# Electronic Supplementary Information

## Ligand exchange processes between molybdenum and zinc additives in lubricants: evidence from NMR ($^{1}$H, $^{13}$C, $^{31}$P) and HPLC-MS analysis

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# Supplementary Material

**Figure 1S: (a)** Mass spectra and **(b)** Extracted Ion Chromarogram (HPLC-MS, APPI, positive mode) of compounds: **(i) 2a**; **(ii) 2b**; **(iii) 2c**.

**Figure 2S:** Calibration curves for $Mo(DTC)_2$. **(a) 2a**; **(b) 2b**; **(c) 2c** (HPLC-MS, APPI, positive mode). IS: Internal standard.

**Figure 3S:** Reference NMR spectra ($CDCl_3$, 25 °C) of $Mo(DTP)_2$ **1** used for the investigation of DTC/DTP ligand exchange reactions. **(a)** $^{1}$H-NMR spectrum (0.0-5.0 ppm, 500 MHz); **(b)** $^{13}$C-NMR spectrum (0-210 ppm, 125 MHz). *: Impurities.

**Figure 4S:** Reference NMR spectra ($CDCl_3$, 25 °C) of $Mo(DTC)_2$ **2d** used for the investigation of DTC/DTP ligand exchange reactions **(a)** $^{1}$H-NMR spectrum (0.0-5.0 ppm, 500 MHz); **(b)** $^{13}$C-NMR spectrum (0-210 ppm, 125 MHz). *: Impurities.

**Figure 5S:** Reference NMR spectra ($CDCl_3$, 25 °C) of $Zn(DTC)_2$ **3a** used for the investigation of DTC/DTP ligand exchange reactions. **(a)** $^{1}$H-NMR spectrum (0.0-5.0 ppm, 500 MHz); **(b)** $^{13}$C-NMR spectrum (0-210 ppm, 125 MHz). *: Impurities.

**Figure 6S:** Reference NMR spectra ($CDCl_3$, 25 °C) of $Zn(DTP)_2$ **4a** used for the investigation of DTC/DTP ligand exchange reactions. **(a)** $^{1}$H-NMR spectrum (0.0-5.0 ppm, 500 MHz); **(b)** $^{13}$C-NMR spectrum (0-210 ppm, 125 MHz). *: Impurities.

**Figure 7S:** Partial $^{1}$H-NMR reference spectra (3.0-5.0 ppm, 500 MHz, $D_8$-toluene, 105 °C) of additives **(a) 1**; **(b) 2d**; **(c) 3a**; **(d) 4a** used for the investigation of DTC/DTP ligand exchange reactions.*: Impurities.

**Figure 8S:** $^{31}$P-NMR reference spectra (90-115 ppm, 121 MHz, $CDCl_3$, 25 °C) of additives **(a) 1**; **(b) 4a** used for the investigation of DTC/DTP ligand exchange reactions. *: Impurities.

**Figure 9S:** Partial $^{31}$P-NMR spectrum (90-115 pp, 162 MHz, $D_8$-toluene, 105 °C) of a mixture of $Mo(DTP)_2$ **1** and $Zn(DTC)_2$ **3a** in a 4:1 molar ratio after 15 min. *: Impurities.

**Figure 10S:** Partial $^{1}$H-NMR spectra (3.0-5.0 ppm, 500 MHz, $CDCl_3$, 25 °C) of a mixture of $Mo(DTP)_2$ **1** and $Zn(DTC)_2$ **3a** in a 1:1 molar ratio after **(a)** 1 h; **(b)** 17 h; **(c)** 95 h. * : Impurities.

**Figure 11S:** Partial $^{31}$P-NMR spectra (90-115 ppm, 121 MHz, $CDCl_3$, 25 °C) of a mixture of $Mo(DTP)_2$ **1** and $Zn(DTC)_2$ **3a** in a 1:1 molar ratio after **(a)** 1 h, **(b)** 17 h; **(c)** 95 h. * : Impurities.

**Figure 12S:** Partial NMR spectra ($CDCl_3$, 25 °C) of a mixture of $Mo(DTC)_2$ **2d** and $Zn(DTP)_2$ **4a** in a 2:1 molar ratio after 24 h. **(a)** $^1$H-NMR spectrum (3.0-5.0 ppm, 500 MHz); **(b)** $^{31}$P-NMR spectrum (90-115 ppm, 121 MHz).

**Figure 13S: (a)** Mass spectra and **(b)** Extracted Ion Chromatogram (HPLC-MS, APPI, positive mode) of compounds **2e**, **2f**, and **2g**.

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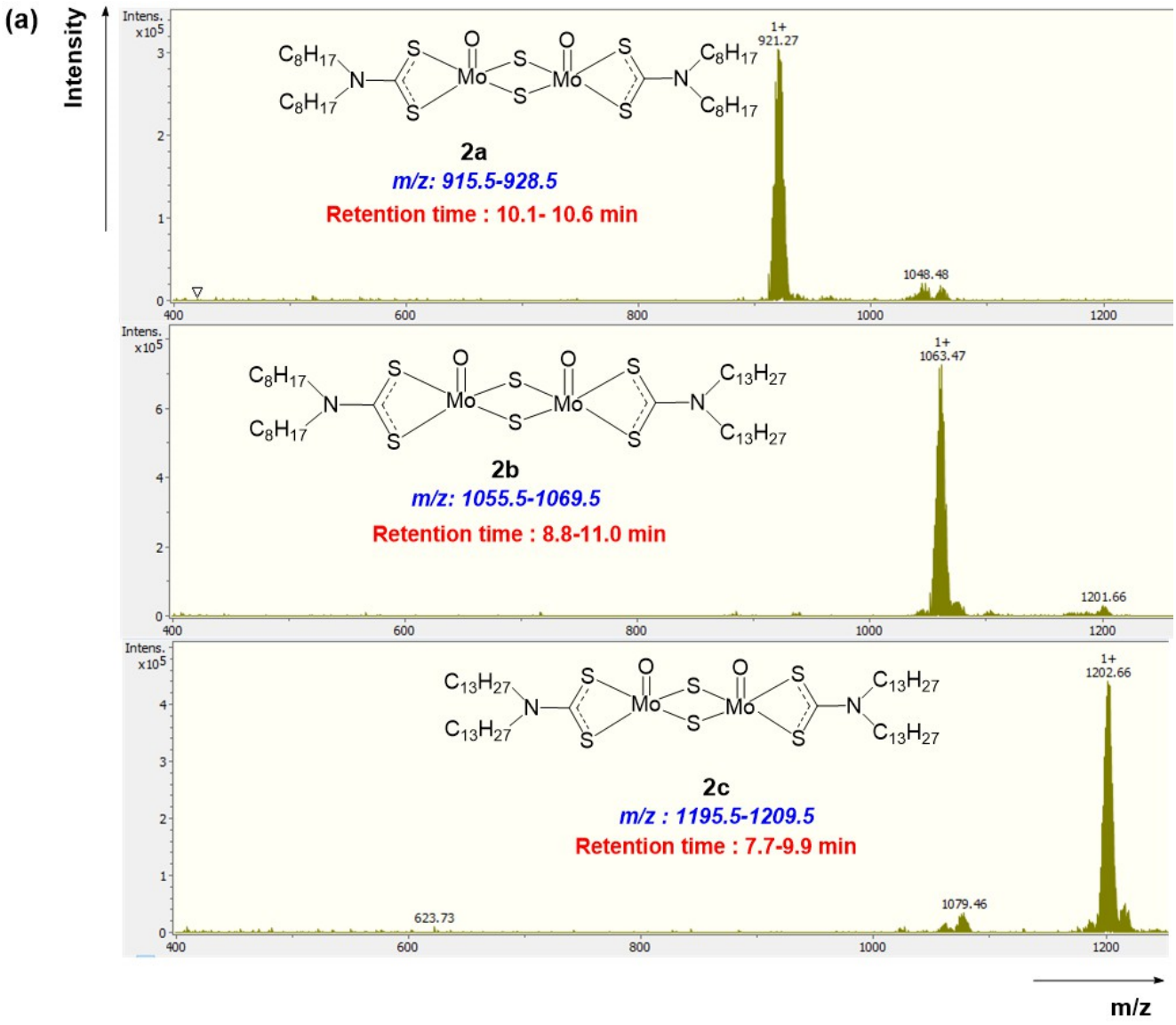


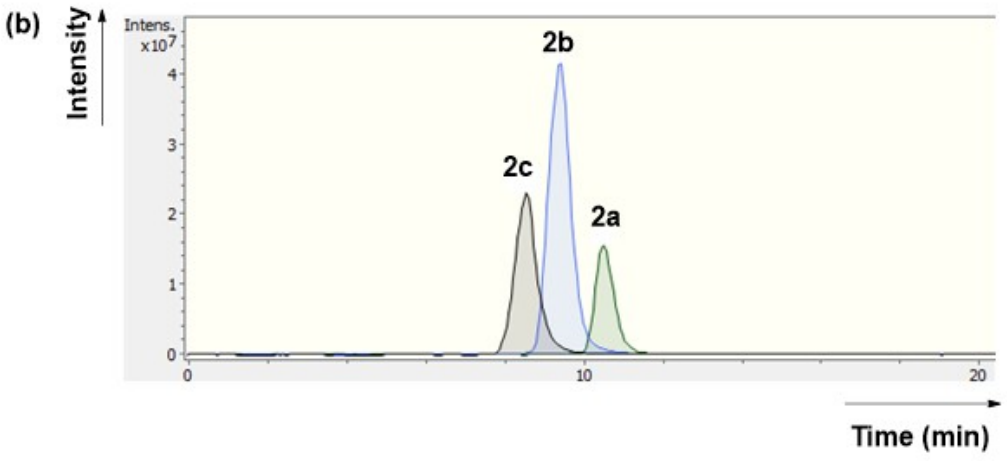

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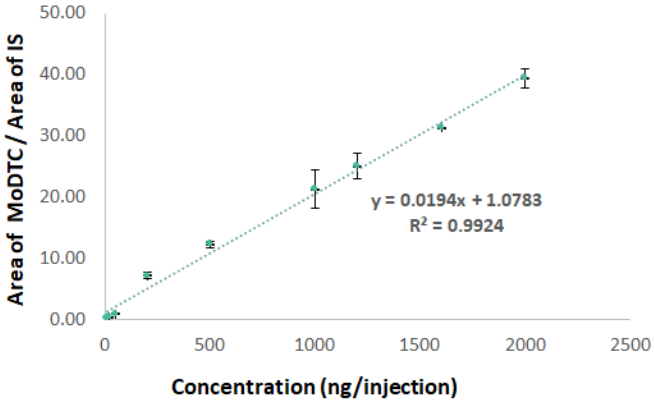
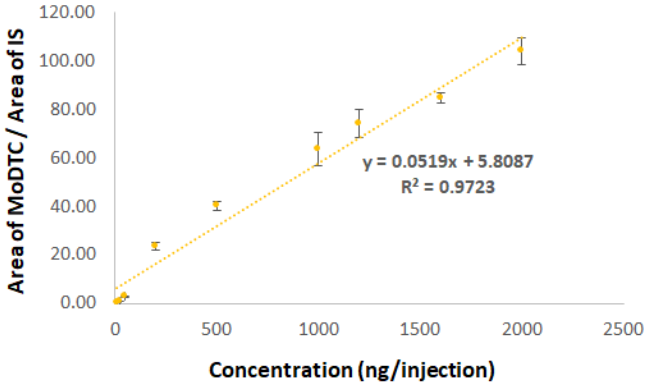



(a) **2a**

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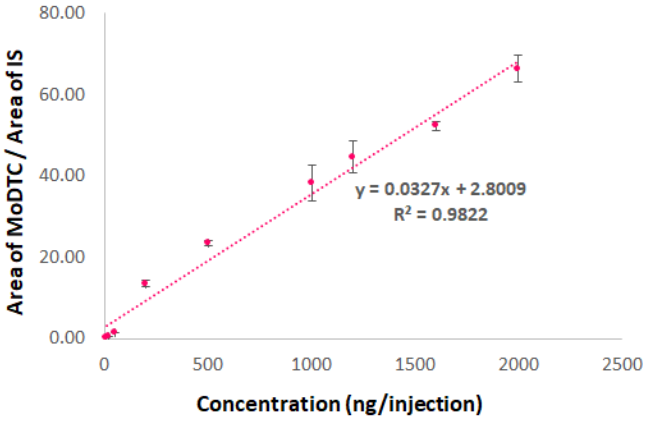


(c) **2c**

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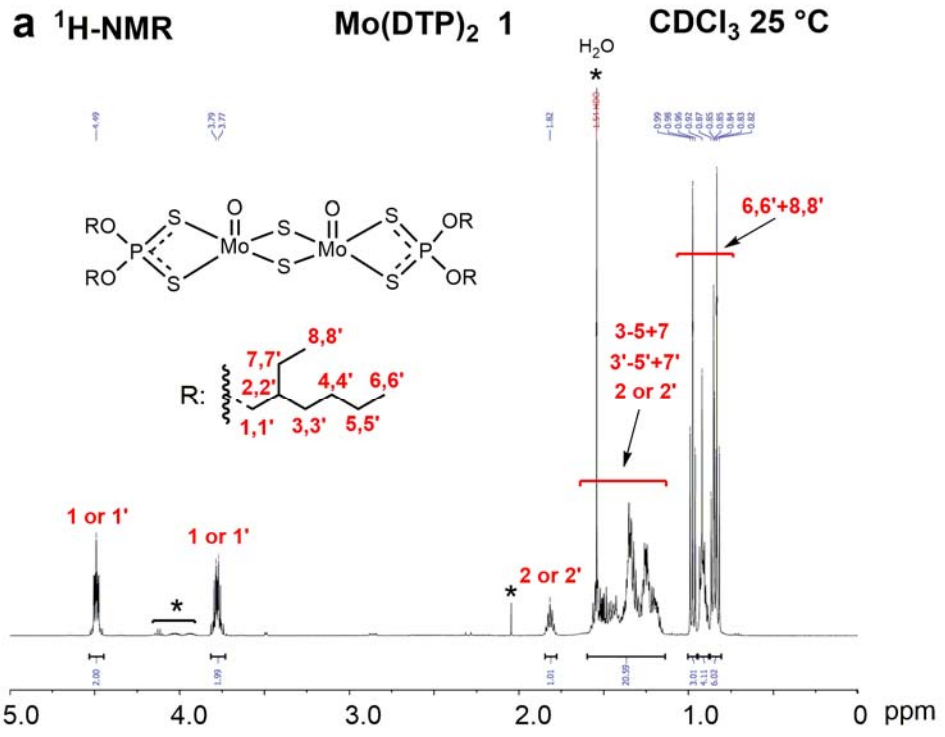


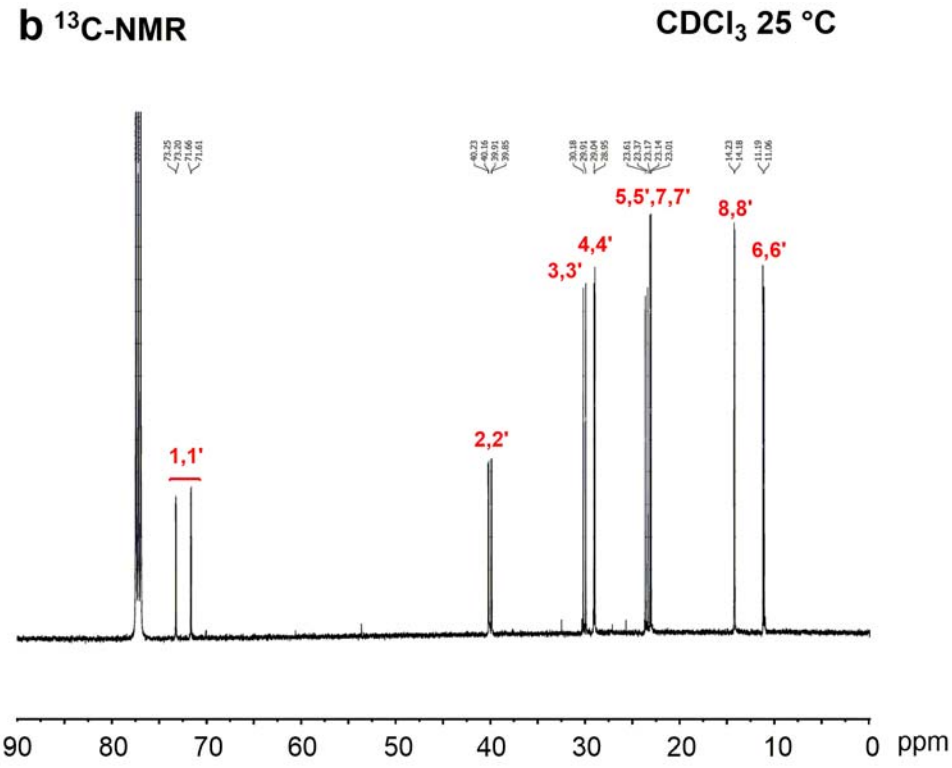

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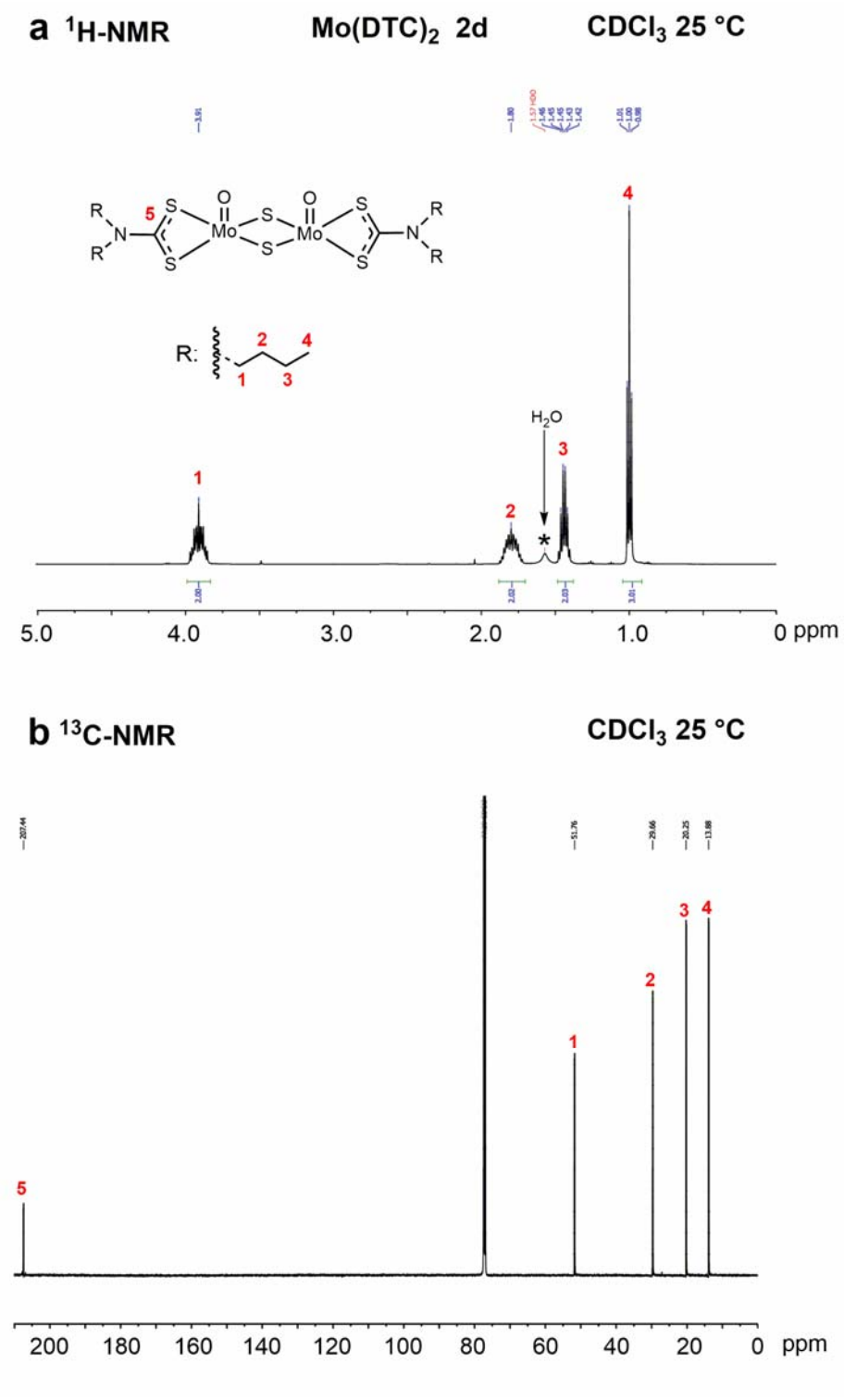

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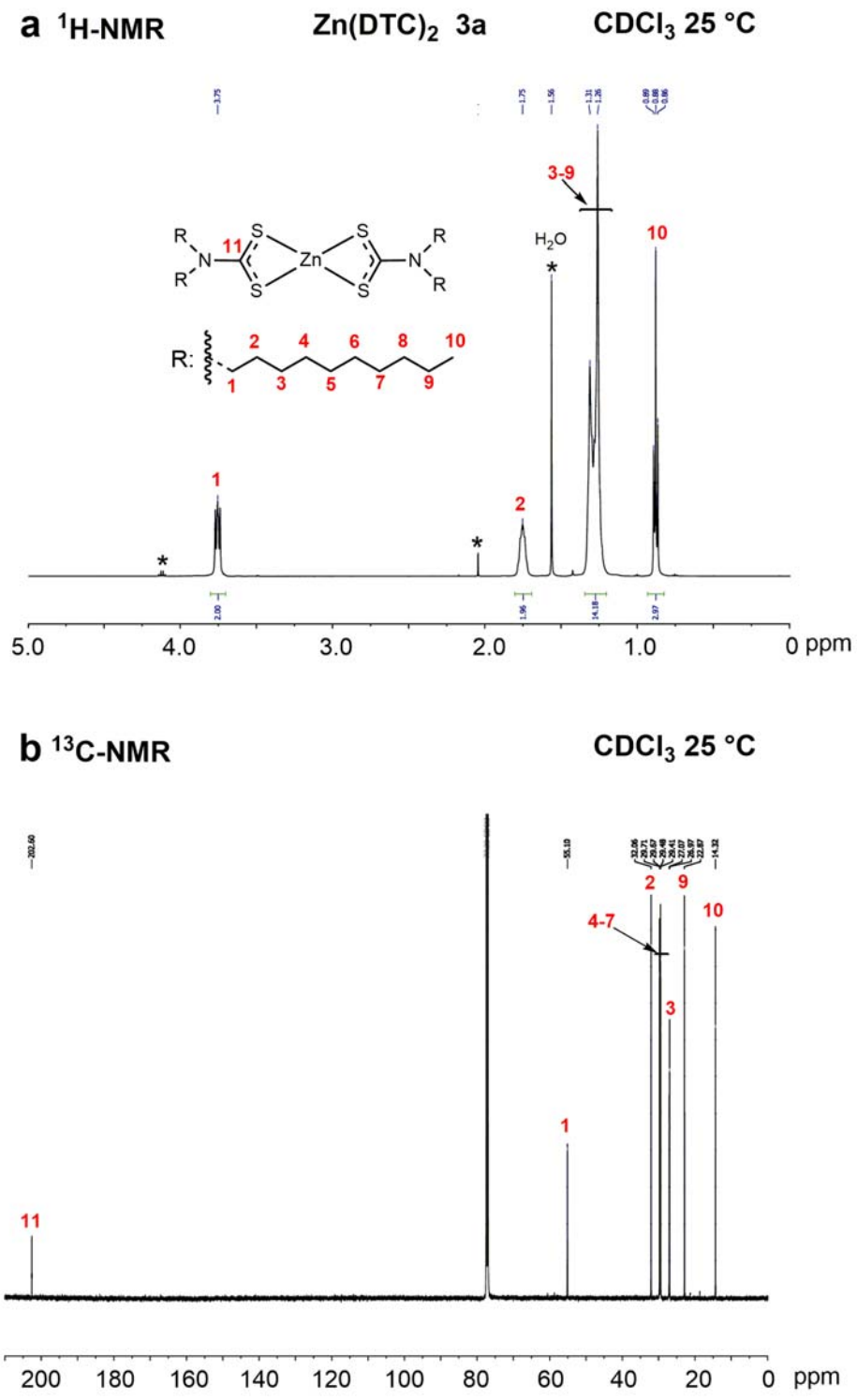

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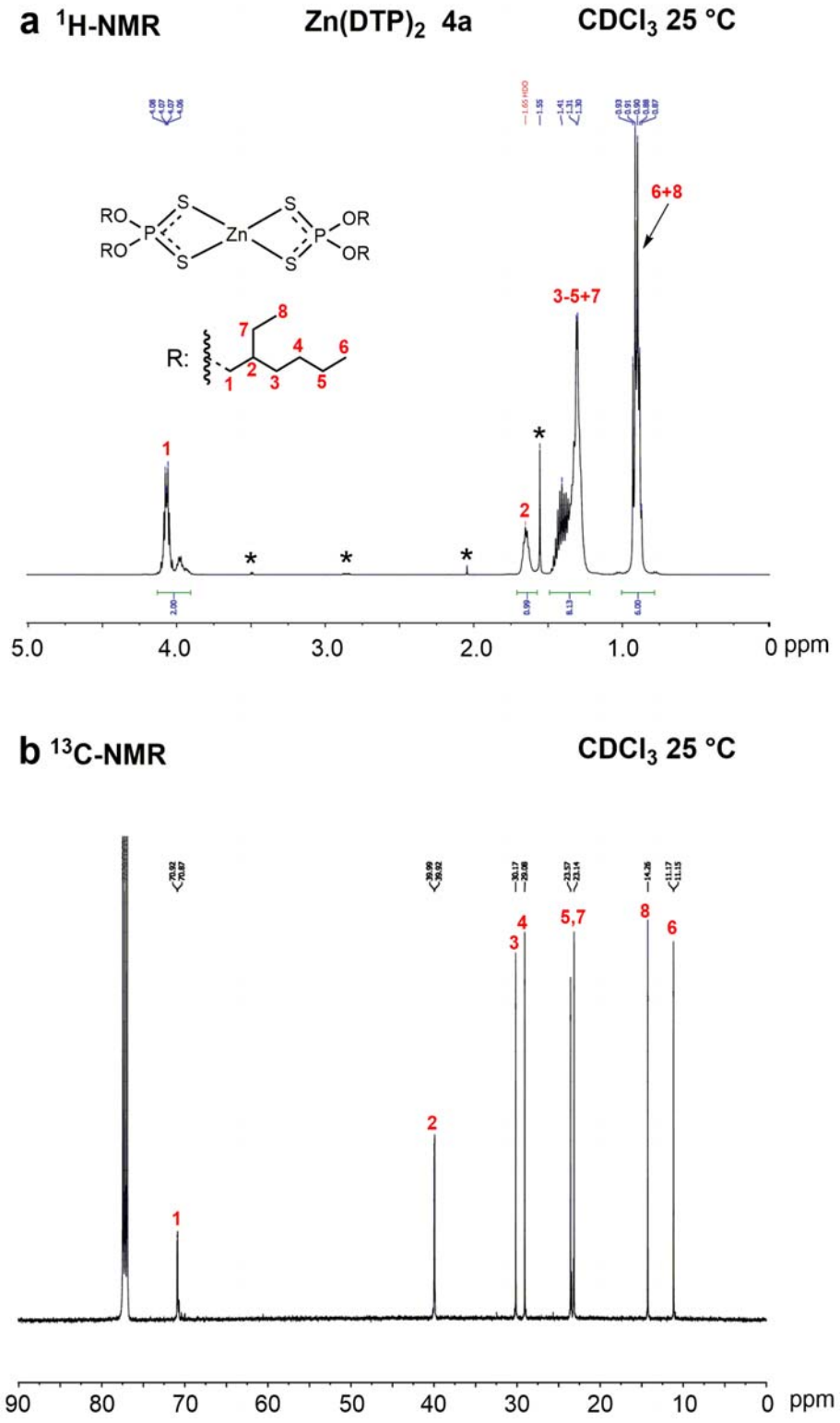

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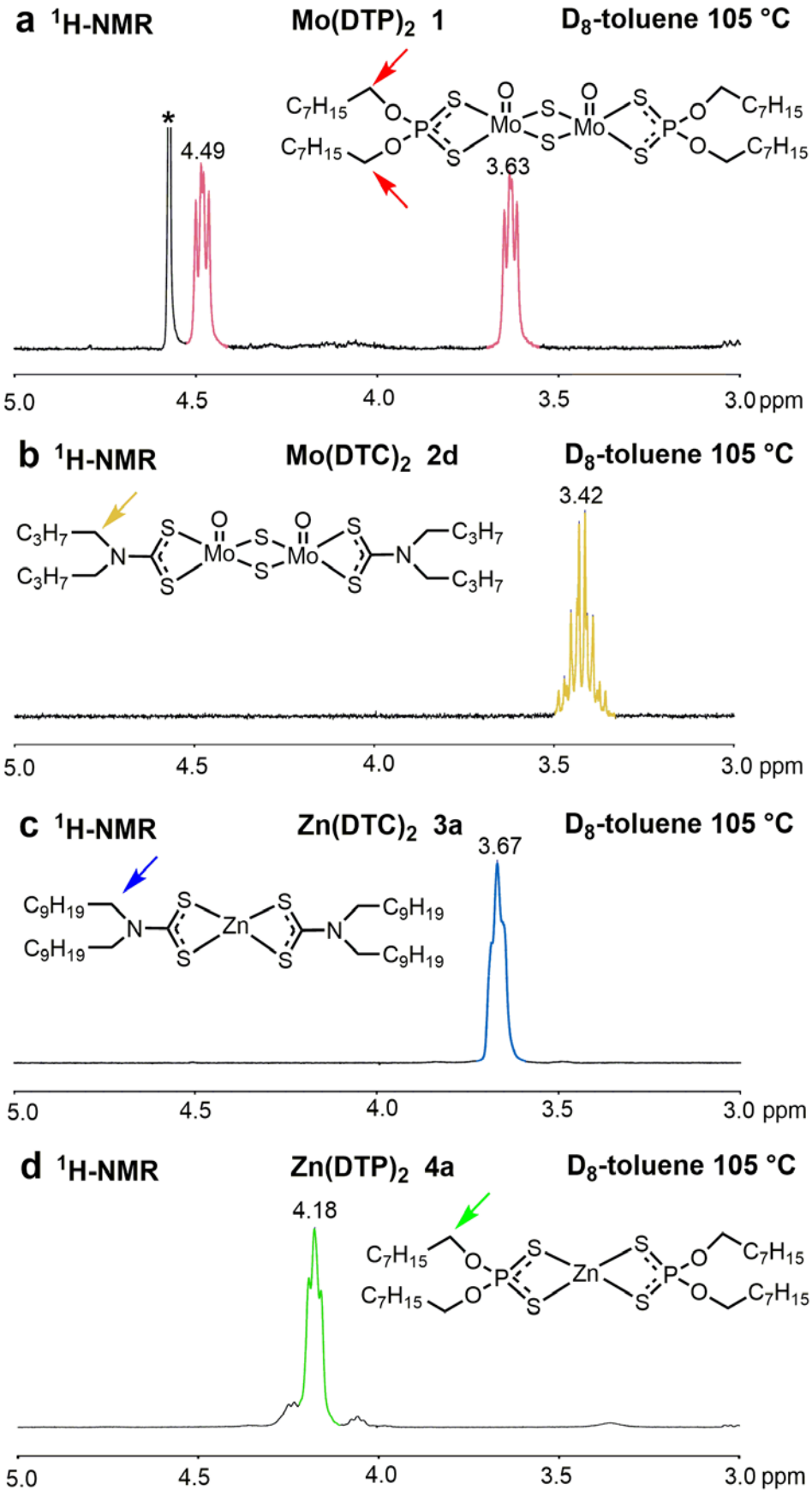

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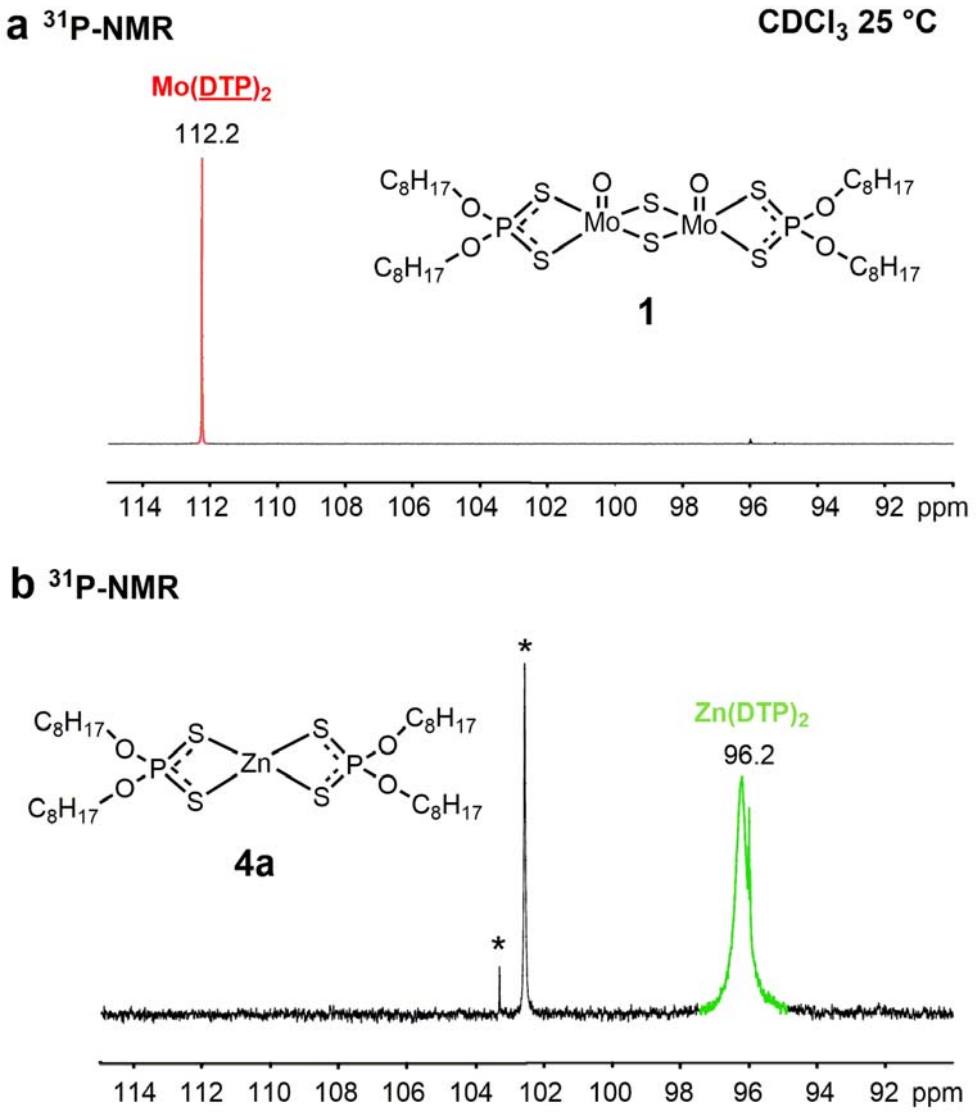

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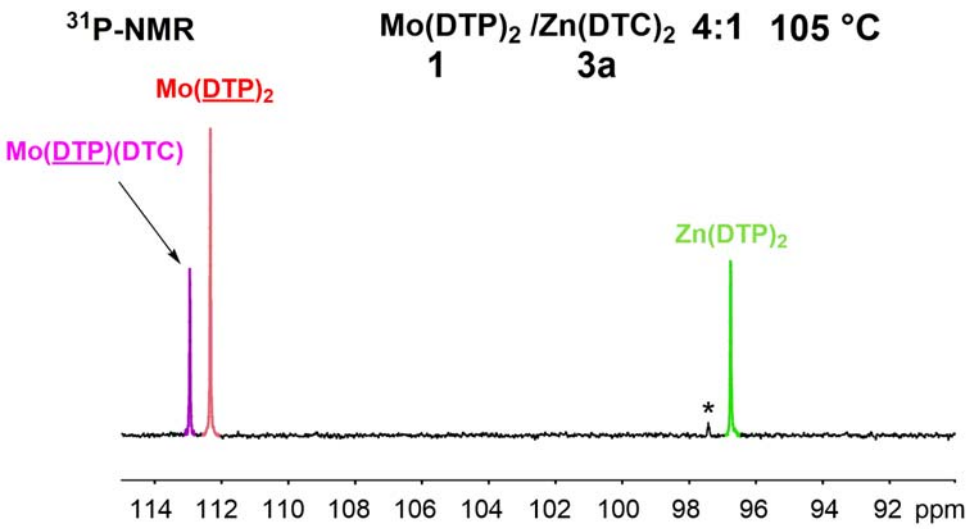

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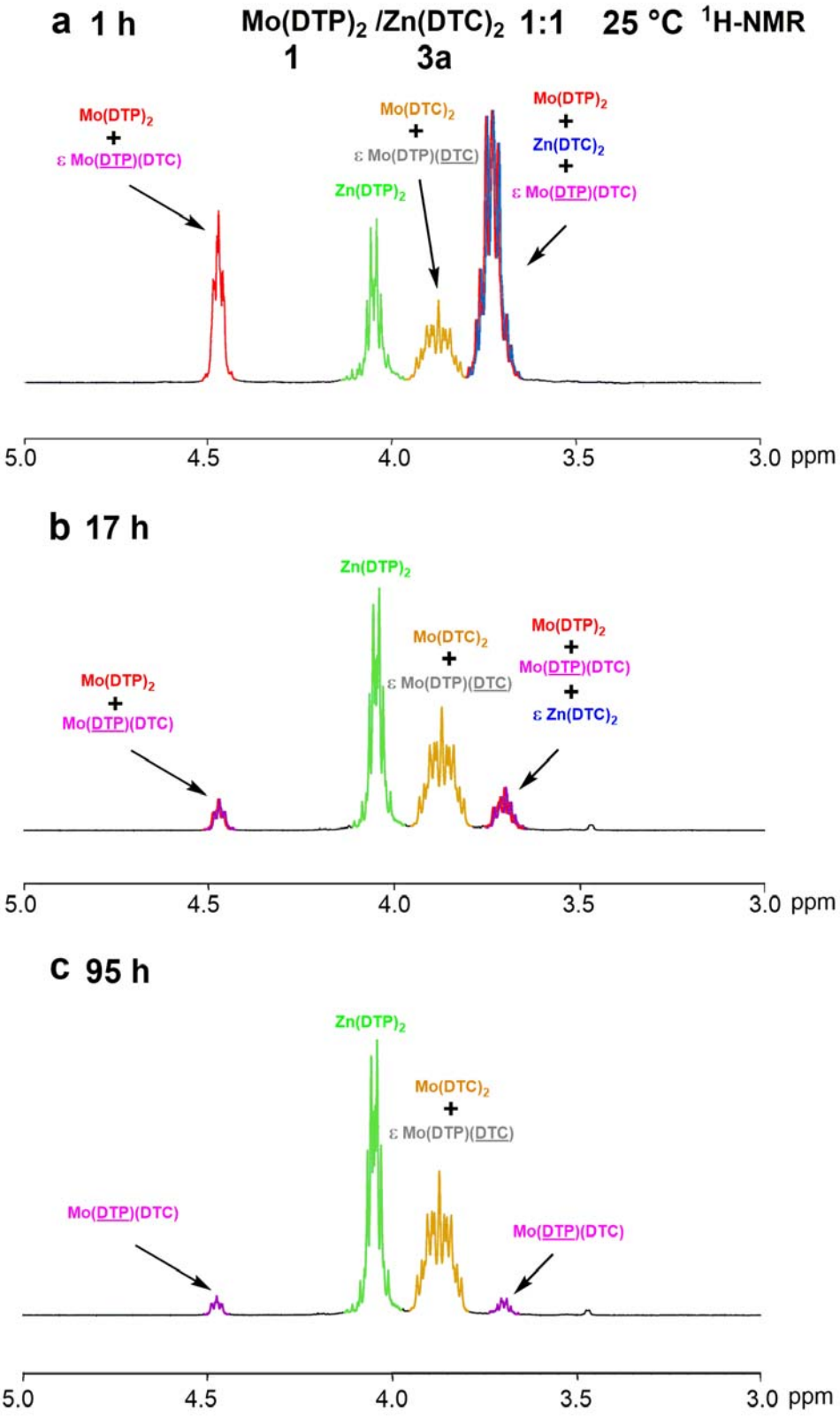

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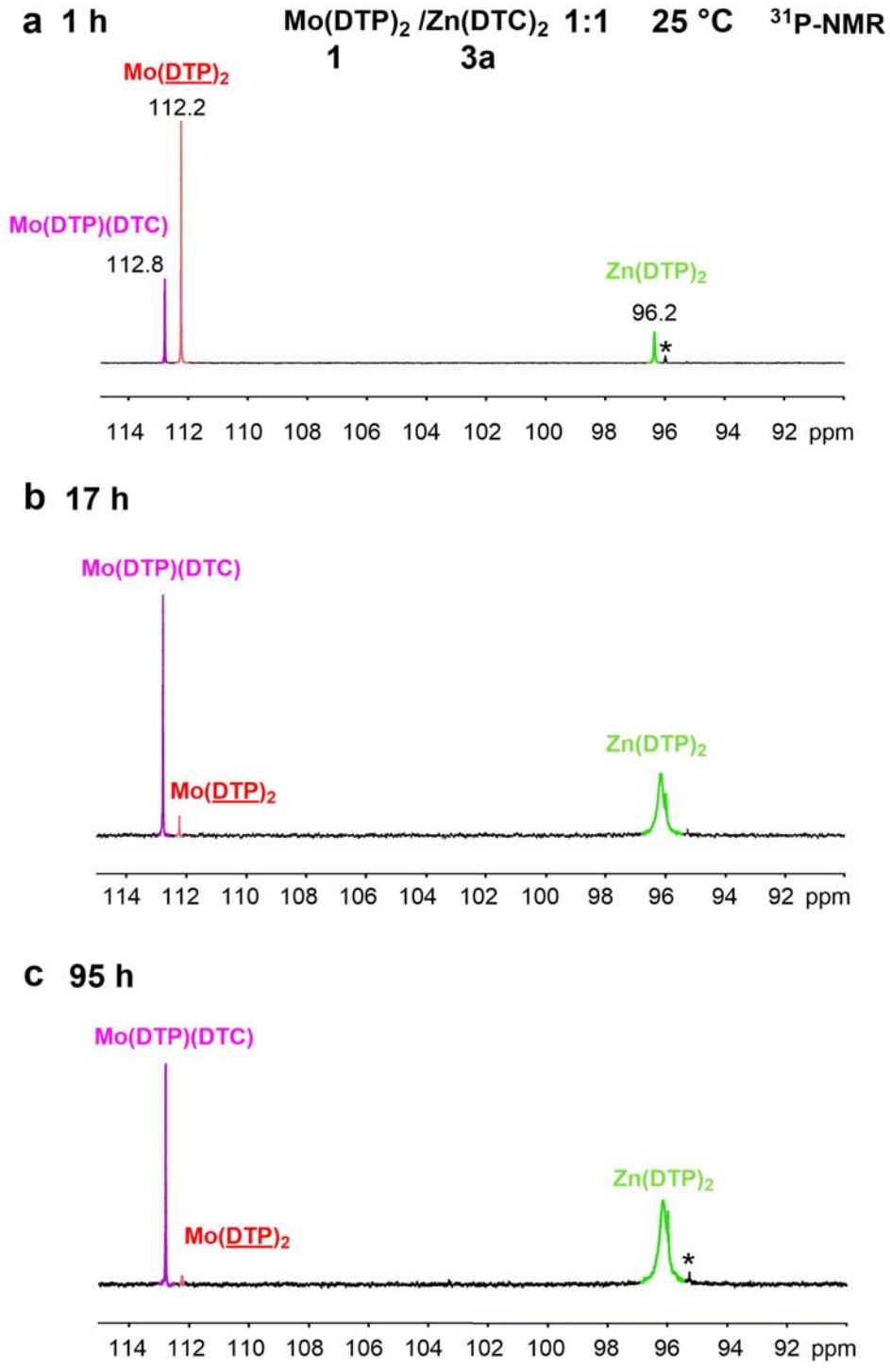

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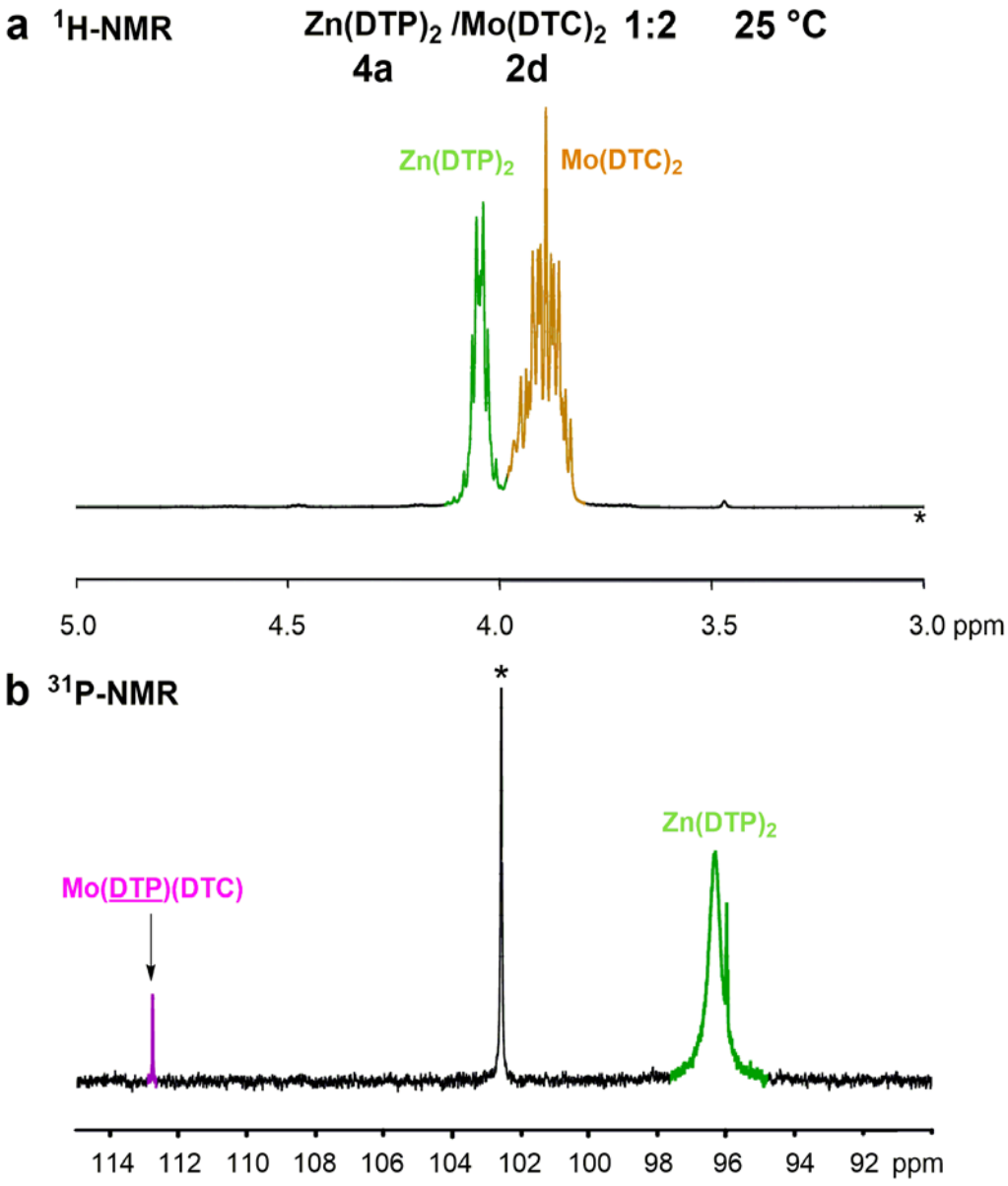

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