Supplementary Information

Heterometallic $Co^{III}Zn^{II}$ Schiff base catalyst for mild hydroxylation of $C(sp^3)$–H bonds of unactivated alkanes: evidence for dual mechanism controlled by the promoter

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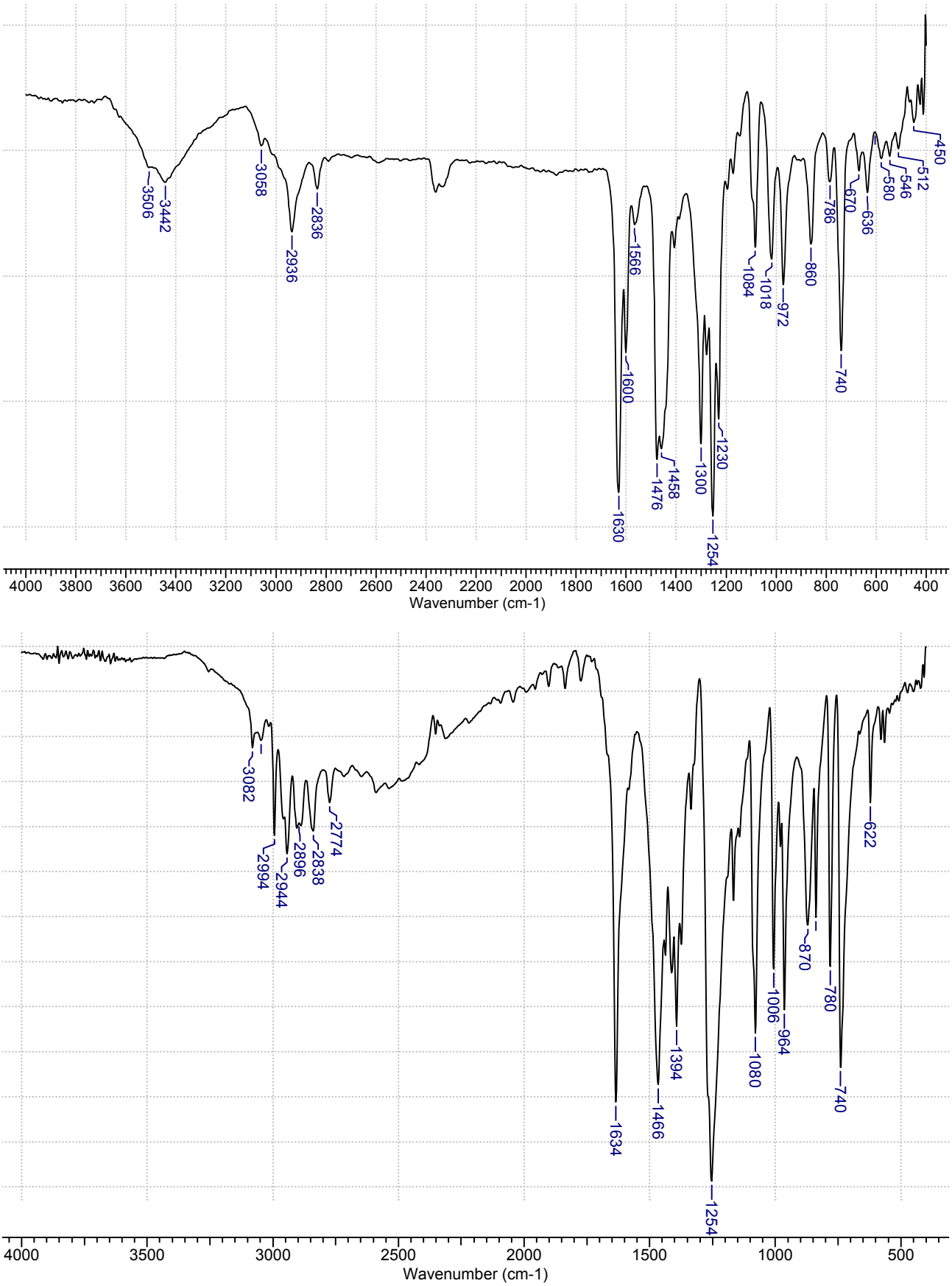
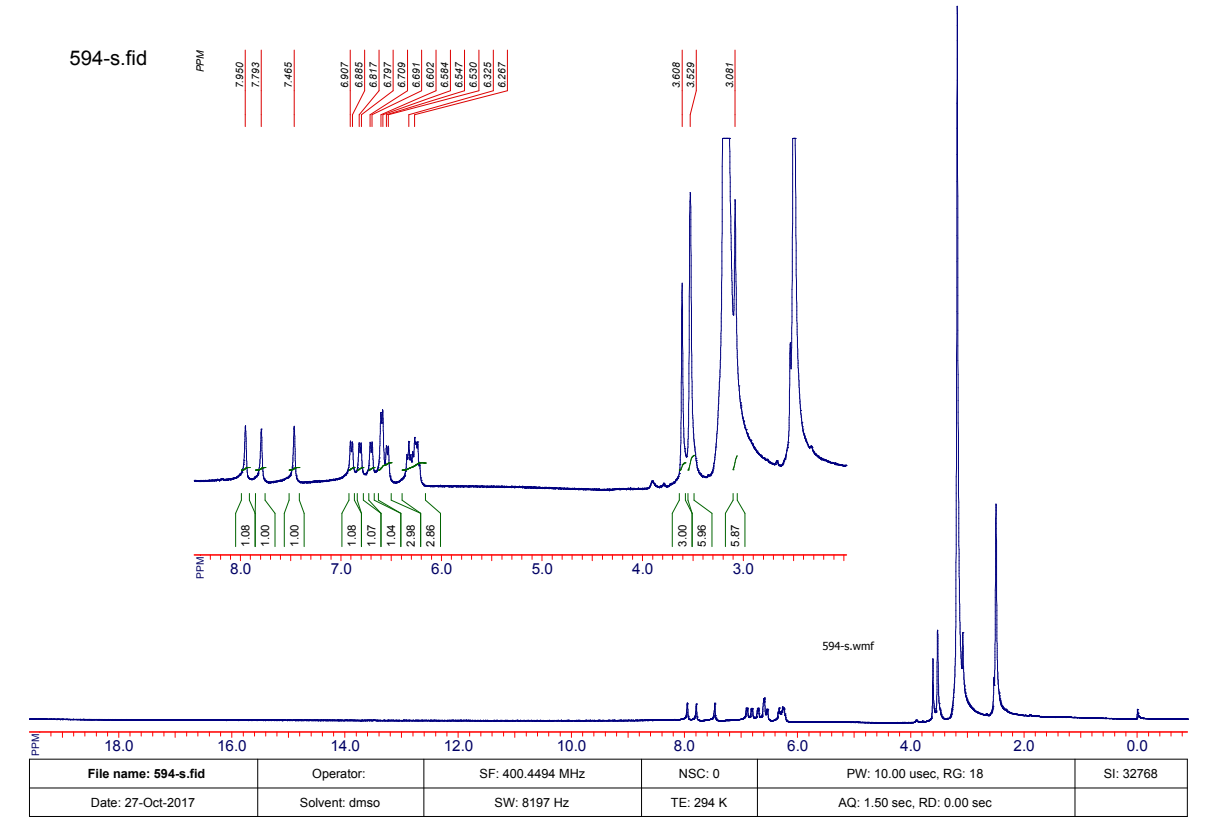


Figure S1. IR-spectra of $[CoZnL_3Cl_2]\cdot CH_3OH$ (**1**) (top) and HL (bottom).



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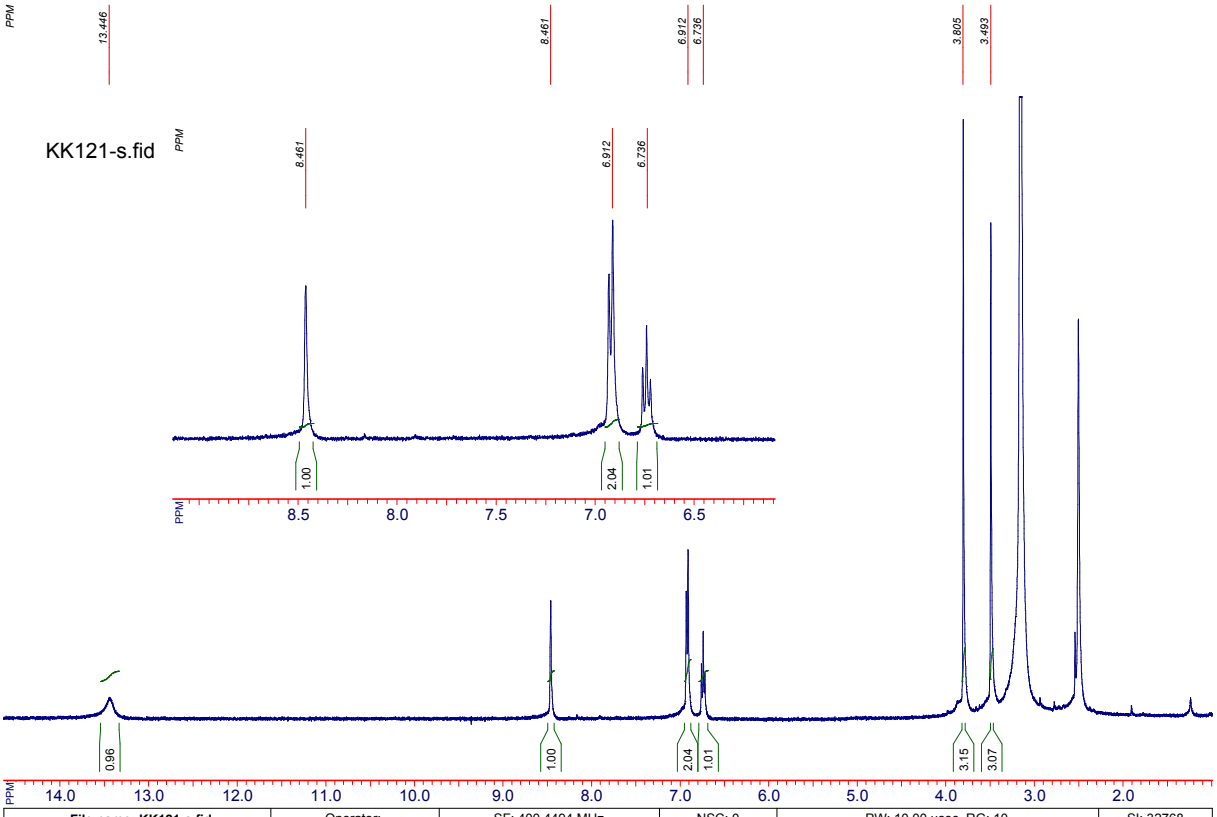

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Figure S2. 400 MHz ^{1}H NMR spectra of $[CoZnL_3Cl_2]\cdot CH_3OH$ (**1**) (top) and HL (bottom) in DMSO-d_6 at 294 K in the ranges of 0–18 and 1–14 ppm, respectively.

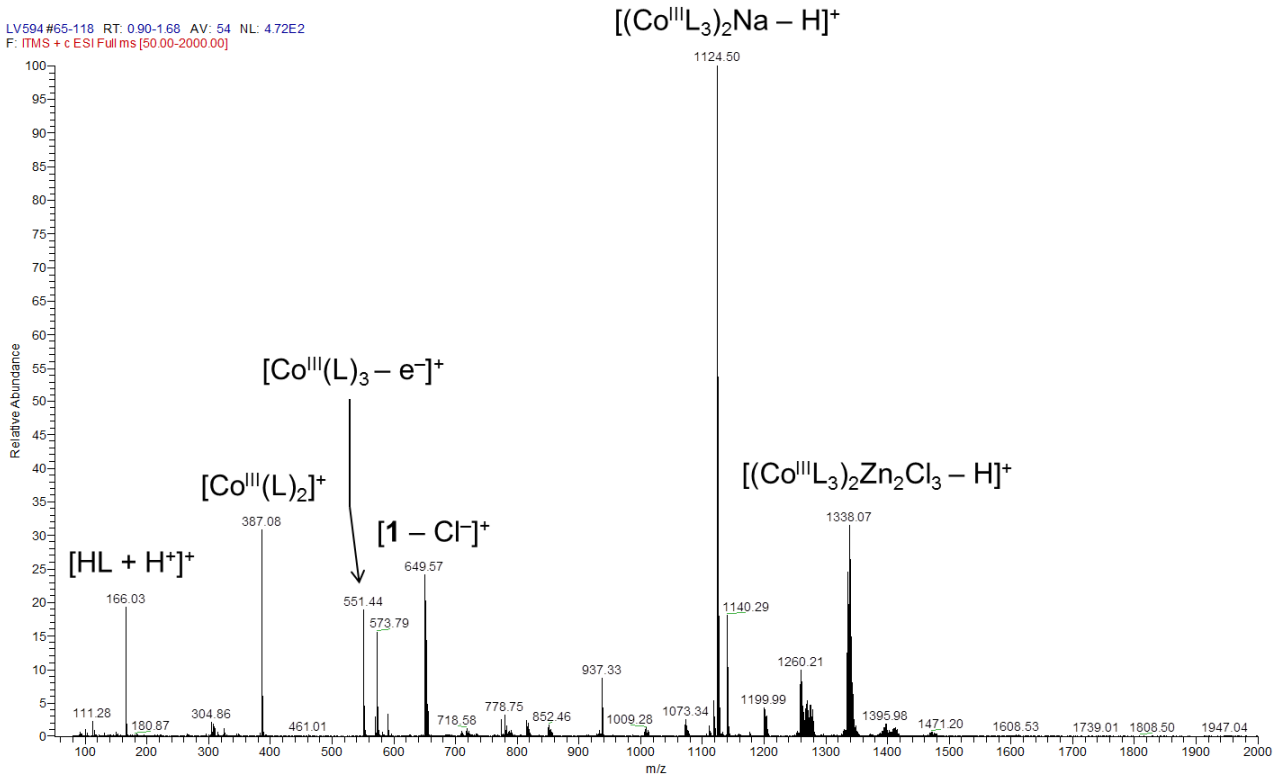

Figure S3. ESI-MS spectrum of a solution of **1** in acetonitrile.

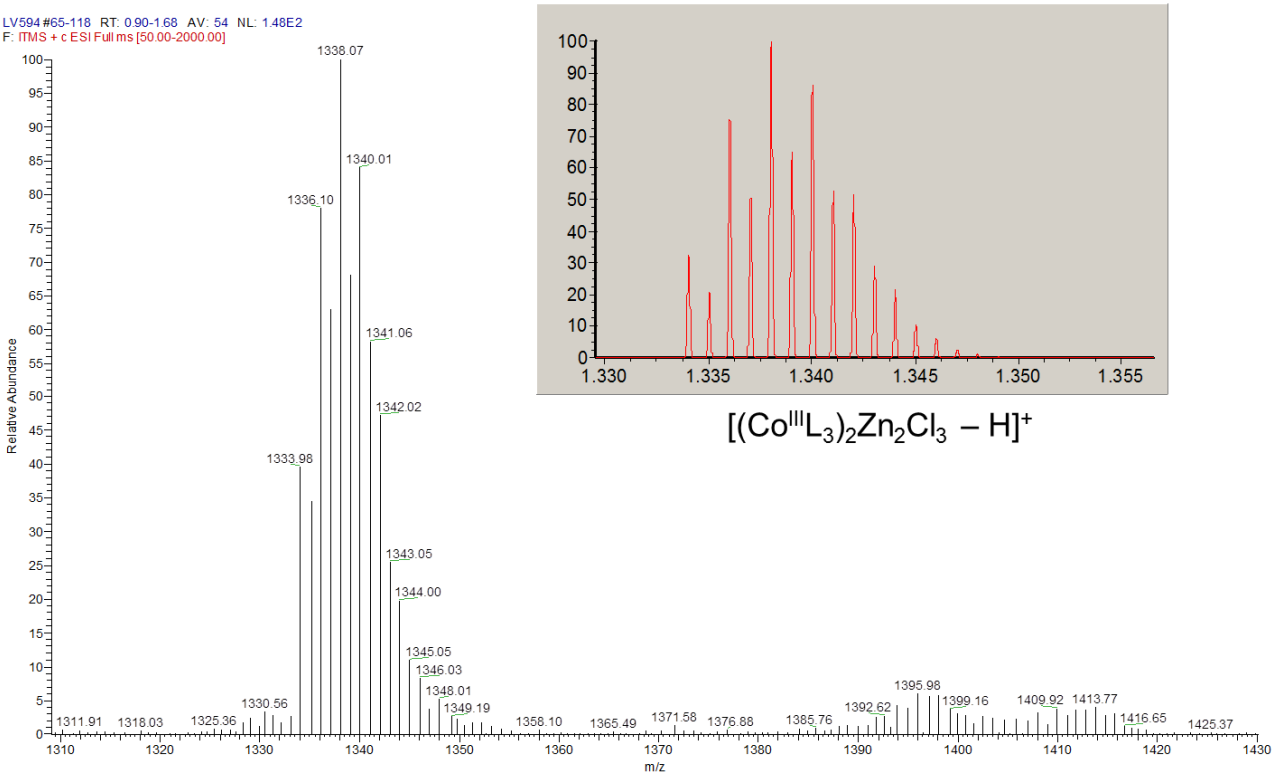

Figure S4. Fragment of the ESI-MS spectrum of **1** (Figure S3) showing the isotopic distribution for the peak at 1338 *m/z*. The inset shows calculated distribution for the proposed species.

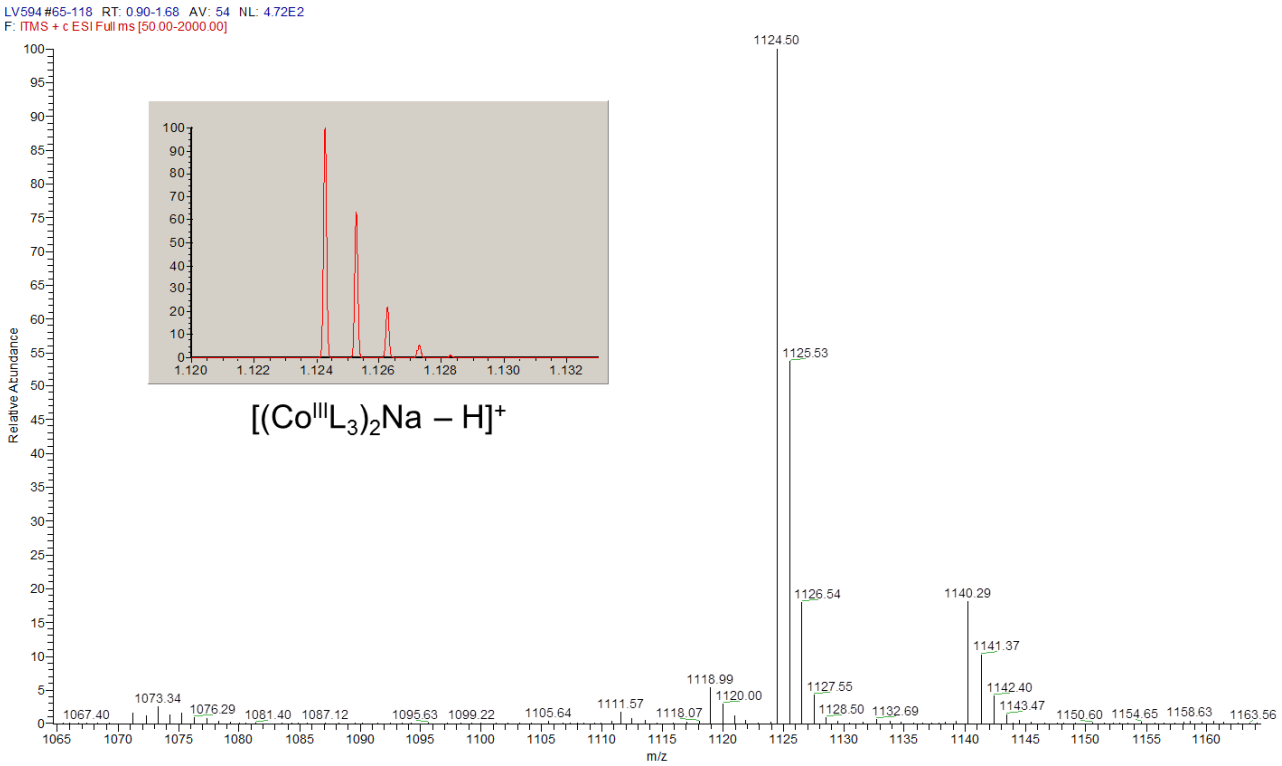

Figure S5. Fragment of the ESI-MS spectrum of **1** (Figure S3) in acetonitrile showing the isotopic distribution for the peak at 1125 *m/z*. The inset shows calculated distribution for the proposed species.

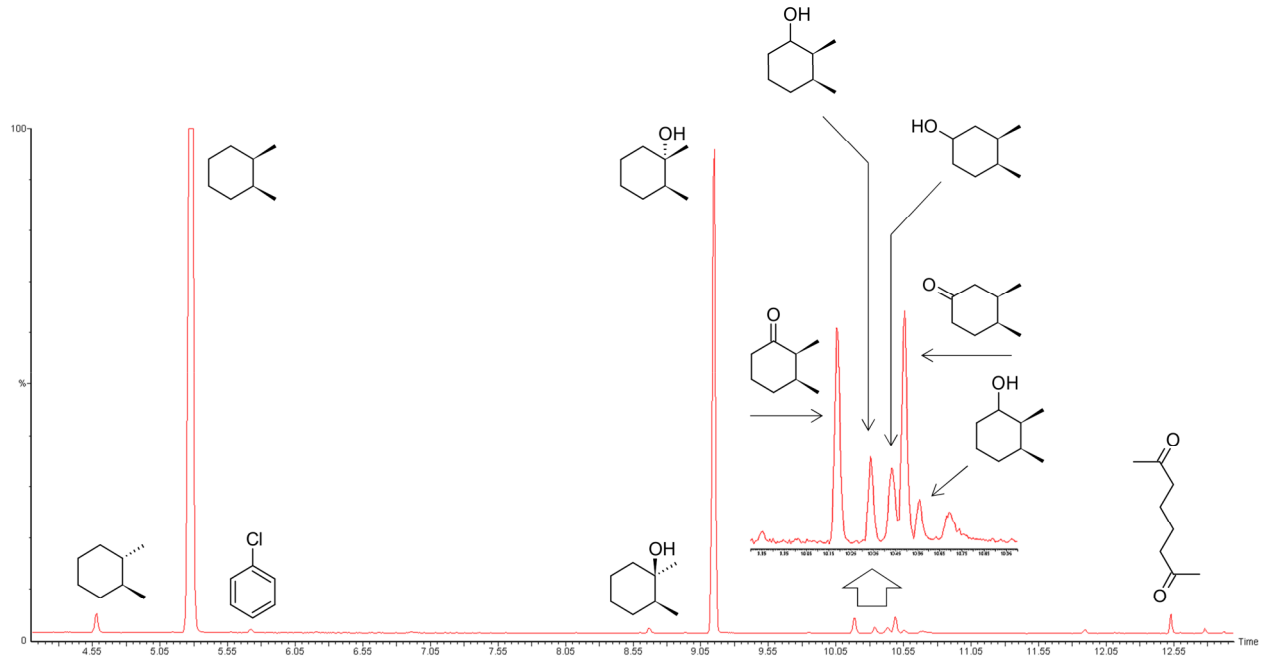

Figure S6. Fragment of the chromatogram showing the main reaction products and by-products in the course of *cis*-1,2-dimethylcyclohexane oxidation with *m*-CPBA catalysed by **1** in the presence of HNO_3 promoter (Table 1, Entry 3).

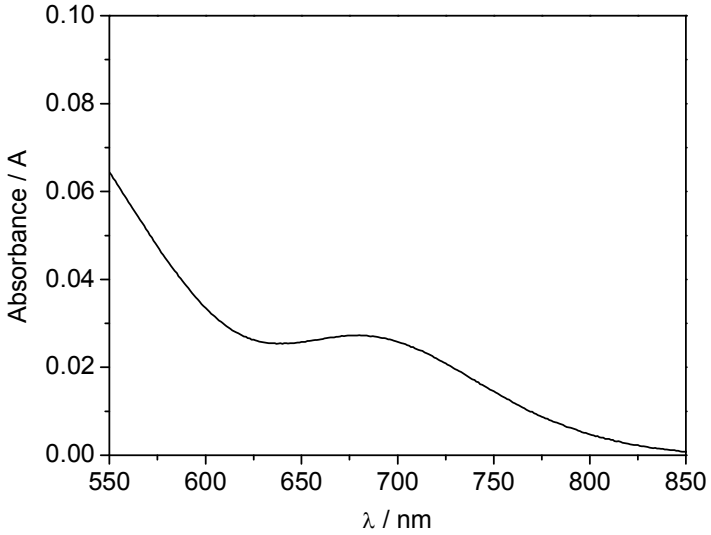

Figure S7. Fragment of the UV/Vis spectrum of **1** in acetonitrile showing the band at 680 nm.

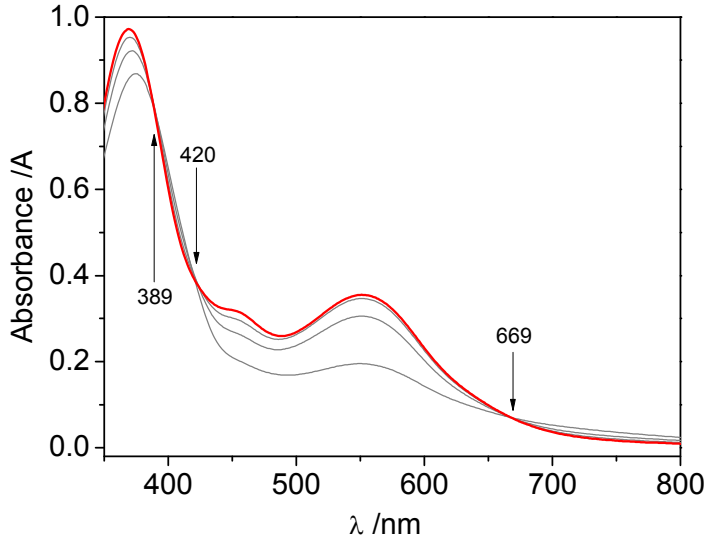

Figure S8. Fragment of the UV/Vis spectra depicted in Figure 6, (**a**), inset (**1** + *cis*-1,2-DMCH + HNO_3), showing isosbestic points.

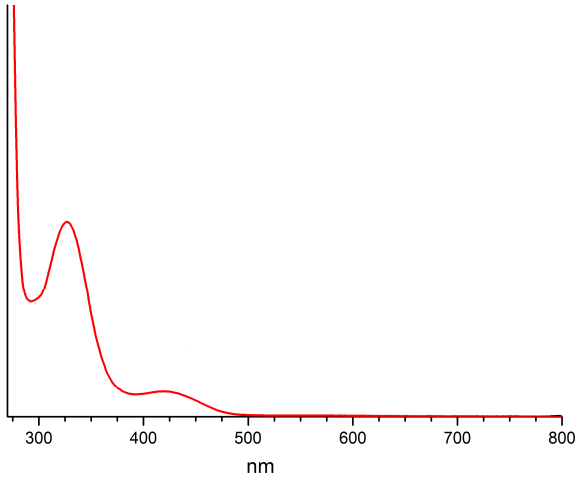

Figure S9. UV/Vis spectrum of free HL in acetonitrile (10^{-4} M).

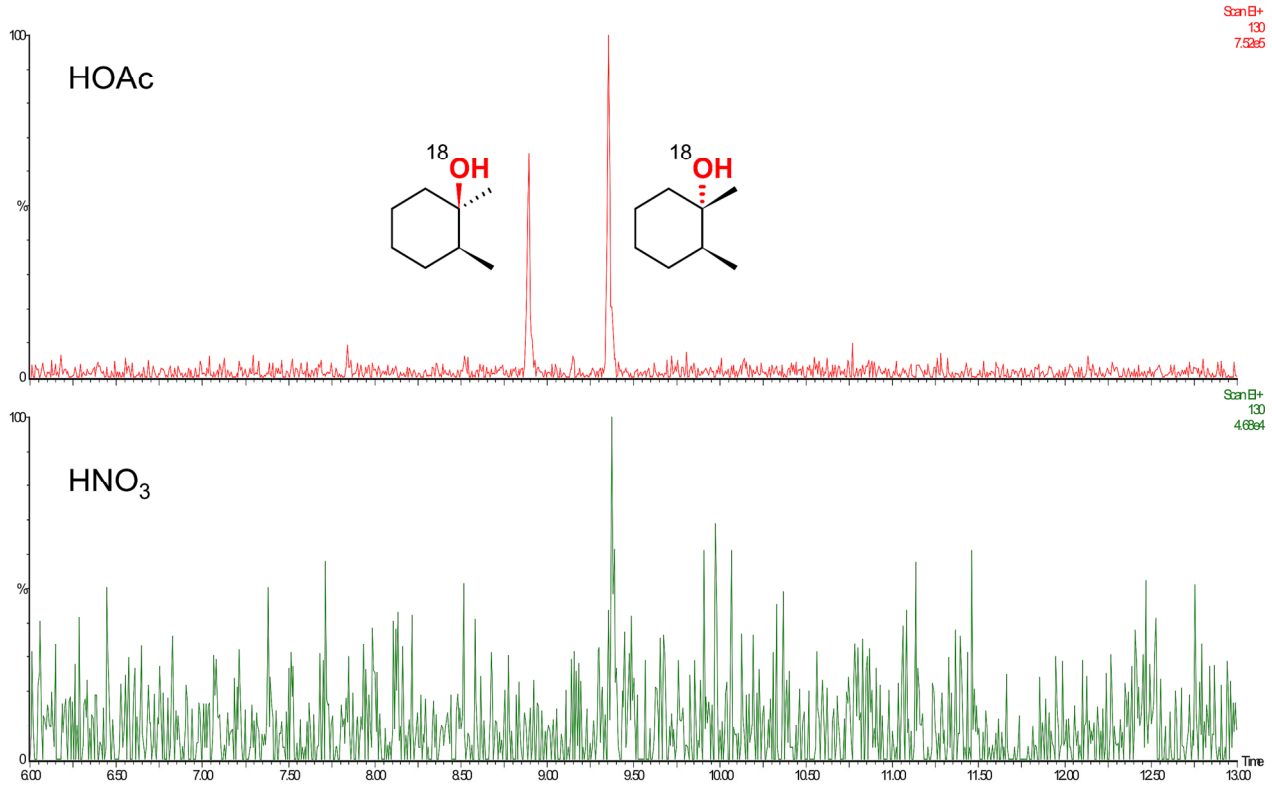

Figure S10. Fragments of the chromatograms, showing the intensities of 130 *m/z* signals (corresponding to the molecular ion, M^+, of the ^{18}O-labelled tertiary alcohols) for the **1**/HOAc/*m*-CPBA (top) and **1**/HNO_3/*m*-CPBA (bottom) tests (Figure 7, 90 min).

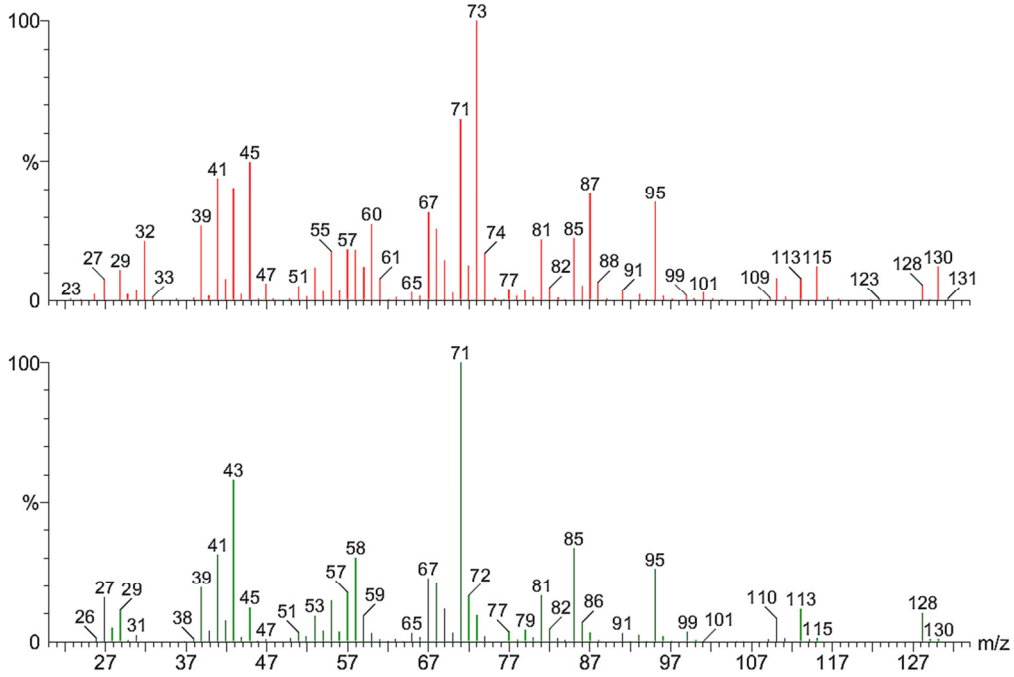

Figure S11. EI-MS spectra of the partially ^{18}O-labelled tertiary *trans*- (top) and *cis*- (bottom) alcohols, formed in the course of *cis*-1,2-DMCH oxidation catalysed by **1** in the presence of HOAc promoter (Figure 7, 40 min).

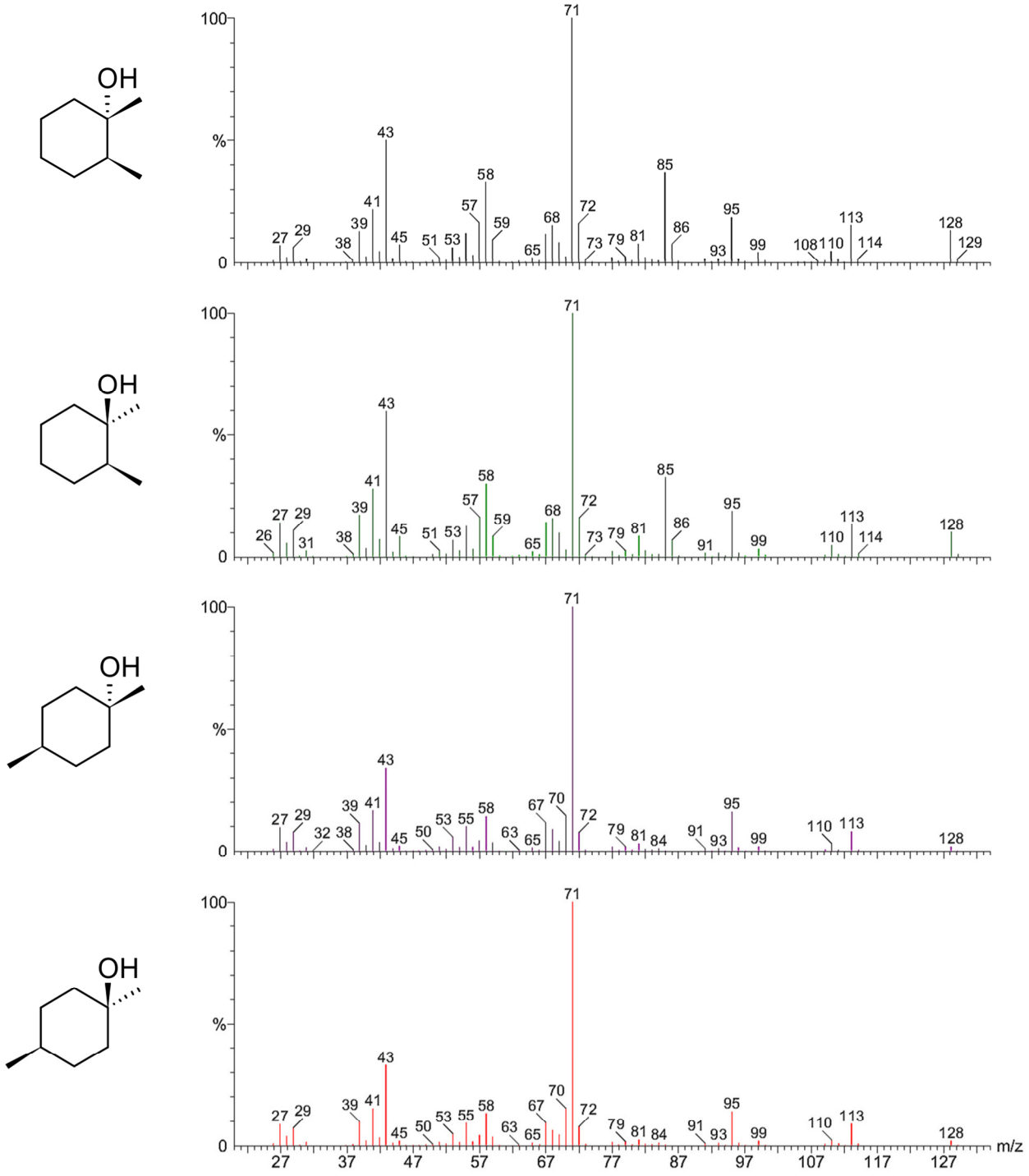

Figure S12. EI-MS spectra of the tertiary alcohols formed as the reaction products in the **1**/HNO_3/*m*-CPBA system (Table 2).

Table S1. Selected bond lengths (Å) and angles (°) for $[CoZnL_3Cl_2]\cdot CH_3OH$ (**1**)

Zn1–O11	2.0300(14)	Co1–O31	1.8788(14)
Zn1–O21	2.1186(14)	Co1–O11	1.9083(14)
Zn1–Cl2	2.2183(6)	Co1–O21	1.9094(14)
Zn1–Cl1	2.2242(6)	Co1–N16	1.9436(17)
Zn1–O12	2.4038(15)	Co1–N26	1.9475(17)
		Co1–N36	1.9506(17)
O11–Zn1–O21	72.96(5)	O31–Co1–O11	172.66(6)
O11–Zn1–Cl2	122.32(5)	O31–Co1–O21	93.32(6)
O21–Zn1–Cl2	103.67(4)	O11–Co1–O21	80.53(6)
O11–Zn1–Cl1	112.07(5)	O31–Co1–N16	93.97(7)
O21–Zn1–Cl1	106.52(4)	O11–Co1–N16	92.50(7)
Cl2–Zn1–Cl1	123.23(2)	O21–Co1–N16	171.38(7)
O11–Zn1–O12	70.79(5)	O31–Co1–N26	84.82(7)
O21–Zn1–O12	143.30(5)	O11–Co1–N26	91.19(7)
Cl2–Zn1–O12	91.01(4)	O21–Co1–N26	90.43(7)
Cl1–Zn1–O12	92.23(4)	N16–Co1–N26	94.81(7)
		O31–Co1–N36	91.17(7)
		O11–Co1–N36	92.54(7)
		O21–Co1–N36	87.44(7)
		N16–Co1–N36	87.80(7)
		N26–Co1–N36	175.35(7)

Table S2. Crystal data and structure refinement for $[CoZnL_3Cl_2]\cdot CH_3OH$ (**1**)

Empirical formula	$C_{28}H_{34}Cl_2CoN_3O_7Zn$
Formula weight	719.78
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.1472(5)
b (Å)	14.9777(5)
c (Å)	16.8684(7)
α (°)	90
β (°)	104.292(4)
γ (°)	90
Volume ($Å^3$)	2974.0(2)
Z	4
Density (mg/m^3)	1.608
μ (mm^{-1})	1.595
θ range for data collection, (°)	2.73; 34.63
Reflections collected	43972
Independent reflections	12011
Data / restraints / parameters	12011 / 0 / 390
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0543, $wR2$ = 0.0955
R indices (all data)	$R1$ = 0.0792, $wR2$ = 0.1032
Goodness-of-fit on F^2	1.106
Largest diff. peak and hole ($eÅ^{-3}$)	0.654; -0.636

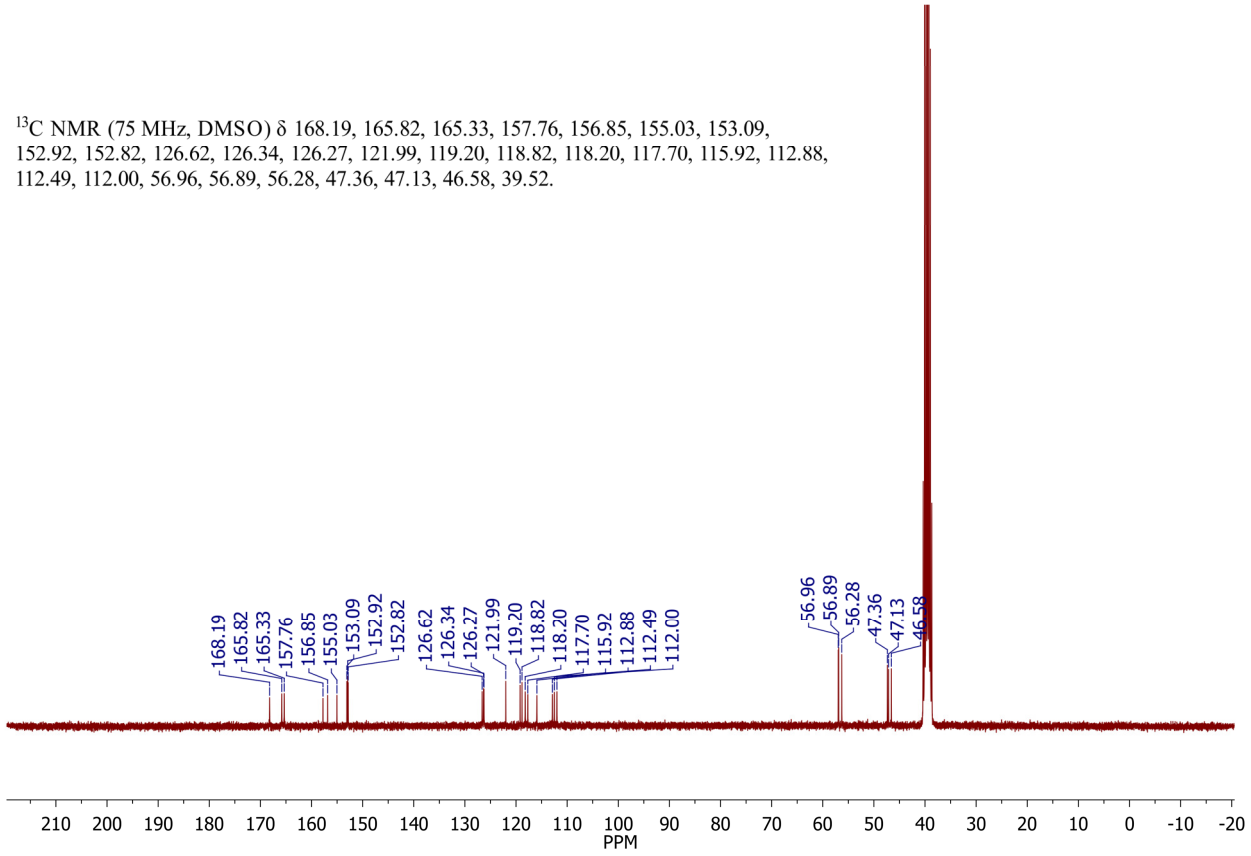

Figure S13. ^{13}C NMR spectrum of $[CoZnL_3Cl_2]\cdot CH_3OH$ (**1**) in DMSO-d_6.