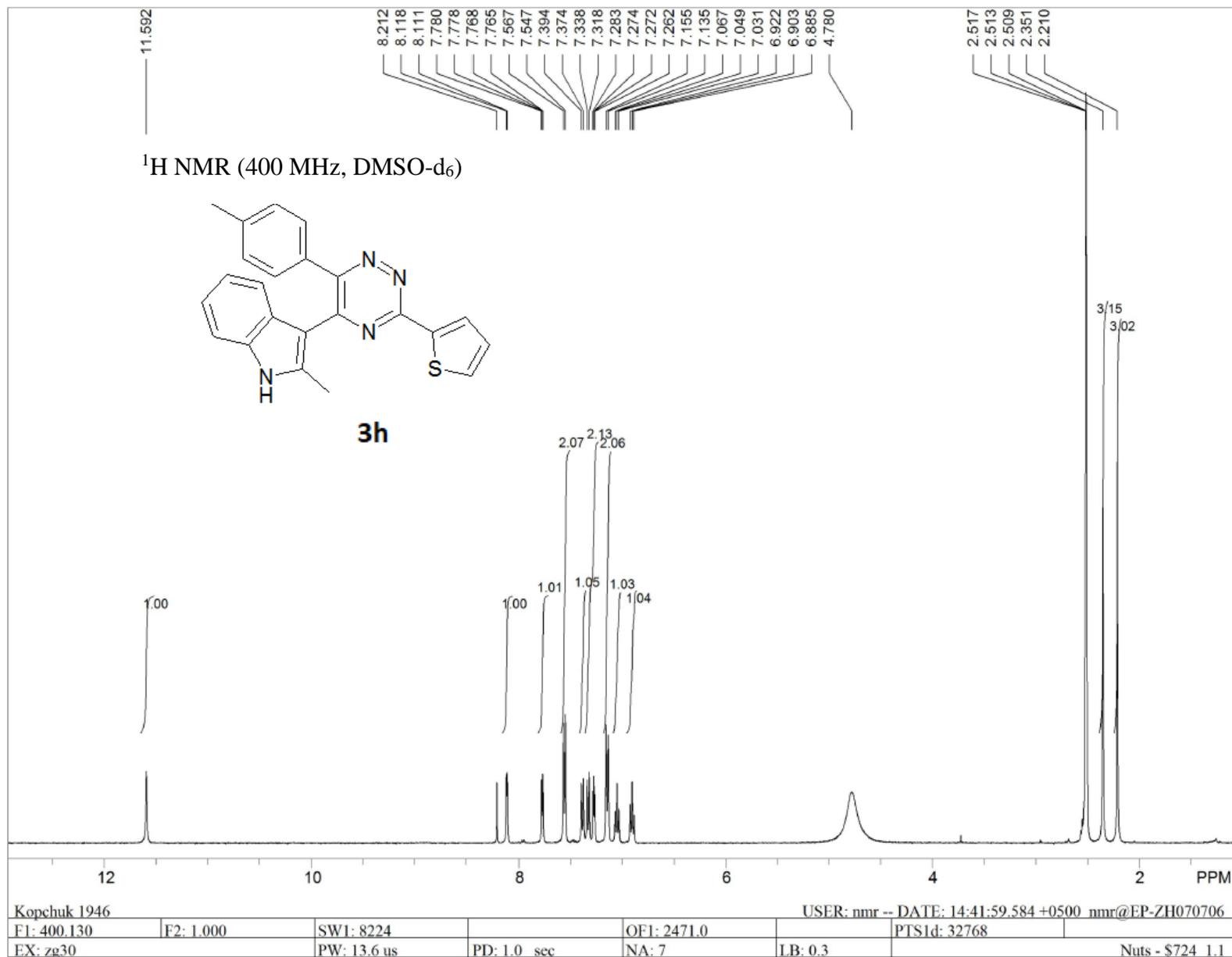
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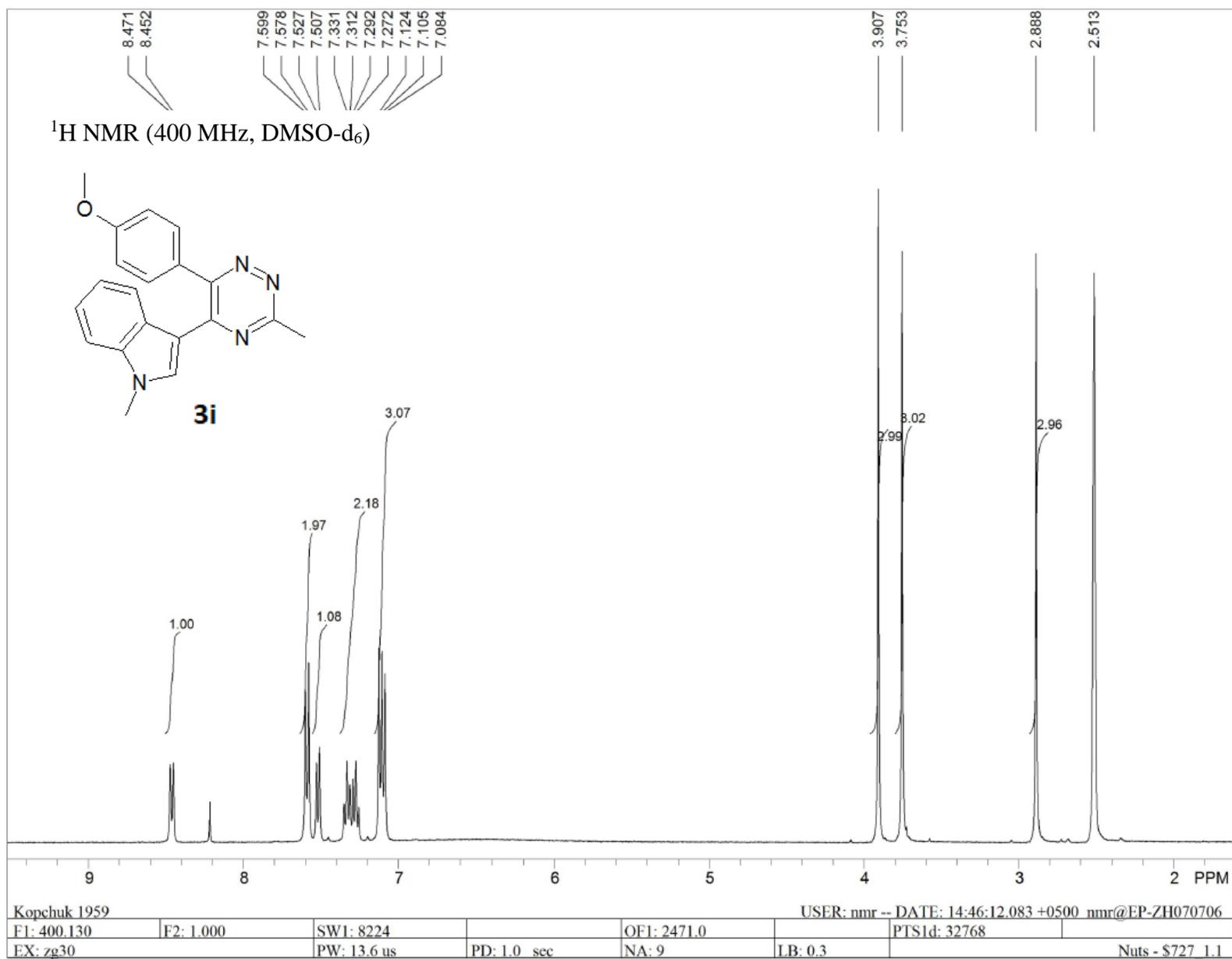


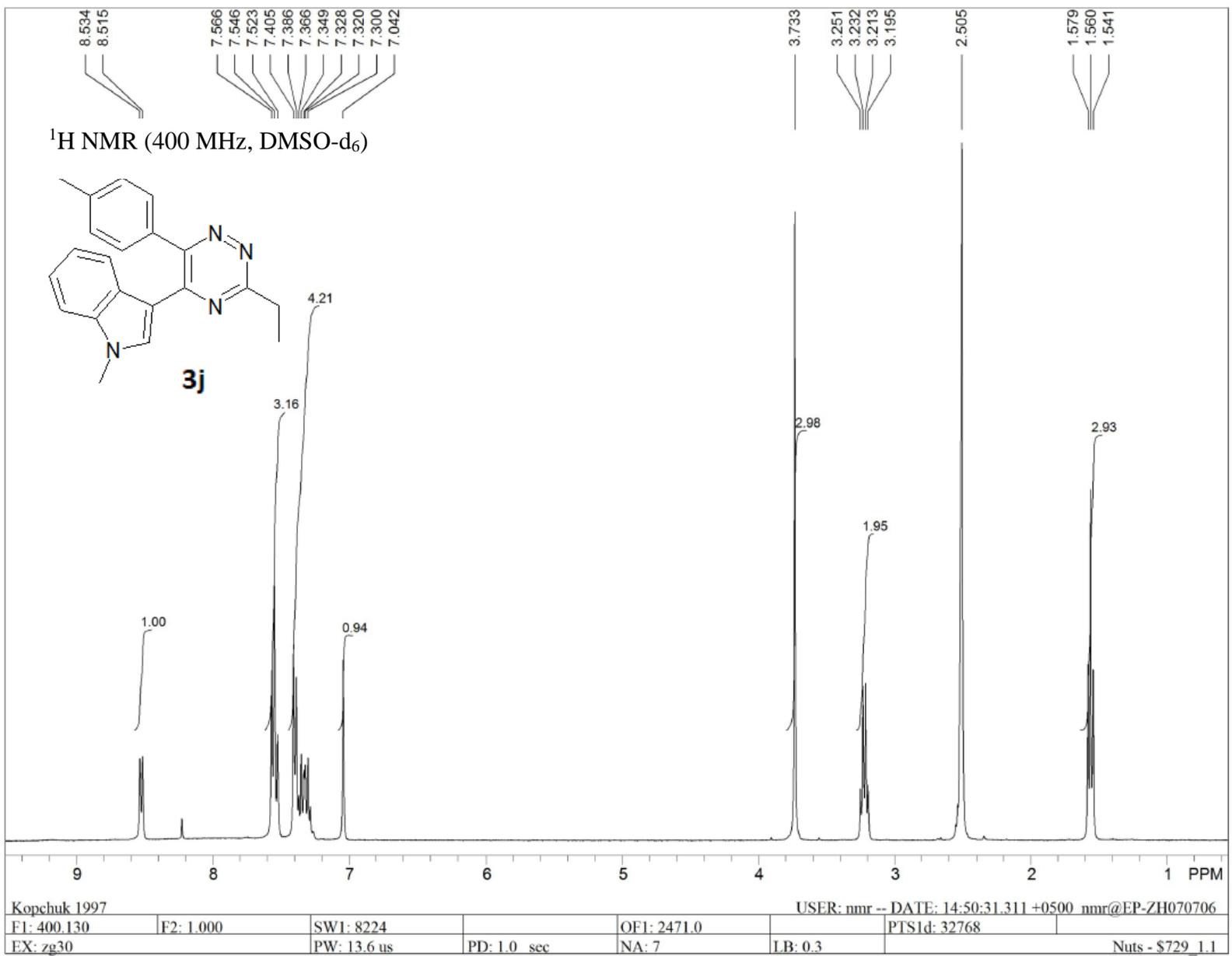
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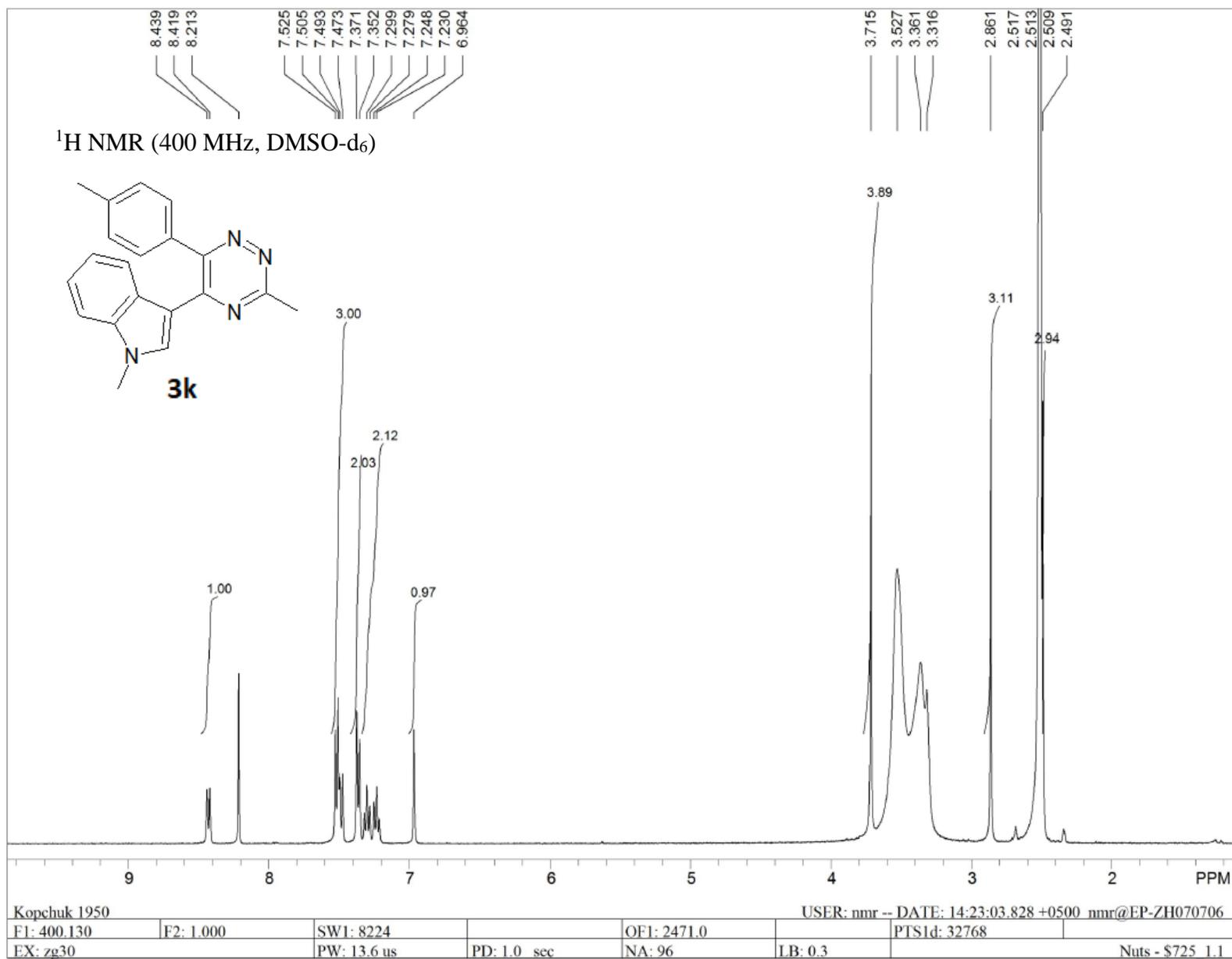
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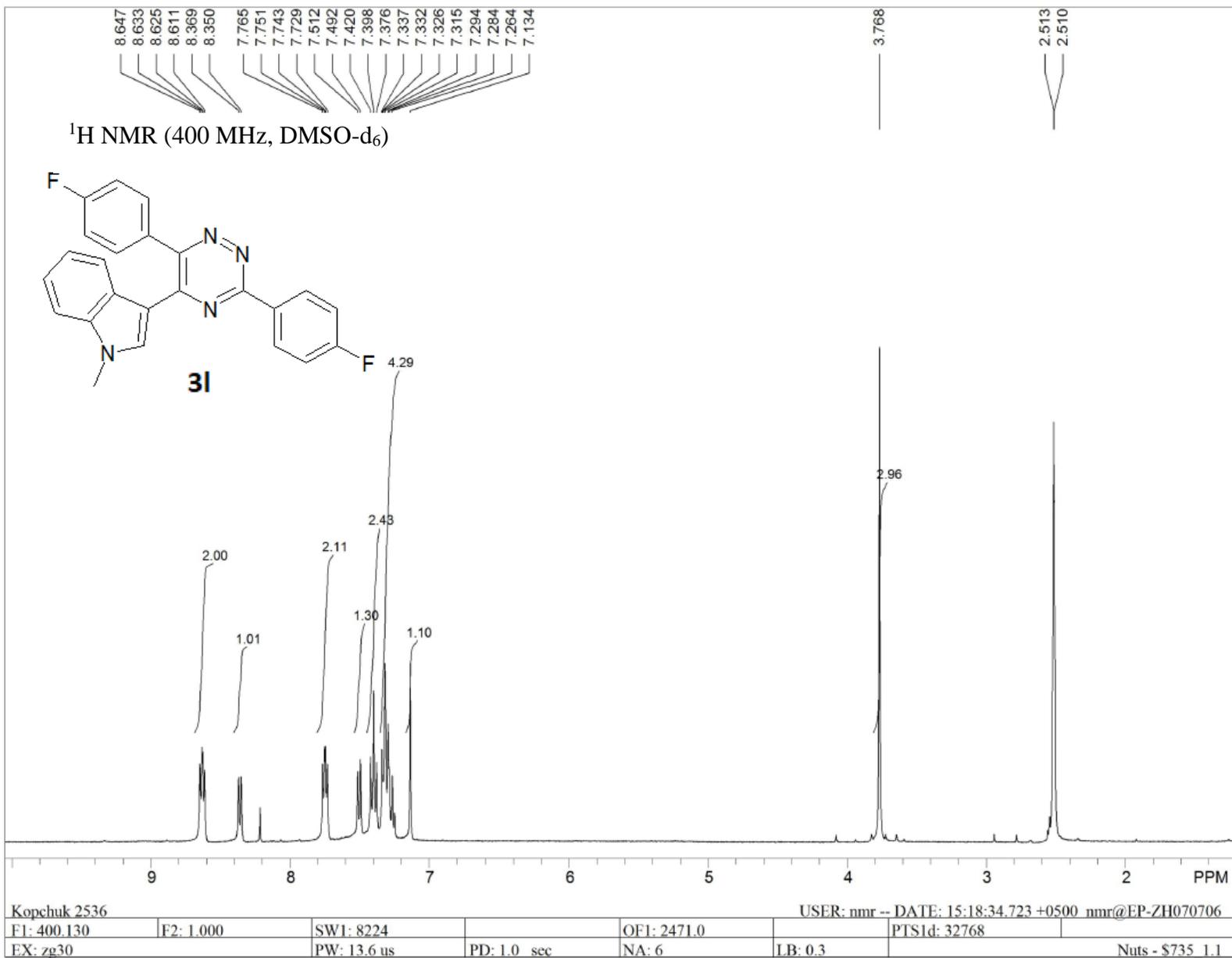
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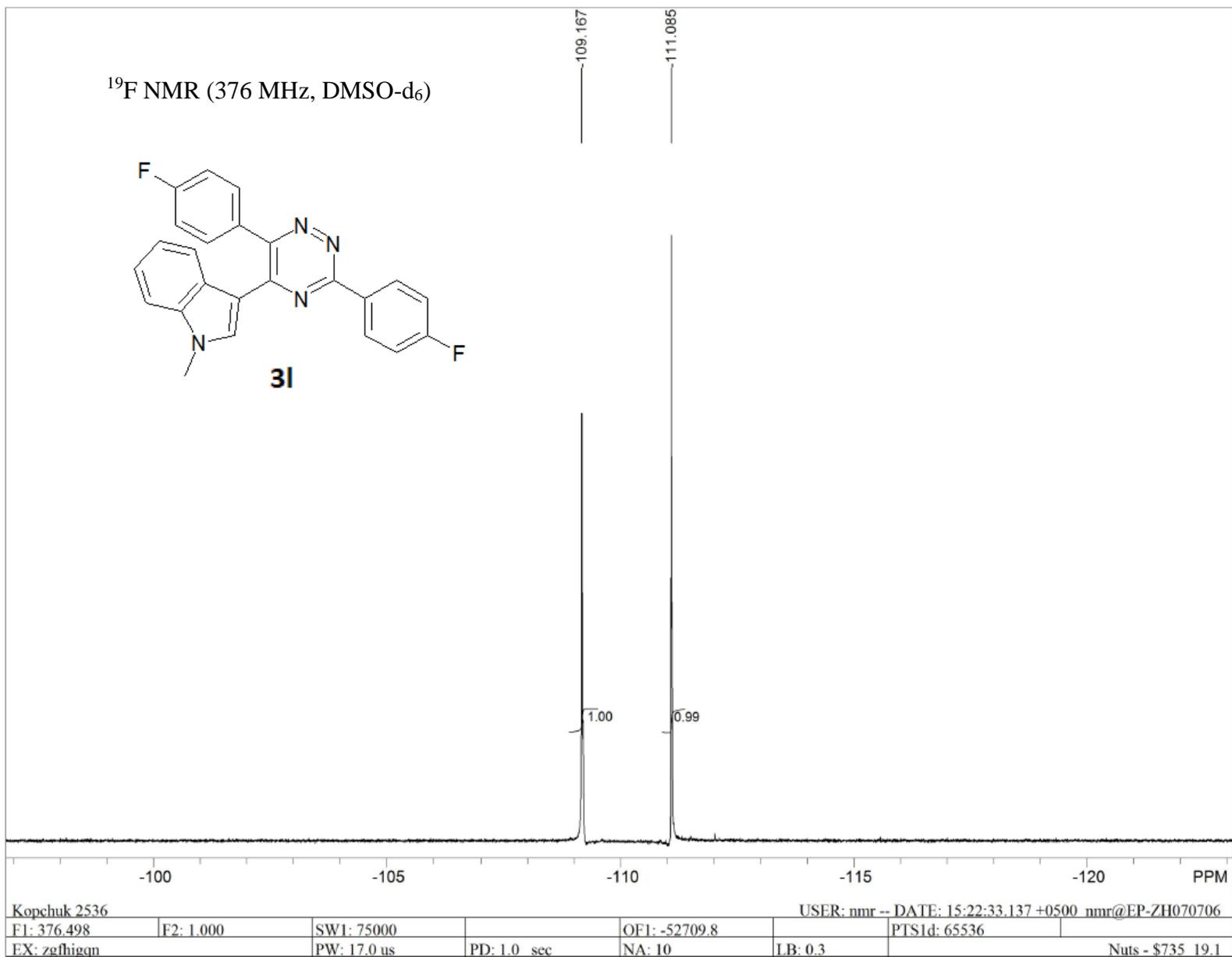


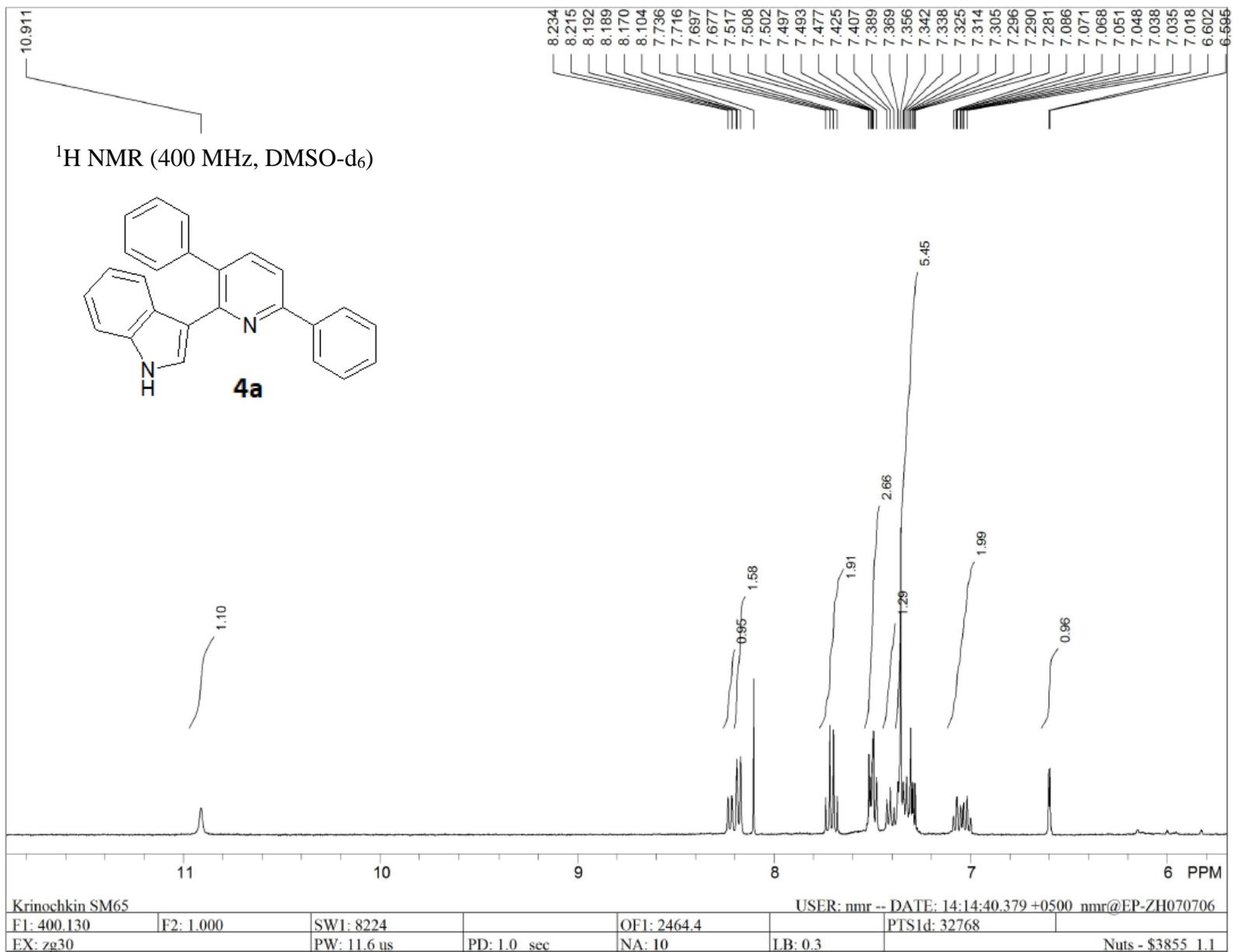


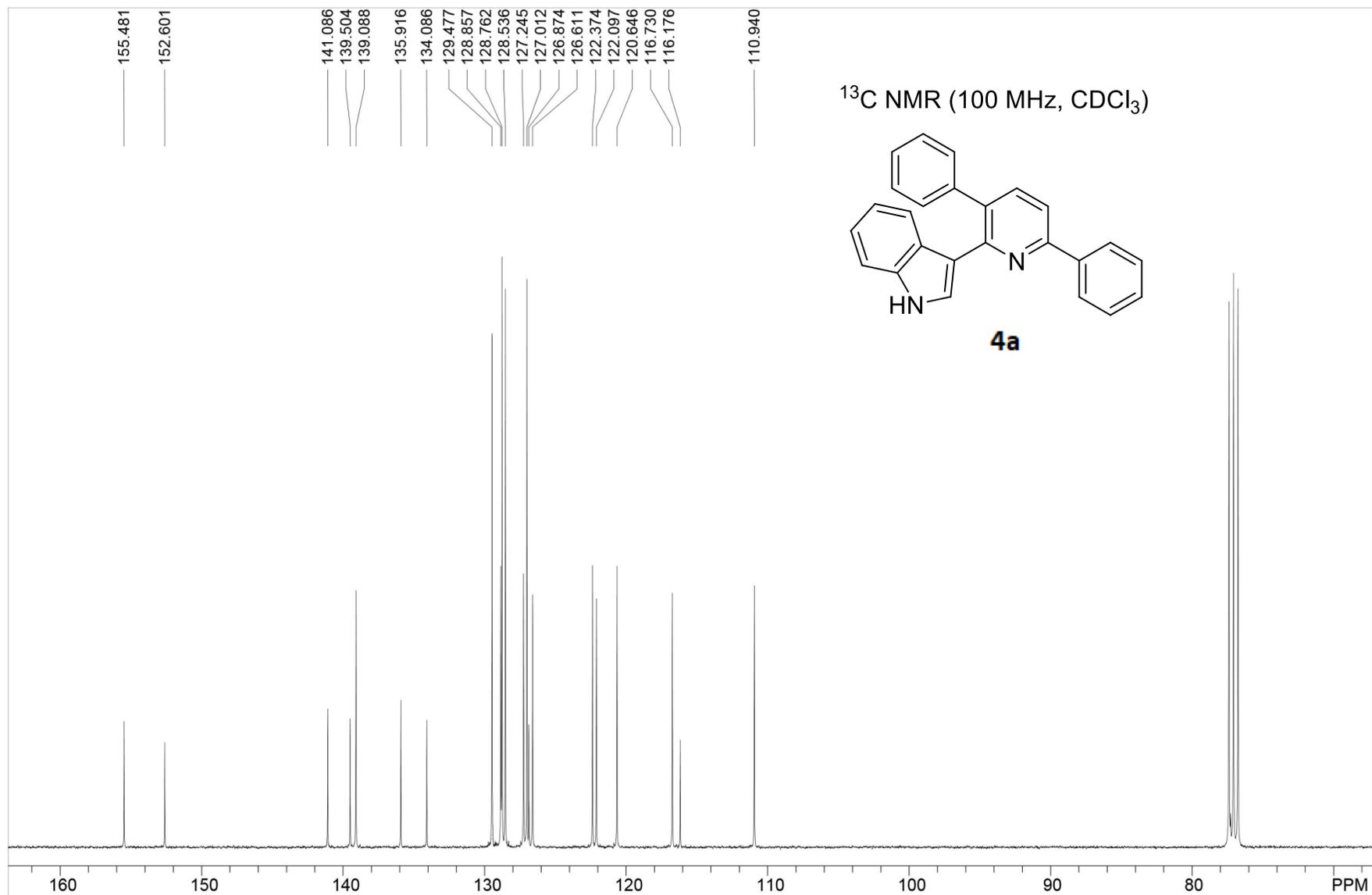




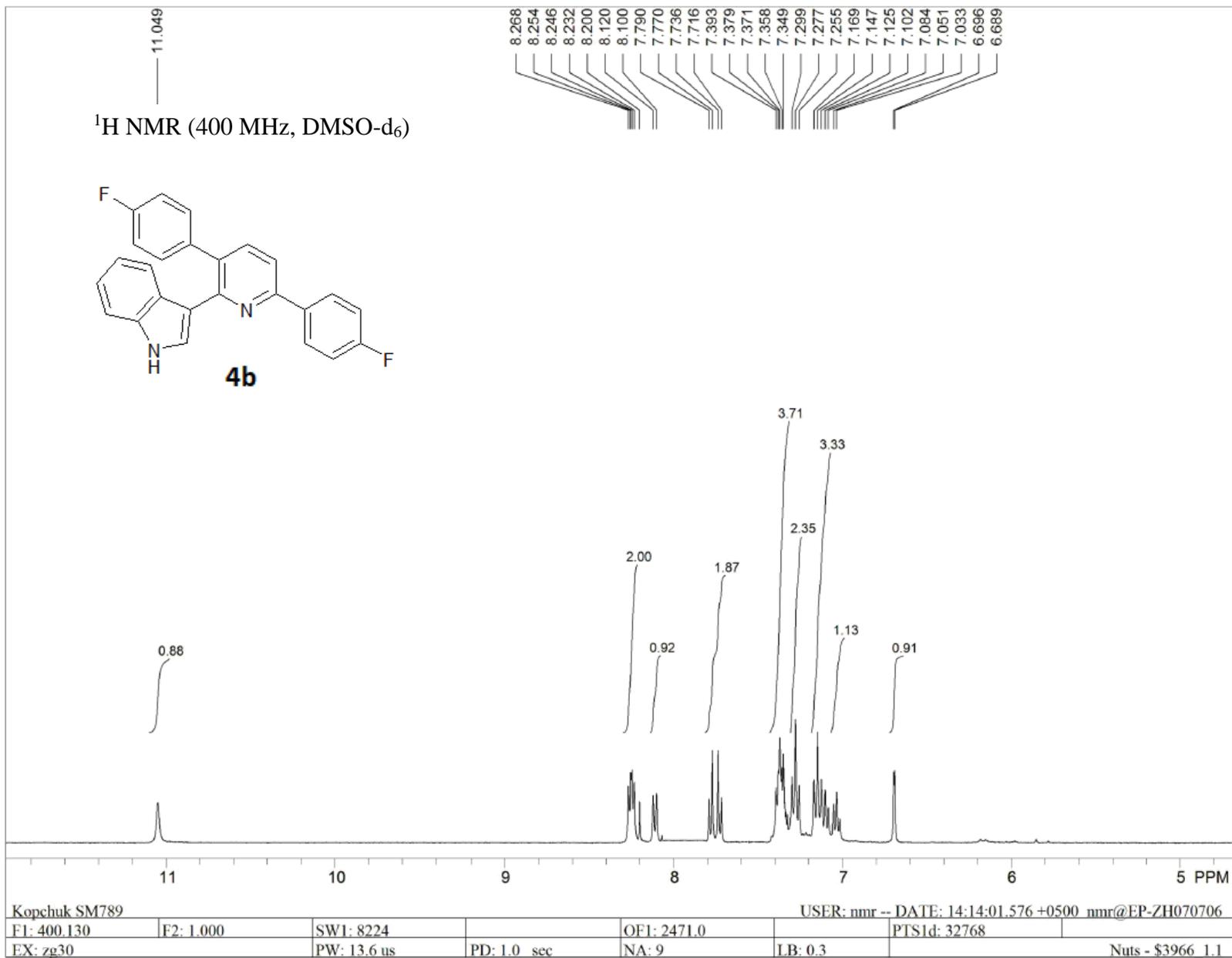


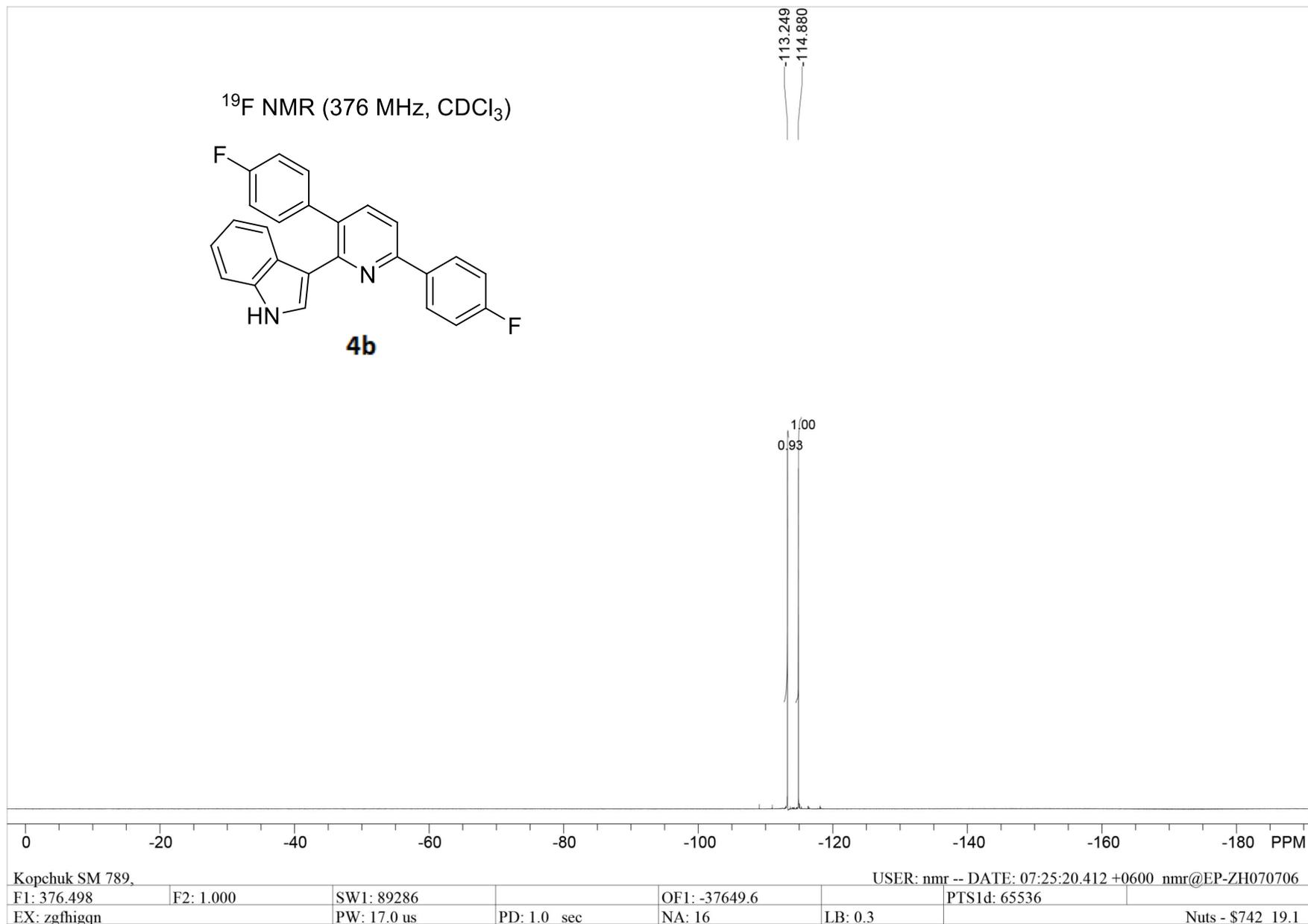


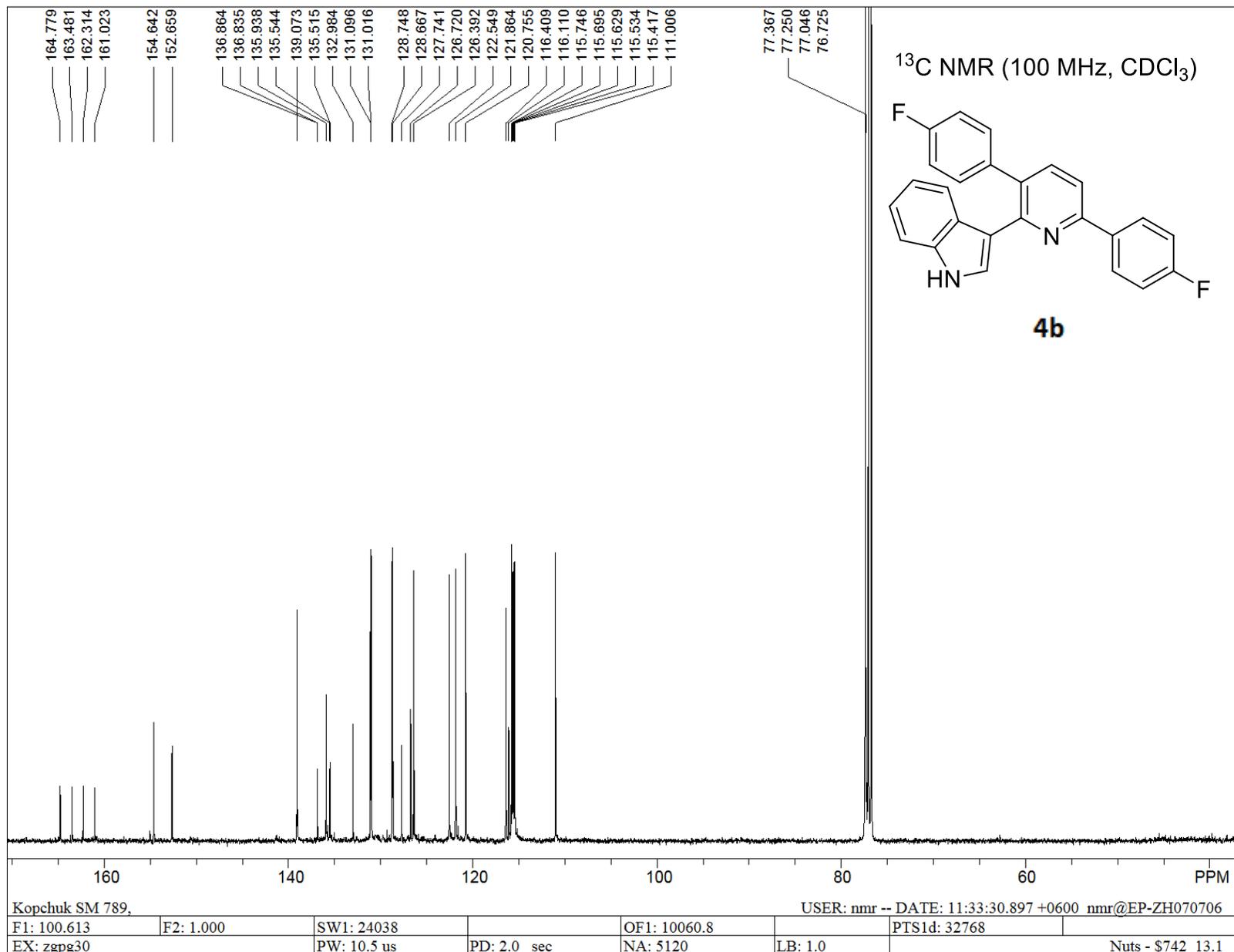


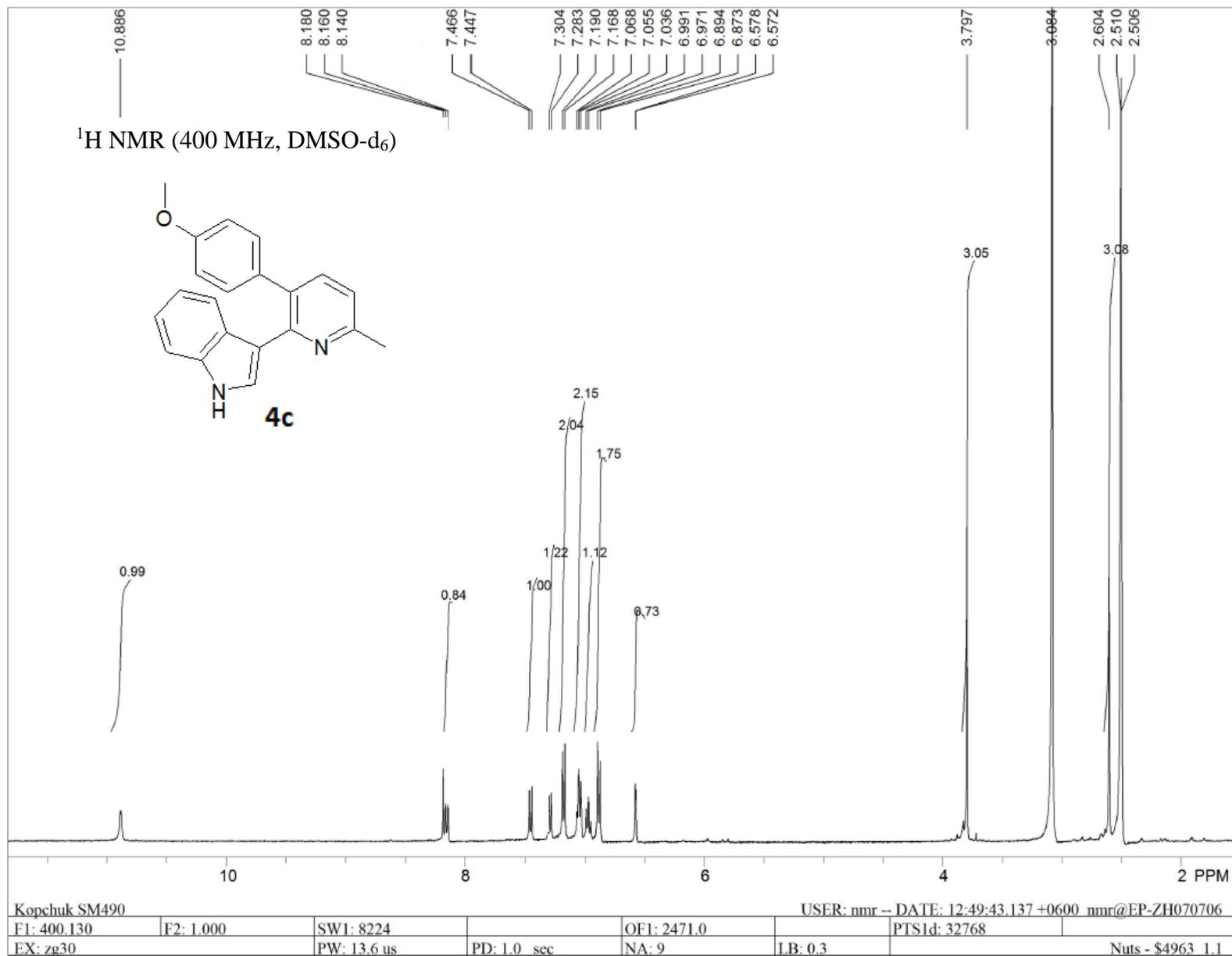


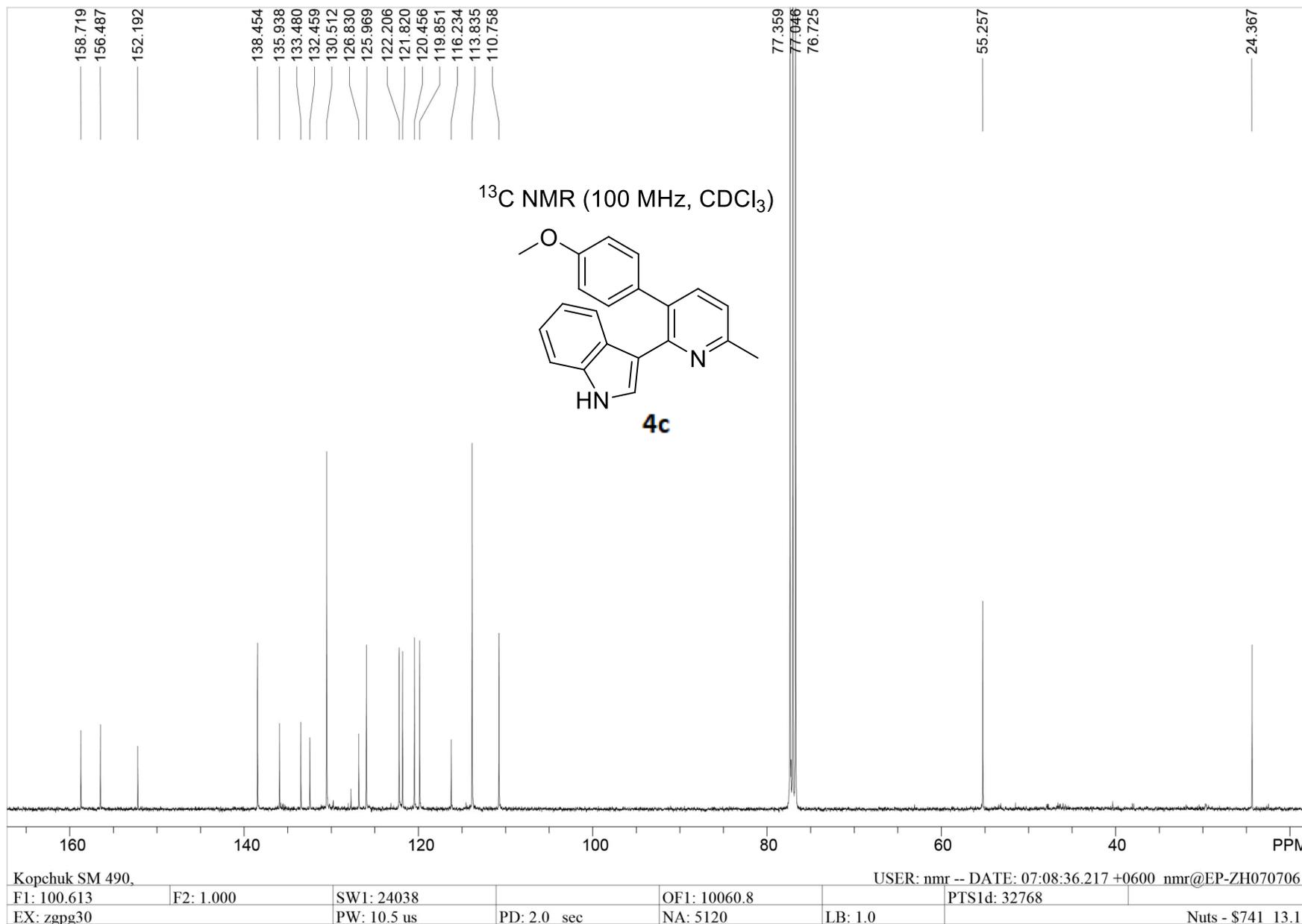
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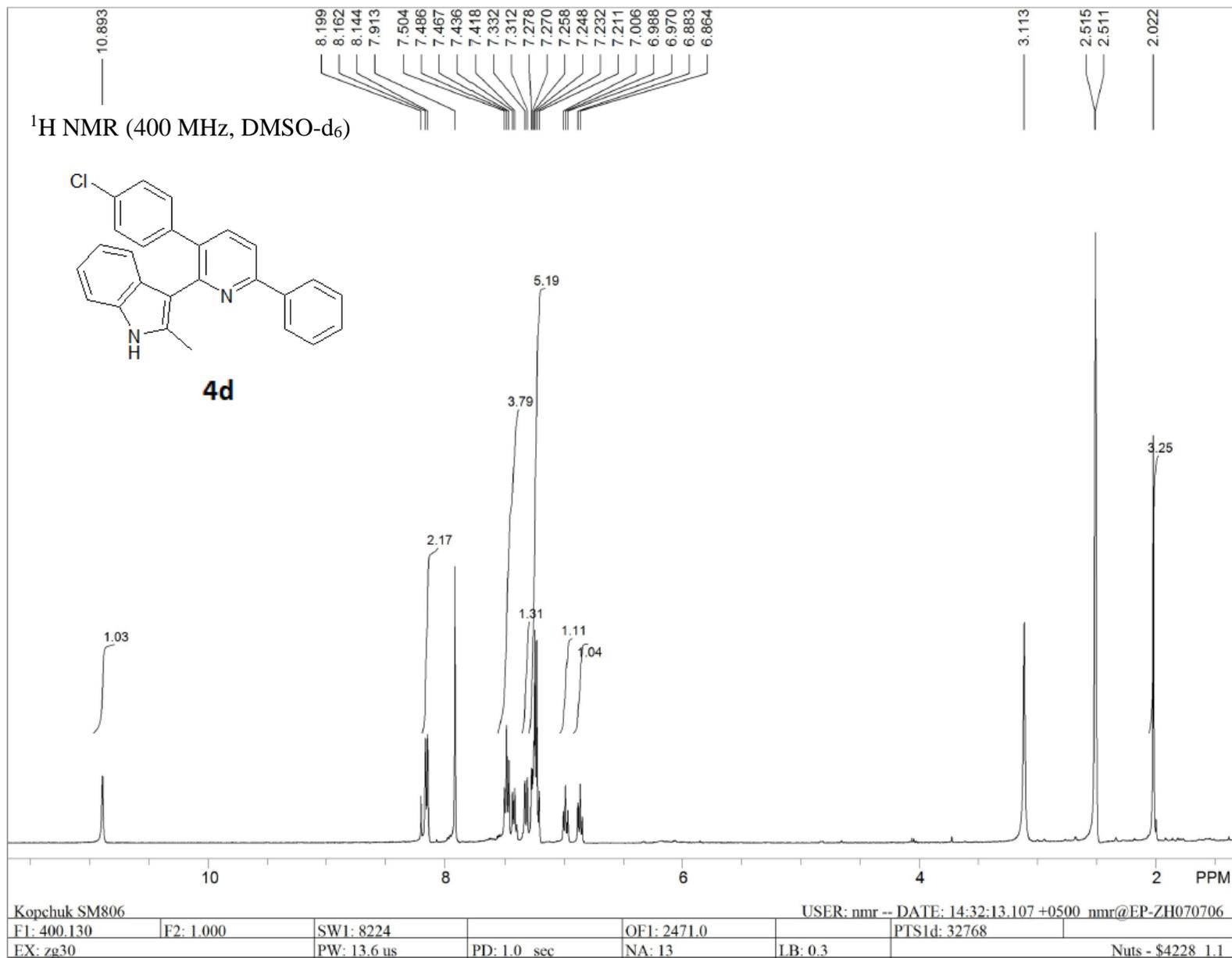


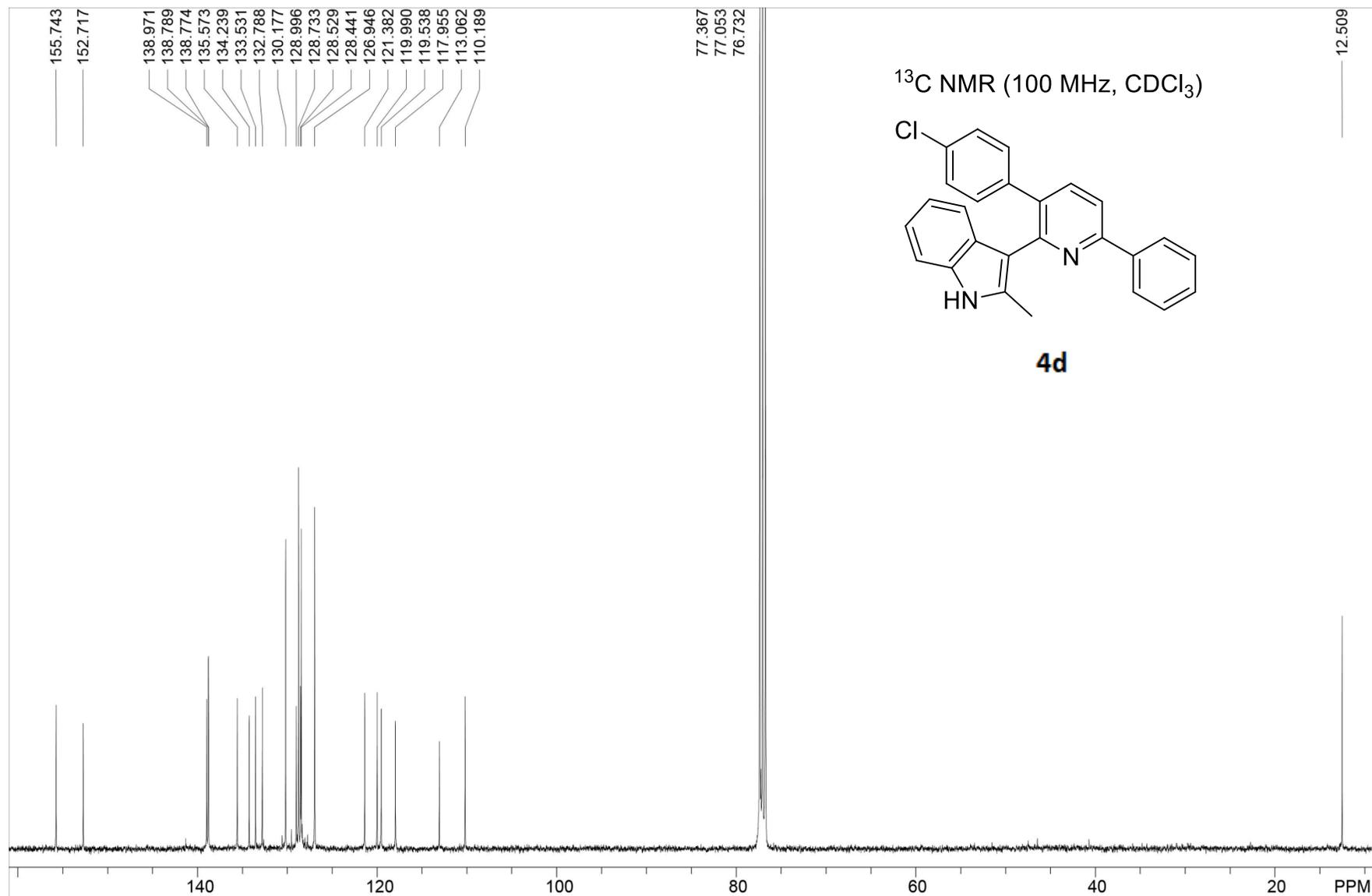




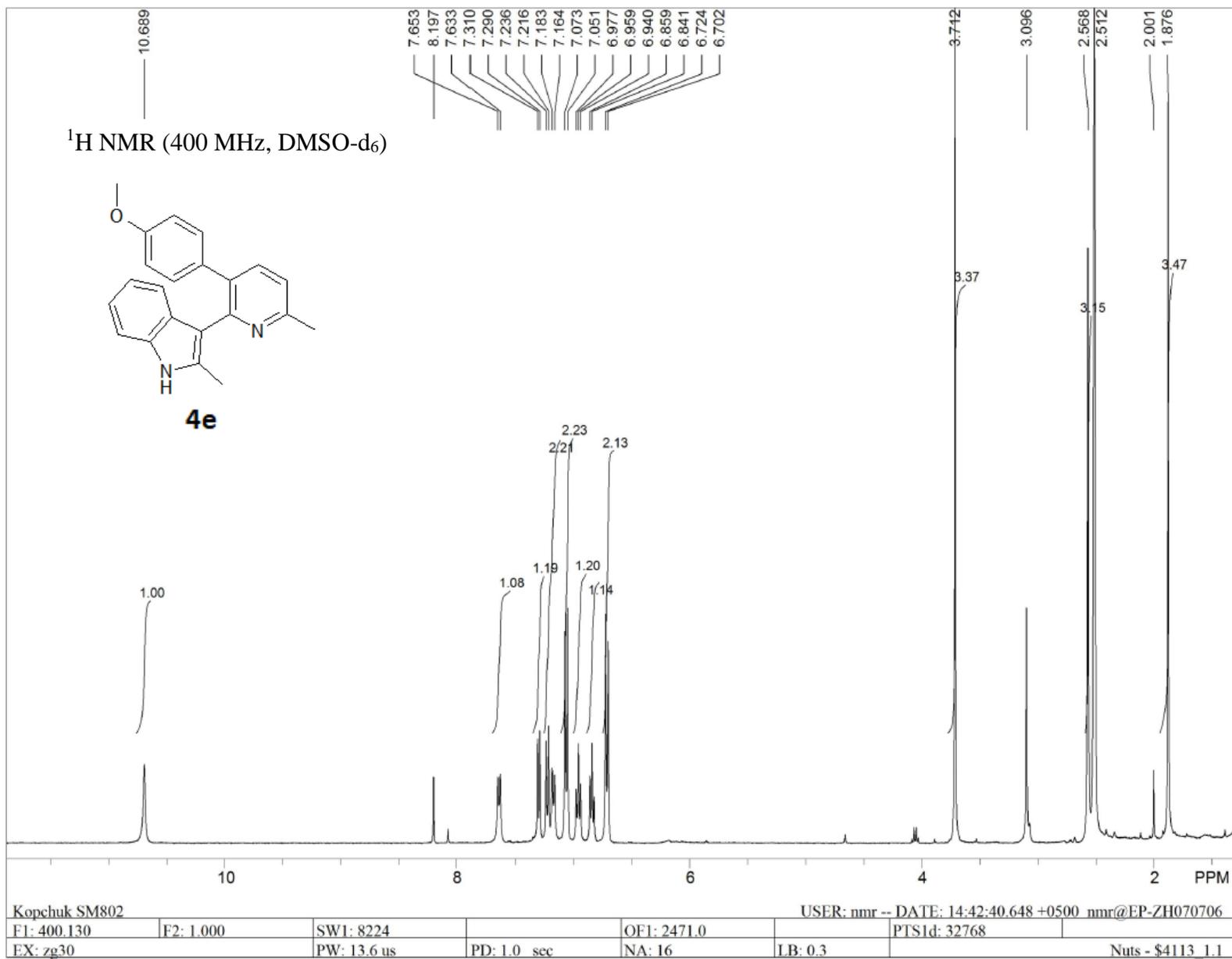


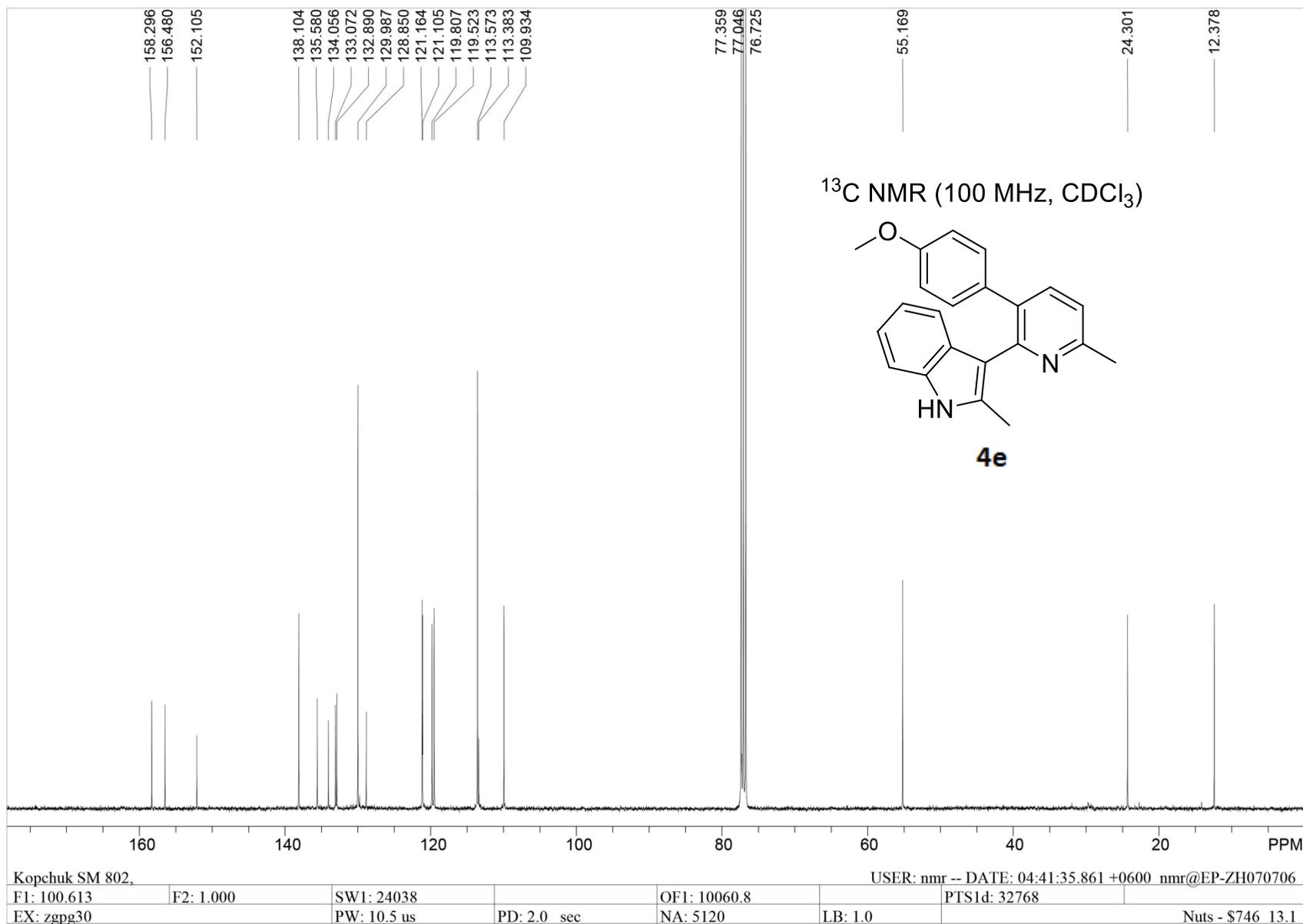


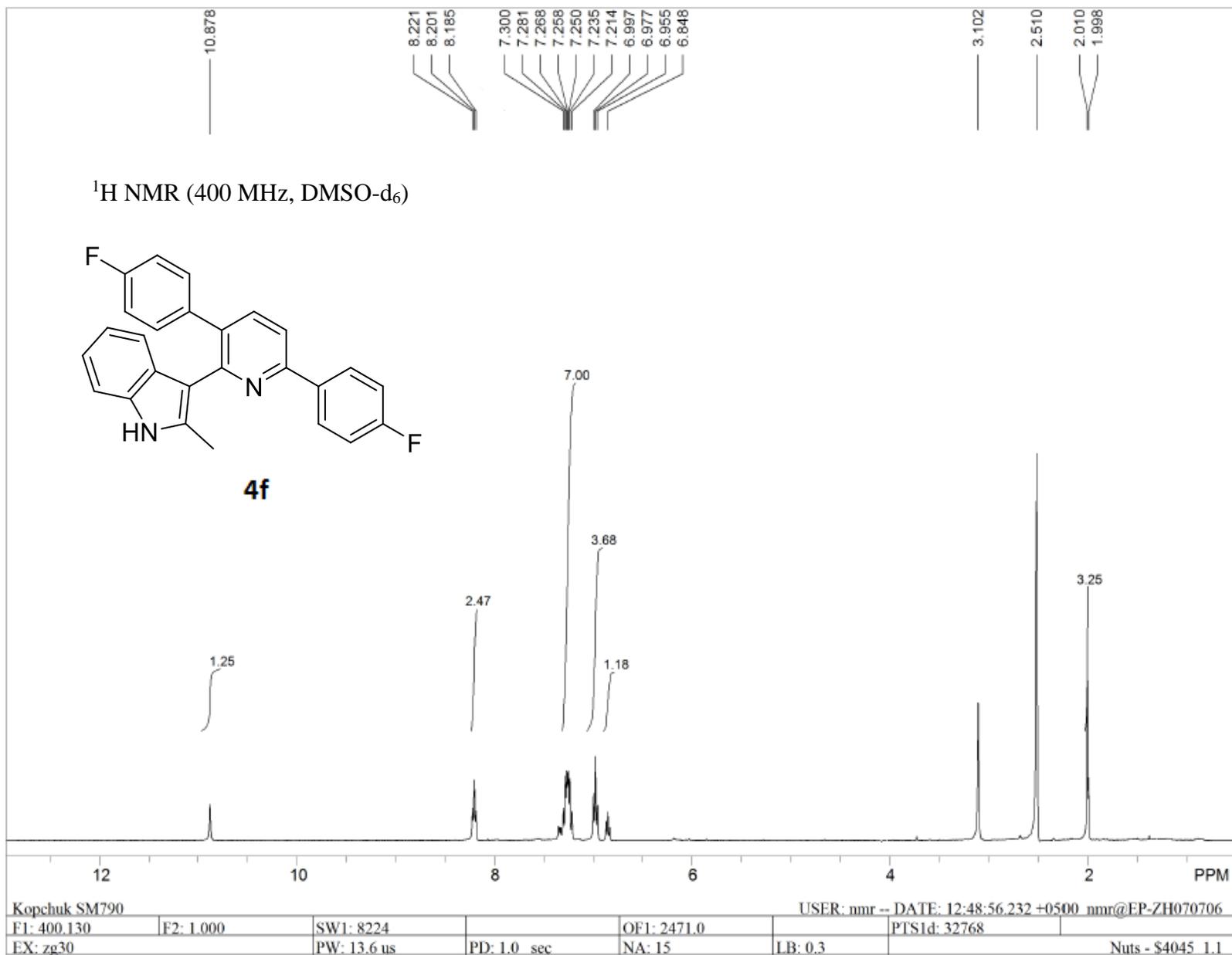


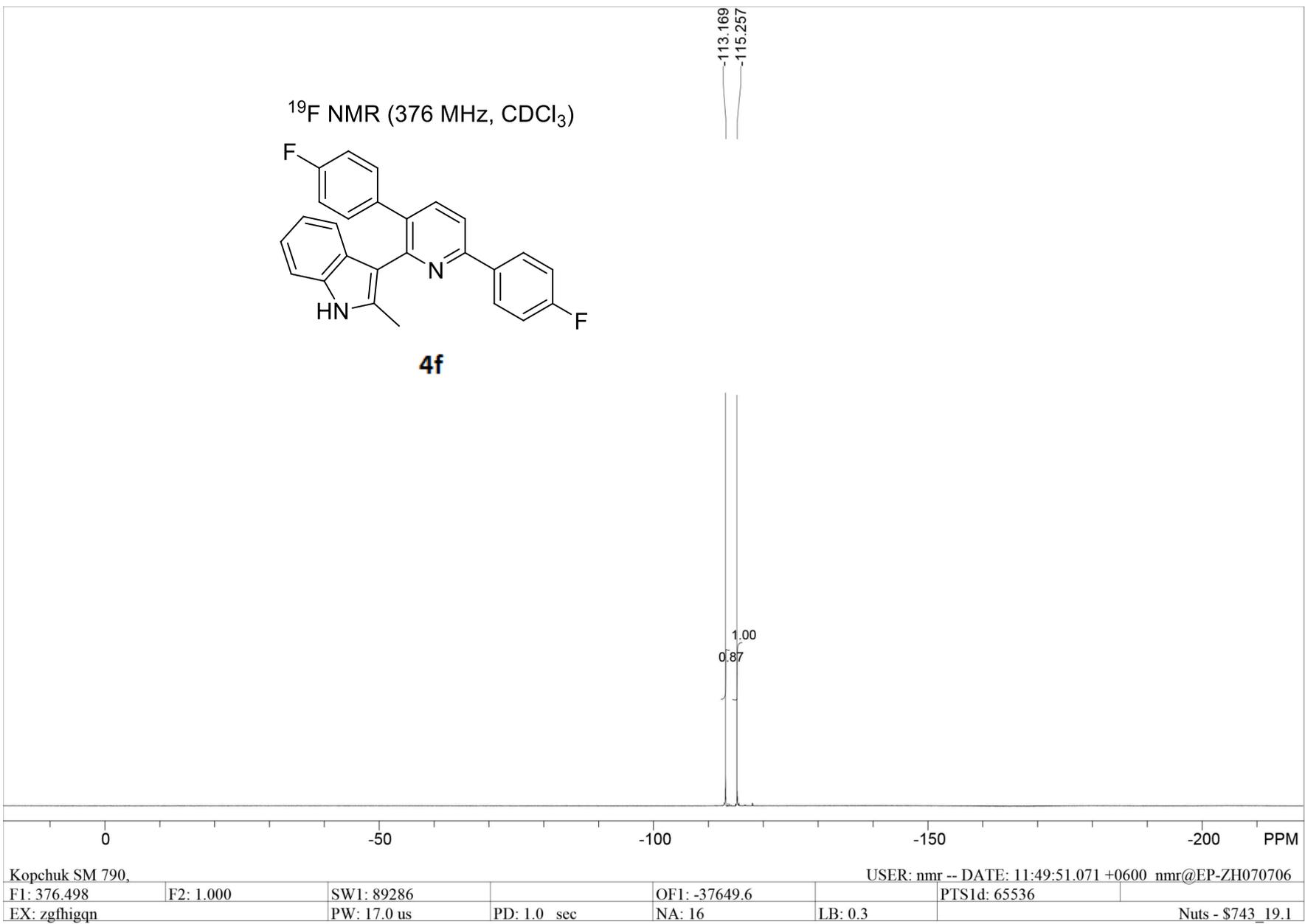


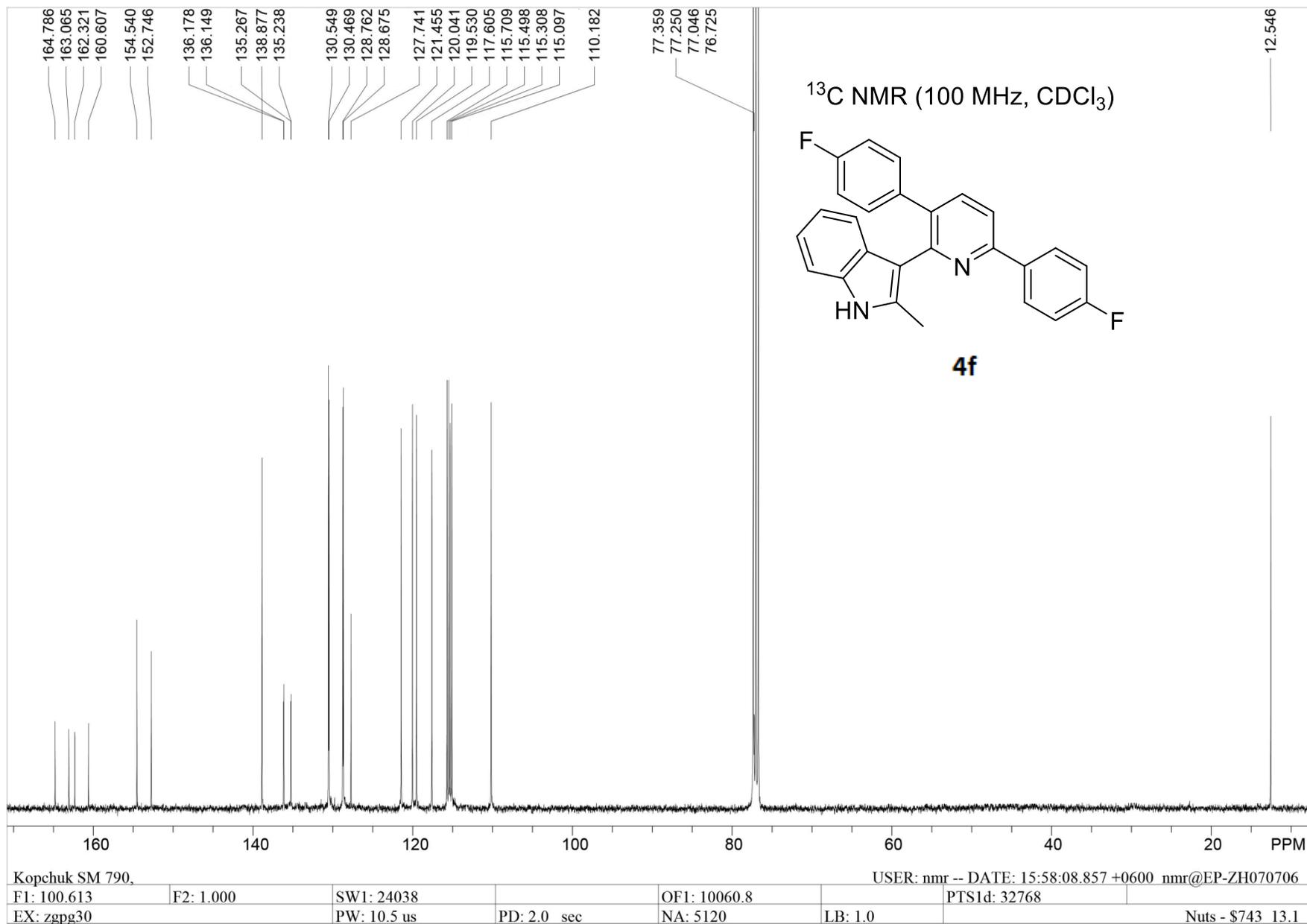
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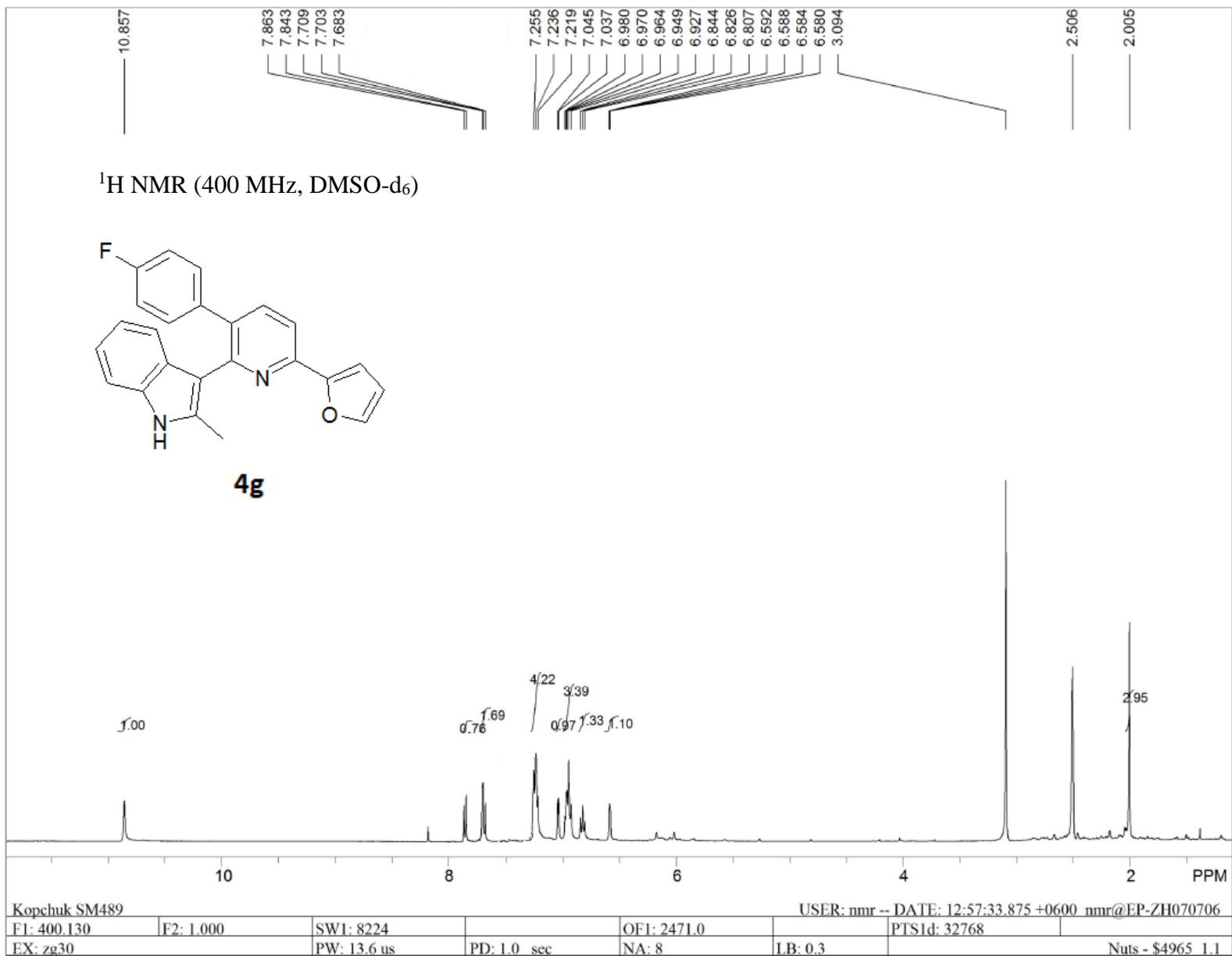


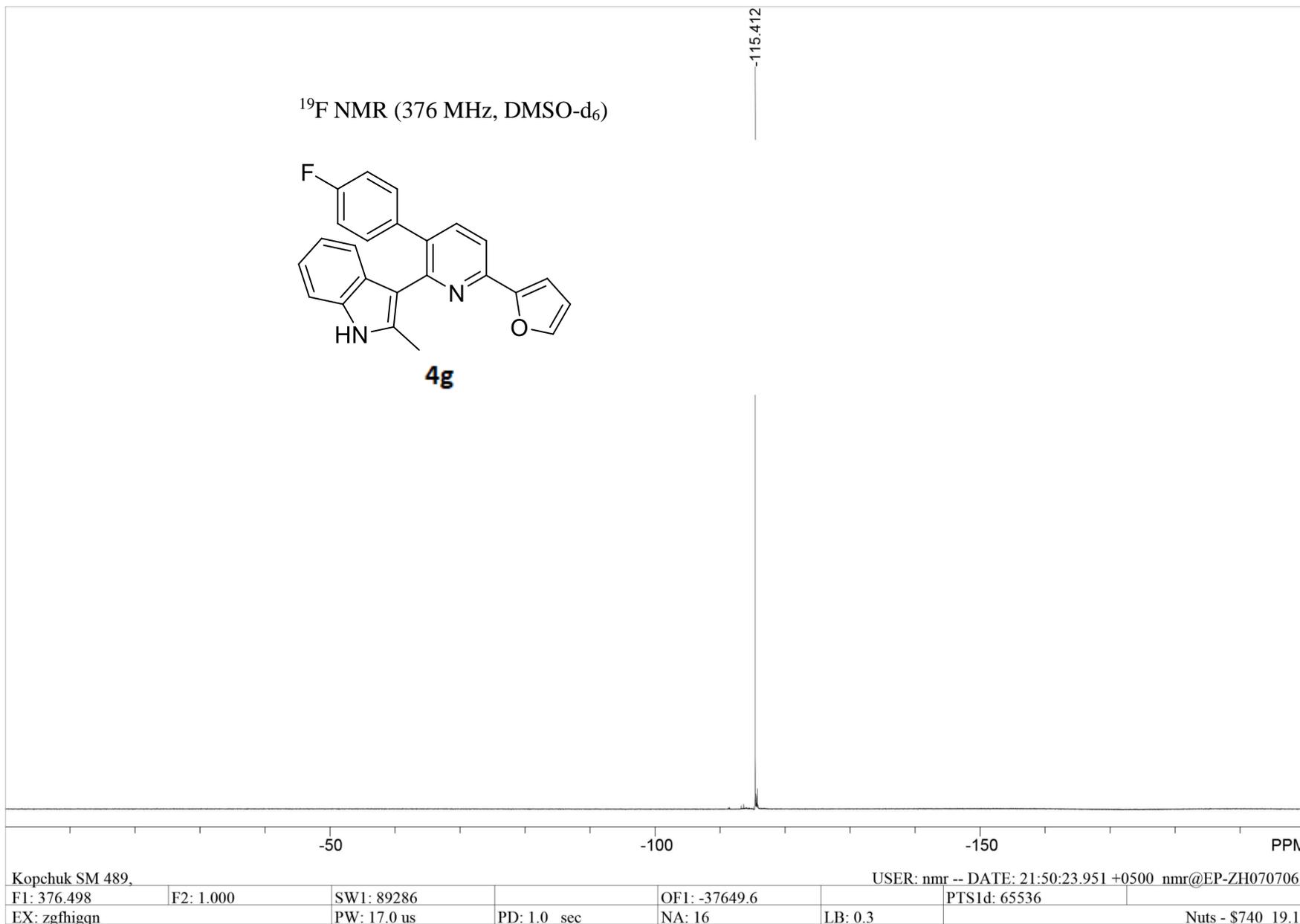


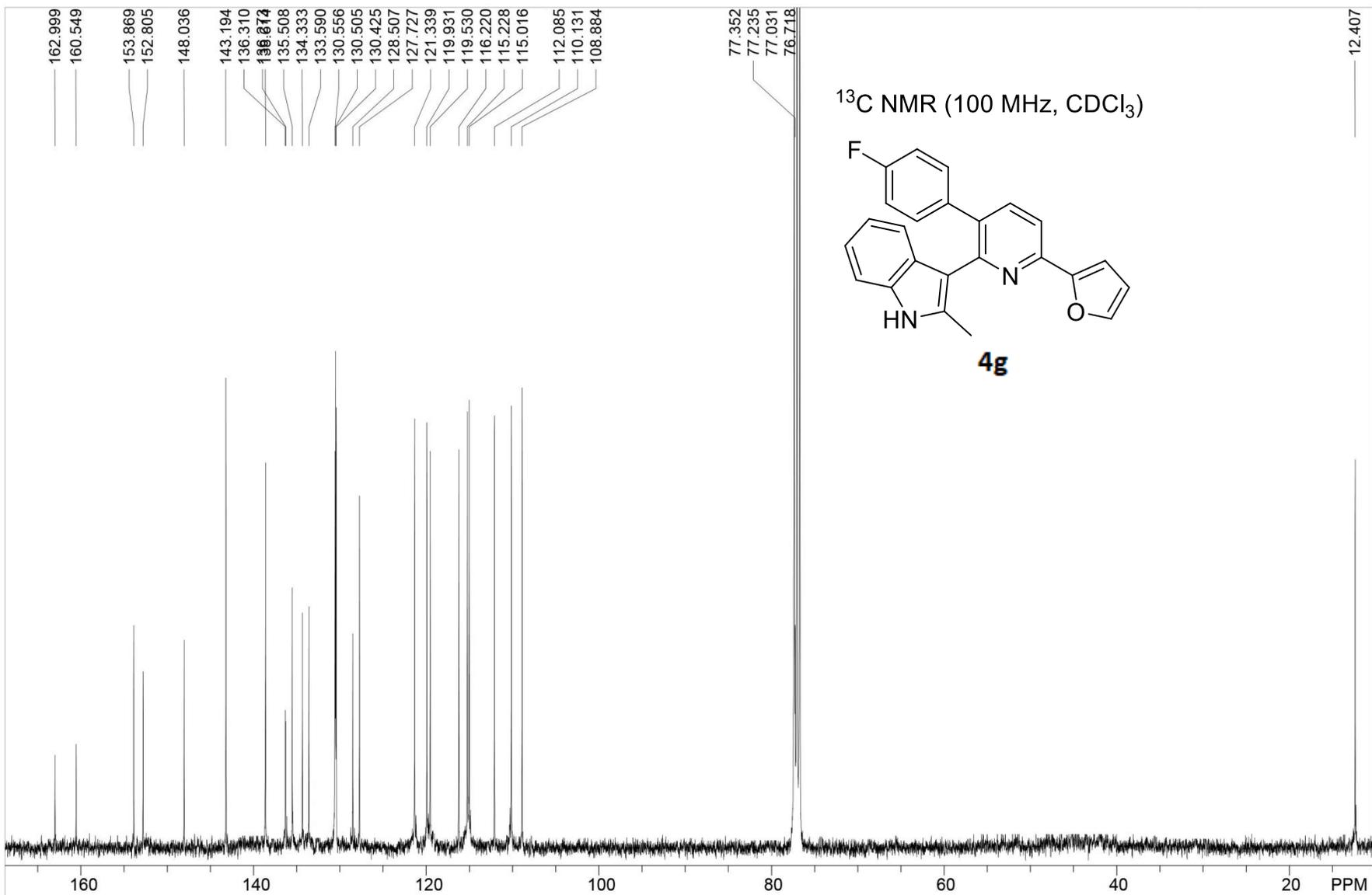




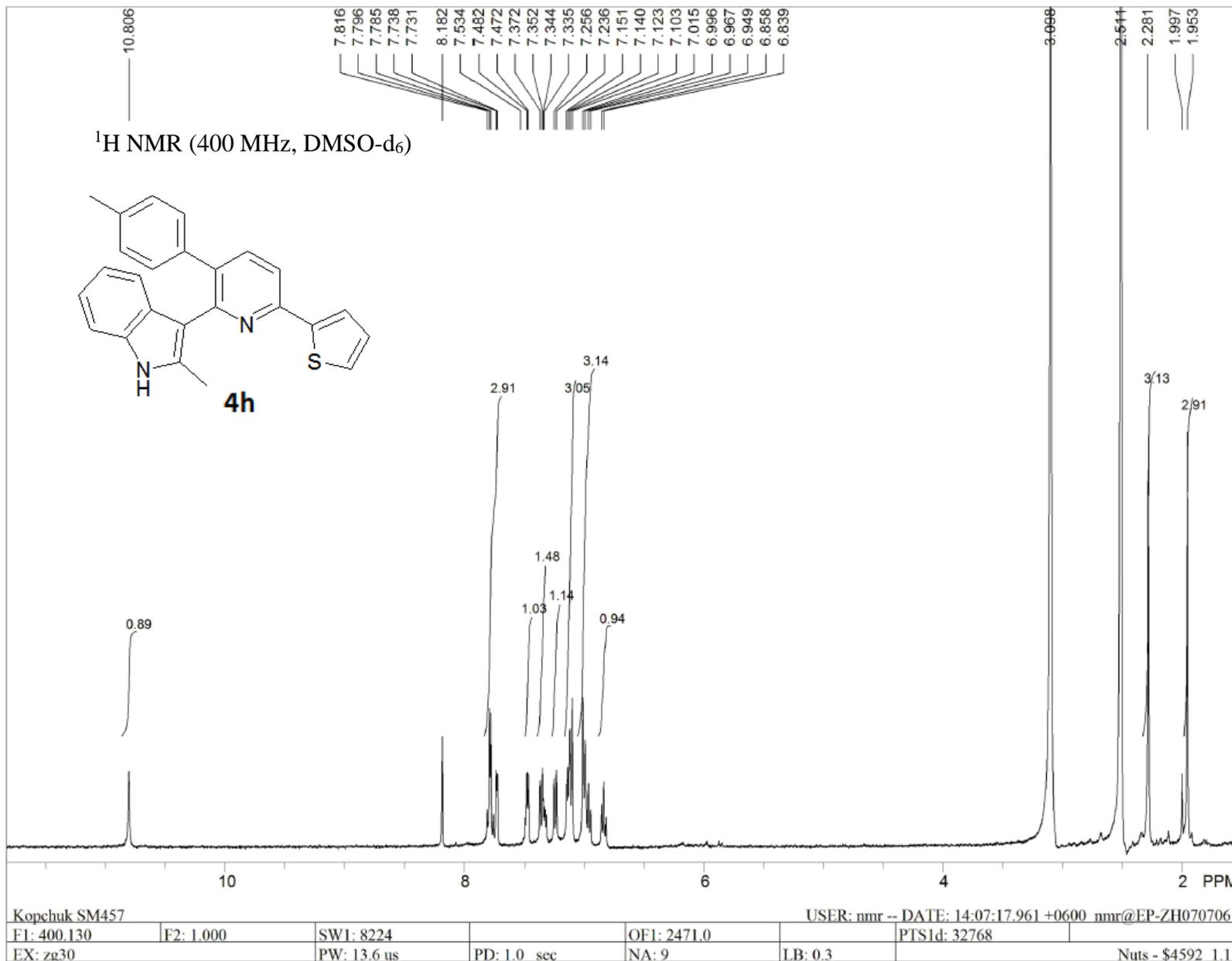


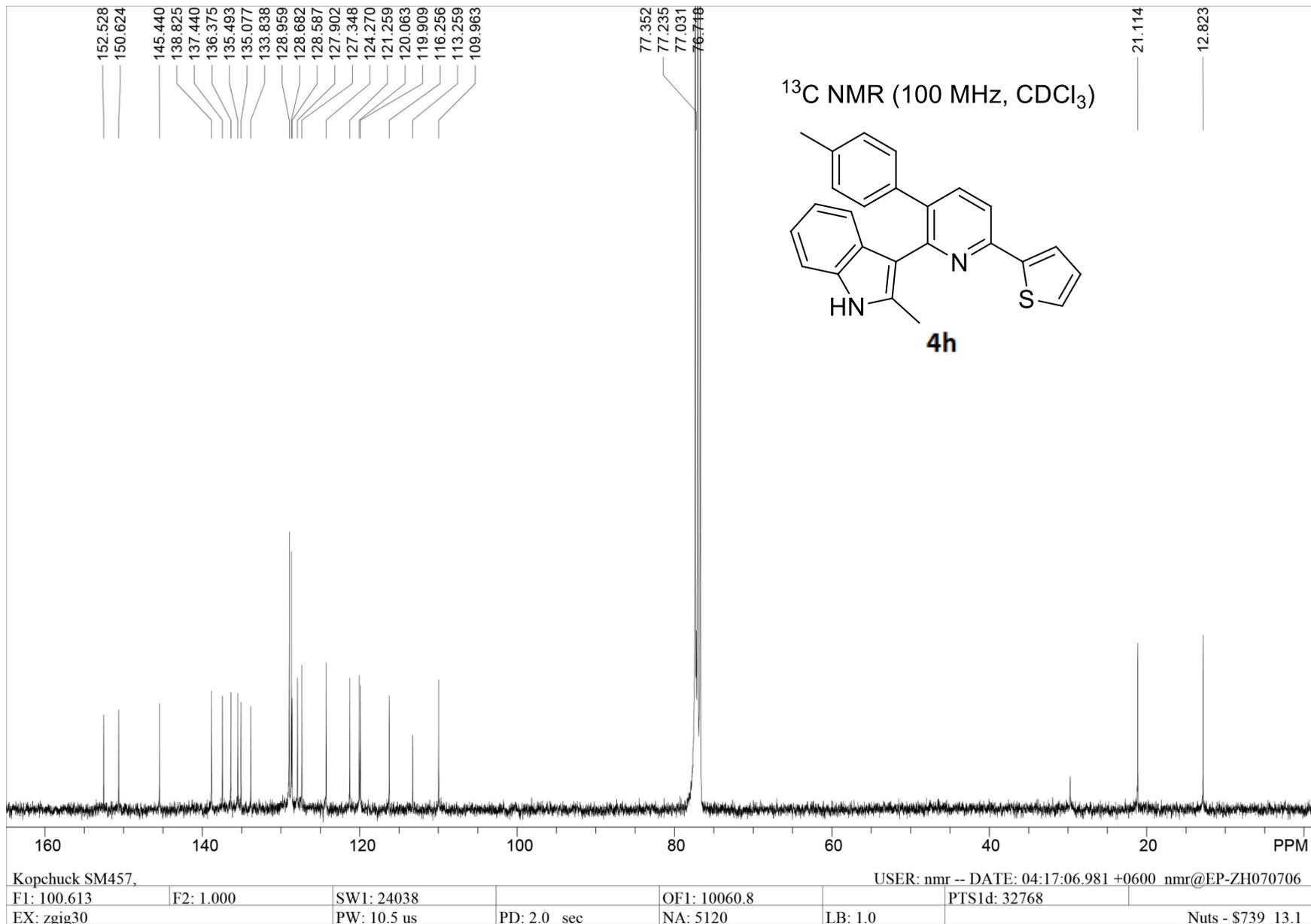


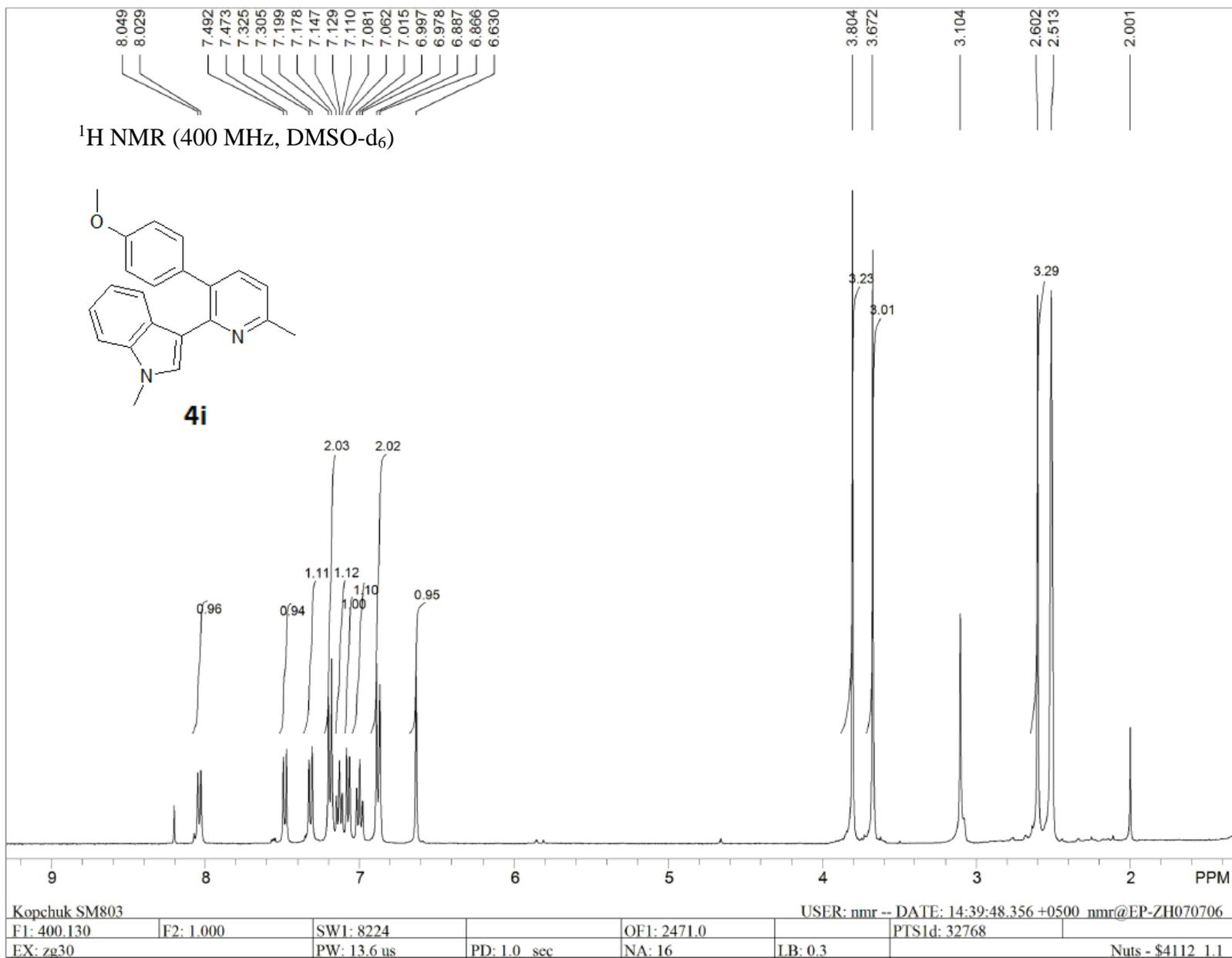


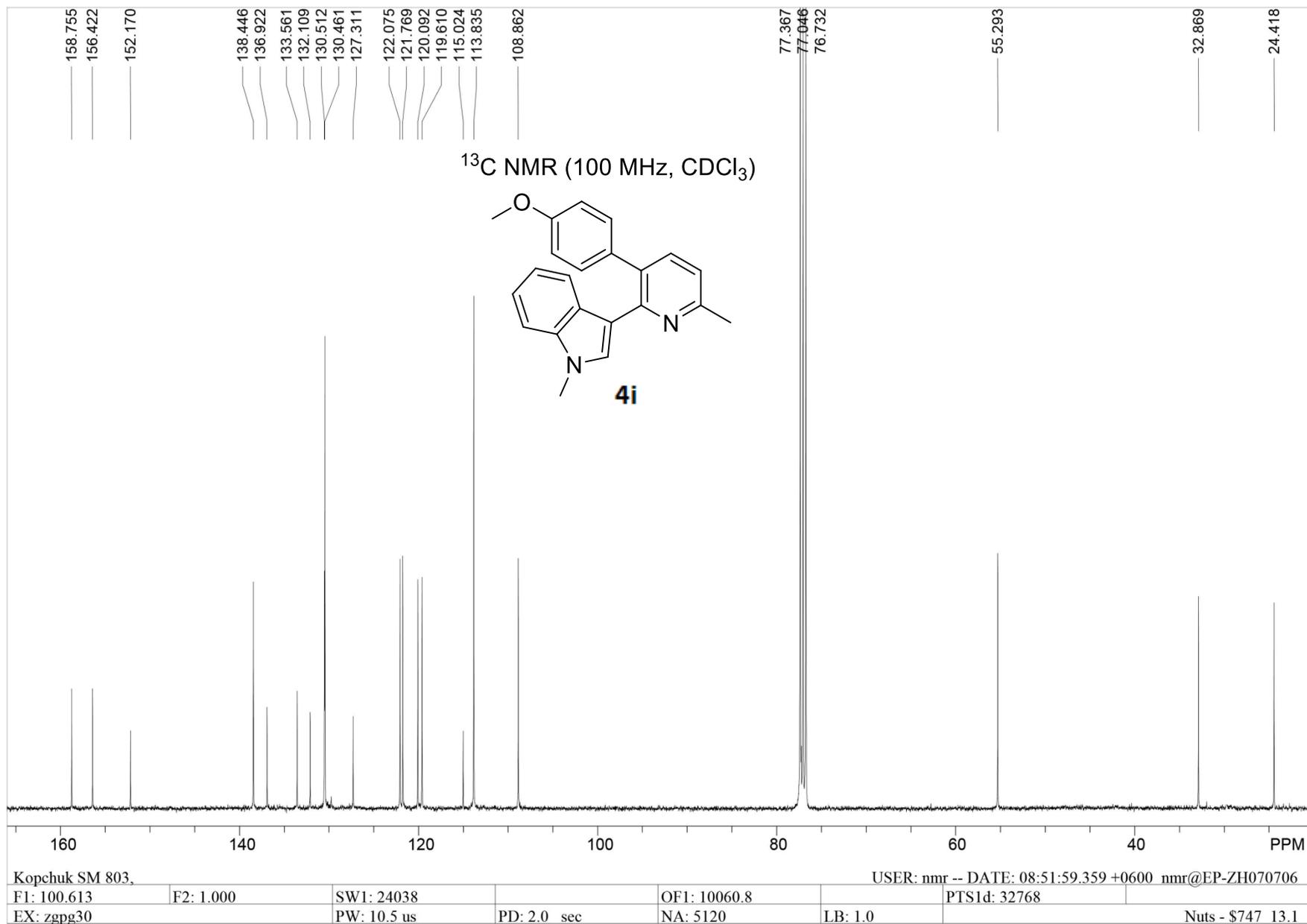


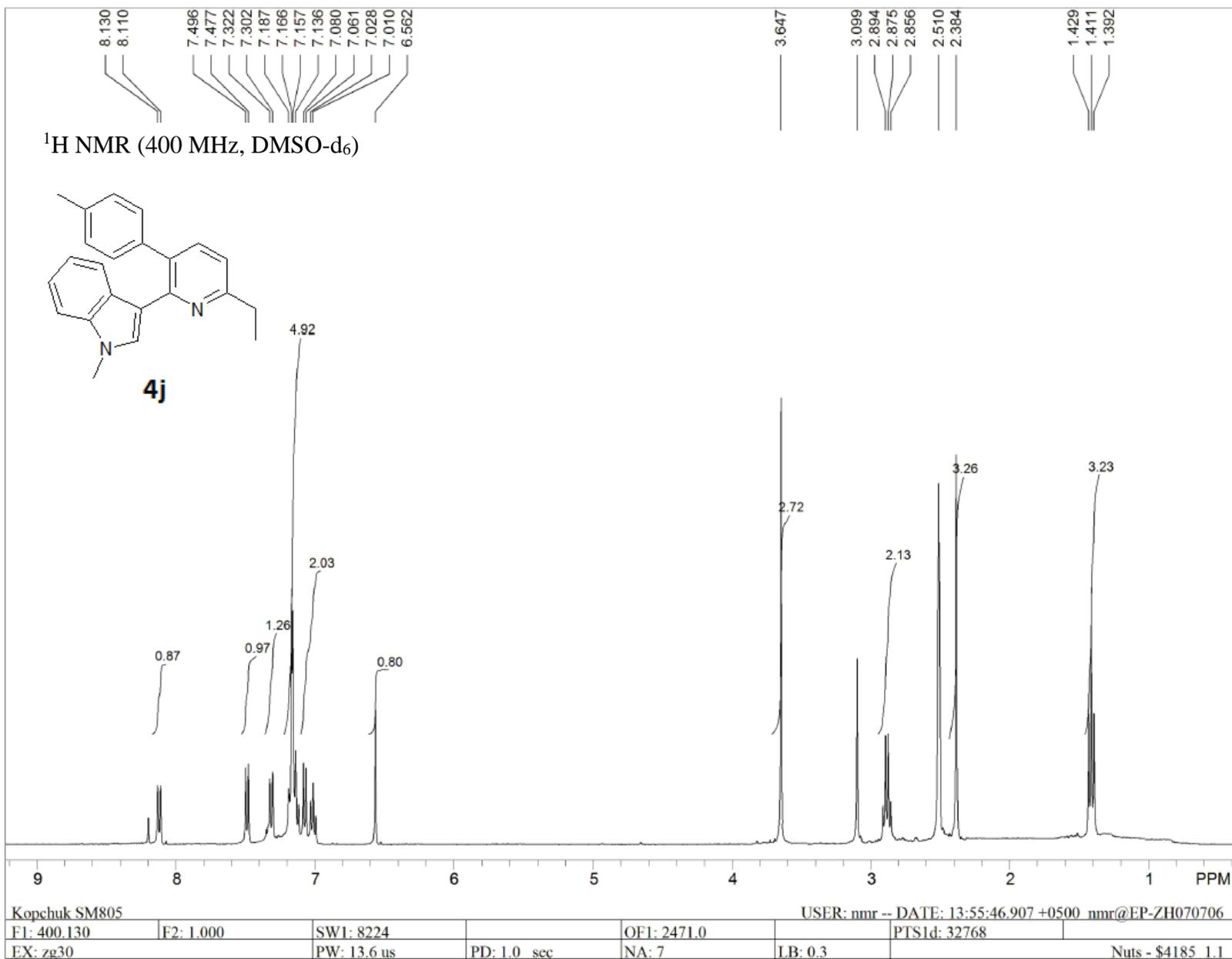
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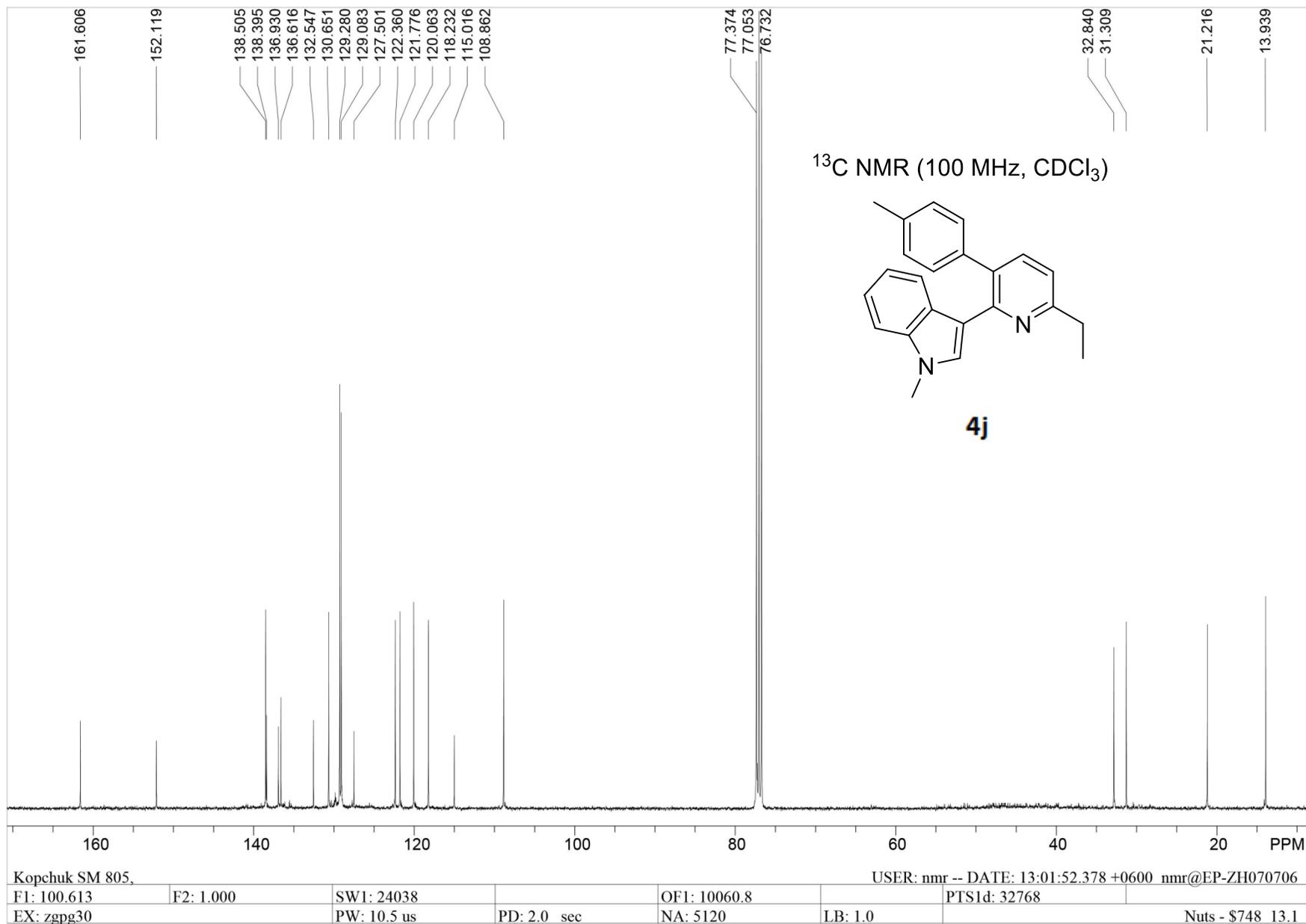


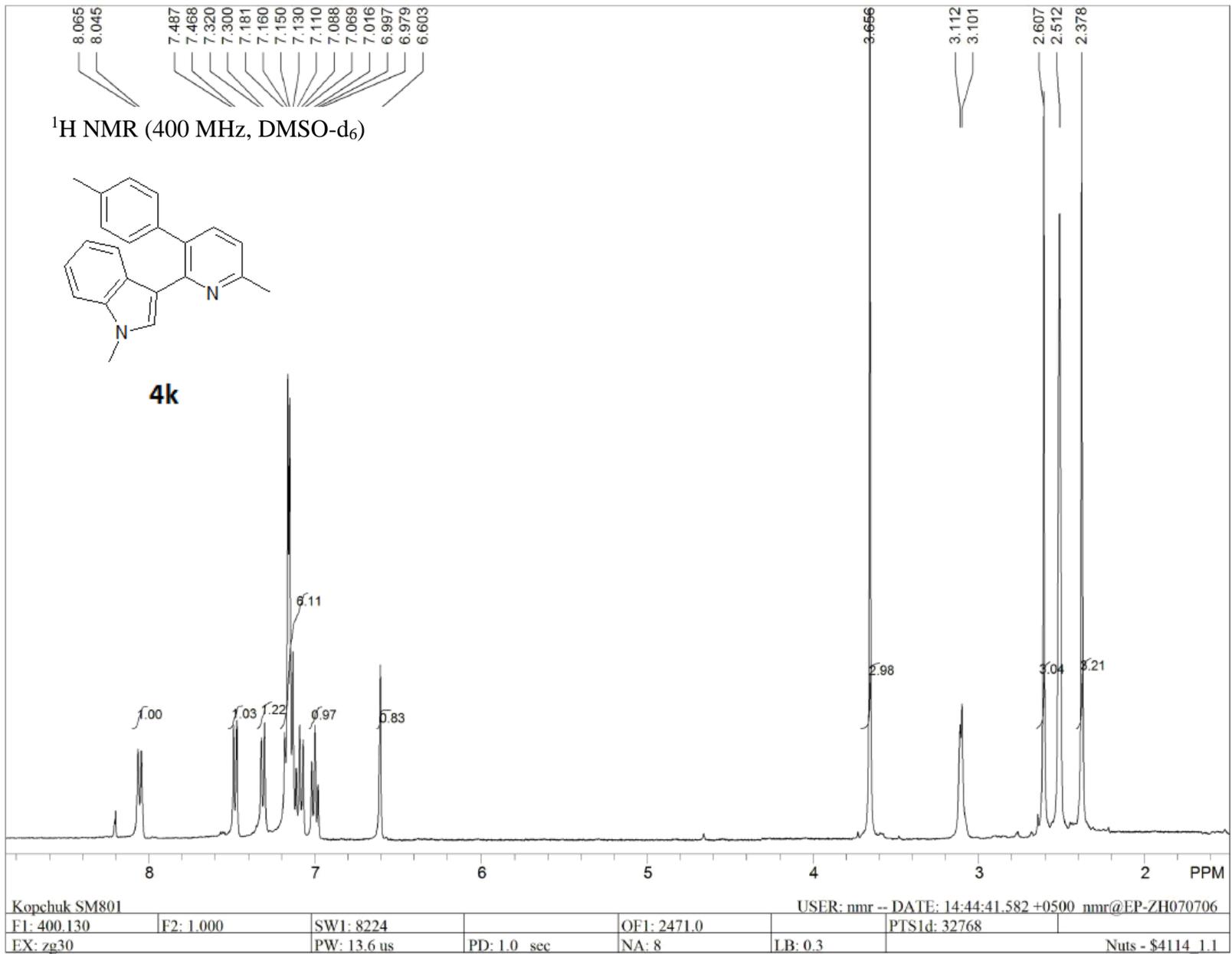


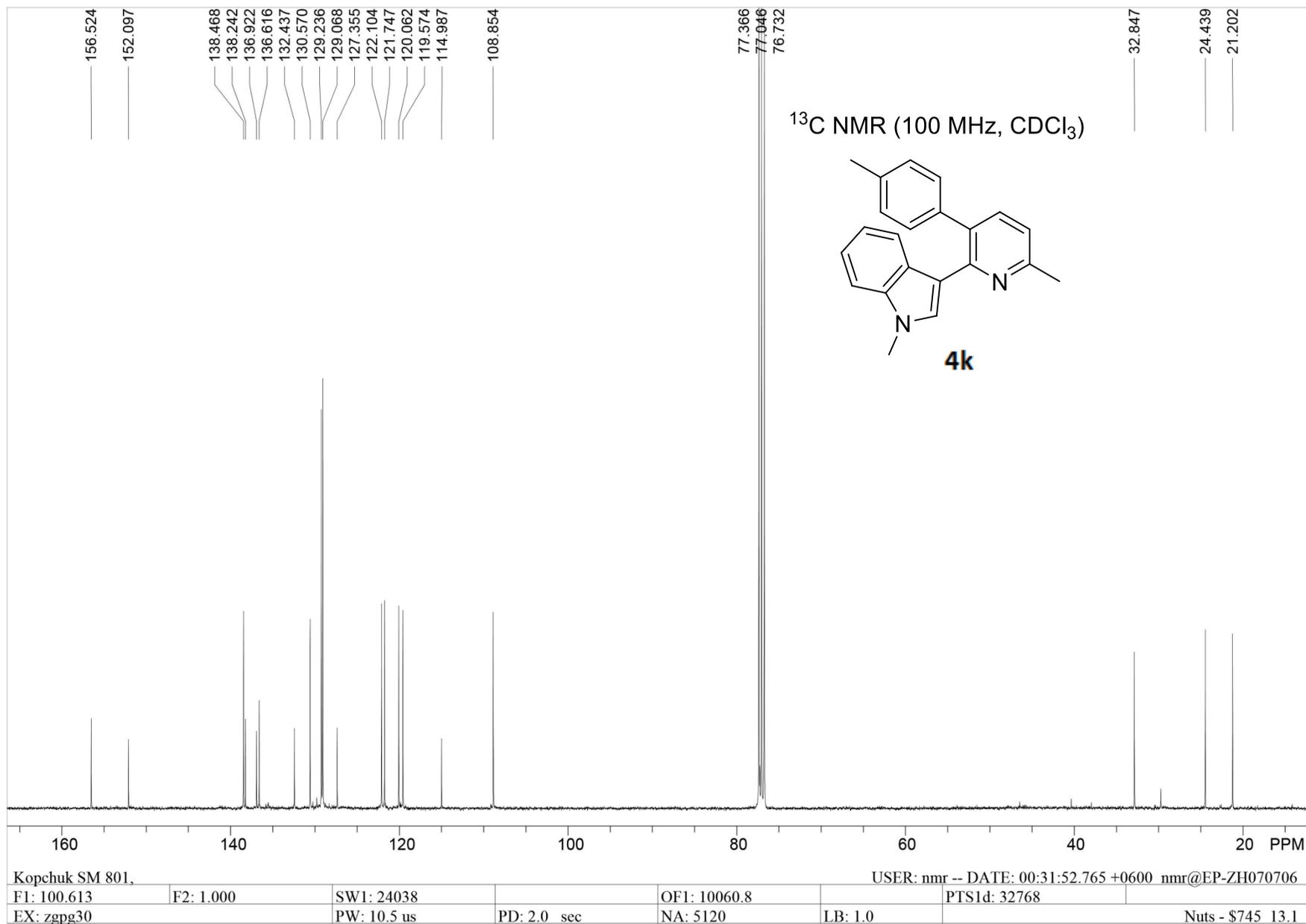


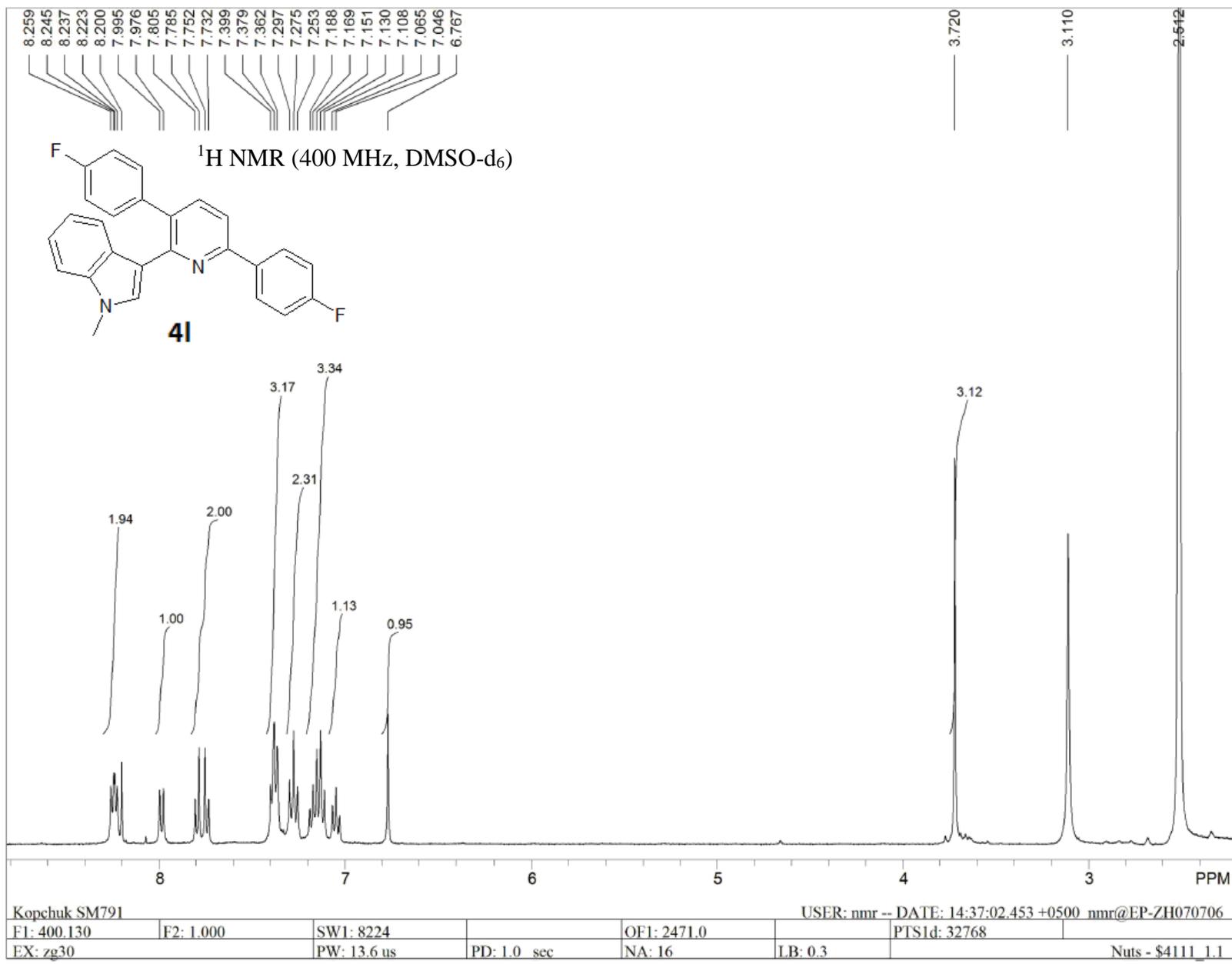


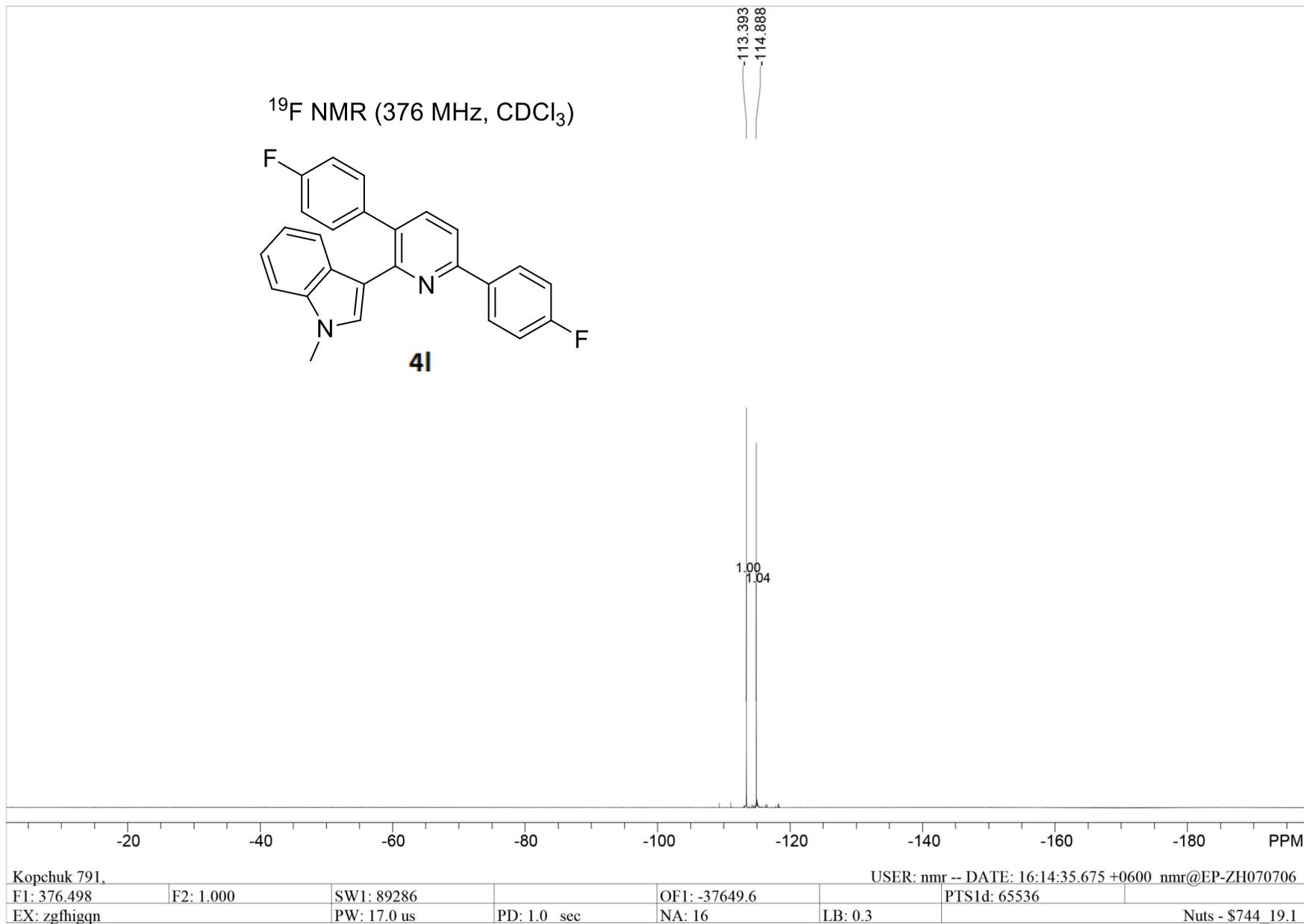


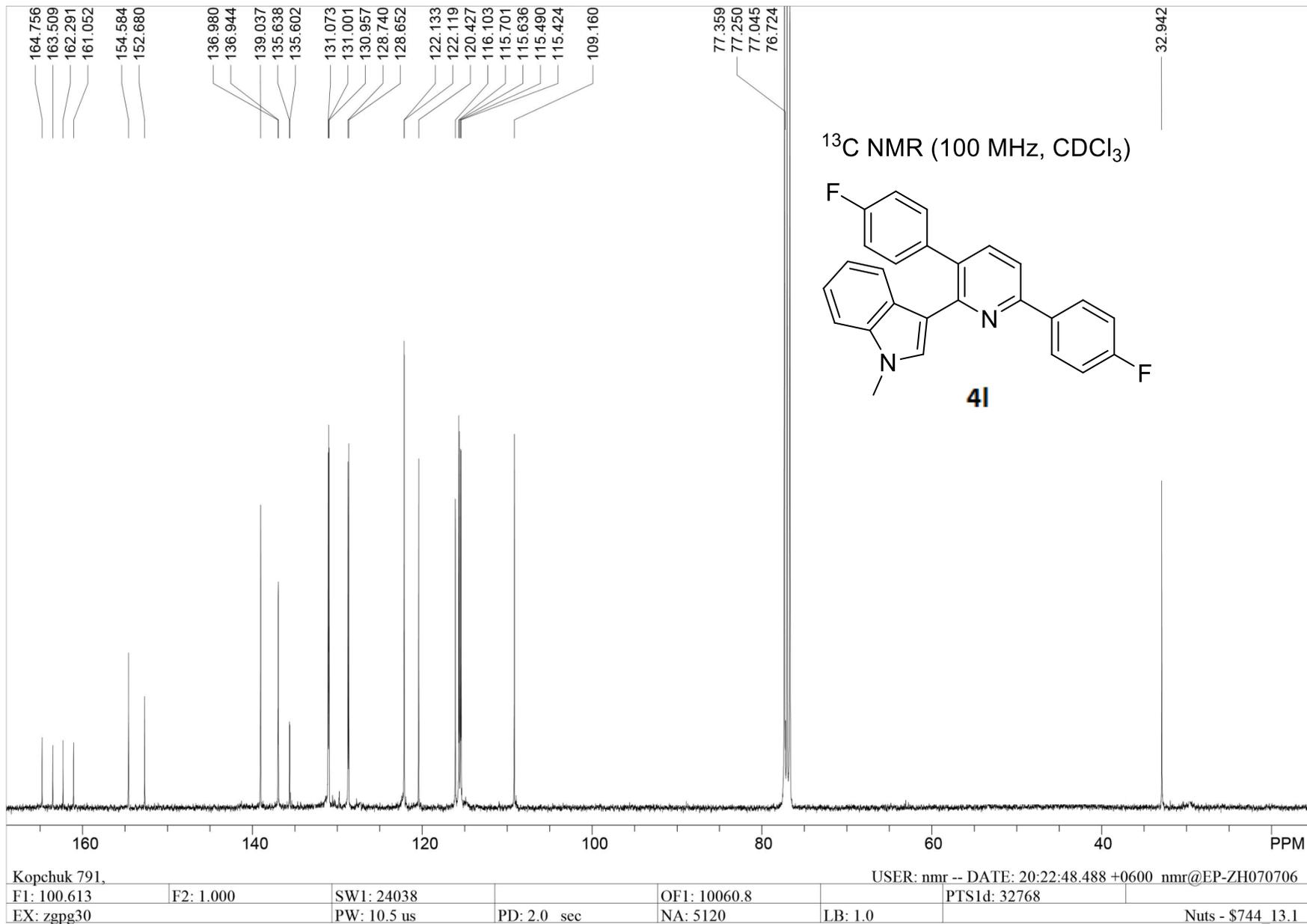












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- S3 V. L. Rusinov, D. N. Kozhevnikov, I. S. Kovalev, O. N. Chupakhin and G. G. Aleksandrov, *Russ. J. Org. Chem.*, 2000, **36**, 1050.