Supplementary Information

p-tert-Butylcalix[6]arene hexacarboxylic acid conformational switching and octahedral coordination with Pb(II) and Sr(II)

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General Information

Reagents, materials and instrumentation

All reagents were of reagent grade and used without further purification unless mentioned otherwise. Generally, solvents were dried by storing them over molecular sieves (Linde type 3A and 4A) or anhydrous $CaCl_2$. Analytical TLC was performed on precoated silica gel plates (SiO_2, 60 F_{254}). NMR experiments were done using Bruker 300 or 400 MHz NMR instruments and processed using iNMR software. The chemical shift of NMR signals are with reference to the solvent signal and the data are reported as follows: chemical shifts in ppm (δ), multiplicity (as singlet, doublet, triplet and broad singlet), integration ratio and interpretation their of. In NMR interpretation, Ar notation indicates the aromatic rings of calixarene backbone.

Synthesis

Syntheses of 5,11,17,23,29,35-hexakis(1,1-dimethylethyl)calix[6]arene-37,38,39,40,41, 42-hexol (**1**) and 37,38,39,40,41,42-hexakis(ethoxycarbonylmethoxy)-5,11,17,23,29,35-hexakis-(1,1-dimethylethyl)calix[6]arene (**2a)** (Scheme 1) has been describe*d.*[10] Purity of the synthesized compounds

was checked by TLC and ^{1}H NMR. The compound 37,38,39,40,41,42-hexakis(methoxycarbonylmethoxy)-5,11,17,23,29,35-hexakis(1,1- dimethylethyl) calix[6]arene **(2b)** was obtained in high yield by following the procedure reported for the synthesis of **2a**. ^{1}H NMR (300 MHz, $CDCl_3$) **2a** δ 0.95 (s, 54 H, ^{t}Bu), 1.24 (t, J = 7.6 Hz, 18 H, CH_3), 3.88-4.36 (bs, buried inside the quartet peak, Ar*CH*$_2$Ar), 4.17 (q, J = 7.0Hz, *CH*$_2$), 4.54 (s, 12 H, ArO*CH*$_2$), 6.96 (s, 12H, Ar*H*). **2b**; the signals were ill defined broad except the singlet at 1.14 due to *tert*-butyl resonance.

37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17,23,29,35-hexakis(1,1-dimethylethyl)calix[6]arene (**3)**

Synthesis of **3** has been described.[10] We synthesized this compound from **2a** based on the previously reported procedure employed for the synthesis of pentameric analogue.[9] In a typical run, the mixture of 4.0 g (2.68 mmol) **2a** and 1.8 g (32 mmol) KOH in 100 cm^3 THF/H_2O (70:30) was refluxed for 24 h under nitrogen flow. After completion of reaction (monitored by TLC), THF was evaporated and remaining suspension was diluted with water. The residue collected after filtration was suspended with 50% HCl (v/v) for several hours to affect the protonation of the carboxylate salt. The solid obtained was then filtered and washed several times with water. Recrystallization from THF/water yielded compound **3** in 93% yield. ^{1}H NMR (300 MHz) $CDCl_3$: δ 1.07 (s, 54H, ^{t}Bu), 3.41 (d, J = 15.6 Hz, 6H, Ar*CH*$_2$Ar, *exo*), 4.18 (bs, 12H ArO*CH*$_2$), 4.49 (d, J = 15.9 Hz, 6H, Ar*CH*$_2$Ar, *endo*), 6.94 (s, 12H, Ar*H*); CD_3CN:$CDCl_3$(1/1): δ 0.86 (s, 54H, ^{t}Bu), 3.22 (bs, 6H, Ar*CH*$_2$Ar), 3.91 (s, 12H, ArO*CH*$_2$), 4.24 (bs, 6H, Ar*CH*$_2$Ar), 6.76 (s, 12H, Ar*H*); Acetone-d6: δ 1.15 (s, 54H, ^{t}Bu), 3.65-4.22 (bs, Ar*CH*$_2$Ar), 4.22 (bs, 12H, ArO*CH*$_2$), 7.10 (s, 12H, Ar*H*); CD_3OD: δ 1.12 (s, 54H, ^{t}Bu), 3.54 (bs, 6H, Ar*CH*$_2$Ar), 4.22 (s, 12H, ArO*CH*$_2$), 4.49 (bs, 6H, Ar*CH*$_2$Ar), 7.05 (s, 12H, Ar*H*).

Figure SI1. 1H NMR spectra of 3 in different solvents.
(a) CDCl3, (b) CDCl3/CD3CN (1/1), (c) Acetone-d6, (d) MeOH-d4.

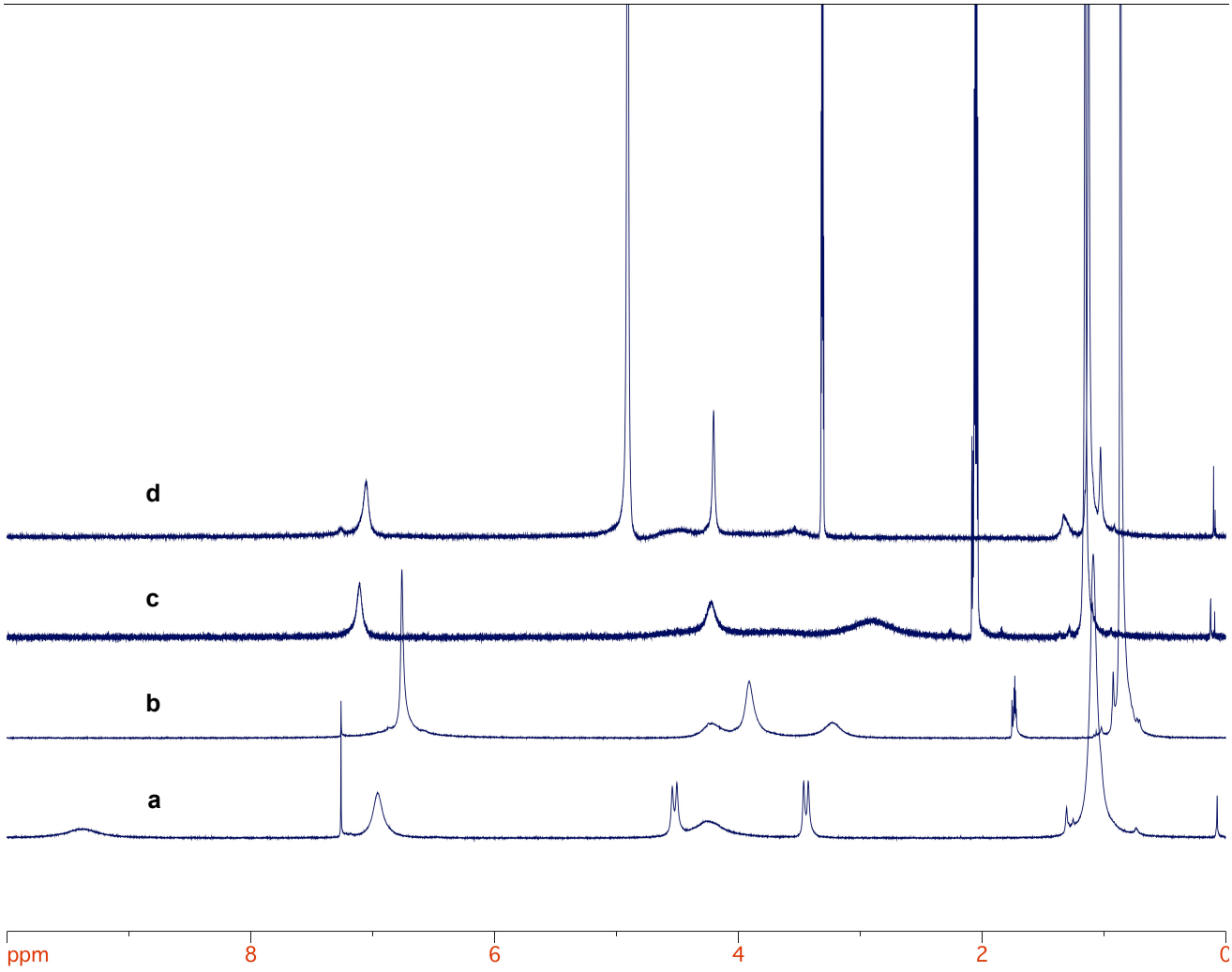
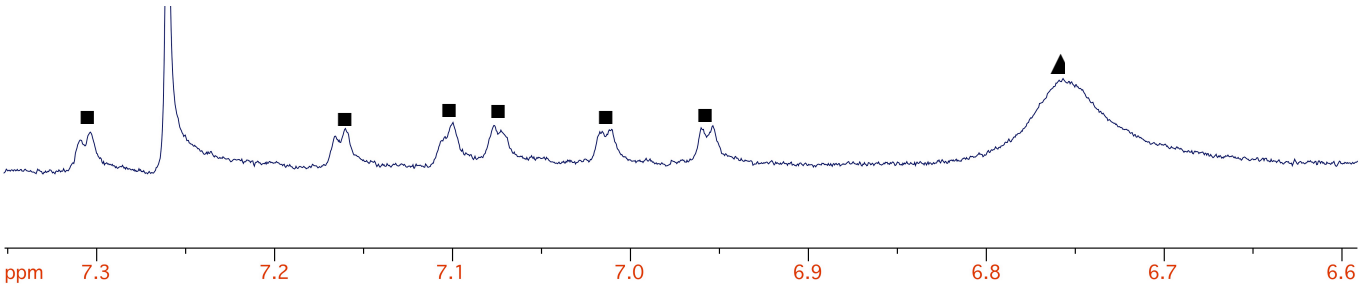
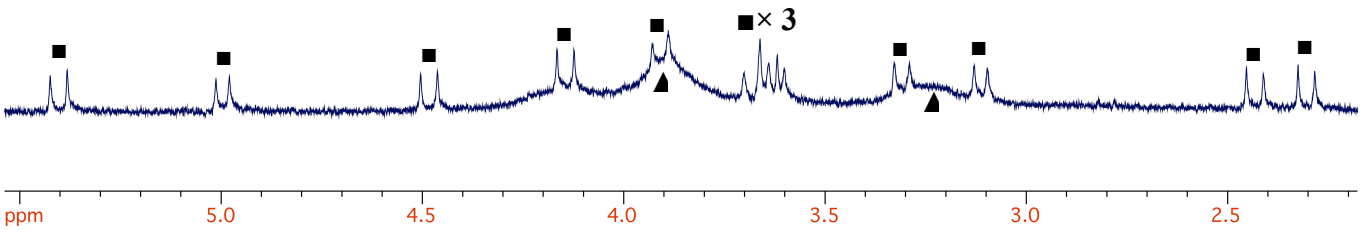


Figure SI2. 300 MHz ^{1}H NMR spectra of 3 in presence of 0.5 equivalent Pb(II) at the time of mixing.

(a) Three pairs of doublets for Ar*H* protons of the complexed ligand (■) and a singlet for non-complexed ligand (▲).



(b) Six pairs of doublets in the region of ArCH_2Ar and ArOCH_2 proton resonances (■). The broad humps (▲) are the signals due to non-complexed ligand.



(c) Three singlets for *tert*-butyl signal of Pb(II) complexed ligand (■) and a singlet for non-complexed ligand (▲).

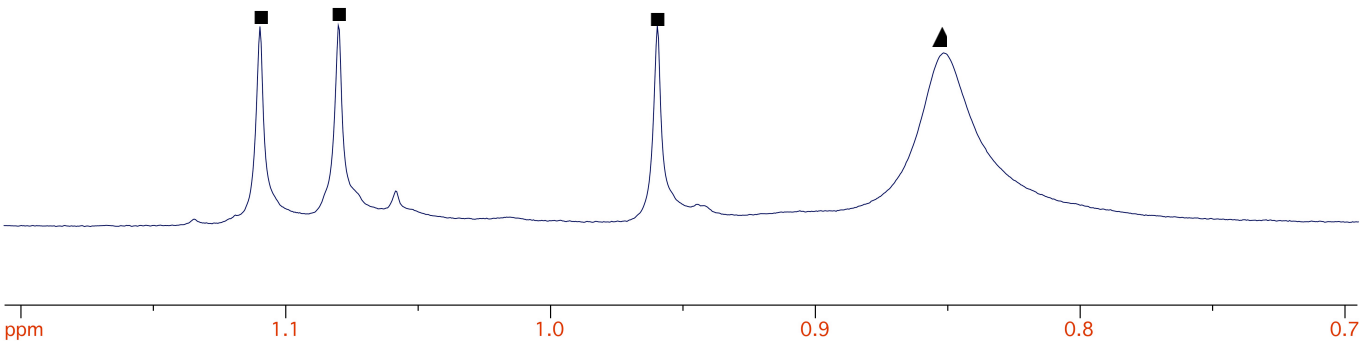
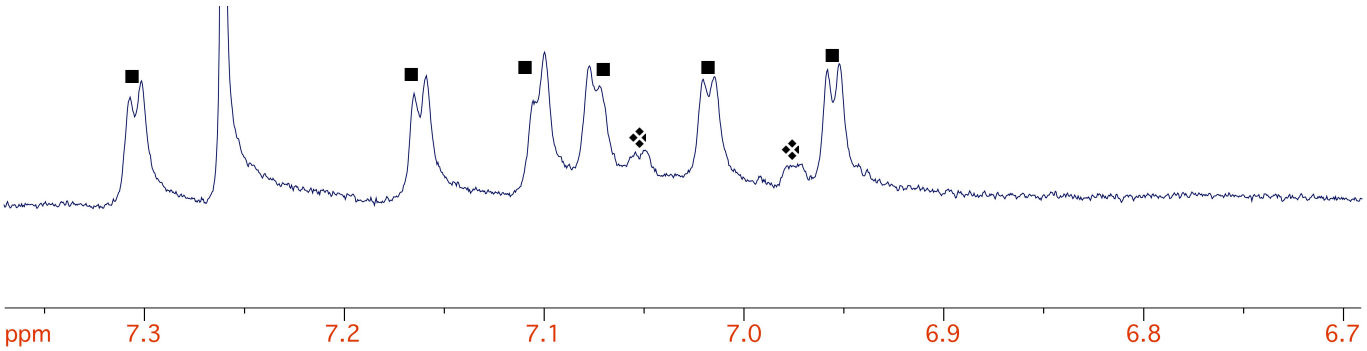
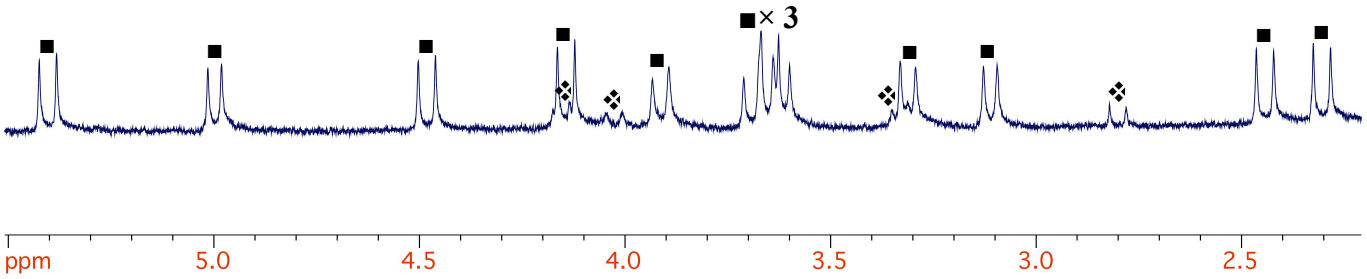


Figure SI3. 300 MHz ^{1}H NMR spectra of 3 in presence of 1.0 equivalent Pb(II) at the time of mixing.

(a) Three pairs of doublets for Ar*H* protons (■), the signal due to free ligand at 6.7 ppm vanished and a pair of doublet appeared as rudimentary signals (❖) at 6.97 and 7.05 ppm for new species.



(b) Six pairs of doublets (■) in the region of ArCH_2Ar and ArOCH_2 proton resonances. Two pairs of doublets (❖) appeared at 2.80, 3.33, 4.02 and 4.14 ppm for new species.



(c) Three singlets for *tert*-butyl signal of Pb(II)-complexed ligand (■), disappearance of the signal due to non-complexed ligand and appearance of a rudimentary signal (❖) for new species at 1.06 ppm.

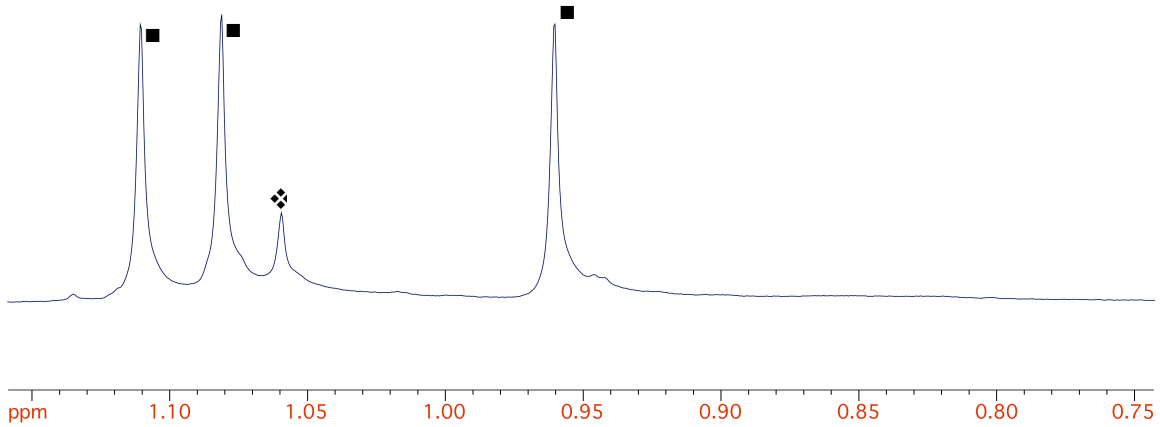


Figure SI4. 300 MHz ^{1}H NMR spectrum of 3·Pb(II) complex after 26 hours

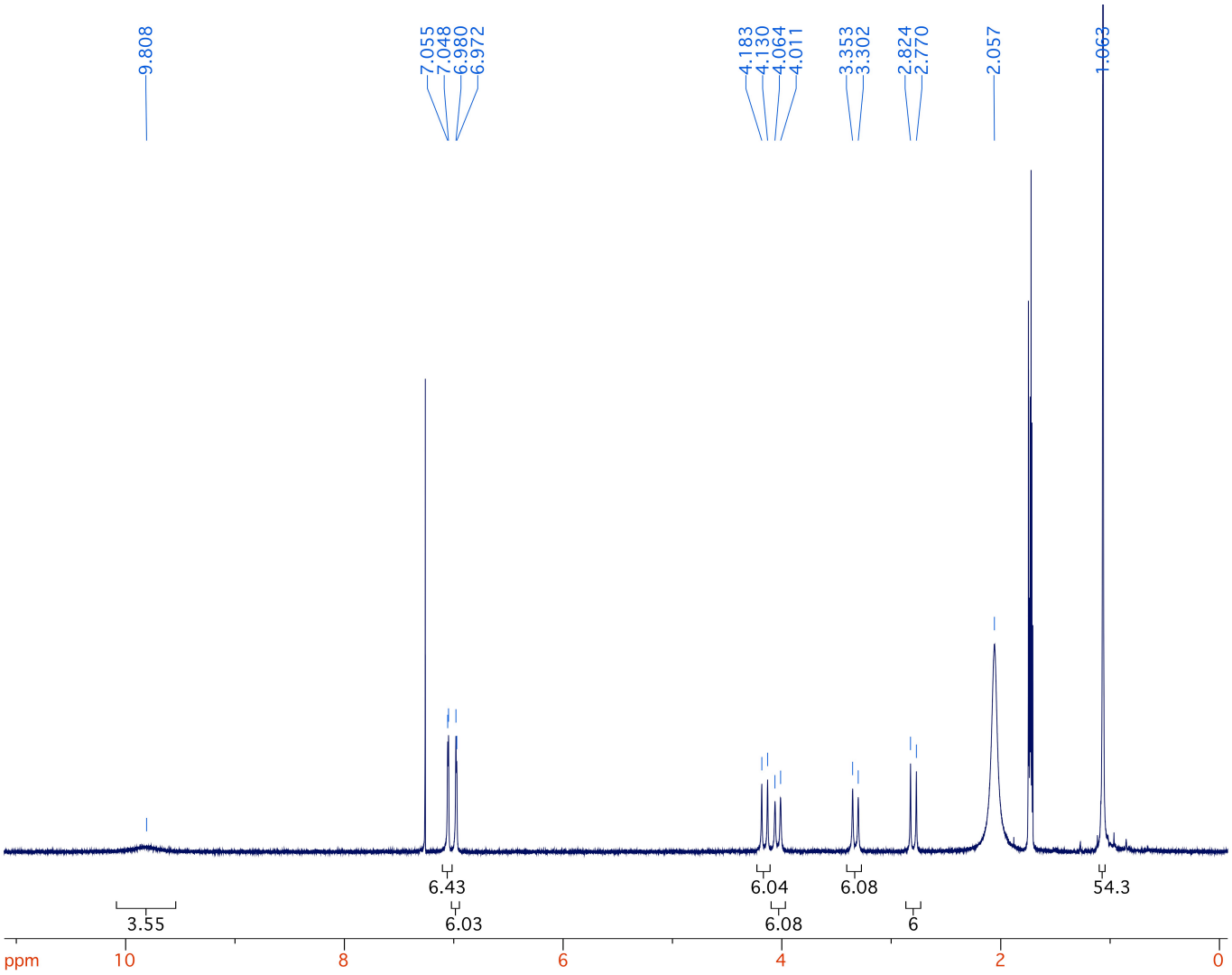


Figure SI5. 300 MHz ^{1}H NMR spectrum of 3·Pb(II) complex after 15 days.

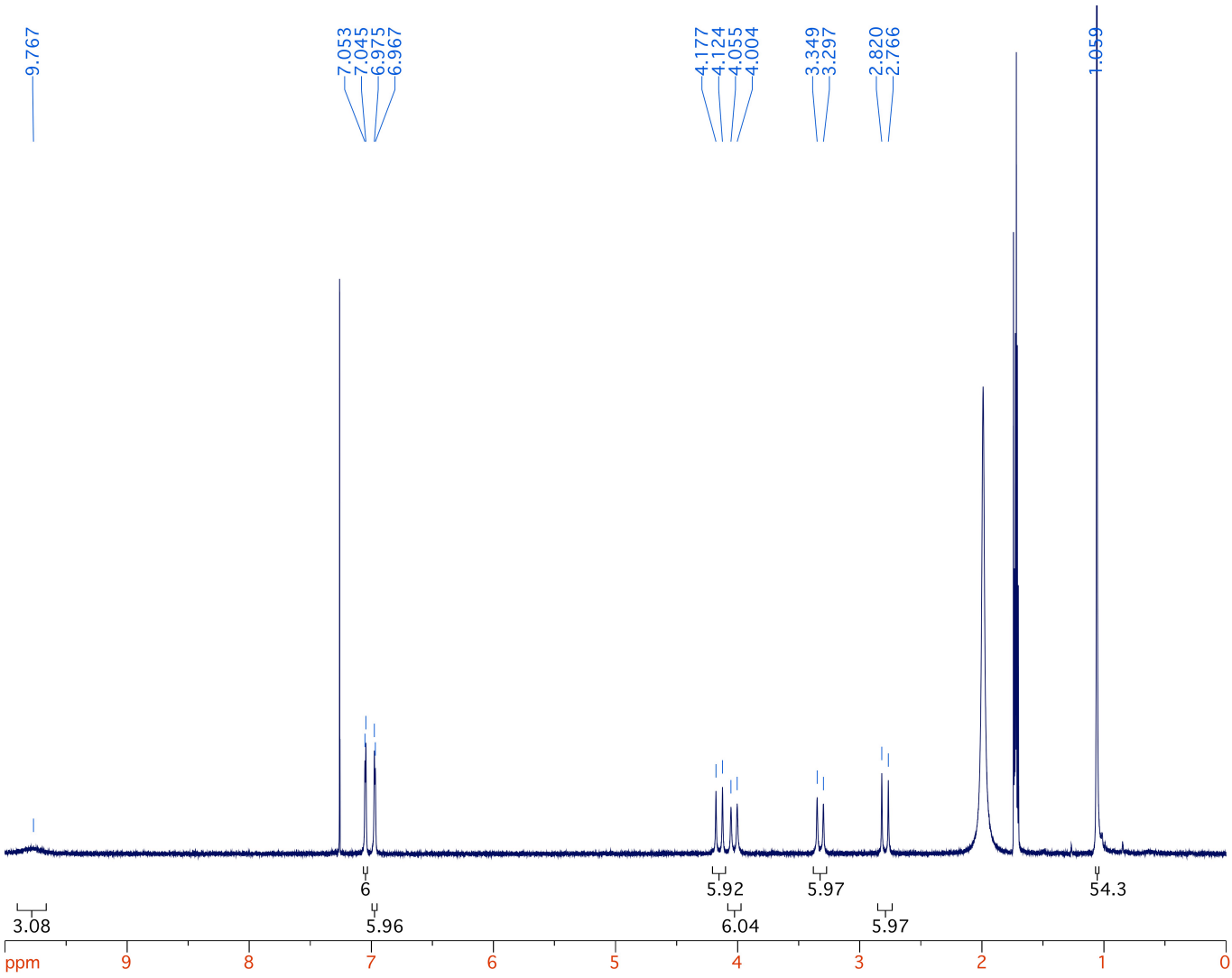
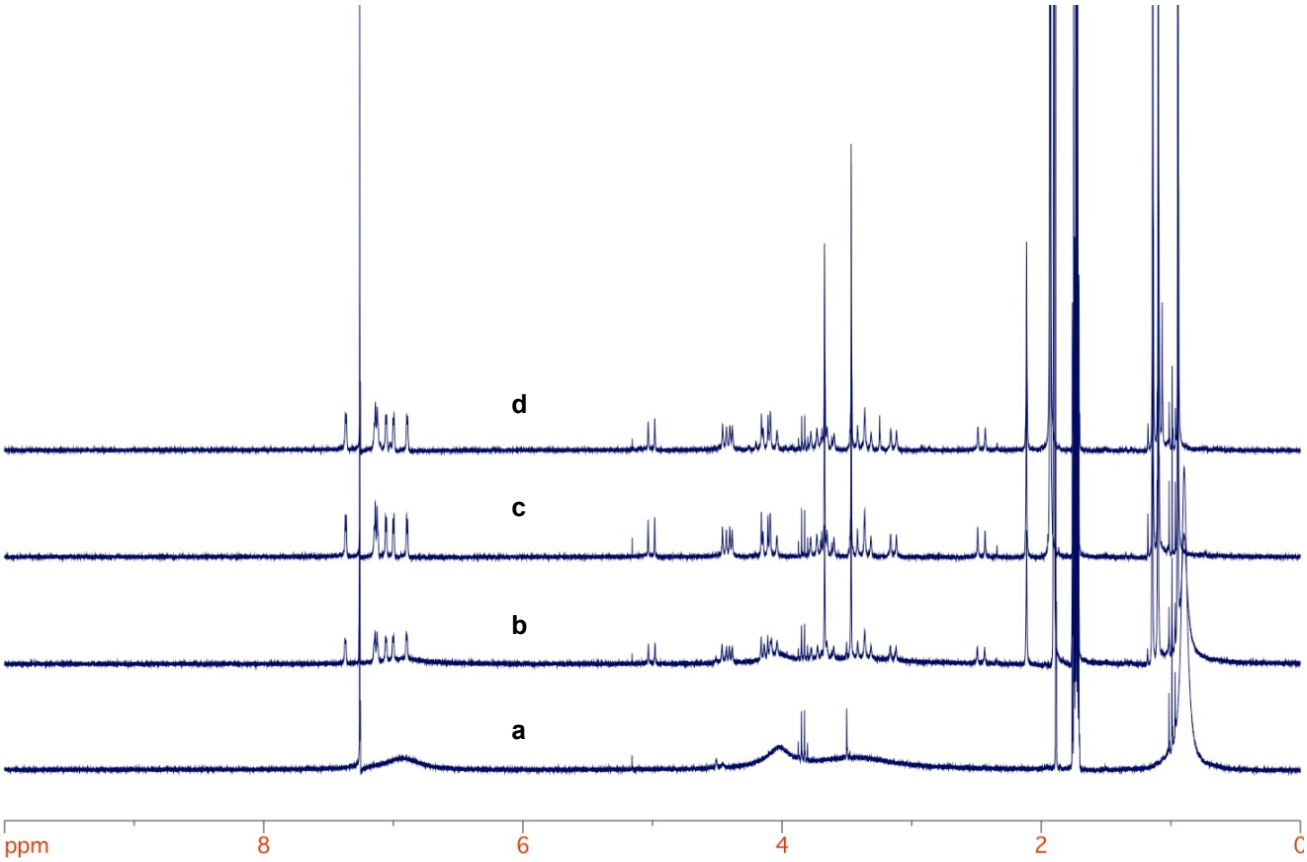


Figure SI6. 300 MHz ^{1}H NMR from titration of TBC[6]CH_2COOMe (2b) with Pb(II)



^{1}H NMR titration of **2b** with $Pb(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1/1).(a) free host, (b) and (c) in presence of 0.5 and 1.0 equivalents Pb(II) respectively, (d) in presence of 1.0 equivalents Pb(II) after 24 hours. Residual solvent peak due to $CHCl_3$ is at 7.26 ppm and due to CH_3CN is at 1.73 ppm.

Figure SI7. 300 MHz ^{1}H NMR spectrum of 3·Pb(II) complex at 253 K and 333 K.

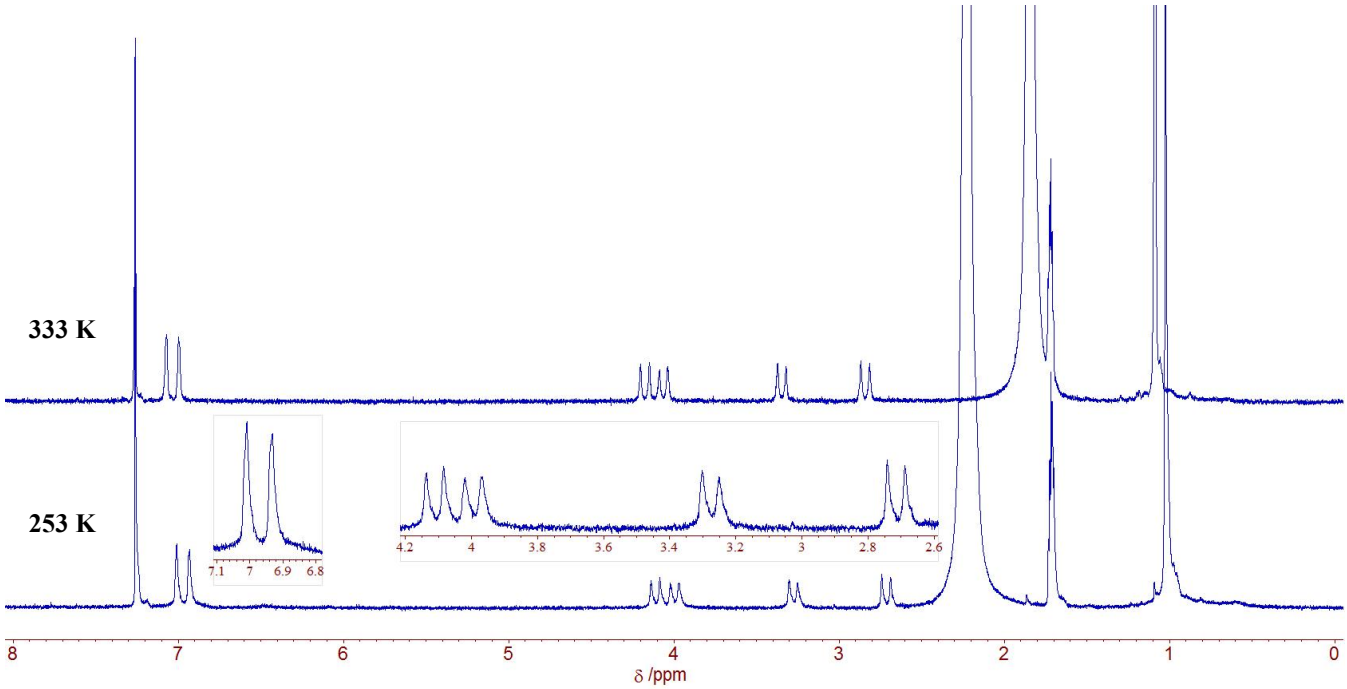


Figure SI8. 75 MHz ^{13}C NMR spectrum of equilibrium sample of 3·Pb(II) complex.

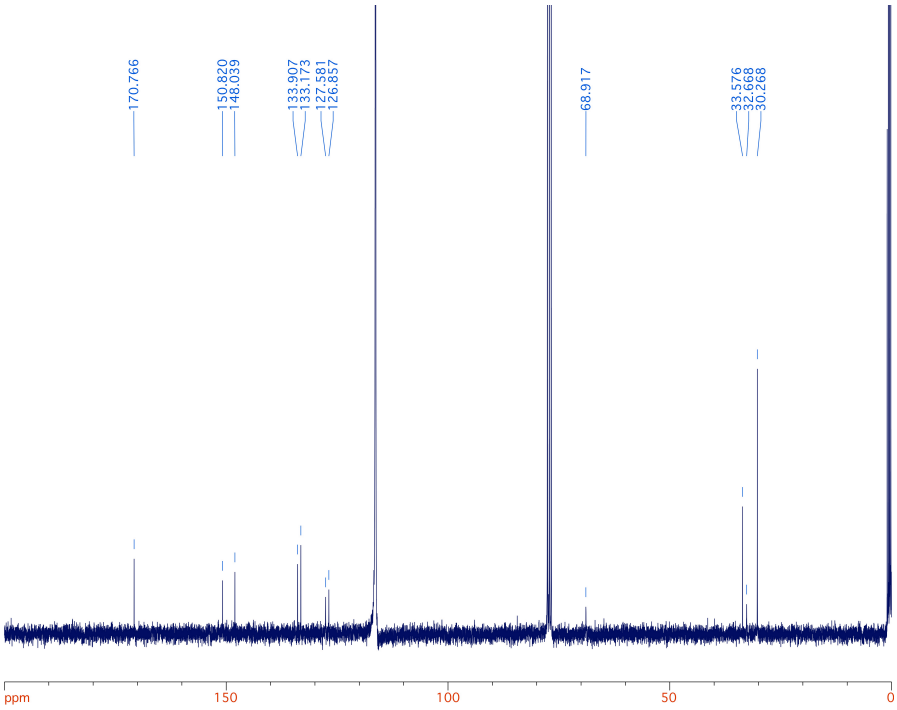


Figure SI9. 75 MHz DEPT-135 spectrum of equilibrium sample of 3·Pb(II) complex.

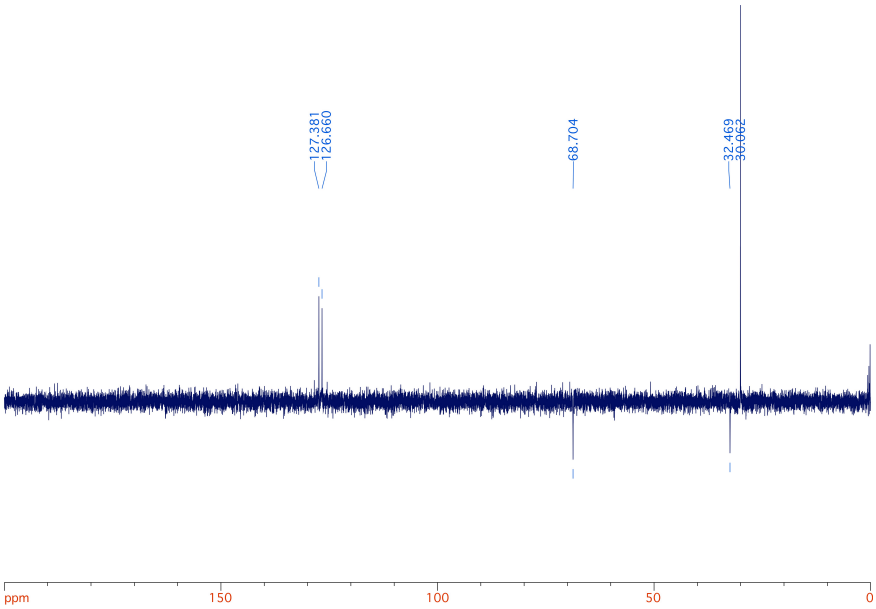


Figure SI10. 300 MHz ^{1}H NMR spectra of 3·Pb(II) complex at equilibrium.
The expanded signals show the non-equivalent nature of ArH protons with meta-coupling and diastereotopic nature of ArOCH2 protons.

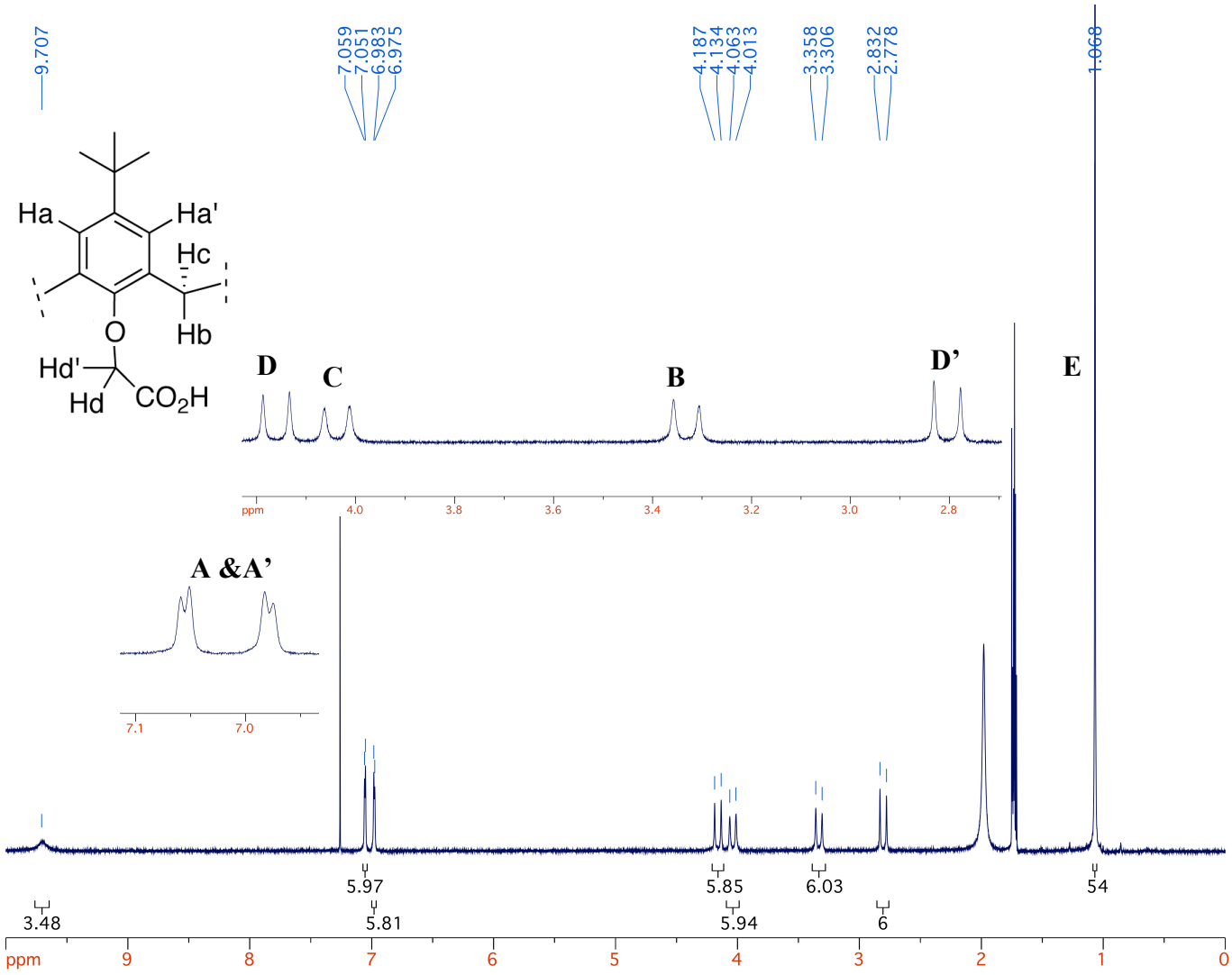


Figure SI11. 300 MHz COSY data of equilibrium sample of 3 in presence of 1.0 equivalent $Pb(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1/1).

COSY NMR data was acquired on a Bruker 300 MHz Fourier spectrometer using the cosygpqf pulse program, 128 X 48 scans, AQ = 0.168 s, TE = 294.7 K, D1 = 2.01 s.

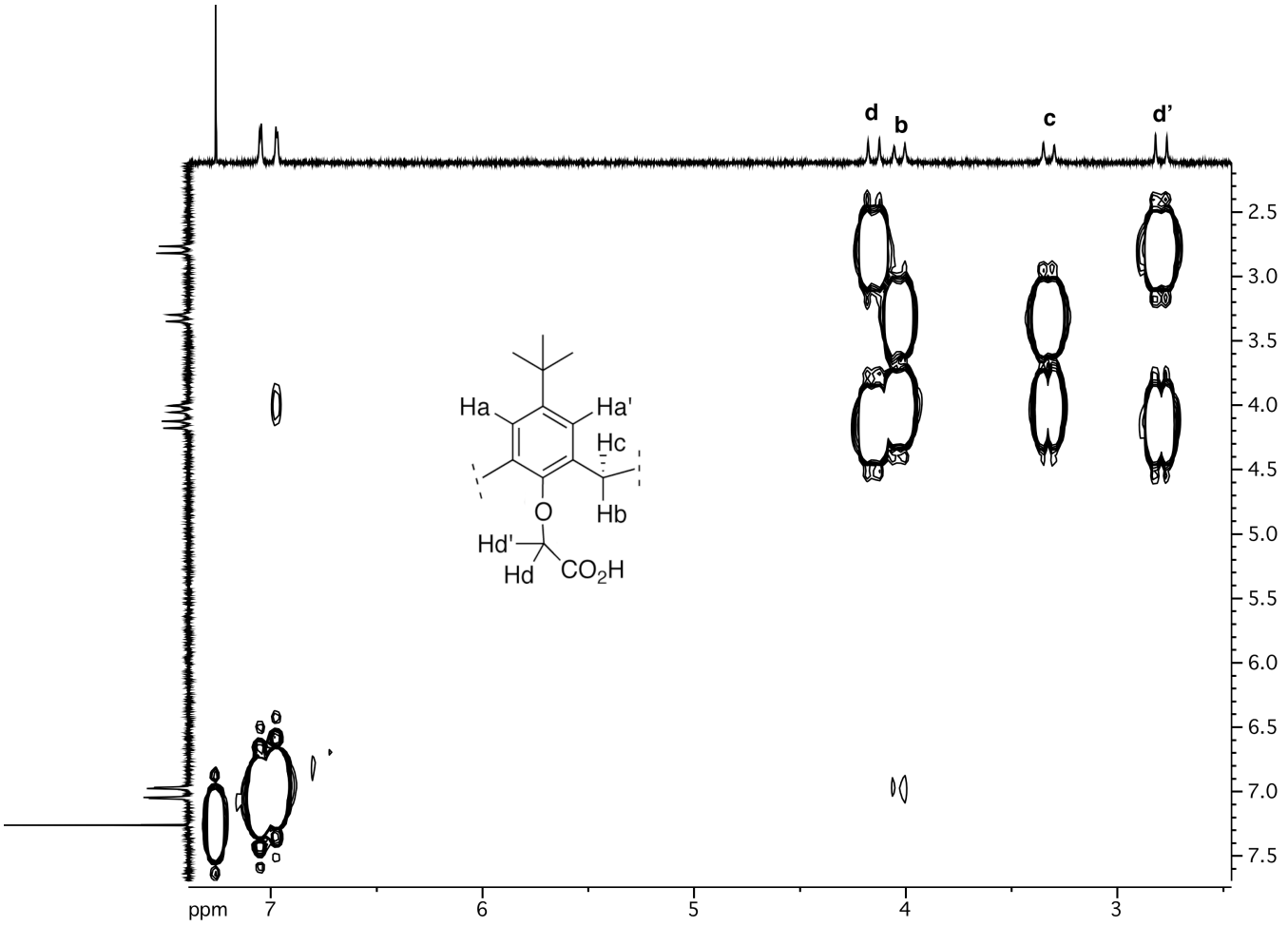


Figure SI12. 300 MHz NOESY data of equilibrium sample of 3 in presence of 1.0 equivalent $Pb(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1/1).

NOESY NMR data was acquired on a Bruker 300 MHz Fourier spectrometer using the noesygpph pulse program, 256 X 24 scans, AQ = 0.168 s, TE = 294.6 K, D1 = 2.01 s, D8 = 0.30 s. Results were nearly identical for D8 = 0.45 s.

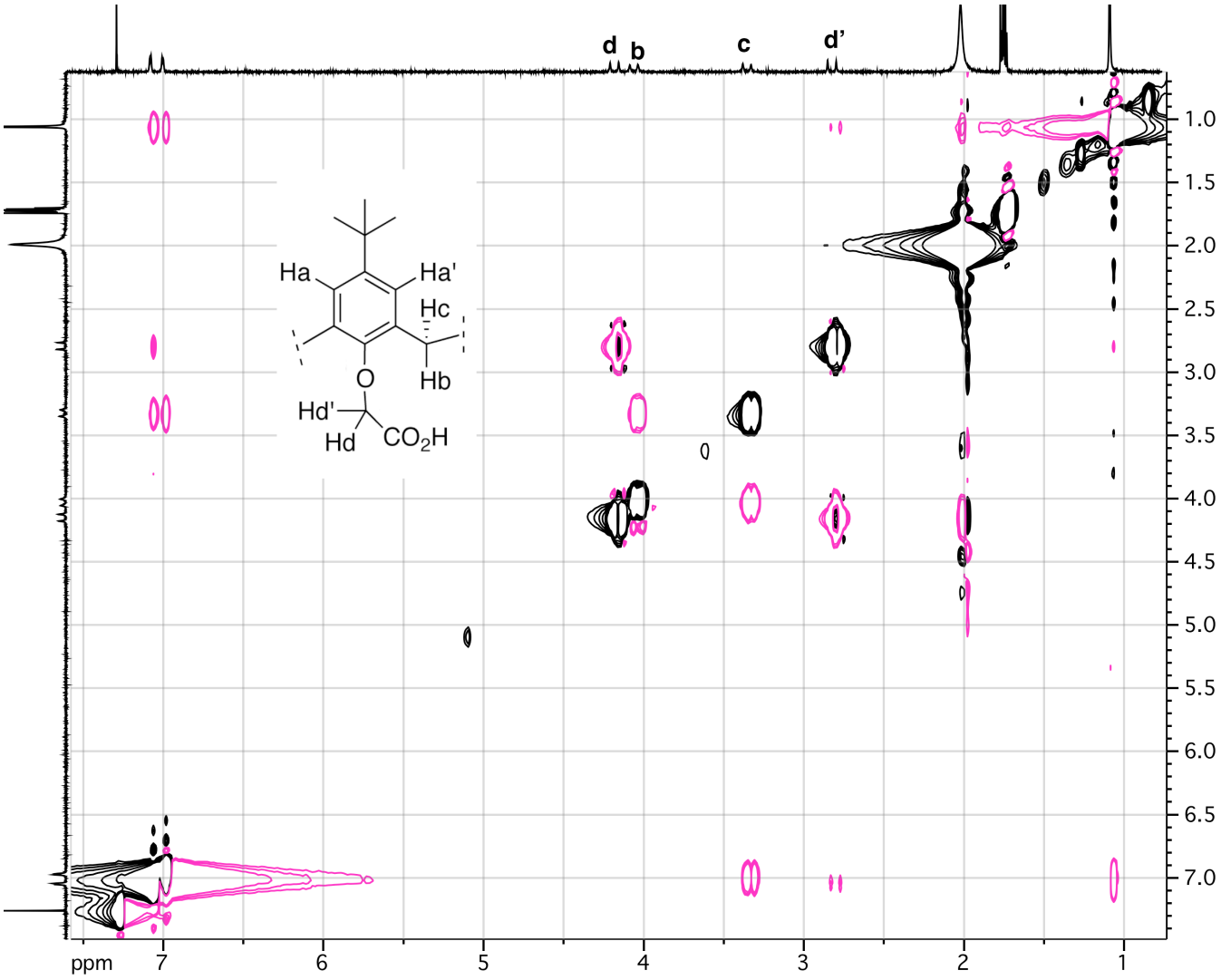
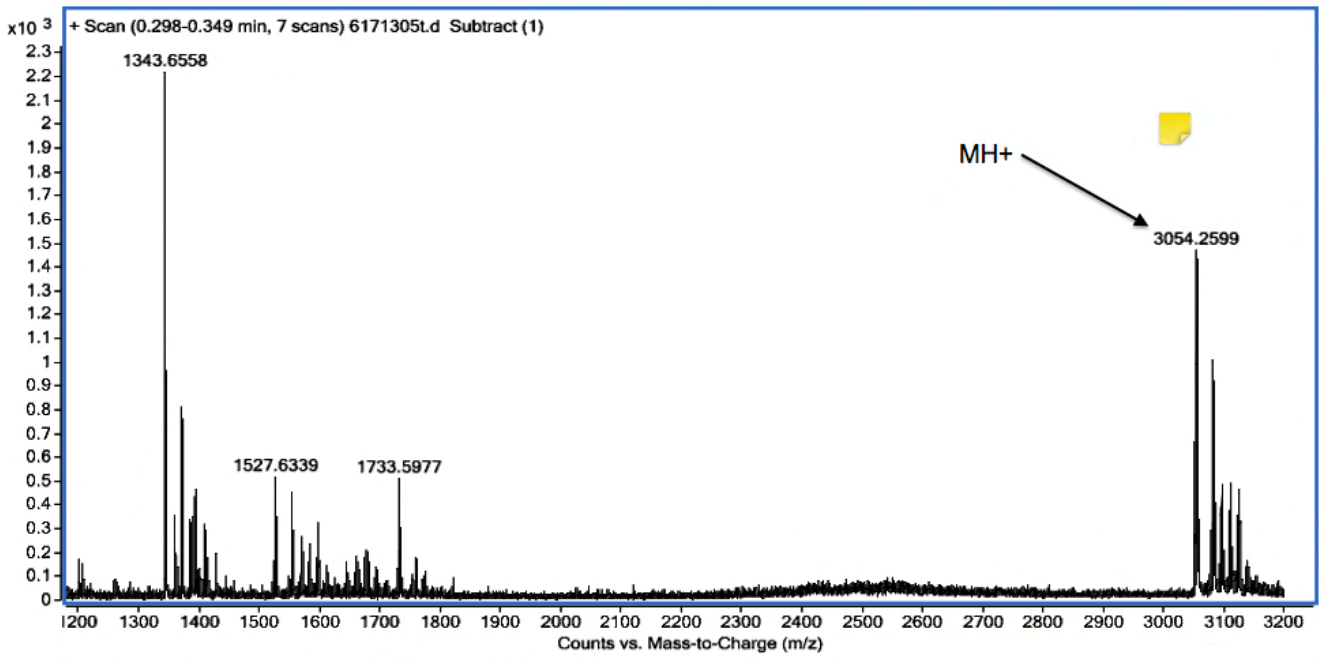
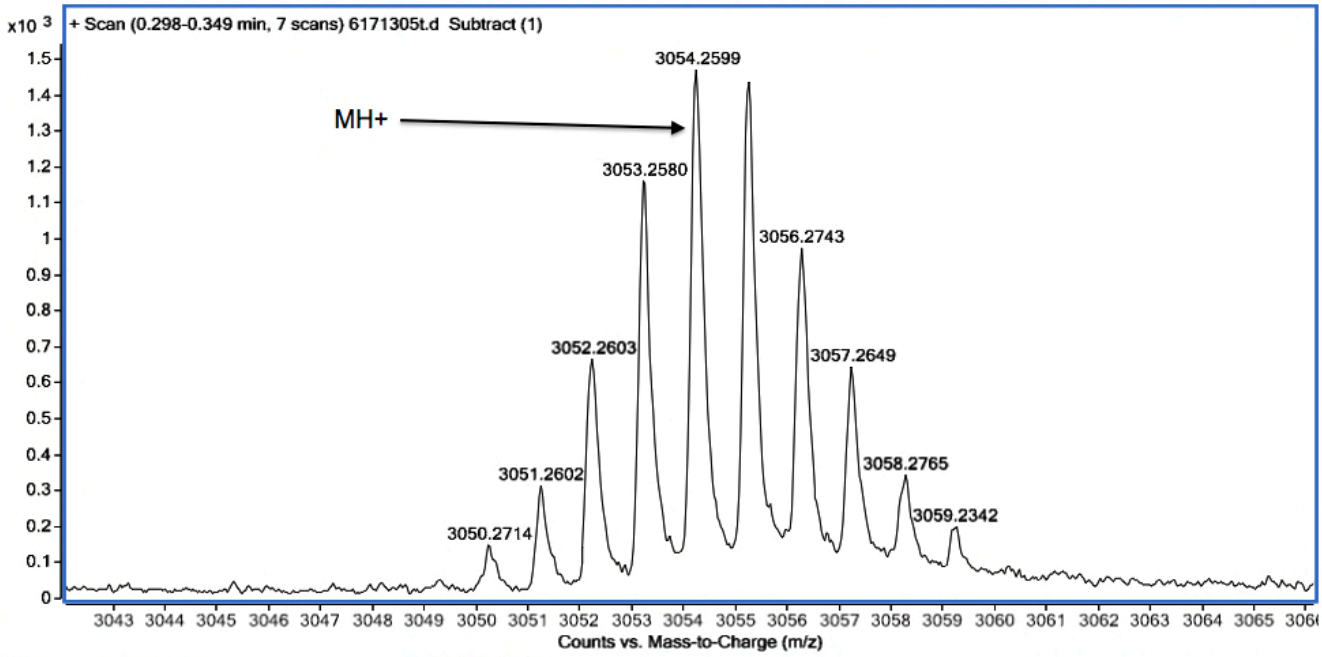


Figure SI13. Mass spectrum of equilibrium sample of 3 complexed with 1 equivalent Pb(II) ion.





Measured Mass 3054.2599

Figure SI14. DOSY data of equilibrium sample of 3 in presence of 0.5 equivalent $Pb(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1/1).

4 identifies peaks for the 1:1 **3**•Pb(II) complex, **3** identifies peaks for the free host.

DOSY NMR data was acquired at 300 MHz with 256 scans using 25 gradients exponentially spaced from 5 to 95%. Diffusion data was extracted from peak integrals using the standard parameters in Topspin and reported as calculated from Simfit results. DOSY plot prepared using DOSY Toolbox v1.5.

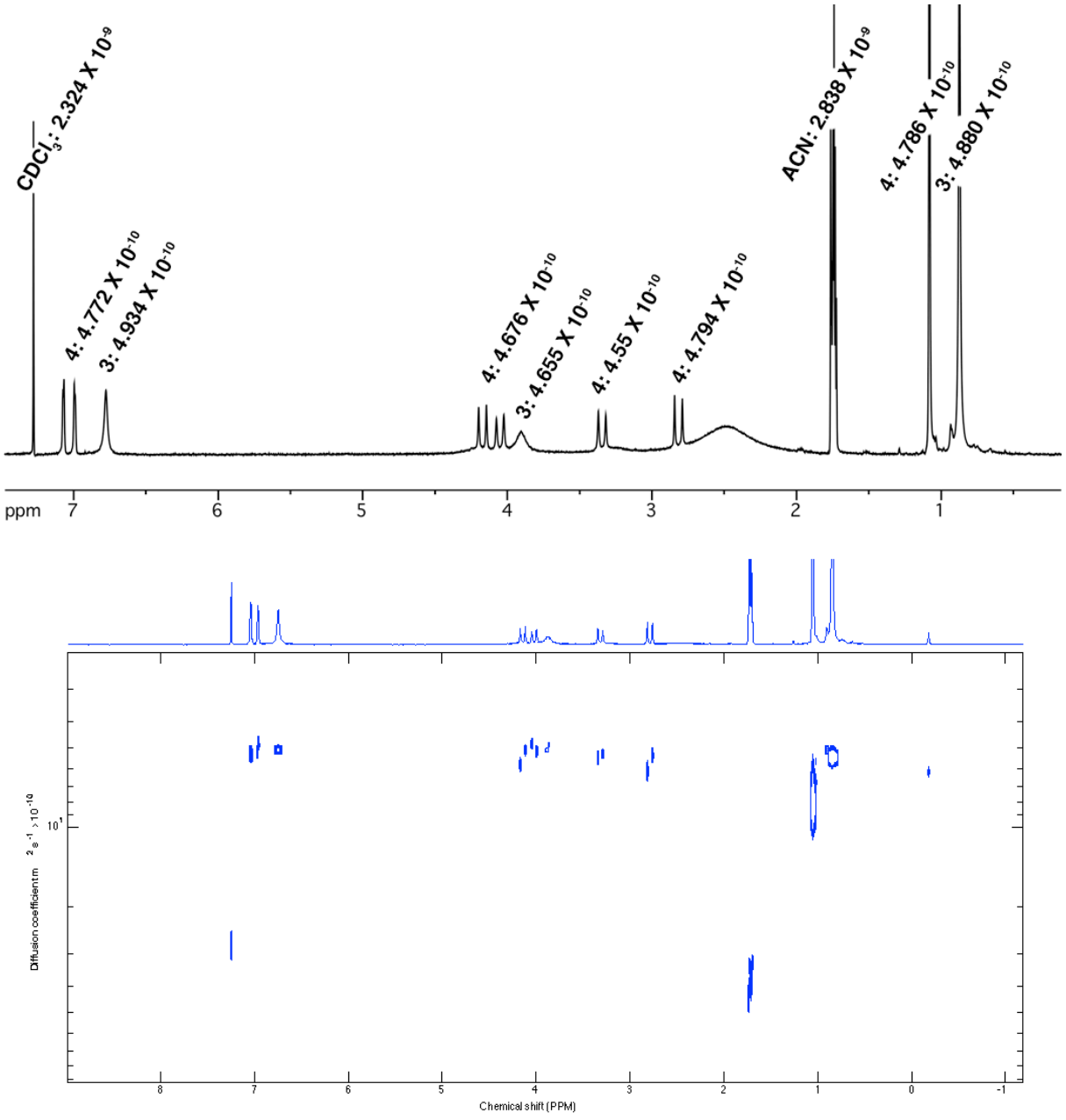


Figure SI15. Mass spectrum of 3 in presence of 1 equivalent Pb(II) ion after 30 minutes.

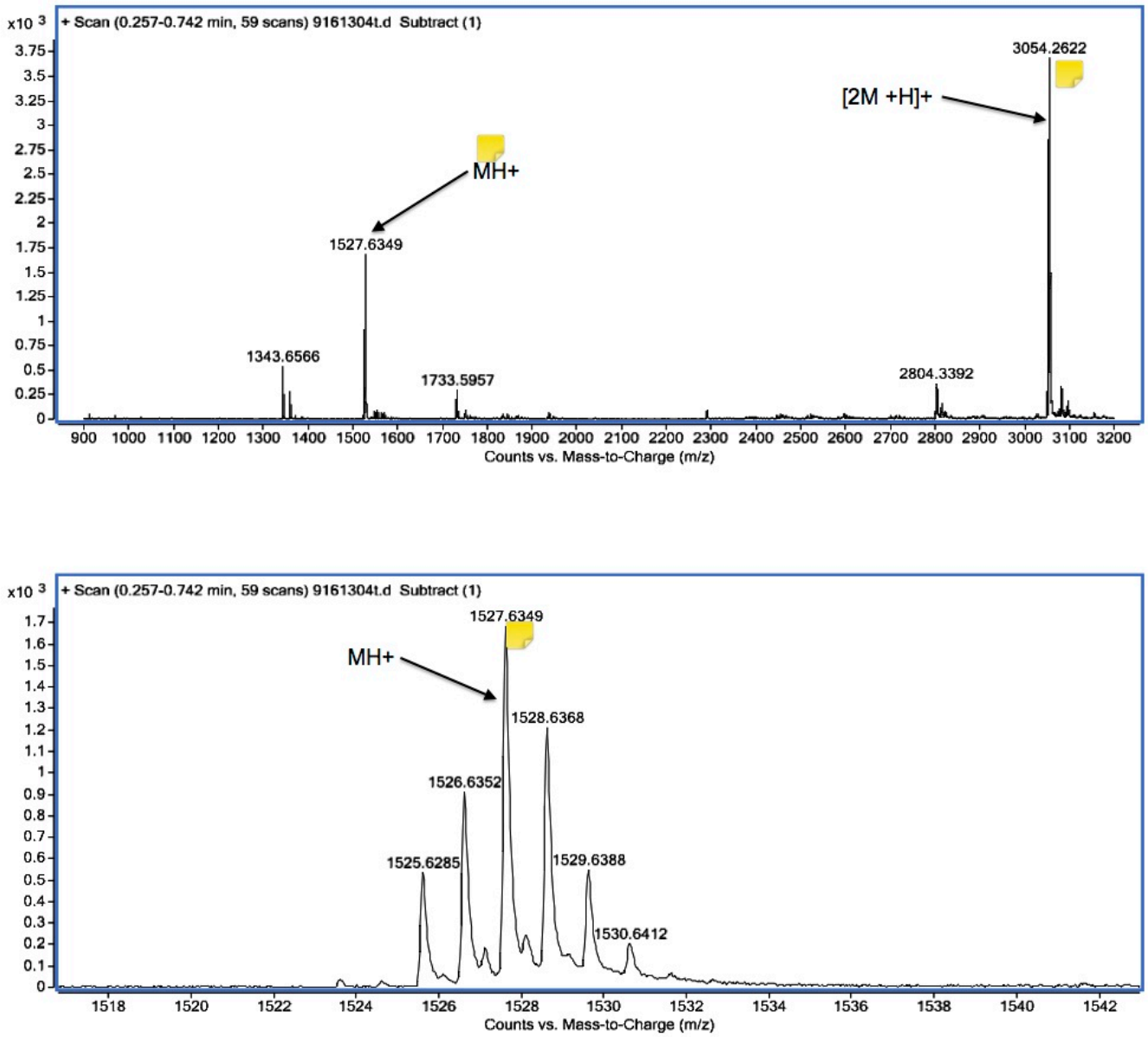
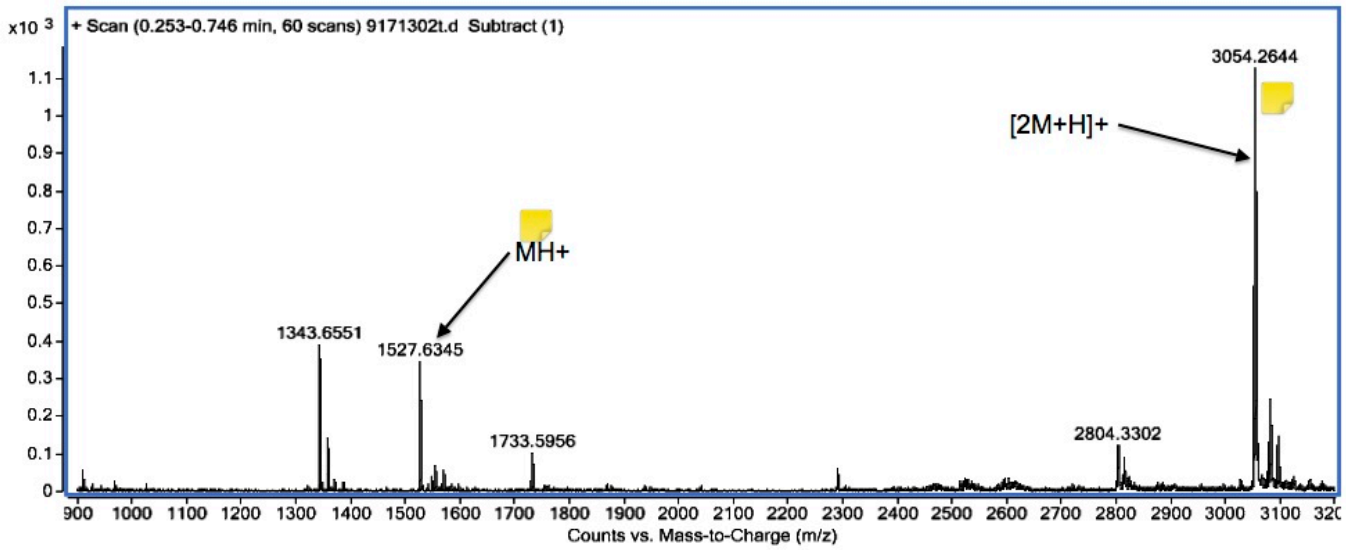


Figure SI16. Mass spectrum of 3 in presence of 1 equivalent Pb(II) ion after 24 hours.



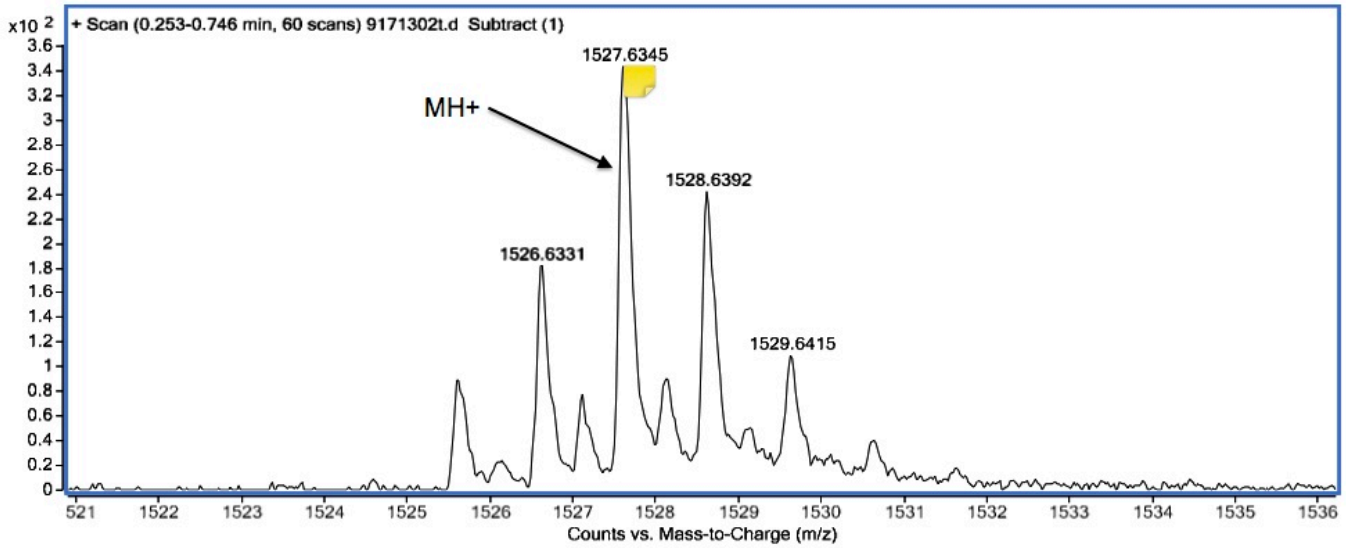
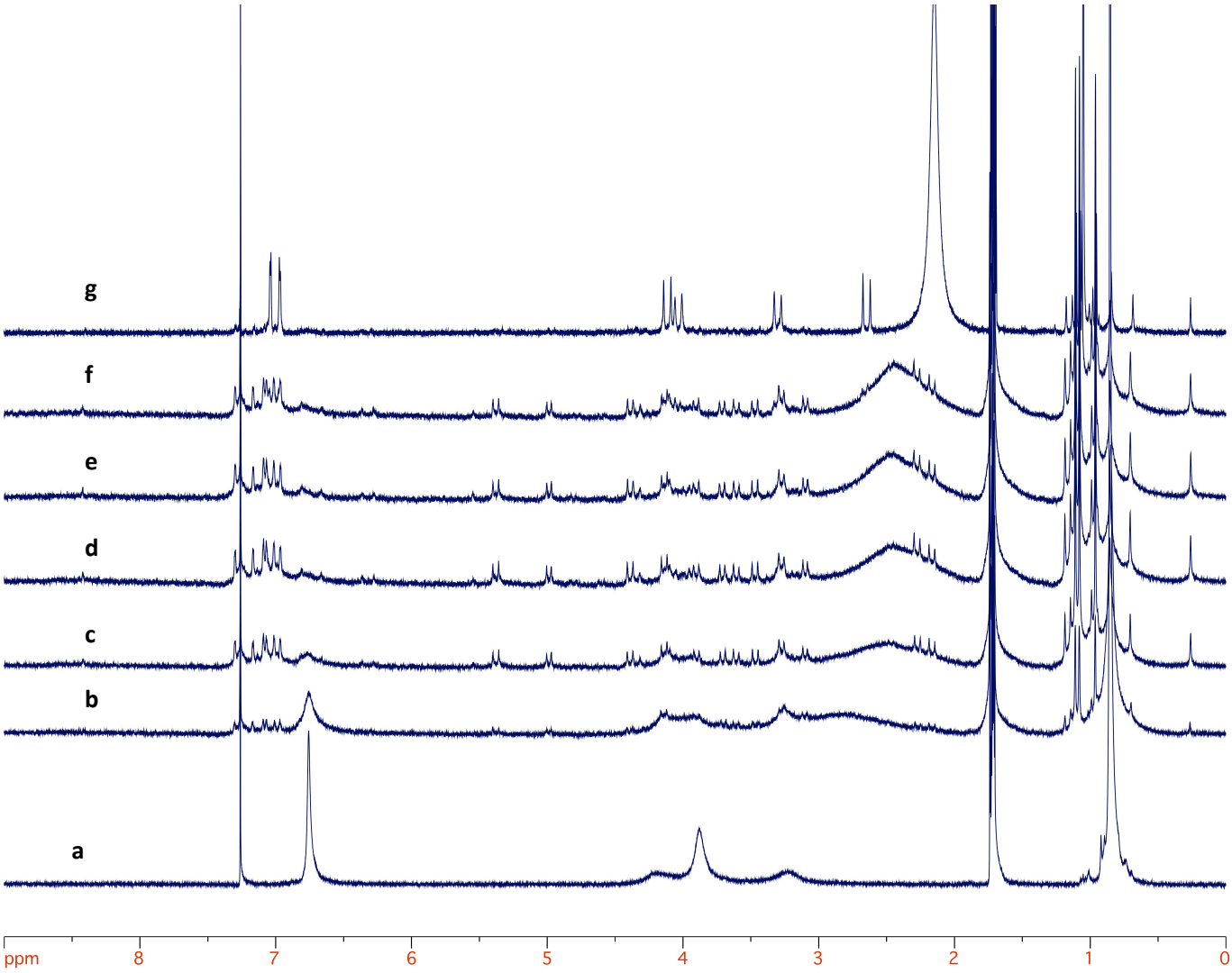


Figure SI17. ^{1}H NMR titration of 3 with $Sr(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1/1).



^{1}H NMR titration (400 MHz) of **3** (5.0 mM) with various equivalents of $Sr(ClO_4)_2.3H_2O$ in $CDCl_3/CD_3CN$ =1/1. (a) free ligand, (b)-(e) in presence of 0.5, 0.75, 1.0 and 2.0 equivalents Sr(II), respectively, (f) in presence of 1.0 equivalent Sr(II) after 24 hours and (g) in presence of 1.0 equivalent Sr(II) after two weeks. Residual solvent peak due to CH_3CN is at 1.73 ppm and due to $CHCl_3$ is at 7.26 ppm.

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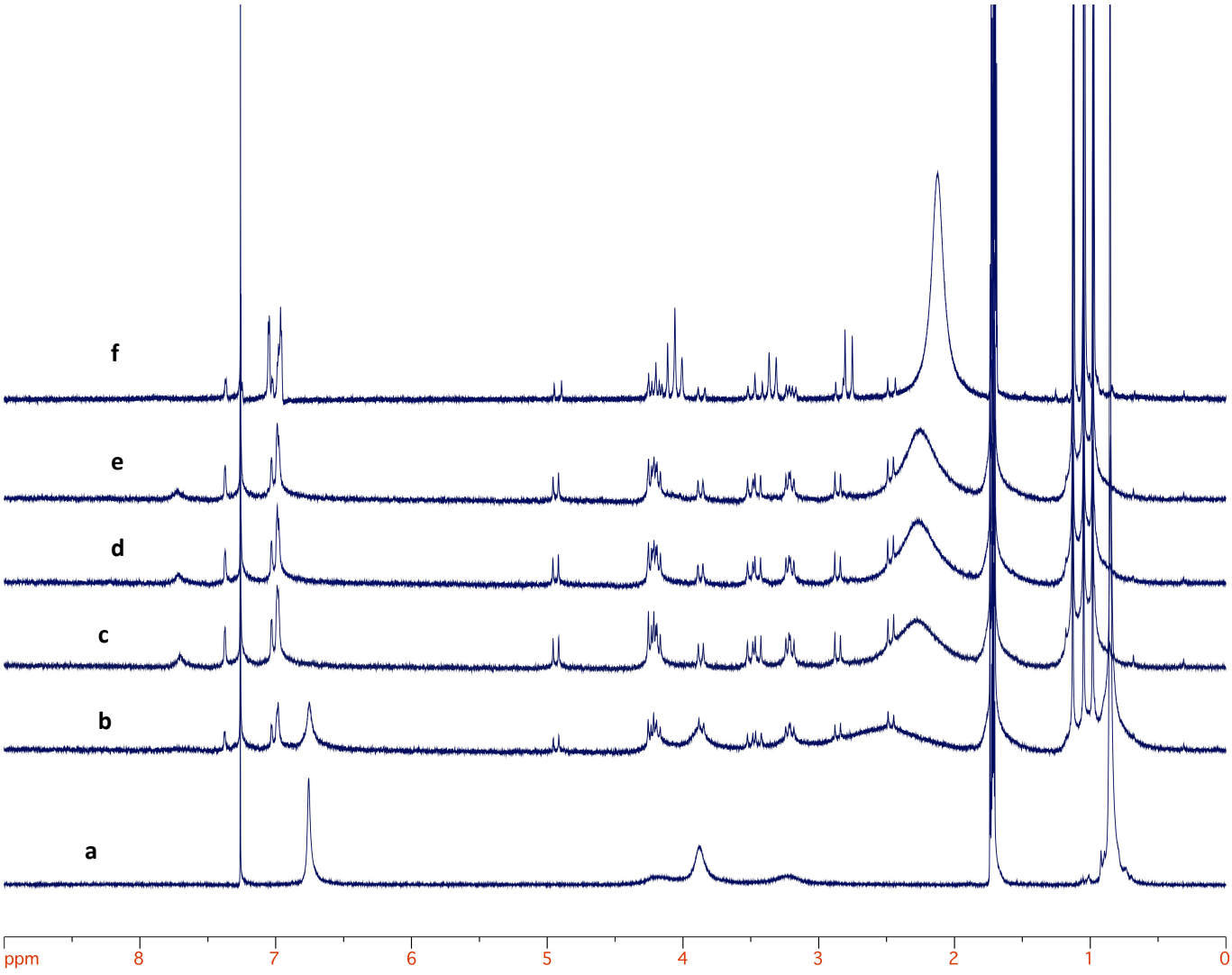
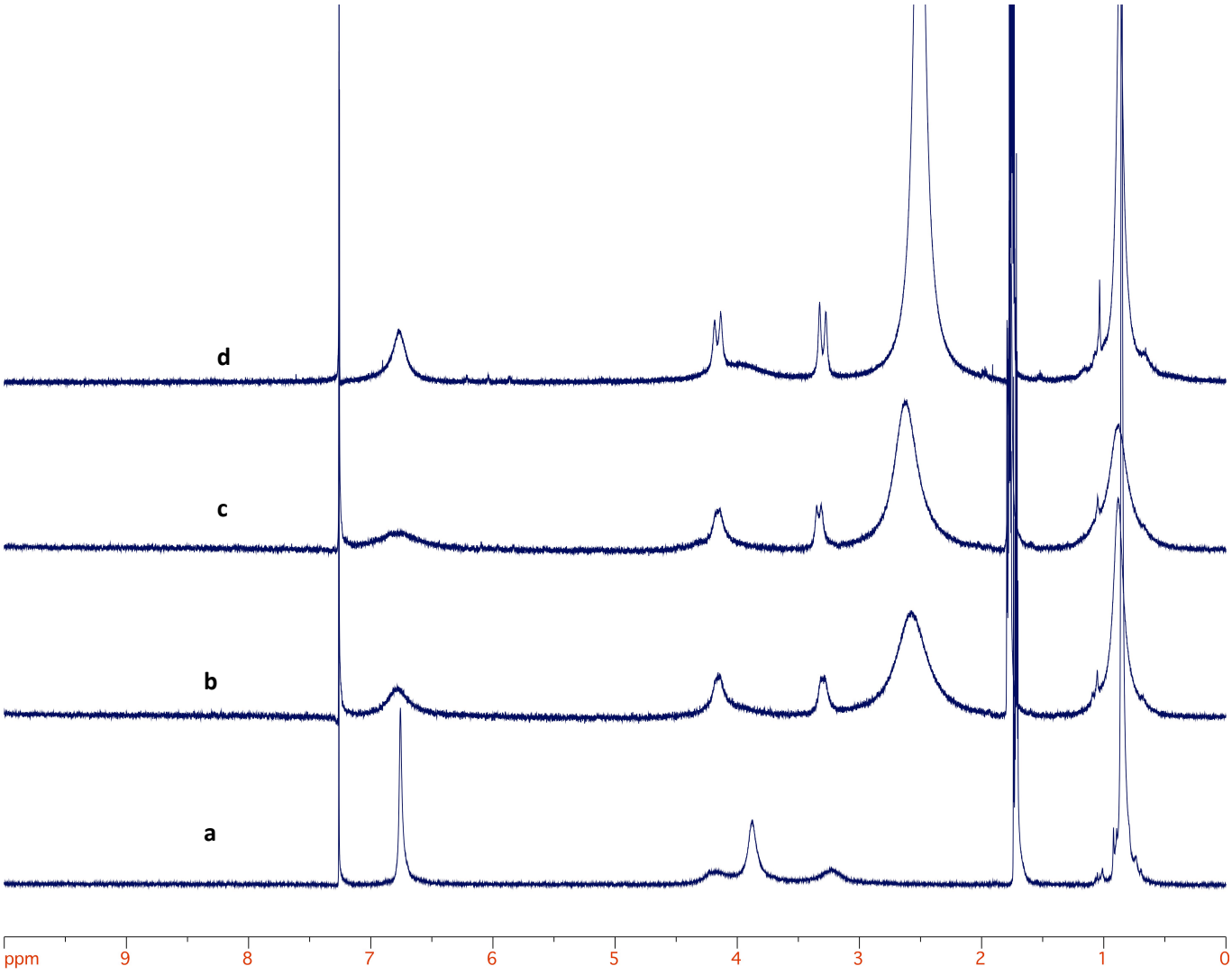
Figure SI18. ^{1}H NMR titration of 3 with $Ba(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1/1).



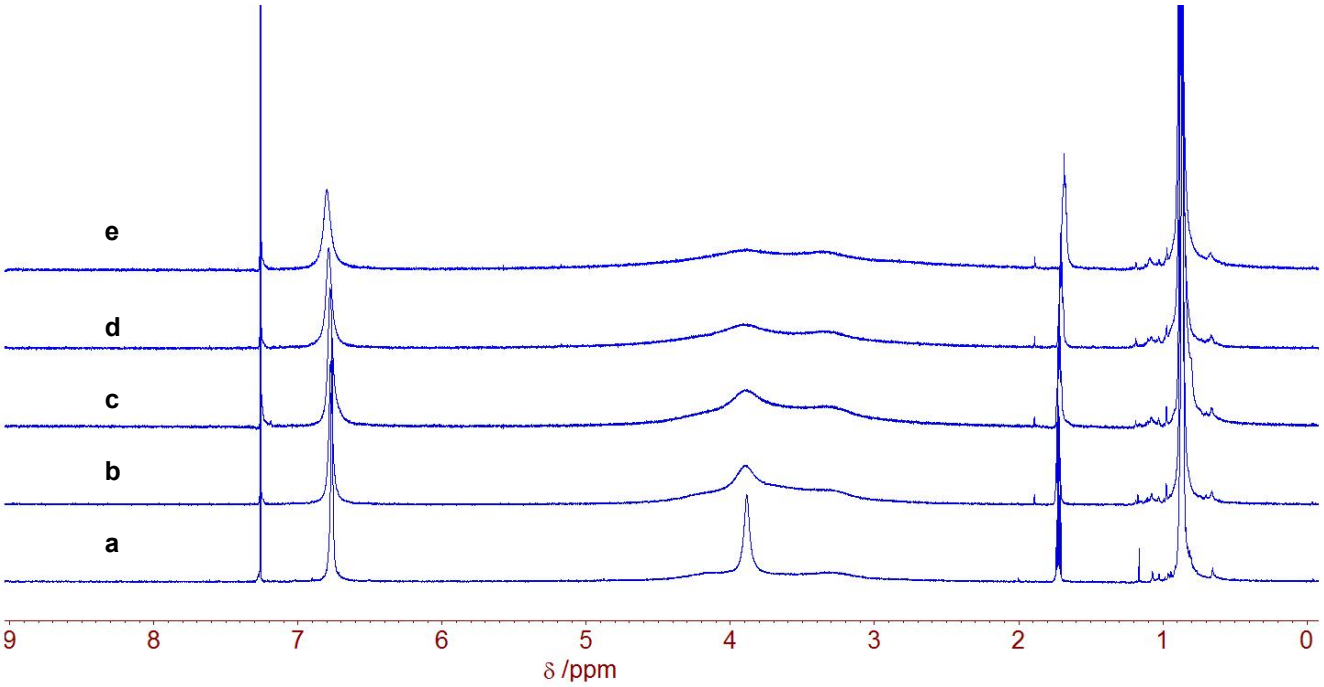
^{1}H NMR titration (400 MHz) of **3** (5.0 mM) with various equivalents of $Ba(ClO_4)_2.3H_2O$ in $CDCl_3/CD_3CN$ =1/1. (a) free ligand, (b)-(d) in presence of 0.5, 1.0 and 2.0 equivalents Ba(II), respectively, (e) in presence of 1.0 equivalent Ba(II) after 24 hours and (f) in presence of 1.0 equivalent Ba(II) after two weeks, respectively. Residual solvent peak due to CH_3CN is at 1.73 ppm and due to $CHCl_3$ is at 7.26 ppm.

Figure SI19. ^{1}H NMR titration of 3 with $Ca(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1/1).



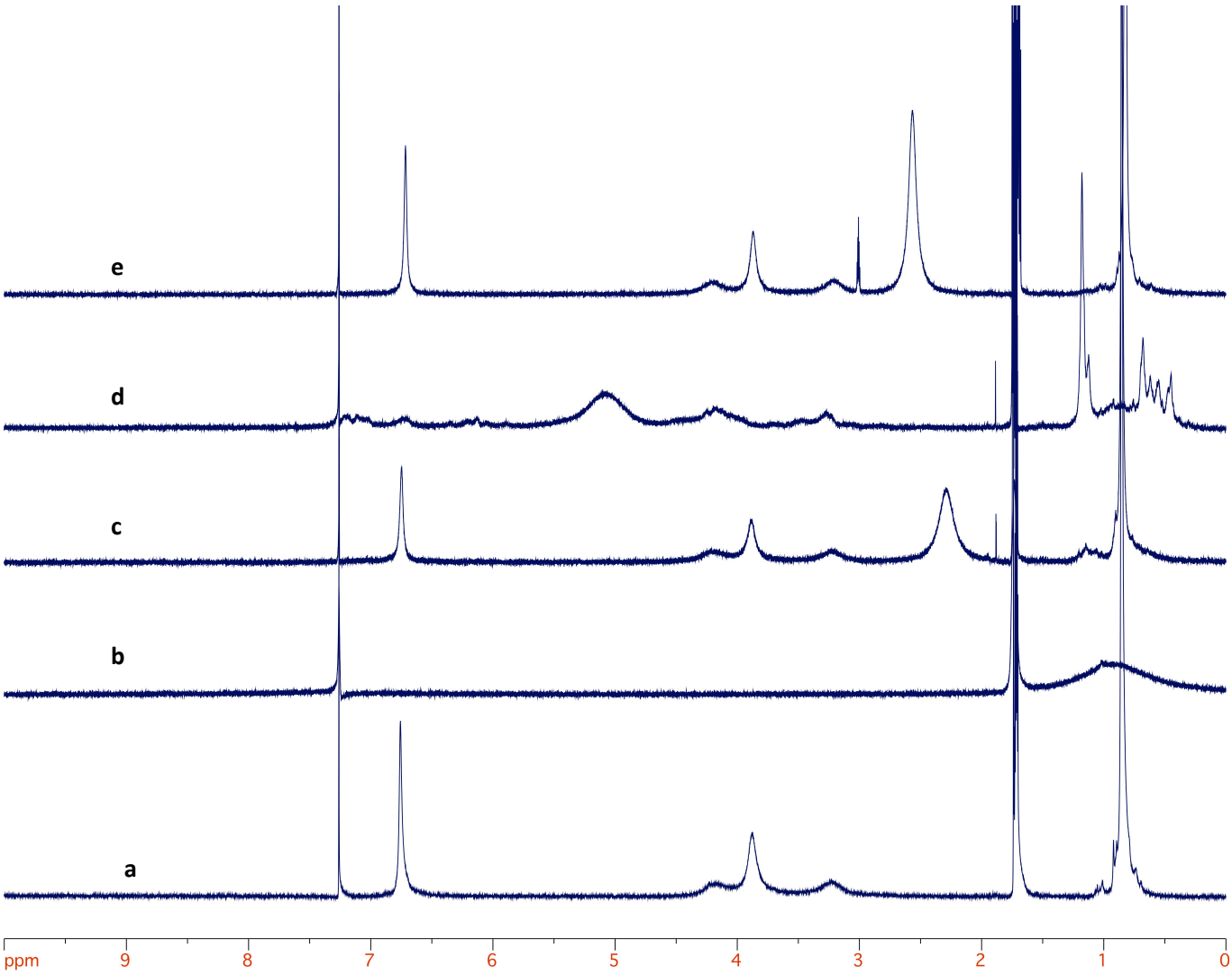
^{1}H NMR titration (300 MHz) of **3** (5.0 mM) with various equivalents of $Ca(ClO_4)_2$.3H2O in $CDCl_3/CD_3CN$ =1/1. (a) free ligand (b) in presence of 0.5 eq Ca(II), (c) in presence of 1.0 equivalent Ca(II) and (d) in presence of 1 equivalent Ca(II) after two weeks, respectively. Residual solvent peak due to CH_3CN is at 1.73 ppm and due to $CHCl_3$ is at 7.26 ppm.

Figure SI20. ^{1}H NMR titration of 3 with $Cu(ClO_4)_2 \cdot 3H_2O$ in $CDCl_3/CD_3CN$ (1/1).



^{1}H NMR titration (300 MHz) of **3** (5.0 mM) with various equivalents of $Cu(ClO_4)_2$ in $CDCl_3/CD_3CN$ =1/1. (a) free ligand and (b) - (e) = in presence of 0.25, 0.5, 1.0 and 2.0 equivalents Cu(II), respectively. Residual solvent peak due to CH_3CN is at 1.73 ppm and due to $CHCl_3$ is at 7.26 ppm.

Figure SI21. ^{1}H NMR of 3 in presence of 1 equivalent Gd(III), Y(III), Bi(III) and UO_2(II) in $CDCl_3/CD_3CN$ (1/1).



^{1}H NMR (300 MHz) of **3** (5.0 mM) in presence of 1 equivalents of different cations in $CDCl_3/CD_3CN$ =1/1. (a) free ligand and (b) - (e) = in presence of 1 equivalents Gd(III), Y(III), Bi(III) and UO_2(II), respectively. Residual solvent peak due to CH_3CN is at 1.73 ppm and due to $CHCl_3$ is at 7.26 ppm.

Figure SI22. 400 MHz ^{1}H NMR spectrum of 3•Pb(II) octahedral complex upon addition of CD_3OD.

(a) Precipitated solid taken up in $CDCl_3/CD_3CN$ (1:1) and (b)-(f) upon addition of CD_3OD: (b) immediately, (c) after 24 h, (d) after 48 h, (e) after 15 days and (f) after 20 days. NMR signals are with reference to $CHCl_3$ signal at 7.26 ppm. The sharp, prominent signals are residual solvent signals.

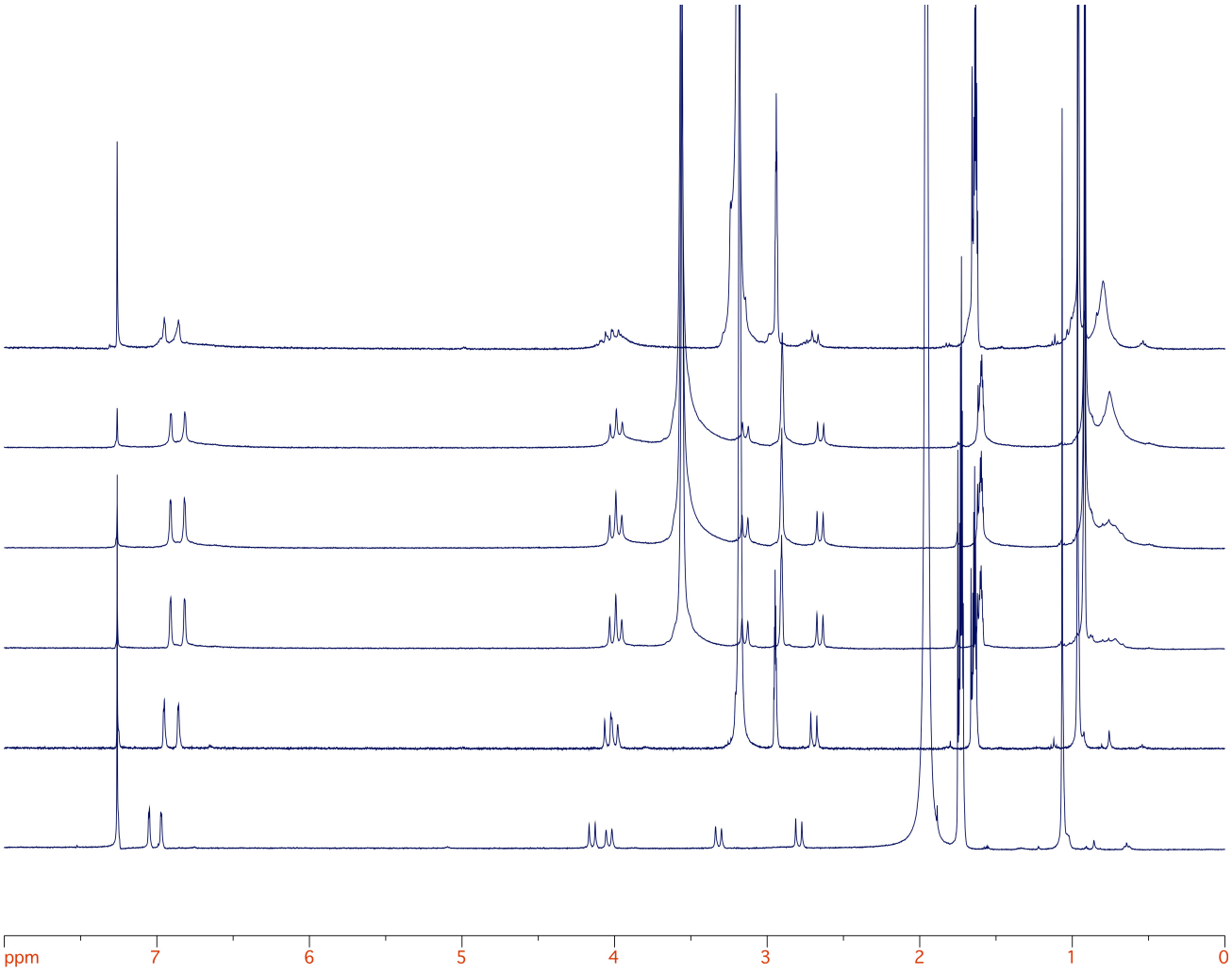


Figure SI23. Expanded rendering from fully refined X-ray data of 3•Pb(II) complex. CIF file found elsewhere in ESI. Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer using MoKα radiation (λ = 0.71073 Å), 65 operating in the ω and ϕ scan mode over a range of $1.02 \leq \theta \leq 25.01$, SADABS was used and the structure was solved by direct methods, all non-hydrogen atoms were refined anisotropically and disordered solvent in void spaces was resolved with SQUEEZE, SHELXTL 97 was used for final full-matrix refinements were against F^2. $C_{78}H_{96}O_{18}Pb$, 1528.7970 g/mol, Cubic, 28.3035(7) Å, 90.00°, 22673.6(17) $Å^3$, su max = 0.000, su mean = 0.000, 150 K, Pn3n, Z = 8, independent reflections = 3367, R = 0.0424, wR = 0.1243 and S = 1.080. CCDC 970239.

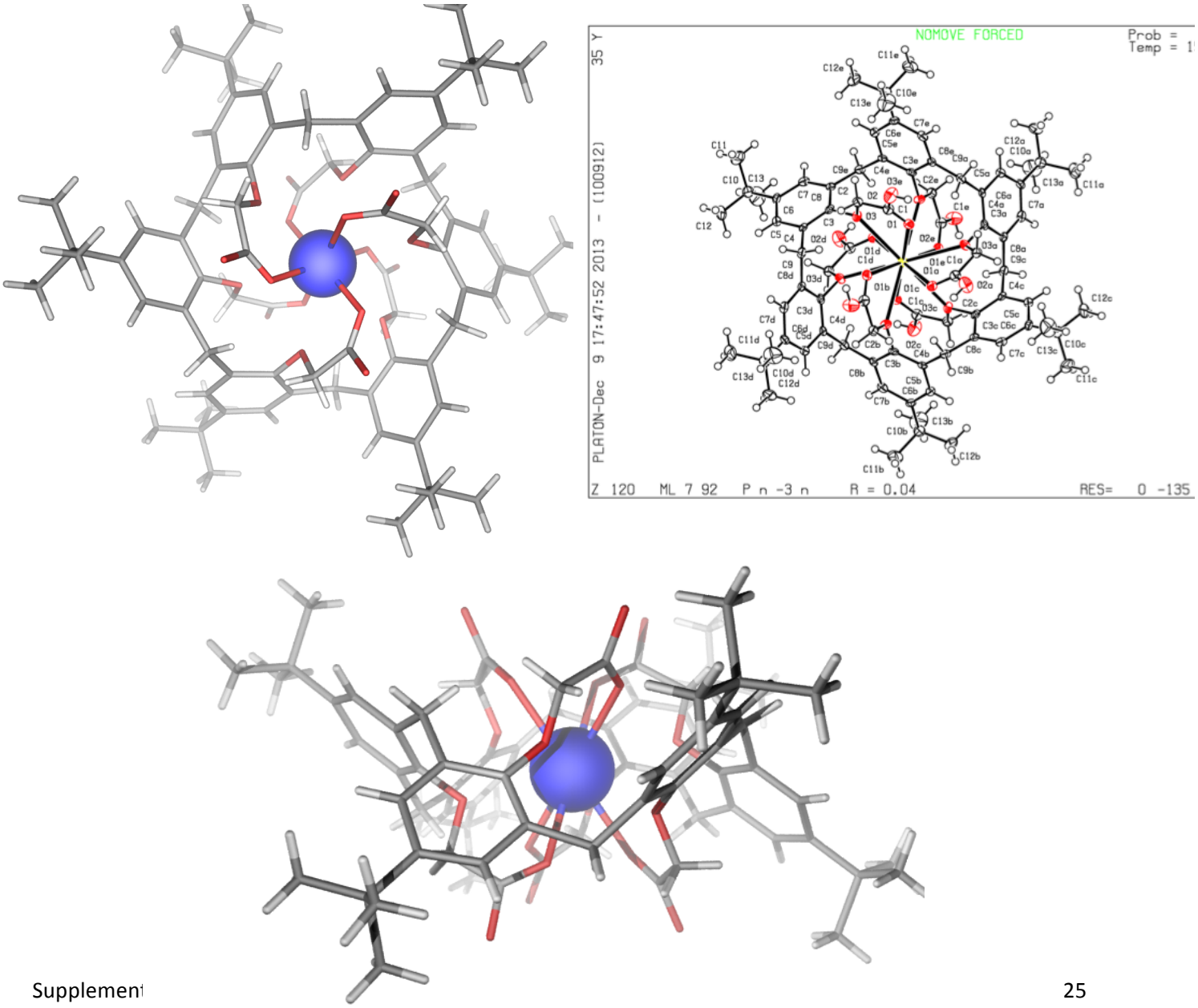


Figure SI24. Unit cell parameters from partially refined X-ray structure of 3•Sr(II) complex.

Complete details will be published in a sequel, H NMR, unit cell and space group matches that of the **3**•Pb(II) complex.

symmetry_cell_setting	Cubic
symmetry_space_group_name_H-M	Pn-3n
cell_length_a	28.32330(10)
cell_length_b	28.32330(10)
cell_length_c	28.32330(10)
cell_angle_alpha	90.00
cell_angle_beta	90.00
cell_angle_gamma	90.00
cell_volume	22721.21(14)