Supporting Information

Synthesis of α -nitro ketoximes from styrenes and *tert*-butyl nitrite

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General Consideration

All solvents and reagents were purchased from the suppliers and used directly. ^1H NMR and ^{13}C NMR were recorded in CDCl_3 or d_6 -DMSO at room temperature on the spectrometer (400 MHz ^1H , 100 MHz ^{13}C). The chemical-shifts scale is based on internal TMS. Data for ^1H NMR and ^{13}C NMR are reported as follows: chemical shift (δppm), multiplicity, integration, and coupling constant (Hz). All reactions were carried out in the air atmosphere.

Experimental Section:

To a 25 mL round bottom flask charged with a magnetic stir-bar was added H_2O (0.5 mL), Styrene (0.5 mmol), *tert*-butyl nitrite (1 mmol) and DMSO (1 mL). Then the reaction mixture was stirred at room temperature for 12h. After the reaction was finished, the mixture was diluted with CH_2Cl_2 , washed with brine and extracted with CH_2Cl_2 . The combined organic extracts were dried over Na_2SO_4 , concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate=5:1) to afford the desired product. The *Z/E* ratios were determined from the signals of CH_2 groups connected to the nitro group.

Characterization Data for Selected Compounds

2-Nitro-1-phenyl-ethanone oxime (3a)

(*Z/E* mixture ratios=20:1)

Yield: 84%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.01 (s, 1H), 7.55-7.53 (m, 2H), 7.38-7.33 (m, 3H), 5.57 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.6, 132.8, 130.5, 129.0, 126.1, 68.4; HRMS (ESI)

calcd for $C_8H_8N_2O_3K$ (M+K)⁺ 219.0172, found 219.0165.

2-Nitro-1-p-tolyl-ethanone oxime (3b)

(*Z/E* mixture ratios=13.4:1)

Yield: 64%; Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 9.26 (s, 1H), 7.42 (d, *J*=8.0 Hz, 2H), 7.16 (d,

J=8.0 Hz, 2H), 5.56 (s, 2H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.4, 140.7, 130.1, 129.7,

126.0, 68.3, 21.3; HRMS (ESI) calcd for $C_9H_{10}N_2O_3K$ (M+K)⁺ 233.0329, found 233.0324.

1-(2,5-Dimethyl-phenyl)-2-nitro-ethanone oxime (3c)

(*Z/E* mixture ratios= 7.0:1)

Yield: 46%; Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 9.10 (s, 0.89H), 8.46 (s, 0.11H), 7.18 (s,

0.24H), 7.06 (s, 1.76H), 7.03 (s, 0.89H), 6.85 (s, 0.11H), 5.44 (s, 1.75H), 4.79 (s, 0.25H), 2.25 (ss,

5.49H), 2.13 (ss, 0.51H); ¹³C NMR (100 MHz, CDCl₃) δ 149.6, 135.8, 133.4, 132.3, 131.0, 130.6,

129.1, 71.2, 23.6, 20.8, 19.4; HRMS (ESI) calcd for $C_{10}H_{12}N_2O_3K$ (M+K)⁺ 247.0485, found 247.0485.

1-(4-tert-Butyl-phenyl)-2-nitro-ethanone oxime (3d)

(*Z/E* mixture ratios>20:1)

Yield: 82%; Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 9.28 (s, 1H), 7.47 (d, *J*=8.4 Hz, 2H), 7.37 (d,

J=8.4 Hz, 2H), 5.57 (s, 2H), 1.25 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 153.9, 148.3, 130.0, 126.0,

125.7, 68.4, 34.8, 31.1; HRMS (ESI) calcd for $C_{12}H_{16}N_2O_3K$ (M+K)⁺ 275.0798, found 275.0794.

1-(4-Chloromethyl-phenyl)-2-nitro-ethanone oxime (3e)

(*Z/E* mixture ratios>20:1)

Yield: 73%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.23 (s, 1H), 7.53 (d, $J=8.0$ Hz, 2H), 7.37 (d, $J=8.0$ Hz, 2H), 5.56 (s, 2H), 4.51 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 139.7, 132.8, 129.2, 126.5, 68.3, 45.4; HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{ClN}_2\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 251.0199, found 251.0198.

1-(4-Methoxy-phenyl)-2-nitro-ethanone oxime (3f)

(*Z/E* mixture ratios=12.5:1)

Yield: 76%; Yellow oil; ^1H NMR (400 MHz, d_6 -DMSO) δ 12.05 (s, 1H), 7.69 (d, $J=8.8$ Hz, 2H), 7.00 (d, $J=8.8$ Hz, 2H), 5.82 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, d_6 -DMSO) δ 160.3, 147.0, 127.4, 126.5, 114.2, 68.9, 55.3; HRMS (ESI) calcd for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_4\text{K}$ ($\text{M}+\text{K}$) $^+$ 249.0278, found 249.0270.

1-(2-Methoxy-phenyl)-2-nitro-ethanone oxime (3g)

(*Z/E* mixture ratios=4.9:1)

Yield: 59%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.55 (s, 0.83H), 8.90 (s, 0.17H), 7.42-7.40 (m, 1.00H), 7.36-7.30 (m, 1.00H), 6.95-6.92 (m, 1.00H), 6.90-6.84 (m, 1.00H), 5.54 (s, 1.66H), 5.32 (s, 0.34H), 3.74 (s, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.2, 155.8, 148.8, 148.2, 131.7, 131.5, 131.0, 130.1, 122.3, 121.2, 120.6, 111.1, 70.0, 55.4; HRMS (ESI) calcd for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_4\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 233.0538, found 233.0548.

1-(4-Ethoxy-phenyl)-2-nitro-ethanone oxime (3h)

(*Z/E* mixture ratios>20:1)

Yield: 71%; Yellow oil; ^1H NMR (400 MHz, d_6 -DMSO) δ 12.05 (s, 1H), 7.69 (d, $J=8.8$ Hz, 2H), 7.00 (d, $J=8.8$ Hz, 2H), 5.83 (s, 2H), 4.11-4.05 (m, 2H), 1.36 (t, $J=6.8$ Hz, 3H); ^{13}C NMR (100 MHz, d_6 -DMSO) δ 159.6, 146.9, 127.3, 126.3, 114.6, 68.8, 63.2, 14.6; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4\text{K}$ ($\text{M}+\text{K}$) $^+$ 263.0434, found 263.0431.

1-(4-Acetic acid phenyl ester)-2-nitro-ethanone oxime (3i)

(*Z/E* mixture ratios>20:1)

Yield: 61%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.11 (s, 1H), 7.56 (d, $J=8.4$ Hz, 2H), 7.08 (d, $J=8.4$ Hz, 2H), 5.52 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 152.0, 147.4, 130.8, 127.4, 122.2, 88.2, 21.1; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_5\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 261.0487, found 261.0464.

1-(4-Cyano-phenyl)-2-nitro-ethanone oxime (3j)

(*Z/E* mixture ratios>20:1)

Yield: 64%; Yellow oil; ^1H NMR (400 MHz, d_6 -DMSO) δ 12.76 (s, 1H), 7.94-7.88 (m, 4H), 5.87 (s, 2H); ^{13}C NMR (100 MHz, d_6 -DMSO) δ 146.7, 138.5, 132.7, 126.6, 118.6, 111.9, 68.5; HRMS (ESI) calcd for $\text{C}_9\text{H}_7\text{N}_3\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 228.0385, found 228.0377.

2-Nitro-1-(4-nitro-phenyl)-ethanone oxime (3k)

(*Z/E* mixture ratios>20:1)

Yield: 51%; Yellow oil; ^1H NMR (400 MHz, d_6 -DMSO) δ 12.90 (s, 1H), 8.31 (d, $J=8.8$ Hz, 2H), 8.04 (d, $J=8.8$ Hz, 2H), 5.94 (s, 2H); ^{13}C NMR (100 MHz, d_6 -DMSO) δ 147.8, 146.5, 140.3, 127.0, 123.9, 68.5; HRMS (ESI) calcd for $\text{C}_8\text{H}_7\text{N}_3\text{O}_5\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 248.0283, found 248.0289.

1-(4-Chloro-phenyl)-2-nitro-ethanone oxime (3l)

(*Z/E* mixture ratios>20:1)

Yield: 69%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.20 (s, 1H), 7.47 (d, $J=8.8$ Hz, 2H), 7.32 (d, $J=8.8$ Hz, 2H), 5.54 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.7, 136.6, 131.3, 129.3, 127.4, 68.2; HRMS (ESI) calcd for $\text{C}_8\text{H}_7\text{ClN}_2\text{O}_3\text{K}$ ($\text{M}+\text{K}$) $^+$ 252.9782, found. 252.9780.

1-(3-Chloro-phenyl)-2-nitro-ethanone oxime (3m)

(*Z/E* mixture ratios=9.5:1)

Yield: 50%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.10 (s, 0.90H), 8.75 (s, 0.10H), 7.55 (s, 1.00H), 7.41-7.26 (m, 3.00H), 5.54 (s, 1.81H), 5.31 (s, 0.19H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.5, 135.1, 134.6, 130.4, 130.3, 126.3, 124.3, 68.1; HRMS (ESI) calcd for $\text{C}_8\text{H}_7\text{ClN}_2\text{O}_3\text{K}$ ($\text{M}+\text{K}$) $^+$ 252.9782, found. 252.9780.

1-(2-Chloro-phenyl)-2-nitro-ethanone oxime (3n)

(*Z/E* mixture ratios=1.7:1)

Yield: 40%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.28 (s, 0.66H), 8.57 (s, 0.34H), 7.44-7.26 (m, 4.00H), 5.53 (s, 1.27H), 5.34 (s, 0.73H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.8, 147.9, 132.5, 132.4, 131.6, 131.4, 131.2, 130.6, 129.9, 129.7, 129.5, 127.4, 127.0, 70.1; HRMS (ESI) calcd for $\text{C}_8\text{H}_7\text{ClN}_2\text{O}_3\text{K}$ ($\text{M}+\text{K}$) $^+$ 252.9782, found.252.9780.

1-(4-Bromo-phenyl)-2-nitro-ethanone oxime (3o)

(*Z/E* mixture ratios>20:1)

Yield: 62%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.13 (s, 1H), 7.48 (d, $J=8.8$ Hz, 2H), 7.40 (d, $J=8.8$ Hz, 2H), 5.54 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 132.2, 131.7, 127.6, 125.0, 68.1; HRMS (ESI) calcd for $\text{C}_8\text{H}_7\text{BrN}_2\text{O}_3\text{K}$ ($\text{M}+\text{K}$) $^+$ 296.9277, found 296.9273.

1-(3-Bromo-phenyl)-2-nitro-ethanone oxime (3p)

(*Z/E* mixture ratios>20:1)

Yield: 52%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.95 (s, 1H), 7.72 (s, 1H), 7.51-7.44 (m, 2H), 7.25-7.18 (m, 1H), 5.54 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 134.8, 133.3, 130.5, 129.2, 124.7, 123.1, 68.1; HRMS (ESI) calcd for $\text{C}_8\text{H}_7\text{BrN}_2\text{O}_3\text{K}$ ($\text{M}+\text{K}$) $^+$ 296.9277, found 296.9273.

1-(4-Methoxy-phenyl)-2-nitro-propan-1-one oxime (3q)

(*Z/E* mixture ratios=1.8:1)

Yield: 75%; Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 9.56 (s, 0.62H), 9.08 (s, 0.38H), 7.34-7.28 (m, 2.00H), 6.87-6.81 (m, 2.00H), 5.84-5.79 (m, 0.64H), 5.50-5.47 (m, 0.36H), 3.73 (s, 3.00H), 1.75 (d, $J=6.8$ Hz, 1.91H), 1.67 (d, $J=6.8$ Hz, 1.09H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.9, 160.5, 153.3, 152.3, 129.7, 128.3, 124.7, 121.7, 114.2, 113.9, 85.0, 77.5, 55.3, 55.2, 16.8, 15.3; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4\text{K}$ ($\text{M}+\text{K}$) $^+$ 263.0434, found. 263.0432.

2-Nitro-1-phenyl-ethanone oxime

2-Nitro-1-p-tolyl-ethanone oxime

1-(2,5-Dimethyl-phenyl)-2-nitro-ethanone oxime

1-(4-tert-Butyl-phenyl)-2-nitro-ethanone oxime

1-(4-Chloromethyl-phenyl)-2-nitro-ethanone oxime

1-(4-Methoxy-phenyl)-2-nitro-ethanone oxime

1-(2-Methoxy-phenyl)-2-nitro-ethanone oxime

1-(4-Ethoxy-phenyl)-2-nitro-ethanone oxime

1-(4-Acetic acid phenyl ester)-2-nitro-ethanone oxime

1-(4-Cyano-phenyl)-2-nitro-ethanone oxime

2-Nitro-1-(4-nitro-phenyl)-ethanone oxime

1-(4-Chloro-phenyl)-2-nitro-ethanone oxime

1-(3-Chloro-phenyl)-2-nitro-ethanone oxime

1-(2-Chloro-phenyl)-2-nitro-ethanone oxime

1-(4-Bromo-phenyl)-2-nitro-ethanone oxime

1-(3-Bromo-phenyl)-2-nitro-ethanone oxime

1-(4-Methoxy-phenyl)-2-nitro-propan-1-one oxime