

Reaction of lithium 2-arylethylnides with 6-aryl-3-(2-pyridyl)-1,2,4-triazines as an access to 6-aryl-5-arylvinyl-3-(2-pyridyl)-1,2,4-triazines

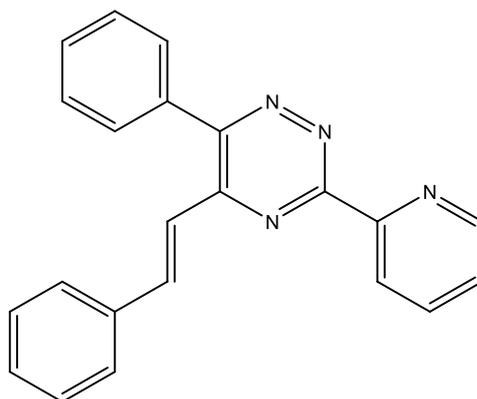
Albert F. Khasanov, Dmitry S. Kopchuk, Igor S. Kovalev, Olga S. Taniya, Grigory V. Zyryanov, Vladimir L. Rusinov and Oleg N. Chupakhin

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.

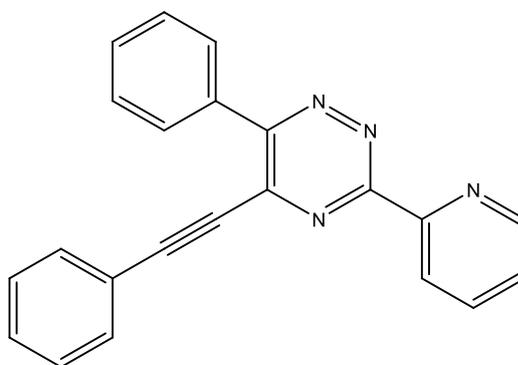
6-Aryl-3-(2-pyridyl)-1,2,4-triazines **1** were synthesized according to the literature method¹.

General method for the preparation of compounds 2 and 4

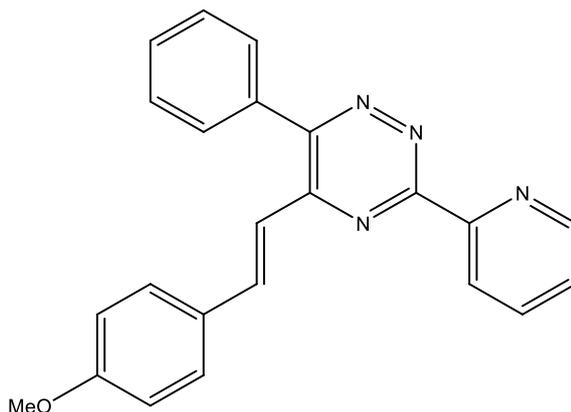
The corresponding arylacetylene (2 mmol) was dissolved in dry THF (4 ml) in a Schlenk flask under argon atmosphere and cooled to -78 °C. *n*-BuLi solution in hexane (2.5 M, 0.8 ml) was added and the resulting mixture was stirred at -78 °C for 5 min. Solution of corresponding 1,2,4-triazine **1** (1.6 mmol) in dry toluene (35 ml) was added and the resulting mixture was stirred overnight at room temperature. Methanol (10 ml), then water (10 ml) were added. The products were extracted with CH_2Cl_2 (3 x 25 ml). The extract was dried with anhydrous sodium sulfate. Solvents were removed under reduced pressure. Products were isolated from the residue by column chromatography (silica gel, eluent: ethyl acetate– CH_2Cl_2 (4:1), $R_f = 0.4$). In case of synthesis of compound **2a**, the residue was dissolved in CH_2Cl_2 (20 ml), then DDQ (45 mg, 0.2 mmol) was added and the resulting mixture was stirred at room temperature for 30 min. Then the reaction mass was purified by column chromatography (neutral Al_2O_3 , eluent: ethyl acetate). The products **2a** and **4** were separated by column chromatography (silica gel, eluent: ethyl acetate– CH_2Cl_2 (4:1)).



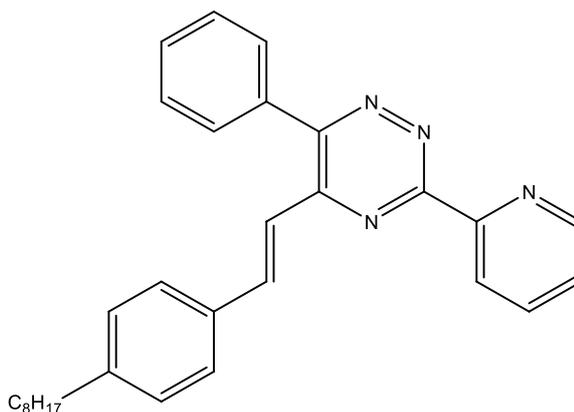
(E)-6-Phenyl-3-(2-pyridyl)-5-styryl-1,2,4-triazine (2a). Yield 480 mg (1.44 mmol, 90%). $R_f = 0.1$. Mp 154–156 °C. $^1\text{H NMR}$ (CDCl_3 , δ , ppm): 7.26 (1H, d, 3J 16.0 Hz, PhCHCH), 7.37-7.41 (3H, m, Ph), 7.53-7.55 (1H, m, H-5 (Py)), 7.58-7.62 (5H, m, PhCHCH), 7.82-7.84 (2H, m, Ph), 8.00 (1H, ddd, 3J 7.7, 7.7 Hz, 4J 2.0 Hz, H-4 (Py)), 8.54 (1H, d, 3J 16.0 Hz, PhCHCH), 8.77 (1H, dd, 3J 7.7 Hz, 4J 1.0 Hz, H-3 (Py)), 8.99 (1H, dd, $^3J = 4.8$ Hz, $^4J = 2.0$ Hz, H-6 (Py)). $^{13}\text{C NMR}$ (CDCl_3 , δ , ppm): 121.5, 124.3, 125.4, 128.3, 128.9, 128.9, 129.7, 130.0, 130.1, 134.6, 135.5, 137.2, 142.1, 150.4, 152.1, 153.2, 156.6, 160.7. **ESI-MS**, m/z : found 337.14, calc. 337.15 ($\text{M}+\text{H}$) $^+$. Found, %: C 78.43, H 4.65, N 16.42. $\text{C}_{22}\text{H}_{16}\text{N}_4$. Calc., %: C 78.55, H 4.79, N 16.65.



6-Phenyl-5-phenylethynyl-3-(2-pyridyl)-1,2,4-triazine (4). Yield 16 mg (0.05 mmol, 3%). $R_f = 0.6$. Mp 142–144 °C. $^1\text{H NMR}$ (CDCl_3 , δ , ppm): 7.37-7.41 (2H, m, PhC \equiv C), 7.43-7.55 (4H, m, PhC \equiv C, H-5 (Py)), 7.59-7.63 (3H, m, Ph), 7.94-7.99 (1H, ddd, 3J 8.0, 8.0 Hz, 4J 2.0 Hz, H-4 (Py)), 8.19-8.22 (2H, m, Ph), 8.75 (1H, dd, 3J 8.0 Hz, 4J 1.0 Hz, H-3 (Py)), 8.96 (1H, dd, $^3J = 4.8$ Hz, $^4J = 2.0$ Hz, H-6 (Py)). $^{13}\text{C NMR}$ (CDCl_3 , δ , ppm): 86.5 (C-sp), 100.8 (C-sp), 120.8, 124.2, 125.7, 128.5, 128.7, 129.5, 130.7, 132.6, 133.9, 137.2, 142.6, 150.6, 152.4, 157.7, 160.7. **ESI-MS**, m/z : found 335.13, calc. 335.13 ($\text{M}+\text{H}$) $^+$. Found, %: C 78.82, H 4.01, N 16.55. $\text{C}_{22}\text{H}_{14}\text{N}_4$. Calc., %: C 79.02, H 4.22, N 16.76.

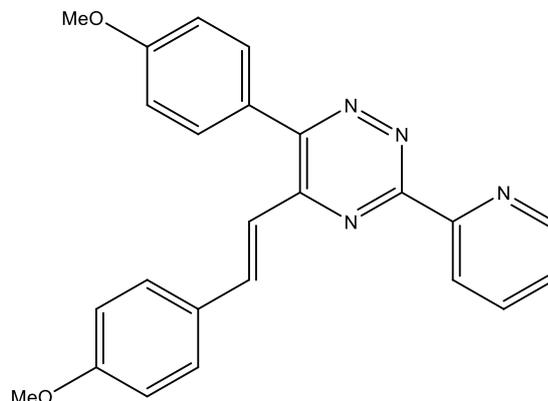


(E)-5-(4-Methoxystyryl)-6-phenyl-3-(2-pyridyl)-1,2,4-triazine (2b). Yield 560 mg (1.53 mmol, 96%). Mp 118–120 °C. $^1\text{H NMR}$ (CDCl_3 , δ , ppm): 3.84 (3H, s, MeO), 6.91 (2H, m, 4-MeOPh), 7.12 (1H, d, 3J 15.5 Hz, 4-MeOPhCH), 7.46–7.56 (3H, m, 4-MeOPh, H-5 (Py)), 7.59 (3H, m, Ph), 7.82 (2H, m, Ph), 7.95 (1H, ddd, 3J 7.7, 7.7 Hz, 4J 2.0 Hz, H-4 (Py)), 8.44 (1H, d, 3J 15.5 Hz, 4-MeOPhCHCH), 8.73 (1H, dd, 3J 7.7 Hz, 4J 1.0 Hz, H-3 (Py)), 8.94 (1H, dd, 3J = 4.8 Hz, 4J = 2.0 Hz, H-6 (Py)). $^{13}\text{C NMR}$ ($\text{DMSO}-d_6$, δ , ppm): 55.4, 99.5, 114.7, 118.5, 124.6, 127.8, 128.5, 129.5, 130.0, 130.1, 130.2, 134.3, 142.0, 148.2, 150.7, 152.0, 156.5, 158.7, 161.3. **ESI-MS**, m/z : found 367.16, calc. 367.16 ($\text{M}+\text{H}$) $^+$. Found, %: C 75.27, H 4.77, N 15.11. **C₂₃H₁₈N₄O**. Calc., %: C 75.39, H 4.95, N 15.29.

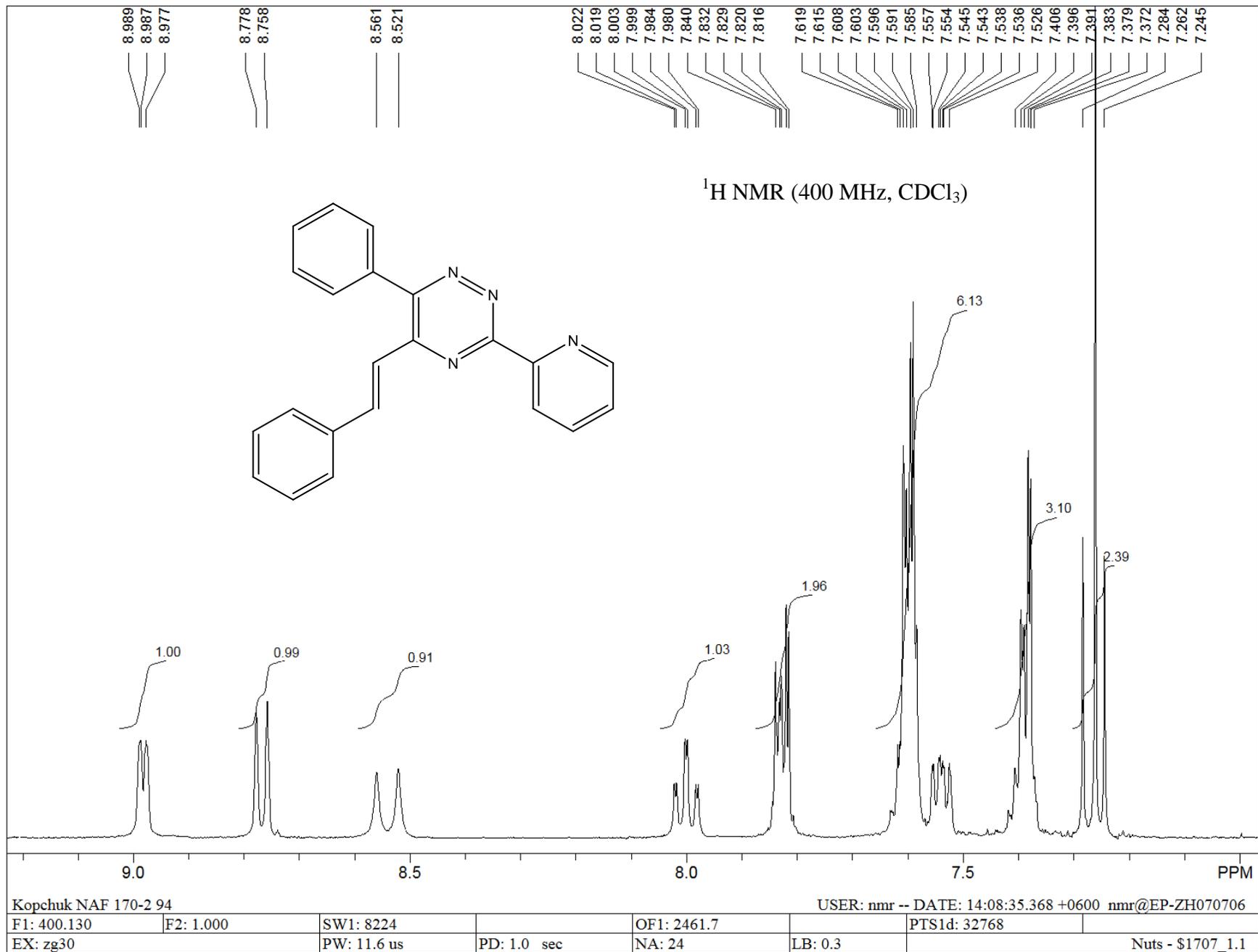


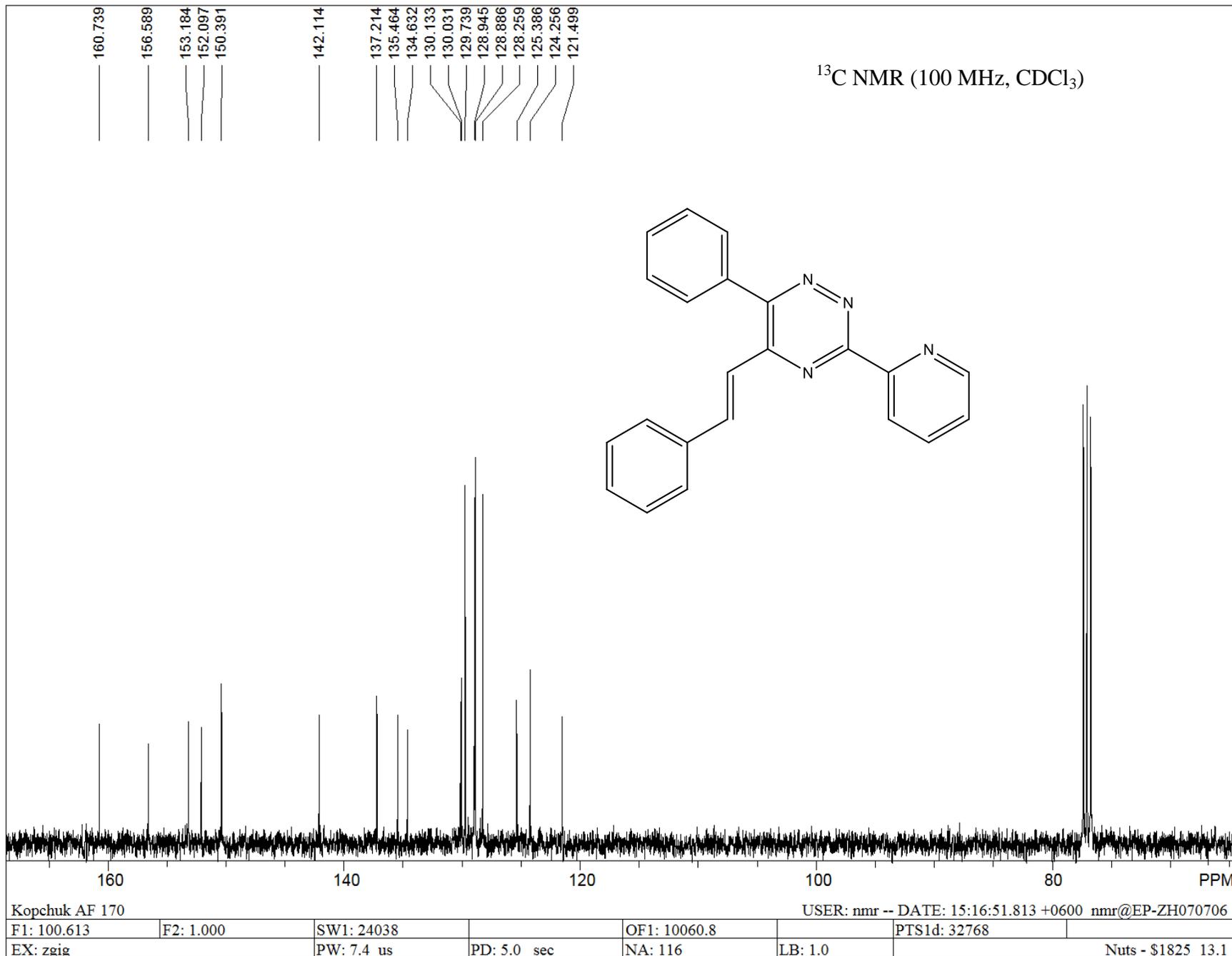
(E)-5-(4-Octylstyryl)-6-phenyl-3-(2-pyridyl)-1,2,4-triazine (2c). Yield 285 mg (0.64 mmol, 40%). Mp 70–72 °C. $^1\text{H NMR}$ (CDCl_3 , δ , ppm): 0.88 (3H, t, 3J 7.2 Hz, CH_3), 1.16–1.38 (12H, m, $\text{ArCH}_2(\text{CH}_2)_6$), 2.62 (2H, t, 3J 7.2 Hz, ArCH_2), 7.17–7.24 (3H, m, 4-OctPhCHCH, 4-OctPh), 7.50 (3H, m, 4-OctPh, H-5 (Py)), 7.56–7.62 (3H, m, Ph), 7.82 (1H, m, Ph), 7.97 (1H, ddd, 3J 7.7, 7.7 Hz, 4J 2.0 Hz, H-4 (Py)), 8.47 (1H, d, 3J 16.0 Hz, PhCHCH), 8.74 (1H, dd, 3J 7.7 Hz, 4J 1.0 Hz, H-3 (Py)), 8.96 (1H, dd, 3J = 4.8 Hz, 4J = 2.0 Hz, H-6 (Py)). **ESI-MS**, m/z : found

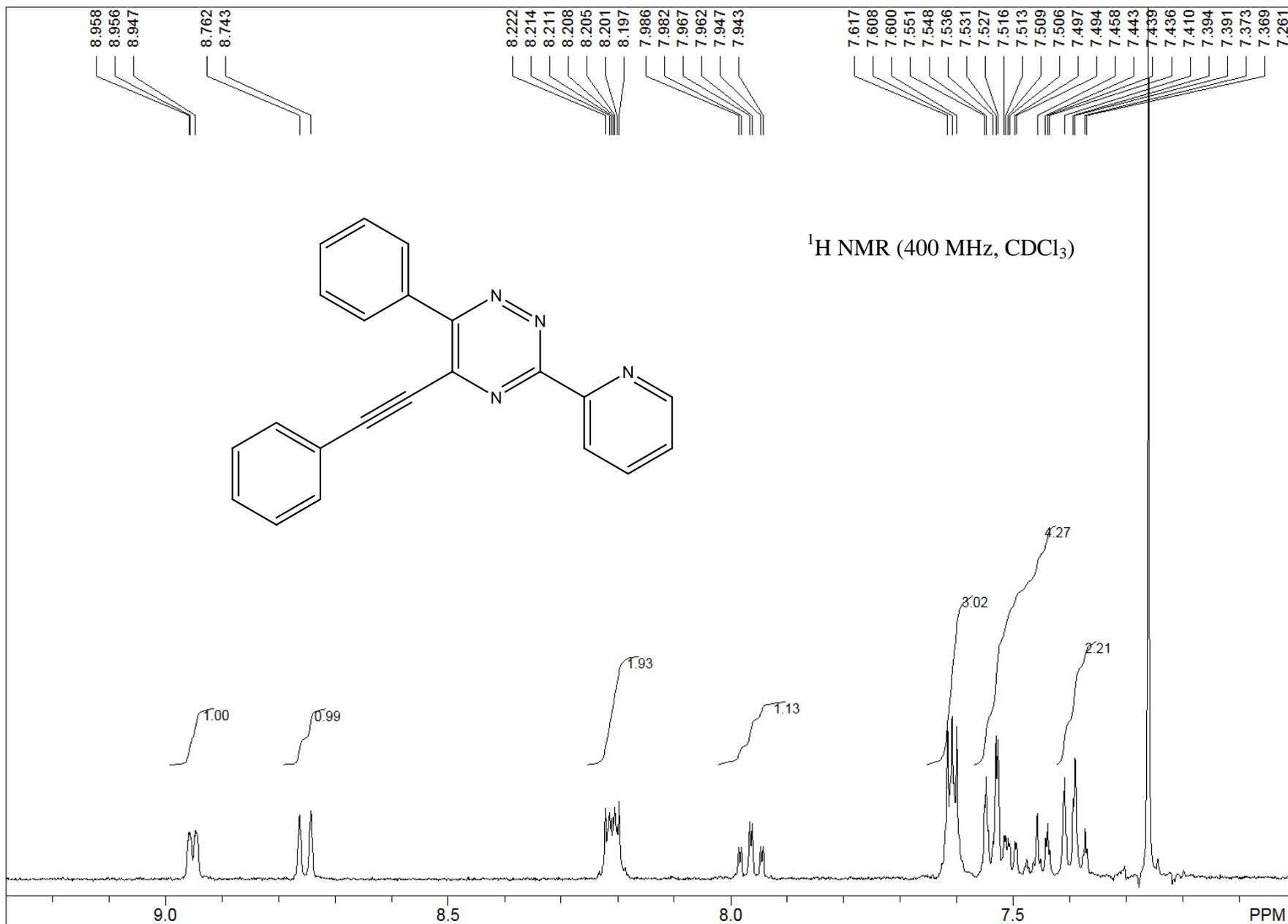
449.27, calc. 449.27 (M+H)⁺. Found, %: C 80.07, H 6.98, N 12.24. **C₃₀H₃₂N₄**. Calc., %: C 80.32, H 7.19, N 12.49.



(E)-6-(4-Methoxyphenyl)-5-(4-methoxystyryl)-3-(2-pyridyl)-1,2,4-triazine (2d). Yield 545 mg (1.38 mmol, 86%). Mp 109-111 °C. ¹H NMR (CDCl₃, δ, ppm): 3.84 (3H, s, MeO), 3.92 (3H, s, MeO), 6.91 (2H, m, 4-MeOPh), 7.10 (2H, m, 4-MeOPh), 7.14 (1H, d, ³J 15.5 Hz, 4-MeOPhCHCH), 7.48 (1H, m, H-5 (Py)), 7.54 (2H, m, 4-MeOPh), 7.79 (2H, m, 4-MeOPh), 7.94 (1H, ddd, ³J 7.7, 7.7 Hz, ⁴J 2.0 Hz, H-4 (Py)), 8.14 (1H, d, ³J 15.5 Hz, 4-MeOPhCHCH), 8.71 (1H, dd, ³J 7.7 Hz, ⁴J 1.0 Hz, H-3 (Py)), 8.94 (1H, dd, ³J = 4.8 Hz, ⁴J = 2.0 Hz, H-6 (Py)). **ESI-MS**, *m/z*: found 397.17, calc. 397.17 (M+H)⁺. Found, %: C 72.53, H 4.88, N 13.97. **C₂₄H₂₀N₄O₂**. Calc., %: C 72.71, H 5.08, N 14.13.







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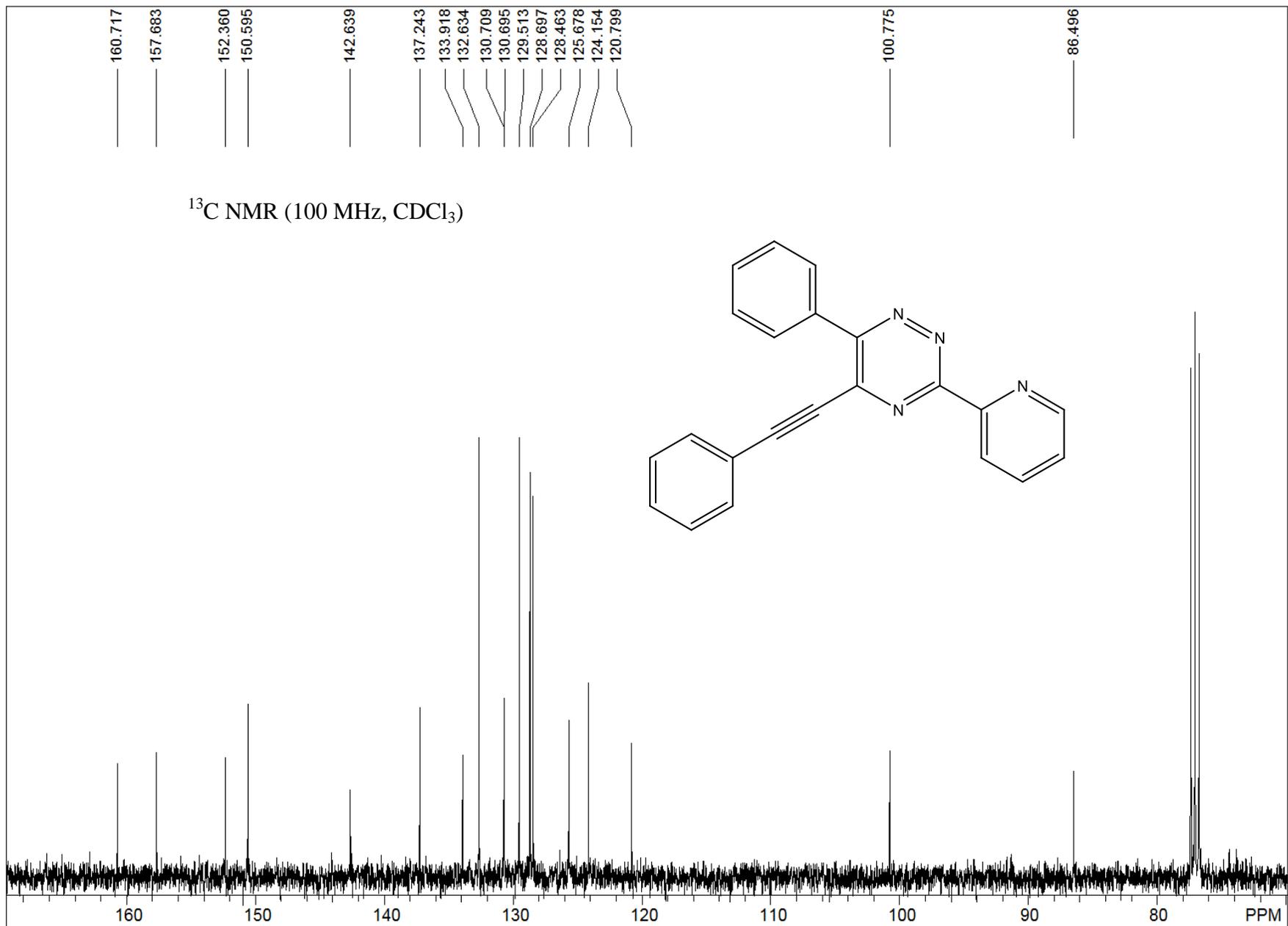
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References

1 V. N. Kozhevnikov, O. V. Shabunina, D. S. Kopchuk, M. M. Ustinova, B. König and D. N. Kozhevnikov, *Tetrahedron*, 2008, **64**, 8963.