Supporting Information

Synthesis of Novel Oxime Sulfonate Derivatives of 2′(2′,6′)-(di)Chloropicropodophyllotoxins as Insecticidal Agents

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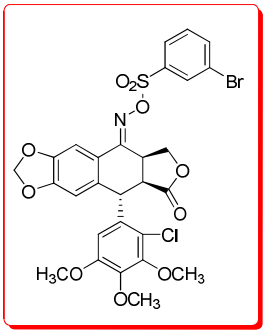
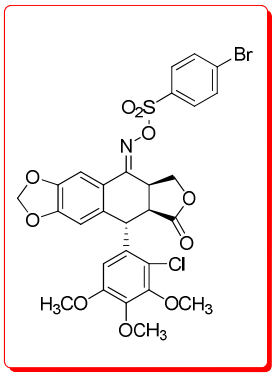
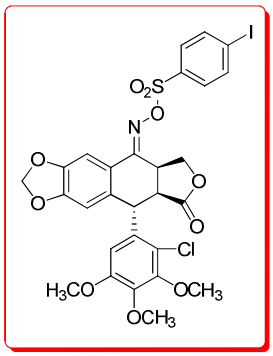


Data for ***4f*****:** Yield: 52%, yellow solid, m.p. 108-110 °C, $[\alpha]^{20}_{D}$ = 24 (*c* 3.2 mg/mL, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.18 (s, 1H, H-2″), 7.97 (d, *J* = 8.0 Hz, 1H, H-6″), 7.84-7.86 (m, 1H, H-4"), 7.51 (t, *J* = 8.0 Hz, 1H, H-5″), 7.13 (s, 1H, H-5), 6.72 (s, 1H, H-8), 6.03 (s, 2H, OCH_2O), 5.77 (s, 1H, H-6'), 5.09 (d, *J* = 2.0 Hz, 1H, H-1),

4.55 (dd, J = 10.0, 7.0 Hz, 1H, H-11), 4.32 (d, J = 10.0 Hz, 1H, H-11), 3.93 (s, 3H, 3′-OCH_3), 3.89-3.91 (m, 1H, H-3), 3.85 (s, 3H, 5′-OCH_3), 3.42 (s, 3H, 4′-OCH_3), 3.40-3.42 (m, 1H, H-2); HRMS (ESI): Calcd for $C_{28}H_{24}O_{10}NBrClS$ ($[M+H]^+$), 679.9987; Found, 679.9993.

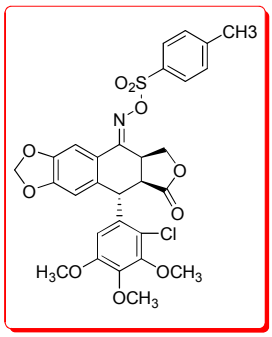


Data for ***4g*****:** Yield: 55%, yellow solid, m.p. 95-97 °C, $[\alpha]^{20}_D$ = 13 (*c* 1.5 mg/mL, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.5 Hz, 2H, H-2″, H-6″), 7.76 (d, J = 8.5 Hz, 2H, H-3″, H-5″), 7.14 (s, 1H, H-5), 6.72 (s, 1H, H-8), 6.03 (s, 2H, OCH_2O), 5.74 (s, 1H, H-6′), 5.08 (d, J = 2.0 Hz, 1H, H-1), 4.52-4.55 (m, 1H, H-11), 4.29-4.33 (m, 1H, H-11), 3.92 (s, 3H, 3′-OCH_3), 3.90 (t, J = 7.5 Hz, 1H, H-3), 3.84 (s, 3H, 5′-OCH_3), 3.40-3.42 (m, 1H, H-2), 3.36 (s, 3H, 4′-OCH_3); HRMS (ESI): Calcd for $C_{28}H_{23}O_{10}NBrClS$ (M^+), 678.9909; Found, 678.9901.

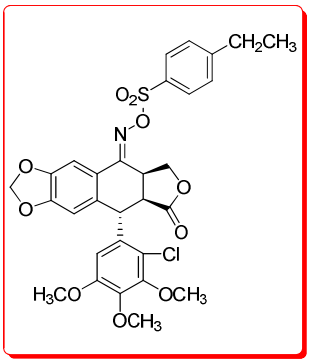


Data for ***4h*****:** Yield: 76%, white solid, m.p. 112-114 °C, $[\alpha]^{20}_D$ = 21 (*c* 3.0 mg/mL,

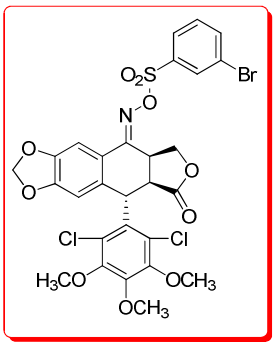
acetone) ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96-7.98 (m, 2H, H-2″, H-6″), 7.71-7.73 (m, 2H, H-3″, H-5″), 7.14 (s, 1H, H-5), 6.72 (s, 1H, H-8), 6.03 (s, 2H, OCH_2O), 5.75 (s, 1H, H-6′), 5.08 (d, J = 2.5 Hz, 1H, H-1), 4.51-4.64 (m, 1H, H-11), 4.32 (d, J = 10.0 Hz, 1H, H-11), 3.92 (s, 3H, 3′-OCH_3), 3.89 (m, 1H, H-3), 3.85 (s, 3H, 5′-OCH_3), 3.41 (dd, J = 8.5, 2.5 Hz, 1H, H-2), 3.37 (s, 3H, 4′-OCH_3); HRMS (ESI): Calcd for $C_{28}H_{24}O_{10}NClIS$ ($[M+H]^+$), 727.9849; Found, 727.9844.



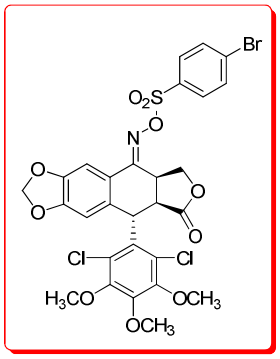
Data for ***4i*****:** Yield: 85%, yellow solid, m.p. 86-88 °C, $[\alpha]^{20}_{D}$ = 5 (*c* 4.0 mg/mL, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.5 Hz, 2H, H-2″, H-6″), 7.40 (d, J = 8.0 Hz, 2H, H-3″, H-5″), 7.15 (s, 1H, H-5), 6.71 (s, 1H, H-8), 6.02 (s, 2H, OCH_2O), 5.78 (s, 1H, H-6′), 5.07 (d, J = 2.5 Hz, 1H, H-1), 4.53 (dd, J = 10.0, 7.0 Hz, 1H, H-11), 4.28-4.30 (m, 1H, H-11), 3.92 (s, 3H, 3′-OCH_3), 3.90 (m, 1H, H-3), 3.84 (s, 3H, 5′-OCH_3), 3.39 (d, J = 2.5 Hz , 1H, H-2), 3.37 (s, 3H, 4′-OCH_3), 2.49 (s, 3H, CH_3); HRMS (ESI): Calcd for $C_{29}H_{27}O_{10}NClFS$ ($[M+H]^+$), 616.1039; Found, 616.1035.



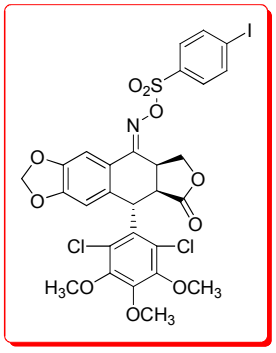
Data for ***4j*****:** Yield: 91%, yellow solid, m.p. 150-152°C, $[\alpha]^{20}_{D}$ = 8 (*c* 3.0 mg/mL, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.5 Hz, 2H, H-2″, H-6″), 7.42 (d, *J* = 8.5 Hz, 2H, H-3″, H-5″), 7.16 (s, 1H, H-5), 6.71 (s, 1H, H-8), 6.02 (s, 2H, OCH_2O), 5.79 (s, 1H, H-6′), 5.08 (d, *J* = 2.0 Hz, 1H, H-1), 4.53 (dd, *J* = 10.0, 7.0 Hz, 1H, H-11), 4.30 (d, *J* = 10.0 Hz, 1H, H-11), 3.92 (s, 3H, 3′-OCH_3), 3.87-3.90 (m, 1H, H-3), 3.84 (s, 3H, 5′-OCH_3), 3.38 (s, 3H, 4′-OCH_3), 3.35-3.37 (m, 1H, H-2), 2.80 (q, *J* = 7.5 Hz, 2H, -CH_2CH_3), 1.29-1.32 (m, 3H, CH_3); HRMS (ESI): Calcd for $C_{30}H_{29}O_{10}NClS$ ($[M+H]^+$), 630.1195; Found, 630.1190.



Data for ***5f*****:** Yield: 67%, yellow solid, m.p. 102-104 °C, $[\alpha]^{20}_{D}$ = 20 (*c* 3.2 mg/mL, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.20 (t, *J* = 2.0 Hz, 1H, H-2″), 8.01 (dt, *J* = 7.5, 1.0 Hz, 1H, H-6″), 7.85 (dt, *J* = 7.5, 1.0 Hz, 1H, H-4"), 7.51 (t, *J* = 7.5 Hz, 1H, H-5″), 7.30 (s, 1H, H-5), 6.22 (d, *J* = 1.0 Hz, 1H, H-8), 6.00 (dd, *J* = 9.0, 1.0 Hz, 2H, OCH_2O), 5.25 (d, *J* = 10.0 Hz, 1H, H-1), 4.93-4.99 (m, 1H, H-11), 4.26-4.27 (m, 1H, H-11), 3.98 (s, 3H, 4′-OCH_3), 3.92 (s, 4H, H-3 and 3′-OCH_3), 3.87 (s, 3H, 5′-OCH_3), 3.50-3.53 (m, 1H, H-2); HRMS (ESI): Calcd for $C_{28}H_{23}O_{10}NBrCl_2S$ ($[M+H]^+$), 713.9598; Found, 713.9592.

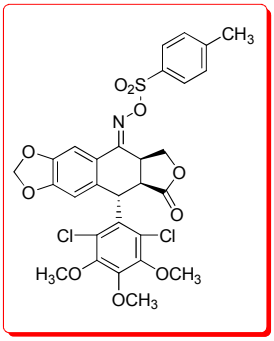


Data for ***5g*****:** Yield: 54%, yellow solid, m.p. 106-108 °C, $[\alpha]^{20}_{D}$ = 26 (*c* 3.5 mg/mL, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.5 Hz, 2H, H-2″, H-6″), 7.76 (d, *J* = 9.0 Hz, 2H, H-3″, H-5″), 7.30 (s, 1H, H-5), 6.22 (s, 1H, H-8), 5.99 (dd, *J* = 10.0, 1.0 Hz, 2H, OCH_2O), 5.25 (d, *J* = 10.0 Hz, 1H, H-1), 4.91-4.96 (m, 1H, H-11), 4.21-4.26 (m, 2H, H-11, H-3), 3.97 (s, 3H, 4′-OCH_3), 3.91 (s, 3H, 3′-OCH_3), 3.87 (s, 3H, 5'-OCH_3), 3.48-3.51 (m, 1H, H-2); HRMS (ESI): Calcd for $C_{28}H_{23}O_{10}NBrCl_2S$ ($[M+H]^+$), 713.9598; Found, 713.9608.

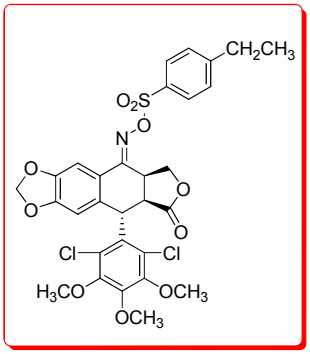


Data for ***5h*****:** Yield: 37%, white solid, m.p. 105-107 °C, $[\alpha]^{20}_{D}$ = 3 (*c* 4.5 mg/mL, acetone): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.0 Hz, 2H, H-2″, H-6″), 7.76 (d, *J* = 8.0 Hz, 2H, H-3″, H-5″), 7.30 (s, 1H, H-5), 6.22 (s, 1H, H-8), 5.99 (d, *J* = 10.0 Hz, 2H, OCH_2O), 5.25 (d, *J* = 10.0 Hz, 1H, H-1), 4.91-4.96 (m, 1H, H-11), 4.22-4.26 (m, 2H, H-11, H-3), 3.97 (s, 3H, 4′-OCH_3), 3.91 (s, 3H, 3′-OCH_3), 3.87 (s, 3H, 5′-OCH_3), 3.48-3.51 (m, 1H, H-2); HRMS (ESI): Calcd for $C_{28}H_{23}O_{10}NCl_2IS$ ($[M+H]^+$),

761.9459; Found, 761.9456.

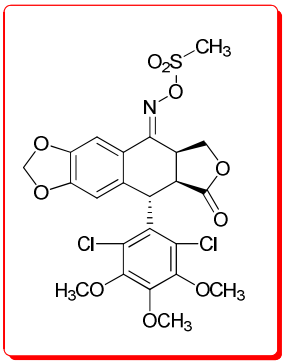


Data for ***5i*****:** Yield: 87%, yellow solid, m.p. 98-100 °C, $[\alpha]^{20}_{D}$ = 23 (*c* 2.1 mg/mL, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.5 Hz, 2H, H-2″, H-6″), 7.40 (d, *J* = 8.5 Hz, 2H, H-3″, H-5″), 7.34 (s, 1H, H-5), 6.20 (s, 1H, H-8), 5.98 (dd, *J* = 10.5, 1.0 Hz, 2H, OCH_2O), 5.23 (d, *J* = 10.0 Hz, 1H, H-1), 4.92-4.98 (m, 1H, H-11), 4.20-4.25 (m, 2H, H-11, H-3), 3.97 (s, 3H, 4′-OCH_3), 3.91 (s, 3H, 3'-OCH_3), 3.87(s, 3H, 5′-OCH_3), 3.47-3.51 (m, 1H, H-2), 2.47 (s, 3H, CH_3); HRMS (ESI): Calcd for $C_{29}H_{26}O_{10}NCl_2S$ ($[M+H]^+$), 650.0649; Found, 650.0647.



Data for ***5j*****:** Yield: 62%, yellow solid, m.p. 92-94 °C, $[\alpha]^{20}_{D}$ = 19 (*c* 3.6 mg/mL, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 2H, H-2″, H-6″), 7.42 (d, *J* = 8.5 Hz, 2H, H-3″, H-5″), 7.35 (s, 1H, H-5), 6.20 (s, 1H, H-8), 5.96 (dd, *J* = 10.5, 1.0 Hz, 2H, OCH_2O), 5.23 (d, *J* = 10.0 Hz, 1H, H-1), 4.94-4.97 (m, 1H, H-3), 4.20-4.25 (m, 2H, H-11), 3.97 (s, 3H, 4′-OCH_3), 3.91 (s, 3H, 3′-OCH_3), 3.87 (s, 3H,

5′-OCH_3), 3.48-3.51 (m, 1H, H-2), 2.79 (q, J = 7.5 Hz, 2H, -CH_2CH_3), 1.31 (t, J = 7.5 Hz, 3H, CH_3); HRMS (ESI): Calcd for $C_{30}H_{28}O_{10}NCl_2S$ ($[M+H]^+$), 664.0805; Found, 664.0812.



Data for ***5k*****:** Yield: 44%, yellow solid, m.p. 114-116 °C, $[\alpha]^{20}_D$ = 20 (*c* 3.8 mg/mL, acetone) ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51 (s, 1H, H-5), 6.27 (s, 1H, H-8), 6.01 (dd, J = 9.5, 1.0 Hz, 2H, OCH_2O), 5.31 (d, J = 10.5 Hz, 1H, H-1), 4.96-4.99 (m, 1H, H-11), 4.31-4.36 (m, 2H, H-11, H-3), 3.99 (s, 3H, 4′-OCH_3), 3.93 (s, 3H, 3′-OCH_3), 3.89(s, 3H, 5′-OCH_3), 3.54-3.57 (m, 1H, H-2), 3.28 (s, 3H, CH_3); HRMS (ESI): Calcd for $C_{23}H_{22}O_{10}NCl_2S$ ($[M+H]^+$), 574.0336; Found, 574.0338.