Supporting information

Transition metal(IV) complexes of nitro-substituted 2,4,9-triazaadamantane-based tris-hydroxylamines: evidence for nitrogen α-effect on stabilization of higher oxidation states

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1. General Methods and Instrumentation

All reactions were carried out in oven-dried (150°C) glassware. CH_2Cl_2, CH_3CN and Et_2O were distilled over CaH_2, other solvents were distilled without drying agents. Ene-nitrosoacetals **3a**[1] and **3b**,[1] $[Co(TACN)(H_2O)_3](CF_3SO_3)_3$,[2] and $[Fe(TACN)]Cl_3$[3] were prepared according to previously described protocols. 1,4,7-Triazacyclononane trihydrochloride (**TACN·3HCl**), CH_3NO_2, DBU, phenylboronic acid, *N*,*N*-Di(octyl)octan-1-amine (trioctylamine), *p*-thiocresol, glutathione, diphenyl ketone, *m*CPBA, 9,10-dihydroanthracene and all inorganic reagents were commercial grade and used as received.

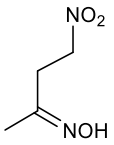
NMR spectra were recorded at room temperature with residual solvent peaks as internal standards.[4] Multiplicities are indicated by s (singlet), d (doublet), dd (doublet of doublets), dddd (doublet of doublets of doublets), td (triplet of doublets), tt (triplet of triplets), m (multiplet), and br (broad). Chemical shifts in ^{11}B spectra are given relative to $BF_3{\cdot}Et_2O$ (0 ppm). W values correspond to the full width at half-maximum of the signal in Hz. Chemical shifts of ^{15}N in 2D $\{^1H\}–\{^{15}N\}$ HMBC spectrum of **7-Ni**(Cl) are given relative to CH_3NO_2 (0 ppm).

Melting points were determined on a Kofler heating stage and were not corrected. Thermogravimetric analysis was studied using STA 449 F3(Netzsch) with ~1mg samples poured in aluminum crucibles covered with pierced lids. HRMS experiments were performed on a mass-spectrometer with electrospray ionization and a time-of-flight (TOF) detector. Peaks in FT-IR spectra data are reported in cm^{-1} with the following relative intensities: s (strong), m (medium), w (weak), br (broad), sh (shoulder). UV-Vis spectra were recorded on a SF2000 spectrophotometer for the solutions of the investigated compounds. Peaks in UV-Vis spectra data are reported in nm. X-band EPR spectra for **7-Mn**(Cl) was recorded from 2mM solution in acetonitrile at 25°C with microwave frequency 9.448 GHz, modulation amplitude 100 μT and 20 db attenuation.

2. Experimental procedures

2.1. Synthesis of mono- and bis-oximes 4 and 5

Synthesis of 4a



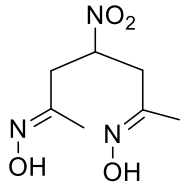
4-Nitrobutan-2-one oxime (4a). Under argon atmosphere, DBU (0.45 mL, 3 mmol) was added to a Schlenk flask with a solution of nitromethane (0.195 mL, 3.6 mmol) in diethyl ether (15 mL) cooled to 0 °C. The reaction mixture was stirred for 30 min at 0 °C, then cooled to -30 °C, and 1M solution of ene-nitrosoacetal **3a** in dry dichloromethane (3 mL, 3 mmol) was added dropwise. The reaction mixture was stirred for 4 h at -30 °C and then warmed to room temperature. After that, NH_4F (1000 mg, 27 mmol) and 5 ml of methanol were added to the resulting solution. The mixture was stirred for 15 min at room temperature. The resulting solution was poured into a mixture of saturated aqueous $NaHCO_3$ solution (50 mL) and EtOAc (50 mL). After separation of the organic layer, the aqueous layer was washed with an additional 50 mL of EtOAc. The combined organic layers were washed with a saturated NaCl solution (50 mL) and dried over Na_2SO_4. The volatiles were removed in vacuo (80 Torr, 37°C). The residue was pre-adsorbed on silica gel and chromatographed (a hexane-EtOAc mixture, 5:1, as the eluent). The resulting residue was dried in a vacuum until constant weight to give 52 mg (yield 13%) of **4a** as a colorless oil. R_f = 0.7 (Hex:EtOAc=1:1). Dynamic mixture of isomers, E : Z = 12.5:1.

E-isomer: ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.93 (s, 3H, C*H*$_3$), 2.89 (t, J = 6.8 Hz, 2H, C*H*$_2$-C=N), 4.60 (t, J = 6.8 Hz, 2H, C*H*$_2$-NO_2), 8.00 (s, 1H, N-O*H*).

Z-isomer: ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.04 (s, 3H, C*H*$_3$), 3.01 (t, J = 7.1 Hz, 2H, C*H*$_2$-C=N), 4.64 (t, J = 7.1 Hz, 2H, C*H*$_2$-NO_2), 8.37 (s, 1H, N-O*H*).

The ^{1}H NMR spectrum is in agreement with literature data.[5]

Synthesis of 5a

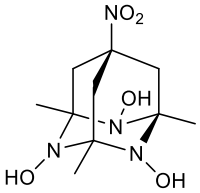


4-Nitroheptane-2,6-dione dioxime (5a). Under argon atmosphere, DBU (0.45 mL, 3 mmol) was added to a Schlenk flask with a solution of nitromethane (0.162 mL, 3 mmol) in diethyl ether (10 mL) cooled to 0 °C. The reaction mixture was stirred for 30 min at 0 °C, then cooled to -30 °C, and 1 M solution of ene-nitrosoacetal **3a** in dry dichloromethane (6 mL, 6 mmol) was added dropwise. The reaction mixture was stirred for 4 h at -30 °C and then warmed to room temperature. After that, NH_4F (2000 mg, 54 mmol) and 5 ml of methanol were added to the resulting solution. The mixture was stirred for 15 min at room temperature. The resulting solution was poured into a mixture of saturated aqueous $NaHCO_3$ (50 mL) and ethyl acetate (50 mL). After separation of the organic layer, the aqueous layer was washed with an additional 50 mL of ethyl acetate. The combined organic layers were washed with a saturated NaCl solution (50 mL) and dried (Na_2SO_4). The volatiles were removed in vacuo (80 Torr, 37°C). The residue was pre-adsorbed on silica gel and chromatographed (a hexane-ethyl acetate mixture, 5:1→2:1, as eluent). The resulting solid material was dried in a vacuum until constant weight to give 218 mg (yield 36%) of **5a** as a white solid. Mp. 139-141°C. R_f = 0.5 (Hex:EtOAc=1:1). Dynamic mixture of isomers, E,E : E,Z = 2:1. E,E-isomer: ^{1}H NMR (300 MHz, COSY, CD_3OD, E,E-isomer, δ, ppm): 1.89 (s, 6H, 2 C*H*$_3$), 2.69 (dd, *J* = 15.9, 4.9 Hz, 2H, C*H*$_2$), 2.86 (dd, *J* = 15.9, 9.1 Hz, 2H, C*H*$_2$), 5.21 (tt, *J* = 9.1, 4.9 Hz, 1H, C*H*-NO_2), N-O*H* not observed.^{13}C {1H} NMR (75 MHz, HSQC, CD_3OD, E,E-isomer, δ, ppm): 13.6 (2*C*H_3), 40.1 (2*C*H_2), 82.9 (*C*H-NO_2), 153.5 (2*C*=N).

E,Z-isomer: ^{1}H NMR (300 MHz, COSY, CD_3OD, E,Z - isomer δ, ppm): 1.88 (s, 3H, C*H*$_3$, Z-fragment), 1.89 (s, 3H, C*H*$_3$, E-fragment), 2.75-2.62 (m, 2H, C*H*$_2$), 2.99-2.86 (m, 2H, C*H*$_2$), 5.30 (dddd, J = 9.3, 7.2, 7.2, 4.9 Hz, 1H, C*H*-NO_2). N-O*H* not observed.^{13}C {1H} NMR (75 MHz, HSQC, CD_3OD, E,Z - isomer δ, ppm): 13.6 (CH_3, E-fragment), 20.5 (CH_3, Z-fragment), 34.2 (CH_2, Z-fragment), 40.2 (CH_2, E-fragment), 82.5 (CH-NO_2), 153.4 (C=N), 153.6 (C=N). ESI-HRMS m/z: $[M+Ag]^+$ Calcd for $[C_7H_{13}N_3O_4Ag]^+$ 309.9952; Found 309.9951.

2.2. Synthesis of NO_2-TRIADs

Synthesis of NO_2-TRIAD (1a)



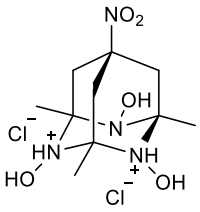
Under argon atmosphere, DBU (0.45 mL, 3 mmol) was added to a Schlenk flask with a solution of nitromethane (0.162 mL, 3 mmol) in diethyl ether (25 mL) cooled to 0 °C. The reaction mixture was stirred for 30 min at 0 °C, then cooled to -30 °C, and 1M solution of ene-nitrosoacetal **3a** in dry dichloromethane (9.3 mL, 9.3 mmol) was added dropwise. The reaction mixture was stirred for 4 h at -30 °C and then warmed to room temperature. After that, 5 mL of methanol were added to the resulting solution. The mixture was stirred for 15 min at room temperature. The resulting solution was poured into a mixture of saturated aqueous $NaHCO_3$ solution (50 mL) and EtOAc (50 mL). After separation of the organic layer, the aqueous layer was washed with an additional 50 mL of EtOAc. The combined organic layers were washed with a saturated NaCl solution (50 mL) and dried over anhydrous Na_2SO_4. The volatiles were removed in a vacuum (20 Torr, 37°C). The residue was adsorbed on silica gel and chromatographed (a hexane-EtOAc mixture 5:1→3:1→2:1, then EtOAc, as eluent). The resulting residue was dried in a vacuum until constant weight to give 310 mg (yield 38%) of **1a** as a colorless oil. Also, dioxime **5a** was isolated as a by-product (130 mg, yield 21%).

To the obtained oilish **NO_2-TRIAD 1a**, 2 ml of Et_2O and 10 ml of hexane were added, and the mixture was kept at 0°C for 4 h. After that, the mother liquor was collected and resulting solid material was dried in a vacuum until constant weight to give 304 mg (yield 37%) as a white solid. Mp. 147-152°C. R_f = 0.4 (EtOAc).

^{1}H NMR (300 MHz, 330K, HMBC, DMSO-d_6, δ, ppm): 1.29 (s, 9 H, 3 C*H*$_3$), 2.13 (s, br, 6 H, 3 C*H*$_2$), (3 O*H* not observed). ^{13}C {1H} NMR (125 MHz, 330K HMBC, DEPT135, DMSO-d_6, δ, ppm): 23.5 (*C*H$_3$), 35.8 (*C*H$_2$), 78.5 (*C*), 81.7 (*C*-*NO*$_2$). FT-IR (KBr): 3435 (br), 2929 (sh), 2872 (m), 1729 (s), 1640 (s), 1544 (s), 1467 (s), 1436 (s), 1372 (s), 1307 (m), 1213 (s), 1155 (w), 1077 (m), 1039 (s), 1014 (s), 950 (s), 870 (w), 827 (m), 769 (m), 747 (w), 710 (s), 677 (s), 621 (m), 480 (m), 458 (w), 412 (w). ESI-HRMS m/z: $[M+H]^+$ Calcd for $[C_{10}H_{19}N_4O_5]^+$ 275.1350; Found 275.1356. Anal. Calcd for $C_{10}H_{18}N_4O_5 \cdot 0.5Et_2O$: C, 45.12; H, 7.06; N, 19.13. Found: C, 45.25; H, 6.85; N, 19.33.

Preparation of crystals for X-ray analysis: **1a** (40 mg) was dissolved in 0.5 mL of $CDCl_3$ in a NMR tube. The solution was left to stay in a refrigerator at 4°C for 1 day. White crystals of **1a**·0.5$CDCl_3$ suitable for X-Ray diffraction analysis were formed.

Synthesis of 1a·2HCl

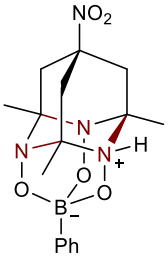


2M HCl in Et_2O (0.373 mL, 0.75 mmol) was added dropwise, with vigorous stirring, within 2 min, to a solution of **NO_2-TRIAD 1a** (100 mg, 0.37 mmol) in 2 mL of Et_2O. The reaction mixture was stirred for 5 min. The mother liquor was separated from the precipitate. Et_2O (2 mL) was added to the latter and the mixture was then stirred for 2 minutes. This operation was repeated two more times. Then, 2 mL of hexane was added to the solid residue and stirring was continued for 2 min. The mother liquor was collected, while the solid material was dried in a vacuum until constant weight to give 94 mg (yield 66%) of **1a·2HCl** as a yellow solid.

Mp. 78-83°C. ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 1.44 (s, 9 H, 3 CH_3), 2.37 (s, 6 H, 3 CH_2), 4.33 (s, br, 5 H, 3 OH and 2 NH). ^{13}C {1H} NMR (75 MHz, DEPT135, DMSO-d_6, δ, ppm): 22.2 (*C*H_3), 34.9 (*C*H_2), 79.9 (*C*), 81.1 (*C*-NO_2). FT-IR (KBr): 3401 (br), 3305 (br), 2997 (w), 2517 (w), 1721 (w), 1702 (w), 1639 (s), 1581 (m), 1547 (s), 1432 (s,sh), 1379 (s), 1312 (m), 1239 (s), 1224 (s), 1193 (s), 1113 (w), 1069 (w), 1023 (s), 1014 (s), 950 (m), 933 (m) 886 (w), 827 (m), 765 (m), 739 (m), 712 (m), 658 (s), 588 (s,br), 479 (m), 457 (w), 432 (w). ESI-HRMS m/z: $[M\text{-}H\text{-}2Cl]^+$ Calcd for $[C_{10}H_{19}N_4O_5]^+$ 275.1350; Found 275.1357. Anal. Calcd for $C_{10}H_{18}N_4O_5 \cdot 0.5Et_2O \cdot 2HCl$: C, 37.51; H, 6.56; N, 14.58. Found: C, 37.47; H, 6.78; N, 14.46.

2.3. Synthesis of boron derivatives 6

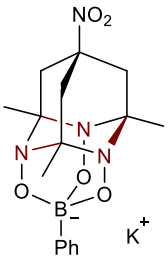
Synthesis of **6a**(H)



A solution of phenylboronic acid (7 mg, 0.06 mmol) in 0.5 mL of Et_2O was added to a solution of **NO_2-TRIAD 1a** (15 mg, 0.06 mmol) in 0.5 mL of Et_2O. The reaction mixture was stirred at room temperature for 1 hour. Then resulting precipitate was separated from the mother liquor and washed 5 times with 1 mL Et_2O. The resulting solid material was dried in a vacuum until constant weight to give 19 mg (yield 95%) of **6a**(H) as a white solid. Mp. above 260°C. ^{1}H NMR (300 MHz, CD_3OD, δ, ppm): 1.94 (s, 9 H, 3 C*H*$_3$), 2.65 (s, 6 H, 3 C*H*$_2$), 7.20 (m, 3 H, *m*- and *p*-C$_6$*H*$_5$), 7.43 (m, 2 H, *o*-C$_6$*H*$_5$), (N*H* not observed). ^{13}C {1H} NMR (75 MHz, DEPT135, CD_3OD, δ, ppm): 23.5 (*C*H$_3$), 43.5 (*C*H$_2$), 78.7 (*C*), 79.8 (*C*-NO_2), 128.1, 128.5, 132.0 (*o*, *m*, *p*-*C*$_6$H$_5$), (*C*-B not observed). ^{11}B NMR (96 MHz, CD_3OD, δ, ppm): 3.09 (s, br). ESI-HRMS m/z: $[M-H]^-$ Calcd for $[C_{16}H_{20}BN_4O_5]^-$ 359.1535; Found 359.1524.

Preparation of crystals for X-ray analysis: **6a**(H) (15 mg) was dissolved in 1 mL of methanol and the solution was filtered through a syringe filter. Slow vapor diffusion of diethyl ether into the methanol solution produced colorless crystals of **6a**(H) suitable for X-Ray diffraction analysis.

Synthesis of 6a(K)

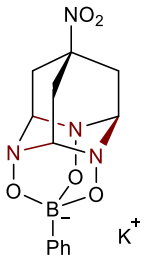


Procedure **A**. Phenylboronic acid (38 mg, 0.32 mmol) was added to a solution of **NO_2-TRIAD 1a** (73 mg, 0.32 mmol) in 2 mL of methanol. The reaction mixture was stirred at room temperature for 36 hours. Then, K_2CO_3 (22 mg, 0.16 mmol) was added and the reaction mixture was stirred for additional 2 hours. The resulting solution was concentrated under reduced pressure and the remaining residue was dried in a vacuum until constant weight to give 73 mg (yield 58%) of **6a**(K) as white solid. Mp. above 260°C. ^{1}H NMR (300 MHz, D_2O, δ, ppm): 1.78 (s, 9 H, 3 CH_3), 2.49 (s, 6 H, 3 CH_2), 7.33 (m, 3 H, *m*- and *p*-C_6H_5), 7.49 (m, 2 H, *o*-C_6H_5). ^{13}C {1H} NMR (75 MHz, HMBC, DEPT135, D_2O, δ, ppm): 23.6 (*C*H_3), 43.1 (*C*H_2), 75.7 (*C*), 79.0 (*C*-NO_2), 127.5, 127.6, 131.0 (*o*, *m*, *p*-*C*$_6H_5$), (*C*-B not observed). ^{11}B NMR (96 MHz, D_2O, δ, ppm): 2.70 (br, W = 256 Hz). FT-IR (KBr): 3348 (br), 3184 (m), 3070 (w), 3045 (m), 3015 (m), 2981 (s), 2942 (s), 1620 (s), 1531 (s), 1462 (s), 1432 (s), 1383 (s), 1369 (s), 1331 (w), 1309 (s), 1229 (s), 1202 (s), 1150 (m), 1079 (s), 1037 (m), 1006 (s), 953 (s), 932 (s), 920 (s), 896 (s), 871 (s), 806 (m), 761 (s), 743 (s), 707 (s), 677 (s), 642 (w), 615 (m), 559 (m), 545 (m), 517 (w), 447 (m), 412 (m). ESI-HRMS m/z: $[M-K]^-$ Calcd for $[C_{16}H_{20}BN_4O_5]^-$ 359.1535; Found 359.1523. Anal. Calcd for $C_{16}H_{20}BN_4O_5K{\cdot}1H_2O$: C, 46.16; H, 5.33; N, 13.46. Found: C, 45.81; H, 5.28; N, 13.23.

Preparation of crystals for X-ray analysis: **6a**(K) (50 mg) was dissolved in 1 mL of methanol and the solution was filtered through a syringe filter. Slow vapor diffusion of diethyl ether into the methanol solution produced colorless crystals of **6a**(K) suitable for X-Ray diffraction analysis.

Procedure **B**. A solution of phenylboronic acid (20 mg, 0.16 mmol) in 1 mL of Et_2O was added to a stirred solution of **NO_2-TRIAD 1a** (44 mg, 0.16 mmol) in 1 mL of Et_2O. The reaction mixture was stirred at room temperature for 1 hour. The resulting precipitate was separated from the mother liquor, washed 5 times with 1 mL Et_2O and dried in vacuum to constant weight (57 mg). After that, K_2CO_3 (11 mg, 0.08 mmol) and 1 mL H_2O were added and the reaction mixture was stirred for additional 1 hour at rt. The resulting solution was concentrated under reduced pressure and the remaining residue was dried in a vacuum until constant weight to give 53 mg (yield 82%). ^{1}H NMR (300 MHz, D_2O, δ, ppm): 1.83 (s, 9 H, 3 CH_3), 2.53 (s, 6 H, 3 CH_2), 7.38 (m, 3 H, *m*- and *p*-C_6H_5), 7.54 (m, 2 H, *o*-C_6H_5).

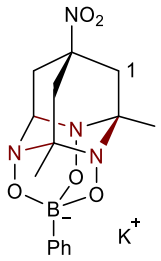
Synthesis of 6b(K)



DBU (0.285 mL, 1.9 mmol) was added to a solution of nitromethane (0.1 mL, 1.9 mmol) in Et_2O (15 mL) cooled to 0°C. The mixture was stirred for about 30 min, then cooled to -30°C, and a 1M solution of ene-nitrosoacetal **3b** in dry dichloromethane (5.9 mmol, 5.9 mL) was added dropwise. The reaction mixture was stirred at -30°C for 4 hours, then warmed to room temperature. MeOH (5 mL) was added and the mixture was stirred at room temperature for 30 min. The resulting solution was poured into a mixture of saturated aqueous $NaHCO_3$ solution (50 mL) and EtOAc (50 mL). The organic layer was separated, and the aqueous layer was washed with an additional 50 mL of EtOAc. The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and the solution was concentrated under reduced pressure (25°C, 20 Torr). To the residue, 3 mL of Et_2O was added, the insoluble material was filtered off, and the solution was transferred to a 10 mL flask. To this solution, 50 mg of phenylboronic acid was added and the mixture was stirred at room temperature for 2 hours. The resulting precipitate was separated from the solution, washed with Et_2O (5×1 mL) and dried in a vacuum (~ 2 h) until constant weight (40 mg). Then, H_2O (1 mL) and K_2CO_3 (9 mg, 0.07 mmol) were added. The resulting mixture was stirred for 1 hour at rt and concentrated under reduced pressure. The remaining solid was dried in a vacuum until constant weight to give 44 mg (yield 7% based on nitromethane) of **6b**(K) as a white solid.

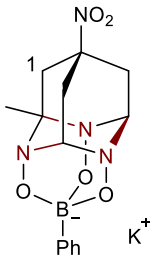
Mp. above 260°C. ^{1}H NMR (300 MHz, D_2O, δ, ppm): 2.71 (s, 6 H, 3 CH_2), 5.15 (s, 3 H, 3 C*H*), 7.36 (m, 3 H, *m*- and *p*-C_6H_5), 7.47 (m, 2 H, *o*-C_6H_5). ^{13}C {1H} NMR (75 MHz, DEPT135, D_2O, δ, ppm): 37.0 (CH_2), 73.3 (*C*H), 77.9 (*C*-NO_2), 127.7, 127.9, 130.9 (*o*, *m*, *p*-C_6H_5), (*C*-B not observed). ^{11}B NMR (96 MHz, D_2O, δ, ppm): 4.33 (s, br). ESI-HRMS m/z: $[M-K]^-$ Calcd for $[C_{13}H_{14}BN_4O_5]^-$ 317.1065; Found 317.1069.

Synthesis of 6c(K)



DBU (0.062 mL, 0.42 mmol) was added to a solution of 4-nitroheptane-2,6-dione dioxime (**5a**) (85 mg, 0.42 mmol) in Et_2O (15 mL) cooled to 0°C. The mixture was stirred for about 30 min, then cooled to -30°C, and a solution of ene-nitrosoacetal **3b** in dry dichloromethane (0.46 mmol, 0.46 mL) was added dropwise. The reaction mixture was stirred at -30°C for 4 hours, then warmed to room temperature. MeOH (3 mL) was added and the mixture was stirred at room temperature for 30 min. The resulting solution was poured into a mixture of saturated aqueous $NaHCO_3$ solution (50 mL) and EtOAc (50 mL). The organic layer was separated, and the aqueous layer was washed with an additional 50 mL of EtOAc. The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4. The solution was concentrated under reduced pressure (25°C, 20 Torr). To the residue, 5 mL of Et_2O was added, the insoluble material was filtered off, and the solution was transferred to a 10 mL flask. To this solution, 50 mg of phenylboronic acid was added and the mixture was stirred at room temperature for 2 hours. The resulting precipitate was separated from the solution, washed with Et_2O (5×1 mL) and dried in a vacuum (~ 2 h) until constant weight to give 20 mg of white precipitate. Then, H_2O (1 mL) and K_2CO_3 (4 mg, 0.029 mmol) were added. The reaction mixture was stirred for 1 hour at rt and concentrated under reduced pressure. The remaining residue was dried in a vacuum until constant weight to give 23 mg (yield 14%) of **6c**(K) as a white solid. Mp. above 260°C.^{1}H NMR (300 MHz, D_2O, δ, ppm): 1.79 (s, 6 H, 2 CH_3), 2.55 (s, 4 H, 2 CH_2), 2.69 (s, 2 H, 1 CH_2), 5.34 (s, 1 H, C*H*), 7.38 (m, 3 H, *m*- and *p*-C_6H_5), 7.52 (m, 2 H, *o*-C_6H_5). ^{13}C {1H} NMR (75 MHz, D_2O, δ, ppm): 24.7 (*C*H_3), 38.2 (*C*H_2), 44.3 (*C*H_2, *C*-1), 76.0 (*C*H), 76.7 (*C*), 80.5 (*C*-NO_2), 128.8, 128.9, 132.3 (*o*, *m*, *p*-C_6H_5), 168.3 (*C*-B). ^{11}B NMR (96 MHz, D_2O, δ, ppm): -3.57 (s, br).ESI-HRMS m/z: $[M-K]^-$ Calcd for $[C_{15}H_{18}BN_4O_5]^-$ 345.1378; Found 345.1383.

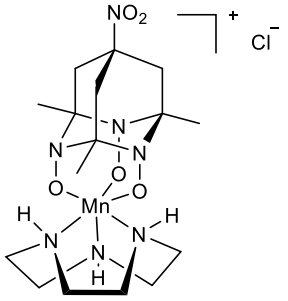
Synthesis of 6d(K)



DBU (0.091 mL, 0.61 mmol) was added to a solution of 4-nitrobutan-2-one oxime **4a** (80 mg, 0.61 mmol) in Et_2O (5 mL) cooled to 0°C. The mixture was stirred for about 30 min, then cooled to -30°C, and a solution of ene-nitrosoacetal **3b** in dry dichloromethane (1.3 mmol, 1.3 mL) was added dropwise. The reaction mixture was stirred at -30°C for 4 hours, then warmed to room temperature. MeOH (3 mL) was added and the mixture was stirred at room temperature for 30 min. The resulting solution was poured into a mixture of saturated aqueous $NaHCO_3$ solution (50 mL) and EtOAc (50 mL). The organic layer was separated, and the aqueous layer was washed with an additional 50 mL of EtOAc. The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4, and the solution was concentrated under reduced pressure (25°C, 20 Torr). To the residue, 5 mL of Et_2O was added, the insoluble material was filtered off, and the solution was transferred to a 10 mL flask. To this solution, 50 mg of phenylboronic acid was added and the mixture was stirred at room temperature for 2 hours. The resulting precipitate was separated from the solution, washed with Et_2O (5×1 mL) and dried in a vacuum (~ 2 h) until constant weight (35 mg). Then, H_2O (1 mL) and K_2CO_3 (7 mg, 0.05 mmol) were added. The reaction mixture was stirred for 1 hour at rt and concentrated under reduced pressure. The remaining residue was dried in a vacuum until constant weight to give 39 mg (yield 17%) of **6d**(K) as a white solid. Mp. above 260°C. ^{1}H NMR (300 MHz, D_2O, δ, ppm): 1.77 (s, 3 H, 1 CH_3), 2.57 (s, 2 H, 1 CH_2), 2.72 (s, 4 H, 2 CH_2), 5.26 (s, 2 H, 2 C*H*), 7.38 (m, 3 H, *m*- and *p*-C_6H_5), 7.51 (m, 2 H, *o*-C_6H_5). ^{13}C {1H} NMR (75 MHz, DEPT135, D_2O, δ, ppm): 24.6 (*C*H_3), 38.2 (*C*H_2), 44.3 (*C*H_2, *C*-1), 74.8 (*C*), 75.7 (*C*H), 80.1 (*C*-NO_2), 128.9, 129.0, 132.2 (*o*, *m*, *p*-C_6H_5), 168.0 (*C*-B). ^{11}B NMR (96 MHz, D_2O, δ, ppm): -3.30 (s, br). ESI-HRMS m/z: $[M-K]^-$ Calcd for $[C_{14}H_{16}BN_4O_5]^-$ 331.1222; Found 331.1217.

2.4. Synthesis of NO_2-TRIAD complexes 7-M

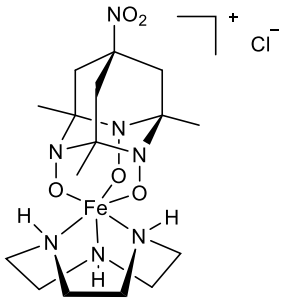
Synthesis of 7-**Mn**(Cl)



Trioctylamine (1.75 mL, 4 mmol) was added to a mixture of **NO_2-TRIAD 1a** (110 mg, 0.4 mmol), **TACN·3HCl** (96 mg, 0.4 mmol), and $MnCl_2 \cdot 4H_2O$ (79 mg, 0.4 mmol) in 10 mL of MeOH. The reaction mixture was stirred for 3 hours at room temperature under air and then kept for additional 24 hours with a closed cap. The precipitate was centrifuged off and a clear solution containing the **7-Mn**(Cl) complex was concentrated in a vacuum. The residue was dried at 0.1 Torr for 5 hours and triturated with Et_2O (7 × 10 mL). The remaining solid material was dried at 0.1 Torr to give 151 mg (yield 66%) of the **7-Mn**(Cl) complex as a black solid. Mp. 227-230°C (with dec.). FT-IR (KBr): 3431 (br), 3200 (br), 2982 (m), 2942 (s), 2884 (m), 1636 (s), 1541 (s), 1490 (w), 1455 (s), 1377 (s,br), 1260 (w), 1211 (s), 1190 (s), 1146 (m), 1100 (s), 1066 (w), 1027 (s), 953 (s), 871 (m), 825 (m), 793 (w), 766 (s), 702 (s), 649 (s), 618 (w), 578 (w), 505 (m), 489 (s), 446 (m), 419 (s). UV−vis spectrum: (MeOH, c = 1.3×10^{-3} M) peaks λ nm: 205, 253, 295, 459, 545. EPR g-factor = 2.0053, A =76G. ESI-HRMS m/z: $[M\text{-}Cl]^+$ Calcd for $[C_{16}H_{30}MnN_7O_5]^+$ 455.1683; Found 455.1680. Anal. Calcd for $C_{16}H_{30}ClMnN_7O_5 \cdot CH_3OH \cdot 3H_2O$: C, 35.39; H, 6.99; N, 16.99. Found: C, 35.21; H, 6.60; N, 16.97.

Preparation of crystals for X-ray analysis: complex **7-Mn**(Cl) (25 mg) was dissolved in 1 mL of methanol and the solution was filtered through a syringe filter. Slow vapor diffusion of diethyl ether into the methanol solution produced black crystals of **7-Mn**(Cl)·$2CH_3OH$ suitable for X-Ray diffraction analysis.

Synthesis of 7-Fe(Cl)

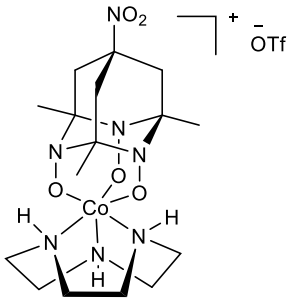


Trioctylamine (1.3 mL, 3 mmol) was added to a mixture of **1a·2HCl** (131 mg, 0.38 mmol), **TACN·3HCl** (60 mg, 0.25 mmol), and anhydrous $FeCl_3$ (41 mg, 0.25 mmol) in 10 mL of MeCN. The reaction mixture was stirred for 3 hours at room temperature under air and then kept for additional 24 hours with a closed cap. The precipitate was centrifuged off and a clear solution containing the **7-Fe**(Cl) complex was concentrated in a vacuum. The residue was dried at 0.1 Torr for 3 hours and washed with Et_2O (5 × 10 mL). Then, a mixture of Et_2O (8 mL) and CH_2Cl_2 (4 mL) was added to the crude product. The mixture was left to stay in a refrigerator at 4°C for 3 days. The precipitate was separated from the mother liquor and dried at 0.1 Torr for 30 min. The resulting solid material was placed in a centrifuge cup and centrifuged with CH_2Cl_2 (1 × 10 mL). The residual solid material was separated from a clear solution and dried in a vacuum at 0.1 Torr to give 36 mg (yield 28%) of the **7-Fe**(Cl) complex as a black solid. Mp. above 260°C.

FT-IR (KBr): 3400 (br), 3157 (br), 2941 (s), 2882 (m), 1637 (m), 1543 (s), 1455 (s), 1377 (s), 1261 (m), 1210 (s), 1189 (s), 1145 (m), 1102 (s), 1032 (s), 946 (s), 871 (m), 826 (m), 797 (m), 767 (s), 699 (s), 655 (m), 624 (w), 586 (w), 504 (s), 486 (s), 455 (w), 434 (w), 418 (w). UV−vis spectrum: (MeOH, c = 4.0×10^{-3} M) peaks λ nm: 271, 349, 498, 574. Mössbauer spectrum, 298K: δ, (mm/s) = 0.2451; $|\Delta E_Q|$, (mm/s) = 3.143(1). ESI-HRMS m/z: $[M\text{-}Cl]^+$ Calcd for $[C_{16}H_{30}FeN_7O_5]^+$ 456.1652; Found 456.1661. Anal. Calcd for $C_{16}H_{30}ClFeN_7O_5 \cdot H_2O$: C, 37.70; H, 6.33; N, 19.23. Found: C, 37.87; H, 6.70; N, 18.65.

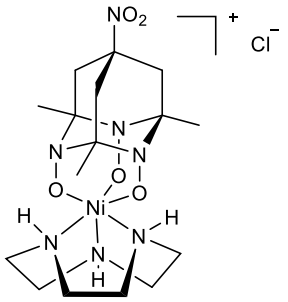
Preparation of crystals for X-ray analysis: complex **7-Fe**(Cl) (25 mg) was dissolved in 1 mL of methanol and the solution was filtered through a syringe filter. Slow vapor diffusion of diethyl ether into the methanol solution produced black crystals of **7-Fe**(Cl)·$2CH_3OH$ suitable for X-Ray diffraction analysis.

Synthesis of 7-Co(OTf)



Trioctylamine (0.4 mL, 0.9 mmol) was added to a mixture of **NO_2-TRIAD 1a** (69 mg, 0.27 mmol) and $[Co(TACN)(H_2O)_3](CF_3SO_3)_3$ (187 mg, 0.27 mmol) in 5 mL of MeOH. The reaction mixture was stirred for 2 hours at room temperature under air and then kept for additional 24 hours with a closed cap. The precipitate was centrifuged off and a clear solution containing the **7-Co**(OTf) complex was concentrated in a vacuum. The residue was dried at 0.1 Torr for 2 hours and triturated with Et_2O (5 × 10 mL). The remaining solid material was dried at 0.1 Torr for 2 hours to give 89 mg (yield 49%) of the **7-Co**(OTf) complex as brown solid. Mp. above 250°C. FT-IR (KBr): 3541 (br), 3469 (br), 3231(br), 2945 (sh,br), 1709 (w), 1631 (m), 1548 (s), 1458 (s), 1432 (s), 1404 (m), 1378 (s), 1352 (m), 1325 (m), 1280 (s), 1253 (s), 1225 (s), 1162 (s), 1099 (m), 1057 (s), 1029 (s), 979 (s), 898 (w), 874 (w), 849 (w), 822 (m), 759 (m), 731 (w), 639 (s), 574 (s), 550 (m), 518 (s), 416 (w). UV−vis spectrum: (MeOH, c = 1.6 × 10^{-4} M) peaks λ nm: 252, 326, 566. ESI-HRMS m/z: $[M\text{-}CF_3SO_3]^+$ Calcd for $[C_{16}H_{30}CoN_7O_5]^+$ 459.1635; Found 459.1638. M/z: $[M\text{-}CF_3SO_3\text{+}H]^+$ Calcd for $[C_{16}H_{31}CoN_7O_5]^+$ 460.1718; Found 460.1695. Anal. Calcd for $C_{17}H_{30}CoF_3SN_7O_8 \cdot 2H_2O \cdot CH_3OH$: C, 31.96; H, 5.66; N, 14.49. Found: C, 32.38; H, 5.04; N, 14.45.

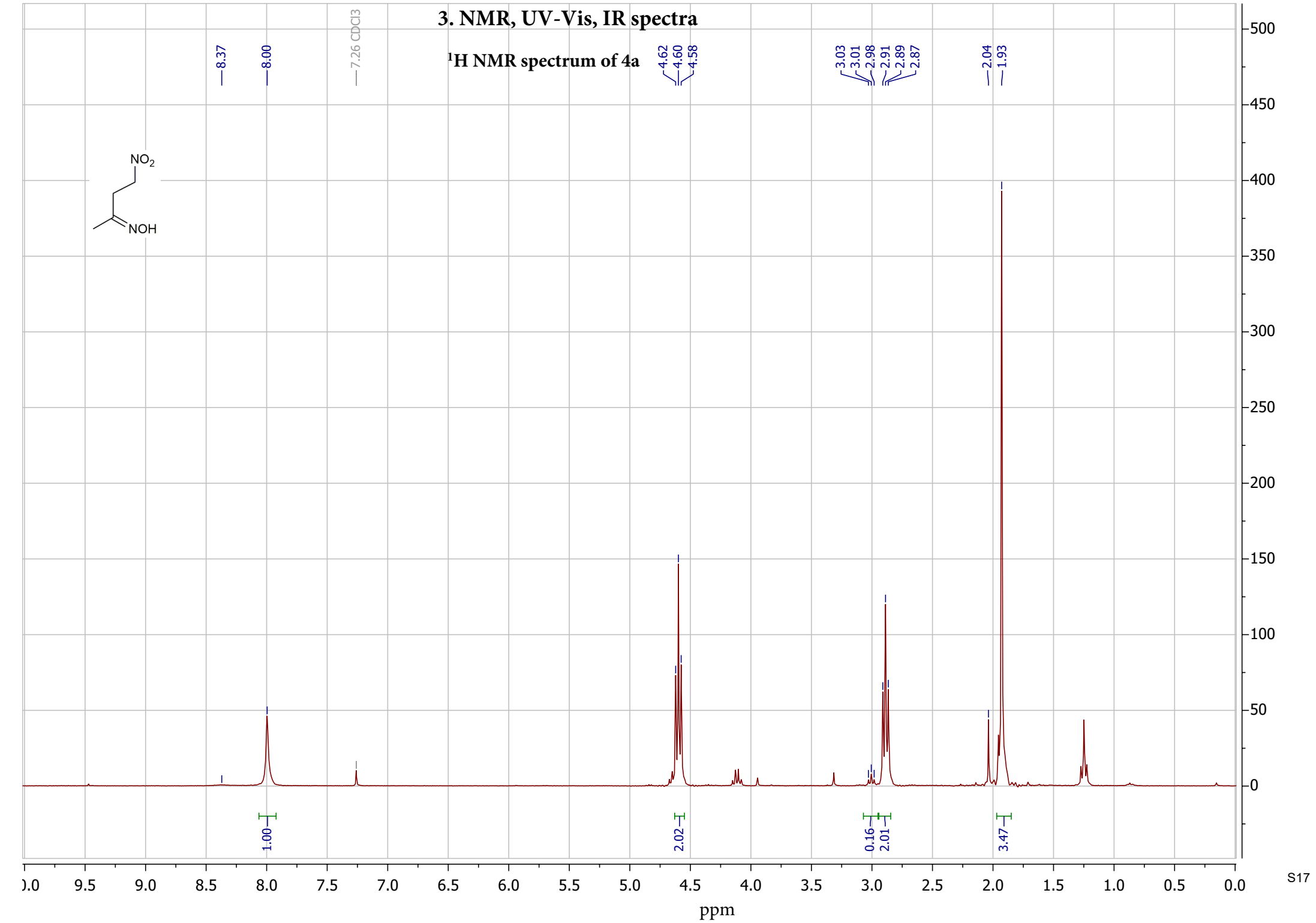
Synthesis of 7-Ni(Cl)

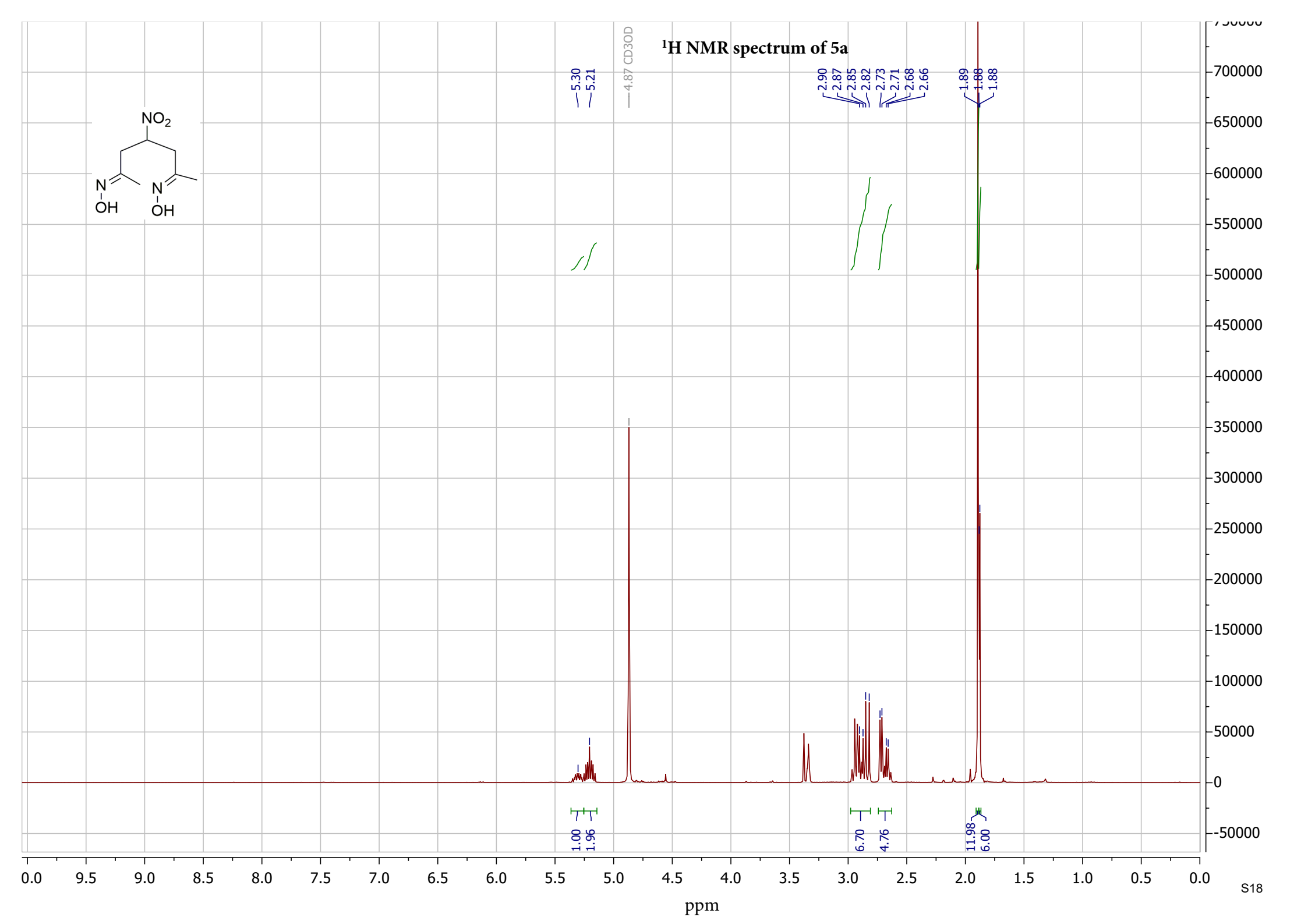


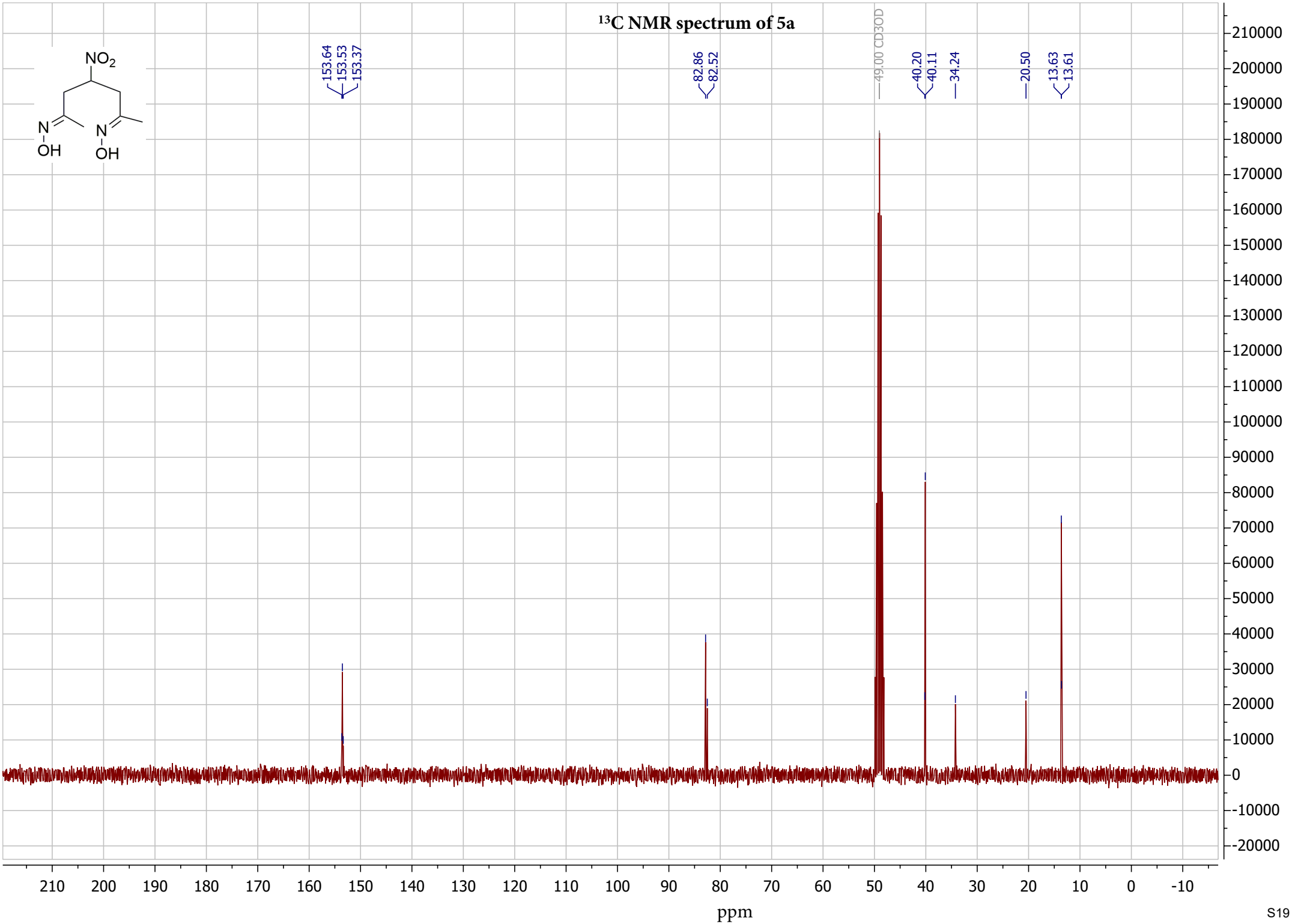
Trioctylamine (1.05 mL, 2.4 mmol) was added to a mixture of **NO_2-TRIAD 1a** (110 mg, 0.4 mmol), **TACN·3HCl** (95 mg, 0.4 mmol) and $NiCl_2$ (52 mg, 0.4 mmol) in 5 mL of MeOH. The reaction mixture was stirred for 3 hours at room temperature under air and then kept for additional 24 hours with a closed cap. The precipitate was centrifuged off and a clear solution containing complex **7-Ni**(Cl) was concentrated in a vacuum. The residue was dried at 0.1 Torr for 5 hours and triturated with Et_2O (7 × 5 mL). The remaining solid material was dried at 0.1 Torr to give 120 mg (yield 59%) of complex **7-Ni**(Cl) as a black solid. Mp. 163-165°C (with dec.). ^{1}H NMR (300 MHz, D_2O, δ, ppm): 1.39 (s, 9 H, 3 C*H*$_3$), 2.97 (s, 6 H, 3 C*H*$_2$), 2.92 – 3.12 (m, 6 H, 6 C*H*$_2$ (TACN)), 3.22 – 3.39 (m, 6 H, 6 C*H*$_2$ (TACN)), 3.90 (s, 3 H, 3 N*H*). ^{13}C {1H} NMR (75 MHz, HSQC, DEPT135, D_2O, δ, ppm): 19.3 (*C*H$_3$), 41.7 (*C*H$_2$), 45.8 (*C*H$_2$ (TACN)), 77.8 (*C*-NO_2), 91.6 (*C*). ^{15}N {1H} NMR (300 MHz, HMBC, D_2O, δ, ppm): -258.1 (*N*O_2). FT-IR (KBr): 3470 (br), 3197 (br), 2943 (m), 2874 (m), 1624 (m), 1545 (s), 1487 (m), 1455 (s), 1379 (s), 1273 (m), 1211 (s), 1190 (m), 1135 (m), 1106 (s), 1065 (m), 1030 (s), 940 (s), 865 (m), 825 (s), 781 (s), 740 (s), 696 (s), 660 (s), 583 (s), 535 (s), 499 (s), 469 (s), 417 (s). UV−vis spectrum: (MeOH, c = 1.8 × 10^{-4} M) peaks λ nm: 304, 360, 465. ESI-HRMS m/z: $[M\text{-}Cl]^+$ Calcd for $[C_{16}H_{30}NiN_7O_5]^+$ 458.1656; Found 458.1655. Anal. Calcd for $C_{16}H_{30}ClNiN_7O_5 \cdot H_2O$: C, 37.49; H, 6.29; N, 19.13. Found: C, 36.86; H, 5.76; N, 18.92.

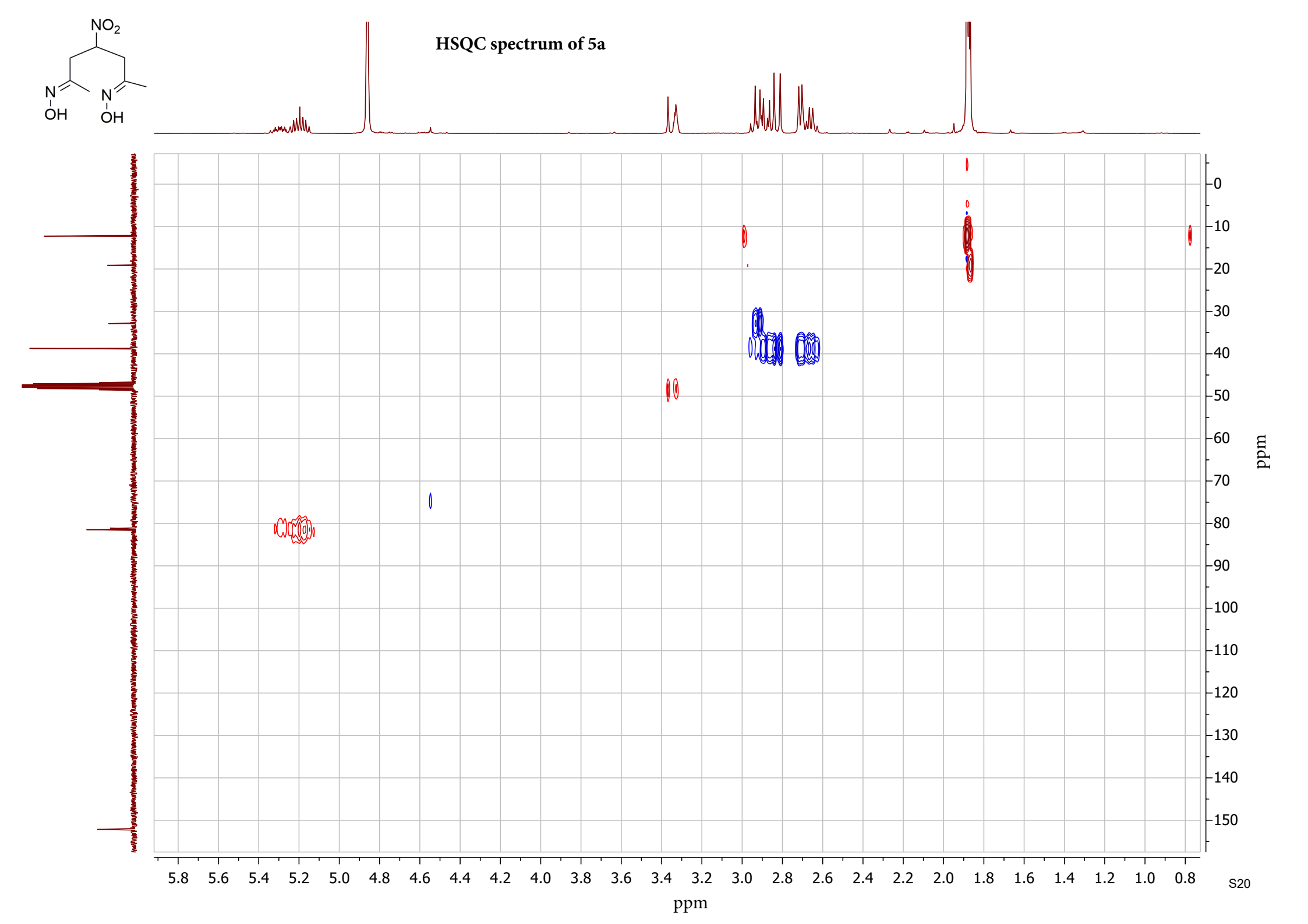
Preparation of crystals for X-ray analysis: complex **7-Ni**(Cl) (15 mg) was dissolved in 1.5 mL of methanol and the solution was filtered through a syringe filter. Slow vapor diffusion of diethyl ether into the methanol solution produced black crystals of **7-Ni**(Cl)·2CH_3OH·H_2O suitable for X-Ray diffraction analysis.

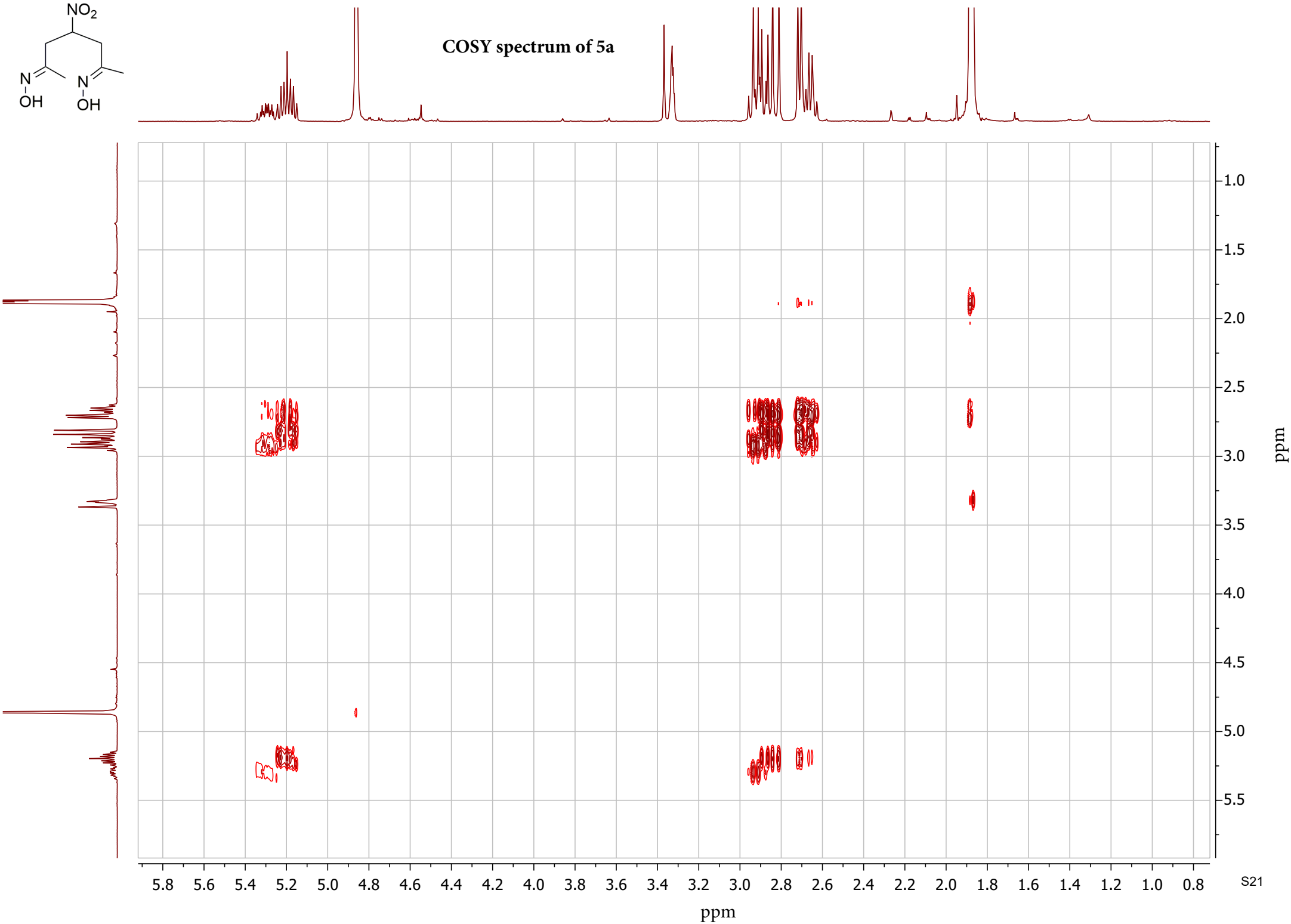
^{1}H NMR spectrum of 4a

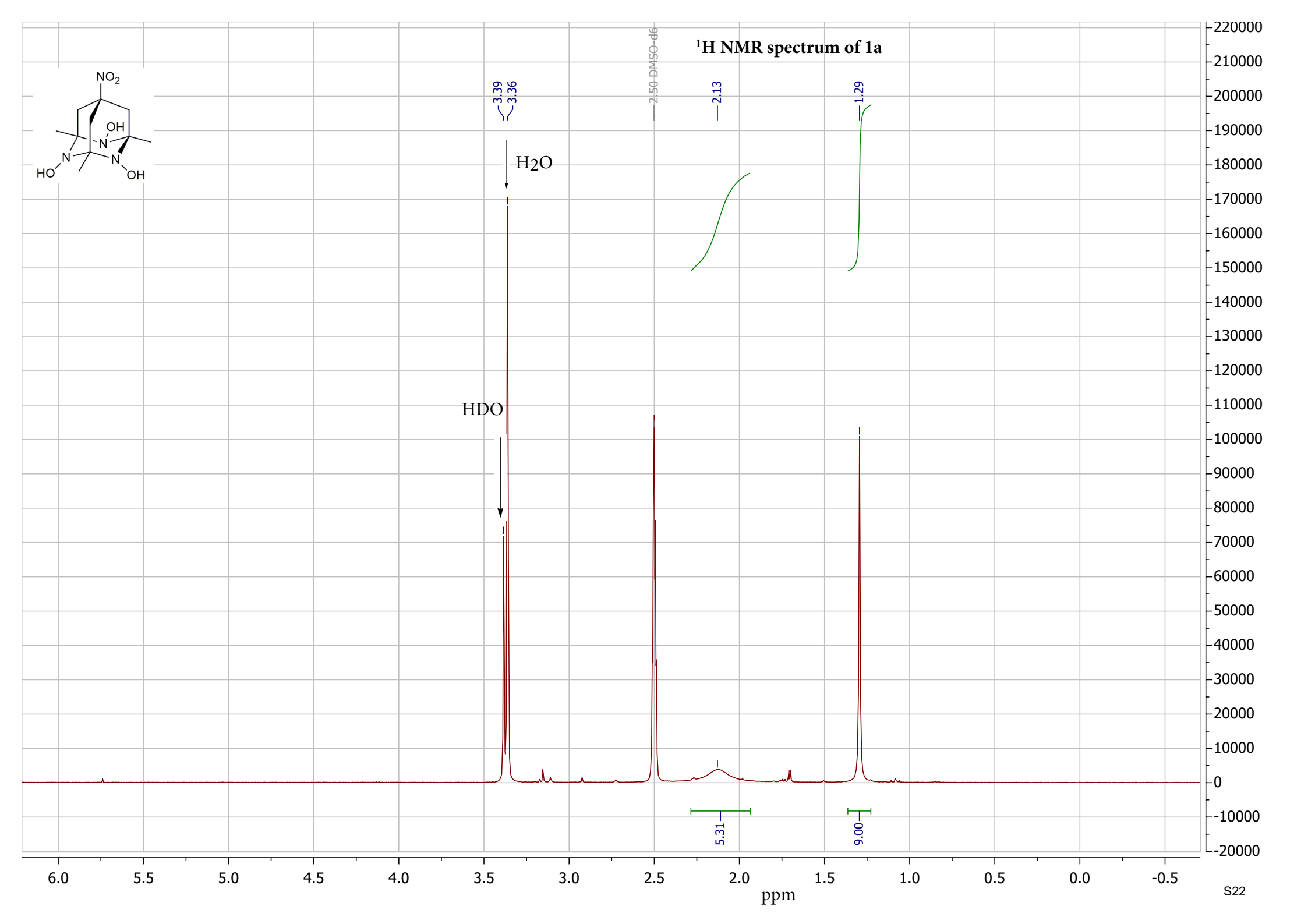



^{1}H NMR spectrum of 5a
NO2
N
OH
N
OH
5.30
5.21
4.87 CD3OD
2.90
2.87
2.85
2.82
2.73
2.71
2.68
2.66
1.89
1.88
1.88
1.00
1.96
6.70
4.76
11.98
6.00
ppm
S18

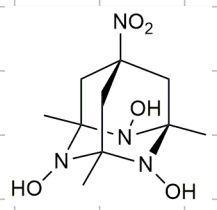

^{13}C NMR spectrum of 5a
NO2
N
OH
N
OH
153.64
153.53
153.37
82.86
82.52
49.00 CD3OD
40.20
40.11
34.24
20.50
13.63
13.61
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


HSQC spectrum of 5a
NO2
N
OH
N
OH
ppm
ppm
S20

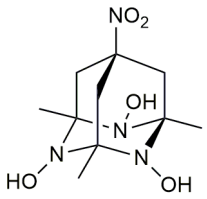

NO2
N
OH
N
OH
COSY spectrum of 5a
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
ppm
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm

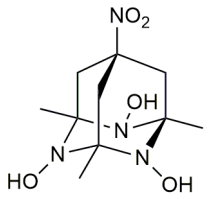

¹H NMR spectrum of 1a
NO2
OH
N
HO
N
N
OH
3.39
3.36
2.50 DMSO-d6
2.13
1.29
H2O
HDO
5.31
9.00
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

^{13}C NMR spectrum of 1a

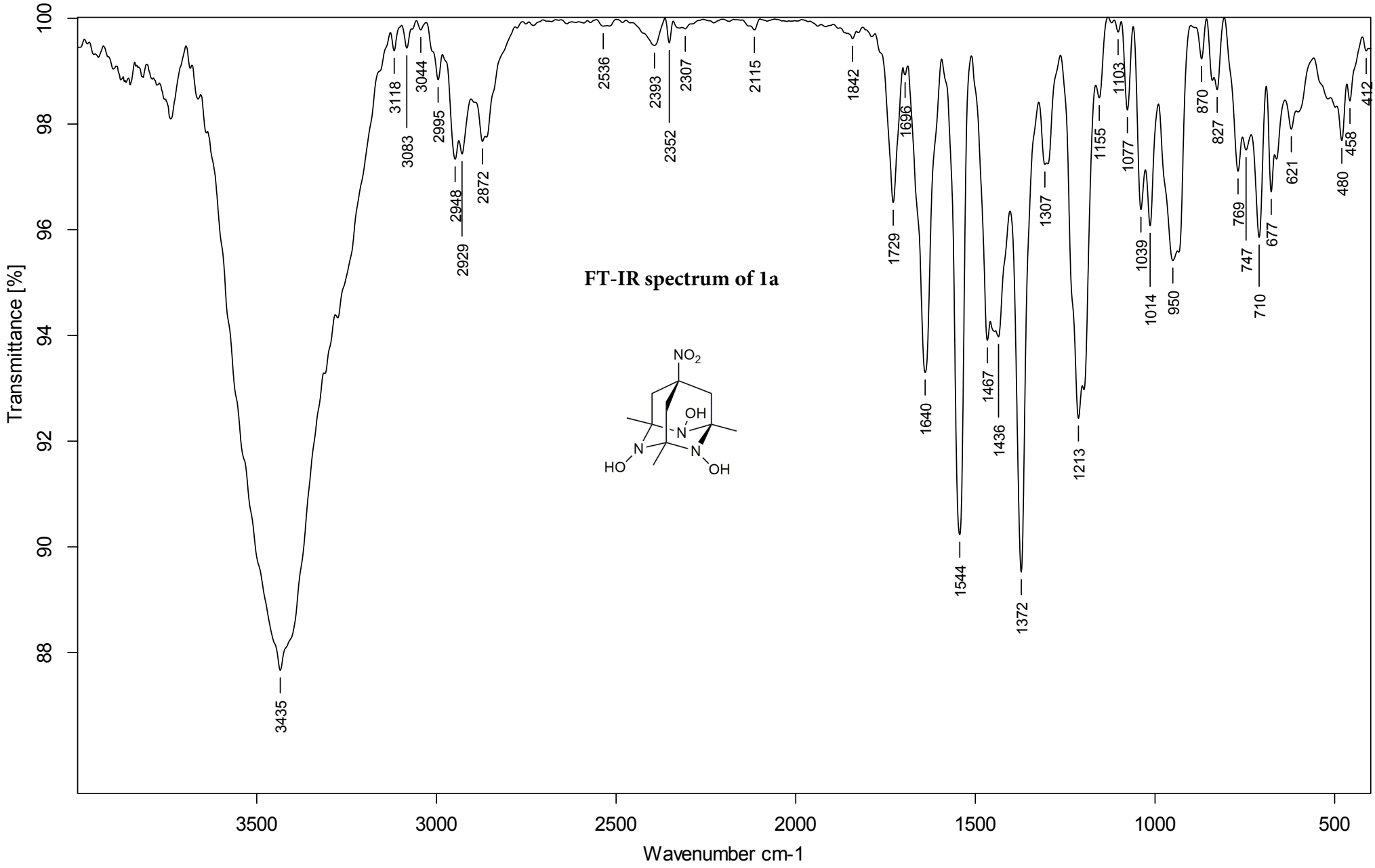


^{13}C NMR spectrum of 1a 330K

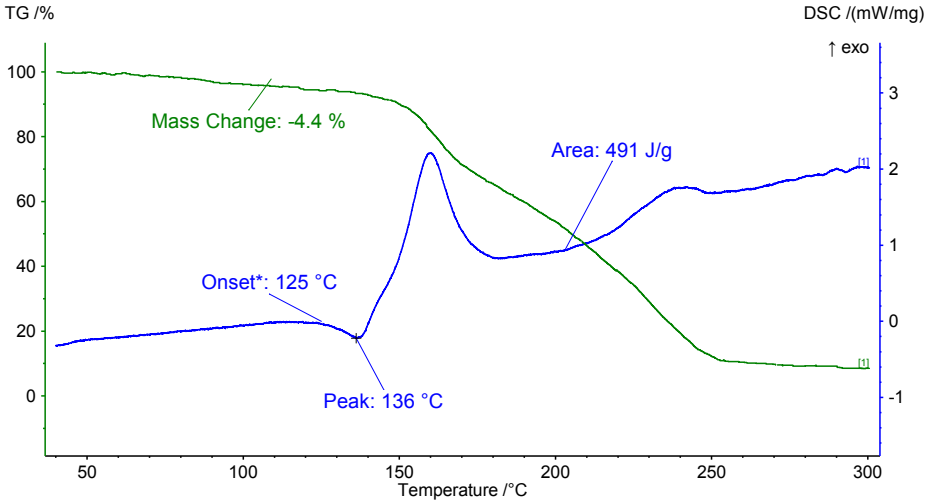




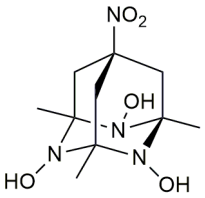
HMBC spectrum of 1a 330K

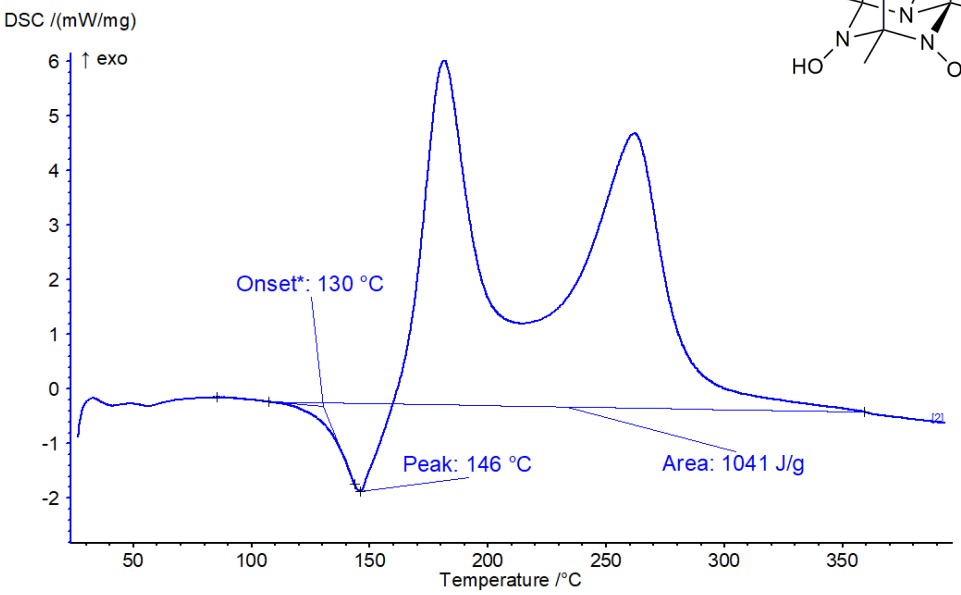

FT-IR spectrum of 1a
Transmittance [%]
Wavenumber cm-1
100
98
96
94
92
90
88
3500
3000
2500
2000
1500
1000
500
3435
3118
3083
3044
2995
2948
2929
2872
2536
2393
2352
2307
2115
1842
1729
1696
1640
1544
1467
1436
1372
1307
1213
1155
1103
1077
1039
1014
950
870
827
769
747
710
677
621
480
458
412
NO2
OH
N
HO
OH

TGA for **1a**, 5 K min^{-1} rate

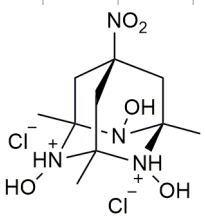


TGA for **1a**, 20 K min^{-1} rate

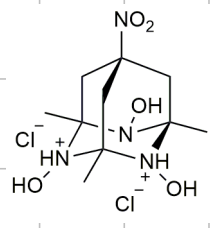




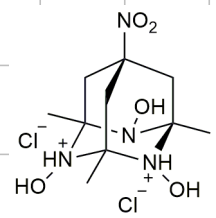
^{1}H NMR spectrum of 1a·2HCl

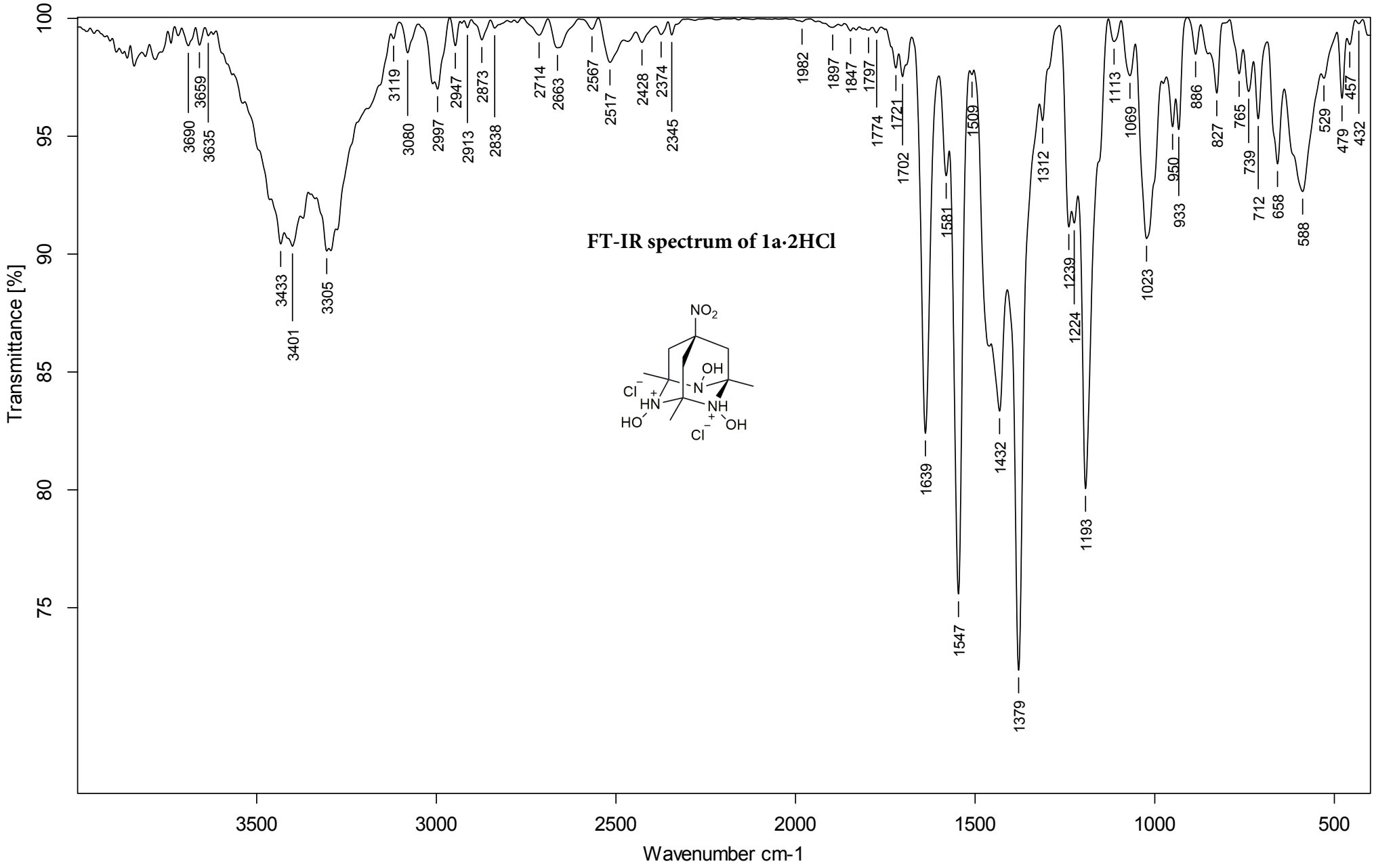


^{13}C NMR spectrum of 1a·2HCl

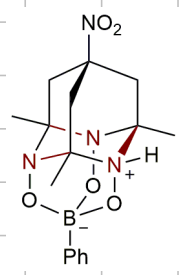


^{13}C DEPT135 NMR spectrum of 1a·2HCl

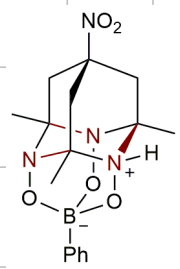


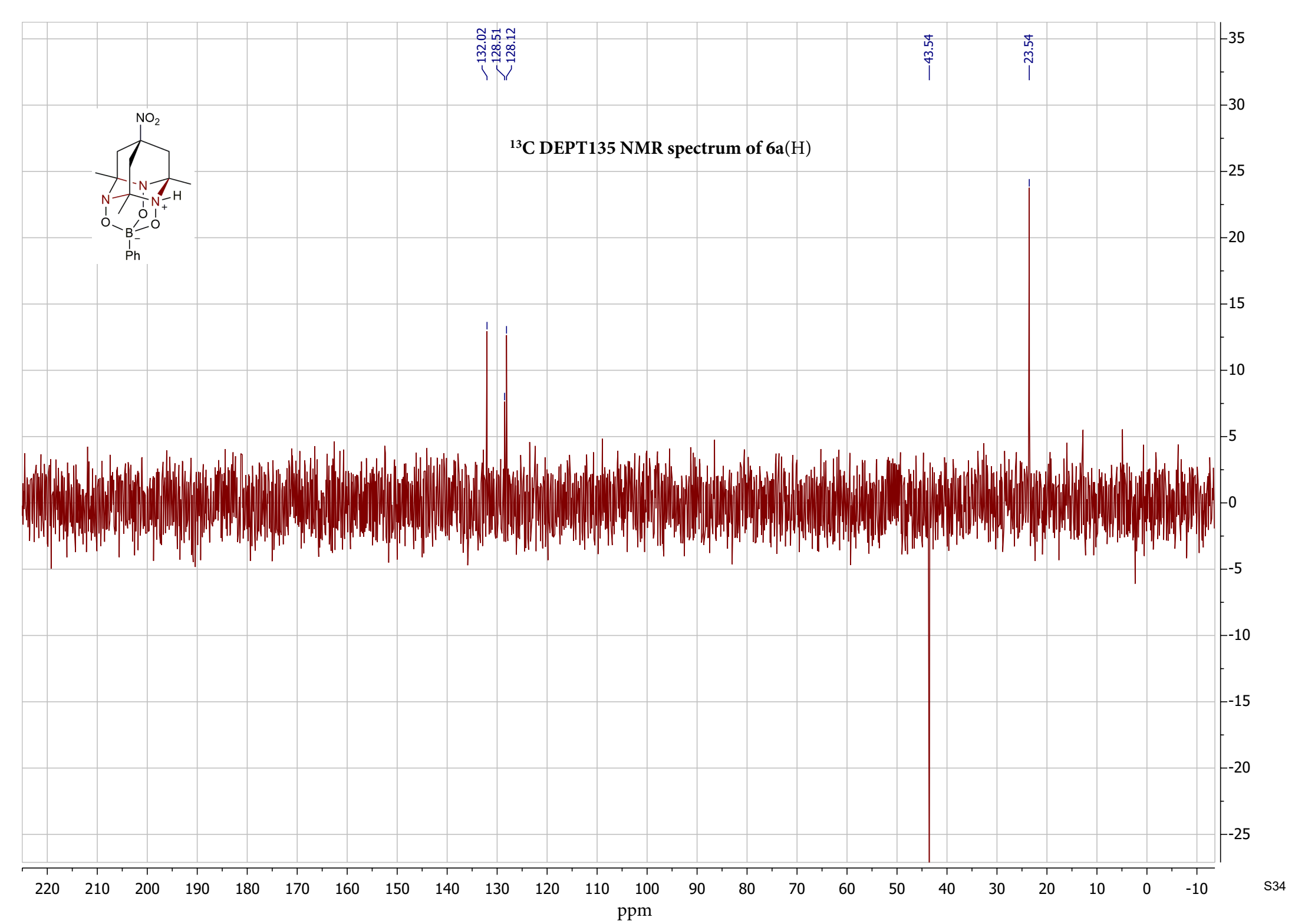

FT-IR spectrum of 1a·2HCl
Transmittance [%]
Wavenumber cm-1
100
95
90
85
80
75
3500
3000
2500
2000
1500
1000
500
3690
3659
3635
3433
3401
3305
3119
3080
2997
2947
2913
2873
2838
2714
2663
2567
2517
2428
2374
2345
1982
1897
1847
1797
1774
1721
1702
1639
1581
1547
1509
1432
1379
1312
1239
1224
1193
1113
1069
1023
950
933
886
827
765
739
712
658
588
529
479
457
432
NO2
OH
N
Cl−
HN+
NH
HO
+
OH
Cl−

^{1}H NMR spectrum of 6a(H)

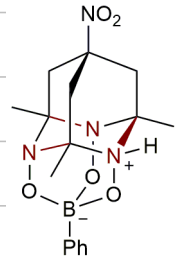


^{13}C NMR spectrum of 6a(H)

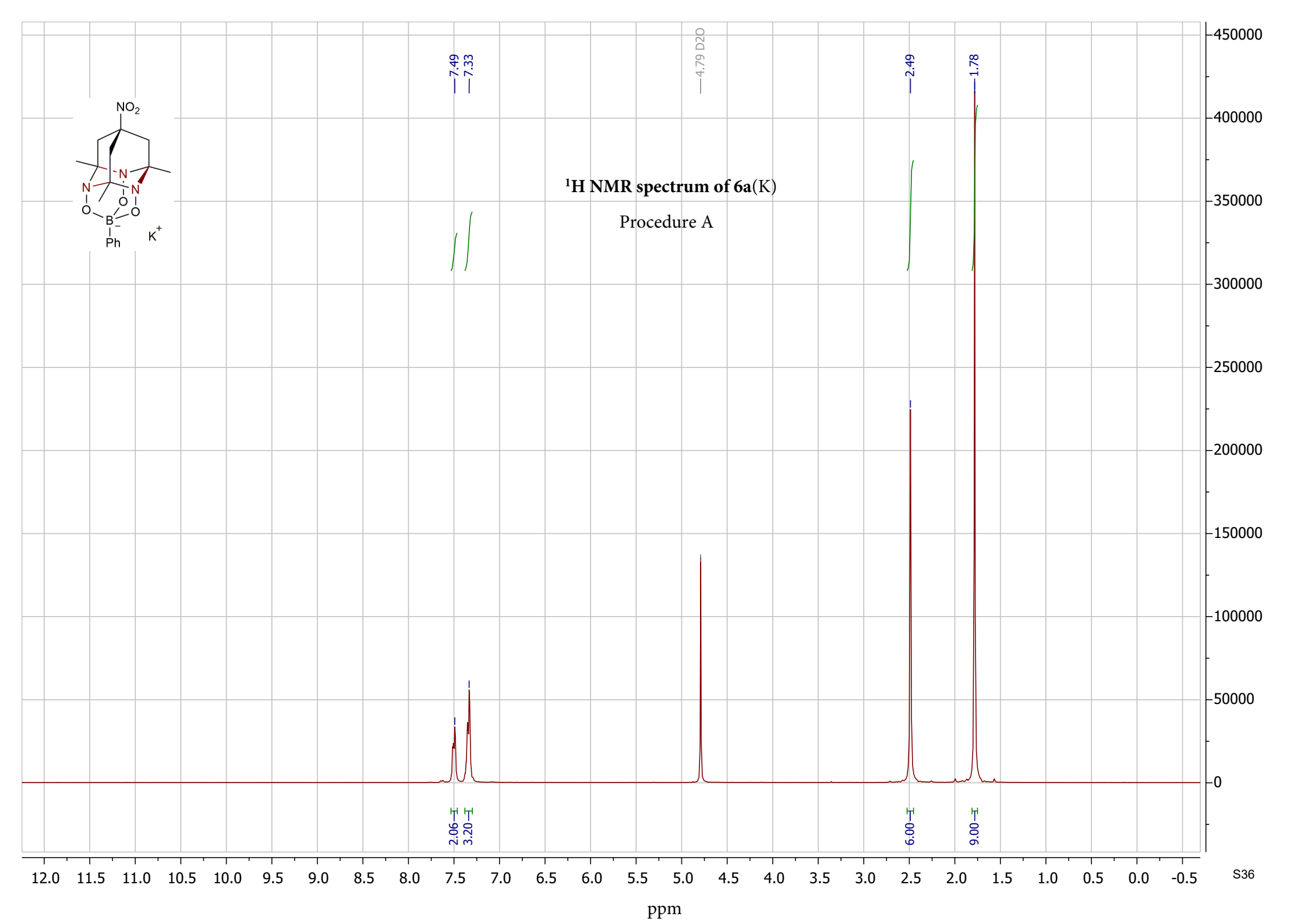


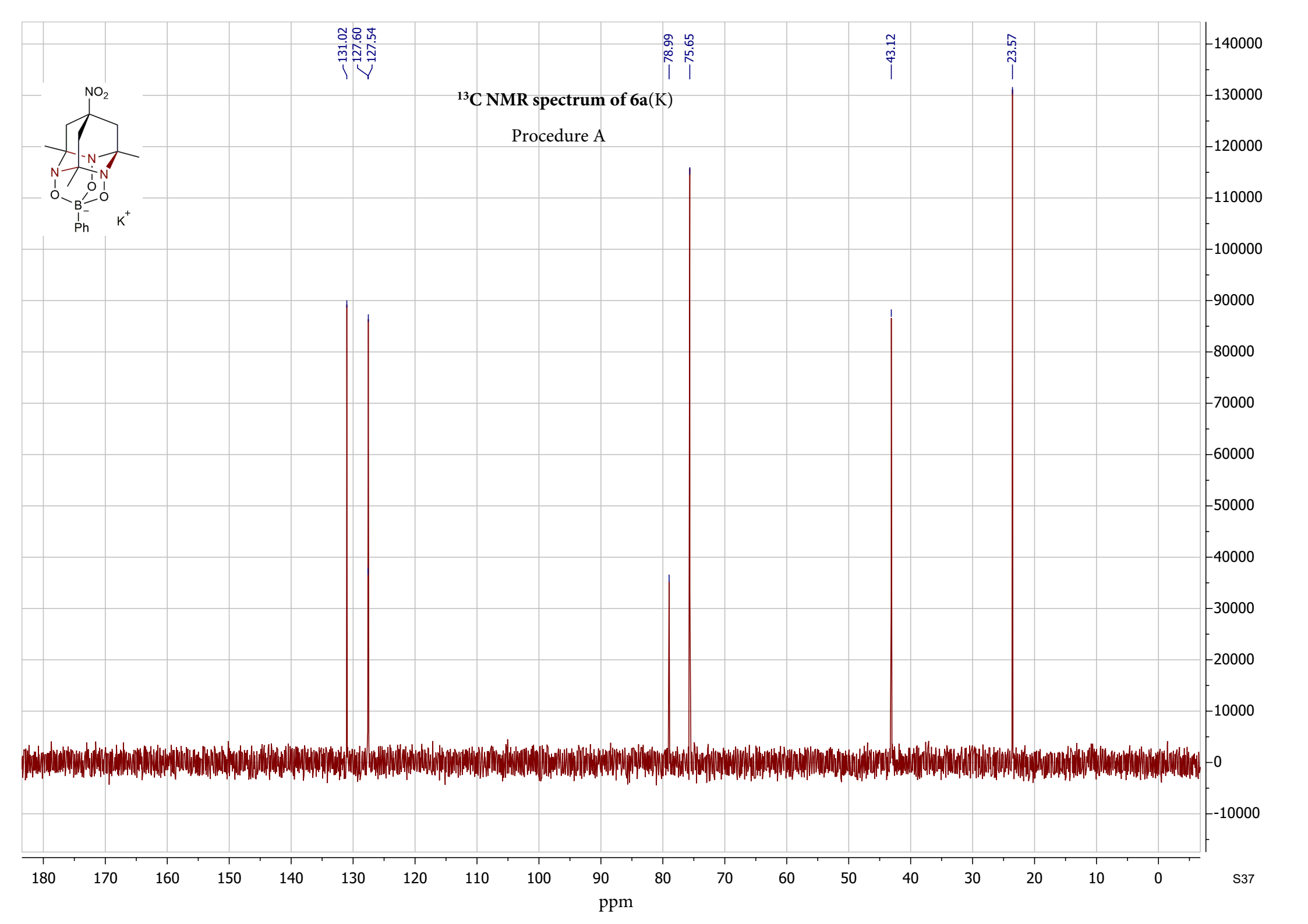


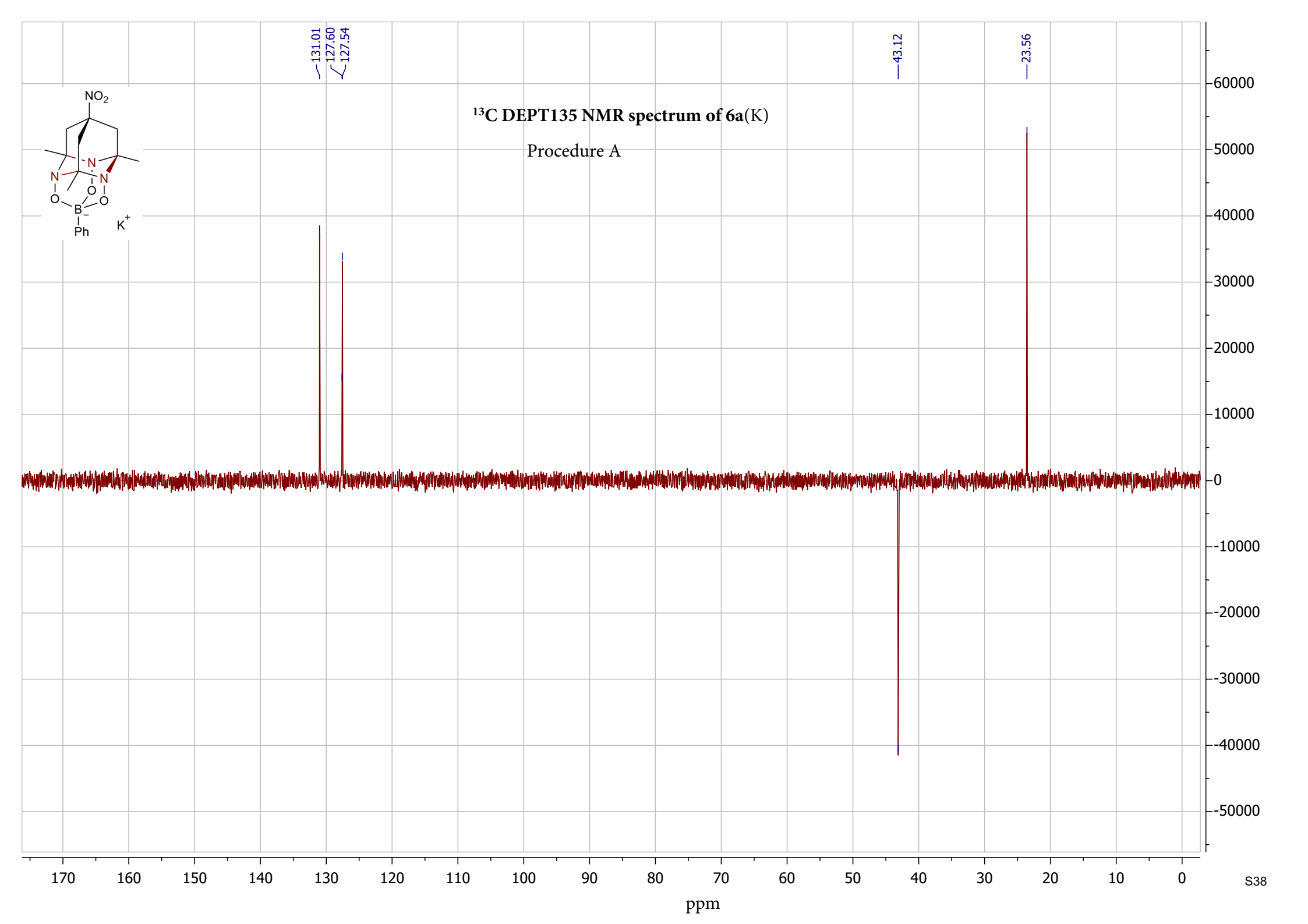
^{13}C DEPT135 NMR spectrum of 6a(H)

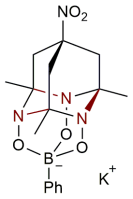


^{11}B NMR spectrum of 6a(H)


7.49
7.33
4.79 D2O
2.49
1.78
2.06
3.20
6.00
9.00
¹H NMR spectrum of 6a(K)
Procedure A
NO2
N
N
N
O
O
O
B
Ph
K+
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

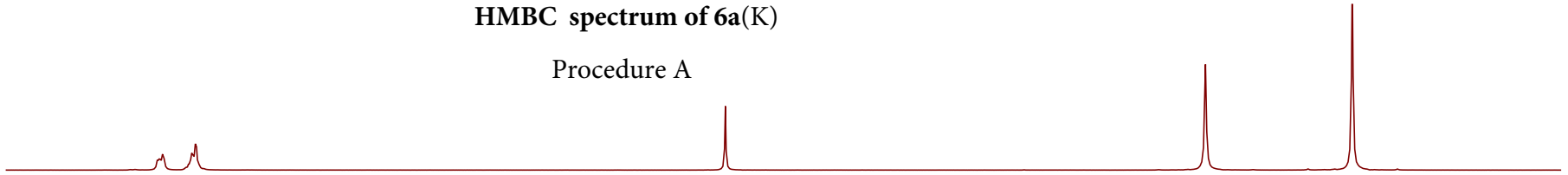

131.02
127.60
127.54
78.99
75.65
43.12
23.57
^{13}C NMR spectrum of 6a(K)
Procedure A
NO2
N
N
N
O
O
O
B
Ph
K+
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

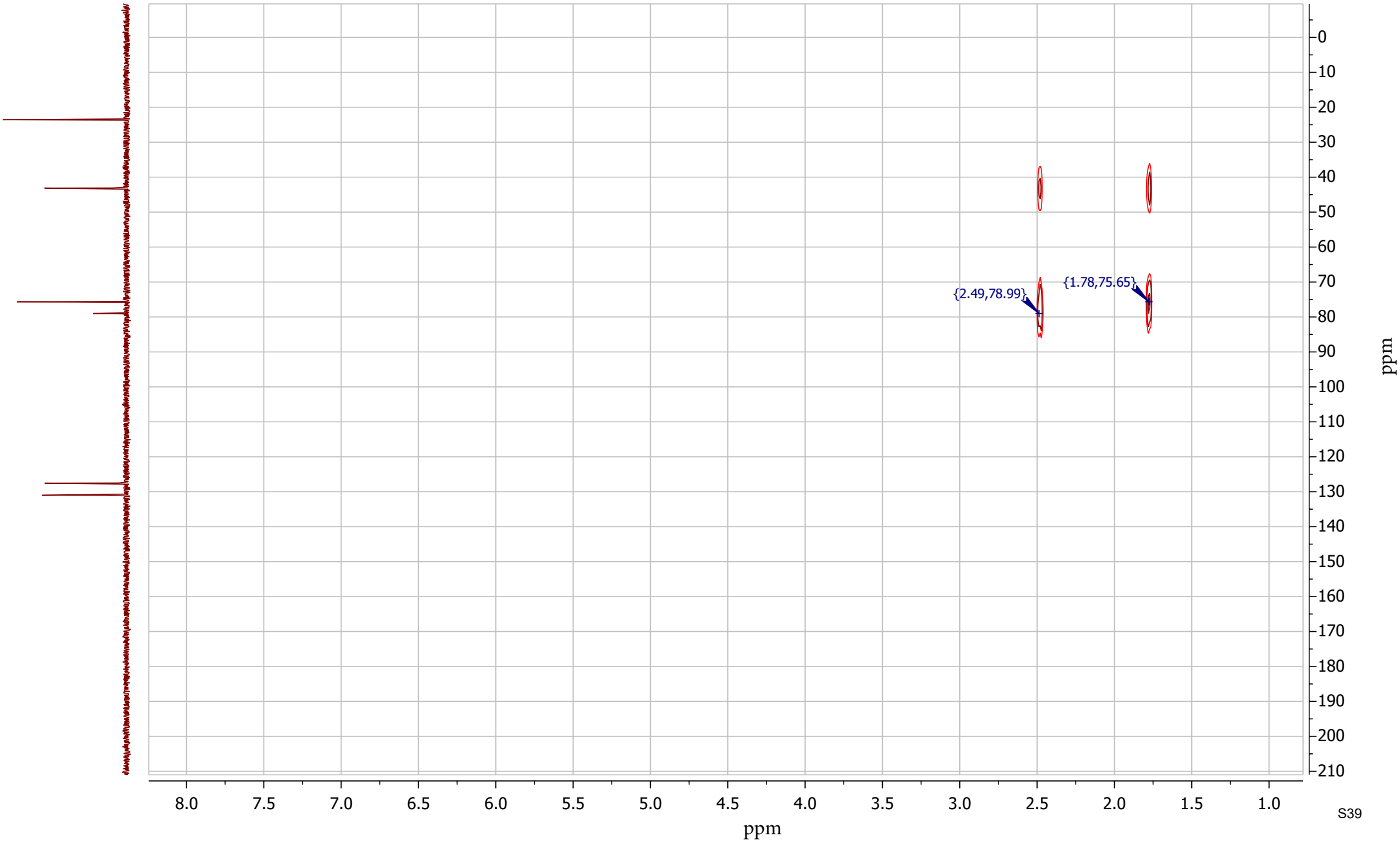

131.01
127.60
127.54
43.12
23.56
NO2
N
N
N
O
O
O
B
Ph
K+
13C DEPT135 NMR spectrum of 6a(K)
Procedure A
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

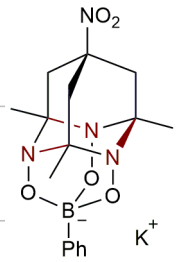


HMBC spectrum of 6a(K)

Procedure A

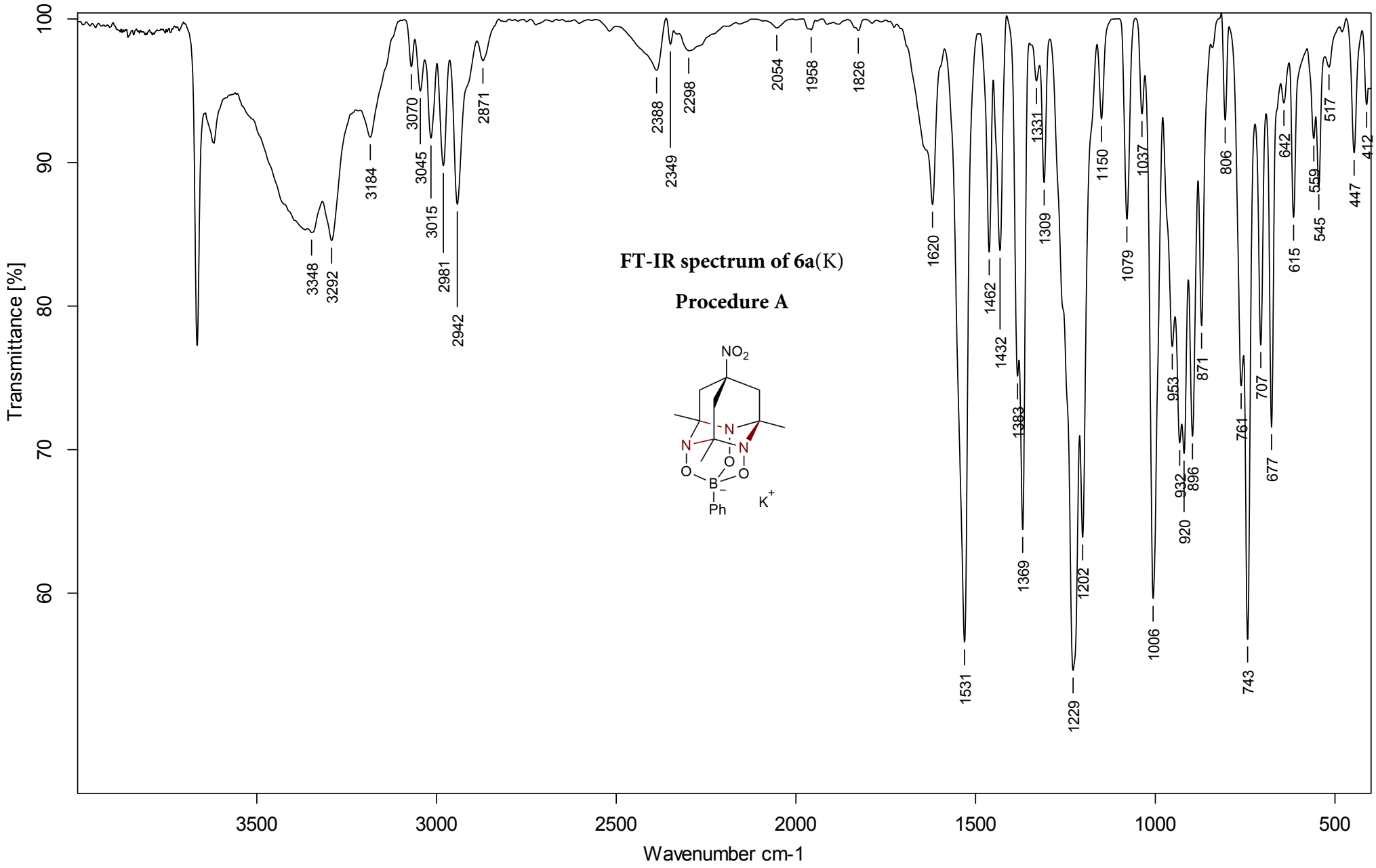


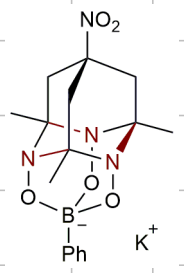




^{11}B NMR spectrum of 6a(K)

Procedure A

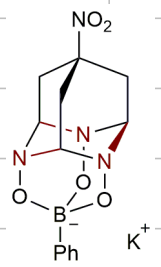

FT-IR spectrum of 6a(K)
Procedure A
Transmittance [%]
Wavenumber cm-1
100
90
80
70
60
3500
3000
2500
2000
1500
1000
500
3348
3292
3184
3070
3045
3015
2981
2942
2871
2388
2349
2298
2054
1958
1826
1620
1531
1462
1432
1383
1369
1331
1309
1229
1202
1150
1079
1037
1006
953
932
920
896
871
806
761
743
707
677
642
615
559
545
517
447
412
NO2
N
O
B
Ph
K+

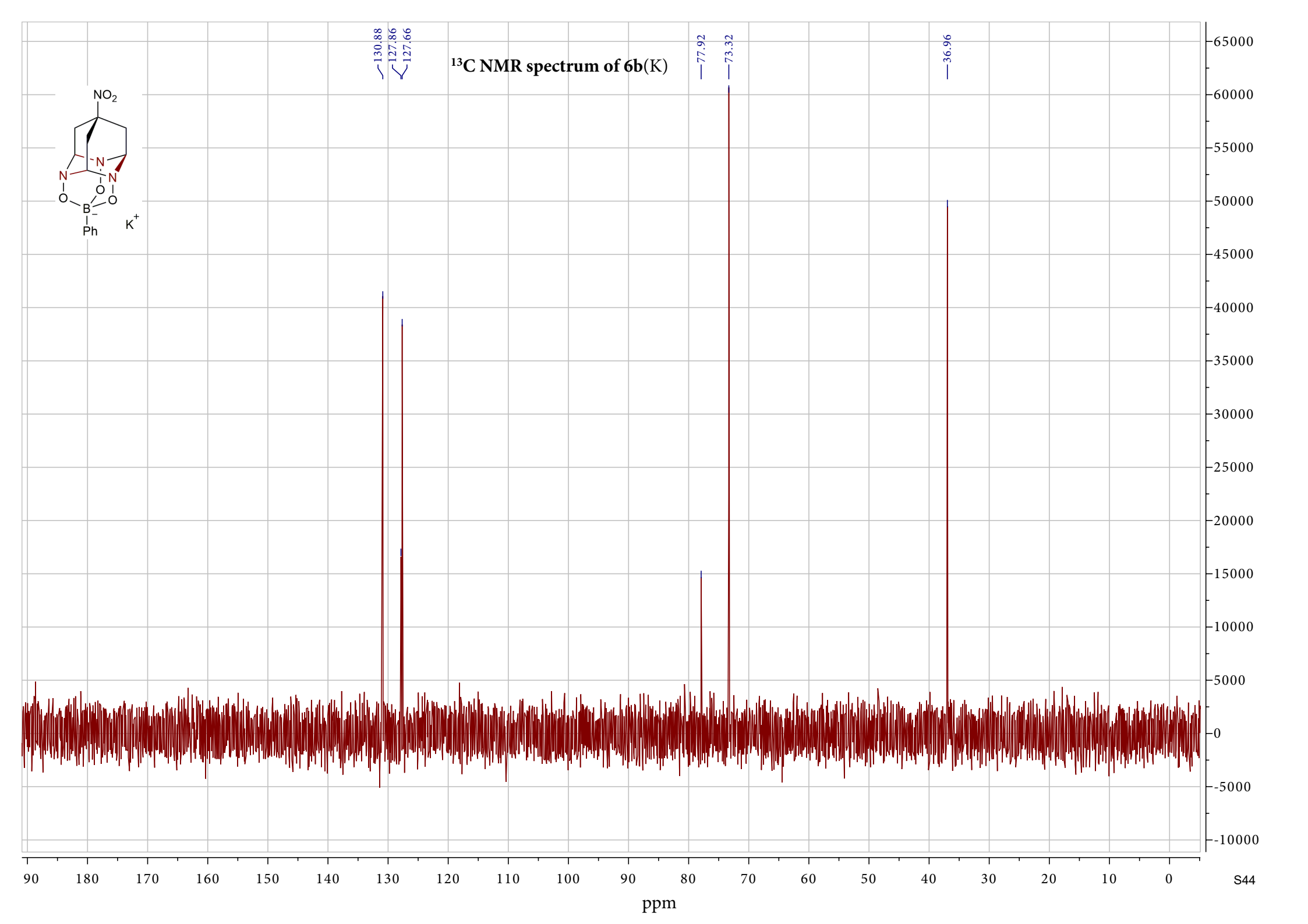


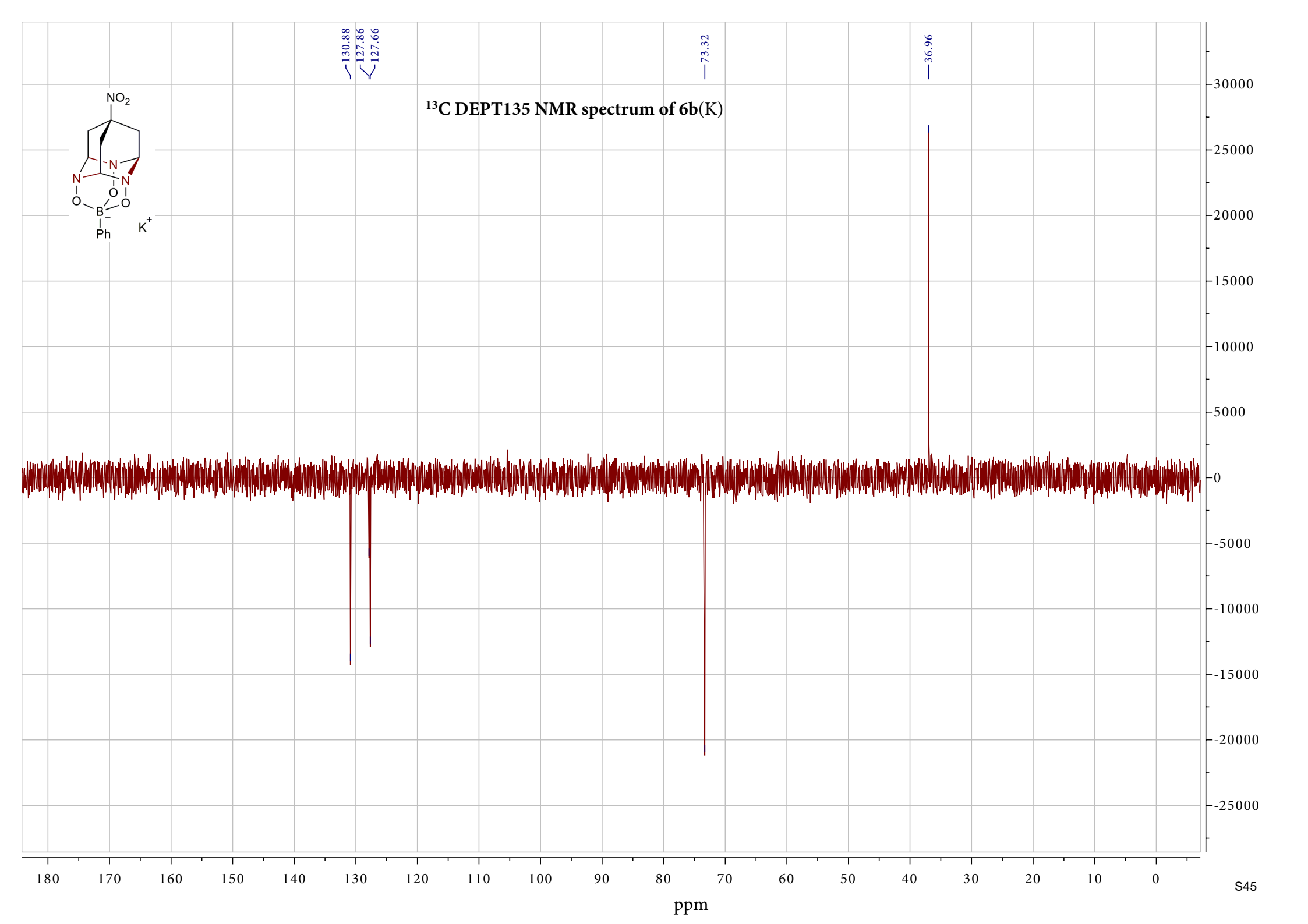
^{1}H NMR spectrum of 6a(K)

Procedure B

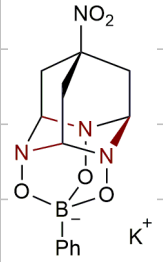
^{1}H NMR spectrum of 6b(K)



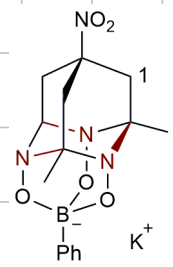

^{13}C NMR spectrum of 6b(K)
130.88
127.86
127.66
77.92
73.32
36.96
NO2
N
N
N
O
O
O
B
Ph
K+
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

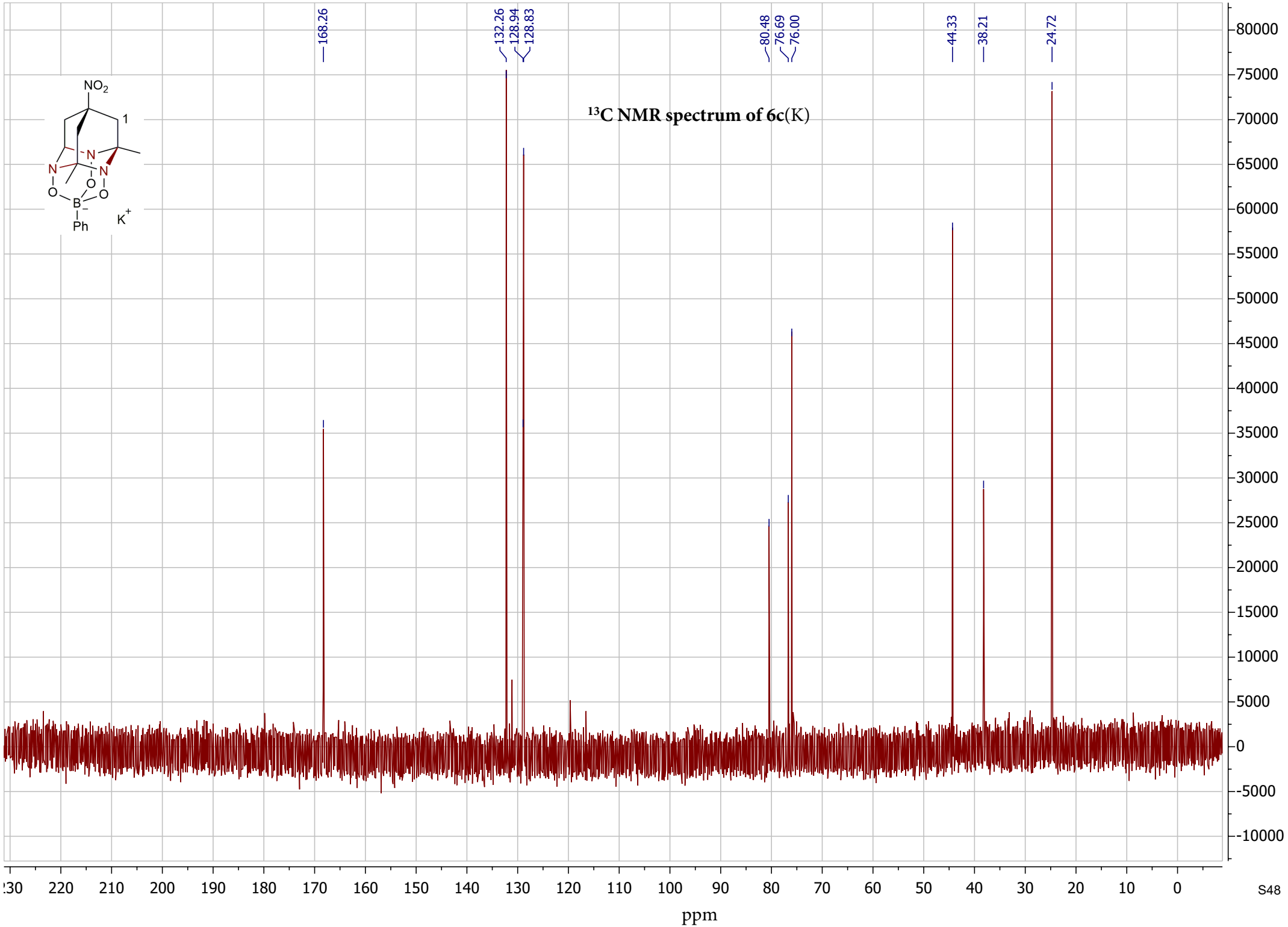

130.88
127.86
127.66
73.32
36.96
^{13}C DEPT135 NMR spectrum of 6b(K)
NO2
N
N
N
O
O
O
O
B
Ph
K+
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

^{11}B NMR spectrum of 6b(K)

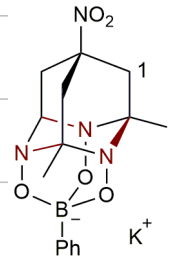


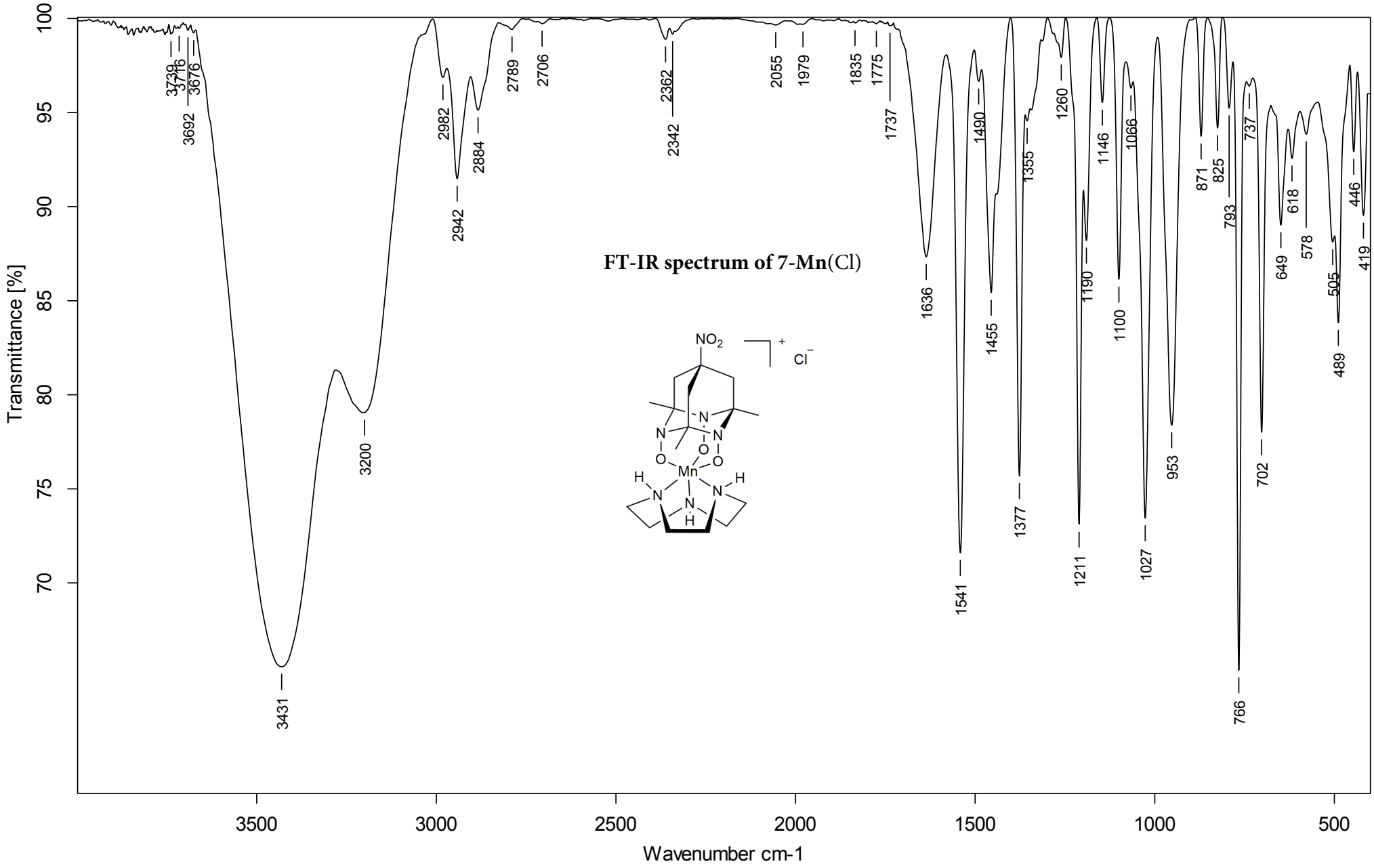
^{1}H NMR spectrum of 6c(K)



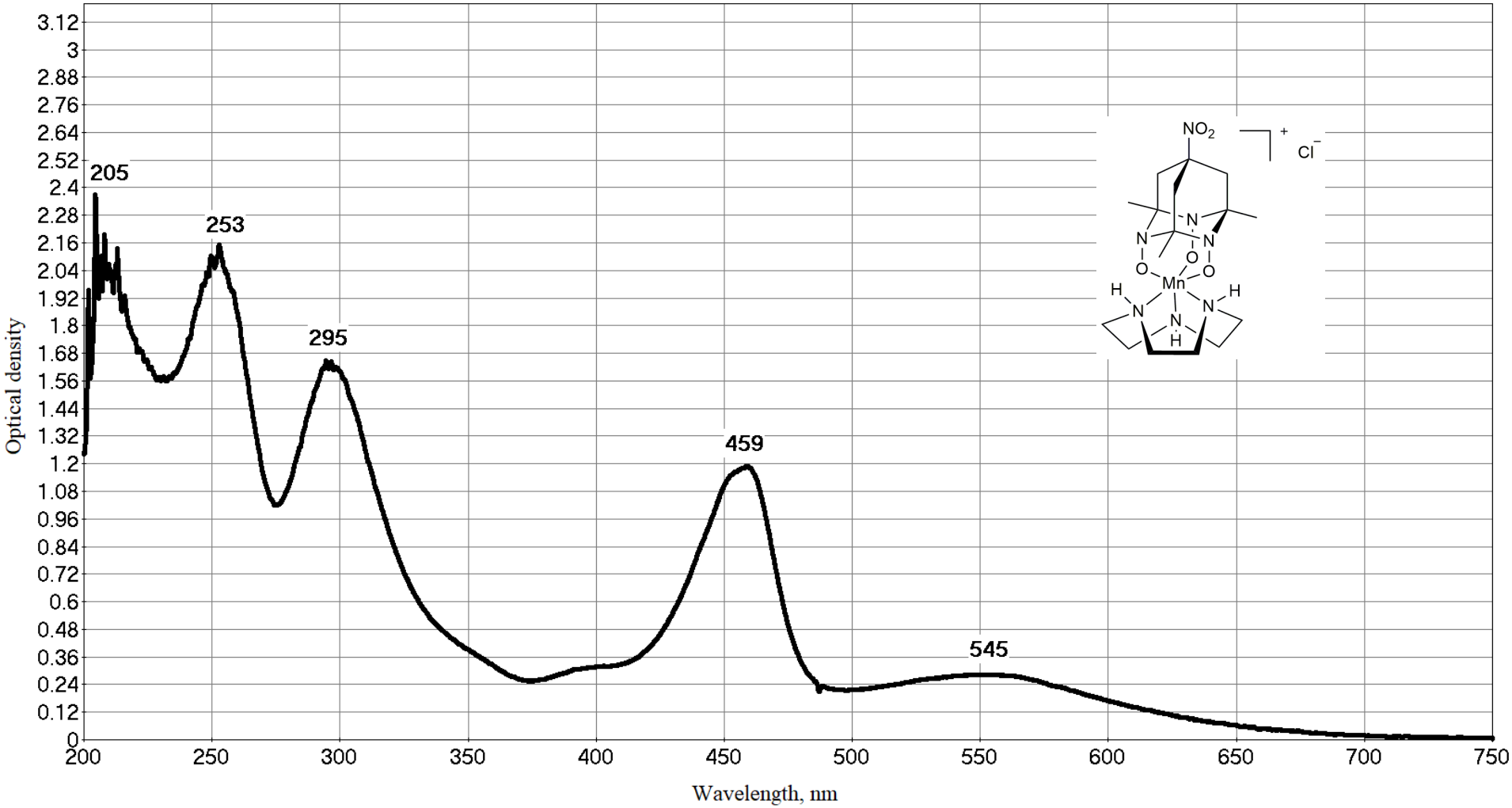

168.26
132.26
128.94
128.83
80.48
76.69
76.00
44.33
38.21
24.72
NO2
1
N
N
N
O
O
O
B
Ph
K+
13C NMR spectrum of 6c(K)
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

^{11}B NMR spectrum of 6c(K)

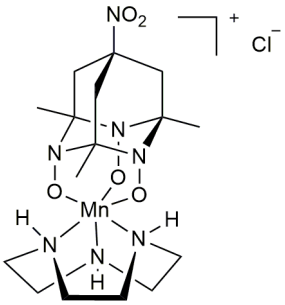



FT-IR spectrum of 7-Mn(Cl)
Transmittance [%]
Wavenumber cm-1
100
95
90
85
80
75
70
3500
3000
2500
2000
1500
1000
500
3739
3716
3692
3676
3431
3200
2982
2942
2884
2789
2706
2362
2342
2055
1979
1835
1775
1737
1636
1541
1490
1455
1377
1355
1260
1211
1190
1146
1100
1066
1027
953
871
825
793
766
737
702
649
618
578
505
489
446
419
NO2
Cl−
Mn

UV–vis spectrum of 7-Mn(Cl)



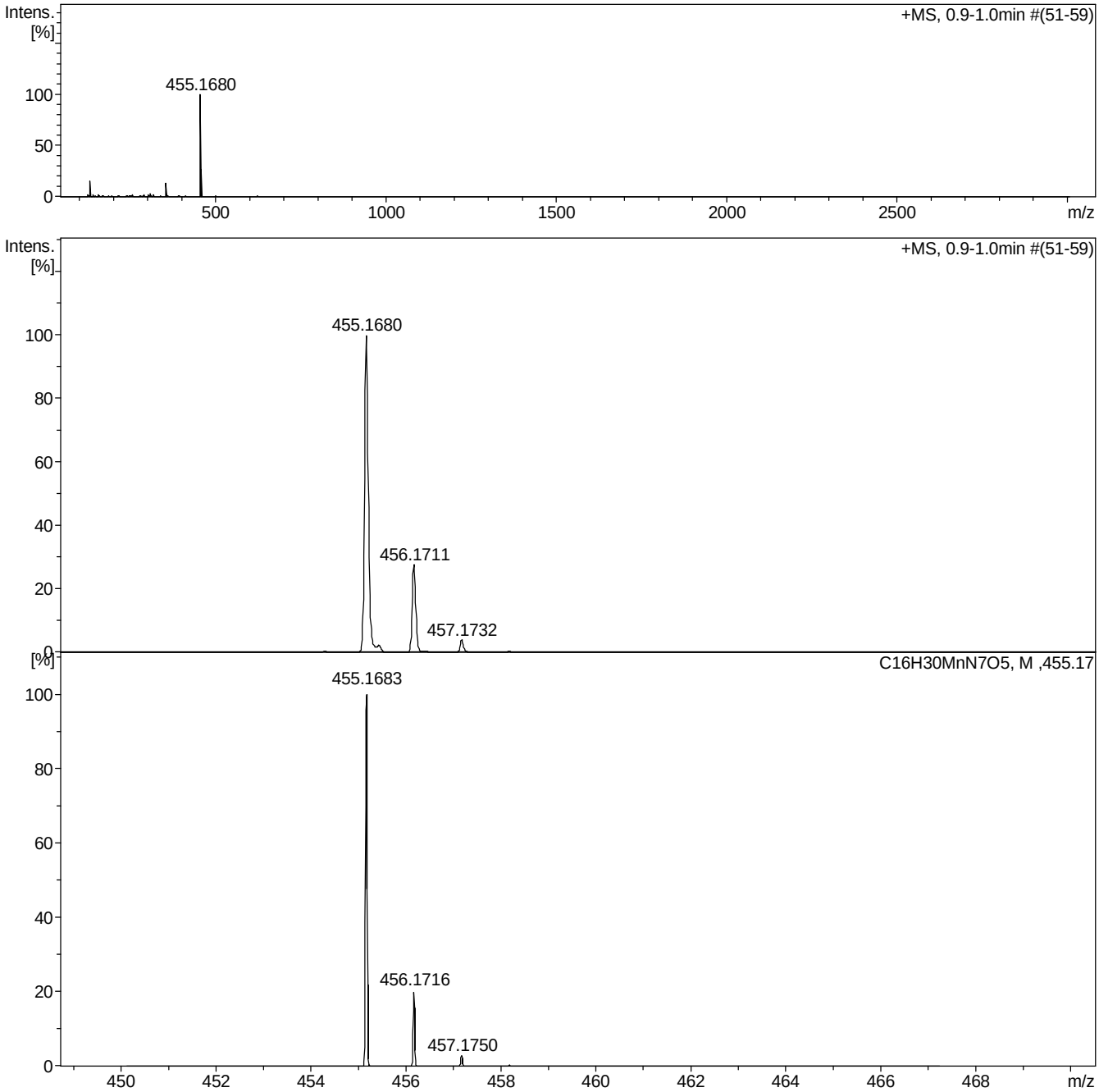
ESI-HRMS of 7-Mn(Cl)



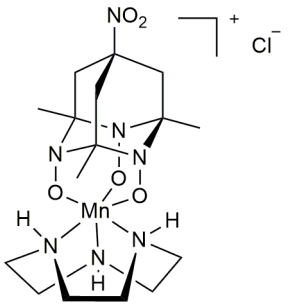
Instrument / Ser# micrOTOF

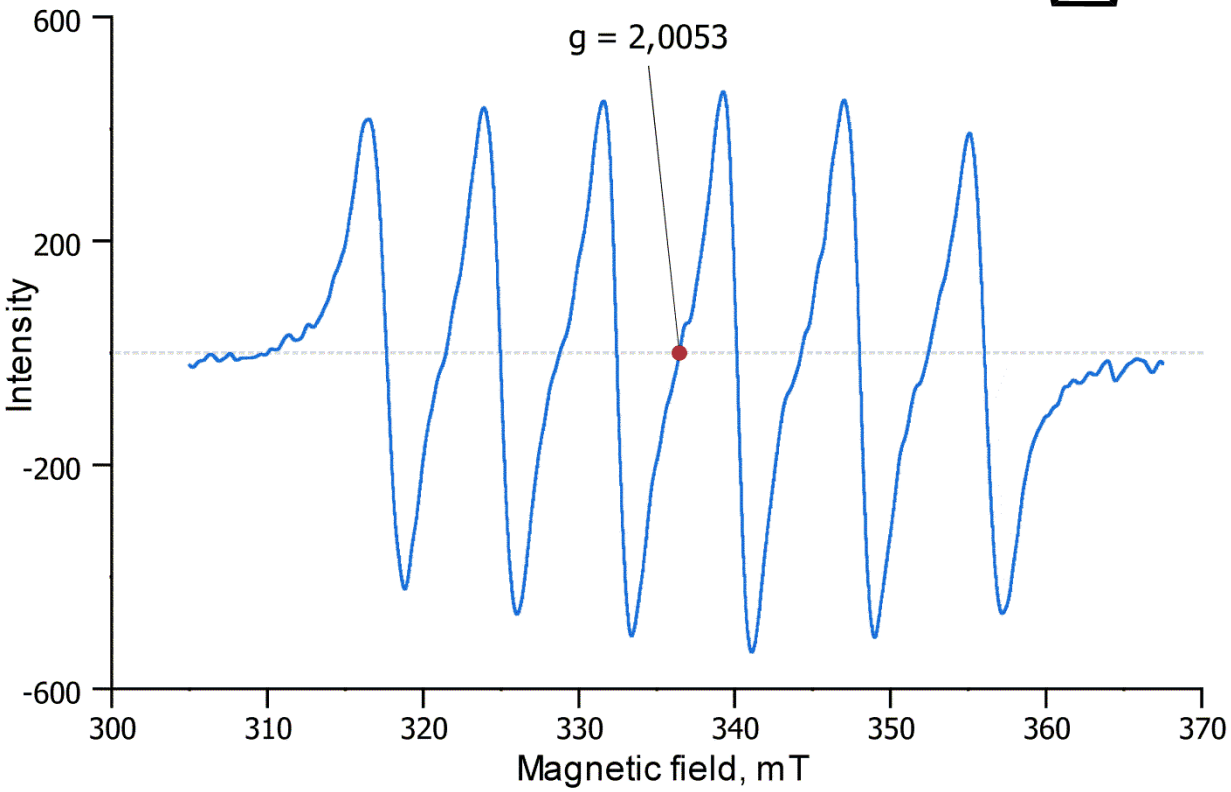
Acquisition Parameter

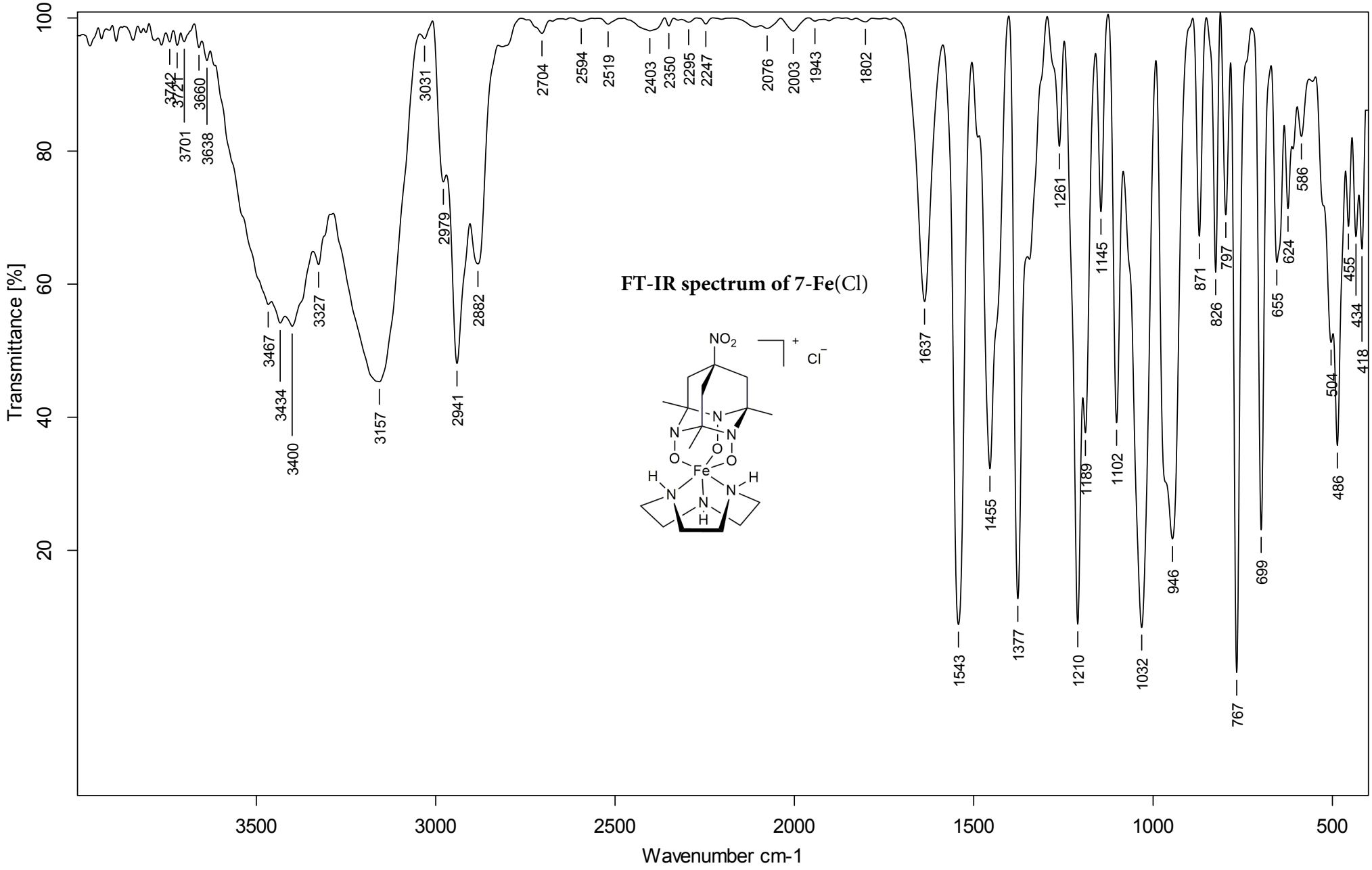
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

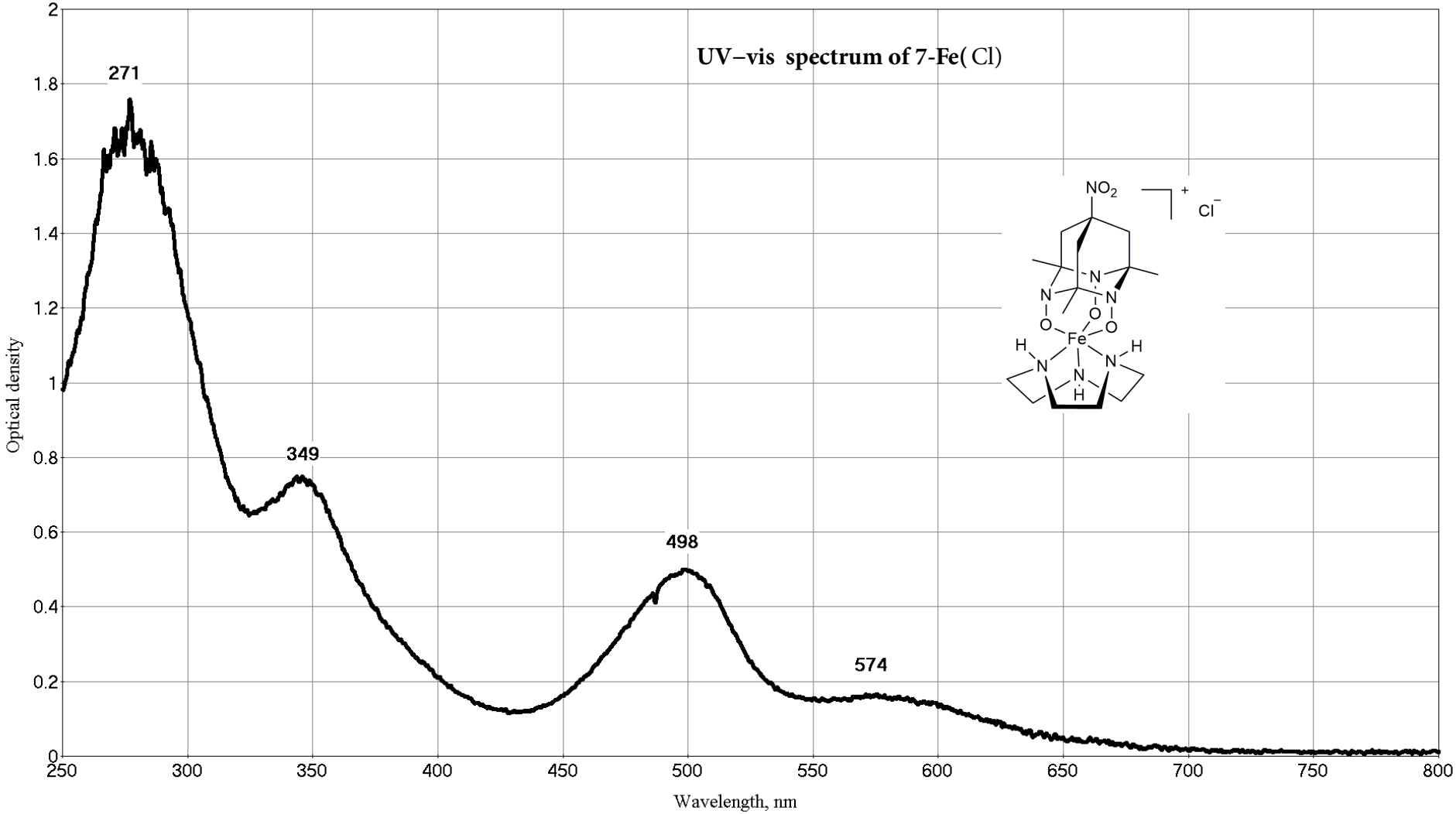


EPR spectrum of 7-Mn(Cl)

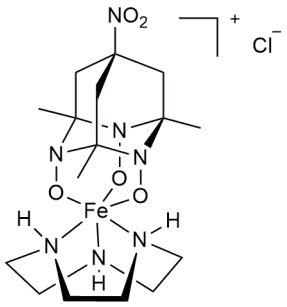





FT-IR spectrum of 7-Fe(Cl)
Transmittance [%]
Wavenumber cm-1
100
80
60
40
20
3500
3000
2500
2000
1500
1000
500
3742
3721
3701
3660
3638
3467
3434
3400
3327
3157
3031
2979
2941
2882
2704
2594
2519
2403
2350
2295
2247
2076
2003
1943
1802
1637
1543
1455
1377
1261
1210
1189
1145
1102
1032
946
871
826
767
797
699
655
624
586
504
486
455
434
418
NO2
Cl
Fe


UV–vis spectrum of 7-Fe(Cl)
271
349
498
574
Optical density
Wavelength, nm
NO2
Cl
Fe

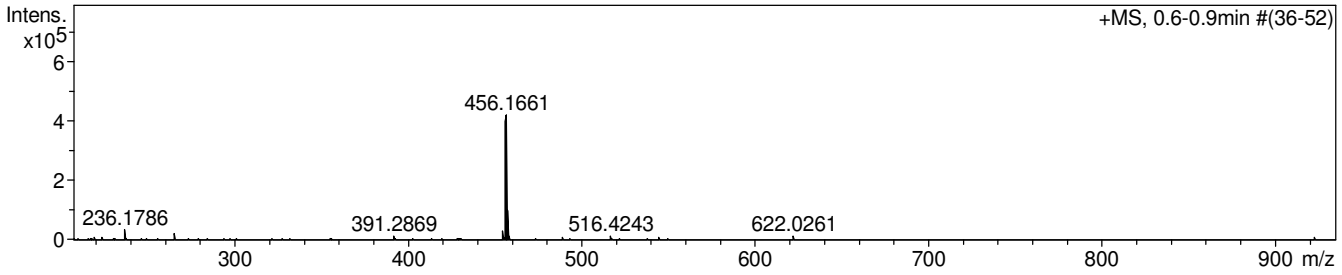
ESI-HRMS of 7-Fe(Cl)

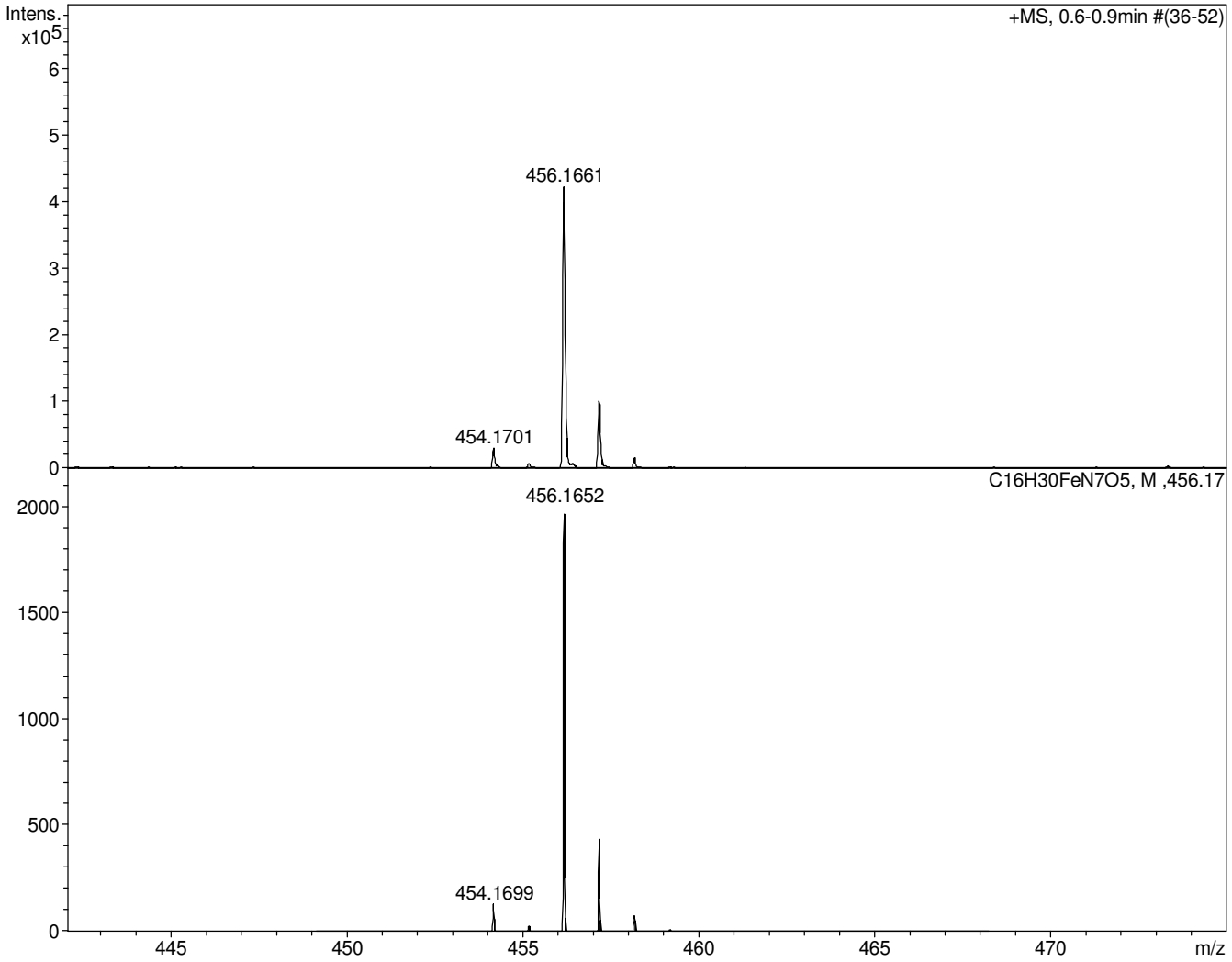


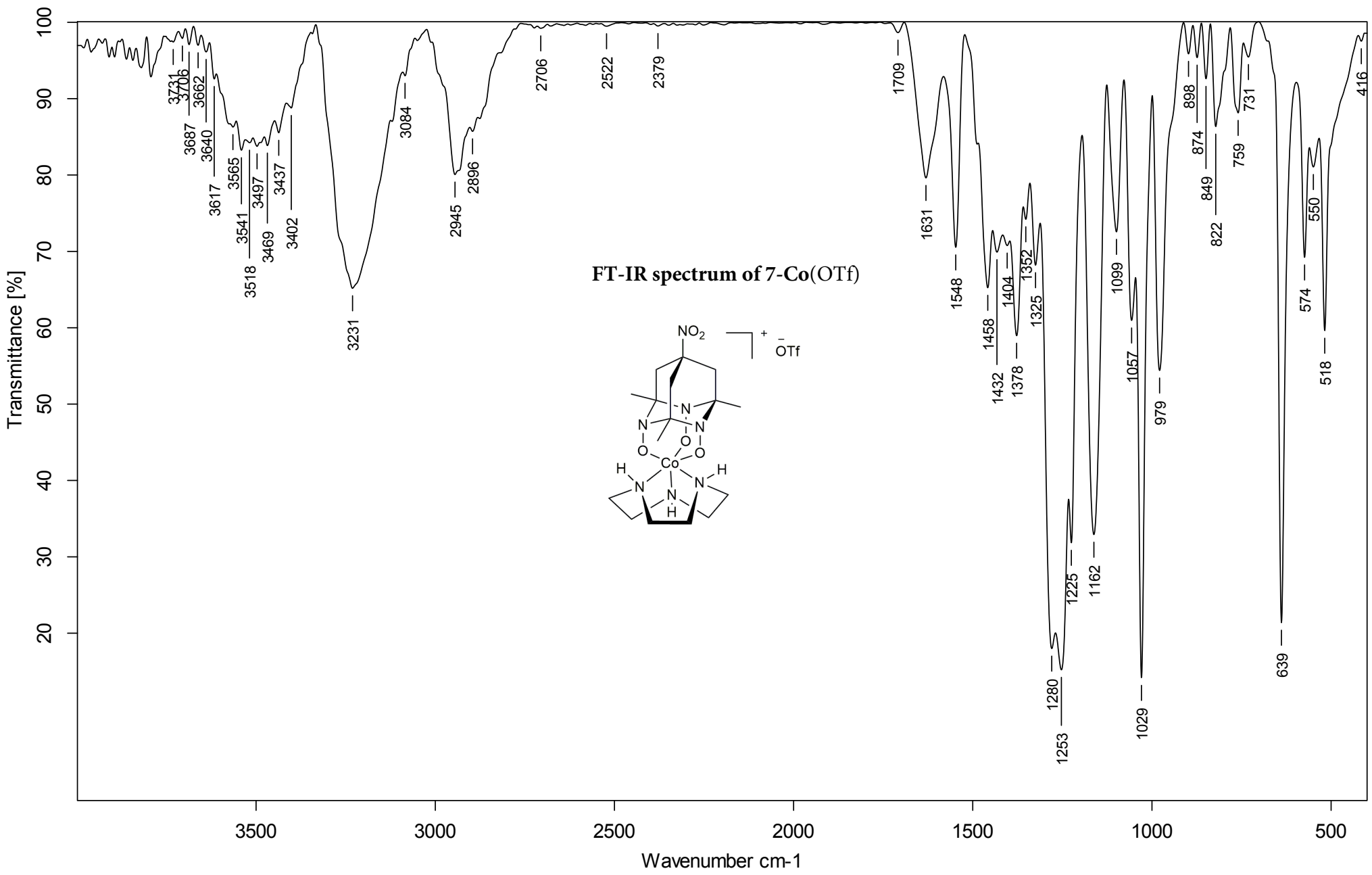
Instrument / Ser# micrOTOF

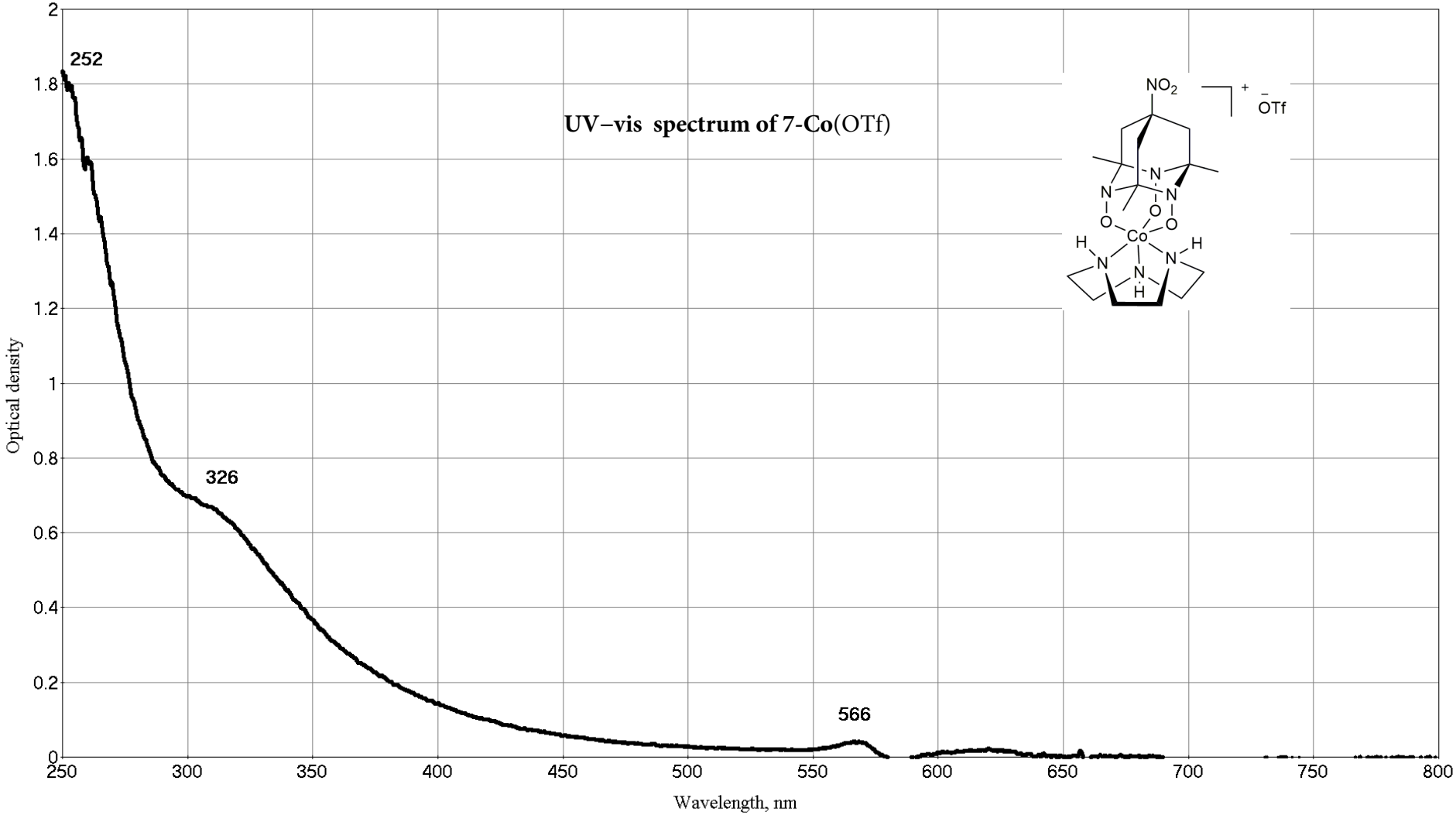
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

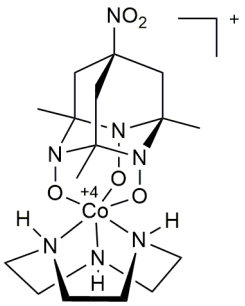




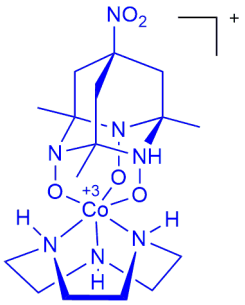

FT-IR spectrum of 7-Co(OTf)
Transmittance [%]
Wavenumber cm-1
3731
3706
3687
3662
3640
3617
3565
3541
3518
3497
3469
3437
3402
3231
3084
2945
2896
2706
2522
2379
1709
1631
1548
1458
1432
1404
1378
1352
1325
1280
1253
1225
1162
1099
1057
1029
979
898
874
849
822
759
731
639
574
550
518
416
NO2
OTf
Co


UV–vis spectrum of 7-Co(OTf)
252
326
566
Optical density
Wavelength, nm
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
250
300
350
400
450
500
550
600
650
700
750
800
NO2
OTf
Co
N
O
H

ESI-HRMS of 7-Co(OTf)



M^+ $(7\text{-Co})^+$



M_2^+

Instrument / Ser# micrOTOF

Acquisition Parameter

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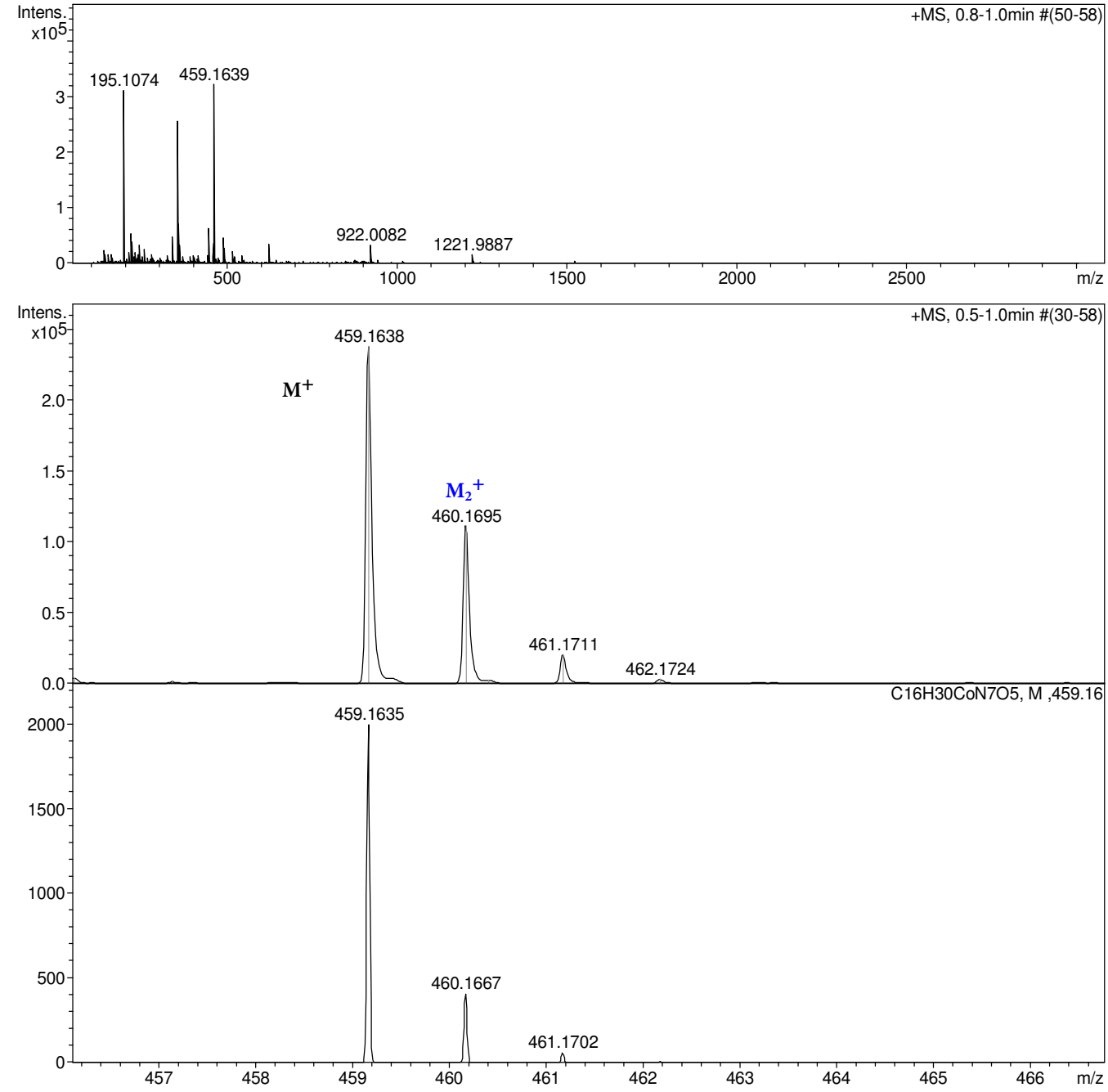
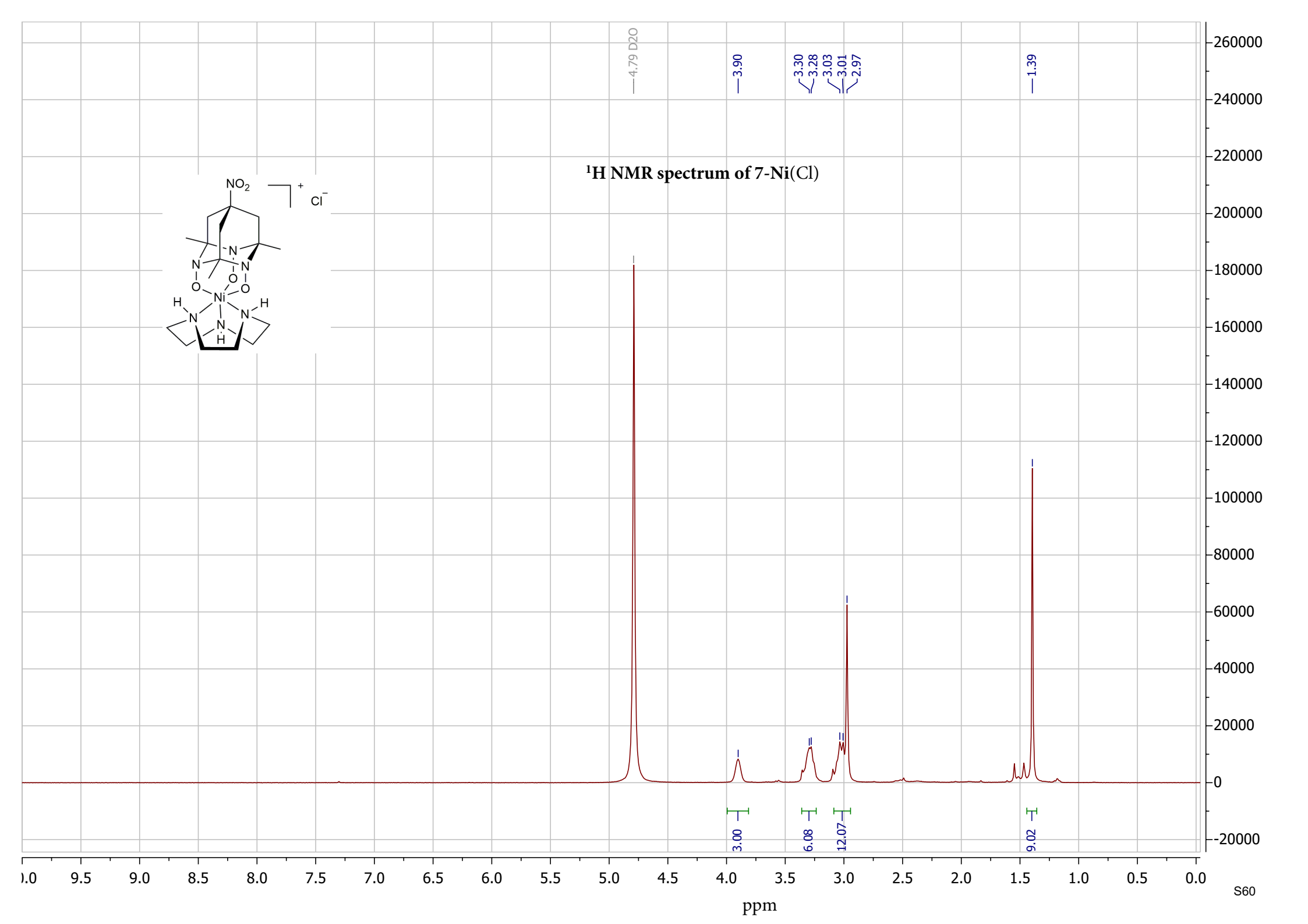
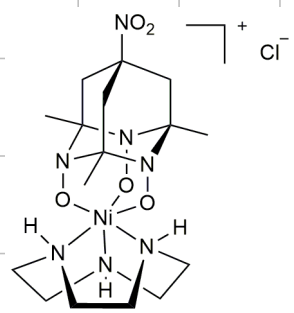
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

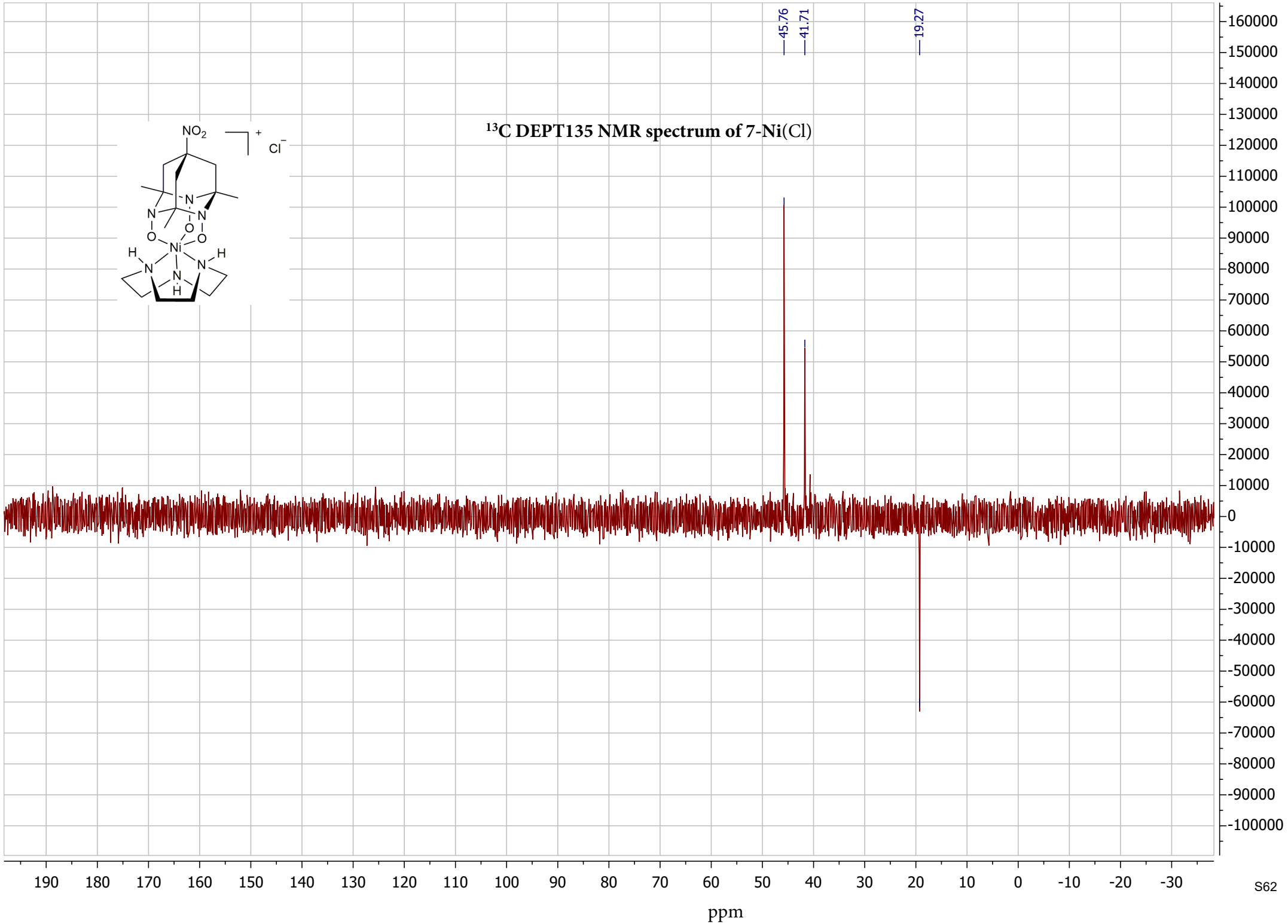




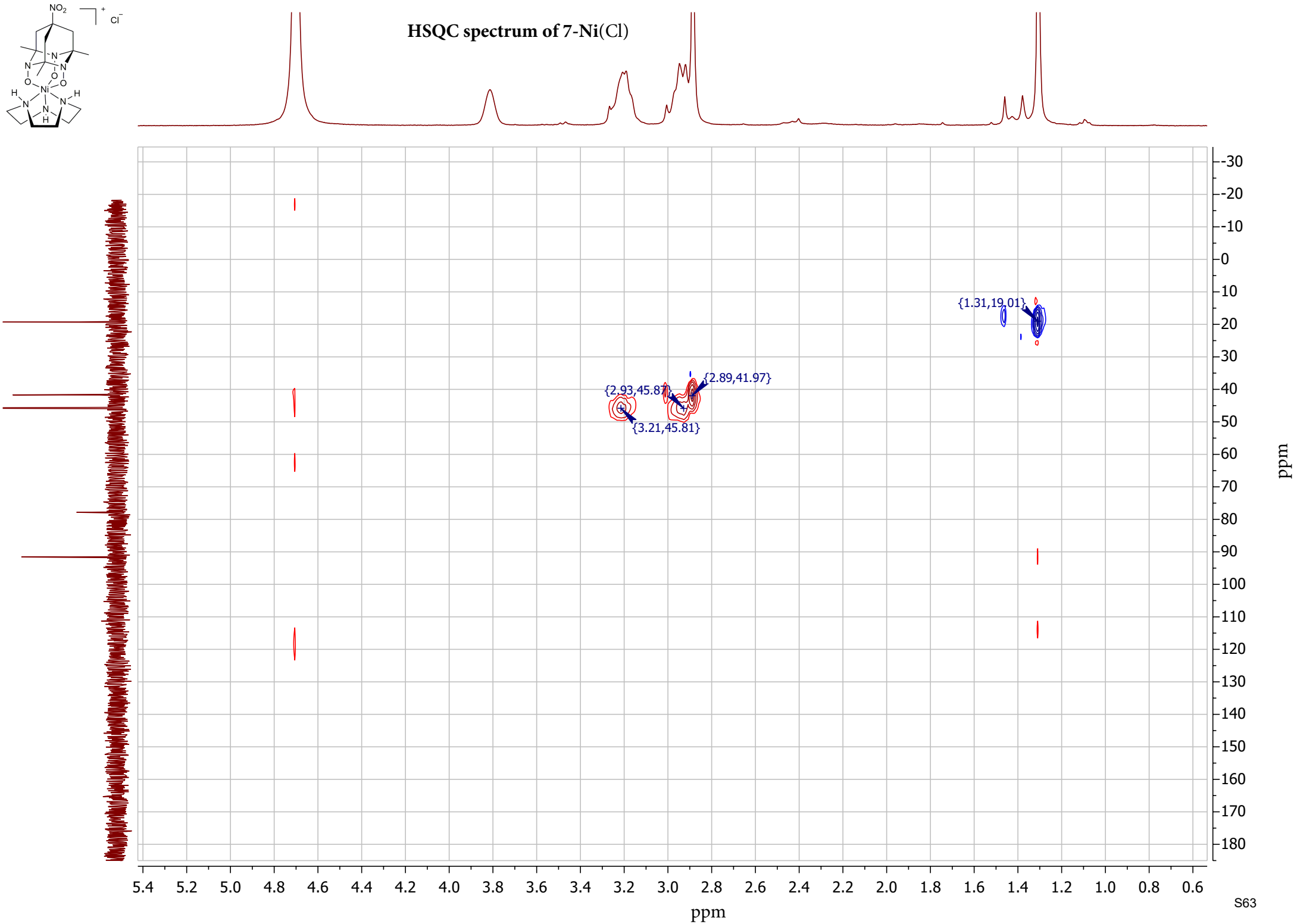
^{1}H NMR spectrum of 7-Ni(Cl)

^{13}C NMR spectrum of 7-Ni(Cl)

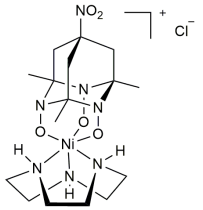




^{13}C DEPT135 NMR spectrum of 7-Ni(Cl)


HSQC spectrum of 7-Ni(Cl)
{1.31,19.01}
{2.89,41.97}
{2.93,45.87}
{3.21,45.81}
ppm
ppm

^{1}H-^{15}N HMBC spectrum of 7-Ni(Cl)



{2.89,-258.47}

{1.31,-258.14}

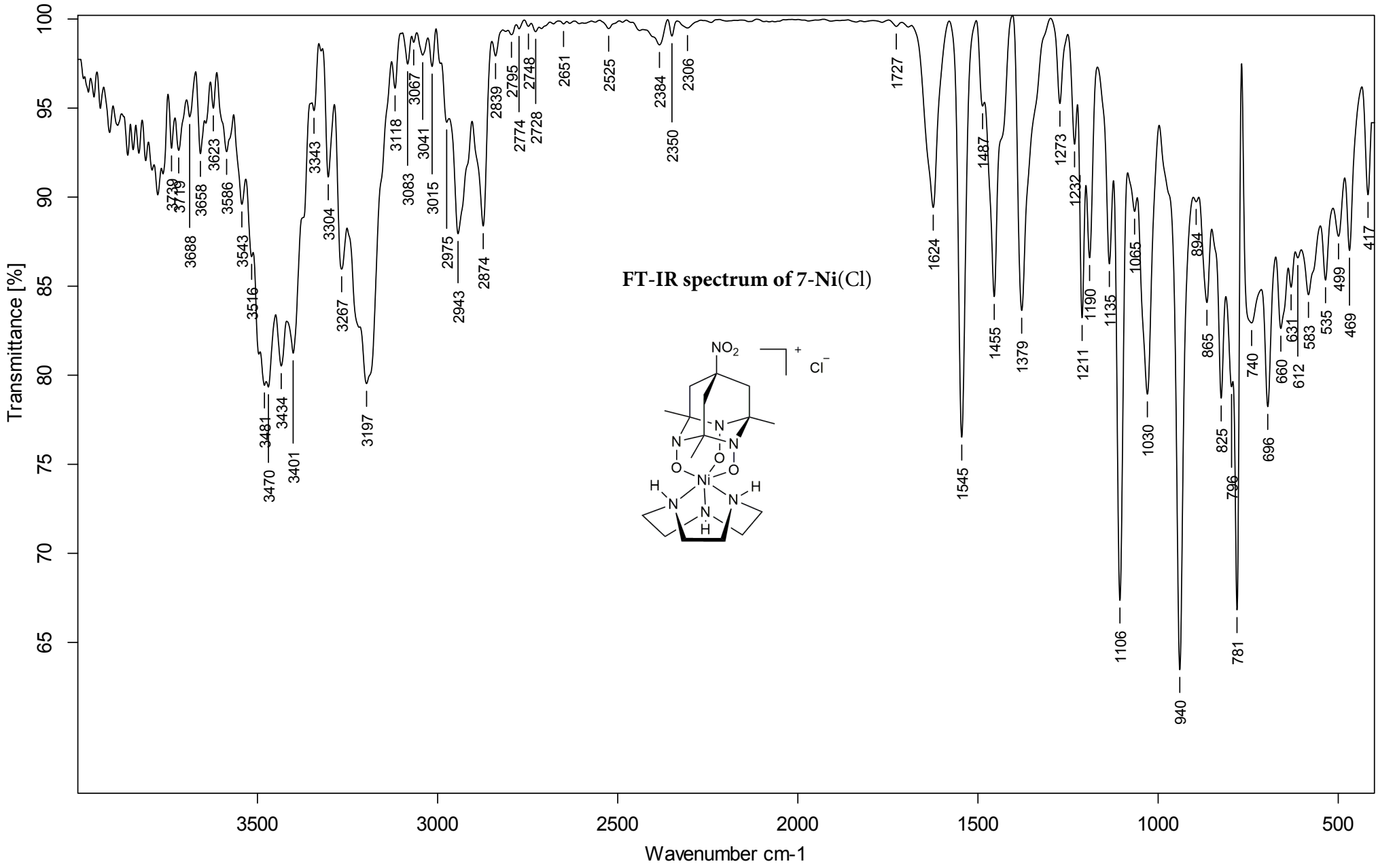
-400 -350 -300 -250 -200 -150 -100 -50 0 50 100 150

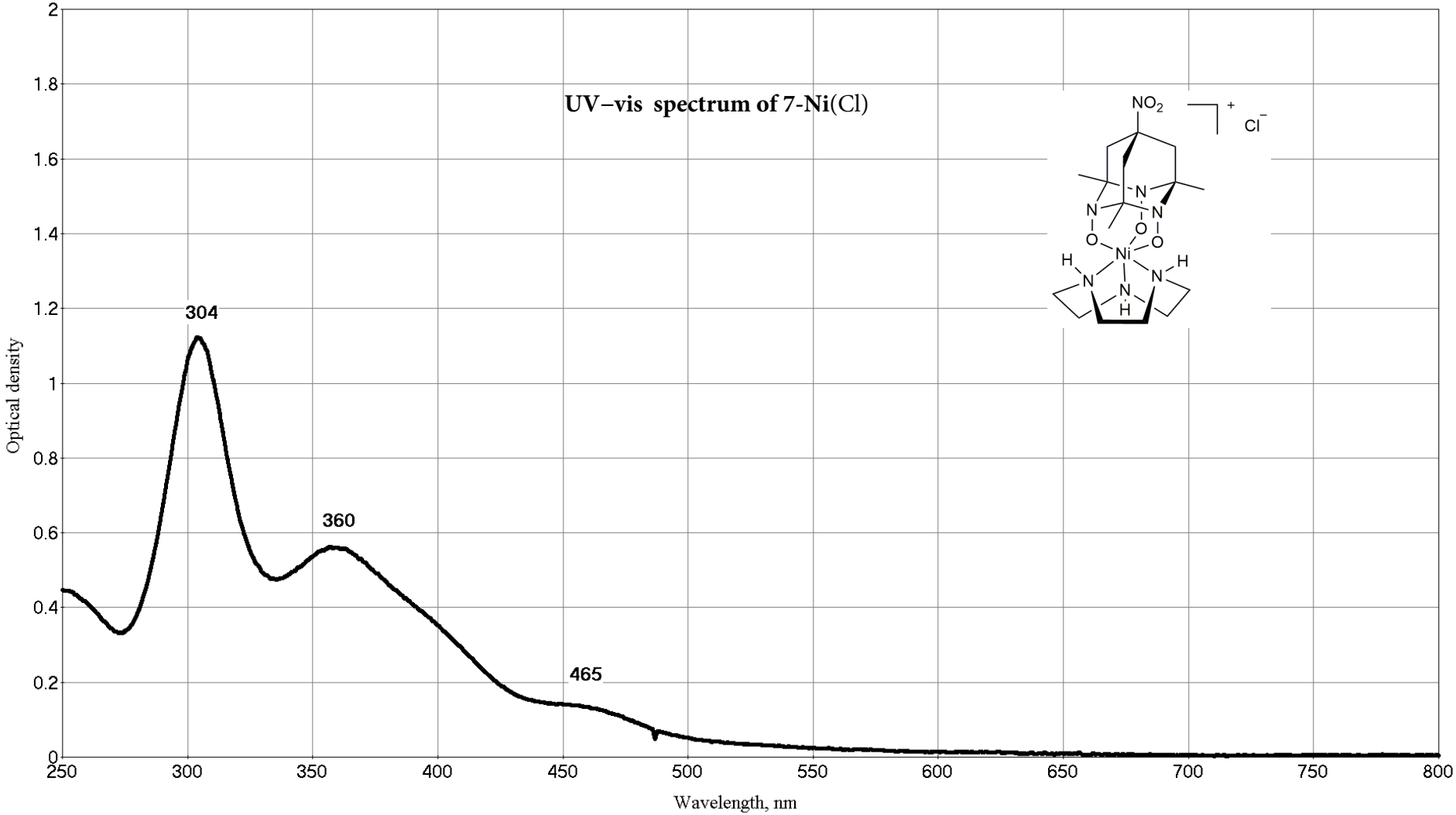
ppm

5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6

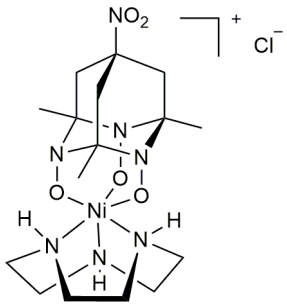
ppm

S64


FT-IR spectrum of 7-Ni(Cl)
Transmittance [%]
Wavenumber cm-1
100
95
90
85
80
75
70
65
3500
3000
2500
2000
1500
1000
500
3729
3719
3688
3658
3623
3586
3543
3516
3481
3470
3434
3401
3343
3304
3267
3197
3118
3083
3067
3041
3015
2975
2943
2874
2839
2795
2774
2748
2728
2651
2525
2384
2350
2306
1727
1624
1545
1487
1455
1379
1273
1232
1211
1190
1135
1106
1065
1030
940
894
865
825
796
781
740
696
660
631
612
583
535
499
469
417
NO2
Cl−
+
N
O
Ni
H


UV–vis spectrum of 7-Ni(Cl)
NO2
Cl−
304
360
465
Optical density
Wavelength, nm
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
250
300
350
400
450
500
550
600
650
700
750
800

ESI-HRMS of 7-Ni(Cl)



Instrument / Ser# micrOTOF

Acquisition Parameter

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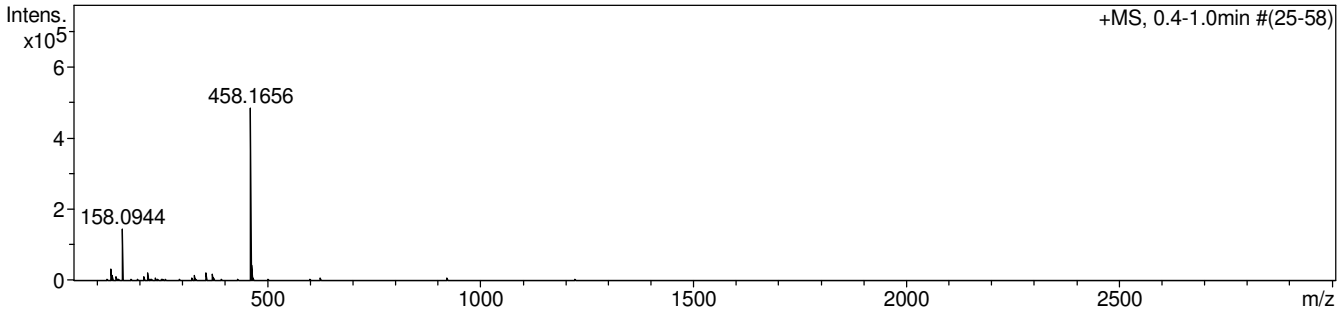
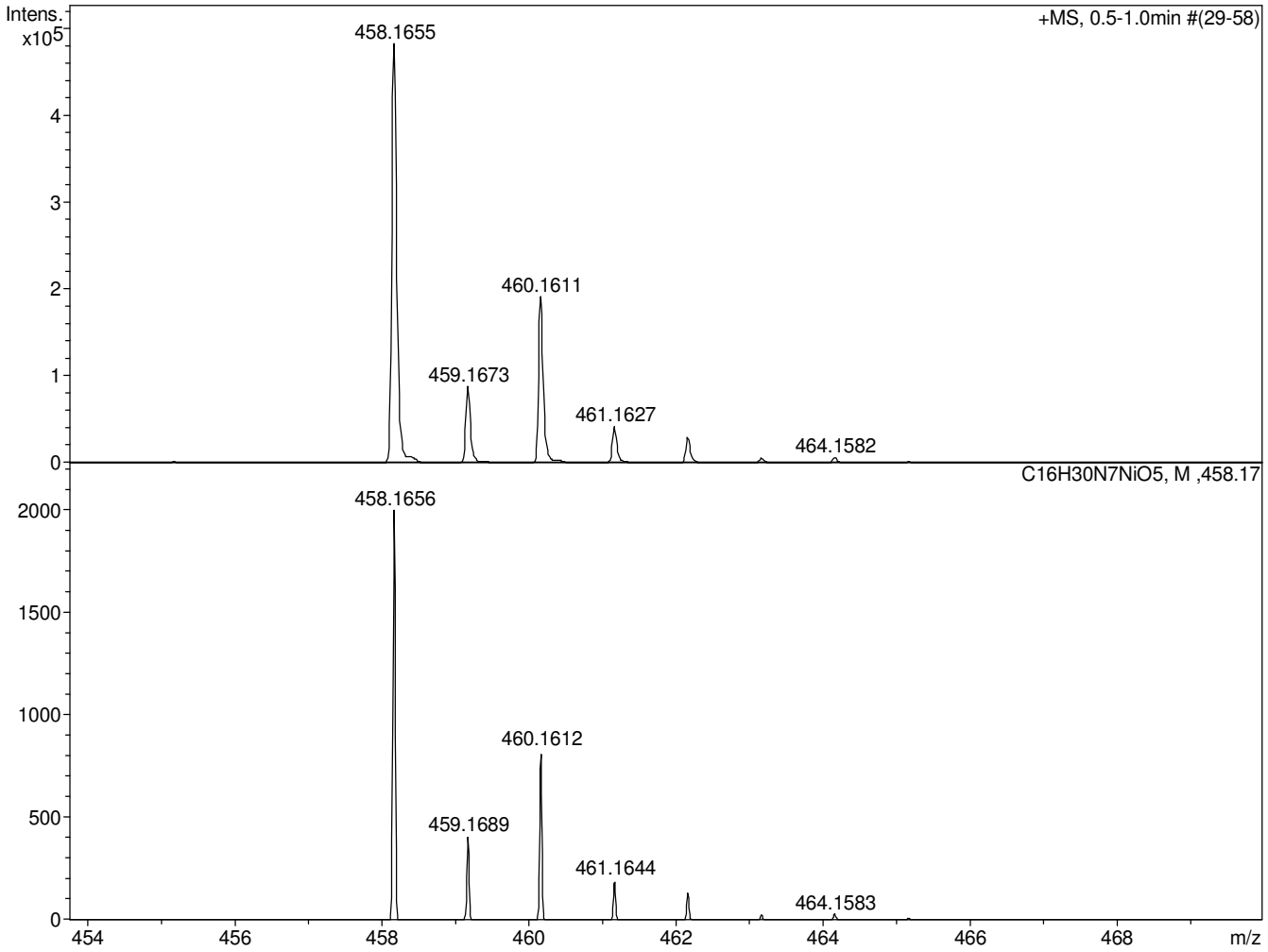
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





4. Catalytic activity of NO_2-TRIAD complexes in oxidation reactions

4.1. Aerobic oxidation of S–H bonds (thiol-oxidase activity)

Aerobic oxidation of *p*-thiocresol catalyzed by complex 7-Mn(Cl)

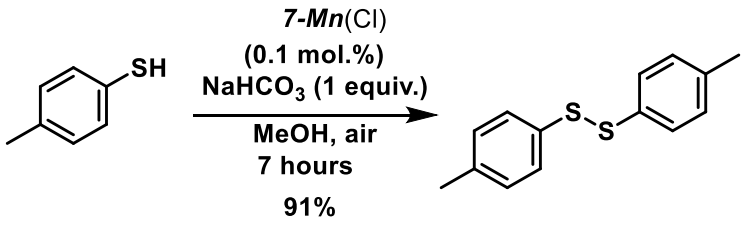
p-Thiocresol (50 mg, 0.4 mmol, 1 equiv.) and $NaHCO_3$ (34 mg, 0.4 mmol, 1 equiv.) were added to 2 mL of methanol. Complex **7-Mn***(Cl)* (10 μL of 41 mM methanolic solution) was added to this mixture. The mixture was stirred in a closed vessel equipped with a magnetic stirrer and an air-filled balloon for 7 hours. The resulting solution was concentrated under reduced pressure. Hexane (2 mL) and water (1 mL) were added to the residue. The organic phase was collected and the aqueous layer was washed with hexane (2 × 2 mL). The combined organic phase was dried over sodium sulfate, concentrated under reduced pressure and analyzed by GC-MS and NMR. The disulfide content in the product was 91% based on NMR spectroscopy with internal standard (1,1,2,2-tetrachloroethane).

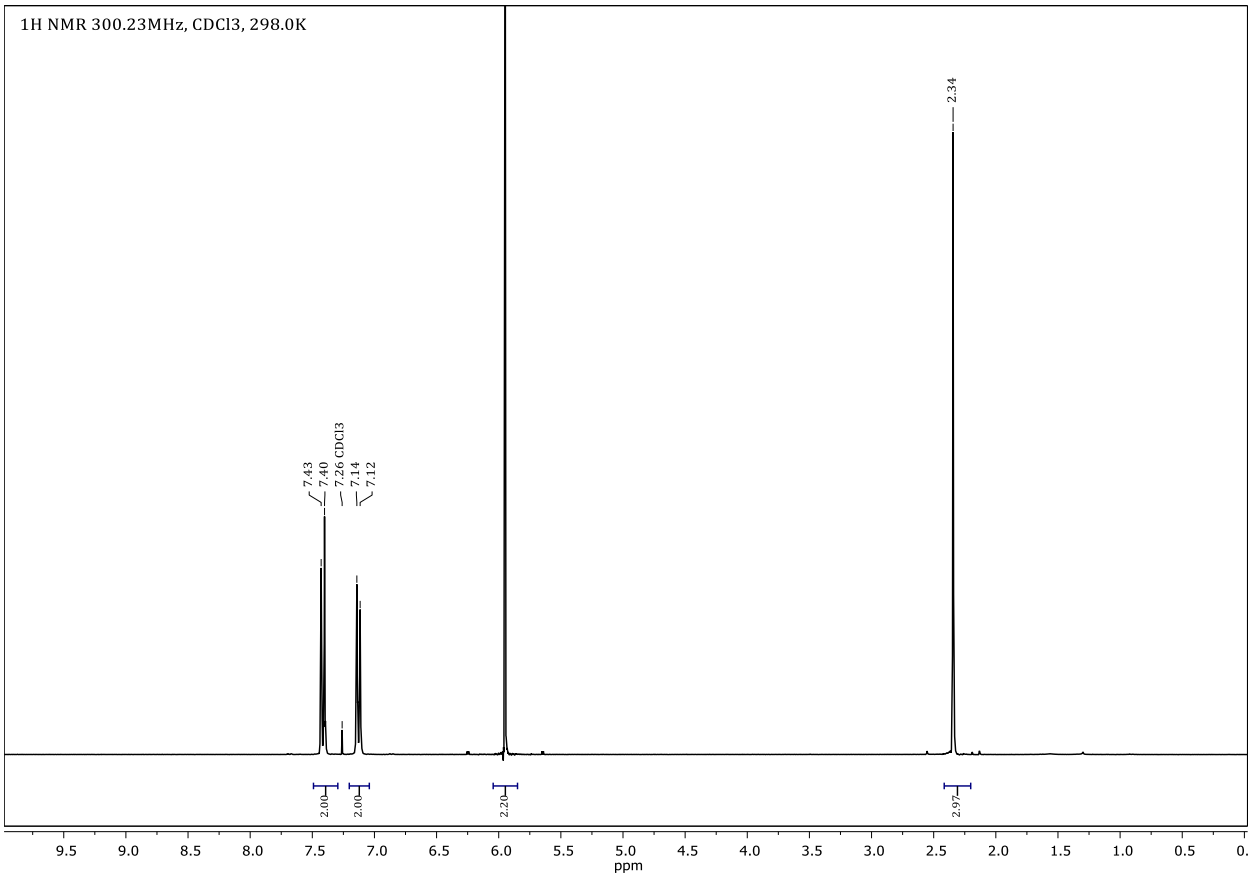
***p*-Tolyl disulfide.** White solid. Mp. 46 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.34 (s, 6 H), 7.14 (m, 4 H), 7.43 (m, 4 H). ^{1}H NMR spectrum and melting point are in agreement with literature data.[6]

Control experiment without a catalyst

p-Thiocresol (50 mg, 0.4 mmol) was stirred in a closed vessel equipped with a magnetic stirrer and an air-filled balloon for 7 hours in methanol (2 mL). The resulting solution was concentrated under reduced pressure. Hexane (2 mL) and water (1 mL) were added to the residue. The organic phase was collected and the aqueous layer was washed with hexane (2 × 2 mL). The combined organic phase was dried over sodium sulfate, concentrated under reduced pressure and analyzed by ^{1}H NMR. The disulfide content in the product was 57% based on NMR spectroscopy with internal standard (1,1,2,2-tetrachloroethane).

^{1}H NMR spectrum of aerobic oxidation of *p*-thiocresol catalyzed by complex **7-Mn**(Cl)





Aerobic oxidation of glutathione catalyzed by complex 7-Mn(Cl)

Glutathione (31 mg, 0.1 mmol, 1 equiv.) and $NaHCO_3$ (27 mg, 0.3 mmol, 3 equiv.) were added to a 1 mM solution of *complex* **7-Mn**(Cl) (10 μL of 10.2 mM aqueous solution) in 3 mL of water. The solution was stirred in a closed vessel equipped with a magnetic stirrer and an air-filled balloon for 24 hours. The resulting solution was concentrated under reduced pressure. MeOH was added to the residue and the resulting precipitate was washed with MeOH until the solution became colorless. The residue was dried under reduced pressure until constant weight and after analyzed by NMR spectroscopy with internal standard (hydroquinone). The disulfide content in the product was 98% based on NMR spectroscopy (internal standard hydroquinone).

Glutathione (GSH). ^{1}H NMR (300 MHz, D_2O, δ, ppm): 2.05-2.20 (m, 2H), 2.52 (t, J = 7.6 Hz, 2H), 2.8-3.0 (m, 2H), 3.71 (t, J = 6.2 Hz, 1H), 3.74 (s, 2H), 4.47 (t, J = 6.2 Hz, 1H). ^{1}H NMR spectrum is in agreement with literature data.[6]

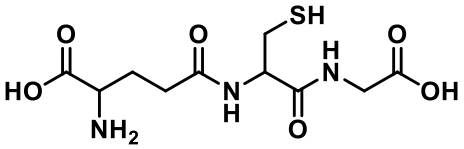
Glutathione disulfide sodium salt. White solid. ^{1}H NMR (300 MHz, D_2O, δ, ppm): 1.95 (m, 4H), 2.25 – 2.52 (m, 4H), 2.87 (dd, J = 14.3, 9.7 Hz, 2H), 3.16 – 3.26 (dd, J = 14.3, 4.5 Hz, 2H), 3.45 (t, J = 6.3 Hz, 2H), 3.73 (d, J = 20.9 Hz, 2H), 3.78 (d, J = 20.9 Hz, 2H), 4.70 – 4.74 (m, 2H).^{1}H NMR spectrum is in agreement with literature data.[6]

Control experiment without a catalyst

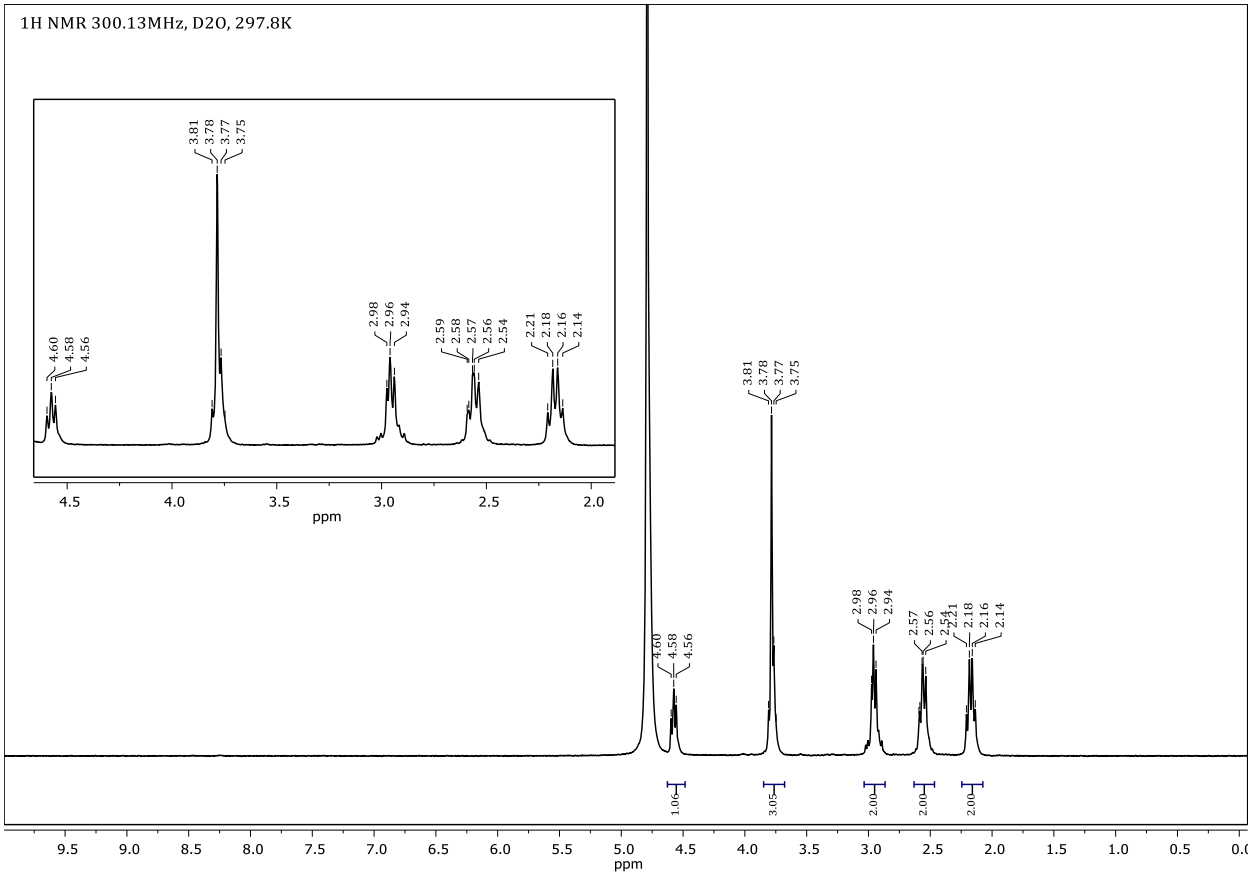
Glutathione (31 mg, 0.1 mmol, 1 equiv.) and $NaHCO_3$ (27 mg, 0.3 mmol, 3 equiv.) were dissolved in water (3 mL). The solution was stirred in a closed vessel equipped with a magnetic stirrer and an air-filled balloon for 8 hours. The resulting solution was evaporated under reduced pressure. MeOH was added to the residue and the resulting precipitate was dried under reduced pressure until constant weight and after analyzed by NMR spectroscopy. The disulfide content in the product was 27% based on NMR.

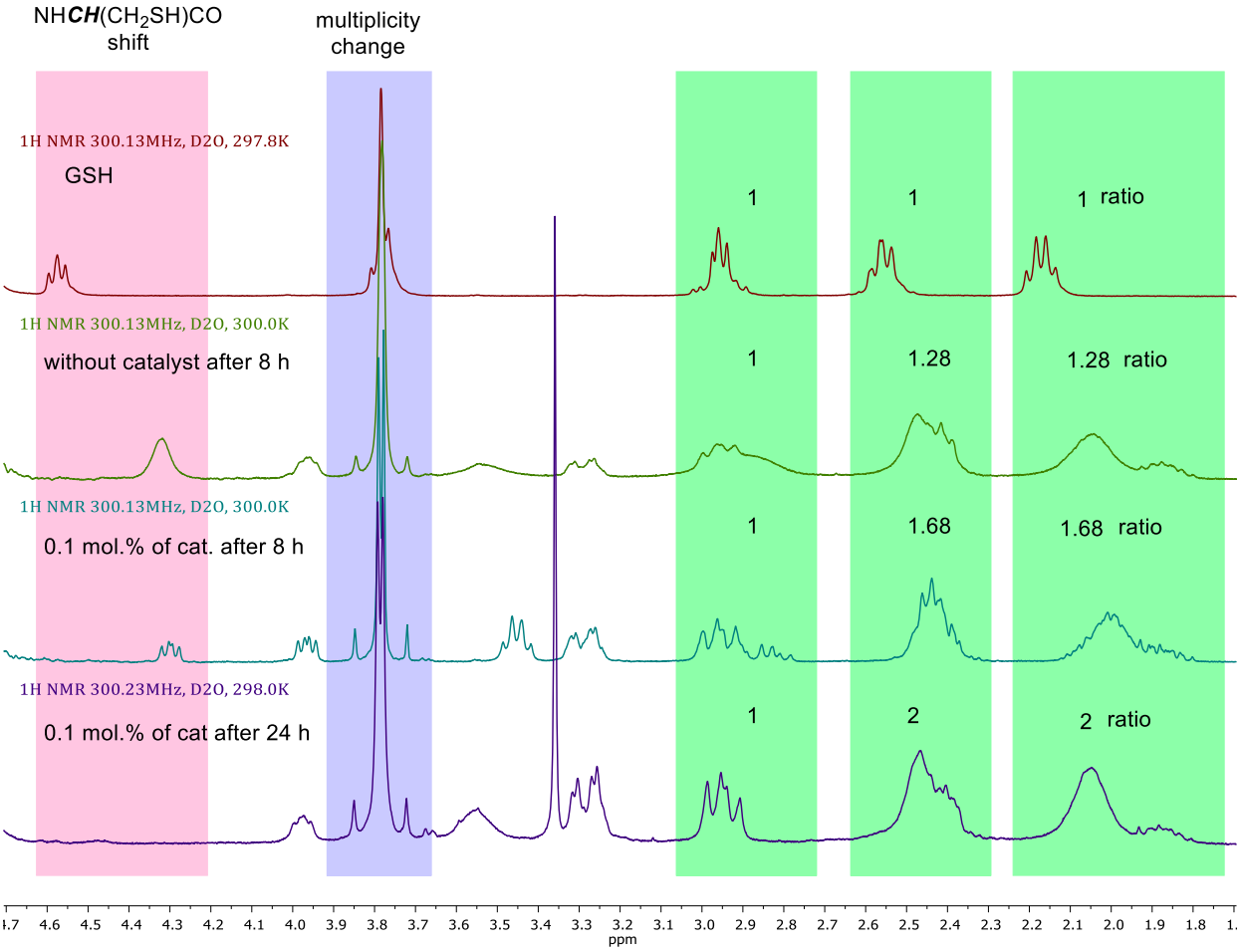
NMR analysis of aerobic oxidation reactions of glutathione

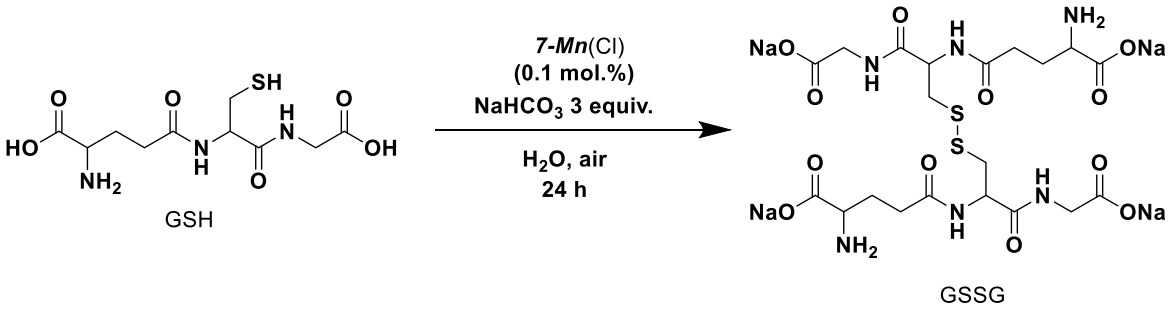
^{1}H NMR spectrum of glutathione



GSH



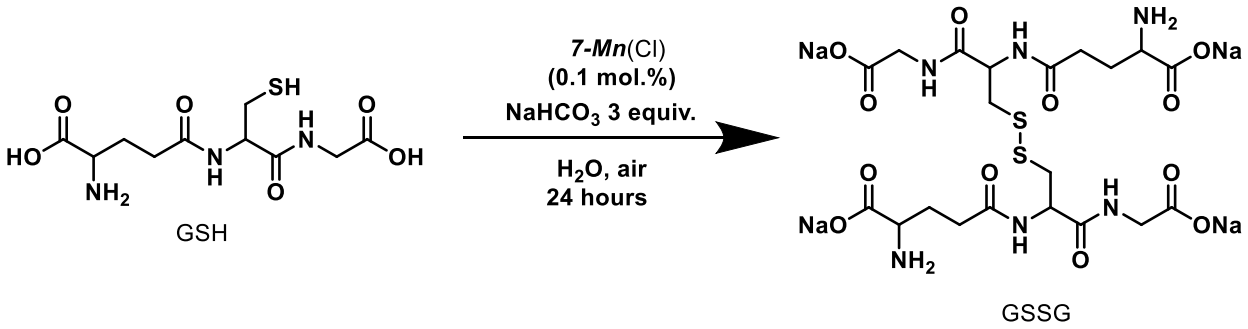

NHCH(CH2SH)CO
shift
multiplicity
change
1H NMR 300.13MHz, D2O, 297.8K
GSH
1
1
1 ratio
1H NMR 300.13MHz, D2O, 300.0K
without catalyst after 8 h
1
1.28
1.28 ratio
1H NMR 300.13MHz, D2O, 300.0K
0.1 mol.% of cat. after 8 h
1
1.68
1.68 ratio
1H NMR 300.23MHz, D2O, 298.0K
0.1 mol.% of cat after 24 h
1
2
2 ratio
ppm

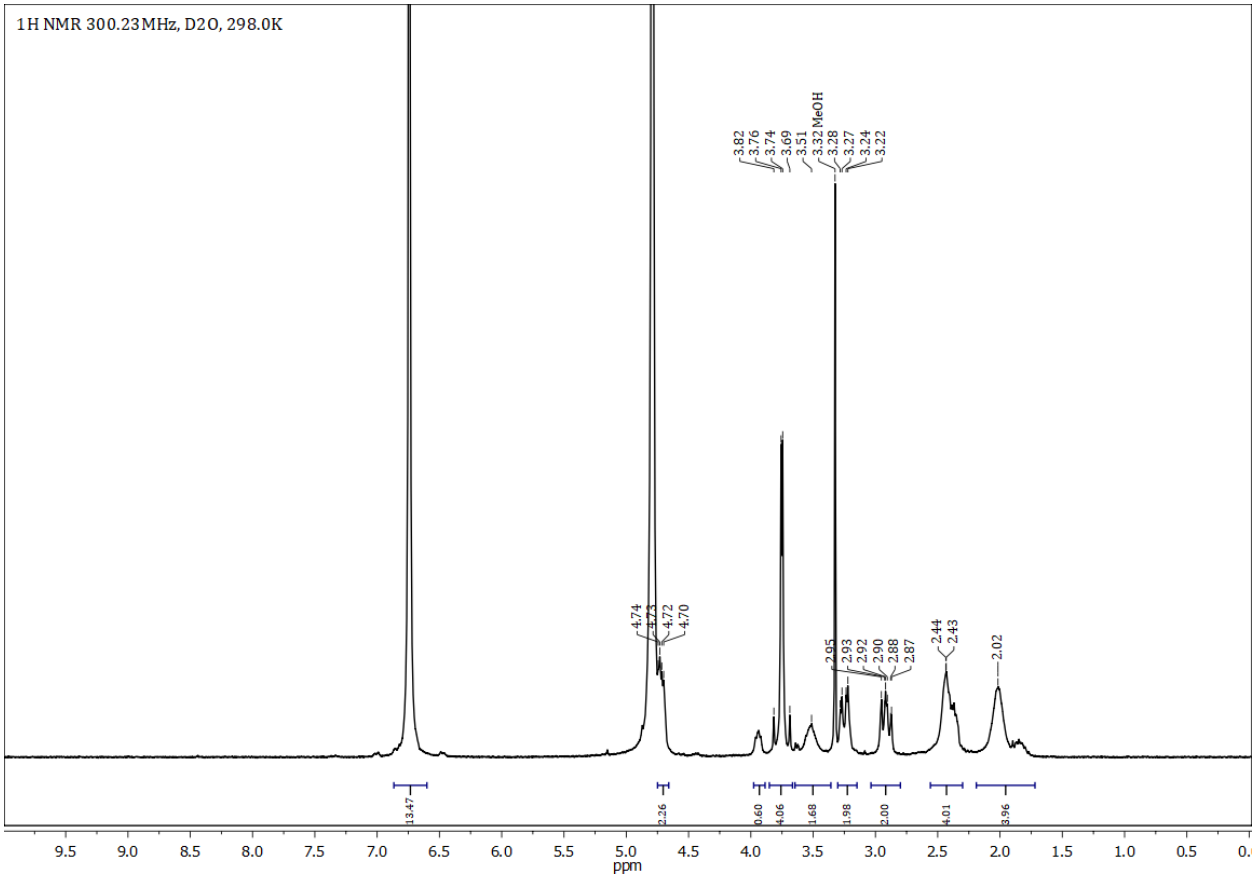

7-Mn(Cl)
(0.1 mol.%)
NaHCO3 3 equiv.
H2O, air
24 h

GSH

GSSG

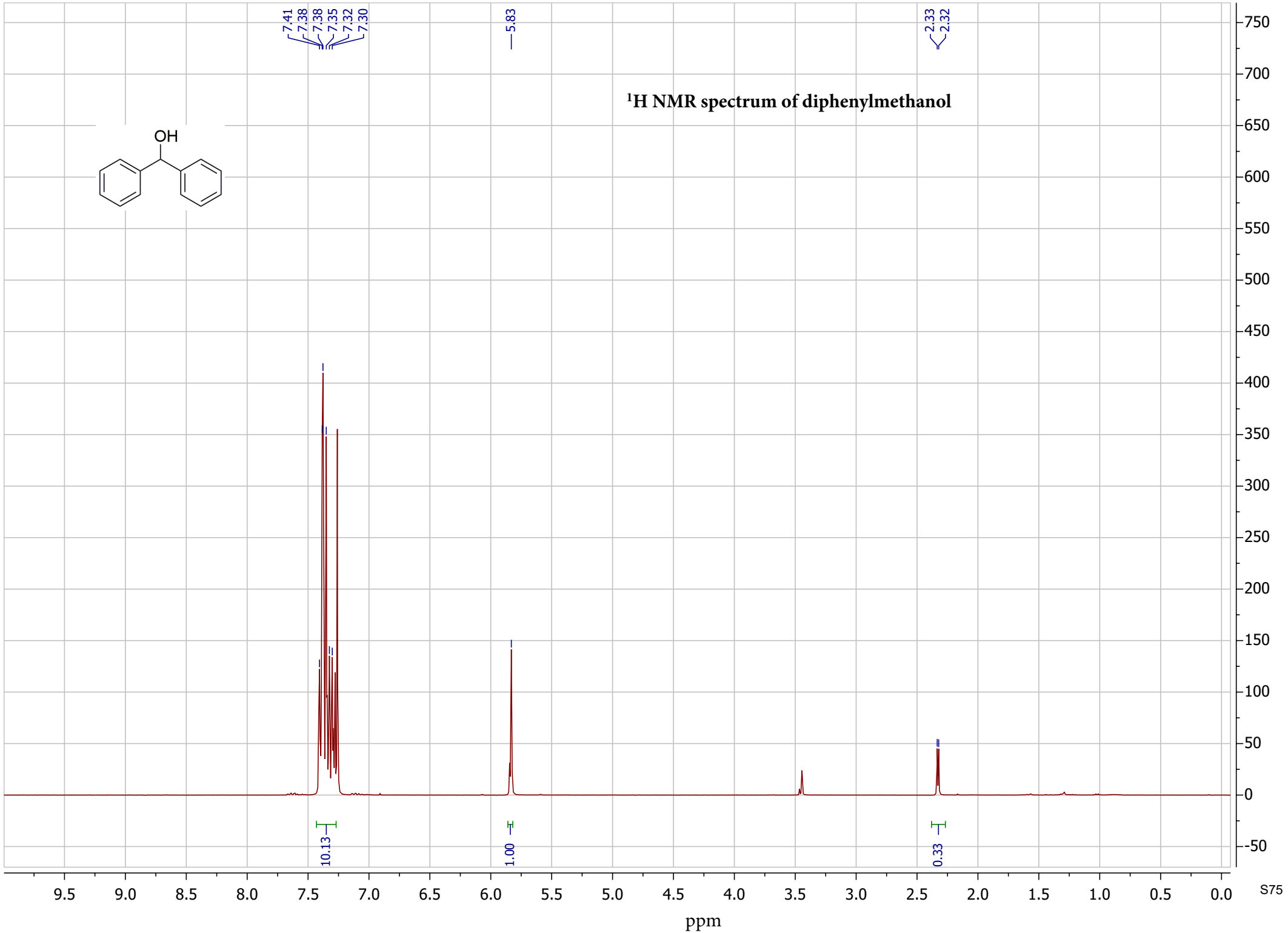
^{1}H NMR spectrum of aerobic oxidation of GSH catalyzed by complex **7-Mn**(Cl)





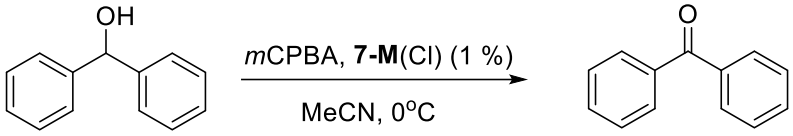
4.2.Synthesis of diphenylmethanol

$NaBH_4$ (0.77 g, 21.4 mmol) was added to a solution of diphenyl ketone (1.0 g, 5.4 mmol) in 30 mL of EtOH at room temperature and with vigorous stirring. The mixture was stirred at room temperature for 1.5 hours. Then, a 10 % NaOH solution was added to the reaction mixture until a clear solution formed (approximately 10 mL of 10 % NaOH solution was added). The volatiles were removed in a vacuum, and the residue was transferred to a separatory funnel containing 20 mL of water and 20 mL of CH_2Cl_2. After separation of the organic layer, the aqueous phase was additionally washed with 20 mL of CH_2Cl_2. The combined organic phase was washed with 20 mL of a saturated NaCl solution, dried over anhydrous Na_2SO_4. The resulting residue was dried in a vacuum until constant weight to give 1.010 g (99 %) of diphenylmethanol as a white solid. Mp. 66-68°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.32 (s, 1H, CHO*H*), 5.83 (s, 1H, C*H*OH), 7.25-7.43 (m, 10H, 2Ph). ^{1}H NMR spectrum and melting point are in agreement with literature data.[7]



^{1}H NMR spectrum of diphenylmethanol

4.3. C–H oxidation of diphenylmethanol with *m*CPBA



To a solution of diphenylmethanol (50 mg, 0.27 mmol) in CH_3CN (2.7 mL) cooled to 0°C, *m*CPBA (334 mg (70%), 1.36 mmol) and a **7-M**(Cl) solution (1.3 mg of **7-Mn**(Cl), 0.0027 mmol in 0.3 mL of CH_3CN, 1.3 mg of **7-Fe**(Cl), 0.0024 mmol in 0.3 mL of CH_3CN, or 1.2 mg of **7-Ni**(Cl), 0.0027 mmol in 0.3 mL of CH_3CN) were added successively with vigorous stirring. The mixture was stirred at 0°C for 6 h and then kept overnight in a fridge (0-5°C). The reaction mixture was then transferred to a separatory funnel containing 20 mL of saturated aqueous $NaHCO_3$ solution and 20 mL of EtOAc. After separation of the organic layer, the aqueous phase was additionally washed with 10 mL of EtOAc. The combined organic phase was washed with 20 mL of saturated NaCl solution, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR spectroscopy with internal standard (1,1,2,2-tetrachloroethane). Results are given in **Table S1**. A preparative experiment with **7-Fe**(Cl) as a catalyst resulted in 86 mg of diphenyl ketone (86%), isolated using column chromatography (hexane : EtOAc = 15: 1).

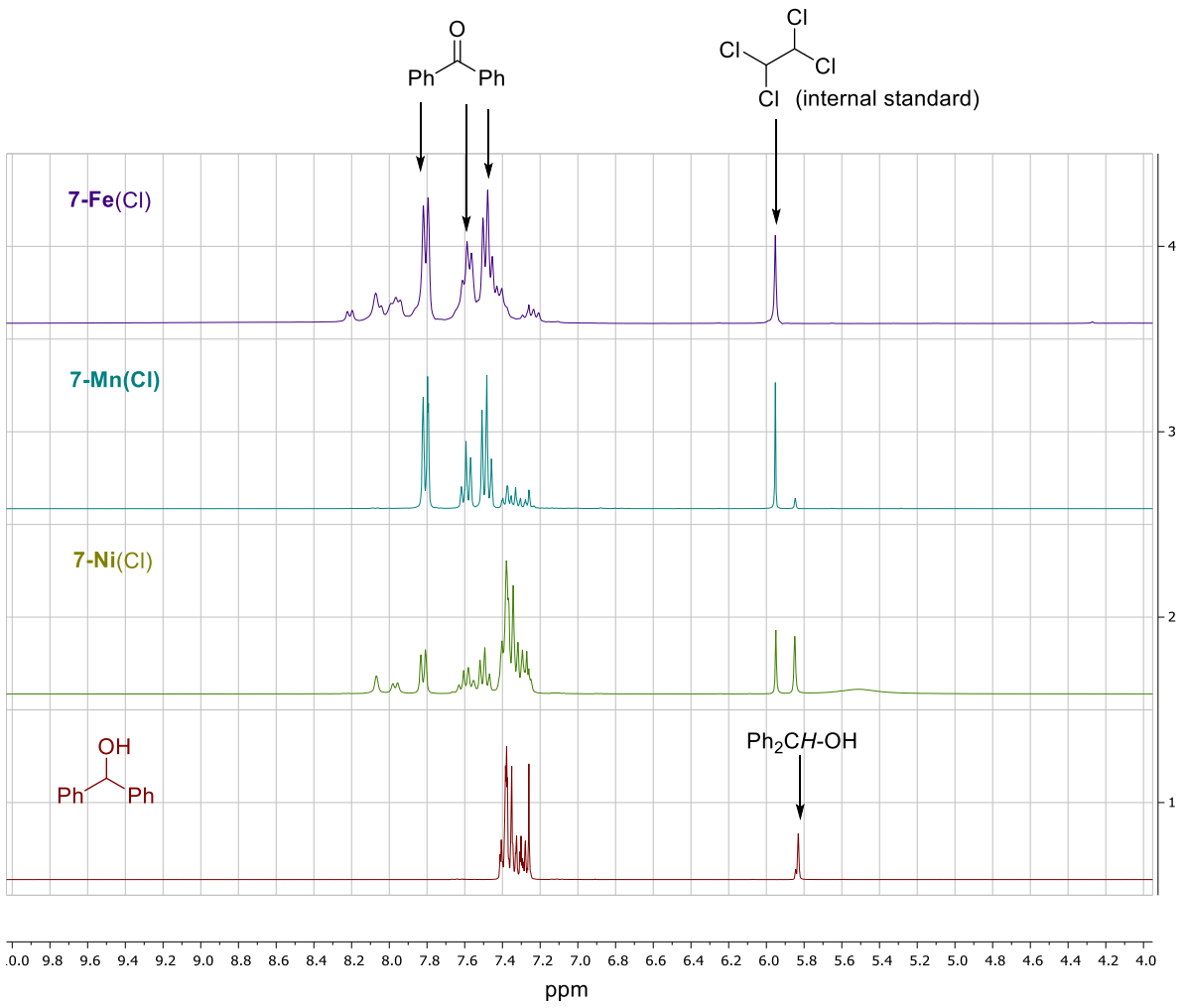
Diphenyl ketone. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.47-7.54 (m, 4H, 4 m-Ph), 7.58-7.66 (m, 2H, 2 p-Ph), 7.78-7.87 (m, 4H, 4 o-Ph). ^{1}H NMR spectrum is in agreement with literature data.[8]

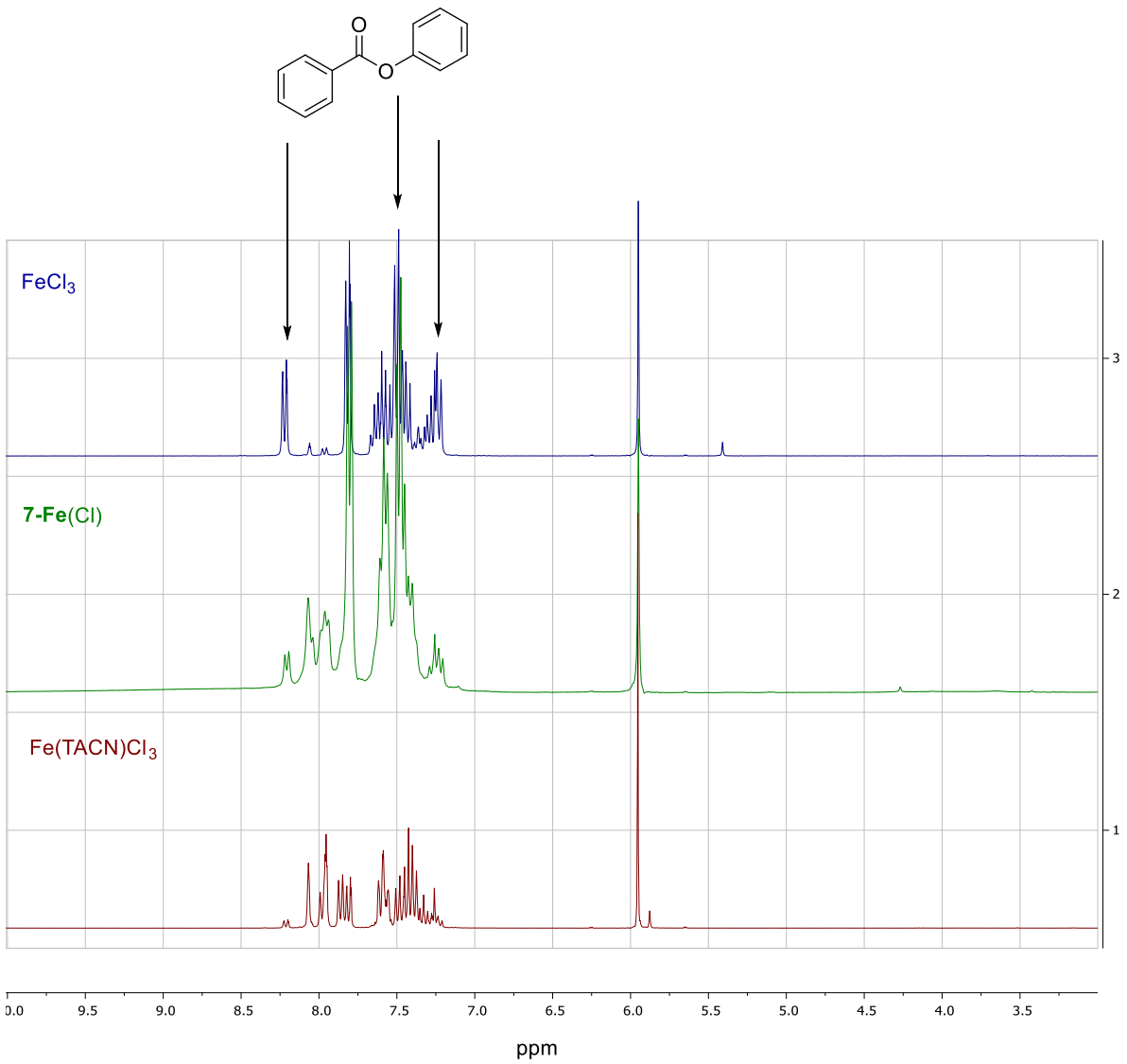
Control experiment without a catalyst

To a solution of diphenylmethanol (50 mg, 0.27 mmol) in CH_3CN (3 mL) cooled to 0°C, *m*CPBA (334 mg (70%), 1.36 mmol) was added with vigorous stirring. The mixture was stirred at 0°C for 6 h and then kept overnight in a fridge (0-5°C). The reaction mixture was then transferred to a separatory funnel containing 20 mL of saturated aqueous $NaHCO_3$ solution and 20 mL of EtOAc. After separation of organic layer, the aqueous phase was additionally washed with 10 mL of EtOAc. The combined organic phase was washed with 20 mL of saturated NaCl solution, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR spectroscopy with internal standard (1,1,2,2-tetrachloroethane). The yield of diphenyl ketone was ≤ 5 % based on NMR data.

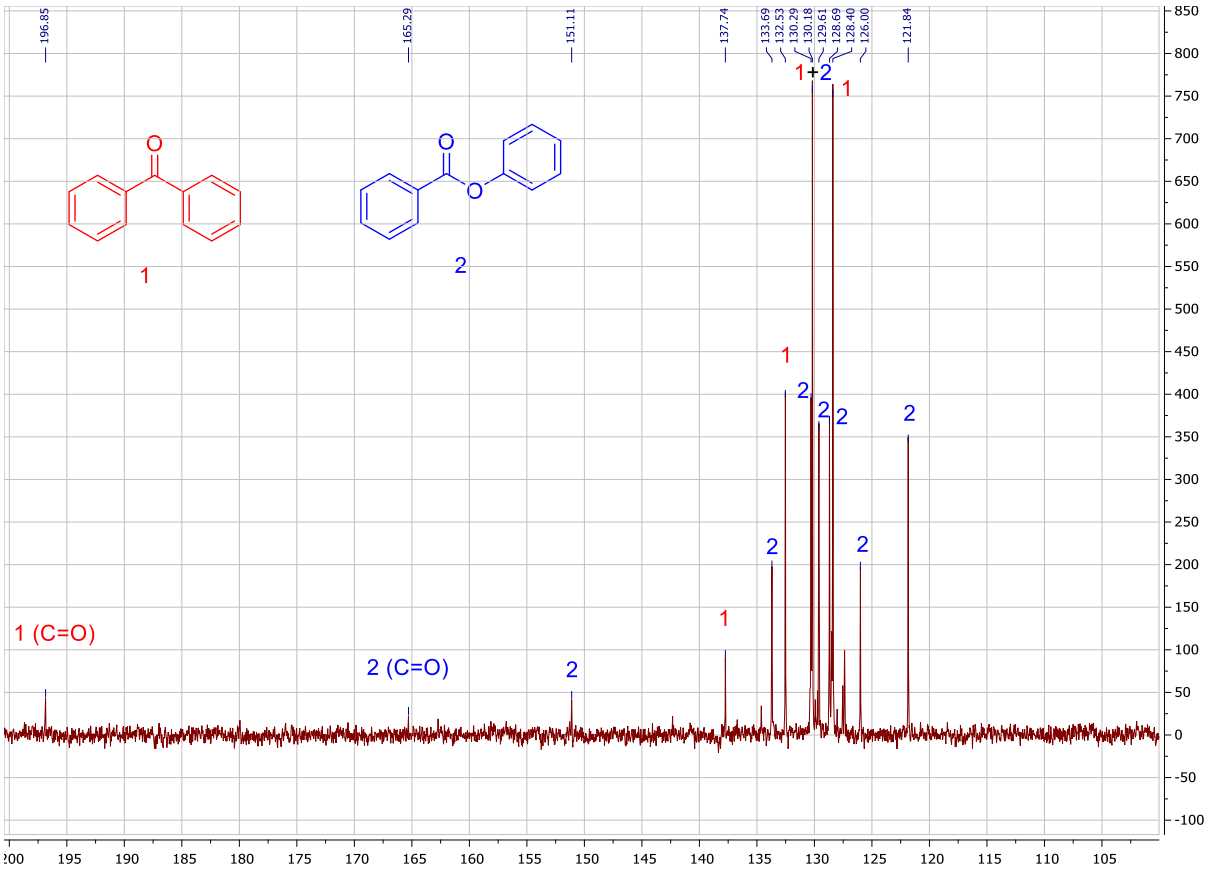
Table S1. Catalytic performance of NO_2-TRIAD complexes **7-M**(Cl) in C–H oxidation of diphenylmethanol with *m*CPBA.

Entry	Catalyst	Conversion of diphenylmethanol, %	Yield of diphenyl ketone, %	Yield of phenyl benzoate, %
1	**7-Mn**(Cl)	88	69	0
2	**7-Fe**(Cl)	>95	74	8
3	**7-Ni**(Cl)	31	28	0
4	$FeCl_3$	>95	18	17
5	$Fe(TACN)Cl_3$	74	38	18
6	No catalyst	<5	<5	0

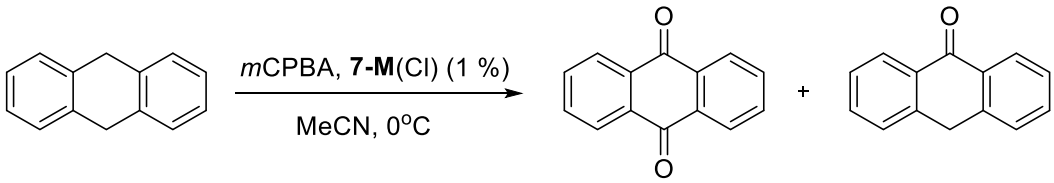

O
Ph
Ph
Cl
Cl
Cl
Cl (internal standard)
7-Fe(Cl)
7-Mn(Cl)
7-Ni(Cl)
OH
Ph
Ph
Ph2CH-OH
4
3
2
1
.0.0 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0
ppm


O
O
FeCl3
7-Fe(Cl)
Fe(TACN)Cl3
3
2
1
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

^{13}C spectrum of optimization experiment ($FeCl_3$ as catalyst)



4.4.Oxidation of 9,10-dihydroanthracene with *m*CPBA (with a catalyst)



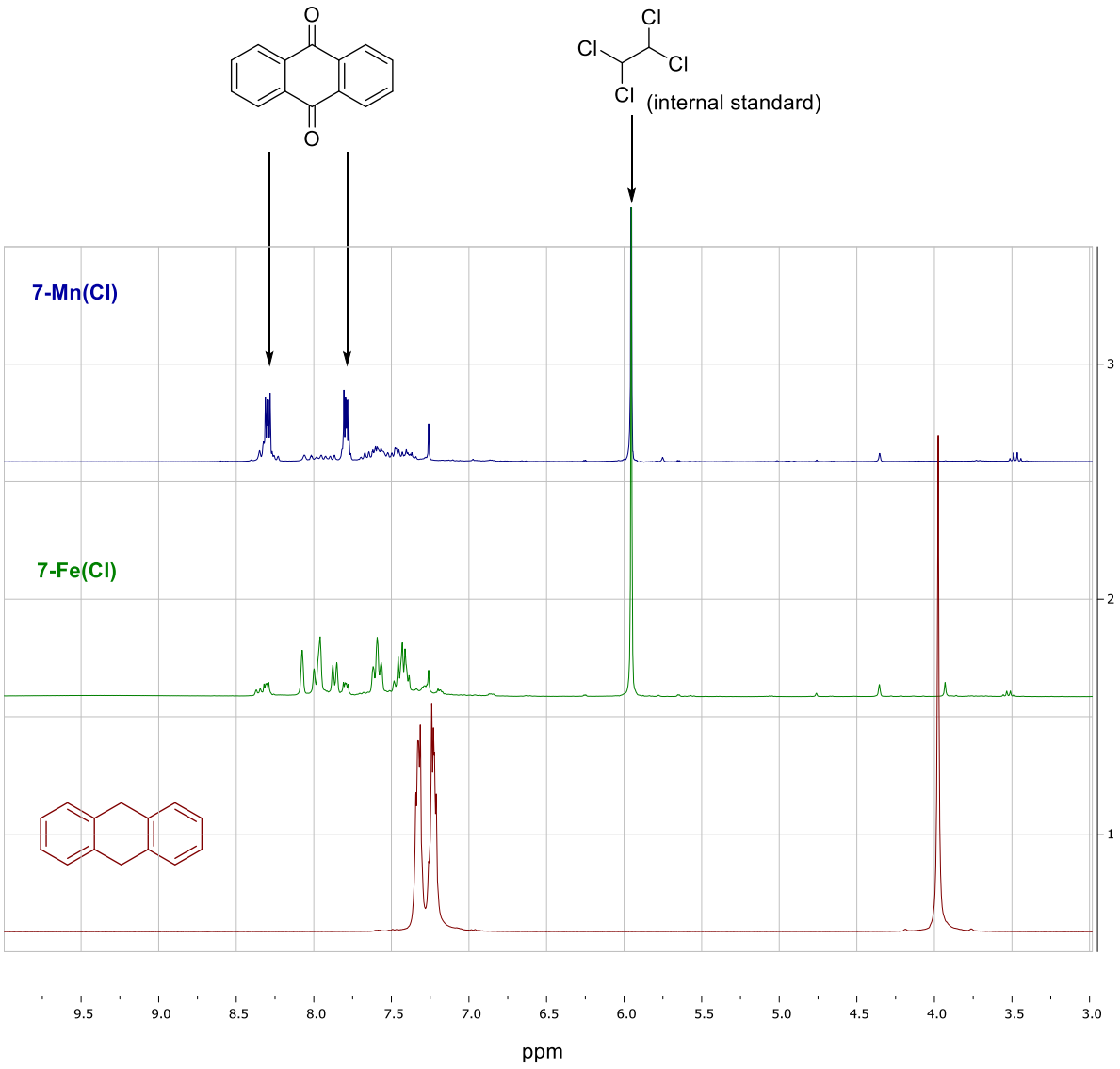
To a solution of 9,10-dihydroanthracene (50 mg, 0.28 mmol) in CH_3CN (2.7 mL) cooled to 0 °C, *m*CPBA (342 mg (70%), 1.39 mmol) and a **7-M**(Cl) solution (1.6 mg of **7-Mn**(Cl), 0.0033 mmol in 0.3 mL of CH_3CN, or 1.6 mg of **7-Fe**(Cl), 0.0028 mmol in 0.3 mL of CH_3CN) were added successively with vigorous stirring. The mixture was stirred at 0°C for 6 h and then kept overnight in a fridge (0-5°C). The reaction mixture was then transferred to a separatory funnel containing 20 mL of saturated aqueous $NaHCO_3$ solution and 20 mL of EtOAc. After separation of the organic layer, the aqueous phase was additionally washed with 10 mL of EtOAc. The combined organic phase was washed with 20 mL of saturated NaCl solution, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR spectroscopy with internal standard (1,1,2,2-tetrachloroethane). Results are given in **Table S2**.

Control experiment without a catalyst

To a solution of 9,10-dihydroanthracene (50 mg, 0.28 mmol) in CH_3CN (3 mL) cooled to 0°C, *m*CPBA (342 mg (70%), 1.39 mmol) was added with vigorous stirring. The mixture was stirred at 0°C for 6 h and then kept overnight in a fridge (0-5°C). The reaction mixture was then transferred to a separatory funnel containing 20 mL of saturated aqueous $NaHCO_3$ solution and 20 mL of EtOAc. After separation of organic layer, the aqueous phase was additionally washed with 10 mL of EtOAc. The combined organic phase was washed with 20 mL of saturated NaCl solution, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR spectroscopy with internal standard (1,1,2,2-tetrachloroethane). The yield of anthracene-9,10-dione was ≤ 5 % based on NMR data, anthracen-9(10H)-one was not observed in NMR spectrum.

Table S2. Catalytic performance of NO_2-TRIAD complexes **7-M**(Cl) in C–H oxidation of dihydroanthracene with mCPBA.

Entry	Catalyst	Conversion of 9,10-dihydroanthracene, %	Yield of anthracene-9,10-dione, %	Yield of anthracen-9(10H)-one, %
1	**7-Mn**(Cl)	>95	51	7
2	**7-Fe**(Cl)	86	22	13
3	$MnCl_2 \cdot 4H_2O$	>95	16	<5
4	No catalyst	22	<5	0


O
O
Cl
Cl
Cl
Cl
(internal standard)
7-Mn(Cl)
7-Fe(Cl)
3
2
1
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm

5. X-ray crystallography

X-ray diffraction data for **7-Mn**(Cl) were collected at 100 K with a Bruker APEXII CCD diffractometer and for others, at 100 K (**7-Fe**(Cl)) and **6a**(K) or at 200 K (**1a**) with a Bruker Quest D8 CMOS diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Using Olex2[9] the structures were solved with the ShelXT[10] structure solution program using Intrinsic Phasing and refined with the XL[11] refinement package using Least Squares minimization against F^2_{hkl} in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of NH groups, as well as those of OH groups of **1a** and of lattice methanol in **7-Fe**(Cl), were located from the difference Fourier synthesis, positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation within the riding model. CCDC 2162202 (**7-Fe**(Cl)), 2161787 (**7-Mn**(Cl)), 2162229 (**6a**(K)) and 2162230 (**1a**) contain the supplementary crystallographic data for this paper.

X-ray diffraction data for **7-Ni**(Cl) (CCDC 2423394) and **6a**(H) (CCDC 2423393) were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K_α-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program[12]. The structure was solved by direct methods using SHELXT[10] and refined on F^2 using SHELXL-2018[13] in the OLEX2 program.[9] All non-hydrogen atoms were refined with individual anisotropic displacement parameters.

Hydrogen atoms (H5, H6 and H7) of amino-groups for **7-Ni**(Cl) were found from the electron density-difference map but were refined as riding atoms with relative displacement parameters.

Locations of amino hydrogen atom (H4) and hydroxyl hydrogen atom (H6) for **6a**(H) were found from the electron density-difference map; these hydrogen atoms were refined with individual isotropic displacement parameters.

Other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters.

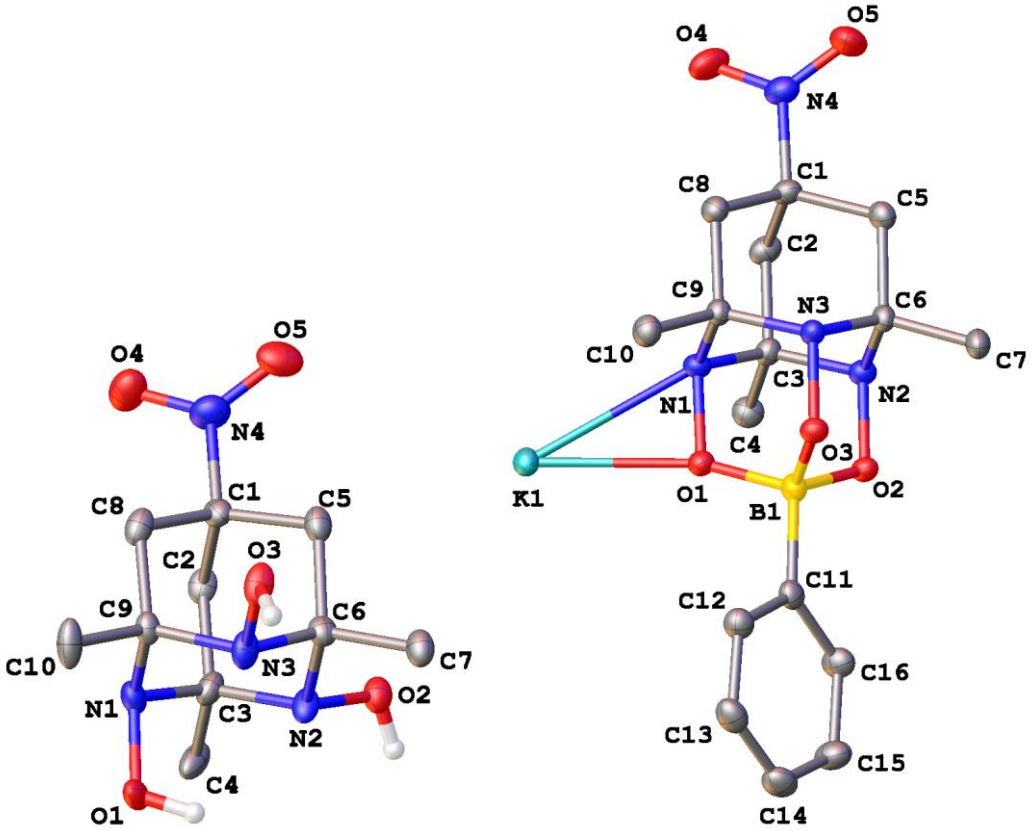


Figure S1. General view of **1a** (left) and **6a**(K) (right) with atoms shown as thermal ellipsoids (p = 50% and 30%, respectively). Hydrogen atoms except those of the OH groups in **1a** are omitted, as well as the minor component of the disordered nitro group and the second symmetry-independent molecule of **1a** and molecules of lattice methanol in **6a**(K) and chloroform in **1a**.

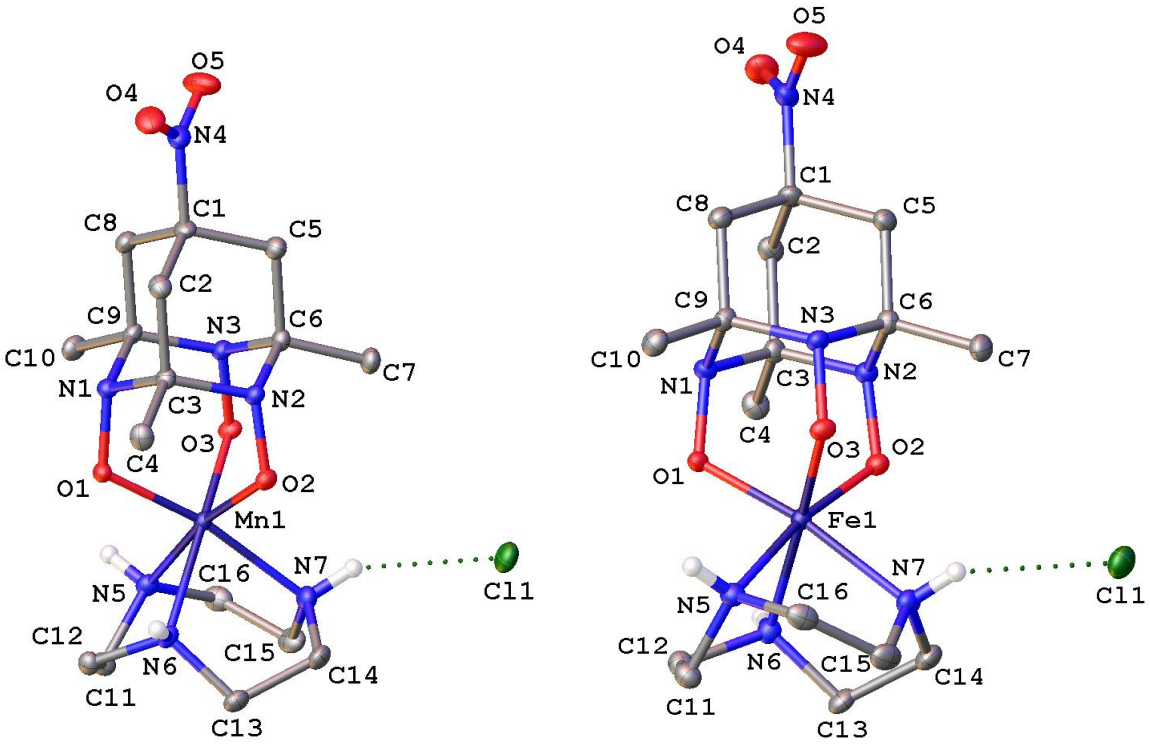


Figure S2. General view of **7-Mn**(Cl) (left) and **7-Fe**(Cl) (right) with atoms shown as thermal ellipsoids (p = 50%). Hydrogen atoms except those of the NH groups are omitted, as well as molecules of lattice methanol.

Table S3. Crystal data and structure refinement parameters for **1a, 6a**(K), **7-Mn**(Cl), **7-Fe**(Cl).

	1a	**6a**(K)	**7-Mn**(Cl)	**7-Fe**(Cl)
Empirical formula	$C_{10.5}H_{18.5}Cl_{1.5}N_4O_5$	$C_{19}H_{32}BKN_4O_8$	$C_{37}H_{81}Cl_2Mn_2N_{14}O_{15}$	$C_{18}H_{38}ClFeN_7O_7$
Formula weight	333.97	494.39	1142.93	555.85
T, K	200	100	100	100
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	C2/c	$P2_1/n$	Pbca	Pbca
Z	16	4	4	8
a, Å	20.5159(18)	8.9221(3)	18.2215(3)	18.2038(5)
b, Å	11.1570(9)	12.6921(4)	13.4869(2)	13.4923(4)
c, Å	25.254(2)	23.3835(6)	21.4452(4)	21.3344(6)
α, °	90	90	90	90
β, °	97.915(5)	97.970(2)	90	90
γ, °	90	90	90	90
V, $Å^3$	5725.6(9)	2622.37(14)	5270.19(15)	5240.0(3)
D_{calc} (g cm^{-1})	1.550	1.252	1.440	1.409
Linear absorption, μ (cm^{-1})	3.88	2.49	6.55	7.27
F(000)	2800	1048	2420	2352
2θmax, °	50	54	63	56
Reflections measured	23107	29325	95823	61871
Independent reflections	5030	5723	8766	6314
Observed reflections [I > 2σ(I)]	3759	4014	5973	4916
Parameters	401	324	348	332
R1	0.1017	0.0523	0.0414	0.0393
wR2	0.2730	0.1417	0.0953	0.0960
GOF	1.114	1.017	1.011	1.040
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e $Å^{-3}$)	1.374/-0.534	0.607/-0.362	0.513/-0.418	0.610/-0.390
CCDC	2162230	2162229	2161787	2162202

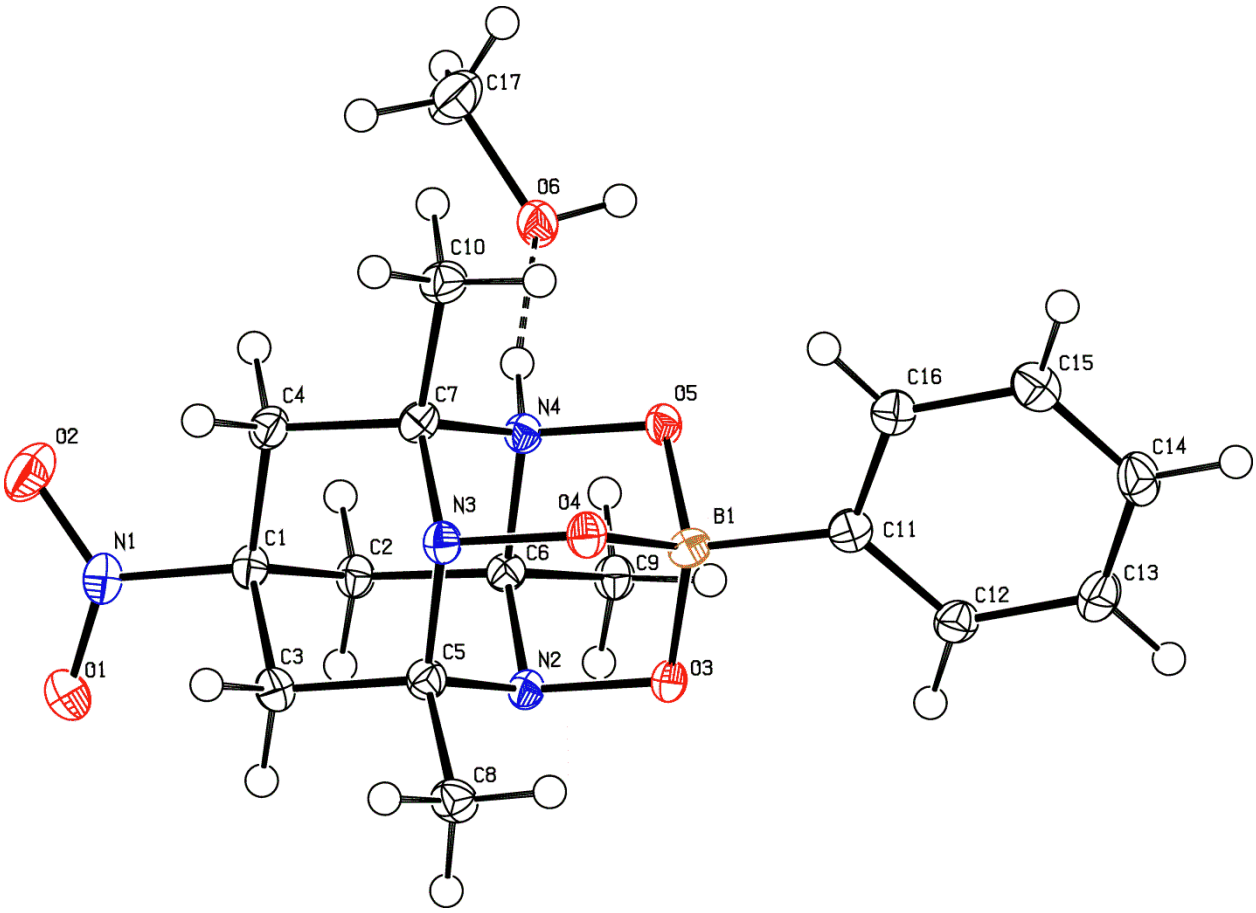


Figure S3. General view of **6a**(H).

Table S4. Crystal data and structure refinement for **6a**(H).

Identification code	CCDC 2423393	
Empirical formula	$C_{17}H_{25}BN_4O_6$	
Formula weight	392.22	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.25318(6) Å	a= 90°.
	b = 10.89893(7) Å	b= 90°.
	c = 16.74915(12) Å	g = 90°.
Volume	1871.70(2) $Å^3$	
Z	4	
Density (calculated)	1.392 g/cm^3	
Absorption coefficient	0.877 mm^{-1}	
F(000)	832	
Crystal size	0.362 x 0.269 x 0.213 mm^3	
Theta range for data collection	4.841 to 80.062°.	
Index ranges	-11<=h<=13, -13<=k<=13, -21<=l<=21	
Reflections collected	16509	
Independent reflections	3925 [R(int) = 0.0306]	
Observed reflections	3871	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.440	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3925 / 0 / 263	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0810	
R indices (all data)	R1 = 0.0308, wR2 = 0.0814	
Absolute structure parameter	0.03(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.221 and -0.211 $e.Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6a**(H). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	152(1)	9200(1)	6811(1)	28(1)
O(2)	1718(2)	10148(1)	7418(1)	29(1)
O(3)	3606(1)	5350(1)	5378(1)	15(1)
O(4)	4680(1)	5218(1)	6676(1)	16(1)
O(5)	5472(1)	6652(1)	5677(1)	14(1)
O(6)	5907(1)	9541(1)	5481(1)	21(1)
N(1)	1288(2)	9296(1)	7024(1)	19(1)
N(2)	2730(1)	6286(1)	5680(1)	14(1)
N(3)	3807(1)	6158(1)	6990(1)	15(1)
N(4)	4612(1)	7561(1)	5980(1)	14(1)
C(1)	2227(2)	8300(2)	6744(1)	16(1)
C(2)	2438(2)	8502(2)	5851(1)	15(1)
C(3)	1618(2)	7041(2)	6879(1)	17(1)
C(4)	3518(2)	8376(2)	7185(1)	17(1)
C(5)	2550(2)	6063(2)	6554(1)	15(1)
C(6)	3323(2)	7496(1)	5523(1)	14(1)
C(7)	4421(2)	7357(2)	6877(1)	15(1)
C(8)	1963(2)	4799(2)	6677(1)	19(1)
C(9)	3591(2)	7678(2)	4640(1)	16(1)
C(10)	5742(2)	7422(2)	7287(1)	20(1)
C(11)	5881(2)	4444(1)	5423(1)	16(1)
C(12)	5620(2)	3847(2)	4701(1)	18(1)
C(13)	6569(2)	3153(2)	4313(1)	22(1)
C(14)	7802(2)	3028(2)	4647(1)	22(1)
C(15)	8087(2)	3608(2)	5365(1)	21(1)
C(16)	7136(2)	4311(2)	5746(1)	18(1)
C(17)	6444(2)	10512(2)	5947(1)	34(1)
B(1)	4863(2)	5380(2)	5810(1)	16(1)

Table S6. Bond lengths [Å] and angles [°] for **6a**(H).

O(1)-N(1)	1.223(2)
O(2)-N(1)	1.221(2)
O(3)-N(2)	1.4506(17)
O(3)-B(1)	1.478(2)
O(4)-N(3)	1.4586(17)
O(4)-B(1)	1.473(2)
O(5)-N(4)	1.4200(17)
O(5)-B(1)	1.536(2)
O(6)-H(6)	0.83(3)
O(6)-C(17)	1.426(2)
N(1)-C(1)	1.525(2)
N(2)-C(5)	1.495(2)
N(2)-C(6)	1.475(2)
N(3)-C(5)	1.484(2)
N(3)-C(7)	1.463(2)
N(4)-H(4)	0.86(3)
N(4)-C(6)	1.529(2)
N(4)-C(7)	1.531(2)
C(1)-C(2)	1.528(2)
C(1)-C(3)	1.524(2)
C(1)-C(4)	1.517(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(6)	1.526(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3)-C(5)	1.532(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(7)	1.535(2)
C(5)-C(8)	1.518(2)
C(6)-C(9)	1.517(2)
C(7)-C(10)	1.520(2)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800

C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.400(2)
C(11)-C(16)	1.403(2)
C(11)-B(1)	1.597(2)
C(12)-H(12)	0.9500
C(12)-C(13)	1.393(3)
C(13)-H(13)	0.9500
C(13)-C(14)	1.390(3)
C(14)-H(14)	0.9500
C(14)-C(15)	1.389(3)
C(15)-H(15)	0.9500
C(15)-C(16)	1.394(3)
C(16)-H(16)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
N(2)-O(3)-B(1)	110.71(11)
N(3)-O(4)-B(1)	110.44(12)
N(4)-O(5)-B(1)	109.00(12)
C(17)-O(6)-H(6)	107(2)
O(1)-N(1)-C(1)	116.81(14)
O(2)-N(1)-O(1)	124.50(15)
O(2)-N(1)-C(1)	118.63(15)
O(3)-N(2)-C(5)	107.64(12)
O(3)-N(2)-C(6)	108.16(12)
C(6)-N(2)-C(5)	111.74(13)
O(4)-N(3)-C(5)	107.84(12)
O(4)-N(3)-C(7)	108.45(12)
C(7)-N(3)-C(5)	111.90(13)
O(5)-N(4)-H(4)	104.1(17)
O(5)-N(4)-C(6)	108.99(11)
O(5)-N(4)-C(7)	109.16(12)
C(6)-N(4)-H(4)	109.4(16)
C(6)-N(4)-C(7)	111.97(12)
C(7)-N(4)-H(4)	112.8(16)
N(1)-C(1)-C(2)	106.75(13)

C(3)-C(1)-N(1)	109.69(13)
C(3)-C(1)-C(2)	109.42(13)
C(4)-C(1)-N(1)	111.27(13)
C(4)-C(1)-C(2)	110.16(14)
C(4)-C(1)-C(3)	109.51(14)
C(1)-C(2)-H(2A)	109.8
C(1)-C(2)-H(2B)	109.8
H(2A)-C(2)-H(2B)	108.2
C(6)-C(2)-C(1)	109.46(13)
C(6)-C(2)-H(2A)	109.8
C(6)-C(2)-H(2B)	109.8
C(1)-C(3)-H(3A)	110.0
C(1)-C(3)-H(3B)	110.0
C(1)-C(3)-C(5)	108.59(13)
H(3A)-C(3)-H(3B)	108.4
C(5)-C(3)-H(3A)	110.0
C(5)-C(3)-H(3B)	110.0
C(1)-C(4)-H(4A)	109.9
C(1)-C(4)-H(4B)	109.9
C(1)-C(4)-C(7)	108.92(13)
H(4A)-C(4)-H(4B)	108.3
C(7)-C(4)-H(4A)	109.9
C(7)-C(4)-H(4B)	109.9
N(2)-C(5)-C(3)	108.15(13)
N(2)-C(5)-C(8)	109.22(14)
N(3)-C(5)-N(2)	111.28(13)
N(3)-C(5)-C(3)	108.56(13)
N(3)-C(5)-C(8)	109.95(13)
C(8)-C(5)-C(3)	109.66(14)
N(2)-C(6)-N(4)	107.99(12)
N(2)-C(6)-C(2)	109.46(13)
N(2)-C(6)-C(9)	111.42(13)
C(2)-C(6)-N(4)	107.48(12)
C(9)-C(6)-N(4)	108.97(13)
C(9)-C(6)-C(2)	111.37(13)
N(3)-C(7)-N(4)	108.13(13)
N(3)-C(7)-C(4)	110.05(13)
N(3)-C(7)-C(10)	111.54(14)
N(4)-C(7)-C(4)	107.51(13)
C(10)-C(7)-N(4)	108.81(13)

C(10)-C(7)-C(4)	110.67(14)
C(5)-C(8)-H(8A)	109.5
C(5)-C(8)-H(8B)	109.5
C(5)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(6)-C(9)-H(9A)	109.5
C(6)-C(9)-H(9B)	109.5
C(6)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	117.38(16)
C(12)-C(11)-B(1)	121.53(15)
C(16)-C(11)-B(1)	120.61(15)
C(11)-C(12)-H(12)	119.2
C(13)-C(12)-C(11)	121.51(16)
C(13)-C(12)-H(12)	119.2
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-C(12)	120.02(17)
C(14)-C(13)-H(13)	120.0
C(13)-C(14)-H(14)	120.2
C(15)-C(14)-C(13)	119.69(16)
C(15)-C(14)-H(14)	120.2
C(14)-C(15)-H(15)	120.0
C(14)-C(15)-C(16)	119.94(17)
C(16)-C(15)-H(15)	120.0
C(11)-C(16)-H(16)	119.3
C(15)-C(16)-C(11)	121.45(17)
C(15)-C(16)-H(16)	119.3
O(6)-C(17)-H(17A)	109.5
O(6)-C(17)-H(17B)	109.5
O(6)-C(17)-H(17C)	109.5

H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(3)-B(1)-O(5)	107.70(13)
O(3)-B(1)-C(11)	110.92(13)
O(4)-B(1)-O(3)	111.55(14)
O(4)-B(1)-O(5)	107.60(13)
O(4)-B(1)-C(11)	113.96(14)
O(5)-B(1)-C(11)	104.63(13)

Table S7. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6a**(H). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	17(1)	30(1)	36(1)	-8(1)	2(1)	4(1)
O(2)	35(1)	22(1)	30(1)	-10(1)	-8(1)	7(1)
O(3)	15(1)	13(1)	17(1)	-2(1)	1(1)	2(1)
O(4)	18(1)	13(1)	17(1)	1(1)	1(1)	3(1)
O(5)	14(1)	12(1)	17(1)	-1(1)	2(1)	2(1)
O(6)	21(1)	17(1)	24(1)	-3(1)	8(1)	-3(1)
N(1)	22(1)	19(1)	16(1)	-1(1)	2(1)	3(1)
N(2)	15(1)	12(1)	15(1)	-2(1)	1(1)	0(1)
N(3)	16(1)	14(1)	16(1)	-1(1)	1(1)	2(1)
N(4)	14(1)	13(1)	15(1)	-1(1)	1(1)	1(1)
C(1)	17(1)	15(1)	15(1)	-2(1)	1(1)	2(1)
C(2)	16(1)	15(1)	15(1)	-1(1)	0(1)	2(1)
C(3)	16(1)	18(1)	16(1)	0(1)	2(1)	0(1)
C(4)	18(1)	17(1)	14(1)	-3(1)	0(1)	1(1)
C(5)	16(1)	15(1)	15(1)	0(1)	1(1)	0(1)
C(6)	14(1)	14(1)	13(1)	0(1)	-1(1)	0(1)
C(7)	18(1)	15(1)	13(1)	-1(1)	-1(1)	0(1)
C(8)	18(1)	17(1)	21(1)	2(1)	2(1)	-3(1)
C(9)	18(1)	17(1)	14(1)	0(1)	1(1)	1(1)
C(10)	18(1)	22(1)	19(1)	-3(1)	-4(1)	0(1)
C(11)	19(1)	12(1)	18(1)	2(1)	1(1)	-1(1)
C(12)	18(1)	14(1)	22(1)	-1(1)	-1(1)	0(1)
C(13)	27(1)	16(1)	22(1)	-4(1)	2(1)	1(1)
C(14)	22(1)	17(1)	28(1)	0(1)	6(1)	5(1)
C(15)	19(1)	18(1)	26(1)	4(1)	1(1)	2(1)
C(16)	20(1)	14(1)	18(1)	2(1)	1(1)	0(1)
C(17)	43(1)	31(1)	29(1)	-12(1)	11(1)	-16(1)
B(1)	17(1)	13(1)	17(1)	-1(1)	-1(1)	-2(1)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **6a**(H).

	x	y	z	U(eq)
H(6)	6450(30)	9380(30)	5131(17)	31
H(4)	5000(20)	8240(20)	5874(14)	21
H(2A)	1588	8485	5570	18
H(2B)	2843	9315	5760	18
H(3A)	769	6990	6600	20
H(3B)	1467	6907	7456	20
H(4A)	3372	8276	7765	20
H(4B)	3924	9188	7093	20
H(8A)	1784	4673	7246	28
H(8B)	2577	4173	6490	28
H(8C)	1148	4735	6374	28
H(9A)	4064	8450	4561	24
H(9B)	2763	7708	4349	24
H(9C)	4119	6994	4441	24
H(10A)	6150	8216	7173	29
H(10B)	6302	6761	7087	29
H(10C)	5627	7330	7865	29
H(12)	4777	3917	4470	22
H(13)	6372	2765	3819	26
H(14)	8447	2547	4387	27
H(15)	8929	3527	5595	25
H(16)	7342	4707	6235	21
H(17A)	5920	10624	6431	51
H(17B)	6438	11272	5634	51
H(17C)	7342	10308	6095	51

Table S9. Torsion angles [°] for **6a**(H).

O(1)-N(1)-C(1)-C(2)	71.67(19)
O(1)-N(1)-C(1)-C(3)	-46.8(2)
O(1)-N(1)-C(1)-C(4)	-168.10(15)
O(2)-N(1)-C(1)-C(2)	-105.85(17)
O(2)-N(1)-C(1)-C(3)	135.70(16)
O(2)-N(1)-C(1)-C(4)	14.4(2)
O(3)-N(2)-C(5)-N(3)	61.25(15)
O(3)-N(2)-C(5)-C(3)	-179.59(12)
O(3)-N(2)-C(5)-C(8)	-60.31(16)
O(3)-N(2)-C(6)-N(4)	-62.00(14)
O(3)-N(2)-C(6)-C(2)	-178.73(12)
O(3)-N(2)-C(6)-C(9)	57.64(16)
O(4)-N(3)-C(5)-N(2)	-61.31(16)
O(4)-N(3)-C(5)-C(3)	179.78(12)
O(4)-N(3)-C(5)-C(8)	59.83(16)
O(4)-N(3)-C(7)-N(4)	61.62(15)
O(4)-N(3)-C(7)-C(4)	178.78(12)
O(4)-N(3)-C(7)-C(10)	-57.99(16)
O(5)-N(4)-C(6)-N(2)	63.28(15)
O(5)-N(4)-C(6)-C(2)	-178.72(12)
O(5)-N(4)-C(6)-C(9)	-57.90(15)
O(5)-N(4)-C(7)-N(3)	-62.70(15)
O(5)-N(4)-C(7)-C(4)	178.51(12)
O(5)-N(4)-C(7)-C(10)	58.61(16)
N(1)-C(1)-C(2)-C(6)	-177.38(13)
N(1)-C(1)-C(3)-C(5)	177.15(13)
N(1)-C(1)-C(4)-C(7)	-179.84(13)
N(2)-O(3)-B(1)-O(4)	57.50(16)
N(2)-O(3)-B(1)-O(5)	-60.37(15)
N(2)-O(3)-B(1)-C(11)	-174.31(12)
N(3)-O(4)-B(1)-O(3)	-57.28(16)
N(3)-O(4)-B(1)-O(5)	60.65(16)
N(3)-O(4)-B(1)-C(11)	176.17(12)
N(4)-O(5)-B(1)-O(3)	60.03(15)
N(4)-O(5)-B(1)-O(4)	-60.36(16)
N(4)-O(5)-B(1)-C(11)	178.10(12)
C(1)-C(2)-C(6)-N(2)	57.90(17)

C(1)-C(2)-C(6)-N(4)	-59.14(16)
C(1)-C(2)-C(6)-C(9)	-178.44(14)
C(1)-C(3)-C(5)-N(2)	-60.68(17)
C(1)-C(3)-C(5)-N(3)	60.18(17)
C(1)-C(3)-C(5)-C(8)	-179.69(14)
C(1)-C(4)-C(7)-N(3)	-57.86(17)
C(1)-C(4)-C(7)-N(4)	59.69(16)
C(1)-C(4)-C(7)-C(10)	178.40(14)
C(2)-C(1)-C(3)-C(5)	60.37(17)
C(2)-C(1)-C(4)-C(7)	-61.66(17)
C(3)-C(1)-C(2)-C(6)	-58.76(17)
C(3)-C(1)-C(4)-C(7)	58.73(17)
C(4)-C(1)-C(2)-C(6)	61.69(17)
C(4)-C(1)-C(3)-C(5)	-60.47(17)
C(5)-N(2)-C(6)-N(4)	56.29(16)
C(5)-N(2)-C(6)-C(2)	-60.43(16)
C(5)-N(2)-C(6)-C(9)	175.94(13)
C(5)-N(3)-C(7)-N(4)	-57.21(16)
C(5)-N(3)-C(7)-C(4)	59.95(16)
C(5)-N(3)-C(7)-C(10)	-176.81(14)
C(6)-N(2)-C(5)-N(3)	-57.36(17)
C(6)-N(2)-C(5)-C(3)	61.80(16)
C(6)-N(2)-C(5)-C(8)	-178.92(13)
C(6)-N(4)-C(7)-N(3)	58.07(16)
C(6)-N(4)-C(7)-C(4)	-60.72(16)
C(6)-N(4)-C(7)-C(10)	179.39(13)
C(7)-N(3)-C(5)-N(2)	57.87(17)
C(7)-N(3)-C(5)-C(3)	-61.04(16)
C(7)-N(3)-C(5)-C(8)	179.01(14)
C(7)-N(4)-C(6)-N(2)	-57.60(15)
C(7)-N(4)-C(6)-C(2)	60.41(16)
C(7)-N(4)-C(6)-C(9)	-178.77(13)
C(11)-C(12)-C(13)-C(14)	0.8(3)
C(12)-C(11)-C(16)-C(15)	-0.2(2)
C(12)-C(11)-B(1)-O(3)	9.0(2)
C(12)-C(11)-B(1)-O(4)	135.83(16)
C(12)-C(11)-B(1)-O(5)	-106.91(17)
C(12)-C(13)-C(14)-C(15)	-0.7(3)
C(13)-C(14)-C(15)-C(16)	0.1(3)
C(14)-C(15)-C(16)-C(11)	0.3(3)

C(16)-C(11)-C(12)-C(13)	-0.4(2)
C(16)-C(11)-B(1)-O(3)	-179.13(14)
C(16)-C(11)-B(1)-O(4)	-52.2(2)
C(16)-C(11)-B(1)-O(5)	65.01(19)
B(1)-O(3)-N(2)-C(5)	-57.83(15)
B(1)-O(3)-N(2)-C(6)	63.05(15)
B(1)-O(4)-N(3)-C(5)	58.06(15)
B(1)-O(4)-N(3)-C(7)	-63.29(15)
B(1)-O(5)-N(4)-C(6)	-61.48(15)
B(1)-O(5)-N(4)-C(7)	61.10(15)
B(1)-C(11)-C(12)-C(13)	171.79(16)
B(1)-C(11)-C(16)-C(15)	-172.44(16)

Table S10. Hydrogen bonds for **6a**(H) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(6)-H(6)...O(3)#1	0.83(3)	2.39(3)	3.1219(18)	148(3)
O(6)-H(6)...N(2)#1	0.83(3)	2.03(3)	2.8440(19)	171(3)
N(4)-H(4)...O(6)	0.86(3)	1.82(3)	2.6680(19)	169(2)

Symmetry transformations used to generate equivalent atoms:

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

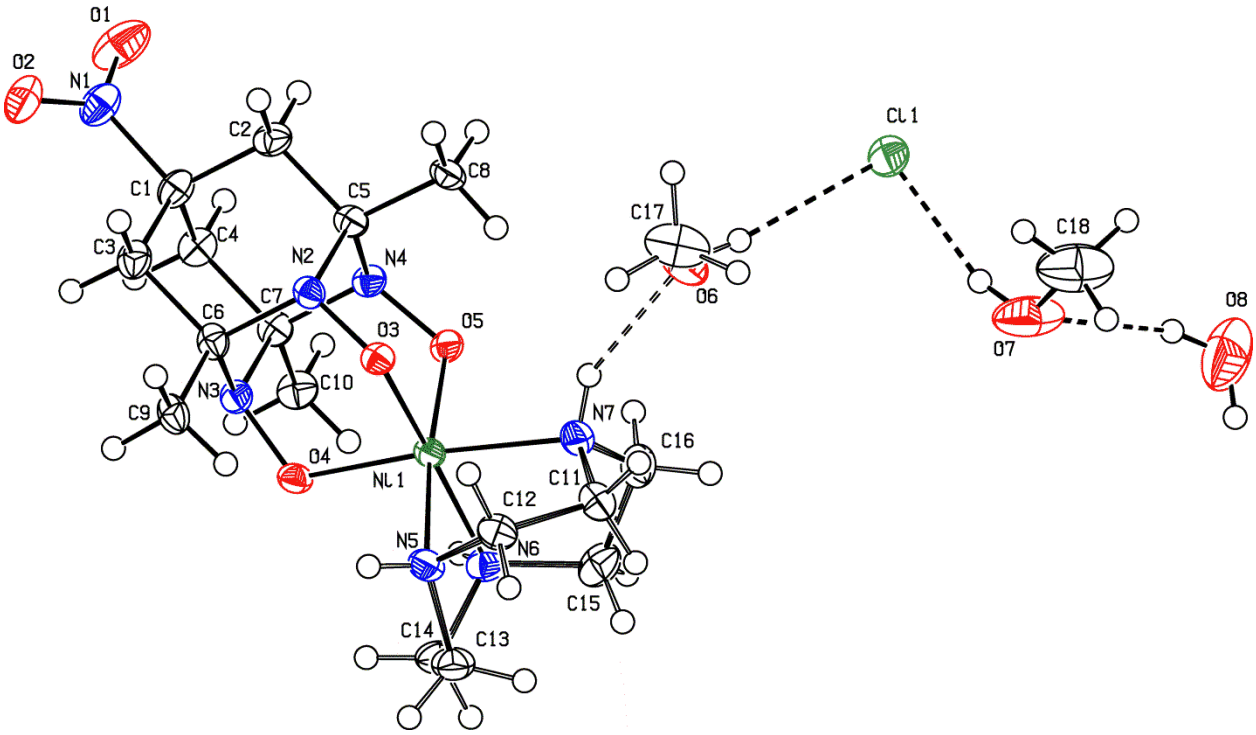


Figure S4. General view of **7-Ni**(Cl).

Table S11. Crystal data and structure refinement for **7-Ni**(Cl).

Identification code	CCDC 242394	
Empirical formula	$C_{36}H_{78}Cl_2N_{14}Ni_2O_{15}$	
Formula weight	1135.44	
Temperature	99.97(12) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 18.30780(10) Å	a= 90°.
	b = 13.51830(10) Å	b= 90°.
	c = 21.2684(2) Å	g = 90°.
Volume	5263.72(7) $Å^3$	
Z	4	
Density (calculated)	1.433 g/cm^3	
Absorption coefficient	2.452 mm^{-1}	
F(000)	2408	
Crystal size	0.261 x 0.248 x 0.134 mm^3	
Theta range for data collection	4.157 to 79.949°.	
Index ranges	-23<=h<=18, -17<=k<=16, -27<=l<=27	
Reflections collected	43580	
Independent reflections	5694 [R(int) = 0.0333]	
Observed reflections	5567	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.486	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5694 / 50 / 413	
Goodness-of-fit on F^2	1.159	
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1815	
R indices (all data)	R1 = 0.0648, wR2 = 0.1818	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.697 and -0.535 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7-Ni**(Cl). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(6)	3808(2)	4714(2)	8324(2)	42(1)
N(5)	1098(2)	6007(2)	8172(1)	24(1)
N(6)	913(2)	4278(2)	7526(2)	27(1)
N(7)	2225(2)	4696(2)	8081(2)	24(1)
C(11)	2048(2)	5070(3)	8722(2)	26(1)
C(12)	1662(2)	6069(3)	8674(2)	26(1)
C(13)	459(2)	5392(3)	8346(2)	29(1)
C(14)	247(2)	4756(3)	7791(2)	32(1)
C(15)	1230(2)	3499(3)	7937(2)	32(1)
C(16)	2052(2)	3634(3)	7982(2)	30(1)
C(17)	4095(3)	5474(4)	8709(3)	51(1)
C(18)	5100(3)	2672(6)	10201(3)	67(2)
Ni(1)	1627(1)	5430(1)	7408(1)	17(1)
O(1)	3051(2)	7090(3)	4494(2)	47(1)
O(2)	2648(2)	8495(2)	4815(1)	36(1)
O(3)	2263(1)	6561(2)	7387(1)	18(1)
O(4)	988(1)	6033(2)	6798(1)	20(1)
O(5)	2173(1)	4802(2)	6748(1)	20(1)
N(1)	2735(2)	7603(2)	4875(2)	29(1)
N(2)	2428(2)	6916(2)	6817(1)	18(1)
N(3)	1314(2)	6455(2)	6298(1)	19(1)
N(4)	2352(2)	5376(2)	6253(1)	19(1)
C(1)	2456(2)	7106(3)	5476(2)	24(1)
C(2)	3116(2)	6723(3)	5832(2)	23(1)
C(3)	2036(2)	7838(3)	5874(2)	24(1)
C(4)	1964(2)	6241(3)	5294(2)	24(1)
C(5)	2857(2)	6203(2)	6432(2)	19(1)
C(6)	1778(2)	7318(2)	6475(2)	20(1)
C(7)	1704(2)	5730(2)	5893(2)	21(1)
C(8)	3503(2)	5818(3)	6799(2)	23(1)
C(9)	1350(2)	8025(3)	6880(2)	24(1)
C(10)	1200(2)	4871(3)	5731(2)	25(1)
Ni(1A)	1514(7)	5368(9)	7052(8)	17(1)

O(1A)	2640(50)	7210(40)	4130(20)	47(1)
O(2A)	2660(50)	8620(30)	4590(30)	36(1)
O(3A)	2160(20)	6480(20)	7100(20)	18(1)
O(4A)	911(18)	6040(30)	6450(18)	20(1)
O(5A)	2080(20)	4770(30)	6405(18)	20(1)
N(1A)	2510(50)	7740(30)	4580(20)	29(1)
N(2A)	2320(20)	6920(30)	6550(20)	18(1)
N(3A)	1210(20)	6590(30)	5990(20)	19(1)
N(4A)	2200(20)	5440(30)	5940(20)	19(1)
C(1A)	2310(30)	7240(40)	5200(20)	24(1)
C(2A)	2960(30)	6760(60)	5530(30)	23(1)
C(3A)	1850(50)	7910(50)	5610(30)	24(1)
C(4A)	1770(40)	6420(50)	5020(30)	24(1)
C(5A)	2730(20)	6240(40)	6130(30)	19(1)
C(6A)	1680(30)	7400(30)	6240(30)	20(1)
C(7A)	1560(30)	5820(40)	5590(20)	21(1)
C(8A)	3370(30)	5780(60)	6460(30)	23(1)
C(9A)	1280(40)	8090(60)	6670(30)	24(1)
C(10A)	1000(40)	5030(50)	5400(30)	25(1)
Cl(1)	4945(1)	2956(1)	8453(1)	30(1)
Cl(1A)	4759(9)	3007(10)	8775(11)	30(1)
Cl(1B)	4630(20)	3050(30)	9140(20)	30(1)
O(7)	4498(3)	2381(6)	9804(2)	62(2)
O(7A)	4815(11)	1864(17)	9822(8)	62(2)
O(8)	4599(5)	139(7)	10092(4)	72(3)

Table S13. Bond lengths [Å] and angles [°] for**7-Ni**(Cl).

O(6)-H(6A)	0.8400
O(6)-C(17)	1.416(6)
N(5)-C(12)	1.487(5)
N(5)-C(13)	1.482(5)
N(5)-Ni(1)	2.046(3)
N(5)-H(5)	0.86(5)
N(6)-H(6)	0.92(5)
N(6)-C(14)	1.492(5)
N(6)-C(15)	1.486(5)
N(6)-Ni(1)	2.049(3)
N(6)-Ni(1A)	2.096(13)
N(7)-C(11)	1.490(5)
N(7)-C(16)	1.485(5)
N(7)-H(7)	0.86(7)
N(7)-Ni(1)	2.057(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(11)-C(12)	1.528(5)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(13)-C(14)	1.511(6)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(15)-C(16)	1.518(6)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(18)-H(18D)	0.9800

C(18)-H(18E)	0.9800
C(18)-H(18F)	0.9800
C(18)-O(7)	1.442(7)
C(18)-O(7A)	1.454(15)
Ni(1)-O(3)	1.922(2)
Ni(1)-O(4)	1.927(3)
Ni(1)-O(5)	1.920(3)
O(1)-N(1)	1.214(5)
O(2)-N(1)	1.223(5)
O(3)-N(2)	1.339(4)
O(4)-N(3)	1.347(4)
O(5)-N(4)	1.350(4)
N(1)-C(1)	1.532(5)
N(2)-C(5)	1.490(4)
N(2)-C(6)	1.497(5)
N(3)-C(6)	1.492(4)
N(3)-C(7)	1.488(4)
N(4)-C(5)	1.500(4)
N(4)-C(7)	1.490(5)
C(1)-C(2)	1.518(5)
C(1)-C(3)	1.513(5)
C(1)-C(4)	1.526(5)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(5)	1.532(5)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3)-C(6)	1.533(5)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(7)	1.525(5)
C(5)-C(8)	1.508(5)
C(6)-C(9)	1.505(5)
C(7)-C(10)	1.523(5)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800

C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
Ni(1A)-O(3A)	1.919(19)
Ni(1A)-O(4A)	1.919(19)
Ni(1A)-O(5A)	1.903(19)
O(1A)-N(1A)	1.21(2)
O(2A)-N(1A)	1.22(2)
O(3A)-N(2A)	1.34(2)
O(4A)-N(3A)	1.35(2)
O(5A)-N(4A)	1.35(2)
N(1A)-C(1A)	1.54(2)
N(2A)-C(5A)	1.49(2)
N(2A)-C(6A)	1.50(2)
N(3A)-C(6A)	1.49(2)
N(3A)-C(7A)	1.49(2)
N(4A)-C(5A)	1.50(2)
N(4A)-C(7A)	1.49(2)
C(1A)-C(2A)	1.52(2)
C(1A)-C(3A)	1.51(2)
C(1A)-C(4A)	1.53(2)
C(2A)-H(2C)	0.9900
C(2A)-H(2D)	0.9900
C(2A)-C(5A)	1.53(2)
C(3A)-H(3C)	0.9900
C(3A)-H(3D)	0.9900
C(3A)-C(6A)	1.53(2)
C(4A)-H(4C)	0.9900
C(4A)-H(4D)	0.9900
C(4A)-C(7A)	1.52(2)
C(5A)-C(8A)	1.50(2)
C(6A)-C(9A)	1.50(2)
C(7A)-C(10A)	1.53(2)
C(8A)-H(8D)	0.9800
C(8A)-H(8E)	0.9800
C(8A)-H(8F)	0.9800
C(9A)-H(9D)	0.9800
C(9A)-H(9E)	0.9800
C(9A)-H(9F)	0.9800
C(10A)-H(10D)	0.9800

C(10A)-H(10E)	0.9800
C(10A)-H(10F)	0.9800
O(7)-H(7A)	0.8400
O(7A)-H(7B)	0.8400
O(8)-H(1)	0.8695
O(8)-H(2)	0.8696
C(17)-O(6)-H(6A)	109.5
C(12)-N(5)-Ni(1)	105.2(2)
C(12)-N(5)-H(5)	105(3)
C(13)-N(5)-C(12)	113.6(3)
C(13)-N(5)-Ni(1)	111.0(2)
C(13)-N(5)-H(5)	112(3)
Ni(1)-N(5)-H(5)	110(3)
C(14)-N(6)-H(6)	105(3)
C(14)-N(6)-Ni(1)	103.8(2)
C(14)-N(6)-Ni(1A)	107.8(4)
C(15)-N(6)-H(6)	116(3)
C(15)-N(6)-C(14)	113.8(3)
C(15)-N(6)-Ni(1)	111.2(2)
C(15)-N(6)-Ni(1A)	125.2(5)
Ni(1)-N(6)-H(6)	106(3)
Ni(1A)-N(6)-H(6)	84(3)
C(11)-N(7)-H(7)	112(4)
C(11)-N(7)-Ni(1)	110.9(2)
C(16)-N(7)-C(11)	114.3(3)
C(16)-N(7)-H(7)	106(4)
C(16)-N(7)-Ni(1)	104.8(2)
Ni(1)-N(7)-H(7)	108(4)
N(7)-C(11)-H(11A)	109.7
N(7)-C(11)-H(11B)	109.7
N(7)-C(11)-C(12)	109.8(3)
H(11A)-C(11)-H(11B)	108.2
C(12)-C(11)-H(11A)	109.7
C(12)-C(11)-H(11B)	109.7
N(5)-C(12)-C(11)	108.6(3)
N(5)-C(12)-H(12A)	110.0
N(5)-C(12)-H(12B)	110.0
C(11)-C(12)-H(12A)	110.0
C(11)-C(12)-H(12B)	110.0
H(12A)-C(12)-H(12B)	108.3

N(5)-C(13)-H(13A)	109.9
N(5)-C(13)-H(13B)	109.9
N(5)-C(13)-C(14)	109.1(3)
H(13A)-C(13)-H(13B)	108.3
C(14)-C(13)-H(13A)	109.9
C(14)-C(13)-H(13B)	109.9
N(6)-C(14)-C(13)	109.4(3)
N(6)-C(14)-H(14A)	109.8
N(6)-C(14)-H(14B)	109.8
C(13)-C(14)-H(14A)	109.8
C(13)-C(14)-H(14B)	109.8
H(14A)-C(14)-H(14B)	108.2
N(6)-C(15)-H(15A)	109.7
N(6)-C(15)-H(15B)	109.7
N(6)-C(15)-C(16)	109.9(3)
H(15A)-C(15)-H(15B)	108.2
C(16)-C(15)-H(15A)	109.7
C(16)-C(15)-H(15B)	109.7
N(7)-C(16)-C(15)	109.7(3)
N(7)-C(16)-H(16A)	109.7
N(7)-C(16)-H(16B)	109.7
C(15)-C(16)-H(16A)	109.7
C(15)-C(16)-H(16B)	109.7
H(16A)-C(16)-H(16B)	108.2
O(6)-C(17)-H(17A)	109.5
O(6)-C(17)-H(17B)	109.5
O(6)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
H(18D)-C(18)-H(18E)	109.5
H(18D)-C(18)-H(18F)	109.5
H(18E)-C(18)-H(18F)	109.5
O(7)-C(18)-H(18A)	109.5
O(7)-C(18)-H(18B)	109.5
O(7)-C(18)-H(18C)	109.5
O(7A)-C(18)-H(18D)	109.5

O(7A)-C(18)-H(18E)	109.5
O(7A)-C(18)-H(18F)	109.5
N(5)-Ni(1)-N(6)	83.74(13)
N(5)-Ni(1)-N(7)	83.32(13)
N(6)-Ni(1)-N(7)	83.55(13)
O(3)-Ni(1)-N(5)	90.12(11)
O(3)-Ni(1)-N(6)	173.71(12)
O(3)-Ni(1)-N(7)	94.44(12)
O(3)-Ni(1)-O(4)	90.93(10)
O(4)-Ni(1)-N(5)	94.93(11)
O(4)-Ni(1)-N(6)	90.93(12)
O(4)-Ni(1)-N(7)	174.35(12)
O(5)-Ni(1)-N(5)	174.28(12)
O(5)-Ni(1)-N(6)	94.85(12)
O(5)-Ni(1)-N(7)	91.02(12)
O(5)-Ni(1)-O(3)	91.13(10)
O(5)-Ni(1)-O(4)	90.63(11)
N(2)-O(3)-Ni(1)	116.25(19)
N(3)-O(4)-Ni(1)	116.24(19)
N(4)-O(5)-Ni(1)	116.28(19)
O(1)-N(1)-O(2)	123.8(4)
O(1)-N(1)-C(1)	117.8(3)
O(2)-N(1)-C(1)	118.4(3)
O(3)-N(2)-C(5)	112.6(3)
O(3)-N(2)-C(6)	113.0(3)
C(5)-N(2)-C(6)	112.8(3)
O(4)-N(3)-C(6)	112.6(3)
O(4)-N(3)-C(7)	113.0(3)
C(7)-N(3)-C(6)	112.8(3)
O(5)-N(4)-C(5)	112.3(3)
O(5)-N(4)-C(7)	113.1(3)
C(7)-N(4)-C(5)	112.5(3)
C(2)-C(1)-N(1)	107.5(3)
C(2)-C(1)-C(4)	109.5(3)
C(3)-C(1)-N(1)	110.5(3)
C(3)-C(1)-C(2)	110.4(3)
C(3)-C(1)-C(4)	110.1(3)
C(4)-C(1)-N(1)	108.8(3)
C(1)-C(2)-H(2A)	109.9
C(1)-C(2)-H(2B)	109.9

C(1)-C(2)-C(5)	109.0(3)
H(2A)-C(2)-H(2B)	108.3
C(5)-C(2)-H(2A)	109.9
C(5)-C(2)-H(2B)	109.9
C(1)-C(3)-H(3A)	109.9
C(1)-C(3)-H(3B)	109.9
C(1)-C(3)-C(6)	108.9(3)
H(3A)-C(3)-H(3B)	108.3
C(6)-C(3)-H(3A)	109.9
C(6)-C(3)-H(3B)	109.9
C(1)-C(4)-H(4A)	110.0
C(1)-C(4)-H(4B)	110.0
H(4A)-C(4)-H(4B)	108.3
C(7)-C(4)-C(1)	108.6(3)
C(7)-C(4)-H(4A)	110.0
C(7)-C(4)-H(4B)	110.0
N(2)-C(5)-N(4)	107.2(3)
N(2)-C(5)-C(2)	108.9(3)
N(2)-C(5)-C(8)	110.6(3)
N(4)-C(5)-C(2)	108.7(3)
N(4)-C(5)-C(8)	111.0(3)
C(8)-C(5)-C(2)	110.3(3)
N(2)-C(6)-C(3)	109.1(3)
N(2)-C(6)-C(9)	111.5(3)
N(3)-C(6)-N(2)	107.0(3)
N(3)-C(6)-C(3)	108.8(3)
N(3)-C(6)-C(9)	110.2(3)
C(9)-C(6)-C(3)	110.2(3)
N(3)-C(7)-N(4)	107.2(3)
N(3)-C(7)-C(4)	109.6(3)
N(3)-C(7)-C(10)	110.0(3)
N(4)-C(7)-C(4)	109.0(3)
N(4)-C(7)-C(10)	110.7(3)
C(10)-C(7)-C(4)	110.2(3)
C(5)-C(8)-H(8A)	109.5
C(5)-C(8)-H(8B)	109.5
C(5)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5

C(6)-C(9)-H(9A)	109.5
C(6)-C(9)-H(9B)	109.5
C(6)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(3A)-Ni(1A)-N(6)	148.2(15)
O(4A)-Ni(1A)-N(6)	110.6(14)
O(4A)-Ni(1A)-O(3A)	91.1(11)
O(5A)-Ni(1A)-N(6)	109.7(13)
O(5A)-Ni(1A)-O(3A)	91.9(11)
O(5A)-Ni(1A)-O(4A)	91.8(11)
N(2A)-O(3A)-Ni(1A)	116(3)
N(3A)-O(4A)-Ni(1A)	121(3)
N(4A)-O(5A)-Ni(1A)	110(3)
O(1A)-N(1A)-O(2A)	124(3)
O(1A)-N(1A)-C(1A)	117(2)
O(2A)-N(1A)-C(1A)	117(2)
O(3A)-N(2A)-C(5A)	111(4)
O(3A)-N(2A)-C(6A)	114(4)
C(5A)-N(2A)-C(6A)	113(4)
O(4A)-N(3A)-C(6A)	113(4)
O(4A)-N(3A)-C(7A)	101(4)
C(7A)-N(3A)-C(6A)	118(3)
O(5A)-N(4A)-C(5A)	113(4)
O(5A)-N(4A)-C(7A)	118(4)
C(7A)-N(4A)-C(5A)	113(3)
C(2A)-C(1A)-N(1A)	113(5)
C(2A)-C(1A)-C(4A)	108(6)
C(3A)-C(1A)-N(1A)	112(4)
C(3A)-C(1A)-C(2A)	115(6)
C(3A)-C(1A)-C(4A)	103(6)
C(4A)-C(1A)-N(1A)	105(4)
C(1A)-C(2A)-H(2C)	109.3

C(1A)-C(2A)-H(2D)	109.3
C(1A)-C(2A)-C(5A)	112(5)
H(2C)-C(2A)-H(2D)	108.0
C(5A)-C(2A)-H(2C)	109.3
C(5A)-C(2A)-H(2D)	109.3
C(1A)-C(3A)-H(3C)	109.7
C(1A)-C(3A)-H(3D)	109.7
C(1A)-C(3A)-C(6A)	110(5)
H(3C)-C(3A)-H(3D)	108.2
C(6A)-C(3A)-H(3C)	109.7
C(6A)-C(3A)-H(3D)	109.7
C(1A)-C(4A)-H(4C)	109.6
C(1A)-C(4A)-H(4D)	109.6
H(4C)-C(4A)-H(4D)	108.1
C(7A)-C(4A)-C(1A)	110(5)
C(7A)-C(4A)-H(4C)	109.6
C(7A)-C(4A)-H(4D)	109.6
N(2A)-C(5A)-N(4A)	106.7(18)
N(2A)-C(5A)-C(2A)	111(5)
N(2A)-C(5A)-C(8A)	112(5)
N(4A)-C(5A)-C(2A)	106(5)
C(8A)-C(5A)-N(4A)	109(5)
C(8A)-C(5A)-C(2A)	111(2)
N(2A)-C(6A)-C(3A)	115(6)
N(2A)-C(6A)-C(9A)	112(4)
N(3A)-C(6A)-N(2A)	107.1(19)
N(3A)-C(6A)-C(3A)	98(5)
N(3A)-C(6A)-C(9A)	113(4)
C(9A)-C(6A)-C(3A)	111(2)
N(3A)-C(7A)-C(4A)	101(5)
N(3A)-C(7A)-C(10A)	110(5)
N(4A)-C(7A)-N(3A)	107.3(19)
N(4A)-C(7A)-C(4A)	113(5)
N(4A)-C(7A)-C(10A)	115(5)
C(4A)-C(7A)-C(10A)	110(2)
C(5A)-C(8A)-H(8D)	109.5
C(5A)-C(8A)-H(8E)	109.5
C(5A)-C(8A)-H(8F)	109.5
H(8D)-C(8A)-H(8E)	109.5
H(8D)-C(8A)-H(8F)	109.5

H(8E)-C(8A)-H(8F)	109.5
C(6A)-C(9A)-H(9D)	109.5
C(6A)-C(9A)-H(9E)	109.5
C(6A)-C(9A)-H(9F)	109.5
H(9D)-C(9A)-H(9E)	109.5
H(9D)-C(9A)-H(9F)	109.5
H(9E)-C(9A)-H(9F)	109.5
C(7A)-C(10A)-H(10D)	109.5
C(7A)-C(10A)-H(10E)	109.5
C(7A)-C(10A)-H(10F)	109.5
H(10D)-C(10A)-H(10E)	109.5
H(10D)-C(10A)-H(10F)	109.5
H(10E)-C(10A)-H(10F)	109.5
C(18)-O(7)-H(7A)	109.5
C(18)-O(7A)-H(7B)	109.5
H(1)-O(8)-H(2)	109.4

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7-Ni**(Cl). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(6)	26(1)	41(2)	59(2)	-4(2)	-4(1)	6(1)
N(5)	18(1)	23(1)	31(2)	1(1)	4(1)	2(1)
N(6)	27(2)	22(2)	33(2)	0(1)	3(1)	-8(1)
N(7)	22(1)	20(1)	30(2)	2(1)	2(1)	4(1)
C(11)	24(2)	26(2)	30(2)	0(1)	-2(1)	3(1)
C(12)	24(2)	27(2)	27(2)	-3(1)	2(1)	2(1)
C(13)	22(2)	29(2)	37(2)	1(2)	6(2)	-4(1)
C(14)	21(2)	41(2)	36(2)	0(2)	3(2)	-8(2)
C(15)	42(2)	19(2)	36(2)	2(2)	4(2)	-7(2)
C(16)	39(2)	18(2)	34(2)	2(1)	6(2)	8(2)
C(17)	35(2)	63(3)	56(3)	-17(2)	8(2)	-5(2)
C(18)	49(3)	101(5)	52(3)	-19(3)	7(2)	-22(3)
Ni(1)	15(1)	13(1)	24(1)	-1(1)	1(1)	0(1)
O(1)	71(2)	38(2)	33(2)	-4(1)	20(2)	-12(2)
O(2)	44(2)	30(2)	33(2)	12(1)	-3(2)	-6(1)
O(3)	17(1)	15(1)	22(1)	-2(1)	0(1)	-3(1)
O(4)	14(1)	22(1)	24(1)	0(1)	1(1)	-2(1)
O(5)	23(1)	12(1)	25(1)	1(1)	5(1)	0(1)
N(1)	35(2)	27(2)	25(2)	3(1)	-2(1)	-10(1)
N(2)	18(1)	14(1)	23(1)	-1(1)	0(1)	1(1)
N(3)	19(1)	17(1)	23(1)	1(1)	-1(1)	-2(1)
N(4)	21(1)	14(1)	23(1)	-1(1)	3(1)	-2(1)
C(1)	30(2)	19(2)	24(2)	2(1)	0(2)	-6(1)
C(2)	24(2)	19(2)	27(2)	-1(1)	4(1)	-4(1)
C(3)	26(2)	18(2)	27(2)	2(1)	-2(2)	-2(1)
C(4)	28(2)	23(2)	22(2)	-2(1)	-1(1)	-4(2)
C(5)	17(2)	14(2)	26(2)	-2(1)	1(1)	-2(1)
C(6)	21(2)	14(2)	26(2)	0(1)	-3(1)	-1(1)
C(7)	21(2)	15(2)	25(2)	-2(1)	-1(1)	-3(1)
C(8)	16(2)	21(2)	32(2)	0(2)	3(1)	3(1)
C(9)	23(2)	15(2)	33(2)	0(2)	-5(2)	2(1)
C(10)	27(2)	19(2)	29(2)	-4(1)	0(2)	-6(1)

Ni(1A)	15(1)	13(1)	24(1)	-1(1)	1(1)	0(1)
O(1A)	71(2)	38(2)	33(2)	-4(1)	20(2)	-12(2)
O(2A)	44(2)	30(2)	33(2)	12(1)	-3(2)	-6(1)
O(3A)	17(1)	15(1)	22(1)	-2(1)	0(1)	-3(1)
O(4A)	14(1)	22(1)	24(1)	0(1)	1(1)	-2(1)
O(5A)	23(1)	12(1)	25(1)	1(1)	5(1)	0(1)
N(1A)	35(2)	27(2)	25(2)	3(1)	-2(1)	-10(1)
N(2A)	18(1)	14(1)	23(1)	-1(1)	0(1)	1(1)
N(3A)	19(1)	17(1)	23(1)	1(1)	-1(1)	-2(1)
N(4A)	21(1)	14(1)	23(1)	-1(1)	3(1)	-2(1)
C(1A)	30(2)	19(2)	24(2)	2(1)	0(2)	-6(1)
C(2A)	24(2)	19(2)	27(2)	-1(1)	4(1)	-4(1)
C(3A)	26(2)	18(2)	27(2)	2(1)	-2(2)	-2(1)
C(4A)	28(2)	23(2)	22(2)	-2(1)	-1(1)	-4(2)
C(5A)	17(2)	14(2)	26(2)	-2(1)	1(1)	-2(1)
C(6A)	21(2)	14(2)	26(2)	0(1)	-3(1)	-1(1)
C(7A)	21(2)	15(2)	25(2)	-2(1)	-1(1)	-3(1)
C(8A)	16(2)	21(2)	32(2)	0(2)	3(1)	3(1)
C(9A)	23(2)	15(2)	33(2)	0(2)	-5(2)	2(1)
C(10A)	27(2)	19(2)	29(2)	-4(1)	0(2)	-6(1)
Cl(1)	28(1)	23(1)	40(1)	3(1)	-2(1)	-7(1)
Cl(1A)	28(1)	23(1)	40(1)	3(1)	-2(1)	-7(1)
Cl(1B)	28(1)	23(1)	40(1)	3(1)	-2(1)	-7(1)
O(7)	34(3)	109(5)	42(2)	-4(3)	4(2)	-23(3)
O(7A)	34(3)	109(5)	42(2)	-4(3)	4(2)	-23(3)
O(8)	88(6)	71(6)	58(5)	25(4)	-27(5)	-16(5)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7-Ni**(Cl).

	x	y	z	U(eq)
H(6A)	4066	4203	8360	63
H(6)	780(30)	4080(40)	7130(20)	33
H(11A)	2503	5143	8969	32
H(11B)	1729	4590	8941	32
H(12A)	1430	6236	9080	31
H(12B)	2020	6594	8571	31
H(13A)	45	5823	8466	35
H(13B)	583	4967	8710	35
H(14A)	-105	4242	7927	39
H(14B)	9	5169	7465	39
H(15A)	1119	2838	7761	39
H(15B)	1011	3542	8361	39
H(16A)	2245	3239	8337	36
H(16B)	2287	3398	7591	36
H(17A)	4570	5685	8543	77
H(17B)	4157	5225	9139	77
H(17C)	3758	6037	8712	77
H(7)	2680(40)	4760(50)	7990(30)	61
H(18A)	5259	3340	10085	101
H(18B)	5506	2208	10144	101
H(18C)	4943	2666	10641	101
H(18D)	4693	3045	10384	101
H(18E)	5393	3112	9935	101
H(18F)	5406	2404	10538	101
H(2A)	3444	7279	5942	28
H(2B)	3392	6252	5566	28
H(3A)	1610	8090	5637	28
H(3B)	2353	8406	5984	28
H(4A)	1540	6483	5051	29
H(4B)	2239	5767	5029	29
H(8A)	3332	5523	7193	34
H(8B)	3837	6365	6892	34

H(8C)	3759	5316	6550	34
H(9A)	911	8238	6654	35
H(9B)	1653	8603	6977	35
H(9C)	1209	7694	7271	35
H(10A)	1460	4399	5462	38
H(10B)	770	5121	5508	38
H(10C)	1046	4540	6119	38
H(2C)	3328	7271	5627	28
H(2D)	3187	6273	5240	28
H(3C)	1391	8080	5394	28
H(3D)	2121	8537	5693	28
H(4C)	1331	6724	4829	29
H(4D)	2001	5988	4700	29
H(8D)	3222	5519	6869	34
H(8E)	3754	6280	6519	34
H(8F)	3567	5238	6201	34
H(9D)	1187	7760	7073	35
H(9E)	808	8275	6479	35
H(9F)	1568	8688	6741	35
H(10D)	743	4794	5779	38
H(10E)	1251	4474	5201	38
H(10F)	647	5316	5109	38
H(5)	980(30)	6610(40)	8100(20)	36
H(7A)	4547	2638	9448	93
H(7B)	4652	1419	10059	93
H(1)	4253	114	10371	108
H(2)	4643	743	9955	108

Table S16. Torsion angles [°] for **7-Ni**(Cl).

N(5)-C(13)-C(14)-N(6)	47.2(4)
N(6)-C(15)-C(16)-N(7)	44.5(4)
N(7)-C(11)-C(12)-N(5)	44.7(4)
C(11)-N(7)-C(16)-C(15)	72.8(4)
C(12)-N(5)-C(13)-C(14)	-137.7(3)
C(13)-N(5)-C(12)-C(11)	71.5(4)
C(14)-N(6)-C(15)-C(16)	-134.0(3)
C(15)-N(6)-C(14)-C(13)	70.3(4)
C(16)-N(7)-C(11)-C(12)	-135.0(3)
Ni(1)-N(5)-C(12)-C(11)	-50.1(3)
Ni(1)-N(5)-C(13)-C(14)	-19.3(4)
Ni(1)-N(6)-C(14)-C(13)	-50.7(3)
Ni(1)-N(6)-C(15)-C(16)	-17.2(4)
Ni(1)-N(7)-C(11)-C(12)	-16.9(3)
Ni(1)-N(7)-C(16)-C(15)	-48.8(3)
Ni(1)-O(3)-N(2)-C(5)	-64.8(3)
Ni(1)-O(3)-N(2)-C(6)	64.5(3)
Ni(1)-O(4)-N(3)-C(6)	-64.6(3)
Ni(1)-O(4)-N(3)-C(7)	64.7(3)
Ni(1)-O(5)-N(4)-C(5)	64.1(3)
Ni(1)-O(5)-N(4)-C(7)	-64.6(3)
O(1)-N(1)-C(1)-C(2)	63.1(4)
O(1)-N(1)-C(1)-C(3)	-176.4(4)
O(1)-N(1)-C(1)-C(4)	-55.4(5)
O(2)-N(1)-C(1)-C(2)	-114.6(4)
O(2)-N(1)-C(1)-C(3)	5.9(5)
O(2)-N(1)-C(1)-C(4)	126.9(4)
O(3)-N(2)-C(5)-N(4)	70.8(3)
O(3)-N(2)-C(5)-C(2)	-171.7(3)
O(3)-N(2)-C(5)-C(8)	-50.3(4)
O(3)-N(2)-C(6)-N(3)	-70.5(3)
O(3)-N(2)-C(6)-C(3)	171.9(3)
O(3)-N(2)-C(6)-C(9)	50.0(4)
O(4)-N(3)-C(6)-N(2)	70.3(3)
O(4)-N(3)-C(6)-C(3)	-172.0(3)
O(4)-N(3)-C(6)-C(9)	-51.0(4)
O(4)-N(3)-C(7)-N(4)	-69.6(3)

O(4)-N(3)-C(7)-C(4)	172.1(3)
O(4)-N(3)-C(7)-C(10)	50.8(4)
O(5)-N(4)-C(5)-N(2)	-70.3(3)
O(5)-N(4)-C(5)-C(2)	172.1(3)
O(5)-N(4)-C(5)-C(8)	50.6(4)
O(5)-N(4)-C(7)-N(3)	69.6(3)
O(5)-N(4)-C(7)-C(4)	-171.8(3)
O(5)-N(4)-C(7)-C(10)	-50.4(4)
N(1)-C(1)-C(2)-C(5)	-179.0(3)
N(1)-C(1)-C(3)-C(6)	-179.0(3)
N(1)-C(1)-C(4)-C(7)	178.5(3)
C(1)-C(2)-C(5)-N(2)	-58.1(4)
C(1)-C(2)-C(5)-N(4)	58.5(4)
C(1)-C(2)-C(5)-C(8)	-179.7(3)
C(1)-C(3)-C(6)-N(2)	57.9(4)
C(1)-C(3)-C(6)-N(3)	-58.5(4)
C(1)-C(3)-C(6)-C(9)	-179.4(3)
C(1)-C(4)-C(7)-N(3)	57.8(4)
C(1)-C(4)-C(7)-N(4)	-59.3(4)
C(1)-C(4)-C(7)-C(10)	179.0(3)
C(2)-C(1)-C(3)-C(6)	-60.2(4)
C(2)-C(1)-C(4)-C(7)	61.3(4)
C(3)-C(1)-C(2)-C(5)	60.4(4)
C(3)-C(1)-C(4)-C(7)	-60.3(4)
C(4)-C(1)-C(2)-C(5)	-61.0(4)
C(4)-C(1)-C(3)-C(6)	60.8(4)
C(5)-N(2)-C(6)-N(3)	58.7(3)
C(5)-N(2)-C(6)-C(3)	-58.8(3)
C(5)-N(2)-C(6)-C(9)	179.2(3)
C(5)-N(4)-C(7)-N(3)	-59.0(3)
C(5)-N(4)-C(7)-C(4)	59.6(4)
C(5)-N(4)-C(7)-C(10)	-179.0(3)
C(6)-N(2)-C(5)-N(4)	-58.6(3)
C(6)-N(2)-C(5)-C(2)	58.8(3)
C(6)-N(2)-C(5)-C(8)	-179.8(3)
C(6)-N(3)-C(7)-N(4)	59.5(3)
C(6)-N(3)-C(7)-C(4)	-58.7(4)
C(6)-N(3)-C(7)-C(10)	179.9(3)
C(7)-N(3)-C(6)-N(2)	-59.1(4)
C(7)-N(3)-C(6)-C(3)	58.6(4)

C(7)-N(3)-C(6)-C(9)	179.6(3)
C(7)-N(4)-C(5)-N(2)	58.7(4)
C(7)-N(4)-C(5)-C(2)	-58.9(4)
C(7)-N(4)-C(5)-C(8)	179.6(3)
Ni(1A)-N(6)-C(14)-C(13)	-73.1(6)
Ni(1A)-N(6)-C(15)-C(16)	2.1(7)
Ni(1A)-O(3A)-N(2A)-C(5A)	-64(4)
Ni(1A)-O(3A)-N(2A)-C(6A)	65(4)
Ni(1A)-O(4A)-N(3A)-C(6A)	-58(4)
Ni(1A)-O(4A)-N(3A)-C(7A)	69(4)
Ni(1A)-O(5A)-N(4A)-C(5A)	71(4)
Ni(1A)-O(5A)-N(4A)-C(7A)	-64(4)
O(1A)-N(1A)-C(1A)-C(2A)	74(10)
O(1A)-N(1A)-C(1A)-C(3A)	-154(9)
O(1A)-N(1A)-C(1A)-C(4A)	-43(10)
O(2A)-N(1A)-C(1A)-C(2A)	-94(9)
O(2A)-N(1A)-C(1A)-C(3A)	38(11)
O(2A)-N(1A)-C(1A)-C(4A)	149(9)
O(3A)-N(2A)-C(5A)-N(4A)	69(5)
O(3A)-N(2A)-C(5A)-C(2A)	-176(4)
O(3A)-N(2A)-C(5A)-C(8A)	-51(5)
O(3A)-N(2A)-C(6A)-N(3A)	-72(5)
O(3A)-N(2A)-C(6A)-C(3A)	180(4)
O(3A)-N(2A)-C(6A)-C(9A)	52(4)
O(4A)-N(3A)-C(6A)-N(2A)	66(5)
O(4A)-N(3A)-C(6A)-C(3A)	-175(4)
O(4A)-N(3A)-C(6A)-C(9A)	-58(4)
O(4A)-N(3A)-C(7A)-N(4A)	-72(4)
O(4A)-N(3A)-C(7A)-C(4A)	170(4)
O(4A)-N(3A)-C(7A)-C(10A)	54(4)
O(5A)-N(4A)-C(5A)-N(2A)	-76(5)
O(5A)-N(4A)-C(5A)-C(2A)	166(4)
O(5A)-N(4A)-C(5A)-C(8A)	46(5)
O(5A)-N(4A)-C(7A)-N(3A)	79(5)
O(5A)-N(4A)-C(7A)-C(4A)	-171(4)
O(5A)-N(4A)-C(7A)-C(10A)	-44(5)
N(1A)-C(1A)-C(2A)-C(5A)	-178(4)
N(1A)-C(1A)-C(3A)-C(6A)	-178(6)
N(1A)-C(1A)-C(4A)-C(7A)	176(6)
C(1A)-C(2A)-C(5A)-N(2A)	-53(7)

C(1A)-C(2A)-C(5A)-N(4A)	62(6)
C(1A)-C(2A)-C(5A)-C(8A)	-179(6)
C(1A)-C(3A)-C(6A)-N(2A)	47(7)
C(1A)-C(3A)-C(6A)-N(3A)	-66(7)
C(1A)-C(3A)-C(6A)-C(9A)	176(5)
C(1A)-C(4A)-C(7A)-N(3A)	61(6)
C(1A)-C(4A)-C(7A)-N(4A)	-53(7)
C(1A)-C(4A)-C(7A)-C(10A)	178(6)
C(2A)-C(1A)-C(3A)-C(6A)	-47(8)
C(2A)-C(1A)-C(4A)-C(7A)	56(7)
C(3A)-C(1A)-C(2A)-C(5A)	52(8)
C(3A)-C(1A)-C(4A)-C(7A)	-67(7)
C(4A)-C(1A)-C(2A)-C(5A)	-63(7)
C(4A)-C(1A)-C(3A)-C(6A)	70(7)
C(5A)-N(2A)-C(6A)-N(3A)	56(5)
C(5A)-N(2A)-C(6A)-C(3A)	-52(5)
C(5A)-N(2A)-C(6A)-C(9A)	180(4)
C(5A)-N(4A)-C(7A)-N(3A)	-55(5)
C(5A)-N(4A)-C(7A)-C(4A)	55(4)
C(5A)-N(4A)-C(7A)-C(10A)	-178(4)
C(6A)-N(2A)-C(5A)-N(4A)	-61(5)
C(6A)-N(2A)-C(5A)-C(2A)	54(5)
C(6A)-N(2A)-C(5A)-C(8A)	179(4)
C(6A)-N(3A)-C(7A)-N(4A)	52(5)
C(6A)-N(3A)-C(7A)-C(4A)	-66(4)
C(6A)-N(3A)-C(7A)-C(10A)	178(4)
C(7A)-N(3A)-C(6A)-N(2A)	-52(6)
C(7A)-N(3A)-C(6A)-C(3A)	68(4)
C(7A)-N(3A)-C(6A)-C(9A)	-176(4)
C(7A)-N(4A)-C(5A)-N(2A)	61(5)
C(7A)-N(4A)-C(5A)-C(2A)	-57(4)
C(7A)-N(4A)-C(5A)-C(8A)	-178(4)

Table S17. Hydrogen bonds for **7-Ni**(Cl) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(6)-H(6A)...Cl(1)	0.84	2.34	3.172(3)	170.8
O(6)-H(6A)...Cl(1A)	0.84	2.24	3.046(15)	161.7
O(6)-H(6A)...Cl(1B)	0.84	2.51	3.22(4)	143.7
N(7)-H(7)...O(6)	0.86(7)	2.18(7)	2.943(4)	148(6)
N(5)-H(5)...Cl(1)#1	0.86(5)	2.59(5)	3.308(3)	141(4)
N(5)-H(5)...Cl(1A)#1	0.86(5)	2.72(5)	3.379(15)	134(4)

Symmetry transformations used to generate equivalent atoms:

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

6. Mössbauer spectrum of 7-**Fe**(Cl) and DFT calculations of δ and ΔE_Q

Mossbauer measurements were performed on powder samples of the **7-Fe**(Cl), lightly pressed into a flat container made of 8-μm-thick aluminum foil. Absorption spectra on ^{57}Fe nuclei were recorded at the room temperature T = 298 K on a standard MS-2020DM spectrometer. A ^{57}Co(Cr) MK57.VR (JSC Cyclotron) gamma ray source operated at room temperature. Isomeric shifts were measured relative to a Ritverc MRA.1.6 reference absorber (3-μm-thick ^{57}Fe-enriched α-Fe foil at room temperature). Computer analysis of the Mossbauer spectra was performed using the Univem-MS program (delivered with the MS-2020DM spectrometer) and the SpectrRelax program.[14,15]

Doublet D1 has a pronounced asymmetry in the intensities and widths of the spectral lines, which in our opinion cannot be due to the Goldansky-Karyagin effect, but indicates a small distribution of the Mössbauer parameters probably associated with two different solid phases: crystalline phase containing **7-Fe**(Cl) with some solvent molecules and amorphous phase without solvent.

Low-intensity doublet D2 with a relative area A of about 10% corresponds to impurity iron in the aluminum foil of the sample container.

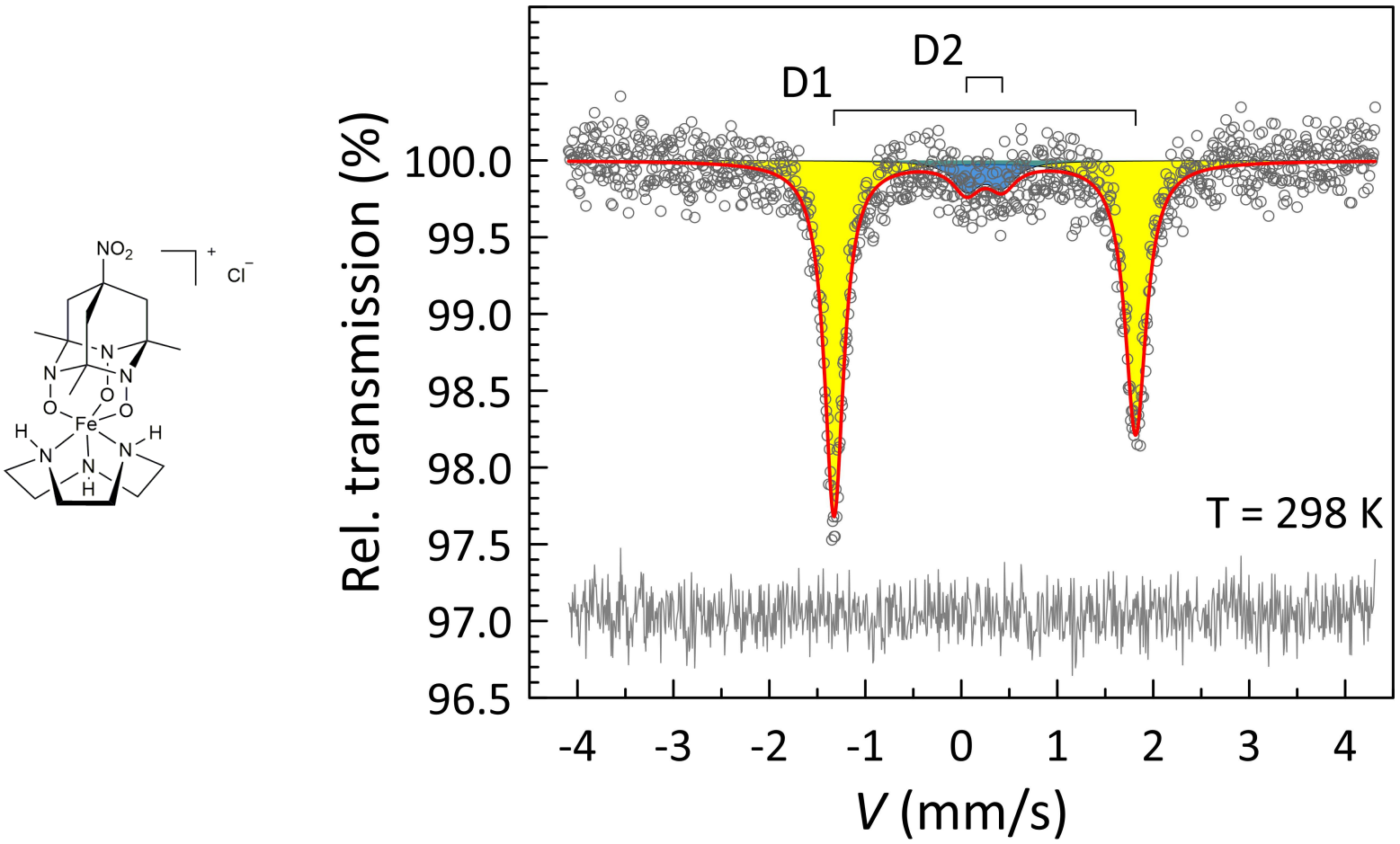


Figure S5. Mössbauer spectrum of complex **7-Fe**(Cl)

Table S18. Resonance parameters of the hyperfine interactions calculated from Mössbauer spectrum.

Component	δ, (mm/s)	$\|\Delta E_Q\|$, (mm/s)	A rel, %	Γ_1, (mm/s)	Γ_2, (mm/s)
Doublet 1 **7-Fe**(Cl)	0.245(1)	3.143(1)	90(1)	0.243(5)	0.269(5)
Doublet 2 Fe in Al foil	0.240(1)	0.372(1)	10(1)	0.343(2)	0.343(2)

‹δ› – average isomer shift, ‹ΔE_Q› – average quadrupole splitting of the paramagnetic doublet, Γ_i – width of the paramagnetic doublet 1 and 2 spectral lines at half-maximum of the signal, *A* – the relative area of the component.

DFT calculations of Mössbauer isomer shift (δ) and quadrupole splitting (ΔE_Q) were performed for several structures:

1) DFT optimized geometry of cation **7.1-Fe**$^+$. Charge +1; multiplicity 1.

2) DFT optimized geometry of cation **7.2-Fe**$^+$. Charge +1; multiplicity 3.

3) DFT optimized geometry of cation **7.3-Fe**$^+$. Charge +1; multiplicity 5.

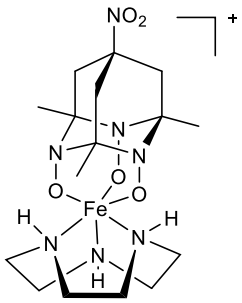


Table S19. Calculated parameters of Mössbauer spectrum.

#	Structure	δ	ΔE_Q
1	DFT optimized geometry of cation **7.1-Fe**$^+$	0.21 mm/s	-1.53 mm/s
	RHO = 23615.538		
	V_{zz} = -0.9395 V_{yy} = 0.5571 V_{xx} = 0.3825		
2	DFT optimized geometry of cation **7.2-Fe**$^+$	0.235 mm/s	-2.23 mm/s
	RHO = 23615.410		
	V_{zz} = -1.3786 V_{yy} = 0.6905 V_{xx} = 0.6881		
3	DFT optimized geometry of cation **7.3-Fe**$^+$	0.48 mm/s	-0.96 mm/s
	RHO = 23613.927		
	V_{zz} = -0.5913 V_{yy} =0.3640 V_{xx} = 0.2272		

RHO – calculated contact electron density on Fe nucleus, a.u.$^{-3}$ V_{xx}, V_{yy}, V_{zz} - eigenvalues of the electric field gradient.

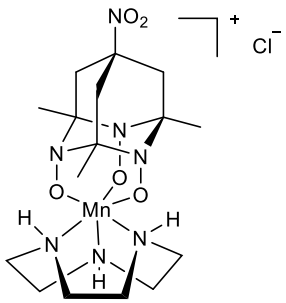
Table S20. Comparison of experimental and calculated Mössbauer parameters for **7-Fe**(Cl).

Parameter	**7-Fe**(Cl)
$\delta_{exp,}$ (mm/s)	0.245
$\lvert\Delta E_Q\rvert_{exp,}$ (mm/s)	3.143
$\delta_{calc,}$ (mm/s)	0.235
$\Delta E_{Q\ calc,}$ (mm/s)	-2.23

7. Determination of magnetic susceptibility of 7-**M**(Cl) by the Evans method

The magnetic susceptibility of the paramagnetic complexes **7-Mn**(Cl)·CH_3OH·$3H_2O$ and **7-Fe**(Cl)·$3H_2O$ in a CD_3OD solution was evaluated by the Evans method[16] at 298K and 300 K respectively, using a Wilmad NMR tube with a coaxial insert. The outer (reference) tube was filled with CD_3OD with approximately 1% of Me_4Si, the inner tube contained a CD_3OD solution of the paramagnetic complexes **7-M**(Cl) with a known concentration and the same amount of Me_4Si. The molar magnetic susceptibility was calculated from the difference between the chemical shift of Me_4Si and residual CD_3OH in pure CD_3OD and its shift in the CD_3OD solution of the paramagnetic complex by the standard Evans method procedure.[17] The molar diamagnetic contribution to the paramagnetic susceptibility was estimated using Pascal's constants.[18]

7-Mn(Cl) **7-Fe**(Cl)



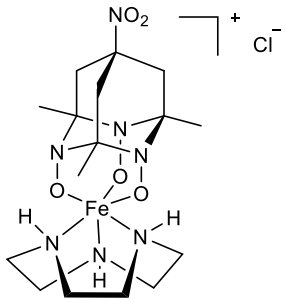
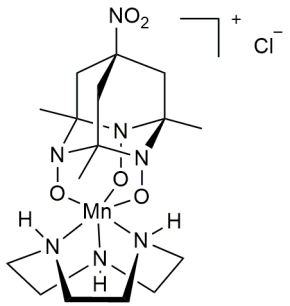


Table S21. Magnetic susceptibility of the complex **7-M**(Cl) complexes (300 MHz, CD_3OD).

Compound	**Δδ, ppm**	**C (M)**	**χM, $cm^3 \cdot mol^{-1}$**	**μ_{eff}, μ_B**
7-Mn(Cl)·CH_3OH·$3H_2O$ **vs TMS**	0.90	$3.26 \cdot 10^{-2}$	$6.31 \cdot 10^{-3}$	3.96; for n = 3 μ = 3.87 (2.3%)
7-Mn(Cl)·CH_3OH·$3H_2O$ **vs CD_3OH**	0.91	$3.26 \cdot 10^{-2}$	$6.39 \cdot 10^{-3}$	3.99; for n = 3 μ = 3.87 (2.8%)
7-Fe(Cl)·$3H_2O$ **vs TMS**	0.33	$2.24 \cdot 10^{-2}$	$3.34 \cdot 10^{-3}$	2.91; for n = 2 μ = 2.83 (2.8%)
7-Fe(Cl)·$3H_2O$ **vs CD_3OH**	0.33	$2.24 \cdot 10^{-2}$	$3.34 \cdot 10^{-3}$	2.91; for n = 2 μ = 2.83 (2.8%)

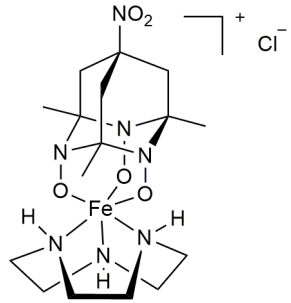
1H NMR 300.23MHz, MeOD, 298.0K



HDO in the solution of the paramagnetic compound
5.81
HDO in pure solution
4.85
CH3OH in the solution of the paramagnetic compound
4.25
CH3OH pure solution
3.34
3.31
CD3OD pure solution
TMS in the solution of the paramagnetic compound
0.90
TMS in pure solution
0.00

7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

1H NMR 300.13MHz, MeOD, 300.0K



5.18 HDO in the solution of the paramagnetic compound

4.84 HDO in pure solution

3.68 CH_3OH in the solution of the paramagnetic compound

3.64 CHD_2OD in the solution of the paramagnetic compound

3.31 CHD_2OD pure solution

0.33 TMS in the solution of the paramagnetic compound

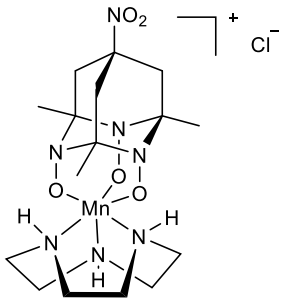
0.00 TMS in pure solution

5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0

ppm

8. CVA for 7-**M**(Cl)

Cyclic voltammetry (CV) experiments were performed for acetonitrile solutions of **7-M**(Cl) with 0.25 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte using a Metrohm Autolab PGSTAT128N potentiostat with a conventional one-compartment three-electrode cell (5 mL of solution) and 100mV/s scan rate. The Pt-disk electrode, which was used as a working electrode, was thoroughly polished with a 0.05 μm alumina slurry, sonicated for two minutes in deionized water and rinsed before every measurement. A Pt counter electrode and a platinum wire reference electrode were used. To account for a drift of the reference electrode, ferrocene was added after the measurements as an internal standard and all the potential is reported relative to the Fc/Fc^+ redox couple. The solutions were thoroughly deaerated by passing argon through them before the CV experiments and above these solutions during the measurements.



7-Mn(Cl)

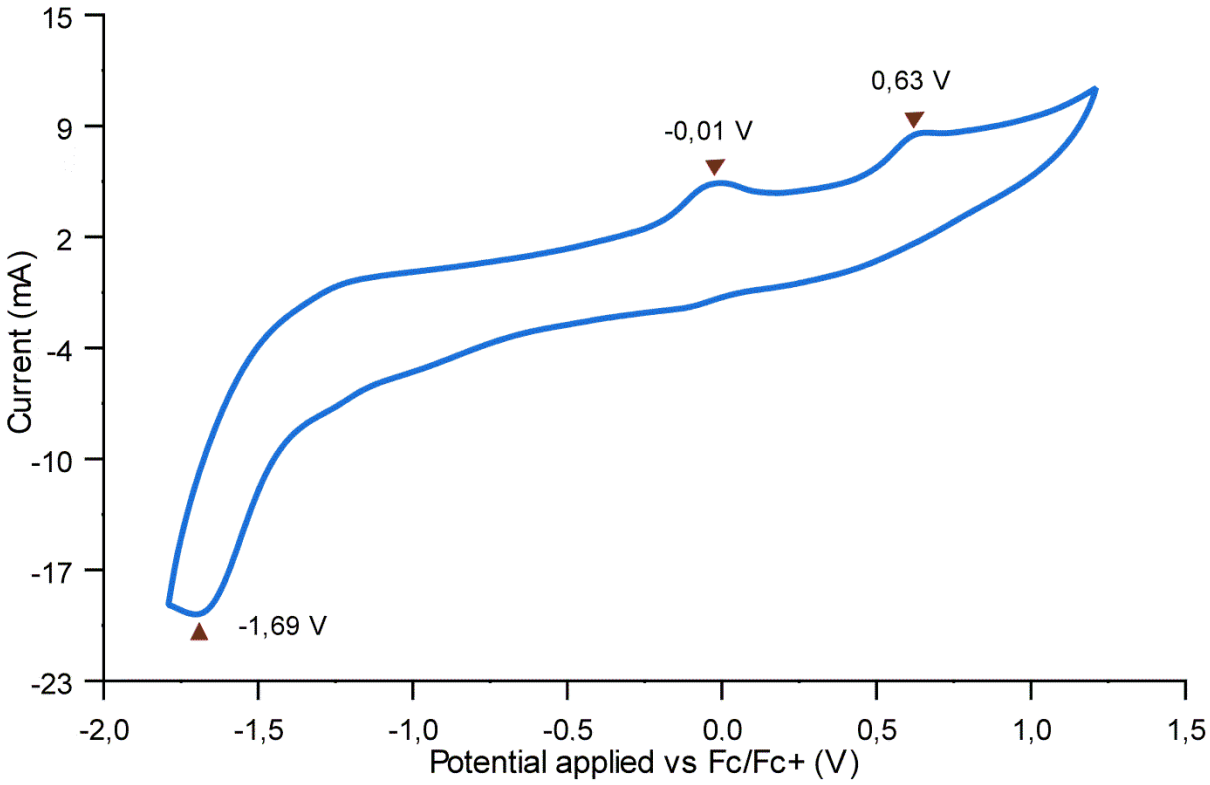
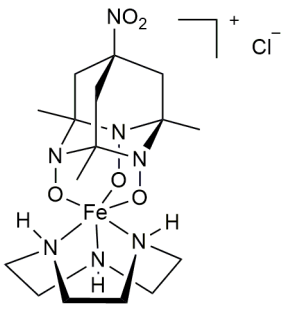


Figure S6. Characteristic cyclic voltammogram of **7-Mn**(Cl) (conditions: 250mM $TBAPF_6$ in MeCN, with Pt disk working and counter electrodes, Pt wire ref. electrode., scan rate 100 mV/s, vs. Fc/Fc^+).



7-Fe(Cl)

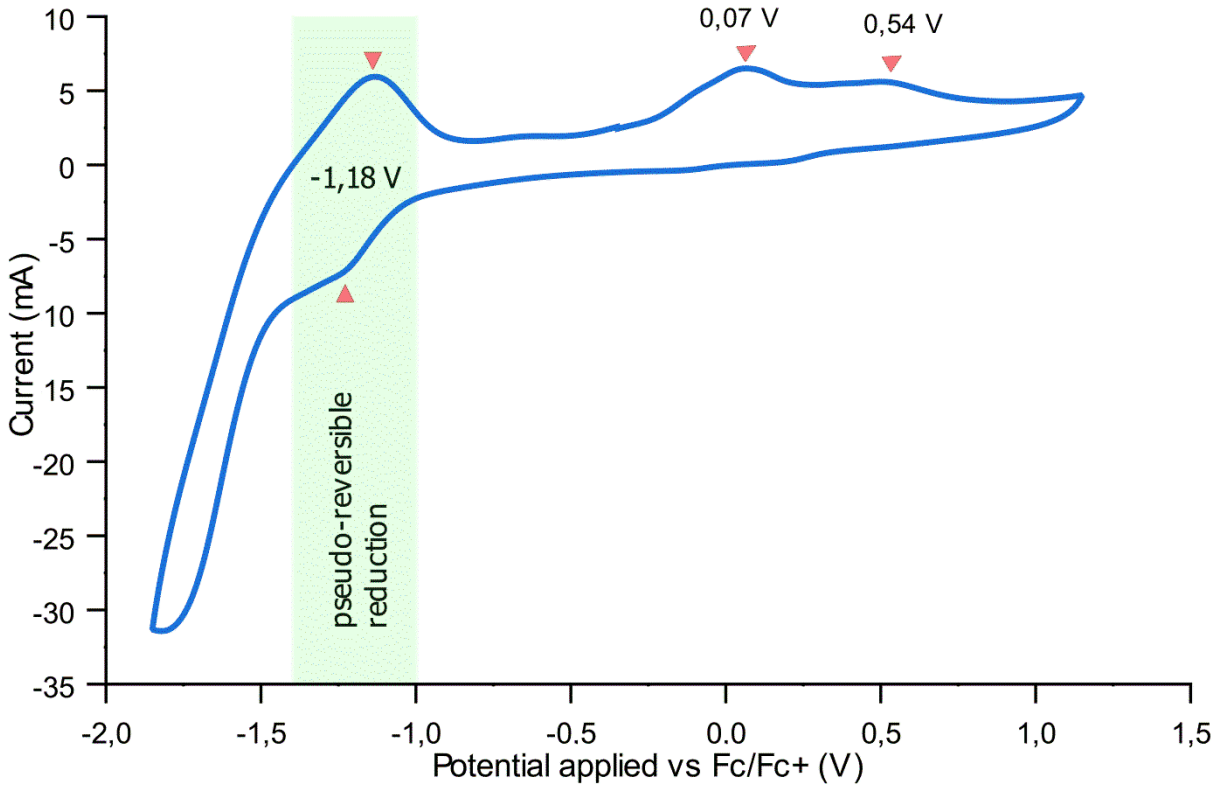
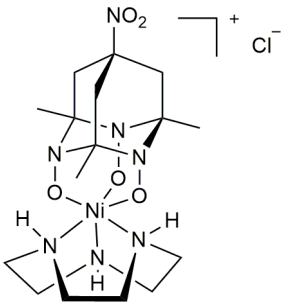


Figure S7. Characteristic cyclic voltammogram of **7-Fe**(Cl) (conditions: 250mM $TBAPF_6$ in MeCN, with Pt disk working and counter electrodes, Pt wire ref. electrode., scan rate 100 mV/s, vs. Fc/Fc^+).



7-Ni(Cl)

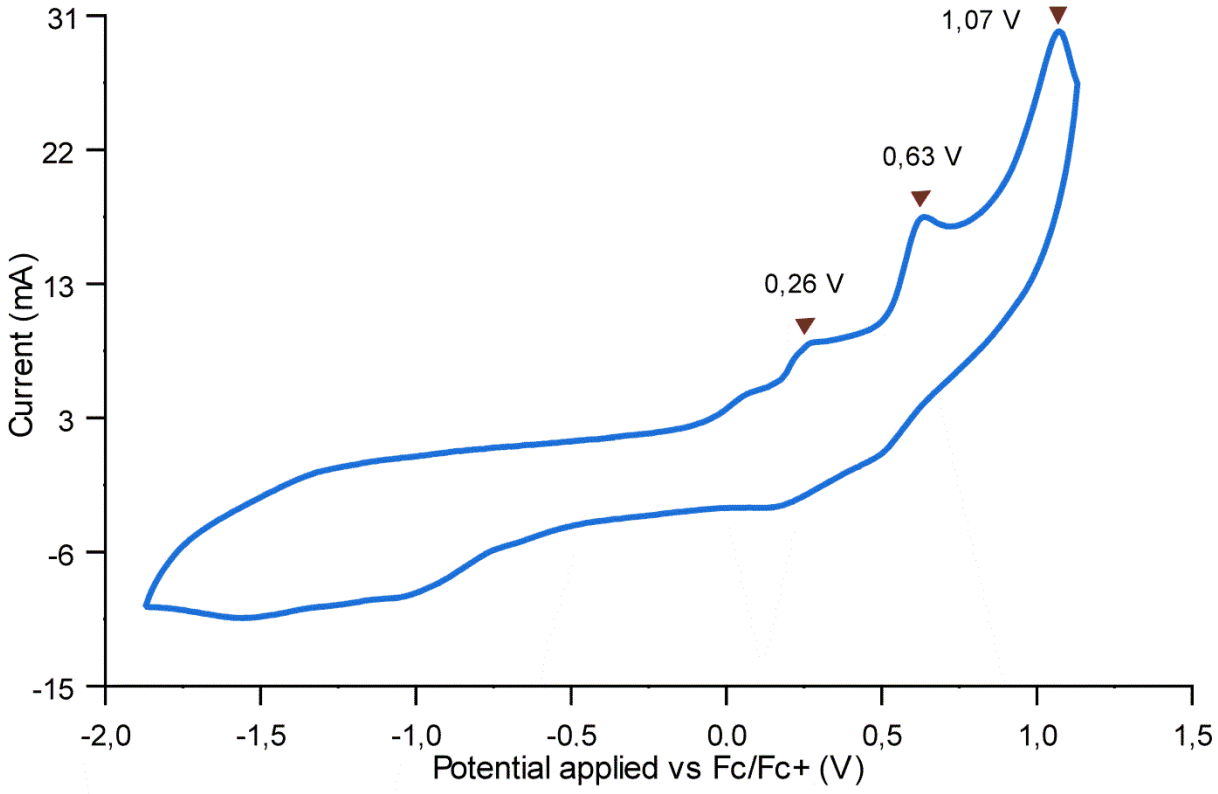


Figure S8. Characteristic cyclic voltammogram of **7-Ni**(Cl) (conditions: 250mM $TBAPF_6$ in MeCN, with Pt disk working and counter electrodes, Pt wire ref. electrode., scan rate 100 mV/s, vs. Fc/Fc^+).

9. DFT calculations

9.1 General information

Calculations were performed with the Gaussian 16 Rev C.01 program.[19] BP86 DFT functional with GD3BJ empirical dispersion correction and jorgetzp basis set[20,21] was used for geometry optimization and calculations of thermodynamics, unless otherwise stated. Cartesian coordinates are given in angstroms; absolute energies for all substances are given in hartrees. Calculations were performed in methanol (SMD model). The approach of Martin and co-workers was followed.[22] Data from X-ray diffraction experiments were used as starting points for geometry optimizations, where applicable. Analysis of vibrational frequencies was performed for all optimized structures. All compounds were characterized by only real vibrational frequencies. Wavefunction stability, using *stable* keyword, was also checked for each molecule before and after geometry optimization. Interpretation of metal spin and oxidation states in DFT optimized structures was performed on the basis of Mulliken atom spin density.

Keywords[23] for geometry optimization and calculations of thermodynamics are:

 # opt freq BP86/Gen nosymm EmpiricalDispersion=GD3BJ pressure=605 temperature=298.15 scf=xqc scrf=(solvent=Methanol,smd) test

9.2 DFT calculations of N-O bond length, Mulliken and CM5 charges, MESP

N-O bond length and Mulliken charges were calculated as single point jobs for optimized geometries of neutral **7-M**(Cl) complexes. CM5[24] charges were calculated, using *population=CM5* keyword.

MESP[25,26] for neutral **7-M**(Cl) complexes were calculated using Multiwfn, using steepest descent method in topology analysis module.[27-29] V_{min} were calculated for nitrogen atom which is the farthest from the chlorine. Numerical values of V_{min} are given in kcal/mol; Cartesian coordinates of V_{min} are given in angstroms.

Table S22. Calculated N-O bond length in **7-M**(Cl) complexes.

Metal complex	S	Calculated N–O bond length, Å
7-Ti(Cl)	S=0	1.43;1.43;1.43
7-V(Cl)	S=0.5	1.42;1.41;1.41
7-Cr(Cl)	S=1	1.39; 1.41; 1.40
7-Mn(Cl)	S =1.5	1.40; 1.40; 1.40
7-Fe(Cl)	S =2	1.39; 1.39; 1.39
7-Co(Cl)	S =0.5	1.36; 1.37; 1.37
7-Ni(Cl)	S=0	1.35; 1.35; 1.35
low-spin **7-Cu**(Cl) ΔE_0 =0.0 kcal	S=0.5	1.32; 1.32; 1.32
high-spin **7-Cu**(Cl)* ΔE_0 = +21.0 kcal	S=1.5	1.34; 1.34; 1.34

* - Used in correlation with experimental ionization energies

Table S23. Calculated summed Mulliken charges only for nitrogen atoms of three N-O fragments in **7-M**(Cl) complexes.

Metal complex	S	Summed Mulliken charges only for nitrogen of three N–O fragments	Experimental ionization energies[30] (IE) for $M^0 \rightarrow M^{+4}$
7-Ti(Cl)	S=0	-0.23	8795
7-V(Cl)	S=0.5	-0.19	9399
7-Cr(Cl)	S=1	-0.13	9972
7-Mn(Cl)	S =1.5	-0.08	10414
7-Fe(Cl)	S =2	-0.04	10567
7-Co(Cl)	S =0.5	0.06	10588
7-Ni(Cl)	S=0	0.1	11183
low-spin **7-Cu**(Cl)	S=0.5	0.28	11583
high-spin **7-Cu**(Cl)*	S=1.5	0.24	11583

* - Used in correlation with experimental ionization energies

Table S24. Calculated summed Mulliken charges for nitrogen and oxygen atoms of three N-O fragments in **7-M**(Cl) complexes.

Metal complex	S	Summed Mulliken charges for nitrogen and oxygen atoms of three N–O fragments
7-Ti(Cl)	S=0	-1.51
7-V(Cl)	S=0.5	-1.34
7-Cr(Cl)	S=1	-1.48
7-Mn(Cl)	S =1.5	-1.63
7-Fe(Cl)	S =2	-1.37
7-Co(Cl)	S =0.5	-1.33
7-Ni(Cl)	S=0	-1.21
low-spin **7-Cu**(Cl)	S=0.5	-0.94
high-spin **7-Cu**(Cl)	S=1.5	-1.14

Table S25. Calculated summed Mulliken charges only for oxygen atoms of three N-O fragments in **7-M**(Cl) complexes.

Metal complex	S	Summed Mulliken charges only for oxygen atoms of three N–O fragments
7-Ti(Cl)	S=0	-1.28
7-V(Cl)	S=0.5	-1.15
7-Cr(Cl)	S=1	-1.34
7-Mn(Cl)	S =1.5	-1.55
7-Fe(Cl)	S =2	-1.33
7-Co(Cl)	S =0.5	-1.39
7-Ni(Cl)	S=0	-1.31
low-spin **7-Cu**(Cl)	S=0.5	-1.22
high-spin **7-Cu**(Cl)	S=1.5	-1.38

Table S26. Calculated summed CM5 charges for nitrogen and oxygen atoms of three N-O fragments in **7-M**(Cl) complexes.

Metal complex	S	Summed CM5 charges for nitrogen and oxygen atoms of three N–O fragments
7-Ti(Cl)	S=0	-1.81
7-V(Cl)	S=0.5	-1.71
7-Cr(Cl)	S=1	-1.64
7-Mn(Cl)	S =1.5	-1.54
7-Fe(Cl)	S =2	-1.41
7-Co(Cl)	S =0.5	-1.29
7-Ni(Cl)	S=0	-1.32
low-spin **7-Cu**(Cl)	S=0.5	-1.24
high-spin **7-Cu**(Cl)	S=1.5	-1.36

Table S27. Calculated summed CM5 charges only for nitrogen atoms of three N-O fragments in **7-M**(Cl) complexes.

Metal complex	S	Summed CM5 charges only for nitrogen of three N–O fragments
7-Ti(Cl)	S=0	-0.70
7-V(Cl)	S=0.5	-0.69
7-Cr(Cl)	S=1	-0.67
7-Mn(Cl)	S =1.5	-0.66
7-Fe(Cl)	S =2	-0.63
7-Co(Cl)	S =0.5	-0.59
7-Ni(Cl)	S=0	-0.58
low-spin **7-Cu**(Cl)	S=0.5	-0.49
high-spin **7-Cu**(Cl)	S=1.5	-0.53

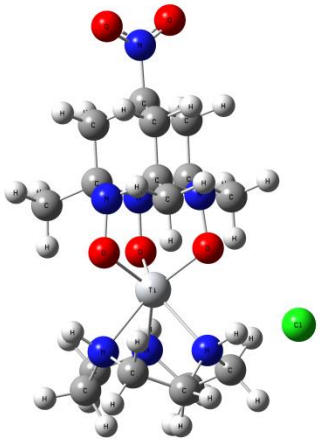
Table S28. Calculated summed Mulliken charges only for oxygen atoms of three N-O fragments in **7-M**(Cl) complexes.

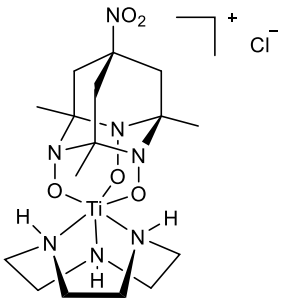
Metal complex	S	Summed CM5 charges only for oxygen atoms of three N–O fragments
7-Ti(Cl)	S=0	-1.11
7-V(Cl)	S=0.5	-1.02
7-Cr(Cl)	S=1	-0.96
7-Mn(Cl)	S =1.5	-0.88
7-Fe(Cl)	S =2	-0.77
7-Co(Cl)	S =0.5	-0.69
7-Ni(Cl)	S=0	-0.74
low-spin **7-Cu**(Cl)	S=0.5	-0.75
high-spin **7-Cu**(Cl)	S=1.5	-0.83

Table S29. Molecular electrostatic potential (MESP) calculations for **7-M**(Cl) complexes.

Metal complex	S	V_{min} for nitrogen atom* kcal/mol
7-Ti(Cl)	S=0	-34.3
7-V(Cl)	S =0.5	-31.6
7-Cr(Cl)	S=1	-21.8
7-Mn(Cl)	S =1.5	-25.2
7-Fe(Cl)	S=1	-19.3
7-Co(Cl)	S =0.5	-8.5
7-Ni(Cl)	S =0	-10.43

*- the farthest from chlorine atom.





7-Ti(Cl)

Charge 0; multiplicity 1

O	14.62566200	4.30083400	15.68362000
O	16.31981000	5.87799100	14.17134700
O	13.72389300	6.73258100	14.67797400
O	13.72439500	2.16710200	9.92076100
O	12.18649500	3.70224100	9.77318400
N	14.19743200	3.78913800	14.41800400
N	15.73286900	5.19815100	13.05837800
N	13.40817600	5.97077800	13.51063600
N	13.15671300	3.18125200	10.32997800
N	14.40568500	7.82862400	16.94953000
H	13.49391900	8.02194300	16.52388900
N	15.48421100	5.46777700	17.83073200
H	15.40837300	4.44749300	17.76776800
N	17.02819900	7.22431800	16.39682000
H	17.65263700	7.41011700	15.57011100
C	13.67288200	3.85156200	11.60888200
C	14.86395700	3.10002100	12.17266900
H	15.69508400	3.08247600	11.45583000
H	14.59382200	2.06738000	12.42915200
C	15.33682300	3.81480800	13.45237700
C	16.53222000	3.07329500	14.03080400
H	16.90440100	3.54920900	14.94362200
H	17.34116800	3.05475900	13.28741000
H	16.24051000	2.03970000	14.26379900
C	14.07620600	5.28562600	11.27182200
H	13.22189100	5.84460000	10.86943900
H	14.89352400	5.29475000	10.53750300
C	14.55894700	5.97511200	12.55895100
C	14.97316200	7.40397700	12.24068700
H	14.11039200	7.95050600	11.83517700
H	15.77252100	7.39013400	11.48706100
H	15.33978700	7.92804600	13.12913700
C	12.54003000	3.87008100	12.63289800

H	12.23605000	2.84651900	12.89217400
H	11.67257500	4.41676200	12.24169600
C	13.03914900	4.57743200	13.90437600
C	11.92162900	4.60121100	14.93635500
H	11.62340100	3.57012200	15.17163700
H	11.05548700	5.13573500	14.52216800
H	12.23241800	5.09787800	15.86120500
C	14.22140000	7.49221000	18.38745500
H	13.25153600	7.86167800	18.74971900
H	14.99995500	8.00316000	18.96973300
C	14.31288300	5.98435100	18.57745400
H	14.36745300	5.73060800	19.64948100
H	13.42426800	5.49130400	18.15527600
C	16.81055500	5.82823100	18.40581700
H	17.24269300	4.97076600	18.94090200
H	16.66697600	6.63038300	19.14167500
C	17.74083800	6.28168600	17.28884100
H	18.65773200	6.73115900	17.70711900
H	18.04141200	5.42229700	16.66963800
C	16.74107100	8.55139200	17.00801600
H	17.45087400	9.29398900	16.61324600
H	16.89580500	8.49614900	18.09425800
C	15.31333300	8.97043200	16.68801900
H	15.02906700	9.86382300	17.26946800
H	15.21860500	9.21385000	15.61891800
Cl	19.17702200	8.26096200	14.34853300
Ti	15.21841800	6.11552900	15.68816700

DFT-D3 BP86/jorgeTZP, solvent methanol, SMD model		
Total electronic energy=	-2697.768089	E_0
Sum of electronic and zero-point Energies=	-2697.286116	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2697.257081	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2697.256137	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2697.337736	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.481972	
Cartesian coordinates of V_{min}		
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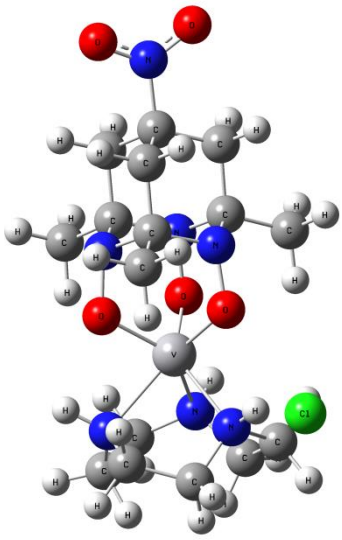

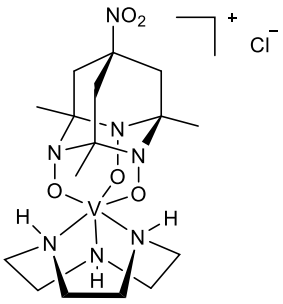

7-V(Cl)

Charge 0; multiplicity 2

O	14.63072700	4.31572700	15.69214900
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O	13.71918500	6.70739700	14.73830700
O	13.75837000	2.23397700	9.91520500
O	12.21086300	3.76088600	9.78244500
N	14.20983400	3.80611500	14.44021000
N	15.72222300	5.24236400	13.11751300
N	13.40499000	5.97929300	13.56775800
N	13.18218500	3.23850600	10.33595300
N	14.40995100	7.80515000	16.90230200
H	13.49929400	8.01579500	16.48143800
N	15.44751700	5.43316100	17.80154300
H	15.34984800	4.41357700	17.75503500
N	17.01475000	7.15329700	16.33808300
H	17.63349100	7.32243600	15.50748700
C	13.68825900	3.89432800	11.62655400
C	14.88513400	3.14602700	12.18282000
H	15.71841600	3.14715100	11.46807300
H	14.62426100	2.10686500	12.42247700
C	15.34696300	3.84487100	13.47315900
C	16.54817900	3.11140600	14.04912800
H	16.90935500	3.58422000	14.96830000
H	17.36089500	3.10950400	13.30965900
H	16.26756700	2.07223400	14.27074600
C	14.07832400	5.33727400	11.31216500
H	13.22003700	5.89360500	10.91431300
H	14.89818600	5.36522700	10.58098800
C	14.54915300	6.01150000	12.60930800
C	14.95207600	7.44968700	12.32101900

H	14.08641500	7.99745200	11.92345600
H	15.75429500	7.45806200	11.57035100
H	15.31121800	7.95686500	13.22255500
C	12.55214900	3.88557500	12.64745400
H	12.25741400	2.85502400	12.88945600
H	11.68022400	4.42946800	12.26194300
C	13.03896700	4.57755100	13.92993400
C	11.92156400	4.57868100	14.96198000
H	11.63086900	3.54253700	15.18397900
H	11.05130300	5.11209800	14.55499800
H	12.23049700	5.06642300	15.89242400
C	14.22931100	7.48851600	18.34826500
H	13.26938300	7.88309200	18.70958700
H	15.02244000	7.99040500	18.91815000
C	14.29199900	5.98238100	18.55464900
H	14.35650300	5.73895200	19.62827000
H	13.39062500	5.50042300	18.14805000
C	16.78760200	5.77733800	18.36179800
H	17.20589700	4.91564400	18.90056800
H	16.66367100	6.58819900	19.09151700
C	17.71729000	6.20396600	17.23427500
H	18.64317700	6.64401400	17.64231800
H	17.99922200	5.33519600	16.62023400
C	16.75685400	8.48978600	16.94585900
H	17.48075900	9.21276200	16.54085800
H	16.91560000	8.43737900	18.03153400
C	15.33717400	8.93165600	16.62819000
H	15.06528600	9.83019200	17.20699200
H	15.24103400	9.16969100	15.55840700
Cl	19.17431100	8.23251900	14.31056000
V	15.19655900	6.11648900	15.75332900

DFT-D3 BP86/jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-2792.292725 E_0
Sum of electronic and zero-point Energies=	-2791.809234 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2791.780819 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2791.779875 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2791.859765 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.483491
Mulliken atom spin density	
V: 1.22	
Cartesian coordinates of V_{min}	
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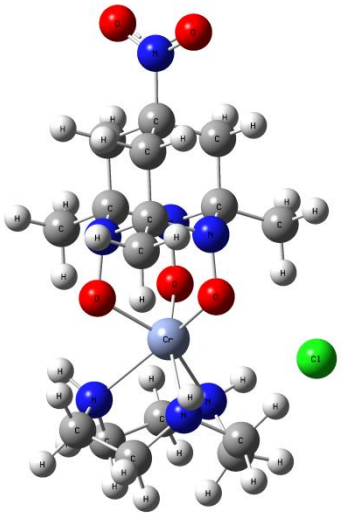

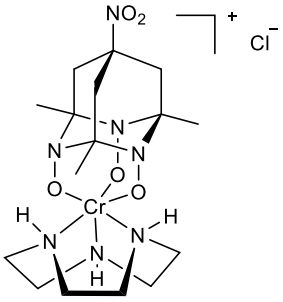

7-Cr(Cl)

Charge 0; multiplicity 3

O	14.30793100	4.52478700	15.73733300
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O	13.96493100	6.89774400	14.51497300
O	13.60969100	2.03970500	10.11044800
O	12.38086500	3.78656300	9.68291400
N	13.93928300	4.01260200	14.49939200
N	15.81382800	4.97363500	13.22108800
N	13.62860100	6.15919300	13.37047700
N	13.18786200	3.16556200	10.37982200
N	14.21297500	7.50804100	17.19162700
H	13.23030700	7.56645300	16.90967400
N	15.87743400	5.36645800	17.57070700
H	15.98097300	4.37635900	17.32823100
N	16.83394900	7.52029100	16.25706600
H	17.28608900	7.92066600	15.38884300
C	13.68540300	3.85477400	11.65624500
C	14.66596000	2.97028300	12.40267500
H	15.54303200	2.74356800	11.78274100
H	14.19353500	2.02663500	12.70650100
C	15.13737300	3.71134100	13.66427700
C	16.11452200	2.83950200	14.43500000
H	16.51867100	3.35810500	15.31003700
H	16.94799600	2.56225100	13.77476900
H	15.60537600	1.92384100	14.76660500
C	14.36161000	5.16581900	11.26306700
H	13.65845800	5.81942500	10.73124200
H	15.23310000	4.97561600	10.62148800
C	14.84130500	5.87906200	12.53729700
C	15.51725000	7.18706800	12.15910200
H	14.79972400	7.82549200	11.62503400

H	16.36622000	6.97526100	11.49435000
H	15.89719300	7.72460100	13.03453500
C	12.47831700	4.15762800	12.54057000
H	11.97010200	3.22916800	12.83652100
H	11.76607800	4.80663600	12.01473100
C	12.96210600	4.87998700	13.80419100
C	11.77935400	5.18813600	14.70752200
H	11.27546200	4.24958100	14.97763500
H	11.06866800	5.82974500	14.16854700
H	12.09408900	5.69642000	15.62476000
C	14.31224900	6.96606700	18.57322400
H	13.34893300	7.05478300	19.09520800
H	15.04037100	7.56738800	19.13455700
C	14.74878000	5.50687300	18.52328000
H	15.02693300	5.14958700	19.52879800
H	13.93369600	4.87525600	18.14521200
C	17.17705900	5.90963900	18.06222200
H	17.82047600	5.09593900	18.42593100
H	16.97426300	6.57238800	18.91396400
C	17.84944800	6.67404100	16.93342800
H	18.68778400	7.28408100	17.30887900
H	18.24343400	5.98153600	16.17573500
C	16.36926000	8.67839600	17.08017800
H	16.85867200	9.59354700	16.71423900
H	16.68827100	8.53082500	18.12093300
C	14.85520800	8.83179300	16.99822100
H	14.50769300	9.57143300	17.73968800
H	14.56246500	9.18548700	15.99869500
Cl	18.39346700	9.00663900	14.03203100
Cr	15.24508400	6.25602800	15.66881600

DFT-D3 BP86/jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-2892.744758 E_0
Sum of electronic and zero-point Energies=	-2892.261054 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2892.232588 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2892.231644 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2892.311691 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.483704
Mulliken atom spin density	
Cr: 2.44	
Cartesian coordinates of V_{min}	
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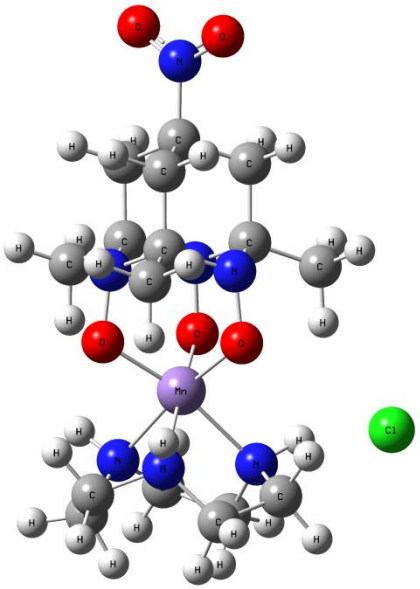
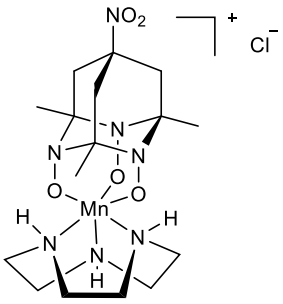




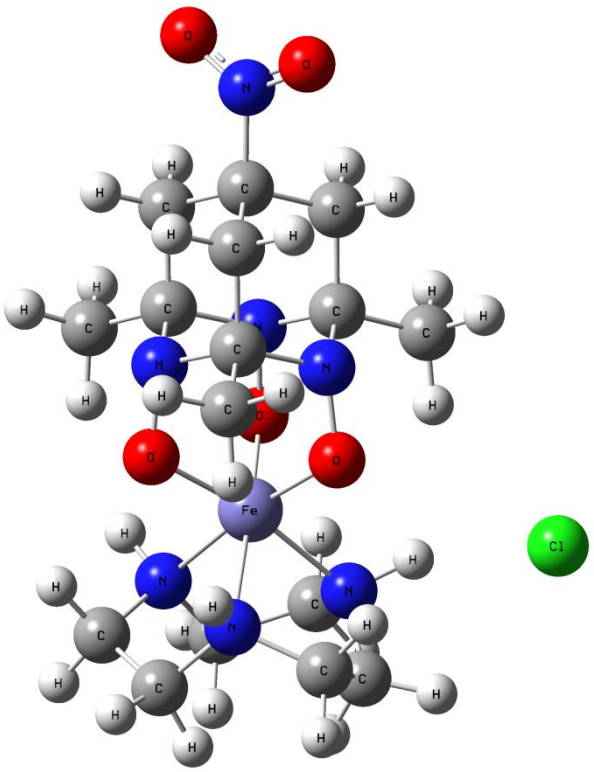
7-Mn(Cl)

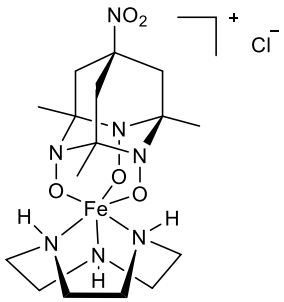
Charge 0; multiplicity 4

Mn	15.12729800	6.13508300	5.58847800
N	13.62756200	4.16468900	6.84331400
O	13.48029400	2.07942000	11.19042800
O	13.93896000	4.69282000	5.58459800
O	12.67338700	4.00067600	11.82484500
O	14.23895700	7.05412700	6.95493300
N	15.79365600	4.71729400	7.88825100
O	16.34975900	5.30546800	6.74570400
N	13.89771000	6.28598000	8.07286000
N	16.47634200	7.76175900	5.27538700
N	14.11058000	7.16382800	4.04415300
N	16.20612700	5.41000400	3.89265300
C	14.84880400	3.62008800	7.51260800
C	15.12237000	5.74502600	8.74044900
C	16.08669400	6.87087100	9.07547900
H	16.95598100	6.45747200	9.60525200
H	15.58356000	7.59575800	9.73015300
H	16.43841700	7.39216200	8.18080800
C	12.95117500	5.19131000	7.69675400
C	11.73940700	5.76101500	6.98213400
H	11.99232500	6.23731500	6.02958000
H	11.25303600	6.50245600	7.63159000
H	11.02655600	4.94898400	6.78012600
C	12.49637500	4.50165800	8.99110600
H	11.98976300	5.24130100	9.62430700
H	11.78799100	3.70220000	8.73293300
C	13.71778200	3.92867300	9.70322700
N	13.25486300	3.27749700	11.01159700
C	14.68114900	5.06198800	10.04315200

H	15.57155100	4.67335500	10.55682200
H	14.19213700	5.80733700	10.68352000
C	14.40658500	2.91843000	8.80768600
H	13.72732900	2.09713200	8.54430000
H	15.29621100	2.49923800	9.29598100
C	15.53926200	2.60825400	6.61374100
H	14.85110200	1.77553100	6.41285800
H	16.42917700	2.21670100	7.12556300
H	15.84477000	3.04444500	5.65920700
C	15.88591900	8.82095000	4.40375000
H	16.37226400	8.77391400	3.42046200
H	16.09440700	9.81565200	4.82188400
C	14.38372000	8.60146000	4.27460600
H	13.87059100	8.87603200	5.20743500
H	13.97038000	9.22359300	3.46329100
C	14.50110400	6.68007000	2.68791800
H	15.15351800	7.42333900	2.21014100
H	13.59803800	6.58640800	2.06644700
C	15.20641700	5.33645700	2.79835300
H	14.49272600	4.54728400	3.07380400
H	15.67553600	5.06020400	1.83970400
C	17.40365400	6.24802300	3.58572900
H	17.18774400	6.84435900	2.68959700
H	18.26534300	5.60811900	3.35035100
C	17.72956500	7.15348500	4.76722800
H	18.15555000	6.57010100	5.59499400
H	18.46209600	7.92246300	4.47198300
H	16.65204600	8.15328200	6.20499400
H	16.51330600	4.46234400	4.12828200
H	13.06986200	7.02683300	4.11406800
Cl	11.03810900	7.03218300	3.54264000

DFT-D3 BP86/jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-2999.230811 E_0
Sum of electronic and zero-point Energies=	-2998.747620 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2998.718997 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2998.718053 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2998.798733 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.483191
Mulliken atom spin density	
Mn: 3.05	
Cartesian coordinates of V_{min}	
16.913416875667 4.237809354591 8.443904230834	





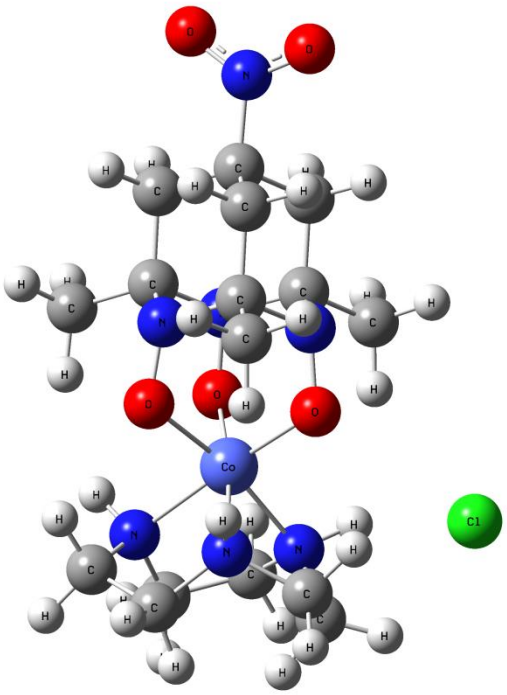
7-Fe(Cl)

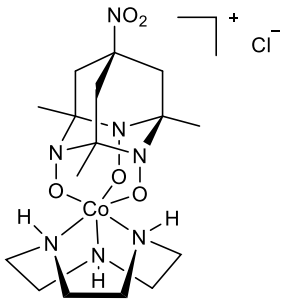
Charge 0; multiplicity 3

Fe	15.23884800	6.12283200	15.76941500
O	14.03141800	4.69965500	15.79438400
O	16.40923000	5.28159400	14.58991900
O	14.32759300	7.03512900	14.42487300
O	13.44748400	2.06340500	10.21734900
O	12.59343200	3.97494900	9.61577600
N	13.69173300	4.17114300	14.55879200
N	15.82658300	4.70061500	13.47311800
N	13.95294100	6.27542900	13.32634500
N	13.20961700	3.25724200	10.40780300
N	14.13952500	7.02221800	17.29856400
H	13.15073300	6.82095700	17.12182300
N	16.29527300	5.33788100	17.39155100
H	16.63434100	4.41342600	17.10940500
N	16.49587300	7.74522400	16.10120900
H	16.71915800	8.27932000	15.22635900
C	13.70673800	3.91147300	11.70235000
C	14.41048700	2.90023400	12.58558500
H	15.28544600	2.47364200	12.07769800
H	13.73310200	2.08388200	12.86897200
C	14.88722200	3.60397300	13.86550300
C	15.58926600	2.59880500	14.76242200
H	15.91009400	3.04705300	15.70694100

H	16.47031200	2.19996400	14.24125100
H	14.90249200	1.77015200	14.98379200
C	14.67192200	5.03460100	11.33390600
H	14.17437800	5.78075700	10.70098400
H	15.54651300	4.63600100	10.80106700
C	15.15140600	5.72309900	12.61921600
C	16.11728100	6.83773800	12.26152200
H	15.61962700	7.53898100	11.57697900
H	16.99087200	6.40816100	11.75133500
H	16.45839500	7.40050700	13.13611500
C	12.50732500	4.50228000	12.43730200
H	11.79483300	3.71326900	12.71622700
H	11.99621100	5.24357800	11.80979600
C	12.99847000	5.19369900	13.71571100
C	11.81095200	5.78049400	14.46000800
H	11.13036400	4.97070600	14.75661700
H	11.27383900	6.47155500	13.79582600
H	12.12172200	6.32823100	15.35432900
C	14.51889600	6.47662200	18.63710800
H	13.62022500	6.30919200	19.24703900
H	15.12750400	7.22778600	19.15708400
C	15.29500600	5.17522700	18.47505200
H	15.77385600	4.89170700	19.42694100
H	14.62422500	4.36072600	18.16945000
C	17.46316700	6.20042500	17.74460100
H	18.34084400	5.57751800	17.96752900
H	17.21978700	6.75592600	18.65979300
C	17.76262200	7.15671900	16.59829200
H	18.46671900	7.94101300	16.92394400
H	18.21892800	6.61992100	15.75433000
C	15.87740800	8.72337900	17.04452400
H	16.07508800	9.74381300	16.68341000
H	16.35213100	8.62755300	18.03041700
C	14.37881800	8.47911900	17.14068600
H	13.94098900	9.05209800	17.97495300
H	13.87869600	8.78488700	16.21106600
Cl	17.42043100	9.87851600	13.99694100

DFT-D3 BP86/jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-3112.005560 E_0
Sum of electronic and zero-point Energies=	-3111.522119 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-3111.493597 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-3111.492652 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-3111.572685 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.483441
Mulliken atom spin density	
Fe: 1.83	
Cartesian coordinates of V_{min}	
12.841808908116 3.201782738459 14.982842151707	





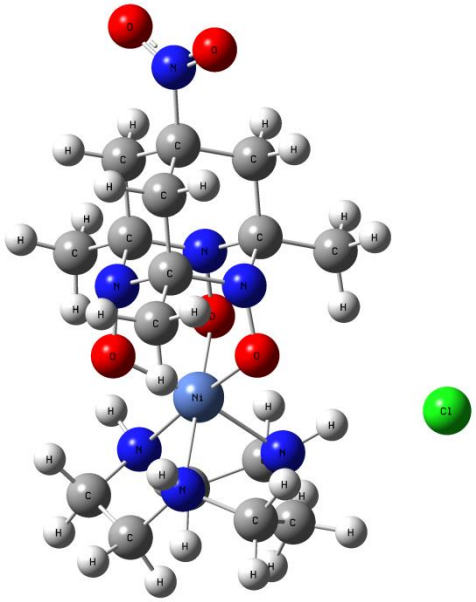
7-Co(Cl)

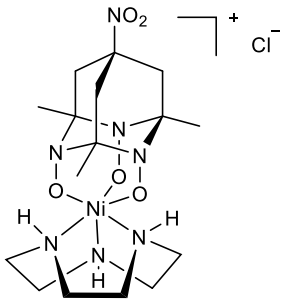
Charge 0; multiplicity 2

O	14.04173100	4.67825000	15.80217900
O	16.42033800	5.27380200	14.59704400
O	14.28303400	7.04200800	14.44688400
O	13.45885700	2.07635700	10.21703800
O	12.59751800	3.98909600	9.62982000
N	13.72708300	4.19258400	14.57474600
N	15.82735300	4.71093200	13.49722700
N	13.93136700	6.27954400	13.36005900
N	13.21545500	3.26751400	10.41686100
N	14.16228200	7.04523600	17.23715700
H	13.18486300	6.83545100	17.01586200
N	16.27786900	5.35871400	17.34971800
H	16.59819400	4.44118200	17.02750200
N	16.52263600	7.74909800	16.10933200
H	16.74867800	8.27900400	15.23020900
C	13.70699100	3.91324800	11.71790900
C	14.41804600	2.89893800	12.59122700
H	15.29498400	2.48196200	12.07861300
H	13.74615000	2.07531500	12.86737000
C	14.89377500	3.59126100	13.87492100
C	15.59780100	2.58485100	14.76517700
H	15.91948200	3.02994100	15.71019700
H	16.47690700	2.18928900	14.23853000
H	14.91259700	1.75435200	14.98497800
C	14.66157300	5.04875800	11.36168200

H	14.15733400	5.79514200	10.73444300
H	15.53985600	4.66307400	10.82539700
C	15.13447500	5.73169200	12.65303000
C	16.09160200	6.85638100	12.30209400
H	15.58860400	7.55891800	11.62298000
H	16.96927500	6.43836600	11.78957900
H	16.42765200	7.41406300	13.18154800
C	12.50192100	4.48432700	12.45813300
H	11.79788900	3.68509200	12.73014700
H	11.98174800	5.22456100	11.83667400
C	12.98278200	5.17394300	13.73940000
C	11.78881300	5.73376800	14.49027800
H	11.12338000	4.91054200	14.78460700
H	11.23781300	6.41738800	13.83000100
H	12.09115700	6.28180400	15.38644400
C	14.49625600	6.48469200	18.58085400
H	13.57891000	6.31839500	19.16261400
H	15.09626900	7.22593600	19.12454900
C	15.26890800	5.18064300	18.41998800
H	15.73721600	4.88713300	19.37394400
H	14.60003700	4.37205300	18.09764000
C	17.45958500	6.18624900	17.73819100
H	18.32098400	5.54085000	17.96070300
H	17.21476500	6.73073100	18.65987300
C	17.78460700	7.15482000	16.61069300
H	18.48459600	7.93499400	16.95408700
H	18.24768900	6.62797900	15.76457700
C	15.90379700	8.73346500	17.04789300
H	16.12771900	9.75216800	16.69789100
H	16.35637900	8.61894300	18.04210400
C	14.40245200	8.50353400	17.10554300
H	13.94678000	9.06666600	17.93698100
H	13.92649400	8.82228300	16.16801600
Cl	17.49373800	9.84391000	14.01349600
Co	15.29135500	6.19481000	15.76466200

DFT-D3 BP86/jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-3231.080925 E_0
Sum of electronic and zero-point Energies=	-3230.597827 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-3230.569029 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-3230.568084 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-3230.648777 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.483097
Mulliken atom spin density	
Co: 0.58	
Cartesian coordinates of V_{min}	
12.862819452702 3.197918873738 15.169331479384	





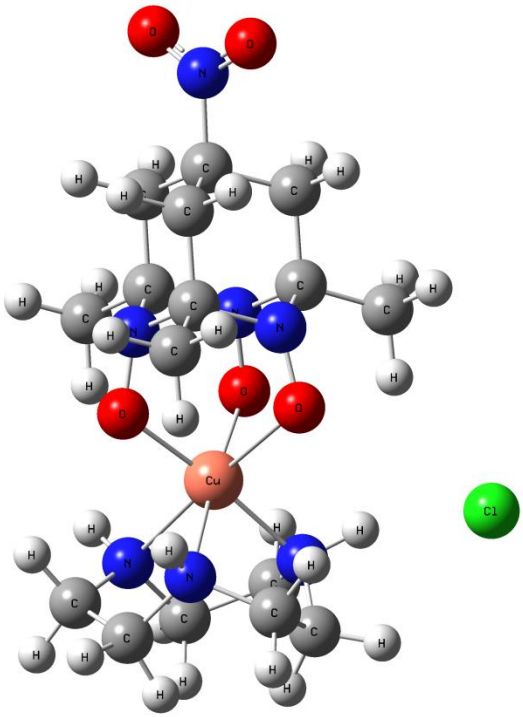
7-Ni(Cl)

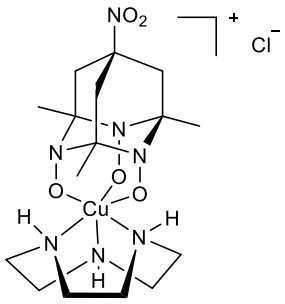
Charge 0; multiplicity 1

O	14.03711800	4.66682600	15.79218400
O	16.41470900	5.30066300	14.56387500
O	14.28889400	7.03137000	14.42385300
O	13.47070100	2.06958300	10.21427700
O	12.58822500	3.97251300	9.62631800
N	13.72161100	4.17791900	14.57419400
N	15.81587300	4.73808400	13.49441700
N	13.94677500	6.26555100	13.36788300
N	13.21749200	3.25896000	10.41155700
N	14.13986900	7.05471500	17.28535300
H	13.15680900	6.85470600	17.08197300
N	16.26698900	5.33137000	17.40538500
H	16.58059600	4.40508400	17.10328700
N	16.51815200	7.72492700	16.10153300
H	16.74248900	8.23594800	15.21603700
C	13.71175000	3.91369700	11.70723600
C	14.43425500	2.90740100	12.58086400
H	15.31164900	2.49540600	12.06466400
H	13.76945700	2.07935900	12.86102300
C	14.90781600	3.60401600	13.86199200
C	15.62812200	2.60781400	14.75065300
H	15.93162900	3.05498900	15.70092400
H	16.52030700	2.23469200	14.22970700
H	14.95926900	1.76157000	14.95950100
C	14.65780000	5.05231600	11.33841000
H	14.14533500	5.79294500	10.71052100
H	15.53452900	4.66879400	10.79750600
C	15.13681100	5.74351300	12.61839500

C	16.08424500	6.87204000	12.26480000
H	15.57653300	7.56489200	11.57917900
H	16.96485600	6.45644900	11.75530600
H	16.41551000	7.43865500	13.14023000
C	12.50712900	4.48285900	12.45015800
H	11.80675200	3.68165900	12.72584500
H	11.98222800	5.21898300	11.82745900
C	12.98694300	5.17414300	13.72946800
C	11.79727700	5.73980000	14.48186700
H	11.11837900	4.92095700	14.75634500
H	11.26037800	6.44412600	13.83182100
H	12.10473700	6.26509800	15.39004900
C	14.49762600	6.50701500	18.62550800
H	13.59255300	6.35576000	19.23064000
H	15.11687700	7.24775400	19.14812400
C	15.25282600	5.18942700	18.47341500
H	15.70983800	4.89744100	19.43388300
H	14.57045800	4.38806400	18.15879800
C	17.44787000	6.17070500	17.75638800
H	18.31473500	5.53404600	17.98393600
H	17.21322200	6.73616900	18.66803200
C	17.76862000	7.11671600	16.60460400
H	18.48994100	7.88610300	16.92930900
H	18.21584200	6.56660700	15.76435900
C	15.90818800	8.72101500	17.02773500
H	16.12434200	9.73519900	16.65916000
H	16.37093900	8.62703400	18.01969000
C	14.40331000	8.50142000	17.11217400
H	13.96800500	9.09595700	17.93308700
H	13.91752900	8.80234700	16.17341500
Cl	17.48580900	9.84580900	13.99028700
Ni	15.24987000	6.14701600	15.82270800

DFT-D3 BP86/jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-3356.614291 E_0
Sum of electronic and zero-point Energies=	-3356.130486 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-3356.101832 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-3356.100887 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-3356.180358 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.483805
Cartesian coordinates of V_{min}	
12.867715686449 3.179674832897 15.096043496676	





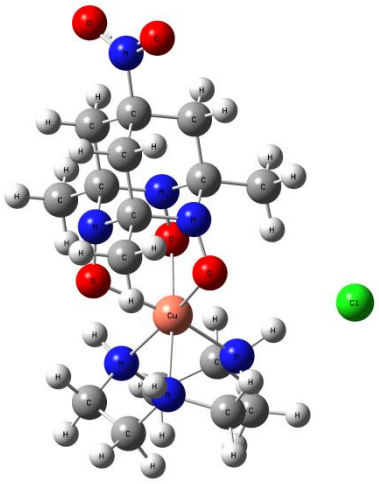
Low spin 7-Cu(Cl)

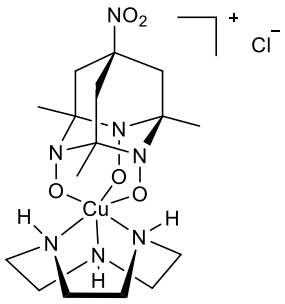
Charge 0; multiplicity 2

O	13.97228200	4.71210300	15.68848500
O	16.37616800	5.42705000	14.38877200
O	14.07954700	7.17748000	14.14228700
O	13.49051900	1.96738700	10.20101100
O	12.54084200	3.81916000	9.55539200
N	13.72008300	4.24147100	14.47599000
N	15.74220000	4.84039400	13.38469700
N	13.82337700	6.29174900	13.19811300
N	13.19841600	3.15334000	10.35835500
N	14.18438200	7.04765500	17.36544600
H	13.19805000	6.86107200	17.16861300
N	16.38336200	5.24792000	17.70695500
H	16.72102700	4.30063500	17.53534400
N	16.61628200	7.66611600	16.21752400
H	16.89607700	8.14598700	15.32929100
C	13.67850100	3.86850500	11.62845100
C	14.44826400	2.91525900	12.52286800
H	15.33602500	2.52296600	12.00927200
H	13.81977500	2.07080200	12.83578600
C	14.90878900	3.66112700	13.77692100
C	15.68049300	2.74021200	14.69973000
H	16.02005400	3.26303700	15.59852900
H	16.55350100	2.34548400	14.16256400
H	15.03470000	1.90154700	14.99284400
C	14.57947000	5.02838100	11.21152800
H	14.03767200	5.72451800	10.55811800

H	15.46689600	4.65624300	10.68046800
C	15.03460600	5.79020300	12.45922600
C	15.94468600	6.93847300	12.08157000
H	15.40494300	7.61212000	11.40136800
H	16.82445100	6.54108000	11.55659800
H	16.27945500	7.51380800	12.95180900
C	12.45507900	4.40866200	12.36442900
H	11.79504600	3.58575400	12.67351300
H	11.89113000	5.09798300	11.72279300
C	12.91235700	5.16866000	13.61175400
C	11.72176700	5.70504000	14.37917100
H	11.08512700	4.86654700	14.69237300
H	11.14025900	6.36651000	13.72272800
H	12.03588000	6.26851300	15.26263100
C	14.53089800	6.54768900	18.72203400
H	13.61777500	6.42527200	19.32331500
H	15.14040600	7.31147900	19.22362000
C	15.28821400	5.21728500	18.68395500
H	15.63124300	4.99198100	19.71241000
H	14.60878700	4.40783100	18.37612200
C	17.50683500	6.15859800	17.99814200
H	18.41341800	5.59714200	18.27419700
H	17.25225100	6.78116800	18.86848800
C	17.82935700	7.04236400	16.78878400
H	18.56984500	7.81084300	17.07519800
H	18.27533900	6.43314800	15.98757900
C	15.98193700	8.69558700	17.08755300
H	16.20474500	9.69649000	16.68717100
H	16.42120900	8.64388200	18.09338200
C	14.47286900	8.48565600	17.14804600
H	14.02851000	9.11435500	17.93948100
H	14.01174500	8.76240300	16.18949600
Cl	17.67314600	9.60590400	13.98429800
Cu	15.28833300	6.14597300	15.85472000

DFT-D3 BP86/jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-3488.778545 E_0
Sum of electronic and zero-point Energies=	-3488.297799 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-3488.267813 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-3488.266869 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-3488.350506 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.480747
Mulliken atom spin density	
Cu: 0.058; summed for nitrogen and oxygen atoms of three N-O fragments: 0.95	





High spin 7-Cu(Cl)

Charge 0; multiplicity 4

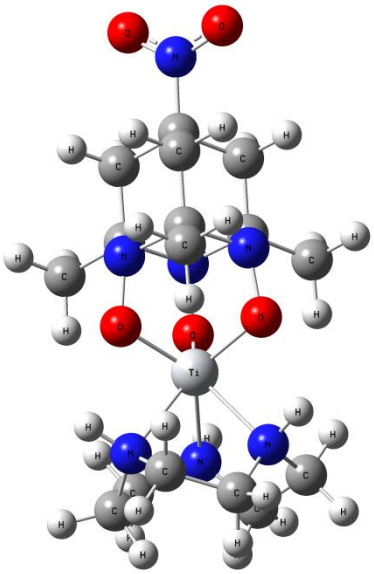
O	14.04564900	4.50565300	15.71008400
O	16.46750100	5.23025600	14.39695100
O	14.11669700	7.01034400	14.32033000
O	13.44577800	2.03434800	10.08823300
O	12.51886600	3.92990700	9.54651700
N	13.76024600	4.09180600	14.47275600
N	15.79536200	4.71342900	13.36017800
N	13.84615600	6.19008300	13.29290000
N	13.17371300	3.21524800	10.30932900
N	14.13520100	7.26798000	17.38536400
H	13.14379500	7.13938600	17.17424300
N	16.26091900	5.38488700	17.56226900
H	16.52250700	4.44190300	17.26802200
N	16.63742700	7.79322300	16.25201600
H	16.90361700	8.28357000	15.35542000
C	13.67329300	3.85678500	11.61053600
C	14.44555500	2.85303500	12.44520500
H	15.32205200	2.47849300	11.90027300
H	13.81222600	1.99951100	12.72180900
C	14.93097800	3.53664000	13.72852800
C	15.70216400	2.55861200	14.59147200
H	16.06569700	3.03215900	15.50801400
H	16.55915900	2.17486600	14.02111600
H	15.04806800	1.71655100	14.85671400
C	14.57336000	5.03611200	11.24840200
H	14.02407500	5.76958500	10.64408100
H	15.45162600	4.69180100	10.68447900
C	15.05244200	5.72047900	12.53513600
C	15.95231800	6.89308500	12.20136100
H	15.39921000	7.60344200	11.57120000
H	16.82496300	6.53017900	11.64070600
H	16.30153900	7.41833200	13.09640300

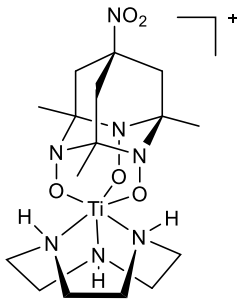
C	12.46076600	4.35857200	12.39054900
H	11.80299300	3.52097600	12.66301900
H	11.89037700	5.08359100	11.79562000
C	12.94025000	5.04749300	13.67119400
C	11.75943000	5.55035700	14.47762500
H	11.10928400	4.70261600	14.73448000
H	11.18721200	6.26544400	13.87096000
H	12.08631300	6.04263600	15.39829300
C	14.47213200	6.68127400	18.69794800
H	13.56484800	6.54093400	19.30423100
H	15.11575500	7.38447800	19.24411700
C	15.18166900	5.32473100	18.55861700
H	15.55440200	5.01939200	19.55297300
H	14.47121200	4.56100200	18.21204200
C	17.45701600	6.17909900	17.93258500
H	18.30443000	5.52160400	18.17781500
H	17.22909600	6.75710700	18.83900700
C	17.83785300	7.10585300	16.78272000
H	18.59212000	7.84298600	17.10905700
H	18.26608700	6.52887700	15.95046300
C	16.03705000	8.80236700	17.16659600
H	16.32757200	9.80725300	16.82351900
H	16.45449200	8.66664800	18.17336600
C	14.51966400	8.68129900	17.19267200
H	14.10854600	9.33767900	17.98089200
H	14.09766900	9.00022500	16.22851300
Cl	17.71513200	9.62794900	14.03411600
Cu	15.32287400	6.29186600	15.82826100

DFT-D3 BP86/jorgeTZP, solvent methanol, SMD model	
Total electronic energy=	-3488.745052 E_0
Sum of electronic and zero-point Energies=	-3488.266082 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-3488.235697 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-3488.234753 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-3488.319731 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.478970
Mulliken atom spin density	
Cu: 0.58; summed for nitrogen and oxygen atoms of three N-O fragments: 1.92	

9.3 DFT calculations of ETS-NOCV, MO and NBO

The extended transition state with natural orbitals for chemical valence approach (ETS-NOCV[31]) were calculated for **7-Ti**$^{+}$ and **7-Ni**$^{+}$ cations with Multiwfn (consult section 3.26 of the manual). Wavefunctions were calculated in gas phase. Each molecule was divided into two fragments: (TACN)M^{4+} and triply deprotonated **1a**. According to wavefunction stability calculations, ground electronic state of anion of **1a** (charge in fragment = -3) is triplet with excess of spin density mostly located on NO_2 group. So broken symmetry solution with stabilized wavefunction for **1a** fragment was used in ETS-NOCV analysis. Since final complexes are singlets, ETS-NOCV pair with the highest value ΔE_{orb} corresponds to electron transfer from NO_2 group. As one of the fragments is an open-shell, the ETS-NOCV analysis was automatically conducted in open-shell form. In this case, the alpha and beta NOCV orbitals are solved independently, and their energies are estimated using alpha and beta Fock matrices respectively. Also for ETS-NOCV analysis atoms must be numbered in a special way, so their numbers and Cartesian coordinates are specially provided below.





7-Ti^{+} (Cartesian coordinates for ETS-NOCV)

Charge 1; multiplicity 1

N	14.50004300	7.86639200	16.88362300
H	13.61569200	8.08618500	16.41273900
N	15.39518000	5.45820000	17.85618600
H	15.23712000	4.44727400	17.78400000
N	17.07826300	7.05662300	16.38858700
H	17.60721500	7.08417100	15.51017100
C	14.26902500	7.59020500	18.32647600
H	13.32698000	8.04017400	18.67179100
H	15.07243000	8.06419500	18.90771900
C	14.25283000	6.08115300	18.56671900
H	14.26096100	5.86127500	19.64797800
H	13.33802300	5.63728200	18.14507100
C	16.73766900	5.73705600	18.43187800
H	17.11043000	4.87702800	19.00683600
H	16.64890400	6.57165800	19.14149300
C	17.71605900	6.08788000	17.31177600
H	18.66346900	6.46838600	17.73030200
H	17.95236000	5.19243200	16.71674500
C	16.89083000	8.42940300	16.92870900
H	17.64868700	9.12015700	16.53158500
H	17.03514900	8.40096500	18.01790100
C	15.48839300	8.93089300	16.58691400
H	15.27021500	9.86823400	17.12665700
H	15.41082900	9.14288500	15.50952800
Ti	15.16171800	6.05455200	15.66886100
O	14.62264100	4.26157200	15.71894200
O	16.33147600	5.91540800	14.21275000
O	13.68594200	6.72404000	14.72929600
O	13.80767500	2.21479600	9.91985800

O	12.23319200	3.73305900	9.79290100
N	14.22124800	3.78007300	14.43331500
N	15.73659000	5.23866000	13.10208800
N	13.39655800	5.95943100	13.55545100
N	13.20857600	3.20674200	10.32528500
C	13.71028100	3.87042400	11.62357300
C	14.91294000	3.13419500	12.18509800
H	15.74576400	3.13428700	11.47070700
H	14.66340600	2.09232100	12.42213200
C	15.36993700	3.83895400	13.47764400
C	16.57593400	3.11108100	14.05283000
H	16.92962700	3.57249500	14.97985100
H	17.39130300	3.12989100	13.31859100
H	16.30067400	2.07001600	14.26448600
C	14.08779000	5.31512600	11.31193400
H	13.22448600	5.85759500	10.90640600
H	14.91026300	5.35535000	10.58406500
C	14.55103600	6.00377100	12.60741000
C	14.93602500	7.44501300	12.30696400
H	14.06228000	7.97538700	11.90753900
H	15.74150300	7.45518600	11.56158600
H	15.28474000	7.96935200	13.20177700
C	12.57462400	3.85740900	12.64180200
H	12.28490100	2.82690300	12.89074000
H	11.70005500	4.38928900	12.24652300
C	13.04670000	4.55491000	13.92952000
C	11.92228900	4.54335500	14.95486500
H	11.65207700	3.50420600	15.18191200
H	11.05062000	5.06477800	14.53931600
H	12.21331400	5.03956100	15.88564300

Table S30. Characteristics of selected NOCV pairs of **7-Ti$^+$**.

NOCV pair	ΔE kcal/mol	Eigenvalue
α_1	-90.48	0.94123
α_2	-35.67	0.48775
α_3	-26.13	0.43359
α_4	-27.19	0.42484
β_1	-35.13	0.48594
β_2	-33.96	0.48218
β_3	-27.23	0.42427
β_4	-27.32	0.42264

Table S31. Contribution of selected atoms to selected NOCV pairs of **7-Ti$^+$**.

Atom	NOCV pair α_2	NOCV pair β_1	NOCV pair β_2
31 (N)	0.04 %*	0.01 %	-0.90 %
32 (N)	-0.01 %	-0.13 %	-0.72 %
33 (N)	-0.37 %	-0.45 %	0.31 %
Overall electron donation: 0.011e$^-$			

*- + sign: atom A gain electron; – sign: atom A lost electron due to the interaction characterized by NOCV pair.

Table S32. Contribution of Ti to selected NOCV pairs of **7-Ti$^+$**.

Atom	NOCV pair α_3	NOCV pair α_4	NOCV pair β_3	NOCV pair β_4
25 (Ti)	-8.87 %	-4.35 %	-4.49 %	-4.72 %
Overall electron donation: 0.0959e$^-$				

*- + sign: atom A gain electron; – sign: atom A lost electron due to the interaction characterized by NOCV pair.

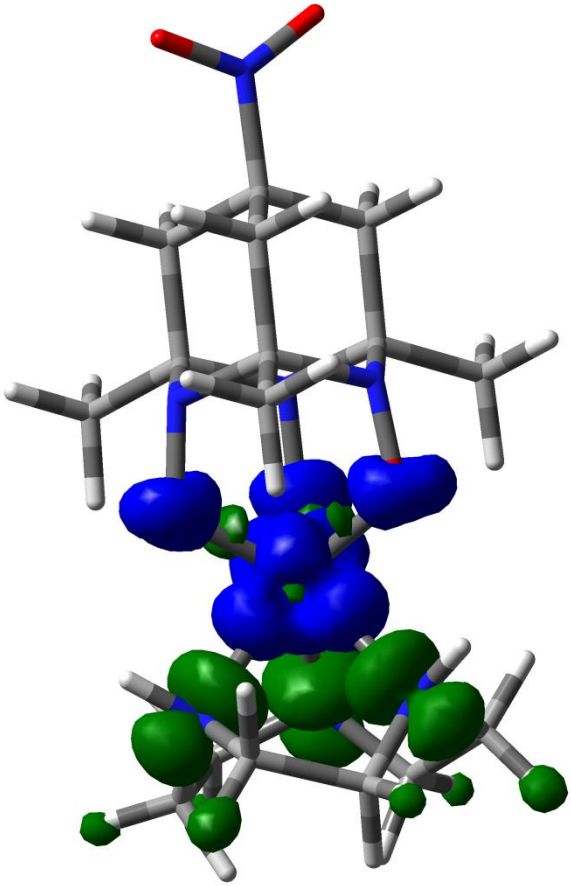


Figure S9. Visualization of sum of α_3, α_4, β_3, β_4 NOCV pairs density isosurface for **7-Ti**$^+$. Isovalue = 0.005.

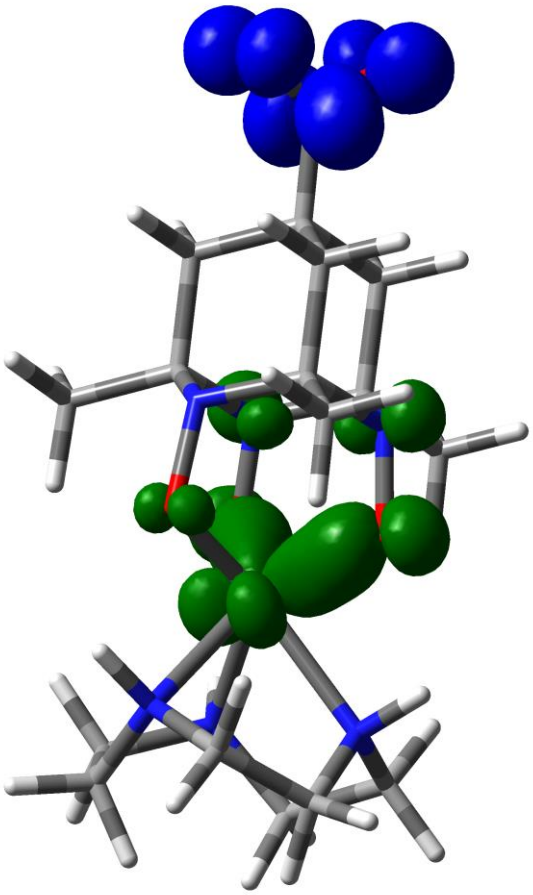


Figure S10. Visualization of α_1 NOCV pair density isosurface for **7-Ti$^+$**. Isovalue = 0.005.

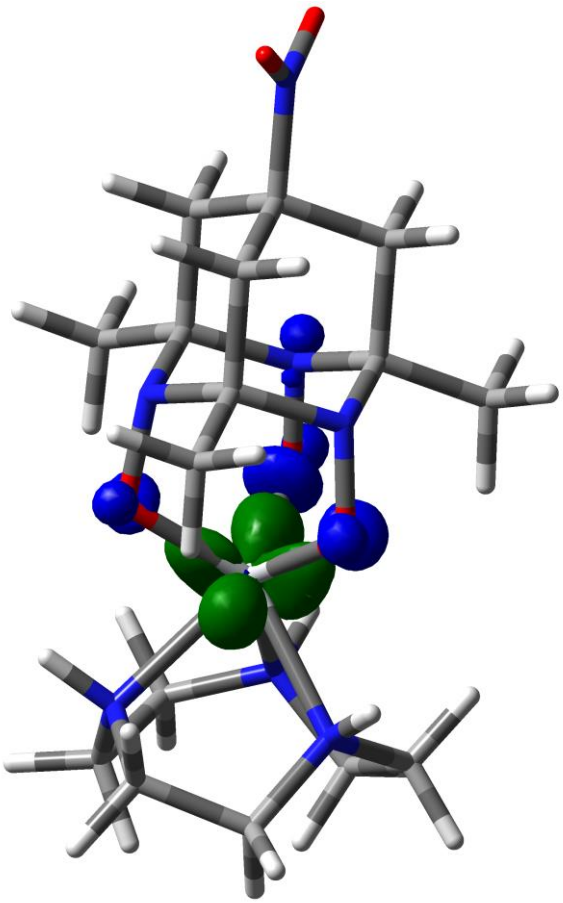


Figure S11. Visualization of α_2 NOCV pair density isosurface for **7-Ti**$^+$. Isovalue = 0.005.

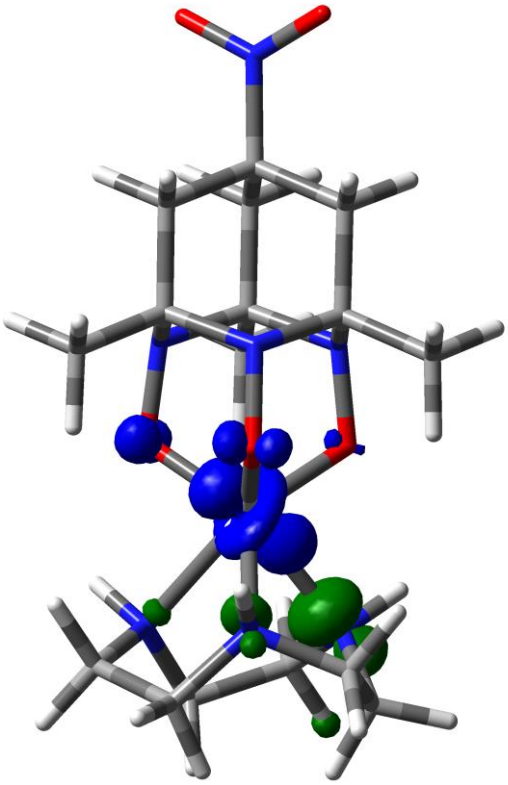


Figure S12. Visualization of α_3 NOCV pair density isosurface for **7-Ti$^+$**. Isovalue = 0.005.

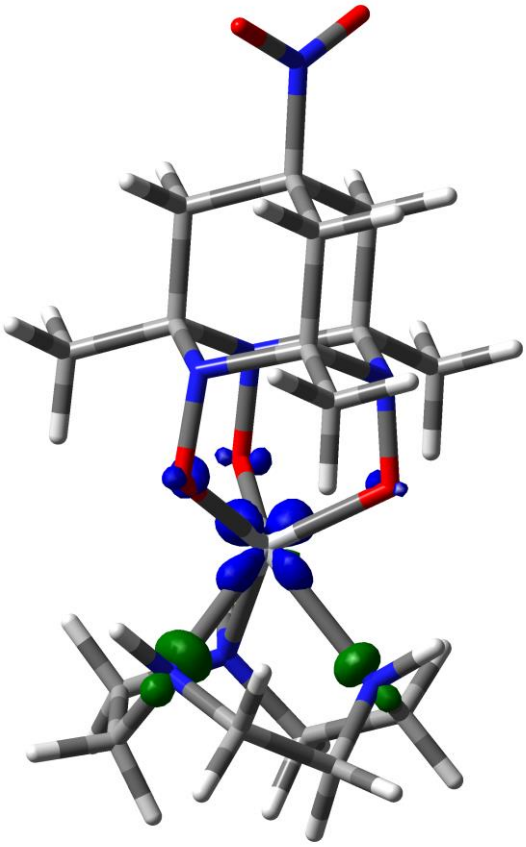


Figure S13. Visualization of α_4 NOCV pair density isosurface for **7-Ti**$^+$. Isovalue = 0.001.

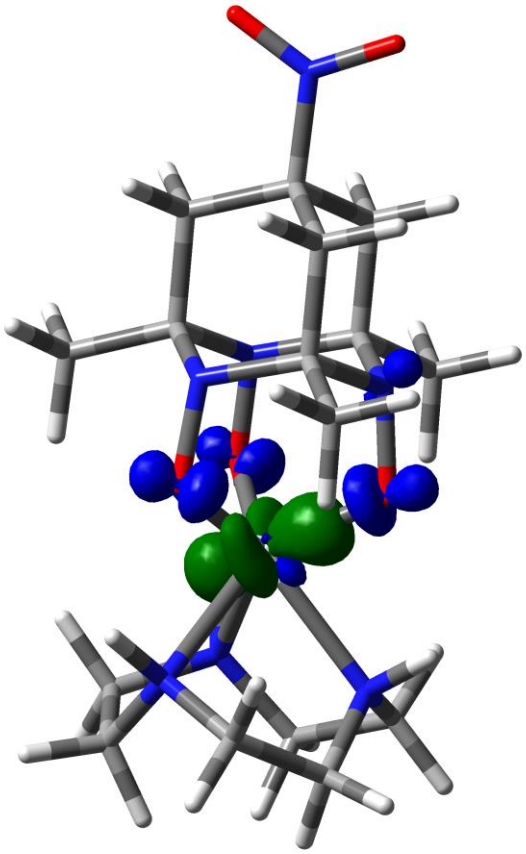


Figure S14. Visualization of β_1 NOCV pair density isosurface for **7-Ti**$^+$. Isovalue = 0.005.

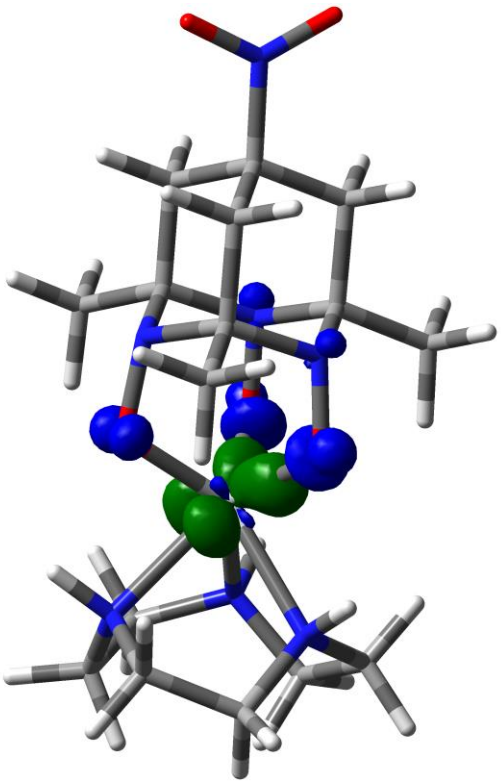


Figure S15. Visualization of β_2 NOCV pair density isosurface for **7-Ti**$^+$. Isovalue = 0.005.

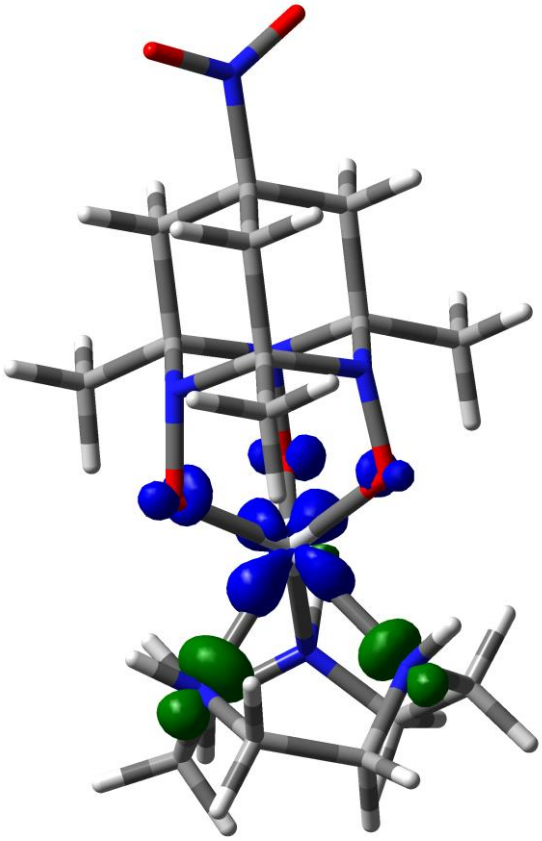


Figure S16. Visualization of β_3 NOCV pair density isosurface for **7-Ti**$^+$. Isovalue = 0.005.

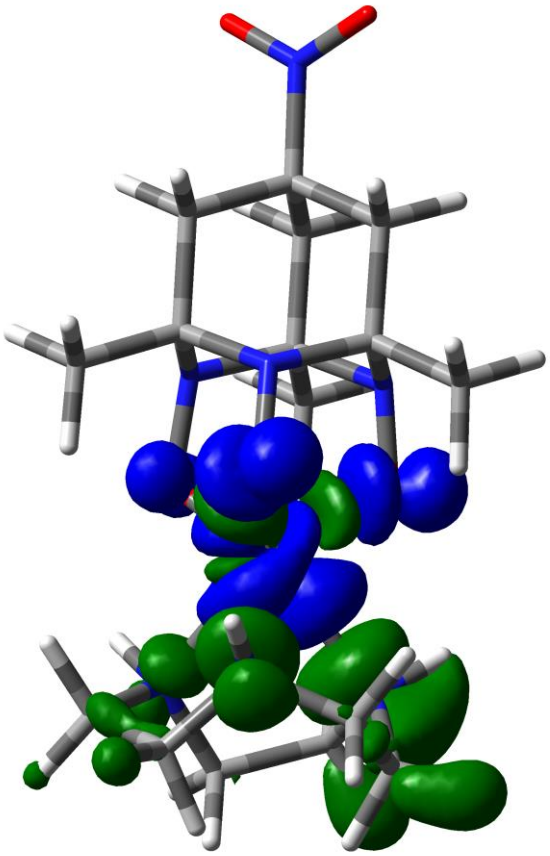
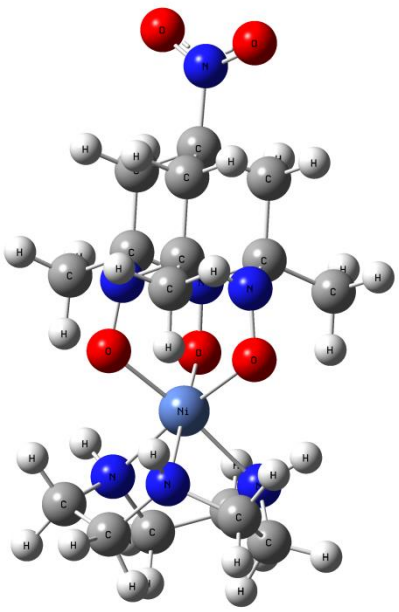
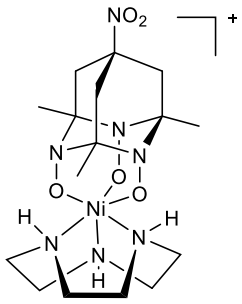


Figure S17. Visualization of β_4 NOCV pair density isosurface for **7-Ti**$^+$. Isovalue = 0.001.





7-Ni^{+} (Cartesian **coordinates for ETS-NOCV)**

Charge 1; multiplicity 1

N	14.13228700	7.06419900	17.30575900
H	13.15363000	6.84617800	17.10553900
N	16.27766100	5.32967600	17.43352500
H	16.58504600	4.40124900	17.13515700
N	16.51776200	7.72430600	16.07977700
H	16.66244400	8.11334900	15.14535900
C	14.51484100	6.53913100	18.64478200
H	13.63177500	6.40607200	19.28669200
H	15.15001200	7.28681100	19.14074400
C	15.26052800	5.20923000	18.50183300
H	15.69972800	4.91364800	19.47026700
H	14.56566700	4.42012300	18.18174700
C	17.45288900	6.18536200	17.75154200
H	18.33438300	5.57499600	17.99643600
H	17.22014800	6.77109200	18.65215900
C	17.77098000	7.11190000	16.57451300
H	18.51816800	7.86629300	16.87573800
H	18.18411700	6.53064700	15.73821700
C	15.89723400	8.74127900	16.97182800
H	16.09044800	9.76063400	16.60692800
H	16.37225600	8.66986000	17.96058300
C	14.38823200	8.50440600	17.08098800
H	13.96081600	9.13764800	17.87751100
H	13.89683300	8.76289100	16.13247100
Ni	15.23113000	6.11395200	15.82020100
O	14.02890000	4.63913800	15.78425600
O	16.40226200	5.28088300	14.57303500
O	14.28166000	7.01143400	14.43656600

O	13.45561400	2.08927800	10.20360000
O	12.62390000	4.02788500	9.60985900
N	13.72775200	4.17244200	14.57006100
N	15.81284300	4.73765600	13.50522100
N	13.94795600	6.25855700	13.38545800
N	13.22197300	3.28094700	10.38164800
C	13.71773000	3.92364700	11.69361400
C	14.43689300	2.90901800	12.56231100
H	15.30938900	2.49190800	12.04200600
H	13.77282600	2.07497700	12.82534400
C	14.90955700	3.58942000	13.85184200
C	15.63140800	2.59226200	14.73890300
H	15.93954000	3.04926900	15.68241500
H	16.52097400	2.21796200	14.21668500
H	14.96161700	1.75133100	14.95952300
C	14.66367900	5.06642000	11.34259100
H	14.15258000	5.80422900	10.70975400
H	15.54396700	4.69047500	10.80088400
C	15.13894800	5.74963200	12.62663300
C	16.08818300	6.88715300	12.29804600
H	15.56050100	7.64030800	11.69934900
H	16.93767700	6.49737700	11.72272700
H	16.47041300	7.35917700	13.20637000
C	12.51249300	4.48236000	12.44141300
H	11.81168100	3.67756200	12.70791700
H	11.98298300	5.21439500	11.81719800
C	12.97968400	5.16518500	13.72864800
C	11.79235000	5.72498700	14.48991000
H	11.12162500	4.90422000	14.77401900
H	11.24949400	6.43085200	13.84842400
H	12.11270200	6.24968300	15.39324200

Table S33. Characteristics of selected NOCV pairs of **7-Ni$^+$**.

NOCV pair	ΔE kcal/mol	Eigenvalue
α_1	-49.16	0.78024
α_2	-47.90	0.77757
α_3	-9.03	0.16206
β_1	-80.88	0.99606
β_2	-51.25	0.78412
β_3	-14.57	0.33168

Table S34. Contribution of selected atoms to selected NOCV pairs of **7-Ni$^+$**.

Atom	NOCV pair α_1	NOCV pair α_2	NOCV pair β_2	NOCV pair β_3
31 (N)	-3.80 %*	-0.56 %	-2.06 %	-
32 (N)	-0.35 %	-6.11 %	0.11 %	-
33 (N)	-2.23 %	-2.81 %	-1.99 %	-
Overall electron donation: 0.154e$^-$				
25 (Ni)	-	-	-	-7.82 %
Overall electron donation: 0.0259e$^-$				

*- + sign: atom A gain electron; – sign: atom A lost electron due to the interaction characterized by NOCV pair.

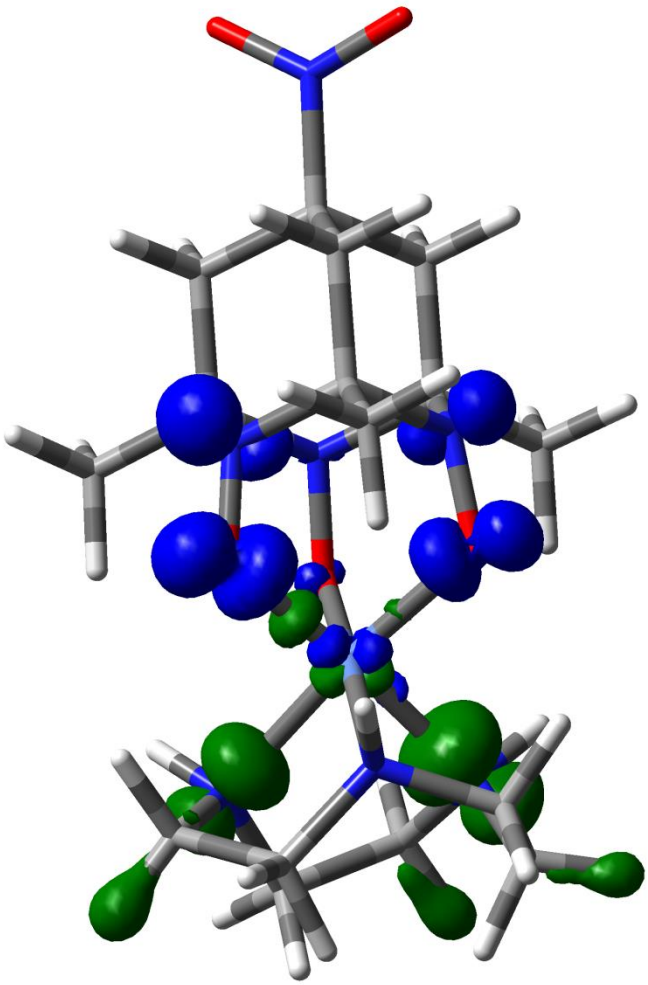


Figure S18. Visualization of α_1 NOCV pair density isosurface for **7-Ni**$^+$. Isovalue = 0.005.

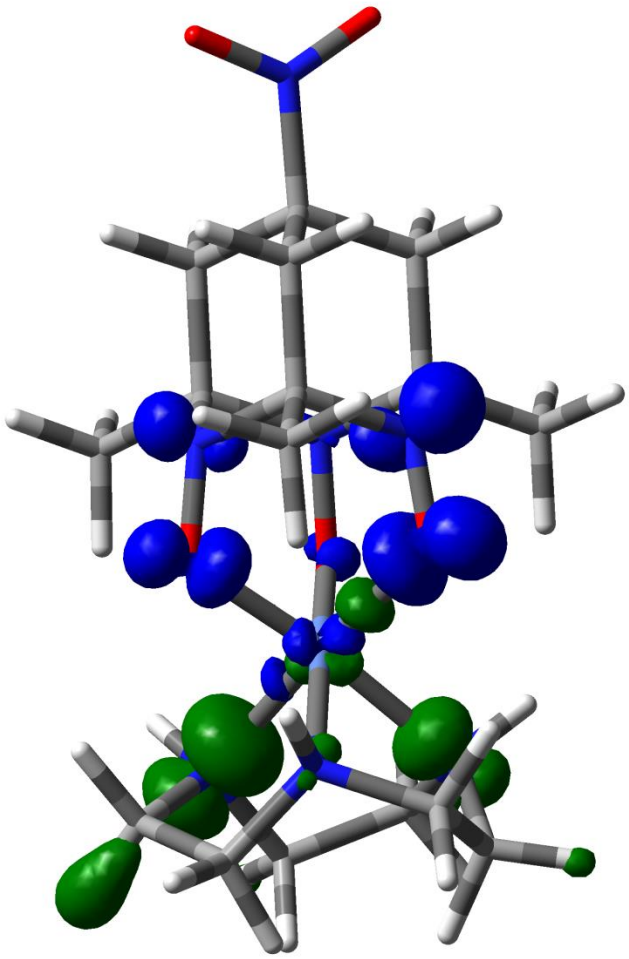


Figure S19. Visualization of α_2 NOCV pair density isosurface for **7-Ni**$^{+}$. Isovalue = 0.005.

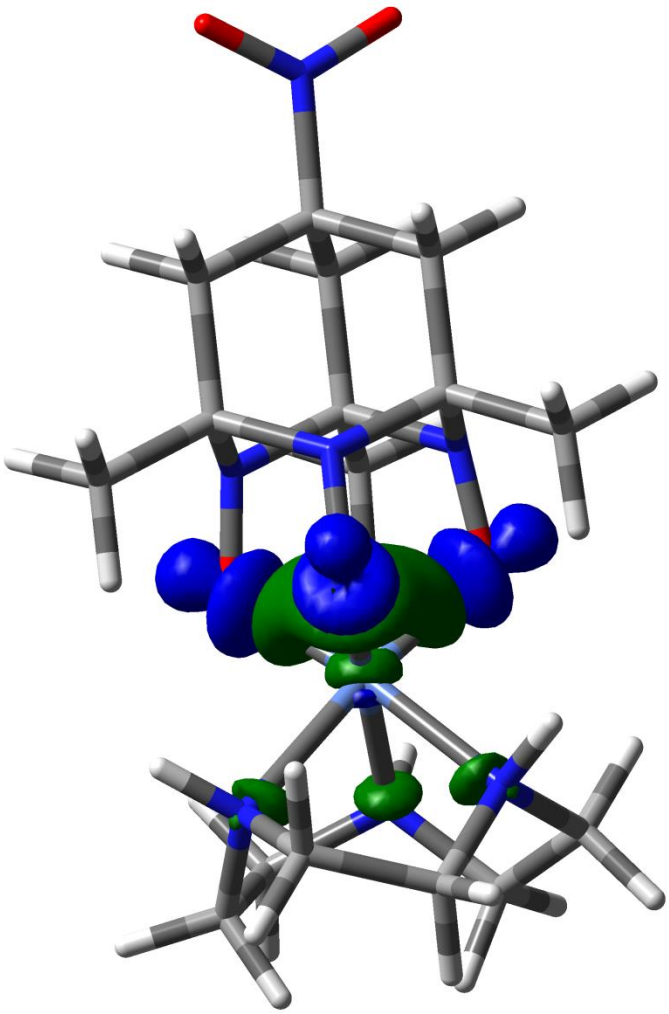


Figure S20. Visualization of α_3 NOCV pair density isosurface for **7-Ni**$^+$. Isovalue = 0.001.

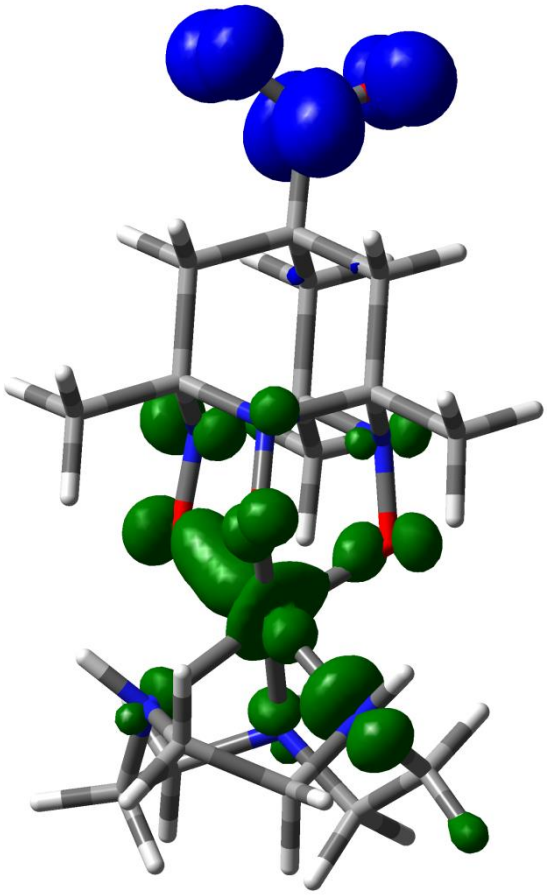


Figure S21. Visualization of β_1 NOCV pair density isosurface for **7-Ni**$^+$. Isovalue = 0.005.

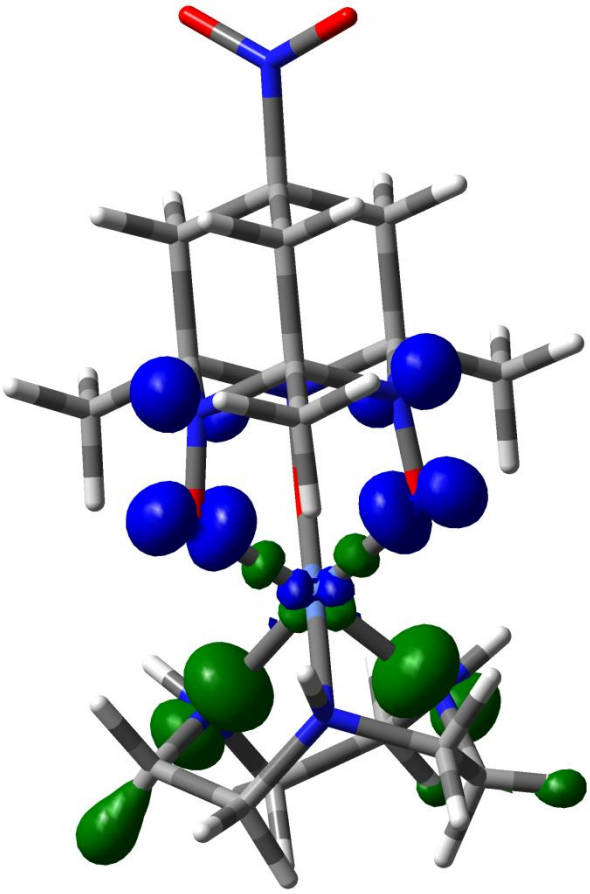


Figure S22. Visualization of β_2 NOCV pair density isosurface for **7-Ni**$^+$. Isovalue = 0.005.

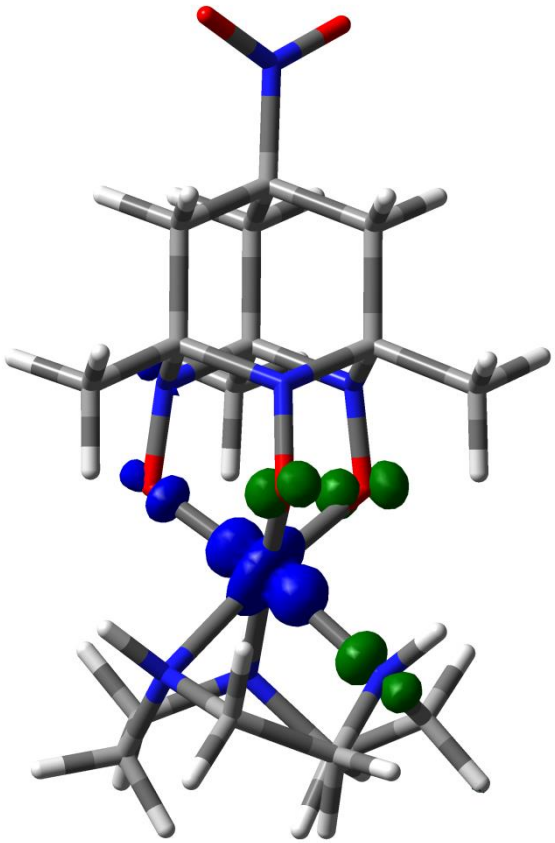


Figure S23. Visualization of β_3 NOCV pair density isosurface for **7-Ni$^+$**. Isovalue = 0.005.

MO orbitals analysis for cations **7-Ti**$^{+}$ and **7-Ni**$^{+}$:

 # sp BP86/Gen nosymm EmpiricalDispersion=GD3BJ scf=xqc

Orbital-by-orbital population analysis (orbital composition analysis) was done for cations **7-Ti**$^{+}$ and **7-Ni**$^{+}$ using Mulliken method for decomposition:

 # Pop=Orbitals=1 RBP86/Gen nosymm EmpiricalDispersion=GD3BJ scf=xqc

NBO orbitals analysis for cations **7-Ti**$^{+}$ and **7-Ni**$^{+}$:

 # sp BP86/Gen nosymm EmpiricalDispersion=GD3BJ scf=xqc Pop=NBORead

…

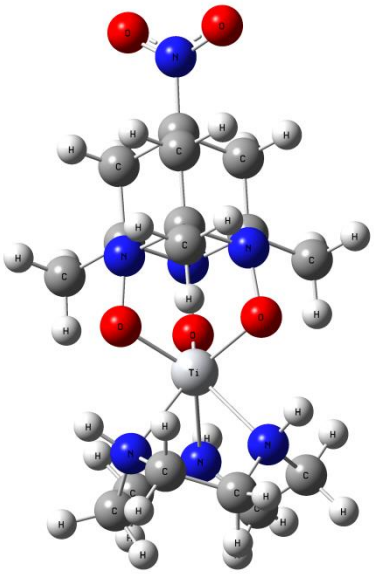
$nbo 3CBOND RESONANCE $end

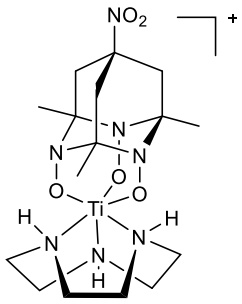
Table S35. Calculated E(2) in kcal/mol for N lone pairs of N-O fragments in **7-Ti**$^{+}$.

Donor NBO (i)	Acceptor NBO (j)	E(2)
116. LP (1) N 31	/***. BD*(1)Ti 25 - O 26	4.32
117. LP (1) N 32	/***. BD*(1)Ti 25 - O 27	4.33
118. LP (1) N 33	/***. BD*(1)Ti 25 - O 28	4.32

Table S36. Calculated E(2) in kcal/mol for N lone pairs of N-O fragments in **7-Ni**$^{+}$.

Donor NBO (i)	Acceptor NBO (j)	E(2)
114. LP (1) N 7	/***. BD*(1) O 2 -Ni 59	8.00
115. LP (1) N 8	/***. BD*(1) O 3 -Ni 59	7.99
113. LP (1) N 6	/***. BD*(1) O 1 -Ni 59	8.00





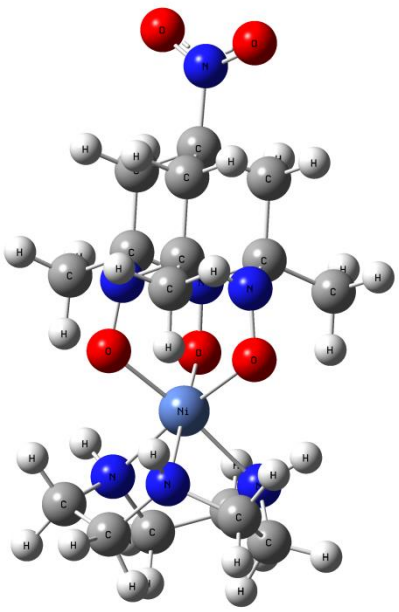
7-Ti^{+}

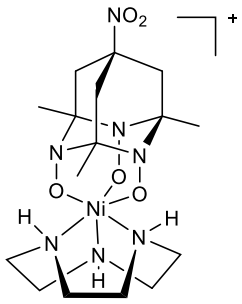
Charge 1; multiplicity 1

N	14.50004300	7.86639200	16.88362300
H	13.61569200	8.08618500	16.41273900
N	15.39518000	5.45820000	17.85618600
H	15.23712000	4.44727400	17.78400000
N	17.07826300	7.05662300	16.38858700
H	17.60721500	7.08417100	15.51017100
C	14.26902500	7.59020500	18.32647600
H	13.32698000	8.04017400	18.67179100
H	15.07243000	8.06419500	18.90771900
C	14.25283000	6.08115300	18.56671900
H	14.26096100	5.86127500	19.64797800
H	13.33802300	5.63728200	18.14507100
C	16.73766900	5.73705600	18.43187800
H	17.11043000	4.87702800	19.00683600
H	16.64890400	6.57165800	19.14149300
C	17.71605900	6.08788000	17.31177600
H	18.66346900	6.46838600	17.73030200
H	17.95236000	5.19243200	16.71674500
C	16.89083000	8.42940300	16.92870900
H	17.64868700	9.12015700	16.53158500
H	17.03514900	8.40096500	18.01790100
C	15.48839300	8.93089300	16.58691400
H	15.27021500	9.86823400	17.12665700
H	15.41082900	9.14288500	15.50952800
Ti	15.16171800	6.05455200	15.66886100
O	14.62264100	4.26157200	15.71894200
O	16.33147600	5.91540800	14.21275000
O	13.68594200	6.72404000	14.72929600
O	13.80767500	2.21479600	9.91985800

O	12.23319200	3.73305900	9.79290100
N	14.22124800	3.78007300	14.43331500
N	15.73659000	5.23866000	13.10208800
N	13.39655800	5.95943100	13.55545100
N	13.20857600	3.20674200	10.32528500
C	13.71028100	3.87042400	11.62357300
C	14.91294000	3.13419500	12.18509800
H	15.74576400	3.13428700	11.47070700
H	14.66340600	2.09232100	12.42213200
C	15.36993700	3.83895400	13.47764400
C	16.57593400	3.11108100	14.05283000
H	16.92962700	3.57249500	14.97985100
H	17.39130300	3.12989100	13.31859100
H	16.30067400	2.07001600	14.26448600
C	14.08779000	5.31512600	11.31193400
H	13.22448600	5.85759500	10.90640600
H	14.91026300	5.35535000	10.58406500
C	14.55103600	6.00377100	12.60741000
C	14.93602500	7.44501300	12.30696400
H	14.06228000	7.97538700	11.90753900
H	15.74150300	7.45518600	11.56158600
H	15.28474000	7.96935200	13.20177700
C	12.57462400	3.85740900	12.64180200
H	12.28490100	2.82690300	12.89074000
H	11.70005500	4.38928900	12.24652300
C	13.04670000	4.55491000	13.92952000
C	11.92228900	4.54335500	14.95486500
H	11.65207700	3.50420600	15.18191200
H	11.05062000	5.06477800	14.53931600
H	12.21331400	5.03956100	15.88564300

DFT-D3 RBP86/ jorgeTZP, gas phase	
Total electronic energy=	-2237.203608 E_0
Sum of electronic and zero-point Energies=	-2236.720775 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2236.694034 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2236.693090 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2236.773499 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.482833





7-Ni^{+}

Charge 1; multiplicity 1

O	14.02890000	4.63913800	15.78425600
O	16.40226200	5.28088300	14.57303500
O	14.28166000	7.01143400	14.43656600
O	13.45561400	2.08927800	10.20360000
O	12.62390000	4.02788500	9.60985900
N	13.72775200	4.17244200	14.57006100
N	15.81284300	4.73765600	13.50522100
N	13.94795600	6.25855700	13.38545800
N	13.22197300	3.28094700	10.38164800
N	14.13228700	7.06419900	17.30575900
H	13.15363000	6.84617800	17.10553900
N	16.27766100	5.32967600	17.43352500
H	16.58504600	4.40124900	17.13515700
N	16.51776200	7.72430600	16.07977700
H	16.66244400	8.11334900	15.14535900
C	13.71773000	3.92364700	11.69361400
C	14.43689300	2.90901800	12.56231100
H	15.30938900	2.49190800	12.04200600
H	13.77282600	2.07497700	12.82534400
C	14.90955700	3.58942000	13.85184200
C	15.63140800	2.59226200	14.73890300
H	15.93954000	3.04926900	15.68241500
H	16.52097400	2.21796200	14.21668500
H	14.96161700	1.75133100	14.95952300
C	14.66367900	5.06642000	11.34259100
H	14.15258000	5.80422900	10.70975400
H	15.54396700	4.69047500	10.80088400
C	15.13894800	5.74963200	12.62663300

C	16.08818300	6.88715300	12.29804600
H	15.56050100	7.64030800	11.69934900
H	16.93767700	6.49737700	11.72272700
H	16.47041300	7.35917700	13.20637000
C	12.51249300	4.48236000	12.44141300
H	11.81168100	3.67756200	12.70791700
H	11.98298300	5.21439500	11.81719800
C	12.97968400	5.16518500	13.72864800
C	11.79235000	5.72498700	14.48991000
H	11.12162500	4.90422000	14.77401900
H	11.24949400	6.43085200	13.84842400
H	12.11270200	6.24968300	15.39324200
C	14.51484100	6.53913100	18.64478200
H	13.63177500	6.40607200	19.28669200
H	15.15001200	7.28681100	19.14074400
C	15.26052800	5.20923000	18.50183300
H	15.69972800	4.91364800	19.47026700
H	14.56566700	4.42012300	18.18174700
C	17.45288900	6.18536200	17.75154200
H	18.33438300	5.57499600	17.99643600
H	17.22014800	6.77109200	18.65215900
C	17.77098000	7.11190000	16.57451300
H	18.51816800	7.86629300	16.87573800
H	18.18411700	6.53064700	15.73821700
C	15.89723400	8.74127900	16.97182800
H	16.09044800	9.76063400	16.60692800
H	16.37225600	8.66986000	17.96058300
C	14.38823200	8.50440600	17.08098800
H	13.96081600	9.13764800	17.87751100
H	13.89683300	8.76289100	16.13247100
Ni	15.23113000	6.11395200	15.82020100

DFT-D3 RBP86/ jorgeTZP, gas phase	
Total electronic energy=	-2896.066840 E_0
Sum of electronic and zero-point Energies=	-2895.583117 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2895.556365 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2895.555421 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2895.635578 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.483724

9.4. Details of DFT calculations of δ and ΔE_Q for 7-Fe^+

For DFT calculation of Mössbauer parameters **7-Fe**$^+$ cations were used as models of **7-Fe**(Cl) complex. Geometry optimization and calculations of thermodynamics were performed in methanol (PCM model). Initial charge of Fe atom was set to +4, the charge of NO_2TAAD ligand was set to -3. For better results, ***initial wavefunction*** was generated using division of the molecule into fragments.[32]

First step of calculation job:

Keywords:

 # BP86/Gen guess(only,fragment=3) pop=none SCF=XQC

A structure complex 1 mult 3 jorge-tzp

1 3 4 3 -3 1 0 1

Fe(Fragment=1)	1.406684000	-0.002979000	-0.002234000
O(Fragment=2)	0.420906000	0.730118000	-1.392297000
O(Fragment=2)	0.412157000	-1.567668000	0.063040000

….

Second step of calculation job:

 # opt freq UBP86/Gen nosymm guess=read geom=checkpoint EmpiricalDispersion=GD3BJ pressure=605 temperature=298.15 scf=xqc scrf=(PCM, Surface=SES, solvent=Methanol)

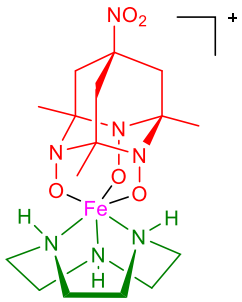
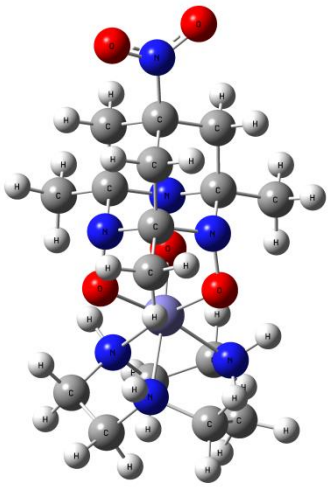
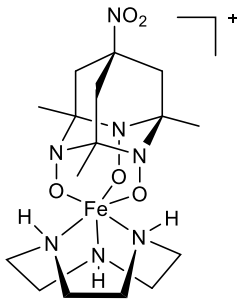


Figure S24. Fragmentation of **7-Fe**$^+$.

Table S37. Calculated relative energies of cations **7.1-Fe**$^+$**– 7.3-Fe**$^+$.

cation	$\Delta G°_{298,15\ K}$ Kcal/mol	ΔE_0 Kcal/mol
7.1-Fe$^+$	+9.2	+9.2
7.2-Fe$^+$	0.0	0.0
7.3-Fe$^+$	+16.6	+19.9





7.1-Fe$^+$

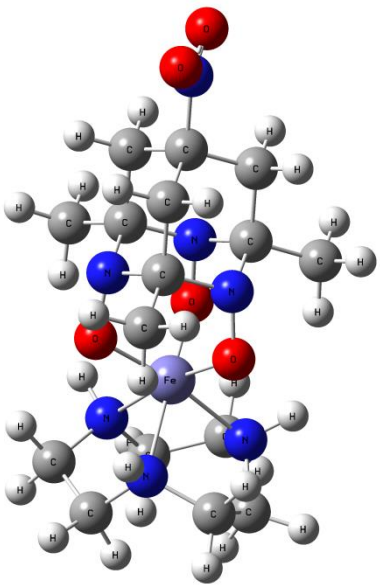
Cation **7.1-Fe$^+$** was calculated with unrestricted formalism (BS-DFT) and *stable = opt* additional step prior *opt freq* job due to RHF-UHF wavefunction instability.

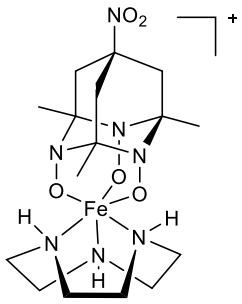
Charge 1; multiplicity 1

Fe	-1.42194300	0.00350000	0.00429600
O	-0.42942400	0.80357100	1.34870900
O	-0.42949100	-1.56708600	0.01757600
O	-0.43804800	0.77580600	-1.36886200
O	5.60158300	1.03528500	-0.03582100
N	0.94604800	0.74152400	1.20562700
N	-2.77229600	1.56310800	-0.20885200
N	0.94375200	-1.40653300	0.02479900
O	5.50226500	-1.14550600	-0.00478600
N	-2.77061300	-0.96507900	-1.23779900
N	-2.76544100	-0.59123600	1.46735500
N	0.93628400	0.69015400	-1.24390400
N	4.98257800	-0.02801500	-0.01919700
C	-3.80142900	1.25371100	-1.24926400
H	-4.00347000	2.13941500	-1.86593600
H	-4.74076100	0.99982100	-0.74098000
C	1.41037300	-0.68227000	1.24306600
C	1.40405700	1.43741400	-0.03384500
C	0.89894500	-1.37487700	2.49636800
H	1.22014600	-0.81055900	3.38119400
H	1.31562100	-2.38941600	2.54413000
H	-0.19137400	-1.44761900	2.49694100
C	-3.79393100	0.46455700	1.72304400
H	-3.99263900	0.55597000	2.79905500
H	-4.73466300	0.15151700	1.25183600
C	2.94142100	1.44899700	-0.03988000
H	3.28177700	1.97346400	-0.94201700
H	3.29056900	2.00612000	0.83880000
C	-3.32401400	0.09635100	-2.11883300

H	-4.14489400	-0.28295300	-2.74810700
H	-2.50439800	0.42332400	-2.77258000
C	-3.79411400	-1.71658800	-0.44713200
H	-3.99127000	-2.69514700	-0.90438500
H	-4.73722200	-1.15589600	-0.48008100
C	0.87772200	-1.46522700	-2.45200300
H	1.19004800	-2.51631400	-2.40537600
H	1.29307400	-1.00458000	-3.35782700
H	-0.21260900	-1.41910700	-2.50855200
C	3.44492900	0.01844900	-0.01498700
C	-3.31419900	-1.88730200	0.98958300
H	-4.13345900	-2.24506400	1.63355700
H	-2.49184500	-2.61364100	1.03369400
C	0.88123100	2.86483300	-0.05675200
H	-0.20844900	2.89446500	0.02076200
H	1.18660100	3.34966400	-0.99283600
H	1.30539100	3.41827500	0.79119400
C	1.40091400	-0.72786500	-1.22963400
C	2.93549100	-0.73039000	-1.24275400
H	3.28760600	-1.76979900	-1.23459600
H	3.27844700	-0.24378800	-2.16634800
C	-3.31956400	1.79634300	1.15305800
H	-4.14149500	2.52994700	1.14187700
H	-2.49807700	2.20091300	1.75907900
C	2.94512500	-0.68352800	1.24420000
H	3.29329600	-0.16281900	2.14717000
H	3.29915900	-1.72181000	1.27191200
H	-2.23315600	2.38136800	-0.50502300
H	-2.22534900	-0.74551200	2.32311600
H	-2.23178200	-1.62802200	-1.80179000

DFT-D3 UBP86/ jorgeTZP, solvent methanol, PCM model		
Total electronic energy=	-2651.512815	E_0
Sum of electronic and zero-point Energies=	-2651.029691	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2651.002974	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2651.002030	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2651.075916	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.483124	
Selected structural parameters of **7.1-Fe**$^+$		
Fe-O bond distances, Å: 1.86, 1.86, 1.85		
Fe-N bond distances, Å: 2.07, 2.07, 2.07		





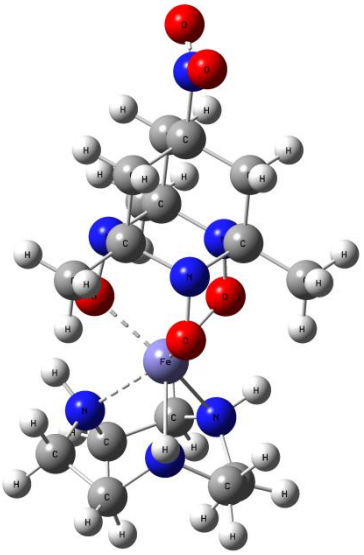
7.2-Fe^{+}

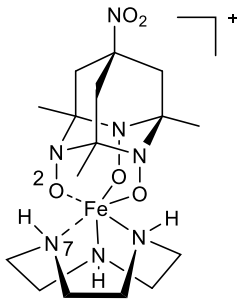
Charge 1; multiplicity 3

Fe	1.40668400	-0.00297900	-0.00223400
O	0.42090600	0.73011800	-1.39229700
O	0.41215700	-1.56766800	0.06304000
O	0.42451800	0.84212500	1.32554000
O	-5.61024900	1.05021600	-0.02626700
N	-0.95141300	0.66674000	-1.25081500
N	2.78097400	1.57795900	-0.04176900
N	-0.95949700	-1.40573300	0.05538000
O	-5.51835200	-1.12985700	0.04876000
N	2.77508200	-0.77012100	1.38796100
N	2.76952300	-0.83377500	-1.36018700
N	-0.94820100	0.76216100	1.19623400
N	-4.99493800	-0.01475900	0.00855700
C	3.80818500	1.42609200	1.03338500
H	4.01810300	2.39547100	1.50483500
H	4.74514900	1.08968000	0.57049000
C	-1.42205800	-0.75235900	-1.20712900
C	-1.41182600	1.43784500	-0.05573500
C	-0.91134600	-1.51915200	-2.41647300
H	-1.25896900	-1.02548200	-3.33308400
H	-1.30301700	-2.54419300	-2.38715200
H	0.18023200	-1.56292600	-2.43100900
C	3.79827300	0.16921300	-1.77202700
H	4.00288600	0.09172500	-2.84814100
H	4.73694700	-0.06568900	-1.25356600
C	-2.94888400	1.45406700	-0.05332300
H	-3.29012100	2.03099200	0.81584500
H	-3.29381200	1.96066000	-0.96380400
C	3.32951700	0.42342200	2.07787000

H	4.15170600	0.15401400	2.75996900
H	2.51066500	0.85113600	2.67181800
C	3.79468100	-1.63482000	0.71883600
H	3.99611000	-2.52964700	1.32280000
H	4.73742100	-1.07534200	0.65865200
C	-0.90383300	-1.32162000	2.53072100
H	-1.24874900	-2.36318200	2.55894800
H	-1.29469800	-0.78744200	3.40642700
H	0.18769600	-1.30864100	2.57313700
C	-3.45714300	0.02628400	0.00343400
C	3.31142000	-2.03382800	-0.67160700
H	4.12851400	-2.49946100	-1.24565700
H	2.48455400	-2.75304400	-0.59693100
C	-0.88654100	2.86302400	-0.11389900
H	0.20501500	2.88724400	-0.15471000
H	-1.22138900	3.40993100	0.77688100
H	-1.28141400	3.35774000	-1.01076400
C	-1.41861100	-0.65476300	1.26535400
C	-2.95295800	-0.65191100	1.27364700
H	-3.30871300	-1.68885100	1.32416700
H	-3.29636100	-0.11245700	2.16727500
C	3.32590300	1.57689000	-1.42408000
H	4.14971100	2.29959200	-1.53757800
H	2.50378300	1.87926600	-2.08659600
C	-2.95665700	-0.74882800	-1.21155200
H	-3.30177400	-0.27974300	-2.14348300
H	-3.31380100	-1.78603300	-1.18039900
H	2.25914000	2.44480000	0.11149300
H	2.24213500	-1.13149100	-2.18492300
H	2.25049000	-1.33176200	2.06359100

DFT-D3 UBP86/ jorgeTZP, solvent methanol, PCM model	
Total electronic energy=	-2651.527445 E_0
Sum of electronic and zero-point Energies=	-2651.043531 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2651.017104 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2651.016160 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2651.090592 $E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.483913
Selected structural parameters of **7.2-Fe$^+$**	
Fe-O bond distances, Å: 1.86, 1.86, 1.86	
Fe-N bond distances, Å: 2.10, 2.10, 2.10	





7.3-Fe^{+}

Charge 1; multiplicity 5

Fe	-1.41233400	-0.06193000	-0.02976400
O	-0.32058500	1.35973700	0.87472300
O	-0.27085100	-1.45109600	0.69509000
O	-0.28966200	0.07758500	-1.59570700
O	5.70901500	0.96770400	-0.46562400
N	1.05817000	1.21503900	0.78397100
N	-2.93804900	1.39811500	0.76638300
N	1.06137800	-1.24339500	0.59420700
O	5.62606600	-0.99148900	0.49455100
N	-2.96386800	-0.04069900	-1.58668800
N	-2.92345600	-1.36515800	0.85480300
N	1.03974400	0.08672300	-1.39023100
N	5.09839800	0.00699500	0.00096600
C	-3.96148500	1.76125500	-0.23802400
H	-4.16556000	2.84161800	-0.22662400
H	-4.90428100	1.26222100	0.02537800
C	1.51982800	-0.06264900	1.40796800
C	1.51044300	1.29984900	-0.63817800
C	0.98389600	-0.17879100	2.82525600
H	1.35141700	0.67015700	3.41625500
H	1.34098500	-1.11347300	3.27707100
H	-0.10973500	-0.16959100	2.83122900
C	-3.92354800	-0.65040100	1.69240800
H	-4.10912700	-1.19775900	2.62676700
H	-4.87737800	-0.62282300	1.14837000
C	3.04656800	1.31175700	-0.66160500
H	3.38677000	1.39691400	-1.70174300
H	3.39149200	2.19574700	-0.11052000
C	-3.50687400	1.33582300	-1.63589300
H	-4.34163700	1.42421800	-2.35115100

H	-2.69228200	1.98677200	-1.98462100
C	-3.97745700	-1.10635300	-1.35743500
H	-4.20466600	-1.63612100	-2.29296200
H	-4.91246600	-0.63213800	-1.03005200
C	1.02246100	-2.38399700	-1.60798600
H	1.39882100	-3.30966700	-1.15376200
H	1.38961600	-2.31581400	-2.64028800
H	-0.07067100	-2.41051400	-1.61956300
C	3.55999900	0.03464200	-0.02197600
C	-3.48549500	-2.09869100	-0.30493500
H	-4.30664900	-2.77152200	-0.00603600
H	-2.67489700	-2.71860700	-0.71354000
C	0.96156200	2.55646000	-1.29227300
H	-0.13159300	2.56596500	-1.26927200
H	1.30500100	2.60817400	-2.33375600
H	1.33623900	3.43250200	-0.74691300
C	1.54245100	-1.19694300	-0.81634100
C	3.07287800	-1.17493300	-0.81648700
H	3.43840400	-2.10591000	-0.36472800
H	3.42053900	-1.12442800	-1.85798900
C	-3.44319800	0.76768400	2.00014600
H	-4.25795800	1.34759400	2.46704900
H	-2.60329600	0.73666800	2.70897600
C	3.05495800	-0.06721500	1.41567300
H	3.40235300	0.78800100	2.01142200
H	3.41067400	-0.99446800	1.88288700
H	-2.34133200	2.19648500	0.99682100
H	-2.37663300	-2.01080700	1.43084300
H	-2.44008800	-0.23070300	-2.44528700

DFT-D3 UBP86/ jorgeTZP, solvent methanol, PCM model		
Total electronic energy=	-2651.495768	E_0
Sum of electronic and zero-point Energies=	-2651.014530	$E_0 + E_{ZPE}$
Sum of electronic and thermal Energies=	-2650.987045	$E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies=	-2650.986101	$E_0 + H_{corr}$
Sum of electronic and thermal Free Energies=	-2651.064082	$E_0 + G_{corr}$
Zero-point correction *(unscaled)* =	0.481238	
Selected structural parameters of **7.3-Fe$^+$**		
Fe-O bond distances, Å: 2.01 - (Fe-O*2*), 1.94, 1.93		
Fe-N bond distances, Å: 2.26 - (Fe-N*7*), 2.20, 2.18		
Mulliken atom spin density		
Fe: 3.50; O*2*: 0.26		

Calculations of Mössbauer isomer shift were performed with the ORCA 4.2.1[33] quantum chemistry program. Calibration line for ^{57}Fe Mössbauer isomer shift was taken from Golovanov et al.[34]

Electric field gradient[35] was calculated for cations **7.1-Fe^{+}** - **7.3-Fe^{+}** as a single point job. Calculations were performed with the ORCA 4.2.1 quantum chemistry program. TPSS DFT functional with DKH-def2-QZVPP basis set on all atoms was used. Relativistic effects were taken into account by requesting a Douglas-Kroll-Hess 2nd order scalar relativistic calculation with inclusion of picture change effects and finite nucleus model.

Sample input file:

```
! SP UKS TPSS NORI DKH2 DKH-def2-QZVPP VERYTIGHTSCF Grid7 NoFinalGrid
SlowConv

%method

IntAcc 7.0

end

%scf MaxIter 2000 end

*xyz 1 3

Fe       1.406684000     -0.002979000     -0.002234000

...

H        2.250490000     -1.331762000      2.063591000

*

%eprnmr nuclei = all 26 {fgrad}

end

%rel PictureChange true FiniteNuc true end
```

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