Y. ANO, M. TOBISU,* N. CHATANI* (OSAKA UNIVERSITY, SUITA, JAPAN)
Palladium-Catalyzed Direct Ethynylation of C(sp³)–H Bonds in Aliphatic Carboxylic Acid Derivatives

Pd-Catalyzed Direct Alkynylation of Aliphatic C–H Bonds

**Significance:** The first palladium-catalyzed alkynylation of unactivated C(sp³)–H bonds in aliphatic carboxylic acid derivatives has been disclosed. 8-Aminoquinoline proved to be the best directing group to promote the desired alkynylation reaction.

**Comment:** Interestingly, replacement of the 8-aminoquinoline moiety with a 1-aminonaphthyl group or N-methylation of the amide group completely inhibited the ethynylation reaction, indicating that both, the nitrogen of the quinoline moiety and the NH group of the amide are essential for the reaction.

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**Selected examples:**

- R = substituted Alk, Ar, CF₃, OMe
- TIPS = trisopropylsilyl

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\begin{align*}
\text{Ac} & \quad \text{+ Br-TIPS} \\
\text{N} & \quad \text{Pd(OAc)₂ (5 mol%)} \\
\text{AgOAc (1 equiv)} & \quad \text{LiCl (1 equiv)} \\
\text{PhMe, 110 °C, 15 h} & \quad \text{up to 75% yield}
\end{align*}
\]

Selected examples:

- up to 75% yield
- 64% yield
- 60% yield
- 60% yield
- 75% yield
- 62% yield