

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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$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the $\text{L}_1\text{-L}_5$ ligands.

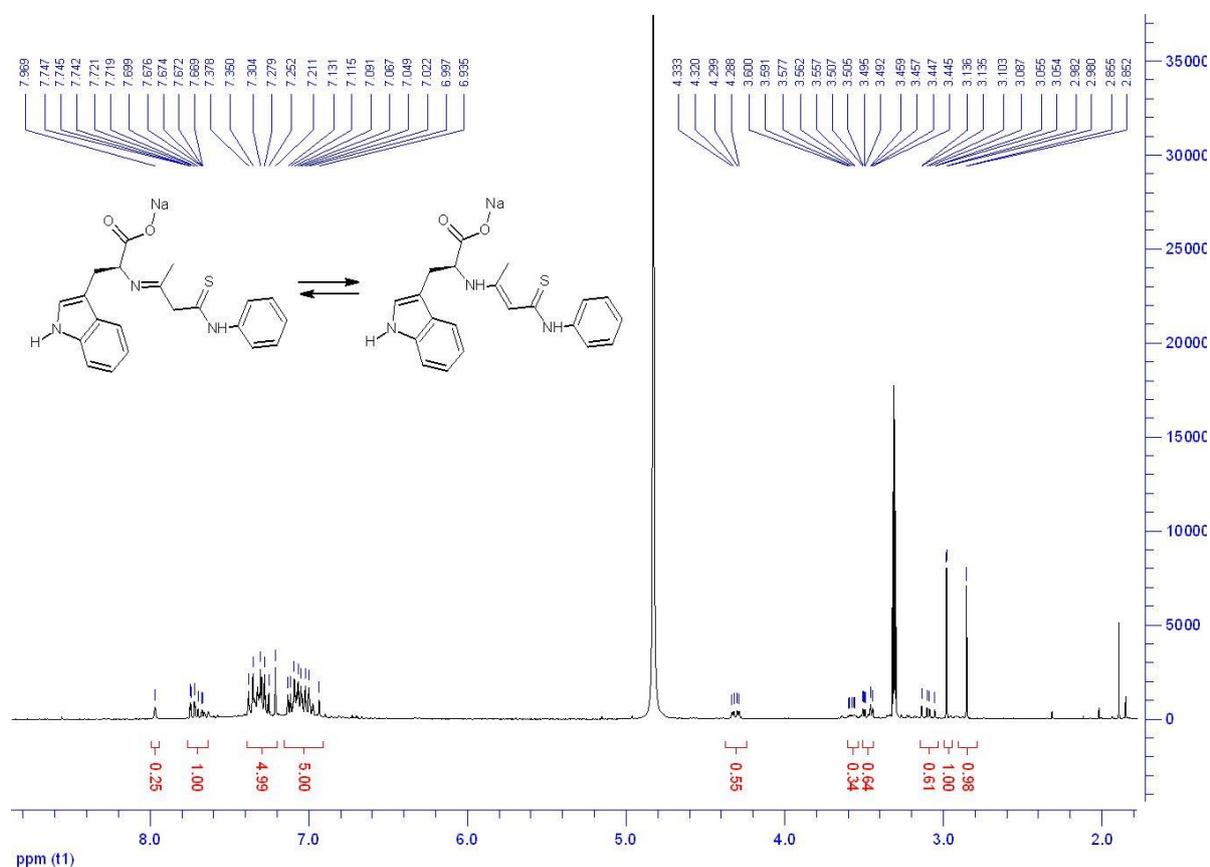


Figure S1. $^1\text{H-NMR}$ spectrum of L_1 . (CD_3OD). σ [ppm] = 7.96 (br. s, NH), 7.74 (m, 1H, Ar-H), 7.72 (m, 1H, Ar-H), 7.28 (m, 4H, Ar-H), 7.21 (br. s, NH), 7.05 (m, 5H, Ar-H), 4.31 (dd, 1H, $J_{\text{HH}} = 3.6$ and 9.9 Hz, CH imine), 3.58 (m, 1H, CH enamine), 3.47 (dd, 2H, $J_{\text{HH}} = 3.7$ and 15.0 Hz, CH_aH_b enamine), 2.94 (dd, 1H, $J_{\text{HH}} = 10.0$ and 15.0 Hz, CH_aH_b imine), 2.99 (s, 3H, CH_3 enamine), 2.85 (s, 3H, CH_3 imine).

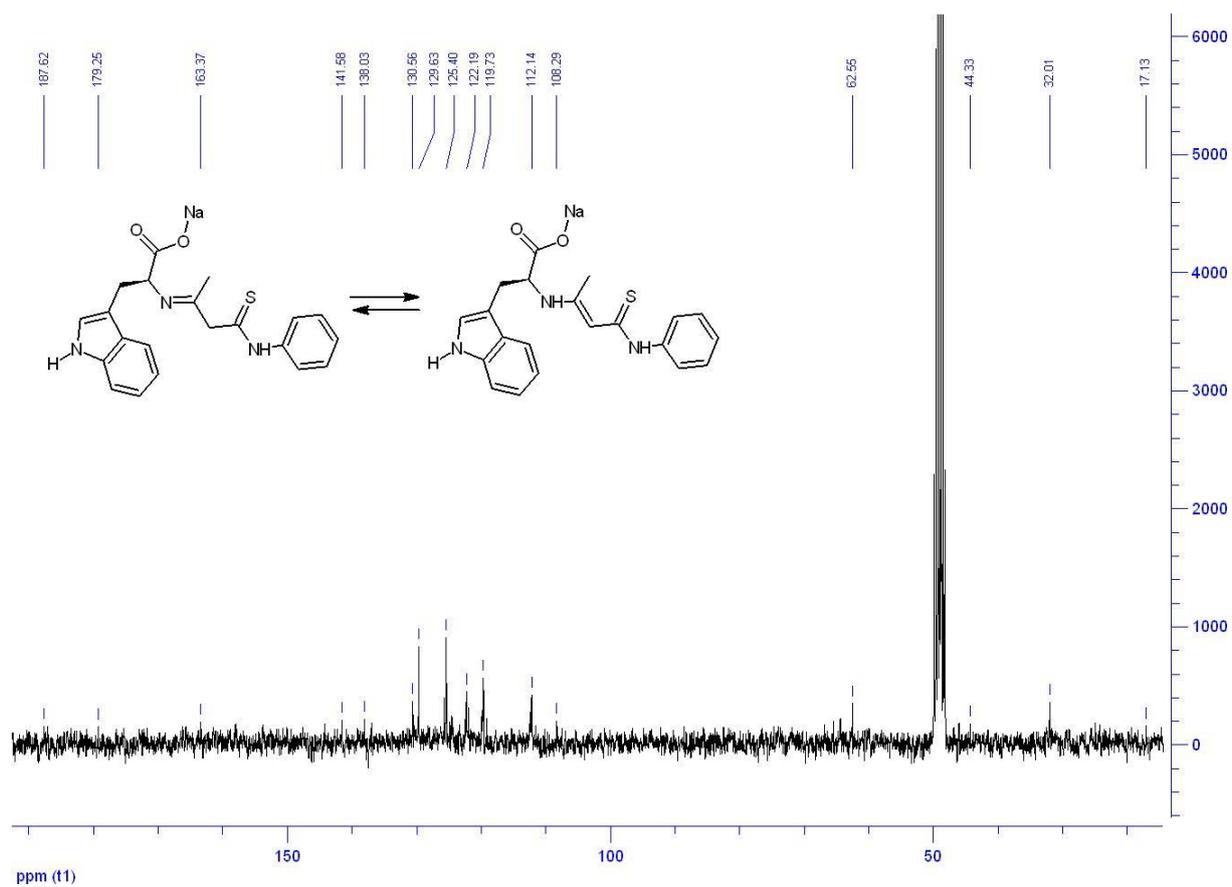


Figure S2. ^{13}C -NMR spectrum of L_1 . $(\text{CD}_3\text{OD})_\sigma$ [ppm] = 187.6 (C=S), 179.2 (COONa), 163.4 (C=N), 141.6 (Ar), 138.0 (Ar), 130.5 (Ar), 129.6 (Ar), 125.4 (Ar), 122.2 (Ar), 119.7 (Ar), 112.1 (Ar), 108.3 (Ar), 62.5 (CH), 44.3 (CH_2), 32.0 (CH_2), 17.1 (CH_3).

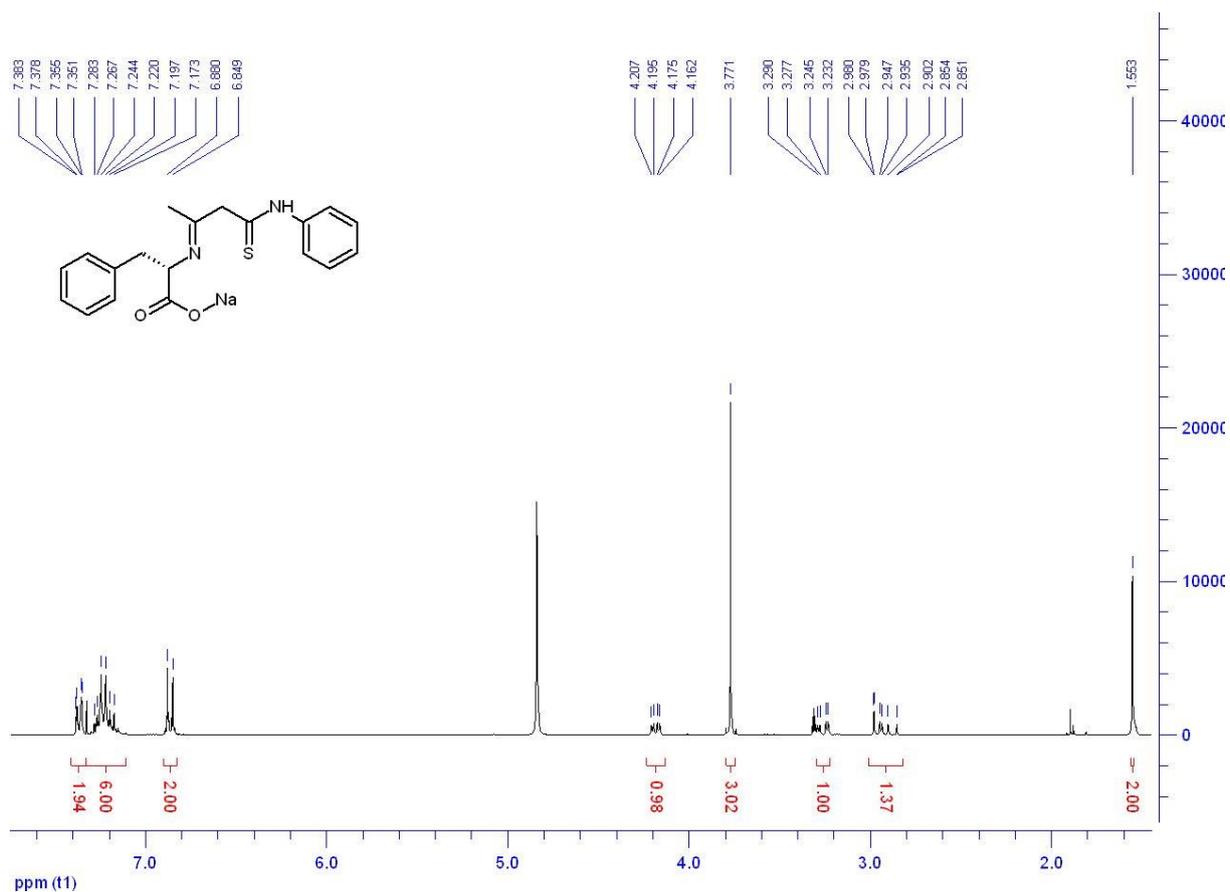


Figure S3. ¹H-NMR spectrum of L₂. (CD₃OD). σ [ppm] = 7.37 (d, 2H, $J_{\text{HH}} = 6.7$ Hz, Ph-H), 7.23 (m, 6H, Ph-H), 6.86 (d, 2H, $J_{\text{HH}} = 9.1$ Hz, Ph-H), 4.18 (dd, 1H, $J_{\text{HH}} = 3.8$ and 9.7 Hz, CH), 3.77 (s, 3H, CH₃), 3.26 (dd, 1H, $J_{\text{HH}} = 3.8$ and 13.8 Hz, CH_aH_b), 2.94 (dd, 1H, $J_{\text{HH}} = 9.8$ and 13.8 Hz, CH_aH_b), 1.55 (s, 2H, CH₂).

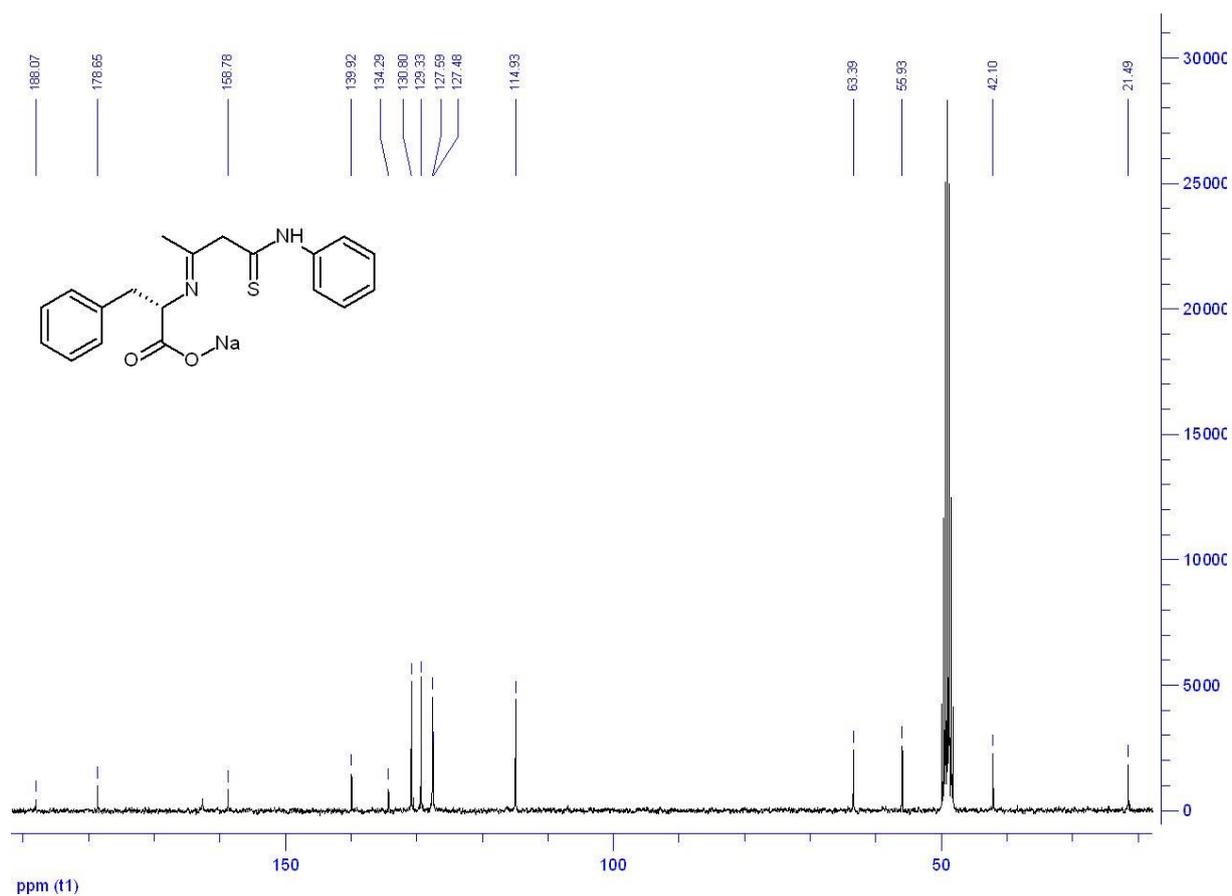


Figure S4. ^{13}C -NMR spectrum of L₂. (CD₃OD) σ [ppm] = 188.1 (C=S), 178.6 (COONa), 158.8 (C=N), 139.9 (Ph), 134.3 (Ph), 130.8 (Ph), 129.3 (Ph), 127.6 (Ph), 127.5 (Ph), 114.9 (Ph), 63.4 (CH), 55.9 (CH₂), 42.1 (CH₂), 21.5 (CH₃).

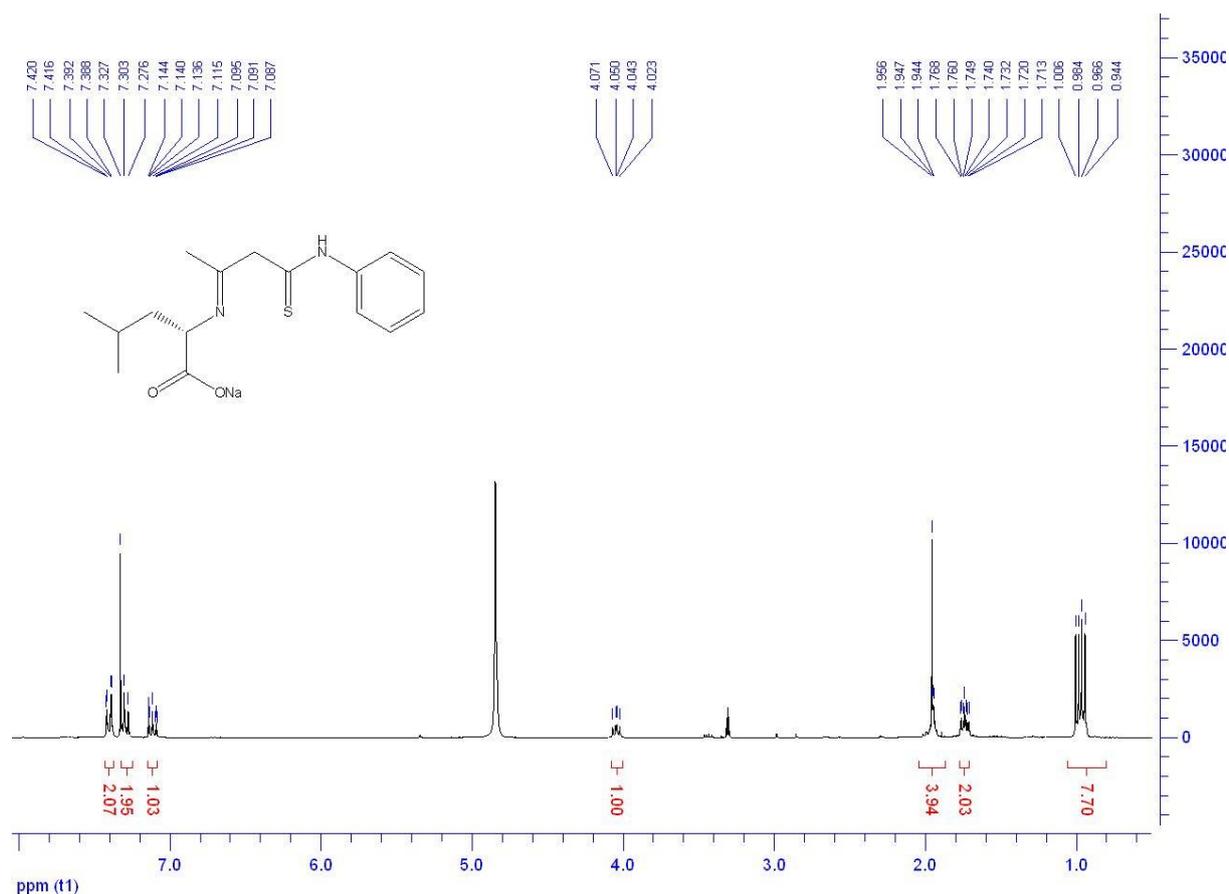


Figure S5. ¹H-NMR spectrum of L₃. (CD₃OD). σ [ppm] = 7.40 (d, 2H, $J_{\text{HH}} = 8.5$ Hz, Ph-H), 7.33 (s, 1H, NH), 7.30 (t, 2H, $J_{\text{HH}} = 8.2$ Hz, Ph-H), 7.12 (t, 1H, $J_{\text{HH}} = 7.3$ Hz, Ph-H), 4.04 (dd, 1H, $J_{\text{HH}} = 6.1$ and 8.2 Hz, CH), 1.96 (s, 3H, CH₃), 1.95 (m, 1H, CH), 1.75 (ddd, 1H, $J_{\text{HH}} = 2.3, 5.8$ and 8.2 Hz, CH_aH_b), 0.99 (d, 3H, $J_{\text{HH}} = 6.6$ Hz, CH₃), 0.99 (br. s, 2H, CH₂), 0.95 (d, 3H, $J_{\text{HH}} = 6.6$ Hz, CH₃).

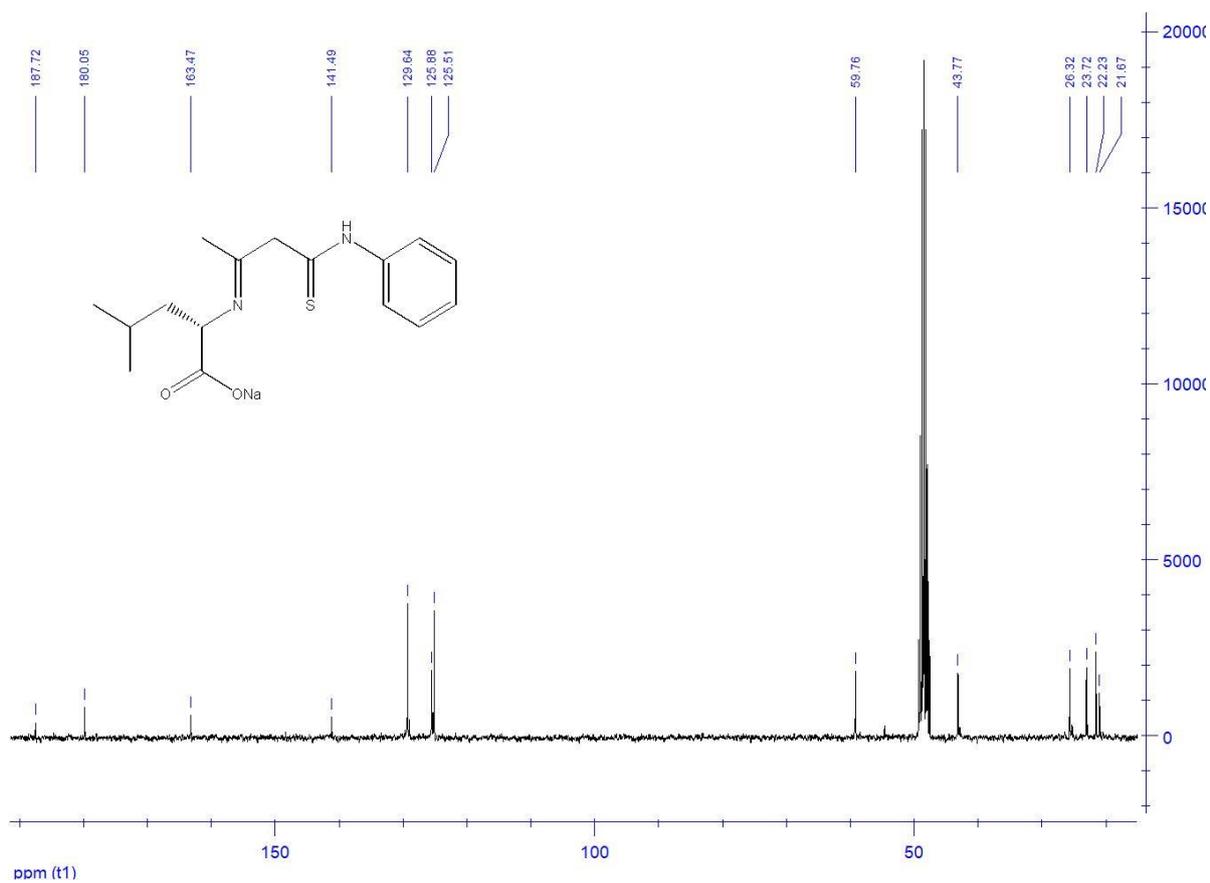


Figure S6. ^{13}C -NMR spectrum of L_3 . (CD_3OD). σ [ppm] = 187.7 (C=S), 180.1 (COONa), 163.5 (C=N), 141.5 (Ph), 129.6 (Ph), 125.9 (Ph), 125.5 (Ph), 59.8 (CH), 43.8 (CH₂), 26.3 (CH₂), 23.7 (CH), 22.2 (CH₃), 21.7 (CH₃).

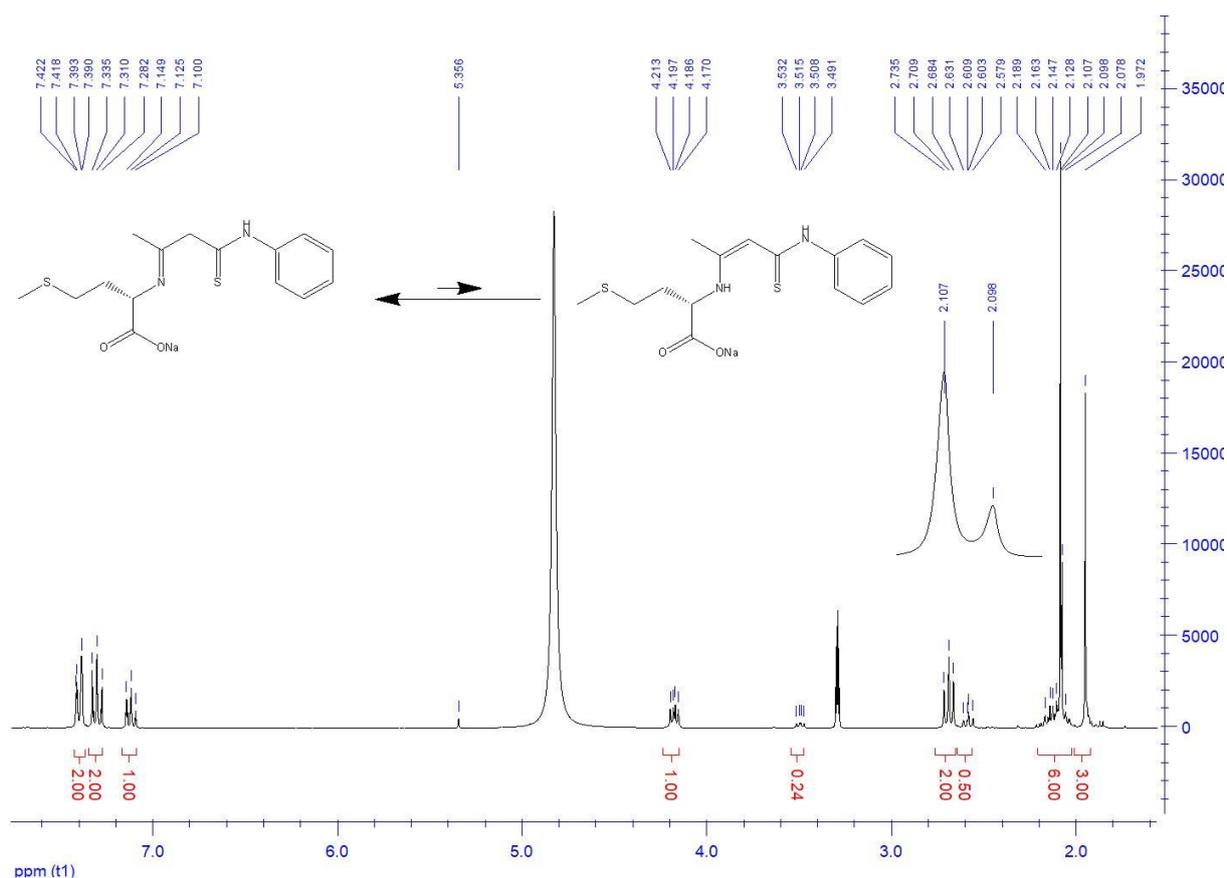


Figure S7. ¹H-NMR spectrum of L₄. (CD₃OD). σ [ppm] = 7.41 (d, 2H, $J_{\text{HH}} = 8.3$ Hz, Ph-H), 7.31 (t, 2H, $J_{\text{HH}} = 8.3$ Hz, Ph-H), 7.13 (t, 1H, $J_{\text{HH}} = 7.3$ Hz, Ph-H), 5.36 (s, =CH enamine), 4.19 (dd, 1H, $J_{\text{HH}} = 4.8$ and 8.1 Hz, CH imine), 3.51 (dd, $J_{\text{HH}} = 5.2$ and 7.3 Hz, CH enamine), 2.71 (t, 2H, $J_{\text{HH}} = 7.4$ Hz, SCH₂ imine), 2.60 (dd, $J_{\text{HH}} = 6.8$ and 8.8 Hz, SCH₂ enamine), 2.15 (m, 3H, CH and CH₂), 2.11 (s, 3H, SCH₃ imine), 2.10 (s, SCH₃ enamine), 1.97 (s, 3H, CH₃).

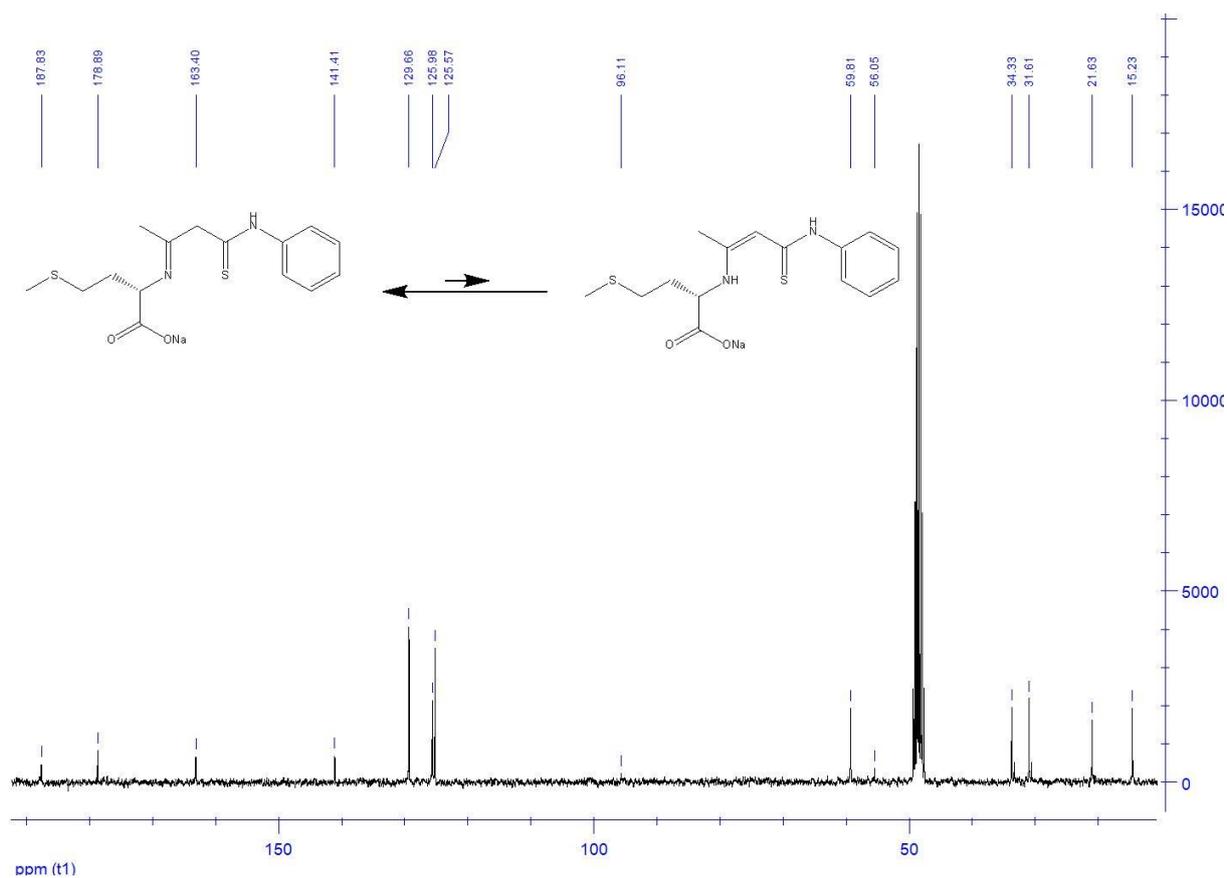


Figure S8. ^{13}C -NMR spectrum of L₄. (CD_3OD). σ [ppm] = 187.8 (C=S), 178.9 (COONa), 163.4 C=N), 141.4 (Ph), 129.7 (Ph), 126.0 (Ph), 125.6 (Ph), 96.1 (=CH enamine), 59.8 (CH_2), 56.1 (CH), 34.3 (SCH_2), 31.6 (CH_2), 21.6 (CH_3), 15.2 (SCH_3).

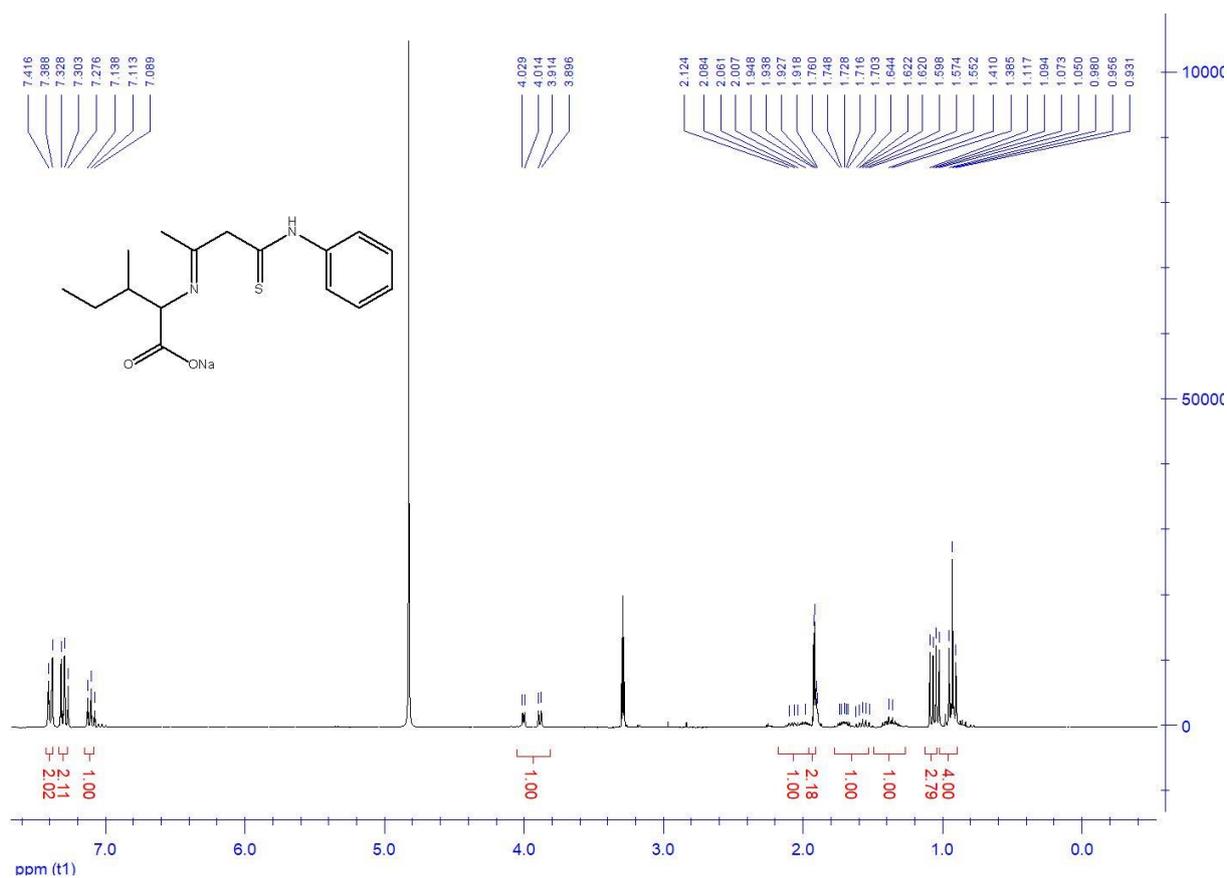


Figure S9. $^1\text{H-NMR}$ spectrum of L_5 . (CD_3OD). σ [ppm] = 7.40 (d, 2H, $J_{\text{HH}} = 7.3$ Hz, Ph-H), 7.30 (t, 2H, $J_{\text{HH}} = 8.2$ Hz, Ph-H), 7.11 (t, 1H, $J_{\text{HH}} = 7.3$ Hz, Ph-H), 4.02 and 3.91 (d, 1H, $J_{\text{HH}} = 4.3$ and 5.6 Hz, CH), 2.07 (m, 1H, CH), 1.95 and 1.94 (s, 3H, CH_3), 1.64 (m, 1H, CH_aH_b), 1.39 (m, 1H, CH), 1.10 and 1.06 (d, 3H, $J_{\text{HH}} = 6.9$ and 6.8 Hz, CH_3), 0.96 (t, 3H, $J_{\text{HH}} = 7.4$ Hz, CH_3).

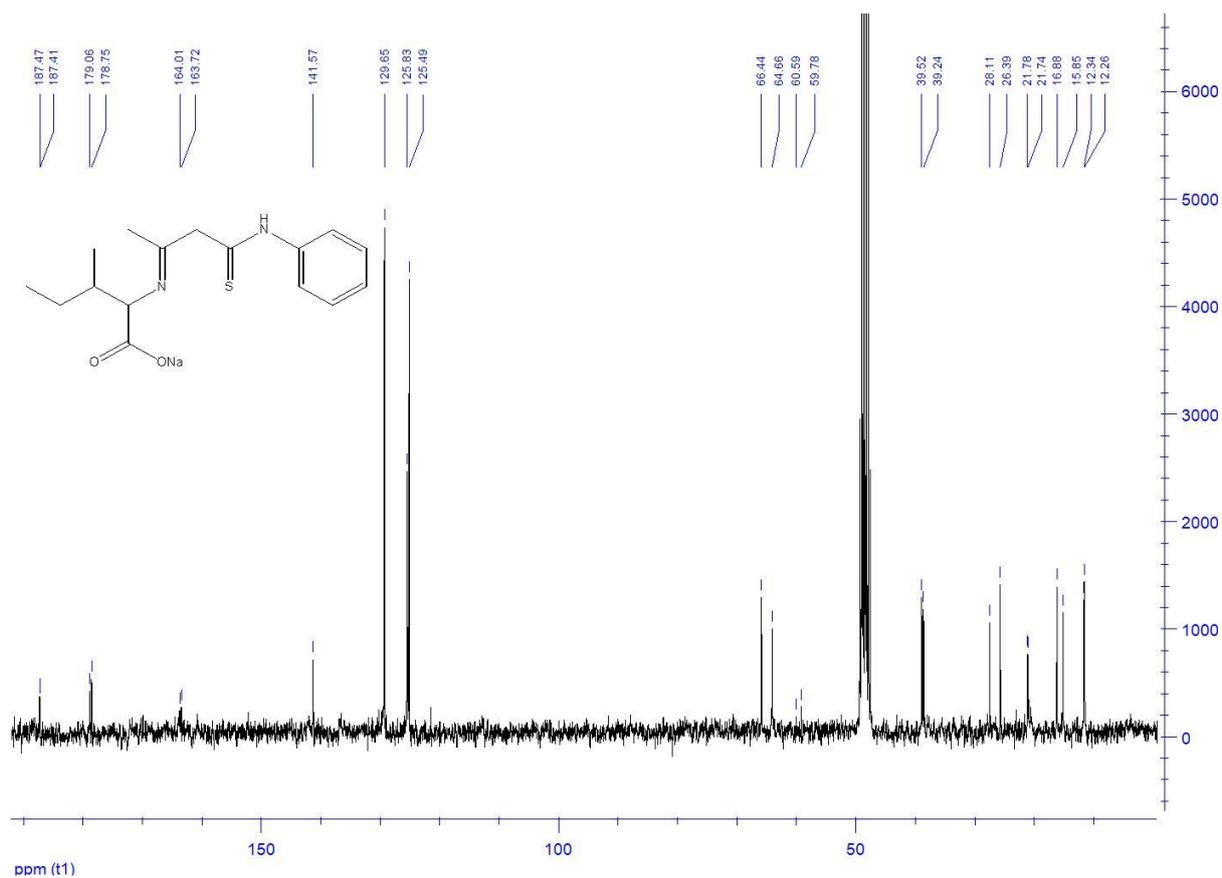


Figure S10. ^{13}C -NMR spectrum of L₅. (CD₃OD). σ [ppm] = 187.5 and 187.4 (C=S), 179.1 and 178.8 (COONa), 164.0 and 163.7 (=CN), 141.6 (Ph), 129.6 (Ph), 125.8 (Ph), 125.5 (Ph), 66.4 and 64.7 (CH₂), 60.6 and 59.8 (CH), 39.5 and 39.2 (CH), 28.1 and 26.4 (CH₂), 21.7 and 21.7 (CH₃), 16.9 and 15.8 (CH₃), 12.3 and 12.2 (CH₃).

IR spectra of ligands L1-L5

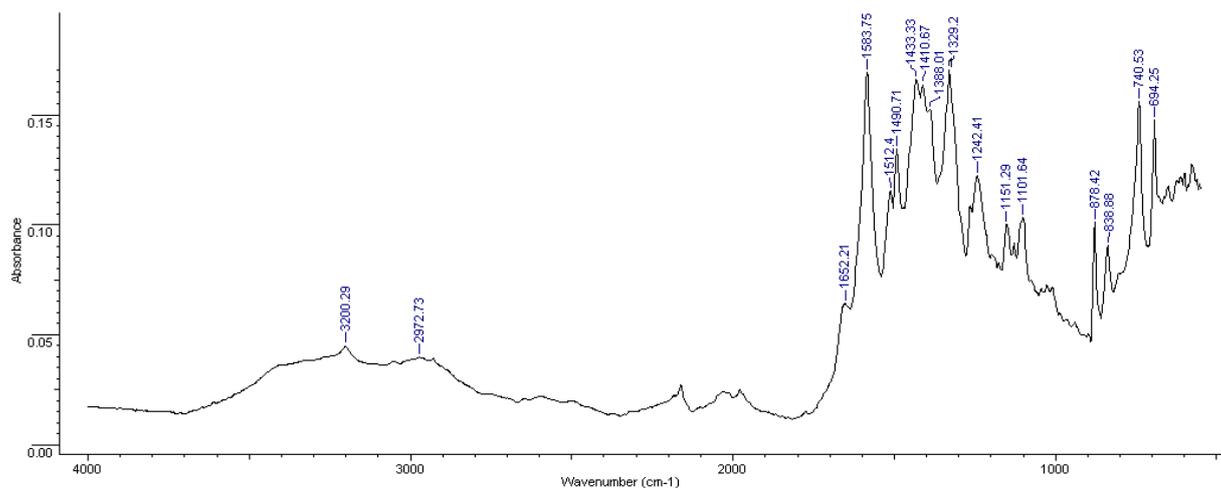


Figure S11. IR-ATR spectrum of L₁

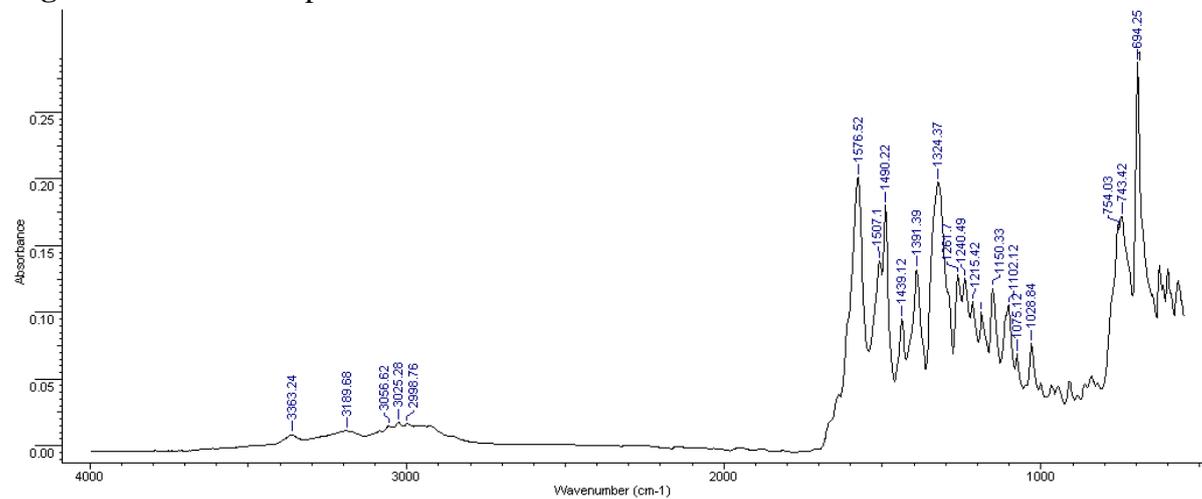


Figure S12. IR-ATR spectrum of L₂

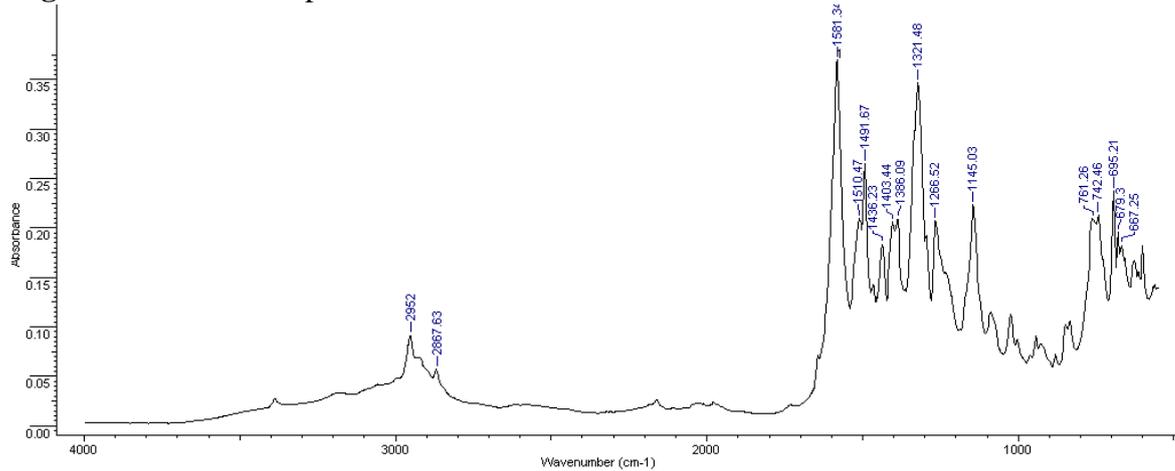


Figure S13. IR-ATR spectrum of L₃

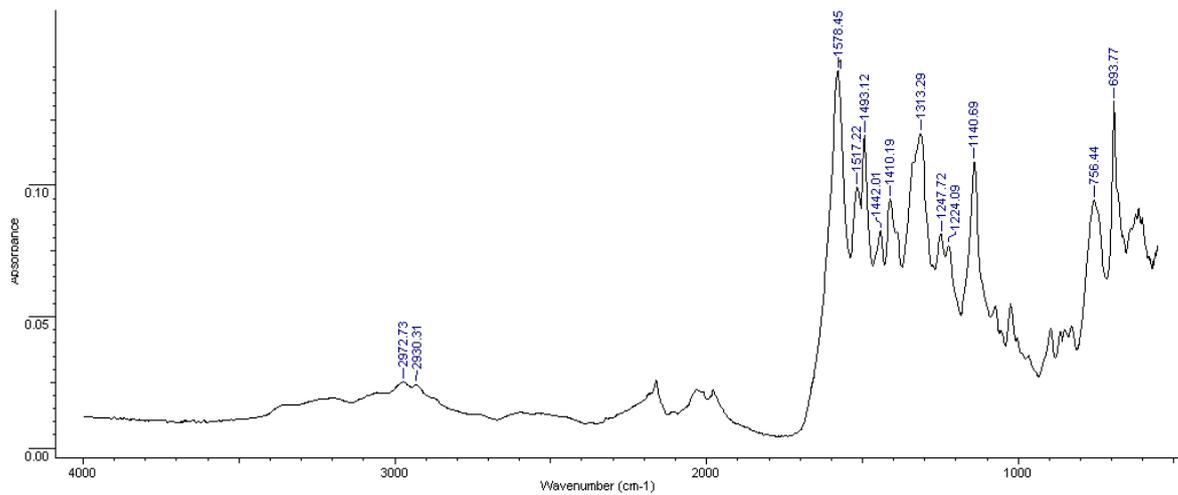


Figure S14. IR-ATR spectrum of L₄

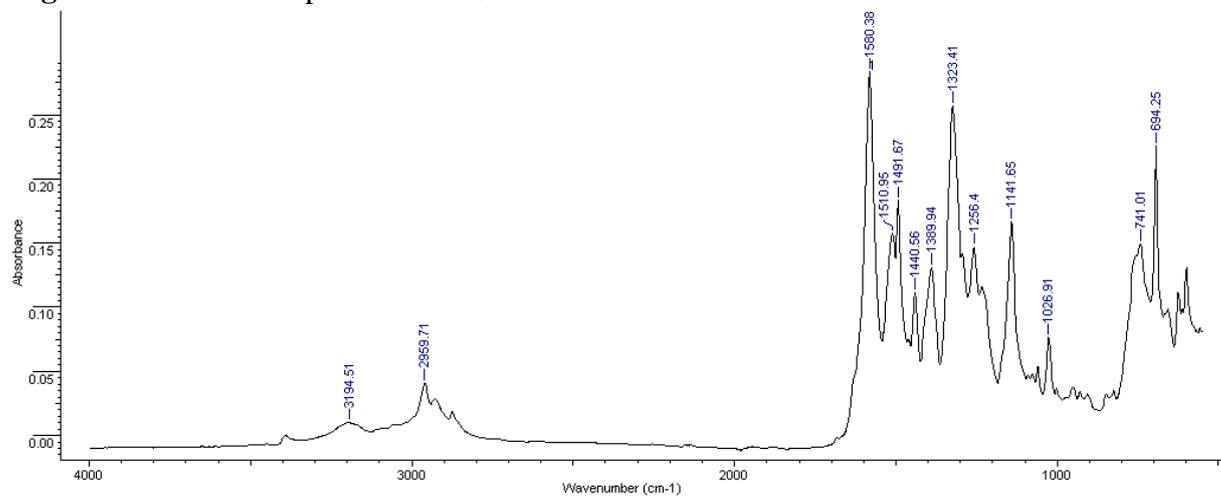


Figure S15. IR-ATR spectrum of L₅

IR spectra of complexes.

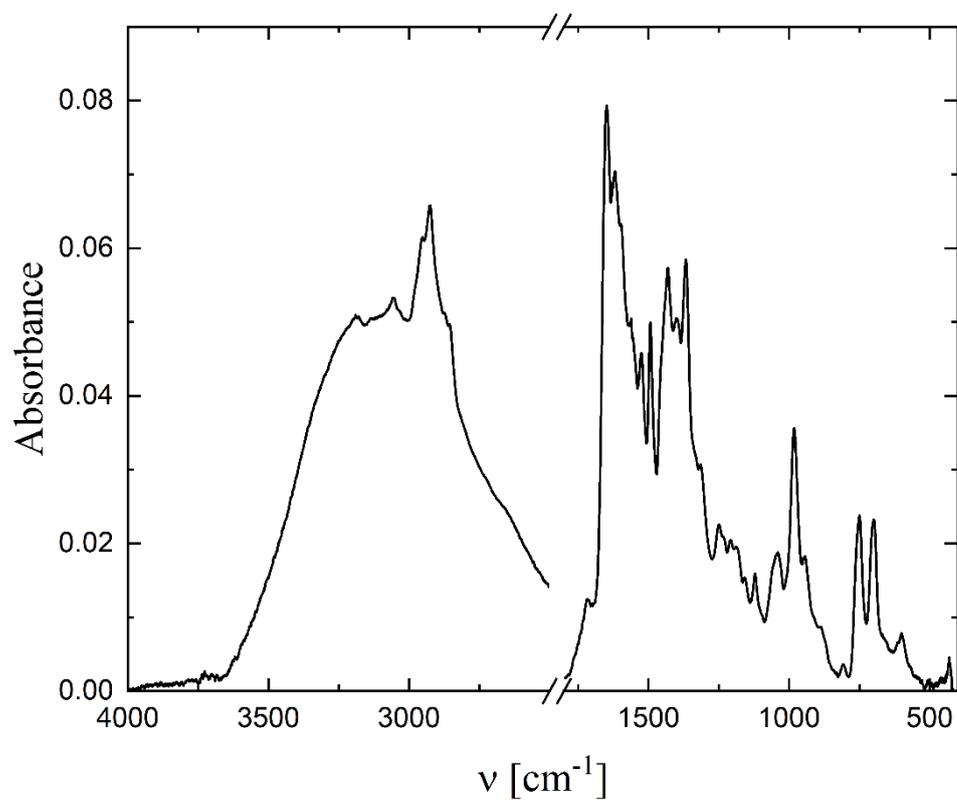


Figure S16. IR-ATR spectrum of VC054.

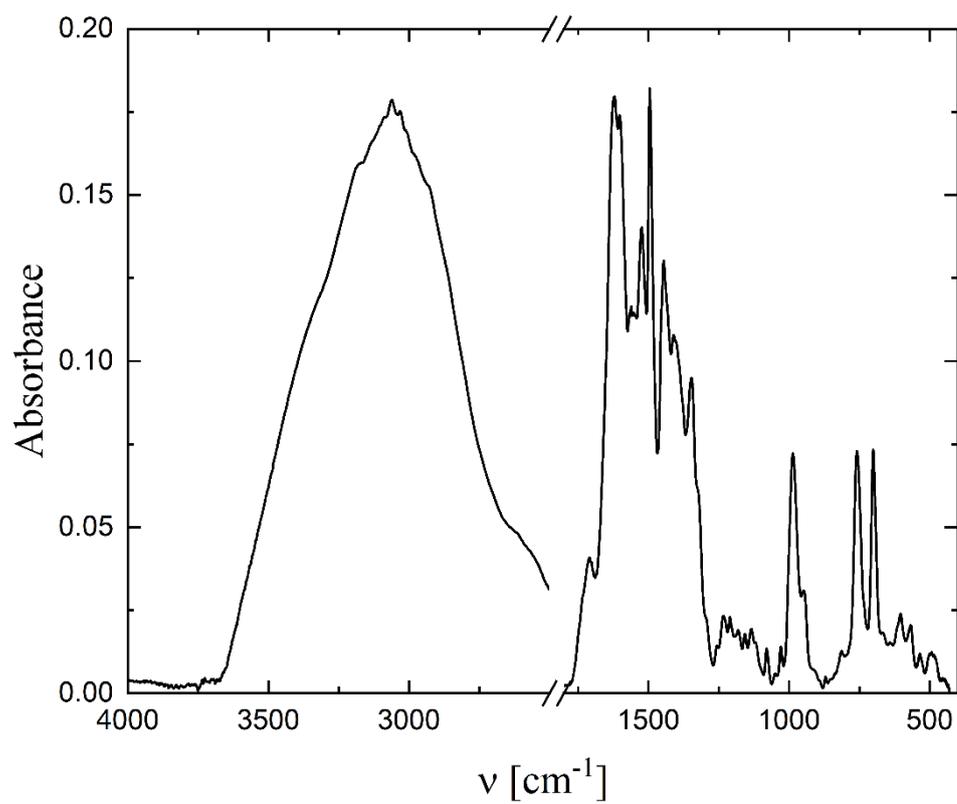


Figure S17. IR-ATR spectrum of VC059.

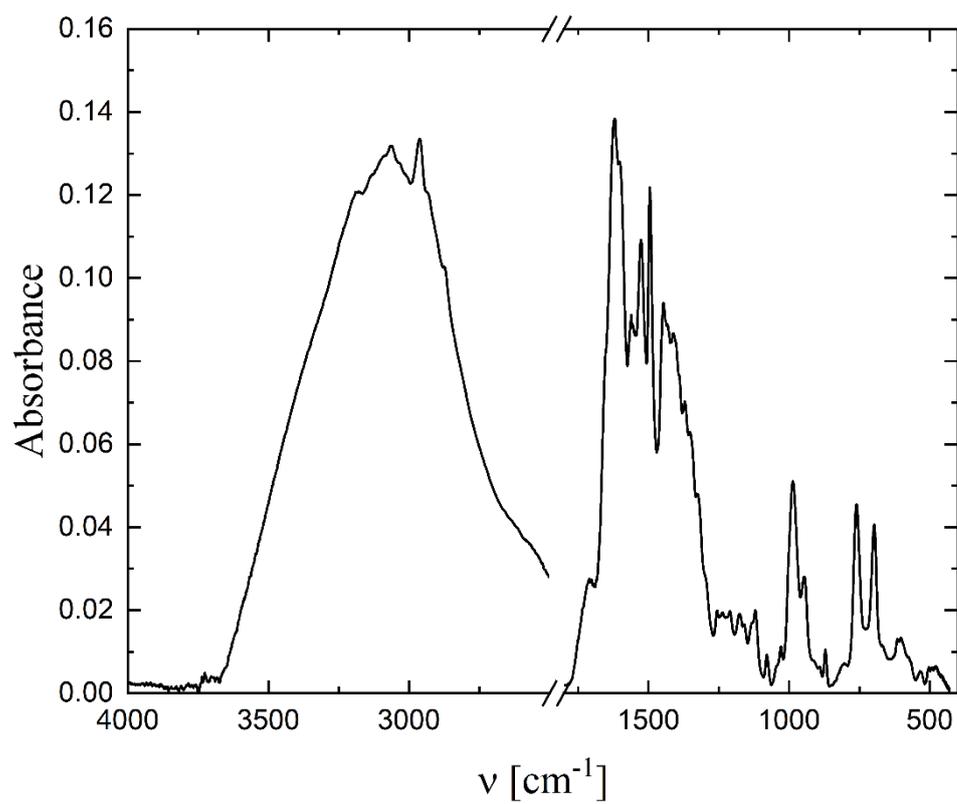


Figure S18. IR-ATR spectrum of VC070.

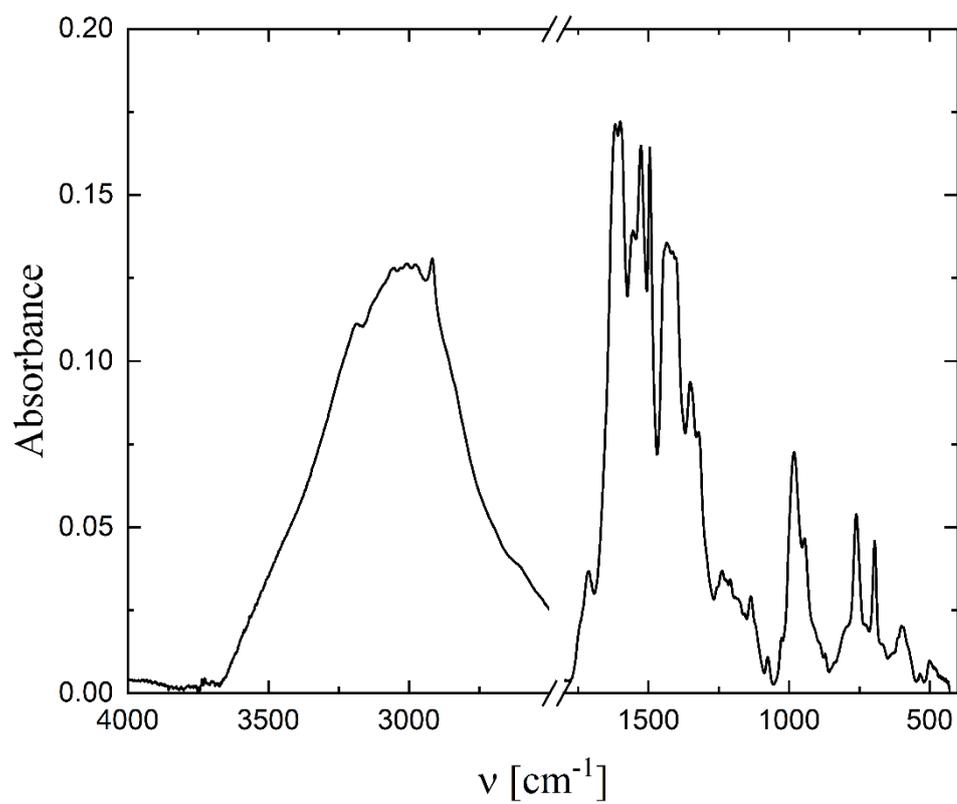


Figure S19. IR-ATR spectrum of VC073.

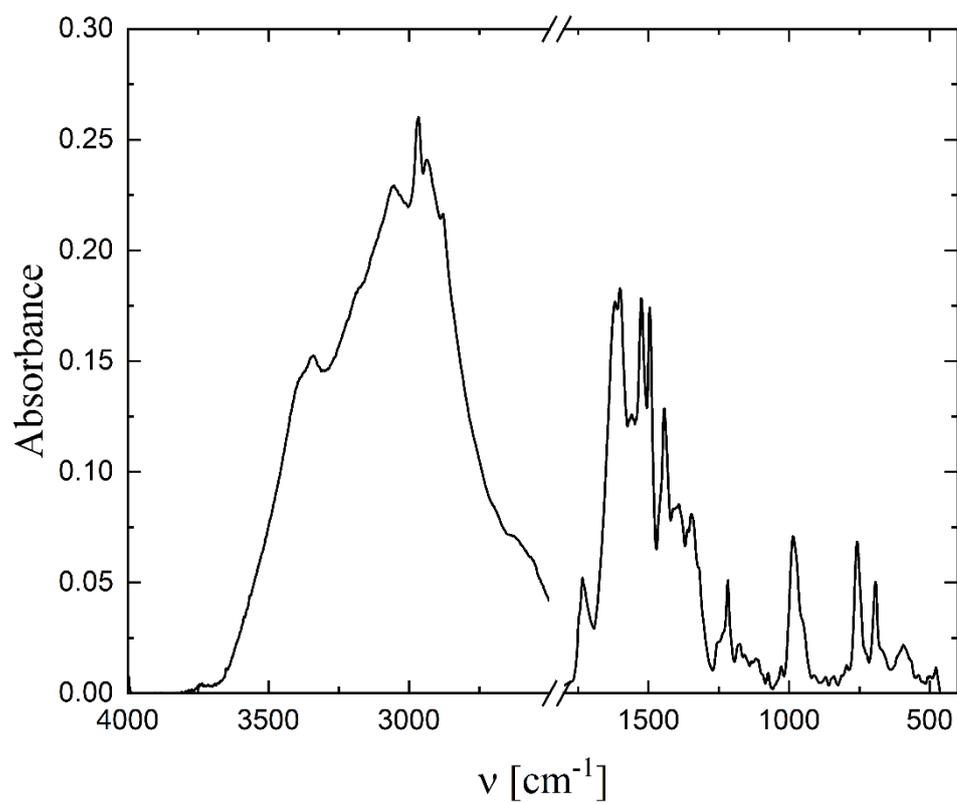


Figure S20. IR-ATR spectrum of VC109.

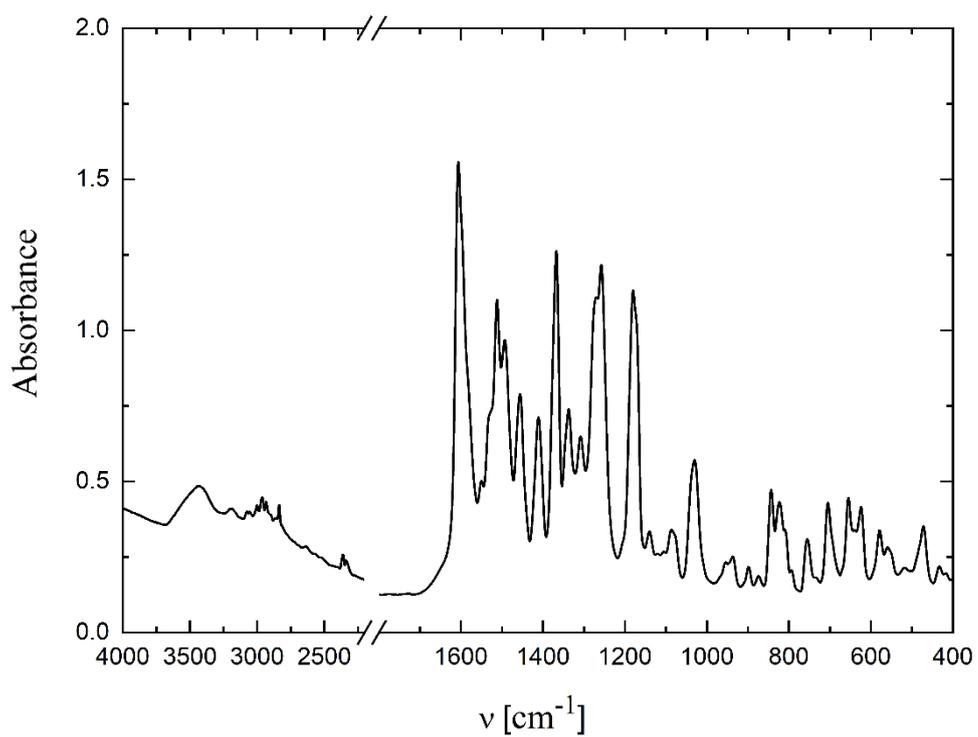


Figure S21. IR-ATR spectrum of VC055.

UV-Vis spectra of complexes

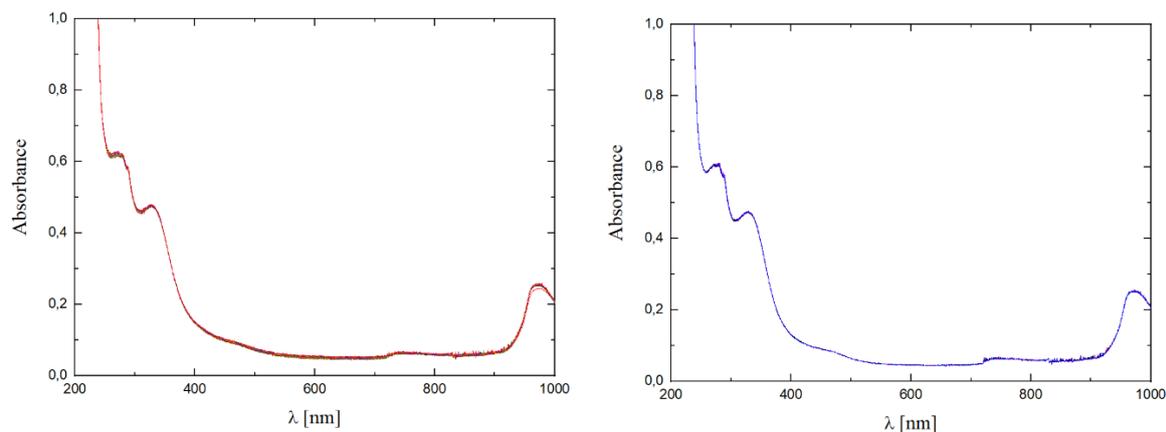


Figure S22. UV-Vis spectra of complex VC054 in DMSO-H₂O mixture (20 μl + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37 °C, d = 1 cm, 15 spectra measured in 340 s intervals.

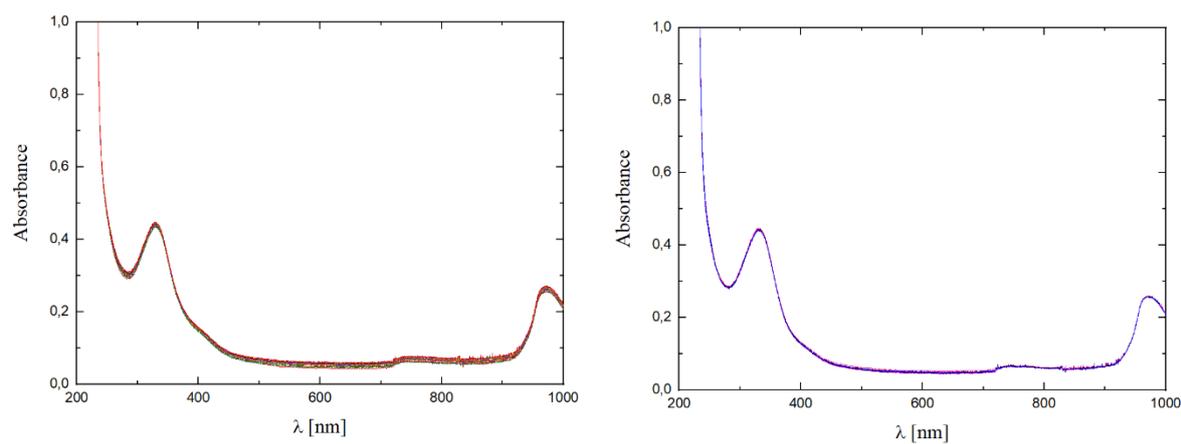


Figure S23. UV-Vis spectra of complex VC059 in DMSO-H₂O mixture (20 μl + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37 °C, d = 1 cm, 15 spectra measured in 340 s intervals.

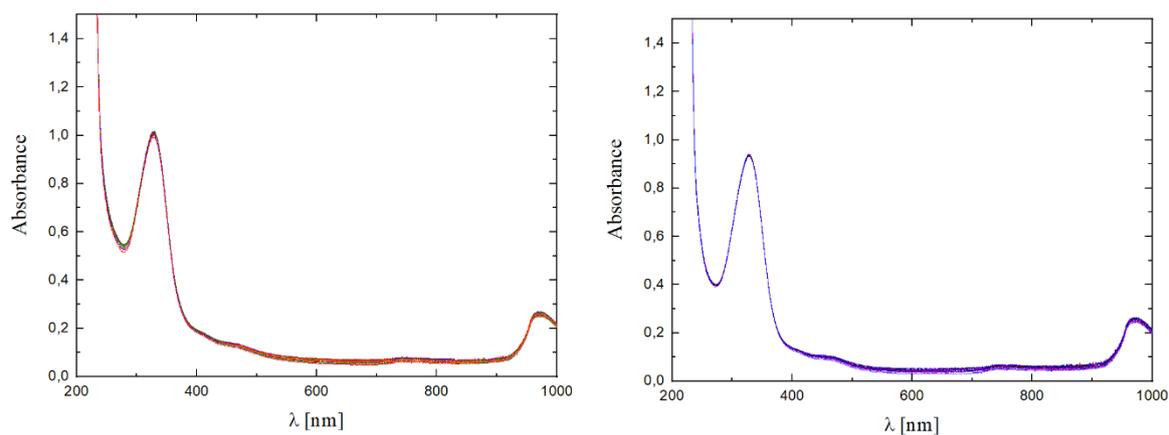


Figure S24. UV–Vis spectra of complex **VC070** in DMSO-H₂O mixture (20 μl + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37 °C, d = 1 cm, 15 spectra measured in 340 s intervals.

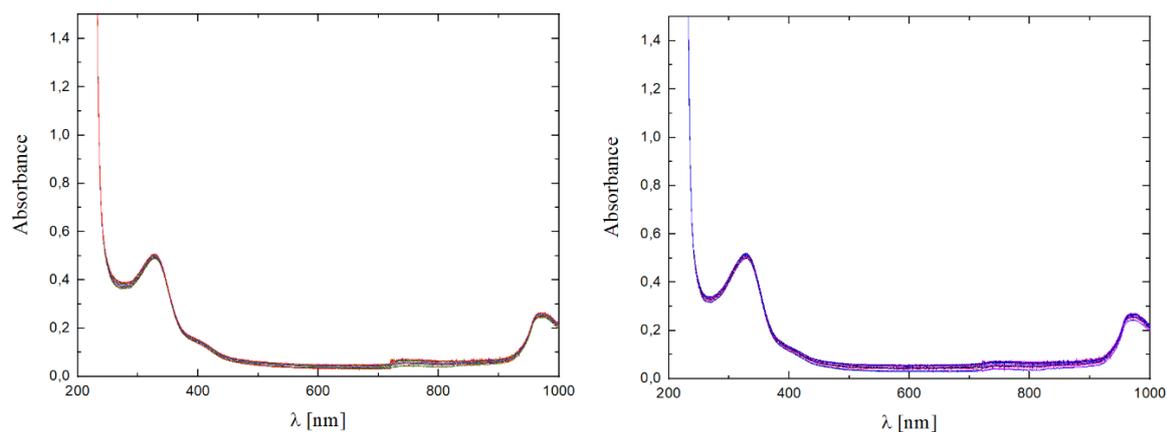


Figure S25. UV–Vis spectra of complex **VC073** in DMSO-H₂O mixture (20 μl + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37 °C, d = 1 cm, 15 spectra measured in 340 s intervals.

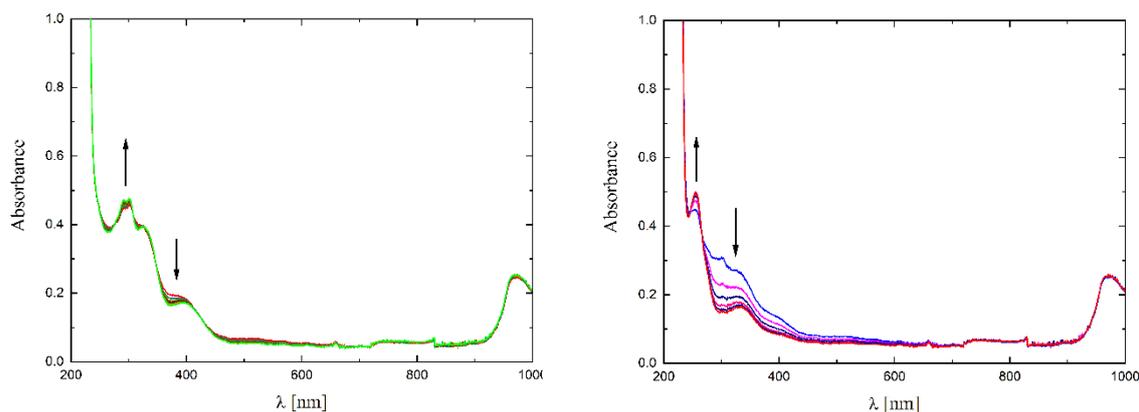


Figure S26. UV-Vis spectra of complex **VC055** in DMSO-H₂O mixture (20 μl + 3 ml respectively) at pH = 7 (left side) and pH = 2 (right side). T = 37 °C, d = 1 cm, 7 spectra measured in 340 s intervals. The arrows show direction of changes in spectra.

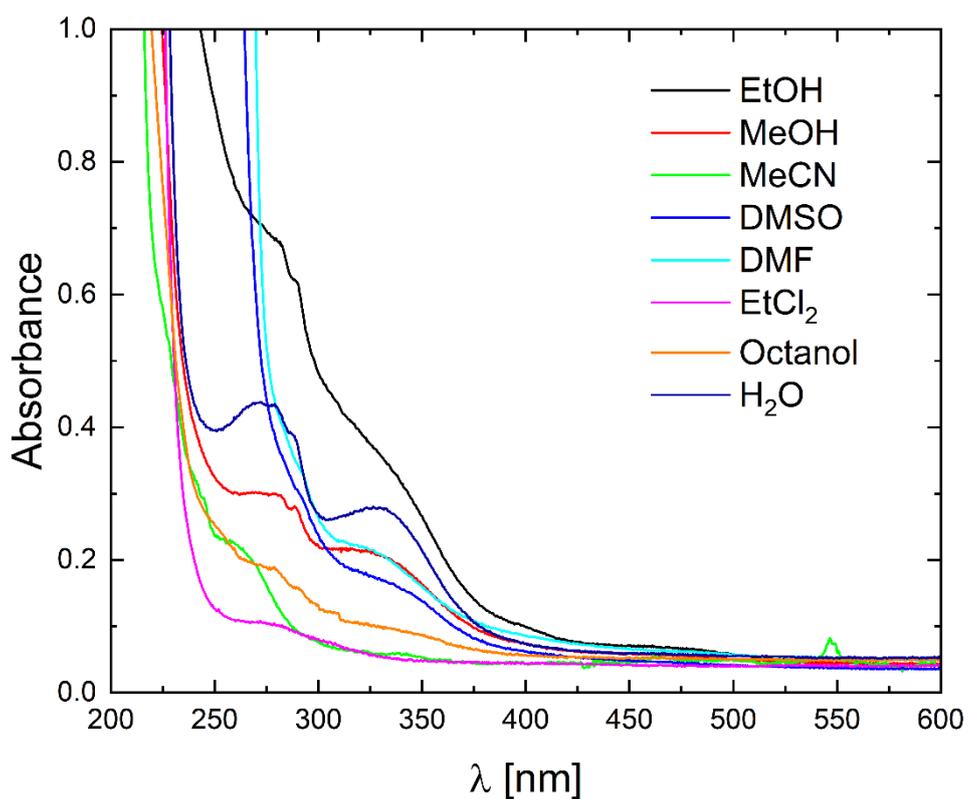


Figure S27. Qualitative UV-Vis spectra of complex **VC054** in different solvents; d = 1 cm.

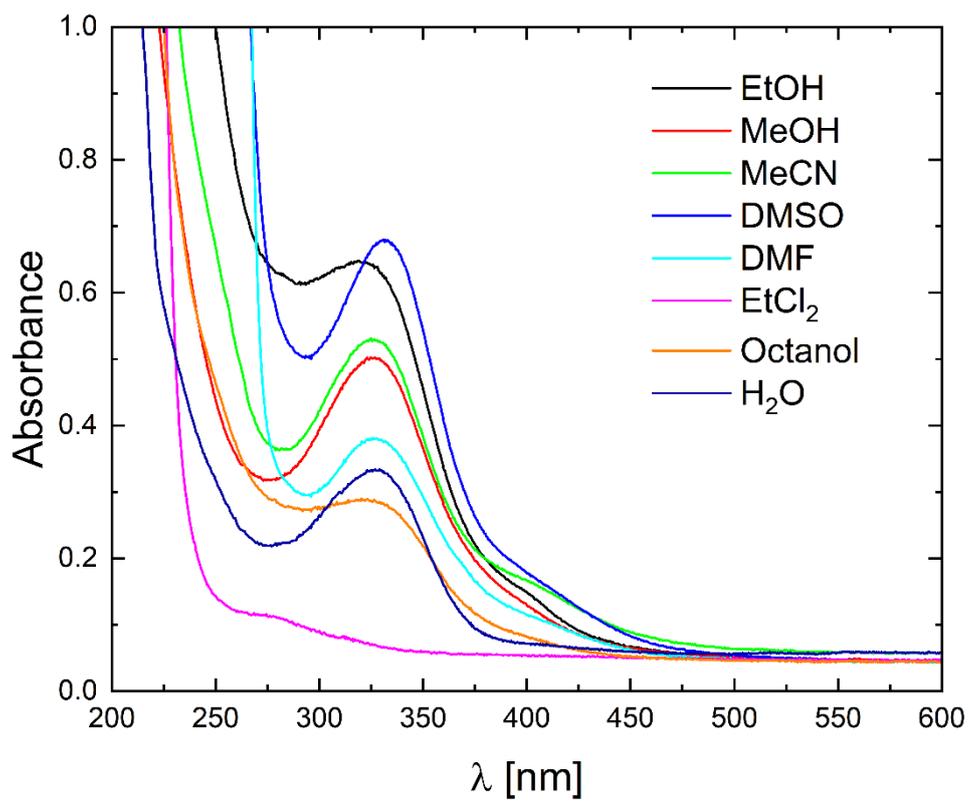


Figure S28. Qualitative UV–Vis spectra of complex **VC059** in different solvents; $d = 1$ cm.

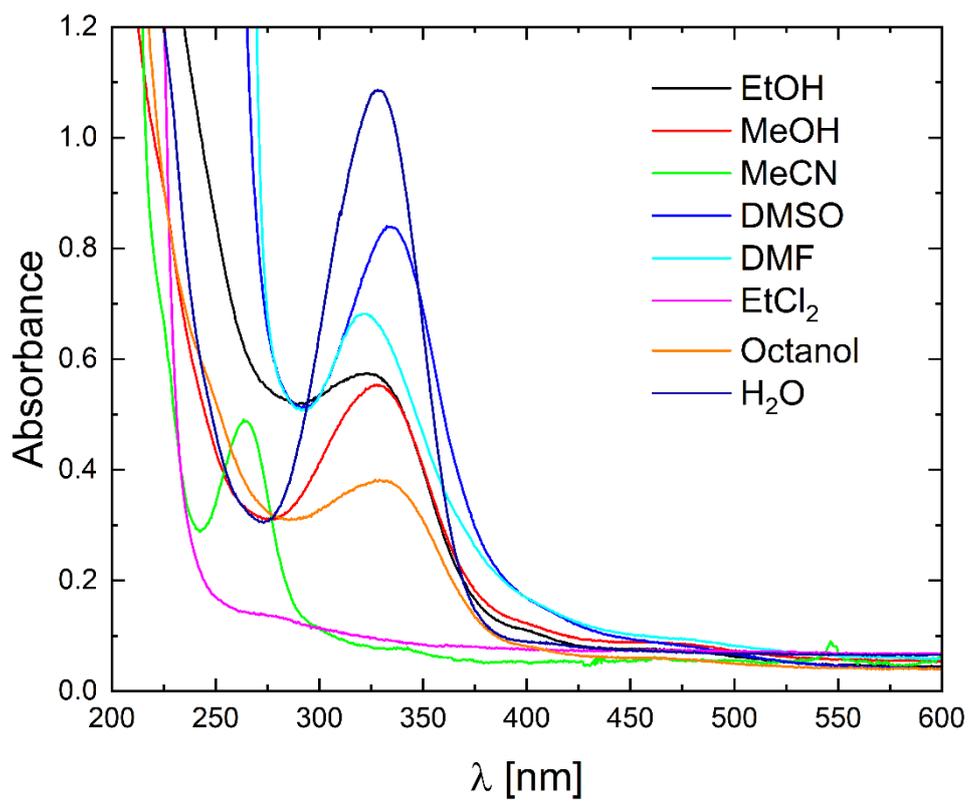


Figure S29. Qualitative UV–Vis spectra of complex **VC070** in different solvents; $d = 1$ cm.

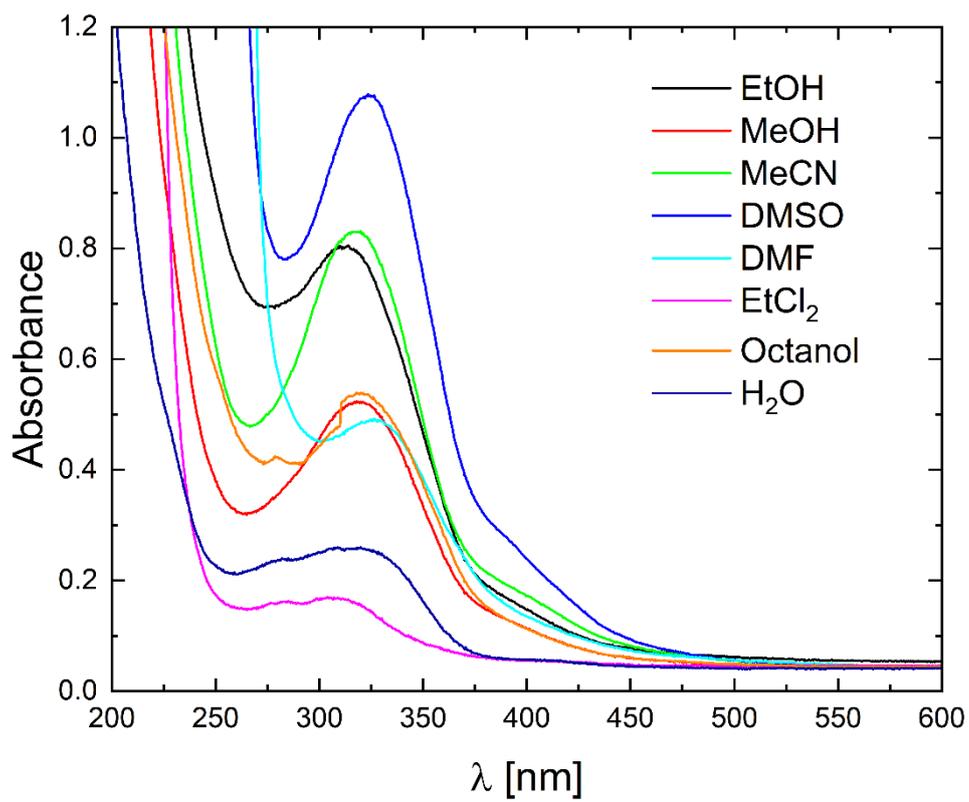


Figure S30. Qualitative UV–Vis spectra of complex **VC073** in different solvents; $d = 1$ cm.

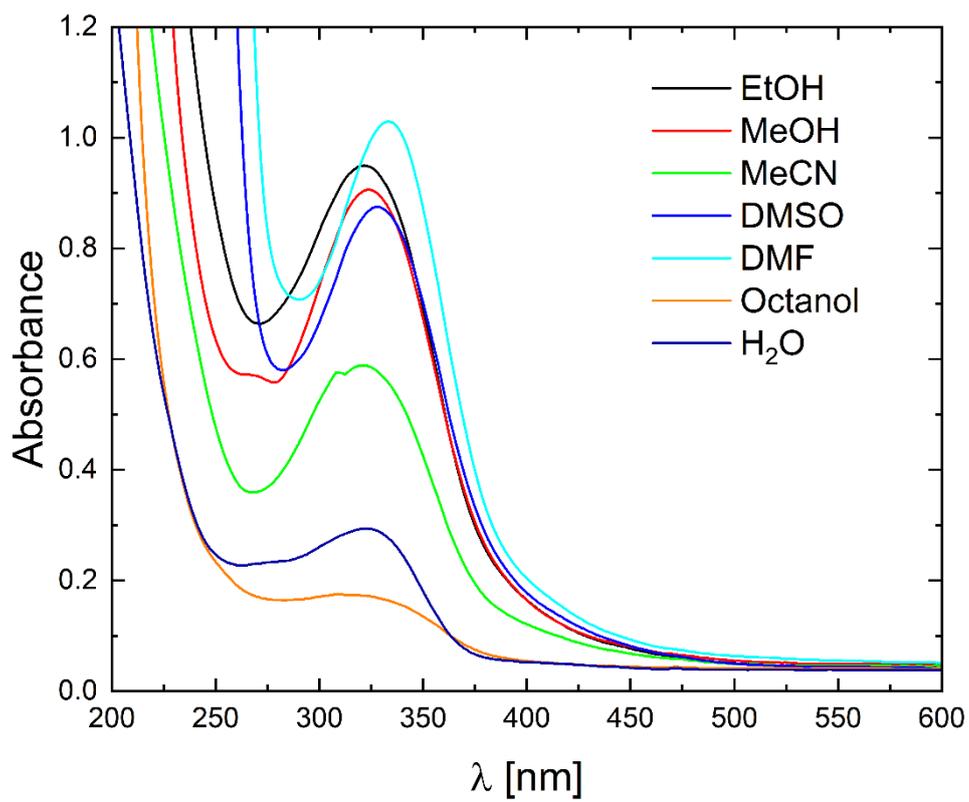


Figure S31. Qualitative UV–Vis spectra of complex **VC109** in different solvents; $d = 1$ cm.

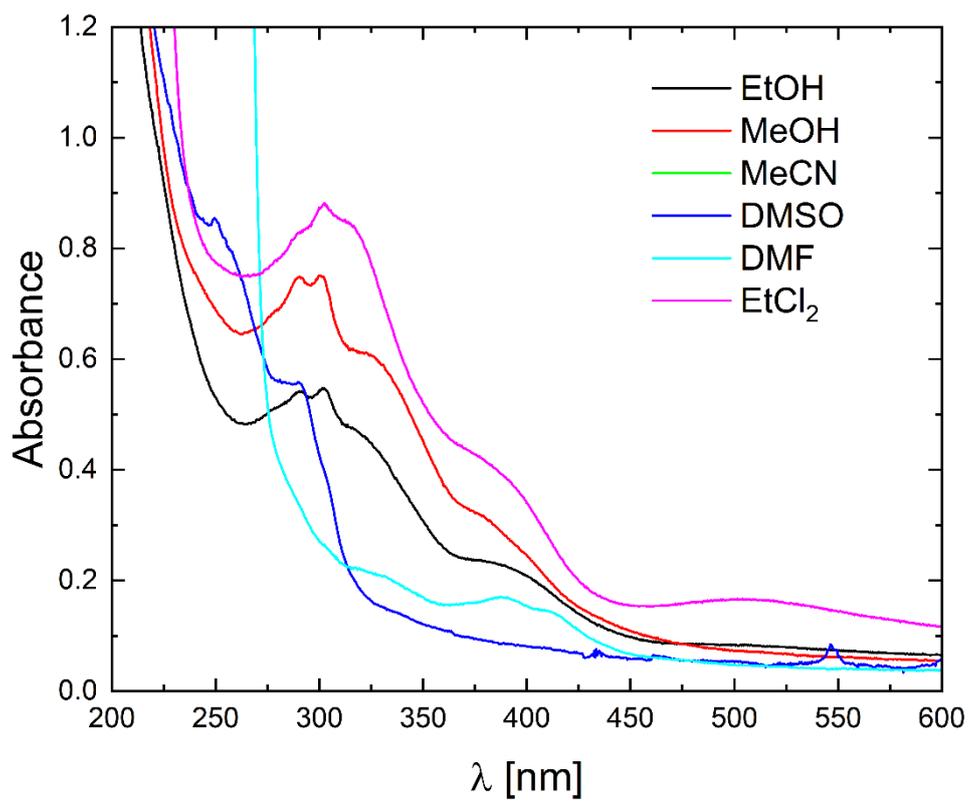


Figure S32. Qualitative UV-Vis spectra of complex **VC055** in different solvents; $d = 1$ cm.