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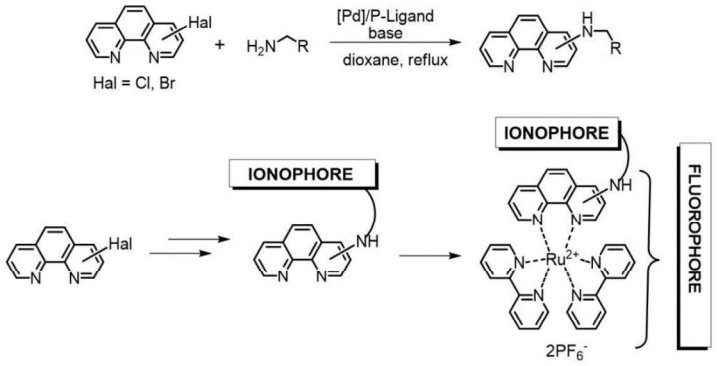
P130 Pd-catalyzed amination of 1,10-phenantrolines and its application for detection of heavy metal ions

by A.S. Abel[a], A.D. Averin[a], A. Bessmertnykh-Lemeune[b], I.P. Beletskaya[a] | [a]M.V. Lomonosov Moscow State University, Department of Chemistry, Leninskie gory, 1-3 Moscow, 119991, Russia, [b]Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR CNRS 6302, 9 avenue A. Savary, 21078 Dijon Cedex, France

1,10-Phenanthrolines are versatile ligands which are widely used in supramolecular chemistry, biochemistry and material science. For instance, Ru(II), Ir(III) and Cu(I) complexes with 1,10-phenanthrolines exhibit appropriate photophysical and electrochemical properties for the development of luminescent biomarkers and sensors and photoactive devices. Accordingly, synthetic approaches to these ligands are widely studied. Transition metal-catalyzed amination reaction is well known to be a useful for functionalization of aromatic compounds. However, catalytic amination of 1,10-phenanthroline derivatives is by far a trivial task as these compounds strongly coordinate catalytic species inhibiting the catalytic cycle.

In this work, we report Pd-catalyzed synthesis of 1,10-phenanthrolines bearing amino substituents at positions 2, 3, 4 or 5 of the phenanthroline core. Catalytic substitution of phenanthroline halides with aliphatic amines was optimized to obtain target products in good yields. Interestingly, amination of halogenophenantrolines with polyamines proceeds chemoselectively and primary amino groups react in the presence of non-protecting secondary amino groups affording ditopic chelators. The diamination of symmetric dihalogeno-substituted 1,10-phenanthrolines was also investigated. In the case of 4,7-dibromo-1,10-phenanthroline polyazamacrocycles bearing phenanthroline moiety were also synthesized in moderate yields. Pd-catalyzed amination of halogenophenanthrolines incorporated in Ru(II)-complex as alternative way was also studied.



As a result, a series of novel chelators was prepared and their sensing properties for toxic metal ions were investigated to develop fluorescent chemosensors for Cu(II) ions.

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