Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Direct preparation of unprotected aminimides ($R_3N^+–NH^–$) from natural aliphatic tertiary alkaloids (R_3N) by [Mn(TDCPP)Cl]-catalysed *N*-amination reaction

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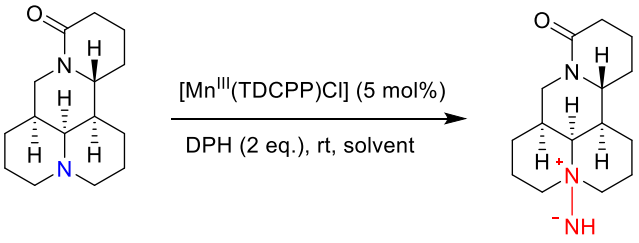
1. Experimental section

a) General information

All chemicals and solvents were purchased as reagent grade and used without further purification unless otherwise noted. Reactions were monitored by TLC plate (precoated with 60 Å silica gel, GF254) purchased from Yantai Jiangyou Silica Gel and visualized by UV light (254, 365 nm) or iodine stain. Porphyrin ligands and the metal complexes[1-4] and carbonyl and sulfonyl hydroxylamonium salt[5] were synthesized according to the literature methods.

NMR spectra were recorded on a Bruker Ascend^{TM} 400 MHz or 500 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA). The electronic absorption spectra were recorded on a Thermo Scientific Evolution 201UV/Visible Spectrophotometer. X-Ray diffraction data of the single crystals were collected on a Bruker X8 Proteum diffractometer.

b) Synthesis and characterization data for aminimide 3a

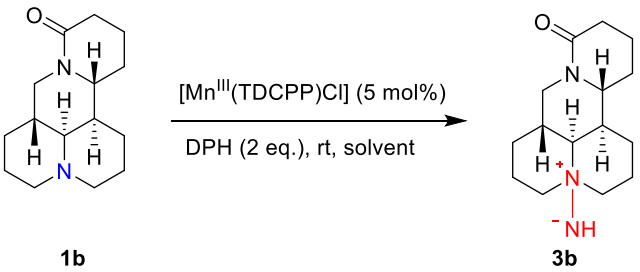


1a **3a**

[Mn^{III}(TDCPP)Cl] (0.05 eq) and DPH (2 eq) were added to a solution of matrine (1 eq) in DCM (50 mM) at room temperature. The reaction mixture was stirred for about 24 h (until the free base alkaloid was completely consumed as monitored by TLC), and then concentrated under vacuum to remove the solvent. The residue was purified by alumina column chromatography with DCM/MeOH (10:1 v/v) as the eluent. The desired product was obtained as a brown and viscous liquid in 89% yield.

^{1}**H NMR** (400 MHz, MeOD): δ ppm 5.60 (d, J = 5.85 Hz, 1H), 4.50 (dd, J_1 = 13.21 Hz, J_2 = 5.56 Hz, 1H), 4.43-4.36 (m, 1H), 3.77 (t, J = 4.04 Hz, 1H), 3.69-3.61 (m, 2H), 3.54-3.48 (m, 3H), 2.52-2.30 (m, 5H), 2.19-1.81(m, 9H), 1.74-1.64 (m, 1H), 1.46-1.36 (m, 1H); **^{13}C NMR** (100 MHz, MeOD): δ ppm 171.59, 68.04, 67.90, 67.45, 53.29, 41.13, 40.63, 33.23, 32.05, 28.28, 24.00, 22.35, 18.27, 16.50, 16.49. **HRMS** (ESI): calcd for $C_{15}H_{26}N_3O^+$ ([M + H]$^+$) 264.2070, found 264.2067.

c) Synthesis and characterization data for aminimide 3b

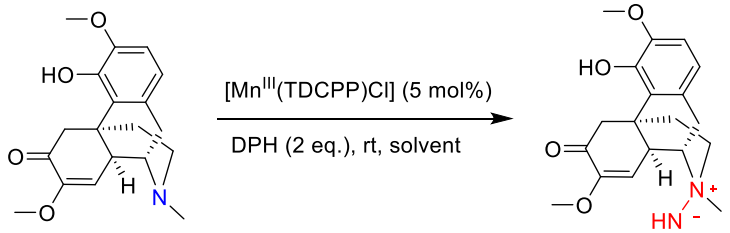


1b **3b**

The procedure is the same as that for **3a**, except that sophoridine (instead of matrine) was used and the reaction mixture was stirred for about 2 h. The desire product was obtained as a brown and viscous liquid in 98% yield.

^{1}**H NMR** (400 MHz, MeOD): δ ppm 4.01-3.90 (m, 2H), 3.75 (d, *J* = 11.58 Hz, 1H), 3.59-3.53 (m, 1H), 3.32-3.19 (m, 4H), 2.81-2.73 (m, 1H), 2.62-2.49 (m, 1H), 2.40-2.25 (m, 3H), 2.15-1.99 (m, 3H), 1.94-1.77 (m, 6H), 1.62-1.52 (m, 1H), 1.46-1.31 (m, 1H); **^{13}C NMR** (100 MHz, MeOD): δ ppm 171.00, 70.12, 69.84, 58.86, 56.13, 46.64, 34.80, 31.55, 28.62, 26.90, 26.66, 22.53, 20.42, 18.21, 17.43. **HRMS** (ESI): calcd for $C_{15}H_{26}N_3O^+$ ($[M + H]^+$) 264.2070, found 264.2066.

d) Synthesis method and characterization data for aminimide 3c

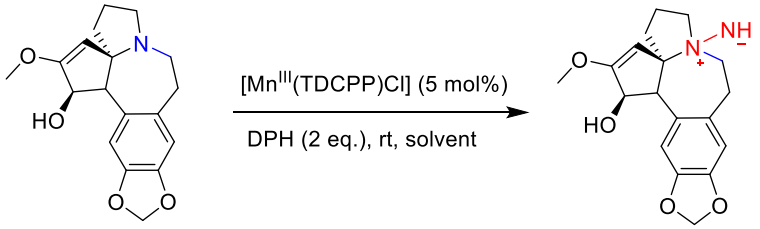


1c **3c**

The procedure is the same as that for **3a**, except that sinomenine (instead of matrine) was used and the reaction mixture was stirred for about 2 h. The desired product was obtained as a pale yellow solid (liable to deliquescence) in 90% yield (90% product yield was obtained with $[Mn^{III}$(4-*N*-MePy-TDCPP)Cl$]PF_6$ as catalyst).

^{1}**H NMR** (400 MHz, CD_3CN): δ ppm 6.88 (d, *J* = 8.21 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 6.22 (s, 2H), 5.60 (s, 1H), 4.28 (s, 1H), 4.07 (s, 1H), 3.84 (s, 3H), 3.68-3.63 (m, 1H), 3.53 (s, 3H), 3.48 (s, 3H), 3.44-3.39 (dd, J_1 =20.5 Hz, J_2 =5.84 Hz, 1H), 3.28-3.23 (d, *J* = 20.89 Hz, 1H), 2.90-2.84 (m, 1H), 2.65 (s, 1H), 2.52-2.45 (m, 1H); **^{13}C NMR** (100 MHz, MeOD): δ ppm 193.38, 152.44, 146.89, 145.44, 124.74, 120.06, 118.50, 112.48, 110.55, 71.02, 59.35, 56.39, 55.19, 54.20, 48.46, 39.03, 38.62, 30.43, 27.09. **HRMS** (ESI): calcd for $C_{19}H_{25}N_2O_4^+$ ($[M + H)]^+$) 345.1809, found 345.1804.

e) Synthesis method and characterization data for aminimide 3d

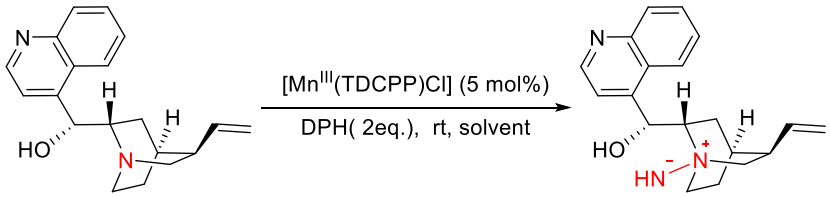


1d **3d**

The procedure is the same as that for **3a**, except that cephalotaxine (instead of matrine) was used and the reaction mixture was stirred for about 2 h. The desired product was obtained as a pale yellow solid in 90% yield.

^{1}**H NMR** (400 MHz, MeOD): δ ppm 6.87 (d, *J* = 3.62 Hz, 2H), 6.01 (s, 2H), 5.29 (s, 1H), 4.84 (d, *J* = 7.16 Hz, 1H), 4.05 (d, *J* = 9.55 Hz, 1H), 4.01-3.89 (m, 2H), 3.84 (s, 3H), 3.79-3.73 (m, 3H), 2.85-2.77 (m, 1H), 2.73-2.64 (m, 1H), 2.27-2.11 (m, 3H); ^{13}**C NMR** (100 MHz, MeOD): δ ppm 166.73, 148.00, 147.68, 129.81, 127.36, 112.35, 110.18, 101.61, 95.86, 88.43, 71.84, 67.56, 63.08, 57.25, 53.39, 37.66, 27.85, 17.60. **HRMS** (ESI): calcd for $C_{18}H_{23}N_2O_4^+$ ([M + H]$^+$) 331.1652, found 331.1658.

f) Synthesis method and characterization data for aminimide 3e

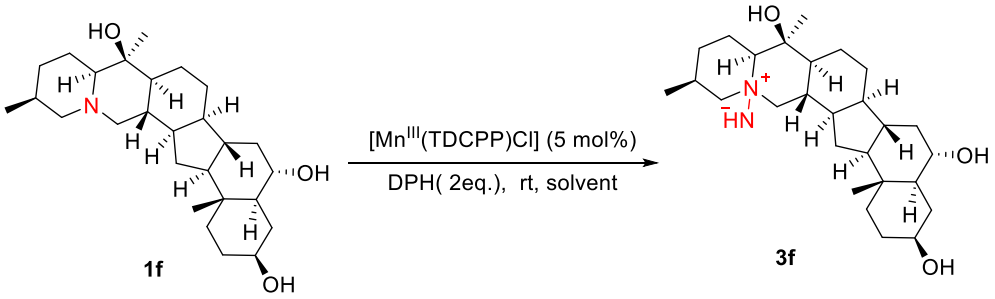


1e **3e**

The procedure is the same as that for **3a**, except that cinchonidine (instead of matrine) was used and the reaction mixture was stirred for about 2 h. The desired product was obtained as a pale yellow oily liquid in 97% yield.

^{1}**H NMR** (400 MHz, MeOD): δ ppm 8.92 (d, *J* = 4.37 Hz, 1H), 8.28 (d, *J* = 8.50 Hz, 1H), 8.11 (d, *J* = 8.50 Hz, 1H), 7.91 (d, *J* = 4.14 Hz, 1H), 7.85 (t, *J* = 7.12 Hz, 1H), 7.77 (t, *J* = 7.35 Hz, 1H), 6.65 (s, 1H), 5.83-5.75 (m, 1H), 5.17 (d, *J* = 17.01 Hz, 1H), 5.08 (d, *J* = 11.04 Hz, 1H), 4.50-4.42 (m, 1H), 3.96 (t, *J* = 10.54 Hz, 1H), 3.76-3.71 (m, 1H), 3.65-3.57 (m, 2H), 3.04 (m, 1H), 2.48-2.40 (m, 2H), 2.16-2.09 (m, 2H), 1.66 (t, *J* = 10.54 Hz, 1H); ^{13}**C NMR** (100 MHz, MeOD): δ ppm 149.68, 147.32, 147.26, 136.98, 129.73, 128.90, 127.57, 124.81, 122.71, 119.40, 116.27, 71.48, 68.54, 63.40, 57.44, 39.59, 26.74, 25.28, 19.47. **HRMS** (ESI): calcd for $C_{19}H_{24}N_3O^+$ ([M + H]$^+$) 310.1914, found 310.1915.

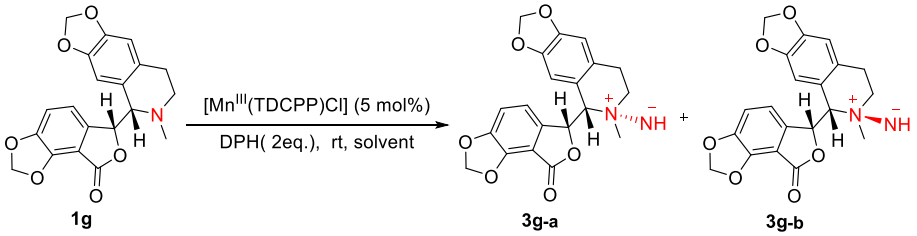
g) Synthesis method and characterization data for aminimide 3f



[Mn^{III}(TDCPP)Cl] (0.05 eq) and DPH (2 eq) were added to a solution of peimine (1 eq) in DCM/MeOH (20:1 v/v) (50 mM) at room temperature. The reaction mixture was stirred for about 2 h (until the free base alkaloid was completed consumed as monitored by TLC), and then concentrated under vacuum to remove the solvent. The residue was purified by alumina column chromatography with DCM/MeOH (10:1 v/v) as the eluent. The desired product was obtained as a colorless solid in 91% yield.

^{1}**H NMR** (400 MHz, MeOD): δ ppm 3.57-3.35 (m, 5H), 3.27 (d, *J* = 12.89 Hz, 1H), 3.17 (t, *J* = 10.86 Hz, 1H), 2.45-2.36 (m, 1H), 2.26-2.17 (m, 3H), 1.98-1.74 (m, 8H), 1.71-1.59 (m, 4H), 1.57-1.46 (m, 3H), 1.42 (d, *J* = 7.79 Hz, 3H), 1.31 (dd, J_1 = 10.92 Hz, J_2 = 3.63 Hz, 1H), 1.27 (s, 3H), 1.23-1.13 (m, 3H), 1.19-1.01 (m, 2H), 0.96-0.91 (m, 1H), 0.88 (s, 3H); **^{13}C NMR** (100 MHz, MeOD): δ ppm 75.48, 72.02, 71.98, 71.21, 70.77, 69.59, 56.70, 51.83, 47.32, 43.32, 39.76, 39.08, 38.70, 37.54, 34.82, 33.51, 31.65, 30.27, 28.77, 27.91, 27.08, 23.79, 22.23, 19.59, 19.52, 15.48, 11.62. **HRMS** (ESI): calcd for $C_{27}H_{47}N_2O_3^+$ ([M + H]$^+$) 447.3581, found 447.3574.

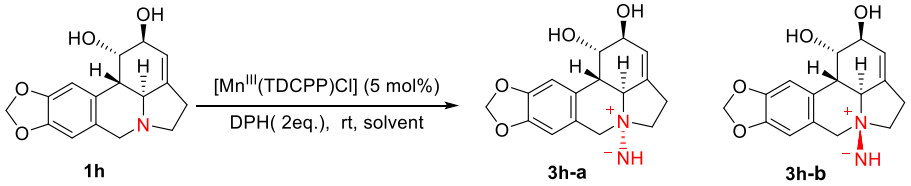
h) Synthesis method and characterization data for aminimide 3g



The procedure is the same as that for **3a**, except that bicuculline (instead of matrine) was used and the reaction mixture was stirred for about 2 h. The desired product **3ga** was obtained as a pale yellow solid in 65% yield, and **3g-b** was obtained as a pale yellow solid in 29% yield. ^{1}**H NMR** of **3g-a (**400 MHz, MeOD): δ ppm 7.52 (d, *J* = 7.51 Hz, 1H), 7.37 (d, *J* = 8.16 Hz, 1H), 6.76 (s, 1H), 6.50 (s, 1H), 6.22 (s, 2H), 5.88 (d, *J* = 8.52 Hz, 2H), 5.65 (s, 1H), 5.42 (s, 1H), 4.28-4.21 (m, 1H), 3.96-3.93 (m, 1H), 3.91 (s, 3H), 3.31-3.19 (m, 2H); **^{13}C NMR** of **3g-a (**100 MHz, MeOD): δ ppm 165.67, 150.40, 148.93, 145.97, 145.54, 137.92, 125.61, 116.15, 115.50, 114.13, 108.10, 107.55, 107.22, 104.07, 101.60, 77.36, 76.92, 59.28, 54.69, 23.61. ^{1}**H NMR** of **3g-b (**400 MHz, MeOD): δ ppm 7.55 (d, *J* = 7.21 Hz, 1H), 7.37 (d, *J* = 7.21 Hz, 1H), 6.83 (s, 1H), 6.78 (s, 1H), 6.22 (d, *J* = 1.91 Hz, 2H), 5.91 (s, 1H), 5.89 (s, 1H), 5.67 (s, 1H), 5.39 (s, 1H), 4.25-4.16 (m, 1H), 3.90-3.85 (m, 1H), 3.49 (s, 3H), 3.31-3.26 (m, 2H); **^{13}C**

NMR of **3g-b (**100 MHz, MeOD): δ ppm 165.85, 150.30, 149.28, 146.11, 145.42, 138.22, 125.10, 116.04, 115.93, 114.11, 108.10, 107.78, 106.93, 103.99, 101.74, 76.63, 76.30, 58.36, 54.50, 24.23. **HRMS** (ESI): calcd for $C_{20}H_{19}N_2O_6^+$ ([M + H]$^+$) 383.1238, found 383.1232.

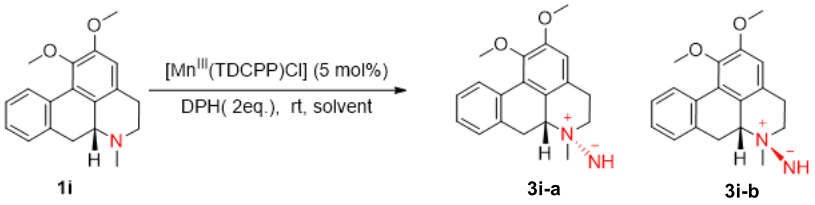
i) Synthesis method and characterization data for aminimide 3h



The procedure is the same as that for **3f**, except that lycorine (instead of peimine) was used. The desired product **3h-a** was obtained as a pale yellow solid in 60% yield, and **3h-b** was obtained as a pale yellow solid in 36% yield.

^{1}**H NMR** of **3h-a** (400 MHz, MeOD): δ ppm 7.09 (s, 1H), 7.02 (s, 1H), 6.05 (d, *J* = 5.02 Hz, 2H), 5.79 (s, 1H), 4.74 (d, *J* = 12.88 Hz, 1H), 4.58 (s, 1H), 4.56 (d, *J* = 13.74 Hz, 1H), 4.25 (s, 1H), 4.13-4.08 (m, 1H), 3.90-3.78 (m, 2H), 3.26-3.17 (m, 1H), 2.93 (d, *J* = 11.48 Hz, 1H), 2.87 (dd, J_1 = 14.72 Hz, J_2 = 5.74 Hz, 1H); ^{13}**C NMR** of **3h-a** (100 MHz, MeOD): δ ppm 149.39, 146.91, 135.86, 130.60, 122.62, 121.83, 109.29, 105.34, 101.65, 76.28, 69.94, 68.44, 68.25, 67.34, 37.76, 29.02. ^{1}**H NMR** of **3h-b** (400 MHz, MeOD): δ ppm 7.03 (s, 1H), 6.77 (s, 1H), 6.02 (s, 2H), 5.89 (s, 1H), 4.98 (d, *J* = 14.41 Hz, 1H), 4.88 (s, 1H), 4.85 (s, 1H), 4.63 (s, 1H), 4.37 (d, *J* = 11.32 Hz, 1H), 4.29-4.24 (m, 2H), 4.02-3.94 (m, 1H), 3.23 (d, *J* = 11.32 Hz, 1H), 3.14-2.98 (m, 2H); ^{13}**C NMR** of **3h-b** (100 MHz, MeOD): δ ppm 148.46, 147.61, 133.55, 125.81, 123.17, 121.76, 107.05, 105.00, 101.72, 71.70, 70.24, 69.73, 66.60, 66.53, 34.29, 25.43. **HRMS** (ESI): calcd for $C_{16}H_{19}N_2O_4^+$ ([M + H]$^+$) 303.1339, found 303.1336.

j) Synthesis method and characterization data for aminimide 3i

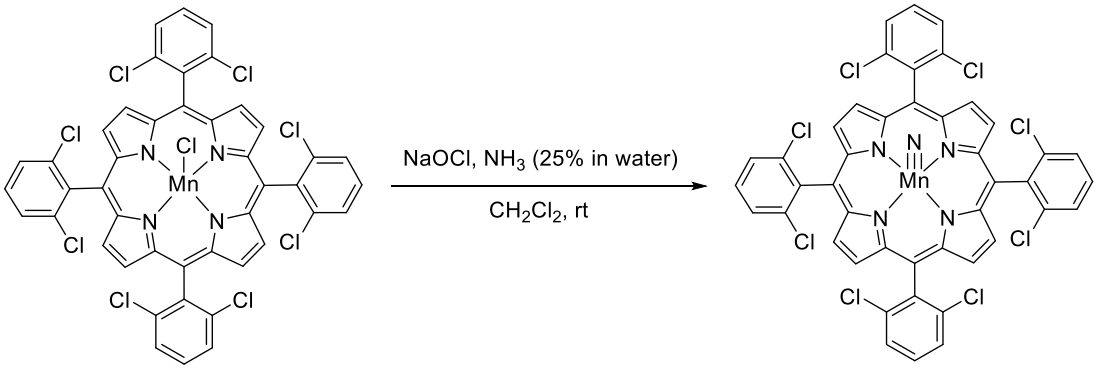


The procedure is the same as that for **3a**, except that nuciferine (instead of matrine) was used and the reaction mixture was stirred for about 2 h. The desired product **3i-a** was obtained as a pale yellow solid in 77% yield, and **3i-b** was obtained as a pale yellow solid in 21% yield.

^{1}**H NMR** of **3i-a** (400 MHz, MeOD): δ ppm 8.33 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 6.96 Hz, 1H), 7.39-7.31 (m, 2H), 6.96 (s, 1H), 4.77 (dd, J_1 = 13.75 Hz, J_2 = 3.66 Hz, 1H), 3.97-3.95 (m, 2H), 3.94 (s, 3H), 3.69 (s, 3H), 3.61 (s, 3H), 3.56-3.47 (m, 1H), 3.38 (dd, J_1 = 13.40 Hz, J_2 = 3.94 Hz, 1H), 3.18 (t, *J* = 13.95 Hz, 1H), 3.13-3.08 (m, 1H); ^{13}**C NMR** of **3i-a** (100 MHz, MeOD): δ ppm 153.90, 146.34, 132.37, 130.86, 128.14, 128.08, 127.55, 127.15, 125.05, 119.53, 111.31, 70.97, 63.07, 59.38, 55.11, 54.88, 29.14, 23.29. ^{1}**H NMR** of **3i-b** (400 MHz, MeOD): δ ppm 8.33 (d, *J* = 7.99 Hz, 1H), 7.42 (d, *J* = 8.05 Hz, 1H), 7.40-7.32 (m,

2H), 6.96 (s, 1H), 4.65 (dd, J_1 = 14.29 Hz, J_2 = 3.41 Hz, 1H), 4.03-3.91 (m, 2H), 3.94 (s, 3H), 3.70 (s, 3H), 3.58 (dd, J_1 = 13.49 Hz, J = 3.92 Hz, 1H), 3.52-3.42 (m, 1H), 3.25 (s, 3H), 3.21 (dd, J_1 = 14.29 Hz, J_2 = 3.21 Hz, 1H), 3.08 (t, J = 13.90 Hz, 1H); **^{13}C NMR** of **3i-b** (100 MHz, MeOD): δ ppm 154.15, 146.48, 132.22, 130.95, 128.20, 128.14, 127.97, 127.65, 127.05, 124.31, 120.21, 111.22, 72.66, 65.03, 59.42, 55.11, 45.16, 28.91, 25.26. **HRMS** (ESI): calcd for $C_{19}H_{23}N_2O_2^+$ ($[M + H]^+$) 311.1754, found 311.1750.

k) Synthesis and characterization data for [Mn^V(TDCPP)(N)]



Method 1. [Mn^{III}(TDCPP)Cl] (200 mg, 0.2 mmol) was dissolved in DCM (40 mL) at room temperature. Excess amounts of aqueous NaOCl (3 mL, 6.5%) and aqueous ammonia (4 mL, 25%) were then added to the solution. The reaction mixture was stirred for about 3 h (until [Mn^{III}(TDCPP)Cl] was completely consumed as monitored by TLC), and then extracted twice with DCM. The organic phase was dried with anhydrous $MgSO_4$, followed by removal of the solvent. The residue was purified by alumina column chromatography with DCM as the eluent. The desired product was obtained as a purple solid (with metallic luster) in 90% yield.

Method 2. [Mn^{III}(TDCPP)Cl] (200 mg, 0.2 mmol) and DPH (0.2 mmol) were dissolved in DCM (40 mL) at room temperature, with subsequent addition of an aqueous solution of NaOH (2.5 M, 10 mL). The mixture was stirred for 1–3 min and then extracted with DCM. The organic phase was collected and evaporated to remove the solvent, giving the desired product in 96% yield.

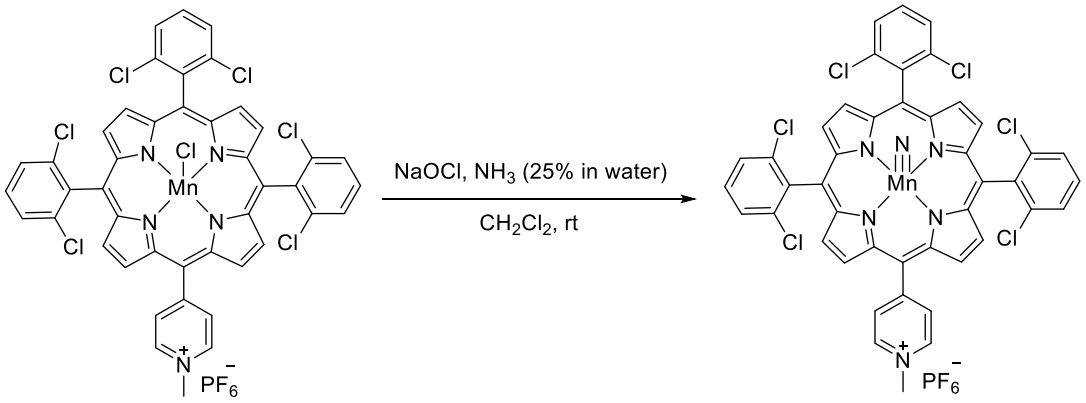
^{1}H NMR (400 MHz, CD_2Cl_2): δ ppm 8.86 (s, 8H), 7.90 (dd, J_1 = 8.09 Hz, J_2 = 1.51 Hz, 4H), 7.84 (dd, J_1 = 8.09 Hz, J_2 = 1.25 Hz, 4H), 7.79 (t, J = 7.91 Hz, 4H); **^{13}C NMR** (100 MHz, CD_2Cl_2): δ ppm 145.49, 138.76, 138.22, 138.18, 131.17, 130.92, 128.14, 128.05, 116.62. **UV-vis** (main peak): 418, 537, 571 nm. **HRMS** (ESI): calcd for $C_{44}H_{21}Cl_8MnN_5^+$ ($[M + H]^+$) 957.8627, found 957.8621.

l) Synthesis and characterization data for [Mn^{III}(4-*N*-MePy-TDCPP)Cl]PF$_6$

(4-Py)TDCPPH$_2$ (30 mg, 0.036 mmol; prepared according to the literature method[6,7]) was dissolved in DMF (4 mL) at room temperature. After addition of CH_3I (50 μL, 0.8 mmol), the mixture was stirred at 60 °C for 6 h under argon, followed by addition of $MnCl_2$ (60 mg, 0.48 mmol) with the resulting mixture being stirred at 130 °C for 12 h. The mixture was then cooled to room temperature, and H_2O (with its volume equal to 2-fold of the DMF in the reaction mixture) was added. The iodide salt [Mn^{III}(4-*N*-MePy-TDCPP)Cl]I was obtained as a deep-green solid after filtration, which was then subjected to counterion exchange by stirring its CH_3CN solution mixed with a solution of NH_4PF_6 (aq, 2 M). After evaporation of the volatiles and purification of the residue by alumina column chromatography with the DCM/MeOH (5:1 v/v) as the eluent, the desired [Mn^{III}(4-*N*-MePy-TDCPP)Cl]PF$_6$ was obtained in 77% yield as a deep-green solid.

HRMS (ESI): calcd for $C_{44}H_{24}Cl_6MnN_5$ $[(M - Cl - PF_6)]^{2+}$ 444.4757, found 444.4747.

m) Synthesis and characterization data for [Mn(4-*N*-MePy-TDCPP)(N)]PF$_6$

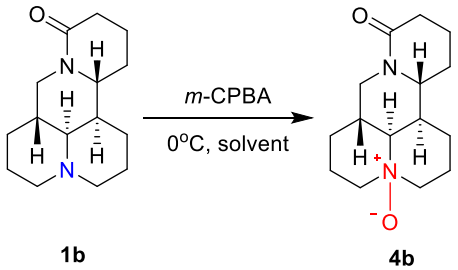


[Mn^{III}(4-*N*-MePy-TDCPP)Cl]PF$_6$ (30 mg, 0.2 mmol) was dissolved in DCM (10 mL) at room temperature. Excess amounts of aqueous NaOCl (1 mL, 6.5%) and aqueous ammonia (1 mL, 25%) were then added. The mixture was stirred for about 3 h (until [Mn^{III}(4-*N*-MePy-TDCPP)Cl]PF$_6$ was completed consumed as monitored by TLC (MeOH/DCM =1:10 v/v)), and then extracted twice with DCM. The organic phase was dried with anhydrous $MgSO_4$, followed by filtration and removal of the solvent. The residue was purified by alumina column chromatography with MeOH/DCM (1:10 v/v) as the eluent. The desired product was

obtained as a purple solid (with metallic luster) in 90% yield.

^{1}H NMR (400 MHz, CD_3CN): δ ppm 9.06-8.97 (m, 6H), 8.92 (s, 4H), 8.80 (s, 2H), 7.96-7.83 (m, 9H), 4.65 (s, 3H); **^{13}C NMR** (100 MHz, CD_3CN): δ ppm 157.94, 137.67, 132.44, 132.12, 132.05, 131.96, 131.85, 131.79, 128.42, 117.60, 115.99, 48.29. **^{19}F NMR (**377 MHz, CD_3CN): δ ppm -72.89 (d, *J* = 706.4 Hz). **HRMS** (ESI): calcd for $C_{44}H_{24}Cl_6MnN_6^+$ ([M – PF_6]$^+$) 902.9539, found 902.9530.

n) Synthesis and characterization data for sophoridine *N*-oxide (4b)

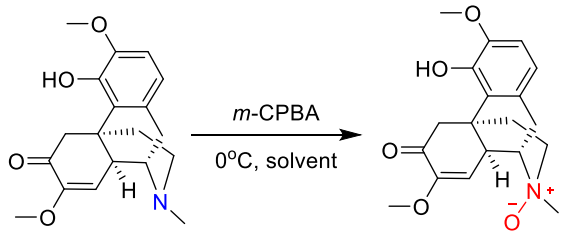


1b **4b**

To a stirred solution of sophoridine (1 eq) in DCM (50 mM) was added *m*-CPBA (1.2 eq) at 0 °C. The mixture was stirred at that temperature for 30 min. The volatiles were removed under vacuum, and the residue was purified by alumina column chromatography with DCM/MeOH (10:1 v/v) as the eluent. Removal of the solvent gave the desired product as a colorless solid in 90% yield.

^{1}H NMR (400 MHz, CD_3OD): δ ppm 4.10-3.99 (m, 2H), 3.81 (m, 1H), 3.7 (t, *J* = 12.85 Hz, 1H), 3.41 (dd, J_1 = 12.99 Hz, J_2 = 5.65 Hz, 2H), 3.27 (m, 1H), 2.69-2.53 (m, 2H), 2.42-2.21 (m, 3H), 2.14-1.96 (m, 4H), 1.92-1.79 (m, 6H), 1.64-1.57 (m, 1H), 1.54-1.45 (m, 1H); **^{13}C NMR** (100 MHz, D_2O): δ ppm 173.37, 70.99, 68.88, 58.54, 57.97, 47.07, 34.72, 31.30, 28.04, 27.59, 25.75, 22.23, 21.18, 18.03, 16.67. **HRMS** (ESI): calcd for $C_{15}H_{25}N_2O_2^+$ ([M + H]$^+$) 265.1911, found 265.1906.

o) Synthesis and characterization data for sinomenine *N*-oxide (4c)



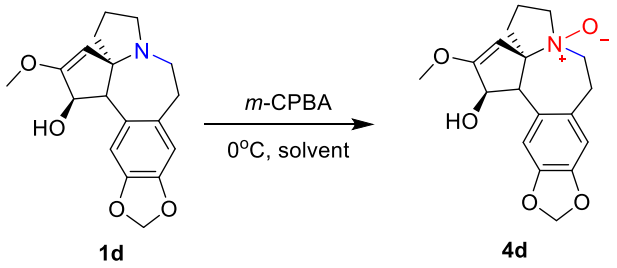
1c **4c**

The procedure is the same as that for **4b** except that sinomenine (instead of sophoridine) was used. The desired product was obtained as a pale-yellow solid in 76% yield.

^{1}H NMR (400 MHz, MeOD): δ ppm 6.81 (d, *J* = 7.66 Hz, 1H), 6.60 (d, *J* = 8.32 Hz, 1H), 5.77 (d, *J* = 2.15 Hz, 1H), 4.41 (d, *J* = 15.45 Hz, 1H), 4.07 (m, 1H), 3.79 (s, 3H), 3.7 (m, 1H), 3.49 (s, 3H), 3.35 (m, 1H), 3.27 (s, 3H), 3.21 (m, 1H), 3.10 (m, 1H), 2.93 (t, *J* = 12.55 Hz, 1H), 2.56 (d, *J* = 15.44 Hz, 1H), 2.45 (t, *J* = 13.32 Hz, 1H), 1.89 (d, *J* = 12.44 Hz, 1H); **^{13}C**

NMR (100 MHz, MeOD): δ ppm 194.25, 152.22, 146.53, 145.46, 125.67, 120.69, 118.39, 114.36, 110.23, 72.87, 60.42, 56.96, 55.18, 54.13, 39.24, 39.15, 39.13, 31.08, 28.07. **HRMS** (ESI): calcd for $C_{19}H_{24}NO_5^+$ ([M + H]$^+$) 346.1654, found 346.1645.

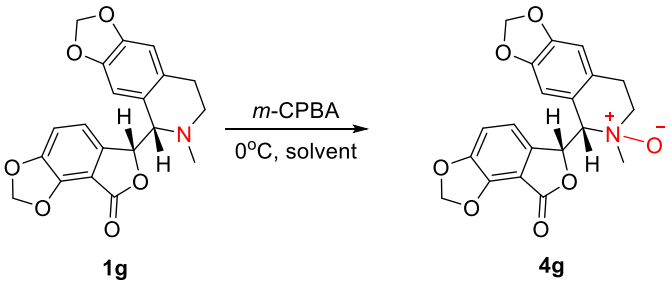
p) Synthesis and characterization data for cephalotaxine *N*-oxide (4d)



The procedure is the same as that for **4b** except that cephalotaxine (instead of sophoridine) was used. *T*he desired product was obtained as a pale-yellow solid in 63% yield.

^{1}**H NMR** (400 MHz, MeOD): δ ppm 6.66 (m, 2H), 5.89 (m, 2H), 5.10 (s, 1H), 4.77 (d, *J* = 9.24 Hz, 1H), 3.84 (d, *J* = 9.24 Hz, 2H), 3.79 (s, 3H), 3.77-3.72 (m, 1H), 3.71-3.66 (m, 1H), 3.62-3.55 (m, 1H), 3.45 (m, 1H), 2.69 (m, 1H), 2.47 (m, 1H), 2.04 (m, 3H); ^{13}**C NMR** (100 MHz, MeOD): δ ppm 165.88, 145.80, 131.19, 129.87, 111.29, 109.07, 100.62, 96.93, 86.68, 71.86, 69.36, 61.72, 56.87, 54.08, 38.69, 28,15, 17.52. **HRMS** (ESI): calcd for $C_{18}H_{22}NO_5^+$ ([M + H]$^+$) 332.1498, found 332.1488;

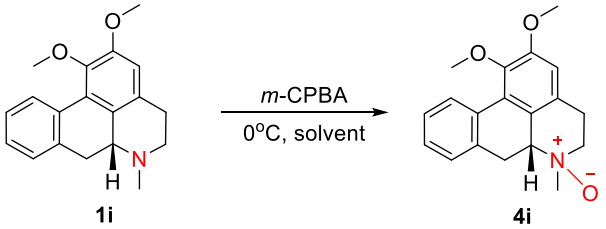
q) Synthesis and characterization data for bicuculline *N*-oxide (4g)



The procedure is the same as that for **4b** except that bicuculline (instead of sophoridine) was used. The desire product was obtained as a pale-yellow solid in 45% yield.

^{1}**H NMR** (400 MHz, MeOD): δ ppm 7.38 (m, 2H), 6.71 (s, 1H), 6.41 (s, 1H), 6.23 (d, *J* = 2.3, 2H), 5.84 (d, *J* = 2.91 Hz, 2H), 5.56 (s, 1H), 4.78 (s, 1H), 4.06 (m, 1H), 3.61 (s, 3H), 3.57 (m, 1H), 3.28 (m, 1H), 3.05 (m, 1H); ^{13}**C NMR** (100 MHz, MeOD): δ ppm 166.15, 150.20, 147.88, 145.47, 139.06, 126.55, 118.40, 115.49, 114.04, 107.90, 107.80, 106.65, 103.95, 101.21, 79.53, 78.32, 61.05, 56.03, 24.85. **HRMS** (ESI): calcd for $C_{20}H_{18}NO_7^+$ ([M + H]$^+$) 384.1083, found 384.1074;

r) Synthesis and characterization data for nuciferine *N*-oxide (4i)



The procedure is the same as that for **4b** except that nuciferine (instead of sophoridine) was used. The desired product was obtained as a pale-yellow solid in 84% yield.

^{1}**H NMR** (400 MHz, MeOD): δ ppm 8.31 (dd, J_1 = 8.04 Hz, J_2 = 1.37 Hz, 1H), 7.39 (d, J = 6.55 Hz, 1H), 7.33-7.25 (m, 2H), 6.88 (s, 1H), 4.49 (dd, J_1 = 12.46 Hz, J_2 = 4.46 Hz, 1H), 3.90 (s, 3H), 3.82-3.75 (m, 1H), 3.63 (s, 3H), 3.61-3.53 (m, 2H), 3.43 (s, 3H), 3.31-3.21 (m, 2H), 2.84 (m, 1H); **^{13}C NMR** (100 MHz, MeOD): δ ppm 153.08, 145.75, 134.08, 131.15, 128.13, 127.87, 127.70, 127.17, 127.00, 126.79, 121.65, 111.16, 70.64, 63.81, 59.29, 56.78, 55.06, 29.37, 24.11. **HRMS** (ESI): calcd for $C_{19}H_{22}NO_3^+$ ([M + H]$^+$) 312.1600, found 312.1589.

Crystal structure determination of 3c, 3h-a and [Mn^{III}(TDCPP)N]

Diffraction-quality crystals of **3c** and **3h-a** were grown by slow cooling of their acetonitrile solution with the addition of 1 M HCl (V_{HCl}:$V_{Acetonitrile}$=1:200). A crystal of [Mn^{V}(TDCPP)N] suitable for X-ray diffraction analysis was grown by slow diffusion of hexane to a toluene solution of this complex. The X-ray diffraction data were collected on a Bruker X8 Proteum diffractometer equipped with a 'Bruker APEX-II CCD' detector. The crystal was kept at 100 K during data collection. The diffraction images were interpreted, and the diffraction intensities were integrated by using the program SAINT. Multi-scan SADABS was applied for absorption correction. By using Olex2, the structure was solved with the XS structure solution program using direct methods and refined with the XL refinement package using least squares minimization. The positions of the H atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, 1.5 times that of the C atoms in methyl group and these positions participated in the calculation of the final R indices. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically.

Table S1. Crystal data and structure refinement for **3c**.

Identification code	**3c**
Empirical formula	$C_{19}H_{29}ClN_2O_6$
Formula weight	416.89
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.2666 (5)
b/Å	14.4440 (9)
c/Å	19.5127 (13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2048.0 (2)
Z	4
ρ_{calc}g/cm^3	1.352
μ/mm^{-1}	1.980
F (000)	888.0
Crystal size/mm^3	0.4 × 0.32 × 0.31
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	3.807 to 68.553
Index ranges	-8⩽ h ⩽ 8, -17 ⩽ k ⩽ 17, -23 ⩽ l ⩽ 23
Reflections collected	32519
Independent reflections	3771 [R_{int} = 0.0383, R_{sigma} = 0.0198]
Data/restraints/parameters	3771/0/257
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0214, wR_2 = 0.0567
Final R indexes [all data]	R_1 = 0.0214, wR_2 = 0.0567
Largest diff. peak/hole / e Å^{-3}	0.22/-0.14
Flack parameter	-0.001 (3)

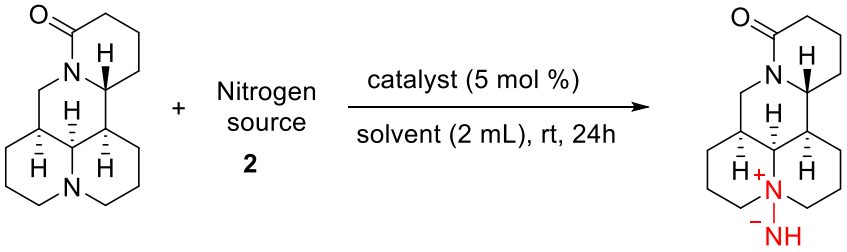
Table S2. Crystal data and structure refinement for **3h-b**.

Identification code	**3h-b**
Empirical formula	$C_{16}H_{20}ClN_2O_5$
Formula weight	356.79
Temperature/K	100
Crystal system	trigonal
Space group	$P3_2$
a/Å	11.3090 (4)
b/Å	11.3090 (4)
c/Å	11.3065 (4)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	1252.30 (10)
Z	3
ρ_{calc}g/cm^3	1.415
μ/mm^{-1}	2.290
F (000)	561.0
Crystal size/mm^3	0.1468 × 0.1253 × 0.1106
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.51 to 79.51
Index ranges	-14≤ h ≤ 13, -14 ≤ k ≤ 13, -13 ≤ l ≤ 14
Reflections collected	13796
Independent reflections	3426 [R_{int} = 0.0317, R_{sigma} = 0.0257]
Data/restraints/parameters	3426/1/228
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0347, wR_2 = 0.0898
Final R indexes [all data]	R_1 = 0.0347, wR_2 = 0.0898
Largest diff. peak/hole / e Å^{-3}	0.20/-0.29
Flack parameter	0.018 (13)

Table S3. Crystal data and structure refinement for [Mn^{V}(TDCPP)(N)].

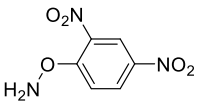
Identification code	[Mn^{V}(TDCPP)(N)]
Empirical formula	$C_{58}H_{36}Cl_8MnN_5$
Formula weight	1141.46
Temperature/K	100
Crystal system	orthorhombic
Space group	P b c a
a/Å	12.6724 (19)
b/Å	19.811 (3)
c/Å	20.784 (3)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	5217.9 (13)
Z	4
$\rho_{calc}g/cm^3$	1.453
μ/mm^{-1}	0.708
F (000)	2320
Crystal size/mm^3	0.48 ×0.35 × 0.04
Radiation	MoK\a (λ = 0.71073)
2Θ range for data collection/°	2.145 to 28.527
Index ranges	-17≤ h ≤17, -26 ≤ k ≤26, -27 ≤ l ≤ 27
Reflections collected	70468
Independent reflections	6616 [R_{int} = 0.0684, R_{sigma} = 0.0321]
Data/restraints/parameters	6616/0/341
Goodness-of-fit on F^2	1.362
Final R indexes [I>=2σ (I)]	R_1 = 0.1003, wR_2 = 0.2327
Final R indexes [all data]	R_1 = 0.1003, wR_2 = 0.2327
Largest diff. peak/hole / e $Å^{-3}$	0.83/-0.71
Flack parameter	-

Table S4. Optimization of reaction conditions by using matrine as the substrate. Porphyrin ligands[1] and the metal complexes,[2-4] and carbonyl and sulfonyl hydroxylamonium salt **2c-2e** [5] were synthesized according to the literature methods.

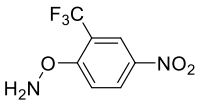


1a **3a**

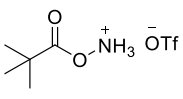
entry	catalyst	**Nitrogen source**	solvent	yield
1	[Fe^{III}(TPP)Cl]	**2a**	DCM	0
2	[Fe^{III}(TDCPP)Cl]	**2a**	DCM	0
3	[Fe^{III}(F_{20}TPP)Cl]	**2a**	DCM	0
4	[Mn^{III}(TPP)Cl]	**2a**	DCM	36%
5	[Mn^{III}(TDCPP)Cl]	**2a**	DCM	89%
6	[Mn^{III}(F_{20}TPP)Cl]	**2a**	DCM	57%
7	[Ru^{IV}(TPP)Cl_2]	**2a**	DCM	24%
8	[Ru^{IV}(TDCPP)Cl_2]	**2a**	DCM	32%
9	[Ru^{IV}(F_{20}TPP)Cl_2]	**2a**	DCM	21%
10	[Mn^{III}(TDCPP)Cl]	**2b**	DCM	7%
11	[Mn^{III}(TDCPP)Cl]	**2c**	DCM	0
12	[Mn^{III}(TDCPP)Cl]	**2d**	DCM	0
13	[Mn^{III}(TDCPP)Cl]	**2e**	DCM	0
14	[Mn^{III}(TDCPP)Cl]	**2a**	DMF	63%
15	[Mn^{III}(TDCPP)Cl]	**2a**	DCE	54%
16	[Mn^{III}(TDCPP)Cl]	**2a**	$CHCl_3$	19%
17	[Mn^{III}(TDCPP)Cl]	**2a**	CH_3CN	37%
18	-	**2a**	DCM	0



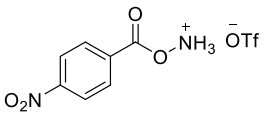
2a



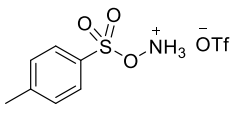
2b



2c

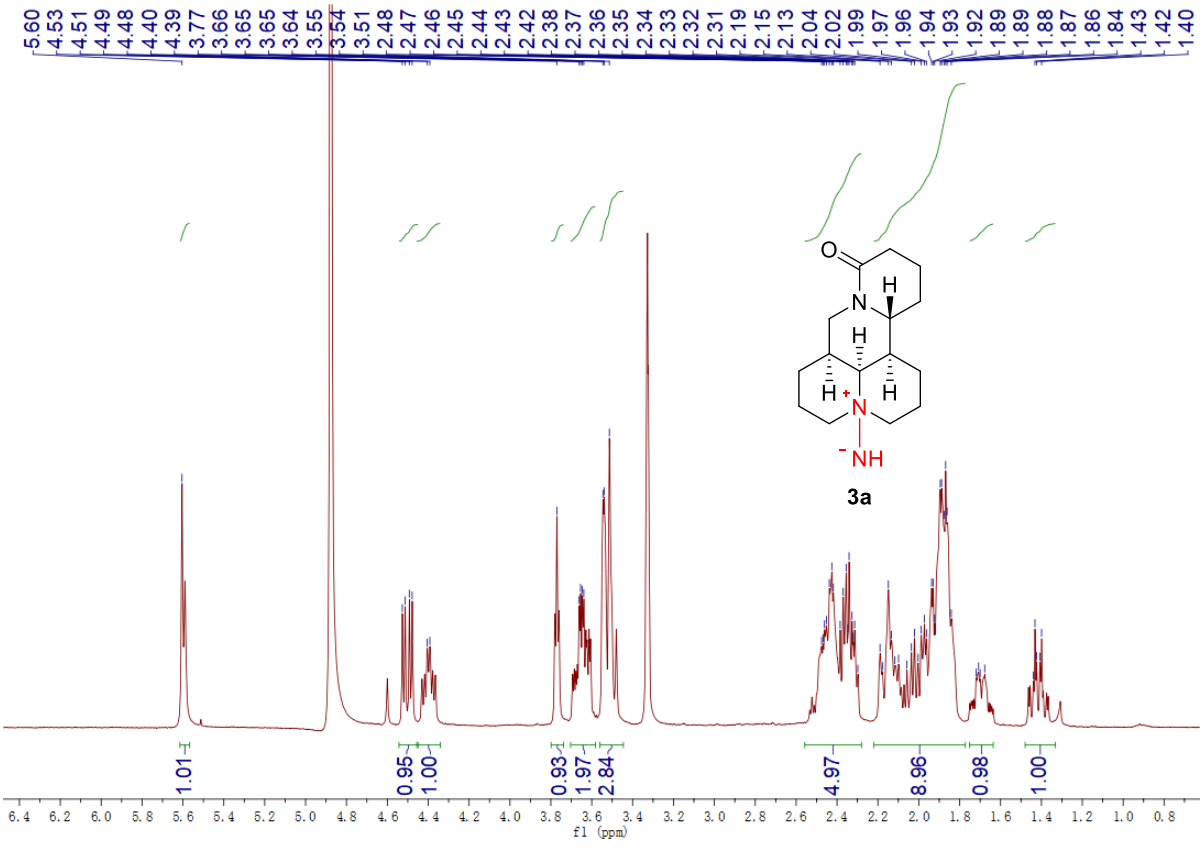


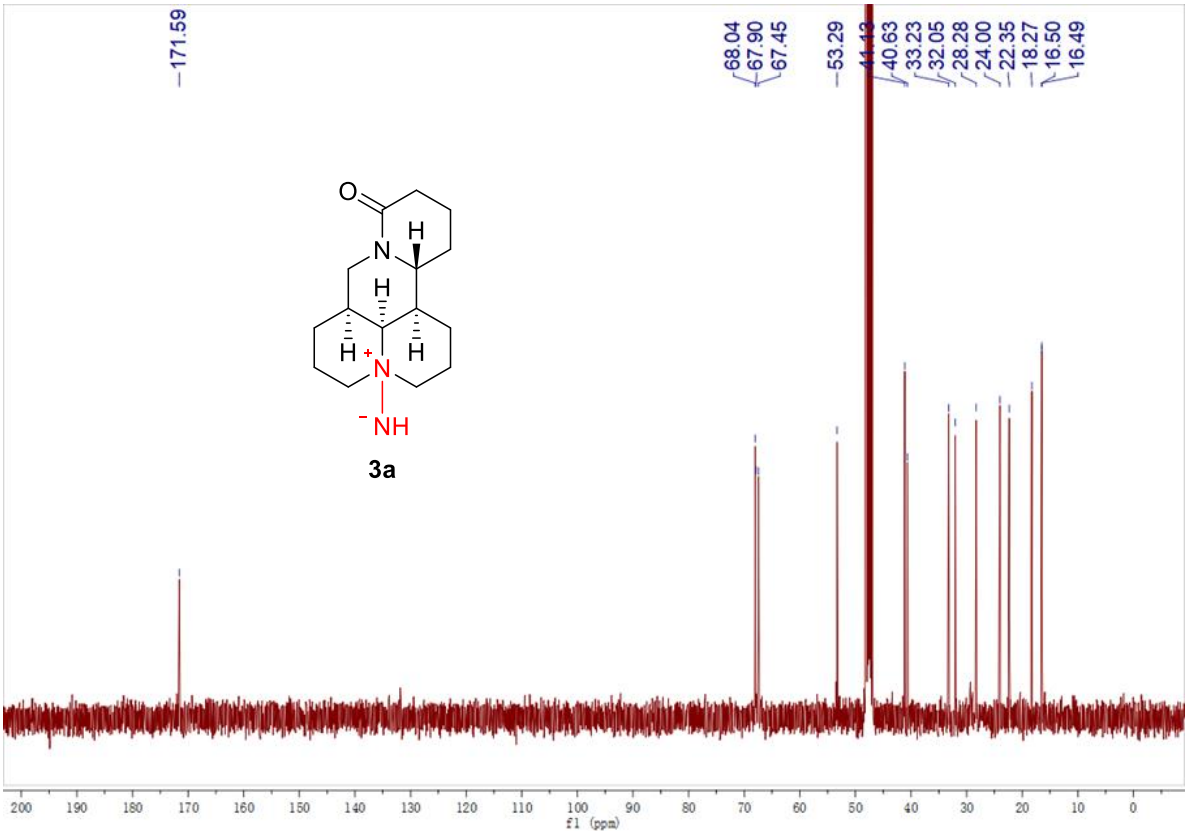
2d

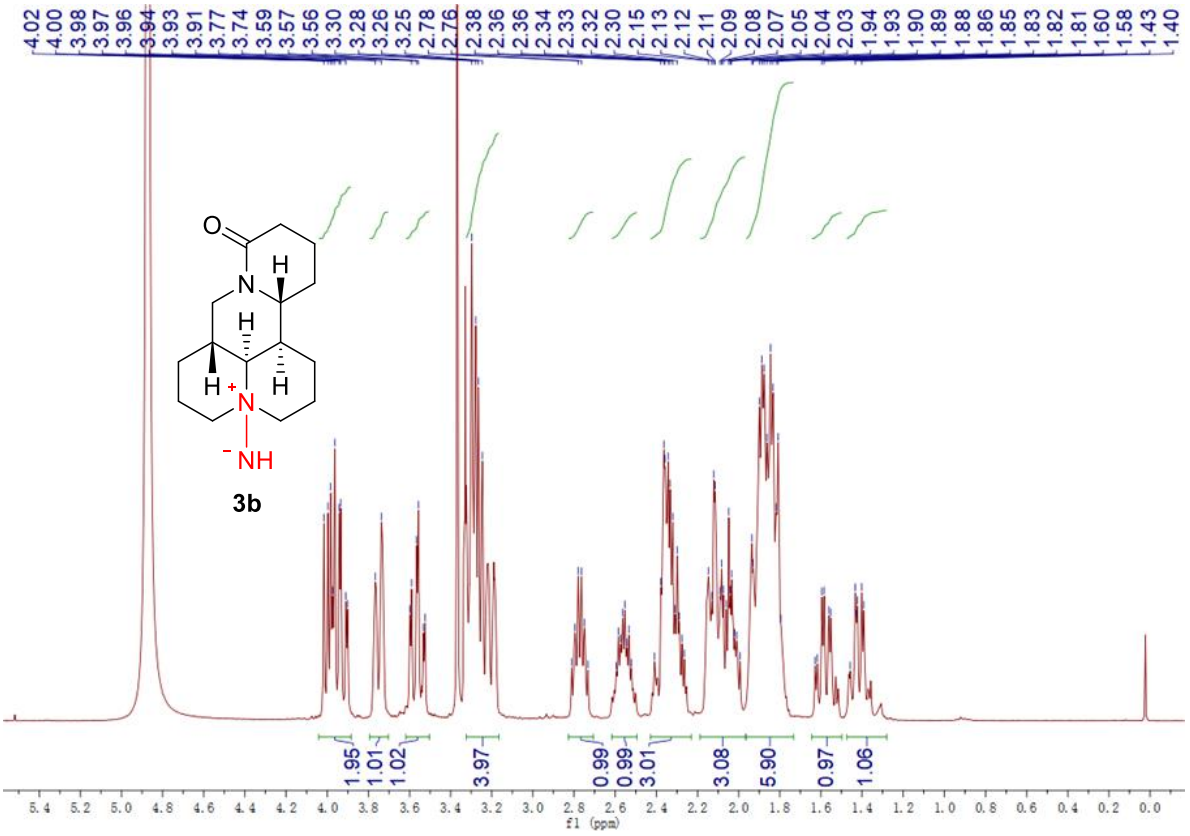


2e

2. NMR spectra



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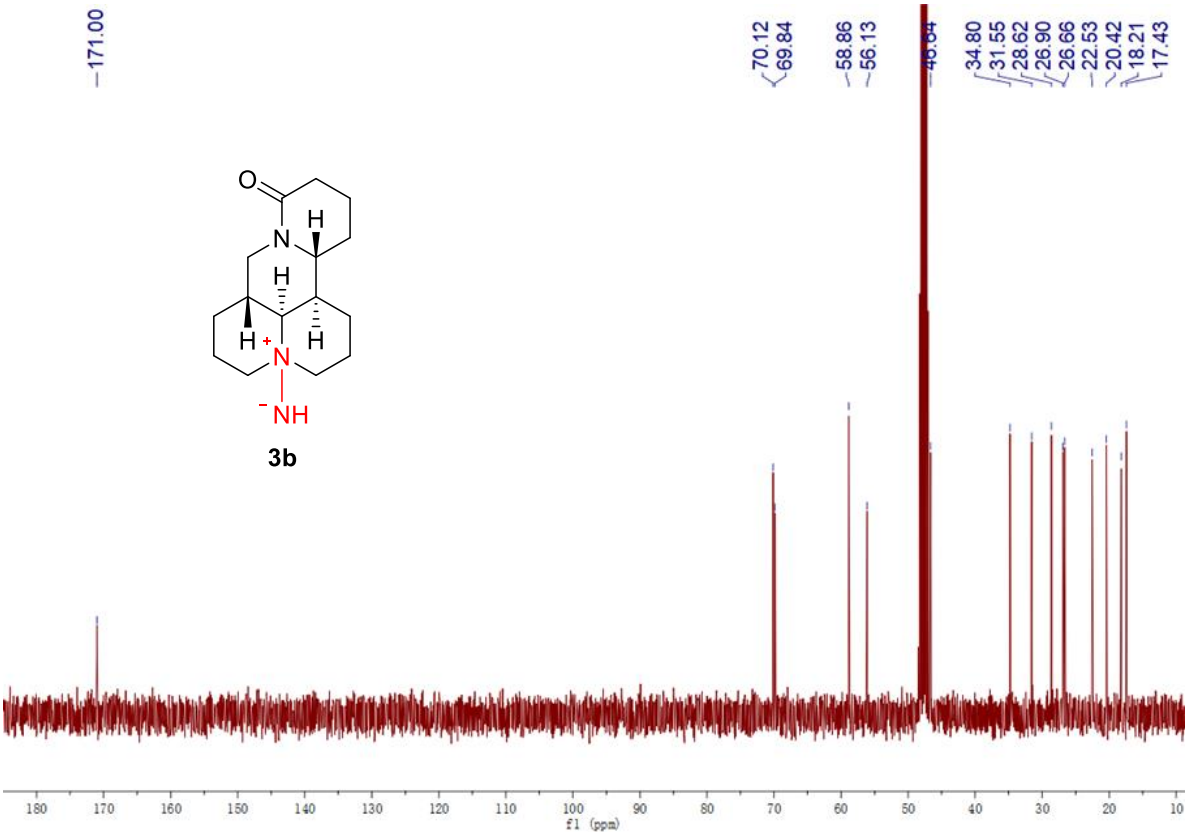
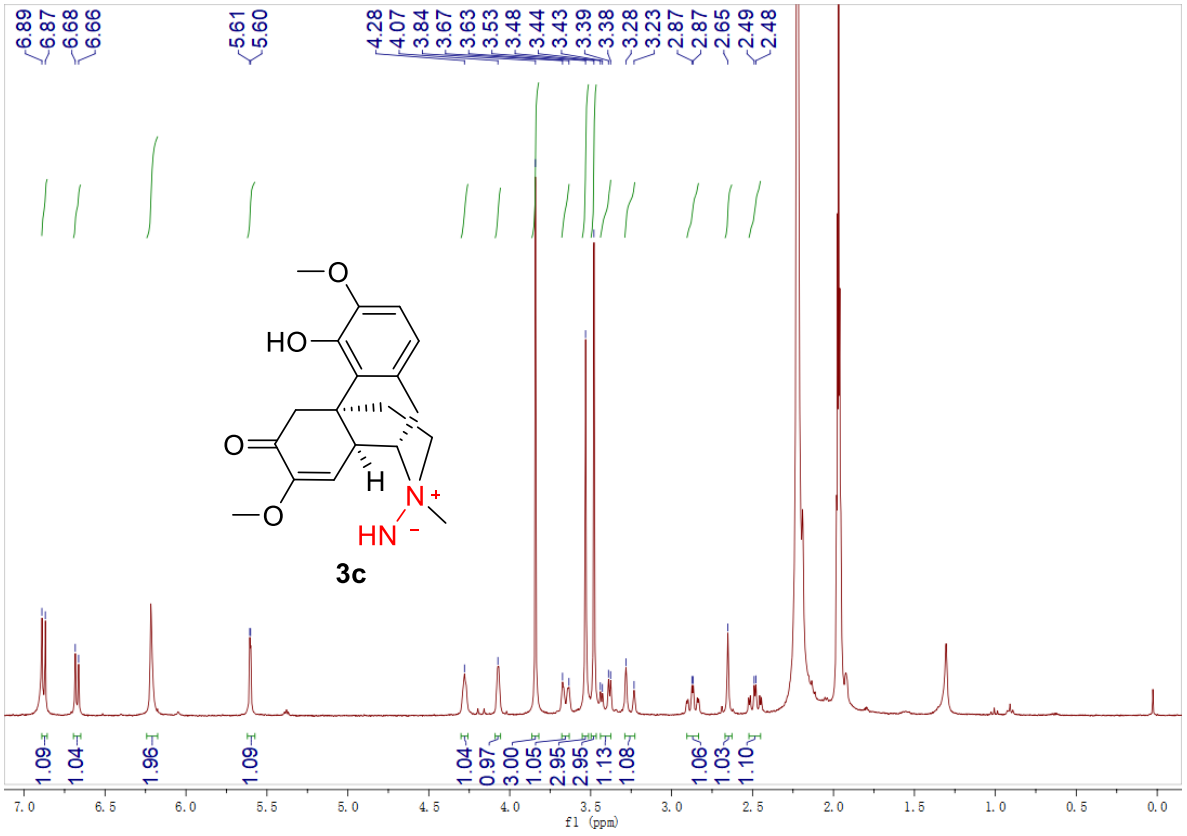
1.95 1.01 1.02 3.97 0.99 0.99 3.01 3.08 5.90 0.97 1.06
f1 (ppm)
3b


171.00
70.12 69.84 58.86 56.13 48.84 34.80 31.55 28.62 26.90 26.66 22.53 20.42 18.21 17.43
f1 (ppm)
3b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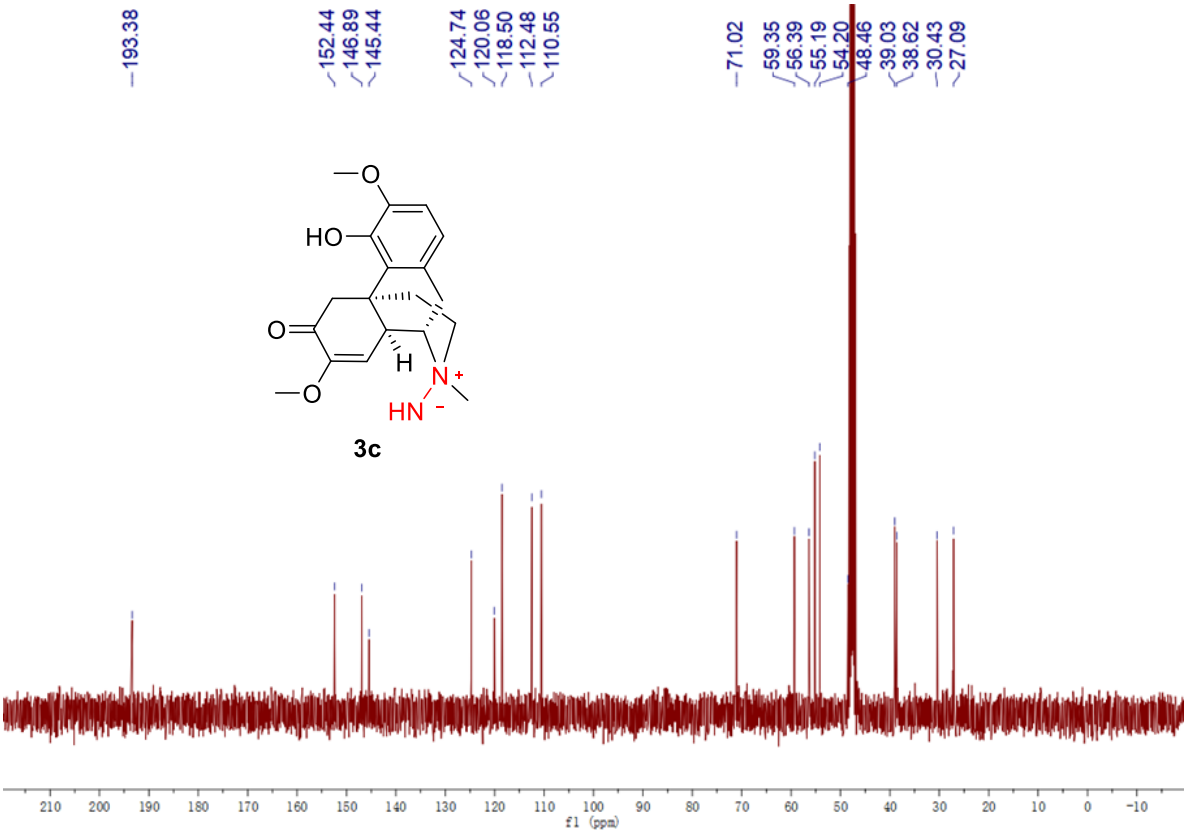
3.44
3.43
3.39
3.38
3.28
3.23
2.87
2.87
2.65
2.49
2.48
HO
O
O
H
N+
HN -
O
3c
1.09
1.04
1.96
1.09
1.04
0.97
3.00
1.05
2.95
2.95
1.13
1.08
1.06
1.03
1.10
f1 (ppm)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110.55
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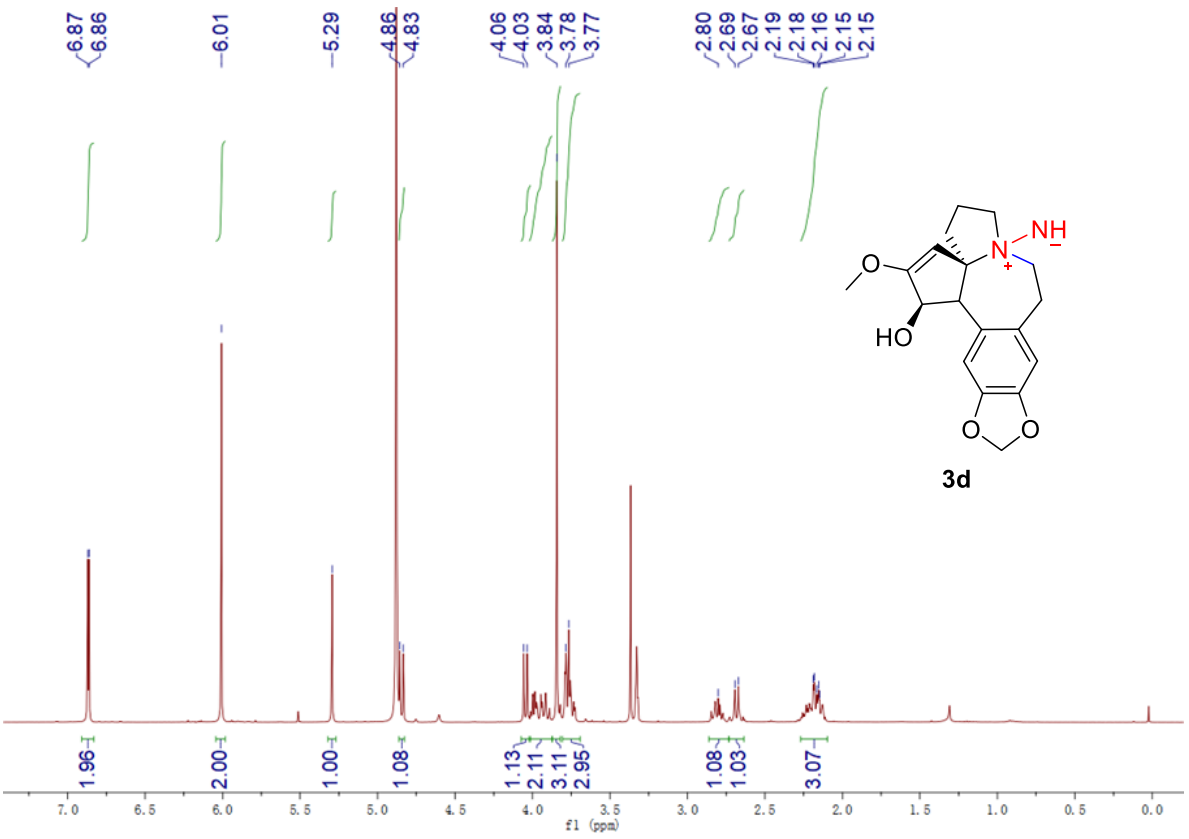
59.35
56.39
55.19
54.20
48.46
39.03
38.62
30.43
27.09
HO
O
O
H
N+
HN -
O
3c
f1 (ppm)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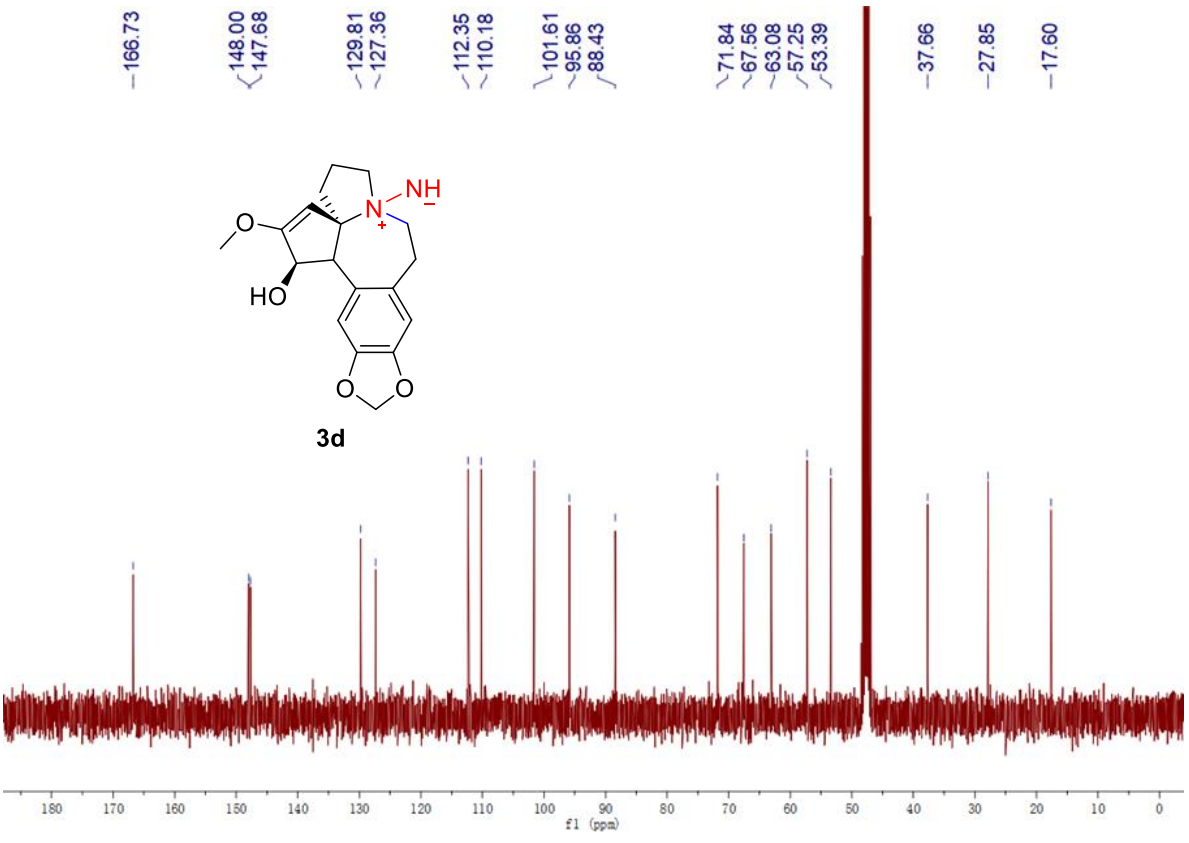
2.67
2.19
2.18
2.16
2.15
2.15
NH
N
O
HO
O
O
1.96
2.00
1.00
1.08
1.13
2.11
3.11
2.95
1.08
1.03
3.07
f1 (ppm)

3d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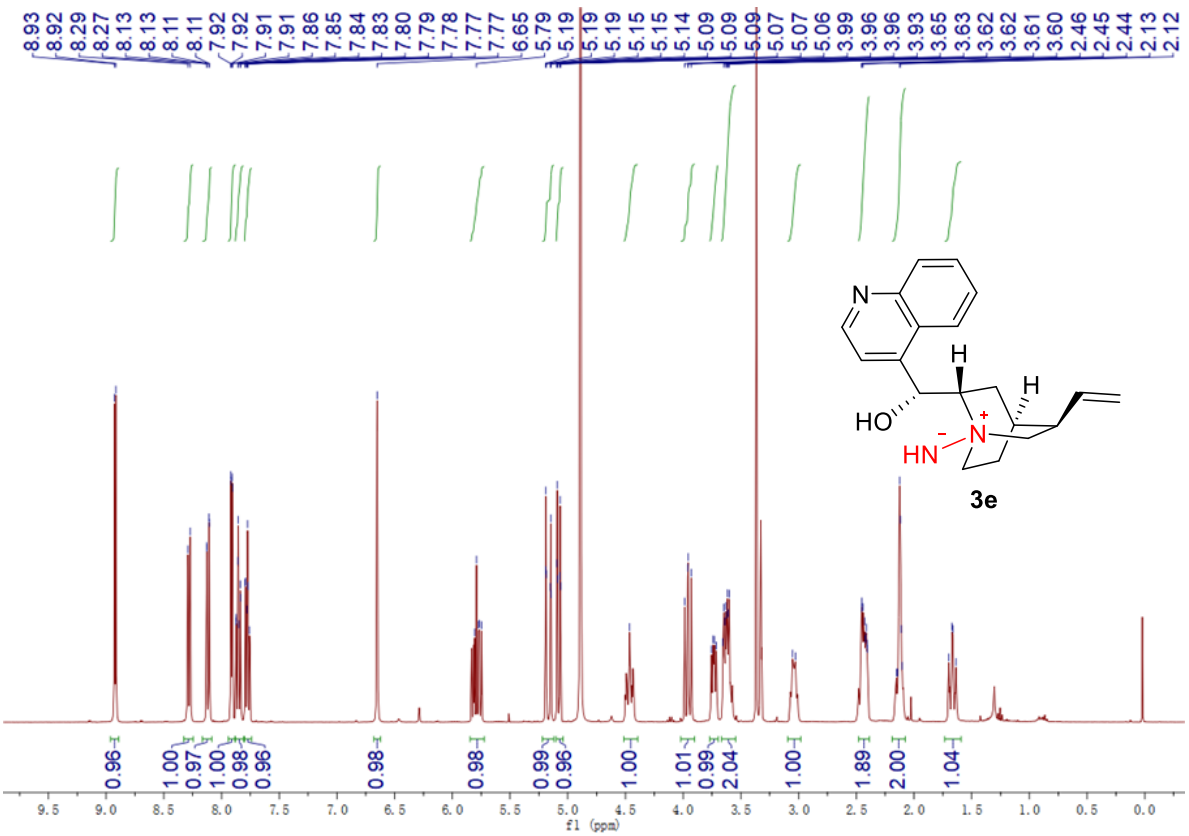
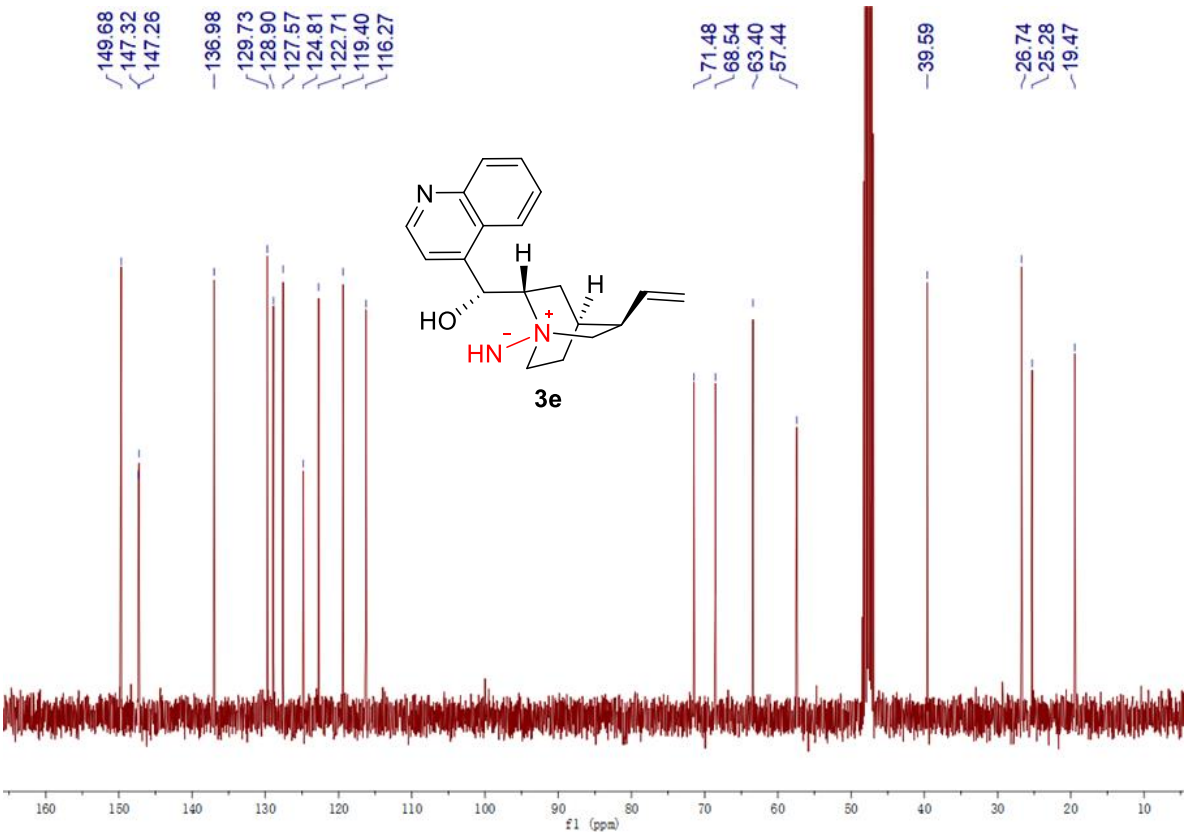
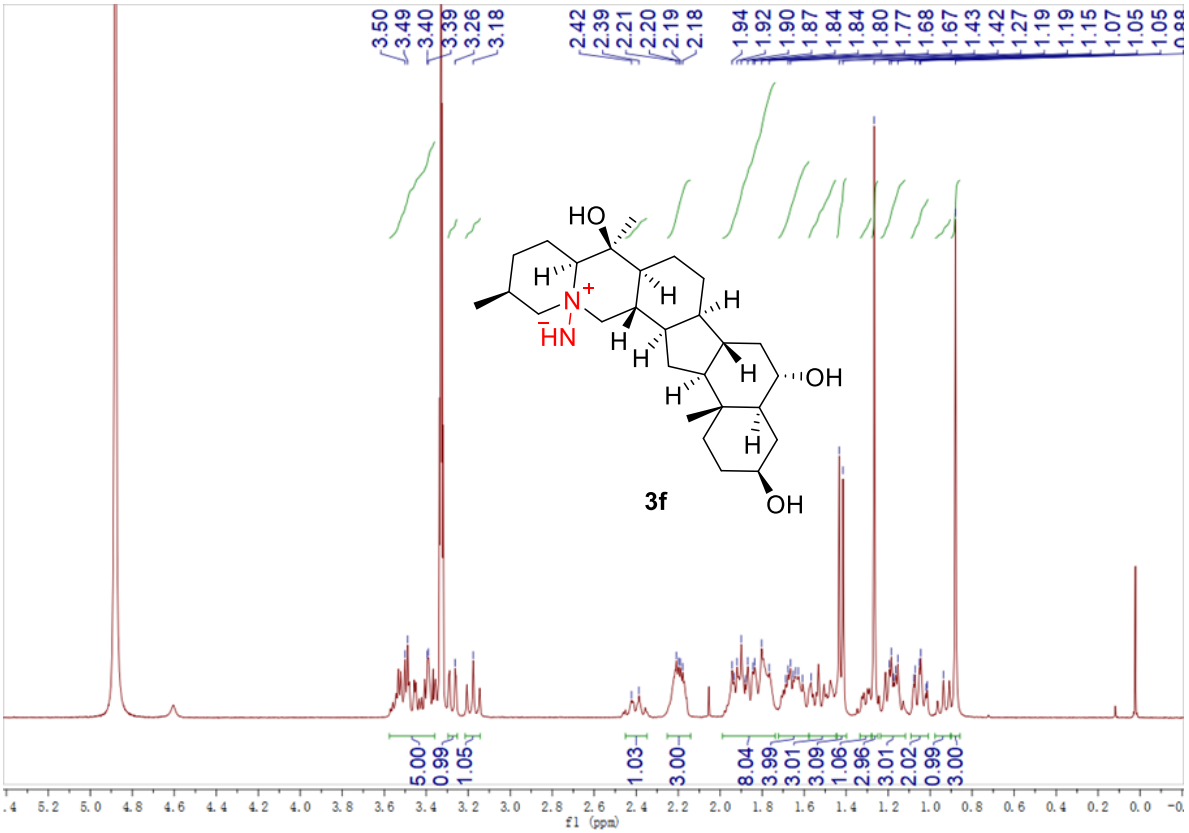
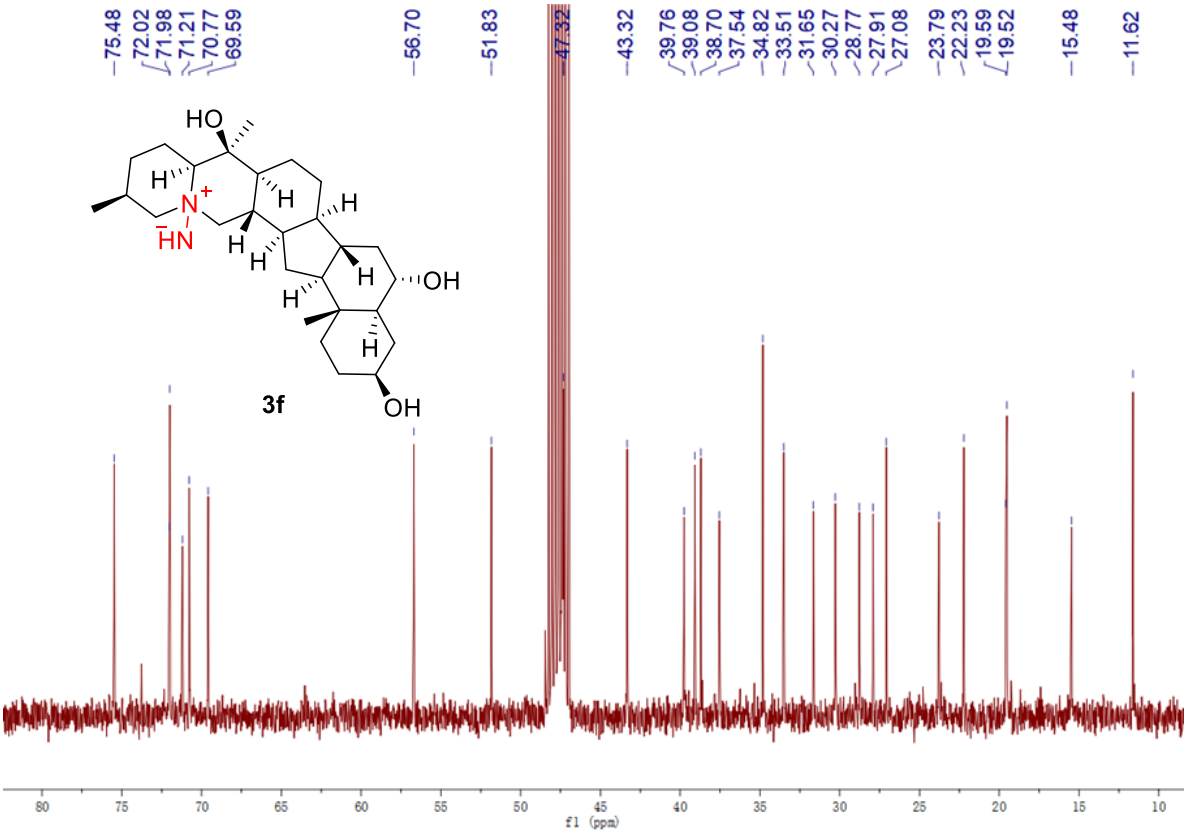
112.35
110.18
101.61
95.86
88.43
71.84
67.56
63.08
57.25
53.39
37.66
27.85
17.60
NH
N
O
HO
O
O
f1 (ppm)

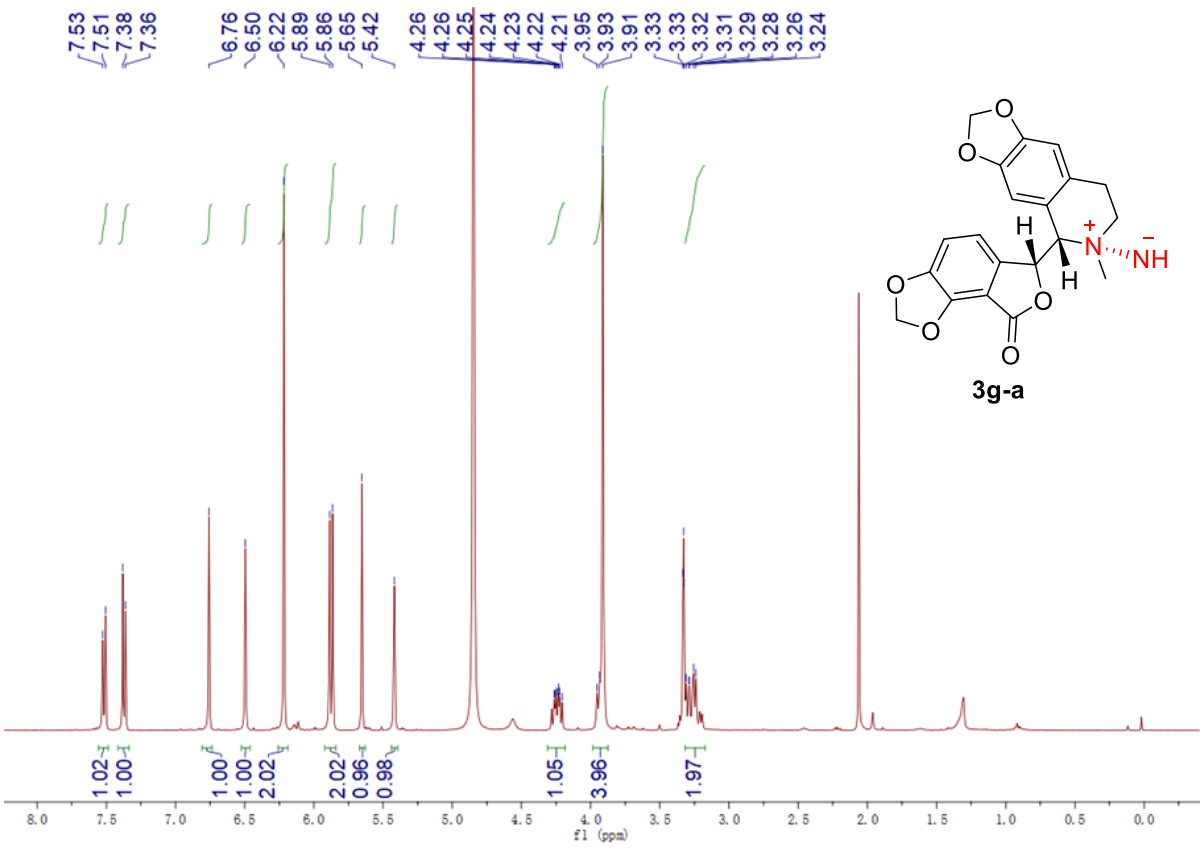
3d

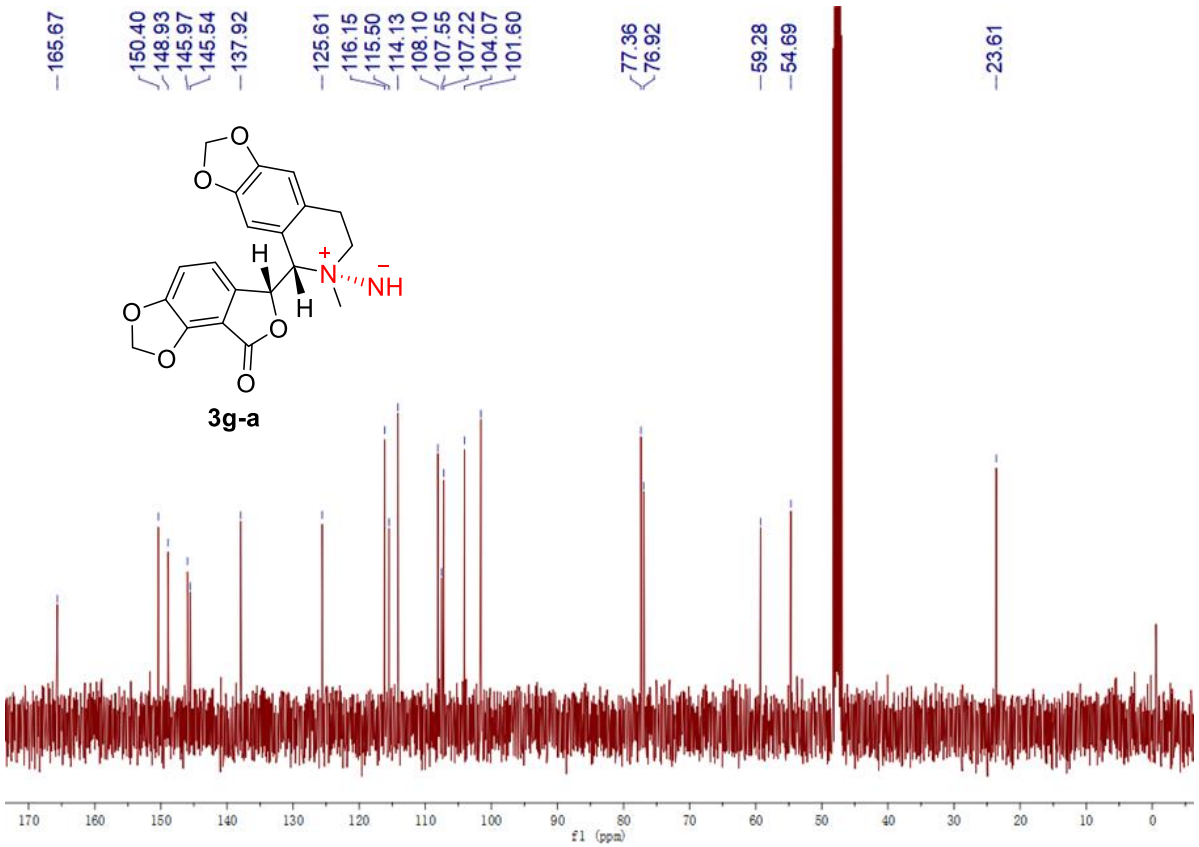

8.93 8.92 8.29 8.27 8.13 8.13 8.11 8.11 7.92 7.92 7.91 7.91 7.86 7.85 7.84 7.83 7.80 7.79 7.78 7.77 7.77 6.65 5.79 5.19 5.19 5.19 5.15 5.15 5.14 5.09 5.09 5.09 5.07 5.07 5.06 3.99 3.96 3.96 3.93 3.65 3.63 3.62 3.62 3.61 3.60 2.46 2.45 2.44 2.13 2.12
0.96 1.00 0.97 1.00 0.98 0.96 0.98 0.98 0.99 0.96 1.00 1.01 0.99 2.04 1.00 1.89 2.00 1.04
f1 (ppm)
N
H
H
HO
HN
3e

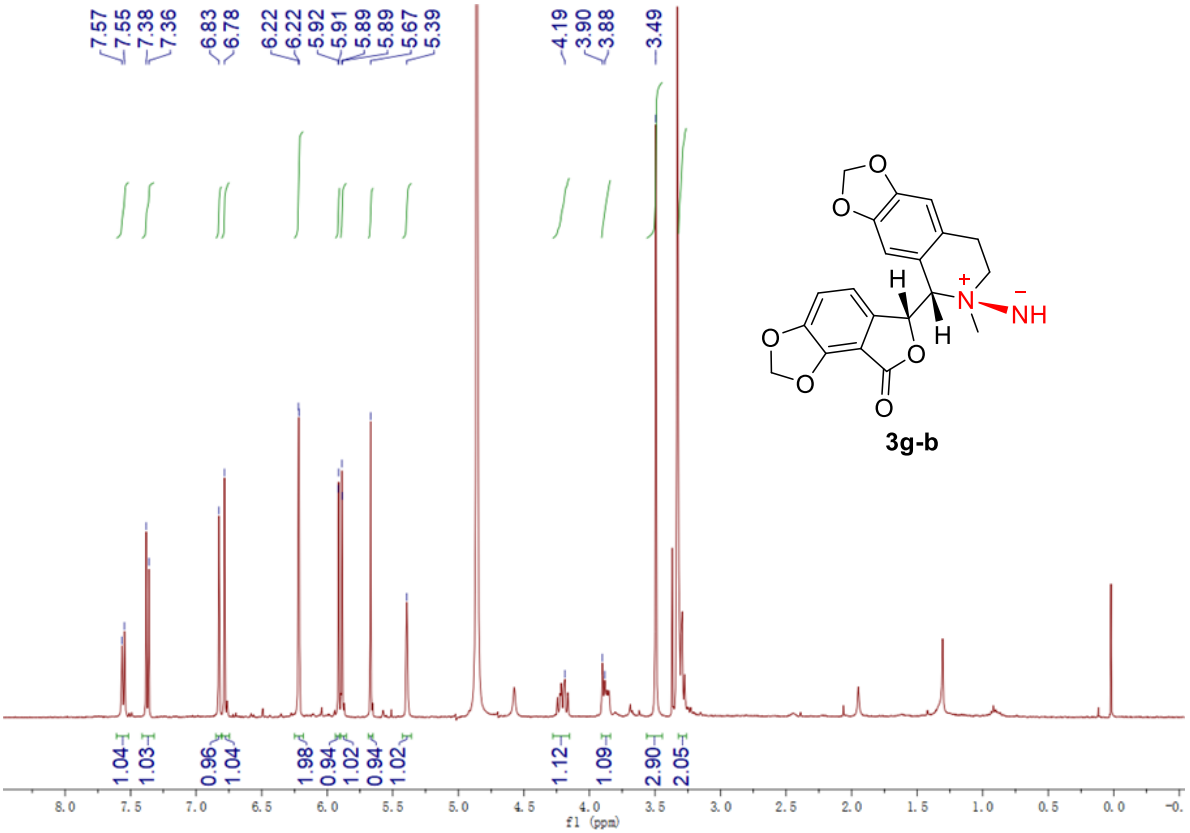

149.68 147.32 147.26 136.98 129.73 128.90 127.57 124.81 122.71 119.40 116.27 71.48 68.54 63.40 57.44 39.59 26.74 25.28 19.47
f1 (ppm)
N
H
H
HO
HN
3e

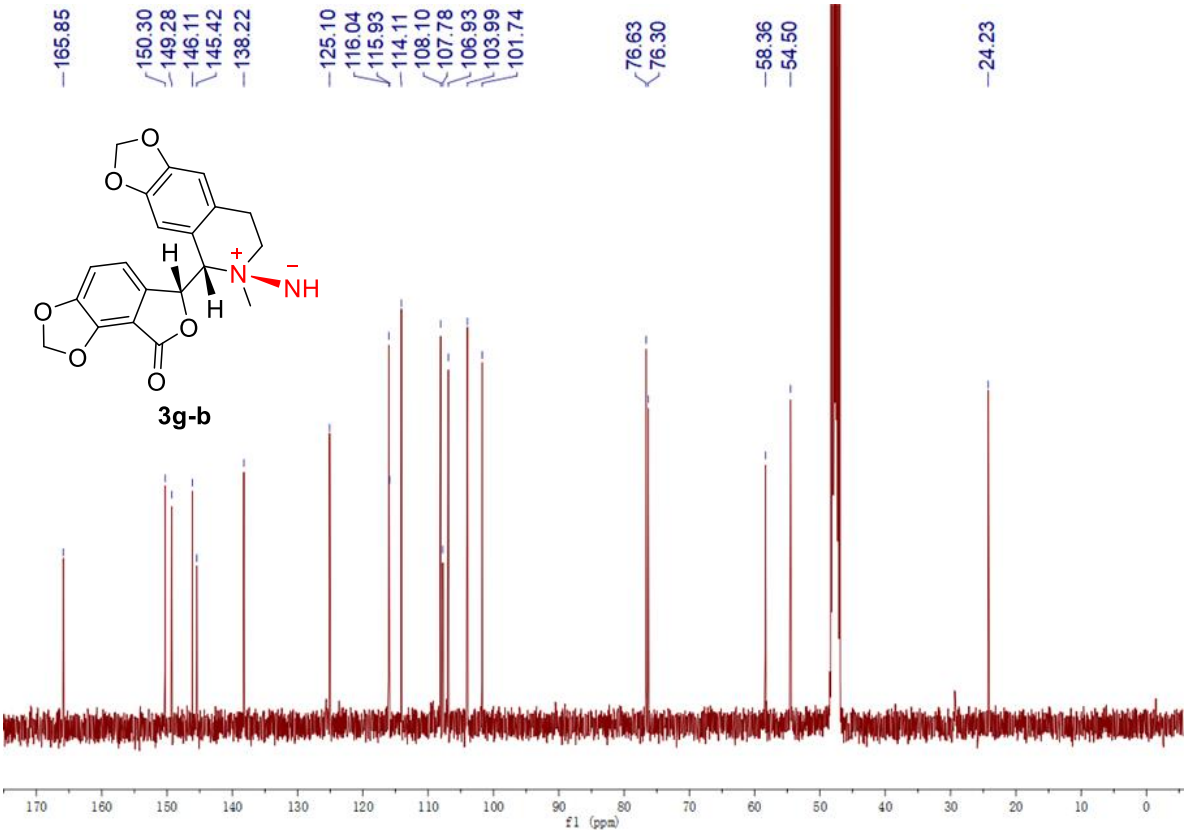

3.50
3.49
3.40
3.39
3.26
3.18
2.42
2.39
2.21
2.20
2.19
2.18
1.94
1.92
1.90
1.87
1.84
1.84
1.80
1.77
1.68
1.67
1.43
1.42
1.27
1.19
1.19
1.15
1.07
1.05
1.05
HO
H
N+
HN
H
H
H
H
H
H
OH
H
OH
3f
5.00
0.99
1.05
1.03
3.00
8.04
3.99
3.01
3.09
1.06
2.96
3.01
2.02
0.99
3.00
f1 (ppm)

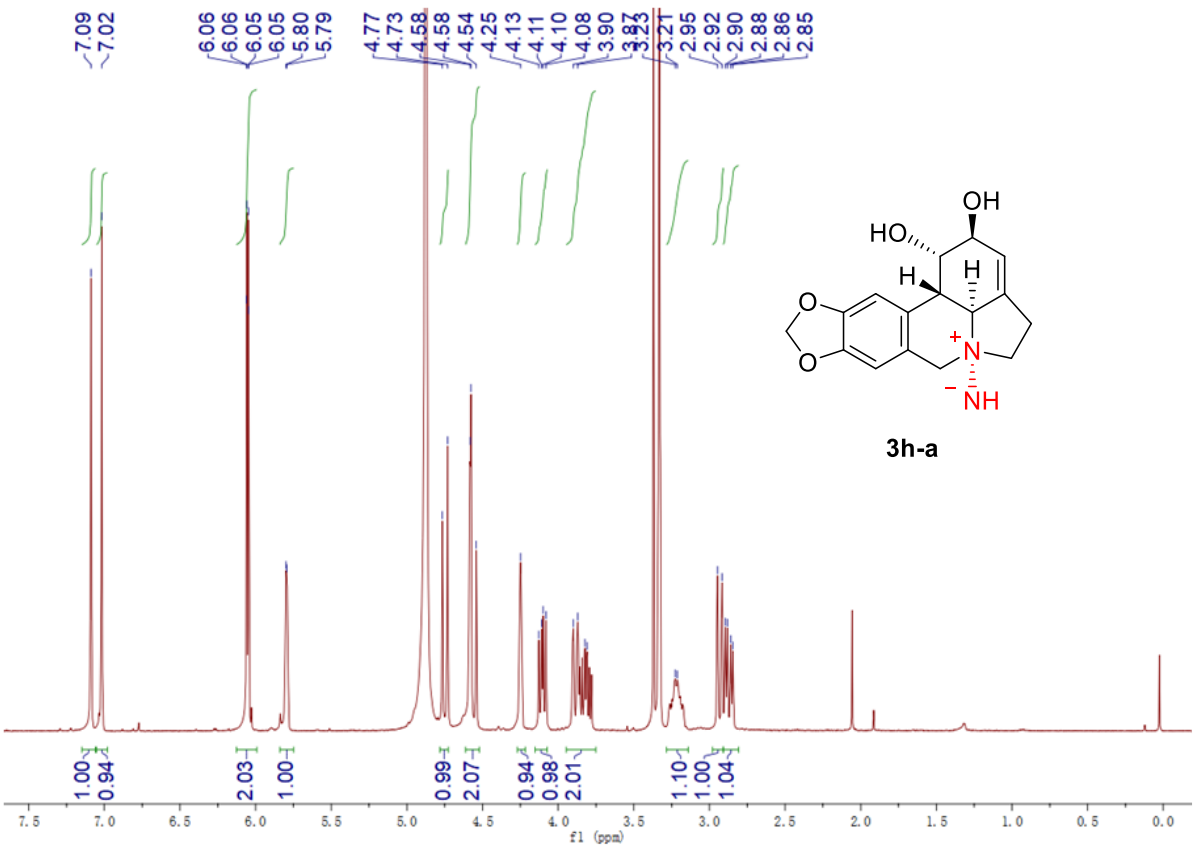

75.48
72.02
71.98
71.21
70.77
69.59
56.70
51.83
47.32
43.32
39.76
39.08
38.70
37.54
34.82
33.51
31.65
30.27
28.77
27.91
27.08
23.79
22.23
19.59
19.52
15.48
11.62
HO
H
N+
HN
H
H
H
H
H
H
OH
H
OH
3f
f1 (ppm)

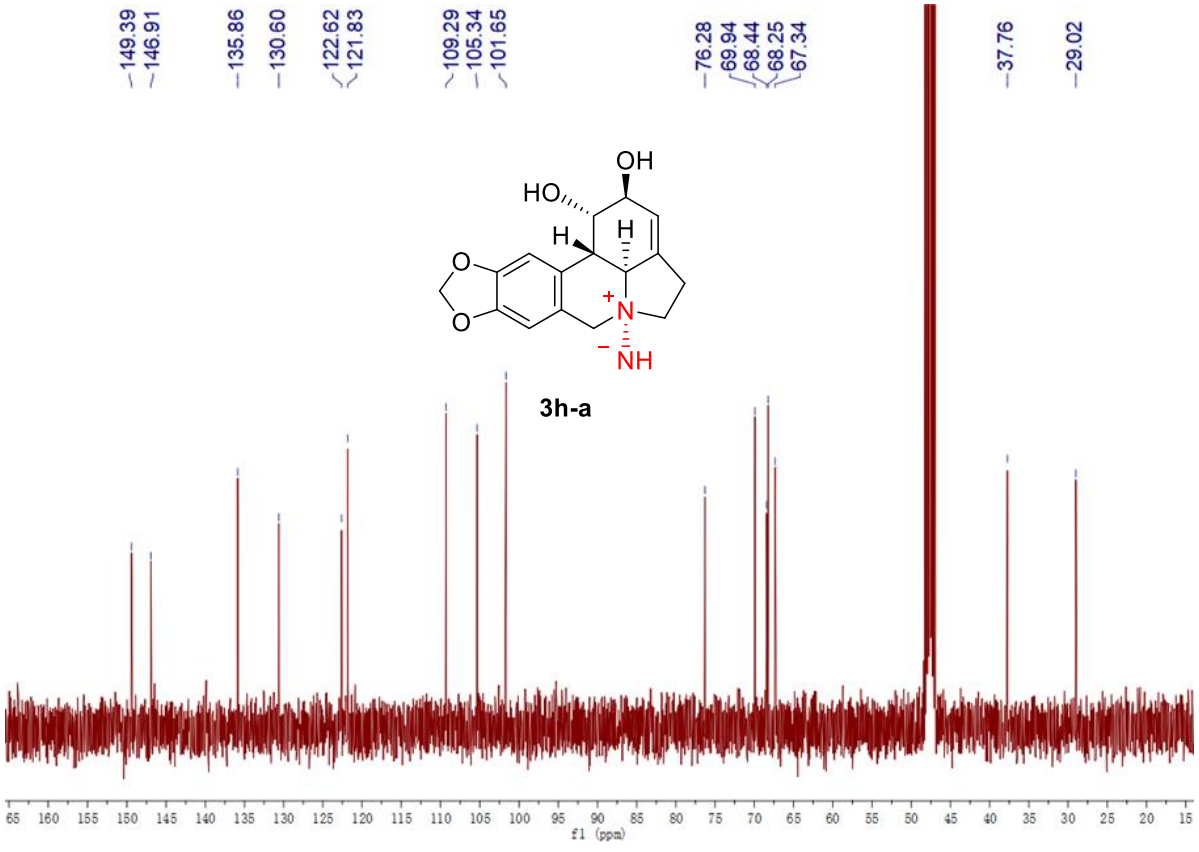

7.53
7.51
7.38
7.36
6.76
6.50
6.22
5.89
5.86
5.65
5.42
4.26
4.26
4.25
4.24
4.23
4.22
4.21
3.95
3.93
3.91
3.33
3.33
3.32
3.31
3.29
3.28
3.26
3.24
1.02
1.00
1.00
1.00
2.02
2.02
0.96
0.98
1.05
3.96
1.97
f1 (ppm)
3g-a

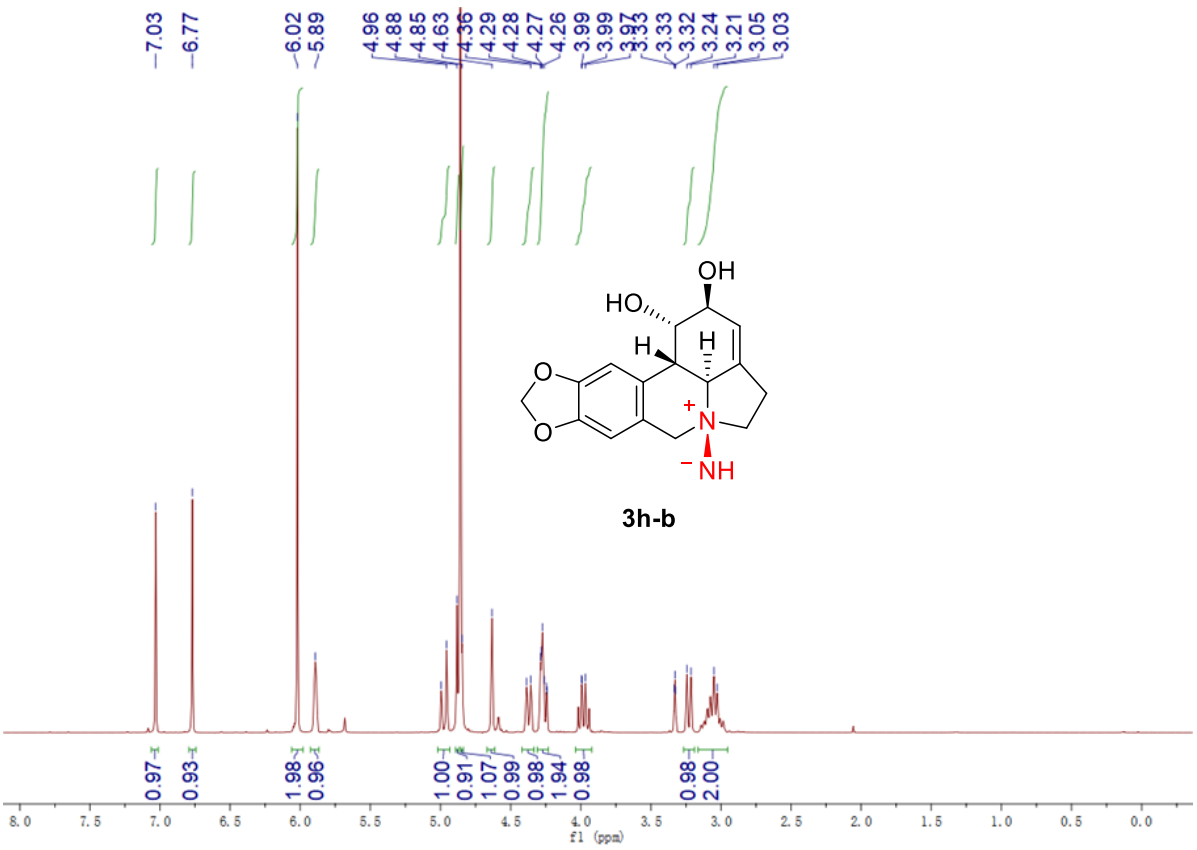

165.67
150.40
148.93
145.97
145.54
137.92
125.61
116.15
115.50
114.13
108.10
107.55
107.22
104.07
101.60
77.36
76.92
59.28
54.69
23.61
f1 (ppm)
3g-a


7.57
7.55
7.38
7.36
6.83
6.78
6.22
6.22
5.92
5.91
5.89
5.89
5.67
5.39
4.19
3.90
3.88
3.49
1.04
1.03
0.96
1.04
1.98
0.94
1.02
0.94
1.02
1.12
1.09
2.90
2.05
f1 (ppm)
3g-b

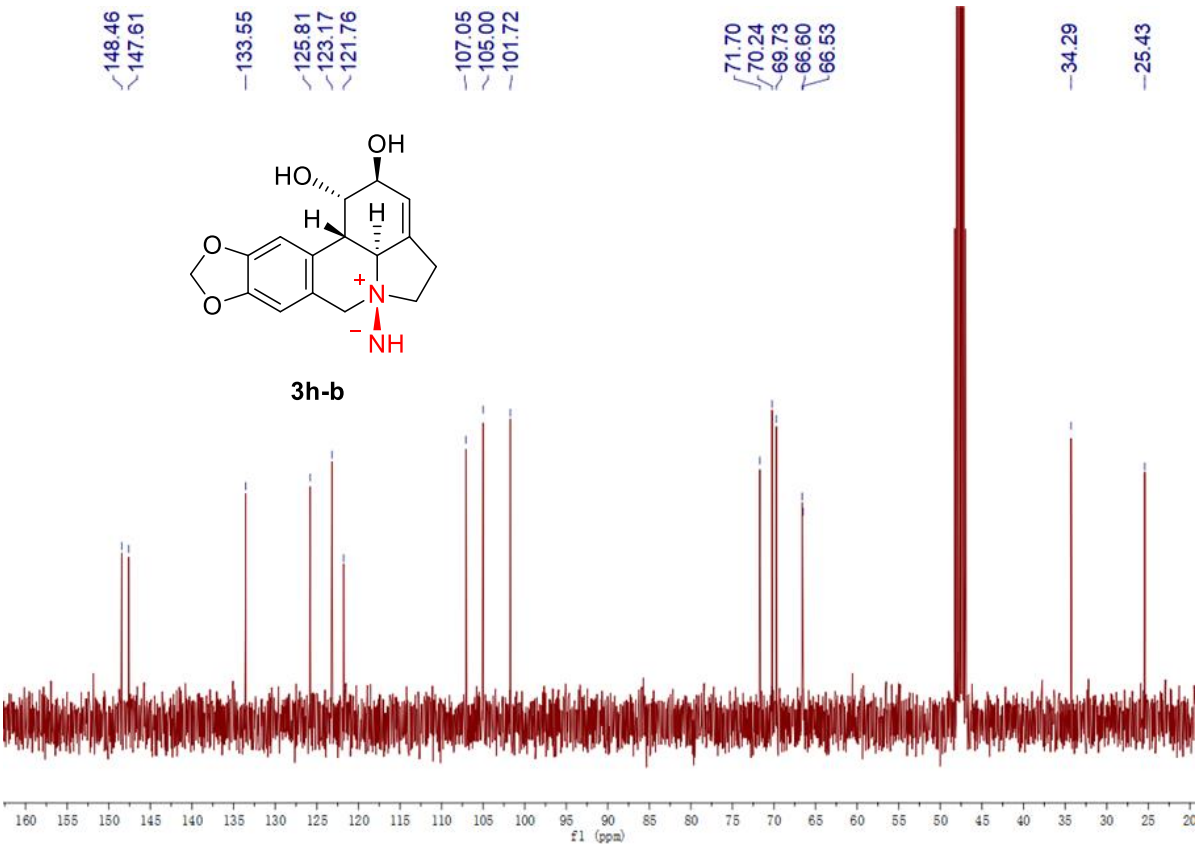

165.85
150.30
149.28
146.11
145.42
138.22
125.10
116.04
115.93
114.11
108.10
107.78
106.93
103.99
101.74
76.63
76.30
58.36
54.50
24.23
f1 (ppm)
3g-b


7.09
7.02
6.06
6.06
6.05
6.05
5.80
5.79
4.77
4.73
4.58
4.58
4.54
4.25
4.13
4.11
4.10
4.08
3.90
3.87
3.83
3.21
2.95
2.92
2.90
2.88
2.86
2.85
1.00
0.94
2.03
1.00
0.99
2.07
0.94
0.98
2.01
1.10
1.00
1.04
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
f1 (ppm)
OH
HO
H
H
O
O
N
NH
3h-a

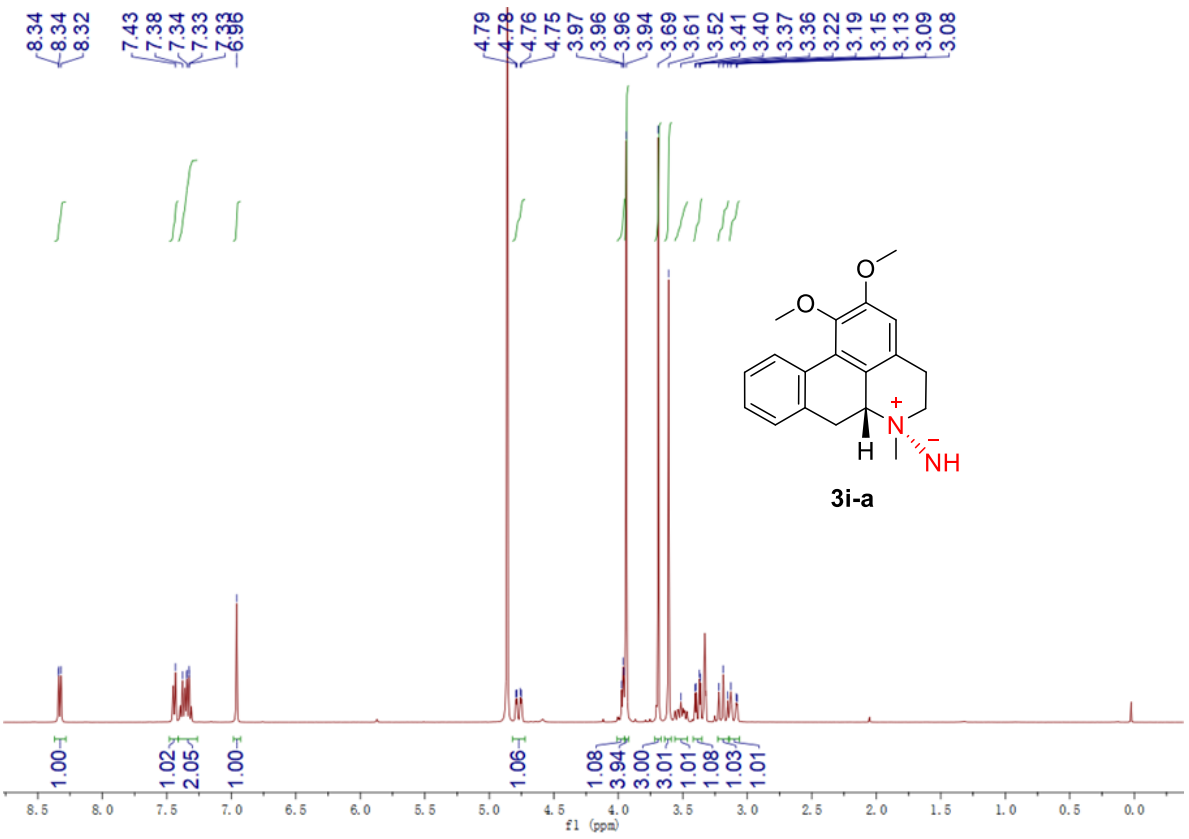

149.39
146.91
135.86
130.60
122.62
121.83
109.29
105.34
101.65
76.28
69.94
68.44
68.25
67.34
37.76
29.02
OH
HO
H
H
O
O
N
NH
3h-a
65
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

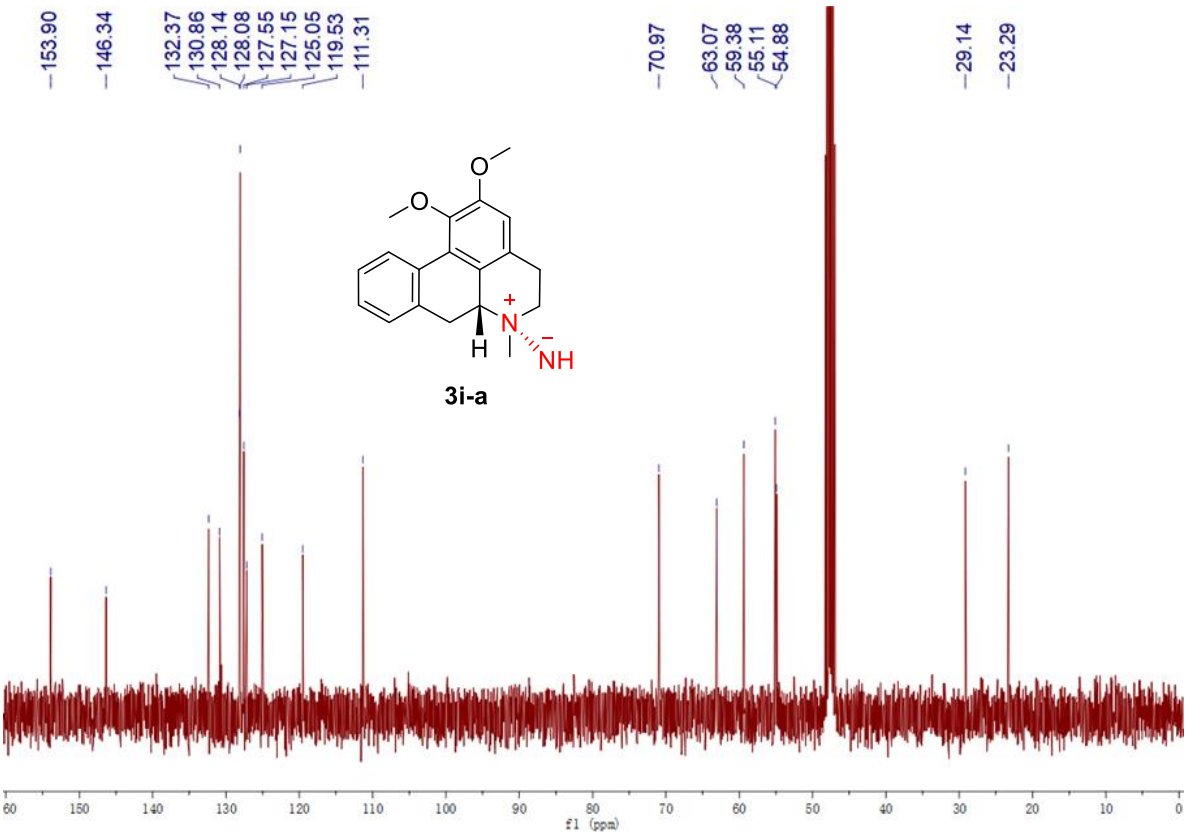

7.03
6.77
6.02
5.89
4.96
4.88
4.85
4.63
4.36
4.29
4.28
4.27
4.26
3.99
3.99
3.97
3.33
3.33
3.32
3.24
3.21
3.05
3.03
OH
HO
H
H
O
O
N
NH
0.97
0.93
1.98
0.96
1.00
0.91
1.07
0.99
0.98
1.94
0.98
0.98
2.00
f1 (ppm)

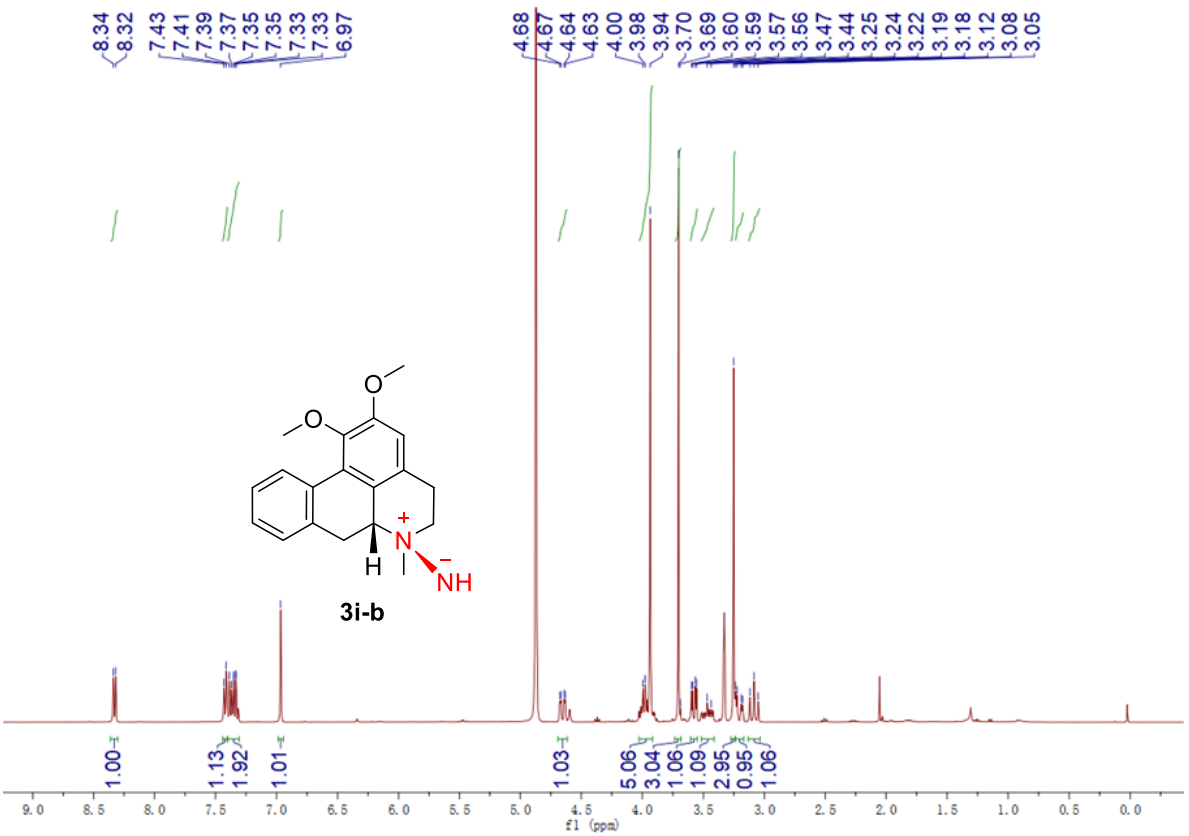
3h-b

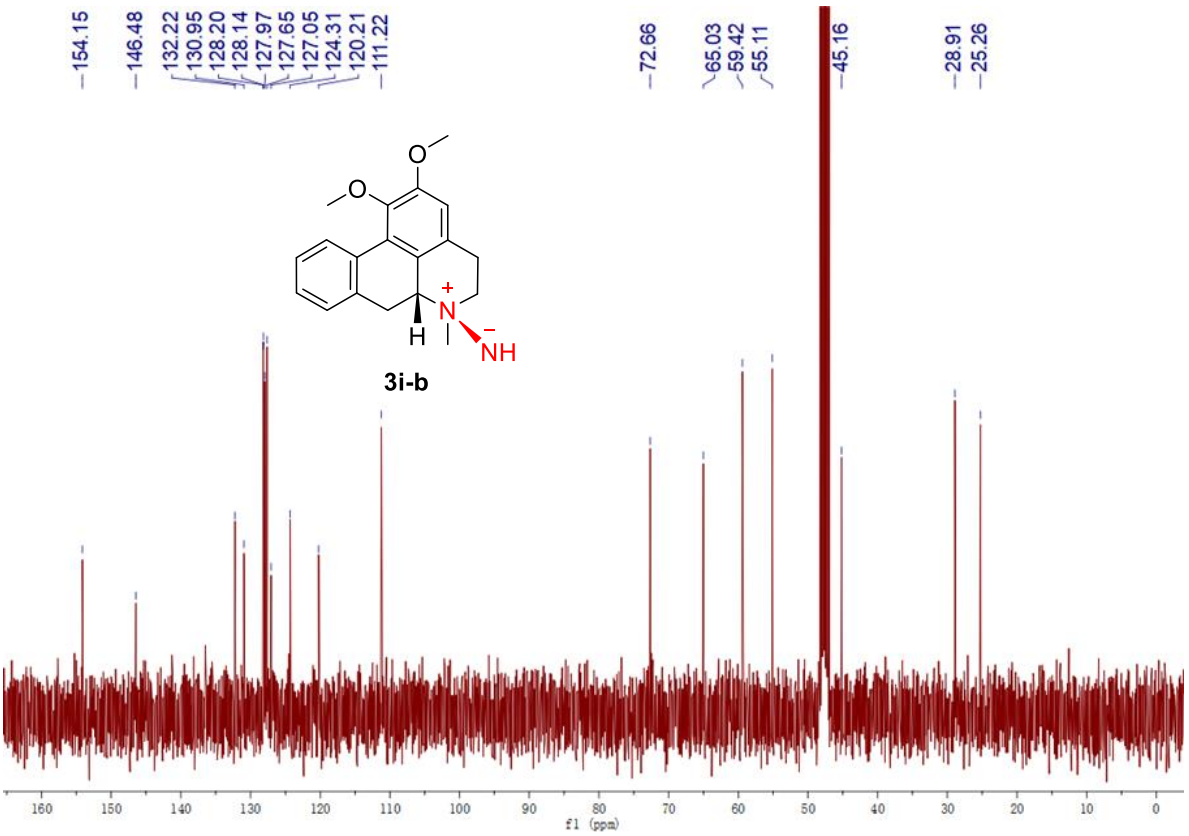

148.46
147.61
133.55
125.81
123.17
121.76
107.05
105.00
101.72
71.70
70.24
69.73
66.60
66.53
34.29
25.43
OH
HO
H
H
O
O
N
NH
f1 (ppm)

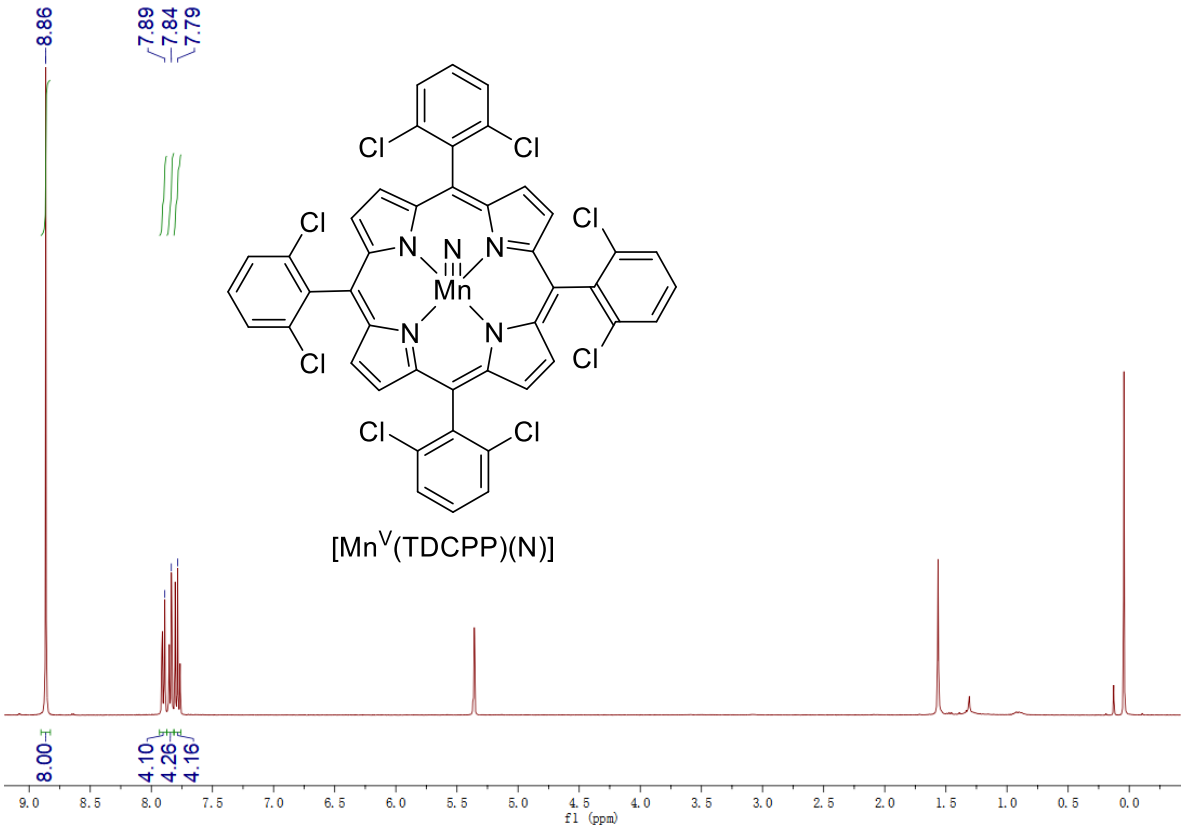
3h-b

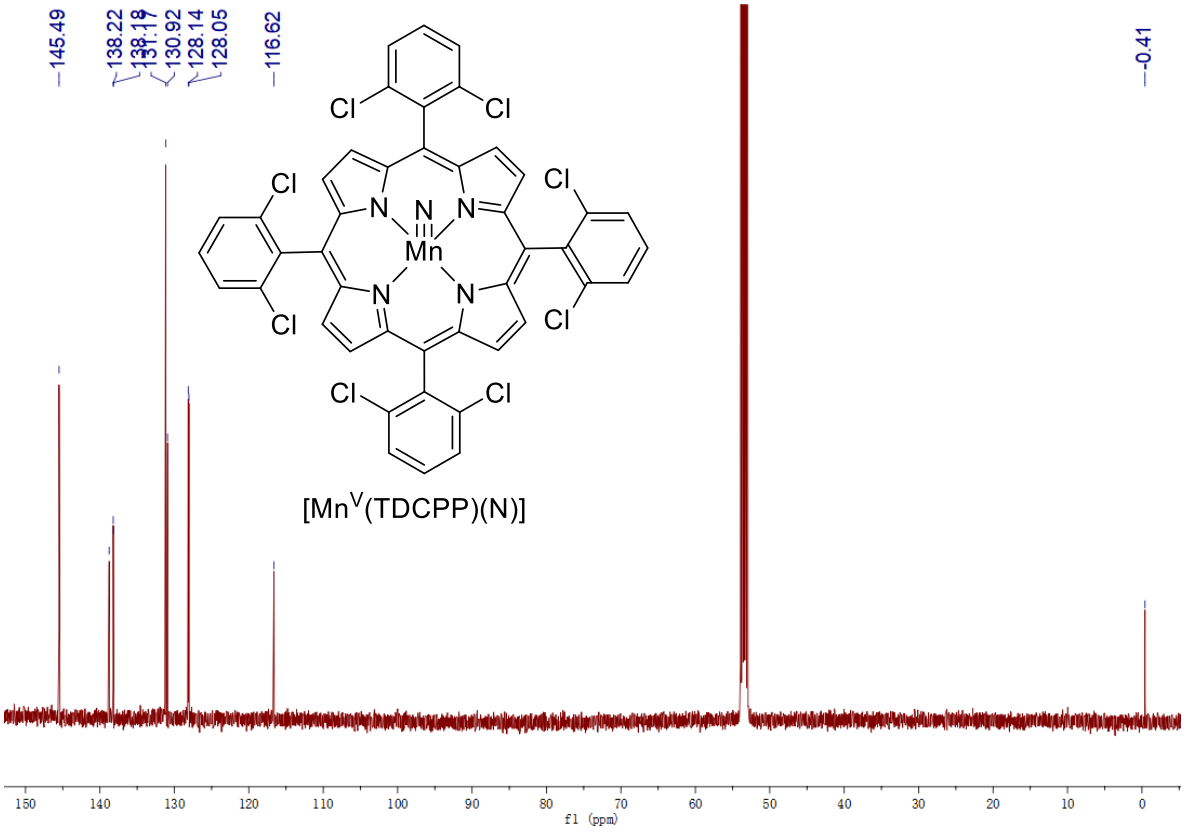

8.34
8.34
8.32
7.43
7.38
7.34
7.33
4.79
4.78
4.76
4.75
3.97
3.96
3.96
3.94
3.69
3.61
3.52
3.41
3.40
3.37
3.36
3.22
3.19
3.15
3.13
3.09
3.08
1.00
1.02
2.05
1.00
1.06
1.08
3.94
3.00
3.01
1.01
1.08
1.03
1.01
f1 (ppm)
3i-a

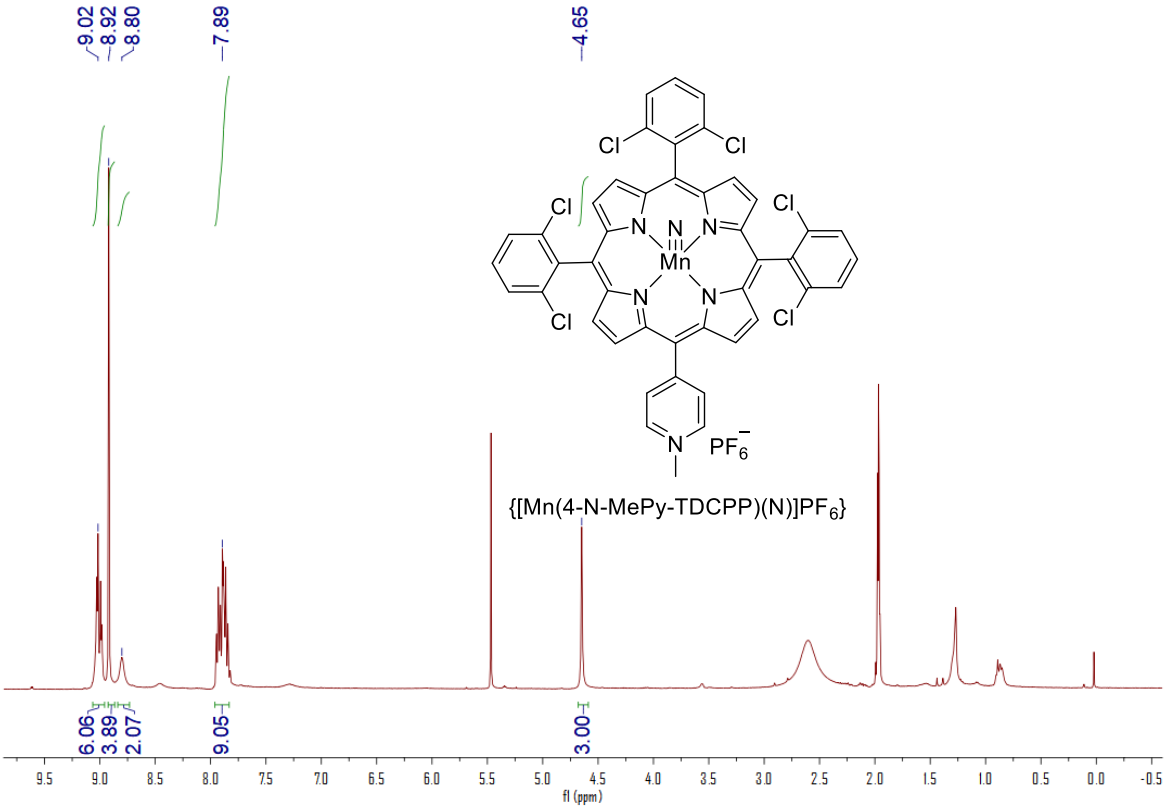

153.90
146.34
132.37
130.86
128.14
128.08
127.55
127.15
125.05
119.53
111.31
70.97
63.07
59.38
55.11
54.88
29.14
23.29
f1 (ppm)
3i-a

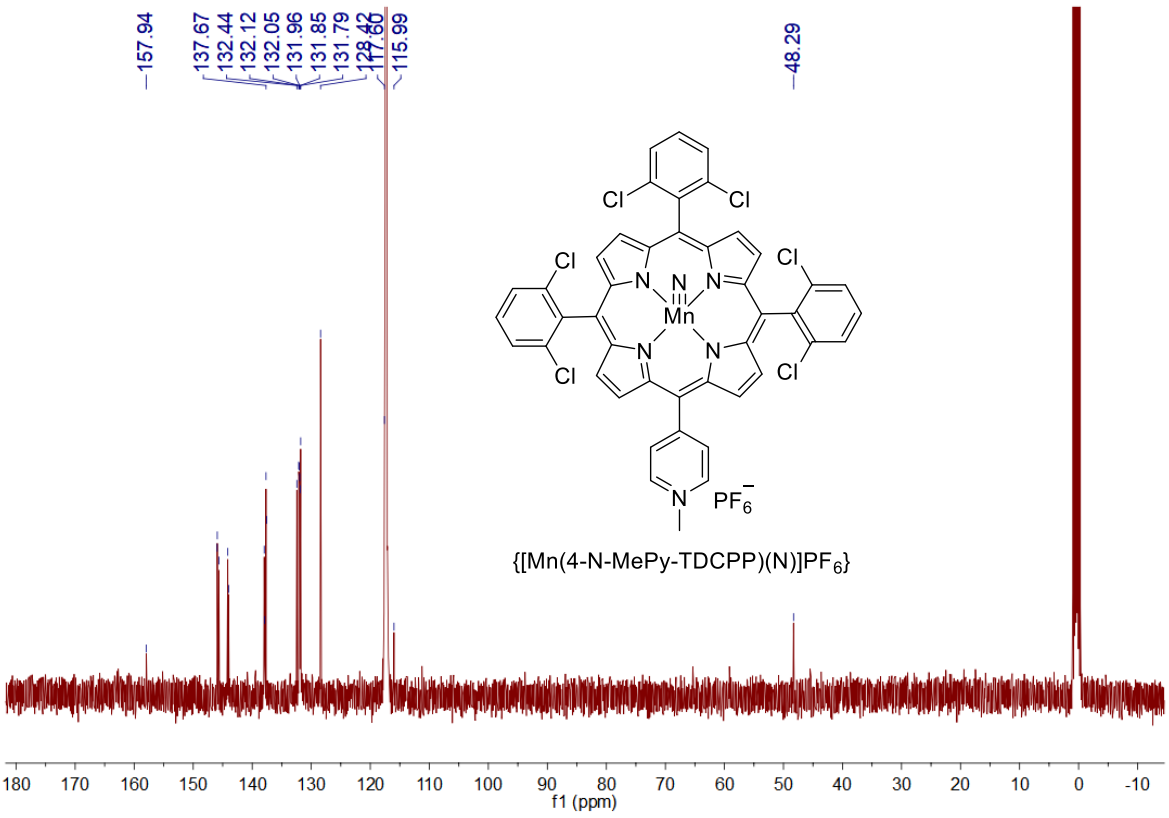

8.34
8.32
7.43
7.41
7.39
7.37
7.35
7.35
7.33
7.33
6.97
4.68
4.67
4.64
4.63
4.00
3.98
3.94
3.70
3.69
3.60
3.59
3.57
3.56
3.47
3.44
3.25
3.24
3.22
3.19
3.18
3.12
3.08
3.05
O
O
N
H
NH
3i-b
1.00
1.13
1.92
1.01
1.03
5.06
3.04
1.06
1.09
2.95
0.95
1.06
f1 (ppm)


154.15
146.48
132.22
130.95
128.20
128.14
127.97
127.65
127.05
124.31
120.21
111.22
72.66
65.03
59.42
55.11
45.16
28.91
25.26
O
O
N
H
NH
3i-b
f1 (ppm)

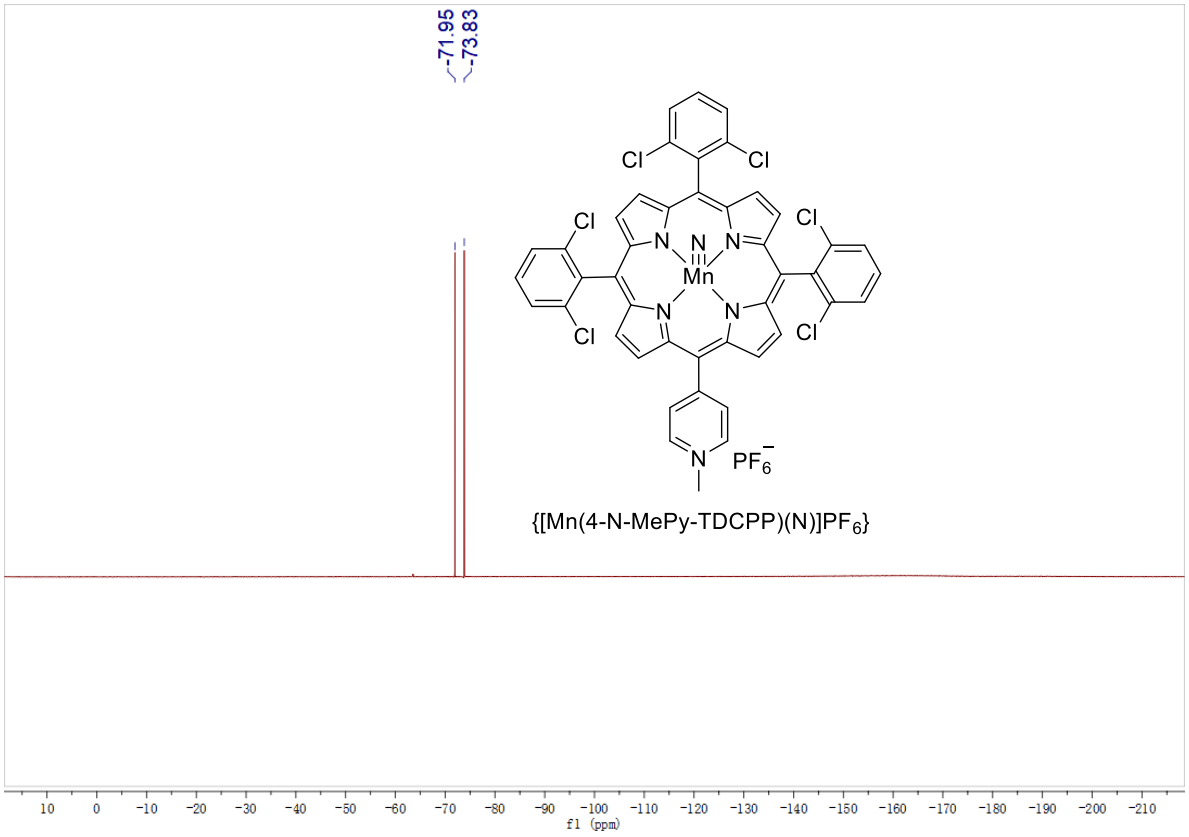

8.86
7.89
7.84
7.79
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
N
N
N
Mn
N
N
[Mn^V(TDCPP)(N)]
8.00
4.10
4.26
4.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

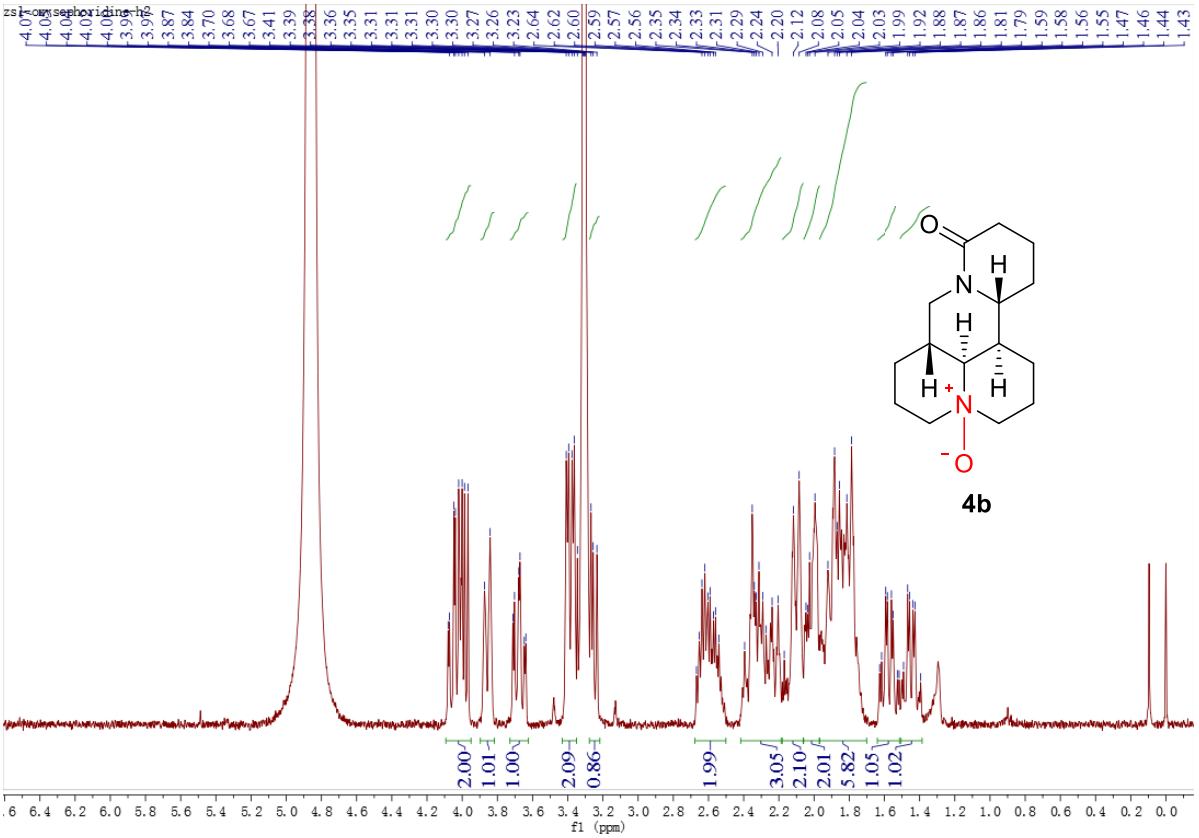

145.49
138.22
138.19
131.17
130.92
128.14
128.05
116.62
-0.41
Cl
Cl
Cl
Cl
Cl
Cl
Cl
Cl
N
N
N
Mn
N
N
[Mn^V(TDCPP)(N)]
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

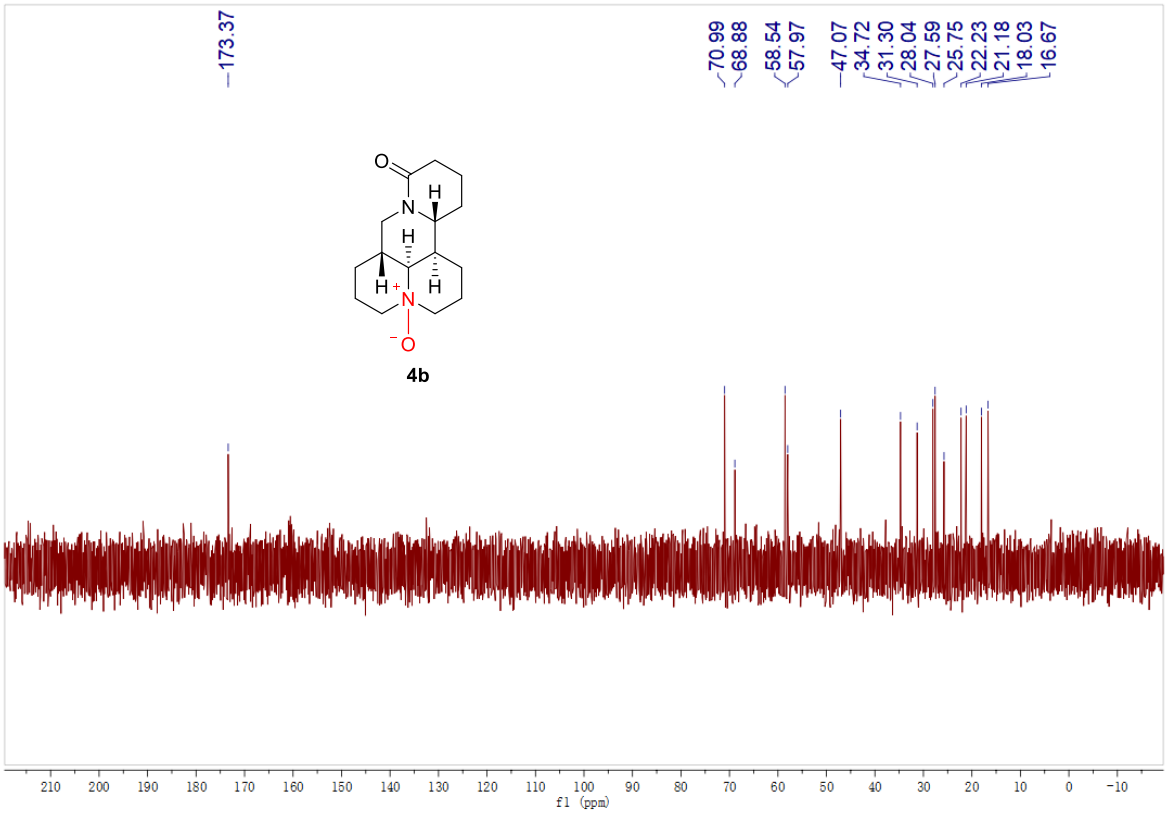

9.02
8.92
8.80
7.89
4.65
6.06
3.89
2.07
9.05
3.00
f1 (ppm)
{[Mn(4-N-MePy-TDCPP)(N)]PF6}

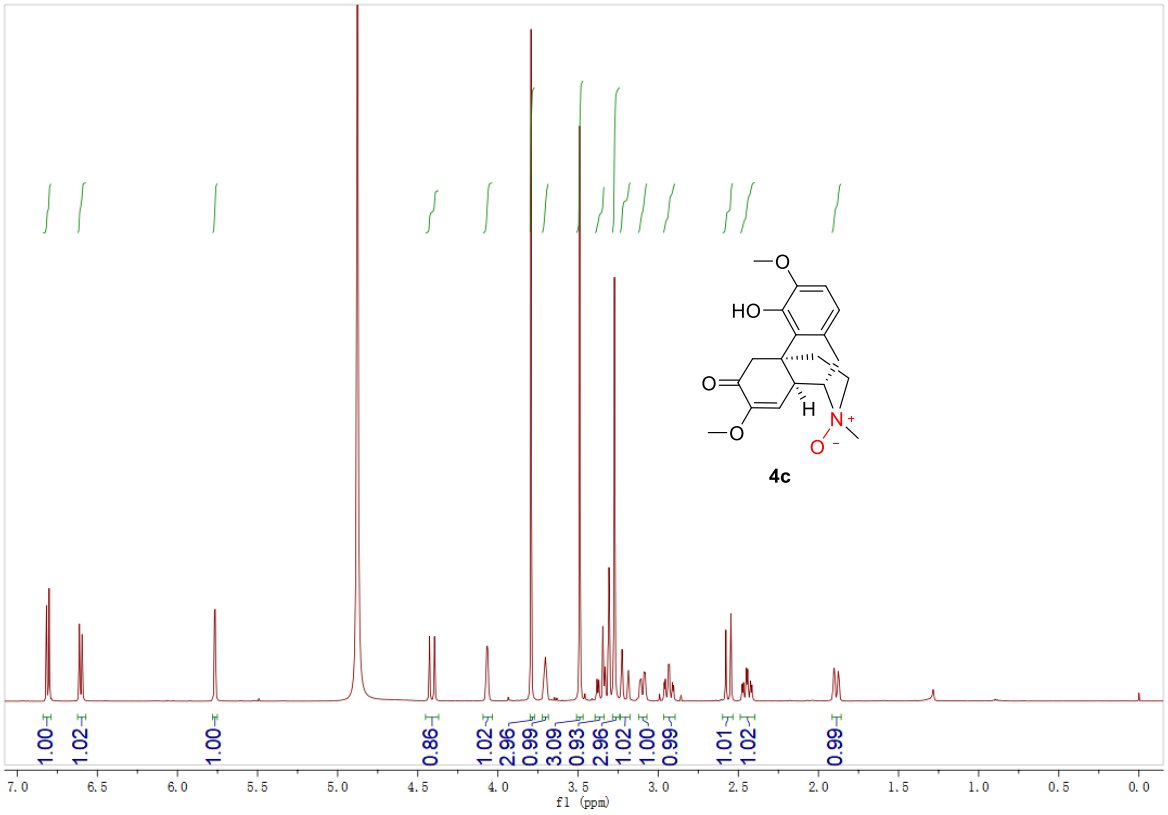

157.94
137.67
132.44
132.12
132.05
131.96
131.85
131.79
115.99
48.29
f1 (ppm)
{[Mn(4-N-MePy-TDCPP)(N)]PF6}

F NMR

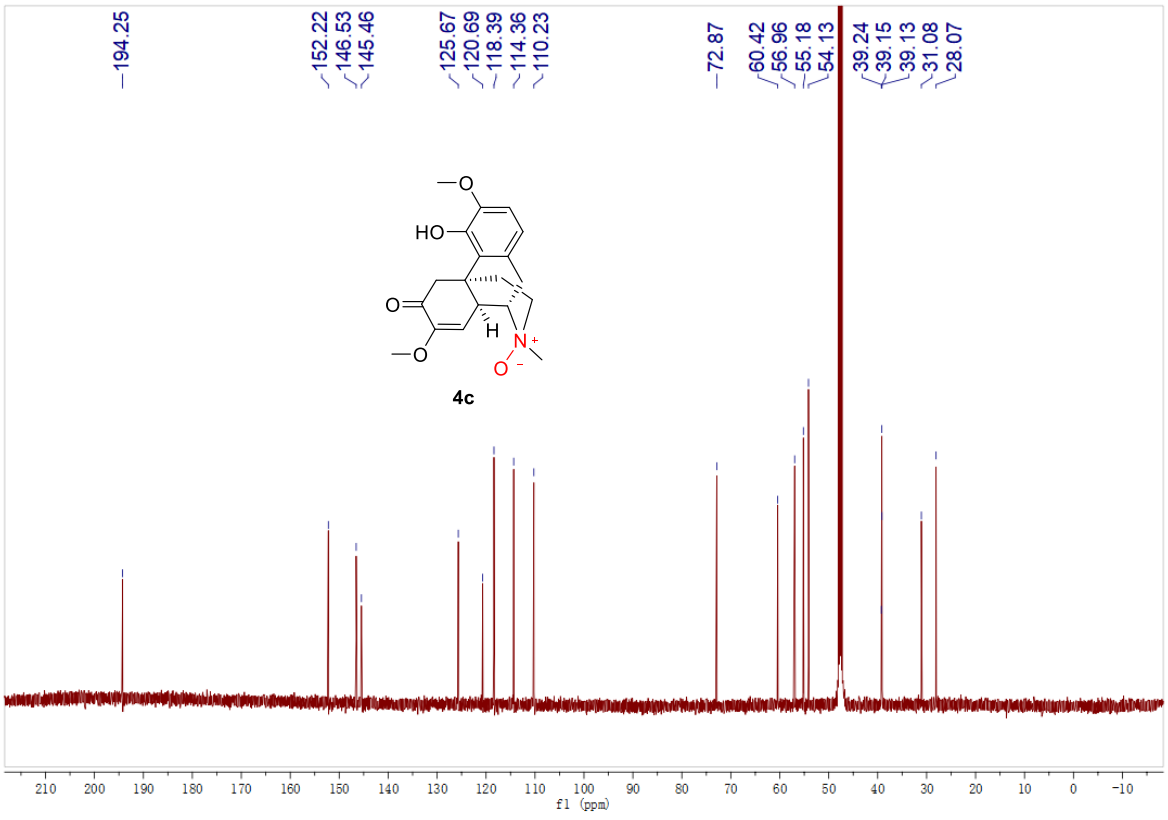

-71.95
-73.83
Cl
Cl
Cl
Cl
Cl
Cl
N
N
N
Mn
N
N
N
PF6
{[Mn(4-N-MePy-TDCPP)(N)]PF6}
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


zsl-cwyseboridine-h2
4.01 4.00 4.00 4.00 4.00 4.00 3.99 3.98 3.87 3.84 3.70 3.68 3.67 3.41 3.39 3.38 3.36 3.35 3.31 3.31 3.31 3.30 3.30 3.27 3.26 3.23 2.64 2.62 2.60 2.59 2.57 2.56 2.35 2.34 2.33 2.31 2.29 2.24 2.20 2.12 2.08 2.05 2.04 2.03 1.99 1.92 1.88 1.87 1.86 1.81 1.79 1.59 1.58 1.56 1.55 1.47 1.46 1.44 1.43
2.00 1.01 1.00 2.09 0.86 1.99 3.05 2.10 2.01 5.82 1.05 1.02
f1 (ppm)
4b

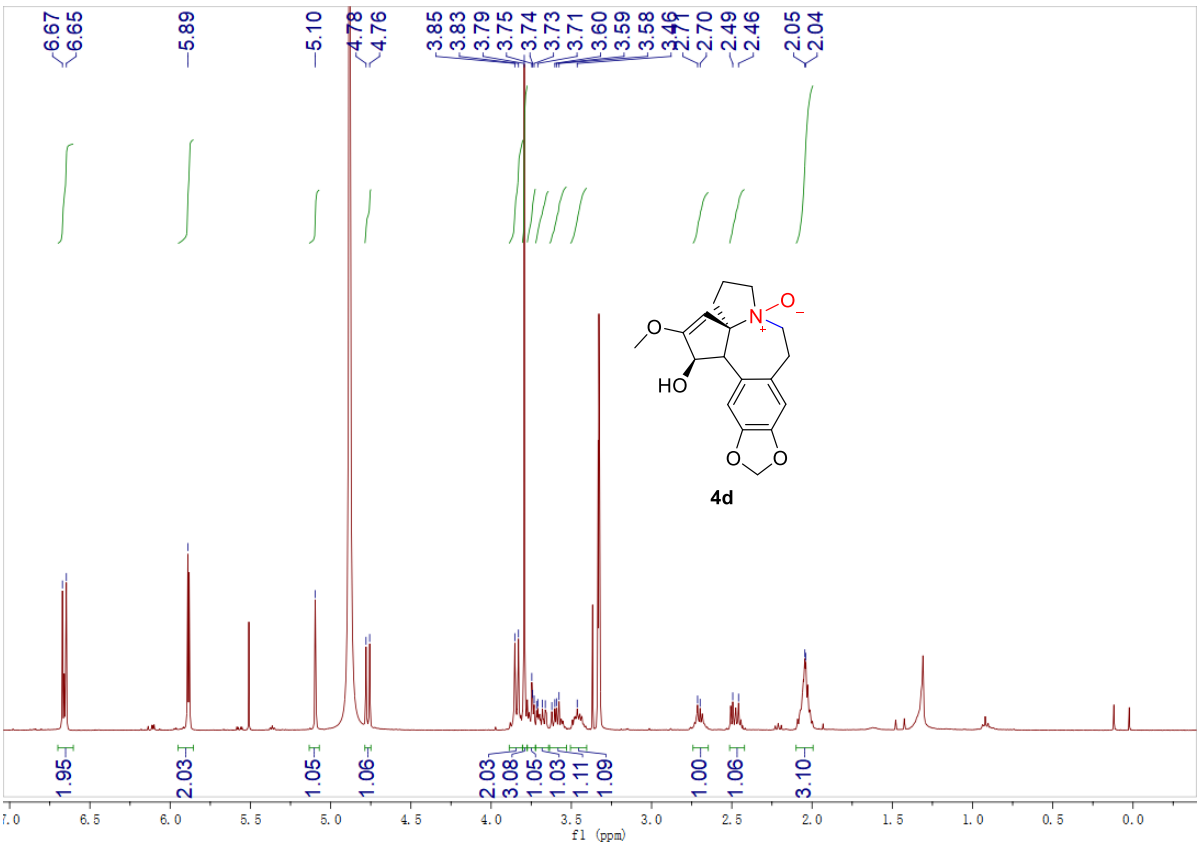

173.37
70.99 68.88 58.54 57.97 47.07 34.72 31.30 28.04 27.59 25.75 22.23 21.18 18.03 16.67
f1 (ppm)
4b

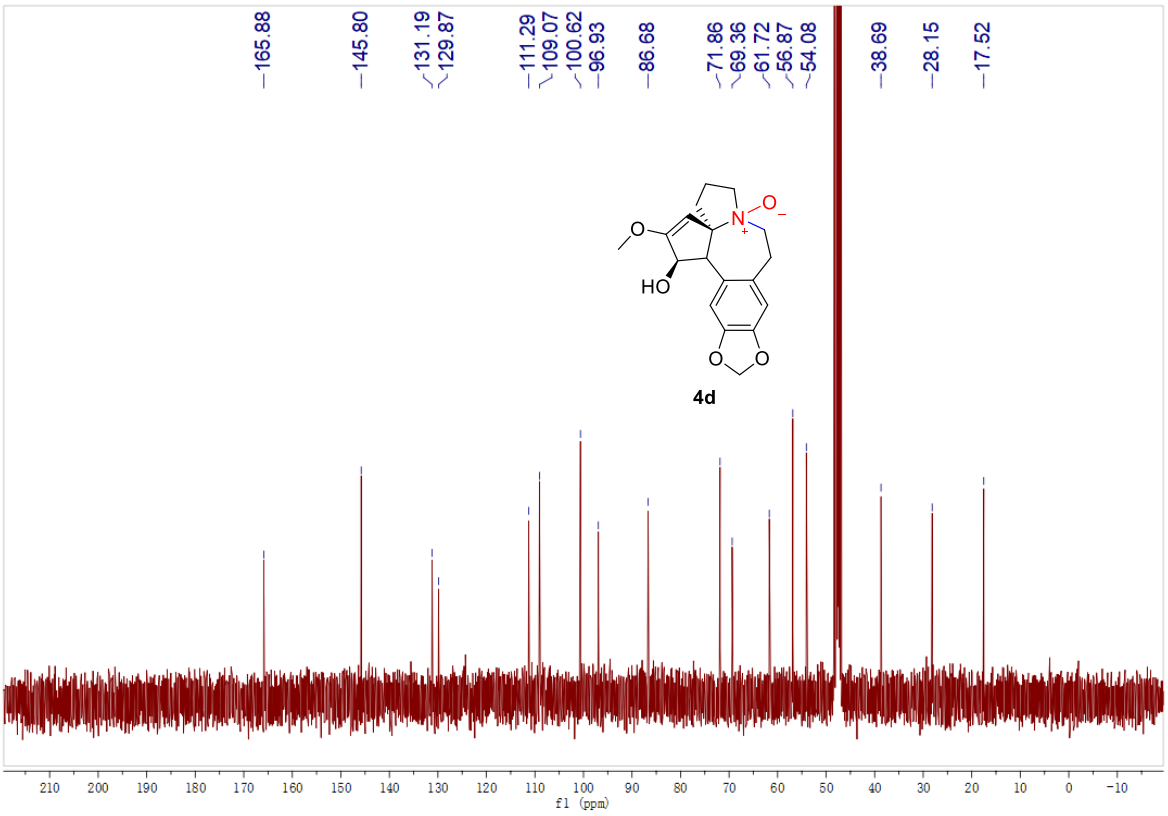

1.00
1.02
1.00
0.86
1.02
2.96
0.99
3.09
0.93
2.96
1.02
1.00
0.99
1.01
1.02
0.99
f1 (ppm)

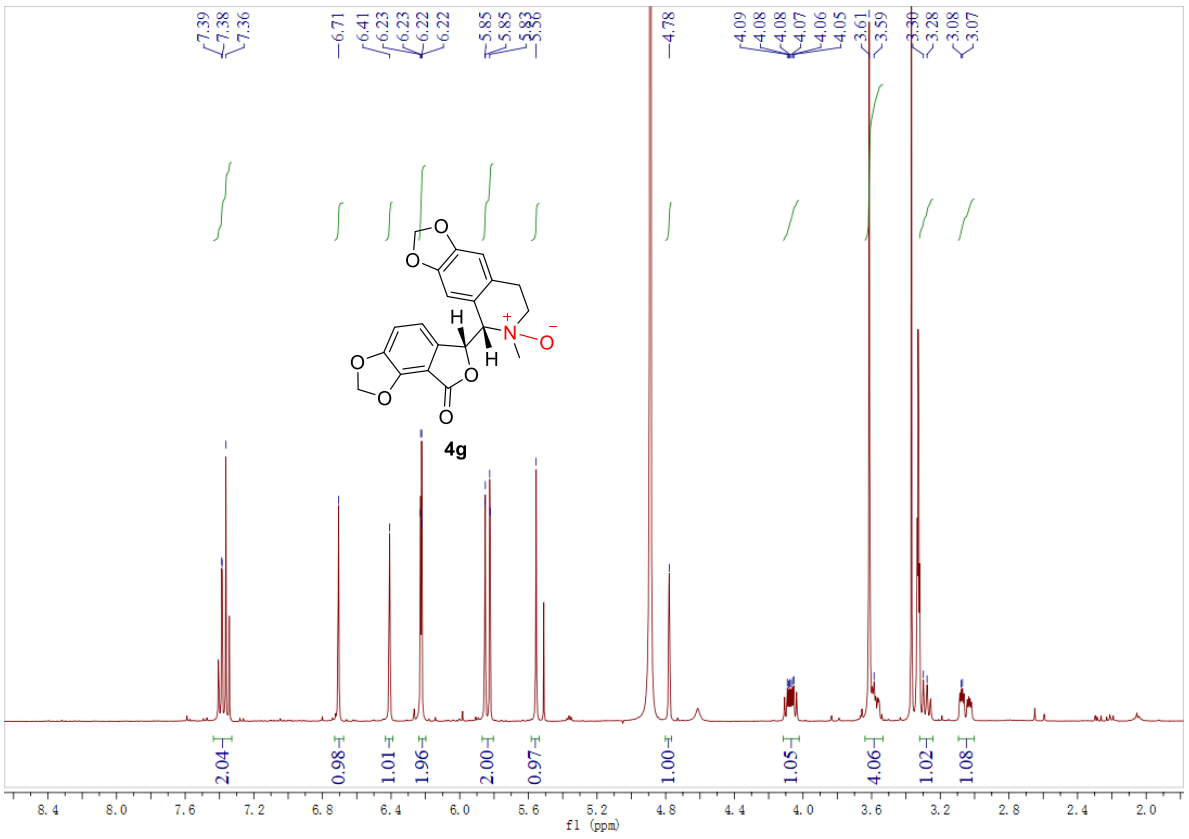
4c


194.25
152.22
146.53
145.46
125.67
120.69
118.39
114.36
110.23
72.87
60.42
56.96
55.18
54.13
39.24
39.15
39.13
31.08
28.07
f1 (ppm)

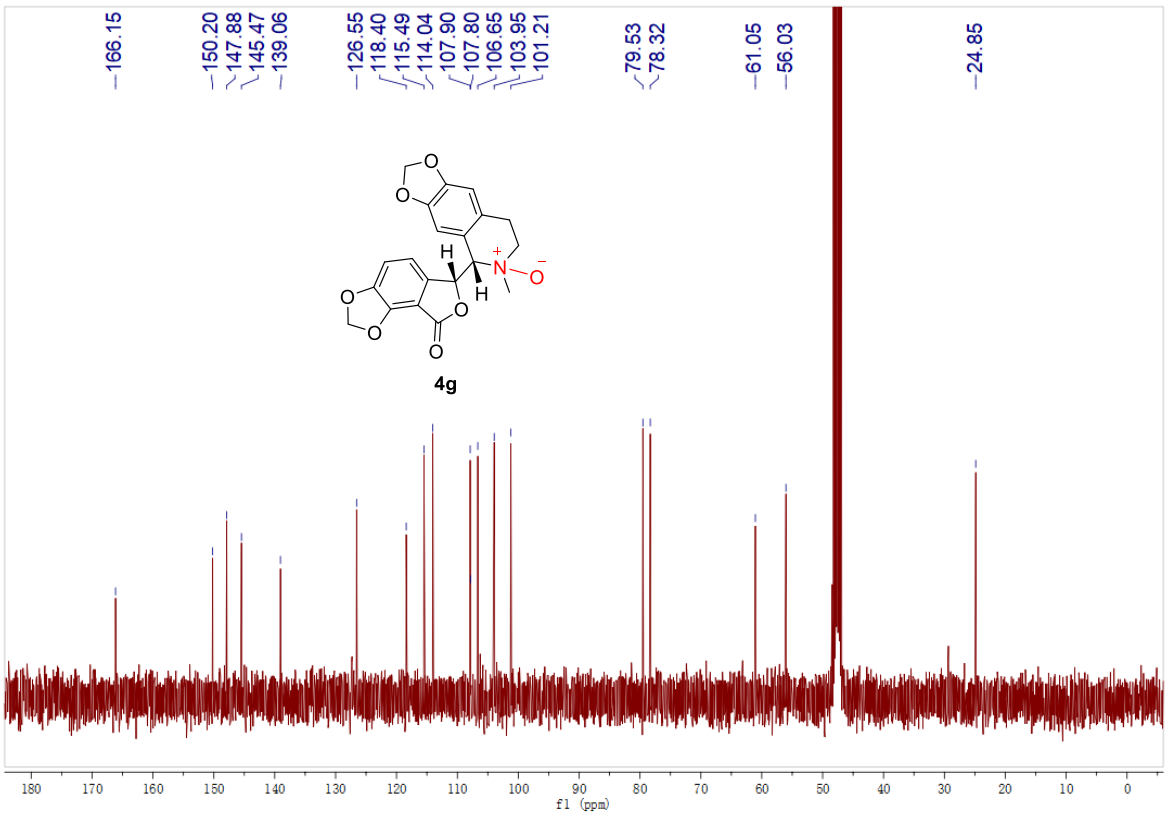
4c


6.67
6.65
5.89
5.10
4.78
4.76
3.85
3.83
3.79
3.75
3.74
3.73
3.71
3.60
3.59
3.58
2.70
2.49
2.46
2.05
2.04
1.95
2.03
1.05
1.06
2.03
3.08
1.05
1.03
1.11
1.09
1.00
1.06
3.10
f1 (ppm)
HO
4d


165.88
145.80
131.19
129.87
111.29
109.07
100.62
96.93
86.68
71.86
69.36
61.72
56.87
54.08
38.69
28.15
17.52
f1 (ppm)
HO
4d


7.39
7.38
7.36
6.71
6.41
6.23
6.23
6.22
6.22
5.85
5.85
5.83
5.56
4.78
4.09
4.08
4.08
4.07
4.06
4.05
3.61
3.59
3.30
3.28
3.08
3.07
2.04
0.98
1.01
1.96
2.00
0.97
1.00
1.05
4.06
1.02
1.08
f1 (ppm)

4g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150.20
147.88
145.47
139.06
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107.90
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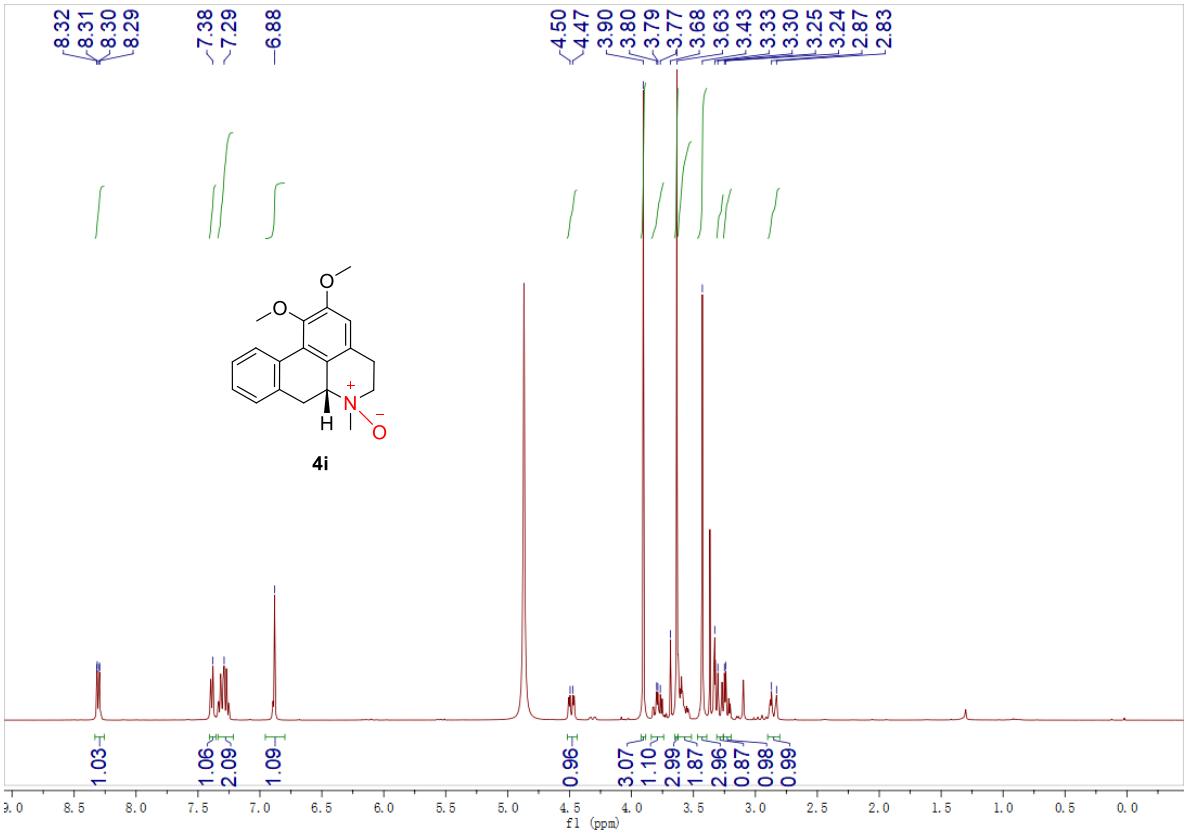
103.95
101.21
79.53
78.32
61.05
56.03
24.85
f1 (ppm)

4g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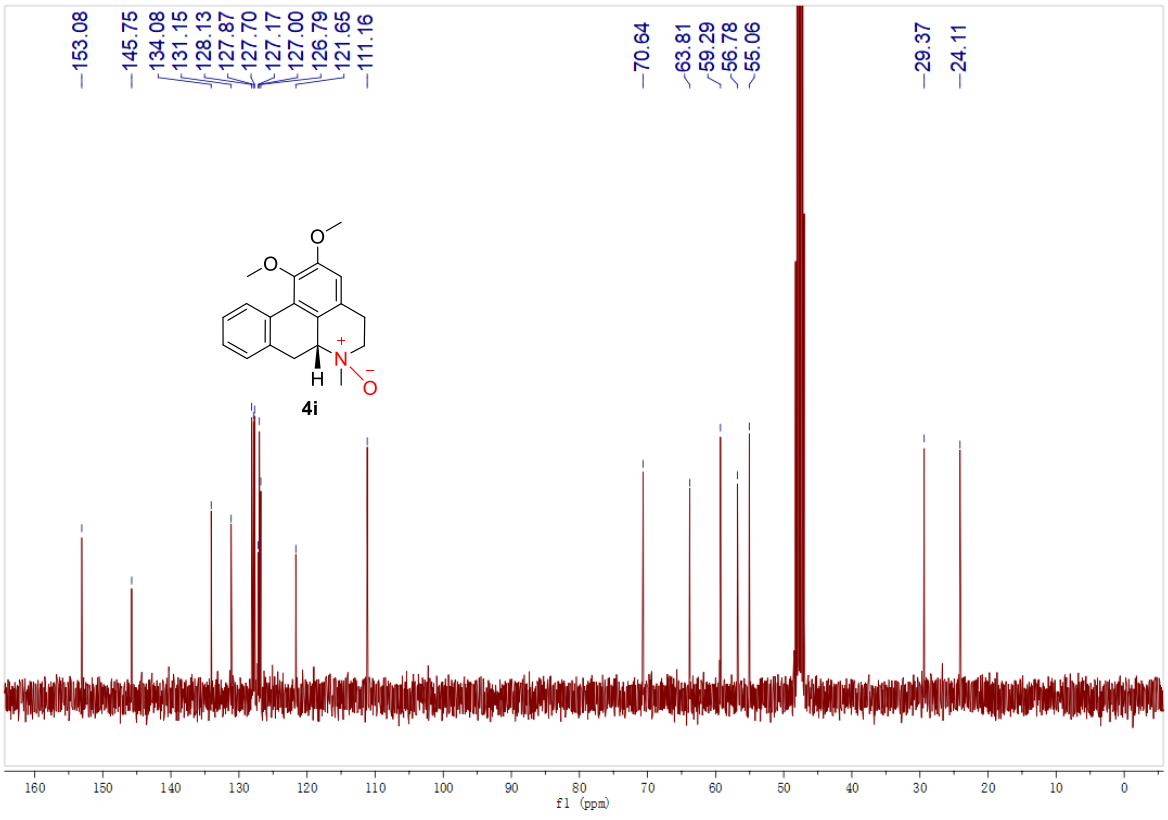
8.31
8.30
8.29
7.38
7.29
6.88
4.50
4.47
3.90
3.80
3.79
3.77
3.68
3.63
3.43
3.33
3.30
3.25
3.24
2.87
2.83
4i
1.03
1.06
2.09
1.09
0.96
3.07
1.10
2.99
1.87
2.96
0.87
0.98
0.99
f1 (ppm)


153.08
145.75
134.08
131.15
128.13
127.87
127.70
127.17
127.00
126.79
121.65
111.16
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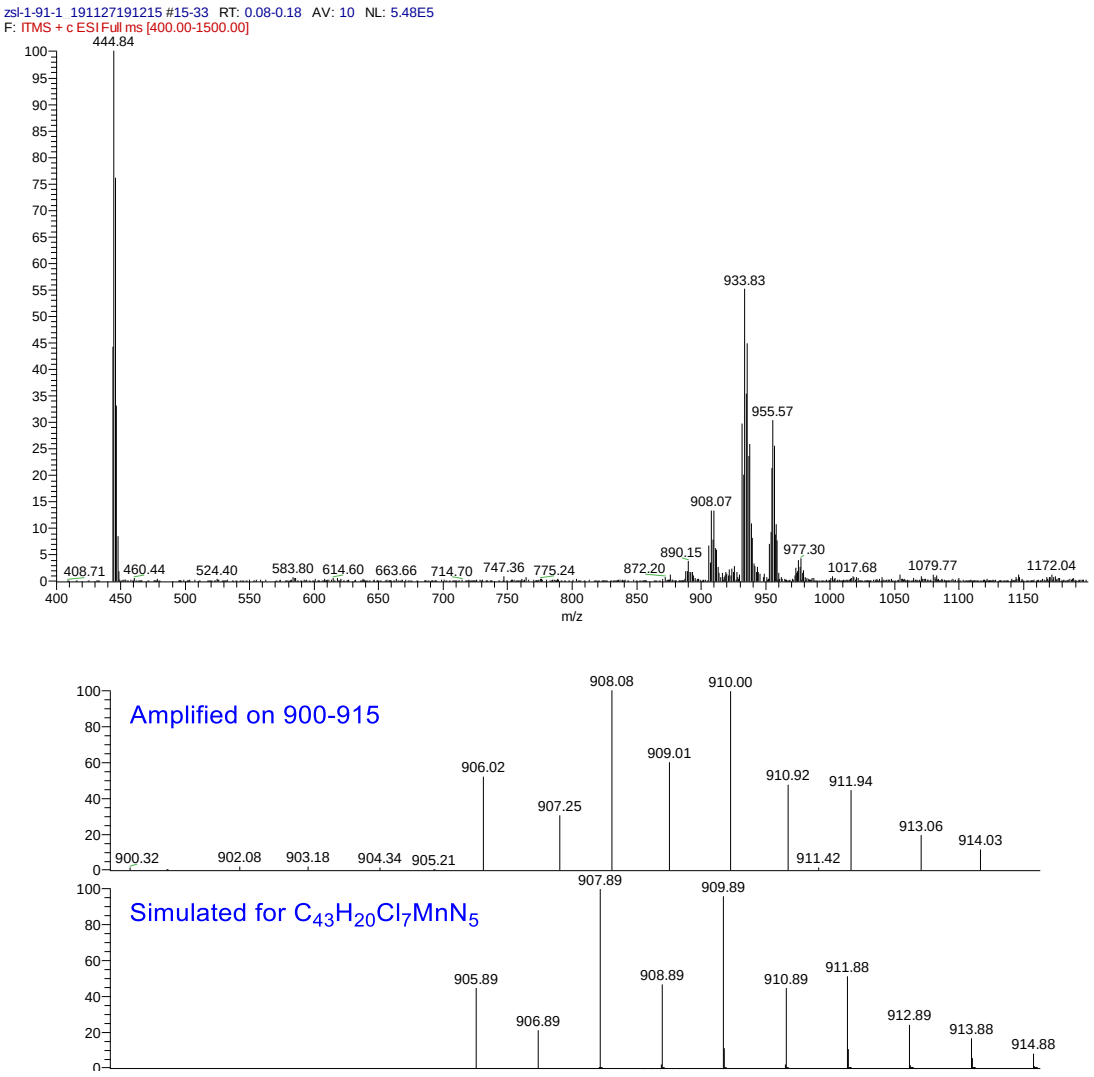
55.06
29.37
24.11
4i
f1 (ppm)



The cluster peak at *m/z* 908 can be assigned as {[Mn^{III}(4-*N*-MePy-TDCPP)Cl] − Me − H}, which is a steady background peak during the MS experiments.

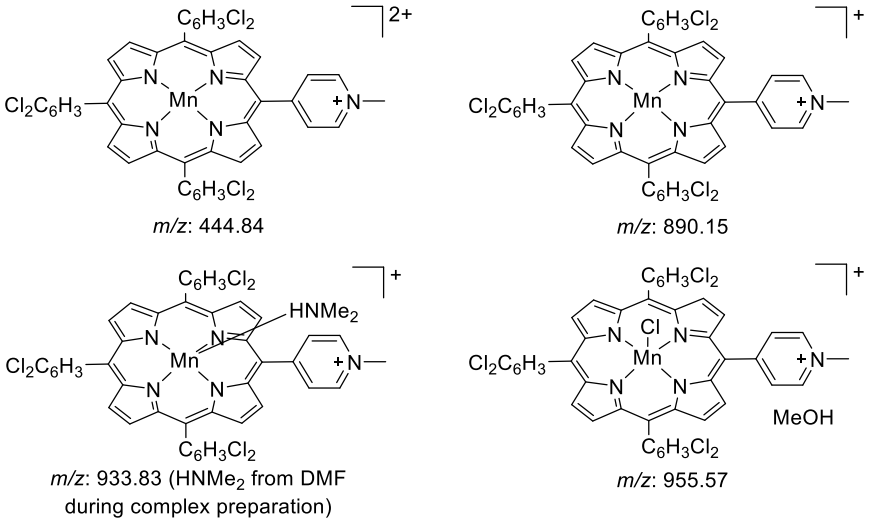
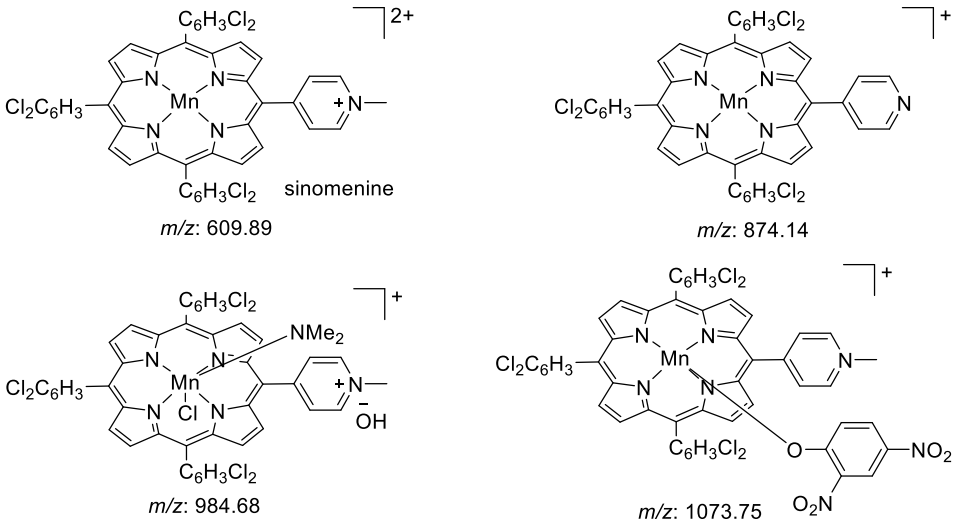


Fig. S1. Mass spectrum of [Mn^{III}(4-*N*-MePy-TDCPP)Cl]PF_6 with assignments of each peaks.



m/z 658.87, $[(\text{sinomenine})_2]^+$; *m/z* 680.98, $[(\text{sinomenine})_2 + \text{Na}]^+$; *m/z* 804.78, $[(\text{sinomenine})_2 + \text{H} + \text{PF}_6]^+$;

Fig. S2. Assignments of the peaks in Fig. 4.

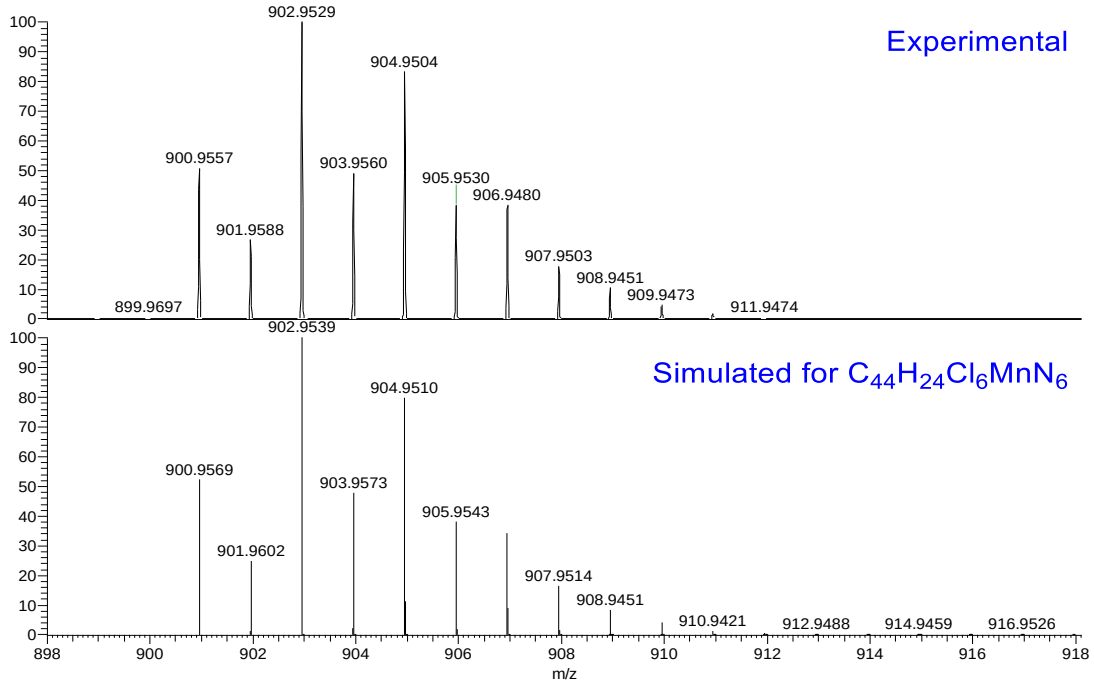


Fig. S3. Experimental and simulated isotopic patterns for $[\text{Mn}(4\text{-}N\text{-MePy-TDCPP})(\text{N})]^+$ by HR-ESI-MS.

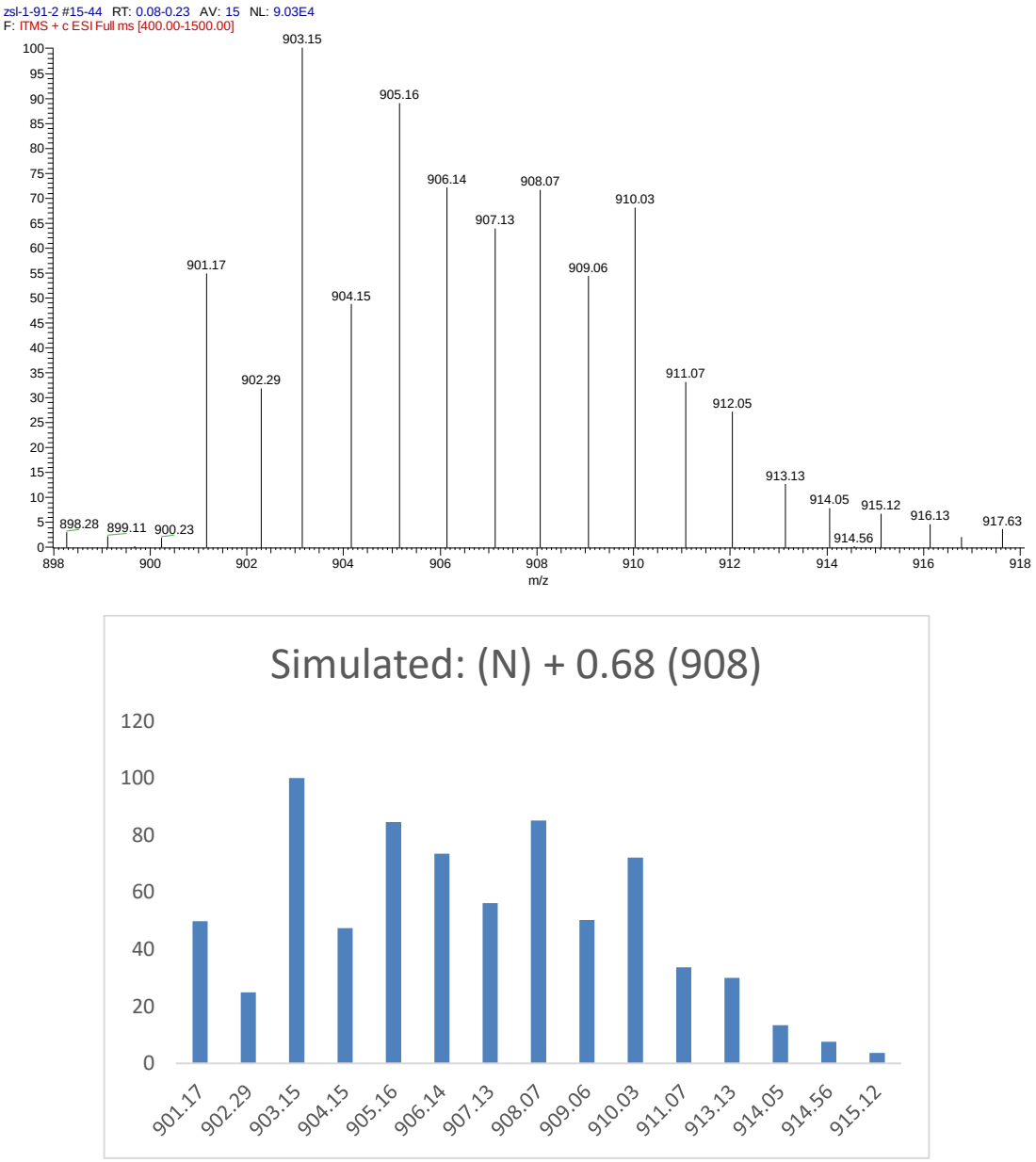


Fig. S4. Amplified on 898-918 of Fig. 4a and the simulated isotopic pattern of [Mn(4-*N*-MePy-TDCPP)(N)]$^+$ + [$C_{43}H_{20}Cl_7MnN_5$]$^+$ (1:0.68).

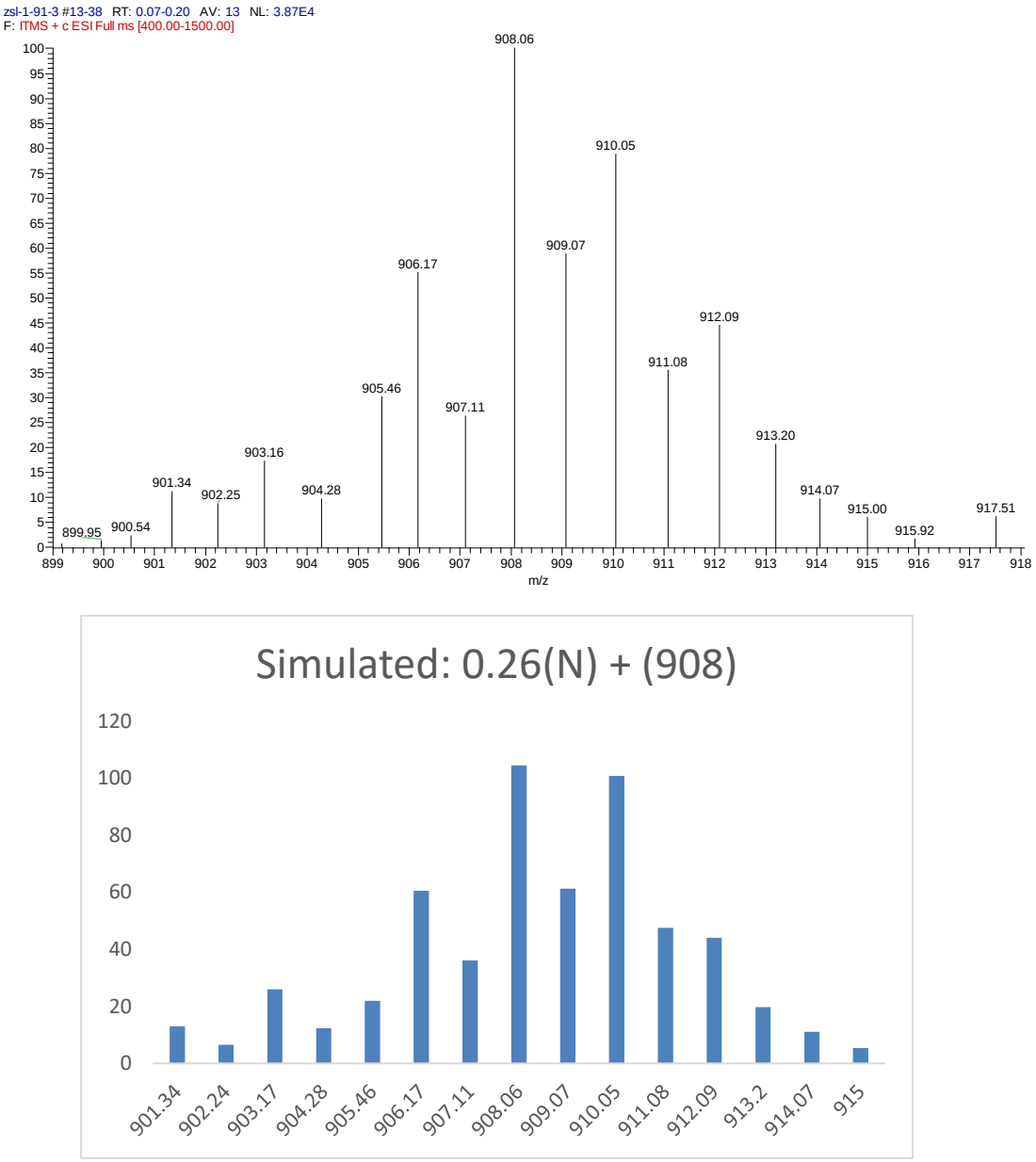


Fig. S5. Amplified on 898-918 of Fig. 4b and the simulated isotopic pattern of $[Mn(4\text{-}\textit{N}\text{-MePy-TDCPP})(N)]^+$ + $[C_{43}H_{20}Cl_7MnN_5]^+$ (0.26:1).

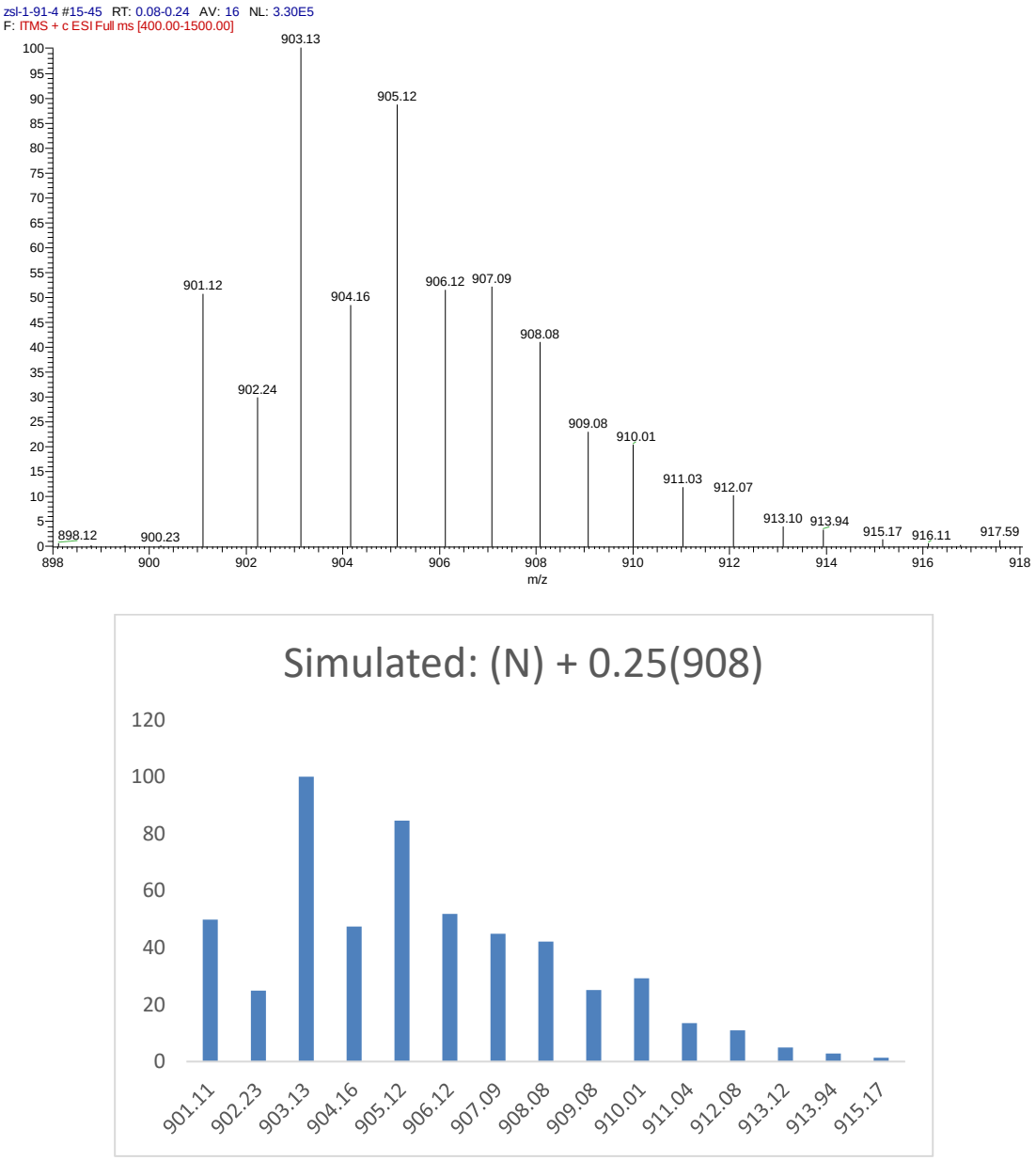


Fig. S6. Amplified on 898-918 of Fig. 4c and the simulated isotopic pattern of $[Mn(4\text{-}N\text{-MePy-TDCPP})(N)]^+$ + $[C_{43}H_{20}Cl_7MnN_5]^+$ (1:0.25).

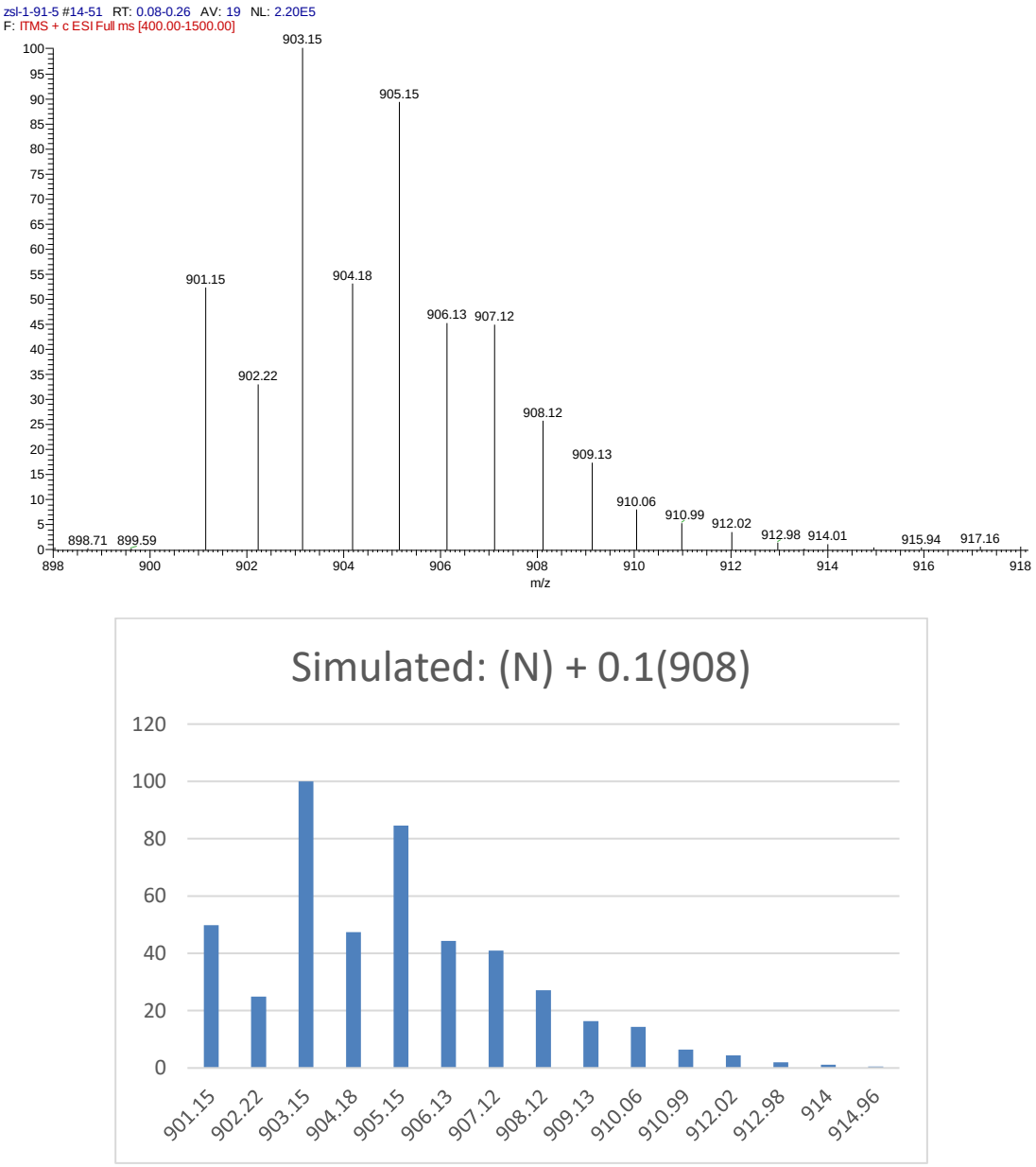


Fig. S7. Amplified on 898-918 of Fig. 4d and the simulated isotopic pattern of [Mn(4-*N*-MePy-TDCPP)(N)]$^+$ + [$C_{43}H_{20}Cl_7MnN_5$]$^+$ (1:0.1).

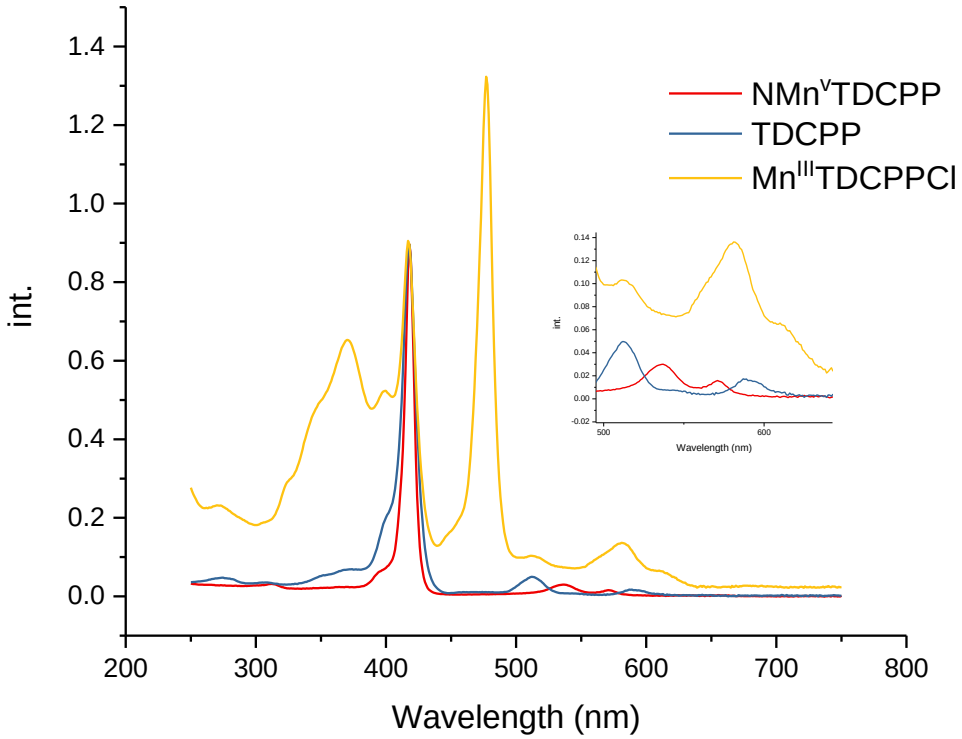


Fig. S8. UV-visible spectra of H_2TDCPP, [Mn^{III}(TDCPP)Cl], and [Mn^{V}(TDCPP)(N)] with enlargement of absorption bands between 480–640 nm.

5. Cytotoxicity assay

The cytotoxicity of the compounds was determined by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay upon 72-h incubation with cancer cell lines. Briefly, HeLa (4000 cells/well), NCI-H460 (3000 cells/well), and A549 (4000 cells/well) were seeded in 96-well flat-bottomed microplate with 100 µL of medium and incubated for 24 h. Compounds were dissolved in DMSO and added serially to the 96-well plates. The cells were exposed with the compounds for 72 h. After that, 10 µL of (3-(4,5-dimethyl-2-thiazoyl)-2,5-diphenyltetrazolium bromide (MTT, 5 mg/mL) was added to each well and incubated for 4 h. Then 100 µL of solubilization solution (10% SDS in 0.01 M HCl) was added to each well. The O.D. 580 nm was measured by a Thermo Scientific VarioskanTM Lux multimode microplate reader. The IC_{50} values of the compounds (concentrations at which could inhibit cellular growth by 50% compared to the negative control) were determined as the percentage ratio of the absorbance of the complex treated cells to the untreated controls.

Compounds	A549 (µM)	HeLa (µM)	H460 (µM)
1b	199.6	424.6	287.2
3b	183.2	328.9	305.2
4b	181.5	387.1	263.8
1c	151.1	245.4	210.4
3c	229.2	> 500	304.3
4c	229.5	220.1	208.2
1d	-	233.7	232.8
3d	-	218.8	345.5
4d	-	257.5	196.8
1g	182.4	244.0	188.6
3g-a	208.4	238.5	187.1
3g-b	130.1	248.5	150.7
4g	199.7	266.1	193.5
1i	114.1	50.3	87.6
3i-b	137.8	500	185.6
4i	176.1	205.5	276.4

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