Photoredox-Catalyzed Hydrocarboxylation of Styrenes in Continuous Flow

Significance: Jamison and co-workers present a photoredox-catalyzed hydrocarboxylation of styrenes using CO₂ and pentamethylpiperidine (PMP). The reactions are performed in flow ($t_R = 8$ min) to provide the anti-Markovnikov adducts in moderate to good yields with high degrees of chemoselectivity. Functional group tolerance and preliminary mechanistic investigations are disclosed.

Comment: This method offers a complementary approach to metal-catalyzed hydrocarboxylation reactions of styrenes, which often afford the corresponding Markovnikov adducts. Metal catalysis has recently been used to affect hydrocarboxylation reactions of simple olefins (M. Gaydou, T. Moragas, F. Juliá-Hernández, R. Martin J. Am. Chem. Soc. 2017, 139, 12161). A similar substrate expansion to simple alkyl olefins would bolster the synthetic capacity of this methodology.

Selected examples:

- $2a$: 87% yield
- $2b$: 48% yield
- $2c$: 57% yield
- $2d$: 61% yield
- $2e$: 33–87% yield

Proposed mechanism:

Continuous flow set-up:

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