

Supplementary Materials:

Interaction of the Fungal Metabolite Harzianic Acid with Rare-Earth Cations (La^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+})

Gaetano De Tommaso ^{1,*}, Maria Michela Salvatore ^{1,2,*}, Antonietta Siciliano ³, Alessia Staropoli ^{2,4}, Francesco Vinale ^{2,5,6}, Rosario Nicoletti ^{4,7}, Marina DellaGreca ¹, Marco Guida ³, Francesco Salvatore ^{1,*}, Mauro Iuliano ^{1,*}, Anna Andolfi ^{1,6,*}

¹ Department of Chemical Sciences, University of Naples Federico II, Naples 80126, Italy; gaetano.detomaso@unina.it (G.D.T.), mariamichela.salvatore@unina.it (M.M.S.), dellagre@unina.it (M.D.G)

² Institute for Sustainable Plant Protection, National Research Council, Portici 80055 (NA), Italy;

³ Department of Biology, University of Naples Federico II, Naples, Italy; antonietta.siciliano@unina.it (A.S.), marco.guida@unina.it (M.G.)

⁴ Department of Agricultural Sciences, University of Naples Federico II, Portici 80055 (NA), Italy; alessia.staropoli@unina.it (A.S.)

⁵ Department of Veterinary Medicine and Animal Productions, University of Naples Federico II, 80137Naples, Italy; frvinale@unina.it (F.V.)

⁶ BAT Center - Interuniversity Center for Studies on Bioinspired Agro-Environmental Technology, University of Naples Federico II, Portici (NA) 80055, Italy

⁷ Council for Agricultural Research and Economics, Research Centre for Olive, Fruit and Citrus Crops, 81100 Caserta, Italy; rosario.nicoletti@crea.gov.it (R.N.)

* Correspondence: frsalvat@unina.it (F.S.), mauro.iuliano@unina.it (M.I.); andolfi@unina.it (A.A.); Tel.: +39-081-2539179 (A.A.)

These authors contributed equally to this work.

Figure S1. Far-UV circular dichroism (CD) spectra (optical path 0.2 cm) of harziaic acid in $\text{CH}_3\text{OH}/0.1 \text{ M NaClO}_4$ (50:50 w/w) at different pH values: $C_{\text{H}_2\text{L}} \leq 1.72 \times 10^{-4} \text{ M}$.

Figure S2. Far-UV circular dichroism (CD) spectra (optical path 1 cm) of $\text{La}(\text{ClO}_4)_3$ in $\text{CH}_3\text{OH}/0.1 \text{ M NaClO}_4$ (50:50 w/w) at different pH values: (A) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{La}}} = 0.995$, $C_{\text{La}} \leq 3.82 \times 10^{-5} \text{ M}$; (B) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{La}}} = 1.992$, $C_{\text{La}} \leq 3.99 \times 10^{-5} \text{ M}$.

Figure S3. Far-UV circular dichroism (CD) spectra (optical path 0.2 cm) of NdCl_3 in $\text{CH}_3\text{OH}/0.1 \text{ M NaClO}_4$ (50:50 w/w) at different pH values: (A) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Nd}}} = 1.000$, $C_{\text{Nd}} \leq 23.3 \times 10^{-4} \text{ M}$; (B) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Nd}}} = 1.935$, $C_{\text{Nd}} \leq 8.26 \times 10^{-5} \text{ M}$.

Figure S4. Far-UV circular dichroism (CD) spectra (optical path 1 cm) of $\text{Sm}(\text{ClO}_4)_3$ in $\text{CH}_3\text{OH}/0.1 \text{ M NaClO}_4$ (50:50 w/w) at different pH values: (A) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Sm}}} = 1.051$, $C_{\text{Sm}} \leq 8.04 \times 10^{-5} \text{ M}$; (B) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Sm}}} = 2.02$, $C_{\text{Sm}} \leq 3.01 \times 10^{-5} \text{ M}$.

Figure S5. Far-UV circular dichroism (CD) spectra (optical path 1 cm) of GdCl_3 in $\text{CH}_3\text{OH}/0.1 \text{ M NaClO}_4$ (50:50 w/w) at different pH values: (A) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Gd}}} = 1.00$, $C_{\text{Gd}} \leq 6.44 \times 10^{-5} \text{ M}$; (B) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Gd}}} = 1.99$, $C_{\text{Gd}} \leq 4.57 \times 10^{-5} \text{ M}$.

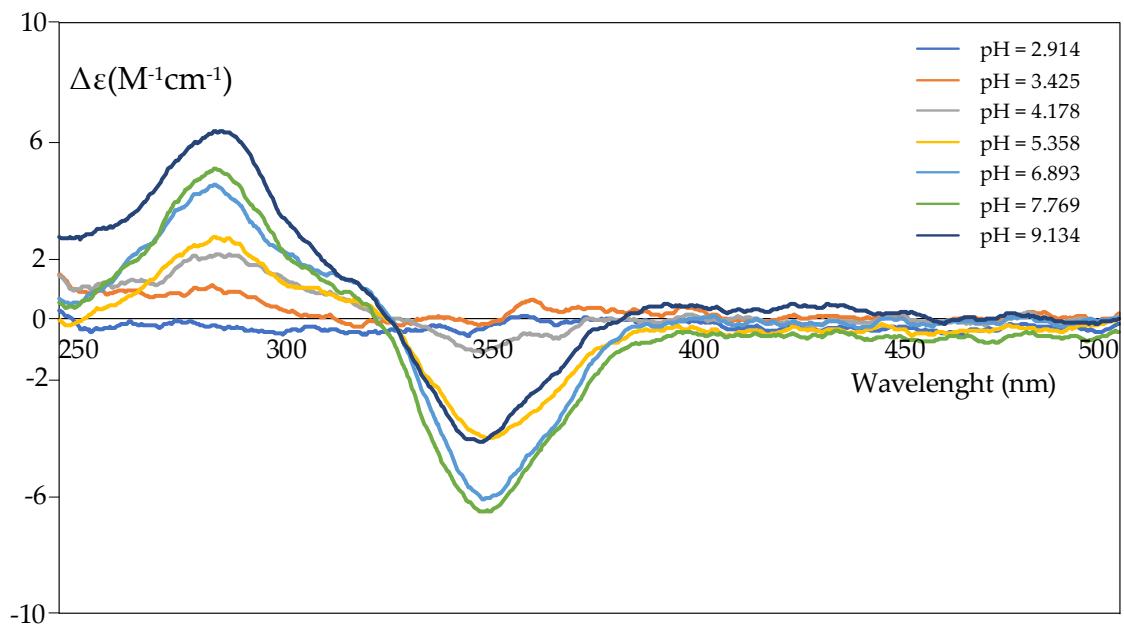
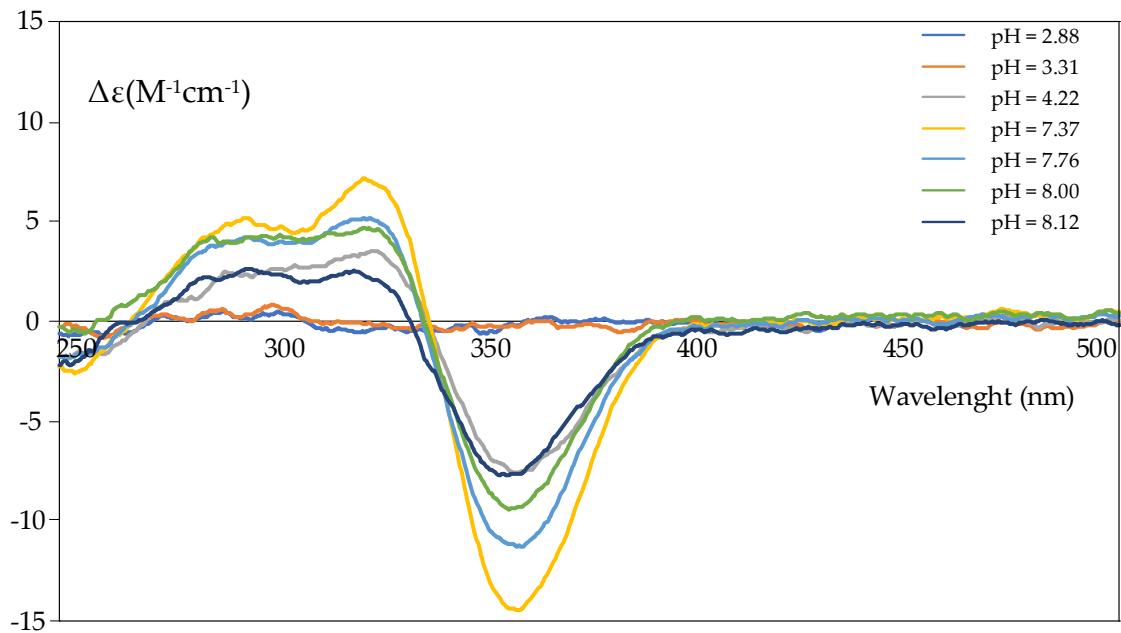


Figure S1. Far-UV circular dichroism (CD) spectra (optical path 0.2 cm) of harziaic acid in $\text{CH}_3\text{OH}/0.1 \text{ M NaClO}_4$ (50:50 w/w) at different pH values: $C_{\text{H}_2\text{L}} \leq 1.72 \times 10^{-4} \text{ M}$.

(A)



(B)

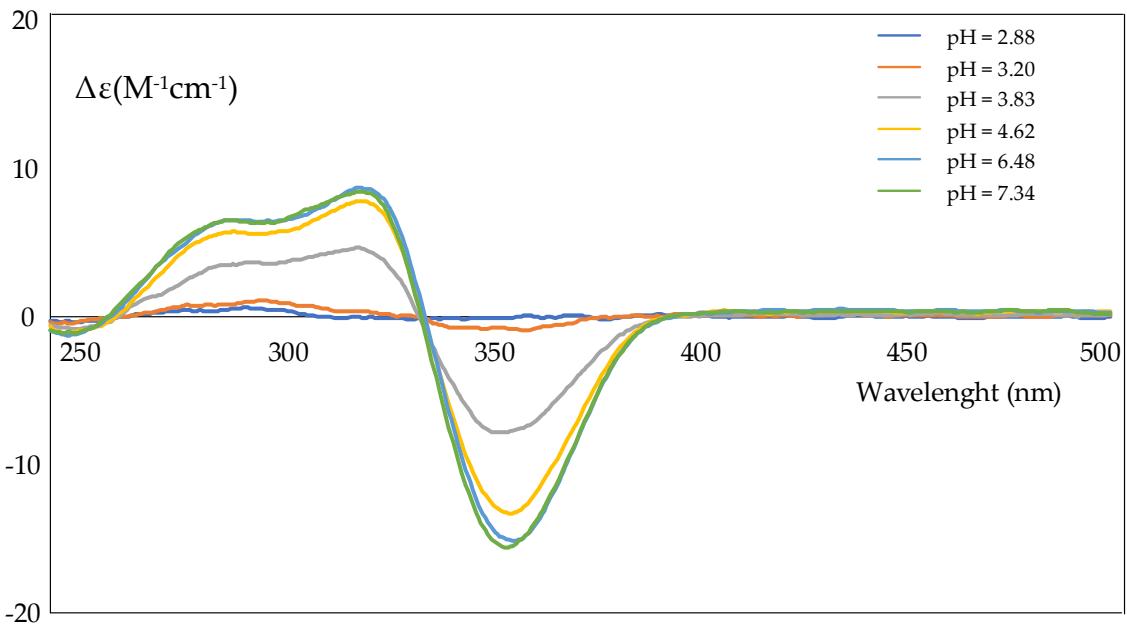
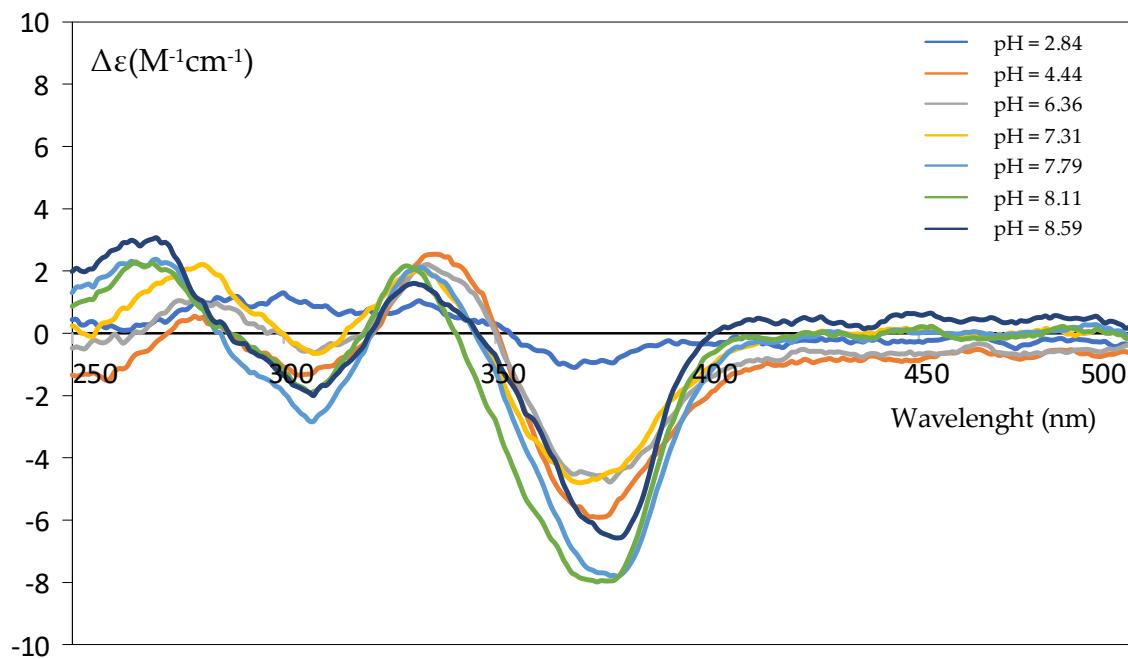


Figure S2. Far-UW circular dichroism (CD) spectra (optical path 1 cm) of $\text{La}(\text{ClO}_4)_3$ in $\text{CH}_3\text{OH}/0.1 \text{ M NaClO}_4$ (50:50 w/w) at different pH values: (A) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{La}}} = 0.995$, $C_{\text{La}} \leq 3.82 \times 10^{-5} \text{ M}$; (B) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{La}}} = 1.992$, $C_{\text{La}} \leq 3.99 \times 10^{-5} \text{ M}$.

(A)



(B)

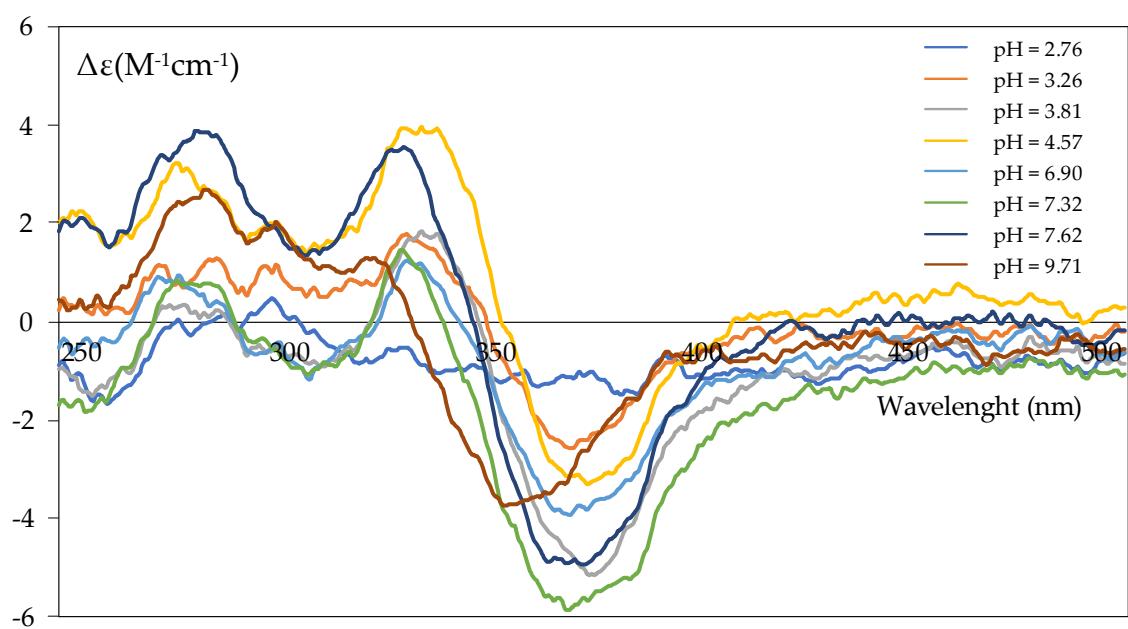
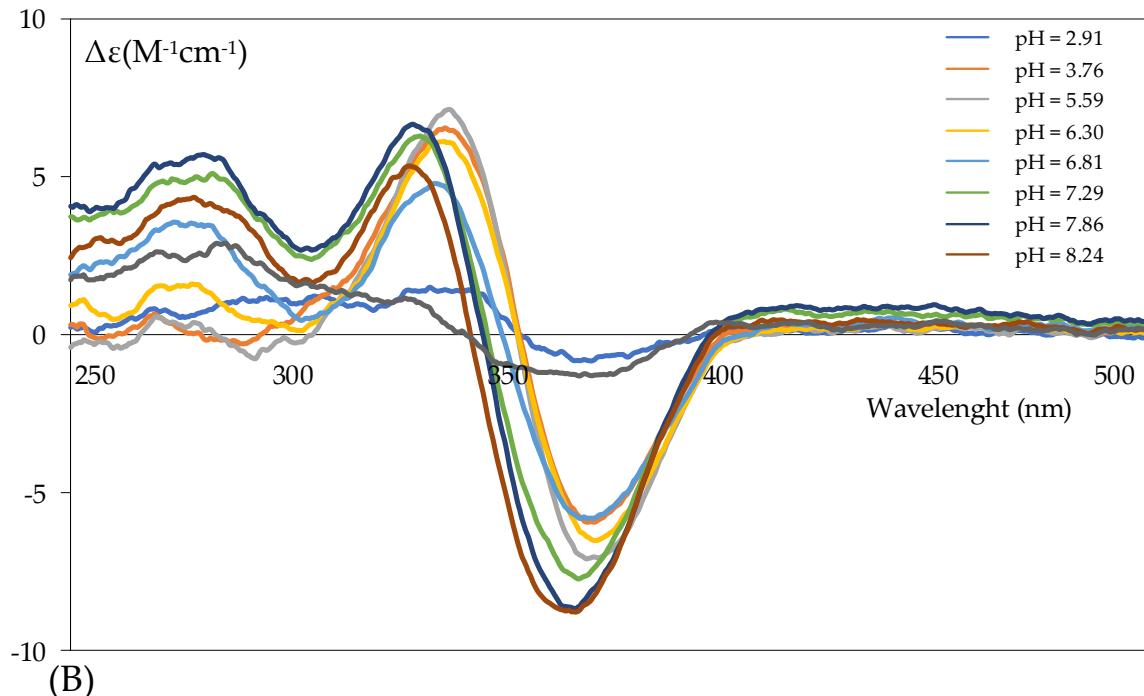


Figure S3. Far-UV circular dichroism (CD) spectra (optical path 0.2 cm) of NdCl₃ in CH₃OH/0.1 M NaClO₄ (50:50 w/w) at different pH values: (A) $\frac{C_{H_2L}}{C_{Nd}} = 1.000$, $C_{Nd} \leq 23.3 \times 10^{-4}$ M; (B) $\frac{C_{H_2L}}{C_{Nd}} = 1.935$, $C_{Nd} \leq 8.26 \times 10^{-5}$ M.

(A)



(B)

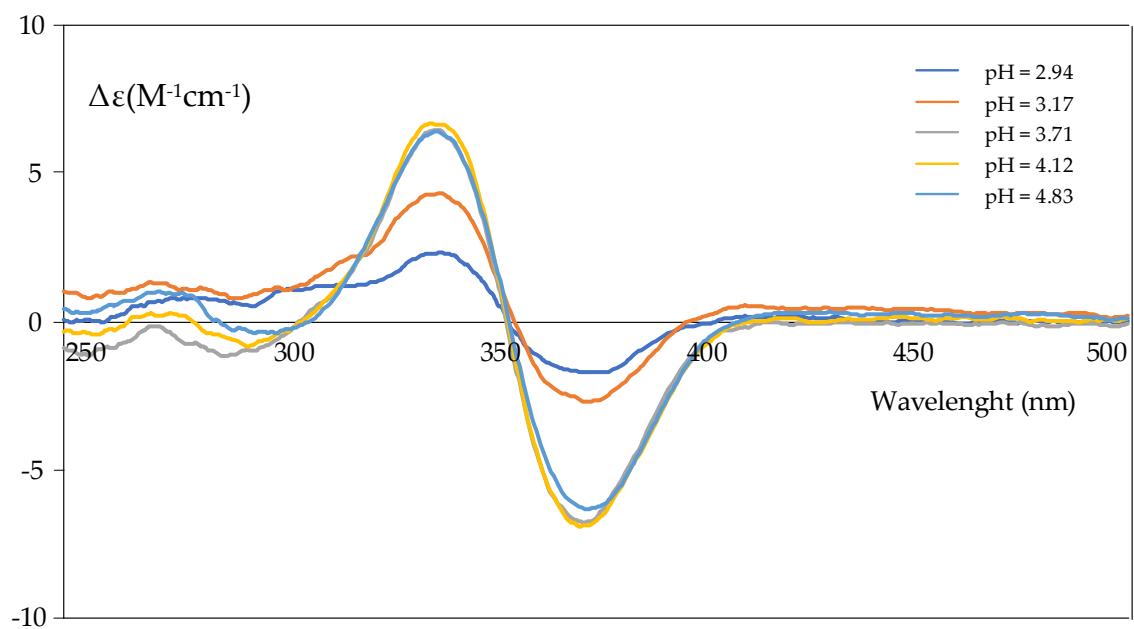


Figure S4. Far-UV circular dichroism (CD) spectra (optical path 1 cm) of $\text{Sm}(\text{ClO}_4)_3$ in $\text{CH}_3\text{OH}/0.1 \text{ M NaClO}_4$ (50:50 *w/w*) at different pH values: (A) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Sm}}} = 1.051$, $C_{\text{Sm}} \leq 8.04 \times 10^{-5} \text{ M}$; (B) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Sm}}} = 2.02$, $C_{\text{Sm}} \leq 3.01 \times 10^{-5} \text{ M}$.

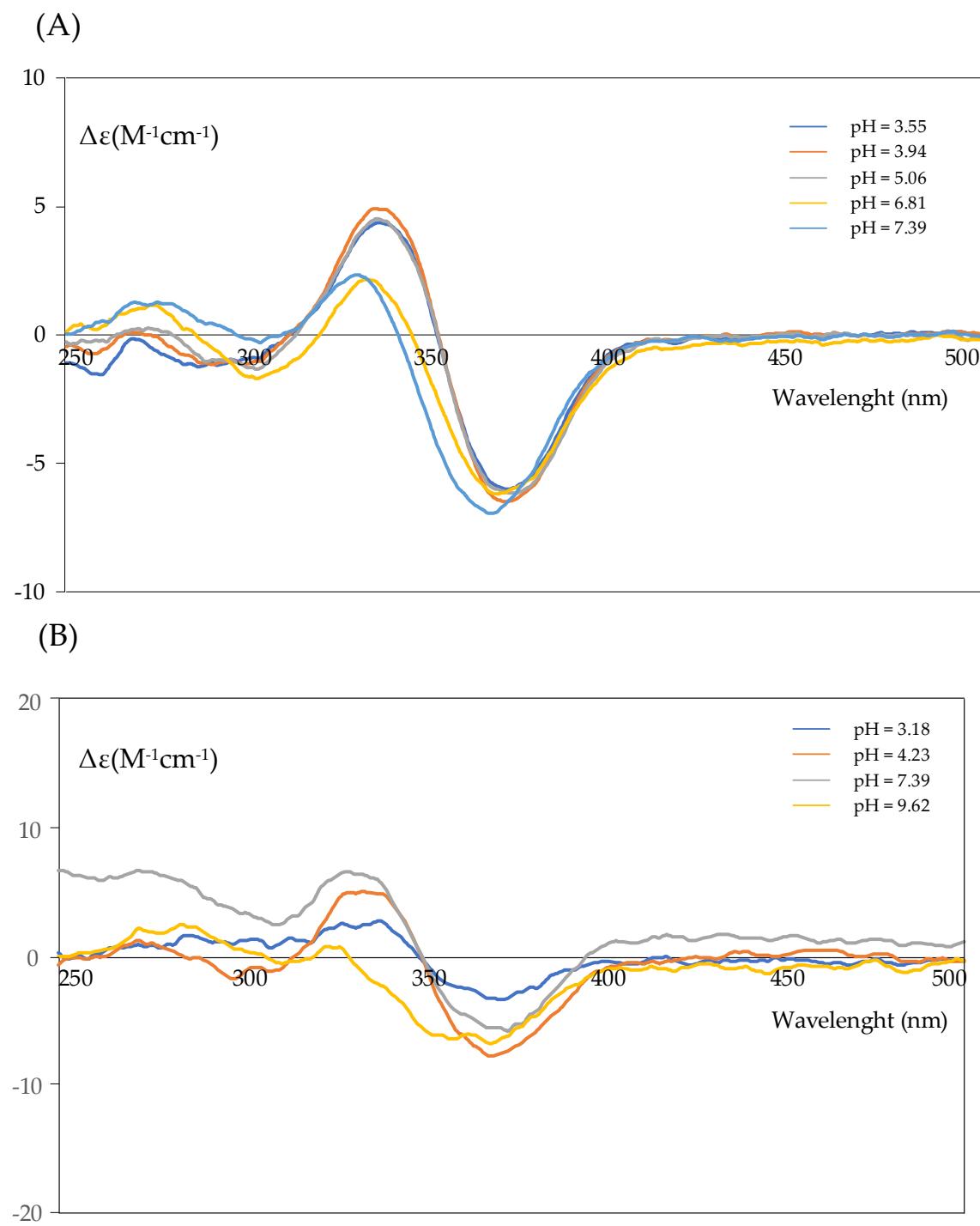


Figure S5. Far-UV circular dichroism (CD) spectra (optical path 1 cm) of GdCl_3 in $\text{CH}_3\text{OH}/0.1 \text{ M NaClO}_4$ (50:50 w/w) at different pH values: (A) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Gd}}} = 1.00$, $C_{\text{Gd}} \leq 6.44 \times 10^{-5} \text{ M}$; (B) $\frac{C_{\text{H}_2\text{L}}}{C_{\text{Gd}}} = 1.99$, $C_{\text{Gd}} \leq 4.57 \times 10^{-5} \text{ M}$.