

Supporting Information

Divergent Synthesis of Oxazolidines and Morpholines via PhI(OAc)₂-Mediated Difunctionalization of Alkenes

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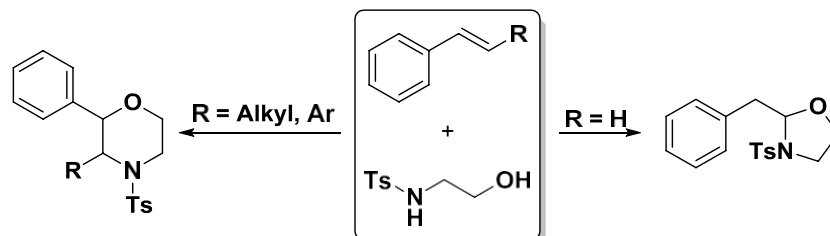
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General information

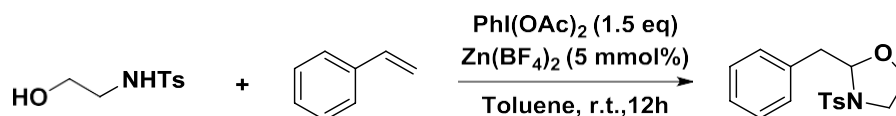
Unless otherwise noted, all commercially available reagents and solvents were used without further purification. All reactions were performed by standard Schlenk techniques in oven-dried reaction vessels under air. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction. Melting points were determined on a ShenGuang WRS-2 melting point apparatus. ^1H NMR, ^{13}C NMR, ^1H - ^1H NOE were recorded in CDCl_3 (internal standard: 7.26 ppm, ^1H ; 77.0 ppm, ^{13}C) using Bruker AV-300 (300 MHz) or AV-400 (400 MHz) NMR spectrometers. ^2H NMR were recorded in CHCl_3 using Bruker AV-300 (300 MHz) spectrometers. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. The mass data (LC-MS) and high resolution mass data (HRMS) were obtained using ESI technique. The *N*-tosyl amino alcohols¹ and β -substituted styrenes² were synthesized according to the reported procedure.

Procedure for difunctionalization of alkenes with *N*-tosyl amino alcohols



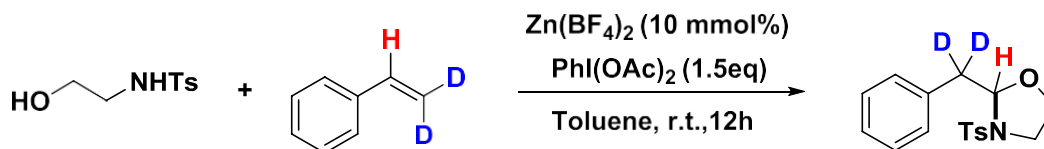
The *N*-tosyl aminoethanol (43.05 mg, 0.2 mmol) and styrene (31.25 mg, 0.3 mmol), $\text{PhI}(\text{OAc})_2$ (96.63 mg, 0.3 mmol), $\text{Zn}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ (4.78 mg, 0.02 mmol) were dissolved in toluene (1 mL) in an oven-dried Schlenk tube. This reaction mixture was stirred at room temperature. After completion of the reaction, the resulting mixture was concentrated and purified by column chromatography (hexane: ethylacetate = 10:1) to give the product **3aa** in 81% yield. Other oxazolidinone derivatives **3ba-3pa**, **3ab-3aj** were obtained by the same procedure. The morpholine derivatives **5aa-5oa**, **5ai** were afforded in toluene (0.3 M) by the same procedure. Besides, **5ae-5ah** were afforded in DCM (0.3 M) by the same procedure.

Procedure for gram scale reaction



The *N*-tosyl aminoethanol (0.86 g, 4 mmol) and $\text{PhI}(\text{OAc})_2$ (1.93 g, 6 mmol), $\text{Zn}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ (47.8 mg, 0.2 mmol) followed by styrene (0.63 g, 6 mmol) were dissolved in toluene (20 mL) in a 100 mL flask. This reaction mixture was stirred at room temperature. After completion of the reaction, the resulting mixture was concentrated and purified by column chromatography to give the product **3aa** in 87% yield.

Procedure for deuterium-labeling experiment



The *N*-tosyl aminoethanol (43.05 mg, 0.2 mmol) and styrene-β, β-d₂ (31.85 mg, 0.3 mmol), PhI(OAc)₂ (96.63 mg, 0.3 mmol), Zn(BF₄)₂·xH₂O (4.78 mg, 0.02 mmol) were dissolved in toluene (1 mL) in an oven-dried Schlenk tube. This reaction mixture was stirred at room temperature. After completion of the reaction, the resulting mixture was concentrated and purified by column chromatography to give the product [D₂]-**3aa** (48 mg, 75% yield).

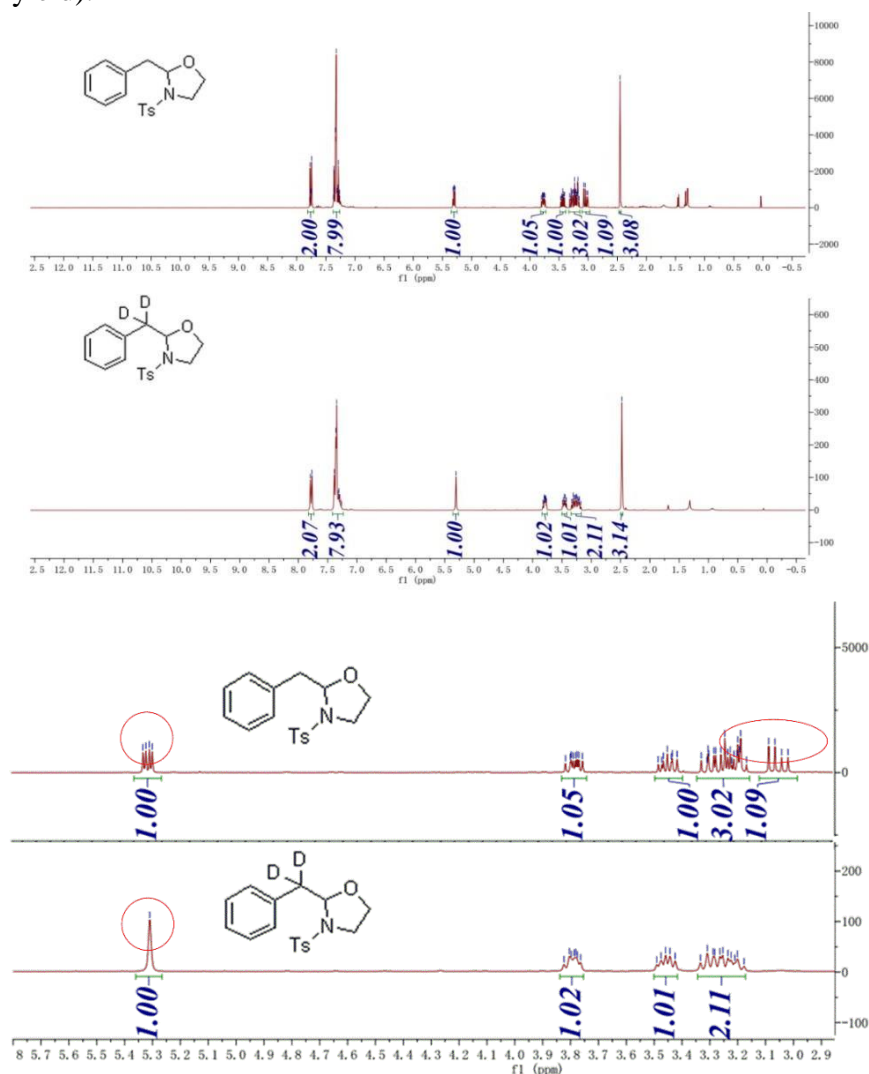


Figure S1. Comparison of ¹H NMR of **3aa** and **3aa-d₂**.

LC-MS Spectra of reaction mixture

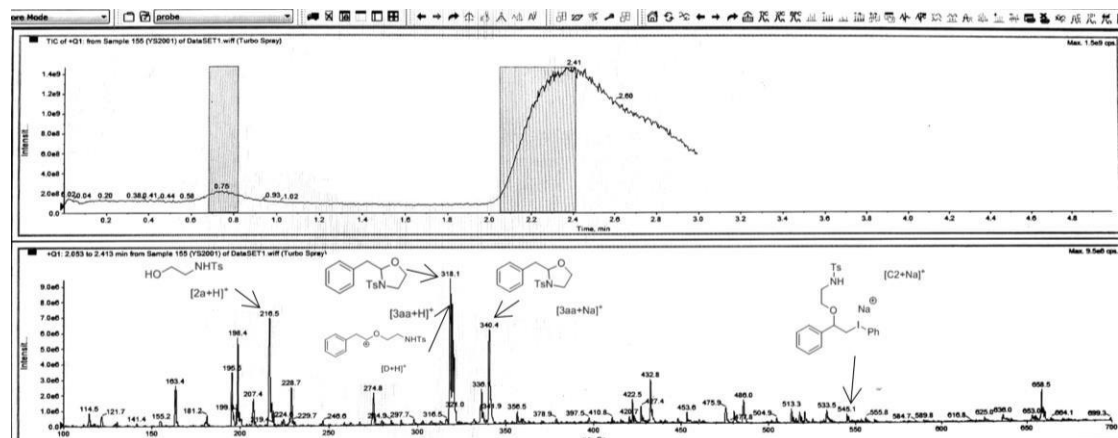


Figure S2. LC-MS of the reaction of **1a** with **2a**. Conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), $\text{PhI}(\text{OAc})_2$ (0.3 mmol), $\text{Zn}(\text{BF}_4)_2$ (0.02 mmol), room temperature, 60 min.

Reference

1. X. Dong, Y. Han, F. Yan, Q. Liu, P. Wang, K. Chen, Y. Li, Z. Zhao, Y. Dong and H. Liu, *Org. Lett.*, 2016, **18**, 3774.
2. L. Zheng, F. Gao, C. Yang, G.-L. Gao, Y. Zhao, Y. Gao and W. Xia, *Org. Lett.*, 2017, **19**, 5086.

