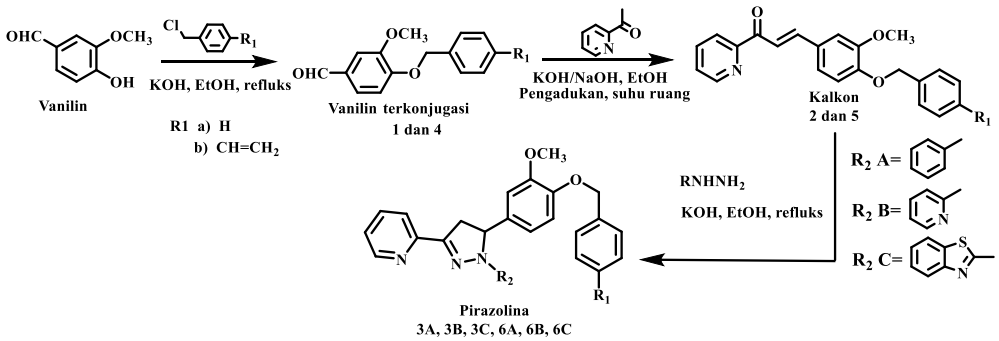
INTISARI



Sintesis senyawa pirazolina **3A**–**3C** dan **6A**–**6C** berbahan dasar 2-asetilpiridin dan vanilin serta uji aktivitasnya sebagai kemosensor telah dilakukan. Vanilin diperpanjang konjugasinya melalui reaksi sintesis eter Williamson antara vanilin dengan benzil klorida atau 1-(klorometil)-4-vinilbenzena untuk menghasilkan senyawa **1** dan **4**, sedangkan kalkon disintesis melalui reaksi *Claisen-Schmidt* dengan mereaksikan 2-asetilpiridin dan vanilin yang telah terkonjugasi yaitu eter vanilin **1** dan **4** membentuk kalkon **2** dan **5**. Selanjutnya, pirazolina disintesis melalui reaksi siklokondensasi antara kalkon dengan fenilhidrazin, 2-hidrazinilpiridin, dan 2-hidrazinilbenzotiazol menggunakan metode refluks dan KOH sebagai katalis. Elusidasi struktur dilakukan dengan instrumentasi FTIR, GC–MS, KLT densitometer, ^{1}H– dan ^{13}C–NMR. Kalkon dan pirazolina diuji aktivitas kemosensornya melalui *screening* terhadap kation Fe(II), Co(II), Mn(II), Cr(III), Zn(II), Cu(II), Fe(III), Cd(II), Pb(II) dan Hg(II), kemudian ditentukan *limit of detection* (LOD), *limit of quantification* (LOQ), *quantum yield* (Φ), dan *binding constant* (K). Interaksi antara ligan dan kation logam dibuktikan menggunakan Job's Plot, FTIR, ^{1}H–NMR, dan pendekatan komputasi melalui *density functional theory* (DFT). Senyawa eter vanilin **1** dan **4** dihasilkan dengan persen hasil 97,38 dan 98,03%, sedangkan kalkon **2** dan **5** berupa padatan kuning dengan persen hasil 87,40 dan 99,48%. Siklisasi kalkon menghasilkan pirazolina **3A**–**3C** dan **6A**–**6C** berupa padatan putih sampai kuning dengan persen hasil lebih besar dari 80%. Uji aktivitas kemosensor menunjukkan bahwa semua pirazolina selektif terhadap kation Hg(II), dengan gugus benzotiazol memberikan selektivitas lebih baik dibandingkan dengan gugus fenil dan piridin. Pirazolina **6C** memberikan kinerja kemosensor terbaik dengan LOD 8,94 nM, LOQ 29,79 nM, Φ 0,73 dan K 1,43. Keberadaan cincin benzotiazol terbukti dapat meningkatkan selektivitas pirazolina, namun tidak demikian dengan keberadaan atom nitrogen pada *binding site*.

Kata kunci: Fluoresensi, kemosensor, pirazolina, siklokondensasi, vanilin.

SYNTHESIS AND ACTIVITY TESTS OF PYRAZOLINE DERIVATIVES AS FLUORESCENCE CHEMOSENSORS OF METAL CATIONS

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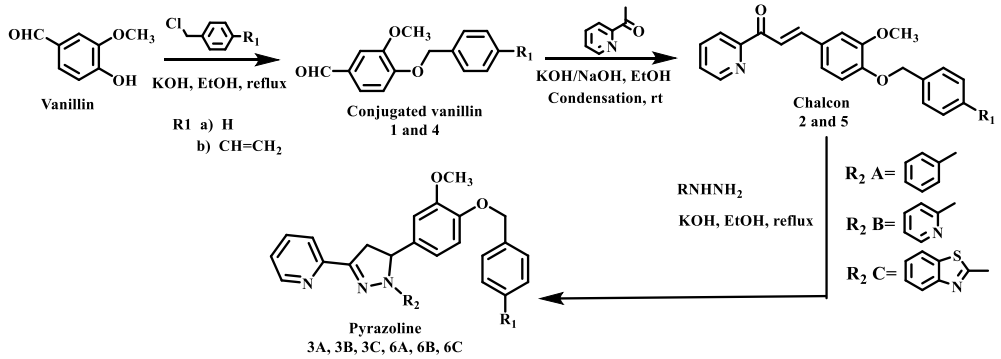
ABSTRACT



The synthesis of pyrazoline compounds **3A**–**3C** and **6A**–**6C** based on 2-acetylpyridine and vanillin and their testing activity as chemosensors have been tested. Vanillin extended its conjugation through the Williamson ether synthesis reaction between vanillin and benzyl chloride or 1-(chloromethyl)-4-vinylbenzene to produce compounds **1** and **4**, while chalcones were synthesized through the Claisen-Schmidt reaction by reacting 2-acetylpyridine and vanillin that had been conjugated, namely vanillin ethers **1** and **4**, to form chalcones **2** and **5**. Furthermore, pyrazoline was synthesized through the cyclocondensation reaction between chalcones with phenylhydrazine, 2-hydrazinylpyridine, and 2-hydrazinyl-benzothiazole using the reflux method and KOH as a catalyst. Structure elucidation were carried out using FTIR, GC–MS, TLC densitometers, ^{1}H– and ^{13}C–NMR instrumentation. Chalcones and pyrazolines were tested for their chemosensory activity by screening against Fe(II), Co(II), Mn(II), Cr(III), Zn(II), Cu(II), Fe(III), Cd(II), Pb(II), and Hg(II) cations, and then the limit of detection (LOD), limit of quantification (LOQ), quantum yield (Φ), and binding constant (K) were determined. The interaction between ligands and metal cations was proven using Job's Plot, FTIR, ^{1}H–NMR, and a computational approach through density functional theory (DFT). Vanillin ether **1** and **4** were produced with 97.38 and 98.03% yields, respectively, while chalcones **2** and **5** were yellow solids with 87.40 and 99.48% yields, respectively. The cyclization of chalcone gave pyrazolines **3A**–**3C** and **6A**–**6C** as white to yellow solids with a yield greater than 80%. Chemosensory activity tests showed that all pyrazolines were selective for Hg(II) cations, with the benzothiazole group providing better selectivity compared to the phenyl and pyridine groups. Pyrazoline **6C** gave the best chemosensory performance with an LOD of 8.94 nM, LOQ of 29.79 nM, Φ of 0.73, and K of 1.43. The presence of the benzothiazole ring was shown to increase the selectivity of pyrazolines, whereas the presence of the nitrogen atom at the binding site did not.
Keywords: Chemosensor, cyclocondensation, fluorescence, pyrazoline, vanillin.