

Synthesis and quantitative structure-activity relationship (QSAR) study of C7-oxime ester derivatives of obacunone as insecticidal agents[†]

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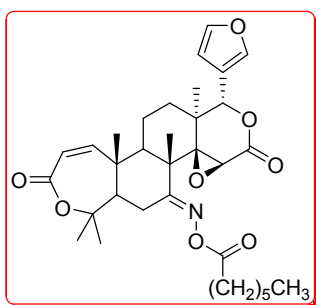
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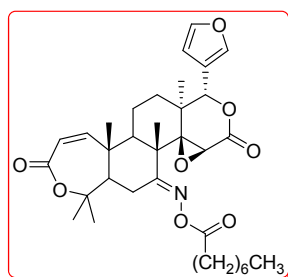
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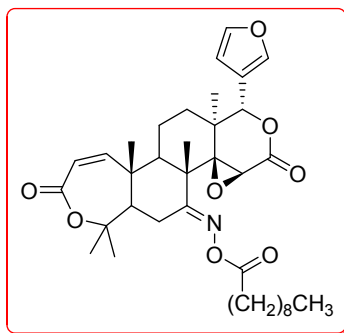


Data for 3f: Yield = 82%, white solid, m.p. 136-138 °C; $[\alpha]_D^{20} = -2$ (*c* 3.7 mg/mL, acetone); IR cm^{-1} (KBr): 2954, 1752, 1704, 1636, 1392, 1283, 1073; ¹H NMR (500 MHz, CDCl₃) δ : 7.42 (s, 1H, H-21), 7.39 (t, *J* = 2.0 Hz, 1H, H-23), 6.49 (d, *J* = 12.0 Hz, 1H, H-1), 6.38 (d, *J* = 1.0 Hz, 1H, H-22), 5.92 (d, *J* = 12.0 Hz, 1H, H-2), 5.50 (s,

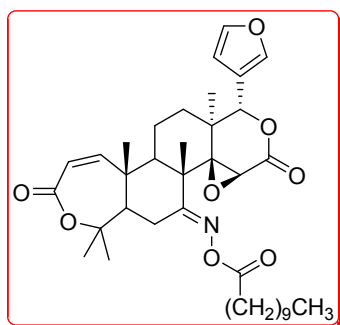
1H, H-17), 3.72 (s, 1H, H-15), 3.14 (dd, $J = 12.5, 3.0$ Hz, 1H, H-6), 2.45-2.49 (m, 2H, -CH₂CH₂(CH₂)₃CH₃), 2.30-2.34 (m, 2H, H-5, 6), 2.14-2.17 (m, 1H, H-9), 1.86-1.92 (m, 3H, H-11, 12), 1.63-1.68 (m, 2H, -CH₂CH₂(CH₂)₃CH₃), 1.52 (s, 3H, H-28), 1.47-1.50 (m, 4H, H-11, 29), 1.42 (s, 3H, H-19), 1.29-1.38 (m, 9H, H-18, -CH₂CH₂(CH₂)₃CH₃), 1.20 (s, 3H, H-30), 0.87 (t, $J = 7.0$ Hz, 3H, -CH₂CH₂(CH₂)₃CH₃); HRMS m/z calcd for C₃₃H₄₃NO₈Na ([M+Na]⁺) 604.2881, found 604.2876.



Data for 3g: Yield = 89%, white solid, m.p. 135-136 °C; $[\alpha]^{20}_D = -2$ (c 3.3 mg/mL, acetone); IR cm⁻¹ (KBr): 2953, 1753, 1703, 1637, 1392, 1282, 1073; ¹H NMR (500 MHz, CDCl₃) δ : 7.42 (s, 1H, H-21), 7.39 (t, $J = 2.0$ Hz, 1H, H-23), 6.49 (d, $J = 12.0$ Hz, 1H, H-1), 6.38 (d, $J = 1.0$ Hz, 1H, H-22), 5.92 (d, $J = 12.0$ Hz, 1H, H-2), 5.50 (s, 1H, H-17), 3.72 (s, 1H, H-15), 3.14 (dd, $J = 12.5, 3.0$ Hz, 1H, H-6), 2.44-2.48 (m, 2H, -CH₂CH₂(CH₂)₄CH₃), 2.30-2.34 (m, 2H, H-5, 6), 2.14-2.17 (m, 1H, H-9), 1.85-1.92 (m, 3H, H-11, 12), 1.63-1.68 (m, 2H, -CH₂CH₂(CH₂)₄CH₃), 1.47-1.52 (m, 7H, H-11, 28, 29), 1.42 (s, 3H, H-19), 1.28-1.37 (m, 11H, H-18, -CH₂CH₂(CH₂)₄CH₃), 1.20 (s, 3H, H-30), 0.87 (t, $J = 7.0$ Hz, 3H, -CH₂CH₂(CH₂)₄CH₃); HRMS m/z calcd for C₃₄H₄₅NO₈Na ([M+Na]⁺) 618.3037, found 618.3037.

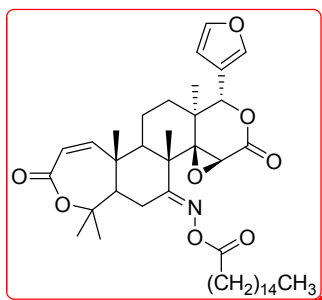


Data for 3h: Yield = 88%, white solid, m.p. 64-65 °C; $[\alpha]^{20}_D = -2$ (*c* 3.9 mg/mL, acetone); IR cm^{-1} (KBr): 2928, 1750, 1704, 1391, 1282, 1073; ^1H NMR (500 MHz, CDCl_3) δ : 7.42 (s, 1H, H-21), 7.40 (s, 1H, H-23), 6.49 (d, $J = 11.5$ Hz, 1H, H-1), 6.38 (s, 1H, H-22), 5.92 (d, $J = 12.0$ Hz, 1H, H-2), 5.49 (s, 1H, H-17), 3.72 (s, 1H, H-15), 3.14 (dd, $J = 12.5, 2.5$ Hz, 1H, H-6), 2.44-2.48 (m, 2H, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 2.27-2.37 (m, 2H, H-5, 6), 2.14-2.27 (m, 1H, H-9), 1.85-1.95 (m, 3H, H-11, 12), 1.63-1.73 (m, 2H, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.52 (s, 3H, H-28), 1.45-1.48 (m, 4H, H-11, 29), 1.42 (s, 3H, H-19), 1.26-1.29 (m, 15H, H-18, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.20 (s, 3H, H-30), 0.86 (t, $J = 7.0$ Hz, 3H, H-2, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$); HRMS m/z calcd for $\text{C}_{36}\text{H}_{49}\text{NO}_8\text{Na}$ ($[\text{M}+\text{Na}]^+$) 646.3350, found 646.3344.



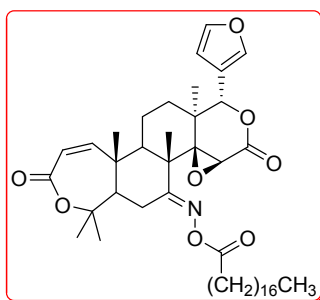
Data for 3i: Yield = 66%, white solid, m.p. 61-62 °C; $[\alpha]^{20}_D = 0.49$ (*c* 4.0 mg/mL, acetone); IR cm^{-1} (KBr): 2927, 1751, 1704, 1634, 1391, 1282, 1072; ^1H NMR (500 MHz, CDCl_3) δ : 7.42 (s, 1H, H-21), 7.39 (t, $J = 2.0$ Hz, 1H, H-23), 6.49 (d, $J = 12.0$

Hz, 1H, H-1), 6.38 (d, $J = 1.0$ Hz, 1H, H-22), 5.92 (d, $J = 12.0$ Hz, 1H, H-2), 5.50 (s, 1H, H-17), 3.72 (s, 1H, H-15), 3.14 (dd, $J = 12.5, 3.0$ Hz, 1H, H-6), 2.44-2.48 (m, 2H, $-CH_2CH_2(CH_2)_7CH_3$), 2.30-2.37 (m, 2H, H-5, 6), 2.14-2.17 (m, 1H, H-9), 1.85-1.92 (m, 3H, H-11, 12), 1.63-1.67 (m, 2H, $-CH_2CH_2(CH_2)_7CH_3$), 1.52 (s, 3H, H-28), 1.47-1.49 (m, 4H, H-11, 29), 1.42 (s, 3H, H-19), 1.26-1.36 (m, 17H, H-18, $-CH_2CH_2(CH_2)_7CH_3$), 1.20 (s, 3H, H-30), 0.86 (t, $J = 7.0$ Hz, 3H, $-CH_2CH_2(CH_2)_7CH_3$); HRMS m/z calcd for $C_{37}H_{51}NO_8Na$ ($[M+Na]^+$) 660.3507, found 660.3510.

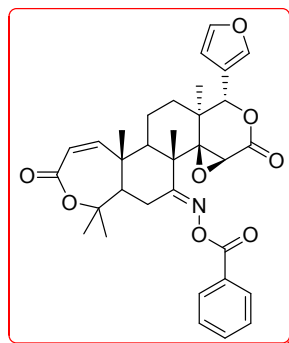


Data for 3j: Yield = 77%, white solid, m.p. 45-47 °C; $[\alpha]_D^{20} = 0.46$ (c 3.1 mg/mL, acetone); IR cm^{-1} (KBr): 2925, 1750, 1704, 1391, 1282, 1072; 1H NMR (500 MHz, $CDCl_3$) δ : 7.42 (s, 1H, H-21), 7.39 (t, $J = 1.5$ Hz, 1H, H-23), 6.49 (d, $J = 12.0$ Hz, 1H, H-1), 6.38 (d, $J = 1.0$ Hz, 1H, H-22), 5.92 (d, $J = 12.0$ Hz, 1H, H-2), 5.50 (s, 1H, H-17), 3.72 (s, 1H, H-15), 3.14 (dd, $J = 12.5, 3.0$ Hz, 1H, H-6), 2.44-2.48 (m, 2H, $-CH_2CH_2(CH_2)_{12}CH_3$), 2.30-2.34 (m, 2H, H-5, 6), 2.14-2.17 (m, 1H, H-9), 1.85-1.95 (m, 3H, H-11, 12), 1.63-1.67 (m, 2H, $-CH_2CH_2(CH_2)_{12}CH_3$), 1.52 (s, 3H, H-28), 1.47-1.50 (m, 4H, H-11, 29), 1.42 (s, 3H, H-19), 1.25-1.36 (m, 27H, H-18, $-CH_2CH_2(CH_2)_{12}CH_3$), 1.20 (s, 3H, H-30), 0.86 (t, $J = 7.0$ Hz, 3H, $-CH_2CH_2(CH_2)_7CH_3$); HRMS m/z calcd for $C_{42}H_{61}NO_8Na$ ($[M+Na]^+$) 730.4289, found

730.4297.

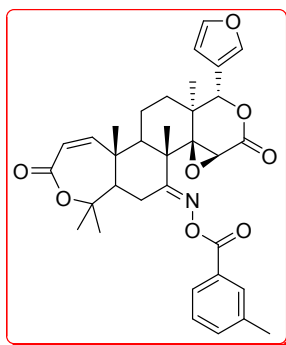


Data for 3k: Yield = 72%, white solid, m.p. 39-40 °C; $[\alpha]^{20}_D = 0.5$ (c 3.2 mg/mL, acetone); IR cm^{-1} (KBr): 2925, 1751, 1705, 1391, 1282, 1072; 1H NMR (500 MHz, $CDCl_3$) δ : 7.42 (s, 1H, H-21), 7.39 (t, $J = 1.5$ Hz, 1H, H-23), 6.49 (d, $J = 12.0$ Hz, 1H, H-1), 6.38 (d, $J = 1.0$ Hz, 1H, H-22), 5.92 (d, $J = 12.0$ Hz, 1H, H-2), 5.50 (s, 1H, H-17), 3.72 (s, 1H, H-15), 3.14 (dd, $J = 12.5, 3.0$ Hz, 1H, H-6), 2.44-2.48 (m, 2H, $-CH_2CH_2(CH_2)_{14}CH_3$), 2.30-2.37 (m, 2H, H-5, 6), 2.14-2.17 (m, 1H, H-9), 1.85-1.95 (m, 3H, H-11, 12), 1.63-1.67 (m, 2H, $-CH_2CH_2(CH_2)_{14}CH_3$), 1.52 (s, 3H, H-28), 1.46-1.50 (m, 4H, H-11, 29), 1.42 (s, 3H, H-19), 1.25-1.34 (m, 31H, H-18, $-CH_2CH_2(CH_2)_{14}CH_3$), 1.20 (s, 3H, H-30), 0.86 (t, $J = 7.0$ Hz, 3H, $-CH_2CH_2(CH_2)_7CH_3$); HRMS m/z calcd for $C_{44}H_{65}NO_8Na$ ($[M+Na]^+$) 758.4602, found 758.4593.

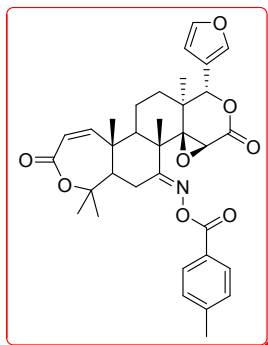


Data for 3l: Yield = 76%, white solid, m.p. 142-144 °C; $[\alpha]^{20}_D = -18$ (c 4.3 mg/mL, acetone); IR cm^{-1} (KBr): 3038, 2950, 1749, 1704, 1634, 1392, 1282, 1121; 1H NMR

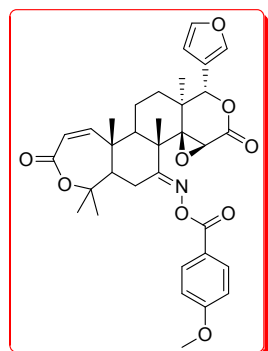
(500 MHz, CDCl₃) δ : 7.99 (d, $J = 7.5$ Hz, 2H, Ar-H), 7.99 (t, $J = 7.5$ Hz, 1H, Ar-H), 7.46-2.49 (m, 2H, Ar-H), 7.43 (s, 1H, H-21), 7.40 (s, 1H, H-23), 6.52 (d, $J = 11.5$ Hz, 1H, H-1), 6.40 (s, 1H, H-22), 5.93 (d, $J = 12.0$ Hz, 1H, H-2), 5.52 (s, 1H, H-17), 3.81 (s, 1H, H-15), 3.13-3.20 (m, 1H, H-6), 2.39-2.46 (m, 2H, H-5, 6), 2.26-2.29 (m, 1H, H-9), 1.88-1.98 (m, 3H, H-11, 12), 1.50-1.53 (m, 4H, H-11, 28), 1.45 (s, 3H, H-29), 1.44 (s, 3H, H-19), 1.39 (s, 3H, H-18), 1.26 (s, 3H, H-30); HRMS m/z calcd for C₃₃H₃₅NO₈Na ([M+Na]⁺) 596.2255, found 596.2253.



Data for 3m: Yield = 94%, white solid, m.p. 251-252 °C; $[\alpha]^{20}_D = -15$ (c 4.2 mg/mL, acetone); IR cm⁻¹ (KBr): 3037, 2990, 1739, 1702, 1644, 1395, 1285, 1121; ¹H NMR (500 MHz, CDCl₃) δ : 7.83 (s, 1H, Ar-H), 7.78 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.39-7.42 (m, 3H, H-21, 23, Ar-H), 7.34 (t, $J = 8.0$ Hz, 1H, Ar-H), 6.51 (d, $J = 12.0$ Hz, 1H, H-1), 6.39 (d, $J = 1.0$ Hz, 1H, H-22), 5.93 (d, $J = 12.0$ Hz, 1H, H-2), 5.51 (s, 1H, H-17), 3.81 (s, 1H, H-15), 3.12-3.19 (m, 1H, H-6), 2.38-2.43 (m, 5H, H-5, 6, -CH₃), 2.26-2.29 (m, 1H, H-9), 1.88-1.96 (m, 3H, H-11, 12), 1.50-1.53 (m, 4H, H-11, 28), 1.45 (s, 3H, H-29), 1.44 (s, 3H, H-19), 1.39 (s, 3H, H-18), 1.26 (s, 3H, H-30); HRMS m/z calcd for C₃₄H₃₇NO₈Na ([M+Na]⁺) 610.2411, found 610.2410.

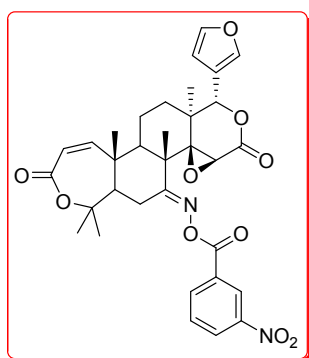


Data for 3n: Yield = 90%, white solid, m.p. 154-156 °C; $[\alpha]^{20}_D = -20$ (*c* 3.4 mg/mL, acetone); IR cm^{-1} (KBr): 3038, 2952, 1749, 1704, 1628, 1391, 1281, 1121; ^1H NMR (500 MHz, CDCl_3) δ : 7.88 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.42 (s, 1H, H-21), 7.39 (s, 1H, H-23), 7.26 (d, $J = 8.5$ Hz, 2H, Ar-H), 6.51 (d, $J = 11.5$ Hz, 1H, H-1), 6.39 (d, $J = 1.0$ Hz, 1H, H-22), 5.92 (d, $J = 11.5$ Hz, 1H, H-2), 5.51 (s, 1H, H-17), 3.81 (s, 1H, H-15), 3.12-3.19 (m, 1H, H-6), 2.41-2.45 (m, 5H, H-5, 6, - CH_3), 2.26-2.28 (m, 1H, H-9), 1.88-1.96 (m, 3H, H-11, 12), 1.49-1.53 (m, 4H, H-11, 28), 1.44 (s, 6H, H-19, 29), 1.39 (s, 3H, H-18), 1.26 (s, 3H, H-30); HRMS m/z calcd for $\text{C}_{34}\text{H}_{37}\text{NO}_8\text{Na}$ ($[\text{M}+\text{Na}]^+$) 610.2411, found 610.2411.

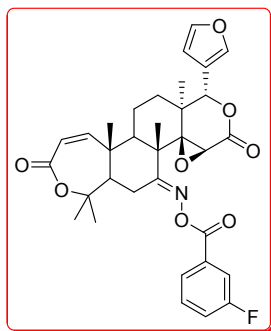


Data for 3o: Yield = 89%, white solid, m.p. 116-118 °C; $[\alpha]^{20}_D = -28$ (*c* 3.3 mg/mL, acetone); IR cm^{-1} (KBr): 3040, 2930, 1748, 1702, 1639, 1390, 1253, 1121; ^1H NMR (500 MHz, CDCl_3) δ : 7.94 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.42 (s, 1H, H-21), 7.39 (s, 1H, H-23), 6.94 (d, $J = 9.0$ Hz, 2H, Ar-H), 6.51 (d, $J = 11.5$ Hz, 1H, H-1), 6.39 (d, $J = 1.0$

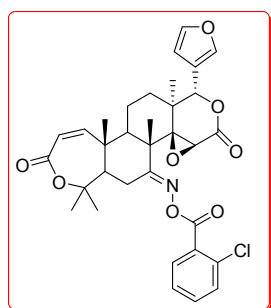
Hz, 1H, H-22), 5.92 (d, $J = 12.0$ Hz, 1H, H-2), 5.51 (s, 1H, H-17), 3.87 (s, 3H, -OCH₃), 3.81 (s, 1H, H-15), 3.09-3.19 (m, 1H, H-6), 2.37-2.46 (m, 2H, H-5, 6), 2.26-2.28 (m, 1H, H-9), 1.88-1.96 (m, 3H, H-11, 12), 1.49-1.53 (m, 4H, H-11, 28), 1.45 (s, 3H, H-29), 1.44 (s, 3H, H-19), 1.39 (s, 3H, H-18), 1.25 (s, 3H, H-30); HRMS m/z calcd for C₃₄H₃₇NO₉Na ([M+Na]⁺) 626.2360, found 626.2355.



Data for 3p: Yield = 88%, white solid, m.p. 226-227 °C; $[\alpha]^{20}_D = -23$ (*c* 4.3 mg/mL, acetone); IR cm⁻¹ (KBr): 3041, 2951, 1760, 1697, 1617, 1392, 1283, 1072; ¹H NMR (500 MHz, CDCl₃) δ : 8.81 (t, $J = 1.5$ Hz, 1H, Ar-H), 8.46-8.48 (m, 1H, Ar-H), 8.36 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.71 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.43 (s, 1H, H-21), 7.40 (t, $J = 2.0$ Hz, 1H, H-23), 6.52 (d, $J = 11.5$ Hz, 1H, H-1), 6.39 (d, $J = 1.5$ Hz, 1H, H-22), 5.94 (d, $J = 12.0$ Hz, 1H, H-2), 5.53 (s, 1H, H-17), 3.81 (s, 1H, H-15), 3.20-3.23 (m, 1H, H-6), 2.43-2.52 (m, 2H, H-5, 6), 2.26-2.28 (m, 1H, H-9), 1.90-1.98 (m, 3H, H-11, 12), 1.56 (s, 3H, H-28), 1.50-1.54 (m, 4H, H-11, 29), 1.46 (s, 3H, H-19), 1.37 (s, 3H, H-18), 1.28 (s, 3H, H-30); HRMS m/z calcd for C₃₃H₃₄N₂O₁₀Na ([M+Na]⁺) 641.2106, found 641.2105.

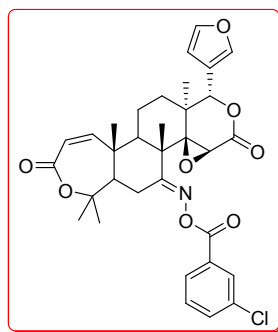


Data for 3q: Yield = 97%, white solid, m.p. 222-223 °C; $[\alpha]^{20}_{\text{D}} = -20$ (*c* 2.9 mg/mL, acetone); IR cm^{-1} (KBr): 3078, 2949, 1746, 1703, 1645, 1393, 1284, 1075; ^1H NMR (500 MHz, CDCl_3) δ : 7.80 (dd, $J_{\text{H,F}} = 6.5, 1.0$ Hz, 1H, Ar-H), 7.66-7.68 (m, 1H, Ar-H), 7.44-7.748 (m, 1H, Ar-H), 7.43 (s, 1H, H-21), 7.39 (t, $J = 2.0$ Hz, 1H, H-23), 7.31-7.39 (m, 1H, Ar-H), 6.51 (d, $J = 11.5$ Hz, 1H, H-1), 6.39 (d, $J = 1.0$ Hz, 1H, H-22), 5.93 (d, $J = 11.5$ Hz, 1H, H-2), 5.52 (s, 1H, H-17), 3.80 (s, 1H, H-15), 3.14-3.15 (m, 1H, H-6), 2.41-2.47 (m, 2H, H-5, 6), 2.25-2.28 (m, 1H, H-9), 1.89-1.94 (m, 3H, H-11, 12), 1.50-1.54 (m, 4H, H-11, 28), 1.46 (s, 3H, H-29), 1.44 (s, 3H, H-19), 1.38 (s, 3H, H-18), 1.26 (s, 3H, H-30); HRMS m/z calcd for $\text{C}_{33}\text{H}_{34}\text{NO}_8\text{FNa}$ ($[\text{M}+\text{Na}]^+$) 614.2161, found 614.2157.

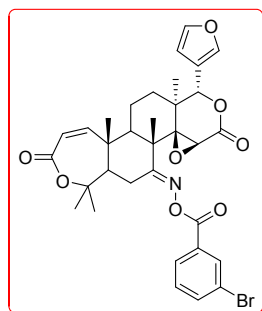


Data for 3r: Yield = 85%, white solid, m.p. 248-250 °C; $[\alpha]^{20}_{\text{D}} = -4$ (*c* 3.6 mg/mL, acetone); IR cm^{-1} (KBr): 3046, 2930, 1742, 1703, 1629, 1373, 1284, 1076; ^1H NMR (500 MHz, CDCl_3) δ : 7.88 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.36-7.47 (m, 5H, H-21, 23, Ar-H), 6.51 (d, $J = 11.5$ Hz, 1H, H-1), 6.39 (s, 1H, H-22), 5.93 (d, $J = 12.0$ Hz, 1H, H-2),

5.50 (s, 1H, H-17), 3.79 (s, 1H, H-15), 3.26-3.32 (m, 1H, H-6), 2.38-2.45 (m, 2H, H-5, 6), 2.06 (d, $J = 12.0$ Hz, 1H, H-9), 1.87-1.95 (m, 3H, H-11, 12), 1.52 (s, 3H, H-28), 1.47-1.49 (m, 4H, H-11, 29), 1.43 (s, 3H, H-19), 1.35 (s, 3H, H-18), 1.25 (s, 3H, H-30); HRMS m/z calcd for $C_{33}H_{34}NO_8ClNa$ ($[M+Na]^+$) 630.1865, found 630.1860.

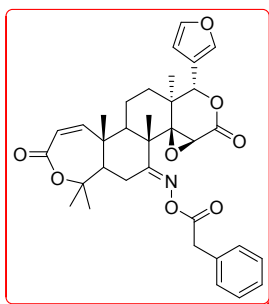


Data for 3s: Yield = 96%, white solid, m.p. 260-262 °C; $[\alpha]^{20}_D = -18$ (c 2.9 mg/mL, acetone); IR cm^{-1} (KBr): 3041, 2948, 1748, 1702, 1629, 1394, 1285, 1075; 1H NMR (500 MHz, $CDCl_3$) δ : 7.97 (s, 1H, Ar-H), 7.88 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.57 (dd, $J = 8.5, 1.5$ Hz, 1H, Ar-H), 7.40-7.44 (m, 3H, H-21, 23, Ar-H), 6.53 (d, $J = 11.5$ Hz, 1H, H-1), 6.39 (d, $J = 1.0$ Hz, 1H, H-22), 5.93 (d, $J = 11.5$ Hz, 1H, H-2), 5.51 (s, 1H, H-17), 3.80 (s, 1H, H-15), 3.13-3.15 (m, 1H, H-6), 2.41-2.47 (m, 2H, H-5, 6), 2.25-2.28 (m, 1H, H-9), 1.89-1.97 (m, 3H, H-11, 12), 1.50-1.54 (m, 4H, H-11, 28), 1.46 (s, 3H, H-29), 1.44 (s, 3H, H-19), 1.37 (s, 3H, H-18), 1.26 (s, 3H, H-30); HRMS m/z calcd for $C_{33}H_{34}NO_8ClNa$ ($[M+Na]^+$) 630.1865, found 630.1861.

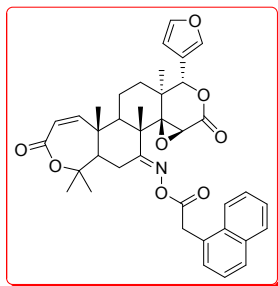


Data for 3t: Yield = 80%, white solid, m.p. 249-251 °C; $[\alpha]^{20}_D = -23$ (c 3.1 mg/mL,

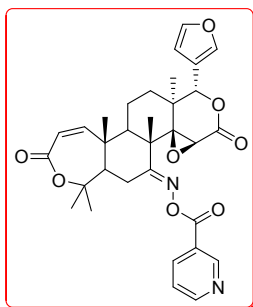
acetone); IR cm^{-1} (KBr): 3040, 2990, 1750, 1701, 1635, 1394, 1285, 1074; ^1H NMR (500 MHz, CDCl_3) δ : 8.12 (t, $J = 1.5$ Hz, 1H, Ar-H), 7.93-7.95 (m, 1H, Ar-H), 7.72-7.74 (m, 1H, Ar-H), 7.43 (s, 1H, H-21), 7.39 (t, $J = 2.0$ Hz, 1H, H-23), 7.35 (t, $J = 8.0$ Hz, 1H, Ar-H), 6.51 (d, $J = 11.5$ Hz, 1H, H-1), 6.39 (d, $J = 1.0$ Hz, 1H, H-22), 5.94 (d, $J = 11.5$ Hz, 1H, H-2), 5.52 (s, 1H, H-17), 3.80 (s, 1H, H-15), 3.11-3.15 (m, 1H, H-6), 2.41-2.47 (m, 2H, H-5, 6), 2.25-2.27 (m, 1H, H-9), 1.89-1.97 (m, 3H, H-11, 12), 1.50-1.55 (m, 4H, H-11, 28), 1.47 (s, 3H, H-29), 1.44 (s, 3H, H-19), 1.37 (s, 3H, H-18), 1.26 (s, 3H, H-30); HRMS m/z calcd for $\text{C}_{33}\text{H}_{34}\text{NO}_8\text{BrNa}$ ($[\text{M}+\text{Na}]^+$) 674.1360, found 674.1377.



Data for 3u: Yield = 96%, white solid, m.p. 110-112 °C; $[\alpha]^{20}_{\text{D}} = -3$ (c 3.6 mg/mL, acetone); IR cm^{-1} (KBr): 3032, 2952, 1747, 1702, 1635, 1391, 1283, 1073; ^1H NMR (500 MHz, CDCl_3) δ : 7.38-7.40 (m, 2H, H-21, 23), 7.27-7.34 (m, 5H, Ar-H), 6.45 (d, $J = 11.5$ Hz, 1H, H-1), 6.36 (d, $J = 1.0$ Hz, 1H, H-22), 5.89 (d, $J = 11.5$ Hz, 1H, H-2), 5.48 (s, 1H, H-17), 3.67-3.82 (m, 3H, H-15, $\text{CH}_2\text{C}_6\text{H}_5$), 2.83-2.88 (m, 1H, H-6), 2.18-2.18 (m, 2H, H-5, 6), 2.12-2.15 (m, 1H, H-9), 1.82-1.93 (m, 3H, H-11, 12), 1.41-1.49 (m, 4H, H-11, 28), 1.37 (s, 3H, H-29), 1.27 (s, 3H, H-19), 1.26 (s, 3H, H-18), 1.17 (s, 3H, H-30); HRMS m/z calcd for $\text{C}_{34}\text{H}_{37}\text{NO}_8\text{Na}$ ($[\text{M}+\text{Na}]^+$) 610.2411, found 610.2412.

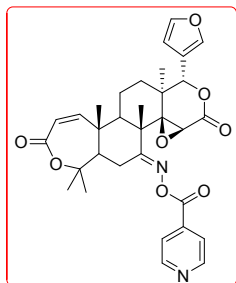


Data for 3v: Yield = 95%, white solid, m.p. 136-138 °C; $[\alpha]_D^{20} = -5$ (*c* 3.4 mg/mL, acetone); IR cm^{-1} (KBr): 3041, 2933, 1747, 1702, 1630, 1393, 1282, 1074; ^1H NMR (500 MHz, CDCl_3) δ : 8.02 (d, $J = 8.5$ Hz, 1H, Nap-H), 7.85 (d, $J = 8.0$ Hz, 1H, Nap-H), 7.78 (d, $J = 8.0$ Hz, 1H, Nap-H), 7.48-7.56 (m, 2H, Nap-H), 7.38-7.44 (m, 4H, H-21, 23, Nap-H), 6.37 (d, $J = 12.0$ Hz, 1H, H-1), 6.35 (s, 1H, H-22), 5.93 (d, $J = 11.5$ Hz, 1H, H-2), 5.46 (s, 1H, H-17), 4.14-4.28 (m, 2H, $-\text{CH}_2\text{C}_{10}\text{H}_7$), 3.73 (s, 1H, H-15), 2.45-2.47 (m, 1H, H-6), 1.99-2.07 (m, 3H, H-5, 6, 9), 1.77-1.90 (m, 3H, H-11, 12), 1.25-1.30 (m, 7H, H-11, 28, 29), 1.16 (s, 3H, H-19), 1.12 (s, 3H, H-18), 0.84 (s, 3H, H-30); HRMS m/z calcd for $\text{C}_{38}\text{H}_{39}\text{NO}_8\text{Na}$ ($[\text{M}+\text{Na}]^+$) 660.2568, found 660.2567.



Data for 3w: Yield = 90%, white solid, m.p. 166-168 °C; $[\alpha]_D^{20} = -19$ (*c* 3.3 mg/mL, acetone); IR cm^{-1} (KBr): 3039, 2952, 1751, 1702, 1638, 1392, 1264, 1071; ^1H NMR (500 MHz, CDCl_3) δ : 9.37 (d, $J = 12.0$ Hz, 1H), 9.00 (s, 1H), 8.77-8.84 (m, 1H), 7.92-7.97 (m, 1H), 7.44 (s, 1H, H-21), 7.40 (t, $J = 1.5$ Hz, 1H, H-23), 6.51 (d, $J = 11.5$ Hz, 1H, H-1), 6.39 (d, $J = 1.0$ Hz, 1H, H-22), 5.94 (d, $J = 11.5$ Hz, 1H, H-2), 5.53 (s, 1H, H-17), 3.79 (s, 1H, H-15), 3.19 (dd, $J = 13.5, 3.5$ Hz, 1H, H-6), 2.43-2.54 (m, 2H, H-5,

6), 2.24-2.26 (m, 1H, H-9), 1.91-1.98 (m, 3H, H-11, 12), 1.57 (s, 3H, H-28), 1.50-1.55 (m, 4H, H-11, 29), 1.45 (s, 3H, H-19), 1.36 (s, 3H, H-18), 1.28 (s, 3H, H-30); HRMS m/z calcd for $C_{32}H_{34}N_2O_8Na$ ($[M+Na]^+$) 597.2207, found 597.2199.



Data for 3x: Yield = 64%, white solid, m.p. 194-196 °C; $[\alpha]^{20}_D = -15$ (c 3.2 mg/mL, acetone); IR cm^{-1} (KBr): 3064, 2954, 1760, 1698, 1635, 1407, 1283, 1072; 1H NMR (500 MHz, $CDCl_3$) δ : 8.99 (d, $J = 6.5$ Hz, 2H), 8.23 (d, $J = 7.0$ Hz, 2H), 7.44 (s, 1H, H-21), 7.41 (t, $J = 1.5$ Hz, 1H, H-23), 6.51 (d, $J = 12.0$ Hz, 1H, H-1), 6.39 (d, $J = 1.0$ Hz, 1H, H-22), 5.94 (d, $J = 11.5$ Hz, 1H, H-2), 5.52 (s, 1H, H-17), 3.78 (s, 1H, H-15), 3.15 (dd, $J = 13.5, 3.5$ Hz, 1H, H-6), 2.42-2.54 (m, 2H, H-5, 6), 2.24-2.26 (m, 1H, H-9), 1.91-1.98 (m, 3H, H-11, 12), 1.57 (s, 3H, H-28), 1.49-1.53 (m, 4H, H-11, 29), 1.45 (s, 3H, H-19), 1.35 (s, 3H, H-18), 1.28 (s, 3H, H-30); HRMS m/z calcd for $C_{32}H_{34}N_2O_8Na$ ($[M+Na]^+$) 597.2207, found 597.2210.