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Innovative Chiral Nanocatalysts: A Green Approach to Asymmetric Heck Carbonylation Reactions

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Extended Abstract

The asymmetric Heck carbonylation reaction is employed in the synthesis of high-value chiral β-carbonyl-substituted molecules, including pharmaceutical compounds containing a chiral oxindole ring with a quaternary carbon stereocenter, such as (+)-physostigmine, (+)-physovenine, and (+)-phenserine [1]. However, previous studies have demonstrated that this reaction, particularly for sterically hindered substrates, requires significantly long reaction times, high catalyst loadings, and elevated temperatures. Therefore, new studies aimed at achieving milder reaction conditions are of great importance. With the careful design and use of catalysts, production protocols can become more economical, environmentally friendly, and sustainable [2]. Additionally, previous research has shown that nanoalloys containing two or more metals exhibit higher stability and selectivity compared to their monometallic counterparts, and they have the potential to be more active due to geometric and electronic effects arising from interactions between the metals [3].

In this study, palladium and palladium-copper alloy nanoparticles stabilized with phosphoramidite ligands containing a C2-symmetric chiral binaphthyl backbone, known for their high efficiency and selectivity in catalytic systems, were synthesized. The structures of the synthesized ligands were elucidated using spectroscopic techniques such as FT-IR, ^{1}H, ^{13}C, and ^{31}P NMR, while the characterization of the mono- and bimetallic nanoparticles was conducted through TEM, XRD, XPS, TGA, and CD analyses. The catalytic activity of these chiral nanoparticles was investigated in asymmetric Heck carbonylation reactions. The possibility of metal atom or ion leaching into the reaction solution during the asymmetric Heck carbonylation reactions was examined via ICP-MS analyses. Furthermore, the recyclability and reusability of the nanoparticles following the catalytic reactions were also investigated. In addition, the homogeneous/heterogeneous behavior of these nanoparticles, known as hybrid catalysts, during catalytic reactions was studied through Hg(0) and CS_2 poisoning tests, with these findings supported by hot filtration tests. The reusability of the mono- and bimetallic nanocatalysts was further explored. During the catalytic applications, the yields and enantioselectivities of the products were determined using GC and HPLC analyses, revealing product formation with complete enantioselectivity (>99% ee) and a yield of 99%.

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