Supporting Information

Preparation of oxazolines and oxazoles via a PhI(OAc)$_2$-promoted cyclization of N-propargylamides

Wei Yi, Qing-Yun Liu, Xing-Xiao Fang, Sheng-Chun Lou and Gong-Qing Liu*

College of Pharmacy, Nantong University, 19 Qixiu Road, Nantong 226001, People’s Republic of China

E-mail: gqliu@ntu.edu.cn

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1. General information

Reagents were used as received without further purification unless otherwise indicated. Solvents were dried and distilled prior to use. Reactions were monitored with thin layer chromatography using silica gel GF$_{254}$ plates. Organic solutions were concentrated in vacuo with a rotavapor. Flash column chromatography was performed using silica gel (200–300 meshes). Petroleum ether used had a boiling point range of 60–90 °C. Melting points were measured on a digital melting point apparatus without correction of the thermometer. Nuclear magnetic resonance spectra were recorded at ambient temperature (unless otherwise stated) at 400 MHz (100 MHz for $^{13}$C) in CDCl$_3$. Chemical shifts were reported in ppm ($\delta$) using TMS as internal standard, and spin–spin coupling constants ($J$) were given in Hz. Infrared (IR) spectra were recorded with KBr pellet, and wavenumbers were given in cm$^{-1}$. High resolution mass spectrometry (HRMS) analyses were carried out on an FTICR HR-ESI-MS.

2. Comparison of the 1H NMR of compound 2a with the literature report.

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<td></td>
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N-propargylamide substrates were prepared by coupling of carboxylic acids and propargylamines according to the literature.\textsuperscript{1-4}


A flame-dried Schlenk flask was charged with 0.50 mmol N-propargylamide, 0.50 mmol PhI(OAc)<sub>2</sub>, 0.50 mmol LiI and 2 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred at room temperature until complete disappearance of the starting material as shown by TLC (usually 12 h). CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was then added, and the mixture was washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to give crude residue, which was purified by flash column chromatography to give the corresponding products.

\((E)-5\)-(Iodomethylene)-2-phenyl-4,5-dihydrooxazole (2a). Compound 2a was prepared according to the general procedure and isolated as a yellow solid (130 mg, 91% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 107–108 °C ( ref,\textsuperscript{4} mp = 104 °C). \textsuperscript{1}H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm= 7.98 – 7.94 (m, 2H), 7.56 – 7.51 (m, 1H), 7.47 – 7.43 (m, 2H), 5.78 (t, J = 3.2 Hz, 1H), 4.62 (d, J = 3.2 Hz,
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.80 (d, $J$ = 7.6 Hz, 1H), 7.49 (dd, $J$ = 7.9, 4.1 Hz, 1H), 7.43 (dd, $J$ = 12.9, 7.0 Hz, 1H), 7.34 (dd, $J$ = 12.4, 5.4 Hz, 1H), 5.78 (t, $J$ = 3.1 Hz, 1H), 4.69 (d, $J$ = 3.1 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$/ppm = 161.1, 156.5, 138.3, 130.5, 130.3, 128.7, 124.8, 124.6, 60.6, 45.7, 20.9. Spectral data are in agreement with literature values.$^3$

$(E)$-5-(Iodomethylene)-2-(o-tolyl)-4,5-dihydrooxazole (2c). Compound 2c was prepared according to the general procedure and isolated as a yellow oil (135 mg, 90% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.84 (d, $J$ = 7.8 Hz, 1H), 7.41 (t, $J$ = 7.0 Hz, 1H), 7.30 – 7.26 (m, 2H), 5.76 (t, $J$ = 3.2 Hz, 1H), 4.69 (d, $J$ = 3.2 Hz, 2H), 2.63 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$/ppm = 163.0, 156.5, 138.3, 130.5, 130.3, 128.7, 124.8, 124.6, 60.6, 45.7, 20.9. Spectral data are in agreement with literature values.$^3$

$(E)$-5-(Iodomethylene)-2-(m-tolyl)-4,5-dihydrooxazole (2d). Compound 2d was prepared according to the general procedure and isolated as a yellow solid (139 mg, 93% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 86–88 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.78 (s, 1H), 7.75 (dd, $J$ = 6.2, 2.6 Hz, 1H), 7.35 – 7.31 (m, 2H), 5.76 (t, $J$ = 3.2 Hz, 1H), 4.61 (d, $J$ = 3.2 Hz, 2H), 2.39 (s, 3H). $^{13}$C
NMR (100 MHz, CDCl₃): δ/ppm= 163.1, 157.0, 137.4, 131.9, 127.47, 127.48, 125.3, 124.1, 60.1, 46.1, 20.3. Spectral data are in agreement with literature values.³

(E)-5-(Iodomethylene)-2-(p-tolyl)-4,5-dihydrooxazole (2e). Compound 2e was prepared according to the general procedure and isolated as a yellow solid (133 mg, 89% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 97–99 °C.¹ H NMR (400 MHz, CDCl₃): δ/ppm= 7.87 (d, J = 6.3 Hz, 2H), 7.27 (d, J = 6.3 Hz, 2H), 5.78 (t, J = 3.2 Hz, 1H), 4.63 (d, J = 3.2 Hz, 2H), 2.42 (s, 3H). 13C NMR (100 MHz, CDCl₃): δ/ppm= 163.2, 156.9, 141.8, 128.4, 127.0, 122.5, 60.0, 46.1, 20.7. Spectral data are in agreement with literature values.³

(E)-5-(Iodomethylene)-2-(4-methoxyphenyl)-4,5-dihydrooxazole (2f). Compound 2f was prepared according to the general procedure and isolated as a yellow solid (139 mg, 88% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 137–139 °C.¹ H NMR (400 MHz, CDCl₃): δ/ppm= 7.89 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.73 (t, J = 3.1 Hz, 1H), 4.58 (d, J = 3.1 Hz, 2H), 3.85 (s, 3H). 13C NMR (100 MHz, CDCl₃): δ/ppm= 162.7, 161.6, 157.1, 128.8, 117.8, 113.0, 60.1, 54.4, 45.8. Spectral data are in agreement with literature values.¹

(E)-2-(4-Fluorophenyl)-5-(iodomethylene)-4,5-dihydrooxazole (2g). Compound 2g was prepared according to the general procedure and isolated as a white solid (133 mg, 88% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 112–113 °C.¹ H NMR (400 MHz, CDCl₃): δ/ppm= 7.97 (d, J = 4.1 Hz, 2H), 7.13 (dd, J = 12.1, 5.2 Hz, 2H), 5.78 (t, J = 3.2 Hz, 1H), 4.61 (d, J = 3.2 Hz, 2H). 19F NMR (376 MHz, CDCl₃) δ/ppm=106.5. 13C NMR (100 MHz, CDCl₃): δ/ppm= 165.1 (d, J_CE =
253.5 Hz), 163.0, 157.9, 130.4 (d, $J_{C,F} = 8.1$ Hz), 122.78, 115.9 (d, $J_{C,F} = 22.1$ Hz), 61.2, 47.4. Spectral data are in agreement with literature values.$^3$

*(E)-2-(4-Bromophenyl)-5-(iodomethylene)-4,5-dihydrooxazole (2h).* Compound 2h was prepared according to the general procedure and isolated as a white solid (147 mg, 81% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 115–117 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.80 (d, $J = 8.6$ Hz, 2H), 7.58 (d, $J = 8.6$ Hz, 2H), 5.77 (t, $J = 3.2$ Hz, 1H), 4.59 (d, $J = 3.2$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$/ppm = 162.1, 156.7, 130.9, 128.4, 125.9, 124.4, 60.2, 46.5. Spectral data are in agreement with literature values.$^3$

*(E)-2-(4-Chlorophenyl)-5-(iodomethylene)-4,5-dihydrooxazole (2i).* Compound 2i was prepared according to the general procedure and isolated as a white solid (126 mg, 79% yield) after flash chromatography (petroleum ether/ethyl acetate = 50/1); mp = 96–98 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.80 (d, $J = 8.6$ Hz, 2H), 7.43 (d, $J = 8.6$ Hz, 2H), 5.78 (t, $J = 3.2$ Hz, 1H), 4.61 (d, $J = 3.2$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$/ppm = 163.1, 157.8, 138.4, 129.3, 129.0, 125.0, 61.3, 47.5. IR (KBr): 3085, 1674, 1649, 1593, 1486, 1321, 1083, 915, 832, 743 cm$^{-1}$. HRMS–ESI: calc. for [C$_{10}$H$_7$ClINO+H]$^+$: m/z = 319.9339, found: 319.9336.

*(E)-5-(Iodomethylene)-2-(4-nitrophenyl)-4,5-dihydrooxazole (2j).* Compound 2j was prepared according to the general procedure and isolated as a yellow solid (101 mg, 61% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 141–142 °C, (ref.$^5$ mp = 125 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 8.31 (d, $J = 8.9$ Hz, 2H), 8.15 (d, $J = 8.9$ Hz, 2H), 5.86 (t, $J = 3.2$ Hz, 1H), 4.67 (d, $J = 3.2$ Hz, 2H). $^{13}$C
NMR (100 MHz, CDCl₃): δ/ppm = 161.2, 156.2, 148.9, 131.2, 128.1, 122.8, 60.3, 47.4. Spectral data are in agreement with literature values.⁵

*(E)*-4-(5-(Iodomethylene)-4,5-dihydrooxazol-2-yl)benzonitrile (2k). Compound 2k was prepared according to the general procedure and isolated as a white solid (112 mg, 72% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 124–126 °C. ¹H NMR (400 MHz, CDCl₃): δ/ppm = 8.06 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 5.83 (t, J = 3.1 Hz, 1H), 4.65 (d, J = 3.1 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm = 161.4, 156.2, 131.4, 129.6, 127.5, 117.0, 114.5, 60.3, 47.2. Spectral data are in agreement with literature values.³

*(E)*-5-(Iodomethylene)-2-(naphthalen-1-yl)-4,5-dihydrooxazole (2l). Compound 2l was prepared according to the general procedure and isolated as a white solid (142 mg, 85% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 97–99 °C. ¹H NMR (400 MHz, CDCl₃): δ/ppm = 9.16 (d, J = 8.6 Hz, 1H), 8.12 (d, J = 7.3 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 8.3, 7.1 Hz, 1H), 7.59 – 7.48 (m, 2H), 5.80 (t, J = 3.1 Hz, 1H), 4.80 (d, J = 3.1 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm = 163.5, 157.3, 133.8, 132.8, 130.9, 129.3, 128.7, 127.8, 126.4, 126.1, 124.6, 122.9, 62.1, 46.8. IR (KBr): 3081, 1666, 1640, 1509, 1304, 1093, 962, 810, 737, 550 cm⁻¹. HRMS–ESI: calc. for [C₁₄H₁₀INO+H]⁺: m/z = 335.9885, found: 335.9886.

*(E)*-5-(Iodomethylene)-2-(2-thienyl)-4,5-dihydrooxazole (2m). Compound 2m was prepared according to the general procedure and isolated as a yellow solid (95 mg, 65% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1); mp = 116–
$118 \, ^\circ \text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl$_3$): $\delta$/ppm$= 7.59$ (d, $J = 1.5$ Hz, 1H), $7.04$ (d, $J = 3.5$ Hz, 1H), $6.52$ (dd, $J = 3.5$, 1.6 Hz, 1H), $5.77$ (t, $J = 3.2$ Hz, 1H), $4.61$ (d, $J = 3.2$ Hz, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): $\delta$/ppm$= 156.1, 155.1, 145.1, 140.6, 114.5, 110.8, 59.9, 46.6$. Spectral data are in agreement with literature values.$^3$

$(E)$-$2$-(Furan-2-yl)-5-(iodomethylene)-4,5-dihydrooxazole ($2n$). Compound $2n$ was prepared according to the general procedure and isolated as a white solid (106 mg, 77% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1); mp = 117–118 $^\circ$C. $^1\text{H NMR}$ (400 MHz, CDCl$_3$): $\delta$/ppm$= 7.58$ (d, $J = 1.5$ Hz, 1H), $7.02$ (d, $J = 3.5$ Hz, 1H), $6.51$ (dd, $J = 3.5$, 1.6 Hz, 1H), $5.76$ (t, $J = 3.2$ Hz, 1H), $4.59$ (d, $J = 3.2$ Hz, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): $\delta$/ppm$= 156.1, 155.1, 145.1, 140.6, 114.4, 110.8, 59.9, 46.6$. Spectral data are in agreement with literature values.$^3$

$(E)$-$5$-(Iodomethylene)-$2$-(1H-pyrrol-2-yl)-4,5-dihydrooxazole ($2o$). Compound $2o$ was prepared according to the general procedure and isolated as a white solid (96 mg, 70% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1); mp = 146–147 $^\circ$C. $^1\text{H NMR}$ (400 MHz, CDCl$_3$): $\delta$/ppm$= 9.91$ (s, 1H), $7.0$ (d, $J = 2.5$ Hz, 1H), $6.84$ (s, 1H), $6.29$ (dd, $J = 6.0$, 2.5 Hz, 1H), $5.77$ (t, $J = 3.1$ Hz, 1H), $4.57$ (d, $J = 3.1$ Hz, 2H).$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): $\delta$/ppm$= 157.7, 156.3, 122.4, 117.5, 113.2, 109.4, 59.0, 46.3$. IR (KBr): 3165, 3078, 1679, 1647, 1452, 1341, 1128, 1007, 947, 738, 603, 489 cm$^{-1}$. HRMS–ESI: calc. for [C$_8$H$_7$IN$_2$O+H]$: m/z = 274.9681$, found: 274.9679.

$(E)$-$5$-(Iodomethylene)-$2$-(pyridin-3-yl)-4,5-dihydrooxazole ($2p$). Compound $2p$ was prepared according to the general procedure and isolated as a yellow solid (103 mg, 72% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1); mp =
115–117 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 9.15 (d, $J$ = 1.5 Hz, 1H), 8.75 (dd, $J$ = 4.8, 1.5 Hz, 1H), 8.22 (dt, $J$ = 7.9, 1.9 Hz, 1H), 7.39 (dd, $J$ = 7.9, 4.8 Hz, 1H), 5.83 (t, $J$ = 3.2 Hz, 1H), 4.63 (d, $J$ = 3.2 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm= 161.0, 156.3, 151.6, 148.1, 134.3, 122.4, 121.9, 60.1, 47.0. IR (KBr): 3054, 2927, 1678, 1650, 1414, 1337, 1235, 1074, 871, 804, 701 cm$^{-1}$. HRMS–ESI: calc. for [C$_9$H$_7$IN$_2$O+H]$^+$: m/z = 286.9681, found: 286.9673.

$(E)$-Cyclopenta-2,4-dien-1-yl(2-(5-(iodomethylene)-4,5-dihydrooxazol-2-yl)cyclopenta-2,4-dien-1-yl)iron (2q). Compound 2q was prepared according to the general procedure and isolated as a brown solid (163 mg, 83% yield) after flash chromatography (petroleum ether/ethyl acetate = 12/1); mp = 141–142 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 5.70 (t, $J$ = 3.1 Hz, 1H), 4.83 – 4.73 (m, 2H), 4.45 (d, $J$ = 3.1 Hz, 2H), 4.42 – 4.37 (m, 2H), 4.21 (s, 4H), 1.67 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm= 166.8, 158.1, 70.9, 69.9, 68.8, 61.1, 46.5. IR (KBr): 3054, 1678, 1648, 1467, 1303, 1105, 929, 772, 507 cm$^{-1}$. HRMS–ESI: calc. for [C$_{14}$H$_{11}$FeINO+H]$^+$: m/z = 392.9313, found: 392.9316.

$(E)$-5-(Iodomethylene)-2-((E)-styryl)-4,5-dihydrooxazole (2r). Compound 2r was prepared according to the general procedure and isolated as a white solid (129 mg, 83% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1); mp = 122–124 °C (ref. $^4$ mp = 118 °C). $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 7.50 (dd, $J$ = 7.4, 2.1 Hz, 2H), 7.43 (d, $J$ = 16.3 Hz, 1H), 7.40 – 7.36 (m, 3H), 6.59 (d, $J$ = 16.3 Hz, 1H), 5.71 (t, $J$ = 3.1 Hz, 1H), 4.54 (d, $J$ = 3.1 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm=
Spectral data are in agreement with literature values.\(^3\)

\textbf{(E)-5-(Iodomethylene)-4,4-dimethyl-2-phenyl-4,5-dihydrooxazole (2s).} Compound 2s was prepared according to the general procedure and isolated as an oil (142 mg, 91\% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta/\text{ppm}= 7.96 – 7.92\) (m, 2H), 7.52 – 7.49 (m, 1H), 7.45 – 7.41 (m, 2H), 5.76 (s, 1H), 1.69 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta/\text{ppm}= 162.3, 157.5, 130.8, 127.5, 127.1, 125.1, 70.3, 44.4, 24.8\). Spectral data are in agreement with literature values.\(^3\)

\textbf{(E)-2-Cyclohexyl-5-(iodomethylene)-4,5-dihydrooxazole (2t).} Compound 2t was prepared according to the general procedure and isolated as a yellow solid (116 mg, 80\% yield) after flash chromatography (petroleum ether/ethyl acetate = 30/1); mp = 41–42 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta/\text{ppm}= 5.57\) (t, \(J = 3.1\) Hz, 1H), 4.37 (dd, \(J = 3.1, 1.3\) Hz, 2H), 2.38 – 2.29 (m, 1H), 1.94 (dd, \(J = 13.2, 2.3\) Hz, 2H), 1.78 (dd, \(J = 12.6, 3.5\) Hz, 2H), 1.51 – 1.38 (m, 2H), 1.35 – 1.19 (m, 4H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta/\text{ppm}= 169.3, 156.7, 59.0, 44.6, 36.0, 27.7, 24.1, 23.8\). IR (KBr): 3077, 2928, 2852, 1681, 1648, 1444, 1383, 1163, 1090, 934, 873, 736, 627, 470 cm\(^{-1}\). HRMS–ESI: calc. for [C\(_{10}\)H\(_{14}\)INO+H]\(^+\): m/z = 292.0198, found: 292.0185.

\textbf{(E)-2-Benzyl-5-(iodomethylene)-4,5-dihydrooxazole (2u).} Compound 2u was prepared according to the general procedure and isolated as a yellow solid (117 mg, 78\% yield) after flash chromatography (petroleum ether/ethyl acetate = 20/1); mp = 68–70 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta/\text{ppm}= 7.29 – 7.19\) (m, 5H), 5.54 (t, \(J = 3.1\) Hz,
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.36 – 7.27 (m, 3H), 7.16 (d, $J = 6.8$ Hz, 2H), 5.74 (t, $J = 3.1$ Hz, 1H), 5.06 (d, $J = 7.6$ Hz, 1H), 4.78 (d, $J = 5.0$ Hz, 1H), 4.40 (t, $J = 3.1$ Hz, 1H), 3.20 (dd, $J = 13.5, 4.9$ Hz, 1H), 3.07 (dd, $J = 13.5, 5.6$ Hz, 1H), 1.44 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$/ppm = 166.5, 157.8, 154.9, 135.6, 129.4, 128.6, 127.1, 80.1, 60.3, 49.9, 47.7, 38.4, 28.3. IR (KBr): 3414, 3343, 2978, 1692, 1524, 1304, 1171, 1019, 861, 753 cm$^{-1}$. HRMS–ESI: calc. for [C$_{17}$H$_{21}$IN$_2$O$_3$+H]$^+$: m/z = 429.0675, found: 429.0672.

(S,E)-Tert-butyl(1-(5-(iodomethylene)-4,5-dihydrooxazol-2-yl)-2-methylpropyl)carbamate (2w). Compound 2w was prepared according to the general procedure and isolated as a brown solid (158 mg, 83% yield) after flash chromatography (petroleum ether/ethyl acetate = 15/1); mp = 89–91 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 5.64 (t, $J = 3.1$ Hz, 1H), 5.09 (d, $J = 9.0$ Hz, 1H), 4.40 (d, $J = 3.1$ Hz, 2H), 4.34 (dd, $J = 8.9, 5.2$ Hz, 1H), 2.09 (td, $J = 13.0, 6.5$ Hz, 1H), 1.42 (s, 9H), 0.96 (d, $J = 6.8$ Hz, 3H), 0.90 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$/ppm = 165.3, 156.1, 153.7, 78.2, 58.5, 52.4, 45.7, 29.4,
26.6, 17.2, 15.7. IR (KBr): 3337, 2969, 2870, 1681, 1527, 1391, 1249, 1173, 1019, 664 cm\(^{-1}\). HRMS–ESI: calc. for [C\(_{13}\)H\(_{21}\)N\(_2\)O\(_3\) +H]\(^+\): m/z =381.0675, found: 381.0671.

\((E)\)-5-(Iodomethylene)-2-(2,3,6,7-tetramethoxyphenanthren-9-yl)-4,5-dihydrooxazol (2x). Compound 2x was prepared according to the general procedure and isolated as a yellow solid (210 mg, 83% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1); mp = 153–155 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ/ppm= 8.97 (s, 1H), 8.30 (s, 1H), 7.80 (s, 1H), 7.76 (s, 1H), 5.80 (t, \(J = 3.1\) Hz, 1H), 5.30 (s, 1H), 4.83 (d, \(J = 3.1\) Hz, 2H), 4.14 (s, 3H), 4.13 (s, 3H), 4.06 (s, 3H), 4.04 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ/ppm= 162.8, 156.1, 150.2, 148.3, 148.1, 148.1, 128.0, 125.7, 124.1, 123.6, 122.5, 117.3, 108.1, 106.6, 101.8, 101.5, 61.2, 55.1, 55.0, 54.9, 45.3. IR (KBr): 2954, 2926, 1635, 1512, 1475, 1264, 1117, 937, 841, 783, 566 cm\(^{-1}\). HRMS–ESI: calc. for [C\(_{22}\)H\(_{20}\)INO\(_5\)+H]\(^+\): m/z = 506.0464, found: 506.0452.

\((5S,8R,9S,10S,13R,14S,17R)-17-(\(\text{Iodomethylene}\)) \(\text{5H-cyclopenta[a]phenanthrene-3,7,12(2H,4H,8H)-trione}\) (2y). Compound 2y was prepared according to the general procedure and isolated as a brown solid (220 mg, 78% yield) after flash chromatography (petroleum ether/ethyl acetate = 2/1); mp = 148–150 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ/ppm= 5.58 (t, \(J = 3.1\) Hz, 1H), 4.37 (t, \(J = 3.1\) Hz, 2H), 2.93 – 2.87 (m, 2H), 2.83 (dd, \(J = 16.1, 9.2\) Hz, 2H), 2.34 – 2.30 (m, 2H), 2.29 – 2.26 (m, 2H), 2.24 – 2.21 (m, 2H), 2.15 – 2.10 (m, 2H), 2.05 – 2.01 (m, 2H), 1.98 – 1.95 (m, 1H), 1.93 (dd, \(J = 4.9, 2.9\) Hz, 1H), 1.87 – 1.81 (m, 2H), 1.60 (td, \(J = 14.3, 5.0\) Hz, 1H), 1.48 – 1.42 (m, 1H), 1.38 (s, 3H), 1.30 (dd, \(J = 7.9, 4.6\) Hz, 2H), 1.27 – 1.22 (m, 2H), 1.06 (s, 3H), 0.86
(d, J = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm = 210.2, 207.4, 207.1, 166.6, 156.6, 59.0, 55.2, 50.1, 47.3, 45.2, 44.8, 43.9, 43.9, 43.3, 41.1, 37.0, 34.8, 34.4, 34.0, 33.6, 29.4, 26.0, 23.9, 23.5, 20.3, 17.0, 10.2. IR (KBr): 3398, 2961, 2827, 1718, 1663, 1533, 1384, 1273, 1008, 916, 731, 619, 525 cm$^{-1}$. HRMS–ESI: calc. for [C$_{27}$H$_{36}$INO$_4$+H]$^+$: m/z = 566.1767, found: 566.1767.

(3R,5αS,6R,8αS,9R,10R,12R,12αR)-3,6,9-Trimethyldecahydro-3H-3,12-epoxy[1,2]dioxepino[4,3-i]isochromen-10-yl

3-((E)-5-(iodomethylene)-4,5-dihydrooxazol-2-yl)propanoate (2z). Compound 2z was prepared according to the general procedure and isolated as an oil (211 mg, 77% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1). $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm = 5.78 (d, J = 9.9 Hz, 1H), 5.61 (t, J = 3.1 Hz, 1H), 5.42 (s, 1H), 4.36 (t, J = 3.1 Hz, 2H), 4.10 (q, J = 7.1 Hz, 1H), 2.78 (t, J = 6.7 Hz, 2H), 2.67 (dd, J = 15.7, 7.8 Hz, 2H), 2.36 (dd, J = 14.0, 10.1 Hz, 1H), 2.04 (d, J = 14.6 Hz, 2H), 1.90 – 1.85 (m, 1H), 1.77 – 1.69 (m, 2H), 1.60 (dt, J = 13.8, 4.3 Hz, 1H), 1.41 (s, 3H), 1.36 (dd, J = 13.5, 3.2 Hz, 1H), 1.26 (t, J = 3.1 Hz, 1H), 1.23 (d, J = 7.1 Hz, 2H), 0.95 (d, J = 5.9 Hz, 3H), 0.82 (d, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm = 169.6, 165.4, 157.0, 103.5, 91.3, 90.5, 79.1, 59.5, 50.6, 46.0, 44.3, 36.3, 35.2, 33.1, 30.8, 28.8, 25.0, 23.6, 22.3, 21.0, 19.2, 11.0. IR (KBr): 3401, 2927, 2873, 1751, 1656, 1573, 1377, 1160, 1013, 875, 731 cm$^{-1}$. HRMS–ESI: calc. for [C$_{22}$H$_{31}$INO$_7$+H]$^+$: m/z = 548.1145, found: 548.1143.
5. **Suzuki coupling of 2s and p-tolylboronic acid**

A vial in a glove box under nitrogen atmosphere was charged with Pd(OAc)$_2$ (0.025 mmol, 7 mg), PPh$_3$ (0.050 mmol, 13 mg), Cs$_2$CO$_3$ (0.70 mmol, 228 mg), and p-tolylboronic acid (0.60 mmol, 82 mg) and 2 mL of dixoane. Compound 2s (0.50 mmol, 157 mg) were subsequently added. The reaction vial was removed from the glove box and heated in oil bath at 70 °C overnight. The resulting mixture was washed with water and extracted with dichloromethane. The combined organic layer was dried over Na$_2$SO$_4$ and concentrated to give crude residue, which was purified by flash column chromatography (petroleum ether/ethyl acetate = 60/1) to give 3 (53 mg, 38%, yellow solid) and 4 (47 mg, 34%, yellow solid).

**(E)-4,4-Dimethyl-5-(4-methylbenzylidene)-2-phenyl-4,5-dihydrooxazole** (3). R$_f$ = 0.20, SiO$_2$, petroleum ether/ethyl acetate = 30/1. mp = 85–87 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm = 8.00 (dd, $J$ = 8.3, 1.3 Hz, 2H), 7.51 (dt, $J$ = 2.8, 2.0 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.21 (d, $J$ = 8.0 Hz, 2H), 7.14 (d, $J$ = 8.0 Hz, 2H), 6.49 (s, 1H), 2.36 (s, 3H), 1.45 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm = 160.3, 158.4, 135.4, 130.6, 130.2, 128.4, 127.7, 127.4, 127.0, 126.0, 102.7, 68.1, 27.1, 20.1. IR (KBr): 2972, 2927, 1694, 1652, 1450, 1304, 1021, 960, 809, 701, 621, 513 cm$^{-1}$. HRMS–ESI: calc. for [C$_{19}$H$_{19}$NO+H]$^+$: m/z = 278.1545, found: 278.1543.

**(Z)-4,4-Dimethyl-5-(4-methylbenzylidene)-2-phenyl-4,5-dihydrooxazole** (4). R$_f$ = 0.21, SiO$_2$, petroleum ether/ethyl acetate = 30/1. mp = 72–74 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm = 8.11 – 8.07 (m, 2H), 7.54 (d, $J$ = 7.9 Hz, 3H), 7.52 – 7.47 (m, 2H), 7.21 (d, $J$ = 8.0 Hz, 2H), 5.52 (s, 1H), 2.37 (s, 3H), 1.53 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm = 160.3, 158.4, 135.4, 130.6, 128.4, 127.7, 127.4, 127.0, 126.0, 102.7, 68.1, 27.1, 20.1. IR (KBr): 2972, 2927, 1694, 1652, 1450, 1304, 1021, 960, 809, 701, 621, 513 cm$^{-1}$. HRMS–ESI: calc. for [C$_{19}$H$_{19}$NO+H]$^+$: m/z = 278.1545, found: 278.1543.
CDCl₃): δ/ppm = 158.9, 158.8, 134.8, 131.1, 130.8, 128.2, 127.6, 127.2, 126.8, 125.9, 98.2, 69.7, 28.7, 20.2. IR (KBr): 2968, 2923, 1696, 1650, 1452, 1286, 1175, 1045, 958, 799, 696, 522 cm⁻¹. HRMS–ESI: calc. for [C₁₉H₁₉NO+H]⁺: m/z = 278.1545, found: 278.15430.


A solution of N-propargylamide (0.5 mmol, 1.0 equiv.), PhI(OAc)₂ (0.05 mmol, 0.1 equiv.), and LiI (0.05 mmol, 0.1 equiv.) in 2 mL of CH₂Cl₂ was irradiated under oxygen atmosphere with a 24 W fluorescent household bulb at room temperature. Upon completion (monitored by TLC), CH₂Cl₂ (10 mL) was added, and the mixture was washed with aqueous Na₂S₂O₃. The organic layer was dried over Na₂SO₄ and concentrated to give crude residue, which was purified by flash column chromatography to give the corresponding products.

2-Phenyloxazole-5-carbaldehyde (5a). Compound 5a was prepared according to the general procedure and isolated as a white solid (71 mg, 82% yield) after flash chromatography (petroleum ether/ethyl acetate = 6/1); mp = 71–73 °C, (ref.⁶ mp = 74–76 °C).¹H NMR (400 MHz, CDCl₃): δ/ppm = 9.82 (s, 1H), 8.19 – 8.16 (m, 2H), 7.95 (s, 1H), 7.59 – 7.49 (m, 3H).¹³C NMR (100 MHz, CDCl₃): δ/ppm = 176.3, 165.5, 149.6, 139.1, 132.3, 129.1, 127.7, 125.9. Spectral data are in agreement with literature values.⁷

2-(o-Tolyl)oxazole-5-carbaldehyde (5b). Compound 5b was prepared according to the general procedure and isolated as a yellow solid (69 mg, 74% yield) after flash chromatography (petroleum ether/ethyl acetate = 12/1); mp = 67–68 °C.¹H NMR (400 MHz, CDCl₃): δ/ppm = 9.83 (s, 1H), 8.15 – 8.11 (m, 1H), 7.97 (s, 1H), 7.42 (td, J = 7.6,
1.3 Hz, 1H), 7.35 – 7.29 (m, 2H), 2.74 (s, 3H). $^1$C NMR (100 MHz, CDCl$_3$): δ/ppm= 175.3, 164.9, 148.1, 138.0, 137.6, 131.0, 130.7, 128.9, 125.3, 123.8, 21.2. Spectral data are in agreement with literature values.$^7$

2-(m-Tolyloxazole-5-carbaldehyde (5c). Compound 5c was prepared according to the general procedure and isolated as a white solid (77 mg, 82% yield) after flash chromatography (petroleum ether/ethyl acetate = 12/1); mp = 60–61 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 9.79 (s, 1H), 7.98 (s, 1H), 7.97 – 7.94 (m, 1H), 7.93 (s, 1H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 2.5$ Hz, 1H), 2.42 (s, 3H). $^1$C NMR (100 MHz, CDCl$_3$): δ/ppm= 176.3, 165.7, 149.6, 139.2, 139.0, 133.2, 129.0, 128.2, 125.7, 124.9, 21.3. Spectral data are in agreement with literature values.$^7$

2-(p-Tolyloxazole-5-carbaldehyde (5d). Compound 5d was prepared according to the general procedure and isolated as a yellow solid (74 mg, 79% yield) after flash chromatography (petroleum ether/ethyl acetate = 12/1); mp = 103–105 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 9.77 (s, 1H), 8.03 (d, $J = 8.2$ Hz, 2H), 7.91 (s, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 2.40 (s, 3H). $^1$C NMR (100 MHz, CDCl$_3$): δ/ppm= 175.2, 164.7, 148.4, 142.0, 138.3, 128.8, 126.7, 122.1, 20.7. Spectral data are in agreement with literature values.$^7$

2-(4-Fluorophenyl)oxazole-5-carbaldehyde (5e). Compound 5e was prepared according to the general procedure and isolated as a white solid (83 mg, 87% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1); mp = 118–120 °C, (ref.$^8$ mp = 123–125°C). $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 9.81 (s, 1H), 8.21 – 8.17 (m, 2H), 7.94 (s, 1H), 7.23 – 7.18 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$): δ/ppm=
13C NMR (100 MHz, CDCl₃): δ/ppm = 176.2, 165.6 (d, J_C-F = 190.6 Hz), 164.0, 149.7, 139.2, 130.1 (d, J_C-F = 9.1 Hz), 122.3, 116.5 (d, J_C-F = 22.3 Hz). Spectral data are in agreement with literature values.

2-(4-Bromophenyl)oxazole-5-carbaldehyde (5f). Compound 5f was prepared according to the general procedure and isolated as a yellow solid (111 mg, 88% yield) after flash chromatography (petroleum ether/ethyl acetate = 6/1); mp = 140 –142 °C. ¹H NMR (400 MHz, CDCl₃): δ/ppm = 9.82 (s, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.94 (s, 1H), 7.66 (d, J = 7.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm = 176.2, 164.6, 149.7, 139.0, 132.5, 129.1, 127.3, 124.8. Spectral data are in agreement with literature values.

2-(4-Methoxyphenyl)oxazole-5-carbaldehyde (5g). Compound 5g was prepared according to the general procedure and isolated as a yellow solid (92 mg, 91% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1); mp = 147–149 °C, (ref, mp = 140–142°C). ¹H NMR (400 MHz, CDCl₃): δ/ppm = 9.77 (s, 1H), 8.13 (d, J = 8.9 Hz, 2H), 7.92 (s, 1H), 7.01 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm = 176.0, 165.8, 163.0, 149.3, 139.7, 129.7, 118.4, 114.6, 55.6. Spectral data are in agreement with literature values.

2-(4-Chlorophenyl)oxazole-5-carbaldehyde (5h). Compound 5h was prepared according to the general procedure and isolated as a white solid (90 mg, 87% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1); mp = 136–138 °C. ¹H NMR (400 MHz, CDCl₃): δ/ppm = 9.82 (s, 1H), 8.12 (d, J = 8.5 Hz, 2H), 7.94 (s, 1H), 7.50 (d, J = 8.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm = 175.2, 163.5, 148.7, 138.0, 137.7, 128.5, 127.9, 123.3. Spectral data are in agreement with literature values.
2-(2-Chlorophenyl)oxazole-5-carbaldehyde (5i). Compound 5i was prepared according to the general procedure and isolated as a white solid (91 mg, 88% yield) after flash chromatography (petroleum ether/ethyl acetate = 12/1); mp = 75–77 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 9.88 (s, 1H), 8.13 (dd, J = 7.8, 1.8 Hz, 1H), 8.02 (s, 1H), 7.56 (dd, J = 8.0, 1.3 Hz, 1H), 7.48 (td, J = 7.7, 1.8 Hz, 1H), 7.42 (td, J = 7.6, 1.3 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm= 175.6, 162.2, 148.6, 136.9, 132.5, 131.6, 130.7, 130.6, 126.1, 123.8. Spectral data are in agreement with literature values. $^7$

2-(Naphthalen-1-yl)oxazole-5-carbaldehyde (5j). Compound 5j was prepared according to the general procedure and isolated as a yellow solid (100 mg, 90% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1); mp = 110–112 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 9.90 (s, 1H), 9.31 (d, J = 8.7 Hz, 1H), 8.43 (d, J = 7.3 Hz, 1H), 8.08 (s, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.70 (t, J = 7.7 Hz, 1H), 7.60 (t, J = 7.7 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm= 176.4, 165.5, 149.2, 138.8, 134.0, 133.3, 130.4, 129.8, 128.9, 128.3, 126.7, 125.8, 125.0, 122.2. IR (KBr): 3046, 1688, 1505, 1322, 1262, 1149, 984, 766, 530 cm$^{-1}$. HRMS–ESI: calc. for [C$_{14}$H$_9$NO$_2$+H]$^+$: m/z = 224.0712, found: 224.0704.

2-(Thiophen-2-yl)oxazole-5-carbaldehyde (5k). Compound 5k was prepared according to the general procedure and isolated as a yellow solid (81 mg, 91% yield) after flash chromatography (petroleum ether/ethyl acetate = 10/1); mp = 100–102 °C, (ref.$^2$ mp = 57–59 °C). $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 9.76 (s, 1H), 7.88 – 7.87 (m, 2H), 7.58 (dd, J = 5.0, 1.1 Hz, 1H), 7.16 (dd, J = 5.0, 3.8 Hz, 1H). $^{13}$C NMR (100
MHz, CDCl$_3$): $\delta$/ppm = 174.9, 160.6, 148.1, 138.3, 130.6, 130.0, 127.6, 127.2. Spectral data are in agreement with literature values.$^7$

2-(Pyridin-3-yl)oxazole-5-carbaldehyde (5l). Compound 5l was prepared according to the general procedure and isolated as a white solid (53 mg, 61% yield) after flash chromatography (petroleum ether/ethyl acetate = 1/1); mp = 101–103 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 9.85 (s, 1H), 9.39 (d, $J = 1.6$ Hz, 1H), 8.78 (dd, $J = 4.8$, 1.3 Hz, 1H), 8.43 (dt, $J = 8.0$, 1.8 Hz, 1H), 7.98 (s, 1H), 7.47 (dd, $J = 8.0$, 4.8 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$/ppm = 175.3, 162.0, 151.5, 149.0, 147.6, 137.6, 133.9, 122.9, 121.4. IR (KBr): 3124, 3093, 2959, 1667, 1580, 1525, 1259, 1154, 974, 774, 701, 621, 454 cm$^{-1}$. HRMS–ESI: calc. for [C$_9$H$_6$N$_2$O$_2$+H]$^+$: m/z = 175.0508, found: 175.0500.

(E)-2-Styryloxazole-5-carbaldehyde (5m). Compound 5m was prepared according to the general procedure and isolated as a yellow solid (79 mg, 79% yield) after flash chromatography (petroleum ether/ethyl acetate = 6/1); mp = 97–99 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 9.75 (s, 1H), 7.89 (s, 1H), 7.79 (d, $J = 16.4$ Hz, 1H), 7.56 (dd, $J = 7.5$, 2.0 Hz, 2H), 7.42–7.38 (m, 3H), 6.98 (d, $J = 16.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$/ppm = 176.1, 165.4, 149.1, 141.3, 139.5, 134.6, 130.4, 129.1, 127.8, 112.5. Spectral data are in agreement with literature values.$^7$

2-(2,4-Dichlorophenyl)oxazole-5-carbaldehyde (5n). Compound 5n was prepared according to the general procedure and isolated as a white solid (85 mg, 70% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1); mp = 103–105 °C, (ref., mp = 120–121 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 9.86 (s, 1H), 8.07 (d, $J = 8.5$ Hz, 1H), 8.00 (s, 1H), 7.56 (d, $J = 1.7$ Hz, 1H), 7.39 (dd, $J = 8.5$, 1.8 Hz, 1H). $^{13}$C
NMR (100 MHz, CDCl₃): δ/ppm = 176.45, 162.3, 149.7, 138.4, 137.9, 134.3, 132.4, 131.5, 127.7, 123.3. Spectral data are in agreement with literature values.⁸

2-(3,4,5-Trimethoxyphenyl)oxazole-5-carbaldehyde (5o). Compound 5o was prepared according to the general procedure and isolated as a white solid (110 mg, 84% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1); mp = 128–130 °C. ¹H NMR (400 MHz, CDCl₃): δ/ppm = 9.79 (s, 1H), 7.93 (s, 1H), 7.40 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm = 176.1, 165.5, 153.7, 149.6, 141.8, 139.6, 120.9, 104.9, 61.1, 56.4. IR (KBr): 2951, 2828, 1683, 1593, 1489, 1416, 1236, 1125, 1002, 858, 781, 740 cm⁻¹. HRMS–ESI: calc. for [C₁₃H₁₃NO₅+H]⁺: m/z = 264.0872, found: 264.0871.

2-(2'-(5-Formyloxazol-2-yl)-[1,1'-biphenyl]-2-yl)oxazole-4-carbaldehyde (5p). Compound 5p was prepared according to the general procedure and isolated as a yellow solid (132 mg, 77% yield) after flash chromatography (petroleum ether/ethyl acetate = 2/1); mp = 35–36 °C. ¹H NMR (400 MHz, CDCl₃): δ/ppm = 9.53 (s, 2H), 8.17 (dd, J = 7.6, 1.5 Hz, 2H), 7.64 (s, 2H), 7.62 – 7.53 (m, 4H), 7.35 (dd, J = 7.3, 1.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm = 175.2, 163.9, 148.2, 140.0, 136.8, 130.5, 130.0, 128.5, 127.2, 124.2. IR (KBr): 2847, 1683, 1523, 1431, 1146, 985, 780, 752, 719, 619 cm⁻¹. HRMS–ESI: calc. for [C₂₀H₁₂N₂O₄+H]⁺: m/z = 345.0875, found: 345.0870.

2-Benzylloxazole-5-carbaldehyde (5q). Compound 5q was prepared according to the general procedure and isolated as a colourless oil (74 mg, 79% yield) after flash chromatography (petroleum ether/ethyl acetate = 8/1). ¹H NMR (400 MHz, CDCl₃): δ/ppm = 9.72 (s, 1H), 7.77 (s, 1H), 7.36 – 7.30 (m, 5H), 4.21 (s, 2H). ¹³C NMR (100
MHz, CDCl$_3$): δ/ppm= 175.4, 166.9, 149.1, 136.8, 132.8, 128.0, 127.9, 126.6, 33.9. Spectral data are in agreement with literature values.$^2$

2-Cyclohexyloxazole-5-carbaldehyde (5r). Compound 5r was prepared according to the general procedure and isolated as a colourless oil (76 mg, 85% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1). $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 9.71 (s, 1H), 7.75 (s, 1H), 2.90 (tt, $J = 11.4, 3.7$ Hz, 1H), 2.12 – 2.06 (m, 2H), 1.85 – 1.80 (m, 2H), 1.63 (dd, $J = 12.3, 3.0$ Hz, 2H), 1.42 – 1.35 (m, 2H), 1.29 (dt, $J = 11.9, 3.0$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm= 175.6, 172.1, 148.5, 137.0, 36.8, 29.2, 28.5, 24.7, 24.5, 24.4. IR (KBr): 3330, 2933, 1688, 1628, 1525, 1450, 1140, 982, 839, 762, 661 cm$^{-1}$. HRMS–ESI: calc. for [C$_{10}$H$_{13}$NO$_2$]+: m/z = 180.1025, found: 180.1023.

(S)-Tert-butyl (1-(5-formyloxazol-2-yl)-2-phenylethyl)carbamate (5s). Compound 5s was prepared according to the general procedure and isolated as a white solid (112 mg, 71% yield) after flash chromatography (petroleum ether/ethyl acetate = 4/1); mp = 71-73 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 9.67 (s, 1H), 7.69 (s, 1H), 7.18 (t, $J = 7.4$ Hz, 3H), 6.97 (d, $J = 6.0$ Hz, 2H), 5.09 (d, $J = 8.3$ Hz, 1H), 3.21 – 3.14 (m, 1H), 2.02 – 1.83 (m, 1H), 1.67 – 1.48 (m, 1H), 1.34 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm= 175.4, 167.1, 153.8, 148.9, 136.1, 134.2, 128.2, 127.7, 126.3, 79.5, 38.9, 32.8, 27.2. Spectral data are in agreement with literature values.$^9$

2-((R)-3-((5S,8R,9S,10S,13R,14S,17R)-10,13-Dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)butyl)oxazole-5-carbaldehyde (5t). Compound 5t was prepared according to the general procedure and isolated as a white
solid (163 mg, 72% yield) after flash chromatography (petroleum ether/ethyl acetate = 1/2); mp = 179–181 °C. 1H NMR (400 MHz, CDCl3): δ/ppm= 9.72 (s, 1H), 7.76 (s, 1H), 2.94 (dd, J = 9.8, 5.5 Hz, 2H), 2.89 (t, J = 5.9 Hz, 1H), 2.86 – 2.81 (m, 2H), 2.36 (dd, J = 12.6, 5.1 Hz, 2H), 2.32 – 2.29 (m, 2H), 2.25 (t, J = 5.0 Hz, 2H), 2.15 (t, J = 6.2 Hz, 2H), 2.08 (dd, J = 6.2, 2.4 Hz, 1H), 2.06 – 2.03 (m, 2H), 1.98 (dd, J = 7.1, 3.0 Hz, 1H), 1.94 (dd, J = 4.9, 3.0 Hz, 1H), 1.87 (dd, J = 11.2, 7.1 Hz, 1H), 1.66 – 1.60 (m, 2H), 1.40 (s, 3H), 1.34 (dd, J = 6.3, 3.3 Hz, 1H), 1.30 (dd, J = 8.9, 5.6 Hz, 2H), 1.07 (s, 3H), 0.92 (d, J = 6.7 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ/ppm= 210.8, 208.0, 207.6, 175.3, 169.3, 148.8, 137.0, 55.9, 50.7, 48.0, 45.8, 44.5, 44.0, 41.8, 37.6, 35.5, 35.0, 34.7, 34.3, 31.3, 26.7, 24.8, 24.1, 20.9, 17.6, 10.8. IR (KBr): 3433, 2966, 1707, 1528, 1388, 1271, 1138, 772, 620, 526 cm⁻¹. HRMS–ESI: calc. for [C27H35NO5+H]+: m/z = 454.2593, found: 454.2586.

7. Derivatizations of aldehyde 5a.

2-Phenyloxazole-5-carbonitrile (6). To compound 5a (87 mg, 0.5 mmol) in toluene (2 mL) at room temperature was added DPPH (233 mg, 1 mmol) in one portion. The resulting suspension was stirred at room temperature for 3 h and then gradually warmed over 45 min to 90 °C. The reaction mixture became clear as the temperature reached 90 °C. After being heated at 90 °C for 7 h, the reaction was allowed to cool to room temperature and then diluted by addition of CH2Cl2 (20 mL) and a saturated aqueous NaHCO3 (20 mL). The aqueous layer was extracted with CH2Cl2 (3×20 ml). All of the organic layers were combined and then dried over Na2SO4. The solvents were removed by rotary evaporation, and the crude residue was purified by column
chromatography (SiO$_2$, petroleum ether/ethyl acetate = 10/1) to afford compound 6 (70 mg, 82% yield) as a white solid. mp = 92–93 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ/ppm= 8.14 – 8.03 (m, 2H), 7.82 (s, 1H), 7.60 – 7.46 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ/ppm= 164.9, 139.1, 132.3, 129.2, 127.4, 125.6, 124.2, 109.5. Spectral data are in agreement with literature values.\(^{10}\)

**2-Phenyloxazole-5-carboxylic acid (8).** The aldehyde 5a (87 mg, 0.5 mmol) was dissolved in the mixture of t-BuOH (5 mL), acetonitrile (5 mL) and 2-methyl-1-butene (2 mL). The mixture was cooled to 0 °C followed by addition of a newly prepared solution of NaH$_2$PO$_4$ (240 mg) and NaClO$_2$ (200 mg) in water (8 mL). The mixture was then slowly warmed to room temperature before it was quenched with saturated Na$_2$S$_2$O$_3$. The aqueous layer was extracted with EtOAc (5 x 10 mL), and the combined organic layers were dried over Na$_2$SO$_4$, filtered, and evaporated to give a residue, which was chromatographed (CH$_2$Cl$_2$/MeOH = 10/1) to give acid 8 (68 mg, 72%) as a white solid. mp= 212–214 °C. $^1$H NMR (400 MHz, DMSO-d$_6$): δ/ppm= 8.01–7.98 (m, 2H), 7.56–7.52 (m, 4H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ/ppm= 162.0, 150.5, 131.8, 131.5, 130.2, 128.2, 127.2, 126.9. Spectral data are in agreement with literature values.\(^{10}\)

**2-Phenyloxazol-5-yl)methanol (7).** To compound 5a (87 mg, 0.5 mmol) in MeOH (20 mL) at room temperature was added NaBH$_4$ (38 mg, 1 mmol) and the mixture was stirred overnight. The resulting mixture was treated with water (20 mL), 1 M NaOH (20 mL) and then was extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated. The resulting residue was chromatographed (petroleum ether/ethyl acetate = 1/1) to give 7 (81 mg, 92%) as a white solid. mp = 90–
92 °C, (ref,\textsuperscript{11} mp = 74.5–76.0 °C). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ/ppm= 8.03 (dd, J = 6.6, 3.0 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.10 (s, 1H), 4.74 (s, 2H), 1.64 (s, 1H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ/ppm= 162.1, 150.8, 130.5, 128.8, 127.3, 126.4, 126.1, 55.3. Spectral data are in agreement with literature values.\textsuperscript{11}

4-Chloro-N-((2-phenyloxazol-5-yl)methyl)aniline (9). A solution of 5a (87 mg, 0.5 mmol) and 4-chloroaniline (64 mg, 0.5 mmol) in MeOH (20 mL) was stirred at room temperature for 2 h, then treated with NaBH\textsubscript{4} (38 mg, 1 mmol) and the mixture was stirred overnight. The resulting mixture was treated with water (20 mL), 1 M NaOH (20 mL) and then was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 30 mL). The combined organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated. The resulting residue was chromatographed (petroleum ether/ethyl acetate = 4/1) to give 9 (126 mg, 89%) as a white solid. mp = 79–81 °C, (ref,\textsuperscript{8} mp = 98–99 °C). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ/ppm= 8.00 (dd, J = 6.7, 2.9 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.16 (d, J = 8.7 Hz, 2H), 7.05 (s, 1H), 6.63 (d, J = 8.8 Hz, 2H), 4.42 (s, 2H), 4.10 (s, 1H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ/ppm= 161.7, 149.3, 145.7, 130.4, 129.2, 128.8, 127.4, 126.3, 125.7, 123.2, 114.3, 39.5. Spectral data are in agreement with literature values.\textsuperscript{8}

8. References

9. Copies of NMR spectra

\[^1\text{H NMR (400 MHz, CDCl}_3\text{)}\] of 2a

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}\] of 2a
$^1$H NMR (400 MHz, CDCl$_3$) of 2b

$^{13}$C NMR (100 MHz, CDCl$_3$) of 2b
\(^1\text{H NMR (400 MHz, CDCl}_3\text{) of 2c}\)

\(^{13}\text{C NMR (100 MHz, CDCl}_3\text{) of 2c}\)
$^1$H NMR (400 MHz, CDCl$_3$) of 2d

$^{13}$C NMR (100 MHz, CDCl$_3$) of 2d
$^1$H NMR (400 MHz, CDCl$_3$) of 2e

$^{13}$C NMR (100 MHz, CDCl$_3$) of 2e
$^{1}$H NMR (400 MHz, CDCl$_3$) of 2f

$^{13}$C NMR (100 MHz, CDCl$_3$) of 2f
$^1$H NMR (400 MHz, CDCl$_3$) of 2g

$^{19}$F NMR (376 MHz, CDCl$_3$) of 2g
\(^{13}\text{C NMR (100 MHz, CDCl}_3\text{) of 2g}\)

\(^{1}\text{H NMR (400 MHz, CDCl}_3\text{) of 2h}\)
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2h

$^1$H NMR (400 MHz, CDCl$_3$) of 2i
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2i

$^1$H NMR (400 MHz, CDCl$_3$) of 2j
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2j

$^1$H NMR (400 MHz, CDCl$_3$) of 2k
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2k

$^1$H NMR (400 MHz, CDCl$_3$) of 2l
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2l

$^1$H NMR (400 MHz, CDCl$_3$) of 2m
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2m

$^1$H NMR (400 MHz, CDCl$_3$) of 2n
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2n

$^1$H NMR (400 MHz, CDCl$_3$) of 2o
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2p

$^1$H NMR (400 MHz, CDCl$_3$) of 2q
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2q

$^1$H NMR (400 MHz, CDCl$_3$) of 2r
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2r

$^1$H NMR (400 MHz, CDCl$_3$) of 2s
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2s

$^1$H NMR (400 MHz, CDCl$_3$) of 2t
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2t

$^1$H NMR (400 MHz, CDCl$_3$) of 2u
^13C NMR (100 MHz, CDCl3) of 2u

^1H NMR (400 MHz, CDCl3) of 2v
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2v

$^1$H NMR (400 MHz, CDCl$_3$) of 2w
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2w

$^1$H NMR (400 MHz, CDCl$_3$) of 2x
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2x

$^1$H NMR (400 MHz, CDCl$_3$) of 2y
$^{13}$C NMR (100 MHz, CDCl$_3$) of $2y$

$^1$H NMR (400 MHz, CDCl$_3$) of $2z$
$^{13}$C NMR (100 MHz, CDCl$_3$) of 2x

$^1$H NMR (400 MHz, CDCl$_3$) of 3
$^{13}$C NMR (100 MHz, CDCl$_3$) of 3

$^1$H NMR (400 MHz, CDCl$_3$) of 4
$^{13}$C NMR (100 MHz, CDCl$_3$) of 4

NOE of 4
$^1$H NMR (400 MHz, CDCl$_3$) of 5a

$^{13}$C NMR (100 MHz, CDCl$_3$) of 5a
^1H NMR (400 MHz, CDCl3) of 5b

^13C NMR (100 MHz, CDCl3) of 5b
$^1$H NMR (400 MHz, CDCl$_3$) of 5c

$^{13}$C NMR (100 MHz, CDCl$_3$) of 5c
$^1$H NMR (400 MHz, CDCl$_3$) of 5d

$^{13}$C NMR (100 MHz, CDCl$_3$) of 5d
$^1$H NMR (400 MHz, CDCl$_3$) of 5e

$^{19}$F NMR (376 MHz, CDCl$_3$) of 5e
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5e

$^1$H NMR (400 MHz, CDCl$_3$) of 5f
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5f

$^1$H NMR (400 MHz, CDCl$_3$) of 5g
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5g

$^1$H NMR (400 MHz, CDCl$_3$) of 5h
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5h

$^1$H NMR (400 MHz, CDCl$_3$) of 5i
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5i

$^1$H NMR (400 MHz, CDCl$_3$) of 5j
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5j

$^1$H NMR (400 MHz, CDCl$_3$) of 5k
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5k

$^1$H NMR (400 MHz, CDCl$_3$) of 5I
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5I

$^1$H NMR (400 MHz, CDCl$_3$) of 5m
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5m

$^1$H NMR (400 MHz, CDCl$_3$) of 5n
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5n

$^1$H NMR (400 MHz, CDCl$_3$) of 5o
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5e

$^1$H NMR (400 MHz, CDCl$_3$) of 5p
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5p

$^1$H NMR (400 MHz, CDCl$_3$) of 5q
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5q

$^1$H NMR (400 MHz, CDCl$_3$) of 5r
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5r

$^1$H NMR (400 MHz, CDCl$_3$) of 5s
$^{13}$C NMR (100 MHz, CDCl$_3$) of 5s

$^1$H NMR (400 MHz, CDCl$_3$) of 5t
$^1$H NMR (400 MHz, CDCl$_3$) of 6

$^1$C NMR (100 MHz, CDCl$_3$) of 5t
$^{13}$C NMR (100 MHz, CDCl$_3$) of 6

$^1$H NMR (400 MHz, CDCl$_3$) of 7
$^{13}$C NMR (100 MHz, CDCl$_3$) of 7

$^{1}$H NMR (400 MHz, DMSO-d$_6$) of 8
$^{13}$C NMR 100 MHz, DMSO-$d_6$ of 8

$^1$H NMR (400 MHz, CDCl$_3$) of 9