

論文内容の要旨

Abstract

Development of Methodologies for Selective Synthesis of Aromatic Compounds Using Metal Catalyst

金属触媒を用いた芳香族化合物の選択的合成法の開発

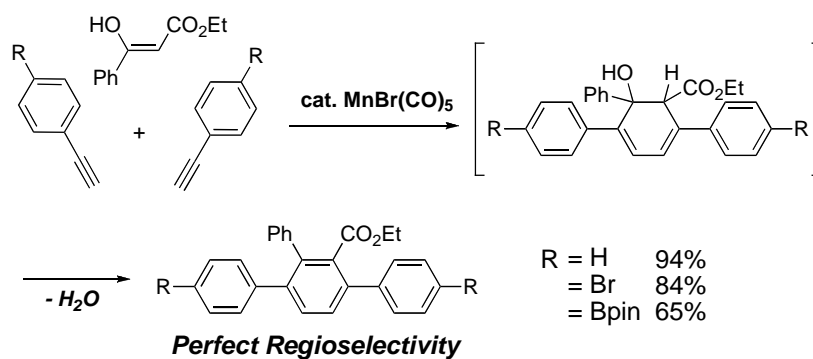
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Densely-functionalized aromatic compounds often appear in the structure of natural products, pharmaceuticals, agrochemicals, and organic semiconductors. Synthesis of these kinds of compounds has been basically achieved by means of derivatization of existing aromatic ring substrates. It requires multi-step synthesis to obtain poly-substituted aromatic compounds. Direct, ideally single-step synthesis of multi-substituted aromatic compounds is desirable. In this thesis, I succeeded development of the selective synthesis of multi-substituted benzenes via manganese-catalyzed [2 + 2 + 2] coupling reaction of 1,3-dicarbonyl compounds and alkynes and indium-catalyzed construction of furan and pyrrole derivatives.

In chapter 1, I mentioned historical and contemporary scientific aspects of aromatic compounds represented by benzene. Selected examples of researches about synthesis of benzene ring by cycloaromatization of aliphatic substrates were also described. Especially, transition metal-catalyzed [2 + 2 + 2] alkyne cyclotrimerization reaction was referred to clarify the motivation and importance of my work.

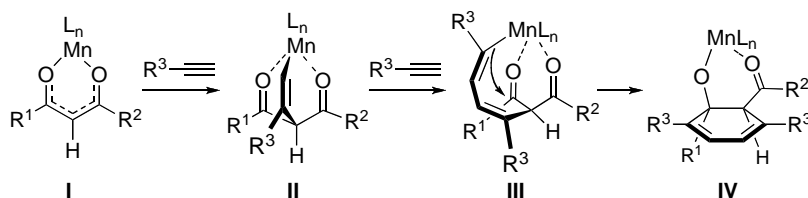
In Chapter 2, manganese-catalyzed [2 + 2 + 2] coupling reaction of 1,3-dicarbonyl compounds and terminal alkynes were demonstrated (Scheme 1). This reaction affords the tetrasubstituted benzene derivatives in high yield and high selectivity. Various functional groups including bromine and boryl substituent were tolerated under the reaction conditions. The use of non-toxic and naturally abundant manganese catalyst is also synthetic virtue of this reaction. The reaction offers key transformation in the synthesis of functional π molecules.

Scheme 1. Mn-catalyzed [2 + 2 + 2] coupling of 1,3-dicarbonyl compound and alkyne



In Chapter 3, mechanistic study of manganese-catalyzed [2 + 2 + 2] reaction was introduced. Suggesting experimental results led me to postulate sequential carbometallation pathway (Scheme 2). Theoretical calculation reasoned the presented reaction pathway and explained origin of regioselectivity and driving force of the reaction. It was disclosed that versatile reactivity of organomanganese (I) species was key of success of the reaction.

Scheme 2. Sequential carbometallation pathway of Mn-catalyzed [2 + 2 + 2] reaction



Chapter 4 is about the indium-catalyzed furan and pyrrole synthesis. I discovered that indium trifluoromethanesulfonate is excellent catalyst to promote the cycloaromatization of α -propargyl ketone (eq. 1). Pyrrole was also obtained utilizing alkynyl enamine (eq. 2). This reaction features small requirement of catalyst and mild reaction conditions.

