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Novel (1*H*-tetrazol-5-yl-*NNO*-azoxy)furazans and their energetic salts: synthesis, characterization and energetic properties

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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 DRX-500 (500.1, 125.8, 36.1, 50.7 MHz, respectively) and 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. 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·min^{-1} rate up to 400 °C. The impact and friction sensitivities of compounds **3a,b** were determined using a STANAG protocol and BAM-type impact and friction machines.[1,2] Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F254 aluminum sheets. *Solvents were purified* before use, according to standard procedures. All other reagents were used without further purification. 3-Amino-4-(2-cyano-1-oxidodiazenyl)furazan **5** and 3-amino-4-{2-[4-(2-cyano-1-oxidodiazenyl)furazan-3-yl]-1-oxidodiazenyl}-furazan **6** were prepared according to the reported procedures.[3]

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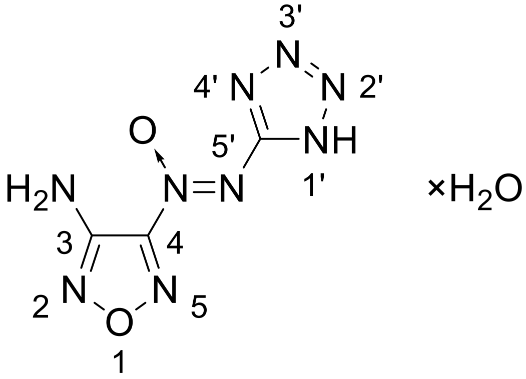
[1] STANAG 4489, Explosives, Impact Sensitivity Tests, 1st ed., NATO standardization agreement, NATO, Brussels (Belgium), 1999.

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

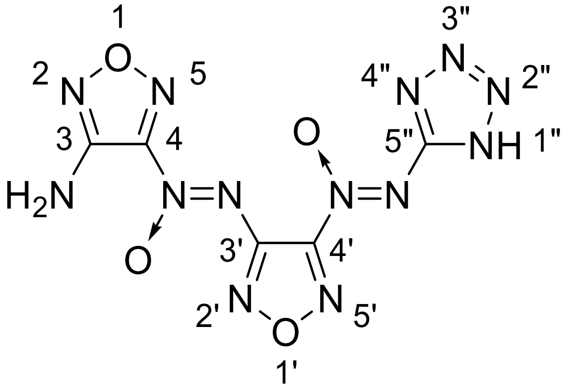
[3] N. E. Leonov, F. M. Sidorov, M. S. Klenov, A. M. Churakov, Yu. A. Strelenko, A. N. Pivkina, I. V. Fedyanin, D. B. Lempert, T. S. Kon’kova, Yu. N. Matyushin and V. A. Tartakovsky, *Mendeleev Commun.*, 2021, **31**, 792.

3-Amino-4-(1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan monohydrate 1·H_2O. Sodium azide (234 mg, 3.6 mmol) was added to a suspension of (cyano-*NNO*-azoxy)furazan **5** (462 mg, 3.0 mmol) in H_2O (8 ml) at 25 °C. The mixture was warmed to 50 °C and stirred at this temperature for 4.5 h (TLC monitoring, eluent – EtOAc/MeOH, 5 : 1). Then H_2O (12 ml) was added and the mixture was acidified to pH ≈ 1 with 10% aqueous HCl solution at 25 °C. The precipitate was filtered off, washed with water (4×10 ml), and dried under reduced pressure to give tetrazole **1**·H_2O (433 mg, 67%) as yellow fine-crystalline powder. The combined filtrate was extracted with ethyl acetate (5×50 ml). The combined extract was washed with water (25 ml), brine (25 ml), dried with $MgSO_4$ and concentrated under reduced pressure at 35 °C. The residue was dissolved in ethyl acetate (6 ml) and petroleum ether (6 ml) was added. The resulting precipitate was collected by filtration, washed with petroleum ether (2×5 ml), and dried under reduced pressure to give an additional amount of tetrazole **1** (136 mg, 21%). DSC (5 °C·min^{-1}): T_{onset} = 183 °C (dec.).



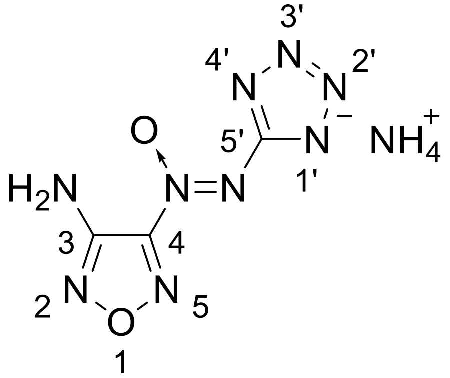
^1H NMR (600.1 MHz, [D$_6$]acetone): δ = 6.62 (br. s, 2 H, NH_2), 5.57 (br. s, 1 H, NH) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]acetone): δ = 152.0 (C-3), 152.5 (br., C-4), 155.0 (C-5') ppm. ^{14}N NMR (43.4 MHz, [D$_6$]acetone): δ = –67 ($\underline{N}$(O)=N, $\Delta\nu_{1/2}$ = 90 Hz), –341 (NH_2, $\Delta\nu_{1/2}$ = 790 Hz) ppm. ^1H NMR (600.1 MHz, [D$_6$]DMSO): δ = 6.91 (br. s, 2 H, NH_2), 8.39 (br. s, 1 H, NH) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]DMSO): δ = 151.2 (C-3), 151.8 (br., C-4), 154.6 (br., C-5') ppm. ^{14}N NMR (43.4 MHz, [D$_6$]DMSO): δ = –68 ($\underline{N}$(O)=N, $\Delta\nu_{1/2}$ = 380 Hz) ppm. ^{15}N NMR (60.8 MHz, [D$_6$]DMSO): δ = 29.0 (N-5), –2.8 (N-2), –8.0 (N-2'/N-3'), –67.9 ($\underline{N}$(O)=N), –77.4 (N-1'/N-4'), –333.1 (NH_2) ppm. IR (KBr): ν = 3626 (s), 3524 (s), 3418 (s), 3322 (s), 3258 (w), 3212 (w), 3173 (w), 1850 (w), 1634 (s), 1603 (m), 1521 (m), 1493 (m), 1466 (s), 1411 (m), 1372 (w), 1325 (w), 1236 (w), 1201 (m), 1117 (w) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_3H_3N_9O_2$ [M – H]$^-$ 196.0337; found 196.0333. Anal. calcd for $C_3H_5N_9O_3$: C 16.75, H 2.34, N 58.60, found C 16.80, H 2.36, N 58.47.

3-Amino-4-{[4-(1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan-3-yl]-*NNO*-azoxy}furazan 2. Sodium azide (78 mg, 1.2 mmol) was added to a suspension of (cyano-*NNO*-azoxy)furazan **6** (266 mg, 1.0 mmol) in H_2O (5 ml) at 25 °C. The mixture was warmed to 50 °C and stirred at this temperature for 2 h (TLC monitoring, eluent – EtOAc/MeOH, 5 : 1). Then H_2O (10 ml) was added and the mixture was acidified to pH ≈ 1 with 10% aqueous HCl solution at 25 °C. Yellow precipitate was filtered off, dissolved in ethyl acetate (6 ml) and petroleum ether (18 ml) was added. The resulting precipitate was collected by filtration, washed with petroleum ether (2 × 5 ml), and dried under reduced pressure to give tetrazole **2** (229 mg, 74%) as yellow fine-crystalline powder. DSC (5 °C·min^{-1}): T_{onset} = 147 °C (dec.).



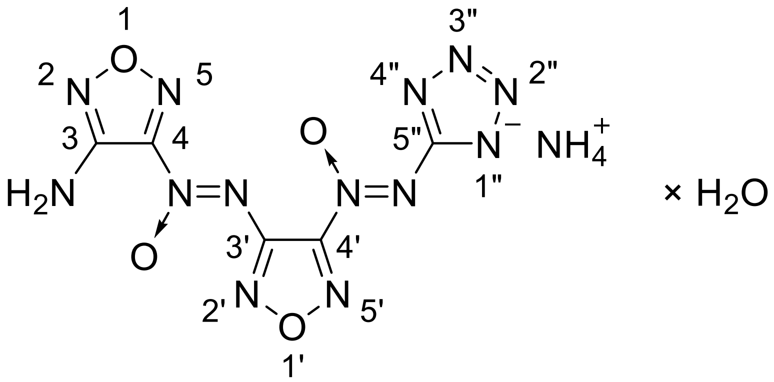
^{1}H NMR (600.1 MHz, [D$_6$]DMSO): δ = 7.19 (br. s, 2 H, NH_2) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]DMSO): δ = 148.6 (C-3 or C-3'), 151.0 (C-3' or C-3), 152.0 (br., C-4 or C-4'), 155.3 (br., C-5"), 155.5 (br., C-4' or C-4) ppm. ^{14}N NMR (43.4 MHz, [D$_6$]DMSO): δ = –60 (Fz–$\underline{N}$(O)=N–Fz, $\Delta\nu_{1/2}$ = 710 Hz), –71 (Fz–$\underline{N}$(O)=N–Tet, $\Delta\nu_{1/2}$ = 460 Hz) ppm. ^{15}N NMR (60.8 MHz, [D$_6$]DMSO): δ = 34.8, 31.7, 31.5 (N-5 and N-2' and N-5'), –0.8 (N-2), –59.5 (Fz–$\underline{N}$(O)=N–Fz), –70.0 (Fz–N(O)=$\underline{N}$–Fz or Fz–N(O)=$\underline{N}$–Tet), –73.5 (Fz–$\underline{N}$(O)=N–Tet), –82.3 (Fz–N(O)=$\underline{N}$–Fz or Fz–N(O)=$\underline{N}$–Tet), –331.4 (NH_2) ppm. IR (KBr): 3425 (s), 3276 (m), 3241 (m), 3193 (m), 3152 (m), 1634 (s), 1552 (w), 1510 (m), 1484 (m), 1460 (m), 1434 (w), 1415 (w), 1396 (w), 1384 (m), 1354 (w), 1215 (w), 1162 (w) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_5H_3N_{13}O_4$ [M + Na]$^+$ 332.0323; found 332.0319. Anal. calcd for $C_5H_3N_{13}O_4$: C 19.42, H 0.98, N 58.90, found C 19.44, H 0.99, N 58.78.

Ammonium salt of 3-amino-4-(1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan 3a. A 25% aqueous ammonia solution (0.2 ml, 188 mg, 2.76 mmol) in MeOH (1 ml) was added dropwise to a stirred suspension of (1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan **1** (495 mg, 2.30 mmol) in MeOH (4 ml) at 0 °C. The mixture was vigorously stirred at this temperature for 1 h. The precipitate was filtered off, washed with cold MeOH (2 × 2 ml), and dried under reduced pressure to give salt **3a** (168 mg, 34%) as yellow fine-crystalline powder. The combined filtrate was concentrated under reduced pressure, the residue was dissolved in boiling MeOH (5 ml). Then MeCN (25 ml) was added, and the solution was cooled to –20 °C. The precipitate was filtered off, washed with MeCN (5 ml), and dried under reduced pressure to give an additional amount of salt **3a** (197 mg, 40%). DSC (5 °C·min^{-1}): T_{onset} = 199 °C (dec.).



^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 6.82 (br. s, 2 H, NH$_2$), 7.46 (br. s, 4 H, NH$_4^+$) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 151.1 (C-3), 151.6 (br., C-4), 162.4 (br., C-5') ppm. ^{14}N NMR (36.1 MHz, [D$_6$]DMSO): δ = –81 ($\underline{\text{N}}$(O)=N, $\Delta\nu_{1/2}$ = 300 Hz), –358 (NH$_4^+$, $\Delta\nu_{1/2}$ = 10 Hz) ppm. ^{15}N NMR (60.8 MHz, [D$_6$]DMSO): δ = 23.9 (N-5), 14.6 (N-2'/N-3'), –6.0 (N-2), –58.1 (N(O)=$\underline{\text{N}}$ or N-1'/N-4'), –63.5 (N(O)=$\underline{\text{N}}$ or N-1'/N-4'), –82.0 ($\underline{\text{N}}$(O)=N), –334.3 (NH$_2$), –357.7 (NH$_4^+$) ppm. IR (KBr): ν = 3401 (m), 3240 (m), 3181 (m), 3050 (w), 2765 (m), 1678 (m), 1637 (s), 1625 (s), 1514 (s), 1484 (m), 1451 (s), 1429 (s), 1404 (s), 1337 (w), 1208 (m), 1178 (m), 1122 (w) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_3H_6N_{10}O_2$ [M – NH$_4$]$^-$ 196.0337; found 196.0339. Anal. calcd for $C_3H_6N_{10}O_2$: C 16.83, H 2.82, N 65.41, found C 16.84, H 2.82, N 65.32.

Ammonium salt of 3-amino-4-{[4-(1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan-3-yl]-*NNO*-azoxy}furazan monohydrate 4a·H$_2$O. A 25% aqueous ammonia solution (0.06 ml, 53 mg, 0.78 mmol) in MeOH (1 ml) was added dropwise to a stirred suspension of (1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan **2** (201 mg, 0.65 mmol) in MeOH (4 ml) at 0 °C. The mixture was vigorously stirred at this temperature for 1 h. The precipitate was filtered off, washed with cold MeOH (2 × 1 ml), and dried under reduced pressure to give salt **4a**·H$_2$O (143 mg, 64%) as yellow fine-crystalline powder. DSC (5 °C·min^{-1}): T_{onset} = 146 °C (dec.).



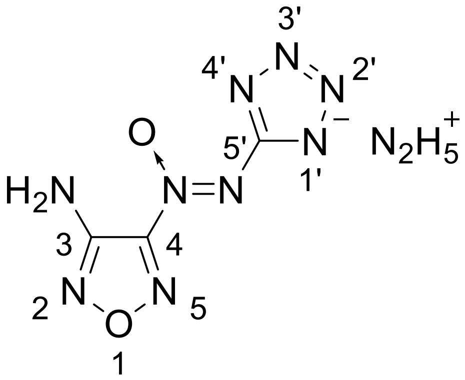
^{1}H NMR (600.1 MHz, [D$_6$]DMSO): δ = 7.22 (br. s, 2 H, NH$_2$), 7.36 (br. s, 4 H, NH$_4^+$) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]DMSO): δ = 148.8, 151.2, 152.0, 155.7 (furazan rings), 162.8 (C-5") ppm. ^{14}N NMR (43.4 MHz, [D$_6$]DMSO): δ = –59 (Fz–$\underline{\text{N}}$(O)=N–Fz, $\Delta\nu_{1/2}$ = 850 Hz), –85 (Fz–$\underline{\text{N}}$(O)=N–Tet, $\Delta\nu_{1/2}$ = 850

Hz), –358 (NH_4^+, Δ$\nu_{½}$ = 70 Hz) ppm. ^{15}N NMR (60.8 MHz, [D_6]DMSO): δ = 33.0, 31.2, 28.6 (N-5 or N-2' or N-5'), 16.2 (N-2''/N-3''), –1.0 (N-2), –55.2 (Fz–N(O)=$\underline{N}$–Fz or Fz–N(O)=$\underline{N}$–Tet or N-1''/N-4''), –57.7 (Fz–N(O)=$\underline{N}$–Fz or Fz–N(O)=$\underline{N}$–Tet or N-1''/N-4''), –59.8 (Fz–$\underline{N}$(O)=N–Fz), –79.4 (Fz–N(O)=$\underline{N}$–Fz or Fz–N(O)=$\underline{N}$–Tet or N-1''/N-4''), –87.9 (Fz–$\underline{N}$(O)=N–Tet), –331.1 (NH_2), –357.5 (NH_4^+) ppm. IR (KBr): 3644 (m), 3573 (m), 3440 (m), 3310 (w), 3203 (w), 3079 (w), 2872 (w), 1725 (w), 1646 (s), 1551 (w), 1515 (m), 1490 (s), 1450 (s), 1433 (m), 1413 (w), 1394 (m), 1361 (w), 1221 (w), 1193 (w), 1169 (w), 1156 (w) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_5H_6N_{14}O_4$ [M – NH_4]$^-$ 308.0358; found 308.0359. Anal. calcd for $C_5H_8N_{14}O_5$: C 17.45, H 2.34, N 56.97, found C 17.47, H 2.38, N 56.84.

General procedure for the synthesis of hydrazinium salts of (1*H*-tetrazol-5-yl-*NNO*-azoxy)furazans 3b,4b

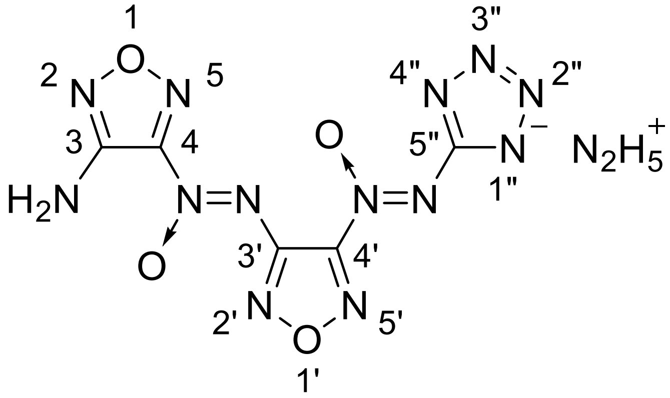
A 64% aqueous hydrazine solution (60 mg, 1.2 mmol) in MeOH (3 ml) was added dropwise to a stirred suspension of appropriate (1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan **1**,**2** (1.0 mmol) in MeOH (3 ml) at 0 °C. The mixture was stirred at this temperature for 1 h. The precipitate was filtered off, washed with methanol (2×2 ml), and dried under reduced pressure.

Hydrazinium salt of 3-amino-4-(1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan 3b. Yield 79%. Yellow fine-crystalline powder. DSC (5 °C·min^{-1}): T_{onset} = 177 °C (dec.).



^{1}H NMR (600.1 MHz, [D_6]DMSO): δ = 6.87 (br. s, 2 H, NH_2), 7.30 (br. s, 5 H, $N_2H_5^+$) ppm. ^{13}C NMR (150.9 MHz, [D_6]DMSO): δ = 151.2 (C-3), 151.6 (br., C-4), 162.5 (br., C-5') ppm. ^{14}N NMR (43.4 MHz, [D_6]DMSO): δ = –81 ($\underline{N}$(O)=N, Δ$\nu_{½}$ = 400 Hz), –331 ($N_2H_5^+$ & NH_2, Δ$\nu_{½}$ = 1430 Hz) ppm. ^{15}N NMR (60.8 MHz, [D_6]DMSO): δ = 24.1 (N-5), 13.9 (N-2'/N-3'), –5.9 (N-2), –59.5 (N(O)=$\underline{N}$ or N-1'/N-4'), –63.8 (N(O)=$\underline{N}$ or N-1'/N-4'), –81.5 ($\underline{N}$(O)=N), –331.2 ($N_2H_5^+$ or NH_2), –334.2 ($N_2H_5^+$ or NH_2) ppm. IR (KBr): ν = 3422 (s), 3310 (m), 3197 (m), 3141 (m), 3065 (m), 2801 (w), 2695 (w), 2615 (w), 1663 (s), 1633 (s), 1528 (w), 1511 (s), 1468 (s), 1433 (m), 1393 (s), 1206 (m), 1173 (m), 1130 (m) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_3H_7N_{11}O_2$ [M – N_2H_5]$^-$ 196.0337; found 196.0346. Anal. calcd for $C_3H_7N_{11}O_2$: C 15.72, H 3.08, N 67.23, found C 15.73, H 3.10, N 67.13.

Hydrazinium salt 3-amino-4-{[4-(1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan-3-yl]-*NNO*-azoxy}furazan 4b. Yield 67%. Yellow-orange fine-crystalline powder. DSC (5 °C·min^{-1}): T_{onset} = 149 °C (dec.).



^{1}H NMR (600.1 MHz, [D$_6$]DMSO): δ = 7.21 (br. s, 7 H, NH$_2$ & N$_2$H$_5^+$) ppm. ^{13}C NMR (150.9 MHz, [D$_6$]DMSO): δ = 148.8, 151.1, 152.2, 155.6 (furazan rings), 162.8 (C-5") ppm. ^{14}N NMR (43.4 MHz, [D$_6$]DMSO): δ = –59 (Fz–$\underline{\text{N}}$(O)=N–Fz, $\Delta\nu_{½}$ = 650 Hz), –88 (Fz–$\underline{\text{N}}$(O)=N–Tet, $\Delta\nu_{½}$ = 980 Hz), –333 (N$_2$H$_5^+$ & NH$_2$, $\Delta\nu_{½}$ = 1920 Hz) ppm. IR (KBr): 3424 (s), 3382 (m), 3314 (w), 3258 (m), 3165 (w), 3107 (w), 1637 (s), 1551 (w), 1518 (m), 1495 (m), 1445 (w), 1429 (w), 1410 (w), 1384 (m), 1355 (w), 1218 (w), 1194 (w), 1165 (w), 1153 (w) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_5H_7N_{15}O_4$ [M – N$_2$H$_5$]$^-$ 308.0358; found 308.0360. Anal. calcd for $C_5H_7N_{15}O_4$: C 17.60, H 2.07, N 61.58, found C 17.56, H 2.02, N 61.45.

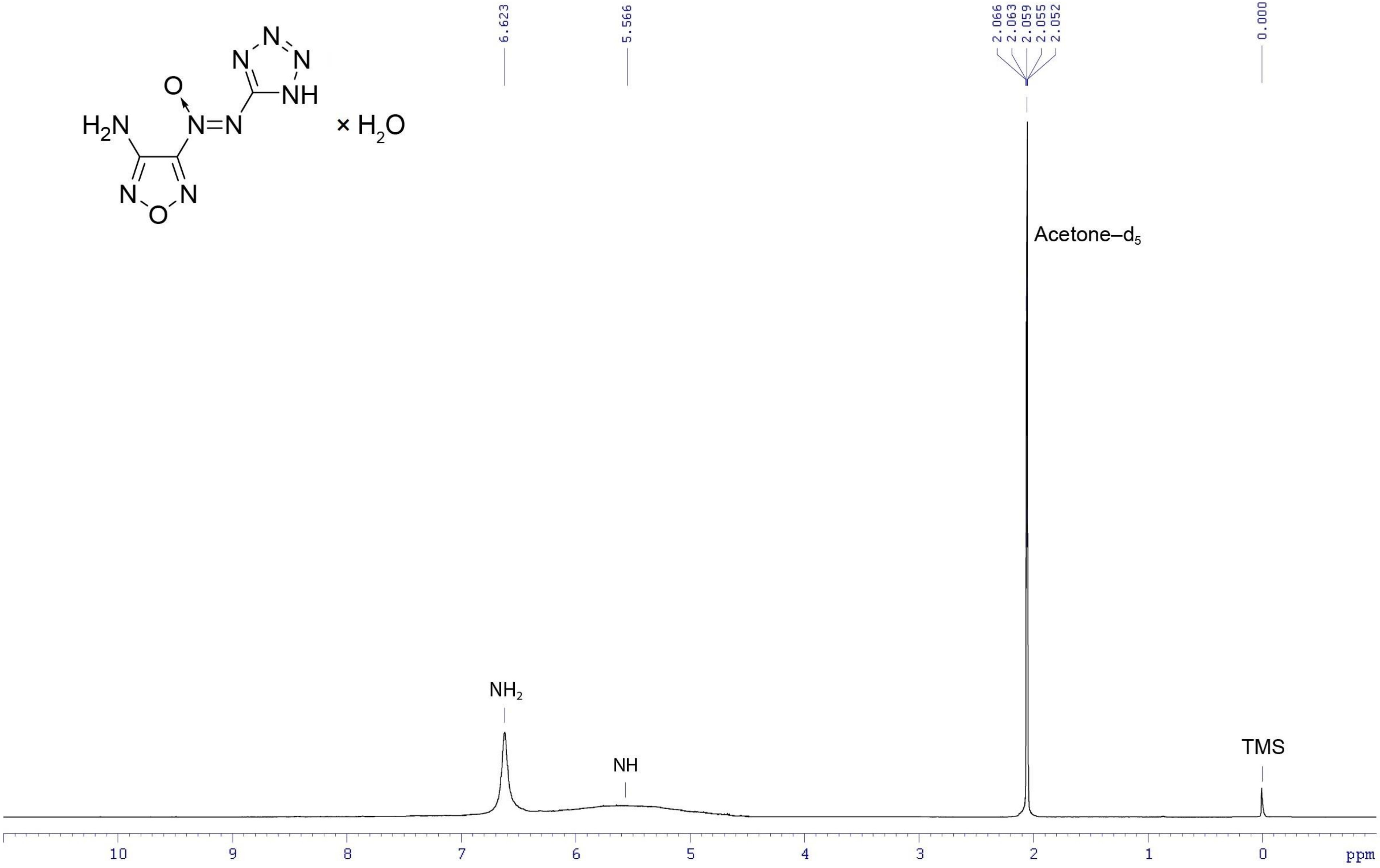
General procedure for the one-stage synthesis of ammonium salts of (1*H*-tetrazol-5-yl-*NNO*-azoxy)furazans 3a,4a

Trimethylsilyl azide (0.33 ml, 2.5 mmol) was added dropwise to a stirred solution of appropriate (cyano-*NNO*-azoxy)furazan **5** or **6** (1.0 mmol) in dry MeCN (5 ml) at 25 °C under an argon atmosphere, and then NH_4F (1.0 mmol) was added. The mixture was vigorously stirred at this temperature for 24 h. The precipitate was filtered off, washed with dry MeCN (3 × 5 ml), and dried under reduced pressure.

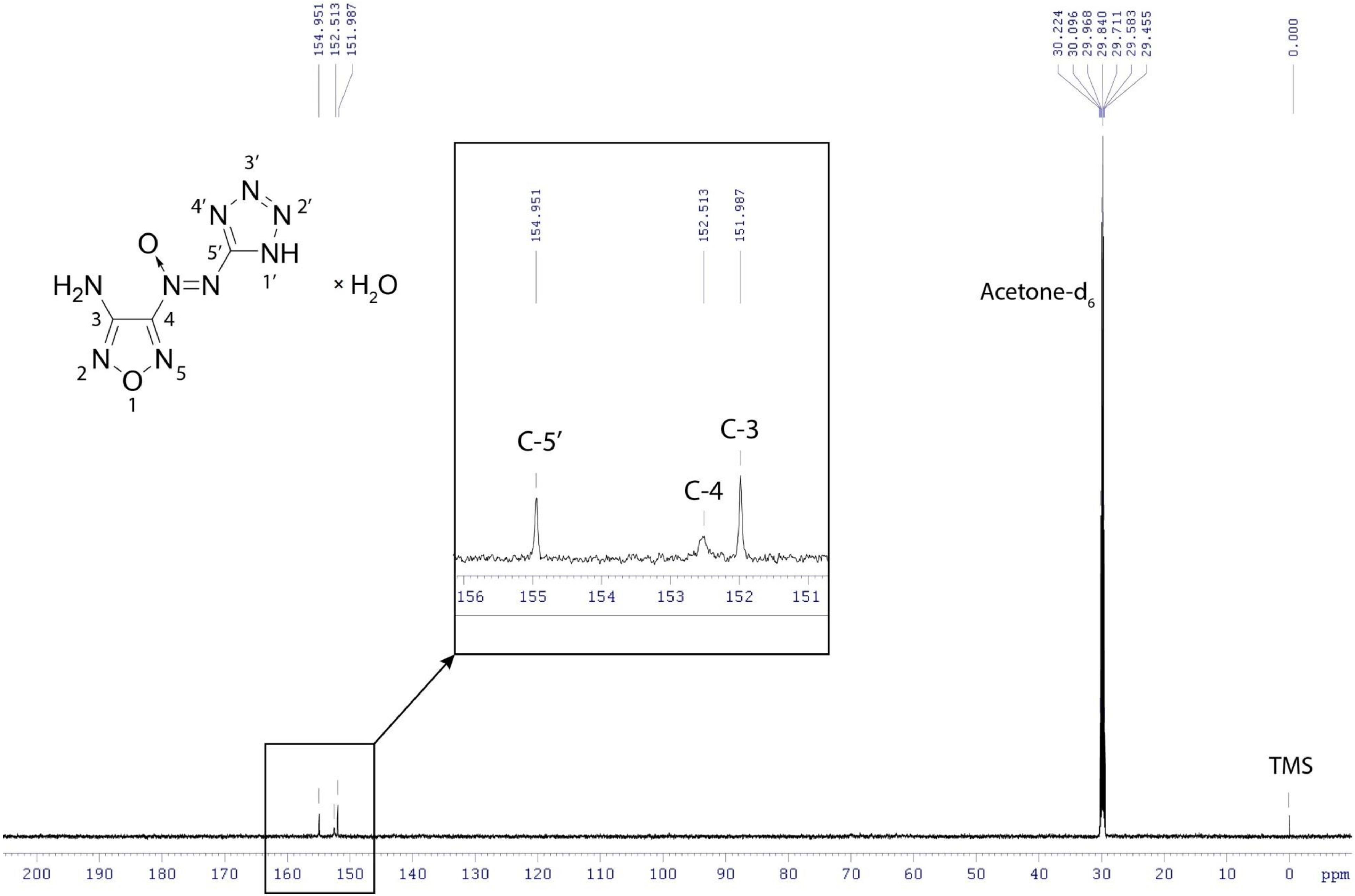
Ammonium salt of 3-amino-4-(1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan 3a. Compound **3a** (78%) was obtained as a yellow fine-crystalline powder, identical (^{1}H, ^{13}C NMR) to the product prepared according to the procedure above.

Ammonium salt of 3-amino-4-{[4-(1*H*-tetrazol-5-yl-*NNO*-azoxy)furazan-3-yl]-*NNO*-azoxy}furazan monohydrate 4a$\cdot H_2O$. Salt **4a**$\cdot H_2O$ (69%) was obtained as a yellow fine-crystalline powder, identical (^{1}H, ^{13}C NMR) to the product prepared according to the procedure above.

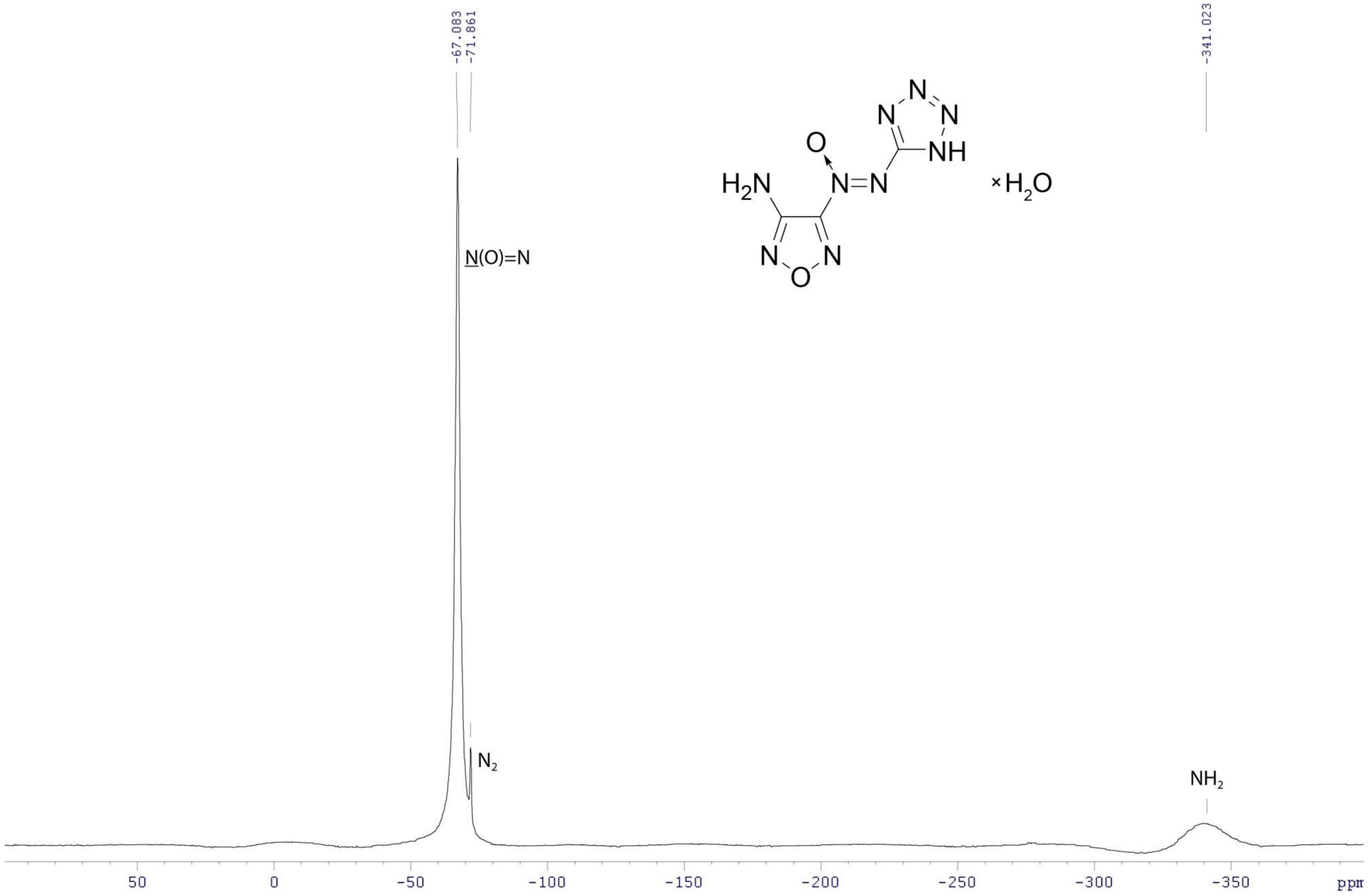
^{1}H NMR (600.1 MHz, [D$_6$]acetone) of tetrazole 1·H_2O



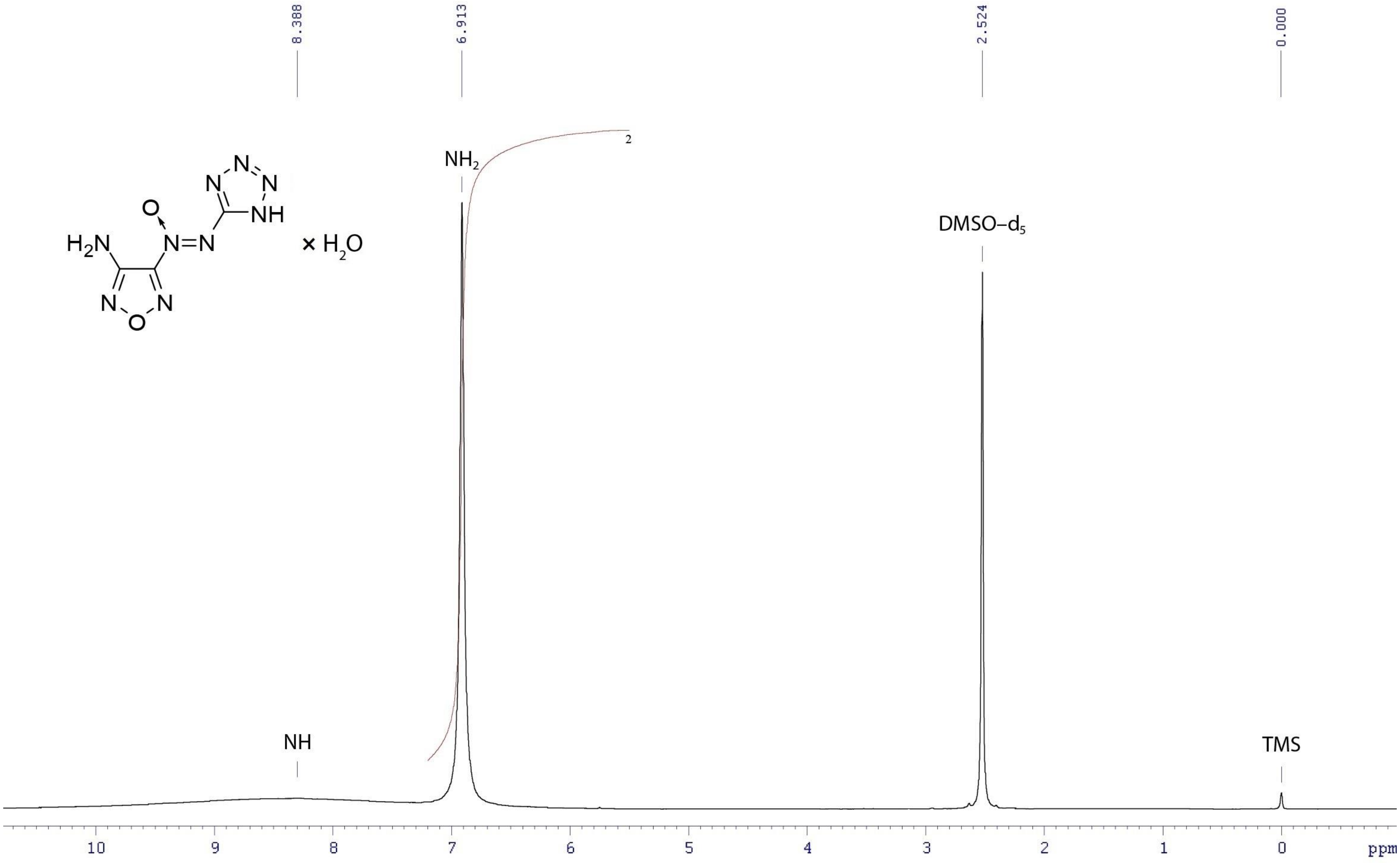
^{13}C NMR (150.9 MHz, [D$_6$]acetone) of tetrazole 1·H_2O



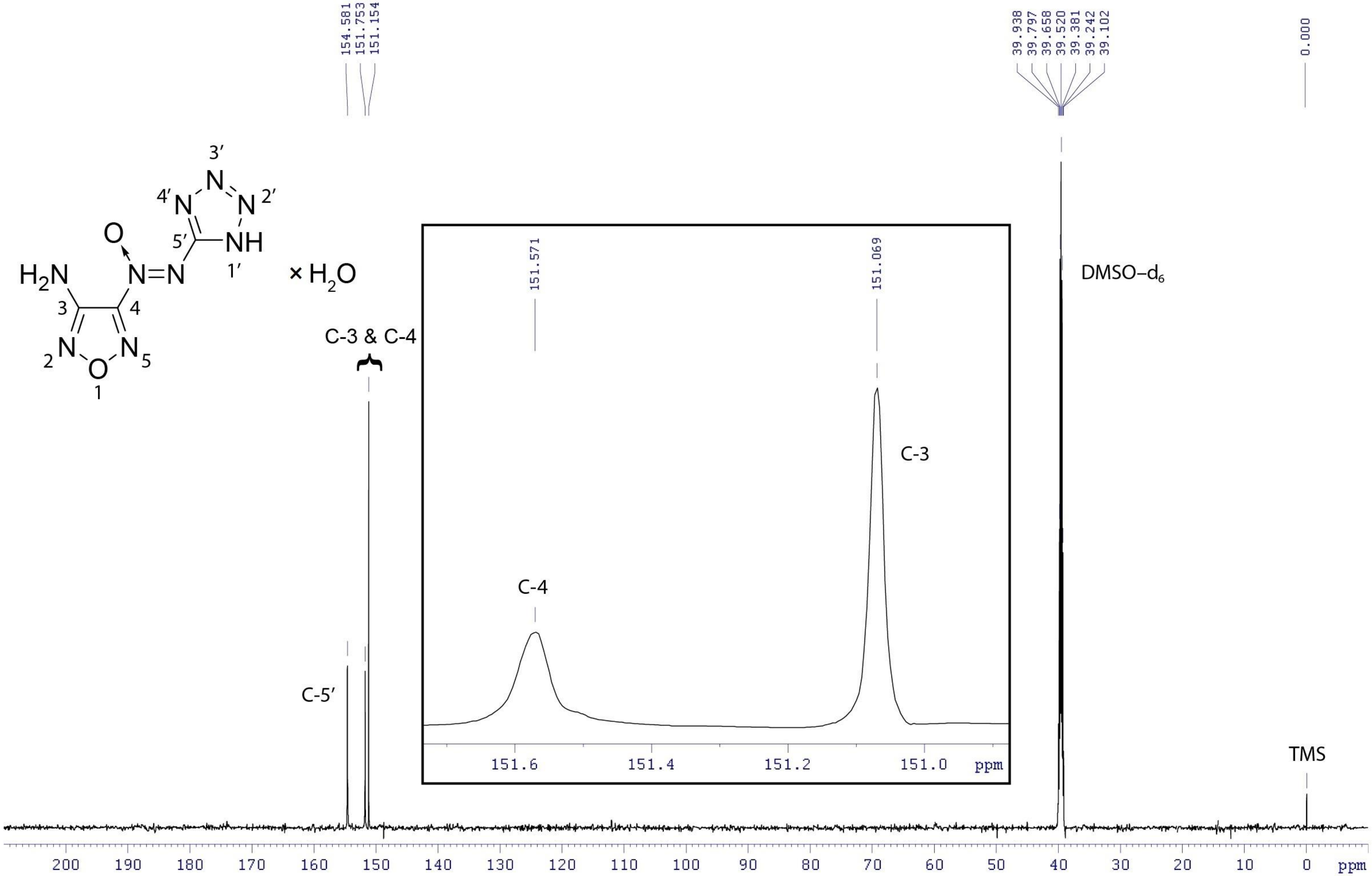
^{14}N NMR (43.4 MHz, [D$_6$]acetone) of tetrazole 1·H$_2$O



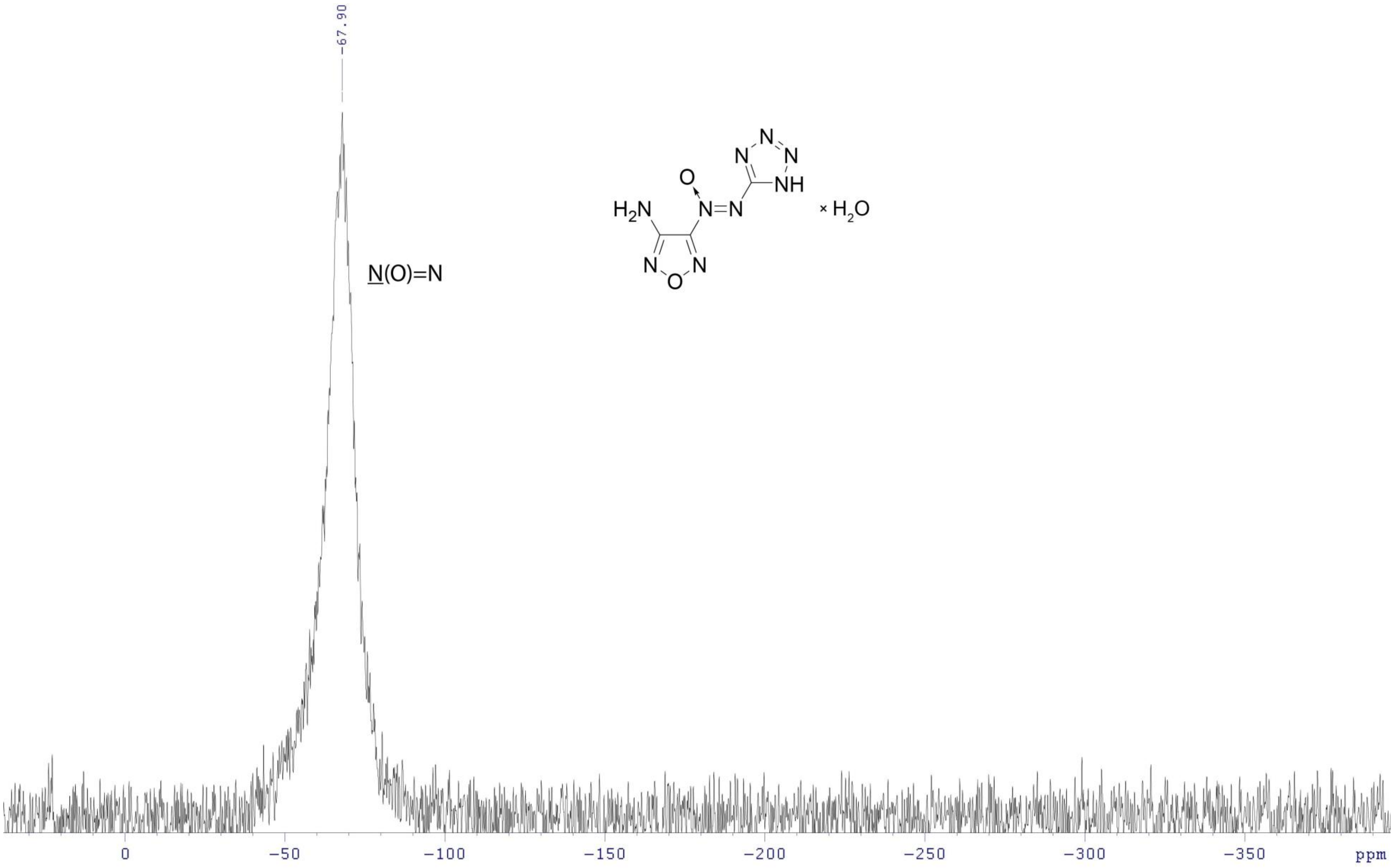
^{1}H NMR (600.1 MHz, [D_6]DMSO) of tetrazole 1·H_2O



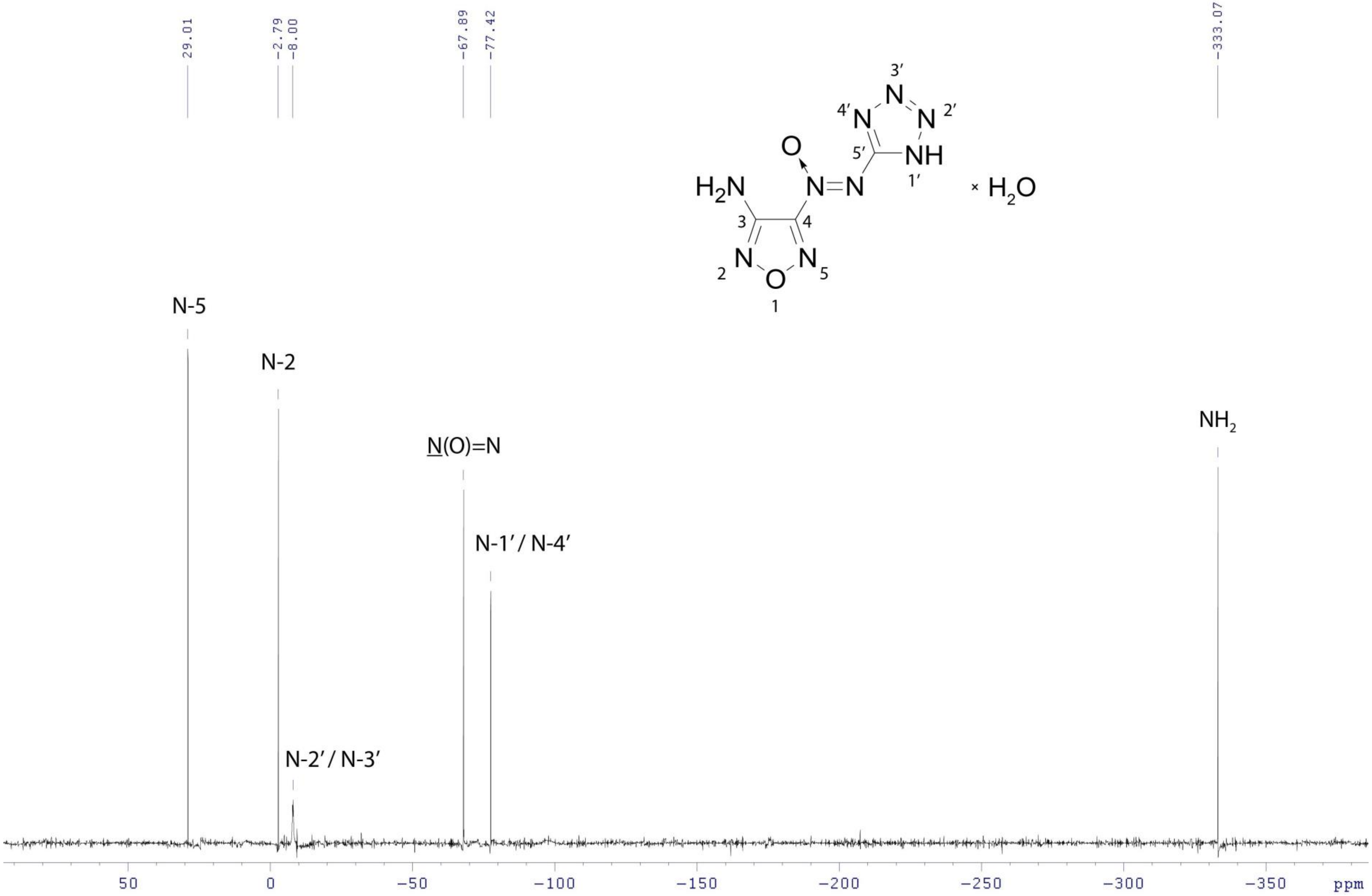
^{13}C NMR (600.1 MHz, [D$_6$]DMSO) of tetrazole 1·H$_2$O



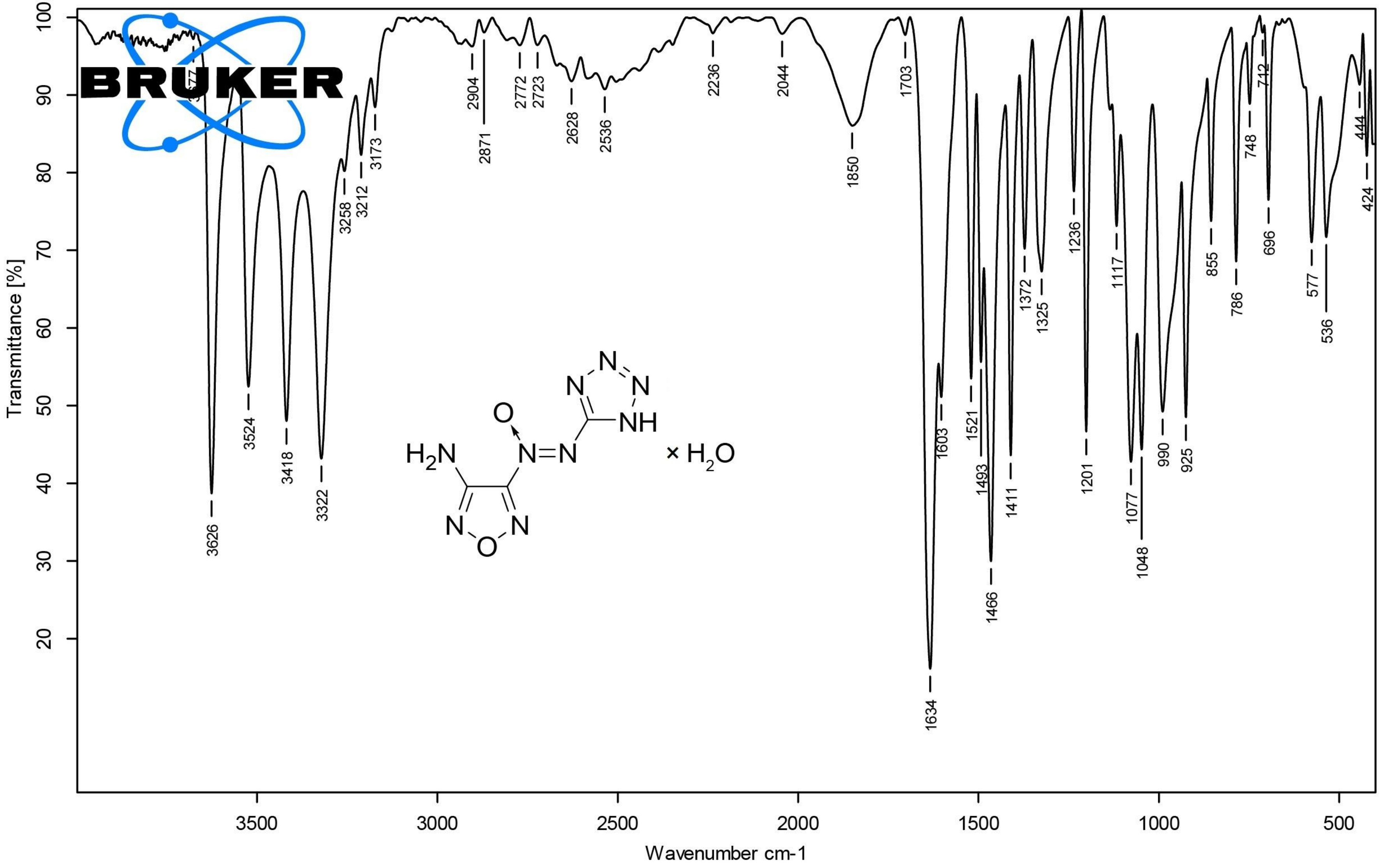
^{14}N NMR (600.1 MHz, [D_6]DMSO) of tetrazole 1·H_2O



^{15}N NMR ([INVGATED}, 60.8 MHz, [D$_6$]DMSO) of tetrazole 1·H$_2$O



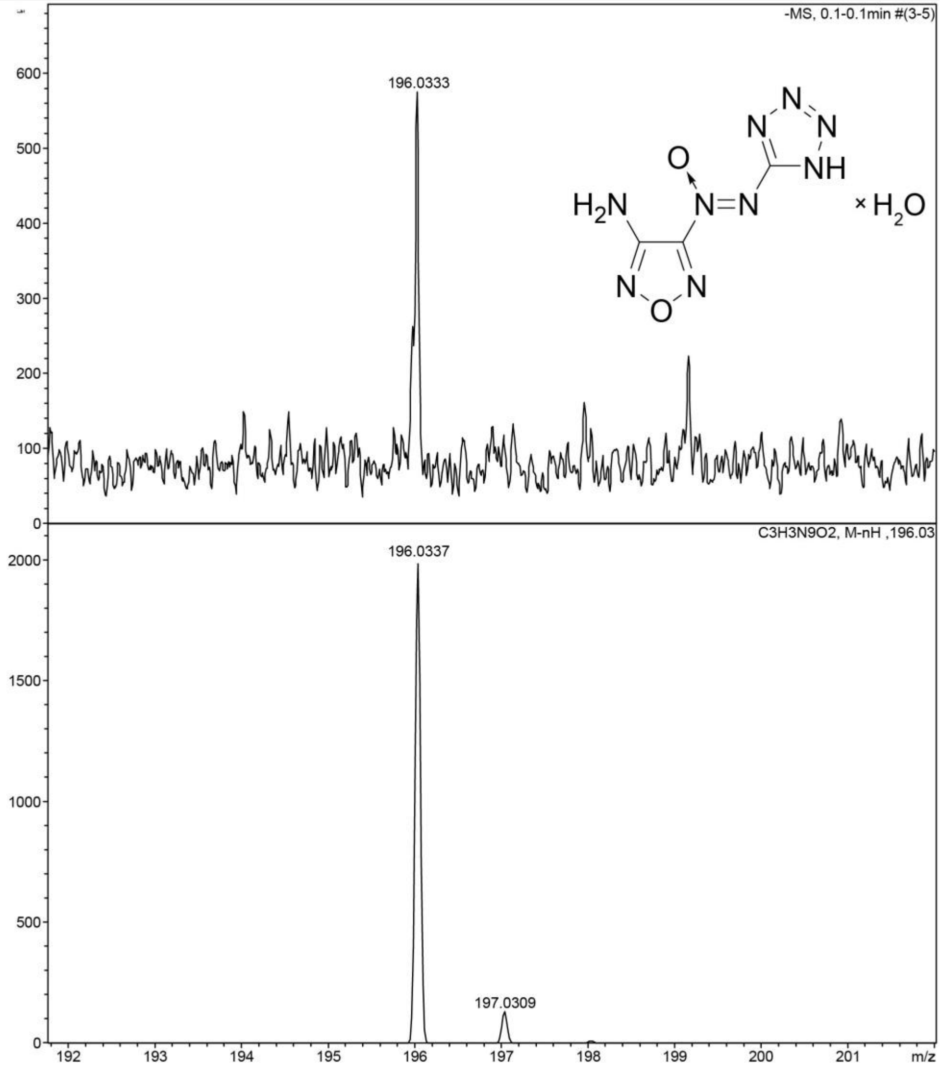
IR of tetrazole $1\cdot H_2O$



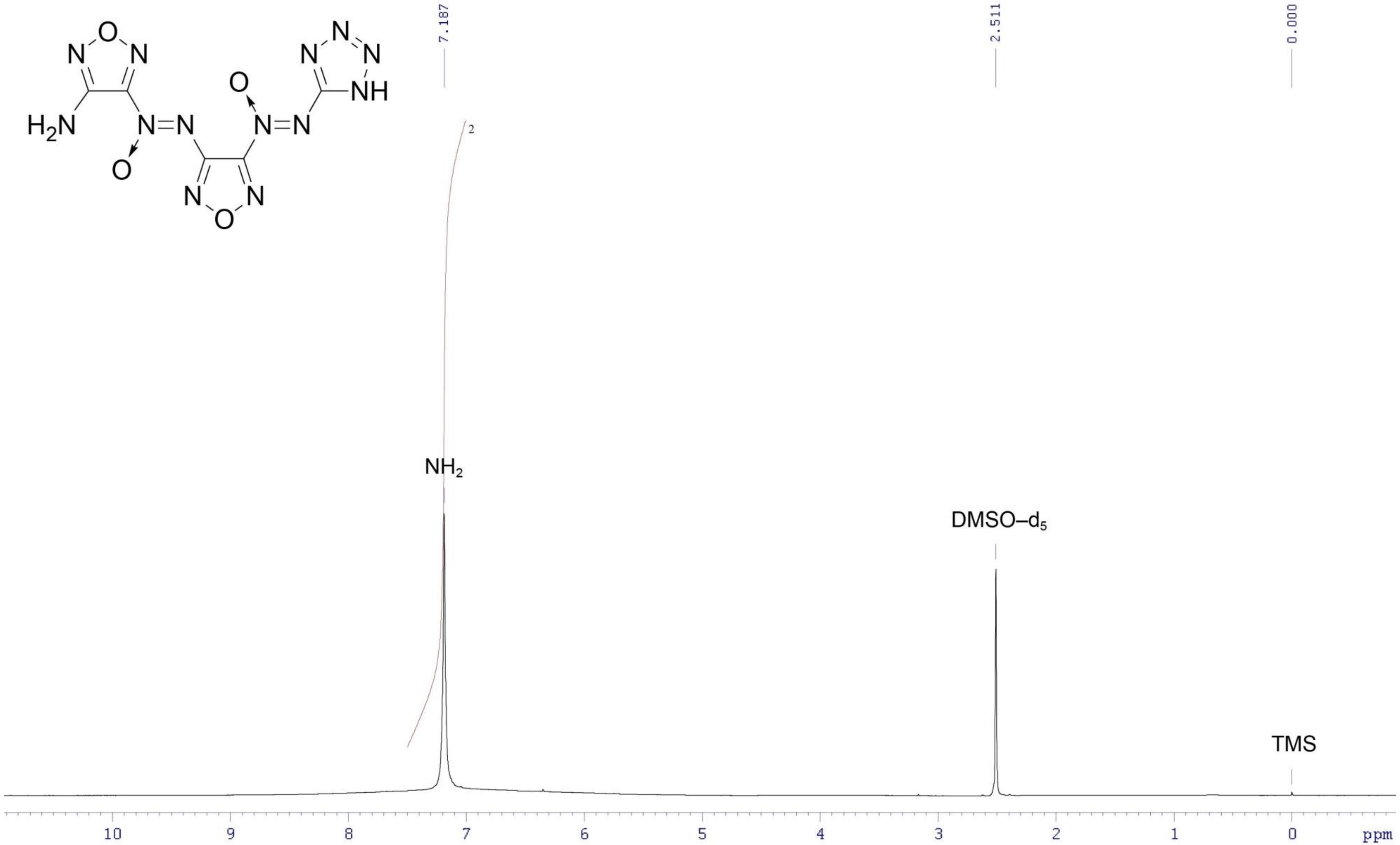
HRMS of tetrazole 1·H_2O

Acquisition Parameter

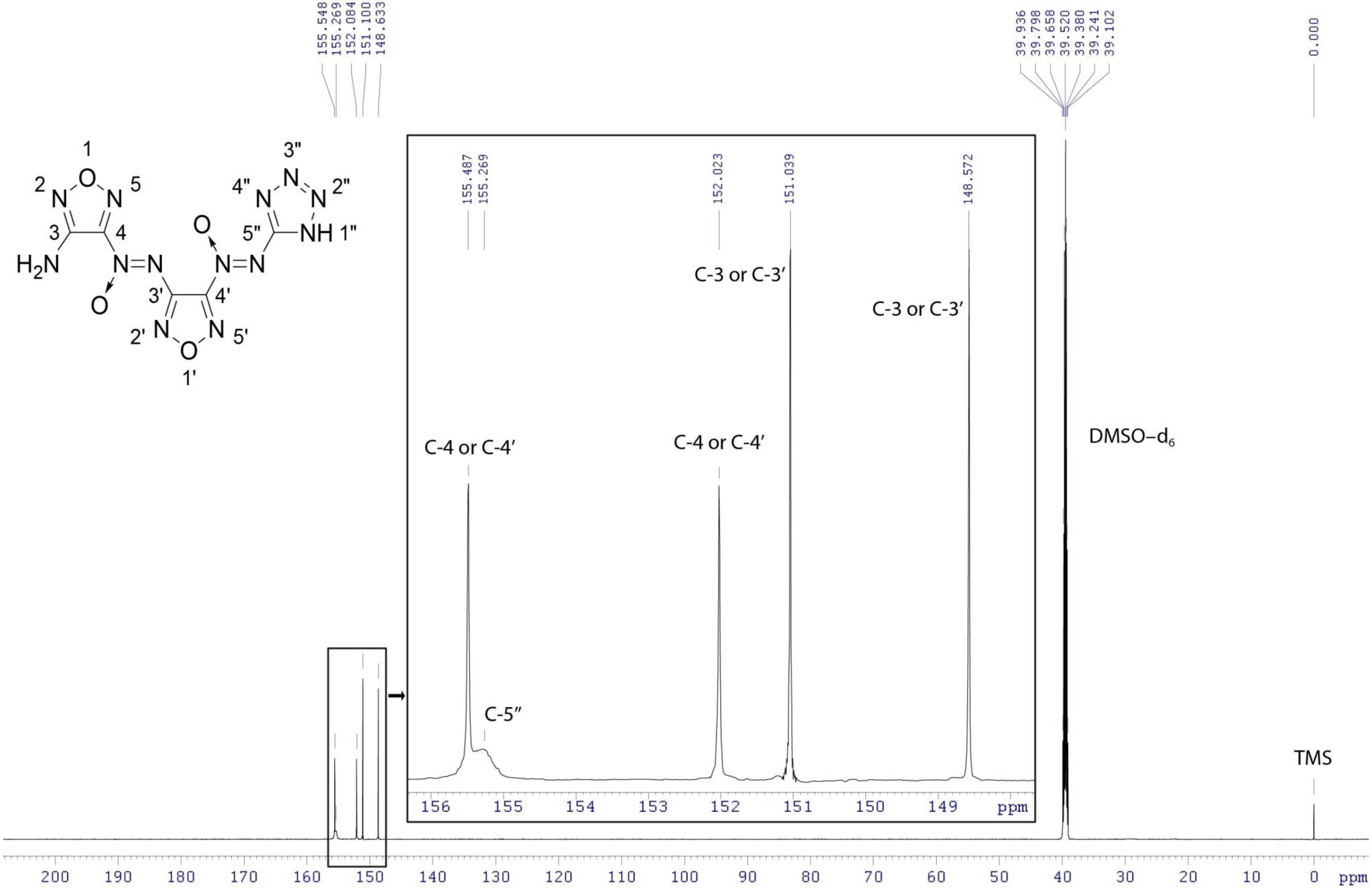
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	3200 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



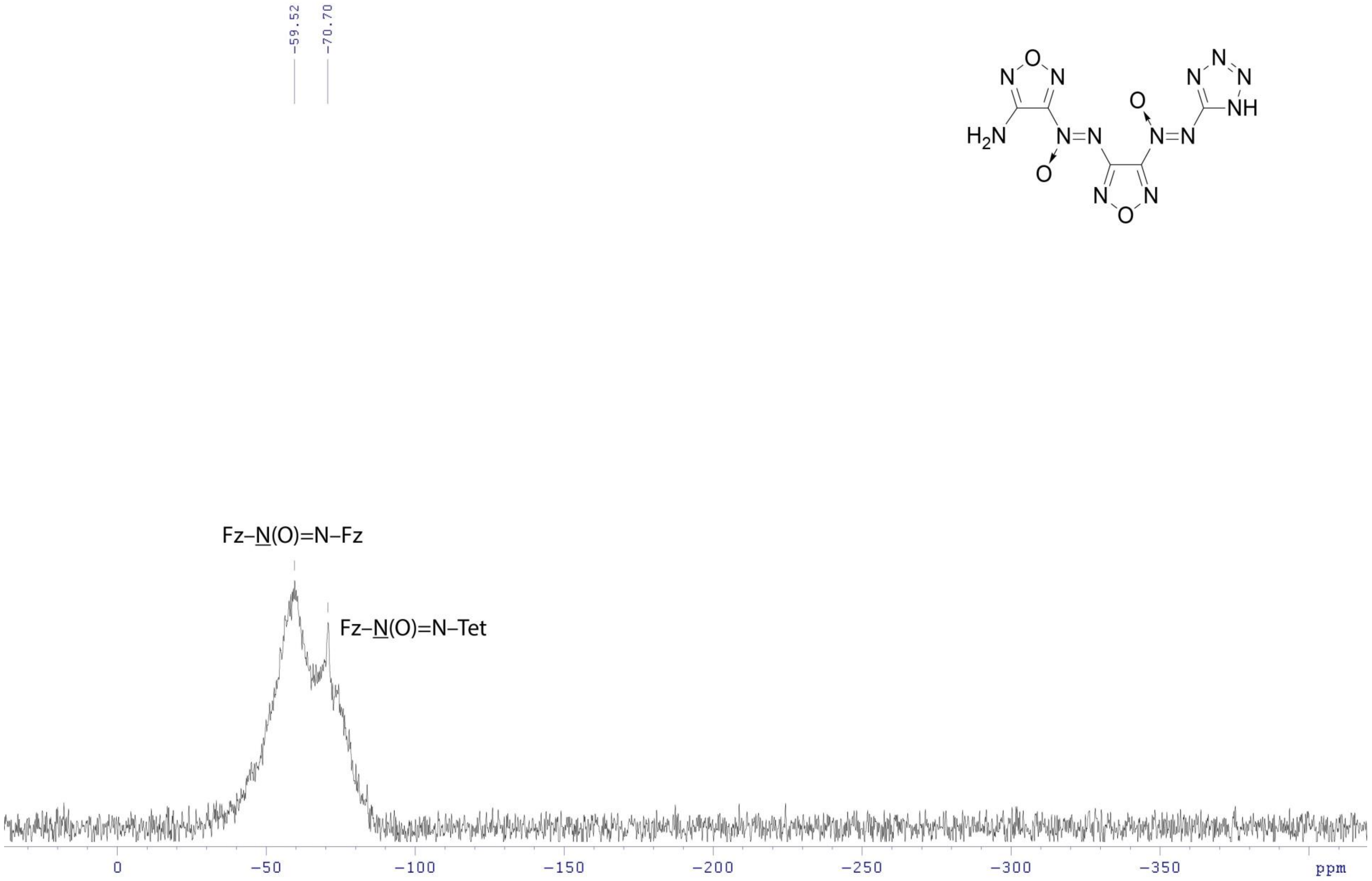
^{1}H NMR (600.1 MHz, [D$_6$]DMSO) spectrum of tetrazole 2



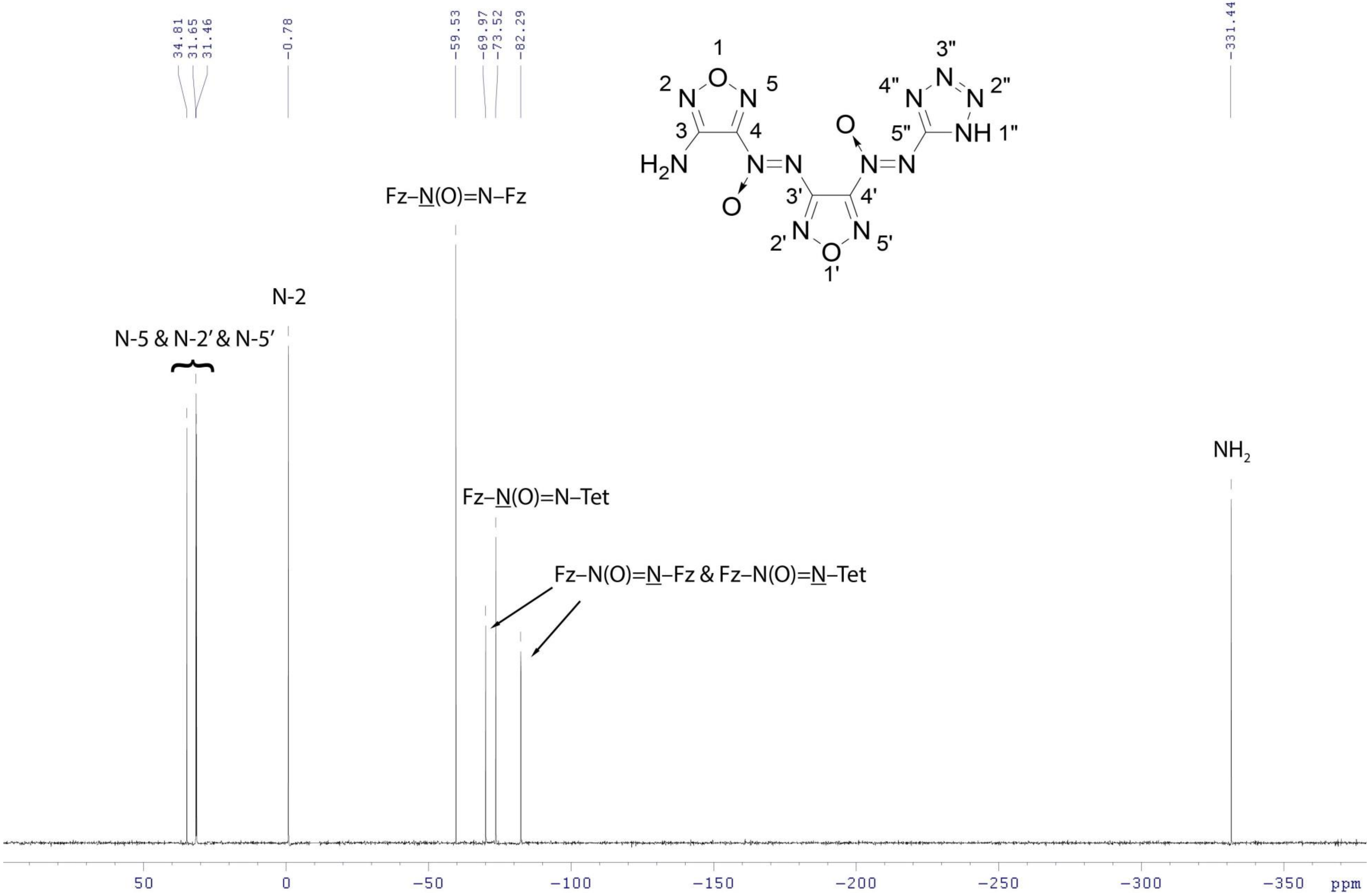
^{13}C NMR (150.9 MHz, [D$_6$]DMSO) spectrum of tetrazole 2



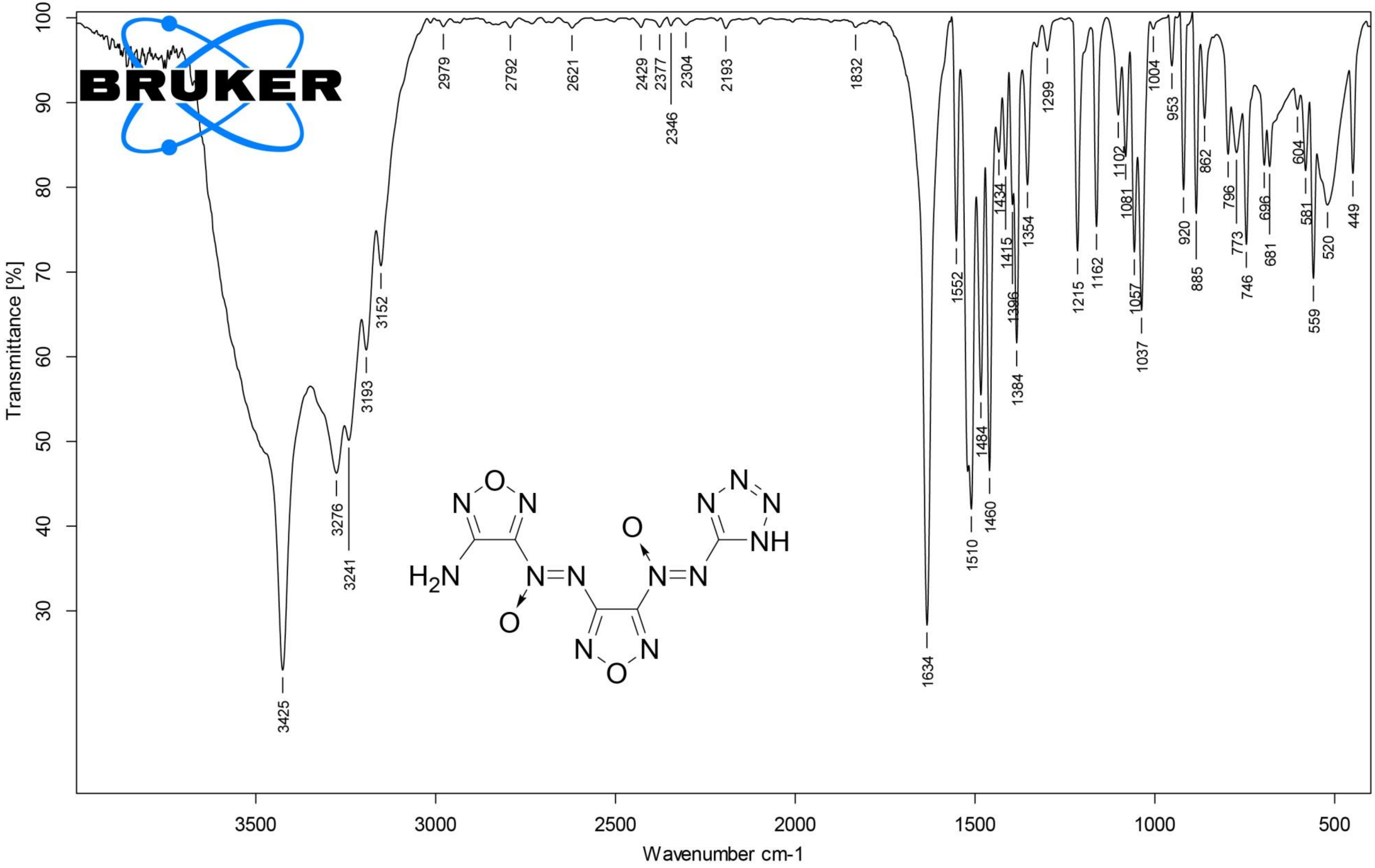
^{14}N NMR (43.4 MHz, [D$_6$]DMSO) spectrum of tetrazole 2



^{15}N NMR ([INVGATED], 60.8 MHz, [D$_6$]DMSO) of tetrazole 2



IR of tetrazole 2



HRMS of tetrazole 2

Acquisition Parameter

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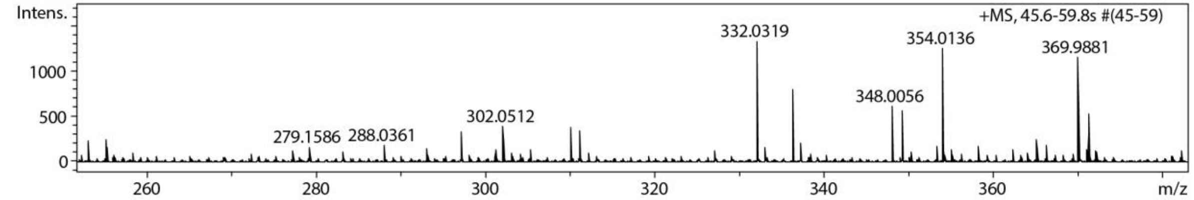
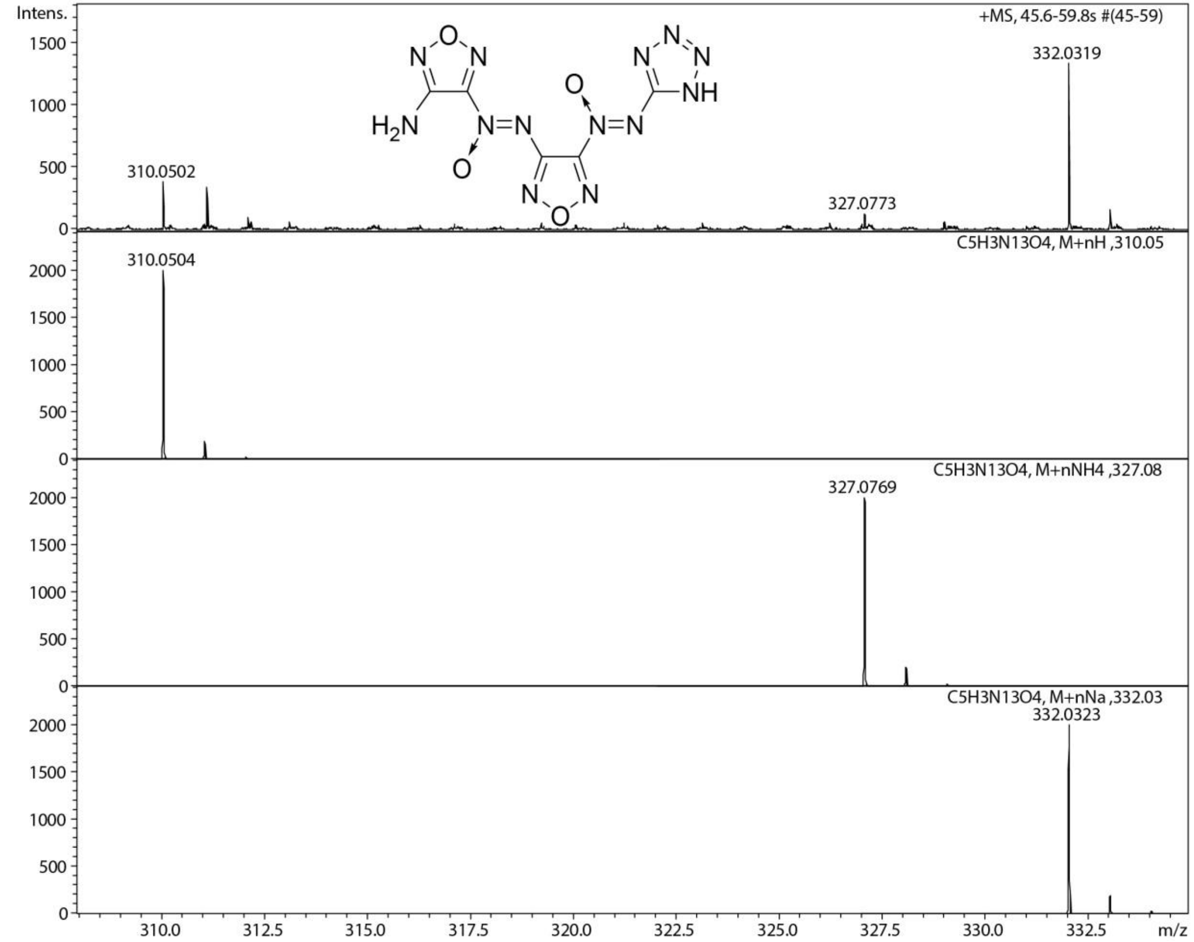
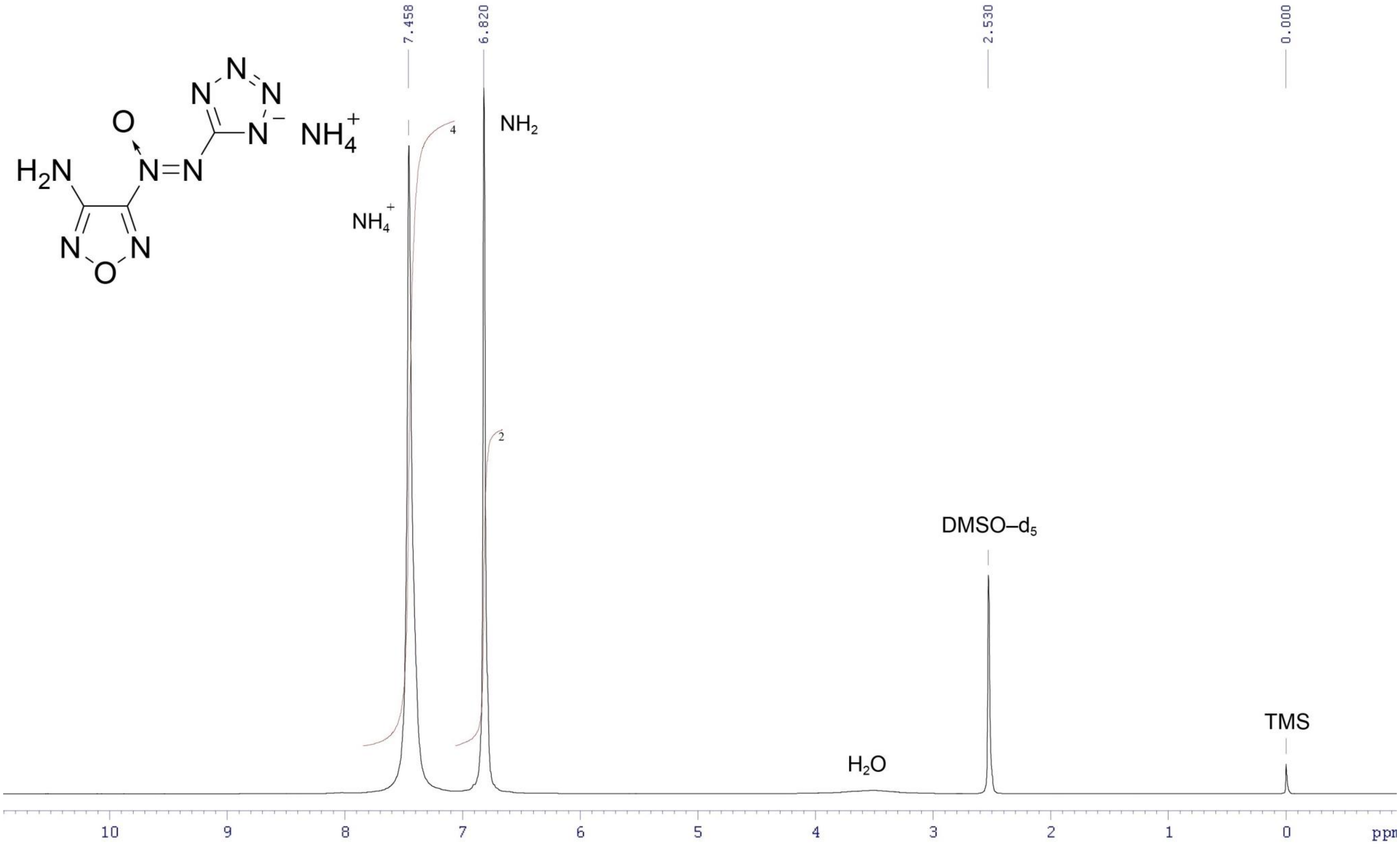
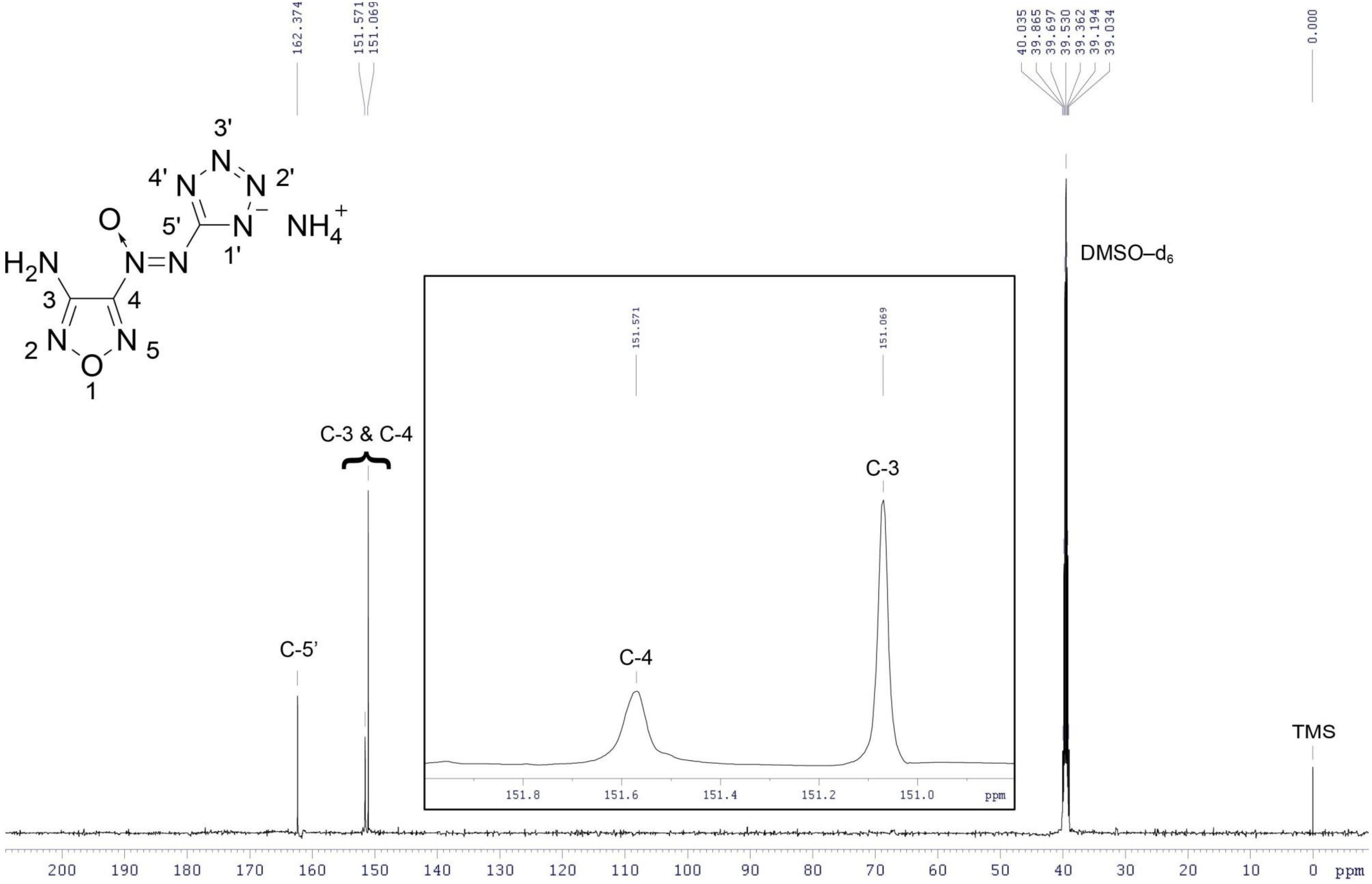




^{1}H NMR (500.1 MHz, [D$_6$]DMSO) spectrum of salt 3a



^{13}C NMR (125.8 MHz, [D$_6$]DMSO) spectrum of salt 3a



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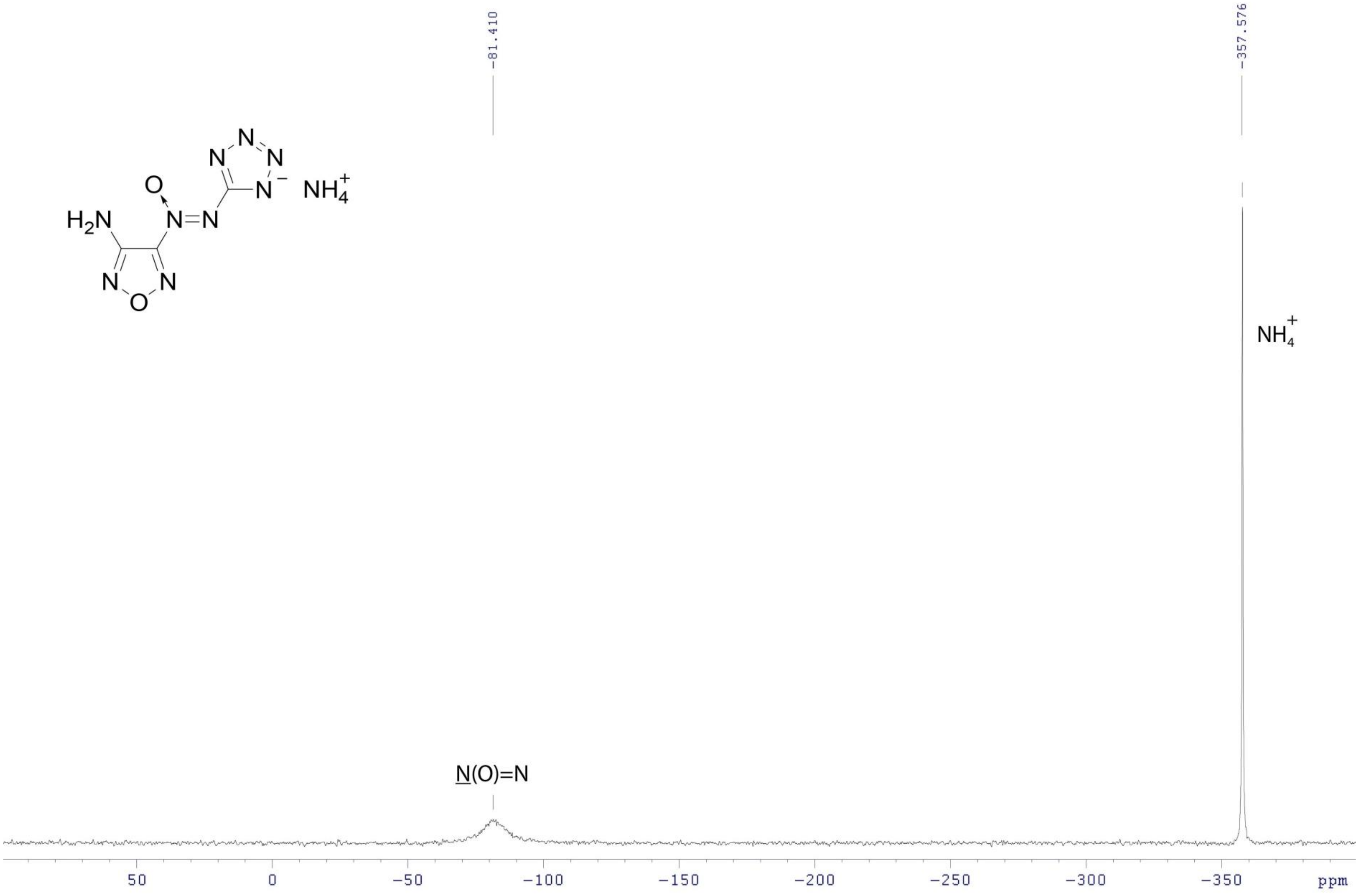
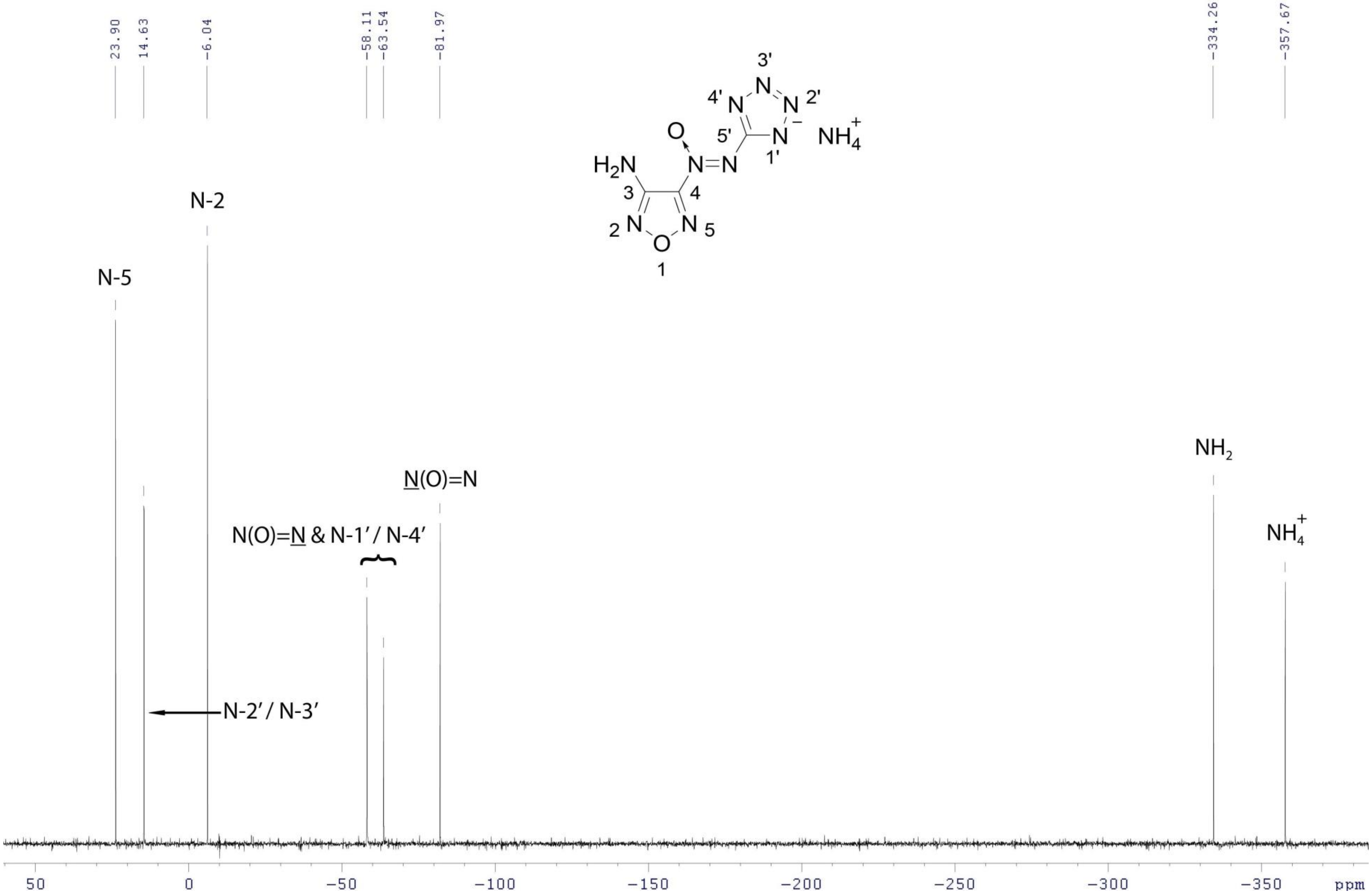
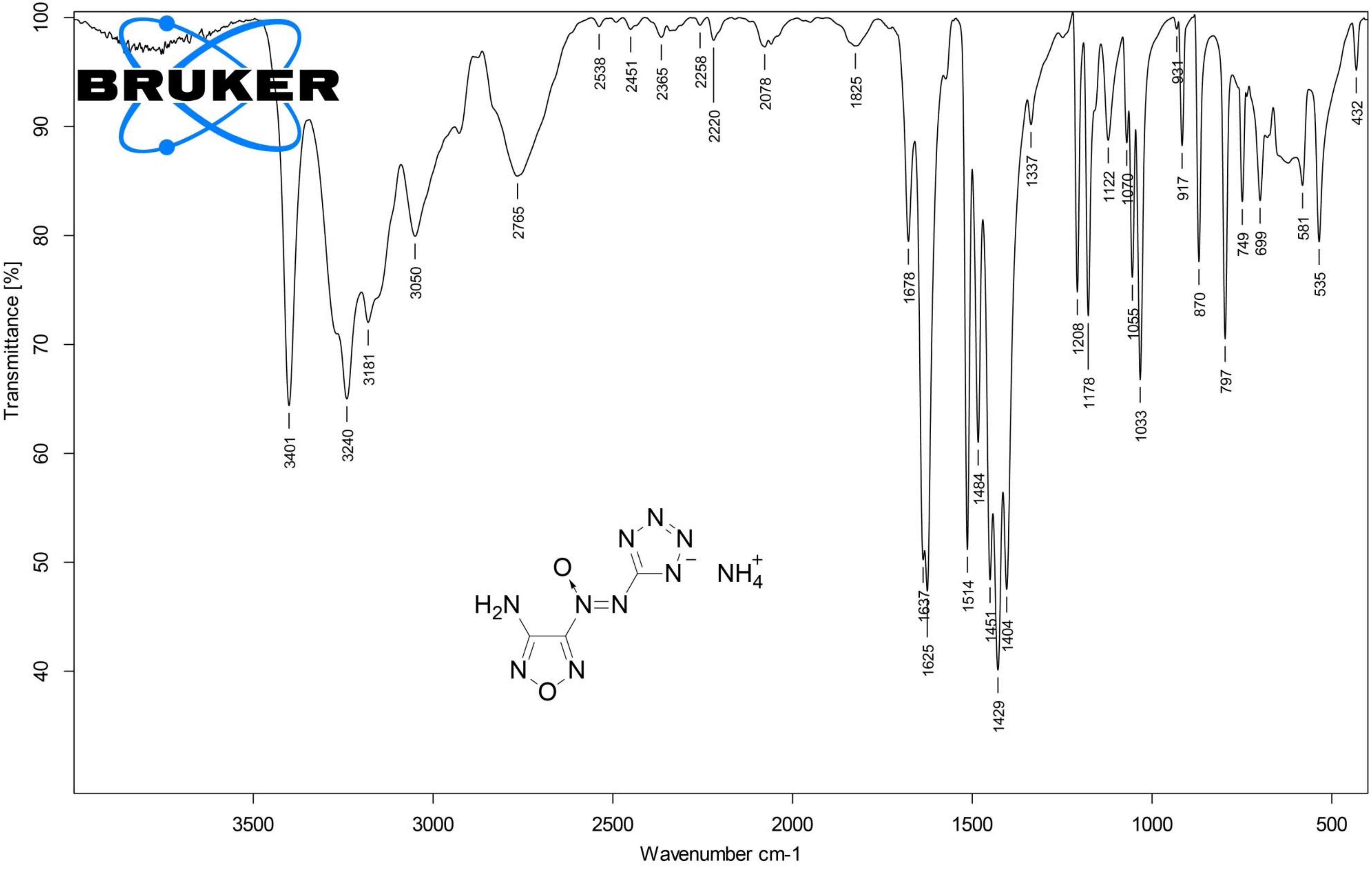


^{15}N NMR ([INVGATED], 60.8 MHz, [D$_6$]DMSO) spectrum of salt 3a



IR of salt 3a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N
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N
N–
NH4+
N
O
N

HRMS of salt 3a

Acquisition Parameter

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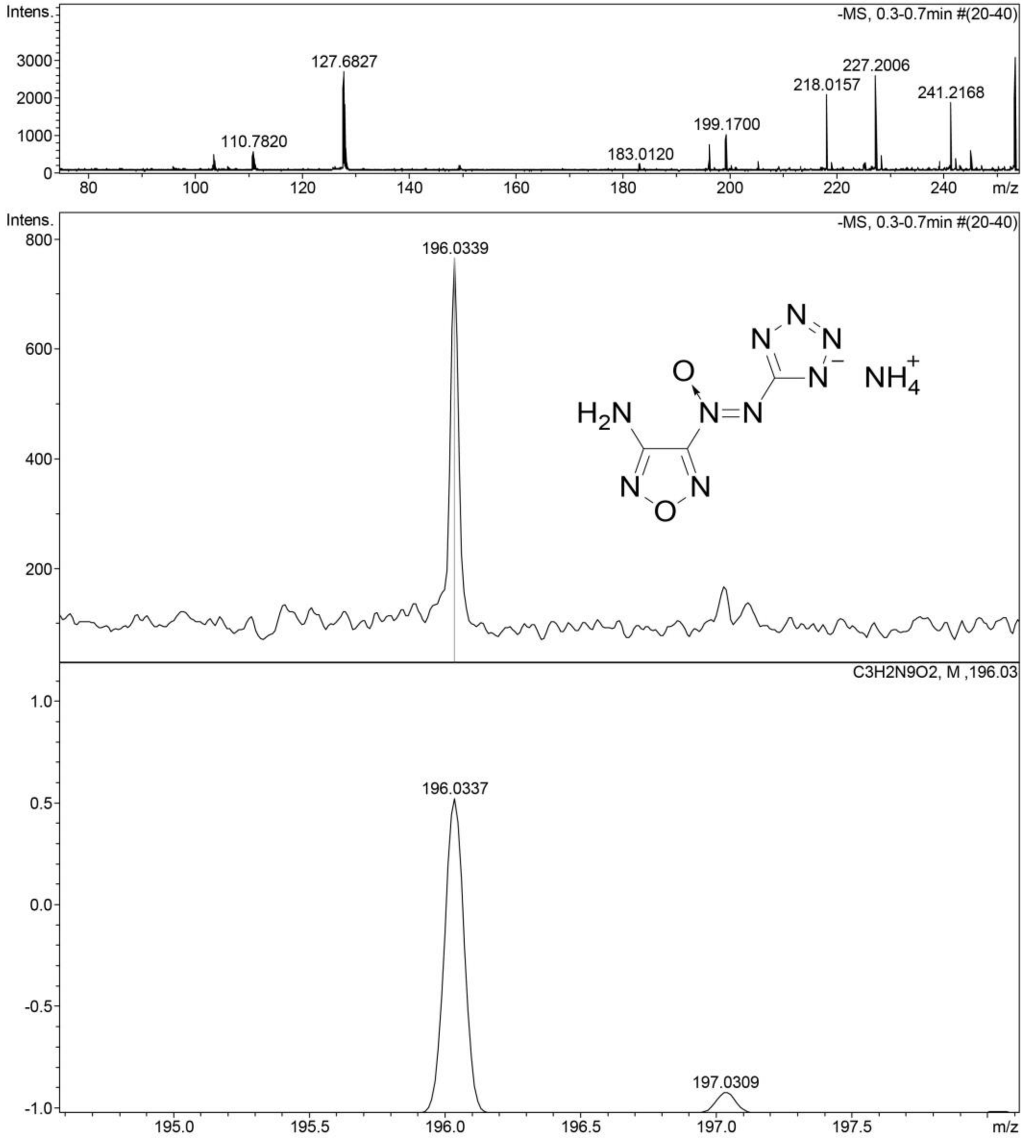
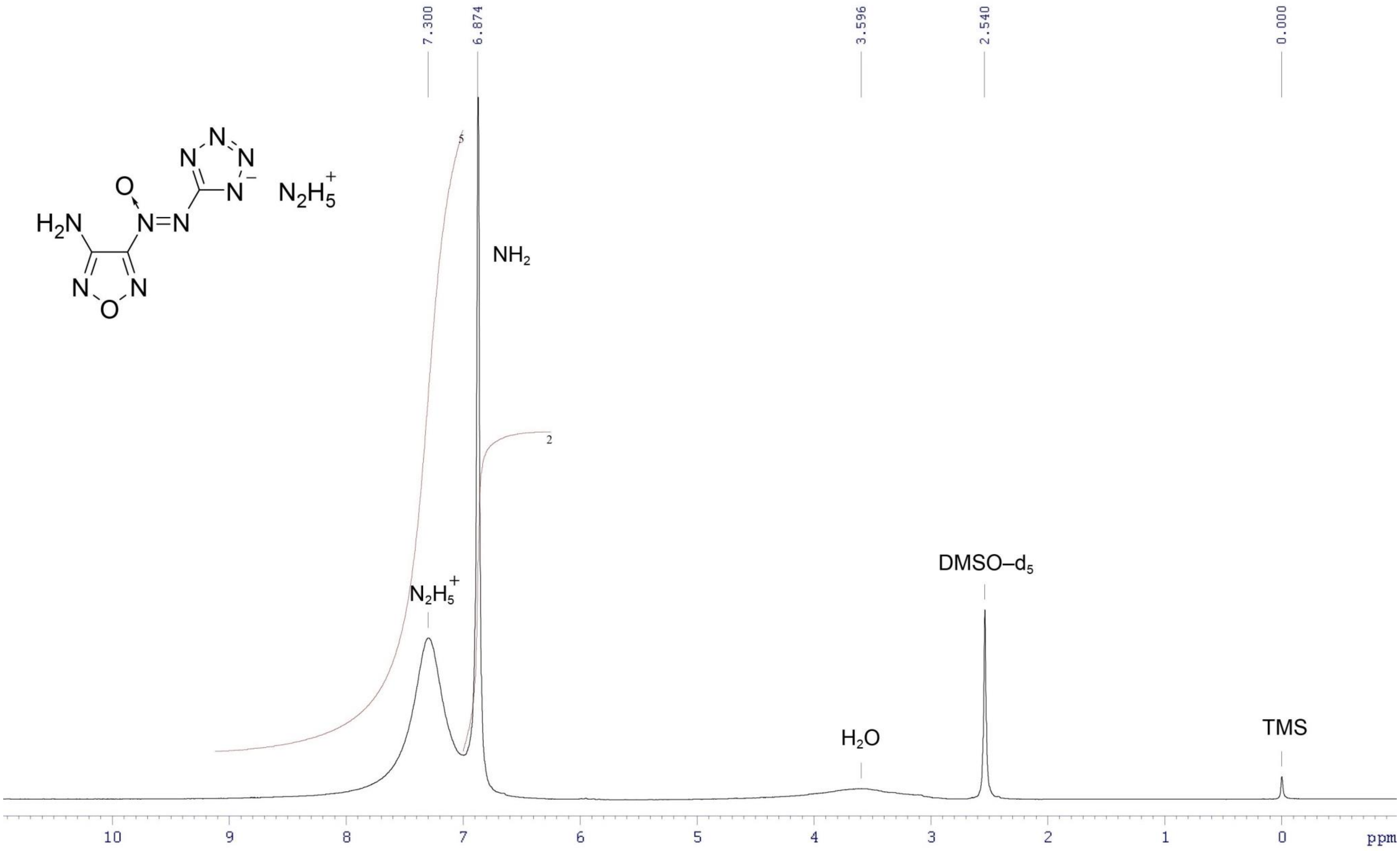
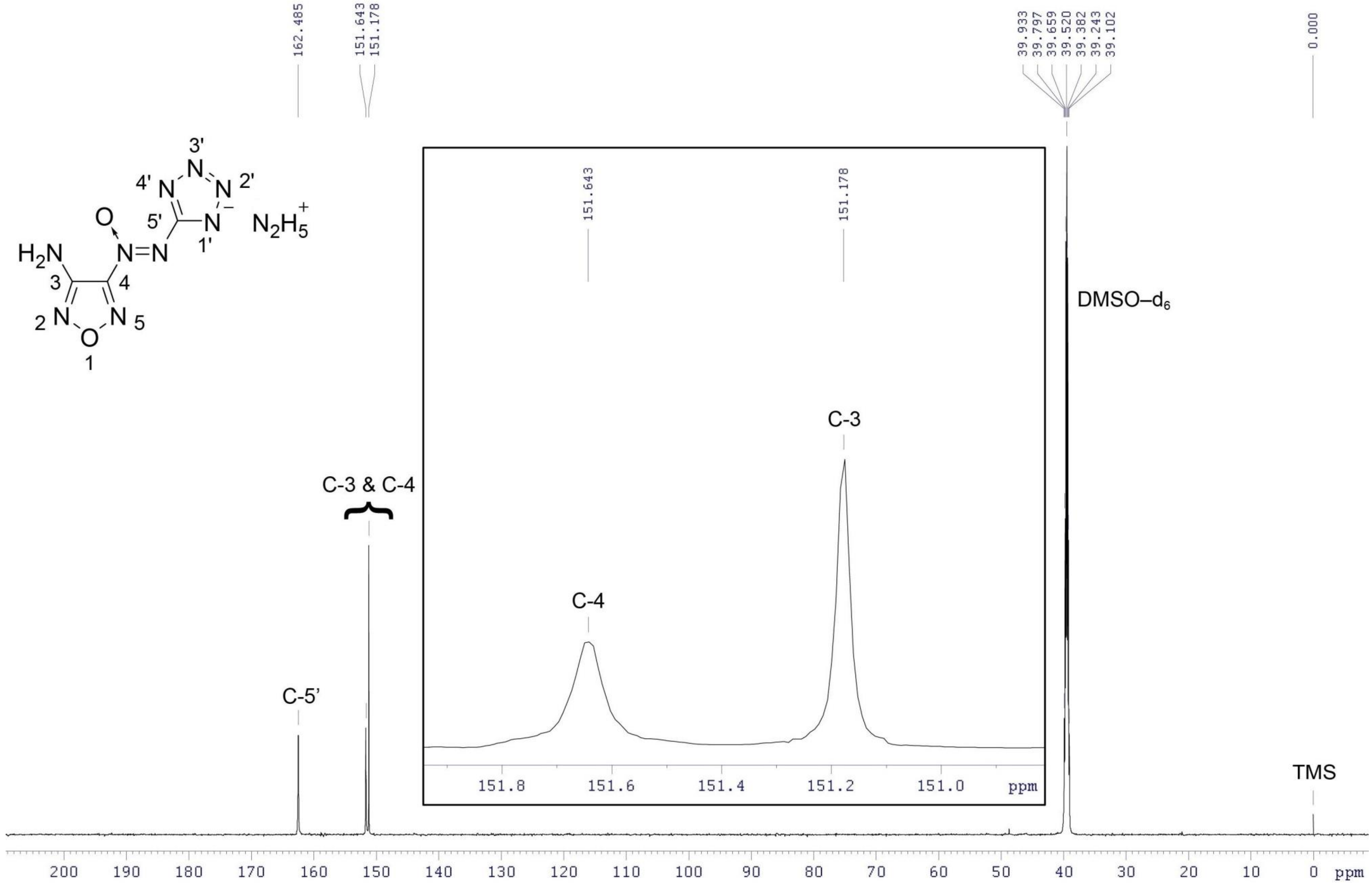


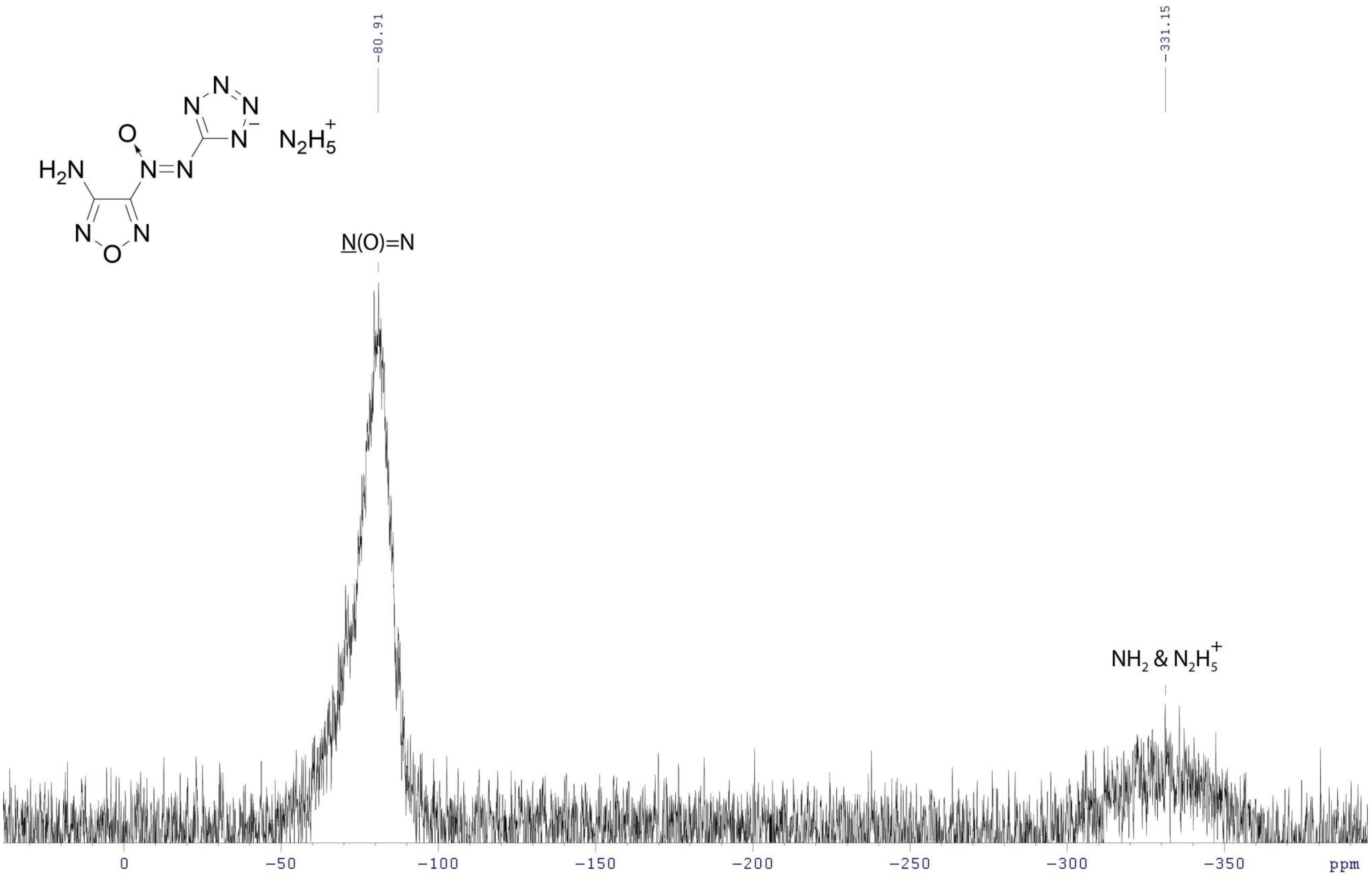
^{1}H NMR (600.1 MHz, [D$_6$]DMSO) of salt 3b



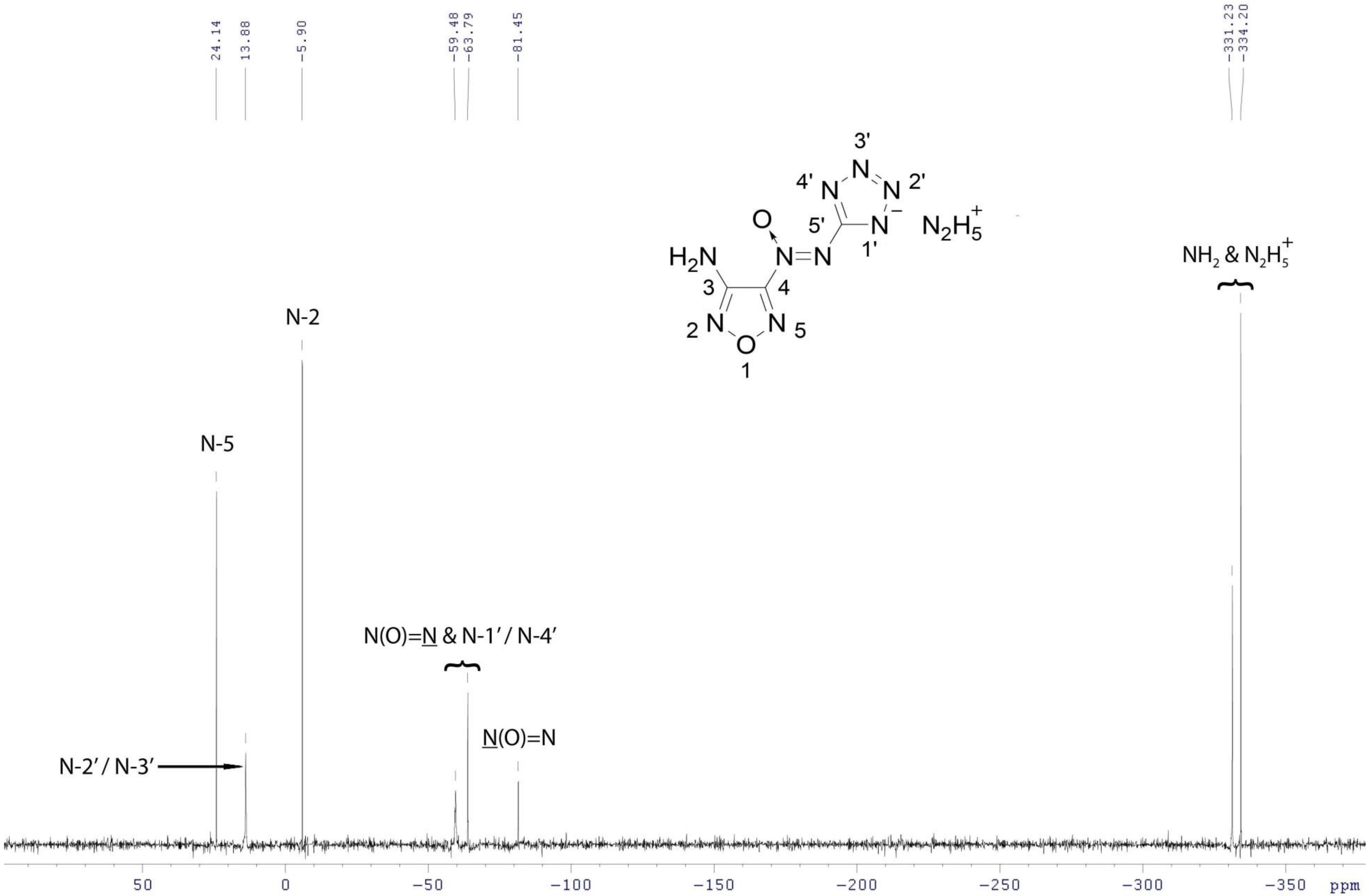
^{13}C NMR (150.9 MHz, [D$_6$]DMSO) of salt 3b



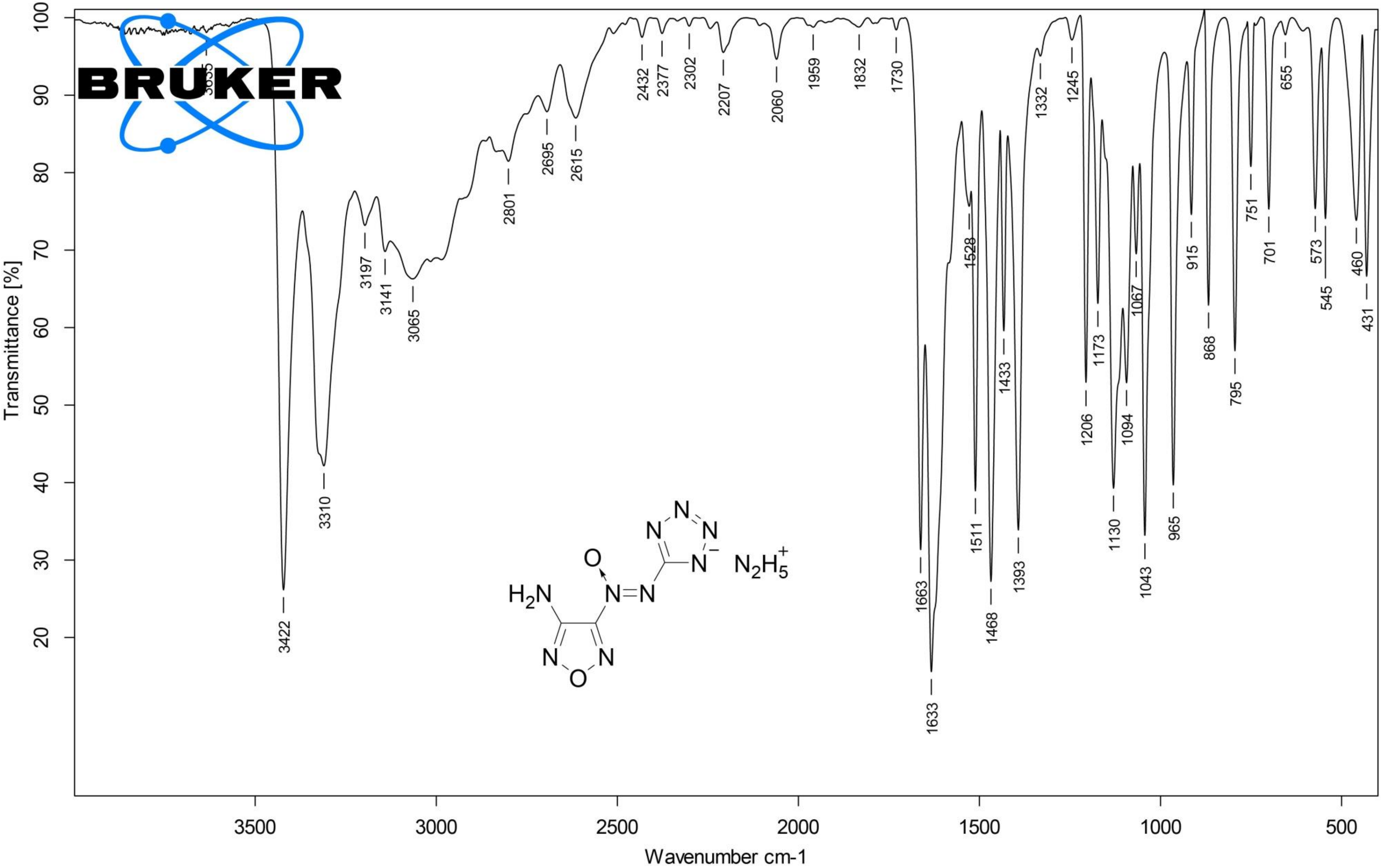
^{14}N NMR (43.4 MHz, [D$_6$]DMSO) of salt 3b



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



IR of salt 3b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$N_2H_5^+$

HRMS of salt 3b

Acquisition Parameter

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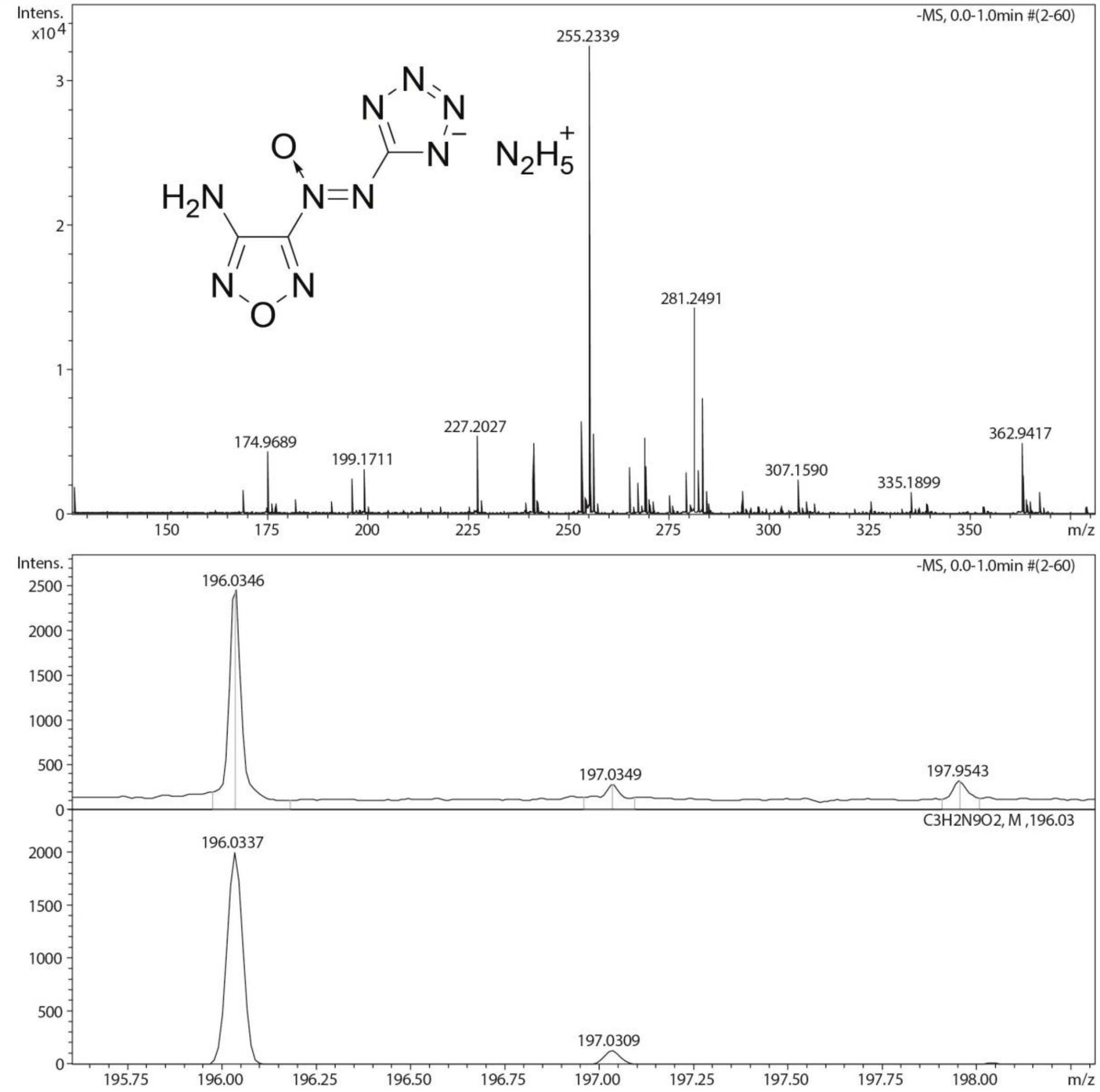
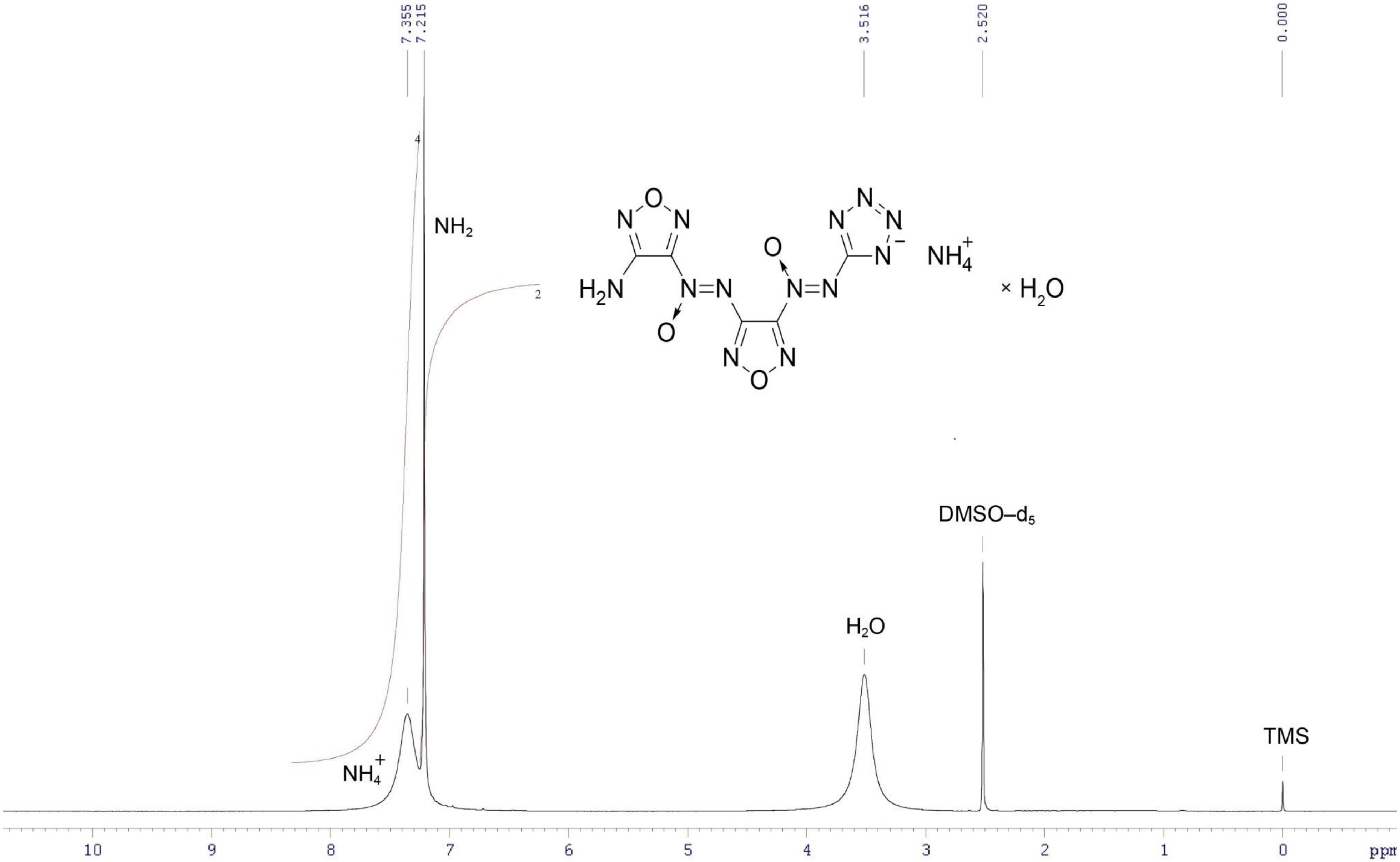
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR (600.1 MHz, [D$_6$]DMSO) of salt 4a·H$_2$O



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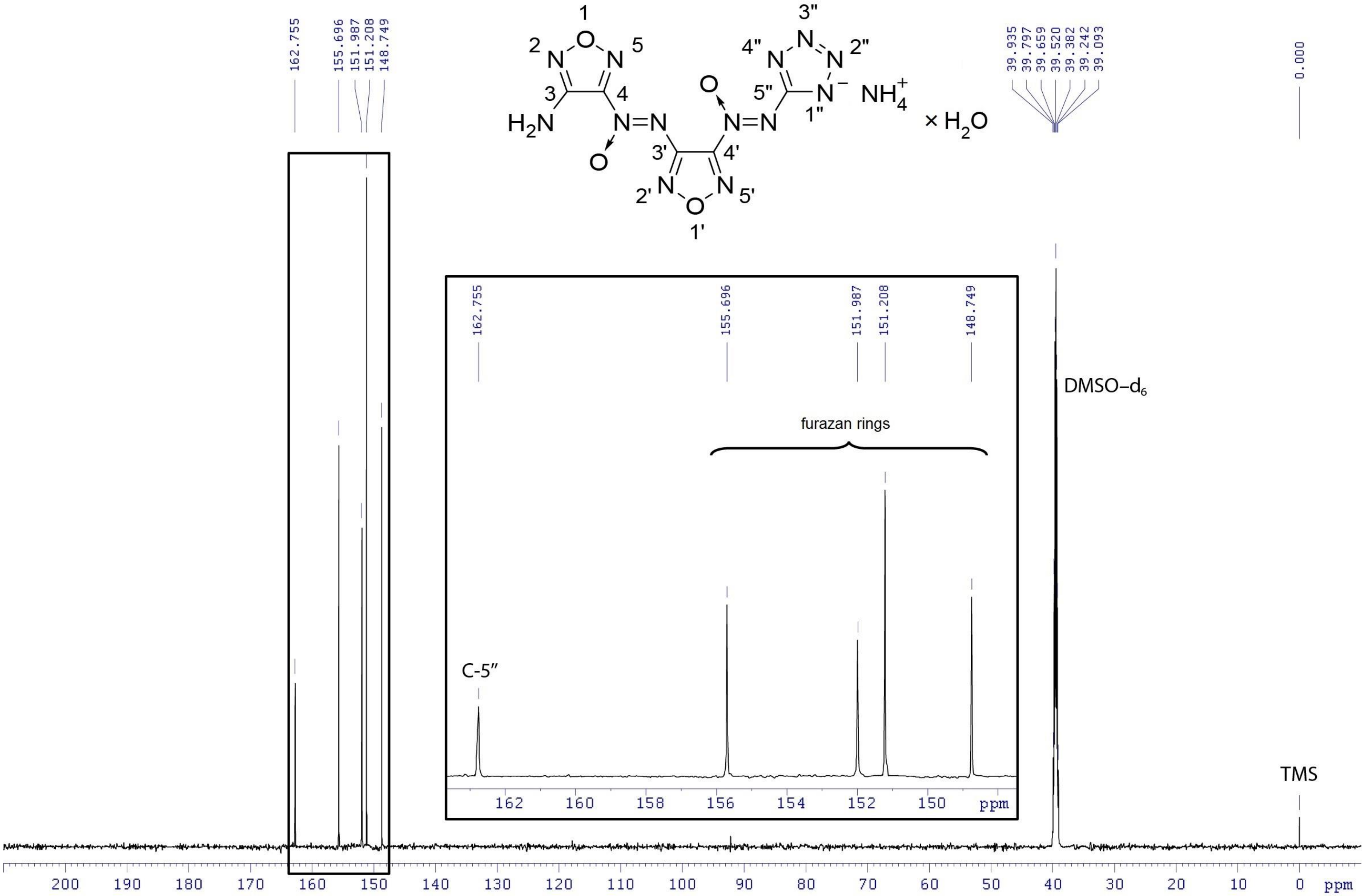
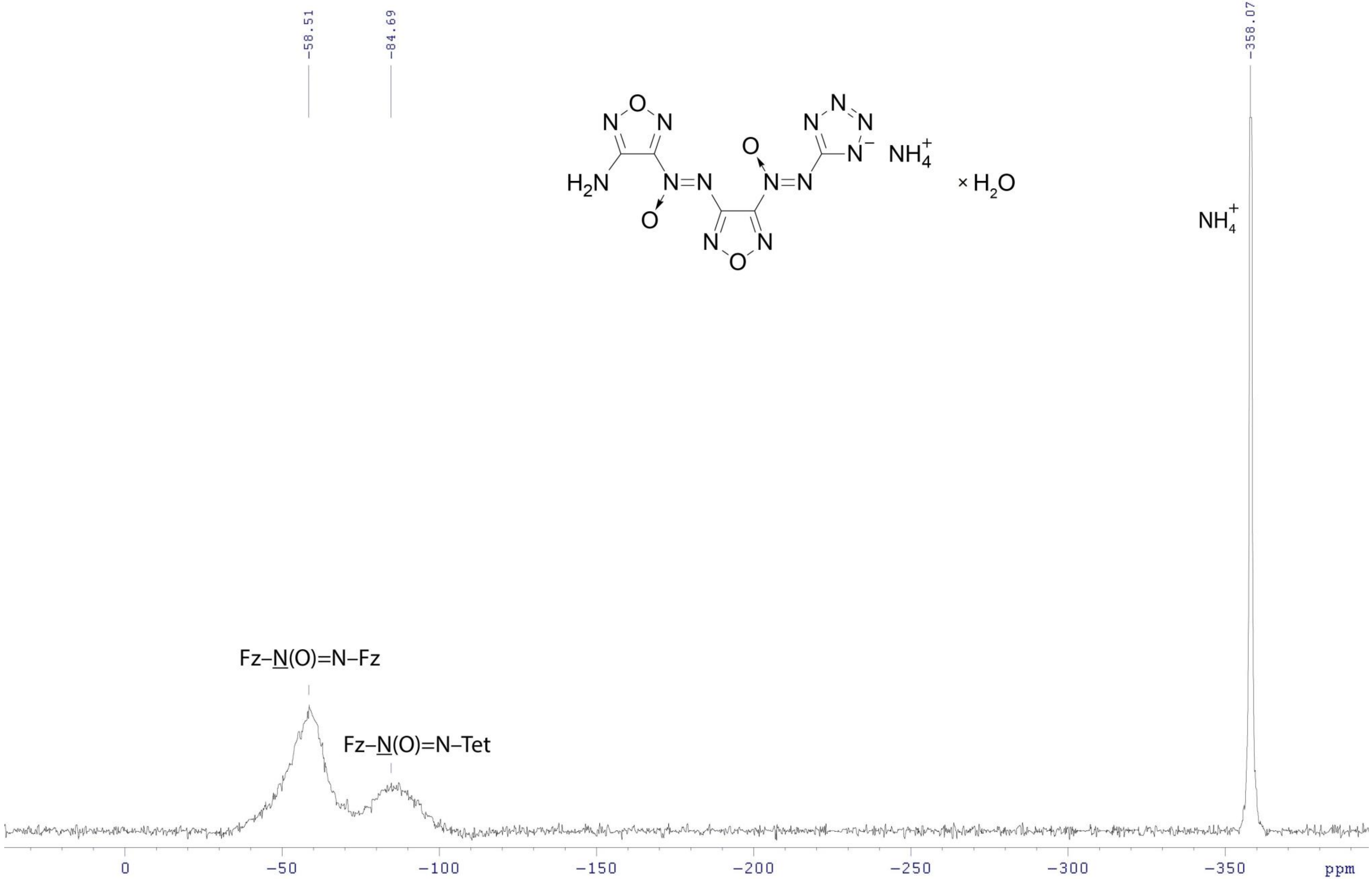
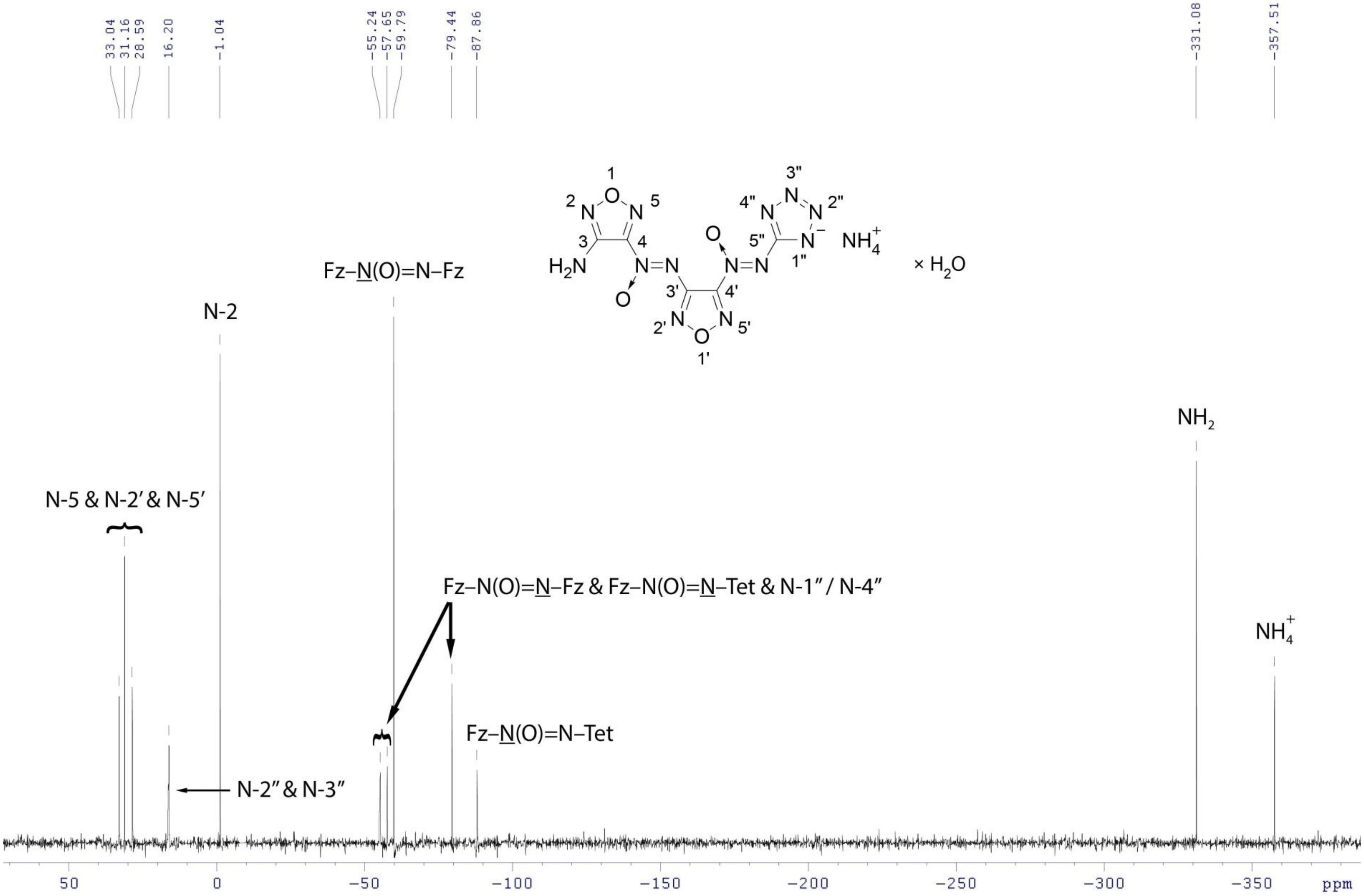


^{14}N NMR (43.4 MHz, [D$_6$]DMSO) of salt 4a·H_2O



^{15}N NMR (60.8 MHz, [D$_6$]DMSO) of salt 4a·H_2O



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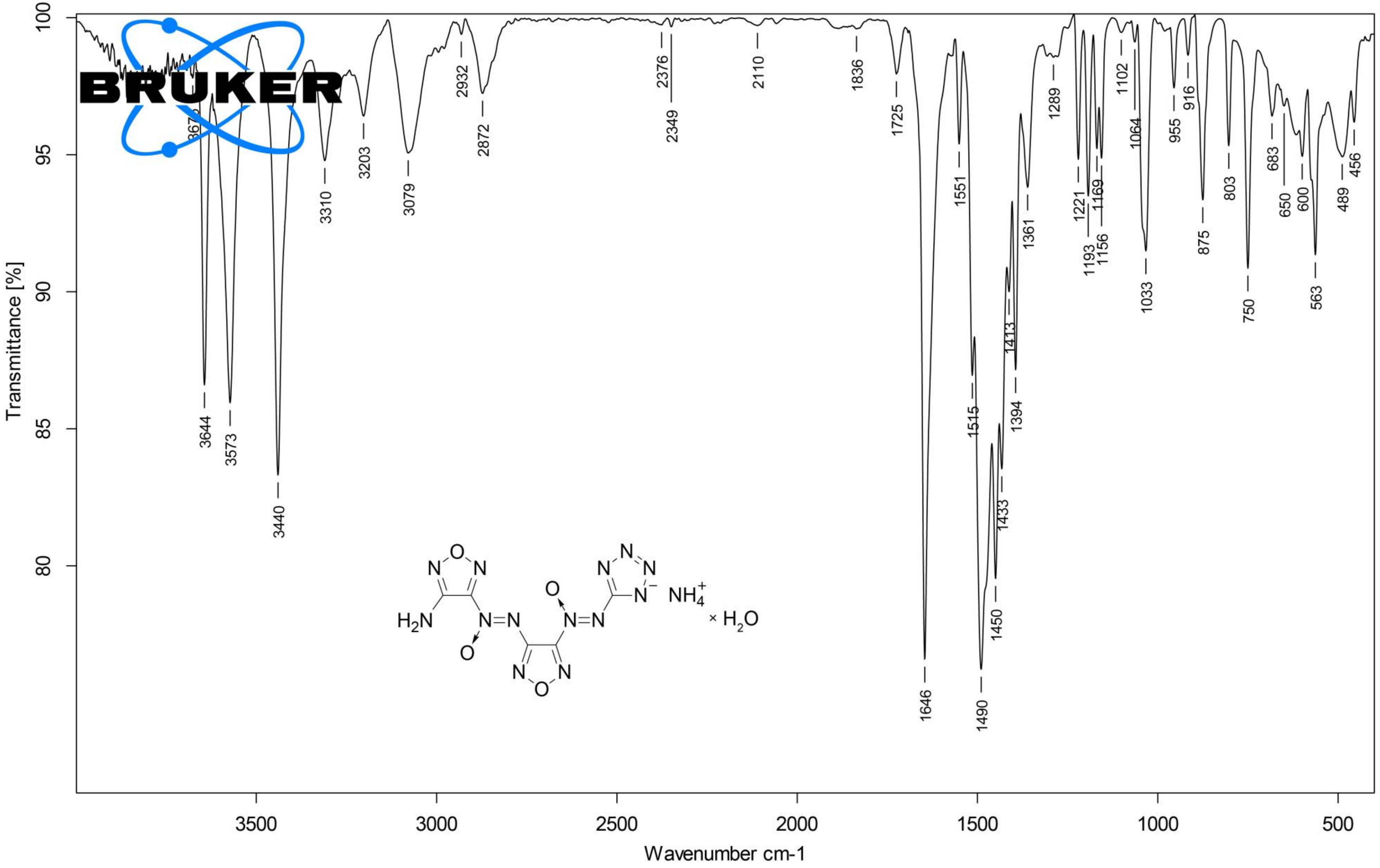
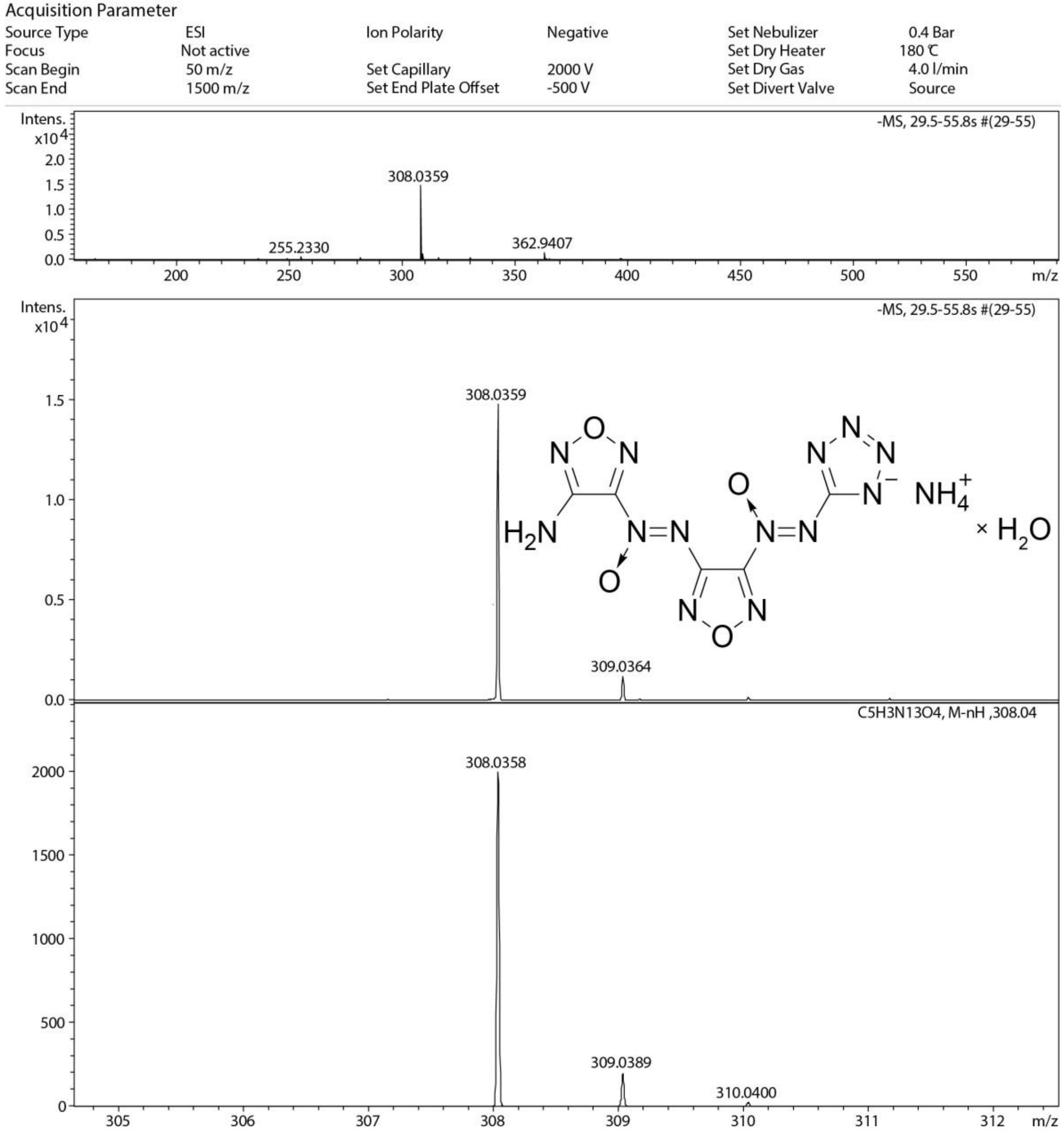


HRMS of salt 4a·H_2O



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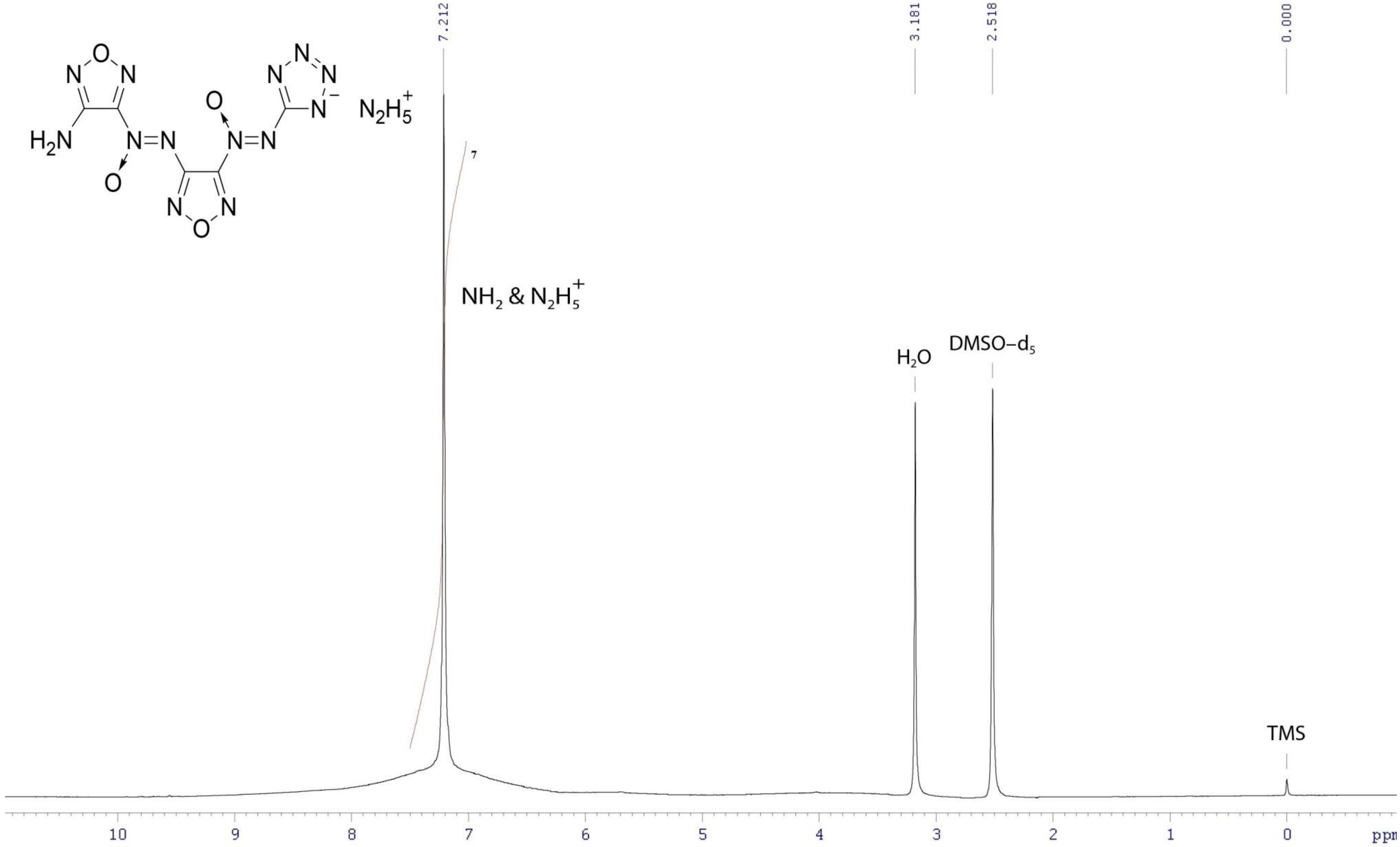
^{1}H NMR (600.1 MHz, [D$_6$]DMSO) of salt 4b



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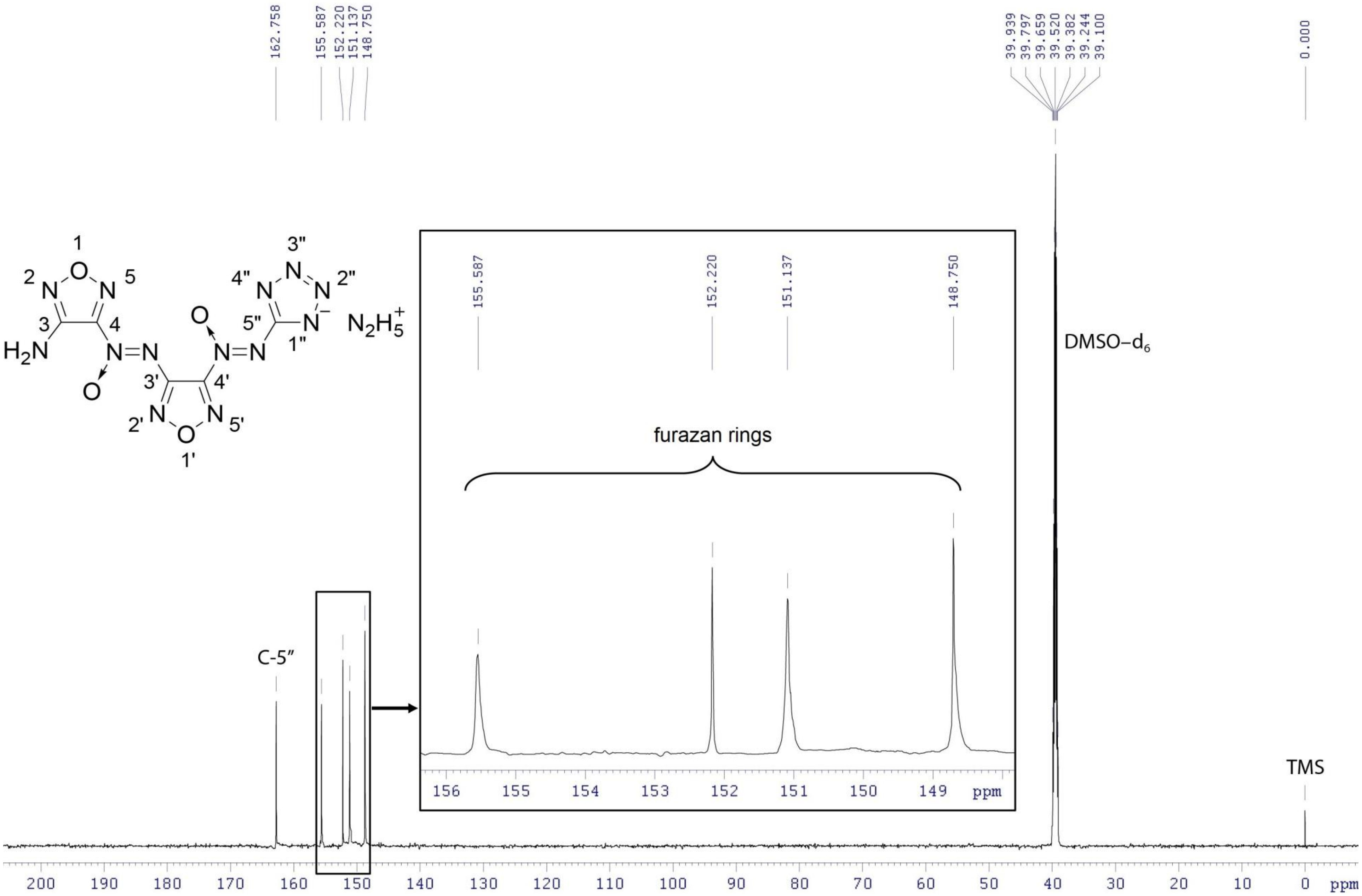
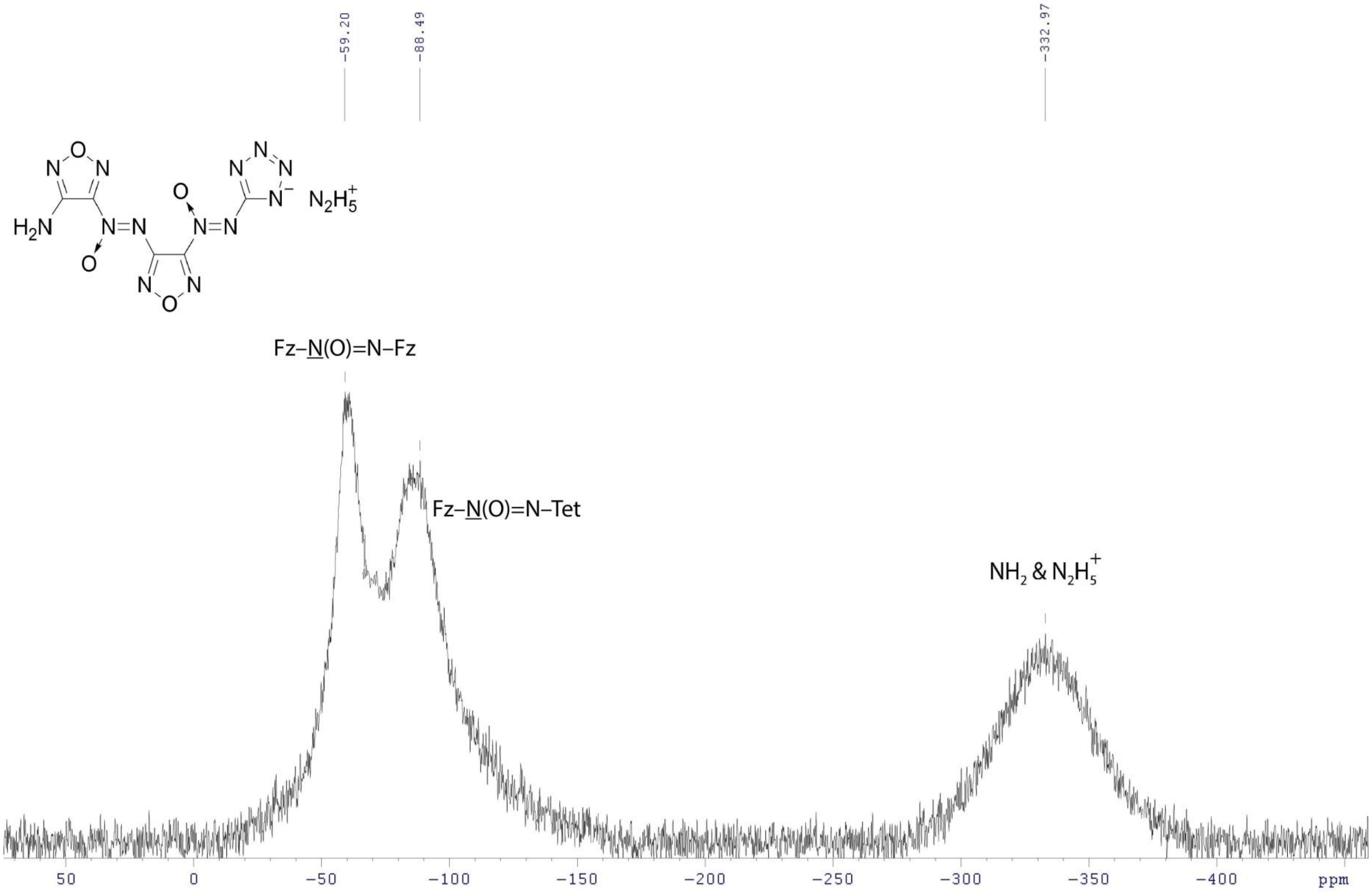


^{14}N NMR (43.4 MHz, [D$_6$]DMSO) of salt 4b



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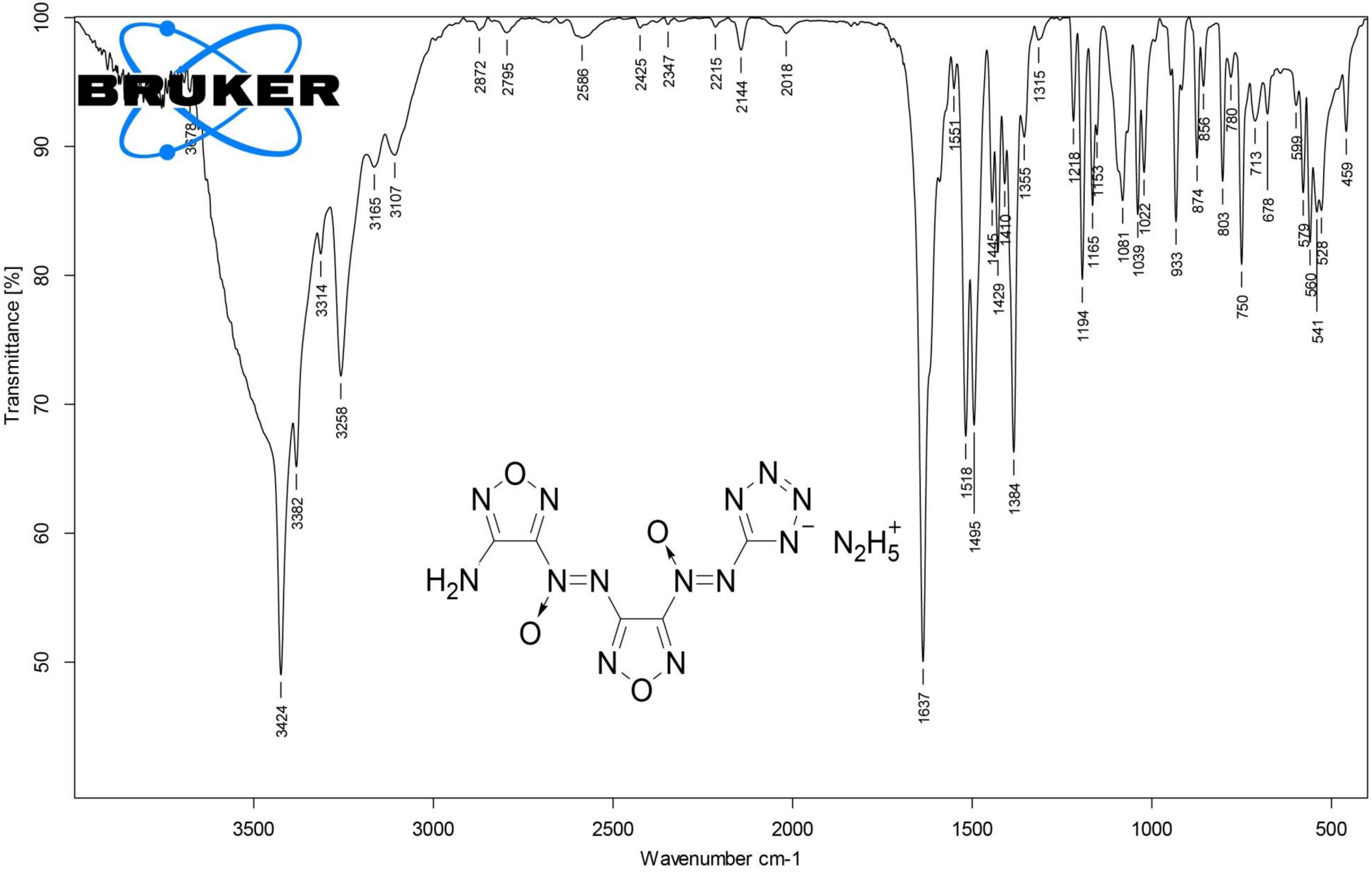
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N2H5+

HRMS of salt 4b

Acquisition Parameter

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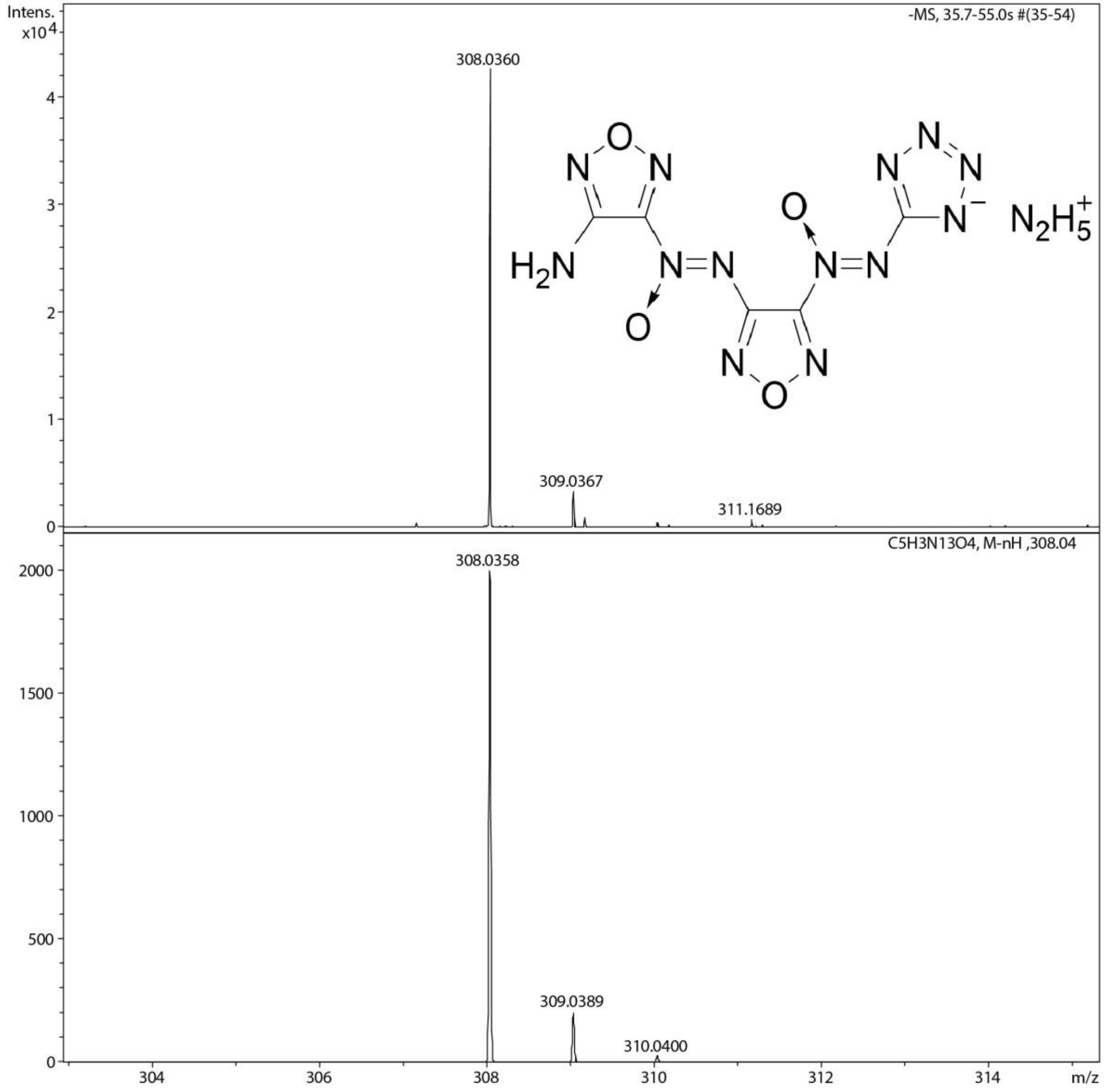

X -ray crystal structure determination

The single crystal X-ray diffraction experiment was performed on a Bruker Apex II diffractometer equipped with a PHOTON 2 detector using the graphite-monochromated MoKα radiation (λ = 0.71073 Å). Frames were integrated using the Bruker SAINT[4] software package by a narrow-frame algorithm. A semi-empirical absorption correction was applied with the SADABS program[5] using the intensity data of equivalent reflections. The structure was solved with the dual-space method with SHELXT program[6] and refined by the full-matrix least-squares technique against F^2_{hkl} in the anisotropic approximation with SHELXL program.[6] Hydrogen atoms were found from difference Fourier synthesis and refined in isotropic approximation.

X-ray powder diffraction studies were performed on a Bruker AXS D8 diffractometer equipped with a primary monochromator (CuKα1 , λ =1.54056 Å) and a LynxEye position sensitive detector. Samples were deposited on a zero-background silicon plate and were rotated with a speed of 60 $\mathrm{deg{\cdot}min^{-1}}$. Data collections was performed in the reflection mode at ambient temperature (ca. 298 K) with a step size of 0.01° for 2θ ranges of 6–60° for phase analysis and 3–90° for structure solution and refinement. The unit cell parameters and phase purity of the bulk sample **3a**·H_2O at room temperature were evaluated by a Pawley fit starting from the single-crystal unit cell parameters.

The diffraction patterns of the sample **3a** was indexed using the SVD (singular value decomposition) index algorithm[7] as implemented in the Bruker TOPAS 5.0 software,[8] the space group was determined using the analysis of systematic absences. The parallel tempering approach implemented in FOX package[9] was used for the crystal structure solution in direct space. The restrained Rietveld refinement (in TOPAS 5.0) was carried out using the methodology described elsewhere.[10] The positions of the hydrogen atoms of the amino group and the ammonium cation could be found from PXRD data or calculated, and were therefore assigned based on the results of periodic DFT calculations (see below). Reference bond lengths and angles for the restrained refinement were taken from the single-crystal structure of the hydrate **3a**·H_2O (averaged for two symmetry-independent molecules). Additional restraints were applied to ensure the planarity of the heterocyclic fragments.

---

[4] SAINT v. 8.34A, Bruker, 2013.

[5] L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10

[6] G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3.

[7] A. A. Coelho, *J. Appl. Crystallogr.*, 2003, **36**, 86.

[8] A. A. Coelho, *J. Appl. Crystallogr.*, 2018, **51**, 210.

[9] V. Favre-Nicolin, R. Černý, *J. Appl. Crystallogr.*, 2002, **35**, 734.

[10] A. O. Dmitrienko and I. S. Bushmarinov, *J Appl Crystallogr*, 2015, **48**, 1777.

Periodic DFT calculations were performed with CRYSTAL17 software package[11] using dispersion-corrected PBE0-D3 functional[12] with Becke–Jonson damping[13] and POB-TZVP basis set.[14] Atomic coordinates for crystal **3a** were optimized using the experimental unit cell parameters, symmetry and initial coordinates from the crystal structure solution; the positions of hydrogen atoms were initially assigned using the information about the strongest potential H-bonds. A shrinking factor 2 2 2 was used for Monkhorst-Pack grid, yielding in total 8 k-points in irreducible Brillouin zone. Harmonic frequencies in Γ-point for crystals were calculated using the numerical algorithm, with two atomic displacements in each Cartesian direction, the absence of imaginary frequencies proved the optimized models to be minima. Note that the resulting geometry and the position of the nitrogen atom of the ammonium cation are very closed to the starting values from the FOX solution. The constrained Rietveld refinement of **3** using the DFT-optimized atomic positions shows fairy good description of PXRD pattern. Such a coincidence of the DFT-optimized and refined structures can serve as an additional indication of the validity of the refined model.[15] Fits are shown in Figures S1,S2.

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[11] R. Dovesi, A. Erba, R. Orlando, C. M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rérat, S. Casassa, J. Baima, S. Salustro and B. Kirtman, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2018, **8**, e1360.

[12] C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.

[13] S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.

[14] M. F. Peintinger, D. V. Oliveira and T. Bredow, *J. Comput. Chem.*, 2013, **34**, 451.

[15] J. van de Streek and M. A. Neumann, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2014, **70**, 1020.

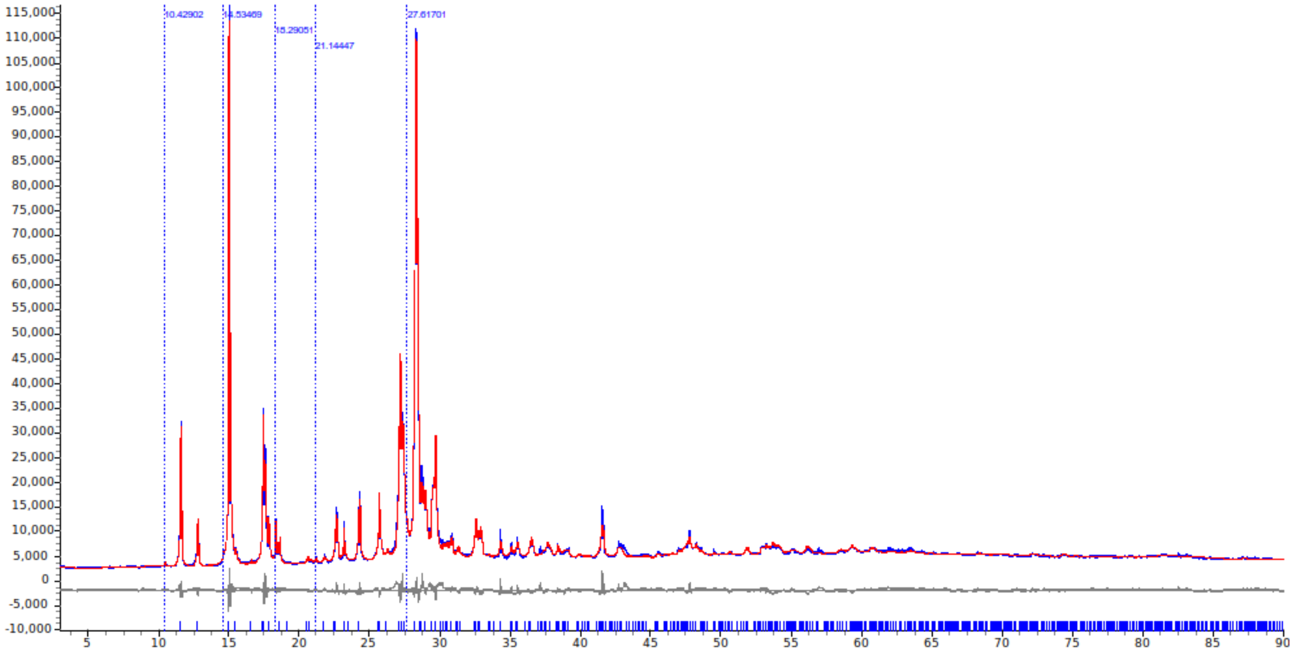


Figure S1. The restrained Rietveld fit of PXRD data for ammonium salt **3a** (R_{bragg} = 0.0099, R_{wp} = 0.0450).

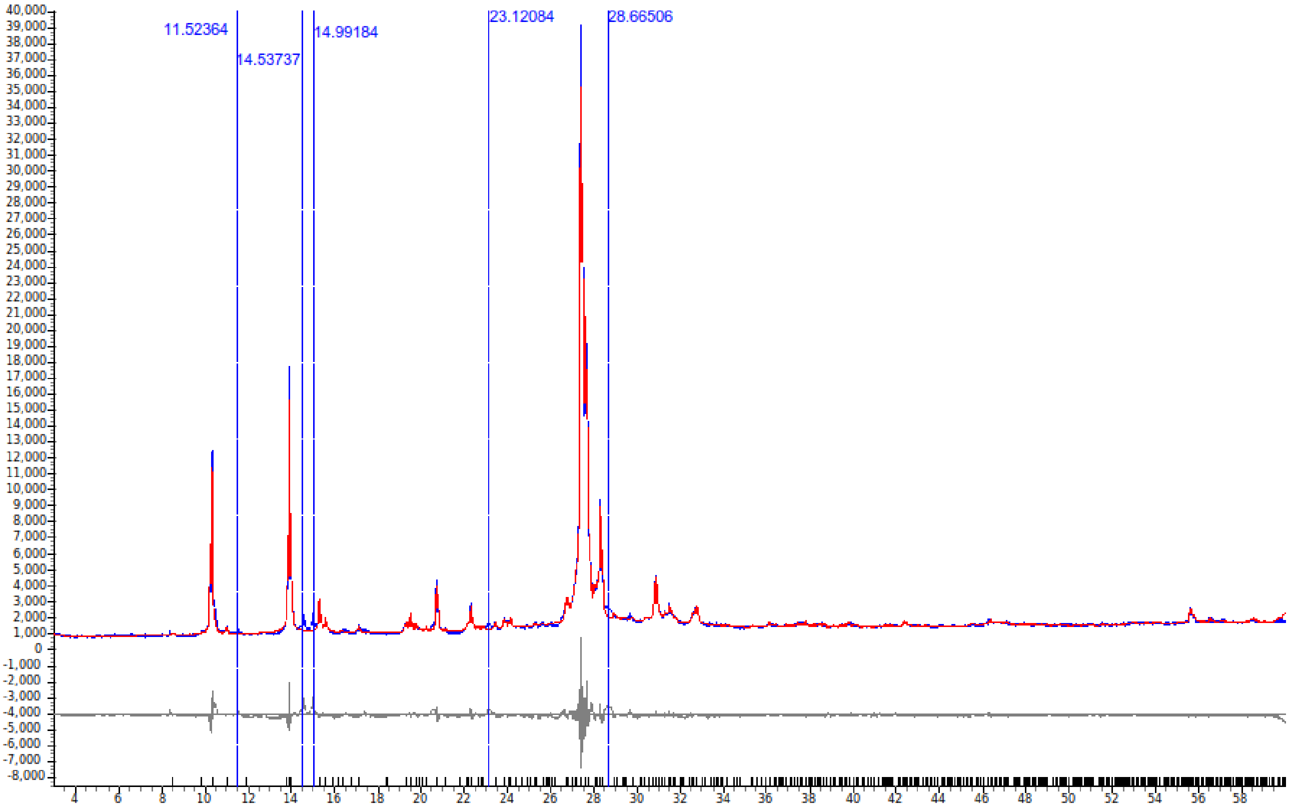


Figure S2. Pawley fit of PXRD data for aminofurazan **3a**·H_2O (R_{wp} = 0.067).

Powder diffraction crystal data for **3a**·H_2O. $C_3H_8N_{10}O_3$ (M = 232.19) at room temperature (ca. 298 K): monoclinic, space group $P2_1/n$, a = 12.2324(15), b = 12.7206(12), c = 13.3676(8) Å, β = 108.694(8)°, V = 1970.3(3) Å^3, Z = 8, Z' = 2, d_{calc} = 1.566 g·cm^{-3}, Pawley fit resulted in R_{wp} = 0.067.

The powder sample separated from the reaction mixture contained pure salt **3a**, while single crystals obtained after recrystallization from ethanol lead to monohydrate **3a**·H_2O. The single crystal structure **3a**·H_2O provides detailed information about the geometry of the anion. The unit cell of **3a**·H_2O contains two symmetry independent sets of anions (as well as cations and solvating water molecules), whose geometries virtually coincide. The anions adopt nearly the planar conformation with intramolecular H-bonds between one of the hydrogen atoms of the amino group and nitrogen atom of the azoxy group with N···N distances equal to 2.9111(16) and 2.8943(15) Å (Figure S3). The valence bonds and angles in the anion are within typical for related compounds that was confirmed by a Mogul geometry.[16] The remaining hydrogen atom of the amino group and hydrogen atoms of the ammonium cation and water molecules form multiple intermolecular H-bonds, leading to a complex H-bonded network.

The model of the anion in structure **3a** obtained from the PXRD experiment does not allow a detailed discussion of its geometry. However, the conformation of the anion is the same that is found in the hydrate structure (Figure S4), with the intermolecular H-bond N6–H6B···N8 (N···N 2.883(14) Å). Hydrogen atoms of the cation participate in multiple H-bonds with nitrogen atoms of the amino group and furazan and tetrazole rings.

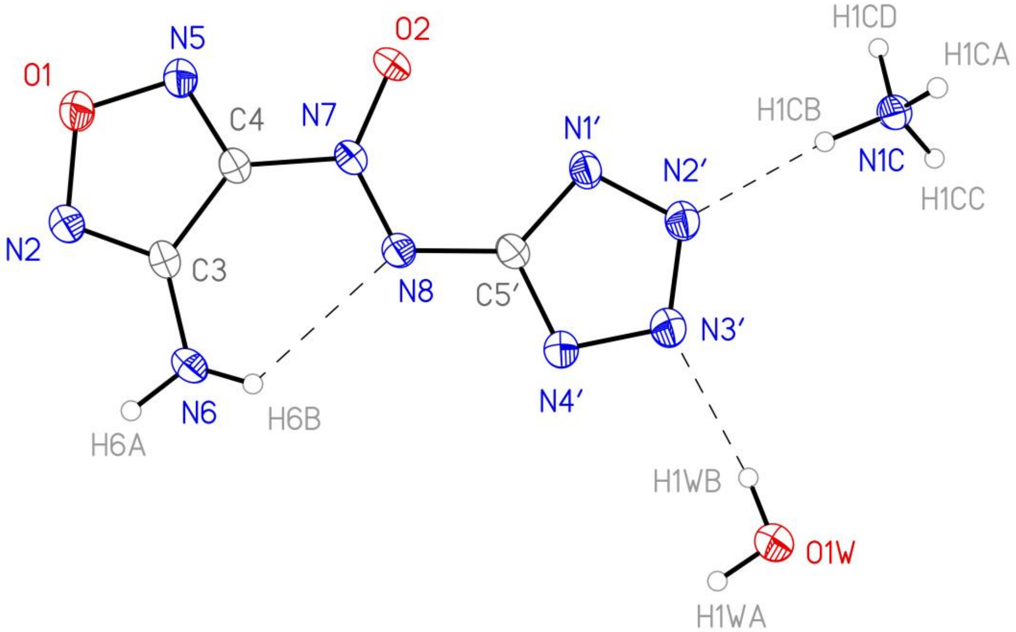


Figure S3. General view of the anion, the cation and solvating water molecule in crystal **3a**·H_2O; non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50 %).

---

[16] I. J. Bruno, J. C. Cole, M. Kessler, J. Luo, W. D. S. Motherwell, L. H. Purkis, B. R. Smith, R. Taylor, R. I. Cooper, S. E. Harris, A. G. Orpen, *J. Chem. Inf. Comp. Sci.*, 2004, 44, 2133.

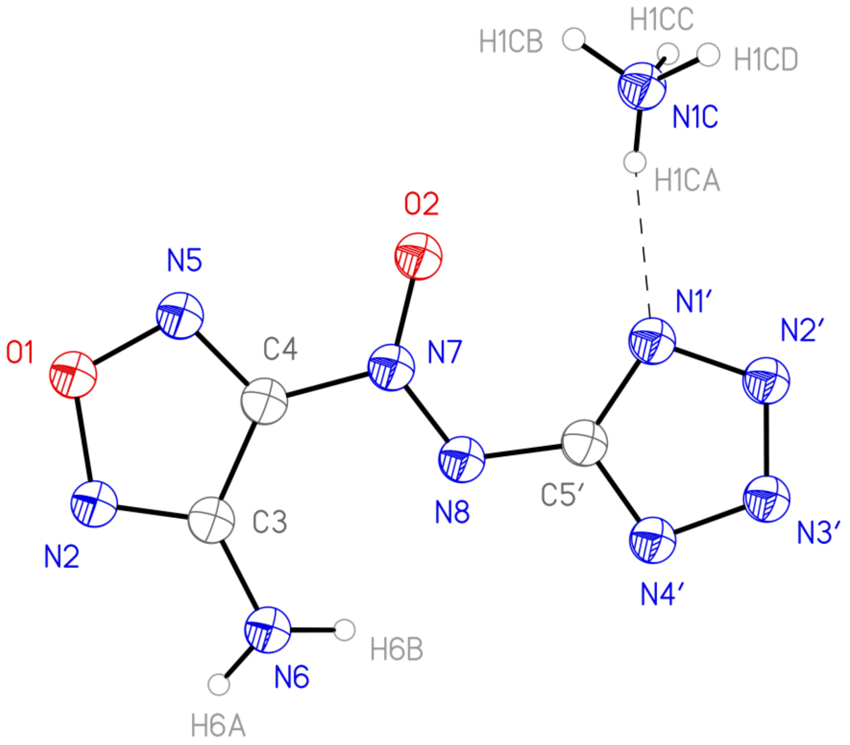
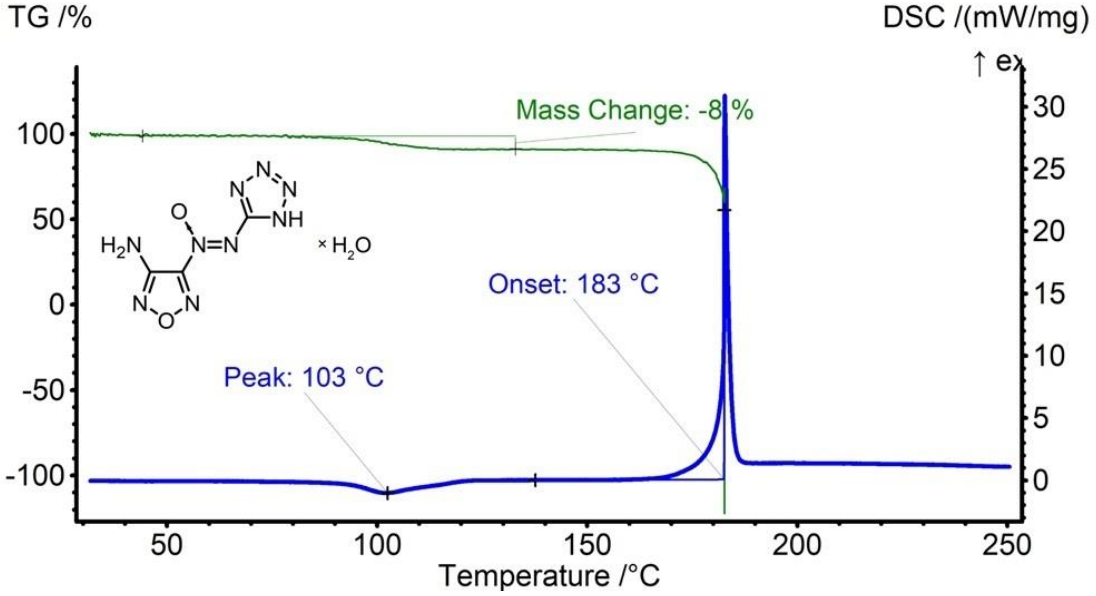
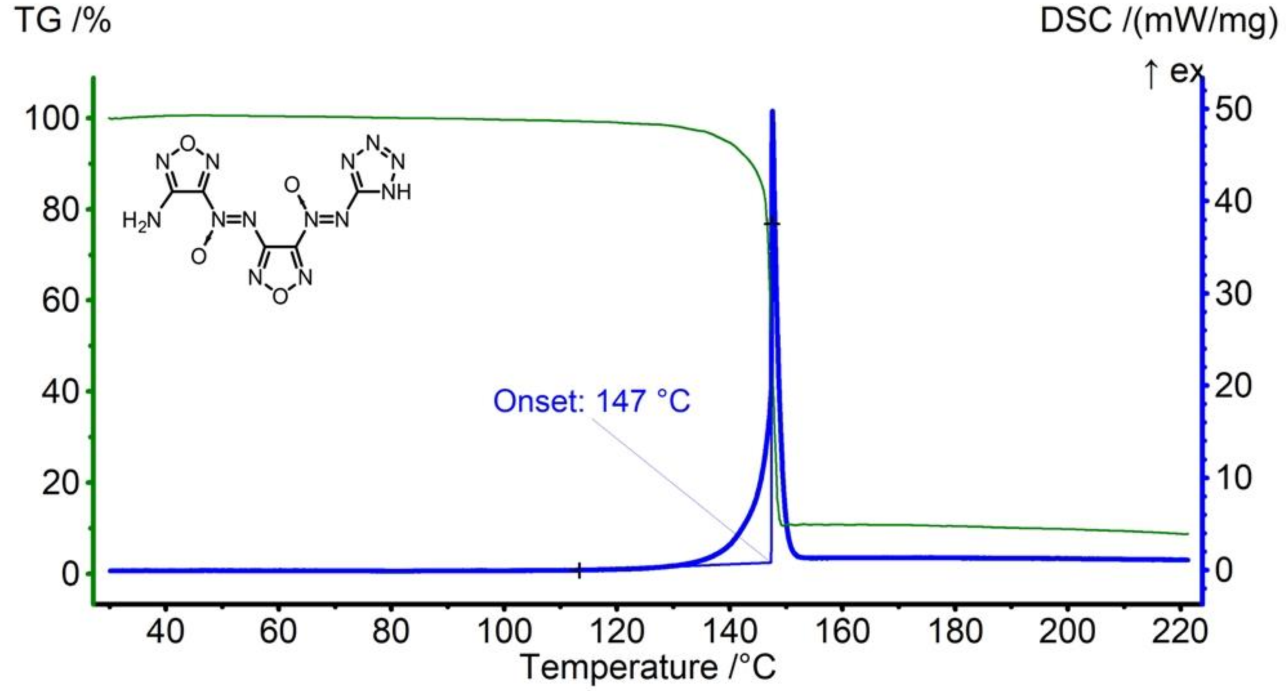


Figure S4. General view of the anion and the cation of ammonium salt **3a**; from powder X-ray diffraction experiment; non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50%).

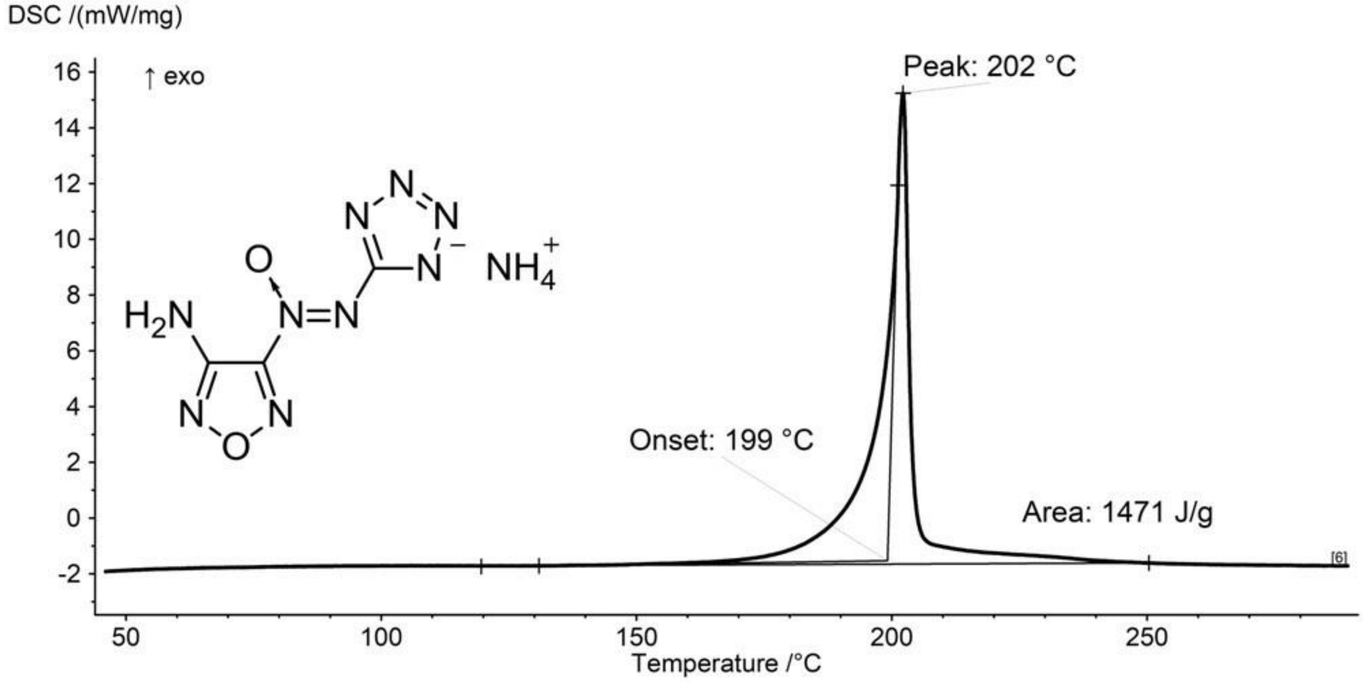
DSC of tetrazole 1·H_2O



DSC of tetrazole 2



DSC of salt 3a



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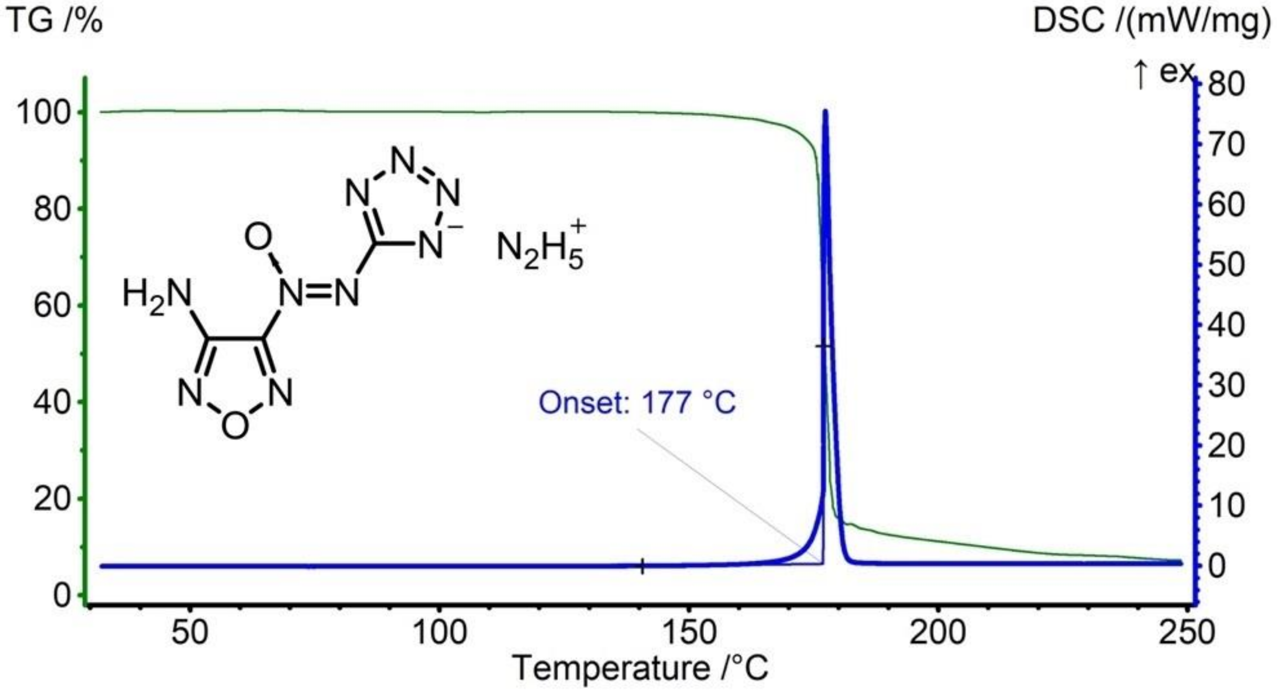
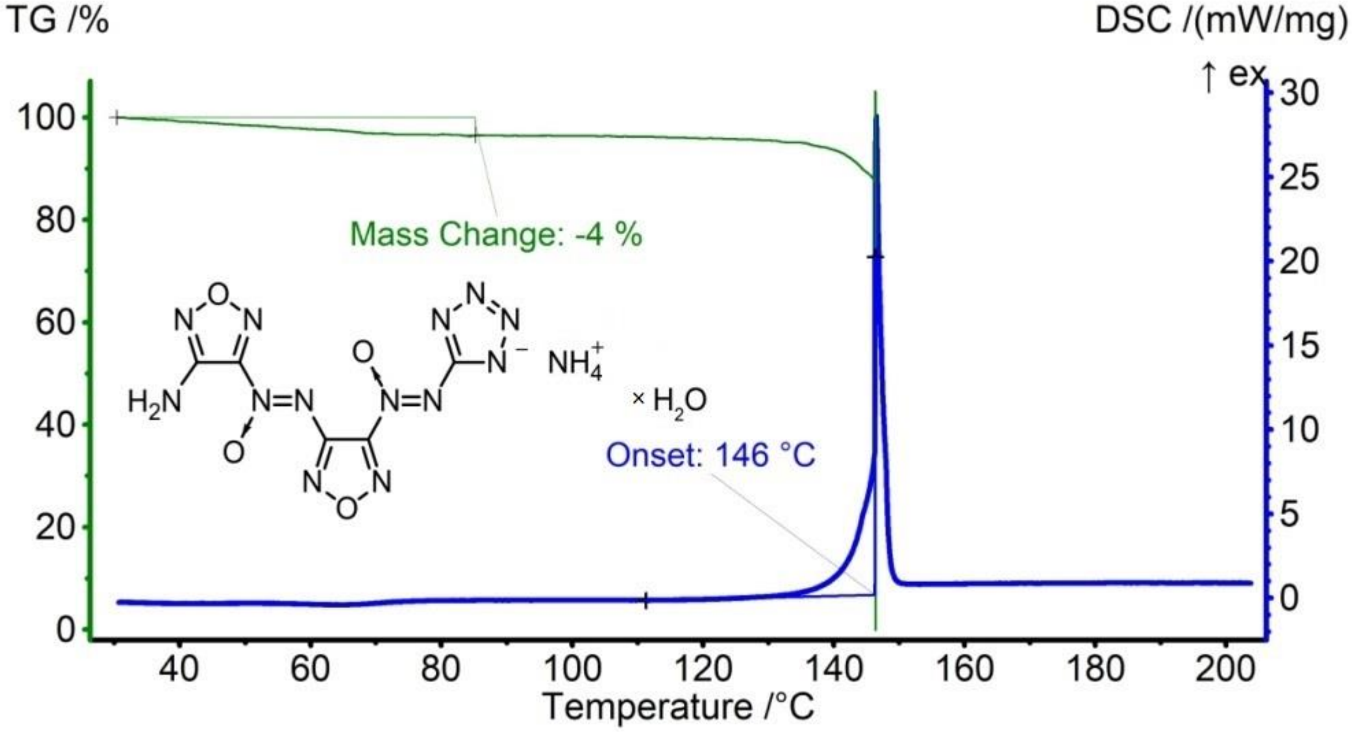
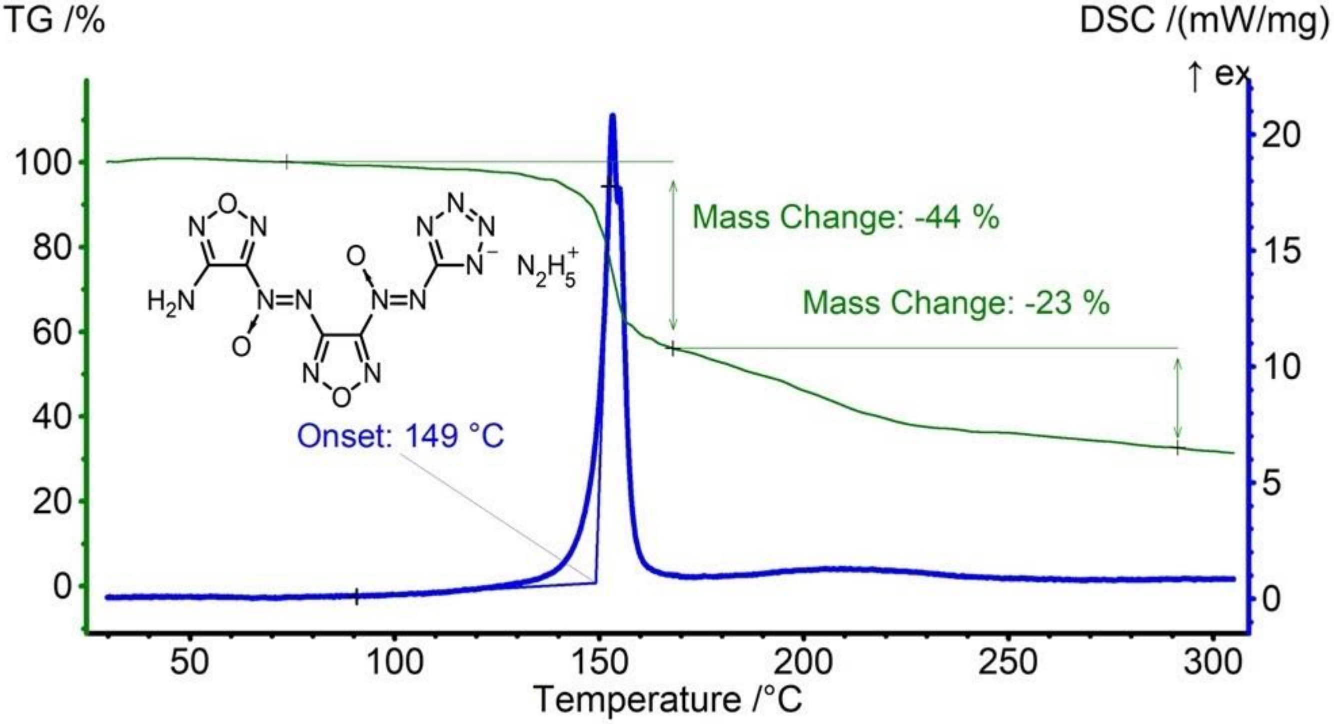


DSC of salt 4a·H_2O



DSC of salt 4b



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).[17]

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 substances **3a** and **3b** 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.[18]

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

[18] 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 compounds **3a** and **3b** is given in Table S1, S2.

Table S1. Results of determination of the combustion energy of the compound **3a**.

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	0.090112	2.41211	1296.73	1025.02	7.20	2.55	7.81	2820.4
2	0.073861	2.16373	1163.20	935.83	7.24	2.10	9.55	2822.6
3	0.070160	2.15052	1156.10	939.30	7.22	1.98	9.46	2824.1
4	0.071611	2.14658	1153.98	932.99	7.26	2.02	9.68	2821.2
5	0.074992	2.22043	1193.68	963.14	7.28	2.12	9.64	2820.3
$-\Delta U'_B = 2821.7 \pm 1.9$ cal·g^{-1}								

Table S2. Results of determination of the combustion energy of compound **3b**.

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	0.068948	2.09739	1127.54	907.01	7.25	2.01	10.52	2911.6
2	0.071070	2.12727	1143.60	915.68	7.22	2.07	11.48	2914.7
3	0.069423	2.13992	1150.41	929.30	7.22	2.01	9.56	2914.3
4	0.070858	2.15791	1160.07	934.79	7.24	2.04	9.72	2911.2
5	0.074203	2.18693	1175.67	940.32	7.20	2.16	9.91	2912.0
$-\Delta U'_B = 2912.8 \pm 1.8$ 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 compounds 3a,b

The combustion reactions of compounds **3a,b** proceed in accordance with the stoichiometry presented in equations (I, II), respectively:

$$C_3H_6N_{10}O_{2(cr)} + 3.5O_{2(g)} = 3CO_{2(g)} + 3H_2O_{(l)} + 5N_{2(g)} \qquad \text{(I)}$$

$$C_3H_7N_{11}O_{2(cr)} + 3.75O_{2(g)} = 3CO_{2(g)} + 3.5H_2O_{(l)} + 5.5N_{2(g)} \qquad \text{(II),}$$

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

The standard enthalpies of formation of substances **3a,b** are calculated based on the enthalpies of combustion in accordance with equations (I, II):

$$\Delta H^{\circ}_{f}[C_3H_6N_{10}O_2]_{(cr)} = 3\Delta H^{\circ}_{f}[CO_2]_{(g)} + 3\Delta H^{\circ}_{f}[H_2O]_{(l)} - \Delta H^{\circ}_{c} \qquad \text{(III)}$$

$$\Delta H^{\circ}_{f}[C_3H_7N_{11}O_2]_{(cr)} = 3\Delta H^{\circ}_{f}[CO_2]_{(g)} + 3.5\Delta H^{\circ}_{f}[H_2O]_{(l)} - \Delta H^{\circ}_{c} \qquad \text{(IV),}$$

where ΔH°_{c} – the standard enthalpy of combustion of the corresponding compound, $kcal \cdot mol^{-1}$, and ΔH°_{f} – the standard enthalpy of its formation, $kcal \cdot mol^{-1}$.

When calculating the standard enthalpy of formation of the studied compounds **3** and **4**, the reference values of the enthalpies of formation of combustion products were used:

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

$\Delta H^{\circ}_{f}[H_2O]_{(l)} = -68.315 \pm 0.009\ kcal \cdot mol^{-1}$.[19]

Table S3. Thermochemical characteristics in the standard state of compounds **3a,b**.

Compound	$-\Delta U'_B$ / $cal \cdot g^{-1}$	ΔH°_{c} / $kcal \cdot mol^{-1}$	ΔH°_{f} / $kcal \cdot mol^{-1}$	ΔH°_{f} / $kcal \cdot kg^{-1}$
3a	2821.7 ± 1.9	–600.9 ± 0.4	113.8 ± 0.4	531.4 ± 1.9
3b	2912.8 ± 1.8	–663.9 ± 0.4	142.7 ± 0.4	622.7 ± 1.7

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[19] 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.

Calculation of the enthalpies of combustion and formation of compound 2 and 4b

The enthalpies of combustion and formation of compounds **2** and **4b** (Table S4) were calculated by an additive method using the contributions values of functional groups to the enthalpy of combustion.

In accordance with the thermochemical data on cyano and tetrazole derivatives,[20] the substitution of the cyano group by the tetrazole ring increases the enthalpy of formation by 31 kcal·mol^{-1}. Using the latter value and the experimentally measured enthalpy of formation of compound **6**, the standard enthalpy of formation of compound **2** was calculated.

The contribution value of azoxyfurazanyl moiety (99.4 kcal·mol^{-1}) was calculated using the experimentally measured enthalpies of formation of compounds **5** (114.3 ± 0.3 kcal·mol^{-1}) and **6** (213.7 ± 1.4 kcal·mol^{-1}).[3]

Using the contribution value of azoxyfurazanyl moiety and the experimentally measured enthalpy of formation of hydrazinium salt **3b**, the standard enthalpy of formation of hydrazinium salt **4b** was calculated.

Table S4. Calculated thermochemical characteristics in the standard state of compounds **2** and **4b**.

Compound	$-\Delta U'_B$ / cal·g^{-1}	ΔH°_c / kcal·mol^{-1}	ΔH°_f / kcal·mol^{-1}	ΔH°_f / kcal·kg^{-1}
2	–	–	244.7	791.5
4b	–	–951.4	242.1	709.5

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[20] J. B. Pedley, *Thermochemical data and structures of organic compounds. Vol 1*, Thermodynamic Research Center: College Station, Texas, USA, 1994, p. 579.