

Supplementary Information

Structural and Sensory Characterization of Key Pungent and Tingling Compounds from Pepper (*Piper nigrum* L.)

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piperyne, 1a, Figure 1: UV/Vis (MeOH/water; pH 3.5): $\lambda_{\text{max}} = 348 \text{ nm}$; LC-MS (ESI⁺): m/z 286 (100, [M+H]⁺), 571 (77, [2M+H]⁺), 593 (37, [2M+Na]⁺), 308 (34, [M+Na]⁺); LC-TOF-MS: m/z 286.1467 ([M+H]⁺, measured), m/z 286.1443 ([M+H]⁺, calcd for C₁₇H₂₀NO₃); ¹H NMR (400 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 1.42–1.48 [m, 4H, H-C(14a, b)], 1.54–1.61 [m, 2H, H-C(15)], 3.50 [t, 4H, J=5.6 Hz, H-C(13a, b)], 6.03 [s, 2H, H-C(1)], 6.66 [d, 1H, J=14.8 Hz, H-C(11)], 6.87–6.98 [m, 3H, J=8.5 Hz, J=14.6 Hz, H-C(6, 8, 9)], 6.95 [dd, 1H, J=1.5 Hz, J=8.0 Hz, H-C(5)], 7.15 [d, 1H, J=1.5 Hz, H-C(3)], 7.21 [dd, 1H, J=10.9 Hz, J=14.6 Hz, H-C(10)]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ 24.7 [C(15)], 25.6 [C(14a)], 25.6 [C(14b)], 44.8 [C(13b)], 47.2 [C(13a)], 101.9 [C(1)], 105.7 [C(3)], 108.7 [C(6)], 121.4 [C(11)], 122.7 [C(5)], 126.0 [C(9)], 131.0 [C(4)], 137.7 [C(8)], 142.4 [C(10)], 148.3 [C(7)], 148.4 [C(2)], 165.4 [C(12)].

piperyline, 1b, Figure 1: UV/Vis (MeOH/water; pH 3.5): $\lambda_{\text{max}} = 348 \text{ nm}$; LC-MS (ESI⁺): m/z 272 (100, [M+H]⁺), 543 (71, [2M+H]⁺), 565 (60, [2M+Na]⁺), 294 (46, [M+Na]⁺); LC-TOF-MS: m/z 272.1294 ([M+H]⁺, measured), m/z 274.1287 ([M+H]⁺, calcd for C₁₆H₁₈NO₃); ¹H NMR (400 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 1.71–1.76 [m, 2H, H-C(14b)], 1.82–1.88 [m, 2H, H-C(14a)], 3.39 [t, 2H, J=7.1 Hz, H-C(13b)], 3.48 [t, 2H, J=7.1 Hz, H-C(13a)], 6.08 [s, 2H, H-C(1)], 6.42 [d, 1H, J=14.7 Hz, H-C(11)], 6.86–6.98 [m, 3H, H-C(6, 8, 9)], 6.96 [dd, 1H, J=1.5 Hz, J=8.0 Hz, H-C(5)], 7.20 [d, 1H, J=1.5 Hz, H-C(3)], 7.21 [dd, 1H, J=10.5 Hz, J=14.7 Hz, H-C(10)]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ 24.9 [C(14b)], 25.9 [C(14a)], 46.2 [C(13b)], 46.5 [C(13a)], 102.0 [C(1)], 106.3 [C(3)], 107.9 [C(6)], 123.2 [C(11)], 123.3 [C(5)], 125.9 [C(9)], 132.4 [C(4)], 138.5 [C(8)], 141.2 [C(10)], 148.3 [C(7)], 148.5 [C(2)], 165.1 [C(12)].

pipperlonguminine, 1c, Figure 1: UV/Vis (MeOH/water; pH 3.5): $\lambda_{\text{max}} = 318 \text{ nm}$; LC-MS (ESI⁺): m/z 274 (100, [M+H]⁺), 296 (76, [M+Na]⁺), 569 (63, [2M+Na]⁺), 547

(43, $[2M+H]^+$); LC-TOF-MS: m/z 274.1450 ($[M+H]^+$, measured), m/z 274.1443 ($[M+H]^+$, calcd for $C_{16}H_{20}NO_3$); 1H NMR (400 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 0.85 [d, 6H, $J=7.0$ Hz, H-C(3', 4')], 1.61–1.76 [m, 1H, H-C(2')], 2.96 [t, 2H, $J=6.4$ Hz, H-C(1')], 6.04 [s, 2H, H-C(1)], 6.11 [d, 1H, $J=15.0$ Hz, H-C(11)], 6.82–6.94 [m, 3H, $J=14.8$ Hz, $J=8.0$ Hz, H-C(6, 8, 9)], 6.98 [dd, 1H, $J=1.2$ Hz, $J=8.0$ Hz, H-C(5)], 7.13 [dd, 1H, $J=10.2$ Hz, $J=15.0$ Hz, H-C(10)], 7.25 [d, 1H, $J=1.7$ Hz, H-C(3)]; ^{13}C NMR (100 MHz, DMSO- d_6 ; HMQC, HMBC): δ 20.6 [C(3')], 20.6 [C(4')], 28.6 [C(2')], 46.6 [C(1')], 101.7 [C(1)], 106.0 [C(3)], 108.9 [C(6)], 123.1 [C(5)], 125.1 [C(11)], 125.7 [C(9)], 131.9 [C(4)], 138.1 [C(8)], 139.6 [C(10)], 148.1 [C(7)], 148.4 [C(2)], 165.6 [C(12)].

Piperettine, 2a, Figure 1: UV/Vis (MeOH/water; pH 3.5): λ_{max} = 366 nm; LC-MS (ESI $^+$): m/z 312 (100, $[M+H]^+$), 623 (55, $[2M+H]^+$), 334 (28, $[M+Na]^+$), 645 (24, $[2M+Na]^+$); LC-TOF-MS: m/z 312.1615 ($[M+H]^+$, measured), m/z 312.1600 ($[M+H]^+$, calcd for $C_{19}H_{22}NO_3$); 1H NMR (400 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 1.42–1.55 [m, 4H, H-C(16a, b)], 1.56–1.63 [m, 2H, H-C(17)], 3.47–3.55 [m, 4H, H-C(15a, b)], 6.04 [s, 2H, H-C(1)], 6.41 [d, 1H, $J=14.5$ Hz, H-C(13)], 6.52 [dd, 1H, $J=12.1$ Hz, $J=14.6$ Hz, H-C(11)], 6.70 [dd, 1H, $J=15.9$ Hz, H-C(8)], 6.76 [dd, 1H, $J=9.3$ Hz, $J=14.6$ Hz, H-C(10)], 6.88–6.93 [m, 2H, H-C(6, 9)], 6.96 [dd, 1H, $J=1.7$ Hz, $J=8.4$ Hz, H-C(5)], 7.17 [dd, 1H, $J=11.3$ Hz, $J=14.6$ Hz, H-C(12)], 7.22 [d, 1H, $J=1.7$ Hz, H-C(3)]; ^{13}C NMR (100 MHz, DMSO- d_6 ; HMQC, HMBC): δ 24.5 [C(17)], 25.2 [C(16a, b)], 45.3 [C(15b)], 46.4 [C(15a)], 101.2 [C(1)], 106.2 [C(3)], 108.9 [C(6)], 121.9 [C(13)], 122.8 [C(5)], 127.4 [C(9)], 130.8 [C(11)], 131.1 [C(4)], 135.6 [C(8)], 139.7 [C(10)], 141.2 [C(12)], 147.9 [C(7)], 148.6 [C(2)], 164.2 [C(14)].

Piperoleine, 2b, Figure 1: UV/Vis (MeOH/water; pH 3.5): λ_{max} = 354 nm; LC-MS (ESI $^+$): m/z 298 (100, $[M+1]^+$), 320 (82, $[M+Na]^+$), 595 (31, $[2M+1]^+$), 617 (41, $[2M+Na]^+$); LC-TOF-MS: m/z 298.1449 ($[M+H]^+$, measured), m/z 298.1443 ($[M+H]^+$,

calcd for $C_{18}H_{20}NO_3$); 1H NMR (400 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 1.75-1.82 [m, 2H, H-C(16b)], 1.84-1.93 [m, 2H, H-C(16 a)], 3.36 [t, 2H, $J=7.5$ Hz, H-C(15 b)], 3.52 [t, 2H, $J=7.5$ Hz, H-C(15 a)], 6.04 [s, 2H, H-C(1)], 6.38 [d, 1H, $J=14.6$ Hz, H-C(13)], 6.52 [dd, 1H, $J=12.1$ Hz, $J=14.6$ Hz, H-C(11)], 6.70 [dd, 1H, $J=15.9$ Hz, H-C(8)], 6.76 [dd, 1H, $J=9.3$ Hz, $J=14.6$ Hz, H-C(10)], 6.88-6.93 [m, 2H, H-C(6, 9)], 6.97 [dd, 1H, $J=1.5$ Hz, $J=8.5$ Hz, H-C(5)], 7.17 [dd, 1H, $J=11.3$ Hz, $J=14.6$ Hz, H-C(12)], 7.21 [d, 1H, $J=1.5$ Hz, H-C(3)]; ^{13}C NMR (100 MHz, DMSO- d_6 ; HMQC, HMBC): δ 24.1 [C(16b)], 26.1 [C(16a)], 45.8 [C(15b)], 46.5 [C(15a)], 101.5 [C(1)], 105.9 [C(3)], 108.7 [C(6)], 122.3 [C(13)], 122.6 [C(5)], 127.9 [C(9)], 131.1 [C(11)], 131.6 [C(4)], 135.4 [C(8)], 139.7 [C(10)], 140.4 [C(12)], 147.6 [C(7)], 148.3 [C(2)], 164.6 [C(14)].

Dehydropipernonaline, 3a, Figure 1: UV/Vis (MeOH/water; pH 3.5): λ_{max} = 264 nm; LC-MS (ESI $^+$): m/z 340 (100, [M+H] $^+$), 362 (69, [M+Na] $^+$), 679 (46, [2M+H] $^+$), 701 (23, [2M+Na] $^+$); LC-TOF-MS: m/z 340.1922 ([M+H] $^+$, measured), m/z 340.1913 ([M+H] $^+$, calcd for $C_{21}H_{26}NO_3$); 1H NMR (400 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 1.35-1.68 [m, 2H, H-C(19)], 1.55-1.61 [m, 4H, H-C(18a, b)], 2.02-3.24 [m, 4H, H-C(10, 11)], 3.45-3.50 [m, 4H, H-C(17a, b)], 5.98 [s, 2H, H-C(1)], 6.06-6.21 [m, 2H, $J=14.8$ Hz, $J=15.4$ Hz, H-C(9, 12)], 6.30 [dd, 1H, $J=11.6$ Hz, $J=14.8$ Hz, H-C(13)], 6.33 [d, 1H, $J=15.4$ Hz, H-C(8)], 6.54 [d, 1H, $J=15.4$ Hz, H-C(15)], 6.79 [dd, 1H, $J=1.7$ Hz, $J=8.0$ Hz, H-C(6)], 6.83 [dd, 1H, $J=1.7$ Hz, $J=8.0$ Hz, H-C(5)], 7.03 [d, 1H, $J=1.7$ Hz, H-C(3)], 7.04 [dd, 1H, $J=10.0$ Hz, $J=14.8$ Hz, H-C(14)]; ^{13}C NMR (100 MHz, DMSO- d_6 ; HMQC, HMBC): δ 24.6 [C(19)], 25.1 [C(18b)], 27.1 [C(18a)], 32.2 [C(11)], 32.7 [C(10)], 42.8 [C(17b)], 46.4 [C(17a)], 101.3 [C(1)], 105.6 [C(3)], 108.6 [C(6)], 120.2 [C(5)], 120.8 [C(15)], 128.3 [C(9)], 129.8 [C(13)], 130.1 [C(8)], 132.2 [C(4)], 141.1 [C(12)], 142.1 [C(14)], 146.8 [C(7)], 148.1 [C(2)], 164.7 [C(16)].

1-[1-Oxo-9(3,4-methylenedioxyphenyl)-2E,4E,8E-nonatrienyl] pyrrolidine, 3b, Figure 1: UV/Vis (MeOH/ water; pH 3.5): λ_{max} = 264 nm; LC-MS (ESI $^+$): m/z 326

(100, [M+H]⁺), 348 (85, [M+Na]⁺), 673 (24, [2M+Na]⁺), 651 (15, [2M+H]⁺); LC-TOF-MS: m/z 326.1763 ([M+H]⁺, measured), m/z 326.1756 ([M+H]⁺, calcd for C₂₀H₂₄NO₃); ¹H NMR (400 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 1.73-1.91 [m, 4H, H-C(18a, b)], 2.28 [m, 4H, H-C(10, 11)], 3.22 [t, 2H, J=6.8 Hz, H-C(17 b)], 3.47 [t, 2H, J=6.8 Hz, H-C(17a)], 5.98 [s, 2H, H-C(1)], 6.09-6.16 [m, J=15.2 Hz, H-C(9,12)], 6.25-6.35 [m, 3H, J=14.8, J=15.8 Hz, H-C(8, 13, 15)], 6.79 [dd, 1H, J=1.7 Hz, J=8.0 Hz, H-C(6)], 6.82 [dd, 1H, J=1.7 Hz, J=8.0 Hz, H-C(5)], 7.03 [d, 1H, J=1.7Hz, H-C(3)], 7.04 [dd, 1H, J=10.8 Hz, J=14.8 Hz, H-C(14)]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ 24.3 [(18b)], 26.1 [C(18a)], 32.2 [C(11)], 32.7 [C(10)], 45.9 [C(17b)], 46.5 [C(17a)], 101.3 [C(1)], 105.7 [C(3)], 108.7 [C(6)], 120.8 [C(5)], 121.8 [C(15)], 128.3 [C(9)], 129.7 [C(13)], 130.2 [C(8)], 132.2 [C(4)], 141.1 [C(12)], 141.7 [C(14)], 146.8 [C(7)], 148.1 [C(2)], 164.2 [C(16)].

Retrofractamide A, **3c**, **Figure 1**: UV/Vis (MeOH/water; pH 3.5): λ_{max} = 264 nm; LC-MS (ESI⁺): m/z 328 (100, [M+H]⁺), 655 (96, [2M+H]⁺), 350 (84, [M+Na]⁺), 677 (79, [2M+Na]⁺); LC-TOF-MS: m/z 328.1914 ([M+H]⁺, measured), m/z 328.1913 ([M+H]⁺, calcd for C₂₀H₂₆NO₃); ¹H NMR (400 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 0.83 [d, 6H, J=7.2 Hz, H-C(3', 4')], 1.66-1.70 [m, 1H, H-C(2')], 2.27 [m, 4H, H-C(10, 11)], 2.93 [t, 2H, J= 6.0 Hz, H-C(1')], 5.92 [d, 1H, J=15.6 Hz, H-C(15)], 5.98 [s, 2H, H-C(1)], 6.08-6.18 [m, 2H, J=15.4 Hz, J=15.8 Hz, H-C(9, 12)], 6.20 [dd, 1H, J=10.4 Hz, J=15.4 Hz, H-C(13)], 6.31 [d, 1H, J=15.6 Hz, H-C(8)], 6.78 [dd, 1H, J=8.2 Hz, H-C(6)], 6.82 [dd, 1H, J=1.2 Hz, J=8.2 Hz, H-C(5)], 6.98 [dd, 1H, J=10.4 Hz, J=14.9 Hz, H-C(14)], 7.05 [d, 1H, J=1.2 Hz, H-C(3)], 7.92 [t, N-H]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ 20.6 [(3', 4')], 28.6 [C(2')], 32.2 [C(11)], 32.6 [C(10)], 46.5 [C(1')], 101.3 [C(1)], 105.6 [C(3)], 108.8 [C(6)], 120.7 [C(5)], 124.1 [C(15)], 128.3 [C(9)], 129.4 [C(13)], 130.1 [C(8)], 132.2 [C(4)], 140.8 [C(12)], 141.1 [C(14)], 146.8 [C(7)], 148.1 [C(2)], 165.6 [C(16)].

Pipernonaline, 4a, Figure 1: UV/Vis (MeOH/water; pH 3.5): $\lambda_{\max}$ = 208 nm, 268 nm; LC-MS (ESI⁺): m/z 342 (100, [M+1]⁺), 364 (78, [M+Na]⁺), 683 (52, [2M+1]⁺), 705 (44, [2M+Na]⁺); LC-TOF-MS: m/z 342.2078 ([M+H]⁺, measured), m/z 342.2069 ([M+H]⁺, calcd for C₂₁H₂₈NO₃); ¹H NMR (400 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 1.35-1.49 [m, 4H, H-C(18a, b)], 1.49-1.68 [m, 6H, H-C(11, 12, 19)], 2.02-3.24 [m, 4H, H-C(10, 13)], 3.48 [br. t, 4H, J=5.6Hz, H-C(17a, b)], 5.98 [s, 2H, H-C(1)], 6.06-6.21 [m, 1H, J=15.9 Hz, H-C(9)], 6.30 [d, 1H, J=15.8 Hz, H-C(8)], 6.60 [d, 1H, J=14.8 Hz, H-C(15)], 6.76 [dd, 1H, J=1.6 Hz, J=8.0 Hz, H-C(6)], 6.80 [dd, 1H, J=1.6 Hz, J=8.0 Hz, H-C(5)], 7.01-7.08 [m, 1H, H-C(14)], 7.03 [d, 1H, J=1.6 Hz, H-C(3)]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ 24.6 [C(19)], 25.8 [C(18b)], 26.9 [C(18a)], 28.3 [C(12)], 29.2 [C(11)], 29.9 [C(13)], 32.7 [C(10)], 42.8 [C(17b)], 46.4 [C(17a)], 101.3 [C(1)], 105.6 [C(3)], 108.6 [C(6)], 120.2 [C(15)], 120.8 [C(5)], 129.8 [C(9)], 130.1 [C(8)], 132.2 [C(4)], 145.1 [C(14)], 146.8 [C(7)], 148.1 [C(2)], 164.7 [C(16)].

Piperroleine B, 5a, Figure 1: UV/Vis (MeOH/ water; pH 3.5): $\lambda_{\max}$ = 260 nm, 304 nm; LC-MS (ESI⁺): m/z 687 (100, [2M+H]⁺), 344 (86, [M+H]⁺), 366 (76, [M+Na]⁺), 709 (55, [2M+Na]⁺), 382 (41, [M+K]⁺); LC-TOF-MS: m/z 344.2236 ([M+H]⁺, measured), m/z 344.2226 ([M+H]⁺, calcd for C₂₁H₃₀NO₃); ¹H NMR (400 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 1.21-1.60 [m, 14H, H-C(11, 12, 13, 14, 18a, 18b, 19)], 2.10-2.15 [q, 2H, H-C(10)], 2.62 [t, 2H, J=7.5 Hz, H-C(15)], 3.34-3.40 [m, 4H, H-C(17a, b)], 5.98 [s, 2H, H-C(1)], 6.08-6.18 [m, 1H, H-C(9)], 6.29 [d, 1H, J=15.2 Hz, H-C(8)], 6.79 [dd, 1H, J=1.6 Hz, J=7.8 Hz, H-C(5)], 6.80-6.83 [m, 1H, H-C(6)], 7.03 [d, 1H, J=1.6 Hz, H-C(3)]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ 24.6 [C(19)], 25.3 [C(14)], 28.9 [C(12)], 29.3 [C(18b)], 29.9 [C(18a)], 29.1 [C(13)], 30.3 [C(11)], 32.7 [C(10, 15)], 42.9 [C(17b)], 46.4 [C(17a)], 101.3 [C(1)], 105.6 [C(3)], 108.6 [C(6)], 120.8 [C(5)], 129.8 [C(9)], 130.2 [C(8)], 132.2 [C(4)], 146.1 [C(7)], 148.1 [C(2)], 170.5 [C(16)].

Brachyamide A, **6b**, **Figure 1**: UV/Vis (MeOH/water; pH 3.5): $\lambda_{\text{max}} = 260 \text{ nm}$; LC-MS (ESI⁺): m/z 382 (100, [M+1]⁺), 763 (90, [2M+H]⁺), 785 (74, [2M+Na]⁺), 404 (70, [M+Na]⁺); LC-TOF-MS: m/z 382.2382 ([M+H]⁺, measured), m/z 382.2382 ([M+H]⁺, calcd for C₂₄H₃₂NO₃); ¹H NMR (400 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 1.23-1.34 [m, 8H, H-C(12, 13, 22a, b)], 1.34-1.70 [m, 4H, H-C(11, 14)], 3.47 [t, 2H, J=7.1 Hz, H-C(21a, b)], 2.09-2.16 [m, 4H, H-C(10, 15)], 5.97 [s, 2H, H-C(1)], 6.06-6.12 [m, 2H, m, J=15.8 Hz, H-C(9, 16)], 6.21-6.28 [m, 2H, J=10.8 Hz, J=14.6 Hz, J=15.2 Hz, H-C(17, 19)], 6.28 [d, 1H, J=16.0 Hz, H-C(8)], 6.78 [dd, 1H, J=1.2 Hz, J=8.2 Hz, H-C(5)], 6.82 [dd, 1H, J=1.2 Hz, J=8.2 Hz, H-C(6)], 7.03 [dd, 1H, J=10.9 Hz, J=14.6 Hz, H-C(18)], 7.03 [d, 1H, J=1.5 Hz, H-C(3)]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ 24.3 [C(22b)], 26.1 [C(22a)], 28.7 [C(13)], 28.9 [C(12)], 29.2 [C(14)], 29.4 [C(11)], 32.7 [C(10)], 32.8 [C(15)], 45.9 [C(21b)], 46.5 [C(21a)], 101.3 [C(1)], 105.6 [C(3)], 108.6 [C(6)], 120.6 [C(5)], 121.5 [C(19)], 129.1 [C(17)], 129.3 [C(8)], 129.6 [C(16)], 132.3 [C(4)], 141.2 [C(18)], 142.5 [C(9)], 146.6 [C(7)], 148.1 [C(2)], 164.7 [C(20)].

Guineensine, **6c**, **Figure 1**: UV/Vis (MeOH/water; pH 3.5): $\lambda_{\text{max}} = 260 \text{ nm}$; LC-MS (ESI⁺): m/z 384 (100, [M+H]⁺), 406 (86, [M+Na]⁺), 767 (31, [2M+H]⁺), 789 (24, [2M+Na]⁺); LC-TOF-MS: m/z 384.2536 ([M+H]⁺, measured), m/z 384.2539 ([M+H]⁺, calcd for C₂₄H₃₄NO₃). ¹H NMR (400 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 0.86 [d, 6H, J=7.0 Hz, H-C(3', 4')], 1.29-1.36 [m, 4H, H-C(12, 13)], 1.37-1.46 [m, 4H, H-C(11, 14)], 1.70-1.72 [m, 1H, H-C(2')], 2.10-2.18 [m, 4H, H-C(10, 15)], 2.96 [t, 2H, J=6.4 Hz, H-C(1')], 5.96 [d, 1H, J=15.2 Hz, H-C(19)], 6.00 [s, 2H, H-C(1)], 6.02-6.12 [m, 2H, J=15.9 Hz, H-C(9, 16)], 6.14-6.22 [m, 1H, J=10.8 Hz, J=15.4 Hz, H-C(17)], 6.31 [d, 1H, J=16.1 Hz, H-C(8)], 6.80 [dd, 1H, J=1.2 Hz, J=8.2 Hz, H-C(5)], 6.87 [dd, 1H, J=1.2 Hz, J=8.2 Hz, H-C(6)], 6.99 [dd, 1H, J=10.8 Hz, J=15.4 Hz, H-C(18)], 7.05 [d, 1H, J=1.5 Hz, H-C(3)]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ 20.6 [C(3',

4'), 28.6 [C(2')], 28.8 [C(13)], 28.9 [C(12)], 29.0 [C(14)], 29.3 [C(11)], 32.6 [C(15)], 32.7 [C(10)], 46.5 [C(1')], 101.3 [C(1)], 105.6 [C(3)], 108.6 [C(6)], 120.6 [C(5)], 123.8 [C(19)], 129.1 [C(17)], 129.3 [C(8)], 129.6 [C(16)], 132.4 [C(4)], 139.5 [C(18)], 141.9 [C(9)], 146.7 [C(7)], 148.1 [C(2)], 165.7 [C(20)].

1-(octadeca-2E,4E,13Z-trienyl)piperidine, 7a, Figure 1: UV/Vis (MeOH/water; pH 3,5): $\lambda_{\max}$ = 260 nm; LC-MS (ESI⁺): m/z 346 (100, [M+H]⁺), 691 (86, [2M+H]⁺), 713 (81, [2M+Na]⁺), 368 (62, [M+Na]⁺), 384 (12, [M+K]⁺); MS/MS (DP = 116 V): m/z (%) 346 (100), 138 (3), 112 (6), 95 (4), 86 (5), 81 (11), 69 (7), 67 (7), 55 (11), 53 (10); LC-TOF-MS: m/z 346.3139 ([M+H]⁺, measured), m/z 346.3110 ([M+H]⁺, calcd for C₂₃H₄₀NO); ¹H NMR (500 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 0.81–0.87 [m, 3H, H-C(18)], 1.20–1.31 [m, 12H, H-C(8, 9, 10, 11, 16, 17)], 1.33–1.41 [m, 2H, H-C(7)], 1.40–1.51 [m, 4H, H-C(20a, b)], 1.55–1.60 [m, 2H, H-C(21)], 1.90–2.04 [m, 4H, H-C(12, 15)], 2.15 [dt, 2H, J=7.3 Hz, H-C(6)], 3.44–3.51 [m, 4H, H-C(19a, b)], 5.30–5.34 [m, 2H, J=5.6 Hz, J=11.2 Hz, H-C(13, 14)], 6.00–6.14 [m, 1H, H-C(5)], 6.13–6.29 [m, 1H, J=10.7 Hz, J=15.4 Hz, H-C(4)], 6.50 [d, 1H, J=15.4 Hz, H-C(2)], 6.98–7.05 [m, 1H, J=10.7 Hz, J=15.4 Hz, H-C(3)]; ¹³C NMR (125 MHz, DMSO-*d*₆; HMQC, HMBC): δ 13.8 [C(18)], 21.6 [C(17)], 23.8 [C(21)], 24.8 [C(20b)], 26.3 [C(12)], 26.3 [C(15)], 26.8 [C(20a)], 28.5 [C(7)], 28.6, 28.7, 28.8, 28.9 [C(8, 9, 10, 11)], 31.1 [C(16)], 33.7 [C(6)], 42.0 [C(19b)], 45.8 [C(19a)], 119.3 [C(2)], 128.9 [C(4)], 129.3 [C(13)], 129.3 [C(14)], 141.1 [C(3)], 141.4 [C(5)], 164.3 [C(1)].

1-(octadeca-2E,4E,13Z-trienyl)pyrrolidine, 7b, Figure 1: UV/Vis (MeOH/water; pH 3,5): $\lambda_{\max}$ = 260 nm; LC-MS (ESI⁺): m/z 332 (100, [M+H]⁺), 663 (87, [2M+H]⁺), 685 (78, [2M+Na]⁺), 354 (72, [M+Na]⁺), 370 (28, [M+K]⁺); MS/MS (DP = 96 V): m/z (%) 332 (100), 164 (3), 150 (4), 136 (3), 124 (5), 107 (3), 98 (11), 67 (9), 55 (24); LC-TOF-MS:); LC-TOF-MS: m/z 332.2983 ([M+H]⁺, measured), m/z 332.2953 ([M+H]⁺, calcd for C₂₂H₃₈NO); ¹H NMR (500 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 0.83–0.87 [m,

3H, H-C(18)], 1.18–1.32 [m, 12H, H-C(8, 9, 10, 11, 16, 17)], 1.33–1.45 [m, 2H, H-C(7)], 1.73–1.78 [m, 2H, H-C(20b)], 1.82–1.90 [m, 2H, H-C(20a)], 1.93–2.02 [m, 4H, H-C(12, 15)], 2.16 [dt, 2H, J=7.4 Hz, H-C(6)], 3.27–3.40 [m, 2H, H-C(19b)], 3.47 [t, 2H, J=7.1 Hz, H-C(19a)], 5.28–5.34 [m, 2H, J=5.5 Hz, J=11.0 Hz, H-C(13, 14)], 6.01–6.14 [m, 1H, H-C(5)], 6.16–6.29 [m, 1H, J=10.2 Hz, J=15.3 Hz, H-C(4)], 6.25 [d, 1H, J=15.3 Hz, H-C(2)], 7.02 [dd, 1H, J=10.2 Hz, J=15.3 Hz, H-C(3)]; ^{13}C NMR (125 MHz, DMSO- d_6 ; HMQC, HMBC): δ 14.0 [C(18)], 22.1 [C(17)], 23.9 [C(20b)], 25.7 [C(20a)], 26.6 [C(12)], 26.6 [C(15)], 28.5, 28.6, 28.7, 28.9 [C(8, 9, 10, 11)], 29.1 [C(7)], 31.3 [C(16)], 33.8 [C(6)], 45.5 [C(19b)], 46.0 [C(19a)], 121.1 [C(2)], 128.9 [C(4)], 129.7 [C(13)], 129.7 [C(14)], 140.8 [C(3)], 142.3 [C(5)], 163.8 [C(1)].

1(2E,4E,13Z)-N-isobutyl-octadeca-2,4,13-trienamide, **7c**, **Figure 1**: UV/Vis (MeOH/water; pH 3,5): λ_{max} = 260 nm; LC-MS (ESI $^{+}$): m/z 334 (100, [M+H] $^{+}$), 667 (96, [2M+H] $^{+}$), 689 (91, [2M+Na] $^{+}$), 356 (85, [M+Na] $^{+}$), 372 (18, [M+K] $^{+}$); MS/MS (DP = 71 V): m/z (%) 334 (100), 109 (5), 95 (8), 81 (15), 67 (16), 55 (20); LC-TOF-MS: m/z 334.3110 ([M+H] $^{+}$, measured), m/z 334.3110 ([M+H] $^{+}$, calcd for C₂₂H₄₀NO); ^1H NMR (500 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 0.83 [d, 6H, J=6.6 Hz, H-C(3', 4')], 0.83–0.87 [m, 3H, H-C(18)], 1.18–1.31 [m, 12H, H-C(8, 9, 10, 11, 16, 17)], 1.31–1.40 [m, 2H, H-C(7)], 1.62–1.73 [m, 1H, H-C(2')], 1.90–2.03 [m, 4H, H-C(12, 15)], 2.11 [dt, 2H, J=7.3 Hz, H-C(6)], 2.93 [t, 2H, J=6.6 Hz, H-C(1')], 5.31 [pt, 2H, J=5.5 Hz, J=11.1 Hz, H-C(13, 14)], 5.92 [d, 1H, J=15.5 Hz, H-C(2)], 6.00–6.07 [m, 1H, H-C(5)], 6.15 [dd, 1H, J=10.2 Hz, J=15.5 Hz, H-C(4)], 6.96 [dd, 1H, J=10.2 Hz, J=15.5 Hz, H-C(3)], 7.91 [t, 1H, J=5.6 Hz, N-H]; ^{13}C NMR (125 MHz, DMSO- d_6 ; HMQC, HMBC): δ 13.8 [C(18)], 20.2 [C(3', 4')], 21.6 [C(17)], 26.3 [C(12)], 26.3 [C(15)], 28.1 [C(2')], 28.1 [C(7)], 28.3, 28.5, 28.6, 28.7 [C(8, 9, 10, 11)], 31.3 [C(16)], 32.1 [C(6)], 46.1 [C(1')], 123.4 [C(2)], 128.6 [C(4)], 129.6 [C(13)], 129.6 [C(14)], 139.0 [C(3)], 141.4 [C(5)], 165.2 [C(1)].

1-(octadeca-2E,4E,12Z-trienyl)piperidine, 8a, Figure 1: UV/Vis (MeOH/water; pH 3,5): $\lambda_{\text{max}} = 260 \text{ nm}$; LC-MS (ESI⁺): m/z 346 (100, [M+H]⁺), 691 (86, [2M+H]⁺), 713 (81, [2M+Na]⁺), 368 (62, [M+Na]⁺), 384 (12, [M+K]⁺); MS/MS (DP = 116 V): m/z (%) 346 (100), 138 (3), 112 (6), 95 (4), 86 (5), 81 (11), 69 (7), 67 (7), 55 (11), 53 (10); LC-TOF-MS: m/z 346.3139 ([M+H]⁺, measured), m/z 346.3110 ([M+H]⁺, calcd for C₂₃H₄₀NO); ¹H NMR (500 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 0.81–0.87 [m, 3H, H-C(18)], 1.20–1.31 [m, 12H, H-C(8, 9, 10, 15, 16, 17)], 1.33–1.41 [m, 2H, H-C(7)], 1.40–1.51 [m, 4H, H-C(20a, b)], 1.55–1.60 [m, 2H, H-C(21)], 1.90–2.04 [m, 4H, H-C(11, 14)], 2.15 [dt, 2H, J=7.3 Hz, H-C(6)], 3.44–3.51 [m, 4H, H-C(19a, b)], 5.30–5.34 [m, 2H, J=5.6 Hz, J=11.2 Hz, H-C(12, 13)], 6.00–6.14 [m, 1H, H-C(5)], 6.13–6.29 [m, 1H, J=10.7 Hz, J=15.4 Hz, H-C(4)], 6.50 [d, 1H, J=15.4 Hz, H-C(2)], 6.98–7.05 [m, 1H, J=10.7 Hz, J=15.4 Hz, H-C(3)]; ¹³C NMR (125 MHz, DMSO-*d*₆; HMQC, HMBC): δ 13.8 [C(18)], 21.9 [C(17)], 23.8 [C(21)], 24.8 [C(20b)], 26.3 [C(11)], 26.3 [C(14)], 26.8 [C(20a)], 28.5 [C(7)], 28.6, 28.7, 28.8, 28.9 [C(8, 9, 10, 15)], 31.0 [C(16)], 33.7 [C(6)], 42.0 [C(19b)], 45.8 [C(19a)], 119.3 [C(2)], 128.9 [C(4)], 129.3 [C(12)], 129.3 [C(13)], 141.1 [C(3)], 141.4 [C(5)], 164.3 [C(1)].

1-(octadeca-2E,4E,12Z-trienyl)pyrrolidine, 8b, Figure 1: UV/Vis (MeOH/water; pH 3,5): $\lambda_{\text{max}} = 260 \text{ nm}$; LC-MS (ESI⁺): m/z 332 (100, [M+H]⁺), 663 (87, [2M+H]⁺), 685 (78, [2M+Na]⁺), 354 (72, [M+Na]⁺), 370 (28, [M+K]⁺); MS/MS (DP = 96 V): m/z (%) 332 (100), 164 (3), 150 (4), 136 (3), 124 (5), 107 (3), 98 (11), 67 (9), 55 (24); LC-TOF-MS: m/z 332.2983 ([M+H]⁺, measured), m/z 332.2953 ([M+H]⁺, calcd for C₂₂H₃₈NO); ¹H NMR (500 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 0.83–0.87 [m, 3H, H-C(18)], 1.18–1.32 [m, 12H, H-C(8, 9, 10, 15, 16, 17)], 1.33–1.49 [m, 2H, H-C(7)], 1.73–1.78 [m, 2H, H-C(20b)], 1.82–1.90 [m, 2H, H-C(20a)], 1.93–2.02 [m, 4H, H-C(11, 14)], 2.16 [dt, 2H, J=7.4 Hz, H-C(6)], 3.27–3.40 [m, 2H, H-C(19b)], 3.47 [t, 2H, J=7.1 Hz, H-C(19a)], 5.28–5.34 [m, 2H, J=5.5 Hz, J=11.0 Hz, H-C(12, 13)], 6.01–

6.14 [m, 1H, H-C(5)], 6.16–6.29 [m, 1H, J=10.2 Hz, J=15.3 Hz, H-C(4)], 6.25 [d, 1H, J=15.3 Hz, H-C(2)], 7.02 [dd, 1H, J=10.2 Hz, J=15.3 Hz, H-C(3)]; ^{13}C NMR (125 MHz, DMSO- d_6 ; HMQC, HMBC): δ 14.0 [C(18)], 22.9 [C(17)], 23.9 [C(20b)], 25.7 [C(20a)], 26.6 [C(11)], 26.6 [C(14)], 28.5, 28.6, 28.7, 28.9 [C(8, 9, 10, 15)], 29.1 [C(7)], 31.2 [C(16)], 33.8 [C(6)], 45.5 [C(19b)], 46.0 [C(19a)], 121.1 [C(2)], 128.9 [C(4)], 129.7 [C(12)], 129.7 [C(13)], 140.8 [C(3)], 142.3 [C(5)], 163.8 [C(1)].

(2*E*,4*E*,12*Z*)-*N*-isobutyl-octadeca-2,4,12-trienamide, **8c**, **Figure 1**: UV/Vis (MeOH/water; pH 3,5): λ_{max} = 260 nm; LC-MS (ESI $^{+}$): m/z 334 (100, [M+H] $^{+}$), 667 (96, [2M+H] $^{+}$), 689 (91, [2M+Na] $^{+}$), 356 (85, [M+Na] $^{+}$), 372 (18, [M+K] $^{+}$); MS/MS (DP = 71 V): m/z (%) 334 (100), 109 (5), 95 (8), 81 (15), 67 (16), 55 (20); LC-TOF-MS: m/z 334.3110 ([M+H] $^{+}$, measured), m/z 334.3110 ([M+H] $^{+}$, calcd for C₂₂H₄₀NO+H); ^1H NMR (500 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 0.83 [d, 6H, J=6.6 Hz, H-C(3', 4')], 0.83–0.87 [m, 3H, H-C(18)], 1.18–1.31 [m, 12H, H-C(8, 9, 10, 15, 16, 17)], 1.31–1.40 [m, 2H, H-C(7)], 1.62–1.73 [m, 1H, H-C(2')], 1.90–2.03 [m, 4H, H-C(11, 14)], 2.11 [dt, 2H, J=7.3 Hz, H-C(6)], 2.93 [t, 2H, J=6.6 Hz, H-C(1')], 5.32 [pt, 2H, J=5.5 Hz, J=11.1 Hz, H-C(12, 13)], 5.92 [d, 1H, J=15.5 Hz, H-C(2)], 6.00–6.07 [m, 1H, H-C(5)], 6.15 [dd, 1H, J=10.2 Hz, J=15.5 Hz, H-C(4)], 6.96 [dd, 1H, J=10.2 Hz, J=15.5 Hz, H-C(3)], 7.91 [t, 1H, J=5.6 Hz, N-H]; ^{13}C NMR (125 MHz, DMSO- d_6 ; HMQC, HMBC): δ 13.8 [C(18)], 20.2 [C(3')], 20.2 [C(4')], 22.1 [C(17)], 26.3 [C(11)], 26.3 [C(14)], 28.1 [C(2')], 28.1 [C(7)], 28.3, 28.5, 28.6, 28.7 [C(8, 9, 10, 15)], 31.1 [C(16)], 32.1 [C(6)], 46.1 [C(1')], 123.4 [C(2)], 128.6 [C(4)], 129.6 [C(12)], 129.6 [C(13)], 139.0 [C(3)], 141.4 [C(5)], 165.2 [C(1)].

(2*E*,4*E*)-*N*-isobutyloctadeca-2,4-dienamide, **9c**, **Figure 1**: UV/Vis (MeOH/water; pH 3,5): λ_{max} = 260 nm; LC-MS (ESI $^{+}$): m/z 336 (100, [M+H] $^{+}$), 358 (29, [M+Na] $^{+}$), 671 (18, [2M+H] $^{+}$), 693 (11, [2M+Na] $^{+}$); MS/MS (DP = 136 V): m/z (%) 336 (100), 280,0 (3), 94,8 (6), 81,0 (12), 67,2 (11), 57,1 (16); LC-TOF-MS: m/z 336.3292 ([M+H] $^{+}$,

measured), m/z 336.3266 ($[M+H]^+$, calcd for $C_{22}H_{42}NO$); 1H NMR (500 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 0.86 [d, 6H, $J=6.6$ Hz, H-C(3', 4')], 0.81–0.89 [m, 3H, H-C(18)], 1.23–1.34 [m, 22H, H-C(7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17)], 1.68–1.72 [m, 1H, H-C(2')], 2.17 [dt, 2H, $J=7.1$ Hz, H-C(6)], 2.95 [t, 2H, $J=6.6$ Hz, H-C(1')], 5.95 [d, 1H, $J=15.3$ Hz, H-C(2)], 6.09–6.11 [m, 1H, H-C(5)], 6.15–6.23 [m, 1H, H-C(4)], 6.97 [dd, 1H, $J=10.5$ Hz, $J=15.3$ Hz, H-C(3)], 7.97 [t, 1H, $J=6.0$ Hz, N-H]; ^{13}C NMR (125 MHz, DMSO- d_6 ; HMQC, HMBC): δ 14.4 [C(18)], 20.6 [C(3', 4')], 22.3 [C(17)], 24.5 [C(7)], 28.4 [C(2')], 29.0, 29.1, 29.1, 29.2, 29.2, 29.4, 29.4, 29.5 [C(8, 9, 10, 11, 12, 13, 14, 15)], 31.5 [C(16)], 31.8 [C(6)], 46.5 [C(1')], 123.7 [C(2)], 129.2 [C(4)], 139.4 [C(3)], 141.8 [C(5)], 165.4 [C(1)].

1-(eicosa-2E,4E,15Z-trienoyl)piperidine, **10a**, **Figure 1**: UV/Vis (MeOH/water; pH 3,5): λ_{max} = 260 nm; LC-MS (ESI $^+$): m/z 374 (100, $[M+H]^+$), 396 (75, $[M+Na]^+$), 747 (55, $[2M+H]^+$), 769 (12, $[2M+Na]^+$); MS/MS (DP = 141 V): m/z (%) 374 (100), 138 (4), 112 (4), 95 (4), 86 (6), 81 (9), 69 (7), 67 (7), 55 (9), 53 (10); LC-TOF-MS: m/z 374.3427 ($[M+H]^+$, measured), m/z 374.3423 ($[M+H]^+$, calcd for $C_{25}H_{44}NO$); 1H NMR (400 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 0.80–0.88 [m, 3H, H-C(20)], 1.14–1.32 [m, 16H, H-C(8, 9, 10, 11, 12, 13, 18, 19)], 1.32–1.39 [m, 4H, H-C(7)], 1.39–1.50 [m, 4H, H-C(22a, b)], 1.54–1.61 [m, 2H, H-C(23)], 1.90–2.03 [m, 4H, H-C(14, 17)], 2.16 [dt, 2H, $J=7.3$ Hz, H-C(6)], 3.42–3.52 [m, 4H, H-C(21a, b)], 5.31 [pt, 2H, $J=5.0$ Hz, $J=10.2$ Hz, H-C(15, 16)], 6.00–6.12 [m, 1H, H-C(5)], 6.09–6.28 [m, 1H, $J=10.8$ Hz, $J=15.2$ Hz, H-C(4)], 6.51 [d, 1H, $J=15.0$ Hz, H-C(2)], 7.02 [dd, 1H, $J=10.8$ Hz, $J=15.0$ Hz, H-C(3)]; ^{13}C NMR (100 MHz, DMSO- d_6 ; HMQC, HMBC): δ /ppm: δ 14.0 [C(20)], 22.1 [C(19)], 24.0 [C(23)], 24.2 [C(22b)], 26.6 [C(22a)], 26.7 [C(14)], 26.7 [C(17)], 29.0 [C(7)], 28.3, 28.5, 28.6, 28.8, 28.9, 28.9 [C(8, 9, 10, 11, 12, 13)], 31.1 [C(18)], 32.3 [C(6)], 42.4 [C(21b)], 45.7 [C(21a)], 119.5 [C(2)], 129.0 [C(4)], 129.7 [C(15)], 129.7 [C(16)], 141.4 [C(3)], 141.8 [C(5)], 164.5 [C(1)].

1-(eicosa-2E,4E,15Z-trienoyl)pyrrolidine, **10b**, **Figure 1**: UV/Vis (MeOH/water; pH 3,5): $\lambda_{\max}$ = 260 nm; LC-MS (ESI⁺): m/z 360 (100, [M+H]⁺), 382 (32, [M+Na]⁺), 719 (18, [2M+H]⁺), 731 (12, [2M+Na]⁺); MS/MS (DP = 101 V): m/z (%) 360 (100), 138 (2), 85 (4), 69 (3), 67 (3), 55 (2); LC-TOF-MS: m/z 360.3272 ([M+H]⁺, measured), m/z 360.3266 ([M+H]⁺, calcd for C₂₄H₄₂NO); ¹H NMR 400 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 0.81–0.88 [m, 3H, H-C(20)], 1.16–1.33 [m, 16H, H-C(8, 9, 10, 11, 12, 13, 18, 19)], 1.33–1.42 [m, 2H, H-C(7)], 1.72–1.80 [m, 2H, H-C(22b)], 1.82–1.91 [m, 2H, H-C(22a)], 1.92–2.04 [m, 4H, H-C(14, 17)], 2.06–2.19 [m, 2H, H-C(6)], 3.27–3.39 [m, 2H, H-C(21b)], 3.43–3.51 [m, 2H, H-C(21a)], 5.31 [pt, 2H, J=4.9 Hz, J=10.0 Hz, H-C(15, 16)], 6.04–6.15 [m, 1H, H-C(5)], 6.12–6.26 [m, 1H, J=10.6 Hz, J=15.2 Hz, H-C(4)], 6.25 [d, 1H, J=15.2 Hz, H-C(2)], 7.02 [dd, 1H, J=10.6 Hz, J=15.2 Hz, H-C(3)]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ /ppm: δ 13.7 [C(20)], 22.8 [C(19)], 23.6 [C(22b)], 25.4 [C(22a)], 26.3 [C(14)], 26.3 [C(17)], 28.7 [C(7)], 28.0, 28.3, 28.4, 28.5, 28.7, 28.7 [C(8, 9, 10, 11, 12, 13)], 31.0 [C(18)], 33.0 [C(6)], 45.2 [C(21b)], 45.6 [C(21a)], 120.8 [C(2)], 128.6 [C(4)], 129.4 [C(15)], 129.4 [C(16)], 140.5 [C(3)], 141.8 [C(5)], 163.6 [C(1)].

(2E,4E,15Z)-N-isobutyl-eicosa-2,4,15-trienamide, **10c**, **Figure 1**: UV/Vis (MeOH/water; pH 3,5): $\lambda_{\max}$ = 260 nm; LC-MS (ESI⁺): m/z 362 (100, [M+H]⁺), 384 (56, [M+Na]⁺), 723 (12, [2M+H]⁺), 745 (10, [2M+Na]⁺); MS/MS (DP = 106 V): m/z (%) 362 (100), 276 (5), 220 (5), 138,0 (11), 112 (6), 95 (5), 86 (28), 69 (12), 67 (10), 55 (22); LC-TOF-MS: m/z 362.3456 ([M+H]⁺, measured), m/z 362.3423 ([M+H]⁺, calcd for C₂₄H₄₄NO); ¹H NMR (500 MHz, DMSO-*d*₆; COSY): δ /ppm: δ 0.81 [d, 6H, J=6.6 Hz, H-C(3', 4')], 0.81-0.84 [m, 3H, C(20)], 1.17–1.29 [m, 16H, H-C(8, 9, 10, 11, 12, 13, 18, 19)], 1.30–1.38 [m, 2H, H-C(7)], 1.62–1.70 [m, 1H, H-C(2')], 1.91–2.00 [m, 4H, H-C(14, 17)], 2.05–2.15 [m, 2H, J=7.1 Hz, H-C(6)], 2.91 [t, 2H, J=6.4 Hz, H-C(1')], 5.26–5.33 [m, 2H, J=5.5 Hz, J=11.0 Hz, H-C(15, 16)], 5.91 [d, 1H, J=15.2, H-C(2)],

5.99–6.06 [m, 1H, H-C(5)], 6.08–6.18 [m, 1H, J=10.2 Hz, J=15.2 Hz, H-C(4)], 6.94 [dd, 1H, J=10.2 Hz, J=15.2 Hz, H-C(3)], 7.96 [t, 1H, J=5.7 Hz, N-H]; ¹³C NMR (125 MHz, DMSO-*d*₆; HMQC, HMBC): δ/ppm: δ 14.2 [C(20)], 20.4 [C(3')], 20.4 [C(4')], 22.0 [C(19)], 26.6 [C(14)], 26.6 [C(17)], 28.4 [C(2')], 28.4 [C(7)], 28.5, 28.6, 28.8, 28.9, 29.0, 29.2 [C(8, 9, 10, 11, 12, 13)], 31.2 [C(18)], 32.5 [C(6)], 46.5 [C(1')], 123.4 [C(2)], 128.8 [C(4)], 129.9 [C(15)], 129.9 [C(16)], 139.6 [C(3)], 142.1 [C(5)], 165.9 [C(1)].

1-(eicosa-2E,4E,14Z-trienoyl)piperidine, 11a, Figure 1: UV/Vis (MeOH/water; pH 3,5): λ_{max} = 260 nm; LC-MS (ESI⁺): *m/z* 374 (100, [M+H]⁺), 396 (75, [M+Na]⁺), 747 (55, [2M+H]⁺), 769 (12, [2M+Na]⁺); MS/MS (DP = 141 V): *m/z* (%) 374 (100), 138 (4), 112 (4), 95 (4), 86 (6), 81 (9), 69 (7), 67 (7), 55 (9), 53 (10); LC-TOF-MS: *m/z* 374.3427 ([M+H]⁺, measured), *m/z* 374.3423 ([M+H]⁺, calcd for C₂₅H₄₄NO); ¹H NMR (400 MHz, DMSO-*d*₆; COSY): δ/ppm: δ 0.80–0.88 [m, 3H, H-C(20)], 1.14–1.32 [m, 16H, H-C(8, 9, 10, 11, 12, 17, 18, 19)], 1.32–1.39 [m, 4H, H-C(7)], 1.39–1.50 [m, 4H, H-C(22a, b)], 1.54–1.61 [m, 2H, H-C(23)], 1.90–2.03 [m, 4H, H-C(13, 16)], 2.16 [dt, 2H, J=7.3 Hz, H-C(6)], 3.42–3.52 [m, 4H, H-C(21a, b)], 5.31 [pt, 2H, J=5.0 Hz, J=10.2 Hz, H-C(14, 15)], 6.00–6.12 [m, 1H, H-C(5)], 6.09–6.28 [m, 1H, J=10.8 Hz, J=15.2 Hz, H-C(4)], 6.51 [d, 1H, J=15.0 Hz, H-C(2)], 7.02 [dd, 1H, J=10.8 Hz, J=15.0 Hz, H-C(3)]; ¹³C NMR (100 MHz, DMSO-*d*₆; HMQC, HMBC): δ/ppm: δ 14.0 [C(20)], 22.1 [C(19)], 24.0 [C(23)], 24.2 [C(22b)], 26.6 [C(22a)], 26.7 [C(13)], 26.7 [C(16)], 29.0 [C(7)], 28.3, 28.5, 28.6, 28.8, 28.9, 28.9 [C(8, 9, 10, 11, 12, 17)], 31.4 [C(18)], 32.3 [C(6)], 42.4 [C(21b)], 45.7 [C(21a)], 119.5 [C(2)], 129.0 [C(4)], 129.7 [C(14)], 129.7 [C(15)], 141.4 [C(3)], 141.8 [C(5)], 164.5 [C(1)].

1-(eicosa-2E,4E,14Z-trienoyl)pyrrolidine, 11b, Figure 1: UV/Vis (MeOH/water; pH 3,5): λ_{max} = 260 nm; LC-MS (ESI⁺): *m/z* 360 (100, [M+H]⁺), 382 (32, [M+Na]⁺), 719 (18, [2M+H]⁺), 731 (12, [2M+Na]⁺); MS/MS (DP = 101 V): *m/z* (%) 360 (100), 138 (2),

85 (4), 69 (3), 67 (3), 55 (2); LC-TOF-MS: m/z 360.3272 ($[M+H]^+$, measured), m/z 360.3266 ($[M+H]^+$, calcd for $C_{24}H_{42}NO$); 1H NMR 400 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 0.81–0.88 [m, 3H, H-C(20)], 1.16–1.33 [m, 18H, H-C(8, 9, 10, 11, 12, 17, 18, 19)], 1.33–1.42 [m, 2H, H-C(7)], 1.72–1.80 [m, 2H, H-C(22b)], 1.82–1.91 [m, 2H, H-C(22a)], 1.92–2.04 [m, 4H, H-C(13, 16)], 2.06–2.19 [m, 2H, H-C(6)], 3.27–3.39 [m, 2H, H-C(21b)], 3.43–3.51 [m, 2H, H-C(21a)], 5.31 [pt, 2H, $J=4.9$ Hz, $J=10.0$ Hz, H-C(14, 15)], 6.04–6.15 [m, 1H, H-C(5)], 6.12–6.26 [m, 1H, $J=10.6$ Hz, $J=15.2$ Hz, H-C(4)], 6.25 [d, 1H, $J=15.2$ Hz, H-C(2)], 7.02 [dd, 1H, $J=10.6$ Hz, $J=15.2$ Hz, H-C(3)]; ^{13}C NMR (100 MHz, DMSO- d_6 ; HMQC, HMBC): δ /ppm: δ 13.7 [C(20)], 22.8 [C(19)], 23.6 [C(22b)], 25.4 [C(22a)], 26.3 [C(13)], 26.3 [C(16)], 28.7 [C(7)], 28.0, 28.3, 28.4, 28.5, 28.7, 28.7 [C(8, 9, 10, 11, 12, 17)], 31.1 [C(18)], 33.0 [C(6)], 45.2 [C(21b)], 45.6 [C(21a)], 120.8 [C(2)], 128.6 [C(4)], 129.4 [C(14)], 129.4 [C(15)], 141.8 [C(5)], 140.5 [C(3)], 163.6 [C(1)].

(2*E*,4*E*,14*Z*)-*N*-isobutyl-eicosa-2,4,14-trienamide, **11c**, **Figure 1**: UV/Vis (MeOH/water; pH 3,5): λ_{max} = 260 nm; LC-MS (ESI $^+$): m/z 362 (100, $[M+H]^+$), 384 (56, $[M+Na]^+$), 723 (12, $[2M+H]^+$), 745 (10, $[2M+Na]^+$); MS/MS (DP = 106 V): m/z (%) 362 (100), 276 (5), 220 (5), 138,0 (11), 112 (6), 95 (5), 86 (28), 69 (12), 67 (10), 55 (22); LC-TOF-MS: m/z 362.3456 ($[M+H]^+$, measured), m/z 362.3423 ($[M+H]^+$, calcd for $C_{24}H_{44}NO$); 1H NMR (500 MHz, DMSO- d_6 ; COSY): δ /ppm: δ 0.81 [d, 6H, $J=6.6$ Hz, H-C(3', 4')], 0.81–0.84 [m, 3H, C(20)], 1.17–1.29 [m, 16H, H-C(8, 9, 10, 11, 12, 17, 18, 19)], 1.30–1.38 [m, 2H, H-C(7)], 1.62–1.70 [m, 1H, H-C(2')], 1.91–2.00 [m, 4H, H-C(13, 16)], 2.05–2.15 [m, 2H, $J=7.1$ Hz, H-C(6)], 2.91 [t, 2H, $J=6.4$ Hz, H-C(1')], 5.26–5.33 [m, 2H, $J=5.5$ Hz, $J=11.0$ Hz, H-C(14, 15)], 5.91 [d, 1H, $J=15.2$ Hz, H-C(2)], 5.99–6.06 [m, 1H, H-C(5)], 6.08–6.18 [m, 1H, $J=10.2$ Hz, $J=15.2$ Hz, H-C(4)], 6.94 [dd, 1H, $J=10.2$ Hz, $J=15.2$ Hz, H-C(3)], 7.96 [t, 1H, $J=5.7$ Hz, N-H]; ^{13}C NMR (125 MHz, DMSO- d_6 ; HMQC, HMBC): δ /ppm: δ 14.2 [C(20)], 20.4 [C(3')], 20.4

[C(4')], 22.3 [C(19)], 26.6 [C(13)], 26.6 [C(16)], 28.4 [C(2')], 28.4 [C(7)], 28.5, 28.6, 28.8, 28.9, 29.0, 29.2 [C(8, 9, 10, 11, 12, 17)], 31.4 [C(18)], 32.5 [C(6)], 46.5 [C(1')], 123.4 [C(2)], 128.8 [C(4)], 129.9 [C(14)], 129.9 [C(15)], 139.6 [C(3)], 142.1 [C(5)], 165.9 [C(1)].