Electronic Supplementary Material (ESI) for Dalton Transactions
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Supporting Information

Asymmetric Zinc(II) Complexes as Functional and Structural Models for Phosphoesterases

Lena J. Daumann, Laurene Marty, Gerhard Schenk, and Lawrence R. Gahan

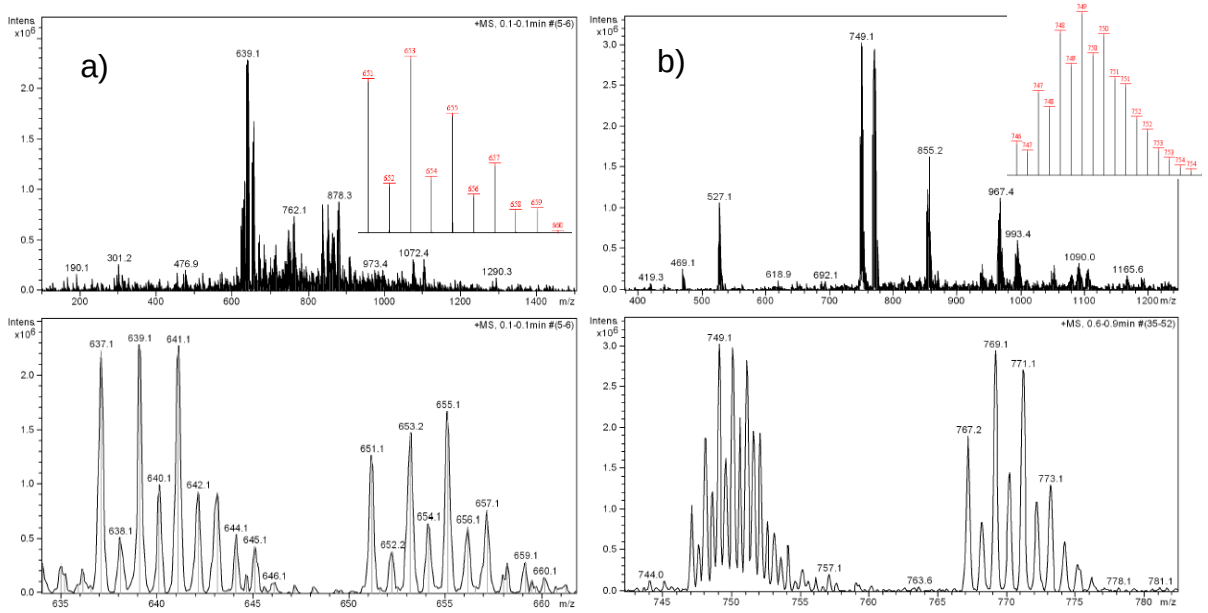

Figure S1. Mass spectrum of $[Zn_2(CH_3\mathbf{L4})(CH_3COO)_2]PF_6$ in MeOH (a) and MeCN (b). Inset with red numbers shows the calculated isotope pattern for the major (identified) ion peak.

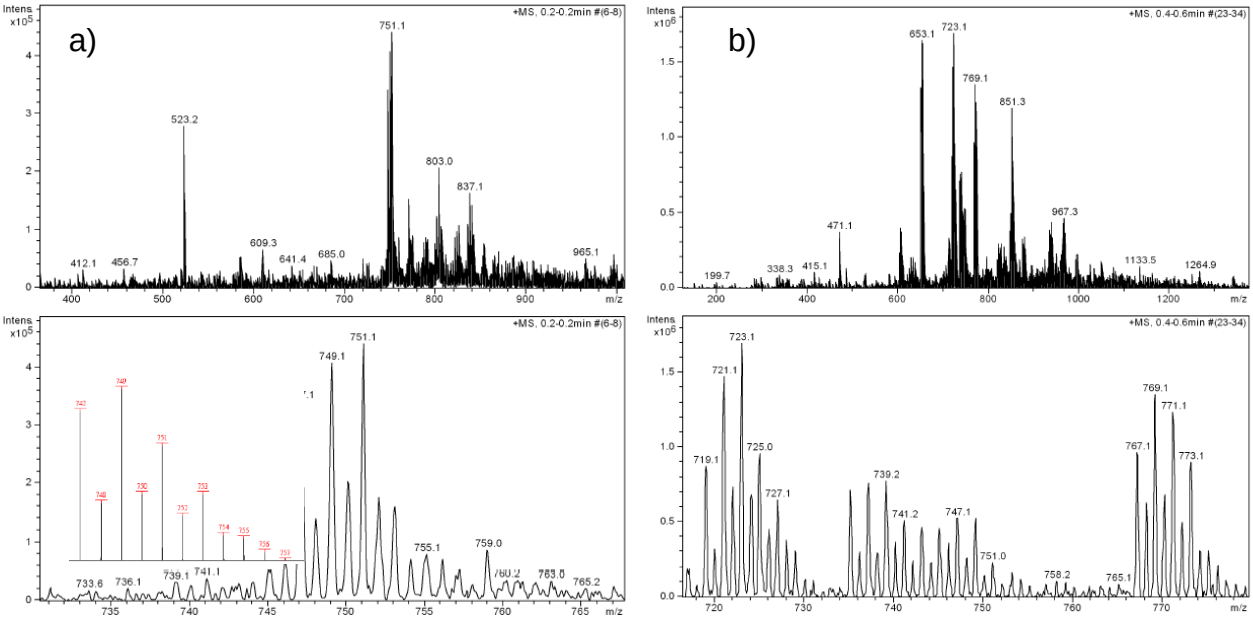

Figure S2 Mass spectrum of $[Zn_2(CH_3\mathbf{L5})(CH_3COO)_2]PF_6$ in MeOH (a) and MeCN (b). Inset with red numbers shows the calculated isotope pattern for the major peak.

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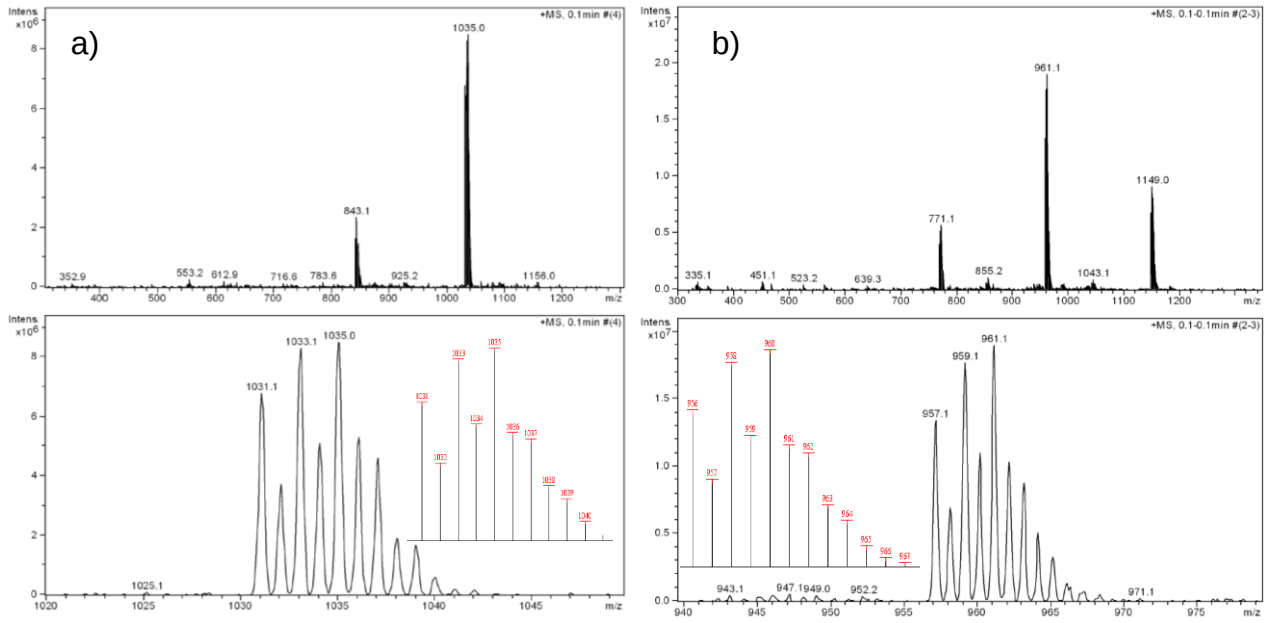

Figure S3 a) Mass spectrum of $[Zn_2(CH_3\mathbf{L4})(CH_3COO)_2]PF_6$ in the presence of 1 eq. diphenylphosphate in MeCN. Final concentration of complex and substrate were both 10 µM. b) Mass spectrum of $[Zn_2(CH_3\mathbf{L5})(CH_3COO)_2]PF_6$ in the presence of 1 eq. diphenylphosphate in MeCN. Final concentration of complex and substrate were both 10 µM.

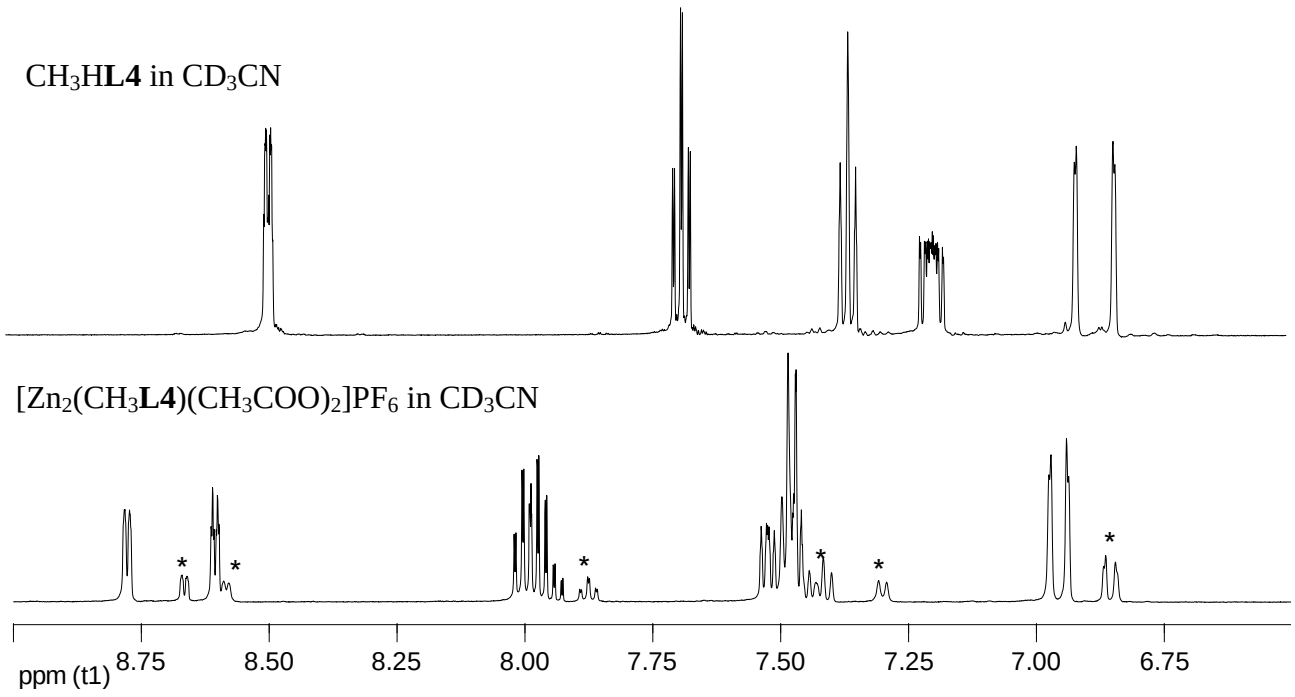

Figure S4 Aromatic region of $CH_3H\mathbf{L4}$ and its zinc complex.

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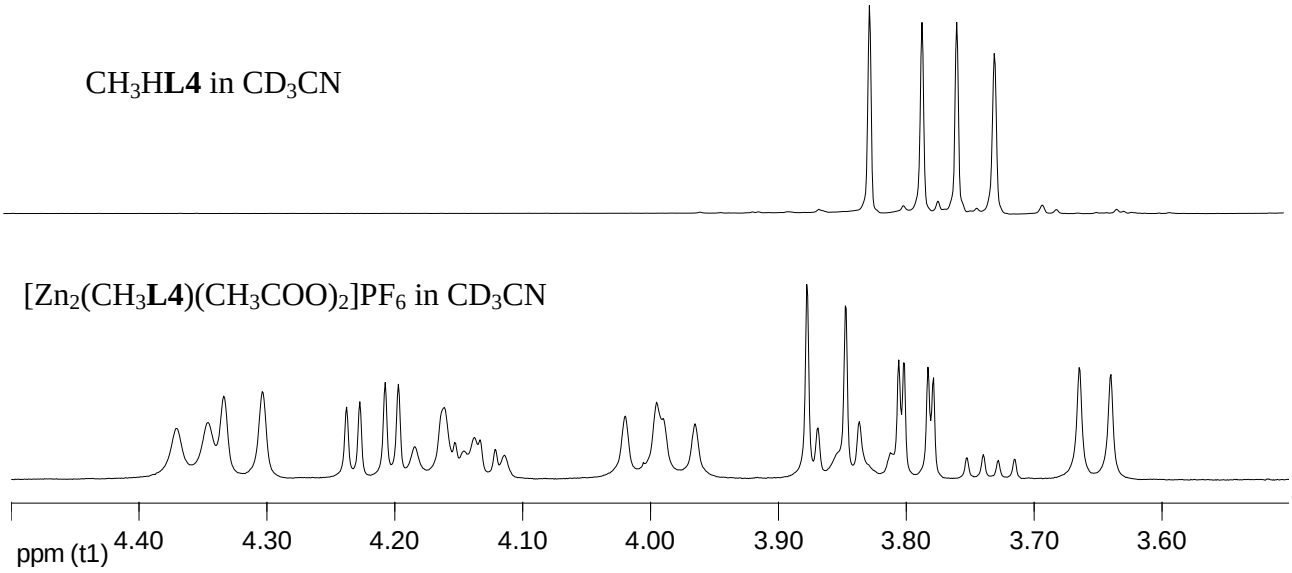

Figure S5 Aliphatic region of CH_3H**L4** and its zinc complex.

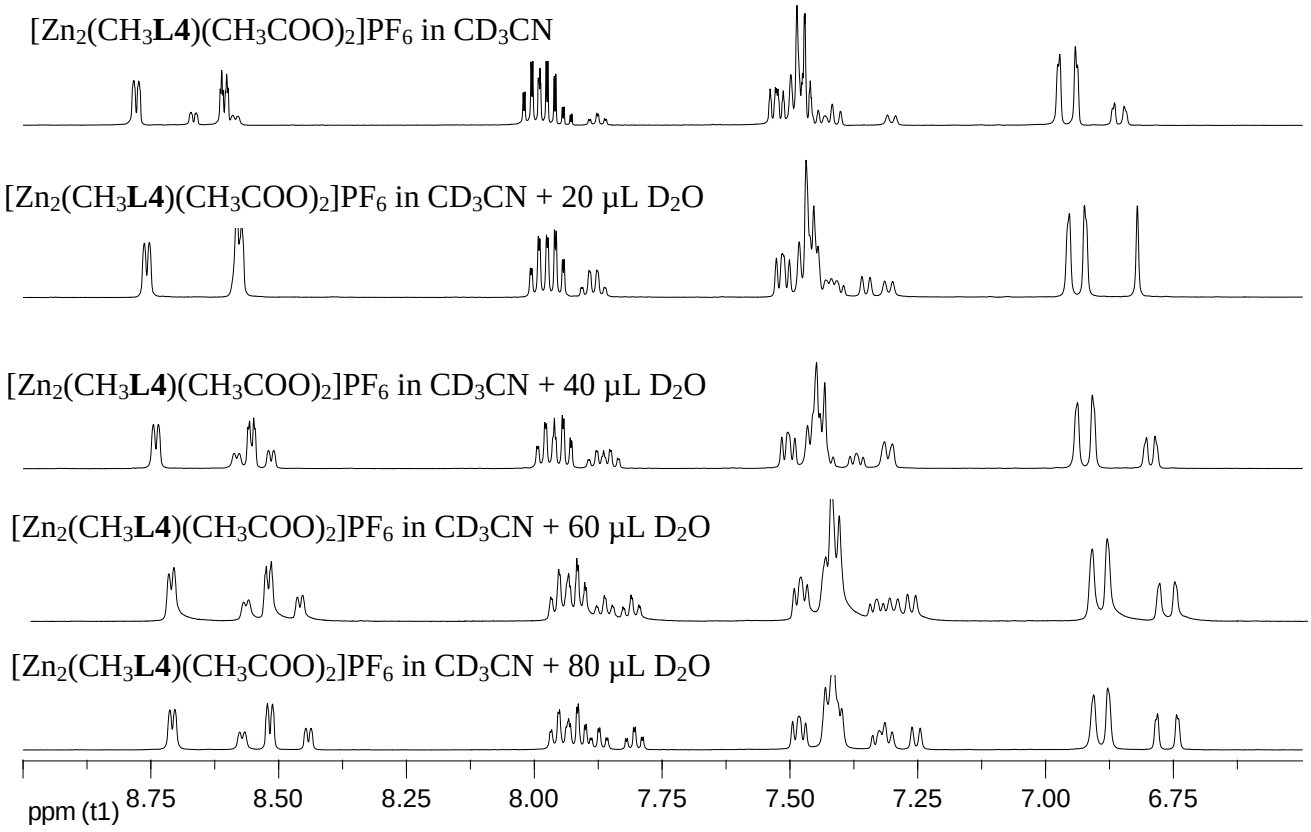

Figure S6 D_2O titration experiment for the complex $[Zn_2(CH_3L4)(CH_3COO)_2]PF_6$

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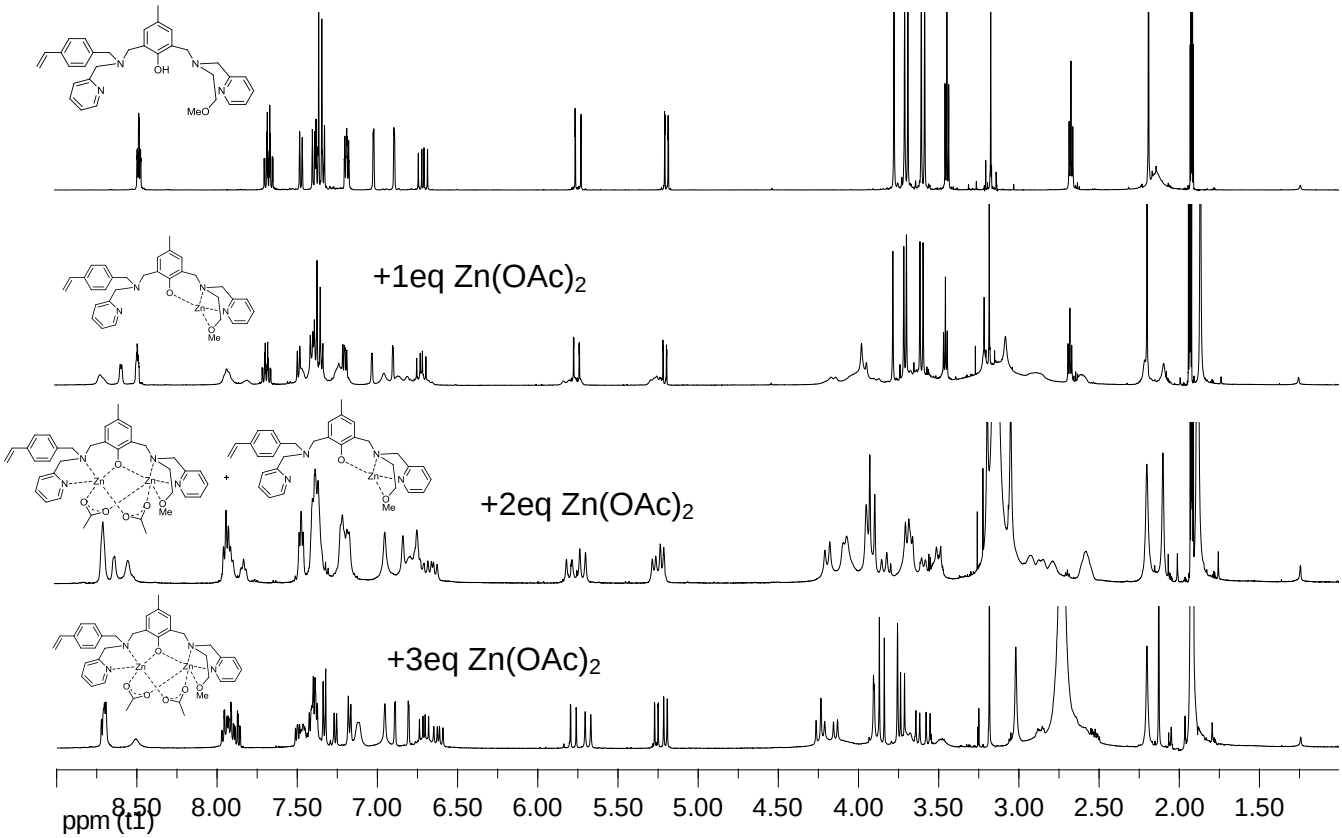

Figure S7 ^{1}H-NMR titration of $Zn(OAc)_2 4H_2O$ into the CH_3H**L5** ligand in CD_3CN and proposed species.

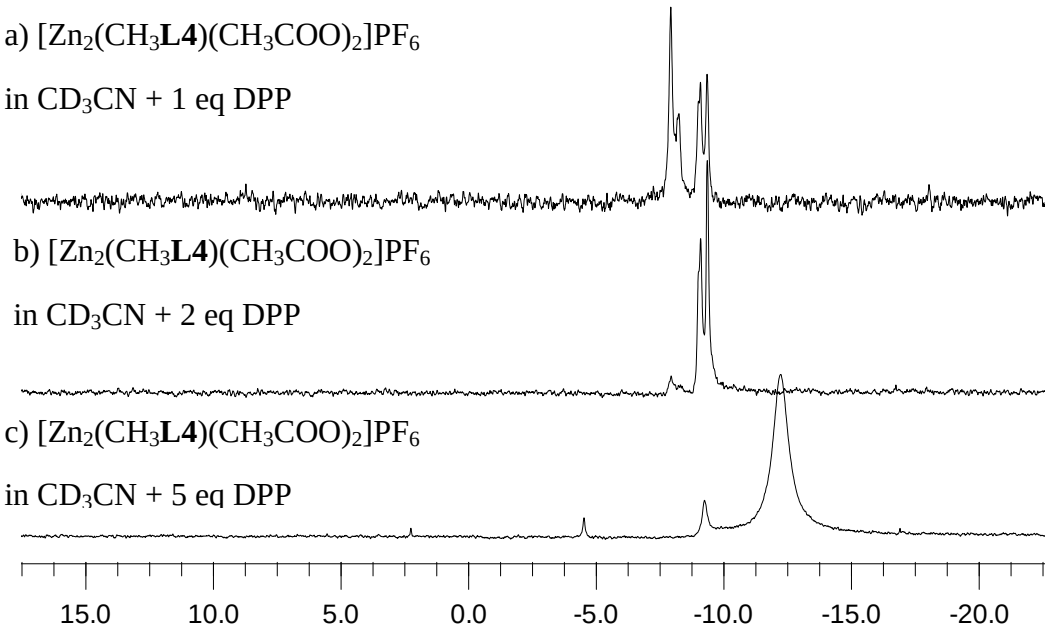

Figure S8 ^{31}P-NMR spectra of $[Zn_2(CH_3$**L4**$)(CH_3COO)_2]PF_6$ measured in CD_3CN in the presence of a) one equivalent DPP, b) two equivalents DPP and c) five equivalents DPP.

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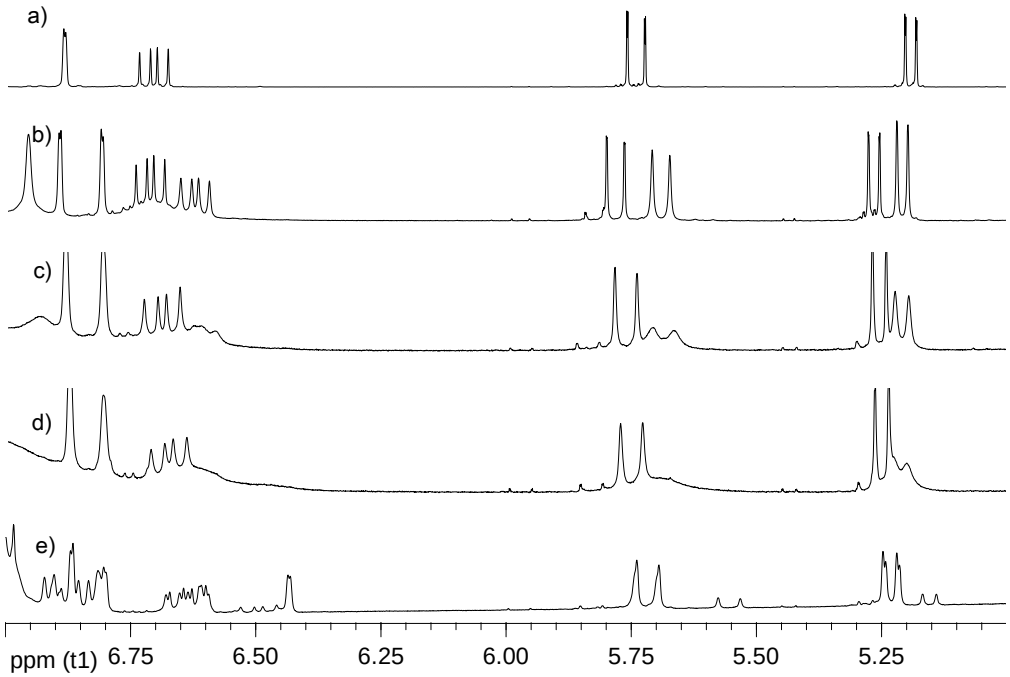

Figure S9 The ^{1}H-NMR spectrum of a) CH_3HL5; b) $[Zn_2(CH_3\mathbf{L5})(CH_3OO)_2]^+$ and c) $[Zn_2(CH_3\mathbf{L5})(CH_3OO)_2]^+$ + 1 equivalent DPP; d) $[Zn_2(CH_3\mathbf{L5})(CH_3OO)_2]^+$ + 2 equivalents DPP; e) $[Zn_2(CH_3\mathbf{L5})(CH_3OO)_2]^+$ + 5 equivalents DPP

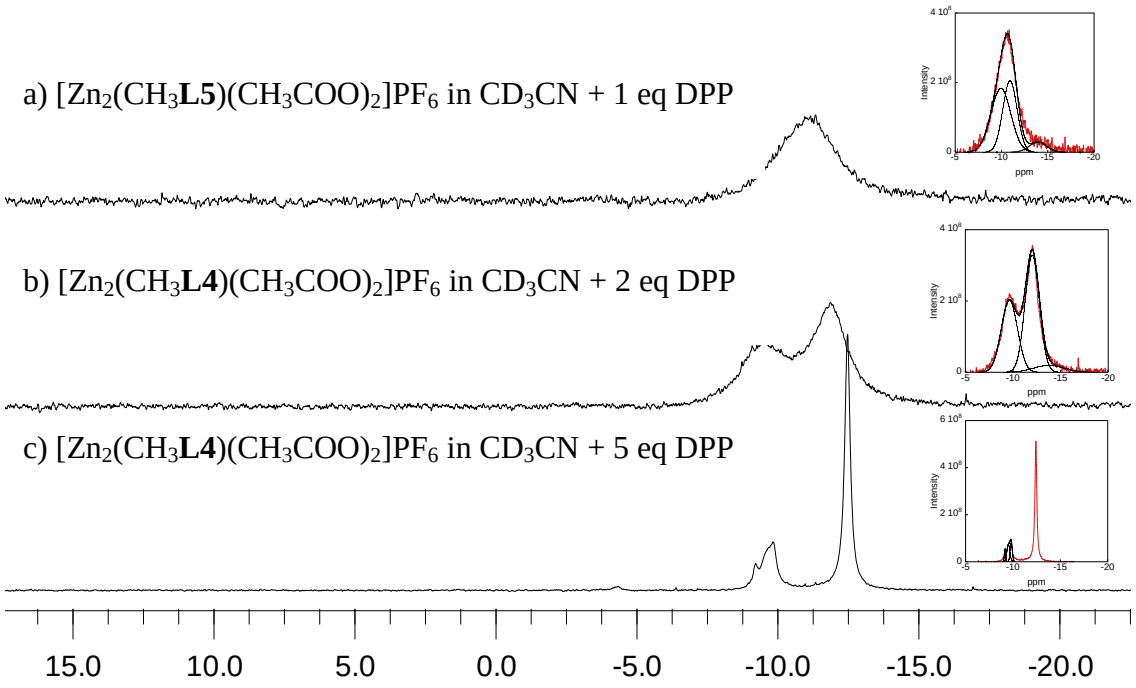

Figure S10 ^{31}P-NMR spectra of $[Zn_2(CH_3\mathbf{L5})(CH_3OO)_2]^+$ in CD_3CN the presence of a) 1 equivalent DPP, b) 2 equivalents DPP c) 5 equivalents DPP at room temperature.

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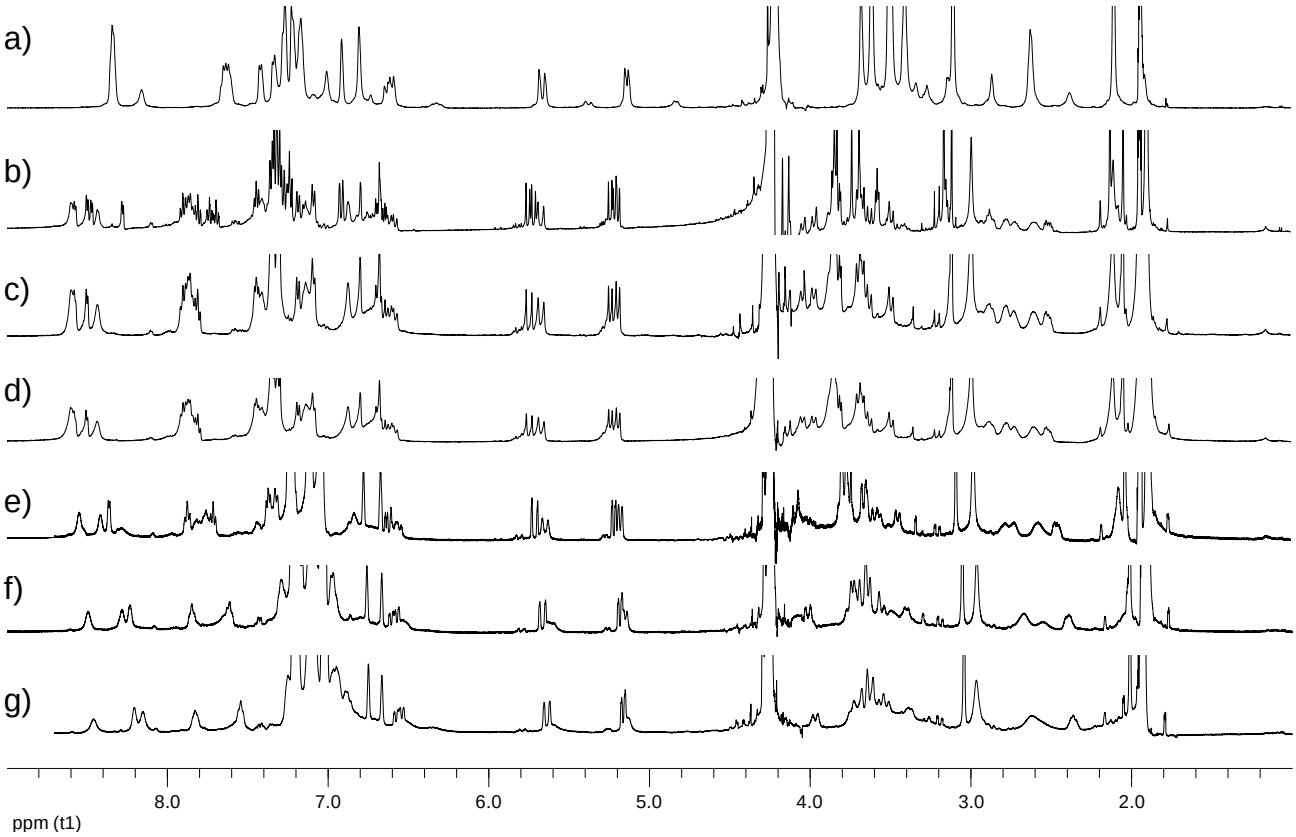

Figure S11 The ^{1}H-NMR spectrum in D_2O:CD_3CN (1:1) of a) CH_3HL5; b) CH_3HL5 + 1 eq. $Zn(OAc)_2$; c) CH_3HL5 + 2 eq. $Zn(OAc)_2$; d) CH_3HL5 + 3 eq. $Zn(OAc)_2$; e) CH_3HL5 + 3 eq. $Zn(OAc)_2$; + 1 eq. DPP; f) CH_3HL5 + 3 eq. $Zn(OAc)_2$; + 2 eq. DPP; g) [CH_3HL5 + 3 eq. $Zn(OAc)_2$; + 3 eq. DPP.

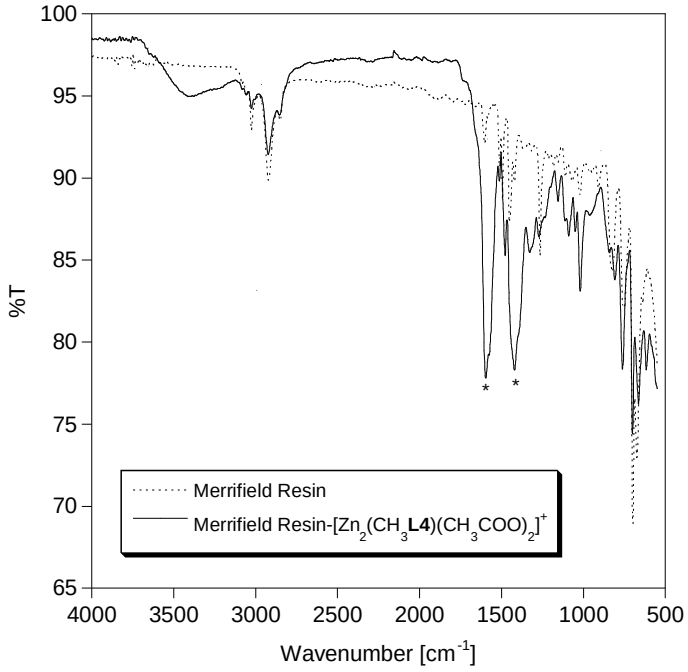

Figure S12 IR spectra of plain MR and $[Zn_2(CH3\mathbf{L4})(CH_3COO)_2]^+$ immobilized on MR

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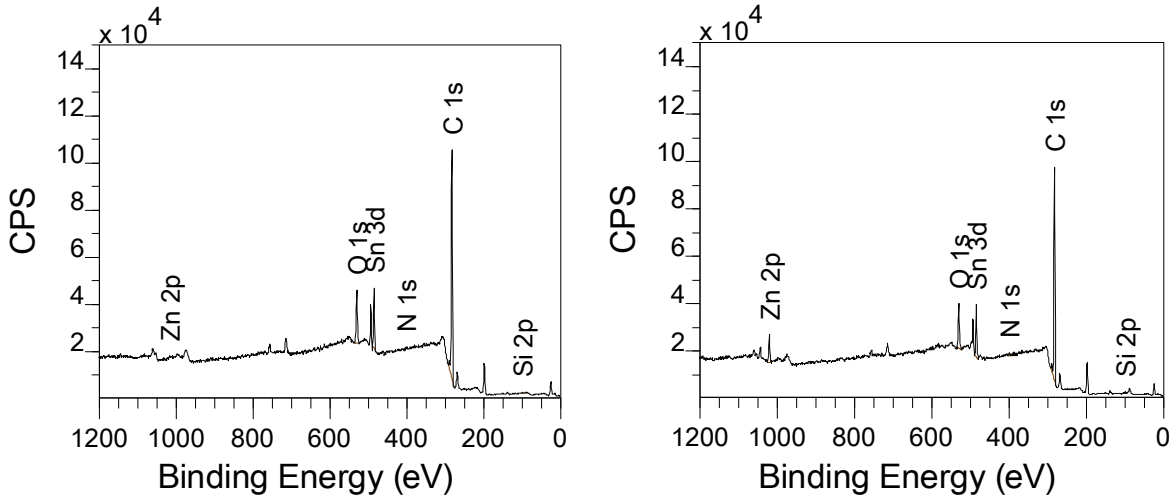

Figure S13 XPS survey spectra of MR (left) and MR treated with $Zn(CH_3COO)_2$ (right)

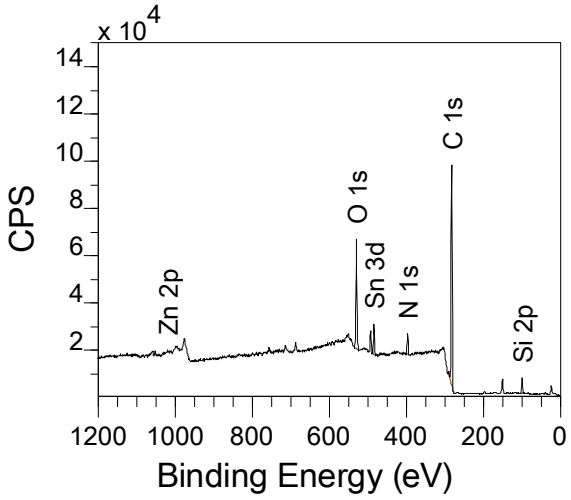

Figure S14 XPS survey spectrum of MR-CH_3H**L4**