

UNIVERSITI TEKNOLOGI MARA

**SYNTHESIS AND
CHARACTERIZATION OF
PALLADIUM(II) AND NICKEL(II)
SCHIFF BASE COMPLEXES FOR
HOMOGENOUS CATALYTIC AND
ANTICANCER STUDIES**

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Thesis submitted in fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Chemistry)

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ABSTRACT

This thesis reports the synthesis, characterization, catalytic investigation as well as anticancer screening of palladium(II) and nickel(II) Schiff base complexes in homogenous copper-free Sonogashira reaction. Two groups of symmetrical tetradentate *ONNO* Schiff bases namely L1 and L2 series were successfully prepared from condensation reaction between salicylaldehyde and its derivatives with two different primary amines namely *ortho*-phenylenediamine and 2,2-dimethyl-1,3-propanediamine, in 2:1 ratio. The synthesized ligands were reacted with palladium(II) acetate and nickel(II) acetate tetrahydrate in 1:1 ratio, yielding palladium(II) and nickel(II) Schiff base complexes. A total of 12 ligands and 17 complexes were successfully isolated and characterized through elemental analysis, melting point, ¹H and ¹³C Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FTIR), UV-Visible spectroscopy and molar conductivity and magnetic susceptibility studies. All spectral and physicochemical data supported the proposed chemical structures. Low molar conductivity values suggested non-electrolytic nature of all complexes. The diamagnetism of all complexes suggested their square planar geometry. This was corroborated by single crystal X-ray crystallography which revealed the square planar geometry of PdL2F and PdL2OMe with crystal structures showing the tetradentate dinitrogen dioxygen [*ONNO*] nature of L1H, L1C and L2F. Coordination to metal centres occur through two phenolic oxygen and two imine nitrogen donor atoms, assenting to the indication through FTIR, NMR and UV-Visible spectroscopy. Palladium(II) complexes of the L2 series were employed to find the optimum reaction conditions for copper-free Sonogashira reaction by varying type of bases, amount of catalysts, and temperature. Copper salt was not used as co-catalyst to avoid the possible homocoupling of diphenylacetylene. All palladium(II) and nickel(II) complexes were employed as catalysts in the reaction after optimization. All palladium(II) complexes were found to be effective as catalysts with 100% conversion of iodobenzene after 3 hours of reaction. Nickel(II) complexes revealed lower catalytic activities than palladium(II) complexes, with fairly moderate efficiency of 91% conversion after 12 hours of reaction. From GC-FID, a single peak of the product, diphenylacetylene, was detected at 11.69 min with no extra peaks, suggesting the absence of homocoupling products. The product of the catalysed reaction was isolated with a yield of 38% and successfully characterized via ¹H and ¹³C Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FTIR) spectroscopy. All compounds were also tested against human colon cancer cell lines (HCT116) where PdL2H showed the highest potency with IC₅₀ of 0.60 µg/ml, lower than that of the standard drug used in this study, 5-FU with IC₅₀ of 1.70 µg/ml. A moderate binding affinity was observed between PdL2H with DNA with a binding constant of 5.715 x 10⁵ M⁻¹. Hypochromism value of 24-33% indicated intercalation mode of interaction with π-π end stacking of the complex with DNA.

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