

Supplementary Information

p-tert-Butylcalix[6]arene hexacarboxylic acid as host for Pb(II), Sr(II) and Ba(II)

Birendra Babu Adhikari,^a Xiang Zhao,^a Shahab Derakhshan,^a Michael P. Schramm^{a*}

^aDepartment of Chemistry and Biochemistry, California State University, Long Beach
1250 Bellflower Blvd., Long Beach, 90840, CA, USA;
Fax: (+)1-562-985-8557; E-mail: michael.schramm@csulb.edu

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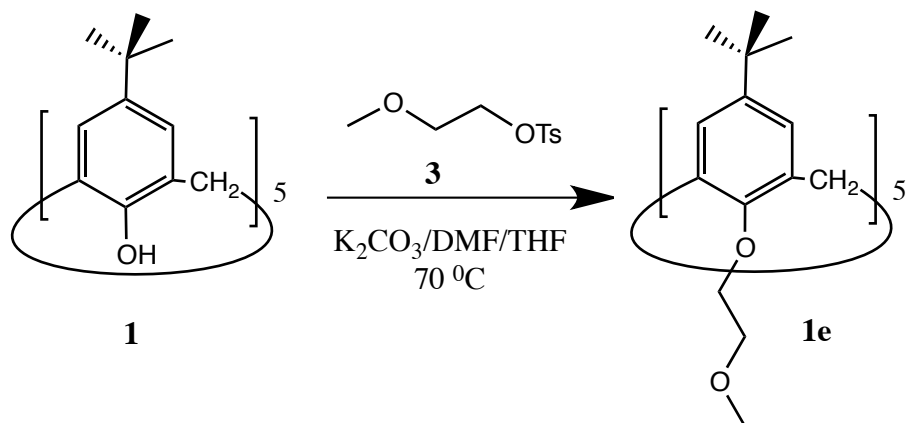
General Information

All reagents were of reagent grade and used without further purification unless mentioned. NMR were acquired on Bruker Fourier 300-MHz or Bruker Avance III 400-MHz (NSF MRI CHE-1337559) systems. Data was processed (iNMR 3.5.1) using a Fourier transform with exponential weighting. NMR solvents were purchased from Cambridge Isotope Laboratories and residual solvent peak was used as an internal standard. All chemicals were used as received unless otherwise noted. SiliaFlash® P60 Silica Gel, 40-63 μm , 60A was purchased from Silicycle. Mass analyses were conducted at the University of California, Riverside High Resolution Mass Spectrometry Facility, Riverside, CA, USA.

Synthesis

Synthesis of **1e**

A slurry of 0.2 g (0.246 mmol) **1**, 0.56 g (2.46 mmol, 10 eq) **3** and 0.34 g (2.46 mmol, 10 eq) K_2CO_3 in 8 cm^3 dry DMF/THF (2:1) mixture was stirred at 70°C for 3 days checking the progress of reaction with TLC. The reaction mixture was cooled to room temperature, THF was removed by rotary evaporation, and water was added to the remaining mixture. The resulting white precipitate was collected by filtration, washed with water, taken up in chloroform (20 mL) and washed again with water (2x20 mL). Drying of chloroform layer (anhydrous MgSO_4) and solvent removal by rotary evaporation afforded an off-white solid. The crude material was then subjected to flash chromatography using 20% EtOAc in hexane to get pure product as a white solid (0.2 g, 74% yield); R_f 0.21 (SiO_2 , 20% EtOAc in Hexane). ^1H NMR (400 MHz, CDCl_3 , 25°C) δ ppm 1.11 (s, 18H), 1.35 (s, 18H), 1.42 (s, 8H), 1.90 (bs, 2H), 2.26 (bs, 3H), 2.92 (bs, 2H), 3.18-3.91 (m, 35H), 4.18(d, $J = 14$ Hz, 1H), 4.37 (d, $J = 13.2$ Hz, 2H), 6.89 (s, 2H), 7.16 (s, 2H), 7.24 (s, 2H), 7.39 (s, 2H), 7.49 (s, 2H).



Scheme: Synthesis of **1e**.

Figure S11. ^1H NMR spectrum of **1e.**

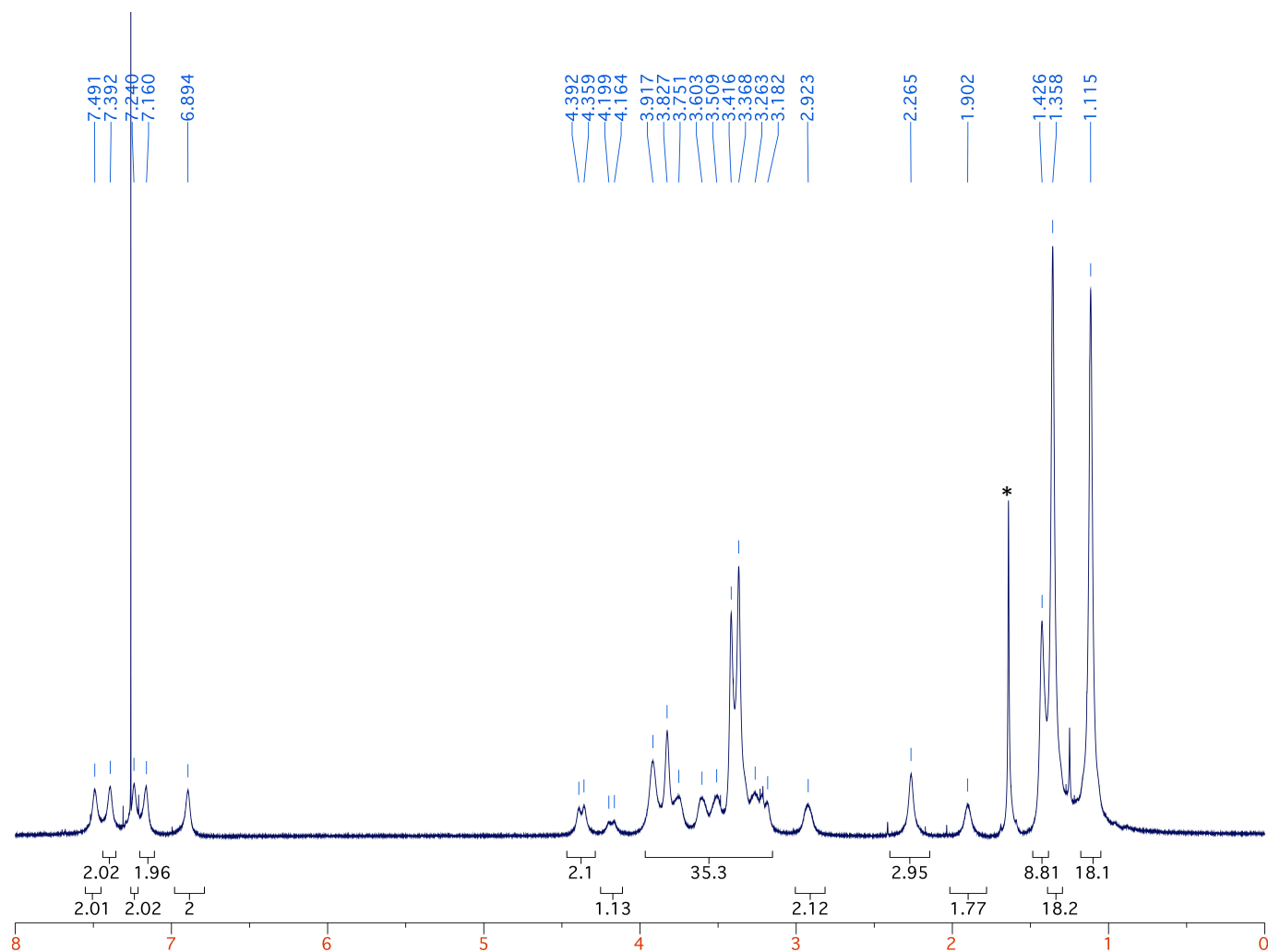
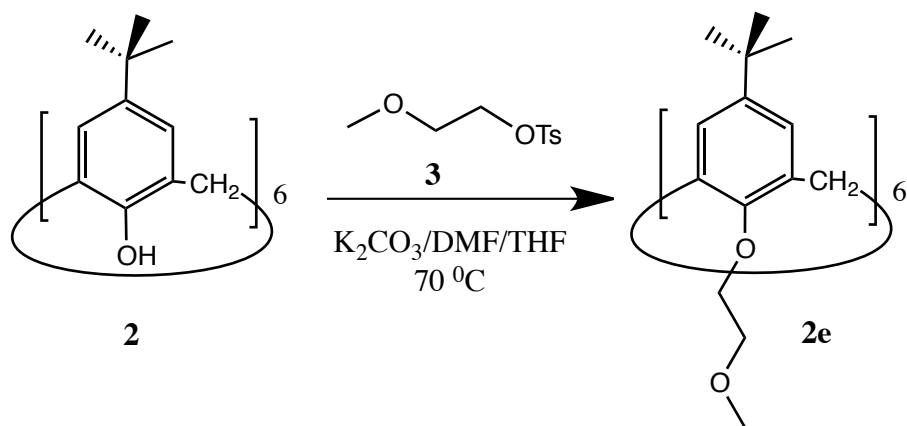


Figure: ^1H NMR (400 MHz) of **1e** in CDCl_3 . A sharp signal at 1.56 ppm (*) is due to residual H_2O .

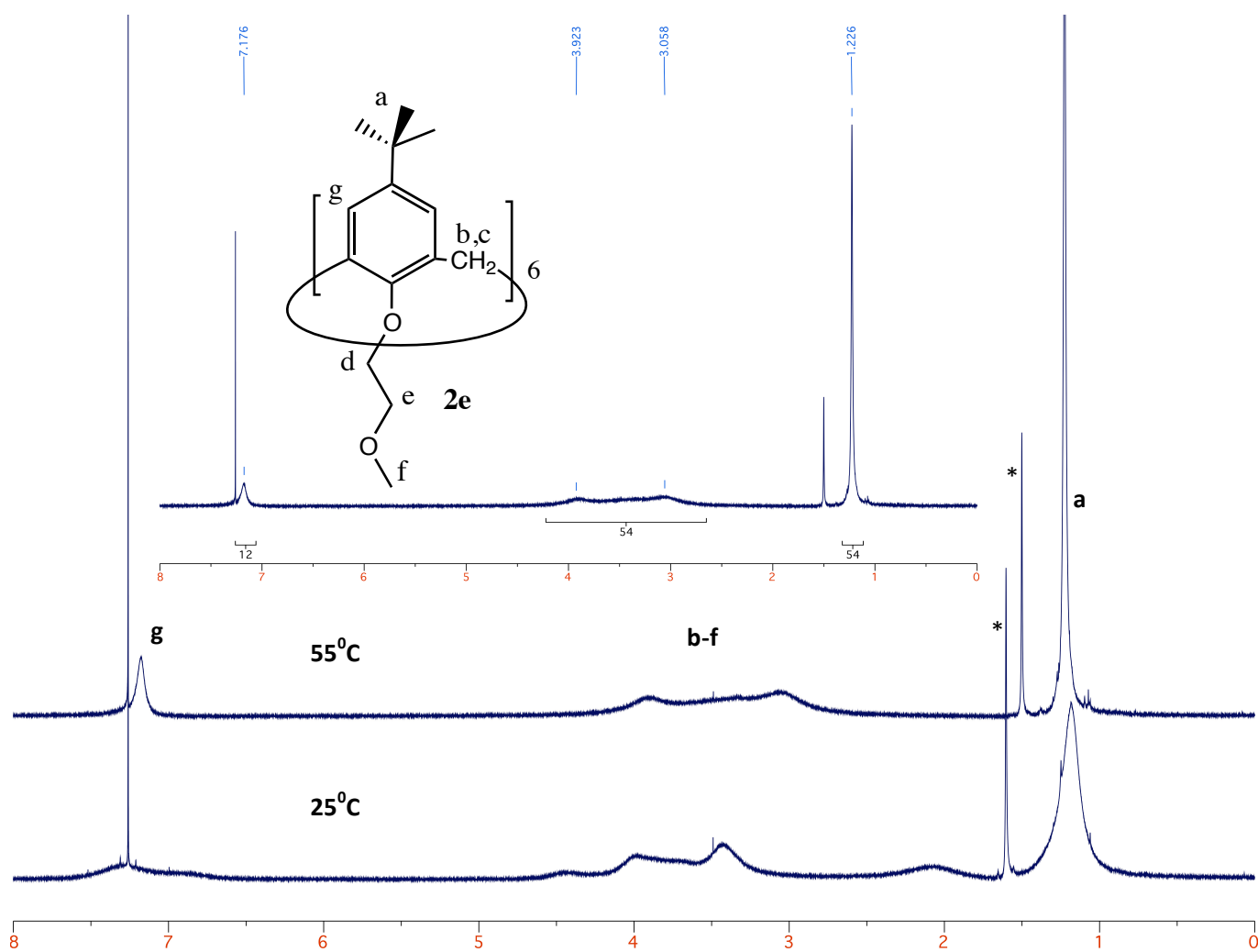
Synthesis of **2e**.

A slurry of 0.3 g (0.3 mmol) **2**, 0.83 g (3.6 mmol, 12 eq) **3** and 0.5 g (3.6 mmol, 12 eq) K_2CO_3 in 10 cm³ dry DMF/THF (2:1) mixture was stirred at 70°C for 3 days checking the progress of reaction with TLC. The reaction mixture was cooled to room temperature and THF was removed by rotary evaporation. Addition of water to the remaining mixture resulted in a thick paste, which was taken up in chloroform (20 mL) and washed with 1 M HCl (20 mL) followed by water (2x20 mL). Solvent removal from the dried organic layer by rotary evaporation afforded a crude white solid. The crude material was then subjected to flash chromatography using 20% EtOAc in hexane to get pure product as a white solid (0.16 g, 40% yield). ¹H NMR (400 MHz, CDCl₃, 25°C) displayed ill-defined broad signals. High temperature ¹H NMR improved the resolution of some signals and gave a spectrum good enough for characterization. ¹H NMR (400 MHz, CDCl₃, 55°C) δ ppm 1.22 (s, 54H), 3.05-3.92 (bs, 54H), 7.17 (s, 12H). The compound **2e** was a single spot on TLC; R_f 0.44 (SiO₂, 20% EtOAc in Hexane) and displayed only one signal on mass spectrum at m/z 1322. $[M+H]^+$ for molecular formula C₈₄H₁₂₀O₁₂: calculated 1321.88; found 1322.



Scheme: synthesis of **2e**.

Figure SI2NMR. ^1H NMR spectra of **2e**.



^1H NMR (400 MHz) of **2e** in CDCl_3 at different temperatures. Inset shows the ^1H NMR of **2e** at 55°C with integration of the signals. * represents a signal due to residual H_2O .

Figure SI2MS. MS spectra of 2e.

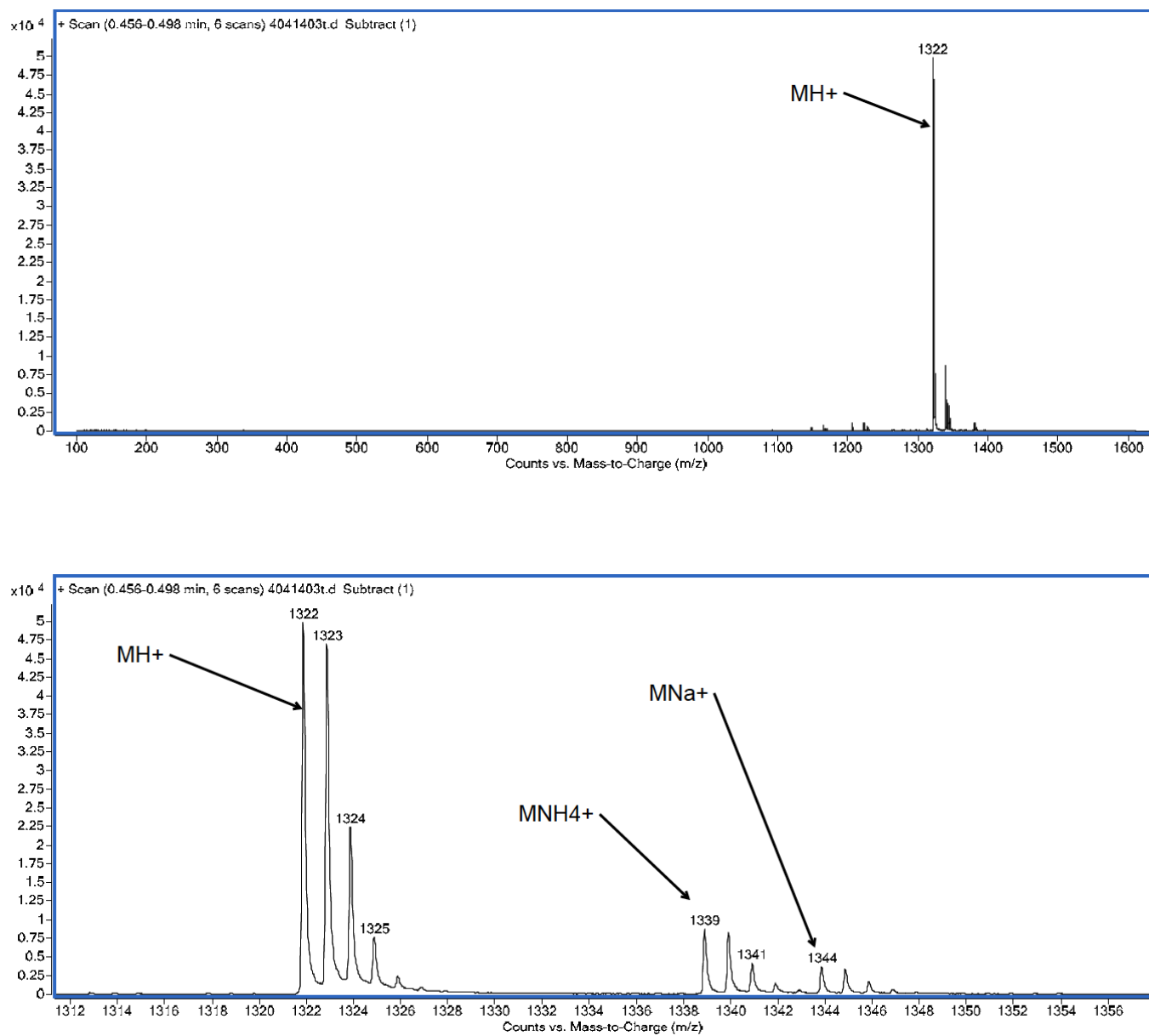


Figure. Mass spectrum of 2e. The molecular ion peak at m/z 1322 corresponds to $[M+H]^+$ for molecular formula $C_{84}H_{120}O_{12}$.

Figure SI3Xray. Single Crystal X-ray data and ORTEP for 2d•Sr(II).

CIF file found elsewhere in ESI. Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$), 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 . $C_{78}H_{96}O_{18}Pb$ (H_2O), 1421.19 g/mol, Cubic, 28.3335(2) \AA , 90.00°, 22745.8(5) \AA^3 , $\mu_{max} = 0.001$, $\mu_{mean} = 0.000$, 174 K, Pn3n, Z = 8, independent reflections = 3015, R = 0.0517, wR = 0.1309 and S = 1.127. CCDC 1014654.

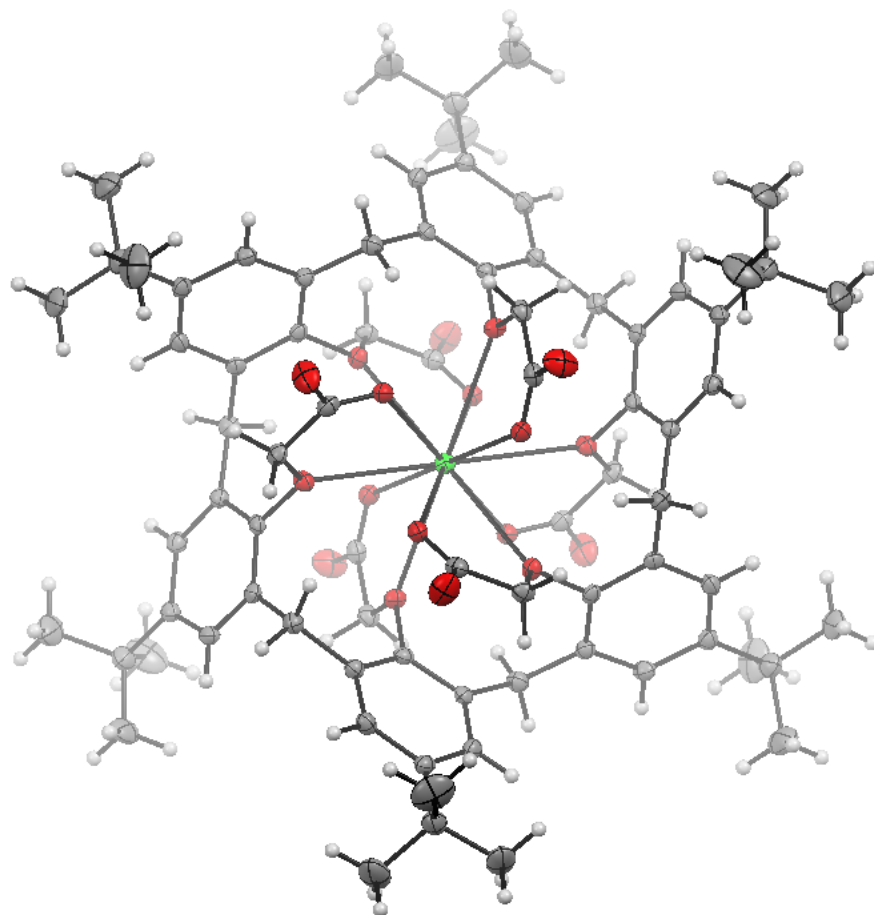
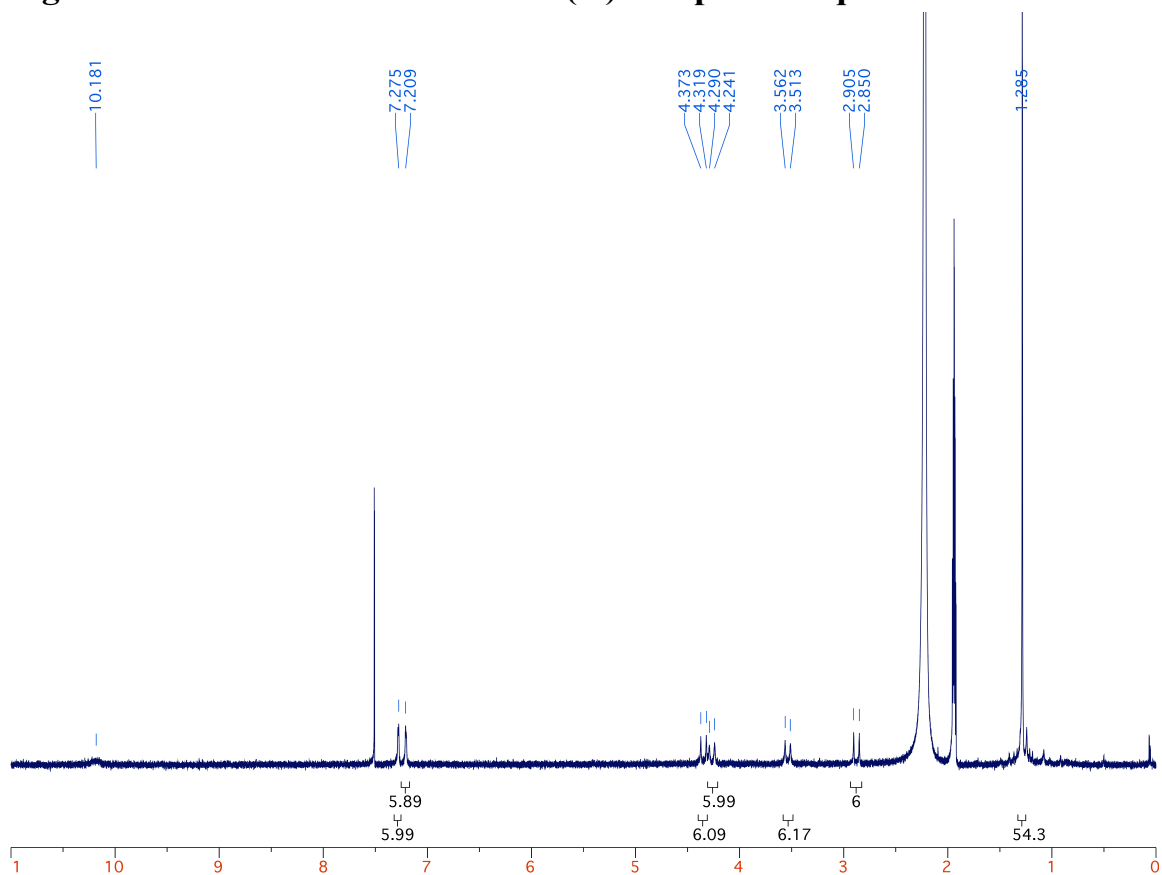


Figure SI3NMR. ^1H NMR of $2\mathbf{d}\cdot\text{Sr}(\text{II})$ complex at equilibrium.



^1H NMR (400 MHz) of $2\mathbf{d}\cdot\text{Sr}(\text{II})$ complex at equilibrium in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1). The ^1H NMR signals are with reference to residual CH_3CN signal at 1.94 ppm. A signal at 7.49 ppm is due to residual CHCl_3 and a prominent signal at 1.22 ppm is due to H_2O from $\text{Sr}(\text{ClO}_4)_2\cdot 3\text{H}_2\text{O}$.

Figure SI4Xray. Powder X-ray data for 2d•Ba(II).

Powder X-ray diffraction data were collected, employing a PANalytical X'Pert Pro MPD diffractometer, equipped with a linear X'Celerator detector, with Cu- $K\alpha_1$ radiation. The data were collected at room temperature in the range $3^\circ \leq 2\theta \leq 40^\circ$ with $\approx 0.008^\circ$ intervals. The X'Pert HighScore Plus software was used to determine the background, the peak positions and the peak shapes. Treor method was used to index the peaks and all the peaks were indexed based a cubic unit cell with $a = 28.499(4)$ Å.

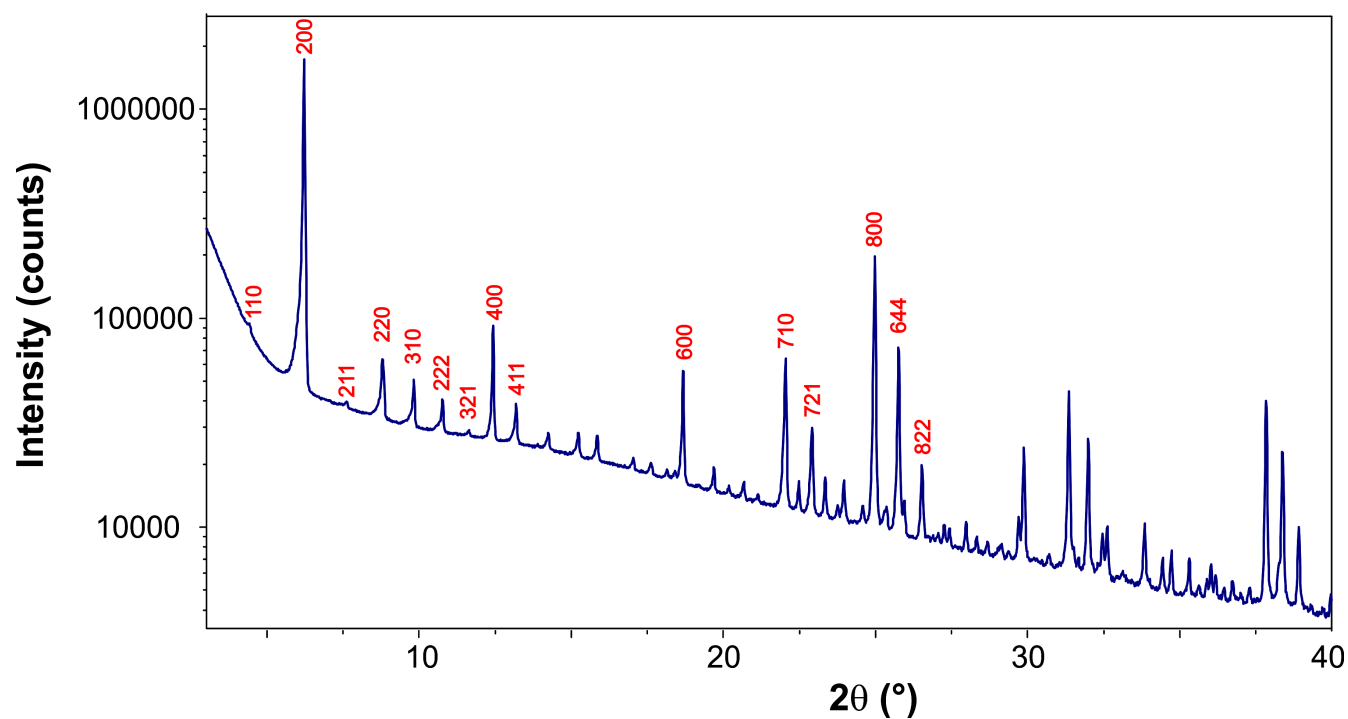
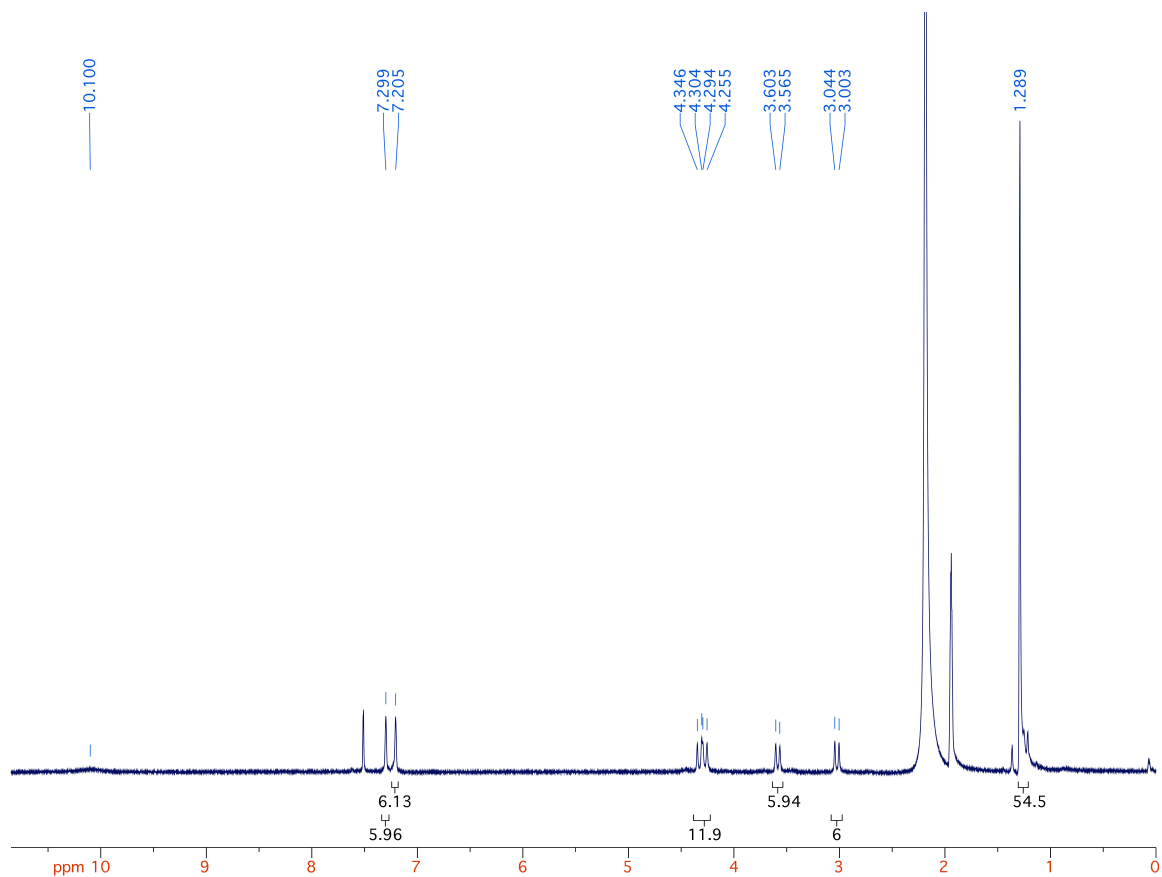
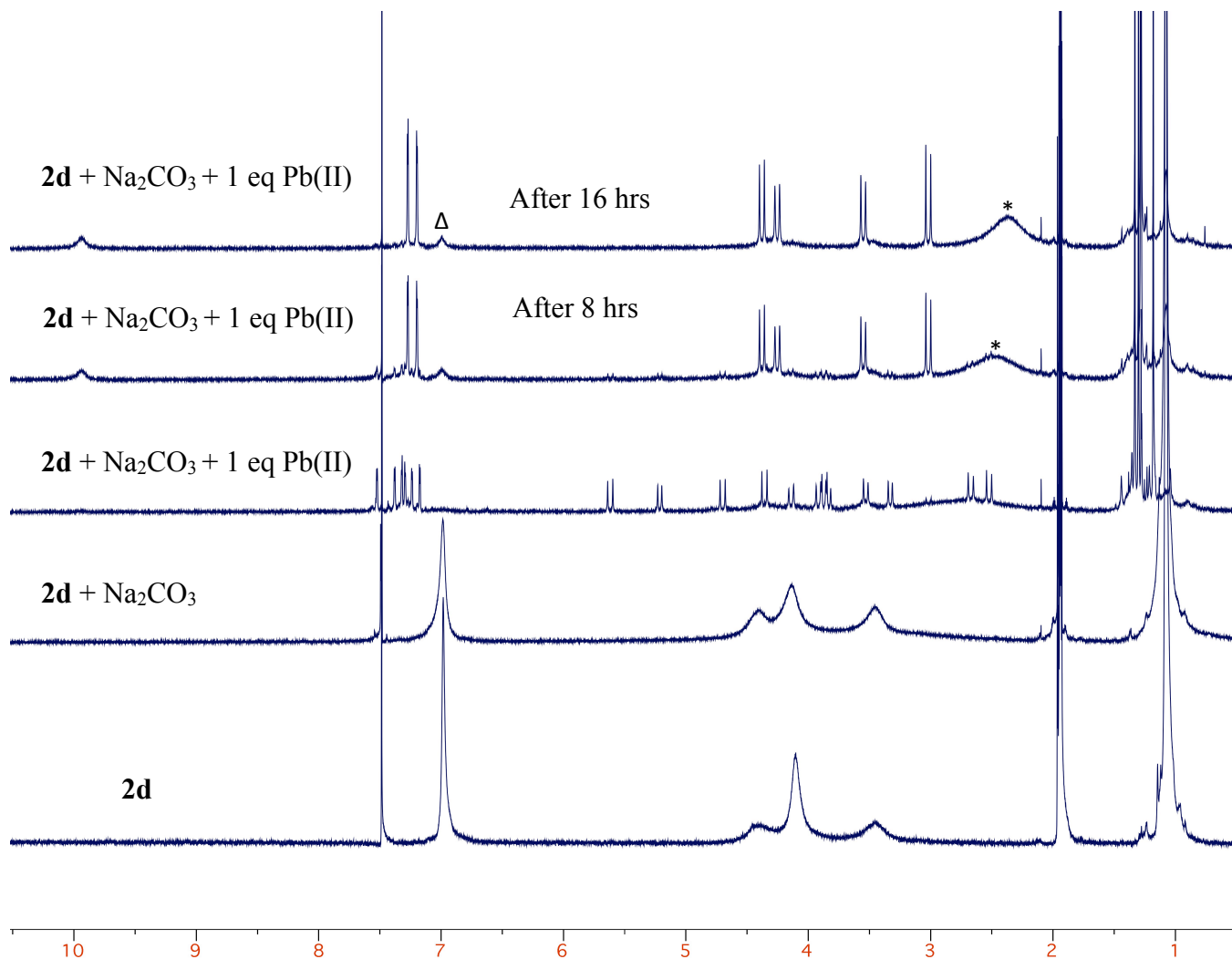


Figure SI4NMR. ^1H NMR of $2\mathbf{d}\cdot\text{Ba(II)}$ complex at equilibrium.



^1H NMR (400 MHz) of $2\mathbf{d}\cdot\text{Ba(II)}$ complex at equilibrium in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1). The ^1H NMR signals are with reference to residual CH_3CN signal at 1.94 ppm. A signal at 7.49 ppm is due to residual CHCl_3 and a prominent signal at 1.18 ppm is due to H_2O from $\text{Ba}(\text{ClO}_4)_2\cdot 3\text{H}_2\text{O}$.

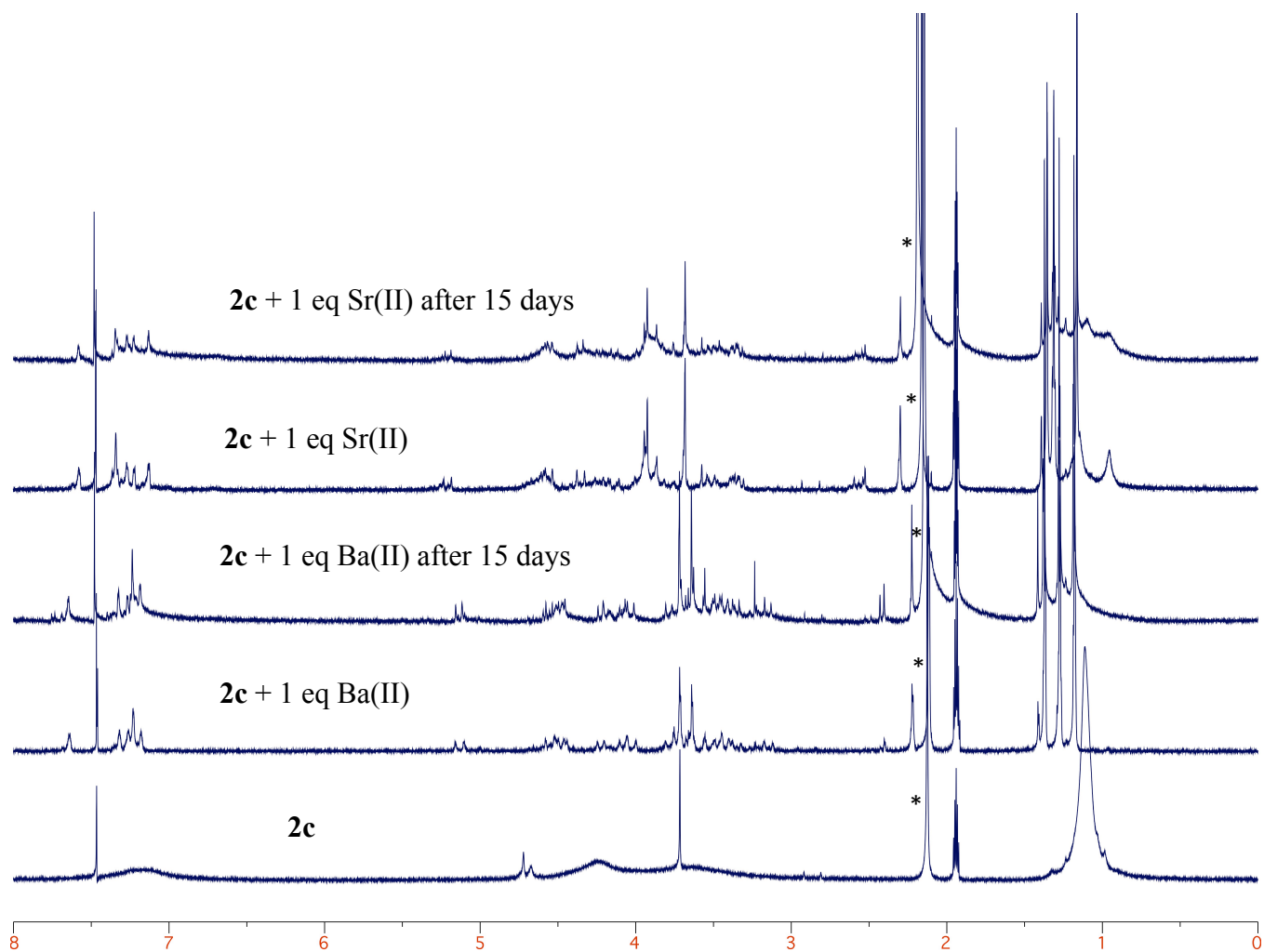
Figure SI5. Effect of Na₂CO₃ addition on complexation of Pb(II) with 2d.



¹H NMR changes on addition of Na₂CO₃ to a solution of **2d** in CDCl₃/CD₃CN (1/1) followed by addition of 1 eq Pb(II). NMR signals are with reference to CH₃CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to residual CHCl₃. * represents a signal from residual H₂O. Δ is a residual signal from free ligand (because the added Pb(II) was probably slightly lower than 1 equivalent).

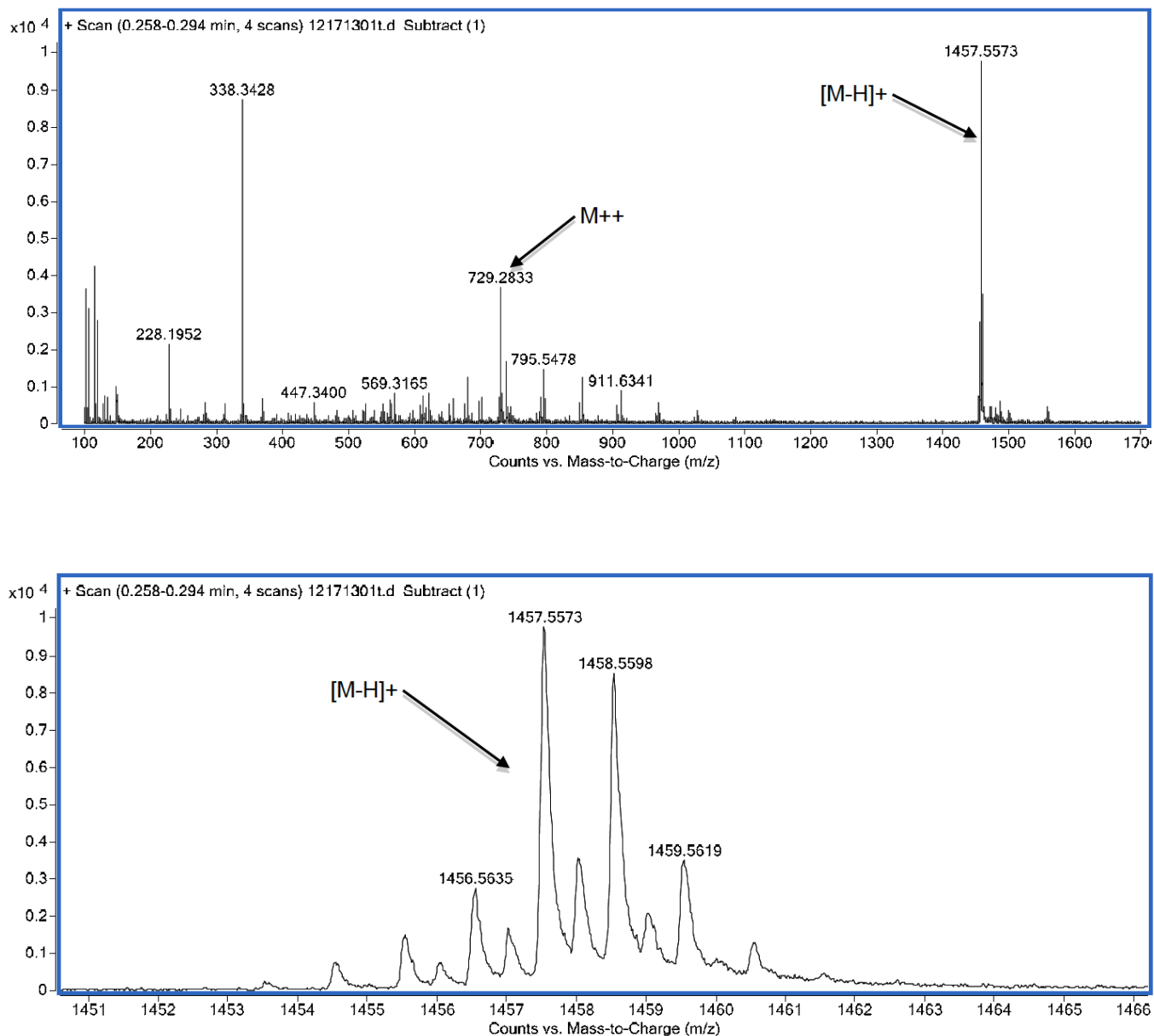
Slight change was observed in peak position of ArCH₂Ar protons, especially endo-proton was upfield shifted by 0.017 ppm. In absence of Na₂CO₃, the NMR signals are at: 3.458 (exo H), 4.102 (OCH₂) and 4.422 (endo H) ppm. After addition of Na₂CO₃, they appeared at 3.448 (exo), 4.136 (OCH₂) and 4.405 (endo).

Figure SI6. Complexation of Ba(II) and Sr(II) with hexaester 2c.



¹H NMR (400 MHz) of **2c** in CDCl₃/CD₃CN (1/1) in presence of 1 equivalent Ba(II) and Sr(II) at the time of addition and after 15 days. NMR signals are with reference to CH₃CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to CDCl₃. * represents a residual signal from H₂O.

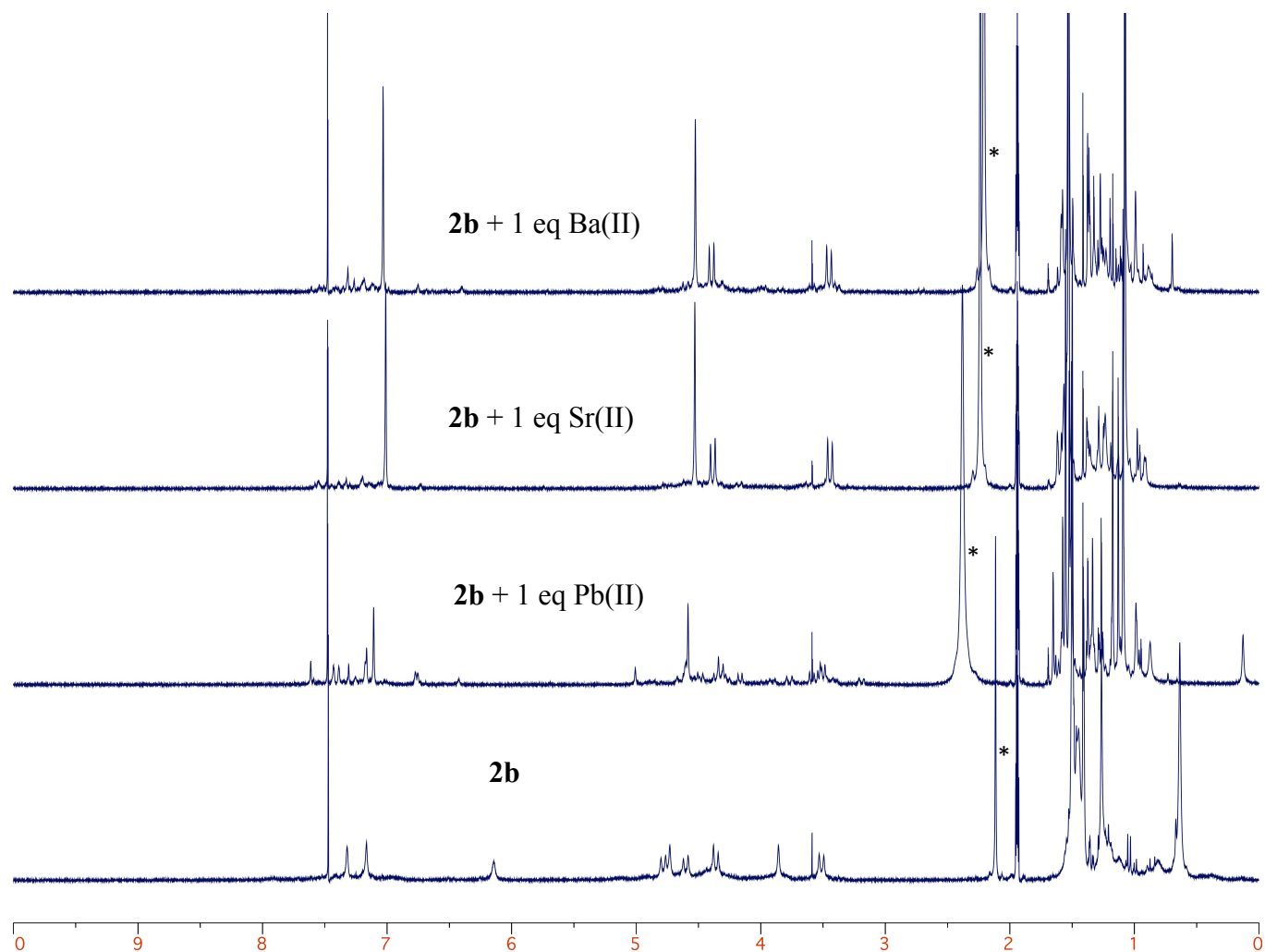
Figure SI7. Mass spectrum of 2d•Ba(II) complex



Mass spectrum of **2d**•Ba(II) complex.

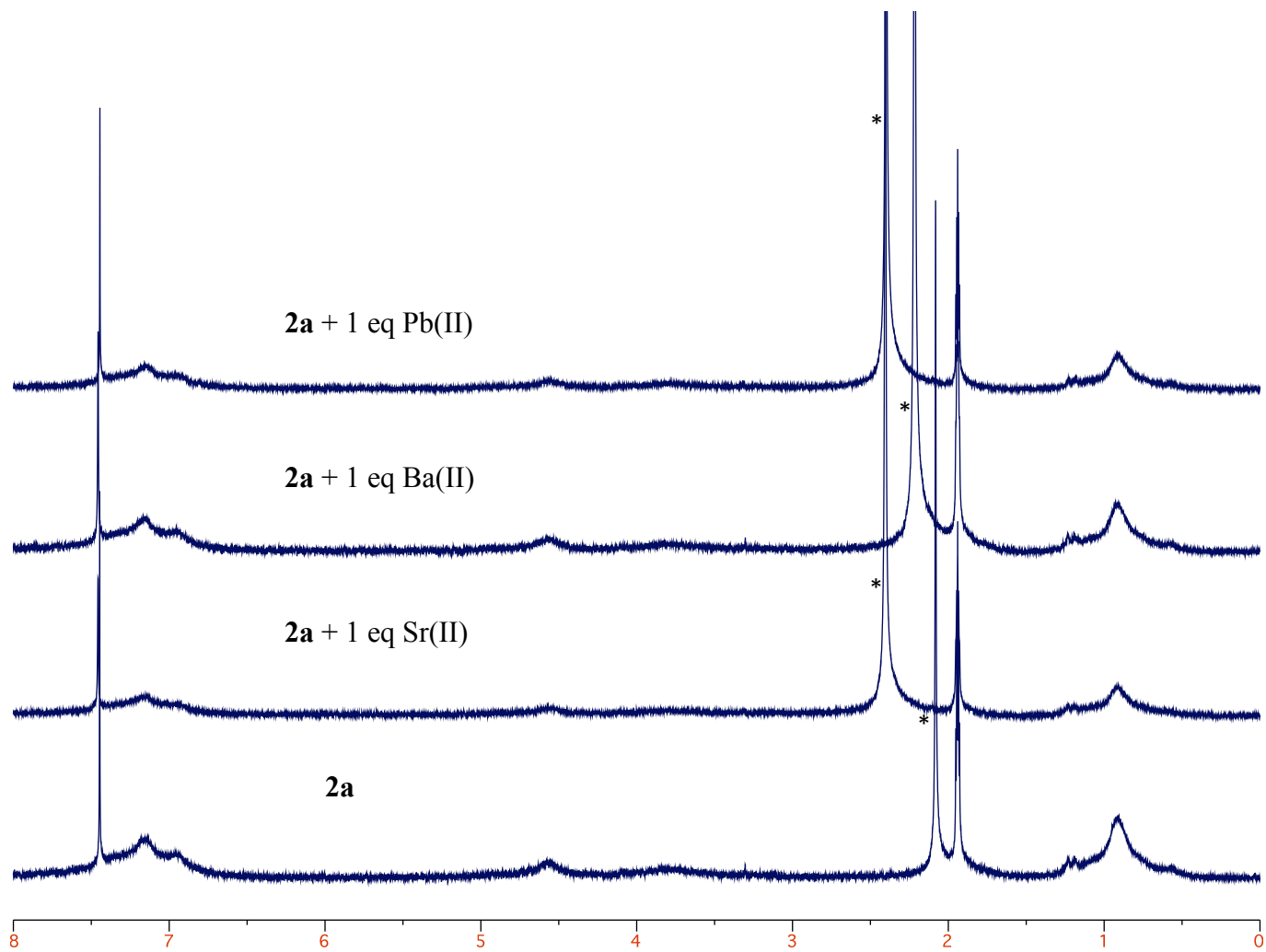
Molecular mass calculated for **2d**•Ba complex (C₇₈H₉₆BaO₁₈) is 1458.5649. The molecular ion peak at 1457.5573 corresponds to [M-H]⁺ and indicates that the electro neutral complex was formed by the loss of two protons for a Ba(II) ion.

Figure SI8. ^1H NMR spectra of **2b in presence of 1 eq Pb(II), Sr(II) and Ba(II).**



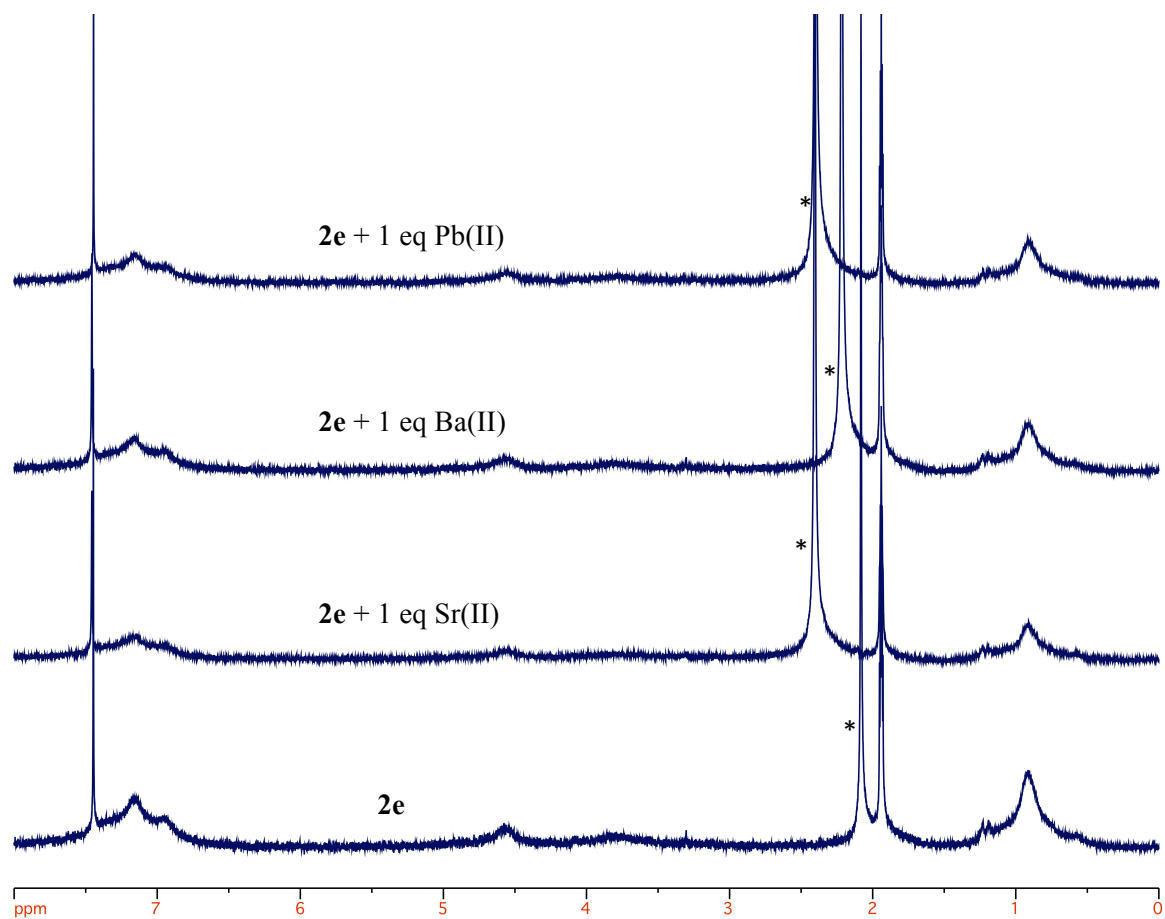
^1H NMR (400 MHz) of **2b** in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1) in presence of 1 equivalent Pb(II), Sr(II) and Ba(II) at the time of addition. NMR signals are with reference to CH_3CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to residual CHCl_3 . * represents a residual signal due to H_2O .

Figure SI9. ^1H NMR spectra of **2a** in presence of 1 eq Sr(II), Ba(II) and Pb(II).



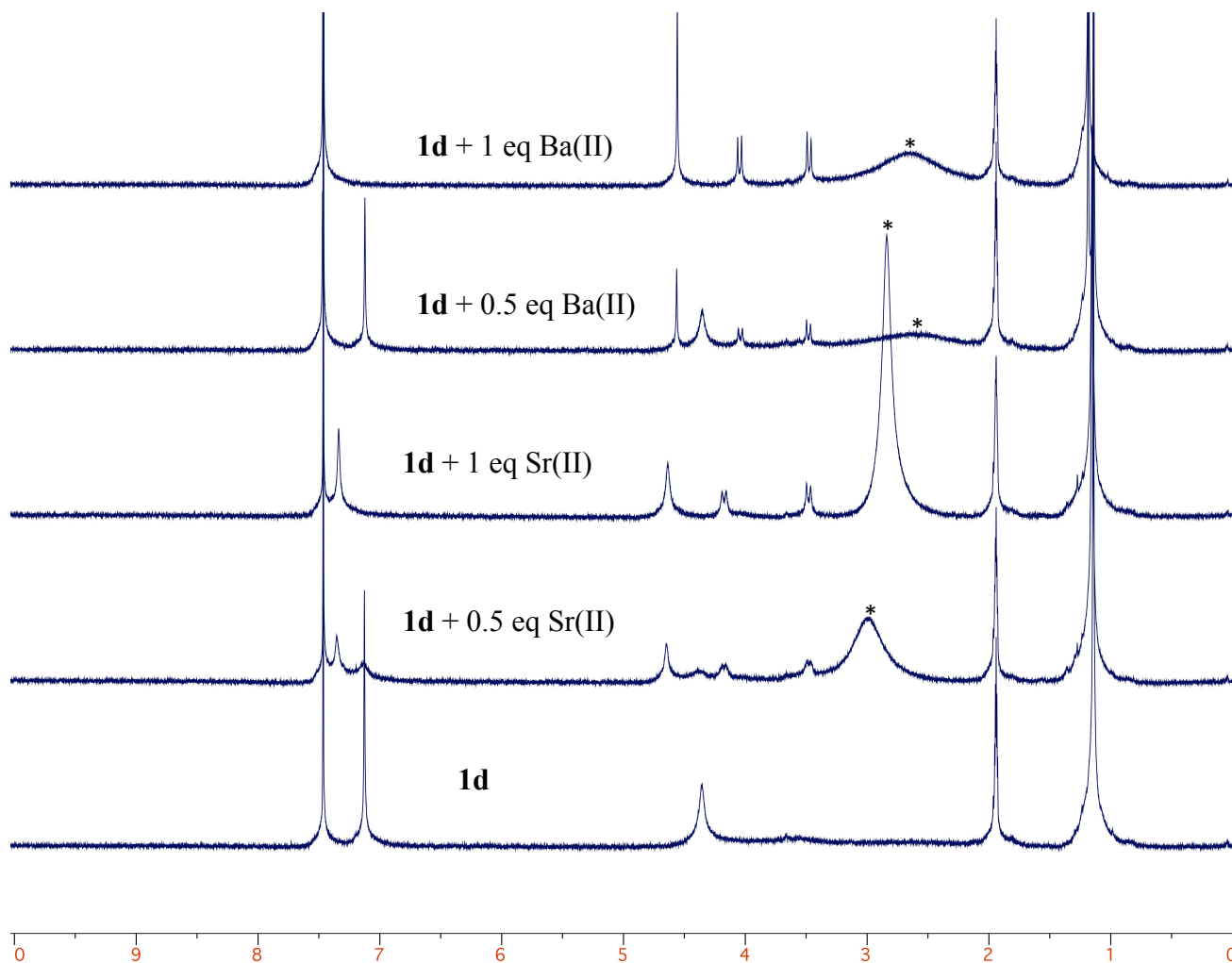
^1H NMR (400 MHz) of **2a** in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1) in presence of some divalent cations. From bottom to top: free ligand **2a**, and in presence of 1 eq Sr(II), Ba(II) and Pb(II), respectively. NMR signals are with reference to CH_3CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to residual CHCl_3 . * represents a residual signal from H_2O .

Figure SI10. ^1H NMR spectra of **2e in presence of 1 eq Sr(II), Ba(II) and Pb(II).**



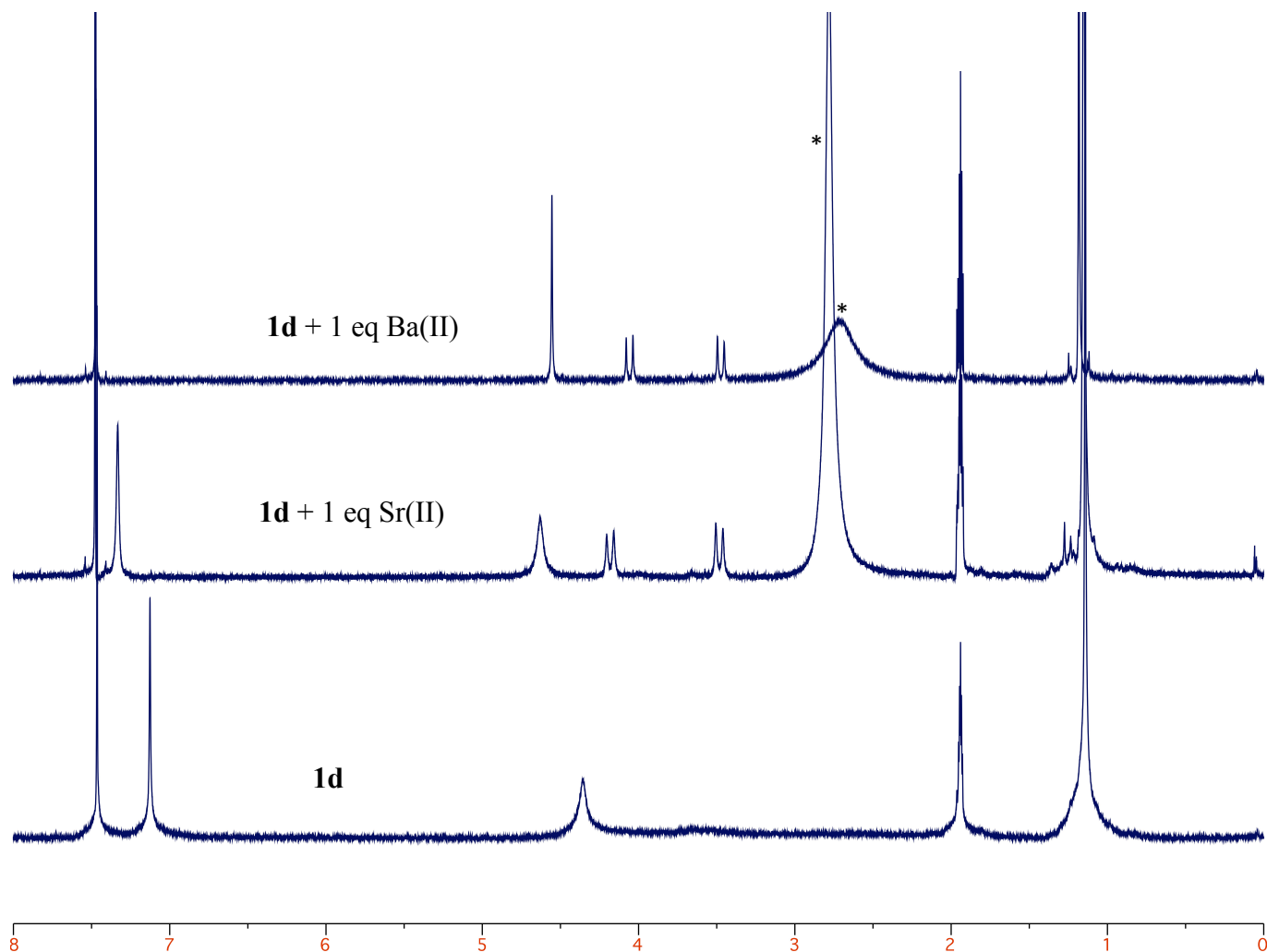
^1H NMR (400 MHz) of **2e** in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1) in presence of some divalent cations. From bottom to top: free ligand **2e**, and in presence of 1 eq Sr(II), Ba(II) and Pb(II), respectively. NMR signals are with reference to CH_3CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to residual CHCl_3 . * represents a residual H_2O signal.

Figure SI11. ^1H NMR spectra of **1d in presence of Sr(II) and Ba(II).**



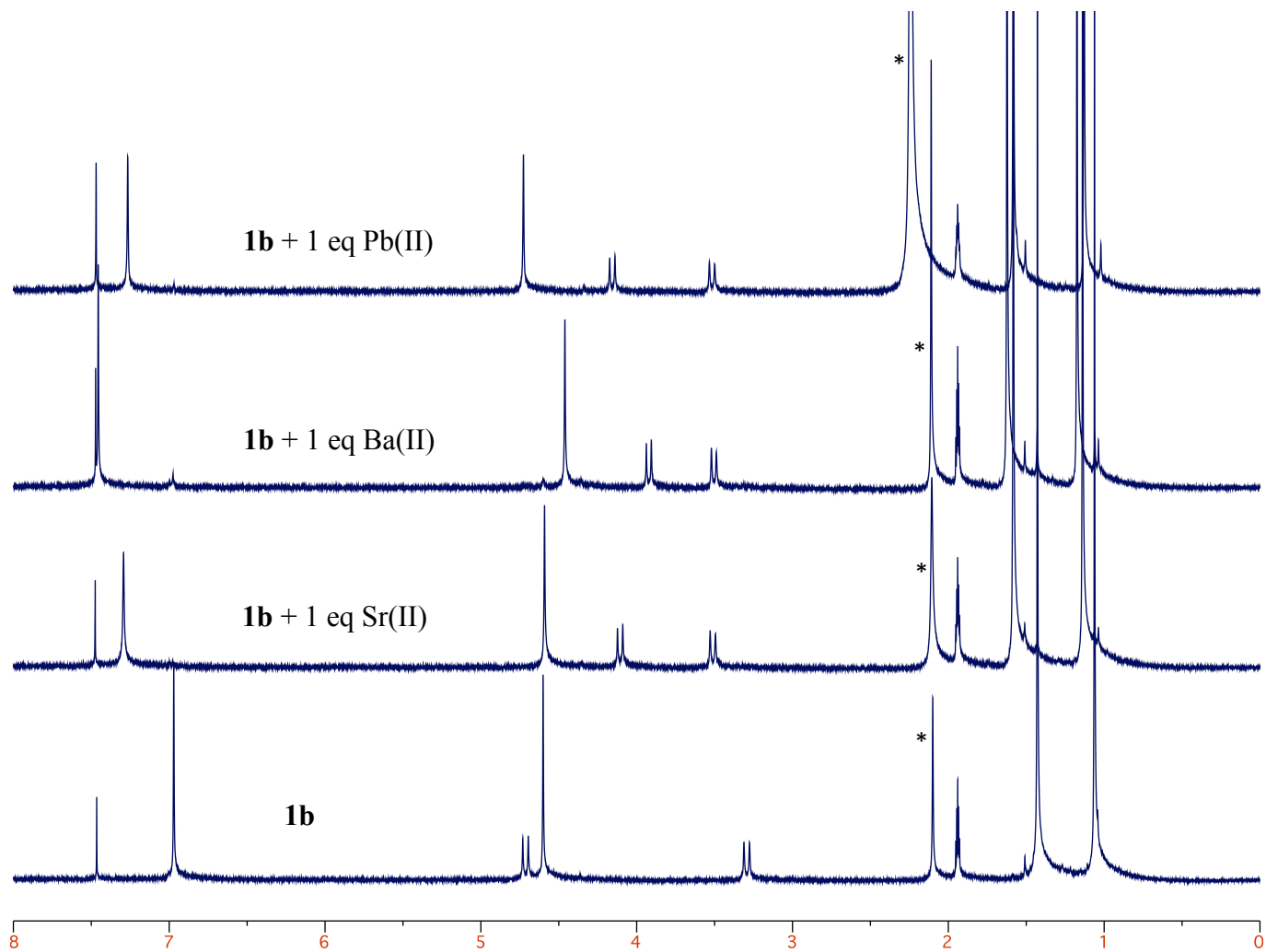
^1H NMR (400 MHz) spectra of **1d** with Sr(II) and Ba(II) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1) at the time of addition. NMR signals are with reference to CH_3CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to residual CHCl_3 . * represents a signal due to residual H_2O from hydrated metal perchlorate salt.

Figure SI12. ^1H NMR spectra of **1d** in presence of 1 eq Sr(II) and Ba(II) after 15 days.



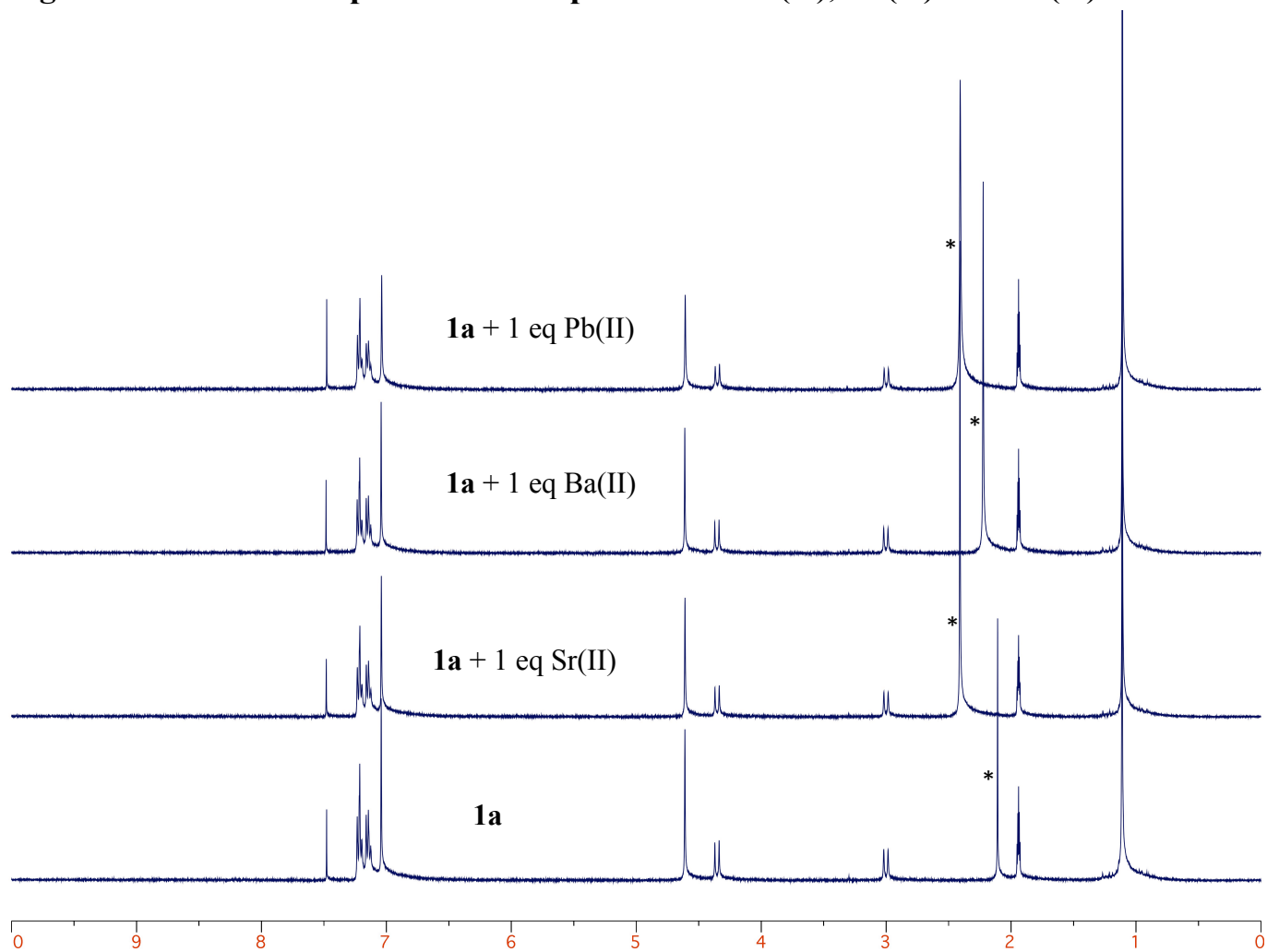
^1H NMR (400 MHz) spectra of **1d** with 1 eq Sr(II) and Ba(II) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1) after 15 days. From bottom to top: **1d**, **1d** + Sr(II), **1d** Ba(II). NMR signals are with reference to CH_3CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to residual CHCl_3 . The ArH signal in case of Ba(II) complex is buried inside the residual CHCl_3 signal at 7.49 ppm. * represents a residual signal due to H_2O from hydrated metal chloride salt.

Figure SI13. ^1H NMR spectra of **1b in presence of Sr(II), Ba(II) and Pb(II).**



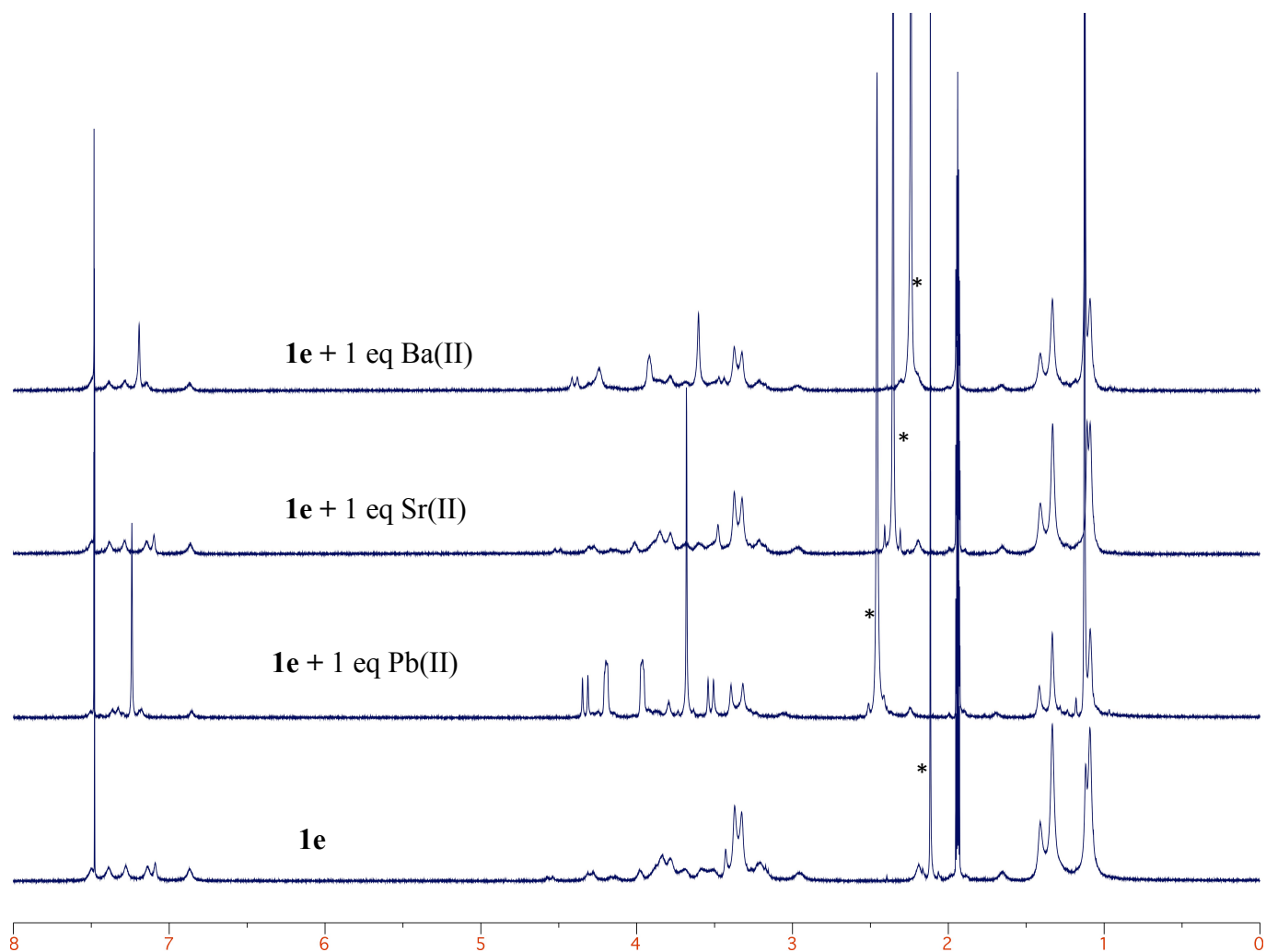
^1H NMR (400 MHz) spectra of **1b** in presence of Sr(II), Ba(II) and Pb(II) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1). NMR signals are with reference to CH_3CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to residual CHCl_3 . * represents a signal due to residual H_2O .

Figure SI14. ^1H NMR spectra of **1a in presence of Sr(II), Ba(II) and Pb(II).**



^1H NMR (400 MHz) spectra of **1a** in presence of Sr(II), Ba(II) and Pb(II) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1). NMR signals are with reference to CH_3CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to residual CHCl_3 . * represents a signal due to residual H_2O .

Figure SI15. ^1H NMR spectra of **1e in presence of Pb(II), Sr(II) and Ba(II).**



^1H NMR (400 MHz) spectra of **1e** in presence of Pb(II), Sr(II) and Ba(II) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1/1). NMR signals are with reference to CH_3CN at 1.94 ppm. The sharp signal at 7.49 ppm is due to residual CHCl_3 . * represents a signal due to residual H_2O .