Supporting Information

For

Design and Synthesis of Nitro Containing Cage Heterocycles as High-Density Materials Derived from Pentacycloundecane (PCUD) Systems

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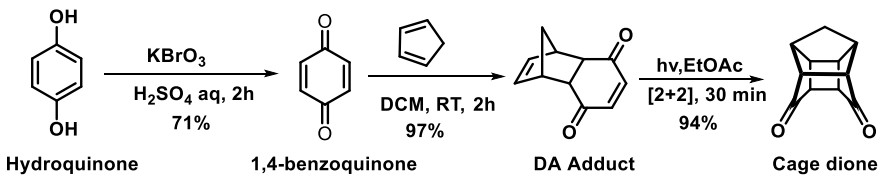
Experimental Section

General Remarks:

All the reactions were monitored by thin layer chromatography (TLC) using appropriate solvent systems. Reactions involving oxygen-sensitive reagents or catalysts were performed in degassed solvents. Anhydrous ethyl acetate, methanol, and dichloromethane were obtained by distillation from sodium benzophenone immediately prior to use. Dichloromethane (CH_2Cl_2) and was distilled from CaH_2. Sodium sulphate was dried in an oven at 130 °C for 1 d. All solvent extracts were washed successively with water and brine (aq. sat. NaCl solution), dried with anhyd. Na_2SO_4, and concentrated at reduced pressure in a rotary evaporator. Yields refer to the chromatographically isolated samples. All the commercial grade reagents such as dicyclopentadiene, hydroquinone, nitromethane and sodium methoxide were used without further purification. NMR samples were generally analysed in $CDCl_3$ solvent, and chemical shifts are reported in δ values using tetramethylsilane (TMS) as an internal standard. The standard abbreviation s, bs, d, t, q, quint, sext, sept and m, refer to singlet, broad singlet, doublet, triplet, quartet, quintet, sextet, septet, and multiplet, respectively. Coupling constants (*J*) are reported in Hz. All ^{1}H NMR and ^{13}C NMR spectroscopic data were recorded with Bruker (AVANCE IIITM) 500 MHz and Bruker (AVANCE IIITM) 400 MHz spectrometers. High-resolution mass spectrometry (HRMS) measurements of unknown compounds were done by using Bruker (Maxis Impact)/Micromass Q-ToF spectrometers and Agilent (AdvanceBio 6545XT LC/Q-TOF). The melting points (M.P.'s) of solid compounds were obtained from a Buchi 560 melting point apparatus and are uncorrected. X-ray diffraction data were collected on a Bruker D8 QUEST (APEX-II CCD) diffractometer by using Mo Kα (λ = 0.71073)/Cu Kα (λ = 1.54184).

General Experimental Procedure for [2+2] Photocycloaddition: Synthesis of Cage Diones Under UV Irradiation (125 W Hg Lamp)

All cage diones **11, 12, 13, 14, 15, 16, 17,** and **18** were prepared based on known literature methods using respective Diels-Alder (DA) adducts under UV irradiation from 125 W Hg lamp for 30–60 min with Pyrex immersion well in dry ethyl acetate solvent. [1–7]



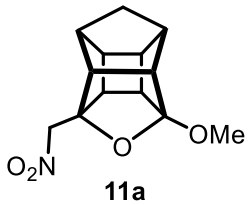
General Procedures and Characterisation Data for All (Known/New) Compounds

To a precooled (0°C) solution of methanol (5 ml) in two necks round bottom flask, sodium methoxide (4.0 equiv.) was added. Later, nitromethane (excess) was added dropwise with constant stirring. After 5 min, pentacyclic dione (200 mg, 1.0 equiv.) was added. After the addition of pentacyclic dione had been completed, the reaction mixture was allowed to stir for 2 h at room temperature. Then, water was added to the reaction mixture and the resulting mixture was extracted with methylene chloride (3×10 ml). The combined organic extracts were washed with water, dried (sodium sulphate) and filtered and the compound was obtained by drying under reduced pressure.

Preparation of nitro compounds 11a, 11b, and 11c

Prepared according to the above general procedure using cage dione **11** (200 mg, 1.14 mmol). Column chromatography (5% ethyl acetate in petroleum ether) afforded the pure liquid cage compound **11a**. Colourless liquid; Yield: 94 mg (33%).

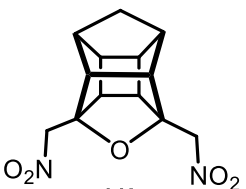
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.74 (d, *J* = 0.4 Hz, 2H), 3.45 (s, 3H), 2.83-2.90 (m, 4H), 2.69-2.75 (m, 2H), 2.50-2.58 (m, 2H), 1.92 (d, *J* = 10.7 Hz, 1H), 1.58 (d, *J* = 10.7 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 122.58, 87.89, 77.35, 57.29, 54.42, 53.79, 47.22, 45.05, 43.68, 43.61, 43.56, 42.03, 41.68 ppm. **HRMS (ESI) m/z:** calculated for $C_{13}H_{16}NO_4$ $[M+H]^+$: 250.1076; found 250.1075.



11a

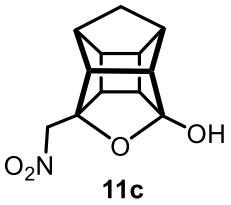
Continued elution of the column chromatography (5% ethyl acetate in petroleum ether) afforded the pure solid cage compound **11b**.Colourless crystalline solid; Yield: 73 mg (23%); M.P. 108-110 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.79 (s, 4H), 2.92 (t, *J* = 3.2 Hz, 2H), 2.85 (s, 2H), 2.75 (m, 2H), 2.53 (d, *J* = 1.3 Hz, 2H), 1.98 (d, *J* = 10.8 Hz, 1H), 1.62 (d, *J* = 10.8 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 93.40, 76.76, 57.98, 47.40, 44.52, 43.88, 41.76 ppm. **HRMS (ESI) m/z:** calculated for $C_{13}H_{14}NaN_2O_5$ $[M+Na]^+$: 301.0793; found 301.0793.



11b

Further elution of the column chromatography (12-15% ethyl acetate in petroleum ether) afforded the pure solid cage compound **11c**. Colourless microcrystalline solid; Yield: 110 mg (41%); M.P. 134-136 °C

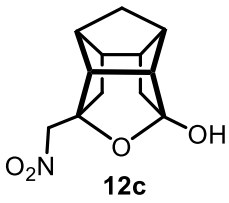


11c

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.74 (s, 2H), 4.34 (bs, 1H), 2.86-2.90 (m, 2H), 2.80-2.83 (m, 2H), 2.67-2.68 (m, 3H), 2.50 (t, *J* = 4.92 Hz, 1H), 1.92 (d, *J* = 10.8 Hz, 1H), 1.58 (d, *J* = 10.8 Hz, 1H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 119.27, 88.36, 77.09, 57.65, 57.30, 47.68, 47.24, 44.96, 43.87, 43.64, 42.17, 41.82 ppm. **HRMS (ESI) m/z:** calculated for $C_{12}H_{14}NO_4$ $[M+H]^+$: 236.0913; found 236.0912

Preparation of nitro compound 12c

Prepared according to the above general procedure using cage dione **12** (200 mg, 1.13 mmol). Column chromatography (20% ethyl acetate in petroleum ether) afforded the pure solid cage compound **12c**. Colourless crystalline solid; Yield: 215 mg (80%); M.P. 108-110 °C

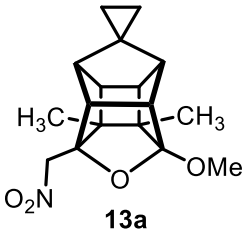


12c

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.66 (d, *J* = 11.6 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 3.17 (d, *J* = 24.2 Hz, 1H), 2.97 (d, *J* = 4.6 Hz, 1H), 2.49-2.53 (m, 2H), 2.32 (s, 1H), 2.28 (s, 1H), 2.14 (d, *J* = 13.6 Hz, 1H), 2.02 (d, *J* = 13.6 Hz, 1H), 1.77-1.82 (m, 2H), 1.65-1.73 (m, 2H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 116.26, 87.70, 80.69, 59.48, 56.60, 49.17, 47.71, 43.10, 42.45, 41.72, 40.79, 37.85 ppm. **HRMS (ESI) m/z:** calculated for $C_{12}H_{15}NaNO_4$ $[M+Na]^+$: 260.0896; found 260.0896.

Preparation of nitro compounds 13a, 13b, and 13c

Prepared according to the above general procedure using cage dione **13** (200 mg, 0.876 mmol). Column chromatography (5% ethyl acetate in petroleum ether) afforded the pure solid cage compound **13a**. White solid; Yield: 80 mg (30%); M.P. 96-98 °C

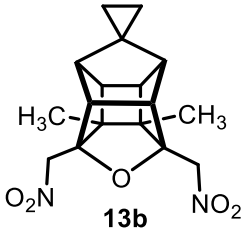


13a

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.71 (d, *J* = 11.8 Hz, 1H), 4.54 (d, *J* = 11.8 Hz, 1H), 3.49 (s, 3H), 3.11-3.13 (m, 2H), 2.46-2.47 (m, 2H), 1.85 (d, *J* = 2.2 Hz, 2H), 1.0 (s, 3H), 0.93 (s, 3H), 0.48-.51 (m, 2H), 0.31-.35 (m, 2H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 120.64, 87.57, 75.87, 56.58, 55.28, 54.25, 53.71, 50.56, 50.03, 48.62, 47.00, 46.33, 40.21, 12.54, 11.24, 5.26, 5.13 ppm. **HRMS (ESI) m/z:** calculated for $C_{17}H_{22}NO_4$ $[M+H]^+$: 304.1549; found 304.1548.

Continued elution of the column chromatography (5% ethyl acetate in petroleum ether) afforded the pure sticky solid cage compound **13b**. off White sticky solid; Yield: 15 mg (5%).

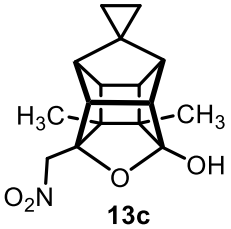
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.76 (d, *J* = 12.4 Hz, 2H), 4.62 (d, *J* = 12.4 Hz, 2H), 3.33-3.36 (m, 1H), 3.11-3.16 (m, 2H), 2.93-2.95 (m, 1H), 2.46-2.58 (m, 1H), 2.09 (t, *J* = 4.4 Hz, 1H), 1.23 (s, 3H), 1.05 (s, 3H), 0.51-.58 (m, 2H), 0.32-.39 (m, 2H) ppm. **HRMS (ESI) m/z:** calculated for $C_{17}H_{20}NaN_2O_5$ $[M+Na]^+$: 355.1264; found 355.1264.



13b

Further elution of the column chromatography (15% ethyl acetate in petroleum ether) afforded the pure solid cage compound **13c**. Colourless crystalline solid; Yield: 81 mg (32%); M.P. 164-166 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 3.57 (s, 1H), 3.12-3.17 (m, 1H), 2.79-2.84 (m, 2H), 2.47-2.52 (m, 2H), 1.95 (t, *J* = 4.8 Hz, 1H), 1.85 (t, *J* = 4.8 Hz, 1H), 1.0 (s, 3H), 0.98 (s, 3H), 0.48-.52 (m, 2H), 0.32-.34 (m, 2H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 117.55, 88.06, 75.80, 57.92, 56.74, 55.37, 52.99, 49.90, 48.46, 46.86, 46.85, 40.12, 12.49, 10.95, 5.24, 5.09 ppm. **HRMS (ESI) m/z:** calculated for $C_{16}H_{20}NO_4$ $[M+H]^+$: 290.1391; found 290.1391.

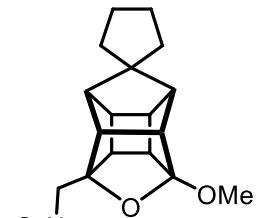


13c

Preparation of nitro compounds 14a, 14b, and 14c

Prepared according to the above general procedure using cage dione **14** (200 mg, 0.876 mmol). Column chromatography (5% ethyl acetate in petroleum ether) afforded the pure liquid cage compound **14a**. Viscous liquid; Yield: 93 mg (35%).

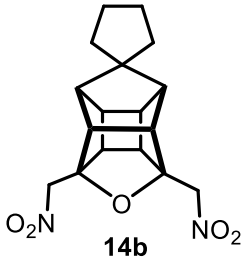
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73 (d, *J* = 1.0 Hz, 2H), 3.45 (s, 3H), 2.78-2.91 (m, 6H), 2.16-2.18 (m, 1H), 2.08-2.10 (m, 1H), 1.32-1.59 (m, 8H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 122.54, 87.85, 77.40, 68.75, 56.95, 54.11, 53.78, 53.00, 51.49, 47.11, 43.46, 42.08, 41.69, 33.19, 31.07, 25.67, 25.39 ppm. **HRMS (ESI) m/z:** calculated for $C_{17}H_{22}NO_4$ $[M+H]^+$: 304.1546; found 304.1545.



14a

Continued elution of the column chromatography (5% ethyl acetate in petroleum ether) afforded the pure solid cage compound **14b**. Colourless crystalline solid; Yield: 52 mg (18%); M.P. 98-100 °C

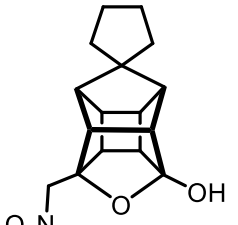
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.78 (d, *J* = 0.5 Hz, 4H), 2.91-2.93 (m, 4H), 2.83-2.84 (m, 2H), 2.12-2.14 (m, 2H) 1.50-1.59 (m, 6H), 1.30-1.33 (m, 2H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 93.35, 76.83, 69.11, 57.63, 52.43, 47.54, 41.79, 33.15, 31.23, 25.67, 25.35 ppm. **HRMS (ESI) m/z:** calculated for $C_{17}H_{20}NaN_2O_5$ $[M+Na]^+$: 355.1249; found 355.1249.



14b

Further elution of the column chromatography (12-15% ethyl acetate in petroleum ether) afforded the pure solid cage compound **14c**. Off white solid; Yield: 99 mg (39%); M.P. 102-104 ℃

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.87 (bs, 1H), 4.71 (s, 2H), 2.72-2.77 (m, 2H), 2.62-2.66 (m, 2H), 2.25-2.28 (m, 2H), 2.07-2.15 (m, 2H), 1.49-1.59 (m, 6H), 1.30-1.33 (m, 2H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 119.27, 88.27, 77.04, 68.65, 57.19, 56.80, 52.84, 51.71, 47.31, 46.99, 42.09, 41.79, 33.09, 31.00, 25.60, 25.33 ppm. **HRMS (ESI) m/z:** calculated for $C_{16}H_{20}NO_4$ $[M+H]^+$: 312.1207; found 312.1207.

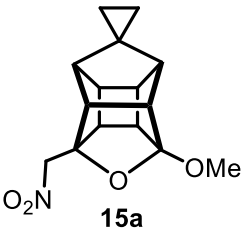


14c

Preparation of nitro compounds 15a, 15b, and 15c

Prepared according to the above general procedure using cage dione **15** (200 mg, 0.998 mmol). Column chromatography (5% ethyl acetate in petroleum ether) afforded the pure liquid cage compound **15a**. Colourless viscous liquid; Yield: 91 mg (33%).

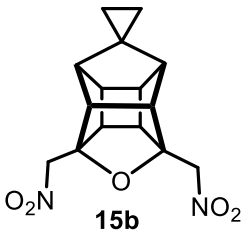
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73 (d, *J* = 1.4 Hz, 2H), 3.45 (s, 2H), 3.0 (s, 2H), 2.85-2.91 (m, 4H), 1.84 (m, 2H), 0.50-.54 (m, 2H), 0.33-.37 (m, 2H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 122.48, 87.78 77.32, 57.21, 54.32, 53.75, 51.25, 49.71, 47.65, 44.07, 42.25, 41.83, 39.97, 5.30, 5.16 ppm. **HRMS (ESI) m/z:** calculated for $C_{15}H_{18}NO_4$ $[M+H]^+$: 276.1232; found 276.1232.



15a

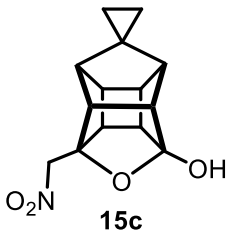
Continued elution of the column chromatography (5% ethyl acetate in petroleum ether) afforded the pure solid cage compound **15b**. Colourless crystalline solid; Yield: 85 mg (28%); M.P. 146-148 ℃

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.79 (d, *J* =1.4 Hz, 4H), 3.0 (s, 2H), 2.92-2.95 (m, 4H), 1.89 (s, 2H), 0.53-.56 (m, 2H), 0.35-.39 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 93.30, 76.80, 57.98, 50.73, 48.16, 41.99, 40.15, 5.33, 5.28 ppm. **HRMS (ESI) m/z:** calculated for $C_{15}H_{16}NaN_2O_5$ $[M+Na]^+$: 327.0951; found 327.0951.



15b

Further elution of the column chromatography (15% ethyl acetate in petroleum ether) afforded the pure solid cage compound **15c**. White colour solid; Yield: 94 mg (36%); M.P. 120-122 ℃

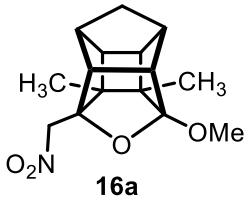


15c

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70 (s, 2H), 3.04 (bs, 1H), 2.89-3.03 (m, 4H), 2.81-2.86 (m, 1H), 2.68-2.72 (m, 1H), 2.03 (t, *J* = 4.7 Hz, 1H), 1.89 (t, *J* = 4.64 Hz, 1H), 0.51-.57 (m, 2H), 0.36-.43 (m, 2H) ppm. **^{13}C NMR (100.6 MHz, DMSO-d_6):** δ 118.29, 87.40 76.88, 56.78, 56.37, 50.27, 49.31, 47.20, 47.14, 46.66, 41.57, 41.53, 5.05, 4.91 ppm. **HRMS (ESI) m/z:** calculated for $C_{14}H_{16}NO_4$ $[M+H]^+$: 262.1087; found 262.1087.

Preparation of nitro compounds 16a, 16b, and 16c

Prepared according to the above general procedure using cage dione **16** (200 mg, 0.988 mmol). Column chromatography (5% ethyl acetate in petroleum ether) afforded the pure liquid cage compound **16a**. Colourless viscous liquid; Yield: 100 mg (36%).

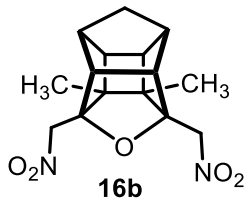


16a

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.68 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 11.6 Hz, 1H) 3.47 (s, 3H), 2.92 (s, 2H), 2.50 (t, *J* = 1.52 Hz, 2H), 2.27-2.29 (m, 2H), 1.89 (d, *J* = 10.5 Hz, 1H), 1.54 (d, *J* = 10.5 Hz, 1H), 0.98 (s, 3H), 0.92 (s, 3H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 120.63, 87.56, 75.87, 56.48, 54.90, 53.83, 53.68, 50.47, 46.75, 46.12, 43.90, 43.73, 42.41, 12.46, 11.19 ppm. **HRMS (ESI) m/z:** calculated for $C_{15}H_{20}NO_4$ $[M+H]^+$: 278.1394; found 278.1393.

Continued elution of the column chromatography (5% ethyl acetate in petroleum ether) afforded the pure colourless

crystalline solid cage compound **16b**. Colourless crystalline solid; Yield: 24 mg (8%); M.P. 146-148 ℃

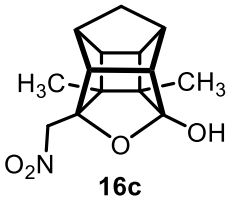


16b

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73 (d, *J*= 12.0 Hz, 2H), 4.61 (d, *J*= 12.0 Hz, 2H), 2.93-3.00 (m, 2H), 2.52-2.57 (m, 2H), 2.35-2.40 (m, 2H), 1.93-2.00 (m, 1H), 1.59-1.63 (m, 1H), 1.03 (s, 6H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 93.38, 75.43, 61.35, 57.19, 55.95, 46.59, 43.95, 43.40, 12.40 ppm. **HRMS (ESI) m/z:** calculated for $C_{15}H_{19}N_2O_5$ $[M+H]^+$: 329.1106; found 329.1105.

Further elution of the column chromatography (12-15% ethyl acetate in petroleum ether) afforded the pure colourless crystalline solid cage compound **16c**. Colourless crystalline solid; Yield: 105 mg (40%); M.P. 144-146 ℃

^{1}H NMR (400 MHz, DMSO-d_6): δ 4.75 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 2.73-2.77 (m, 1H), 2.32-2.44 (m, 3H), 2.12 (s, 1H), 1.71 (d, *J* = 10.2 Hz, 1H), 1.35 (d, *J* = 10.2 Hz, 1H), 0.78 (s, 3H), 0.74 (s, 3H) ppm. **^{13}C NMR (100.6 MHz, DMSO-d_6):** δ 116.91, 87.14, 76.01, 56.93, 55.71, 54.33, 52.00, 46.20, 43.27, 42.78, 41.76, 12.08, 11.33 ppm. **HRMS (ESI) m/z:** calculated for $C_{14}H_{18}NO_4$ $[M+H]^+$: 264.1230; found 264.1229.

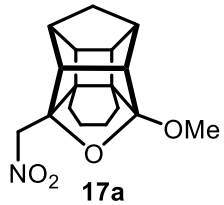


16c

Preparation of nitro compounds 17a, 17b, and 17c

Prepared according to the above general procedure using cage dione **17** (200 mg, 0.876 mmol). Column chromatography (5% ethyl acetate in petroleum ether) afforded the pure solid cage compound **17a**. Colourless crystalline solid; Yield: 98 mg (37%); M.P. 98-100 ℃

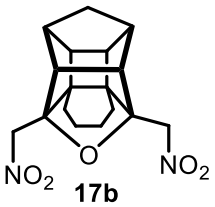
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.72 (d, *J* = 11.72 Hz, 1H), 4.56 (d, *J* = 11.72 Hz, 1H), 3.48 (s, 3H), 2.92-2.95 (m, 2H), 2.49-2.51 (m, 4H), 1.90-1.93 (d, *J* = 10.6 Hz, 1H), 1.57-1.60 (m, 8H), 1.46 (m, 1H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 121.07, 87.80, 75.65, 56.74, 54.40, 53.75, 52.32, 50.67, 44.18, 43.94, 43.80, 42.51, 21.63, 19.69, 17.77, 17.18 ppm. **HRMS (ESI) m/z:** calculated for $C_{17}H_{21}KN_2O_5$ $[M+K]^+$: 342.1102; found 342.1106.



17a

Continued elution of the column chromatography (5% ethyl acetate in petroleum ether) afforded the pure solid cage compound **17b**. Colourless crystalline solid; Yield: 58 mg (20%); M.P. 122-124 ℃

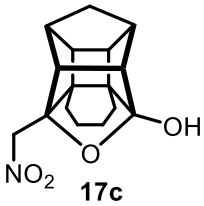
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73 (d, *J* = 11.92 Hz, 2H), 4.61 (d, *J* = 11.92 Hz, 2H), 2.92-2.98 (m, 2H), 2.50-2.59 (m, 4H), 1.95-1.97 (d, *J* = 10.8 Hz, 1H), 1.60-1.66 (m, 6H), 1.49-1.53 (m, 2H), 1.40-1.45 (m, 1H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 93.37, 75.05, 57.31, 55.15, 43.97, 43.37, 43.22, 20.25, 16.49 ppm. **HRMS (ESI) m/z:** calculated for $C_{17}H_{20}NaN_2O_5$ $[M+Na]^+$: 355.1264; found 355.1264.



17b

Further elution of the column chromatography (12-15% ethyl acetate in petroleum ether) afforded the pure solid cage compound **17c**. Colourless crystalline; Yield: 96 mg (38%); M.P. 156-158 ℃

^{1}H NMR (400 MHz, DMSO-d_6): δ 4.73 (d, *J* = 12.1 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 2.71-2.75 (m, 1H), 2.40-2.46 (m, 2H), 2.32-2.34 (m, 3H) 1.73 (d, *J* = 10.2, 1H), 1.37-1.41 (m, 6H), 1.19-1.22 (m, 2H) ppm. **^{13}C NMR (100.6 MHz, DMSO-d_6):** δ 117.15, 87.28, 75.76, 56.96, 55.89, 53.88, 50.39,

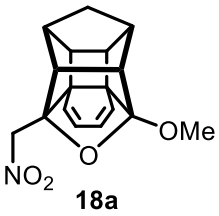


17c

43.90, 43.59, 43.28, 42.82, 41.83, 21.01, 19.75, 17.44, 17.05 ppm. **HRMS (ESI) m/z:** calculated for $C_{16}H_{20}NO_4$ $[M+H]^+$: 290.1376; found 290.1375.

Preparation of nitro compounds 18a, 18b, and 18c

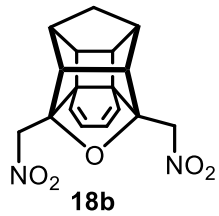
Prepared according to the above general procedure using cage dione **18** (200 mg, 0.891 mmol). Column chromatography (5% ethyl acetate in petroleum ether) afforded the pure solid cage compound **18a**. Colourless crystalline solid; Yield: 72 mg (27%); M.P. 134-136 ℃



18a

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82-5.92 (m, 2H), 5.47-5.59 (m, 2H), 4.76 (d, *J* =11.9 Hz, 1H), 4.69 (d, *J* =11.96 Hz, 1H), 3.52 (s, 3H), 3.00-3.04 (m, 2H), 2.86-2.92 (m, 2H), 1.83 (d, *J* = 10.7 Hz, 1H), 1.44 (d, *J* = 10.7 Hz, 1H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 125.60, 123.03, 122.72, 122.08, 120.09, 90.74, 75.05, 57.16, 55.46, 54.47, 53.99, 53.96, 53.48, 51.54, 44.79, 43.14, 42.00 ppm. **HRMS (ESI) m/z:** calculated for $C_{17}H_{18}NO_4$ $[M+H]^+$: 322.1049; found 322.1049.

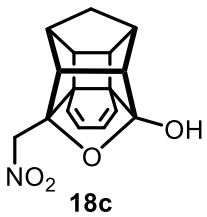
Continued elution of the column chromatography (5% ethyl acetate in petroleum ether) afforded the pure solid cage compound **18b**. Colourless crystalline solid; Yield: 44 mg (15%); M.P. 124-126 ℃



18b

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89-5.93 (m, 2H), 5.55-5.57 (m, 2H), 4.77 (d, *J* = 12.1 Hz, 2H), 4.72 (d, *J* = 12.1 Hz, 2H), 3.02 (d, *J* = 1.76 Hz, 2H), 2.95 (t, *J* = 1.56 Hz, 2H), 2.58-2.63 (m, 2H), 1.87 (d, *J* = 10.9 Hz, 1H), 1.45 (d, *J* = 10.9 Hz, 1H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 125.11, 120.89, 95.98, 74.77, 58.00, 56.53, 54.31, 44.39, 41.96 ppm. **HRMS (ESI) m/z:** calculated for $C_{17}H_{16}NaN_2O_5$ $[M+Na]^+$: 351.0955; found 351.0955.

Further elution of the column chromatography (12-15% ethyl acetate in petroleum ether) afforded the pure solid cage compound **18c**. Colourless crystalline solid; Yield: 99 mg (39%); M.P. 152-154 ℃

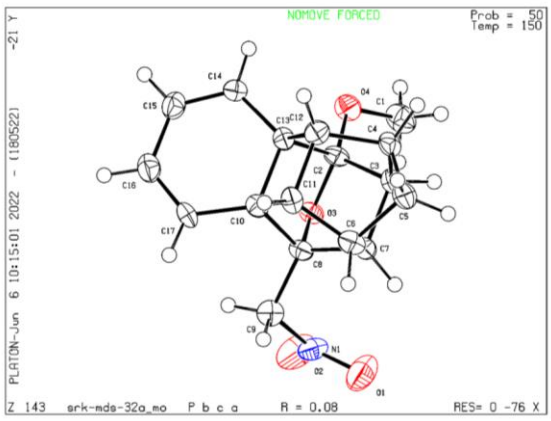


18c

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89-5.92 (m, 2H), 5.47-5.56 (m, 2H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 3.44 (bs, 1H), 3.02-3.07 (m, 1H), 2.91-2.96 (m, 2H), 2.76-2.81 (m, 1H), 2.71 (t, *J* = 4.7 Hz, 1H), 2.56 (t, *J* = 4.8 Hz, 1H), 1.82 (d, *J* = 10.8 Hz, 1H), 1.42 (d, *J* = 10.8 Hz, 1H) ppm. **^{13}C NMR (100.6 MHz, $CDCl_3$):** δ 125.53, 125.10, 120.63, 120.28, 119.42,

91.28, 75.06, 58.21, 57.34, 55.76, 54.42, 54.38, 53.07, 44.64, 43.07, 41.90 ppm. **HRMS (ESI) m/z:** calculated for $C_{16}H_{15}NaNO_4$ $[M+Na]^+$: 308.0893; found 308.0893.

(1R,2R,2aR,4S,9S,10S)-1-methoxy-10-(nitromethyl)-2,2a,2a1,3,4,4a-hexahydro-1H-1,4b,2,4-(epoxyethane[1,1,2,2]tetrayl)benzo[1,4]cyclobuta[1,2,3-cd]pentalene (18a) CCDC (2174597)



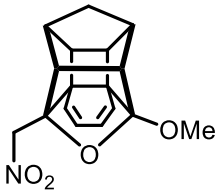
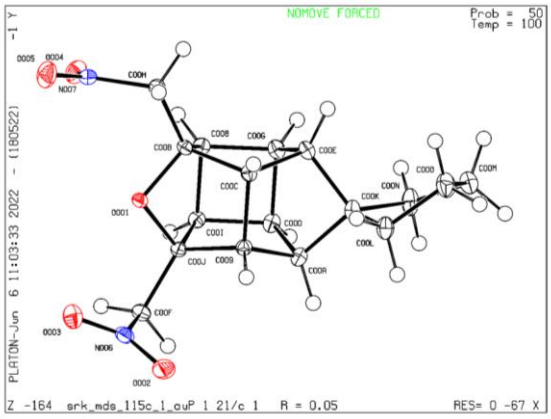


Table S1. X-ray crystallographic data and refinement parameters for **18a (CCDC 2174597)**

Identification code	SRK-MDS-32A_Mo
Empirical formula	$C_{17}H_{17}NO_4$
Formula weight	299.31
Temperature/K	150
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.2844(15)
b/Å	9.1450(8)
c/Å	24.787(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2784.6(5)
Z	8
ρ_{calc}g/cm^3	1.428
μ/mm^{-1}	0.102
F (000)	1264.0
Crystal size/mm^3	0.156 × 0.118 × 0.032
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.286 to 49.99
Index ranges	$-14 \leq h \leq 11$, $-10 \leq k \leq 10$, $-29 \leq l \leq 29$
Reflections collected	10475
Independent reflections	2454 [R_{int} = 0.1481, R_{sigma} = 0.1247]
Data/restraints/parameters	2454/0/200
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0760, wR_2 = 0.1612
Final R indexes [all data]	R_1 = 0.1404, wR_2 = 0.2125
Largest diff. peak/hole / e Å^{-3}	0.38/-0.44

(1'R,2a'S,2a1'R,4a'R,6'S,6a'S)-1',2a'-bis(nitromethyl)hexahydro-1'H,3'H-spiro[cyclopentane-1,5'-[1,3,4,6](epiethane[1,1,2,2]tetrayl)pentaleno[1,6-bc]furan] (14b) CCDC (2174974)



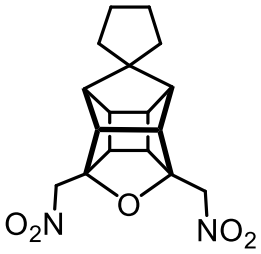
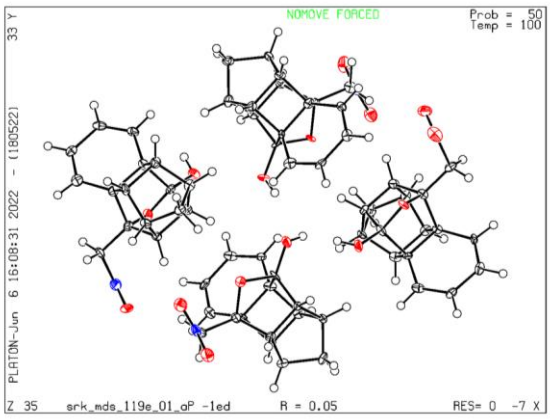


Table S1. X-ray crystallographic data and refinement parameters for **14b (CCDC 2174974)**

Identification code	SRK_MDS_115C_1_autored
Empirical formula	$C_{17}H_{20}N_2O_5$
Formula weight	332.35
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3658(4)
b/Å	10.8470(2)
c/Å	11.7593(4)
α/°	90
β/°	109.713(3)
γ/°	90
Volume/Å^3	1484.86(8)
Z	4
ρ_{calc}g/cm^3	1.487
μ/mm^{-1}	0.110
F(000)	704.0
Crystal size/mm^3	0.876 × 0.582 × 0.485
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.134 to 74.476
Index ranges	$-17 \leq h \leq 19$, $-17 \leq k \leq 17$, $-19 \leq l \leq 16$
Reflections collected	37476
Independent reflections	6540 [R_{int} = 0.0487, R_{sigma} = 0.0522]
Data/restraints/parameters	6540/0/217
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1101
Final R indexes [all data]	R_1 = 0.0772, wR_2 = 0.1232
Largest diff. peak/hole / e Å^{-3}	0.48/-0.31

(1R,2R,2aR,4S,9S,10S)-10-(nitromethyl)-2,2a,2a1,3,4,4a-hexahydro-1H-1,4b,2,4-(epoxyethane[1,1,2,2]tetrayl)benzo[1,4]cyclobuta[1,2,3-cd]pentalen-1-ol (18c) CCDC (2175009)



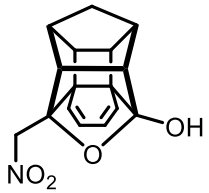
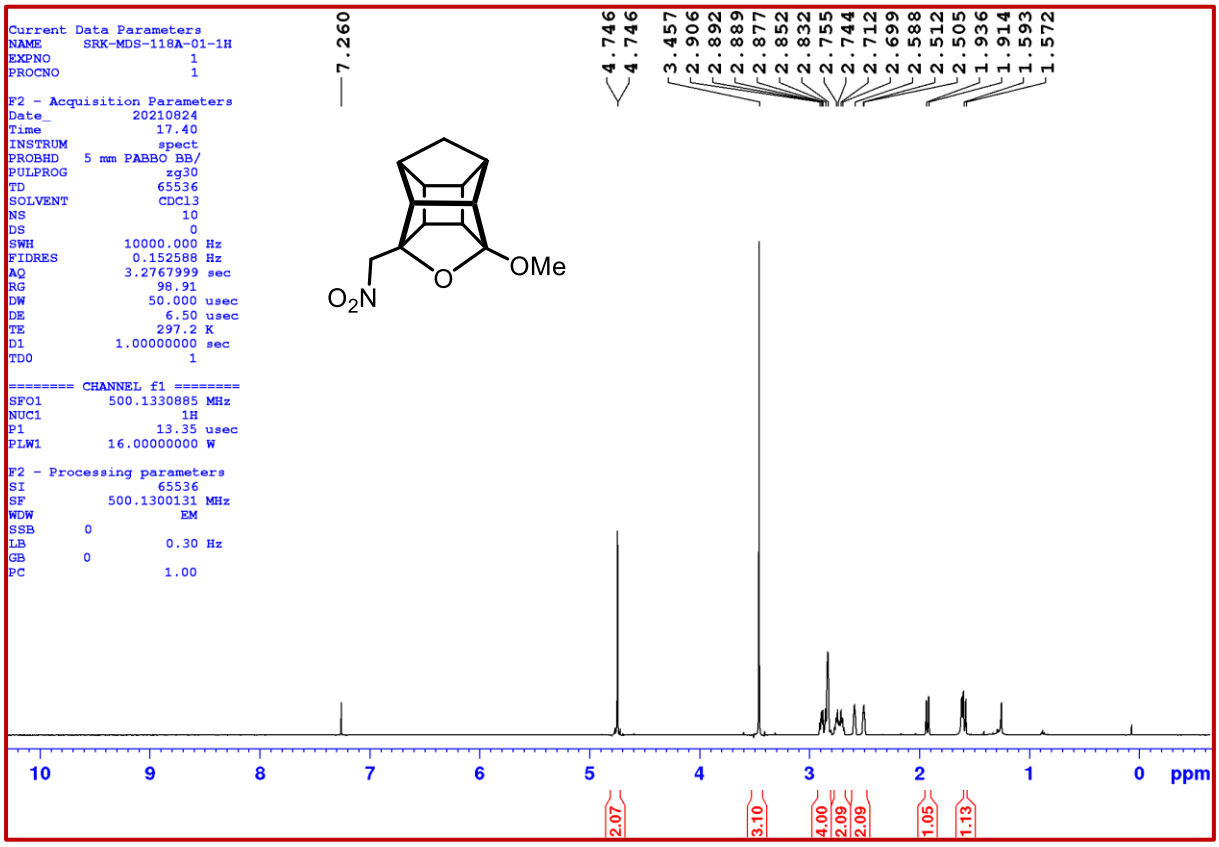


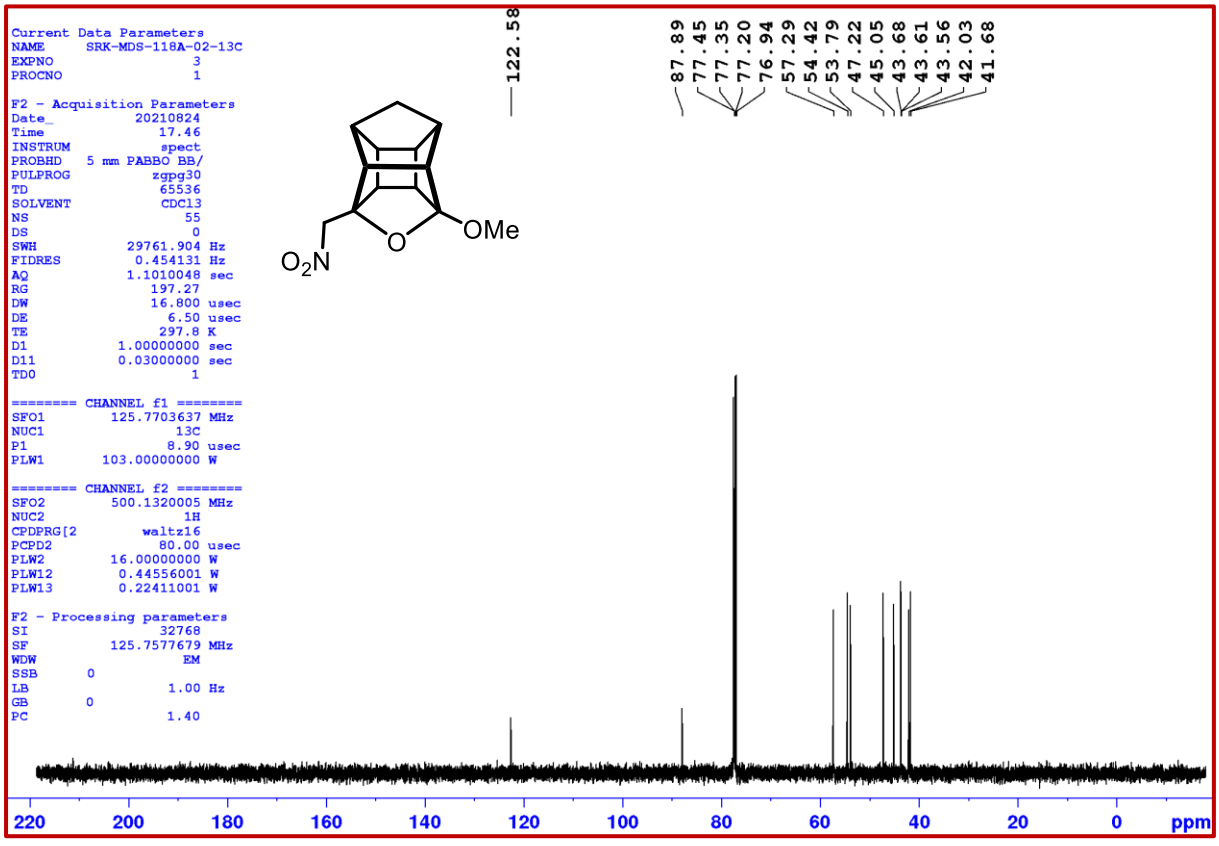
Table S1. X-ray crystallographic data and refinement parameters for **18c (CCDC 2175009)**

Identification code	SRK_MDS_119E_01_autored
Empirical formula	$C_{64}H_{60}N_4O_{16}$
Formula weight	1141.16
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.9853(11)
b/Å	14.012(2)
c/Å	19.196(2)
α/°	70.016(12)
β/°	89.958(10)
γ/°	82.431(10)
Volume/Å^3	2499.2(6)
Z	2
ρ_{calc}g/cm^3	1.516
μ/mm^{-1}	0.110
F (000)	1200.0
Crystal size/mm^3	0.485 × 0.246 × 0.0132
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.162 to 49.994
Index ranges	$-11 \le h \le 11$, $-16 \le k \le 16$, $-22 \le l \le 22$
Reflections collected	50004
Independent reflections	8794 [R_{int} = 0.1024, R_{sigma} = 0.0777]
Data/restraints/parameters	8794/0/761
Goodness-of-fit on F^2	0.951
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1165
Final R indexes [all data]	R_1 = 0.1249, wR_2 = 0.1585
Largest diff. peak/hole / e Å^{-3}	0.32/-0.36

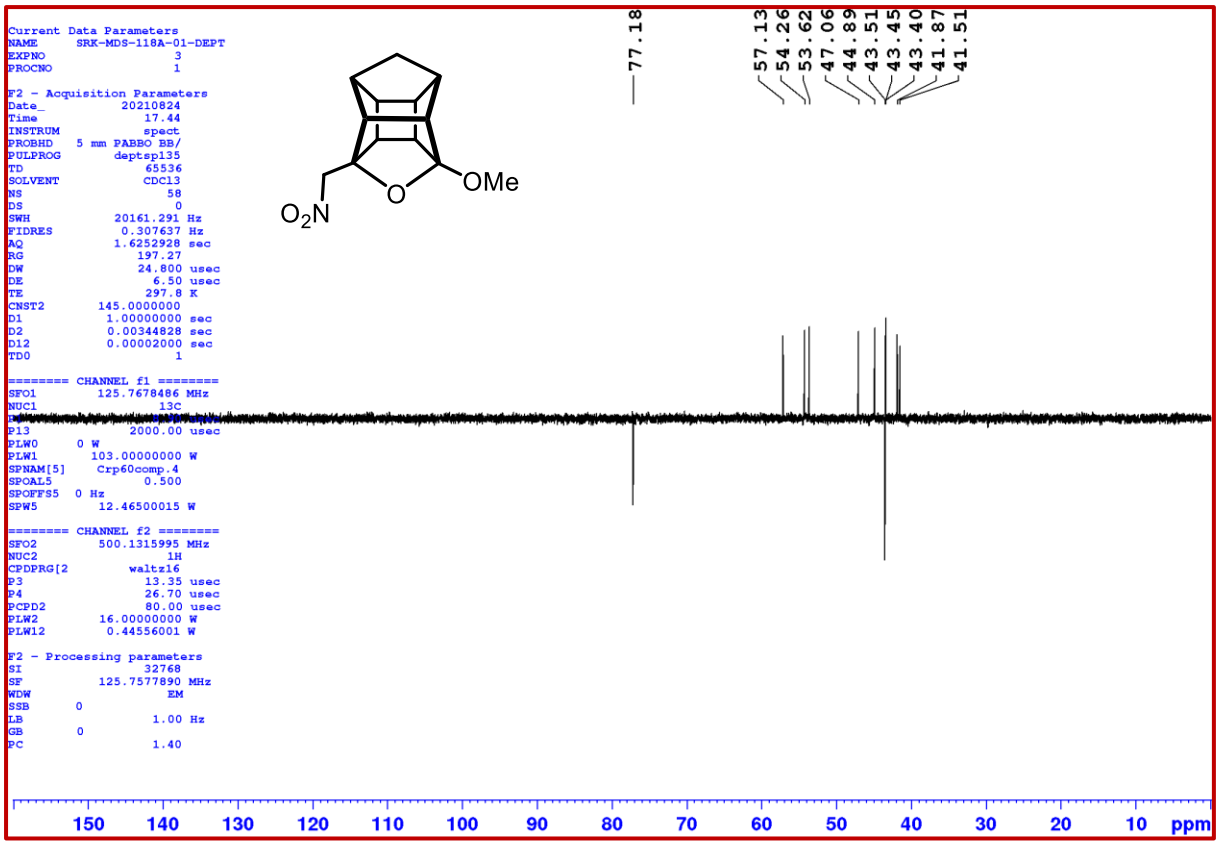
^{1}H NMR of Compound 11a (500 MHz, $CDCl_3$)



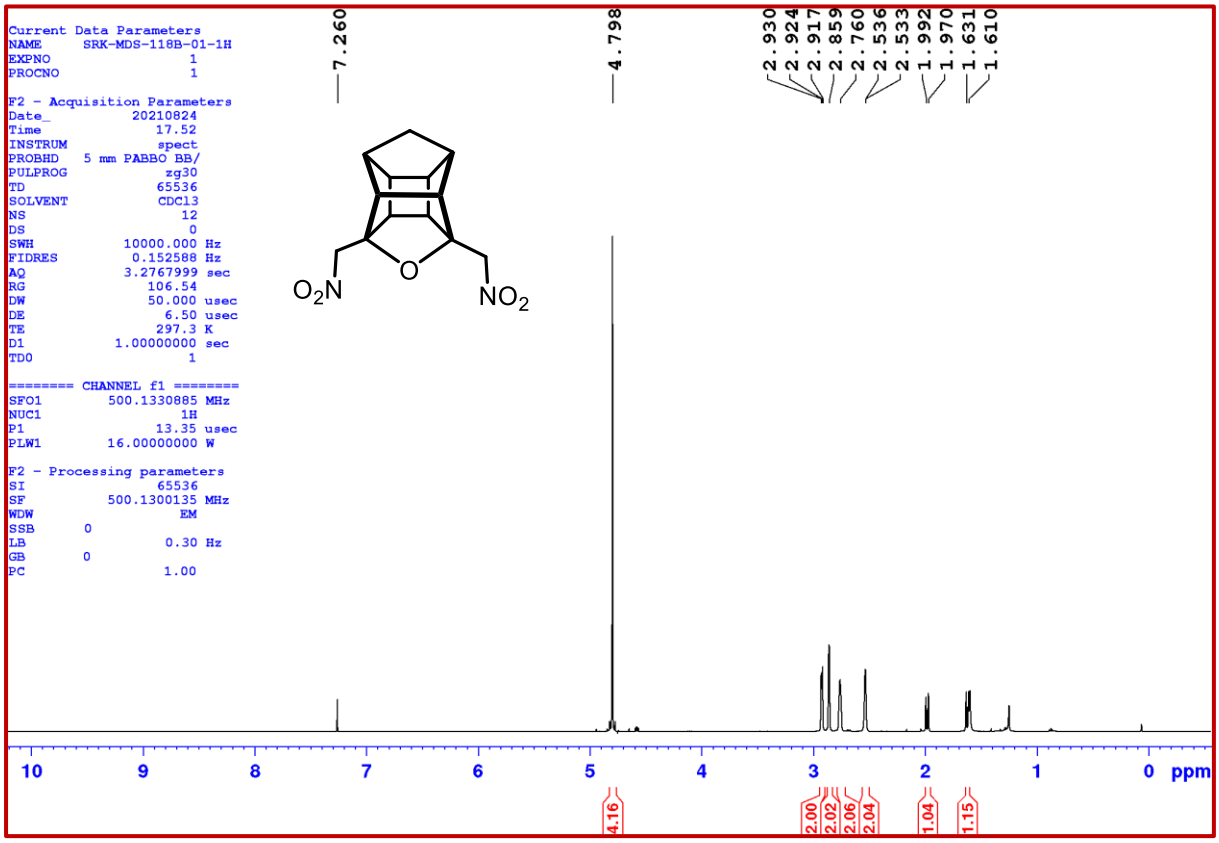
^{13}C NMR of Compound 11a (125 MHz, $CDCl_3$)



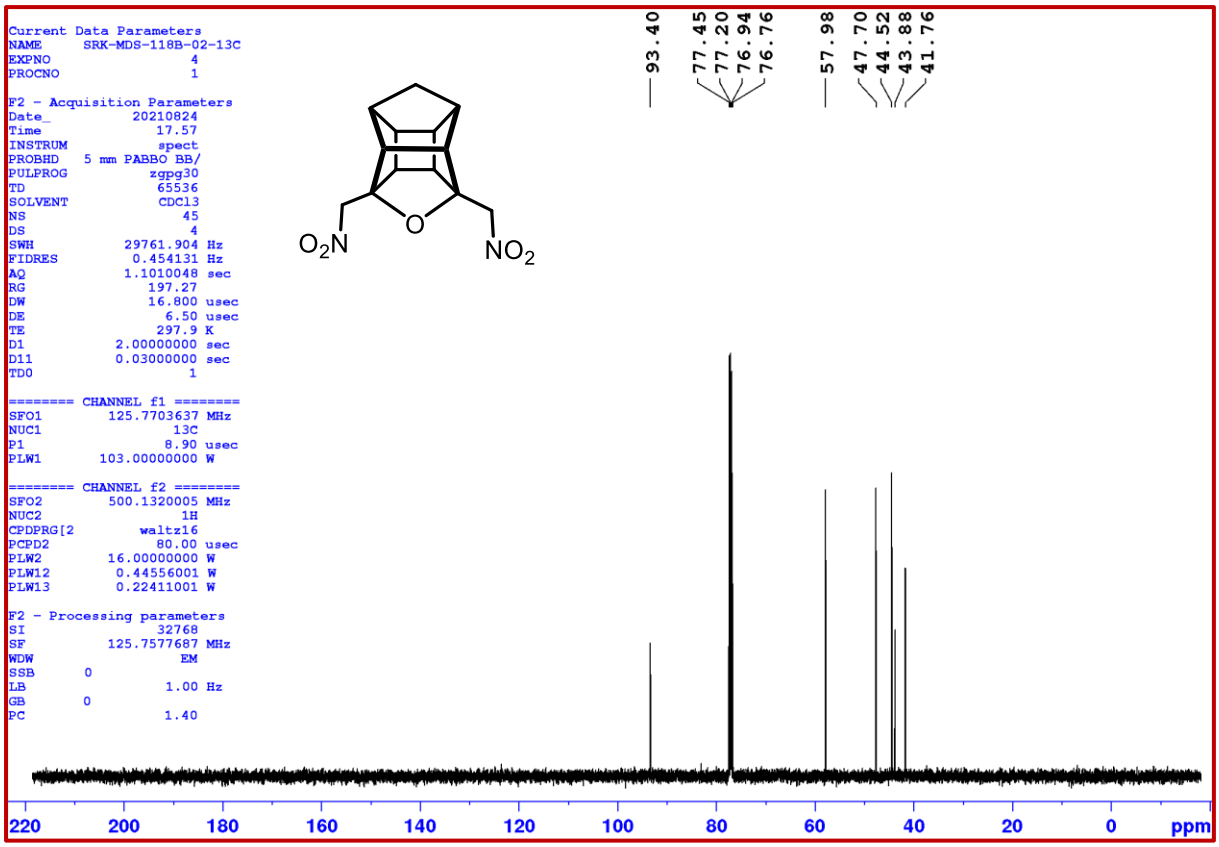
DEPT 135 NMR of Compound 11a (125 MHz, $CDCl_3$)



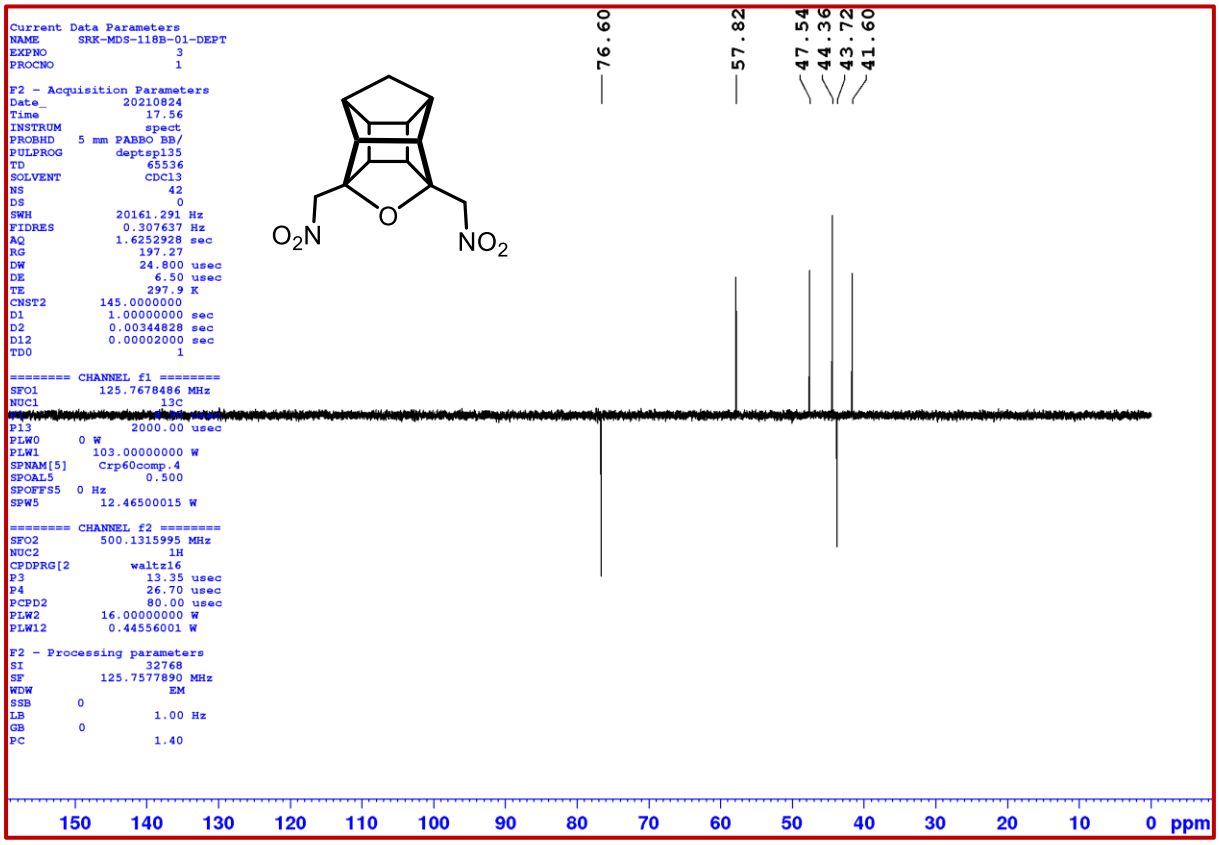
^{1}H NMR of Compound 11b (500 MHz, $CDCl_3$)



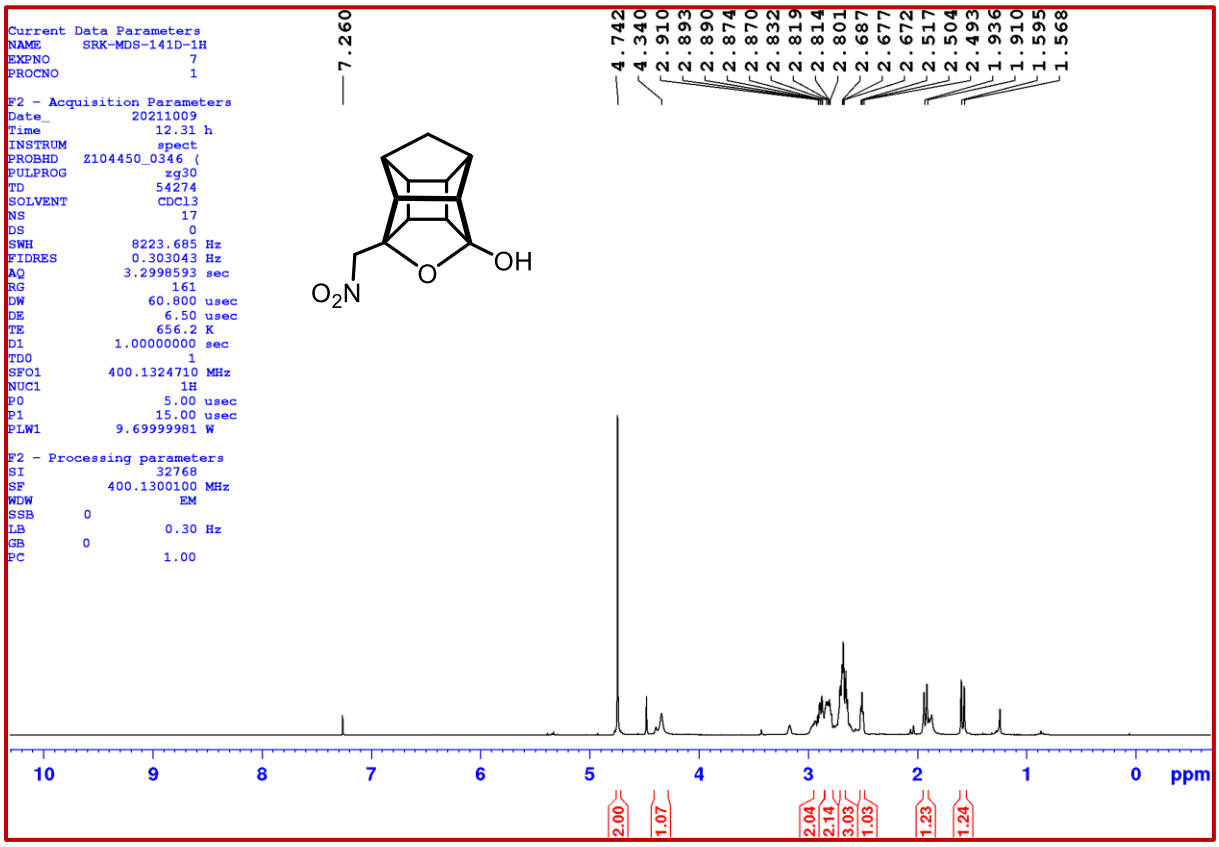
^{13}C NMR of Compound 11b (125 MHz, $CDCl_3$)



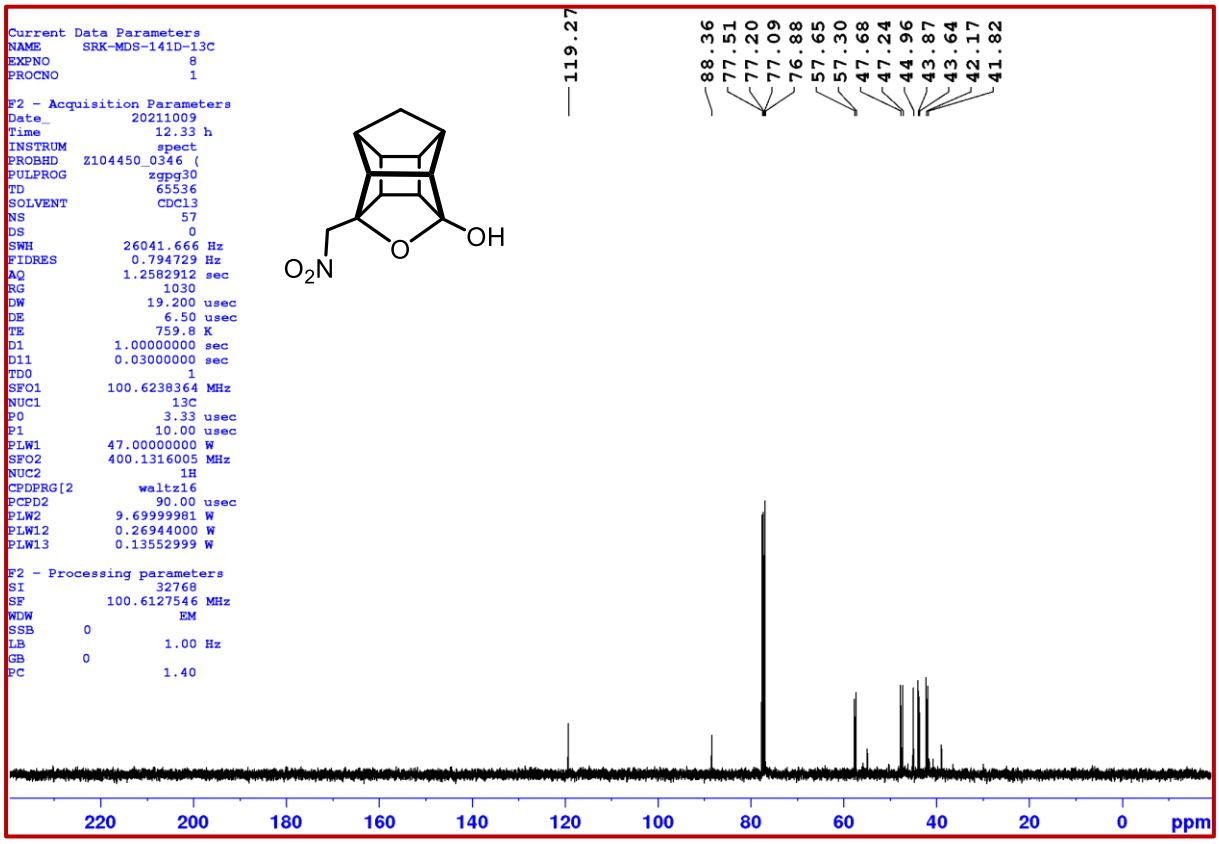
DEPT 135 NMR of Compound 11b (125 MHz, $CDCl_3$)



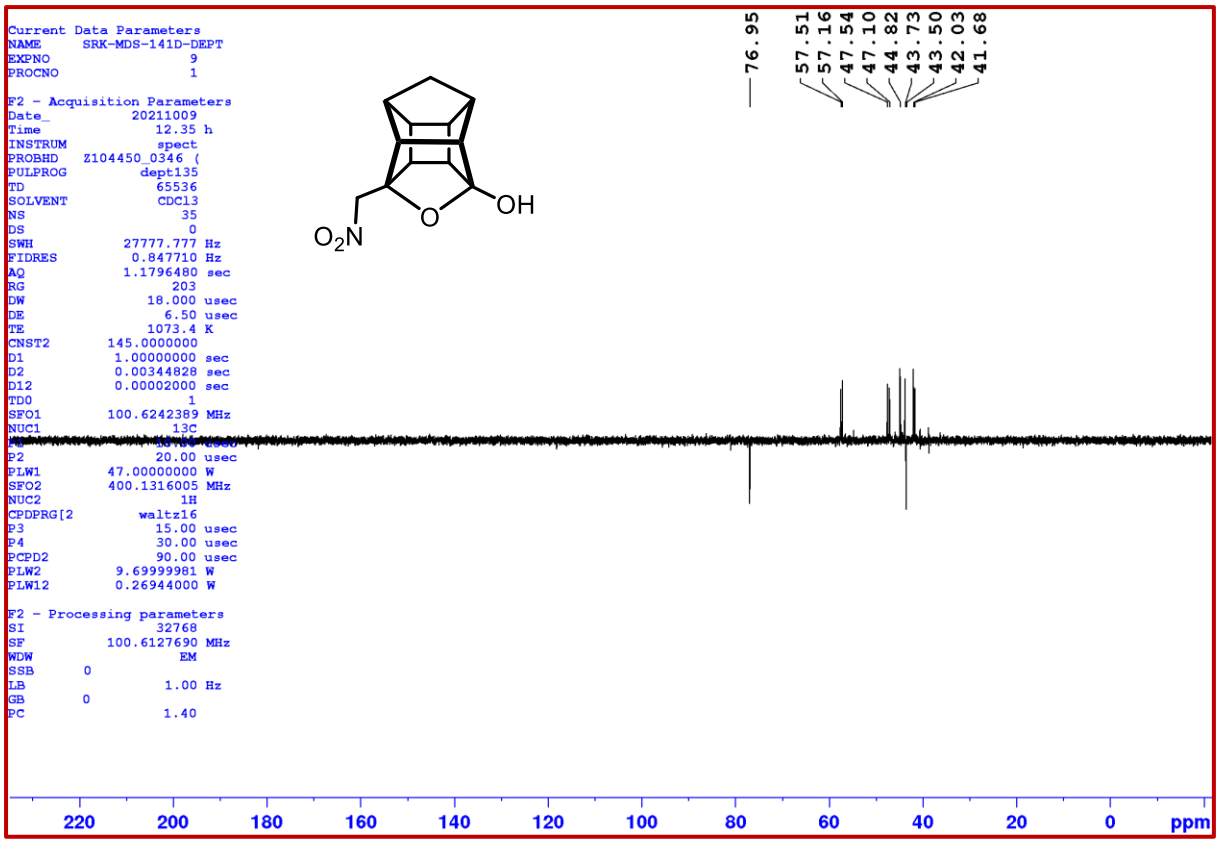
^{1}H NMR of Compound 11c (400 MHz, $CDCl_3$)



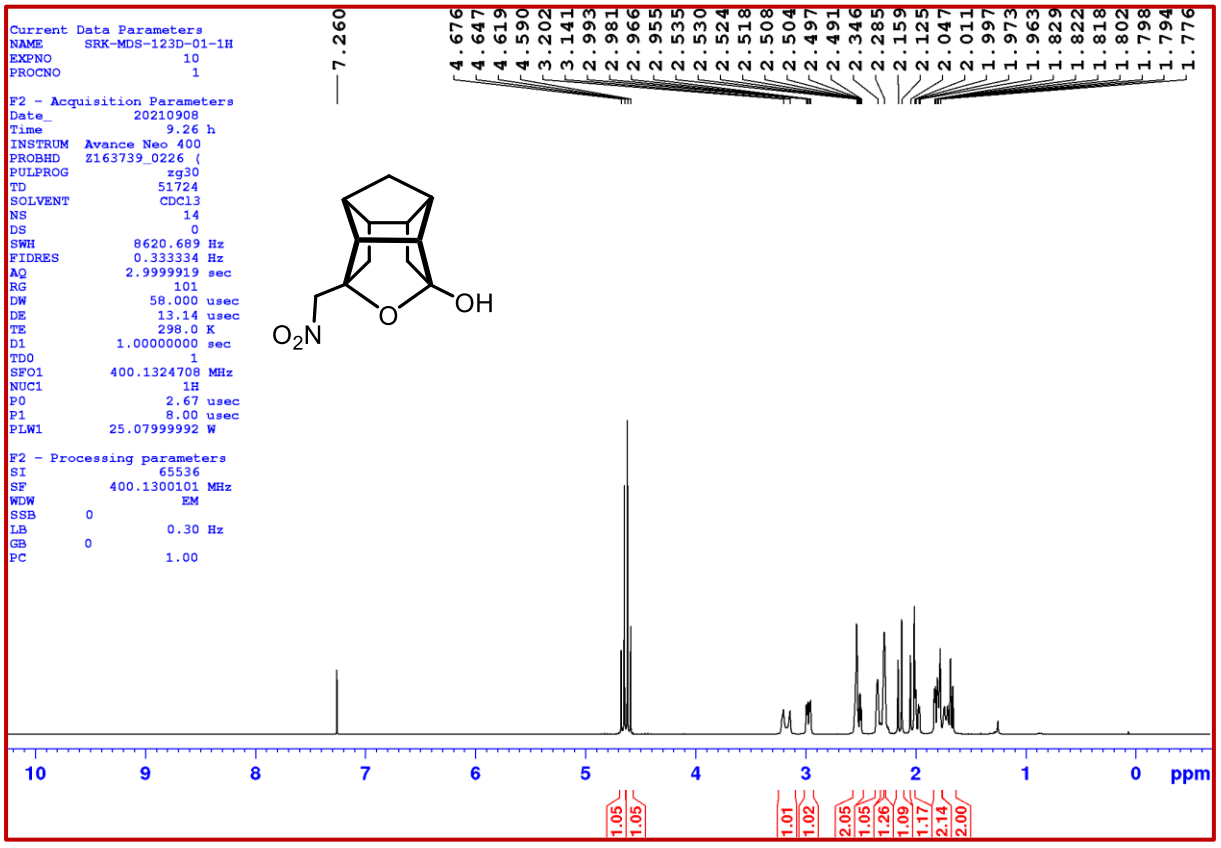
^{13}C NMR of Compound 11c (100.6 MHz, $CDCl_3$)



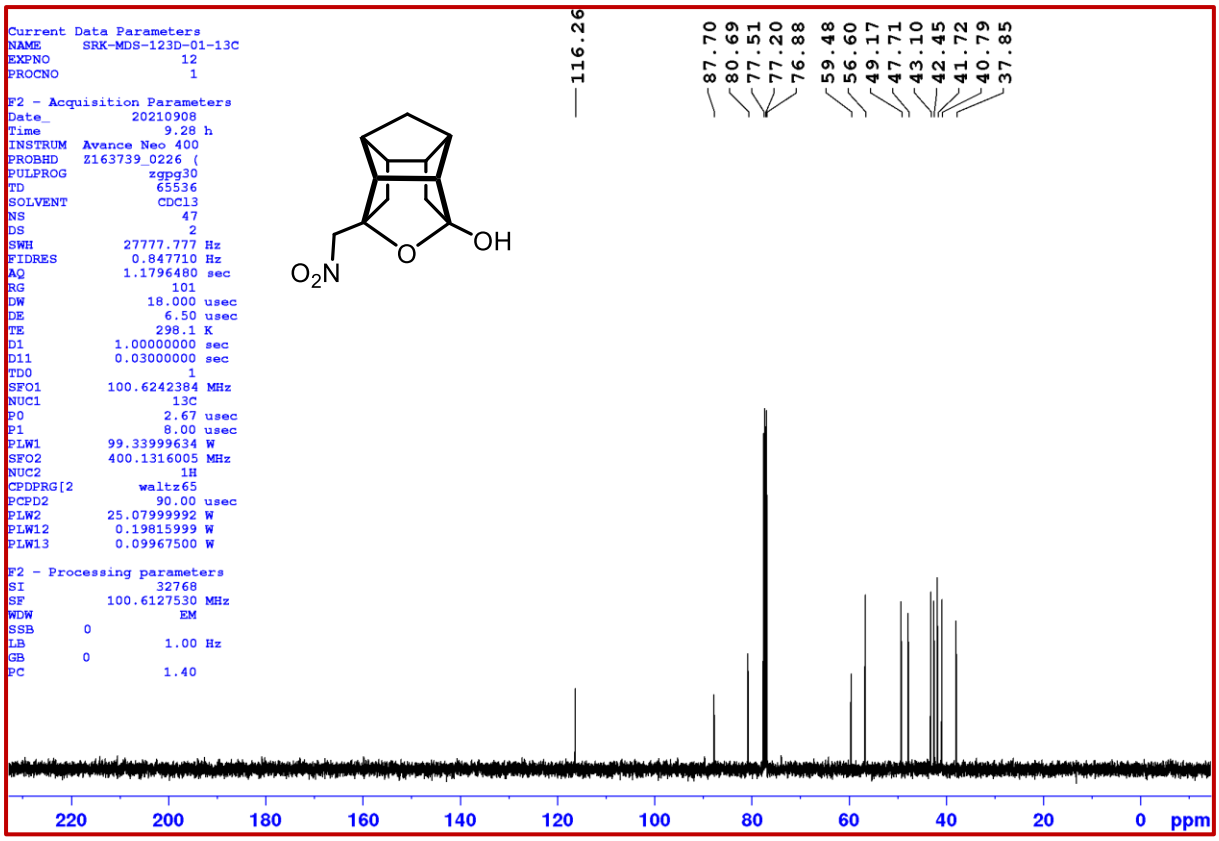
DEPT 135 NMR of Compound 11c (100.6 MHz, $CDCl_3$)



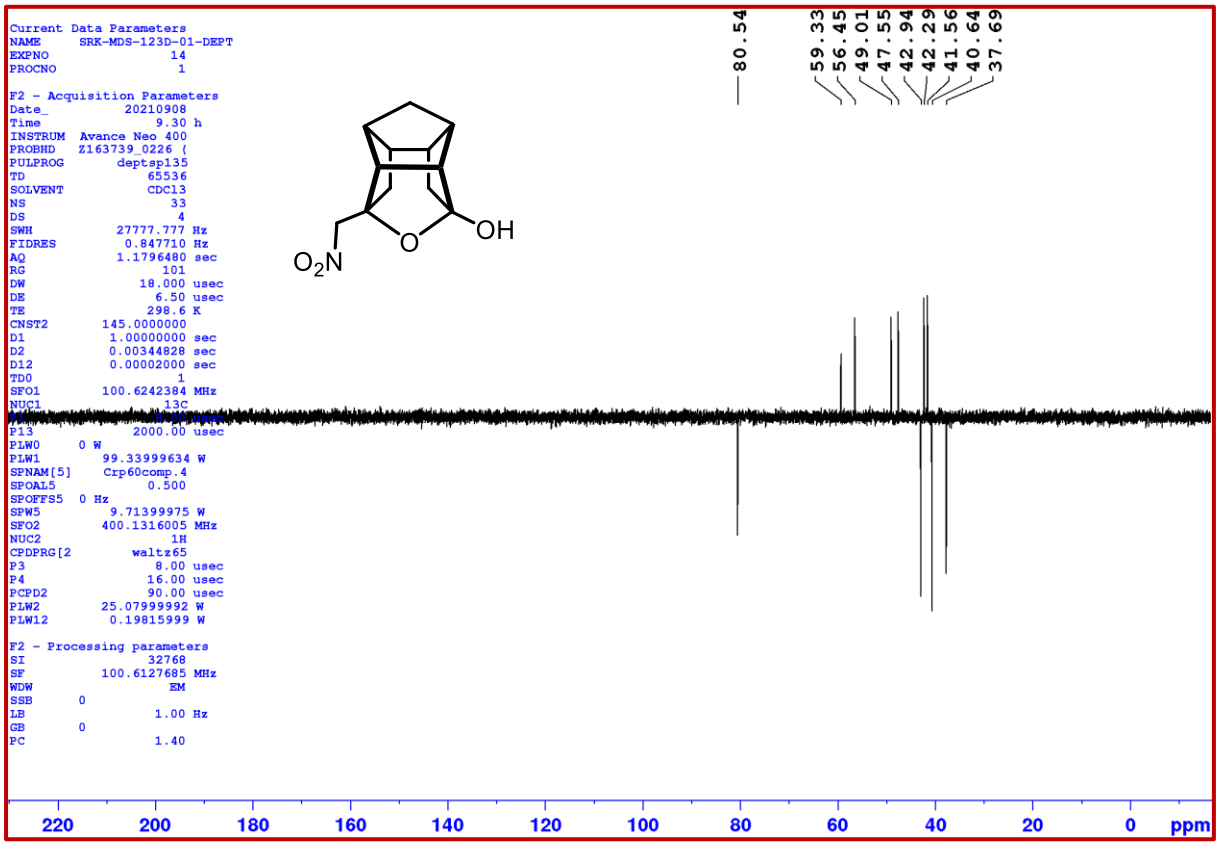
^{1}H NMR of Compound 12c (400 MHz, $CDCl_3$)



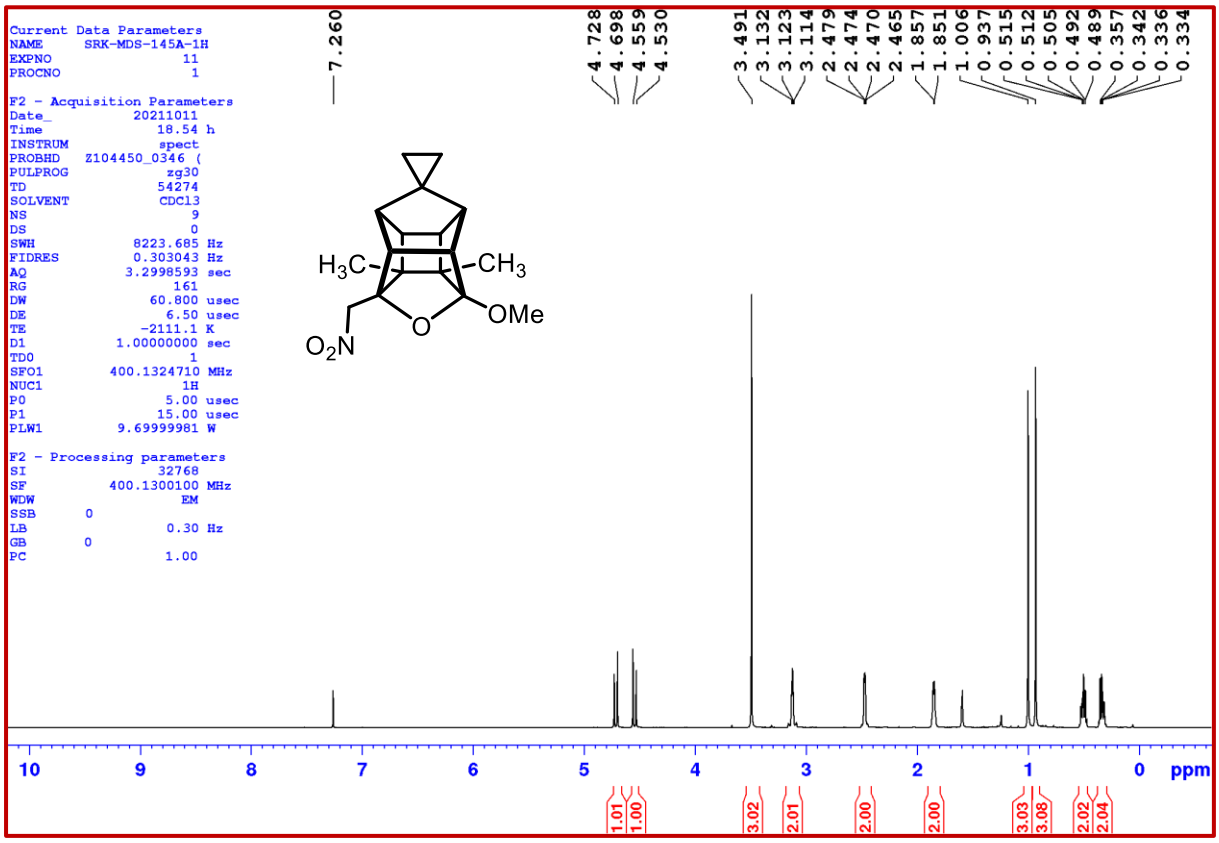
^{13}C NMR of Compound 12c (100.6 MHz, $CDCl_3$)



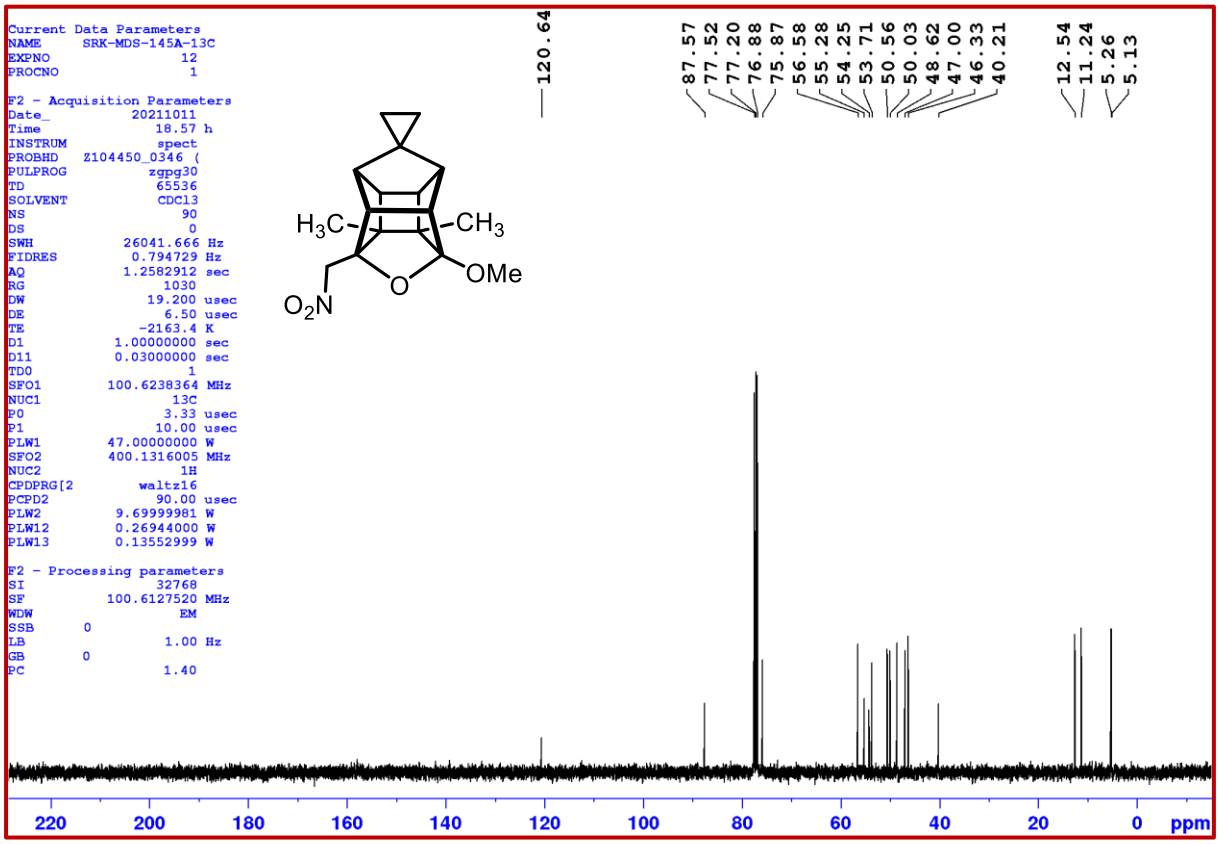
DEPT 135 NMR of Compound 12c (100.6 MHz, $CDCl_3$)



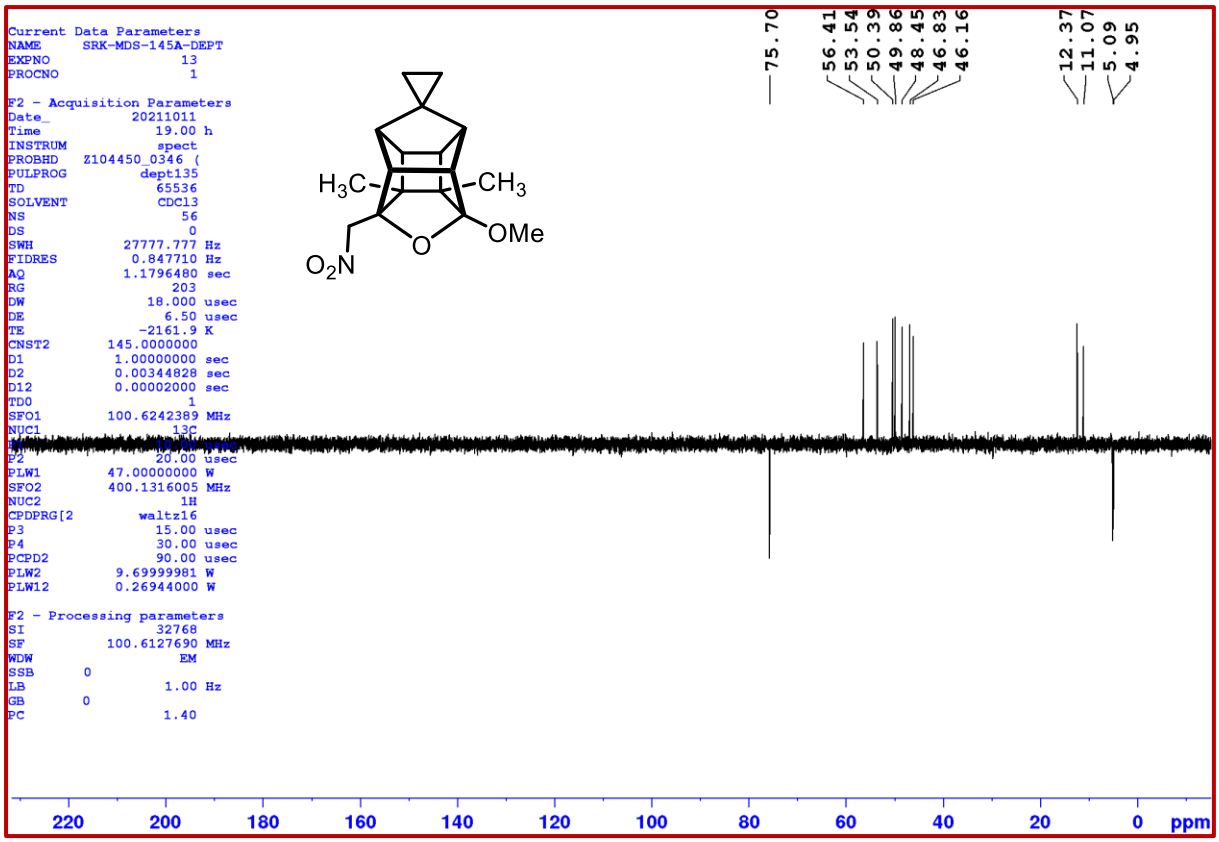
^{1}H NMR of Compound 13a (400 MHz, $CDCl_3$)



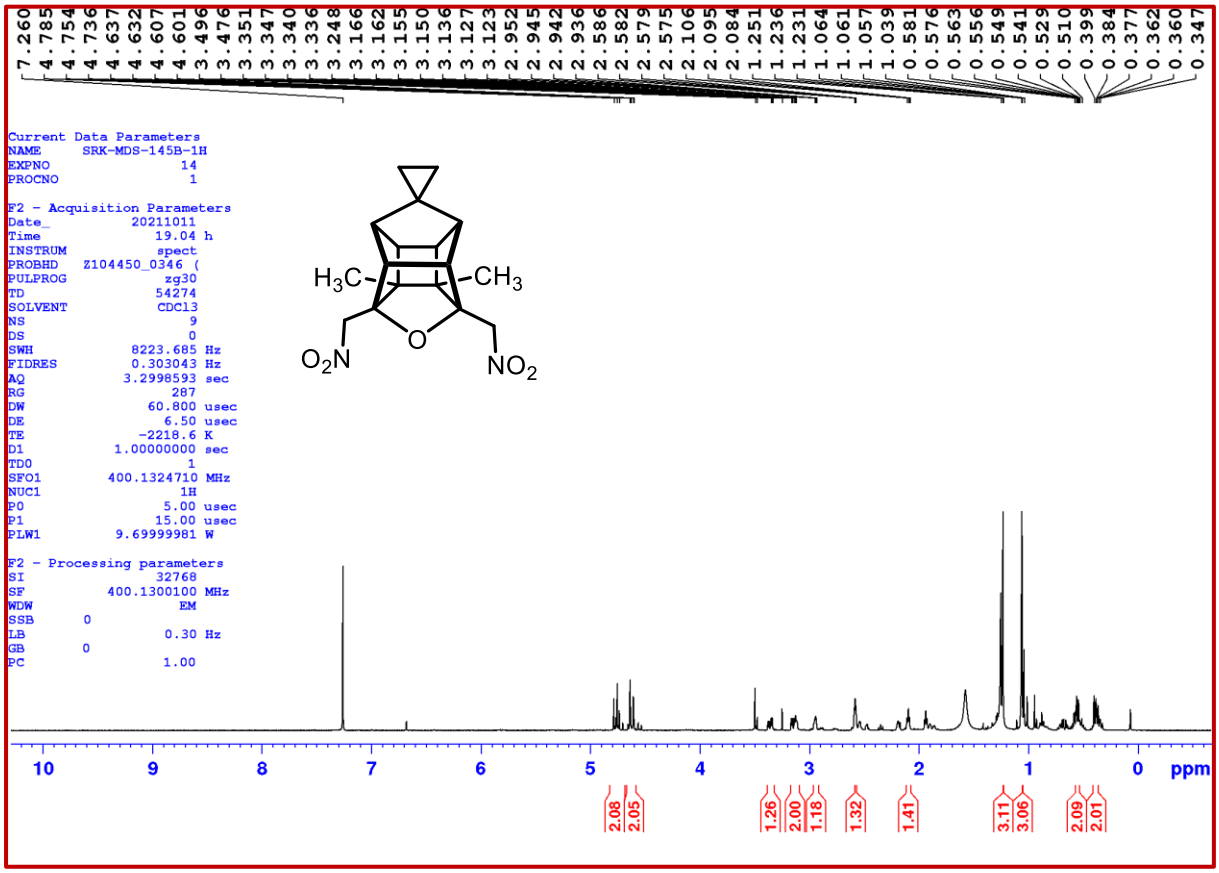
^{13}C NMR of Compound 13a (100.6 MHz, $CDCl_3$)



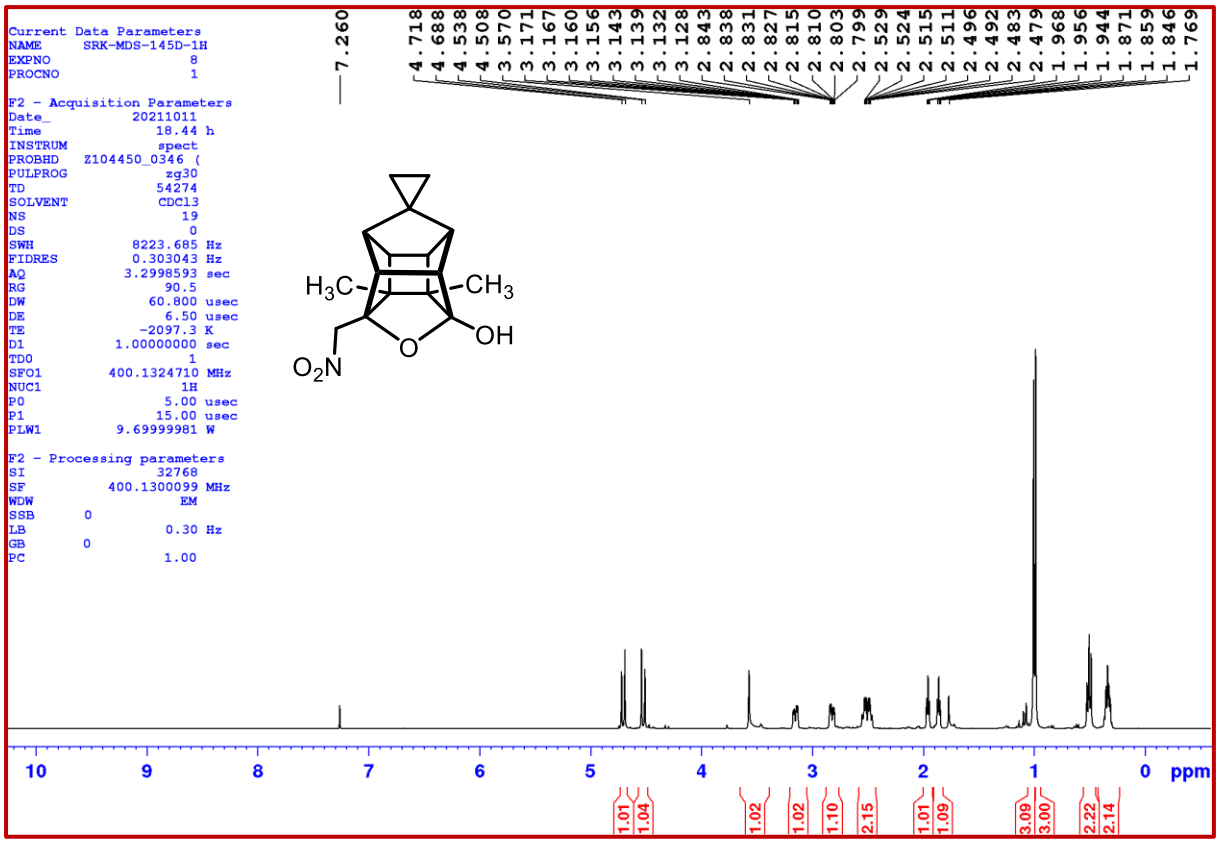
DEPT 135 NMR of Compound 13a (100.6 MHz, $CDCl_3$)



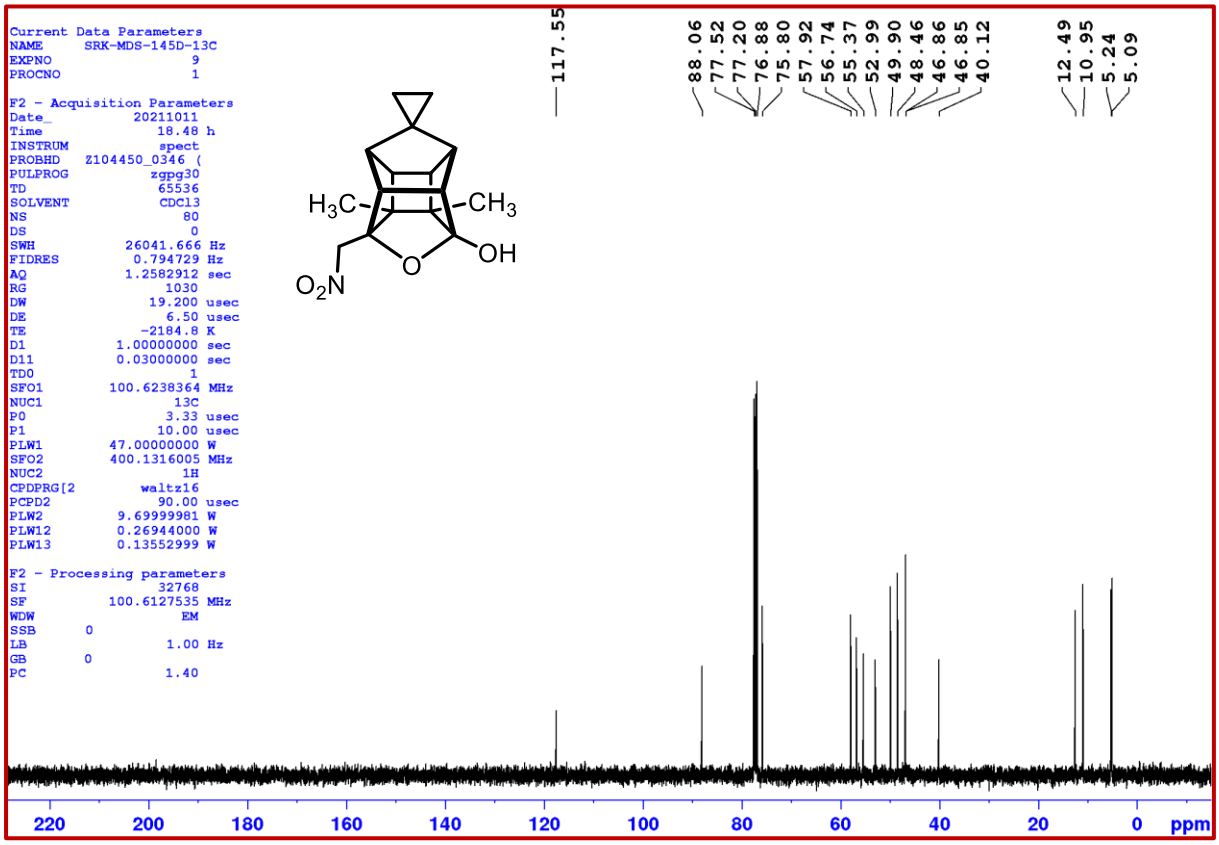
^{1}H NMR of Compound 13b (400 MHz, $CDCl_3$)



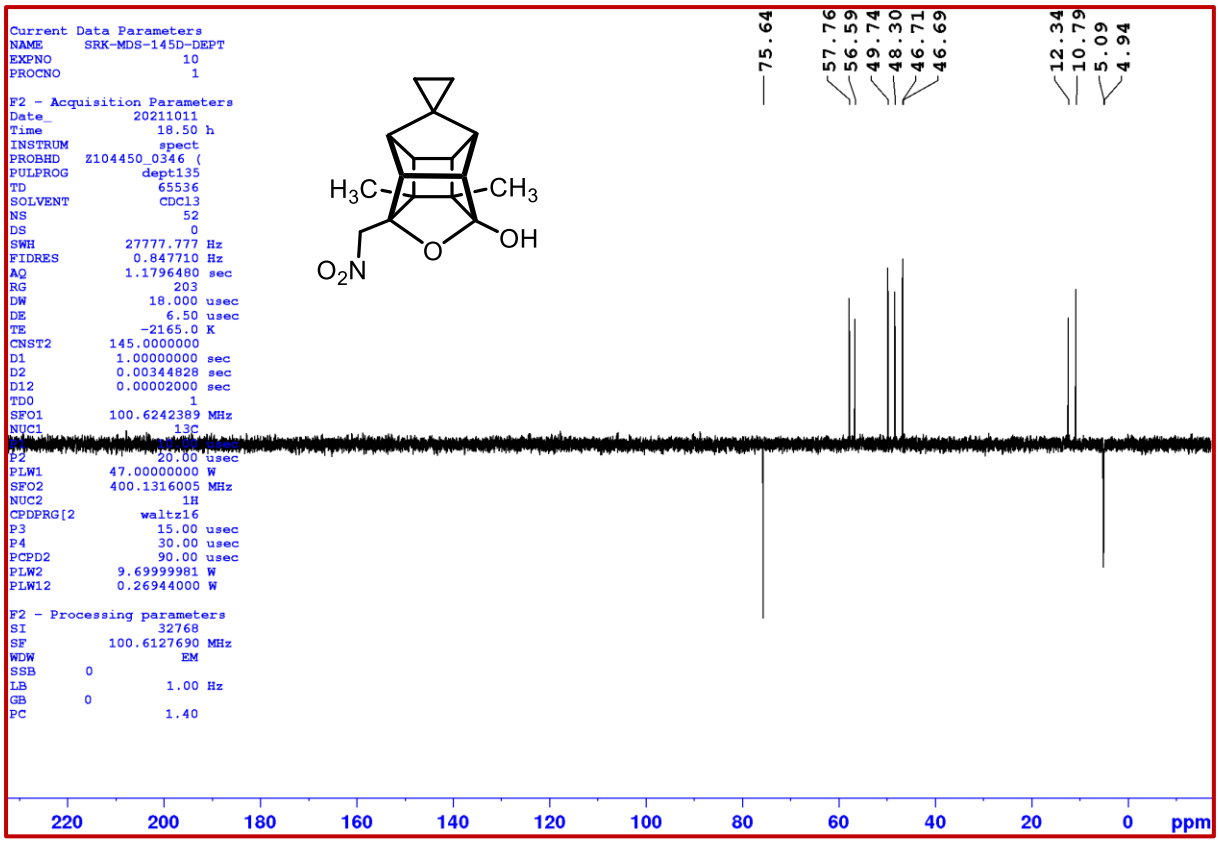
^{1}H NMR of Compound 13c (400 MHz, $CDCl_3$)



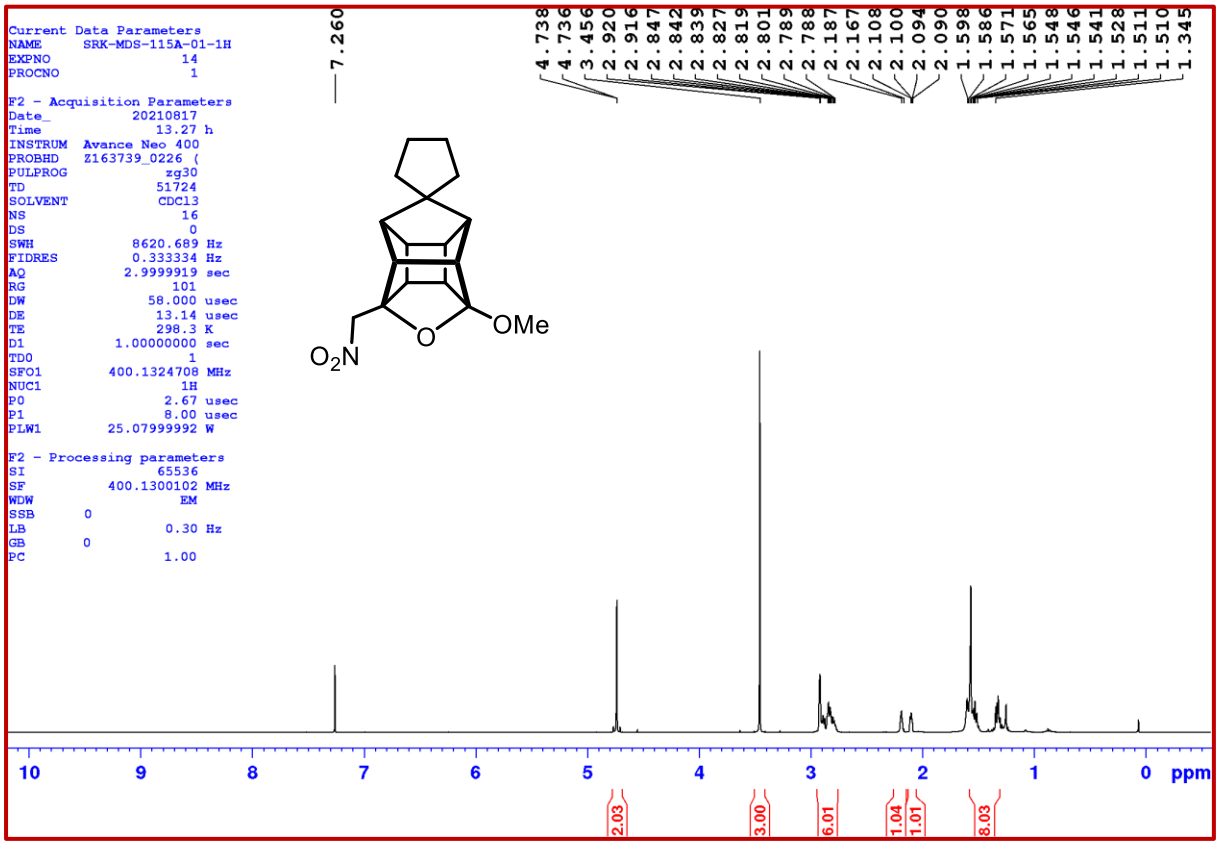
^{13}C NMR of Compound 13c (100.6 MHz, $CDCl_3$)



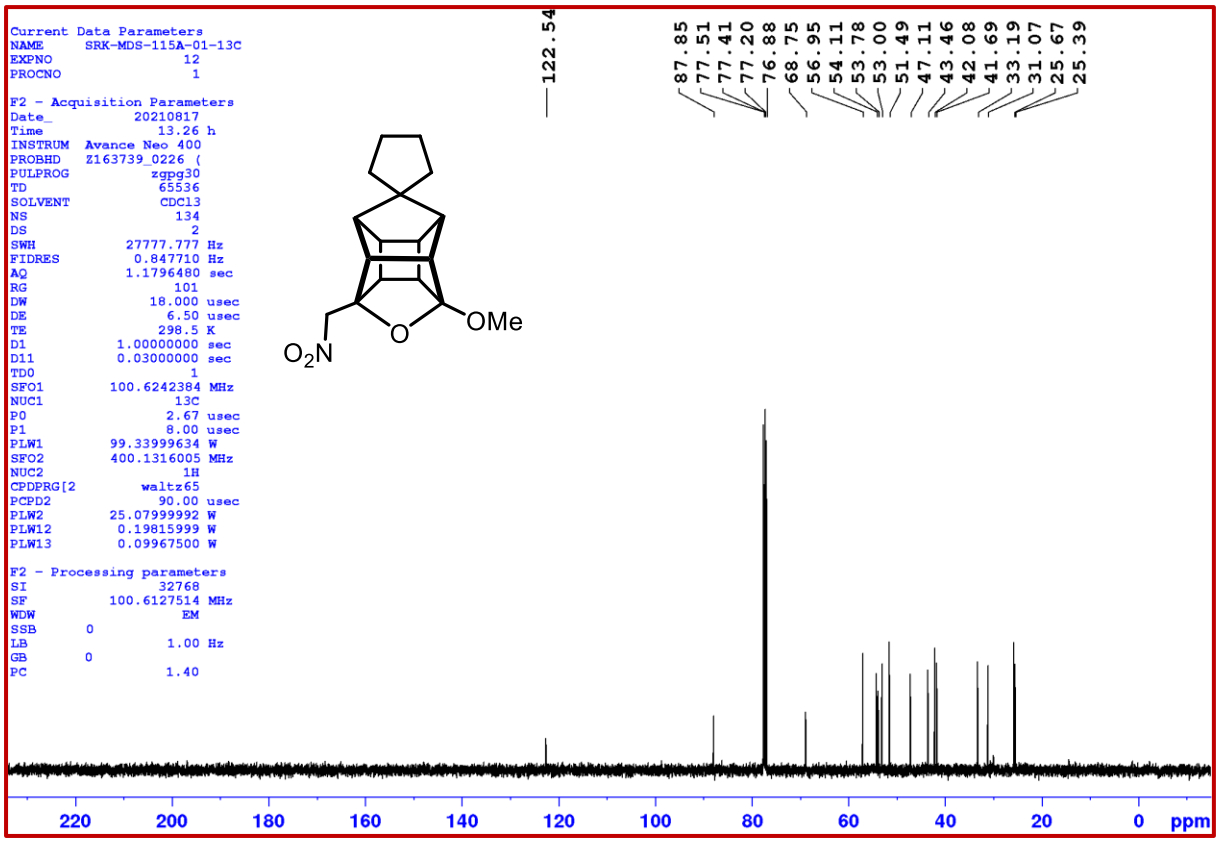
DEPT 135 NMR of Compound 13c (100.6 MHz, $CDCl_3$)



^{1}H NMR of Compound 14a (400 MHz, $CDCl_3$)



^{13}C NMR of Compound 14a (100.6 MHz, $CDCl_3$)



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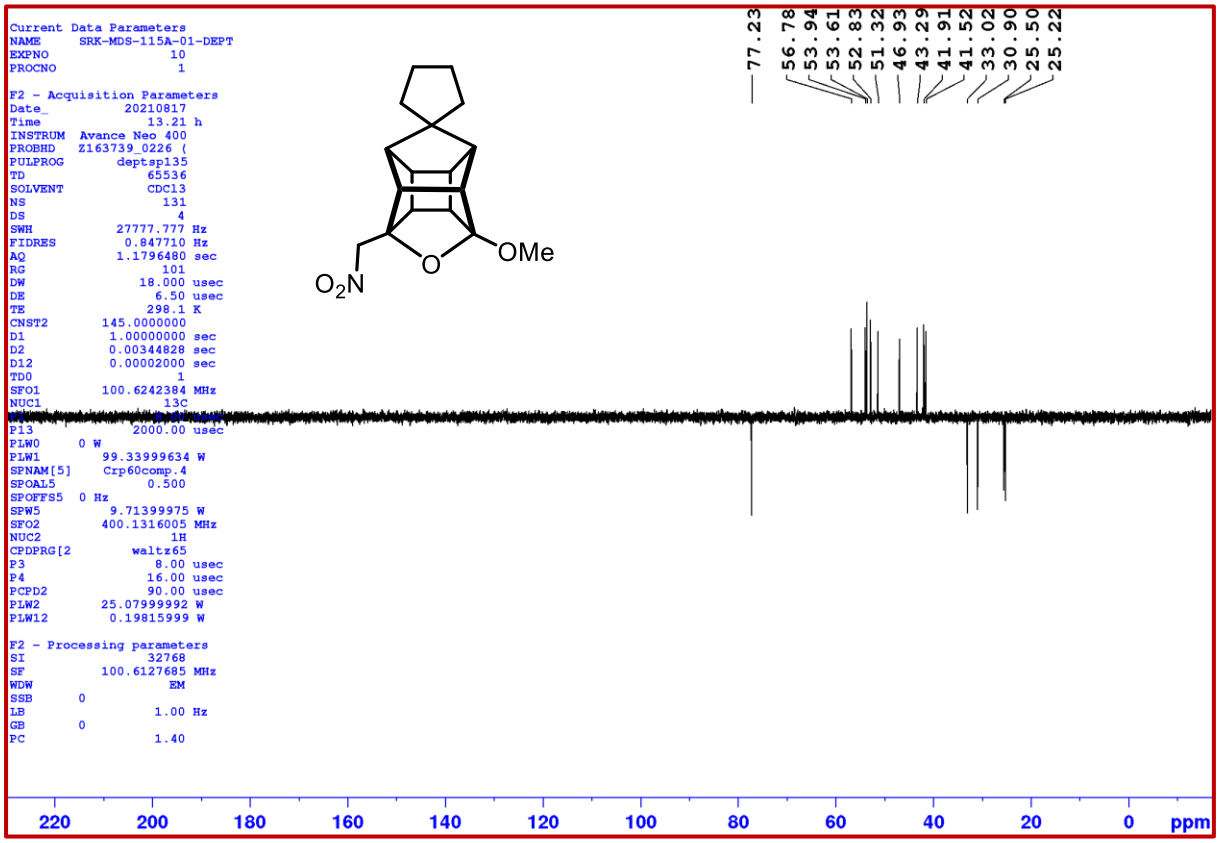

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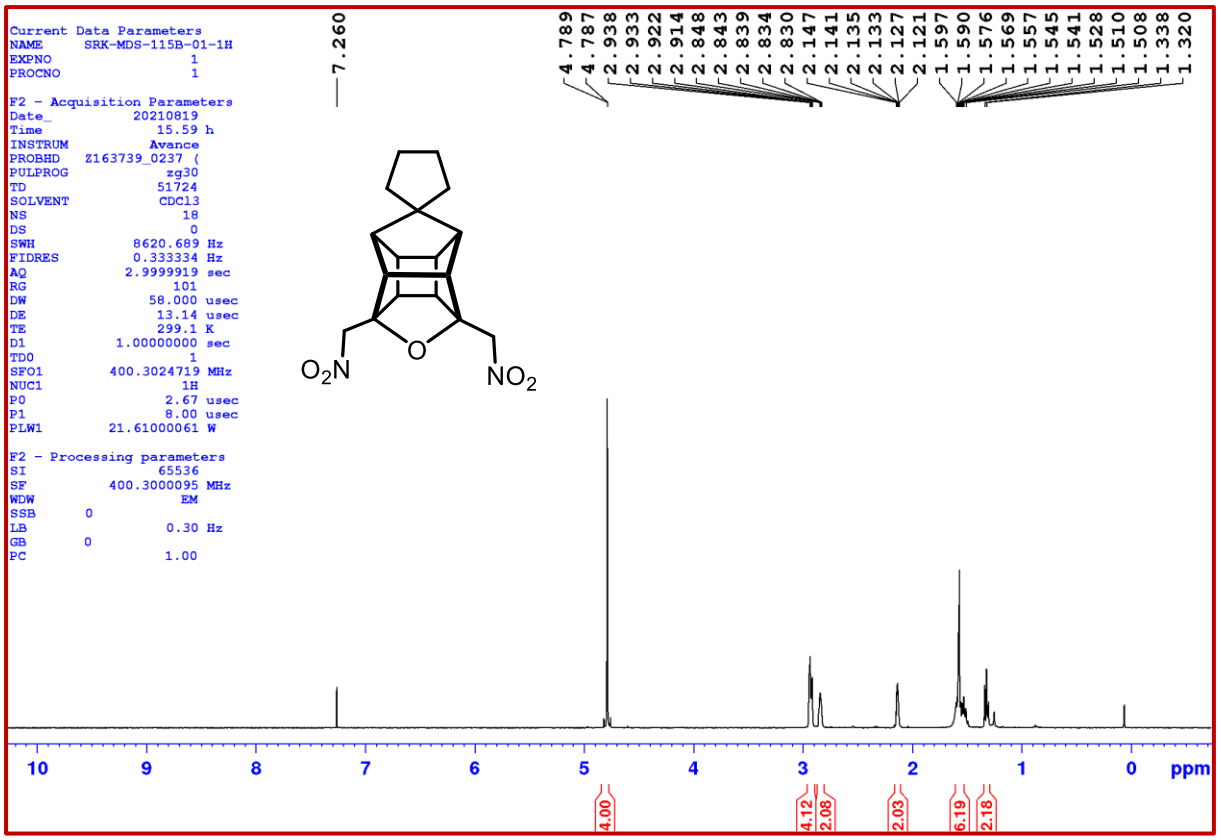
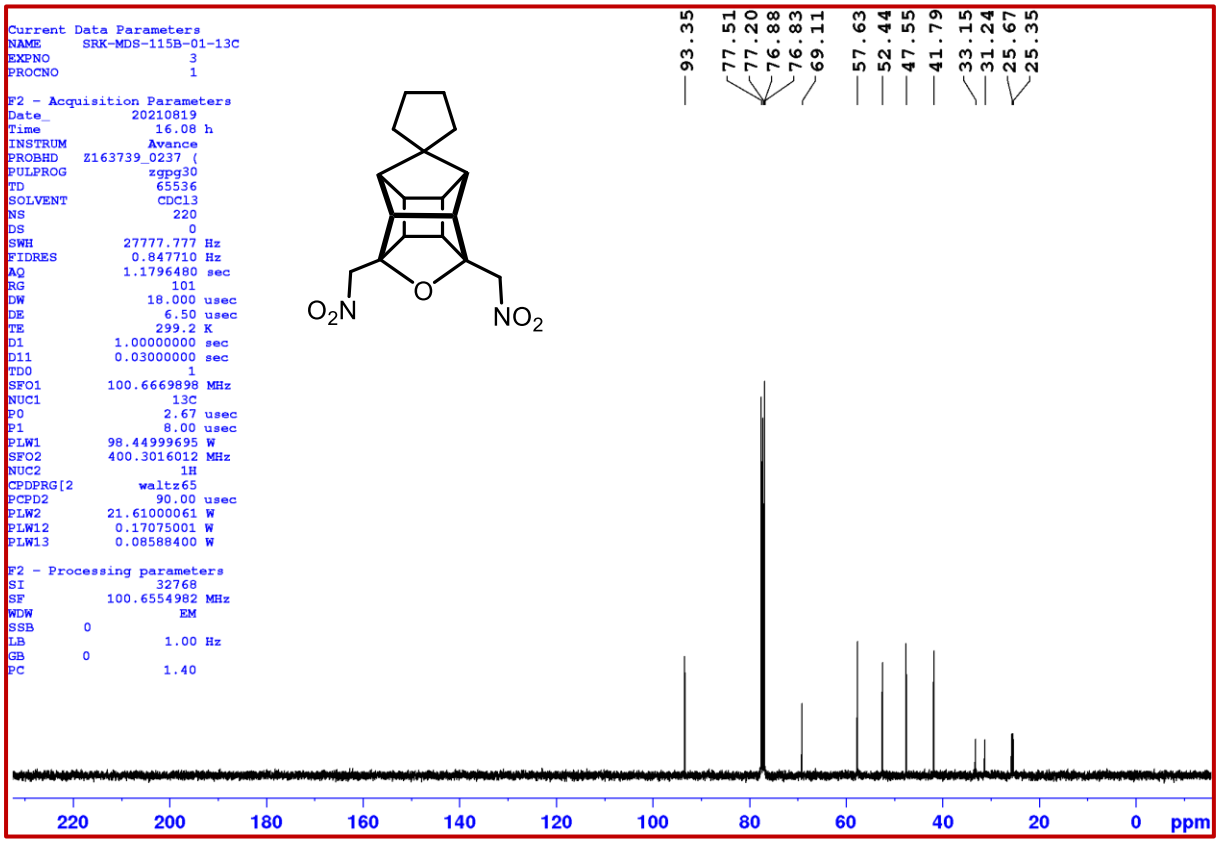
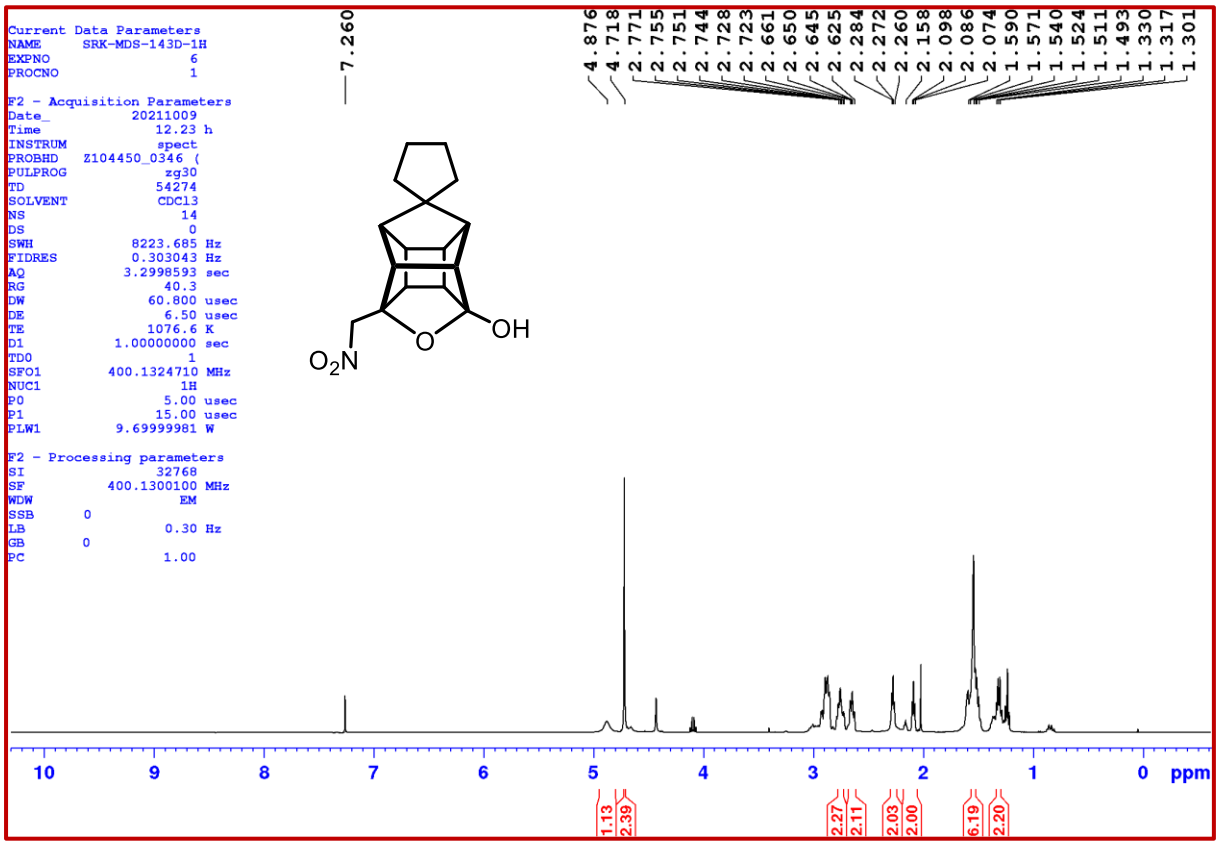


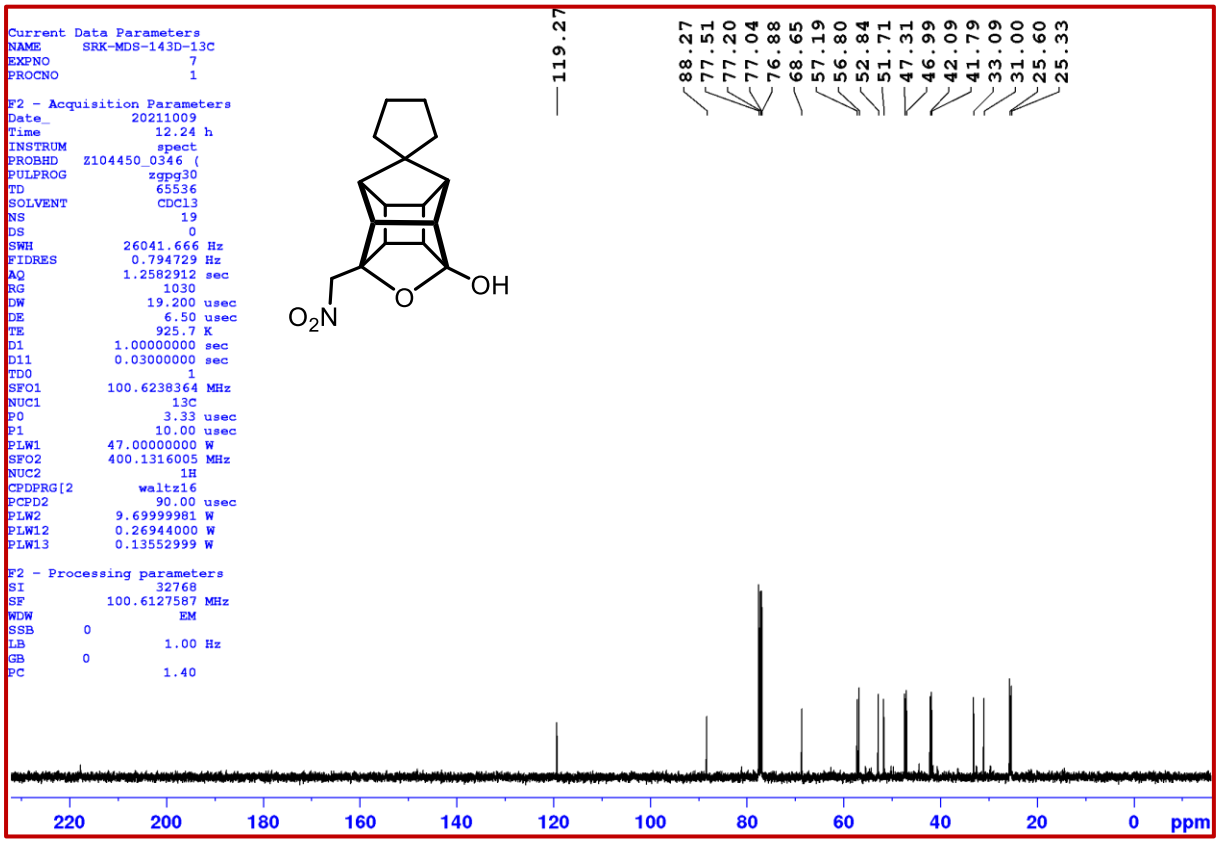
^{13}C NMR of Compound 14b (100.6 MHz, $CDCl_3$)



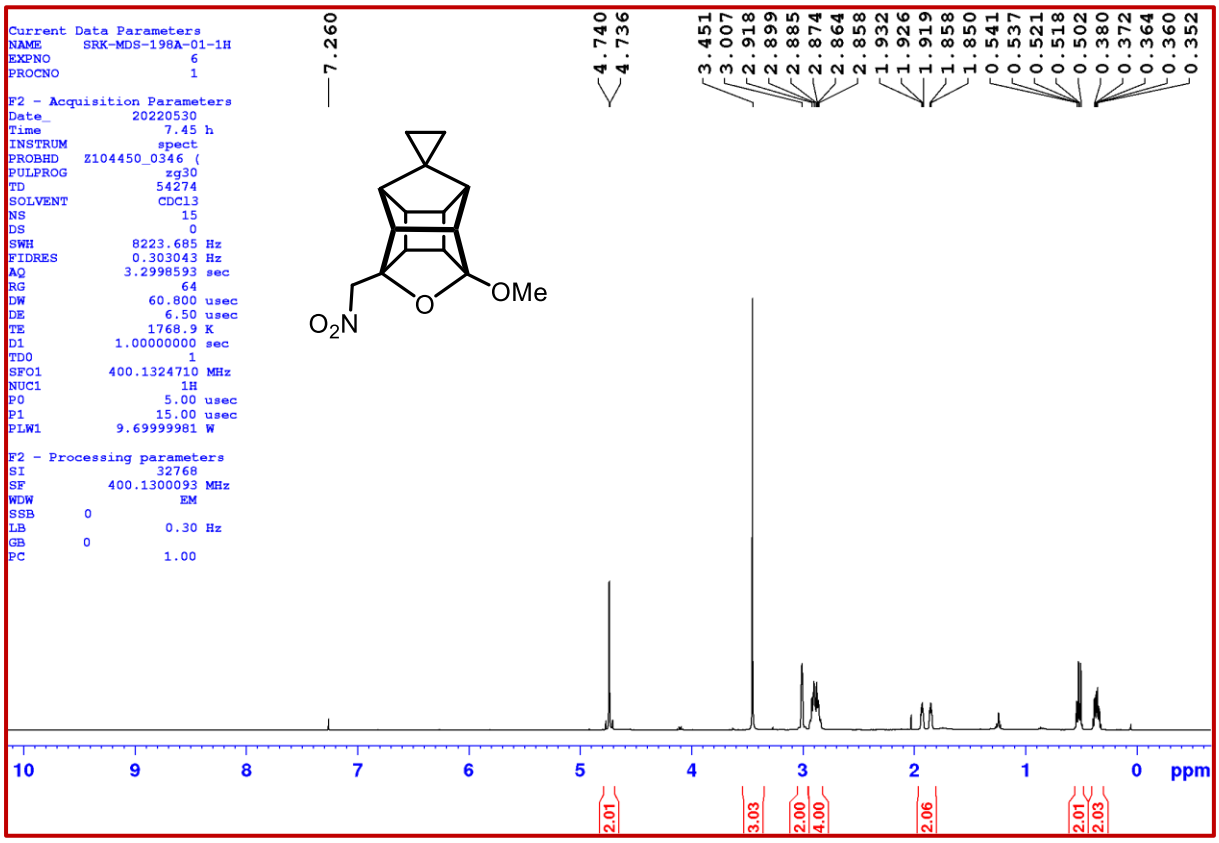
^{1}H NMR of Compound 14c (400 MHz, $CDCl_3$)



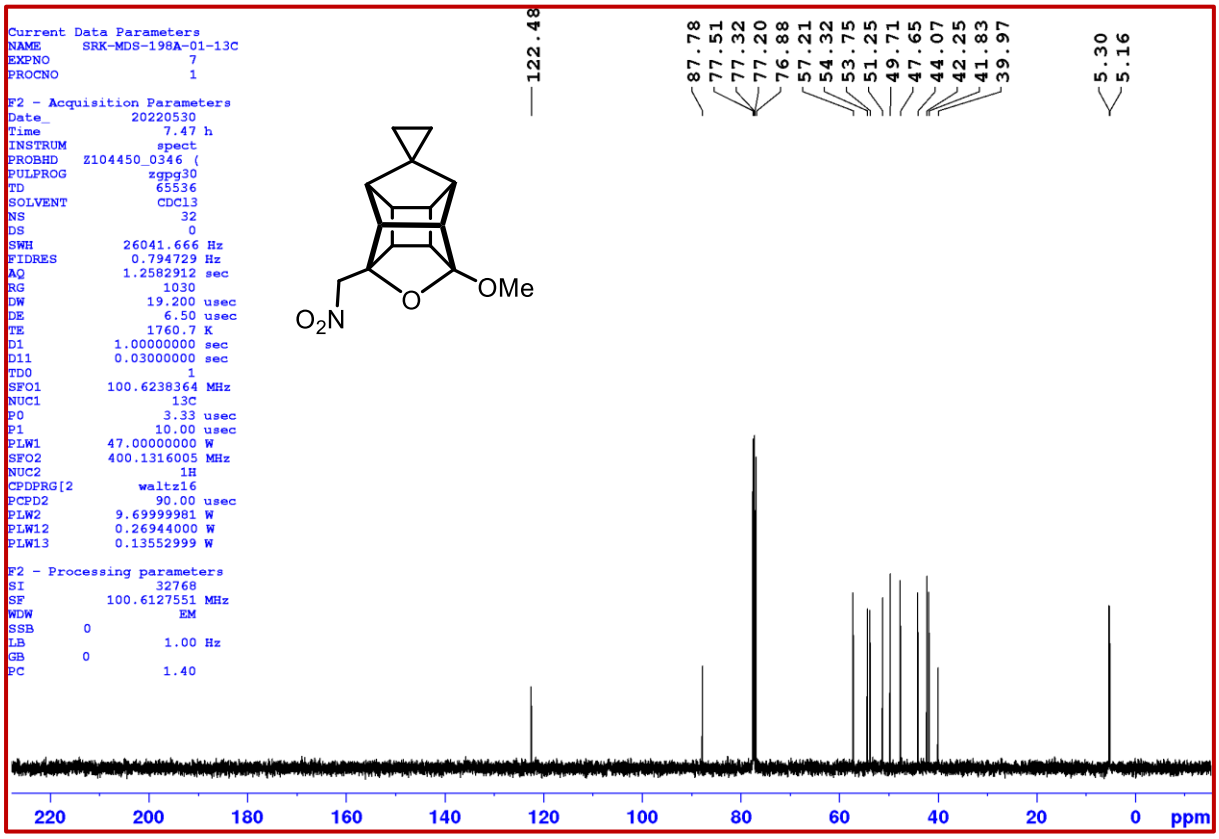
^{13}C NMR of Compound 14c (100.6 MHz, $CDCl_3$)



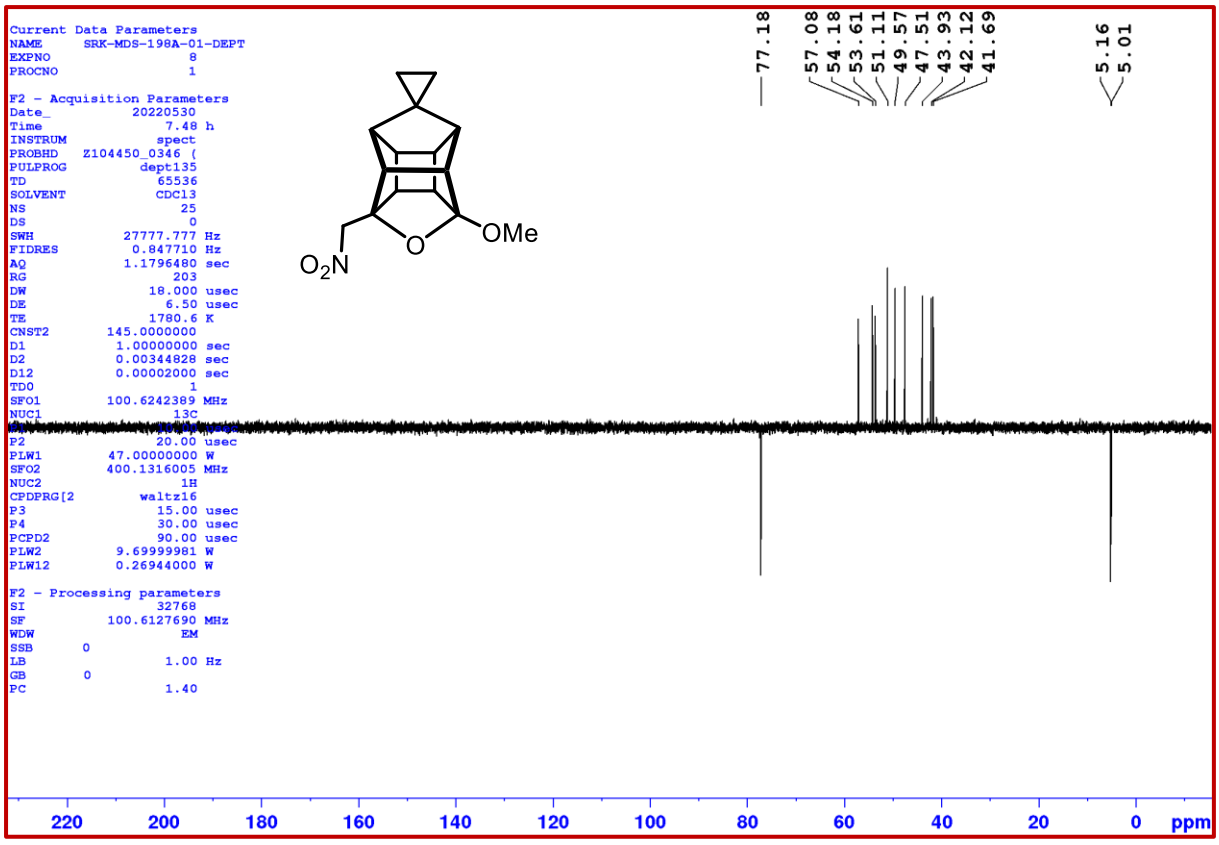
^{1}H NMR of Compound 15a (400 MHz, $CDCl_3$)



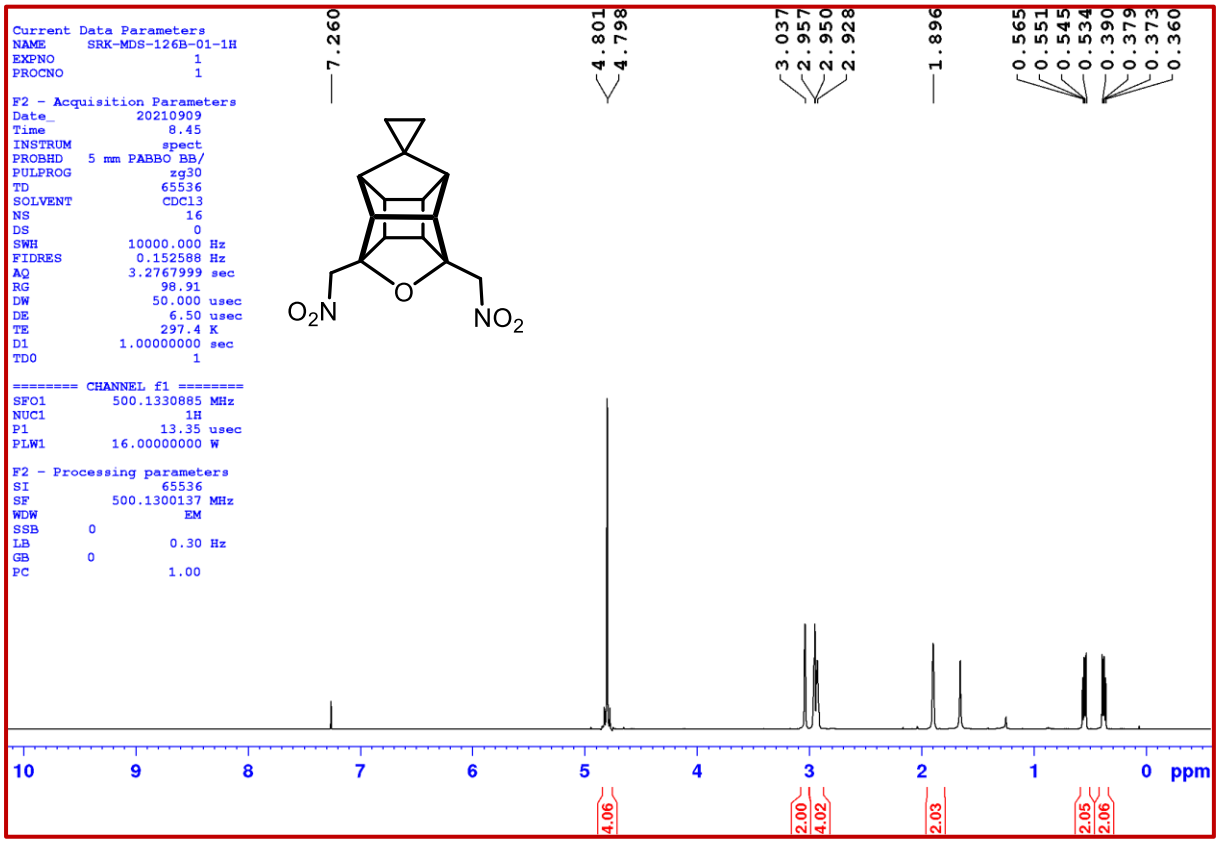
^{13}C NMR of Compound 15a (100.6 MHz, $CDCl_3$)



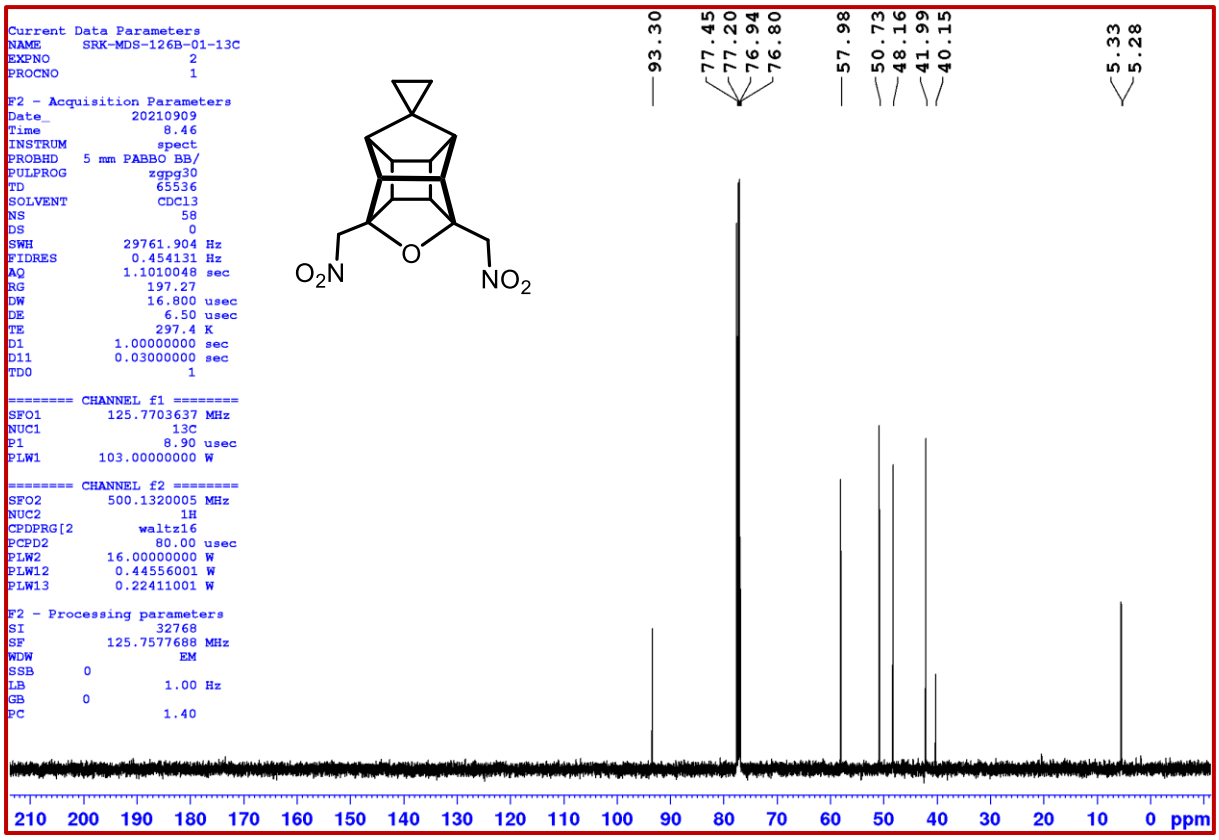
DEPT 135 NMR of Compound 15a (100.6 MHz, $CDCl_3$)



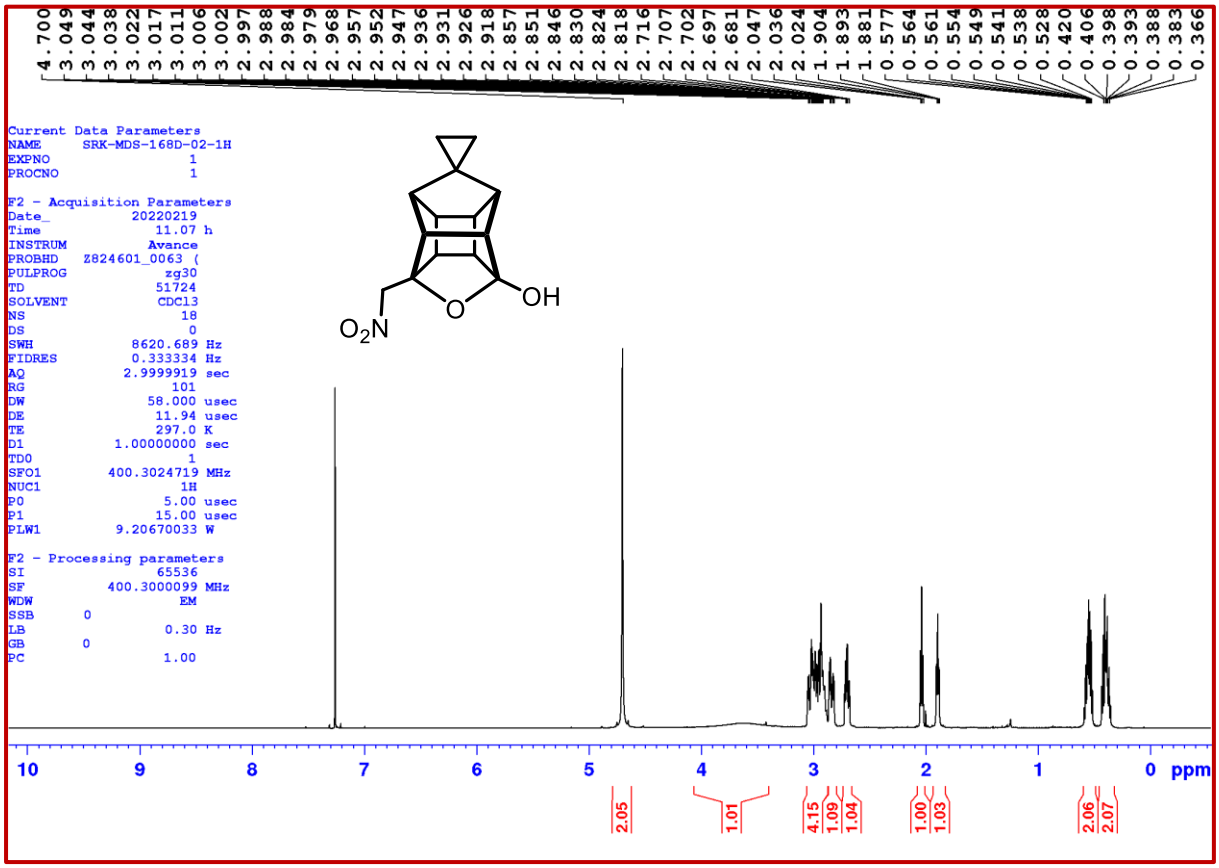
^{1}H NMR of Compound 15b (500 MHz, $CDCl_3$)



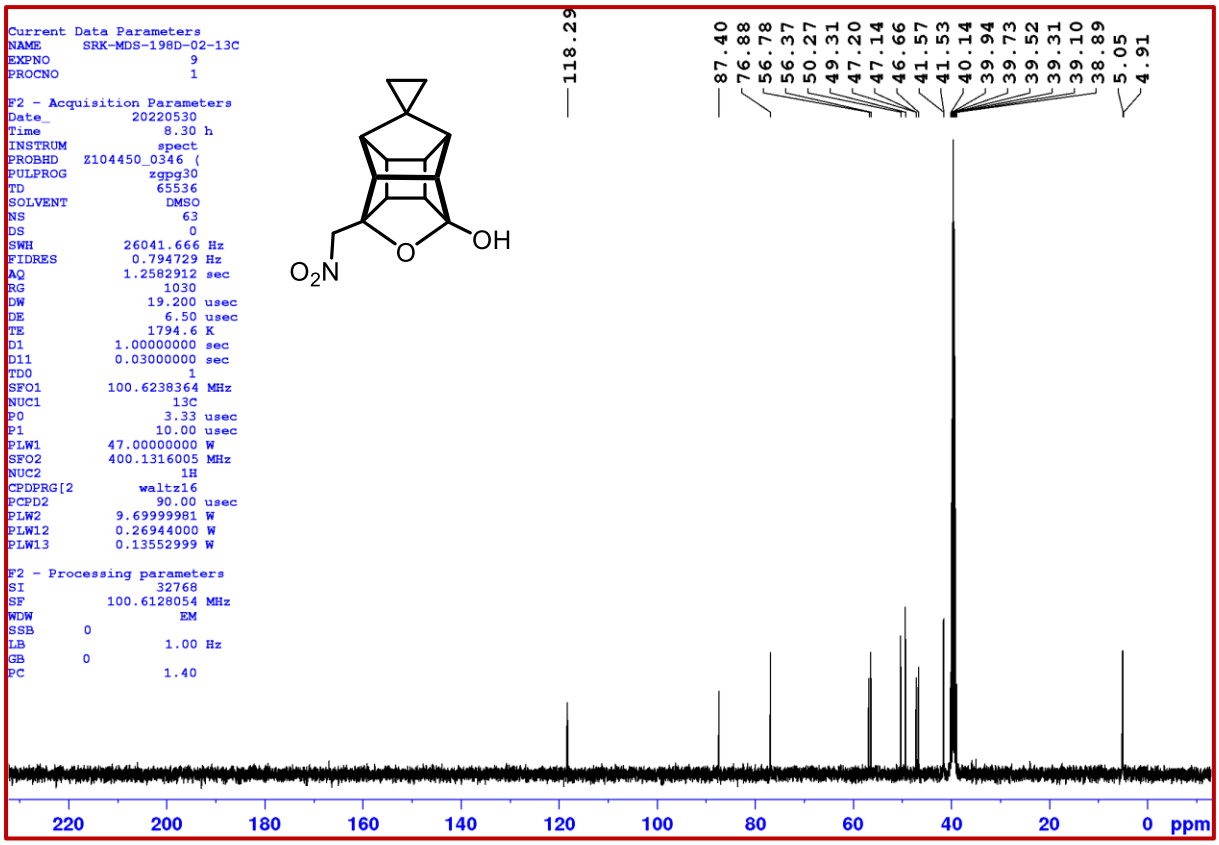
^{13}C NMR of Compound 15b (125 MHz, $CDCl_3$)



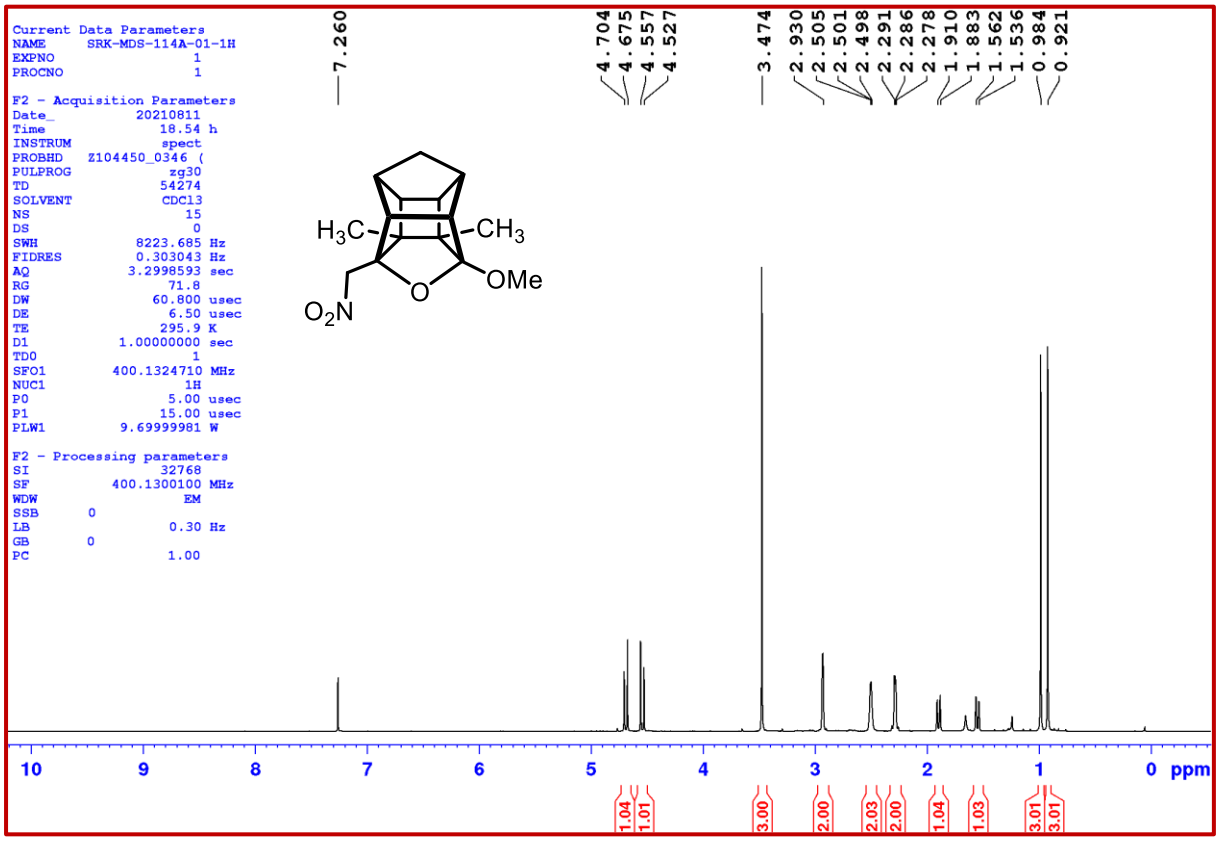
^{1}H NMR of Compound 15c (400 MHz, $CDCl_3$)



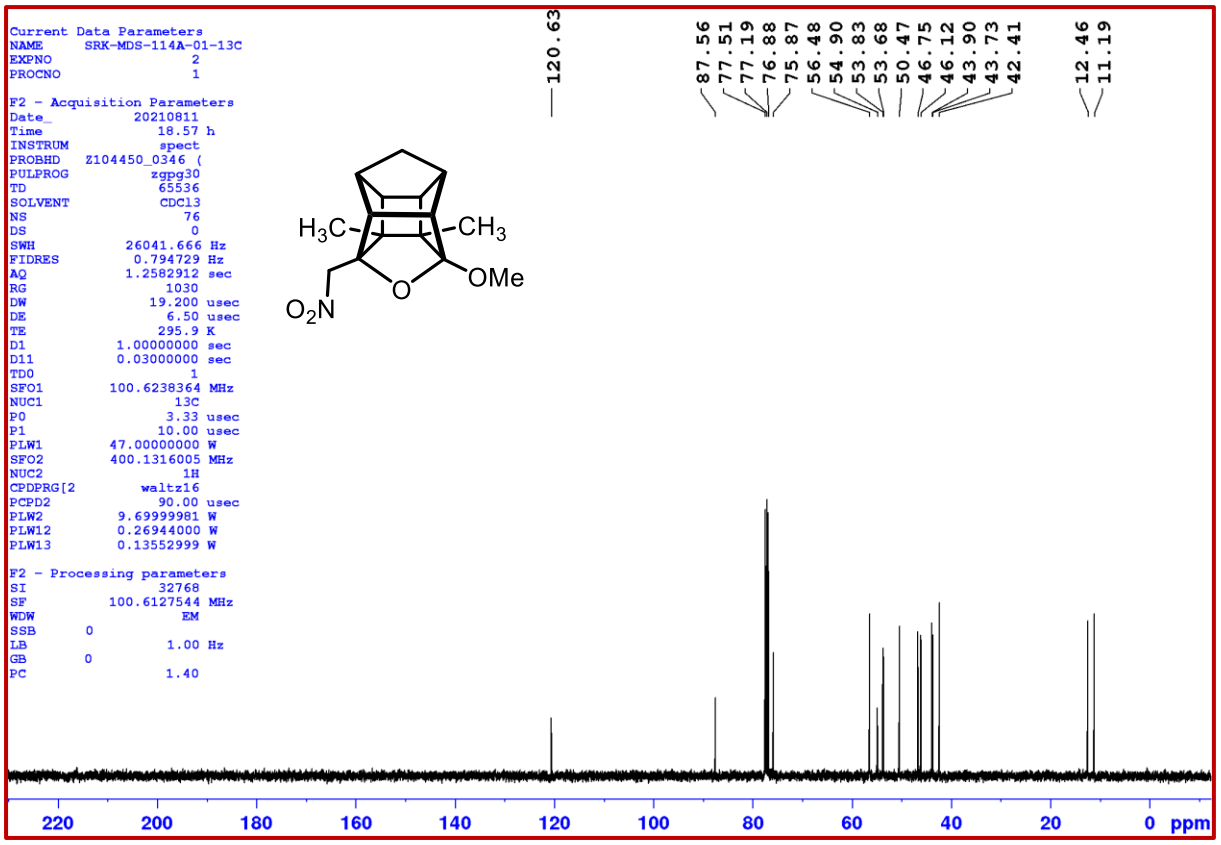
^{13}C NMR of Compound 15c (100.6 MHz, DMSO-d_6)



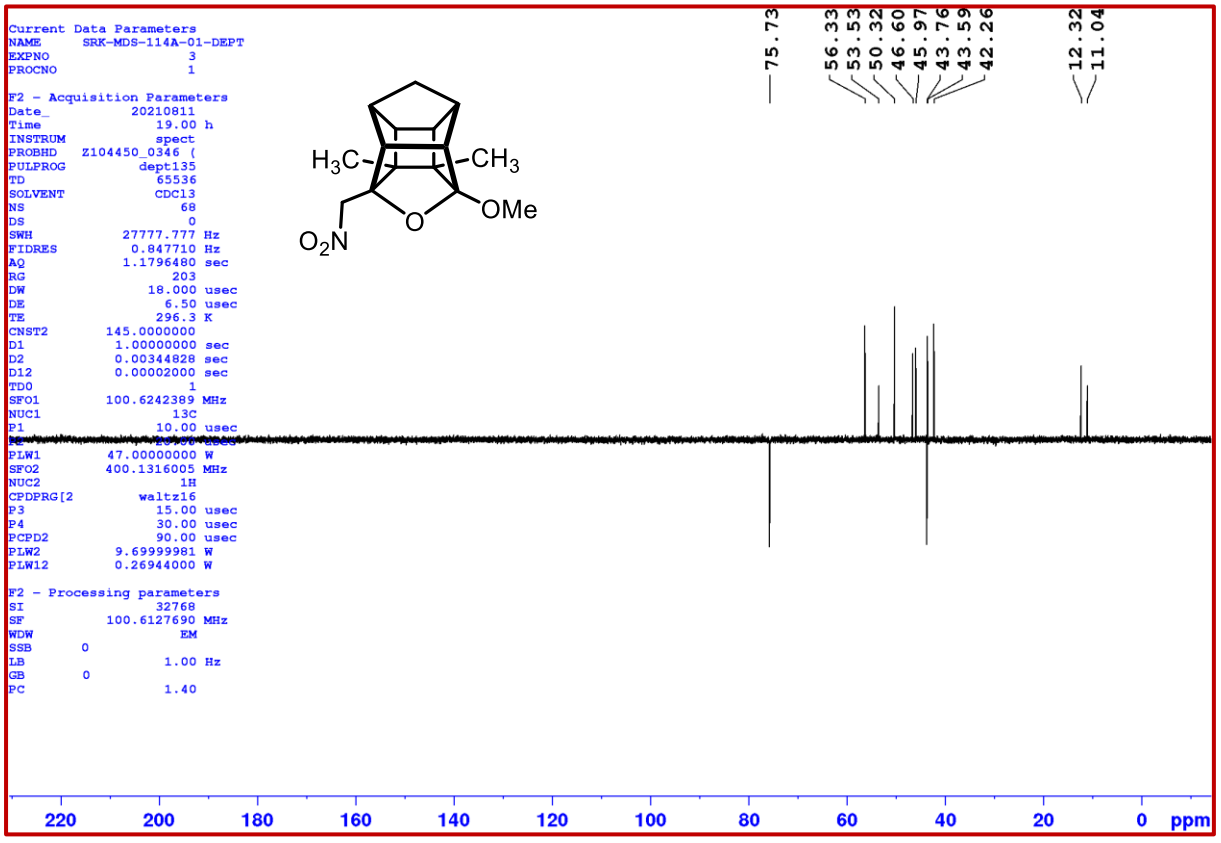
^{1}H NMR of Compound 16a (400 MHz, $CDCl_3$)



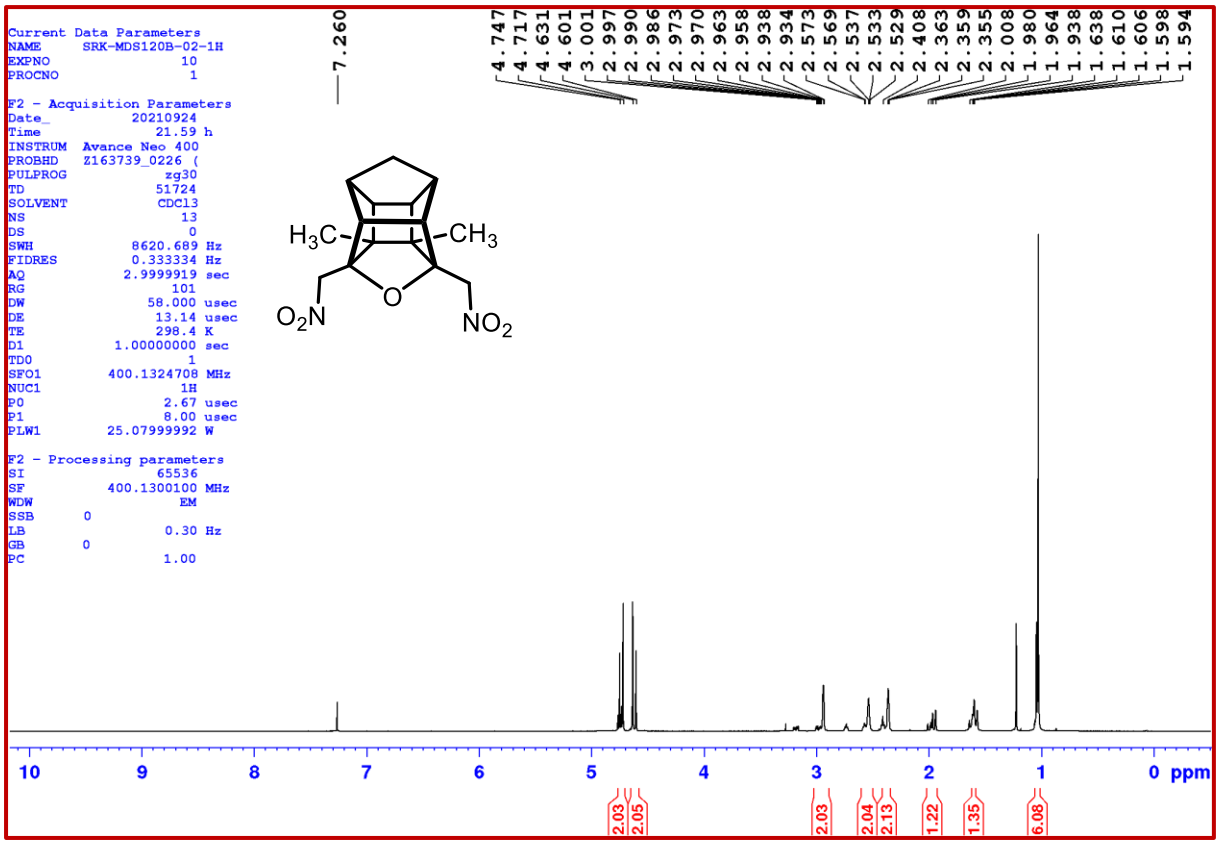
^{13}C NMR of Compound 16a (100.6 MHz, $CDCl_3$)



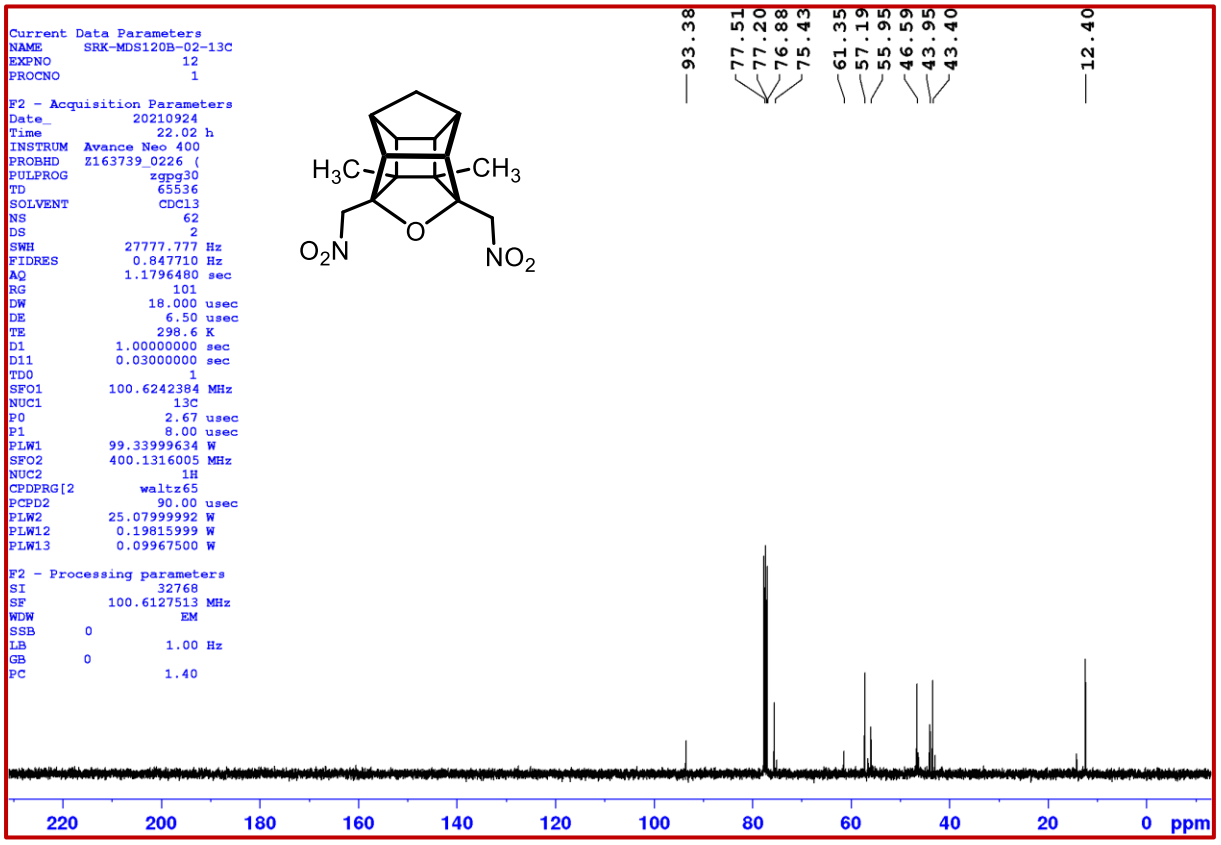
DEPT 135 NMR of Compound 16a (100.6 MHz, $CDCl_3$)



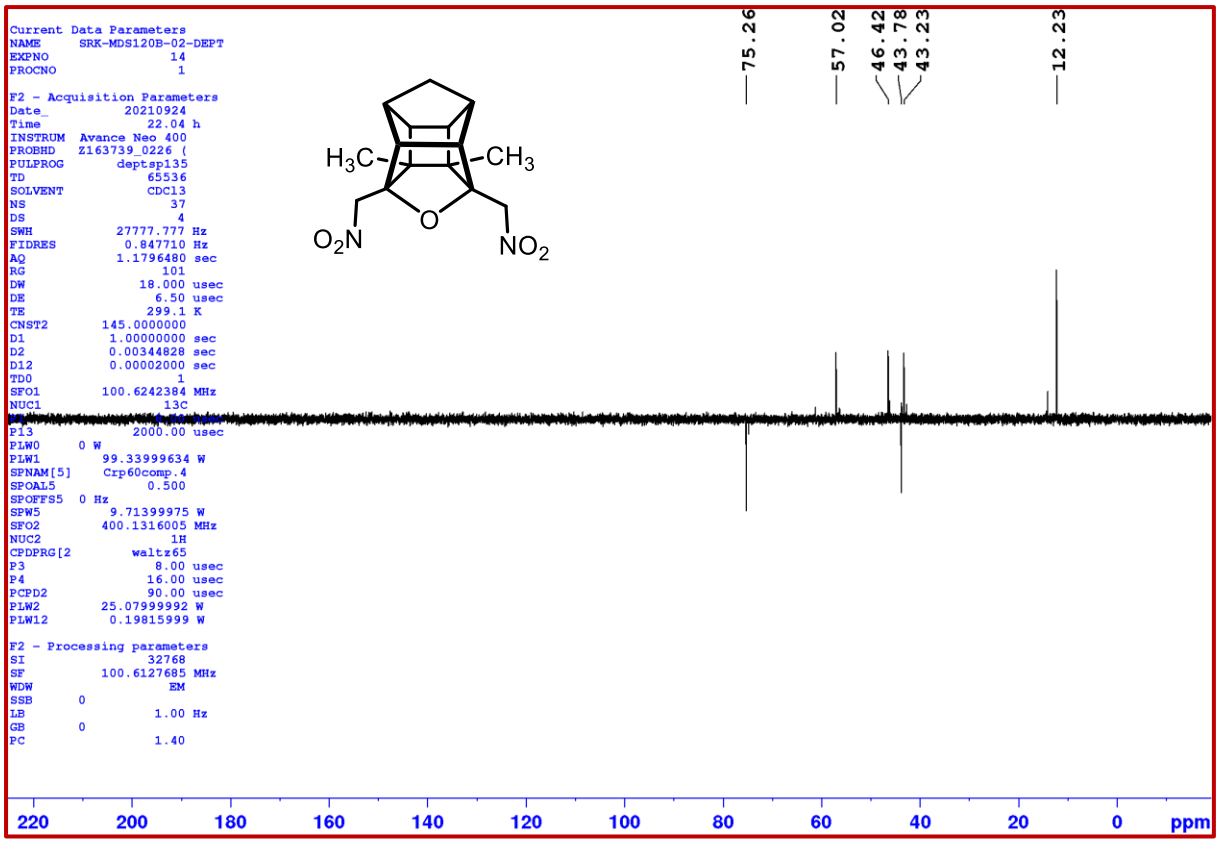
^{1}H NMR of Compound 16b (400 MHz, $CDCl_3$)



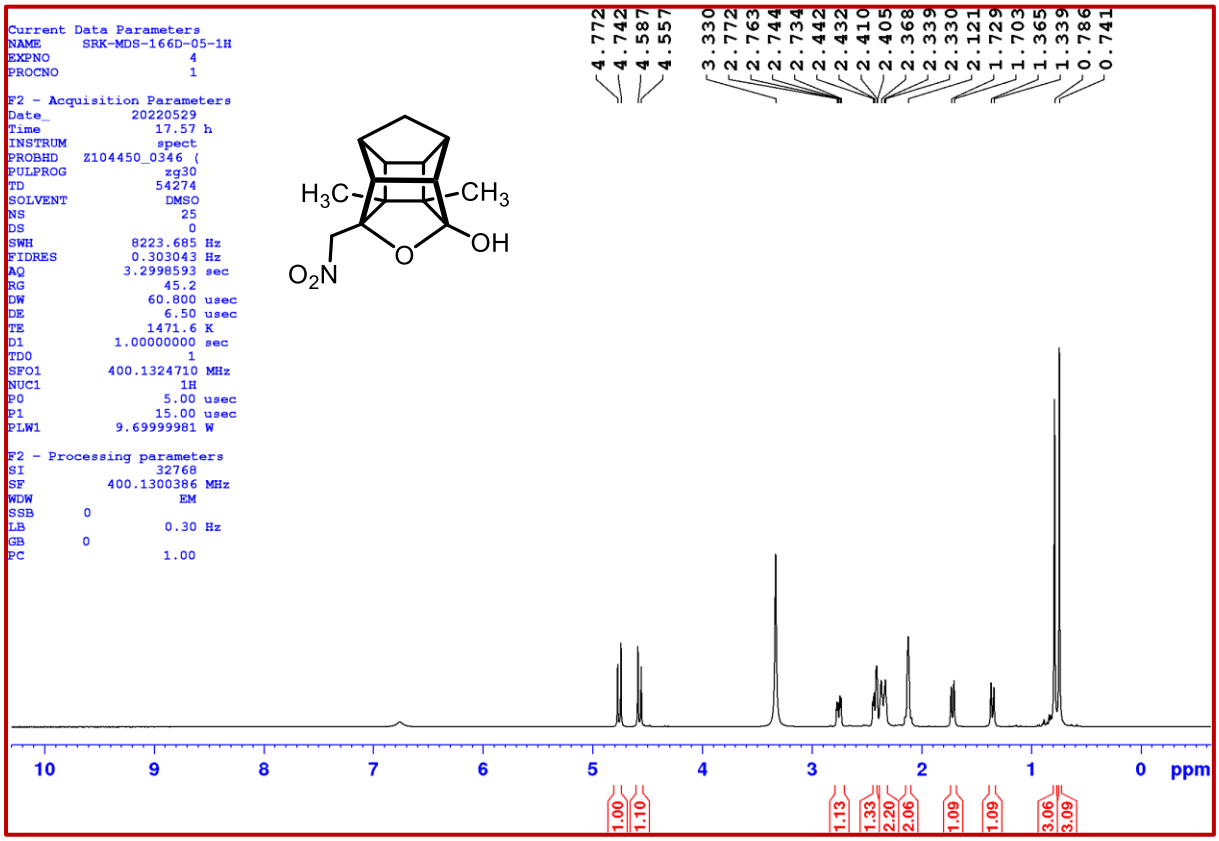
^{13}C NMR of Compound 16b (100.6 MHz, $CDCl_3$)



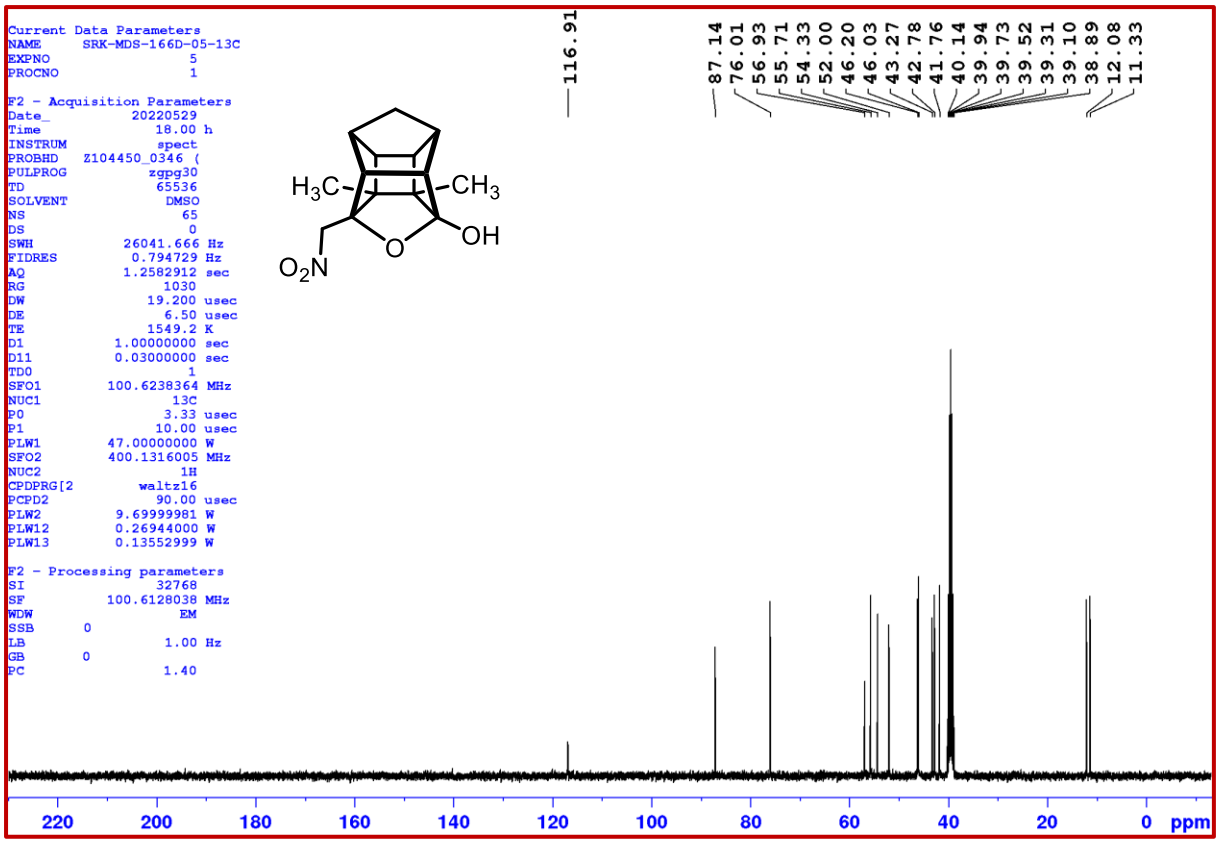
DEPT 135 NMR of Compound 16b (100.6 MHz, $CDCl_3$)



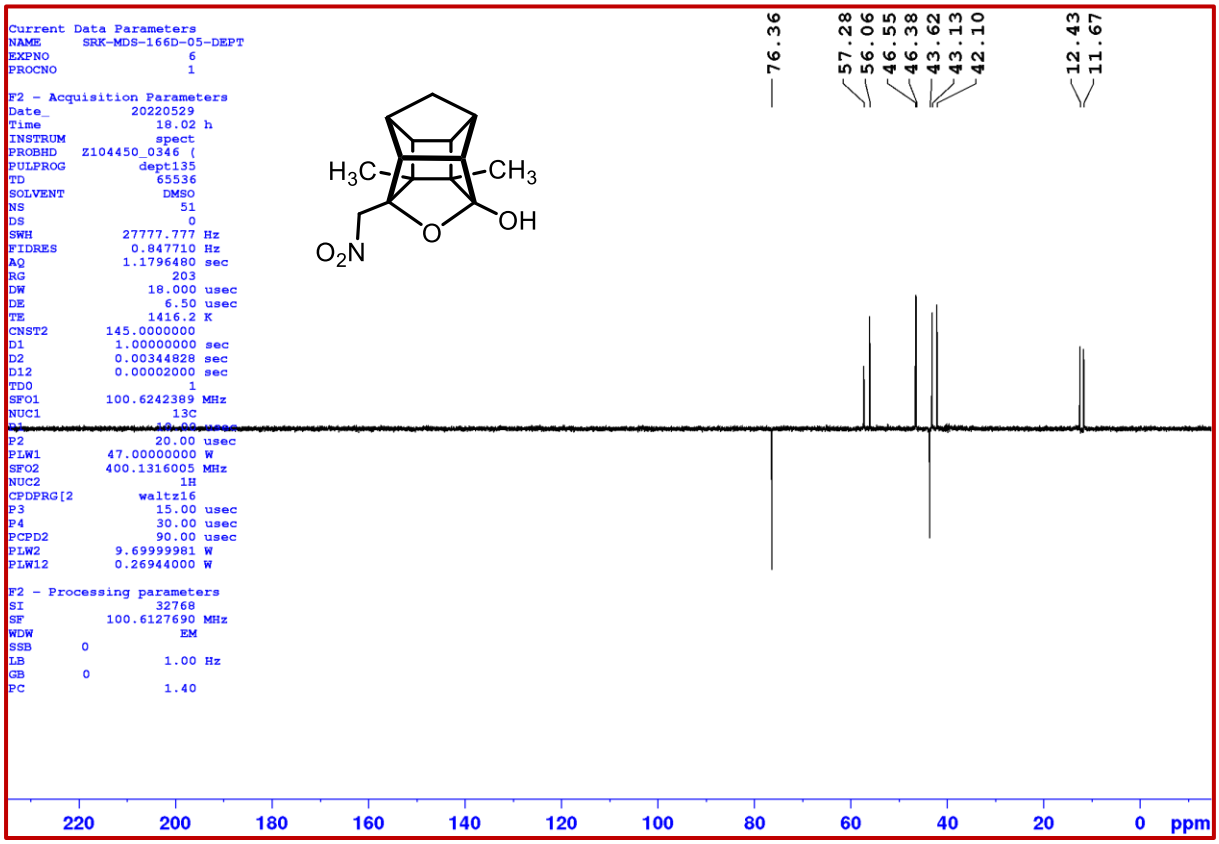
^{1}H NMR of Compound 16c (400 MHz, DMSO-d_6)



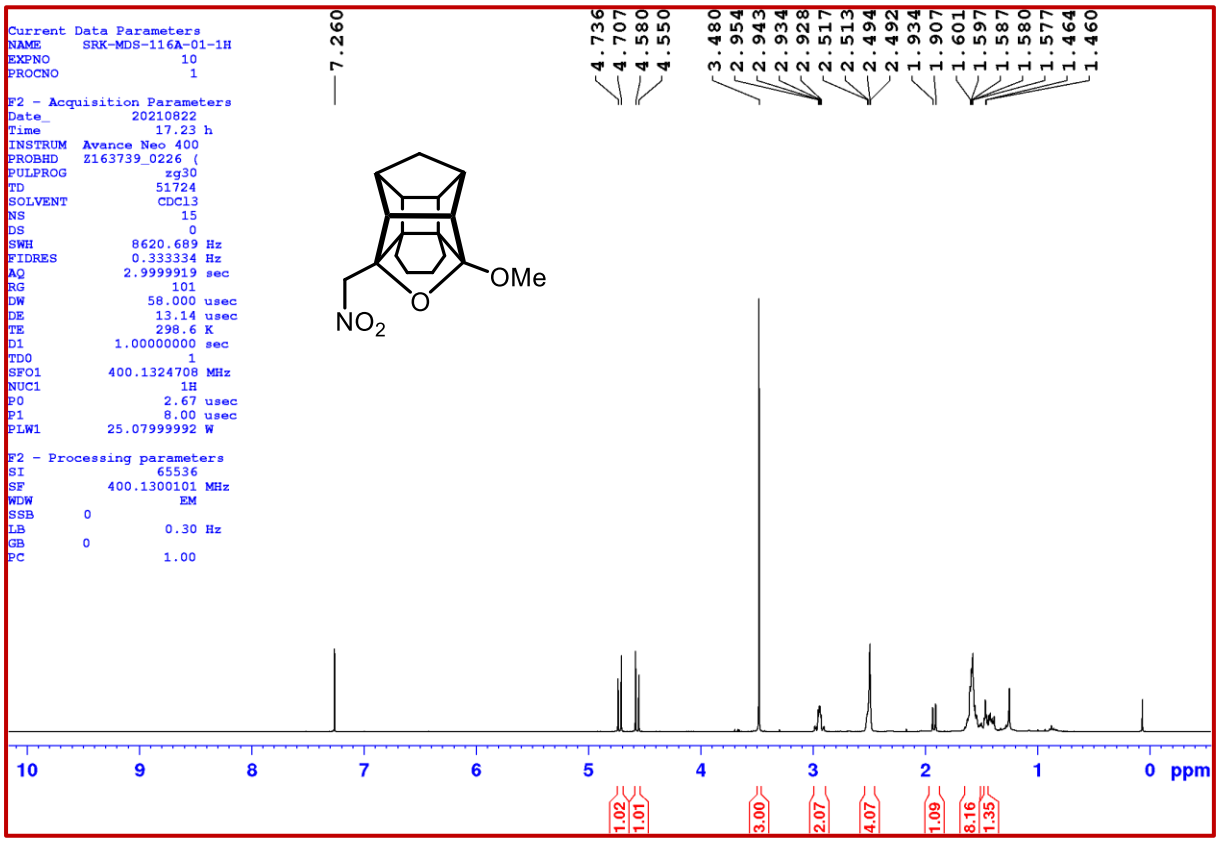
^{13}C NMR of Compound 16c (100.6 MHz, DMSO-d_6)



DEPT 135 NMR of Compound 16c (100.6 MHz, DMSO-d_6)



^{1}H NMR of Compound 17a (400 MHz, $CDCl_3$)



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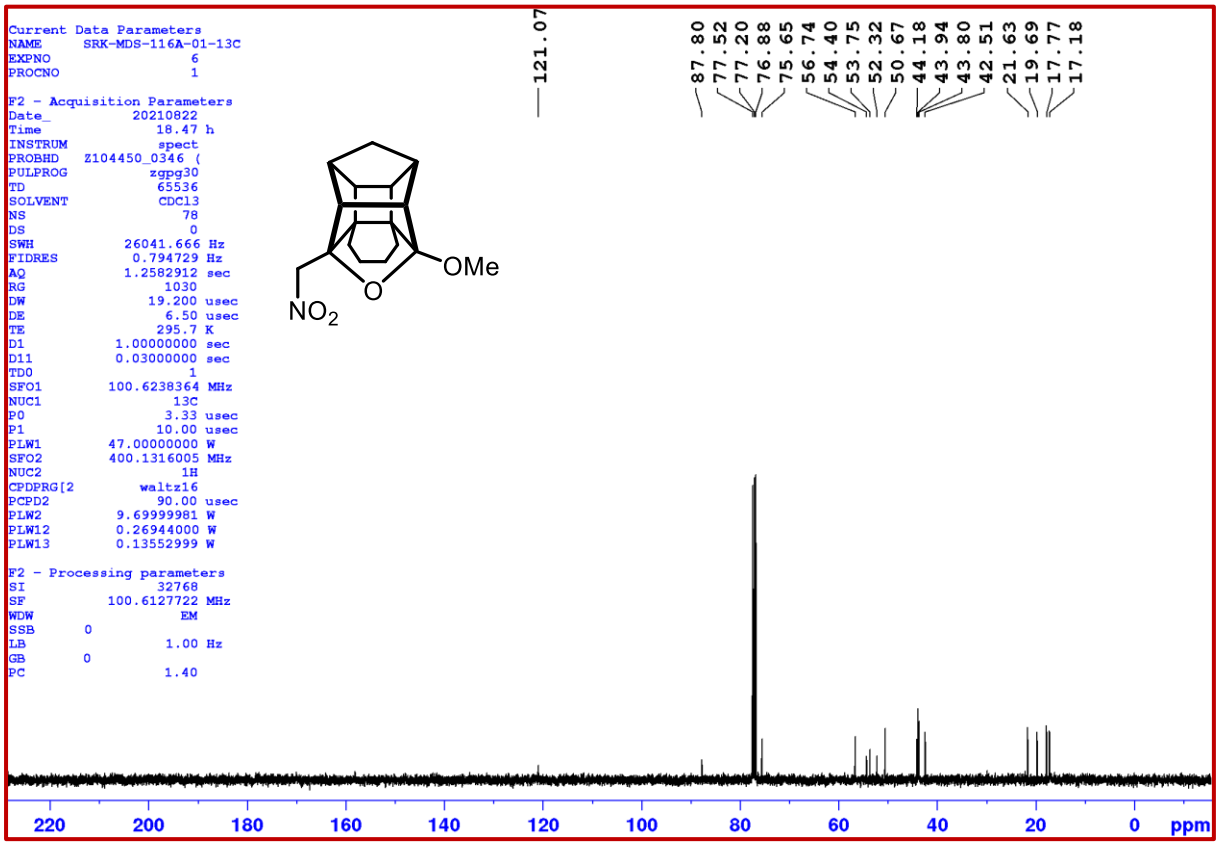

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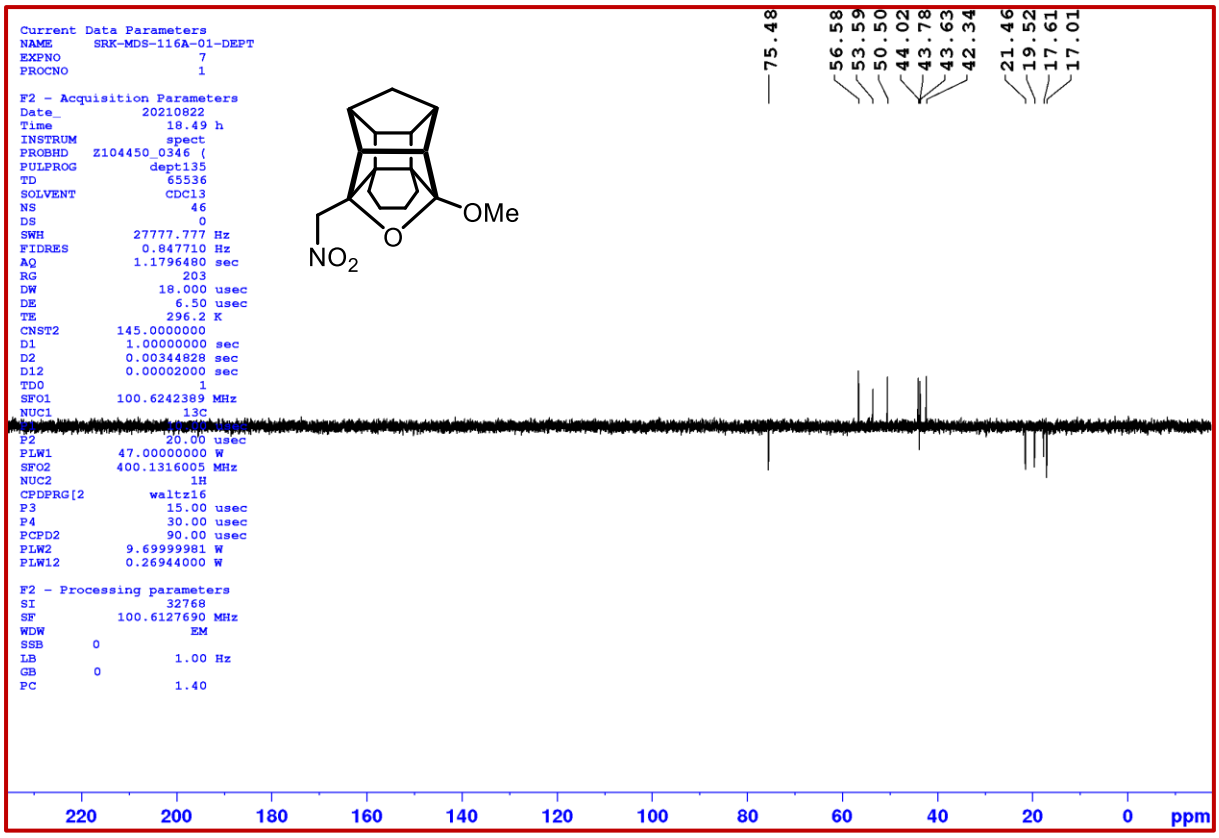
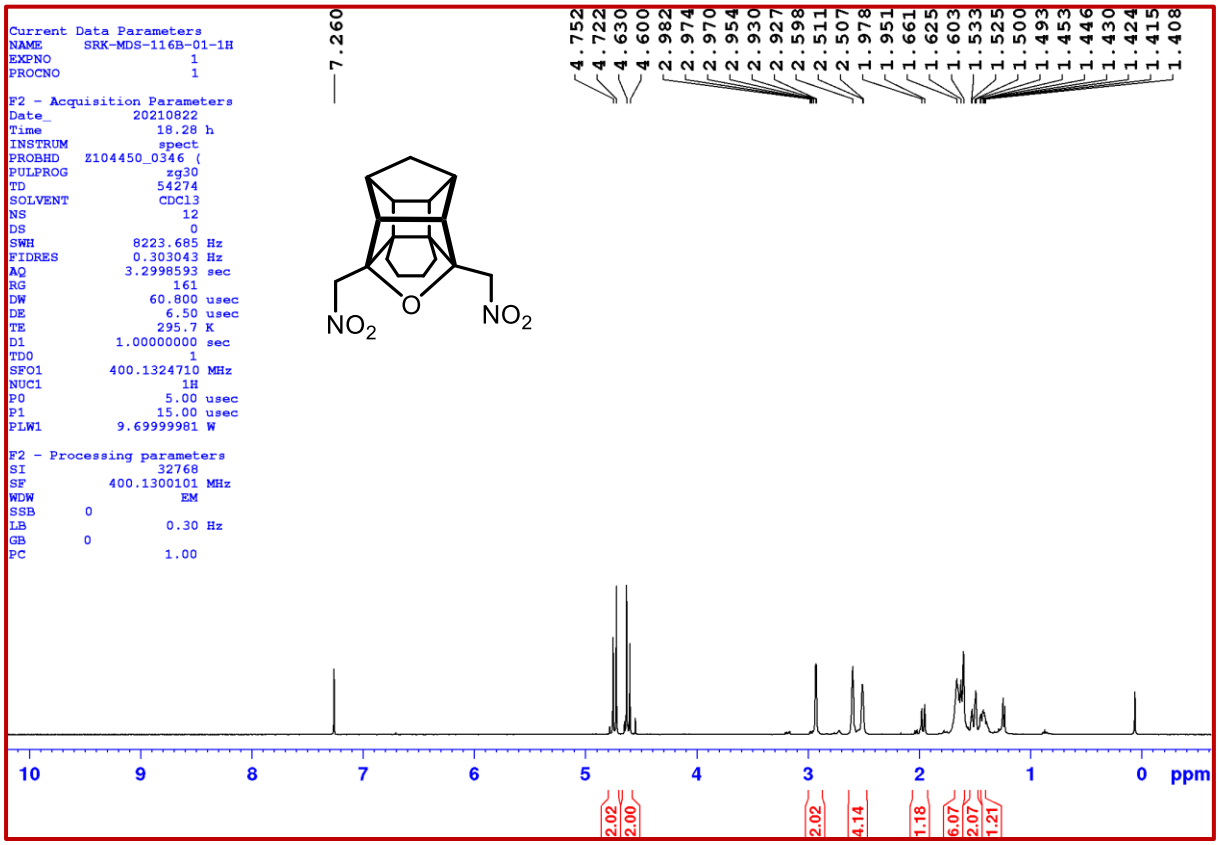
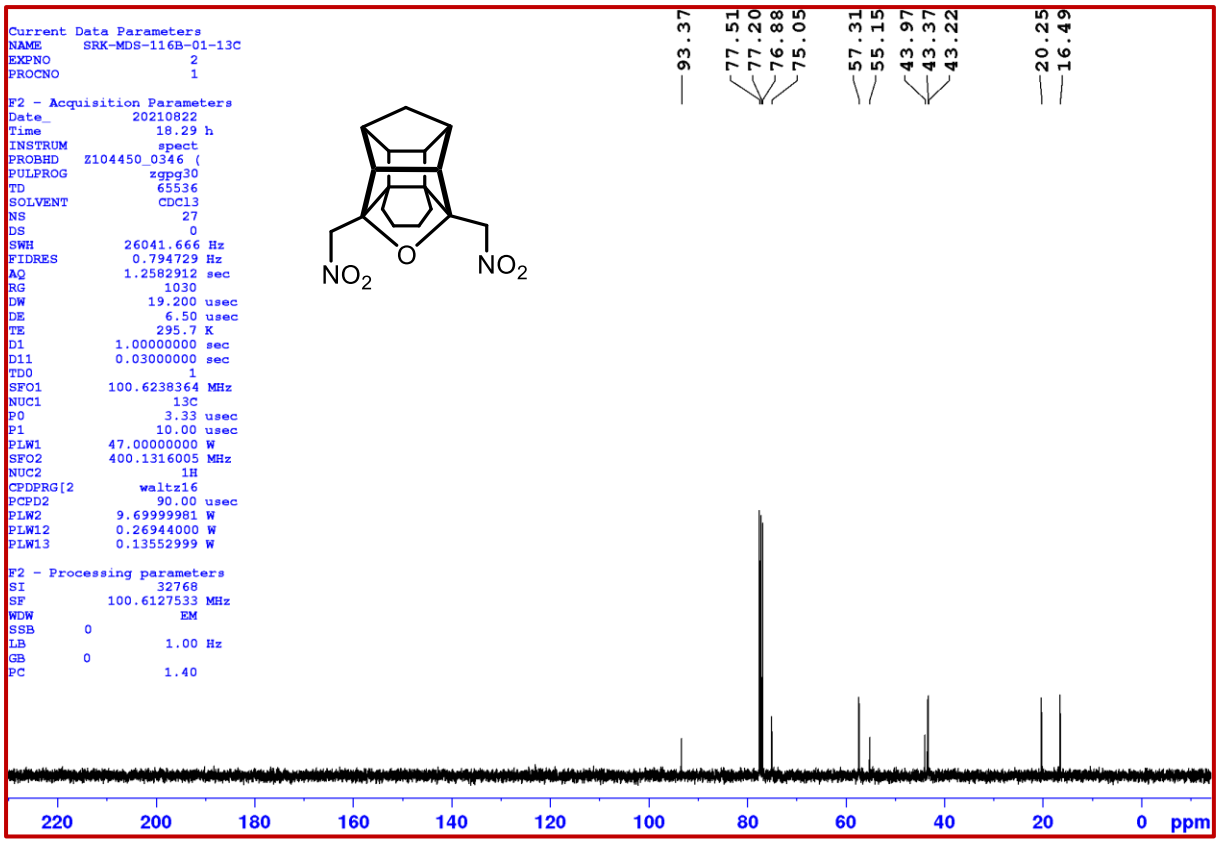


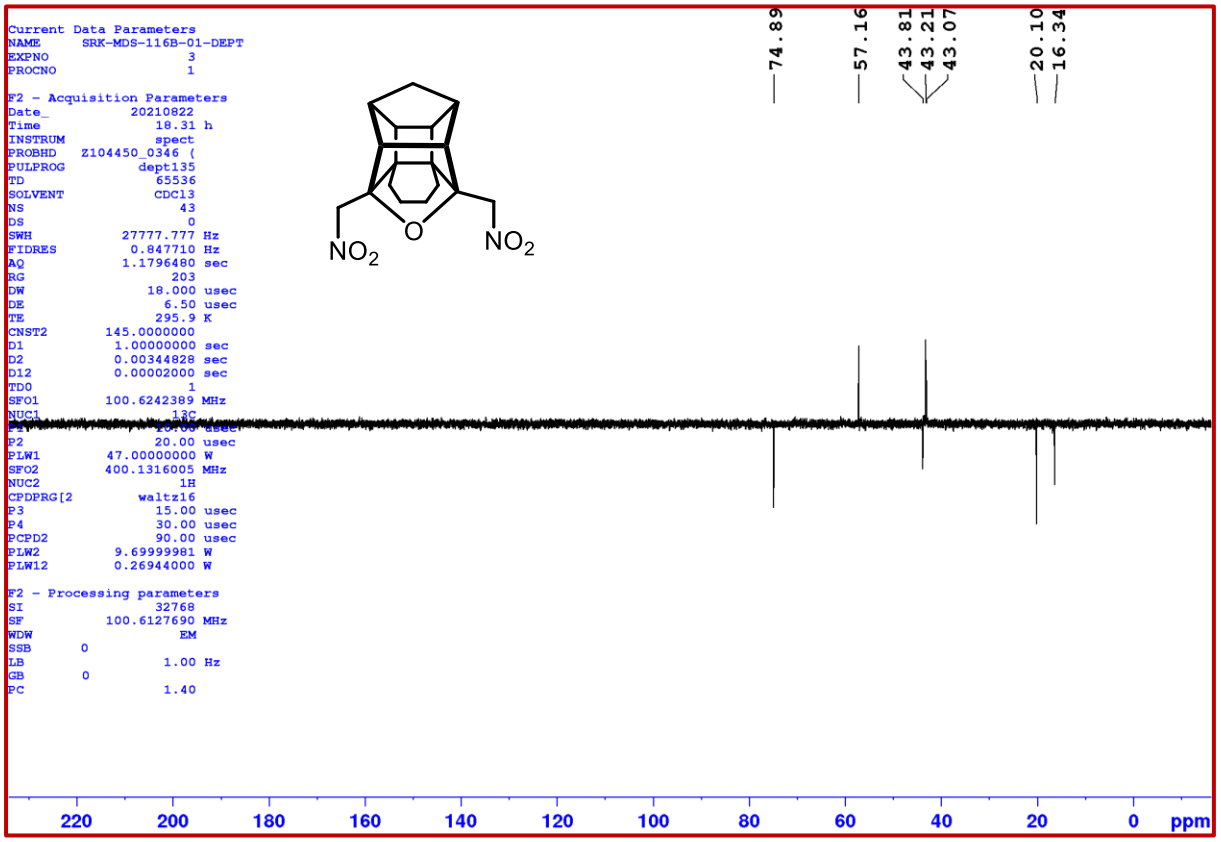
^{1}H NMR of Compound 17b (400 MHz, $CDCl_3$)



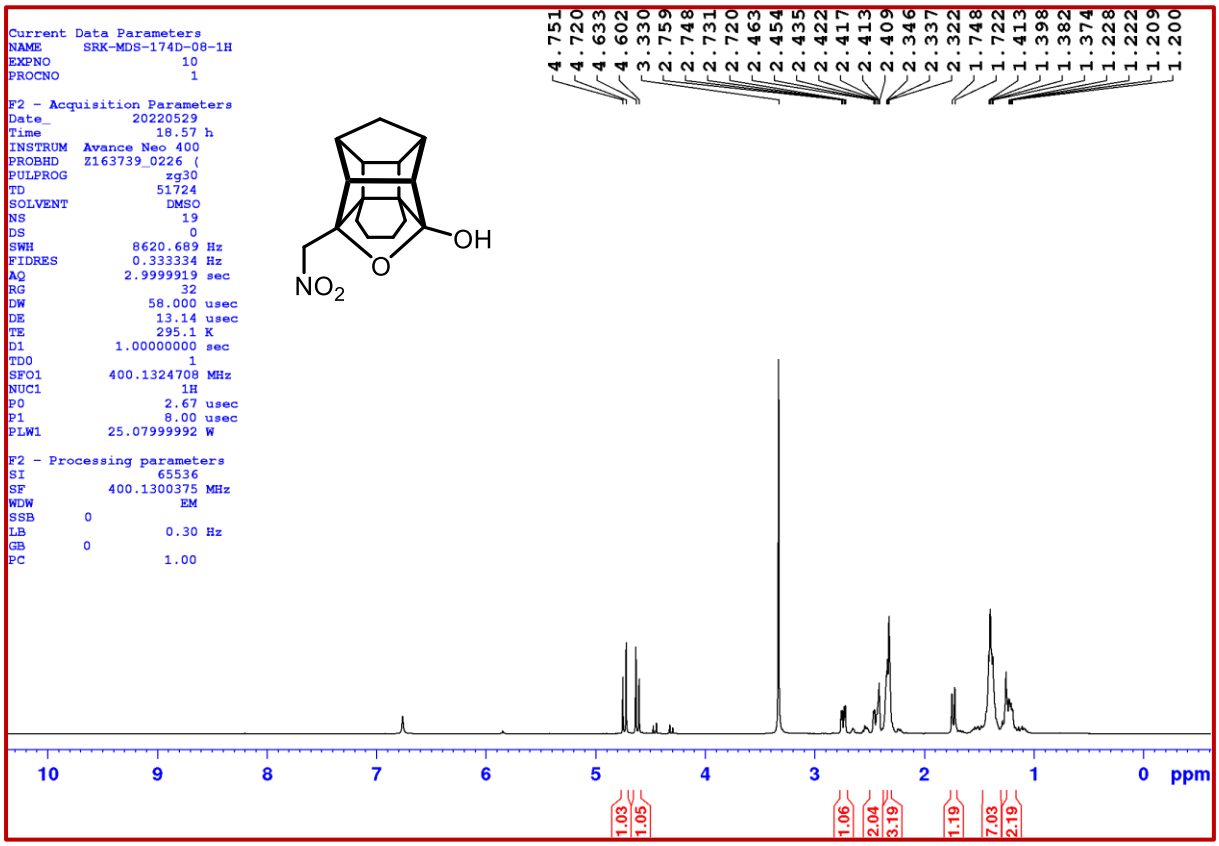
^{13}C NMR of Compound 17b (100.6 MHz, $CDCl_3$)



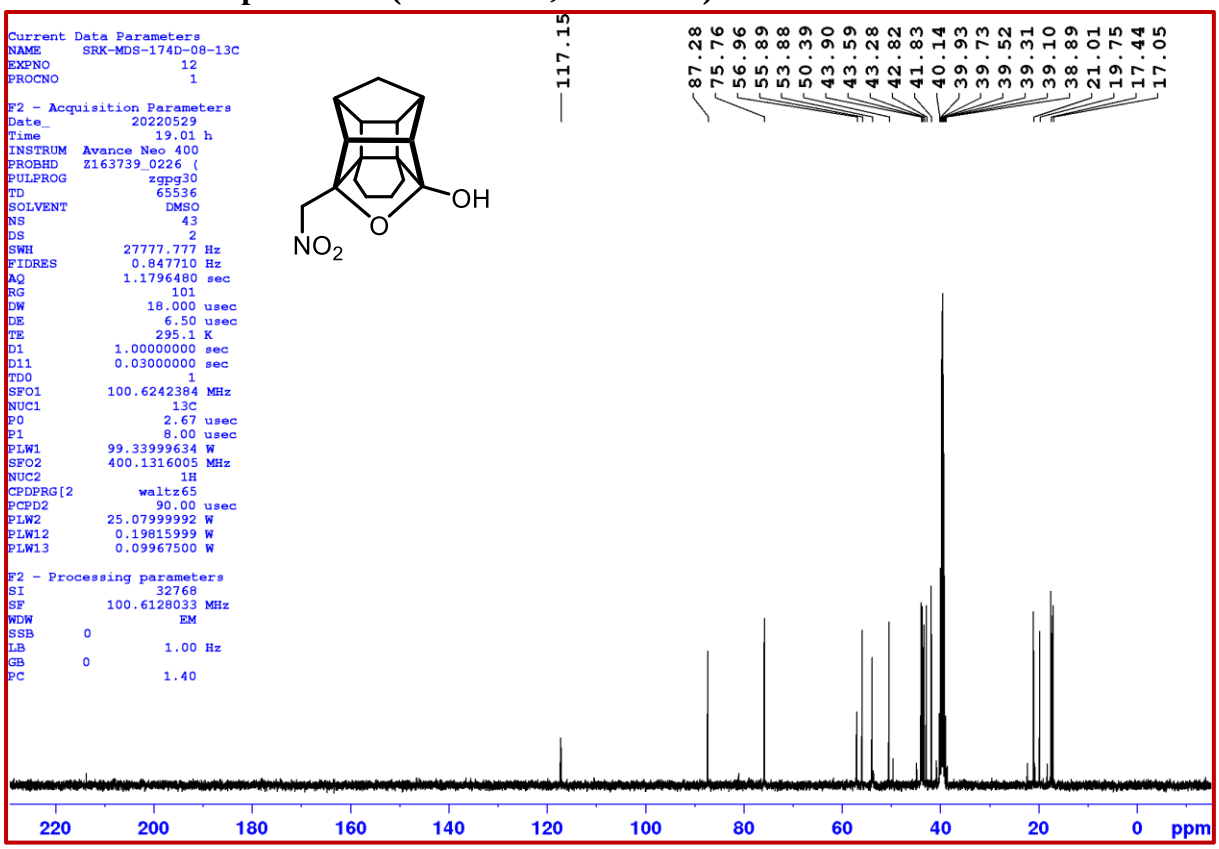
DEPT 135 NMR of Compound 17b (100.6 MHz, $CDCl_3$)



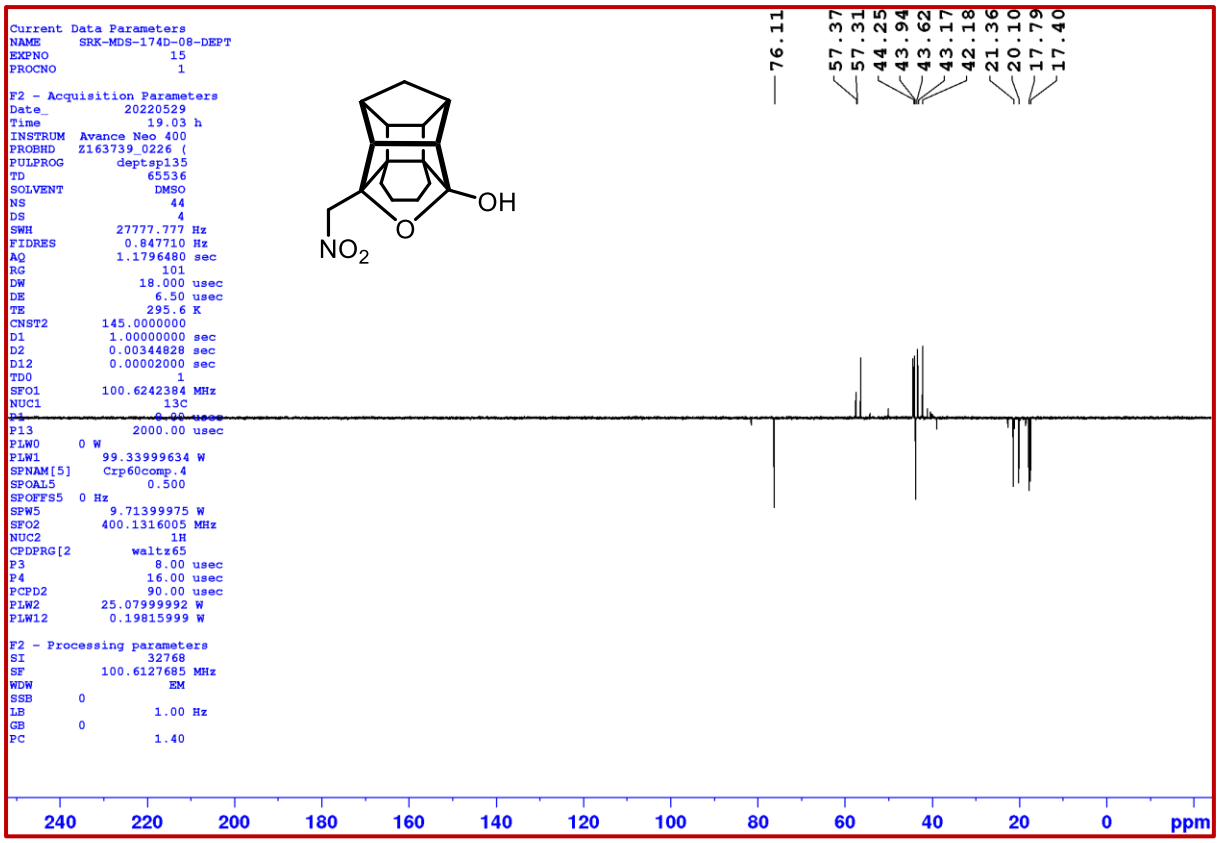
^{1}H NMR of Compound 17c (400 MHz, DMSO-d$_6$)



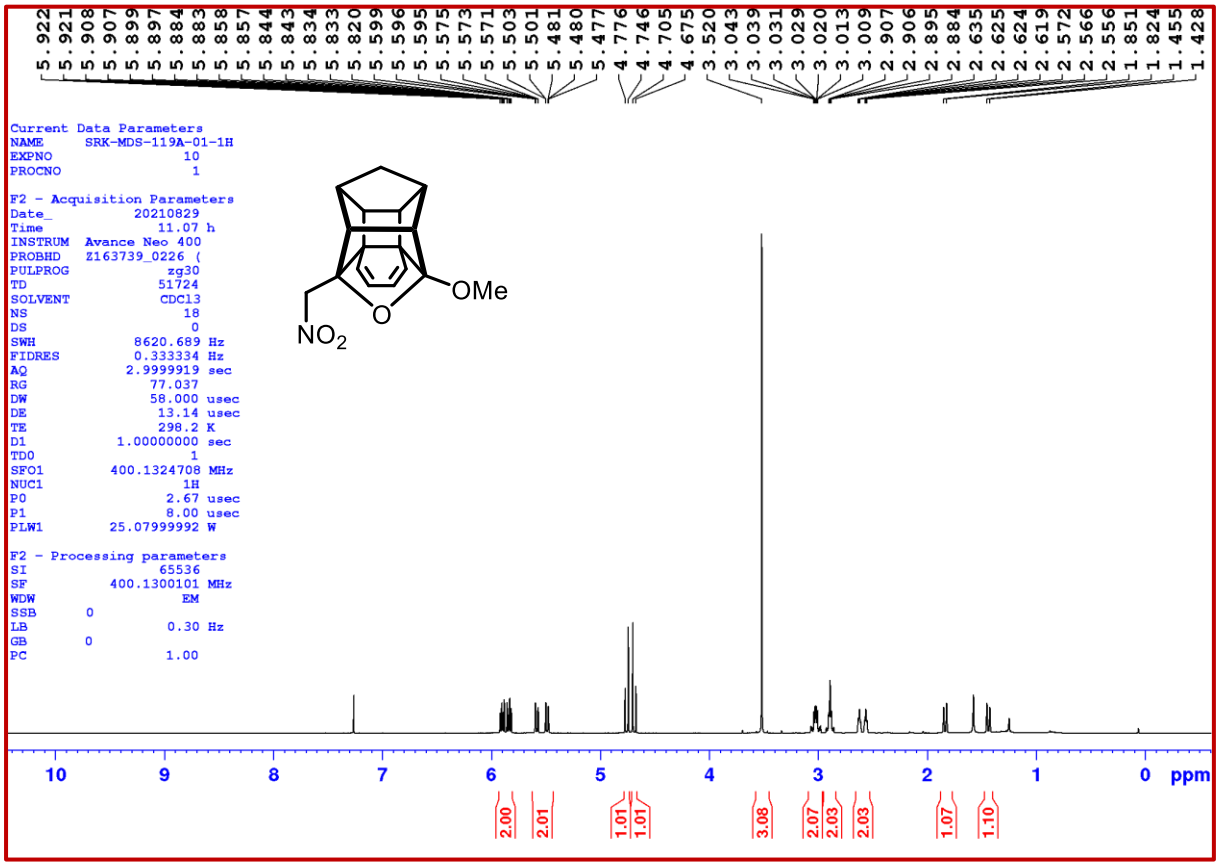
^{13}C NMR of Compound 17c (100.6 MHz, DMSO-d$_6$)



DEPT 135 NMR of Compound 17c (100.6 MHz, DMSO-d_6)



^{1}H NMR of Compound 18a (400 MHz, $CDCl_3$)



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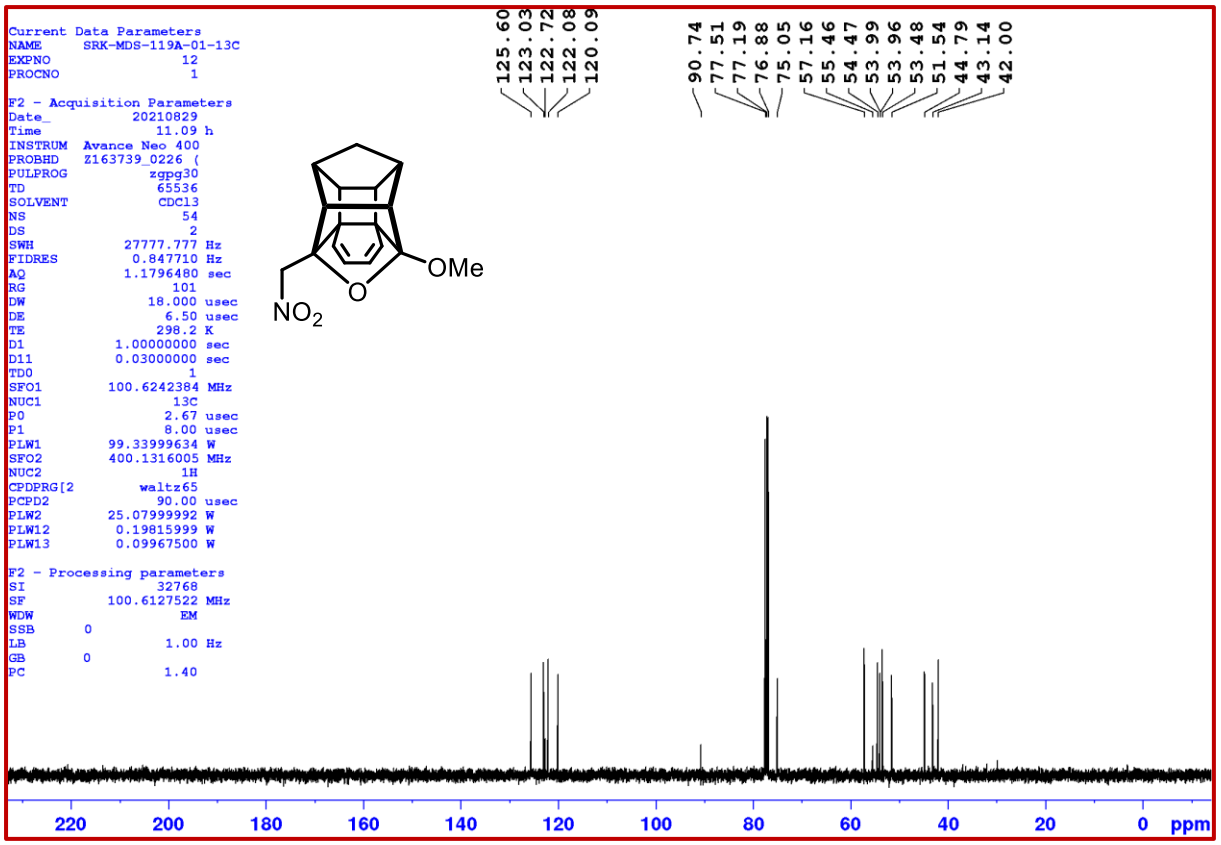

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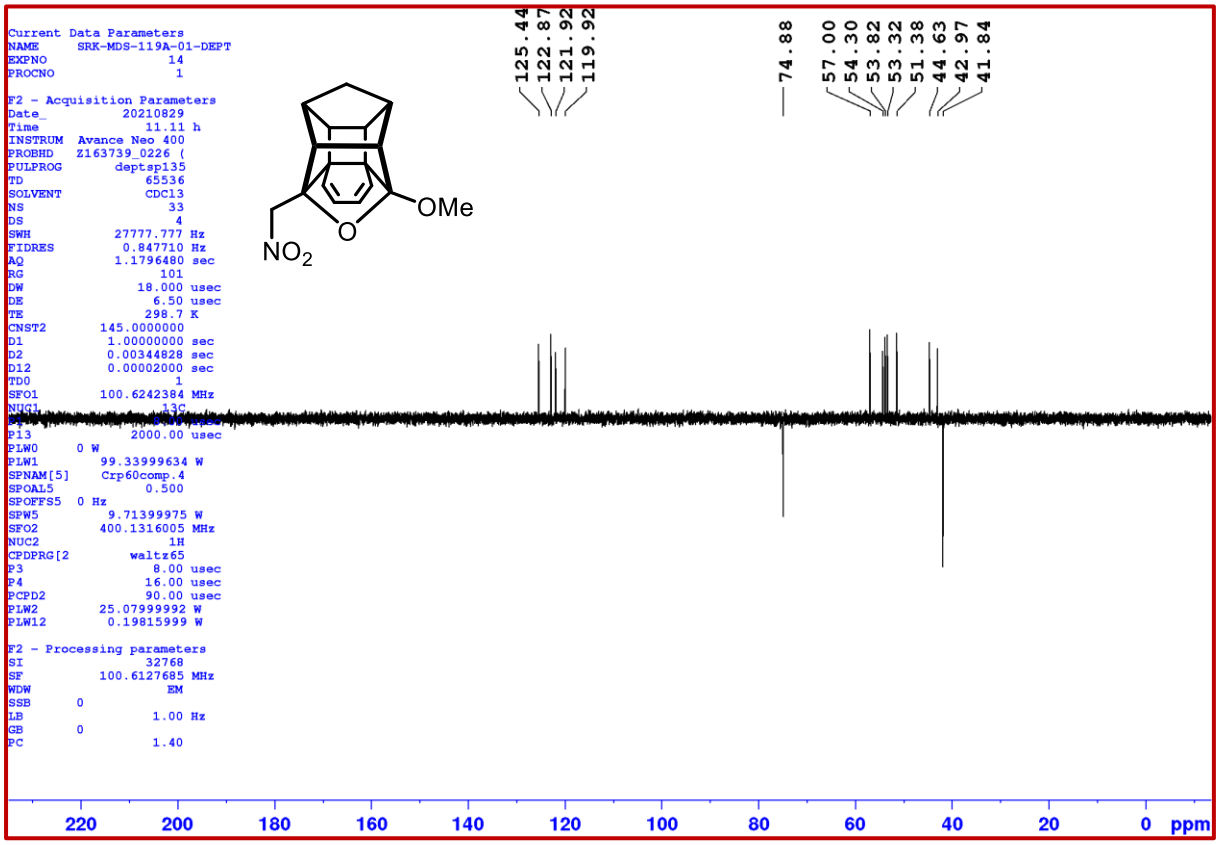
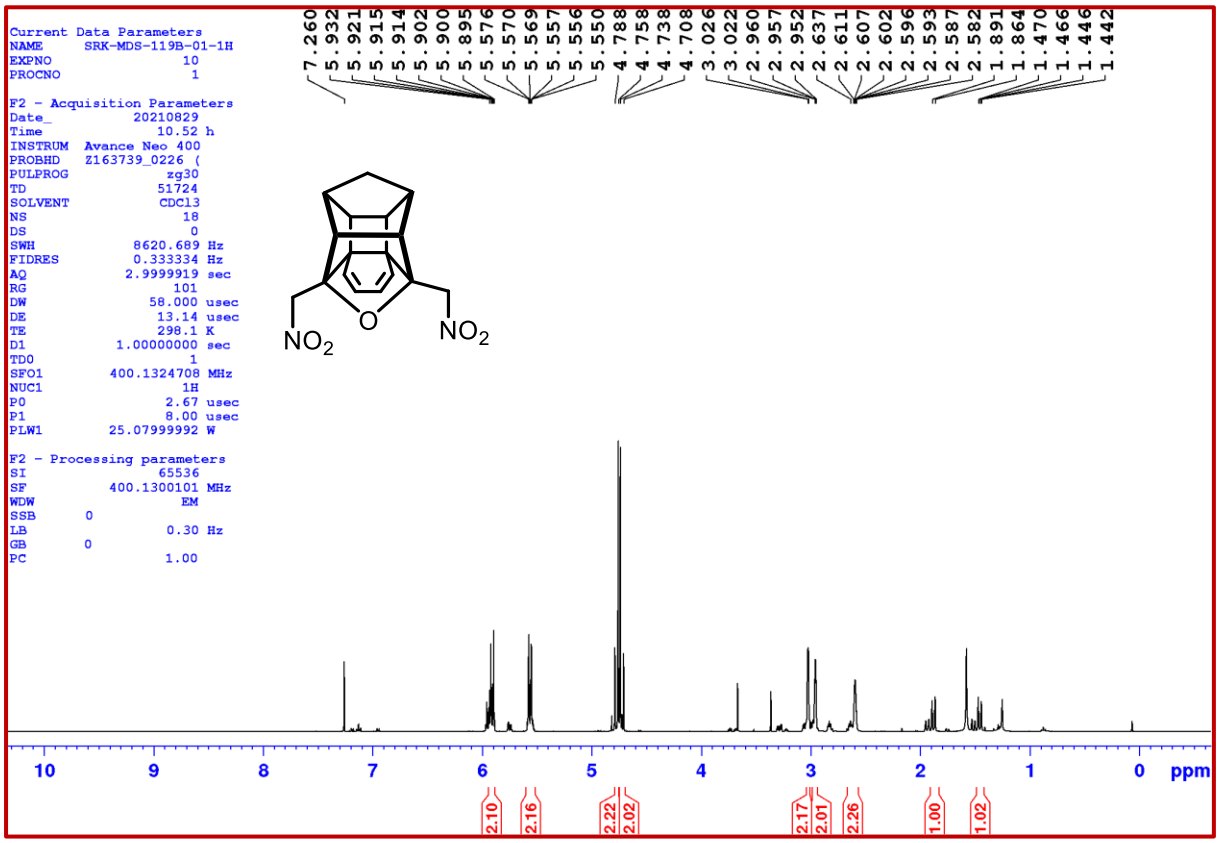
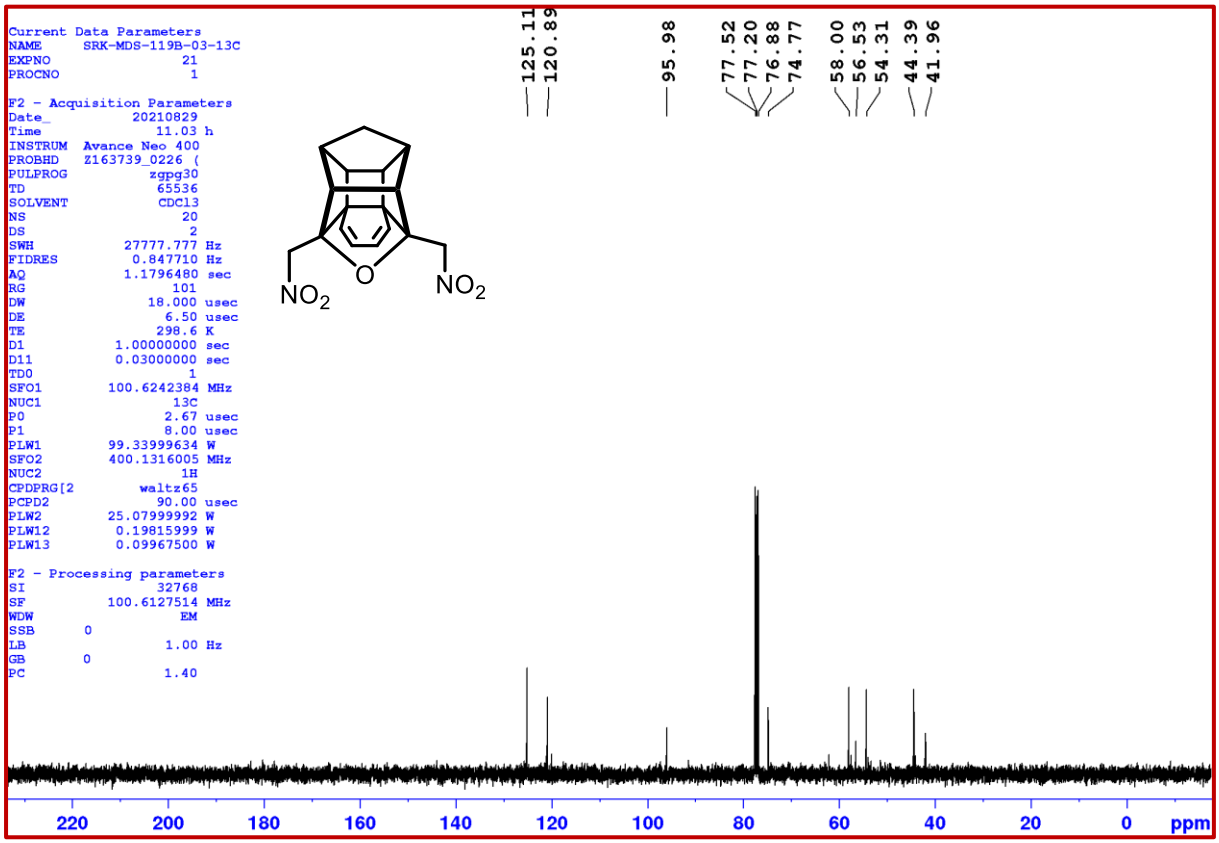


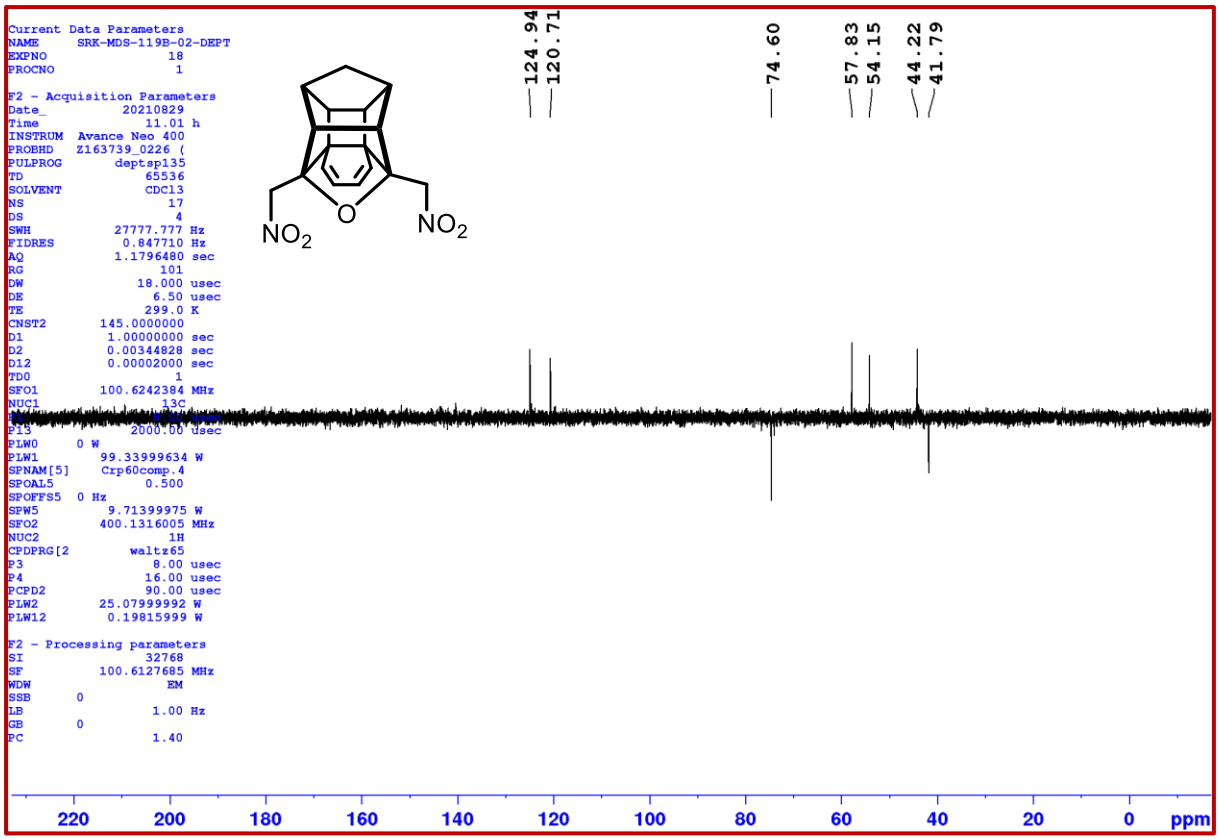
^{1}H NMR of Compound 18b (400 MHz, $CDCl_3$)



^{13}C NMR of Compound 18b (100.6 MHz, $CDCl_3$)



DEPT 135 NMR of Compound 18b (100.6 MHz, $CDCl_3$)



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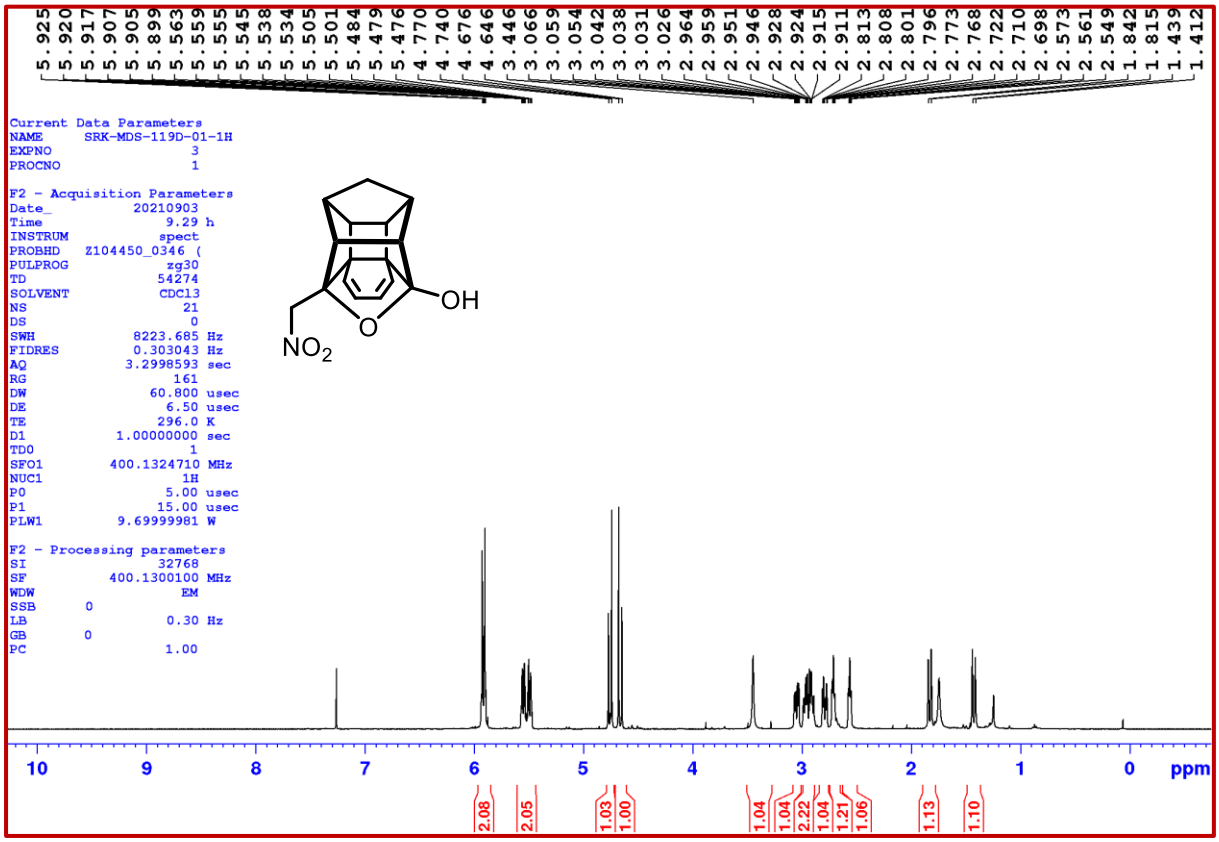

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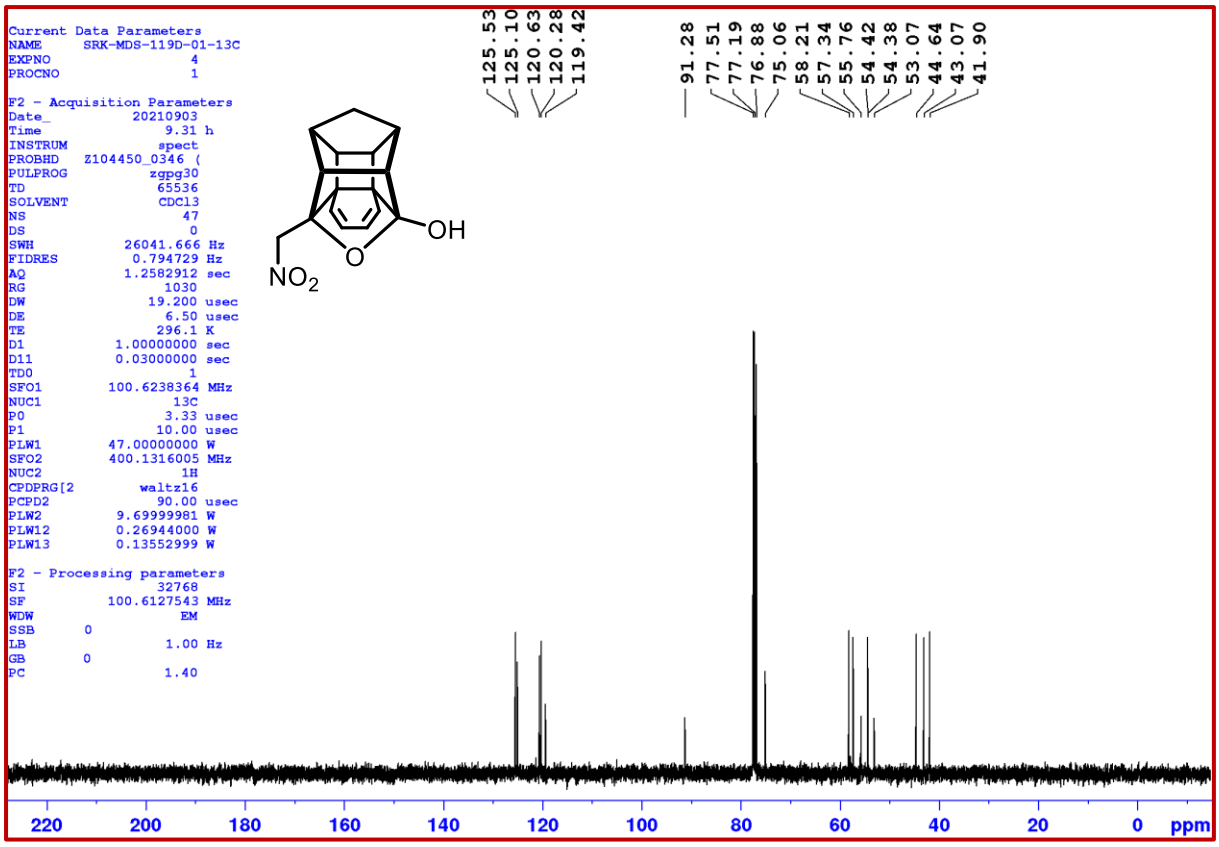
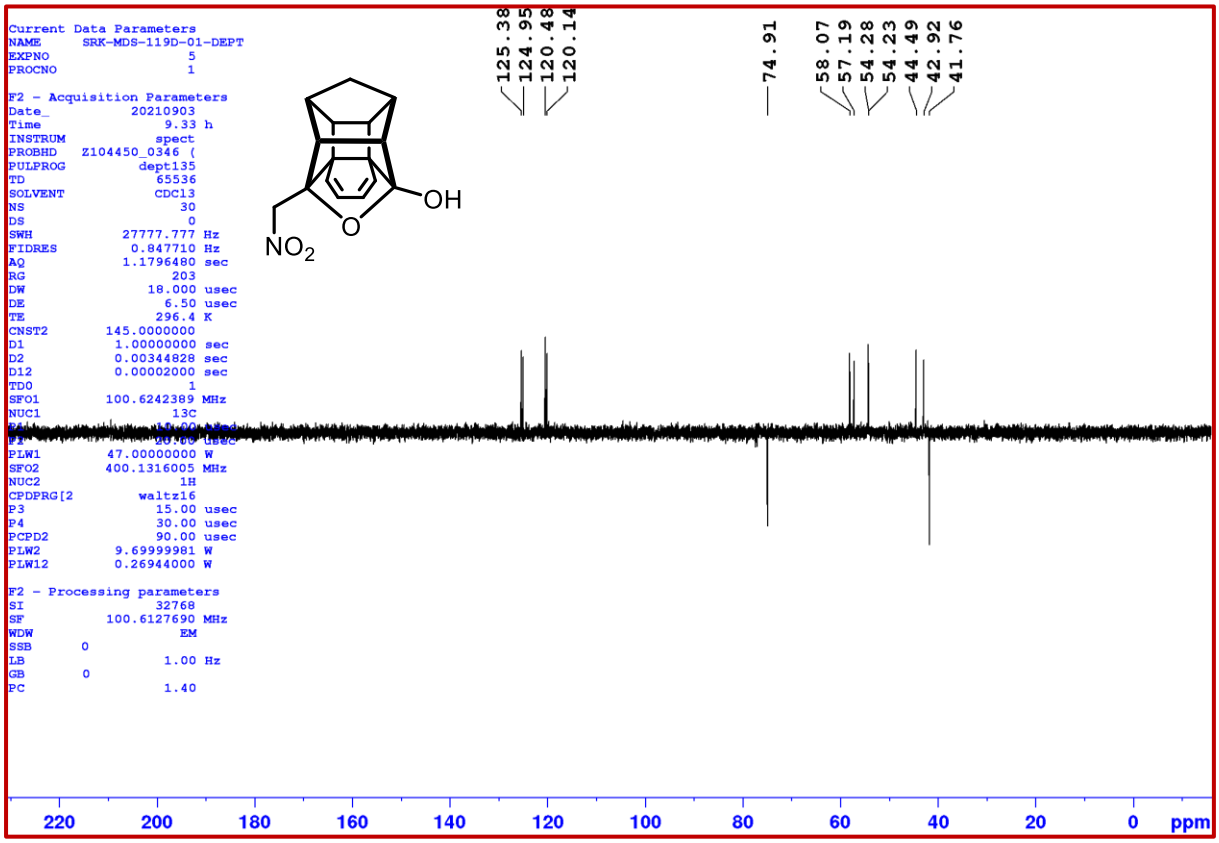


DEPT 135 NMR of Compound 18c (100.6 MHz, $CDCl_3$)



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3. Mehta, G.; Srikrishna, A.; Reddy, A. V.; Nair, M. S. *Tetrahedron* **1981**, *37*, 4543.
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