Supporting Information

Brønsted Acid-Catalyzed Meyer–Schuster Rearrangement for the Synthesis of α,β -Unsaturated Carbonyl Compounds

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1. General Experimental Methods

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker ADVANCE III 400 NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.26 for ^1H and δ 77.0 for ^{13}C). 1,2-Dichloroethane was distilled from CaCl_2 . Commercial available reagents were used without purification. All reactions involving air- and moisture-sensitive compounds were performed in oven- or flame dried glassware under nitrogen. Organic extracts were dried over anhydrous MgSO_4 and the solvents were removed on a rotary evaporator under reduced pressure. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230-400 mesh).

2. Preparation and characterization of compounds 1d and 2d

1) General procedure for the synthesis of propargyl alcohol (1d)

A solution of ethynylmagnesium bromide (2.4 mL) in THF (0.5 M, 1.2 mmol) was added dropwise over 5 min to a stirred solution of 4-methoxybenzaldehyde (136.15 mg, 1.0 mmol) in anhydrous THF (10 mL) at 0 °C under N_2 . The mixture was allowed to warm to room temperature and stirred for 1 h. After, saturated aqueous ammonium chloride solution (20 mL) were added, and the organic layer was then separated. The aqueous layer was extracted with ether (2 x 20 mL). The combine with organic layer were dried over MgSO_4 , filtered, and concentrated. The residue was purified by column chromatography ($n\text{-Hex/EtOAc} = 7/1$) to give 1-(4-methoxyphenyl)prop-2-yn-1-ol (**1d**, 150.30 mg, 92%) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 7.7$ Hz, 2H), 6.84 (d, $J = 7.7$ Hz, 2H), 5.32 (s, 1H), 3.73 (s, 3H), 3.39 (d, $J = 7.8$ Hz, 1H), 2.63 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 159.5, 132.5, 128.1, 113.9, 83.9, 77.5, 77.2, 76.9, 74.6, 63.7, 55.3.

This compound is known and the spectroscopic data match those reported.

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2) General procedure for the synthesis of α,β -unsaturated carbonyl compounds from aryl propargyl alcohols (**2d**)

To a suspension of *p*-toluenesulfonic acid (98%, Alfa Aesar, 28.35 mg, 30 mol%) in dry 1,2-dichloroethane (3.0 mL) was added 1-(4-methoxyphenyl)prop-2-yn-1-ol (**1d**, 81.09 mg, 0.5 mmol). The stirred solution was heated at 60 °C for 2 h. And then, the solvent was removed at reduced pressure and the residue was purified by column chromatography with *n*-Hex/EtOAc (5/1) as the eluent to give 4-methoxycinnamaldehyde (**2d**, 69.30 mg, 82%) as a yellow color oil. ¹H NMR (400 MHz, CDCl₃) δ 9.66 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 15.9 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.61 (dd, *J* = 7.7 Hz, *J* = 15.9 Hz, 1H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 193.6, 162.1, 152.6, 130.2, 126.6, 126.4, 114.4, 55.3.

All products reported in this article are known compounds, and their full data can be obtained from the reported literature.

3) NMR spectra of compounds 1d,