Supporting Information

For

One-Pot Synthesis of Polyfunctionalized Quinolines via a Copper-Catalyzed Tandem Cyclization

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1. General procedure for substrates

The amide (1.0 mmol) was added to SOCl$_2$ (2 mL, 27.5 mmol) at room temperature under a N$_2$ atmosphere. Then, the resulting solution was heated to reflux for 2 hours. Corresponding imidoyl chloride was obtained by the removal of excessive SOCl$_2$, and the crude product could be directly used in the next step.

To a solution of the aldehyde (5 mmol) in dry THF (5 mL) was added ethynylmagnesium bromide (6 mmol) at 0 °C under N$_2$ atmosphere. The resulting solution was stirred for 1 hour at room temperature. The reaction was monitored by TLC, and then quenched by adding 20 mL water and extracted with ether (3×10 mL). The combined organics were dried over anhydrous Na$_2$SO$_4$. After removal of solvent the residue, left was purified by flash column chromatography with silica gel using mixture of petroleum ether and ethyl acetate to give the title substrates.

A mixture of (Boc)$_2$O (5 mmol), Et$_3$N (6 mmol) and DMAP (1 mmol) in THF (10 mL) were stirred at room temperature, followed by dropwise addition of the propargyl alcohol derivative (4 mmol). The reaction was monitored by TLC, and then quenched with aqueous NH$_4$Cl (20 mL) and extracted with ether (3×10 mL). The organic phase was washed with brine after which it was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the title substrates.
To a solution of the propargyl alcohol derivative (4 mmol) in DCM (10 mL) was added pyridine (6 mmol) and acetic anhydride (5 mmol) at room temperature, and stirring was continued for 1 h. The reaction mixture was diluted with aqueous NH₄Cl (20 mL) and extracted with ether (3×10 mL). The combined organics were dried over anhydrous Na₂SO₄. The crude product was purified by flash column chromatography on silica gel to give the title substrates.

\[
\begin{align*}
R^4-NH_2 + (\text{Boc})_2O & \xrightarrow{\text{DMAP, Et}_3\text{N, DCM, rt}} R^4-NHBoc \\
\end{align*}
\]

A mixture of amine (10 mmol), Et₃N (15 mmol) and DMAP (1 mmol) in DCM (20 mL) were stirred at room temperature, followed by dropwise addition of the (Boc)₂O (12 mmol). The resulting solution was stirred for 6 hours, and then quenched with aqueous NH₄Cl (20 mL) and extracted with ether (3×10 mL). The organic phase was washed with brine after which it was dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the title substrates.

\[
\begin{align*}
R^4-NHBoc + \text{Br} & \xrightarrow{\text{NaH, THF, 0 °C to rt}} N^\text{Boc}
\end{align*}
\]

Sodium hydride (6 mmol, 60% in mineral oil) was added to a solution of substrates (5mmol) in dry THF (10 mL) at 0°C. The resulting mixture was stirred for 30 minutes at room temperature. Then, propargyl bromide (6 mmol) in dry THF (5mL) was added slowly at 0°C and the solution was stirred for 2 h at room temperature. The reaction was monitored by TLC, and then quenched by adding 20 mL water and extracted with ether (3×10 mL). The combined organics were dried over anhydrous Na₂SO₄. After removal of solvent the residue, left was purified by flash column chromatography on silica gel to give the title substrates.
chromatography with silica gel using mixture of petroleum ether and ethyl acetate to give the title substrates.

2. General procedure for the reaction

Under nitrogen condition, CuI (0.05 mmol) was successively added to a 25mL vial equipped with a stir bar at -78 °C. A solution of the imidoyl chloride (0.5 mmol) in DCE (2 mL) was added using a syringe. Then, the corresponding alkyne (0.6 mmol) was added to the mixture. Et$_3$N (0.75 mmol) was added at last. The reaction was stirred for 30 minutes at -78 °C, and stirred for another 12 hours at room temperature. Solvent was removed in vacuo to leave a crude mixture, which is purified by silica gel column chromatography to afford pure product.

3. The $^1$H and $^{13}$C NMR spectra of compounds