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Benzylic C-H Arylation with Visible-Light/Nickel Catalysis: The Dual Role of Benzophenone

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PURPOSE OF THE ABSTRACT

The formation of new bonds is one of the most common ventures in synthetic organic chemistry. The rising environmental awareness also influenced the approach of organic chemists. Atom-economical catalytic reactions performed under mild reaction conditions using non-toxic reagents and catalysts are becoming more important while designing new methods.

Therefore, we developed a mild approach for the direct functionalization of non-activated benzylic C(sp³)-H bonds combining photoredox and nickel catalysis. This allows an atom-economical pathway for the C-C bond formation at ambient temperature.[1]

To circumvent the need of harsh conditions (strong acids, peroxides, UV light) for the activation of aliphatic C-H bonds we chose a benzophenone derivative which upon excitation to its triplet state by visible light irradiation abstracts an aliphatic hydrogen atom from toluene derivatives. The so formed benzylic radical is entering the nickel catalytic cycle to participate in the cross-coupling reaction with a variety of aryl-halides. In our case the benzophenone catalyst is not only playing the role of a photoactive hydrogen atom transfer agent but also serves as an electron transfer agent allowing the base-assisted reduction of a nickel intermediate to close the catalytic cycle after reductive elimination of the arylated product.

The ease of scaling up the reaction is particularly interesting as the diarylmethanes are important structural motifs in bio-active compounds, drug molecules and organic materials [2].

FIGURES

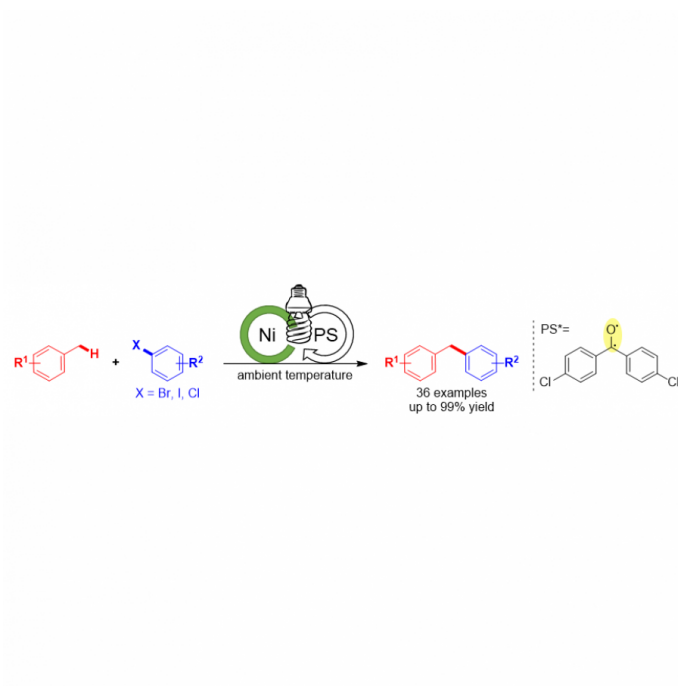


FIGURE 1

Dual catalyzed arylation of toluene derivatives.

FIGURE 2

KEYWORDS

Metallaphotoredox | Visible-light | C(sp³)-H-Functionalization | Energy transfer

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