Electronic supplementary materials *Mendeleev Commun.*, 2016, **26**, 172−173

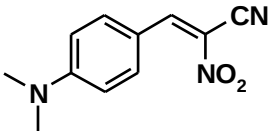
New stable form of nitroacetonitrile

Egor K. Voinkov, Evgeny N. Ulomskiy, Vladimir L. Rusinov, Oleg N. Chupakhin, Konstantin V. Savateev, Victor V. Fedotov, Evgeny B. Gorbunov, Maksim L. Isenov and Oleg S. Eltsov

General. Unless otherwise indicated, all common reagents and solvents were used from commercial suppliers without further purification. Melting points were determined on a Staffordshire ST15 OSA apparatus. ^{1}H, ^{13}C NMR spectra were acquired on a Bruker Avance-400 spectrometer, using DMSO-d_6 with TMS as internal reference. ^{13}C NMR spectra were recorded both decoupling (BB) and without decoupling of protons (GATE). The chemical shifts in ^{15}N NMR spectrum were determined on the basis of data of ^{1}H–^{15}N experiment. Elemental analysis was performed on a Perkin Elmer 2400 CHN instrument. IR spectra were recorded on the IR spectrometer «Bruker Alpha, ZnSe (FTIR)." Monitoring of the reaction course was carried out by TLC on Silufol UV-254 plates using EtOAc as eluent.

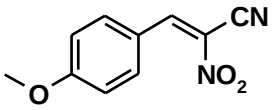
Starting compound **3** was synthesized as described in literature[1]. Compound **1** was synthesized similar to source[2].

3-(4-*N*,*N*-Dimethylphenyl)-2-nitroacrylonitrile (5b). To a suspension of 0.228 g (0.002 mol) trifluoracetic acid, 5 ml ethanol and 0.248 g (0.002 mol) nitroacetonitrile potassium salt (**2**) is added a solution of 0.298 g (0.002 mol) 4-dimethylaminobenzaldehyde (**4b**) in 5 ml ethanol. The reaction mixture is stirred for 3 hours at room temperature, the precipitate is filtered, washed with an aqueous alcohol solution and dried. Yield 0.24 g (69%), purple powder, mp 183 °C (183°C, lit.[4]). ^{1}H NMR, δ, p.m.: 3.20 (6H, s, 2CH_3), 6.88 (2H, d, *J*=9.10, 2CH), 7.97 (2H, d, *J*=9.10, 2CH), 8.59 (1H, s, CH). Found (%): C, 60.77, H, 5.08, N, 19.27. Calc. for $C_{11}H_{11}N_3O_2$ (%): C, 60.82, H, 5.10, N, 19.34. IR, ν, cm^{-1}: 817, 876, 938, 1061, 1169, 1185, 1251, 1278, 1389, 1438, 1462, 1487, 1525, 1542, 1567, 1618, 2213, 2911.

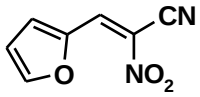


3-(4-Methoxyphenyl)-2-nitroacrylonitrile (5c). To a stirred solution of 0.456 g (0.004 mol) trifluoracetic acid are added sequentially 1 ml of ethanol, 0.248 g (0.002 mol) of nitroacetonitrile potassium salt (**2**) and 0.272 g (0.002 mol) of 4-methoxybenzaldehyde (**4c**). The reaction mixture

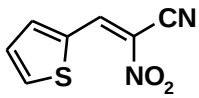
is stirred for 3 hours at room temperature and evaporated to dryness. The product (**5c**) is extracted with boiling CCl_4 and crystallized from it under cooling in ice bath. The precipitate is filtered, washed with CCl_4 and dried. Yield 0.228 g (56%), yellow crystals, mp 101°C (98°C, lit.[5]). ^{1}H NMR, δ, p.m.: 3.93 (3H, s, CH_3), 7.16 (2H, d, *J*=9,00, 2CH), 8.13 (2H, d, *J*=9,00, 2CH), 8.91 (1H, s, CH). Found (%): C, 58.64, H, 4.11, N, 13.71. Calc. for $C_{10}H_8N_2O_3$ (%): C, 58.82, H, 3.95, N, 13.72. IR spectrum, ν, cm^{-1}: 837, 1178, 1271, 1317, 1433, 1505, 1589, 2229, 3042.



3-(2-Furyl)-2-nitroacrylonitrile (5d). To a stirred solution of 0.456 g (0.004 mol) trifluoracetic acid are added sequentially 1 ml of ethanol, 0.248 g (0.002 mol) of nitroacetonitrile potassium salt (**2**) and 0.192 g (0.002 mol) of furaldehyde (**4d**). The reaction mixture is stirred for 3 hours at room temperature and evaporated to dryness. The product (**5d**) is extracted with boiling CCl_4 and crystallized from it under cooling in ice bath. The precipitate is filtered, washed with CCl_4 and dried. Yield 0.233 g (71%), brown crystals, mp 130°C (126°C, lit.[3]). ^{1}H NMR, δ, p.m.: 6.90 (1H, dd, J^1=3.7, J^2=1.7, CH), 7.76 (1H, d, J^1=3.7, CH), 8.30 (1H, d, J^2=1.7, CH), 8.83 (1H, s, CH). Found (%): C, 51.03, H, 2.28, N, 16.93. Calc. for $C_7H_4N_2O_3$ (%): C, 51.23, H, 2.46, N, 17.07. IR spectrum, ν, cm^{-1}: 783, 1026, 1280, 1307, 1514, 1607, 2234, 3044, 3120.



2-Nitro-3-(2-thienyl)acrylonitrile (5e). To a suspension of 0.228 g (0.002 mol) trifluoracetic acid, 5 ml ethanol and 0.248 g (0.002 mol) nitroacetonitrile potassium salt (**2**) is added a solution of 0.224 g (0.002 mol) thiophene-2-carbaldehyde (**4e**) in 5 ml ethanol. The reaction mixture is stirred for 3 hours at room temperature. The solvent is evaporated in vacuo and the residue is treated with water and the precipitate is filtered. Yield 0.23 g (64%), black crystals, mp 168 °C (146°C, lit.[6]). ^{1}H NMR, δ, p.m.: 7.40 (1H, dd, J^1=4.90, J^2=4.00, CH), 8.25 (1H, d, J^2=4.00, CH), 8.37 (1H, d, J^1=4.90, CH), 9.30 (1H, s, CH). Found (%): C, 46.48, H, 2.40, N, 15.49, S, 17.71. Calc. for $C_7H_4N_2O_2S$ (%): C, 46.66, H, 2.24, N, 15.55, S, 17.79. IR, ν, cm^{-1}: 736, 859, 1039, 1057, 1144, 1216, 1253, 1284, 1330, 1409, 1453, 1474, 1504, 1529, 1588, 1682, 2212, 3044, 3090, 3104.



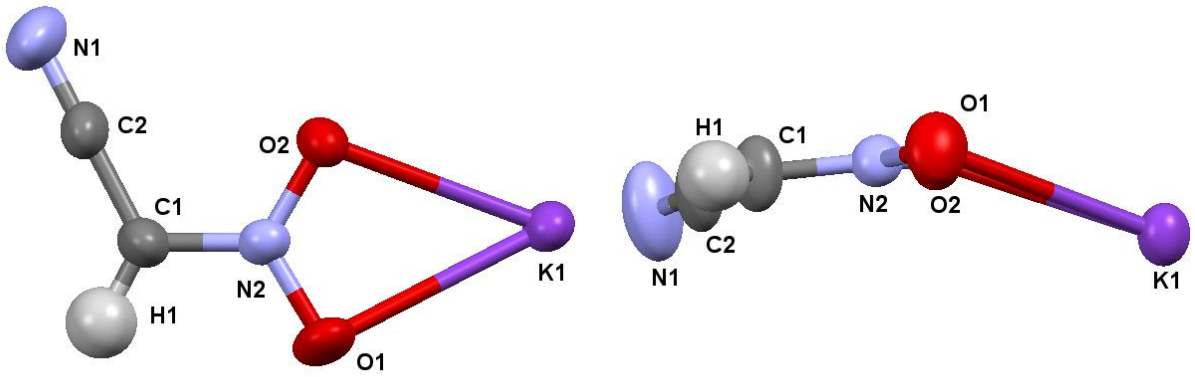


Figure 1S Molecular structures of potassium salt of NAN (**2**).

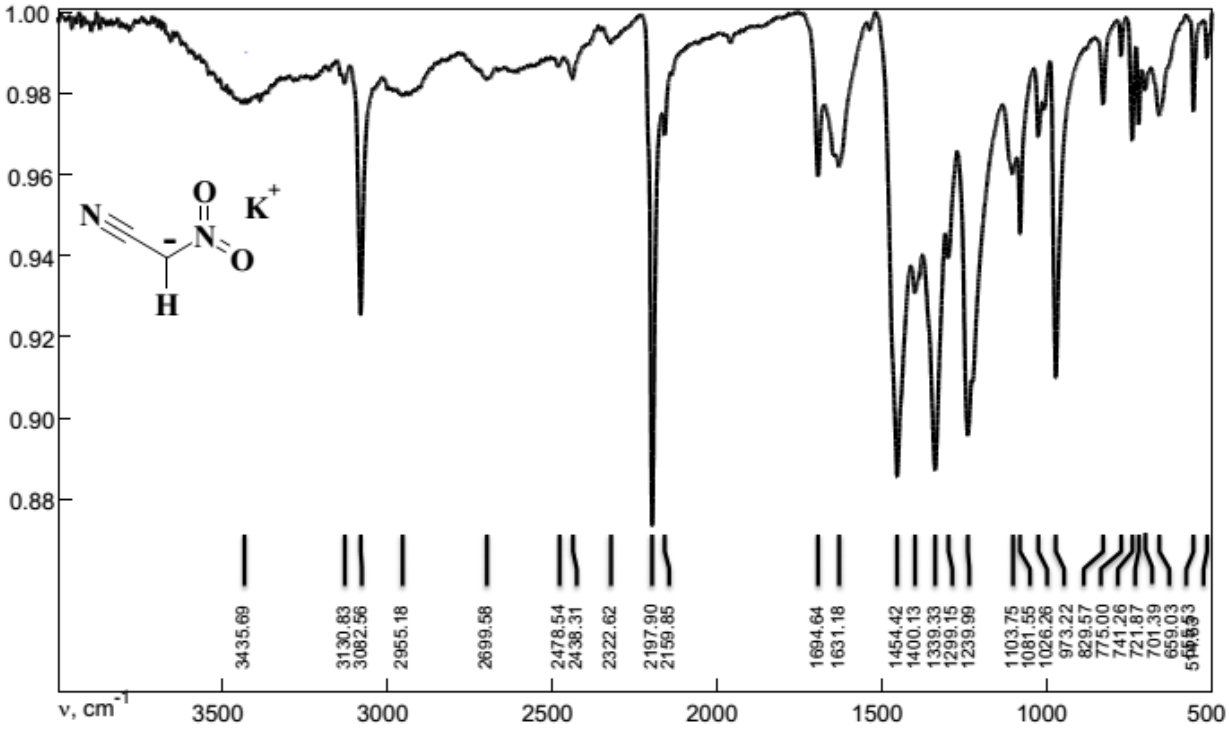


Figure 2S IR spectrum of potassium salt of NAN (**2**).

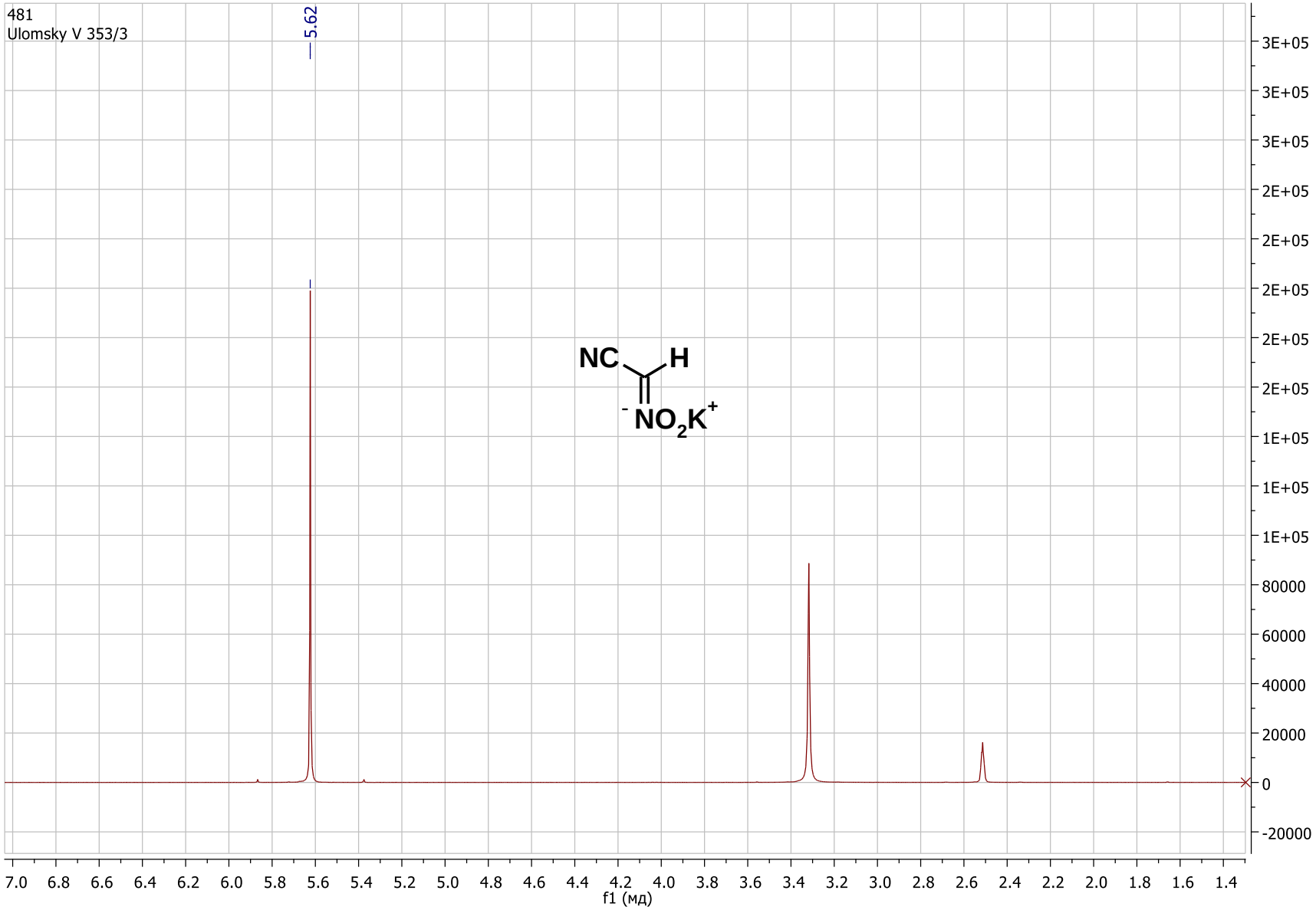


Figure 3S ^{1}H NMR spectrum of compound **2**.

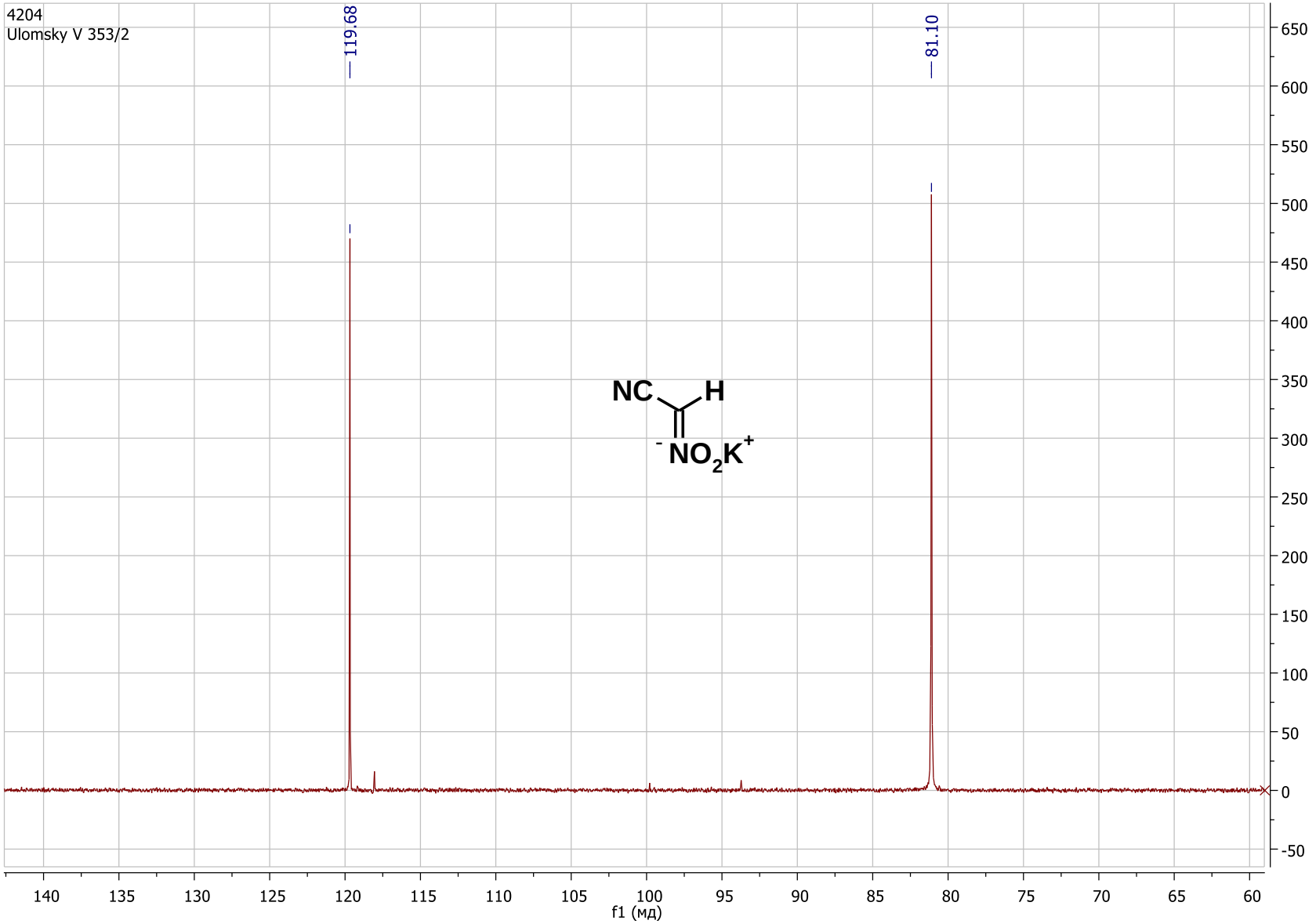


Figure 4S ^{13}C NMR spectrum (Broad band) of compound **2**.

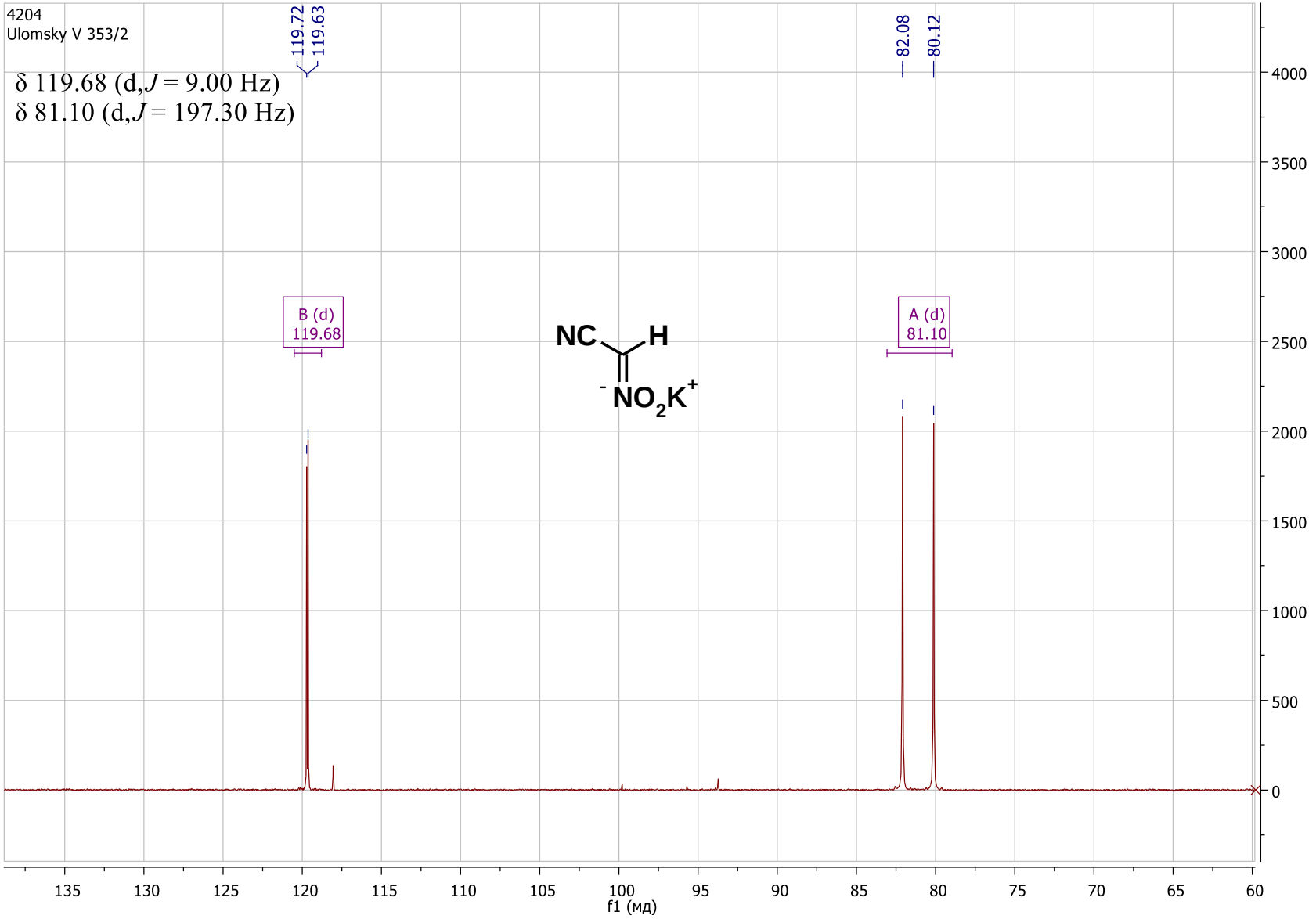


Figure 5S ^{13}C NMR spectrum (GATE) of compound **2**.

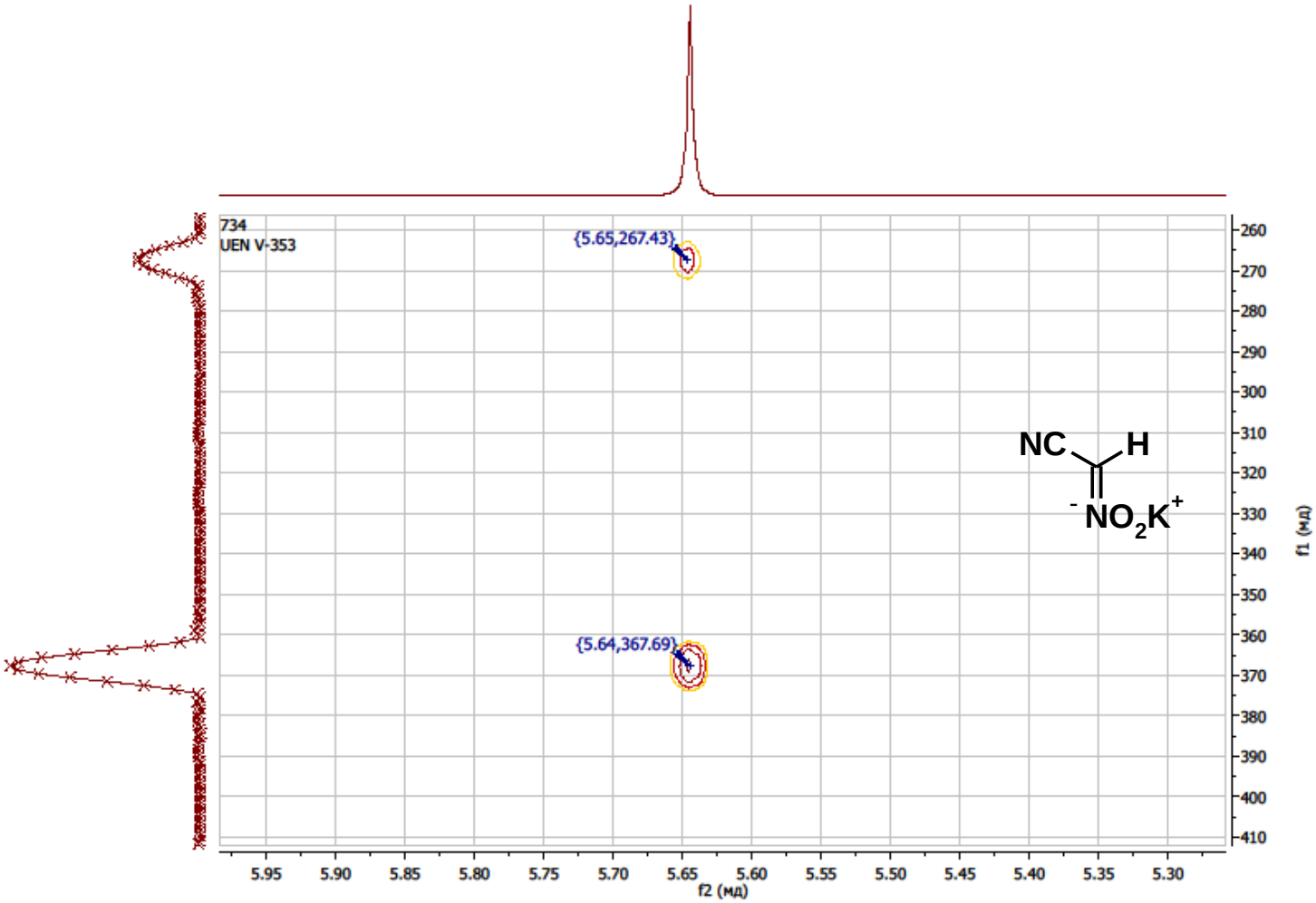


Figure 6S HMBC spectrum of ^{15}N and ^{1}H nucleus of compound **2**.

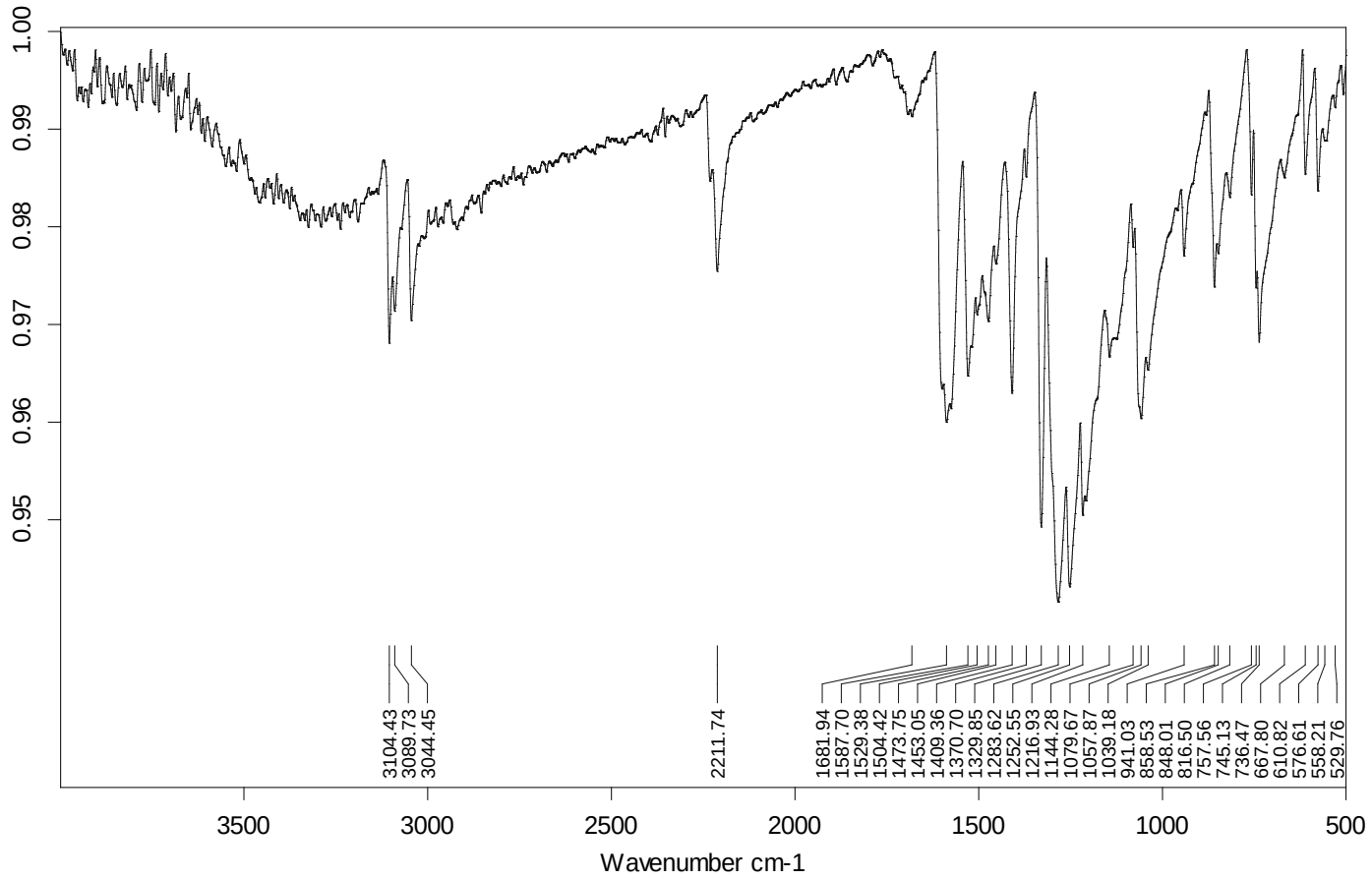


Figure 7S IR spectrum of compound **5e**.

References

1 A. Murray and D. L. Williams, *Organic Syntheses with Isotopes. Part 1*, Interscience Publishers, Michigan, 1958.
2 Darapsky and Hillers, *J. Prakt. Chem.*, 1915, **2**, 325.
3 W. Ried and E. Koehler, *Liebigs Ann. Chem.*, 1956, **598**, 145.
4 Aboskalova, *J. Org. Chem. USSR*, 1972, **8**, 1349 (*Zh. Org. Khim.*, 1972, **8**, 1333).
5 D. Brillon and G. Sauve, *J. Org. Chem.*, 1992, **57**, 1838.
6 Dore and Viel, *Eur. J. Med. Chem.*, 1974, **9**, no. 6, 666.
7 L. S. Pupko, A. I. Dychenko and P. S. Pelkis, *J. Org. Chem. USSR (Engl. Transl.)*, 1972, **8**, 40 (*Zh. Org. Khim.*, 1972, **8**, 39).