13C-NMR (100 MHz, CDCl₃): δ = 172.4 and 172.2 (C-1); 156.3 and 155.5 (C-5); 134.8 and 134.6 (C-10); 2.84-2.73 (m, 3 H, H-3); 2.63-2.34 (m, 2 H, H-8); 1.67 (s, 3 H, H-12); 1.61 (s, 3 H, H-11); 1.49-1.38 (m, 9 H, H-13, H-14). Yield: 19.32 g (58 %). Rf = 0.42 (12.5% EtOAc in petroleum ether). 1H-NMR (400 MHz, CDCl₃): δ = 5.06-4.99 (m, 1 H, H-9); 4.70 (dd, J = 10.5, 5.3 Hz, 0.5 H, H-2); 4.30 (dd, J = 10.3, 5.3 Hz, 0.5 H, H-2); 3.69 (s, 3 H, H-4); 2.84-2.73 (m, 3 H, H-3); 2.63-2.34 (m, 2 H, H-8); 1.67 (s, 3 H, H-12); 1.61 (s, 3 H, H-11). HRMS (ESI): [M + Na]⁺ calcd for C₁₄H₂₅NO₄ + Na: 294.1681; found: 294.1686.3

To a suspension of sarcosine (35.64 g, 0.40 mol) in 350 mL MeOH was added thionyl chloride (29.02 mL, 0.40 mol) at 0 °C. After complete addition the cooling bath was removed and the reaction mixture was stirred for 30 min at r.t. and refluxed for further 6 h. The resulting solution was concentrated in vacuum and the residue was dried in high vacuum over night at r.t. to afford sarcosine methylester.HCl as a white powder which was used in the next step without further purification; yield: 76.65 g (90 %), Rf = 0.36 (12.5% EtOAc in petroleum ether). 1H-NMR (400 MHz, CDCl₃): δ = 3.89 and 3.82 (2 x s, 2 H, CH₃); 3.65 and 3.64 (2 x s, 3 H, H-4); 2.84 and 2.83 (2 x s, 3 H, H-3); 1.38 and 1.33 (2 x s, 9 H, H-7). 13C-NMR (100 MHz, CDCl₃): δ = 166.7 (C-1), 53.3 (C-2), 48.9 (C-3), 33.4 (C-4). 1 To a suspension of sarcosine methylester.HCl (59.80 g, 0.43 mol) and (Boc)₂O (138.01 mL, 0.65 mol) in 1.0 L CH₂Cl₂, TEA (119.09 mL, 0.86 mol) was added dropwise at 0 °C. After complete addition the cooling bath was removed and the reaction mixture was stirred for two days at r.t. Aq. HCl (1 M) was added until the aqueous layer showed pH = 6. The resulting two layers were separated and the organic layer was washed with dist. H₂O, dried (Na₂SO₄), concentrated in vacuum and volatile impurities were removed in high vacuum over night at r.t. to afford a clear oil; yield: 22.16 g (59 %), Rf = 0.29 (12.5% EtOAc in petroleum ether). 1H-NMR (400 MHz, CDCl₃): δ = 5.06-4.99 (m, 1 H, H-9); 4.70 (dd, J = 10.5, 5.3 Hz, 0.5 H, H-2); 4.30 (dd, J = 10.3, 5.3 Hz, 0.5 H, H-2); 3.69 (s, 3 H, H-4); 2.84-2.73 (m, 3 H, H-3); 2.63-2.34 (m, 2 H, H-8); 1.67 (s, 3 H, H-12); 1.61 (s, 3 H, H-11). HRMS (ESI): m/z [M + Na]⁺ calcd for C₂₀H₃₆N₄O₄ + Na: 416.2520; found: 416.2516.2

2-((N-tert-Butyloxycarbonyl-N-methyl)amino)-5-methylhex-4-enioic acid methyl ester 3a: A solution of 2 (30.49 g, 0.15 mol) in 250 mL THF/DME (1:1) was added to NaHMDS (75 mL, 0.15 mol, 2.0 M in THF) dropwise at -78 °C. The reaction mixture was stirred for 1 h before prenyl bromide (44.71 g, 0.30 mol) was added dropwise. Stirring was continued overnight, while the reaction was allowed to warm to r.t. Work-up started by quenching with some drops of sat. aq NH₄Cl. All solvents were removed in vacuum and the residue was partitioned between EtOAc (300 mL) and dist. H₂O (50 mL). The aqueous layer was removed and the organic layer was washed with brine (50 mL), dried (Na₂SO₄) and concentrated in vacuum. The residue was purified by column chromatography (10 -> 50 % EtOAc in petroleum ether) to afford 3a as a clear oil; yield: 19.32 g (58 %), Rf = 0.42 (12.5% EtOAc in petroleum ether). 1H-NMR (400 MHz, CDCl₃): δ = 5.06-4.99 (m, 1 H, H-9); 4.70 (dd, J = 10.5, 5.3 Hz, 0.5 H, H-2); 4.30 (dd, J = 10.3, 5.3 Hz, 0.5 H, H-2); 3.69 (s, 3 H, H-4); 2.84-2.73 (m, 3 H, H-3); 2.63-2.34 (m, 2 H, H-8); 1.67 (s, 3 H, H-12); 1.61 (s, 3 H, H-11). HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₅H₂₅NO₄ + Na: 294.1681; found: 294.1686.3

(N-tert-Butyloxycarbonyl-N-methyl)phenylalanine-methyl ester 3b: Synthesis of ester 3b following the procedure as described for 3a using reactant 2 (30.49 g, 0.15 mol) in 250 mL THF/DME (1:1), NaHMDS (75.00 mL, 0.15 mol, 2 M in THF), BnBr (28.22 g, 0.17 mol). Ester 3b was isolated as a clear oil; yield: 29.22 g (66 %), Rf = 0.33 (12.5% EtOAc in petroleum ether). 1H-NMR (400 MHz, CDCl₃): δ = 7.37-7.16 (m, 5 H, H-10, H-11, H-12); 4.96 (dd, J = 10.7, 5.3 Hz, 0.5 H, H-2); 4.56 (dd, J = 10.8, 4.4 Hz, 0.5 H, H-2); 3.79-3.73 (m, 3 H, H-4), 1H-NMR (300 MHz, CDCl₃): δ = 9.76 (s, 2 H, NH₂); 3.88 (t, J = 5.6 Hz, 2 H, H-2), 3.82 (s, 3 H, H-4), 2.84 (t, J = 5.2 Hz, 3 H, H-3).
2-((N-tert-Butoxycarbonyl-N-methyl)amino)-5-methylhex-4-enoic acid-N,O-dimethylhydroxylamide 4a:
To a suspension of 3a (21.12 g, 77.83 mmol) and N,O-dimethylhydroxylamine HCl (12.15 g, 124.53 mmol) in 200 mL THF was added i-PrMgBr (123.29 mL, 246.58 mmol, 2M in THF) dropwise at -25 °C. After complete addition, stirring was continued for 2 h at -10 °C before the reaction was quenched by the addition of sat. aq NH₄Cl (50 mL). The resulting layers were separated and the aqueous layer was extracted with Et₂O (3x 50 ml). The combined organic extracts were dried (Na₂SO₄) and concentrated in vacuum. The residue was purified by column chromatography (10 % EtOAc in petroleum ether) to afford 4a as yellow oil; yield: 19.13 g (82 %), Rf = 0.36 (12.5% EtOAc in petroleum ether).

1H-NMR (400 MHz, CDCl₃): δ = 5.10 (bs, 0.5 H, H-2), 4.98 (m, 1 H, H-9), 4.85 (bs, 0.5 H, H-2), 3.64 and 3.59 (2x s, 3 H, H-4B), 3.10 (s, 3 H, H-4A), 2.77-2.70 (m, 3 H, H-3), 2.33 (m, 2 H, H-8), 1.60 (d, J = 4.8 Hz, 3 H, H-12), 1.56 (s, 3 H, H-11), 1.41-1.35 (d, 9 H, H-7).

3C-NMR (100 MHz, CDCl₃): δ = 172.6 and 171.9 (C-1), 156.0 and 155.3 (C-5), 134.4 and 134.3 (C-10), 119.6 and 119.5 (C-9), 79.8 and 79.5 (C-6), 61.5 and 61.3 (C-4B), 55.4 and 53.8 (C-2), 32.2 and 32.0 (C-4A), 30.0 and 29.6 (C-3), 28.4 and 28.3 (C-7), 27.6 (C-8), 25.8 (C-12), 17.8 and 17.7 (C-11). IR (neat): 2973, 2928, 1692, 1443, 1365, 1328, 1166, 1138, 991, 863, 768. HRMS (ESI): m/z [M + Na⁺] calcd for C₁₅H₂₈N₂O₄ + Na: 323.1947; found: 323.1958.

(300 MHz, CDCl₃): δ = 5.10 (bs, 0.5 H, H-2), 4.98 (m, 1 H, H-9), 4.85 (bs, 0.5 H, H-2), 3.64 and 3.59 (2x s, 3 H, H-4B), 3.10 (s, 3 H, H-4A), 2.77-2.70 (m, 3 H, H-3), 2.33 (m, 2 H, H-8), 1.60 (d, J = 4.8 Hz, 3 H, H-12), 1.56 (s, 3 H, H-11), 1.41-1.35 (d, 9 H, H-7).

3C-NMR (100 MHz, CDCl₃): δ = 172.6 and 171.9 (C-1), 156.0 and 155.3 (C-5), 134.4 and 134.3 (C-10), 119.6 and 119.5 (C-9), 79.8 and 79.5 (C-6), 61.5 and 61.3 (C-4B), 55.4 and 53.8 (C-2), 32.2 and 32.0 (C-4A), 30.0 and 29.6 (C-3), 28.4 and 28.3 (C-7), 27.6 (C-8), 25.8 (C-12), 17.8 and 17.7 (C-11). IR (neat): 2973, 2928, 1692, 1668 1443, 1365, 1328, 1166, 1138, 991, 863, 768. HRMS (ESI): m/z [M + Na⁺] calcd for C₁₅H₂₈N₂O₄ + Na: 323.1947; found: 323.1958.

(E)-1-(2-Iodovinyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane 6:
To a solution of oxetane 5 (20.65 g, 73.21 mmol) in CH₂Cl₂ (180 mL) was added BF₃·OEt₂ (1.04 mL, 7.32 mmol) dropwise at r.t. The mixture was stirred until no starting material remained according to detection (petroleum ether/EtOAc/TEA 1:10:0.1; ca. 2 h). The reaction was quenched by the addition of TEA (2.03 mL, 14.64 mmol), stirred for 10 min and concentrated to half of its original volume in vacuum. The solution was decanted off the precipitated BF₃·NEt₃-Komplex and the solvent was removed in vacuum to afford 5 (20.55 g, quant.) as a white solid. 1H-NMR (300 MHz, CDCl₃): δ = 6.86 (d, J = 14.7 Hz, 1 H, H-3), 6.48 (d, J = 14.7 Hz, 1 H, H-2), 3.94 (s, 6 H, H-4), 0.82 (s, 3 H, H-6). 13C-NMR (75 MHz, CDCl₃): δ = 140.0 (C-2), 106.4 (C-3), 84.4 (c-1), 72.8 (C-4), 30.5 (C-5), 14.3 (C-6).

(E)-1-(4-Methyl-2,6,7-trioxabicyclo[2.2.2]octan-1-yl)-4-(N-tert-butoxycarbonyl-N-methyl)amino-7-methyl-
octa-1,6-dien-3-one 7a: NMR data for structure elucidation: 1H-NMR (400 MHz, CDCl₃): δ = 6.65-6.47 (m, 2 H, H-5 and H-6), 5.7-4.97 (m, 1 H, H-10), 4.47 (dd, J = 9.4, 5.7 Hz, 0.5 H, H-8), 4.31 (dd, J = 9.3, 5.3 Hz, 0.5 H, H-8), 3.94 (s, 6 H, H-3), 2.72 and 2.63 (2x s, 3 H, H-14), 2.58-2.26 (m, 2 H, H-9), 1.72-1.65 (m, 3 H, H-13), 1.62 (s, 3 H, H-12), 1.48-1.37 (m, 9 H, H-17), 0.81 (s, 3 H, H-11). 13C-NMR (100 MHz, CDCl₃): δ = 198.4 and 197.6 (C-7), 156.5 and 154.5 (C-15), 138.6 (C-5), 135.0 and 134.8 (C-11), 129.1 and 128.6(C-6), 120.2 and 120.0 (C-10), 106.3 (C-4), 81.1 and 80.6 (C-16), 73.4 (C-3), 65.4
and 62.9 (C-8), 32.5 and 31.3 (C-14), 31.1 (C-2), 28.6 and 28.5 (C-17), 26.9 and 26.3 (C-9), 26.1 (C-13), 18.1 (C-12), 14.7 (C-1).

*(E)-1-(4-Methyl-2,6,7-trioxabicyclo[2.2.2]octan-1-yl)-4-((N-tert-butoxycarbonyl-N-methyl)amino)-5-phenylpent-1-en-3-one 7b: NMR data for structure elucidation: 1H-NMR (400 MHz, CDCl3): δ = 7.36-7.13 (m, 5 H, H-11, H-12, H-13), 6.62-6.53 (m, 2 H, H-5, H-6), 4.97 (dd, J = 9.8, 5.4 Hz, 0.5 H, H-8), 4.55 (dd, J = 10.6, 4.5 Hz, 0.5 H, H-8), 3.95 (s, 6 H, H-3), 3.25-3.14 (m, 1 H, H-9), 2.97-2.81 (m, 1 H, H-9), 2.59 (s, 3 H, H-14), 1.37 and 1.29 (2 x s, 9 H, H-17), 0.81 (s, 3 H, H-1). 13C-NMR (100 MHz, CDCl3): δ = 197.8 and 197.2 (C-7), 156.2 and 155.0 (C-15), 138.9 (C-5), 138.8 and 138.5 (C-10), 129.7 and 129.6 (C-11), 129.0 and 128.8 (C-12), 128.4 (C-6), 126.9 and 126.8 (C-13), 106.2 (C-4), 81.2 and 80.7 (C-16), 73.4 (C-3), 67.1 and 64.4 (C-8), 34.1 and 33.4 (C-9), 32.8 and 31.9 (C-14), 31.0 (C-2), 28.5 and 28.3 (C-17), 14.7 (C-1).

*(E)-3-(1-Methyl-2-mercaptop-1H-imidazole-4-yl)-2(E)-propenoic acid methyl ester 8a: NMR data for structure elucidation: 1H-NMR (300 MHz, CDCl3): δ = 11.44 (s, 1 H, S-H), 7.39 (d, J = 15.8 Hz, 1 H, H-5), 6.21 (d, J = 15.8 Hz, 1 H, H-6), 5.06-4.95 (m, 1 H, H-10), 3.75 (s, 3 H, H-8), 3.52 (s, 3 H, H-4), 3.37 (d, J = 6.7 Hz, 2 H, H-9), 1.75 (s, 3 H, H-12), 1.73 (d, J = 1.5 Hz, 3 H, H-13). 13C-NMR (75 MHz, CDCl3): δ = 167.6 (C-7), 163.9 (C-1), 136.5 (C-3), 134.8 (C-9), 128.0 (C-5), 121.5 (C-2), 118.4 (C-10), 115.5 (C-6), 52.2 (C-8), 31.9 (C-4), 25.8 (C-12), 23.8 (C-9), 18.3 (C-13).

*(E)-3-(1-Methyl-2-mercaptop-5-(3-methylbut-2-en-1-yl)-1H-imidazole-4-yl)-2(E)-propenoic acid methyl ester 8b: NMR data for structure elucidation: 1H-NMR (400 MHz, CDCl3): δ = 12.19 (s, 1 H, S-H), 7.41 (d, J = 15.8 Hz, 1 H, H-5), 7.31-7.19 (m, 3 H, H-12, H-13), 7.05 (d, J = 7.0 Hz, 2 H, H-11), 6.41 (d, J = 15.8 Hz, 1 H, H-6), 4.00 (s, 2 H, H-9), 3.73 (s, 3 H, H-8), 3.36 (s, 3 H, H-4). 13C-NMR (75 MHz, CDCl3): δ = 167.4 (C-7), 163.8 (C-1), 135.2 (C10), 132.7 (C-3), 129.3 (C-11), 128.1 (C-12), 127.6 (C-13), 127.4 (C-5), 122.8 (C-2), 116.6 (C-6), 52.0 (C-8), 31.9 (C-4), 29.8 (C-9).

*(E)-3-(1-Methyl-5-(3-methylbut-2-en-1-yl)-1H-imidazole-4-yl)-2(E)-propenoic acid methyl ester (Fungerin) 1a: NMR data for structure elucidation: 1H-NMR (400 MHz, CDCl3): δ = 7.58 (d, J = 15.3 Hz, 1 H, H-5), 7.36 (s, 1 H, H-1), 6.44 (d, J = 15.3 Hz, 1 H, H-6), 5.08-5.00 (m, 1 H, H-10), 3.72 (s, 3 H, H-8), 3.50 (s, 3 H, H-4), 3.41 (d, J = 6.9 Hz, 2 H, H-9), 1.76 (s, 3 H, H-12), 1.72 (d, J = 1.0 Hz, 3 H, H-13). 13C-NMR (75 MHz, CDCl3): δ = 168.5 (C-7), 139.0 (C-1), 135.8 (C-5), 134.7 (C-11), 134.6 (C-3), 134.4 (C-2), 119.8 (C-10), 114.0 (C-6), 51.5 (C-8), 31.9 (C-4), 25.7 (C-12), 22.7 (C-9), 18.0 (C-13).

*(E)-3-(1-Methyl-5-(1H-imidazole-4-yl)-2(E)-propenoic acid methyl ester 1b: NMR data for structure elucidation: 1H-NMR (400 MHz, CDCl3): δ = 7.62 (d, J = 15.4 Hz, 1 H, H-5), 7.45 (s, 1 H, H-1), 7.29-7.16 (m, 3 H, H-12, H-13), 7.03 (d, J = 7.1 Hz, 2 H, H-11), 6.60 (d, J = 15.4 Hz, 1 H, H-6), 4.06 (s, 2 H, H-9), 3.73 (s, 3 H, H-8), 3.36 (s, 3 H, H-4). 13C-NMR (75 MHz, CDCl3): δ = 168.3 (C-7), 139.0 (C-1), 136.7 (C-10), 135.5 (C-3), 134.7 (C-5), 132.6 (C-2), 128.9 (C-11), 128.0 (C-12), 126.9 (C-13), 115.2 (C-6), 51.4 (C-8), 31.8 (C-4), 28.8 (C-9).

