

## *Supplementary*

### **Vanadium Complexes with Thioanilide Derivatives of Amino Acids: Inhibition of Human Phosphatases and Specificity in Various Cell Models of Metabolic Disturbances**

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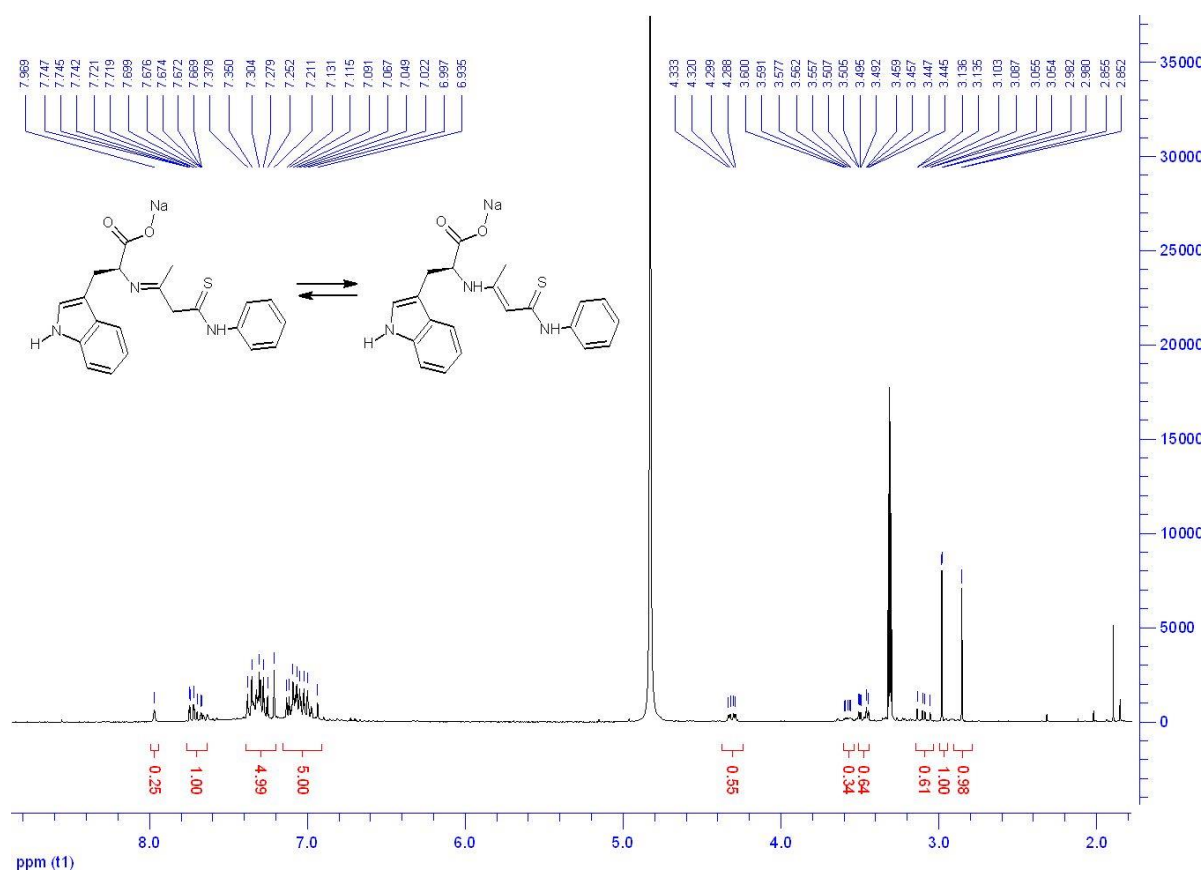
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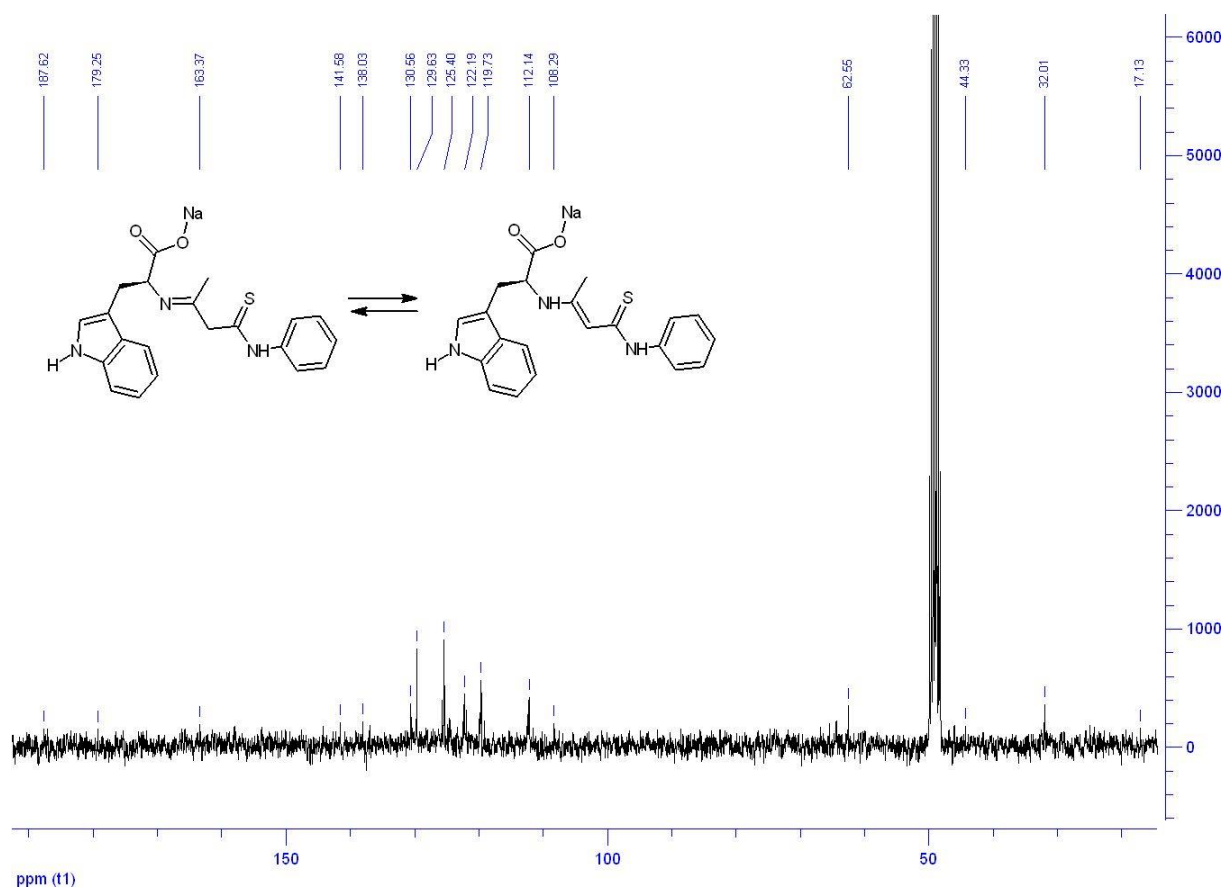
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**$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the L<sub>1</sub>-L<sub>5</sub> ligands.**



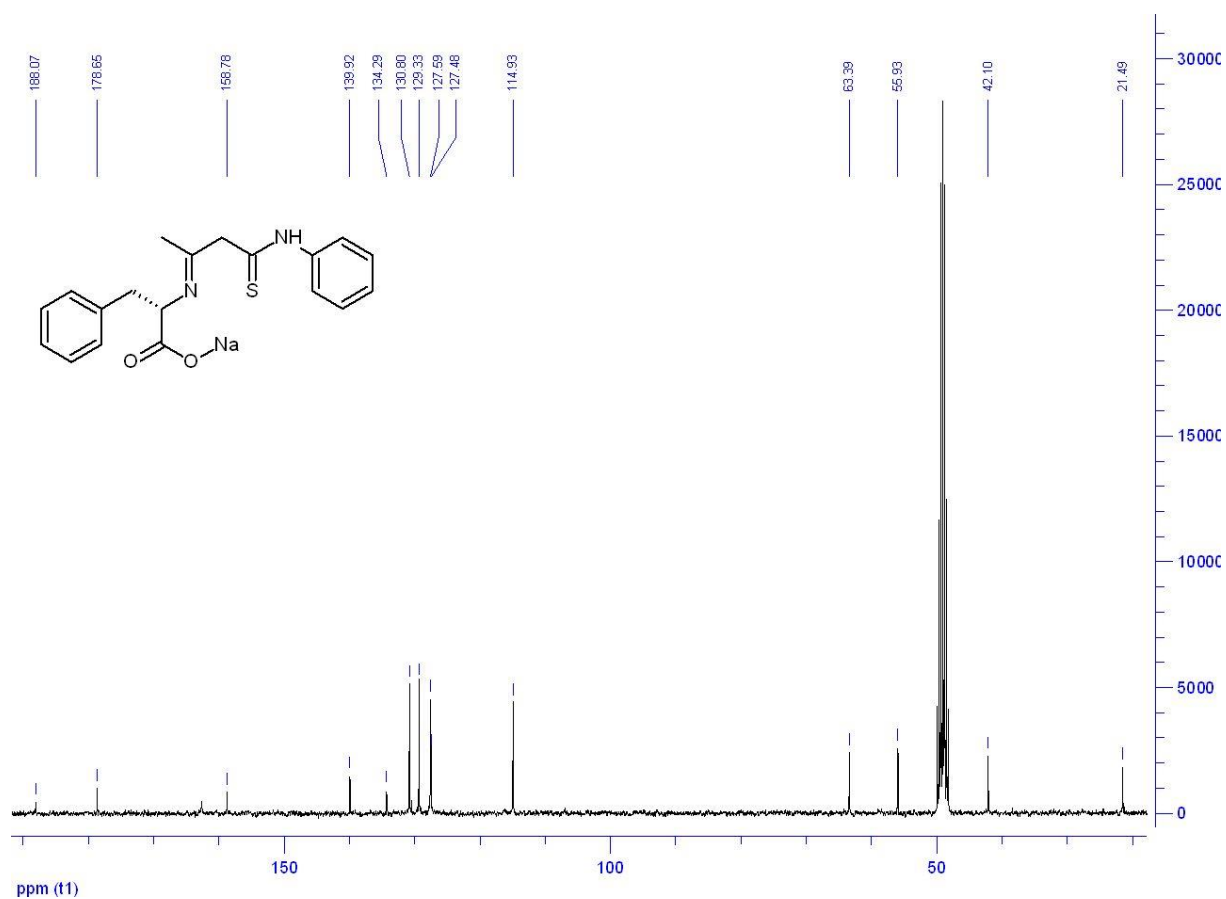
**Figure S1.**  $^1\text{H}$ -NMR spectrum of L<sub>1</sub>. ( $\text{CD}_3\text{OD}$ ).  $\sigma$  [ppm] = 7.96 (br. s, NH), 7.74 (m, 1H, Ar-H), 7.72 (m, 1H, Ar-H), 7.28 (m, 4H, Ar-H), 7.21 (br. s, NH), 7.05 (m, 5H, Ar-H), 4.31 (dd, 1H,  $J_{\text{HH}}$  = 3.6 and 9.9 Hz, CH imine), 3.58 (m, 1H, CH enamine), 3.47 (dd, 2H,  $J_{\text{HH}}$  = 3.7 and 15.0 Hz,  $\text{CH}_\text{a}\text{H}_\text{b}$  enamine), 2.94 (dd, 1H,  $J_{\text{HH}}$  = 10.0 and 15.0 Hz,  $\text{CH}_\text{a}\text{H}_\text{b}$  imine), 2.99 (s, 3H,  $\text{CH}_3$  enamine), 2.85 (s, 3H,  $\text{CH}_3$  imine).



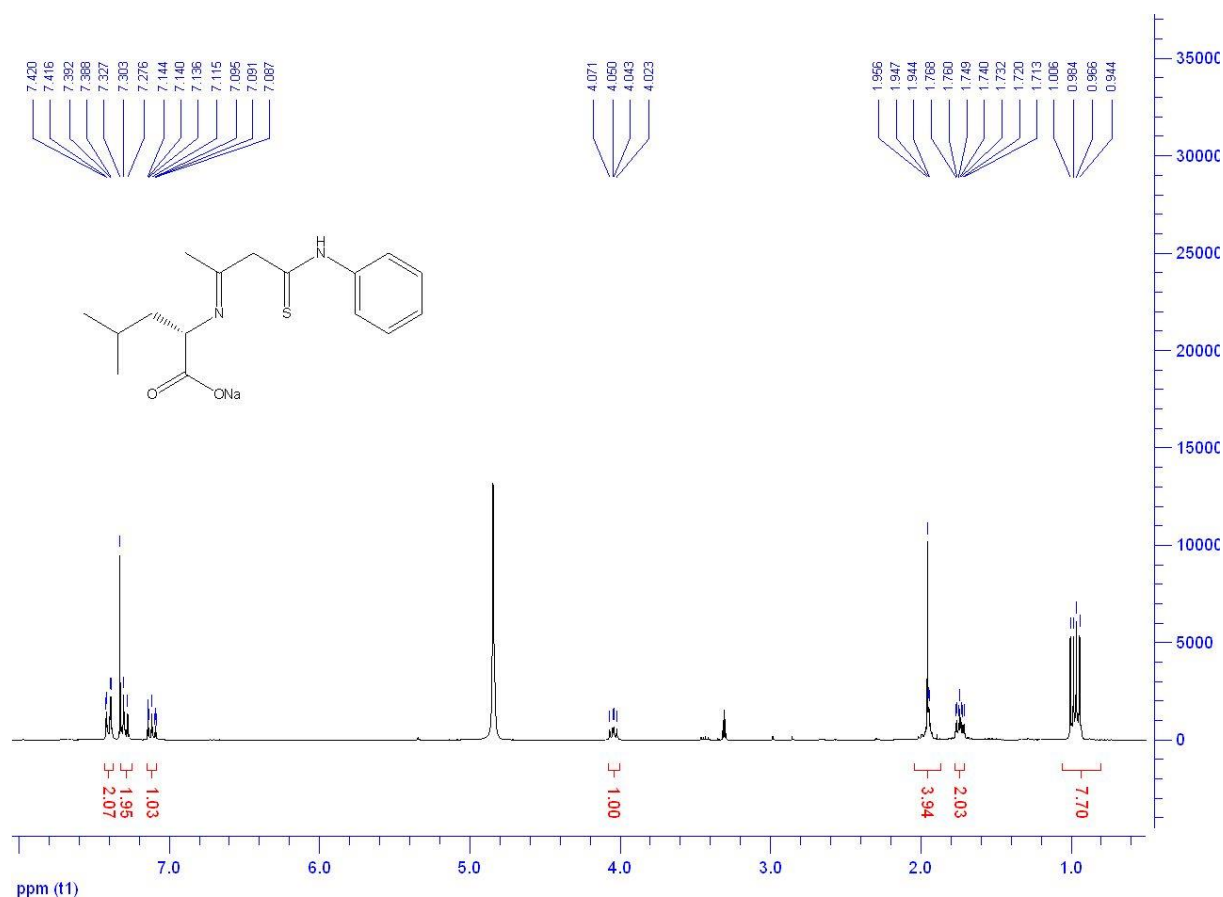
**Figure S2.** <sup>13</sup>C-NMR spectrum of **L1**. (CD<sub>3</sub>OD)σ [ppm] = 187.6 (C=S), 179.2 (COONa), 163.4 (C=N), 141.6 (Ar), 138.0 (Ar), 130.5 (Ar), 129.6 (Ar), 125.4 (Ar), 122.2 (Ar), 119.7 (Ar), 112.1 (Ar), 108.3 (Ar), 62.5 (CH), 44.3 (CH<sub>2</sub>), 32.0 (CH<sub>2</sub>), 17.1 (CH<sub>3</sub>).



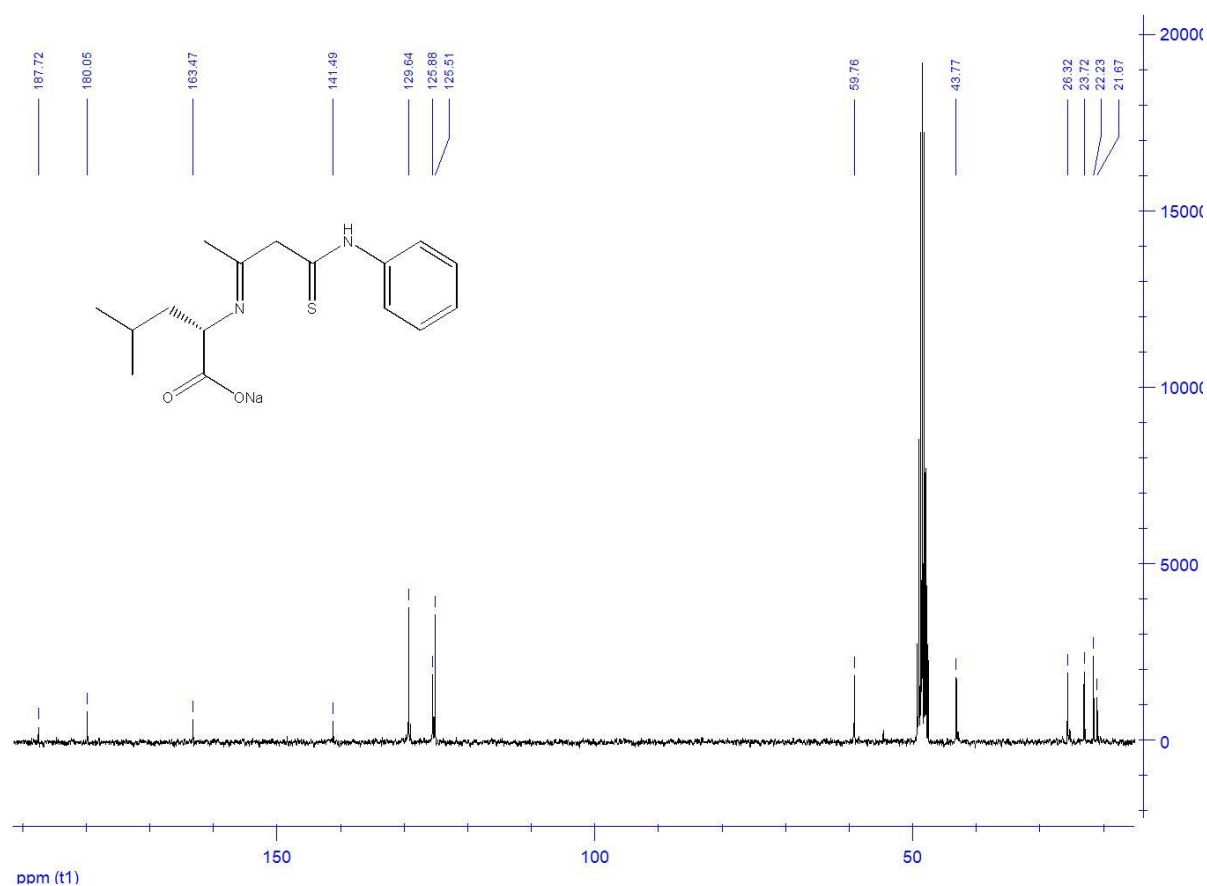
**Figure S3.**  $^1\text{H-NMR}$  spectrum of  $L_2$ . ( $\text{CD}_3\text{OD}$ ).  $\sigma$  [ppm] = 7.37 (d, 2H,  $J_{\text{HH}} = 6.7$  Hz, Ph-H), 7.23 (m, 6H, Ph-H), 6.86 (d, 2H,  $J_{\text{HH}} = 9.1$  Hz, Ph-H), 4.18 (dd, 1H,  $J_{\text{HH}} = 3.8$  and 9.7 Hz, CH), 3.77 (s, 3H,  $\text{CH}_3$ ), 3.26 (dd, 1H,  $J_{\text{HH}} = 3.8$  and 13.8 Hz,  $\text{CH}_a\text{H}_b$ ), 2.94 (dd, 1H,  $J_{\text{HH}} = 9.8$  and 13.8 Hz,  $\text{CH}_a\text{H}_b$ ), 1.55 (s, 2H,  $\text{CH}_2$ ).



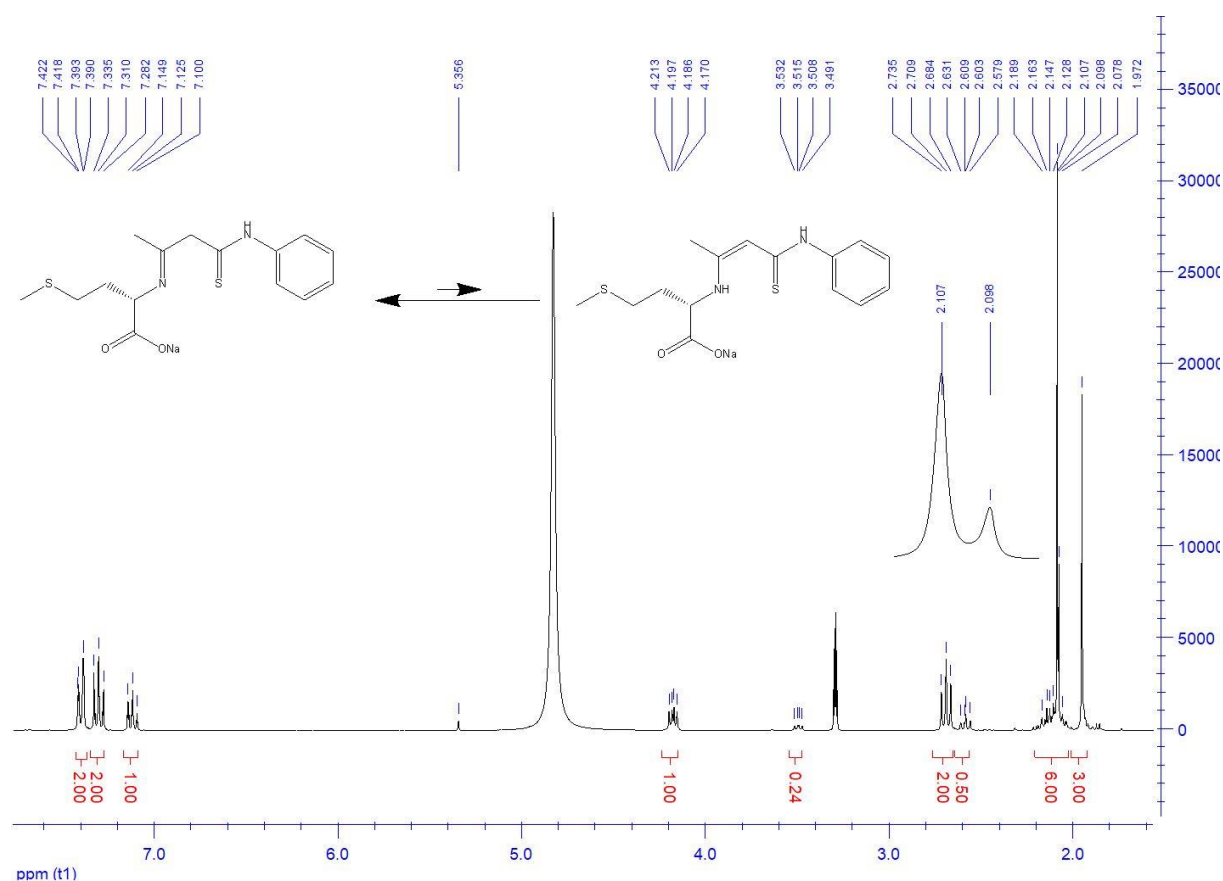
**Figure S4.** <sup>13</sup>C-NMR spectrum of L<sub>2</sub>. (CD<sub>3</sub>OD)σ [ppm] = 188.1 (C=S), 178.6 (COONa), 158.8 (C=N), 139.9 (Ph), 134.3 (Ph), 130.8 (Ph), 129.3 (Ph), 127.6 (Ph), 127.5 (Ph), 114.9 (Ph), 63.4 (CH), 55.9 (CH<sub>2</sub>), 42.1 (CH<sub>2</sub>), 21.5 (CH<sub>3</sub>).



**Figure S5.** <sup>1</sup>H-NMR spectrum of L<sub>3</sub>. (CD<sub>3</sub>OD).  $\sigma$  [ppm] = 7.40 (d, 2H,  $J_{\text{HH}} = 8.5$  Hz, Ph-H), 7.33 (s, 1H, NH), 7.30 (t, 2H,  $J_{\text{HH}} = 8.2$  Hz, Ph-H), 7.12 (t, 1H,  $J_{\text{HH}} = 7.3$  Hz, Ph-H), 4.04 (dd, 1H,  $J_{\text{HH}} = 6.1$  and 8.2 Hz, CH), 1.96 (s, 3H, CH<sub>3</sub>), 1.95 (m, 1H, CH), 1.75 (ddd, 1H,  $J_{\text{HH}} = 2.3$ , 5.8 and 8.2 Hz, CH<sub>a</sub>H<sub>b</sub>), 0.99 (d, 3H,  $J_{\text{HH}} = 6.6$  Hz, CH<sub>3</sub>), 0.99 (br. s, 2H, CH<sub>2</sub>), 0.95 (d, 3H,  $J_{\text{HH}} = 6.6$  Hz, CH<sub>3</sub>).

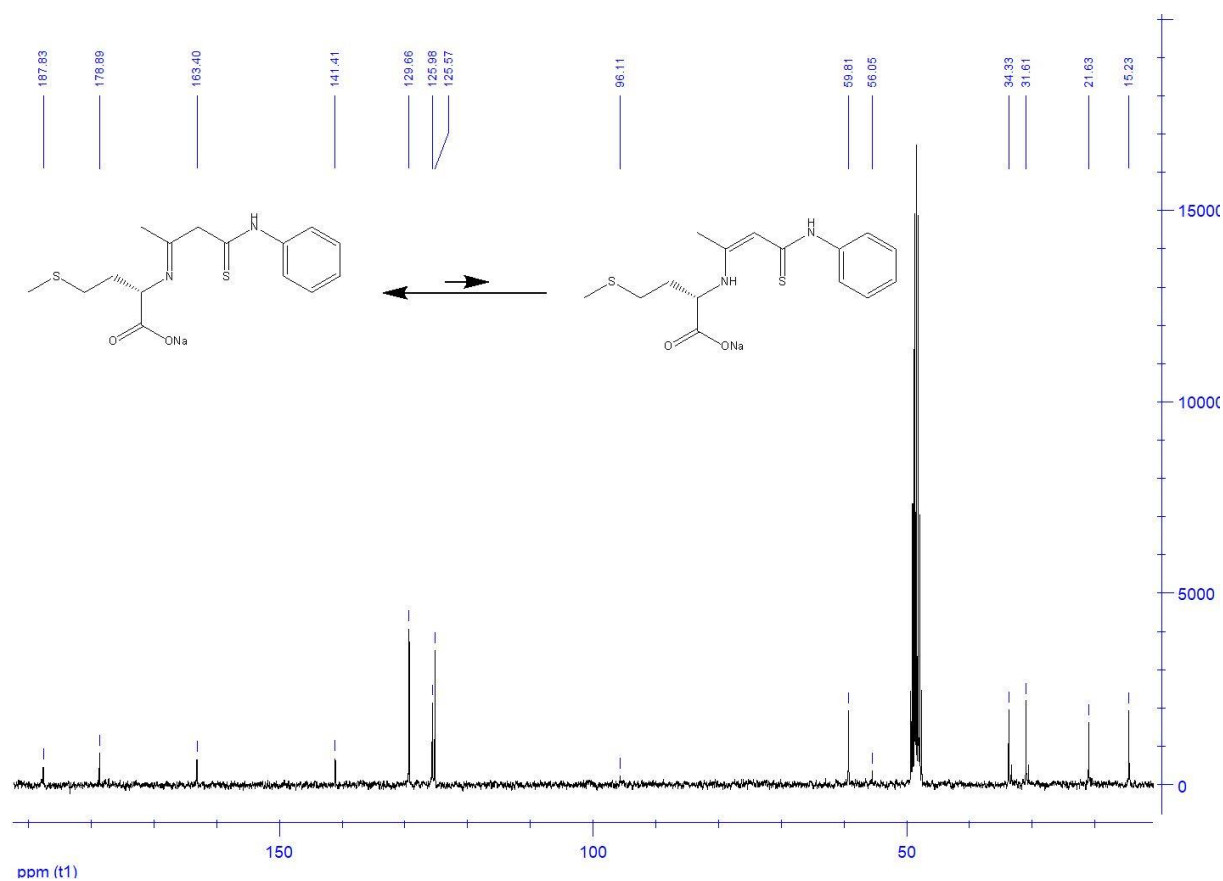


**Figure S6.** <sup>13</sup>C-NMR spectrum of L<sub>3</sub>. (CD<sub>3</sub>OD).  $\sigma$  [ppm] = 187.7 (C=S), 180.1 (COONa), 163.5 (C=N), 141.5 (Ph), 129.6 (Ph), 125.9 (Ph), 125.5 (Ph), 59.8 (CH), 43.8 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 23.7 (CH), 22.2 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub>).

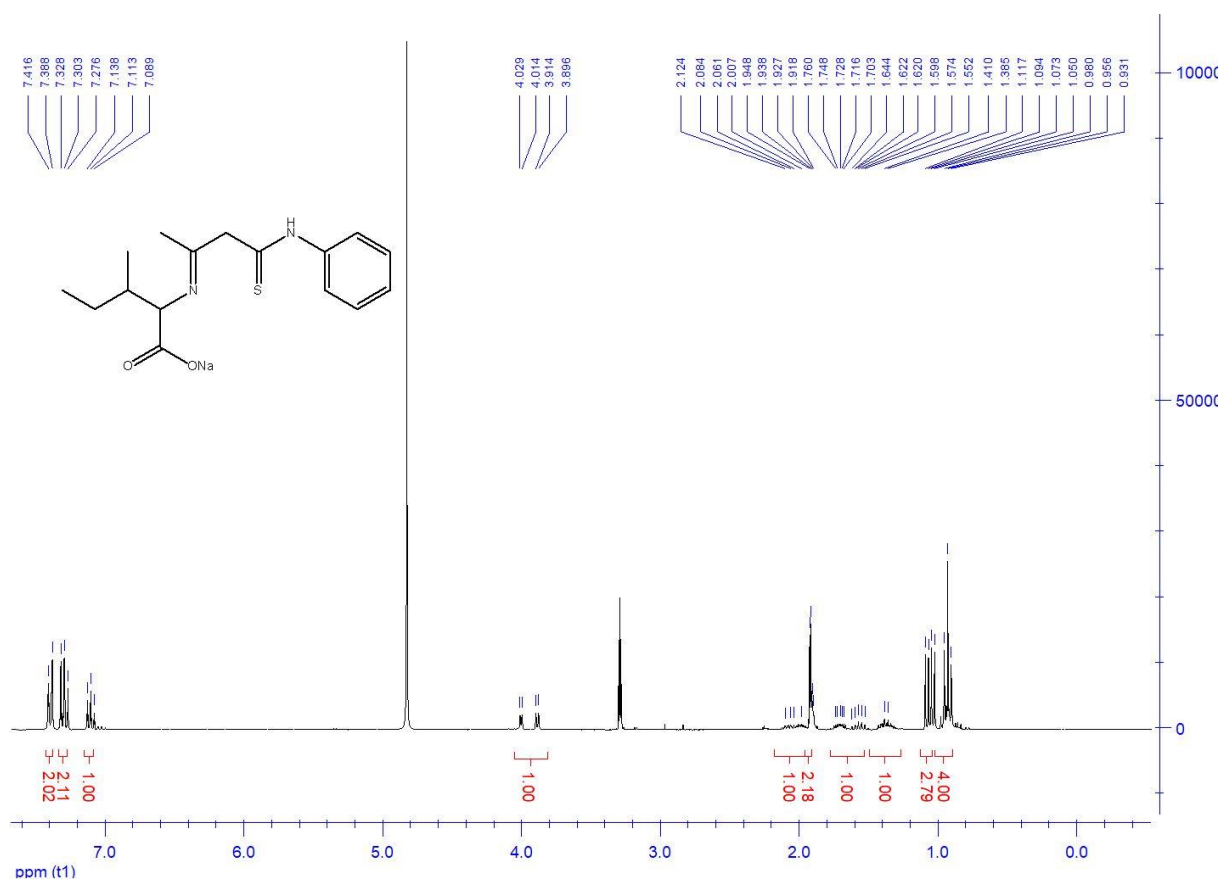


**Figure S7.** <sup>1</sup>H-NMR spectrum of L4. (CD<sub>3</sub>OD).  $\sigma$  [ppm] = 7.41 (d, 2H,  $J_{\text{HH}}$  = 8.3 Hz, Ph-H), 7.31 (t, 2H,  $J_{\text{HH}}$  = 8.3 Hz, Ph-H), 7.13 (t, 1H,  $J_{\text{HH}}$  = 7.3 Hz, Ph-H), 5.36 (s, =CH enamine), 4.19 (dd, 1H,  $J_{\text{HH}}$  = 4.8 and 8.1 Hz, CH imine), 3.51 (dd,  $J_{\text{HH}}$  = 5.2 and 7.3 Hz CH enamine), 2.71 (t, 2H,  $J_{\text{HH}}$  = 7.4 Hz, SCH<sub>2</sub> imine), 2.60 (dd,  $J_{\text{HH}}$  = 6.8 and 8.8 Hz, SCH<sub>2</sub> enamine), 2.15 (m, 3H, CH and CH<sub>2</sub>), 2.11 (s, 3H, SCH<sub>3</sub> imine), 2.10 (s, SCH<sub>3</sub> enamine), 1.97 (s, 3H, CH<sub>3</sub>).

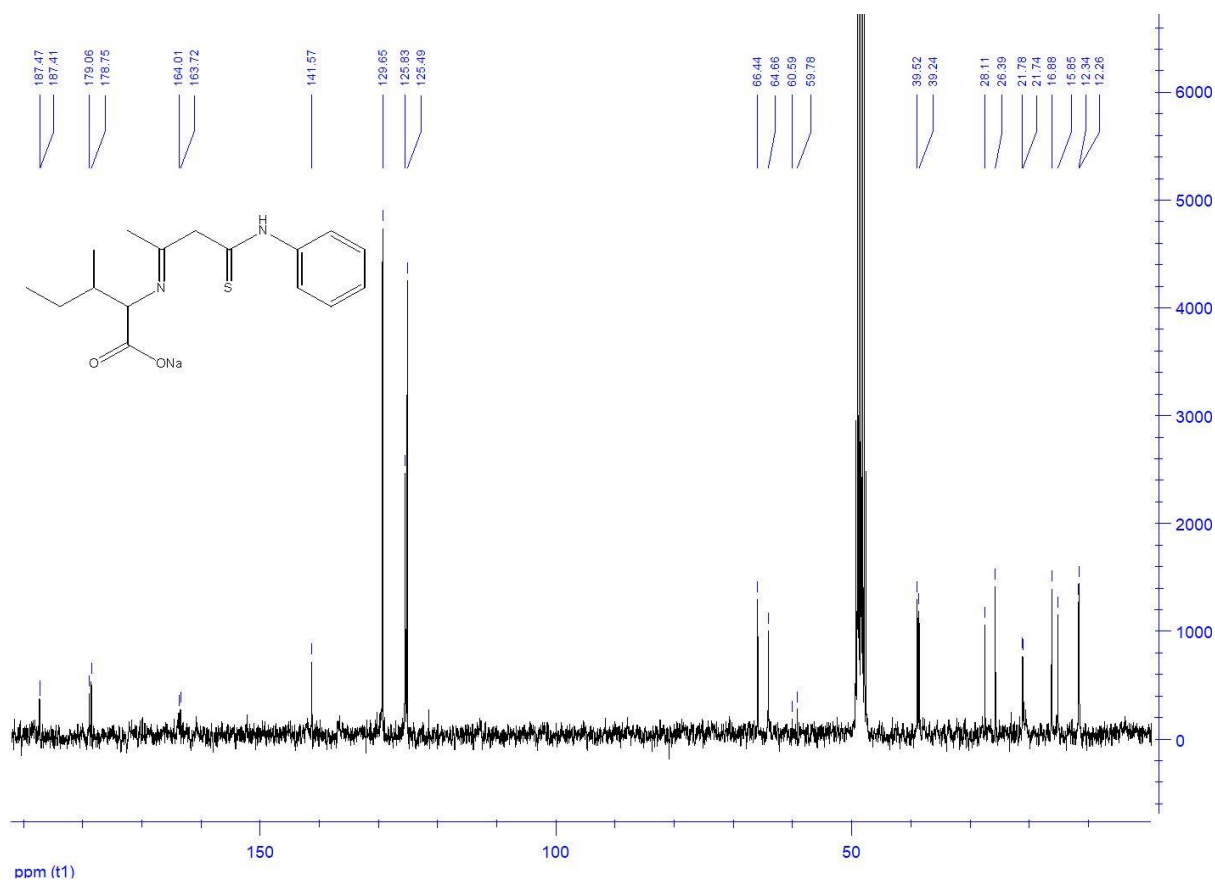




**Figure S8.**  $^{13}\text{C}$ -NMR spectrum of  $\text{L}_4$ . ( $\text{CD}_3\text{OD}$ ).  $\sigma$  [ppm] = 187.8 (C=S), 178.9 (COONa), 163.4 C=N), 141.4 (Ph), 129.7 (Ph), 126.0 (Ph), 125.6 (Ph), 96.1 (=CH enamine), 59.8 ( $\text{CH}_2$ ), 56.1 (CH), 34.3 ( $\text{SCH}_2$ ), 31.6 ( $\text{CH}_2$ ), 21.6 ( $\text{CH}_3$ ), 15.2 ( $\text{SCH}_3$ ).



**Figure S9.** <sup>1</sup>H-NMR spectrum of L<sub>5</sub>. (CD<sub>3</sub>OD).  $\sigma$  [ppm] = 7.40 (d, 2H,  $J_{\text{HH}} = 7.3$  Hz, Ph-H), 7.30 (t, 2H,  $J_{\text{HH}} = 8.2$  Hz, Ph-H), 7.11 (t, 1H,  $J_{\text{HH}} = 7.3$  Hz, Ph-H), 4.02 and 3.91 (d, 1H,  $J_{\text{HH}} = 4.3$  and 5.6 Hz, CH), 2.07 (m, 1H, CH), 1.95 and 1.94 (s, 3H, CH<sub>3</sub>), 1.64 (m, 1H, CH<sub>a</sub>H<sub>b</sub>), 1.39 (m, 1H, CH), 1.10 and 1.06 (d, 3H,  $J_{\text{HH}} = 6.9$  and 6.8 Hz, CH<sub>3</sub>), 0.96 (t, 3H,  $J_{\text{HH}} = 7.4$  Hz, CH<sub>3</sub>).



**Figure S10.** <sup>13</sup>C-NMR spectrum of L<sub>5</sub>. (CD<sub>3</sub>OD).  $\sigma$  [ppm] = 187.5 and 187.4 (C=S), 179.1 and 178.8 (COONa), 164.0 and 163.7 (=CN), 141.6 (Ph), 129.6 (Ph), 125.8 (Ph), 125.5 (Ph), 66.4 and 64.7 (CH<sub>2</sub>), 60.6 and 59.8 (CH), 39.5 and 39.2 (CH), 28.1 and 26.4 (CH<sub>2</sub>), 21.7 and 21.7 (CH<sub>3</sub>), 16.9 and 15.8 (CH<sub>3</sub>), 12.3 and 12.2 (CH<sub>3</sub>).

## IR spectra of ligands L<sub>1</sub>-L<sub>5</sub>

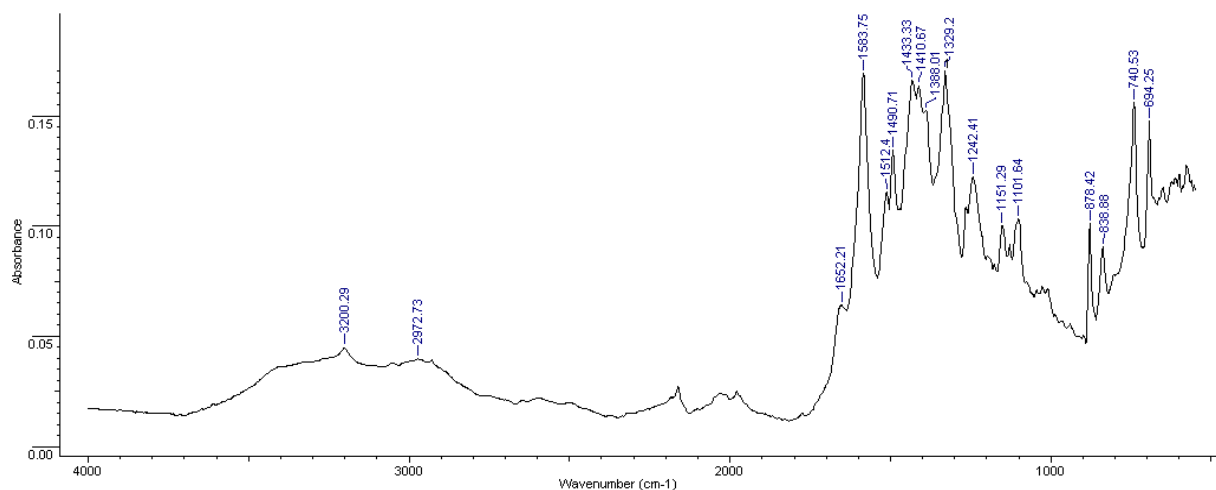


Figure S11. IR-ATR spectrum of L<sub>1</sub>

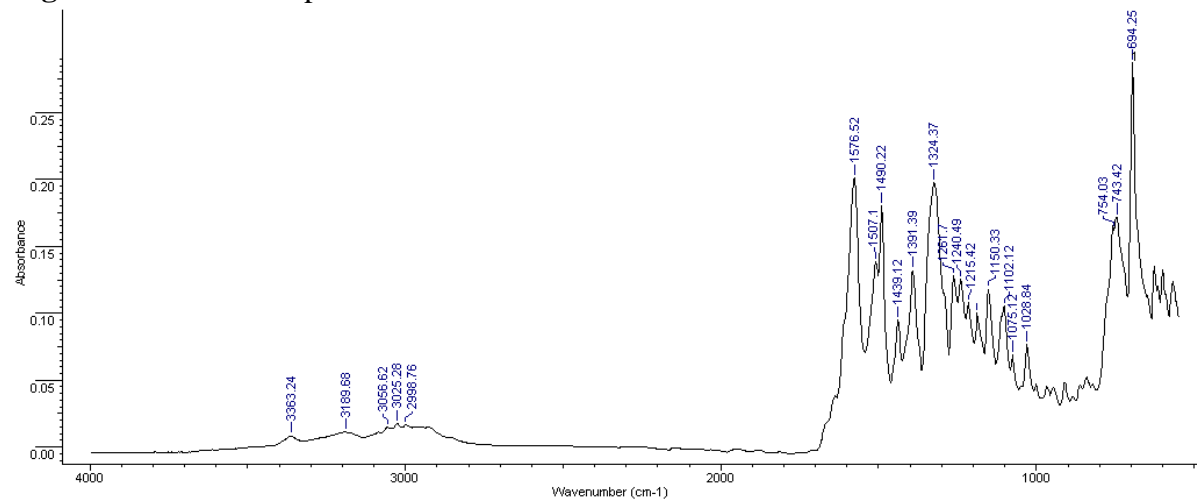


Figure S12. IR-ATR spectrum of L<sub>2</sub>

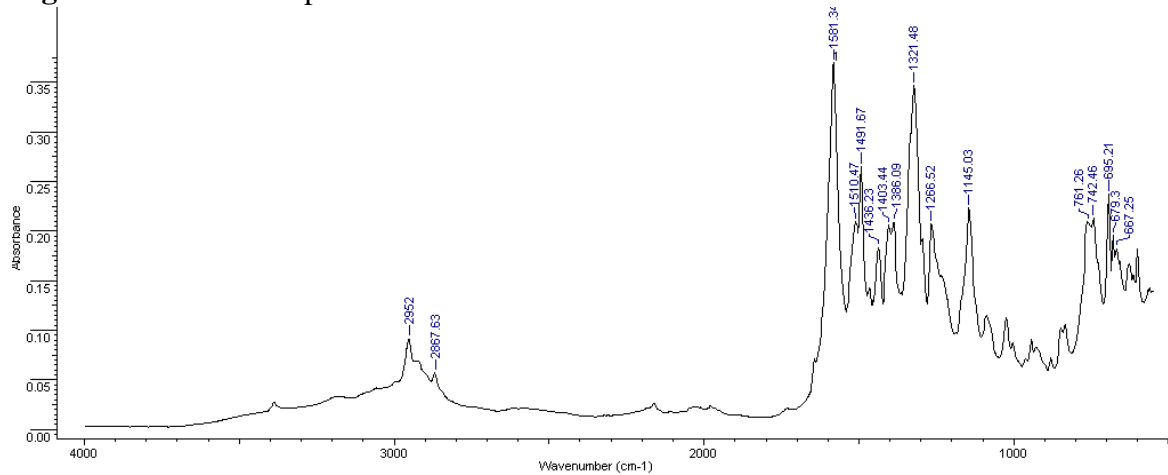
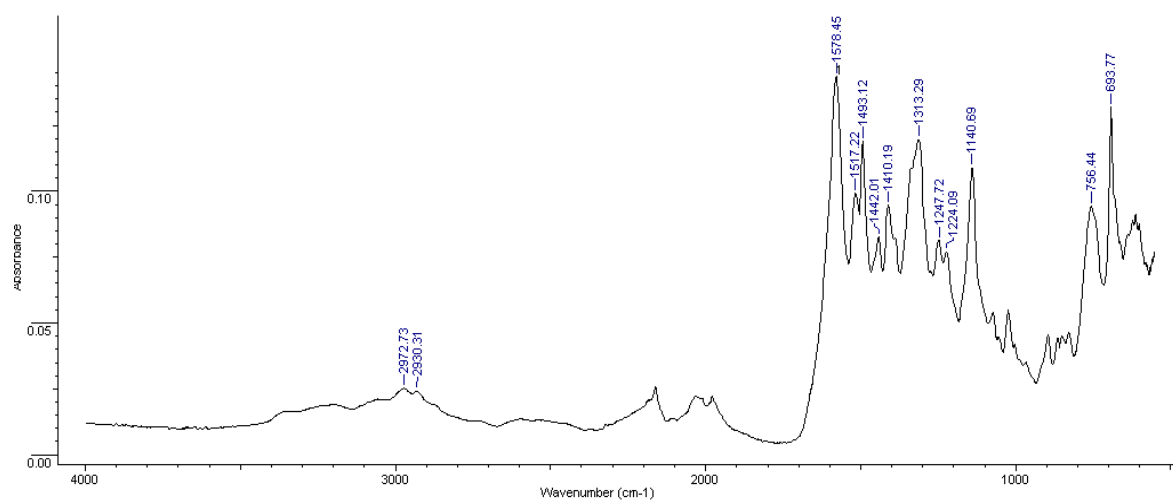
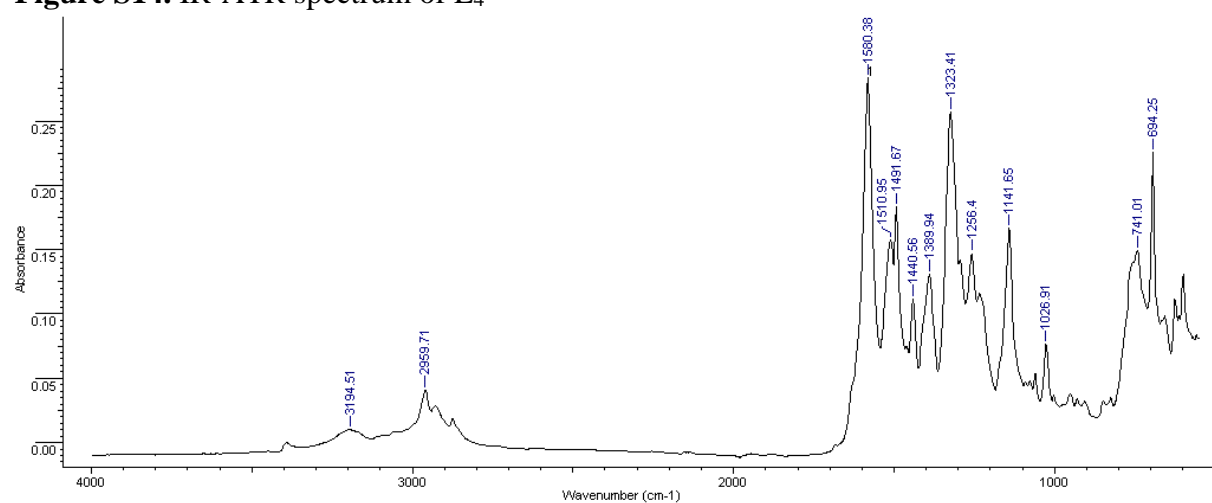


Figure S13. IR-ATR spectrum of L<sub>3</sub>

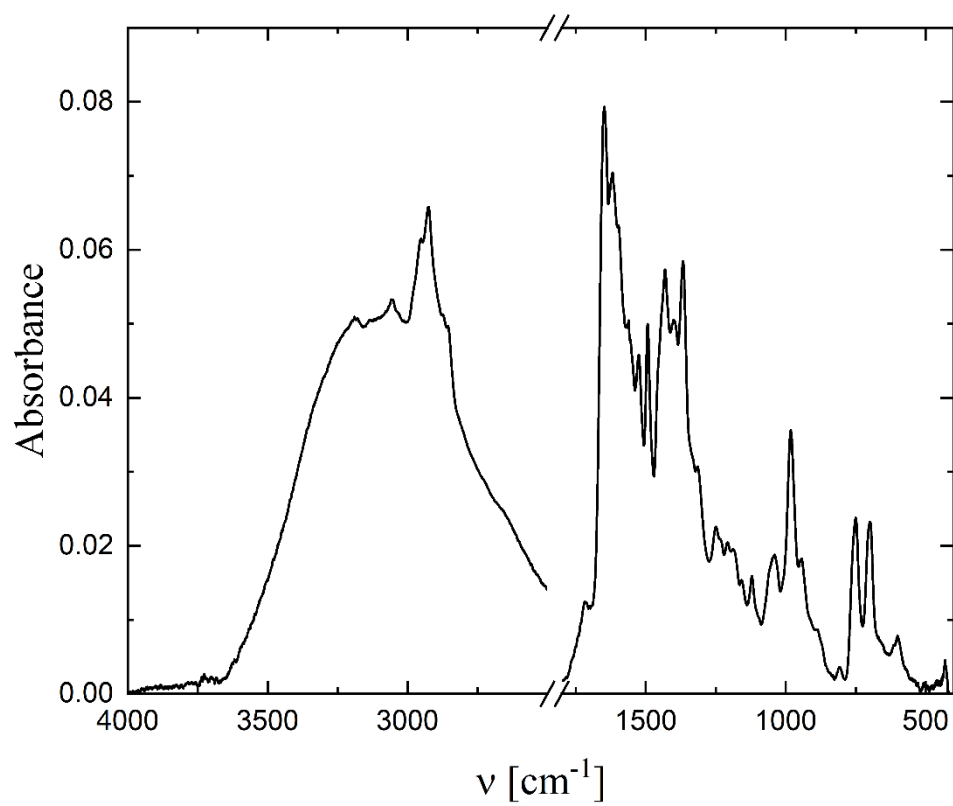


**Figure S14.** IR-ATR spectrum of L<sub>4</sub>

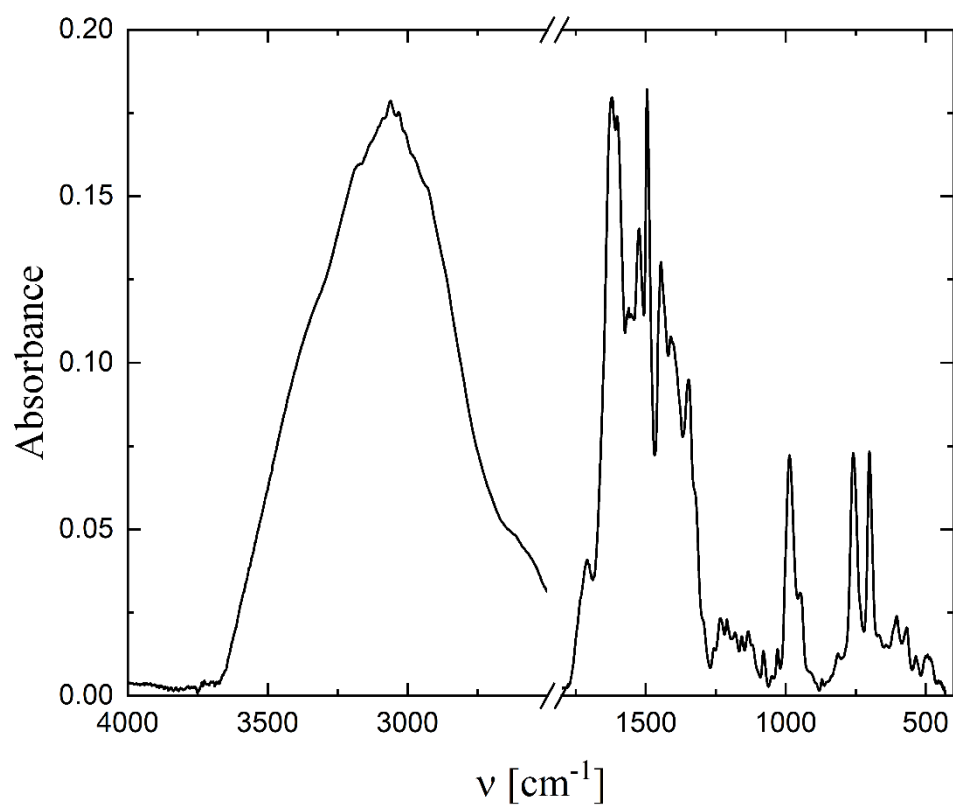


**Figure S15.** IR-ATR spectrum of L<sub>5</sub>

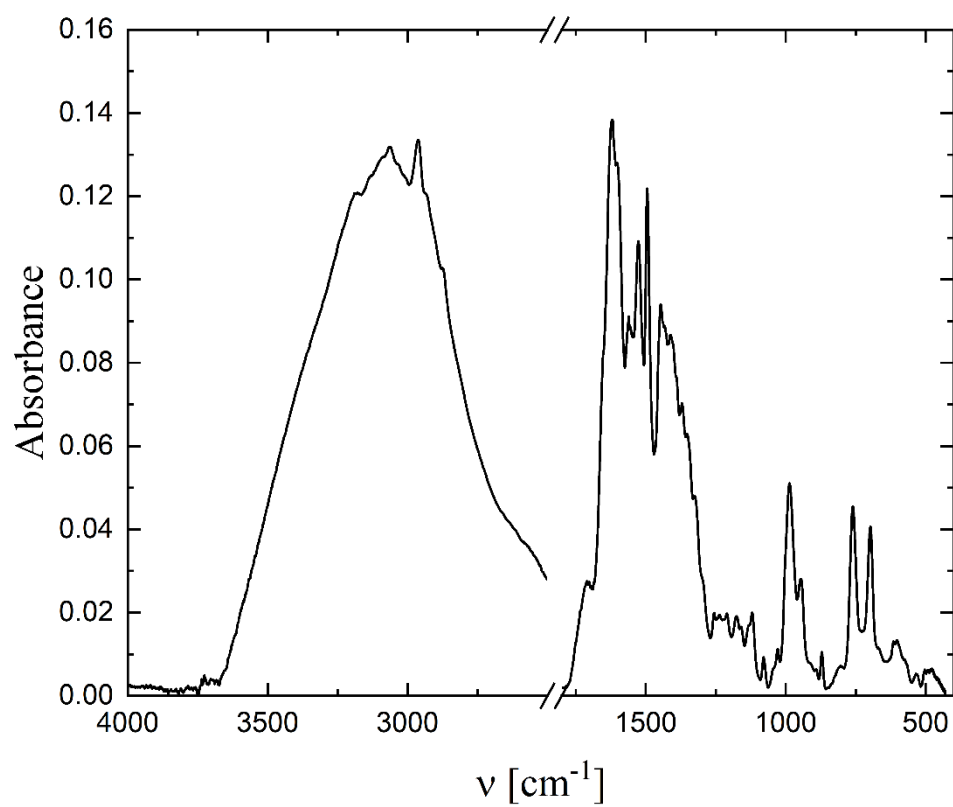
**IR spectra of complexes.**



**Figure S16.** IR-ATR spectrum of **VC054**.

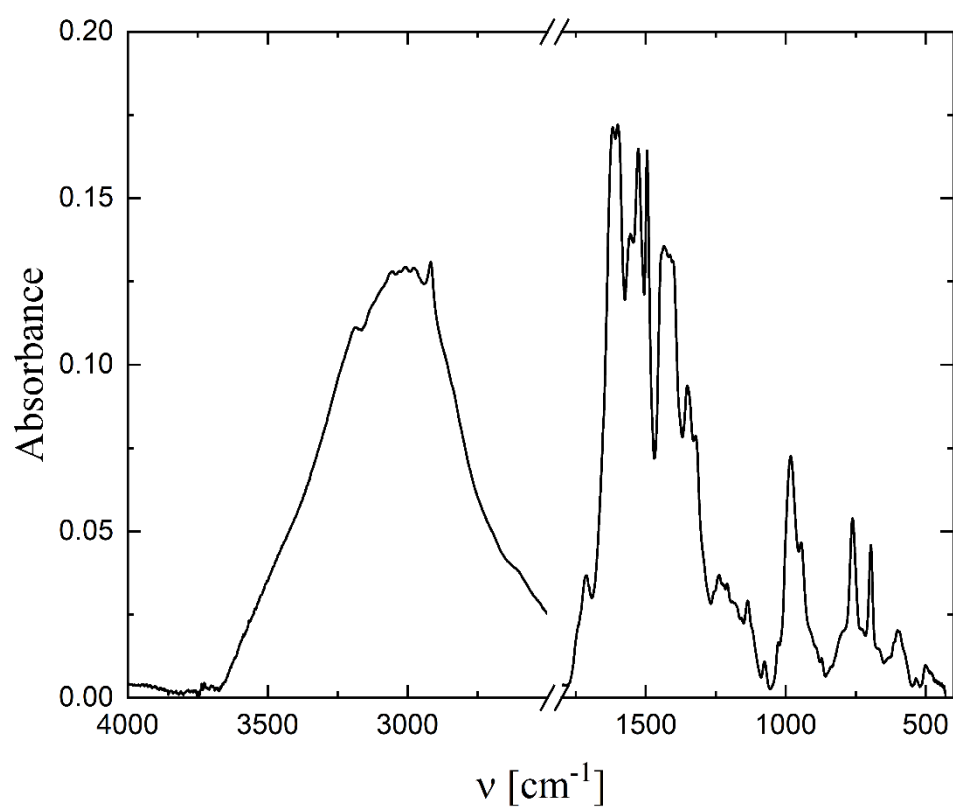


**Figure S17.** IR-ATR spectrum of **VC059**.

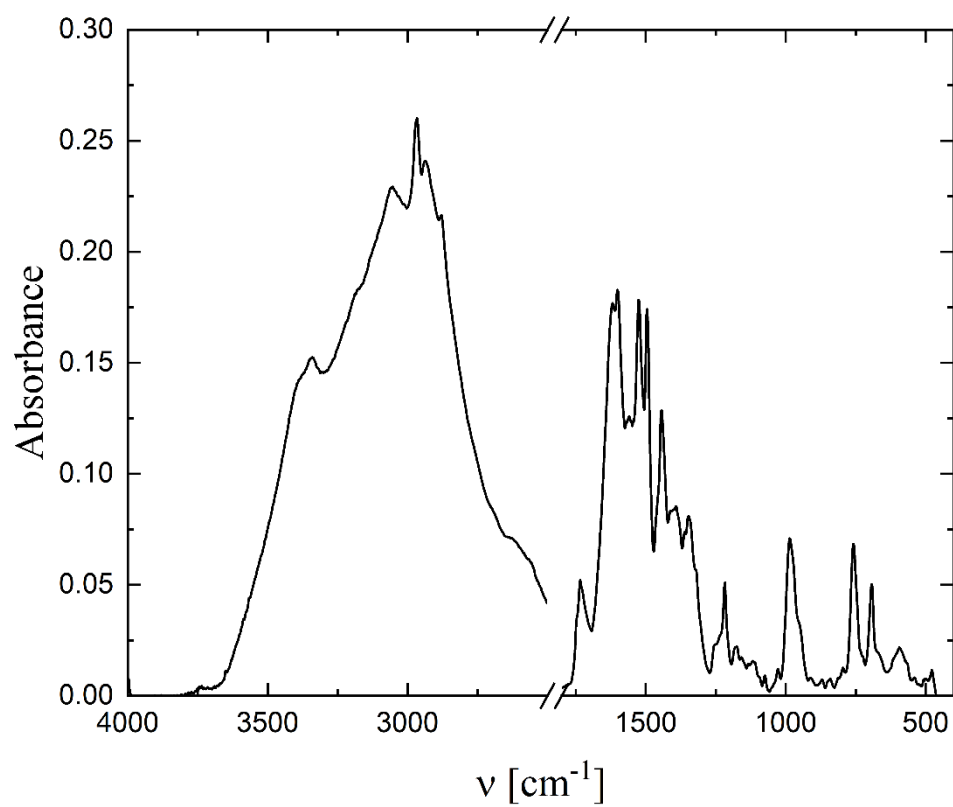


**Figure S18.** IR-ATR spectrum of **VC070**.

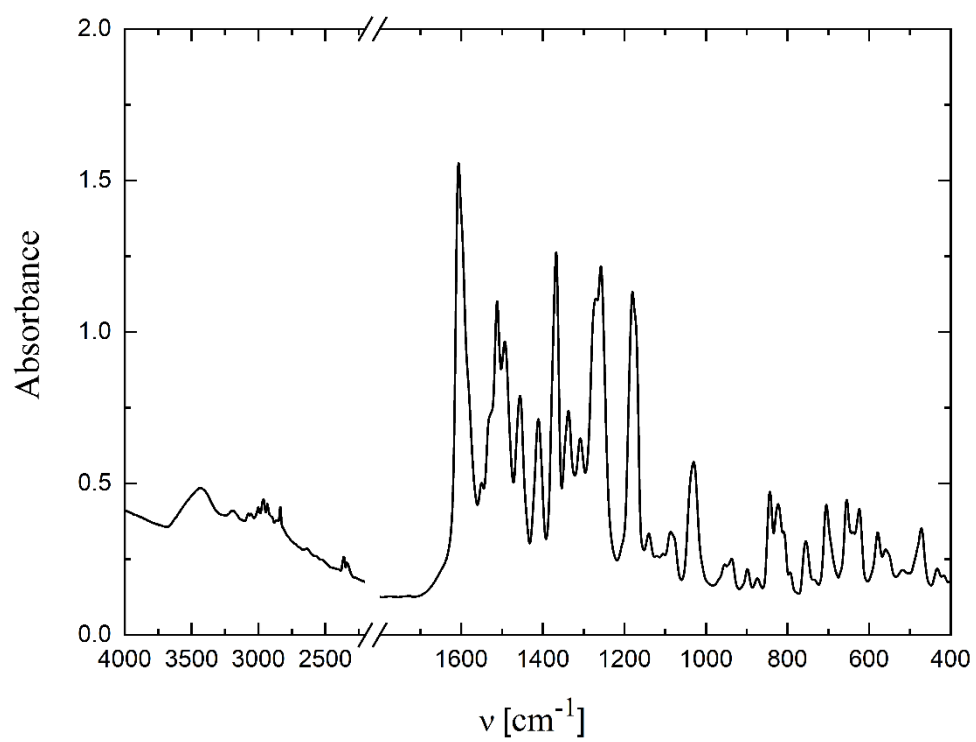




**Figure S19.** IR-ATR spectrum of **VC073**.

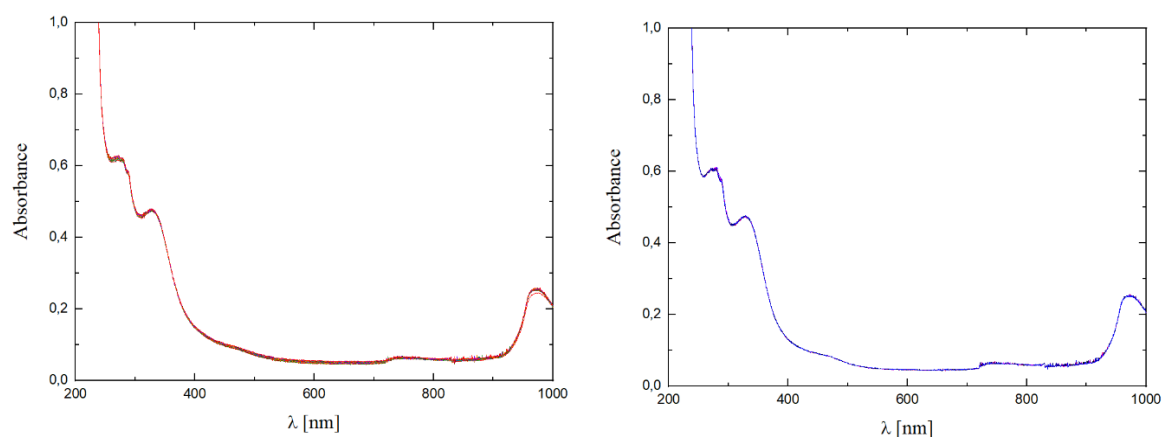


**Figure S20.** IR-ATR spectrum of **VC109**.

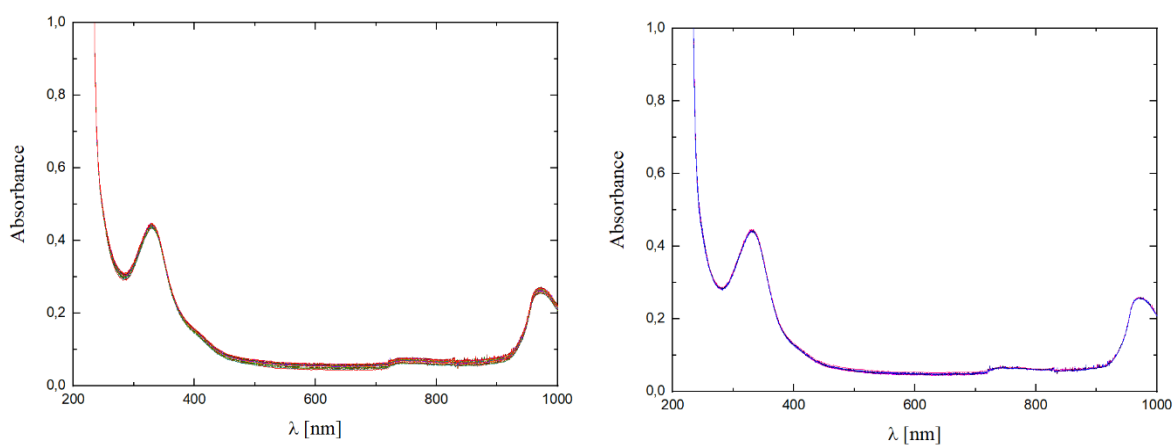


**Figure S21.** IR-ATR spectrum of **VC055**.

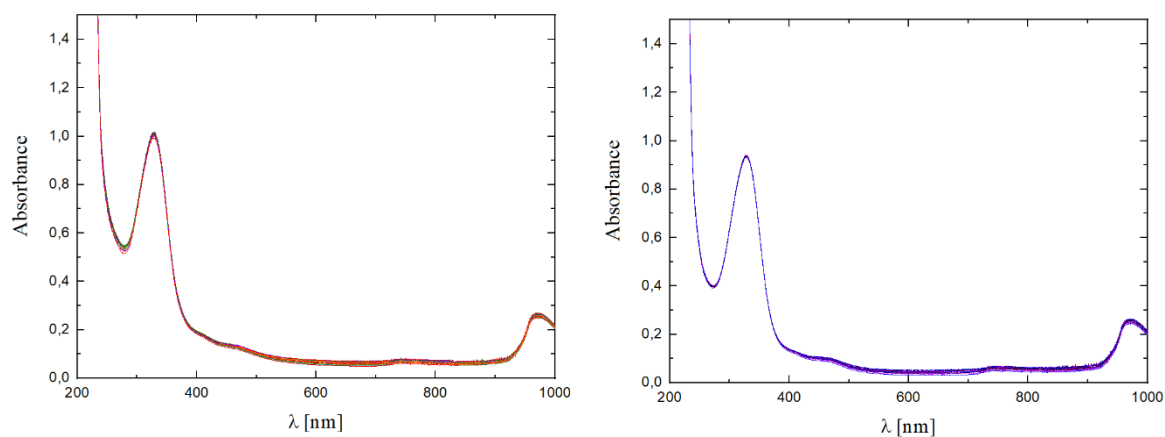
## UV-Vis spectra of complexes



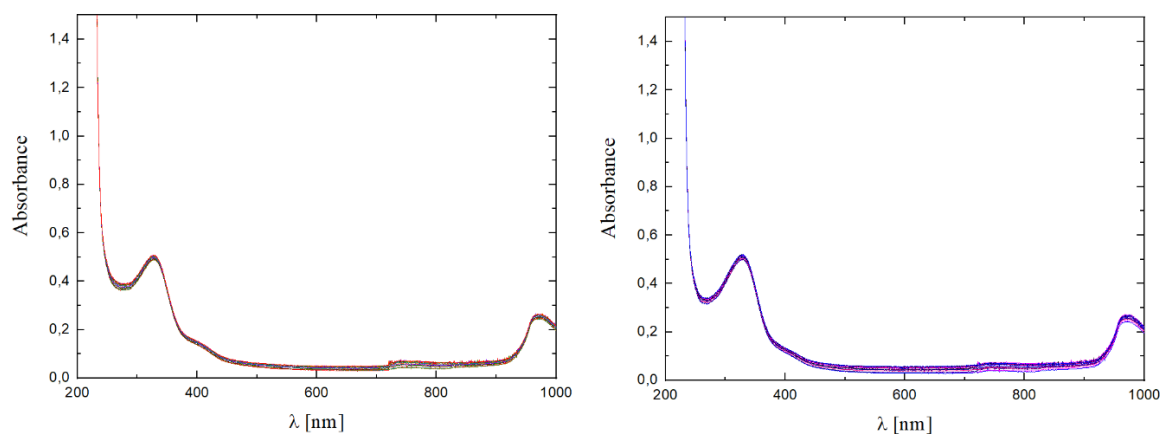
**Figure S22.** UV-Vis spectra of complex **VC054** in DMSO-H<sub>2</sub>O mixture (20  $\mu$ l + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37  $^{\circ}$ C, d = 1 cm, 15 spectra measured in 340 s intervals.



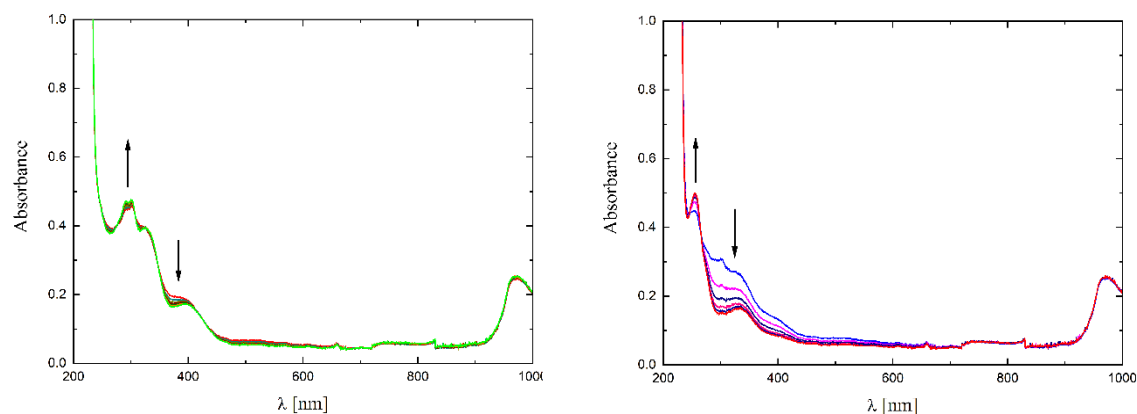
**Figure S23.** UV-Vis spectra of complex **VC059** in DMSO-H<sub>2</sub>O mixture (20  $\mu$ l + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37  $^{\circ}$ C, d = 1 cm, 15 spectra measured in 340 s intervals.



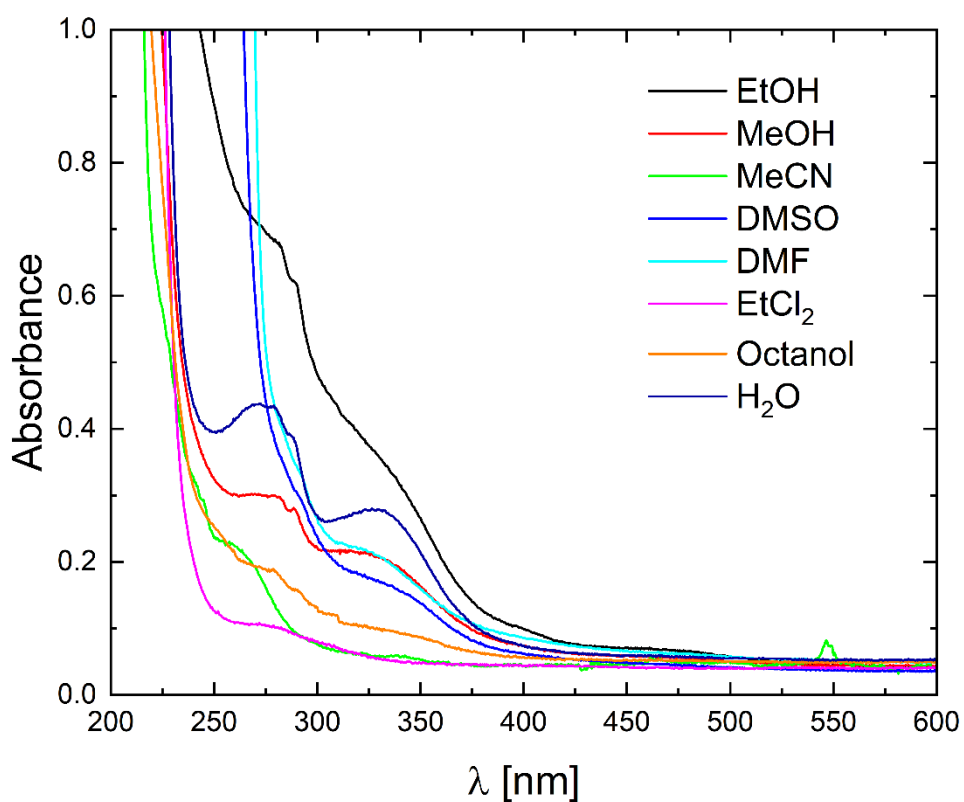
**Figure S24.** UV-Vis spectra of complex **VC070** in DMSO-H<sub>2</sub>O mixture (20  $\mu$ l + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37  $^{\circ}$ C, d = 1 cm, 15 spectra measured in 340 s intervals.



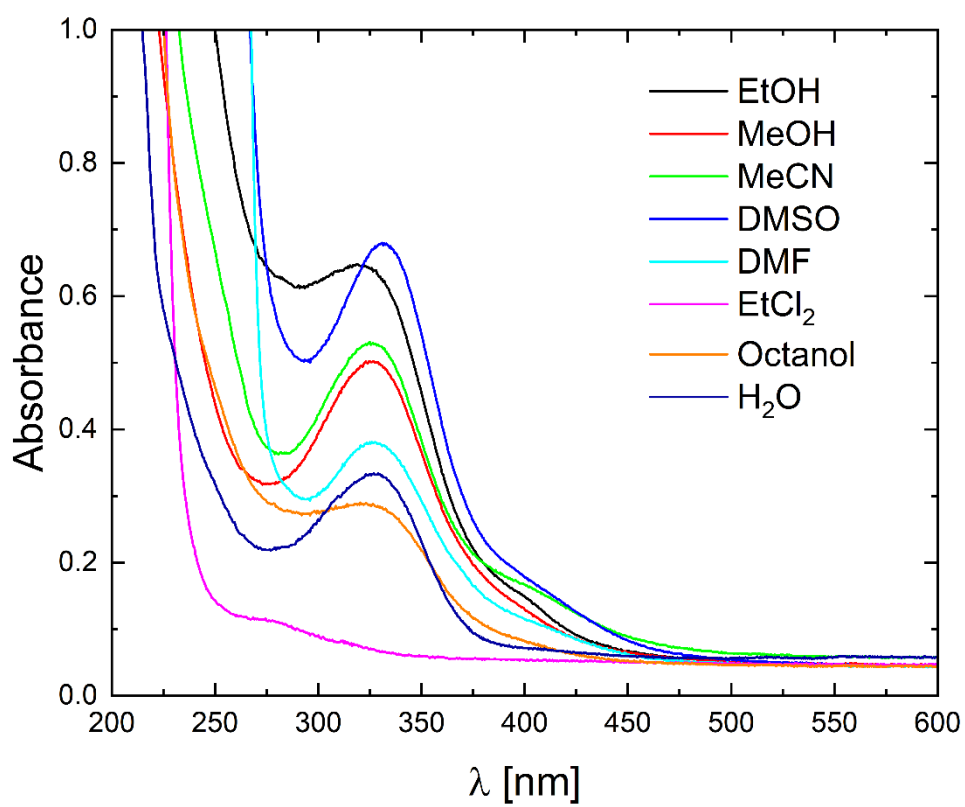
**Figure S25.** UV-Vis spectra of complex **VC073** in DMSO-H<sub>2</sub>O mixture (20  $\mu$ l + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37  $^{\circ}$ C, d = 1 cm, 15 spectra measured in 340 s intervals.



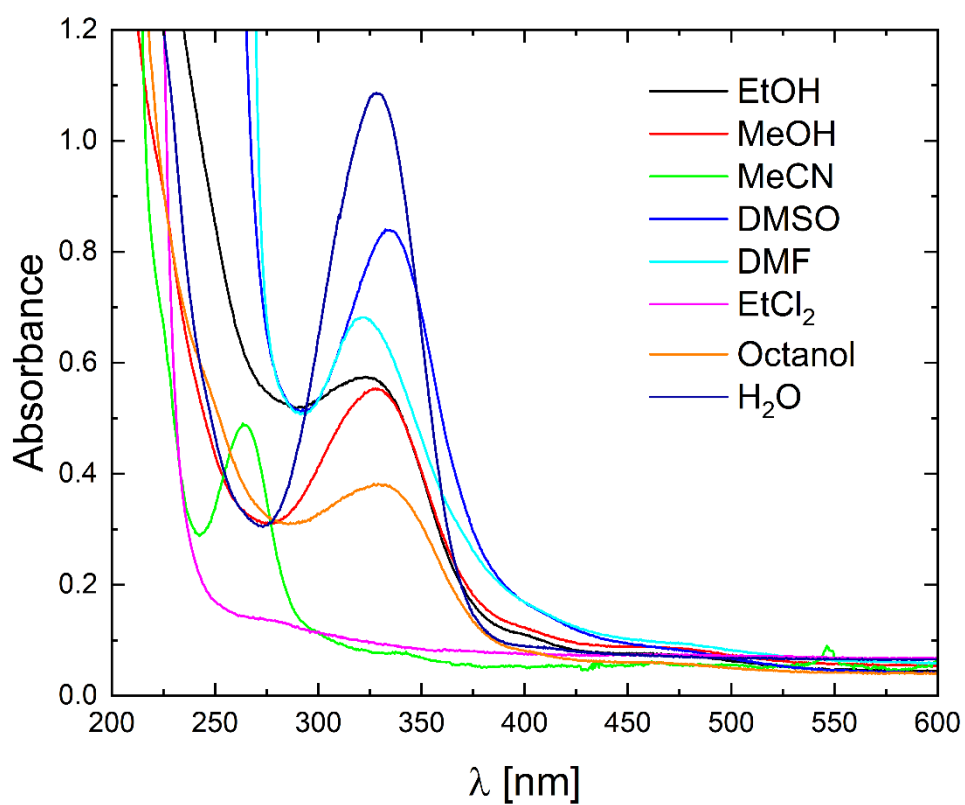
**Figure S26.** UV-Vis spectra of complex **VC055** in DMSO-H<sub>2</sub>O mixture (20  $\mu$ l + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37  $^{\circ}$ C, d = 1 cm, 7 spectra measured in 340 s intervals. The arrows show direction of changes in spectra.



**Figure S27.** Qualitative UV-Vis spectra of complex **VC054** in different solvents; d = 1 cm.

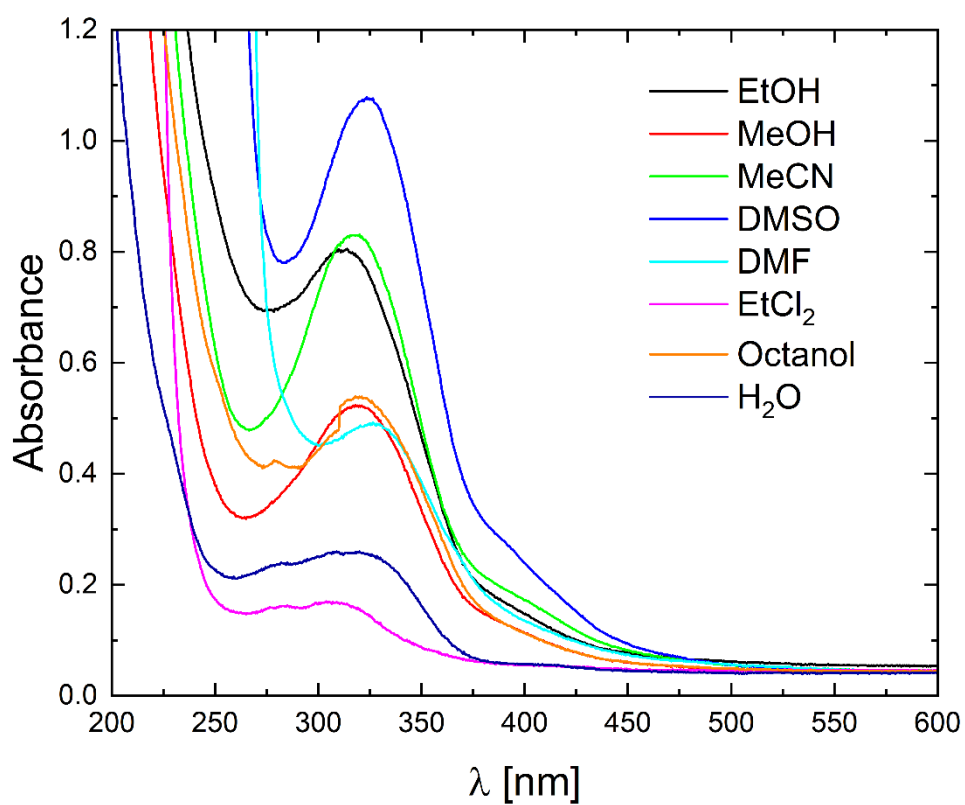


**Figure S28.** Qualitative UV–Vis spectra of complex **VC059** in different solvents;  $d = 1$  cm.

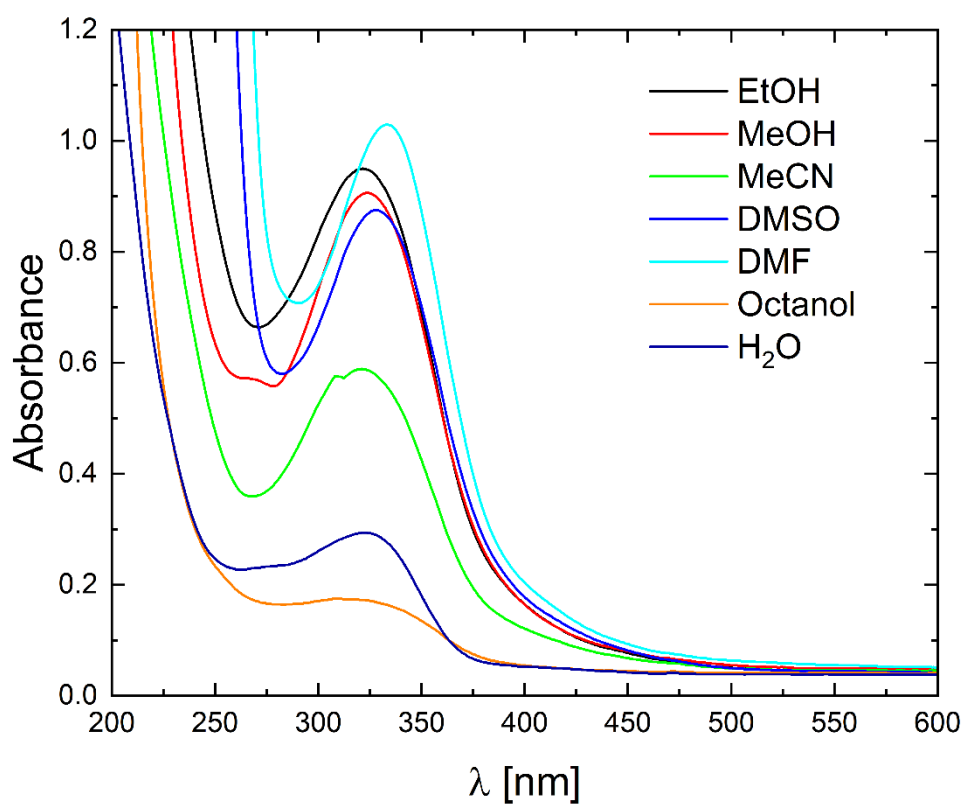


**Figure S29.** Qualitative UV–Vis spectra of complex **VC070** in different solvents;  $d = 1$  cm.

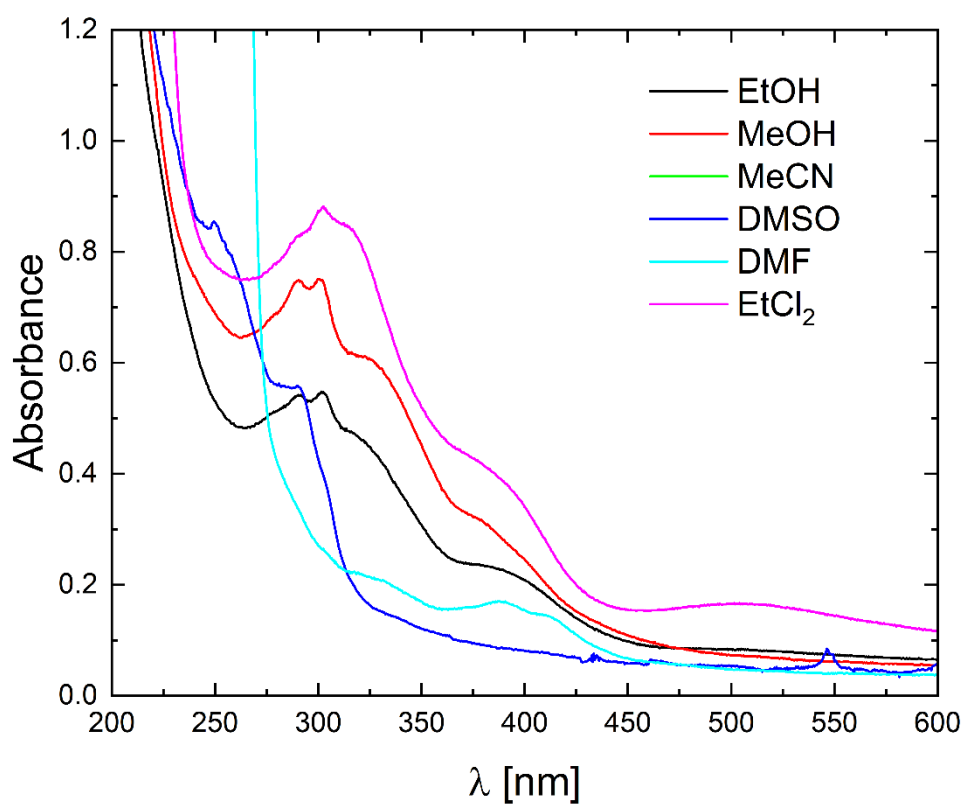




**Figure S30.** Qualitative UV–Vis spectra of complex **VC073** in different solvents;  $d = 1$  cm.



**Figure S31.** Qualitative UV–Vis spectra of complex **VC109** in different solvents;  $d = 1$  cm.



**Figure S32.** Qualitative UV–Vis spectra of complex **VC055** in different solvents;  $d = 1$  cm.