
Dynamic equilibration of η^1 -carbene and η^2 -alkyne moieties within an alkynylcarbene dimanganese complex

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SUPPORTING INFORMATION

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General

The complexes $[\text{Cp}(\text{CO})_2\text{Mn}\equiv\text{CPh}][\text{BPh}_4]$ and $[\text{MeCp}(\text{CO})_2\text{Mn}\equiv\text{CR}'][\text{BPh}_4]$ ($\text{R} = \text{Ph}$, Tol) were prepared by slight modifications of the procedure described for the synthesis of $[\text{Cp}(\text{CO})_2\text{Re}\equiv\text{CPh}][\text{BPh}_4]$ (Handwerker, B. M.; Garrett, K. E.; Nagle, K. L., Geoffroy, G. L. *Organometallics* **1990**, *9*, 1562). The complex $(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})\text{C}\equiv\text{CPh}$ was synthesized as described in the literature (Dötz, K. H., Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23). Lithium phenylacetylide $\text{PhC}\equiv\text{CLi}$ (1M solution in THF), and tolylacetylene were obtained from Aldrich. The complexes $\text{CpMn}(\text{CO})_3$ and $\text{MeCpMn}(\text{CO})_3$ were obtained from Aldrich and Alfa, respectively. Tetrahydrofuran and diethyloxide used for the synthesis were distilled under nitrogen from sodium benzophenone ketyl just before use. Other solvents were purified following standard procedures, and stored under nitrogen. All synthetic manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. A liquid N_2 /isopropanol slush bath was used to maintain samples at the desired low temperature. Chromatographic separation of the complexes was performed on alumina (neutral, activity III (Aldrich)). Solution IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer with 0.1 mm cells equipped with CaF_2 windows. ^1H and ^{13}C NMR spectra were obtained on Bruker WM250, DPX300, or AMX400 spectrometers and were referenced to the residual signals of the deuterated solvent. Mass spectra were recorded on AEI-MS9, or Nermag R10-10 mass spectrometers (EI). Microanalyses of C and H elements were performed on a Perkin-Elmer 2400 CHN analyser.

Synthesis of $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{C}\equiv\text{CPh}$ (**1a**), $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{R}')\text{C}\equiv\text{CR}''$ (**1b**: $\text{R}' = \text{R}'' = \text{Ph}$; **1c**: $\text{R}' = \text{Ph}$, $\text{R}'' = \text{Tol}$; **1d**: $\text{R}' = \text{Tol}$, $\text{R}'' = \text{Ph}$)

*Typical procedure as illustrated for $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{C}\equiv\text{CPh}$ (**1b**).* Lithium phenylacetylide (2.0 mL of a 1M solution in THF, 2 mmol) was added dropwise to a solution of $[\text{MeCp}(\text{CO})_2\text{Mn}\equiv\text{CPh}][\text{BPh}_4]$ (1.21 g, 2.02 mmol) in CH_2Cl_2 (15 mL) cooled at -80°C . The yellow solution turned rapidly dark red. The cold solution was filtered on a short column of alumina. The solvents were removed under high vacuum and the oily black residue was purified by chromatography on alumina. An initial elution with a 1:20 diethyloxide/pentane mixture gave a yellow band containing trace amount of $\text{MeCpMn}(\text{CO})_3$. A second elution with 1:5 diethyloxide/pentane mixture afforded a dark red band containing complex $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{C}\equiv\text{CPh}$ (**1b**), which was isolated as a brown-red oil after removal of the solvent under high vacuum (0.63 g, 82% yield).

The complexes $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{C}\equiv\text{CPh}$ (**1a**), $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{C}\equiv\text{CTol}$ (**1c**), and $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{Tol})\text{C}\equiv\text{CPh}$ (**1d**) were obtained in 82%, 81%, and 85% yield, respectively, following the above procedure and using the appropriate combination of cationic carbyne complex and alkynyllithium reagent.

1a: ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.1\text{-}7.1$ (m, 10H, *Ph*), 5.26 (s, 5H, *Cp*); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2): $\delta = 302.4$ ($\text{Mn}=\text{C}$), 234.1 (*CO*), 156-123.7 (*Ph* and $\text{C}\equiv$), 105.9 ($\text{C}\equiv$), 94.1 (*Cp*); IR: $\nu = 2124$ ($\nu\text{C}\equiv\text{C}$), 1969, 1905 (νCO) cm^{-1} .

1b: ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.1\text{-}7.5$ (m, 10H, *Ph*), 5.22, 5.13 (m, 4H, *MeCp*), 2.06 (s, 3H, *MeCp*); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2): $\delta = 300.9$ ($\text{Mn}=\text{C}$), 234.6 (*CO*), 156.3-125.7 (*Ph*), 125.5, 106.1 ($\text{C}\equiv\text{C}$), 108.6, 95.2, 94.2 (*MeCp*), 13.8 (*MeCp*). IR (CH_2Cl_2):

$\nu = 2124$ ($\nu\text{C}\equiv\text{C}$), 1969, 1905 (νCO) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{17}\text{O}_2\text{Mn}$: C 72.64; H 4.51; found: C 72.55; H 4.49.

1c: ^1H NMR (250 MHz, C_6D_6): $\delta = 8.3$ -6.7 (m, 9H, *Ph* et $\text{C}_6\text{H}_4\text{Me}$), 4.72, 4.58 (m, 4H, *MeCp*), 1.99 (s, 3H, *MePh*), 1.55 (s, 3H, *MeCp*); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): $\delta = 301.5$ ($\text{Mn}=\text{C}$), 234.5 (CO), 153.2-125.4 (*Ph* and *MePh*), 113.2, 102.9 ($\text{C}\equiv\text{C}$), 107.5, 94.5, 93.2 (*MeCp*), 21.2 (*MePh*), 12.9 (*MeCp*); IR (CH_2Cl_2): $\nu = 2121$ ($\nu\text{C}\equiv\text{C}$), 1969, 1907 (νCO) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{19}\text{O}_2\text{Mn}$: C 73.08, H 4.86; found: C 73.15, H 4.68.

1d: ^1H NMR (250 MHz, CD_2Cl_2): $\delta = 8.1$ -7.3 (m, *Ph* and *MePh*), 5.2, 5.1 (m, *MeCp*), 2.4 (s, *MePh*), 1.7 (s, *MeCp*); $^{13}\text{C}\{^1\text{H}\}$ NMR (63 MHz, CD_2Cl_2): $\delta = 299.5$ ($\text{Mn}=\text{C}$), 234.9 (CO), 153.2-131.3 (*Ph* and *MePh*), 125.5, 105.5 ($\text{C}\equiv\text{C}$), 108.4, 95.3, 94.1 (*MeCp*), 21.7 (*MePh*), 13.8 (*MeCp*); IR (THF): $\nu = 2126$ ($\nu\text{C}\equiv\text{C}$); 1970, 1907 (νCO) cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{19}\text{O}_2\text{Mn}$: C 73.08, H 4.86; found C 72.98, H 4.59.

Synthesis of $[\text{Cp}(\text{CO})_2\text{Mn}]_2[\mu\text{-}\eta^3\text{-PhCCCPh}]$ (**3a**), $[\text{MeCp}(\text{CO})_2\text{Mn}]_2[\mu\text{-}\eta^3\text{-PhCCCPh}]$, (**3b**), $[\text{MeCp}(\text{CO})_2\text{Mn}][\text{Cp}(\text{CO})_2\text{Mn}][\mu\text{-}\eta^3\text{-PhCCCPh}]$ (**3c**), and $[\text{MeCp}(\text{CO})_2\text{Mn}]_2[\mu\text{-}\eta^3\text{-PhCCCTol}]$ (**3d**).

*Typical procedure as illustrated for $[\text{MeCp}(\text{CO})_2\text{Mn}][\mu\text{-}\eta^3\text{-PhCCCPh}]$ (**3b**).* A solution of $\text{MeCp}(\text{CO})_3\text{Mn}$ (0.22 mL, 1.4 mmol) in THF (100 mL) was irradiated for one hour using a Pyrex-filtered Original Hanau TQ 150 medium-pressure Hg vapor lamp. The resulting purple solution of $\text{MeCp}(\text{CO})_2\text{Mn}(\text{THF})$ (**2b**) was transferred by means of a canula into in a Schlenk flask containing $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{C}\equiv\text{CPh}$ (**1b**, 0.53 g, 1.40 mmol). After stirring for 4 hours, the solvent was removed under vacuum to leave a brown oil, which was chromatographed on alumina. An initial elution with a 1:20 diethyloxide/pentane mixture gave a yellow band containing trace amount of $\text{MeCpMn}(\text{CO})_3$. A second elution with a 1:10 diethyloxide/pentane mixture gave a brown band containing the complex $[\text{MeCp}(\text{CO})_2\text{Mn}]_2[\mu\text{-}\eta^3\text{-PhCCCPh}]$ (**3b**), which was isolated as a brown oil after the solvents were removed under high vacuum (0.414 g, 0.73 mmol, 52% yield).

The complex $[\text{Cp}(\text{CO})_2\text{Mn}]_2[\mu\text{-}\eta^3\text{-PhCCCPh}]$, **3a**, was prepared from $\text{CpMn}(\text{CO})_2(\text{THF})$ (**2a**) and $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{C}\equiv\text{CPh}$ (**1a**) as starting material and was obtained as a brown microcrystalline solid after chromatographic workup (65% isolated yield). Crystals suitable for an X-ray structure determination were grown from a pentane solution in the cold.

The complex $[\text{MeCp}(\text{CO})_2\text{Mn}][\text{Cp}(\text{CO})_2\text{Mn}][\mu\text{-}\eta^3\text{-PhCCCPh}]$, **3c/3c'**, was prepared by reaction of **1a** with **2b** (48% isolated yield), and by reaction **1b** with **2a** (32% isolated yield) respectively.

The complex $[\text{MeCp}(\text{CO})_2\text{Mn}]_2[\mu\text{-}\eta^3\text{-PhCCCTol}]$, **3d/3d'**, was prepared by reaction of **1c** with **2b** (38% isolated yield), and by reaction **1d** with **2d** (43% isolated yield).

3a: ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): $\delta = 7.7$ -7.1 (m, 10H, *Ph*), 4.61 (s, 10H, *Cp*); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298K): $\delta = 232.9$ (CO), 145.5-125.0 (*Ph*), 88.5 (*Cp*), 75.4 (*PhCCCPh*); ^1H NMR (400 MHz, CD_2Cl_2 , 188 K): $\delta = 8.0$ -7.2 (m, 10H, *Ph*), 4.75 (s, 5H, *Cp*), 4.22 (s, 5H, *Cp*). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 183 K): $\delta = 317.9$ ($\text{Mn}=\text{C}$), 235.6, 235.4, 232.6, 231.4 (CO), 157.6 (C_{ipso} phenyl ring 1), 133.9 (C_{ipso} phenyl ring 2), 132.0-122.0 (*Ph*), 106.3 ($=\text{CC}\equiv\text{C}$), 91.9, 85.9 (*Cp*), 76.9 ($=\text{CC}\equiv\text{C}$). MS (EI): m/z : 542 $[\text{M}]^+$, 486 $[\text{M}$ -

2CO]⁺, 458 [M-3CO]⁺, 430 [M-4CO]⁺; IR (Et₂O): ν = 1980, 1961, 1915, 1910 (ν CO) cm⁻¹; elemental analysis calcd (%) for C₂₉H₂₀O₄Mn₂: C 64.22, H 3.72; found: C 64.44, H 3.48.

3b: ¹H NMR (400 MHz, toluene-D₈, 298 K): δ = 7.8-7.0 (m, 5H, *Ph*), 4.22, 4.02 (m, 4H, *MeCp*), 1.52 (s, 3H, *MeCp*); ¹³C{¹H} NMR (75.5 MHz, toluene-D₈, 298 K): δ = 234.2 (CO), 147.0-125.5 (*Ph*), 105.5, 90.1, 88.1 (*MeCp*), 78.2 (=CC≡C), 13.3 (*MeCp*); ¹H NMR (400 MHz, toluene-D₈, 188 K): δ = 8.3-7.1 (m, 10H, *Ph*), 4.55, 4.30, 4.22, 4.03, 3.60, 3.48, 3.40 (m, 8H, *MeCp*), 1.82 (s, 3H, *MeCp*), 1.41 (s, 3H, *MeCp*); ¹³C{¹H} NMR (100 MHz, toluene-D₈, 188 K): δ = 318.5 (Mn=C), 237.9, 237.3, 233.9, 233.1 (CO), 158.3 (*Ph*, C_{ipso} phenyl ring 1), 134.9 (*Ph*, C_{ipso} phenyl ring 2), 130.2-122.0 (*Ph*), 110.9 (=CC≡C) 108.6, 106.2, 95.8, 94.8, 93.9, 88.0, 87.5, 87.5, 86.8, 81.6 (*MeCp*), 77.8 (=CC≡C), 14.7, 13.7 (*MeCp*); MS (EI): m/z (%): 570 [M]⁺, 514 [M-2CO]⁺, 486 [M-3CO]⁺, 458 [M-4CO]⁺; IR (Et₂O): ν = 1980, 1961, 1915, 1910 (ν CO) cm⁻¹; elemental analysis calcd (%) for C₃₁H₂₄O₄Mn₂: C 65.26, H 4.24; found: C 65.51, H 4.05.

3c/3c' (isomers **3c** and the **3c'** can be differentiated at LT only): ¹H NMR (300 MHz, benzene-D₆, 298 K): δ = 7.8-6.9 (m, 10H, *Ph*), 4.64 (s, 5H, *Cp*), 4.42, 4.31 (m, 4H, *MeCp*), 1.77 (s, 3H, *MeCp*); ¹³C{¹H} NMR (75.5 MHz, benzene-D₆, 298 K): δ = 234.0 (CO), 131.9-125.2 (*Ph*), 105.2, 89.7, 87.6 (*MeCp*), 89.9 (*Cp*), 77.4 (=CC≡C), 13.5 (*MeCp*); ¹H NMR (300 MHz, CD₂Cl₂, 188 K): δ = 7.9-7.3 (m, 20H, *Ph*), 4.7, 4.5 (broad singlets, 10H, *Cp*), 4.5-3.7 (broad multiplets, 8H, *MeCp*), 1.69 (broad singlet, 6H, *MeCp*); ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂, 188 K): δ = 319.5 (br, Mn=C), 236.9, 236.5, 233.1 (br, CO), 157.7-122.5 (*Ph*), 111.4, 108.5, 105.2(=CC≡C and *MeCp*), 92.6-85.2 (*MeCp* and *Cp*), 77.0, 76.1 (=CC≡C, each isomer), 13.7 (br, *MeCp*); IR (CH₂Cl₂): ν = 1975, 1953, 1905(br) (ν CO) cm⁻¹.

Note that at 188 K, most of the signals attributable to the 3c and the 3c' isomers are isochronous.

3d/3d' (isomers **3d** and the **3d'** can be differentiated at LT only): ¹H NMR (300 MHz, toluene-D₈, 298 K): δ = 7.7-7.0 (m, 9H, *Ph* and *MePh*), 4.30, 4.22, 4.08, 4.00 (m, 8H, *MeCp*), 2.19 (s, 3H, *MePh*), 1.56, 1.52 (s, 6H, *MeCp*); ¹³C{¹H} NMR (75.5 MHz, toluene-D₈, 298 K): δ = 234.5 (br, CO), 148.3-122.8 (*Ph* and *PhMe*), 105.5, 105.4, 90.4, 89.7, 88.4, 87.7 (*MeCp*), 77.2 (=CC≡C), 21.2 (*MePh*), 13.3, 13.2 (*MeCp*); ¹H NMR (400 MHz, CD₂Cl₂, 188 K): δ = 7.7-7.1 (m, 9H, *Ph* and *MePh*), 4.5-4.3 (m, 8H, *MeCp*), 2.4 (s, 3H, *MePh*), 1.80, 1.75 (s, 6H, *MeCp*); NMR ¹³C{¹H} (100 MHz, CD₂Cl₂, 188 K): δ = 318.6 (br, Mn=C), 236.2, 232.9, 231.9 (CO), 157.0-121.9 (*Ph* and *MePh*), 107.3, 105.1, 104.6 (=CC≡C and *MeCp*), 93.4-86.6 (*MeCp*), 76.2, 74.5 (=CC≡C, each isomer), 20.9 (*MePh*), 13.2 (*MeCp*); MS (EI): m/z (%): 584 [M]⁺, 528 [M-2CO]⁺, 500 [M-3CO]⁺, 472 [M-4CO]⁺; IR (CH₂Cl₂): ν = 1975, 1953, 1905(br) (ν CO) cm⁻¹.

Note that at 188 K, most of the signals attributable to the 3d and the 3d' isomers are isochronous.

Reaction of [MeCp(CO)₂Mn]₂[μ - η^3 -PhCCCTol] (**3d**) with carbon monoxide

A solution of [MeCp(CO)₂Mn]₂[μ - η^3 -PhCCCTol] (**3d**, 0.205 g, 0.35 mmol) in THF (10 mL) was introduced in a Fischer-Porter bottle. The vessel was pressurized under carbon monoxide (4 atm), and heated for 1 hours at 80°C. After cooling, the autoclave was depressurized, and the solution was transferred into a Schlenk tube. The solution was

concentrated under vacuum to give a brown-red oily residue, which was chromatographed on alumina. An initial elution with a 1:20 diethyloxide/pentane mixture gave a yellow band containing $\text{MeCpMn}(\text{CO})_3$, which was discarded. A second elution with 1:5 diethyloxide/pentane mixture afforded two bands. The first one, red in color, contained a 1:1 mixture of $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{C}\equiv\text{CTol}$ (**1c**) and $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{Tol})\text{C}\equiv\text{CPh}$ (**1d**), which was isolated as a brown-red oil after removal of the solvent under high vacuum (0.07 g, 0.18 mmol, 53% yield). The second band, brown in color, contained unreacted starting material (0.02 g, 0.034 mmol, 10%).

Reaction of $(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})\text{C}\equiv\text{CPh}$ (**4**) with $\text{MeCp}(\text{CO})_2\text{Mn}(\text{THF})$ (**2b**)

A solution of $\text{MeCp}(\text{CO})_3\text{Mn}$ (0.32 ml, 2 mmol) in THF (100 mL) was irradiated for three hours using a Pyrex-filtered Original Hanau TQ 150 medium-pressure Hg vapor lamp. The resulting purple solution of **2b** was transferred by means of a canula into a Schlenk flask containing $(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})\text{C}\equiv\text{CPh}$ (**4**, 0.330 g, 1 mmol) and the mixture was stirred overnight. The solvent was removed under vacuum to leave a brown oil, which was chromatographed on alumina. An initial elution with a 1:20 diethyloxide/pentane mixture gave a yellow band containing $\text{MeCpMn}(\text{CO})_3$ and $\text{Cr}(\text{CO})_6$. A second elution with a 1:10 diethyloxide/pentane mixture gave two bands, an orange one followed by a brown one. Removal of the solvents from the collected bands gave $\text{MeCp}(\text{CO})_2\text{Mn}=\text{C}(\text{Ph})\text{C}\equiv\text{COEt}$ (**6**) as an orange oil (0.080 g, 0.23 mmol, 23% yield), and $\text{MeCp}(\text{CO})_2\text{Mn}\{\eta^2-(\text{CO})_5\text{Cr}=\text{C}(\text{OEt})\text{C}\equiv\text{CPh}\}$ (**5**) as a brown oil (0.11 g, 0.20 mmol, 20% yield).

Complete conversion of **5** into **6** was achieved as follows. The complex $[\text{MeCp}(\text{CO})_2\text{Mn}][(\text{CO})_5\text{Cr}=\text{C}(\text{Ph})\text{C}\equiv\text{CPh}]$ (**7**, 0.11 g, 0.20 mmol) in solution in THF (10 ml) was heated in THF under reflux for 1 hour. After cooling, the solvent was removed under vacuum and the oily residue was treated by column chromatography. Elution with a 1:10 diethyl oxide/pentane mixture gave an orange band. Removal of the solvents from that band gave **6** as an orange oil (0.06 g, 0.017 mmol, 85 % yield).

5. NMR ^1H (300 MHz, CD_2Cl_2): $\delta = 7.9\text{-}7.0$ (m, 5H, *Ph*), 4.8 (m, *MeCp*), 4.4 (q, OCH_2CH_3), 2.0 (s, *MeCp*), 1.6 (t, OCH_2CH_3); NMR $^{13}\text{C}\{^1\text{H}\}$ (75.5 MHz, CD_2Cl_2): $\delta = 330.0$ (Cr=C), 234.5 (Mn-CO), 225.7, 217.0 (Cr-CO), 133.3-128.0 (*Ph*), 104.0, 87.6, 85.9 (*MeCp*), 89.8 ($\text{C}\equiv\text{C}$), 75.8 (OCH_2CH_3), 71.8 ($\text{C}\equiv\text{C}$), 15.4 (OCH_2CH_3), 13.6 (*MeCp*). IR (THF): $\nu = 2055, 1984, 1942, 1925$ (sh), 1887 (s) (νCO) cm^{-1} ; MS (EI): m/z : 540 $[\text{M}]^+$, 456 $[\text{M}-3(\text{CO})]^+$, 428 $[\text{M}-4(\text{CO})]^+$, 400 $[\text{M}-5(\text{CO})]^+$, 344 $[\text{M}-7(\text{CO})]^+$.

6. NMR ^1H (250 MHz, CD_2Cl_2): $\delta = 7.6\text{-}7.3$ (m, *Ph*), 4.84, 3.74 (m, *MeCp*), 4.54 (q, OCH_2CH_3), 1.97 (s, *MeCp*), 1.46 (t, OCH_2CH_3); NMR $^{13}\text{C}\{^1\text{H}\}$ (63 MHz, CD_2Cl_2): $\delta = 293.4$ (Mn=C), 234.6 (CO), 134.6-124.4 (*Ph*), 107.0, 91.0, 90.7 (*MeCp*), 117.5, 94.0 ($\text{C}\equiv\text{C}$), 73.4 (OCH_2CH_3), 17.0 (OCH_2CH_3), 15.3 (*MeCp*); IR (THF): $\nu = 2157$ ($\nu\text{C}\equiv\text{C}$), 1961, 1902 (νCO) cm^{-1} ; MS (EI): m/z : 348 $[\text{M}]^+$, 292 $[\text{M}-2(\text{CO})]^+$.

X-ray Diffraction Studies

Crystals of **3a** suitable for X-ray diffraction were obtained through recrystallisation from pentane in the cold. Data were collected on a Stoe IPDS diffractometer. All calculations were performed on a PC-compatible computer using the WinGX system (Farrugia, L. J. J.

Appl. Crystallogr. **1999**, 32, 837-838). Full crystallographic data are given in Table S1 and in the attached CIF file. The structure was solved by using the SIR92 program (*SIR92: A program for crystal structure solution*. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. J. *Appl. Crystallogr.* **1993**, 26, 343-350), which revealed the position of all the non-hydrogen atoms. The structure was refined by using the SHELXS97 program (*[Includes SHELXS97, SHELXL97, CIFTAB] - Programs for Crystal Structure Analysis (Release 97-2)*. Sheldrick, G.M., Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, **1998**). Atomic scattering factors were taken from the usual tabulations (Hahn, T. Ed., *International Tables for Crystallography, Volume A*, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1995**). Anomalous dispersion terms for Mn were included in F_C . All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms were set in idealized position (C-H = 0.96 Å; $U = 1.2U_{eq}$ attached C) and held fixed during refinements. Selected distances and angles for **3a** are given in Tables S2 and S3, respectively. Final atomic coordinates for non-hydrogen atoms, anisotropic temperature factors, and atomic coordinates for hydrogen atoms are given in Table S4 to S6, respectively.

Table S1. Crystal data and structure refinement for complexes **3a**.

compound	3a
empirical formula	C ₂₉ H ₂₀ Mn ₂ O ₄
formula weight	542.33
temperature, K	160 K
wavelength, Å	0.71073 Å
crystal system	monoclinic
space group	P2 ₁ /c
a, Å	12.843(2) Å
b, Å	8.358(1) Å
c, Å	22.265(6) Å
β (deg)	97.62(3)
volume, Å ³	2368.8(8)
Z	4
D _{calcd.} (g.cm ⁻³)	1.521
μ (mm ⁻¹)	1.100
F(000)	1104
θ max (deg)	24.18
index ranges	-14•h•14 -8•k•9, -25•l•25
reflections collected	14485
independent reflections	3520 [R(int) = 0.039]
completeness to θ max, %	85.6
refinement method	Full-matrix least-squares on F ²
restraints / parameters	0 / 316
g. o. f on F ²	0.956
R [I>2σ(I)]	0.0247
R _w [I>2σ(I)]	0.0591
R (all data)	0.0362
R _w (all data)	0.0628
resid. el. density (e.Å ⁻³)	0.260 / -0.212

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

	x	y	z	$U(\text{eq})$
Mn(1)	6554(1)	2818(1)	613(1)	19(1)
Mn(2)	8668(1)	-1461(1)	1371(1)	18(1)
O(1)	5977(1)	5376(2)	1409(1)	39(1)
O(2)	4509(1)	1407(3)	758(1)	50(1)
O(6)	6680(1)	-1912(2)	560(1)	38(1)
O(7)	9760(2)	-2180(3)	328(1)	55(1)
C(1)	6218(2)	4376(3)	1096(1)	26(1)
C(2)	5324(2)	1931(3)	708(1)	29(1)
C(3)	7284(2)	1748(3)	1288(1)	18(1)
C(4)	8296(2)	1089(3)	1293(1)	20(1)
C(5)	9260(2)	832(3)	1278(1)	21(1)
C(6)	7454(2)	-1696(3)	878(1)	24(1)
C(7)	9325(2)	-1872(3)	736(1)	29(1)
C(11)	6982(2)	1716(4)	-195(1)	44(1)
C(12)	7811(2)	2684(4)	64(1)	40(1)
C(13)	7461(2)	4237(4)	69(1)	43(1)
C(14)	6422(2)	4267(4)	-196(1)	49(1)
C(15)	6121(2)	2737(5)	-358(1)	48(1)
C(21)	6869(2)	1543(3)	1882(1)	19(1)
C(22)	7269(2)	2485(3)	2377(1)	27(1)
C(23)	6901(2)	2317(3)	2929(1)	33(1)
C(24)	6138(2)	1198(4)	3001(1)	36(1)
C(25)	5741(2)	252(4)	2518(1)	38(1)
C(26)	6100(2)	422(3)	1961(1)	28(1)
C(31)	10279(2)	1568(3)	1243(1)	20(1)
C(32)	10341(2)	3189(3)	1108(1)	26(1)
C(34)	12215(2)	3007(3)	1156(1)	34(1)
C(36)	11207(2)	668(3)	1330(1)	28(1)
C(33)	11299(2)	3907(3)	1063(1)	32(1)
C(35)	12164(2)	1413(4)	1288(1)	35(1)
C(45)	8614(2)	-1408(3)	2344(1)	26(1)
C(44)	8020(2)	-2689(3)	2082(1)	28(1)
C(41)	9666(2)	-1628(3)	2236(1)	27(1)
C(42)	9718(2)	-3046(3)	1908(1)	29(1)
C(43)	8693(2)	-3726(3)	1804(1)	29(1)

Table S3. Bond lengths [Å] and angles [°] for complex **3a**.

Mn(1)-C(1)	1.779(3)
Mn(1)-C(2)	1.783(2)
Mn(1)-C(3)	1.888(2)
Mn(1)-C(11)	2.155(2)
Mn(1)-C(12)	2.152(2)
Mn(1)-C(13)	2.145(2)
Mn(1)-C(14)	2.157(3)
Mn(1)-C(15)	2.159(2)
Mn(2)-C(4)	2.186(2)
Mn(2)-C(5)	2.082(2)
Mn(2)-C(6)	1.795(2)
Mn(2)-C(7)	1.774(2)
Mn(2)-C(43)	2.122(3)
Mn(2)-C(42)	2.138(2)
Mn(2)-C(44)	2.145(2)
Mn(2)-C(41)	2.172(2)
Mn(2)-C(45)	2.176(2)
O(1)-C(1)	1.157(3)
O(2)-C(2)	1.154(3)
O(6)-C(6)	1.155(3)
O(7)-C(7)	1.155(3)
C(3)-C(4)	1.411(3)
C(3)-C(21)	1.501(3)
C(4)-C(5)	1.261(3)
C(5)-C(31)	1.457(3)
C(1)-Mn(1)-C(2)	86.69(11)
C(1)-Mn(1)-C(3)	90.00(10)
C(2)-Mn(1)-C(3)	93.58(10)
C(7)-Mn(2)-C(6)	87.53(10)
C(7)-Mn(2)-C(5)	83.11(10)
C(6)-Mn(2)-C(5)	109.81(10)
C(7)-Mn(2)-C(4)	104.28(10)
C(6)-Mn(2)-C(4)	83.97(9)
C(5)-Mn(2)-C(4)	34.27(8)
C(43)-Mn(2)-C(4)	153.60(8)
C(42)-Mn(2)-C(4)	139.78(8)
C(44)-Mn(2)-C(4)	115.07(9)
C(41)-Mn(2)-C(4)	103.34(9)
C(45)-Mn(2)-C(4)	91.39(9)
O(1)-C(1)-Mn(1)	178.5(2)

O(2)-C(2)-Mn(1)	177.4(2)
C(4)-C(3)-C(21)	112.55(17)
C(4)-C(3)-Mn(1)	123.41(15)
C(21)-C(3)-Mn(1)	124.02(14)
C(5)-C(4)-C(3)	166.7(2)
C(5)-C(4)-Mn(2)	68.35(14)
C(3)-C(4)-Mn(2)	124.93(16)
C(4)-C(5)-C(31)	145.2(2)
C(4)-C(5)-Mn(2)	77.38(15)
C(31)-C(5)-Mn(2)	137.44(17)
O(6)-C(6)-Mn(2)	177.3(2)
O(7)-C(7)-Mn(2)	178.1(2)

Symmetry transformations used to generate equivalent atoms:

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

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Mn(1)	16(1)	22(1)	19(1)	3(1)	3(1)	2(1)
Mn(2)	18(1)	20(1)	17(1)	0(1)	1(1)	1(1)
O(1)	41(1)	33(1)	44(1)	-8(1)	16(1)	7(1)
O(2)	25(1)	78(2)	47(1)	15(1)	1(1)	-16(1)
O(6)	33(1)	37(1)	38(1)	4(1)	-14(1)	-7(1)
O(7)	51(1)	79(2)	38(1)	-17(1)	22(1)	5(1)
C(1)	20(1)	28(2)	30(1)	9(1)	5(1)	3(1)
C(2)	23(1)	39(2)	25(1)	7(1)	-1(1)	2(1)
C(3)	17(1)	16(2)	21(1)	-2(1)	3(1)	-3(1)
C(4)	23(1)	21(2)	16(1)	3(1)	4(1)	1(1)
C(5)	23(1)	21(2)	20(1)	2(1)	4(1)	2(1)
C(6)	30(1)	19(2)	24(1)	3(1)	3(1)	1(1)
C(7)	25(1)	32(2)	29(1)	-2(1)	0(1)	2(1)
C(11)	84(2)	27(2)	26(1)	-2(1)	27(1)	0(2)
C(12)	27(1)	74(3)	22(1)	16(1)	11(1)	17(1)
C(13)	58(2)	47(2)	29(1)	-1(1)	21(1)	-23(2)
C(14)	57(2)	56(2)	36(2)	27(2)	20(1)	27(2)
C(15)	34(2)	90(3)	19(1)	5(1)	0(1)	-16(2)
C(21)	16(1)	20(1)	22(1)	3(1)	4(1)	4(1)
C(22)	23(1)	29(2)	29(1)	-1(1)	4(1)	-3(1)
C(23)	32(1)	44(2)	24(1)	-9(1)	6(1)	-1(1)
C(24)	33(1)	53(2)	24(1)	3(1)	11(1)	0(1)
C(25)	31(1)	50(2)	32(1)	6(1)	9(1)	-14(1)
C(26)	25(1)	35(2)	24(1)	-1(1)	2(1)	-6(1)
C(31)	21(1)	24(2)	16(1)	-1(1)	5(1)	-1(1)
C(32)	30(1)	25(2)	24(1)	-1(1)	8(1)	1(1)
C(34)	28(1)	38(2)	37(1)	-3(1)	13(1)	-11(1)
C(36)	23(1)	24(2)	38(1)	4(1)	7(1)	2(1)
C(33)	42(1)	27(2)	29(1)	0(1)	13(1)	-7(1)
C(35)	19(1)	44(2)	45(1)	2(1)	8(1)	2(1)
C(45)	36(1)	29(2)	14(1)	2(1)	3(1)	5(1)
C(44)	29(1)	32(2)	23(1)	7(1)	7(1)	0(1)
C(41)	27(1)	29(2)	22(1)	4(1)	-5(1)	3(1)
C(42)	29(1)	28(2)	28(1)	5(1)	-1(1)	9(1)
C(43)	39(1)	17(2)	30(1)	2(1)	0(1)	-1(1)

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

	x	y	z	U(eq)
H(11)	6997	613	-248	53
H(12)	8486	2335	209	48
H(13)	7853	5116	223	52
H(14)	6000	5173	-254	58
H(15)	5460	2427	-544	57
H(22)	7789	3235	2334	32
H(23)	7169	2961	3253	40
H(24)	5894	1083	3373	43
H(25)	5228	-505	2566	45
H(26)	5824	-221	1638	34
H(32)	9731	3799	1049	31
H(34)	12860	3486	1128	40
H(36)	11183	-419	1415	34
H(33)	11329	4989	970	38
H(35)	12779	815	1350	42
H(45)	8362	-557	2552	32
H(44)	7305	-2840	2089	34
H(41)	10225	-948	2362	32
H(42)	10320	-3472	1778	34
H(43)	8500	-4666	1595	35

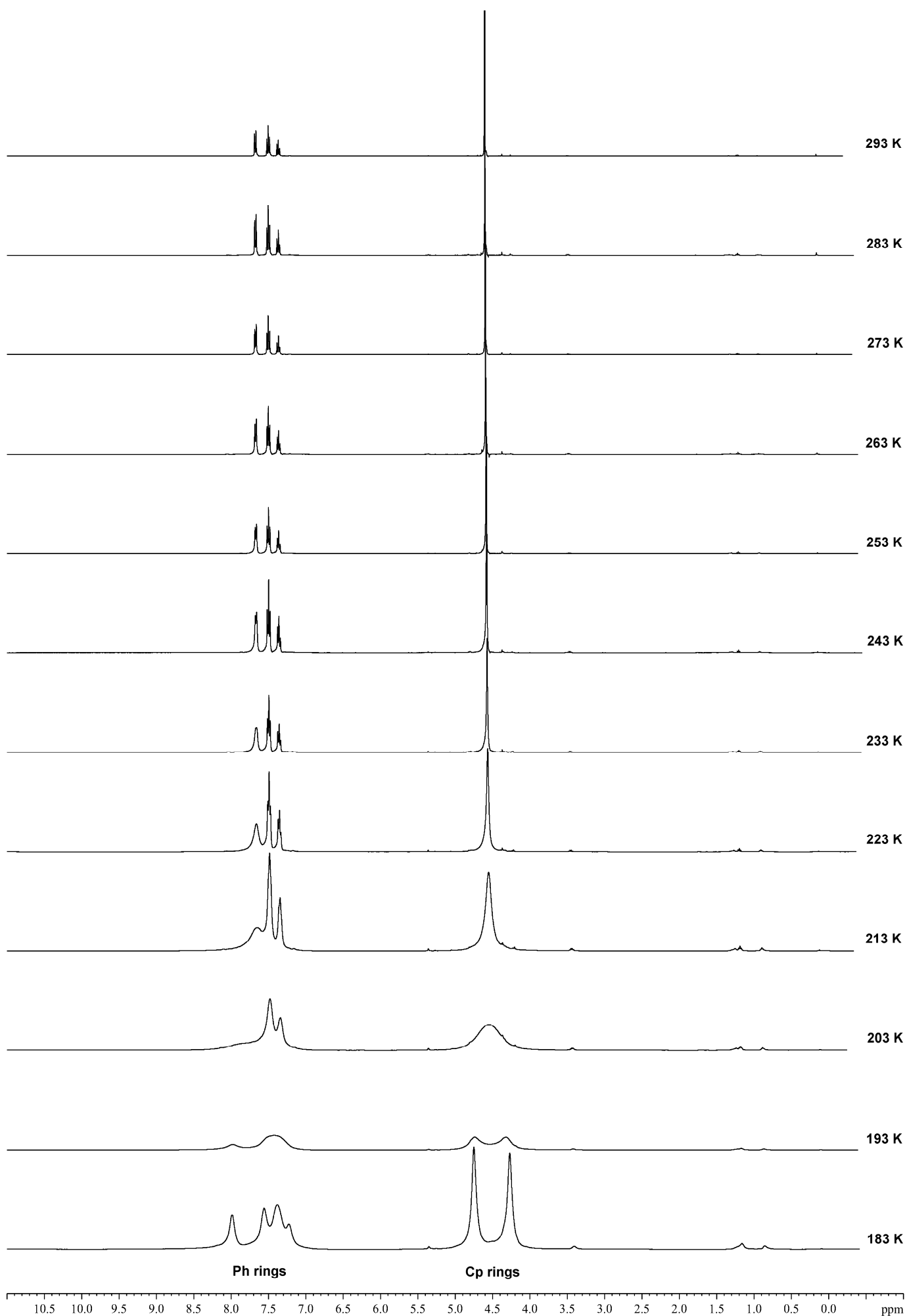


Figure S1. Proton NMR spectra (400 MHz, dichloromethane-D₂) of complex **3a**.

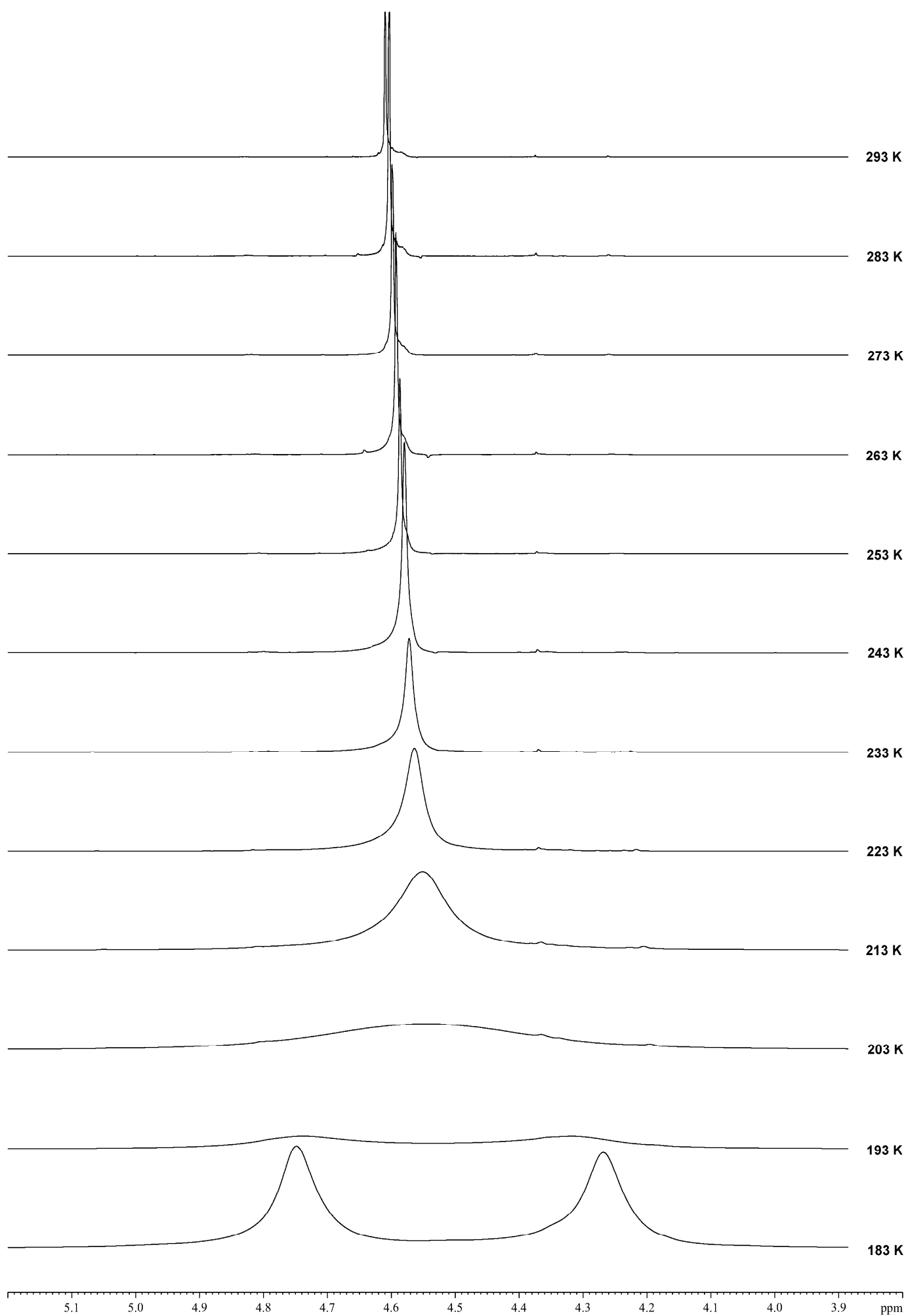


Figure S2. Proton NMR spectra (400 Mhz, dichloromethane-D₂) of compound **3a**.

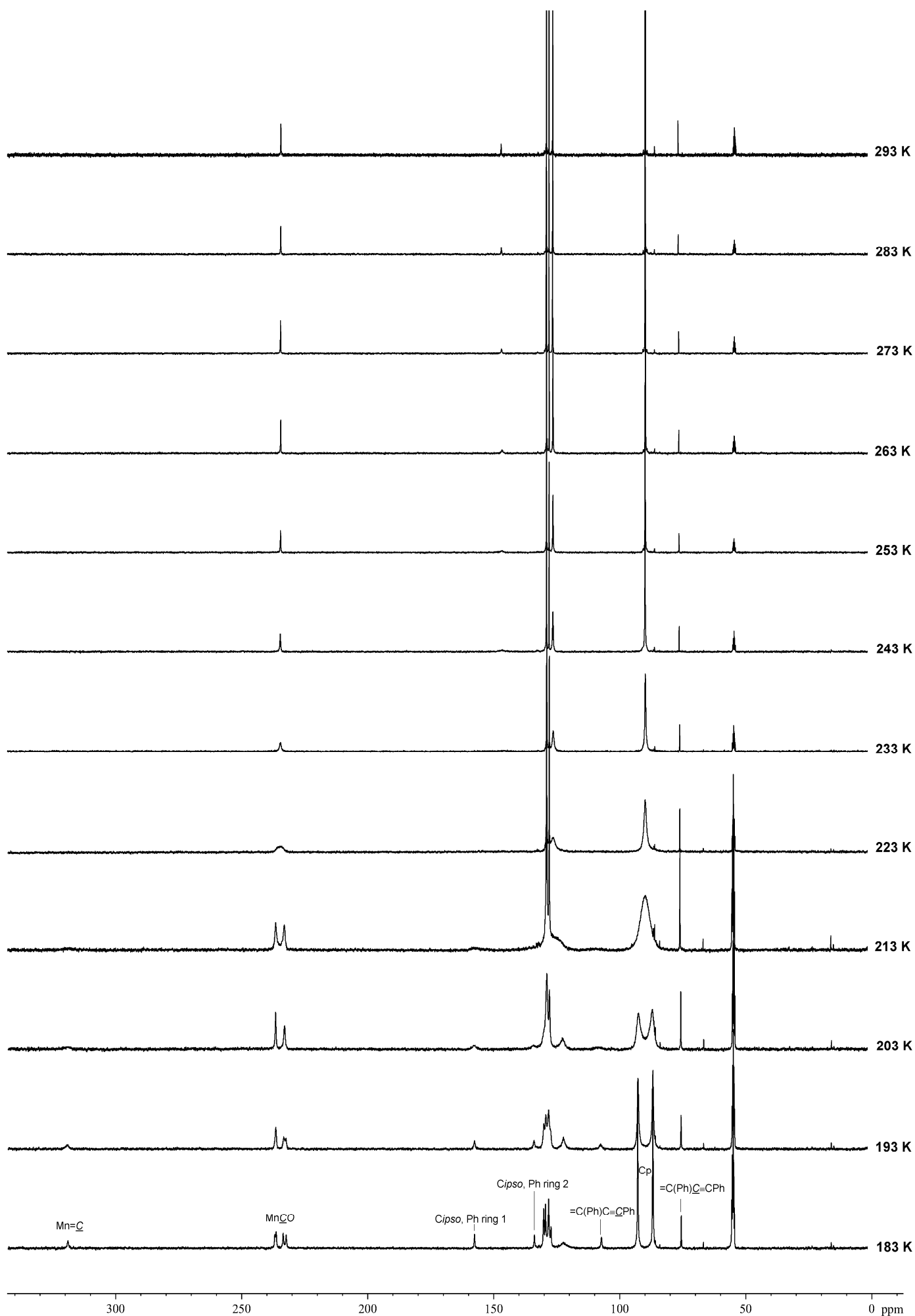


Figure S3. Carbon 13 NMR spectra (100 Mhz, dichloromethane-D2) of compound **3a**.

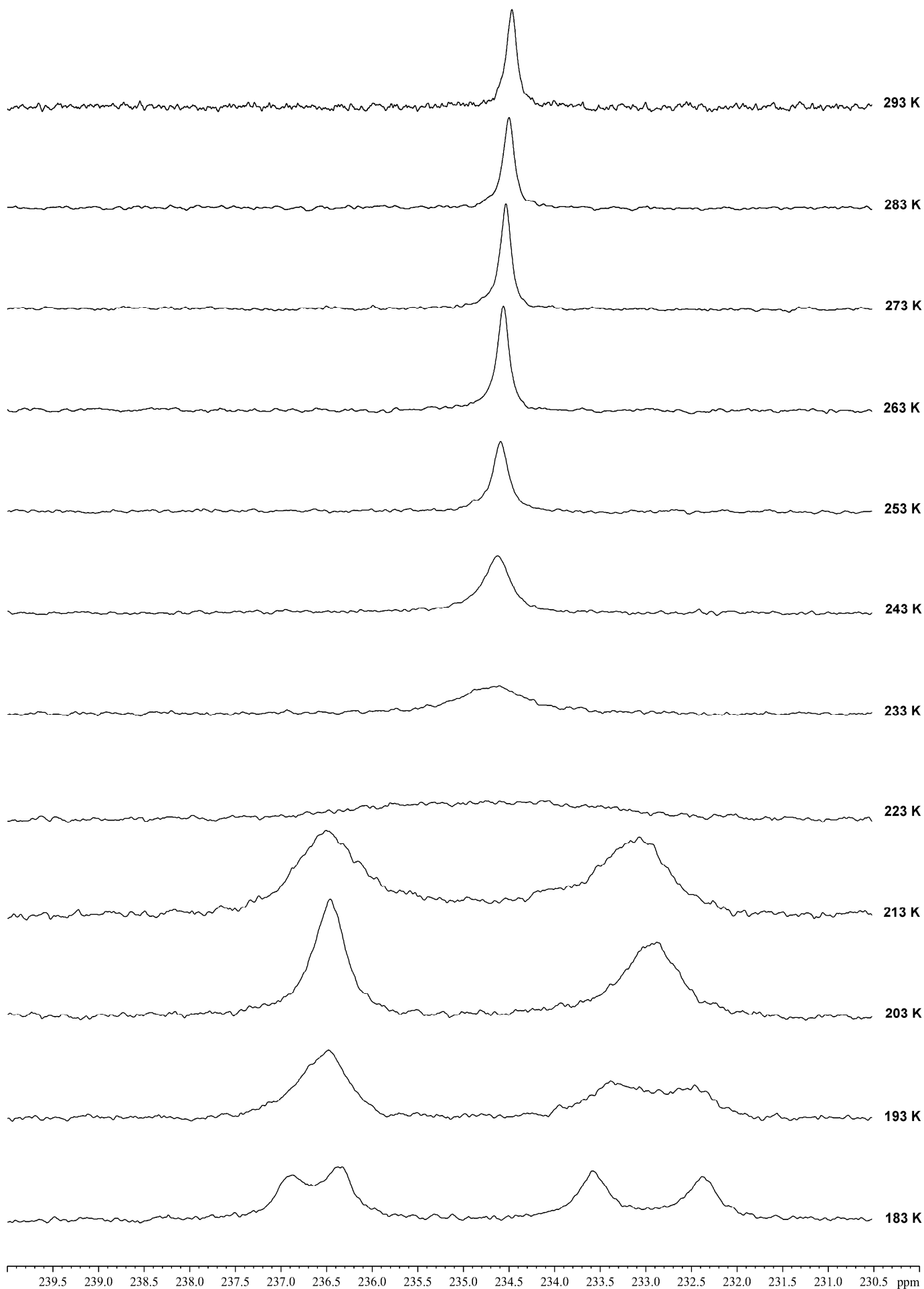


Figure S4. Carbon 13 NMR spectra (100 Mhz, dichloromethane-D₂) of compound **3a**, CO's area.

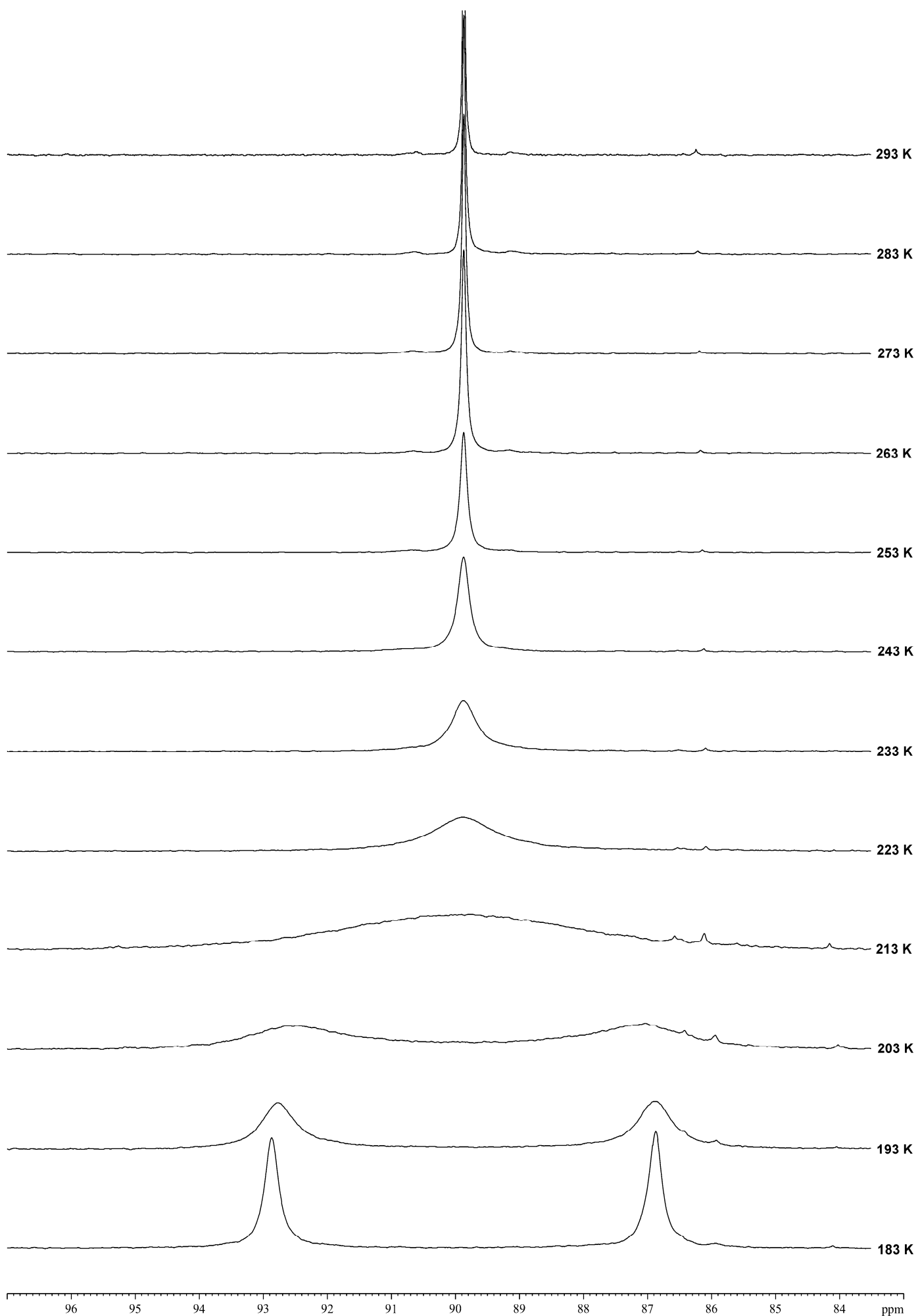


Figure S5. Carbon 13 NMR spectra (100 Mhz, dichloromethane-D2) of compound **3a**, Cp's area.

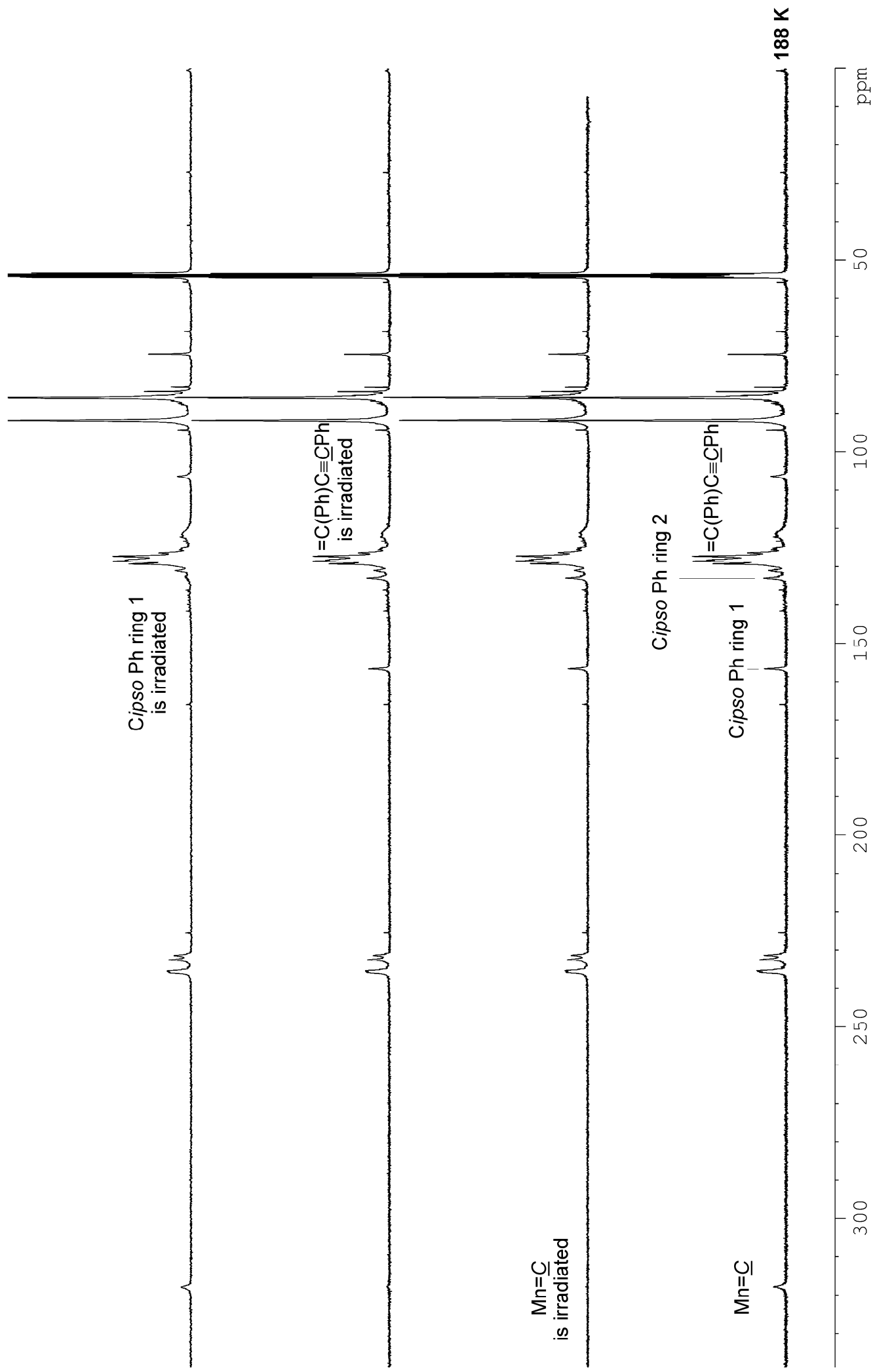


Figure S6. Carbon ^{13}C NMR spectra (100 Mhz, dichloromethane- D_2) of compound **3a**, spin saturation transfer experiments (188 K).