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Novel energetic aminofurazans with a nitro-*NNO*-azoxy group

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Contents

Experimental Section

Safety precautions

While we have experienced no difficulties in syntheses and characterization of these energetic materials, proper protective measures should be used. Manipulations must be carried out in a hood behind a safety shield. Face shield and leather gloves must be worn. Mechanical actions involving scratching or scraping must be avoided.

General Remarks: ^{1}H, ^{13}C, ^{14}N and ^{15}N NMR spectra were recorded with Bruker AV600 (600.1, 150.9, 43.4, 60.8 MHz, respectively) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from internal TMS (^{1}H, ^{13}C) or external CH_3NO_2 (^{14}N, ^{15}N negative values of δ_N correspond to upfield shifts). The IR spectra were recorded with a Bruker ALPHA-T spectrometer in the range 400–4000 cm^{-1} (resolution 2 cm^{-1}) as pellets with KBr. High-resolution ESI mass spectra (HRMS) were recorded with a Bruker micrOTOF II instrument. Melting points were determined with a Kofler melting point apparatus and are uncorrected. Thermal behavior was studied using Netzsch DSC 204 HP in nitrogen flow. A sample of ca. 0.5 mg was placed in closed aluminum crucibles with pierced lids and heated linearly at 5 $K \cdot min^{-1}$ rate up to 400 °C. The impact and friction sensitivities of compound **2a** were determined using a STANAG protocol and BAM-type impact and friction machines.[1,2] Silica gel "Silpearl UV 254" was used for preparative column and thin-layer chromatography. Analytical thin-layer chromatography (TLC) was carried out on "Silufol" TLC silica gel UV-254 aluminum sheets. Solvents were purified before use according to standard procedures. All other reagents were used without further purification. 3-Nitro-4-{[4'-(nitro-*NNO*-azoxy)furazan-3'-yl]-*NNO*-azoxy}furazan (**1a**), 3-(nitro-*NNO*-azoxy)-4-{[4'-(nitro-*NNO*-azoxy)furazan-3'-yl]-*NNO*-azoxy}furazan (**1b**) and bis-4,4'-(nitro-*NNO*-azoxy)-3,3'-azofurazan (**1c**) were prepared according to the reported procedures.[3]

1 STANAG 4489, Explosives, Impact Sensitivity Tests, 1st ed., NATO standardization agreement, NATO, Brussels (Belgium), 1999.

2 STANAG 4487, Explosives, Friction Sensitivity Tests, 1st ed., NATO standardization agreement, NATO, Brussels (Belgium), 2002.

3 N. E. Leonov, M. S. Klenov, O. V. Anikin, A. M. Churakov, Yu. A. Strelenko, A. A. Voronin, D. B. Lempert, N. V. Muravyev, I. V. Fedyanin, S. E. Semenov and V. A. Tartakovsky, *ChemistrySelect*, 2020, **5**, 12243.

Table S1 The reactions of (nitro-*NNO*-azoxy)furazans **1a–c** with ammonia

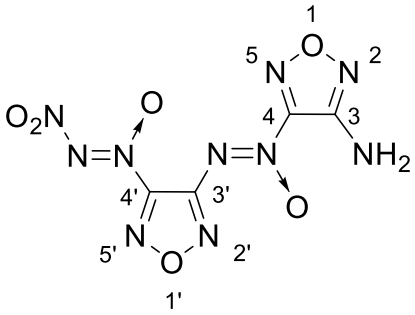
Entry	Starting compound	Method	Time, min	Temperature, °C	Product	Yield (%)
1	**1a**	A	60	25	**2a**	25
2	**1a**	B	30	25	**2a**	38
3	**1a**	B	90	0	**2a**	20
4	**1b**	A	15	25	**2a**	29
5	**1b**	B	30	25	**2a**	43
6	**1c**	C	1	0	**2b**	38
7	**1c**	C	1	15	**2b**	44[4]
8	**1c**	B	30	25	**2b**	10

Method A: A saturated solution of NH_3 in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of starting compound (1.0 mmol) in dry CH_2Cl_2 (15 mL) at 25 °C under argon (see Table S1). The mixture was vigorously stirred at this temperature until the starting compound disappeared (TLC control). The precipitate was then filtered off, washed with CH_2Cl_2 (2 × 25 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by preparative thin-layer chromatography (petroleum ether/ethyl acetate, 10 : 1, then 5 : 1, containing 0.1% v/v of trifluoroacetic acid).

Method B: A concentrated aqueous ammonia solution (2 mL) was added dropwise to a stirred solution of starting compound (1.0 mmol) in CH_2Cl_2 (10–20 mL) at 25 °C (see Table S1). The mixture was vigorously stirred at this temperature until the starting compound disappeared (TLC control). Then H_2O (20 mL) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic extracts were washed with water (20 mL), brine (20 mL), dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (in the case of product **2a** – petroleum ether/ethyl acetate, 10 : 1, then 5 : 1, containing 0.1% v/v of trifluoroacetic acid; in the case of product **2b** – petroleum ether/ethyl acetate, 20 : 1, then 10 : 1, containing 0.1% v/v of trifluoroacetic acid).

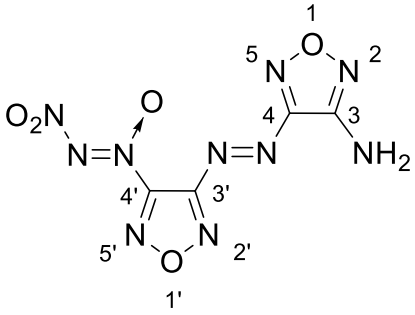
[4] The conversion of compound **1c** is 62%.

3-Amino-4-{[4'-(nitro-*NNO*-azoxy)-furazan-3'-yl]-*NNO*-azoxy}furazan (2a). R_f = 0.28 (eluent petroleum ether/ethyl acetate, 5 : 1). Yellow needles, m.p.: 114 °C (CH_2Cl_2 – hexane, 3 : 1). DSC (5 °C·min^{-1}): T_{onset} = 114 °C (dec.).



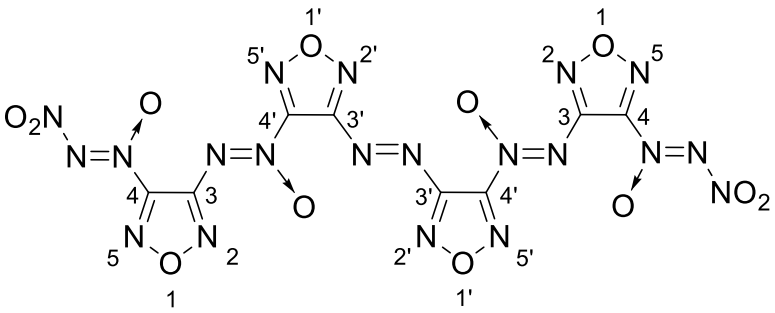
^{1}H NMR (600.1 MHz, [D$_6$]acetone): δ = 6.67 (br. s, 2 H, NH_2) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]acetone): δ = 149.8 (C-3 or C-3'), 152.0 (C-3' or C-3), 153.0 (br., C-4 or C-4'), 153.6 (br., C-4' or C-4) ppm. ^{14}N NMR (43.4 MHz, [D$_6$]acetone): δ = –42 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 20 Hz), –59 ($\underline{N}$(O)=N, $\Delta\nu_{½}$ = 55 Hz), –66 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 30 Hz), –339 (NH_2, $\Delta\nu_{½}$ = 725 Hz). ^{15}N NMR ([INVGATED], 60.8 MHz, [D$_6$]acetone): δ = 38.5, 34.7, 34.4, 2.4 (furazan rings), –41.3 (N(O)=N–$\underline{N}O_2$), –58.8 ($\underline{N}$(O)=N), –65.7 ($\underline{N}$(O)=N–NO_2), –337.2 (NH_2). IR (KBr): ν = 3453 (s), 3319 (m), 3260 (w), 3202 (w), 1641 (s), 1625 (s), 1582 (w), 1549 (w), 1514 (s), 1497 (m), 1480 (s), 1459 (w), 1433 (w), 1408 (w), 1361 (w), 1321 (w), 1280 (s), 1213 (w), 1153 (m) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_4H_2N_{10}O_6$ [M + Na]$^+$ 309.0051; found 309.0050. Anal. calcd for $C_4H_2N_{10}O_6$: C 16.79, H 0.70, N 48.95, found: C 16.82, H 0.74, N 48.85.

3-Amino-4'-(nitro-*NNO*-azoxy)-4,3'-azofurazan (2b). Method C: Ammonia gas was passed through a stirred solution of compound **1c** (1.84 g, 5.35 mmol) in dry CH_2Cl_2 (45 mL) for 60 s at 15 °C. The precipitate was filtered off and washed with CH_2Cl_2 (2 × 25 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by preparative column chromatography (petroleum ether/ethyl acetate, 10 : 1, containing 0.5% v/v of trifluoroacetic acid, R_f (**2b**) = 0.05) to give aminofurazan **2b** (0.39 g, 27% or 44% with the conversion of **1c** being 62%) as an orange solid, m.p. 62–63 °C, and the unreacted azofurazan **1c** (0.7 g, 38%, R_f (**1c**) = 0.68) as an orange solid, m.p. 83–84 °C (dec.).



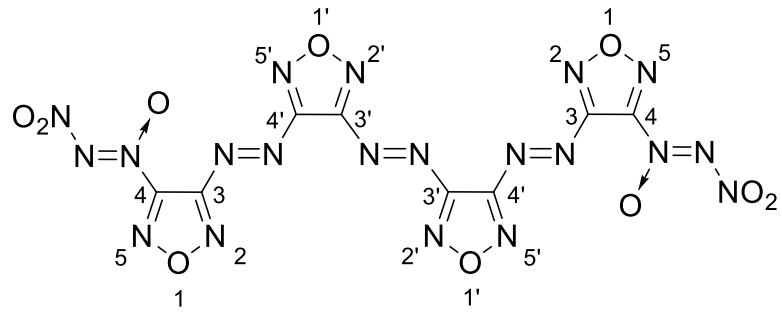
^{1}H NMR (600.1 MHz, [D$_6$]acetone): δ = 6.54 (br. s, 2 H, NH_2) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]acetone): δ = 150.2 (C-3), 153.2 (br., C-4'), 157.5 (C-4 or C-3'), 157.6 (C-3' or C-4) ppm. ^{14}N NMR (43.4 MHz, [D$_6$]acetone): δ = 7 (N(O)=$\underline{N}$–NO_2, $\Delta\nu_{½}$ = 1100 Hz), –42 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 20 Hz), –67 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 40 Hz), –336 (NH_2, $\Delta\nu_{½}$ = 740 Hz). ^{15}N NMR ([INVGATED], 60.8 MHz, [D$_6$]acetone): δ = 148.0, 102.7 (N=N), 49.9, 38.5, 32.2 (furazan rings), –41.3 (N(O)=N–$\underline{N}O_2$), –66.6 ($\underline{N}$(O)=N–NO_2), –335.7 (NH_2). IR (KBr): ν = 3461 (s), 3322 (m), 1629 (s), 1550 (w), 1487 (m), 1454 (w), 1429 (w), 1398 (w), 1278 (m), 1238 (m), 1163 (m) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_4H_2N_{10}O_5$ [M + Ag]$^+$ 376.9255; found 376.9261. Anal. calcd for $C_4H_2N_{10}O_5$: C 17.79, H 0.75, N 51.85, found: C 17.84, H 0.76, N 51.68.

3,3'-Diazene-1,2-diylbis(4-{[4-(nitro-*NNO*-azoxy)furazan-3-yl]-*NNO*-azoxy}furazan) (3a). Finely powdered dibromoisocyanuric acid (DBI, 301 mg, 1.05 mmol) was added in one portion to a stirred solution of compound **2a** (200 mg, 0.70 mmol) in dry CH_2Cl_2 (1 mL) at 25 °C under argon. The mixture was vigorously stirred at this temperature for 12 h. The precipitate was then filtered off, washed with CH_2Cl_2 (2 × 25 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by preparative thin-layer chromatography (petroleum ether/ethyl acetate, 5 : 1, containing 0.1% v/v of trifluoroacetic acid, R_f (**3a**) = 0.47) to give furazan **3a** (129 mg, 65%) as a red-orange oil.



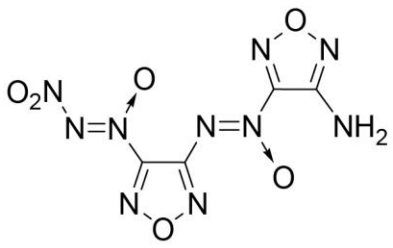
^{13}C NMR (150.9 MHz, [D$_6$]acetone): δ = 149.9 (C-3 or C-3'), 153.3 (br., C-4 or C-4'), 155.1 (br., C-4' or C-4), 157.9 (C-3' or C-3) ppm. ^{14}N NMR (43.4 MHz, [D$_6$]acetone): δ = –42 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 35 Hz), –67 ($\underline{N}$(O)=N–NO$_2$ & $\underline{N}$(O)=N, $\Delta\nu_{½}$ = 75 Hz). ^{15}N NMR ([INVGATED], 60.8 MHz, [D$_6$]acetone): δ = 144.0 (N=N), 39.6, 39.2, 36.5, 34.6 (furazan rings), 7.0 (N(O)=$\underline{N}$), –41.1 (N(O)=N–$\underline{N}O_2$), –66.0 & –66.4 ($\underline{N}$(O)=N–NO$_2$ & $\underline{N}$(O)=N). Anal. calcd for $C_8N_{20}O_{12}$: C 16.91, N 49.30, found: C 16.94, N 49.21.

3,3'-Diazene-1,2-diylbis(4-{(*E*)-[4-(nitro-*NNO*-azoxy)furazan-3-yl]diazenyl}furazan) (3b). Finely powdered DBI (0.62 g, 2.17 mmol) was added in one portion to a stirred solution of compound **2b** (390 mg, 1.44 mmol) in dry CH_2Cl_2 (2 mL) at 25 °C under an argon atmosphere. The mixture was vigorously stirred at this temperature for 12 h. The precipitate was then filtered off, washed with CH_2Cl_2 (2 × 25 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by preparative thin-layer chromatography (petroleum ether/ethyl acetate, 5 : 1, containing 0.1% v/v of trifluoroacetic acid, R_f (**3b**) = 0.80) to give furazan **3b** (356 mg, 92%) as a red oil.



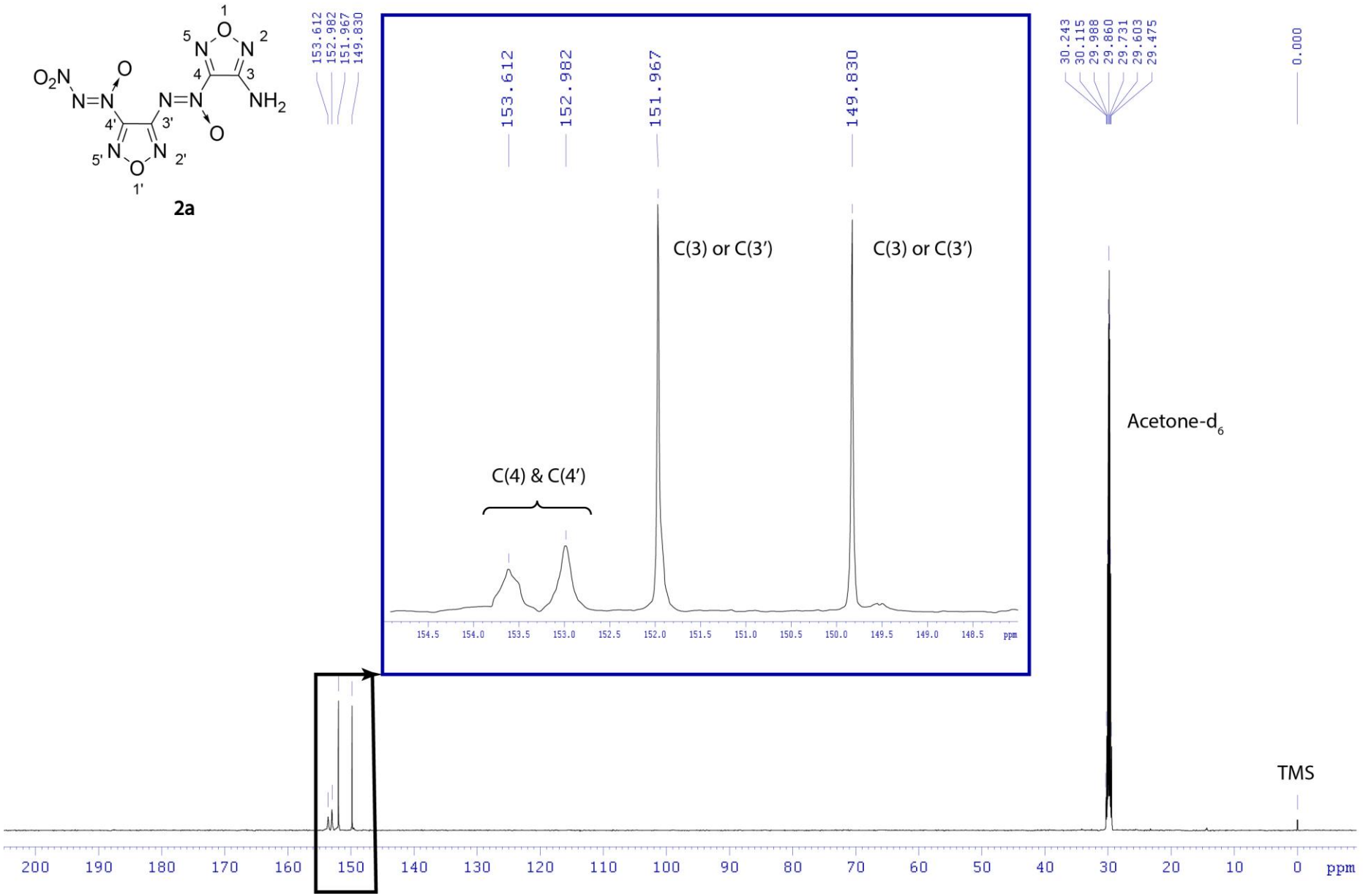
^{13}C NMR (150.9 MHz, [D$_6$]acetone): δ = 152.4 (br., C-4), 157.9, 158.8, 158.9 (C-3 or C-3' or C-4') ppm. ^{14}N NMR (43.4 MHz, [D$_6$]acetone): δ = –42 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 35 Hz), –68 ($\underline{N}$(O)=N–NO$_2$, $\Delta\nu_{½}$ = 60 Hz). ^{15}N NMR ([INVGATED], 60.8 MHz, [D$_6$]acetone): δ = 148.1, 146.5, 139.1 (N=N), 39.2, 38.1, 37.1, 35.9 (furazan rings), 7.8 (N(O)=$\underline{N}$–NO$_2$), –41.5 (N(O)=N–$\underline{N}O_2$), –67.4 ($\underline{N}$(O)=N–NO$_2$). IR (KBr): ν = 1643 (s), 1633 (s), 1577 (m), 1556 (m), 1504 (s), 1468 (m), 1407 (m), 1378 (m), 1313 (m), 1278 (s), 1243 (m), 1171 (s) cm^{-1}. Anal. calcd for $C_8N_{20}O_{10}$: C 17.92, N 52.24, found: C 17.94, N 52.14.

^{1}H NMR (600.1 MHz, [D$_6$]acetone) of compound 2a

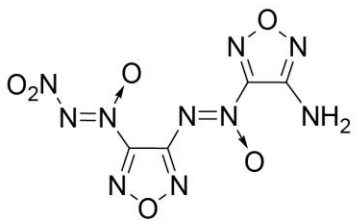


2a

^{13}C NMR (150.9 MHz, [D$_6$]acetone) of compound 2a

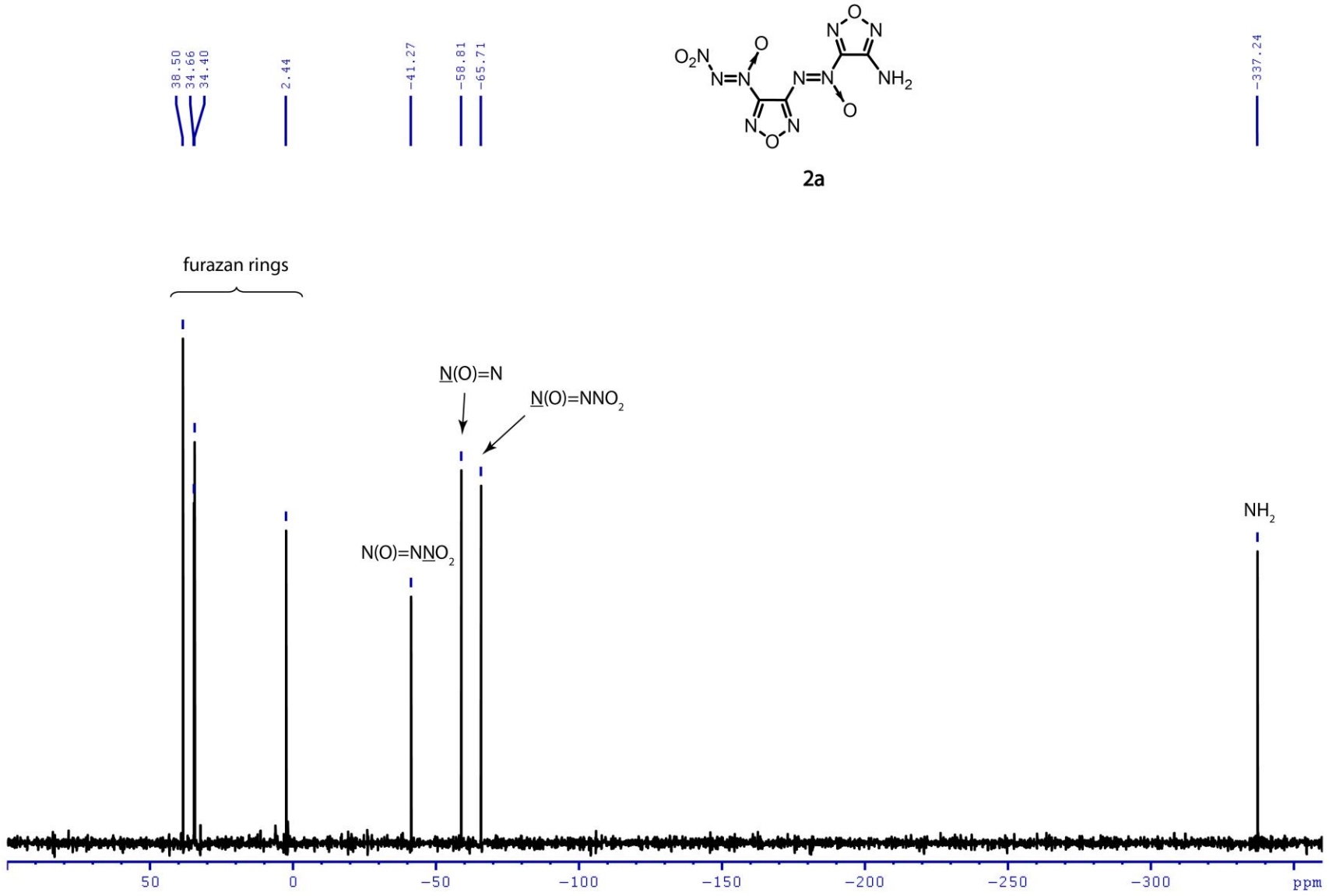


^{14}N NMR (43.4 MHz, [D$_6$]acetone) of compound 2a

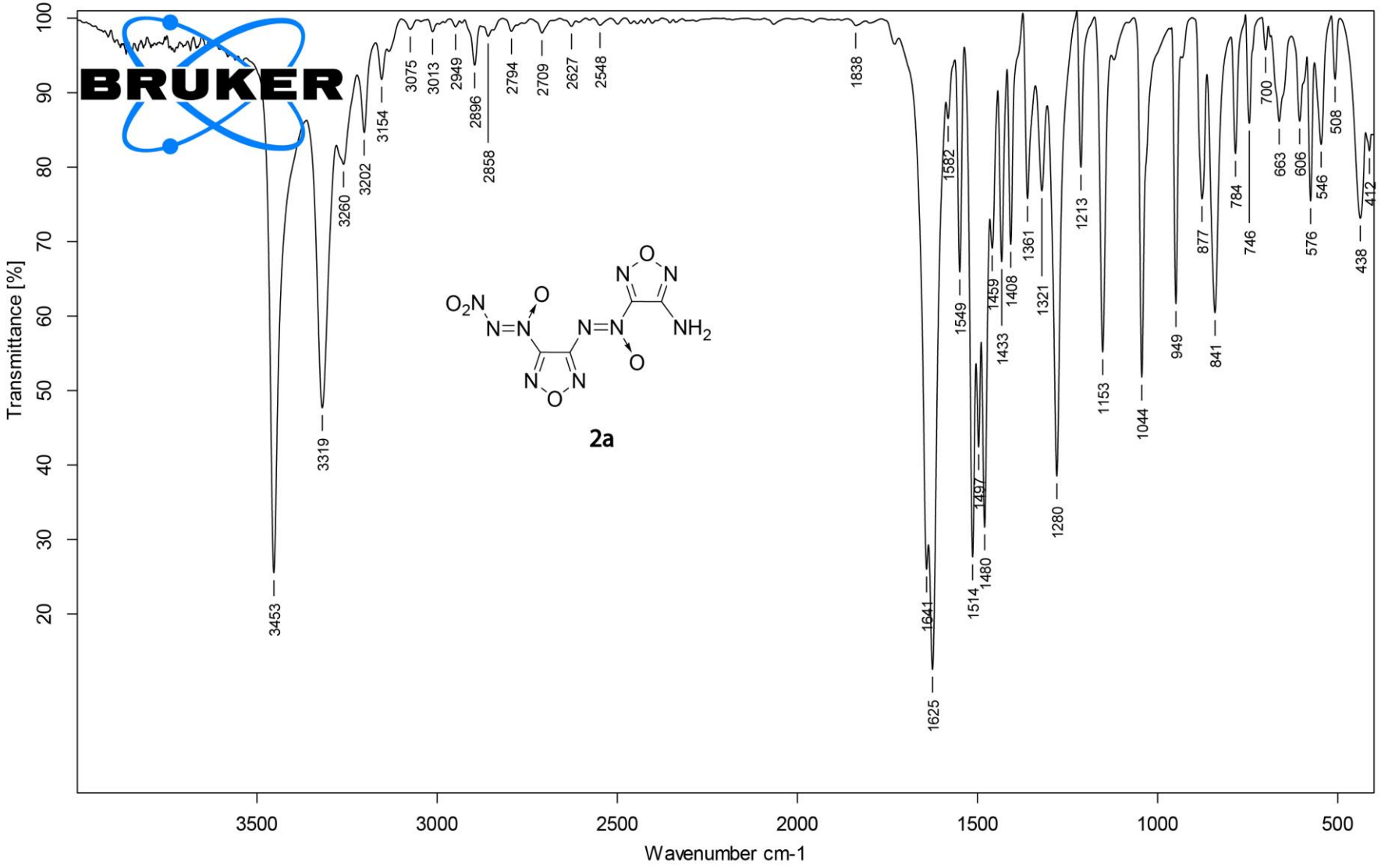


2a

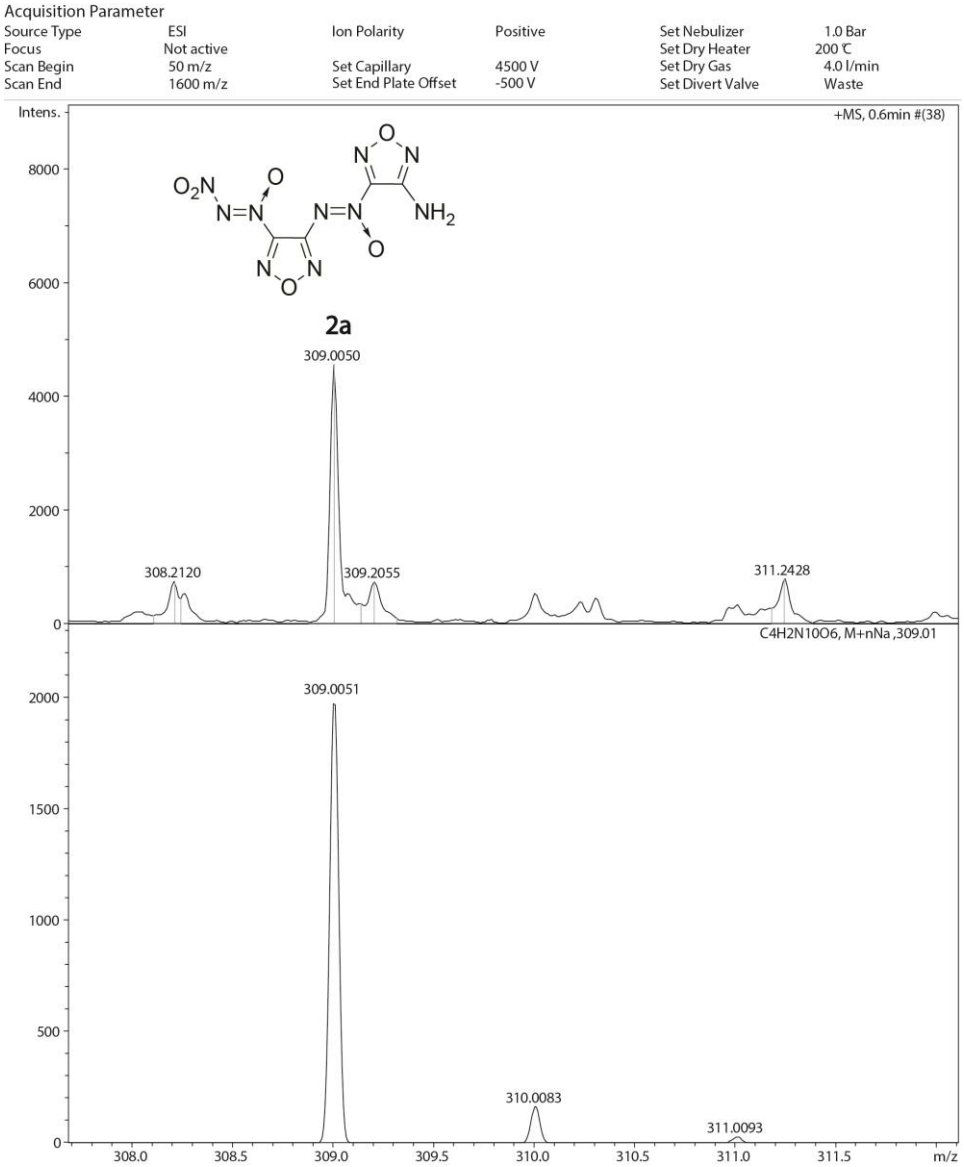
^{15}N NMR ([INVGATED}, 60.8 MHz, [D$_6$]acetone) of compound 2a



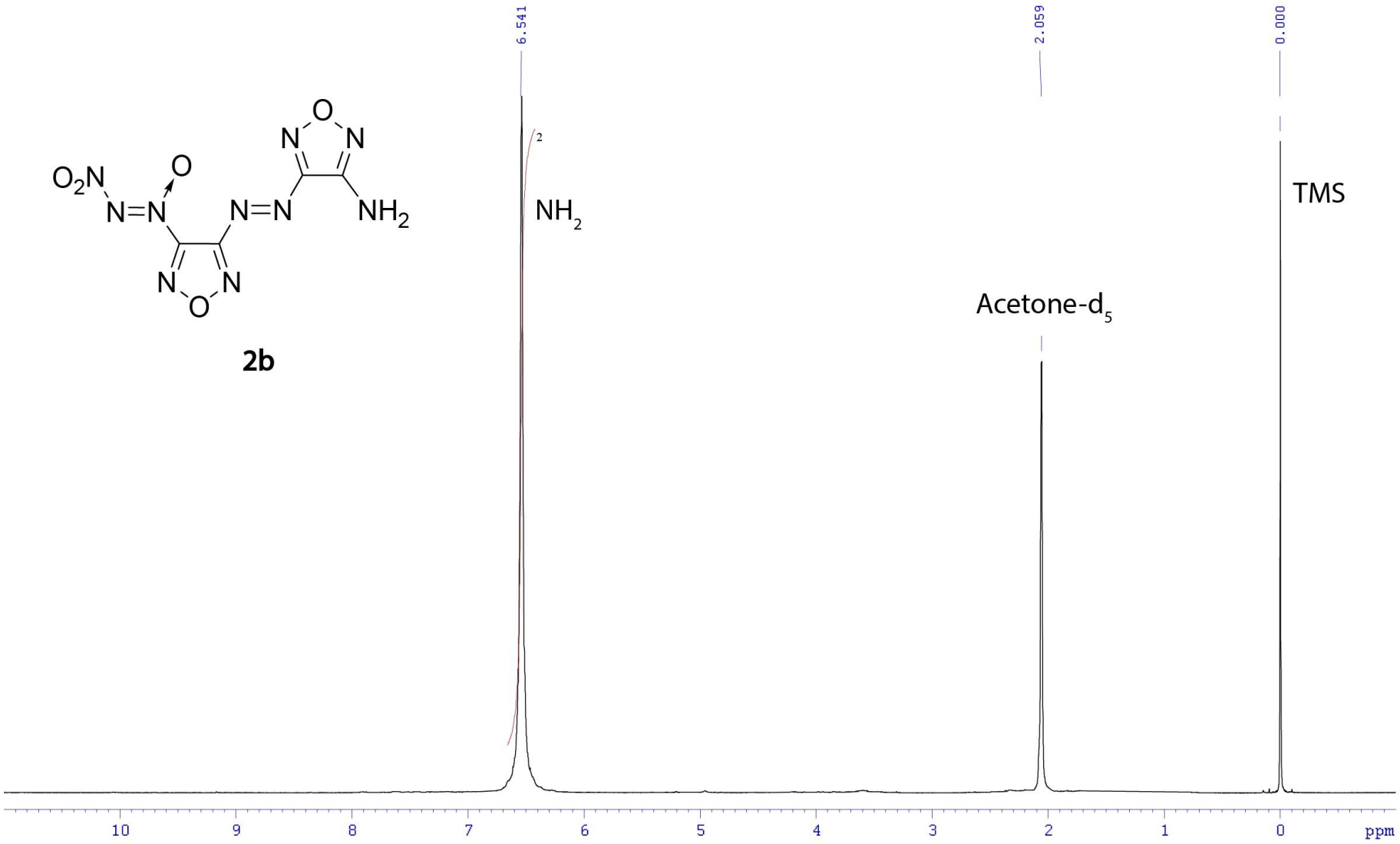
IR of compound 2a



HRMS of compound 2a

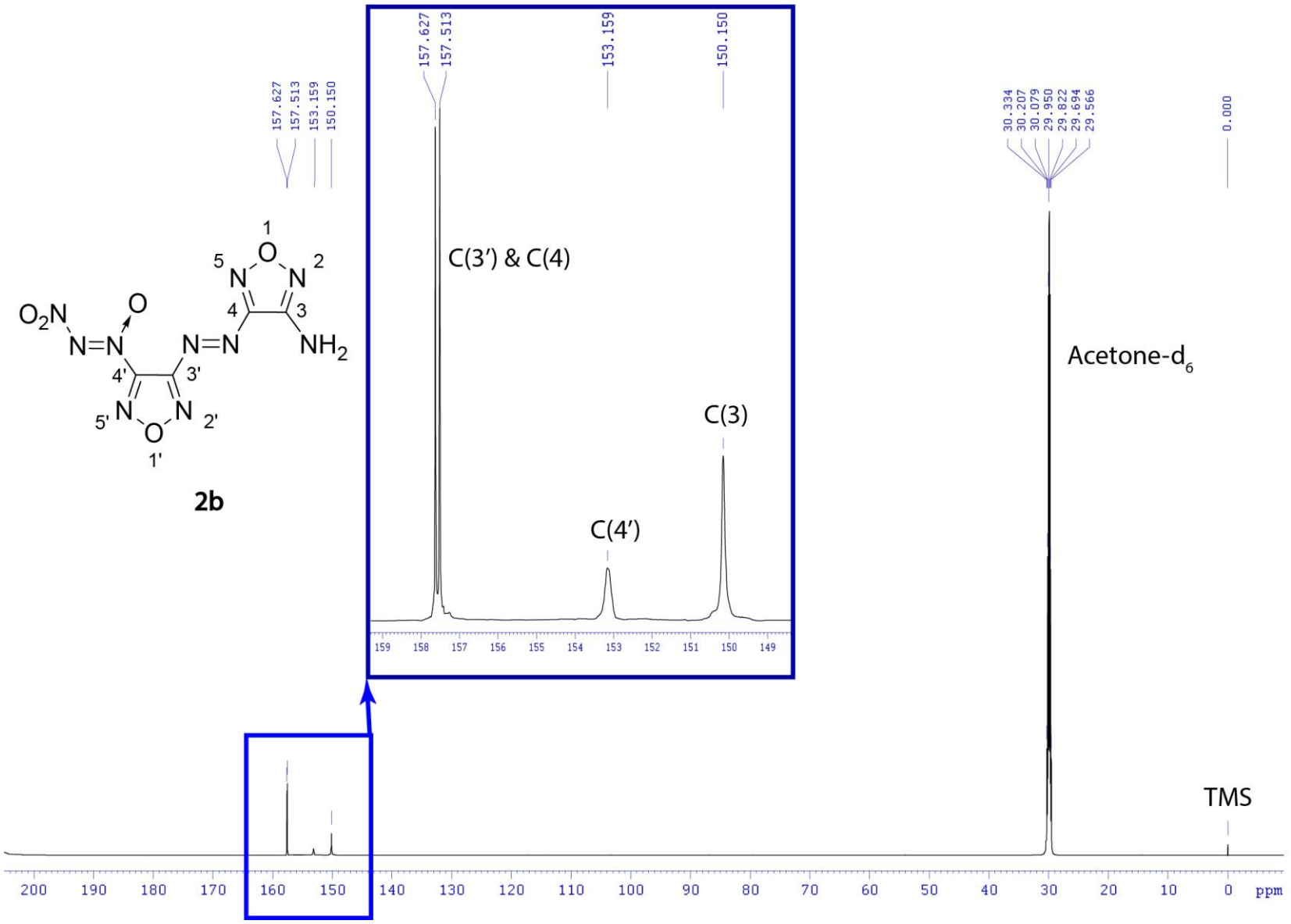


^{1}H NMR (600.1 MHz, [D$_6$]acetone) spectrum of compound 2b

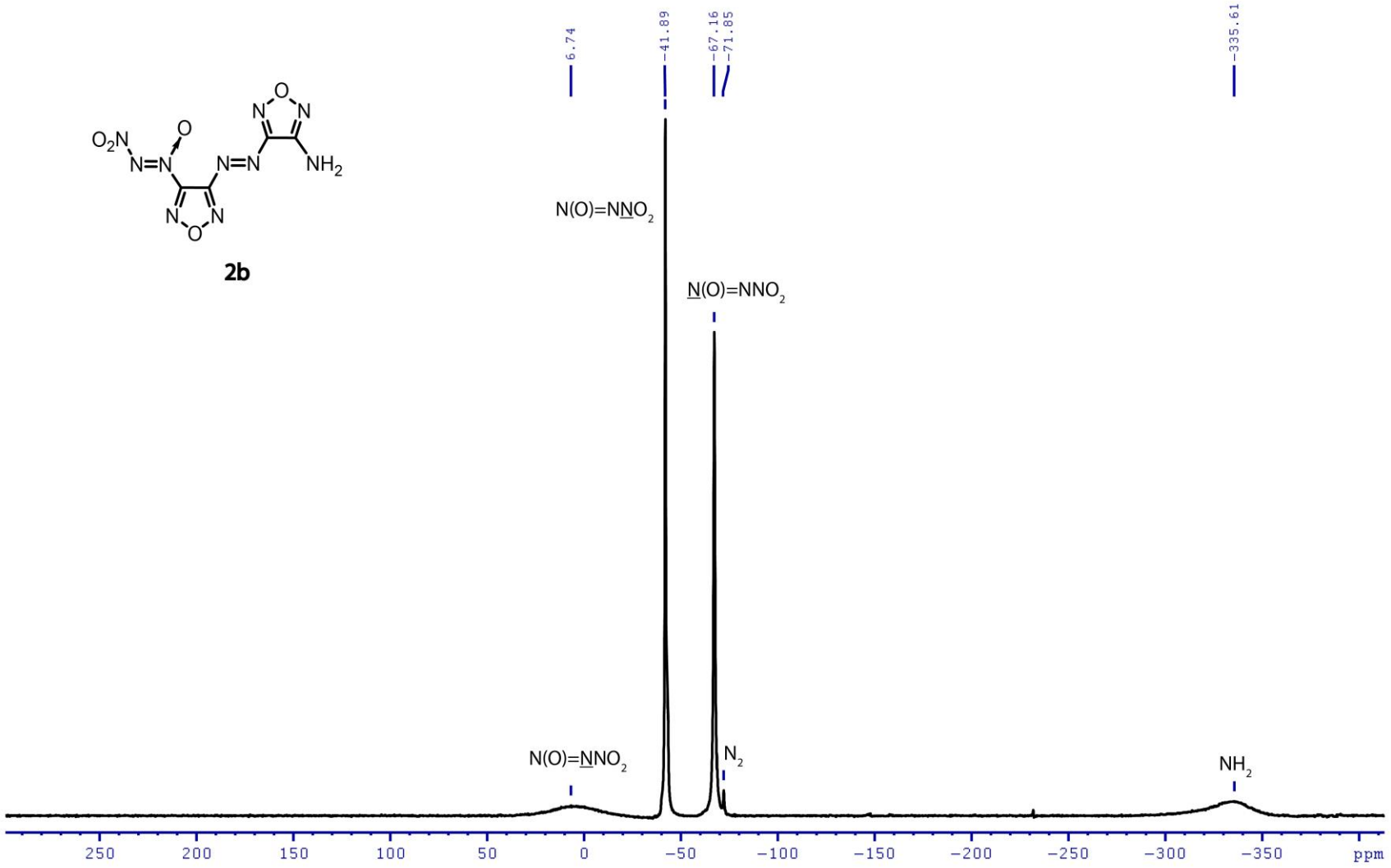


2b

^{13}C NMR (150.9 MHz, [D$_6$]acetone) spectrum of compound 2b

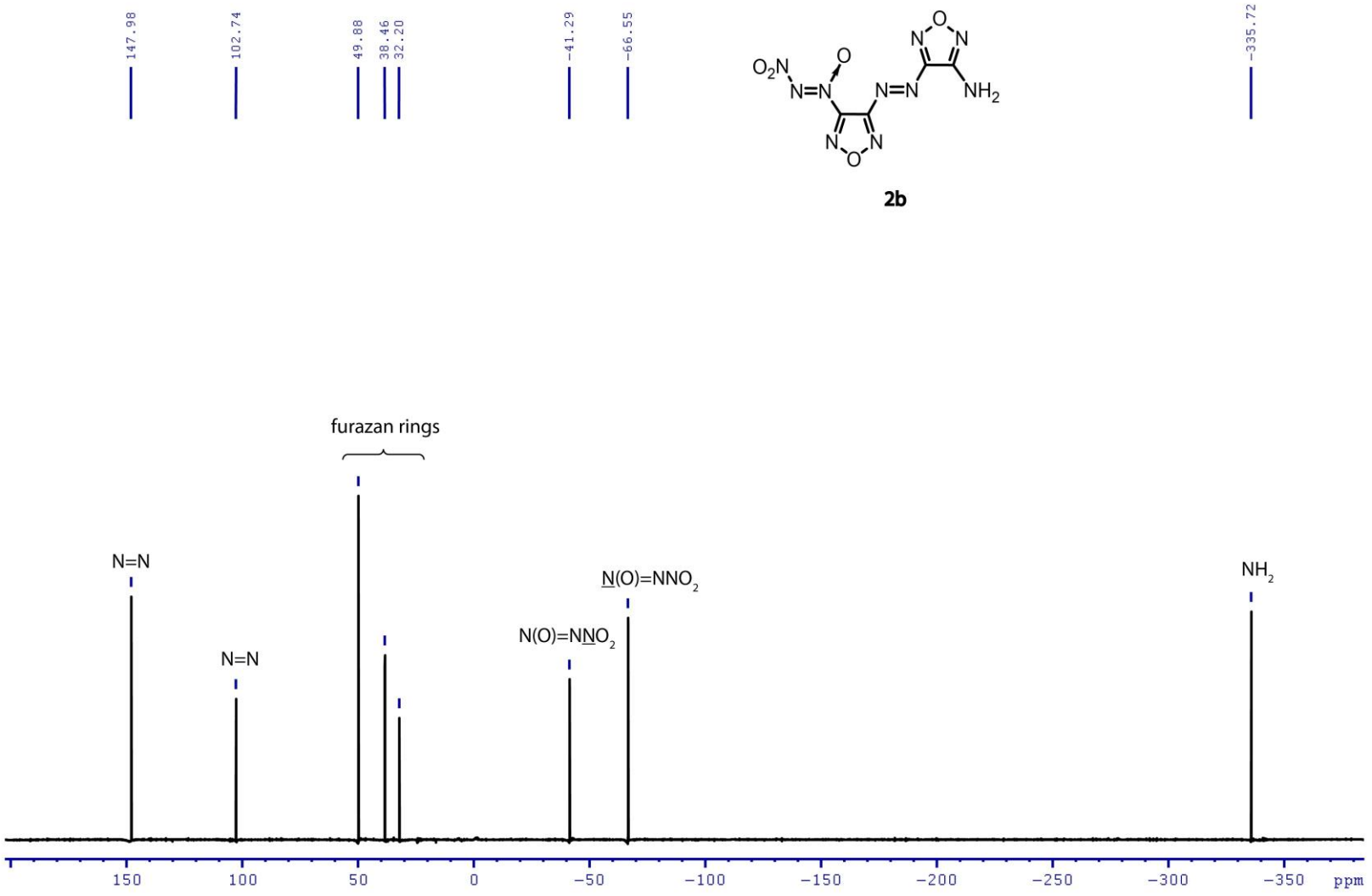


^{14}N NMR (43.4 MHz, [D$_6$]acetone) spectrum of compound 2b



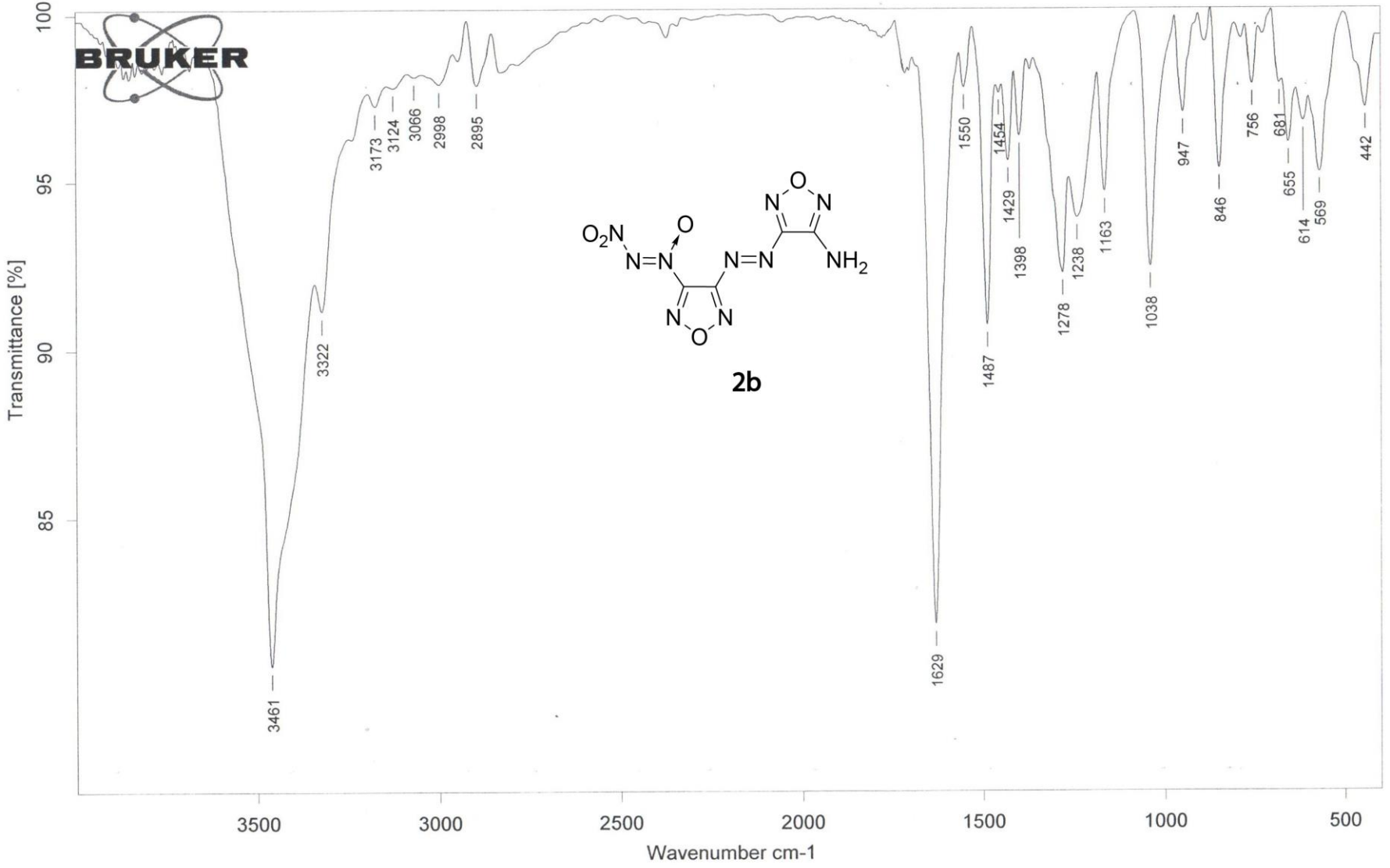
2b

^{15}N NMR ([INVGATED], 60.8 MHz, [D_6]acetone) of compound 2b

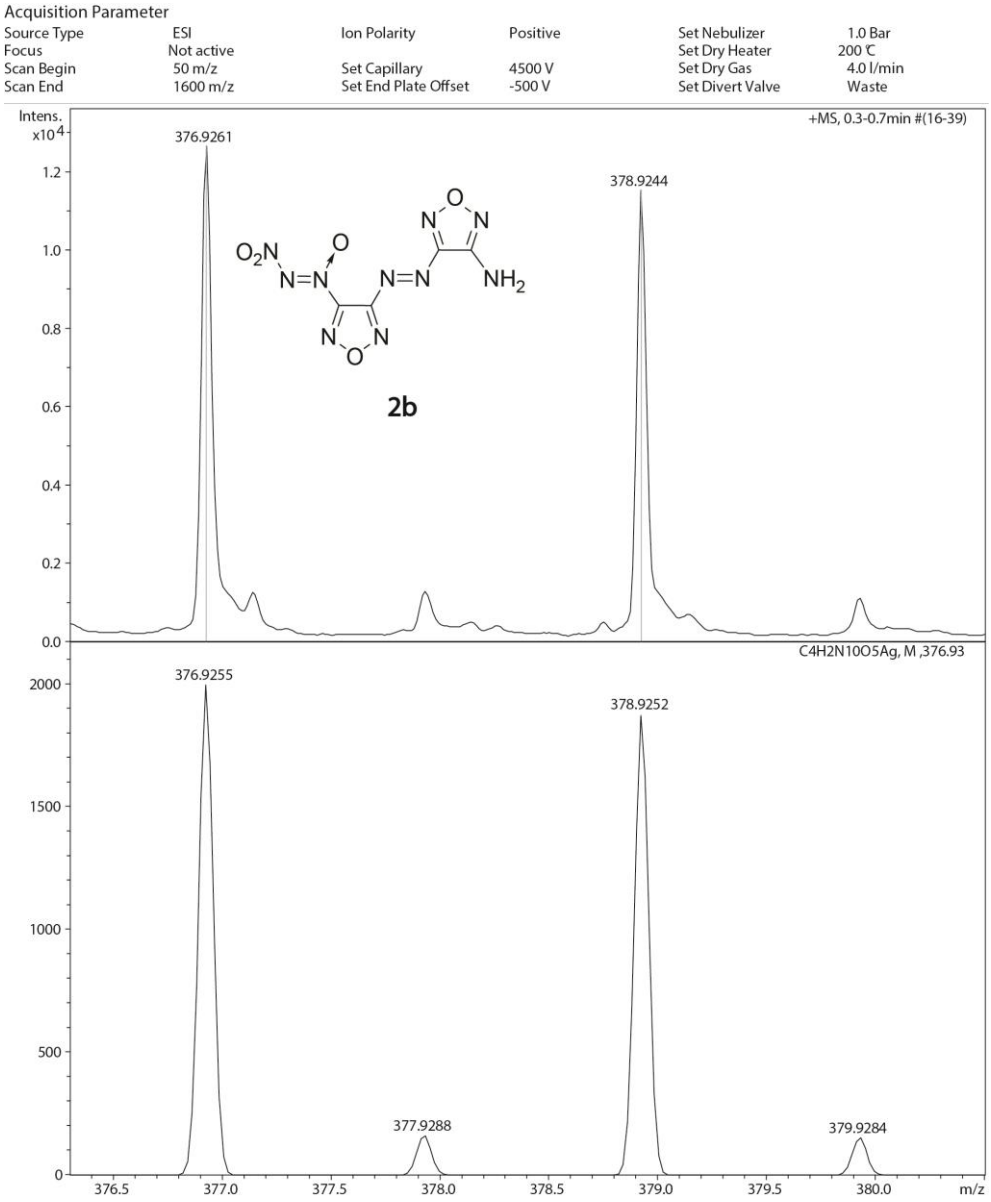


2b

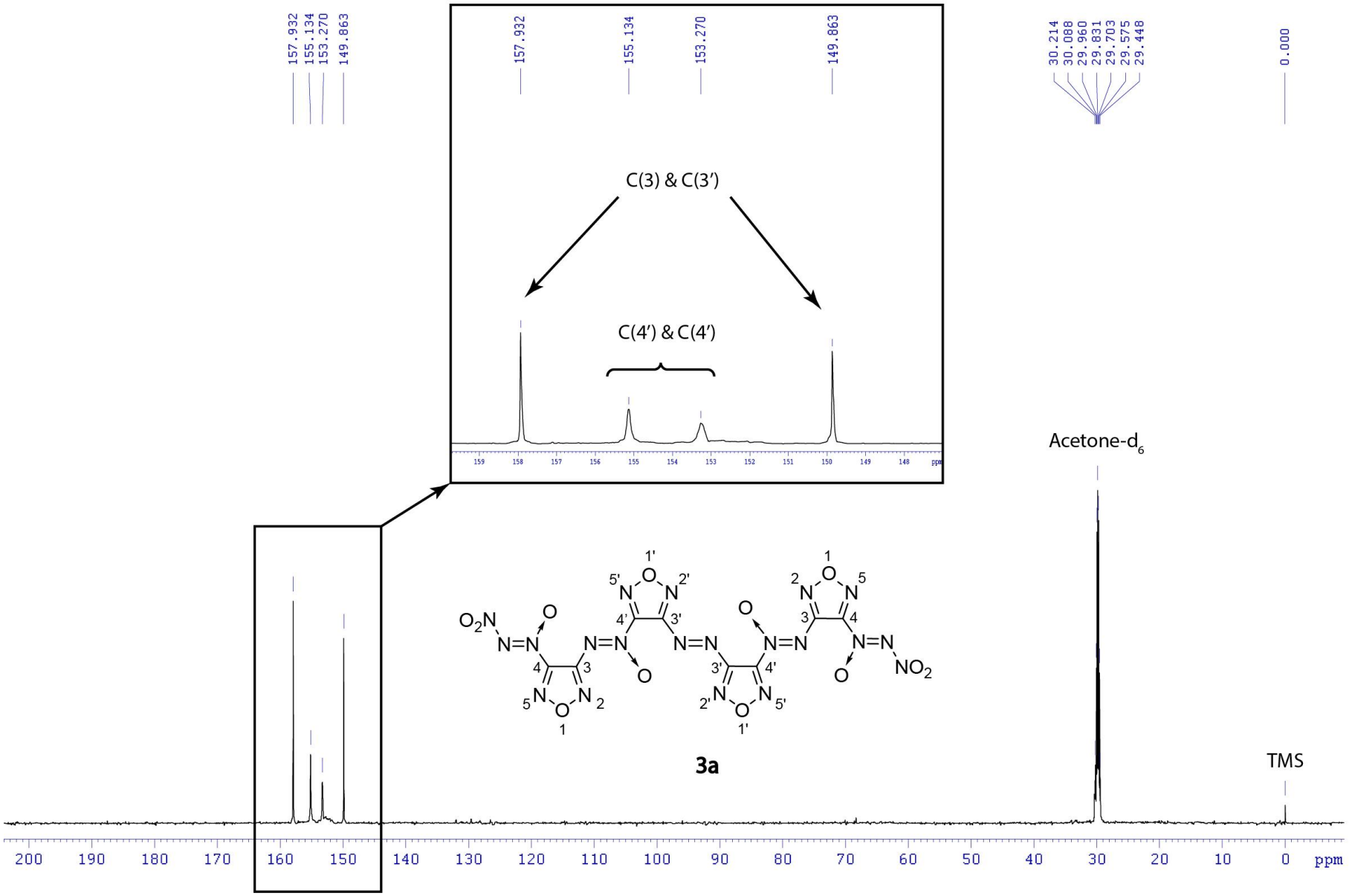
IR of compound 2b



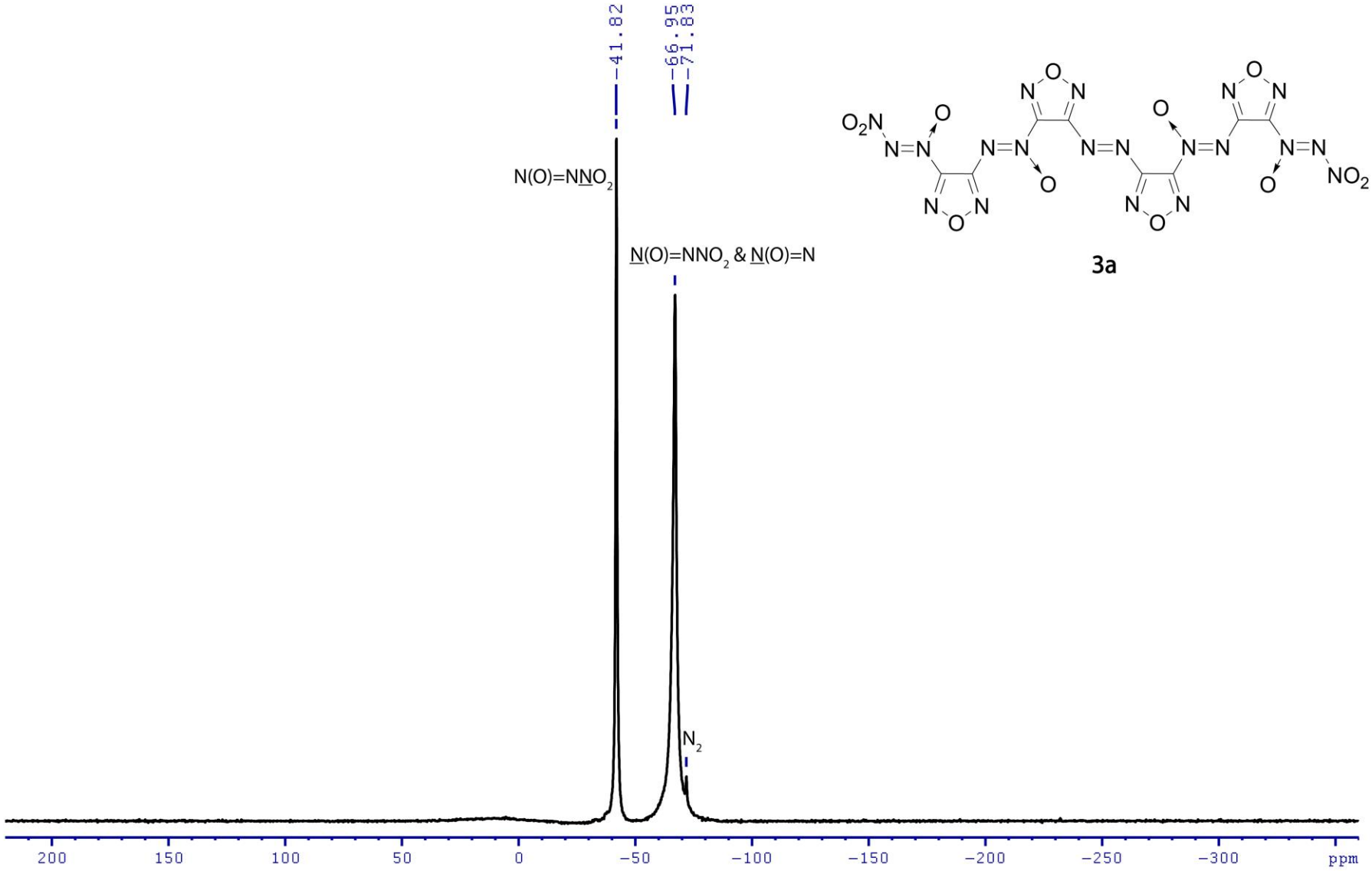
HRMS of compound 2b



^{13}C NMR (150.9 MHz, [D$_6$]acetone) spectrum of compound 3a

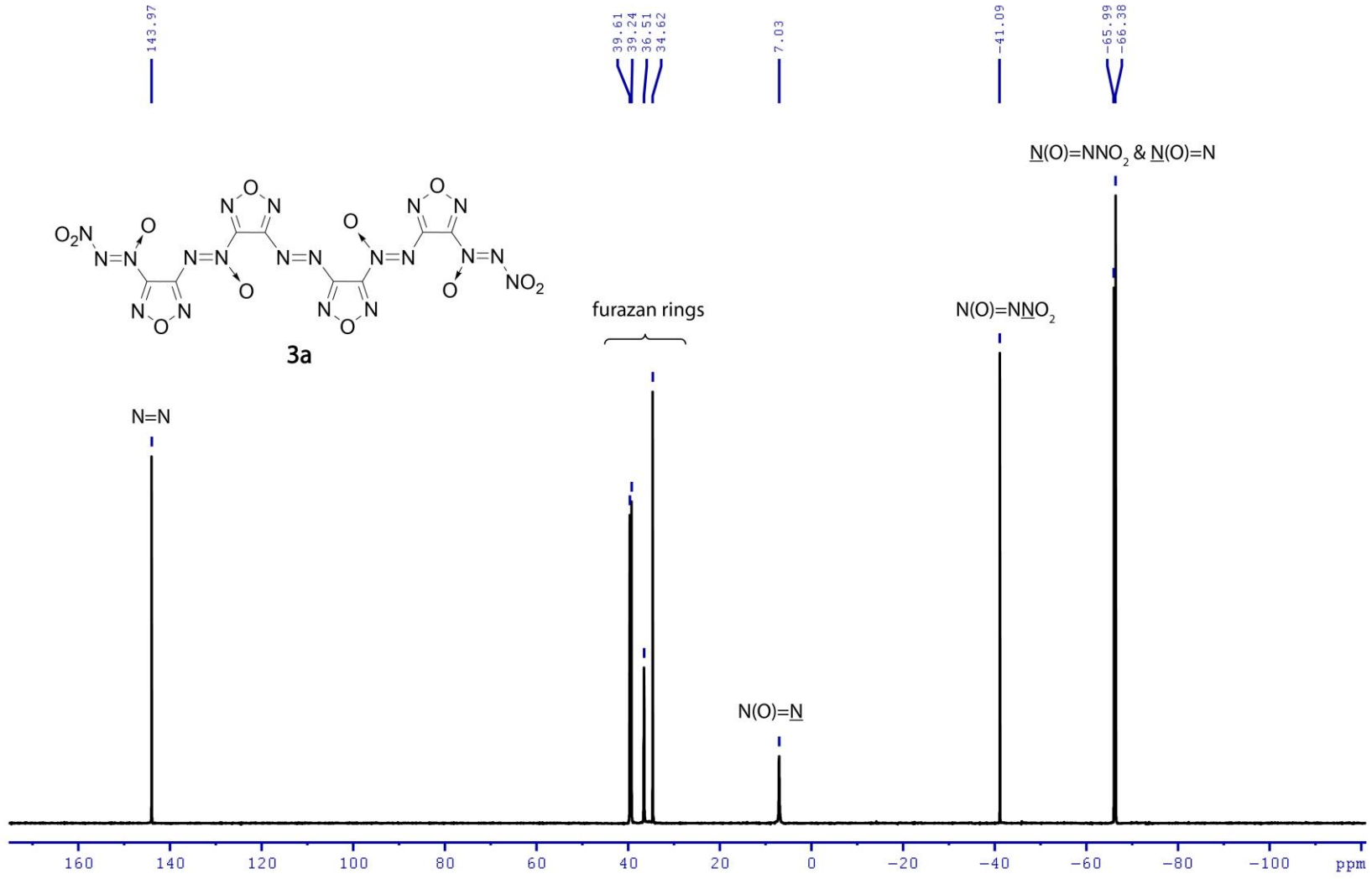


^{14}N NMR (43.4 MHz, [D$_6$]acetone) spectrum of compound 3a



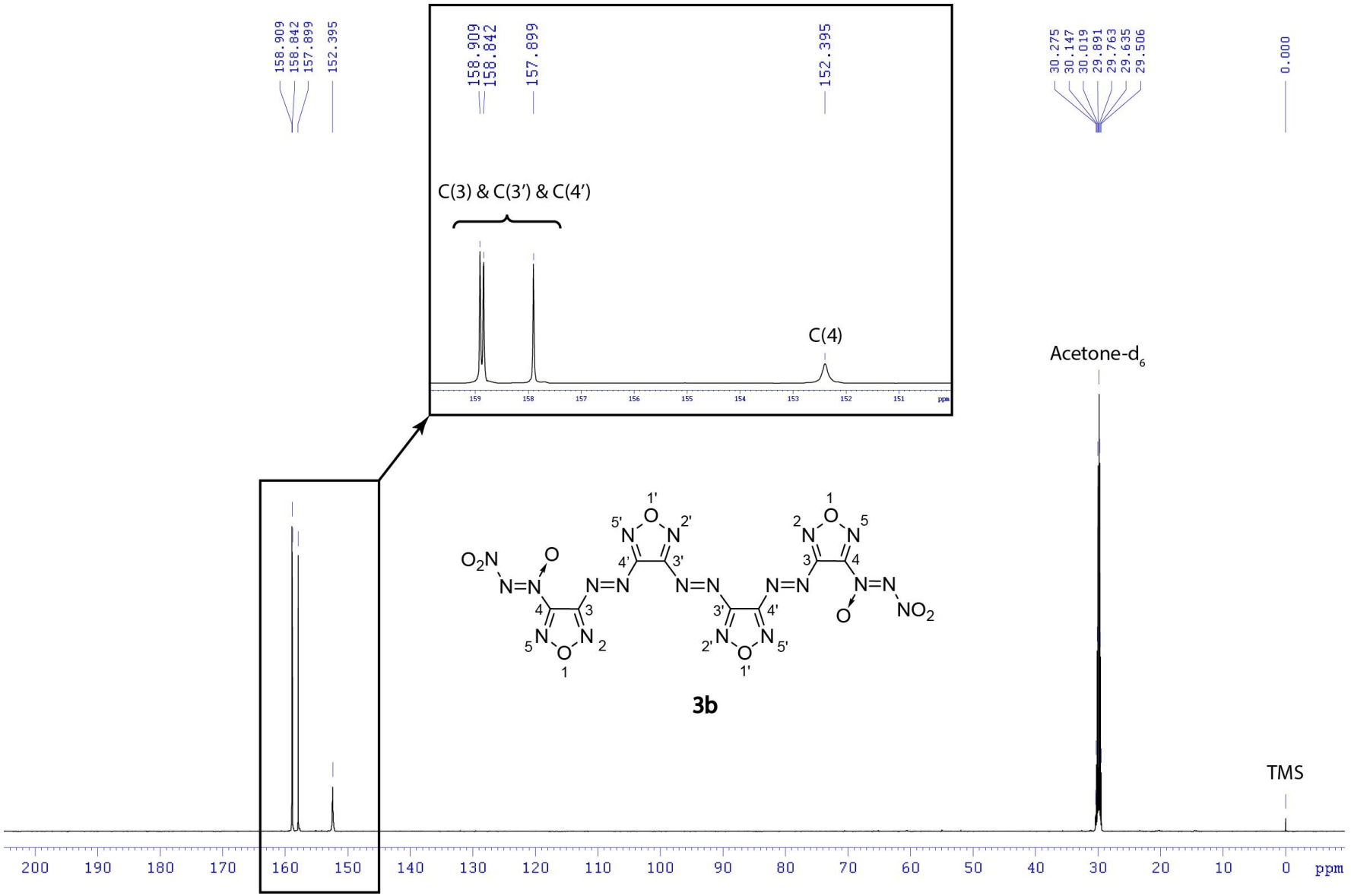
3a

^{15}N NMR ([INVGATED], 60.8 MHz, [D$_6$]acetone) of compound 3a

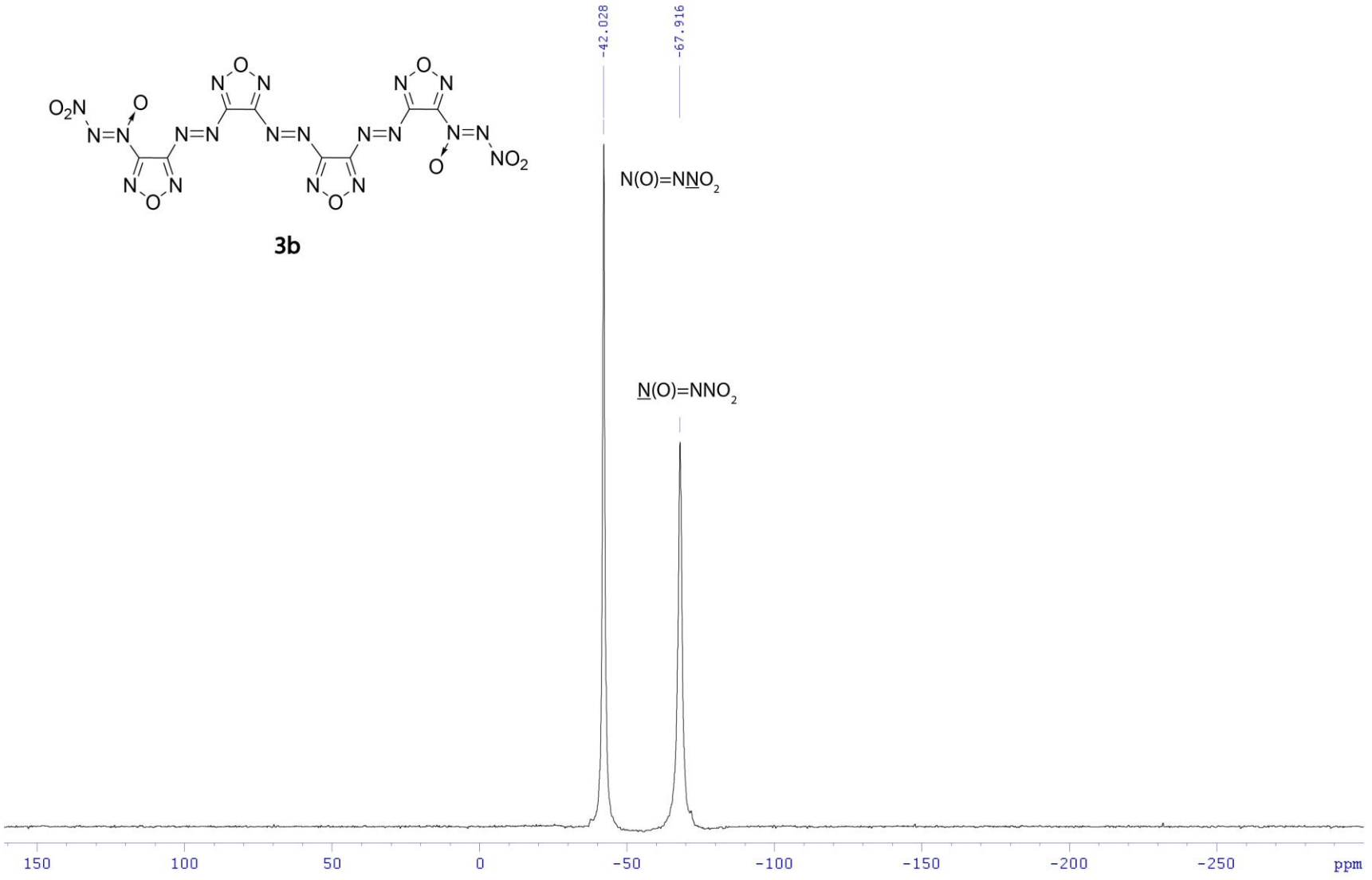


3a

^{13}C NMR (150.9 MHz, [D$_6$]acetone) spectrum of compound 3b

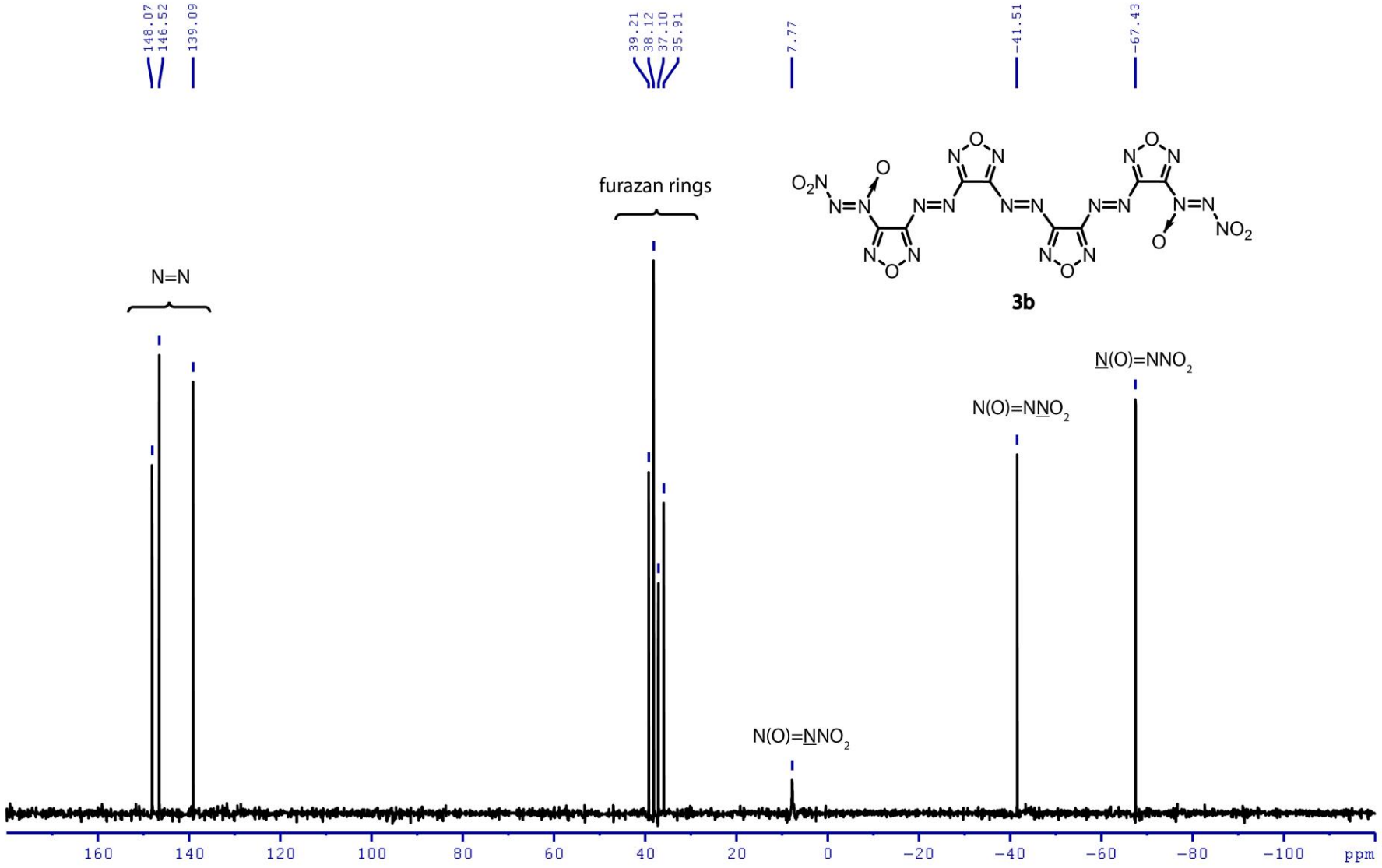


^{14}N NMR (43.4 MHz, [D$_6$]acetone) spectrum of compound 3b

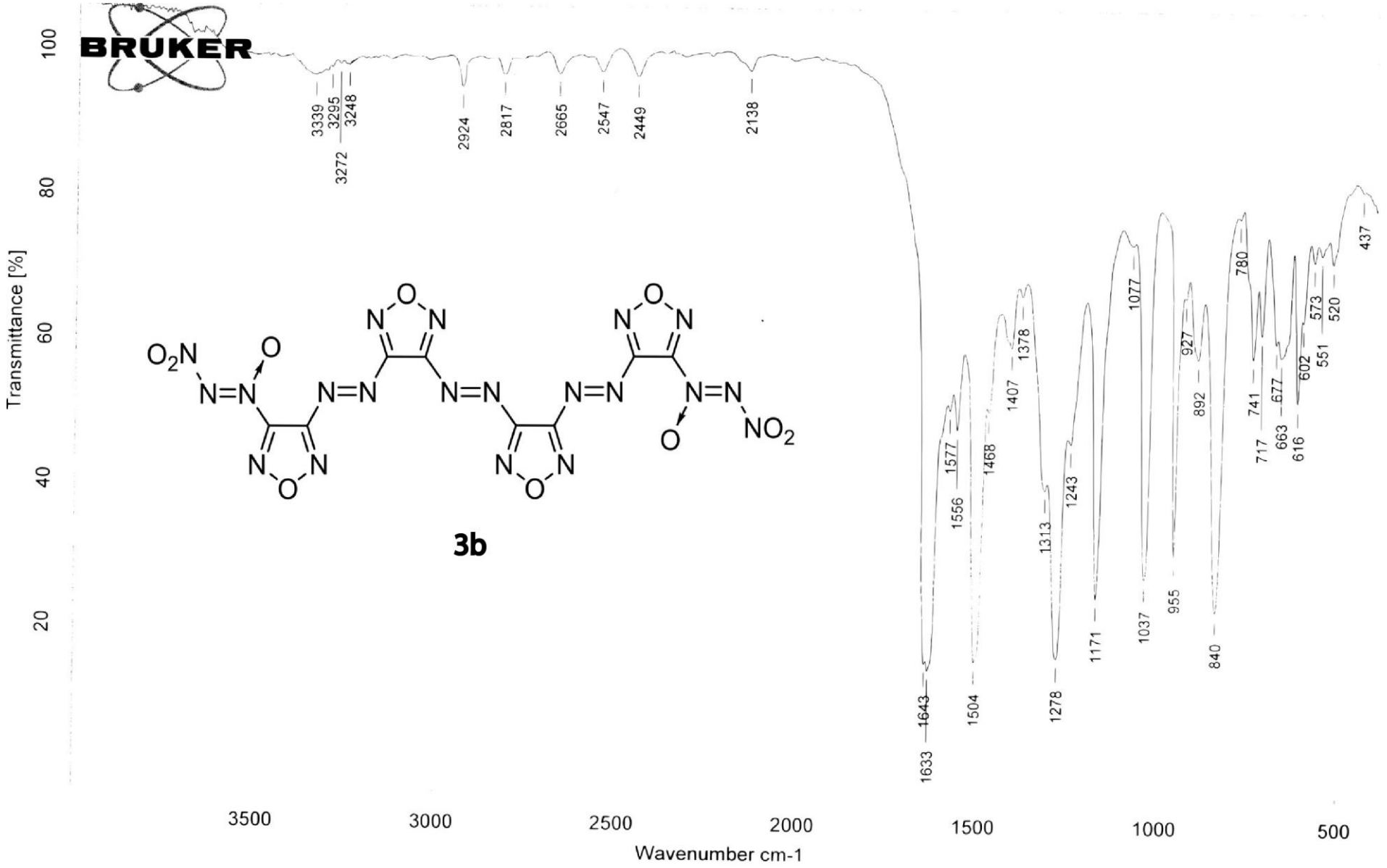


3b

^{15}N NMR ([INVGATED], 60.8 MHz, [D$_6$]acetone) of compound 3b



IR of compound 3b



3b

X -ray crystal structure determination

X-ray powder diffraction measurements were performed on a Bruker AXS D8 diffractometer (CuKα, λ =1.534 Å, reflection mode) equipped with a LynxEye position sensitive detector. Data collection was performed at ambient temperature with a step size of 0.02° and 1 s per step exposure for the 2θ range of 4–60°. Unit cell parameters were refined with a Pawley method using starting unit cell parameters taken from low-temperature single-crystal experiments. Final unit cell data are provided in Table S2, and fits are shown in Figures S1 and S2.

Table S2 Unit cell parameters and crystal density for compounds **2a** and **2b** determined by powder diffraction at room temperature (~298 K)

Compound	**2a**	**2b**
Space group	$P2_1/n$	$C2/c$
Z / Z'	4 / 1	8 / 1
a, Å	11.7874(4)	15.4497(17)
b, Å	5.2236(2)	7.4855(7)
c, Å	17.3785(6)	17.7812(19)
β, °	98.504(2)	96.856(5)
V, Å^3	1058.28(6)	2041.7(4)
d, g·cm^{-1}	1.796	1.758

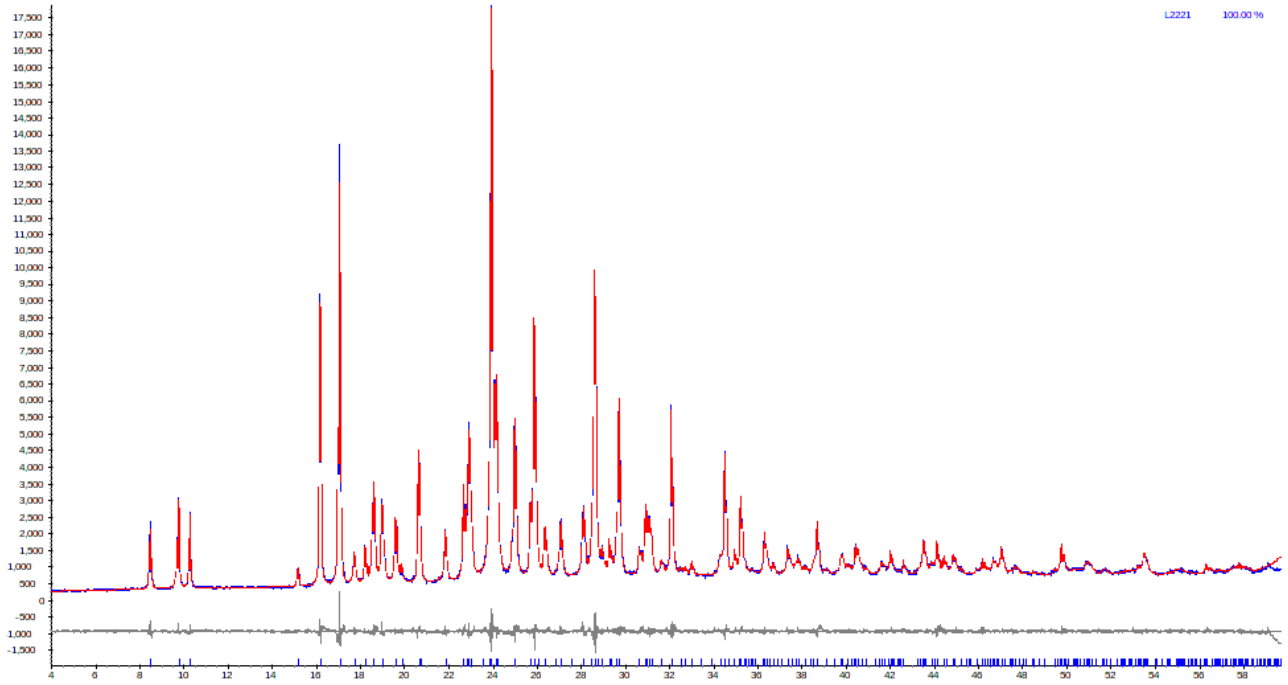


Figure S1 Pawley fit of PXRD data for aminofurazan **2a** (Rwp = 4.7).

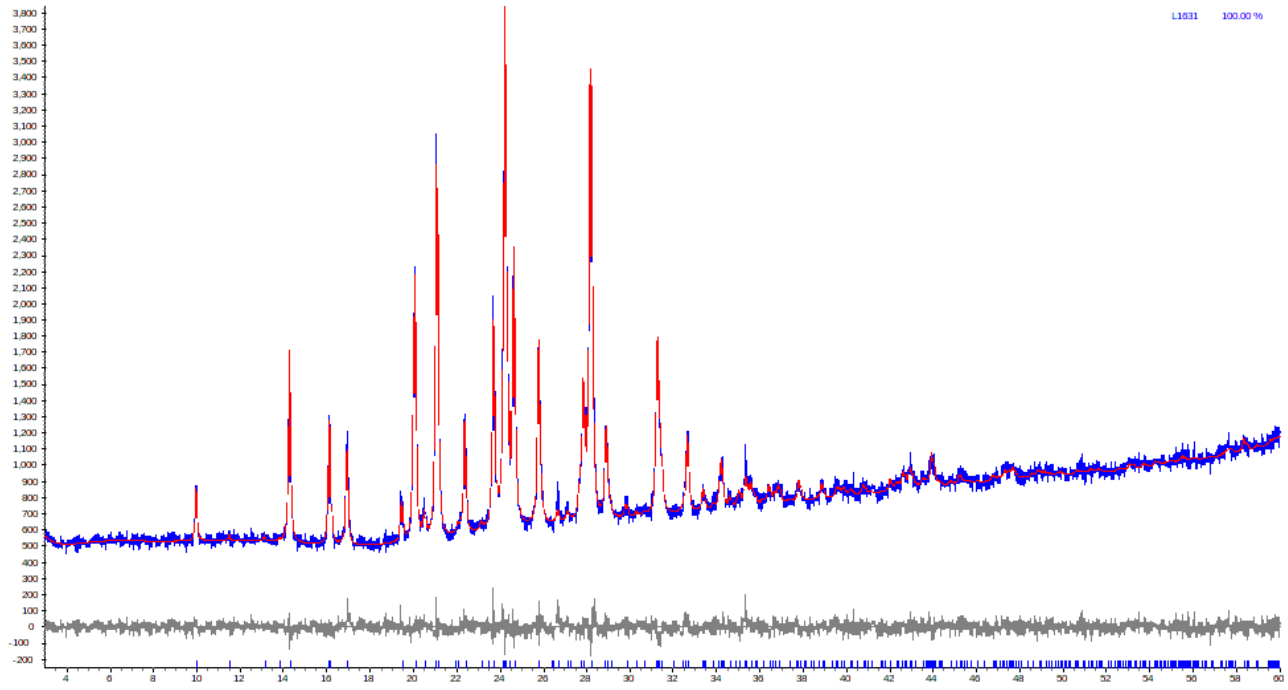


Figure S2 Pawley fit of PXRD data for aminofurazan **2b** (Rwp = 4.0).

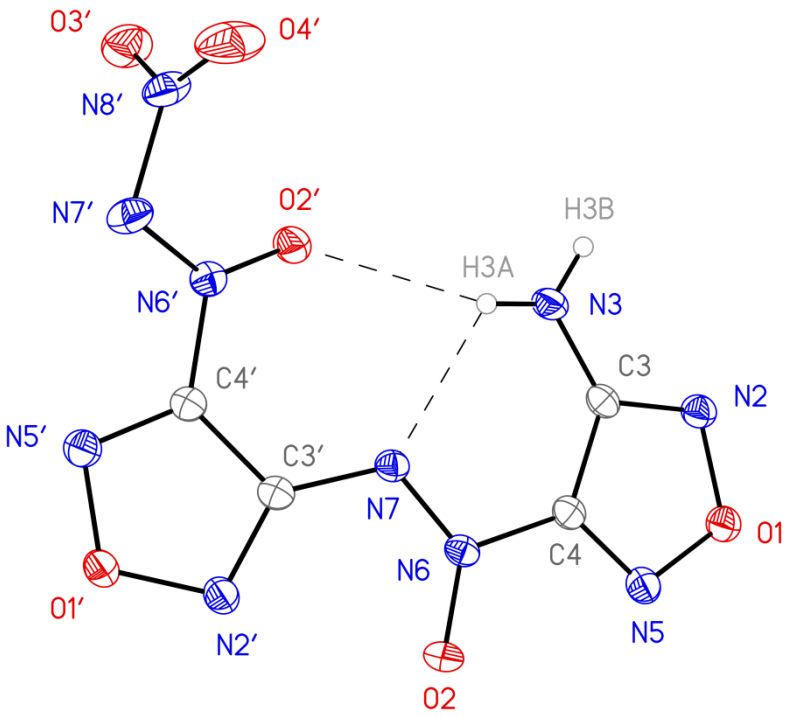


Figure S3 General view of aminofurazan **2a** in a crystal; non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50%)

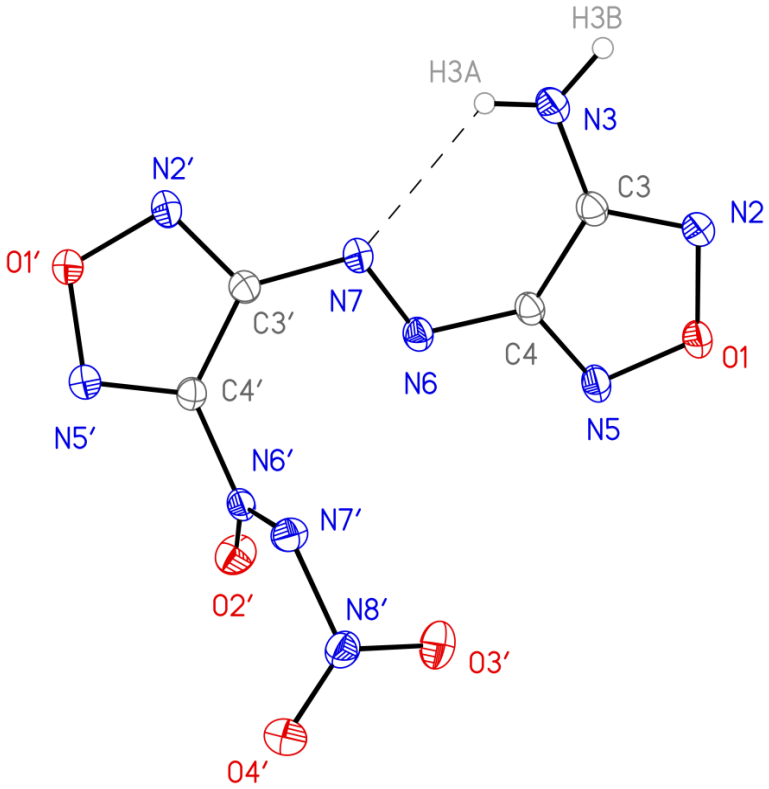
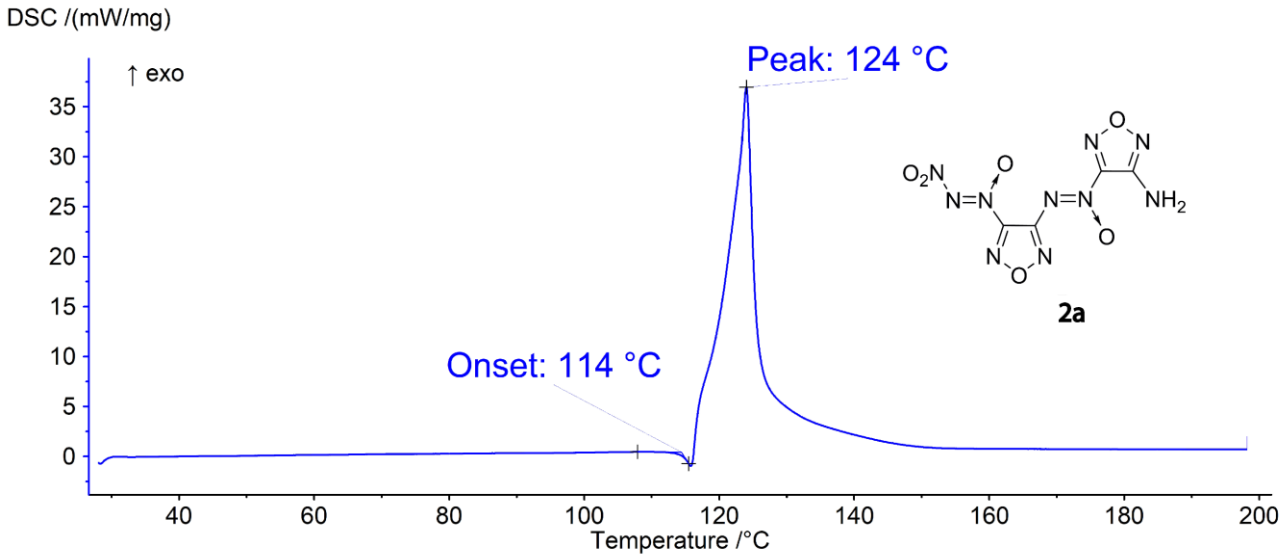
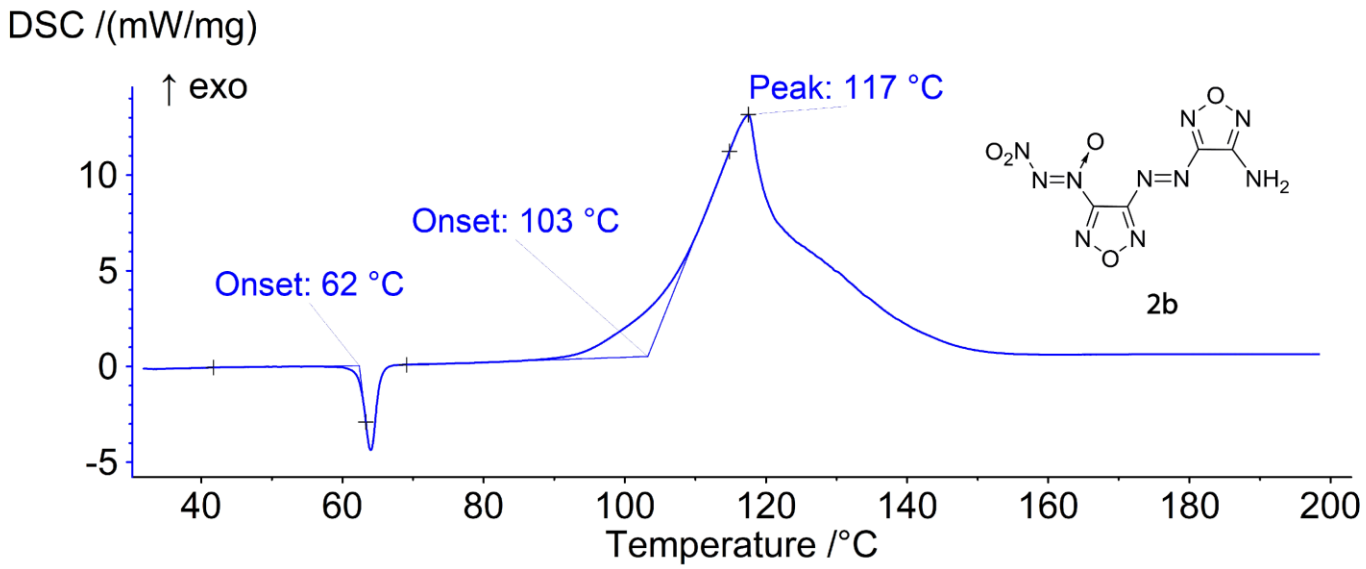


Figure S4 General view of aminofurazan **2b** in a crystal; non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50%)

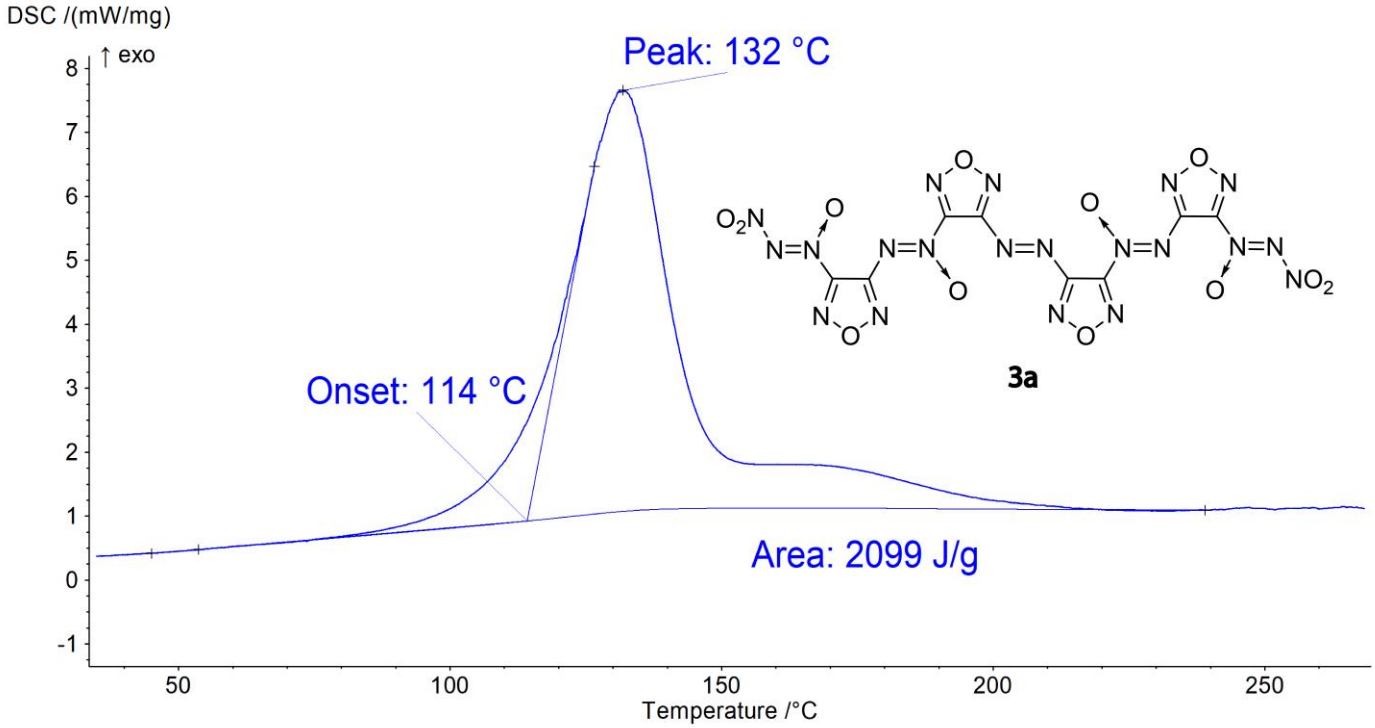
DSC of compound 2a



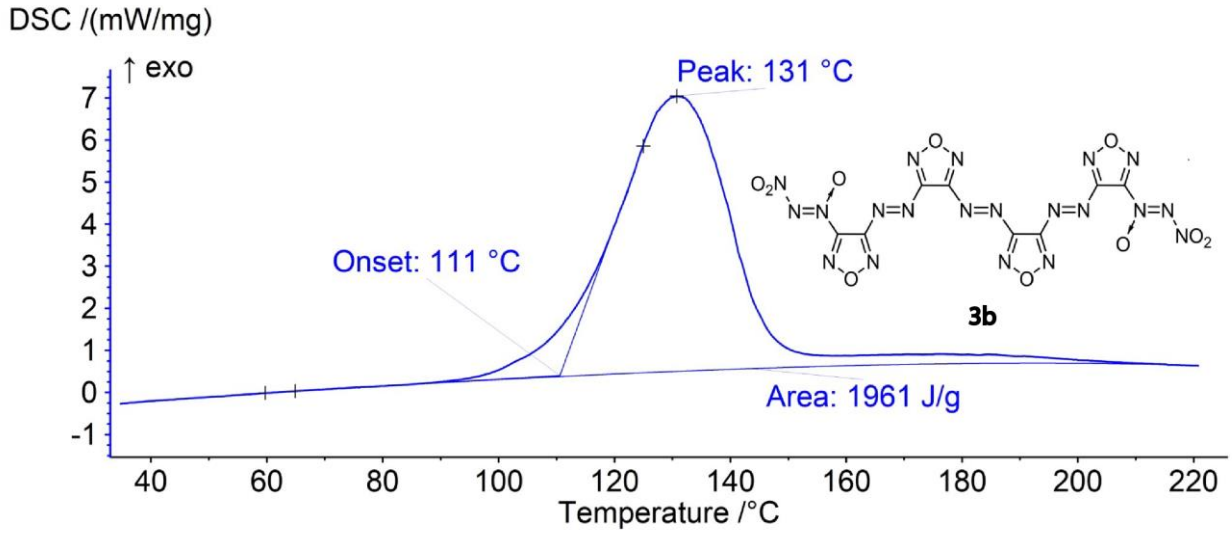
DSC of compound 2b



DSC of compound 3a



DSC of compound 3b



Calorimetric measurements

The main method for determining the enthalpy of formation of energetic compounds is combustion calorimetry. The measurements were performed on a precision automatic combustion calorimeter with an isothermal shell (designed by the Laboratory of Thermodynamics of High-Energy Systems of the Federal Research Center of Chemical Physics named after N. N. Semenov of the Russian Academy of Sciences for the combustion of energetic compounds).[5]

Basic design features of the calorimeter used in this study: 1) small heat equivalent (~500 cal·degree^{-1}) with a large volume of bomb (200 cm^3); 2) simple installation bomb calorimeter – just remove the cap shell and the calorimetric vessel, drop the bomb and close the cover; 3) continuously thermostatic shell; 4) permanently fixed to the sheath liquid hermetic calorimeter vessel is in the form of a glass with double walls (calorimeter constant volume of fluid that delivers constant heat equivalent); 5) low measurement error. The calorimeter allows you to measure the thermal effect of the combustion reaction of substances with an extended uncertainty of 0.01–0.02%. Calibration of the calorimeter was carried out with the reference benzoic acid of the K-1 brand produced by the D. I. Mendeleev Institute of Metrology. The combustion energy of benzoic acid under standard conditions was 6322.6±1.2 cal·g^{-1}. The absence of a systematic error in calorimetric measurements was controlled by burning secondary reference substances-succinic and hippuric acids, whose combustion energies on this calorimeter were 3020.3±0.6 cal·g^{-1} (0.02%) and 5631.4±3.4 cal·g^{-1} (0.06%), respectively. Samples of the studied substance **2a** were burned in a platinum crucible. Pressed tablets of substances were weighed on Bunge microanalytic scales with an error of $2\cdot10^{-6}$ g. The suspended sample of the substance was placed in a calorimetric bomb and filled with oxygen. The initial oxygen pressure during the combustion of all substances is about 30 atm (3 MPa). Before the experiment, 1 mL of distilled water was injected into the bomb to create a saturated vapor pressure and dissolve the nitrogen oxides formed during the combustion process.

The samples were ignited with a cotton thread, which in turn was ignited by incandescent platinum wire (diameter 0.3 mm) with a dosed pulse of current supplied from a special device. The combustion energy of cotton yarn was measured in a series of seven experiments and amounted to 3968.9 ±1.6 cal·g^{-1}. When determining the combustion energy, corrections for the thermal effects of nitric acid formation, heat exchange of a calorimetric vessel with an isothermal shell, and the combustion energy of the auxiliary substance and cotton thread were taken into account. A detailed procedure for preparing samples and conducting an incineration experiment was described earlier.[6]

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5 Ya. O. Inozemtsev, A. B. Vorob'ev, A. V. Inozemtsev and Yu. N. Matyushin, *Combustion and Explosion (Gorenie i vzryv)*, 2014, **7**, 260.

6 T. S. Kon'kova, Yu. N. Matyushin, E. A. Miroshnichenko and A. B. Vorob'ev, *Russ. Chem. Bull.*, 2009, **58**, 2020.

The combustion energy ($-\Delta U'_B$, cal·g^{-1}) under calorimetric bomb conditions for the studied compound **2a** is given in Table S3.

Table S3 Results of determination of the combustion energy of the compound **2a**

Entry	*m*, g	ΔT, °C	*Q*, cal	q_a, cal	q_i, cal	q_N, cal	q_{cot}, cal	$-U'_B$, cal·g^{-1}
1	0.089855	1.96147	1054.47	836.72	7.30	3.15	8.54	2212.0
2	0.076293	2.05002	1102.07	914.60	7.19	2.68	8.97	2210.3
3	0.069981	1.91603	1030.04	856.60	7.18	2.44	9.17	2209.9
4	0.088054	2.07715	1116.66	902.04	7.27	3.15	9.01	2216.7
5	0.084344	2.06564	1110.47	905.13	7.29	3.02	8.55	2210.9
$-\Delta U'_B = 2212.0 \pm 3.2$ cal·g^{-1}								

N – the ordinal number of the experiment;

m – weight of the sample of the compound in vacuum, g;

ΔT – corrected temperature rise in the calorimeter, degrees;

Q – the amount of heat measured in the experiment, cal;

q_a – heat of the combustion of the auxiliary substance benzoic acid, cal;

q_i – ignition energy, cal;

q_N − correction for the formation of nitric acid, cal;

q_{cot} − heat generation from combustion of the cotton thread, cal;

$\Delta U'_B$ − combustion energy of a substance in the bomb, cal·g^{-1}.

Calculation of the standard enthalpies of combustion and formation of compound 2a

Reaction of combustion of compound **2a** proceeds in accordance with the stoichiometry presented by equation (I):

$$C_4H_2N_{10}O_{6(cr)} + 1.5O_{2(g)} = 4CO_{2(g)} + H_2O_{(l)} + 5N_{2(g)} \qquad (I),$$

where the subscripts cr, g, and l correspond to the crystalline, gaseous, and liquid states, respectively, in this and subsequent equations.

The enthalpy of formation of the studied compound for the standard state was calculated from the corresponding enthalpy of combustion in accordance with the stoichiometry of the reaction (I):

$$\Delta H^\circ_f[C_4H_2N_{10}O_6]_{(cr)} = 4\Delta H^\circ_f[CO_2]_{(g)} + \Delta H^\circ_f[H_2O]_{(l)} - \Delta H^\circ_c \qquad (II),$$

where ΔH°_c – the standard enthalpy of combustion of the compound **2a**, kcal·mol^{-1}, and ΔH°_f – the standard enthalpy of its formation, kcal·mol^{-1}.

$\Delta H^\circ_c = -627.3 \pm 0.9$ kcal·mol^{-1};

$\Delta H^\circ_f [C_4H_2N_{10}O_6]_{(cr)} =$ **182.8 ± 0.9** kcal·mol^{-1}.

When calculating the standard enthalpy of formation of the studied compound **2a**, the reference values of the enthalpies of formation of combustion products were used:

$\Delta H^\circ_f[CO_2]_{(g)} = -94.051 \pm 0.031$ kcal·mol^{-1} and

$\Delta H^\circ_f[H_2O]_{(l)} = -68.315 \pm 0.009$ kcal·mol^{-1}.[7]

Calculation of the enthalpies of combustion and formation of compound 2b

The enthalpies of combustion and formation of compound **2b** (Table S4) were calculated by an additive method using the contributions values of functional groups to the enthalpy of combustion. The contribution value of the 3-aminofurazanyl moiety (–259.5 kcal·mol^{-1}) was calculated using the enthalpy of formation of 3,4-diaminofurazan ($\Delta H°_f$ = +24.8 kcal·mol^{-1})[8] and the "contribution" to the enthalpy of combustion of amino group (NH_2) (–90 kcal·mol^{-1}). The latter was calculated from the thermochemical data

7 J. D. Cox, D. D. Wagman and V. A. Medvedev Eds., *CODATA key values for thermodynamics. Final Report of the CODATA Task Group on Key Values for Thermodynamics*, New York, Washington, Philadelphia, London, 1989.

8 Yu. N. Matyushin, V. P. Lebedev, *Proceedings of 28th International Annual Conference of ICT*, 1997, p. 98.

on amino derivatives of benzene.[9] The contribution value of the azo group (–98 kcal·mol^{-1}) was calculated using thermochemical data on azobenzene[10] and the enthalpy of formation of benzene (+11.72 kcal·mol^{-1}).[11] The contribution value of 4-(nitro-*NNO*-azoxy)furazanyl moiety (–284 kcal·mol^{-1}) was calculated using the experimentally measured enthalpy of combustion of compound **2a** (–627.3 ± 0.9 kcal·mol^{-1}) and the contribution value of the azoxy group to the enthalpy of combustion (–84.0 kcal·mol^{-1}). The latter was calculated from the experimental thermochemical characteristics of the known compound 3-nitro-4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazan.[12]

Table S4 Thermochemical characteristics in the standard state of compounds **2a** and **2b**

Compound	$-\Delta U'_B$	ΔH°_c	ΔH°_f
	cal·g^{-1}	kcal·mol^{-1}	kcal·mol^{-1}
2a	2212.0 ± 3.2	–627.3 ± 2.0	182.8 ± 2.0
2b	–	–641.5*	197.0*

* – calculated values

9 J. B. Pedley, *Thermochemical data and structures of organic compounds*, 1st edn., vol. 1, Thermodynamic Research Center, CRC Press, Texas, USA, 1994.
10 D. R. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
11 J. D. Cox and G. Pilcher, *Thermodynamics of Organic and Organometallic Compounds*, Academic Press, London, 1970.
12 D. A. Gulyaev, M. S. Klenov, A. M. Churakov, Yu. A. Strelenko, I. V. Fedyanin, D. B. Lempert, E. K. Kosareva, T. S. Kon'kova,Yu. N. Matyushin and V. A. Tartakovsky. *RSC Adv.*, 2021, **11**, 24013.

Combustion performance

Energy potential of aminofurazans 2a and 2b as energetic fillers for solid composite propellants (SCP)

The effectiveness of aminofurazans **2a** and **2b** as energetic fillers for SCP has been studied. Being high-enthalpy compounds (enthalpies of formation above 2500 kJ kg^{-1}), they are most effective for creating SCP compositions that do not contain metals and their hydrides. Compared to known energetic fillers such as **RDX**, **HMX** and **CL-20**, the enthalpies of formation of compounds **2a** and **2b** are much higher. The oxygen content in aminofurazan **2a** is the same as in **RDX** and **HMX**, and lower than in **CL-20**. The hydrogen content in compounds **2a** and **2b** is significantly lower than in **RDX**, **HMX**, and **CL-20**. The densities of aminofurazans **2a** and **2b** are lower than the densities of **RDX**, **HMX**, and **CL-20**.

For a correct comparison of the effectiveness of aminofurazans **2a** and **2b** with **RDX**, **HMX**, and **CL-20**, binary compositions containing the investigated component and an active binder (**AB**) with a volume content of the latter 18% were considered. If the volume fraction of the binder is below 18 vol.%, the processing of the propellant mass is difficult, while if it is higher, almost always this leads to a decrease in the energy parameters.

We considered as an active binder (**AB**) the composition, consisting of polyvinylmethyltetrazole plasticized with a mixture of nitroglycerin with a phlegmatizer (molecular formula of **AB** is $C_{18.962}H_{34.64}N_{19.157}O_{29.317}$, enthalpy of formation is –757 kJ·kg^{-1}, density 1.49 g·cm^{-3}).[13]

The main parameter describing the energy properties of SCP is the specific impulse (I_{sp}). It was calculated at pressures in the combustion chamber of 4.0 MPa and at the nozzle exit section of 0.1 MPa using the TERRA standard code for calculating high-temperature chemical equilibria,[14] which is used in a wide range of papers to evaluate I_{sp} values of various formulations.

Table S5 represents the results of calculating the values of the specific impulse (I_{sp}), density (ρ) and combustion temperature (T_c) of model formulations of SCPs containing one of the energetic fillers + **AB** (18 vol.%).

13 D. Lempert, G. Nechiporenko, G. Manelis, *Cent. Eur. J. Energ. Mater.*, 2006, **4**, 73.
14 B. G. Trusov, *"Program System TERRA for Simulation Phase and Thermal Chemical Equilibrium", XIV Int. Symp. on Chemical Thermodynamics*, St-Petersburg, 2002, p. 483.

Table S5 Specific impulse (I_{sp}), density (ρ) and combustion temperature (T_c) of binary compositions: energetic filler + **AB** (18 vol.% or 13.8–15.7 w.%)

Energetic filler		AB,	I_{sp}, s	ρ,	T_c, K
compound	w.%	w.%		g·cm^{-3}	
2a	84.6	15.4	**262.7**	1.744	3665
2b	84.3	15.7	**260.9**	1.711	**3635**
CL-20	86.2	13.8	255.7	1.944	3455
RDX	84.75	15.25	251.1	1.757	3175
HMX	85.3	14.7	250.9	1.831	3180

The calculation results show that the model composition of SCP based on aminofurazan **2a** in terms of specific impulse (I_{sp}) is ~2 s higher than the similar composition based on aminofurazan **2b**, and is 7–12 s higher than compositions based on known components (RDX, HMX, and CL-20) (see Table S5, Figure S5). The composition of SCP based on compound **2b** has a specific impulse 5–10 s higher than that of similar compositions based on **RDX**, **HMX**, and **CL-20**.

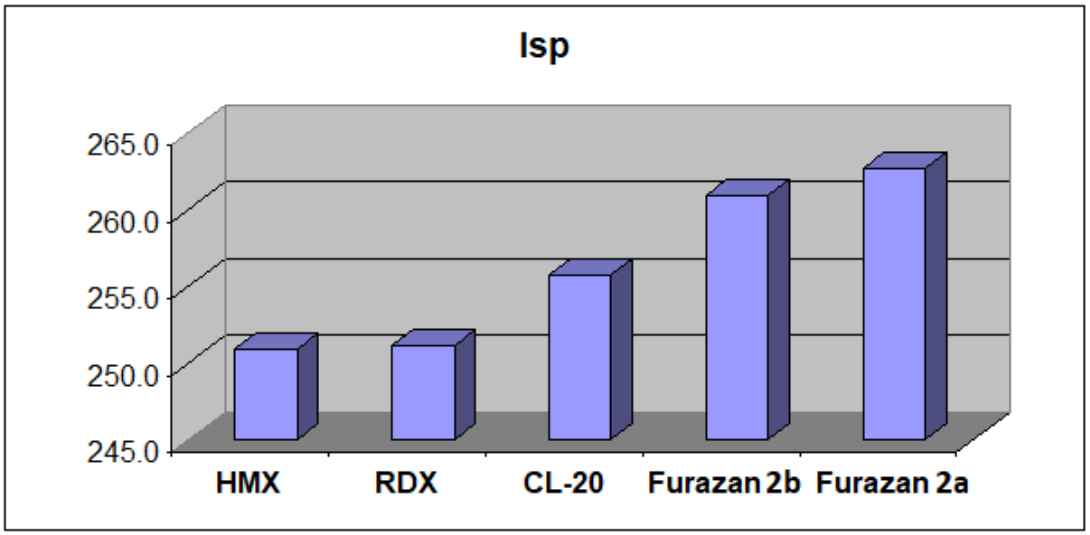

Figure S5 Relative efficiency of aminofurazans **2a** and **2b**, **RDX**, **HMX**, and **CL-20** as energetic fillers of SCP.

Note that the replacement of a part of compound **2a** (the oxidizer excess coefficient (α) of compound **2a** is equal 0.67 as in **HMX** and **RDX**) in the model composition of SCP with oxidizers – ammonium perchlorate (**AP**) or ammonium dinitramide (**ADN**) while maintaining the volume fraction of the active binder leads to a decrease in the specific impulse. A similar replacement of a part of compound **2b** (the oxidizer excess coefficient α = 0.56) in the composition with **AP** leads to a decrease in the specific impulse; replacing it with **ADN** (5–15%) only slightly (by 0.2–0.4 s) increases the I_{sp}, and a further increase in the proportion of **ADN** (above 20–25%) decreases I_{sp}.