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Supporting Information

Synthesis of Oxazolines via Cascade Reaction between

Azaoxyallyl Cations and 1, 2-Benzisoxazoles

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Table of Contents

General Information	.S2
General Procedures for the Preparation of α - Halohydroxamates	
General Procedures for 1, 2-benzisoxazoles	
Preparation of [3+2] Cyclization Reactions	.S4
X-ray Crystallography Data of 3ao (CCDC 1900697)	S5
Copies of 1H NMR and 13C NMR spectra of the Titled Compounds	S6

General Information

Reagents and Solvents: All solvents were purified and dried according to standard methods. PE refers to petroleum ether (b.p. 60 – 90 $^{\circ}$ C) and EA refers to ethyl acetate.

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure and conducted by eluting with PE/EA, which are listed as volume/volume ratios.

Data collection: Melting point (m.p.) was measured on a microscopic melting point apparatus. ¹H NMR and ¹³C NMR spectra were collected on BRUKER AV-300 (300MHz) or BRUKER AV-400 (400MHz) spectrometer using CDCl₃ as solvent. Chemical shifts of ¹H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard (CDCl₃, δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, brs = broad singlet, m= multiplet), coupling constant (Hz), and integration. Chemical shifts of ¹³C NMR were reported in ppm with the solvent as the internal standard (CDCl₃, δ = 77.0 ppm). High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer electron spray ionization (ESI) as the ion source. Unless otherwise indicated, all other reagents and solvents were obtained from commercial suppliers and used without further purification. Absorption measurements were performed either using а Shimadzu UV-3600 Plus UV-Vis spectrophotometer. Emission measurements were performed using a Horiba,Ltd Fluoro Max-4 photoluminescence spectrometer.

General Procedures for the Preparation of α- Halohydroxamates¹



To a suspension of the *O*-alkyloxyamine hydrochloride and triethylamine in DCM (0.25 M) was added dropwise the alpha-haloacid halide at 0 °C. The reaction mixture was stirred at this temperature until complete consumption of starting material (detected by TLC). The mixture was warmed to room temperature and quenched with water. The organic phase was washed with water (×3), then washed with brine (×1), dried over sodium sulfate, filtered and evaporated. Purification *via* a flash column chromatography (PE/EA=8/1) provided the α -halohydroxamates.

General Procedures for 1, 2-benzisoxazoles²



A mixture of Ph_3P (1.5 eq.) and DDQ (1.5 eq.) in dry DCM (5.0 mL) was stirred at room temperature for 1 min. Substituted salicylaldoximes (1.0 mmol) were then added. The green color of the reaction mixture changed to brown after 1 min. TLC monitoring showed completion of the reaction. The solvent was evaporated. Column chromatography of the crude mixture on silica gel using (PE/EA=3/1) as eluent gave the desired products.

^{1.} C. S. Jeffrey, K. L. Barnes, J. A. Eickhoff and C. R. Carson, J. Am. Chem. Soc., 2011, 133, 7688-7691.

2. N. Iranpoor, H. Firouzabadi and N. Nowrouzi, *Tetrahedron Lett.*, 2006, **47**, 8247-8250.

Preparation of [3+2] Cyclization Reactions



To a 10 mL round-bottom flask was sequentially added α -halohydroxamate **1** (0.2 mmol, 1.0 eq.), Na₂CO₃ (0.40 mmol, 2.0 eq.), substituted 1, 2-benzisoxazoles **2** (0.3 mmol, 1.5 eq.) and HFIP (1.0 mL). The reaction mixture was stirred at room temperature for 3 hours. Upon completion of the reaction (monitored by TLC), the reaction mixture was diluted with EA. The crude material was then filtered through celite and washed with EA. The filtrate was concentrated under reduced pressure and purified by flash column chromatography on silica gel (PE/EA = 20/1) to afford the pure product.

X-ray Crystallography Data of 3ao (CCDC 1900697)



Empirical formula	$C_{18}H_{16}Br_2N_2O_3$
Formula weight	468.15
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P-1
a/Å	5.5740(11)
b/Å	12.623(3)
c/Å	14.179(3)
α/°	110.91(3)
β/°	95.03(3)
γ/°	95.13(3)
Volume	920.5(4)
Z	2
Dx, g/cm ³	1.689
F(000)	464.0
Crystal size/mm ³	$0.200 \times 0.100 \times 0.100$
Mu/mm ⁻¹	4.422
T _{min} , T _{max}	0.594, 0.643
Radiation	ΜοΚ \α (λ = 0.71073)
Reflections collected	3762
h,k,l(max)	6,15,17
Data/restraints/parameters	3384/0/214
Final R indexes [I>=2σ (I)]	$R_1 = 0.1018$, $wR_2 = 0.2194$
Final R indexes [all data]	$R_1 = 0.2092$, $wR_2 = 0.2571$
S	1.216
N _{par}	214

Copies of 1H NMR and 13C NMR spectra of the Titled Compounds

(Z)-2-(2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime

BnO 54.0 mg, 87% yield, $R_f = 0.32$ (PE/EA = 10/1); white solid, m.p. 72.8 – 73.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.15 (s, 1H), 7.79 (dd, J = 7.9, 1.7 Hz, 1H), 7.47 – 7.29 (m, 6H), 7.03 (dd, J = 8.4, 1.2 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 5.12 (s, 2H), 1.52 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) 160.4, 159.9, 157.7, 137.2, 134.3, 128.5, 128.4, 128.4, 128.1, 119.2, 117.0, 109.0, 77.1, 67.3, 28.0; HRMS (ESI) calcd for C₁₈H₁₈N₂O₃⁺ [M+H]⁺: m/z = 311.1390, found 311.1391.

(Z)-2-(3-bromo-2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime



(Z)-2-(2-hydroxy-3-methoxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime

BnQ

0

OH

3ac

٦N

53.0 mg, 78% yield, $R_f = 0.39$ (PE/EA = 10/1); white solid, m.p. 84.2 – 85.6 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.38 (s, 1H), 7.47 – 7.22 (m, 6H), 7.01 (dd, J = 8.1, 1.4 Hz, 1H), 6.85 (td, J = 8.0, 0.9 Hz, 1H), 5.11 (s, 2H), 3.90 (s, 3H), 1.52 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 160.6, 157.6, 150.2, 148.3, 137.2, 128.4, 128.4, 128.1, 119.9, 118.8, 115.8, 109.3, 77.0, 67.3, 56.2, 28.0; HRMS (ESI) calcd for C₁₉H₂₀N₂O₄⁺ [M+H]⁺: m/z= 341.1496, found 341.1497.

(Z)-2-(3-(tert-butyl)-2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime



found 367.2012.

(Z)-2-(4-fluoro-2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime

BnO N 56.0 mg, 85% yield, $R_f = 0.44$ (PE/EA = 10/1); white solid, m.p. 83.5 - 84.4 °C; ¹H NMR (300 MHz, CDCl₃) δ , ppm 11.43 (s, 1H), 7.76 (dd, J = 8.8, 6.4 Hz, 1H), 7.47 - 7.25 (m, 5H), 6.72 (dd, J = 10.4, 2.5 Hz, 1H), 6.63 (ddd, J = 8.8, 8.1, 2.5 Hz, 1H), 5.11 (s, 2H), 1.51 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 166.4 (d, J = 252.0 Hz), 162.0 (d, J = 13.0 Hz), 159.9, 157.4, 137.1, 130.3 (d, J = 11.0 Hz), 128.5, 128.4, 128.1, 107.2 (d, J = 23.0 Hz), 105.8 (d, J = 3.0 Hz),

104.3 (d, *J* = 24.0 Hz), 77.1, 67.2, 28.0; HRMS (ESI) calcd for C₁₈H₁₇FN₂O₃⁺ [M+H]⁺: *m/z* = 329.1296, found 329.1291.

(Z)-2-(4-chloro-2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime

BnO, N 57.0 mg, 83% yield, $R_f = 0.50$ (PE/EA = 10/1); white solid, m.p. 101.6 - 102.3 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.30 (s, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.47 - 7.25 (m, 5H), 7.04 (d, J = 2.0 Hz, 1H), 6.89 (dd, J = 8.5, 2.0 Hz, 1H), 5.11 (s, 2H), 1.51 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) 160.5, 159.9, 157.2, 140.2, 137.0, 129.4, 128.5, 128.4, 128.1, 119.8, 117.4, 107.7, 77.2, 67.3, 28.0; HRMS (ESI) calcd for C₁₈H₁₇ClN₂O₃⁺[M+H]⁺: m/z = 345.1000, found 345.1003.

(Z)-2-(4-bromo-2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime



70.0 mg, 90% yield, $R_f = 0.50$ (PE/EA = 10/1); white solid, m.p. 99.8 – 100.7 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.20 (s, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.39 – 7.18 (m, 5H), 7.13 (d, J = 1.8 Hz, 1H), 6.96 (dd, J = 8.5, 1.8 Hz, 1H), 5.02 (s, 2H), 1.43 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) 160.4, 160.0, 157.2, 137.0, 129.4, 128.5, 128.5, 128.4, 128.1, 122.7, 120.4, 108.1, 77.2, 67.3, 28.0; HRMS (ESI) calcd for C₁₈H₁₇BrN₂O₃⁺ [M+H]⁺: m/z = 389.0495, found 389.0491.

(Z)-2-(2-hydroxy-4-methylphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime

52.5 mg, 81% yield, $R_f = 0.42$ (PE/EA = 10/1); white solid, m.p. 70.3 - 71.2 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.05 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.47 - 7.19 (m, 5H), 6.83 (s, 1H), 6.71 (dd, J = 8.0, 1.5 Hz, 1H), 5.11 (s, 2H), 2.33 (s, 3H), 1.50 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) 160.4, 159.9, 157.9, 145.5, 137.2, 128.5, 128.4, 128.2, 128.1, 120.4, 117.3, 106.5, 77.0, 67.18, 28.1, 22.0; HRMS (ESI) **3ah**

S7

calcd for $C_{19}H_{20}N_2O_3^+$ [M+H]⁺: m/z = 325.1547, found 325.1545.

(Z)-2-(2-hydroxy-4-methoxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime

BnQ N O O H 3ai

54.4 mg, 80% yield, $R_f = 0.40$ (PE/EA = 10/1); white solid, m.p. 106.1 – 107.2 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.28 (s, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.47 – 7.25 (m, 5H), 6.52 (d, J = 2.4 Hz, 1H), 6.46 (dd, J = 8.8, 2.4 Hz, 1H), 5.11 (s, 2H), 3.81 (s, 3H), 1.50 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 164.6, 161.9, 160.2, 158.0, 137.2, 129.6, 128.4, 128.4, 128.0, 107.1, 102.2, 100.9, 77.00, 67.0, 55.5, 28.1; HRMS (ESI) calcd for C₁₉H₂₀N₂O₄⁺[M+H]⁺: m/z= 341.1496,

found 341.1493.

(Z)-2-(5-chloro-2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime



(Z)-2-(5-bromo-2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime



(Z)-2-(2-hydroxy-5-methylphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime



Br

53.8 mg, 83% yield, $R_f = 0.39$ (PE/EA = 10/1); white solid, m.p. 104.3 – 105.3 °C; ¹H NMR (300 MHz, CDCl₃) δ 10.92 (s, 1H), 7.57 (d, J = 2.4 Hz, 1H), 7.51 – 7.26 (m, 5H), 7.21 (dd, J = 8.4, 2.2 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 5.13 (s, 2H), 2.28 (s, 3H), 1.51 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 160.4, 157.9, 157.8, 137.3, 135.3, 128.5, 128.4, 128.3, 128.1, 128.1, 116.8, 108.6, 77.3, 67.3, 28.0, 20.3; HRMS (ESI) calcd for C₁₉H₂₀N₂O₃⁺ [M+H]⁺: m/z = 325.1547, found 325.1542.

(Z)-2-(2-hydroxy-6-methoxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime

BnQ N N O H 3am

52.4 mg, 77% yield, $R_f = 0.51$ (PE/EA = 10/1); white solid, m.p. 87.8 - 88.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 12.33 (s, 0H), 7.49 – 7.21 (m, 6H), 6.64 (dd, J = 8.5, 1.1 Hz, 1H), 6.40 (d, J = 8.4 Hz, 1H), 5.13 (s, 2H), 3.85 (s, 3H), 1.51 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 162.2, 161.3, 159.9, 158.5, 137.4, 134.2, 128.3, 128.1, 127.8, 109.9, 102.0, 99.4, 76.8, 65.0, 56.2, 28.0; HRMS (ESI) calcd for C₁₉H₂₀N₂O₄⁺ [M+H]⁺: m/z = 341.1496, found 341.1493.

(Z)-2-(1-hydroxynaphthalen-2-yl)-4, 4-dimethyloxazol-5(4H)-one O-benzyl oxime

BnO N $33.7 - 134.9 \ ^{\circ}C; \ ^{1}H \ NMR \ (300 \ MHz, \ CDCl_3) \ \delta \ 13.24 \ (s, \ 1H), \ 8.83 \ (dd, J = 8.8, \ 1.0 \ Hz, \ 1H), \ 7.86 \ (d, J = 9.0 \ Hz, \ 1H), \ 7.75 \ (dd, J = 8.5, \ 1.1 \ Hz, \ 1H), \ 7.55 \ (ddd, J = 8.6, \ 6.9, \ 1.5 \ Hz, \ 1H), \ 7.50 - 7.43 \ (m, \ 2H), \ 7.42 - 7.30 \ (m, \ 4H), \ 7.22 \ (d, J = 9.0 \ Hz, \ 1H), \ 5.19 \ (s, \ 2H), \ 1.58 \ (s, \ 6H); \ ^{13}C \ NMR \ (100 \ MHz, \ CDCl_3) \ 162.9, \ 162.7, \ 158.1, \ 137.5, \ 135.6, \ 131.4, \ 129.9, \ 129.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 123.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 123.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 123.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 123.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 123.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 123.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 123.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 123.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 123.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 128.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 128.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 124.9, \ 128.7, \ 119.0, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 128.5, \ 128.4, \ 128.0, \ 127.9, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128.4, \ 128.5, \ 128$

100.9, 78.2, 65.0, 28.1; HRMS (ESI) calcd for $C_{22}H_{20}N_2O_3^+$ [M+H]⁺: m/z = 361.1547, found 361.1548.

(*Z*)-2-(3, 5-dibromo-2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4*H*)-one *O*-benzyl oxime



83.9 mg, 90% yield, $R_f = 0.43$ (PE/EA = 10/1); white solid, m.p. 140.1 – 141.4 °C; ¹H NMR (300 MHz, CDCl₃) δ 12.05 (s, 1H), 7.86 (dd, J = 22.0, 2.4 Hz, 2H), 7.51 – 7.30 (m, 5H), 5.15 (s, 2H), 1.56 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) 159.3, 156.5, 155.8, 139.6, 136.9, 129.8, 128.5, 128.5, 128.2, 111.9, 111.1, 110.8, 77.3, 67.5, 27.9; HRMS (ESI) calcd for C₁₈H₁₆Br₂N₂O₃⁺ [M+H]⁺: m/z = 466.9600, found 466.9598.

(Z)-2-(2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-methyl oxime

MeO 30.4 mg, 65% yield, $R_f = 0.35$ (PE/EA = 10/1); white solid, m.p. 83.9 – 84.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.16 (s, 1H), 7.81 (dd, J = 7.9, 1.6 Hz, 1H), 7.52 – 7.34 (m, 1H), 7.06 (dd, J = 8.4, 1.2 Hz, 1H), 7.01– 6.89 (m, 1H), 3.95 (s, 3H), 1.57 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 160.3, 159.9, 157.3, 134.3, 128.4, 119.2, 117.1, 109.0, 67.2, 63.0, **3**ca

28.0; HRMS (ESI) calcd for $C_{12}H_{14}N_2O_3^+[M+H]^+$: m/z= 235.1077, found 235.1077.

(Z)-2-(2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-ethyl oxime

Eto N
29.8 mg, 60% yield, $R_f = 0.40$ (PE/EA = 10/1); white solid, m.p. 84.1 – 85.2 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.21 (s, 1H), 7.83 (dt, J = 7.9, 1.4 Hz, 1H), 7.45 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.06 (dd, J = 8.4, 1.2 Hz, 1H), 6.95 (m, 1H), 4.18 (q, J = 7.0 Hz, 2H), 1.57 (s, 6H), 1.36 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 160.4, 159.9, 157.0, 134.3, 128.5, 119.1, 117.0, 109.1, 70.7, 67.1, 28.0, 14.4; HRMS (ESI) calcd for C₁₃H₁₆N₂O₃⁺ [M+H]⁺: m/z = 249.1234, found 249.1235.

(Z)-2-(2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-ally oxime

38.0 mg, 86.3 °C; 0 1.4 Hz, 1 0 6.95 (td, 2H), 4.62 0H 109.0, 75

38.0 mg, 73% yield, $R_f = 0.36$ (PE/EA = 10/1); white solid, m.p. 85.6 – 86.3 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.18 (s, 1H), 7.83 (dt, J = 7.9, 1.4 Hz, 1H), 7.45 (tt, J = 8.5, 1.4 Hz, 1H), 7.06 (dd, J = 8.2, 1.2 Hz, 1H), 6.95 (td, J = 7.7, 7.2, 1.1 Hz, 1H), 6.18 – 5.98 (m, 1H), 5.43 – 5.26 (m, 2H), 4.62 (dt, J = 5.9, 1.3 Hz, 2H), 1.57 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) 160.3, 159.9, 157.5, 134.3, 133.6, 128.5, 119.2, 118.3, 117.0, 109.0, 75.9, 67.3, 28.0; HRMS (ESI) calcd for C₁₄H₁₆N₂O₃⁺ [M+H]⁺: m/z = 261.1234, found 261.1234.

(Z)-2-(2-hydroxyphenyl)-4, 4-dimethyloxazol-5(4H)-one O-(tert-butyl) oxime



3ea

42.0 mg, 76% yield, R_f = 0.35 (PE/EA = 10/1); white solid, m.p. 97.7 – 98.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.34 (s, 1H), 7.84 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.43 (m, 1H), 7.05 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.01 – 6.88 (m, 1H), 1.55 (s, 6H), 1.38 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) 160.7, 159.9, 155.7, 134.1, 128.6, 119.0, 116.9, 109.3, 79.6, 67.0, 28.1, 27.2; HRMS (ESI) calcd for C₁₅H₂₀N₂O₃⁺[M+H]⁺: m/z= 277.1547, found 277.1545.

(Z)-2-(2-hydroxyphenyl)-4-methyloxazol-5(4H)-one O-benzyl oxime

BnO 19.5 mg, 33% yield, $R_f = 0.33$ (PE/EA = 10/1); white solid, m.p. 90.1 – 91.4 °C; ¹H NMR (300 MHz, CDCl₃) δ 11.05 (s, 1H), 7.70 (dd, J = 7.9, 1.7 Hz, 1H), 7.40 – 7.13 (m, 6H), 6.95 (dd, J = 8.4, 1.1 Hz, 1H), 6.89 – 6.77 (m, 1H), 5.03 (d, J = 2.1 Hz, 2H), 4.73 (q, J = 7.1 Hz, 1H), 1.45 (d, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 162.4, 160.0, 155.4, 137.2, 3ga 134.5, 128.5, 128.5, 128.4, 128.1, 119.2, 117.1, 108.9, 77.0, 60.9,

20.4; HRMS (ESI) calcd for $C_{15}H_{20}N_2O_3^+$ [M+H]⁺: m/z = 297.1234, found 297.1236.

(Z)-2-(2-hydroxyphenyl)-4,4-dimethyloxazol-5(4H)-one oxime

To an 10 mL round-bottom flask equipped with a magnetic stir bar, Pd/C (0.0075



5

mmol, 0.1 eq.), and (Z)-2-(2-(benzyloxy)phenyl)-4,4-dimethyloxazol -5(4H)-one O-benzyl oxime(3aa) (30.0 mg, 0.075 mmol, 1.0 eq.) were added. The tube was sealed with rubber stopper, evacuated and backfilled with H₂ (this process was repeated for 3 times), then MeOH (1.5 mL) via syringe was added at room temperature. The mixture was stirred at room temperature for 24 h. Upon completion, the reaction mixture was then purified by preparative

thin layer chromatography using petroleum ether/ethyl acetate system (petroleum ether / ethyl acetate = 15/1) to give product 5 as a thick colorless oil in 97% yield(12.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 11.12 (s, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.31 (s, 1H), 7.05 (d, J = 8.3 Hz, 1H), 6.95 (t, J = 8.1 Hz, 1H), 1.56 (s, 6H).¹³C NMR (100 MHz, CDCl₃) δ 160.25, 159.94, 159.14, 134.44, 128.39, 119.28, 117.09, 108.98, 67.26, 27.88; HRMS (ESI) calcd for $C_{11}H_{12}N_2O_3^+$ [M+H]⁺: m/z = 221.0881, found 221.0922.

Ethyl (E)-3-(2-((Z)-5-((benzyloxy)imino)-4,4-dimethyl-4,5-dihydrooxazol-2yl)phenoxy)acrylate



6

To an 10 mL round-bottom flask equipped with a magnetic stir bar, Dabco (0.0075 mmol, 0.1 eq.), ethyl propiolate (0.0825 mmol, 1.1 eq.) and (Z)-2-(2-(benzyloxy)phenyl)-4,4-dimethyloxazol-5(4H)-one O-benzyl oxime(3aa) (30.0 mg, 0.075 mmol, 1.0 eq.) were added. The tube was sealed with rubber stopper, evacuated and backfilled with N_2 (this process was repeated for 3 times), then DCM (1.5mL)

via syringe was added at room temperature. The mixture was stirred at room temperature for 24 h. Upon completion, the reaction mixture was then purified by preparative thin layer chromatography using petroleum ether/ethyl acetate system (petroleum ether / ethyl acetate = 10/1) to give product 6 as a thick colorless oil in 78% yield(29.0mg).¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, J = 7.7, 2.2 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.57 – 7.51 (m, 1H), 7.43 – 7.32 (m, 3H), 7.29 – 7.25 (m, 1H), 7.16 (d, J = 8.1 Hz, 1H), 5.43 (dt, J = 12.4, 1.8 Hz, 1H), 5.10 (d, J = 2.8 Hz, 2H), 4.20 - 4.13 (m, 2H), 1.51 – 1.47 (m, 6H), 1.26 (td, J = 6.5, 3.6 Hz, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 166.96, 159.59, 155.78, 154.24, 144.77, 137.39, 133.54, 131.47, 128.34, 128.26, 127.89, 125.46, 120.42, 118.22, 102.21, 76.80, 68.25, 60.10, 27.64, 14.32; HRMS (ESI) calcd for $C_{23}H_{24}N_2O_5^+$ [M+H]⁺: m/z = 409.1719, found 409.1759.





















































































S33

Optical Properties



(Z)-2-(2-hydroxyphenyl)-4,4-dimethyloxazol-5(4H)-one O-benzyl oxime(3aa)

Figure S1: Normalized absorption (black line), excitation (red line, Detection: 267 nm) and emission (blue line, Ex.: 316 nm) spectra of **3aa**. The concentration of dichloromethane solution is 5×10^{-5} mol L⁻¹.

(Z)-2-(2-hydroxy-4-methoxyphenyl)-4,4-dimethyloxazol-5(4H)-one O-benzyl oxime(3ai)



Figure S2: Normalized absorption (black line), excitation (red line, Detection: 267 nm) and emission (blue line, Ex.: 323 nm) spectra of **3ai**. The concentration of dichloromethane solution is 5×10^{-5} mol L⁻¹.

(Z)-2-(3,5-dibromo-2-hydroxyphenyl)-4,4-dimethyloxazol-5(4H)-one O-benzyl oxime(3ao)



Figure S3: Normalized absorption (black line), excitation (red line, Detection: 266 nm) and

emission (blue line, Ex.: 316 nm) spectra of **3ao**. The concentration of dichloromethane solution is 5×10^{-5} mol L⁻¹.