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"Highly energetic *N*-cyano-substituted CL-20 analogues: challenging the stability limits of polynitro hexaazaisowurtzitanes"

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Contents

Experimental Section

General methods

Analytical thin-layer chromatography (TLC) was carried out on Silufol UV-254 silica gel and Merck 60 F254 silica gel aluminum sheets. Merck 60 (15–40 µm) silica gel was used for preparative column and thin-layer chromatography. Melting points were determined with a Boethius Kofler melting point apparatus (heat rate 5 °C·min^{-1}). ^{1}H, ^{13}C and ^{14}N NMR spectra of compounds **4**, **8**, **10**, **12**, **14**, **20**, **21** were recorded using a 300 MHz (Bruker AM300) nuclear magnetic resonance spectrometer operating at 300.1, 75.5 and 30.4, respectively. ^{1}H, ^{13}C{^{1}H}, ^{14}N and ^{15}N{^{1}H} NMR spectra of compounds **5**, **6**, **15**, **22**, **23** were recorded using a 600 MHz (Bruker AV600) nuclear magnetic resonance spectrometer operating at 600.13, 564,69, 150.9, 43.37 and 60.8 MHz, respectively. DMSO-d$_6$ and acetone-d$_6$ were employed as NMR solvent. Chemical shifts /in the ^{1}H, ^{13}C, ^{19}F, ^{14}N and ^{15}N spectra are reported in delta (δ) units, parts per million (ppm), relative to the internal standard Me$_4$Si (TMS) (^{1}H, ^{13}C − positive values correspond to downfield chemical shifts) and external standard MeNO$_2$ (^{14}N, ^{15}N − negative values correspond to upfield shifts). The values of the spectral parameters J and $\Delta v_{1/2}$ are given in Hz. The signals in the NMR spectra were assigned based on the values of a resonance peaks in similar compounds.[8,27] IR spectra were recorded on a Bruker ALPHA-T spectrometer in the range from 4000 to 400 cm^{-1} (resolution 2 cm^{-1}) using KBr pellets. The IR spectral frequencies were assigned according to commonly observed values reported in the literature.[28] High-resolution mass spectra (HRMS) were recorded by electrospray ionization (ESI) with a Bruker micrOTOF II instrument. Elemental analyses were carried out on Perkin Elmer 2400 elemental analyzer. X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using graphite monochromatized Cu K$_\alpha$-radiation (λ =1.54184 Å). Electron microscopy characterization was performed using Hitachi Regulus8230 field-emission scanning electron microscope (FE-SEM). Target-oriented approach was utilized for the optimization of the analytic measurements.[29] Before measurements the sample was mounted on a 25 mm aluminum specimen stub, fixed by conductive carbon tape and coated with a 30 nm film of carbon. Images were acquired in secondary electron mode at a 4 kV accelerating voltage. Electrostatic potentials (ESP) of

the 0.001 electrons per bohr^3 isosurfaces for the electron density were computed on the basis of XRD results using quantum chemical calculations employing the GAUSSIAN 09 program package[17] and consist of the evaluation of the electron density and electrostatic potential of the optimized molecular structures for the gas phase using the DFT/B3LYP method at the 6-31G(d,p) level. The powders densities were measured at ~30 °C using a Micromeritics AccuPyc 1340 V2.01 helium pycnometer. Thermochemical measurements were carried out on a precision automatic combustion calorimeter with an isothermal coating specifically developed for combustion of energetic compounds.[18] Thermal behavior was studied with simultaneous thermal analysis STA 449 F1 Jupiter (Netzsch). A sample with a mass of ~1.5 mg was placed into capped aluminum crucibles with cracked lids and heated at a linear rate of 5 °C·min^{-1} to 600 °C in argon flow under atmospheric pressure. Sensitivity toward impact and friction was measured on a BAM devices using STANAG[22] standards in sets of 30 experiments. Solvents were purified before use according to the standard procedures.[30] All other reagents were used without further purification. The starting materials were obtained according to previously reported procedures.[12,15,8b]

4-Trifluoroacetyl-2,6,8,12-tetranitrohexaazaisowurtzitane (**1**) was prepared according to method of *Bellamy et al.*[12,15] by di-*N*-trifluoroacetylation of 2,6,8,12-tetraacetylhexaazaisowurtzitane (TADA) with TFAA, followed by nitrolysis of the *N*-acetyl groups using HNO$_3$/30% oleum and removal of the *N*-trifluoroacetyl protecting group with EtOH in ~90% total yield per three steps, dec. >185 °C, ^{1}H NMR (300.1 MHz, acetone-d$_6$): δ 5.99 (brs, 1H, NH), 6.65 (s, 2H, CH), 7.29 (m, 1H, CH), 7.60 (m, 1H, CH), 7.85 (s, 2H, CH) ppm.

4-Methoxymethyl-2,6,8,10,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (**11**) was obtained based on our method[8b] by *N*-chloromethylation of **1** with CH$_2$O/HCl$_{(g)}$, followed by methanolysis and deprotection amino the with group AcONa/EtOH in ~75% total yield per three steps, mp 180–182 °C (dec.). ^{1}H NMR (300.1 MHz, acetone-d$_6$): δ 3.39 (s, 3 H, Me), 4.76 (s, 2 H, CH$_2$), 5.50 (brs, 1 H, NH), 6.35 (d, $J_{H,H}$ = 8 Hz, 2 H, CH^{4,5}), 6.47 (d, $J_{H,H}$ = 8 Hz, 2 H, CH^{2,3}), 7.69 (s, 2 H, CH^{1,6}) ppm.

2,6,8,10,12-Pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane (**16**) was prepared according to previously reported procedures of *Bellamy et al.*[12] was prepared by mono-*N*-trifluoroacetylation of TADA with TFAA/TFA, followed by nitrolysis of the *N*-acetyl groups using HNO3/30% oleum and removal of the *N*-trifluoroacetyl protecting group by

solvolysis with EtOH in ~40% total yield per three steps, dec >165 °C; ^{1}H NMR (300.1 MHz, acetone-d$_6$): δ 6.00 (broad s, 1H, NH), 6.70–6.73 (m, 2 H, 2 CH), 7.91 (s, 2 H, 2 CH), 7.97 (d, $J_{H,H}$ = 8 Hz, 2H, 2CH) ppm.

2,6,8,12-Tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (**17**) was obtained according to previously reported procedures of *Bellamy et al.*[12,15] by di-*N*-trifuoroacetylation of TADA with TFAA, followed by nitrolysis of the *N*-acetyl groups using HNO$_3$/30% oleum and removal the *N*-trifluoroacetyl groups with AcONa/EtOH in ~50% total yield per three steps, dec >185 °C; ^{1}H NMR (300.1 MHz, acetone-d$_6$): 5.44 ppm (s, 2 H, NH), 6.28 ppm (s, 4 H, 4 CH), 7.57 (s, 2 H, 2 CH) ppm.

All physicochemical parameters of starting materials are in agreement with the data given in the literature.

Used trichloroacetyl isocyanate was prepared according to the corresponding reported procedures.[31]

Syntheses

Caution! Although there is no danger in treating these substances, manipulations with such high-energy materials must be carried out by using standard safety precautions. All compounds should be handled with extreme care.

4-Carbomoyl-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (4).
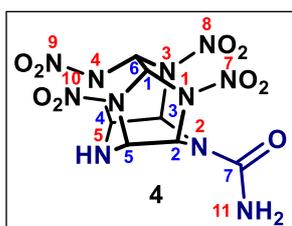
To a solution of **1** (0.500 g, 1.13 mmol) in dry acetonitrile (5 mL), a solution of trichloroacetyl isocyanate (1.30 g, 6.90 mmol) in dry acetonitrile (4 mL) was added dropwise. The reaction mixture was stirred at 20 °C for 24 h, and the solvent was removed *in vacuo*. To the residue, MeOH (7 mL) and 92% H_2SO_4 (0.2 mL) was added, the resulting solution was stirred at 20 °C for 24 h, and the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate (15 mL), washed with distilled water (3x5 mL) to neutral pH of washings, followed by the solution drying over $MgSO_4$, and the solvent was evaporated *in vacuo*. To the residue, a mixture of Et_2O and hexane, 1:1 (2 mL), was added, the precipitate formed was filtered off and air-dried to give trifluoroacetyl derivative **3** (0.460 g, yield: 84%) as a colorless powder, which was directly used in the next step without further purification. To a solution of the resulting compound **3** (0.460 g, 0.945 mmol) in EtOH (4 mL), a solution of NaOAc (0.890 g, 10.9 mmol) in EtOH (8 mL) was added. The reaction mixture was stirred at 20 °C for 1 h, the precipitate formed was filtered off, washed with water (20 mL) and air-dried. Compound **4** (0.218 g, yield: 59% or 50% per two steps) was isolated as a colorless powder, dec. (observed on Kofler's table, 5 °C·min^{-1}): 210 °C.

^{1}H NMR (300.1 MHz, acetone-d$_6$): δ 5.71 (br s, 1 H, NH), 6.32 (br s, 2 H, NH$_2$), 6.42 (d, $J_{H,H}$ = 7 Hz, 2 H, CH^{4,5}), 7.33 (d, $J_{H,H}$ = 8 Hz, 2 H, CH^{2,3}), 7.68 (s, 2 H, CH^{1,6}) ppm. **^{1}H NMR (300.1 MHz, DMSO-d$_6$):** δ 6.30 (br s, 1 H, NH), 7.10 (br s, 2 H, NH$_2$), 6.16 (br s, 2 H, CH^{4,5}), 6.93 (br s, 2 H, CH^{2,3}), 7.65 (s, 2 H, CH^{1,6}) ppm. **^{13}C NMR (75.5 MHz, DMSO-d$_6$):** δ 68.0 (CH^{2,3}), 71.4 (CH^{4,5}), 72.3 (CH^{1,6}), 154.7 (C=O) ppm. **^{14}N NMR (21.7 MHz, DMSO-d$_6$):** δ −36 ($\Delta v_{1/2}$ = 365 Hz) (4 NO$_2$) ppm. **IR (KBr):** $\tilde{v}$ 3460 (m) and 3310 (m) (NH$_2$), 3210 (m) (NH), 3044 (m) (CH), 1708 (s) (C=O), 1587 (vs) and 1548 (s) (*as* N*NO$_2$*), 1324 (s), 1288 (vs) and 1265 (vs) (*sym* N*NO$_2$*) cm^{-1}. **HRMS (ESI):** *m/z* calcd for [C$_7$H$_9$N$_{11}$O$_9$ + NH$_4$$^+$]: 409.0923; found [*M* + NH$_4$]$^+$: 409.0922.

4-Cyano-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (5).

To a solution of $(CF_3SO_2)_2O$ (Tf$_2$O) (0.34 mL, 2.00 mmol) in dry acetonitrile (4 mL), pyridine (0.17 mL, 2.10 mmol) was added dropwise. The resulting mixture was stirred at 20 °C for 10 min and was added dropwise to a solution of **4** (0.200 g, 0.510 mmol) in dry acetonitrile (4 mL). The reaction mixture was stirred at 20 °C for 4.5 h until **4** disappeared by TLC (eluent, ethyl acetate–hexane, 1:1), then diluted with water (20 mL). The product was extracted with ethyl acetate (2×15 mL), the extract was washed with water (3×5 mL). After drying the extract over MgSO$_4$, and evaporating of the solvent *in vacuo*, compound **5** was isolated from the residue by flash column chromatography (elution with ethyl acetate). To the crude product, Et$_2$O (1 mL) was added, the precipitate formed was filtered off and air-dried. The resulting product can be further purified by recrystallisation from ethyl acetate in CCl$_4$ vapor atmosphere. Compound **5** (0.169 g, yield: 88%) was obtained as a colorless powder, DSC. (5 °C·min^{-1}): onset 173 °C, max 210 °C. Density (pycnometer, 26 °C): 1.902 g·cm^{-3}.

^{1}H NMR (600.13 MHz, acetone-d$_6$): δ 5.96 (br s, 1 H, NH), 6.56 (br s, 2 H, CH^{4,5}), 6.88 (d, $J_{H,H}$ = 7 Hz, 2 H, CH^{2,3}), 7.81 (s, 2 H, CH^{1,6}) ppm. **^{13}C{^{1}H} NMR (150.9 MHz, acetone-d$_6$):** δ 71.6 (CH^{4,5}), 72.5 (CH^{2,3}), 72.7 (CH^{1,6}), 111.1 (CN) ppm. **^{14}N NMR (43.37 MHz, acetone-d$_6$):** δ −40 ($\Delta v_{1/2}$ = 72 Hz) (2 N^{9,10}O$_2$), −38 ($\Delta v_{1/2}$ = 75 Hz) (2 N^{7,8}O$_2$) ppm. **^{15}N{^{1}H} NMR ([INVGATED], 60.8 MHz, acetone-d$_6$):** δ −336.3 (N^2), −182.6 (N^{1,3}), −177.6 (N^{4,5}), −172.0 (CN^{11}), −39.9, (N^{7,8}), −37.1, (N^{9,10}) ppm. **IR (KBr):** $\tilde{v}$ 3388 (m) (NH), 3038 (m) (CH), 2243 (s) (CN), 1595 (vs) and 1555 (s) (*as* N*NO$_2$*), 1328 (vs), 1292 (vs) and 1269 (vs) (*sym* N*NO$_2$*) cm^{-1}. **HRMS (ESI):** *m/z* calcd for [C$_7$H$_7$N$_{11}$O$_8$ − H$^+$]: 372.0406; found [*M* − H]$^+$: 372.0398.

4-Nitroso-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (8).

To a solution of **1** (0.50 g, 1.13 mmol) in AcOH (5 mL), NaNO$_2$ (0.35 g, 5 mmol) was added portionwise. The reaction mixture was stirred at 20 °C for 4 h until **1** disappeared by TLC (eluent, ethyl acetate–hexane, 1:1) and then diluted with water (30 mL). The precipitate formed was filtered off, washed with water and air-dried to give trifluoroacetyl derivative **7** (0.450 g, yield: 85%) as a colorless powder, which was directly used in the next step without further purification. The resulting compound **7** (0.450 g, 0.85 mmol) was dissolved in EtOH (8 mL), the reaction mixture was stirred at 20 °C for 45 min, the precipitate formed was filtered off, washed with mixture of EtOH and water, 1:1 (4 mL), and air-dried. Compound **8** (0.311 g, yield: 87%) was isolated as a colorless powder, dec.. (observed on Kofler's table, 5 °C·min^{-1}): 190 °C.

¹H NMR (300.1 MHz, acetone-d₆): δ 5.92 (br s, 1 H, NH), 6.49 and 6.80 (2d, $J_{H,H}$ = 8 Hz, 2 H, CH²,³), 7.84 (dd, $J_{H,H1}$ = 16 Hz, $J_{H,H2}$ = 2 Hz, 2 H, CH⁴,⁵) and 7.96 (dd, $J_{H,H}$ = 8 Hz, $J_{H,H}$ = 2 Hz, 2 H, CH⁴,⁵), 7.85 (d, $J_{H,H}$ = 6 Hz, 2 H, CH¹,⁶) ppm. **¹³C NMR (75.5 MHz, acetone-d₆):** δ 68.0 (CH²,³), 71.4 (CH⁴,⁵), 72.3 (CH¹,⁶), 154.7 (C=O) ppm. **¹⁴N NMR (21.7 MHz, acetone-d₆):** δ −40 ($\Delta\nu_{1/2}$ = 61 Hz) (2 N⁷,⁸O₂) and −37 ($\Delta\nu_{1/2}$ = 59 Hz) (2 N⁹,¹⁰O₂) ppm. **IR (KBr):** $\tilde{\nu}$ 3466 (m) and 3401 (m) (NH), 3037 (m) (CH), 1604 (vs) and 1558 (vs) (*as* N*NO₂*), 1330 (vs), 1289 (vs) and 1266 (vs) (*sym* N*NO₂*) cm⁻¹. **Elemental analysis** for $C_6H_7N_{11}O_9$ (377.19): calcd C, 19.10; H, 1.86; N, 40.85 %; found C, 19.43; H, 1.99; N, 40.60 %.

4-Carbomoyl-10-nitroso-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (10).

To a solution of **8** (0.440 g, 1.17 mmol) in dry acetonitrile (5 mL), a solution of trichloroacetyl isocyanate (1.50 g, 8.00 mmol) in dry acetonitrile (4 mL) was added dropwise. The reaction mixture was stirred at 20 °C for 24 h, and the solvent was removed *in vacuo*. To the residue, MeOH (7 mL) and 92% H_2SO_4 (0.3 mL) was added, the resulting solution was stirred at 20 °C for 24 h, and the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate (20 mL), washed with distilled water (3x5 mL) to neutral pH of washings, followed by the solution drying over MgSO₄, and the solvent was evaporated *in vacuo*. The product was isolated from the residue by preparative TLC (elution with ethyl acetate–hexane, 1:1). Compound **10** (0.299 g, yield: 61%) was obtained as a colorless powder, mp 130–132 °C (dec.).

¹H NMR (300.1 MHz, acetone-d₆): δ 6.51 (br s, 1 H, NH₂), 7.47 and 7.83 (2 dd, $J_{H,H1}$ = 8 Hz, $J_{H,H2}$ = 2 Hz, 2 H, CH²,³), 7.92 and 8.12 (2 dd, $J_{H,H1}$ = 8 Hz, $J_{H,H2}$ = 2 Hz, 2 H, CH⁴,⁵), 7.95 (s, 2 H, CH¹,⁶) ppm. **¹³C NMR (75.5 MHz, acetone-d₆):** δ 61.1 and 71.5 (CH⁴,⁵), 70.6 and 73.2 (CH²,³), 74.9 and 75.1 (CH¹,⁶), 155.3 (C=O) ppm. **¹⁴N NMR (21.7 MHz, acetone-d₆):** δ −40 ($\Delta\nu_{1/2}$ = 100 Hz) (4 NO₂) ppm. **IR (KBr):** $\tilde{\nu}$ 3468 (s) and 3324 (s) (NH₂), 3039 (w) (CH), 1708 (vs) (C=O), 1604 (vs) and 1555 (s) (*as* N*NO₂*), 1325 (s), 1290 (vs) and 1266 (vs) (*sym* N*NO₂*) cm⁻¹. **HRMS (ESI):** *m/z* calcd for $[C_7H_8N_{12}O_{10}$ + Na⁺]: 443.0379; found [*M* + Na] ⁺: 443.0386.

4-Cyano-10-nitroso-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (6).

A. To a solution of **5** (0.055 g, 0.147 mmol) in dry acetonitrile (4 mL), NOBF₄ (0.034 g, 0.290 mmol) was added. The reaction mixture was stirred at 20 °C for 35 min until **5** disappeared by TLC (eluent, ethyl acetate–hexane, 1:1) and then poured into water (10 mL). The product was extracted with ethyl acetate (2×10 mL), the extract was washed with water (2×2 mL). After drying the extract over MgSO₄, and evaporating of the solvent *in vacuo*, compound

6 was isolated from the residue by preparative TLC (elution with ethyl acetate–hexane, 1:2). Compound **6** (0.030 g, yield: 51%) was obtained as a colorless powder, DSC. (5 °C·min^{-1}): onset 209 °C, max 229 °C. Density (pycnometer, 26 °C): 1.899 g·cm^{-3}.

^{1}H NMR (600.13 MHz, acetone-d$_6$): δ 7.14 and 7.43 (br s, 2 H, CH^{2,3}), 8.02 and 8.24 (br s, 2 H, CH^{4,5}), 8.10 (s, 2 H, CH^{1,6}) ppm. **^{13}C{^{1}H} NMR (150.9 MHz, acetone-d$_6$):** δ 60.3 and 72.6 (CH^{4,5}), 73.9 and 74.6 (CH^{2,3}), 72.6 (CH^{1,6}), 110.2 (CN) ppm. **^{14}N NMR (43.37 MHz, acetone-d$_6$):** δ −42 ($\Delta\nu_{1/2}$ = 79 Hz) (4 NO$_2$^{cage}) ppm. **^{15}N NMR ([INVGATED], 60.8 MHz, acetone-d$_6$):** δ −185.8, −182.8, −182.2, −181.9 (N^{1,3} and N^{4,6}), −170.5 (CN^{11}), −172.8 (N^{12}O), −144.6 (N^5), −41.6, −41.4, −41.3, −41.0 (N^{7,8} and N^{9,10}) ppm. **IR (KBr):** 3035 (m) (CH), 2247 (m) (CN), 1606 (vs) and 1565 (s) (*as* N*NO$_2$*), 1326 (s), 1289 (vs) and 1267 (vs) (*sym* N*NO$_2$*) cm^{-1}. **Elemental analysis** for C$_7$H$_6$N$_{12}$O$_9$ (402.20): calcd C, 20.90; H, 1.50; N, 41.79 %; found C, 20.89; H, 1.37; N, 41.45 %.

B. To an emulsion of Tf$_2$O (0.300 mL, 1.80 mmol) in dry dichloroethane (5 mL), pyridine (0.15 mL, 1.86 mmol) was added dropwise. The resulting mixture was stirred at 20 °C for 10 min, and then was added dropwise to a suspension of **10** (0.108 g, 0.257 mmol) in dry dichloroethane (5 mL) at 0–5 °C. The reaction mixture was stirred at 20 °C for 20 min until **10** disappeared by TLC (eluent, ethyl acetate–hexane, 1:1), then the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate (15 mL), washed with water (3×5 mL). After drying the solution over MgSO$_4$, and evaporating of the solvent *in vacuo*, compound **6** was isolated from the residue by flash column chromatography (elution with ethyl acetate–hexane, 1:1). To the crude product, Et$_2$O (1 mL) was added, the precipitate formed was filtered off and air-dried. Compound **6** (0.043 g, yield: 42%) was obtained as a colorless powder. The physicochemical parameters of the sample are in agreement with those of compound **6** obtained by method A.

4-(2,2,2-Trinitroethyl)-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (12).

To a suspension of **11** (0.360 g, 0.900 mmol) in dry acetonitrile (8 mL) trinitromethane (0.277 g, 1.80 mmol) was added dropwise. The reaction mixture was stirred at 20 °C for 0.5 h, then diluted with water (40 mL). The product was extracted with ethyl acetate (3×20 mL), the extract was washed with water (3×10 mL). After drying the extract over MgSO$_4$, and evaporating of the solvent *in vacuo*, compound **15** was isolated from the residue by flash column chromatography (elution with ethyl acetate–hexane, 1:1). To the crude product, a mixture of Et$_2$O and hexane, 1:1 (2 mL), was added, the precipitate formed was filtered off and air-dried. Compound **12** (0.270 g, yield: 58%) was obtained as a colorless powder, mp 202–204 °C (dec.).

¹H NMR (300.1 MHz, acetone-d₆): δ 5.46 (s, 2H, CH₂), 5.69 (br s, 1 H, NH), 6.34 and 6.36 (2 d, $J_{H,H}$ = 3 Hz, 2 H, CH^{2,3}), 6.60 (d, $J_{H,H}$ = 7 Hz, 2 H, CH^{4,5}), 7.71 (s, 2 H, CH^{1,6}) ppm. **¹³C NMR (75.5 MHz, acetone-d₆):** δ 55.7 (CH₂), 72.9 and 73.0 (CH^{2,3}), 73.5 (CH^{1,6}), 77.7 (CH^{4,5}), 128.0 (C(NO₂)₃) ppm. **¹⁴N NMR (21.7 MHz, acetone-d₆):** δ −37 ($\Delta v_{1/2}$ = 80 Hz) (4 NNO_2), −37 ($\Delta v_{1/2}$ = 80 Hz) (3 CNO_2) ppm. **IR (KBr):** $\tilde{v}$ 3042 (m) (CH), 1609 (vs) (*as* CNO_2), 1596 (vs) and 1561 (s) (*as* NNO_2), 1327 (vs), 1286 (vs) and 1270 (vs) (*sym* CNO_2 and NNO_2) cm⁻¹. **HRMS (ESI):** *m/z* calcd for [C₈H₉N₁₃O₁₄ + Cl⁻]: 546.0075; found [*M* + NH₄] ⁻: 546.0077. **Elemental analysis** for C₈H₉N₁₃O₁₄ (377.19): calcd C, 18.79; H, 1.76; N, 35.62 %; found C, 19.25; H, 1.50; N, 35.37 %.

4-Carbomoyl-10-(2,2,2-trinitroethyl)-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (14).

To a solution of **12** (0.600 g, 1.18 mmol) in dry acetonitrile (5 mL), a solution of trichloroacetyl isocyanate (1.33 g, 7.00 mmol) in dry acetonitrile (7 mL) was added dropwise. The reaction mixture was stirred at 20 °C for 6 h, and the solvent was removed *in vacuo*. To the residue, MeOH (8 mL) and 92% H₂SO₄ (0.4 mL) was added, the resulting solution was stirred at 20 °C for 15 h, and the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate (20 mL), washed with distilled water (3x5 mL) to neutral pH of washings, followed by the solution drying over MgSO₄ and the solvent was evaporated *in vacuo*. To the residue, a mixture of Et₂O and hexane, 1:1 (2 mL), was added, the precipitate formed was filtered off and air-dried. Compound **14** (0.63 g, yield: 97%) was isolated as a colorless powder, mp 118–120 °C.

¹H NMR (300.1 MHz, acetone-d₆): δ 5.51 (s, 1 H, CH₂), 6.42 (br s, 2 H, NH₂), 6.72 (d, $J_{H,H}$ = 8 Hz, 2 H, CH^{4,5}), 7.44 (d, $J_{H,H}$ = 8 Hz, 2 H, CH^{2,3}), 7.84 (s, 2 H, CH^{1,6}) ppm. **¹³C NMR (75.5 MHz, acetone-d₆):** δ 55.4 (CH₂), 70.2 (CH^{1,6}), 74.2 (CH^{2,3}), 78.0 (CH^{4,5}), 127.9 (C(NO₂)₃), 155.0 (C=O) ppm. **¹⁴N NMR (21.7 MHz, acetone-d₆):** δ −38 ($\Delta v_{1/2}$ = 113 Hz) (4 NNO_2), −38 ($\Delta v_{1/2}$ = 33 Hz) (3 CNO_2) ppm. **IR (KBr):** $\tilde{v}$ 3486 (vs) and 3419 (vs) (NH₂), 3042 (w) (CH), 1707 (vs) (C=O), 1596 (br vs) (*as* CNO_2 and NNO_2), 1292 (br s) and 1266 (s) (*sym* CNO_2 and NNO_2) cm⁻¹. **HRMS (ESI):** *m/z* calcd for [C₉H₁₀N₁₄O₁₅ + H⁺]: 555.0523; found [*M* + H] ⁺: 555.0511.

4-Cyano-10-(2,2,2-trinitroethyl)-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (15).

To a solution of Tf$_2$O (0.60 mL, 3.64 mmol) in dry acetonitrile (5 mL), pyridine (0.30 mL, 3.70 mmol) was added dropwise. The resulting mixture was stirred at 20 °C for 10 min, and was added dropwise to a solution of **14** (0300 g, 0.540 mmol) in dry acetonitrile (5 mL). The reaction mixture was stirred at 20 °C for 2.5 h, then diluted with water (40 mL). The product was extracted with ethyl acetate (2×20 mL), the extract was washed with water (3×5 mL). After drying the extract over MgSO$_4$, and evaporating of the solvent *in vacuo*, compound **15** was isolated from the residue by flash column chromatography (elution with ethyl acetate–hexane, 1:2). To the crude product, Et$_2$O (1 mL), was added, the precipitate formed was filtered off and air-dried. Compound **15** (0.255 g, yield: 88%) was obtained as a colorless powder, DSC. (5 °C·min^{-1}): onset 203 °C, max 220 °C. Density (pycnometer, 26 °C): 1.868 g·cm^{-3}.

^{1}H NMR (600.13 MHz, acetone-d$_6$): δ 5.49 (s, 2 H, CH$_2$), 6.87 (d, $J_{H,H}$ = 8 Hz, 2 H, CH^{4,5}), 7.07 (d, $J_{H,H}$ = 7 Hz, 2 H, CH^{2,3}), 8.05 (s, 2 H, CH^{1,6}) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, acetone-d$_6$): δ 53.2 (CH$_2$), 72.9 (CH^{1,6}), 73.2 (CH^{2,3}), 77.2 (CH^{4,5}), 110.4 (CN), 126.3 (C(NO$_2$)$_3$) ppm. ^{14}N NMR (43.37 MHz, acetone-d$_6$): δ −41 ($\Delta v_{1/2}$ = 126 Hz) (2 N^{7,8}O$_2$), −39 ($\Delta v_{1/2}$ = 130 Hz) (2 N^{9,10}O$_2$) ppm. ^{15}N{^{1}H} NMR ([INVGATED], 60.8 MHz, acetone-d$_6$): δ −335.7 (N^2), −181.4 (N^{4,6}), −178.3 (N^{1,3}), −170.5 (CN^{11}), −144.6 (N^5), −40.7 (N^{7,8}), −38.5 (N^{9,10}), −30.7 (C(N^{12}O$_2$)$_3$) ppm. IR (KBr): $\tilde{v}$ 3040 (w) (CH), 2247 (m) (CN), 1597 (br vs) (*as* C*NO$_2$* and N*NO$_2$*), 1293 (br s) and 1268 (s) (*sym* C*NO$_2$* and N*NO$_2$*) cm^{-1}. **HRMS (ESI):** *m/z* calcd for [C$_9$H$_8$N$_{14}$O$_{14}$ + NH$_4$$^+$]: 559.0237; found [*M* + NH$_4$]$^+$: 559.0235.

4-Carbomoyl-2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane (20).
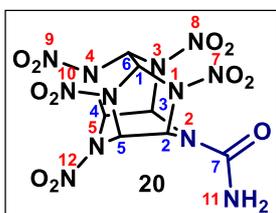
To a solution of **16** (0.500 g, 1.27 mmol) in dry acetonitrile (6 mL), a solution of trichloroacetyl isocyanate (1.05 g, 5.60 mmol) in dry acetonitrile (3 mL) was added dropwise. The reaction mixture was stirred at 20 °C for 24 h, and the solvent was removed *in vacuo*. To the residue, MeOH (10 mL) and 92% H$_2$SO$_4$ (0.2 mL) was added, the resulting solution was stirred at 20 °C for 24 h, and the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate (15 mL), washed with distilled water (3x5 mL) to neutral pH of washings, followed by the solution drying over MgSO$_4$ and the solvent was evaporated *in vacuo*. To the residue, Et$_2$O (1 mL) was added, the precipitate formed was filtered off and air-dried. Compound **20** (0.443 g, yield: 80%) was isolated as a colorless powder, mp 202–204 °C (dec.) (from EtOH–H$_2$O).

^{1}H NMR (300.1 MHz, DMSO-d_6): δ 7.09 (br s, 2 H, NH$_2$), 7.39 (d, $J_{H,H}$ = 7 Hz, 2 H, CH^{2,3}), 7.79 (d, $J_{H,H}$ = 7 Hz, 2 H, CH^{4,5}), 7.93 (s, 2 H, CH^{1,6}) ppm. **^{13}C NMR (75.5 MHz, DMSO-d_6):** δ 70.0 (CH^{2,3}), 70.2 (CH^{4,5}), 73.4 (CH^{1,6}), 154.2 (C=O) ppm. **^{14}N NMR (21.7 MHz, DMSO-d_6):** δ −39 ($\Delta v_{1/2}$ = 431 Hz) (4 NO$_2$) ppm. **IR (KBr):** $\tilde{v}$ 3487 (vs), 3449 (s), 3400 (s) and 3355 (m) (NH$_2$), 3041 (vs) (CH), 1714 (vs) and 1687 (vs) (C=O), 1615 (vs), 1594 (vs) and 1571 (vs) (as NNO$_2$), 1332 (vs), 1295 (vs) and 1269 (vs) (sym NNO$_2$) cm^{-1}. **Elemental analysis** for C$_8$H$_{10}$N$_{12}$O$_{10}$ (434.24): calcd C, 19.27; H, 1.85; N, 38.53 %; found C, 19.37; H, 1.85; N, 38.21 %.

4-Cyano-2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane (22).
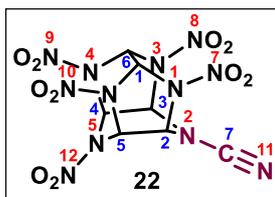
A. To a solution of Tf$_2$O (0.60 mL, 3.64 mmol) in dry acetonitrile (5 mL), pyridine (0.30 mL, 3.90 mmol) was added dropwise. The resulting mixture was stirred at 20 °C for 10 min, and was added dropwise to a solution of **20** (0.200 g, 0.870 mmol) in dry acetonitrile (3 mL). The reaction mixture was stirred at 20 °C for 5 h, then diluted with water (20 mL). The product was extracted with ethyl acetate (2×15 mL), the extract was washed with water (3×5 mL). After drying the extract over MgSO$_4$, and evaporating of the solvent *in vacuo*, compound **22** was isolated from the residue by flash column chromatography (elution with ethyl acetate –hexane, 1:2). To the crude product, Et$_2$O (1 mL) was added, the precipitate formed was filtered off and air-dried. Compound **22** (0.112 g, yield: 58%) was obtained as a colorless powder. The product was further purified by reprecipitation from MeCN with water. DSC (5 °C·min^{-1}): onset 223 °C, max 241 °C. Density (pycnometer, 26 °C): 1.924 g·cm^{-3}.

^{1}H NMR (600.13 MHz, acetone-d_6): 7.30 (d, $J_{H,H}$ = 8 Hz, 2 H, CH^{2,3}), 8.17 (s, 2 H, CH^{1,6}), 8.25 (d, $J_{H,H}$ = 8 Hz, 2 H, CH^{4,5}) ppm. **^{1}H NMR (300.1 MHz, DMSO-d_6):** 7.03 (d, $J_{H,H}$ = 8 Hz, 2 H, CH^{2,3}), 7.81 (d, 2 H, CH^{4,5}), 8.01 (s, 2 H, CH^{1,6}) ppm. **^{13}C{^{1}H} NMR (150.9 MHz, acetone-d_6):** δ 72.2 (CH^{4,5}), 74.9 (CH^{1,6}), 75.2 (CH^{2,3}), 111.4 (CN) ppm. **^{14}N NMR (43.37 MHz, acetone-d_6):** δ −42 ($\Delta v_{1/2}$ = 156 Hz) (5 NNO$_2$) ppm. **^{15}N NMR ([INVGATED], 60.8 MHz, acetone-d_6):** δ −328.6 (N^2), −199.3 (N^5), −182.4 (N^{1,3}), −180.1 (N^{4,6}), −171.1 (CN^{11}), −43.3 (N^{12}), −41.3 (N^{9,10}), −41.0 (N^{7,8}) ppm. **IR (KBr):** $\tilde{v}$ 3042 (s) (CH), 2248 (s) (CN), 1633 (vs), 1593 (vs) and 1571 (vs) (as NNO$_2$), 1329 (vs), 1292 (vs) and 1258 (vs) (sym NNO$_2$) cm^{-1}. **Elemental analysis** for C$_7$H$_6$N$_{12}$O$_{10}$ (418.20): calcd C, 20.10; H, 1.45; N, 40.19; found C, 20.48; H, 1.32; N, 39.85 %.

B. To a solution of **5** (0.060 g, 0.160 mmol) in dry acetonitrile (4 mL), NO$_2$BF$_4$ (0.040 g, 0.300 mmol) was added. The reaction mixture was stirred at 20 °C for 1.5 until **5** disappeared by TLC (eluent, ethyl acetate–hexane, 1:1) and then poured into water (10 mL). The product was extracted with ethyl acetate (2×10 mL), the extract was washed with water (2×2 mL). After drying the extract over MgSO$_4$, and evaporating of the solvent *in vacuo*, compound **15**

was isolated from the residue by preparative TLC (elution with ethyl acetate–hexane, 1:2), Compound **22** (0.037 g, yield: 55%) was obtained as a colorless powder. The physicochemical parameters of the sample are in agreement with those of compound **22** obtained by method A.

4,10-Dicarbomoyl-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (21).
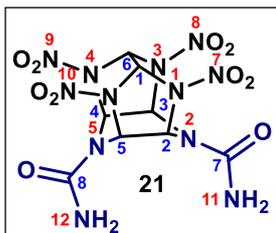
To a suspension of **17** (0.560 g, 1.61 mmol) in dry acetonitrile (15 mL), a solution of trichloroacetyl isocyanate (3.00 g, 15.9 mmol) in dry acetonitrile (10 mL) was added dropwise. The reaction mixture was stirred at 20 °C for 24 h, and the solvent was removed *in vacuo*. To the residue, MeOH (25 mL) and 92% H_2SO_4 (0.3 mL) was added, the resulting solution was stirred at 20 °C for 24 h, and the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate (50 mL), washed with distilled water (2x20 mL) to neutral pH of washings, followed by the solution drying over $MgSO_4$ and the solvent was evaporated *in vacuo*. To the residue, Et_2O (50 mL) was added, the precipitate formed was filtered off, washed with Et_2O (2x20 mL) and air-dried. Compound **21** (0.650 g, yield: 93%) was isolated as a colorless powder, dec. (observed on Kofler's table, 5 °C·min^{-1}): 245 °C.

^{1}H NMR (300.1 MHz, acetone-d$_6$): δ 6.51 (br s, 2 H, NH$_2$), 7.43 (d, $J_{H,H}$ = 7 Hz, 2 H, CH^{2,3} and CH^{4,5}), 7.79 (s, 2 H, CH^{1,6}) ppm. **^{13}C NMR (75.5 MHz, acetone-d$_6$):** δ 68.7 (CH^{2,3} and CH^{4,5}), 73.4 (CH^{1,6}), 154.4 (C=O) ppm. **^{14}N NMR (21.7 MHz, acetone-d$_6$):** δ −38 ($\Delta v_{1/2}$ = 130 Hz) (4 NO$_2$) ppm. **IR (KBr):** $\tilde{v}$ 3426 (vs), 3320 (vs) (NH$_2$), 3268 (s) and 3205 (s) (NH$_2$), 3040 (s) (CH), 1678 (br vs) (C=O), 1611 (vs) and 1557 (vs) (*as* N*NO$_2$*), 1323 (vs), 1288 (vs) and 1263 (vs) (*sym* N*NO$_2$*) cm^{-1}. **HRMS (ESI):** *m/z* calcd for [C$_8$H$_{10}$N$_{12}$O$_{10}$ + H$^+$]: 435.0716; found [*M* + H] $^+$: 435.0707.

4,10-Dicyano-2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazaisowurtzitane (23).
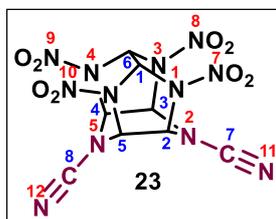
To a solution of Tf$_2$O (0.58 mL, 1.22 mmol) in dry acetonitrile (9 mL), pyridine (0.28 mL, 3.60 mmol) was added dropwise. The resulting mixture was stirred at 20 °C for 5 min, and was added dropwise to a suspension of **21** (0.191 g, 0.440 mmol) in dry acetonitrile (9 mL). The reaction mixture was stirred at 20 °C for 24 h, and the solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate (50 mL), the solution was washed with water (2×20 mL). After drying the solution over $MgSO_4$, and evaporating of the solvent *in vacuo*, compound **23** was isolated from the residue by flash column chromatography (elution with ethyl acetate). To the crude product, Et_2O (50 mL) was added, the precipitate was filtered off and air-dried. Compound **23** (0.160 g, yield: 91%) was

obtained as a colorless powder. The product was further purified by recrystallization from MeCN–H_2O. DSC. (5 °C·min^{-1}): onset 238 °C, max 249 °C (from MeCN–H_2O). Density (pycnometer, 26 °C): 1.858 g·cm^{-3}.

^1H NMR (300.1 MHz, acetone-d$_6$): δ 7.13 (s, 2 H, CH^{2,3} and CH^{4,5}), 8.10 (s, 2 H, CH^{1,6}) ppm. **^1H NMR (600.13 MHz, DMSO-d$_6$):** δ 6.82 (s, 2 H, CH^{2,3} and CH^{4,5}), 7.93 (s, 2 H, CH^{1,6}) ppm. **$^{13}C\{^1H\}$ NMR (150.9 MHz, DMSO-d$_6$):** δ 73.6 (CH^{2,3}, CH^{4,5} and CH^{1,6}), 111.2 (2 CN) ppm. **^{14}N NMR (43.37 MHz, DMSO-d$_6$):** δ −24 ($\Delta\nu_{1/2}$ = 416 Hz) (4 NNO_2) ppm. **^{15}N NMR ([INVGATED], 60.8 MHz, DMSO-d$_6$):** δ −328.6 (N^{2,5}), −182.7 (N^{1,3} and N^{4,6}), −171.6 (CN^{11}), −40.8 (N^{7,8} and N^{9,10}) ppm. **IR (KBr):** $\tilde{v}$ 3031 (vs) (CH), 2246 (vs) (CN), 1616 (vs), 1599 (s) and 1565 (vs) (*as* NNO_2), 1349 (vs), 1330 (vs), 1298 (vs) and 1264 (vs) (*sym* NNO_2) cm^{-1}. **Elemental analysis** for $C_8H_6N_{12}O_8$ (398.21): calcd C, 24.13; H, 1.52; N, 42.21%; found C, 24.12; H, 1.51; N, 42.21 %.

¹H NMR (300.1 MHz, [D₆]acetone) spectrum of compound 4
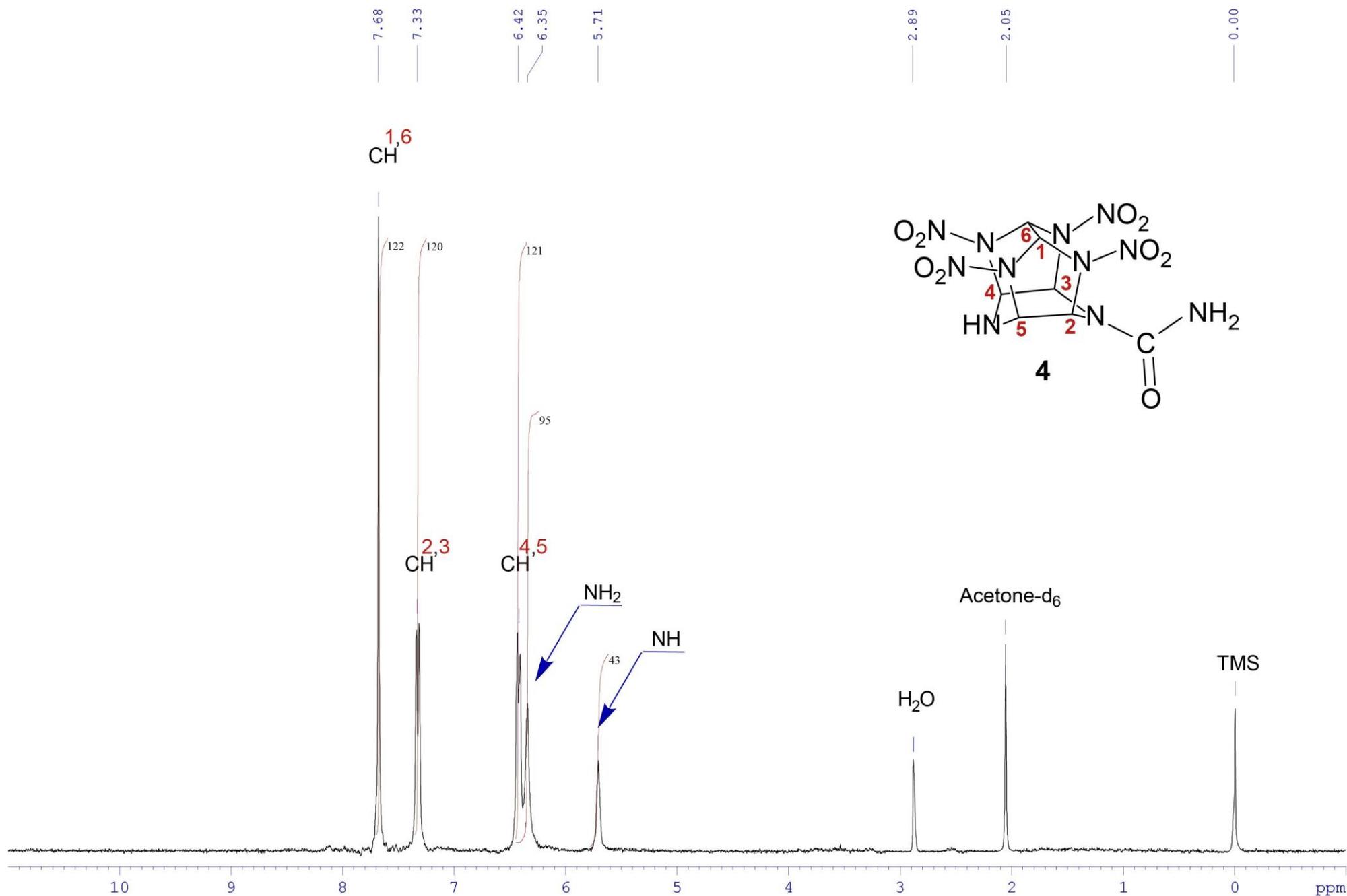
¹H NMR (300.1 MHz, [D₆]DMSO) spectrum of compound 4
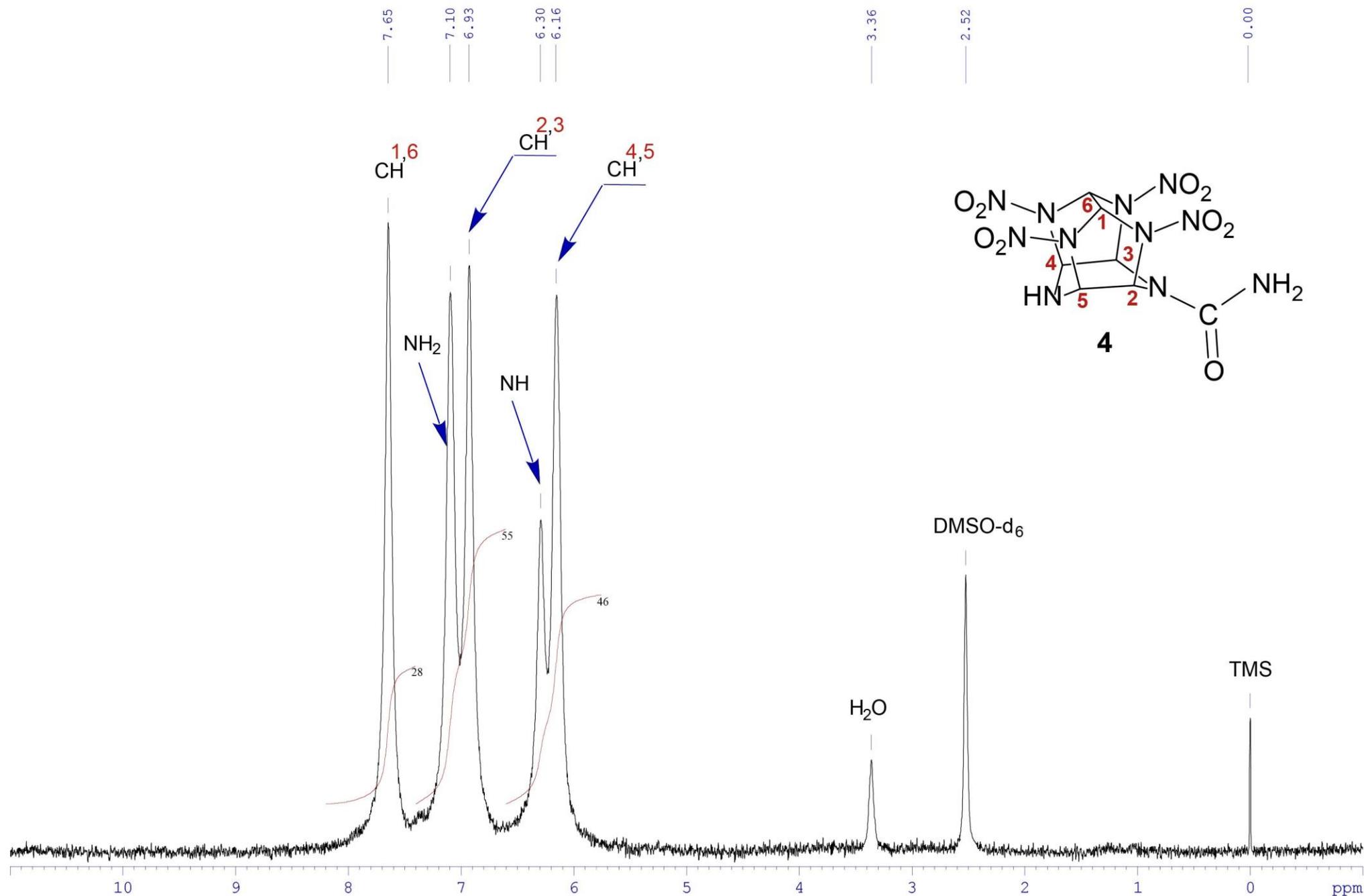
^{13}C NMR (75.1 MHz, [D$_6$]DMSO) spectrum of compound 4
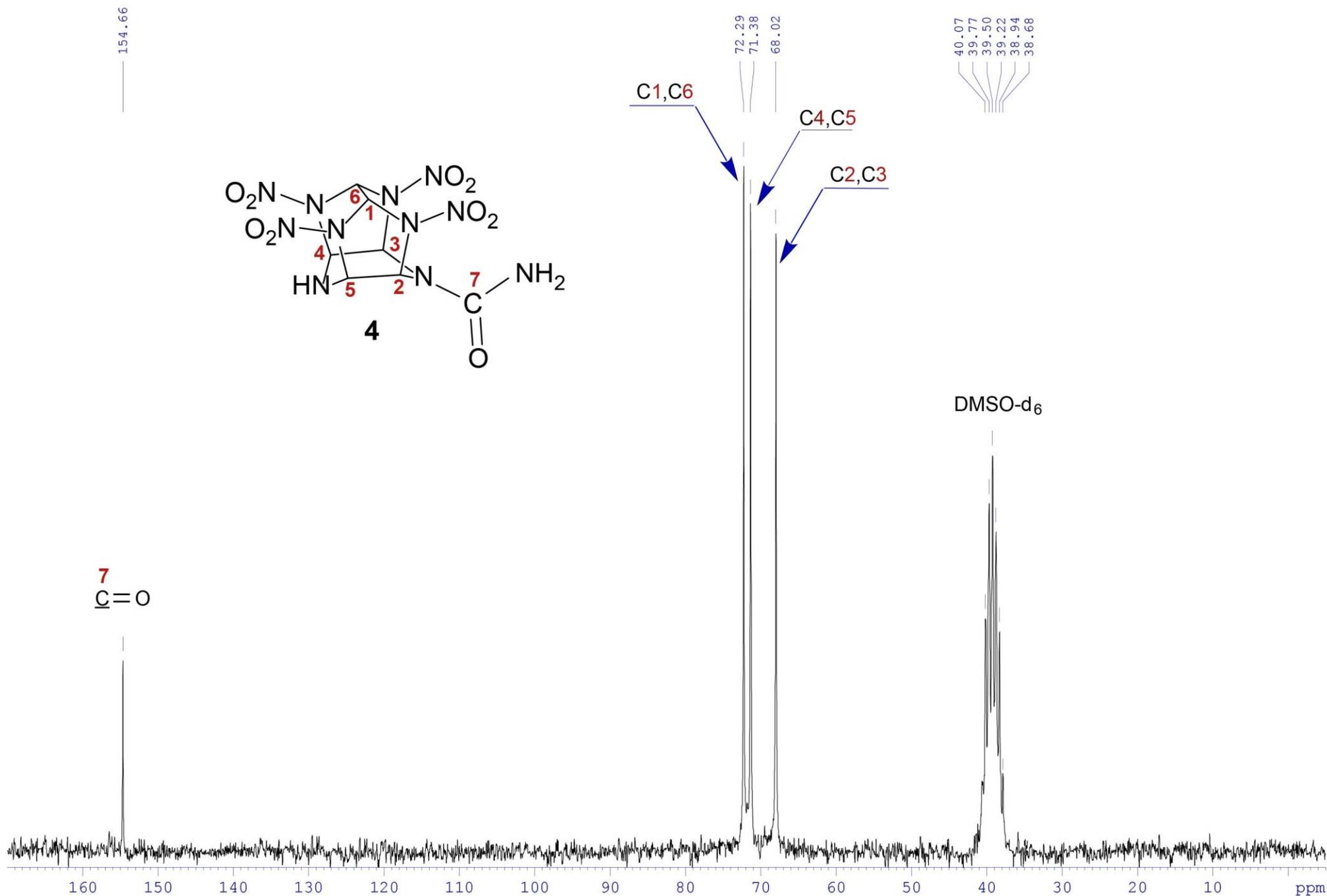
^{14}N NMR (22 MHz, [D$_6$]DMSO) spectrum of compound 4
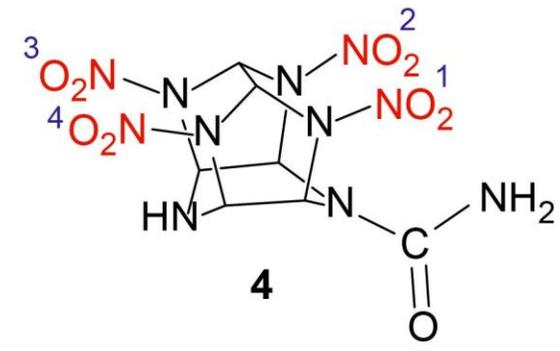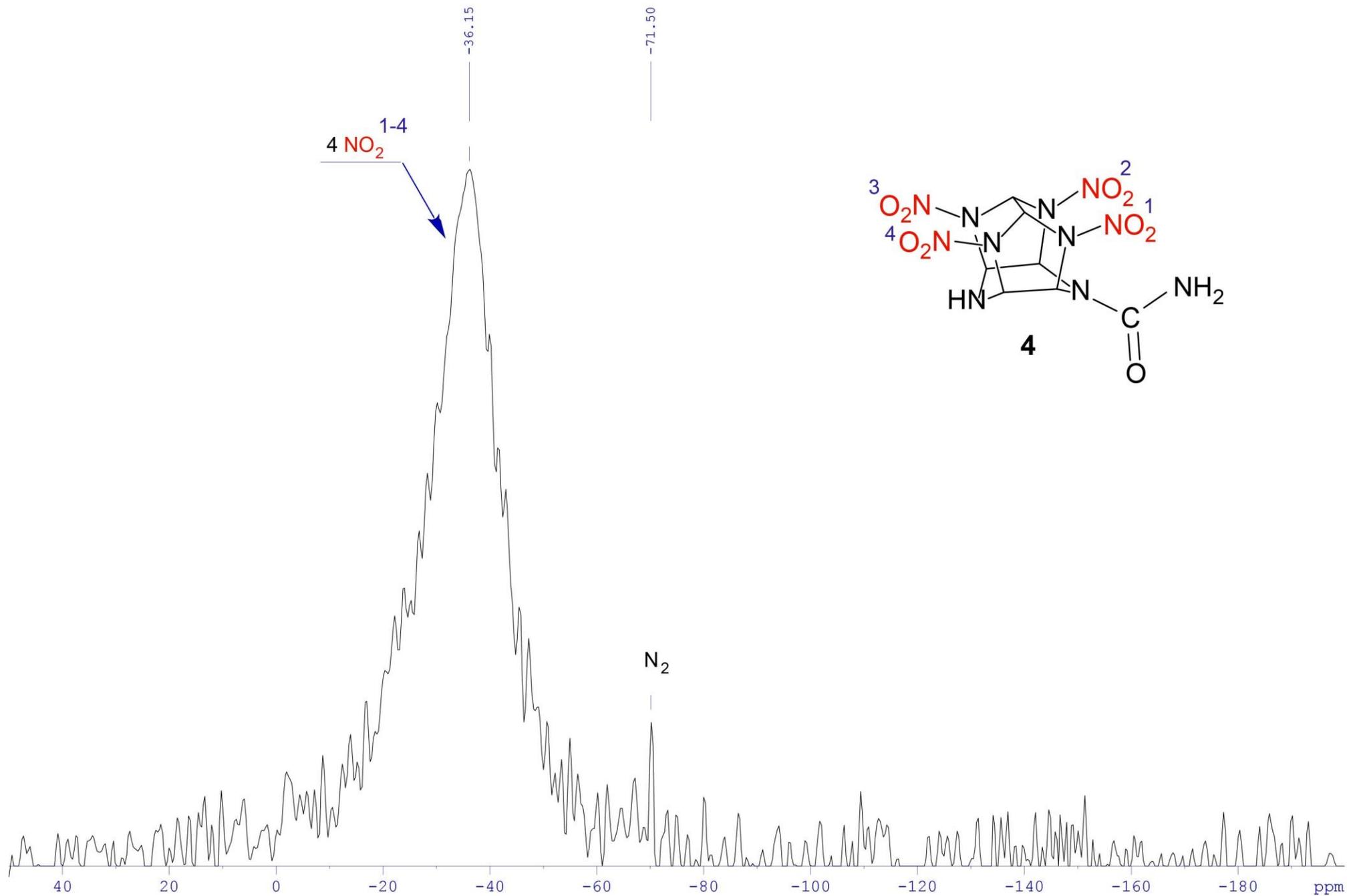
IR (KBr) spectrum of compound 4

Intens.
x10⁴   +MS

409.0922

409.3788

410.0935
410.3790

Intens.
x10⁴   C7H9N11O9, M+nNH4 ,409.09

409.0923

410.0954

408.75   409.00   409.25   409.50   409.75   410.00   410.25   410.50   410.75   m/z
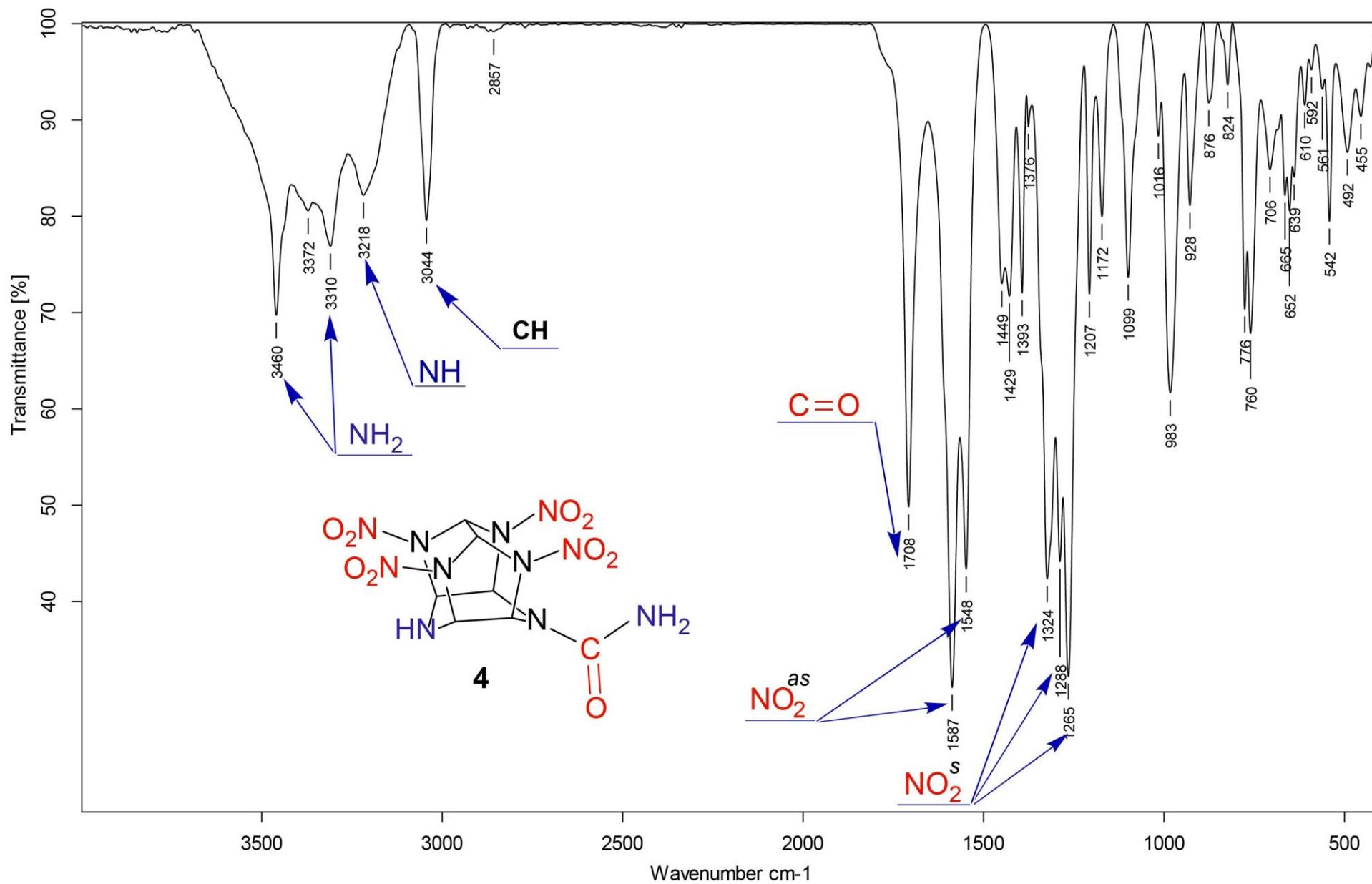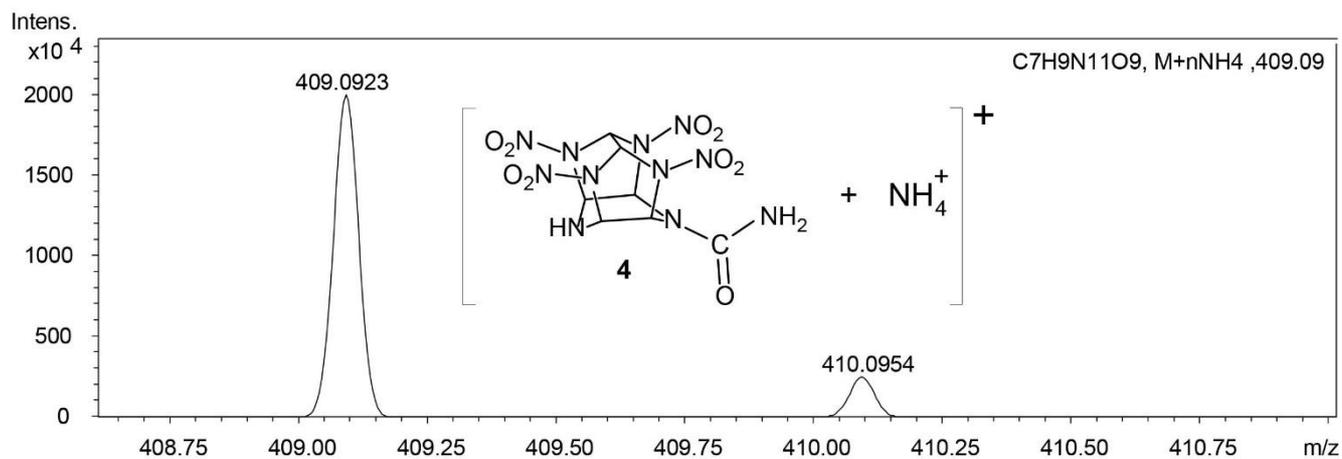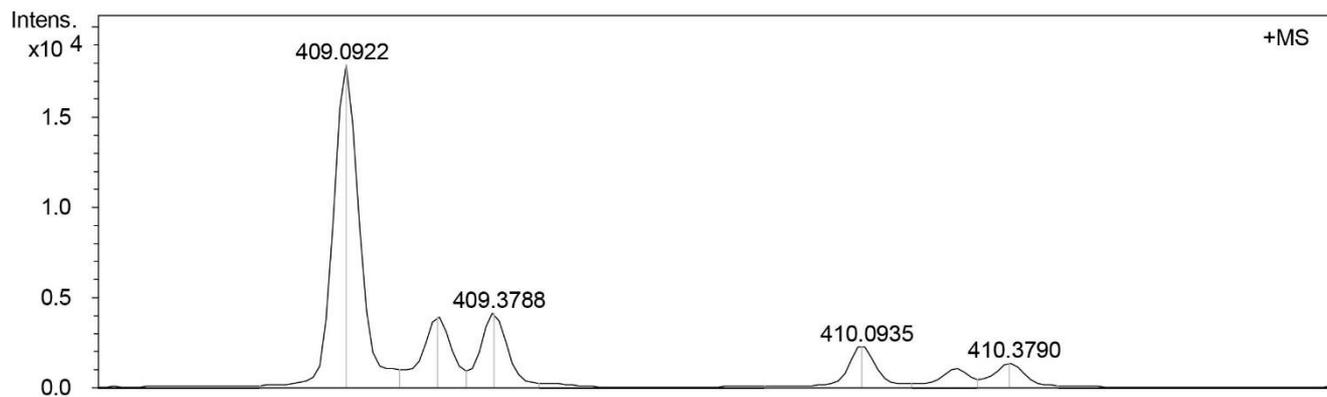
¹H NMR (600.13 MHz,[D₆]acetone) spectrum of compound 5

^{13}C NMR (150.9 MHz,[D$_6$]acetone) spectrum of compound 5

111.12

72.65
72.49
71.62

28.82
28.69
28.57
28.44
28.31

0.00

C1,C6

C2,C3

C4,C5

O_2N-N ... $N-NO_2$
6   1
O_2N-N ... $N-NO_2$
3
4
HN   5   2   N   7
$C \equiv N$

5

7
$\underline{C} \equiv N$

Acetone-d$_6$

TMS

135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm
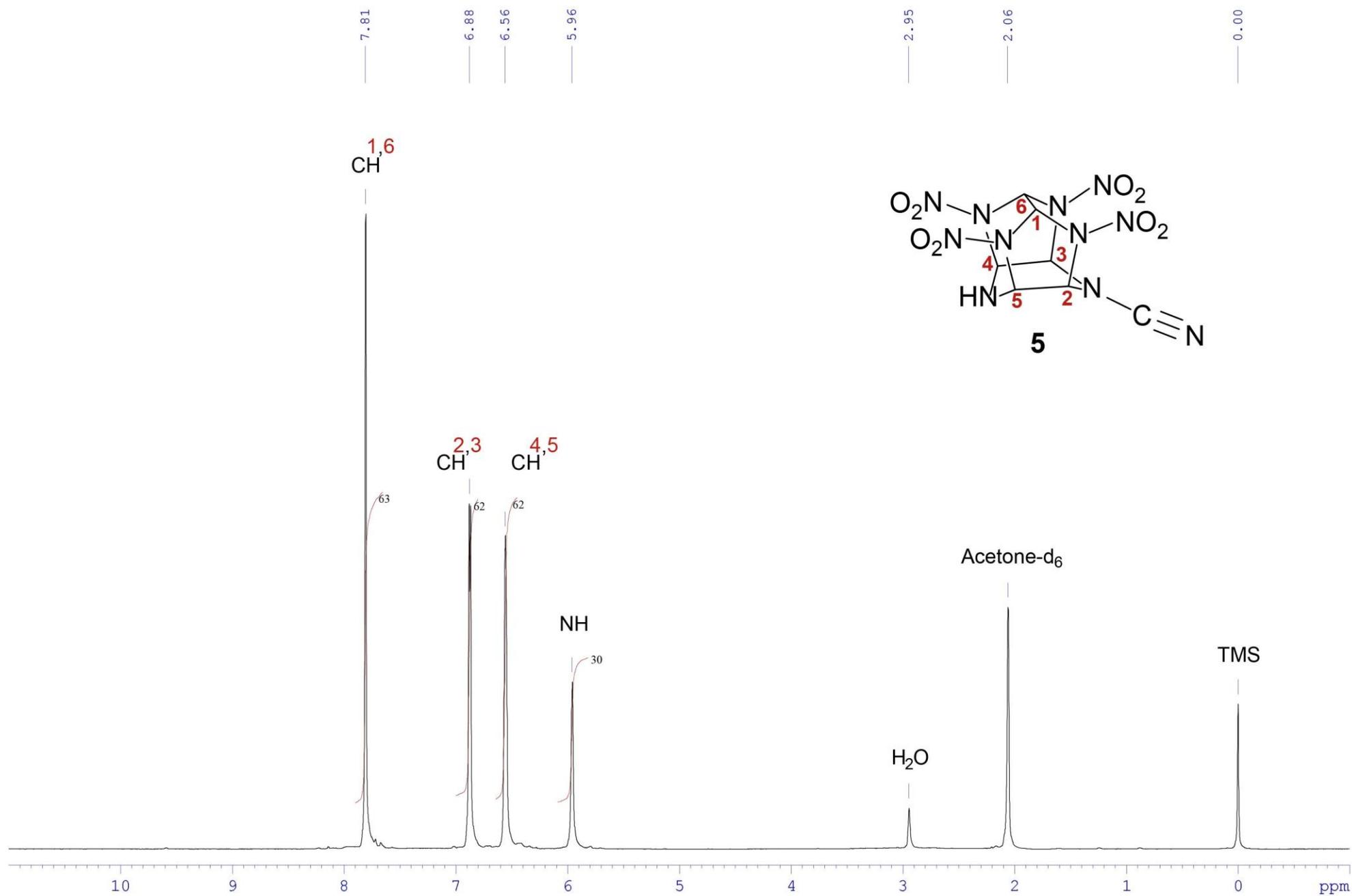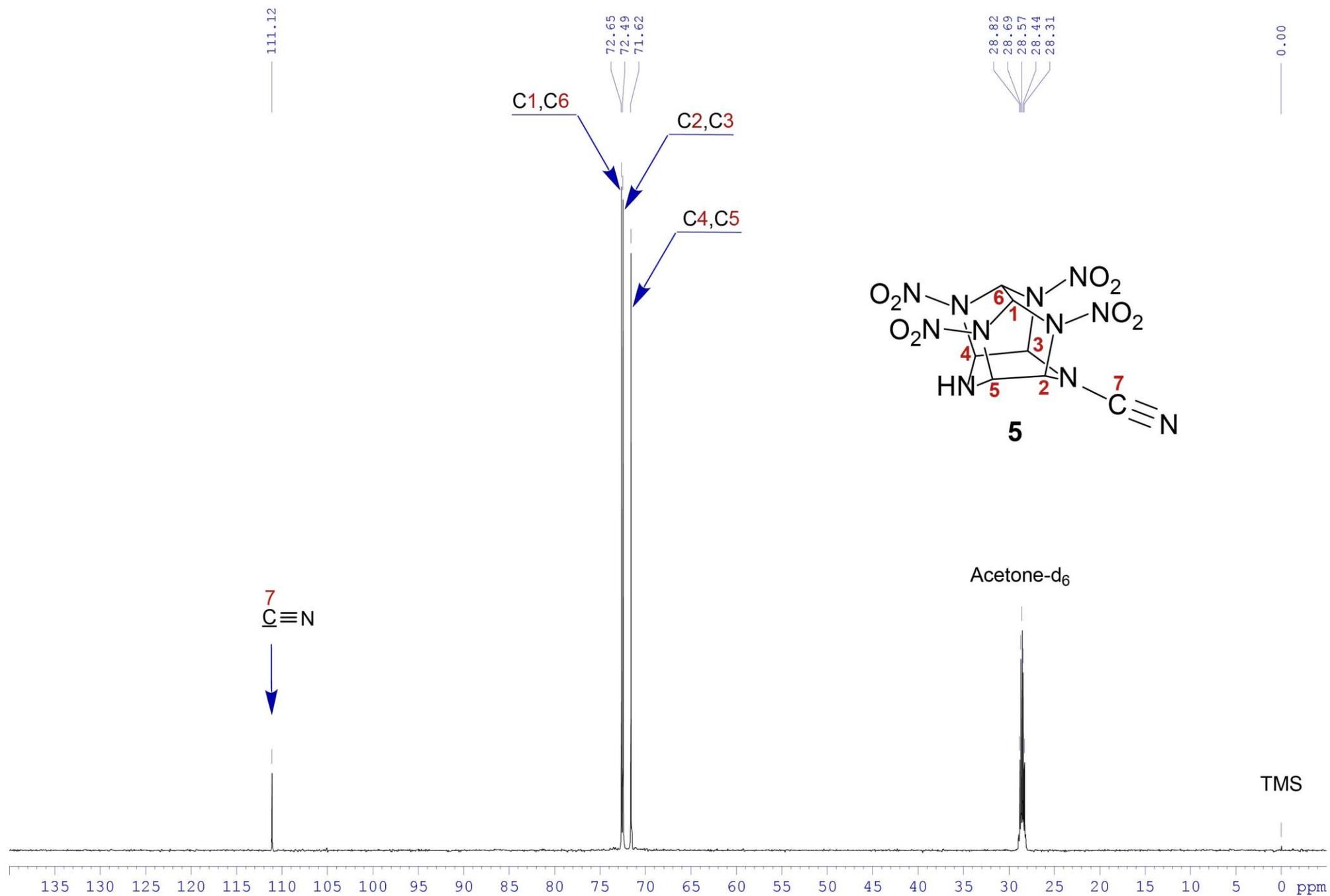
{¹H–¹³C} COSY NMR (600.13 MHz,[D₆]acetone) spectrum of compound 5
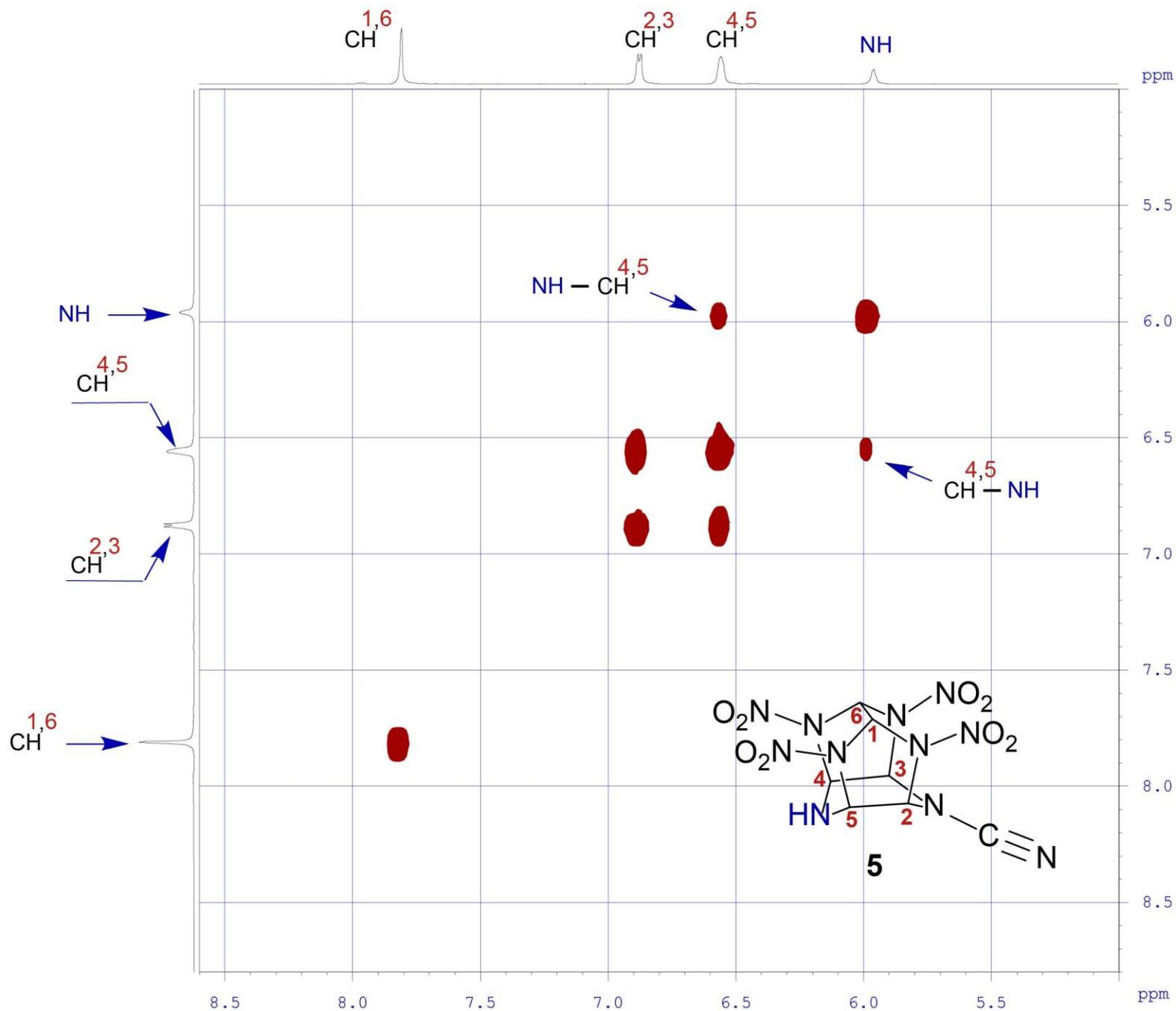
{^{1}H–^{13}C} HSQC NMR (600.13 MHz, [D$_6$]acetone) spectrum of compound 5

{^{1}H–^{13}C} HMBC NMR (600.13 MHz,[D$_6$]acetone) spectrum of compound 5
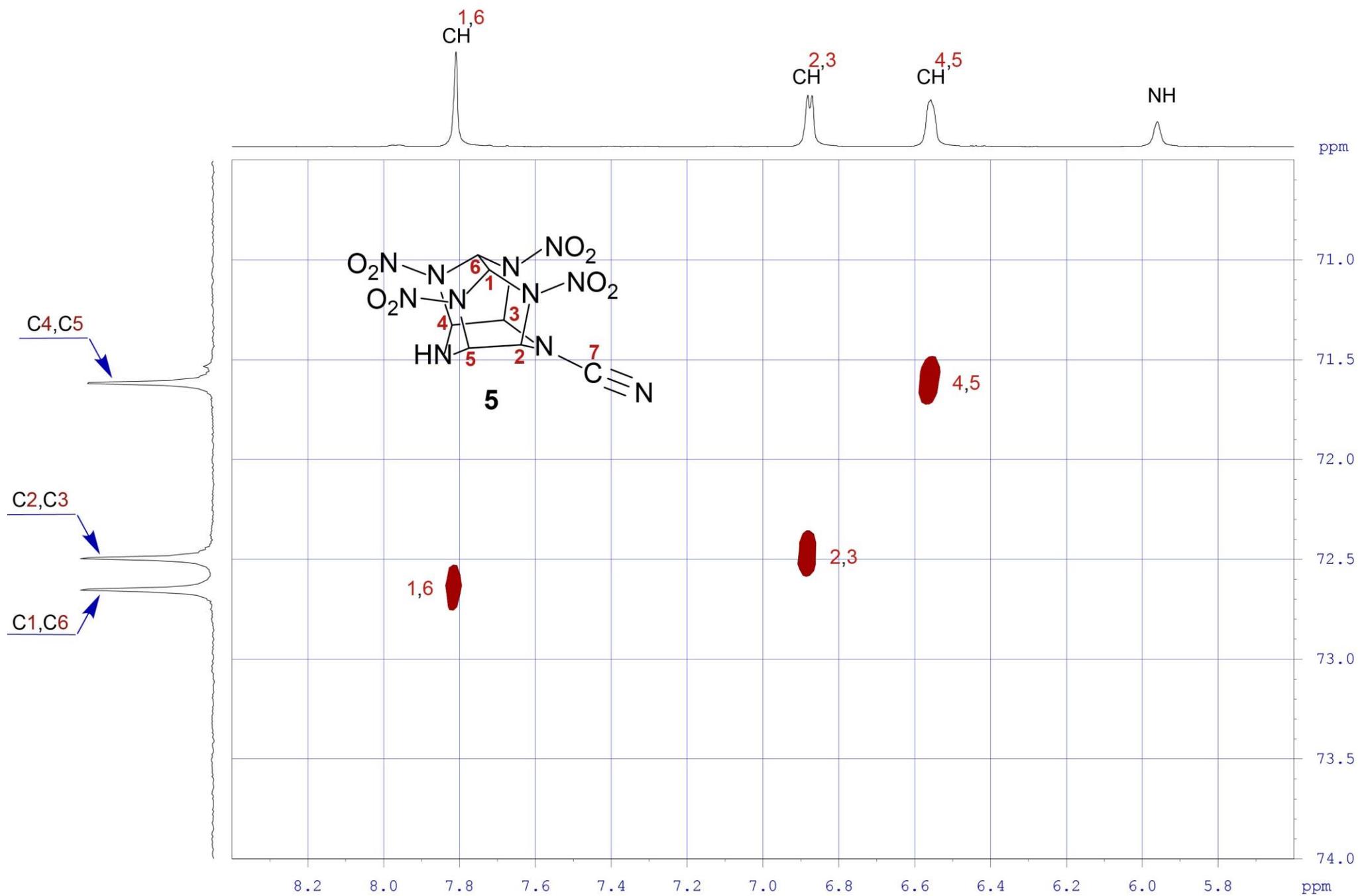
^{14}N NMR (43.37 MHz, [D$_6$]acetone) spectrum of compound 5
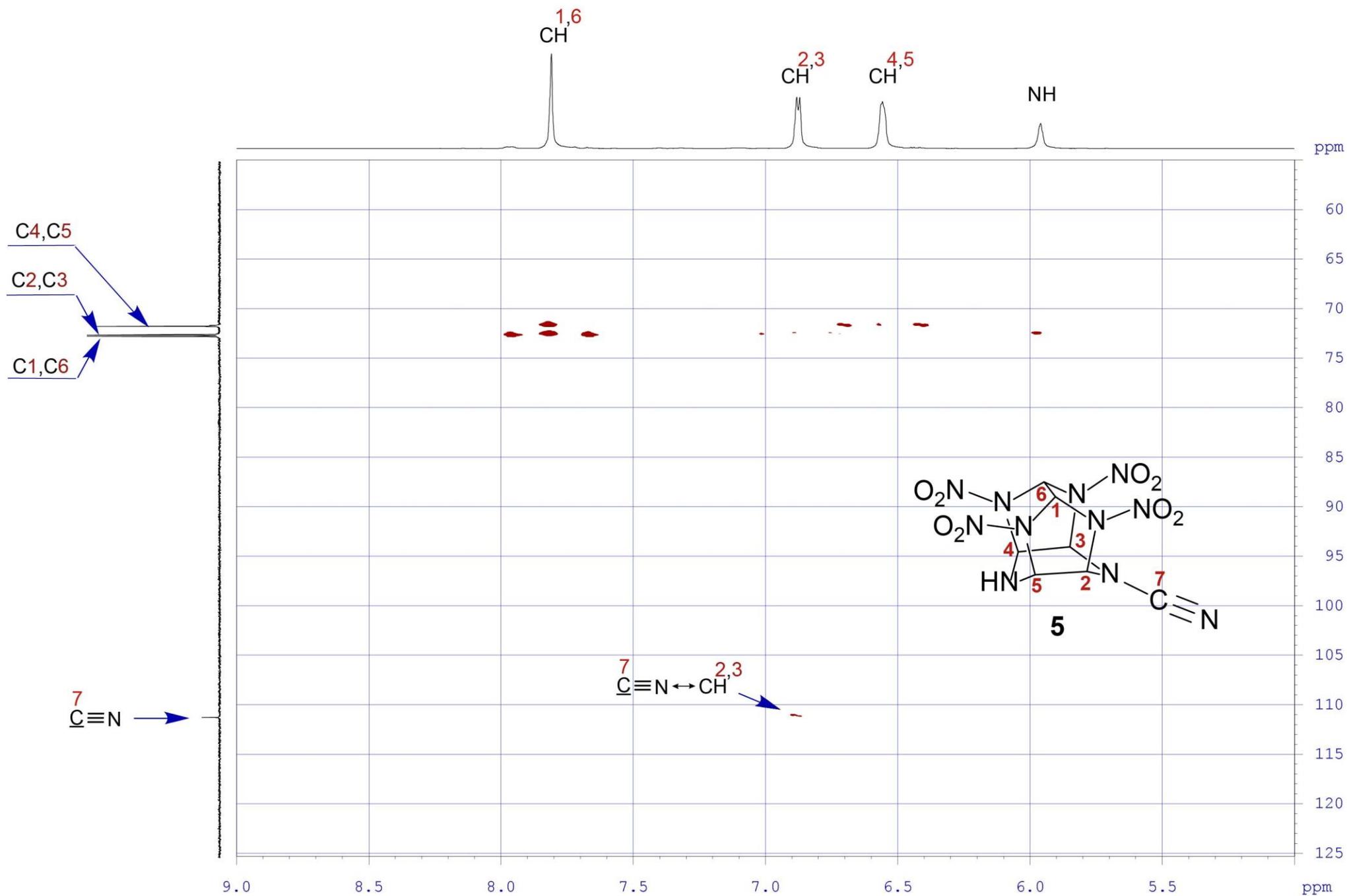
^{15}N NMR ([INVGATED], [INEPT], 60.8 MHz, [D$_6$]acetone) spectrum of compound **5**
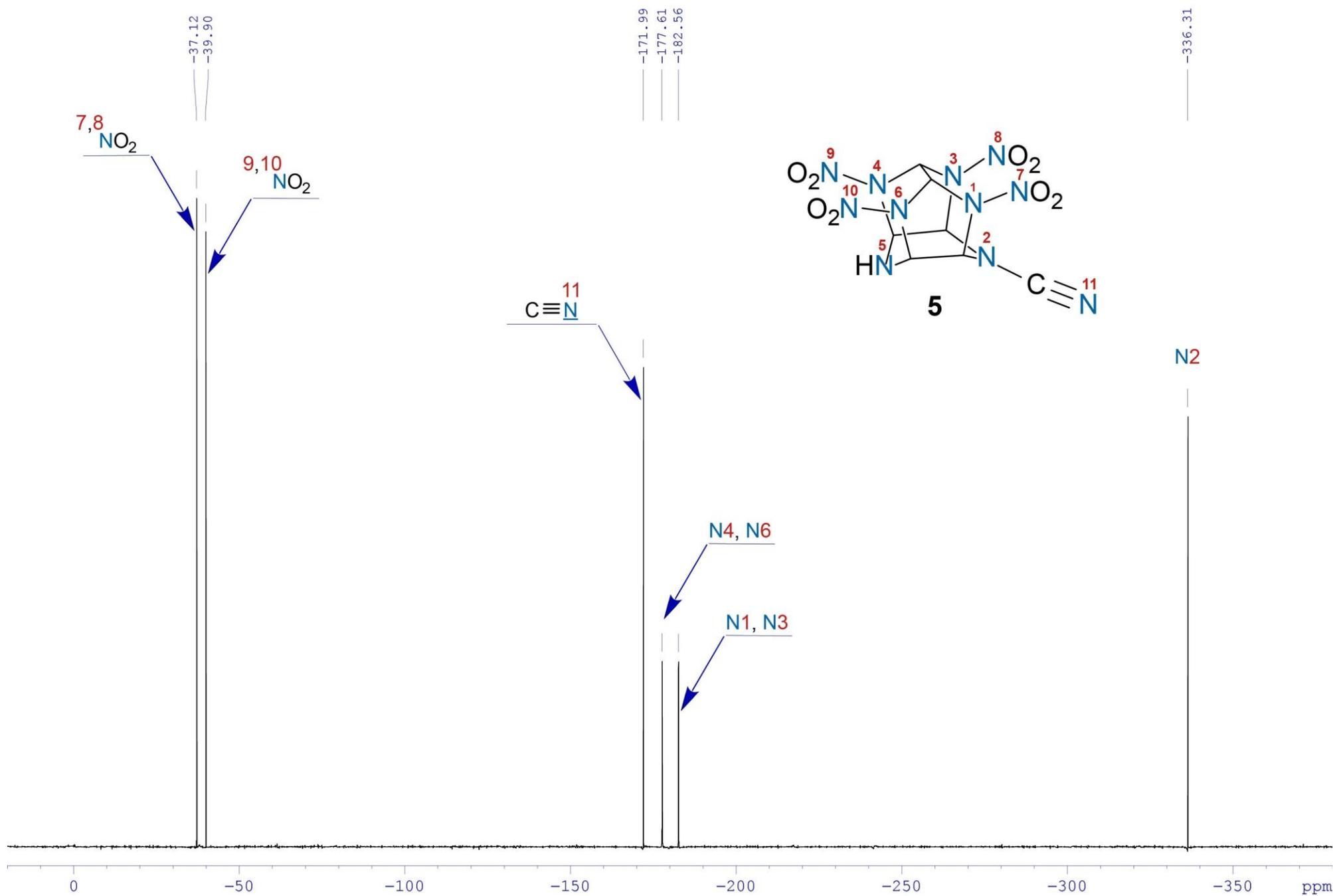
{^{1}H−^{15}N} HMBC NMR (600.13 MHz,[D$_6$]acetone) spectrum of compound 5
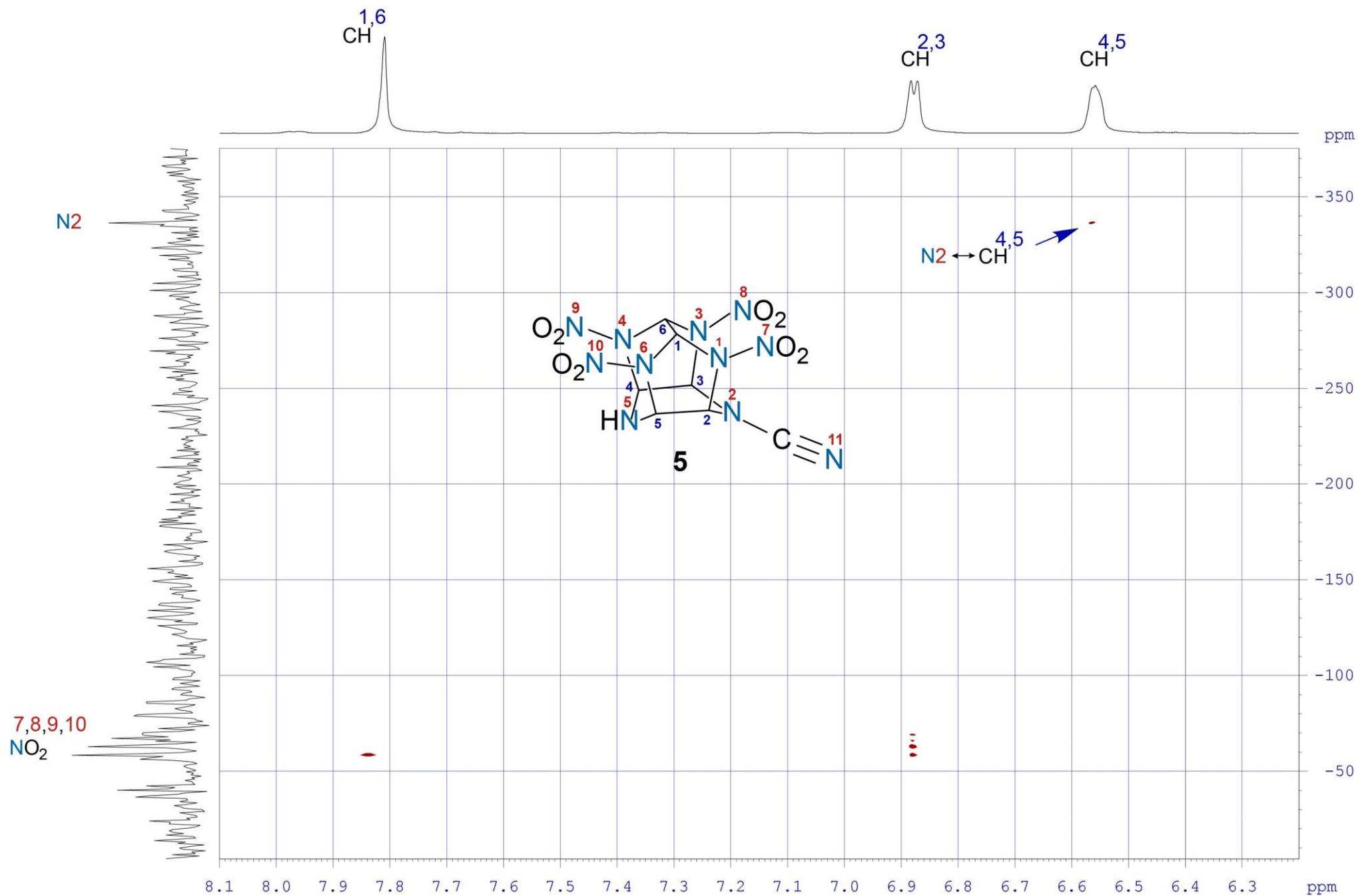
IR (KBr) spectrum of compound 5
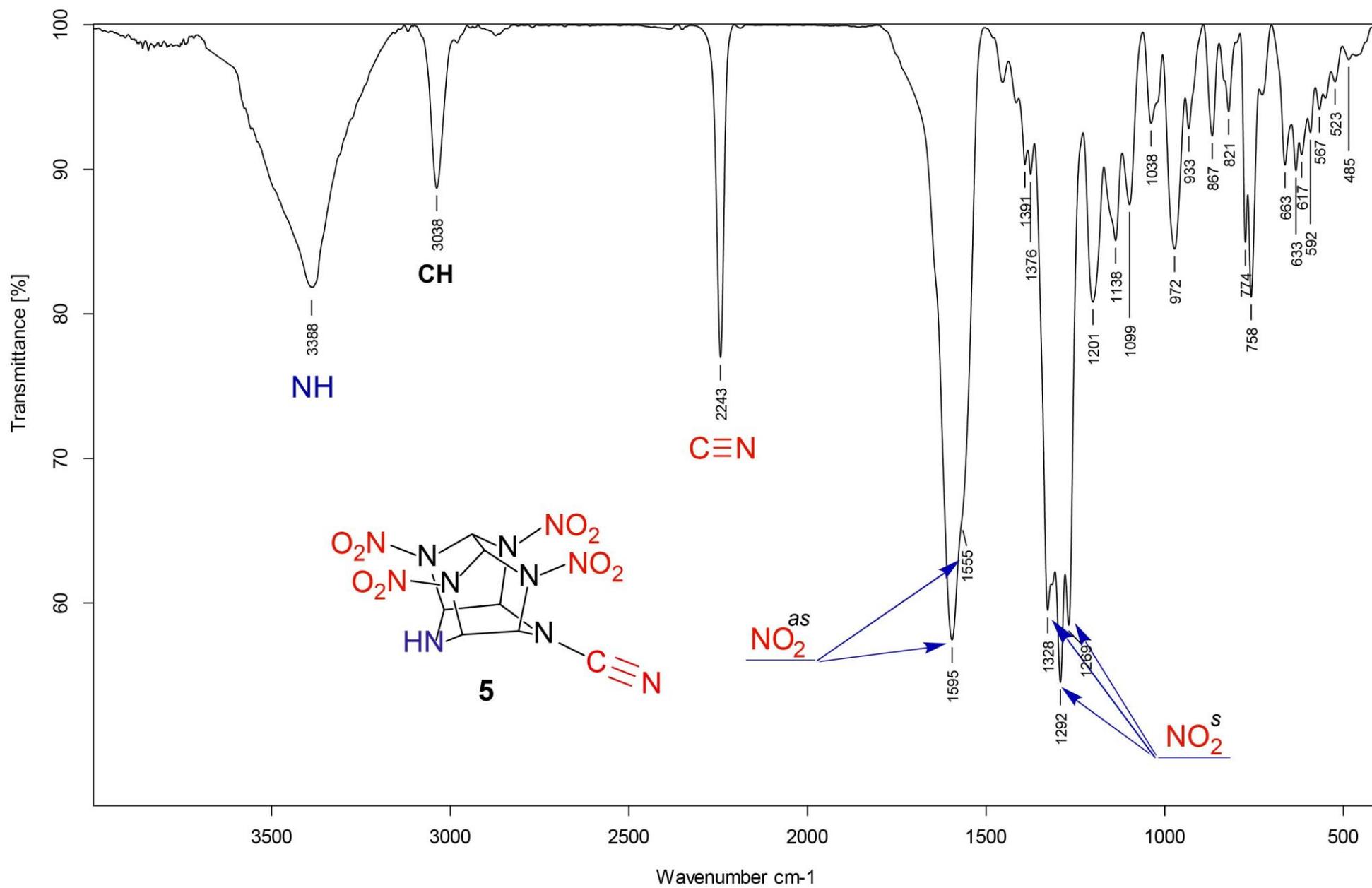
HRMS (ESI) for compound 5
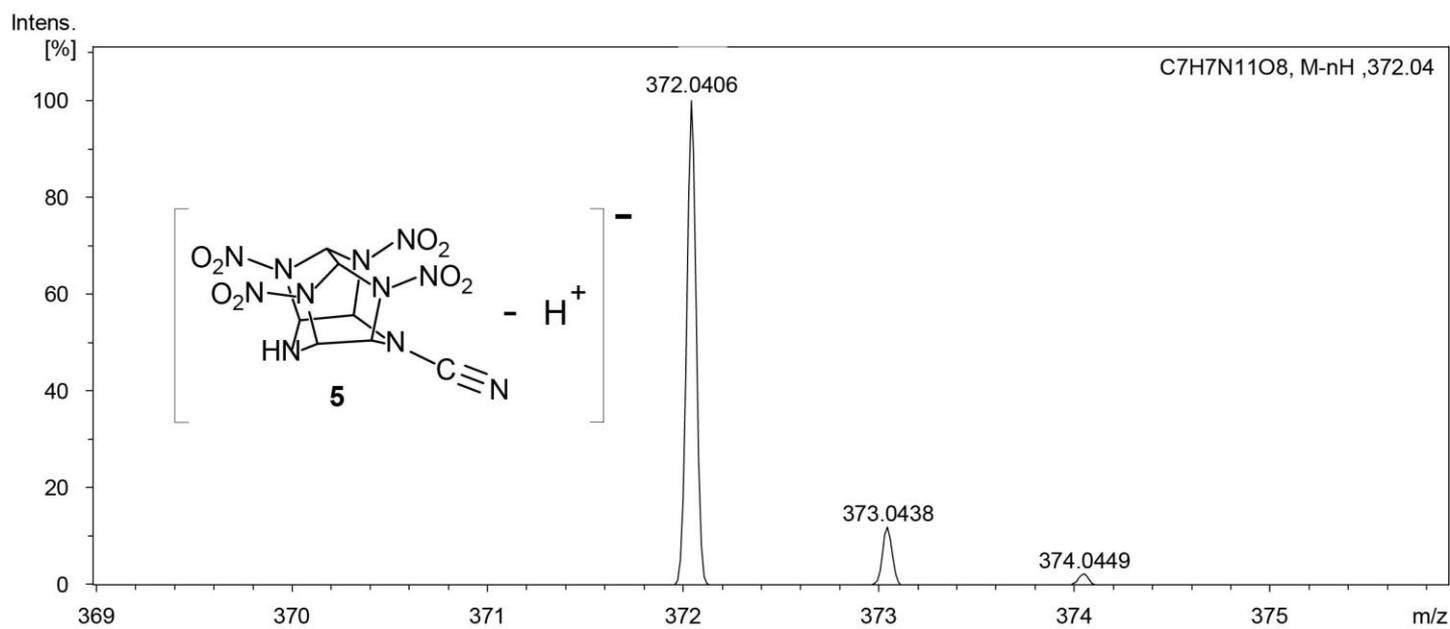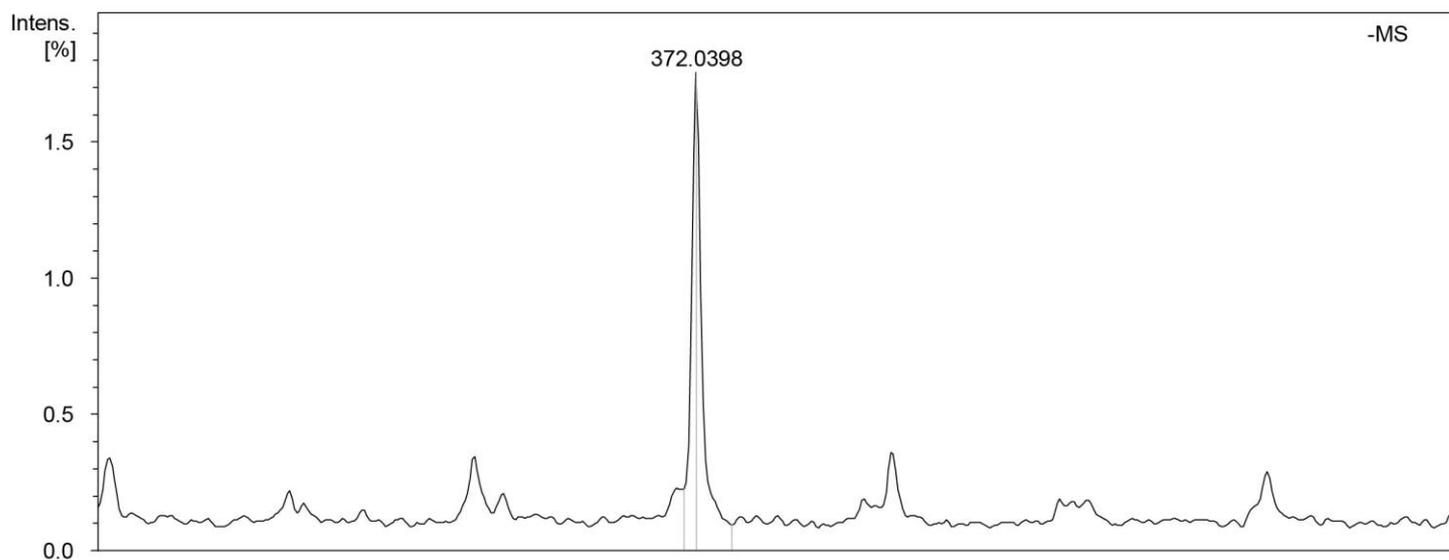
¹H NMR (600.13 MHz,[D₆]acetone) spectrum of compound 6
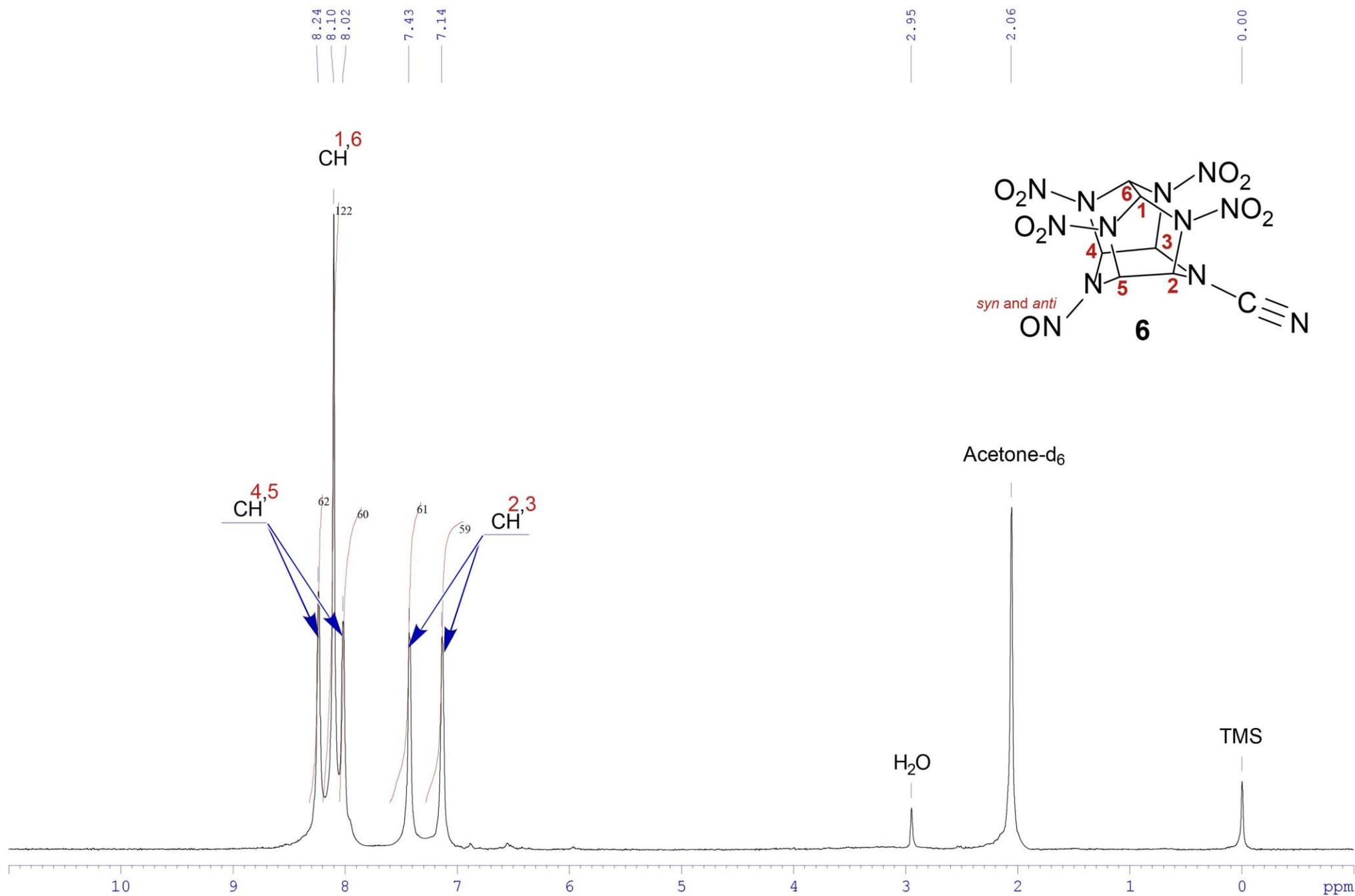
CH^{1,6}

CH^{4,5}

CH^{2,3}

Acetone-d₆

H₂O

TMS

8.24
8.10
8.02

7.43
7.14

2.95

2.06

0.00

122

62
60
61
59

syn and anti

O₂N—N   N—NO₂
O₂N—N   N—NO₂
ON

6

10   9   8   7   6   5   4   3   2   1   0   ppm

^{13}C NMR (150.9 MHz,[D$_6$]acetone) spectrum of compound 6

110.19

74.55
73.91
73.59
72.62

60.32

28.82
28.69
28.56
28.43
28.31

C1,C6

C2,C3

C4(C5)

C5(C4)

O$_2$N—N   N—NO$_2$
          6
          1
O$_2$N—N   N—NO$_2$
      N   3
      4
                      2
syn and anti   N   N
ON   5   C≡N
                6

Acetone-d$_6$

7
C≡N

135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm
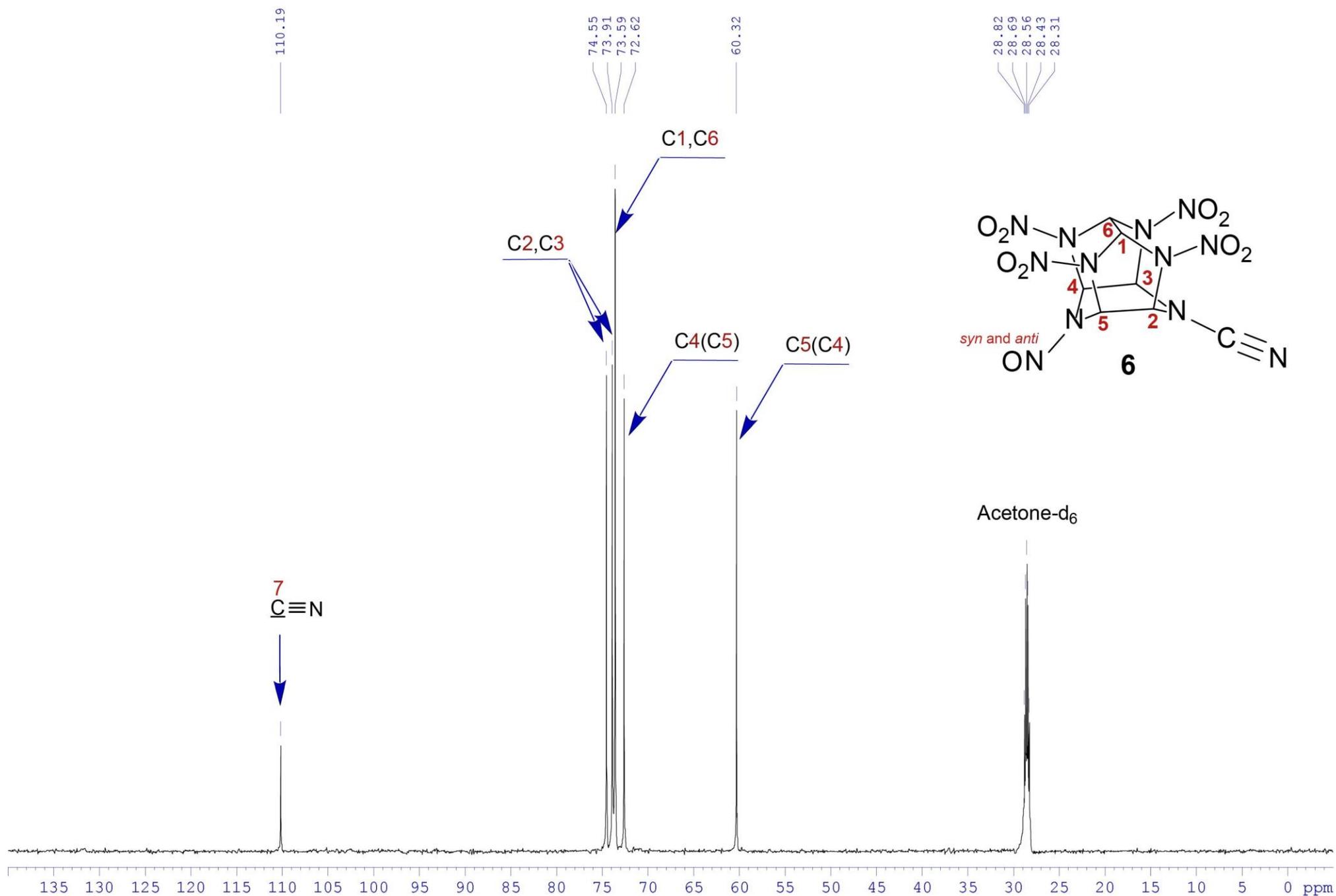
{¹H–¹³C} HSQC NMR (600.13 MHz, [D₆]acetone) spectrum of compound 6

{¹H–¹³C} HMBC NMR (600.13 MHz, [D₆]acetone) spectrum of compound 6

S37
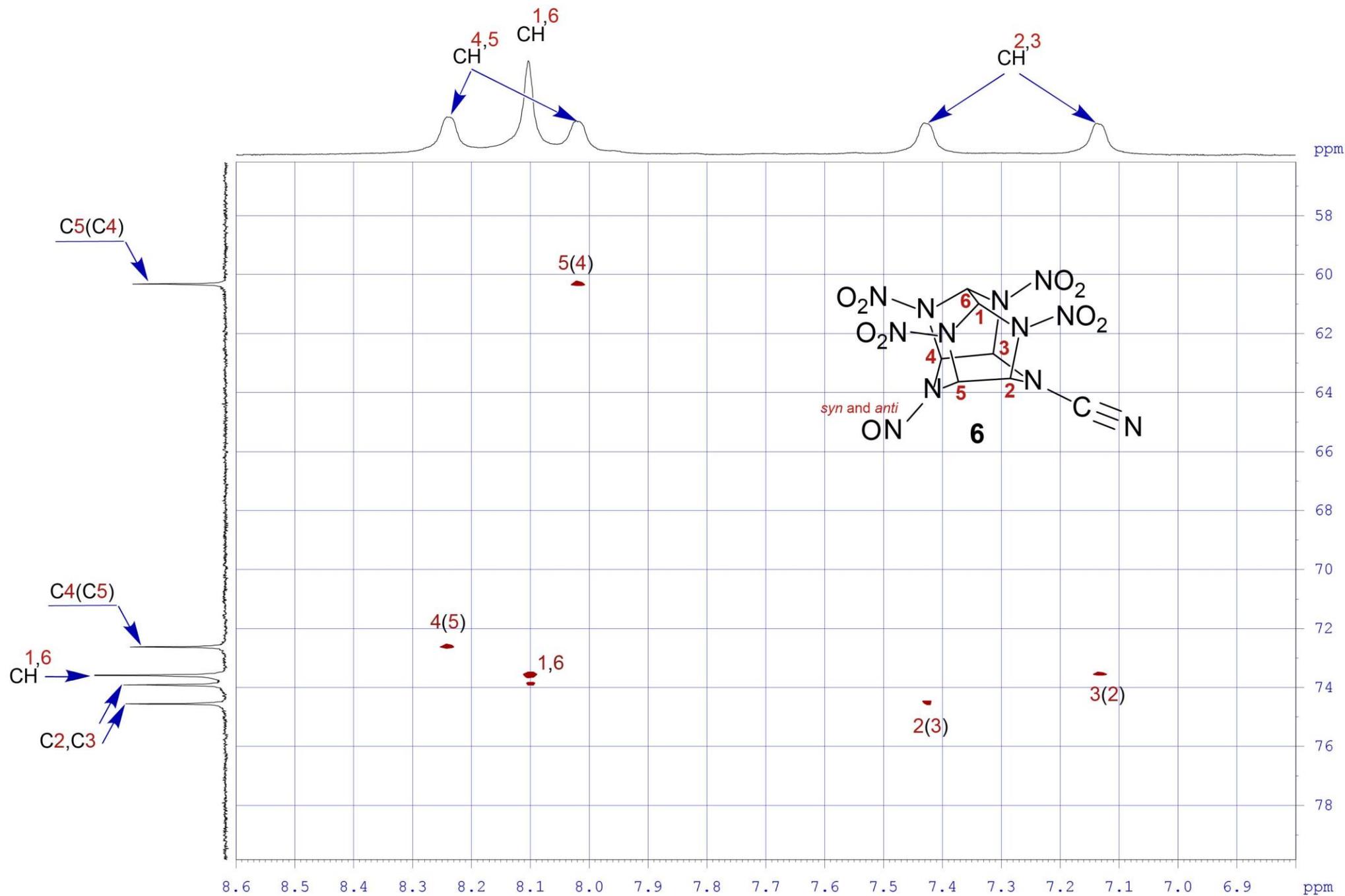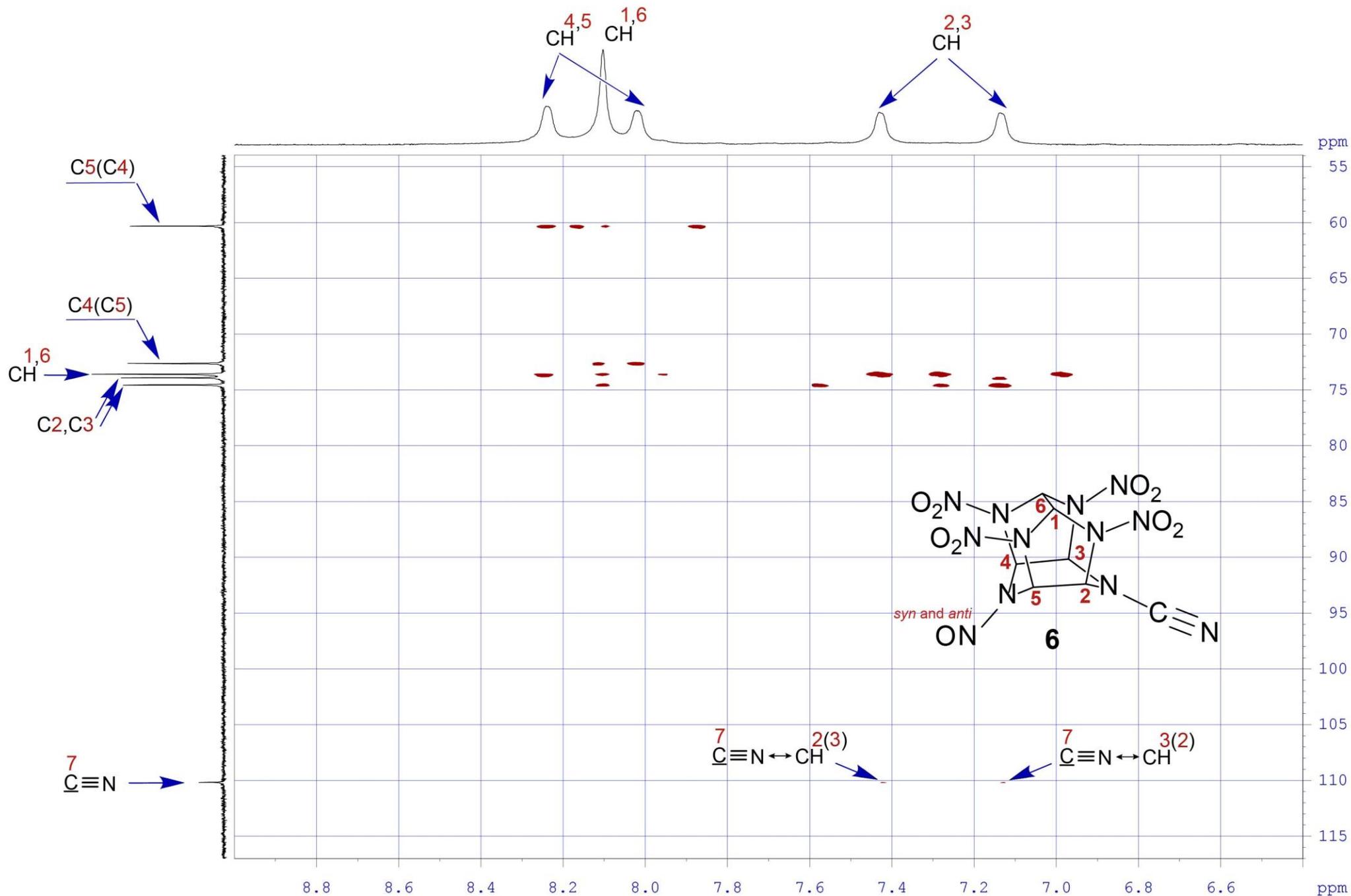
^{14}N NMR (43.37 MHz,[D$_6$]acetone) spectrum of compound 6

^{15}N NMR ([INVGATED], [INEPT], 60.8 MHz, [D$_6$]acetone) spectrum of compound 6

172.75

−41.03
−41.26
−41.43
−41.55

−144.56

−170.51

−181.92
−182.15
−182.84
−185.77

11
C≡N

N5

12
NO

7,8,9,10
NO$_2$

N1, N3, N4, N6

150   100   50   0   −50   −100   −150   −200   −250   −300   −350   ppm

IR (KBr) spectrum of compound 6

S40
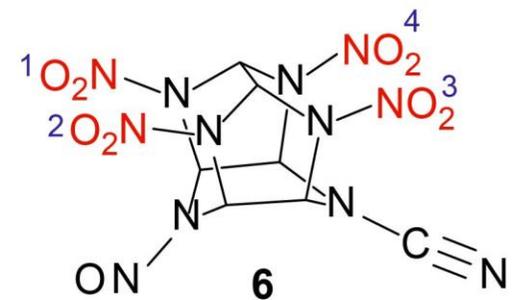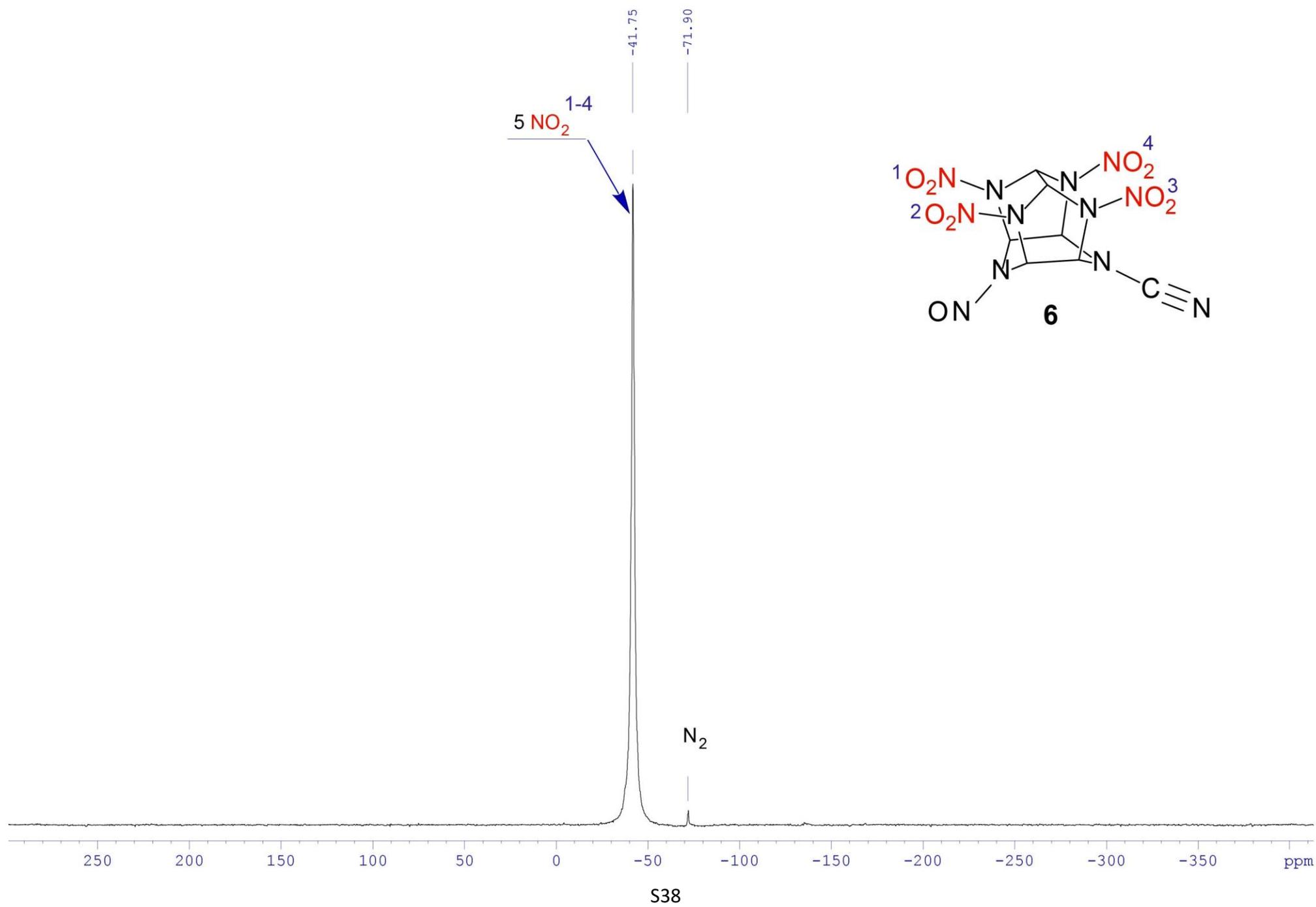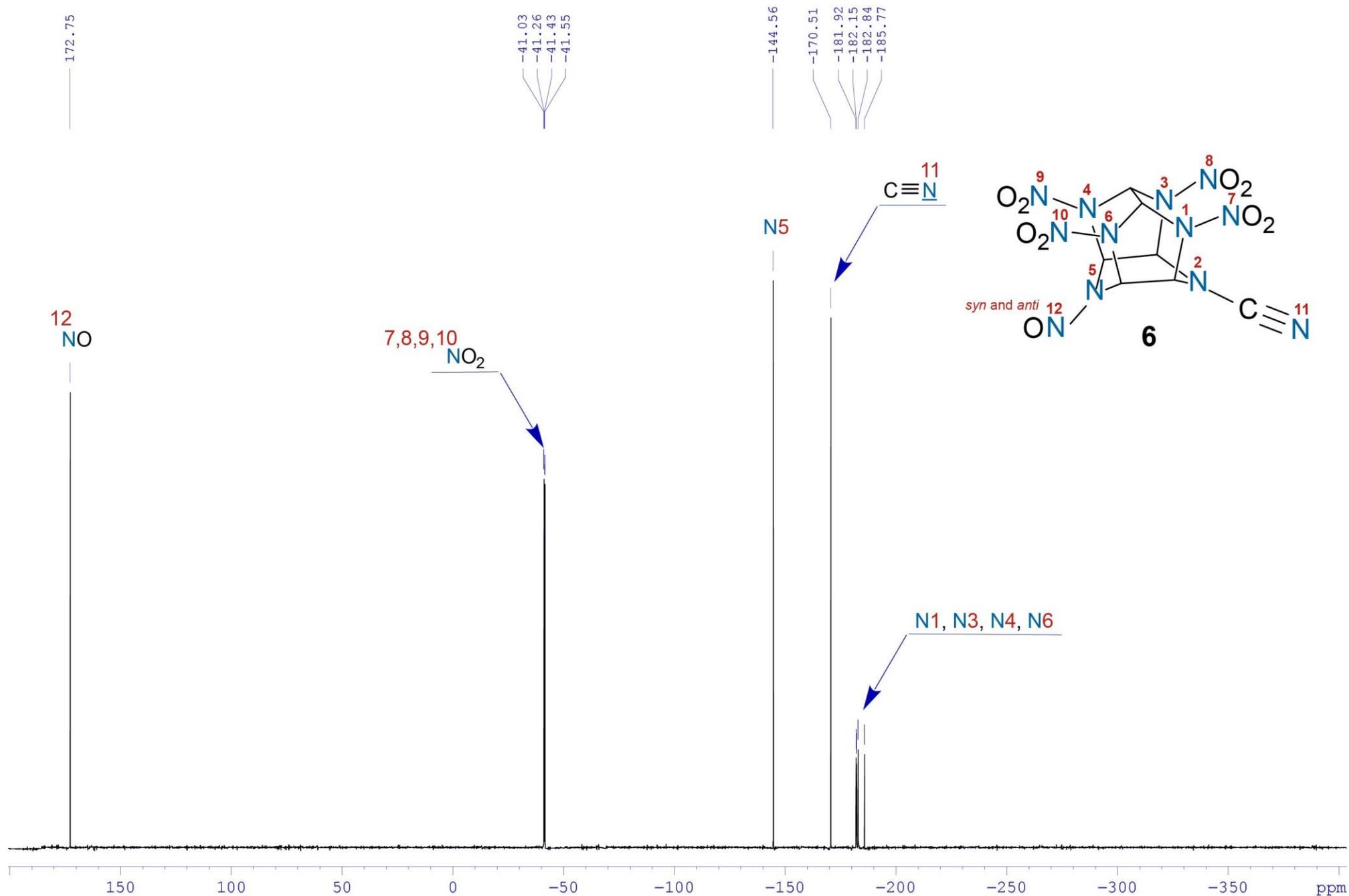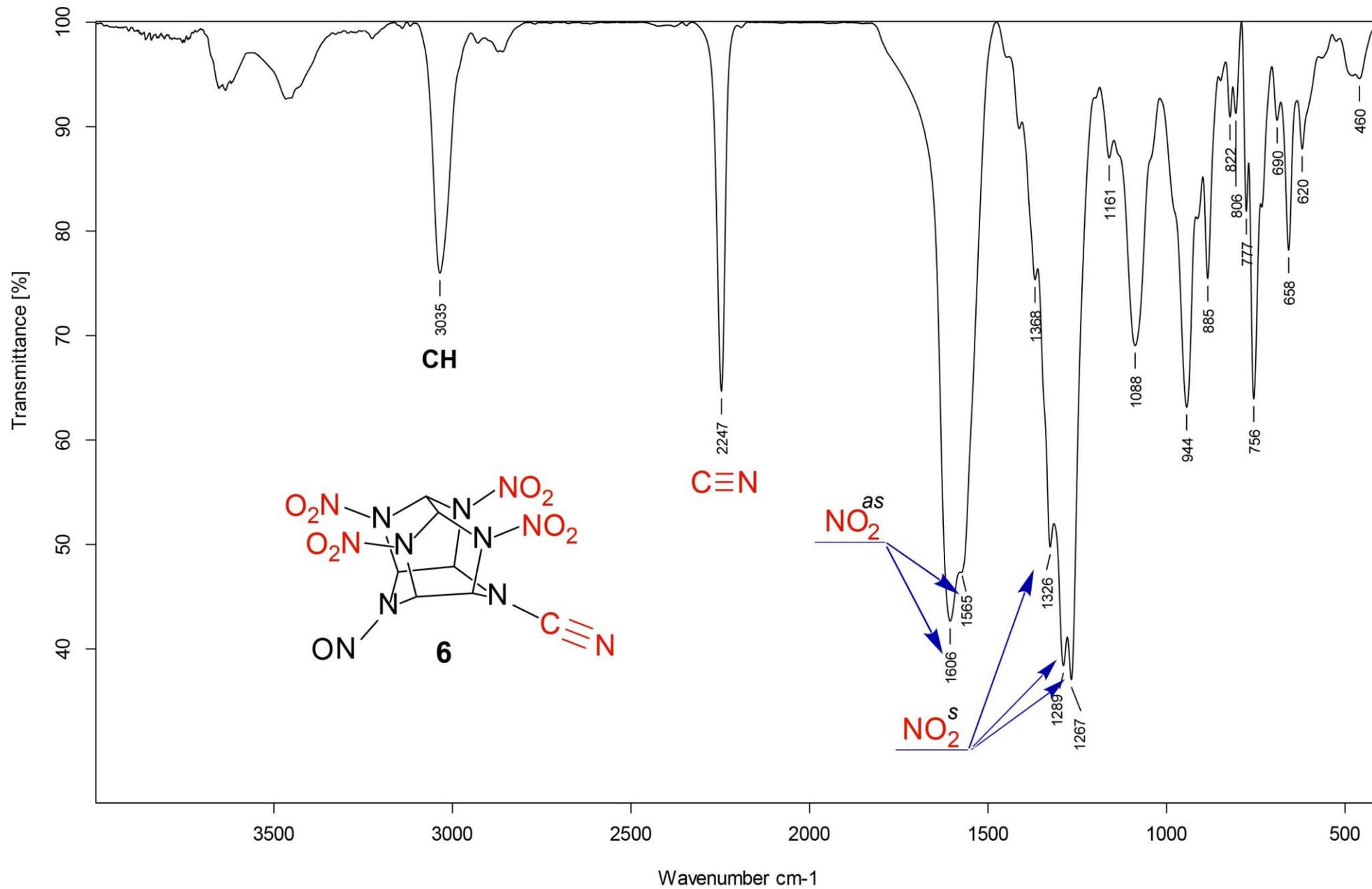
^{1}H NMR (300.1 MHz, [D$_6$]acetone) spectrum of compound 8
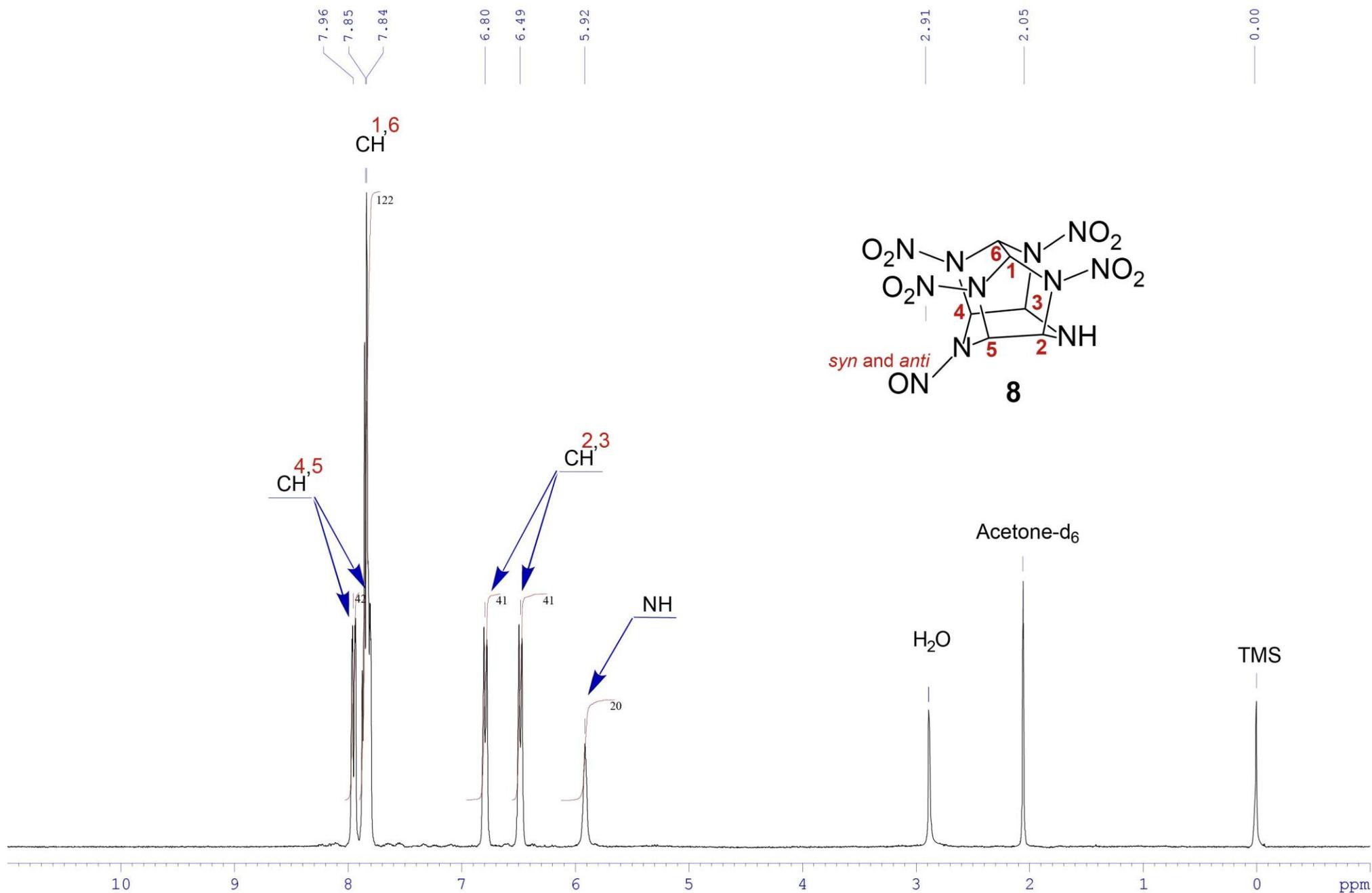
^{13}C NMR (75.5 MHz, [D$_6$]acetone) spectrum of compound 8
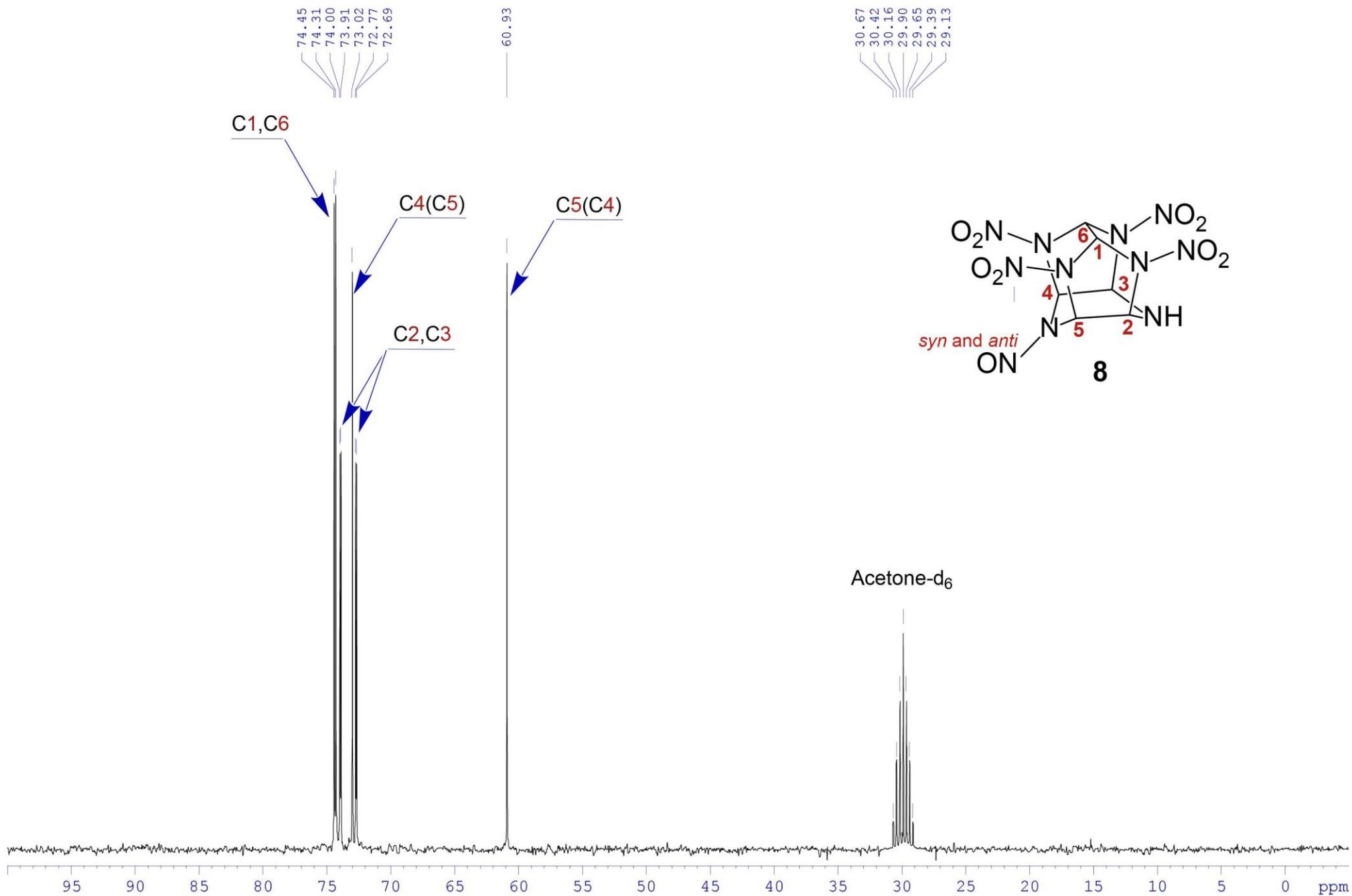
^{14}N NMR (21.7 MHz, [D$_6$]acetone) spectrum of compound 8
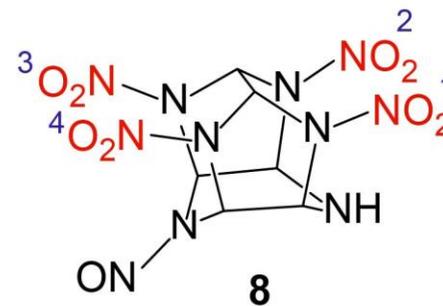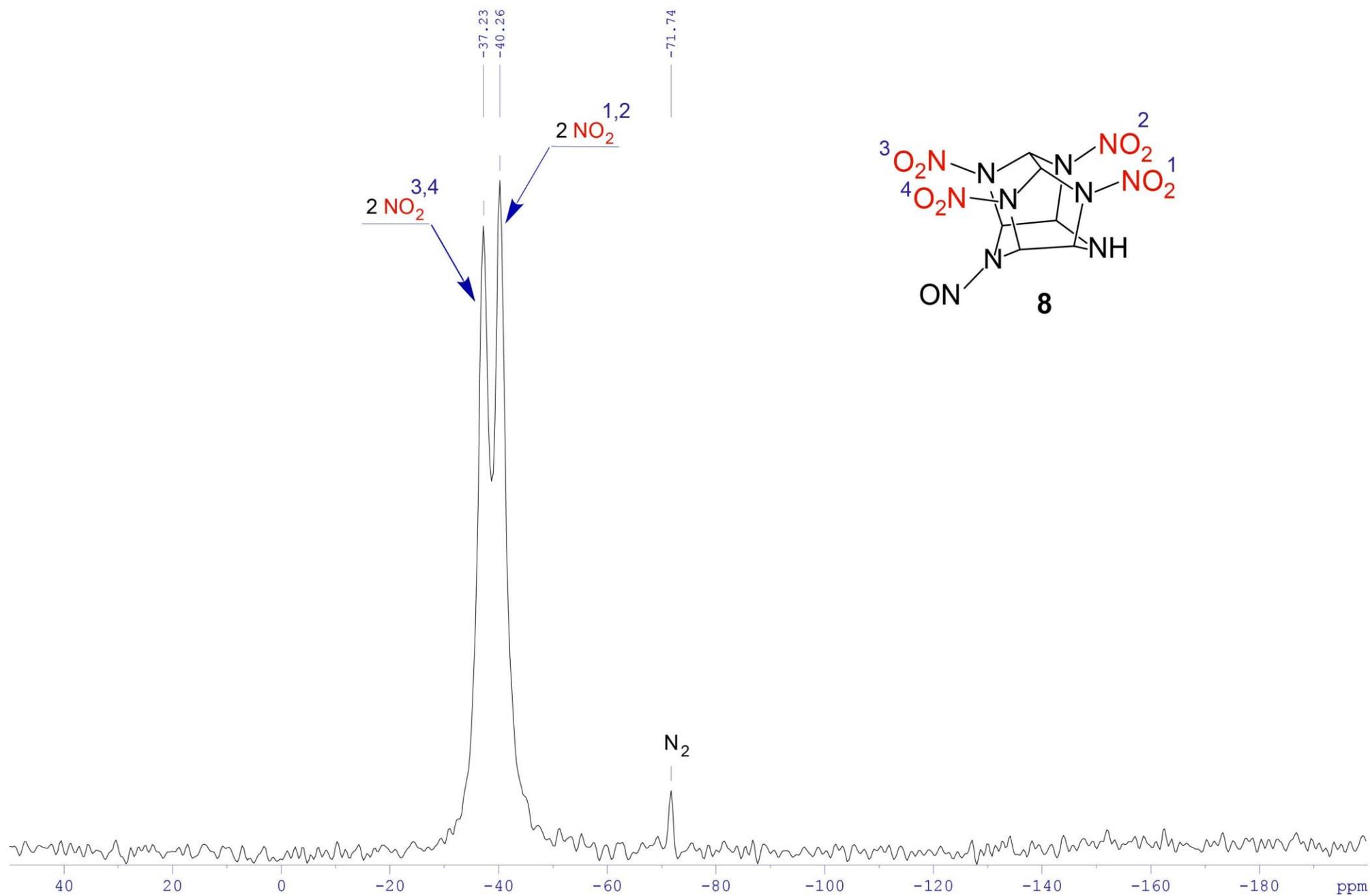
IR (KBr) spectrum of compound 8

HRMS (ESI) for compound 8

Intens. -MS

2500

2000 376.0338

1500

1000

500 374.0262 377.0331

0

C6H7N11O9, M-nH ,376.03

2000 376.0355

1500

1000 377.0387

500 378.0398

0

373   374   375   376   377   378   379   m/z
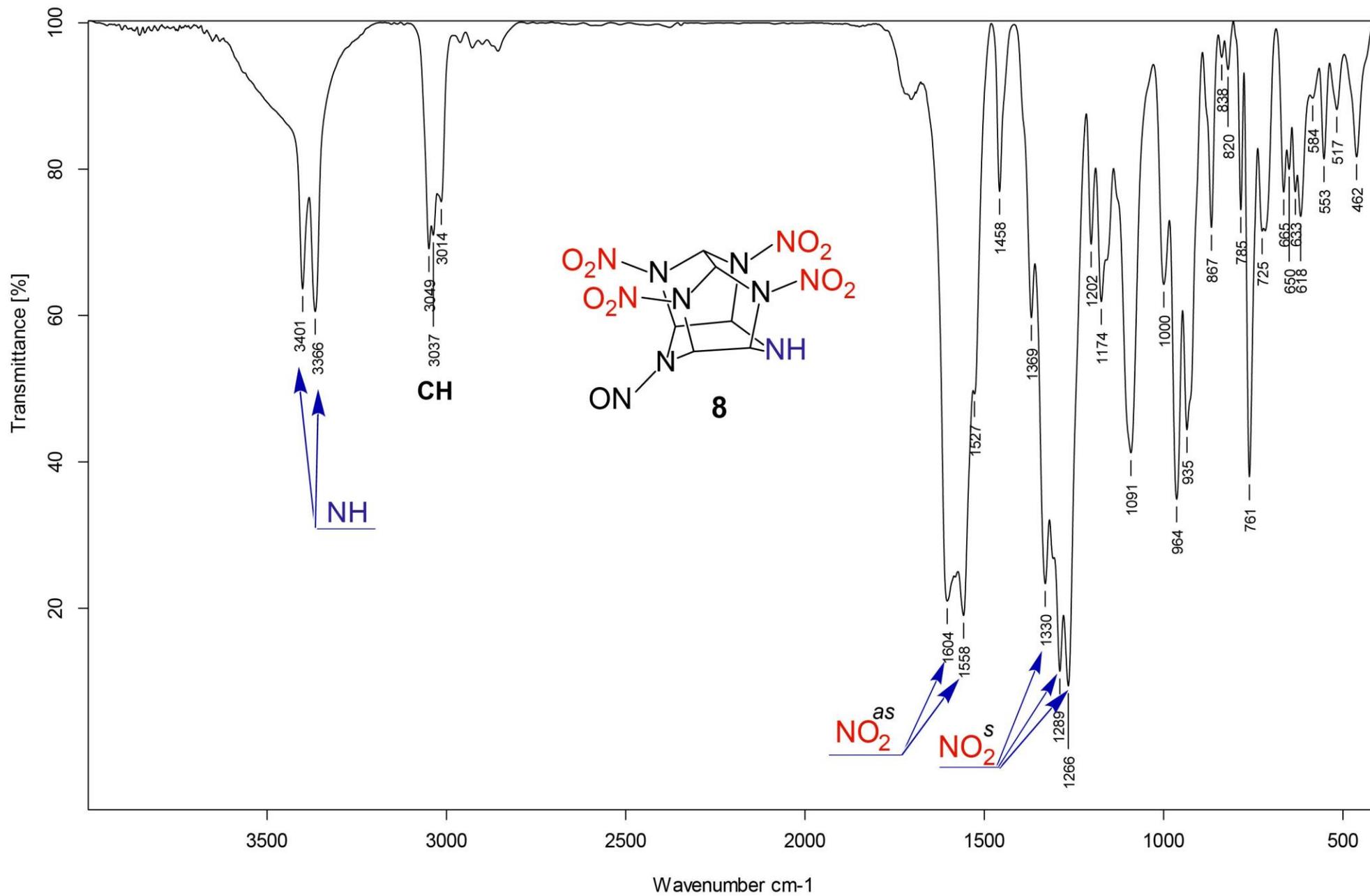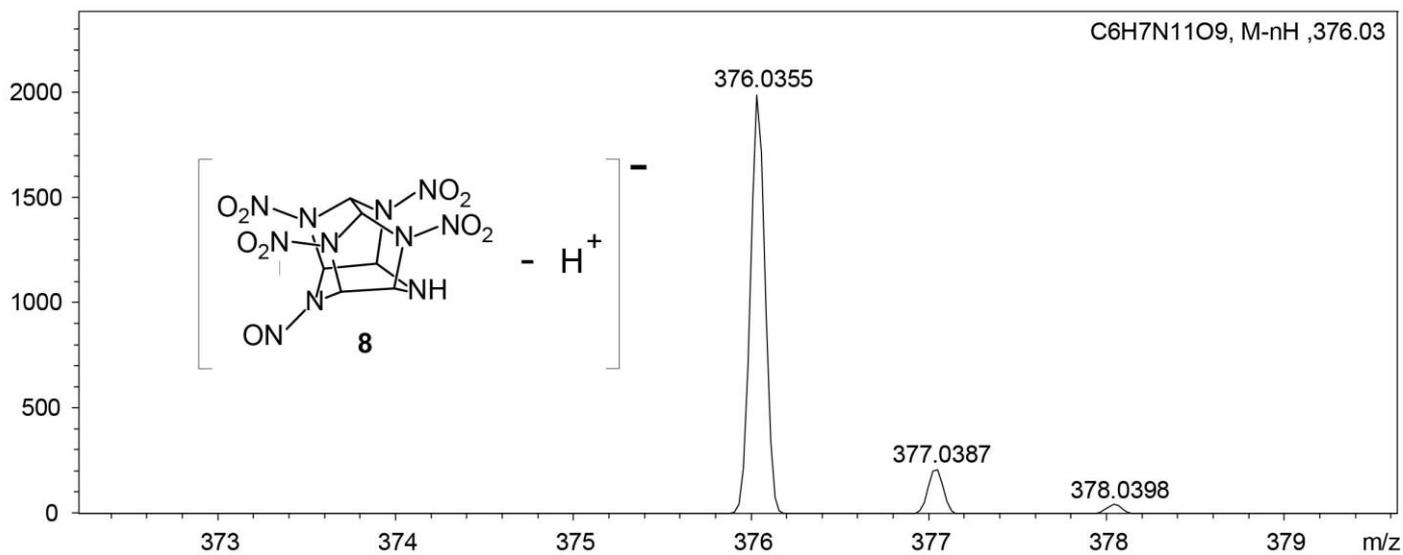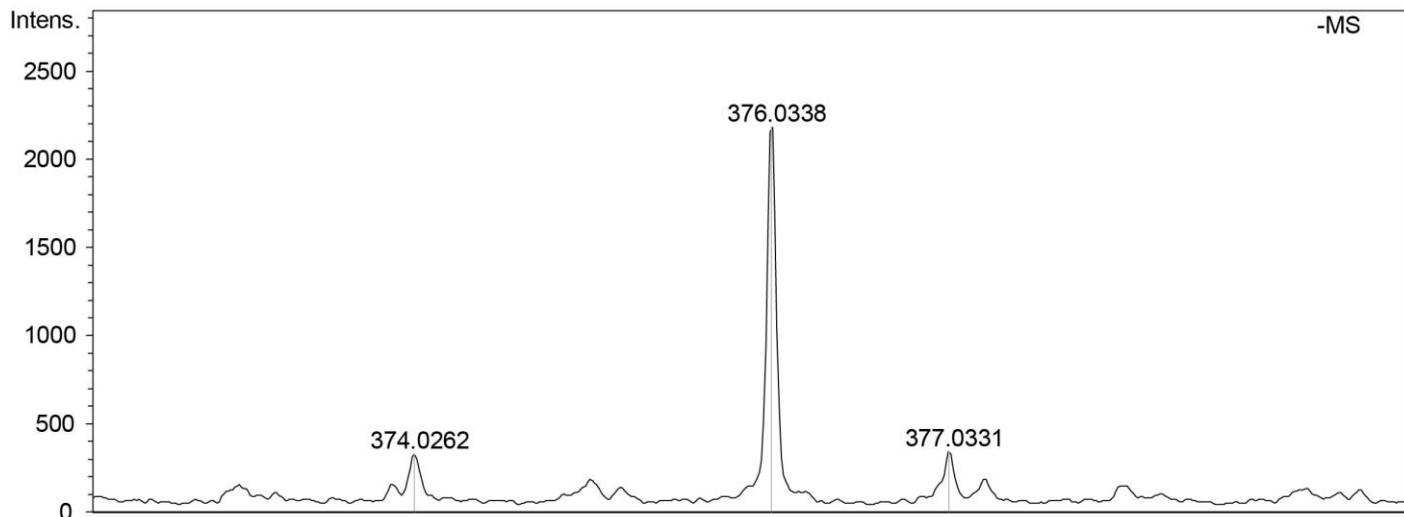
^{1}H NMR (300.1 MHz, [D$_6$]acetone) spectrum of compound 10

^{13}C NMR (75.5 MHz, [D$_6$]acetone) spectrum of compound 10

155.28

75.10
74.92
73.17
71.45
70.61

61.11

30.68
30.42
30.16
29.91
29.65
29.39
29.14

C1,C6

C4(C5)

C5(C4)

C2(C3)

C3(C2)

7
C=O

Acetone-d$_6$

O$_2$N—N   6   N—NO$_2$
O$_2$N—N   1   N—NO$_2$
         4   3
                    N—   7   NH$_2$
syn and anti   N   5   2
ON   C
         10   O

160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   10   ppm
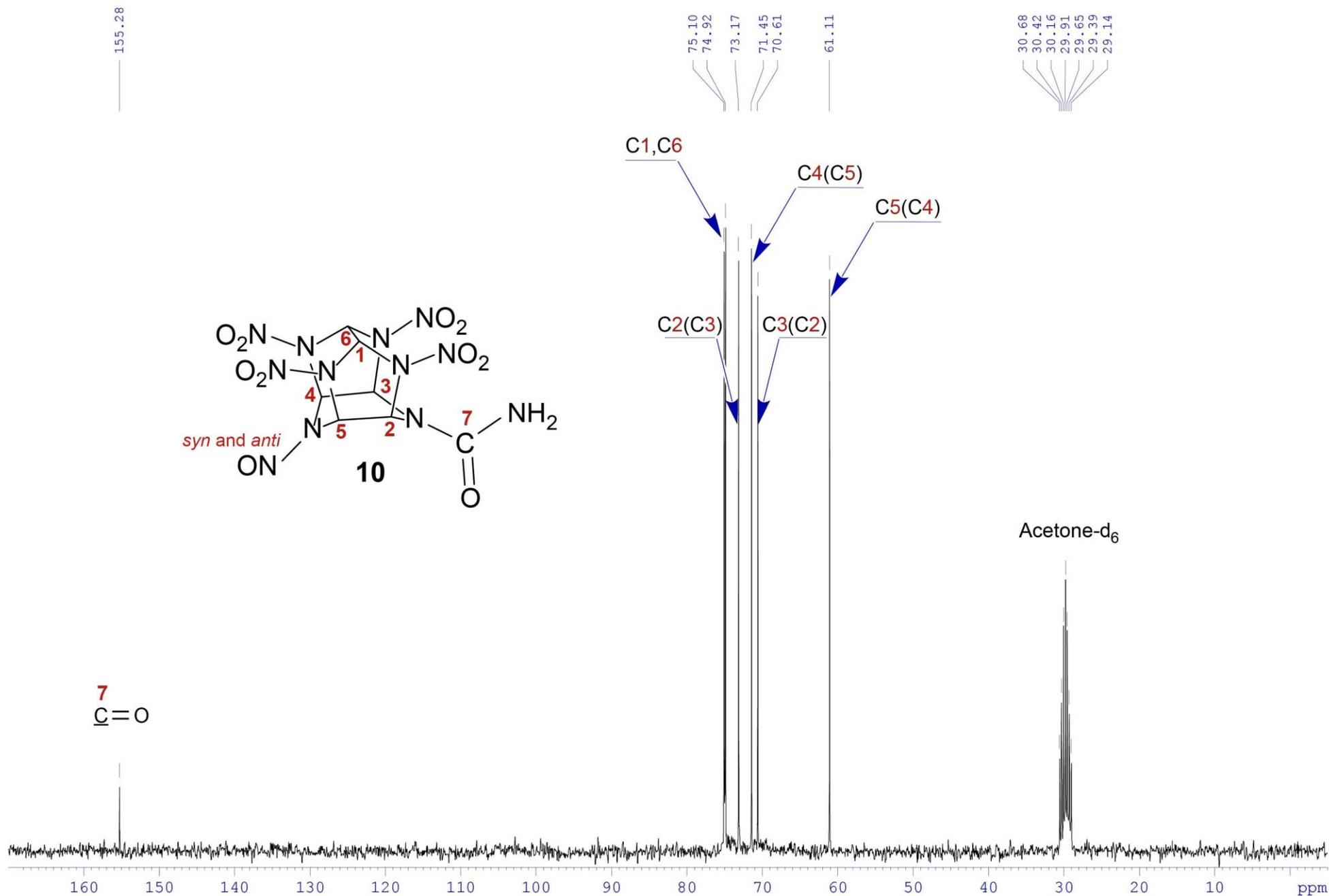
^{14}N NMR (21.7 MHz, [D$_6$]acetone) spectrum of compound 10
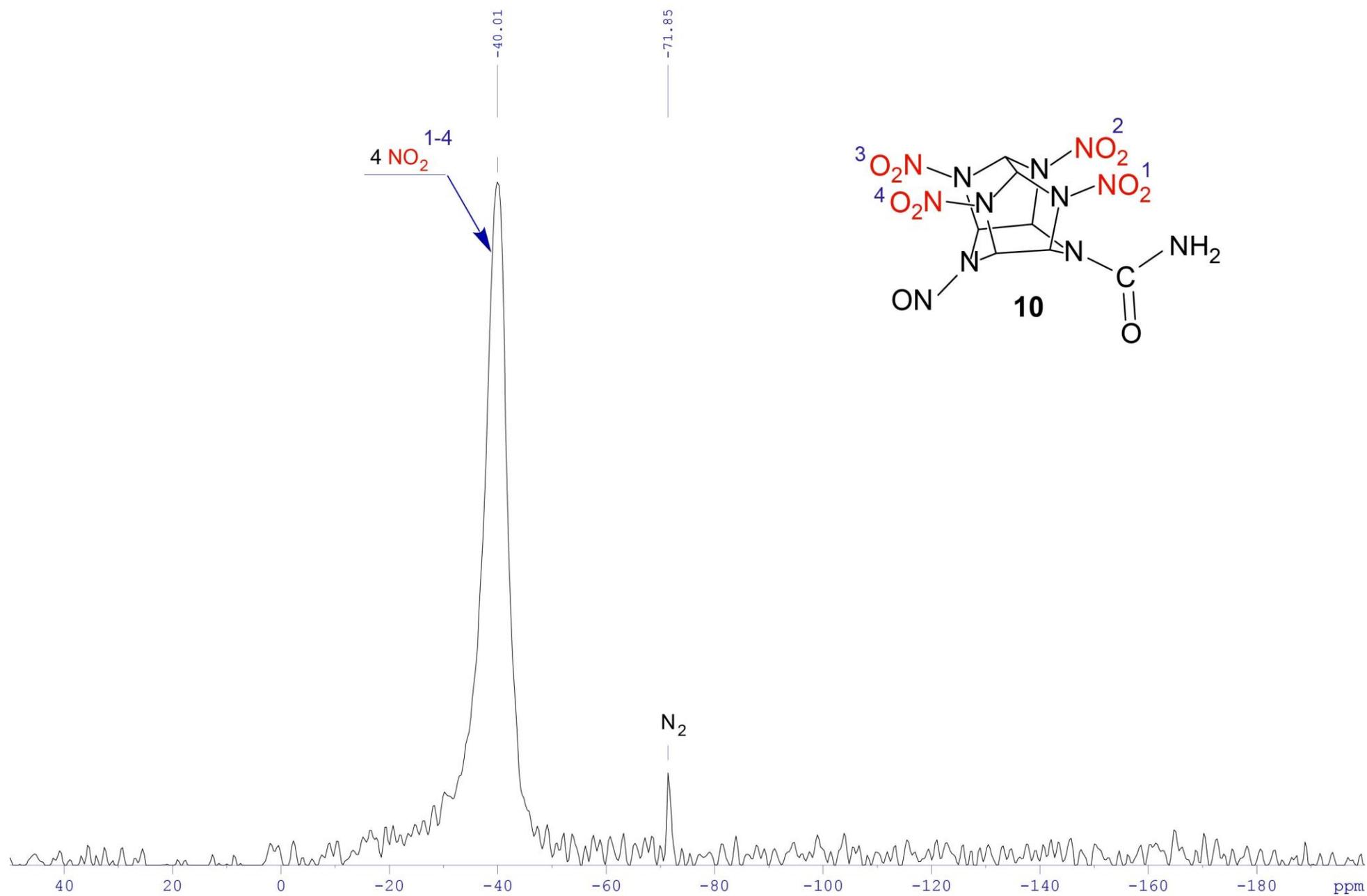
IR (KBr) spectrum of compound 10
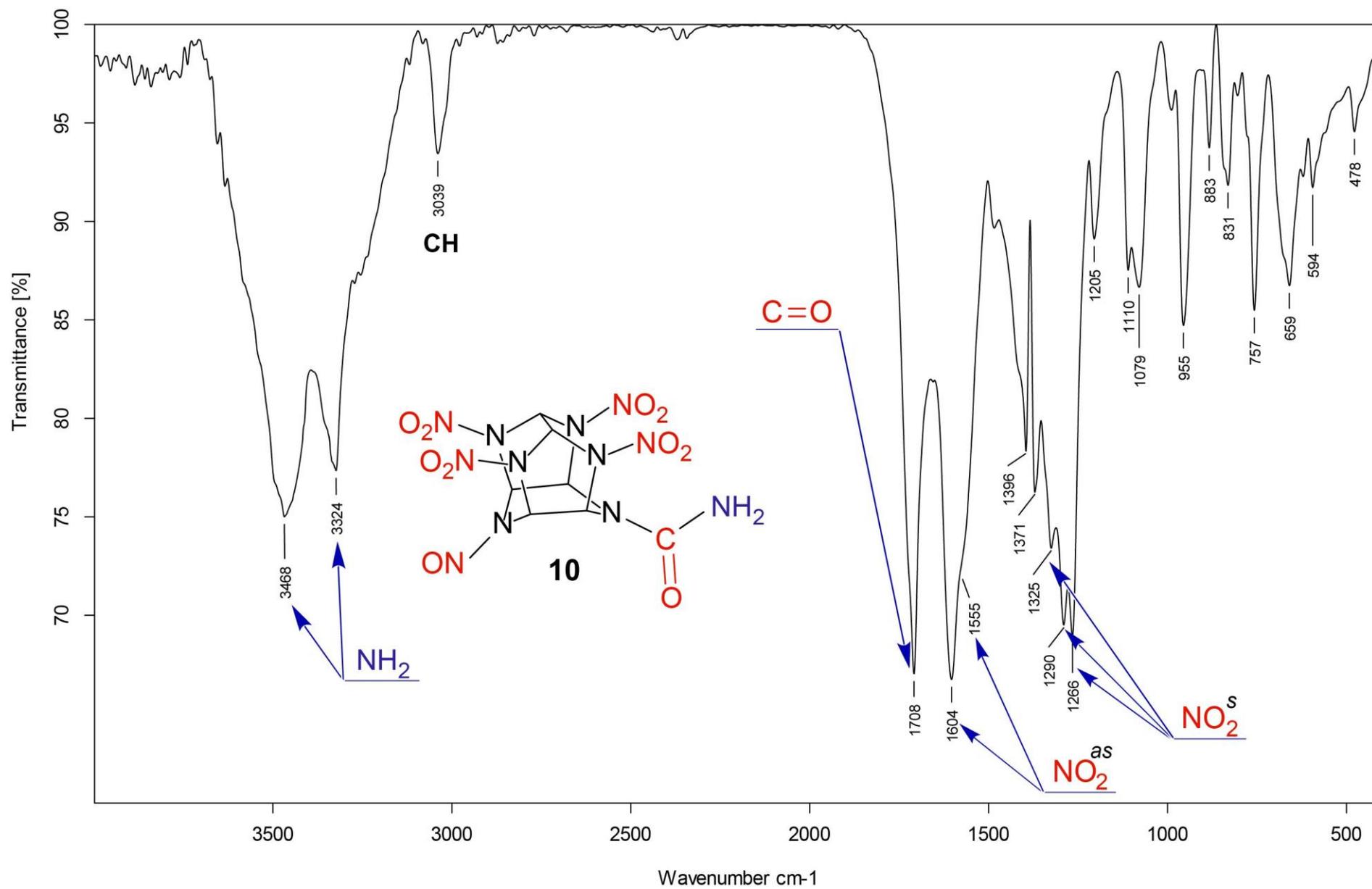
HRMS (ESI) for compound 10
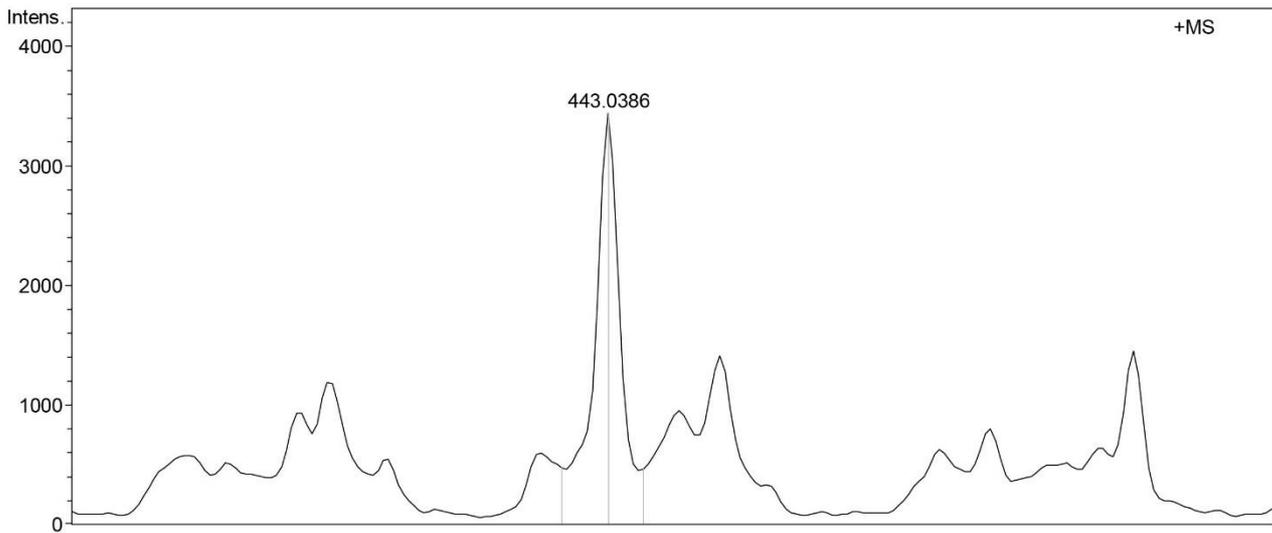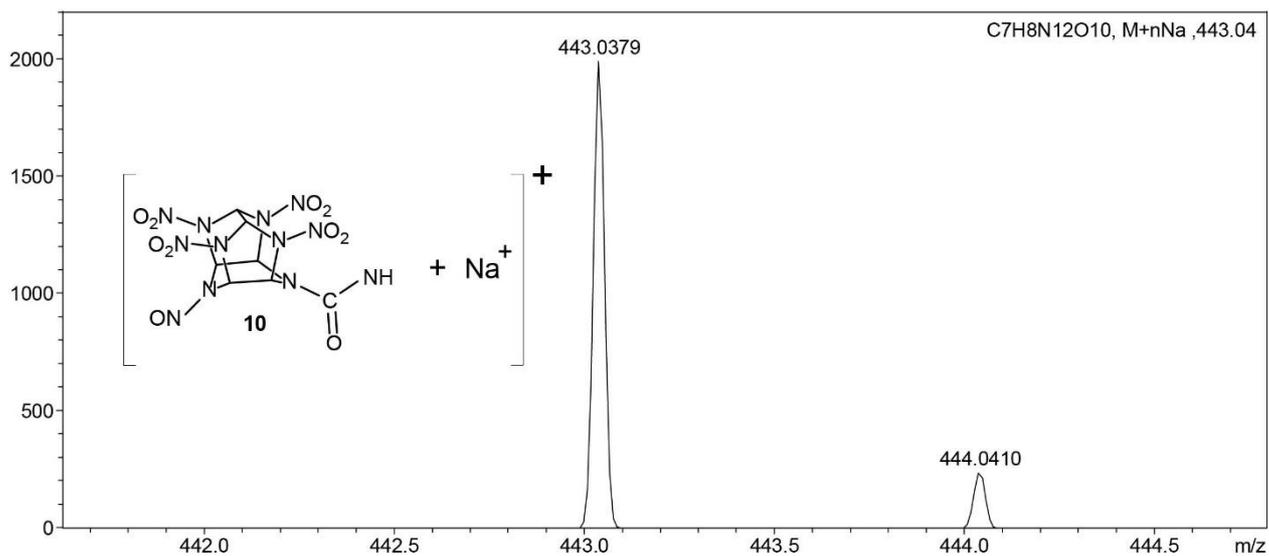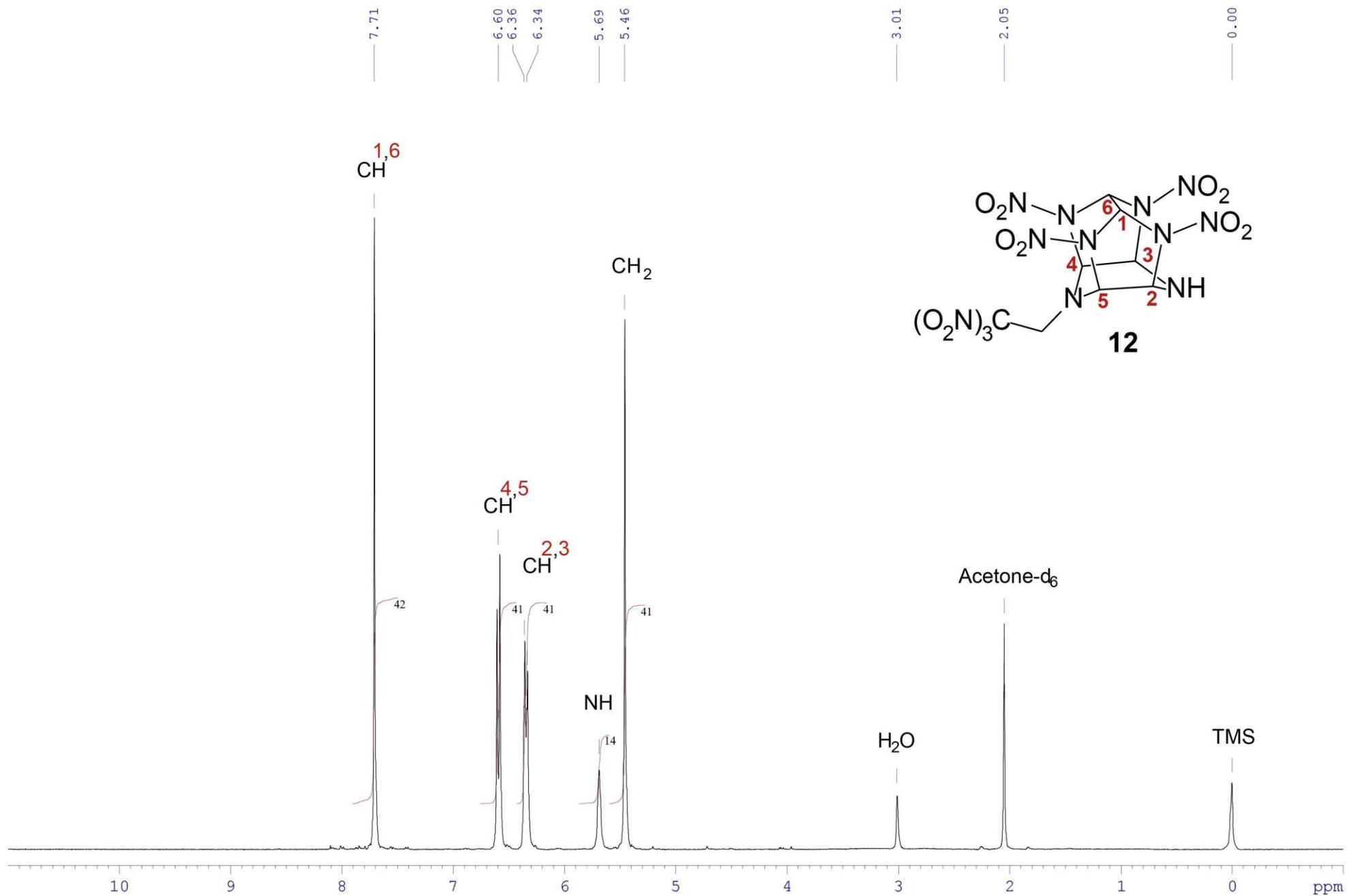
C7H8N12O10, M+nNa ,443.04

443.0379

444.0410

^{1}H NMR (300.1 MHz, [D$_6$]acetone) spectrum of compound 12

7.71

6.60
6.36
6.34

5.69
5.46

3.01

2.05

0.00

CH^{1,6}

CH^{4,5}

CH^{2,3}

CH$_2$

NH

Acetone-d$_6$

H$_2$O

TMS

42

41 41

41

14

O_2N-N $N-NO_2$
O_2N-N $N-NO_2$
$(O_2N)_3C$

NH

12

10 9 8 7 6 5 4 3 2 1 0 ppm

^{13}C NMR (75.5 MHz, [D$_6$]acetone) spectrum of compound 12

127.96

77.65
75.80
73.46
72.96
72.87

55.65

30.67
30.42
30.16
29.90
29.65
29.39
29.14

C1,C6

C4,C5

C2,C3

8
C(NO$_2$)$_3$

7
CH$_2$

Acetone-d$_6$

O$_2$N–N
O$_2$N–N
NO$_2$
NO$_2$
NH
(O$_2$N)$_3$C
12

135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm
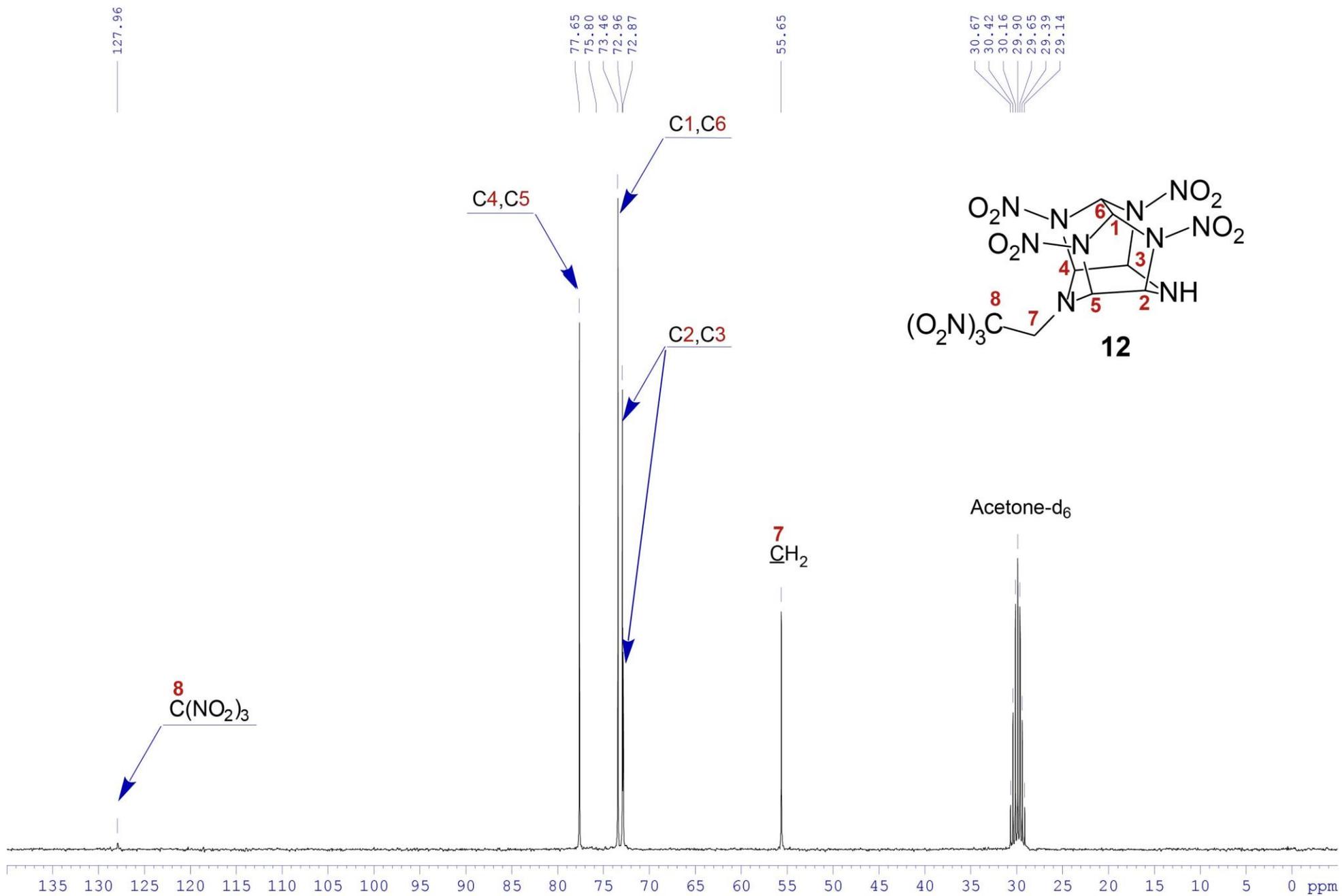
^{14}N NMR (21.7 MHz, [D_6]acetone) spectrum of compound 12
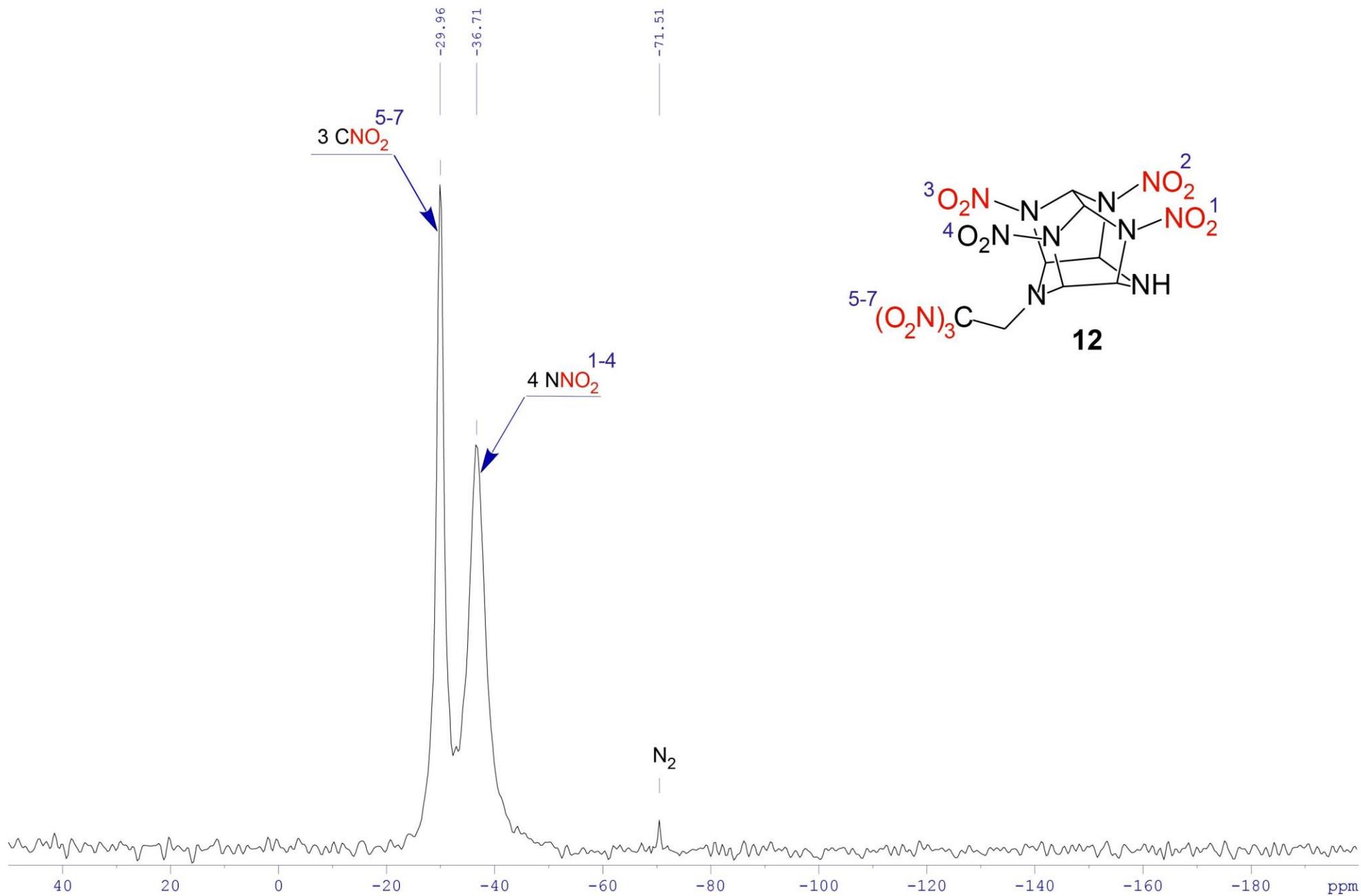
IR (KBr) spectrum of compound 12
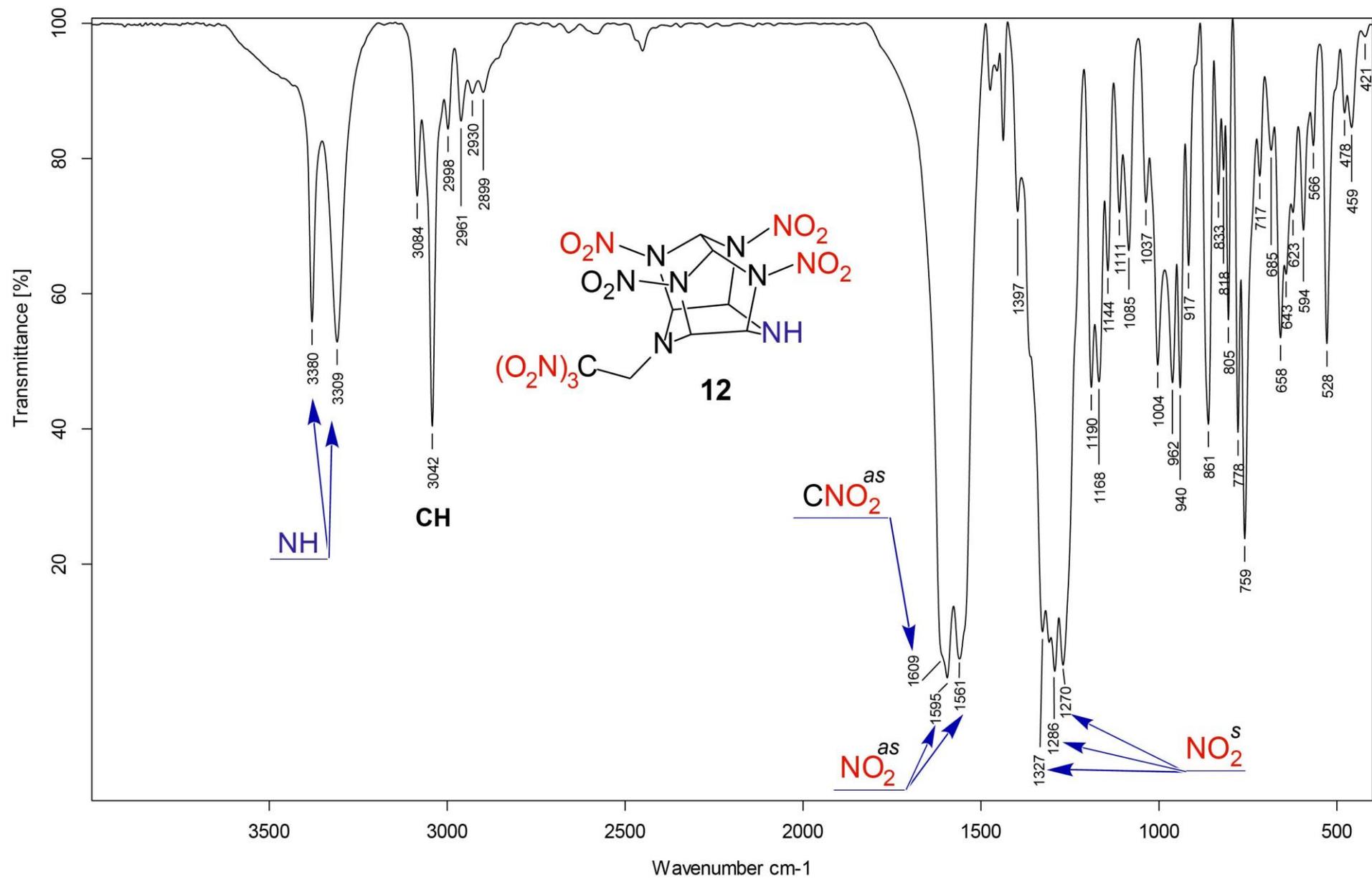
^{1}H NMR (300.1 MHz, [D$_6$]acetone) spectrum of compound 14

CH^{1,6}

CH^{2,3}

CH^{4,5}

CH$_2$

NH$_2$

Acetone-d$_6$

H$_2$O

TMS

7.84 7.44 6.72 6.42 5.51 2.89 2.05 0.00

89 88 88 77 88

10 9 8 7 6 5 4 3 2 1 0 ppm
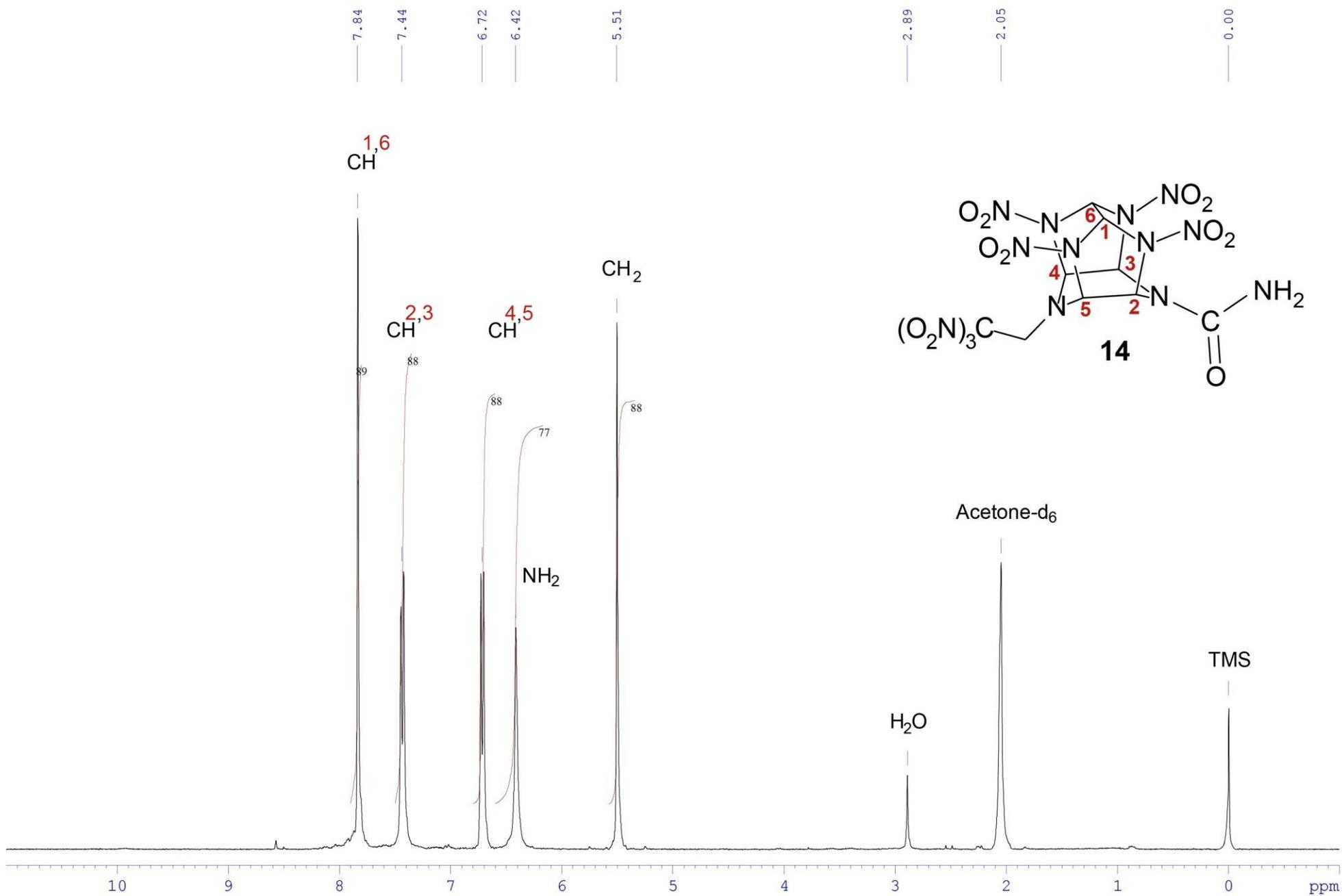
^{13}C NMR (75.5 MHz, [D$_6$]acetone) spectrum of compound 14
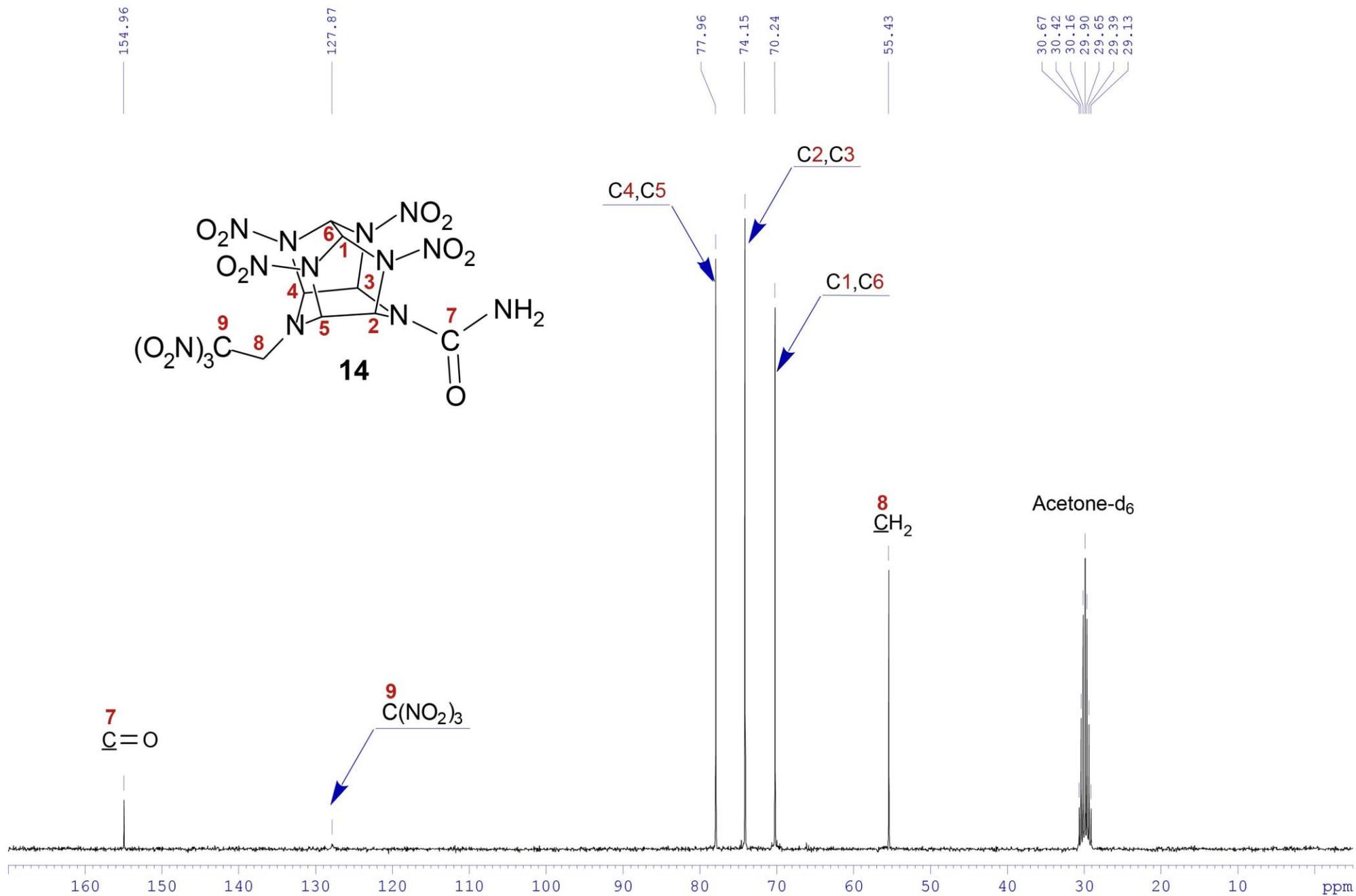
¹⁴N NMR (21.7 MHz, [D₆]acetone) spectrum of compound 14

IR (KBr) spectrum of compound 14

S58

HRMS (ESI) for compound 14

+MS

555.0511 572.0751 577.0323 586.5380 593.0079 596.5125

C9H10N14O15, M+nH ,555.05

555.0523

14

C9H10N14O15, M+nNa ,577.03

577.0342

14

C9H10N14O15, M+nK ,593.01

593.0082
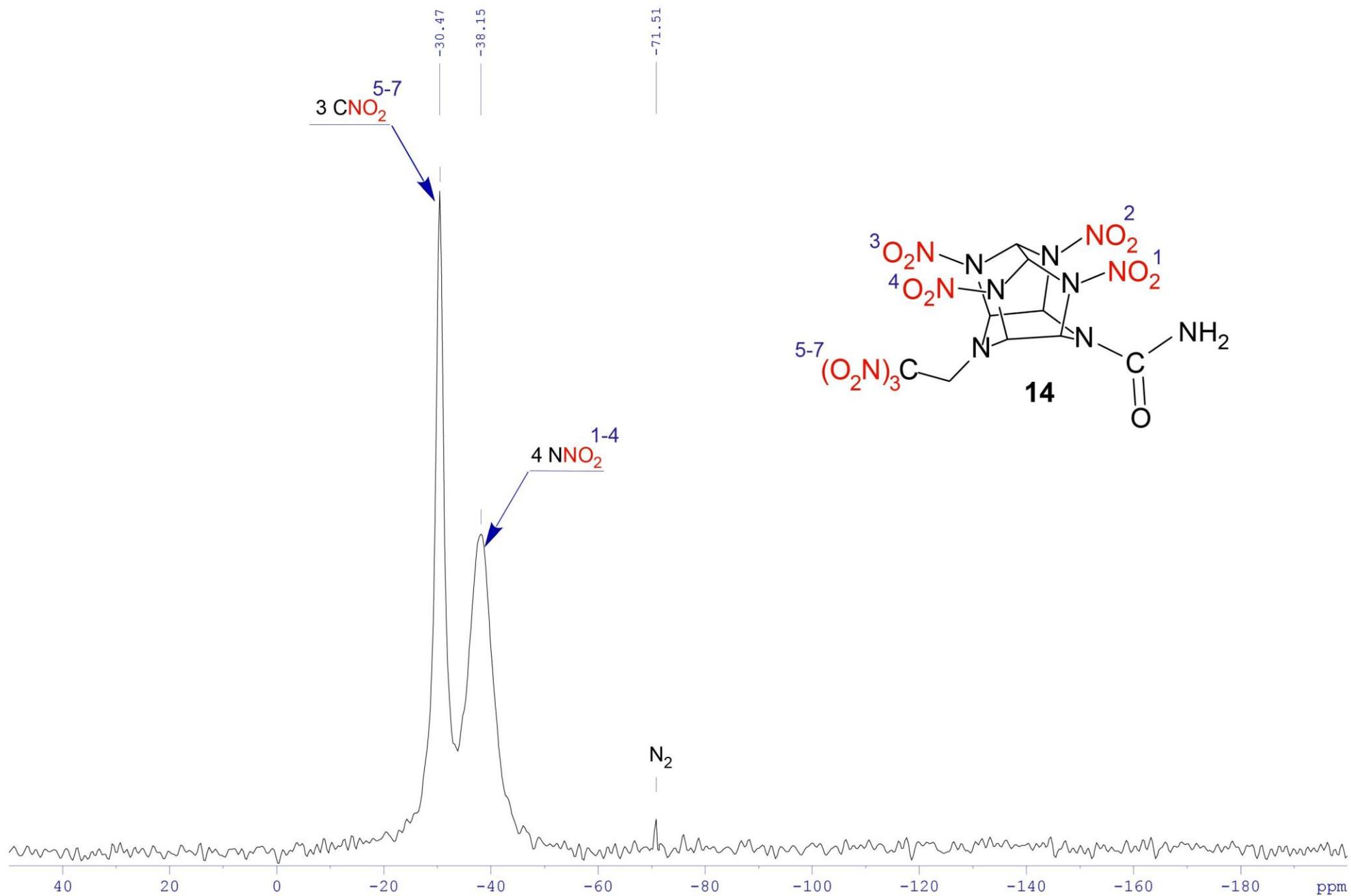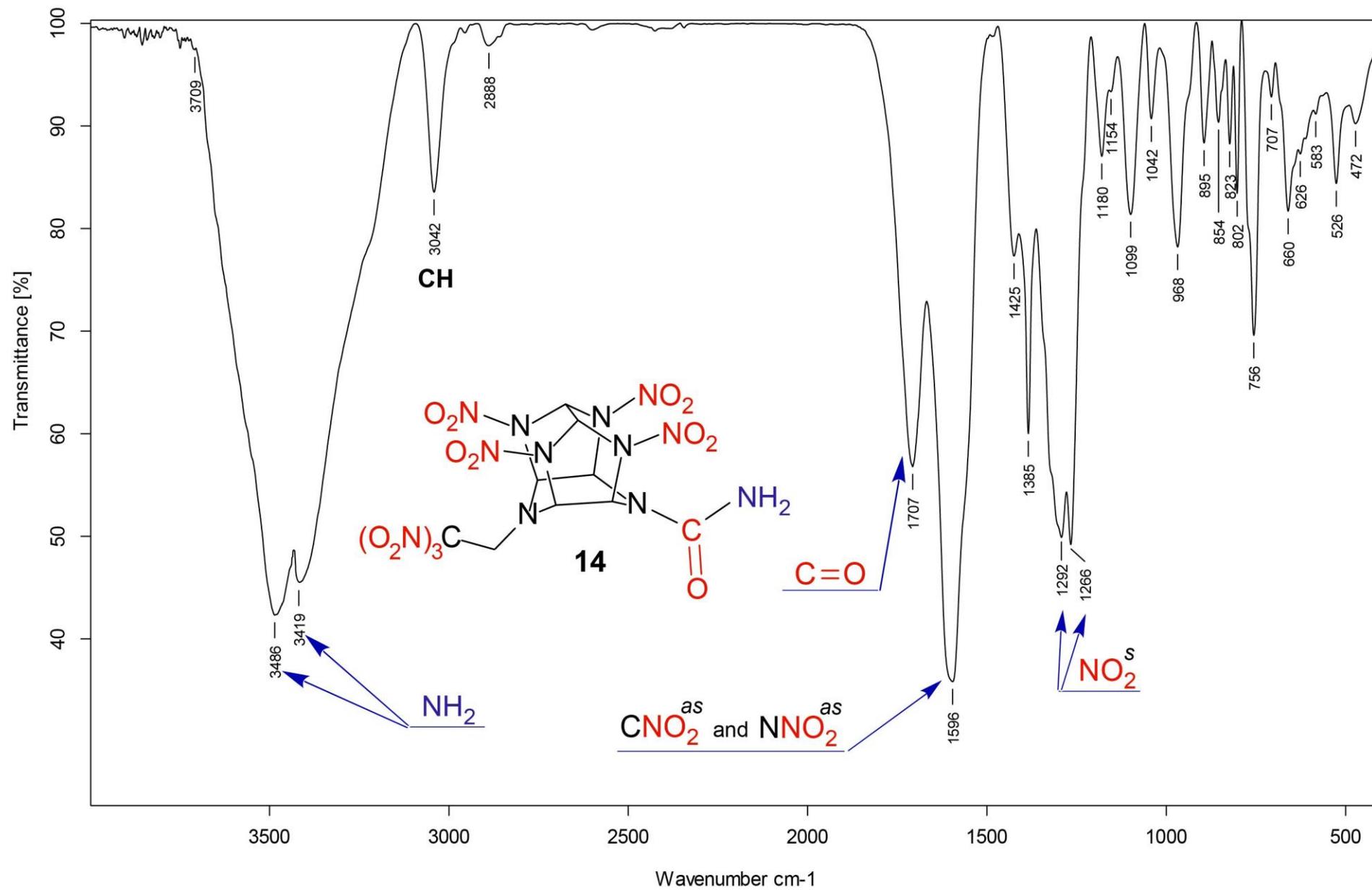
14
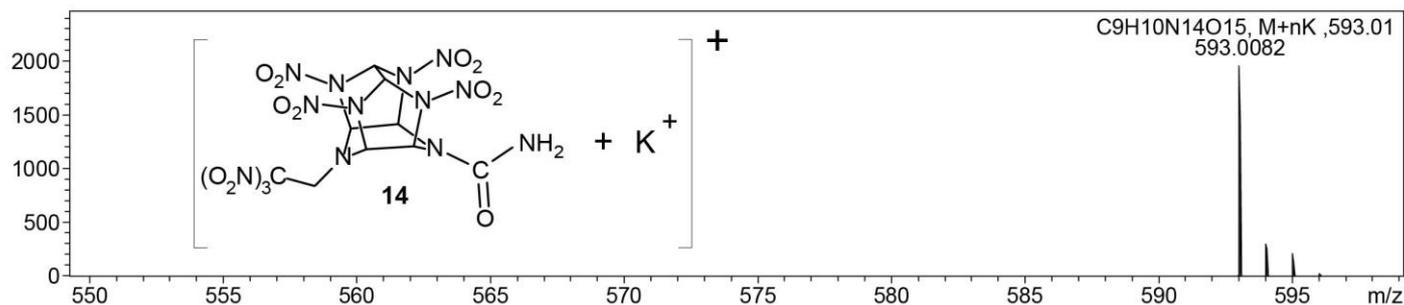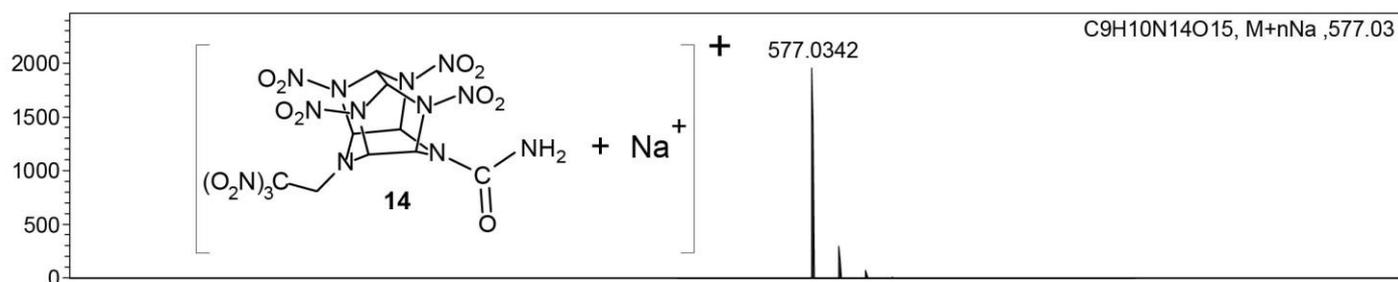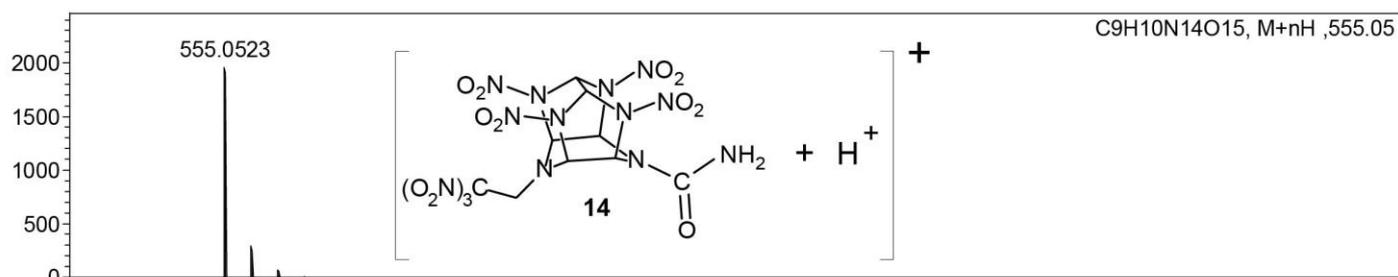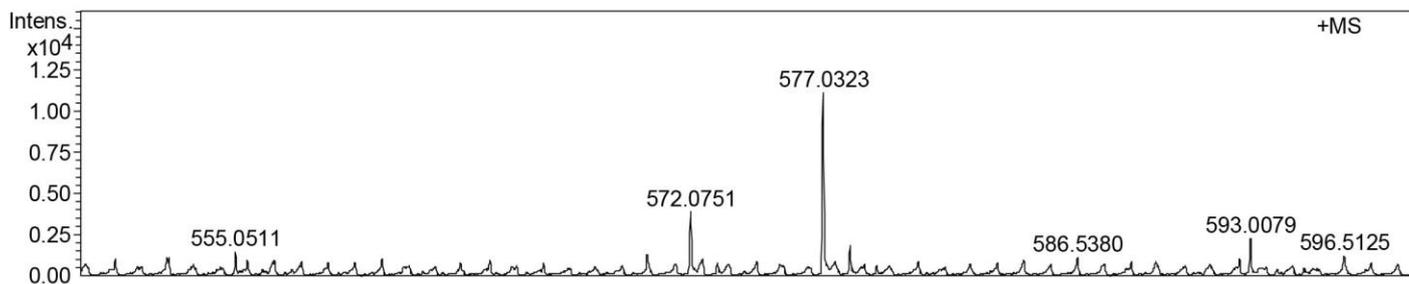
^{1}H NMR (600.13 MHz, [D$_6$]acetone) spectrum of compound 15

^{13}C NMR (150.9 MHz, [D$_6$]acetone) spectrum of compound 15

126.30

110.36

77.20
73.17
72.93

53.21

28.94
28.81
28.68
28.55
28.43
28.30
28.17

C2,C3

C1,C6

C4,C5

$\underline{C}H_2$ **8**

7 $\underline{C}\equiv N$

Acetone-d$_6$

9 $\underline{C}(NO_2)_3$

15

135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm
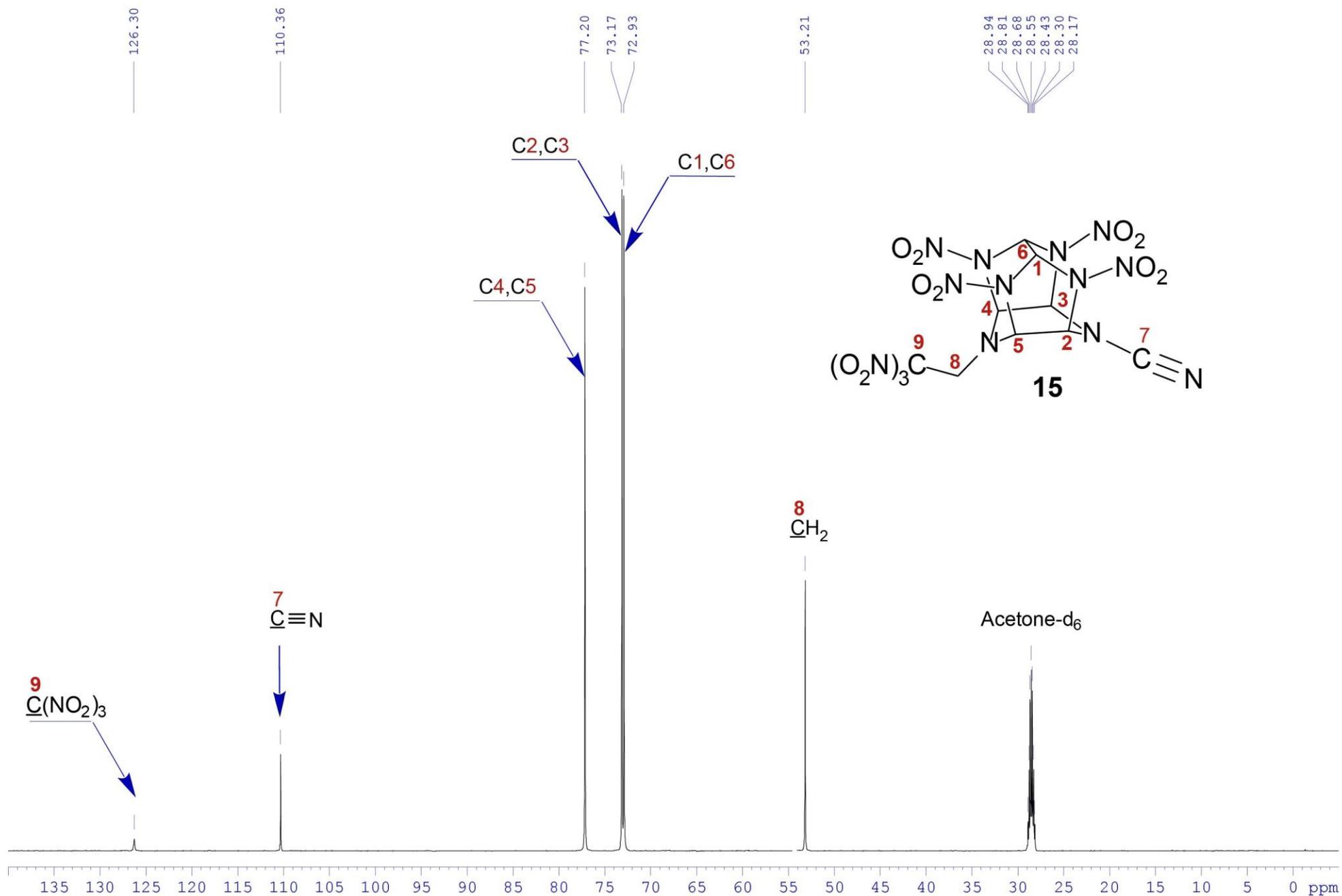
{¹H−¹³C} HSQC NMR (600.13 MHz, [D₆]acetone) spectrum of compound 15
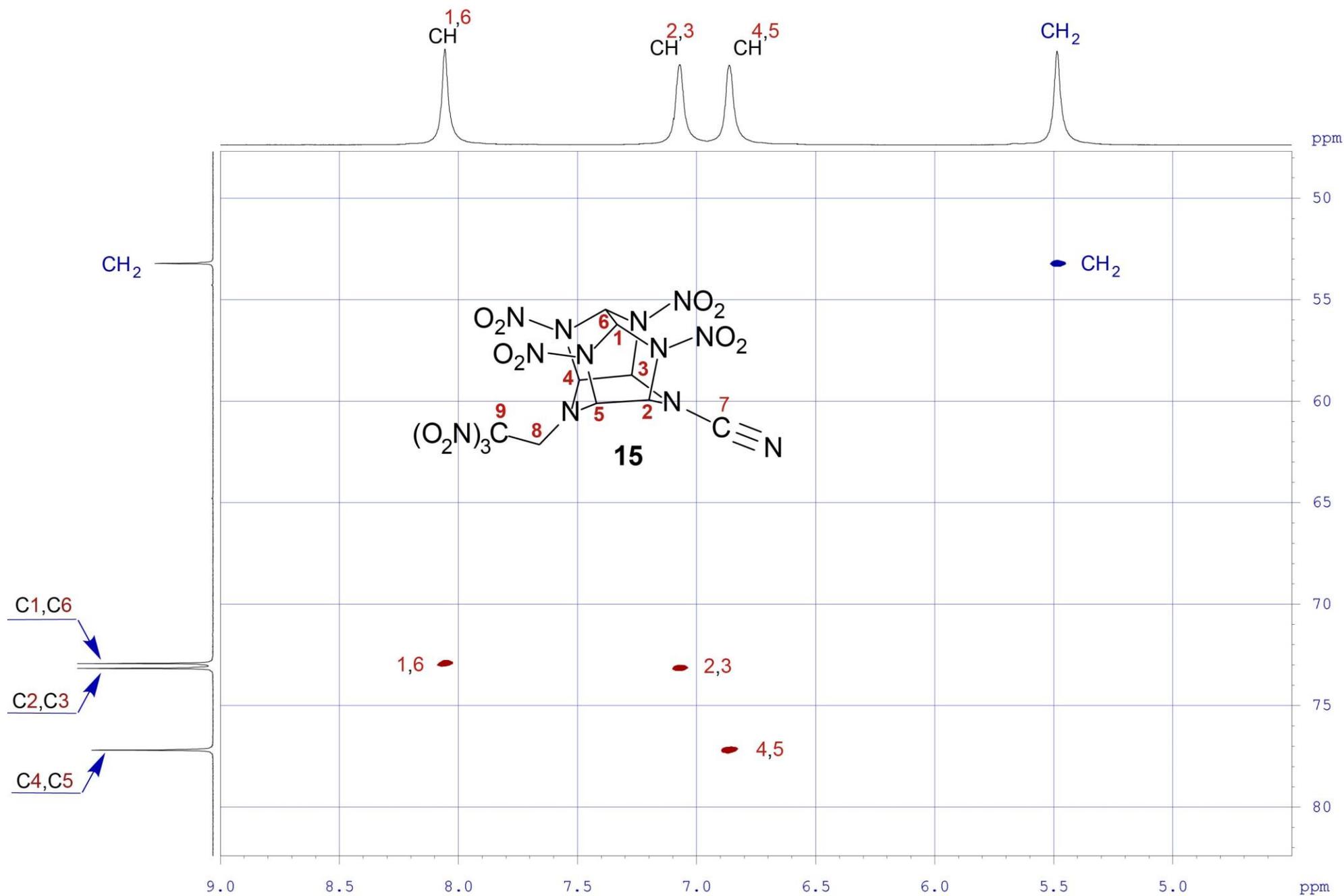
{^{1}H–^{13}C} HMBC NMR (600.13 MHz, [D$_6$]acetone) spectrum of compound 15
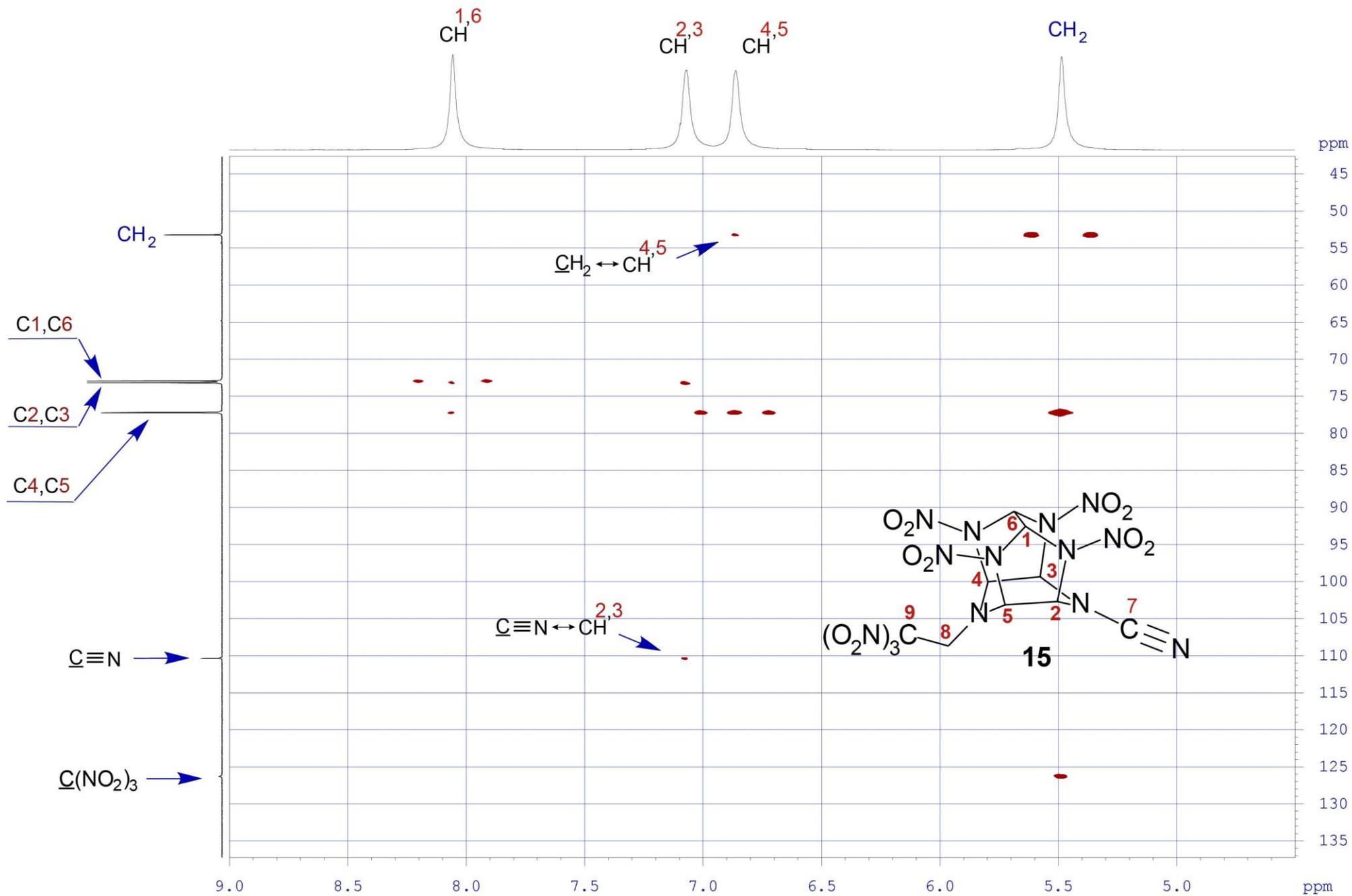
^{14}N NMR (43.37 MHz, [D$_6$]acetone) spectrum of compound 15
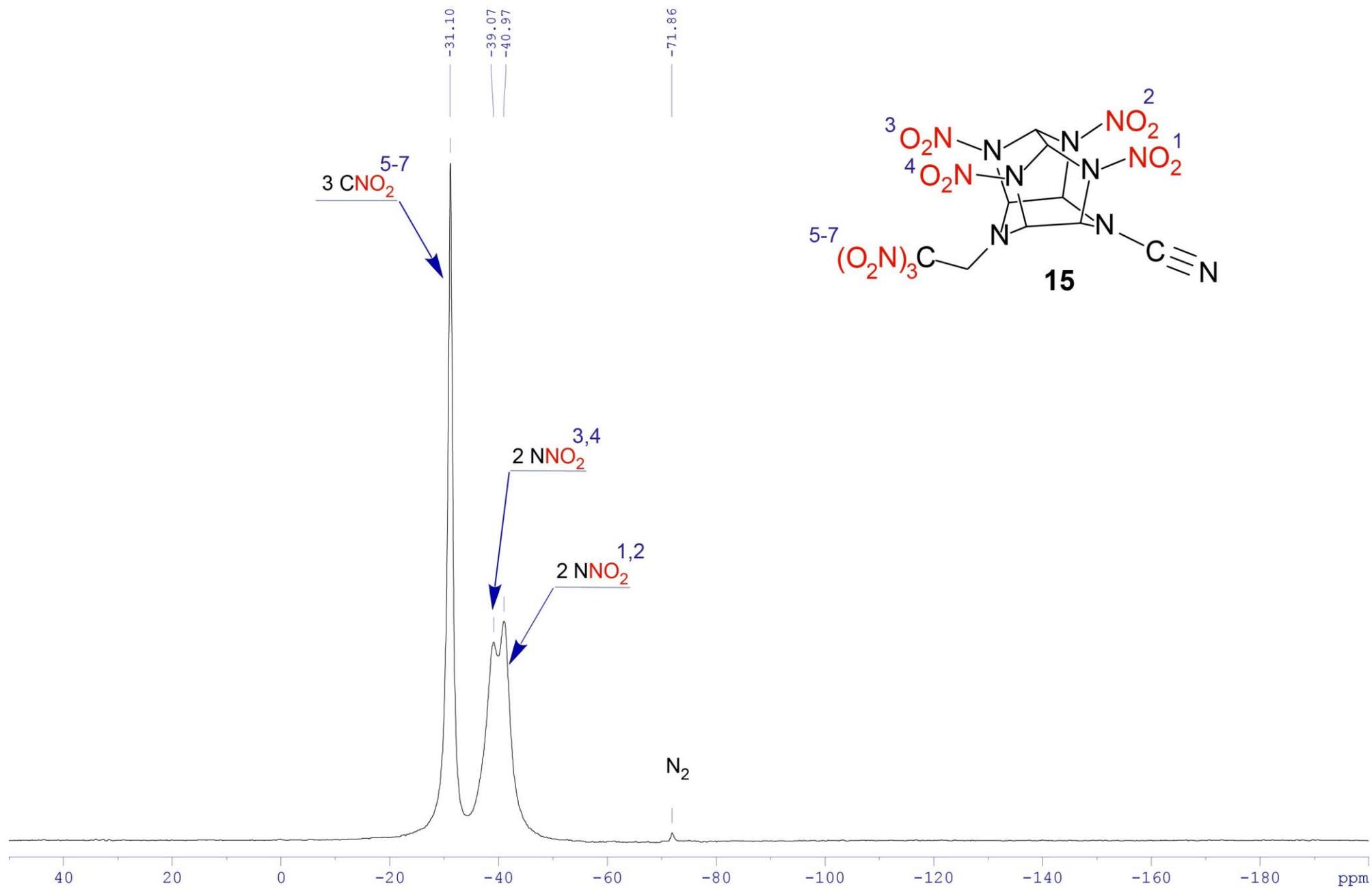
^{15}N NMR ([INVGATED], [INEPT], 60.8 MHz, [D$_6$]acetone) spectrum of compound 15
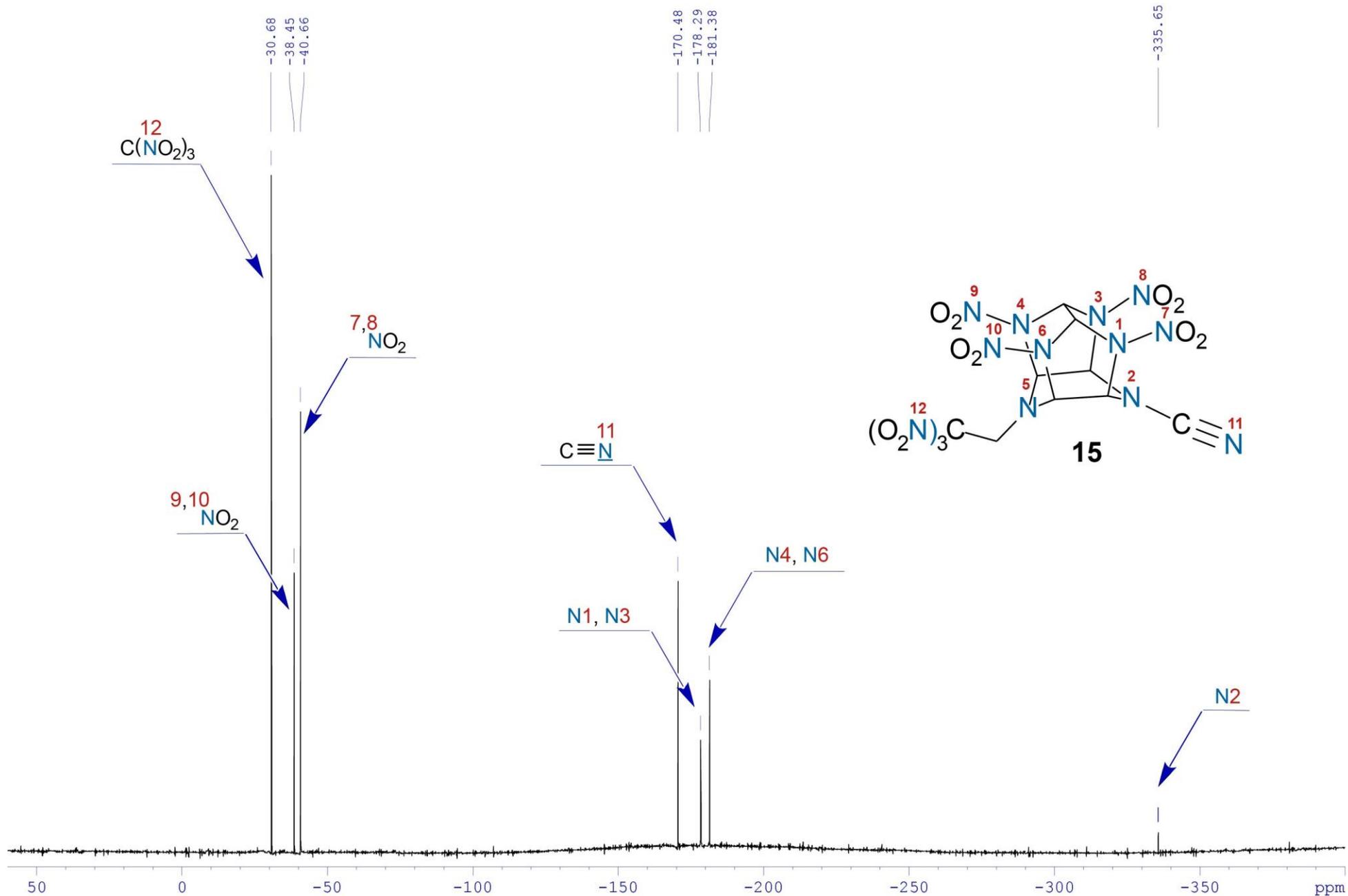
{^{1}H−^{15}N} HSQC NMR (600.13 MHz, [D$_6$]acetone) spectrum of compound 15
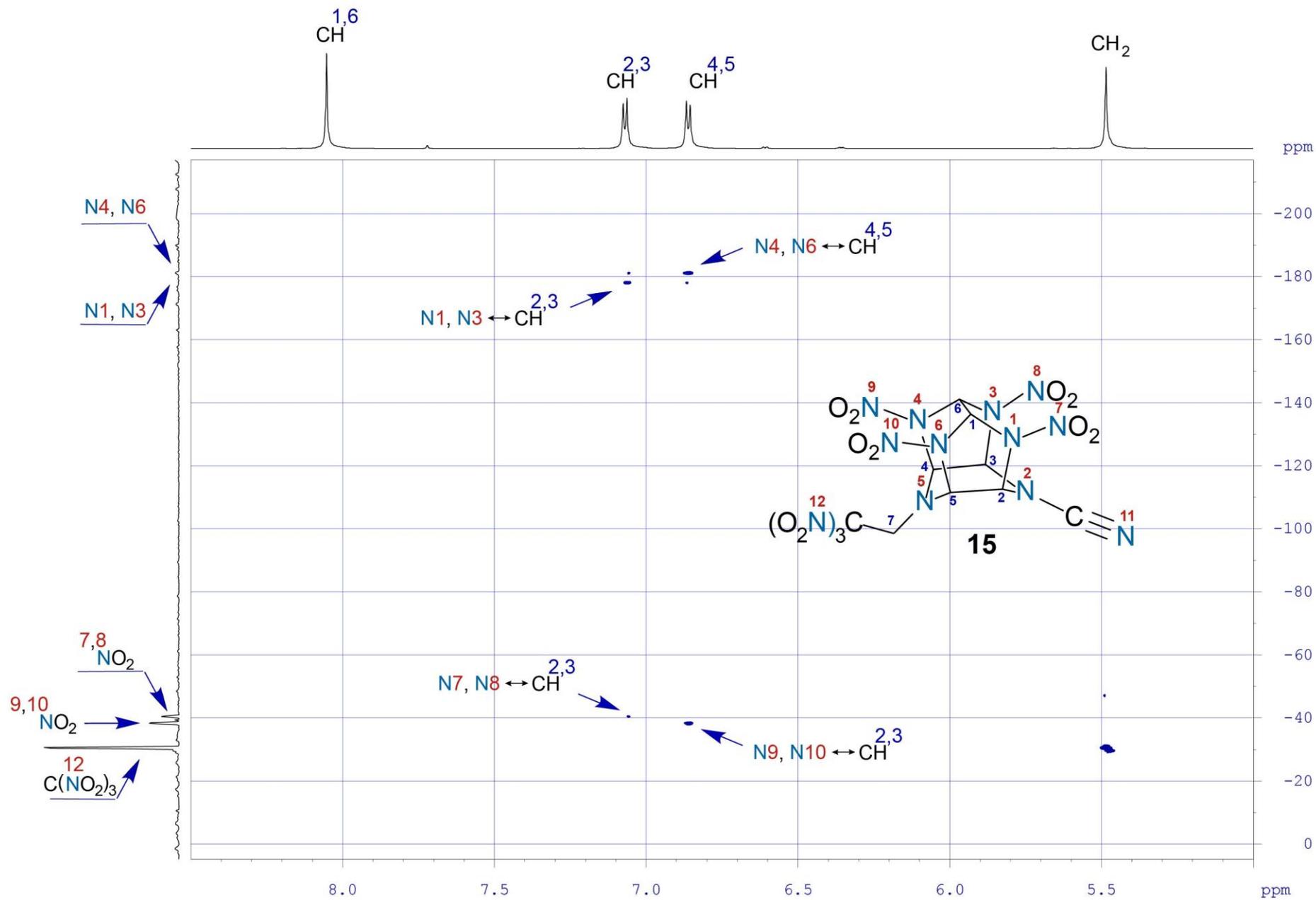
IR (KBr) spectrum of compound 15
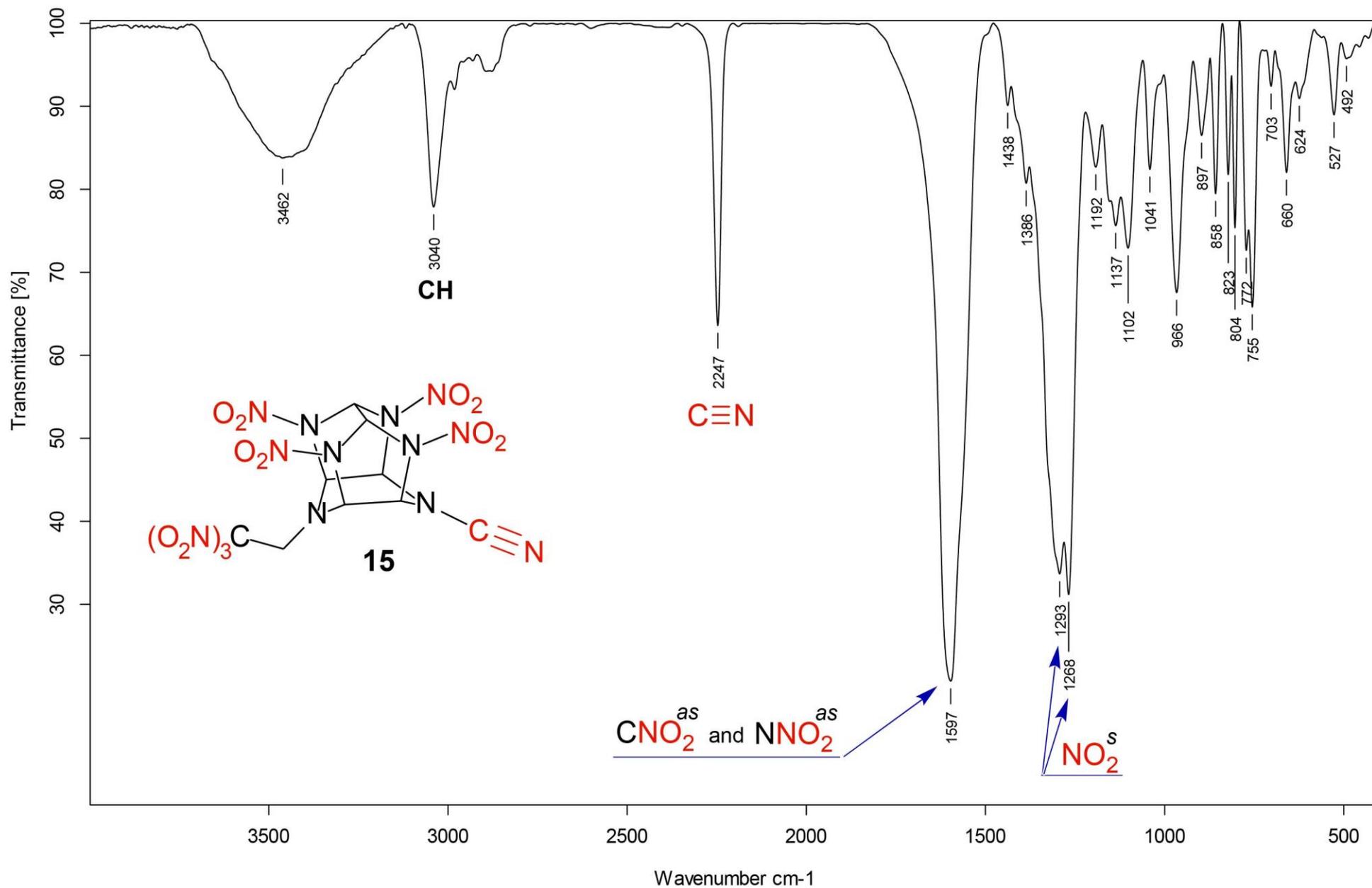
HRMS (ESI) for compound 15

^{1}H NMR (300.1 MHz, [D$_6$]DMSO) spectrum of compound 20

7.93
7.79
7.39
7.09
3.42
2.52
0.00

CH^{1,6}

CH^{4,5}

CH^{2,3}

NH$_2$

49   49

51   51

DMSO-d$_6$

H$_2$O

TMS

10   9   8   7   6   5   4   3   2   1   0   ppm
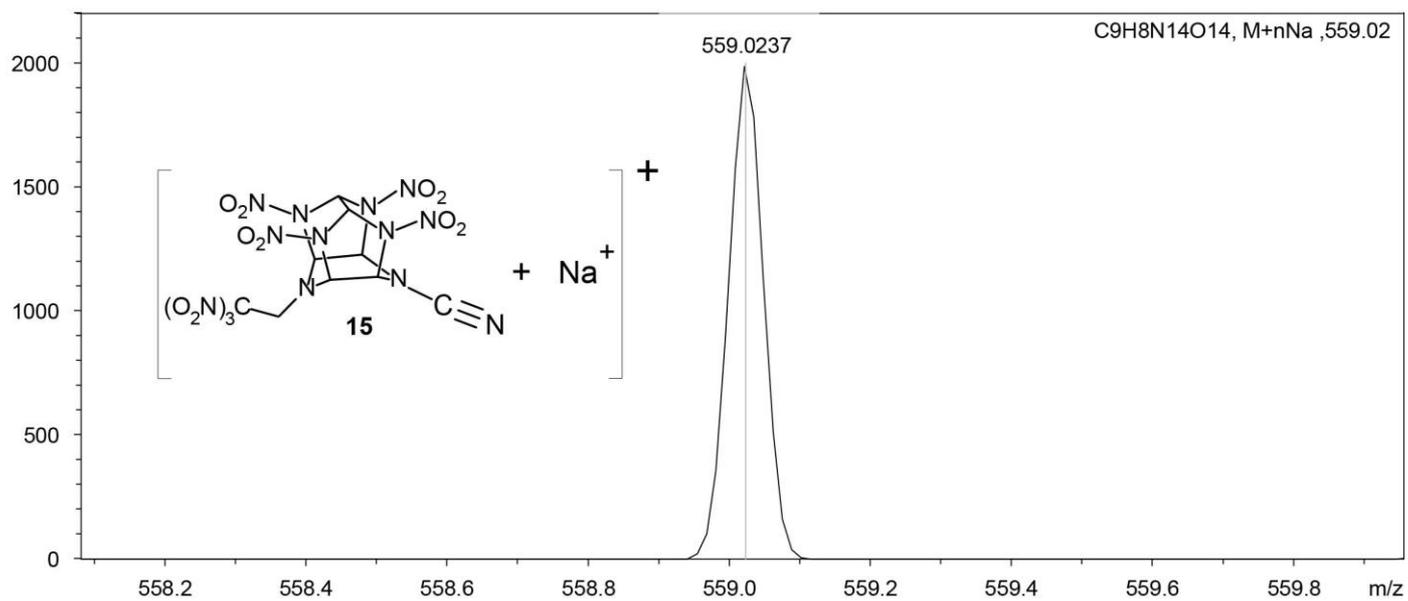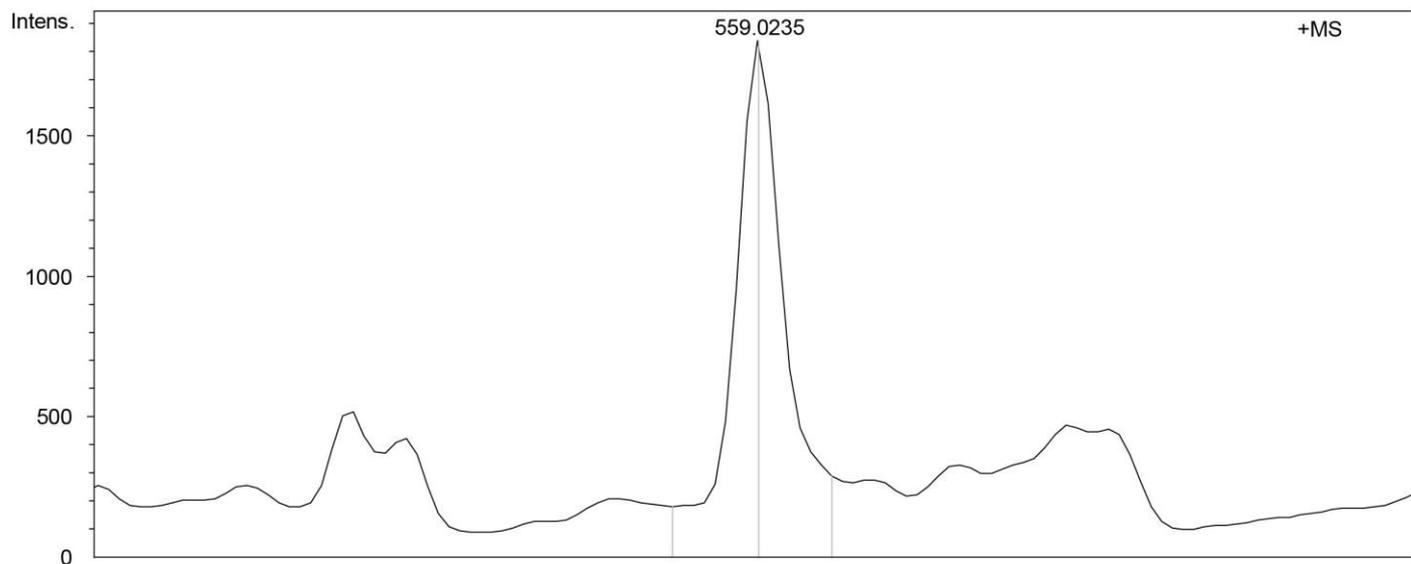
¹³C NMR (75.5 MHz, [D₆]DMSO) spectrum of compound 20

^{13}C NMR (75.5 MHz, [D$_6$]DMSO) spectrum of compound 20

154.17

73.41
70.19
69.98

40.04
39.76
39.49
39.21
38.93

C4,C5

C2,C3

C1,C6

7
C=O

DMSO-d$_6$

20

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{14}N NMR (22 MHz, [D$_6$]DMSO) spectrum of compound 20

-38.99

-71.88

N$_2$

100   50   0   -50   -100   -150   ppm
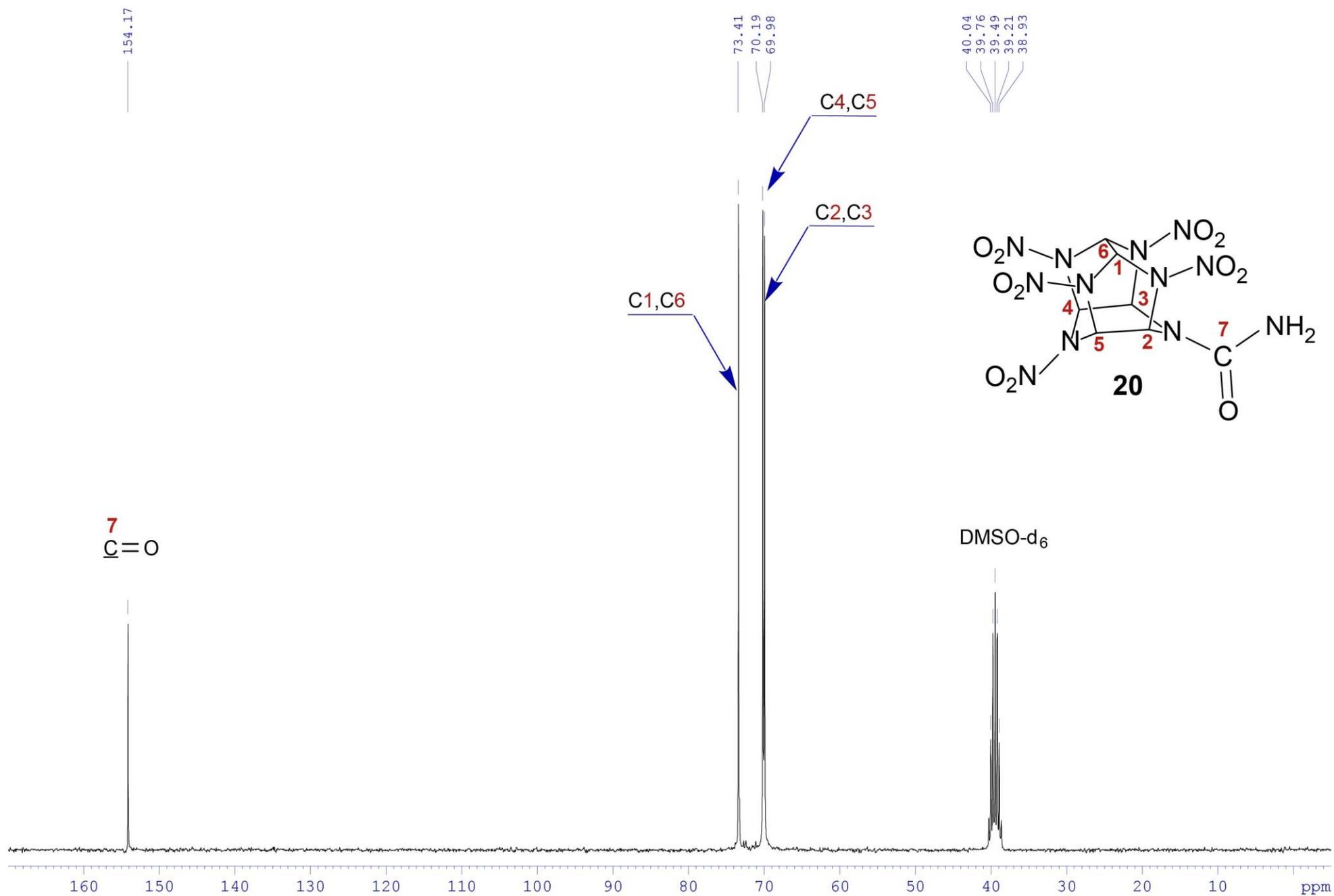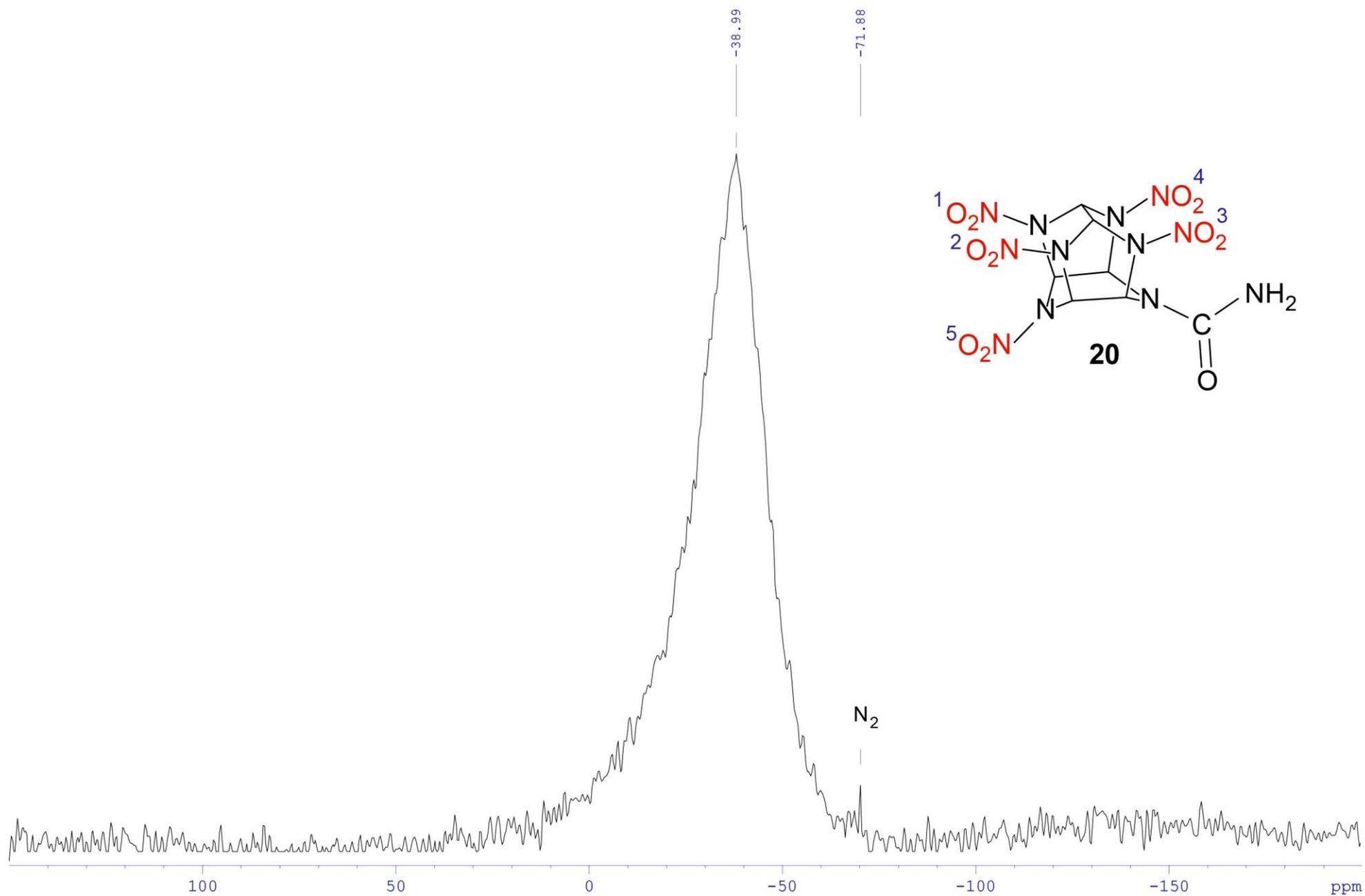
IR (KBr) spectrum of compound 20

^{1}H NMR (600.13 MHz, [D$_6$]acetone) spectrum of compound 22

8.25
8.17
7.30
2.07
0.00

CH^{1,6}

122
120
119

CH^{4,5}

CH^{2,3}

TMS

Acetone-d$_6$

H$_2$O

O$_2$N—N—N—NO$_2$
O$_2$N—N—N—NO$_2$
O$_2$N—N
N—C≡N

22

10   9   8   7   6   5   4   3   2   1   0   ppm
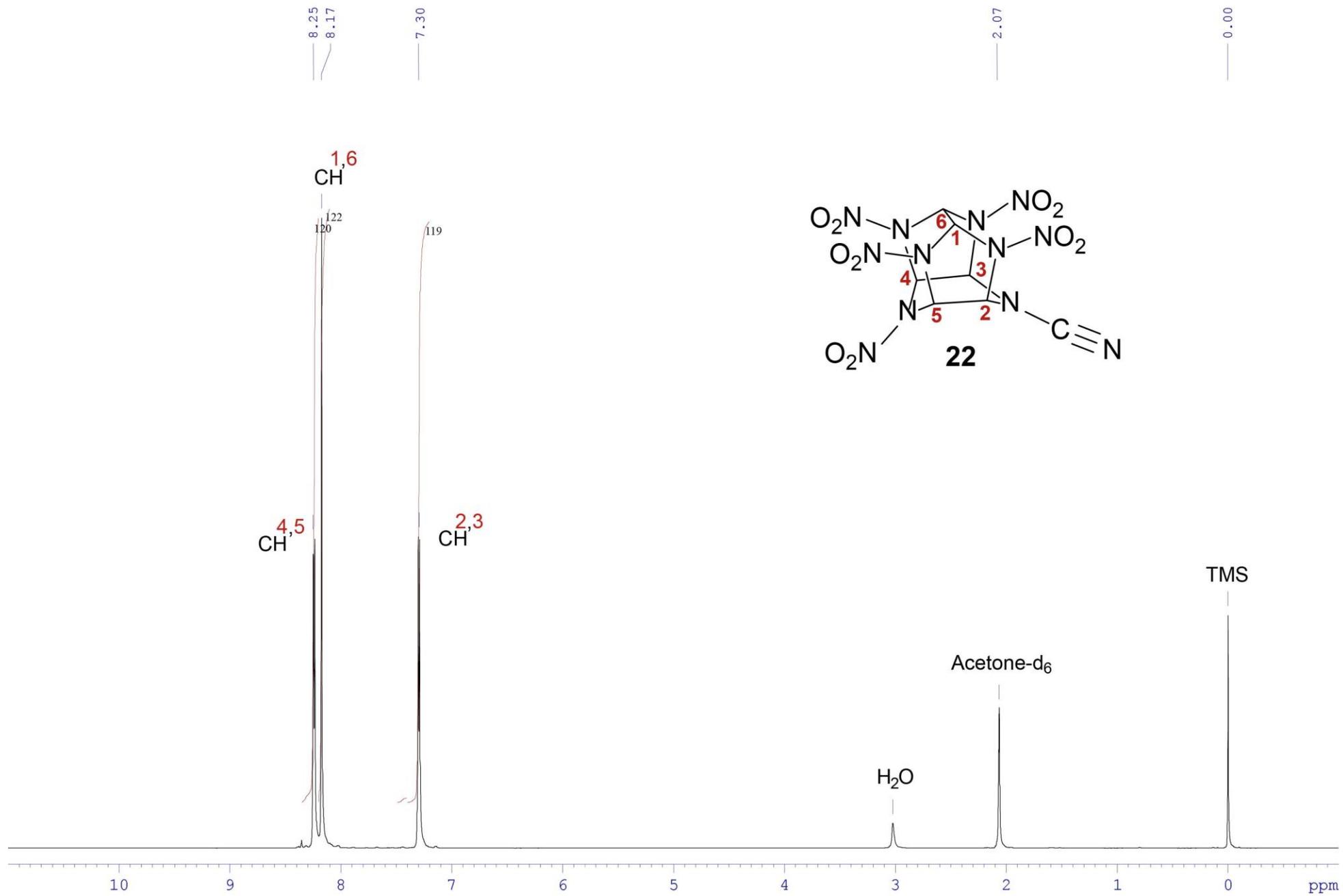
^{1}H NMR (300.1 MHz, [D$_6$]DMSO) spectrum of compound 22

^{13}C NMR (150.9 MHz,[D$_6$]acetone) spectrum of compound 22
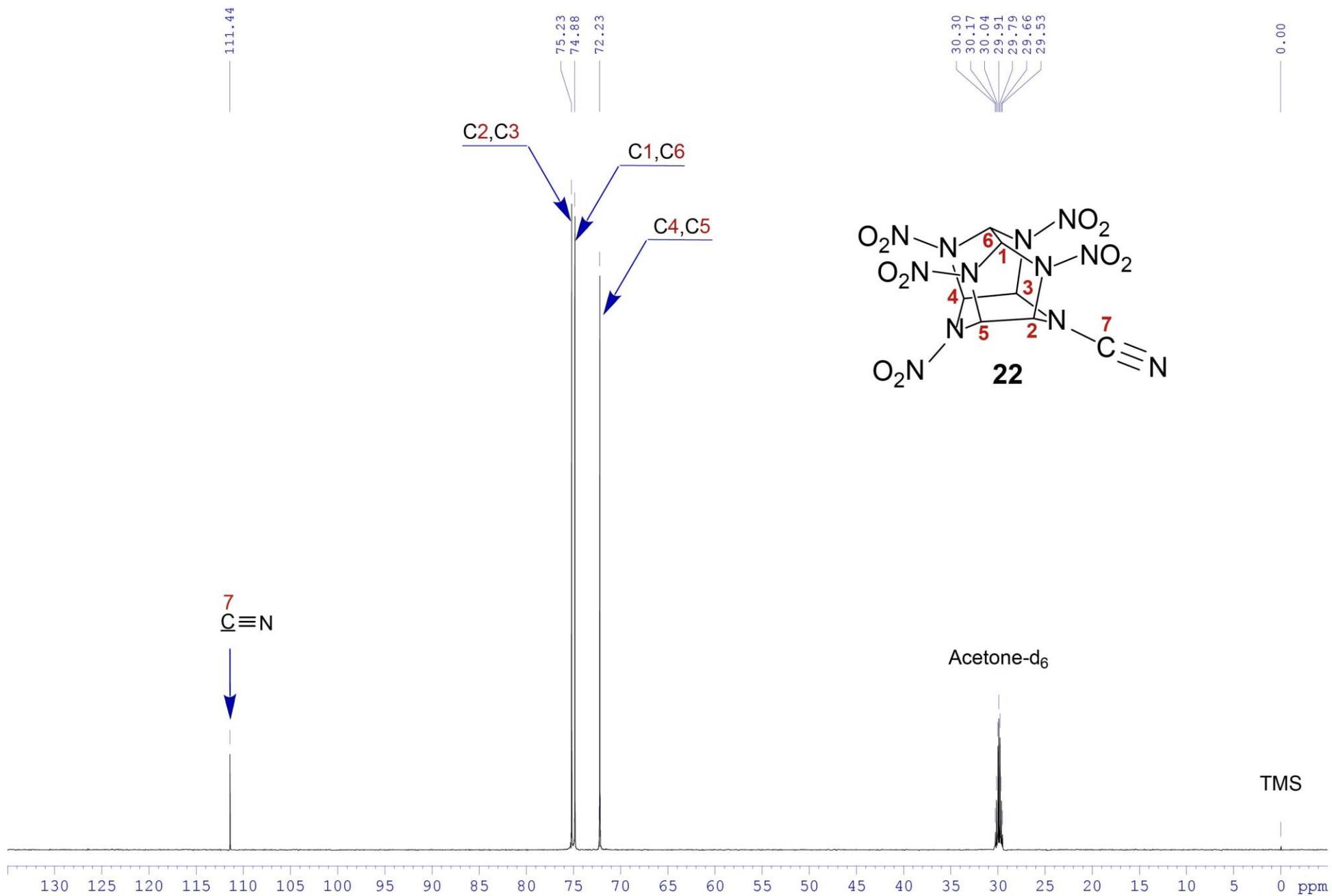
{^{1}H–^{13}C} HSQC NMR (600.13 MHz, [D$_6$]acetone) spectrum of compound 22
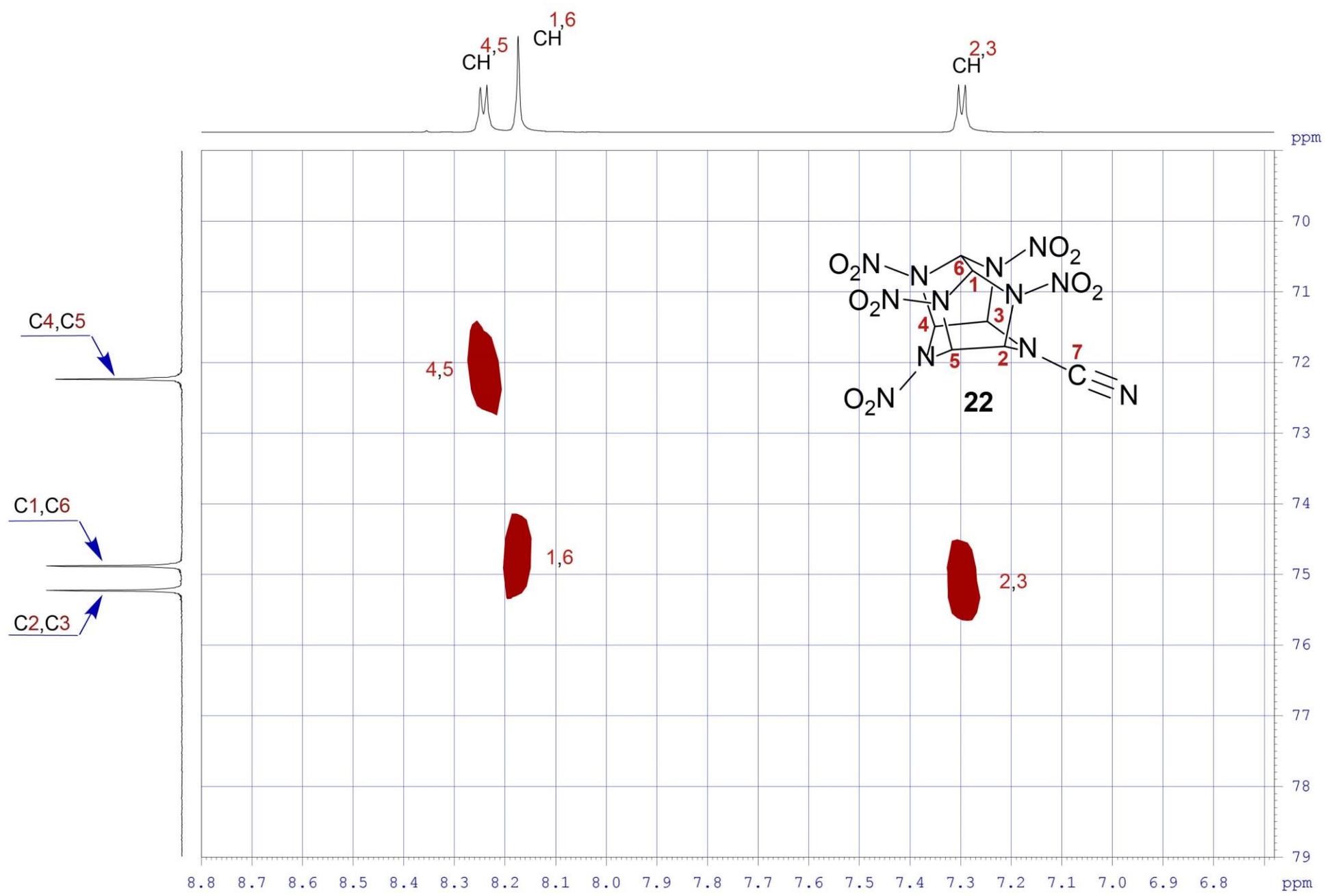
{¹H−¹³C} HMBC NMR (600.13 MHz,[D₆]acetone) spectrum of compound 22
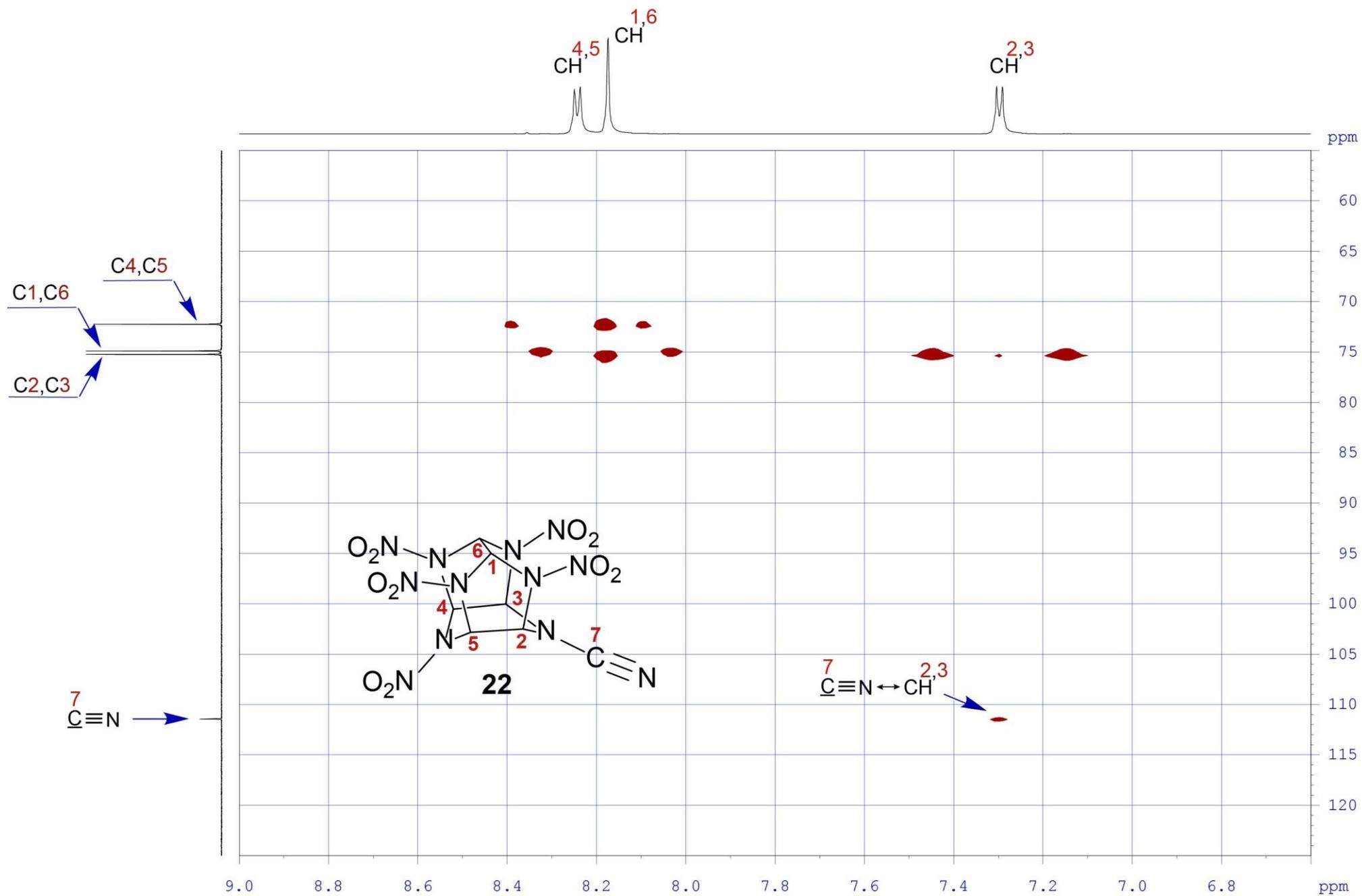
14N NMR (43.37 MHz, [D₆]acetone) spectrum of compound 22
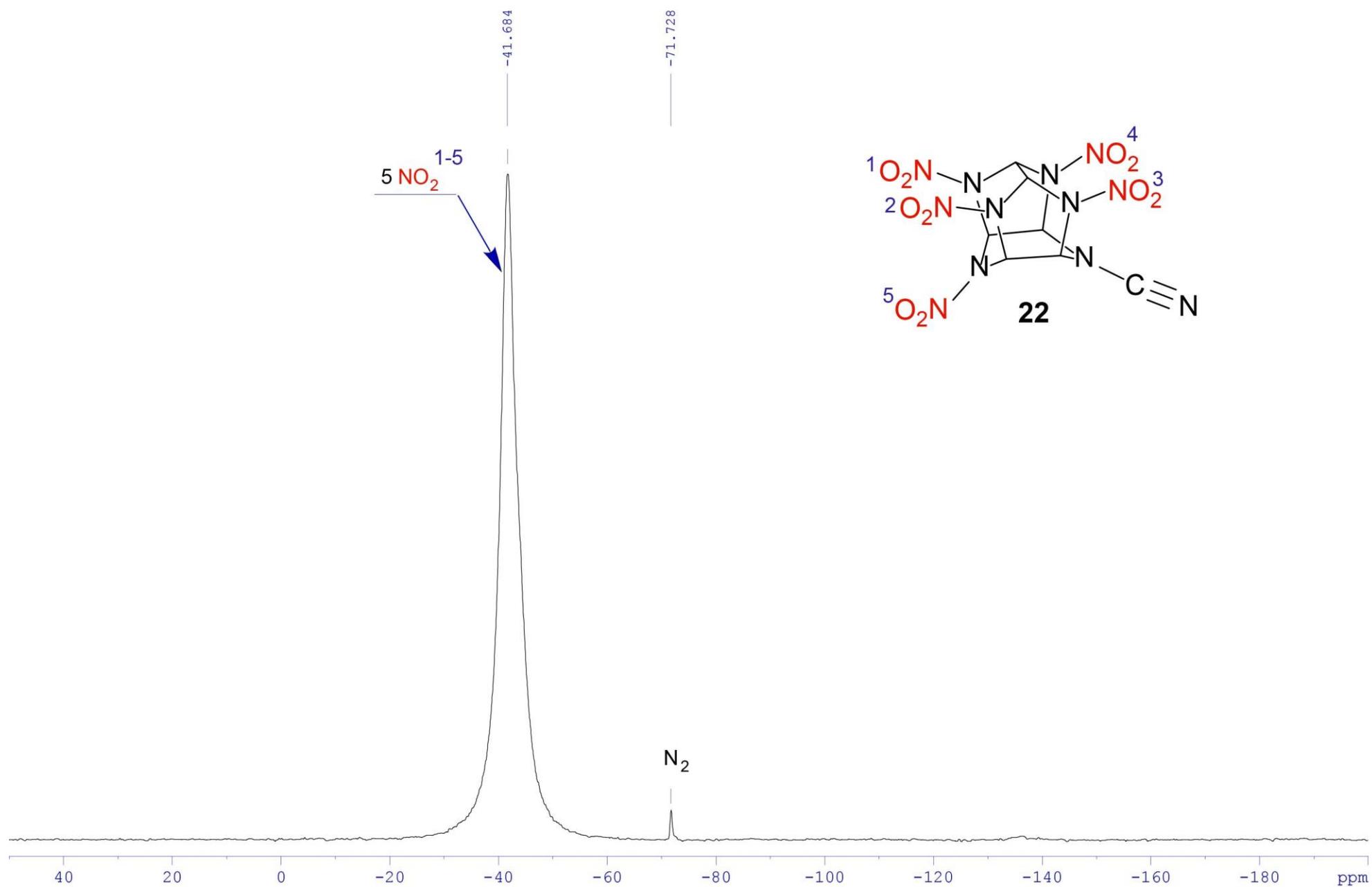
^{15}N NMR ([INVGATED], [INEPT], 60.8 MHz, [D$_6$]acetone) spectrum of compound 22
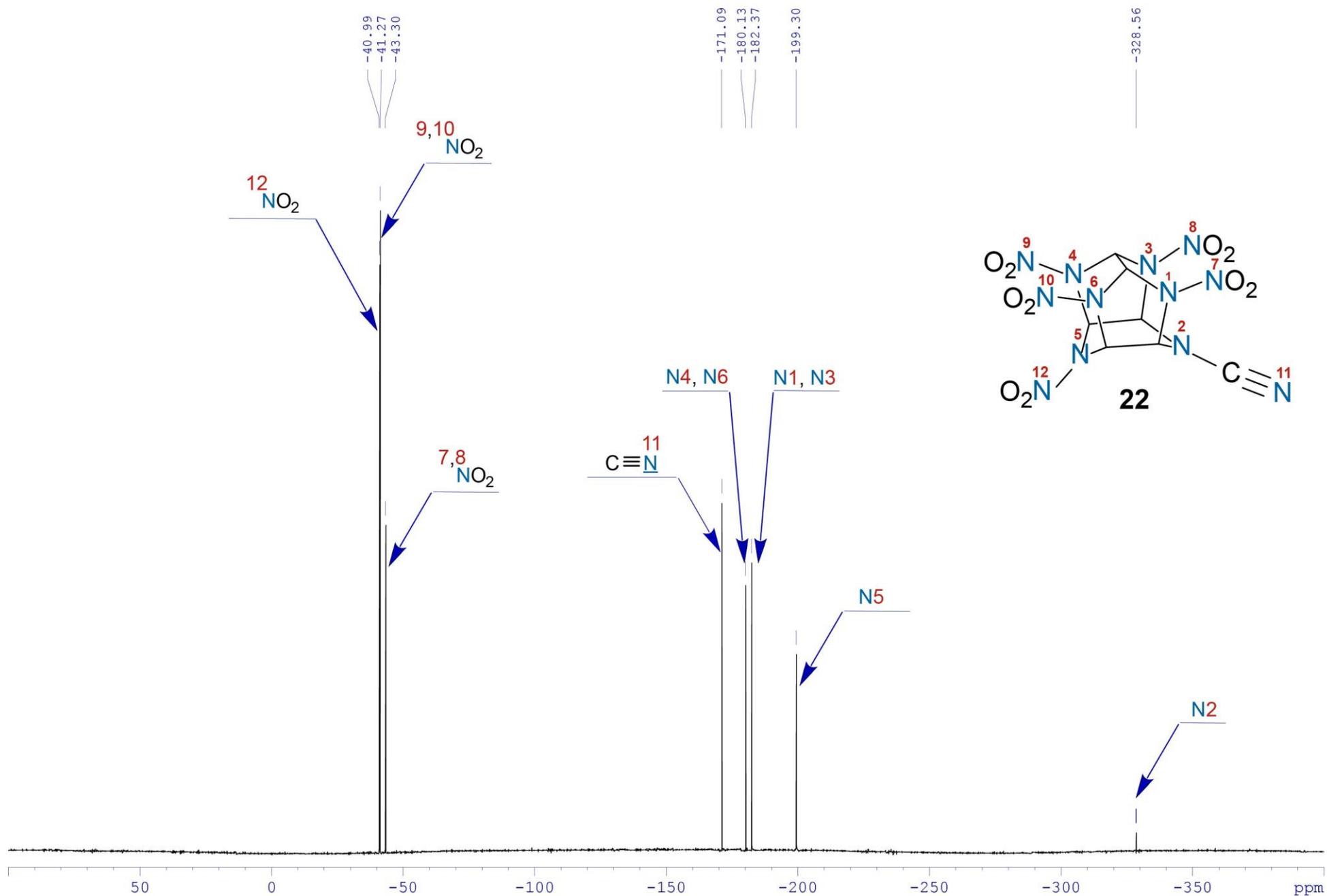
IR (KBr) spectrum of compound 22
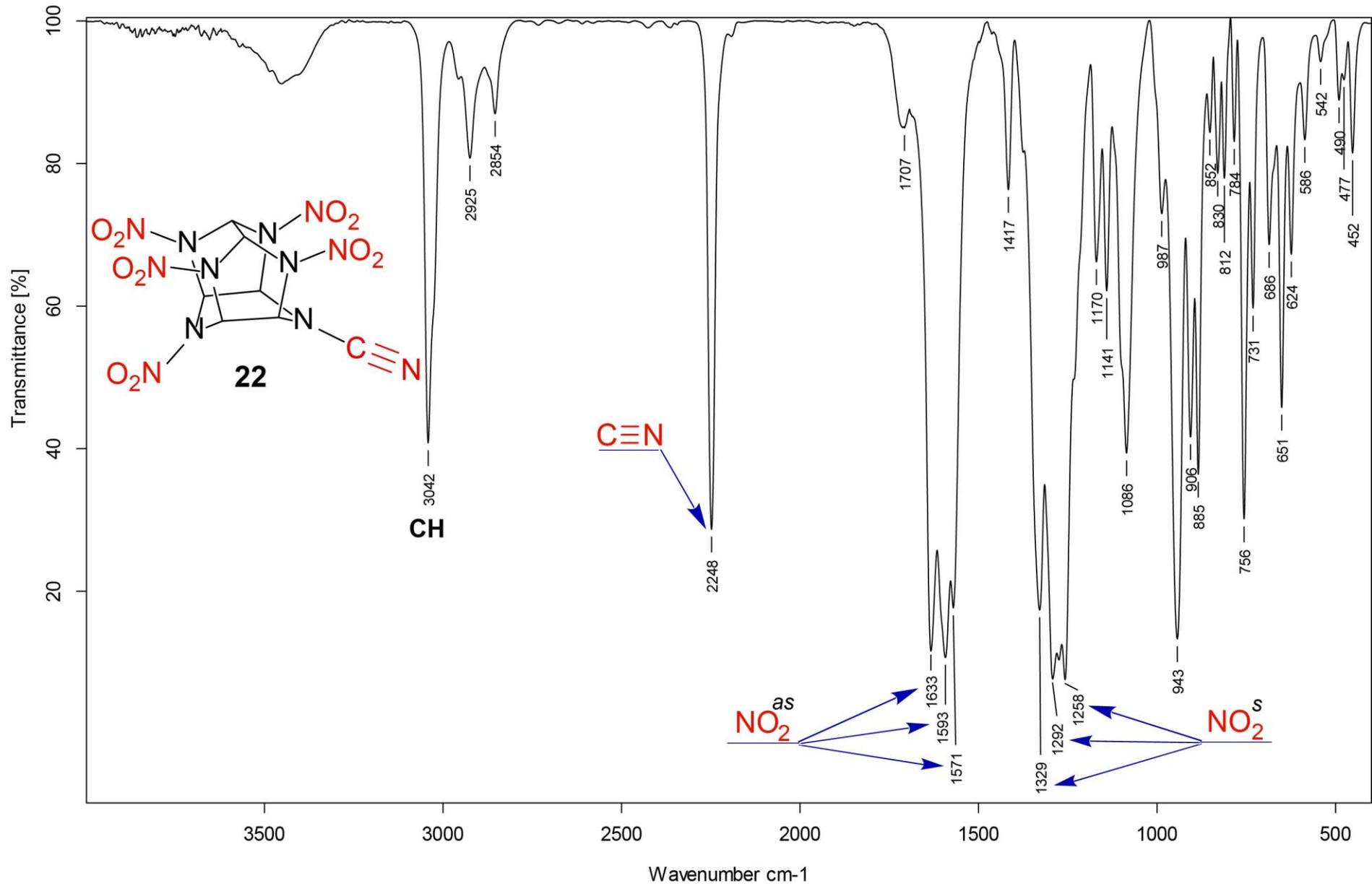
^{1}H NMR (300.1 MHz, [D$_6$]acetone) spectrum of compound 21
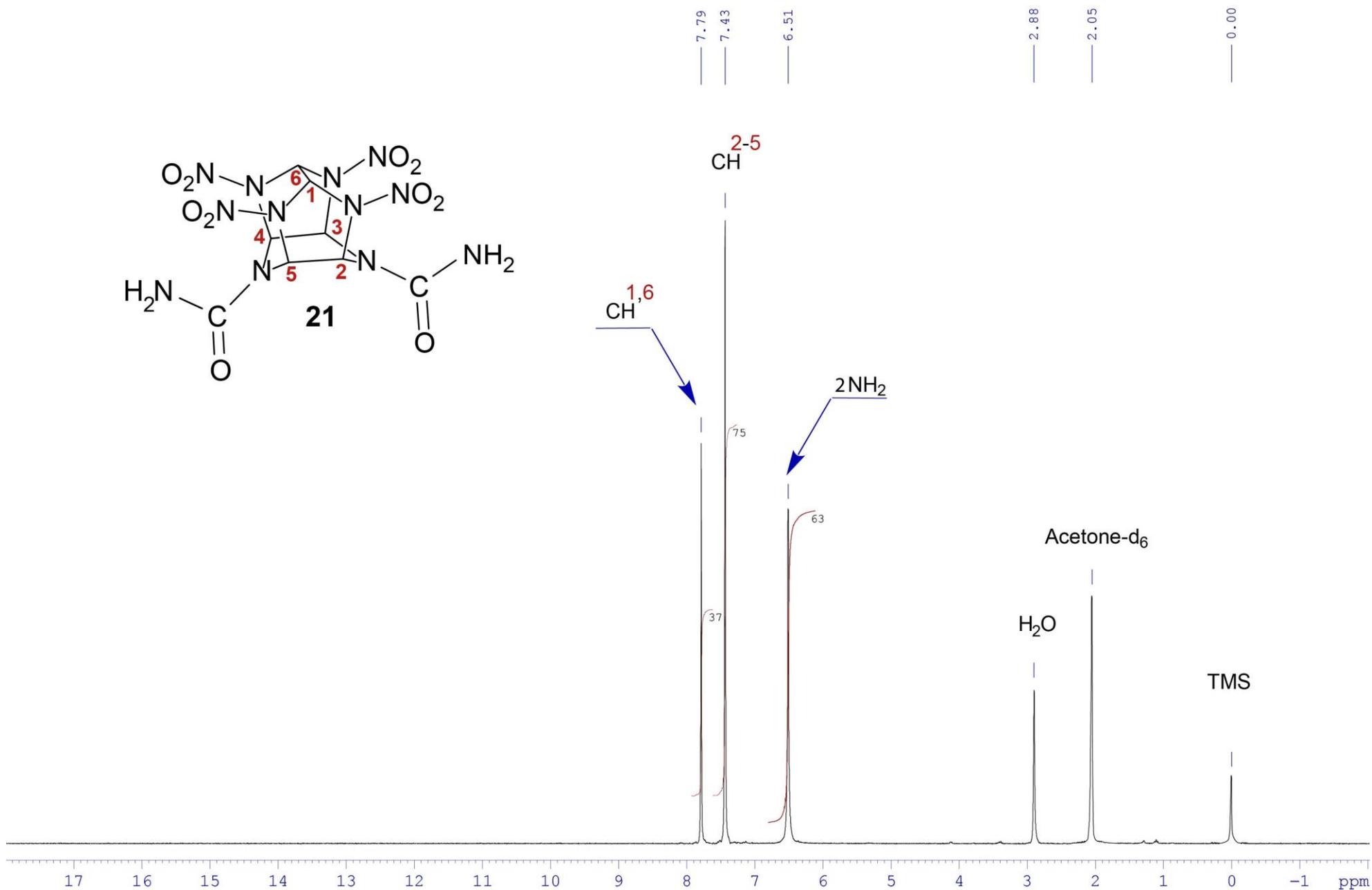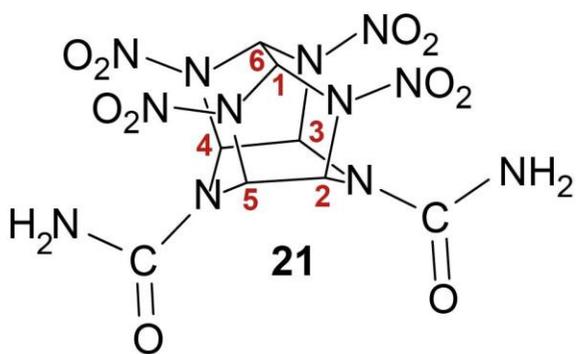
^{13}C NMR (75.5 MHz, [D$_6$]acetone) spectrum of compound 21

154.43

73.41
68.69

29.20
29.14
29.05
28.99
28.89
28.83
28.74
28.59
28.43
28.28

0.00

C2,C3,C4,C5

C1,C6

C7,C8

Acetone-d$_6$

TMS

180   170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   10   ppm
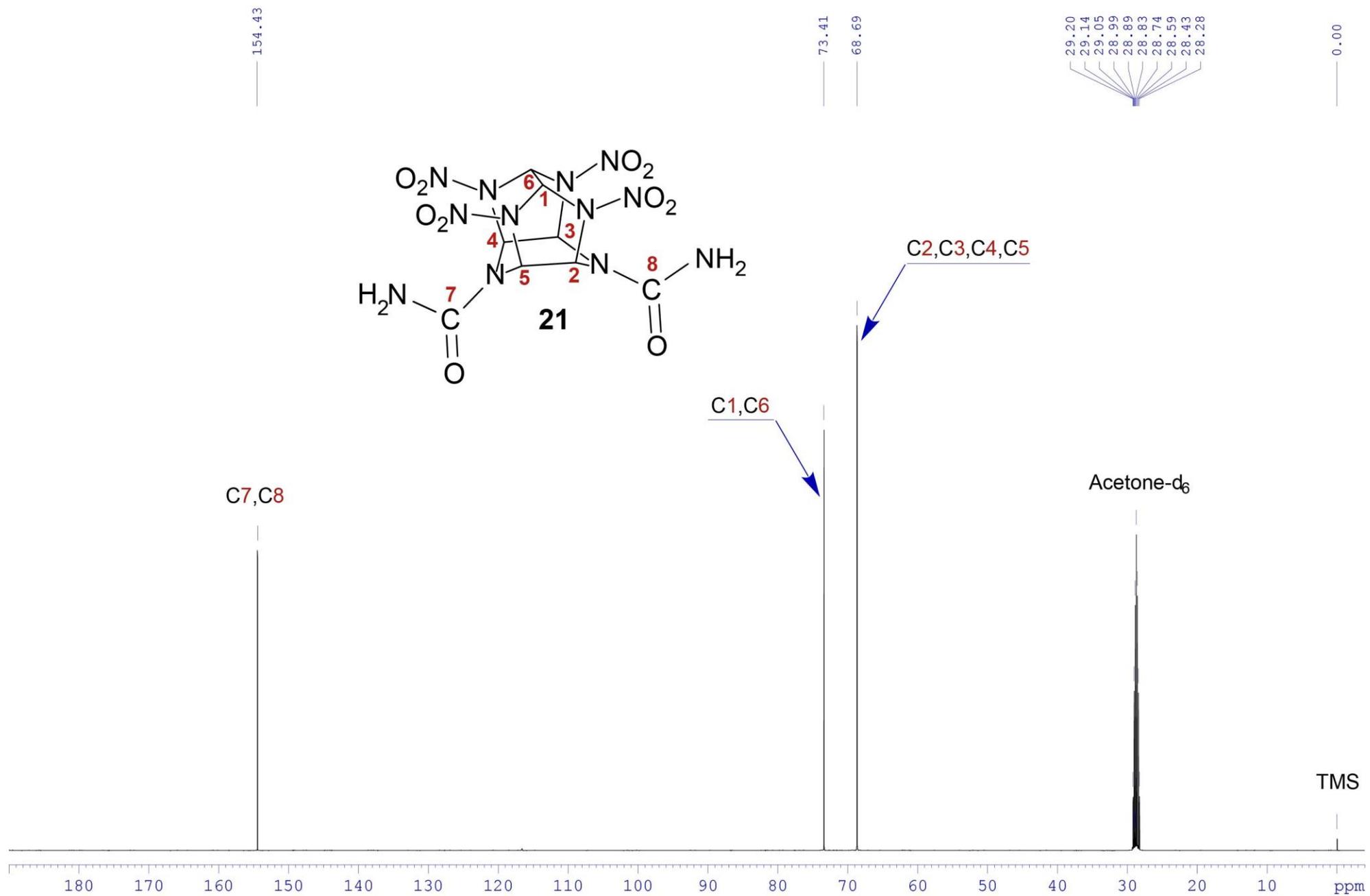
^{14}N NMR (21.7 MHz, [D$_6$]acetone) spectrum of compound 21
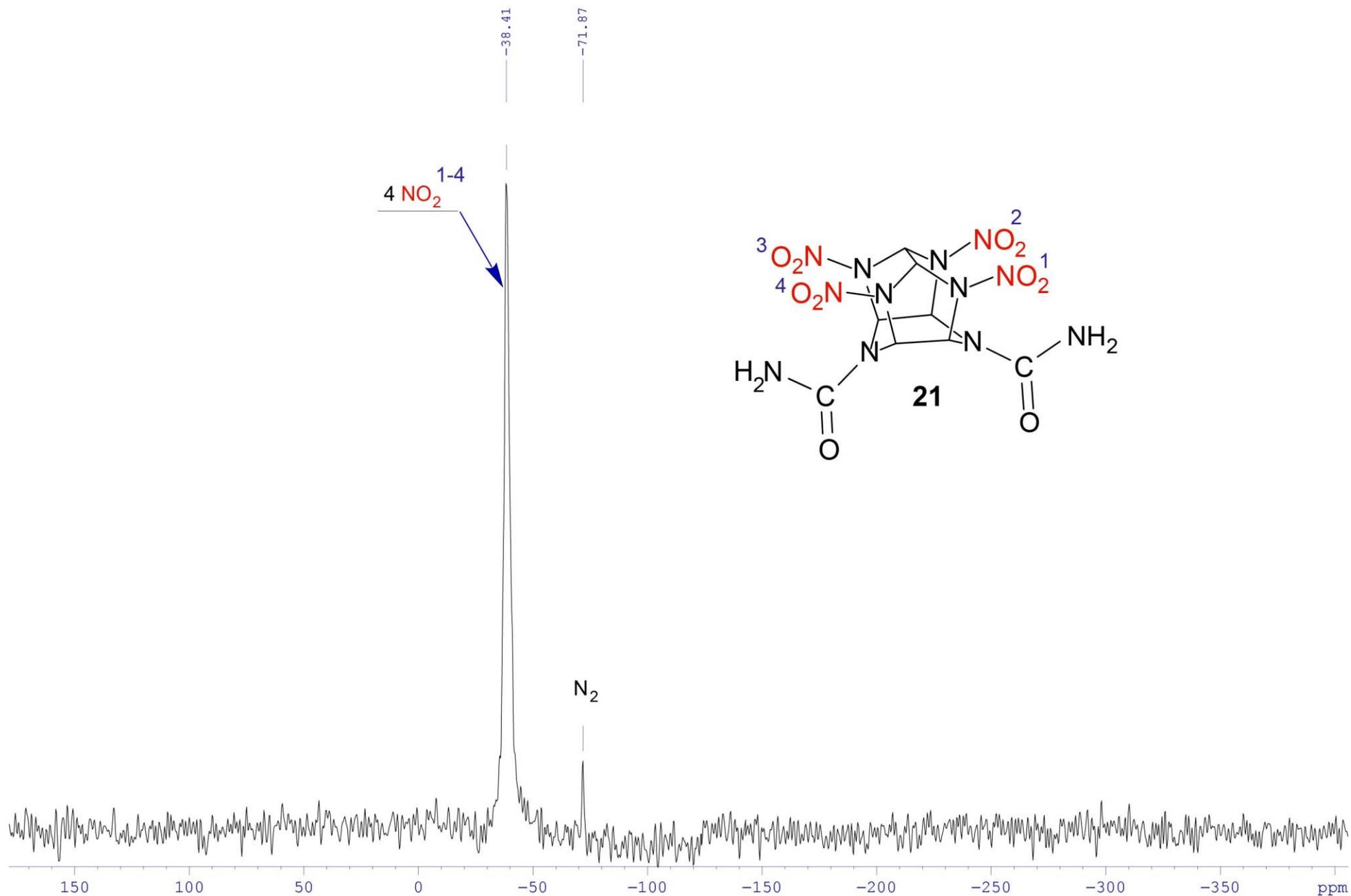
IR (KBr) spectrum of compound 21
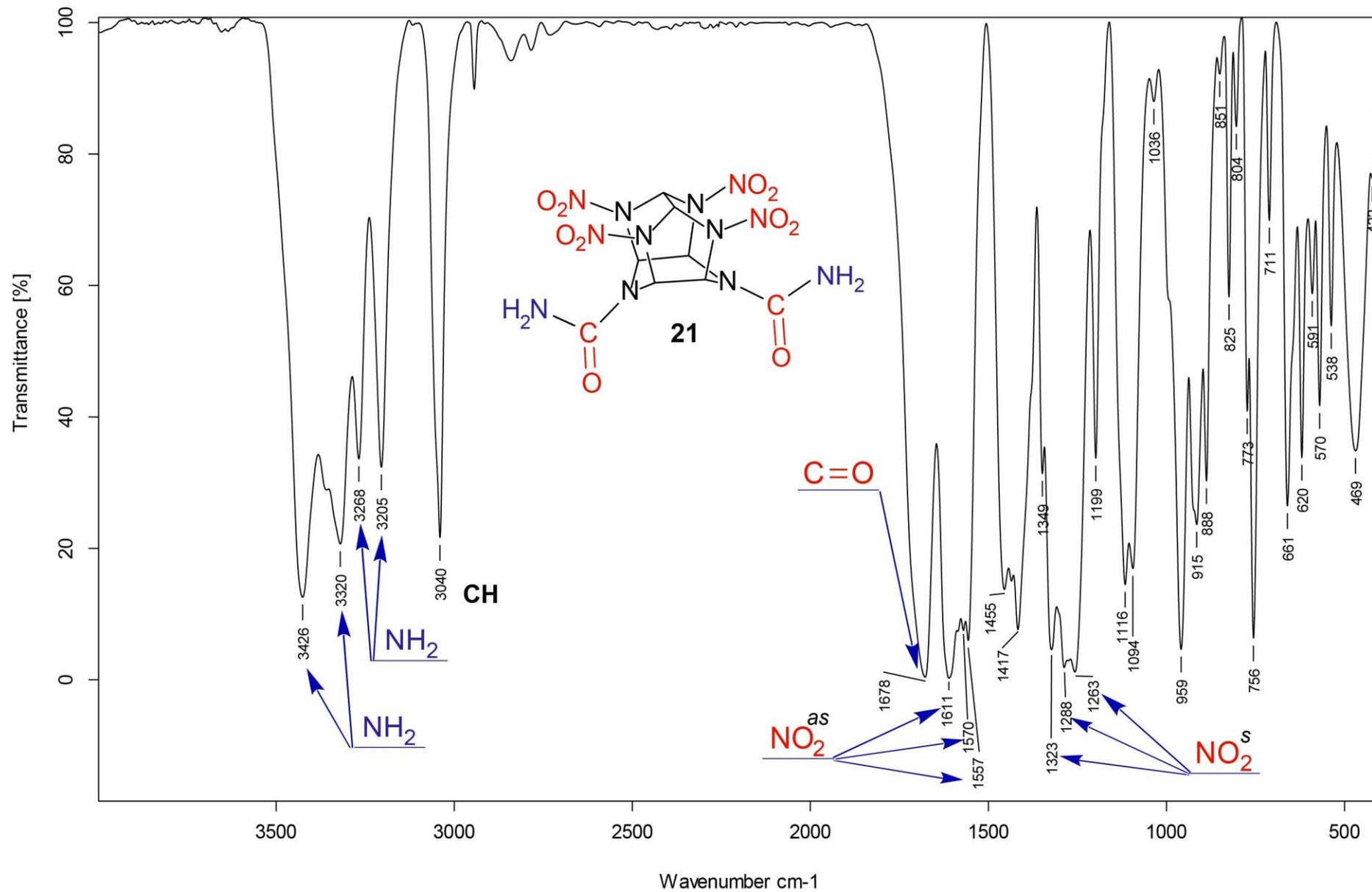
HRMS (ESI) for compound 21
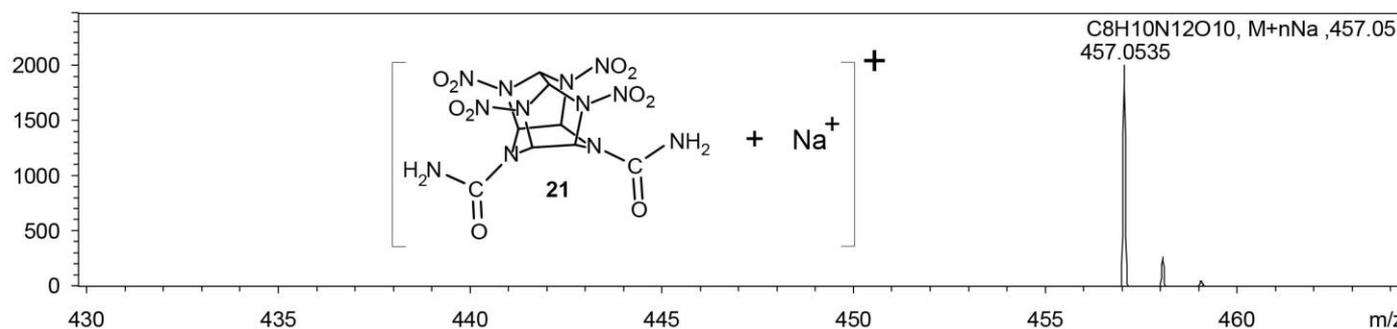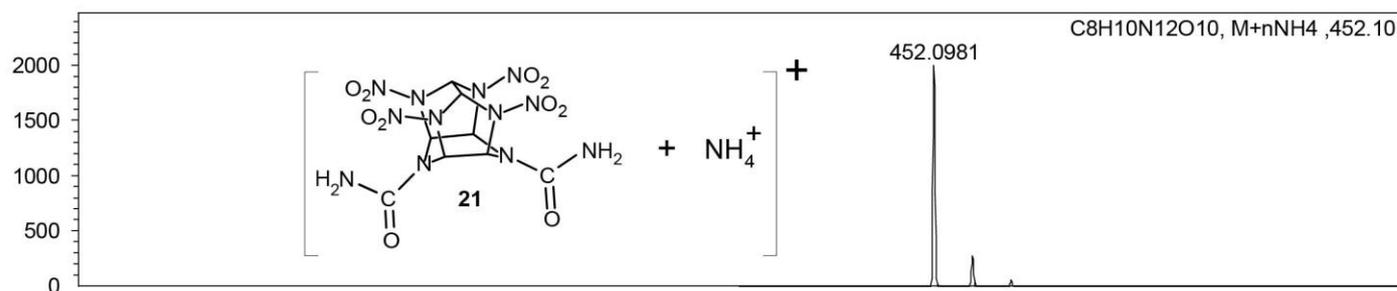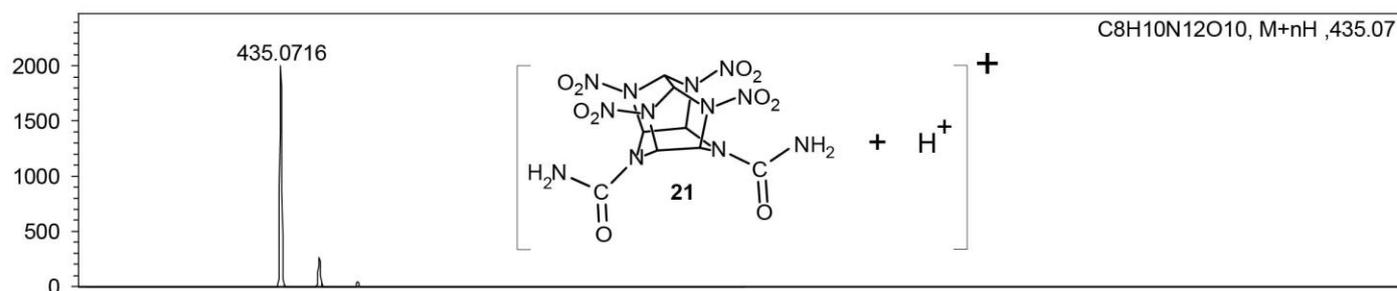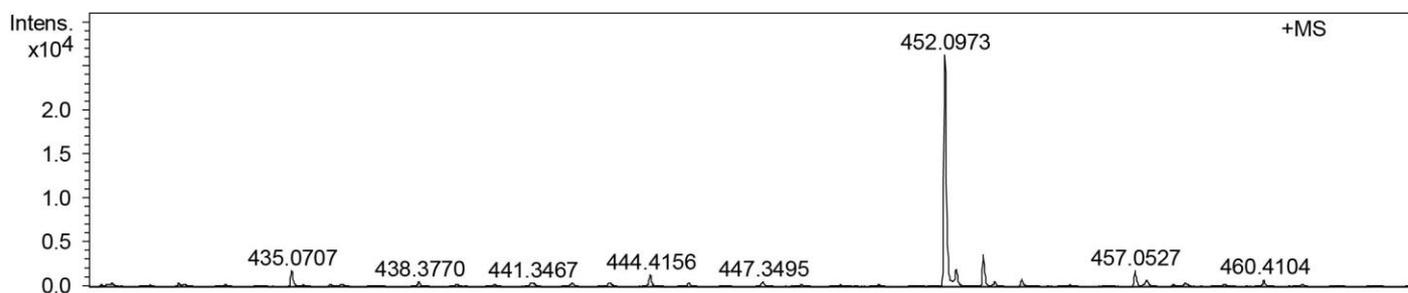
^{1}H NMR (300.1 MHz, [D$_6$]acetone) spectrum of compound 23
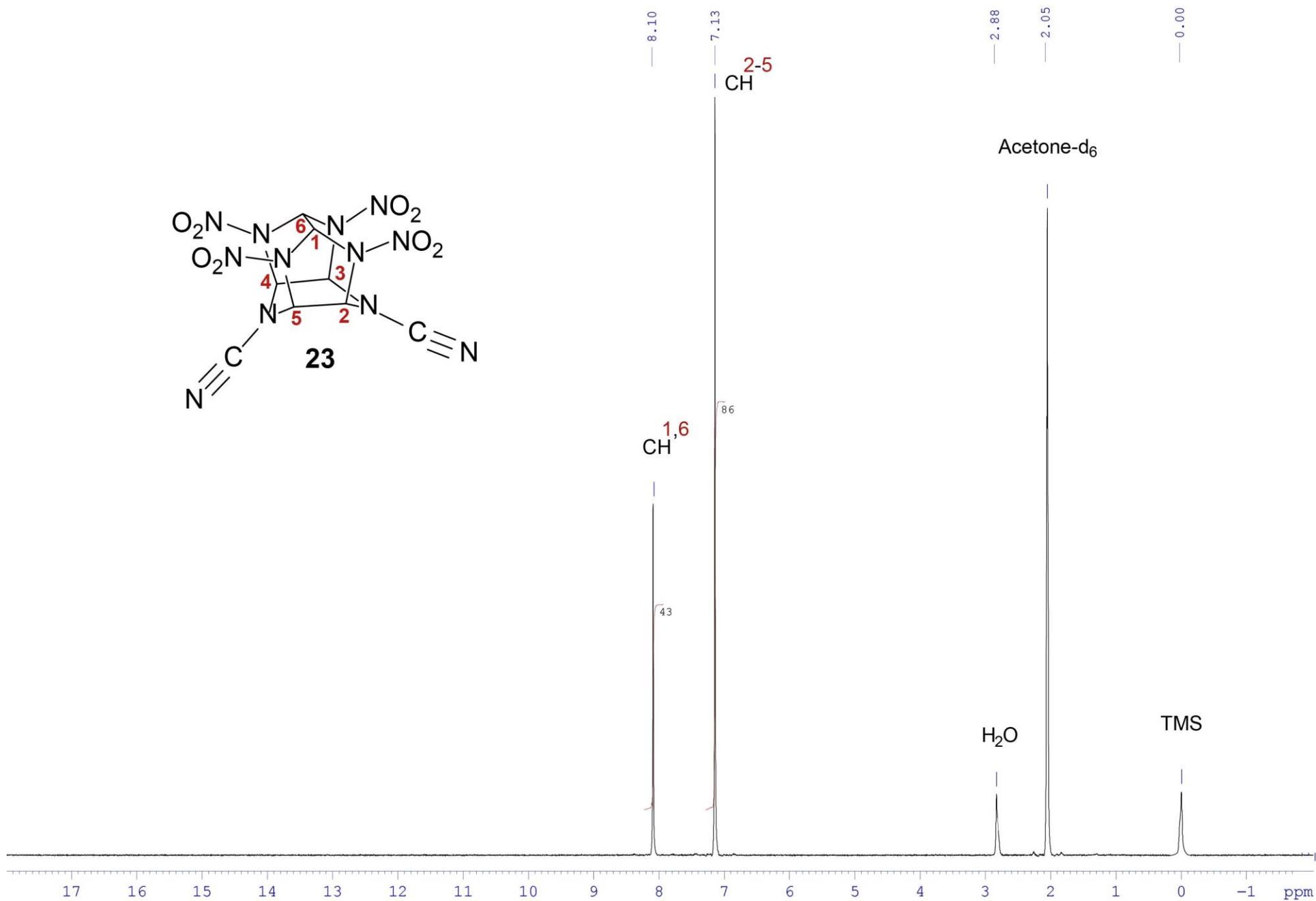
^{1}H NMR (600.13 MHz, [D$_6$]DMSO) spectrum of compound 23
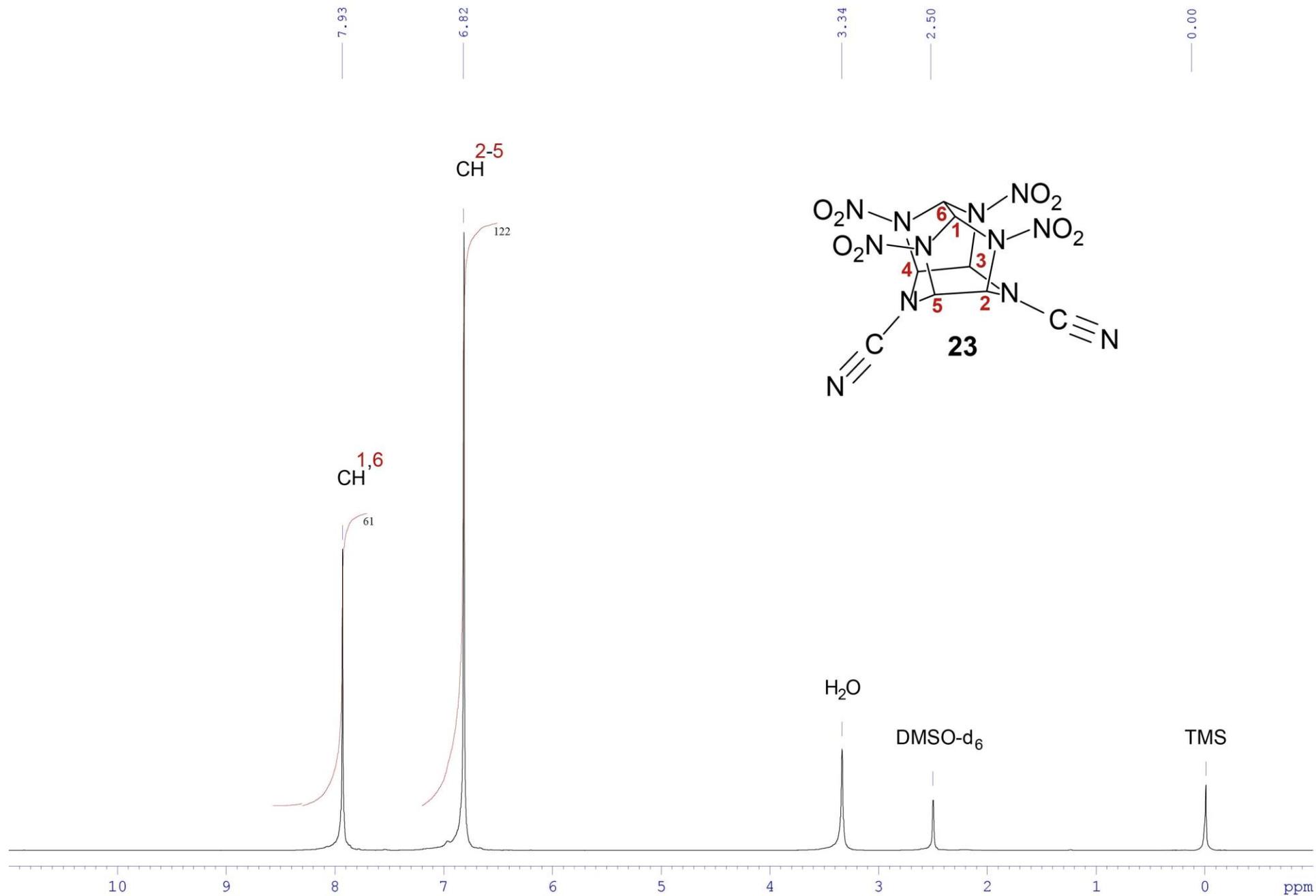
^{13}C NMR (150.9 MHz,[D$_6$]DMSO) spectrum of compound 23
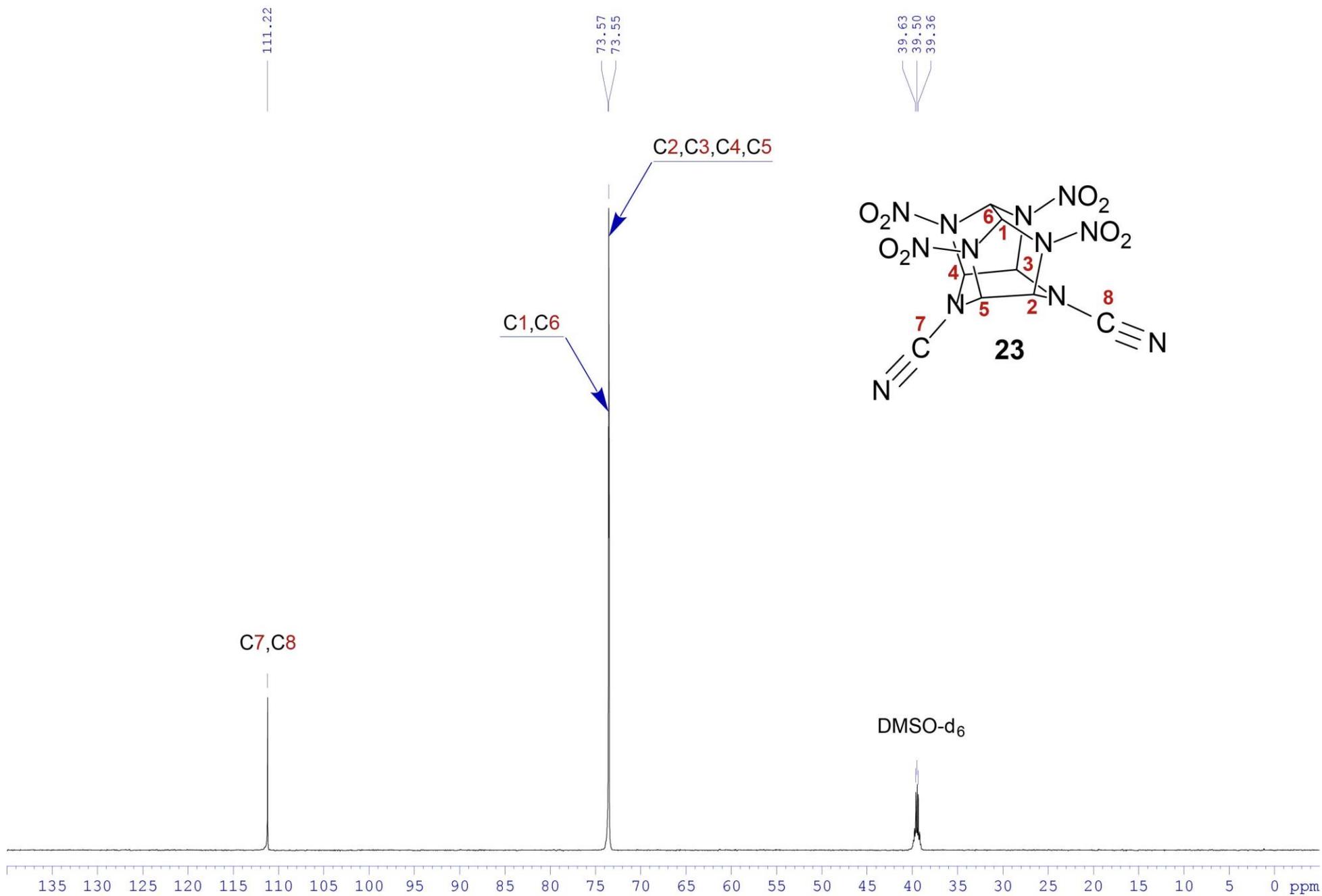
{^{1}H–^{13}C} HSQC NMR (600.13 MHz, [D$_6$]DMSO) spectrum of compound 23
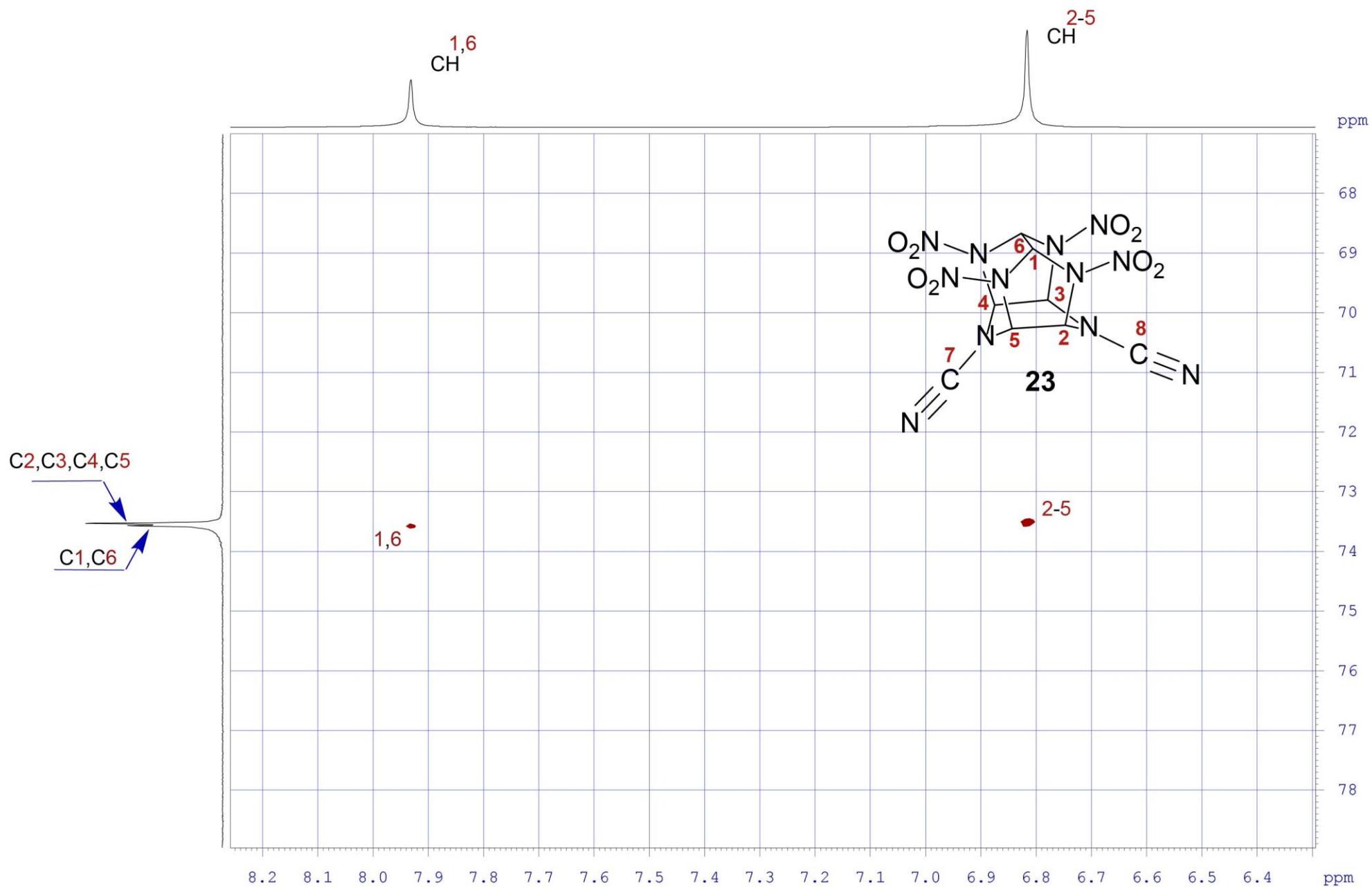
{¹H−¹³C} HMBC NMR (600.13 MHz,[D₆]DMSO) spectrum of compound 23
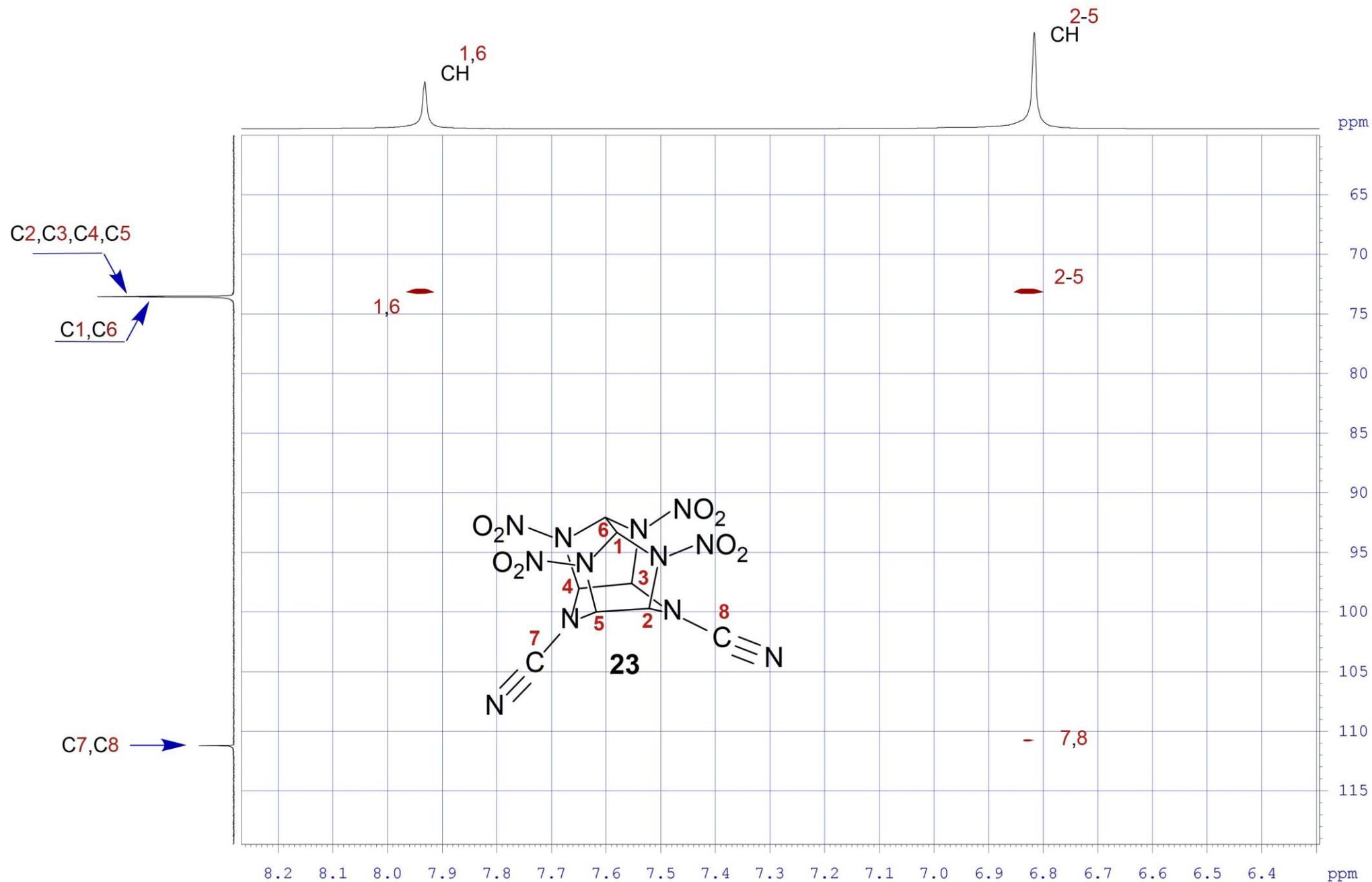
^{14}N NMR (43.37 MHz, [D$_6$]DMSO) spectrum of compound 23
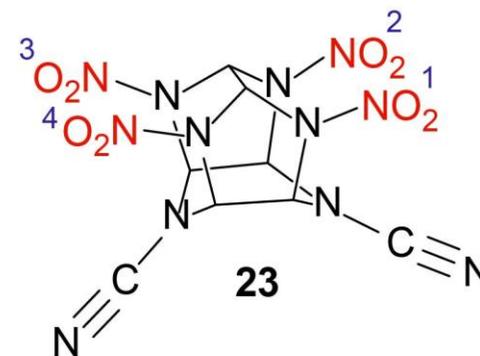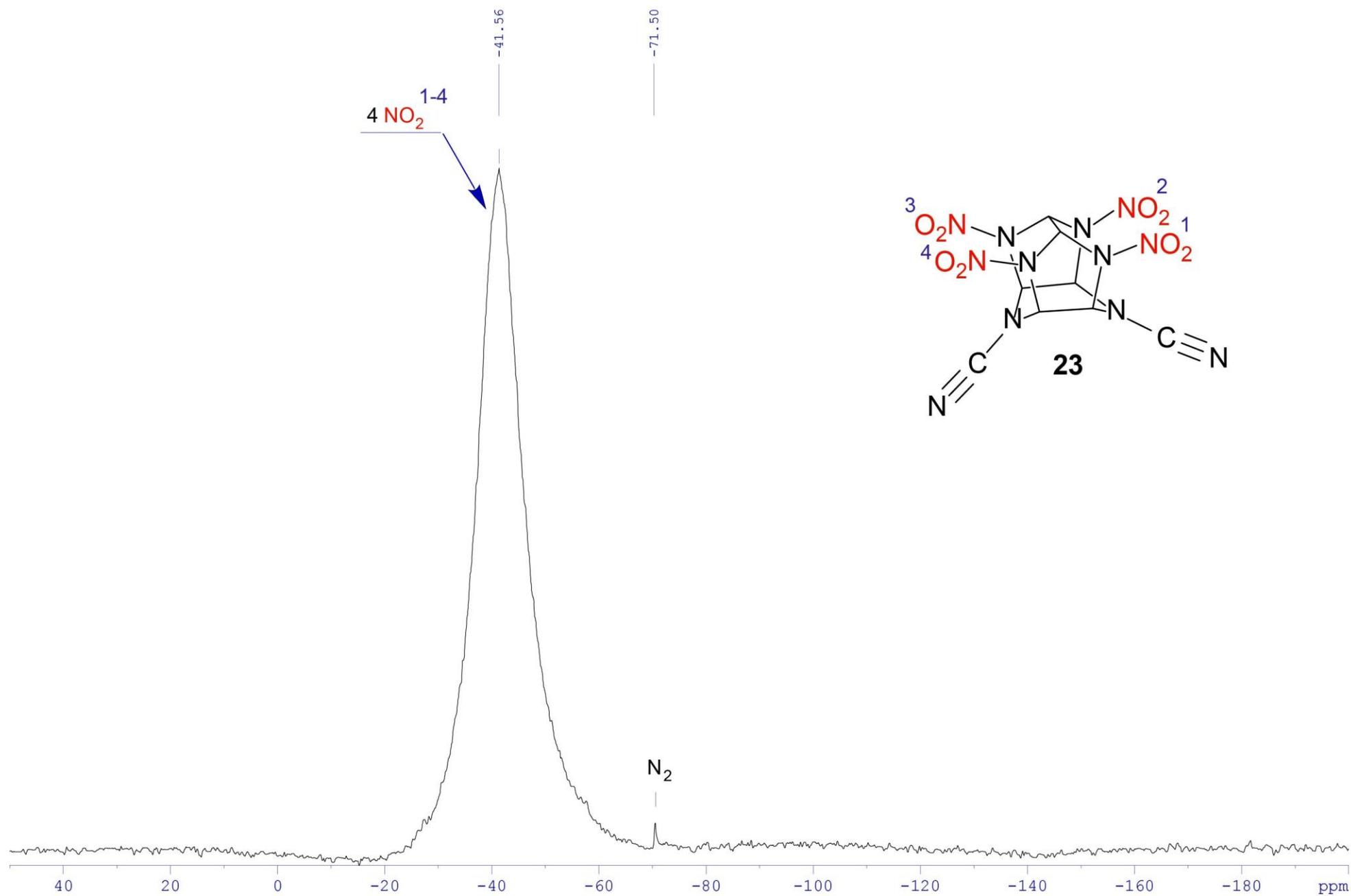
^{15}N NMR ([INVGATED], [INEPT], 60.8 MHz, [D$_6$]DMSO) spectrum of compound 23
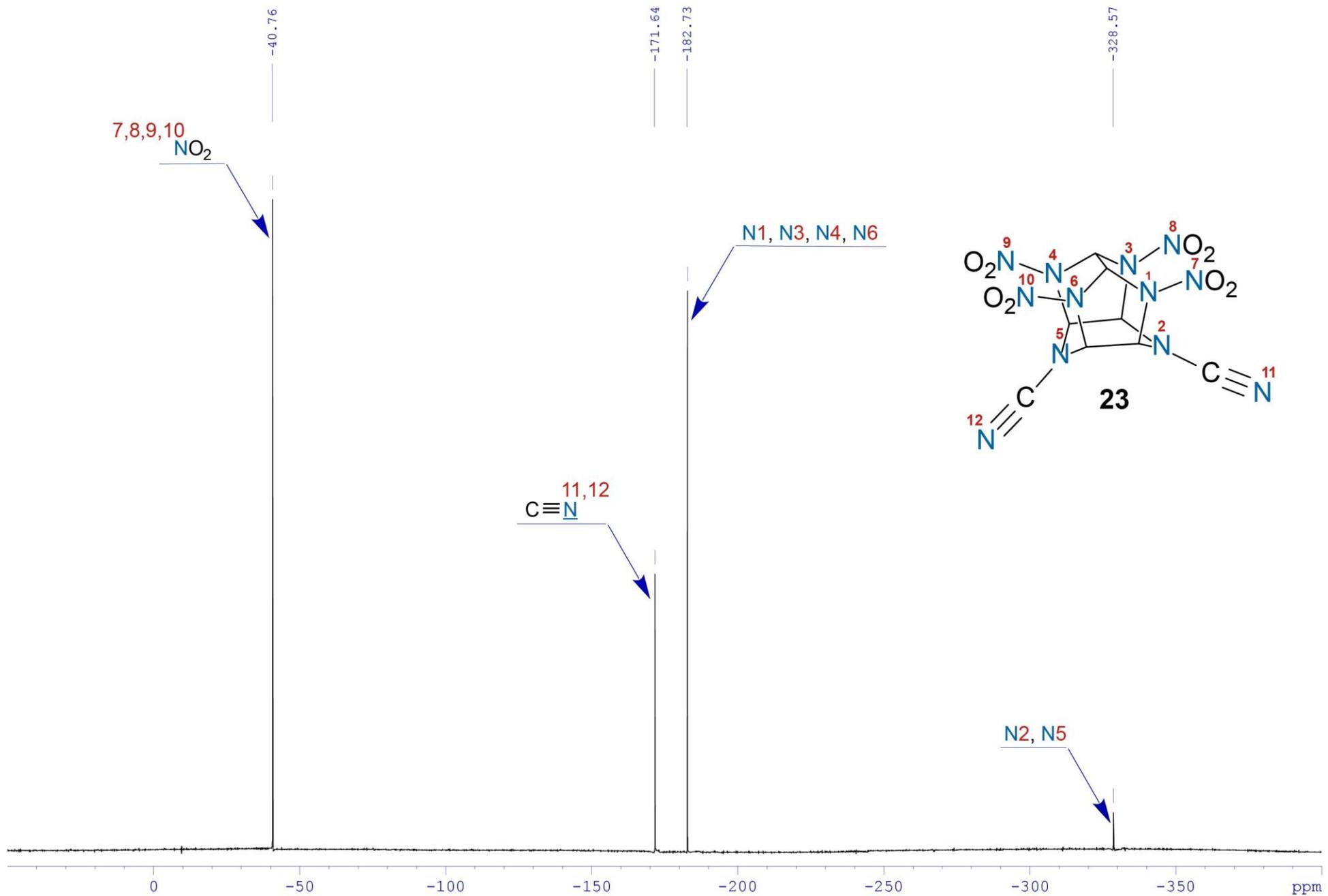
IR (KBr) spectrum of compound 23
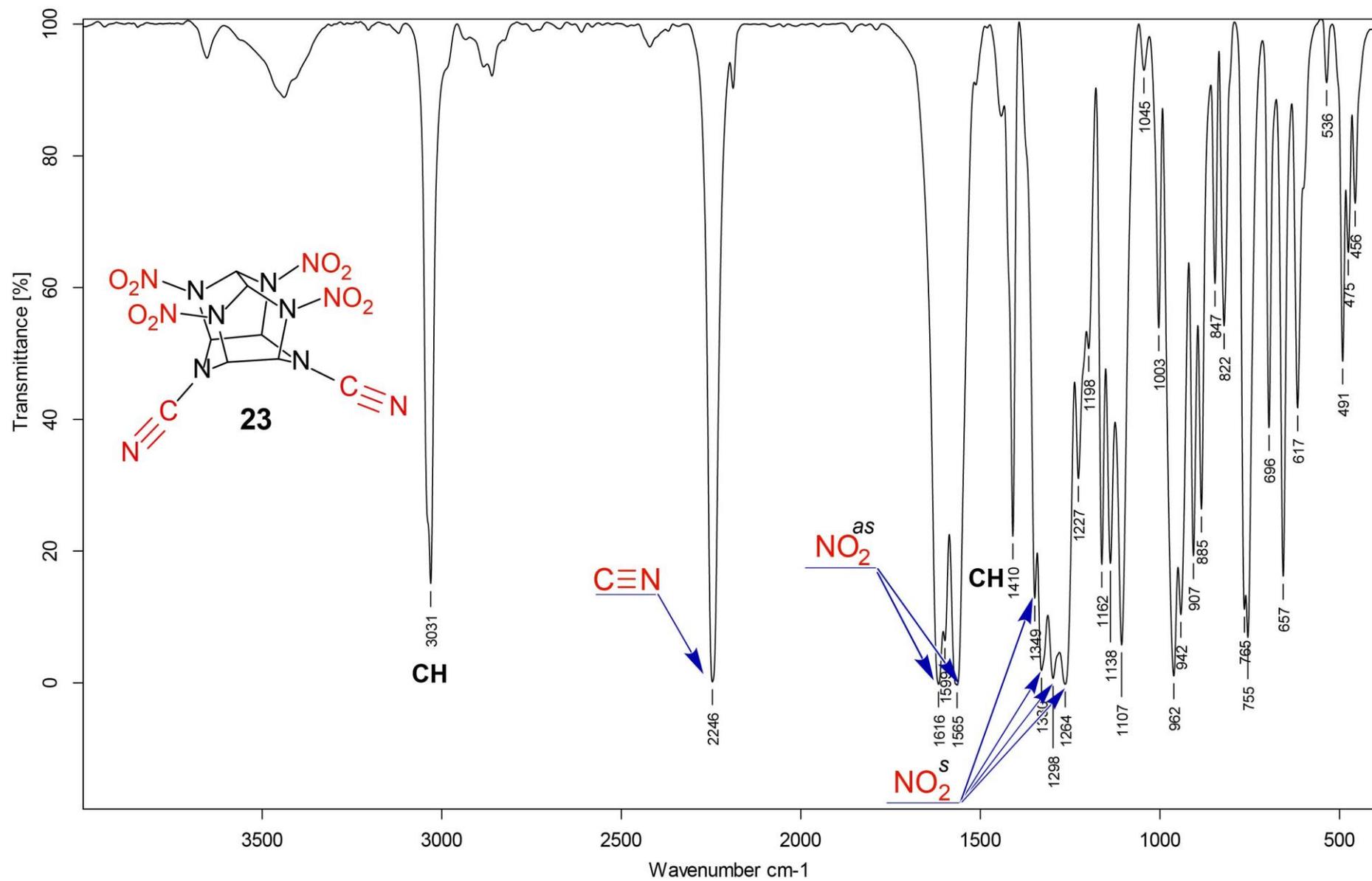
<u>General formula of 4-carbomoyl-2,6,8,12-tetranitroisowutzitanes **4**, **10**, **14**, **20** and **21**</u>
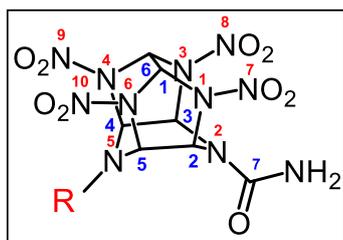
4: R = H;

10: R = NO;

14: R = $^8CH_2{}^9C(^{11}NO_2)_3$;

20: R = $^{11}NO_2$;

21: R = ^8CN.

Table 1 Assigned ^1H, $^{13}C\{^1H\}$, and ^{14}N NMR shifts [ppm] of **4**, **10**, **14**, **20** and **21** in DMSO-d_6 or Acetone-d_6.

Nucleus	Assignment		Compounds Chemical shifts δ, ppm				
	Part	Groups	**4**	**10**	**14**	**20**	**21**
	Solvent		DMSO-d_6 [Acetone-d_6]	Acetone-d_6	Acetone-d_6	DMSO-d_6	Acetone-d_6
^1H ($J_{H,H}$, Hz)	Cage	CH^{1,6}	7.65 s [7.68 s]	7.95 s	7.84 s	7.93 s	7.79 s
		CH^{2,3}	6.93 bs [7.33 d (8)]	7.47 dd (8, 2) 7.83 dd (8, 2)	7.44 d (8)	7.39 d (7)	7.43 s
		CH^{4,5}	6.16 bs [6.42 d (7)]	7.92 dd (8, 2) 8.12 dd (8, 3)	6.72 d (8)	7.79 d (7)	
	Units	NH$_2$	7.10 bs [6.32 bs]	6.51 bs	6.42 bs	7.09 bs	6.51 bs
		N^5–H	6.30 bs [5.71 bs]		–		
		N^5–CH$_2$		–	5.51 s		–
$^{13}C\{^1H\}$ ($J_{C,F}$, Hz)	Cage	C^{1,6}	72.3	74.9 75.1	70.2	73.4	73.4
		C^{2,3}	68.0	70.6 73.2	74.2	70.0	68.7
		C^{4,5}	71.4	61.1 71.5	78.0	70.2	
	Units	C=O	154.7	155.3	155.0	154.2	154.4
		N^5–CH$_2$		–	55.4		–
		C(NO$_2$)$_3$			127.9		
^{14}N ($\Delta\nu_{1/2}$, Hz)	Cage	NNO$_2$ **7–10 (and 11)**	–36 (365)	–40 (100)	–38 (113)	–39 (431)	–38 (130)
	Units	CNO$_2$		–	–31 (33)		–

General formula of 4-cyano-2,6,8,12-tetranitroisowutzitanes **5**, **6**, **15**, **22** and **23**

O_2N ... NO_2 ... $N-NO_2$ ... O_2N-N ... R ... $C{\equiv}N$
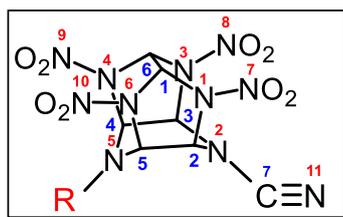
5: R = H;

6: R = ^{12}NO;

15: R = $^8CH_2{}^9C(^{12}NO_2)_3$;

22: R = $^{12}NO_2$;

23: R = $^8C^{12}N$.

Table 2 Assigned ^1H, $^{13}C\{^1H\}$, and ^{14}N NMR shifts [ppm] of **5**, **6**, **15**, **22** and **23** in acetone-d_6 or DMSO-d_6.

Nucleus	Assignment			Compounds Chemical shifts δ, ppm			
	Part	Groups	**5**	**6**	**15**	**22**	**23**
	Solvent		Acetone-d_6	Acetone-d_6	Acetone-d_6	Acetone-d_6 [DMSO-d_6]	DMSO-d_6 [Acetone-d_6]
^1H ($J_{H,H}$, Hz)	Cage	CH^{1,6}	7.81 s	8.10 s	8.05 s	8.17 s [8.01 s]	7.93 s [8.10 s]
		CH^{2,3}	6.88 d (7)	7.14 bs 7.43 bs	7.07 d (7)	7.30 d (8) [7.03 (8)]	6.82 s [7.13 s]
		CH^{4,5}	6.56 bs	8.02 bs 8.24 bs	6.87 d (8)	8.25 d (8) [7.81 d (8)]	
	Units	N^5–H	5.96 bs		–		
		N^5–CH$_2$		–	5.49 s		–
$^{13}C\{^1H\}$ ($J_{C,F}$, Hz)	Cage	C^{1,6}	72.7	72.6	72.9	74.9	
		C^{2,3}	72.5	73.9 74.6	73.2	75.2	73.6
		C^{4,5}	71.6	60.3 72.6	77.2	72.2	
		CN	111.1	110.2	110.4	111.4	111.2
	Units	N^5–CH$_2$		–	53.2		–
		C(NO$_2$)$_3$			126.3		
^{14}N ($\Delta v_{1/2}$, Hz)	Cage	NNO$_2$ **7–10,11**	**7,8** –38 (75) **9,10** –40 (72)	–42 (79)	**7,8** –41 (126) **9,10** –39 (130)	–42 (156)	–24 (416)
	Units	CNO$_2$		–	–31 (43)		–

Table 3 Assigned $^{15}N\{^{1}H\}$ NMR shifts [ppm] of **5**, **6**, **15**, **22** and **23** in acetone-d_6 or DMSO-d_6.

Part	Groups		5	6	15	22	23
					Chemical shifts δ, ppm		
Cage	$N^{1,3}$		−182.6	−185.8 / −182.8	−178.3	−182.4	−182.7
	$N^{4,6}$		−177.6	−182.2 / −181.9	−181.4	−180.1	
	N^5		n.o.*	−144.6	n.o.*	−199.3	−328.6
	N^2		−336.3	n.o.*	−335.7	−328.6	
	N–NO_2	7,8	−37.1	−41.6 / −41.4	−40.7	−43.3	−40.8
		9,10	−39.9	−41.3 / −41.0	−38.5	−41.3	
		12		–		−41.0	–
Units	CN^{11}		−172.0	−170.5	−170.5	−171.1	−171.6
	$CH_2C(N^{12}O_2)_3$		–		−30.7	–	
	N^5–$\underline{N^{12}}O$		–	172.8		–	

* Probably, due to the splitting on ^{1}H and ^{14}N, the signal of this ^{15}N are very broadened, its intensity is highly reduced, the signal did not observed between a "noise" although the measurements were performed in different modes with elongated pulse delays throughout the night.

Table 4 Assigned IR vibrations [cm^{-1}] of isowurtzitanes **4**, **5**, **6**, **8**, **10**, **12**, **14**, **15**, **20**–**23** in KBr.

Assignment	Substrates		Amides					Nitriles				
							Vibration frequencies v, cm^{-1}					
	7	12	4	10	14	20	21	5	6	15	22	23
as N–NO_2	1604 vs	1596 vs	1587 vs	1604 vs		1615 vs	1611 vs	1595 vs	1606 vs		1633 vs	1616 vs
						1594 vs					1593 vs	1599 s
	1558 vs	1561 s	1548 vs	1555 s	1596 b vs	1571 vs	1557 vs	1555 s	1565 vs	1597 b vs	1571 vs	1565 vs
as C–NO_2	–	1609 vs	–			–		–				–
s N–NO_2	1330 vs	1327 vs	1324 vs	1325 s		1332 vs	1323 vs	1328 vs	1326 s		1329 vs	1349 s / 1330 vs
	1289 vs	1286 vs	1288 vs	1290 vs	1292 b s	1295 vs	1288 vs	1292 vs	1289 vs	1293 b s	1292 vs	1298 vs
	1266 vs	1270 vs	1265 vs	1266 vs	1266 s	1269 vs	1263 vs	1269 vs	1267 vs	1268 s	1258 vs	1264 vs
CH	3037 m	3042 m	3044 m	3039 w	3042 w	3041 vs	3040 s	3038 m	3035 w	3040 w	3042 s	3031 vs
CN		–			–			2243 s	2247 m	2247 m	2248 s	2246 vs
C=O		–	1708 s	1708 vs	1707 vs	1714 vs / 1687 vs	1678 b vs					
NH_2		–	3460 m / 3310 m	3468 s / 3324 s	3486 vs / 3419 vs	3487 vs / 3449 s / 3400 s / 3355 m	3426 vs / 3320 vs / 3268 s / 3205 s			–		
NH	3366 m / 3401 m	–	3218 m		–			3388 m			–	

S96

General formula of the substrates 4-R-2,6,8,12-tetranitroisowutzitanes **8** and **12**

7: R = [11]NO;

12: R = [7]CH_2[8]C([12]NO_2)$_3$.
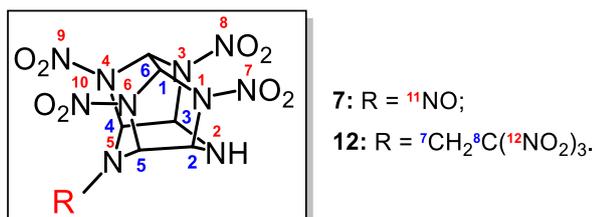
Table 5 Assigned ^1H, $^{13}C\{^1H\}$, and ^{14}N NMR shifts [ppm] of **8** and **12** in acetone-d$_6$.

Nucleus	Assignment		Compounds	
			Chemical shifts δ, ppm	
	Part	Groups	**8**	**12**
	Solvent		Acetone-d$_6$	Acetone-d$_6$
^1H ($J_{H,H}$, Hz)	Cage	CH^{1,6}	7.85 d (6)	7.71 s
		CH^{2,3}	6.49 d (8) 6.80 d (8)	6.34 d (3) 6.36 d (3)
		CH^{4,5}	7.84 dd (16, 2) 7.96 dd (8, 2)	6.60 d (7)
	Units	N^5–H	5.92 bs	5.69 bs
		N^5–CH$_2$	–	5.46 s
$^{13}C\{^1H\}$ ($J_{C,F}$, Hz)	Cage	C^{1,6}	74.3 74.5	73.5
		C^{2,3}	72.7 72.8 73.9 74.0	73.0 72.9
		C^{4,5}	60.9 73.0	77.7
		N^5–CH$_2$	–	55.7
		C(NO$_2$)$_3$		128.0
^{14}N ($\Delta v_{1/2}$, Hz)	Cage	NNO$_2$ **7,8**	–40 (61)	–37 (80)
		9,10	–37 (59)	
	Units	CNO$_2$	–	–30 (33)

Description of the spectra of 4-carbomoyl-polynitro hexaazaisowutzitanes 4, 10, 14, 20, 21

and 4-cyano-polynitro hexaazaisowutzitanes 5, 6, 15, 22, 23

As can be seen in table 4 the IR spectra of the carboxamides and the nitriles show the characteristic absorption bands of the C=O at $\tilde{v}$ 1714 to 1678 cm^{-1} and the band of the CN at $\tilde{v}$ 2248 to 2243 cm^{-1}, respectively. The bands corresponding to the asymmetrical vibrations of the NO$_2$ for the carboxamides are located at $\tilde{v}$ 1615 to 1548 cm^{-1}, and for the nitriles are located at $\tilde{v}$ 1633 to 1555 cm^{-1}, whereas the bands of the symmetrical vibrations of the NO$_2$ for the carboxamides are located at $\tilde{v}$ 1332 to 1263 cm^{-1}, and for the nitriles are located at $\tilde{v}$ 1349 to 1258 cm^{-1}, respectively. The band of the CH units of the hexaazaisowurtzitane cage for the carboxamides appears at $\tilde{v}$ 3044 to 3039 cm^{-1} and for the nitriles appears at $\tilde{v}$ 3042 to 3031 cm^{-1}, respectively. Additionally, in the IR spectra of the carboxamides there are pairs of bands of the NH$_2$ at $\tilde{v}$ 3487–3320 and 3400–3205 cm^{-1}, while in the IR spectra of amines **4** and **5**, the band of the NH is observed at $\tilde{v}$ 3218–3388 cm^{-1}, respectively.

According to tables 1 and 2 the resonance peaks of the CH units of the carboxamides and of the nitriles are observed in the range δ_H 6.2–8.0 ppm and δ_H 6.6–8.3 ppm in the ^{1}H NMR, as well as in the range δ_c 61.1–78.0 ppm and δ_c 60.3–77.2 ppm in the ^{13}C NMR, respectively. The spectra of the carboxamides contain the signals of the carbamoyl group, namely, the broadened peak of the NH$_2$ protons at high field with δ_H 6.5 and 7.1 ppm in the ^{1}H NMR, the peak from the carbon atom of the C=O at δ_c 154.2–155.3 ppm in the ^{13}C NMR. In the ^{13}C NMR spectra of the nitriles there is the signal of the CN group at δ_c 110.2–111.4 ppm. The signals of the protons of the cage secondary amino groups in the ^{1}H NMR of amide **4** and cyanide **5** are broadened and observed at high field with δ_H 5.71 and 5.96 ppm, respectively. In addition, in the spectra of **14** and **15** there are the signals of the trinitroethyl moiety, namely, the peak from CH$_2$ unit at δ_H ~5.5 ppm in the ^{1}H NMR and at δ_c 55.4 and 53.2 ppm, respectively, in the ^{13}C NMR, as well as a strongly broadened peak from C(NO$_2$)$_3$ at δ_C 126.8 ppm. It should be noted that in the ^{1}H, ^{13}C NMR spectra of compounds **6** and **10** there are some splitting due to synperiplanar (sp_ts) or anti-periplanar (ap_ts) conformation of NO bond with respect to the nitrogen lone pair.

The ^{14}N NMR spectra of the new compounds show the signals from the *N*-nitro groups of the polynitro hexaazaisowurtzitane cage at δ_N −40 to −36 ppm ($\Delta v_{1/2}$ 100–365 Hz) and at δ_N −42 to −24 ppm ($\Delta v_{1/2}$ 72–416 Hz) for the carboxamides and the nitriles, respectively. The ^{14}N NMR spectra of **14** and **15** containing the C(NO$_2$)$_3$ unit shows the additional sharp peak of the *C*-nitro group at δ_N −31 ppm ($\Delta v_{1/2}$ ~40 Hz).

The ^{15}N NMR spectra of the target *N*-cyano HAIWs **5**, **6**, **15**, **22**, **23** were recorded in acetone-d$_6$ (or DMSO-d$_6$) and the results are summarized in Table 3 for comparison. The signals of the nitro (niroso) groups are observed at the lowest field in the range δ_N −43 to −30 ppm (173 ppm). The signal for the nitrogen atom of the cyano group appear in the middle field of the spectra at δ_N −172 to −170 ppm. The signals of the nitrogen atoms of the five-membered cage rings are also found in the middle area at the range between δ_N −186 and −177 ppm. The peak of the nitrogen atom of the six-membered cage ring, which is linked to the CN group, appears in the highest field at δ_N −336 to −329 ppm, while the opposite nitrogen atom of the six-membered cage ring, appears in various fields depending on the substituent over a wide range δ_N −329 to −145 ppm. In the ^{15}N NMR spectra of **5**, **6** and **15**, some low-intensity peaks from the nitrogen atoms of the six-membered cage ring did not appear, which is not uncommon, and is probably due to the fact that these ^{15}N are split and very broadened, their intensity is highly reduced, these signals are not observed among the "noise", although the measurements were performed in different modes with elongated pulse delays throughout the night.

1) Single crystal X-ray diffraction of compound 5

X-ray diffraction data **5** were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using graphite monochromatized Cu K$_\alpha$-radiation (λ =1.54184 Å). The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[32] The structure was solved by direct methods using SHELXT[33] and refined on F^2 using SHELXL-2018[34] in the OLEX2 program.[35] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. The location of hydrogen atom H6 was found from the electron density-difference map; this hydrogen atom was refined with individual isotropic displacement parameters. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite[36] was used for molecular graphics. Detailed crystallographic information is provided in Tables 5–8, and structure are presented in Figures 1 and 2. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2308196. Copies of the data can be obtained free of charge *via* https://www.ccdc.cam.ac.uk/structures/

Table 6. Detail Crystallographic data of compounds **5** according to single crystal X-ray diffraction analysis.

Formula	$C_7H_7N_{11}O_8$
Formula weight [g·mol^{-1}]	373.24
Crystal system	monoclinic
Space group	$P\,2_1$/n
Unit cell dimensions	a = 7.67654(7) Å, α = 90°
	b = 15.58666(16) Å, β = 96.3532(9)°
	c = 10.82025(11) Å, γ = 90°
V [Å^3]	1286.71(2)
Z / Z'	4 / 1
ρ_{calc} [g·cm^{-3}]	1.927
μ [mm^{-1}]	1.545
F(000)	760
crystal colour	colorless
crystal size [mm^3]	0.15 × 0.09 × 0.04
θ range [°]	4.996 to 79.670
Index ranges	$-8 \leq h \leq 9, -19 \leq k \leq 19, -13 \leq l \leq 13$
Reflections measured	17390
Independent reflections	2779 [R(int) = 0.0220]
Restraints applied/parameters refined	0 / 239
Goodness-of-fit on F^2	1.031
Reflections with $I > 2\sigma(I)$	2660
Final R indeces [$I \geq 2\sigma(I)$]	R_1 = 0.0303, wR_2 = 0.0769
Final R indeces [all data]	R_1 = 0.0315, wR_2 = 0.0779
Residual electron density (ρ_{max}/ρ_{min}) [e Å^{-3}/ e Å^{-3}]	0.330 / -0.250
CCDC number	2308196
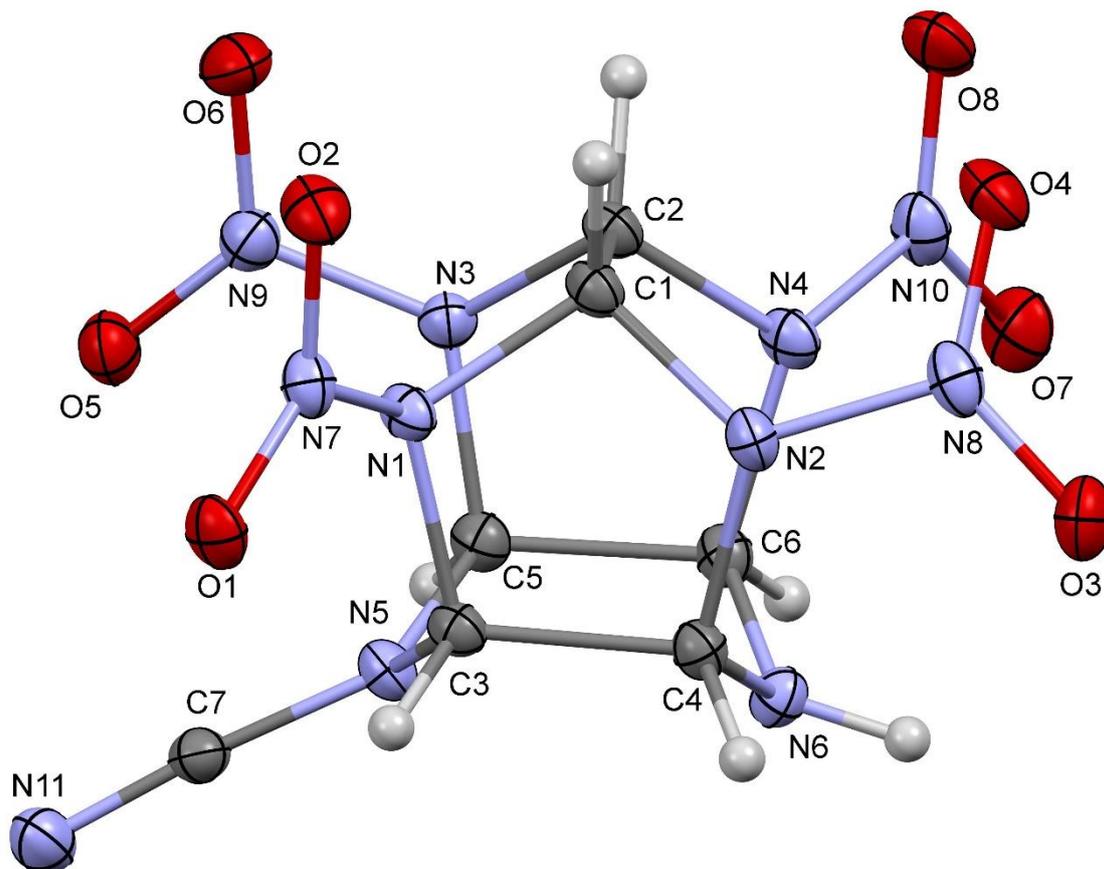
Figure 1. General view of molecule **5** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.

(a)   **(b)**
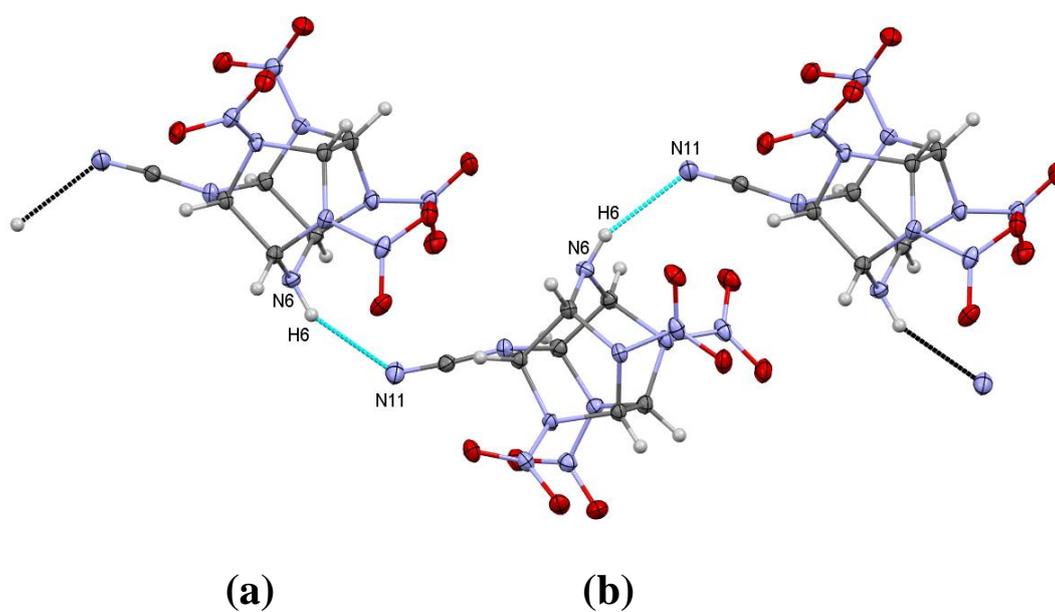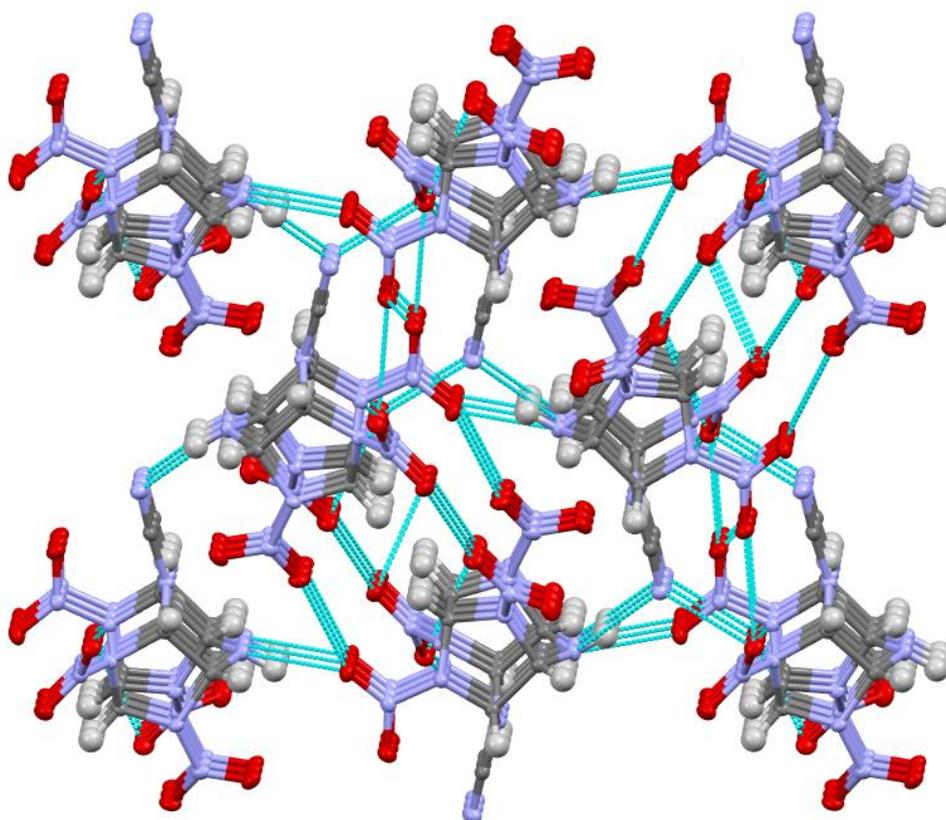
Figure 2. Supramolecular structure in the crystal **5** formed by the classical H-bond interactions, (a) and general view along axis *a* to the crystal packing (b) formed by the classical H-bond interactions, N···O and O···O interactions.

Table 7 Selected bond lengths (Å), bond angles (°) and torsion angles (°) of compound **5**

Bond lengths	
Cage nitro groups	
N(1)–N(7)	1.4301(13)
N(2)–N(8)	1.3669(14)
N(3)–N(9)	1.3756(14)
N(4)–N(10)	1.3950(14)
Cyano group	
N(5)–C(7)	1.3397(15)
N(11)–C(7)	1.1499(17)

Table 7 (continued)

Bond angles	
Cage nitro groups	
N(7)–N(1)–C(1)	114.68(9)
N(7)–N(1)–C(3)	115.70(9)
N(8)–N(2)–C(1)	119.04(9)
N(8)–N(2)–C(4)	119.36(10)
N(9)–N(3)–C(2)	119.83(10)
N(9)–N(3)–C(5)	120.79(10)
N(10)–N(4)–C(2)	117.60(10)
N(10)–N(4)–C(6)	120.10(9)
Cyano group	
C(7)–N(5)–C(3)	117.75(10)
C(7)–N(5)–C(5)	121.32(10)

Torsion angles	
Cage nitro groups	
N(7)–N(1)–C(3)–C(4) (*axial*)	-110.83(10)
N(8)–N(2)–C(4)–C(3) (*equatorial*)	-173.10(9)
N(9)–N(3)–C(5)–C(6) (*equatorial*)	-176.54(9)
N(10)–N(4)–C(6)–C(5) (*axial*)	-119.03(11)
Cyano group	
C(7)–N(5)–C(3)–(C4) (*middle*)	149.10(10)
C(7)–N(5)–C(5)–C(6) (*middle*)	-152.34(10)

Table 8 Intermolecular hydrogen bonds for **5** [Å and °].

D–H···A	D–H, Å	H···A, Å	D···A, Å	∠ DHA, °	symmetry operation
N(6)-H(6)···O(6)	0.870(18)	2.312(18)	2.8605(14)	121.1(13)	-x+1/2,y-1/2,-z+3/2
N(6)-H(6)···N(11)	0.870(18)	2.254(18)	3.0351(15)	149.4(15)	x+1/2,-y+1/2,z+1/2

2) Single crystal X-ray diffraction of compound 15

X-ray diffraction data **15** were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using graphite monochromatized Cu K_α-radiation (λ =1.54184 Å). The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[32] The structure was solved by direct methods using SHELXT[33] and refined on F^2 using SHELXL-2018[34] in the OLEX2 program.[35] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite[36] was used for molecular graphics. Detailed crystallographic information is provided in Tables 9 and 10, and structure are presented in Figures 3 and 4. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2308197. Copies of the data can be obtained free of charge *via* https://www.ccdc.cam.ac.uk/structures/

Table 9. Detail Crystallographic data of compounds **15** according to single crystal X-ray diffraction analysis.

Formula	$C_9H_8N_{14}O_{14}$
Formula weight [g·mol^{-1}]	536.29
Crystal system	monoclinic
Space group	$P\,2_1/n$
Unit cell dimensions	a = 13.5629(4) Å, α = 90° b = 8.4701(3) Å, β = 109.891(3)° c = 17.2484(5) Å, γ = 90°
V [Å^3]	1863.27(11)
Z / Z'	4 / 1
ρ_{calc} [g·cm^{-3}]	1.912
μ [mm^{-1}]	1.608
$F(000)$	1088
crystal colour	colorless
crystal size [mm^3]	0.11 × 0.06 × 0.02
θ range [°]	3.465 to 83.954
Index ranges	$-17 \le h \le 16, -10 \le k \le 10, -21 \le l \le 21$
Reflections measured	23475
Independent reflections	4051 [R(int) = 0.0416]
Restraints applied/parameters refined	0 / 334
Goodness-of-fit on F^2	1.077
Reflections with $I > 2\sigma(I)$	3523
Final R indeces [$I \ge 2\sigma(I)$]	R_1 = 0.0374, wR_2 = 0.0902
Final R indeces [all data]	R_1 = 0.0446, wR_2 = 0.1002
Residual electron density (ρ_{max}/ρ_{min}) [e Å^{-3}/ e Å^{-3}]	0.353 / -0.363
CCDC number	2308197
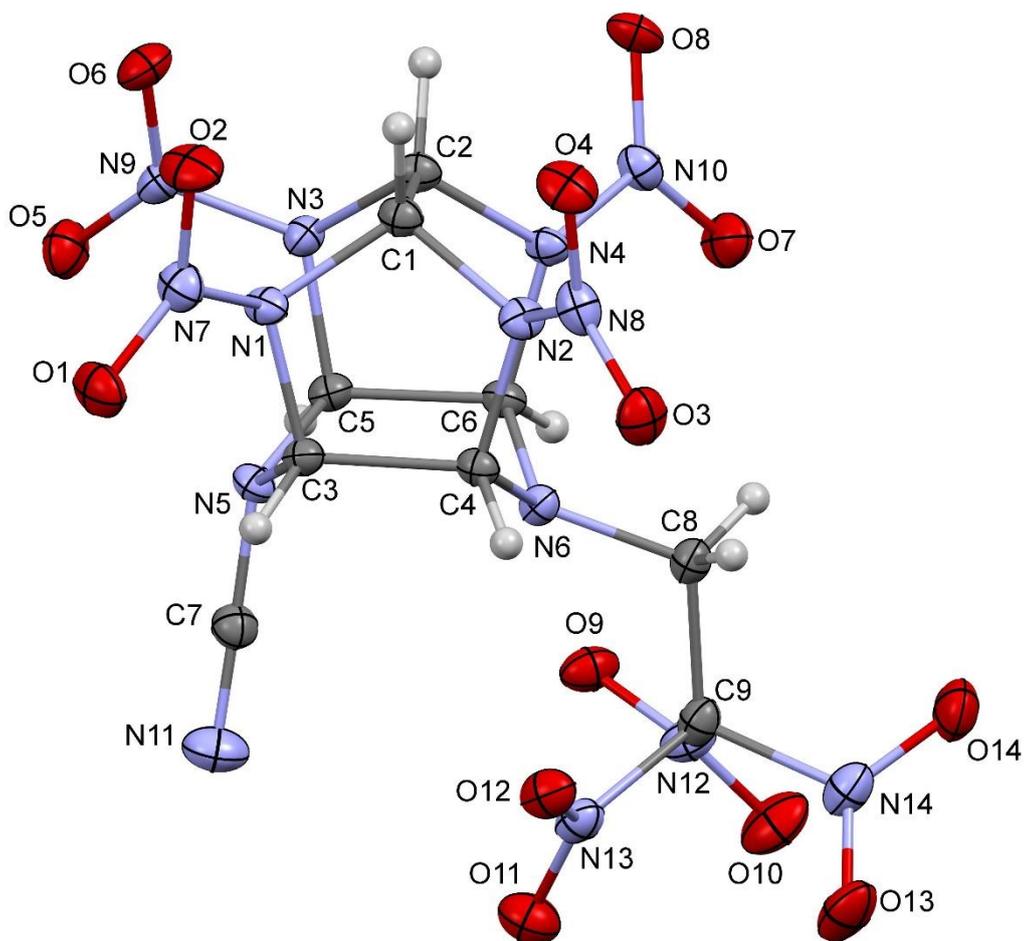
Figures 3. General view of molecule **15** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.
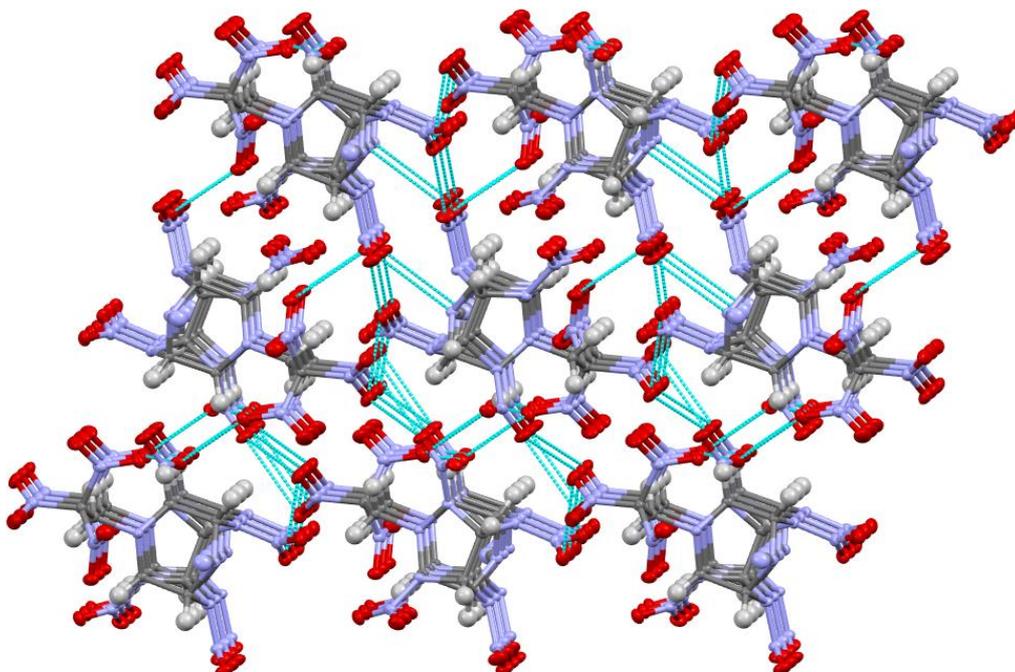
Figures 4. General view along axis *b* to the crystal packing for **15**, formed mainly by N···O and O···O interactions.

Table 10. Selected bond lengths (Å), bond angles (°) and torsion angles (°) of compound **15**

Bond lengths	
Cage nitro groups	
N(1)–N(7)	1.428(2)
N(2)–N(8)	1.4078(19)
N(3)–N(9)	1.381(2)
N(4)–N(10)	1.389(2)
Cyano group	
N(5)–C(7)	1.345(2)
N(11)–C(7)	1.145(3)
Trinitroethyl moiety	
N(6)–C(8)	1.456(2)
C(8)–C(9)	1.537(3)
C(9)–N(12)	1.528(2)
C(9)–N(13)	1.526(2)
C(9)–N(14)	1.523(2)

Bond angles	
Cage nitro groups	
N(7)–N(1)–C(1)	116.81(14
N(7)–N(1)–C(3)	116.73(14)
N(8)–N(2)–C(1)	116.26(14)
N(8)–N(2)–C(4)	117.38(14)
N(9)–N(3)–C(2)	119.53(14)
N(9)–N(3)–C(5)	120.48(14)
N(10)–N(4)–C(2)	118.12(14)
N(10)–N(4)–C(6)	118.54(13)
Cyano group	
C(7)–N(5)–C(3)	113.89(14)
C(7)–N(5)–C(5)	116.99(14)
Trinitroethyl moiety	
N(6)–C(8)–C(9)	112.19(14)
C(8)–C(9)–N(12)	114.50(14)
C(8)–C(9)–N(13)	113.62(14)
C(8)–C(9)–N(14)	110.06(15)

Torsion angles	
Cage nitro groups	
N(7)–N(1)–C(3)–C(4) (*axial*)	-115.10(15)
N(8)–N(2)–C(4)–C(3) (*axial*)	111.47(15)
N(9)–N(3)–C(5)–C(6) (*equatorial*)	-174.95(13)
N(10)–N(4)–C(6)–C(5) (*axial*)	-117.70(15)
Cyano group	
C(7)–N(5)–C(3)–(C4) (*axial*)	86.23(18)
C(7)–N(5)–C(5)–C(6) (*axial*)	-86.40(18)
Trinitroethyl moiety	
C(3)–C(4)–N(6)–C(8) (*equatorial*)	-162.42(14)
C(5)–C(6)–N(6)–C(8) (*equatorial*)	160.98(14)

3) Single crystal X-ray diffraction of compound 22

X-ray diffraction data **22** as solvate **22**·MeCN were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using graphite monochromatized Cu K$_\alpha$-radiation (λ =1.54184 Å). The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[32] The structure was solved by direct methods using SHELXT[33] and refined on F^2 using SHELXL-2018[34] in the OLEX2 program.[35] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite[36] was used for molecular graphics. Detailed crystallographic information is provided in Tables 11 and 12, and structure are presented in Figures 5 and 6. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2308198. Copies of the data can be obtained free of charge *via* https://www.ccdc.cam.ac.uk/structures/

Table 11. Detail Crystallographic data of compounds **22** according to single crystal X-ray diffraction analysis.

Formula	$C_7H_6N_{12}O_{10}$·CH_3CN
Formula weight [g·mol^{-1}]	459.29
Crystal system	monoclinic
Space group	Pna2$_1$
Unit cell dimensions	a = 13.5373(3) Å, α = 90° b = 7.8765(2) Å, β = 90° c = 32.0668(8) Å, γ = 90°
V [Å^3]	3419.17(14)
Z / Z'	8 / 2
ρ_{calc} [g·cm^{-3}]	1.784
μ [mm^{-1}]	1.428
F(000)	1872
crystal colour	colorless
crystal size [mm^3]	0.17 × 0.09 × 0.04
θ range [°]	2.756 to 79.984
Index ranges	$-13 \leq h \leq 16, -10 \leq k \leq 9, -40 \leq l \leq 40$
Reflections measured	41607
Independent reflections	7144 [R(int) = 0.0357]
Restraints applied/parameters refined	3 / 592
Goodness-of-fit on F^2	1.091
Reflections with $I > 2\sigma(I)$	7081
Final R indeces [$I \geq 2\sigma(I)$]	R_1 = 0.0554, wR_2 = 0.1509
Final R indeces [all data]	R_1 = 0.0557, wR_2 = 0.1511
Residual electron density (ρ_{max}/ρ_{min}) [e Å^{-3}/ e Å^{-3}]	0.758 / -0.335
CCDC number	2308198
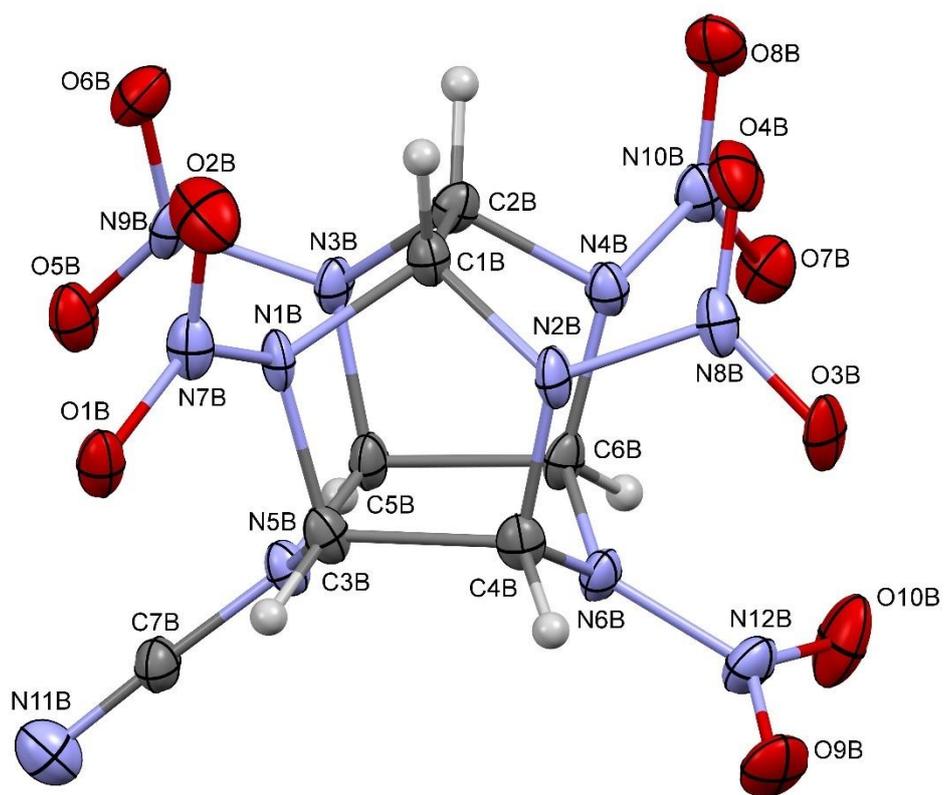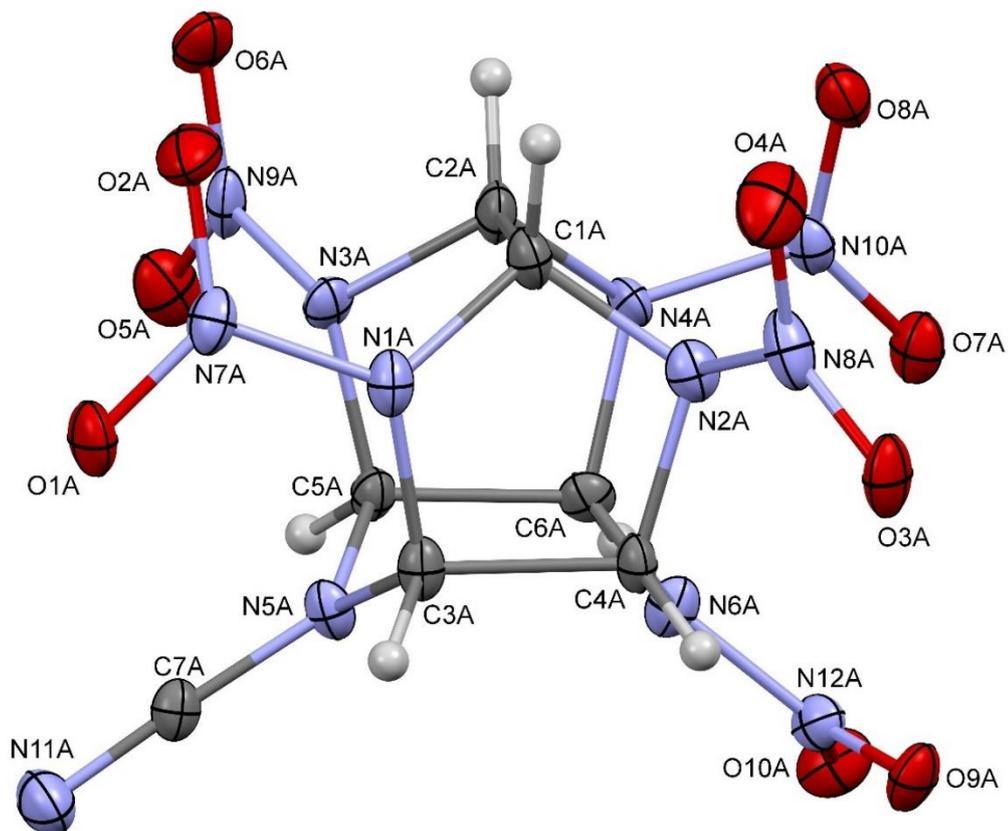
Figure 5. General view of molecule **22** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.
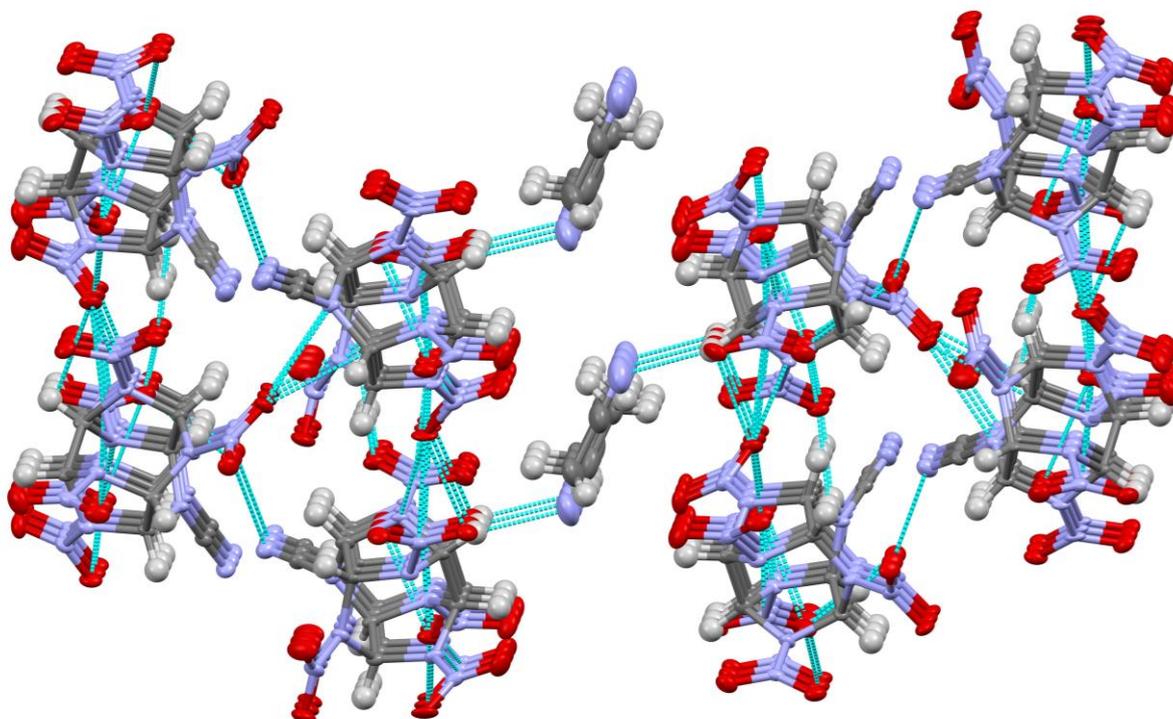
Figure 6. General view to the crystal packing for compound **22**·MeCN along the axis *b*, formed mainly by N···O and O···O interactions.

Table 12. Selected bond lengths (Å), bond angles (°) and torsion angles (°) of compound **22**

Bond lengths	
Cage nitro groups	
N(1A)–N(7A) / N(1B)–N(7B)	1.383(6) / 1.428(6)
N(2A)–N(8A) / N(2B)–N(8B)	1.445(6) / 1.391(6)
N(3A)–N(9A) / N(3B)–N(9B)	1.442(5) / 1.385(6)
N(4A)–N(10A) / N(4B)–N(10B)	1.376(6) / 1.437(6)
N(6A)–N(12A) / N(6B)–N(12B)	1.393(6) / 1.393(6)
Cyano group	
N(5A)–C(7A) / N(5B)–C(7B)	1.339(6) / 1.337(7)
N(11A)–C(7A) / N(11B)–C(7B)	1.159(7) / 1.152(7)

Bond angles	
Cage nitro groups	
N(7A)–N(1A)–C(1A) / N(7B)–N(1B)–C(1B)	118.6(4) / 114.9(4)
N(7A)–N(1A)–C(3A) / N(7B)–N(1B)–C(3B)	119.1(4) / 114.5(4)
N(8A)–N(2A)–C(1A) / N(8B)–N(2B)–C(1B)	114.0(4) / 118.3(4)
N(8A)–N(2A)–C(4A) / N(8B)–N(2B)–C(4B)	113.6(4) / 120.5(4)
N(9A)–N(3A)–C(2A) / N(9B)–N(3B)–C(2B)	114.0(4) / 120.4(4)
N(9A)–N(3A)–C(5A) / N(9B)–N(3B)–C(5B)	115.9(4) / 119.6(4)
N(10A)–N(4A)–C(2A) / N(10B)–N(4B)–C(2B)	121.0(4) / 114.1(4)
N(10A)–N(4A)–C(6A) / N(10B)–N(4B)–C(6B)	119.7(4) / 115.8(4)
N(12A)–N(6A)–C(4A) / N(12B)–N(6B)–C(4B)	118.9(4) / 120.3(4)
N(12A)–N(6A)–C(6A) / N(12B)–N(6B)–C(6B)	121.2(4) / 117.9(4)
Cyano group	
C(7A)–N(5A)–C(3A) / C(7B)–N(5B)–C(3B)	118.5(4) / 121.1(4)
C(7A)–N(5A)–C(5A) / C(7B)–N(5B)–C(5B)	121.4(4) / 121.3(4)

Table 12 (continued)

Torsion angles

Cage nitro groups

N(7A)–N(1A)–C(3A)–C(4A) / N(7B)–N(1B)–C(3B)–C(4B)	(*equatorial*) / (*axial*)	171.1(4) / 106.9(4)
N(8A)–N(2A)–C(4A)–C(3A) / N(8B)–N(2B)–C(4B)–C(3B)	(*axial*) / (*equatorial*)	106.6(4) / -171.3(4)
N(9A)–N(3A)–C(5A)–C(6A) / N(9B)–N(3B)–C(5B)–C(6B)	(*axial*) / (*equatorial*)	110.1(4) / -177.8(4)
N(10A)–N(4A)–C(6A)–C(5A) / N(10A)–N(4A)–C(6B)–C(5B)	(*equatorial*) / (*axial*)	175.6(4) / 110.7(4)
N(12A)–N(6A)–C(4A)–C(3A) / N(12B)–N(6B)–C(4B)–C(3B)	(*middle*) / (*middle*)	-138.0(4) / -148.6(4)
N(12A)–N(6A)–C(6A)–C(5A) / N(12B)–N(6B)–C(6B)–C(5B)	(*middle*) / (*middle*)	140.3(4) / 145.9(4)

Cyano group

C(7A)–N(5A)–C(3A)–(C4A) / C(7B)–N(5B)–C(3B)–(C4B)	(*middle*) / (*middle*)	145.7(4) / 138.4(5)
C(7A)–N(5A)–C(5A)–C(6A) / C(7B)–N(5B)–C(5B)–C(6B)	(*middle*) / (*middle*)	-144.2(4) / -140.7(5)

4) Single crystal X-ray diffraction of compound 23

X-ray diffraction data **23** were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using graphite monochromatized Cu K_α-radiation (λ =1.54184 Å). The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[32] The structure was solved by direct methods using SHELXT[33] and refined on F^2 using SHELXL-2018 [34] in the OLEX2 program.[35] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite[36] was used for molecular graphics. Detailed crystallographic information is provided in Tables 13 and 14, and structure are presented in Figures 7 and 8. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2308199. Copies of the data can be obtained free of charge *via* https://www.ccdc.cam.ac.uk/structures/

Table 13. Detail Crystallographic data of compounds **23** according to single crystal X-ray diffraction analysis.

Formula	$C_8H_6N_{12}O_8$
Formula weight [g·mol^{-1}]	398.25
Crystal system	monoclinic
Space group	$P\,2_1/c$
Unit cell dimensions	a = 7.78897(7) Å, α = 90°
	b = 13.33467(14) Å, β = 93.7723(8)°
	c = 13.43040(12) Å, γ = 90°
V [Å^3]	1391.90(2)
Z / Z'	4 / 1
ρ_{calc} [g·cm^{-3}]	1.900
μ [mm^{-1}]	1.503
F(000)	808
crystal colour	colorless
crystal size [mm^3]	0.24 × 0.05 × 0.04
θ range [°]	4.678 to 77.708
Index ranges	$-9 \le h \le 7, -16 \le k \le 16, -17 \le l \le 16$
Reflections measured	18672
Independent reflections	2957 [R(int) = 0.0277]
Restraints applied/parameters refined	0 / 253
Goodness-of-fit on F^2	1.042
Reflections with $I > 2\sigma(I)$	2852
Final R indeces [$I \ge 2\sigma(I)$]	R_1 = 0.0310, wR_2 = 0.0784
Final R indeces [all data]	R_1 = 0.0317, wR_2 = 0.0789
Residual electron density (ρ_{max}/ρ_{min}) [e Å^{-3}/ e Å^{-3}]	0.302 / -0.314
CCDC number	2308199
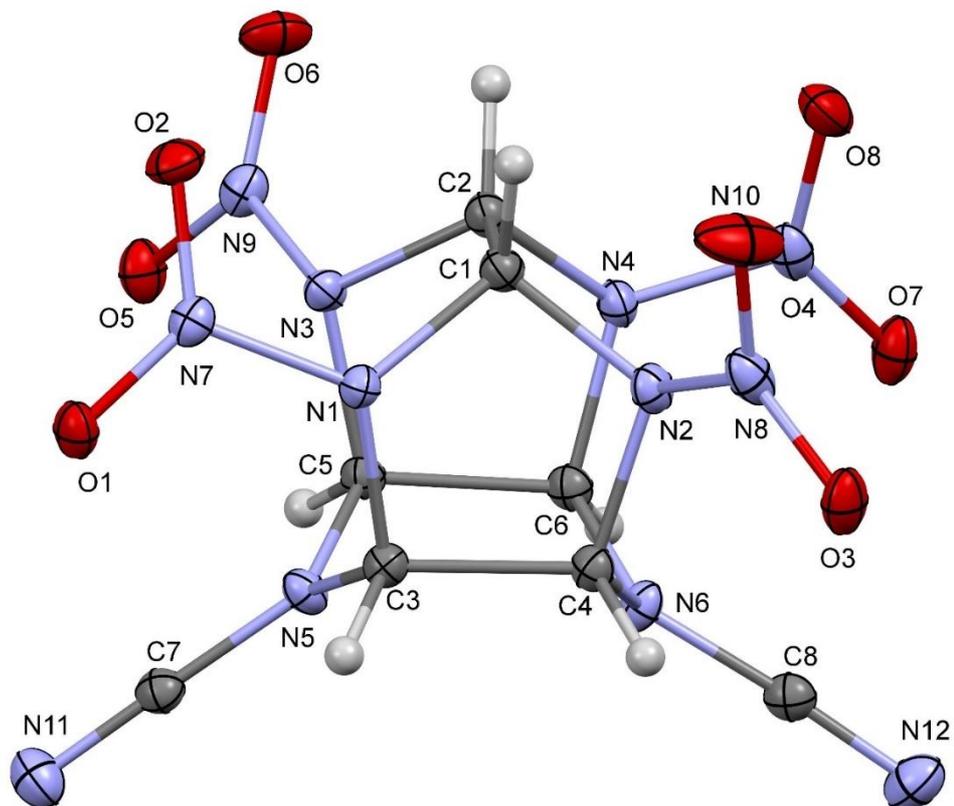
Figure 7. General view of molecule **23** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.
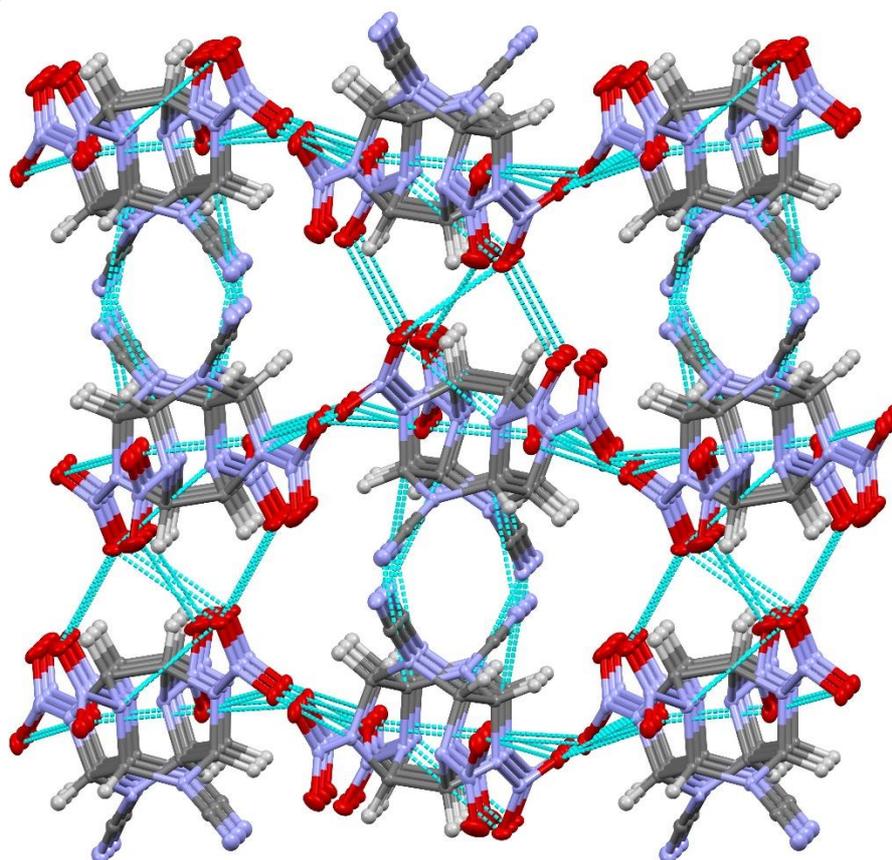
Figure 8. General view to the crystal packing for compound **23** along the axis *a*, formed by the O···O interactions and C···N interactions between acetonitrile fragments.

Table 14. Selected bond lengths (Å), bond angles (°) and torsion angles (°) of compound **23**

Bond lengths	
Cage nitro groups	
N(1)–N(7)	1.3742(13)
N(2)–N(8)	1.4245(13)
N(3)–N(9)	1.4311(13)
N(4)–N(10)	1.3682(13)
Cyano groups	
N(5)–C(7)	1.3388(15)
N(11)–C(7)	1.1506(16)
N(6)–C(8)	1.3440(15)
N(12)–C(8)	1.1506(16)

Bond angles	
Cage nitro groups	
N(7)–N(1)–C(1)	119.97(9)
N(7)–N(1)–C(3)	120.33(9)
N(8)–N(2)–C(1)	116.71(9)
N(8)–N(2)–C(4)	115.06(9)
N(9)–N(3)–C(2)	115.07(9)
N(9)–N(3)–C(5)	114.25(9)
N(10)–N(4)–C(2)	121.15(9)
N(10)–N(4)–C(6)	120.59(9)
Cyano groups	
C(7)–N(5)–C(3)	121.52(10)
C(7)–N(5)–C(5)	120.39(10)
C(8)–N(6)–C(4)	118.34(9)
C(8)–N(6)–C(6)	120.65(9)

Torsion angles	
Cage nitro groups	
N(7)–N(1)–C(3)–C(4) (*equatorial*)	175.29(9)
N(8)–N(2)–C(4)–C(3) (*axial*)	112.11(10)
N(9)–N(3)–C(5)–C(6) (*axial*)	108.43(10)
N(10)–N(4)–C(6)–C(5) (*equatorial*)	178.57(9)
Cyano groups	
C(7)–N(5)–C(3)–(C4) (*middle*)	140.69(10)
C(7)–N(5)–C(5)–C(6) (*middle*)	-137.80(10)
C(8)–N(6)–C(4)–C(3) (*middle*)	-147.62(10)
C(8)–N(6)–C(6)–C(5) (*middle*)	151.06(10)

Molecular surface electrostatic potentials (ESPs) of 0.001 electrons per bohr³ isosurfaces for 5, 15, 22, 23 and CL-20 calculated for optimized molecular structures in the gas phase using the DFT/B3LYP method at the 6-31G(d,p) level

−15 kcal·mol⁻¹
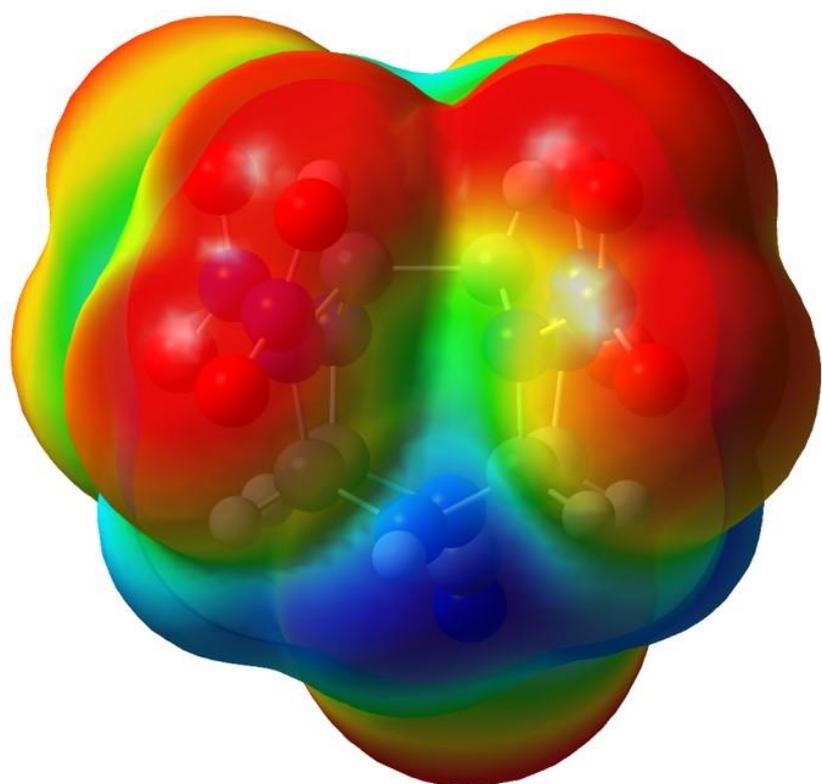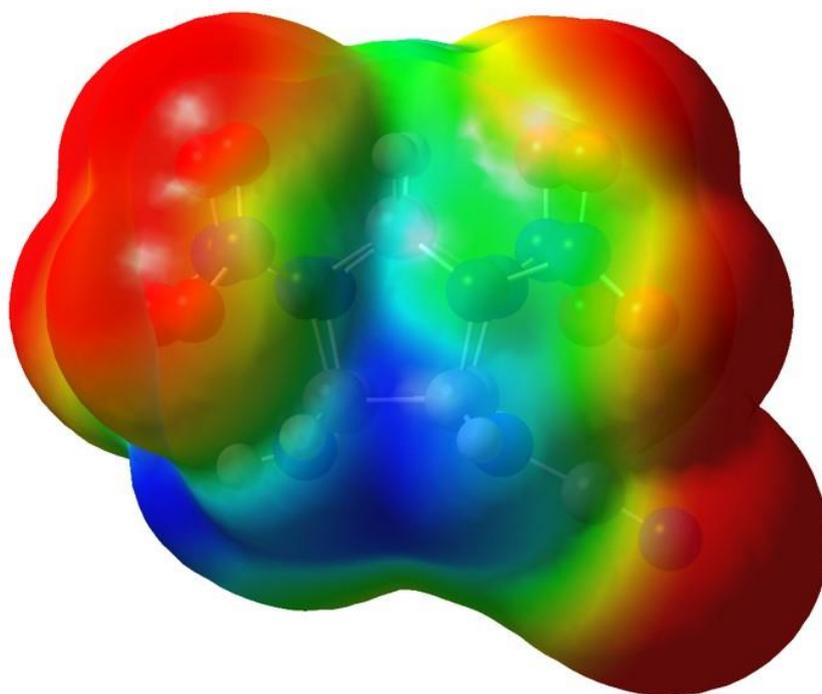
+40 kcal·mol⁻¹

Figure 9. Molecular surface electrostatic potentials (ESPs) for **5**. The ESP surface is divided into local electron-deficient (blue) and electron-rich (red) areas.
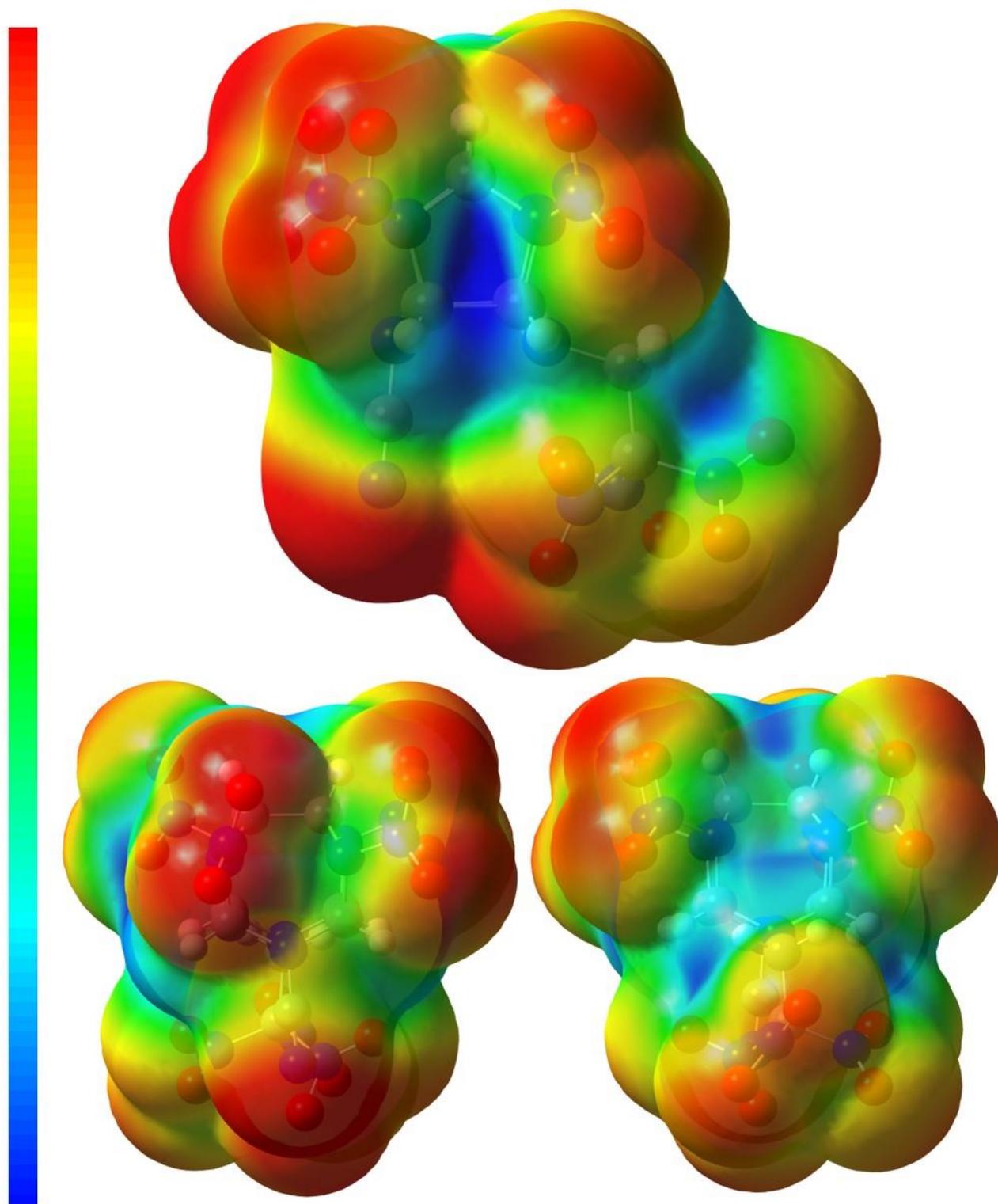
−15 kcal·mol^{-1}

+40 kcal·mol^{-1}

Figure 10. Molecular surface electrostatic potentials (ESPs) for **15**. The ESP surface is divided into local electron-deficient (blue) and electron-rich (red) areas.
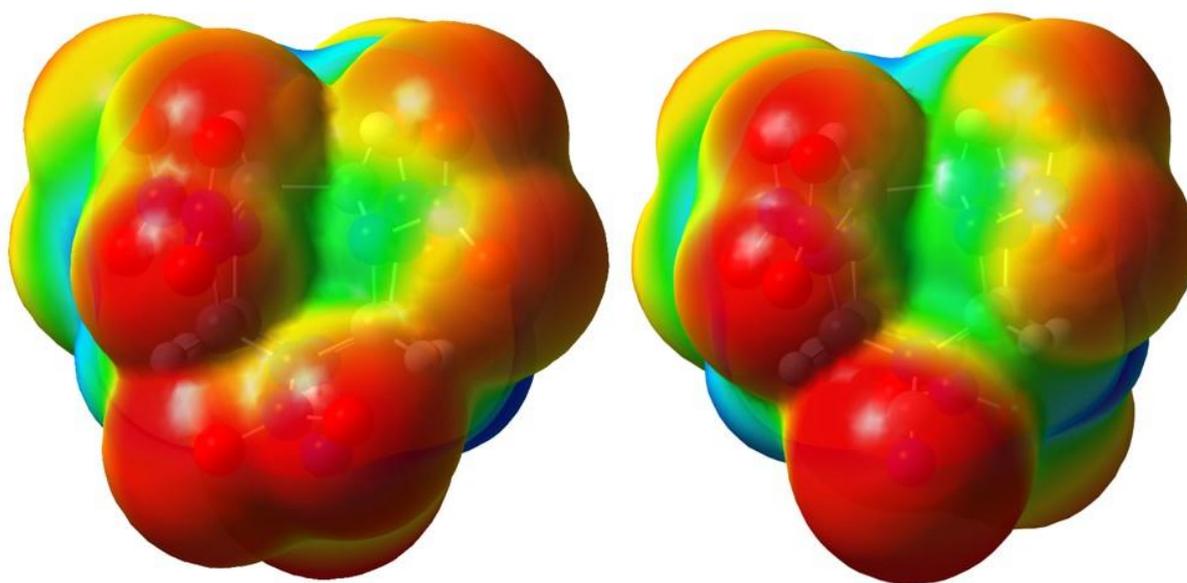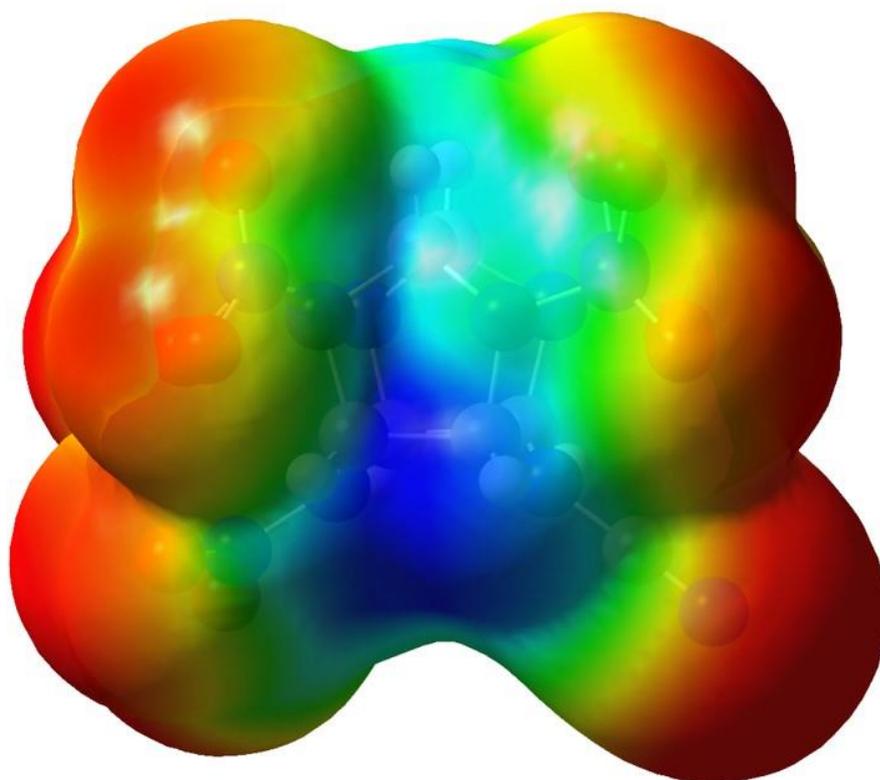
−15 kcal·mol⁻¹

+40 kcal·mol⁻¹

Figure 11. Molecular surface electrostatic potentials (ESPs) for **22**. The ESP surface is divided into local electron-deficient (blue) and electron-rich (red) areas.
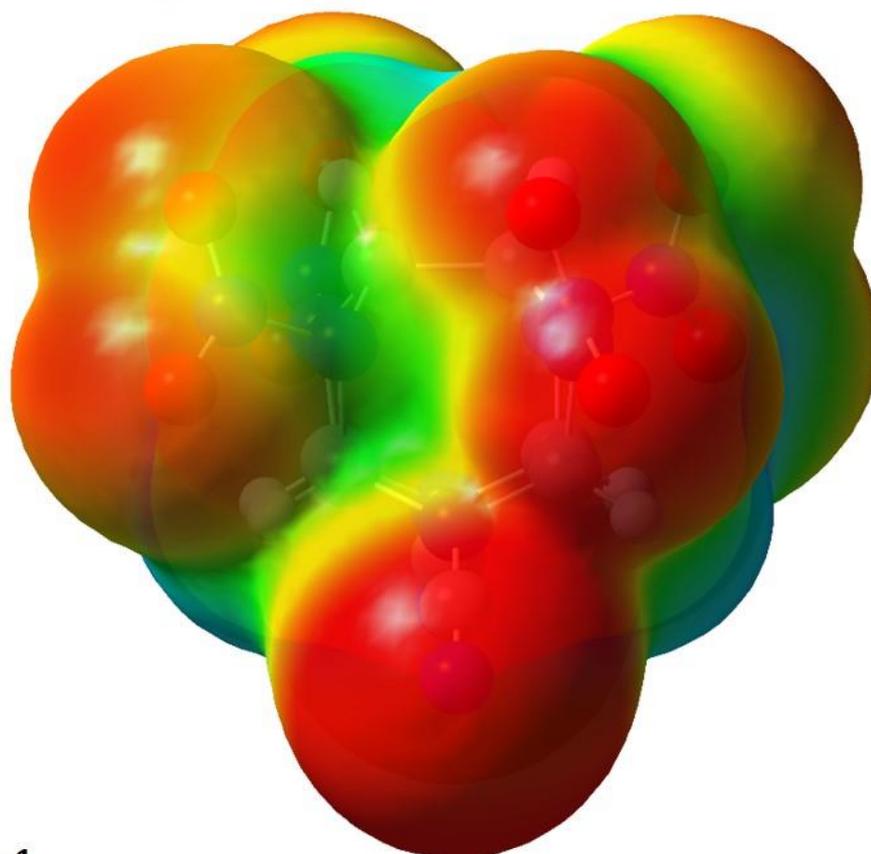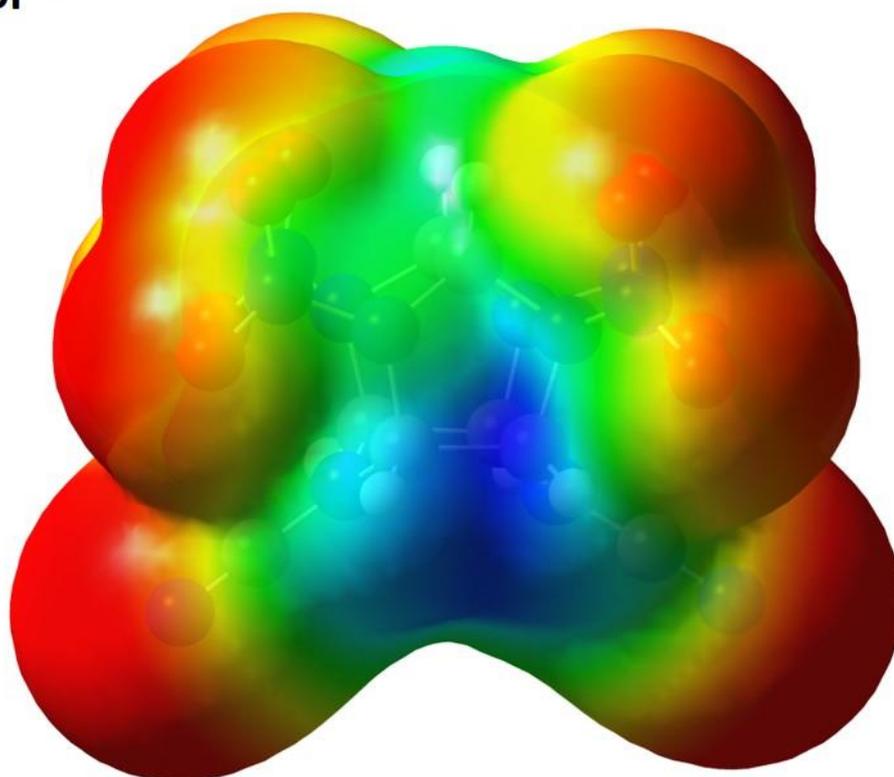
−15 kcal·mol⁻¹

+40 kcal·mol⁻¹

Figure 12. Molecular surface electrostatic potentials (ESPs) for **23**. The ESP surface is divided into local electron-deficient (blue) and electron-rich (red) areas.
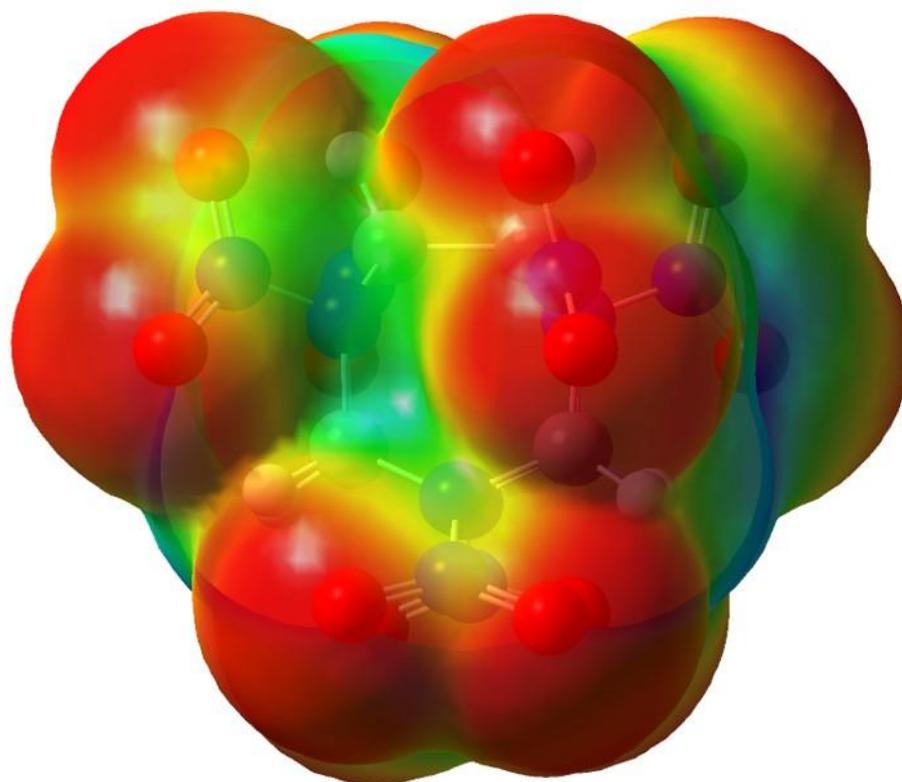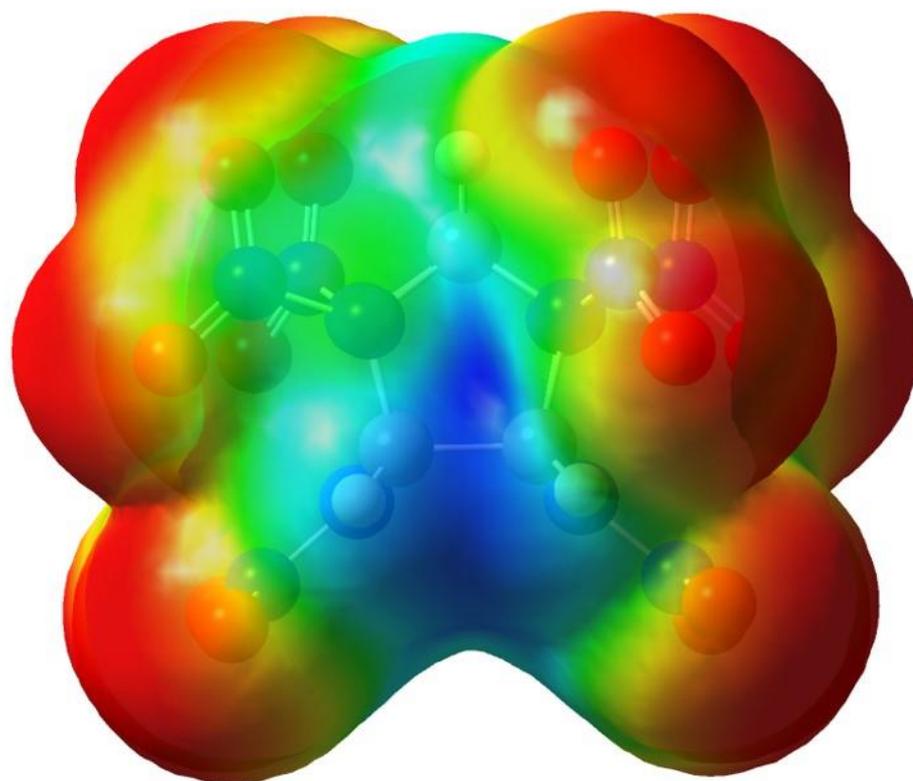
−15 kcal·mol^{-1}

+40 kcal·mol^{-1}

Figure 13. Molecular surface electrostatic potentials (ESPs) for **CL-20**. The ESP surface is divided into local electron-deficient (blue) and electron-rich (red) areas.

Differential scanning calorimetric (DSC) and thermogravimetric (TG) analysis for cyano derivatives of polynitro HAIWs 5, 6, 15, 22 and 23
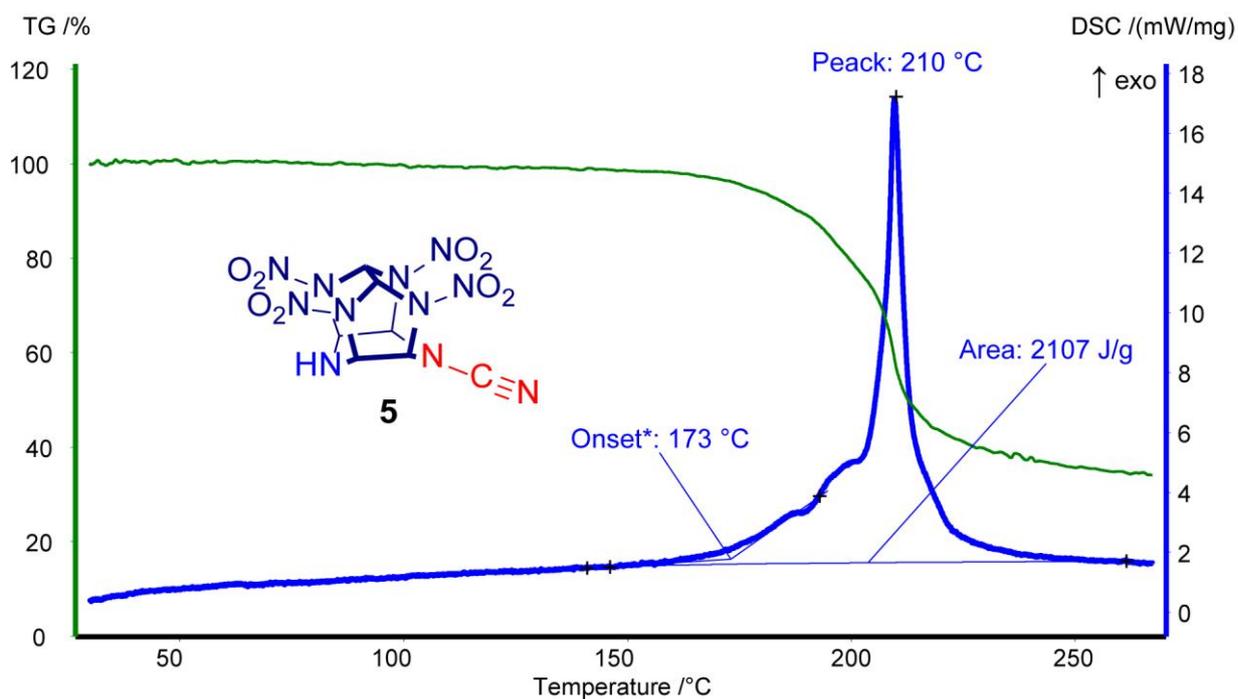
Figure 14. DSC and TG curves of amino derivative **5** (heating rate of 5 °C min^{-1}).
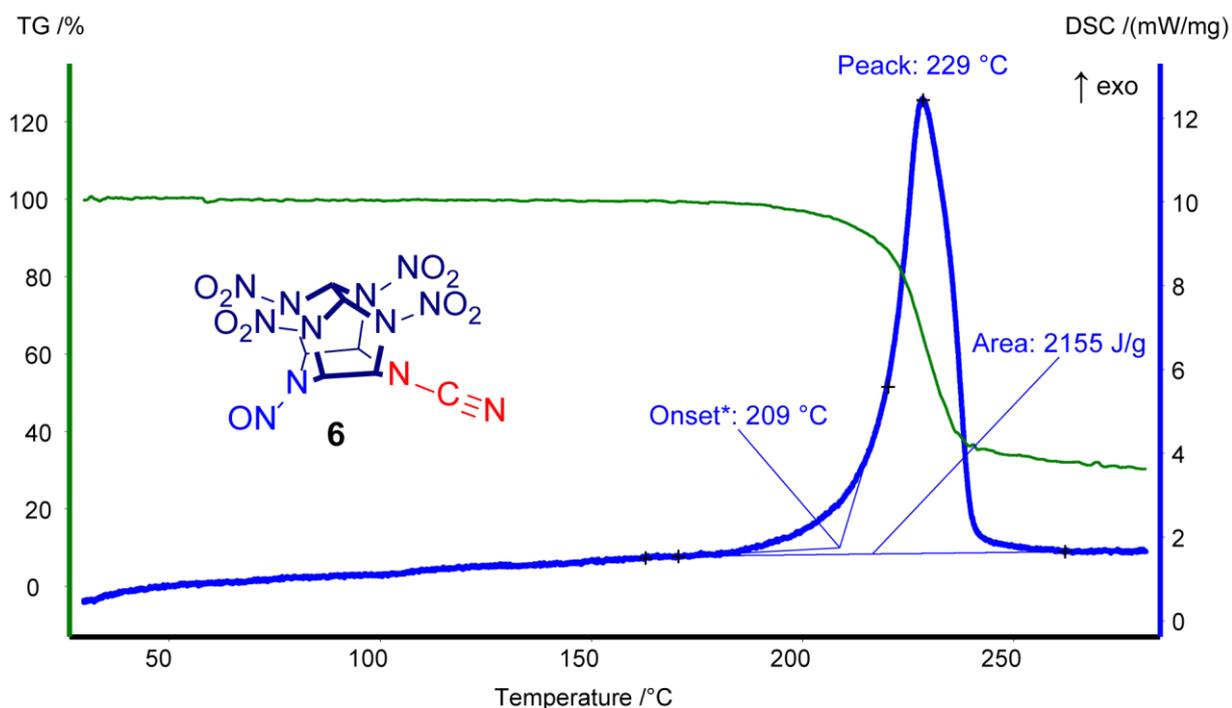
Figure 15. DSC and TG curves of nitroso derivative **6** (heating rate of 5 °C min^{-1}).
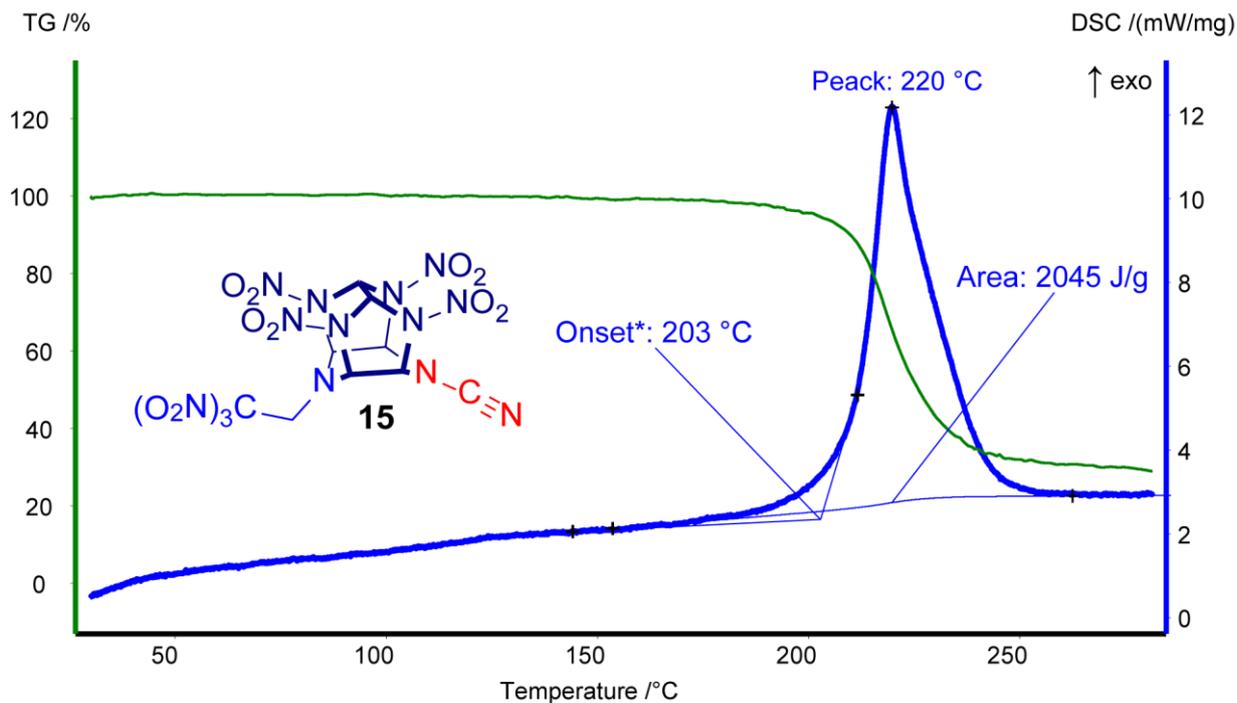
Figure 16. DSC and TG curves of 2,2,2-trinitroethyl derivative **15** (heating rate of 5 °C min⁻¹).
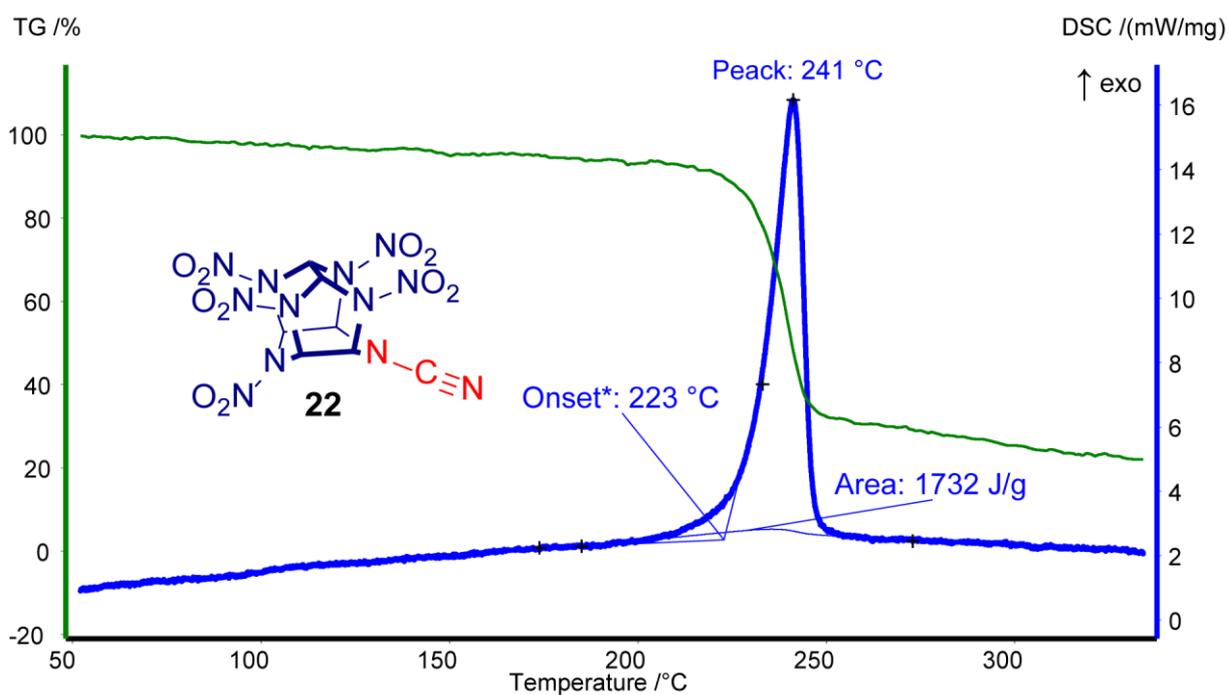
Figure 17. DSC and TG curves of pentanitro HAIW **22** (heating rate of 5 °C min⁻¹).
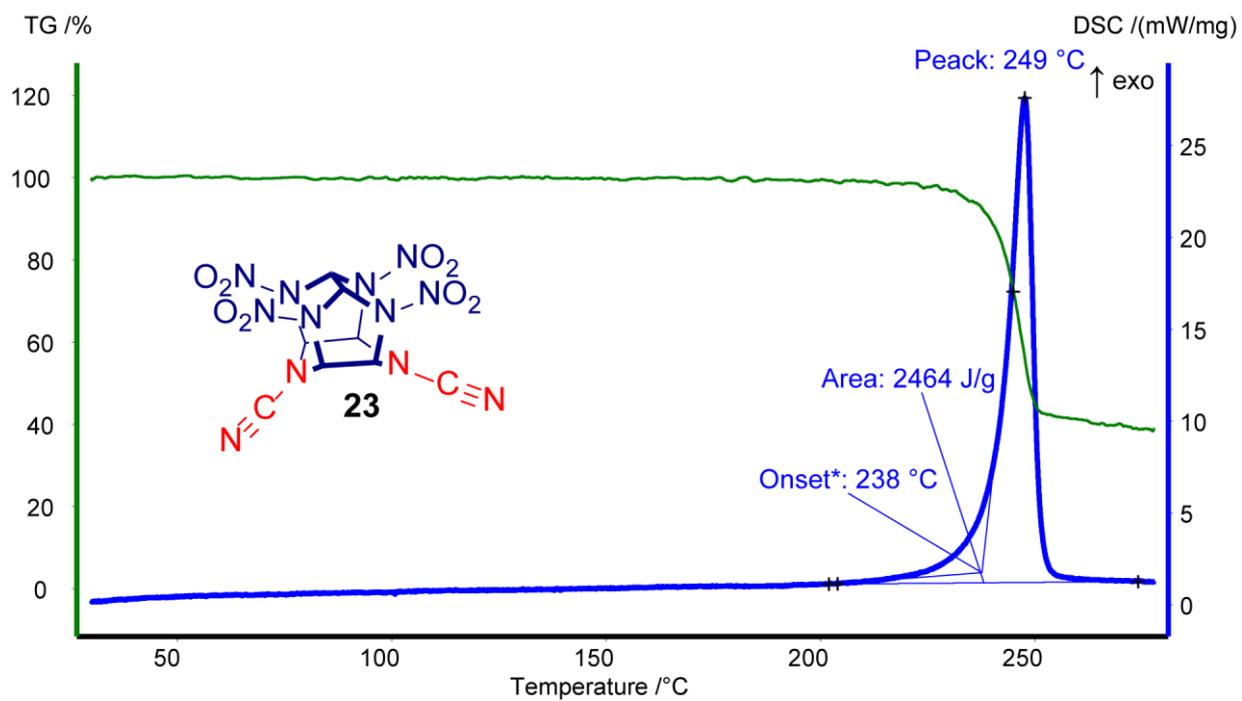
Figure 18. DSC and TG curves of dicyano derivative **23** (heating rate of 5 °C min⁻¹).

Measurements and calculations of enthalpies of combustion and formation for cyano-substituted HAIWs 5, 6, 15, 22, 23

The combustion reactions of bis-cage derivatives **5**, **6**, **15**, **22** and **23** occurs according to Eq. (1) – Eq. (5)

$$C_7H_7N_{11}O_{8(cr)} + 4.75\ O_{2(g)} \rightarrow 7\ CO_{2(g)} + 3.5\ H_2O_{(l)} + 5.5\ N_{2(g)}, \qquad \text{[Eq. (1)]}$$
5

$$C_7H_6N_{12}O_{9(cr)} + 4\ O_{2(g)} \rightarrow 7\ CO_{2(g)} + 3\ H_2O_{(l)} + 6\ N_{2(g)}, \qquad \text{[Eq. (2)]}$$
6

$$C_9H_8N_{14}O_{14(cr)} + 4\ O_{2(g)} \rightarrow 9\ CO_{2(g)} + 4\ H_2O_{(l)} + 7\ N_{2(g)}, \qquad \text{[Eq. (3)]}$$
15

$$C_7H_6N_{12}O_{10(cr)} + 3.5\ O_{2(g)} \rightarrow 7\ CO_{2(g)} + 3\ H_2O_{(l)} + 6\ N_{2(g)}, \qquad \text{[Eq. (4)]}$$
22

$$C_8H_6N_{12}O_{8\ (cr)} + 5.5\ O_{2(g)} \rightarrow 8\ CO_{2(g)} + 3\ H_2O_{(l)} + 6\ N_{2(g)}, \qquad \text{[Eq. (5)]}$$
23
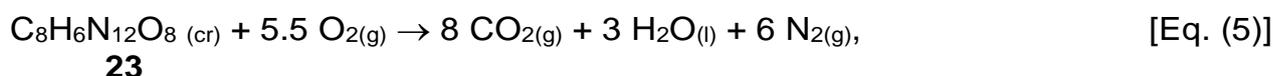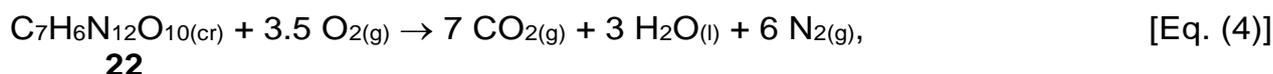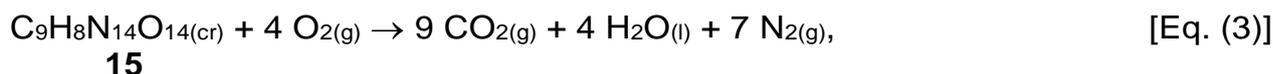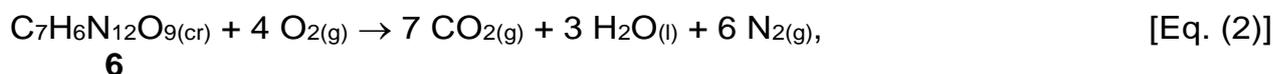
where the subscripts cr, g, and l refer to crystalline, gaseous, and liquid states of the compounds, respectively.

The relationship between the enthalpies of formation and enthalpies of combustion of these compounds are presented by Eq. (6) – Eq. (10) taking into account the stoichiometry of reactions (1) – (5)

$$\Delta H_f\,[C_7H_7N_{11}O_8]_{(cr)} = 7\ \Delta H_f\,[CO_2]_{(g)} + 3.5\ \Delta H_f\,[H_2O]_{(l)} - \Delta H_{comb}(\mathbf{5}), \qquad \text{[Eq. (6)]}$$
5

$$\Delta H_f\,[C_7H_6N_{12}O_9]_{(cr)} = 7\ \Delta H_f\,[CO_2]_{(g)} + 3\ \Delta H_f\,[H_2O]_{(l)} - \Delta H_{comb}(\mathbf{10}), \qquad \text{[Eq. (7)]}$$
6

$$\Delta H_f\,[C_9H_8N_{14}O_{14}]_{(cr)} = 9\ \Delta H_f\,[CO_2]_{(g)} + 4\ \Delta H_f\,[H_2O]_{(l)} - \Delta H_{comb}(\mathbf{15}), \qquad \text{[Eq. (8)]}$$
15

$$\Delta H_f\,[C_7H_6N_{12}O_{10}]_{(cr)} = 7\ \Delta H_f\,[CO_2]_{(g)} + 3\ \Delta H_f\,[H_2O]_{(l)} - \Delta H_{com}(\mathbf{22}), \qquad \text{[Eq. (9)]}$$
22

$$\Delta H_f\,[C_8H_6N_{12}O_8]_{(cr)} = 8\ \Delta H_f\,[CO_2]_{(g)} + 3\ \Delta H_f\,[H_2O]_{(l)} - \Delta H_{comb}(\mathbf{23}), \qquad \text{[Eq. (10)]}$$
23

where $\Delta H_f[CO_2]_{(g)} = -94.051 \pm 0.031$ kcal·mol^{-1} and $\Delta H_f[H_2O]_{(l)} = -68.315 \pm 0.009$ kcal·mol^{-1} .[37]

Measurements of the enthalpies of combustion for **22** and **23** were carried out on a precision automatic combustion calorimeter with an isothermal coating specifically developed for combustion of energetic compounds and are presented in Tables 15 and 16. The mean square error of the measurements was 0.025%.

Table 15. Measurements of combustion energy of compound **22.**

#	m^a [g]	ΔT^b [deg]	$Q_{meas}{}^c$ [cal]	$q_a{}^d$ [cal]	$q_i{}^e$ [cal]	$q_N{}^f$ [cal]	$q_{cot}{}^g$ [cal]	$-\Delta U'_B{}^h$ [cal·g^{-1}]
1	0.058363	2.12627	1143.17	984.01	7.32	1.31	9.66	2413.6
2	0.080126	2.17049	1166.94	954.87	7.24	1.80	9.52	2415.1
3	0.079681	2.15514	1158.69	947.55	7.28	1.80	9.40	2417.9
4	0.078429	2.13695	1148.91	941.47	7.30	1.75	9.28	2411.2
5	0.081207	2.15929	1160.92	946.01	7.26	1.93	9.47	2416.7

$$-\Delta U'_B{}^h = 2414.9 \pm 3.0 \text{ cal·g}^{-1}$$

$$-\Delta H_{comb}{}^i = 1002.7 \pm 1.3 \text{ kcal·mol}^{-1}$$

$$\Delta H_f{}^j = 139.4 \pm 1.3 \text{ kcal·mol}^{-1}$$

Table 16. Measurements of combustion energy of compound **23.**

#	m^a [g]	ΔT^b [deg]	$Q_{meas}{}^c$ [cal]	$q_a{}^d$ [cal]	$q_i{}^e$ [cal]	$q_N{}^f$ [cal]	$q_{cot}{}^g$ [cal]	$-\Delta U'_B{}^h$ [cal·g^{-1}]
1	0.047206	2.01840	1085.17	930.50	7.20	1.35	9.53	2893.5
2	0.074831	2.16654	1164.82	929.64	7.31	2.16	9.30	2892.0
3	0.073209	2.12884	1144.55	913.77	7.28	2.11	9.35	2896.4
4	0.075014	2.17738	1170.66	934.82	7.30	2.16	9.41	2892.2
5	0.078312	2.21650	1191.68	946.07	7.18	2.24	9.55	2894.1

$$-\Delta U'_B{}^h = 2893.6 \pm 2.1 \text{ cal·g}^{-1}$$

$$-\Delta H_{comb}{}^i = 1145.6 \pm 0.8 \text{ kcal·mol}^{-1}$$

$$\Delta H_f{}^j = 188.2 \pm 0.8 \text{ kcal·mol}^{-1}$$

Note for the tables: [a] Sample mass of the test substance (measurement error $2 \cdot 10^{-6}$ g); [b] Corrected temperature rise in the calorimeter; [c] The amount of heat measured in experiment (see formula 1); [d] Heat release from the combustion of the auxiliary substance (benzoic acid, the value on a unit of mass 6322.6 ± 1.2 cal·g^{-1}); [e] Ignition energy; [f] Heat release from the nitric acid solution formation (the value on a unit of mass 1.38 cal·g^{-1}); [g] Heat release from the combustion of cotton thread (the value on a unit of mass measured in a series of seven experiments was 3968.9 ± 1.6 cal·g^{-1}); [h] Combustion energy of compound in a bomb is; [i] The standard enthalpy of combustion of the compound; [j] The standard enthalpy of formation of a compound.

The measured values were used to determine ΔH_f of compounds **22** and **23** according to the standard scheme developed by S. M. Skuratov and V. P. Kolesov (M. V. Lomonosov Moscow State University).[38]

The amount of heat measured in experiment is obtained by the formula (1):

$$Q_{meas} = W \times \Delta T, \qquad\qquad\qquad (1)$$

where W is the energy equivalent, which was measured in a series of six experiments and amounted to 537.59 ± 0.14 cal·deg^{-1}.

The combustion energy of compound in a bomb is:

$$-\Delta U'_B = (Q_{meas} - q_a - q_i - q_N - q_{cot}) \times m^{-1}. \qquad\qquad (2)$$

And the enthalpy of combustion of the compound is:

$$-\Delta H_{comb} = -\Delta U'_B \times M + \pi \times \Delta U'_B + (n - n') \times R \times T, \qquad (3)$$

where M is the molar mass of the test substance, n' and n are the number of moles of gases, respectively, in the right and left sides of the chemical equation of combustion of one mole of a substance, R is the molar gas constant, T is the standard temperature (298 K) and π is the Washburn correction, which for compound $C_aH_bO_cN_d$ is calculated by the formula:

$$\pi = 0.3 \times P \times (-\Delta U_B / a)^{-1} \times \left[-1 + 1.1 \times \left(\frac{b - 2(c+d)}{4a} \right) - \frac{2}{P} \right] \qquad (4),$$

where P is the initial pressure of oxygen in the bomb (30 atm); $-\Delta U_B / a$ is the heat of combustion of carbon contained in a combusted compound, kcal·(g·atom)$^{-1}$.

Based on these thermochemical and literature data,[8b–g] the determination of ΔH_{comb} and ΔH_f for **5**, **6** and **15** was carried out by the additive method for calculating thermodynamic properties to S. W. Benson[19] using the contributions of molecular fragments as well as Eq. (6) – Eq. (8), respectively.

High-temperature chemical equilibria thermodynamic calculations for cyano-substituted HAIWs 5, 6, 15, 22, 23

Metal-free formulations of SCP with an "active" binder, a mixture of polyvinyl methyl tetrazole with nitroglycerin and a phlegmatizer (Act-bnd, $C_{18.96}H_{34.64}N_{19.16}O_{29.32}$; ΔH_F −757 kJ·kg^{-1}; d 1.49 g·cm^{-3})[24] in an amount corresponding to 19% by volume and the rest is a mixture of AP with the material under study (CL-20 or **5**, **6**, **15**, **22** and **23**) by varying the ratio of these HEDMs to AP were considered. The specific impulse I_{sp} (at pressures of 4.0 and 0.1 MPa in the combustion chamber and at the nozzle exit, respectively) and the combustion temperature T_{comb} were determined using the standard code TERRA[26] for high-temperature chemical equilibria calculation. The results of calculation with varying of the content of the organic energetic component are presented in Table 17 and Figures 19, 20.
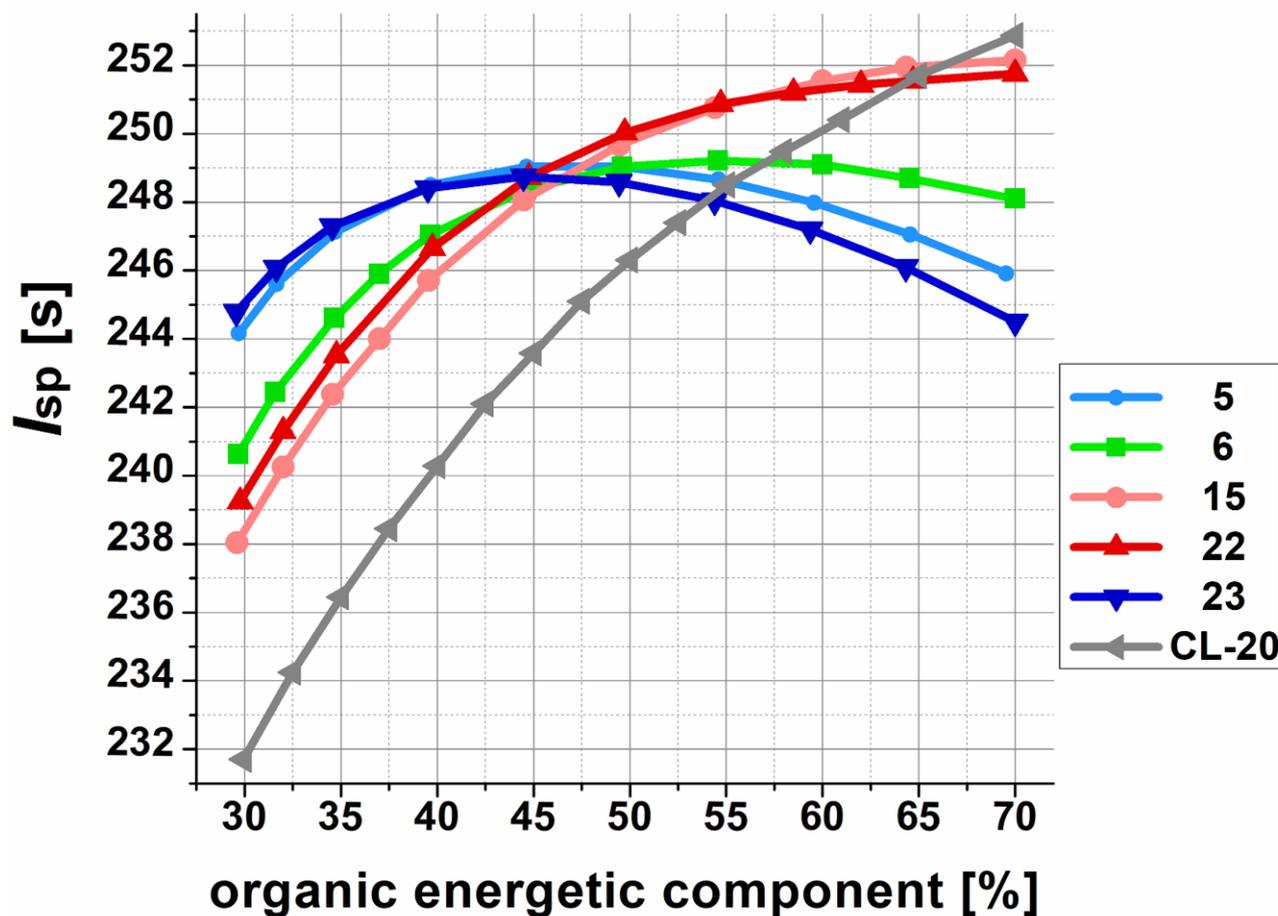
Figure 19. The dependence of I_{sp} on the kind of HEDM (**5**, **6**, **15**, **22**, **23** and CL-20) and its percentage in the SCP formulations containing 19 vol% (15–16 wt%) Active binder, organic energetic component, and AP.

Table 17. The I_{sp} values and other energetic parameters that can be achieved using SCP containing 19 vol% (15.0–15.8 wt%) Active binder, 34.4–39.8 wt% AP and HEDM **5**, **6**, **15**, **22**, **23** or CL-20.

organic component		Act-bnd[a]	AP[b]	d[c]	T_{comb}[d]	I_{sp}[e]
type	[wt%]	[wt%]	[wt%]	[g·cm^{-3}]	[K]	[s]
5	15.48	10	74.52	1.828	3100	244.6
	15.46	15	69.54	1.831	3160	245.9
	15.44	20	64.56	1.833	3200	247.1
	15.42	25	59.58	1.835	3240	248.0
	15.4	30	54.6	1.837	3260	248.7
	15.38	35	49.62	1.840	3265	249.0
	15.36	40	44.64	1.842	3260	249.0
	15.34	45	39.66	1.844	3240	248.5
	15.32	50	34.68	1.847	3210	247.1
	15.3	55	29.7	1.849	3160	244.2
6	15.5	10	74.5	1.827	3260	247.3
	15.46	20	64.54	1.831	3300	248.7
	15.42	30	54.58	1.836	3300	249.2
	15.4	35	49.6	1.839	3290	249.0
	15.38	40	44.62	1.841	3260	248.4
	15.36	45	39.64	1.843	3230	247.0
	15.34	50	34.66	1.846	3190	244.6
	15.32	55	29.68	1.848	3120	240.6
15	15.75	0	84.25	1.798	3370	251.9
	15.7	10	74.3	1.805	3370	252.2
	15.65	20	64.35	1.813	3360	251.9
	15.58	30	54.42	1.820	3320	250.8
	15.55	35	49.45	1.824	3290	249.7
	15.5	40	44.5	1.828	3260	248.1
	15.45	45	39.55	1.832	3215	245.7
	15.42	50	34.58	1.835	3160	242.4
	15.4	55	29.6	1.839	3090	238.0
22	15.3	10	74.7	1.848	3360	251.3
	15.29	20	64.71	1.850	3355	251.6
	15.28	30	54.72	1.852	3330	250.9
	15.27	35	49.73	1.853	3300	250.0
	15.26	40	44.74	1.854	3270	248.7
	15.25	45	39.75	1.855	3230	246.7
	15.24	50	34.76	1.856	3180	243.5
	15.23	55	29.77	1.857	3110	239.2
23	15.76	10	74.24	1.798	3120	243.2
	15.68	20	64.32	1.806	3220	246.1
	15.64	25	59.36	1.811	3250	247.2
	15.6	30	54.4	1.815	3270	248.0
	15.56	35	49.44	1.819	3285	248.6
	15.52	40	44.48	1.823	3280	248.7
	15.48	45	39.52	1.828	3260	248.4
	15.44	50	34.56	1.832	3230	247.3
	15.42	55	29.58	1.836	3180	244.8
CL-20	14.8	10	75.2	1.912	3400	253.8
	14.85	15	70.15	1.908	3380	252.9
	14.9	20	65.1	1.905	3350	251.7
	14.9	25	60.1	1.902	3320	250.2
	14.95	30	55.05	1.898	3280	248.5
	14.95	35.05	50	1.895	3240	246.2
	15	40	45	1.891	3200	243.6
	15	45	40	1.888	3140	240.3
	15.05	55	29.95	1.882	3000	231.7

[a] Active binder. [b] Ammonium perchlorate. [c] Density of composition. [d] Temperature in the combustion chamber. [e] Specific impulse

(A)
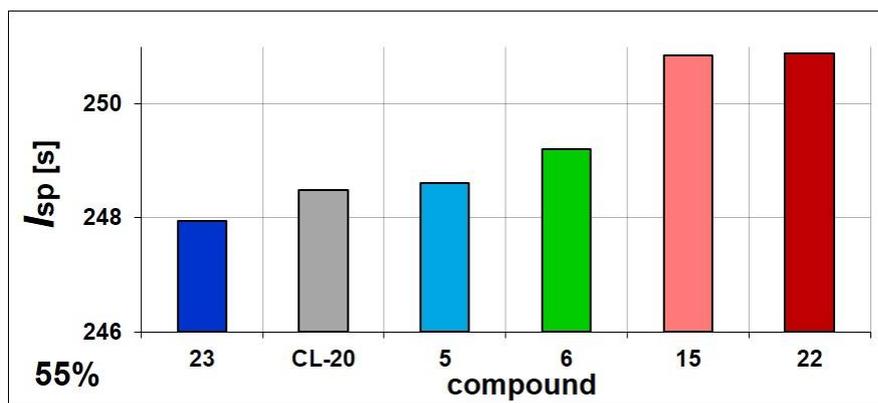
(B)
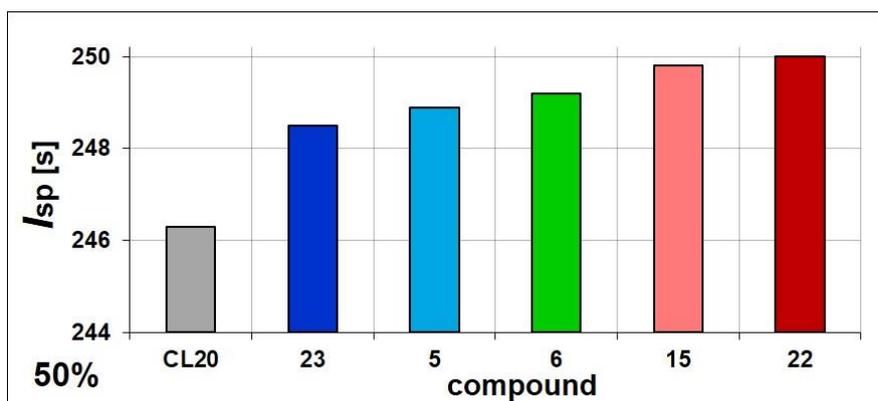
(C)
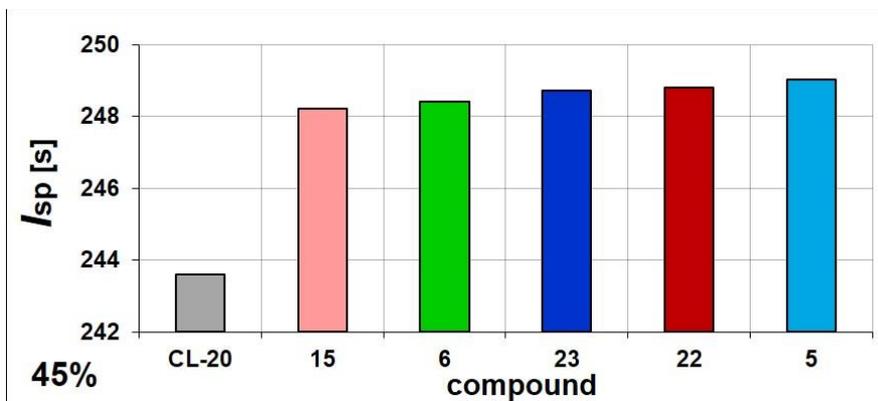
(D)
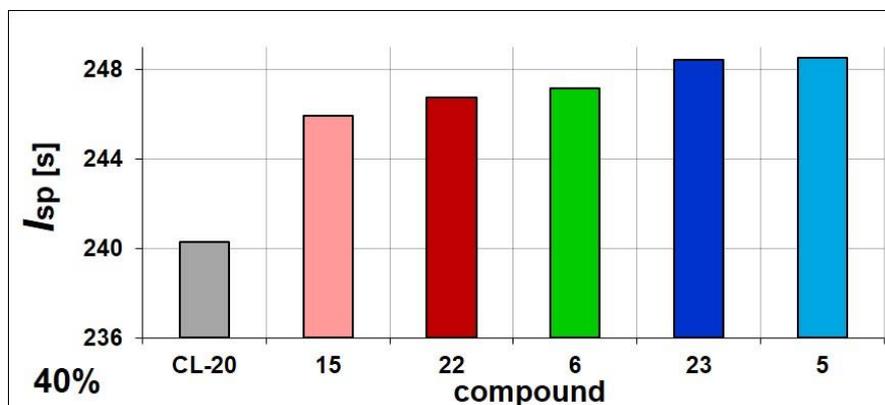
Figure 20. A series of the relative efficiency of the studied energetic components at the maximum I_{sp} values of the SCP compositions containing 19 vol% Active binder, AP, and HEDM **5**, **6**, **15**, **22**, **23** or CL-20 at 55 (A), 50 (B), 45 (C) and 40 (D) wt%.

Explosive performance of compounds 5, 6, 15, 22 and 23

Table 18. Physicochemical and explosive properties of **5**, **6**, **15**, **22** and **23** in comparison with RDX, HMX, and CL-20 (<u>**all density measured using a gas pycnometer at room temperature**</u>).

Compd	Formula	α^a	H%[b]	$T_{dec}{}^c$ [°C]	d^d [g cm^{-3}]	$\Delta H_f{}^e$ [kJ/kg (kJ mol^{-1})]	IS[f] [J]	FS[f] [N]	$D_v{}^g$ [km s^{-1}]	$P_{C\text{-}J}{}^g$ [GPa]	$Q_v{}^g$ [MJ kg^{-1}]
5	$C_7H_7N_{11}O_8$	0.46	1.89	173	1.902	+1590 (+593)	–	–	9.14	39.2	6.22
6	$C_7H_6N_{12}O_9$	0.53	1.50	209	1.899	+1479 (+594)	–	–	9.06	38.8	6.21
15	$C_9H_8N_{14}O_{14}$	0.64	1.50	203	1.868	+1035 (+555)	–	–	8.96	37.4	6.47
22	$C_7H_6N_{12}O_{10}$	0.59	1.45	223	1.924	+1397 (+584)	3.9	220	9.19	40.9	6.44
23	$C_8H_6N_{12}O_8$	0.42	1.52	238	1.858	+1980 (+788)	5.2	210	8.95	36.7	6.30
RDX	$C_3H_6N_6O_6$	0.67	2.72	204[h]	1.799	+301 (+67)[i]	8.0[h]	130[h]	8.96	36.2	6.17
HMX	$C_4H_8N_8O_8$	0.67	2.70	280[h]	1.897	+255 (+76)[i]	7.0[h]	130[h]	9.21	40.3	6.15
CL-20	$C_6H_6N_{12}O_{12}$	0.80	1.37	229[h]	2.021	+857 (+375)[j]	4.0[h]	80[h]	9.43	45.6	6.53

[a] Oxygen coefficient. For a compound with the molecular formula $C_xH_yN_wO_z$, $\alpha = z/(2x+y/2)$. [b] Hydrogen content. [c] Extrapolated decomposition onset temperature at a heating rate of 5 °C min^{-1} (DSC). [d] Density measured using a gas pycnometer at room temperature. [e] Standard enthalpy of formation determined by the method of combustion calorimetry. [f] The impact and friction sensitivity determined by BAM method using the STANAG standards.[22] [g] Detonation parameters: velocity, pressure and heat calculated with S&DV4.5 code.[23] [h] Ref.21 [i] Ref.21 [j] Ref.8d

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