

Supporting Information

Semisynthesis of esters and oxime esters/sulfonates from furyl-ring-based acetylation derivatives of fraxinellone as insecticidal agents

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Data for 8f: Colorless liquid, yield: 98%; $[\alpha]_D^{20} = -18$ (*c* 4.3 mg/mL, acetone); IR cm^{-1} : 3023, 2965, 2940, 1730, 1589, 1266, 1011; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.89 (d, $J = 8.4$ Hz, 2H, -Ph), 7.56 (d, $J = 8.4$ Hz, 2H, -Ph), 7.44 (s, 1H, H-2'), 6.35 (s, 1H, H-4'), 6.14-6.19 (m, 1H, -O(CH)CH₃), 4.84 (s, 1H, H-8), 2.13-2.31 (m, 2H, H-4), 2.11 (s, 3H, H-10), 1.73-1.87 (m, 3H, H-5, 6), 1.70 (d, $J = 2.0$ Hz, 1.5H, -OH(CH)CH₃), 1.69 (d, $J = 2.0$ Hz, 1.5H, -OH(CH)CH₃), 1.40-1.47 (m, 1H, H-6), 0.84-0.86 (m, 3H, H-11). HRMS (ESI): Calcd for $\text{C}_{23}\text{H}_{27}\text{O}_5\text{NBr}$ ($[\text{M}+\text{NH}_4]^+$), 476.1067; found, 476.1062.

Data for 8g: Colorless liquid, yield: 94%; $[\alpha]_D^{20} = -22$ (*c* 4.1 mg/mL, acetone); IR cm^{-1} : 2959, 2924, 2854, 1756, 1719, 1268, 1048, 767; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.13 (d, $J = 8.0$ Hz, 2H, -Ph), 7.73 (d, $J = 8.8$ Hz, 2H, -Ph), 7.44 (s, 1H, H-2'), 6.38 (s, 1H, H-4'), 6.16-6.22 (m, 1H, -O(CH)CH₃), 4.84 (s, 1H, H-8), 2.18-2.31 (m, 2H, H-4), 2.16 (s, 3H, H-10), 1.79-1.87 (m, 2H, H-5, 6), 1.73 (d, $J = 1.6$ Hz, 1.5H, -OH(CH)CH₃), 1.71 (d, $J = 1.6$ Hz, 1.5H, -OH(CH)CH₃), 1.41-1.47 (m, 2H, H-5, 6), 0.86-0.87 (m, 3H, H-11). HRMS (ESI): Calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5\text{N}_2$ ($[\text{M}+\text{NH}_4]^+$), 423.1914;

found, 423.1910.

Data for 8h: Colorless liquid, yield: 90%; $[\alpha]^{20}_D = -13$ (*c* 4.2 mg/mL, acetone); IR cm^{-1} : 2939, 2873, 1755, 1721, 1446, 1269, 1201, 1048; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.83 (dd, $J = 7.6, 1.2$ Hz, 1H, -Ph), 7.70 (d, $J = 9.6$ Hz, 1H, -Ph), 7.44 (s, 1H, H-2'), 7.38-7.42 (m, 1H, -Ph), 7.23-7.28 (m, 1H, -Ph), 6.36 (s, 1H, H-4'), 6.14-6.20 (m, 1H, -O(CH)CH₃), 4.84 (s, 1H, H-8), 2.18-2.31 (m, 2H, H-4), 2.13 (s, 3H, H-10), 1.79-1.83 (m, 3H, H-5, 6), 1.71 (d, $J = 2.0$ Hz, 1.5H, -OH(CH)CH₃), 1.70 (d, $J = 2.0$ Hz, 1.5H, -OH(CH)CH₃), 1.40-1.48 (m, 1H, H-6), 0.87-0.88 (m, 3H, H-11). HRMS (ESI): Calcd for $\text{C}_{23}\text{H}_{27}\text{O}_5\text{NF}$ ($[\text{M}+\text{NH}_4]^+$), 416.1868; found, 416.1864.

Data for 8i: Colorless liquid, yield: 82%; $[\alpha]^{20}_D = -15$ (*c* 3.5 mg/mL, acetone); IR cm^{-1} : 2937, 2873, 1755, 1720, 1254, 1048, 984; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.01 (s, 1H, -Ph), 7.92 (dd, $J = 7.6, 1.2$ Hz, 1H, -Ph), 7.51 (d, $J = 8.8$ Hz, 1H, -Ph), 7.44 (s, 1H, H-2'), 7.36 (t, $J = 8.0$ Hz, 1H, -Ph), 6.36 (s, 1H, H-4'), 6.14-6.20 (m, 1H, -O(CH)CH₃), 4.84 (s, 1H, H-8), 2.17-2.31 (m, 2H, H-4), 2.13 (s, 3H, H-10), 1.80-1.83 (m, 3H, H-5, 6), 1.71 (d, $J = 2.0$ Hz, 1.5H, -OH(CH)CH₃), 1.70 (d, $J = 2.4$ Hz, 1.5H, -OH(CH)CH₃), 1.40-1.48 (m, 1H, H-6), 0.87-0.88 (m, 3H, H-11). HRMS (ESI): Calcd for $\text{C}_{23}\text{H}_{22}\text{O}_5\text{Cl}$ ($[\text{M}-\text{H}]^+$), 413.1150; found, 413.1148.

Data for 8j: Colorless liquid, yield: 83%; $[\alpha]^{20}_D = -12$ (*c* 4.2 mg/mL, acetone); IR cm^{-1} : 2921, 2870, 2853, 1747, 1723, 1420, 1250, 1047; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.16 (t, $J = 1.6$ Hz, 1H, -Ph), 7.96 (dd, $J = 7.6, 1.2$ Hz, 1H, -Ph), 7.67 (d, $J = 8.0$ Hz, 1H, -Ph), 7.44 (s, 1H, H-2'), 7.29 (t, $J = 8.0$ Hz, 1H, -Ph), 6.36 (s, 1H, H-4'), 6.14-6.20 (m, 1H, -O(CH)CH₃), 4.84 (s, 1H, H-8), 2.18-2.31 (m, 2H, H-4), 2.13 (s, 3H, H-

10), 1.79-1.83 (m, 3H, H-5, 6), 1.71 (d, $J = 8.4$ Hz, 1.5H, -OH(CH)CH₃), 1.69 (d, $J = 8.4$ Hz, 1.5H, -OH(CH)CH₃), 1.40-1.48 (m, 1H, H-6), 0.87-0.88 (m, 3H, H-11).

HRMS (ESI): Calcd for C₂₃H₂₇O₅NBr ([M+NH₄]⁺), 476.1067; found, 476.1062.

Data for 9f: White solid, yield: 67%, m.p. 154-156 °C; $[\alpha]^{20}_D = -19$ (c 3.8 mg/mL, acetone); IR cm⁻¹: 2925, 2852, 1748, 1589, 1255, 1055, 910; ¹H NMR (500 MHz, CDCl₃) δ : 7.96 (d, $J = 8.5$ Hz, 2H, -Ph), 7.63 (d, $J = 8.5$ Hz, 2H, -Ph), 7.62 (s, 1H, H-2'), 6.97 (s, 1H, H-4'), 4.88 (s, 1H, H-8), 2.44 (s, 3H, -CH₃), 2.19-2.32 (m, 2H, H-4), 2.14 (s, 3H, H-10), 1.84-1.87 (m, 2H, H-5, 6), 1.72-1.76 (m, 1H, H-5), 1.45-1.49 (m, 1H, H-6), 0.87 (s, 3H, H-11). HRMS (ESI): Calcd for C₂₃H₂₃O₅NBr ([M+H]⁺), 472.0754; found, 472.0749.

Data for 9g: White solid, yield: 70%, m.p. 188-190 °C; $[\alpha]^{20}_D = -27$ (c 3.1 mg/mL, acetone); IR cm⁻¹: 2936, 2865, 1746, 1262, 1070, 910; ¹H NMR (500 MHz, CDCl₃) δ : 8.20 (d, $J = 8.5$ Hz, 2H, -Ph), 7.80 (d, $J = 8.0$ Hz, 2H, -Ph), 7.63 (s, 1H, H-2'), 6.99 (s, 1H, H-4'), 4.89 (s, 1H, H-8), 2.46 (s, 3H, -CH₃), 2.27-2.32 (m, 2H, H-4), 2.14 (s, 3H, H-10), 1.84-1.87 (m, 2H, H-5, 6), 1.71-1.77 (m, 1H, H-5), 1.45-1.50 (m, 1H, H-6), 0.87 (s, 3H, H-11). HRMS (ESI): Calcd for C₂₄H₂₃O₅N₂ ([M+H]⁺), 419.1601; found, 419.1598.

Data for 9h: White solid, yield: 88%, m.p. 194-196 °C; $[\alpha]^{20}_D = -13$ (c 3.3 mg/mL, acetone); IR cm⁻¹: 2926, 2924, 1749, 1674, 1266, 1046, 901; ¹H NMR (500 MHz, CDCl₃) δ : 7.90-7.93 (m, 1H, -Ph), 7.77-7.79 (m, 1H, -Ph), 7.62 (s, 1H, H-2'), 7.47-7.50 (m, 1H, -Ph), 7.32-7.34 (m, 1H, -Ph), 6.97 (s, 1H, H-4'), 4.89 (s, 1H, H-8), 2.46 (s, 3H, -CH₃), 2.27-2.28 (m, 1H, H-4), 2.18-2.21 (m, 1H, H-4), 2.14 (s, 3H, H-10),

1.85-1.87 (m, 2H, H-5, 6), 1.74-1.80 (m, 1H, H-5), 1.45-1.50 (m, 1H, H-6), 0.87 (s, 3H, H-11). HRMS (ESI): Calcd for $C_{23}H_{23}O_5NF$ ($[M+H]^+$), 412.1555; found, 412.1551.

Data for 9i: White solid, yield: 86%, m.p. 206-208 °C; $[\alpha]_D^{20} = -25$ (c 4.0 mg/mL, acetone); IR cm^{-1} : 2927, 2870, 1753, 1675, 1427, 1244, 911; 1H NMR (500 MHz, $CDCl_3$) δ : 8.07 (t, $J = 1.5$ Hz, 1H, -Ph), 7.99 (d, $J = 7.5$ Hz, 1H, -Ph), 7.62 (s, 1H, H-2'), 7.58-7.60 (m, 1H, -Ph), 7.43 (t, $J = 8.0$ Hz, 1H, -Ph), 6.97 (s, 1H, H-4'), 4.89 (s, 1H, H-8), 2.46 (s, 3H, $-CH_3$), 2.27-2.32 (m, 1H, H-4), 2.18-2.21 (m, 1H, H-4), 2.14 (s, 3H, H-10), 1.85-1.87 (m, 2H, H-5, 6), 1.74-1.78 (m, 1H, H-5), 1.45-1.50 (m, 1H, H-6), 0.87 (s, 3H, H-11). HRMS (ESI): Calcd for $C_{23}H_{23}O_5NCl$ ($[M+H]^+$), 428.1259; found, 428.1254.

Data for 9j: White solid, yield: 72%, m.p. 218-220 °C; $[\alpha]_D^{20} = -16$ (c 3.4 mg/mL, acetone); IR cm^{-1} : 2926, 2871, 1753, 1678, 1230, 1206, 1048, 913; 1H NMR (500 MHz, $CDCl_3$) δ : 8.22 (t, $J = 1.5$ Hz, 1H, -Ph), 8.03 (dd, $J = 7.0, 1.0$ Hz, 1H, -Ph), 7.73-7.76 (m, 1H, -Ph), 7.62 (s, 1H, H-2'), 7.36 (t, $J = 8.0$ Hz, 1H, -Ph), 6.97 (s, 1H, H-4'), 4.89 (s, 1H, H-8), 2.46 (s, 3H, $-CH_3$), 2.27-2.32 (m, 1H, H-4), 2.16-2.21 (m, 1H, H-4), 2.14 (s, 3H, H-10), 1.84-1.87 (m, 2H, H-5, 6), 1.73-1.77 (m, 1H, H-5), 1.44-1.50 (m, 1H, H-6), 0.87 (s, 3H, H-11). HRMS (ESI): Calcd for $C_{23}H_{23}O_5NBr$ ($[M+H]^+$), 472.0754; found, 472.0754.

Data for 10f: White solid, yield: 67%, m.p. 128-130 °C; $[\alpha]_D^{20} = 119$ (c 3.4 mg/mL, acetone); IR cm^{-1} : 2953, 2924, 2853, 1746, 1252, 914; 1H NMR (500 MHz, $CDCl_3$) δ : 7.93 (d, $J = 9.0$ Hz, 2H, -Ph), 7.63 (d, $J = 9.0$ Hz, 2H, -Ph), 7.55 (d, $J = 2.0$ Hz, 1H,

H-5'), 6.73 (d, $J = 2.0$ Hz, 1H, H-4'), 5.82 (s, 1H, H-8), 2.48 (s, 3H, $-CH_3$), 2.21-2.24 (m, 2H, H-4), 2.14 (s, 3H, H-10), 2.04-2.09 (m, 1H, H-5), 1.80-1.83 (m, 1H, H-6), 1.62-1.67 (m, 2H, H-5, 6), 0.95 (s, 3H, H-11). HRMS (ESI): Calcd for $C_{23}H_{23}O_5NBr$ ($[M+H]^+$), 472.0754; found, 472.0747.

Data for 10g: White solid, yield: 85%, m.p. 206-208 °C; $[\alpha]^{20}_D = 71$ (c 3.1 mg/mL, acetone); IR cm^{-1} : 2953, 2923, 2851, 1749, 1460, 1256, 1065, 923; 1H NMR (500 MHz, $CDCl_3$) δ : 8.17 (d, $J = 8.5$ Hz, 2H, -Ph), 7.79 (d, $J = 8.5$ Hz, 2H, -Ph), 7.57 (d, $J = 1.5$ Hz, 1H, H-5'), 6.75 (d, $J = 1.5$ Hz, 1H, H-4'), 5.81 (s, 1H, H-8), 2.50 (s, 3H, $-CH_3$), 2.22-2.24 (m, 2H, H-4), 2.15 (s, 3H, H-10), 2.02-2.08 (m, 1H, H-5), 1.79-1.83 (m, 1H, H-6), 1.62-1.68 (m, 2H, H-5, 6), 0.96 (s, 3H, H-11). HRMS (ESI): Calcd for $C_{24}H_{23}O_5N_2$ ($[M+H]^+$), 419.1601; found, 419.1602.

Data for 10h: White solid, yield: 85%, m.p. 80-82 °C; $[\alpha]^{20}_D = 49$ (c 4.3 mg/mL, acetone); IR cm^{-1} : 2932, 2872, 1750, 1444, 1266, 910; 1H NMR (500 MHz, $CDCl_3$) δ : 7.87 (d, $J = 7.5$ Hz, 1H, -Ph), 7.74 (d, $J = 9.0$ Hz, 1H, -Ph), 7.55 (d, $J = 1.5$ Hz, 1H, H-5'), 7.47-7.49 (m, 1H, -Ph), 7.31-7.34 (m, 1H, -Ph), 6.74 (d, $J = 0.8$ Hz, 1H, H-4'), 5.82 (s, 1H, H-8), 2.49 (s, 3H, $-CH_3$), 2.21-2.24 (m, 2H, H-4), 2.14 (s, 3H, H-10), 2.04-2.09 (m, 1H, H-5), 1.81-1.83 (m, 1H, H-6), 1.63-1.65 (m, 2H, H-5, 6), 0.96 (s, 3H, H-11). HRMS (ESI): Calcd for $C_{23}H_{23}O_5NF$ ($[M+H]^+$), 412.1555; found, 412.1551.

Data for 10i: White solid, yield: 70%, m.p. 158-160 °C; $[\alpha]^{20}_D = 111$ (c 3.8 mg/mL, acetone); IR cm^{-1} : 2954, 2926, 2870, 1762, 1745, 1230, 1044, 879; 1H NMR (500

MHz, CDCl₃) δ : 8.04 (t, $J = 2.0$ Hz, 1H, -Ph), 7.96 (d, $J = 7.5$ Hz, 1H, -Ph), 7.58 (d, $J = 8.0$ Hz, 1H, -Ph), 7.56 (d, $J = 1.5$ Hz, 1H, H-5'), 7.42 (t, $J = 8.0$ Hz, 1H, -Ph), 6.74 (d, $J = 2.0$ Hz, 1H, H-4'), 5.82 (s, 1H, H-8), 2.50 (s, 3H, -CH₃), 2.21-2.24 (m, 2H, H-4), 2.14 (s, 3H, H-10), 2.03-2.09 (m, 1H, H-5), 1.80-1.83 (m, 1H, H-6), 1.62-1.66 (m, 2H, H-5, 6), 0.96 (s, 3H, H-11). HRMS (ESI): Calcd for C₂₃H₂₃O₅NCl ([M+H]⁺), 428.1259; found, 428.1254.

Data for 10j: White solid, yield: 72%, m.p. 148-150 °C; [α]_D²⁰ = 114 (*c* 3.8 mg/mL, acetone); IR cm⁻¹: 2933, 2869, 1749, 1237, 1052, 912; ¹H NMR (500 MHz, CDCl₃) δ : 8.20 (s, 1H, -Ph), 8.00 (d, $J = 8.0$ Hz, 1H, -Ph), 7.73 (d, $J = 9.0$ Hz, 1H, -Ph), 7.55 (d, $J = 2.0$ Hz, 1H, H-5'), 7.36 (t, $J = 8.0$ Hz, 1H, -Ph), 6.74 (d, $J = 2.0$ Hz, 1H, H-4'), 5.82 (s, 1H, H-8), 2.49 (s, 3H, -CH₃), 2.21-2.24 (m, 2H, H-4), 2.14 (s, 3H, H-10), 2.03-2.08 (m, 1H, H-5), 1.80-1.83 (m, 1H, H-6), 1.62-1.68 (m, 2H, H-5, 6), 0.96 (s, 3H, H-11). HRMS (ESI): Calcd for C₂₃H₂₃O₅NBr ([M+H]⁺), 472.0754; found, 472.0750.