

Abstract

In the first part, an efficient (hetero)arylation of *ortho*-C–H bonds of the benzene ring of 2-arylpyrimidines is achieved by Ru(II)–carboxylate-catalyzed reaction with (hetero)aryl bromides in water under microwave irradiation. This "green" methodology provides a series of polyconjugated pyrimidines with high site-selectivity. As established from Hammett plots, electron-withdrawing groups on phenyl ring of the pyrimidine substrates facilitate the arylation, while both electron-withdrawing and electron-donating groups on the aryl bromides assure a faster reaction.

In the second part, a series of hexa(heteroaryl)benzenes were synthesized by the Ru(II)–carboxylate-catalyzed multiple C–H activation of benzenes carrying pyridyl, pyrimidyl, or pyrazolyl directing groups using N-heteroaryl bromides as coupling partners. The reactions proceeded with high selectivity under microwave irradiation in water. Iterative penta-arylation was implemented *via* sequential activation of C–H bonds of generated intermediates by cascade chelation assistance of in situ installed pyridyl groups.

In the third part, the preliminary study on *N*-pyridylpyridin-2-one formation from substituted 2-bromopyridines was obtained. The pyridones were formed in the presence of Ru(II)-pivalate- Na_2CO_3 catalytic system. The study suggests that oxygen for 2-pyridone formation comes from pivalate which is regenerated with carbonate during the catalytic cycle.

In the fourth part, the synthesized multiheteroaryl-substituted benzenes were used as ligands in coordination to selected transition metals (Ru, Pd, Pt and Ag) to obtain multinuclear complexes. Novel seven-membered bidentate Ru(II) complexes with one or two metal centres were prepared. The strategy was also employed in coordination of two Pd(II) and two Pt(II) cations as well as mixed Ru(II)-Pd(II) and Ru(II)-Pt(II) complexes. The poly(hetero)arylated benzenes were further used as ligands in coordination with Ag(I) ions, to obtain tetra- and pentanuclear complexes. The Ag(I) ions are in square or pentagon orientation, with F^- ion in the centre of complex, between two hexa-coordinating ligands.

Keywords: ruthenium, water, hexaheteroarylbenzene, pyridones, microwaves, complexes