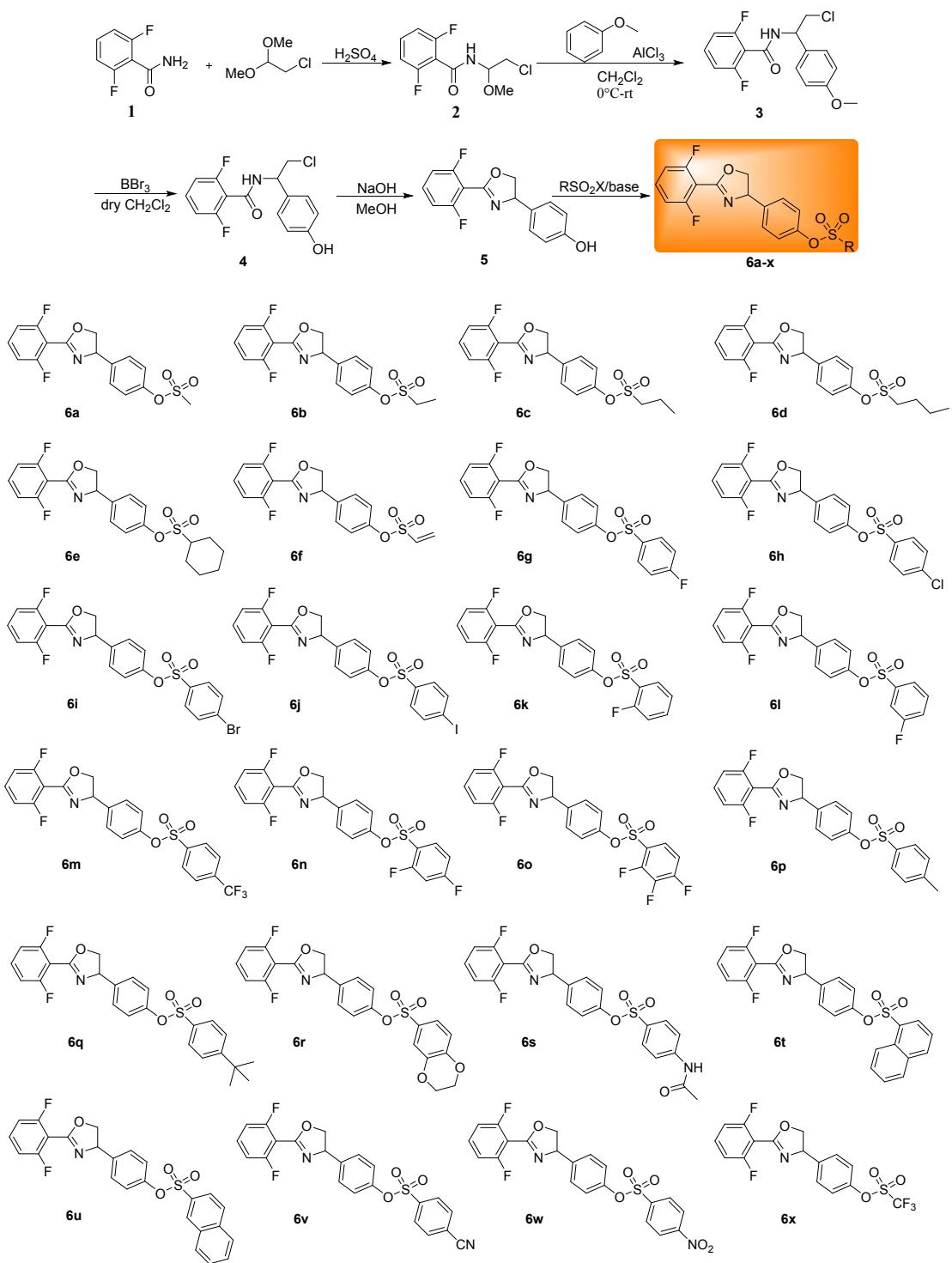


Supporting information

Design, Synthesis, Acaricidal Activities, and Structure–Activity
Relationship Studies of Novel Oxazolines Containing Sulfonate Moieties

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N-(2-chloro-1-methoxyethyl)-2,6-difluorobenzamide (2)

White solid, yield 87%, mp 91-92 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.38 (m, 1H), 6.99 (t, J = 8.0 Hz, 2H), 6.49 (d, J = 8.0 Hz, 1H), 5.66-5.60 (m, 1H), 3.78 (dd, J =

12.0, 3.6 Hz, 1H), 3.71 (dd, J = 12.0, 4.0 Hz, 1H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0 (dd, J = 251.3, J = 6.6 Hz), 160.8, 132.3 (t, J = 10.2 Hz), 113.6 (t, J = 19.8 Hz), 112.2 (dd, J = 23.4, 2.1 Hz), 79.5, 56.4, 46.2.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenol (5)

Light yellow solid, yield 51%, mp 157-158 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.41 (s, 1H), 7.74–7.58 (m, 1H), 7.28 (t, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 5.35 (dd, J = 10.0, 8.0 Hz, 1H), 4.77 (dd, J = 10.0, 8.8 Hz, 1H), 4.14 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 160.6 (dd, J = 252.9, 6.7 Hz), 157.2, 155.8, 133.9 (t, J = 10.6 Hz), 132.8, 128.2, 115.8, 112.8 (dd, J = 17.9, 5.2 Hz), 107.3 (t, J = 18.6 Hz), 75.1, 69.5. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{F}_2\text{NO}_2$ [M+H] $^+$ 276.0831, found: 276.0822

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl methanesulfonate (6a)

Colorless oil, yield 71%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.75–7.62 (m, 1H), 7.44 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.30 (t, J = 8.4 Hz, 2H), 5.55 (dd, J = 10.4, 7.9 Hz, 1H), 4.86 (dd, J = 10.3, 8.7 Hz, 1H), 4.24 (t, J = 8.0 Hz, 1H), 3.39 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 160.1 (dd, J = 253.6, 6.4 Hz), 156.2, 148.3, 141.2, 133.7 (t, J = 10.4 Hz), 128.2, 122.5, 112.4 (dd, J = 20.0, 4.8 Hz), 106.4 (t, J = 18.0 Hz), 74.3, 68.6, 37.3. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{14}\text{F}_2\text{NO}_4\text{S}$ [M+H] $^+$ 354.0606, found 354.0605

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl ethanesulfonate (6b)

Light yellow oil, yield 70%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.71–7.63 (m, 1H),

7.43 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.8$ Hz, 2H), 7.29 (t, $J = 8.4$ Hz, 2H), 5.54 (dd, $J = 10.4, 8.0$ Hz, 1H), 4.86 (dd, $J = 10.4, 8.8$ Hz, 1H), 4.23 (t, $J = 8.0$ Hz, 1H), 3.52 (q, $J = 7.2$ Hz, 2H), 1.38 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.6 (dd, $J = 253.5, 6.2$ Hz), 156.7, 148.6, 141.6, 134.2 (t, $J = 10.4$ Hz), 128.7, 122.9, 112.9 (dd, $J = 19.9, 4.8$ Hz), 106.9 (t, $J = 18.5$ Hz), 74.8, 69.0, 45.0, 8.5. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{F}_2\text{NO}_4\text{S} [\text{M}+\text{H}]^+$ 368.0763, found: 368.0759.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl propane-1-sulfonate (6c)

Light yellow oil, yield 83%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.72–7.63 (m, 1H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.30 (t, $J = 8.8$ Hz, 2H), 5.56 (dd, $J = 9.6, 8.4$ Hz, 1H), 4.87 (dd, $J = 10.0, 9.2$ Hz, 1H), 4.24 (t, $J = 8.4$ Hz, 1H), 3.51 (t, $J = 7.2$ Hz, 2H), 1.91–1.80 (m, 2H), 1.04 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.2 (dd, $J = 253.2, 6.4$ Hz), 156.2, 148.1, 141.1, 133.6 (t, $J = 10.4$ Hz), 128.2, 122.4, 112.3 (dd, $J = 20.0, 4.4$ Hz), 106.5 (t, $J = 18.4$ Hz), 74.3, 68.6, 51.3, 16.9, 12.3. HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{18}\text{F}_2\text{NO}_4\text{S} [\text{M}+\text{H}]^+$ 382.0919, found: 382.0926

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl butane-1-sulfonate (6d)

Colorless oil, yield 78%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.73–7.62 (m, 1H), 7.45 (d, $J = 8.8$ Hz, 2H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.31 (t, $J = 8.4$ Hz, 2H), 5.55 (dd, $J = 10.0, 8.0$ Hz, 1H), 4.87 (dd, $J = 10.0, 8.8$ Hz, 1H), 4.25 (t, $J = 8.4$ Hz, 1H), 3.57–3.50 (m, 2H), 1.88–1.74 (m, 2H), 1.51–1.40 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.2 (dd, $J = 253.4, 6.1$ Hz), 156.2, 148.2, 141.1, 133.6 (t, $J = 10.5$ Hz), 128.2, 122.4, 112.4 (dd, $J = 20.2, 4.3$ Hz), 106.5 (t, $J = 18.4$ Hz), 74.3, 68.6, 49.4,

25.1, 20.6, 13.3. HRMS (ESI): calcd for $C_{19}H_{20}F_2NO_4S$ $[M+H]^+$ 396.1076, found: 396.1082

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl cyclohexanesulfonate

(6e)

Colorless oil, yield 60%. 1H NMR (400 MHz, DMSO- d_6) δ 7.74–7.61 (m, 1H), 7.43 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.30 (t, J = 8.4 Hz, 2H), 5.54 (dd, J = 10.0, 8.0 Hz, 1H), 4.86 (dd, J = 10.0, 8.8 Hz, 1H), 4.24 (t, J = 8.4 Hz, 1H), 3.59–3.49 (m, 1H), 2.20 (d, J = 11.2 Hz, 2H), 1.83 (d, J = 13.2 Hz, 2H), 1.67–1.52 (m, 3H), 1.42–1.32 (m, 2H), 1.26–1.16 (m, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.7 (dd, J = 253.6, 6.0 Hz), 156.7, 148.5, 141.4, 134.2 (t, J = 10.4 Hz), 128.7, 122.8, 112.9 (dd, J = 20.0, 4.8 Hz), 106.9 (d, J = 8.0 Hz), 74.8, 69.1, 59.4, 26.6, 24.9, 24.6. HRMS (ESI): calcd for $C_{21}H_{22}F_2NO_4S$ $[M+H]^+$ 422.1232, found: 422.1240.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl ethenesulfonate (6f)

Light yellow oil, yield 79%. 1H NMR (400 MHz, DMSO- d_6) δ 7.80–7.60 (m, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.37–7.26 (m, 4H), 7.22 (dd, J = 10.0, 6.4 Hz, 1H), 6.39 (d, J = 10.0 Hz, 1H), 6.30 (d, J = 16.4 Hz, 1H), 5.53 (dd, J = 10.0, 8.0 Hz, 1H), 4.85 (dd, J = 10.0, 8.8 Hz, 1H), 4.23 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.1 (dd, J = 253.6, 6.1 Hz), 156.3, 148.2, 141.3, 133.7 (t, J = 10.5 Hz), 133.4, 132.1, 128.2, 122.5, 112.4 (dd, J = 20.0, 4.5 Hz), 106.5 (t, J = 18.3 Hz), 74.3, 68.5. HRMS (ESI): calcd for $C_{17}H_{14}F_2NO_4S$ $[M+H]^+$ 366.0606, found: 366.0612.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-

fluorobenzenesulfonate (6g)

White solid, yield 90%, mp 74-75 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 7.98–7.94 (m, 2H), 7.72–7.63 (m, 1H), 7.57–7.50 (m, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 8.4 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 5.50 (dd, J = 10.0, 8.0 Hz, 1H), 4.83 (dd, J = 10.4, 8.8 Hz, 1H), 4.18 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.3, 164.8, 160.6 (dd, J = 253.6, 6.0 Hz), 156.8, 145.2 (d, J = 672.4 Hz), 134.2 (t, J = 10.4 Hz), 132.1 (d, J = 10.0 Hz), 130.9 (d, J = 3.2 Hz), 128.7, 122.8, 117.7 (d, J = 23.2 Hz), 112.9 (dd, J = 20.0, 4.8 Hz), 106.8 (t, J = 18.0 Hz), 74.7, 68.9. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{15}\text{F}_3\text{NO}_4\text{S}$ [M+H] $^+$ 434.0668, found: 434.0673

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-

chlorobenzenesulfonate (6h)

Light yellow solid, yield 88%, mp 66-67 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 7.89 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.77–7.63 (m, 1H), 7.35 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 8.4 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 5.50 (dd, J = 10.0, 8.0 Hz, 1H), 4.83 (dd, J = 10.4, 8.8 Hz, 1H), 4.18 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 161.4 (dd, J = 253.5, 6.1 Hz), 157.4, 149.3, 142.7, 141.3, 134.9 (t, J = 10.4 Hz), 134.3, 131.3, 131.2, 129.5, 123.5, 113.6 (dd, J = 20.2, 4.4 Hz), 107.6 (t, J = 18.3 Hz), 75.4, 69.7. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{15}\text{ClF}_2\text{NO}_4\text{S}$ [M+H] $^+$ 450.0373, found: 450.0365.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-

bromobenzenesulfonate (6i)

Colorless oil, yield 80%. ^1H NMR (400 MHz, DMSO- d_6) δ 7.90 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.72–7.63 (m, 1H), 7.35 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 5.50 (dd, J = 10.4, 8.0 Hz, 1H), 4.83 (dd, J = 10.0, 8.8 Hz, 1H), 4.18 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.7 (dd, J = 253.6, 6.0 Hz), 156.7, 148.6, 142.0, 134.2 (t, J = 10.4 Hz), 134.0, 133.5, 130.6, 129.8, 128.8, 122.8, 112.9 (dd, J = 20.0, 4.8 Hz), 106.9 (t, J = 18.4 Hz), 74.7, 69.0. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{15}\text{BrF}_2\text{NO}_4\text{S}$ [M+H] $^+$ 493.9868, found: 493.9862.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-iodobenzenesulfonate (6j)

Yellow oil, yield 85%. ^1H NMR (400 MHz, DMSO- d_6) δ 8.06 (d, J = 7.2 Hz, 2H), 7.71–7.65 (m, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2H), 7.29 (t, J = 8.8 Hz, 2H), 7.09 (d, J = 7.6 Hz, 2H), 5.52–5.46 (m, 1H), 4.85–4.80 (m, 1H), 4.18 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.1 (dd, J = 253.6, 6.4 Hz), 156.3, 148.0, 141.4, 138.8, 133.7 (t, J = 10.4 Hz), 129.6, 128.2, 122.3, 115.3, 112.4 (dd, J = 20.0, 4.4 Hz), 106.3 (t, J = 18.4 Hz), 104.0, 74.2, 68.4. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{15}\text{F}_2\text{INO}_4\text{S}$ [M+H] $^+$ 541.9729, found: 541.9728.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 2-fluorobenzenesulfonate (6k)

White solid, yield 83%, mp 50–51 °C. ^1H NMR (400 MHz, DMSO) δ 7.94–7.88 (m, 1H), 7.82–7.77 (m, 1H), 7.71–7.61 (m, 2H), 7.46–7.41 (m, 1H), 7.36 (d, J = 8.8 Hz,

2H), 7.28 (t, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 5.49 (dd, J = 10.0, 8.0 Hz, 1H), 4.82 (dd, J = 10.4, 8.8 Hz, 1H), 4.27–4.04 (m, 1H). ^{13}C NMR (100 MHz, DMSO-*d*₆) δ 160.1 (dd, J = 253.6, 6.4 Hz), 158.5 (d, J = 257.6 Hz), 156.3, 148.0, 141.6, 138.2 (d, J = 8.8 Hz), 133.7 (t, J = 10.4 Hz), 131.1, 128.3, 125.5 (d, J = 3.6 Hz), 122.2 (d, J = 13.6 Hz), 121.9, 117.9 (d, J = 20.4 Hz), 112.4 (dd, J = 20.0, 4.8 Hz), 106.4 (t, J = 18.4 Hz), 74.2, 68.5. HRMS (ESI): calcd for C₂₁H₁₅F₃NO₄S [M+H]⁺ 434.0668, found: 434.0667.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 3-fluorobenzenesulfonate (6l)

Colorless oil, yield 96%. ^1H NMR (400 MHz, DMSO-*d*₆) δ 7.78 (d, J = 8.0 Hz, 1H), 7.76–7.70 (m, 3H), 7.70–7.61 (m, 1H), 7.35 (d, J = 8.8 Hz, 2H), 7.28 (t, J = 8.4 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 5.50 (dd, J = 10.0, 8.0 Hz, 1H), 4.83 (dd, J = 10.0, 8.8 Hz, 1H), 4.17 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ 162.2 (d, J = 250.0 Hz), 160.7 (dd, J = 253.6, 6.2 Hz), 156.7, 148.6, 142.0, 136.6 (d, J = 7.5 Hz), 134.2 (t, J = 10.4 Hz), 132.7 (d, J = 8.2 Hz), 128.7, 125.1 (d, J = 2.8 Hz), 122.9 (d, J = 21.5 Hz), 122.7, 115.8 (d, J = 25.2 Hz), 112.9 (dd, J = 19.9, 4.8 Hz), 106.9 (t, J = 18.4 Hz), 74.7, 69.0. HRMS (ESI): calcd for C₂₁H₁₅F₃NO₄S [M+H]⁺ 434.0668, found: 434.0673

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-(trifluoromethyl)benzene sulfonate (6m)

Colorless oil, yield 90%. ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.12 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.4 Hz, 2H), 7.72–7.63 (m, 1H), 7.36 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 8.4 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 5.50 (dd, J = 10.0, 8.4 Hz, 1H), 4.83 (dd, J =

10.0, 8.8 Hz, 1H), 4.18 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.2 (dd, J = 253.7, 6.1 Hz), 156.2, 148.0, 141.7, 138.2, 134.3 (q, J = 32.3 Hz), 133.7 (t, J = 10.4 Hz), 129.3, 128.3, 127.0 (q, J = 3.6 Hz), 125.9 (q, J = 278 Hz), 122.3, 112.4 (dd, J = 20.0, 4.5 Hz), 106.4 (t, J = 18.4 Hz), 74.2, 68.5. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{15}\text{F}_5\text{NO}_4\text{S} [\text{M}+\text{H}]^+$ 484.0636, found: 484.0641.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 2,4-difluorobenzenesulfonate (6n)

Light yellow solid, yield 87%, mp 80-81 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 7.91–7.84 (m, 1H), 7.82–7.75 (m, 1H), 7.72–7.63 (m, 1H), 7.39–7.26 (m, 5H), 7.16 (d, J = 8.0 Hz, 2H), 5.50 (dd, J = 10.0, 8.0 Hz, 1H), 4.83 (dd, J = 10.4, 8.8 Hz, 1H), 4.18 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 166.6 (dd, J = 257.4, 12.0 Hz), 160.2 (dd, J = 253.5, 6.2 Hz), 159.6 (dd, J = 259.7, 14.1 Hz), 156.2, 147.9, 141.7, 133.7 (t, J = 10.5 Hz), 133.4 (d, J = 11.5 Hz), 128.4, 122.0, 119.0 (dd, J = 13.9, 3.7 Hz), 113.2 (dd, J = 22.7, 3.6 Hz), 112.4 (dd, J = 20.0, 4.5 Hz), 107.0 (dd, J = 27.2, 24.9 Hz), 106.4 (t, J = 18.2 Hz), 74.2, 68.5. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{14}\text{F}_4\text{NO}_4\text{S} [\text{M}+\text{H}]^+$ 452.0574, found: 452.0579.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 2,3,4-trifluorobenzenesulfonate (6o)

Light yellow solid, yield 83%, mp 72-73 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 7.72–7.62 (m, 2H), 7.59–7.51 (m, 1H), 7.36 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 8.8 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 5.51 (dd, J = 10.0, 8.0 Hz, 1H), 4.83 (dd, J = 10.0, 9.2 Hz, 1H), 4.18 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.6 (dd, J = 253.5, 6.2

Hz), 156.7, 155.3 (ddd, $J = 258.8, 10.0, 3.3$ Hz), 148.9 (ddd, $J = 260.8, 11.7, 4.3$ Hz), 148.4, 142.4, 140.7 (dt, $J = 252.3$ Hz, 14.9 Hz), 134.2 (t, $J = 10.5$ Hz), 128.9, 126.6 (dd, $J = 9.8, 4.1$ Hz), 122.8, 120.5 (dd, $J = 11.1, 3.5$ Hz), 114.4 (dd, $J = 18.6, 3.5$ Hz), 112.9 (dd, $J = 19.8, 4.8$ Hz), 106.9 (t, $J = 18.3$ Hz), 74.7, 69.0. HRMS (ESI): calcd for $C_{21}H_{13}F_5NO_4S$ [M+H]⁺ 470.0480, found: 470.0479.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-methylbenzenesulfonate (6p)

Yellow solid, yield 80%, mp 69-70 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.76 (d, $J = 8.0$ Hz, 2H), 7.72-7.62 (m, 1H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.35-7.26 (m, 4H), 7.06 (d, $J = 8.4$ Hz, 2H), 5.52-5.46 (m, 1H), 4.86-4.79 (m, 1H), 4.20-4.15 (m, 1H), 2.42 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 160.6 (dd, $J = 253.6, 6.0$ Hz), 156.7, 148.7, 146.3, 141.7, 134.2 (t, $J = 10.4$ Hz), 131.9, 130.7, 128.7, 128.6, 122.7, 112.9 (dd, $J = 20.0, 4.4$ Hz), 106.9 (t, $J = 18.4$ Hz), 74.7, 69.0, 21.62. HRMS (ESI): calcd for $C_{22}H_{18}F_2NO_4S$ [M+H]⁺ 430.0919, found: 430.0925.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-(*tert*-butyl)benzenesulfonate (6q)

Colorless oil, yield 94%, ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.82 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.72-7.63 (m, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.29 (t, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 5.50 (dd, $J = 10.0, 8.0$ Hz, 1H), 4.83 (dd, $J = 10.0, 8.8$ Hz, 1H), 4.19 (t, $J = 8.4$ Hz, 1H), 1.32 (s, 9H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 160.6 (dd, $J = 253.6, 6.4$ Hz), 158.8, 156.7, 148.7, 141.7, 134.2 (t, $J = 10.4$ Hz), 132.0,

128.6, 128.5, 127.2 122.7, 112.9 (dd, $J = 20.0, 4.4$ Hz), 106.9 (t, $J = 17.6$ Hz), 74.7, 69.0, 35.6 , 31.1. HRMS (ESI): calcd for $C_{25}H_{24}F_2NO_4S$ [M+H]⁺ 472.1389, found: 472.1394.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 2,3-dihydrobenzo[b][1,4]dioxine-6-sulfonate (6r)

White solid, yield 22%, mp 52-53 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.72–7.63 (m, 1H), 7.39–7.25 (m, 6H), 7.13–7.08 (m, 3H), 5.51 (dd, $J = 10.0, 8.0$ Hz, 1H), 4.84 (dd, $J = 10.0, 8.8$ Hz, 1H), 4.40–4.36 (m, 2H), 4.35–4.30 (m, 2H), 4.19 (t, $J = 8.4$ Hz, 1H). ¹³C NMR (100 MHz, DMSO) δ 160.6 (dd, $J = 253.6, 6.1$ Hz), 156.7, 149.4, 148.8, 144.1, 141.7, 134.2 (t, $J = 10.5$ Hz), 128.6, 126.6, 122.8, 122.5, 118.6, 117.5, 112.9 (dd, $J = 19.8, 4.8$ Hz), 106.9 (t, $J = 18.4$ Hz), 74.7, 69.0, 65.0, 64.5. HRMS (ESI): calcd for $C_{23}H_{18}F_2NO_6S$ [M+H]⁺ 474.0817, found: 474.0818.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-acetamidobenzenesulfonate (6s)

White solid, yield 44%, mp 52-53 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.54 (s, 1H), 7.89 (d, $J = 9.2$ Hz, 2H), 7.83 (d, $J = 9.2$ Hz, 2H), 7.71–7.63 (m, 1H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.31–7.25 (m, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 5.52 (dd, $J = 10.0, 8.0$ Hz, 1H), 4.85 (dd, $J = 10.4, 8.8$ Hz, 1H), 4.23–4.17 (m, 1H), 2.14 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 170.0, 160.6 (dd, $J = 253.6, 6.0$ Hz), 156.8, 148.8, 145.3, 141.6, 134.1 (t, $J = 10.4$ Hz), 130.1, 128.5, 127.8, 122.8, 119.3, 112.8 (dd, $J = 20.0, 4.4$ Hz), 106.8 (t, $J = 18.4$ Hz), 74.7, 69.0, 24.6. HRMS (ESI): calcd for $C_{23}H_{19}F_2N_2O_5S$ [M+H]⁺

473.0977, found: 473.0978.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl naphthalene-1-sulfonate

(6t)

Colorless oil, yield 75%. ^1H NMR (400 MHz, DMSO- d_6) δ 8.66 (d, J = 8.4 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 7.2 Hz, 1H), 7.95–7.89 (m, 1H), 7.83–7.77 (m, 1H), 7.68–7.63 (m, 2H), 7.32–7.21 (m, 4H), 6.91 (d, J = 6.8 Hz, 2H), 5.45–5.39 (m, 1H), 4.81–4.75 (m, 1H), 4.14–4.10 (m, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.6 (dd, J = 253.7, 6.1 Hz), 156.7, 148.7, 141.8, 136.9, 134.2, 134.1 (t, J = 10.4 Hz), 131.8, 130.1, 130.0, 129.9, 128.7, 128.11, 128.05, 125.1, 124.5, 122.3, 112.8 (dd, J = 20.3, 4.3 Hz), 106.9 (t, J = 18.4 Hz), 74.6, 69.0. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{18}\text{F}_2\text{NO}_4\text{S} [\text{M}+\text{H}]^+$ 466.0919, found: 466.0921.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl naphthalene-2-sulfonate

(6u)

Colorless oil, yield 76%. ^1H NMR (400 MHz, DMSO- d_6) δ 8.58 (d, J = 1.2 Hz, 1H), 8.23 (t, J = 7.2 Hz, 2H), 8.12 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 8.8, 2.0 Hz, 1H), 7.84–7.77 (m, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.70–7.61 (m, 1H), 7.35–7.22 (m, 4H), 7.08 (d, J = 8.8 Hz, 2H), 5.45 (dd, J = 10.0, 8.0 Hz, 1H), 4.80 (dd, J = 10.0, 8.8 Hz, 1H), 4.14 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 160.1 (dd, J = 253.6, 6.2 Hz), 156.2, 148.3, 141.3, 135.0, 133.7 (t, J = 10.6 Hz), 131.4, 131.3, 130.2, 130.0, 130.0, 129.6, 128.2, 128.1, 128.0, 122.4, 122.3, 112.4 (dd, J = 20.3, 4.3 Hz), 106.4 (t, J = 18.6

Hz), 74.2, 68.5. HRMS (ESI): calcd for $C_{25}H_{18}F_2NO_4S$ $[M+H]^+$ 466.0919, found: 466.0924.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-cyanobenzenesulfonate (6v)

Yellow solid, yield 85%, mp 107-108 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.53-7.38 (m, 1H), 7.30 (d, J = 8.8 Hz, 2H), 7.06-6.94 (m, 4H), 5.45 (dd, J = 10.0, 8.4 Hz, 1H), 4.82 (dd, J = 10.0, 8.8 Hz, 1H), 4.23 (t, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4 (dd, J = 256.4, 5.9 Hz), 153.4, 143.9, 136.7, 134.6, 128.2, 128.0 (t, J = 10.4 Hz), 124.4, 123.6, 117.8, 113.3, 112.1, 107.3 (dd, J = 20.3, 5.2 Hz), 102.1 (t, J = 17.5 Hz), 69.8, 64.7. HRMS (ESI): calcd for $C_{22}H_{15}F_2N_2O_4S$ $[M+H]^+$ 441.0715, found: 441.0717.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl 4-nitrobenzenesulfonate (6w)

Light yellow solid, yield 77%, mp 131-132°C. ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 160.2 (dd, J = 253.6, 6.1 Hz), 156.3, 151.1, 148.0, 141.7, 139.5, 133.7 (t, J = 10.2 Hz), 130.0, 128.4, 125.0, 122.3, 112.4 (dd, J = 20.2, 4.1 Hz), 106.3 (d, J = 18.3 Hz), 74.2, 68.5. 1H NMR (400 MHz, $DMSO-d_6$) δ 8.47 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.8 Hz, 2H), 7.73-7.62 (m, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 5.51 (dd, J = 10.0, 8.0 Hz, 1H), 4.84 (dd, J = 10.4, 8.8 Hz, 1H), 4.19 (t, J = 8.4 Hz, 1H). HRMS (ESI): calcd for $C_{21}H_{15}F_2N_2O_6S$ $[M+H]^+$ 461.0613, found: 461.0618.

4-(2-(2,6-difluorophenyl)-4,5-dihydrooxazol-4-yl)phenyl trifluoromethanesulfonate (6x)

White solid, yield 71%, mp 167–168 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.73–7.64 (m, 1H), 7.58–7.50 (m, 4H), 7.30 (t, *J* = 8.4 Hz, 2H), 5.59 (dd, *J* = 10.0, 8.0 Hz, 1H), 4.88 (dd, *J* = 10.4, 8.8 Hz, 1H), 4.29–4.22 (m, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 160.7 (dd, *J* = 253.6, 6.1 Hz), 157.0, 148.9, 143.5, 134.2 (t, *J* = 10.5 Hz), 129.3, 122.2, 118.7 (q, *J* = 319 Hz), 112.9 (dd, *J* = 20.3, 4.3 Hz), 106.9 (t, *J* = 18.3 Hz), 74.7, 68.9. HRMS (ESI): calcd for C₁₆H₁₁F₅NO₄S [M+H]⁺ 408.0323, found: 408.0328.

Biological Assay. All bioassays were performed on representative test organisms reared in the laboratory. According to statistical requirements the bioassay was repeated at 25 ± 1 °C. Assessments were made on a dead/alive basis. Evaluation were based on a percentage scale of 0–100, where 0 equals no activity and 100 equals total kill. For comparative purpose, etoxazole was tested under the same conditions.

Acaricidal Activity against Eggs of Carmine Spider Mites (*T. cinnabarinus*). The acaricidal activities against the eggs of carmine spider mites of the target compounds **6a–x** and etoxazole as the contrast compound were evaluated using the reported procedure. The test samples were dissolved with acetone in appropriate quantities. The acetone solution of each compound was diluted with distilled water to give the desired final concentrations. Sieva bean plants (*Phaseolus vulgaris* L.) when its primary leaves expanded to 10 cm were selected and cut back to one plant per pot. Female mites were moved using a fine brush from the main colony

to leaves of the test plants to lay eggs; each leaf was let to have seven mites. About 24 h later, the adult mites were removed, leaving about 60–100 eggs per leaf. The leaves were kept for no more than 24 h before test. The mite-egg-infested leaves were dipped into the test solution for 3 s with agitation, excess liquid was got rid of by shaking, and then the leaves were placed in a tube (10 cm inner diameter) lined with a piece of filter paper. Percentage mortalities were evaluated 4 days after test.

Acaricidal Activity against Larvae of Carmine Spider Mites (*T. cinnabarinus*). The acaricidal activities against the larvae of carmine spider mites of the target compounds **6a-x** and etoxazole as the contrast compound were evaluated according to the reported procedure. The mite-egg-infested leaves (eggs that were laid on the same day) were kept at 25 °C for 4 days. After one day, the larvae were hatched and moved to the fresh leaves used for testing. Each leaf had about 60–100 mites. The leaf was cut and dipped into the test solution for 3 s, then the excess liquid was got rid of, and the leaf was placed in a tube (10 cm inner diameter) lined with a piece of filter paper. Percentage mortalities were evaluated 4 days after test.

Stomach Toxicity against Cotton Bollworm (*Helicoverpa armigera*) and Corn Borer (*Ostrinia nubilalis*). The stomach toxicities were evaluated by the leaf-dip method according to the reported procedure. Leaf disks (about 5 cm) were cut from fresh corn leaves, and then dipped into the prepared test solution for 3–5 s. After air-drying, the treated leaf disks were placed individually into a glass surface vessel (7 cm). Each dried treated leaf disk was invaded with 10 third-instar larvae. Percentage mortalities were evaluated 4 days after treatment. Leaves treated with

acetone were provided as controls.

Larvicidal Activity against Oriental Armyworm (*Mythimna separata*). The larvicidal activities of the target compounds **6a-x** and the control compound etoxazole against oriental armyworm were tested by foliar application using the reported procedure. For the foliar armyworm tests, individual corn leaves were placed on moistened pieces of filter paper in Petri dishes. The leaves were then sprayed with the test solution and allowed to dry. The dishes were infested with 10 fourth-instar oriental armyworm larvae. Percentage mortalities were examined 4 days after treatment.

Larvicidal Activity against Mosquito Larvae (*C. Pipiens pallens*). The larvicidal activities against mosquito were tested by using the reported procedure. The compounds **6a-x** were prepared to different concentrations by dissolving each compound in acetone and adding distilled water. Then 20 fourth-instar mosquito larvae were put into 10 mL of the test solution and raised for 8 days. The results were expressed by death percentage. Etoxazole was the control compound.

Statistical analysis

Each treatment was carried out three times. The mortality data given in Tables 1–4 are means \pm SDs for the three replicates. Linear regression equations and correlation coefficients were obtained with four or five sets of data in Tables 2 and 3 by means of the DPS Data Processing System software. LC₅₀ values were auto-calculated and are reported with 95% confidence intervals.

Table. Mortalities of Oxazolines **6a–x** and Etoxazole against lepidopteran pests

compound	oriental armyworm (%)	cotton bollworm (%)	corn borer (%)
	600 mg/L	600 mg/L	600 mg/L
6a	20	5	5
6b	10	5	5
6c	20	20	10
6d	5	10	0
6e	5	0	0
6f	15	10	10
6g	10	0	0
6h	50	20	35
6i	20	15	10
6j	45	30	25
6k	45	20	30
6l	20	10	10
6m	20	10	20
6n	30	10	15
6o	35	25	40
6p	45	30	25
6q	40	25	25
6r	40	25	25
6s	35	20	15
6t	5	0	0
6u	100/40 ^a	80	65
6v	100/50 ^a	75	75
6w	5	0	0
6x	30	20	30
etoxazole	100/100 ^a /10 ^b	100/50 ^a	100/60 ^a

^a200 mg/L. ^b200 mg/L

