Supporting Information:

Unanticipated demetalation of a Zn(salphen) complex provoked by N-heterocycles

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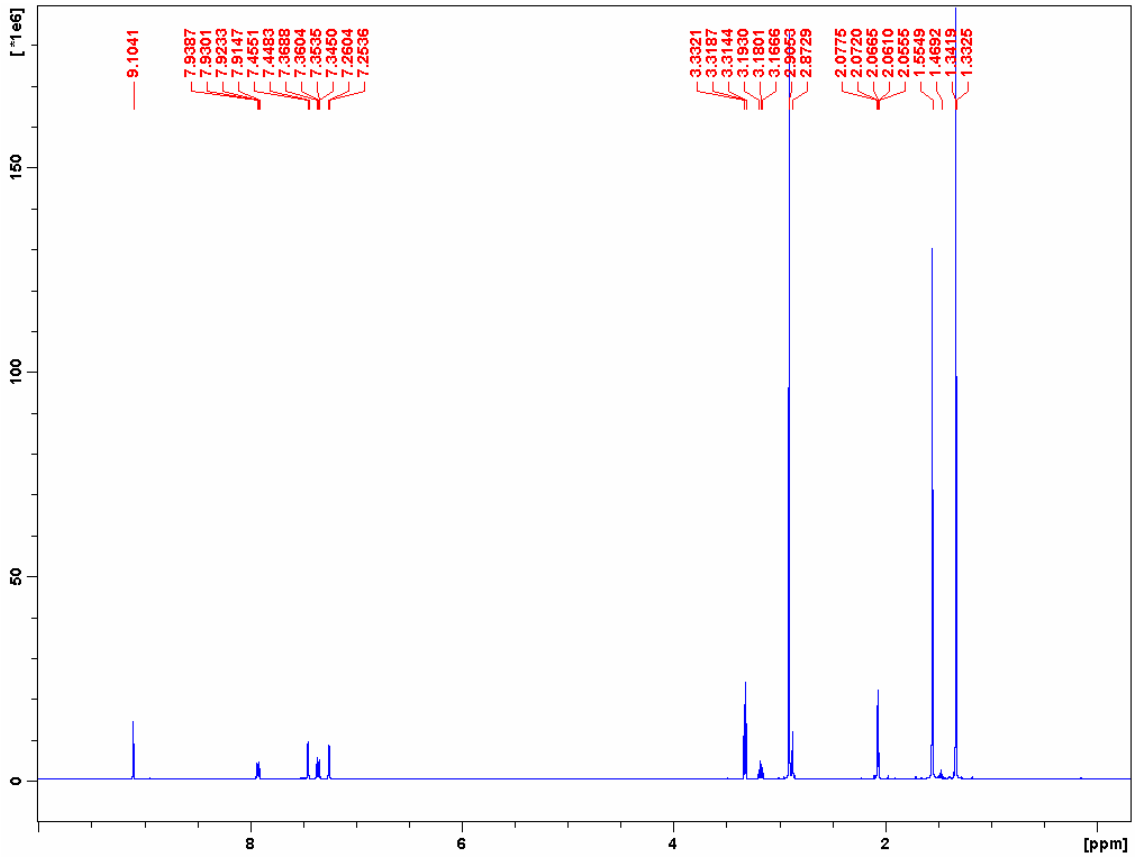
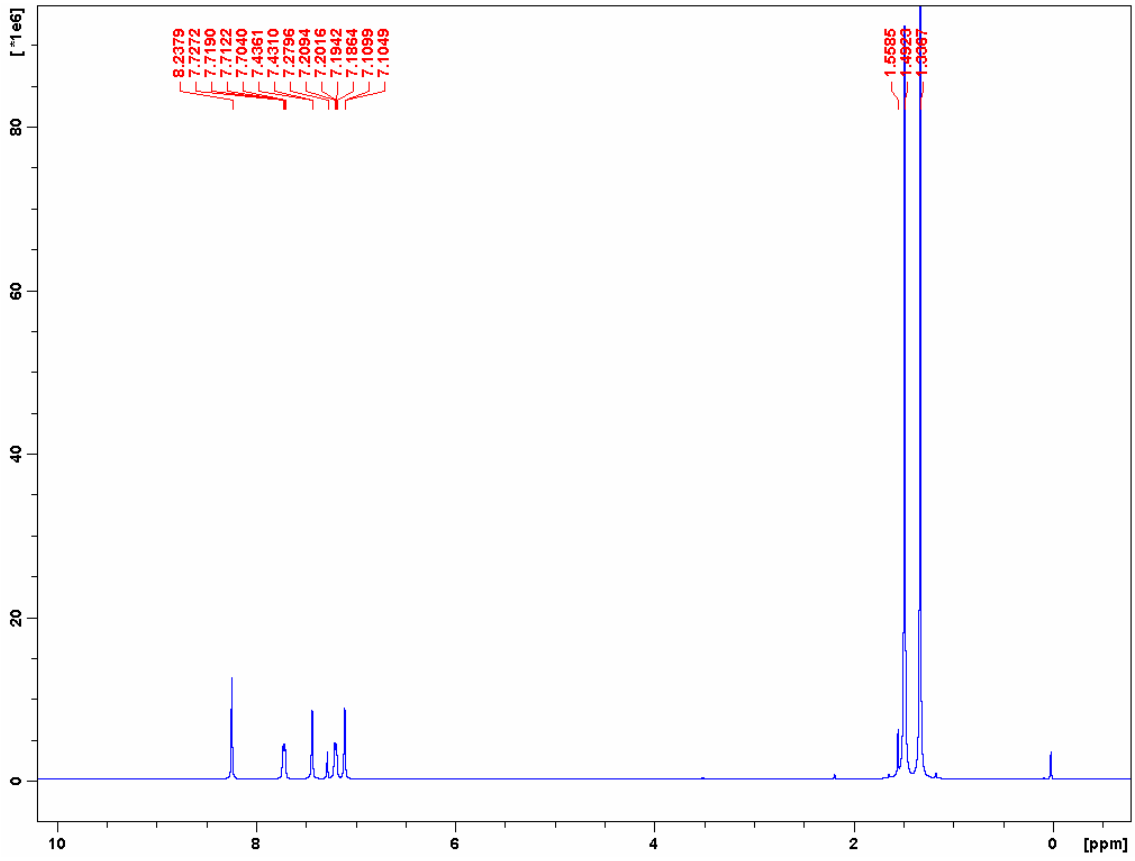
Contents:[1]

[1] All ^{1}H NMR spectra were recorded at 400 MHz. The $CDCl_3$ contained TMS as internal standard.

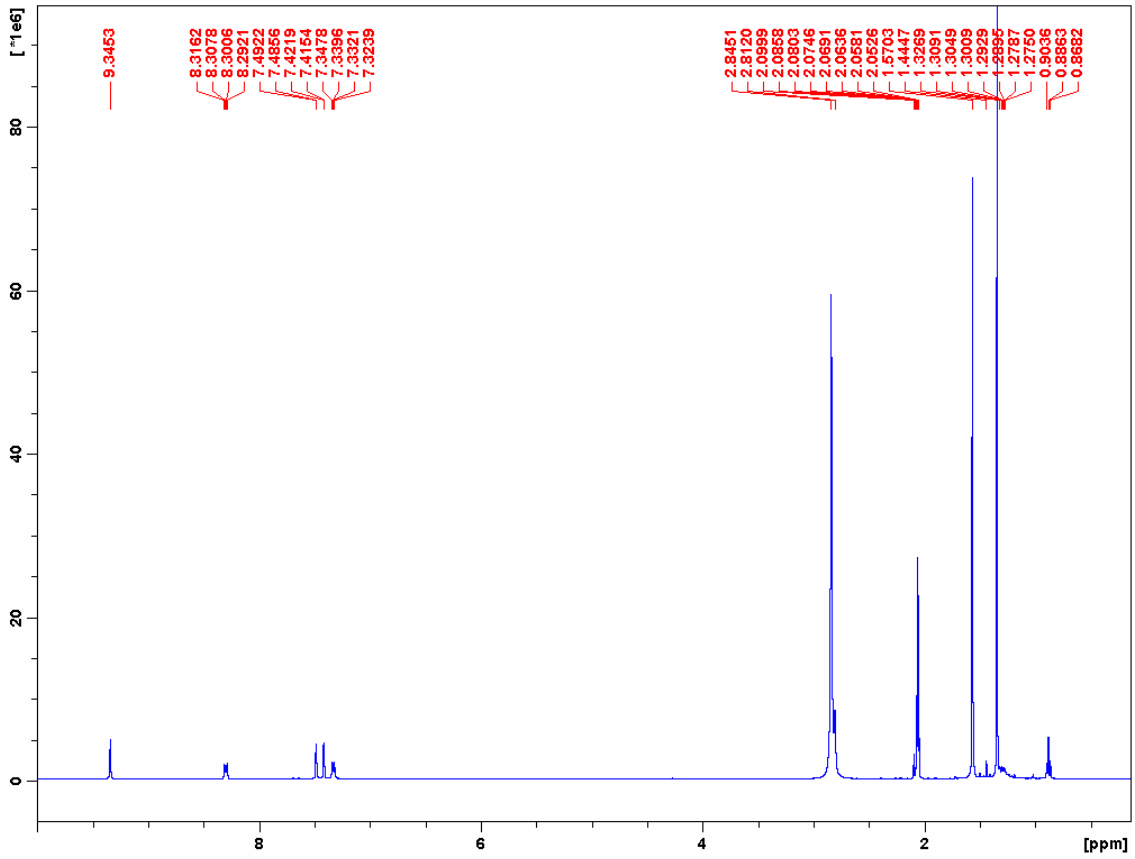
^{1}H NMR spectrum (d_6-acetone) of Zn(salphen)compound **1a**.



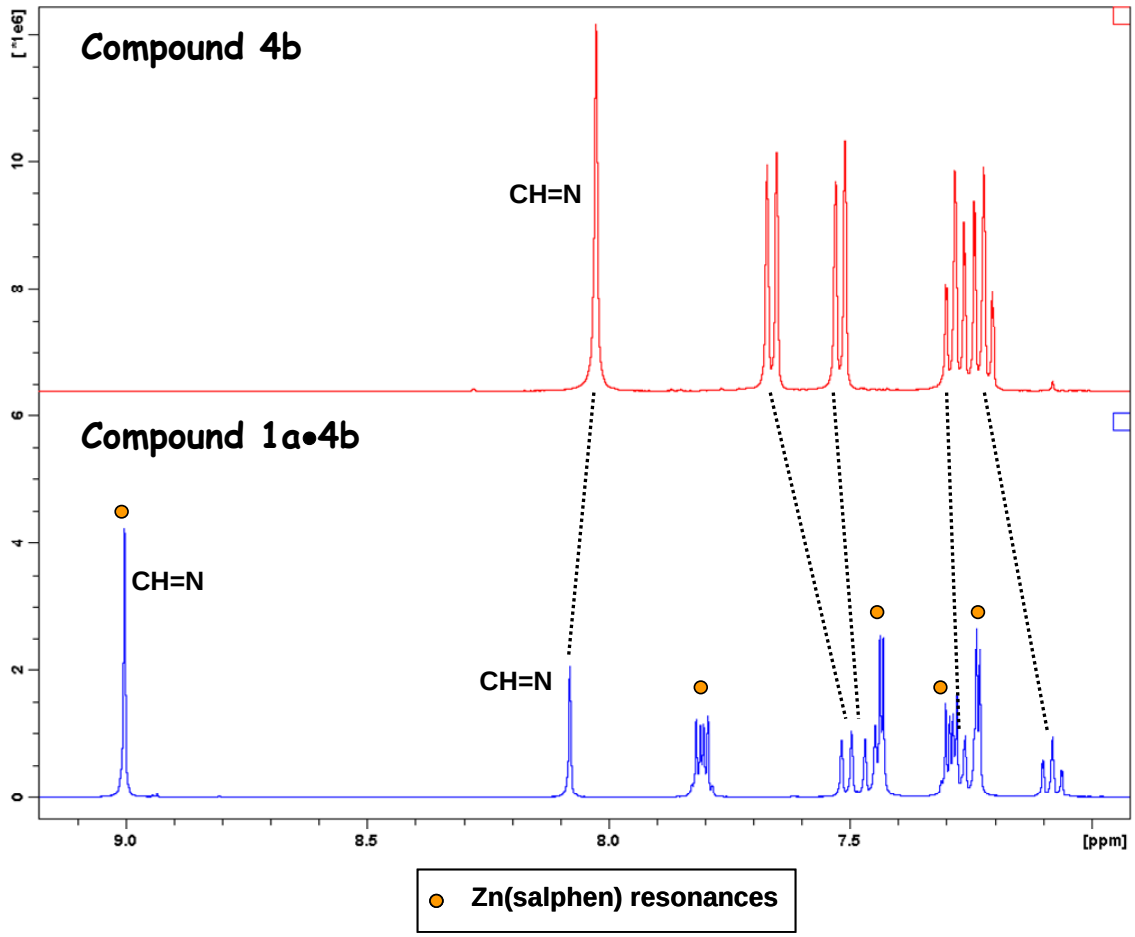
^{1}H NMR spectrum ($CDCl_3$) of Ni(salphen)compound **1b**.



^{1}H NMR spectrum (d_6-acetone) of Ru(CO)(salphen)compound **1c**.



Typical NMR shifts for compound **1a·4b** as compared to free **4b**.



Crystallographic details for **2**, **1a·4b** and **1a·5b.**

Compound	1a·4b	1a·5b	2
Formula	$C_{44}H_{54}N_4O_2\ Zn_1$	$C_{40}H_{52}N_4O_2Zn_1$	$C_{78}H_{105}N_7O_4$*
Solvents in crystal	-------	-------	3/2 × Acetonitrile*
Formula weight	736.28	686.23	1204.69
Crystal size (mm^3)	0.14 × 0.12 × 0.07	0.30 × 0.30 × 0.10	0.20 × 0.10 × 0.10
Crystal color	orange	yellow	orange
Temp (K)	100	100	100
Crystal system	triclinic	orthorhombic	triclinic
Space group	*P*ī	*I*bam	*P*ī
A (Å)	9.4787(6)	32.9872(19)	9.9668(6)
B (Å)	14.6726(11)	9.8259(6)	11.7206(5)
C (Å)	14.9753(10)	23.0204(13)	33.5724(16)
α (deg)	103.503(4)	90.00	81.394(2)
β (deg)	107.774(3)	90.00	82.282(2)
γ (deg)	91.800(4)	90.00	69.164(2)
V ($Å^3$)	1916.6(2)	7461.6(8)	3610.1(3)
Z	2	4	2
ρ (g/cm^3)	1.276	1222	1.108
μ (mm^{-1})	0.683	0.696	0.068
θ_{max} (°)	39.97	39.87	35.18
Reflec. measured	37644	45014	58825
Unique reflections	16419 [R_{int} = 0.0288]	11013 [R_{int} = 0.0370]	29202 [R_{int} = 0.0491]
Absorp. correct.	SADABS (Bruker)	SADABS (Bruker)	SADABS (Bruker)
Trans. min/max	0.8433/1.0000	0.8486/1.0000	0.8123/1.0000
Parameters	473	230	833
R1/wR2 [I>2σ(I)]	0.0332/0.0867	0.0307/0.0850	0.0781/0.1862
R1/wR2 [all data]	0.0404/0.0905	0.0386/0.0899	0.1219/0.2059
Goodness-of-fit (F^2)	1.059	1.033	1.062
Peak/hole ($e/Å^3$)	0.667/-0.301	0.834/-0.297	0.954/-0.532

* The elementary cell contains two independent molecules of the main compound.

X-ray Structure Determination: Crystals of **1a·4b**, **1a·4b** and **2** were obtained from CH_3CN in the presence of suitable ligands. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data Collection: Measurements were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with MoKα radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = –173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection Apex2 V. 1.0-22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius 2001) and absorption correction SADABS V. 2.10 (2003).

Structure Solution and Refinement: SHELXTL Version 6.10 (Sheldrick, 2000) was used.[2]

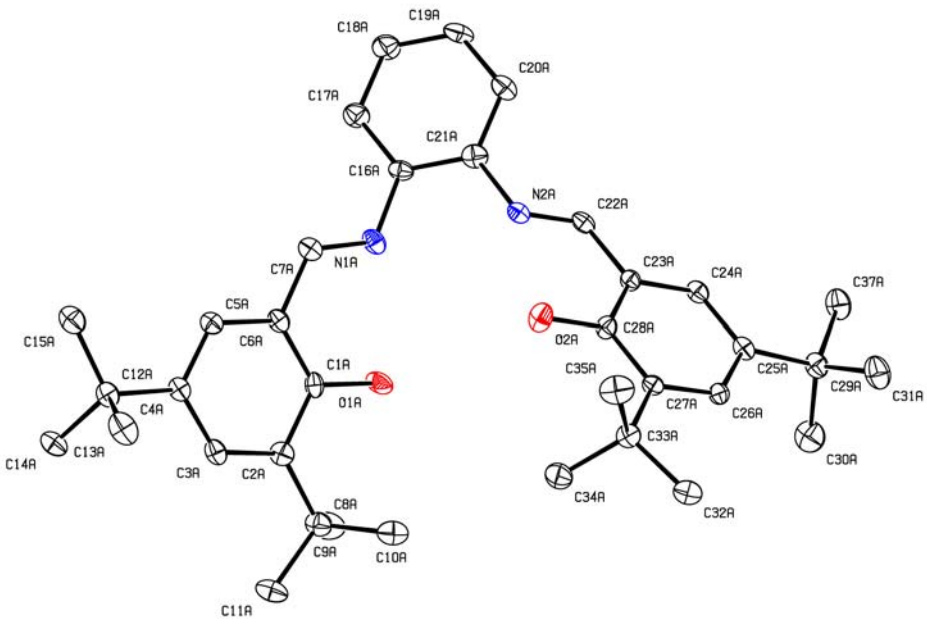
Comments:

The proposed structure for the **1a·4b** could be elucidated unambiguously by single crystal X-ray diffraction. The compound crystallizes in the triclinic space group *P*ī. The elementary cell contains one molecule of the complex.

The structure of **1a·5b** was proved by X-ray single crystal structure analysis. The compound is crystallizing in the orthorhombic space group *I*bam with a *C*m symmetry for the molecule. The hydrogen atoms at C22 are disordered in two orientations.

After different attempts, the structure of **2** could be solved using tiny crystals obtained from acetonitrile. In sake of the bad quality of the crystals, the structure could be elucidated with enough quality for reporting. Compound **2** crystallizes as an acetonitrile solvate with two independent molecules of the main compound and three independent molecules of acetonitrile in the elementary cell.

Structure of ligand 2:



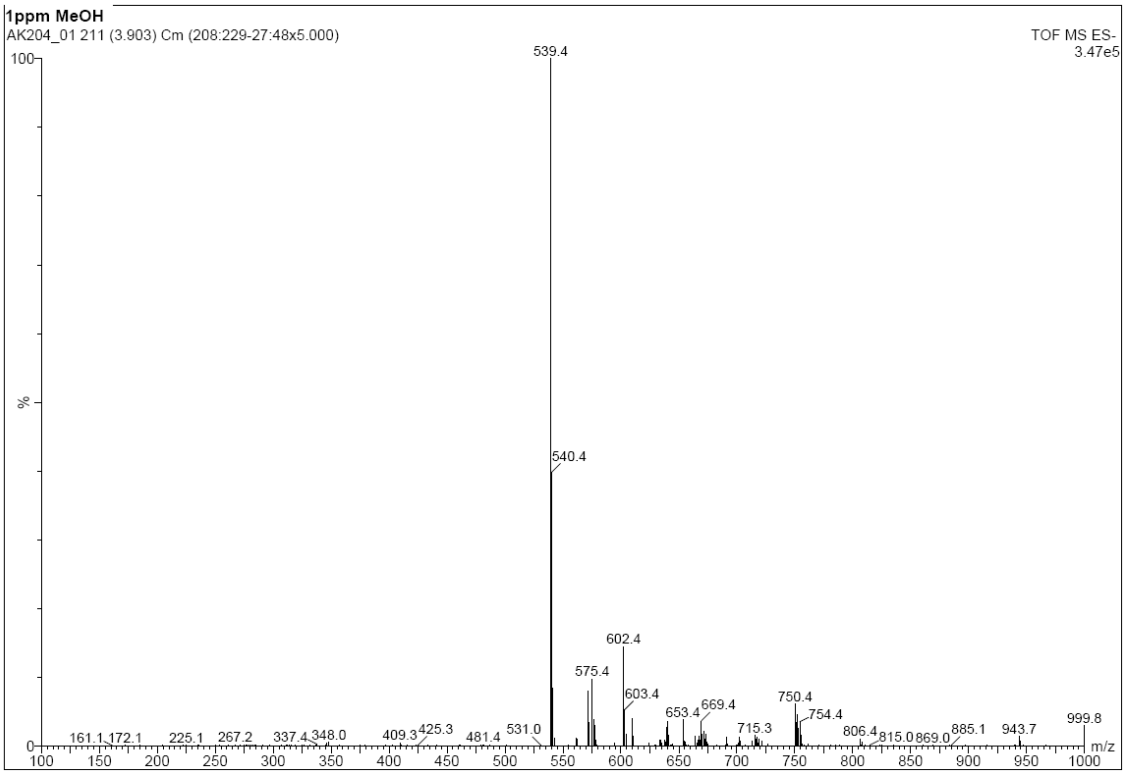
The X-ray molecular structure determined for **2**; hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Only one of the crystallographically independent molecules is shown.

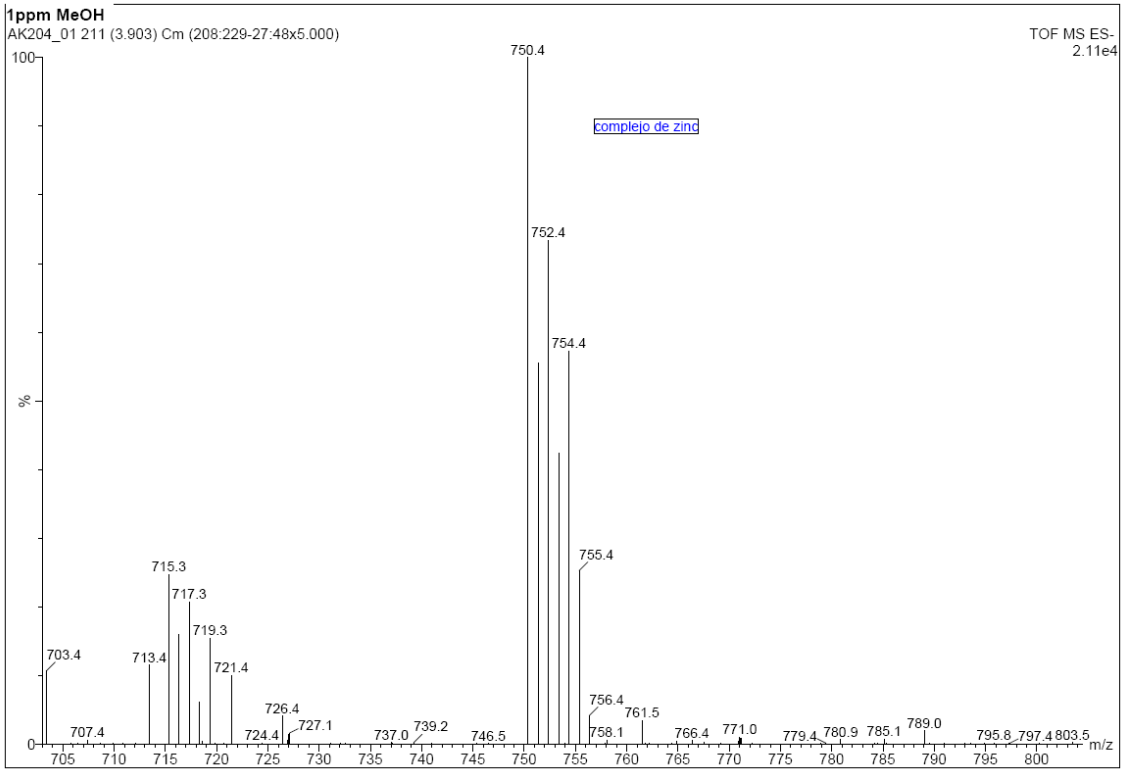
[2] Sheldrick, G. M., *´SHELXTL Crystallographic System Ver. 5.10´*, Bruker AXS Inc., Madison, Wisconsin **1998**.

MALDI-TOF-MS spectrum for the product of the reaction between **1a** and purine **3**.

Please note: MS analysis carried out for the mother liquor

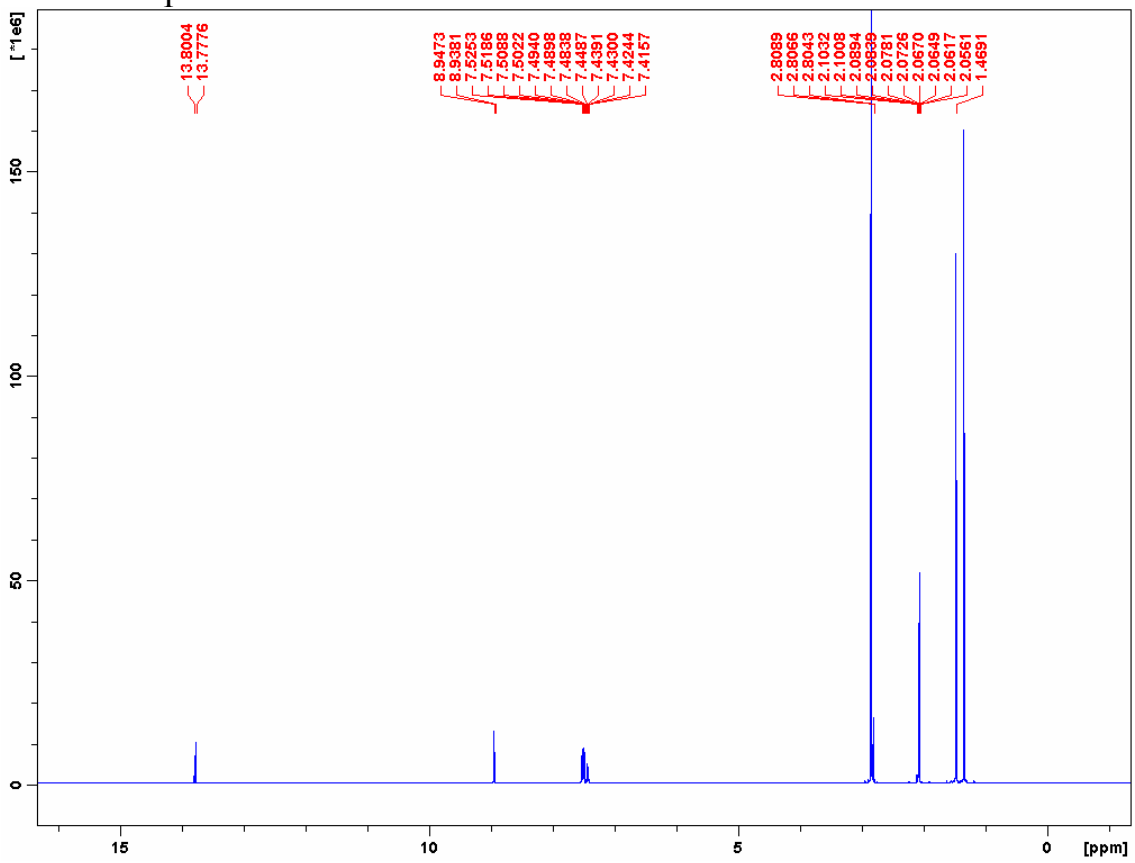
MALDI-TOF-MS spectrum for the product of the reaction between **1a** and imidazole **5a**.



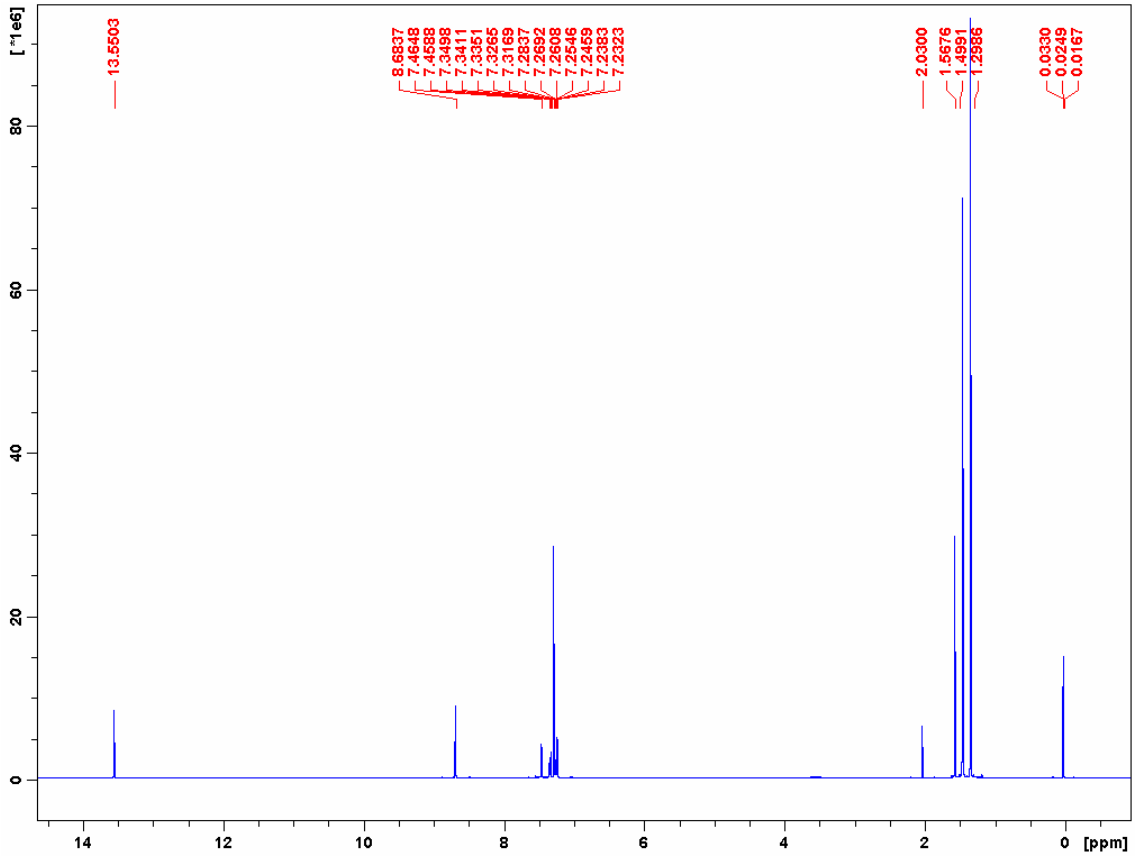


Please note: MS analysis carried out for the mother liquor. An enlargement is presented for part of the higher mass region, showing the presence of mono-Zn species.

^{1}H NMR analysis (d_6-acetone) of the yellow crystals obtained after reaction of **1a** with purine **3.**



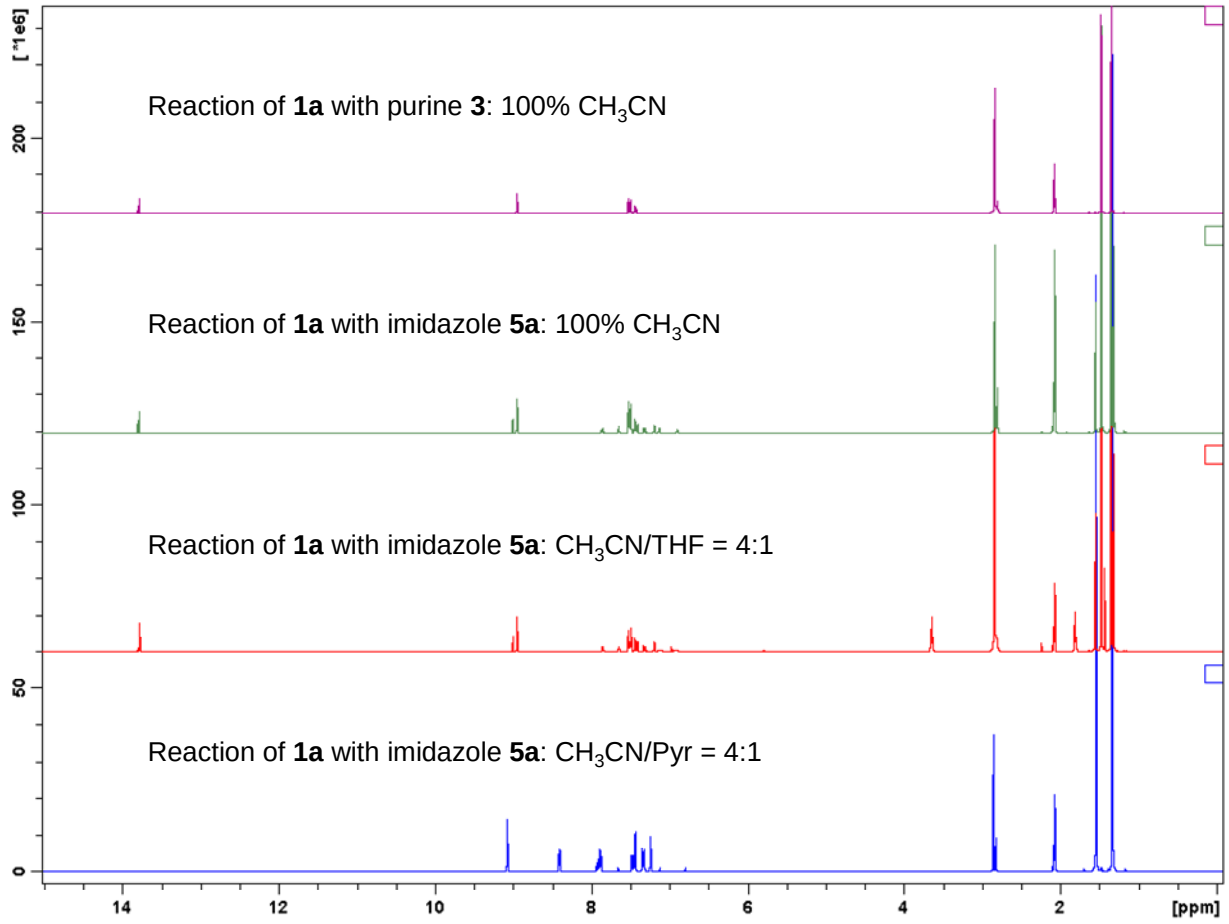
Directly below the spectrum recorded in $CDCl_3$:



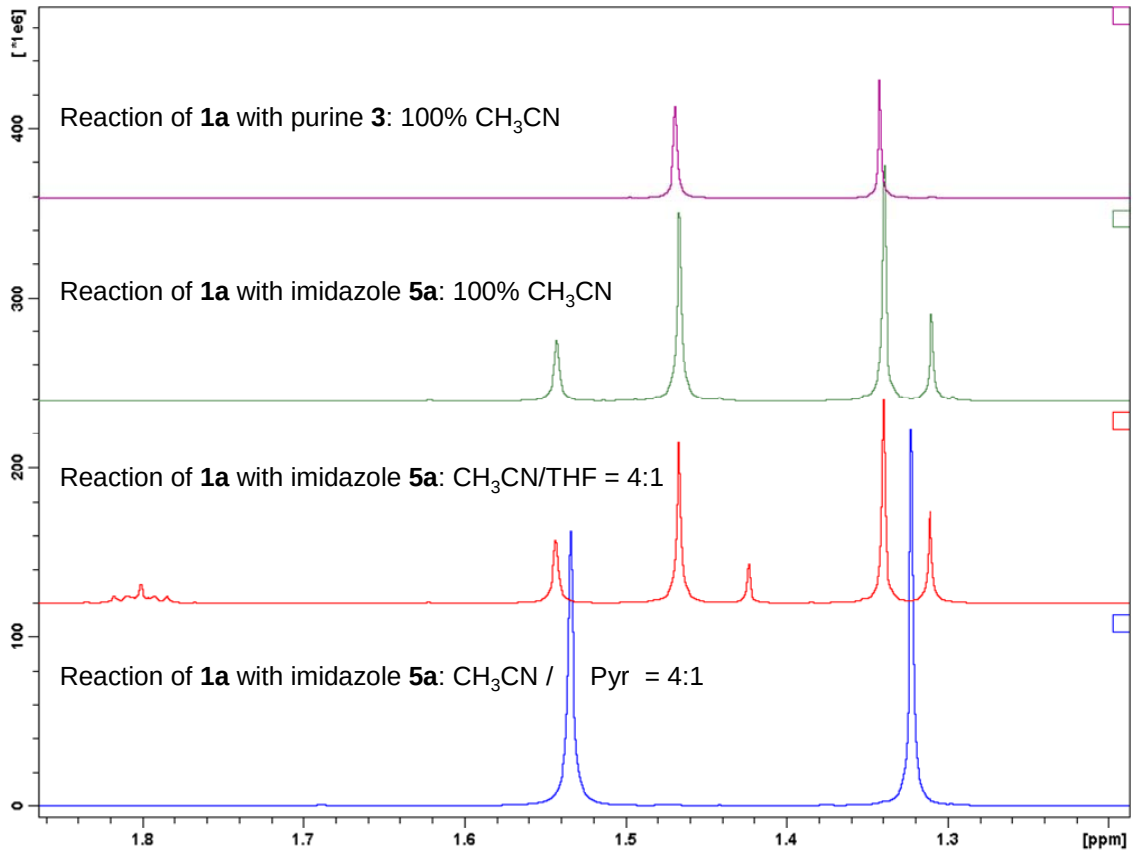
Typical NMR shifts (d_6-acetone) upon demetalation of complex **1a** in the presence of purine **3** and imidazole **5a**.

For the reaction that involved purine, the product after isolation is presented. For the other three spectra the product(s) after 4 h are presented. For all samples both the full spectra as well as the *t*-Bu regions are given. In order to establish a reliable conversion of **1a** into **2**, NMR signal integration was carried out in the *t*-Bu region.

Full spectra:



Enlarged *t*-Bu region of the NMR spectra:



Please note the small changes in shifts of the *t*-Bu resonances for the isolated reaction product in the presence of pyridine; in this case the 1:1 assembly **1a**·pyridine was identified, and the coordination of pyridine to the Zn metal center causes small changes in the magnetic environment of the *t*-Bu groups within the assembly.

Assignments:

δ = 1.47, 1.34 ppm; compound **2**
δ = 1.55, 1.31 ppm; compound **1a**

Literature pKa data for a series of N-heterocyclic compounds[3-6]

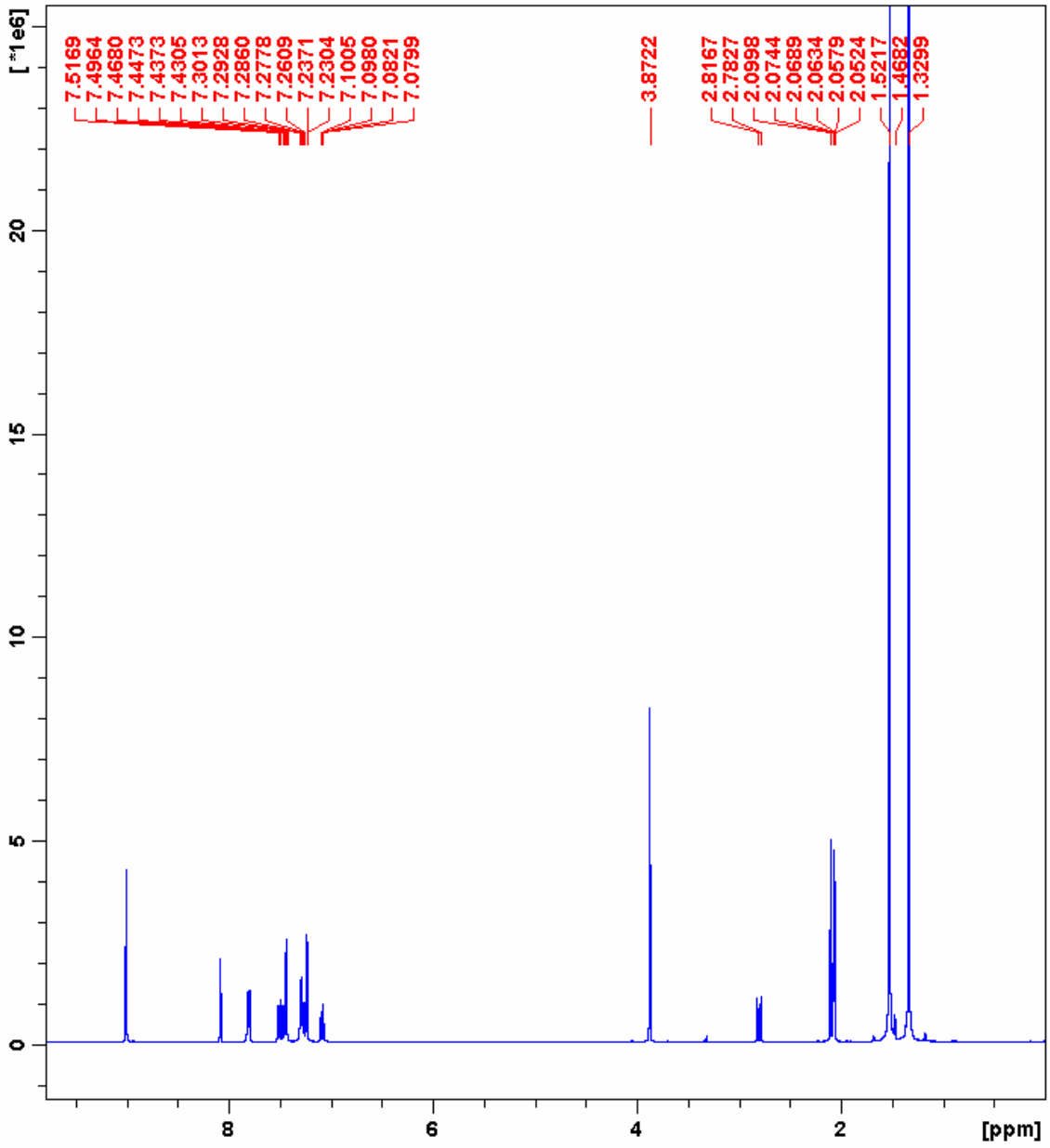
Compound	**pKa (H_2O)**	**pKa (dmso)**
H_2O	15.7	32
Phenol	9.95	18.0
Indole		20.95
Benzimidazole	6.0	16.4
Imidazole		18.6
2-Me-imidazole	7.75	
2-Me-benzimidazole	6.1	
2-Me-pyridine[1]	5.94	
Pyridine[1]	5.14	
Purine	2.39	
MeOH	15.5	27.9
CH_3CN		31.3

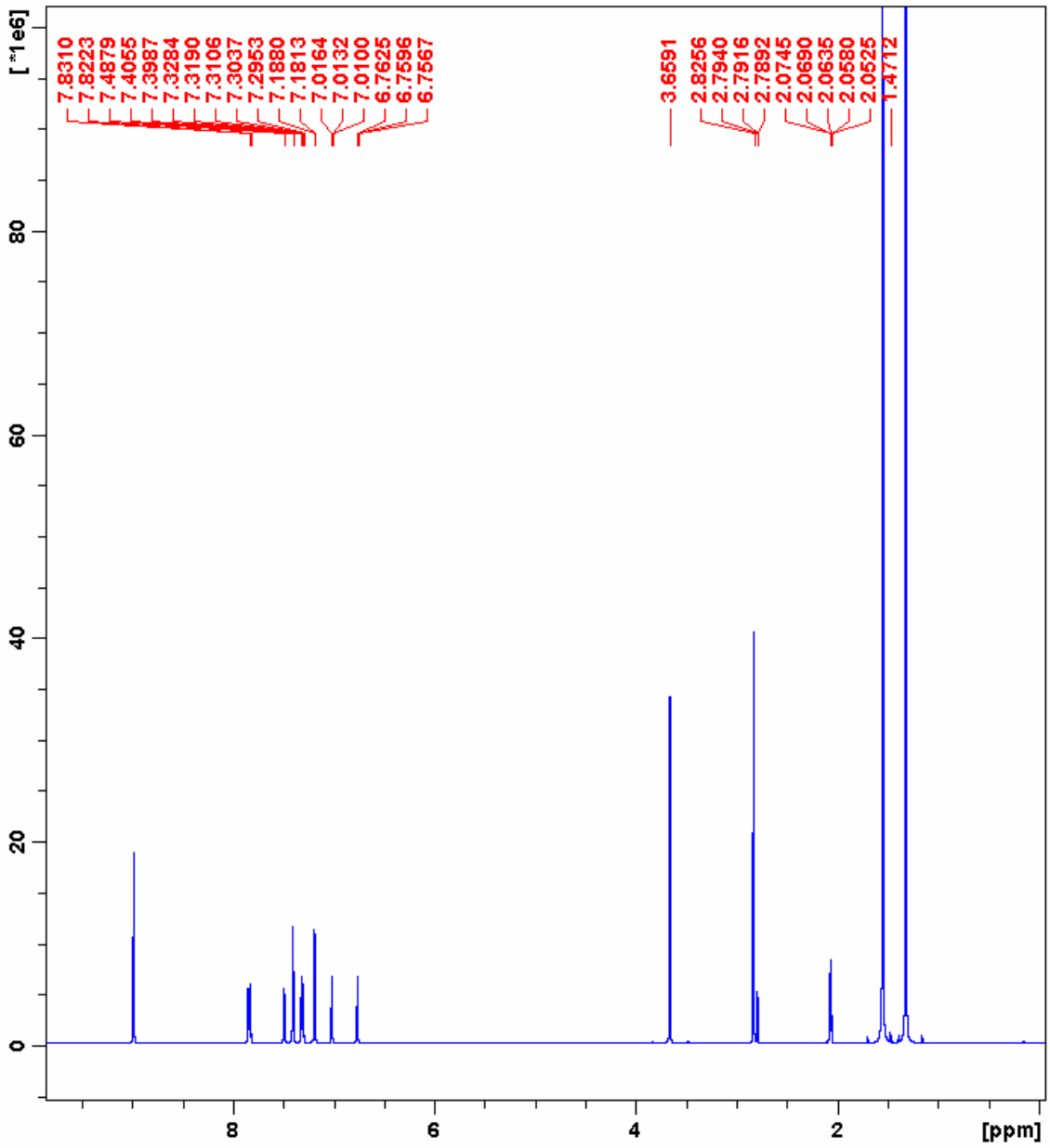
[1] Of the corresponding pyridinium derivative.

[3] http://daecr1.harvard.edu/pdf/evans_pKa_table.pdf.
[4] Lailach, G. E.; Thompson, T. D.; Brindley, G. W. *Clays and Clay Minerals* **1968**, *16*, 285.
[5] http://research.chem.psu.edu/brpgroup/pKa_compilation.pdf
[6] www.chem.wisc.edu/areas/reich/pkatable

Full ^{1}H NMR spectra (d_6-acetone) of compounds **1a·4b**, **1a·5b** and **1a·7**.

In order of mentioning:

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7.1813
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7.0132
7.0100
6.7625
6.7596
6.7567
3.6591
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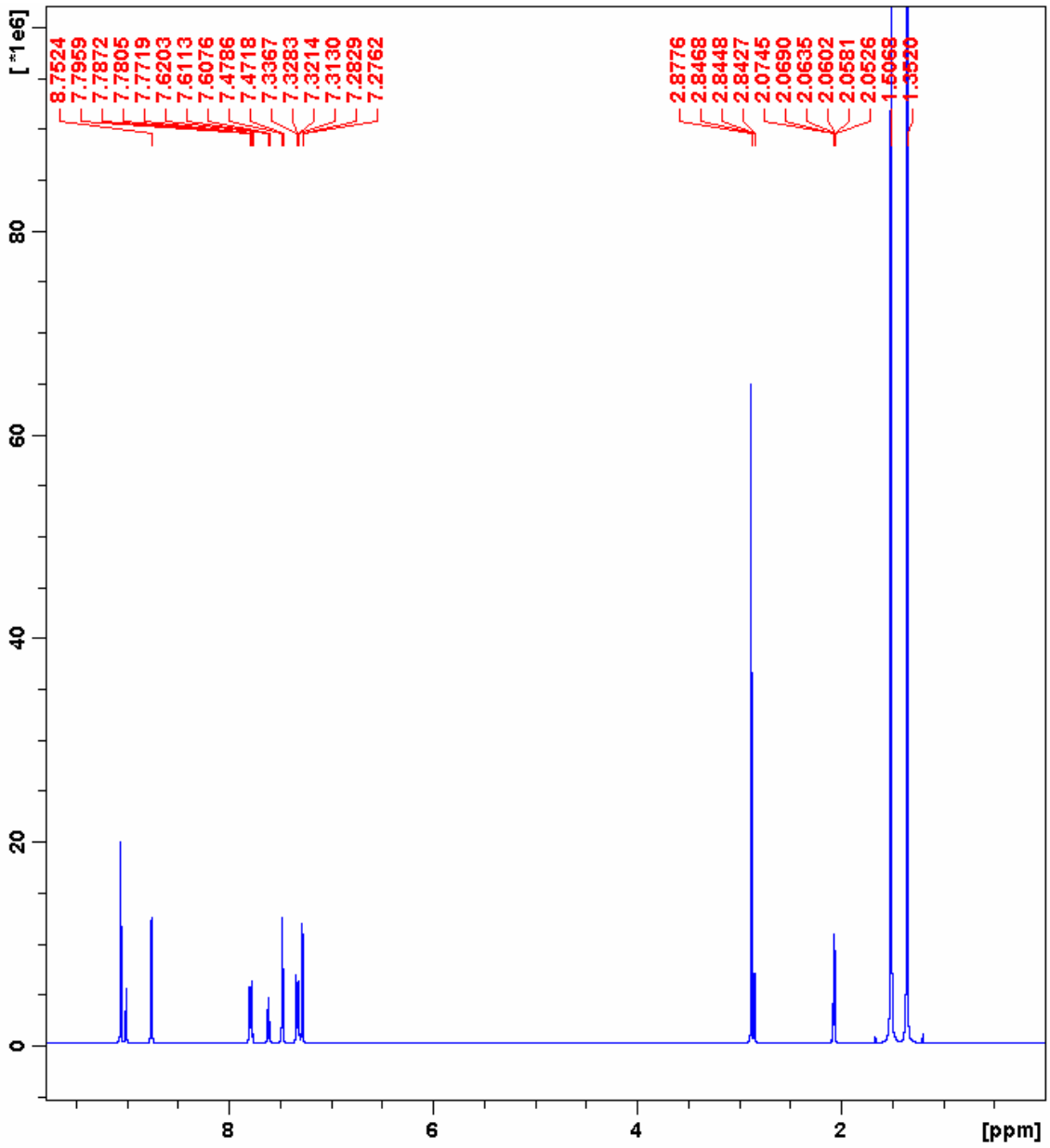
2.0525
1.4712


[*1e6]
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40
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2.0745
2.0690
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2.0526
1.5068
1.3520
8
6
4
2
[ppm]

Typical procedure involving complexes **1** and the N-heterocycles **3-7**.

Typical procedure for the reaction of complexes 1a-c with the N-heterocycles. A mixture of Zn(salphen) **1a** (61.3 mg, 0.101 mmol) and imidazole **5a** (13.0 mg, 0.191 mmol) in acetonitril (6 mL) was heated in a glass vial until all solids had dissolved. After cooling to ambient temperature the mixture was left unstirred for 4 h, and then a homogenized sample was taken for ^{1}H NMR analysis. The solvent was removed in vacuo and the residue dissolved in the appropriate NMR solvent directly followed by analysis. Data for **1a**: ^{1}H NMR (400 MHz, d_6-acetone): δ = 9.10 (s, 2H), 7.94-7.91 (m, 2H), 7.45 (d, ^4J = 2.7 Hz, 2H), 7.37-7.35 (m, 2H), 7.26 (d, ^4J = 2.7 Hz, 2H), 1.55 (s, 18H), 1.34 (s, 18H). MS (MALDI-TOF, positive mode) *m/z* 603.3 $(M+H)^+$. Data for **1b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 2H), 7.73-7.70 (m, 2H), 7.43 (d, ^4J = 2.0 Hz, 2H), 7.21-7.19 (m, 2H), 7.11 (d, ^4J = 2.0 Hz, 2H), 1.49 (s, 18H), 1.34 (s, 18H). Data for **1c**: ^{1}H NMR (400 MHz, d_6-acetone): δ = 9.35 (s, 2H), 8.32-8.29 (m, 2H), 7.49 (d, ^4J = 2.6 Hz, 2H), 7.42 (d, ^4J = 2.6 Hz, 2H), 7.35-7.32 (m, 2H), 1.57 (s, 18H), 1.35 (s, 18H). Data for **2**: ^{1}H NMR (400 MHz, d_6-acetone): δ = 13.78 (s, 2H), 8.95 (s, 2H), 7.52-7.48 (m, 6H), 7.44-7.42 (m, 2H), 1.47 (s, 18H), 1.34 (s, 18H). MS (MALDI-TOF, negative mode) *m/z* 539.4 $(M-H)^-$.