CHEMISTRY
A EUROPEAN JOURNAL

# Supporting Information

# Synthesis and investigation of a chiral enterobactin analogue based on a macrocyclic peptide scaffold

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## 1. Spectrophotometric data

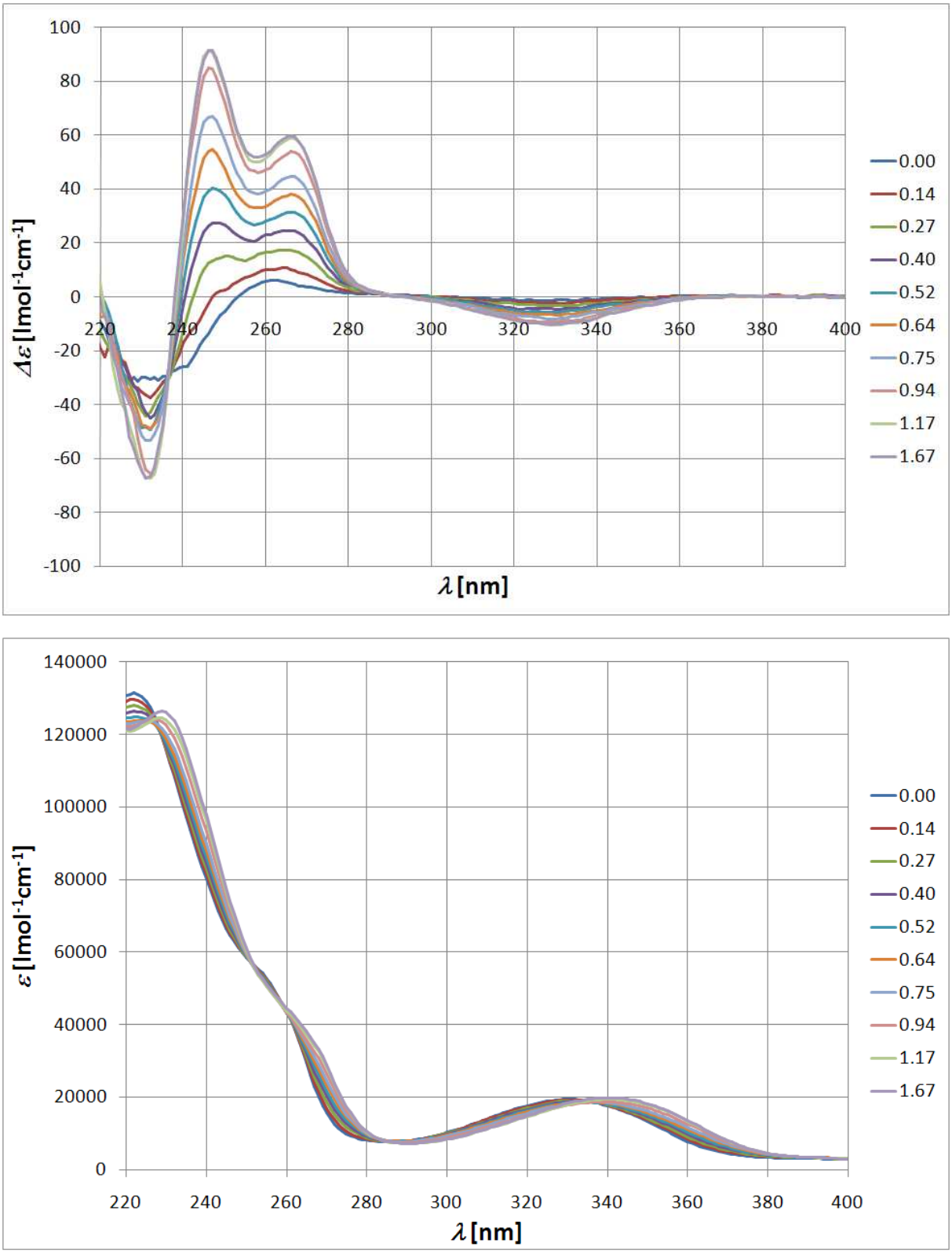
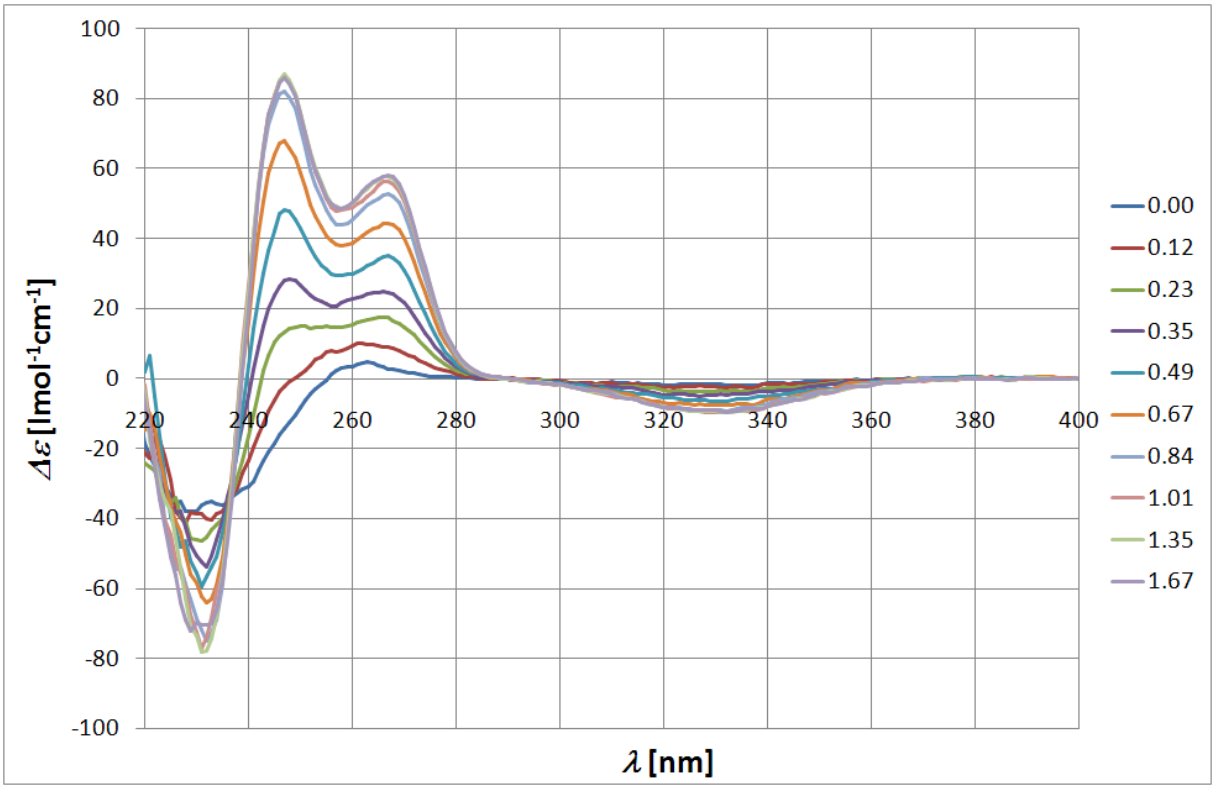



**Figure 1.** Spectrophotometric titration of ligand **1** with $Al^{3+}$ ([**1**] = 2.0*10$^{-5}$ M, MeOH/$H_2O$ : 10/90; 0.10 M TRIS; 0.02 M HCl buffer; pH = 8.95); top: CD spectra; bottom: UV-vis absorption spectra.



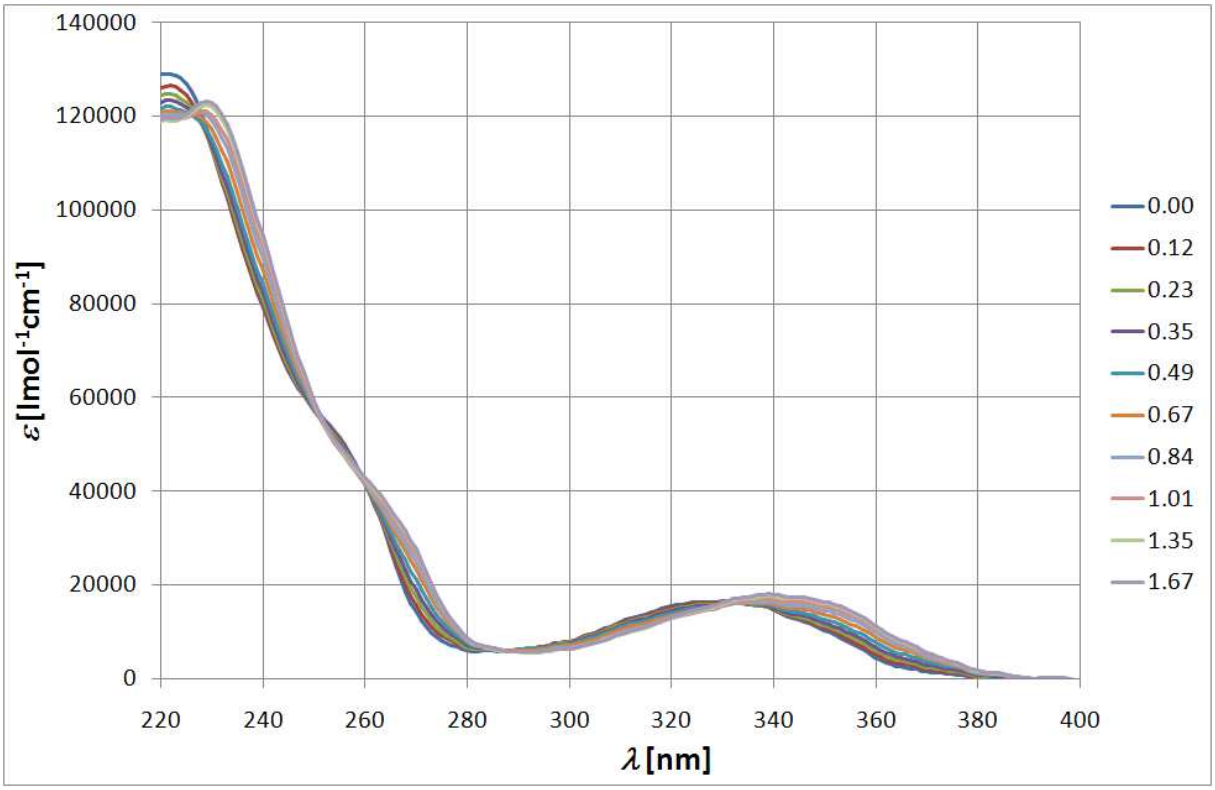
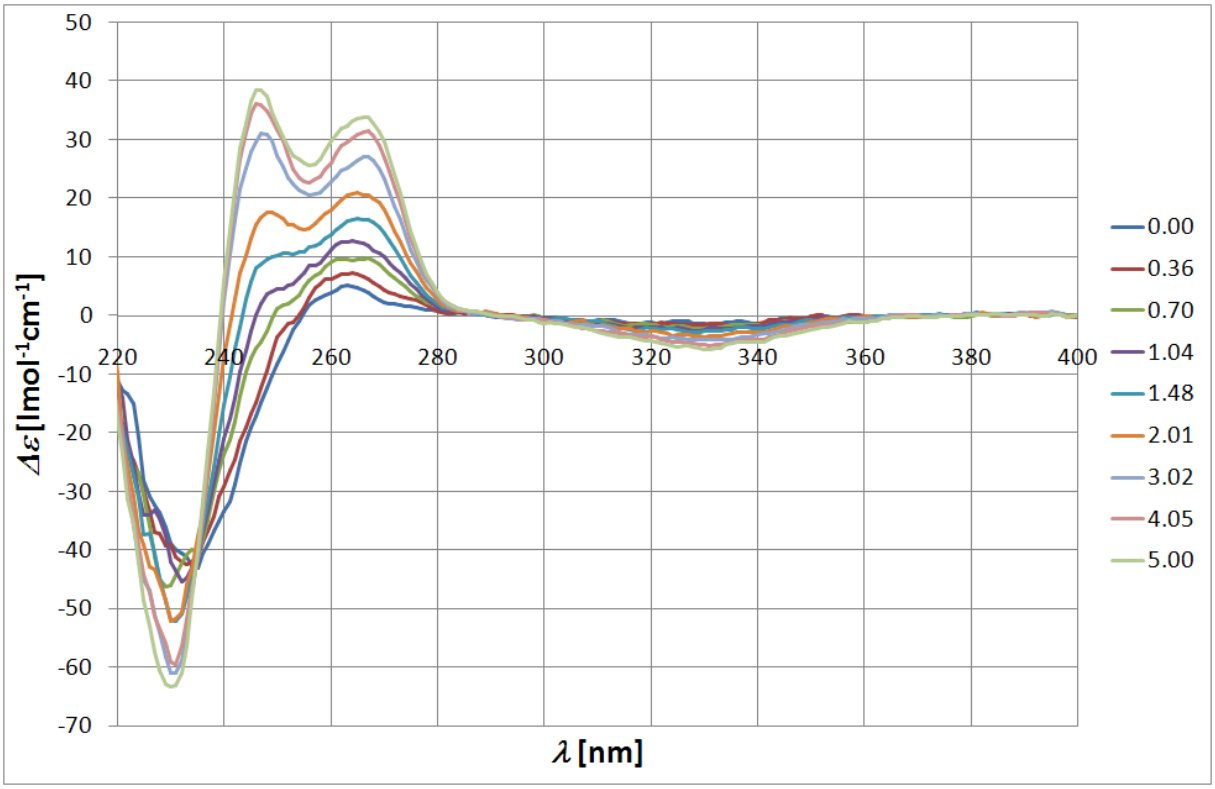




**Figure 2.** Spectrophotometric titration of ligand **1** with $Ga^{3+}$ ([**1**] = $2.0*10^{-5}$ M, MeOH/$H_2O$ : 10/90; 0.10 M TRIS; 0.02 M HCl buffer; pH = 8.95); top: CD spectra; bottom: UV-vis absorption spectra.



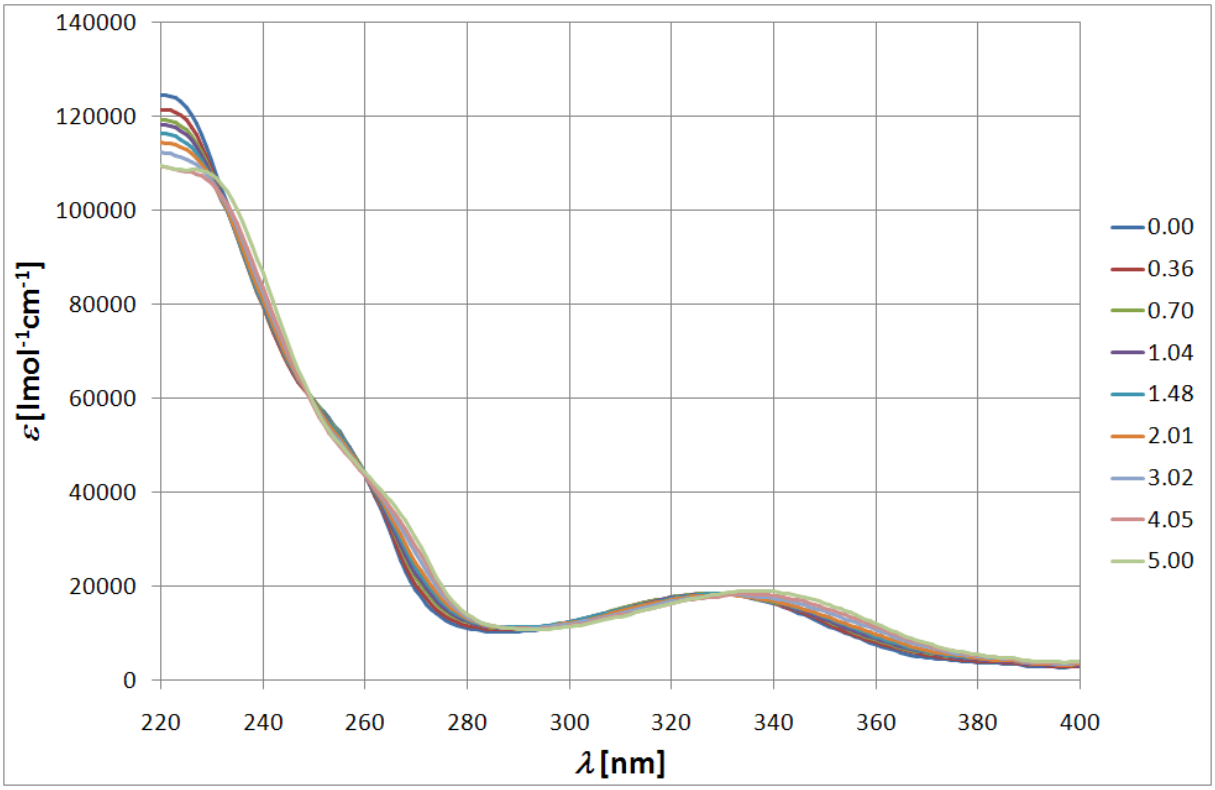
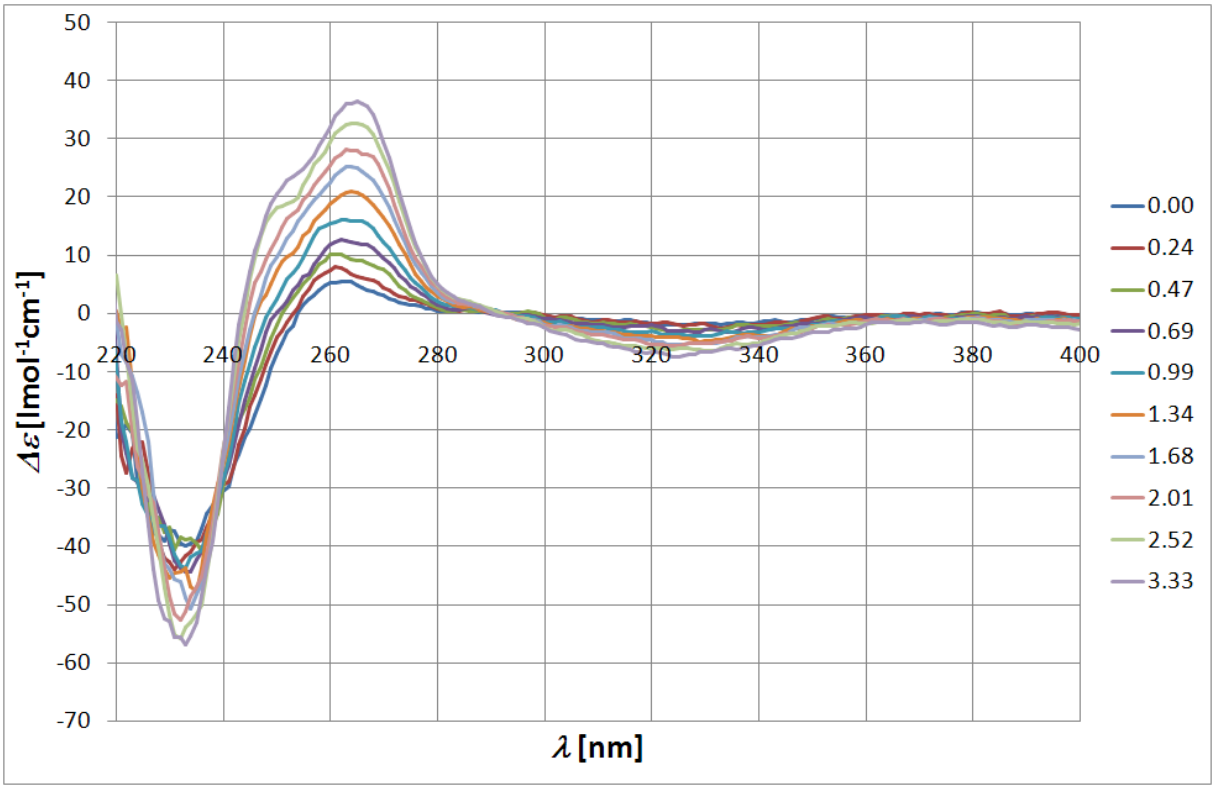




**Figure 3.** Spectrophotometric titration of ligand **1** with $In^{3+}$ ([**1**] = $2.0*10^{-5}$ M, MeOH/$H_2O$ : 10/90; 0.10 M TRIS; 0.02 M HCl buffer; pH = 8.95); top: CD spectra; bottom: UV-vis absorption spectra.



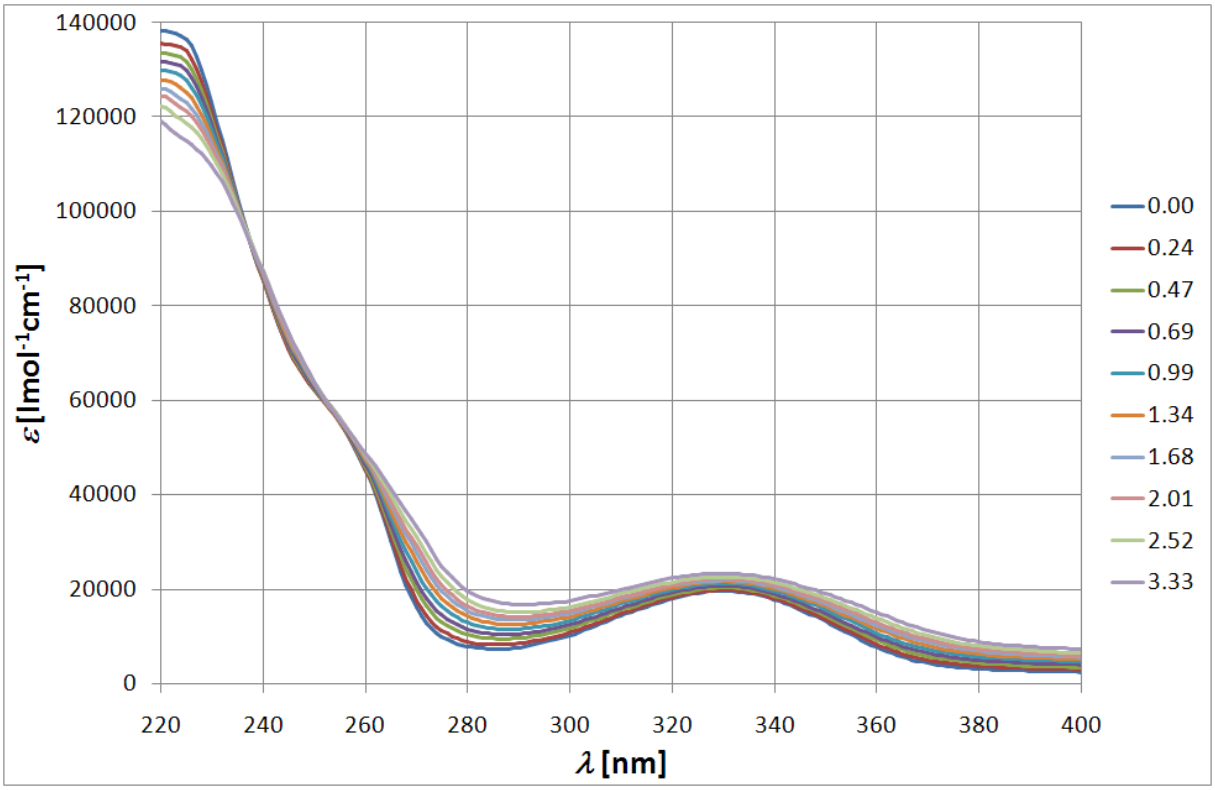
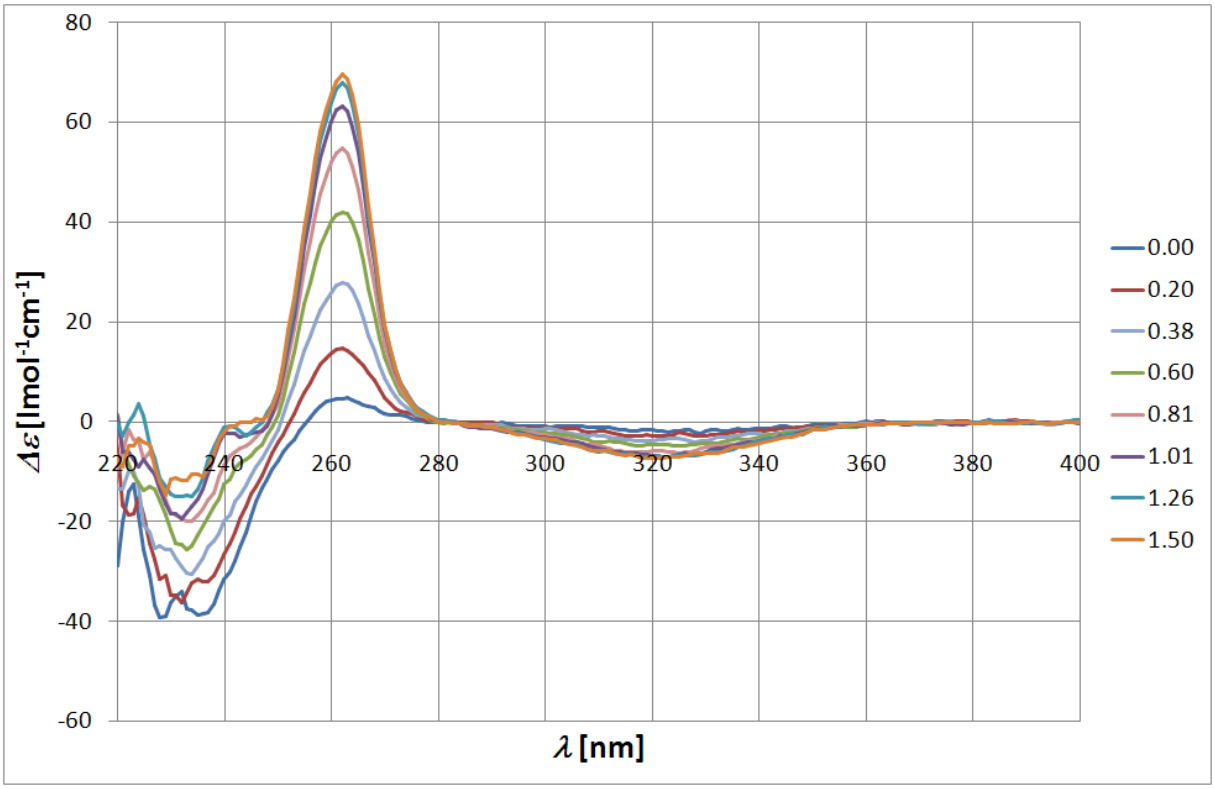




**Figure 4.** Spectrophotometric titration of ligand **1** with $Fe^{3+}$ ([**1**] = $2.0*10^{-5}$ M, MeOH/$H_2O$ : 10/90; 0.10 M TRIS; 0.02 M HCl buffer; pH = 8.95); top: CD spectra; bottom: UV-vis absorption spectra.



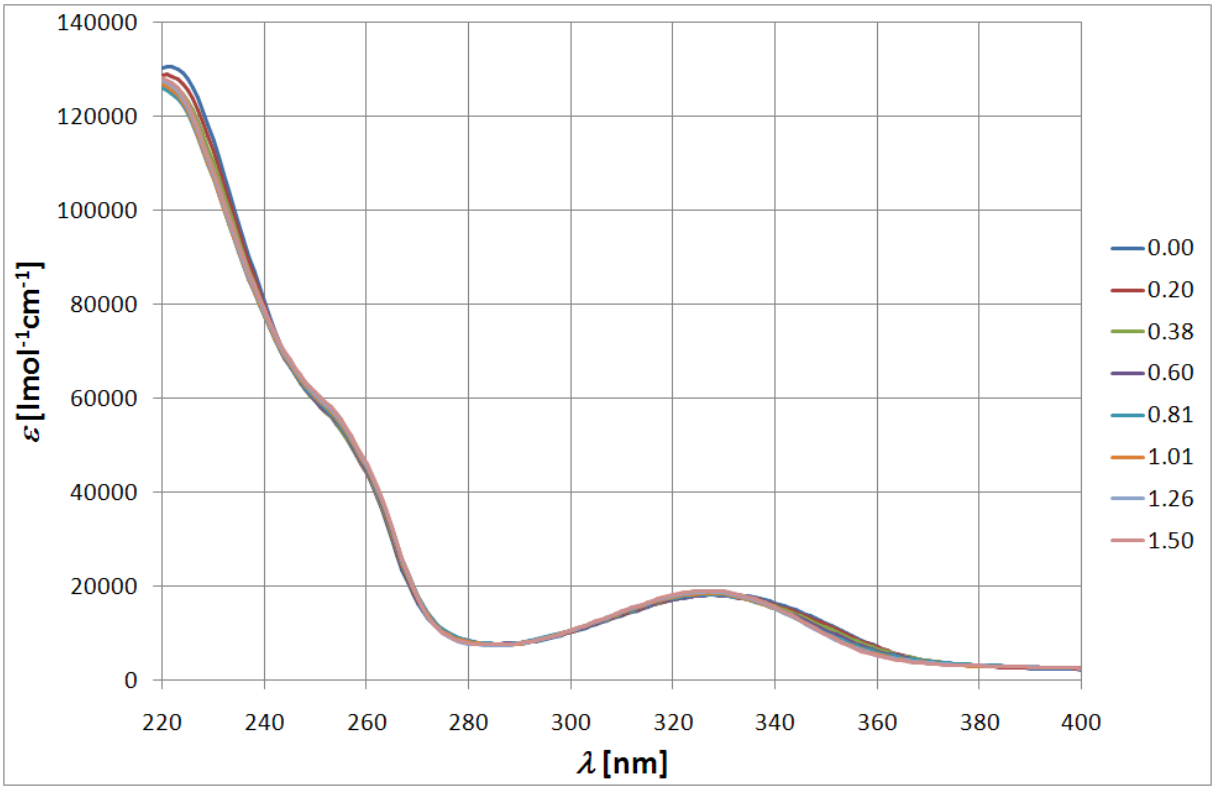
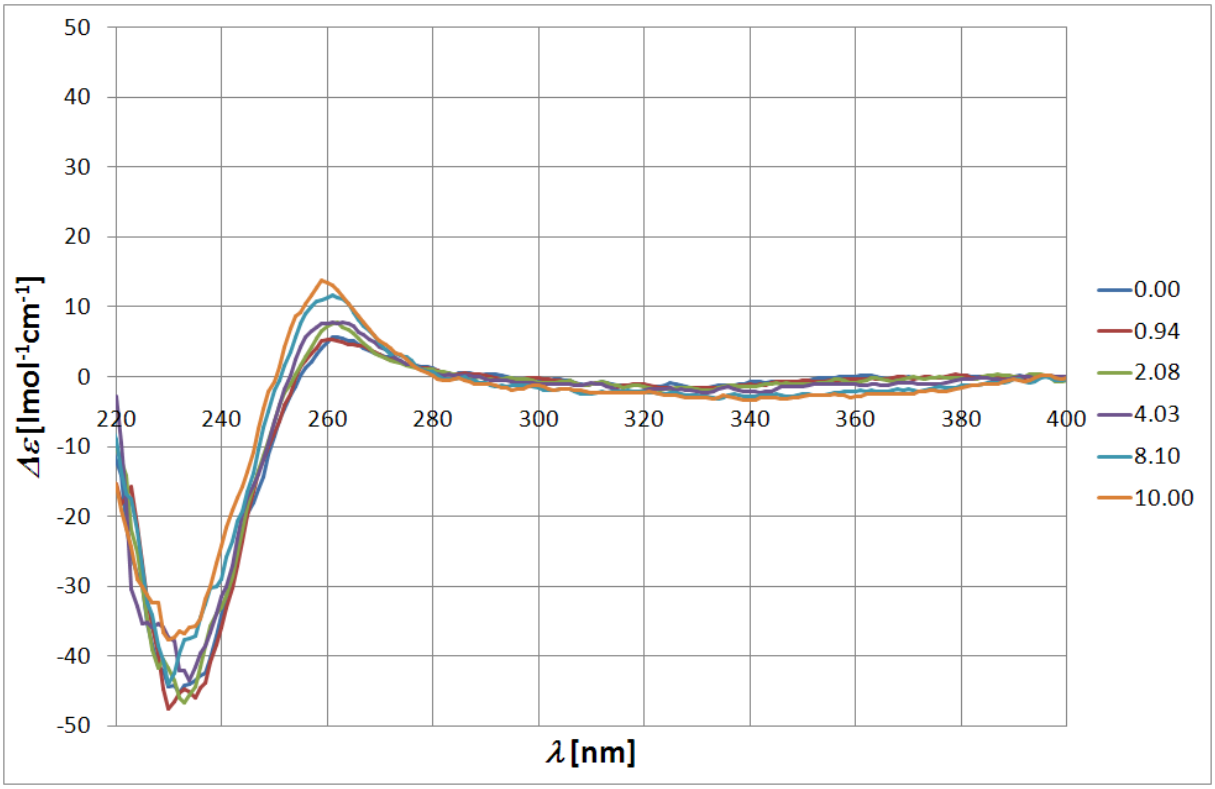




**Figure 5.** Spectrophotometric titration of ligand **1** with $Ge(OCH_3)_4$ ([**1**] = $2.0*10^{-5}$ M, $MeOH/H_2O$ : 10/90; 0.10 M TRIS; 0.02 M HCl buffer; pH = 8.95); top: CD spectra; bottom: UV-vis absorption spectra.



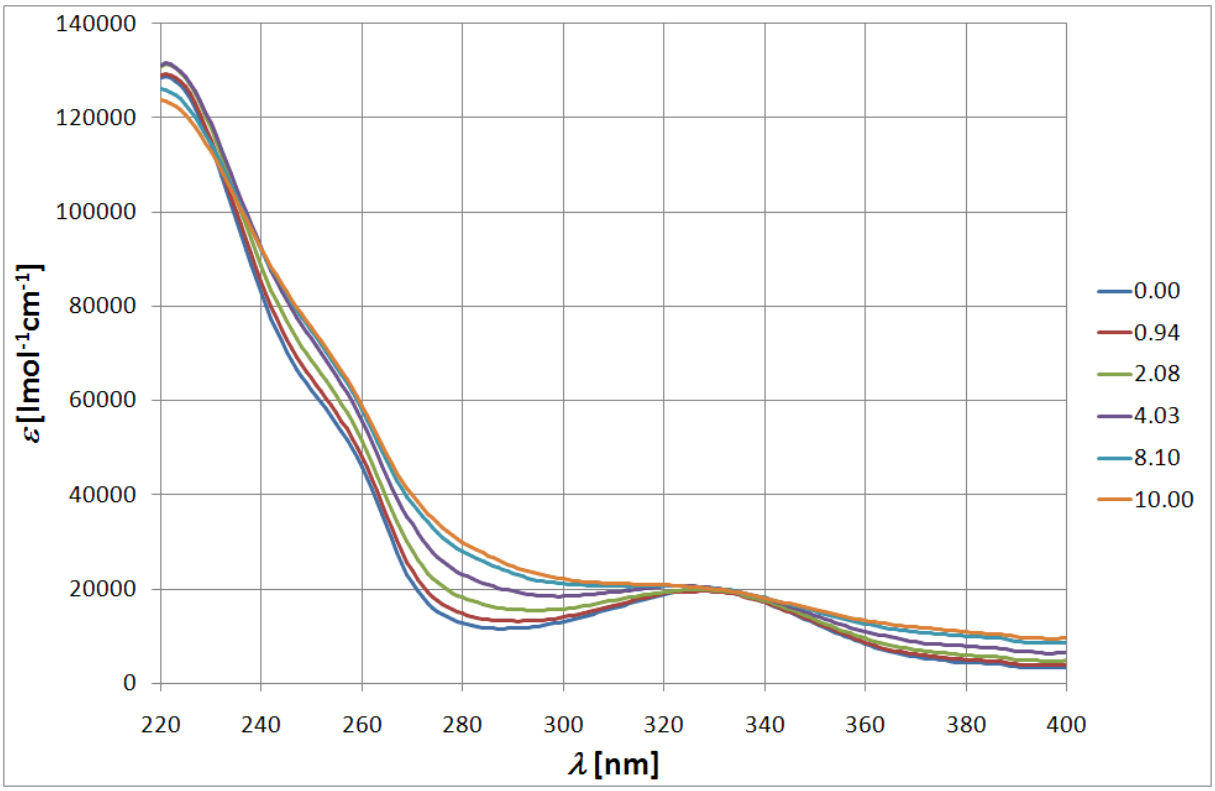




**Figure 6.** Spectrophotometric titration of ligand **1** with Ti(*i*OPr)$_4$ ([**1**] = 2.0*10$^{-5}$ M, MeOH/H$_2$O : 10/90, 0.10 M TRIS / 0.02 M HCl buffer, pH = 8.95); top: CD spectra; bottom: UV-vis absorption spectra.

## 2. Determination of virtual binding constants

Titration experiments for the determination of the association constants were performed with the instrument assembly according to Figure 7. Keeping the concentration of ligand **1** ([L] = $2.0*10^{-5}$ M) constant, the metal to ligand molar ratio (*X = [M]/[L]*) was increased from zero to several equivalents in 50 discrete steps. After each addition, molecular spectra were taken after adequate mixing and equilibration time. From the measured UV-vis absorption (*A(λ,X)*) and ellipticity (*Θ(λ,X)*) data set, molar extinction (*ε(λ,X)*) and molar circular dichroism (*Δε(λ,X)*) values were calculated according to *Lambert-Beer* law. Equations (1) and (2) expressing explicitly the spectral changes as a function of metal to ligand ratio were used to evaluate the virtual association constants (for a particular wavelength) by nonlinear square fitting to the obtained data $\Delta\varepsilon^{\lambda}(X)$ and $\Delta\varepsilon^{\lambda}(X)$, respectively. Numeric analysis was performed with Microcal Origin software program by using *Lewenberg-Marquardt* iteration method.

$$Y^{\lambda}(X) = \varepsilon^{\lambda}_{obs.}(X) =$$
$$= \varepsilon^{\lambda}_{L} + \frac{\varepsilon^{\lambda}_{ML} - \varepsilon^{\lambda}_{L}}{2[L]_{tot}} \left\{ \frac{1}{K} + [L]_{tot}(1+X) - \sqrt{\left( \frac{1}{K} + [L]_{tot}(1+X) \right)^{2} - 4[L]^{2}_{tot} X} \right\} \qquad (1)$$

$$Y^{\lambda}(X) = \Delta\varepsilon^{\lambda}_{obs.}(X) =$$
$$= \Delta\varepsilon^{\lambda}_{L} + \frac{\Delta\varepsilon^{\lambda}_{ML} - \Delta\varepsilon^{\lambda}_{L}}{2[L]_{tot}} \left\{ \frac{1}{K} + [L]_{tot}(1+X) - \sqrt{\left( \frac{1}{K} + [L]_{tot}(1+X) \right)^{2} - 4[L]^{2}_{tot} X} \right\} \qquad (2)$$

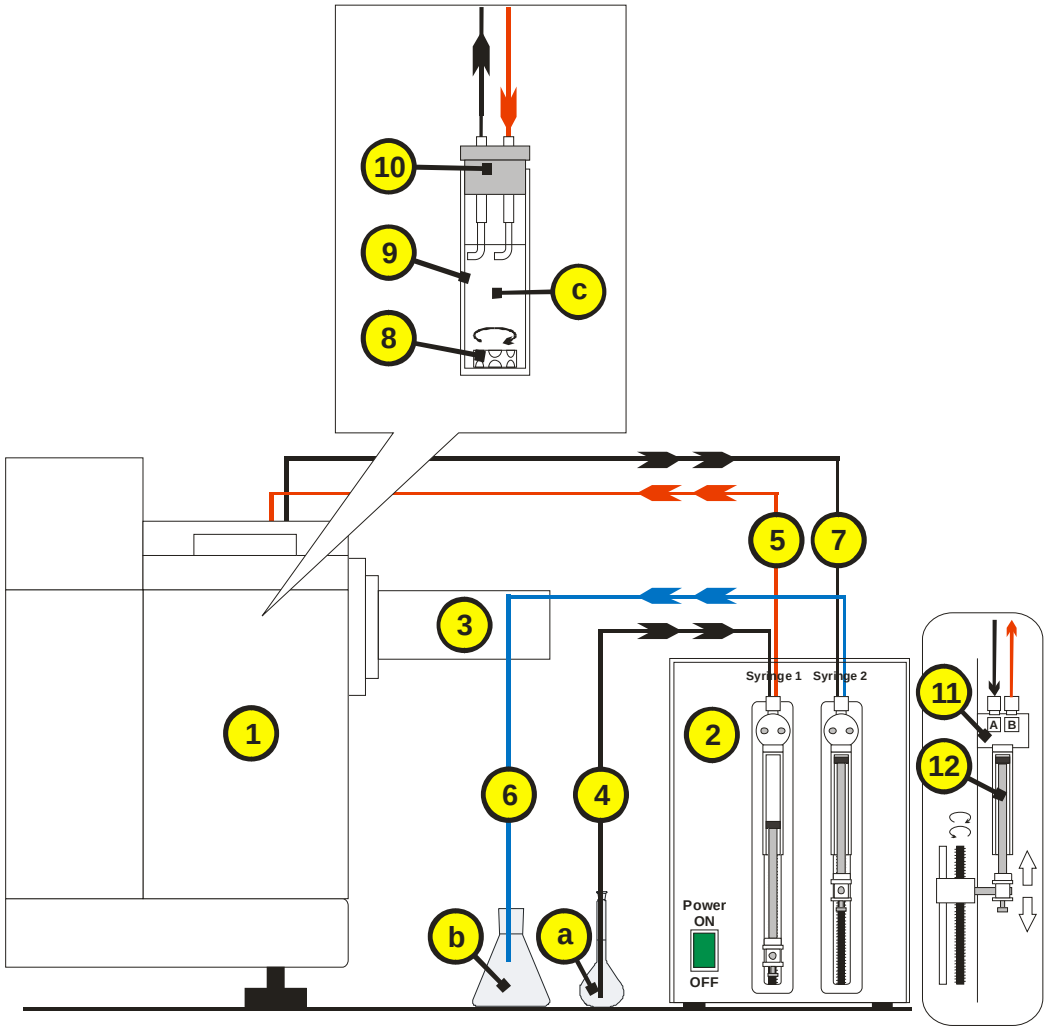



**Figure 7.** 1.) „Jasco J-815“ spectropolarimeter; 2.) „Jasco ATS-443“ automatic titration unit; 3.) detector; 4.) titrant solution intake; 5.) titrant solution inject; 6.) sample solution disposal; 7.) sample solution withdrawal; 8.) stirring magnet; 9.) fluorescence quartz cuvette (l = 1 cm); 10.) cell cap with nozzles; 11.) magnetic valve (changeover the sample inlet/outlet ports.); 12.) Hamilton Microliter™ syringe (V = 2500 µl); a.) titrant solution; b.) waste solution; c.) titrant solution.

## 3. Nuclear magnetic resonance data

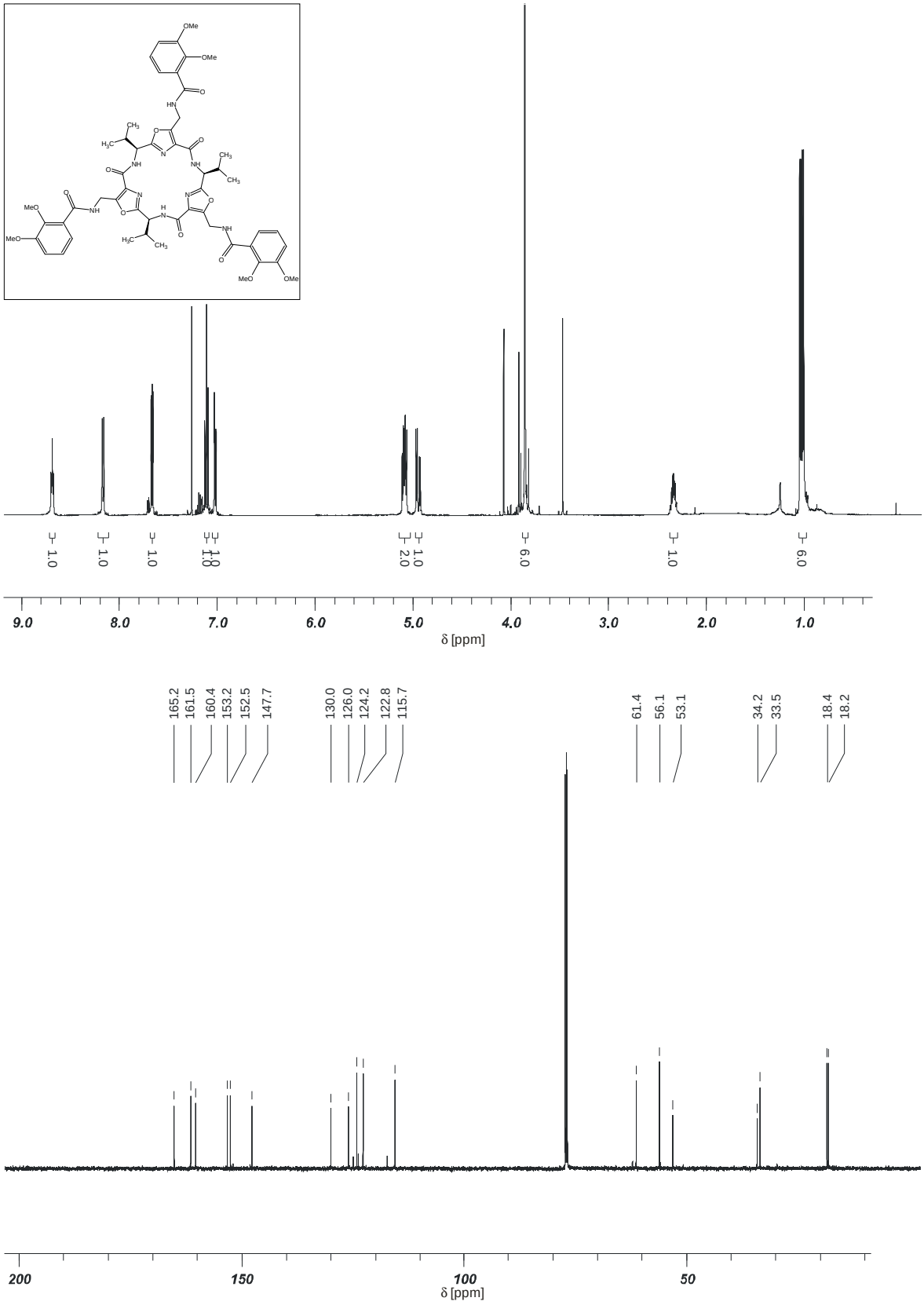



**Figure 8.** $^{1}$H- and $^{13}$C-NMR spectra of methyl protected ligand **8a** in $CDCl_3$.

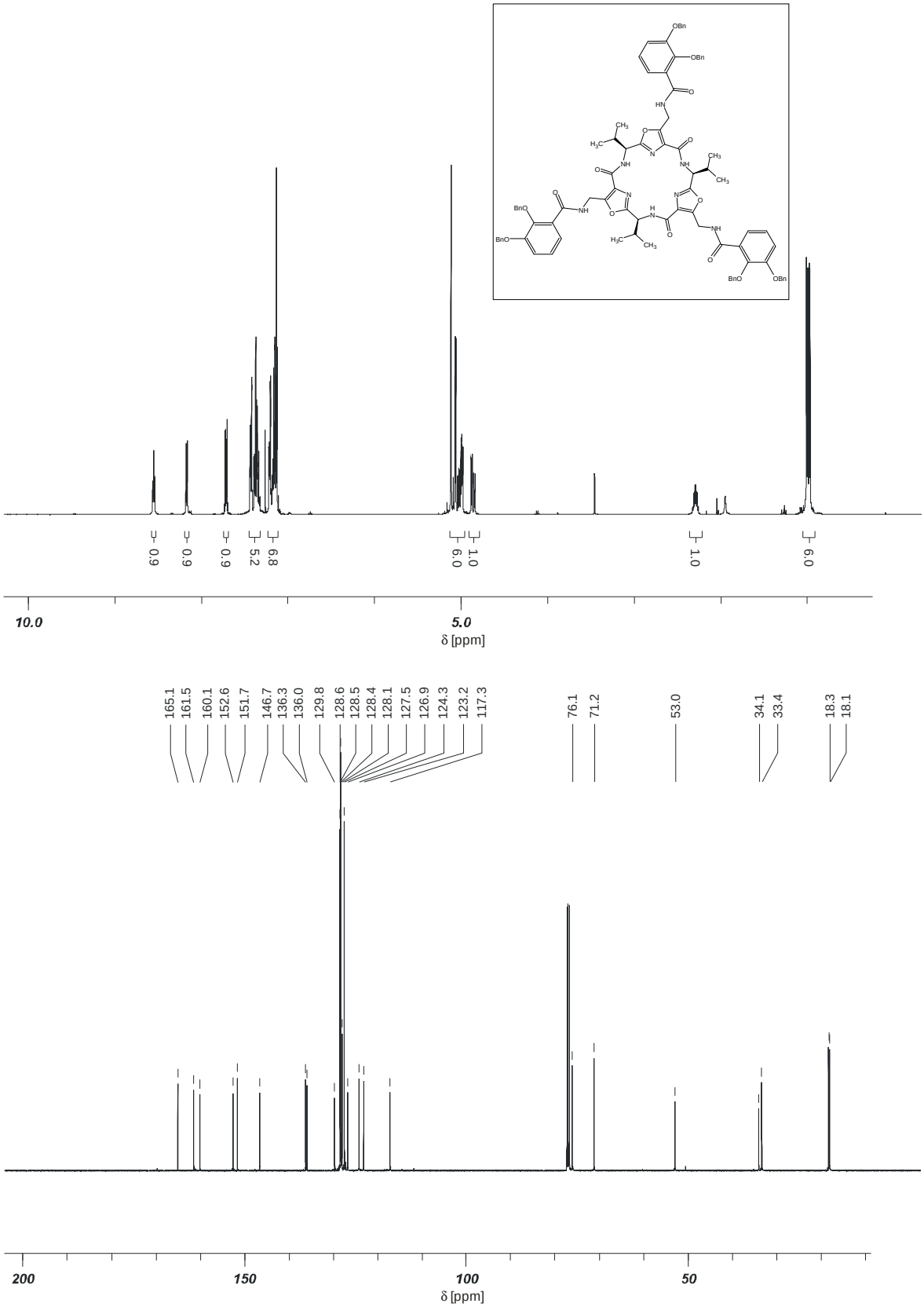



**Figure 9.** $^{1}$H- and $^{13}$C-NMR spectra of benzyl protected ligand **8b** in $CDCl_3$.

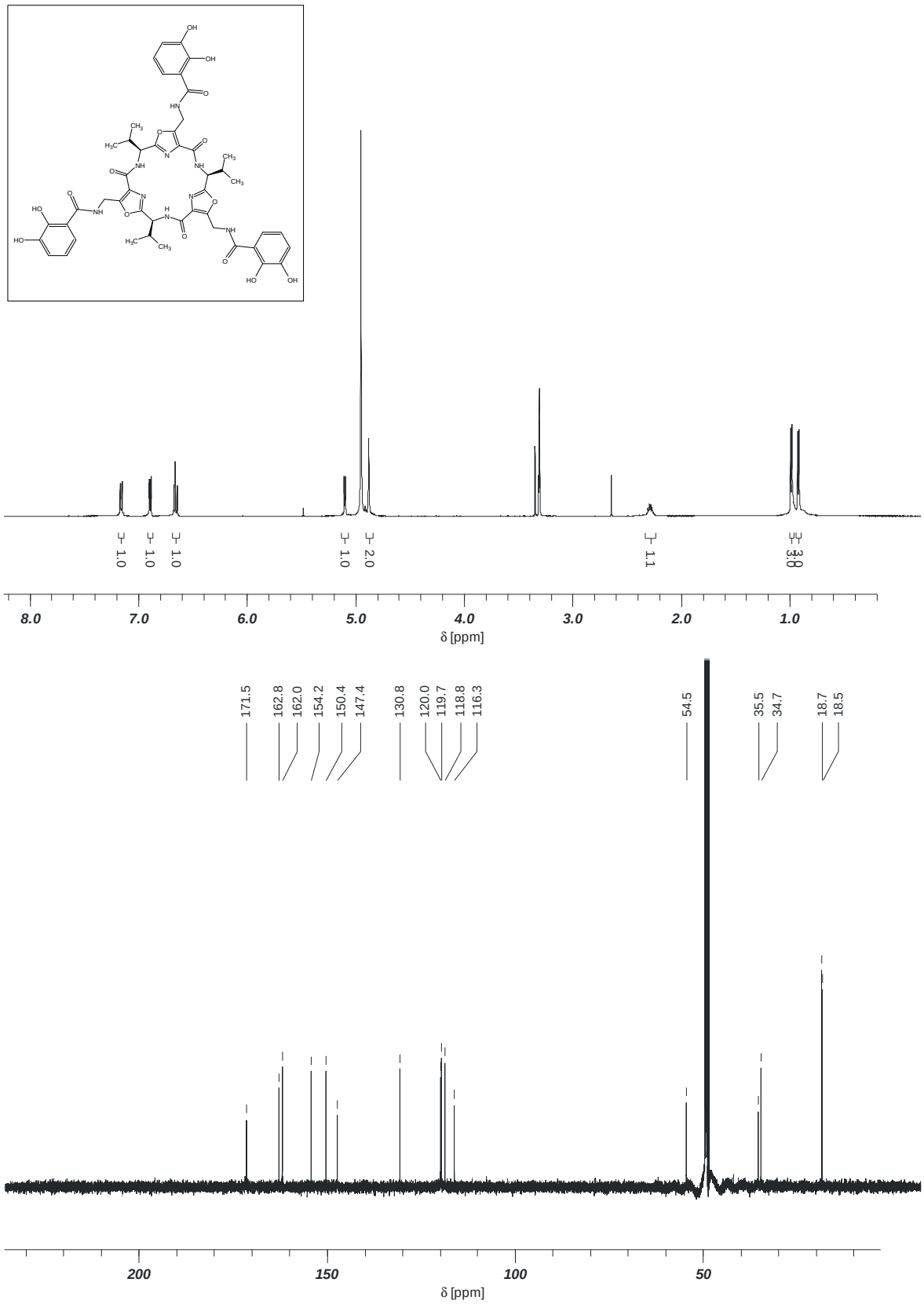



**Figure 10.** $^{1}$H- and $^{13}$C-NMR spectra of ligand **1** in MeOH-d4.