

**π -Extended fluorophores based on 5-aryl-2,2'-bipyridines:
synthesis and photophysical studies**

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General. Unless otherwise mentioned, all common reagents and solvents were used as purchased. Melting points were measured on the Boetius hot stage. ^1H and ^{13}C NMR spectra were acquired on a Bruker Avance-400 spectrometer, 298 K, digital resolution ± 0.01 ppm, as solutions in CDCl_3 and DMSO-d_6 using TMS as internal reference. 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. All reactions involving moisture sensitive reactants were executed using oven dried glassware.

The starting compounds: 6-(4-bromophenyl)-3-(2-pyridyl)-1,2,4-triazine, 5-(4-bromophenyl)-2,2'-bipyridine **1**, 5-(4-tolyl)-2,2'-bipyridine **3** [S1] and 2-tributylstannyl-5-dodecylthiophene [S2] were synthesized as described in literature.

General method for the synthesis of bipyridines 4,7

Bromophenyl bipyridine derivative **1** or **2** (0.5 mmol) was dissolved in toluene (20 ml) followed by addition of phenylboronic acid (0.525 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (10.5 mg, 0.015 mmol) and triphenylphosphine (6.6 mg, 0.025 mmol). A solution of potassium carbonate (0.69 g, 5 mmol) in water (10 ml) was prepared separately. Next, the prepared potassium carbonate solution and ethanol (7 ml) were added successively, the resulting mixture was stirred under reflux in argon atmosphere for 8 h (for the synthesis of cyclopenta[*c*]pyridine **7** reaction time 20 h required). After completion, the reaction mass was washed with potassium hydroxide and ammonium chloride solutions. The organic phase was dried over anhydrous sodium sulfate. The crude residue obtained after evaporation of the solvent in vacuum was purified by recrystallization (toluene).

5-(Biphenyl-4-yl)-2,2'-bipyridine (4). Yield 108 mg (0.35 mmol, 70%). ^1H NMR (DMSO-d_6 , δ , ppm): 7.32-7.41 (m, 2H, Ph, H-5 (Py)), 7.43-7.49 (m, 2H, Ph), 7.65-7.69 (m, 2H, Ph), 7.75-

7.77 (m, 2H, C-H_{arom}), 7.81-7.85 (m, 2H, C-H_{arom}), 7.90 (ddd, 1H, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4'), 8.18 (dd, 1H, ³J 8.3 Hz, ⁴J 2.5 Hz, H-4), 8.46 (dd, 1H, ³J 7.7 Hz, ⁴J 1.0 Hz, H-3'), 8.50 (d, 1H, ³J 8.3 Hz, H-3), 8.66 (dd, 1H, ³J 4.8 Hz, ⁴J 2.0 Hz, H-6'), 8.98 (d, 1H, ⁴J 2.5 Hz, H-6). ¹³C NMR (DMSO-d₆, δ, ppm): 121.1, 121.1, 123.7, 127.1, 127.5, 127.6, 127.9, 128.9, 135.1, 136.0, 136.5, 137.0, 140.4, 141.1, 147.6, 149.3, 155.0, 155.9. **ESI-MS**, *m/z*: found 309.14 [M+H]⁺, required 309.14. Found, %: C 85.53, H 5.31, N 8.90. **C₂₂H₁₆N₂**. Required, %: C 85.69, H 5.23, N 9.08.

4-(Biphenyl-4-yl)-1-(pyridin-2-yl)-6,7-dihydro-5H-cyclopenta[*c*]pyridine (7). Yield 96 mg (0.275 mmol, 55%). ¹H NMR (CDCl₃, δ, ppm): 2.10-2.12 (m, 2H, CH₂-6), 3.10 (t, 2H, ³J 7.5 Hz, CH₂-7), 3.48 (t, 2H, ³J 7.5 Hz, CH₂-5), 7.28 (ddd, 1H, ³J 4.8, 7.7 Hz, ⁴J 1.0 Hz, H-5 (Py)), 7.36-7.40 (m, 1H, Ph), 7.44-7.51 (m, 2H, Ph), 7.58-7.60 (m, 2H, C-H_{arom}), 7.63-7.68 (m, 2H, Ph), 7.70-7.75 (m, 2H, C-H_{arom}), 7.83 (ddd, 1H, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4 (Py)), 8.22 (dd, 1H, ³J 7.7 Hz, ⁴J 1.0 Hz, H-3 (Py)), 8.60 (s, 1H, H-3), 8.72 (dd, 1H, ³J 4.8 Hz, ⁴J 2.0 Hz, H-6 (Py)). ¹³C NMR (CDCl₃, δ, ppm): 25.6, 32.7, 33.4, 122.7, 123.0, 127.1, 127.4, 127.5, 128.9, 129.0, 133.3, 136.4, 136.8, 139.4, 140.6, 146.7, 148.7, 150.9, 153.2, 158.3. **ESI-MS**, *m/z*: found 349.17 [M+H]⁺, required 349.17. Found, %: C 86.02, H 5.49, N 7.99. **C₂₅H₂₀N₂**. Required, %: C 86.17, H 5.79, N 8.04.

5-(4-Bromomethylphenyl)-2,2'-bipyridine. 5-(4-Tolyl)-2,2'-bipyridine **3** (2.0 g, 8.1 mmol) was dissolved in dry CCl₄ (50 ml). *N*-Bromosuccinimide (1.44 g, 8.1 mmol) and benzoyl peroxide (catalytic amount) were added, and the mixture was refluxed for 8 h under light irradiation. The resulting precipitate was filtered off. The analytically pure product was obtained from the filtrate after evaporation of the solvent in vacuum followed by recrystallization (ethanol). Yield 1.58 g (4.86 mmol, 60%). M.p. 142-144 °C. ¹H NMR (CDCl₃, δ, ppm): 4.67 (s, 2H, CH₂Br), 7.38 (ddd, 1H, ³J 4.8, 7.7 Hz, ⁴J 1.0 Hz, H-5'), 7.53-7.58 (m, 2H, C-H_{arom}), 7.70-7.75 (m, 2H, C-H_{arom}), 7.88 (ddd, 1H, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4'), 8.14 (dd, 1H, ³J 8.3 Hz, ⁴J 2.5 Hz, H-4), 8.43-8.47 (m, 2H, H-3,3'), 8.65 (dd, 1H, ³J 4.8 Hz, ⁴J 2.0 Hz, H-6'), 8.93 (d, 1H, ⁴J 2.5 Hz, H-6). **ESI-MS**, *m/z*: found 325.03 [M+H]⁺, required 325.03. Found, %: C 62.68, H 4.19, N 8.80. **C₁₇H₁₃BrN₂**. Required, %: C 62.79, H 4.03, N 8.61.

(*E*)-5-{4-[2-(Thiophen-2-yl)vinyl]phenyl}-2,2'-bipyridine (8). To a solution of 5-(4-bromomethylphenyl)-2,2'-bipyridine (1.00 g, 3.08 mmol) in benzene (50 ml), triphenylphosphine (1.35 g, 5.1 mmol) was added, and the resulting mixture was refluxed for 1 h. The solvent was removed under reduced pressure. The residue was dissolved in dry THF (20 ml). This solution, and

a solution of thiophene-2-carbaldehyde (0.28 ml, 3.08 mmol) in dry THF (10 ml) were added to the suspension of potassium *tert*-butoxide (110.9 mg, 1.54 mmol) in dry THF (10 ml) by portions. The resulting mixture was stirred for 1 h. After completion, the solvent was removed under reduced pressure. Water (20 ml) was added to the residue and the product was extracted with CH₂Cl₂ (3 x 20 ml). The organic phase was dried over anhydrous sodium sulfate. The analytically pure product was obtained after evaporation of the solvent in vacuum and recrystallization (toluene). Yield 400 mg (1.17 mmol, 38%). M.p. 232-234°C. ¹H NMR (CDCl₃, δ, ppm): 6.98 (d, 1H, ³J 16.0 Hz, vinyl), 7.04 (dd, 1H, ³J 5.2, 3.2 Hz, H-4 (thiophene)), 7.12 (d, 1H, ³J 3.2 Hz, thiophene), 7.24 (d, 1H ³J 5.2 Hz, thiophene), 7.25-7.37 (m, 2H, vinyl, H-5'), 7.57-7.61 (m, 2H, C-H_{arom}), 7.65-7.67 (m, 2H, C-H_{arom}), 7.84 (ddd, 1H, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4'), 8.04 (dd, 1H, ³J 8.3 Hz, ⁴J 2.5 Hz, H-4), 8.42-8.50 (m, 2H, H-3,3'), 8.71 (dd, 1H, ³J 4.8 Hz, ⁴J 2.0 Hz, H-6'), 8.93 (d, 1H, ⁴J 2.5 Hz, H-6). ESI-MS, *m/z*: found 341.11 [M+H]⁺, required 341.11. Found, %: C 77.50, H 4.61, N 8.11. C₂₂H₁₆N₂S. Required, %: C 77.62, H 4.74, N 8.23.

The general procedure for the synthesis of ethynyl-derivatives of bipyridine

In a Schlenk flask, the corresponding haloarene (2 mmol), PdCl₂(PPh₃)₂ (10 mg, 14.2 μmol) and triphenylphosphine (20 mg, 7.63 μmol) were suspended in piperidine (15 ml) under argon atmosphere. A solution of the corresponding acetylene (2.2 mmol) in THF (10 ml) was added, and argon was passed through the mixture for 20 min. A solution of CuI (8 mg, 4.20 μmol) and LiBr (41 mg, 0.47 mmol) in THF (5 ml) was added, and the resulting mixture was stirred at 80 °C under argon atmosphere for 7 h. After completion, water (40 ml) was added and the product was extracted with CH₂Cl₂ (3 x 20 ml). The organic phase was dried over anhydrous sodium sulfate. The crude residue was obtained after evaporation of the solvent in vacuum and trituration with diethyl ether. The resulting precipitate was filtered off and dried.

5-[4-(Phenylethynyl)phenyl]-2,2'-bipyridine (6a). Yield 0.29 g (0.87 mmol, 44%). M.p. 153-155 °C. ¹H NMR (CDCl₃, δ, ppm): 7.29-7.33 (m, 4H, Ph, H-5'), 7.50-7.54 (m, 2H, Ph), 7.51-7.56 (m, 2H, C-H_{arom}), 7.63-7.68 (m, 2H, C-H_{arom}), 7.88 (ddd, 1H, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4'), 8.14 (dd, 1H, ³J 8.3 Hz, ⁴J 2.5 Hz, H-4), 8.44-8.47 (m, 2H, H-3,3'), 8.65 (dd, 1H, ³J 4.8 Hz, ⁴J 2.0 Hz, H-6'), 8.93 (d, 1H, ⁴J 2.5 Hz, H-6). ESI-MS, *m/z*: found 333.14 [M+H]⁺, required 333.14. Found, %: C 86.98, H 4.67, N 8.24. C₂₄H₁₆N₂. Required, %: C 86.72, H 4.85, N 8.43.

5-[4-(Trimethylsilylethynyl)phenyl]-2,2'-bipyridine (6b). Yield 0.56 g (1.7 mmol, 85%). M.p. 140-142 °C. ¹H NMR (CDCl₃, δ, ppm): 0.28 (s, 9H, SiMe₃), 7.38 (ddd, 1H, ³J 4.8, 7.7 Hz, ⁴J

1.0 Hz, H-5'), 7.53-7.58 (m, 2H, C-H_{arom}), 7.70-7.75 (m, 2H, C-H_{arom}), 7.88 (ddd, 1H, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4'), 8.14 (dd, 1H, ³J 8.3 Hz, ⁴J 2.5 Hz, H-4), 8.43-8.48 (m, 2H, H-3,3'), 8.65 (dd, 1H, ³J 4.8 Hz, ⁴J 2.0 Hz, H-6'), 8.93 (d, 1H, ⁴J 2.5 Hz, H-6). ESI-MS, *m/z*: found 329.15 [M+H]⁺, required 329.15. Found, %: C 76.55, H 5.98, N 8.44. C₂₁H₂₀N₂Si. Required, %: C 76.78, H 6.14, N 8.53.

5-[4-[4-(2,2'-Bipyridin-5-yl)phenylethynyl]phenyl]-2,2'-bipyridine-6-carbonitrile (9). Yield 0.65 g, (1.27 mmol, 64%). M.p. > 250 °C. ¹H NMR (CDCl₃, δ, ppm): 7.32-7.36 and 7.39-7.42 (both m, 1H, both H-5 of terminal pyridines), 7.65-7.77 (m, 8H, C-H_{arom}), 7.83-7.93 (m, 2H), 8.02 (d, 1H, ³J 8.3 Hz, cyanopyridine), 8.07 (dd, 1H, ³J 8.3 Hz, ⁴J 2.5 Hz, H-4 (bipyridine)), 8.46-8.56 (m, 3H), 8.70-8.77 (m, 3H), 8.98 (d, 1H, ⁴J 2.5 Hz, H-6 (bipyridine)). ESI-MS, *m/z*: found 512.19 [M+H]⁺, required 512.19. Found, %: C 82.12, H 4.06, N 13.61. C₃₅H₂₁N₅. Required, %: C 82.17, H 4.14, N 13.69.

5-(4-Ethynylphenyl)-2,2'-bipyridine (6c). Trimethylsilyl derivative **6b** (1.76 g, 5.36 mmol) was suspended in a solution of sodium (10 mg) in methanol (20 ml), and the mixture was refluxed for 30 min. After completion, water (60 ml) was added and the product was extracted with CH₂Cl₂ (3 x 20 ml). The organic phase was dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure and used in the next step without additional purification. Yield 1.10 g (4.3 mmol, 80%). M.p. 133-135 °C. ¹H NMR (CDCl₃, δ, ppm): 4.32 (s, 1H, C≡C-H), 7.38 (ddd, 1H, ³J 4.8, 7.7 Hz, ⁴J 1.0 Hz, H-5'), 7.52-7.57 (m, 2H, C-H_{arom}), 7.71-7.76 (m, 2H, C-H_{arom}), 7.88 (ddd, 1H, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4'), 8.14 (dd, 1H, ³J 8.3 Hz, ⁴J 2.5 Hz, H-4), 8.44-8.49 (m, 2H, H-3,3'), 8.65 (dd, 1H, ³J 4.8 Hz, ⁴J 2.0 Hz, H-6'), 8.93 (d, 1H, ⁴J 2.5 Hz, H-6). ESI-MS, *m/z*: found 257.11 [M+H]⁺, required 257.11. Found, %: C 84.11, H 4.49, N 10.75. C₁₈H₁₂N₂. Required, %: C 84.35, H 4.72, N 10.93.

5-[4-(5-Dodecylthiophen-2-yl)phenyl]-2,2'-bipyridine (5). 5-(4-Bromophenyl)-2,2'-bipyridine **1** (0.898 g, 2.8 mmol) was dissolved in dry DMF (25 ml) in a Schlenk flask. Argon was passed through the solution for 30 min. Then Pd(PPh₃)₄ (100 mg, 8.65 μmol) and solution of 2-tributylstannyl-5-dodecylthiophene (2.2 g, 4.06 mmol) in dry THF (5 ml) were added. Argon was passed through the resulting mixture for 30 min. Then the reaction mixture was stirred at 100 °C under argon atmosphere for 2 h. After completion of the reaction, the mixture was cooled to room temperature. The resulting precipitate was filtered off, washed with acetone and recrystallized

(DMF). Yield 0.87 g (1.8 mmol, 65%). M.p. 218-220 °C. ¹H NMR (CDCl₃, δ, ppm): 0.89-0.93 (m, 3H, CH₃), 1.27-1.33 (m, 18H, CH₃(CH₂)₉), 1.70-1.75 (m, 2H, CH₂CH₂-thiophene), 2.83 (t, 2H, ³J 6.8 Hz, CH₂-thiophene), 6.77 (d, 1H, ³J 3.2 Hz, thiophene), 7.20 (d, 1H, ³J 3.2 Hz, thiophene), 7.32 (ddd, 1H, ³J 4.8, 7.7 Hz, ⁴J 1.0 Hz, H-5'), 7.62-7.65 (m, 2H, C-H_{arom}), 7.67-7.72 (m, 2H, C-H_{arom}), 7.83 (ddd, 1H, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4'), 8.04 (dd, 1H, ³J 8.3 Hz, ⁴J 2.5 Hz, H-4), 8.44-8.49 (m, 2H, H-3,3'), 8.70 (dd, 1H, ³J 4.8 Hz, ⁴J 2.0 Hz, H-6'), 8.95 (d, 1H, ⁴J 2.5 Hz, H-6). ESI-MS, *m/z*: found 483.28 [M+H]⁺, required 483.28. Found, %: C 79.54, H 7.85, N 5.64. C₃₂H₃₈N₂S. Required, %: C 79.62, H 7.93, N 5.80.

4-(4-Bromophenyl)-1-(pyridin-2-yl)-6,7-dihydro-5H-cyclopenta[c]pyridine (2). A mixture of the triazine precursor (1 g, 3.19 mmol) and 1-morpholinocyclopentene (2.56 ml, 15.97 mmol) was stirred at 200 °C under argon atmosphere for 2 h. More 1-morpholinocyclopentene (1.28 ml, 7.98 mmol) was added, and the mixture was stirred at the same conditions for more 1 h. After completion, the reaction mass was cooled to room temperature. Acetonitrile (15 ml) was added, and the mixture was stirred at room temperature for 1 h. The resulting precipitate was filtered off, washed with acetonitrile and dried. The analytical sample was obtained by recrystallization (acetonitrile). Yield 0.9 g (2.56 mmol, 80%). ¹H NMR (DMSO-d₆, δ, ppm): 2.00-2.10 (m, 2H, CH₂-6), 3.00 (t, 2H, ³J 7.5 Hz, CH₂-7), 3.48 (t, 2H, ³J 7.5 Hz, CH₂-5), 7.33 (ddd, 1H, ³J 4.8, 7.7 Hz, ⁴J 1.0 Hz, H-5 (Py)), 7.45-7.49 (m, 2H, C-H_{arom}), 7.60-7.66 (m, 2H, C-H_{arom}), 7.86 (ddd, 1H, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4 (Py)), 8.30 (dd, 1H, ³J 7.7 Hz, ⁴J 1.0 Hz, H-3 (Py)), 8.43 (s, 1H, H-3), 8.64 (dd, 1H, ³J 4.8 Hz, ⁴J 2.0 Hz, H-6 (Py)). ¹³C NMR (DMSO-d₆, δ, ppm): 24.6, 31.8, 33.2, 121.3, 122.5, 123.0, 130.5, 131.6, 132.1, 136.5, 136.5, 138.8, 146.0, 148.5, 150.4, 152.8, 157.6. ESI-MS, *m/z*: found 351.05 [M+H]⁺, required 351.05. Found, %: C 64.86, H 4.21, N 7.86. C₃₂H₃₈N₂S. Required, %: C 64.97, H 4.30, N 7.98.

References

- S1. V. N. Kozhevnikov, O. V. Shabunina, D. S. Kopchuk, M. M. Ustinova, B. König and D. N. Kozhevnikov, *Tetrahedron*, 2008, **64**, 8963.
- S2. L. Bian, J. Hai, E. Zhu, J. Yu, Y. Liu, J. Zhou, G. Ge and W. Tang, *J. Mater. Chem. A*, 2015, **3**, 1920.

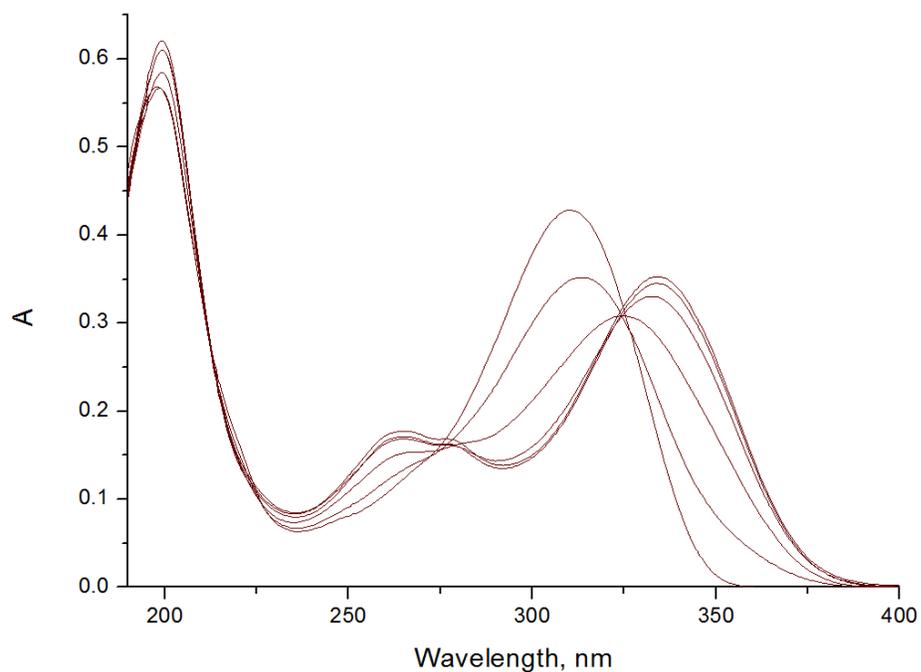


Figure S1 Changing of the absorption spectra of compound **4** (10^{-5} M, MeCN) upon titrating of Zn(ClO₄)₂ solution (0-1 eq., step 0.2 eq.).

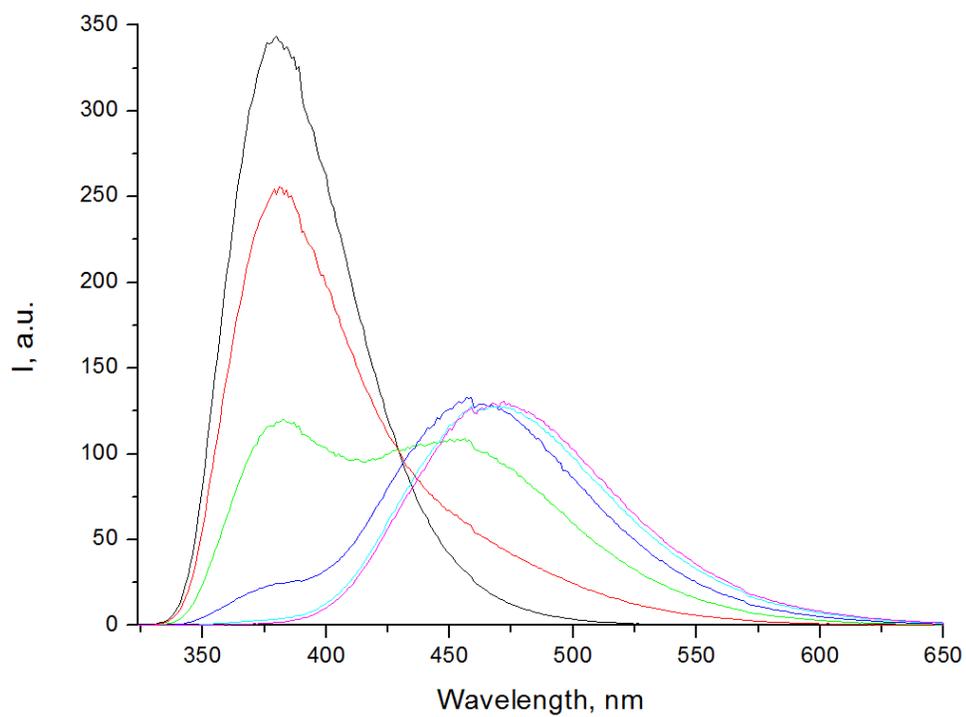


Figure S2 Changing of the luminescence spectra of compound **4** (10^{-5} M, MeCN) upon titrating of Zn(ClO₄)₂ solution (0-1 eq., step 0.2 eq.), excitation at 325 nm.

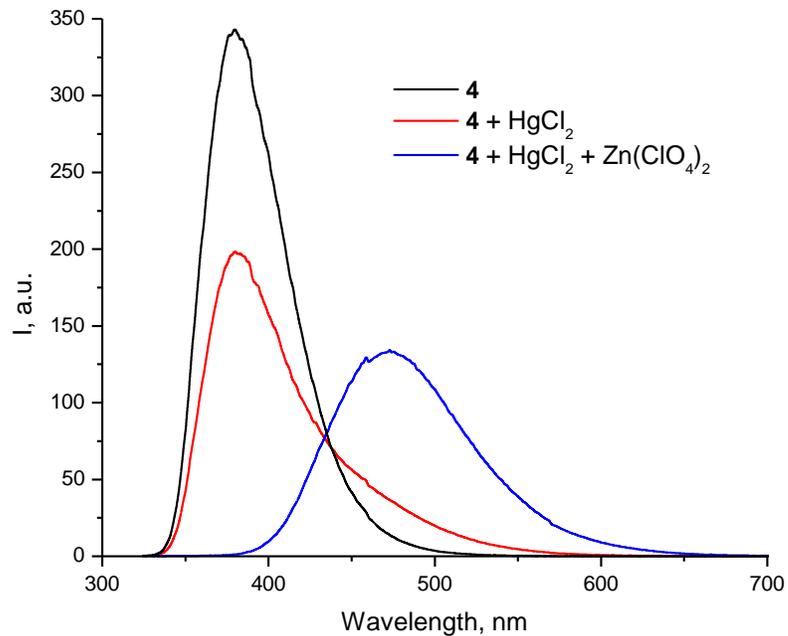


Figure S3 Luminescence of **4** before and after addition of excess of HgCl₂ and after subsequent addition of excess of Zn(ClO₄)₂.

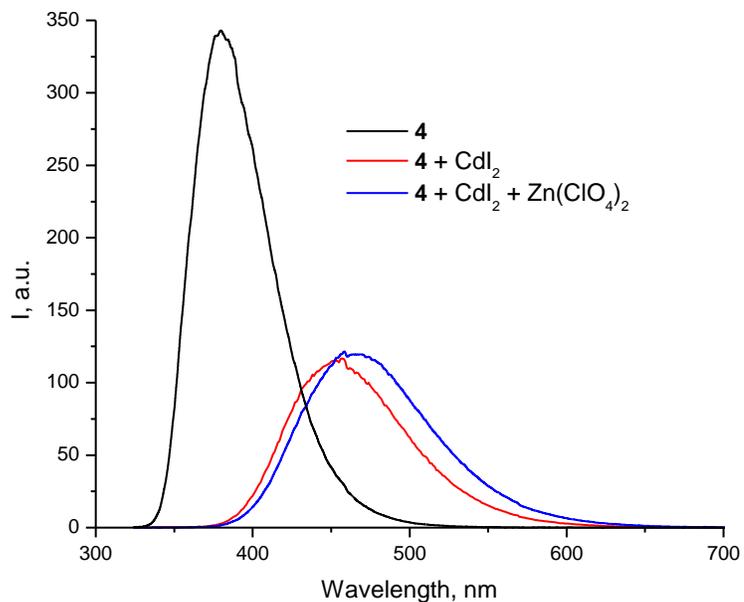


Figure S4 Luminescence of **4** before and after addition of excess of CdI₂ and after subsequent addition of excess of Zn(ClO₄)₂.

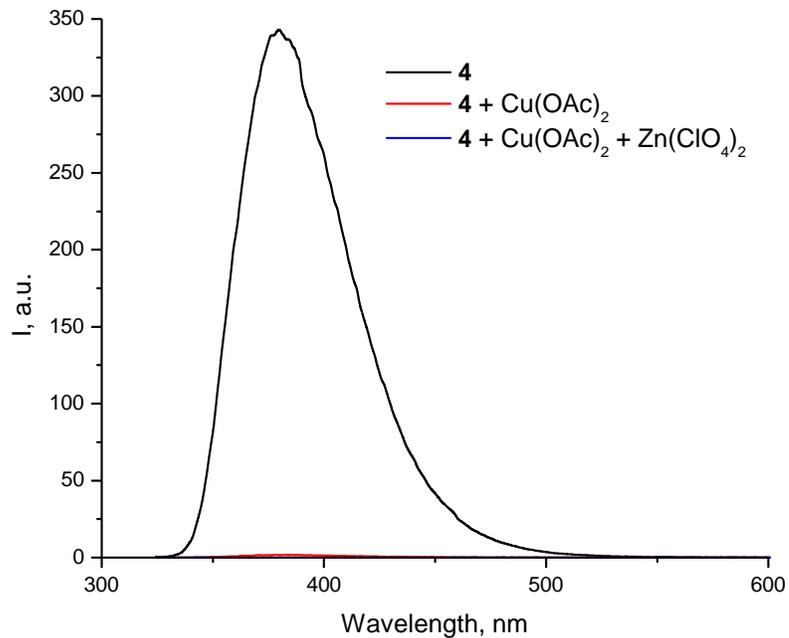


Figure S5 Luminescence of **4** before and after addition of excess of $\text{Cu}(\text{OAc})_2$ and after subsequent addition of excess of $\text{Zn}(\text{ClO}_4)_2$.

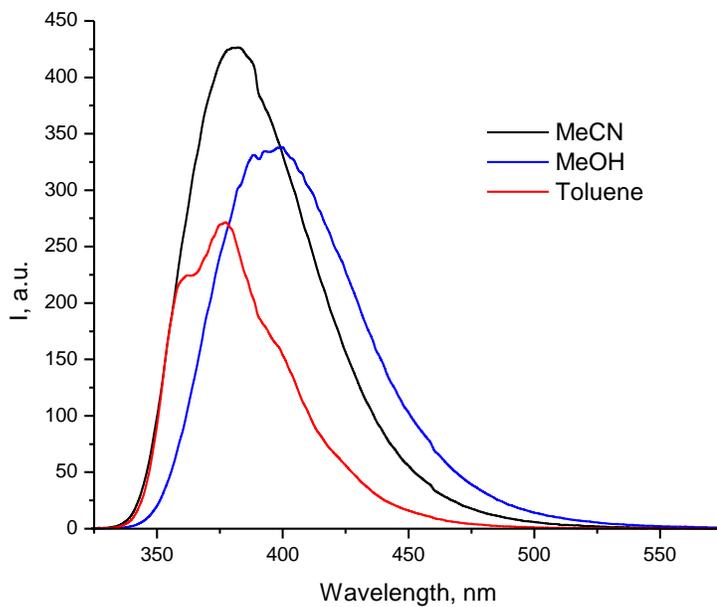
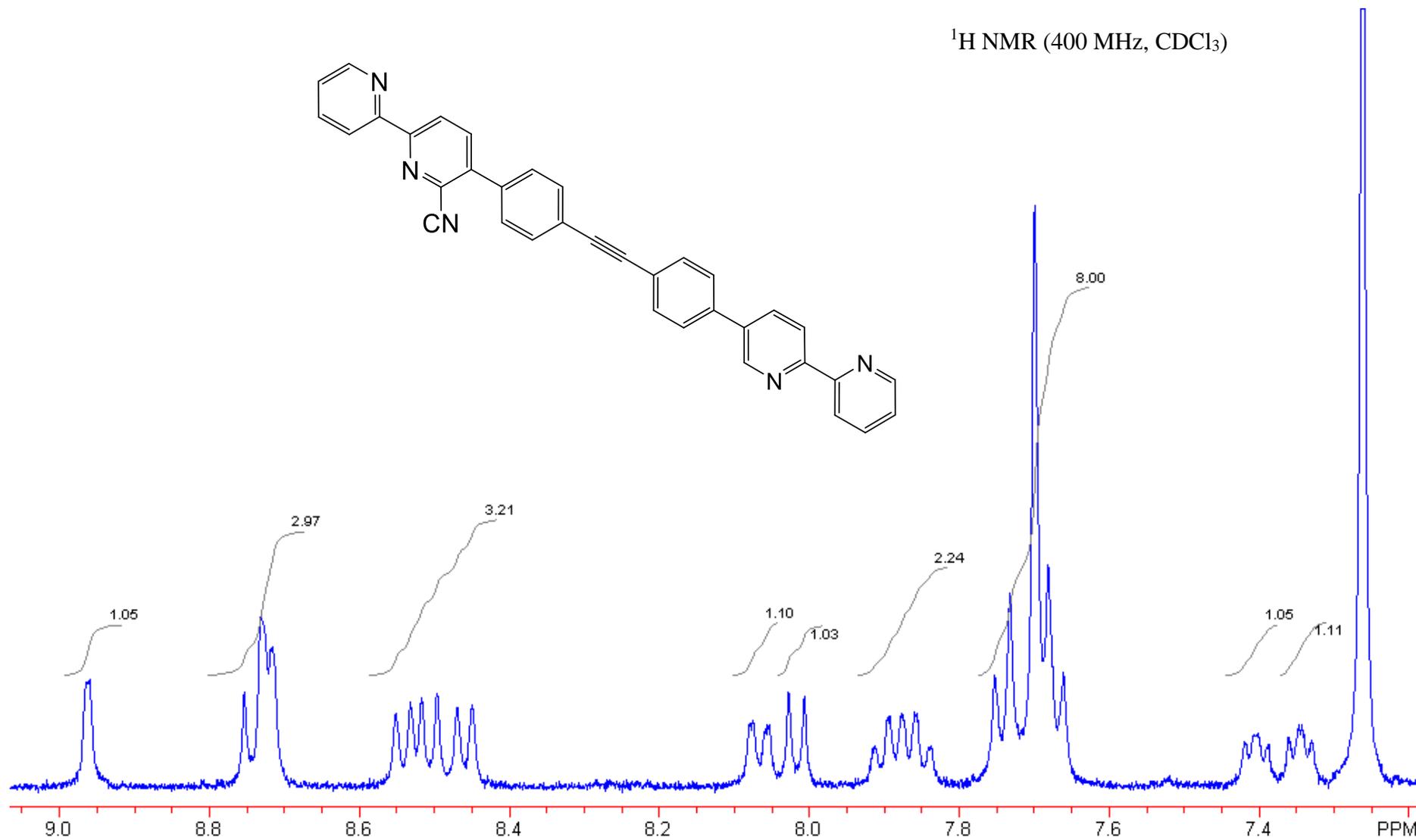
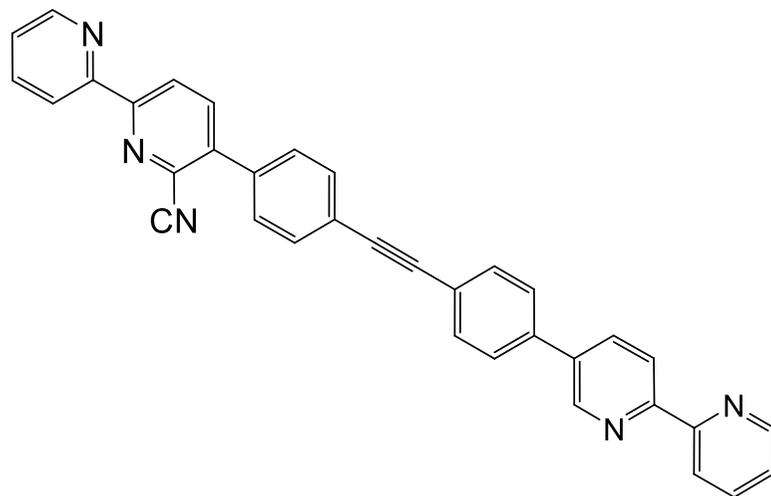
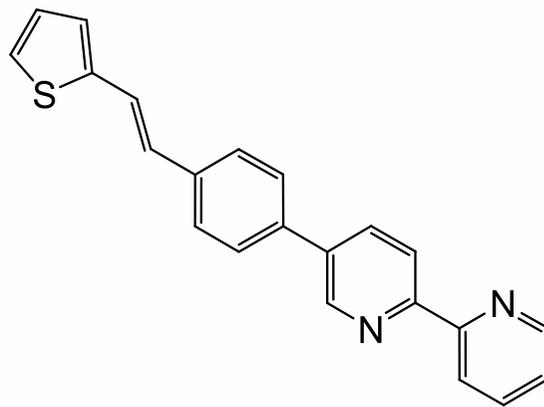


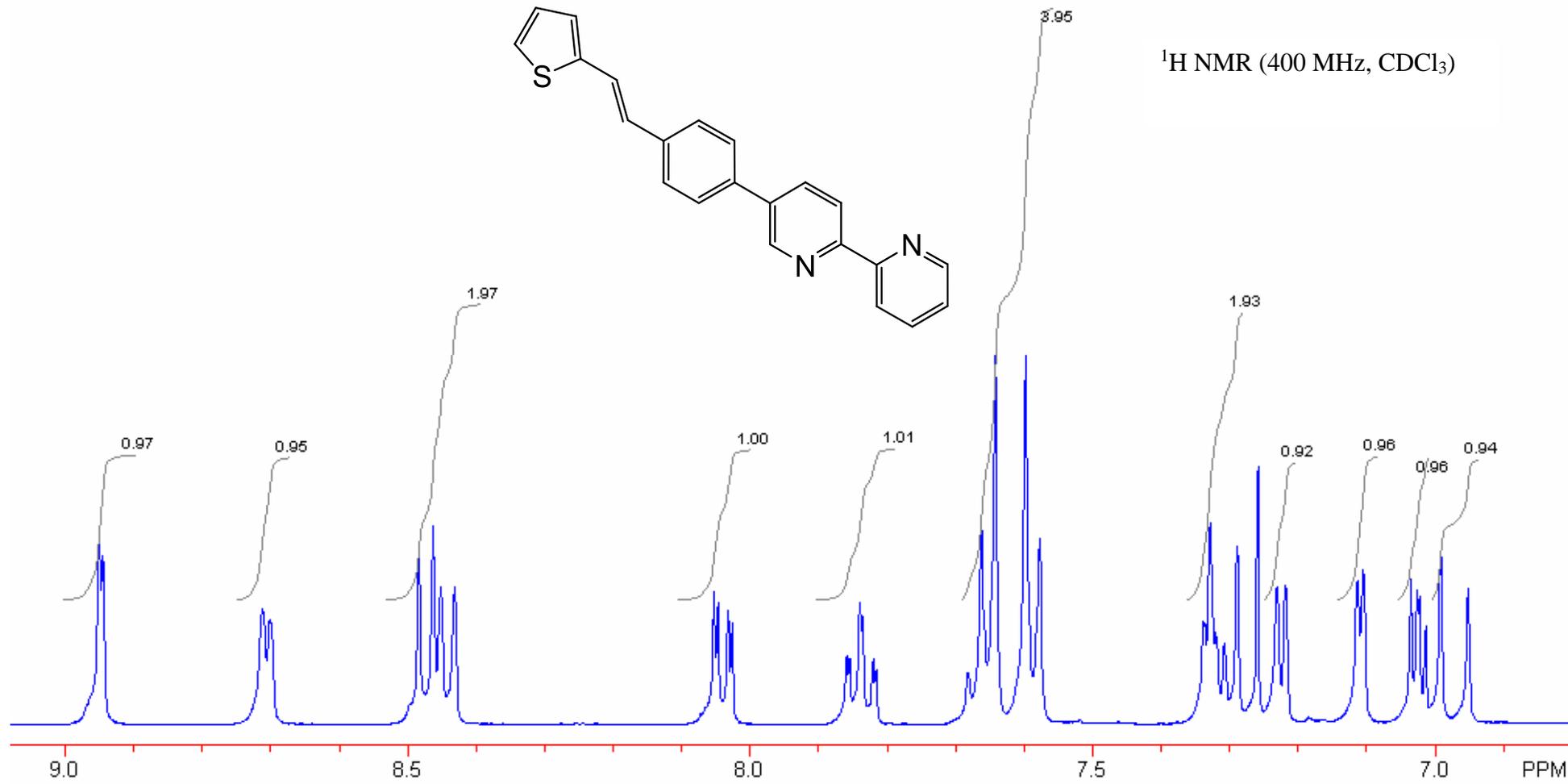
Figure S6 Luminescence spectra of **4** at room temperature in different solvents.

¹H NMR (400 MHz, CDCl₃)

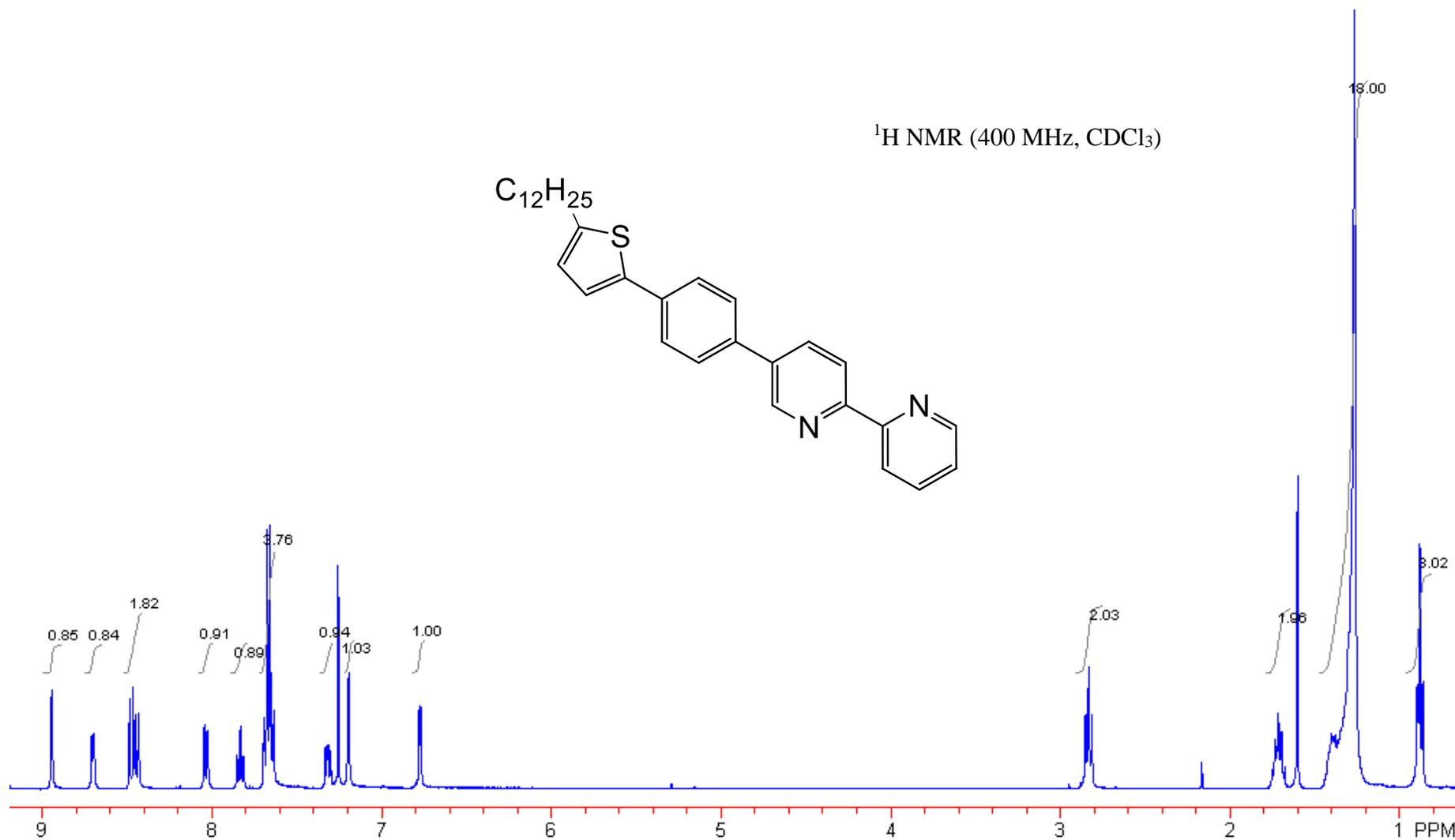
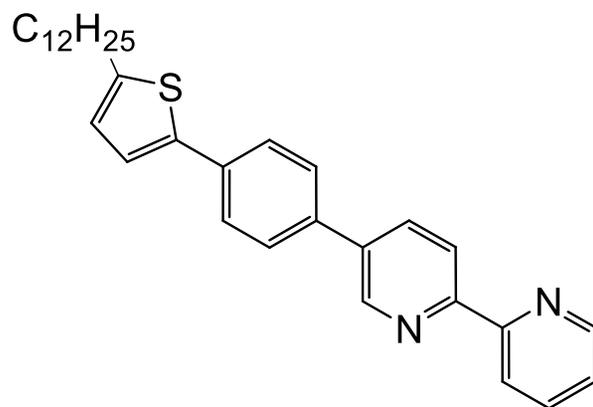


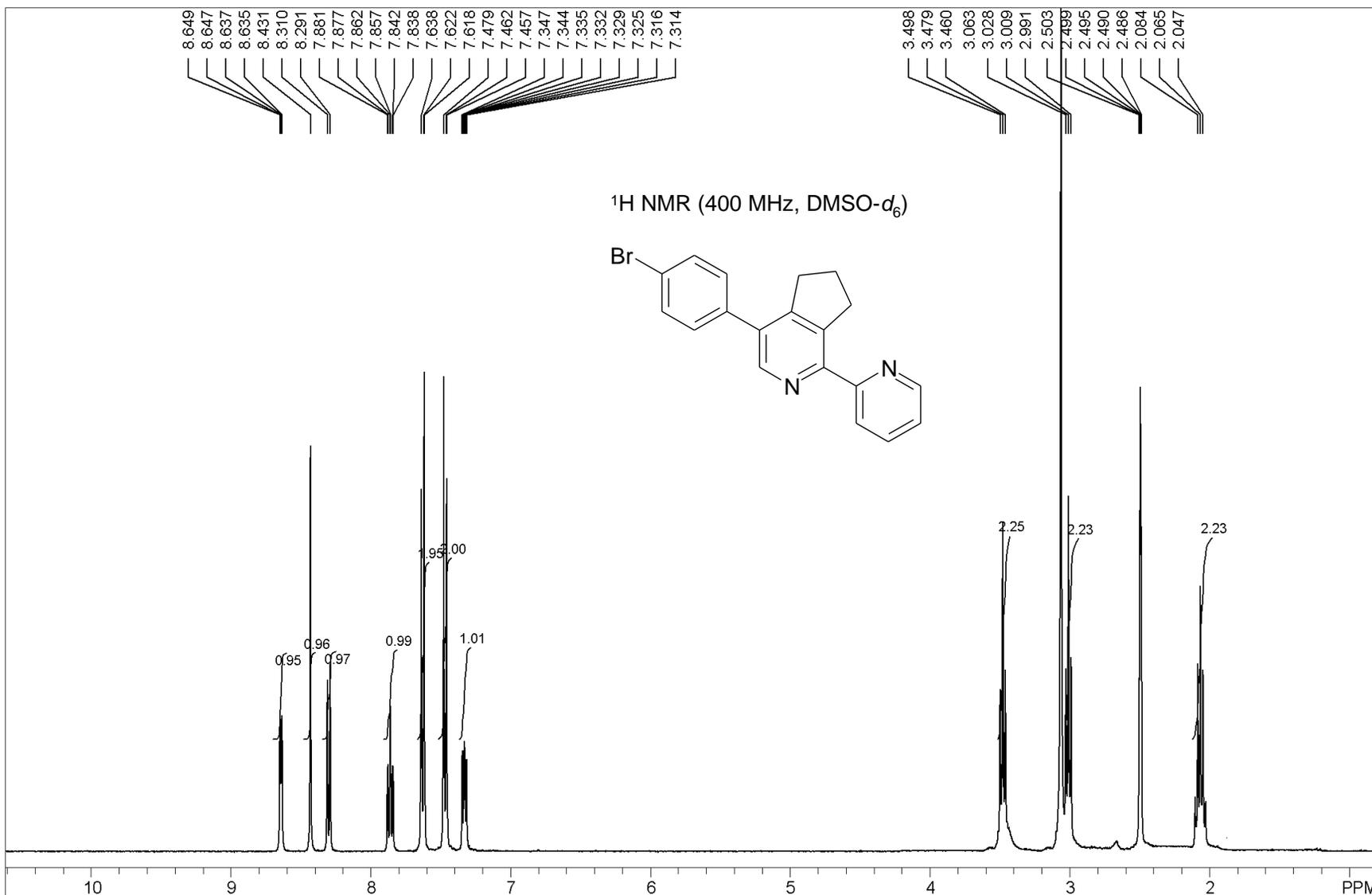


$^1\text{H NMR}$ (400 MHz, CDCl_3)



^1H NMR (400 MHz, CDCl_3)

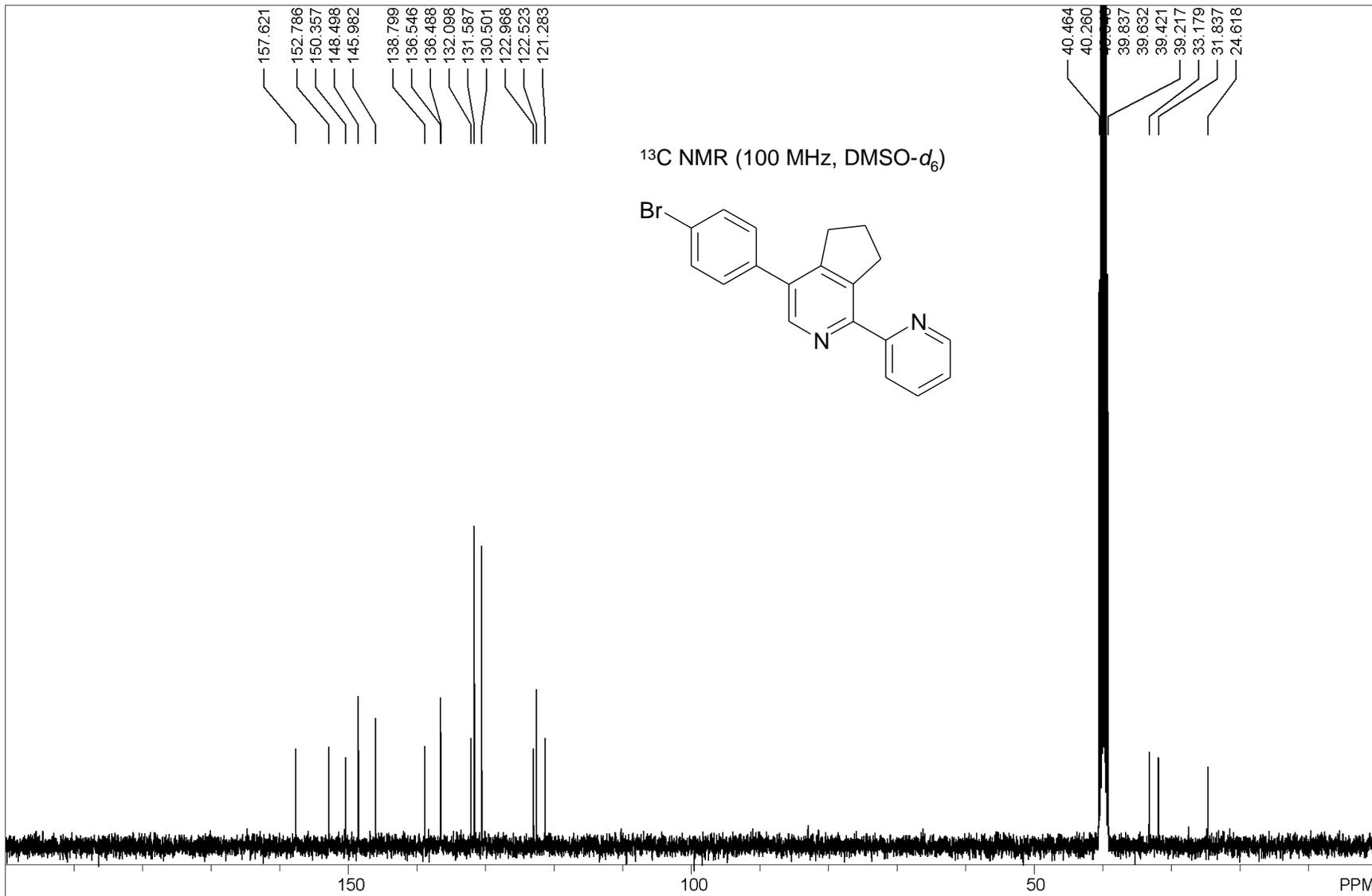




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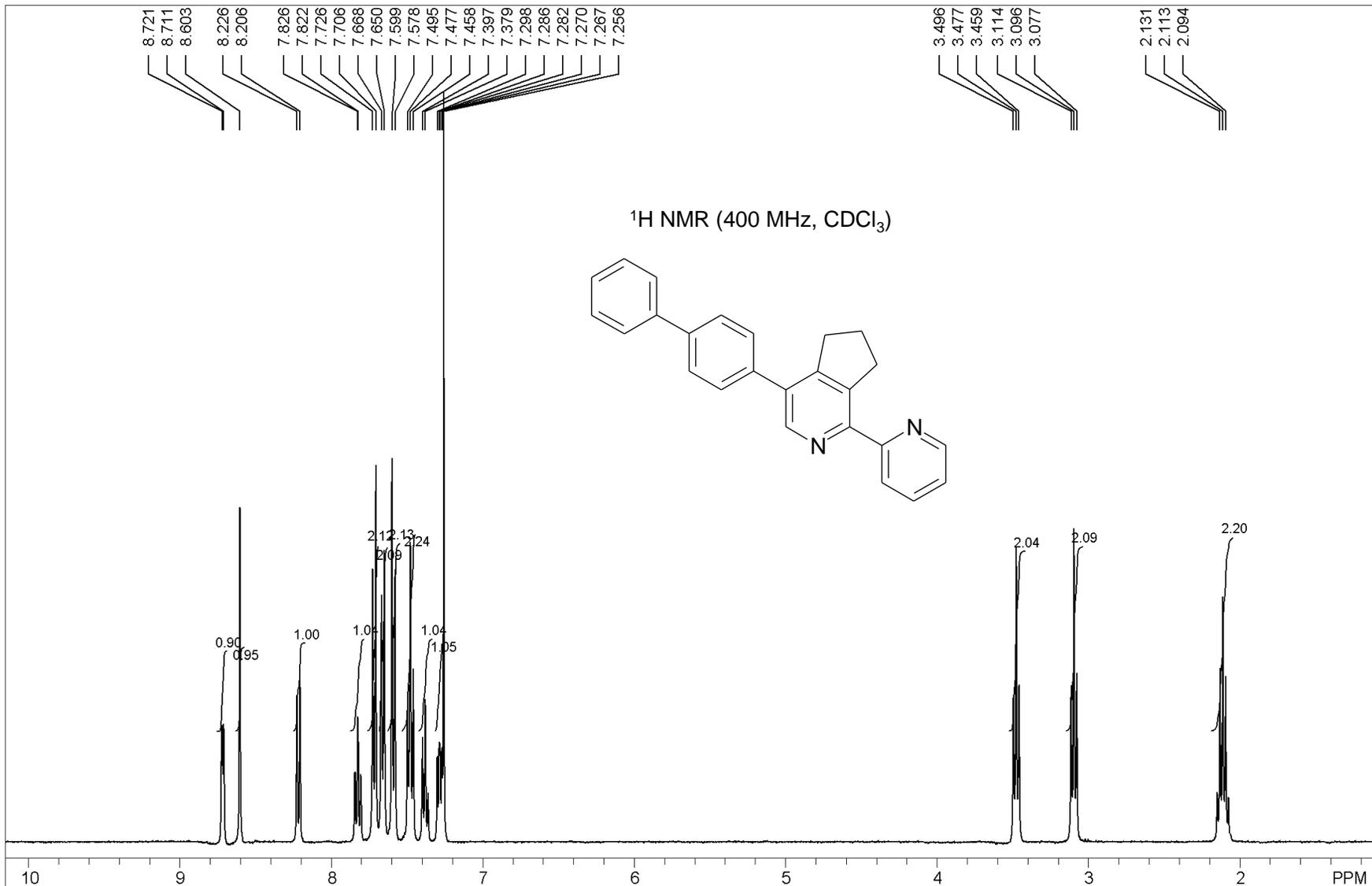
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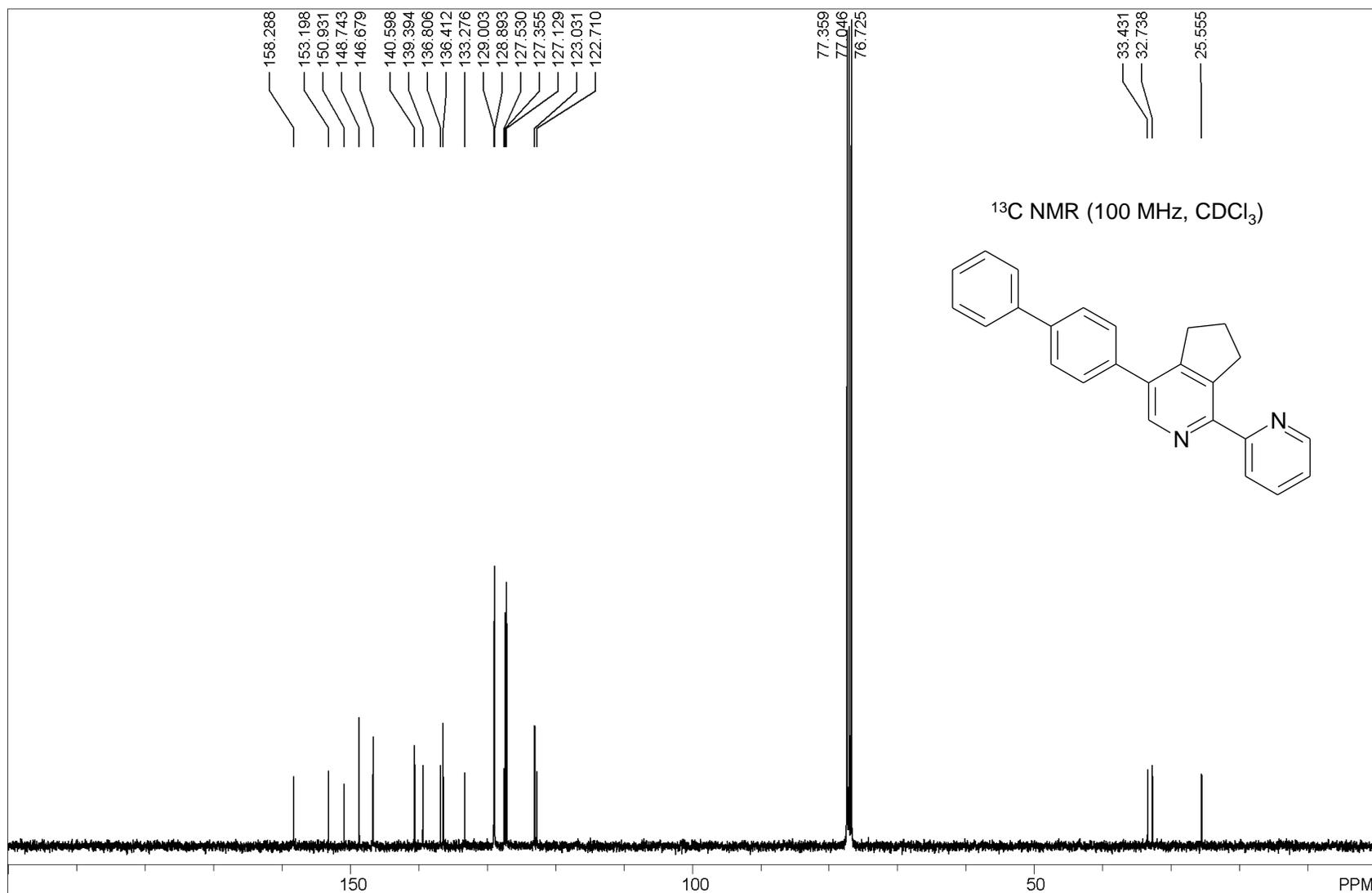
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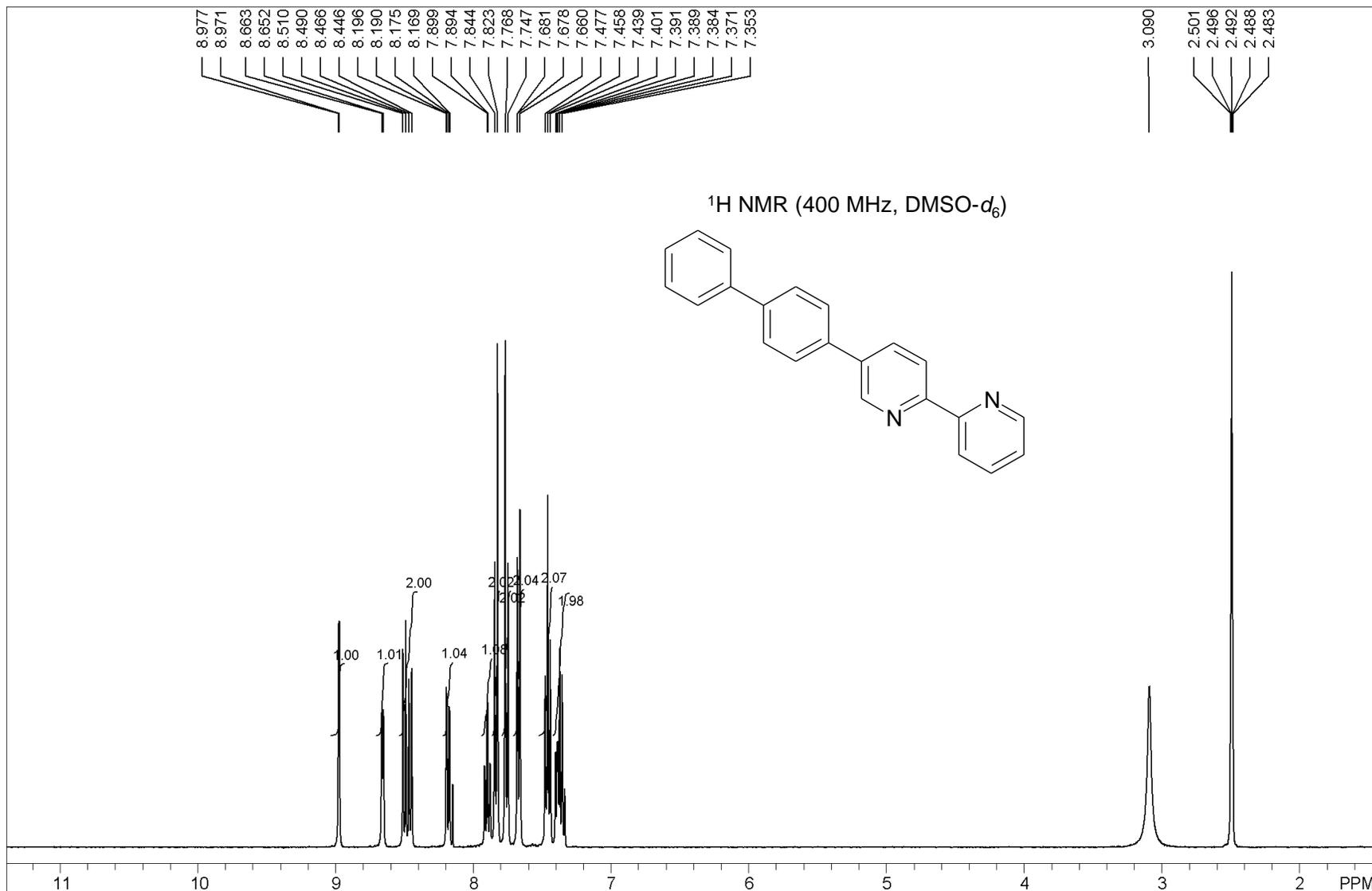
Kopchuk AK 241				USER: nmr -- DATE: 13:43:44.519+0600 nmr@EP-ZH070706			
F1: 400.130	F2: 1.000	SW1: 8224		OF1: 2459.7		PTS1d: 32768	
EX: zg30		PW: 11.6 us	PD: 1.0 sec	NA: 10	LB: 0.3		Nuts - \$236_1.1



Krinochkin AK 241,

USER: nmr -- DATE: 18:23:23.317 +0600 nmr@EP-ZH070706

F1: 100.613	F2: 1.000	SW1: 24038	OF1: 10060.8	PTS1d: 32768
EX: zgig30	PW: 7.4 us	PD: 2.0 sec	NA: 1919	LB: 1.0
				Nuts - \$488_13.1

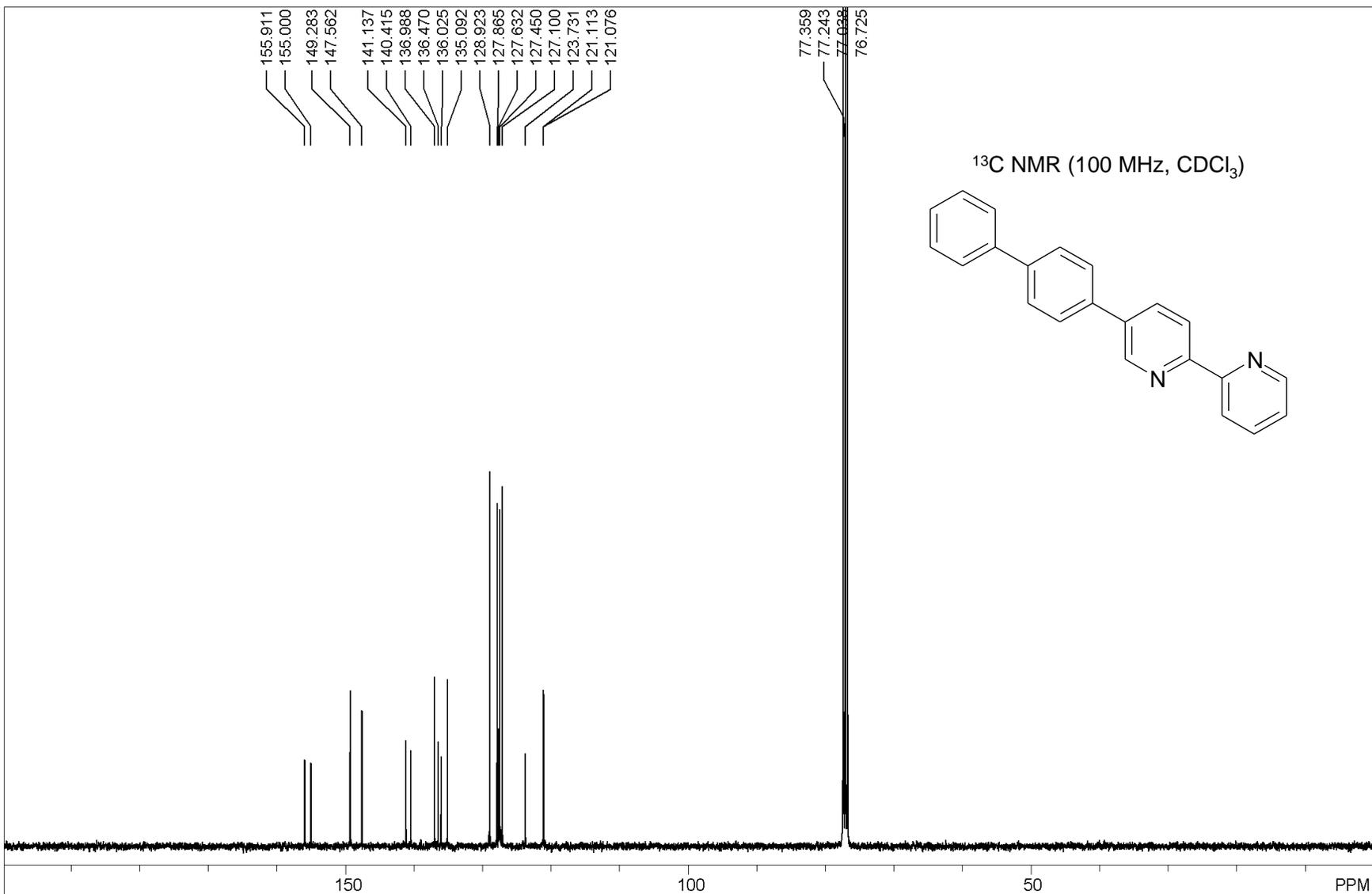


Kopchuk AK 179

USER: nmr -- DATE: 14:56:36.110 +0500 nmr@EP-ZH070706

F1: 400.130	F2: 1.000	SW1: 8224	OF1: 2463.9	PTS1d: 32768
EX: zg30	PW: 11.6 us	PD: 1.0 sec	NA: 7	LB: 0.3

Nuts - \$3974_1.1



Krinochkin AK 177.				USER: nmr -- DATE: 00:27:27.951 +0600 nmr@EP-ZH070706			
F1: 100.613	F2: 1.000	SW1: 24038		OF1: 10060.8		PTS1d: 32768	
EX: zgig30		PW: 7.4 us	PD: 2.0 sec	NA: 5120	LB: 1.0		Nuts - \$490_13.1