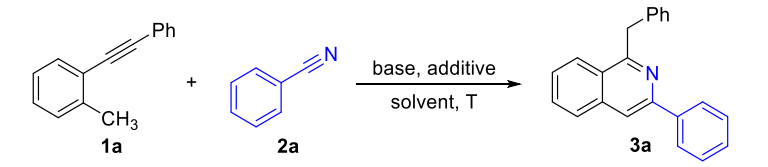
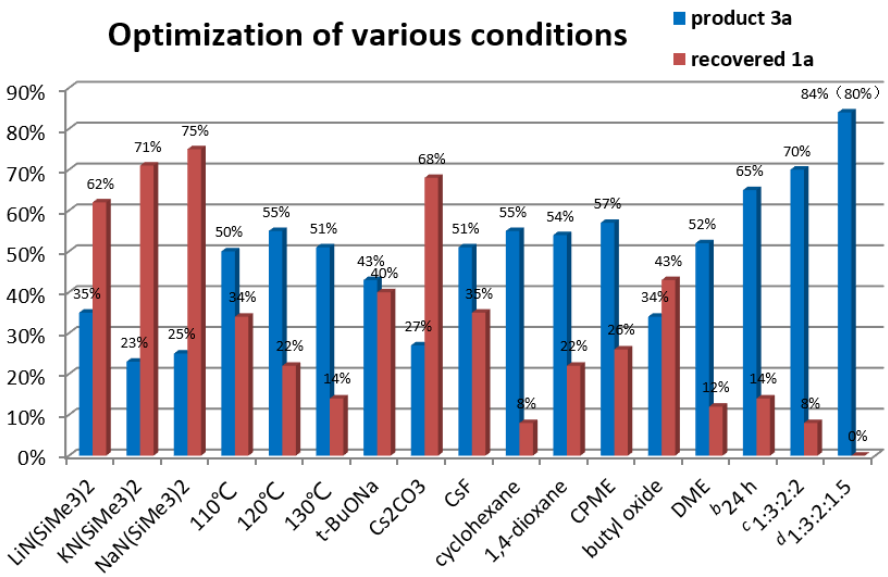
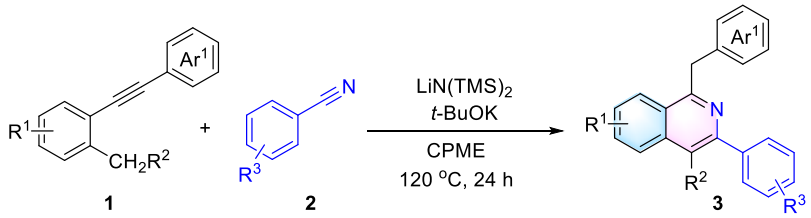
Table 1 Optimization of the Reaction Conditions[a].

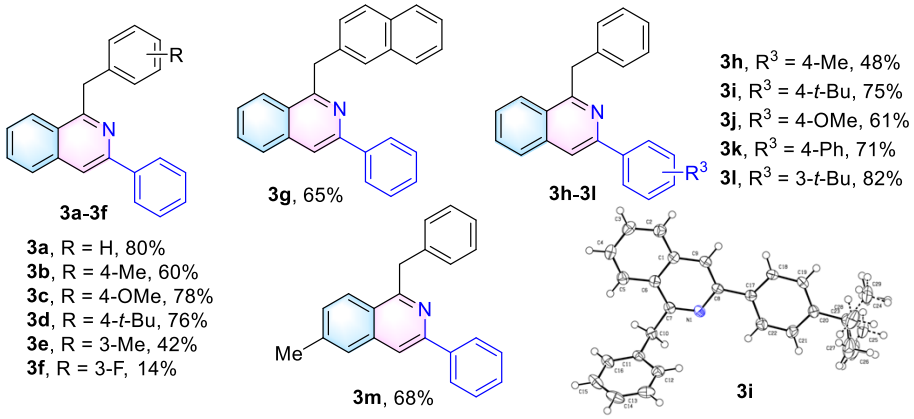




[a]The reaction was firstly performed with **1a** (0.2 mmol), **2a** (2 equiv), $LiN(SiMe_3)_2$ (2 equiv), *t*-BuOK (2 equiv), THF (1 mL, Dry) at 100 °C under N_2 for 12 h. The yield was determined by ^1H NMR using CH_3NO_2 as the internal standard based on **1a**. Then the reaction conditions were optimized by sequentially screening of different bases, temperatures, additives and solvents. [b]24 h. [c]**1a**: **2a**: $LiN(SiMe_3)_2$: *t*-BuOK = 1: 3: 2: 2. [d]**1a**: **2a**: $LiN(SiMe_3)_2$: *t*-BuOK = 1: 3: 2: 1.5. CPME = cyclopentyl methyl ether; DME = 1,2-dimethoxyethane.

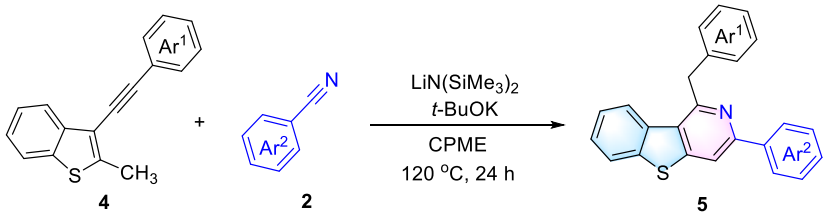
Table 2 Substrate scope of [4 + 2] cycloaddition of *o*-substituted aryl alkynes with nitriles[a].

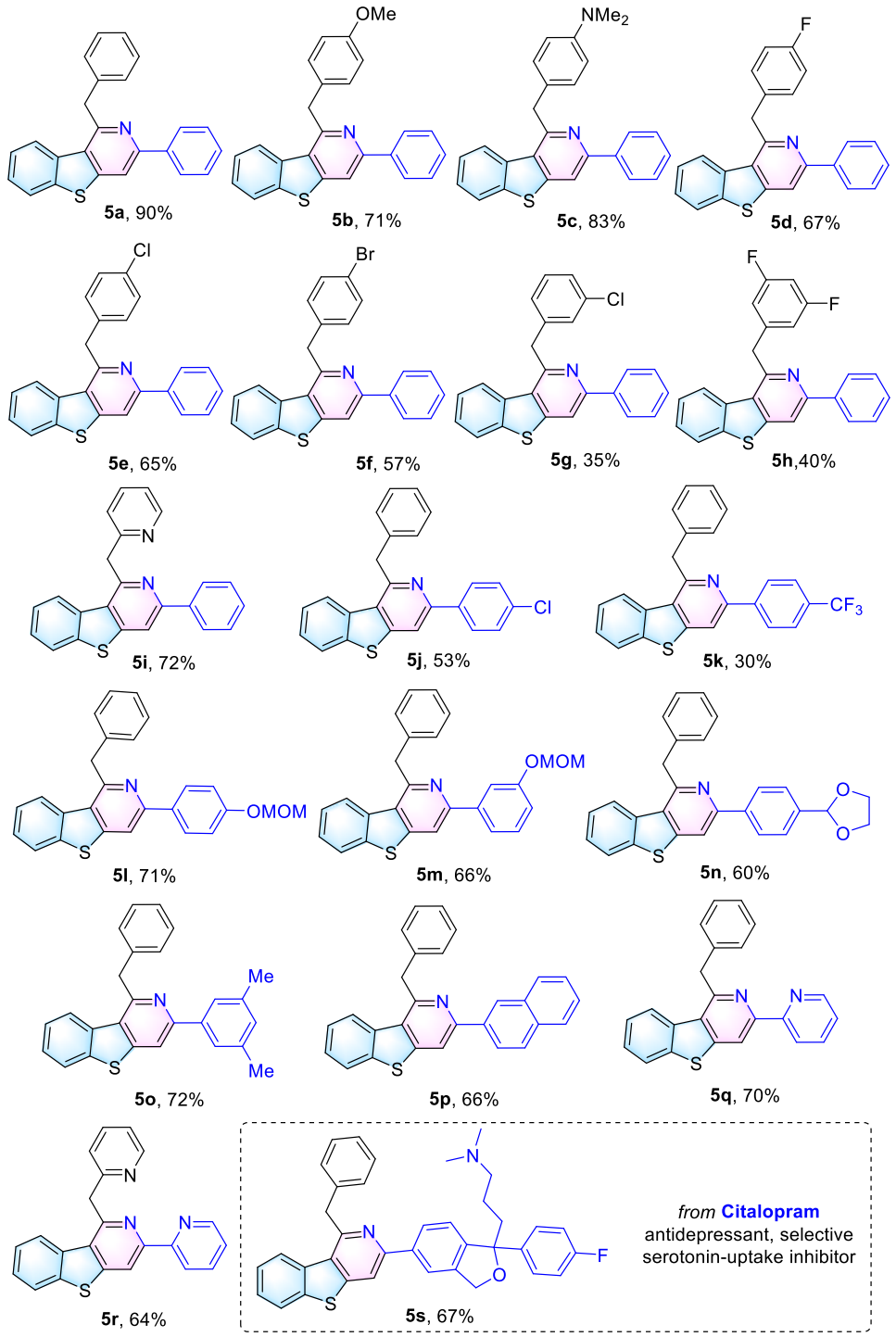




[a]Reaction conditions A: **1** (0.2 mmol), **2** (3 equiv), $LiN(SiMe_3)_2$ (2 equiv), *t*-BuOK (1.5 equiv), dry CPME (1 mL), at 120 °C for 24 h; isolated yields. [b]*t*-BuOK (2.0 equiv) without $LiN(SiMe_3)_2$.

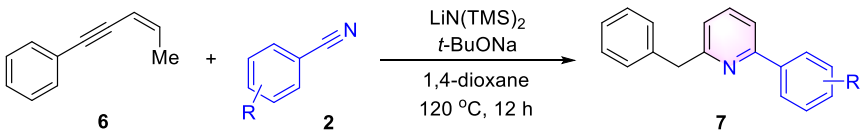
Table 3 Substrate scope of [4 + 2] cycloaddition of *o*-substituted heteroaryl alkynes with nitriles[a].



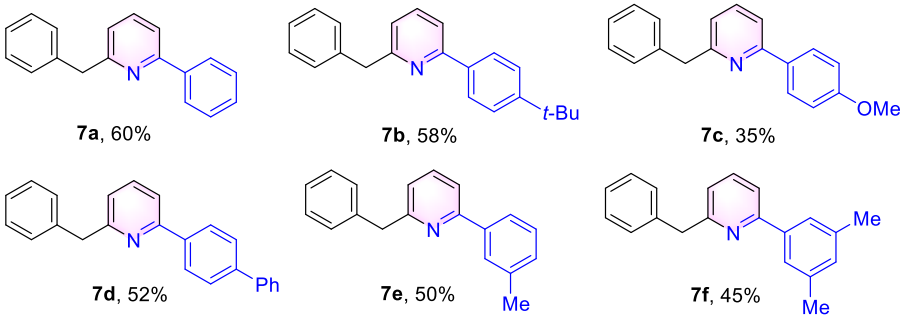


[a]Reaction conditions B: **4** (0.2 mmol), **2** (3 equiv), $LiN(SiMe_3)_2$ (2 equiv), *t*-BuOK (1.2 equiv), dry CPME (0.5 mL), at 120 °C for 24 h; isolated yields. OMOM = OCH_2OCH_3.

Table 4 Substrate scope of [4 + 2] cycloaddition of enyne with nitriles[a].



6 2 7



[a]Reaction conditions C: **6** (0.2 mmol), **2** (3 equiv), $LiN(SiMe_3)_2$ (2 equiv), *t*-BuONa (1.2 equiv), dry 1,4-dioxane (0.5 mL), at 120 °C for 12 h; isolated yields.