Supporting Information

Efficient Microwave-Assisted Synthesis of Aminoxy Acid Conjugates

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General procedure for the synthesis of N-Cbz-protected α-aminoxy acids 3a-d, (3c+3c'). NaH (2 equiv) was added portionwise to a stirring solution of benzylhydroxycarbamate (1 equiv) in THF under argon atmosphere. The resulting reaction mixture was stirred at -20°C for 15 min. A solution of the respective α-bromo carboxylic acid (1 equiv) in THF (3 mL) was added dropwise. The resulting reaction mixture was allowed to warm up to rt and stirred for additional 8h. The solvent was removed under reduced pressure. The resulting residue was washed with hexanes (2 x 20 mL) followed by hexanes:diethyl ether (1:1, 2 x 20 mL) The resulting residue was dissolved in water, acidified to pH = 3 (4N HCl) and extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over MgSO₄, the organic solvent was removed under reduced pressure to give the corresponding N-Cbz-protected α-aminoxy acids 3a-d, (3c+3c'), which were used without further purification.

Compound 2a was purchased from Sigma Aldrich Inc. and was used without any further purification. Compounds 2b-d, (2c+2c') were prepared from commercially available α-amino acids according to literature procedure (2).

2-(((Benzyloxy)carbonyl)amino)oxy)acetic acid (3a). White solid, mp 68.0 - 69.0 °C, lit. mp 67.0 – 67.8 °C (1), 53% yield. ¹H-NMR (300 MHz, CDCl₃) δ, 8.37 (br s, 1H), 7.36 (br s, 5H), 5.21 (s, 2H), 4.49 (s, 2H). ¹³C-NMR (75 MHz, CDCl₃) δ, 172.8, 158.7, 135.0, 129.0, 128.9, 128.7, 73.7, 68.7.

(R)-2-(((Benzyloxy)carbonyl)amino)oxy)propanoic acid (3b). White solid, mp 82.0 – 85.0 °C, 59% yield. ¹H-NMR (300 MHz, CDCl₃) δ, 8.95 (br s, 1H), 8.52 (br s, 1H), 7.43 – 7.28 (m, 5H), 5.18 (s, 2H), 4.50 (q, J = 7.1 Hz, 1H), 1.48 (d, J = 7.1 Hz, 3H). ¹³C-NMR
(75 MHz, CDCl$_3$) $\delta$, 176.2, 158.4, 135.2, 128.8, 128.5, 80.3, 68.3, 16.4. Anal. Calcd for. C$_{11}$H$_{13}$NO$_5$: C 55.23; H 5.48; N 5.85. Found C 55.16; H 5.46; N 5.71.

(R)-2-(((Benzyloxy)carbonyl)amino)oxy)-3-phenylpropanoic acid (3c). Yellow oil, 47% yield. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$, 10.22 (br s, 1H), 8.64 (br s, 1H), 7.31 – 7.28 (m, 3H), 7.20 – 7.17 (m, 7H), 5.05 (s, 2H), 4.60 (dd, $J = 8.5$, 4.1 Hz, 1H), 3.16 (dd, $J = 14.9$, 4.1 Hz, 1H), 3.00 (dd, $J = 14.9$, 8.5 Hz, 1H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$, 174.2, 158.3, 135.7, 134.8, 129.1, 128.4, 128.2, 128.1, 126.8, 84.8, 68.0, 36.9.

(R,S)-2-(((Benzyloxy)carbonyl)amino)oxy)-3-phenylpropanoic acid (3c+3c'). Yellow oil, 53% yield. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$, 8.18 (br s, 1H), 7.41 – 7.20 (m, 10H), 5.13 (s, 2H), 4.61 (dd, $J = 8.9$, 3.7 Hz, 1H), 3.26 (dd, $J = 14.7$, 3.8 Hz, 1H), 3.04 (dd, $J = 14.7$, 8.9 Hz, 1H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$, 173.9, 158.8, 147.6, 129.5, 129.2, 128.9, 128.7, 128.6, 127.2, 86.1, 68.7, 37.4.

(R)-2-(((Benzyloxy)carbonyl)amino)oxy)-4-methylpentanoic acid (3d). Yellow oil, 61% yield. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$, 8.66 (s, 1H), 7.36 – 7.34 (m, 5H), 7.05 (br s, 2H), 5.16 – 5.10 (m, 2H), 4.42 (dd, $J = 9.9$, 3.8 Hz, 1H), 1.90 – 1.67 (m, 1H), 1.61 – 1.51 (m, 1H), 0.94 – 0.87 (m, 6H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$, 176.1, 158.1, 135.2, 128.7, 128.5, 123.3, 82.8, 68.1, 68.0, 39.8, 24.6, 23.2, 21.5. Anal. Calcd. for C$_{14}$H$_{19}$NO$_5$: C 59.78; H 6.81; N 4.98. Found C 59.47; H 7.22; N 5.10.
General procedure for N-Cbz-protected (α-aminoxyacyl)benzotriazoles 4a-d, (4c+4c'). Thionyl chloride (1 equiv) was added dropwise to a stirred solution of benzotriazole (3 equiv) in THF (20 mL). The resulting mixture was stirred at rt. for 30 min under argon. The N-Cbz-protected α-aminoxy acids 3a-d, (3c+3c') (1 equiv) were each added portionwise and the resulting reaction mixtures were stirred at rt for additional 4h. Each precipitate was filtered off and the solvent removed under reduced pressure to give oils that were redissolved in diethylether (10 mL), washed with water (20 mL) and Na$_2$CO$_3$ (10% solution, 2 x 20 mL), and the solvent evaporated to give a colorless oils which were crystallized from diethylether:hexane (1:2) to give N-Cbz-protected (α-aminoxyacyl)benzotriazoles 4a-d, (4c+4c').

**Benzyl 2-(1H-benzotriazol-1-yl)-2-oxoethoxycarbamate (4a).** White solid, mp 88.0 - 90.0 °C, lit. mp 86.0 – 87.0 °C (J), 76% yield. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$, 8.25 (ddd, $J = 8.2, 0.9, 0.9$ Hz, 1H), 8.14 (ddd, $J = 8.2, 0.9, 0.9$ Hz, 1H), 7.69 (ddd, $J = 8.3, 7.2, 1.0$ Hz, 1H), 7.69 (ddd, $J = 8.3, 7.4, 1.0$ Hz, 1H), 7.54 (ddd, $J = 8.3, 7.1, 1.0$ Hz, 1H), 7.38 – 7.35 (m, 5H), 5.55 (s, 2H), 5.22 (s, 2H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$, 168.1, 157.1, 146.0, 135.3, 131.1, 130.9, 128.8, 128.7, 128.5, 126.8, 120.6, 114.1, 74.7, 68.1.

**(R)-Benzyl (1-(1H-benzotriazol-1-yl)-1-oxopropan-2-yl)oxycarbamate (4b).** White prisms, 88.5 – 91.0 °C, 77% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.23 (dd, $J = 8.3, 1.0$ Hz, 1H), 8.15 (dd, $J = 8.3, 1.0$ Hz, 1H), 7.91 (s, 1H), 7.70 (ddd, $J = 8.2, 7.1, 1.0$ Hz, 1H), 7.55 (ddd, $J = 8.2, 7.1, 1.0$ Hz, 1H), 7.26 – 7.36 (m, 5H), 5.94 (q, $J = 6.9$ Hz, 1H), 5.19 (s, 2H), 1.77 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 171.2, 157.3, 146.0, 135.4, 131.2, 131.0, 128.8, 128.7, 128.5, 126.8, 120.6, 114.4, 80.8, 68.0, 17.2., Anal. Calcd. for C$_{17}$H$_{16}$N$_4$O$_4$, C, 60.00; H, 4.74; N, 16.46. found C, 59.93; H, 4.54; N, 16.36.
**(R)-Benzyl(1-((1H-benzotriazol-1-yl)-1-oxo-3-phenylpropan-2-yl)oxycarbamate**

(4c). White prisms, mp 90.0 – 91.0 °C, 88% yield. $^1$H-NMR (300 MHz, CDCl$_3$) δ, 8.28 (ddd, J = 8.2, 0.8, 0.8 Hz, 1H), 8.14 (ddd, J = 8.2, 0.8, 0.8 Hz, 1H), 7.79 (s, 1H), 7.68 (ddd, J = 8.2, 7.5, 0.8 Hz, 1H), 7.54 (ddd, J = 8.2, 7.5, 0.8 Hz, 1H), 7.32 – 7.19 (m, 10H), 6.14 (dd, J = 7.8, 4.3 Hz, 1H), 5.11 (s, 2H), 3.47 (dd, J = 14.7, 4.3 Hz, 1H), 3.36 (dd, J = 14.7, 7.8 Hz, 1H). $^{13}$C-NMR (75 MHz, CDCl$_3$) δ, 169.7, 157.2, 146.0, 135.3, 135.3, 131.0, 129.5, 128.7, 128.6, 128.4, 127.3, 126.8, 120.5, 114.3, 85.1, 68.0, 37.8. Anal. Calcd. for C$_{23}$H$_{20}$N$_4$O$_4$: C 66.34; H 4.84; N 13.43. Found C 66.44; H 5.06; N 13.98.

**(R,S)-Benzyl(1-((1H-benzotriazol-1-yl)-4-methyl-1-oxopentan-2-yl)oxycarbamate**

(4d). Colorless oil, 86% yield. $^1$H-NMR (300 MHz, CDCl$_3$) δ, 8.28 (dd, J = 8.2, 1.0 Hz, 1H), 8.13 (dd, J = 8.1, 1.1 Hz, 1H), 8.10 (s, 1H), 7.66 (ddd, J = 8.2, 7.2, 1.1 Hz, 1H), 7.53 (ddd, J = 8.2, 7.2, 1.1 Hz, 1H), 7.50 – 7.30 (m, 5H), 5.94 (dd, J = 9.8, 3.1 Hz, 1H), 5.18 (s, 2H), 2.18 – 2.08 (m, 1H), 1.94 – 1.80 (m, 2H), 1.10 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$) δ, 171.3, 157.4, 146.0, 135.3, 131.2, 131.0,
128.7, 128.7, 128.6, 126.6, 120.4, 114.5, 83.5, 68.0, 40.5, 25.0, 23.4, 21.4. Anal. Calcd. for C$_{20}$H$_{22}$N$_4$O$_4$: C 62.82; H 5.80; N 14.65. Found C 62.63 H 5.90; N 14.18.
(R)-((3aR,5R,5aS,8aS,8bR)-2,2,7,7-Tetramethyltetrahydro-3aH-bis[1,3]dioxolo[4,5-b:4',5'-d]pyran-5-yl)methyl 2-(benzoyloxycarbaminoxy)propanoate (6b). Colorless oil, 71% yield, \([\alpha]_D^{21} = +20.2\) (c 0.14 in CH$_2$Cl$_2$). Anal. Calcd. for C$_{23}$H$_{31}$NO$_{10}$: C 57.37; H 6.49; N 2.91. Found C 57.48; H 6.76; N 2.81.

$^1$H-NMR (300 MHz, CDCl$_3$) \(\delta\), 8.20 (s, 1H), 7.37-7.32 (m, 5H), 5.54 (d, \(J = 5.0\) Hz, 1H), 5.21-5.12 (m, 2H), 4.62 (dd, \(J = 7.7, 2.5\) Hz, 1H), 4.54 (q, \(J = 7.0\) Hz, 1H), 4.47 (dd, \(J = 11.4, 4.4\) Hz, 1H), 4.33 (dd, \(J = 5.0, 2.5\) Hz, 1H), 4.27-4.17 (m, 2H), 4.06-4.00 (m, 1H), 1.48 (d, \(J = 7.0\) Hz, 1H), 1.45 (s, 3H), 1.43 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$) \(\delta\), 172.0, 157.1, 135.7, 128.8, 128.6, 128.5, 110.1, 109.2, 96.5, 80.5, 71.1, 71.0, 70.5, 67.8, 65.9, 63.9, 26.1, 26.0, 25.0, 24.6, 16.4.

(R)-((3aR,5R,6S,6aR)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl) 2-(benzyloxycarbaminoxy)-4-methylpentanoate (6c). Colorless oil, 60% yield, \([\alpha]_D^{21} = +32.5\) (c 0.24 in CH$_2$Cl$_2$). Anal. Calcd for C$_{26}$H$_{37}$NO$_{10}$: C 59.64; H 7.12; N 2.68. Found: C 59.43; H 7.33; N 2.59. $^1$H-NMR (300 MHz, CDCl$_3$) \(\delta\), 8.81 (s, 1H), 7.41-7.29 (m, 5H), 5.89 (d, \(J = 3.8\) Hz, 1H), 5.23-5.05 (m, 3H), 4.56-4.50 (m, 2H), 4.35-4.29 (m, 1H), 4.22 (dd, \(J = 9.0, 3.6\) Hz, 1H), 4.14 (dd, \(J = 9.0, 5.7\) Hz, 1H), 4.07 (dd, \(J = 9.0, 3.3\) Hz, 1H), 2.03-1.63 (m, 2H), 1.53 (s, 3H), 1.51-1.42 (m, 1H), 1.34 (s, 3H), 1.32 (s, 3H), 1.23 (s, 3H), 1.01-0.91 (m, 6H). $^{13}$C-NMR (75 MHz, CDCl$_3$) \(\delta\), 171.4, 156.7, 135.6, 128.7, 112.6, 110.2, 105.4, 84.0, 83.7, 80.3, 77.7, 73.0, 68.0, 67.8, 39.6, 27.0, 26.5, 24.9, 24.8, 23.2, 21.9.

(R)-((3aR,5R,6S,6aR)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl) 2-(benzyloxycarbaminoxy)-3-phenylpropanoate (6d). Colorless oil, 68% yield, \([\alpha]_D^{21} = +13.1\) (c 0.18 in CH$_2$Cl$_2$). Anal.
Calcd for C_{29}H_{35}NO_{10}: C 62.47; H 6.33; N 2.51. Found: C 62.51; H 6.43; N 2.48. ¹H-NMR (300 MHz, CDCl₃) δ, 8.86 (s, 1H), 7.37-7.23 (m, 10H), 5.62 (d, J = 3.5 Hz, 1H), 5.16 (d, J = 12.0 Hz, 1H), 5.08 (d, J = 12.0 Hz, 1H), 5.02 (d, J = 3.4 Hz, 1H), 4.80 (dd, J = 6.7, 5.2 Hz, 1H), 4.29-4.02 (m, 5H), 3.24-3.06 (m, 2H), 1.49 (s, 3H), 1.32 (s, 3H), 1.28 (s, 3H), 1.21 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃) δ, 169.8, 156.7, 135.5, 135.3, 129.7, 128.7, 128.5, 127.3, 112.5, 105.3, 85.4, 83.3, 80.2, 77.8, 73.2, 67.9, 67.8, 37.0, 27.0, 26.4, 24.7.

(R)-(3aR,5R,5aS,8aS,8bR)-2,2,7,7-Tetramethyltetrahydro-3aH-bis[1,3]dioxolo[4,5-b:4′,5′-d]pyran-5-yl)methyl 2-(benzyl-oxycarbonylaminoxy)-3-phenylpropanoate (6e). Colorless oil, 84% yield, [α]_{D}^{21} = +12.3 (c 0.20 in CH₂Cl₂). Anal. Calcd for C_{29}H_{35}NO_{10}: C 62.47; H 6.33; N 2.51. Found: C 62.52; H 6.36; N 2.38. ¹H-NMR (300 MHz, CDCl₃) δ, 8.18 (s, 1H), 7.39-7.18 (m, 10H), 5.53 (d, J = 5.1 Hz, 1H), 5.17-5.02 (m, 2H), 4.69 (t, J = 6.4 Hz, 1H), 4.60 (dd, J = 7.8, 2.6 Hz, 1H), 4.39 (dd, J = 11.3, 5.1 Hz, 1H), 4.32 (ddd, J = 5.0, 2.6, 0.6 Hz, 1H), 4.25-4.12 (m, 2H), 4.03-3.94 (m, 1H), 3.19-3.06 (m, 2H), 1.45 (s, 3H), 1.43 (s, 3H), 1.31 (s, 3H), 1.25 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃) δ, 170.7, 157.0, 135.9, 135.6, 129.5, 128.7, 128.6, 127.1, 110.0, 109.2, 96.5, 85.2, 71.0, 70.9, 70.5, 67.7, 65.7, 63.8, 37.2, 26.1, 26.0, 25.0, 24.7.

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-Tetramethyltetrahydro-3aH-bis[1,3]dioxolo[4,5-b:4′,5′-d]pyran-5-yl)methyl 2-(benzoyloxy-carbonylaminoxy)-3-phenylpropanoate (6e + 6e'). Colorless oil, 65% yield, [α]_{D}^{21} = -14.1 (c 0.18 in CH₂Cl₂). Anal. Calcd for C_{29}H_{35}NO_{10}: C 62.47; H 6.33; N 2.51. Found: C 62.47; H 6.73; N 2.31. ¹H-NMR (300 MHz, CDCl₃) δ, 8.21 (s, 0.6H), 8.14 (s, 0.4H), 7.32-7.24 (m, 10H), 5.58-5.48 (m, 1H), 5.18-5.04 (m, 2H), 4.75-4.55 (m, 2H), 4.48-3.96 (m, 5H), 3.18-3.10 (m, 2H), 1.50-1.40
(m, 6H), 1.32-1.24 (m, 6H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$, 170.7, 170.7, 157.0, 135.9, 135.7, 135.6, 129.5, 128.7, 128.5, 128.3, 127.0, 110.0, 109.2, 109.0, 96.5, 85.1, 84.7, 70.9, 70.9, 70.6, 70.4, 67.7, 67.6, 66.0, 65.6, 64.0, 63.7, 37.1, 37.0, 26.1, 25.9, 25.0, 24.6. 

(R)-(R)-2-Hydroxy-2-((3aR,5R,6S,6aR)-6-hydroxy-2,2-dimethyltetrahydro-furo[3,2-d][1,3]dioxol-5-yl)ethyl 2-(benzyloxy carbonylaminoxy)propanoate (6f). White microcrystals, mp 112.0-115.0 °C, 62% yield, $[\alpha]_{D}^{21} = +43.3$ (c 0.13 in CH$_2$Cl$_2$). Anal. Calcd for C$_{20}$H$_{27}$NO$_{10}$: C 54.42; H 6.16; N 3.17. Found: C 54.46; H 6.22; N 3.00. $^{1}$H-NMR (300 MHz, DMSO-$d_6$) $\delta$, 10.50 (s, 1H), 7.40-7.30 (m, 5H), 5.79 (d, $J = 3.5$ Hz, 1H), 5.27 (d, $J = 4.5$ Hz, 1H), 5.14-5.04 (m, 3H), 4.43-4.26 (m, 3H), 4.07-3.84 (m, 4H), 1.36 (s, 3H), 1.33 (d, $J = 6.9$ Hz, 3H), 1.22 (s, 3H). $^{13}$C-NMR (75 MHz, DMSO-$d_6$) $\delta$, 171.1, 157.1, 136.2, 128.4, 128.0, 127.9, 110.6, 104.5, 84.6, 80.2, 79.1, 72.8, 67.3, 66.1, 65.1, 26.7, 26.2, 16.3.
(R,Z)-3,7-Dimethylocta-2,6-dien-1-yl 2-(((benzyloxy)-carbonyl)amino)oxy)-propanoate (8a). Colorless oil, 60% yield, $[\alpha]_D^{21} = +91.0$ (c 0.22 in CH$_2$Cl$_2$). HRMS calcd. for [C$_{21}$H$_{29}$NO$_5$+Na]$^+$= 398.1938, found = 398.1949. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$, 8.11 (s, 1H), 7.35-7.33 (m, 5H), 5.34 (t, $J = 7.7$ Hz, 1H), 5.58 (d, $J = 12.3$ Hz, 1H), 5.10-5.06 (m, 1H), 4.64 (d, $J = 7.6$ Hz, 2H), 4.50 (q, $J = 7.0$ Hz, 1H), 2.10-2.05 (m, 4H), 1.76 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.45 (d, $J = 7.0$ Hz, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$, 172.2, 157.1, 143.4, 135.6, 132.3, 128.6, 128.4, 128.3, 123.5, 118.6, 79.8, 67.5, 61.9, 32.2, 26.6, 25.7, 23.5, 17.7, 16.3.

(R,S)-(E)-3,7-Dimethylocta-2,6-dien-1-yl 2-(((benzyloxy) carbonyl)amino)oxy)-3-phenylpropanoate (8b+8b'). Colorless oil, 54% yield, $[\alpha]_D^{21} = +0.01$ (c 1.96 in CH$_2$Cl$_2$). Anal. Calcd for C$_{27}$H$_{33}$NO$_5$: C 71.82; H 7.37; N 3.10. Found: C 72.15; H 7.75; N 3.25. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$, 7.78 (s, 1H), 7.37-7.28 (m, 5H), 7.28-7.18 (m, 5H), 5.24 (t, $J = 7.2$ Hz, 1H), 5.15 (d, $J = 12.1$ Hz, 1H), 5.10 (d, $J = 12.1$ Hz, 1H), 5.10-5.04 (m, 1H), 4.67 (dd, $J = 7.0$, 5.2 Hz, 1H), 4.62 (d, $J = 7.2$ Hz, 2H), 3.16 (dd, $J = 12.1$, 4.9 Hz, 1H), 3.09 (dd, $J = 12.5$, 5.1 Hz, 1H), 2.10-2.03 (m, 4H), 1.68 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$, 170.9, 157.0, 143.3, 135.8, 135.5, 132.1, 129.5, 128.7, 128.5, 128.4, 127.0, 123.7, 117.6, 84.5, 67.7, 62.3, 39.7, 37.3, 26.4, 25.9, 17.9, 16.7.

(R,E)-2,7-Dimethyloct-2,6-dien-1-yl-2-(((benzyloxy)-carbonyl)amino)oxy)-4-methylpentanoate (8c). Colorless oil, 50% yield, $[\alpha]_D^{21} = +56.8$ (c 0.29 in CH$_2$Cl$_2$). Anal. Calcd for C$_{24}$H$_{35}$NO$_5$: C 69.04; H 8.45; N 3.35. Found: C 68.70; H 8.87; N 3.22. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$, 8.24 (br s, 1H), 7.32 (s, 5H), 5.34 (t, $J = 7.2$ Hz, 1H), 5.18 (d, $J = 12.1$ Hz, 1H), 5.12 (d, $J = 12.3$ Hz, 1H), 5.09-5.08 (m, 1H), 4.63 (d, $J = 7.3$ Hz, 2H),
4.44 (dd, $J = 9.8, 3.8$ Hz, 1H), 2.11-2.10 (m, 6H), 1.99-1.88 (m, 1H), 1.76 (s, 3H), 1.67 (s, 3H), 1.59 (s, 3H), 0.93 (d, $J = 5.7$ Hz, 3H), 0.91 (d, $J = 5.1$ Hz, 3H). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$, 172.3, 157.3, 143.2, 135.7, 132.2, 128.6, 128.4, 123.6, 118.7, 82.7, 67.6, 61.8, 61.2, 39.9, 32.2, 26.7, 25.8, 24.6, 23.6, 23.2, 21.6, 17.7.
(2R)-(10R,13R)-17-((2R,5R)-5-Ethyl-6-methylheptan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca-hydro-1H-cyclopenta[a]phenanthren-3-yl 2-(((benzyloxy)-carbonyl)amino)oxy)propanoate (10a). White microcrystals, mp 102.0-103.0 °C, 22% yield, [α]D21 = +25.3 (c 0.23 in CH2Cl2). Anal. Calcd for C40H61NO5: C 75.55; H 9.67; N 2.20. Found: C 75.36; H 10.04; N 2.13. 1H-NMR (300 MHz, CDCl3) δ, 7.88 (s, 1H), 7.37-7.35 (m, 5H), 5.38 (d, J = 3.8 Hz, 1H), 5.20 (d, J = 12.1 Hz, 1H), 5.15 (d, J = 12.1 Hz, 1H), 4.70-4.67 (m, 1H), 4.47 (q, J = 7.0 Hz, 1H), 2.33 (d, J = 7.7 Hz, 2H), 2.02-1.95 (m, 2H), 1.95-1.61 (m, 2H), 1.61-0.76 (m, 41H), 0.67 (s, 3H). 13C-NMR (75 MHz, CDCl3) δ, 171.6, 157.0, 139.4, 135.6, 128.7, 128.6, 128.4, 123.2, 79.2, 75.2, 67.7, 56.8, 56.2, 50.1, 46.0, 42.5, 39.9, 39.0, 38.4, 37.0, 36.7, 36.3, 36.0, 34.1, 33.9, 32.6, 32.1, 32.0, 30.4, 29.3, 28.4, 27.9, 26.2, 24.4, 23.2, 21.2, 20.4, 20.0, 19.5, 19.2, 18.9, 18.4, 16.4, 15.5, 12.2, 12.0.

(2R)-(10R,13R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca-hydro-1H-cyclo-penta[a]phenanthren-3-yl 2-(((benzyloxy)carbonyl) amino)oxy)-3-phenylpropanoate (10b). White microcrystals, mp 114.0-115.0 °C, 25% yield, [α]D21 = +20.4 (c 0.21 in CH2Cl2). Anal. Calcd for C44H61NO5: C 77.27; H 8.99; N 2.05. Found: C 76.92; H 9.33; N 1.96. 1H-NMR (300 MHz, CDCl3) δ, 7.79 (s, 1H), 7.36-7.31 (m, 5H), 7.28-7.21 (m, 5H), 5.36 (d, J = 4.7 Hz, 1H), 5.16 (d, J = 12.1 Hz, 1H), 5.10 (d, J = 12.1 Hz, 1H), 4.64 (dd, J = 6.8, 5.4 Hz, 1H), 4.59 (dd, J = 8.4, 4.8 Hz, 1H), 3.13 (s, 1H), 3.10 (d, J = 1.6 Hz, 1H), 2.25 (d, J = 7.7 Hz, 2H), 2.07-1.90 (m, 2H), 1.90-1.69 (m, 3H), 1.62-1.10 (m, 17H), 1.00-0.82 (m, 13H), 0.67 (s, 3H). 13C-NMR (75 MHz, CDCl3) δ, 170.4, 157.1, 139.4, 135.9, 135.6, 129.6, 128.7, 128.6, 128.4, 128.4, 127.0, 123.1, 84.5, 75.3, 67.7, 56.8, 56.3, 50.1, 42.4,
39.8, 39.7, 38.1, 37.3, 37.0, 36.7, 36.3, 35.9, 32.0, 32.0, 28.4, 28.2, 27.7, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0.

\((10R,13R)\)-10,13-Dimethyl-17-((\(R\))-6-methylheptan-2-yl)tetradecahydro-1\(H\)-cyclo-penta[\(a\)]phenanthren-3-yl 2-(((benzyloxy)carbonyl)amino)-oxy)-3-phenylpropanoate (10b+10b'). White microcrystals, mp 112.0-114.0 °C, 25% yield, \([\alpha]_{D}^{21} = -14.6\) (c 0.19 in CH\(_2\)Cl\(_2\)). Anal. Calcd for C\(_{44}\)H\(_{61}\)NO\(_5\): C 77.27; H 8.99; N 2.05. Found: C 77.04; H 9.33; N 2.13. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\), 7.76 (s, 0.5H), 7.76 (s, 0.5H), 7.37-7.30 (m, 5H), 7.28-7.21 (m, 5H), 5.36-5.34 (m, 1H), 5.16 (d, \(J = 12.1\) Hz, 1H), 5.10 (d, \(J = 12.2\) Hz, 1H), 4.63 (t, \(J = 6.2\) Hz, 1H), 4.60-4.57 (m, 1H), 3.12 (d, \(J = 6.5\) Hz, 2H), 2.28-1.67 (m, 7H), 1.57-0.85 (m, 33H), 0.67 (s, 3H).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\), 170.4, 157.1, 139.4, 135.9, 135.6, 129.6, 128.6, 128.4, 128.4, 127.0, 123.1, 84.5, 75.4, 67.7, 56.8, 56.3, 50.1, 42.5, 39.9, 39.7, 38.1, 38.0, 37.3, 37.0, 36.7, 36.3, 35.9, 32.0, 31.2, 28.4, 28.2, 27.8, 27.7, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0.

\((2R)-(10R,13R)-17 -((2R,5S,E)-5-Ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca-hydro-1\(H\)-cyclopenta[\(a\)]phenanthren-3-yl 2-(((benzyloxy)-carbonyl)amino)oxy)-4-methylpentanoate (10d). White microcrystals, mp 120.0-122.0 °C, 20% yield, \([\alpha]_{D}^{21} = +25.9\) (c 0.10 in CH\(_2\)Cl\(_2\)). HRMS calcd for [C\(_{43}\)H\(_{65}\)NO\(_5\)+Na]\(^+\) = 698.4755, found = 698.4774. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\), 7.79 (s, 1H), 7.36-7.34 (m, 5H), 5.38 (d, \(J = 5.0\) Hz, 1H), 5.20 (d, \(J = 12.1\) Hz, 1H), 5.14 (d, \(J = 12.1\) Hz, 1H), 5.01 (dd, \(J = 15.2, 8.5\) Hz, 1H), 4.69-4.67 (m, 1H), 4.40 (dd, \(J = 9.8, 3.9\) Hz, 1H), 2.33 (d, \(J = 7.7\) Hz, 2H), 2.11-1.82 (m, 6H), 1.78-1.38 (m, 14H), 1.38-1.08 (m, 5H), 1.03-0.98 (m, 8H), 0.95-0.93 (m, 6H), 0.88-0.78 (m, 9H), 0.70 (s, 3H). \(^{13}\)C-
NMR (75 MHz, CDCl$_3$) $\delta$, 171.7, 157.0, 139.4, 138.4, 135.6, 129.4, 128.7, 128.6, 128.5, 123.1, 82.8, 75.1, 67.8, 64.3, 56.9, 56.1, 51.4, 50.2, 42.4, 40.7, 39.9, 39.8, 38.2, 37.1, 36.7, 32.0, 29.1, 27.9, 25.6, 24.7, 24.5, 23.3, 21.7, 21.4, 21.3, 19.5, 19.2, 12.4, 12.2.
Benzyl ((R)-1-((9-((2R,3R,4S,5R)-3,4-dihydroxy-5-(hydroxy-methyl)tetrahydrofuran-2-yl)-9H-purin-6-yl)amino)-1-oxo-3-phenylpropan-2-yl)oxycarbamate (12b).

White microcrystals, mp 110.0-113.0°C, 54% yield, $[\alpha]_D^{21} = -9.6$ (c 0.5 in CH$_3$OH).

HRMS calcd. for [C$_{27}$H$_{28}$N$_6$O$_8$+Na]$^+$ = 587.1861, found = 587.1859. $^1$H-NMR (500 MHz, DMSO-$d_6$) $\delta$, 10.52 (brs, 1H), 8.38 (s, 1H), 8.35 (s, 1H), 7.46 (br s, 1H), 7.38-7.20 (m, 10H), 5.94 (d, J = 7.5 Hz, 2H), 5.36 (d, J = 5.6 Hz, 1H), 5.09 (d, J = 12.8 Hz, 1H), 5.06 (d, J = 12.8 Hz, 1H), 4.72 (dd, J = 7.5, 4.5 Hz, 1H), 4.10 (br s, 1H), 3.68 (dd, J = 12.4, 3.4 Hz, 1H), 3.59 (dd, J = 12.2, 3.0 Hz, 1H), 3.20 (dd, J = 14.9, 4.5 Hz, 1H), 3.04 (dd, J = 14.8, 7.4 Hz, 1H). $^{13}$C-NMR (125 MHz, DMSO-$d_6$) $\delta$, 169.4, 157.0, 152.3, 149.0, 140.0, 136.2, 129.2, 129.0, 128.4, 128.1, 128.0, 127.8, 126.5, 119.4, 87.5, 83.5, 83.2, 74.3, 71.6, 66.1, 61.5, 36.5.
1^13C-NMR (75 MHz, CDCl3)

6b
$^1$H-NMR (75 MHz, CDCl$_3$)
\(^{13}\text{C-}\text{NMR (75 MHz, CDCl})\)
Figure S1. $^1$H–$^{13}$C gHMBC experiment for 6f
Proton connectivity for sugar part of compound 6f – determined by $^1$H-$^1$H gDQCOSY experiment, expansion is provided in Figure S2-S3.

Figure S2. $^1$H-$^1$H DQCOSY of 6f.
**Figure S3.** $^1$H-$^1$H gDQ COSY expansion for sugar part
$^{1}H$-NMR (600 MHz, CDCl$_3$)

![NMR spectrum image]
H-NMR (300 MHz, CDCl₃)
References:
