

Supporting Information

Title: 2,4,4,6,8,8-Hexanitro-2,6-diazaadamantane: A high-energy density compound with high stability

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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 , $\text{DMSO}-d_6$, $\text{CD}_3\text{OD}-d_4$, $\text{C}_3\text{D}_6\text{O}$ 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. Elemental analysis of all new compounds was performed by using a Vario EL III CHN elemental analyzer. 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 comparison of their physical and spectral data with those reported in the literature. Yields refers to isolated yield of analytically pure material unless otherwise noted.

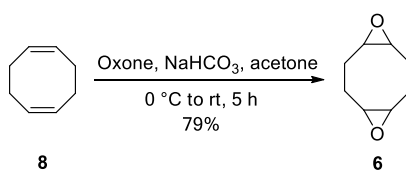
5,10-dioxatricyclo[7.1.0.0^{4,6}]decane (**6**)^[1], 1,2,5,6-Tetrabromocyclooctane (**7**)^[2],

9-azabicyclo[3.3.1]nona-3,7-diene (**14**)^[2] was synthesized according to reported procedures.

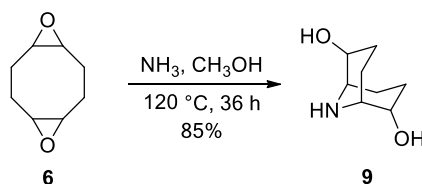
1. B. Vidmantas, R. Dovile, O. Edvinas, S. Sigita, *J. Org. Chem.* **2013**, 78, 5339–5348.
2. G. Q. Li, S. F. Nelsen, A. S. Jalilov, I. A. Guzei, *J. Org. Chem.* **2010**, 75, 2445–2452.

2. Experimental Procedures and Spectroscopic Data of Compounds

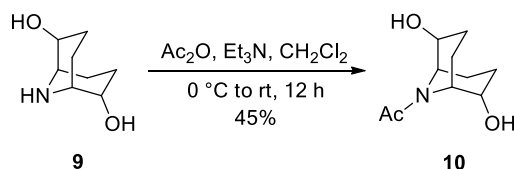
5,10-Dioxatricyclo[7.1.0.0^{4,6}]decane (**6**):



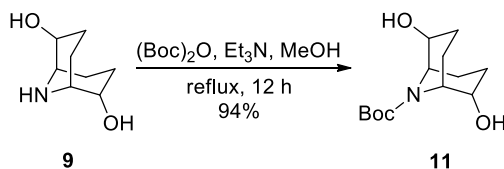
To a 2.0 L three-necked flask equipped with mechanical stirrer, dropping funnel and thermometer were added NaHCO_3 (84 g, 1.00 mol), water (400 mL), acetone (120 mL), dichloromethane (400 mL) and cycloocta-1,5-diene (**8**) (10.8 g, 0.10 mol). A solution of Oxone (154 g, 0.25 mol) in water (500 mL) was added dropwise over 2 h to the vigorously stirred reaction mixture at the rate to keep mixture temperature below 30 °C. After addition, the mixture was stirred for an additional 5 h, and then the organic layer was separated, washed with brine, and dried (Na_2SO_4). The solvent was evaporated to afford **6** (11.06 g, 79%) as colorless oil, which solidified on standing; the product was TLC and NMR pure and was used for the next step without further purification: ^1H NMR (500 MHz, CDCl_3): δ 3.03-3.00 (m, 4H), 2.06-2.01 (m, 4H), 1.94-1.90 (m, 4H) ppm; ^{13}C NMR (126 MHz, CDCl_3): δ 56.3, 22.3 ppm.

9-Azabicyclo[3.3.1]nonane-2,6-diol (9):

To a solution of **6** (5.0 g, 35.69 mmol) in 5 mL of CH₃OH was added 20 mL of ammonia-saturated CH₃OH. The mixture was heated to 120 °C for 36 h in a steel bomb. After cooling, the mixture was concentrated in vacuum. The product was purified by flash chromatography (2:1 ethyl acetate/methanol) to afford diol **9** (4.77 g, 85%) as a white solid. ¹H NMR (500 MHz, CD₃OD): δ 3.90-3.88 (m, 2H), 2.84-2.82 (m, 2H), 2.13-2.11 (m, 2H), 1.88-1.85 (m, 2H), 1.74-1.69 (m, 4H) ppm; ¹³C NMR (126 MHz, CD₃OD): δ 71.1, 51.6, 30.5, 23.8 ppm; IR (thin film, ν cm⁻¹): 3249, 2915, 1485, 1326, 1048, 1000, 889; C₈H₁₅NO₂ (157.11): C 61.12, H 9.62, N 8.91; found: C 61.15, H 9.64, N 8.86; ESI-MS: m/z [(M+H)⁺]: 158.11.

9-Acetyl-9-azabicyclo[3.3.1]nonane-2,6-diol (10):

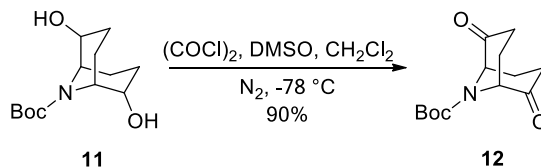
To a mixture of diol **9** (1.47 g, 9.32 mmol), trimethylamine (1.9 mL, 13.98 mmol) and CH₂Cl₂ (20 mL) was added dropwise acetic anhydride (1.94 mL, 20.50 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature. The mixture was concentrated in vacuum. The product was scrubbed with dichloromethane to afford acetamide **10** (0.83 g, 45%) as a white solid. ¹H NMR (500 MHz, CD₃OD): δ 4.54 (t, *J* = 5.35 Hz, 1H), 3.85-3.83 (m, 2H), 3.75-3.70 (m, 1H), 2.23-2.10 (m, 5H), 1.91-1.71 (m, 5H), 1.64-1.60 (m, 1H) ppm; ¹³C NMR (126 MHz, CD₃OD): δ 169.8, 69.3, 68.4, 53.8, 28.9, 28.8, 21.9, 21.0, 19.8 ppm; IR (thin film, ν cm⁻¹): 3327, 2902, 1600, 1449, 1080, 1040; C₁₀H₁₇NO₃ (199.12): C 60.28, H 8.60, N 7.03; found: C 60.32, H 8.62, N 7.00.

9-(tert-Butoxycarbonyl)-9-azabicyclo[3.3.1]nonane-2,6-diol (11):

A mixture of diol **9** (10.14 g, 64.54 mmol), trimethylamine (89.5 mL, 645.40 mol) and CH₃OH (300 mL) was added di-*tert*-butyl dicarbonate (29.7 mL, 129.14 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 (2:1 ethyl acetate/petroleum) to afford diol **11** (15.60 g, 94%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 4.11-4.09 (m, 1H), 4.01-3.99 (m, 1H), 3.89-3.82 (m, 2H), 3.54-3.06 (br, 1H), 2.58-2.24 (br, 1H), 2.16-2.08 (m, 2H), 1.90-1.85 (m, 2H), 1.76-1.64 (m, 4H), 1.42 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 154.7, 80.3, 69.7, 68.9, 50.8, 49.6, 29.9, 29.2, 28.7, 22.0, 21.5 ppm; IR (thin film, ν

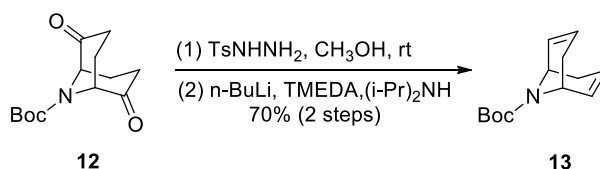
cm⁻¹): 3306, 2943, 1654, 1420, 1163, 1050, 905; C₁₃H₂₃NO₄ (257.16): C 60.68, H 9.01, N 5.44; found: C 60.71, H 9.04, N 5.39.

9-(*tert*-Butoxycarbonyl)-9-azabicyclo[3.3.1]nonane-2,6-dione (12**):**

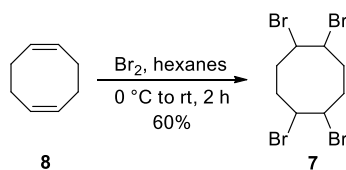


DMSO (18.5 mL, 0.26 mol) was added over about 30 min to a solution of oxalyl chloride (11.2 mL, 0.13 mmol) in CH₂Cl₂ (300 mL) at -78 °C under N₂. The mixture was stirred for 30 min at -78 °C before a solution of **11** (14.1 g, 54.83 mmol) in a mixture of CH₂Cl₂ (100 mL) was added. After stirring at this temperature for 2 h, trimethylamine (109.5 mL, 0.79 mol) was added to the resultant cloudy solution and the mixture stirred for another 1 h at that temperature. The milky white solution was warmed to room temperature and quenched by the addition of water (200 mL). The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (300 mL×3). The combined organic layers were washed sequentially with saturated aqueous NaHCO₃ (150 mL) and brine (150 mL), dried with Na₂SO₄, and filtered. The solvent was removed in vacuum and the residue was purified by flash silica gel column chromatography (1:5 ethyl acetate/petroleum) to afford the dione **12** (12.53 g, 90%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 4.83–4.68 (m, 2H), 2.60–2.57 (m, 2H), 2.43–2.37 (m, 4H), 2.11–2.07 (m, 2H), 1.47 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ: 207.3, 153.2, 82.0, 58.7, 44.7, 40.0, 39.5, 28.5 ppm; IR (thin film, ν cm⁻¹): 2979, 1683, 1394, 1305, 1168, 1104; C₁₃H₁₉NO₄ (253.13): C 61.64, H 7.56, N 5.53; found: C 61.69, H 7.58, N 5.49.

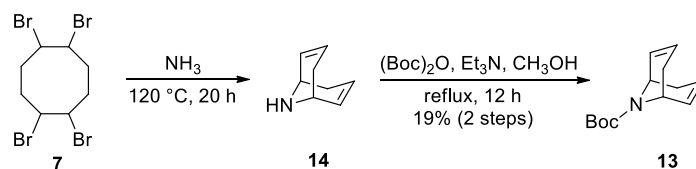
9-(*tert*-Butoxycarbonyl)-9-azabicyclo[3.3.1]nona-2,6-diene (13**):**



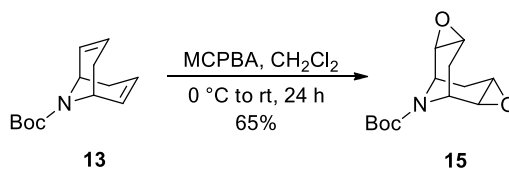
A mixture of dione **12** (11.0 g, 43.45 mmol), *p*-toluenesulfonyl hydrazidine (17.8 g, 95.60 mmol) and CH₃OH 100 mL was stirred at room temperature for 4 h. The reaction mixture was concentrated in vacuum, then washed with ethanol to afford dihydrazone 25.3 g as a white solid. A mixture of *i*-Pr₂NH (49.0 mL, 347.6 mmol) and TMEDA (229.5 mL, 1.52 mol) was chilled to 0 °C under N₂ and then *n*-BuLi (1.6M in hexane, 141.2 mL, 225.94 mmol) was added via cannula over 30 min followed by portion-wise addition of the prepared bis-tosylhydrazone (25.3 g, 42.94 mmol) over 30 min. The cooling bath was removed and the mixture stirred at 15 h, after which the mixture was chilled to 0 °C. Water was slowly added until all the lithium salts were dissolved. The solution was transferred to a pear-shaped funnel and the organic layer was separated. The solvent was removed in vacuum and the residue was purified by flash silica gel column chromatography (1:50 ethyl acetate/petroleum) to afford **13** (6.73 g, 70%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 5.71–5.65 (m, 4H), 4.70 (s, 1H), 4.56 (s, 1H), 2.46–2.38 (m, 2H), 1.83–1.80 (d, *J* = 16.55 Hz, 2H), 1.42 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 153.7, 129.4, 128.7, 124.3, 123.7, 79.4, 47.4, 45.8, 28.8, 28.5 ppm; IR (thin film, ν cm⁻¹): 2975, 2905, 1680, 1415, 1181, 1064, 806, 705; C₁₃H₁₉NO₂ (221.14): C 70.56, H 8.65, N 6.33; found: C 70.59, H 8.68, N 6.31; ESI-MS: *m/z* [(M+H)⁺]: 222.10.

1,2,5,6-Tetrabromocyclooctane (7):

Br₂ (37 mL, 0.73 mol) was added dropwise to cycloocta-1,5-diene **8** (40 mL, 0.33 mol) in hexanes (300 mL) in a 1 L flask with mechanical stirring at 0 °C under a nitrogen atmosphere. The solid product was filtered, washed with hexanes (100 mL×3), and dried to provide the desired product **7** (83.90 g, 60%): ¹H NMR (500 MHz, CDCl₃) δ: 4.78-4.77 (d, *J* = 3.8 Hz, 2H), 4.59-4.58 (d, *J* = 7.3 Hz, 2H), 2.84-2.82 (d, *J* = 13.35 Hz, 2H), 2.46-2.43 (m, 2H), 2.41-2.35 (m, 2H), 2.14-2.12 (d, *J* = 12.65 Hz, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ: 58.6, 31.8 ppm.

9-(tert-Butoxycarbonyl)-9-azabicyclo[3.3.1]nona-2,6-diene (13):

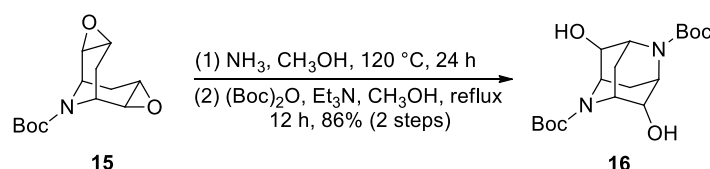
Excess NH₃ (liquid) (30 mL) was condensed using a dry ice bath with 1,2,5,6-tetrabromocyclooctane (35 g, 82.60 mmol) in a steel hydrogenation bomb with magnetic stirring, heated at 120 °C overnight, and the reactor was cooled again with dry ice and opened in a fume hood. NH₃ was evaporated as the temperature increased from -78 °C to room temperature under air. CH₂Cl₂ (200 mL) was added to extract the product. The CH₂Cl₂ extracts were combined and concentrated together with silica gel powder (30 g) and loaded on the top of a silica gel column packed with hexanes. The column was flashed with 20% ethyl acetate in hexanes (2 L) and followed by using 2% methanol and 2% ammonia-water in ethyl acetate (3 L) to elute the desired crude product **14** (2.5 g). A mixture of diene **14** (2.5 g), trimethylamine (28.6 mL, 206.45 mmol) and CH₃OH (100 mL) was added di-*tert*-butyl dicarbonate (9.5 mL, 41.30 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 (1:50 ethyl acetate/petroleum) to afford diene **13** (3.48 g, 19%) as a white solid.

9-(tert-Butoxycarbonyl)-9-aza-2,3;6,7-diepoxybicyclo[3.3.1]nonane (15):

To a suspension of (85%, 9.86 g, 48.58 mmol) of MCPBA in 60 mL of CH₂Cl₂ at 0 °C was added dropwise a solution of **13** (4.3 g, 19.43 mmol) in 30 mL of CH₂Cl₂. After being stirred at room temperature for 24 h, the solution was diluted with an additional 40 mL CH₂Cl₂, washed with 10% aqueous NaHSO₃ (40 mL), 5% NaHCO₃ (80 mL), H₂O (80 mL), and then dried over Na₂SO₄ and concentrated in vacuum. The product was purified by flash chromatography (1:3 ethyl acetate/petroleum) to afford the diepoxide **15** (3.20 g, 65%) as a

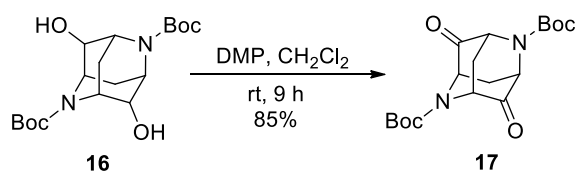
white solid. ^1H NMR (500 MHz, CDCl_3): δ 4.47-4.45 (d, J = 7.2 Hz, 1H), 4.33-4.31 (d, J = 7.15 Hz, 1H), 3.25 (s, 2H), 2.93-2.92 (d, J = 2.75 Hz, 2H), 2.35-2.29 (m, 2H), 1.86-1.82 (m, 2H), 1.44 (s, 9H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ : 155.0, 80.1, 25.7, 48.7, 48.5, 43.3, 41.8, 28.2, 24.0, 23.5 ppm; IR (thin film, ν cm^{-1}): 2974, 2919, 1689, 1399, 1320, 1101, 1054, 905, 803; $\text{C}_{13}\text{H}_{19}\text{NO}_4$ (253.13): C 61.64, H 7.56, N 5.53; found: C 61.67, H 7.59, N 5.50; ESI-MS: m/z [(M+H) $^+$]: 254.06.

2,6-Di(*tert*-butoxycarbonyl)-2,6-diazaadamantane-4,8-diol (16**):**



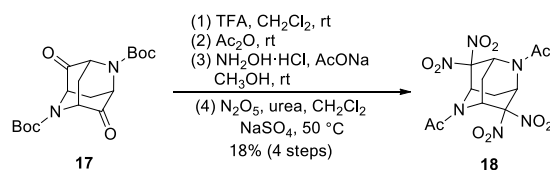
To a solution of (4.08 g, 16.12 mmol) of **15** in 5 mL of CH_3OH was added 20 mL of ammonia-saturated CH_3OH . The mixture was heated to 120 $^\circ\text{C}$ for 24 h in a steel bomb. After cooling, the mixture was concentrated in vacuum to afford the crude product 4.35 g. A mixture of crude product (4.35 g), trimethylamine (22.3 mL, 161.20 mol) and CH_3OH (80 mL) was added di-*tert*-butyl dicarbonate (7.4 mL, 32.24 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 (2:3 ethyl acetate/petroleum) to afford diol **16** (5.13 g, 86%) as a white solid. ^1H NMR (500 MHz, CDCl_3): δ 4.27-4.14 (m, 4H), 3.75-3.70 (d, J = 25.3 Hz, 2H), 3.03 (br, 2H), 2.33-2.30 (m, 2H), 1.57-1.55 (m, 2H), 1.44-1.43 (m, 18H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ : 157.0, 154.3, 80.5, 80.4, 67.9, 67.6, 67.2, 51.8, 51.7, 50.2, 48.9, 47.8, 47.6, 28.4, 26.8, 26.4, 26.0 ppm; IR (thin film, ν cm^{-1}): 3450, 2978, 2923, 1669, 1654, 1417, 1164, 1086, 1038; $\text{C}_{18}\text{H}_{30}\text{N}_2\text{O}_6$ (370.21): C 58.36, H 8.16, N 7.56; found: C 58.40, H 8.18, N 7.53; ESI-MS: m/z [(M+H) $^+$]: 371.14.

2,6-Di(*tert*-butoxycarbonyl)-2,6-diazaadamantane-4,8-dione (17**):**



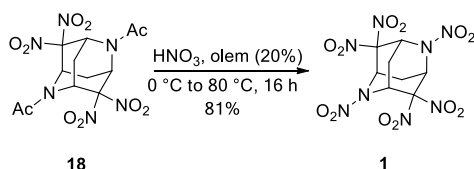
To a solution of the diol **16** (3.0 g, 8.10 mmol) in CH_2Cl_2 was added Dess-Martin eriodinane (20.62g, 48.62 mmol) at room temperature. After stirring for 9 h, the mixture was filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel column chromatography (1:2 ethyl acetate/petroleum) to afford **17** (2.52 g, 85%) as a white solid. ^1H NMR (500 MHz, CD_3OD): δ 4.09-4.08 (m, 4H), 2.12-2.10 (m, 4H), 1.50 (s, 18H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ : 202.0, 200.5, 154.9, 152.8, 82.5, 81.7, 58.2, 53.1, 40.0, 33.1, 28.5, 28.3, 28.2 ppm; IR (thin film, ν cm^{-1}): 2942, 1730, 1676, 1405, 1298, 1158, 1097, 989; $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_6$ (366.18): C 59.00, H 7.15, N 7.65; found: C 59.04, H 7.18, N 7.62; ESI-MS: m/z [(M+Na) $^+$]: 389.04.

2,6-Diacetyl-4,4,8,8-tetranitro-2,6-diazaadamantane (**18**):



To a solution of CH₂Cl₂ (10 mL) and TFA (10 mL) was added **17** (2.16 g, 5.90 mmol) at room temperature. After stirred for 2 h, the mixture was concentrated in vacuum. The crude product was dissolved in Ac₂O (20 mL) and stirred for 12 h, after evaporation of the volatiles in vacuum, the yellow foam thus obtained was dissolved in CH₃OH (30 mL) and treated with hydroxylamine hydrochloride (1.64 g, 23.60 mmol) as well as NaOAc (2.9 g, 35.40 mmol). The resulting mixture was stirred for 2 h. Brine (40 mL) was added and the mixture was extracted with EtOAc (40 mL×3). The combined organic phase was dried with Na₂SO₄. Removal of the solvent in vacuum. A mixture of the crude product (1.85 g), urea (2.15 g, 35.40 mmol), Na₂SO₄ (5 g) and CH₂Cl₂ (60 mL) was stirred and heated to 50 °C. A solution of N₂O₅ (3.83 g, 35.40 mmol) in CH₂Cl₂ (15 mL) was added dropwise within 5 min during which time a green color appeared initially and then faded as more N₂O₅ was added. The reaction mixture was stirred for an additional 30 min and then poured into an iced saturated solution of NaHCO₃ (100 mL). The organic layer was washed with brine (100 mL), dried with Na₂SO₄, and filtered. The solvent was removed in vacuum and the residue was purified by flash silica gel column chromatography (1:4 ethyl acetate/petroleum) to afford the product **18** (0.43 g, 18%) as a white solid. ¹H NMR (500 MHz, C₃D₆O): δ 6.22 (s, 2H), 5.72-5.71 (m, 2H), 2.65-2.59 (m, 2H), 2.40-2.39 (m, 6H), 2.27-2.25 (m, 2H) ppm; ¹³C NMR (126 MHz, DMSO) δ: 169.0, 111.7, 111.4, 111.1, 50.3, 50.2, 44.2, 44.1, 30.1, 29.1, 28.2, 21.4 ppm; IR (thin film, ν cm⁻¹): 3019, 1683, 1569, 1382, 1276, 983, 844; C₁₂H₁₄N₆O₁₀ (402.08): C 35.83, H 3.51, N 20.89; found: C 35.86, H 3.53, N 20.85; ESI-MS: m/z [(M+Cl)⁻]: 436.85.

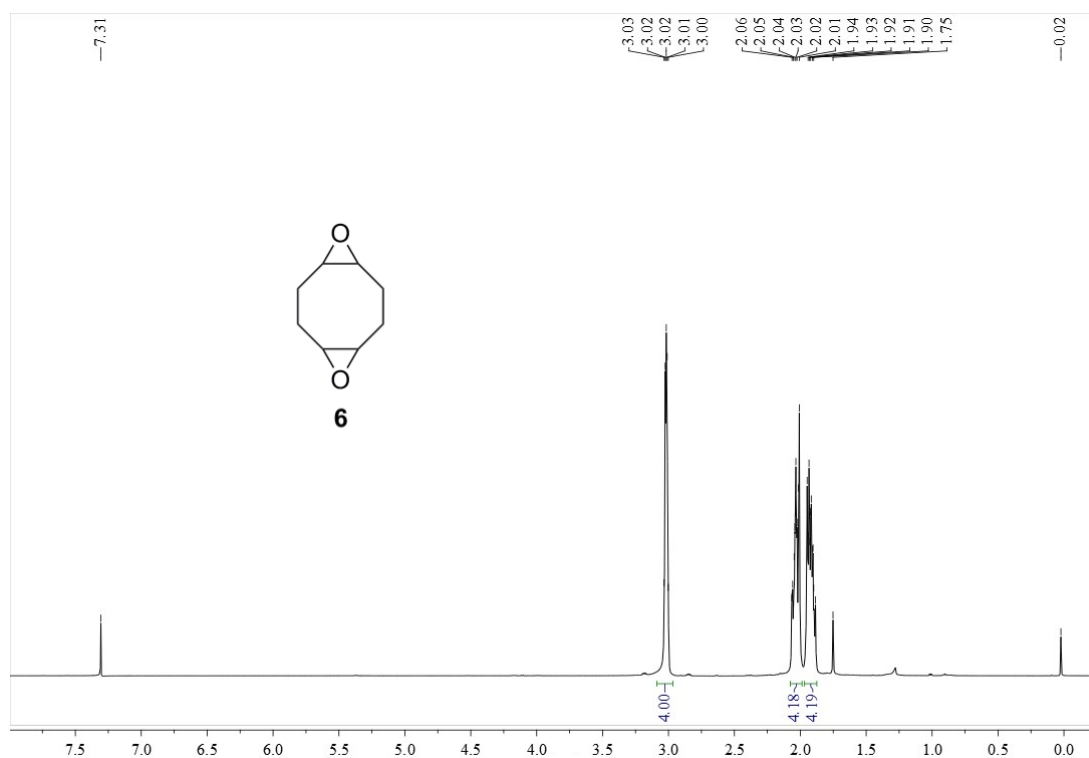
2,4,4,6,8,8-Hexanitro-2,6-diazaadamantane (**1**):



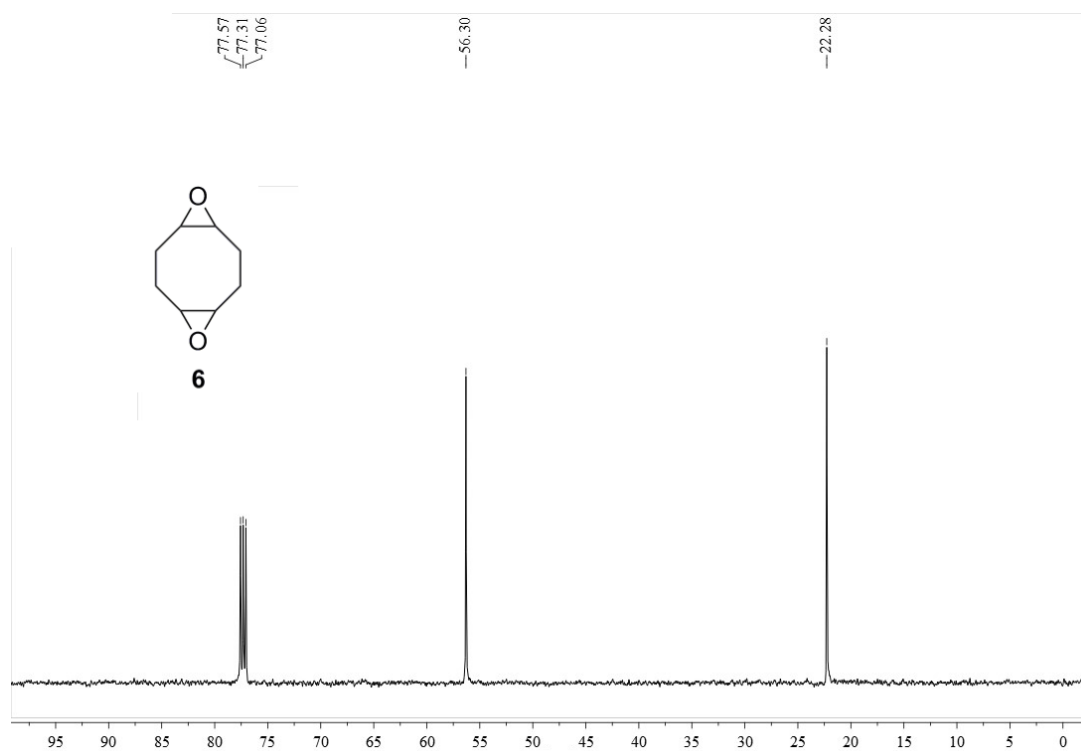
To a mixture of fuming nitric acid (4 mL) and 20% oleum (2 mL) at 0 °C was added diacetamide **18** (200 mg, 0.50 mmol). The reaction mixture was heated to 80 °C. After stirring for 16 h, the reaction mixture was cooled to ambient temperature and poured into ice-water (30 mL) with agitation. The white participate was filtered, washed with water and dried in vacuum. The product **1** (0.16 g, 81%) was afforded as a white solid. ¹H NMR (500 MHz, DMSO): δ 6.4 (s, 4H), 2.68 (s, 4H) ppm; ¹³C NMR (126 MHz, DMSO) δ: 109.3, 50.2, 27.2 ppm; IR (thin film, ν cm⁻¹): 2922, 1576, 1455, 1276, 979, 843, 783; C₈H₈N₈O₁₀ (408.03): C 23.54, H 1.98, N 27.45; found: C 23.58, H 2.01, N 27.42; ESI-MS: m/z [(M+Cl)⁻]: 442.88.

3. ^1H -NMR, ^{13}C -NMR, ^{19}F -NMR and FT-IR Spectra of Compounds

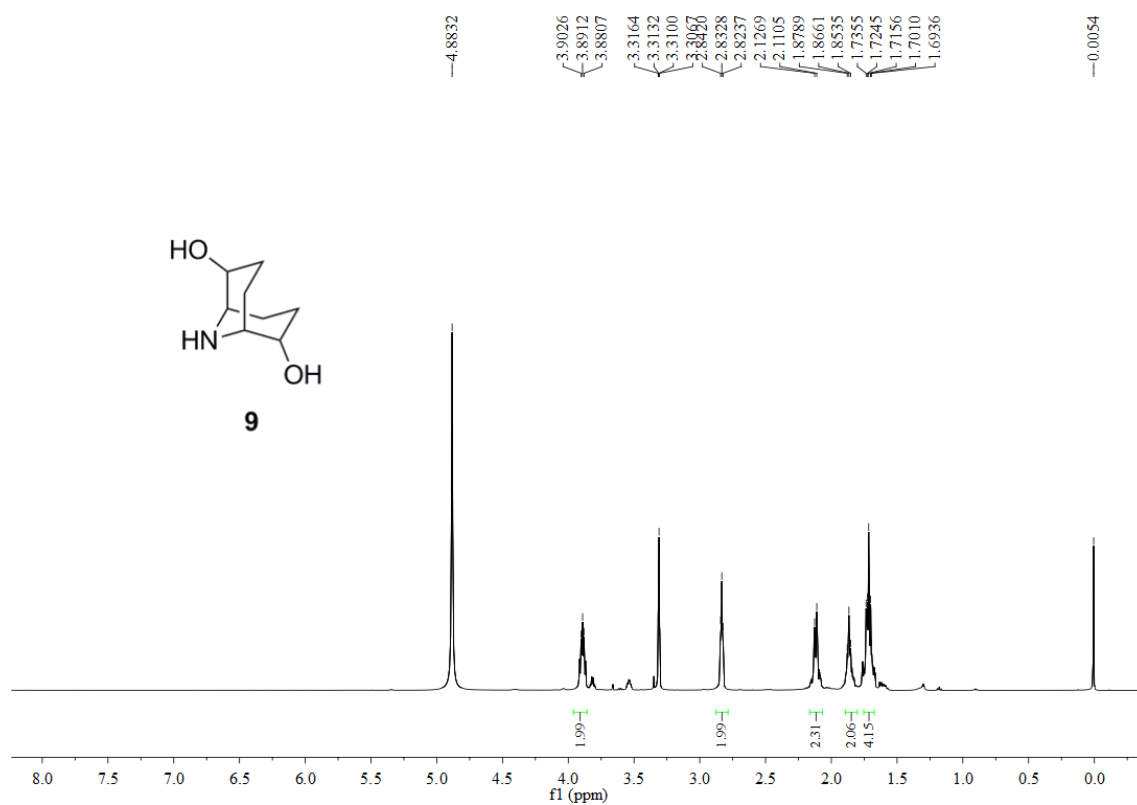
^1H NMR spectrum of compound 6 (CDCl_3 , 500 MHz)



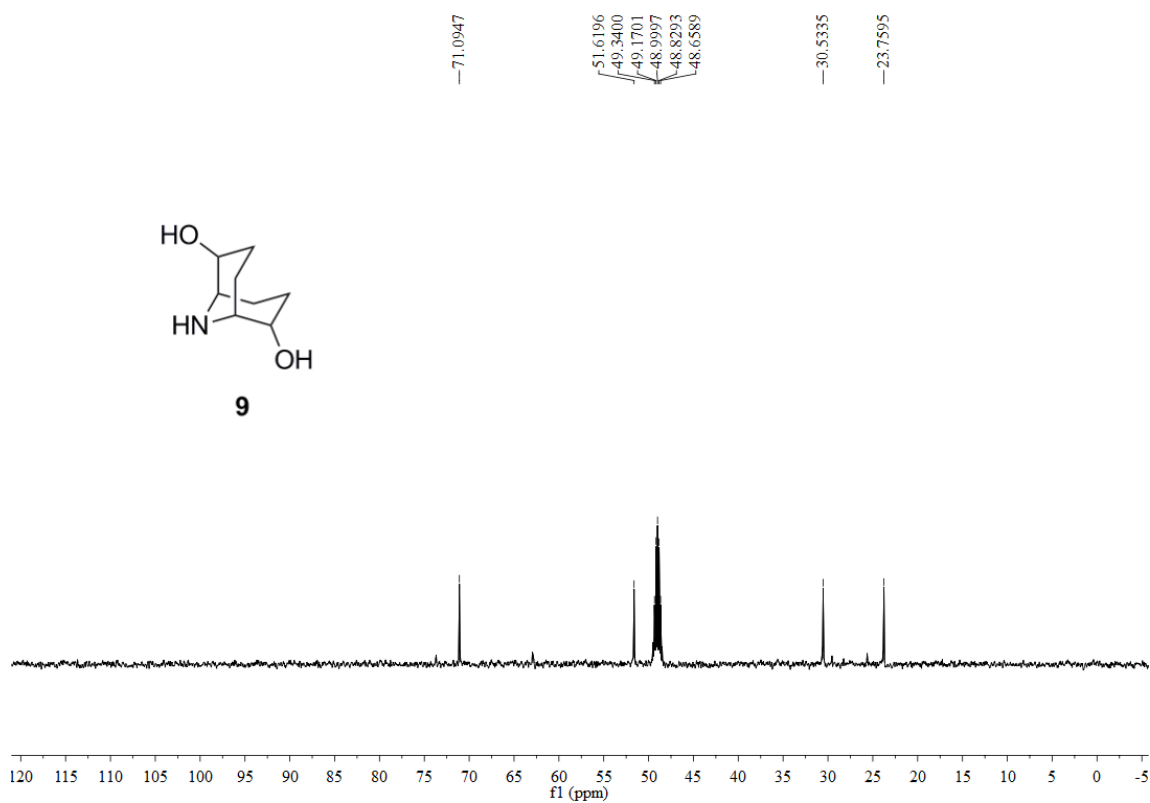
^{13}C NMR spectrum of compound 6 (CDCl_3 , 126 MHz)



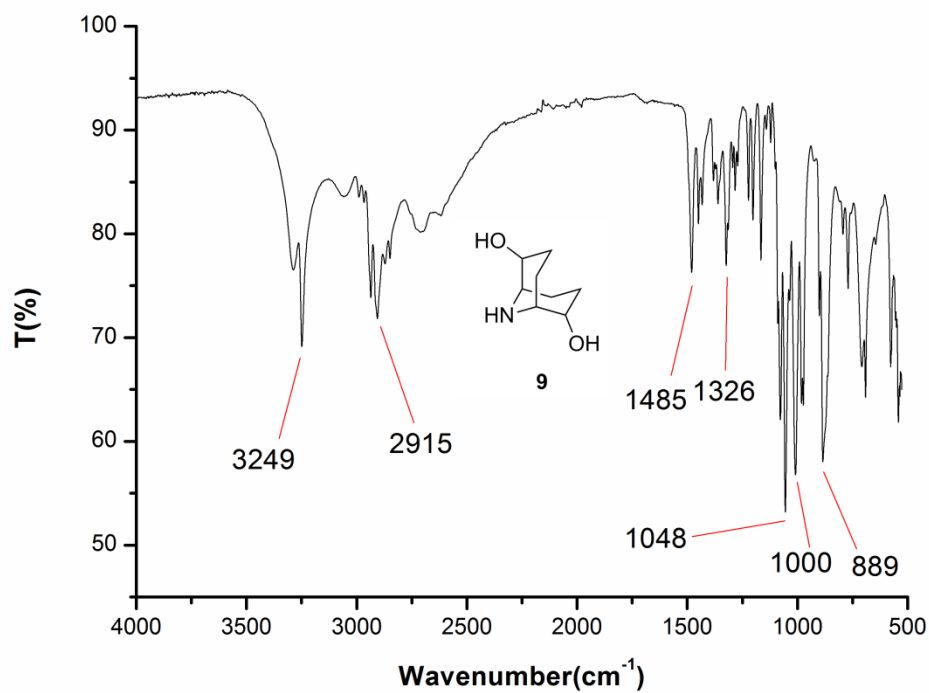
¹H NMR spectrum of compound 9 (CD₃OD-*d*₄, 500 MHz)



¹³C NMR spectrum of compound 9 (CD₃OD-*d*₄, 126 MHz)

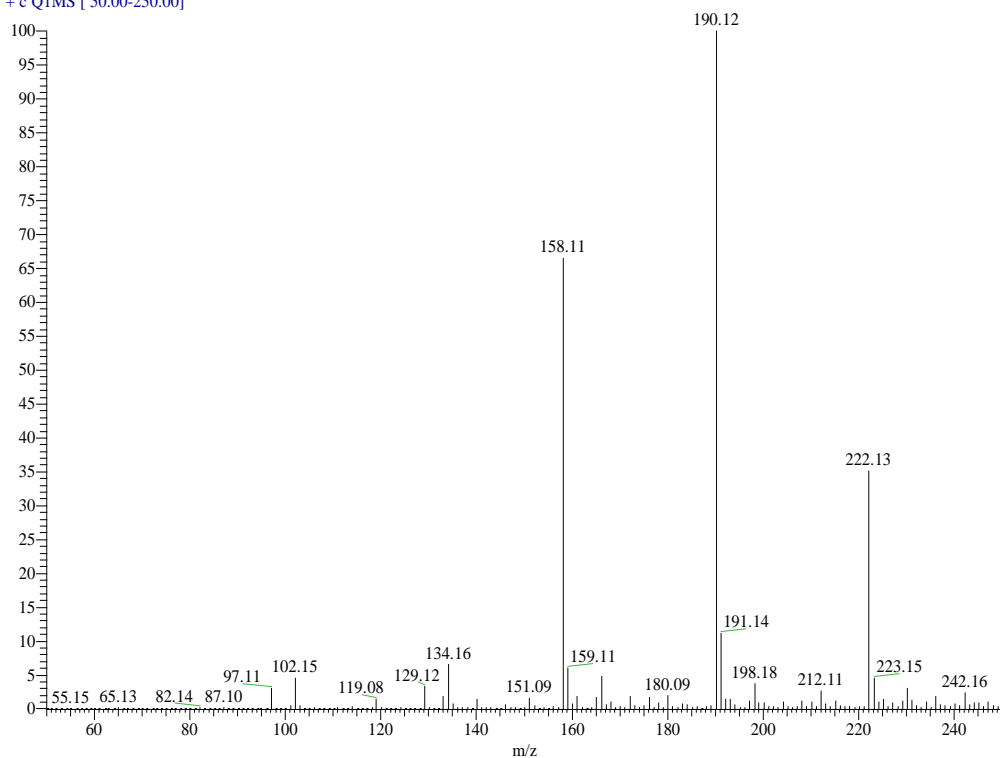


IR spectrum of compound 9

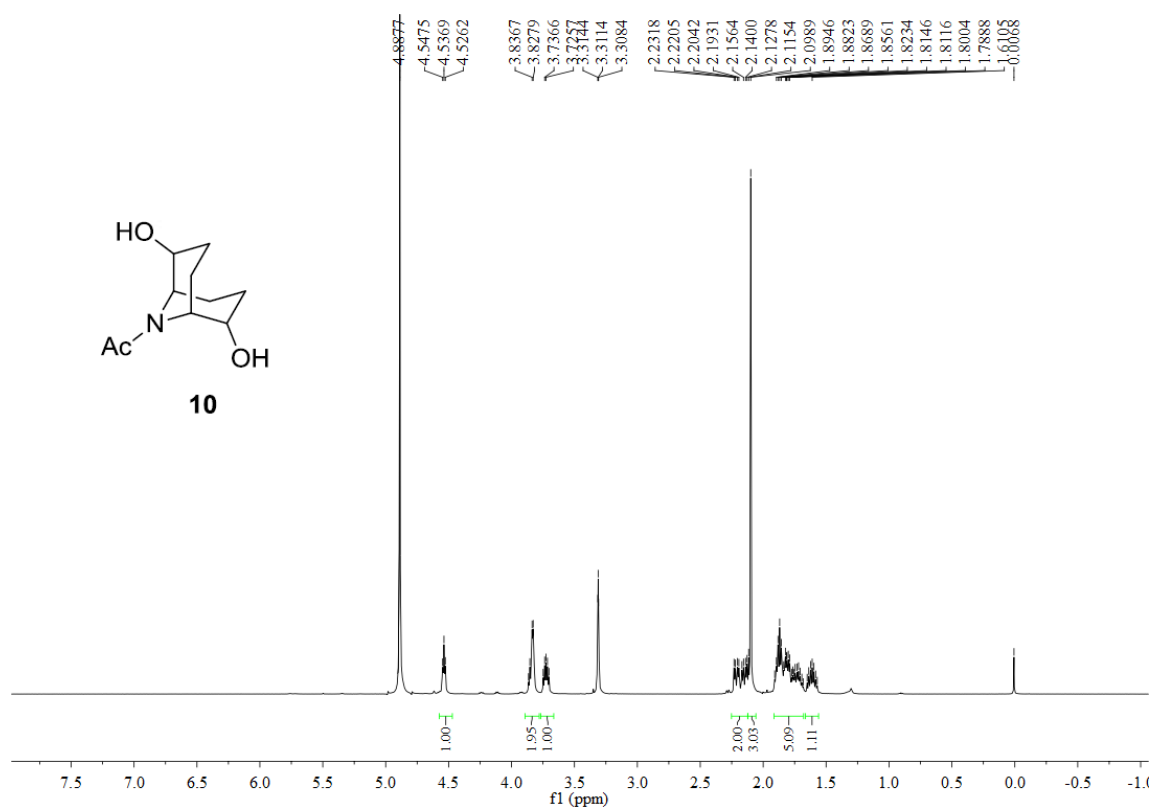


Electrospray Ionization (ESI) Mass Spectrometry of compound 9 (m/z of 158.11)

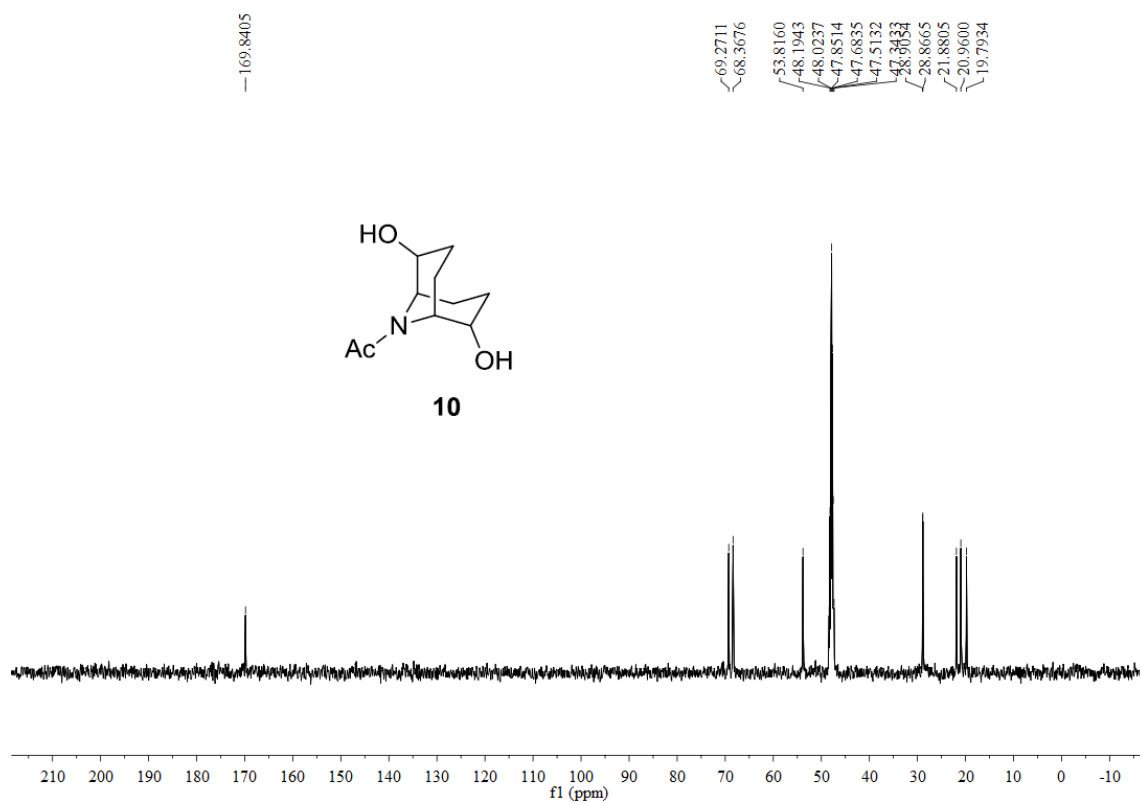
20180605-ZJ-01 #4 RT: 0.04 AV: 1 NL: 6.24E6
T: + c Q1MS [50.00-250.00]



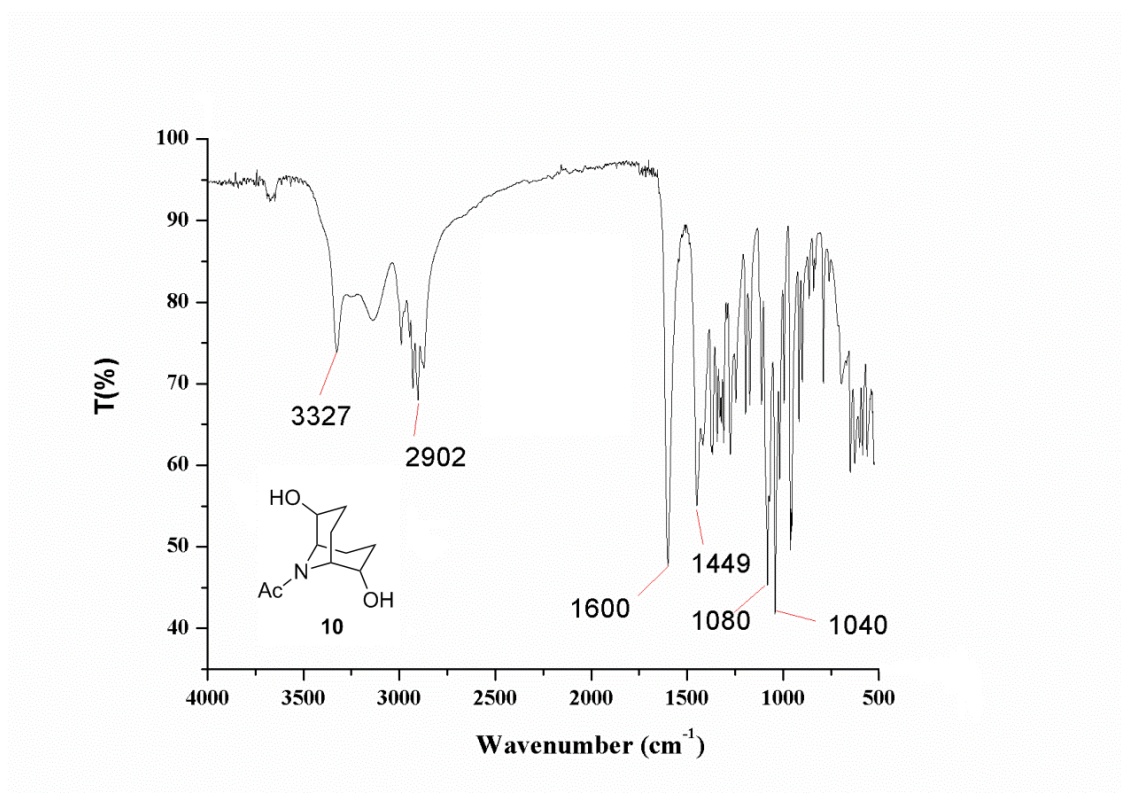
¹H NMR spectrum of compound 10 (CD₃OD-*d*₄, 500 MHz)



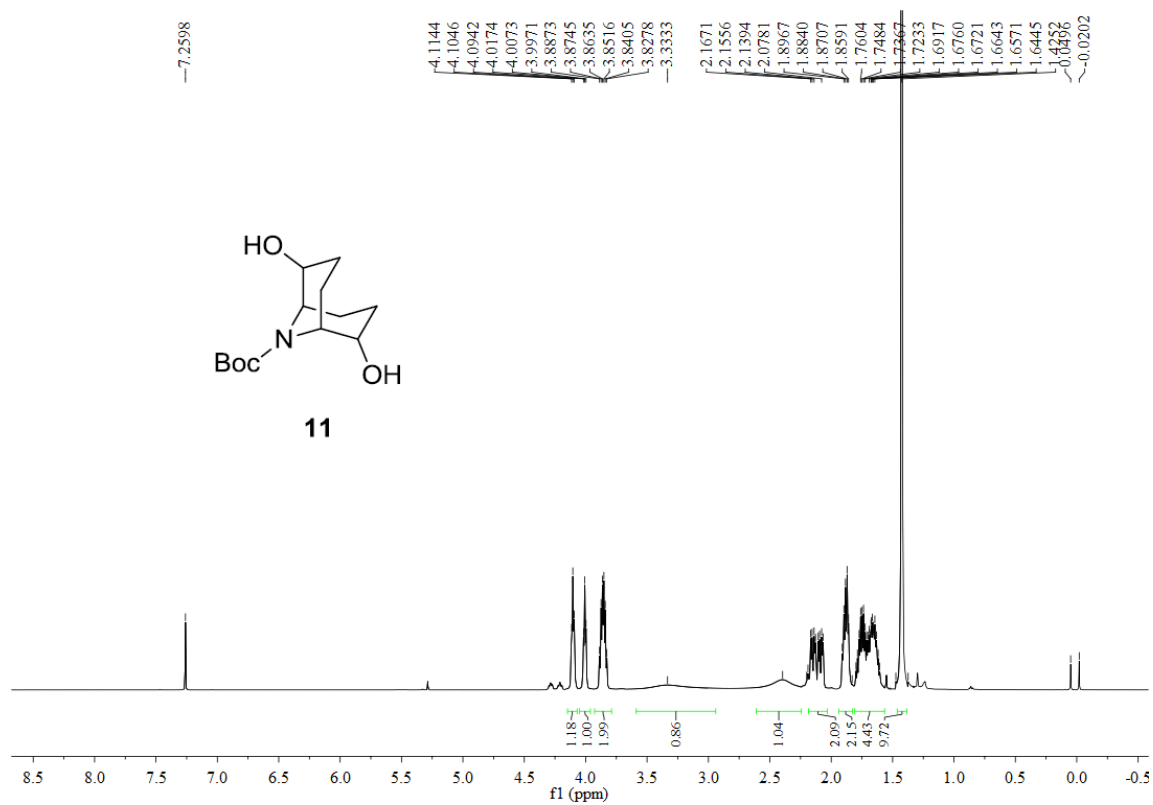
¹³C NMR spectrum of compound 10 (CD₃OD-*d*₄, 126 MHz)



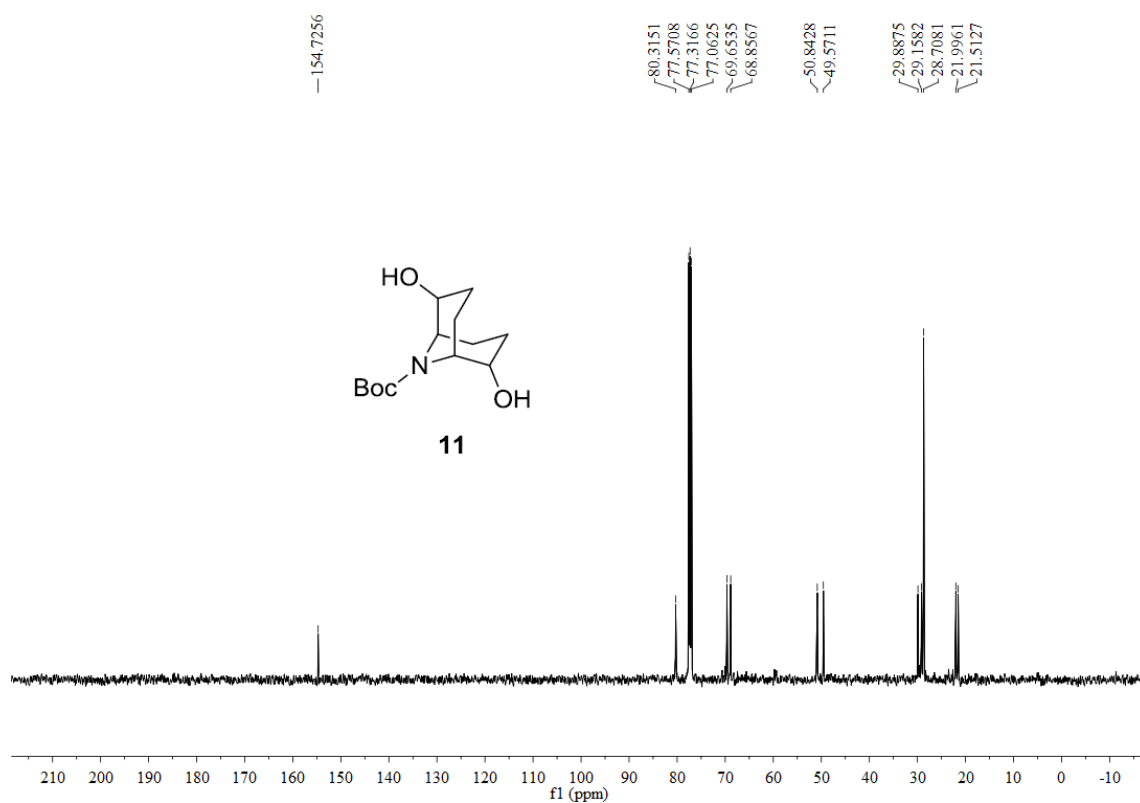
IR spectrum of compound 10



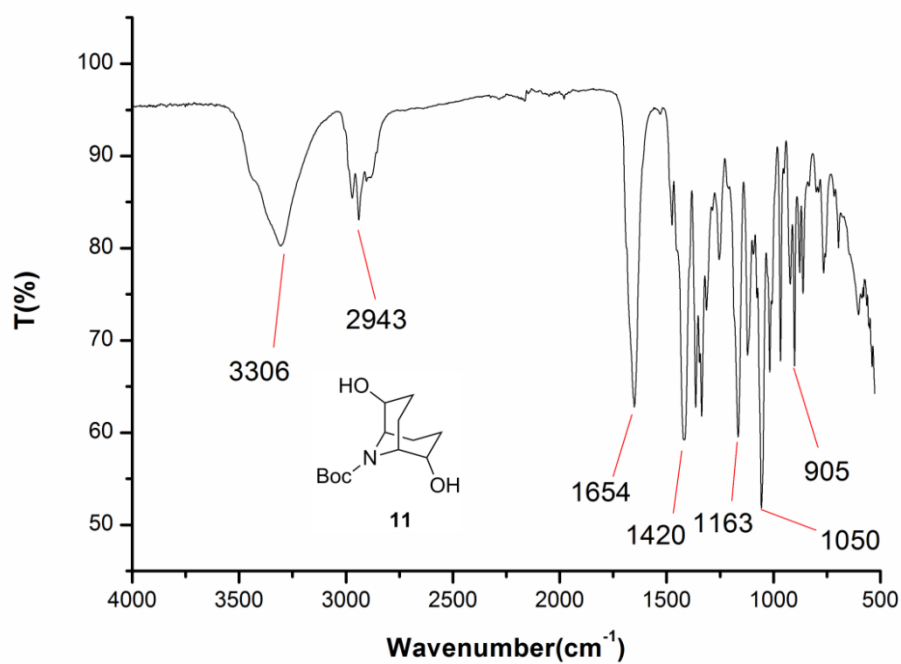
¹H NMR spectrum of compound 11 (CDCl₃, 500 MHz)



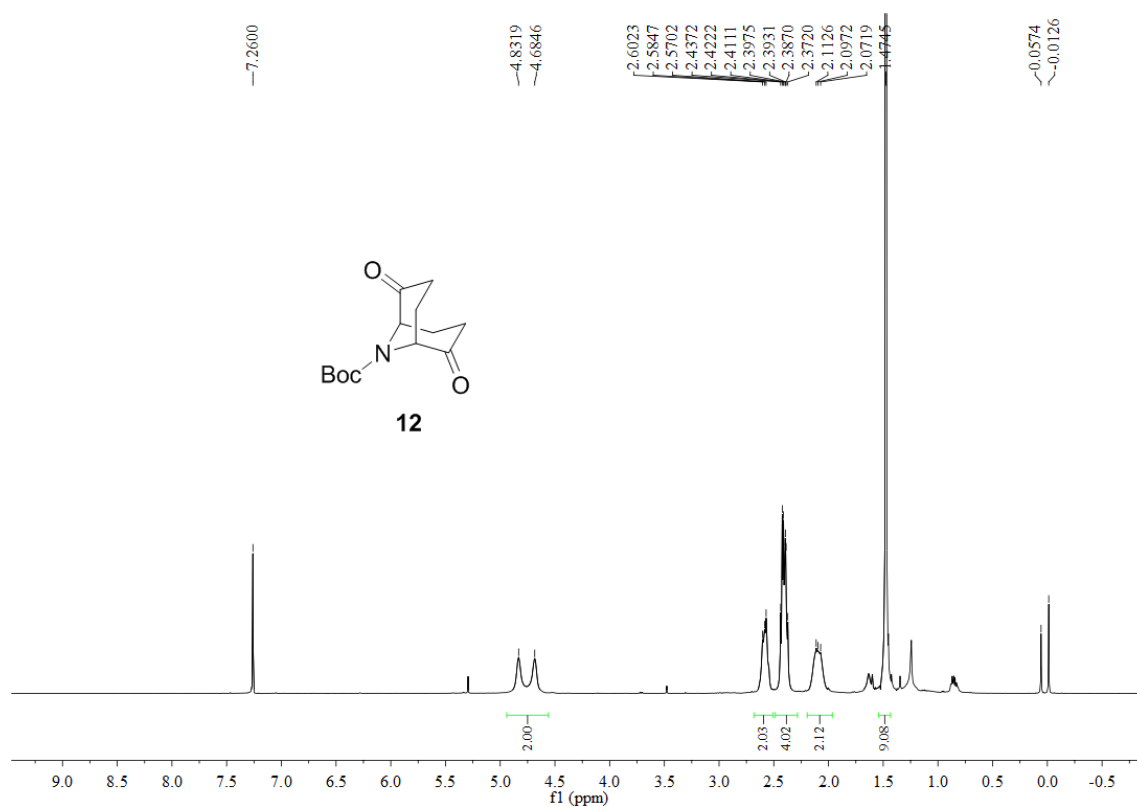
¹³C NMR spectrum of compound 11 (CDCl₃, 126 MHz)



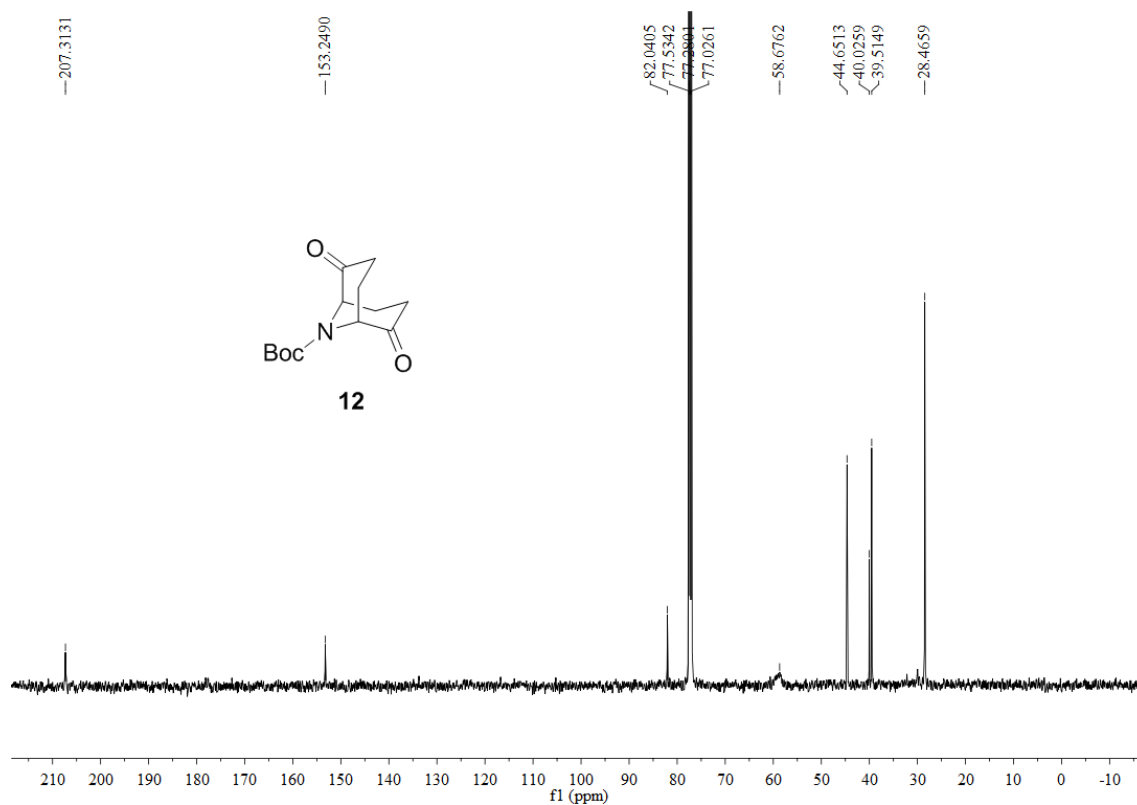
IR spectrum of compound 11



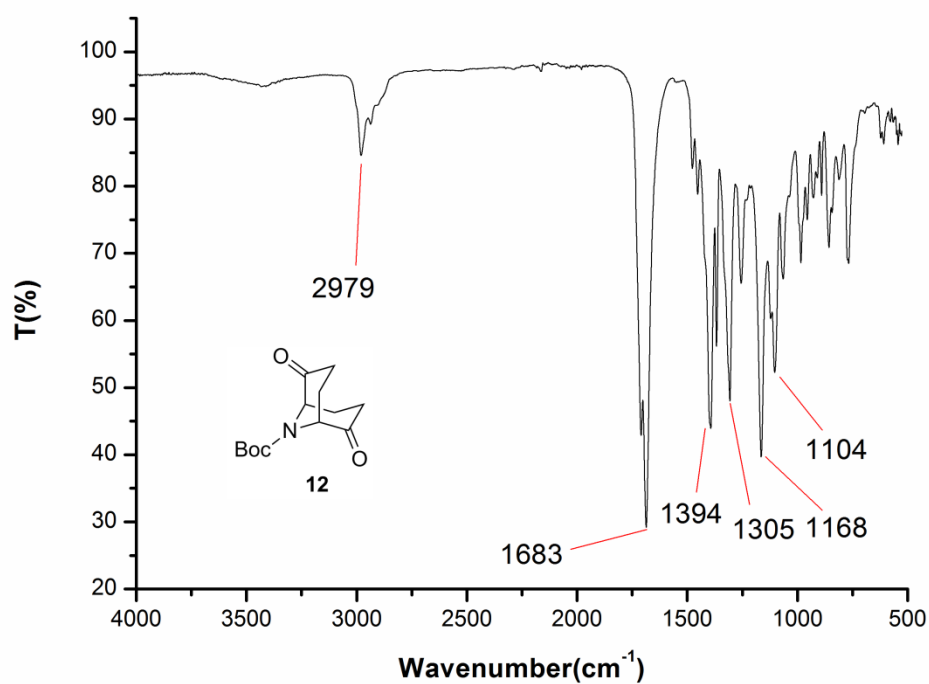
¹H NMR spectrum of compound 12 (CDCl₃, 500 MHz)



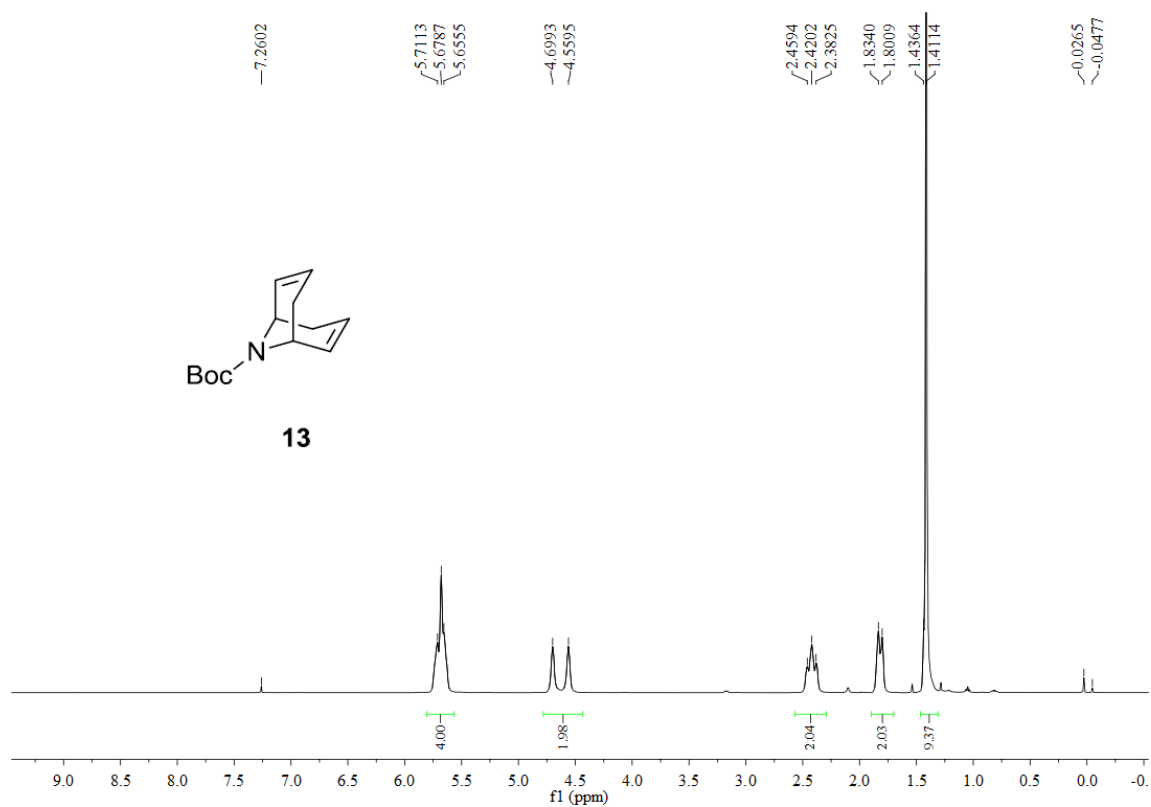
¹³C NMR spectrum of compound 12 (CDCl₃, 126 MHz)



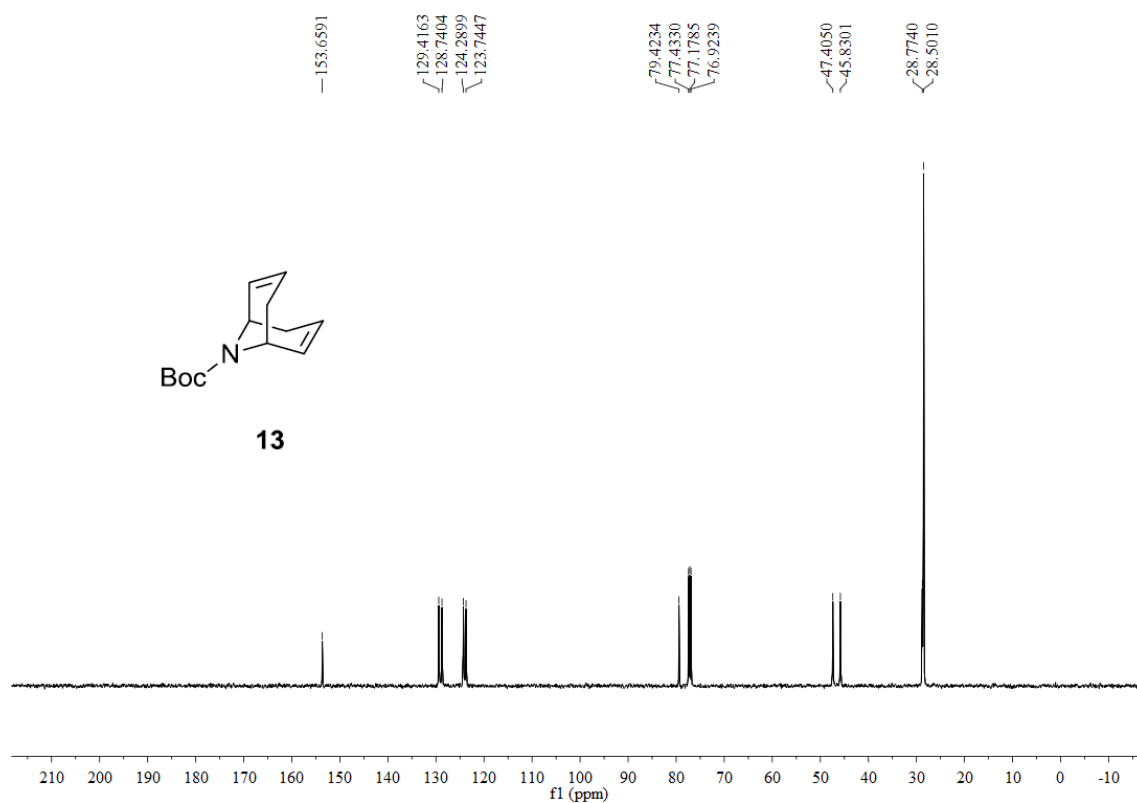
IR spectrum of compound 12



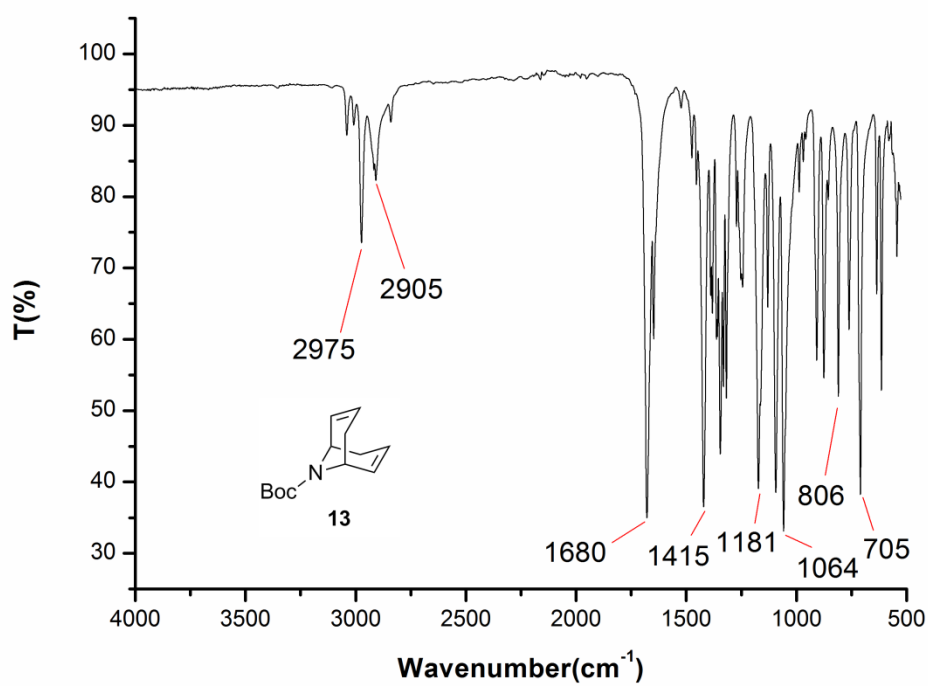
¹H NMR spectrum of compound 13 (CDCl₃, 500 MHz)



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

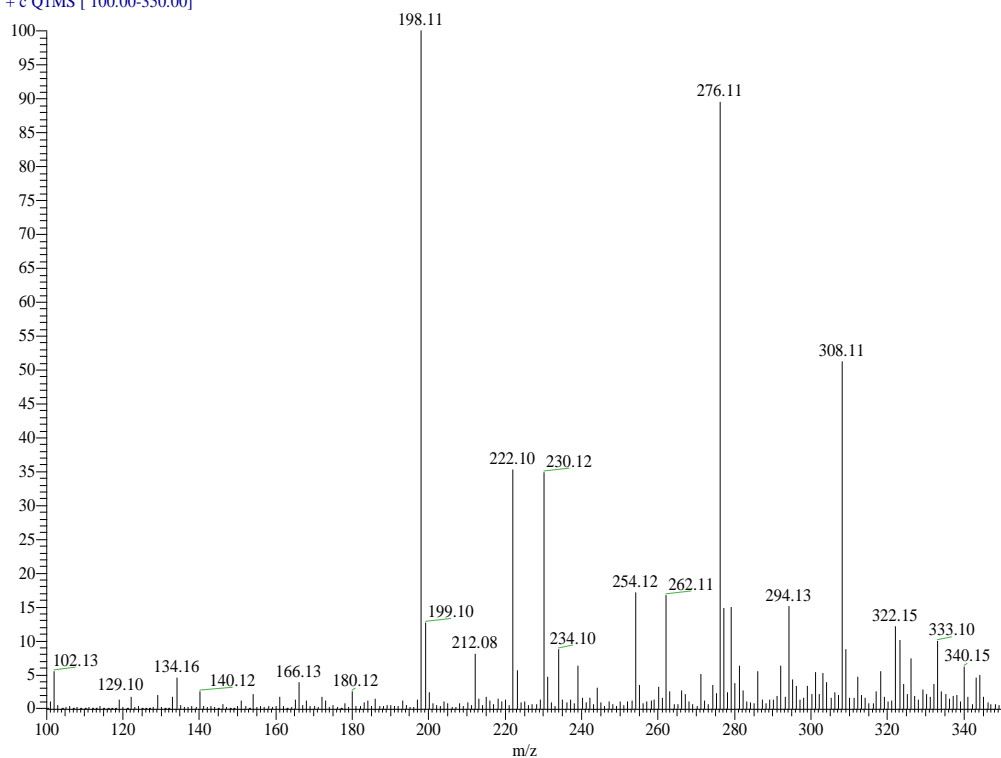


IR spectrum of compound 13

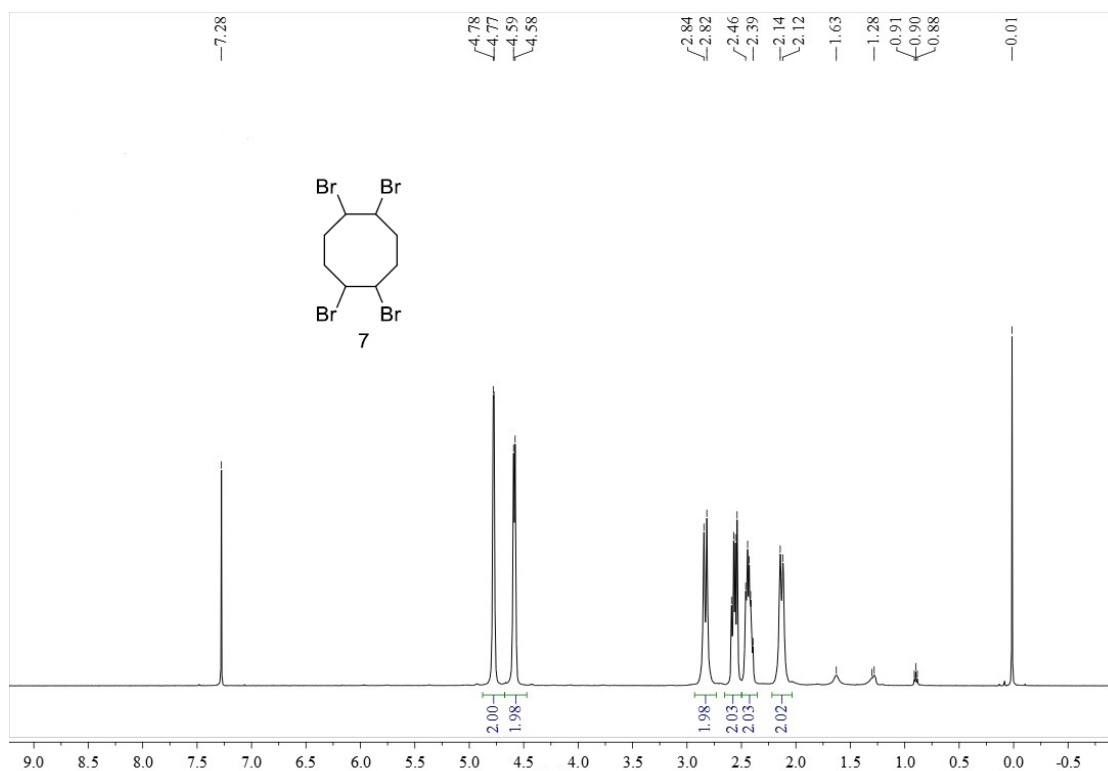


Electrospray Ionization (ESI) Mass Spectrometry of compound 13 (m/z of 222.10)

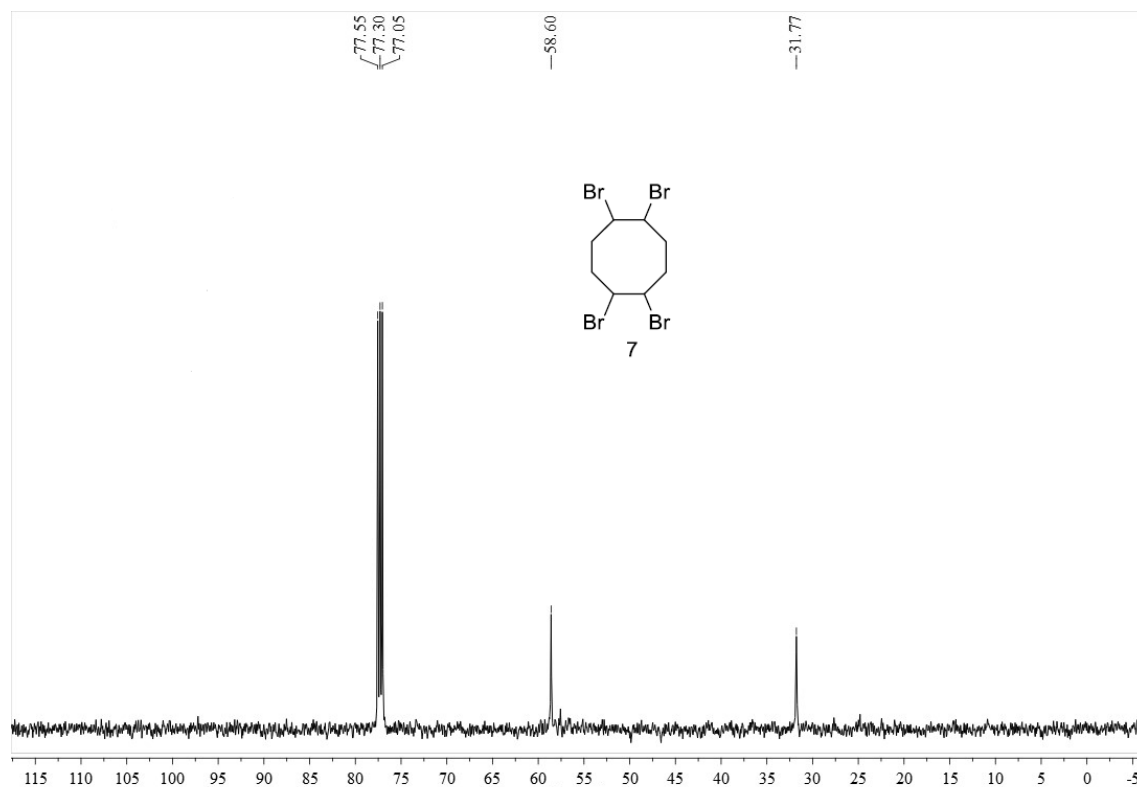
20180605-ZJ-05 #176 RT: 2.45 AV: 1 NL: 6.85E6
T: + c Q1MS [100.00-350.00]



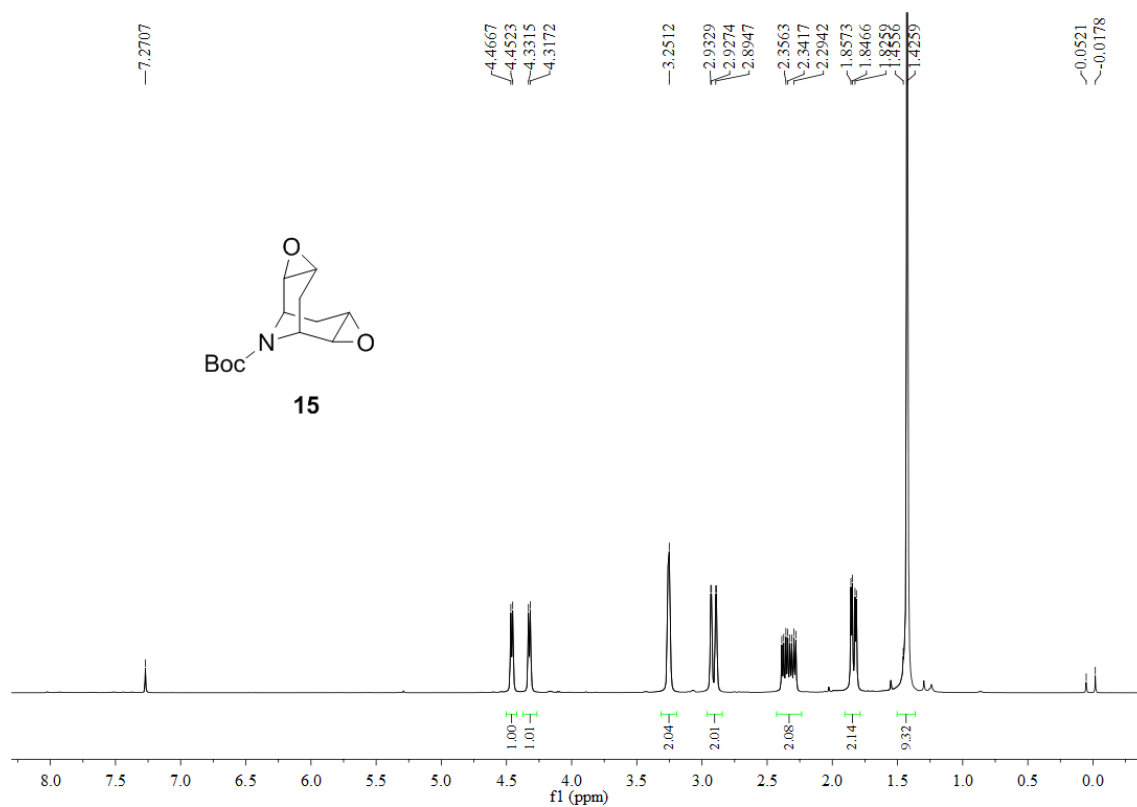
¹H NMR spectrum of compound 7 (CDCl₃, 500 MHz)



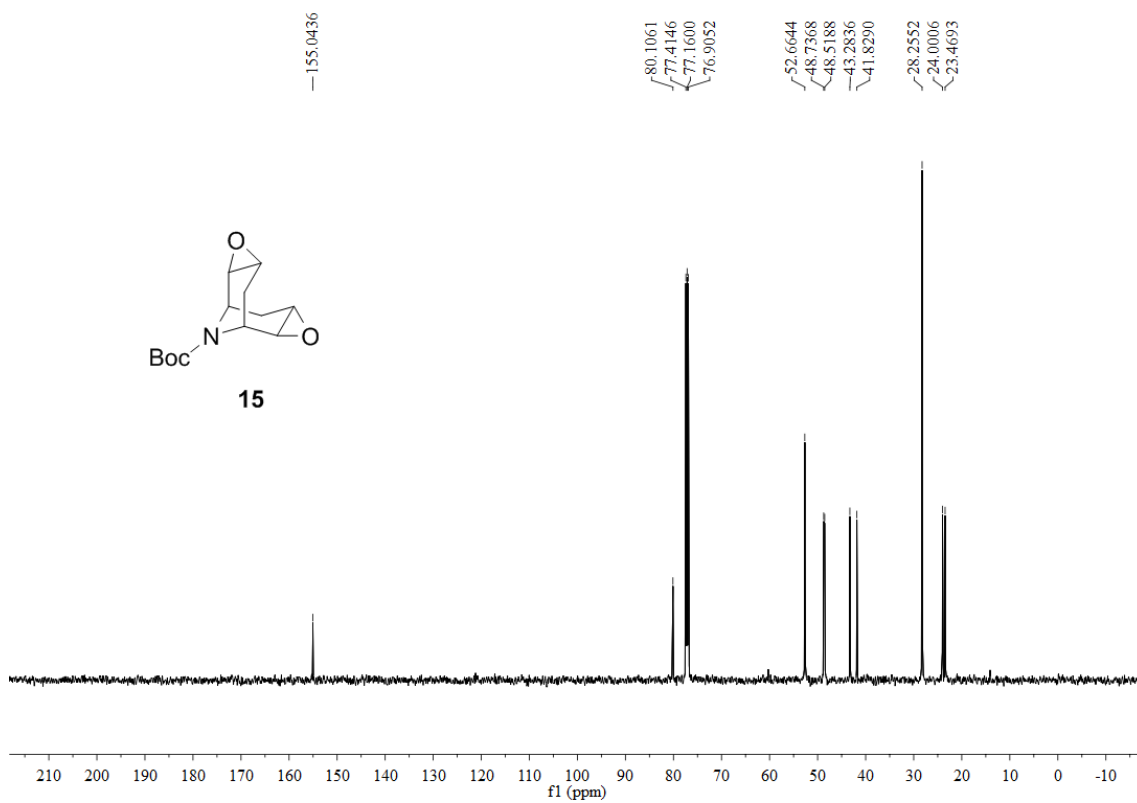
¹³C NMR spectrum of compound 7 (CDCl₃, 126 MHz)



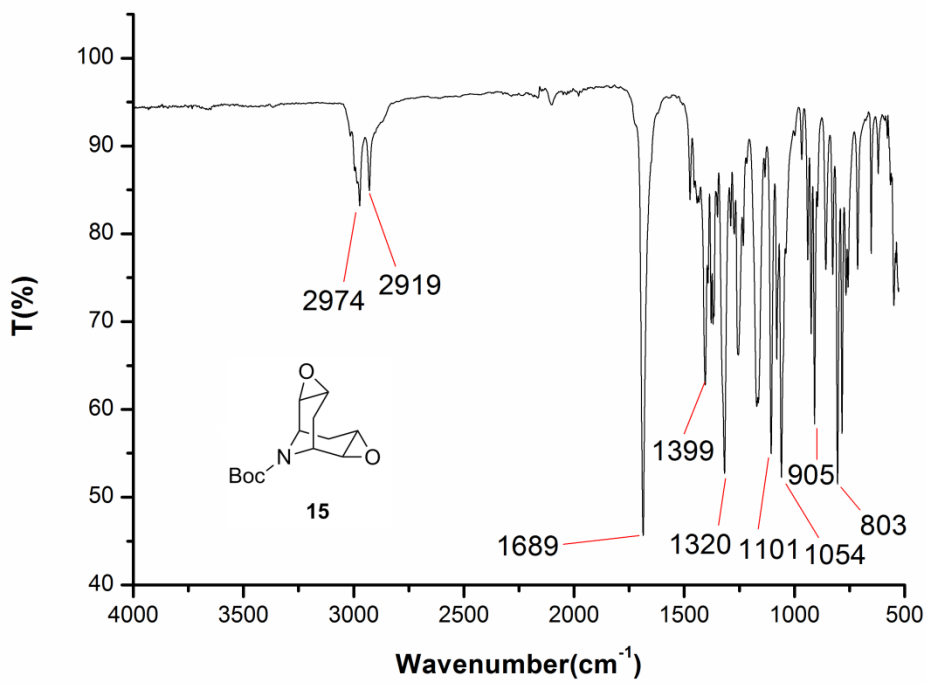
¹H NMR spectrum of compound 15 (CDCl₃, 500 MHz)



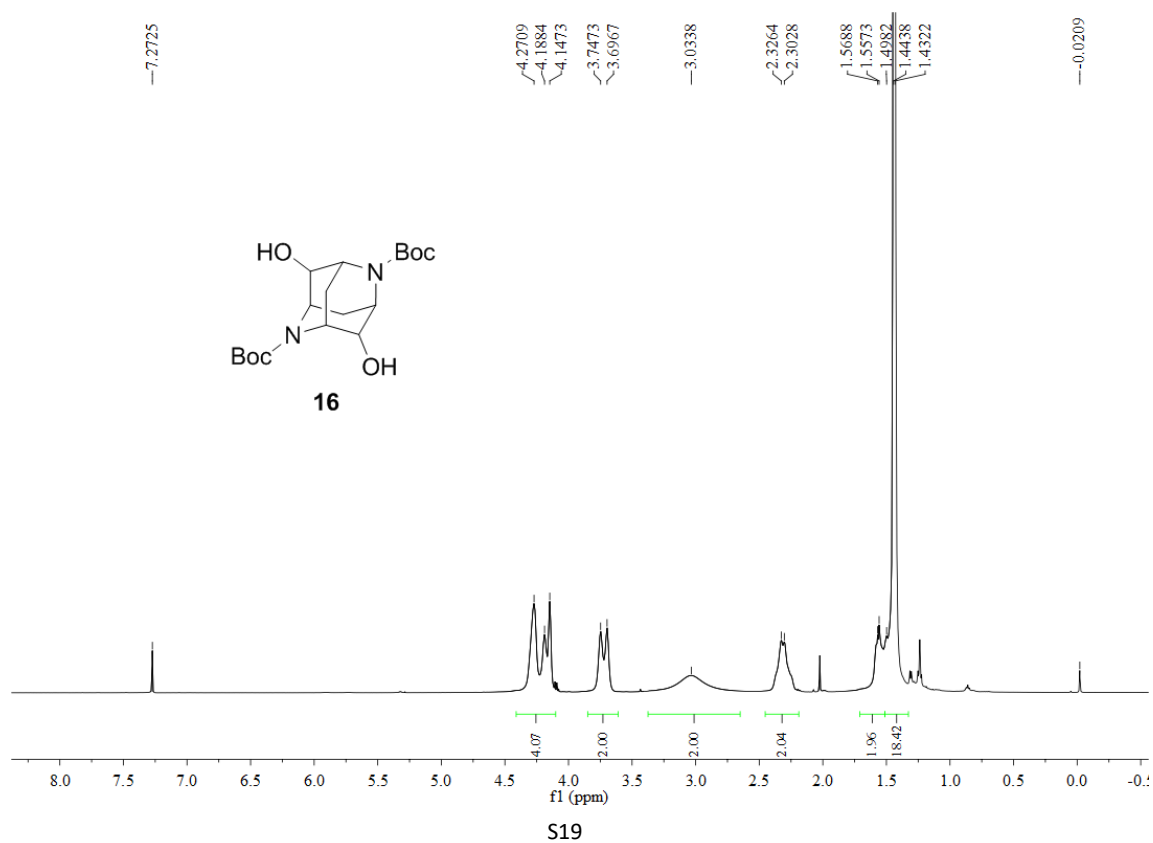
^{13}C NMR spectrum of compound 15 (CDCl_3 , 126 MHz)



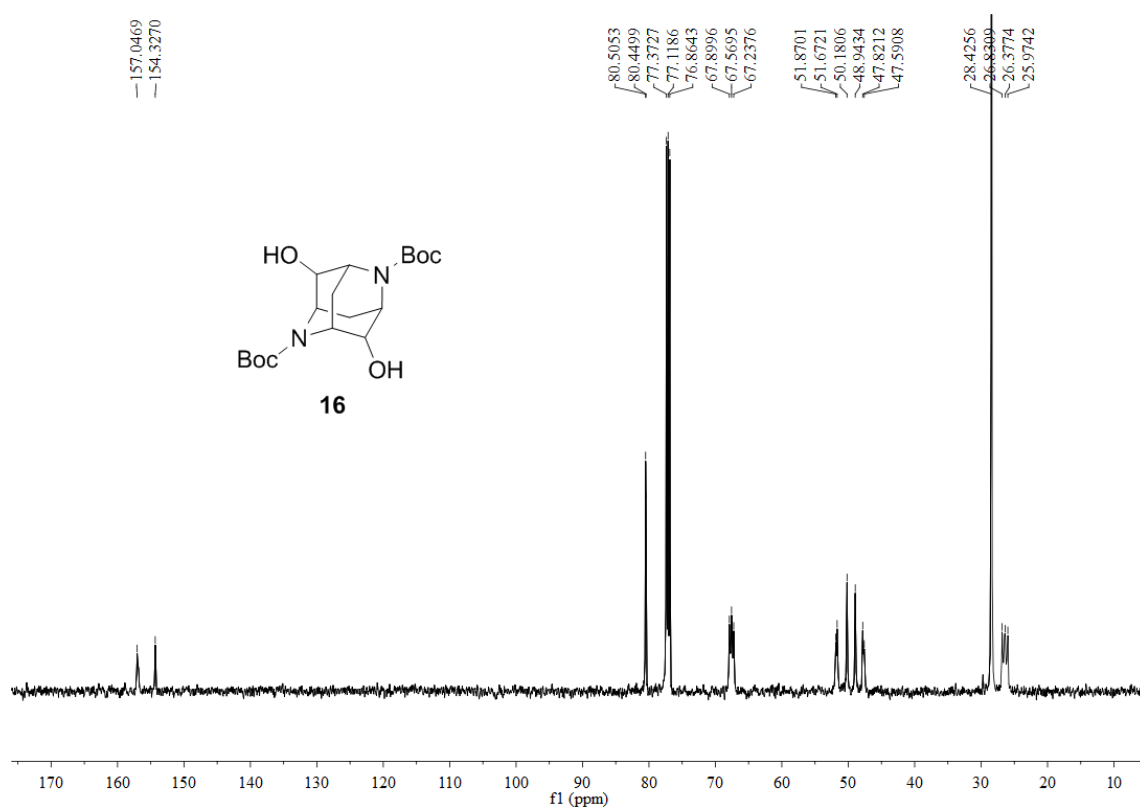
IR spectrum of compound 15



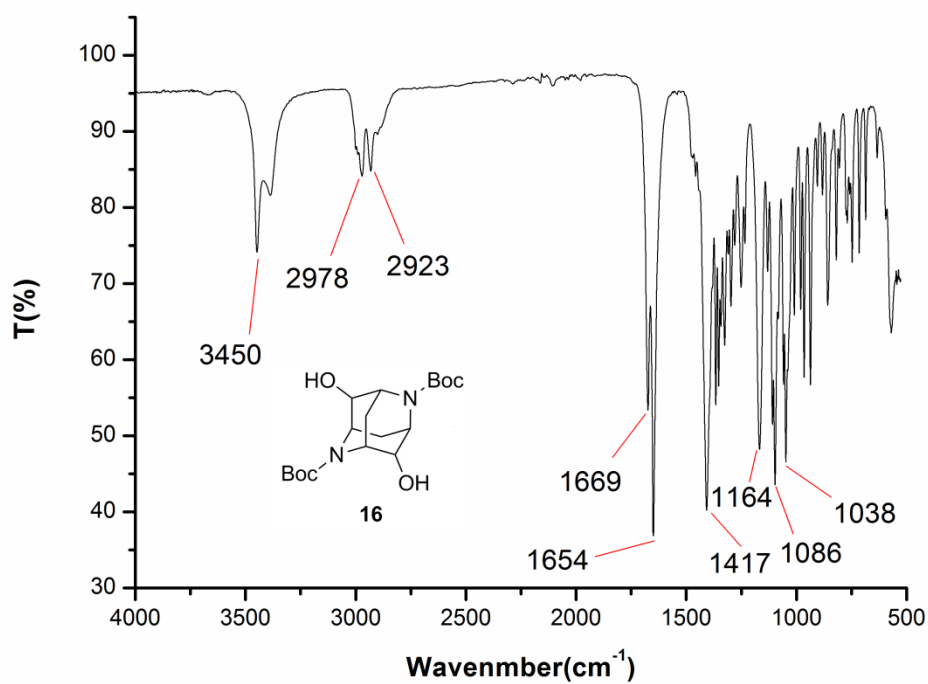
20180605-ZJ-06 #147 RT: 2.10 AV: 1 NL: 1.76E6
T: + c Q1MS [100.00-350.00]



¹³C NMR spectrum of compound 16 (CDCl₃, 126 MHz)



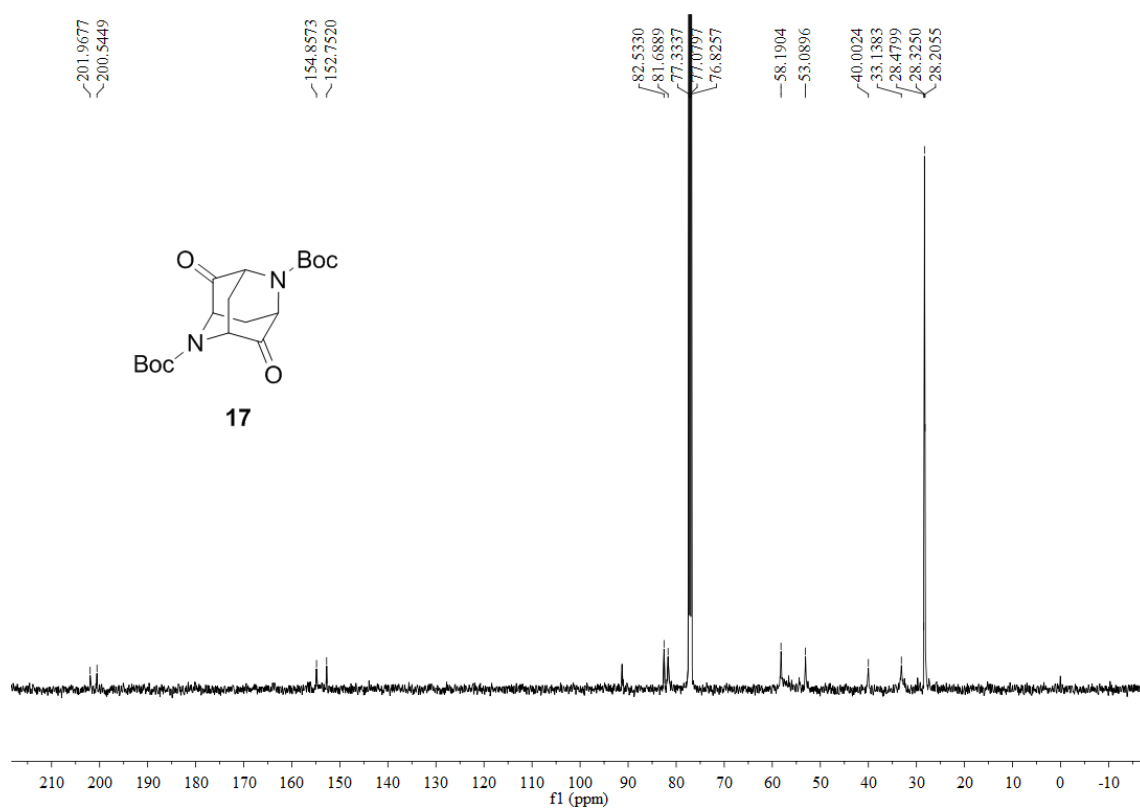
IR spectrum of compound 16



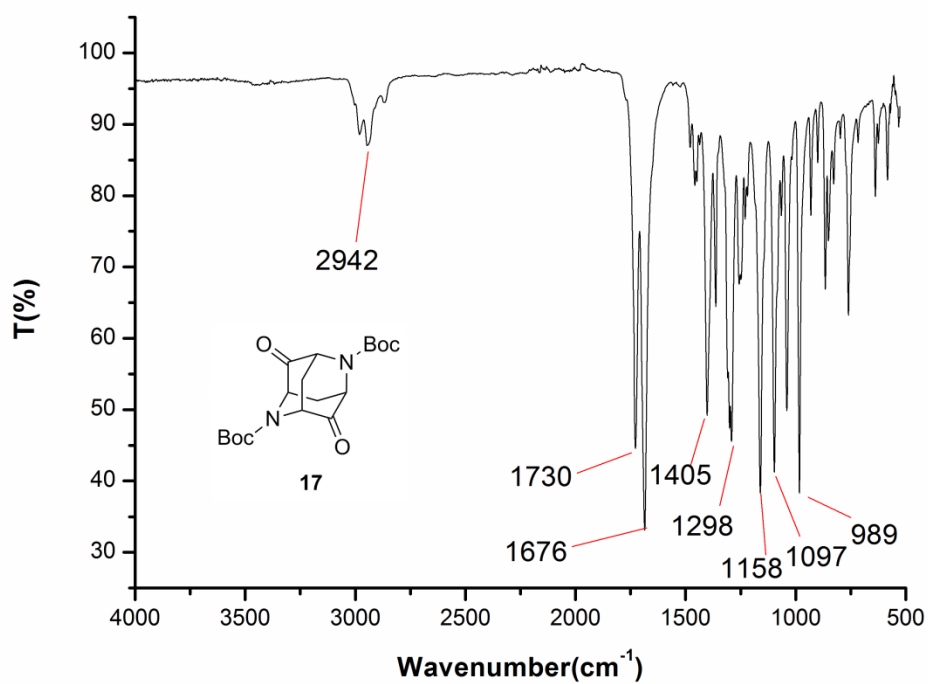
20180408ZJ-4 #43 RT: 0.53 AV: 1 NL: 9.56E7
T: + c Q1MS [300.00-400.00]



¹³C NMR spectrum of compound 17 (CDCl₃, 126 MHz)



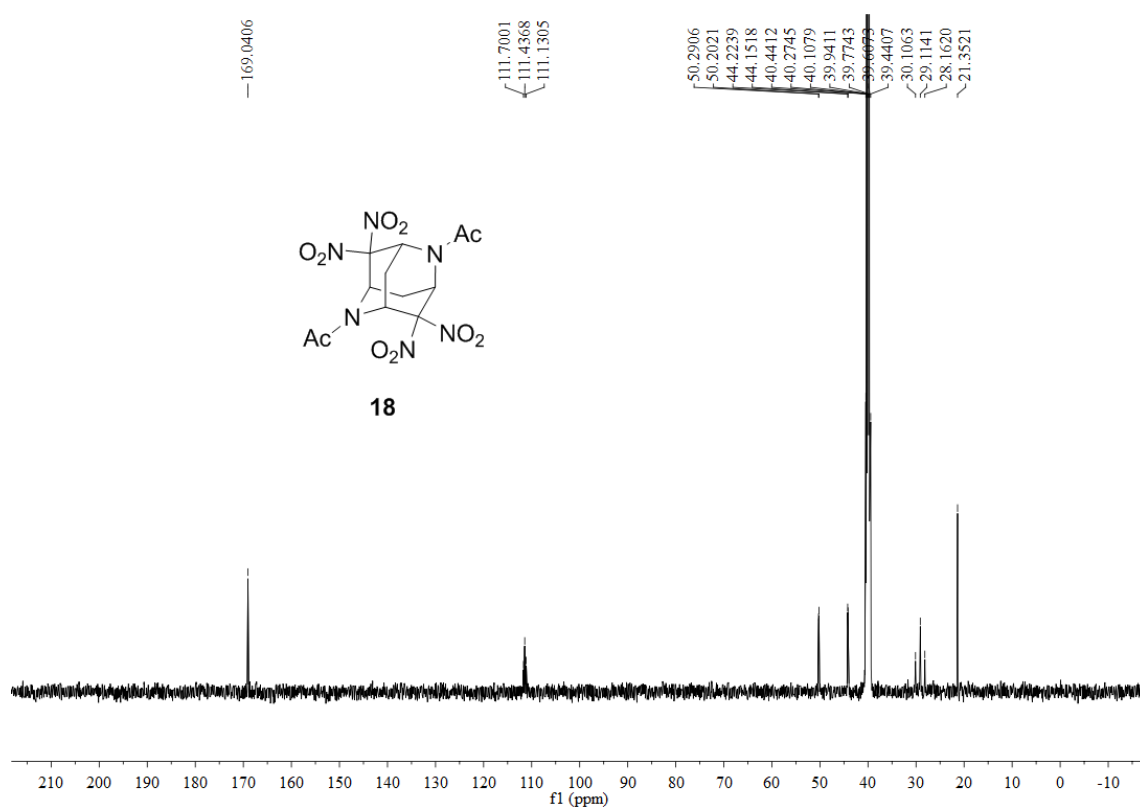
IR spectrum of compound 17



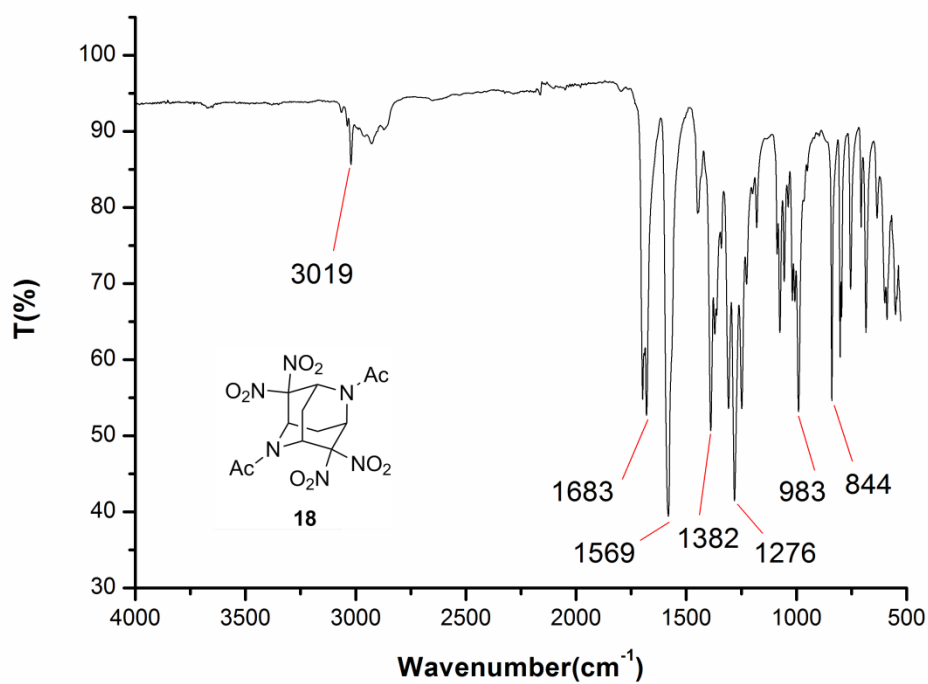
20180412-ZJ01 #399 RT: 4.58 AV: 1 NL: 6.11E5
T: + c Full ms2 384.00@-10.00 [200.00-400.00]



^{13}C NMR spectrum of compound 18 (DMSO- d_6 , 126 MHz)

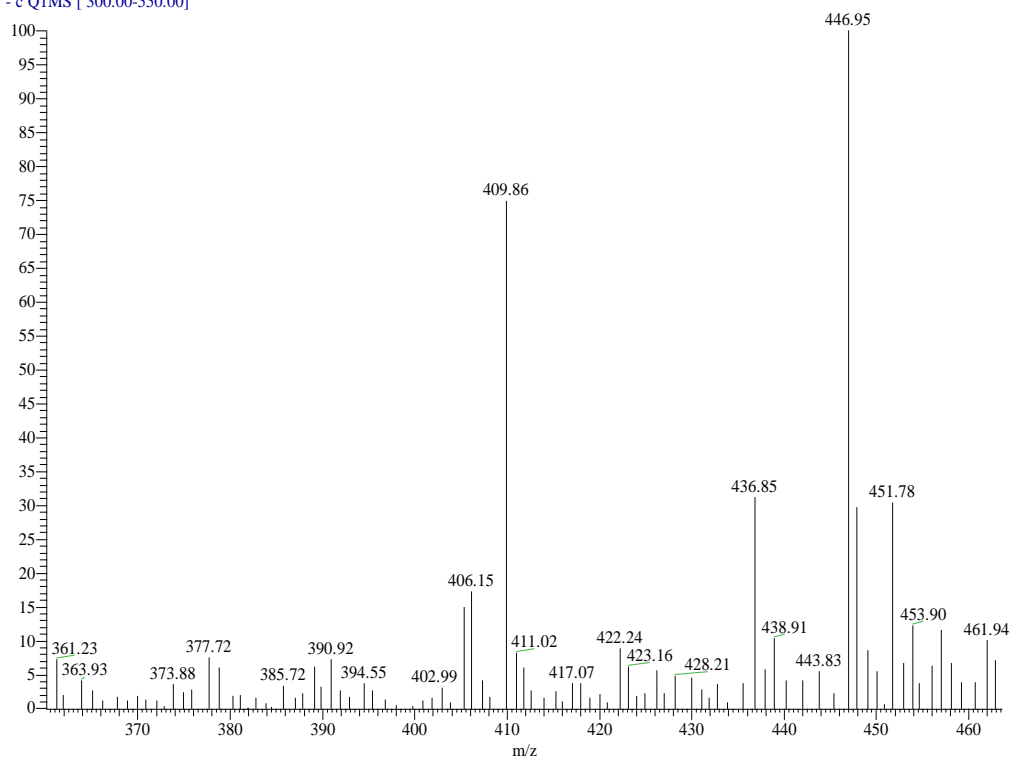


IR spectrum of compound 18

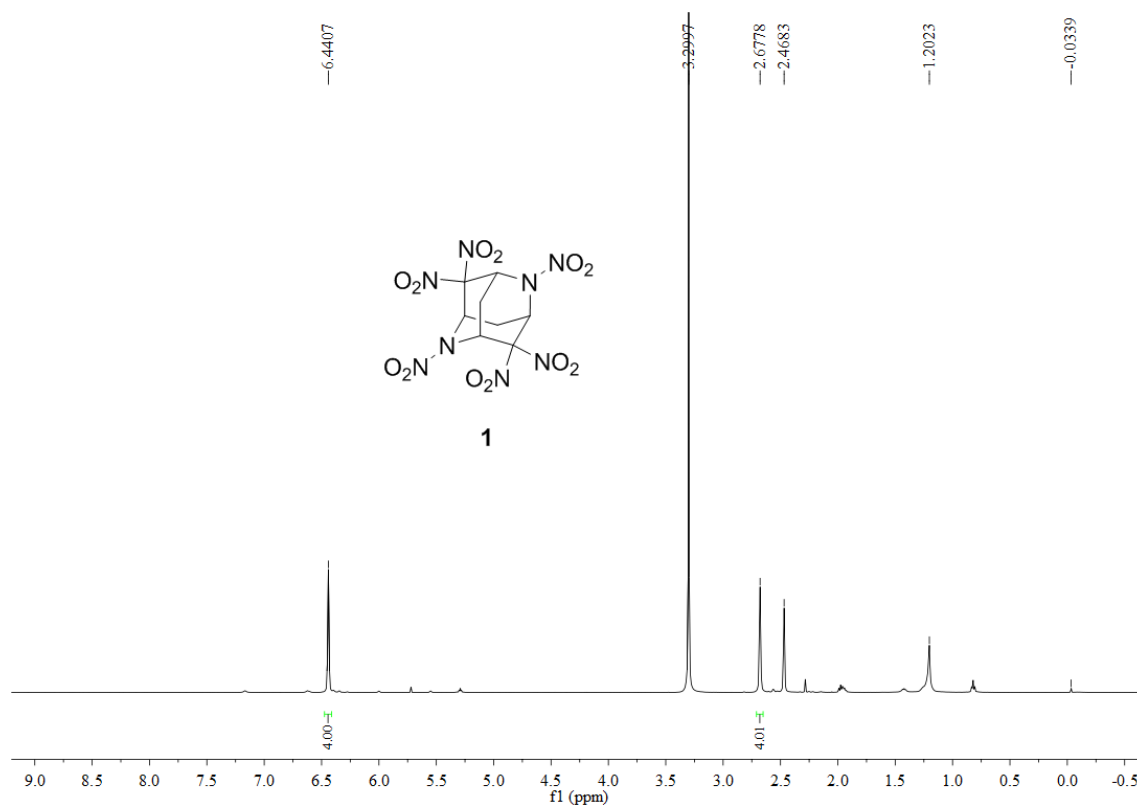


Electrospray Ionization (ESI) Mass Spectrometry of compound 18 (m/z of 436.85)

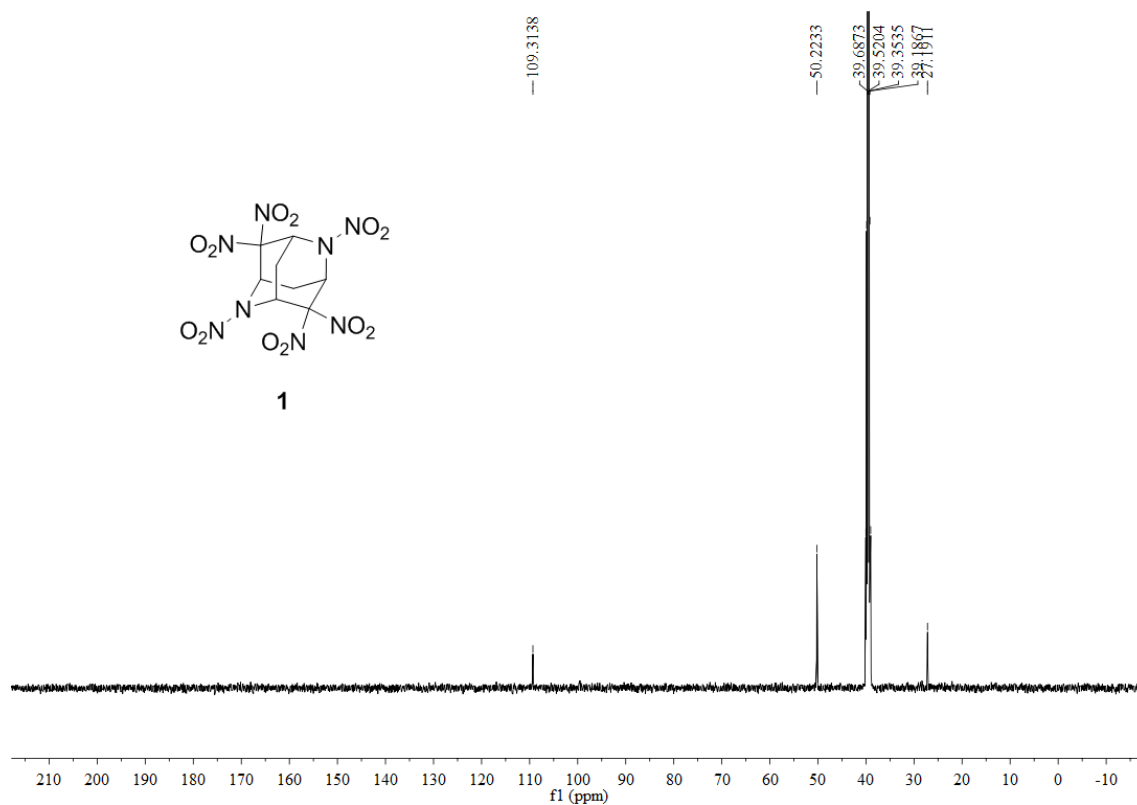
20180605-ZJ-07 #134 RT: 1.92 AV: 1 NL: 7.13E4
T: - c Q1MS [300.00-550.00]



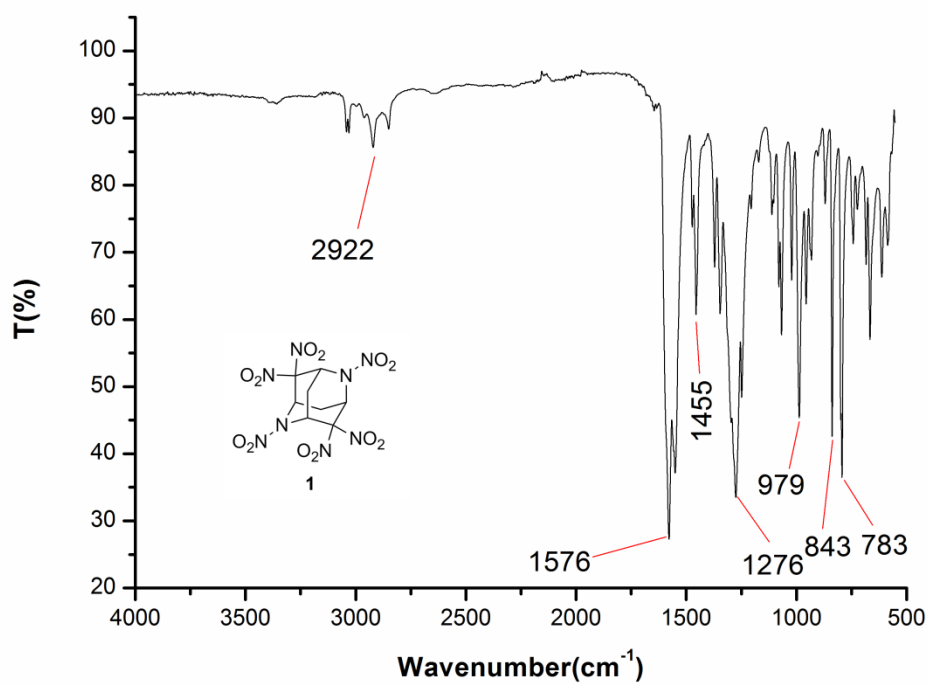
¹H NMR spectrum of compound 1 (DMSO-d₆, 500 MHz)



¹³C NMR spectrum of compound 1 (DMSO-*d*₆, 126 MHz)

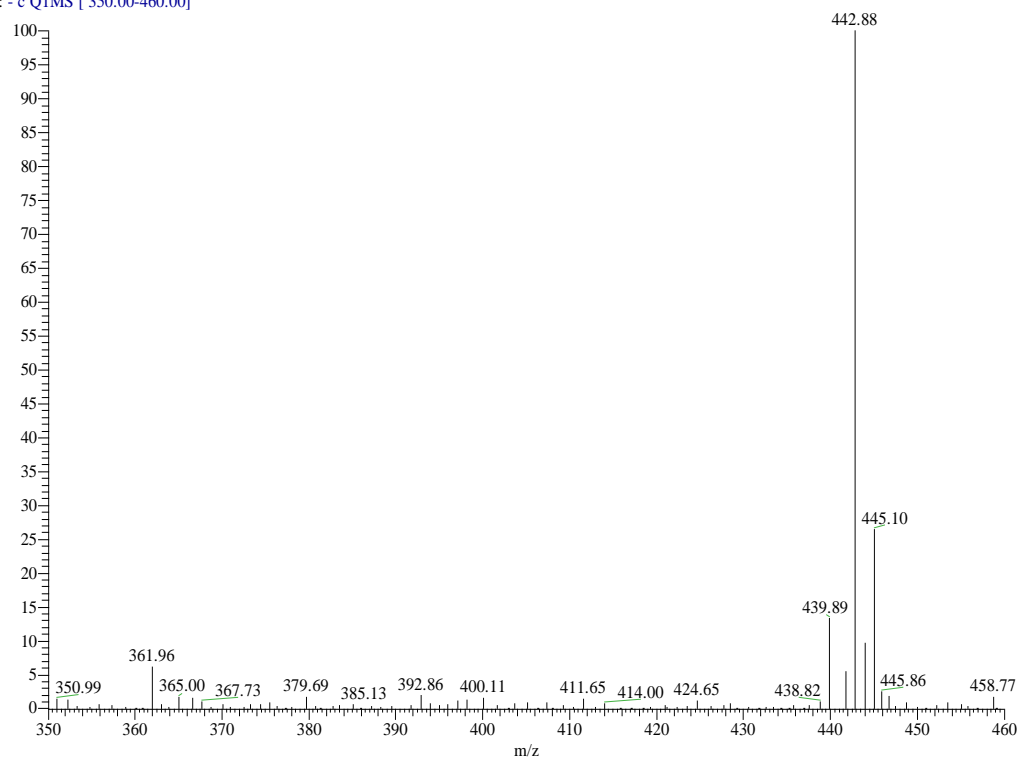


IR spectrum of compound 1



Electrospray Ionization (ESI) Mass Spectrometry of compound 1 (m/z of 442.88)

20180625-zj-2 #9 RT: 0.12 AV: 1 NL: 1.08E5
T: - c Q1MS [350.00-460.00]



4. X-ray Crystal Structures and Data of Compound 1

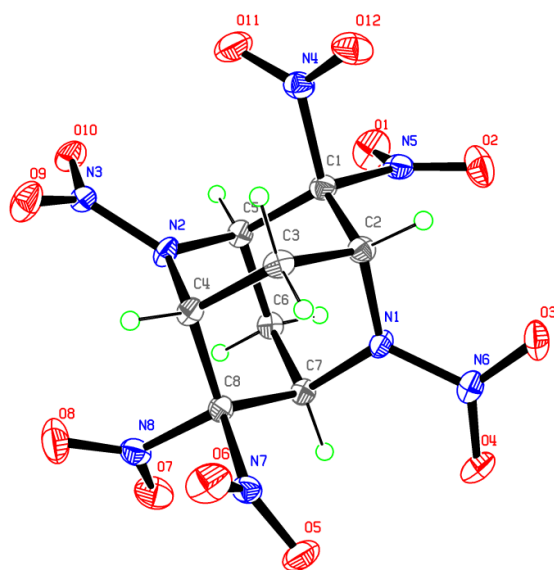


Figure S1. ORTEP diagram of **1** Color code: Carbon (grey), Oxygen (red), Nitrogen (blue).

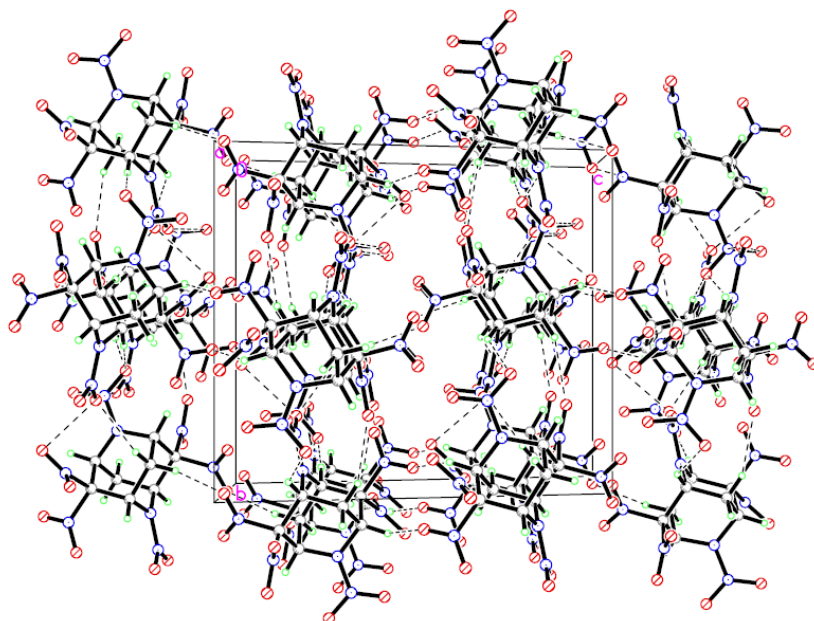


Figure S2. Crystal packing of **1** Color code: Carbon (grey), Oxygen (red), Nitrogen (blue).

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

Identification code	1
Empirical formula	C ₈ H ₈ N ₈ O ₁₂
Formula weight	408.22
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 8.0321(15) Å α = 90°. b = 12.359(2) Å β = 104.253(2)°. c = 14.386(3) Å γ = 90°.
Volume	1384.1(5) Å ³
Z	4
Density (calculated)	1.959 Mg/m ³
Absorption coefficient	0.186 mm ⁻¹
F(000)	832
Crystal size	0.260 x 0.230 x 0.190 mm ³
Theta range for data collection	2.202 to 25.002°.
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	9617
Independent reflections	2425 [R(int) = 0.0270]
Completeness to theta = 25.002°	99.3 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2425 / 0 / 254
Goodness-of-fit on F ²	1.027
Final R indices [I > 2σ(I)]	R ₁ = 0.0292, wR ₂ = 0.0742
R indices (all data)	R ₁ = 0.0322, wR ₂ = 0.0764
Extinction coefficient	0.0199(15)
Largest diff. peak and hole	0.331 and -0.199 e.Å ⁻³
CCDC	1854396

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for **1**.

U(eq) is defined as one third of the trace of the orthogonalized U _{ij} tensor.				
	x	y	z	U(eq)
C(1)	3251(2)	5106(1)	1492(1)	14(1)
C(2)	1686(2)	5828(1)	1452(1)	14(1)
C(3)	395(2)	5224(1)	1889(1)	15(1)
C(4)	1268(2)	4925(1)	2927(1)	13(1)

C(5)	4147(2)	4816(1)	2530(1)	14(1)
C(6)	4740(2)	5857(1)	3087(1)	14(1)
C(7)	3176(2)	6575(1)	3073(1)	13(1)
C(8)	1898(2)	5949(1)	3511(1)	14(1)
N(1)	2309(2)	6765(1)	2063(1)	14(1)
N(2)	2846(2)	4313(1)	2953(1)	15(1)
N(3)	2917(2)	3222(1)	3152(1)	15(1)
N(4)	2717(2)	4089(1)	875(1)	17(1)
N(5)	4511(2)	5628(1)	980(1)	18(1)
N(6)	1942(2)	7794(1)	1709(1)	16(1)
O(9)	1636(1)	2806(1)	3310(1)	25(1)
N(6')	1942(2)	7794(1)	1709(1)	16(1)
O(9')	1636(1)	2806(1)	3310(1)	25(1)
N(7)	378(2)	6659(1)	3595(1)	17(1)
N(8)	2720(2)	5641(1)	4557(1)	18(1)
O(1)	5990(1)	5318(1)	1226(1)	30(1)
O(2)	3930(2)	6273(1)	348(1)	29(1)
O(3)	1255(1)	7882(1)	859(1)	23(1)
O(4)	2338(1)	8543(1)	2282(1)	20(1)
O(5)	682(2)	7616(1)	3756(1)	25(1)
O(6)	-996(1)	6214(1)	3509(1)	28(1)
O(7)	3915(1)	6196(1)	4987(1)	26(1)
O(8)	2103(2)	4874(1)	4878(1)	31(1)
O(10)	4268(1)	2762(1)	3168(1)	20(1)
O(11)	3474(2)	3254(1)	1145(1)	28(1)
O(12)	1594(1)	4215(1)	143(1)	25(1)

Table 3. Bond lengths [Å] and angles [°] for **1**.

C(1)-C(2)	1.531(2)
C(1)-C(5)	1.532(2)
C(1)-N(5)	1.5335(18)
C(1)-N(4)	1.5374(18)
C(2)-N(1)	1.4646(18)
C(2)-C(3)	1.533(2)
C(2)-H(2)	1.0000
C(3)-C(4)	1.530(2)
C(3)-H(3A)	0.9900

C(3)-H(3B)	0.9900
C(4)-N(2)	1.4686(18)
C(4)-C(8)	1.534(2)
C(4)-H(4A)	1.0000
C(5)-N(2)	1.4701(18)
C(5)-C(6)	1.528(2)
C(5)-H(5)	1.0000
C(6)-C(7)	1.5342(19)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-N(1)	1.4673(18)
C(7)-C(8)	1.5396(19)
C(7)-H(7)	1.0000
C(8)-N(7)	1.5318(18)
C(8)-N(8)	1.5345(18)
N(1)-N(6')	1.3746(17)
N(1)-N(6)	1.3746(17)
N(2)-N(3)	1.3773(17)
N(3)-O(10)	1.2204(16)
N(3)-O(9')	1.2205(16)
N(3)-O(9)	1.2205(16)
N(4)-O(11)	1.2122(17)
N(4)-O(12)	1.2160(16)
N(5)-O(2)	1.2124(17)
N(5)-O(1)	1.2155(17)
N(6)-O(3)	1.2171(16)
N(6)-O(4)	1.2282(17)
N(6')-O(3)	1.2171(16)
N(6')-O(4)	1.2282(17)
N(7)-O(6)	1.2123(17)
N(7)-O(5)	1.2174(17)
N(8)-O(8)	1.2125(18)
N(8)-O(7)	1.2169(17)
C(2)-C(1)-C(5)	110.92(11)
C(2)-C(1)-N(5)	111.68(12)
C(5)-C(1)-N(5)	111.08(11)
C(2)-C(1)-N(4)	110.20(11)

C(5)-C(1)-N(4)	111.66(12)
N(5)-C(1)-N(4)	100.93(10)
N(1)-C(2)-C(1)	106.39(11)
N(1)-C(2)-C(3)	107.75(11)
C(1)-C(2)-C(3)	109.41(12)
N(1)-C(2)-H(2)	111.0
C(1)-C(2)-H(2)	111.0
C(3)-C(2)-H(2)	111.0
C(4)-C(3)-C(2)	108.93(11)
C(4)-C(3)-H(3A)	109.9
C(2)-C(3)-H(3A)	109.9
C(4)-C(3)-H(3B)	109.9
C(2)-C(3)-H(3B)	109.9
H(3A)-C(3)-H(3B)	108.3
N(2)-C(4)-C(3)	109.48(11)
N(2)-C(4)-C(8)	104.14(11)
C(3)-C(4)-C(8)	110.21(11)
N(2)-C(4)-H(4A)	110.9
C(3)-C(4)-H(4A)	110.9
C(8)-C(4)-H(4A)	110.9
N(2)-C(5)-C(6)	107.49(11)
N(2)-C(5)-C(1)	106.91(11)
C(6)-C(5)-C(1)	108.98(12)
N(2)-C(5)-H(5)	111.1
C(6)-C(5)-H(5)	111.1
C(1)-C(5)-H(5)	111.1
C(5)-C(6)-C(7)	109.38(11)
C(5)-C(6)-H(6A)	109.8
C(7)-C(6)-H(6A)	109.8
C(5)-C(6)-H(6B)	109.8
C(7)-C(6)-H(6B)	109.8
H(6A)-C(6)-H(6B)	108.2
N(1)-C(7)-C(6)	107.01(11)
N(1)-C(7)-C(8)	106.48(11)
C(6)-C(7)-C(8)	109.28(11)
N(1)-C(7)-H(7)	111.3
C(6)-C(7)-H(7)	111.3
C(8)-C(7)-H(7)	111.3

N(7)-C(8)-C(4)	110.72(11)
N(7)-C(8)-N(8)	102.96(10)
C(4)-C(8)-N(8)	109.69(11)
N(7)-C(8)-C(7)	111.62(11)
C(4)-C(8)-C(7)	110.73(11)
N(8)-C(8)-C(7)	110.88(11)
N(6')-N(1)-C(2)	119.90(11)
N(6)-N(1)-C(2)	119.90(11)
N(6')-N(1)-C(7)	121.36(11)
N(6)-N(1)-C(7)	121.36(11)
C(2)-N(1)-C(7)	118.48(11)
N(3)-N(2)-C(4)	120.04(11)
N(3)-N(2)-C(5)	120.18(11)
C(4)-N(2)-C(5)	117.99(11)
O(10)-N(3)-O(9')	125.92(12)
O(10)-N(3)-O(9)	125.92(12)
O(10)-N(3)-N(2)	116.85(11)
O(9')-N(3)-N(2)	117.23(11)
O(9)-N(3)-N(2)	117.23(11)
O(11)-N(4)-O(12)	126.32(13)
O(11)-N(4)-C(1)	117.68(12)
O(12)-N(4)-C(1)	115.97(12)
O(2)-N(5)-O(1)	126.48(13)
O(2)-N(5)-C(1)	117.34(12)
O(1)-N(5)-C(1)	116.12(12)
O(3)-N(6)-O(4)	125.81(12)
O(3)-N(6)-N(1)	117.25(12)
O(4)-N(6)-N(1)	116.94(12)
O(3)-N(6')-O(4)	125.81(12)
O(3)-N(6')-N(1)	117.25(12)
O(4)-N(6')-N(1)	116.94(12)
O(6)-N(7)-O(5)	126.46(13)
O(6)-N(7)-C(8)	117.08(12)
O(5)-N(7)-C(8)	116.45(12)
O(8)-N(8)-O(7)	126.28(13)
O(8)-N(8)-C(8)	116.69(12)
O(7)-N(8)-C(8)	117.02(12)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	15(1)	13(1)	16(1)	-2(1)	6(1)	-3(1)
C(2)	14(1)	15(1)	13(1)	-1(1)	1(1)	0(1)
C(3)	11(1)	15(1)	17(1)	-3(1)	2(1)	-1(1)
C(4)	11(1)	12(1)	18(1)	1(1)	6(1)	1(1)
C(5)	10(1)	14(1)	18(1)	1(1)	5(1)	0(1)
C(6)	11(1)	16(1)	15(1)	0(1)	1(1)	0(1)
C(7)	12(1)	13(1)	14(1)	0(1)	1(1)	-1(1)
C(8)	13(1)	13(1)	14(1)	2(1)	3(1)	3(1)
N(1)	16(1)	10(1)	15(1)	1(1)	1(1)	0(1)
N(2)	13(1)	10(1)	23(1)	3(1)	8(1)	2(1)
N(3)	18(1)	12(1)	15(1)	0(1)	4(1)	0(1)
N(4)	17(1)	18(1)	17(1)	-3(1)	7(1)	-3(1)
N(5)	21(1)	17(1)	19(1)	-4(1)	10(1)	-5(1)
N(6)	11(1)	14(1)	23(1)	4(1)	7(1)	1(1)
O(9)	22(1)	17(1)	40(1)	4(1)	14(1)	-2(1)
N(6')	11(1)	14(1)	23(1)	4(1)	7(1)	1(1)
O(9')	22(1)	17(1)	40(1)	4(1)	14(1)	-2(1)
N(7)	18(1)	18(1)	15(1)	1(1)	6(1)	5(1)
N(8)	19(1)	21(1)	14(1)	0(1)	4(1)	6(1)
O(1)	20(1)	29(1)	46(1)	4(1)	19(1)	3(1)
O(2)	32(1)	34(1)	21(1)	8(1)	8(1)	-7(1)
O(3)	26(1)	23(1)	19(1)	10(1)	4(1)	4(1)
O(4)	18(1)	11(1)	32(1)	-2(1)	7(1)	-1(1)
O(5)	31(1)	14(1)	33(1)	-2(1)	13(1)	4(1)
O(6)	17(1)	27(1)	42(1)	-3(1)	14(1)	1(1)
O(7)	26(1)	32(1)	18(1)	-6(1)	-1(1)	-2(1)
O(8)	40(1)	30(1)	22(1)	11(1)	6(1)	-5(1)
O(10)	19(1)	15(1)	26(1)	2(1)	6(1)	7(1)
O(11)	36(1)	17(1)	29(1)	-5(1)	4(1)	3(1)
O(12)	23(1)	30(1)	19(1)	-7(1)	-1(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(2)	1145	6058	779	17
H(3A)	-616	5688	1872	18
H(3B)	-2	4560	1515	18
H(4A)	473	4501	3225	16
H(5)	5134	4315	2556	16
H(6A)	5556	6247	2791	17
H(6B)	5337	5680	3757	17
H(7)	3527	7272	3420	16

Single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow recrystallization from acetone. The result of X-ray diffraction indicates that compound **1** crystallizes in the monoclinic space group $P2_1/c$. Due to the introduction of the two nitrogen atoms, the skeleton of the diazaadamantane has a few changes in comparison with 2,2,4,4,6,6-hexanitroadamantane (HNA). The four C-N bond lengths are 1.467 Å, 1.465 Å, 1.469 Å and 1.470 Å, which are shorter than C-C bonds of HNA (1.525 Å) and similar to C-N bonds of 2,4,4,8,8-pentanitro-2-azaadamantane (1.468 Å and 1.466 Å). The C-N-C angles of 2,6-diazaadamantane are 118.48° and 117.99°, which is larger than the C-C-C angle of HNA (109.5°). The crystal density was determined to be 1.959 g cm⁻³, which falls in the range of crystal densities of new high-performance energetic materials (1.8-2.0 g cm⁻³) and is much higher than known energetic materials with adamantane or azaadamantane skeletons.