Supporting Information

Sc(OTf)$_3$-mediated 1,3-dipolar cycloaddition–ring cleavage–rearrangement: a highly stereoselective access to $\textit{Z-}\beta$-enaminonitriles

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Experimental

**General methods and materials.** Proton nuclear magnetic resonance spectra (1H NMR) and carbon nuclear magnetic resonance spectra (13C NMR) were recorded at 500 MHz and 125 MHz, respectively, using CDCl₃ as reference standard (δ 7.26 ppm) for 1H NMR and (δ 77.04 ppm) for 13C NMR. HRMS (ion trap) were recorded using APCI or ESI. Melting points are uncorrected. Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

The α, β-unsaturated nitriles 1b, 1c, 1d, 1f, 1h, 1i, 1j and the azides 2b, 2c, 2d, 2e, 2f, 2g, 2h, 2i, 2j, 2k, 2l, 2m, 2n, 2o were synthesized as previously reported in the literature.

**General experimental procedure for synthesis of Z-β-enaminonitriles 3.** A mixture of α, β-unsaturated nitriles (1.0 equiv, 1 mmol), azide (1.2 equiv, 1.2 mmol), Sc(OTf)₃ (0.05 equiv, 0.05 mmol), and 2 mL of toluene was refluxed at 110 °C for 12 h. The progress of the reaction was monitored by thin-layer chromatography. The mixture was then cooled and evaporated under reduced pressure. The target product 3 was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether.

*CAUTION: Sufficient care has to be exercised while handling organic azides because of their explosive nature.*
References


3aa-d

3ab-d