

Conversion of esters to thioesters under mild conditions.

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Rok wydania

2021

Czasopismo

Organic and Biomolecular
Chemistry

Numer woluminu

19

Strony

2991-2996

DOI

10.1039/d1ob00187f

Kolekcja

Naukowa

Język

Angielski

Streszczenie

We report conversion of esters to thioesters via selective C-O bond cleavage/weak C-S bond formation under transition-metal-free conditions. The method is notable for a general and practical transition-metal-free system, broad substrate scope and excellent functional group tolerance. The strategy was successfully deployed in late-stage thioesterification, site-selective cross-coupling/thioesterification/decarbonylation and easy-to-handle gram scale thioesterification. Selectivity and computational studies were performed to gain insight into the formation of weak C-S bonds by C-O bond cleavage, which contrasts with the traditional trend of nucleophilic additions to carboxylic acid derivatives.

Adres publiczny

<http://dx.doi.org/10.1039/d1ob00187f>

Strona internetowa wydawcy

<https://www.rsc.org/>

Artykuł

Plik został wygenerowany dnia 2026-10-14 15:37:08

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/iaJJcT3>.