New Journal of Chemistry

Electronic Supplementary Information

Dithiocarbamate transfer reaction from methylene-*bis*-(dithiocarbamates) to molybdenum dithiocarbamates in engine lubricants investigated using laboratory experiments

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Supplementary Materials

Figure S1: Reference NMR spectra ($CDCl_3$) of MBDTC **3a (a)** ^{1}H-NMR spectrum (0.5-7.5 ppm, 500 MHz); **(b)** ^{13}C-NMR spectrum (0-220 ppm, 125 MHz). *****: Impurities.

Figure S2: Reference NMR spectra ($CDCl_3$) of MBDTC **3b (a)** ^{1}H-NMR spectrum (0.5-7.5 ppm, 500 MHz); **(b)** ^{13}C-NMR spectrum (0-220 ppm, 125 MHz). *****: Impurities.

Figure S3: Mass spectrum (Probe-MS, EI, 70 eV) of methylene-*bis*(di-*n*-decyl-dithiocarbamate) **3b**

Figure S4: Reference NMR spectra ($CDCl_3$) of methylene-*bis*(dithiophosphate) **4 (a)** ^{1}H-NMR spectrum (0.5-5.0 ppm, 500 MHz); **(b)** ^{13}C-NMR spectrum (0-210 ppm, 125 MHz). *****: Impurities.

Figure S5: (a) Extracted Ion Chromatogram (HPLC-MS, APPI, positive mode) and **(b)** Mass spectrum (HPLC-MS, APPI, positive mode) of methylene-*bis*(dithiophosphate) **4**

Figure S6: Mass spectrum (Probe-MS, EI, 70 eV) of methylene-*bis*(dithiophosphate) **4**

Figure S7: **(a)** Extracted Ion Chromatogram (HPLC-MS, APPI, positive mode, m/z: 804-817; 943-957) showing the distribution of MoDTC **1d** and **1e** formed in the ageing experiments involving MoDTC **1a**-**1c** (1 wt. %) and MBDTC **3a** (2 wt. %) in a hydrocarbon base oil under argon at 135 °C (Experiment 1, Table 1) after 15 h and **(b)** Mass spectrum (HPLC-MS, APPI, positive mode) of MoDTC **1d** and **1e**.

Figure S8: Visual aspect of the samples collected during the oil ageing experiment involving MoDTC **1a**-**1c** (1 wt. %), primary ZnDTP **2a** (1 wt. %) and MBDTC **3a** (2 wt. %) in a hydrocarbon base oil under argon bubbling at 135 °C (Experiment 2, Table 1) and showing the progressive formation of a yellowish precipitate.

Figure S9: Mass spectrum (Probe-MS, EI, 70 eV) obtained from the yellowish precipitate formed during the oil ageing experiment involving MoDTC **1a**-**1c** (1 wt. %), primary ZnDTP **2a** (1 wt. %) and MBDTC **3a** (2 wt. %) in a hydrocarbon base oil under argon bubbling at 135 °C

Figure S10: Evolution of the concentrations of **(a-c)** the mono-sulfurized MoDTC **1S-1d**-**1f** and **(d-f)** the di-sulfurized MoDTC **2S-1d**-**1f** during the experiments involving : (i) MoDTC **1a**-**1c** (1 wt .%), MBDTC **3a** (2 wt. %) and secondary ZnDTP **2b** (1 wt. %), (blue color; Experiment 3, Table 1) and (ii) MoDTC **1a**-**1c** (1 wt. %), MBDTC **3a** (2 wt. %) and primary ZnDTP **2a** (1 wt. %), (red color; Experiment 2, Table 1) in a lubricant base oil under argon bubbling at 135 °C. IS: internal standard. *Y-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses of each sample.

Figure S11: Evolution with time of the percentage of sulfurized MoDTC (sum of **1S-1d**-**1f** and **2S-1d**-**1f**) relative to the total (regular + sulfurized) MoDTC (sum of **1a**-**1f**, **1S-1a**-**1f** and **2S-1a**-**1f**) during the experiment involving : (i) MoDTC **1a**-**1c** (1 wt. %), MBDTC **3a** (2 wt. %) and secondary ZnDTP **2b** (1 wt. %), (blue color; Experiment 3, Table 1) and (ii) MoDTC **1a**-**1c** (1 wt. %), MBDTC **3a** (2 wt. %) and primary ZnDTP **2a** (1 wt. %), (red color; Experiment 2, Table 1) in a lubricant base oil under argon bubbling at 135 °C.

Figure S12: (a-c) Extracted Ion Chromatogram (HPLC-MS, APPI) showing the distribution of residual MoDTC **1a**-**1c** and **(g-i)** their corresponding mass spectra; **(d-f)** Extracted Ion Chromatogram (HPLC-MS, APPI) showing the distributions of MoDTC **1g**-**1i** and **(j-l)** their corresponding mass spectra formed after 18 h in the oil ageing experiment involving MoDTC **1a**-**1c** (1 wt. %), MBDTC **3b** (2 wt. %) and primary ZnDTP **2a** (1 wt. %) in a hydrocarbon base oil under argon bubbling at 135 °C (Experiment 4, Table 1).

Figure S13: Visual aspect of the samples collected during the oil ageing experiment involving MoDTC **1a**-**1c** (1 wt. %)**,** MBDTC **3b** (2 wt. %) and primary ZnDTP **2a** (1 wt. %) in a hydrocarbon base oil under argon bubbling at 135 °C (Experiment 4, Table 1) and showing the absence of precipitate.

Figure S14: (a-g) Extracted Ion Chromatogram (HPLC-MS, APPI) showing the distribution of newly-formed MoDTC bearing ligands with C_4 and/or C_{10} alkyl chains and **(h-n)** their corresponding mass spectra after 18 h of the oil ageing experiment involving MoDTC **1a**-**1c** (1 wt. %), MBDTC **3a** (2 wt. %) and ZnDTC **5a** (1 wt. %) in a hydrocarbon base oil under argon bubbling at 135 °C (Experiment 5, Table 1).

Figure S15: Partial phosphorus-decoupled ^{1}H-NMR spectrum (3.0–5.5 ppm, 500 MHz, $CDCl_3$) of the reference additive MBDTP **4**. *: Impurities

Figure S1: Reference NMR spectra ($CDCl_3$) of MBDTC **3a** **(a)** ^{1}H-NMR spectrum (0.5-7.5 ppm, 500 MHz); **(b)** ^{13}C-NMR spectrum (0-220 ppm, 125 MHz). *: Impurities.

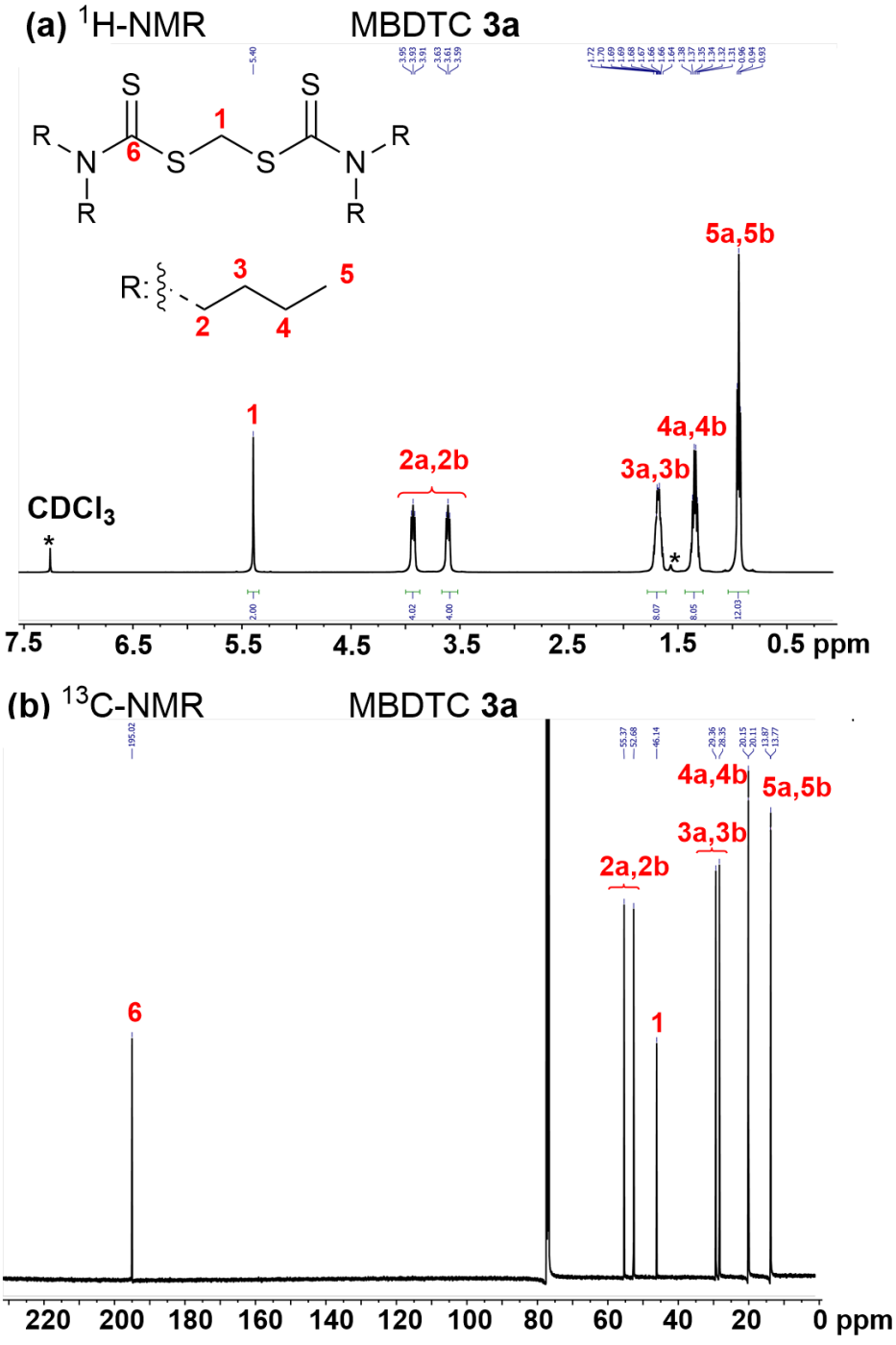


Figure S2: Reference NMR spectra ($CDCl_3$) of MBDTC **3b (a)** ^{1}H-NMR spectrum (0.5-7.5 ppm, 500 MHz); **(b)** ^{13}C-NMR spectrum (0-220 ppm, 125 MHz). *: Impurities.

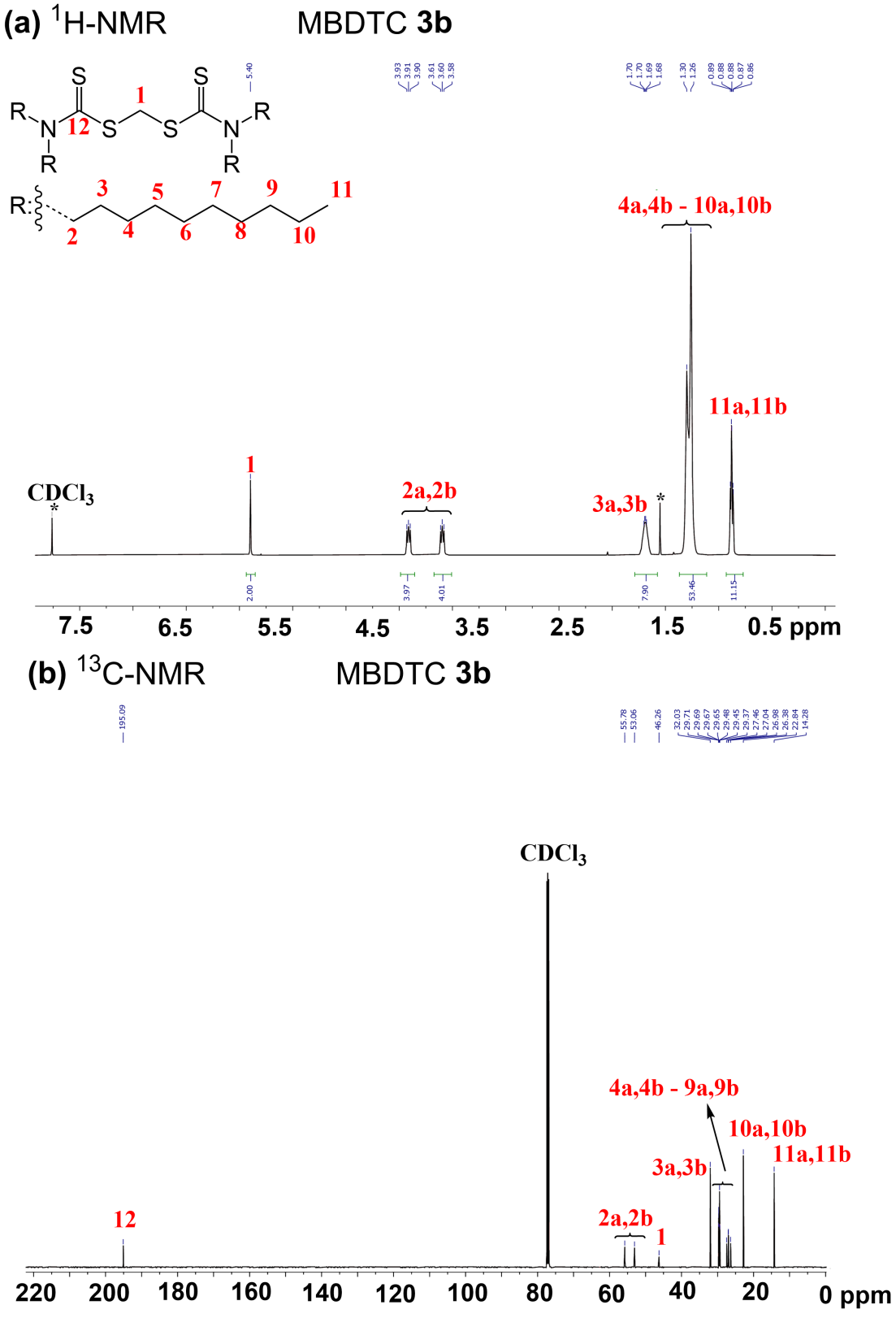


Figure S3: Mass spectrum (Probe-MS, EI, 70 eV) of methylene-*bis*(di-*n*-decyl-dithiocarbamate) **3b**

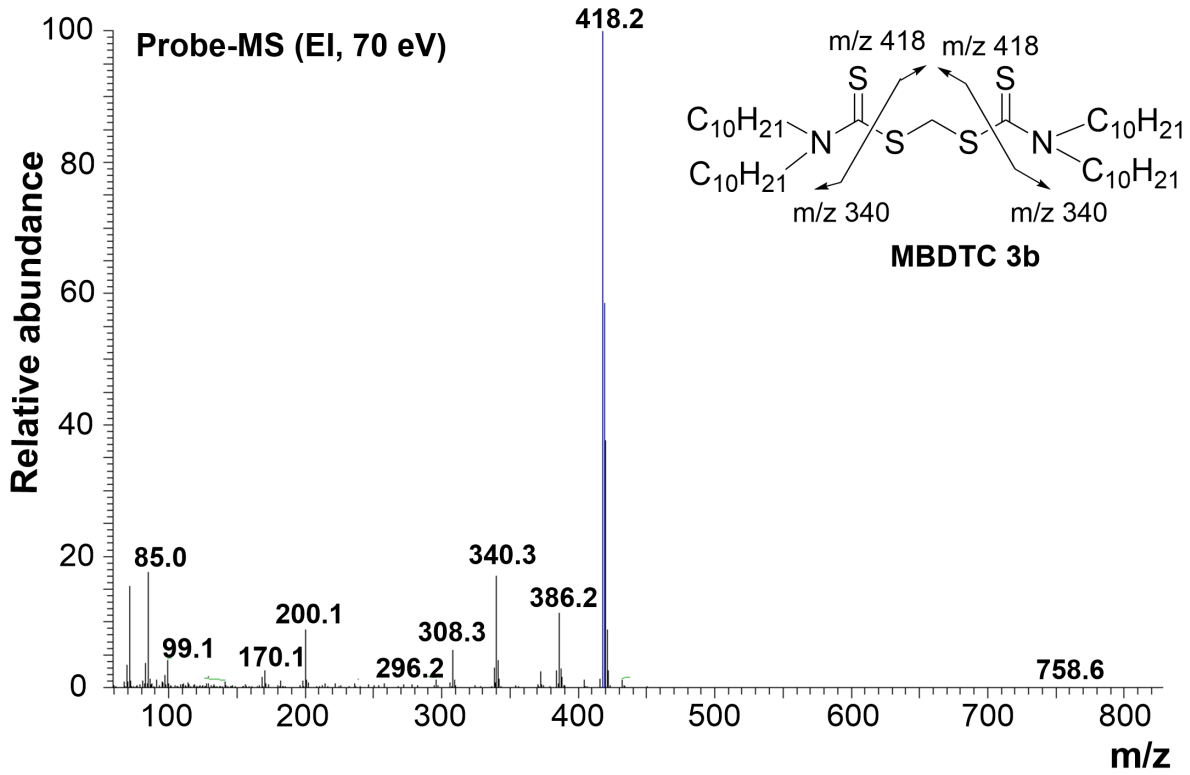


Figure S4: Reference NMR spectra ($CDCl_3$) of methylene-*bis*(dithiophosphate) **4 (a)** ^{1}H-NMR spectrum (0.5-5.0 ppm, 500 MHz); **(b)** ^{13}C-NMR spectrum (0-210 ppm, 125 MHz). *****: Impurities.

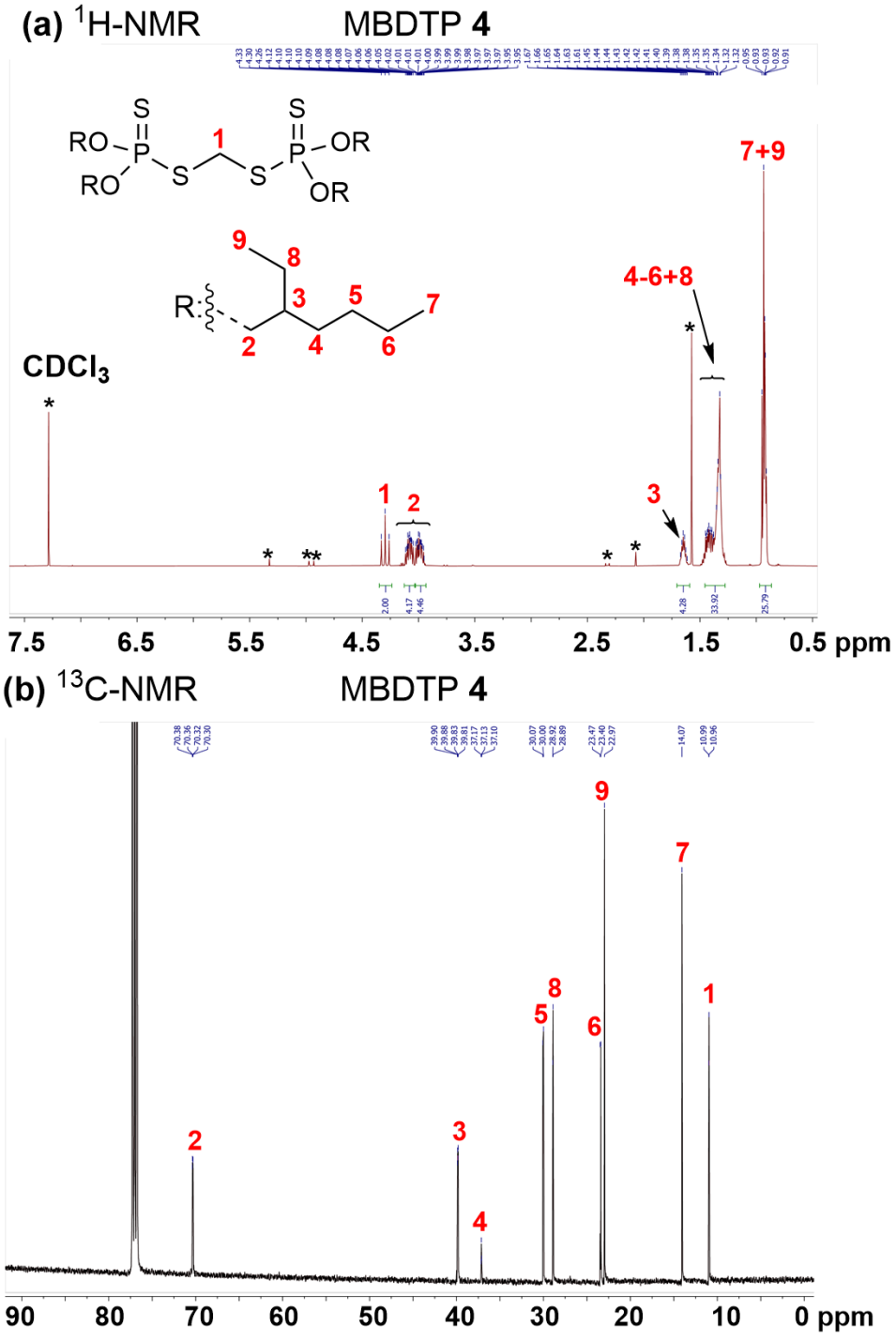


Figure S5: (a) Extracted Ion Chromatogram (HPLC-MS, APPI, positive mode) and **(b)** Mass spectrum (HPLC-MS, APPI, positive mode) of methylene-*bis*(dithiophosphate) **4**

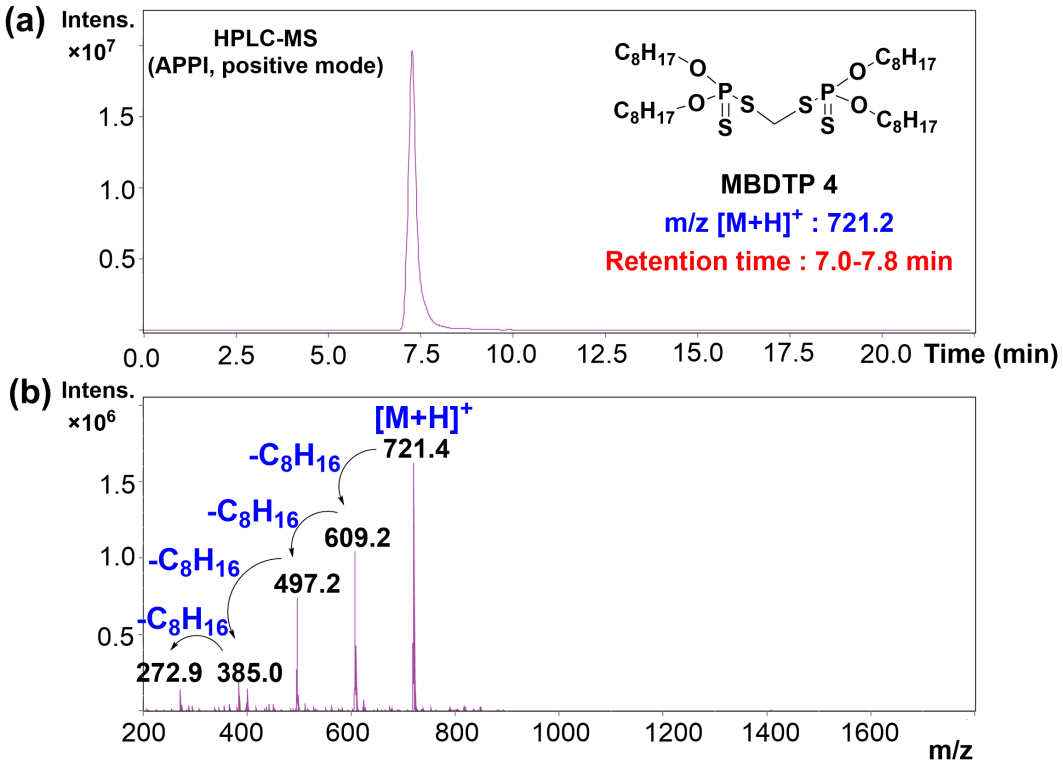


Figure S6: Mass spectrum (Probe-MS, EI, 70 eV) of methylene-*bis*(dithiophosphate) **4**

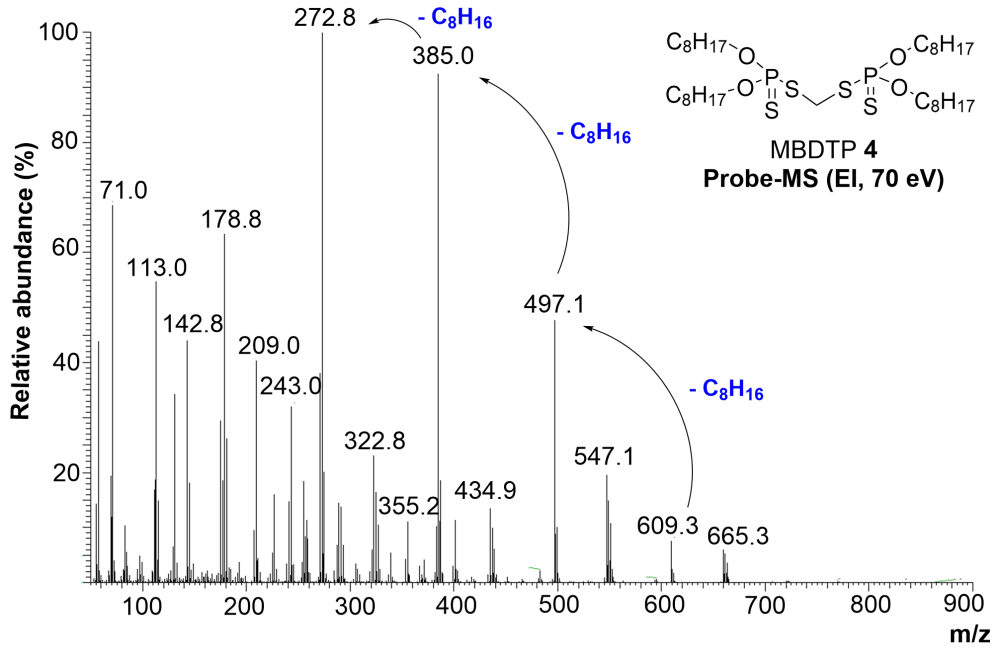


Figure S7: **(a)** Extracted Ion Chromatogram (HPLC-MS, APPI, positive mode, *m/z*: 804-817; 943-957) showing the distribution of MoDTC **1d** and **1e** formed in the ageing experiments involving MoDTC **1a**-**1c** (1 wt. %) and MBDTC **3a** (2 wt. %) in a hydrocarbon base oil under argon at 135 °C (Experiment 1, Table 1) after 15 h and **(b)** Mass spectrum (HPLC-MS, APPI, positive mode) of MoDTC **1d** and **1e**.

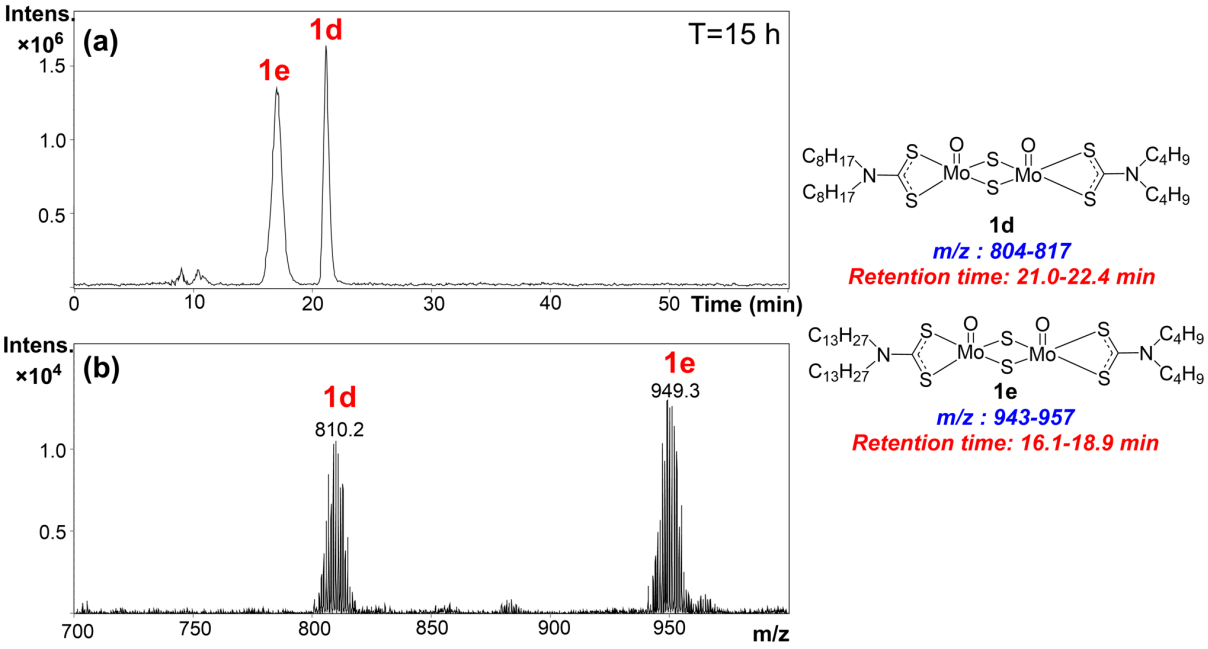


Figure S8: Visual aspect of the samples collected during the oil ageing experiment involving MoDTC **1a**-**1c** (1 wt. %), primary ZnDTP **2a** (1 wt. %) and MBDTC **3a** (2 wt. %) in a hydrocarbon base oil under argon bubbling at 135 °C (Experiment 2, Table 1) showing the progressive formation of a yellowish precipitate.

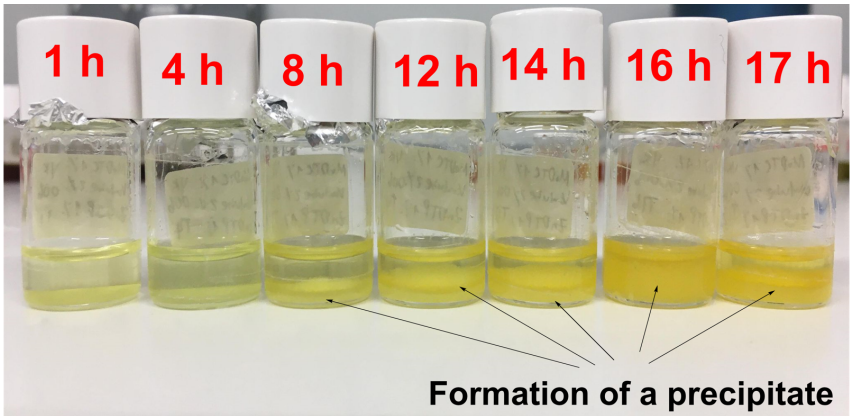
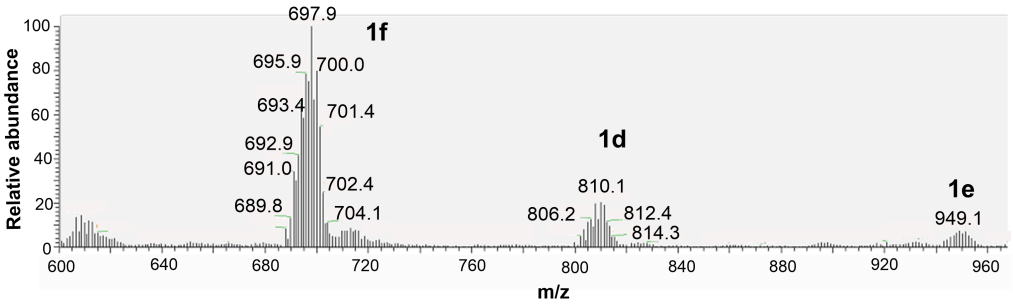
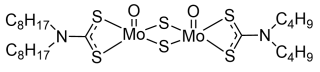


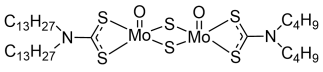
Figure S9: Mass spectrum (Probe-MS, EI, 70 eV) obtained from the yellowish precipitate formed during the oil ageing experiment involving MoDTC **1a**-**1c** (1 wt. %), primary ZnDTP **2a** (1 wt. %) and MBDTC **3a** (2 wt. %) in a hydrocarbon base oil under argon bubbling at 135 °C



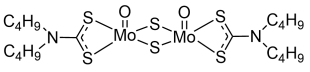
Probe-MS (EI, 70eV) : m/z (relative intensity) 693-700 (M^+, 100%), 943-957 (10), 804-817 (21)



1d
m/z : 804-817

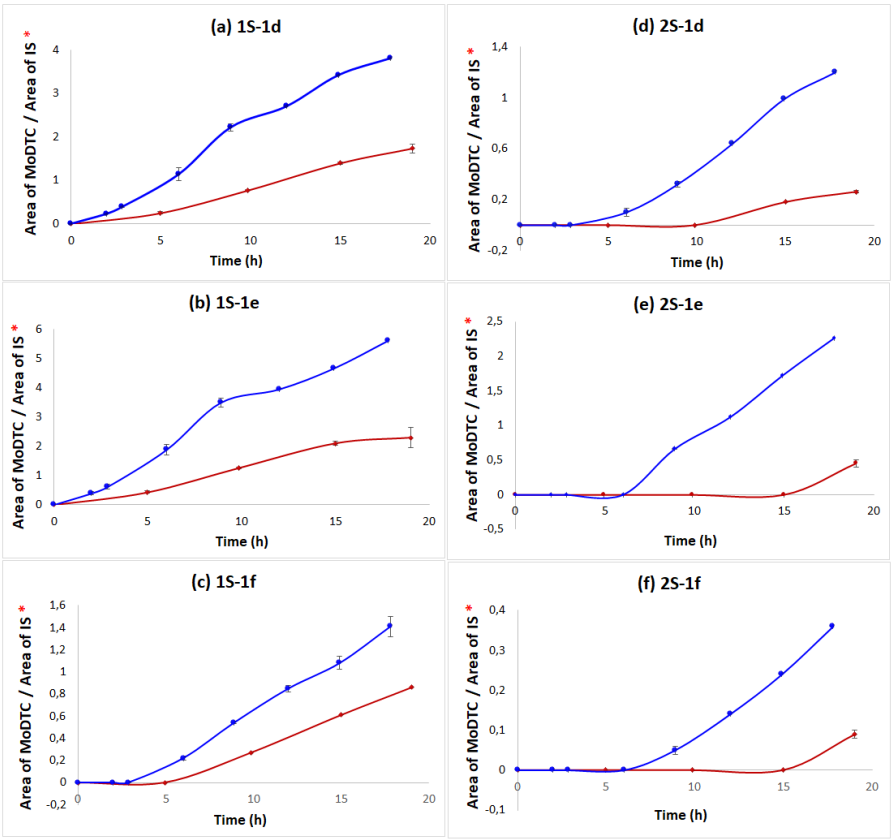


1e
m/z : 943-957



1f
m/z : 693-700

Figure S10: Evolution of the concentrations of **(a-c)** the mono-sulfurized MoDTC **1S-1d**-**1f** and **(d-f)** the di-sulfurized MoDTC **2S-1d**-**1f** during the experiments involving : (i) MoDTC **1a**-**1c** (1 wt .%), MBDTC **3a** (2 wt. %) and secondary ZnDTP **2b** (1 wt. %) (blue color; Experiment 3, Table 1) and (ii) MoDTC **1a**-**1c** (1 wt. %), MBDTC **3a** (2 wt. %) and primary ZnDTP **2a** (1 wt. %), (red color; Experiment 2, Table 1) in a lubricant base oil under argon bubbling at 135 °C. IS: internal standard. *Y-axis: arbitrary units. Error bars correspond to triplicate HPLC-MS analyses of each sample.



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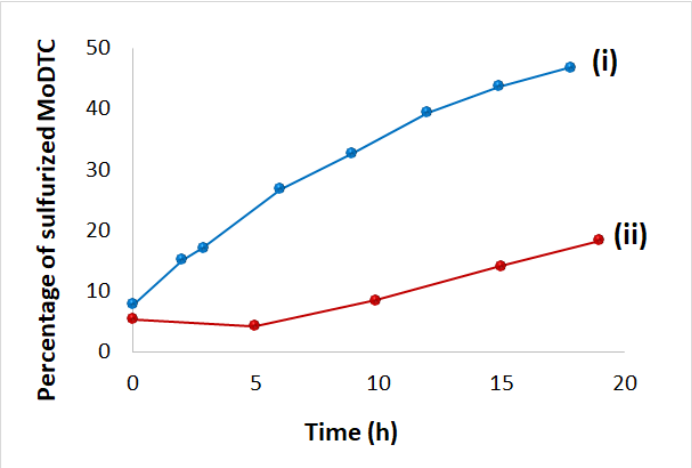

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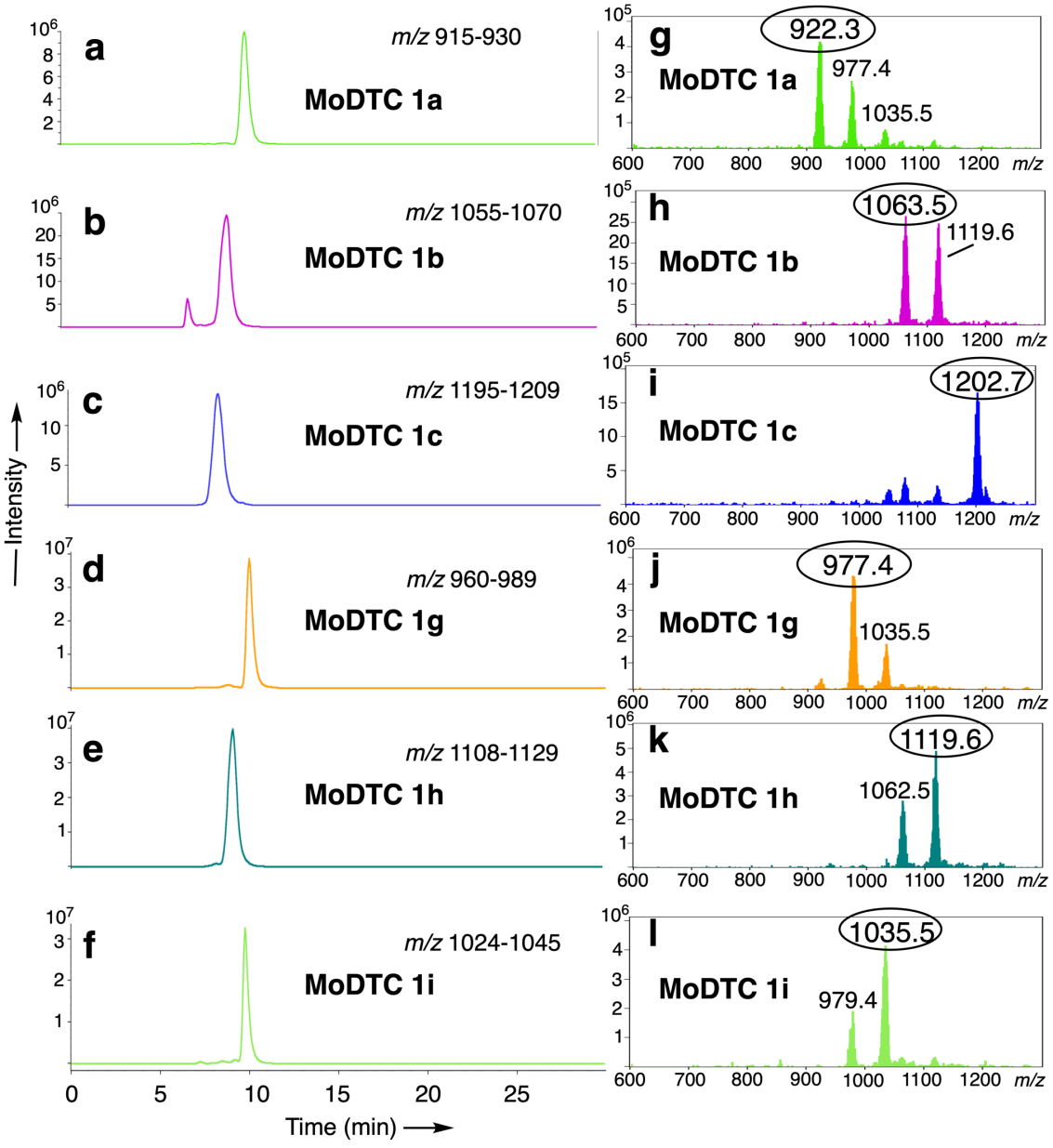

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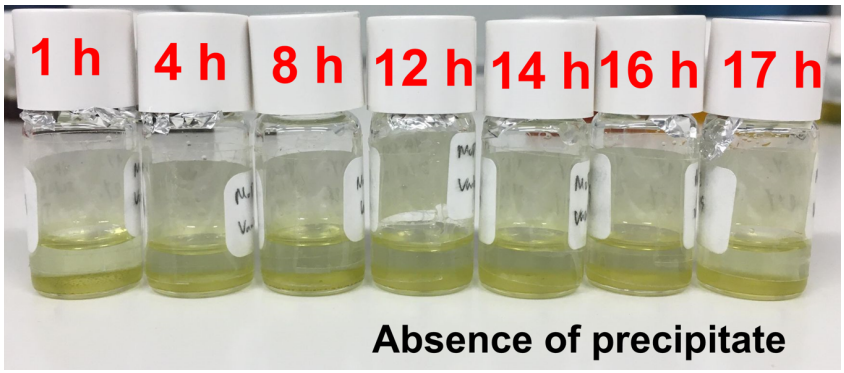

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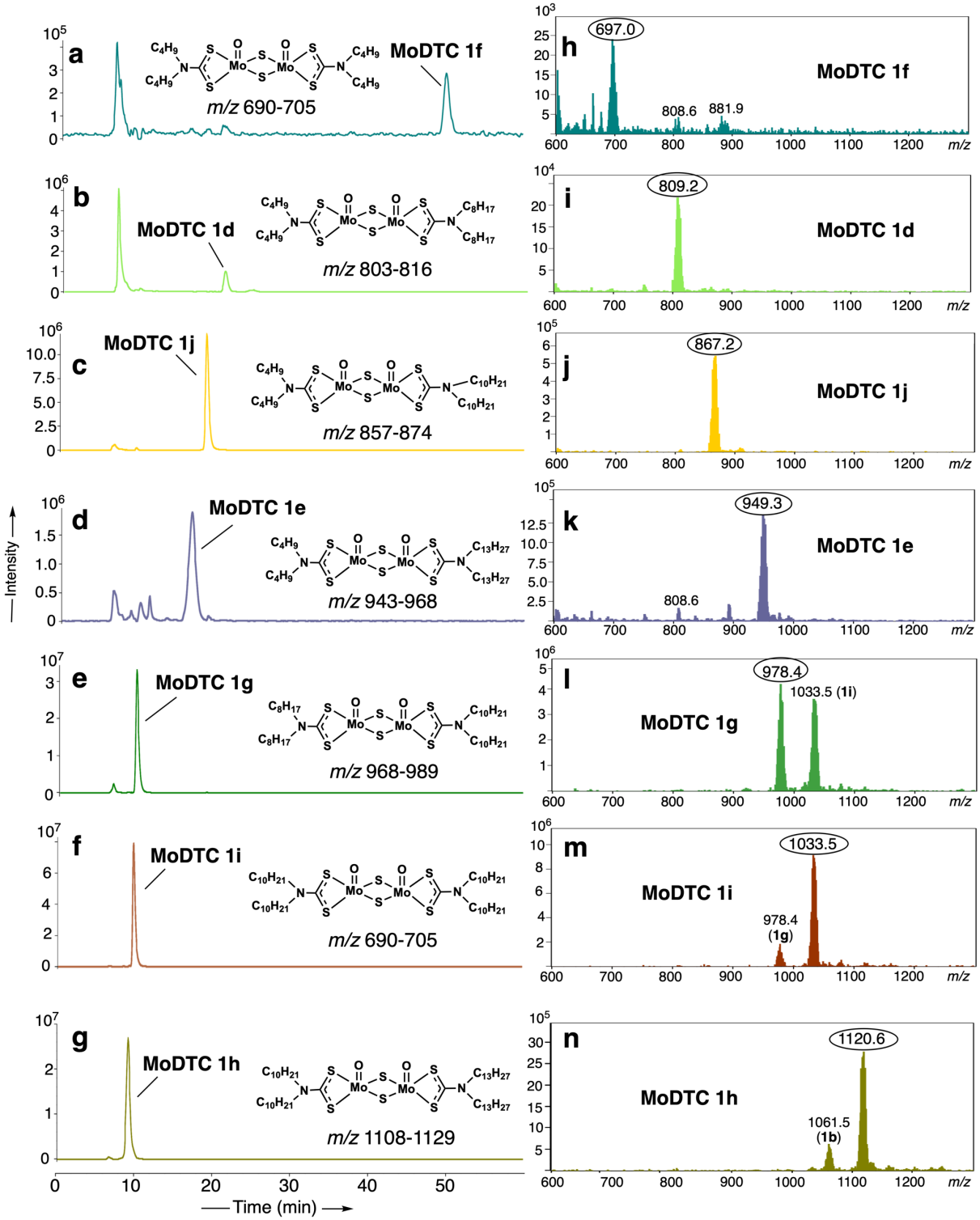

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