

Supporting Information

Title: Introduction of seven nitro groups on 2-azaadamantane scaffold via a two-shell arrangement strategy

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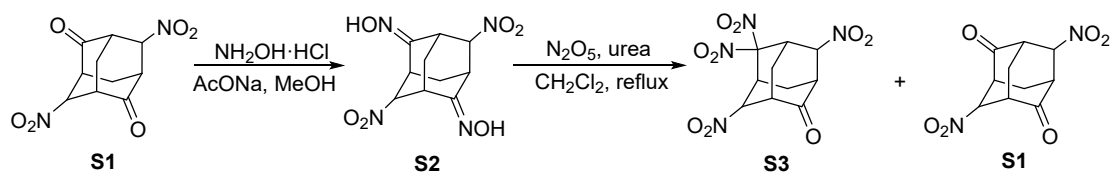
1 General Information

Unless otherwise specified, the chemicals (AR grade) were obtained from commercial sources and were used without further purification. N_2O_5 is a strong oxidizing agent that forms explosive mixtures with organic compounds. The decomposition of N_2O_5 produces highly toxic NO_2 gas. N_2O_5 must be handled in closed systems under a well-ventilated hood. Eye protection and leather gloves must be worn at all times. Petroleum ether refers to the fraction boiling in the 60-90 °C range. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on aluminium oxide gel (spherical, neutral, 200-300 mesh) or silica gel (200-300 mesh). 1H and ^{13}C NMR spectra were obtained at 500 and 126 MHz, respectively, and $CDCl_3$, $DMSO-d_6$, CD_3OD , acetone- d_6 , were used as the solvent with TMS as the internal standard. All FTIR spectra were obtained using a Nicolet FTIR IS10 Spectrometer. TGA and DSC were measured with TGA/SDTA851e and DSC823e, respectively at a heating rate of 5 °C·min⁻¹. MS/MS (ESI) mass spectra were recorded on a Finnigan TSQ Quantum ultra-AM mass spectrometer (Thermo Fisher Scientific, Waltham, MA USA). X-ray intensity data were collected on a Bruker D8 CMOS detector employing graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å). The known compounds were identified by the comparison of their physical and spectral data with those reported in the literature. Yield refers to the isolated yield of the analytically pure material unless otherwise noted.

4,8-dinitroadamantane-2,6-dione (**S1**)¹, bicyclo[3.3.1]nonane-2,6-dione (**6**)²⁻⁴ were prepared according to the reported procedures. Bicyclo[3.3.1]nona-3,7-diene-2,6-dione (**5**)⁵, bicyclo[3.3.1]nona-3,7-diene-2,6-diol (**4a**)⁶ and 4,8-dimethoxybicyclo[3.3.1]nona-2,6-diene (**4b**)⁷ were prepared according to the improved reporting procedure.

2 Experimental Procedures and Spectroscopic Data of the Synthesized Compounds

The attempt to synthesize 2,2,4,6,6,8-hexanitroadamantane (A) :



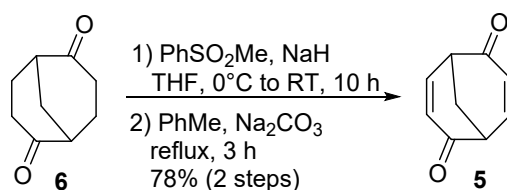
S1 (0.51g, 2mmol) was dissolved in MeOH (50 mL) and treated with hydroxylamine hydrochloride (0.84 g, 12 mmol) and NaOAc (1.31 g, 16 mmol). The resulting mixture was stirred for 24 h. The reaction mixture was concentrated in vacuo to a volume of approximately 5 mL. Water (15 mL) was added and the mixture was extracted with dichloromethane (3×30 mL). The combined organic phase was washed with saturated solution of $NaHCO_3$ (2×5 mL) and brine (5 mL), dried with Na_2SO_4 . After removal of the solvent in vacuum, the crude product was mixed with urea (0.72

g, 12 mmol), Na₂SO₄ (5 g) and CH₂Cl₂ (20 mL) and heated to 50 °C. A solution of N₂O₅ (1.3 g, 12 mmol) in CH₂Cl₂ (8 mL) was added dropwise within 5 min, during this period a green color appeared initially and then faded as more N₂O₅ was added. The reaction mixture was stirred for additional 1 h and then poured into an iced saturated solution of NaHCO₃ (20 mL). And the mixture was extracted with dichloromethane (3 × 30 mL). The combined organic phase was washed with brine (10 mL), dried with Na₂SO₄, and filtered. The solvent was removed in vacuum and the residue was purified by flash silica gel column chromatography (15:1 petroleum/ethyl acetate) to afford the **S3** as a white solid (0.26 g, 40%), then **S1** was recovered as a white solid (0.24 g, 42%).

Compound **S3**: ¹H NMR (500 MHz, Chloroform-*d*) δ 5.05-4.98 (m, 2H), 4.45 (s, 2H), 3.49-3.43 (m, 2H), 2.61 (dt, *J* = 15.7 Hz, 3.3 Hz, 2H), 2.09-2.02 (m, 2H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 199.26, 119.06, 85.37, 44.20, 44.20, 33.89, 27.22; IR (thin film, ν cm⁻¹): 2947, 2886, 1543, 1460, 1380, 1320, 1087, 916.

Compound **S1**: ¹H NMR (500 MHz, DMSO-*d*₆) δ 6.75 (s, 1H), 5.67-5.50 (m, 1H), 5.38 (s, 1H), 3.31 (s, 1H), 3.03 (s, 1H), 2.60 (s, 1H) 2.30-2.14 (m, 3H), 1.74 (dt, *J* = 14 Hz, 3.1 Hz, 1H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 205.51, 202.38, 94.54, 88.97, 88.09, 87.92, 47.73, 47.09, 46.38, 46.17, 45.62, 41.59, 28.28, 27.85, 27.40, 27.20; IR (thin film, ν cm⁻¹): 2964, 2896, 1780, 1567, 1391, 1385, 1013.

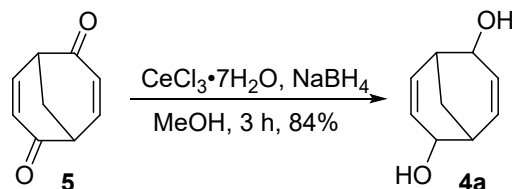
Bicyclo[3.3.1]nona-3,7-diene-2,6-dione (**5**):



Methyl benzenesulphinate (18.94 mL, 144 mmol) was added in one portion to a suspension of sodium hydride (15.79 g, 395 mmol, 60% dispersion in mineral oil) in dry THF (100 mL) under a nitrogen atmosphere. The resulting suspension was cooled to 0 °C and a solution of dione **6** (10 g, 66 mmol) in dry THF (50 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight, then quenched with 10% solution of phosphoric acid to pH 3~4. The aqueous phase was extracted with ethyl acetate (3 × 200 mL), the combined organic fractions were washed with brine, dried (Na₂SO₄) and evaporated under reduced pressure. The obtained residue was subjected to flash chromatography on silica gel with ethyl acetate to remove unreacted methyl benzenesulfinate. The obtained crude products of phenylsulfinyl derivatives were combined and dissolved in toluene (140 mL). Solid sodium carbonate (14 g, 132 mmol) was added and the resulting suspension was heated under reflux for 2 h. After cooling to room temperature, the reaction mixture was filtered, the filter cake was washed with toluene and the filtrate was evaporated. The obtained residue was purified by column chromatography on silica gel with a petroleum ether-ethyl acetate mixture (2:1) to afford compound **5** (7.6 g, 78%) as an off-white solid. ¹H NMR (500 MHz, Chloroform-*d*) δ 6.99 (dd, *J* = 10.0, 6.8 Hz, 2H), 5.87 (d, *J* = 10.0 Hz, 2H),

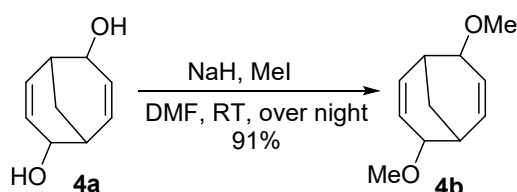
3.33 (dt, $J = 6.2, 2.9$ Hz, 2H), 2.76 (t, $J = 2.9$ Hz, 2H); ^{13}C NMR (126 MHz, Chloroform- d) δ 193.57, 146.44, 126.15, 45.77, 34.44.

Bicyclo[3.3.1]nona-3,7-diene-2,6-diol (**4a**):



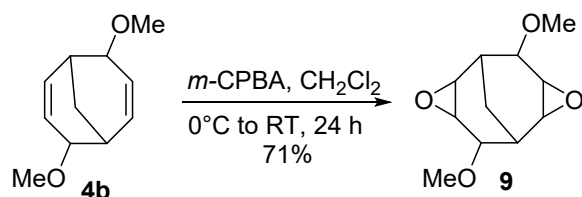
To a solution of **5** (5.4 g, 36 mmol), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (27 g, 72 mmol) in MeOH (100 mL), NaBH_4 was added in portions (4×0.685 g, 72 mmol) over a period of two min at ambient temperature. The reaction mixture was stirred for 3 h and then quenched with HCl (1 M) to pH 3-4 and concentrated in vacuo to a volume of approximately 5 mL. Brine (35 mL) was added and the mixture was extracted with ethyl acetate (5×50 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo yielding white solid crude material. The product was isolated using flash chromatography affording 4.67 g of **4a** in 84% yield. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 5.65 (ddd, $J = 10.2, 5.3, 2.1$ Hz, 2H), 5.50 (dd, $J = 9.9, 1.6$ Hz, 2H), 4.60 (s, 2H), 4.38 – 4.22 (m, 2H), 2.33 (m, 2H), 1.65 (t, $J = 3.3$ Hz, 2H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 132.28, 128.49, 71.32, 35.08, 29.35.

4,8-Dimethoxybicyclo[3.3.1]nona-2,6-diene (**4b**):



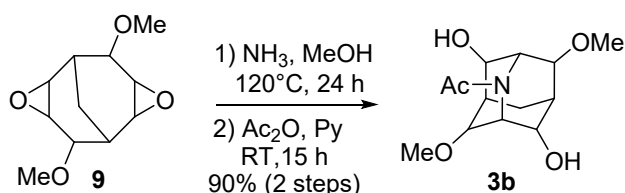
Sodium hydride (4.8 g, 0.12 mol, 60% dispersion in mineral oil) was added to a stirred solution of **4a** (4.56 g, 0.03 mol) in dry DMF (30 mL) at 0°C . The resulting suspension was stirred under a nitrogen atmosphere for 10 min and then MeI (7.84 mL 0.12 mol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight, then quenched by careful addition of 10% HCl solution. The resulting mixture was diluted with water (20 mL) and ethyl acetate (20 mL), layers were separated and the aqueous phase was extracted with ethyl acetate (3×30 mL). Combined organic phase was washed with water (10 mL), saturated solution of NaHCO_3 (2×5 mL) and brine (10 mL), dried (Na_2SO_4) and evaporated. The obtained residue was purified by column chromatography on silica gel to afford compound **4b** (4.3 g, 91% yield) as a yellow oil, which was found to be unstable at room temperature. ^1H NMR (500 MHz, Chloroform- d) δ 5.80 – 5.74 (m, 2H), 5.71 (d, $J = 10.3$ Hz, 2H), 4.02 (d, $J = 5.3$ Hz, 2H), 3.38 (d, $J = 1.3$ Hz, 6H), 2.71 – 2.63 (m, 2H), 1.78 (s, 2H); ^{13}C NMR (126 MHz, Chloroform- d) δ 128.66, 128.40, 80.98, 56.02, 31.69, 28.71.

5,10-Dimethoxy-3,8-dioxatetracyclo[4.4.1.0^{2,4}.0^{7,9}]undecane (**9**):



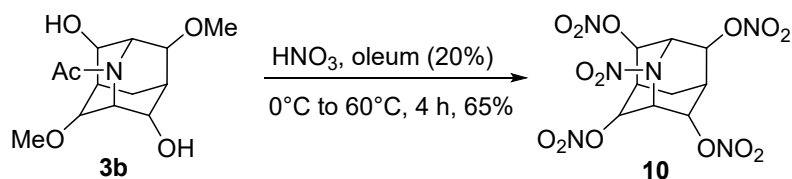
To a suspension of *m*-CPBA (27 g, 133.2 mmol, 85%) in 60 mL of CH₂Cl₂ at 0 °C was added dropwise a solution of **4b** (4 g, 22.2 mmol) in 60 mL of CH₂Cl₂. After being stirred at room temperature for 24 h, the reaction mixture was filtered with diatomite, the filter cake was washed with CH₂Cl₂, then quenched by 10% aqueous NaHSO₃ (40 mL), aqueous phase was extracted with CH₂Cl₂ (3 × 30 mL). Combined organic phase was washed with water (10 mL), saturated solution of NaHCO₃ (10 mL) and brine (10 mL), dried (Na₂SO₄) and concentrated in vacuum. The product was purified by flash chromatography (10:1 petroleum/ethyl acetate) to afford compound **9** (3.35 g, 71%) as a white oil, which solidified into a white solid at 0 °C. ¹H NMR (500 MHz, Chloroform-*d*) δ 3.58 (d, *J* = 5.8 Hz, 2H), 3.50 (s, 6H), 3.38 – 3.30 (m, 2H), 3.08 (dd, *J* = 3.8, 1.6 Hz, 2H), 2.48 (dq, *J* = 3.8, 1.8 Hz, 2H), 1.20 (t, *J* = 3.4 Hz, 2H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 77.39, 57.13, 53.76, 52.63, 28.99, 15.61; IR (thin film, ν cm⁻¹): 2907, 2829, 1432, 1377, 1308, 1256, 1193, 1095, 933, 864, 801, 771, 640; HRMS (ESI): *m/z* calcd for C₁₁H₁₆O₄H⁺ [M+H]⁺ 213.1121, found 213.1448.

2-Acetyl-9,10-dimethoxy-2-azaadamantane-4,8-diol (**3b**):



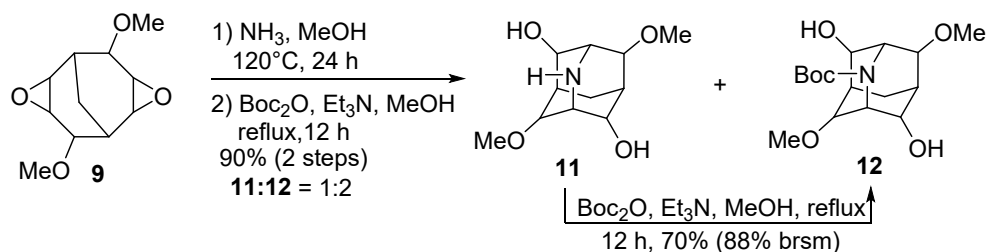
To a solution of **9** (424 mg, 2.0 mmol) in 5 mL of methanol was added 10 mL of ammonia-saturated methanol. The mixture was heated to 120 °C for 24 h in a steel bomb. After cooling, the mixture was concentrated in vacuum. Without further purification, to a mixture of crude products dissolved in pyridine (10 mL) was added dropwise acetic anhydride (0.2 mL, 2.2 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature. The mixture was concentrated in vacuum. The product was purified by flash chromatography (1:1 petroleum/ethyl acetate) to afford acetamide **3b** (412 mg, 90% over 2 steps) as a white solid. ¹H NMR (500 MHz, Methanol-*d*₄) δ 4.97 – 4.75 (m, 4H), 4.18 (d, *J* = 5.3 Hz, 1H), 4.05 (s, 1H), 3.95 (s, 1H), 3.83 (d, *J* = 5.7 Hz, 2H), 3.35 (dt, *J* = 25.2, 4.2 Hz, 6H), 2.20 (s, 1H), 2.17 – 2.03 (m, 4H), 1.96 (s, 2H); ¹³C NMR (126 MHz, Methanol-*d*₄) δ 171.32, 76.37, 75.82, 65.62, 64.91, 56.26, 55.23, 55.13, 49.27, 36.27, 35.17, 21.57, 20.11; IR (thin film, ν cm⁻¹): 2917, 2448, 1613, 1456, 1275, 1107, 1080, 1031, 928, 885, 674; HRMS (ESI): *m/z* calcd for C₁₃H₂₁NO₅H⁺ [M+H]⁺ 272.1492, found 272.1480.

2-Nitro-2-azaadamantane-4,8,9,10-tetrayl tetranitrate (**10**):



To a mixture of fuming nitric acid (4 mL) and 20% oleum (2 mL) at 0°C was added acetamide **3b** (229 mg, 1.0 mmol). The reaction mixture was heated to 60°C. After stirring for 4 h, the reaction mixture was cooled to ambient temperature and poured into ice-water (20 mL) with agitation. The white particulate was filtered, washed with water and dried in vacuum. The product **10** (272 mg, 65%) was afforded as a white solid. ¹H NMR (500 MHz, Chloroform-*d*) δ 5.79 (d, *J* = 3.4 Hz, 2H), 5.77 (s, 2H), 5.71 (s, 2H), 3.04 (s, 2H), 2.37 (t, *J* = 3.2 Hz, 2H); ¹³C NMR (126 MHz, Acetone-*d*₆) δ 205.39, 77.09, 74.04, 52.76, 31.44, 28.96, 22.65; IR (thin film, ν cm⁻¹): 2988, 2901, 1653, 1632, 1543, 1270, 950, 826, 745, 676; HRMS (ESI): *m/z* calcd for C₉H₁₀N₆O₁₄Cl⁻ [M+Cl]⁻ 460.9949, found 460.9657.

2-*tert*-Butoxycarbonyl-9,10-dimethoxy-2-azaadamantane-4,8-diol (**12**):



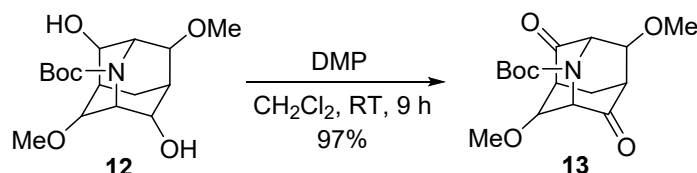
To a solution of **9** (424 mg, 2.0 mmol) in 5 mL of methanol was added 10 mL of ammonia-saturated methanol. The mixture was heated to 120 °C for 24 h in a steel bomb. After cooling, the mixture was concentrated in vacuum to afford the crude product 458 mg. A mixture of crude product (458 mg), triethylamine (2.8 mL, 20 mmol) and MeOH (15 mL) was added di-*tert*-butyl dicarbonate (0.92 mL, 4 mmol) at room temperature. The reaction mixture was refluxed under stirring for 12 h. The mixture was concentrated in vacuum. The product was purified by flash chromatography (10:1 ethyl acetate/methanol) to afford **12** (395 mg, 60% over 2 steps) as a white solid, along with its precursor 9,10-dimethoxy-2-azaadamantane-4,8-diol (**11**, 137 mg, 30% over 2 steps) as a white solid, too. And the compound **11** could continue to react with (Boc)₂O to furnish **12** (70% yield) combined with recovery of **11** (20% yield).

Compound **11**: ¹H NMR (500 MHz, Methanol-*d*₄) δ 4.21 (t, *J* = 3.7 Hz, 2H), 3.78 (dd, *J* = 4.1, 2.4 Hz, 2H), 3.30 (s, 6H), 3.20 – 3.14 (m, 2H), 2.13 (t, *J* = 3.6 Hz, 2H), 1.87 (s, 2H); ¹³C NMR (126 MHz, Methanol-*d*₄) δ 77.29, 66.97, 54.85, 52.48, 35.83, 22.10; IR (thin film, ν cm⁻¹): 2926, 2818, 1452, 1190, 1081, 1055, 1033, 934, 912, 780, 683; HRMS (ESI): *m/z* calcd for C₁₁H₁₉NO₄H⁺ [M+H]⁺ 230.1387, found 230.1377.

Compound **12**: ¹H NMR (500 MHz, Methanol-*d*₄) δ 4.26 (d, *J* = 9.0 Hz, 2H), 4.12 (d, *J* = 10.8

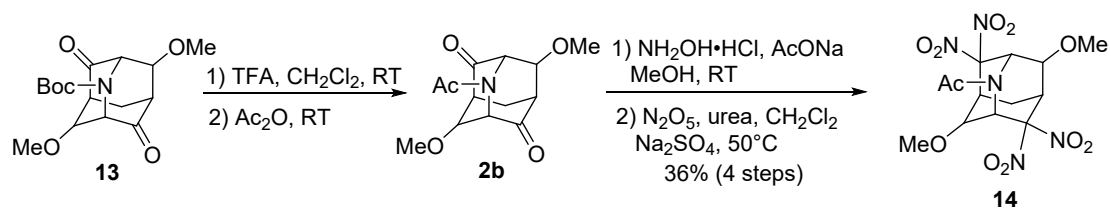
Hz, 2H), 3.78 (d, $J = 3.2$ Hz, 1H), 3.73 (s, 1H), 3.33 (d, $J = 10.6$ Hz, 6H), 2.11 – 2.03 (m, 2H), 1.91 (s, 2H), 1.46 (s, 9H); ^{13}C NMR (126 MHz, Methanol- d_4) δ 155.71, 79.72, 76.43, 76.10, 65.38, 65.14, 55.10, 55.01, 51.90, 50.78, 36.56, 36.25, 27.27, 21.70; IR (thin film, ν cm^{-1}): 2923, 1660, 1422, 1365, 1289, 1248, 1168, 1096, 1031, 943. HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{27}\text{NO}_6\text{K}^+$ $[\text{M}+\text{K}]^+$ 368.1470, found 368.1411.

2-*tert*-Butoxycarbonyl-9,10-dimethoxy-2-azaadamantane-4,8-dione (**13**):



To a solution of the diol **12** (400 mg, 1.2 mmol) in CH_2Cl_2 (25 mL) was added Dess-Martin periodinane (3 g, 7 mmol) at room temperature. After stirring for 9 h, the mixture was filtered and the filtrate was concentrated under reduced pressure. Purification of the crude residue via silica gel column chromatography (1:1 petroleum/ethyl acetate) afforded compound **13** (383 mg, 97%) as a white solid. ^1H NMR (500 MHz, Chloroform- d) δ 5.04 – 4.99 (m, 1H), 4.82 (dd, $J = 2.9, 1.5$ Hz, 1H), 3.77 (t, $J = 3.3$ Hz, 1H), 3.71 (t, $J = 3.3$ Hz, 1H), 3.38 (d, $J = 1.4$ Hz, 6H), 2.95 (dd, $J = 10.2, 3.7$ Hz, 2H), 1.96 – 1.89 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (126 MHz, Chloroform- d) δ 203.34, 203.02, 153.46, 83.41, 83.37, 81.57, 60.98, 59.28, 56.73, 56.49, 48.75, 48.64, 28.20, 26.28; IR (thin film, ν cm^{-1}): 2923, 1726, 1694, 1413, 1320, 1160, 1096, 998, 951, 894, 757; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_6\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 348.1418, found 348.1435.

2-Acetyl-9,10-dimethoxy-4,4,8,8-tetranitro-2-azaadamantane (**14**):



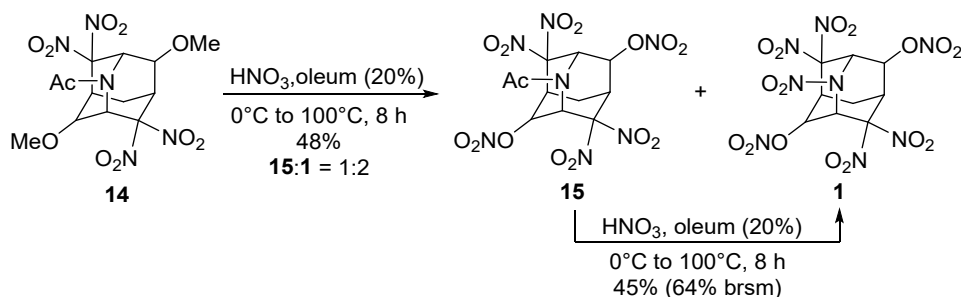
To a solution of CH_2Cl_2 (10 mL) and TFA (10 mL) was added **13** (325 mg, 1.0 mmol) at room temperature. After being stirred for 2 h, the mixture was concentrated in vacuum. The crude product was dissolved in Ac_2O (20 mL) and stirred for 12 h, after evaporation of the volatiles in vacuum, the yellow foam obtained was dissolved in MeOH (20 mL) and treated with hydroxylamine hydrochloride (278 mg, 4.0 mmol) and NaOAc (820 mg, 10.0 mmol). The resulting mixture was stirred for 24 h. Brine (20 mL) was added and the mixture was extracted with EtOAc (3×30 mL). The combined organic phase was dried with Na_2SO_4 . After removal of the solvent in vacuum, the crude product (350 mg) was mixed with urea (360 mg, 6.0 mmol), Na_2SO_4 (5 g) and CH_2Cl_2 (20 mL) and heated to 50 °C. A solution of N_2O_5 (650 mg, 6.0 mmol) in CH_2Cl_2 (5 mL) was added dropwise within 5 min, during this period a green color appeared initially and then faded as more

N₂O₅ was added. The reaction mixture was stirred for additional 1 h and then poured into an iced saturated solution of NaHCO₃ (30 mL). **And the mixture was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was washed with brine (10 mL), dried with Na₂SO₄, and filtered.** The solvent was removed in vacuum and the residue was purified by flash silica gel column chromatography (3:1 petroleum/ethyl acetate) to afford the product **14** (151 mg, 36%) as a white solid.

Compound **2b**: ¹H NMR (500 MHz, DMSO-*d*₆) δ 5.18 – 5.10 (m, 1H), 4.63 – 4.54 (m, 1H), 3.96 (t, *J* = 3.3 Hz, 1H), 3.94 (t, *J* = 3.3 Hz, 1H), 3.34 (s, 3H), 3.22 (s, 3H), 2.95 (d, *J* = 3.7 Hz, 1H), 2.86 (d, *J* = 3.8 Hz, 1H), 2.00 (s, 3H), 1.97 (s, 2H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 203.82, 203.26, 169.08, 83.14, 82.58, 64.11, 58.00, 57.05, 56.43, 48.23, 47.92, 25.19, 21.61; IR (thin film, ν cm⁻¹): 2932, 1728, 1625, 1584, 1416, 1277, 1091, 988, 961, 591; HRMS (ESI): *m/z* calcd for C₁₃H₁₇NO₅H⁺ [M+H]⁺ 268.1179, found 268.1185.

Compound **14**: ¹H NMR (500 MHz, Acetone-*d*₆) δ 6.25 (s, 1H), 5.43 (s, 1H), 3.92 (d, *J* = 2.1 Hz, 2H), 3.86 (dd, *J* = 3.7, 2.1 Hz, 1H), 3.80 (t, *J* = 3.0 Hz, 1H), 3.39 (s, 3H), 3.32 (s, 3H), 2.42 (s, 1H), 2.42 (s, 1H), 2.38 (s, 3H); ¹³C NMR (126 MHz, Acetone-*d*₆) δ 205.41, 169.86, 113.46, 76.71, 76.45, 57.33, 56.77, 54.15, 46.42, 35.27, 34.06, 23.80, 20.72; IR (thin film, ν cm⁻¹): 2920, 1672, 1594, 1582, 1562, 1409, 1305, 1277, 1105, 966, 827, 777, 681; HRMS (ESI): *m/z* calcd for C₁₃H₁₇N₅O₁₁H⁺ [M+H]⁺ 420.0997, found 420.1049.

2,9,9,10,10-pentanitro-2-azaadamantane-4,8-diyl dinitrate (**1**):



To a mixture of fuming nitric acid (4 mL) and 20% oleum (2 mL) at 0°C was added compound **14** (150 mg, 0.36 mmol). The reaction mixture was heated to 100°C. After stirring for 8 h, the reaction mixture was cooled to ambient temperature and poured into ice-water (25 mL) with agitation. The white participate was filtered, washed with water and dried in vacuum. The product was purified by flash chromatography (6:1 petroleum/ethyl acetate) to afford product **1** (155 mg, 32%) as a white solid along with **15** (77 mg, 16%, 4:1 petroleum/ethyl acetate) as a white solid. Compound **15** could undergo the same nitrolysis procedure to provide **1** (45%) combined with recovery of **15** (30%).

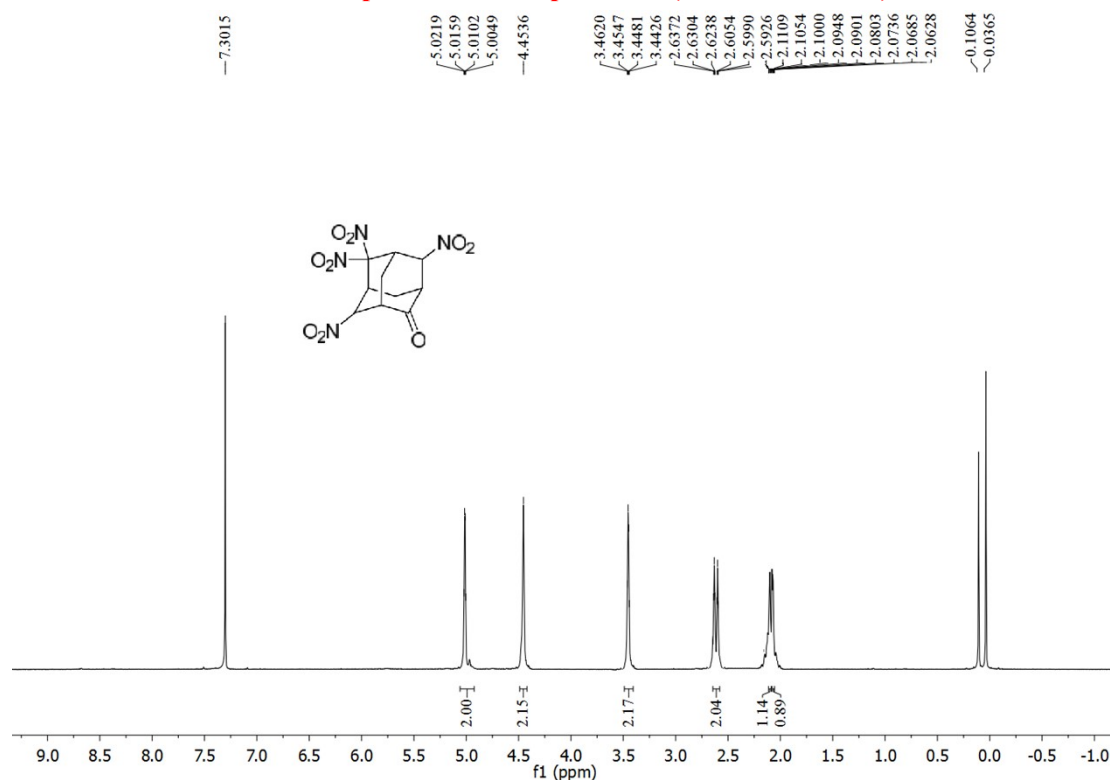
Compound **15**: ¹H NMR (500 MHz, Acetone-*d*₆) δ 6.46 (s, 1H), 5.98 (s, 1H), 5.81 (t, *J* = 2.9 Hz, 1H), 5.71 (t, *J* = 2.8 Hz, 1H), 4.26 (t, *J* = 3.1 Hz, 1H), 4.20 – 4.14 (m, 1H), 3.00 (dt, *J* = 16.8, 3.2 Hz, 1H), 2.91 (dt, *J* = 16.8, 3.2 Hz, 1H), 2.47 (s, 3H); ¹³C NMR (126 MHz, Acetone-*d*₆) δ 169.92, 113.00, 112.37, 75.70, 75.30, 52.53, 45.97, 34.67, 34.41, 23.80, 20.42; IR (thin film, ν cm⁻¹): 1688,

1681, 1662, 1591, 1279, 828, 806, 789, 779, 721; HRMS (ESI): m/z calcd for $C_{11}H_{11}N_7O_{15}Na^+$ $[M+Na]^+$ 504.0205, found 504.0196.

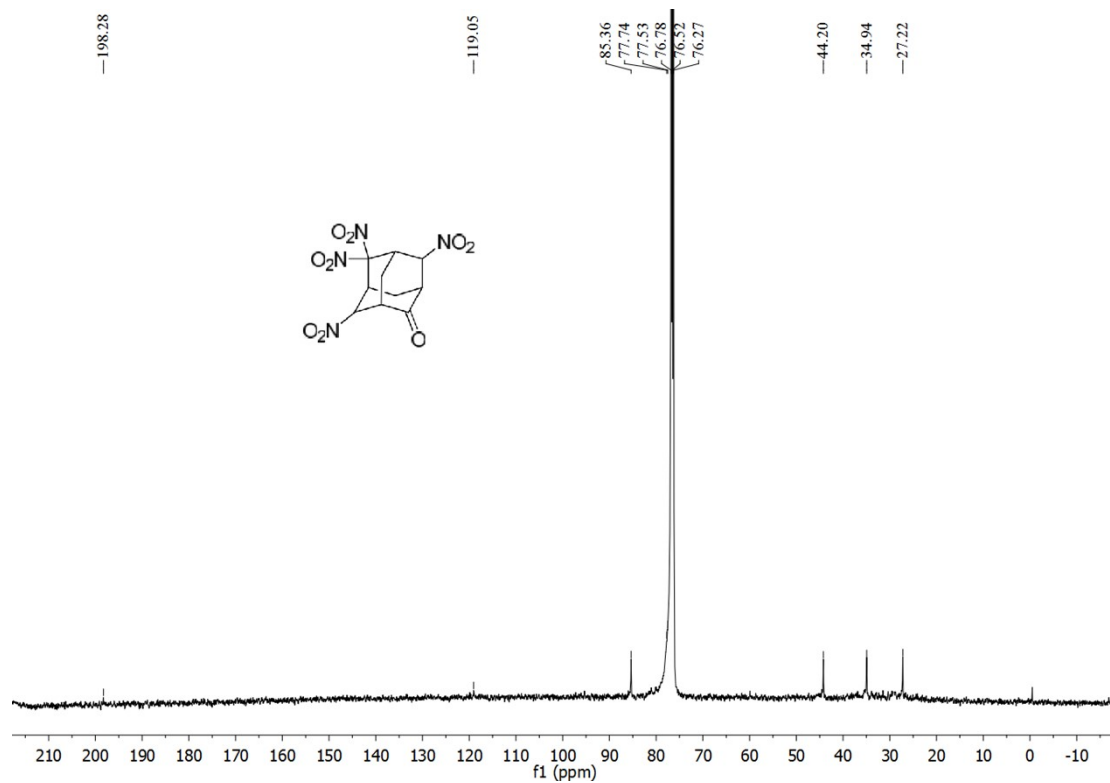
Compound 1: 1H NMR (500 MHz, Acetone- d_6) δ 6.84 (s, 2H), 6.00 – 5.96 (m, 2H), 4.29 (s, 2H), 3.04 (s, 2H); ^{13}C NMR (126 MHz, Acetone- d_6) δ 111.82, 74.67, 52.73, 34.82, 23.64; IR (thin film, ν cm^{-1}): 3029, 1689, 1587, 1268, 977, 938, 802, 717; HRMS (ESI): m/z calcd for $C_9H_8N_8O_{16}Cl^-$ $[M+Cl]^-$ 518.9752, found 518.9806.

3 ¹H-NMR and ¹³C-NMR Spectra of Compounds

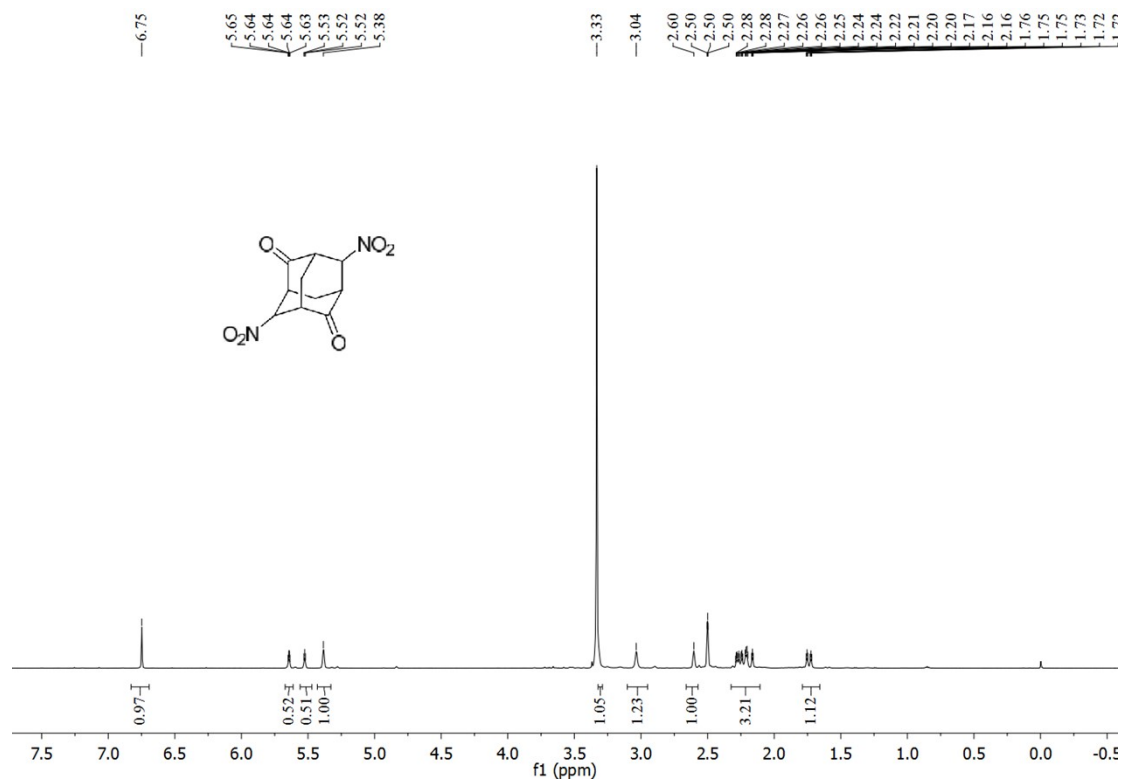
¹H NMR spectrum of compound S3 (CDCl₃, 500 MHz)



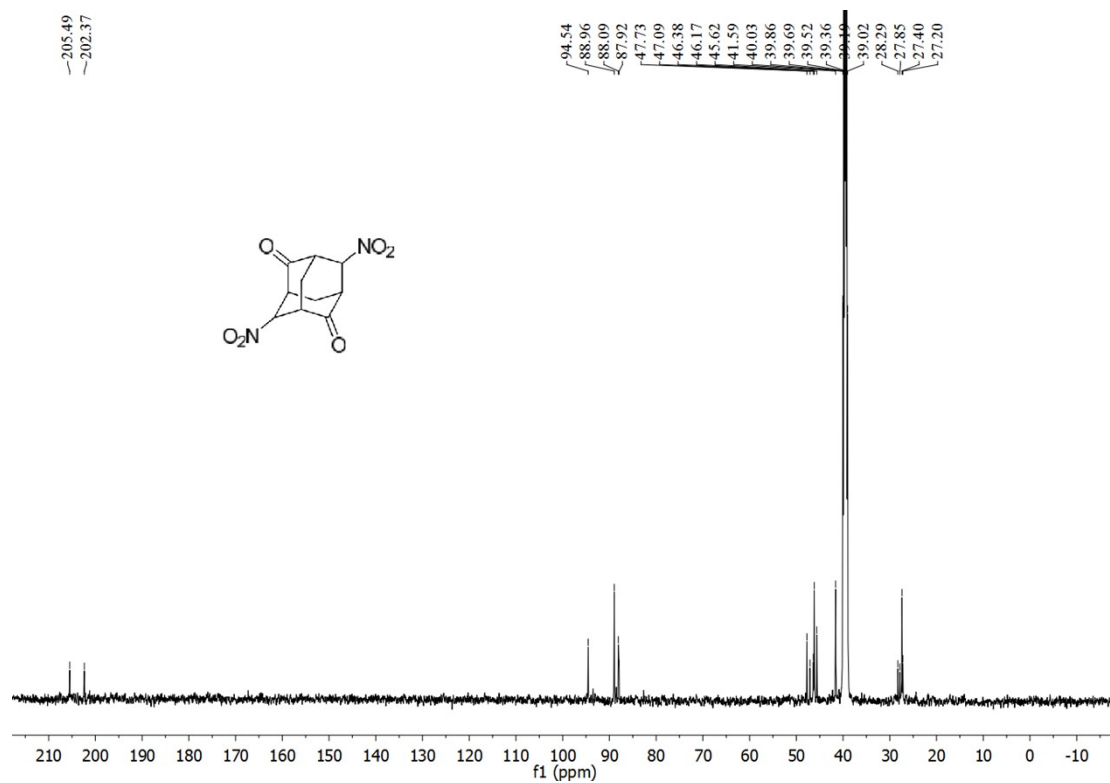
¹³C NMR spectrum of compound S3 (CDCl₃, 126 MHz)



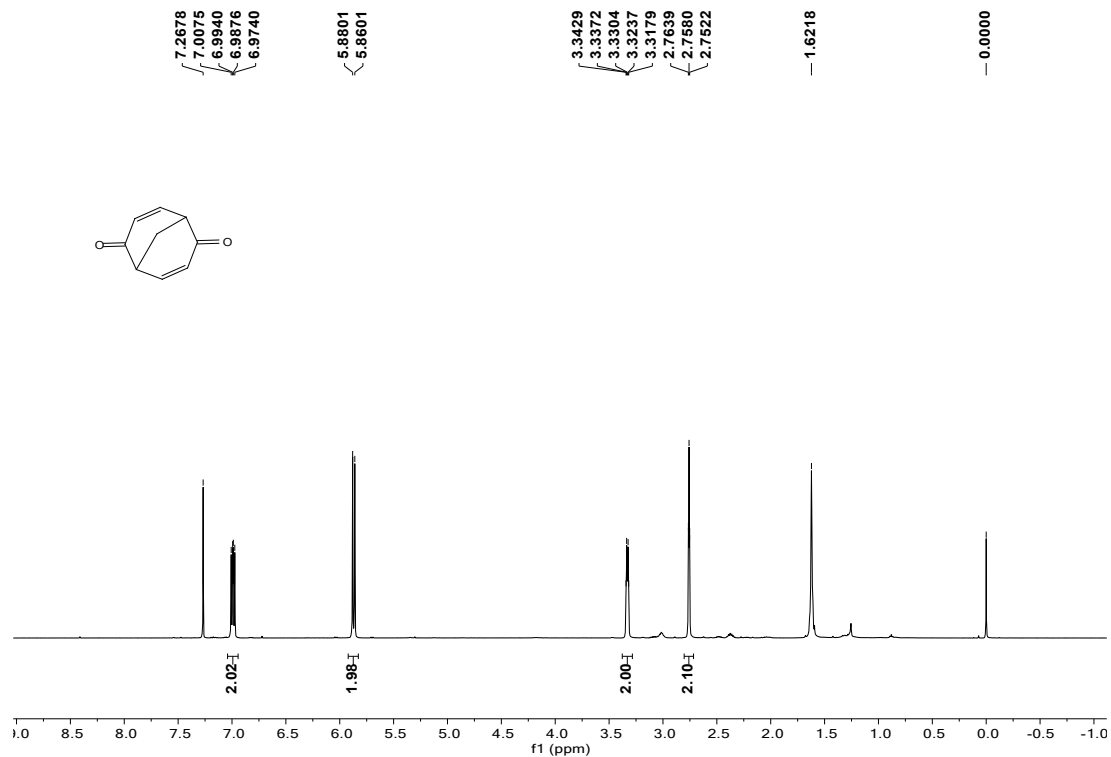
¹H NMR spectrum of compound S1 (DMSO-*d*₆, 500 MHz)



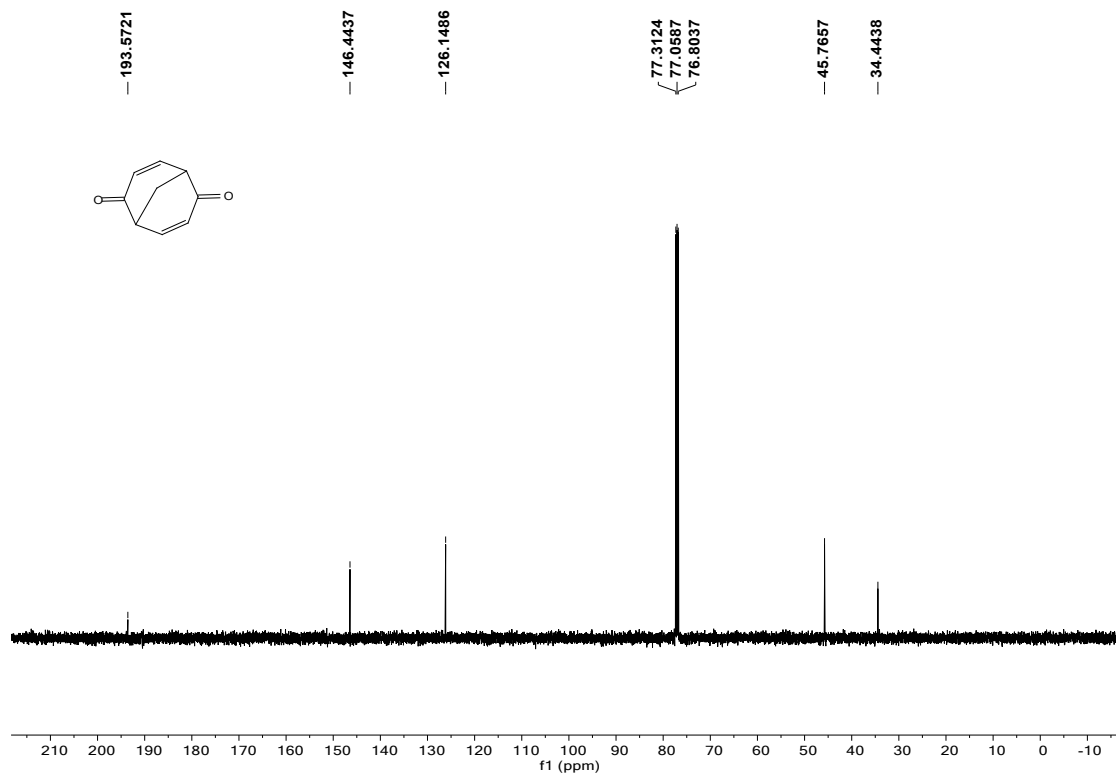
¹³C NMR spectrum of compound S1 (DMSO-*d*₆, 126 MHz)



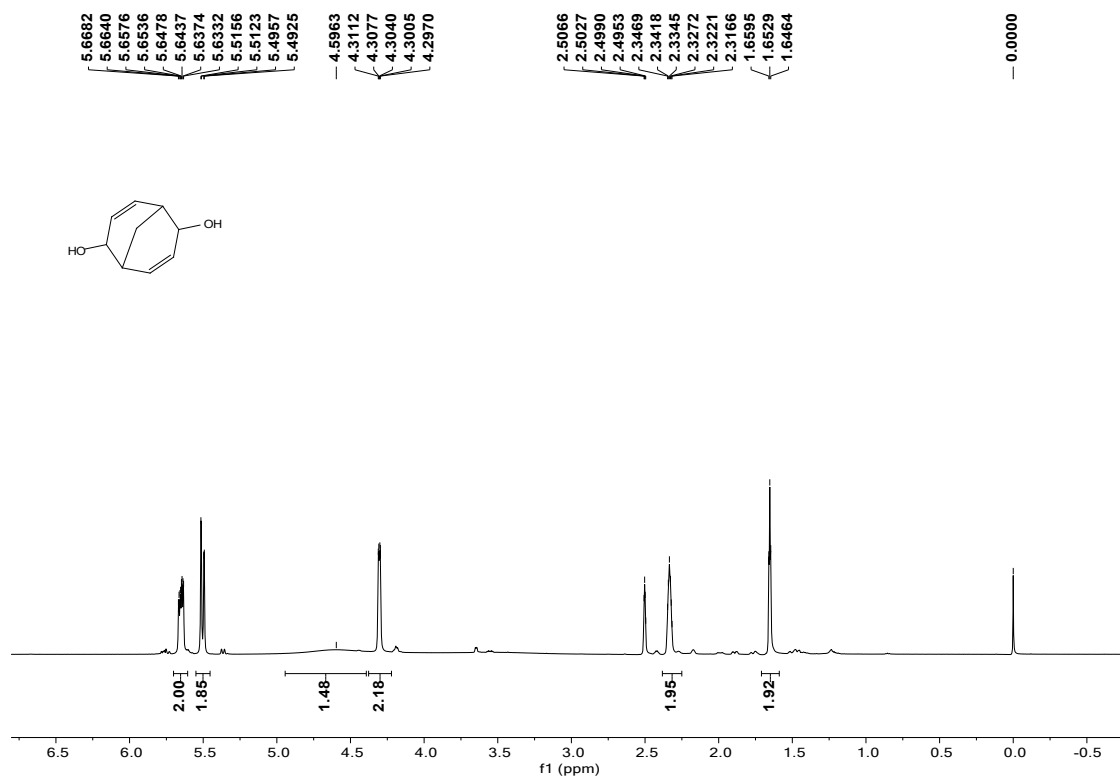
¹H NMR spectrum of compound 5 (CDCl₃, 500 MHz)



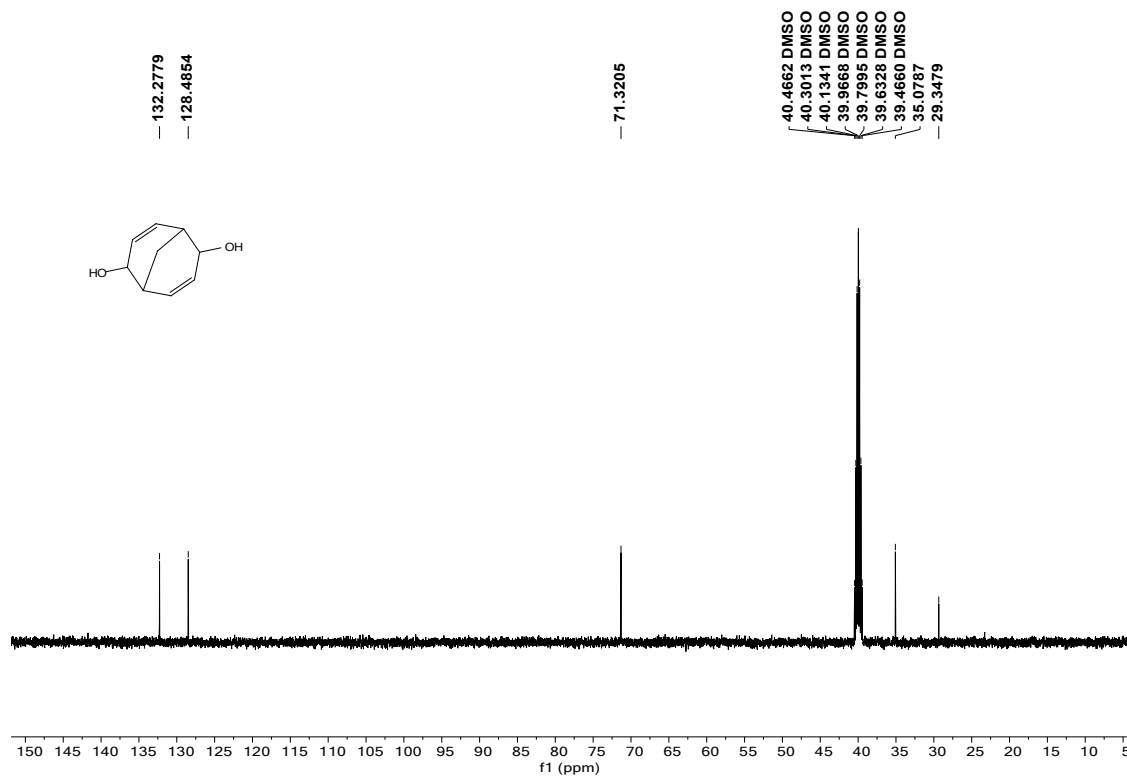
¹³C NMR spectrum of compound 5 (CDCl₃, 126 MHz)



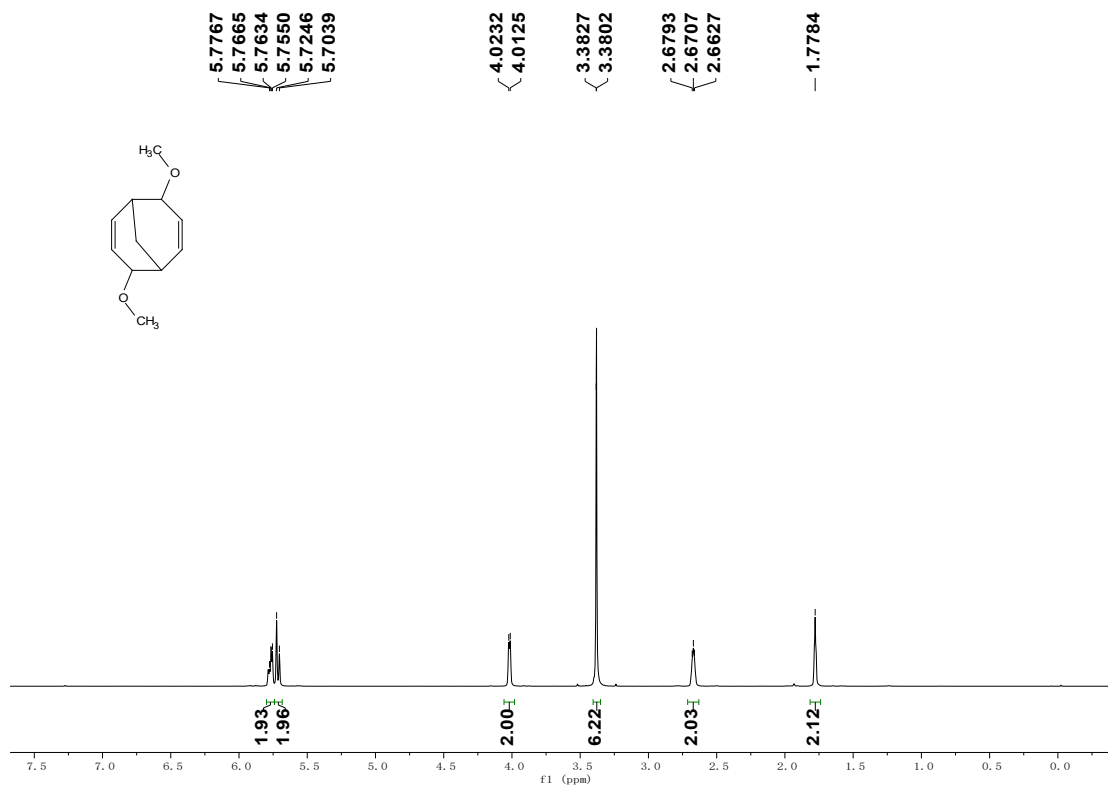
¹H NMR spectrum of compound 4a (DMSO-*d*₆, 500 MHz)



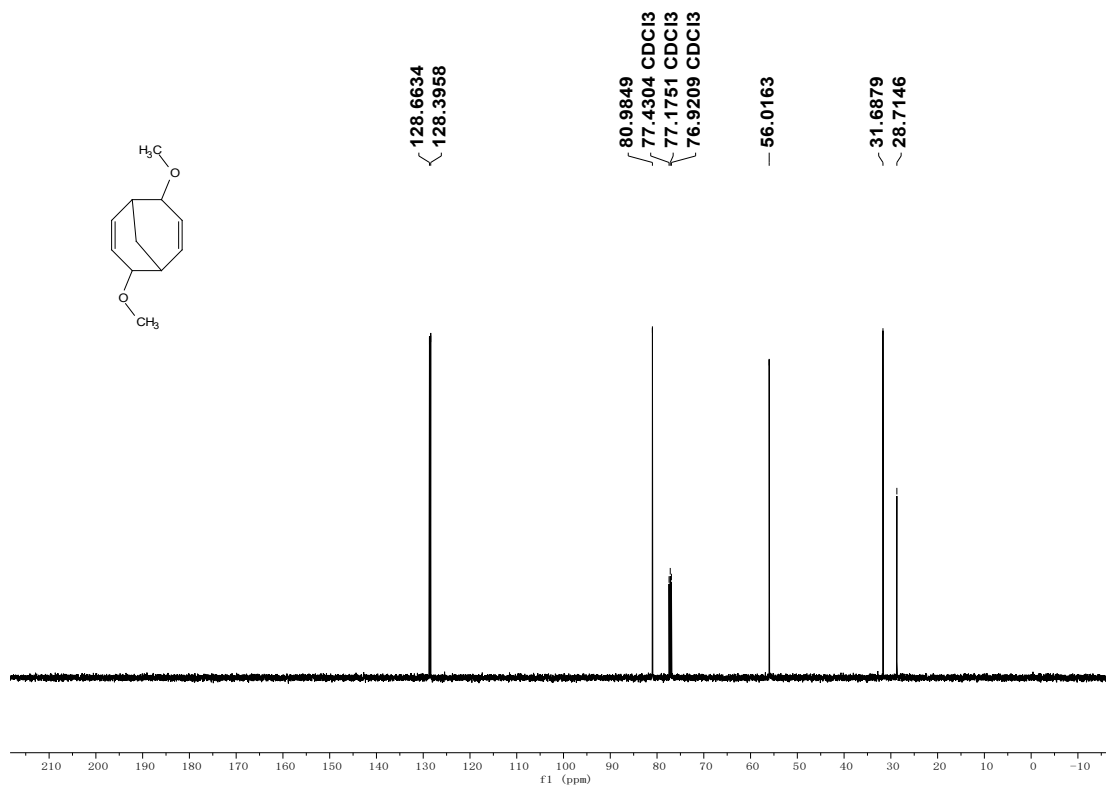
¹³C NMR spectrum of compound 4a (DMSO-*d*₆, 126 MHz)



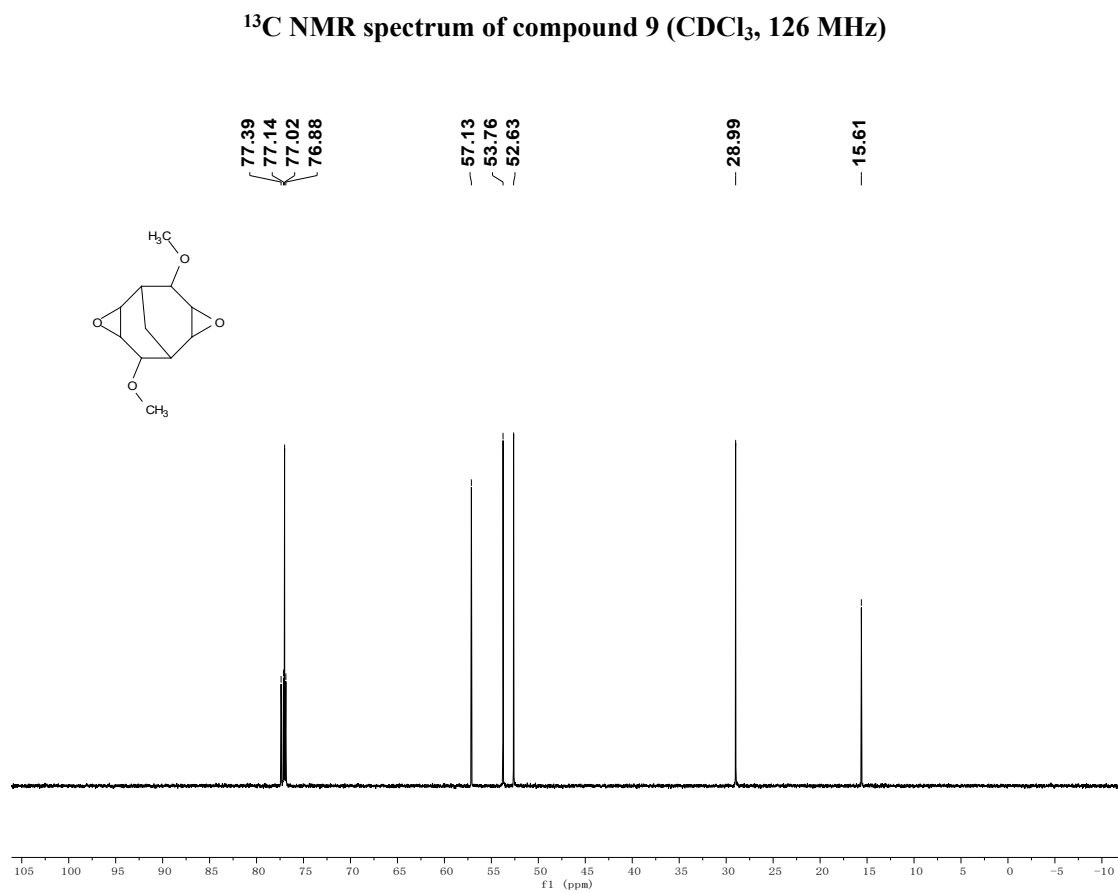
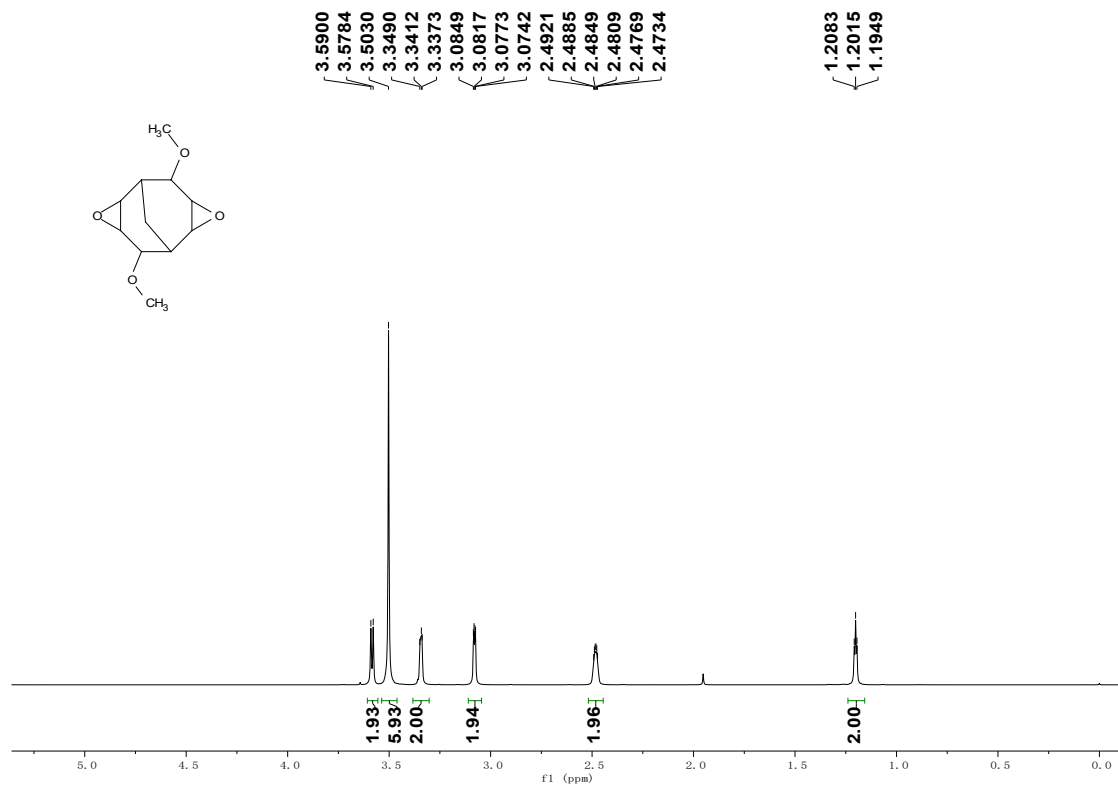
¹H NMR spectrum of compound 4b (CDCl₃, 500 MHz)



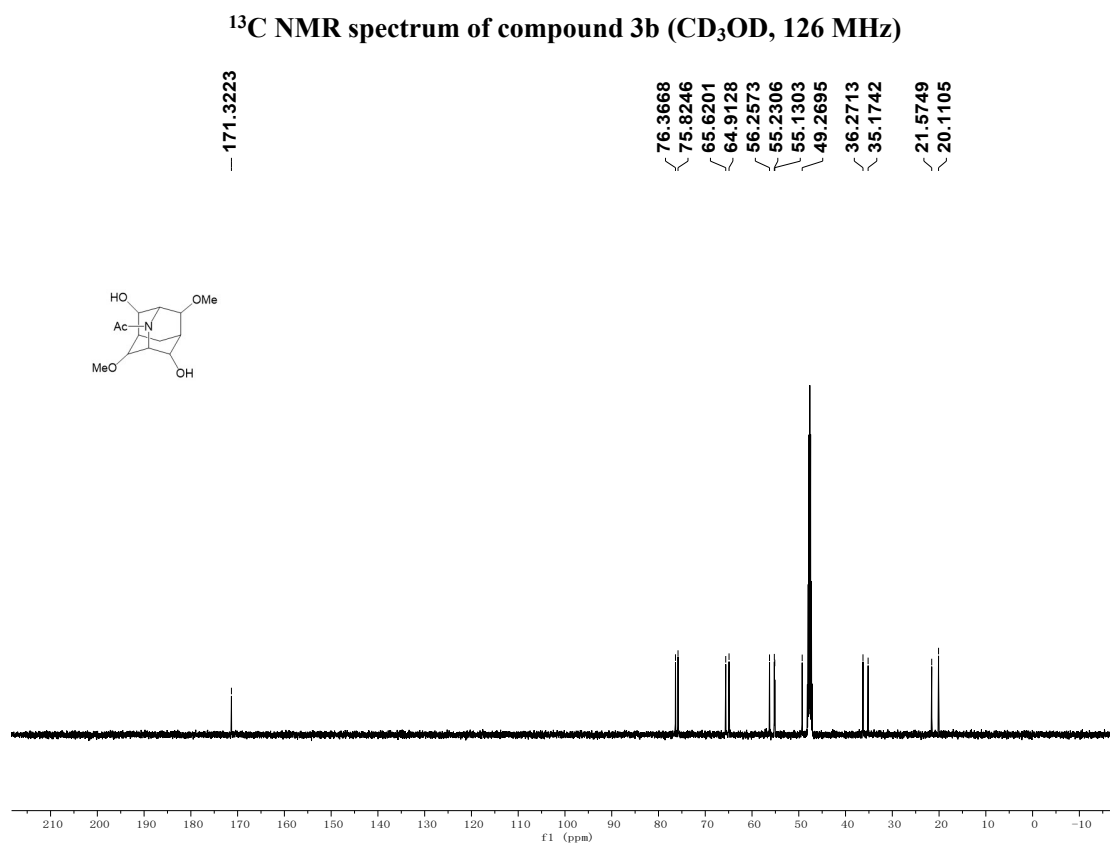
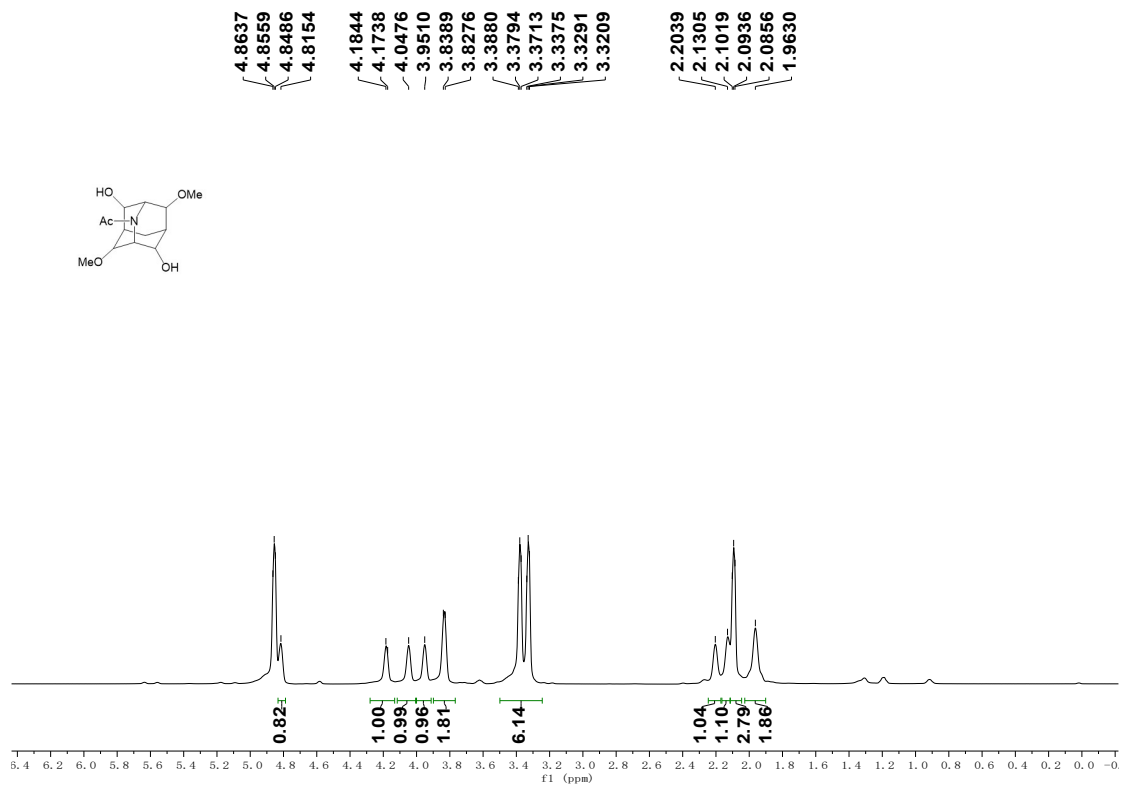
^{13}C NMR spectrum of compound 4b (CDCl_3 , 126 MHz)



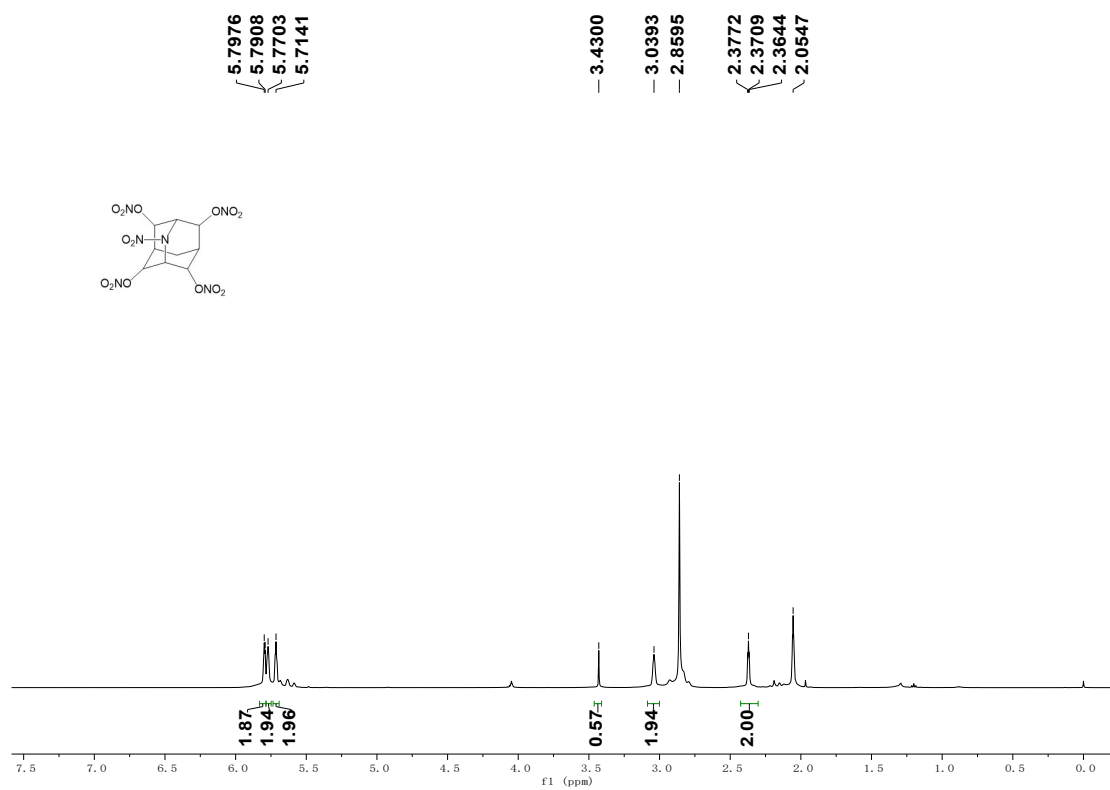
^1H NMR spectrum of compound 9 (CDCl_3 , 500 MHz)



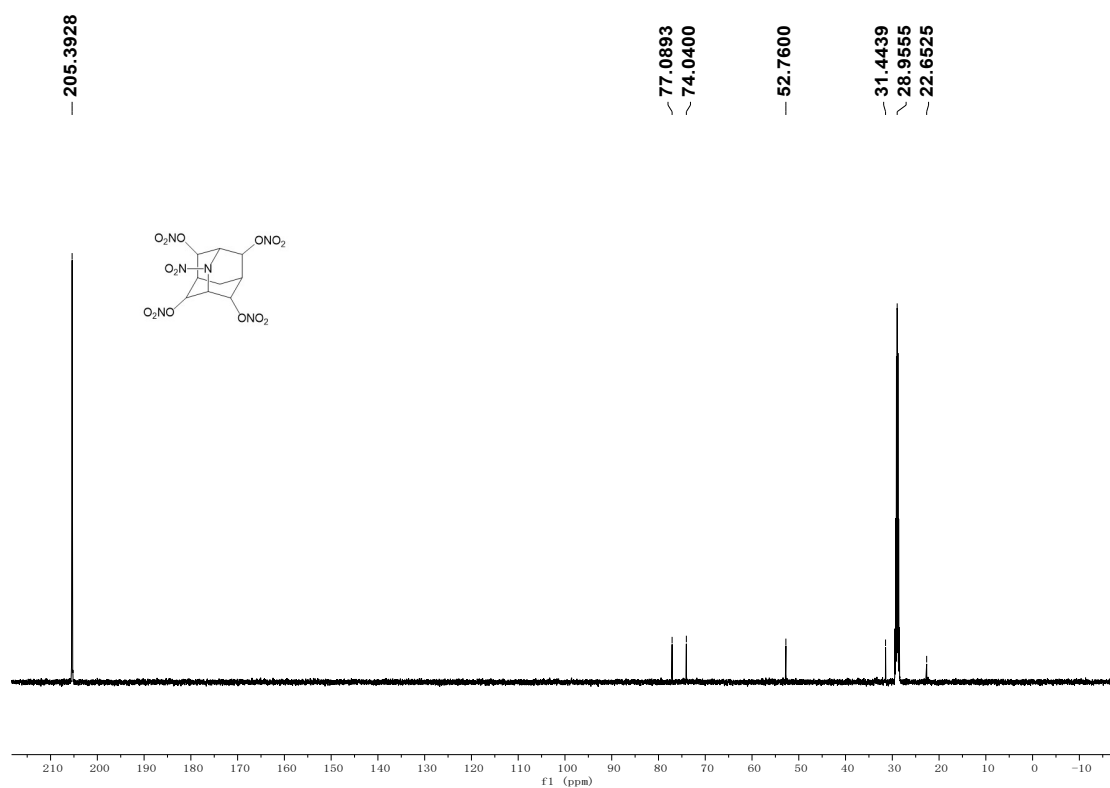
¹H NMR spectrum of compound 3b (CD₃OD, 500 MHz)



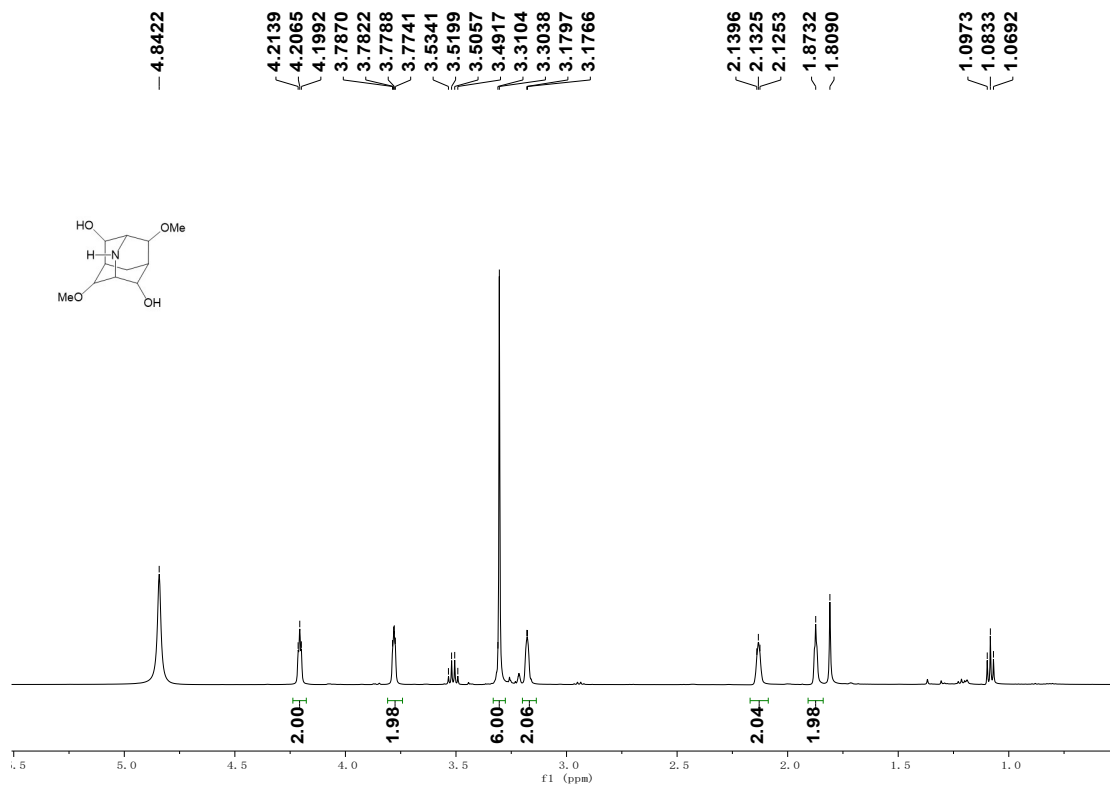
¹H NMR spectrum of compound 10 (CDCl₃, 500 MHz)



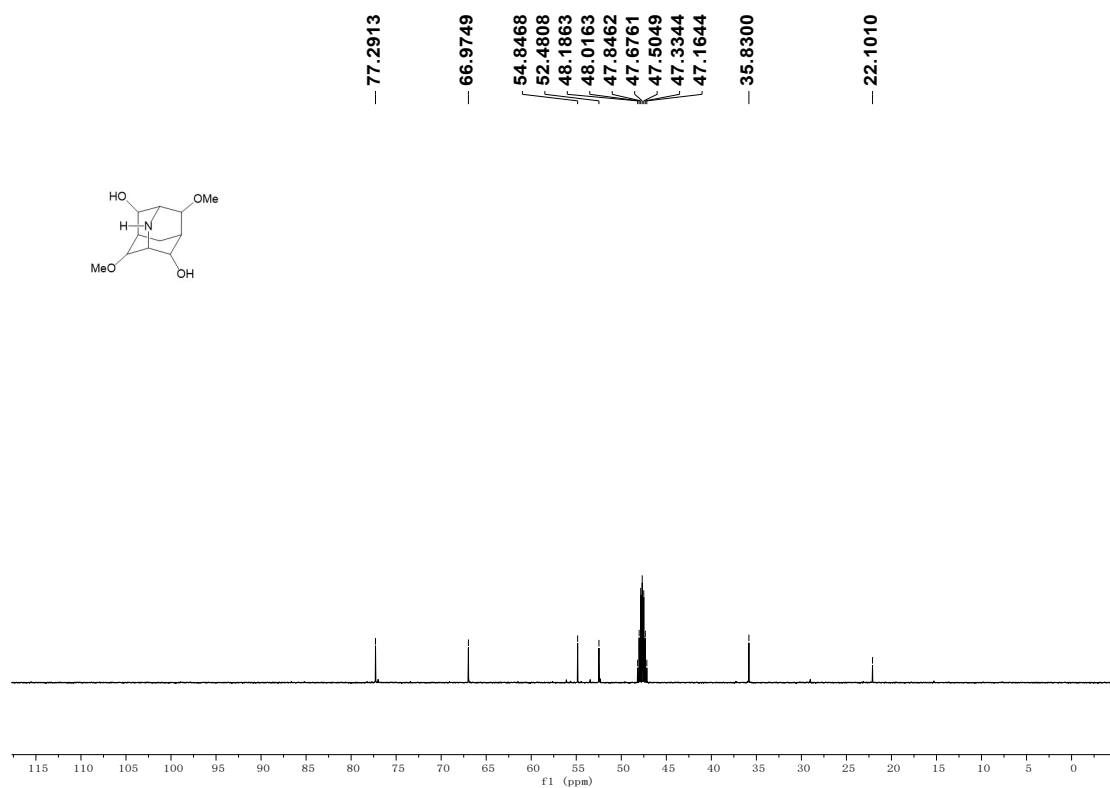
¹³C NMR spectrum of compound 10 (CDCl₃, 126 MHz)



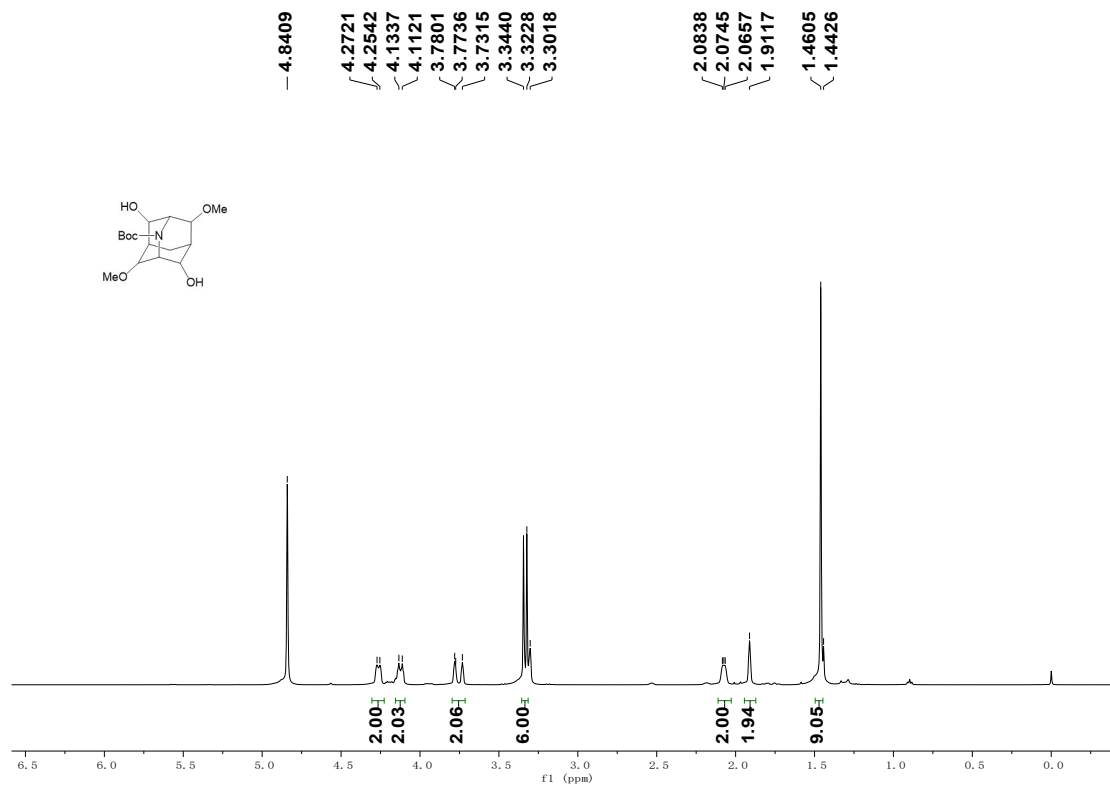
¹H NMR spectrum of compound 11 (CD₃OD, 500 MHz)



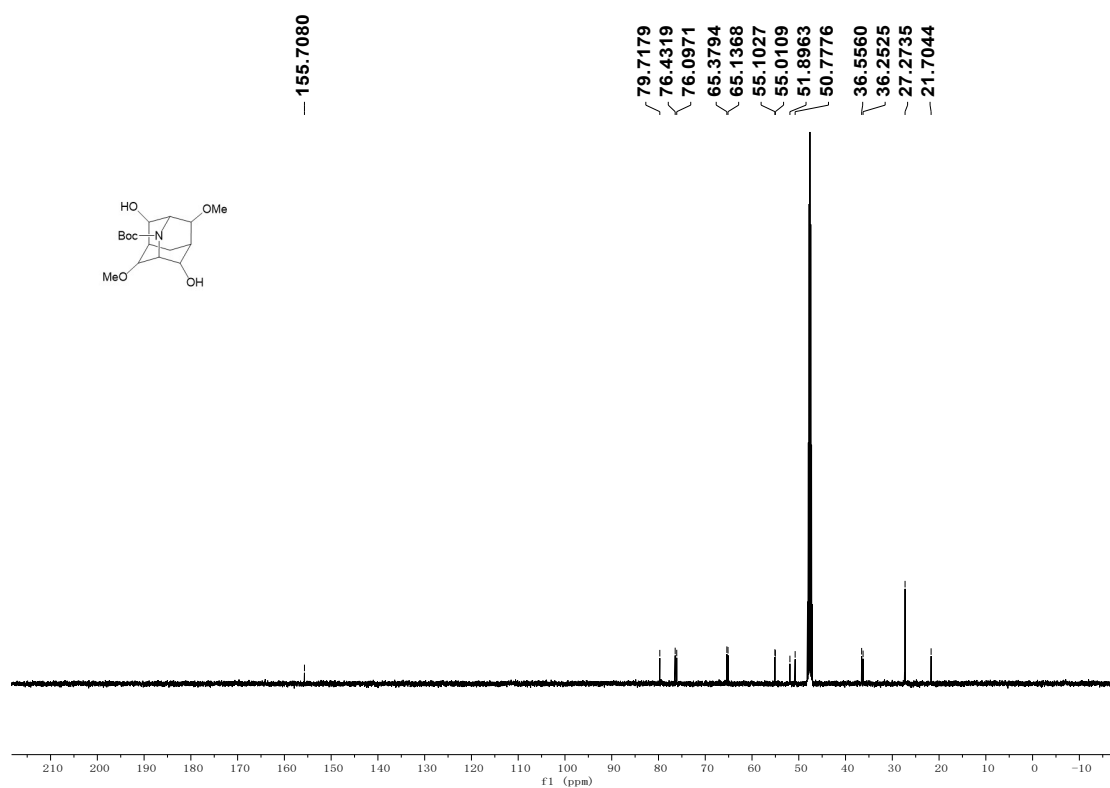
¹³C NMR spectrum of compound 11 (CD₃OD, 126 MHz)



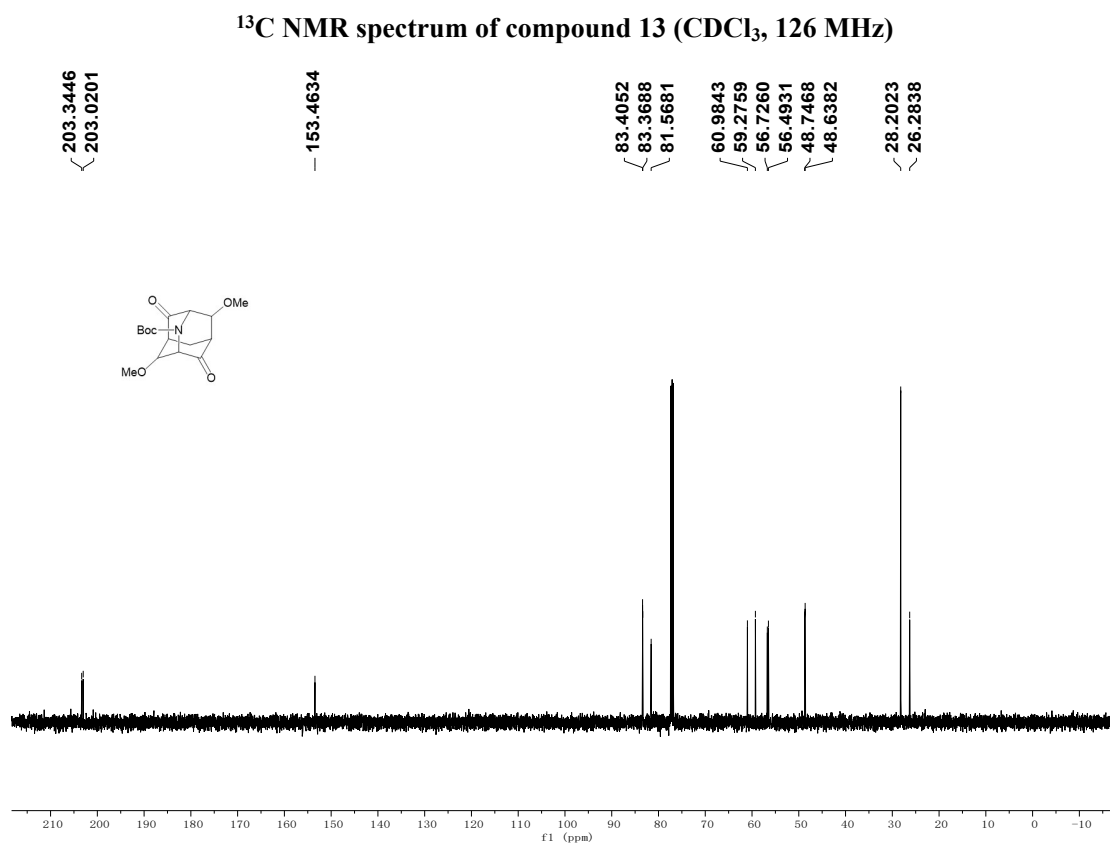
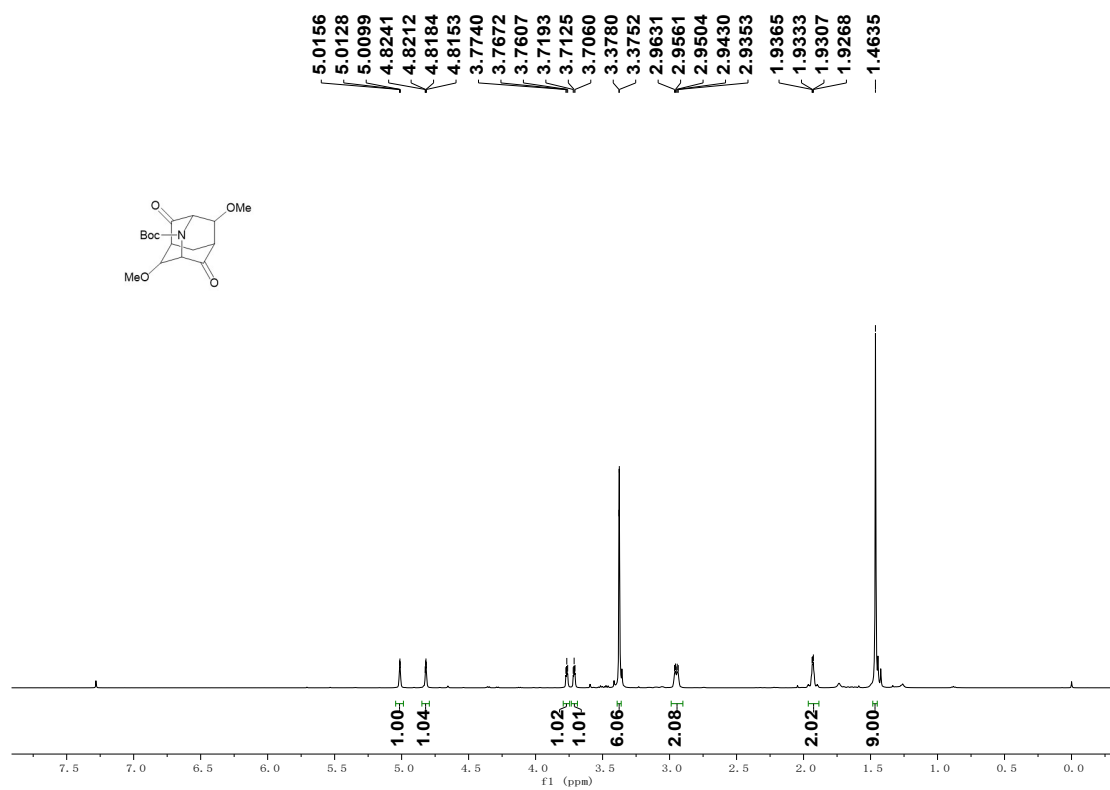
¹H NMR spectrum of compound 12 (CD₃OD, 500 MHz)



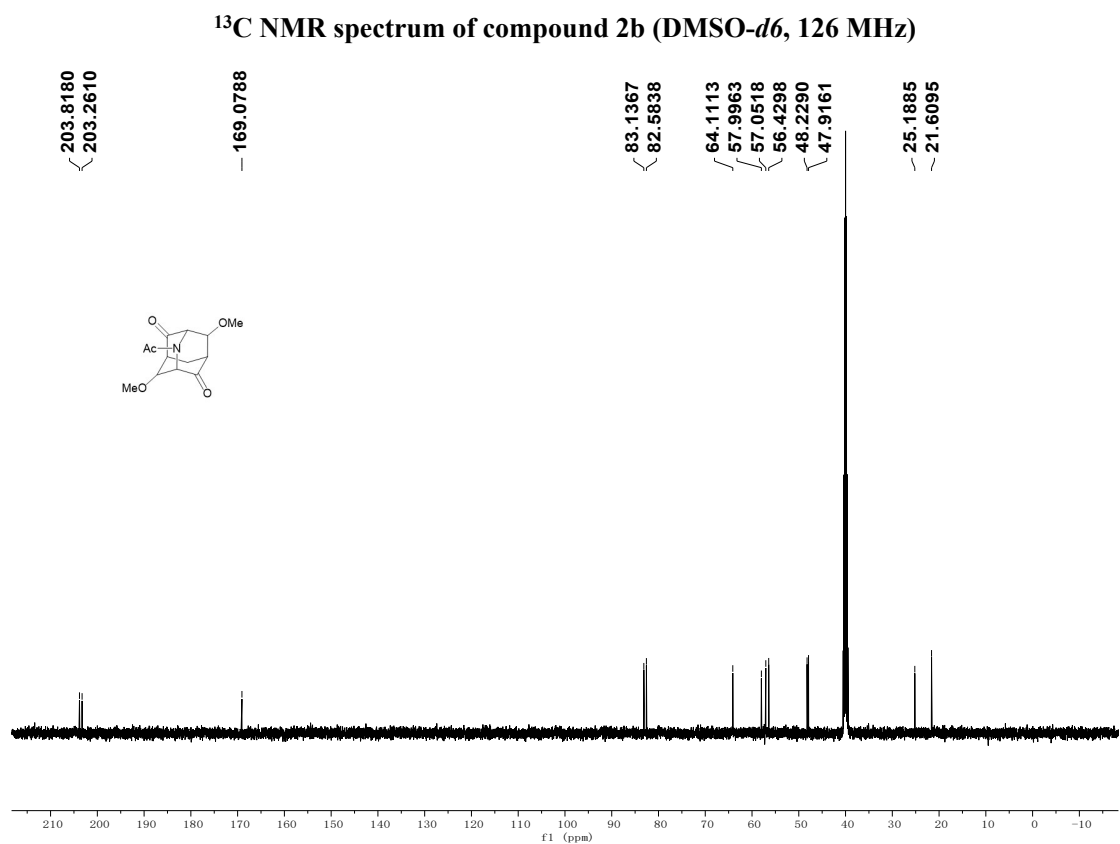
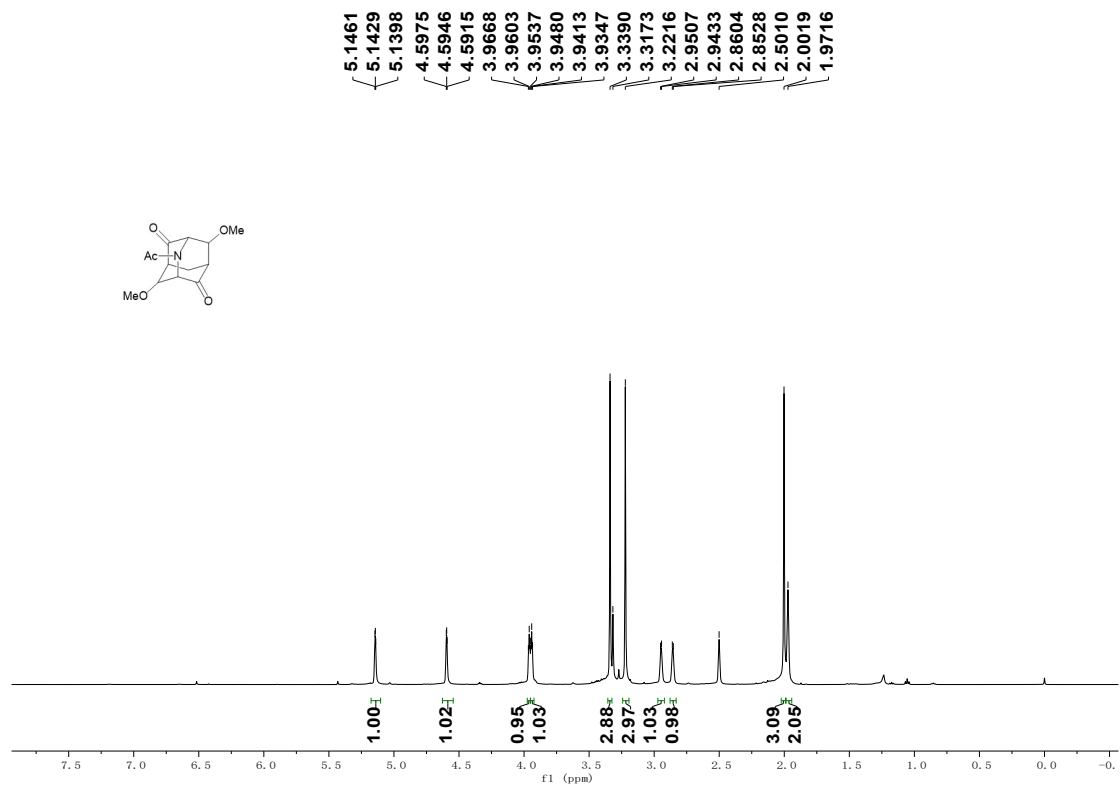
¹³C NMR spectrum of compound 12 (CD₃OD, 126 MHz)



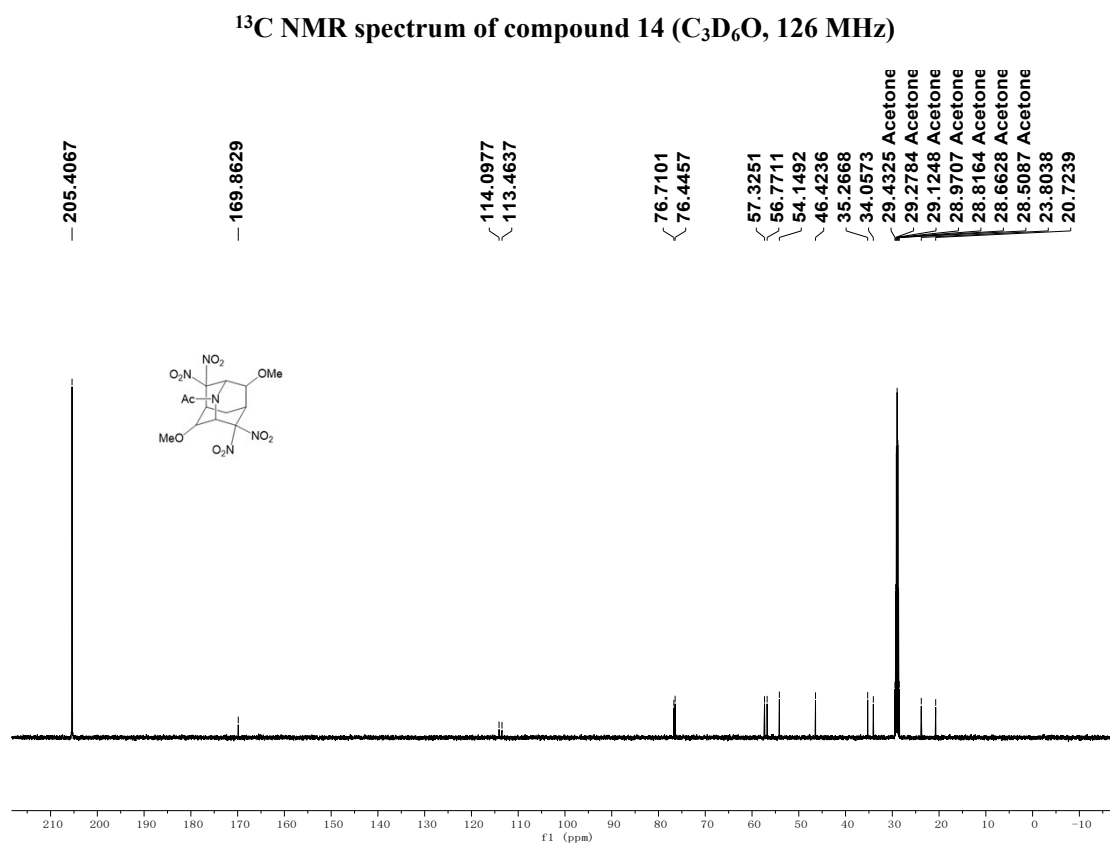
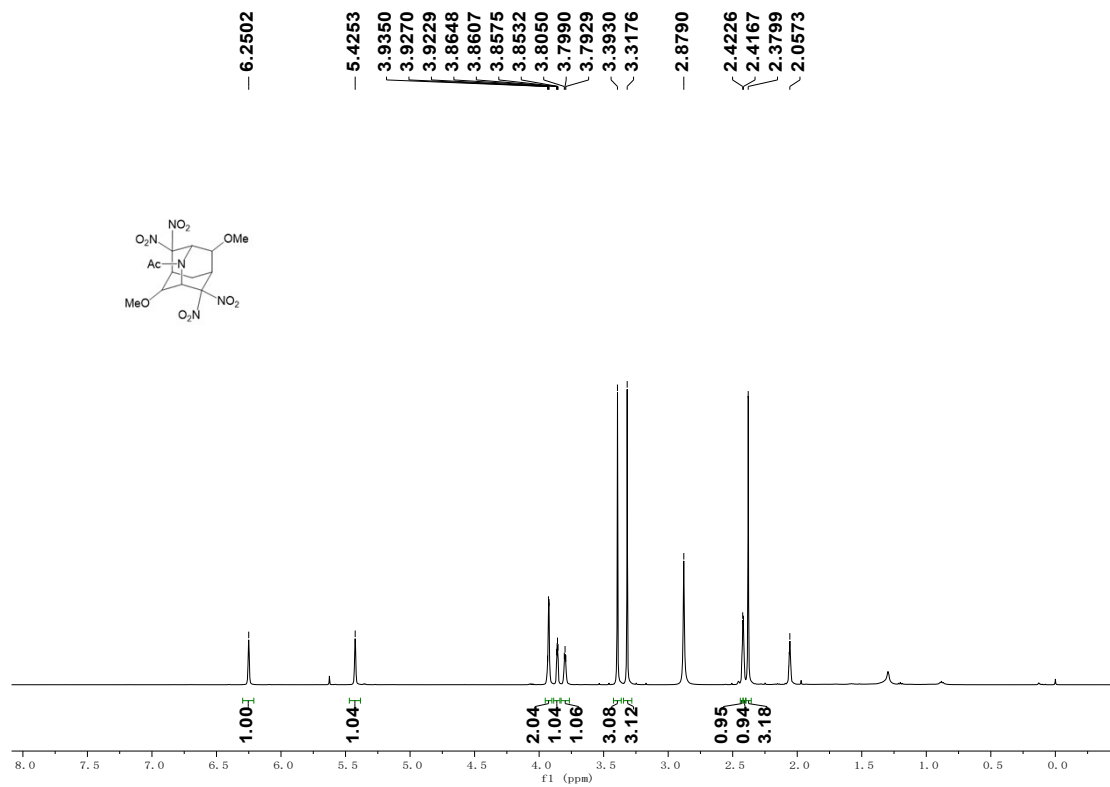
¹H NMR spectrum of compound 13 (CDCl₃, 500 MHz)



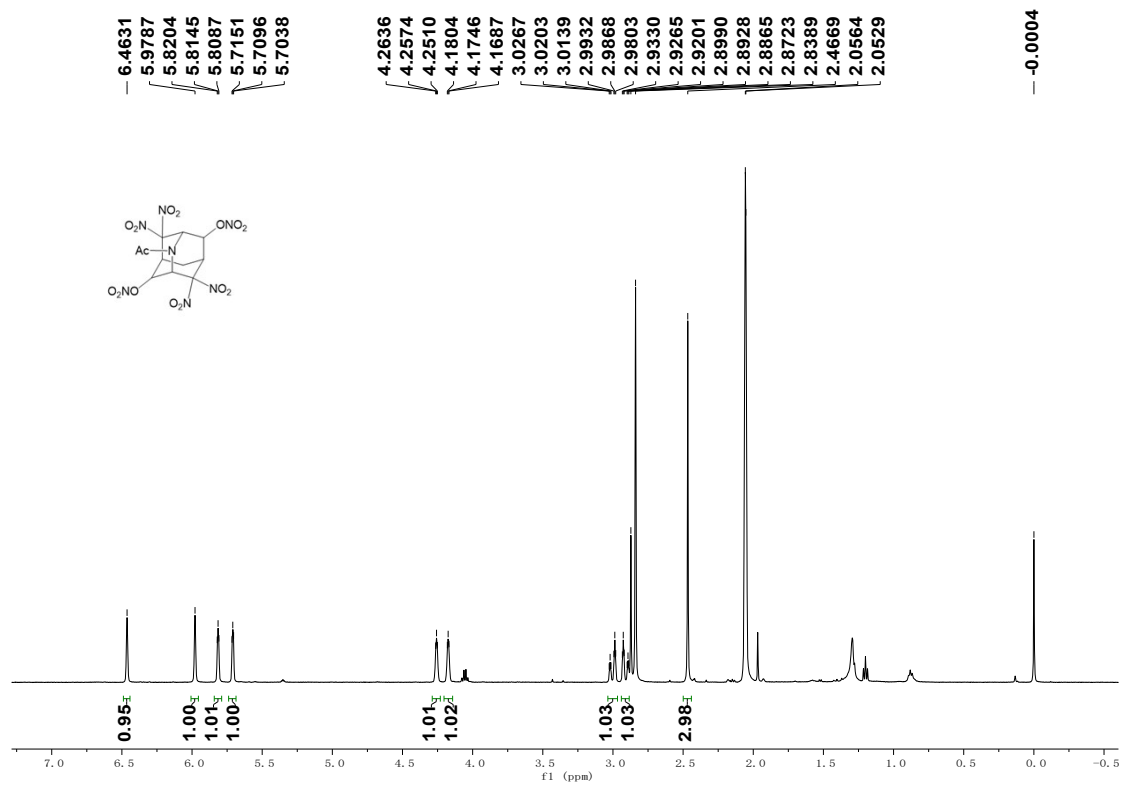
¹H NMR spectrum of compound 2b (DMSO-*d*₆, 500 MHz)



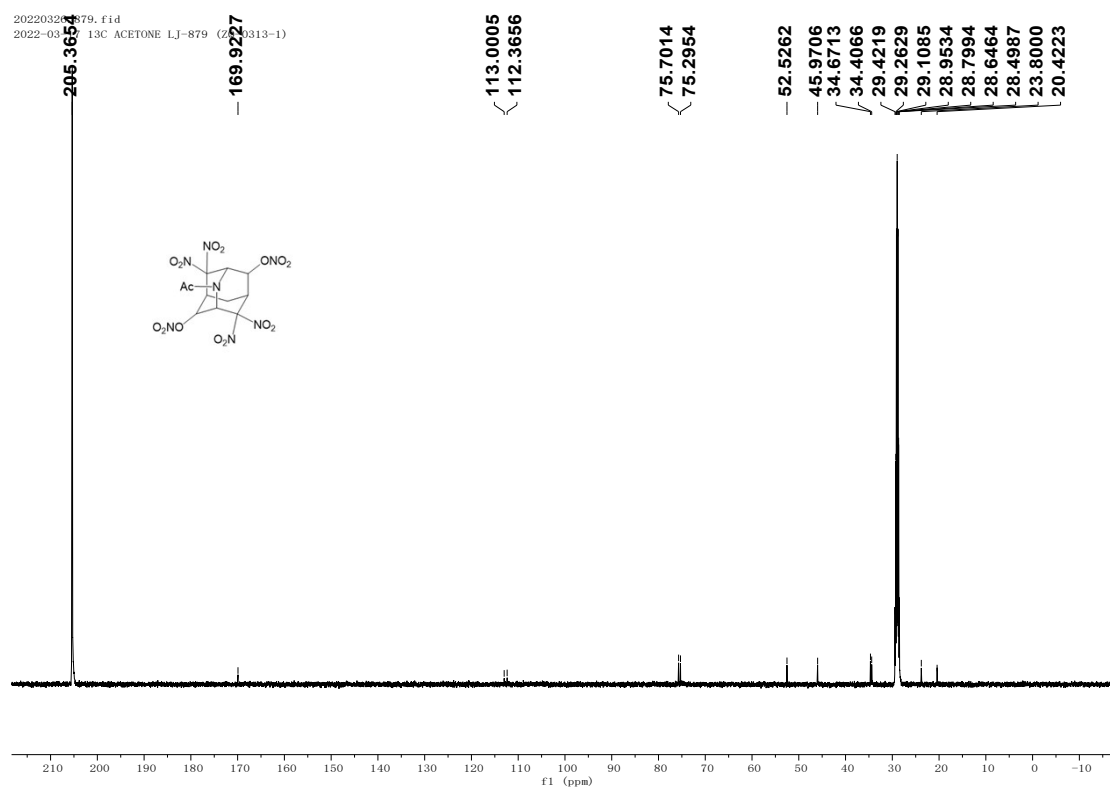
¹H NMR spectrum of compound 14 (C₃D₆O, 500 MHz)



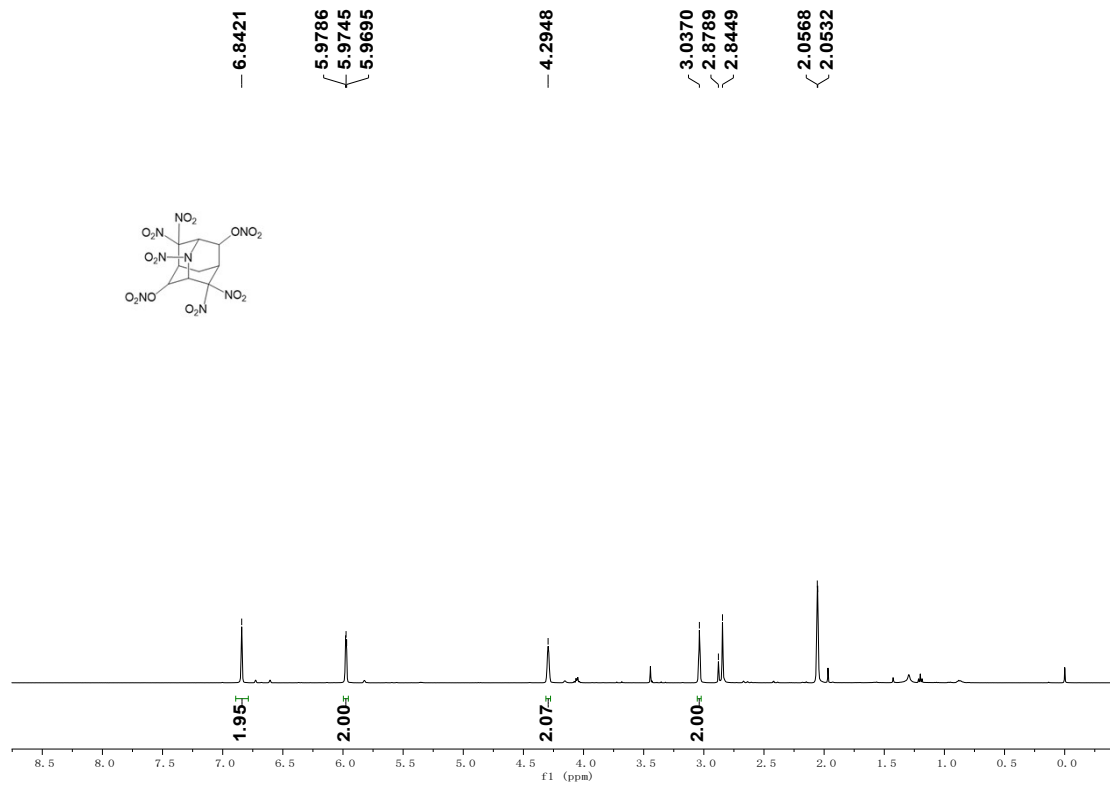
¹H NMR spectrum of compound 15 (C₃D₆O, 500 MHz)



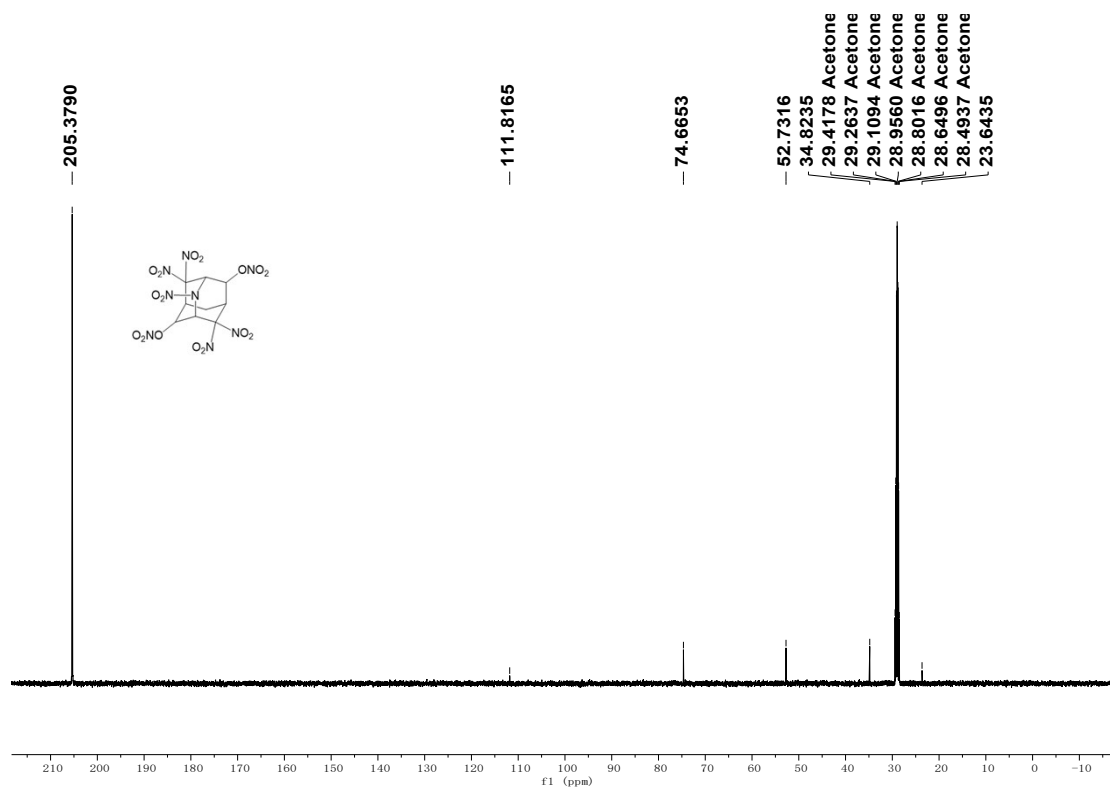
¹³C NMR spectrum of compound 15 (C₃D₆O, 126 MHz)



¹H NMR spectrum of compound 1 (C₃D₆O, 500 MHz)



¹³C NMR spectrum of compound 1 (C₃D₆O, 126 MHz)



4 X-ray Crystal Structures and Data of Compound 10

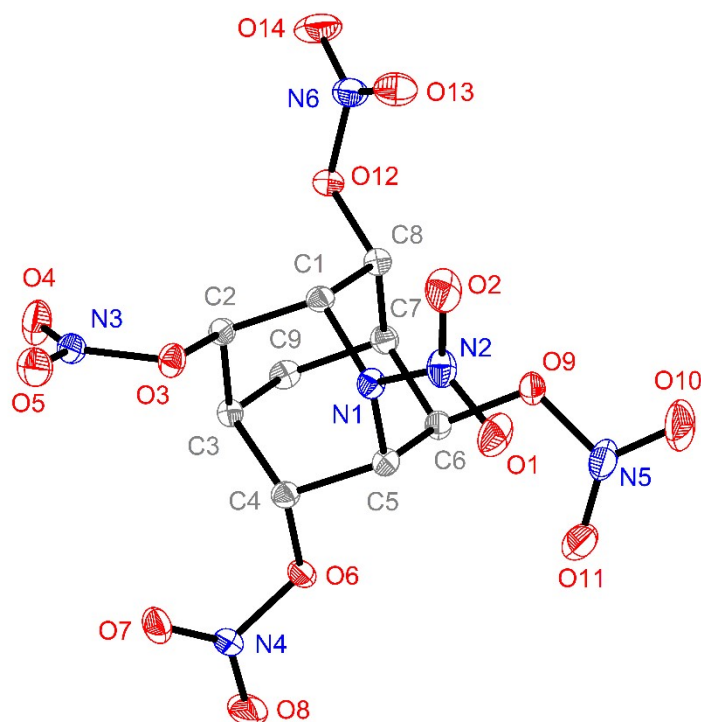


Figure S1. ORTEP diagram of **10** Color code: Carbon (grey), Oxygen (red), Nitrogen (blue).

Single crystals of **10** suitable for X-ray diffraction analysis were obtained by slow recrystallization from a mixture of acetone and chloroform. The result of X-ray diffraction indicates that compound **10** crystallizes in the monoclinic space group $P2_1 2_1 2_1$. The crystal density was determined to be 1.776 g cm^{-3} .

Table S1. Crystal data and structure refinement for **10**.

Identification code	10	
Empirical formula	C ₉ H ₁₀ N ₆ O ₁₄	
Formula weight	426.23	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>P</i> 21 21 21	
Unit cell dimensions	a = 8.7329(11) Å	α = 90°.
	b = 11.6016(15) Å	β = 90°.
	c = 15.738(2) Å	γ = 90°.
Volume	1594.5(4) Å ³	
Z	4	
Density (calculated)	1.776 mg/m ³	
Absorption coefficient	0.171 mm ⁻¹	
F(000)	872	
Crystal size	0.200 x 0.150 x 0.150 mm ³	
Theta range for data collection	2.181 to 27.237°.	
Index ranges	-10 ≤ h ≤ 11, -14 ≤ k ≤ 14, -18 ≤ l ≤ 19	
Reflections collected	12487	
Independent reflections	3266 [R(int) = 0.0453]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.975 and 0.970	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3266 / 0 / 262	
Goodness-of-fit on F ²	1.032	
Final R indices [I > 2σ(I)]	R1 = 0.0367, wR2 = 0.0755	
R indices (all data)	R1 = 0.0503, wR2 = 0.0817	
Absolute structure parameter	0.4(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.159 and -0.175 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7524(3)	5012(2)	5633(2)	29(1)
C(2)	6302(3)	4261(2)	6038(2)	29(1)
C(3)	5540(3)	4882(2)	6781(2)	29(1)
C(4)	4862(3)	6009(2)	6446(2)	30(1)
C(5)	6124(3)	6781(2)	6095(2)	31(1)
C(6)	7330(3)	7010(2)	6775(2)	32(1)
C(7)	8058(3)	5872(2)	7064(2)	31(1)
C(8)	8771(3)	5290(2)	6287(2)	32(1)
C(9)	6781(3)	5126(2)	7447(2)	33(1)
N(1)	6802(3)	6114(2)	5394(1)	32(1)
N(2)	7450(3)	6726(2)	4738(2)	42(1)
N(3)	4469(3)	2924(2)	5445(2)	41(1)
N(4)	2648(3)	6448(2)	7291(2)	38(1)
N(5)	8296(4)	8887(2)	6394(2)	56(1)
N(6)	10707(3)	3842(2)	6121(2)	46(1)
O(1)	7035(3)	7720(2)	4636(2)	61(1)
O(2)	8351(3)	6214(2)	4279(1)	61(1)
O(3)	5226(2)	3997(2)	5357(1)	37(1)
O(4)	4694(3)	2377(2)	6076(2)	60(1)
O(5)	3681(3)	2718(2)	4844(2)	58(1)
O(6)	4189(2)	6697(2)	7121(1)	36(1)
O(7)	2080(2)	5644(2)	6930(2)	49(1)
O(8)	2092(3)	7089(2)	7790(2)	69(1)
O(9)	8589(2)	7690(2)	6434(1)	42(1)
O(10)	9397(4)	9407(2)	6161(2)	99(1)
O(11)	7048(3)	9223(2)	6589(2)	65(1)
O(12)	9462(2)	4241(2)	6609(1)	38(1)
O(13)	10958(3)	4291(2)	5453(2)	59(1)
O(14)	11367(3)	3065(2)	6463(2)	68(1)

Table S3. Bond lengths [\AA] and angles [$^\circ$] for **10**.

C(1)-N(1)	1.475(3)
C(1)-C(2)	1.518(4)
C(1)-C(8)	1.533(4)
C(1)-H(1)	0.9800

C(2)-O(3)	1.457(3)
C(2)-C(3)	1.526(4)
C(2)-H(2)	0.9800
C(3)-C(4)	1.528(4)
C(3)-C(9)	1.534(4)
C(3)-H(3)	0.9800
C(4)-O(6)	1.453(3)
C(4)-C(5)	1.524(4)
C(4)-H(4)	0.9800
C(5)-N(1)	1.471(3)
C(5)-C(6)	1.525(4)
C(5)-H(5)	0.9800
C(6)-O(9)	1.455(3)
C(6)-C(7)	1.534(4)
C(6)-H(6)	0.9800
C(7)-C(8)	1.529(4)
C(7)-C(9)	1.535(4)
C(7)-H(7)	0.9800
C(8)-O(12)	1.450(3)
C(8)-H(8)	0.9800
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
N(1)-N(2)	1.375(3)
N(2)-O(1)	1.220(3)
N(2)-O(2)	1.221(3)
N(3)-O(5)	1.194(3)
N(3)-O(4)	1.194(3)
N(3)-O(3)	1.416(3)
N(4)-O(8)	1.185(3)
N(4)-O(7)	1.199(3)
N(4)-O(6)	1.402(3)
N(5)-O(10)	1.193(4)
N(5)-O(11)	1.198(4)
N(5)-O(9)	1.413(3)
N(6)-O(13)	1.194(3)
N(6)-O(14)	1.197(3)
N(6)-O(12)	1.409(3)

N(1)-C(1)-C(2)	107.7(2)
N(1)-C(1)-C(8)	107.0(2)
C(2)-C(1)-C(8)	109.7(2)
N(1)-C(1)-H(1)	110.8
C(2)-C(1)-H(1)	110.8
C(8)-C(1)-H(1)	110.8
O(3)-C(2)-C(1)	105.4(2)
O(3)-C(2)-C(3)	112.4(2)
C(1)-C(2)-C(3)	110.9(2)
O(3)-C(2)-H(2)	109.3
C(1)-C(2)-H(2)	109.3
C(3)-C(2)-H(2)	109.3
C(2)-C(3)-C(4)	108.0(2)
C(2)-C(3)-C(9)	107.6(2)
C(4)-C(3)-C(9)	110.6(2)
C(2)-C(3)-H(3)	110.2
C(4)-C(3)-H(3)	110.2
C(9)-C(3)-H(3)	110.2
O(6)-C(4)-C(5)	103.58(19)
O(6)-C(4)-C(3)	112.0(2)
C(5)-C(4)-C(3)	110.3(2)
O(6)-C(4)-H(4)	110.2
C(5)-C(4)-H(4)	110.2
C(3)-C(4)-H(4)	110.2
N(1)-C(5)-C(4)	104.7(2)
N(1)-C(5)-C(6)	109.9(2)
C(4)-C(5)-C(6)	110.3(2)
N(1)-C(5)-H(5)	110.6
C(4)-C(5)-H(5)	110.6
C(6)-C(5)-H(5)	110.6
O(9)-C(6)-C(5)	110.9(2)
O(9)-C(6)-C(7)	105.2(2)
C(5)-C(6)-C(7)	110.1(2)
O(9)-C(6)-H(6)	110.2
C(5)-C(6)-H(6)	110.2
C(7)-C(6)-H(6)	110.2
C(8)-C(7)-C(6)	108.2(2)
C(8)-C(7)-C(9)	111.1(2)

C(6)-C(7)-C(9)	107.5(2)
C(8)-C(7)-H(7)	110.0
C(6)-C(7)-H(7)	110.0
C(9)-C(7)-H(7)	110.0
O(12)-C(8)-C(7)	105.1(2)
O(12)-C(8)-C(1)	110.7(2)
C(7)-C(8)-C(1)	109.9(2)
O(12)-C(8)-H(8)	110.3
C(7)-C(8)-H(8)	110.3
C(1)-C(8)-H(8)	110.3
C(3)-C(9)-C(7)	110.4(2)
C(3)-C(9)-H(9A)	109.6
C(7)-C(9)-H(9A)	109.6
C(3)-C(9)-H(9B)	109.6
C(7)-C(9)-H(9B)	109.6
H(9A)-C(9)-H(9B)	108.1
N(2)-N(1)-C(5)	117.2(2)
N(2)-N(1)-C(1)	117.6(2)
C(5)-N(1)-C(1)	115.88(19)
O(1)-N(2)-O(2)	125.0(3)
O(1)-N(2)-N(1)	117.6(3)
O(2)-N(2)-N(1)	117.3(3)
O(5)-N(3)-O(4)	130.3(3)
O(5)-N(3)-O(3)	111.6(2)
O(4)-N(3)-O(3)	118.1(2)
O(8)-N(4)-O(7)	129.2(3)
O(8)-N(4)-O(6)	112.9(2)
O(7)-N(4)-O(6)	117.8(2)
O(10)-N(5)-O(11)	130.3(3)
O(10)-N(5)-O(9)	111.5(3)
O(11)-N(5)-O(9)	118.2(3)
O(13)-N(6)-O(14)	129.4(3)
O(13)-N(6)-O(12)	118.5(3)
O(14)-N(6)-O(12)	112.0(3)
N(3)-O(3)-C(2)	114.5(2)
N(4)-O(6)-C(4)	114.5(2)
N(5)-O(9)-C(6)	114.4(2)
N(6)-O(12)-C(8)	114.1(2)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^*2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	29(1)	30(1)	29(1)	-4(1)	3(1)	2(1)
C(2)	28(1)	28(1)	31(1)	-1(1)	-4(1)	0(1)
C(3)	29(1)	28(1)	31(1)	1(1)	1(1)	-2(1)
C(4)	30(1)	30(1)	31(1)	-3(1)	2(1)	2(1)
C(5)	32(2)	28(1)	34(1)	2(1)	0(1)	1(1)
C(6)	32(2)	29(1)	35(2)	-3(1)	4(1)	-3(1)
C(7)	29(1)	33(1)	32(1)	-2(1)	-4(1)	-2(1)
C(8)	29(2)	29(1)	36(2)	1(1)	1(1)	1(1)
C(9)	39(2)	33(1)	28(1)	1(1)	1(1)	4(1)
N(1)	38(1)	32(1)	26(1)	5(1)	4(1)	-2(1)
N(2)	52(2)	44(2)	32(1)	2(1)	5(1)	-12(1)
N(3)	33(1)	35(1)	56(2)	-16(1)	1(1)	-4(1)
N(4)	26(1)	38(1)	52(2)	-3(1)	2(1)	1(1)
N(5)	73(2)	34(1)	61(2)	-6(1)	19(2)	-14(2)
N(6)	34(1)	46(2)	57(2)	-13(1)	-4(1)	6(1)
O(1)	86(2)	40(1)	58(1)	19(1)	9(1)	-4(1)
O(2)	77(2)	61(2)	46(1)	0(1)	28(1)	-14(1)
O(3)	40(1)	32(1)	38(1)	-1(1)	-10(1)	-6(1)
O(4)	67(2)	42(1)	70(2)	14(1)	-10(1)	-17(1)
O(5)	49(1)	56(1)	67(2)	-24(1)	-12(1)	-9(1)
O(6)	25(1)	37(1)	45(1)	-10(1)	3(1)	-3(1)
O(7)	36(1)	50(1)	61(1)	-9(1)	0(1)	-14(1)
O(8)	44(1)	67(2)	96(2)	-38(2)	24(1)	1(1)
O(9)	39(1)	32(1)	54(1)	-4(1)	11(1)	-9(1)
O(10)	104(2)	55(2)	138(3)	5(2)	57(2)	-32(2)
O(11)	74(2)	36(1)	83(2)	-4(1)	21(2)	3(1)
O(12)	29(1)	36(1)	50(1)	1(1)	0(1)	6(1)
O(13)	57(2)	67(2)	55(2)	-9(1)	13(1)	12(1)
O(14)	55(1)	63(2)	86(2)	-4(1)	-10(1)	30(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**.

	x	y	z	U(eq)
H(1)	7965	4632	5133	35

H(2)	6770	3545	6242	35
H(3)	4732	4399	7026	35
H(4)	4098	5849	6006	36
H(5)	5695	7507	5884	37
H(6)	6867	7407	7261	38
H(7)	8848	6023	7492	38
H(8)	9553	5789	6035	38
H(9A)	7209	4404	7647	40
H(9B)	6331	5522	7929	40

Table S6. Torsion angles [°] for **10**.

N(1)-C(1)-C(2)-O(3)	66.8(2)
C(8)-C(1)-C(2)-O(3)	-177.0(2)
N(1)-C(1)-C(2)-C(3)	-55.1(3)
C(8)-C(1)-C(2)-C(3)	61.1(3)
O(3)-C(2)-C(3)-C(4)	-59.9(3)
C(1)-C(2)-C(3)-C(4)	57.8(3)
O(3)-C(2)-C(3)-C(9)	-179.3(2)
C(1)-C(2)-C(3)-C(9)	-61.6(3)
C(2)-C(3)-C(4)-O(6)	-176.5(2)
C(9)-C(3)-C(4)-O(6)	-59.0(3)
C(2)-C(3)-C(4)-C(5)	-61.7(3)
C(9)-C(3)-C(4)-C(5)	55.8(3)
O(6)-C(4)-C(5)-N(1)	-178.62(19)
C(3)-C(4)-C(5)-N(1)	61.3(2)
O(6)-C(4)-C(5)-C(6)	63.2(3)
C(3)-C(4)-C(5)-C(6)	-56.9(3)
N(1)-C(5)-C(6)-O(9)	61.7(3)
C(4)-C(5)-C(6)-O(9)	176.6(2)
N(1)-C(5)-C(6)-C(7)	-54.4(3)
C(4)-C(5)-C(6)-C(7)	60.6(3)
O(9)-C(6)-C(7)-C(8)	-61.0(3)
C(5)-C(6)-C(7)-C(8)	58.6(3)
O(9)-C(6)-C(7)-C(9)	178.9(2)
C(5)-C(6)-C(7)-C(9)	-61.5(3)
C(6)-C(7)-C(8)-O(12)	178.73(19)
C(9)-C(7)-C(8)-O(12)	-63.5(3)
C(6)-C(7)-C(8)-C(1)	-62.0(3)

C(9)-C(7)-C(8)-C(1)	55.7(3)
N(1)-C(1)-C(8)-O(12)	175.5(2)
C(2)-C(1)-C(8)-O(12)	58.9(3)
N(1)-C(1)-C(8)-C(7)	59.7(3)
C(2)-C(1)-C(8)-C(7)	-56.9(3)
C(2)-C(3)-C(9)-C(7)	59.2(3)
C(4)-C(3)-C(9)-C(7)	-58.5(3)
C(8)-C(7)-C(9)-C(3)	-57.8(3)
C(6)-C(7)-C(9)-C(3)	60.4(3)
C(4)-C(5)-N(1)-N(2)	151.8(2)
C(6)-C(5)-N(1)-N(2)	-89.8(3)
C(4)-C(5)-N(1)-C(1)	-62.3(3)
C(6)-C(5)-N(1)-C(1)	56.1(3)
C(2)-C(1)-N(1)-N(2)	-154.2(2)
C(8)-C(1)-N(1)-N(2)	87.8(3)
C(2)-C(1)-N(1)-C(5)	60.0(3)
C(8)-C(1)-N(1)-C(5)	-58.0(3)
C(5)-N(1)-N(2)-O(1)	-22.0(4)
C(1)-N(1)-N(2)-O(1)	-167.3(3)
C(5)-N(1)-N(2)-O(2)	161.1(2)
C(1)-N(1)-N(2)-O(2)	15.7(4)
O(5)-N(3)-O(3)-C(2)	-175.4(2)
O(4)-N(3)-O(3)-C(2)	4.6(3)
C(1)-C(2)-O(3)-N(3)	150.5(2)
C(3)-C(2)-O(3)-N(3)	-88.6(2)
O(8)-N(4)-O(6)-C(4)	-173.7(2)
O(7)-N(4)-O(6)-C(4)	6.4(3)
C(5)-C(4)-O(6)-N(4)	152.8(2)
C(3)-C(4)-O(6)-N(4)	-88.3(3)
O(10)-N(5)-O(9)-C(6)	175.6(3)
O(11)-N(5)-O(9)-C(6)	-4.2(4)
C(5)-C(6)-O(9)-N(5)	81.0(3)
C(7)-C(6)-O(9)-N(5)	-159.9(2)
O(13)-N(6)-O(12)-C(8)	-9.2(3)
O(14)-N(6)-O(12)-C(8)	171.0(2)
C(7)-C(8)-O(12)-N(6)	-153.4(2)
C(1)-C(8)-O(12)-N(6)	87.9(2)

Symmetry transformations used to generate equivalent atoms:

5 X-ray Crystal Structures and Data of Compound 1

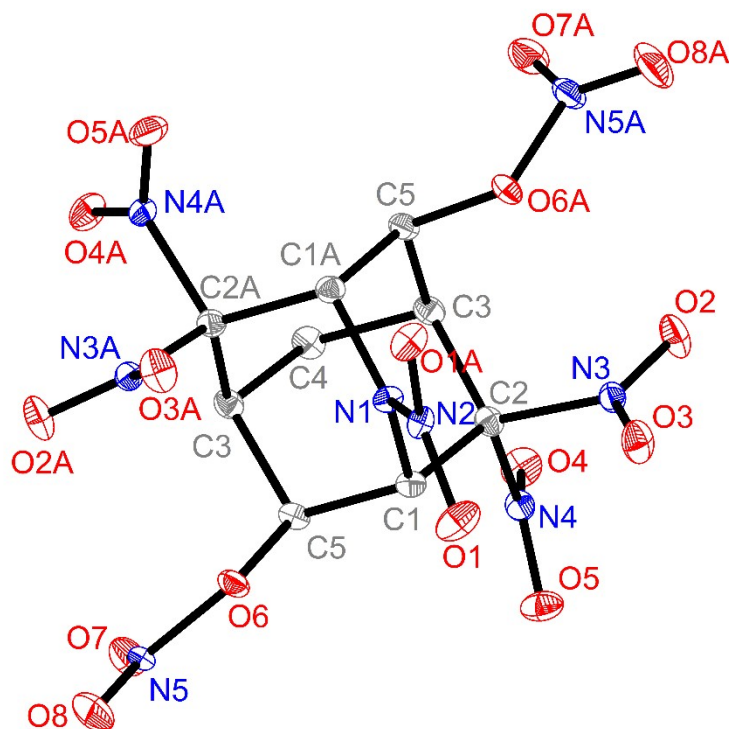


Figure S2. ORTEP diagram of **1** Color code: Carbon (grey), Oxygen (red), Nitrogen (blue).

Single crystals of **1** were obtained by slow recrystallization from a mixture of ethanol and chloroform. The result of X-ray diffraction indicates that compound **1** crystallizes in the monoclinic space group $C2/c$. The crystal density was determined to be 1.878 g cm^{-3} .

Table S7. Crystal data and structure refinement for **1**.

Identification code	1	
Empirical formula	C ₉ H ₈ N ₈ O ₁₆	
Formula weight	484.23	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>C</i> 2/ <i>c</i>	
Unit cell dimensions	a = 10.1396(16) Å	α = 90°.
	b = 11.8452(18) Å	β = 99.443(2)°.
	c = 14.454(2) Å	γ = 90°.
Volume	1712.5(5) Å ³	
Z	4	
Density (calculated)	1.878 mg/m ³	
Absorption coefficient	0.183 mm ⁻¹	
F(000)	984	
Crystal size	0.140 x 0.140 x 0.140 mm ³	
Theta range for data collection	2.665 to 27.226°.	
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -18 ≤ l ≤ 17	
Reflections collected	6550	
Independent reflections	1773 [R(int) = 0.0193]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.975 and 0.975	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1773 / 0 / 151	
Goodness-of-fit on F ²	1.045	
Final R indices [I > 2σ(I)]	R1 = 0.0392, wR2 = 0.1114	
R indices (all data)	R1 = 0.0472, wR2 = 0.1173	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.285 and -0.283 e.Å ⁻³	

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	5007(2)	3094(1)	6637(1)	26(1)
C(2)	6272(2)	3826(1)	6798(1)	26(1)
C(3)	6278(2)	4590(1)	7646(1)	27(1)
C(4)	5000	5327(2)	7500	31(1)
C(5)	3781(2)	3871(1)	6474(1)	28(1)
N(1)	5000	2464(2)	7500	28(1)
N(2)	5000	1294(2)	7500	40(1)
N(3)	7542(1)	3096(1)	6873(1)	34(1)
N(4)	6379(1)	4511(1)	5911(1)	35(1)
N(5)	1481(2)	3644(2)	5739(1)	48(1)
O(1)	4870(2)	835(1)	6733(1)	60(1)
O(2)	8583(1)	3585(1)	7110(1)	59(1)
O(3)	7410(2)	2109(1)	6678(1)	55(1)
O(4)	6765(2)	5473(1)	5998(1)	53(1)
O(5)	6071(2)	4011(1)	5173(1)	54(1)
O(6)	2676(1)	3108(1)	6243(1)	38(1)
O(7)	1544(2)	4631(2)	5570(1)	66(1)
O(8)	591(2)	2996(2)	5565(1)	81(1)

Table S9. Bond lengths [\AA] and angles [$^\circ$] for **1**.

C(1)-N(1)	1.4544(17)
C(1)-C(5)	1.533(2)
C(1)-C(2)	1.534(2)
C(1)-H(1)	0.9800
C(2)-C(3)	1.523(2)
C(2)-N(4)	1.536(2)
C(2)-N(3)	1.541(2)
C(3)-C(5)#1	1.540(2)
C(3)-C(4)	1.547(2)
C(3)-H(3)	0.9800
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-O(6)	1.4350(19)
C(5)-H(5)	0.9800
N(1)-N(2)	1.387(3)

N(2)-O(1)#1	1.2216(17)
N(2)-O(1)	1.2217(17)
N(3)-O(2)	1.204(2)
N(3)-O(3)	1.204(2)
N(4)-O(4)	1.205(2)
N(4)-O(5)	1.215(2)
N(5)-O(8)	1.180(2)
N(5)-O(7)	1.198(3)
N(5)-O(6)	1.454(2)
N(1)-C(1)-C(5)	108.75(12)
N(1)-C(1)-C(2)	106.36(11)
C(5)-C(1)-C(2)	108.72(13)
N(1)-C(1)-H(1)	111.0
C(5)-C(1)-H(1)	111.0
C(2)-C(1)-H(1)	111.0
C(3)-C(2)-C(1)	110.52(13)
C(3)-C(2)-N(4)	111.54(13)
C(1)-C(2)-N(4)	110.13(12)
C(3)-C(2)-N(3)	112.61(12)
C(1)-C(2)-N(3)	111.18(13)
N(4)-C(2)-N(3)	100.49(12)
C(2)-C(3)-C(5)#1	109.91(13)
C(2)-C(3)-C(4)	109.42(11)
C(5)#1-C(3)-C(4)	106.27(12)
C(2)-C(3)-H(3)	110.4
C(5)#1-C(3)-H(3)	110.4
C(4)-C(3)-H(3)	110.4
C(3)#1-C(4)-C(3)	111.34(18)
C(3)#1-C(4)-H(4A)	109.4
C(3)-C(4)-H(4A)	109.4
C(3)#1-C(4)-H(4B)	109.4
C(3)-C(4)-H(4B)	109.4
H(4A)-C(4)-H(4B)	108.0
O(6)-C(5)-C(1)	103.91(12)
O(6)-C(5)-C(3)#1	113.97(13)
C(1)-C(5)-C(3)#1	110.18(12)
O(6)-C(5)-H(5)	109.5

C(1)-C(5)-H(5)	109.5
C(3)#1-C(5)-H(5)	109.5
N(2)-N(1)-C(1)	120.86(8)
N(2)-N(1)-C(1)#1	120.86(8)
C(1)-N(1)-C(1)#1	118.28(17)
O(1)#1-N(2)-O(1)	127.2(2)
O(1)#1-N(2)-N(1)	116.42(11)
O(1)-N(2)-N(1)	116.41(11)
O(2)-N(3)-O(3)	126.29(16)
O(2)-N(3)-C(2)	115.69(15)
O(3)-N(3)-C(2)	118.00(14)
O(4)-N(4)-O(5)	125.81(16)
O(4)-N(4)-C(2)	118.59(15)
O(5)-N(4)-C(2)	115.60(14)
O(8)-N(5)-O(7)	131.0(2)
O(8)-N(5)-O(6)	111.6(2)
O(7)-N(5)-O(6)	117.44(16)
C(5)-O(6)-N(5)	113.34(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

Table S10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	28(1)	26(1)	23(1)	-1(1)	2(1)	-2(1)
C(2)	26(1)	25(1)	27(1)	5(1)	2(1)	2(1)
C(3)	26(1)	24(1)	30(1)	-1(1)	0(1)	-3(1)
C(4)	33(1)	22(1)	37(1)	0	2(1)	0
C(5)	26(1)	30(1)	25(1)	0(1)	-2(1)	-1(1)
N(1)	38(1)	19(1)	26(1)	0	5(1)	0
N(2)	49(1)	23(1)	52(1)	0	20(1)	0
N(3)	29(1)	38(1)	35(1)	4(1)	6(1)	5(1)
N(4)	33(1)	39(1)	34(1)	10(1)	7(1)	-1(1)
N(5)	31(1)	72(1)	38(1)	-10(1)	-5(1)	1(1)
O(1)	94(1)	31(1)	60(1)	-17(1)	29(1)	-12(1)
O(2)	26(1)	61(1)	86(1)	-2(1)	4(1)	-2(1)
O(3)	46(1)	36(1)	82(1)	-6(1)	11(1)	11(1)
O(4)	68(1)	37(1)	55(1)	12(1)	18(1)	-9(1)

O(5)	70(1)	61(1)	30(1)	5(1)	7(1)	-13(1)
O(6)	28(1)	42(1)	38(1)	-7(1)	-6(1)	-6(1)
O(7)	48(1)	82(1)	62(1)	8(1)	-4(1)	16(1)
O(8)	40(1)	109(2)	86(1)	-25(1)	-12(1)	-17(1)

Table S11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **1**.

	x	y	z	U(eq)
H(1)	5011	2583	6105	31
H(3)	7077	5068	7740	33
H(4A)	5001	5808	8043	37
H(4B)	4999	5808	6957	37
H(5)	3832	4367	5939	33

Table S12. Torsion angles [$^\circ$] for **1**.

N(1)-C(1)-C(2)-C(3)	-57.36(15)
C(5)-C(1)-C(2)-C(3)	59.59(15)
N(1)-C(1)-C(2)-N(4)	178.94(12)
C(5)-C(1)-C(2)-N(4)	-64.10(16)
N(1)-C(1)-C(2)-N(3)	68.45(15)
C(5)-C(1)-C(2)-N(3)	-174.59(12)
C(1)-C(2)-C(3)-C(5)#1	59.15(15)
N(4)-C(2)-C(3)-C(5)#1	-177.98(12)
N(3)-C(2)-C(3)-C(5)#1	-65.86(16)
C(1)-C(2)-C(3)-C(4)	-57.18(16)
N(4)-C(2)-C(3)-C(4)	65.69(16)
N(3)-C(2)-C(3)-C(4)	177.81(12)
C(2)-C(3)-C(4)-C(3)#1	58.54(10)
C(5)#1-C(3)-C(4)-C(3)#1	-60.08(9)
N(1)-C(1)-C(5)-O(6)	-70.01(14)
C(2)-C(1)-C(5)-O(6)	174.58(12)
N(1)-C(1)-C(5)-C(3)#1	52.46(16)
C(2)-C(1)-C(5)-C(3)#1	-62.94(16)
C(5)-C(1)-N(1)-N(2)	122.34(9)
C(2)-C(1)-N(1)-N(2)	-120.74(9)
C(5)-C(1)-N(1)-C(1)#1	-57.66(9)
C(2)-C(1)-N(1)-C(1)#1	59.27(9)
C(1)-N(1)-N(2)-O(1)#1	172.88(12)

C(1)#1-N(1)-N(2)-O(1)#1	-7.12(12)
C(1)-N(1)-N(2)-O(1)	-7.12(12)
C(1)#1-N(1)-N(2)-O(1)	172.88(12)
C(3)-C(2)-N(3)-O(2)	-46.8(2)
C(1)-C(2)-N(3)-O(2)	-171.47(15)
N(4)-C(2)-N(3)-O(2)	71.98(18)
C(3)-C(2)-N(3)-O(3)	134.30(16)
C(1)-C(2)-N(3)-O(3)	9.7(2)
N(4)-C(2)-N(3)-O(3)	-106.90(16)
C(3)-C(2)-N(4)-O(4)	17.3(2)
C(1)-C(2)-N(4)-O(4)	140.35(16)
N(3)-C(2)-N(4)-O(4)	-102.31(17)
C(3)-C(2)-N(4)-O(5)	-163.38(14)
C(1)-C(2)-N(4)-O(5)	-40.29(19)
N(3)-C(2)-N(4)-O(5)	77.05(17)
C(1)-C(5)-O(6)-N(5)	-159.04(13)
C(3)#1-C(5)-O(6)-N(5)	81.02(16)
O(8)-N(5)-O(6)-C(5)	-179.63(17)
O(7)-N(5)-O(6)-C(5)	0.5(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

6 Computational Method

For the explosives with CHNO elements, these parameters can be calculated using the Kamlet-Jacobos (K-J) equations:

$$D = (1.011 + 1.312\rho_0) (N \bar{M}^{0.5} Q^{0.5})^{0.5} \quad (1)$$

$$P = 1.558\rho_0^2 N \bar{M}^{0.5} Q^{0.5} \quad (2)$$

here P is the detonation pressure (GPa), D is the detonation velocity (km/s), ρ_0 is the packed density ($\text{g}\cdot\text{cm}^{-3}$), N is the moles of gas produced by per gram of explosives, \bar{M} is an average molar weight of detonation products, and Q is the chemical energy of detonation ($\text{cal}\cdot\text{g}^{-1}$).

In the molecular design of HEDC, we suggested that Q can be calculated as the difference between the heats of formation (HOFs) of products and that of reactants. From the K-J equations, it is found that Q has much less effect than ρ_0 on D and P . In order to save the required time and resources, Q and HOF estimated using the semi-empirical MO PM3 method are precise enough to substitute the experimental data as has been proven in the previous studies⁸⁻¹⁰.

ρ_0 is crucial to the detonation properties. Based on the quantum chemistry, we recommend an

efficient and convenient way to predict the theoretical molecular density ρ_0 replaced by ρ_{cry} ^{11,12}. Studies have indicated that, when the average molar volume V estimated by Monte-Carlo method based on 0.001electrons/bohr³ density space at the B3LYP/6-31G** or 6-31G* level is used, the theoretical molecular density ρ_0 ($\rho_0 = M/V$, M is the molecular weight) is close to the experimental crystal density ρ_{cry} .

Calculated Results

Table S13. Physicochemical properties and detonation performances of **1** and **10**.

Compound	Formula	ρ^a (g·cm ⁻³)	ΔH_f^b (kJ·mol ⁻¹)	D^c (m·s ⁻¹)	Q^d (cal·g ⁻¹)	P^e (GPa)	N^f (mol·g ⁻¹)	\overline{M}^g (g·mol ⁻¹)
1	C ₉ H ₈ N ₈ O ₁₆	1.878	-49.11	8914	1618.66	36.16	0.029	32.00
10	C ₉ H ₁₀ N ₆ O ₁₄	1.776	-304.48	8317	1500.32	30.45	0.029	29.76

^a crystal density determined from single-crystal X-ray diffraction analysis. ^b Heat of formation. ^c Theoretical detonation velocity. ^d Heat of detonation. ^e Theoretical detonation pressure. ^f Moles of gas produced by per gram of explosives. ^g Average molar weight of detonation products.

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