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## **Electronic Supplementary Information (ESI)**

***Energetic alkylnitramines-functionalized pentanitro  
hexaazaisowurtzitanes: towards advanced less sensitive CL-20  
analogs***

Vladimir V. Parakhin,\* Galina V. Pokhvisneva, Tatiana V. Ternikova, Sergei V. Nikitin, Gennady A. Smirnov,  
Tatiana S. Kon'kova, David B. Lempert and Alla N. Pivkina

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# 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  $\mu\text{m}$ ) silica gel was used for preparative column and thin-layer chromatography. Melting points were determined with a Boethius Kofler melting point apparatus (heat rate  $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ ).  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{14}\text{N}$  NMR spectra of compounds **7–9** were recorded using a 300 MHz (Bruker AM300) nuclear magnetic resonance spectrometer operating at 300.1, 75.5 and 30.4, respectively.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{14}\text{N}$  and  $^{15}\text{N}\{^1\text{H}\}$  NMR spectra of compounds **10–14** were recorded using a 600 MHz (Bruker AV600) nuclear magnetic resonance spectrometer operating at 600.13, 150.9, 43.37 and 60.8 MHz, respectively. Acetone- $\text{d}_6$  was employed as NMR solvent. Chemical shifts in the  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$  and  $^{15}\text{N}$  spectra are reported in delta ( $\delta$ ) units, parts per million (ppm), relative to the internal standard  $\text{Me}_4\text{Si}$  (TMS) ( $^1\text{H}$ ,  $^{13}\text{C}$  – positive values correspond to downfield chemical shifts) and external standard  $\text{MeNO}_2$  ( $^{14}\text{N}$ ,  $^{15}\text{N}$  – negative values correspond to upfield shifts). The values of the spectral parameters  $J$  and  $\Delta\nu_{1/2}$  are given in Hz. IR spectra were recorded on a Bruker ALPHA-T spectrometer in the range from 4000 to  $400\text{ cm}^{-1}$  (resolution  $2\text{ cm}^{-1}$ ) using KBr pellets. 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. The powders densities were measured at  $\sim 30\text{ }^{\circ}\text{C}$  using a Micromeritics AccuPyc 1340 V2.01 helium pycnometer. All reagents were purchased from Acros and Sigma-Aldrich. Solvents were purified before use according to the standard procedures.<sup>1</sup> Thermochemical measurements were carried out on a precision automatic combustion calorimeter with an isothermal coating specifically developed for combustion of energetic compounds.<sup>2</sup> Thermal stability was studied on a DSC 204 HP (Netzsch) high-sensitive instrument. A sample with a mass of  $\sim 0.5\text{ mg}$  was placed into capped aluminum crucibles with cracked lids and heated at a linear rate of  $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  to  $300\text{ }^{\circ}\text{C}$  under a nitrogen flow of  $100\text{ mL}\cdot\text{min}^{-1}$ . Sensitivity toward impact and friction was measured on a BAM devices using STANAG<sup>3, 4</sup> standards in sets of 30 experiments. All other reagents were used without further purification. The starting 2,6,8,10,12-pentanitrohexaazaisowurtzitane (**1**) was prepared according to previously reported procedures of A. J. Bellamy<sup>5</sup> by mono-trifluoroacetylation of 2,6,8,12-tetraacetylhexaazaisowurtzitane (TADA) with TFAA/TFA, followed by nitrolysis of the

*N*-acetyl groups using HNO<sub>3</sub>/30% oleum and removal of the *N*-trifluoroacetyl protecting group by solvolysis with EtOH in ~40% total yield on 3 steps, dec >165 °C; <sup>1</sup>H NMR (300.1 MHz): δ 6.00 (broad s, 1H, NH), 6.70–6.73 (m, 2H, 2CH), 7.91 (s, 2H, 2CH), 7.97 (d, *J*<sub>H,H</sub> = 8 Hz, 2H, 2CH), these and other physicochemical parameters of **1** are in agreement with the data given in the literature. Used nitrourethane<sup>6, 7</sup> and ethylenedinitramine<sup>8</sup> were prepared according to the corresponding reported procedures.

## 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.

**Ethyl nitro[(2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitan-4-yl)methyl]carbamate (7).** A suspension of **1** (2.00 g, 5.09 mmol) and paraformaldehyde (1.20 g, 40.1 mmol) in AcCl (39.6 mL, 560 mmol) was stirred at 20 °C for 24 h, and then the excess AcCl was removed *in vacuo*. To the residue, dry MeCN (13.0 mL) was added, then a solution of nitrourethane (0.800 g, 5.97 mmol) and Et<sub>3</sub>N (0.840 mL, 6.03 mmol) in dry MeCN (5.0 mL) were added dropwise. The reaction mixture was stirred at 20 °C for 2 h and then was poured into water (100 mL). The precipitate formed was filtered off, washed with water (100 mL) and air-dried. The resulting solid can be further purified by preparative chromatography (elution with ethyl acetate–hexane, 1:2). Compound **7** (2.71 g, yield: 99%) was isolated as a colorless powder, mp 190–192 °C (dec.). <sup>1</sup>H NMR (300.1 MHz): δ 1.37 (t, *J*<sub>H,H</sub> = 7 Hz, 3 H, Me), 4.40 (k, *J*<sub>H,H</sub> = 7 Hz, 2 H, OCH<sub>2</sub>), 5.75 (s, 2 H, N <sup>cage</sup> CH<sub>2</sub>), 7.08 and 7.97 (d, *J*<sub>H,H</sub> = 8 Hz, 2 H, CH), 8.02 (s, 2 H, CH) ppm. <sup>13</sup>C NMR (75.5 MHz): δ 14.3 (Me), 65.9 (OCH<sub>2</sub>), 150.3 (C=O), 66.0 (N <sup>cage</sup> CH<sub>2</sub>), 71.7, 74.5 and 77.8 (CH) ppm. <sup>14</sup>N NMR (30.4 MHz): δ –46 (Δ*v*<sub>1/2</sub> = 80 Hz, NNO<sub>2</sub> <sup>chain</sup> ), –41 (Δ*v*<sub>1/2</sub> = 120 Hz) and –40 (Δ*v*<sub>1/2</sub> = 106 Hz) (NNO<sub>2</sub> <sup>cage</sup> ) ppm. IR (KBr):  $\tilde{\nu}$  3061 (m) (CH<sub>2</sub>/Me), 1774 (s) (C=O), 1601 (vs), 1579 (vs) and 1546 (m) (asymm. NNO<sub>2</sub> <sup>cage</sup> ), 1529 (m) (asymm. NNO<sub>2</sub> <sup>chain</sup> ), 1331 (s), 1289 (s) and 1269 (vs) (symm. NNO<sub>2</sub>) cm<sup>-1</sup>. HRMS (ESI): *m/z* calcd for [C<sub>10</sub>H<sub>13</sub>N<sub>13</sub>O<sub>14</sub> + Na<sup>+</sup>]: 562.0597; found [*M* + Na]<sup>+</sup>: 562.0609.

***N*-[(2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitan-4-yl)methyl]nitramide (8).** A suspension of **7** (2.71 g, 4.21 mmol) in AcOEt (30.0 mL) was

saturated with gaseous ammonia, the reaction mixture was stirred at 20 °C for ~0.5 h until **7** disappeared by TLC (eluent, ethyl acetate–hexane, 1:2) and the solvent was removed *in vacuo*. To the residue, water (10 mL) was added, the precipitate formed was filtered off, washed with water (10 mL) and air-dried. Compound **8** (1.81 g, yield: 77%) was isolated as a colorless powder, dec. (observed on Kofler's table, 5 °C·min<sup>-1</sup>): 195 °C. Density (pycnometer, 30 °C): 1.901 g·cm<sup>-3</sup>. <sup>1</sup>H NMR (300.1 MHz): δ 5.06 (s, 2 H, N<sup>cage</sup>CH<sub>2</sub>), 6.69 and 7.95 (d, *J*<sub>H,H</sub> = 8 Hz, 2 H, CH), 8.03 (s, 2 H, CH) ppm. <sup>13</sup>C NMR (75.5 MHz): δ 62.7 (N<sup>cage</sup>CH<sub>2</sub>), 71.3, 74.4 and 77.5 (CH) ppm. <sup>14</sup>N NMR (30.4 MHz): δ -41 (Δ*v*<sub>1/2</sub> = 93 Hz) and -39 (Δ*v*<sub>1/2</sub> = 106 Hz) (NNO<sub>2</sub><sup>cage</sup>), -30 (Δ*v*<sub>1/2</sub> = 60 Hz, NNO<sub>2</sub><sup>chain</sup>) ppm. IR (KBr):  $\tilde{\nu}$  3297 (m) (NH), 3044 (m) (CH<sub>2</sub>), 1608 (s), 1590 (vs) and 1553 (s) (asymm. NNO<sub>2</sub><sup>cage</sup>), 1339 (s), 1280 (vs) and 1261 (vs) (symm. NNO<sub>2</sub>) cm<sup>-1</sup>. Elemental analysis for C<sub>7</sub>H<sub>9</sub>N<sub>13</sub>O<sub>12</sub> (467.23): calcd C, 17.99; H, 1.94; N, 38.97 %; found C, 18.29; H, 2.00; N, 38.64 %.

***N*-[2-(nitramino)ethyl]-*N*-[(2,6,8,10,12-pentanitro-2,4,6,8,10,12-**

**hexaazaisowurtzitan-4-yl)methyl]nitramide (**9**).** A suspension of **1** (0.500 g, 1.27 mmol) and paraformaldehyde (0.300 g, 10.0 mmol) in AcCl (9.90 mL, 140 mmol) was stirred at 20 °C for 24 h, and the excess AcCl was removed *in vacuo*. To the residue, dry MeCN (8.0 mL) was added, the resulting suspension was added in portions to the solution of EDNA (0.250 g, 1.67 mmol) and Et<sub>3</sub>N (0.25 mL, 1.80 mmol) in dry MeCN (8.0 mL). The reaction mixture was stirred at 20 °C for 3 h, and then was poured into water (30 mL). The precipitate of **9** (0.400 g, yield: 57%) was filtered off, washed with water (30 mL) and air-dried. An additional amount of **9** (0.170 g, yield: 24%) was isolated by extraction of the mother liquor with AcOEt (3×20 mL), followed by drying the extract over MgSO<sub>4</sub> and evaporating the solvent *in vacuo*. The resulting product can be further purified by preparative chromatography (elution with ethyl acetate–hexane, 1:1). In total, compound **9** (0.570 g, yield: 81%) was obtained as a colorless powder, dec. (observed on Kofler's table, 5 °C·min<sup>-1</sup>): 208 °C. Density (pycnometer, 30 °C): 1.869 g·cm<sup>-3</sup>. <sup>1</sup>H NMR (300.1 MHz): δ 3.94 and 4.25 (t, *J*<sub>H,H</sub> = 6 Hz, 2 H, CH<sub>2</sub><sup>chain</sup>), 5.39 (s, 2 H, N<sup>cage</sup>CH<sub>2</sub>), 7.01 and 7.97 (d, *J*<sub>H,H</sub> = 8 Hz, 2 H, CH), 8.06 (s, 2 H, CH), 10.87 (br s, 2 H, NH) ppm. <sup>13</sup>C NMR (75.5 MHz): δ 43.8 and 50.1 (CH<sub>2</sub><sup>chain</sup>), 68.5 (N<sup>cage</sup>CH<sub>2</sub>), 71.5, 74.4 and 77.6 (CH) ppm. <sup>14</sup>N NMR (30.4 MHz): δ -41 (Δ*v*<sub>1/2</sub> = 106 Hz) and -39 (Δ*v*<sub>1/2</sub> = 106 Hz) (NNO<sub>2</sub><sup>cage</sup>), -31 (Δ*v*<sub>1/2</sub> = 80 Hz) and -28 (Δ*v*<sub>1/2</sub> = 47 Hz) (NNO<sub>2</sub><sup>chain</sup>) ppm. IR (KBr):  $\tilde{\nu}$  3327 (m) (NH), 3037 (m) (CH<sub>2</sub>), 1619 (vs), 1592 (vs) and 1574 (vs) (asymm. NNO<sub>2</sub><sup>cage</sup>), 1520 (m) (asymm. NNO<sub>2</sub><sup>chain</sup>), 1336 (s), 1274 (vs) and 1258 (vs) (symm.

$\text{NNO}_2$ )  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd for  $[\text{C}_9\text{H}_{13}\text{N}_{15}\text{O}_{14} + \text{Na}^+]$ : 578.0659; found  $[M + \text{Na}]^+$ : 578.0663.

***N*-methyl-*N*-[(2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitan-4-yl)methyl]nitramide (10).** To a solution of **8** (0.400 g, 0.857 mmol) in dry MeCN (8.0 mL)  $\text{Et}_3\text{N}$  (0.14 mL, 1.01 mmol) and MeI (0.2 mL, 3.23 mmol) were added. The reaction mixture was stirred at 20 °C for 5 days and then was diluted with water (100 mL). The product was extracted with AcOEt (3×10 mL), the extract was sequentially washed with brine (10 mL), 10% aqueous solution of  $\text{Na}_2\text{SO}_3$  (10 mL) and water (10 mL). After drying the extract over  $\text{MgSO}_4$ , and evaporating of the solvent *in vacuo*, **10** was isolated from the residue by preparative TLC (elution with benzene–acetone, 7:1). The crude product was further purified by boiling in EtOH for 5 min, followed by washing with small amount of EtOH,  $\text{Et}_2\text{O}$  and drying *in vacuo*. Compound **10** (0.206 g, yield: 50%) was obtained as a colorless powder. Density (XRD, 25 °C):  $1.860 \text{ g}\cdot\text{cm}^{-3}$ . Density (pycnometer, 31 °C):  $1.848 \text{ g}\cdot\text{cm}^{-3}$ . DSC (5 °C·min<sup>-1</sup>): onset 222 °C, max 226 °C. Sensitivities: IS = 6.1 J; FS = 180 N. <sup>1</sup>H NMR (600.13 MHz):  $\delta$  3.52 (s, 3 H, Me), 5.35 (s, 2 H,  $\text{N}^{\text{cage}}\text{CH}_2$ ), 6.99 and 7.99 (d,  $J_{\text{H,H}} = 7 \text{ Hz}$ , 2 H, CH), 8.05 (s, 2 H, CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz):  $\delta$  38.9 (Me), 68.7 ( $\text{N}^{\text{cage}}\text{CH}_2$ ), 71.2, 74.2 and 77.3 (CH) ppm. <sup>14</sup>N NMR (43.37 MHz):  $\delta$  -41 ( $\Delta\nu_{1/2} = 102 \text{ Hz}$ ) and -38 ( $\Delta\nu_{1/2} = 97 \text{ Hz}$ ) ( $\text{NNO}_2^{\text{cage}}$ ), -29 ( $\Delta\nu_{1/2} = 34 \text{ Hz}$ ,  $\text{NNO}_2^{\text{chain}}$ ) ppm. <sup>15</sup>N NMR ([INVGATED], 60.8 MHz):  $\delta$  -320.7 ( $\text{N}^{\text{cage}}\text{CH}_2$ ), -203.3 ( $\text{NNO}_2^{\text{chain}}$ ), -199.5, -180.8 and -177.7 ( $\text{N}^{\text{cage}}\text{NO}_2$ ), -40.7, -39.9 and -37.3 ( $\text{NNO}_2^{\text{cage}}$ ), -28.6 ( $\text{NNO}_2^{\text{chain}}$ ) ppm. IR (KBr):  $\nu$  3051 (m) and 3033 (m) ( $\text{CH}_2/\text{Me}$ ), 1610 (s), 1589 (vs) and 1560 (s) (asymm.  $\text{NNO}_2^{\text{cage}}$ ), 1522 (s) (asymm.  $\text{NNO}_2^{\text{chain}}$ ), 1340 (s), 1295 (vs) and 1272 (vs) (symm.  $\text{NNO}_2$ )  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd for  $[\text{C}_8\text{H}_{11}\text{N}_{13}\text{O}_{12} - \text{H}^+]$ : 480.0577; found  $[M - \text{H}]^-$ : 580.0567.

***N*-[2-(methylnitramino)ethyl]-*N*-[(2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitan-4-yl)methyl]nitramide (11).** To a solution of **9** (0.100 g, 0.180 mmol) in dry MeCN (5.0 mL) was added  $\text{Et}_3\text{N}$  (0.03 mL, 0.216 mmol) and MeI (0.02 mL, 0.323 mmol). The reaction mixture was stirred at 20 °C for 5 days, and then was diluted with water (100 mL). The product was extracted with AcOEt (3×5 mL), the extract was sequentially washed with brine (5 mL), 10% aqueous solution of  $\text{Na}_2\text{SO}_3$  (5 mL) and water (5 mL). After drying the extract over  $\text{MgSO}_4$  and evaporating of the solvent *in vacuo*, compound **11** (0.023 g, yield: 22%) was isolated from the residue by preparative TLC (elution with benzene–acetone, 7:1) as a colorless crystals, dec. (observed on Kofler's table, 5 °C·min<sup>-1</sup>): 197°C. Density (pycnometer, 31 °C):  $1.822 \text{ g}\cdot\text{cm}^{-3}$ . <sup>1</sup>H NMR (600.13 MHz):  $\delta$  3.45 (s, 3 H, Me), 4.24 and 4.32 (t,  $J_{\text{H,H}} = 5 \text{ Hz}$ , 2 H,



CH<sub>2</sub><sup>chain</sup>), 5.40 (s, 2 H, N<sup>cage</sup>CH<sub>2</sub>), 7.00 and 7.98 (d, *J*<sub>H,H</sub> = 8 Hz, 2 H, CH), 8.06 (s, 2 H, CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz): δ 39.6 (Me), 49.4 and 51.1 (CH<sub>2</sub><sup>chain</sup>), 68.4 (N<sup>cage</sup>CH<sub>2</sub>), 71.4, 74.4 and 77.5 (CH) ppm. <sup>14</sup>N NMR (43.37 MHz): δ -41 and -38 (Δ*v*<sub>1/2</sub> = 128 Hz, NNO<sub>2</sub><sup>cage</sup>), -30 (Δ*v*<sub>1/2</sub> = 62 Hz) and -28 (Δ*v*<sub>1/2</sub> = 26 Hz) (NNO<sub>2</sub><sup>chain</sup>) ppm. <sup>15</sup>N NMR ([INVGATED], 60.8 MHz): δ -320.0 (N<sup>cage</sup>CH<sub>2</sub>), -210.5 (N<sup>chain</sup>NO<sub>2</sub>), -199.3 (N<sup>cage</sup>NO<sub>2</sub>), -196.5 (N<sup>chain</sup>NO<sub>2</sub>), -180.4 and -177.6 (NNO<sub>2</sub><sup>cage</sup>), -40.8, -39.9 and -37.4 (NNO<sub>2</sub><sup>cage</sup>), -30.2 and -27.3 (NNO<sub>2</sub><sup>chain</sup>) ppm. IR (KBr):  $\tilde{\nu}$  3040 (m) (CH<sub>2</sub>/Me), 1607 (s), 1587 (vs) (asymm. NNO<sub>2</sub><sup>cage</sup>), 1540 (s) and 1510 (s) (asymm. NNO<sub>2</sub><sup>chain</sup>), 1331 (s), 1282 (vs) and 1260 (vs) (symm. NNO<sub>2</sub>) cm<sup>-1</sup>. HRMS (ESI): *m/z* calcd for [C<sub>10</sub>H<sub>15</sub>N<sub>15</sub>O<sub>14</sub> + Na<sup>+</sup>]: 592.0815; found [*M* + Na]<sup>+</sup>: 592.0814.

**2-nitro-1-[(2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitan-4-yl)methyl](nitramino)methyl}guanidine (12).**

A suspension of 1-hydroxymethyl-2-nitroguanidine (0.500 g, 3.73 mmol) and SOCl<sub>2</sub> (2.8 mL, 38.6 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10.0 mL) was stirred at 20 °C for 24 h, then the precipitate was filtered off, washed with dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and dried *in vacuo*. The resulting solid was added in portions to the solution of **8** (1.40 g, 3.00 mmol) and Et<sub>3</sub>N (0.55 mL, 3.96 mmol) in dry MeCN (10.0 mL). The reaction mixture was stirred at 20 °C for 1.5 h, and then, under stirring, was poured into water (100 mL). The precipitate formed was filtered off, washed with water (100 mL) and air-dried. Compound **12** was isolated from the solid mixture by preparative TLC (elution with ethyl acetate–hexane, 1:1). The product was further purified by reprecipitation with water from a solution of compound **8** in MeCN. Compound **12** (0.876 g, yield: 50%) was obtained as a colorless powder. Density (XRD, 25 °C): 1.860 g·cm<sup>-3</sup>. Density (pycnometer, 32 °C): 1.846 g·cm<sup>-3</sup>. DSC (5 °C·min<sup>-1</sup>): onset 203 °C, max 215 °C. Sensitivities: IS = 4.3 J; FS = 180 N. <sup>1</sup>H NMR (600.13 MHz): δ 5.27 (d, *J*<sub>H,H</sub> = 6 Hz, 2 H, CH<sub>2</sub><sup>chain</sup>), 5.54 (s, 2 H, N<sup>cage</sup>CH<sub>2</sub>), 7.20 (d, *J*<sub>H,H</sub> = 8 Hz, 2 H, CH), 7.51 (br t, *J*<sub>H,H</sub> = 5 Hz, 1 H, NH), 7.93 (d, *J*<sub>H,H</sub> = 8 Hz, 2 H, CH), 8.01 (s, 2 H, CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz): δ 55.7 (CH<sub>2</sub><sup>chain</sup>), 68.0 (N<sup>cage</sup>CH<sub>2</sub>), 71.3, 74.4 and 77.2 (CH), 160.2 (C=NNO<sub>2</sub>) ppm. <sup>14</sup>N NMR (43.37 MHz): δ -135 (Δ*v*<sub>1/2</sub> = 80 Hz, C=N–NO<sub>2</sub>), -41 (Δ*v*<sub>1/2</sub> = 121 Hz) and -38 (Δ*v*<sub>1/2</sub> = 140 Hz) (NNO<sub>2</sub><sup>cage</sup>), -31 (Δ*v*<sub>1/2</sub> = 85 Hz, NNO<sub>2</sub><sup>chain</sup>), -14 (Δ*v*<sub>1/2</sub> = 87 Hz, C=N–NO<sub>2</sub>) ppm. <sup>15</sup>N NMR ([INVGATED], 60.8 MHz): δ -321.3 (N<sup>cage</sup>CH<sub>2</sub>), -298.9 (NH<sub>2</sub>), -294.8 (NH), -199.0 (N<sup>cage</sup>NO<sub>2</sub>), -184.6 (N<sup>chain</sup>NO<sub>2</sub>), -181.6 and -178.5 (N<sup>cage</sup>NO<sub>2</sub>), -40.5, -40.0 and -37.5 (NNO<sub>2</sub><sup>cage</sup>), -30.4 (NNO<sub>2</sub><sup>chain</sup>), -13.1 (C=NNO<sub>2</sub>) ppm. IR (KBr):  $\tilde{\nu}$  3464 (m) and 3423 (s) (NH<sub>2</sub>), 3358 (m) (NH), 3044 (m) (CH<sub>2</sub>), 1643 (s) (C=N), 1596 (vs) (asymm. NNO<sub>2</sub><sup>cage</sup>), 1532 (m) (asymm. NNO<sub>2</sub><sup>chain</sup>), 1449 (m) (asymm. C=N–NO<sub>2</sub>), 1308 (s) (symm. C=N–NO<sub>2</sub>), 1330 (s), 1283 (s) and 1261 (vs)

(symm.  $\text{NNO}_2^{\text{cage}}$ )  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd for  $[\text{C}_9\text{H}_{13}\text{N}_{17}\text{O}_{14} + \text{H}^+]$ : 584.0901; found  $[\text{M} + \text{H}]^+$ : 584.0890.

**2-nitro-1-[(2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitan-4-yl)methyl(2-(nitramino)ethyl)](nitramino)methylguanidine (13).**

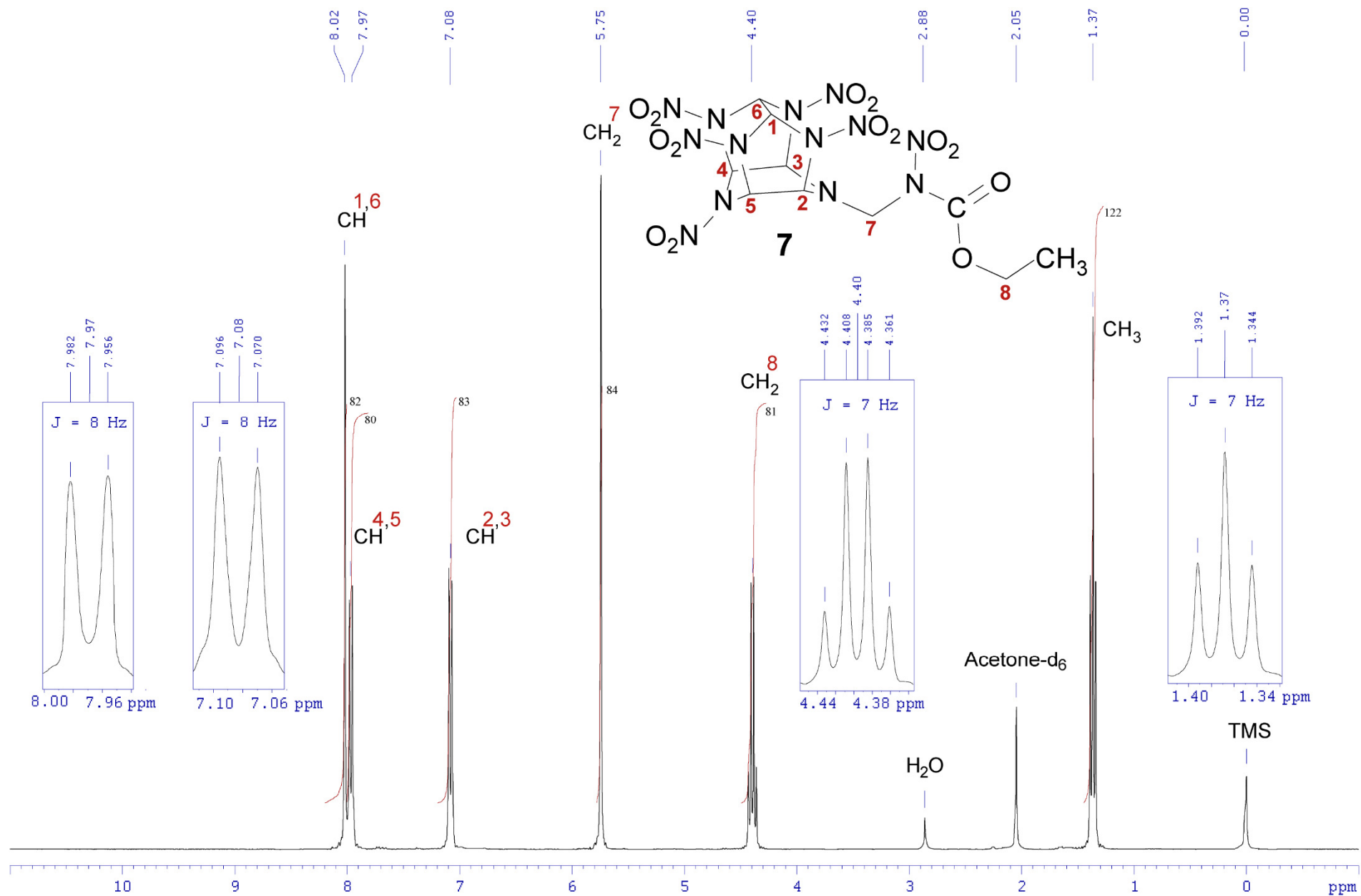
A suspension of 1-hydroxymethyl-2-nitroguanidine (0.100 g, 0.746 mmol) and  $\text{SOCl}_2$  (0.56 mL, 7.72 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (2.0 mL) was stirred at 20 °C for 24 h, then the precipitate was filtered off, washed with dry  $\text{CH}_2\text{Cl}_2$  (2 mL) and dried *in vacuo*. The resulting solid was added in portions to the solution of **9** (0.200 g, 0.360 mmol) and  $\text{Et}_3\text{N}$  (0.06 mL, 0.432 mmol) in dry MeCN (10.0 mL). The reaction mixture was stirred at 20 °C for 2.5 h, and then, under stirring, was poured into water (50 mL). The precipitate formed was filtered off, washed with water (50 mL) and air-dried. Compound **13** (0.065 g, yield: 27%) was isolated from the solid mixture by preparative TLC (elution with ethyl acetate–hexane, 1:1) as a colorless powder, dec. (observed on Kofler's table, 5 °C·min<sup>-1</sup>): 178 °C. Density (pycnometer, 33 °C): 1.804 g·cm<sup>-3</sup>. <sup>1</sup>H NMR (600.13 MHz):  $\delta$  4.36 (s, 4 H,  $\text{CH}_2^{\text{chain}}$ ), 5.18 (d,  $J_{\text{H,H}} = 7$  Hz, 2 H,  $\text{CH}_2^{\text{chain}}$ ), 5.40 (s, 2 H,  $\text{N}^{\text{cage}}\text{CH}_2$ ), 6.99 (d,  $J_{\text{H,H}} = 8$  Hz, 2 H, CH), 7.60 (br s, 1 H, NH), 7.97 (d,  $J_{\text{H,H}} = 8$  Hz, 2 H, CH), 8.02 (s, 2 H, CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz):  $\delta$  49.8, 50.4 and 57.7 ( $\text{CH}_2^{\text{chain}}$ ), 68.7 ( $\text{N}^{\text{cage}}\text{CH}_2$ ), 71.3, 74.2 and 77.3 (CH), 160.2 (C=NNO<sub>2</sub>) ppm. <sup>14</sup>N NMR (43.37 MHz):  $\delta$  -136 ( $\Delta\nu_{1/2} = 111$  Hz, C=N–NO<sub>2</sub>), -41 ( $\Delta\nu_{1/2} = 136$  Hz) and -38 ( $\Delta\nu_{1/2} = 158$  Hz) ( $\text{NNO}_2^{\text{cage}}$ ), -30 ( $\Delta\nu_{1/2} = 102$  Hz,  $\text{NNO}_2^{\text{chain}}$ ), -14 ( $\Delta\nu_{1/2} = 106$  Hz, C=N–NO<sub>2</sub>) ppm. <sup>15</sup>N NMR ([INVGATED], 60.8 MHz):  $\delta$  -320.3 ( $\text{N}^{\text{cage}}\text{CH}_2$ ), -298.5 (NH<sub>2</sub>), -199.1 ( $\text{N}^{\text{cage}}\text{NO}_2$ ), -195.2 and -193.2 ( $\text{N}^{\text{chain}}\text{NO}_2$ ), -180.8 and -177.9 ( $\text{N}^{\text{cage}}\text{NO}_2$ ), -135.6 (C=NNO<sub>2</sub>) -40.6, -39.9 and -37.5 ( $\text{NNO}_2^{\text{cage}}$ ), -29.5 and -29.0 ( $\text{NNO}_2^{\text{chain}}$ ), -13.2 (C=NNO<sub>2</sub>) ppm IR (KBr):  $\tilde{\nu}$  3435 (m) and 3345 (m) (NH<sub>2</sub> and NH), 3039 (w) (CH<sub>2</sub>), 1641 (m) (C=N), 1595 (m) (asymm.  $\text{NNO}_2^{\text{cage}}$ ), 1533 (m) (asymm.  $\text{NNO}_2^{\text{chain}}$ ), 1455 (m) (asymm. C=N–NO<sub>2</sub>), 1330 (m), 1285 (vs) and 1266 (vs) (symm.  $\text{NNO}_2$ )  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  calcd for  $[\text{C}_{11}\text{H}_{17}\text{N}_{19}\text{O}_{16} + \text{H}^+]$ : 672.1173; found  $[\text{M} + \text{H}]^+$ : 672.1166.

**N,N'-bis[(2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitan-4-yl)methyl]nitramide (14).**

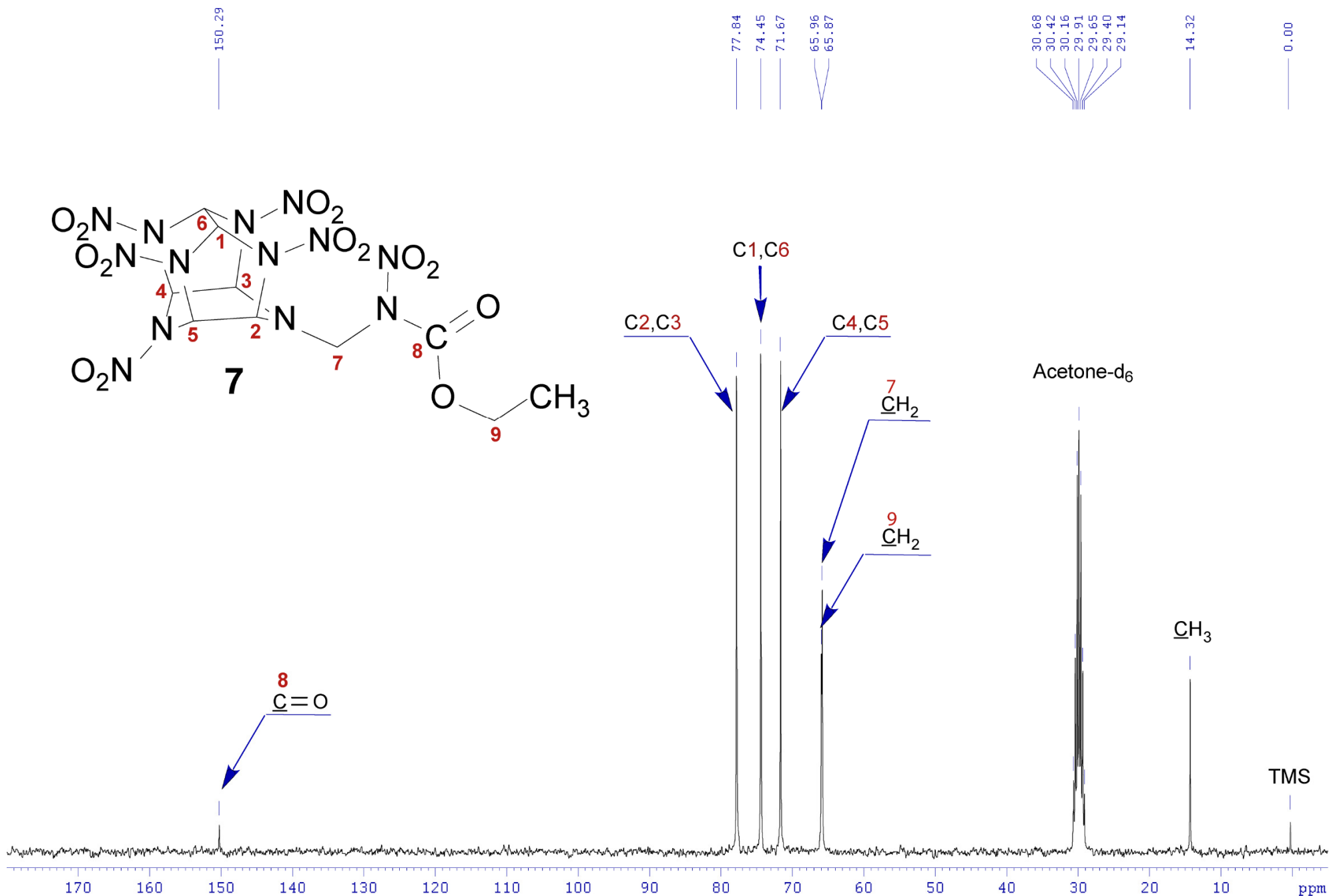
A suspension of **1** (0.500 g, 1.27 mmol) and paraformaldehyde (0.300 g, 10.0 mmol) in AcCl (9.90 mL, 140 mmol) was stirred at 20 °C for 24 h, and the excess AcCl was removed *in vacuo*. To the residue, dry MeCN (13.0 mL) was added, the resulting suspension was added in portions to the solution of **8** (0.420 g, 0.899 mmol) and  $\text{Et}_3\text{N}$  (0.14 mL, 1.01 mmol) in dry MeCN (8.0 mL). The reaction mixture was stirred at 20 °C for 3 h, then the solid was filtered off and filtrate was poured into water (30 mL). The precipitate formed was filtered off, washed with

water (100 mL) and air-dried. Compound **14** was isolated from the solid mixture by preparative TLC (elution with ethyl acetate–hexane, 1:1). The crude product was further purified by boiling in *i*-PrOH for 3 h, followed by heating at 70 °C in water for 3 h and drying under heating at 90 °C *in vacuo*. Compound **14** (0.300 g, yield: 38%) was obtained as a colorless powder. Density (pycnometer, 33 °C): 1.921 g·cm<sup>-3</sup>. DSC (5 °C·min<sup>-1</sup>): onset 223 °C, max 229 °C. Sensitivities: IS = 8.0 J; FS = 150 N. <sup>1</sup>H NMR (600.13 MHz): δ 5.50 (s, 2 H, N<sup>cage</sup>CH<sub>2</sub>), 7.00 and 7.95 (d, *J*<sub>H,H</sub> = 7 Hz, 2 H, CH), 8.07 (s, 2 H, CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz): δ 67.3 (N<sup>cage</sup>CH<sub>2</sub>), 71.3, 74.5 and 77.4 (CH) ppm. <sup>14</sup>N NMR (43.37 MHz): δ -41 (Δ*v*<sub>1/2</sub> = 192 Hz) (NNO<sub>2</sub><sup>cage</sup>), -34 (Δ*v*<sub>1/2</sub> = 174 Hz, NNO<sub>2</sub><sup>chain</sup>) ppm. <sup>15</sup>N NMR ([INVGATED], 60.8 MHz): δ -319.1 (N<sup>cage</sup>CH<sub>2</sub>), -199.6 (N<sup>cage</sup>NO<sub>2</sub>), -190.2 (NNO<sub>2</sub><sup>chain</sup>), -180.1 and -177.3 (N<sup>cage</sup>NO<sub>2</sub>), -41.1, -40.0 and -37.1 (NNO<sub>2</sub><sup>cage</sup>), -33.7 (NNO<sub>2</sub><sup>chain</sup>) ppm. IR (KBr):  $\tilde{\nu}$  3040 (m) (CH<sub>2</sub>), 1595 (vs),(asymm. NNO<sub>2</sub>), 1330 (s), 1284 (vs) and 1264 (vs) (symm. NNO<sub>2</sub>) cm<sup>-1</sup>. Elemental analysis for C<sub>14</sub>H<sub>16</sub>N<sub>24</sub>O<sub>22</sub> (872.43): calcd C, 19.27; H, 1.85; N, 38.53 %; found C, 19.44; H, 2.00; N, 38.16 %. Slow crystallization of compound **14** from MeCN–H<sub>2</sub>O gave a co-crystal of compound **14** with two molecules of MeCN as a colorless crystals, m.p. 117–122 °C (dec.). Density (X-ray, 25 °C): 1.789 g·cm<sup>-3</sup>. Elemental analysis for C<sub>18</sub>H<sub>22</sub>N<sub>26</sub>O<sub>22</sub> (954.53): calcd C, 22.65; H, 2.32; N, 38.15 %; found C, 22.62; H, 1.88; N, 38.09 %.

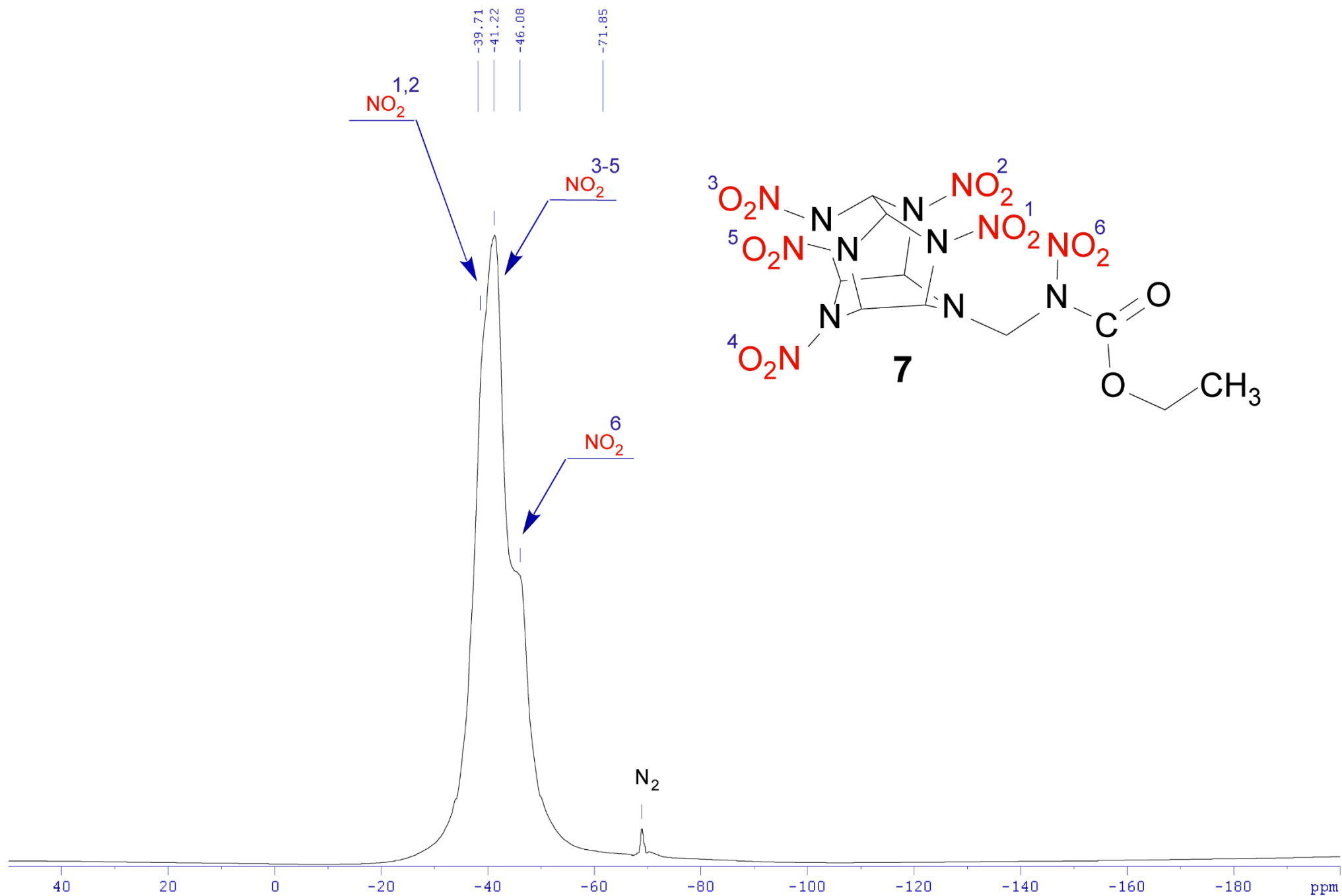
**$^1\text{H}$  NMR (300.1 MHz,  $[\text{D}_6]$ acetone) spectrum of compound 7**



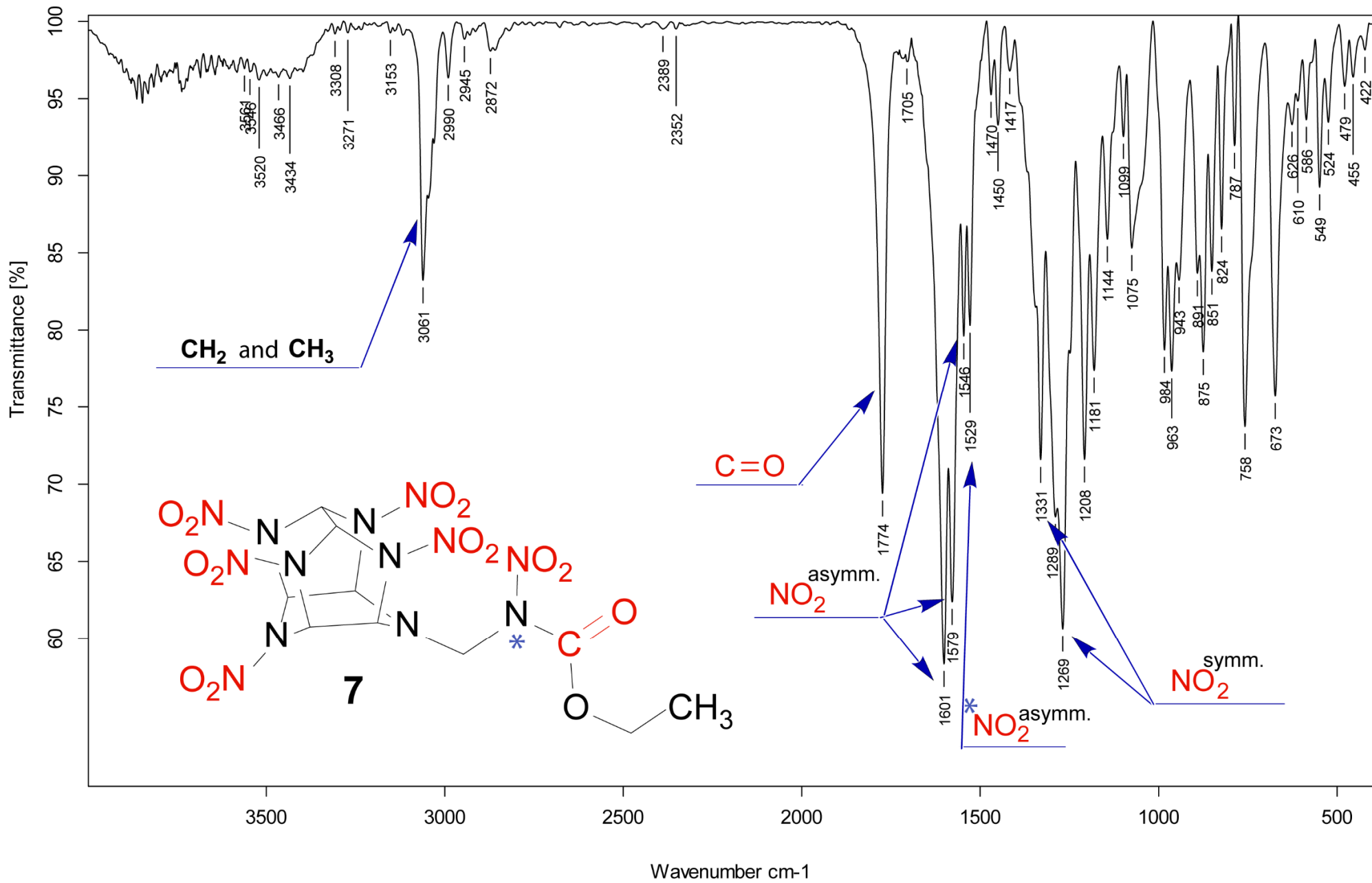
# $^{13}\text{C}$ NMR (75.5 MHz, $[\text{D}_6]$ acetone) spectrum of compound 7



# $^{14}\text{N}$ NMR (21.7 MHz, $[\text{D}_6]$ acetone) spectrum of compound 7



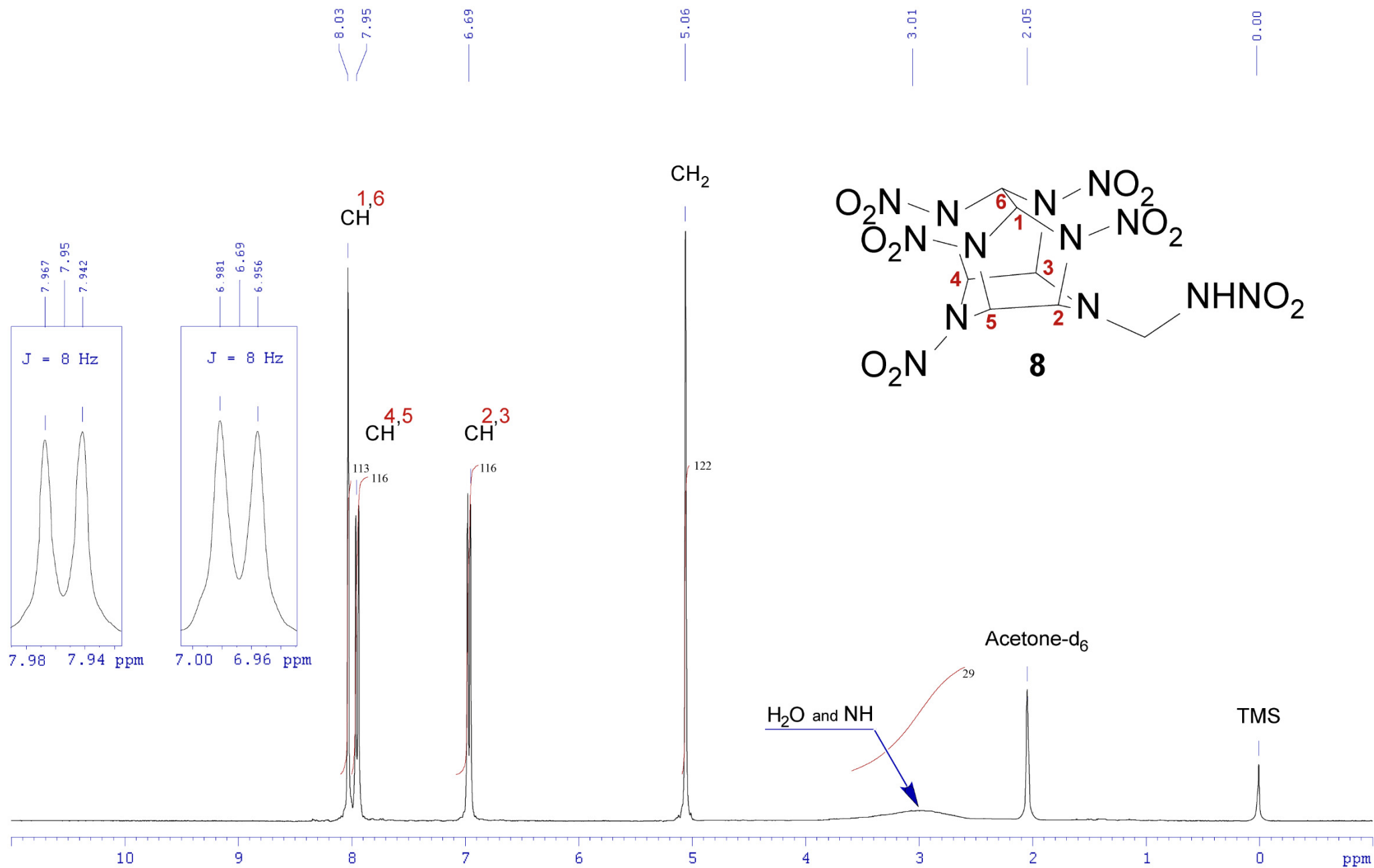
# IR (KBr) spectrum of compound 7



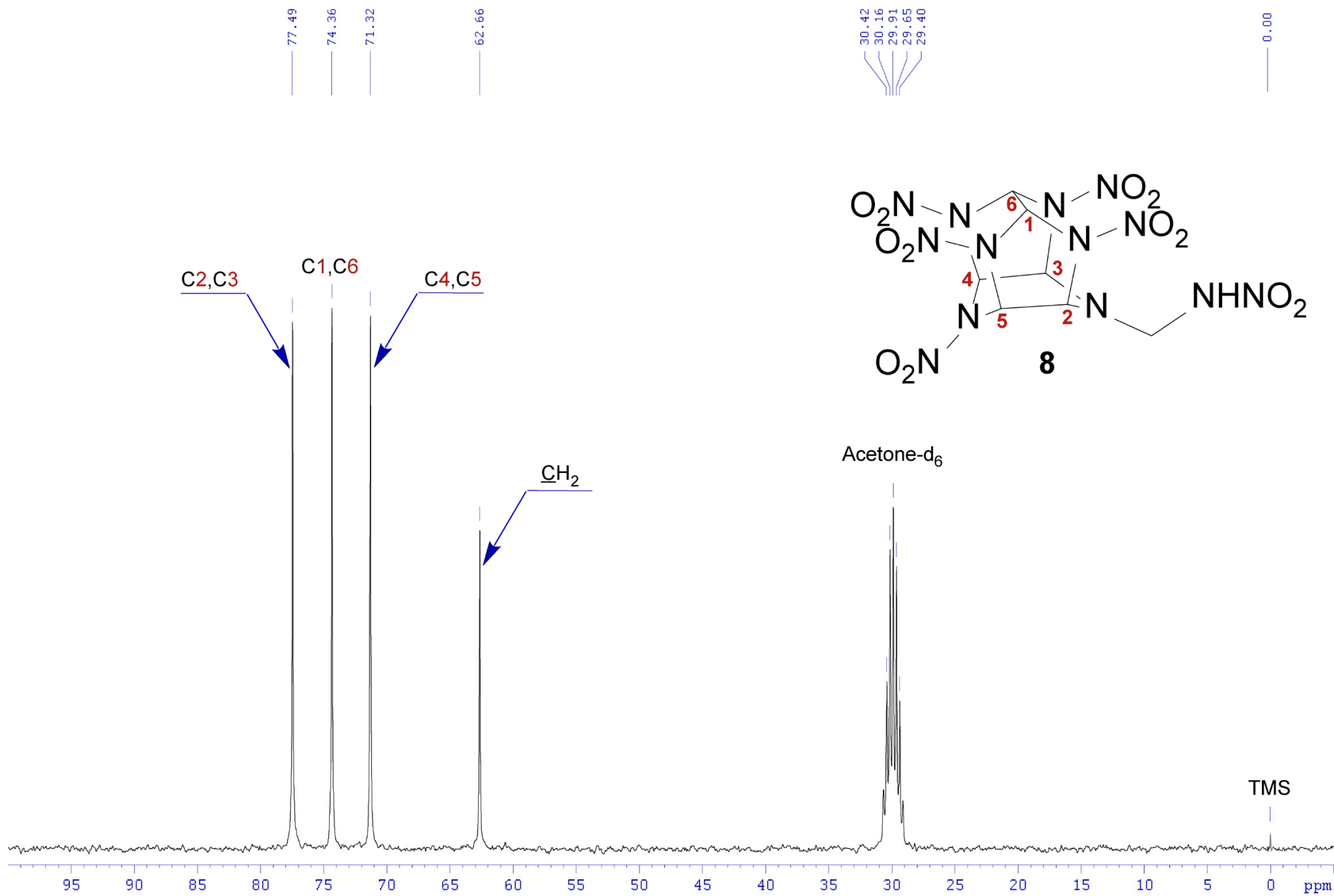




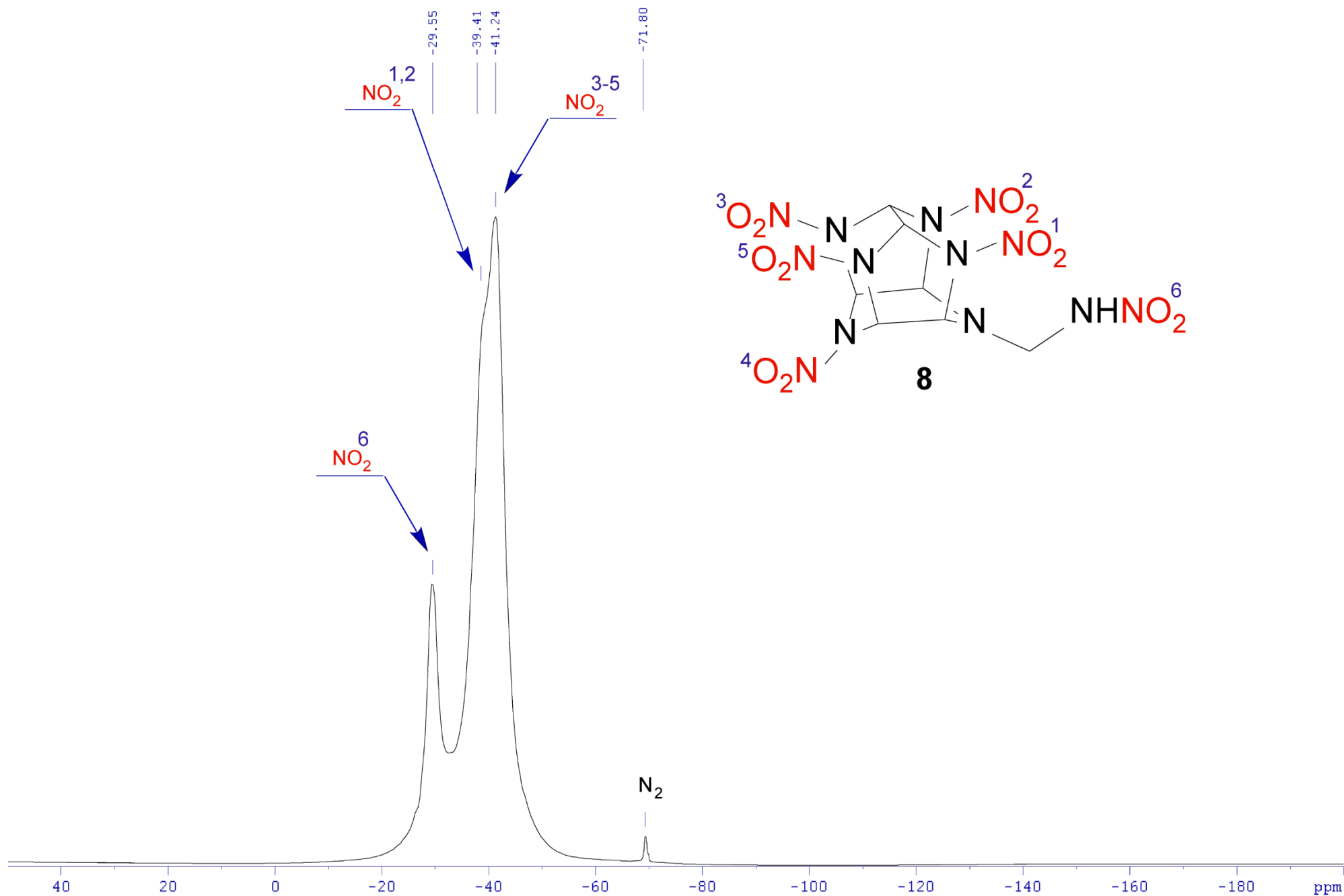
# <sup>1</sup>H NMR (300.1 MHz, [D<sub>6</sub>]acetone) spectrum of compound 8



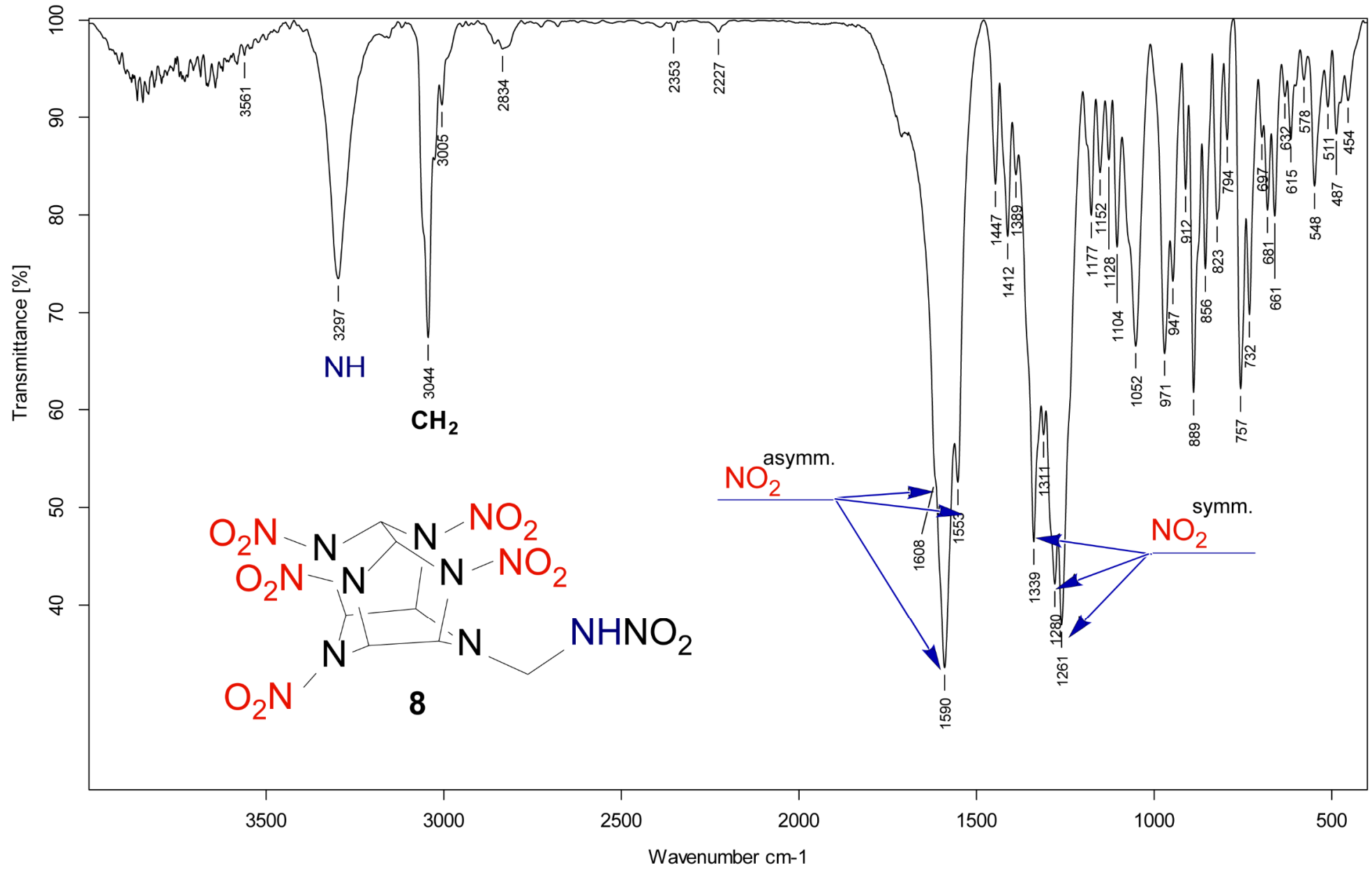
# $^{13}\text{C}$ NMR (75.5 MHz, $[\text{D}_6]$ acetone) spectrum of compound 8



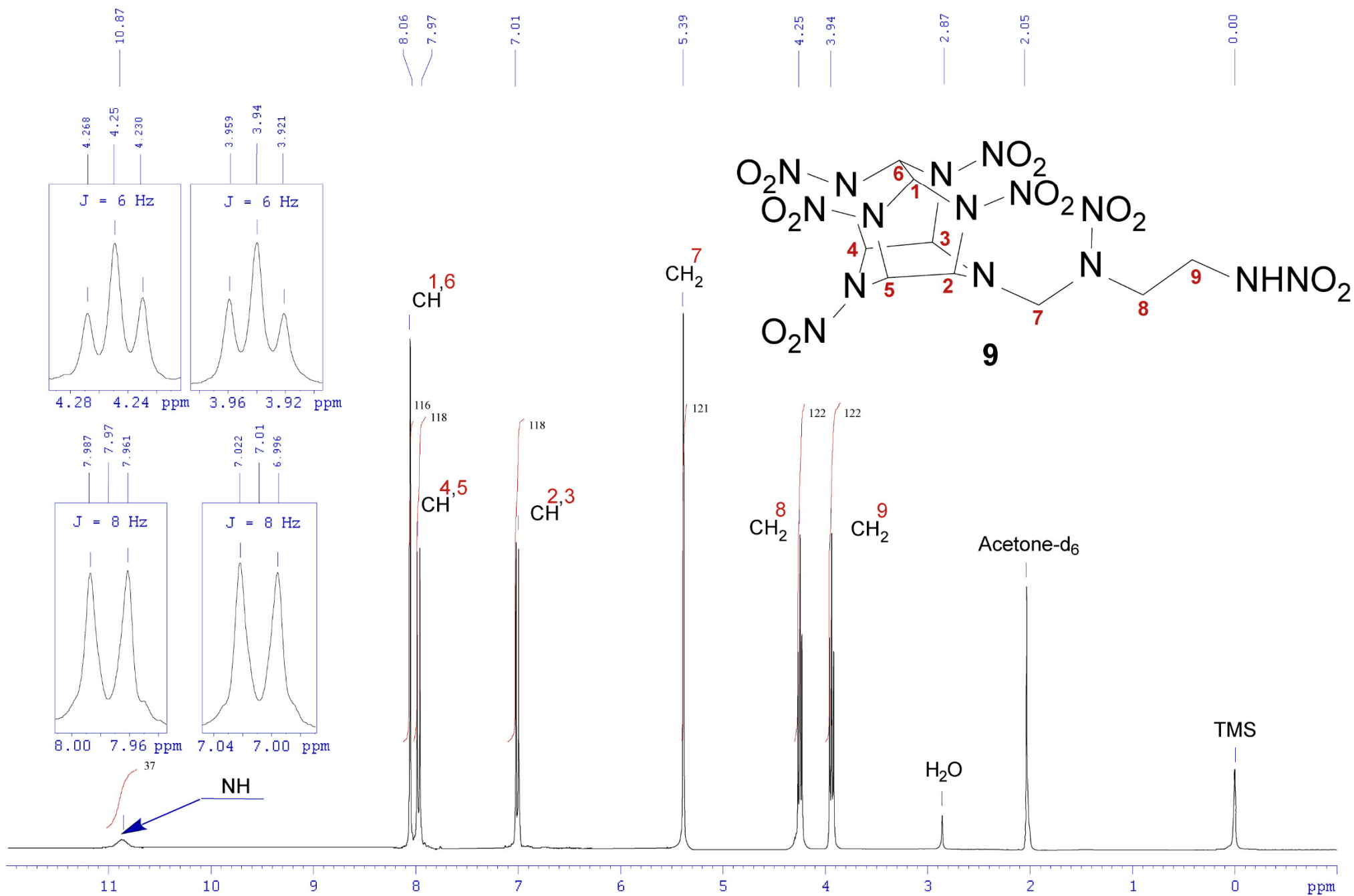
# $^{14}\text{N}$ NMR (21.7 MHz, $[\text{D}_6]$ acetone) spectrum of compound 8



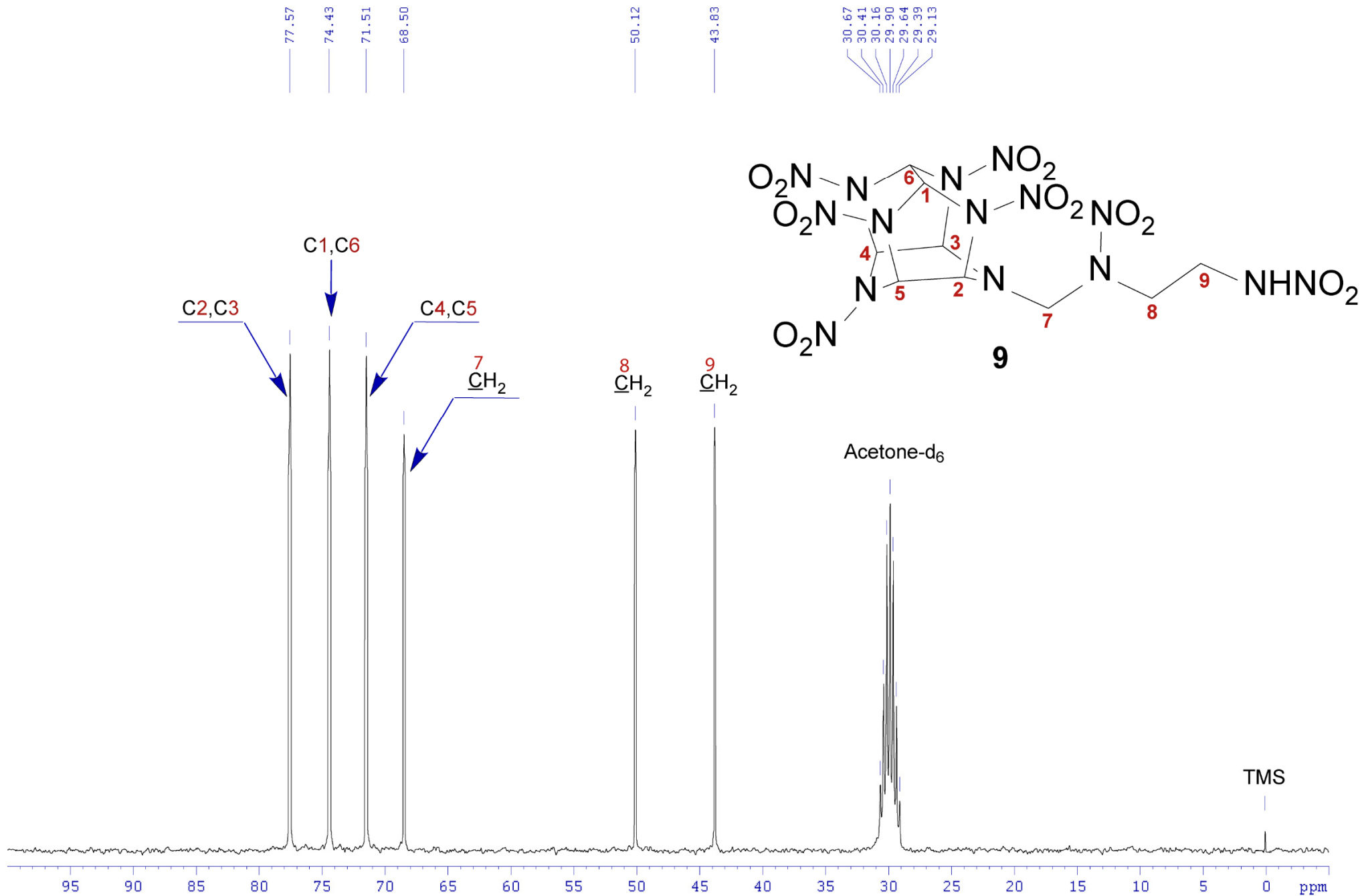
# IR (KBr) spectrum of compound 8



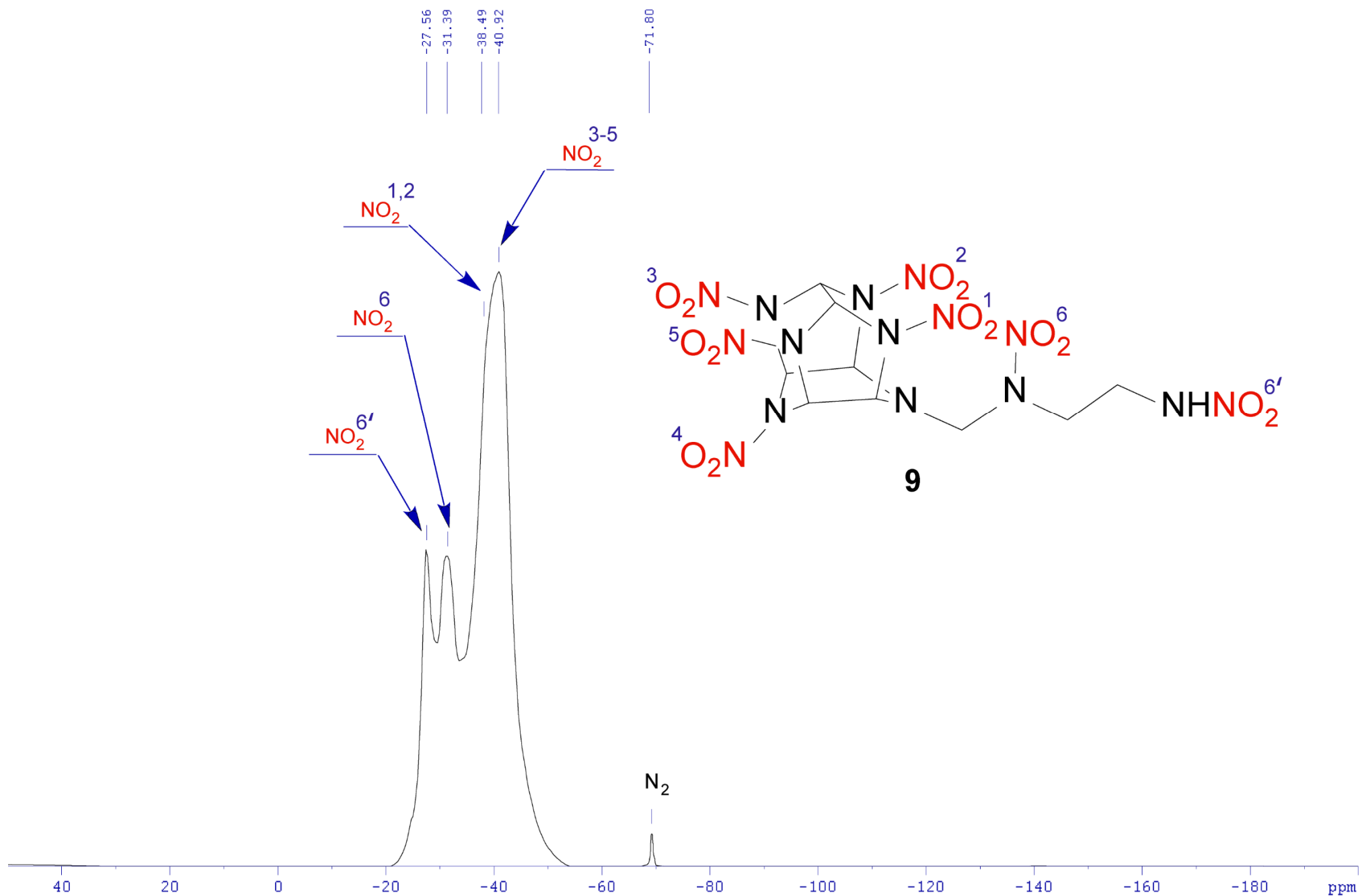
# <sup>1</sup>H NMR (300.1 MHz, [D<sub>6</sub>]acetone) spectrum of compound 9



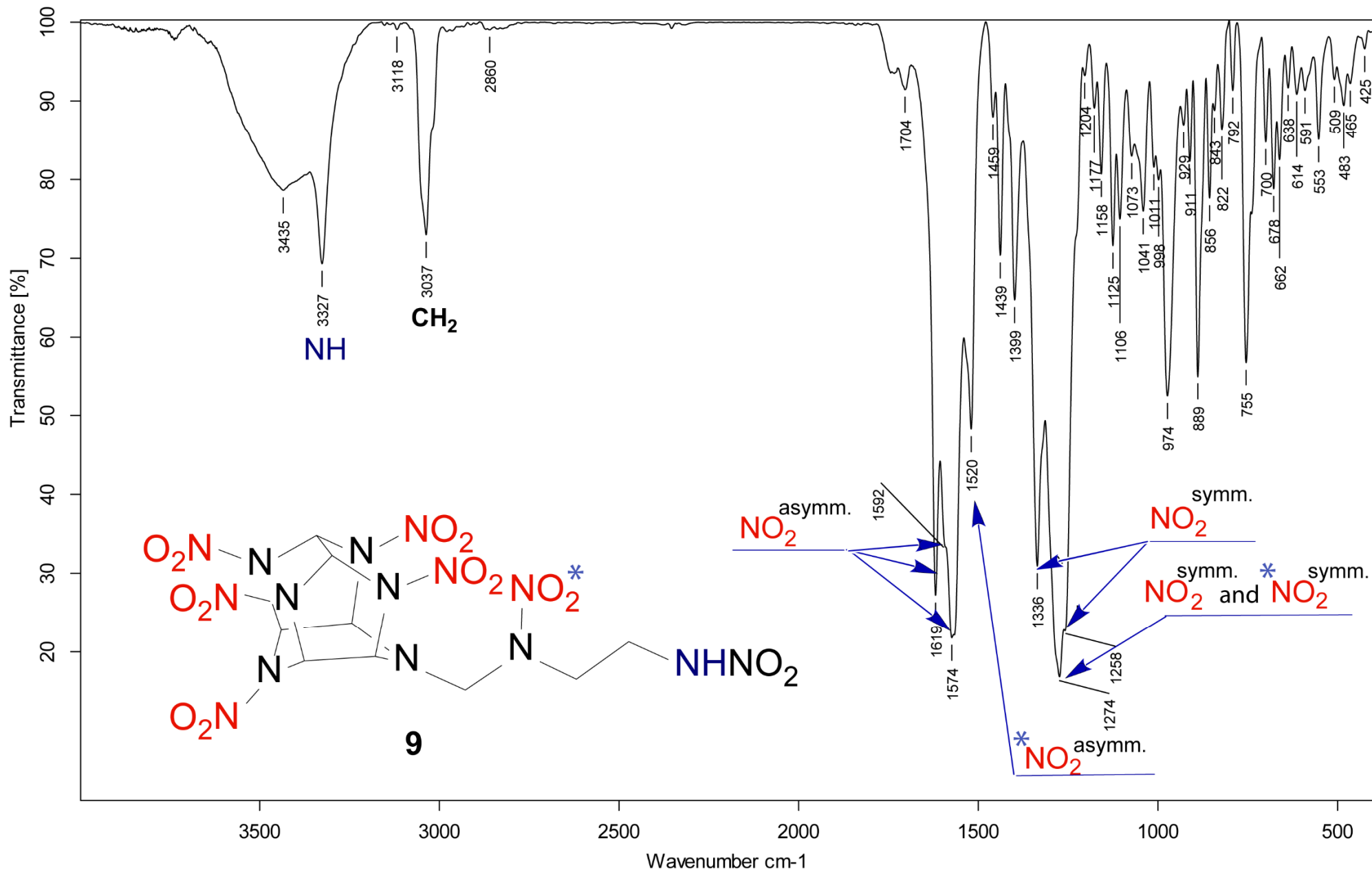
# $^{13}\text{C}$ NMR (75.5 MHz, $[\text{D}_6]$ acetone) spectrum of compound 9



# $^{14}\text{N}$ NMR (21.7 MHz, $[\text{D}_6]$ acetone) spectrum of compound 9

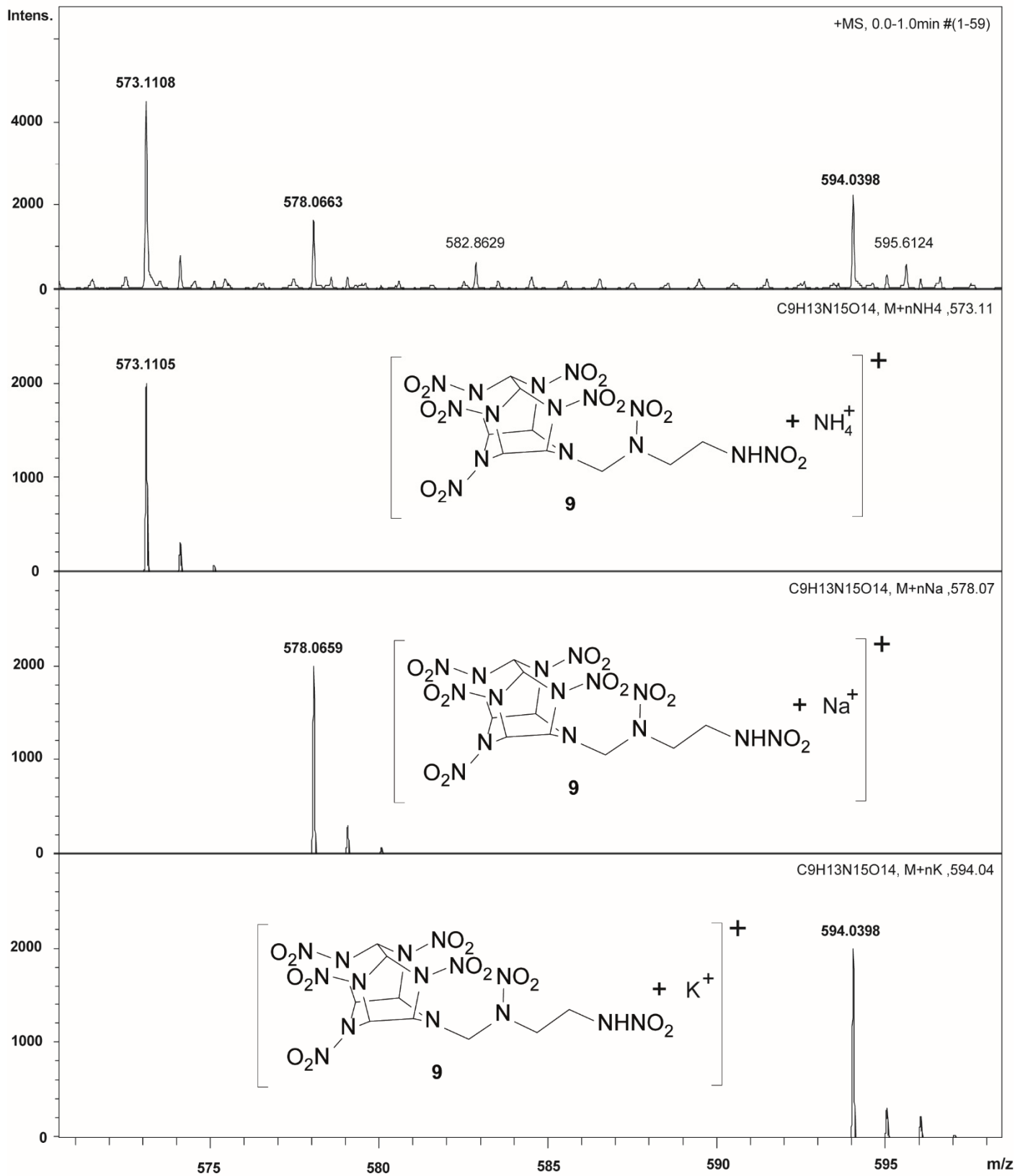


# IR (KBr) spectrum of compound 9

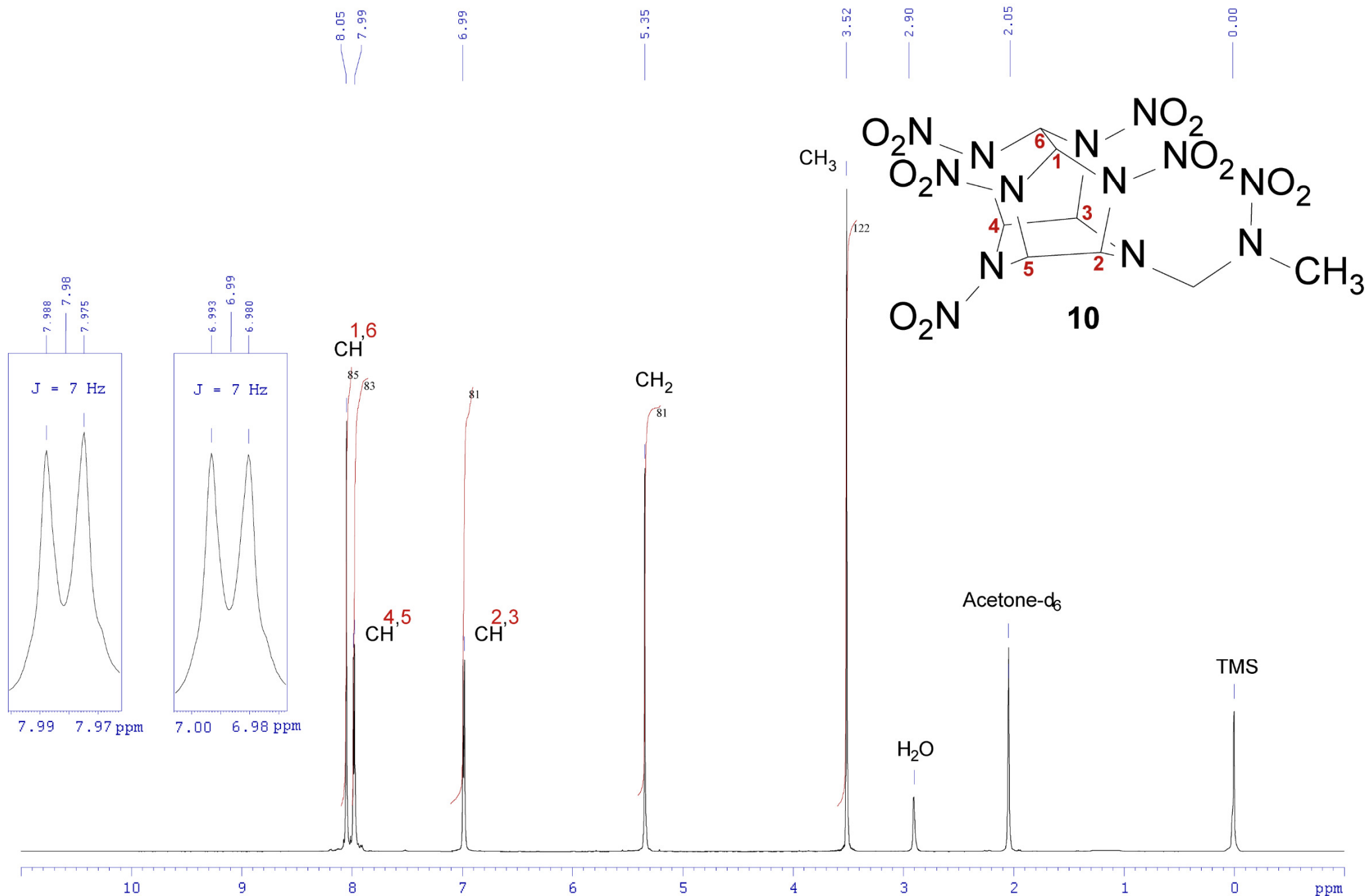




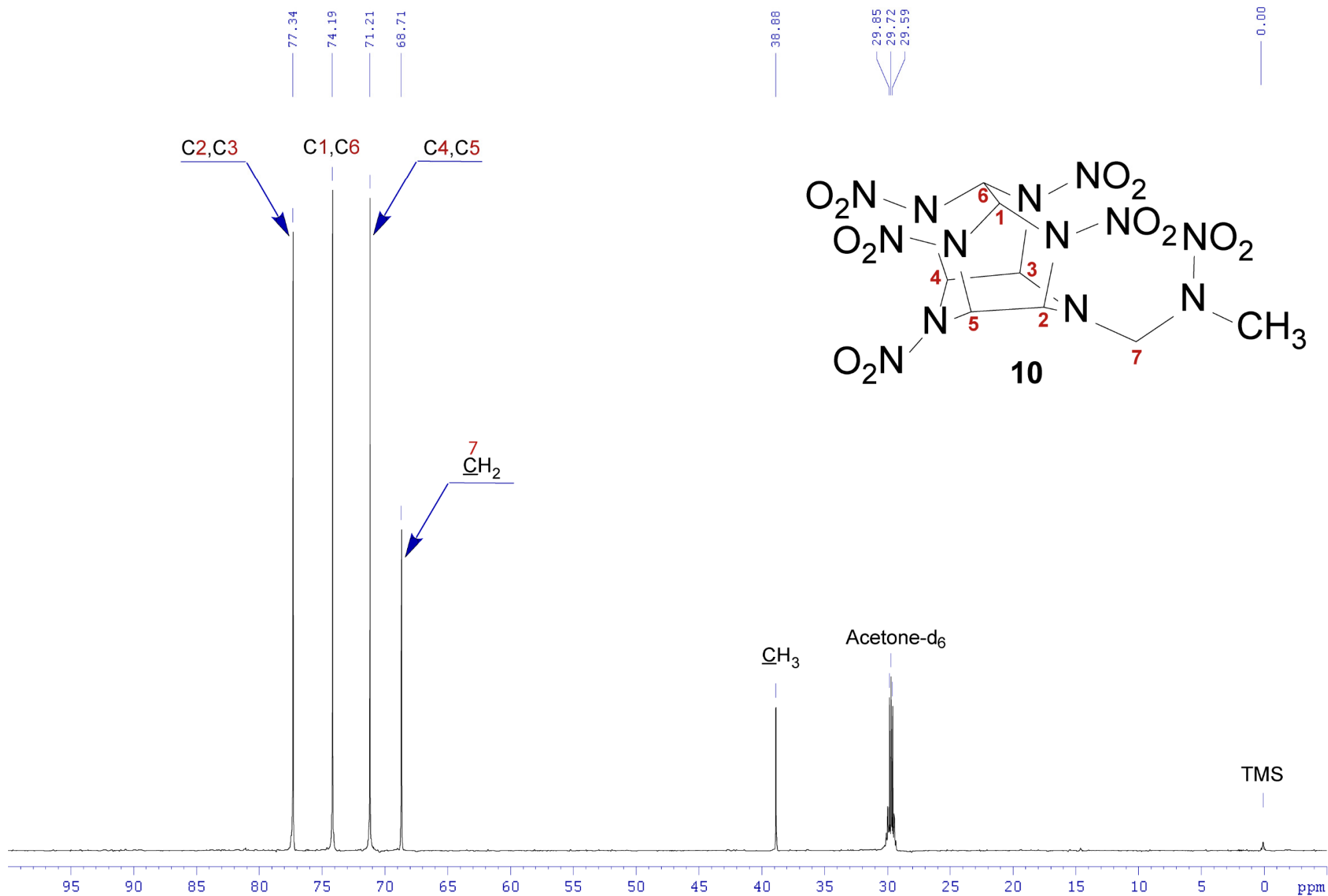
# HRMS (ESI) for compound 9



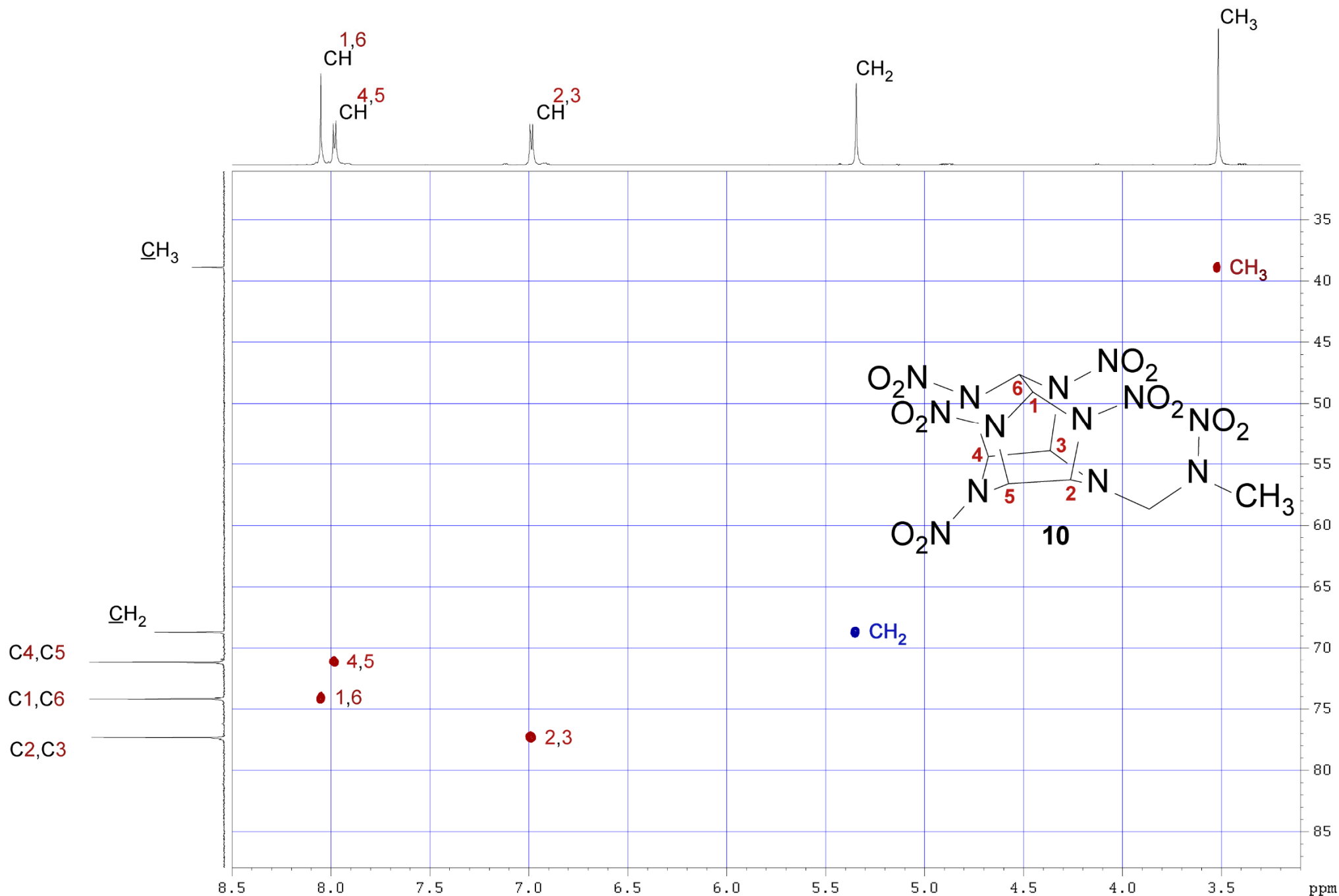
# $^1\text{H}$ NMR (600.13 MHz, $[\text{D}_6]$ acetone) spectrum of compound 10



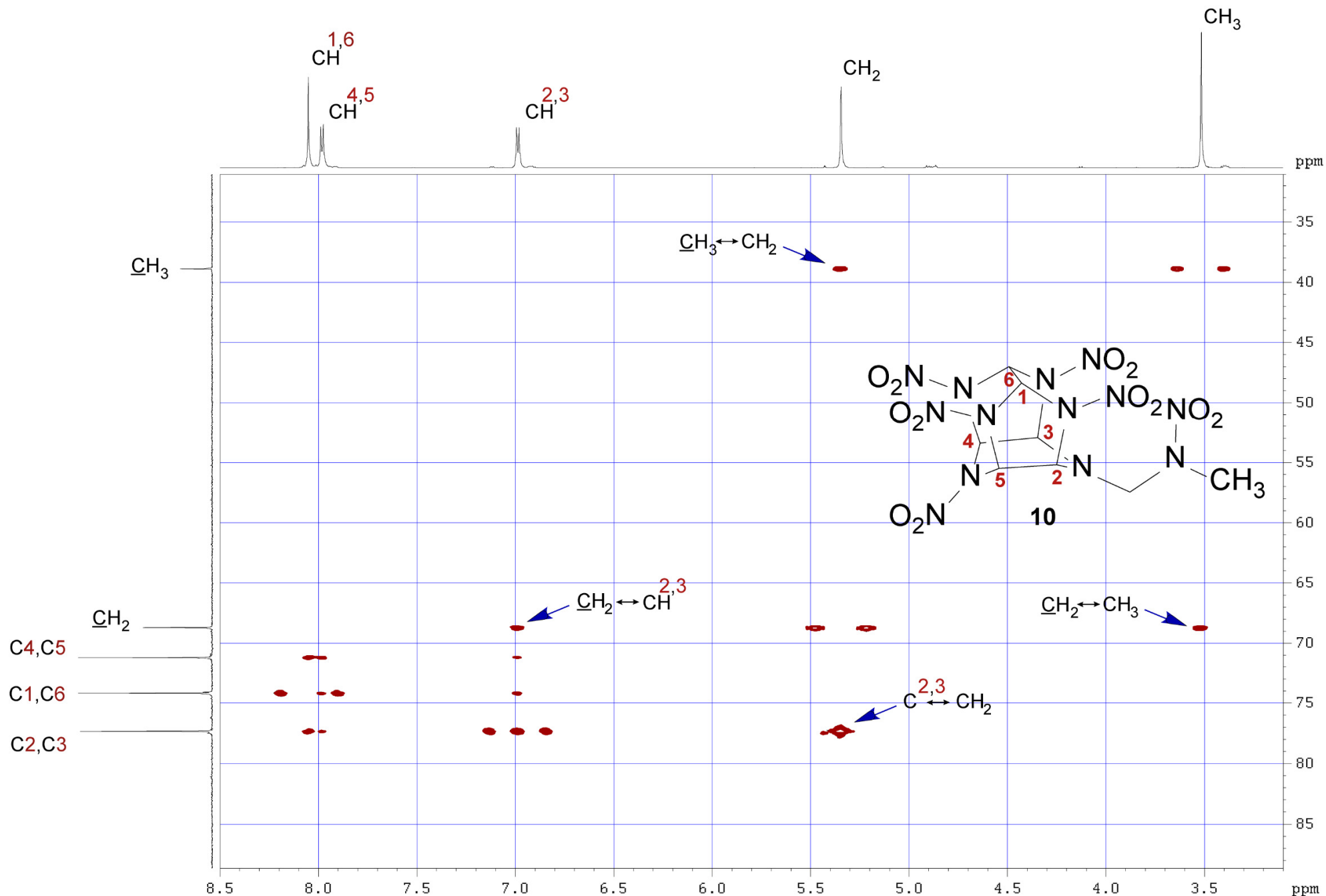
# $^{13}\text{C}$ NMR (150.9 MHz, $[\text{D}_6]$ acetone) spectrum of compound 10



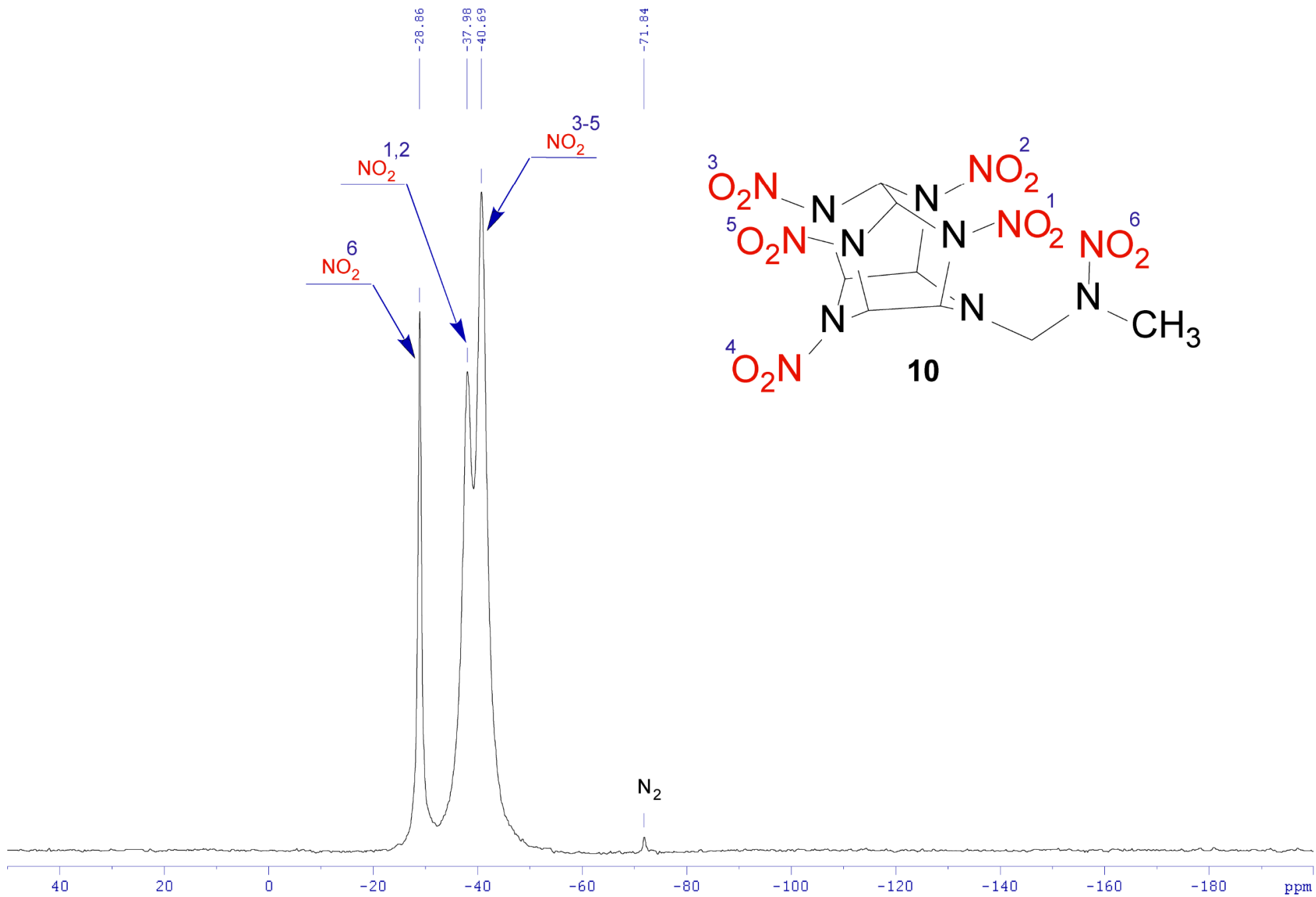
# $\{^1\text{H}-^{13}\text{C}\}$ HSQC NMR (600.13 MHz, $[\text{D}_6]$ acetone) spectrum of compound 10



# $\{^1\text{H}-^{13}\text{C}\}$ HMBC NMR (600.13 MHz, $[\text{D}_6]$ acetone) spectrum of compound 10



# $^{14}\text{N}$ NMR (43.37 MHz, $[\text{D}_6]$ acetone) spectrum of compound 10



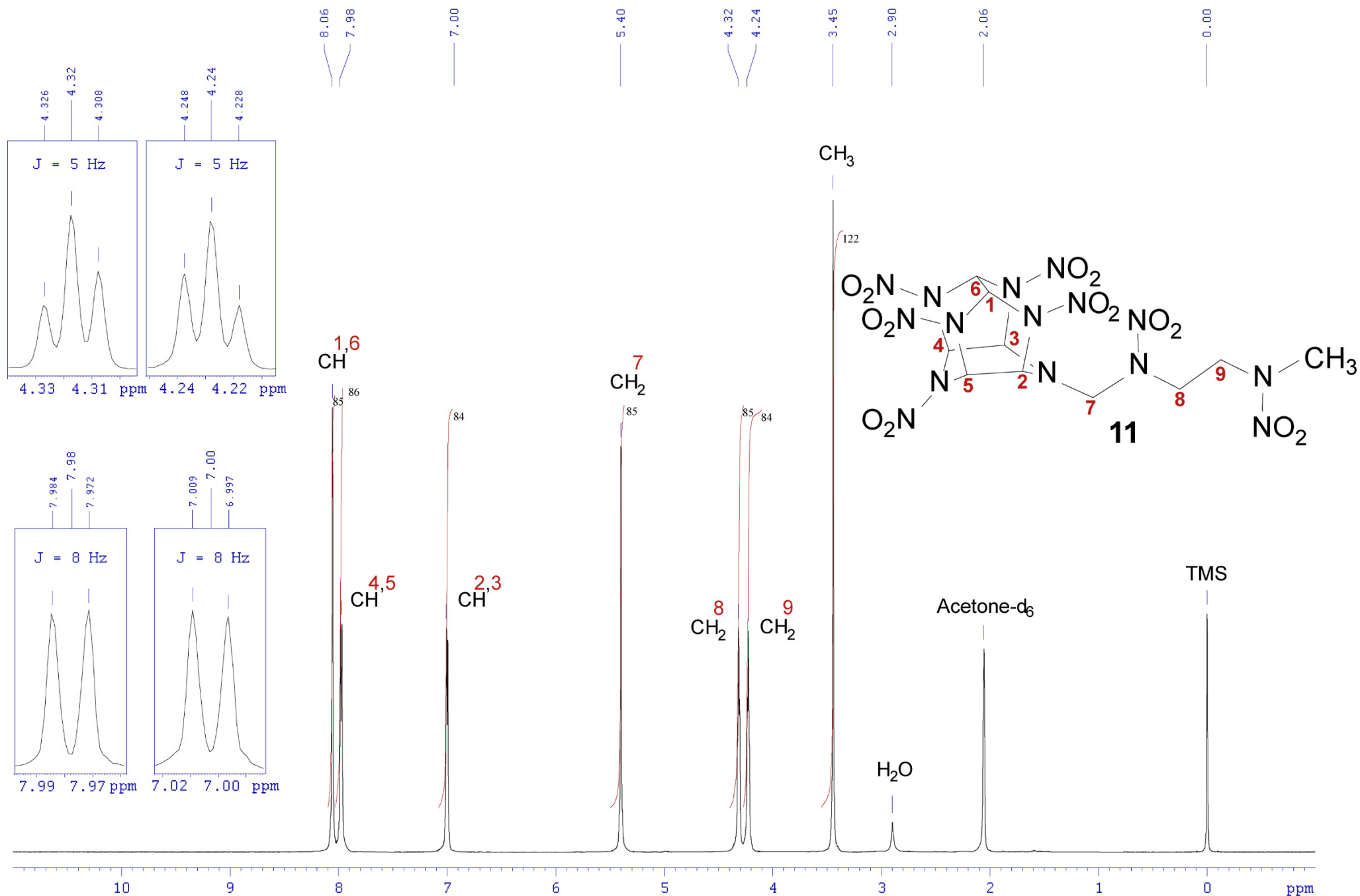




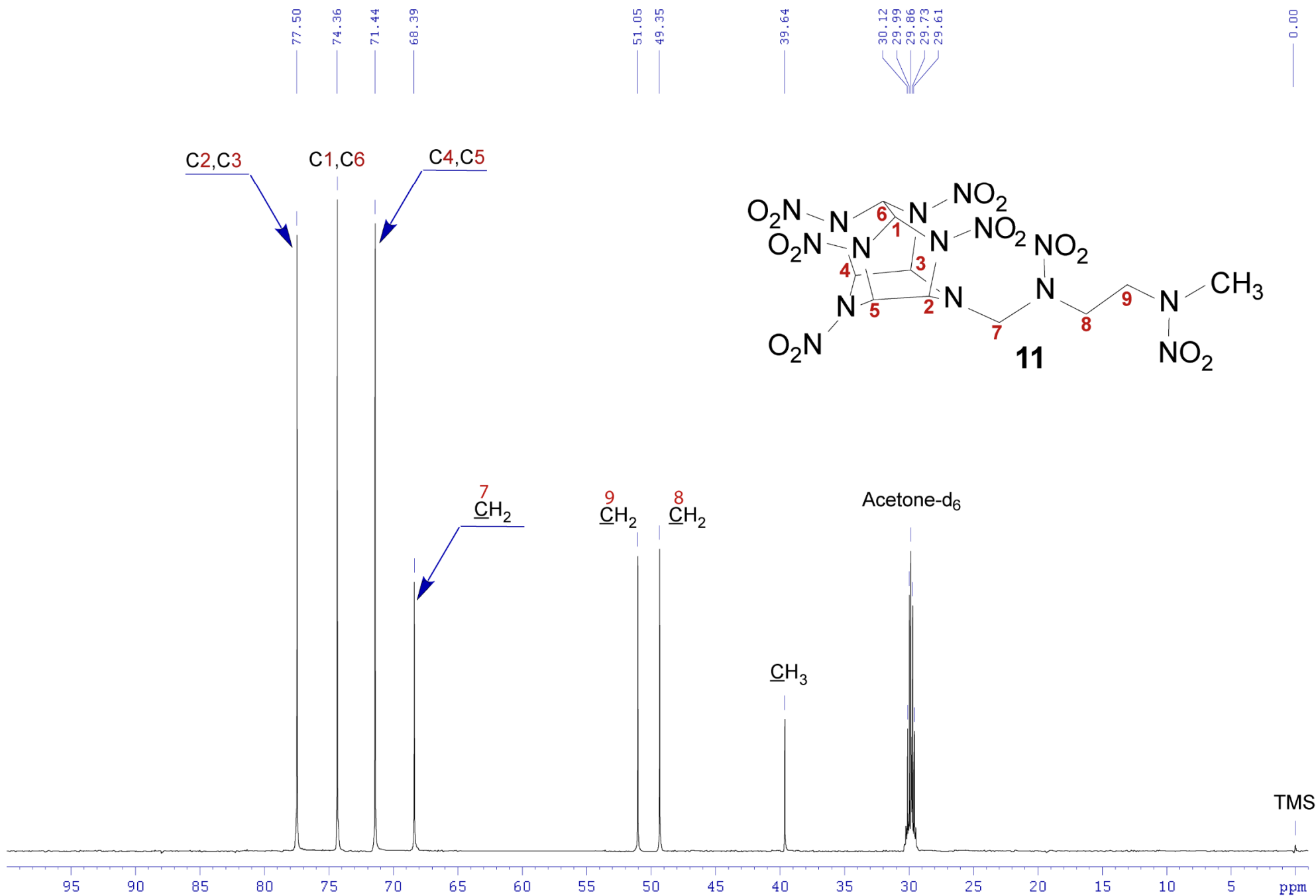




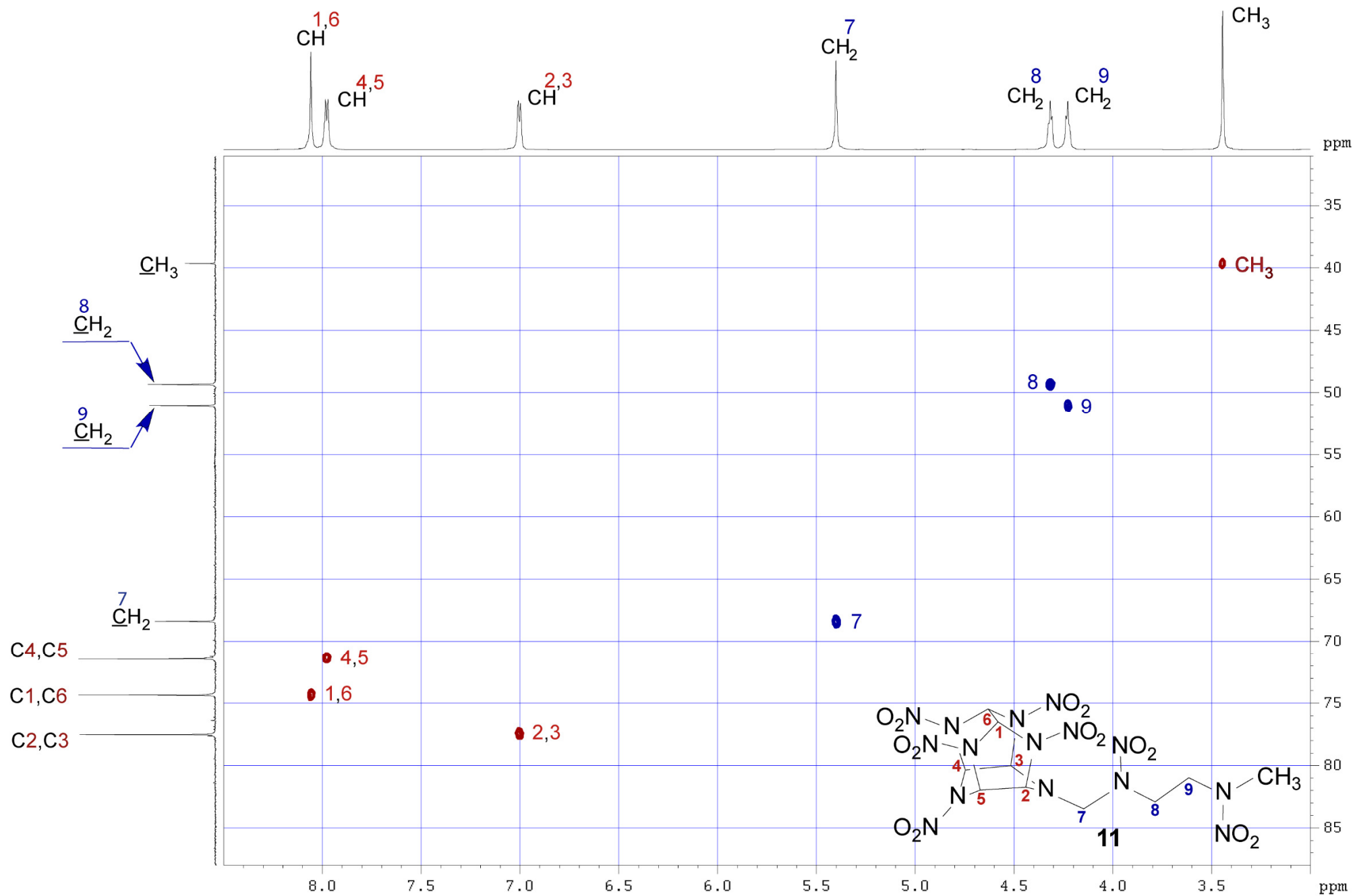
# <sup>1</sup>H NMR (600.13 MHz, [D<sub>6</sub>]acetone) spectrum of compound 11



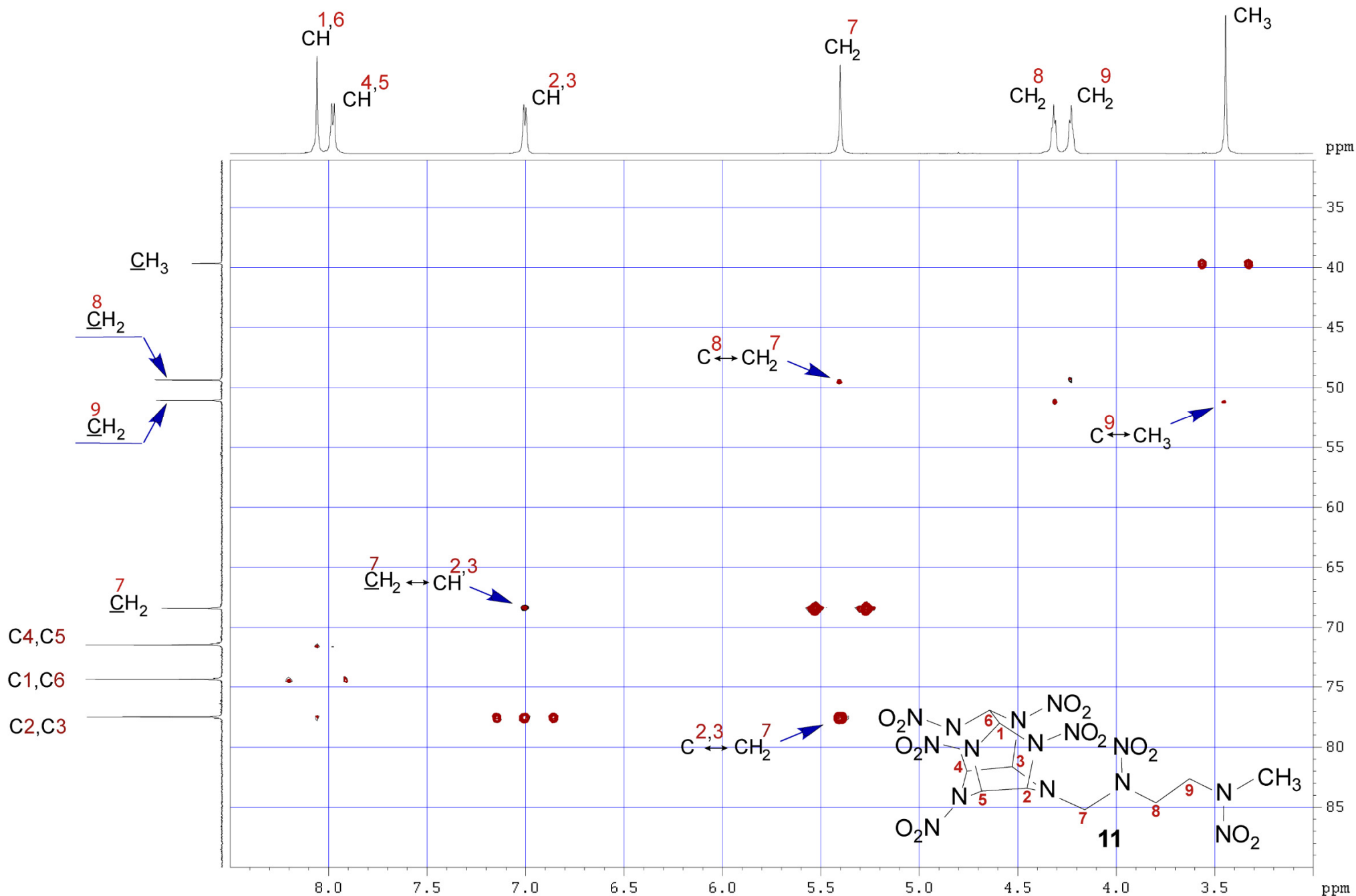
# $^{13}\text{C}$ NMR (150.9 MHz, $[\text{D}_6]$ acetone) spectrum of compound 11



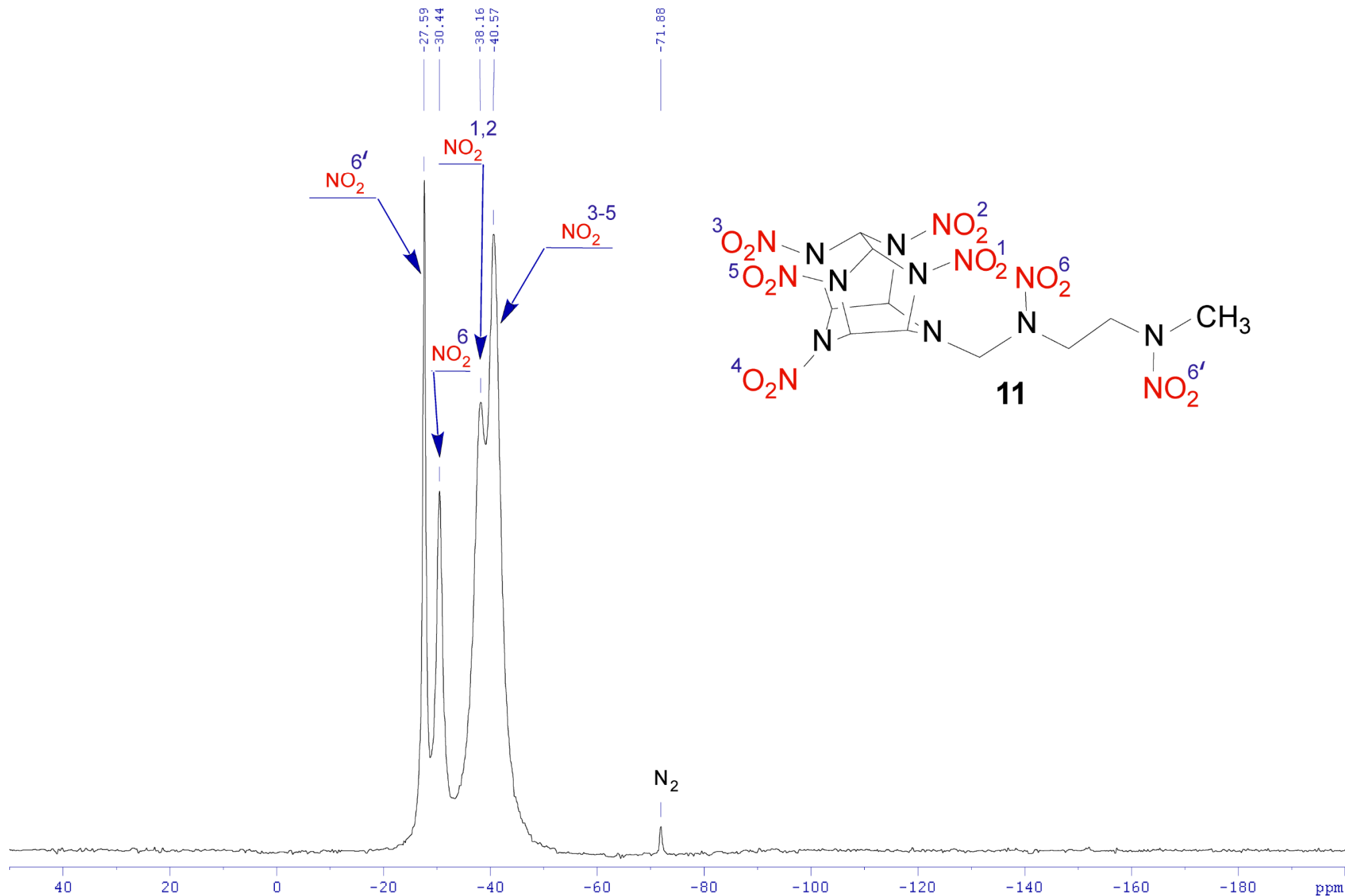
# $\{^1\text{H}-^{13}\text{C}\}$ HSQC NMR (600.13 MHz, $[\text{D}_6]$ acetone) spectrum of compound 11



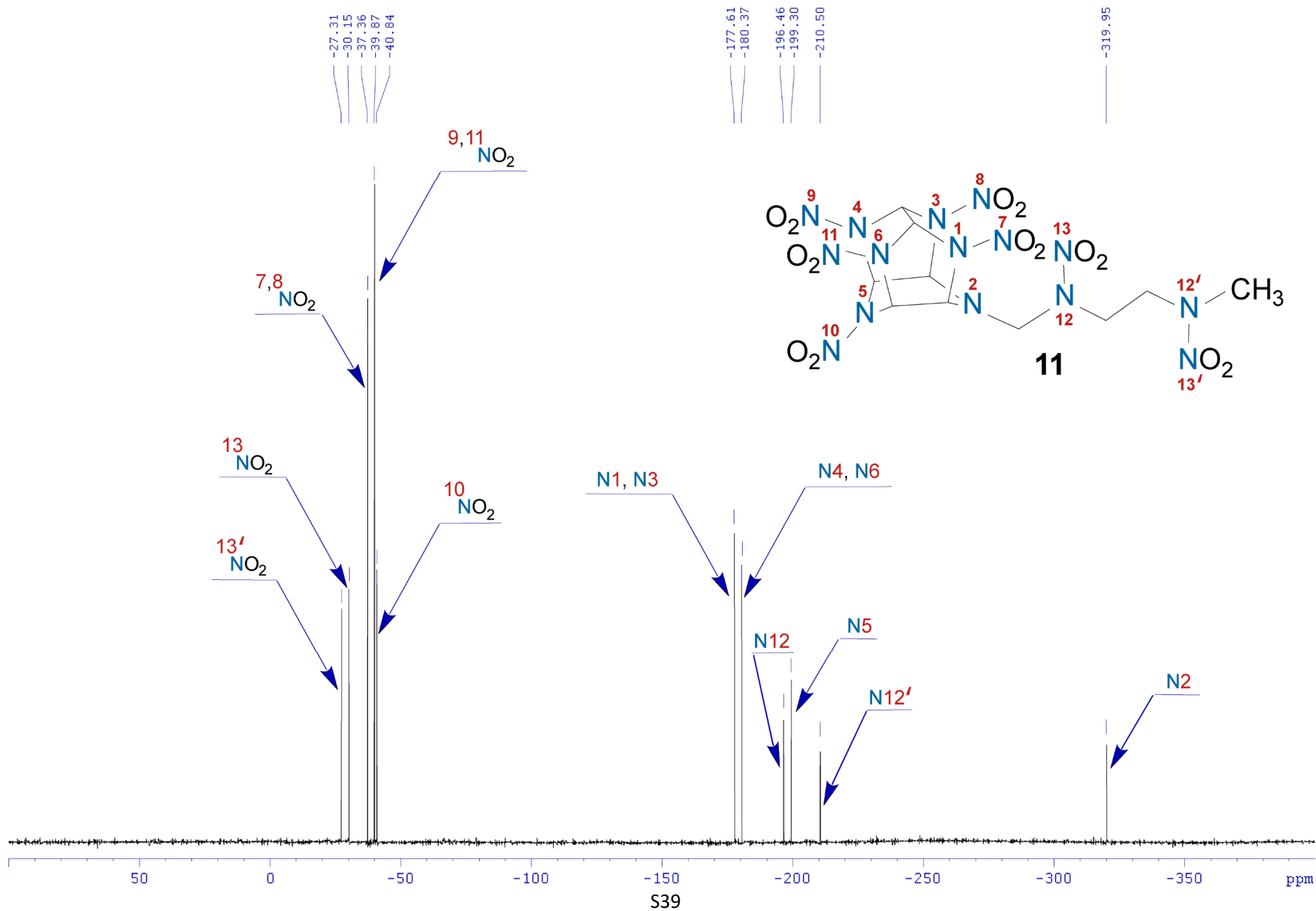
**{<sup>1</sup>H-<sup>13</sup>C} HMBC NMR (600.13 MHz, [D<sub>6</sub>]acetone) spectrum of compound 11**



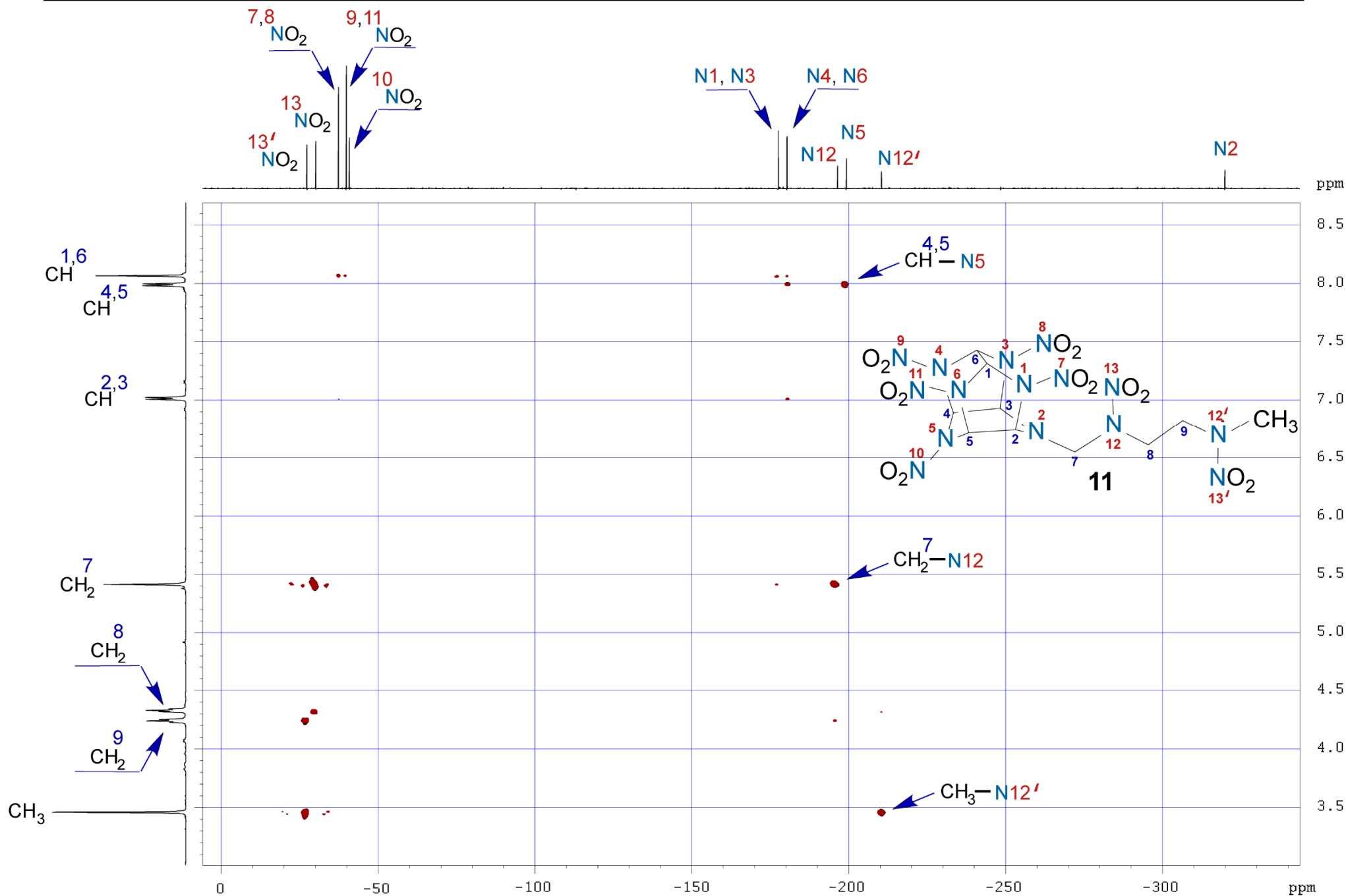
**$^{14}\text{N}$  NMR (43.37 MHz,  $[\text{D}_6]$ acetone) spectrum of compound 11**



# $^{15}\text{N}$ NMR ([INVGATED], 60.8 MHz, $[\text{D}_6]$ acetone) spectrum of compound 11

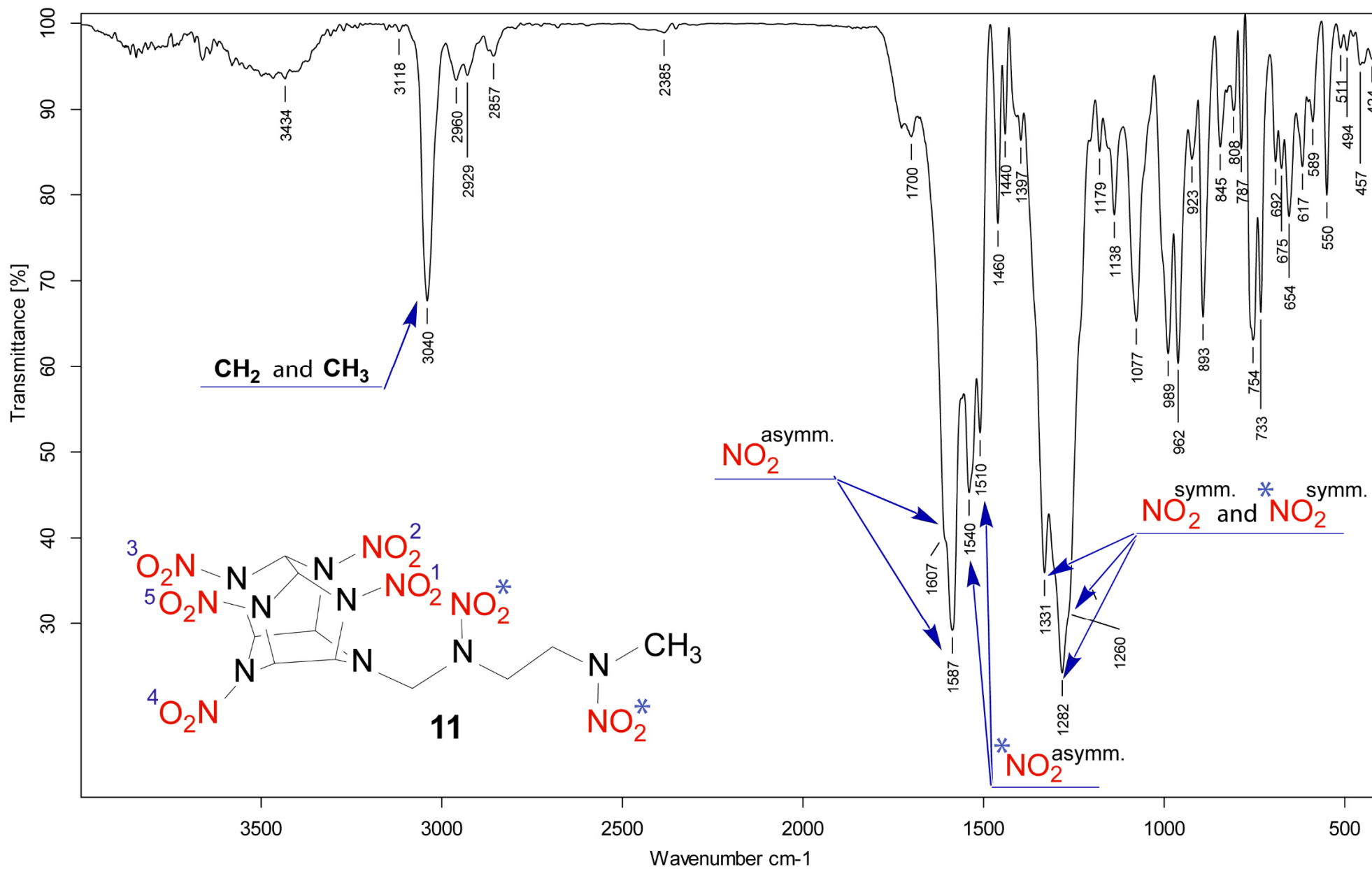


**{<sup>1</sup>H-<sup>15</sup>N} HSQC NMR (600.13 MHz, [D<sub>6</sub>]acetone) spectrum of compound 11**



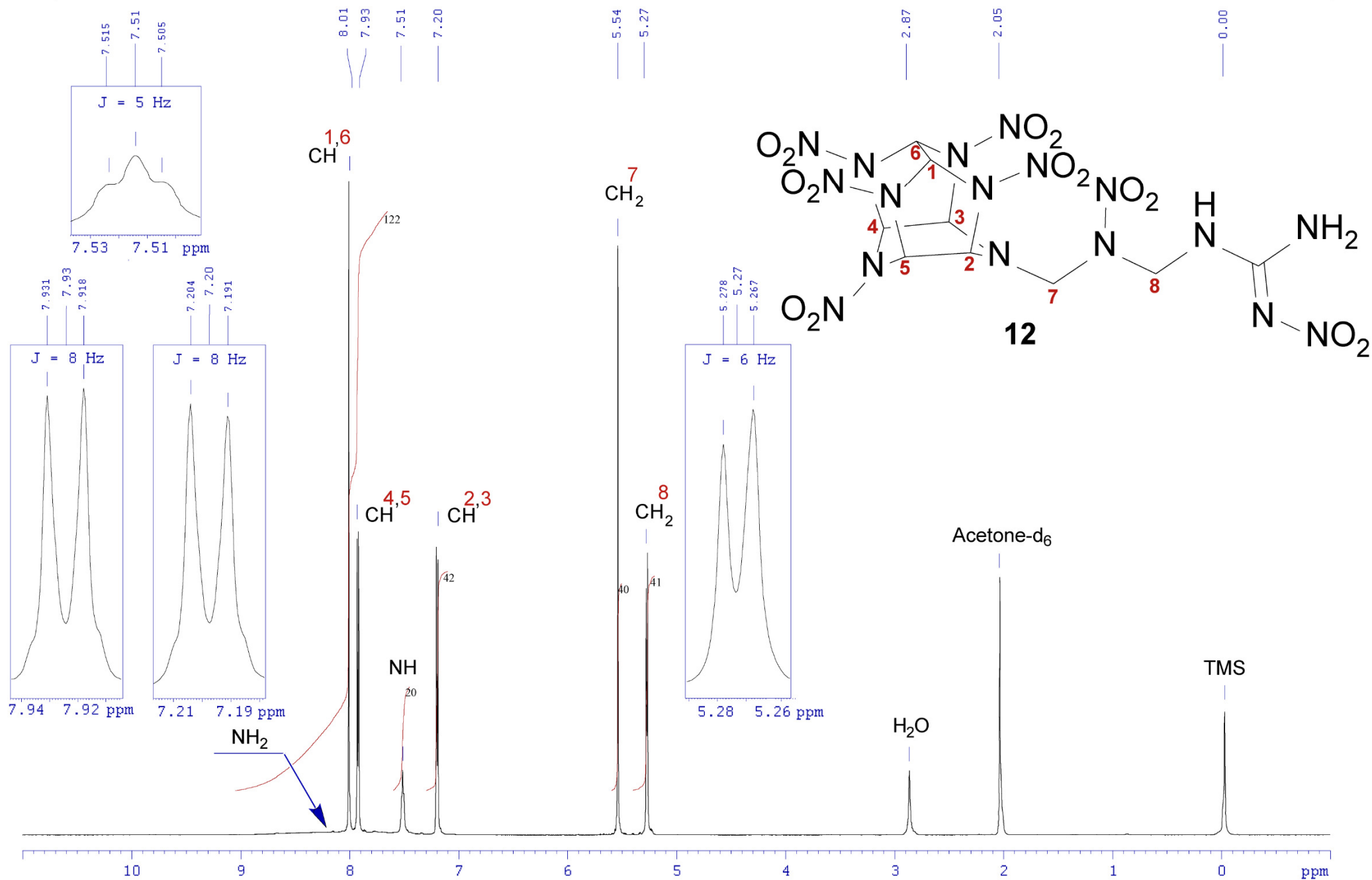


# IR (KBr) spectrum of compound 11

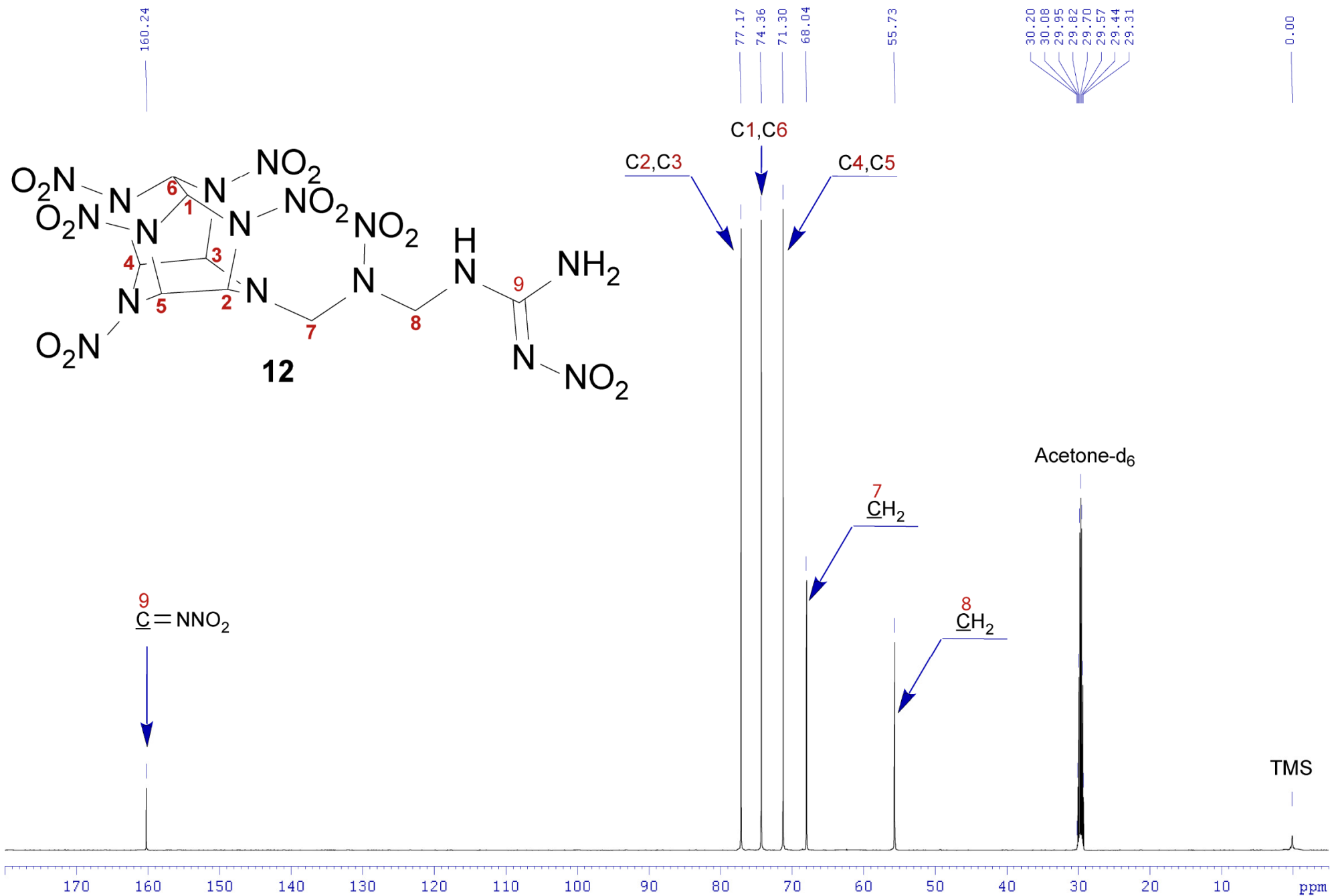




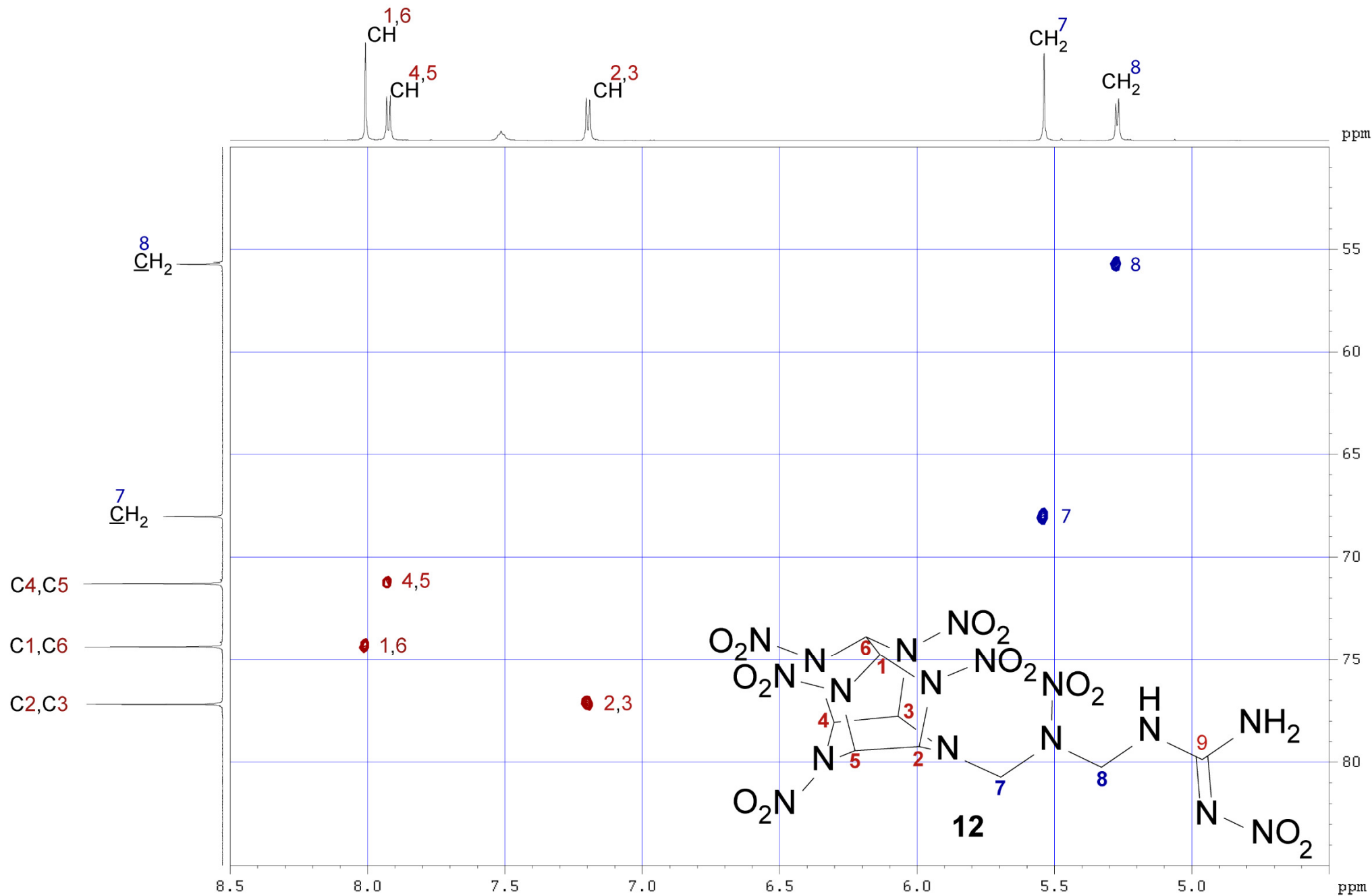
# $^1\text{H}$ NMR (600.13 MHz, $[\text{D}_6]$ acetone) spectrum of compound 12



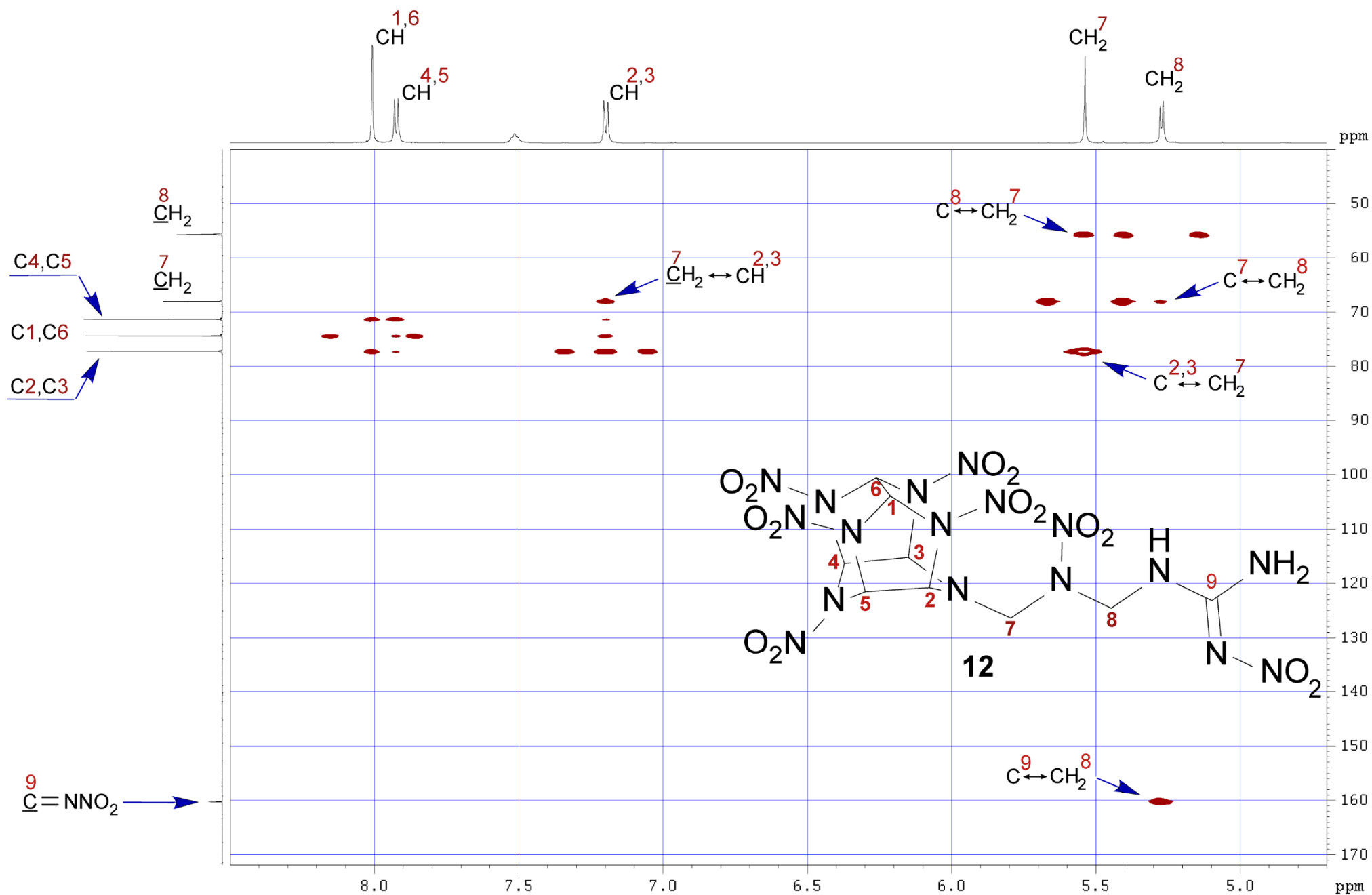
# $^{13}\text{C}$ NMR (150.9 MHz, $[\text{D}_6]$ acetone) spectrum of compound 12



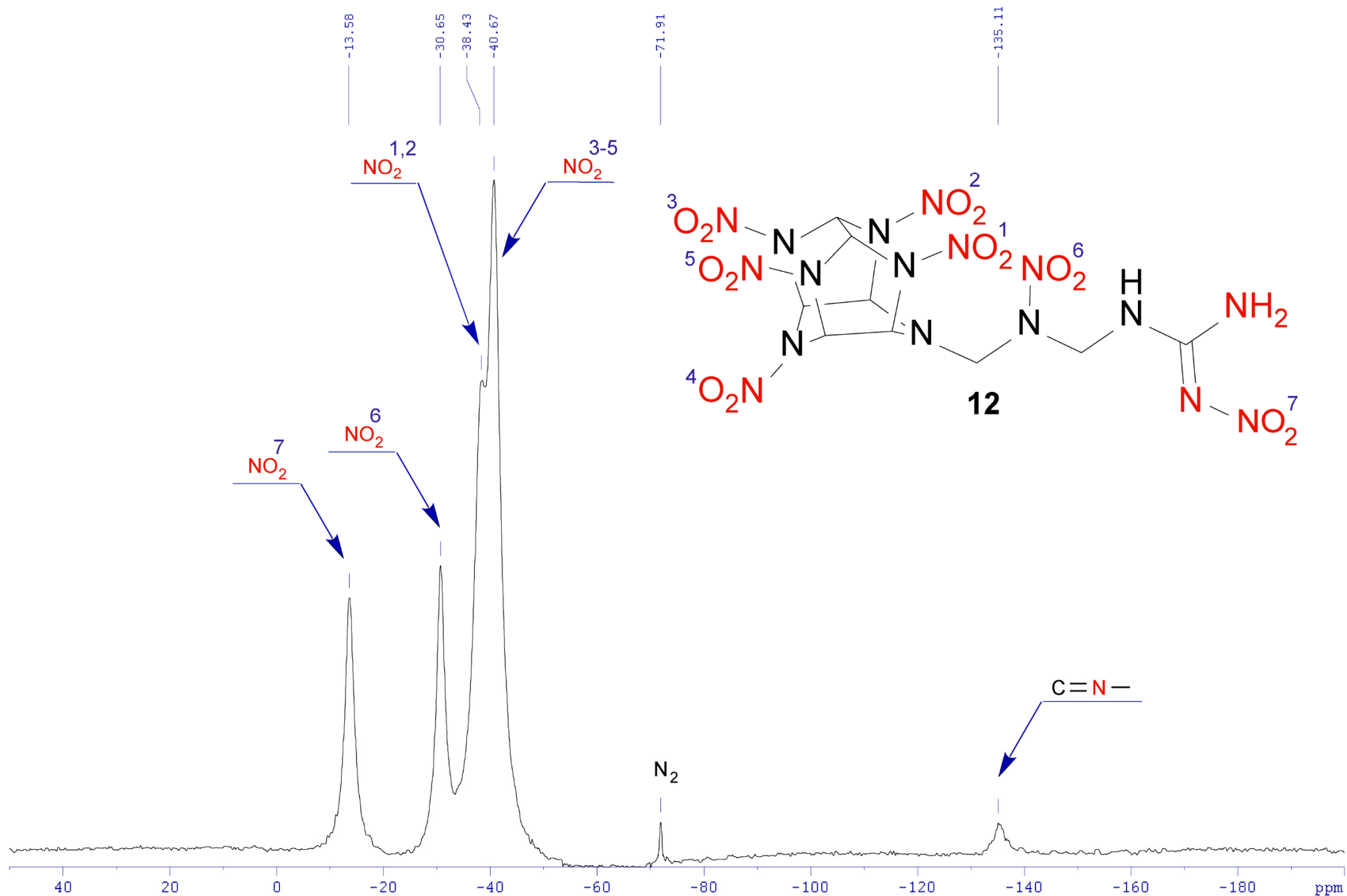
**$\{^1\text{H}-^{13}\text{C}\}$  HSQC NMR (600.13 MHz,  $[\text{D}_6]$ acetone) spectrum of compound 12**



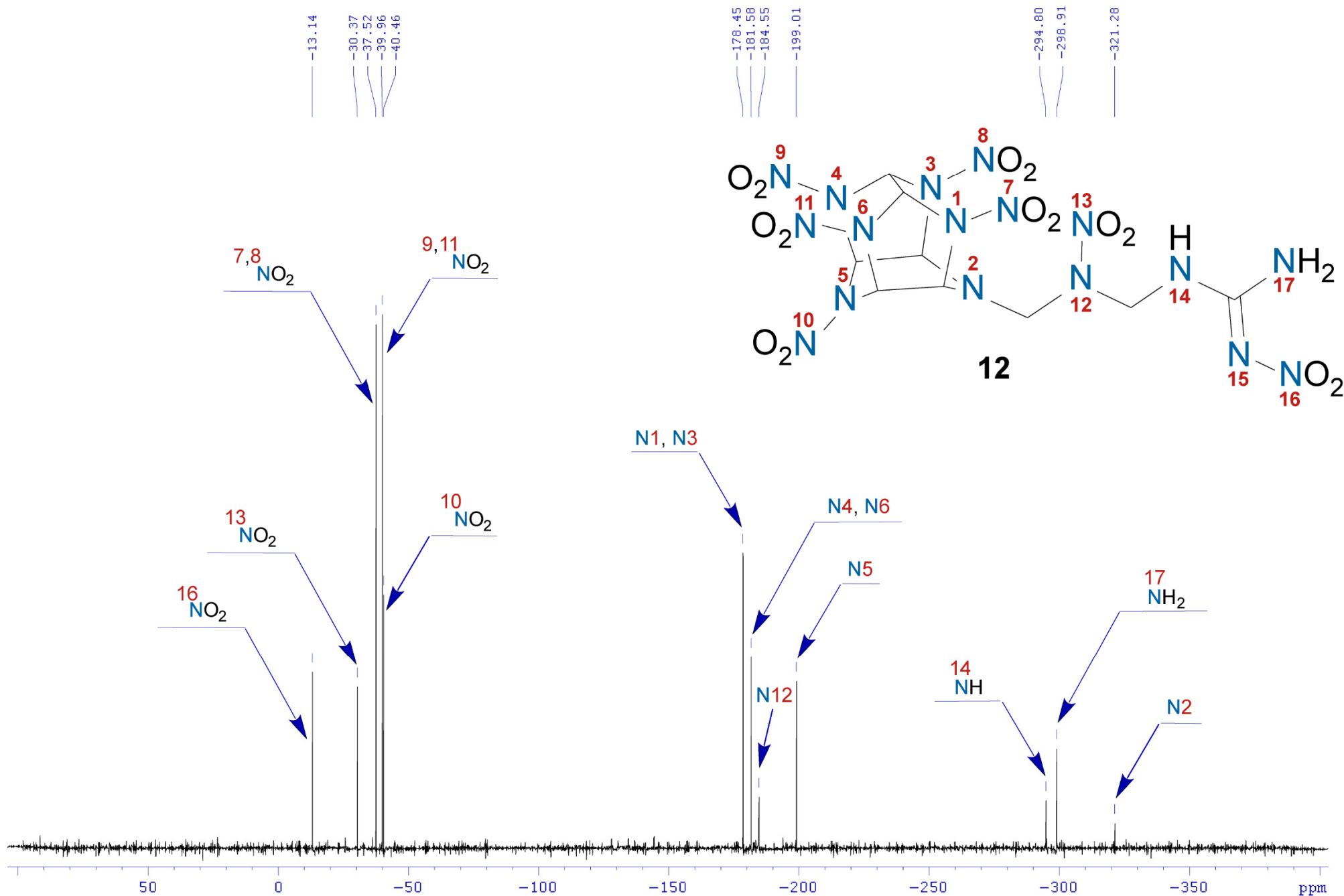
**$\{^1\text{H}-^{13}\text{C}\}$  HMBC NMR (600.13 MHz,  $[\text{D}_6]$ acetone) spectrum of compound 12**



# $^{14}\text{N}$ NMR (43.37 MHz, $[\text{D}_6]$ acetone) spectrum of compound 12

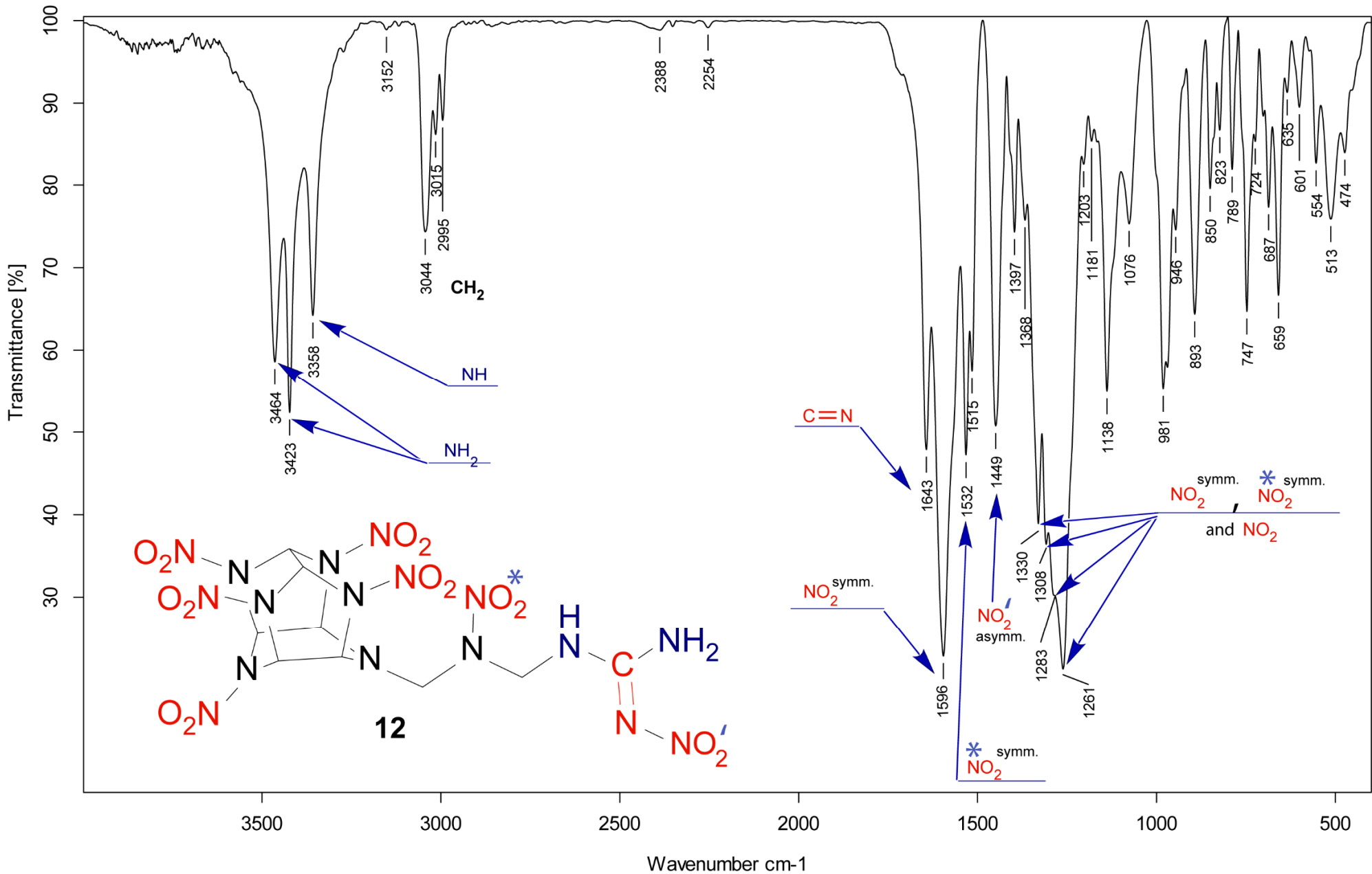


# $^{15}\text{N}$ NMR ([INVGATED], 60.8 MHz, $[\text{D}_6]$ acetone) spectrum of compound 12

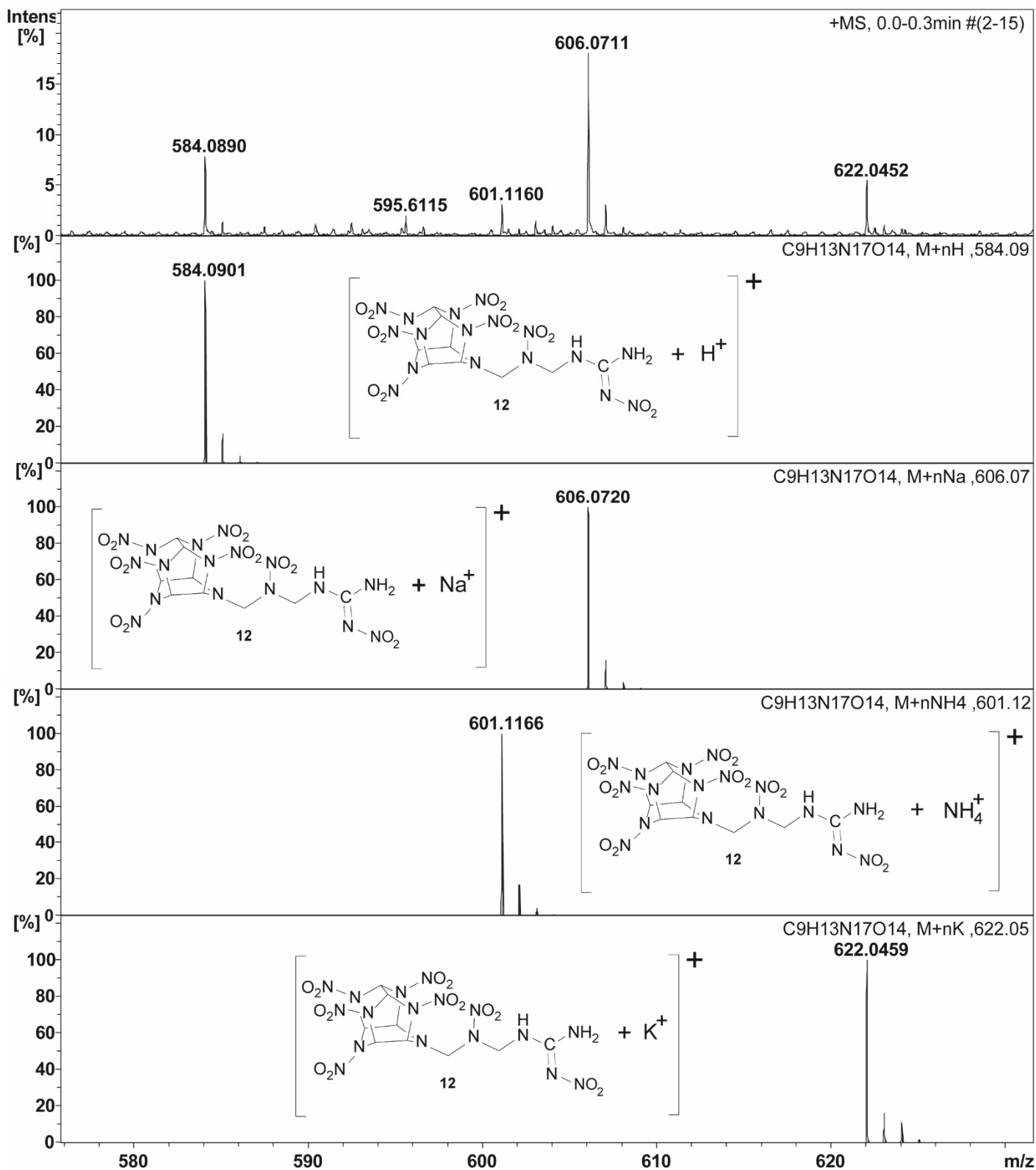




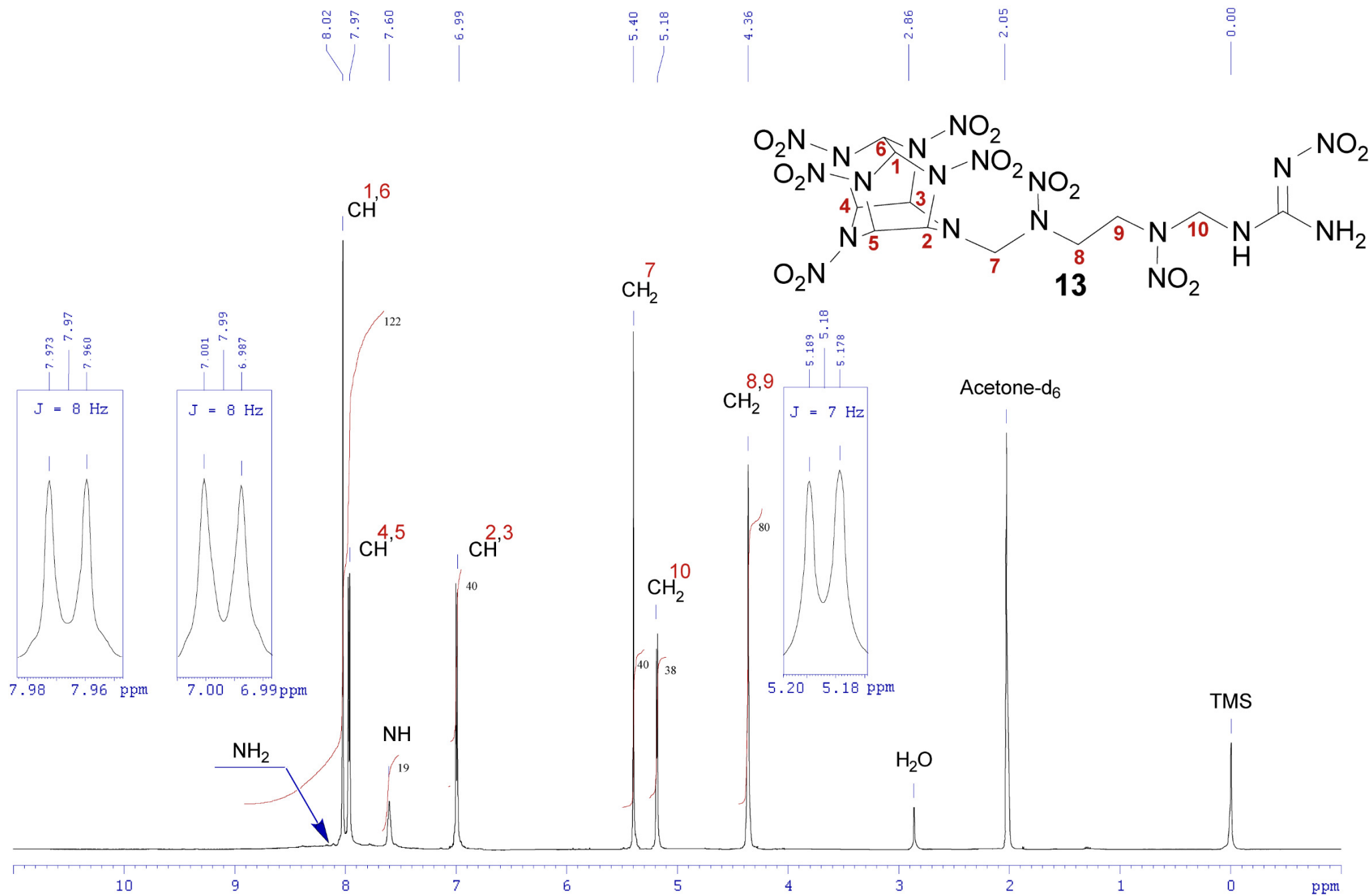
# IR (KBr) spectrum of compound 12



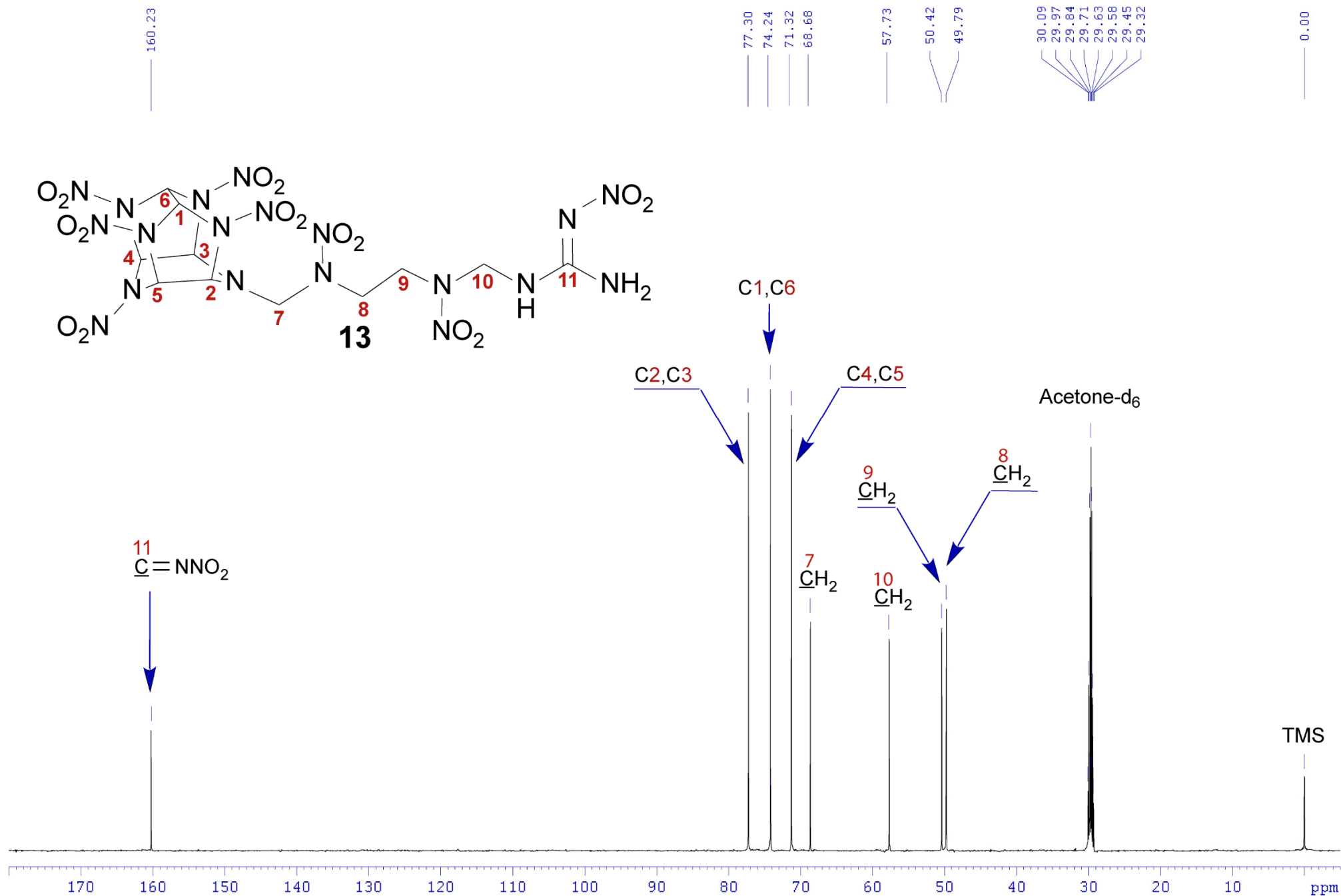
# HRMS (ESI) for compound 12



# <sup>1</sup>H NMR (600.13 MHz, [D<sub>6</sub>]acetone) spectrum of compound 13



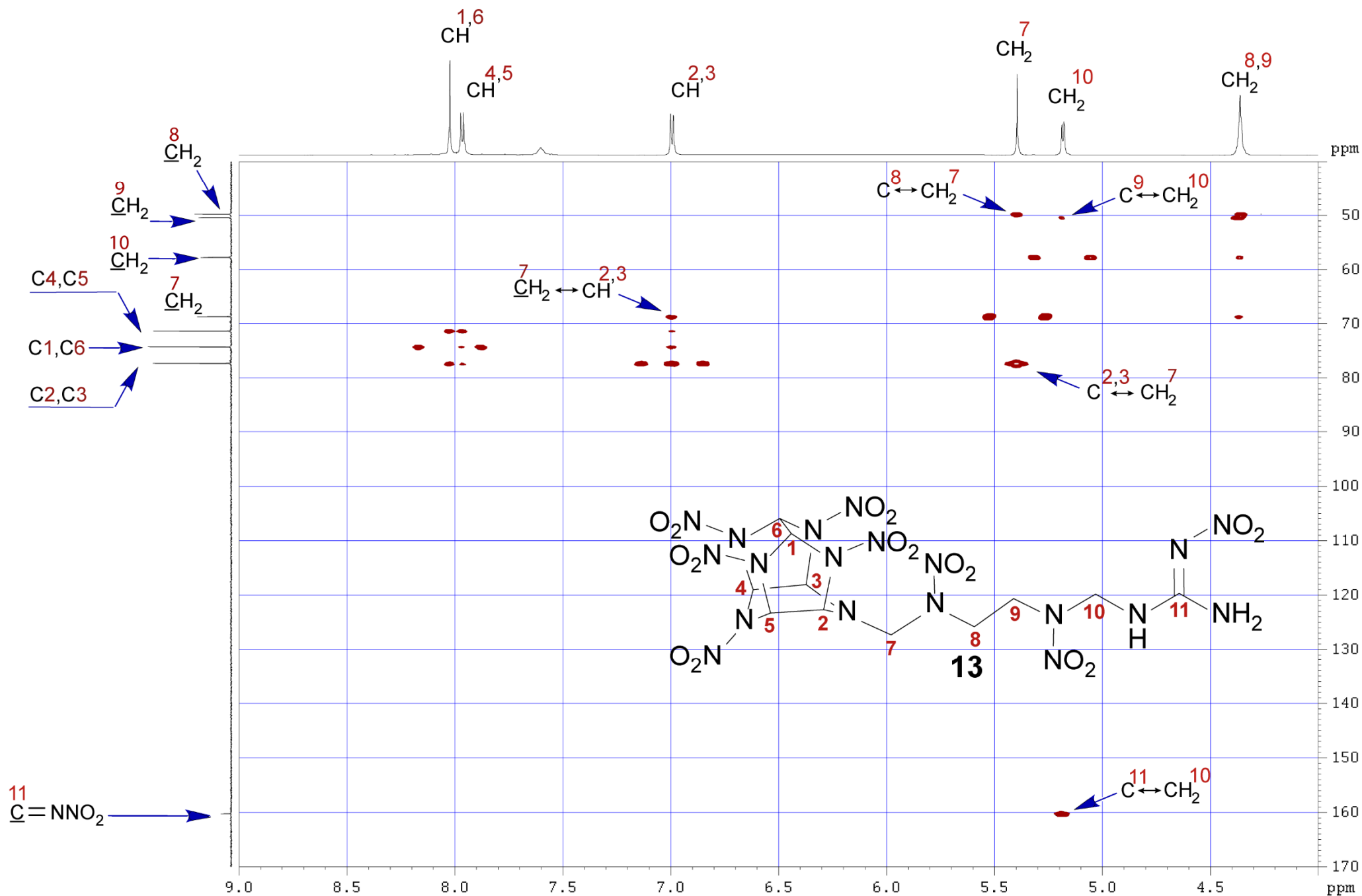
# $^{13}\text{C}$ NMR (150.9 MHz, $[\text{D}_6]$ acetone) spectrum of compound 13



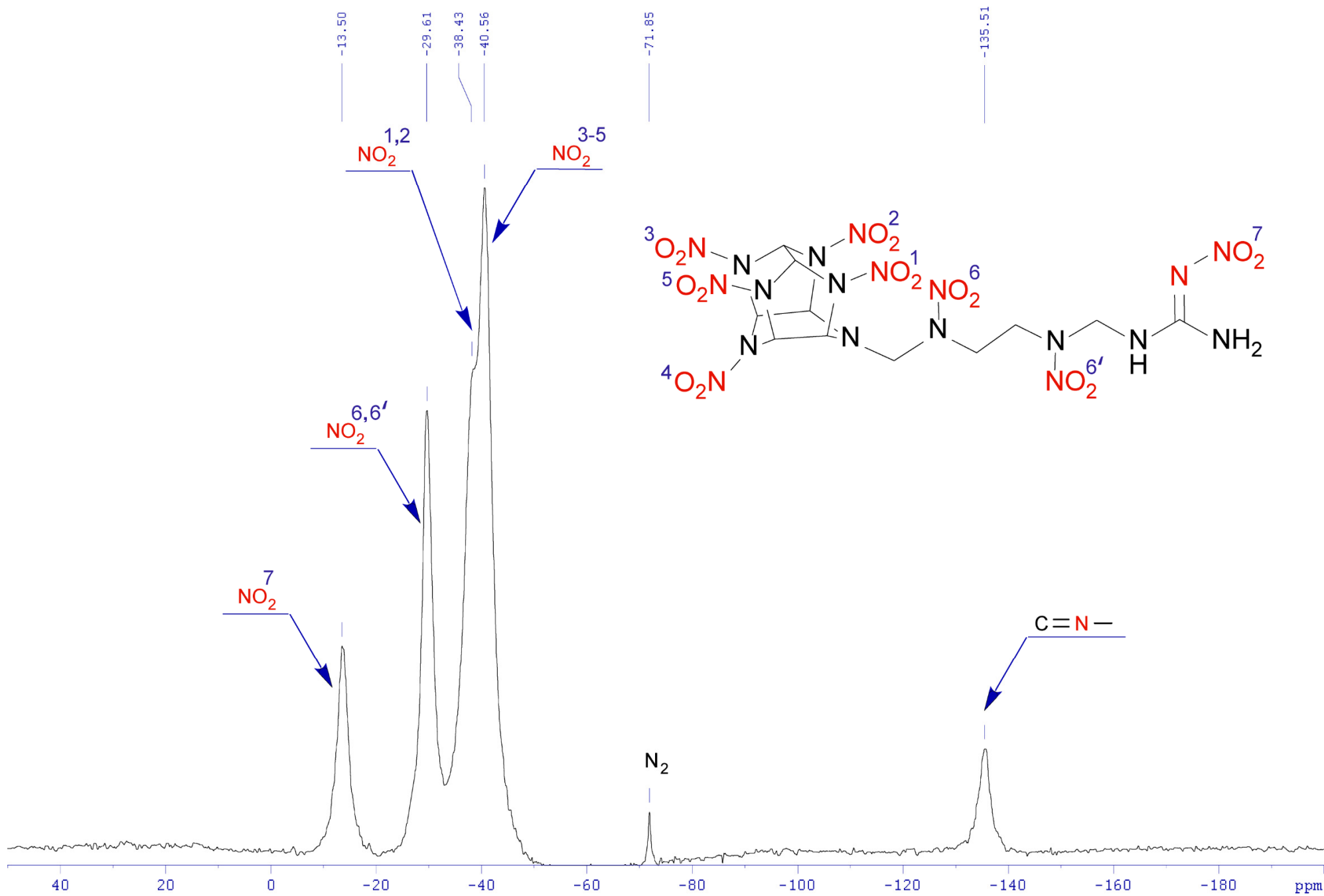
# $\{^1\text{H}-^{13}\text{C}\}$ HSQC NMR (600.13 MHz, $[\text{D}_6]$ acetone) spectrum of compound 13



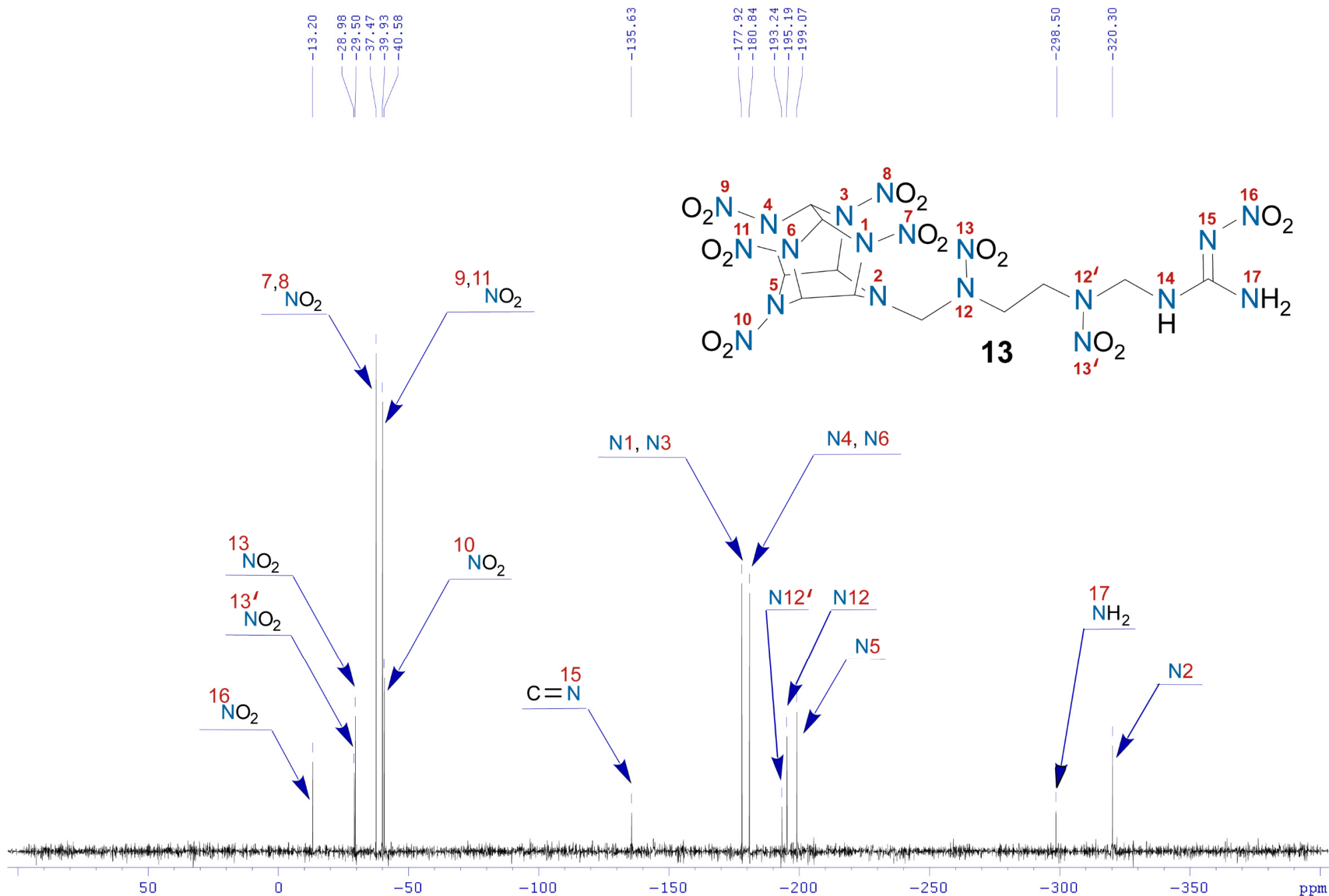
{<sup>1</sup>H-<sup>13</sup>C} HMBC NMR (600.13 MHz, [D<sub>6</sub>]acetone) spectrum of compound 13



# $^{14}\text{N}$ NMR (43.37 MHz, $[\text{D}_6]$ acetone) spectrum of compound 13

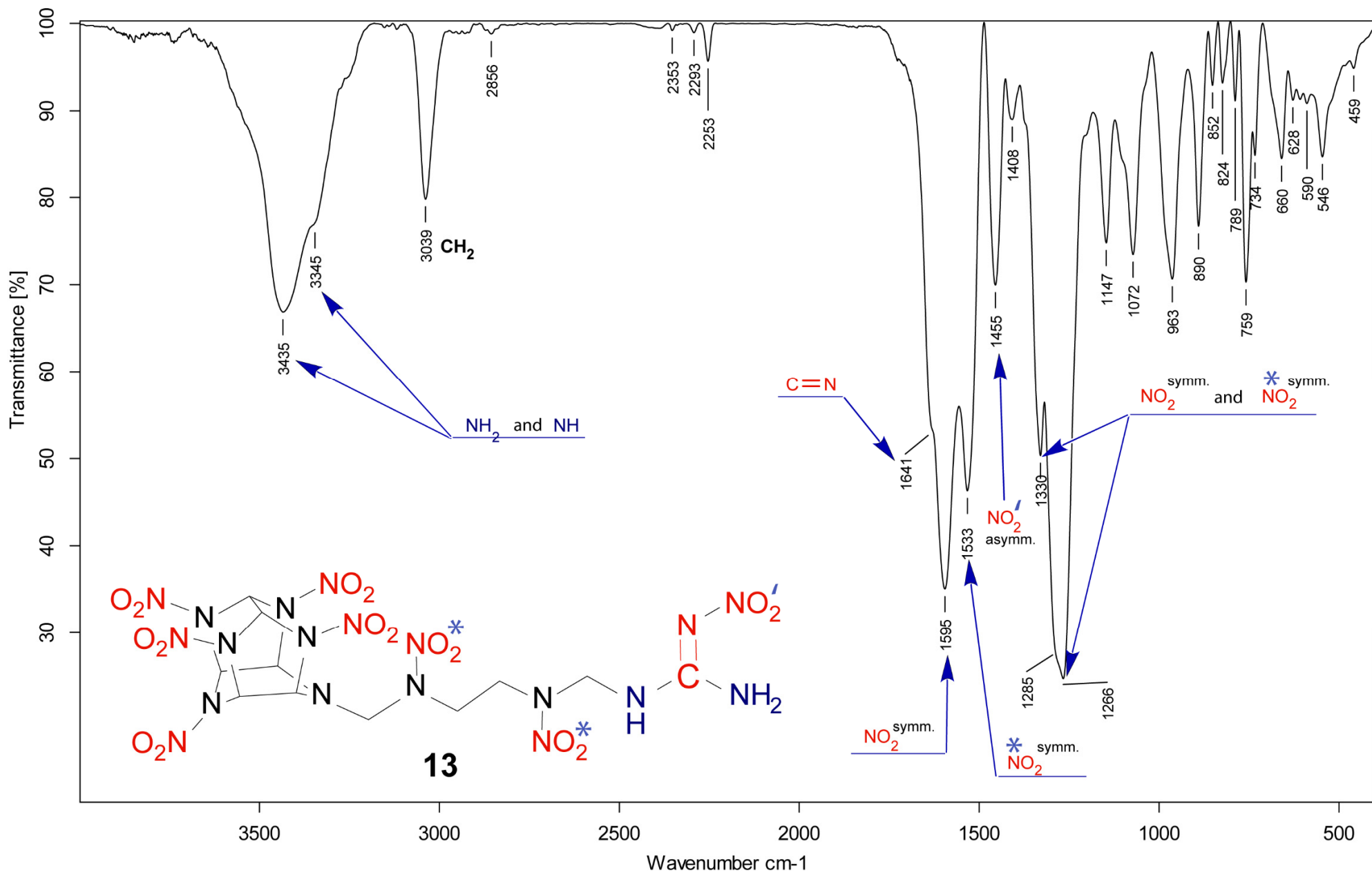


# $^{15}\text{N}$ NMR ([INVGATED], 60.8 MHz, $[\text{D}_6]$ acetone) spectrum of compound 13



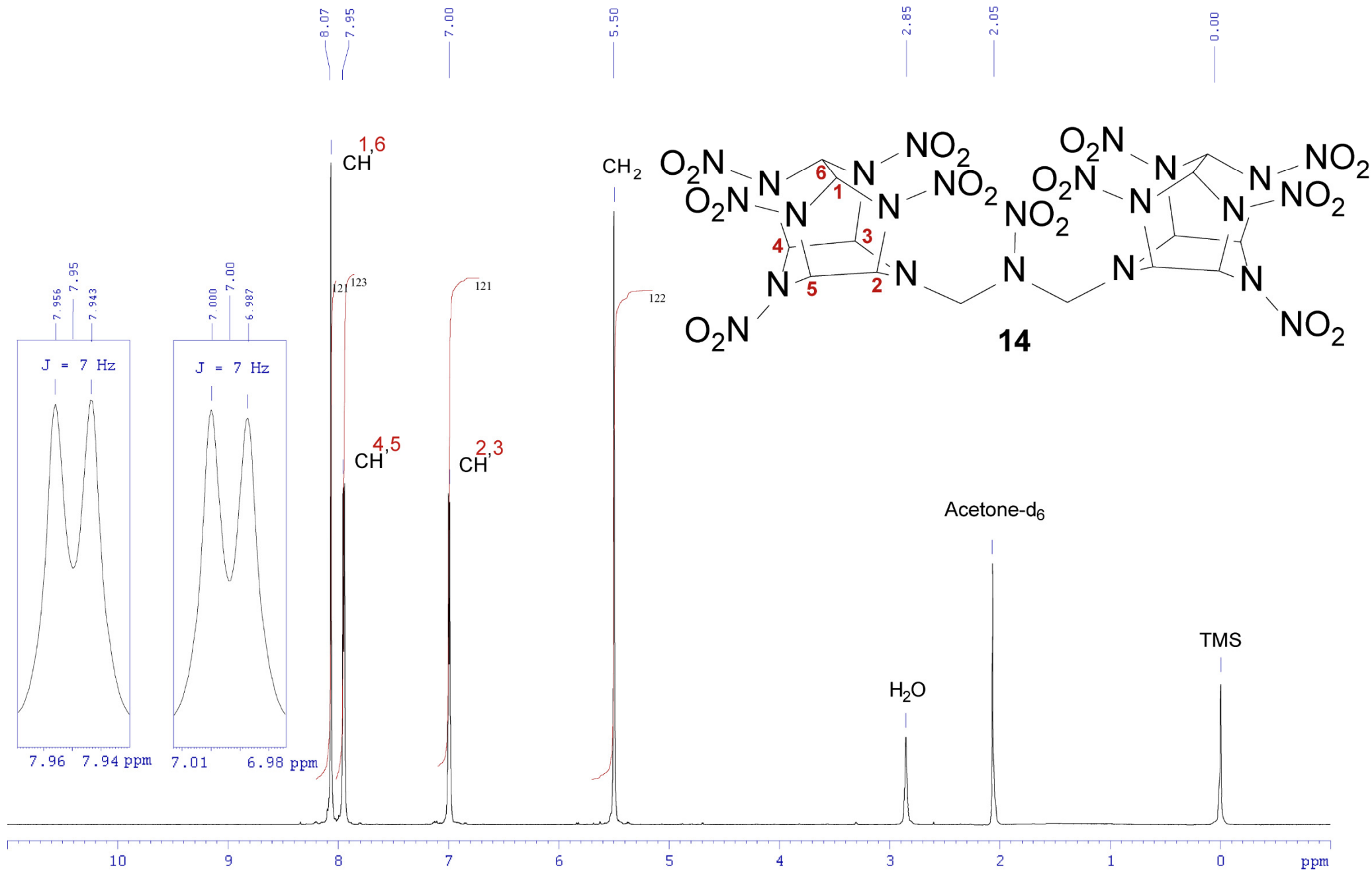


# IR (KBr) spectrum of compound 13

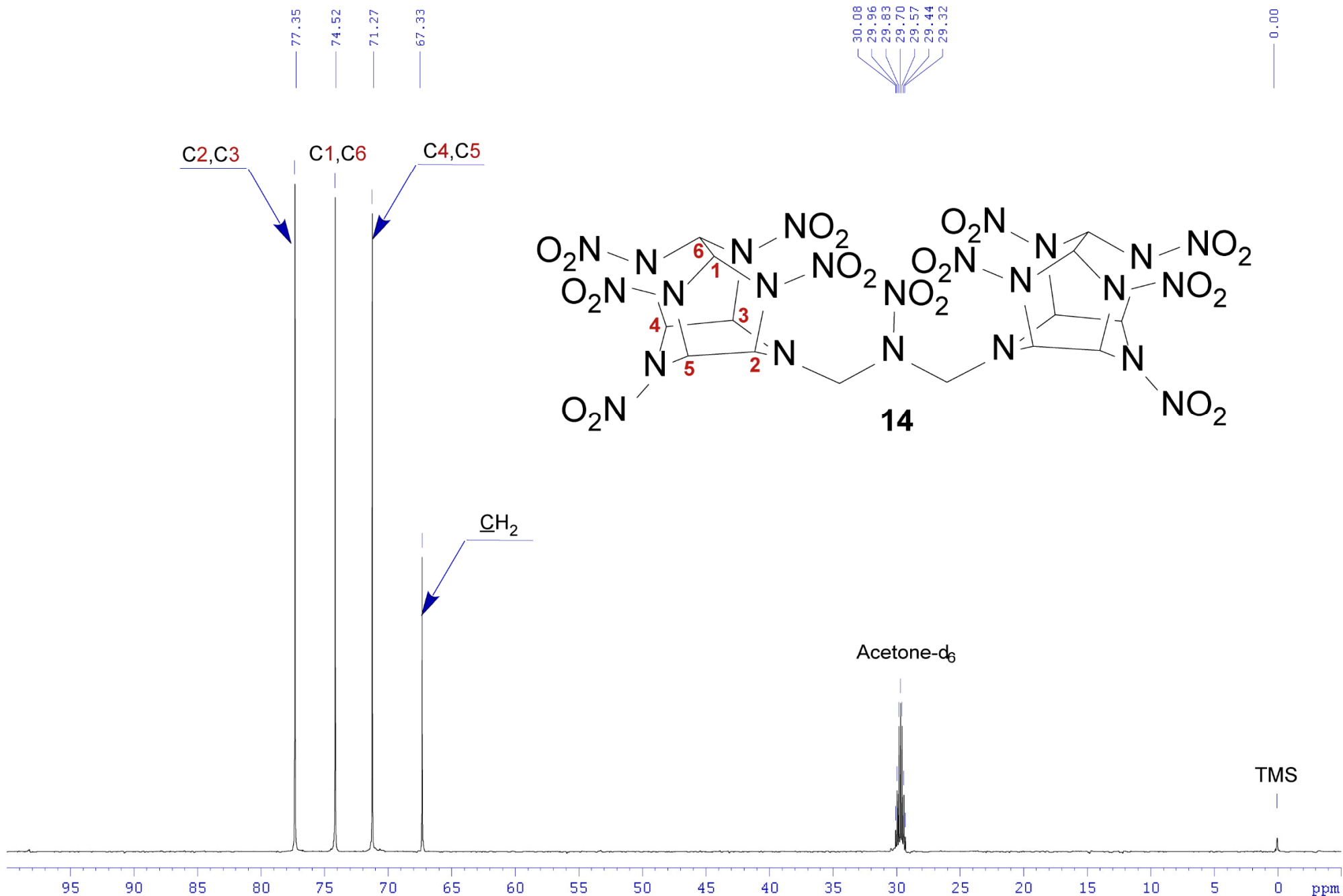




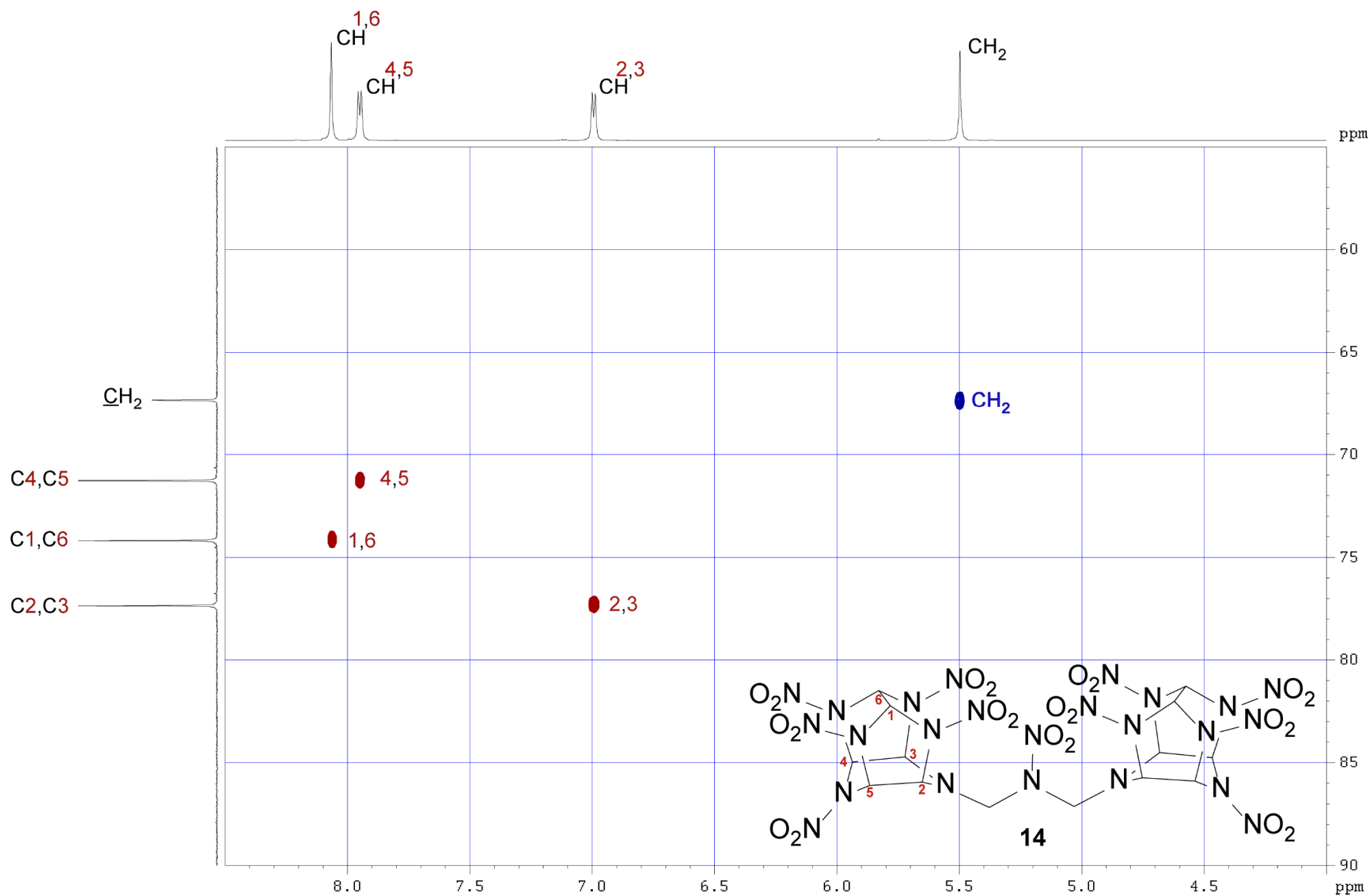
# <sup>1</sup>H NMR (600.13 MHz, [D<sub>6</sub>]acetone) spectrum of compound 14



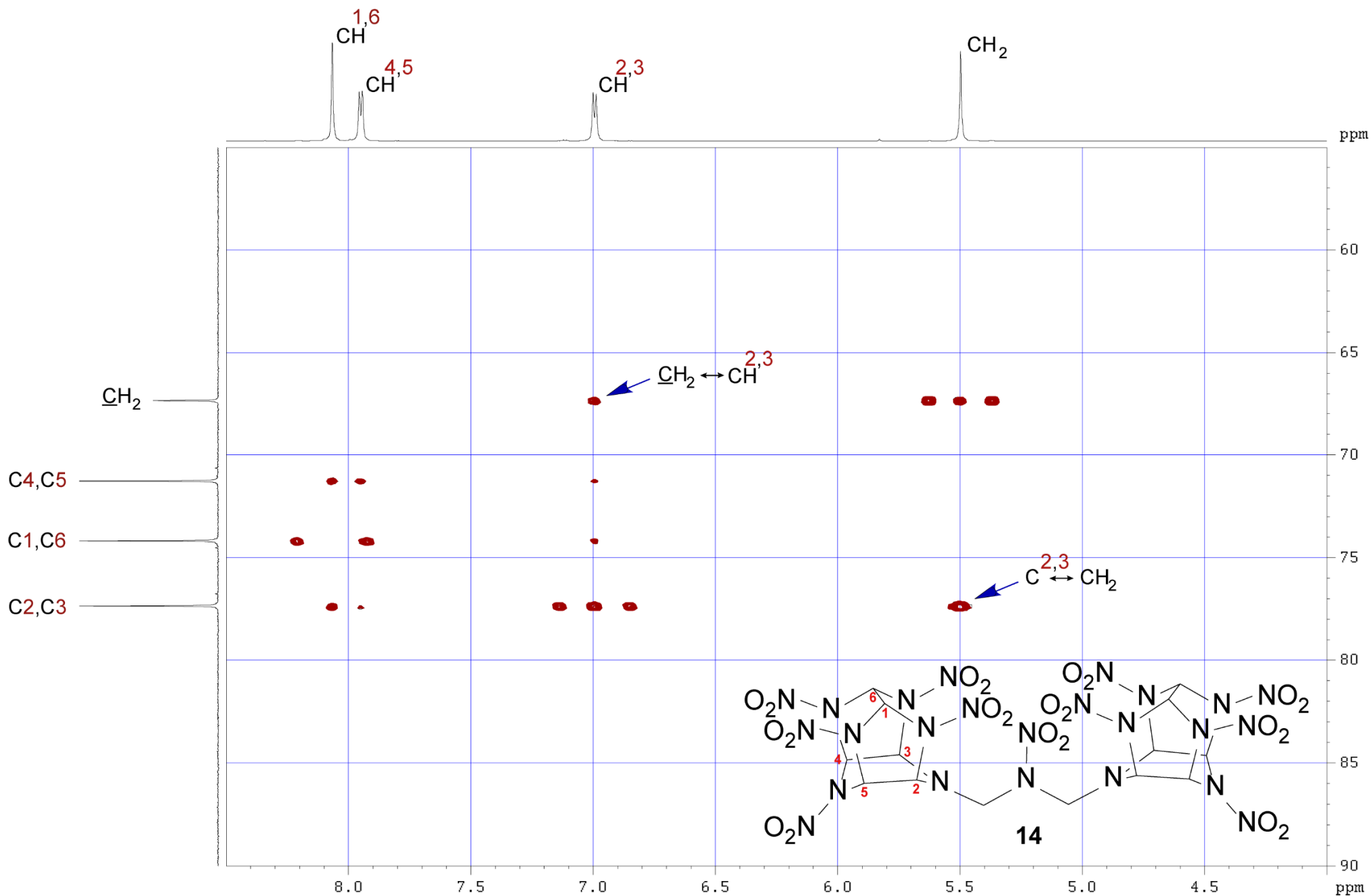
# $^{13}\text{C}$ NMR (150.9 MHz, $[\text{D}_6]$ acetone) spectrum of compound 14



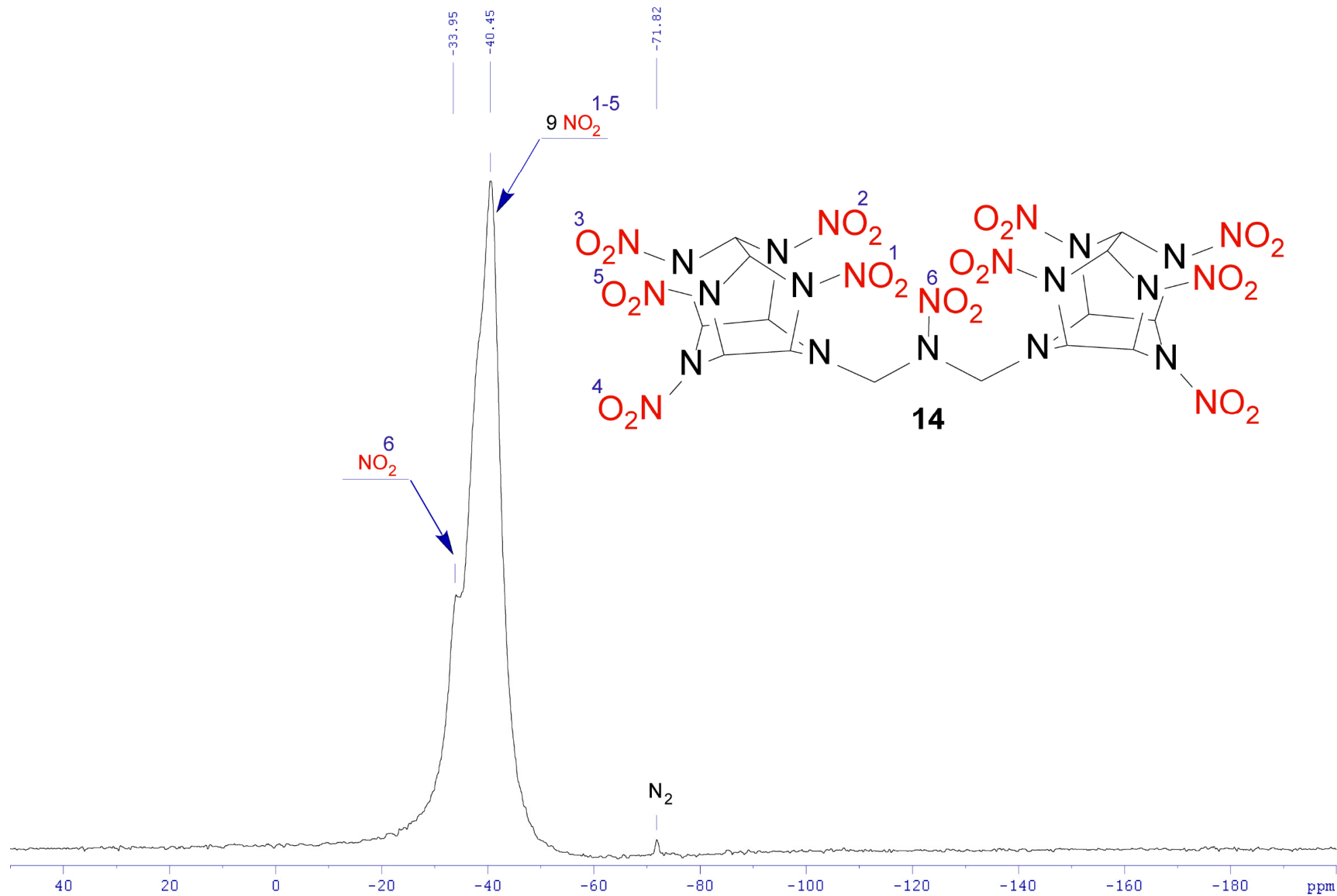
**{<sup>1</sup>H-<sup>13</sup>C} HSQC NMR (600.13 MHz, [D<sub>6</sub>]acetone) spectrum of compound 14**



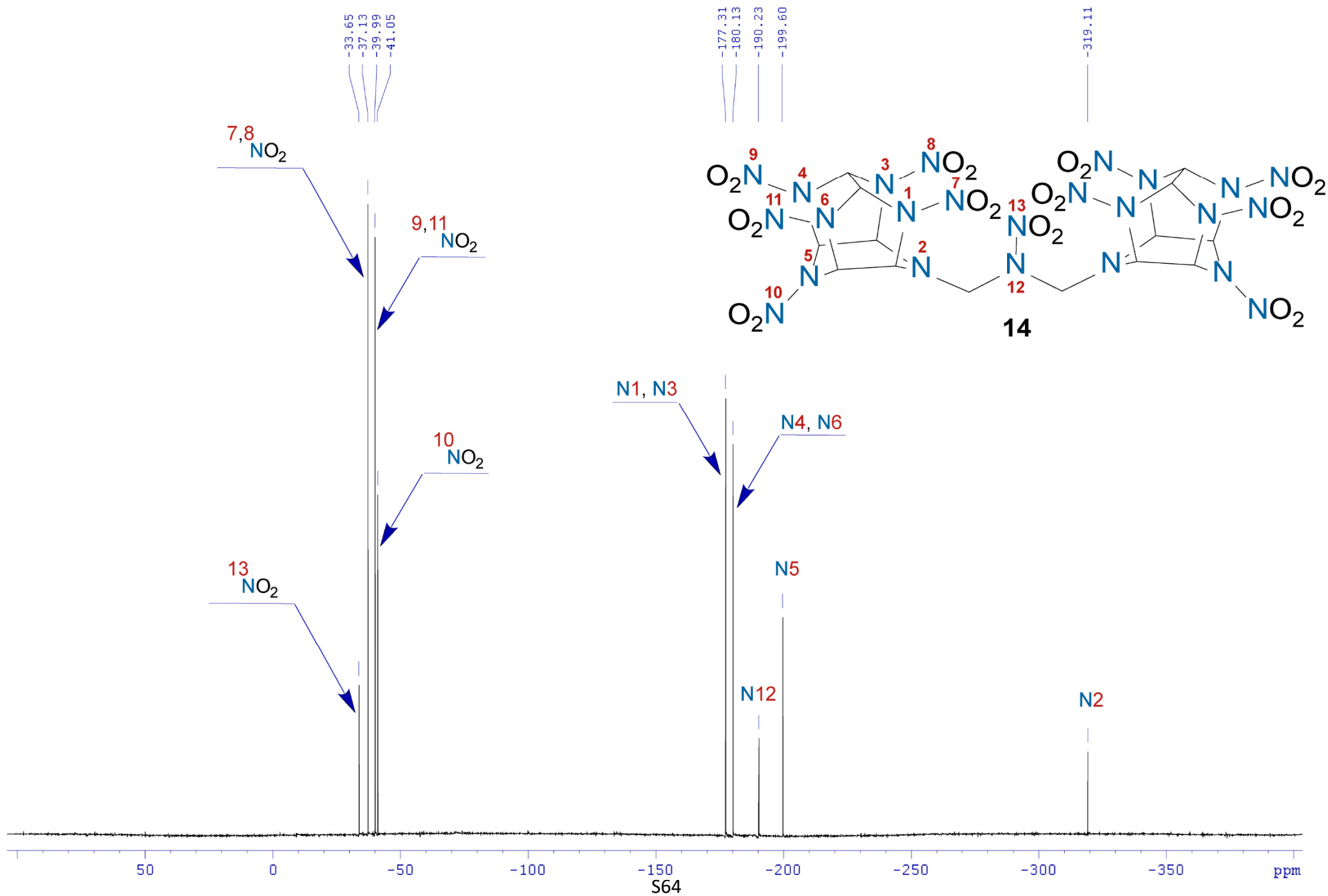
# $\{^1\text{H}-^{13}\text{C}\}$ HMBC NMR (600.13 MHz, $[\text{D}_6]$ acetone) spectrum of compound 14



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

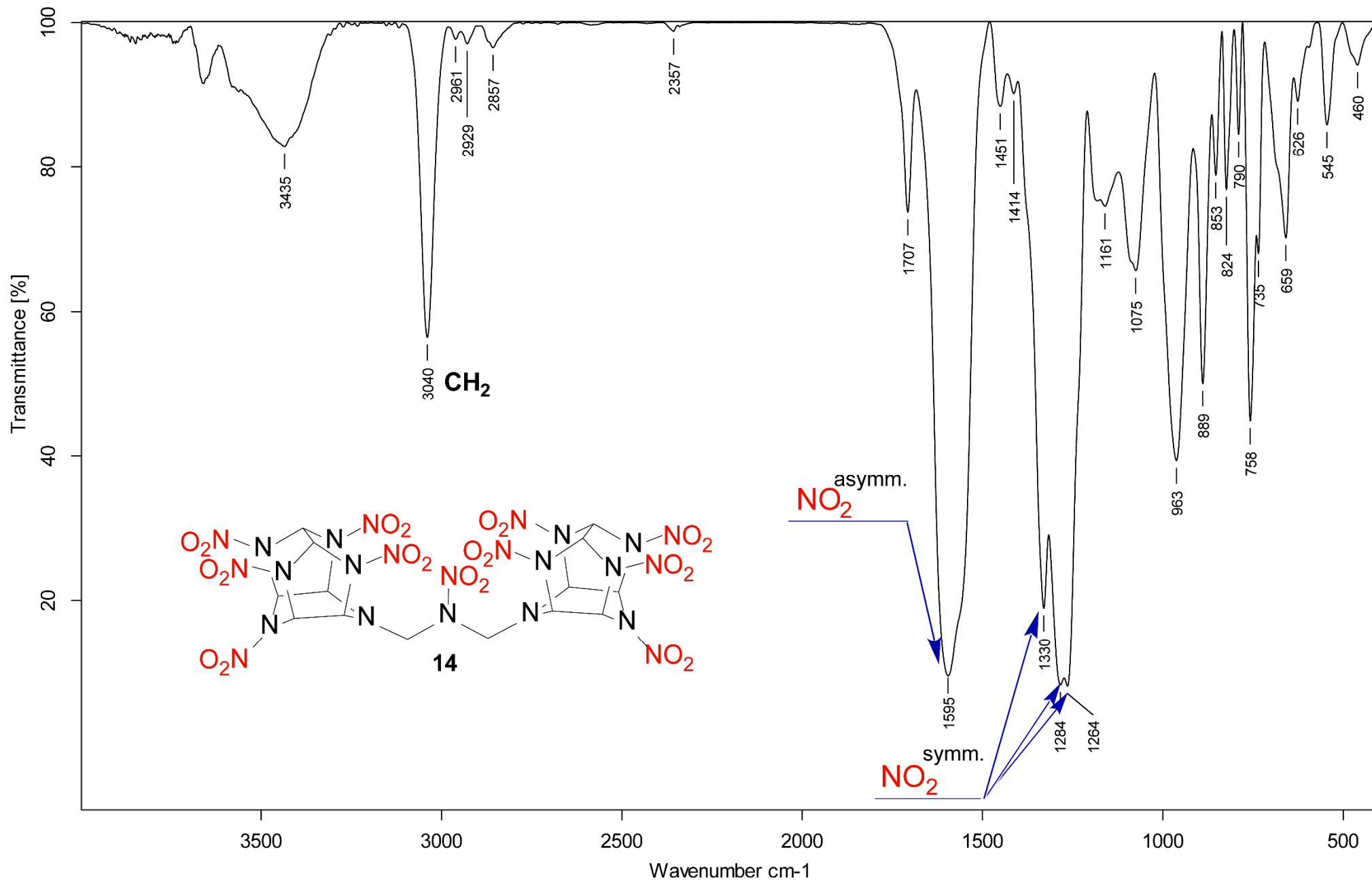


# $^{15}\text{N}$ NMR ([INVGATED], 60.8 MHz, $[\text{D}_6]$ acetone) spectrum of compound 14



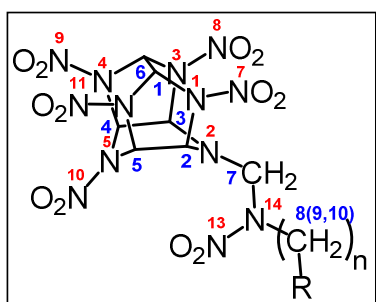


# IR (KBr) spectrum of compound 14



# Analysis of spectral characteristics of nitramines 7–14

## General formula of nitramines 7–14



7: n=0, R = COOEt;

8: n=0, R = H;

9: n = 2, R = N(NO<sub>2</sub>)H;

10: n = 0, R = CH<sub>3</sub>;

11: n = 2, R = N(NO<sub>2</sub>)CH<sub>3</sub>;

12: n = 1, R = HNC(NH<sub>2</sub>)=NNO<sub>2</sub>;

13: n = 2, R = N(NO<sub>2</sub>)CH<sub>2</sub>HNC(NH<sub>2</sub>)=NNO<sub>2</sub>;

14: n = 1, R = W(NO<sub>2</sub>)<sub>5</sub> (pentanitro pexaazaisowurtzitan).

**Table 1** Assigned <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>14</sup>N NMR shifts [ppm] of nitramines 7–14 in acetone-d<sub>6</sub>.

Nucleus	Assignment		Compounds							
	Part	Groups	Chemical shifts δ, ppm							
			7	8	9	10	11	12	13	14
<sup>1</sup> H (J <sub>H,H</sub> , Hz)	Cage	CH <sup>1,6</sup>	8.02 s	8.03 s	8.06 s	8.05 s	8.06 s	8.01 s	8.02 s	8.07 s
		CH <sup>4,5</sup>	7.97 d (8)	7.95 d (8)	7.97 d (8)	7.99 d (7)	7.98 d (8)	7.93 d (8)	7.97 d (8)	7.95 d (7)
		CH <sup>2,3</sup>	7.08 d (8)	6.69 d (8)	7.01 d (8)	6.99 d (7)	7.00 d (8)	7.20 d (8)	6.99 d (8)	7.00 d (7)
	Chain	N <sup>Cage</sup> -CH <sub>2</sub> <sup>7</sup>	5.75 s	5.06 s	5.39 s	5.35 s	5.40 s	5.54 s	5.40 s	5.50 s
		N(NO <sub>2</sub> )-CH <sub>2</sub> <sup>8(9)</sup>	–	–	4.25 t (6)	–	4.32 t (5)	5.27 d (6)	5.18 d (7)	–
		CH <sub>2</sub> <sup>9(10)</sup>	–	–	3.94 t (6)	–	4.24 t (5)	–	4.36 s	–
		N(NO <sub>2</sub> )-Me	–	–	–	3.52 s	3.45 s	–	–	–
		NH	–	n.o.*	10.87 brs	–	–	7.51 brt (5)	7.60 brs	–
		OCH <sub>2</sub>	4.40 k (7)	–	–	–	–	–	–	–
		-Me	1.37 t (7)	–	–	–	–	–	–	–
<sup>13</sup> C{ <sup>1</sup> H}	Cage	C <sup>2,3</sup>	77.8	77.5	77.6	77.3	77.5	77.2	77.3	77.4
		C <sup>1,6</sup>	74.5	74.4	74.4	74.2	74.4	74.4	74.2	74.5
		C <sup>4,5</sup>	71.7	71.3	71.5	71.2	71.4	71.3	71.3	71.3
	Chain	N <sup>Cage</sup> -CH <sub>2</sub> <sup>7</sup>	66.0	62.7	68.5	68.7	68.4	68.0	68.7	67.3
		N(NO <sub>2</sub> )-CH <sub>2</sub> <sup>8</sup>	–	–	50.1	–	49.4	55.7	49.8	–
		CH <sub>2</sub> <sup>9(10)</sup>	–	–	43.8	–	51.1	–	50.4 <sup>9</sup> 57.7 <sup>10</sup>	–
		N(NO <sub>2</sub> )-Me	–	–	–	38.9	39.6	–	–	–
		C=NNO <sub>2</sub>	–	–	–	–	–	160.2	160.2	–
		C=O	150.3	–	–	–	–	–	–	–
		OCH <sub>2</sub>	65.9	–	–	–	–	–	–	–
	-Me	14.3	–	–	–	–	–	–	–	
<sup>14</sup> N (ΔV <sub>1/2</sub> , Hz)	Cage	NNO <sub>2</sub> <sup>7,8</sup>	–40 (106)	–39 (106)	–39 (106)	–38 (97)	–38 (128)	–38 (140)	–38 (158)	–41 (192)
		NNO <sub>2</sub> <sup>9–11</sup>	–41 (120)	–41 (93)	–41 (106)	–41 (102)	–41 (128)	–41 (121)	–41 (136)	–
	Chain	NNO <sub>2</sub> <sup>13</sup>	–46 (80)	–30 (60)	–31 (80) –28 (47)	–29 (34)	–30 <sup>6</sup> (62) –28 <sup>6'</sup> (26)	–31 (85)	–30 (102)	–34 (174)
		C=N-NO <sub>2</sub>	–	–	–	–	–	–14 (87)	–14 (106)	–
	C=N-NO <sub>2</sub>	–	–	–	–	–	–135 (80)	–136 (111)	–	

\* Due to the processes of proton exchange with water, the signal did not observed.

**Table 2** Assigned  $^{15}\text{N}\{^1\text{H}\}$  NMR shifts [ppm] of nitramines **10–14** in acetone- $d_6$ .

Assignment		Compounds				
		Chemical shifts $\delta$ , ppm				
Part	Groups	10	11	12	13	14
Cage	N <sup>1,3</sup>	-177.7	-177.6	-178.5	-177.9	-177.3
	N <sup>4,6</sup>	-180.8	-180.4	-181.6	-180.8	-180.1
	N <sup>5</sup>	-199.5	-199.3	-199.0	-199.1	-199.6
	N <sup>2</sup> CH <sub>2</sub>	-320.7	-320.0	-321.3	-320.3	-319.1
	7,8	-37.3	-37.4	-37.5	-37.5	-37.1
	N-NO <sub>2</sub> 9,11	-39.9	-39.9	-40.0	-39.9	-40.0
	10	-40.7	-40.8	-40.5	-40.6	-41.1
Chain	N <sup>12</sup> -NO <sub>2</sub>	-203.3	-196.5 -210.5	-184.6	-195.2 -193.2	-190.2
	N-N <sup>13</sup> O <sub>2</sub>	-28.6	-30.2 -27.3	-30.4	-29.5 -29.0	-33.7
	C=N-NO <sub>2</sub>			-13.1	-13.2	
	C=N-NO <sub>2</sub>			n.o.*	-135.6	
	NH			-294.8	n.o.*	
	NH <sub>2</sub>			-298.9	-298.5	

\* Probably, due to the splitting on  $^1\text{H}$  and  $^{14}\text{N}$ , the signal of this  $^{15}\text{N}$  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 3** Assigned IR vibrations [ $\text{cm}^{-1}$ ] of nitramines **7–14** in KBr.

Assignment	Compounds							
	Vibration frequencies $\nu$ , $\text{cm}^{-1}$							
	7	8	9	10	11	12	13	14
	1601 vs	1608 s	1619 vs	1610 s	1607 s			
as N-NO <sub>2</sub> <sup>Cage</sup>	1579 vs	1590 vs	1592 vs	1589 vs	1587 vs	1596 vs	1595 m	
	1546 m	1553 s	1574 vs	1560 s	–			1595 vs
as N-NO <sub>2</sub> <sup>Chain</sup>	1529 m	–	1520 m	1522 s	1540 s 1510 s	1532 m	1533 m	
	1331 s	1339 s	1336 s	1340 s	1331 s	1330 s	1330 m	1330 vs
s N-NO <sub>2</sub>	1289 s	1280 vs	1274 vs	1295 vs	1282 vs	1283 s	1285 vs	1284 vs
	1269 vs	1261 vs	1258 vs	1272 vs	1260 vs	1261 vs	1266 vs	1264 vs
C=N-NO <sub>2</sub> <sup>NQ</sup>			–			1449 <sup>as</sup> m	1455 <sup>as</sup> m	–
						1308 <sup>s</sup> s		
CH <sub>2</sub> / Me	3061 m	3044 m	3037 m	3051 m 3033 m	3040 m	3044 m	3039 w	3040 m
NH		3297 m	3327 m			3358 m		
	–			–	–		3435 m	–
NH <sub>2</sub>		–	–			3464 m 3423 s	3345 m	
C=N			–			1643 s	1641 m	–
C=O	1774 s				–			

## Description of the spectra of nitramines 7–10

As can be seen in table 3 the IR spectra of **7–14** show the characteristic absorption bands corresponding to the asymmetrical vibrations of the *n*-nitro groups of at  $\tilde{\nu}$  1619 to 1546  $\text{cm}^{-1}$  (nitramine cage) and at  $\tilde{\nu}$  1540 to 1520  $\text{cm}^{-1}$  (nitramine chain), as well as the bands of the symmetrical vibrations of the *N*-nitro groups at  $\tilde{\nu}$  1340 to 1258  $\text{cm}^{-1}$ . In the IR spectra of **12** and **13** containing the nitroguanyl moiety, additional bands of the *N*-nitro group are observed at  $\tilde{\nu}$   $\sim$ 1450  $\text{cm}^{-1}$  (asymmetrical vibration of the nitrimino group), the imino group at  $\tilde{\nu}$   $\sim$ 1640  $\text{cm}^{-1}$  and amino groups at  $\tilde{\nu}$  3464 to 3297  $\text{cm}^{-1}$ .

According to table 1 the resonance peaks of the methylene units, which are directly linked to the pentanitro isowurtzitane cage, mainly appear in the range  $\delta_{\text{H}}$  5.39–5.75 ppm in the  $^1\text{H}$  NMR and  $\delta_{\text{C}}$  66.0–68.7 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR. While the signals of the  $\text{CH}_2$  located further from the cage along the alkylnitramine chain are slightly shifted to a lower field and are observed at  $\delta_{\text{H}}$  4.24–5.27 ppm in the  $^1\text{H}$  nmr and  $\delta_{\text{C}}$  49.4–57.7 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR. In primary nitramines **8** and **9**, the signal of the  $\text{CH}_2$  adjacent to  $\text{NHNO}_2$  is more shifted than other ones and appears at  $\delta_{\text{H}}$  5.06 and 3.94 ppm in the  $^1\text{H}$  NMR, as well as at  $\delta_{\text{C}}$  62.7 and 43.8 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR, respectively. The protons of amino and primary nitramino groups of **8**, **9**, **12**, and **13** are broadened to varying degrees and are observed at high field in the range  $\delta_{\text{H}}$  7.5–11.0 ppm. Additionally, in the  $^{13}\text{C}$  NMR of **12** and **13** bearing the nitroguanyl moiety the signal from the carbon atom of imino group  $\text{C}=\text{N}$  appears at  $\delta_{\text{C}}$  160.2 ppm.

The  $^{14}\text{N}$  NMR spectra of the new compounds show signals from the *N*-nitro groups of the pentanitro hexaazaisowurtzitane cage at  $\delta_{\text{N}}$  –41 to –38 ppm ( $\text{NO}_2$ ,  $\Delta\nu_{1/2} = 97\text{--}192$  Hz) and of the nitramine open-chain at  $\delta_{\text{N}}$  –34 to –28 ppm ( $\text{NO}_2$ ,  $\Delta\nu_{1/2} = 26\text{--}174$  Hz), except **7**, the peak of the *N*-nitro group in the side chain of which are observed in a lower field at –46 ppm. The  $^{14}\text{N}$  NMR spectra of **12** and **13** containing the nitroguanyl unit show the additional signals of the *N*-nitro group at  $\delta_{\text{N}}$  –14 ppm ( $\Delta\nu_{1/2} \sim 100$  Hz) and the imino group at  $\delta_{\text{N}}$  –135 ppm ( $\Delta\nu_{1/2} \sim 41$  Hz).

The  $^{15}\text{N}$  NMR spectra of **10–14** were measured in acetone- $\text{d}_6$  and are summarized in table 2. The signals of the *N*-nitro groups are observed at the lowest field and in the usual range  $\delta_{\text{N}}$  –41 to –37 ppm (nitramine cage) and  $\delta_{\text{N}}$  –34 to –27 ppm (nitramine chain). The signal for the cage nitrogen atom, which is linked to the alkylnitramine chain, appears at the highest field  $\delta_{\text{N}}$  –321 to –319 ppm. The signals of the nitrogen atoms of the five-membered rings of the cage are found as two close peaks in the middle of the spectra at the range between  $\delta_{\text{N}}$  –182 and –177 ppm. The peak of the nitrogen atom of the six-membered rings of the cage, which is linked to the  $\text{NO}_2$  group, appears at  $\delta_{\text{N}}$  –199 ppm. The other nitrogen atoms of the alkylnitramine open-chain fragment appear as the signals at the range between  $\delta_{\text{N}}$  –184 and –211 ppm. In the spectra of **12** and **13** are also observed some resonance peaks corresponding to the amino and imino nitrogen atoms of the nitroguanyl moiety.

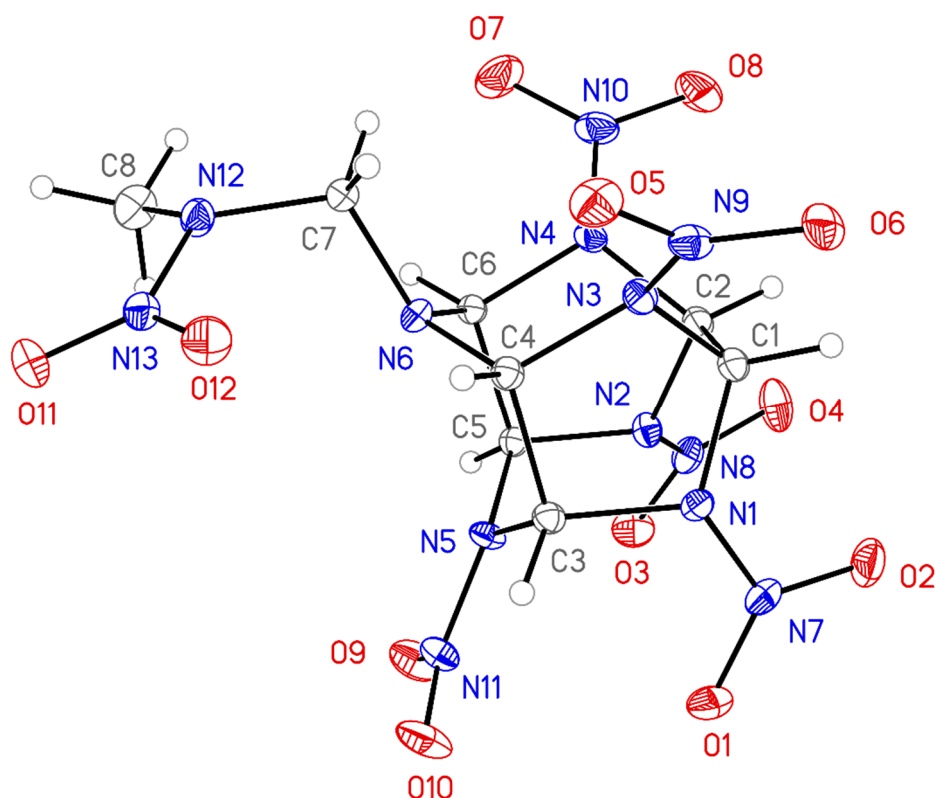
## 1) Single crystal X-ray diffraction of compound 10

The X-ray diffraction study of **10** was carried out on a «Bruker SMART APEX DUO CCD» diffractometer equipped with a Photon-III area-detector (MoK $\alpha$  radiation:  $\lambda = 0.71073 \text{ \AA}$ , graphite monochromator,  $\omega$ -scan) at 120 K. The structures were solved by a direct method and refined by least squares in the anisotropic full-matrix approximation in  $F^2_{\text{hkl}}$ . The positions of hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model. All calculations were performed using the SHELXT program package.<sup>6</sup> Detailed crystallographic information is provided in Tables 4, 5, and structure are presented in Fig. 1, 2. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2111284. Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

Single crystals of **10** suitable for X-ray diffraction measurements were obtained by slow evaporation from a solution of **10** in a mixture of MeCN and H<sub>2</sub>O at room temperature.

**Table 4** Detail Crystallographic data of compounds **10** according to single crystal X-ray diffraction analysis.

Formula	C <sub>8</sub> H <sub>11</sub> N <sub>13</sub> O <sub>12</sub>
Formula weight [g·mol <sup>-1</sup> ]	481.26
Temperature [K]	120
Radiation	MoK $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )
Crystal system	monoclinic
Space group	<i>P</i> 21/ <i>c</i>
Unit cell dimensions	$a = 8.7416(2) \text{ \AA}$ , $\alpha = 90^\circ$ $b = 1.9374(3) \text{ \AA}$ , $\beta = 97.207(1)^\circ$ $c = 16.2335(4) \text{ \AA}$ , $\gamma = 90^\circ$
$V [\text{\AA}^3]$	1680.61(7)
$Z / Z'$	4 / 1
$\rho_{\text{calc}} [\text{g}\cdot\text{cm}^{-3}]$	1.902
$\mu [\text{mm}^{-1}]$	0.177
$F(000)$	984
crystal colour	colourless
crystal size [mm <sup>3</sup> ]	0.33 × 0.28 × 0.08
$\theta$ range [°]	2.35 to 34.73
Index ranges	$-13 \leq h \leq 13$ , $-18 \leq k \leq 18$ , $-24 \leq l \leq 24$
Reflections measured	32903
Independent reflections	6342 [R(int) = 0.0320]
Restraints applied/parameters refined	0 / 299
Goodness-of-fit on $F^2$	1.017
Reflections with $I > 2\sigma(I)$	4984
Final $R$ indices [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0332$ , $wR_2 = 0.0877$
Final $R$ indices [all data]	$R_1 = 0.0453$ , $wR_2 = 0.0916$
Residual electron density ( $\rho_{\text{max}}/\rho_{\text{min}}$ ) [ $\text{e \AA}^{-3}/\text{e \AA}^{-3}$ ]	0.449 / -0.325
CCDC number	2111284



**Fig. 1.** General view of molecule **10** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.

**Table 5** Selected bond lengths (Å), bond angles (°) and torsion angles (°) of compound **10**

<b>Bond lengths</b>	
<i>Cage nitro groups</i>	
N(1)–N(7)	1.3803(11)
N(2)–N(8)	1.4036(11)
N(3)–N(9)	1.4011(11)
N(4)–N(10)	1.3713(11)
N(5)–N(11)	1.3971(11)
<i>Nitramine open-chain</i>	
N(6)–C(7)	1.4683(11)
C(7)–N(12)	1.4597(12)
N(12)–C(8)	1.4616(13)
N(12)–N(13) ( <i>Nitro group</i> )	1.3584(11)

**Table 5** (continued)

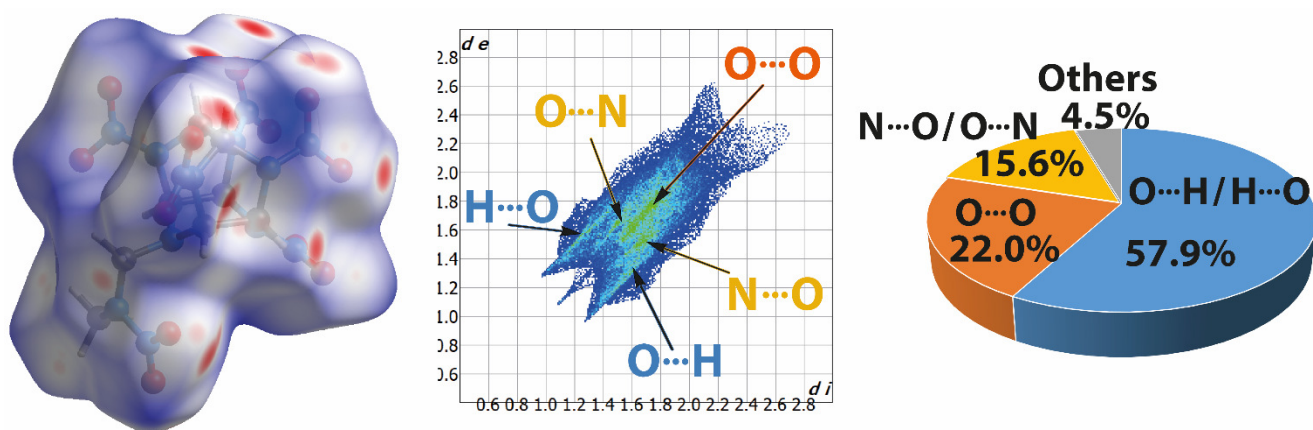
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<b>Bond angles</b>	
<i>Cage nitro groups</i>	
N(7)–N(1)–C(1)	117.41(7)
N(7)–N(1)–C(3)	118.88(7)
N(8)–N(2)–C(2)	119.74(7)
N(8)–N(2)–C(5)	118.93(7)
N(9)–N(3)–C(1)	118.53(7)
N(9)–N(3)–C(4)	117.40(7)
N(10)–N(4)–C(2)	121.20(8)
N(10)–N(4)–C(6)	121.70(7)
N(11)–N(5)–C(3)	120.36(7)
N(11)–N(5)–C(5)	120.50(7)
<i>Nitramine open-chain</i>	
N(6)–C(7)–N(12)	111.31(7)
C(7)–N(12)–C(8)	121.27(8)
N(13)–N(12)–C(7) ( <i>Nitro group</i> )	115.03(7)
N(13)–N(12)–C(8) ( <i>Nitro group</i> )	116.10(8)

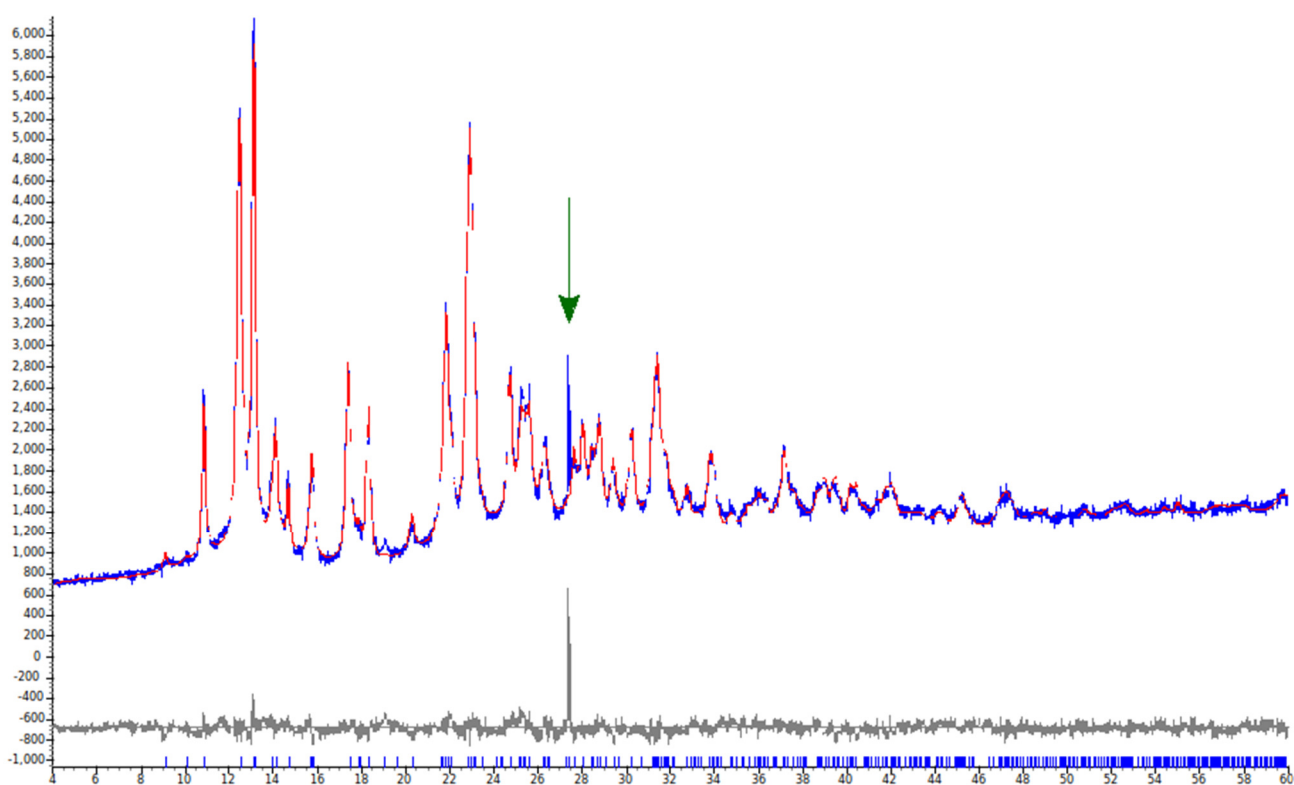
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<b>Torsion angles</b>	
<i>Cage nitro groups</i>	
N(7)–N(1)–C(3)–C(4) ( <i>equatorial</i> )	–165.26(7)
N(8)–N(2)–C(5)–C(6) ( <i>axial</i> )	–124.18(8)
N(9)–N(3)–C(4)–C(3) ( <i>axial</i> )	–116.42(8)
N(10)–N(4)–C(6)–C(5) ( <i>axial</i> )	128.47(8)
N(11)–N(5)–C(5)–C(6) ( <i>middle</i> )	140.50(8)
N(11)–N(5)–C(3)–C(4) ( <i>middle</i> )	–141.89(8)
<i>Nitramine open-chain</i>	
C(4)–N(6)–C(7)–N(12) ( <i>axial</i> )	–119.51(8)
C(6)–N(6)–C(7)–N(12) ( <i>axial</i> )	105.08(9)

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**Fig. 2** Hirshfeld surface calculations, 2D fingerprint plots in crystal stacking and pie graph of percentage contributions of the individual atomic contacts to the Hirshfeld surface of **10**.



**Fig. 3** Experimental (blue) and calculated (red) powder diffraction pattern for **10** at ambient conditions ( $\sim 298$  K, constrained Rietveld refinement). **Calculated crystal density is  $1.860 \text{ g}\cdot\text{cm}^{-3}$** . The most intense reflection corresponding to an unidentified admixture phase is shown with green arrow, the total area of the diffraction pattern corresponding to this phase does not exceed 1.1%.



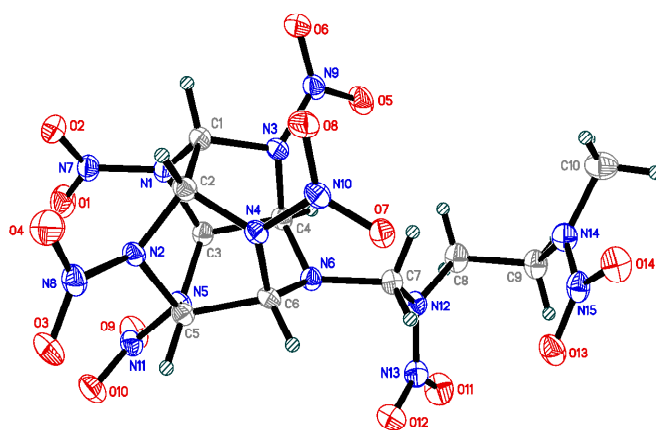
## 2) Single crystal X-ray diffraction of compound 11

The X-ray diffraction study of **11** was carried out on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (CuK $\alpha$  radiation:  $\lambda = 1.54184 \text{ \AA}$ , graphite monochromator, kappa geometry, shutterless  $\omega$ -scan technique) at 100K. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.<sup>10</sup> The structure was solved by direct methods using SHELXT<sup>9</sup> and refined on  $F^2$  using SHELXL-2018<sup>11</sup> in the OLEX2 program.<sup>12</sup> 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. A rotating group model was applied for methyl groups. Detailed crystallographic information is provided in Tables 6, 7 and structure are presented in Fig. 4–6. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2121216. Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

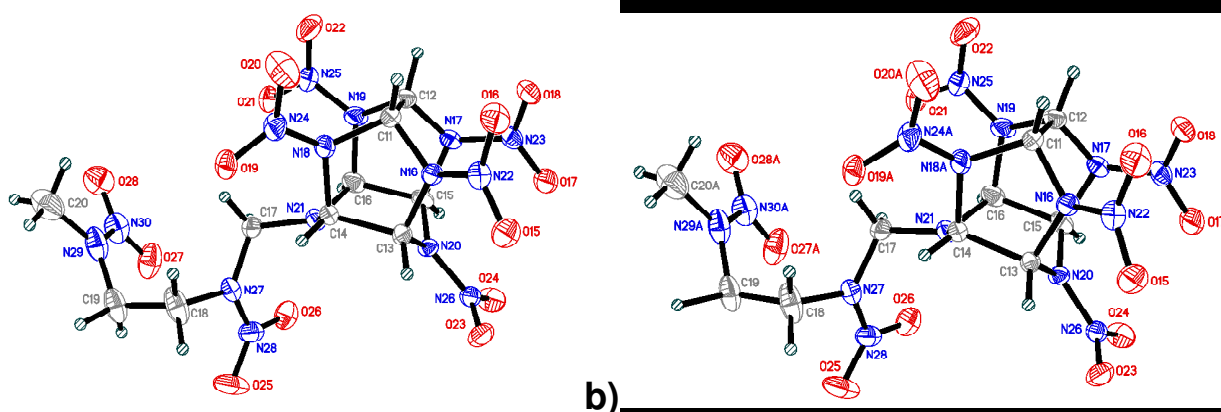
Single crystals of **11** suitable for X-ray diffraction measurements were obtained by slow evaporation from a solution of **11** in a mixture of MeCN and H<sub>2</sub>O at room temperature.

**Table 6** Detail Crystallographic data of **11** according to single crystal X-ray diffraction analysis.

Formula	C <sub>10</sub> H <sub>15</sub> N <sub>15</sub> O <sub>14</sub>
Formula weight [g·mol <sup>-1</sup> ]	569.37
Temperature [K]	100(2)
Radiation	MoK $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )
Crystal system	Monoclinic
Space group	$P 2_1/c$
Unit cell dimensions	$a = 14.18150(10) \text{ \AA}$ , $\alpha = 90^\circ$ $b = 13.83480(10) \text{ \AA}$ , $\beta = 93.9580(10)^\circ$ $c = 21.5145(2) \text{ \AA}$ , $\gamma = 90^\circ$
$V [\text{\AA}^3]$	4211.04(6)
$Z / Z'$	8 / 2
$\rho_{\text{calc}} [\text{g}\cdot\text{cm}^{-3}]$	1.796
$\mu [\text{mm}^{-1}]$	1.474
$F(000)$	2336
crystal colour	Colourless
crystal size [mm <sup>3</sup> ]	0.05 × 0.03 × 0.01
$\theta$ range [°]	3.124 to 78.485
Index ranges	$-18 \leq h \leq 17$ , $-17 \leq k \leq 17$ , $-27 \leq l \leq 25$
Reflections measured	59336
Independent reflections	9011 [R(int) = 0.0488]
Restraints applied/parameters refined	71 / 799
Goodness-of-fit on $F^2$	1.048
Reflections with $I > 2\sigma(I)$	8476
Final $R$ indices [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0505$ , $wR_2 = 0.1384$
Final $R$ indices [all data]	$R_1 = 0.0527$ , $wR_2 = 0.1403$
Residual electron density ( $\rho_{\text{max}} / \rho_{\text{min}}$ ) [ $\text{e \AA}^{-3} / \text{e \AA}^{-3}$ ]	0.624 / -0.587
CCDC number	2121216



**Fig. 4** General view of the first molecule of **11** in the unit cell. Anisotropic displacement parameters are drawn at 50% probability level.



**Fig. 5** General view of the second molecule of **11** in the unit cell, the atoms at the end of the nitramine open-chain as well as one cage nitro group are disordered. Anisotropic displacement parameters are drawn at 50% probability level.

**Table 7** Selected bond lengths (Å), bond angles (°) and torsion angles (°) of compound **11**

**Bond lengths**

*Cage nitro groups*

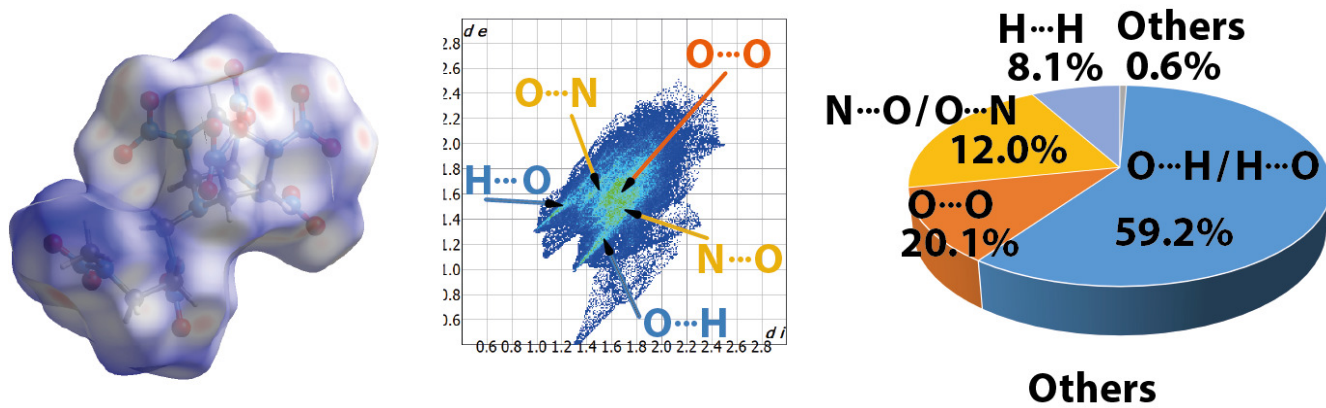
N(1)–N(7) / N(16)–N(22)	1.378(2) / 1.379(2)
N(2)–N(8) / N(17)–N(23)	1.4154(19) / 1.361(2)
N(3)–N(9) / N(18)–N(24), N(18A)–N(24A)	1.4131(19) / 1.394(3), 1.391(4)
N(4)–N(10) / N(19)–N(25)	1.3495(19) / 1.362(3)
N(5)–N(11) / N(20)–N(26)	1.3983(19) / 1.390(2)

*Nitramine open-chain*

N(6)–C(7) / N(21)–C(17)	1.463(2) / 1.460(2)
C(7)–N(12) / C(17)–N(27)	1.455(2) / 1.456(2)
N(12)–C(8) / N(27)–C(18)	1.467(2) / 1.464(3)
N(12)–N(13) / N(27)–N(28) ( <i>Nitro group</i> )	1.363(2) / 1.357(2)
C(8)–C(9) / C(18)–C(19)	1.529(2) / 1.542(3)
C(9)–N(14) / C(19)–N(29), C(19)–N(29A)	1.461(2) / 1.484(4), 1.485(5)
N(14)–C(10) / N(29)–C(20), N(29A)–C(20A)	1.467(3) / 1.461(4), 1.461(5)
N(14)–N(15) / N(29)–N(30), N(29A)–N(30A)	1.348(2) / 1.362(3), 1.363(4)

(*Nitro group*)





**Fig. 6** Hirshfeld surface calculations, 2D fingerprint plots in crystal stacking and pie graph of percentage contributions of the individual atomic contacts to the Hirshfeld surface of **11**.

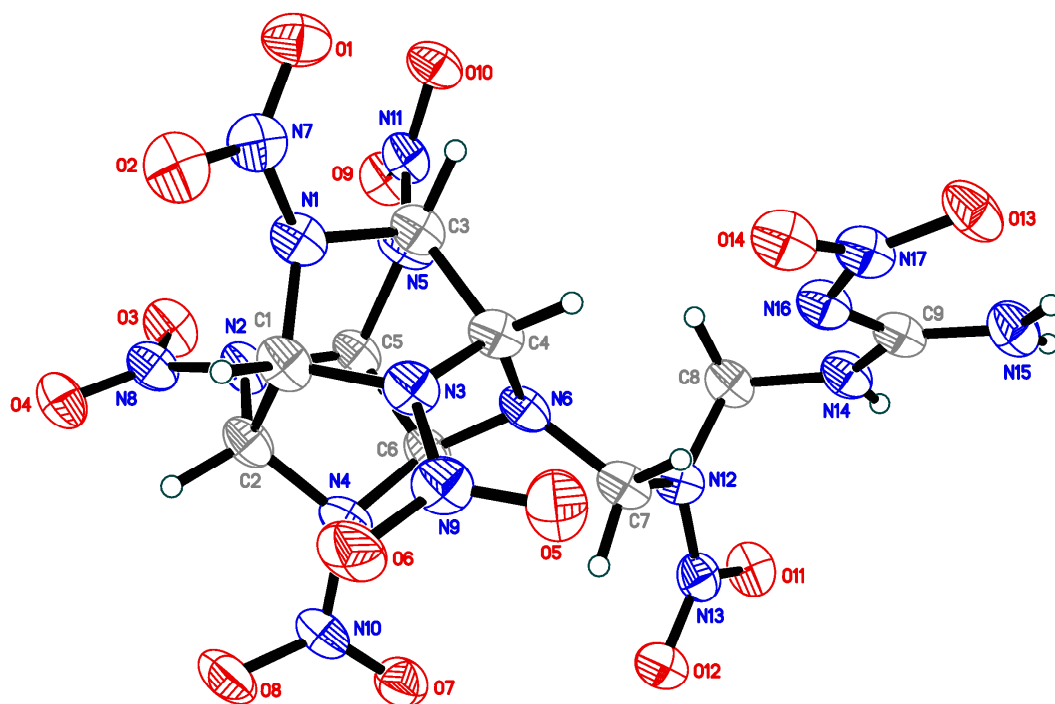
### 3) Single crystal X-ray diffraction of compound 12

The X-ray diffraction study of **12** was carried out on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (CuK $\alpha$  radiation:  $\lambda = 1.54184 \text{ \AA}$ , graphite monochromator, kappa geometry, shutterless  $\omega$ -scan technique) at 100K. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.<sup>10</sup> The structure was solved by direct methods using SHELXT<sup>9</sup> and refined on  $F^2$  using SHELXL-2018<sup>11</sup> in the OLEX2 program.<sup>12</sup> All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Locations of amino hydrogen atoms (H15A, H15B, H14) were found from the electron density-difference map; these hydrogen atoms were 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. Detailed crystallographic information is provided in Tables 8–10 and structure are presented in Fig. 7, 8. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2104897. Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

Single crystals of **12** suitable for X-ray diffraction measurements were obtained by slow evaporation from a solution of **12** in a mixture of MeCN and H<sub>2</sub>O at room temperature.

**Table 8** Detail Crystallographic data of **12** according to single crystal X-ray diffraction analysis.

Formula	C <sub>9</sub> H <sub>13</sub> N <sub>17</sub> O <sub>14</sub>
Formula weight [g·mol <sup>-1</sup> ]	583.36
Temperature [K]	100
Radiation	CuK $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )
Crystal system	orthorhombic
Space group	<i>Pca21</i>
Unit cell dimensions	$a = 17.7402(4) \text{ \AA}$ , $\alpha = 90^\circ$ $b = 9.2797(4) \text{ \AA}$ , $\beta = 90^\circ$ $c = 12.2787(4) \text{ \AA}$ , $\gamma = 90^\circ$
$V [\text{\AA}^3]$	2021.37(12)
$Z / Z'$	4 / 1
$\rho_{\text{calc}} [\text{g}\cdot\text{cm}^{-3}]$	1.917
$\mu [\text{mm}^{-1}]$	1.586
$F(000)$	1192
crystal colour	colourless
crystal size [mm <sup>3</sup> ]	0.05 × 0.04 × 0.005
$\theta$ range [°]	4.765 to 79.343
Index ranges	$-21 \leq h \leq 22$ , $-11 \leq k \leq 11$ , $-15 \leq l \leq 14$
Reflections measured	17943
Independent reflections	3924 [R(int) = 0.0498]
Restraints applied/parameters refined	1 / 375
Goodness-of-fit on $F^2$	1.080
Reflections with $I > 2\sigma(I)$	3539
Final $R$ indices [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0521$ , $wR_2 = 0.1425$
Final $R$ indices [all data]	$R_1 = 0.0574$ , $wR_2 = 0.1471$
Residual electron density ( $\rho_{\text{max}} / \rho_{\text{min}}$ ) [ $\text{e \AA}^{-3} / \text{e \AA}^{-3}$ ]	0.418 / -0.307
CCDC number	2104897



**Fig. 7** General view of molecule **12** in crystal. Anisotropic displacement parameters are drawn at 50% probability level.

**Table 9** Selected bond lengths (Å), bond angles (°) and torsion angles (°) of compound **12**

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**Bond lengths**

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*Cage nitro groups*

N(1)–N(7)	1.415(6)
N(2)–N(8)	1.392(6)
N(3)–N(9)	1.341(6)
N(4)–N(10)	1.398(6)
N(5)–N(11)	1.372(6)

*Nitramine open-chain*

N(6)–C(7)	1.449(7)
C(7)–N(12)	1.468(7)
C(8)–N(12)	1.469(6)
N(12)–N(13) ( <i>Nitro group</i> )	1.359(6)

*Nitroguanyl moiety*

C(8)–N(14)	1.435(7)
C(9)–N(14)	1.344(7)
C(9)–N(15)	1.321(7)
C(9)–N(16)	1.350(7)
N(16)–N(17) ( <i>Nitro group</i> )	1.342(6)

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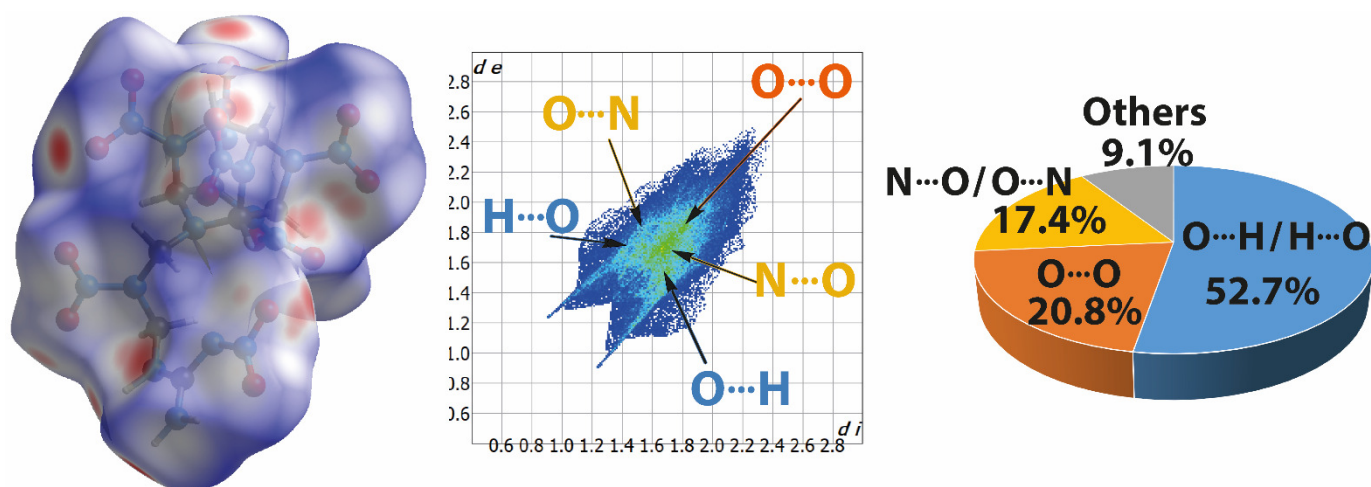
**Table 9** (continued)

<b>Bond angles</b>	
<i>Cage nitro groups</i>	
N(7)–N(1)–C(1)	116.0(4)
N(7)–N(1)–C(3)	118.8(4)
N(8)–N(2)–C(2)	122.2(4)
N(8)–N(2)–C(5)	121.2(4)
N(9)–N(3)–C(1)	121.7(4)
N(9)–N(3)–C(4)	122.8(4)
N(10)–N(4)–C(2)	119.3(4)
N(10)–N(4)–C(6)	118.8(4)
N(11)–N(5)–C(3)	120.2(4)
N(11)–N(5)–C(5)	119.9(4)
<i>Nitramine open-chain</i>	
N(6)–C(7)–N(12)	109.9(4)
C(7)–N(12)–C(8)	122.9(4)
N(13)–N(12)–C(7) ( <i>Nitro group</i> )	120.0(4)
N(13)–N(12)–C(8) ( <i>Nitro group</i> )	116.2(4)
<i>Nitroguanyl moiety</i>	
N(14)–C(8)–N(12)	114.7(4)
C(9)–N(14)–C(8)	122.9(5)
N(15)–C(9)–N(14)	119.1(5)
N(14)–C(9)–N(16)	112.3(4)
N(15)–C(9)–N(16)	128.6(5)
N(17)–N(16)–C(9) ( <i>Nitro group</i> )	119.6(4)
<b>Torsion angles</b>	
<i>Cage nitro groups</i>	
N(7)–N(1)–C(3)–C(4) ( <i>axial</i> )	114.5(4)
N(8)–N(2)–C(5)–C(6) ( <i>axial</i> )	–130.1(4)
N(9)–N(3)–C(4)–C(3) ( <i>equatorial</i> )	–174.2(4)
N(10)–N(4)–C(6)–C(5) ( <i>axial</i> )	120.3(4)
N(11)–N(5)–C(5)–C(6) ( <i>middle</i> )	144.9(4)
N(11)–N(5)–C(3)–C(4) ( <i>middle</i> )	–142.7(4)
<i>Nitramine open-chain</i>	
C(4)–N(6)–C(7)–N(12) ( <i>axial</i> )	–139.7(4)
C(6)–N(6)–C(7)–N(12) ( <i>axial</i> )	76.6(5)
<i>Nitroguanyl moiety</i>	
N(12)–C(8)–N(14)–C(9)	–80.7(6)

**Table 10** Hydrogen bonds for **12** [Å and °].

D—H···A	type	d(D—H)	d(H···A)	d(D···A)	angle (DHA)
N(14)—H(14)···O(10)#1	intermolecular	0.86(9)	2.46(9)	3.241(6)	151(8)
N(15)—H(15A)···O(3)#2	intermolecular	0.96(7)	2.66(6)	3.189(7)	115(4)
N(15)—H(15)···O(13)	intramolecular	0.96(7)	1.96(6)	2.642(7)	126(5)
N(15)—H(15B)···O(7)#3	Intermolecular	0.91(9)	2.22(9)	3.061(7)	154(8)

Symmetry transformations used to generate equivalent atoms: #1  $x, y+1, z$ ; #2  $-x+1/2, y+1, z+1/2$ ; #3  $x-1/2, -y+2, z$ .

**Fig. 8** Hirshfeld surface calculations, 2D fingerprint plots in crystal stacking and pie graph of percentage contributions of the individual atomic contacts to the Hirshfeld surface of **12**.



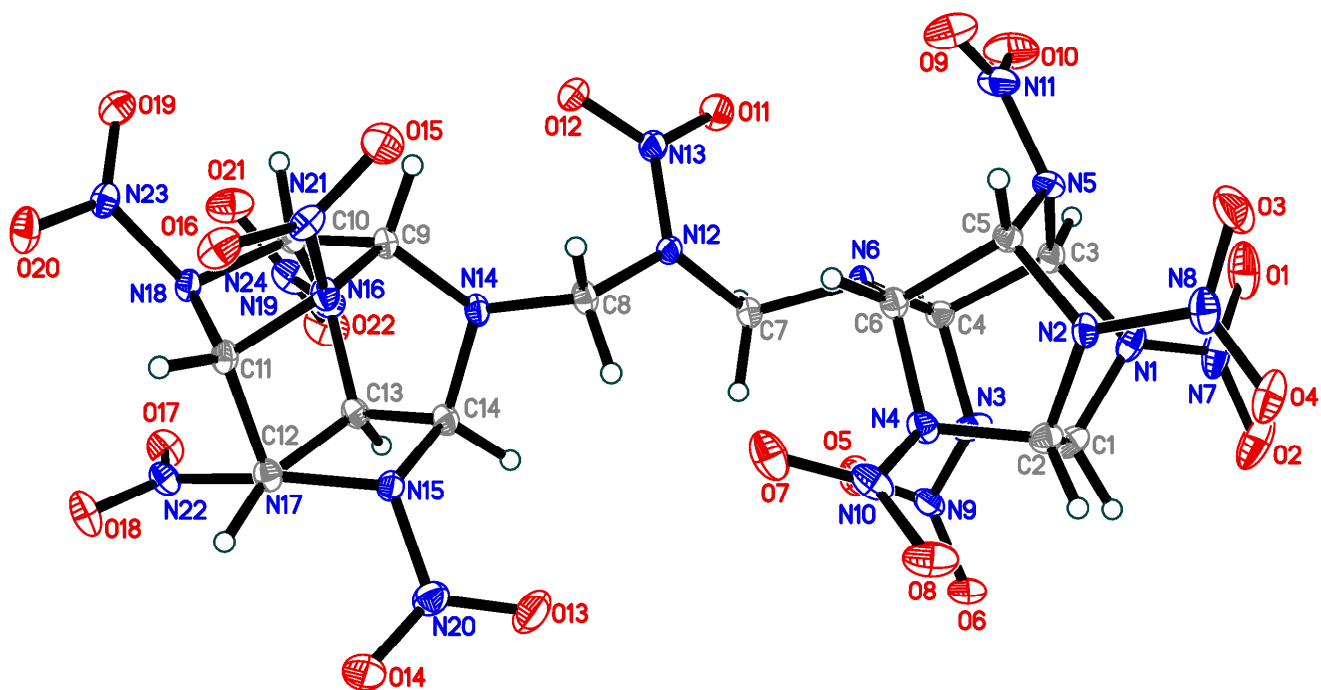
#### 4) Single crystal X-ray diffraction of compound 14·2MeCN

The X-ray diffraction study of 14·2MeCN was carried out on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (MoK $\alpha$  radiation:  $\lambda = 0.71073$  Å graphite monochromator, shutterless  $\omega$ -scan technique) at 100K. The intensity data were integrated by the SAINT program<sup>13</sup> and were corrected for absorption and decay using SADABS.<sup>14</sup> The structure was solved by direct methods using SHELXT<sup>9</sup> and refined on  $F^2$  using SHELXL-2018.<sup>11</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters; a rotating group model was applied for methyl groups. The SHELXTL program suite was used for molecular graphics. Detailed crystallographic information is provided in Table 11, 12 and structure is presented in Fig. 9–13. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2078088. Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

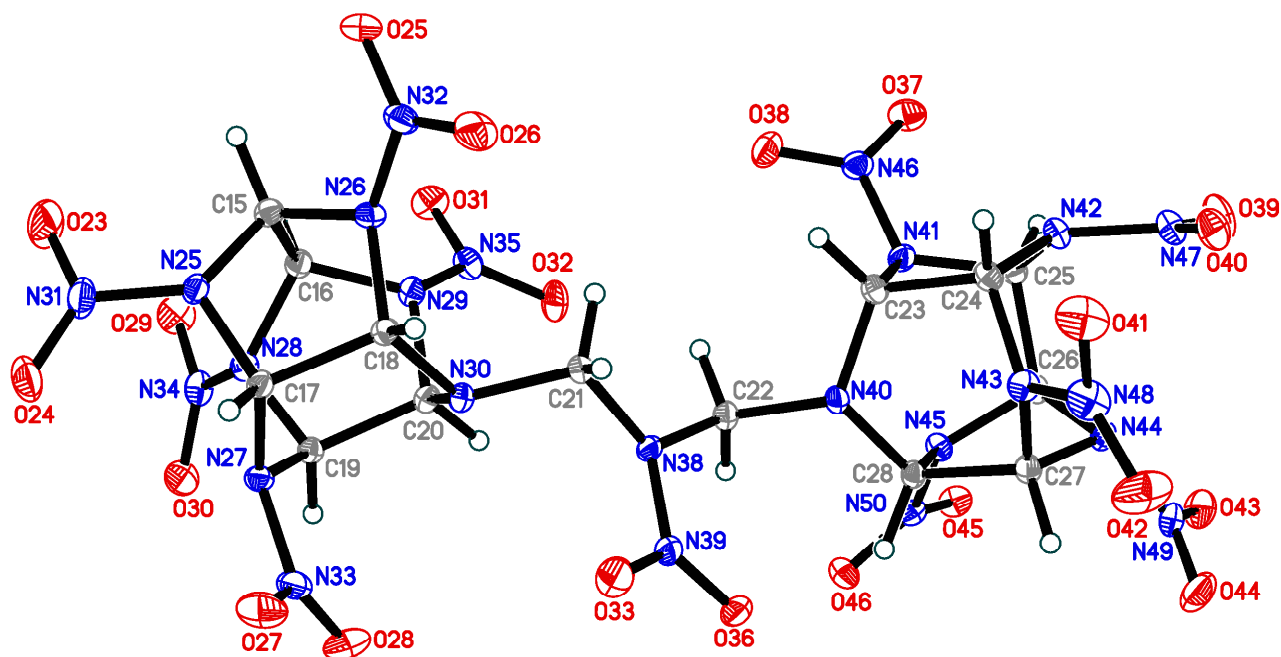
Single crystals of 14·2MeCN suitable for X-ray diffraction measurements were obtained by slow evaporation from a solution of 14 in a mixture of MeCN and H<sub>2</sub>O at room temperature. Upon slow evaporation from a solution of 14 in a mixture of acetone, THF or dioxane and H<sub>2</sub>O crystals are formed, which are solvates 14, containing, one molecule of the corresponding solvent.

**Table 11** Detail Crystallographic data of 14·2MeCN according to single crystal X-ray diffraction analysis.

Formula	C <sub>18</sub> H <sub>22</sub> N <sub>26</sub> O <sub>22</sub>
Formula weight [g·mol <sup>-1</sup> ]	954.61
Temperature [K]	100
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ Å)
Crystal system	triclinic
Space group	<i>P</i> -1
Unit cell dimensions	$a = 11.7431(2)$ Å, $\alpha = 89.4340(10)^\circ$ $b = 15.9679(3)$ Å, $\beta = 82.7850(10)^\circ$ $c = 19.3734(4)$ Å, $\gamma = 73.8080(10)^\circ$
$V$ [Å <sup>3</sup> ]	3459.83(11)
$Z / Z'$	4 / 2
$\rho_{\text{calc}}$ [g·cm <sup>-3</sup> ]	1.833
$\mu$ [mm <sup>-1</sup> ]	0.167
$F(000)$	1952
crystal colour	colourless
crystal size [mm <sup>3</sup> ]	0.21 × 0.19 × 0.08
$\theta$ range [°]	1.986 to 34.349
Index ranges	$-18 \leq h \leq 18$ , $-25 \leq k \leq 25$ , $-30 \leq l \leq 30$
Reflections measured	172779
Independent reflections	28977 [R(int) = 0.0676]
Restraints applied/parameters refined	0 / 1194
Goodness-of-fit on $F^2$	1.030
Reflections with $I > 2\sigma(I)$	19693
Final $R$ indices [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0488$ , $wR_2 = 0.0992$
Final $R$ indices [all data]	$R_1 = 0.0882$ , $wR_2 = 0.1187$
Residual electron density ( $\rho_{\text{max}}/\rho_{\text{min}}$ ) [e Å <sup>-3</sup> / e Å <sup>-3</sup> ]	0.462 / -0.409
CCDC number	2078088



**Fig. 9** General view of the first molecule of **14** in the unit cell. Anisotropic displacement parameters are drawn at 50% probability level.



**Fig. 10** General view of the second molecule of **14** in unit cell. Anisotropic displacement parameters are drawn at 50% probability level.

**Table 12** Selected bond lengths (Å), bond angles (°) and torsion angles (°) of compound **14**·MeCN**Bond lengths***Cage nitro groups*

N(1)–N(7) / N(18)–N(23)	1.4187(16) / 1.4534(15)
N(28)–N(34) / N(42)–N(47)	1.4155(15) / 1.3894(15)
N(2)–N(8) / N(17)–N(22)	1.3768(16) / 1.3929(15)
N(25)–N(31) / N(44)–N(49)	1.3676(16) / 1.4404(15)
N(3)–N(9) / N(16)–N(21)	1.3426(16) / 1.3992(15)
N(29)–N(35) / N(41)–N(46)	1.3836(15) / 1.4068(15)
N(4)–N(10) / N(15)–N(20)	1.4112(15) / 1.4115(16)
N(26)–N(32) / N(45)–N(50)	1.3729(15) / 1.3778(15)
N(5)–N(11) / N(19)–N(24)	1.4187(16) / 1.4086(16)
N(27)–N(33) / N(43)–N(48)	1.4162(15) / 1.3985(16)

*Nitramine open-chain*

N(6)–C(7) / N(14)–C(8)	1.4724(16) / 1.4565(16)
N(30)–C(21) / N(40)–C(22)	1.4722(16) / 1.4633(16)
C(7)–N(12) / C(8)–N(12)	1.4495(17) / 1.4631(16)
C(21)–N(38) / C(22)–N(38)	1.4499(16) / 1.4643(16)
N(12)–N(13) ( <i>Nitro group</i> )	1.3702(15)
N(38)–N(39) ( <i>Nitro group</i> )	

**Bond angles***Cage nitro groups*

N(7)–N(1)–C(1) / N(23)–N(18)–C(10)	118.04(11) / 113.24(10)
N(34)–N(28)–C(16) / N(47)–N(42)–C(25)	118.22(10) / 117.98(10)
N(7)–N(1)–C(3) / N(23)–N(18)–C(11)	117.10(11) / 111.15(10)
N(34)–N(28)–C(19) / N(47)–N(42)–C(24)	117.66(10) / 119.53(10)
N(8)–N(2)–C(2) / N(22)–N(17)–C(12)	120.35(11) / 117.39(10)
N(31)–N(25)–C(15) / N(49)–N(44)–C(26)	120.89(11) / 113.70(10)
N(8)–N(2)–C(5) / N(22)–N(17)–C(13)	120.47(11) / 120.45(10)
N(31)–N(25)–C(17) / N(49)–N(44)–C(27)	121.63(10) / 114.34(10)
N(9)–N(3)–C(1) / N(21)–N(16)–C(9)	124.02(11) / 118.05(10)
N(35)–N(29)–C(16) / N(46)–N(41)–C(25)	119.04(10) / 116.59(10)
N(9)–N(3)–C(4) / N(21)–N(16)–C(11)	124.06(11) / 117.27(10)
N(35)–N(29)–C(20) / N(46)–N(41)–C(23)	120.91(10) / 116.59(10)
N(10)–N(4)–C(2) / N(20)–N(15)–C(12)	115.81(10) / 115.47(10)
N(32)–N(26)–C(15) / N(50)–N(45)–C(26)	119.67(10) / 121.70(10)
N(10)–N(4)–C(6) / N(20)–N(15)–C(14)	115.56(10) / 116.12(10)
N(32)–N(26)–C(18) / N(50)–N(45)–C(28)	119.75(10) / 119.49(10)
N(11)–N(5)–C(3) / N(24)–N(19)–C(10)	113.44(11) / 118.23(11)
N(33)–N(27)–C(19) / N(48)–N(43)–C(24)	114.59(10) / 119.85(11)
N(11)–N(5)–C(5) / N(24)–N(19)–C(13)	113.87(11) / 117.94(10)
N(33)–N(27)–C(17) / N(48)–N(43)–C(27)	112.96(10) / 119.83(11)

**Table 12** (continued)**Bond angles***Nitramine open-chain*

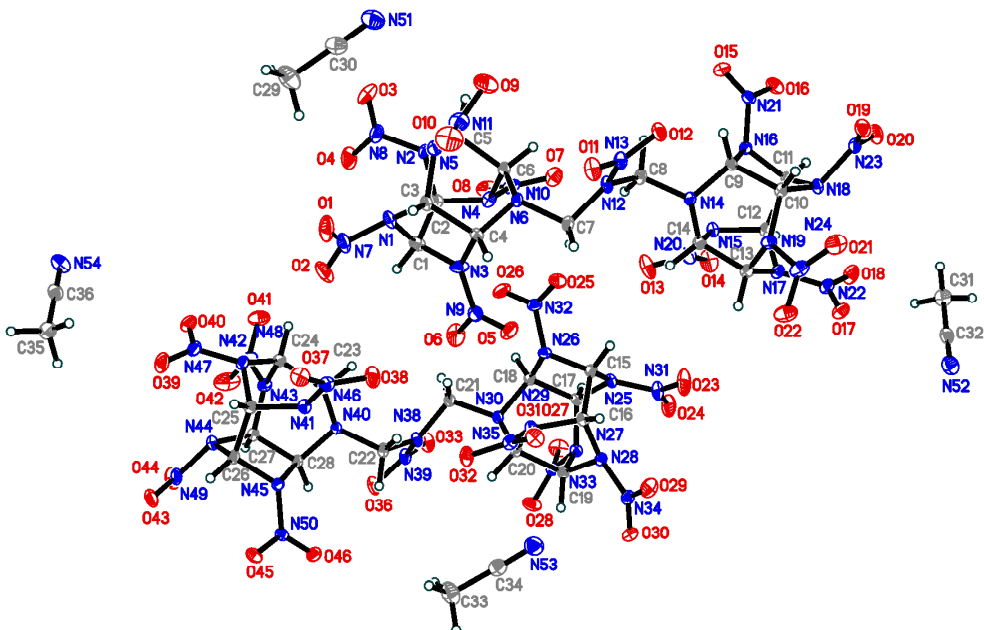
N(6)–C(7)–N(12) / N(14)–C(8)–N(12)	110.24(10) / 113.59(10)
N(30)–C(21)–N(38) / N(40)–C(22)–N(38)	110.52(10) / 112.89(10)
C(7)–N(12)–C(8)	124.73(11)
C(21)–N(38)–C(22)	123.13(10)
N(13)–N(12)–C(7) ( <i>Nitro group</i> )	116.67(10)
N(39)–N(38)–C(21) ( <i>Nitro group</i> )	116.60(10)
N(13)–N(12)–C(8) ( <i>Nitro group</i> )	117.00(10)
N(39)–N(38)–C(22) ( <i>Nitro group</i> )	116.54(10)

**Torsion angles***Cage nitro groups*

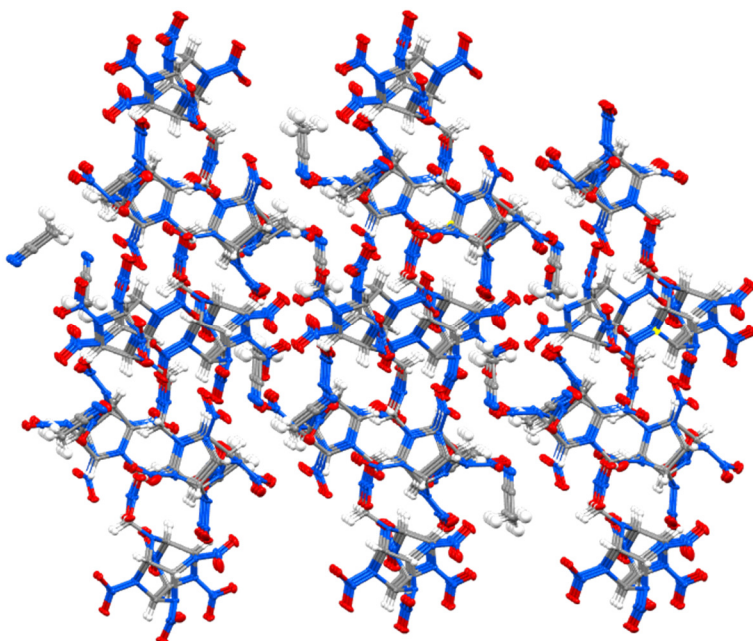
N(7)–N(1)–C(3)–C(4) / N(23)–N(18)–C(10)–C(9) ( <i>axial</i> )/( <i>axial</i> )	119.22(12) / 100.89(11)
N(34)–N(28)–C(19)–C(20) / N(47)–N(42)–C(24)–C(23) ( <i>axial</i> )/( <i>equat</i> )	120.74(11) / –169.01(11)
N(8)–N(2)–C(5)–C(6) / N(22)–N(17)–C(13)–C(14) ( <i>equat</i> )/( <i>equat</i> )	175.12(11) / 169.47(11)
N(31)–N(25)–C(17)–C(18) / N(49)–N(44)–C(27)–C(28) ( <i>equat</i> )/( <i>axial</i> )	178.69(11) / –106.84(11)
N(9)–N(3)–C(4)–C(3) / N(21)–N(16)–C(9)–C(10) ( <i>middle</i> )/( <i>axial</i> )	–145.72(13) / –
N(35)–N(29)–C(20)–C(19) / N(46)–N(41)–C(23)–C(24) ( <i>axial</i> )/( <i>axial</i> )	113.19(11) –121.06(11) / – 111.67(11)
N(10)–N(4)–C(6)–C(5) / N(20)–N(15)–C(14)–C(13) ( <i>axial</i> )/( <i>axial</i> )	109.08(11) / 108.95(12)
N(32)–N(26)–C(18)–C(17) / N(50)–N(45)–C(28)–C(27) ( <i>axial</i> )/( <i>axial</i> )	122.79(11) / 124.13(11)
N(11)–N(5)–C(5)–C(6) / N(24)–N(19)–C(13)–C(14) ( <i>axial</i> )/( <i>middle</i> )	83.31(13) / 154.50(11)
N(33)–N(27)–C(19)–C(20) / N(48)–N(43)–C(24)–C(23) ( <i>axial</i> )/( <i>middle</i> )	–82.39(12) / –145.88(11)
N(11)–N(5)–C(3)–C(4) / N(24)–N(19)–C(10)–C(9) ( <i>axial</i> )/( <i>middle</i> )	–81.15(13) / –153.52(10)
N(33)–N(27)–C(17)–C(18) / N(48)–N(43)–C(27)–C(28) ( <i>axial</i> )/( <i>middle</i> )	83.39(12) / 144.27(11)

*Nitramine open-chain*

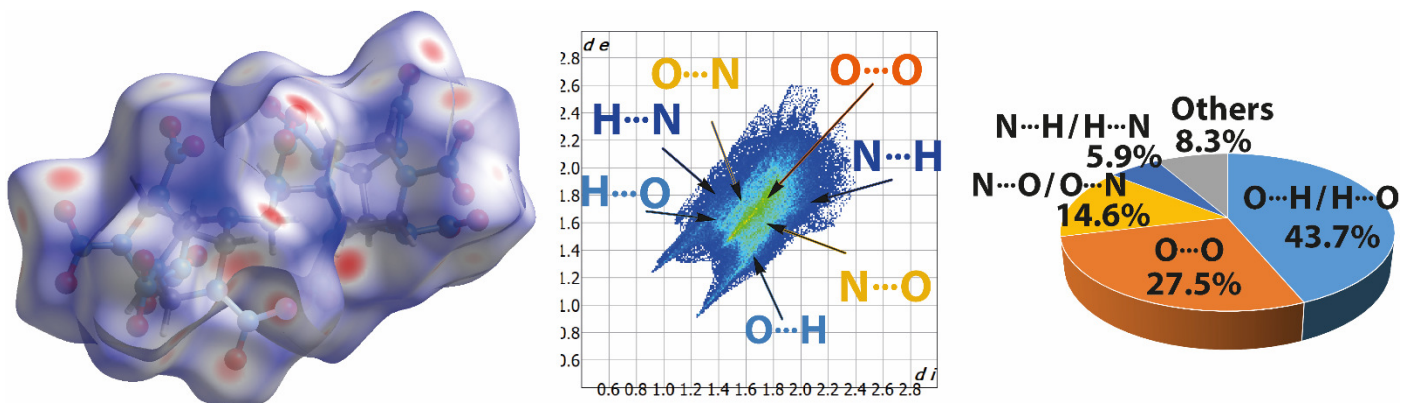
C(4)–N(6)–C(7)–N(12) / C(9)–N(14)–C(8)–N(12) ( <i>equat</i> )/( <i>axial</i> )	–163.07(10) / –
C(18)–N(30)–C(21)–N(38) / C(23)–N(40)–C(22)–N(38) ( <i>equat</i> )/( <i>axial</i> )	114.95(12) 168.77(10) / –110.43(12)
C(6)–N(6)–C(7)–N(12) / C(14)–N(14)–C(8)–N(12)	62.68(14) / 106.43(13)
C(20)–N(30)–C(21)–N(38) / C(28)–N(40)–C(22)–N(38)	–60.00(13) / 114.66(12)



**Fig. 11** A general view of the molecular unit of 14·2MeCN in crystal. Anisotropic displacement parameters are drawn at 50% probability level.



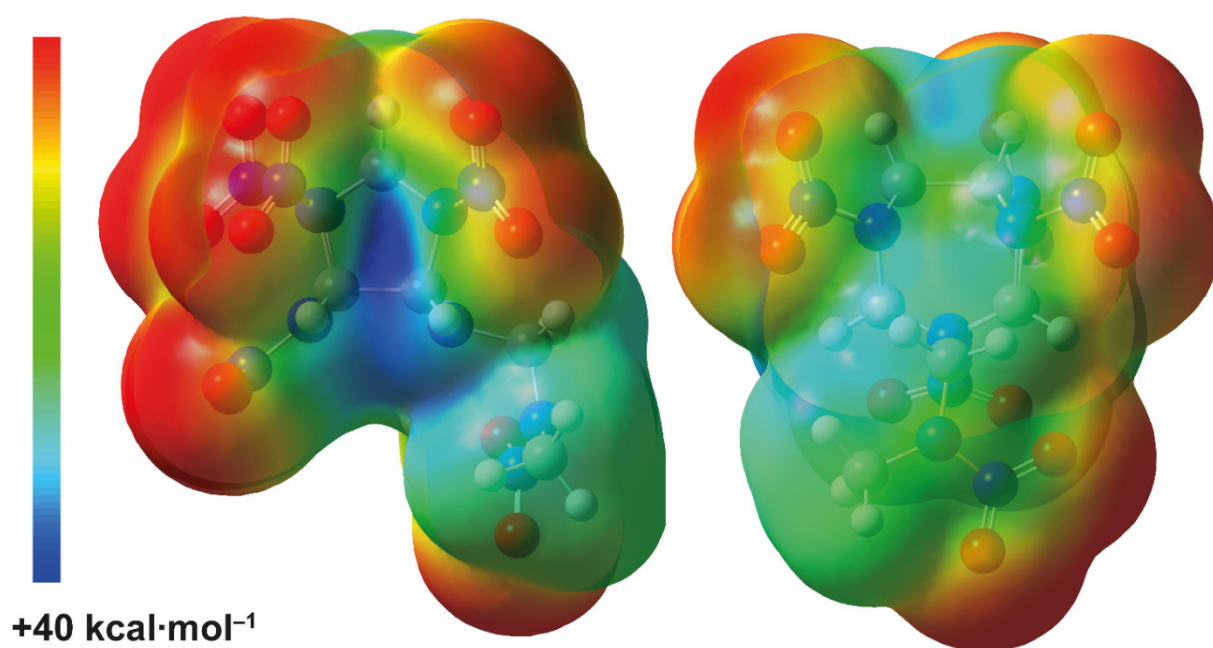
**Fig. 12** A general view of the packing diagram of 14·2MeCN in crystal.



**Fig. 13** Hirshfeld surface calculations, 2D fingerprint plots in crystal stacking and pie graph of percentage contributions of the individual atomic contacts to the Hirshfeld surface of 14.

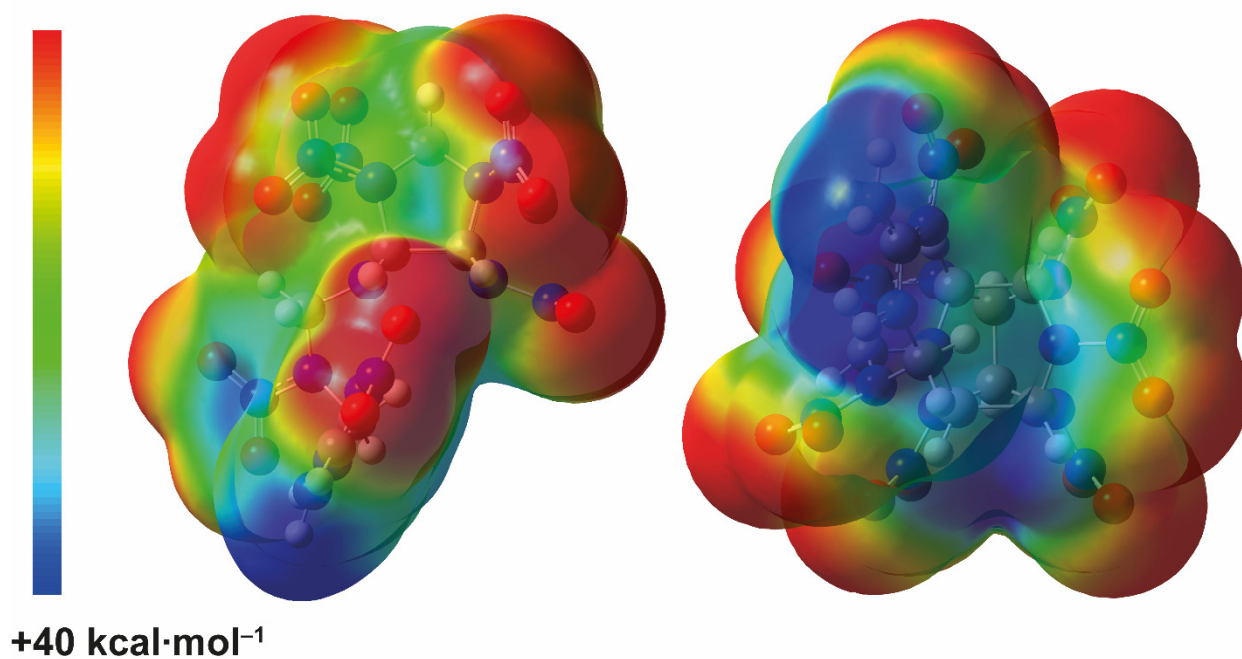
## Molecular surface electrostatic potentials (ESPs) for 10, 12, and 14.

-15 kcal·mol<sup>-1</sup>



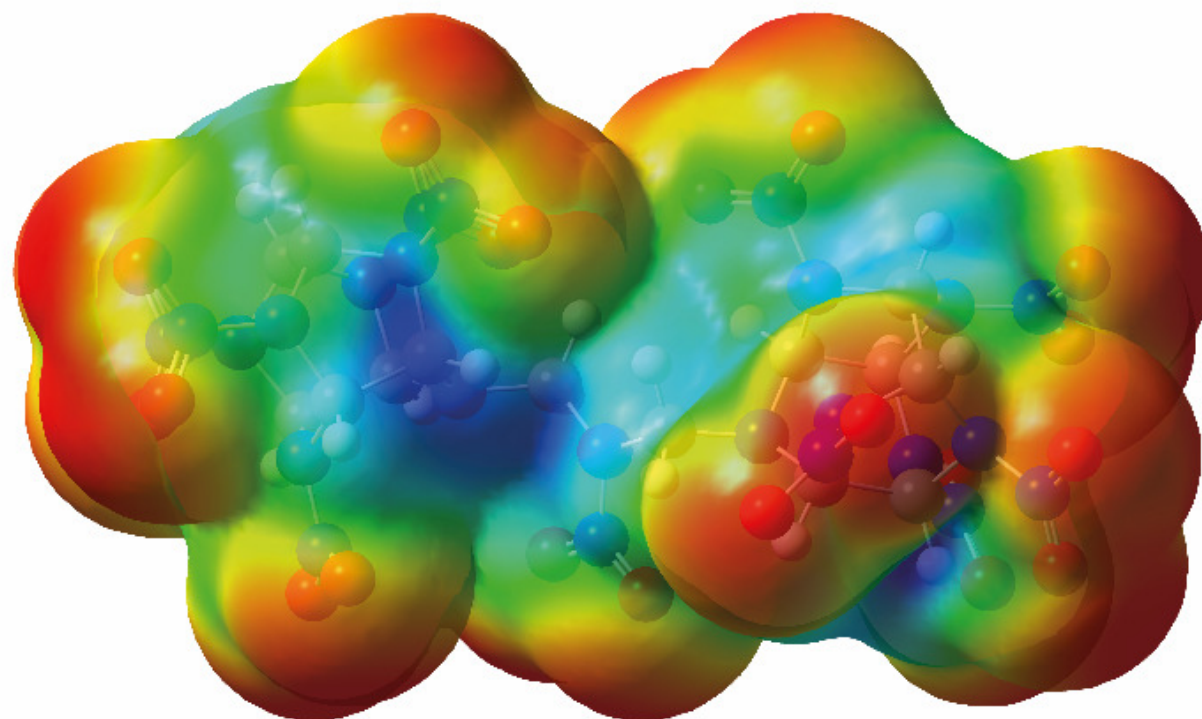
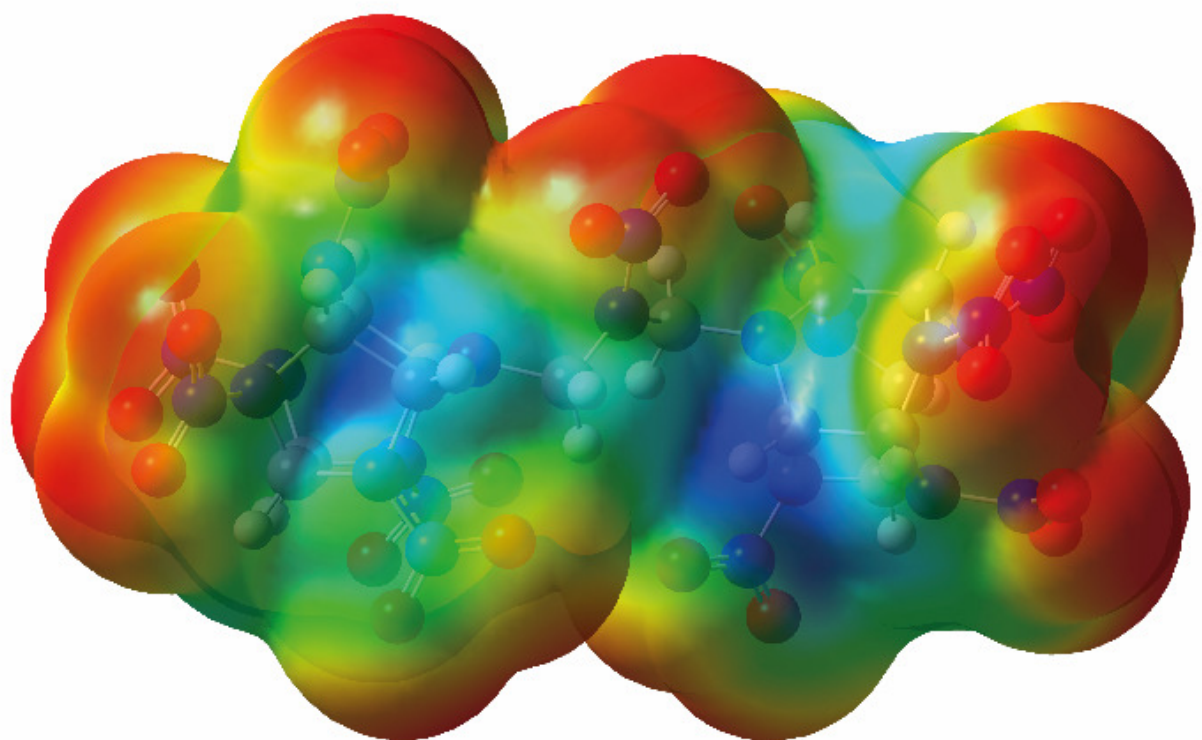
**Fig. 14** Molecular surface electrostatic potentials (ESPs) for 10. The ESP surface is divided into local electron-deficient (blue) and electron-rich (red) areas.

-15 kcal·mol<sup>-1</sup>



**Fig. 15** Molecular surface electrostatic potentials (ESPs) for 12. The ESP surface is divided into local electron-deficient (blue) and electron-rich (red) areas.

-15 kcal·mol<sup>-1</sup>

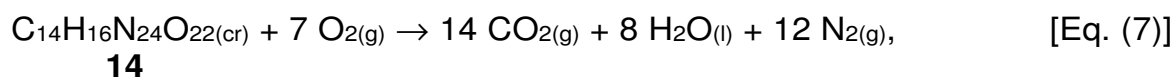
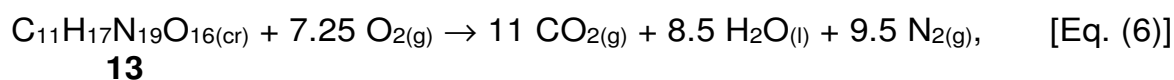
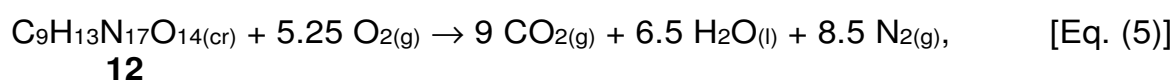
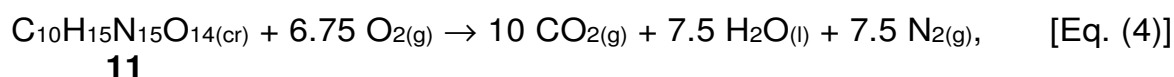
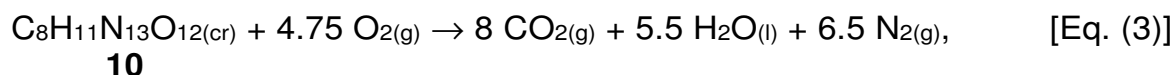
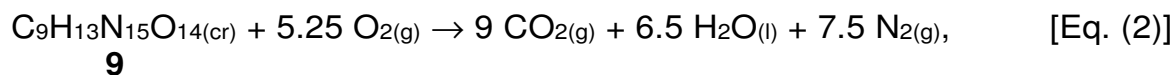
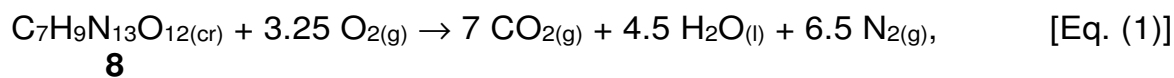


+40 kcal·mol<sup>-1</sup>

**Fig. 16** Molecular surface electrostatic potentials (ESPs) for **14**. The ESP surface is divided into local electron-deficient (blue) and electron-rich (red) areas.

## Measurements and calculations of enthalpies of combustion and formation for compounds 8–14

The combustion reactions of alkylnitramines **8–14** occurs according to Eq. (1) – Eq. (7)



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. (8) – Eq. (14) taking into account the stoichiometry of reactions (1) – (7)

$$\Delta H_f [\text{C}_7\text{H}_9\text{N}_{13}\text{O}_{12}(\text{cr})] = 7 \Delta H_f [\text{CO}_2]_{(\text{g})} + 4.5 \Delta H_f [\text{H}_2\text{O}]_{(\text{l})} - \Delta H_{\text{comb}}(\mathbf{8}), \quad [\text{Eq. (8)}]$$

**8**

$$\Delta H_f [\text{C}_9\text{H}_{13}\text{N}_{15}\text{O}_{14}(\text{cr})] = 9 \Delta H_f [\text{CO}_2]_{(\text{g})} + 6.5 \Delta H_f [\text{H}_2\text{O}]_{(\text{l})} - \Delta H_{\text{comb}}(\mathbf{9}), \quad [\text{Eq. (9)}]$$

**9**

$$\Delta H_f [\text{C}_8\text{H}_{11}\text{N}_{13}\text{O}_{12}(\text{cr})] = 8 \Delta H_f [\text{CO}_2]_{(\text{g})} + 5.5 \Delta H_f [\text{H}_2\text{O}]_{(\text{l})} - \Delta H_{\text{comb}}(\mathbf{10}), \quad [\text{Eq. (10)}]$$

**10**

$$\Delta H_f [\text{C}_{10}\text{H}_{15}\text{N}_{15}\text{O}_{14}(\text{cr})] = 10 \Delta H_f [\text{CO}_2]_{(\text{g})} + 7.5 \Delta H_f [\text{H}_2\text{O}]_{(\text{l})} - \Delta H_{\text{comb}}(\mathbf{11}), \quad [\text{Eq. (11)}]$$

**11**

$$\Delta H_f [\text{C}_9\text{H}_{13}\text{N}_{17}\text{O}_{14}(\text{cr})] = 9 \Delta H_f [\text{CO}_2]_{(\text{g})} + 6.5 \Delta H_f [\text{H}_2\text{O}]_{(\text{l})} - \Delta H_{\text{comb}}(\mathbf{12}), \quad [\text{Eq. (12)}]$$

**12**

$$\Delta H_f [\text{C}_{11}\text{H}_{17}\text{N}_{19}\text{O}_{16}(\text{cr})] = 11 \Delta H_f [\text{CO}_2]_{(\text{g})} + 8.5 \Delta H_f [\text{H}_2\text{O}]_{(\text{l})} - \Delta H_{\text{comb}}(\mathbf{13}), \quad [\text{Eq. (13)}]$$

**13**

$$\Delta H_f [\text{C}_{14}\text{H}_{16}\text{N}_{24}\text{O}_{22}(\text{cr})] = 14 \Delta H_f [\text{CO}_2]_{(\text{g})} + 8 \Delta H_f [\text{H}_2\text{O}]_{(\text{l})} - \Delta H_{\text{comb}}(\mathbf{14}), \quad [\text{Eq. (14)}]$$

**14**

where  $\Delta H_f[\text{CO}_2]_{(\text{g})} = -94.051 \pm 0.031 \text{ kcal} \cdot \text{mol}^{-1}$  and  $\Delta H_f[\text{H}_2\text{O}]_{(\text{l})} = -68.315 \pm 0.009 \text{ kcal} \cdot \text{mol}^{-1}$ .<sup>15</sup>



Measurements of the enthalpies of combustion for **10**, **12**, and **14** 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 13–15. The mean square error of the measurements was 0.025%.

**Table 13.** Measurements of combustion energy of compound **10**.

#	$m^a$ [g]	$\Delta T^b$ [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 <sup>-1</sup> ]
1	0.069111	2.09903	1128.42	934.17	7.28	1.66	8.58	2557.2
2	0.081565	2.23354	1200.73	973.47	7.27	1.94	9.75	2553.8
3	0.083406	2.19459	1179.79	947.87	7.26	1.98	9.47	2556.3
4	0.084217	2.22787	1197.68	964.52	7.29	2.01	8.96	2551.7
5	0.068061	2.18772	1176.10	984.51	7.34	1.64	8.43	2559.2

$$-\Delta U_B^h = 2555.6 \pm 3.4 \text{ cal}\cdot\text{g}^{-1}$$

$$-\Delta H_{comb}^i = 1222.4 \pm 1.6 \text{ kcal}\cdot\text{mol}^{-1}$$

$$\Delta H_f^j = 94.3 \pm 1.6 \text{ kcal}\cdot\text{mol}^{-1}$$

**Table 14.** Measurements of combustion energy of compound **12**.

#	$m^a$ [g]	$\Delta T^b$ [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 <sup>-1</sup> ]
1	0.084123	2.27646	1223.80	1003.29	7.29	1.86	8.02	2417.2
2	0.085600	2.33077	1253.00	1027.66	7.31	1.88	9.29	2416.6
3	0.081369	2.17507	1169.30	954.80	7.28	1.82	8.62	2418.3
4	0.082536	2.16970	1166.41	949.17	7.32	1.82	8.68	2416.1
5	0.083721	2.20237	1183.97	963.67	7.28	1.88	8.75	2417.5

$$-\Delta U_B^h = 2417.1 \pm 0.2 \text{ cal}\cdot\text{g}^{-1}$$

$$-\Delta H_{comb}^i = 1400.6 \pm 0.1 \text{ kcal}\cdot\text{mol}^{-1}$$

$$\Delta H_f^j = 110.1 \pm 0.1 \text{ kcal}\cdot\text{mol}^{-1}$$

**Table 15.** Measurements of combustion energy of compound **14**.

#	$m^a$ [g]	$\Delta T^b$ [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 <sup>-1</sup> ]
1	0.084158	2.19785	1181.54	961.36	7.27	1.96	9.70	2391.4
2	0.082909	2.20372	1184.70	968.23	7.19	1.92	9.36	2388.2
3	0.081694	2.17286	1168.11	954.80	7.25	1.90	9.22	2386.2
4	0.079015	2.17835	1171.06	964.79	7.24	1.84	8.89	2383.1
5	0.070624	2.17250	1167.91	979.85	7.29	1.64	10.07	2393.8

$$-\Delta U_B^h = 2388.5 \pm 4.8 \text{ cal}\cdot\text{g}^{-1}$$

$$-\Delta H_{comb}^i = 2069.7 \pm 4.2 \text{ kcal}\cdot\text{mol}^{-1}$$

$$\Delta H_f^j = 206.5 \pm 4.2 \text{ kcal}\cdot\text{mol}^{-1}$$

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

The measured values were used to determine  $\Delta H_f$  of compounds **10**, **12**, and **14** according to the standard scheme developed by S. M. Skuratov and V. P. Kolesov (M. V. Lomonosov Moscow State University).<sup>16, 17</sup>

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

$$Q_{\text{meas}} = W \times \Delta T^{-1}, \quad (1)$$

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

The combustion energy of compound in a bomb is:

$$-\Delta U_B = (Q_{\text{meas}} - q_a - q_i - q_N - q_{\text{cot}}) \times m^{-1}. \quad (2)$$

And the enthalpy of combustion of the compound is:

$$-\Delta H_{\text{comb}} = -\Delta U_B \times M + \pi \times \Delta U_B + (n' - n) \times R \times T, \quad (3)$$

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  $\pi$  is the Washburn correction, which for compound  $C_aH_bO_cN_d$  is calculated by the formula:

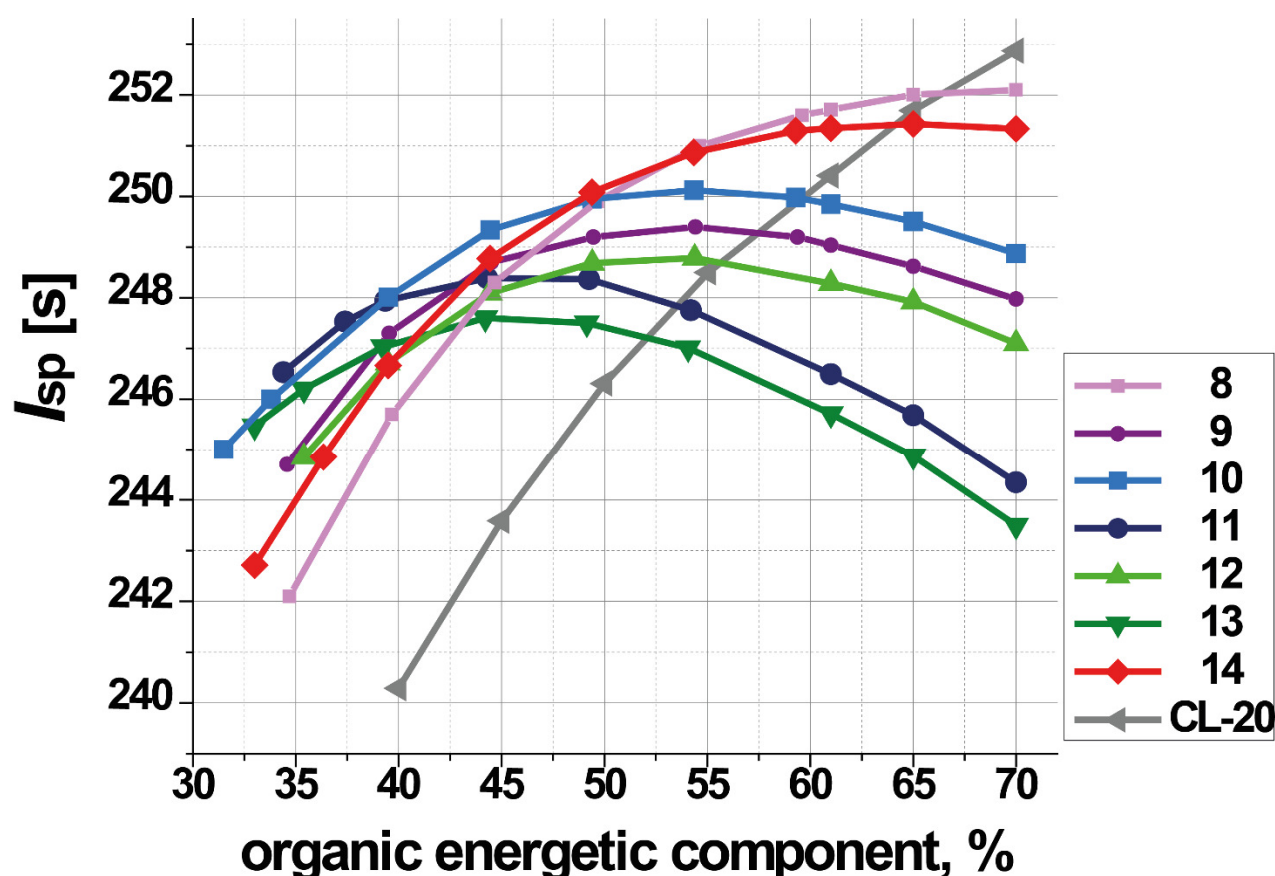
$$\pi = 0.3 \times P \times (-\Delta U_B / a)^{-1} \times \left[ -1 + 1.1 \times \left( \frac{b - 2(c + d)}{4a} \right) - \frac{2}{P} \right] \quad (4),$$

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,  $\text{kcal} \cdot (\text{g} \cdot \text{atom})^{-1}$ .

Based on these thermochemical data, the determination of  $\Delta H_{\text{comb}}$  and  $\Delta H_f$  for **11** and **13** was carried out by the additive method for calculating thermodynamic properties to S. W. Benson<sup>18</sup> using the contributions of molecular fragments as well as Eq. (7) and Eq. (9), respectively.

## High-temperature chemical equilibria thermodynamic calculations for compounds 8–14

Metal-free formulations of SCP with an «active» binder, a mixture of polyvinyl methyl tetrazole with nitroglycerin and a phlegmatizer (Act-bnd,  $C_{18.96}H_{34.64}N_{19.16}O_{29.32}$ ;  $\Delta H_f = -757$   $\text{kJ}\cdot\text{kg}^{-1}$ ;  $d = 1.49$   $\text{g}\cdot\text{cm}^{-3}$ )<sup>19</sup> in an amount corresponding to 19% by volume and the rest is a mixture of AP with the material under study (CL-20 or 8–14) 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  $T_{\text{comb}}$  were determined using the standard code TERRA<sup>20</sup> for high-temperature chemical equilibria calculation. The results of calculation with varying of the content of the organic energetic component are presented in table 16 and Fig. 17, 18.



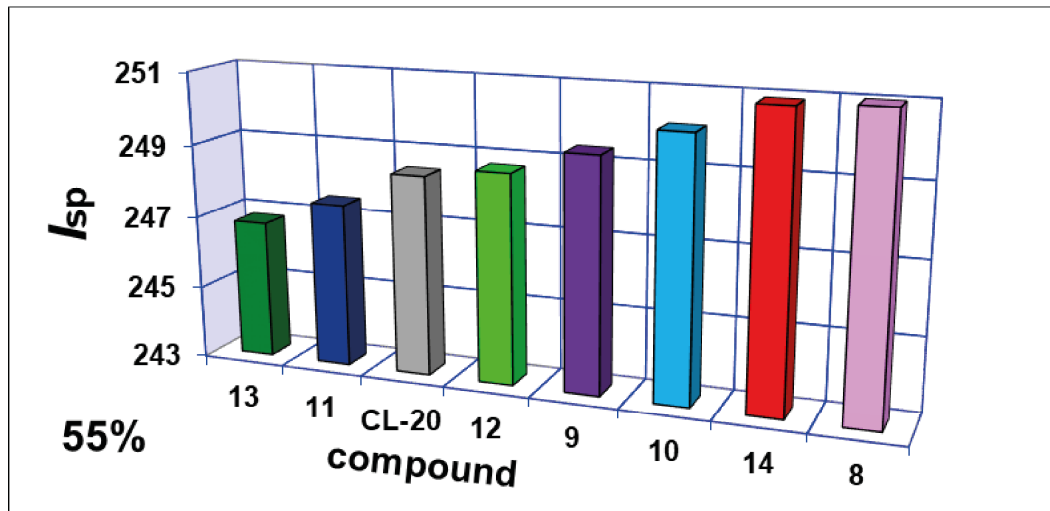
**Fig. 17** The dependence of  $I_{sp}$  on the kind of HEDM (8–14 and CL-20) and its percentage in the SCP formulations containing 19 vol.% (15–16 wt.%) Active binder, organic energetic component, and AP.

**Table 16** 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 **8–14** or CL-20.

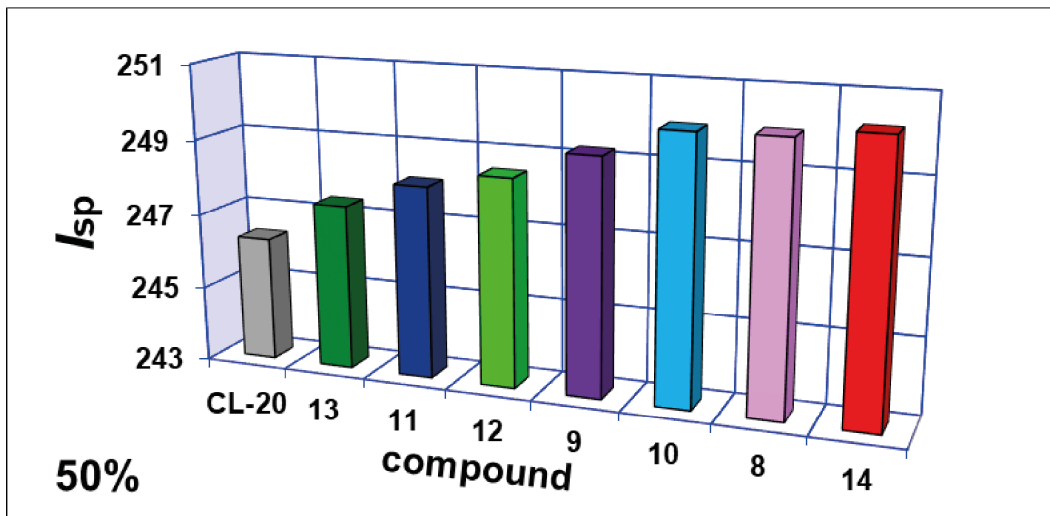
organic component		act-bnd <sup>a</sup> [w.%]	AP <sup>b</sup> [w.%]	$d^c$ [g·cm <sup>-3</sup> ]	$T_{comb}^d$ [K]	$I_{sp}^e$ [s]	
Type	w.%						
8	74.54	15.46	10	1.828	3315	252.1	
	64.58	15.42	20	1.832	3310	252.0	
	59.60	15.4	25	1.835	3300	251.6	
	54.62	15.38	30	1.837	3285	251.0	
	49.64	15.36	35	1.839	3260	249.9	
	44.66	15.34	40	1.842	3230	248.3	
	39.68	15.32	45	1.844	3185	245.7	
	34.70	15.3	50	1.846	3130	242.1	
9	74.29	15.71	10	1.804	3160	247.2	
	64.35	15.65	20	1.812	3215	248.7	
	59.38	15.62	25	1.816	3230	249.2	
	54.42	15.58	30	1.820	3240	249.4	
	49.46	15.54	35	1.823	3230	249.2	
	44.50	15.5	40	1.827	3220	248.7	
	39.54	15.46	45	1.831	3190	247.3	
	34.58	15.42	50	1.835	3150	244.7	
10	74.25	15.75	10	1.798	3180	248.2	
	64.30	15.7	20	1.806	3230	249.6	
	59.30	15.70	25	1.810	3250	250.0	
	54.35	15.65	30	1.815	3255	250.1	
	49.40	15.60	35	1.819	3250	249.9	
	44.45	15.55	40	1.823	3233	249.3	
	39.50	15.50	45	1.828	3200	248.0	
	11	74.00	16.00	10	1.771	3010	243.3
64.10		15.90	20	1.782	3120	245.9	
54.20		15.80	30	1.794	3190	247.8	
49.25		15.75	35	1.800	3200	248.4	
44.30		15.70	40	1.806	3210	248.4	
39.35		15.65	45	1.812	3200	247.9	
37.40		15.60	47	1.815	3180	247.5	
34.40		15.60	50	1.818	3160	246.5	
12	74.26	15.74	10	1.798	3160	246.4	
	64.32	15.68	20	1.806	3215	248.0	
	54.38	15.62	30	1.815	3234	248.8	
	49.41	15.59	35	1.819	3230	248.7	
	44.44	15.56	40	1.823	3210	248.1	
	39.47	15.53	45	1.827	3180	246.7	
	13	73.85	16.15	10	1.757	3020	242.4
		63.95	16.05	20	1.771	3120	245.2
54.07		15.93	30	1.784	3185	247.0	
49.14		15.86	35	1.791	3200	247.5	
44.21		15.79	40	1.798	3200	247.6	
39.25		15.75	45	1.805	3180	247.0	
14		74.14	15.86	10	1.791	3305	251.1
		64.24	15.76	20	1.800	3310	251.4
	59.29	15.71	25	1.805	3310	251.3	
	54.34	15.66	30	1.809	3295	250.9	
	49.39	15.61	35	1.814	3270	250.1	
	44.44	15.56	40	1.819	3245	248.8	
	39.49	15.51	45	1.824	3200	246.7	
	CL-20	75.25	14.75	10	1.912	3400	253.9
65.10		14.9	20	1.905	3350	251.7	
60.05		14.95	25	1.901	3320	250.3	
55.05		14.95	30	1.898	3280	248.5	
50.00		15.00	35	1.895	3240	246.3	
45.00		15.00	40	1.891	3200	243.6	
40.00		15.00	45	1.888	3140	240.3	

<sup>a</sup> Active binder. <sup>b</sup> Ammonium perchlorate. <sup>c</sup> Density of composition. <sup>d</sup> Temperature in the combustion chamber. <sup>e</sup> Specific impulse.

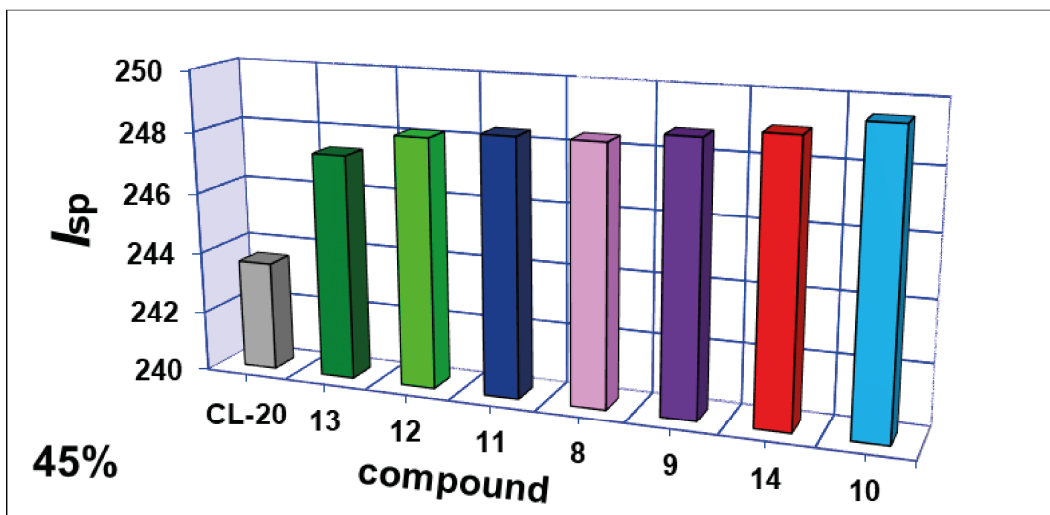
(A)



(B)



(C)



**Fig. 18** 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 10–14 or CL-20 at 55 (a), 50 (b) and 45 (c) w.%

# Explosive performance of compounds 8–14

**Table 17** Physicochemical and explosive properties of 8–14 in comparison with RDX, HMX, and CL-20.

Compd	Formula	$\alpha^a$	H% <sup>b</sup>	$T_{\text{dec}}^c$ [°C]	$d^d$ [g·cm <sup>-3</sup> ]	$\Delta H_f^e$ [kJ·kg <sup>-1</sup> (kJ·mol <sup>-1</sup> )]	IS <sup>g</sup> [J]	FS <sup>g</sup> [N]	$D_v^h$ [km·s <sup>-1</sup> ] <sup>[e]</sup>	$P_{C-J}^h$ [GPa] <sup>[e]</sup>	$Q_v^h$ [MJ·kg <sup>-1</sup> ]
<b>8</b>	C <sub>7</sub> H <sub>9</sub> N <sub>13</sub> O <sub>12</sub>	0.65	1.94	195 <sup>i</sup>	1.901	+807 (+377) <sup>f</sup>	–	–	9.16	40.0	6.28
<b>9</b>	C <sub>9</sub> H <sub>13</sub> N <sub>15</sub> O <sub>14</sub>	0.57	2.36	208 <sup>i</sup>	1.869	+643 (+357) <sup>f</sup>	–	–	9.07	38.2	6.12
<b>10</b>	C <sub>8</sub> H <sub>11</sub> N <sub>13</sub> O <sub>12</sub>	0.56	2.30	222 <sup>c</sup>	1.848	+821 (+395)	6.1	180	9.06	37.8	6.22
<b>11</b>	C <sub>10</sub> H <sub>15</sub> N <sub>15</sub> O <sub>14</sub>	0.51	2.66	197 <sup>i</sup>	1.822	+620 (+353)	–	–	8.94	35.5	6.03
<b>12</b>	C <sub>9</sub> H <sub>13</sub> N <sub>17</sub> O <sub>14</sub>	0.57	2.25	203 <sup>c</sup>	1.846	+791 (+461)	4.3	180	9.04	37.9	6.01
<b>13</b>	C <sub>11</sub> H <sub>17</sub> N <sub>19</sub> O <sub>16</sub>	0.52	2.55	178 <sup>i</sup>	1.804	+626 (+420)	–	–	8.85	34.7	5.87
<b>14</b>	C <sub>14</sub> H <sub>16</sub> N <sub>24</sub> O <sub>22</sub>	0.61	1.85	223 <sup>c</sup>	1.921	+992 (+865)	8.0	150	9.22	40.7	6.36
RDX <sup>j</sup>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	0.67	2.72	203 <sup>k</sup>	1.799	+301 (+67)	7.5	120	8.96	36.2	6.17
HMX <sup>j</sup>	C <sub>4</sub> H <sub>8</sub> N <sub>8</sub> O <sub>8</sub>	0.67	2.70	280 <sup>k</sup>	1.897	+255 (+76)	7.0	112	9.21	40.3	6.15
CL-20 <sup>j</sup>	C <sub>6</sub> H <sub>6</sub> N <sub>12</sub> O <sub>12</sub>	0.80	1.37	229 <sup>k</sup>	2.021	+833 (+365) <sup>l</sup>	4.0	48	9.42	45.6	6.52

<sup>a</sup> Oxygen coefficient. For a compound with the molecular formula C<sub>x</sub>H<sub>y</sub>N<sub>w</sub>O<sub>z</sub>,  $\alpha = z/(2x+y/2)$ . <sup>b</sup> Hydrogen content. <sup>c</sup> Extrapolated decomposition onset temperature at a heating rate of 5 °C·min<sup>-1</sup> (DSC). <sup>d</sup> Density measured using a gas pycnometer at room temperature. <sup>e</sup> Standard enthalpy of formation determined by the method of combustion calorimetry. <sup>f</sup> Calculated enthalpy of formation. <sup>g</sup> The impact and friction sensitivity determined by BAM method using the STANAG standards. <sup>h</sup> Detonation parameters: velocity, pressure and heat calculated with S&DV4.5 code. <sup>i</sup> Decomposition temperature at a heating rate of 5 °C·min<sup>-1</sup> (observed on Kofler's table) <sup>j</sup> Ref.<sup>21</sup>. <sup>k</sup> Ref.<sup>22</sup> <sup>l</sup> Ref.<sup>23</sup>

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