

Synthetic Methods

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Q. Liu* _ 1244 – 1247



Highly Regioselective Copper-Catalyzed Benzylic C-H Amination by N-Fluorobenzenesulfonimide

$$R^{1} \stackrel{\text{CuCl (10 mol\%)}}{\stackrel{\text{N}}{\text{Co}_{2}Ph}} + F \stackrel{\text{N}}{\text{N}} \stackrel{\text{N}}{\text{SO}_{2}Ph} \xrightarrow{\text{DCE, 110 °C}} R^{1} \stackrel{\text{L}}{\text{N}} \stackrel{\text{N}}{\text{N}} \stackrel{\text{N}}{\text{N}}$$

Primary target: A practical and effective copper-catalyzed amination strategy for synthesizing various benzylic amines from benzylic hydrocarbons is described (see scheme; DCE = 1,2-dichloroethane). Xylene substrates can undergo diamination reactions using this method. The remarkable preference for primary over secondary benzylic C-H bonds has been observed for the first time.

Asymmetric Catalysis

D. Shi, Y. Xie, H. Zhou, C. Xia, H. Huang* ______ 1248 - 1251



A Highly Diastereo- and Enantioselective Reaction for Constructing Functionalized Cyclohexanes: Six Contiguous Stereocenters in One Step

Just mix to get six: Six contiguous stereocenters, including one quaternary stereocenter, and three C-C bonds are created by a new copper-catalyzed tandem reaction (see scheme). Rigid chiral diamine ligands enabled this asymmetric tandem reaction to proceed with excellent stereoselectivity (complete diastereoselectivity and high enantioselectivity) and high yield under mild reaction conditions.

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Years Ago .

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

 \mathcal{J} he Nobel Prize in Chemistry 1961 was awarded to M. Calvin for his "research on the carbon dioxide assimilation in plants". Issue 2/1962 contains Calvin's Nobel Lecture, in which he describes how ¹⁴C radiolabeling was used to track carbon that enters a plant as carbon dioxide and is turned to carbohydrate in the photosynthetic carbon cycle. Angewandte Chemie has kept the tradition of publishing the Nobel Lectures to this very day.

These days, the mercury ion is considered an environmental hazard and its sensing and extraction are frequently

reported. In former times however, HgSO₄·2HgO, which was discovered in 1604, was even used medicinally! In 1962, A. Weiss reported on the structure of this salt, which was shown by X-ray studies to consist of polymeric (Hg₃O₂)⁺ cations in slightly undulating twodimensional infinite layers.

The butterfly and the salamander are the sources of natural products that were discussed in two Communications. C. Schöpf outlined how the pigment erythropterin was synthesized by treatment of xanthoperin with oxalacetic acid at pH 4.2 and 80°C. It was postulated that

xanthoperin was the primary product in the biosynthesis of pteridine butterfly pigments. G. Habermehl reported the elucidation of the structure of samandaridine, which was isolated along with a range of other alkaloids from the skin gland venom of the fire and alpine salamanders. The structure was deduced from an X-ray study of the hydrobromide salt, and the configuration was confirmed by the two-dimensional electron density projection—quite an achievement 50 years ago!

Read more in Issue 2/1962