



Review

Metal complex catalysis in the synthesis of quinolines

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ABSTRACT

This review integrates and gives analysis of published data about the synthesis of quinolines by the reactions of anilines with aldehydes, alkenes, alkynes, alkyl amines, allyl amines, alcohols, 1,2-diols, and 1,3-diols using metal complex catalysts based on Ru, Pt, Rh, Pd, Ir, In, Mo, Co, Bi, Ga, Sc, Hf, Ti, Fe, Ni, Au, Ag, Cu, and Ln. Mechanistic aspects of the catalytic reactions are considered and discussed in detail.

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Introduction

Quinoline and its derivatives constitute an important class of nitrogen-containing heterocyclic systems. The quinoline moiety is a structural part of numerous pharmaceuticals possessing antibacterial, antimalarial and anticancer activities. Quinoline derivatives have found wide use in the preparation of herbicidal

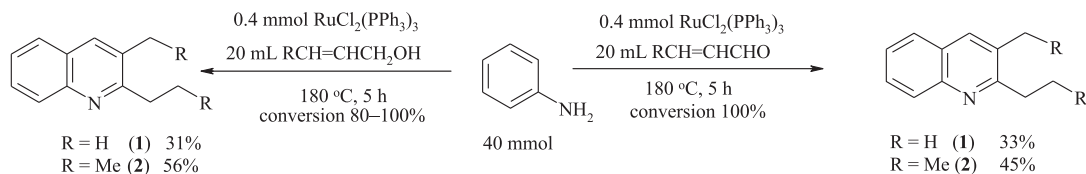
agents, corrosion inhibitors, cyanine dyes, and complexing agents.

Most of the known classical methods of quinoline synthesis by the Skraup, Doebner–von Miller, Combes and Conrad–Limbach reactions are based on the acid-catalyzed condensation of aniline or its derivatives with glycerol or carbonyl compounds. A key drawback of the classical methods for quinoline synthesis is the lack of environmental safety resulting from the necessity to use stoichiometric amounts of acid catalysts due to their binding to nitrogen-containing substrates. In addition, the use of highly reactive acid catalysts markedly restricts the range of functionally substituted substrates that can be involved in the quinoline synthesis.

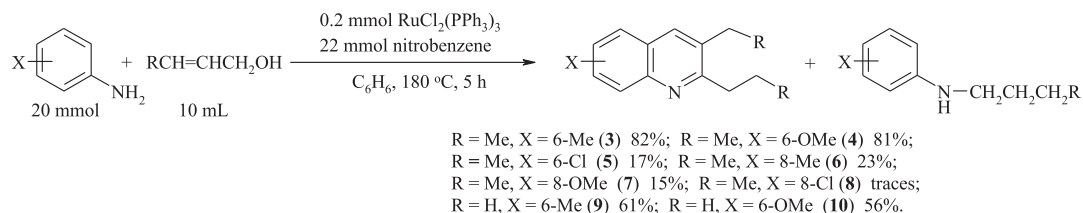
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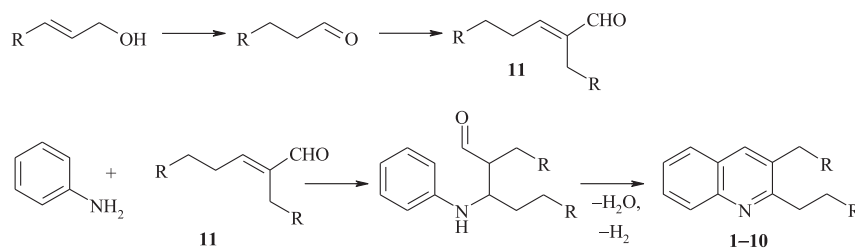
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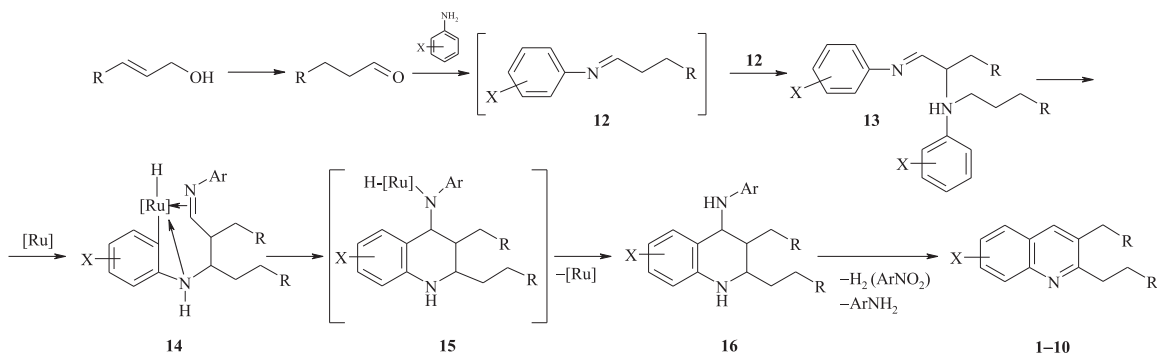
Scheme 1.



Scheme 2.



Scheme 3.

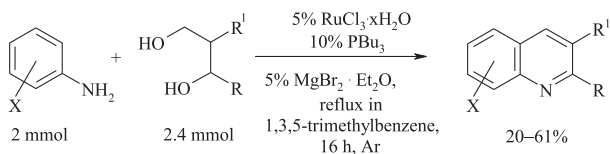


Scheme 4.

A new page of quinoline synthesis was opened by using metal complexes as catalysts. This has three undisputable advantages over the classical methods: tolerance to most of functional groups, considerable extension of the inventory of C₃-synthons suitable as building blocks in the

construction of the quinoline ring, and low consumption of the catalyst.

Some aspects related to the use of metal complexes as catalysts of quinoline synthesis have now been considered in reviews and monographs [1–9].



X = H, R¹ = H, R = H (17); X = H, R¹ = H, R = Me (18);
X = H, R¹ = Me, R = H (19); X = 6-Cl, R¹ = Me, R = H (20);
X = 6-Me, R¹ = Me, R = H (21); X = 6-MeO, R¹ = H, R = H (22);
X = 6-MeO, R¹ = H, R = Me (23); X = 6-MeO, R¹ = Me, R = H (24);
X = 7-Me, R¹ = Me, R = H (25); X = 8-Me, R¹ = Me, R = H (26);
X = 8-Cl, R¹ = Me, R = H (27); X = 8-MeO, R¹ = Ph, R = H (28);
X = H, R¹ = H, R = Hexⁿ (29); X = H, R¹ = Buⁿ, R = H (30);
X = H, R¹ = Ph, R = H (31).

Scheme 5.

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