Supporting Information (SI)

Regioselective Ring Opening of Styrene Oxide Catalyzed by $\text{MoO}_2(\text{acac})_2$

Hongwei Yang, Liming Xu, Cuicui Luo, Chunxu Lu, Guangbin Cheng*

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing,
210094, P. R. China

Email: gcheng@mail.njust.edu.cn

Experimental Section

Most of the chemical reagents were purchased from Aldrich and used without further purification in most cases. Solvents were purchased and dried by a standard method. Analytical gas chromatography was performed on an Agilent model GC-6820 instrument equipped with a capillary column of HP-5 (5% phenyl methylpolysiloxane, 30 m x 0.32 mm x 0.25 μm) using nitrogen as carrier gas. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance III 500 MHz instrument. Chemical shifts are in ppm from tetramethylsilane (TMS). Analyses of C/H/N were performed with a Vario EL III Analyzer. Melting points were determined on an Electrothermal apparatus and uncorrected. All the major products were isolated by flash column chromatography on silica gel, with eluents of mixed solvents (ethyl acetate and petroleum ether). TLC was performed on a Merck Kieselgel F₂₅₄, 0.2 mm thick.

General procedure for the reaction of styrene oxide (1) with different nucleophiles 2

MoO₂(acac)₂ (32 mg, 0.1 mmol) was added to a magnetically stirred mixture of styrene oxide (**1**) (240 mg, 2.0 mmol) and the corresponding nucleophiles **2** (2.0 mmol) in CCl₄ (5 mL). After the feeding course, the mixture was heated to a set temperature and refluxed for a certain time (Tables 1 and 2). After removal of solvent under vacuum, the crude residue obtained was separated by column chromatography on silica gel to afford the corresponding product.

2-(2-nitrophenylamino)-2-phenylethanol (**3a**)^[10]

Red oil; Yield: 464 mg, 90%. IR (KBr) $\nu_{\max}$ (cm⁻¹): 3387 (ν O-H, N-H), 2877 (ν C-H, N-CH), 1417, 1348 (ν NO₂), 1506, 1569, 1620 (ν C=C aromatic ring); H NMR (500 MHz, CDCl₃) δ 7.48 (dt, J = 7.7, 3.9 Hz, 1H), 7.36 (dd, J = 8.2, 4.7 Hz, 5H), 7.34 – 7.27 (m, 1H), 7.20 (t, J = 8.1 Hz, 1H), 6.82 (dd, J = 8.2, 2.3 Hz, 1H), 5.30 (s, 1H), 4.55 (dd, J = 6.5, 4.0 Hz, 1H), 4.01 (dd, J = 11.2, 4.0 Hz, 1H), 3.83 (dd, J = 11.2, 6.5 Hz, 1H), 2.18 (s, 1H). ¹³C NMR (500 MHz, CDCl₃) δ 149.2, 148.3, 139.2, 129.8, 129.2, 128.1, 126.8, 119.6, 112.3, 107.9, 67.2, 59.9.

2-(3-nitrophenylamino)-2-phenylethanol (**3b**)^[11]

Red oil; Yield: 470 mg, 91%. ¹H NMR (500 MHz, CDCl₃) δ 8.77 (d, J = 5.5 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 7.38 (d, J = 4.3 Hz, 4H), 7.34 – 7.29 (m, 1H), 7.28 (t, J = 3.7 Hz, 1H), 6.68 – 6.58 (m, 2H), 4.74 (dd, J = 10.6, 6.0 Hz, 1H), 4.06 – 3.98 (m, 1H), 3.95 – 3.88 (m, 1H), 2.18 (s, 1H).

2-(4-nitrophenylamino)-2-phenylethanol (**3c**)^[12]

Red solid; Yield: 470 mg, 91%. mp 88-90 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.74 (d, J = 5.2 Hz, 1H), 8.20 – 8.17 (m, 1H), 7.39 – 7.35 (m, 5H), 7.33 – 7.29 (m, 1H), 7.29 –

7.27 (m, 1H), 6.64 (dd, $J = 3.2, 1.5$ Hz, 1H), 4.73 (dt, $J = 10.6, 5.3$ Hz, 1H), 4.04 (dd, $J = 11.2, 4.4$ Hz, 1H), 3.94 (dd, $J = 11.2, 6.2$ Hz, 1H), 2.17 (s, 1H).

2-(p-toluidino)-2-phenylethanol (**3d**)^[13]

Yellow solid; yield: 413 mg, 91%. mp 59-61 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.31 (m, 4H), 7.27 – 7.25 (m, 1H), 7.00 – 6.84 (m, 2H), 6.53 – 6.48 (m, 2H), 4.52 – 4.47 (m, 1H), 3.94 (dd, $J = 11.0, 4.1$ Hz, 1H), 3.77 – 3.71 (m, 1H), 2.20 (d, $J = 2.9$ Hz, 3H).

2-(4-methoxyphenylamino)-2-phenylethanol (**3e**)^[14]

White solid; yield: 457 mg, 94%. mp 22-24 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.32 (m, 4H), 7.28 – 7.25 (m, 1H), 6.70 (t, $J = 6.1$ Hz, 2H), 6.55 (d, $J = 8.9$ Hz, 2H), 4.45 (dd, $J = 7.4, 4.2$ Hz, 1H), 3.93 (dd, $J = 11.1, 4.2$ Hz, 1H), 3.73 (dd, $J = 11.1, 7.5$ Hz, 1H), 3.70 (s, 3H).

2-(3-chlorophenylamino)-2-phenylethanol (**3f**)^[15]

White solid; yield: 446 mg, 90%. mp 52-53 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.34 (m, 3H), 7.33 – 7.28 (m, 1H), 7.27 (m, 1H), 7.00 (dd, $J = 10.4, 5.7$ Hz, 1H), 6.64 (dd, $J = 7.8, 1.2$ Hz, 1H), 6.55 (t, $J = 2.1$ Hz, 1H), 6.43 (dd, $J = 8.1, 1.9$ Hz, 1H), 4.48 (dd, $J = 6.6, 4.2$ Hz, 1H), 3.96 (dd, $J = 11.2, 4.1$ Hz, 1H), 3.78 (dd, $J = 11.1, 6.6$ Hz, 1H), 1.69 (s, 2H).

2-phenyl-2-(phenylamino)ethanol (**3g**)^[16]

Yellow solid; Yield: 405 mg, 95%. mp 134-136 °C; ¹H NMR (500 MHz, CDCl₃) δ

7.41-7.35(m, 4H), 7.30-7.27 (m, 1H), 7.13(t, 2H), 6.71(t, 1H), 6.60(d, 2H), 5.30 (s,

1H), 4.51(m, 1H), 3.96-3.93(dd, 1H), 3.78-3.74(dd, 1H).

2-phenoxy-2-phenylethanol (**3h**)^[17]

Yellow solid; Yield: 373 mg, 87%. mp 77-80 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.37

(dt, *J* = 15.0, 7.3 Hz, 4H), 7.33 – 7.29 (m, 1H), 7.21 (t, *J* = 7.9 Hz, 2H), 6.97 – 6.86

(m, 3H), 5.28 (dd, *J* = 8.2, 3.5 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.87 – 3.80 (m, 1H), 2.34

(d, *J* = 5.5 Hz, 1H).

2-(4-phenylphenol)-2phenylethanol (**3i**)

White solid; Yield: 344 mg, 77%. mp 126-128 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.53

– 7.49 (m, 2H), 7.47 – 7.43 (m, 3H), 7.42 (dd, *J* = 4.2, 3.2 Hz, 3H), 7.40 – 7.37 (m,

2H), 7.35 – 7.28 (m, 2H), 7.01 – 6.91 (m, 2H), 5.34 (dd, *J* = 8.3, 3.5 Hz, 1H), 3.97 (dd,

J = 12.0, 8.3 Hz, 1H), 3.90 – 3.80 (m, 1H), 2.29 (s, 1H). ¹³C NMR (126 MHz, CDCl₃)

δ 156.34 (s), 139.65 (s), 136.74 (s), 133.42 (s), 127.86 (s), 127.72 (s), 127.28 (s),

127.15 (s), 125.74 (s), 125.32 (s), 115.17 (s), 80.28(s), 76.31-75.80 (m), 66.64 (s).

Anal. Calcd (%) for C₂₀H₁₈O₂ (290.14): C 82.72, H 6.25, O 11.03; Found :C 83.03,

H 6.12, O 11.95.

2-(4-methoxyphenyl)-2-phenylethanol (**3j**)^[18]

Colorless oil; Yield: 275mg, 63%. ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.31(m, 3H), 7.27-7.23(m, 2H), 7.20-7.18(m, 2H), 6.88-6.86(m, 2H), 4.16-4.13(m, 2H), 3.79(s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 156.4, 140.8, 133.2, 128.7, 128.0, 127.3, 125.9, 114.1, 66.7, 55.6, 53.2.

^1H NMR and ^{13}C NMR spectra for selected product

Figure S1. ^1H NMR spectra (500 MHz) of **1**

Figure S2. ¹H NMR spectra (500 MHz) of **3a**

Figure S3. ¹³C NMR spectra (500 MHz) of **3a**

Figure S4. ^1H NMR spectra (500 MHz) of **3b**

Figure S5. ^1H NMR spectra (500 MHz) of **3c**

Figure S6. ¹H NMR spectra (500 MHz) of **3d**

Figure S7. ¹H NMR spectra (500 MHz) of **3e**

Figure S8. ¹H NMR spectra (500 MHz) of 3f

Figure S9. ¹H NMR spectra (500 MHz) of 3g

Figure S10. ^1H NMR spectra (500 MHz) of **3h**

Figure S11. ^1H NMR spectra (500 MHz) of **3i**

Figure S12. ^{13}C NMR spectra (500 MHz) of **3i**