Photochemical release of aldehydes from α -acetoxy nitroveratryl ethers

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General Experimental

Reactions were generally carried out under an atmosphere of nitrogen or argon using flame dried glassware. Solvents were dried by filtration, under an argon atmosphere, through a purification system similar to the one proposed by Grubbs *et al* ^[1]. Thin layer chromatography (TLC) analyses were done using aluminium sheets coated with silica gel 60 F₂₅₄. Flash column chromatography (FC) was carried out using Brunschwig silica gel 60 Å (32-63 mesh). Commercially available solid products were used without further purification and liquids were freshly distilled before use, unless specified otherwise.

NMR spectra were recorded with Bruker Avance DRX 500 (¹H: 500 and ¹³C: 125.77 MHz) and Bruker Avance DPX 360 (¹H: 360 and ¹³C: 90.55 MHz) spectrometers in CDCl₃ or CD₃CN. Chemical shifts are given in ppm, calibrated to the residual solvent peak (7.27 and 77.0 ppm for CDCl₃, 1.94 and 1.30 ppm for CD₃CN respectively for ¹H and ¹³C), coupling constants “*J*” are expressed in Hertz (multiplicity: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quadruplet, quint = quintet, sext = sextet, m = multiplet). IR were recorded on a FTIR Unicam Mattson 5000 spectrometer. Electron impact (EI) and electrospray ionization (ESI) mass spectra (MS) were obtained with a Vacuum Generators Micromass VG 70/70E

^[1] Pangborn, A.B. ; Giardello, M.A. ; Grubbs, R.H. ; Rosen, R.K. ; Timmers, F.J. *Organometallics* **1996**, *15*, 1518-1520.

spectrometer and with a FT/ICR mass spectrometer Bruker 4.7T BioApex II, relative intensities are given in parenthesis. Photochemical irradiations were made in a Rayonet photoreactor, in a quartz vessel, with 16 lamps of 350 nm. All melting points are uncorrected.

General Procedure A for the Esterification Reaction.

2-Nitroveratrol **1** (1.0 mmol), triethylamine (2.0 mmol) and 4-dimethylaminopyridine (DMAP, 0.1 mmol) were dissolved in anhydrous dichloromethane (10 mL). Acid chloride **2** (1.1 mmol) was then added and the mixture was stirred at 25°C for 20 h. Ethyl acetate was added and the mixture was washed with 10% HCl and aqueous bicarbonate. The organic layer was dried over magnesium sulfate, filtered and concentrated. The residue was purified by recrystallization or FC (silica gel).

Acetic acid 4,5-dimethoxy-2-nitrobenzyl ester **3a**

Following the general procedure A, 2-nitroveratrol **1** (100.0 mg, 0.469 mmol), triethylamine (95.0 mg, 0.938 mmol) and 4-dimethylaminopyridine (6.0 mg, 0.0469 mmol) in the presence of acetyl chloride **2a** (41.0 mg, 0.516 mmol) gave **3a** (106.5 mg, 89 %) as a yellow solid.

TLC (SiO₂, cyclohexane / AcOEt 1:1): R_f = 0.52. **m.p.** 160-166°C. **¹H-NMR** (360 MHz, CDCl₃): δ(ppm) 2.18 (s, 3H), 3.97 (s, 3H), 4.00 (s, 3H), 5.51 (s, 2H), 7.01 (s, 1H), 7.73 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ(ppm) 20.85, 56.37, 56.4, 63.2, 108.25, 110.55, 126.9, 146.08, 148.27, 153.43, 170.3. **EI-MS**: *m/z* (%) 255 (7, M⁺), 209 (4), 196 (51), 180 (5), 167 (34), 151 (15), 136 (100), 124 (7), 108 (8), 95 (5), 78 (2), 69 (2), 43 (5). **FT-IR (CHCl₃)**: ν_{max} 3032, 3021, 1744, 1584, 1524, 1464, 1440, 1383, 1365, 1332, 1279, 1236, 1216, 1204, 1069, 1033, 873, 812, 776, 746, 730, 721, 683 cm⁻¹. **HR-MS (ESI)**: 278.06376 (calcd for C₁₁H₁₃NO₆ + Na: 278.06350).

3a

Propionic acid 4,5-dimethoxy-2-nitrobenzyl ester 3b

Following the general procedure A, 2-nitroveratrol **1** (500.0 mg, 2.345 mmol), triethylamine (477.0 mg, 4.691 mmol) and 4-dimethylaminopyridine (29.2 mg, 0.235 mmol) in the presence of propionyl chloride **2b** (243.6 mg, 2.580 mmol) gave **3b** (595.1 mg, 94 %) as fine yellow needles.

TLC (SiO₂, hexane / AcOEt 2:1): R_f = 0.32. **m.p.** 124-126°C. **¹H-NMR** (360 MHz, CDCl₃): δ(ppm) 1.22 (t, *J* = 7.2 Hz, 3H), 2.46 (q, *J* = 7.3 Hz, 2H), 3.97 (s, 3H), 3.99 (s, 3H), 5.53 (s, 2H), 7.02 (s, 1H), 7.73 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ(ppm) 9.17, 27.60, 56.36, 56.42, 63.09, 108.27, 110.42, 127.18, 140.05, 148.23, 153.44, 173.71. **EI-MS**: *m/z* (%) 269 (11, M⁺), 223 (6), 196 (100), 180 (7), 167 (48), 151 (21), 136 (92), 123 (7), 108 (11), 95 (7), 77 (4), 57 (9). **FT-IR (CHCl₃)**: ν_{max} 3031, 3018, 1740, 1584, 1524, 1464, 1333, 1278, 1213, 1175, 1069, 873, 784, 764, 734, 721 cm⁻¹. **HR-MS (ESI)**: 292.07945 (calcd for C₁₂H₁₅NO₆ + Na: 292.07915).

3b**Butyric acid 4,5-dimethoxy-2-nitrobenzyl ester 3c**

Following the general procedure A, 2-nitroveratrol **1** (500.0 mg, 2.345 mmol), triethylamine (477.0 mg, 4.691 mmol) and 4-dimethylaminopyridine (29.2 mg, 0.235 mmol) in the presence of butyryl chloride **2c** (280.6 mg, 2.580 mmol) gave **3c** (635.0 mg, 96 %) as yellow pellets.

TLC (SiO₂, hexane / AcOEt 2:1): R_f = 0.37. **m.p.** 115-118°C. **¹H-NMR** (360 MHz, CDCl₃): δ(ppm) 0.99 (t, *J* = 7.7 Hz, 3H), 1.73 (sext, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 3.97 (s, 3H), 3.99 (s, 3H), 5.52 (s, 2H), 7.01 (s, 1H), 7.73 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ(ppm) 13.70, 18.45, 36.13, 56.35, 56.40, 63.02, 108.23, 110.37, 127.22, 140.00, 148.19, 153.42, 172.93. **EI-MS**: *m/z* (%) 283 (6, M⁺), 237 (3), 196 (100), 180 (4), 167 (28), 151 (13), 136 (45), 123 (4), 109 (5), 95 (3), 77 (3), 71 (4), 43 (3). **FT-IR (CHCl₃)**: ν_{max} 3016, 2970, 2940, 2925, 1739, 1584, 1524, 1464, 1441, 1384, 1333, 1278, 1173, 1068, 988, 873, 800, 768, 750, 672 cm⁻¹. **HR-MS (ESI)**: 306.0942 (calcd for C₁₃H₁₇NO₆ + Na: 306.0948).

3c**Pentanoic acid 4,5-dimethoxy-2-nitrobenzyl ester 3d**

Following the general procedure A, 2-nitroveratrol **1** (500.0 mg, 2.345 mmol), triethylamine (477.0 mg, 4.691 mmol) and 4-dimethylaminopyridine (29.2 mg, 0.235 mmol) in the presence of valeroyl chloride **2d** (317.4 mg, 2.580 mmol) gave **3d** (669.2 mg, 96 %) as yellow pellets.

TLC (SiO₂, hexane / AcOEt 2:1): R_f = 0.41. **m.p.** 89-91°C. **¹H-NMR** (360 MHz, CDCl₃): δ (ppm) 0.93 (t, J = 7.3 Hz, 3H), 1.39 (sext, J = 7.3 Hz, 2H), 1.68 (quint, J = 7.7 Hz, 2H), 2.43 (t, J = 7.7 Hz, 2H), 3.97 (s, 3H), 3.99 (s, 3H), 5.52 (s, 2H), 7.01 (s, 1H), 7.73 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) 13.69, 22.26, 27.04, 33.97, 56.34, 56.40, 63.03, 108.23, 110.37, 127.22, 140.01, 148.19, 153.41, 173.10. **EI-MS**: m/z (%) 297 (4, M^+), 251 (3), 196 (100), 180 (8), 167 (48), 151 (22), 136 (71), 123 (8), 109 (8), 95 (6), 85 (4), 77 (5), 57 (10). **FT-IR (CHCl₃)**: $\nu_{\max}$ 3037, 3021, 2963, 2940, 1739, 1584, 1524, 1465, 1440, 1383, 1333, 1278, 1226, 1218, 1207, 1169, 1093, 1069, 873, 789, 767, 753, 734, 725, 669 cm⁻¹. **HR-MS (ESI)**: 320.1108 (calcd for C₁₄H₁₉NO₆ + Na: 320.1104).

3d**Hexanoic acid 4,5-dimethoxy-2-nitrobenzyl ester 3e**

Following the general procedure A, 2-nitroveratrol **1** (500.0 mg, 2.345 mmol), triethylamine (477.0 mg, 4.691 mmol) and 4-dimethylaminopyridine (29.2 mg, 0.235 mmol) in the presence of caproyl chloride **2e** (354.4 mg, 2.580 mmol) gave **3e** (689.5 mg, 94 %) as yellow pellets.

TLC (SiO₂, hexane / AcOEt 2:1): R_f = 0.53. **m.p.** 75-78°C. **¹H-NMR** (500 MHz, CDCl₃): δ (ppm) 0.90 (t, J = 5.1 Hz, 3H), 1.32-1.36 (m, 4H), 1.66-1.72 (m, J = 5.3 Hz, 2H), 2.42 (t, J = 5.3 Hz, 2H), 3.97 (s, 3H), 3.99 (s, 3H), 5.52 (s, 2H), 7.01 (s, 1H), 7.73 (s, 1H). **¹³C-NMR** (125 MHz,

CDCl₃): δ (ppm) 13.85, 22.29, 24.67, 31.29, 34.24, 56.34, 56.40, 63.02, 108.23, 110.39, 127.22, 140.02, 148.20, 153.42, 173.11. **EI-MS**: m/z (%) 311 (6, M⁺), 265 (3), 196 (26), 180 (9), 167 (46), 151 (21), 136 (100), 124 (3), 108 (4), 99 (2). **FT-IR (CHCl₃)**: $\nu_{\max}$ 3043, 3034, 2961, 2939, 2964, 1738, 1584, 1524, 1464, 1440, 1383, 1333, 1278, 1240, 1211, 1168, 1098, 1068, 989, 873, 753, 705, 695, 668 cm⁻¹. **HR-MS (ESI)**: 334.12605 (calcd for C₁₅H₂₁NO₆ + Na: 334.12610).

Dodecanoic acid 4,5-dimethoxy-2-nitrobenzyl ester **3f**

Following the general procedure A, 2-nitroveratrol **1** (100.0 mg, 0.469 mmol), triethylamine (95.0 mg, 0.938 mmol) and 4-dimethylaminopyridine (6.0 mg, 0.0469 mmol) in the presence of lauroyl chloride **2f** (113.0 mg, 0.516 mmol) gave **3f** (137.0 mg, 74 %) as a yellow solid.

TLC (SiO₂, cyclohexane / AcOEt 2:1): R_f = 0.61. **m.p.** 76-80°C. **¹H-NMR** (360 MHz, CDCl₃): δ (ppm) 0.88 (t, J = 6.8 Hz, 3H), 1.2-1.4 (16H), 1.68 (m, 2H), 2.43 (t, J = 7.3 Hz, 2H), 3.97 (s, 3H), 3.99 (s, 3H), 5.52 (s, 2H), 7.01 (s, 1H), 7.73 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) 14.1, 22.7, 25.0, 29.2, 29.25, 29.3, 29.4, 29.6, 31.9, 34.3, 56.3, 56.4, 63.0, 108.2, 110.4, 127.2, 140.0, 148.2, 153.4, 173.1. **EI-MS**: m/z (%) 395 (2, M⁺), 196 (35), 180 (25), 167 (40), 151 (49), 136 (100), 123 (4), 108 (7), 96 (2), 79 (2), 71 (2), 57 (1). **FT-IR (CHCl₃)**: $\nu_{\max}$ 3035, 3020, 2960, 2932, 2857, 1739, 1584, 1524, 1464, 1441, 1333, 1278, 1234, 1213, 1169, 1069, 874, 798, 781, 769, 754, 747, 739, 672 cm⁻¹. **HR-MS (ESI)**: 418.2200 (calcd for C₂₁H₃₃NO₆ + Na: 418.2200).

Phenylacetic acid 4,5-dimethoxy-2-nitrobenzyl ester **3g**

In a flask under argon, a mixture of 2-nitroveratrol **1** (200.0 mg, 0.938 mmol) and 4-dimethylaminopyridine (11.7 mg, 0.094 mmol) was dissolved in dry dichloromethane (4.5 mL), and pyridine (223.7 mg, 2.814 mmol) was added. The solution was cooled to 0°C, and phenylacetyl chloride **2g** (296.0 mg, 1.876 mmol) was added dropwise. The reaction was stirred for 20 min at 0°C and then allowed to warm to RT while stirring for two days. The reaction mixture was diluted with water and extracted with dichloromethane. The combined organic layers were washed with saturated aqueous CuSO₄ solution and brine, dried over Na₂SO₄, and concentrated. The residue was purified by FC (silica gel, CH₂Cl₂) giving **3g** (275.3 mg, 89 %) as a yellow orange solid.

TLC (SiO₂, CH₂Cl₂): R_f = 0.68. **m.p.** 113-116°C. **¹H-NMR** (500 MHz, CDCl₃): δ(ppm) 3.64 (s, 3H), 3.77 (s, 2H), 3.94 (s, 3H), 5.57 (s, 2H), 6.68 (s, 1H), 7.28-7.31 (m, 1H), 7.33-7.37 (4H), 7.70 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ(ppm) 41.63, 56.14, 56.36, 63.41, 108.11, 109.29, 127.29, 127.39, 128.77, 129.37, 133.74, 139.47, 147.97, 153.56, 170.61. **EI-MS**: *m/z* (%) 331 (8, M⁺), 285 (8), 240 (1), 212 (2), 196 (100), 180 (12), 167 (68), 151 (63), 136 (89), 123 (26), 108 (11), 91 (64), 77 (8), 65 (8). **FT-IR (CHCl₃)**: ν_{max} 3038, 3022, 3011, 2973, 2940, 2852, 1741, 1584, 1524, 1464, 1441, 1383, 1332, 1279, 1242, 1139, 1068, 1009, 988, 874, 745, 733, 720 cm⁻¹. **¹H-NMR (ESI)**: 354.09478 (calcd for C₁₇H₁₇NO₆ + Na: 354.09480).

3g

3-Methylsulfanylpropionic acid 4,5-dimethoxy-2-nitrobenzyl ester **3h**

Following the general procedure A, 2-nitroveratrol **1** (500.0 mg, 2.345 mmol), triethylamine (477.0 mg, 4.691 mmol) and 4-dimethylaminopyridine (29.2 mg, 0.235 mmol) in the presence of 3-methylthiopropionyl chloride **2h** (368.7 mg, 2.580 mmol) gave **3h** (659.8 mg, 89 %) as a yellow solid.

TLC (SiO₂, CH₂Cl₂): R_f = 0.70. **m.p.** 79-83°C. **¹H-NMR** (500 MHz, CDCl₃): δ(ppm) 2.14 (s, 3H), 2.74-2.84 (4H), 3.96 (s, 3H), 3.40 (s, 3H), 5.55 (s, 2H), 7.03 (s, 1H), 7.72 (s, 1H). **¹³C-NMR**

(125 MHz, CDCl₃): δ (ppm) 15.57, 29.06, 34.37, 56.38, 56.52, 63.48, 108.17, 110.42, 126.88, 139.90, 148.21, 153.49, 171.32. **EI-MS**: m/z (%) 316 (8), 315 (3, M⁺), 269 (39), 254 (9), 212 (3), 196 (100), 180 (93), 165 (33), 151 (21), 136 (67), 123 (27), 107 (12), 95 (25), 75 (36), 61 (26), 55 (6). **FT-IR (CHCl₃)**: $\nu_{\max}$ 3035, 3026, 2939, 1741, 1584, 1524, 1464, 1441, 1385, 1332, 1279, 1230, 1169, 1069, 769, 751 cm⁻¹. **HR-MS (ESI)**: 338.06639 (calcd for C₁₃H₁₇NO₆S + Na: 338.06687).

(3R)-3,7-Dimethyl-oct-6-enoic acid 4,5-dimethoxy-2-nitrobenzyl ester 3i

2-Nitroveratrol **1** (200.0 mg, 0.938 mmol), (*R*)-citronellic acid **2i** (163.0 mg, 0.938 mmol) and 4-dimethylaminopyridine (11.7 mg, 0.094 mmol) were dissolved in chloroform (ethanol-free, stabilized on amylene, 20 mL). *N,N'*-Dicyclohexylcarbodiimide (DCC, 293.3 mg, 1.407 mmol) was then added, and the mixture was stirred at 60°C for two days. The mixture was filtered (PTFE filter) and washed with 10 % HCl, saturated NaHCO₃ solution and brine. The organic layer was dried over magnesium sulfate, filtered and evaporated. The residue was purified by FC (silica gel, CH₂Cl₂) giving **3i** (165.8 mg, 48 %) as a yellow oil.

TLC (SiO₂, hexane / AcOEt 3:1): R_f = 0.31. **¹H-NMR** (360 MHz, CDCl₃): δ (ppm) 0.98 (d, *J* = 6.8 Hz, 3H), 1.20-1.31 (m, 1H), 1.34-1.44 (m, 1H), 1.60 (s, 3H), 1.68 (s, 3H), 1.92-2.09 (3H), 2.24 (dd, *J* = 8.2, 14.5 Hz, 1H), 2.45 (dd, *J* = 5.4, 14.5 Hz, 1H), 3.97 (s, 3H), 3.98 (s, 3H), 5.06-5.10 (m, 1H), 5.52 (s, 2H), 7.01 (s, 1H), 7.73 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) 17.62, 19.64, 25.41, 25.68, 30.07, 36.76, 41.71, 56.34, 56.40, 62.98, 108.24, 110.45, 124.05, 127.21, 131.70, 140.05, 148.21, 153.42, 172.52. **EI-MS**: m/z (%) 366 (3), 348 (5), 302 (3), 206 (3), 196 (100), 180 (88), 169 (49), 151 (32), 136 (27), 123 (21), 109 (64), 95 (13), 81 (6), 69 (41), 55 (5), 41 (6). **FT-IR (CHCl₃)**: $\nu_{\max}$ 3032, 2969, 2938, 2853, 1736, 1584, 1524, 1464, 1333, 1278, 1228, 1150, 1068, 988, 873, 768, 755, 735, 728 cm⁻¹. **HR-MS (ESI)**: 388.1731 (calcd for C₁₉H₂₇NO₆ + Na: 388.1730).

General Procedure B for the Reductive Acetylation Reaction.

Under nitrogen, the ester **3** (1.0 mmol) was dissolved in dry dichloromethane (6 mL). Upon cooling to -78°C , DIBALH (1M in hexanes, 2.0 mL, 2.0 mmol) was added dropwise. After 45 min, the reaction was treated sequentially with pyridine (3.0 mmol) dropwise, a solution of DMAP (2.0 mmol) in dry dichloromethane (3.0 mL) dropwise, and acetic anhydride (6.0 mmol) dropwise. The mixture was stirred at -78°C for 20 h, gradually warmed to 0°C , and stirred for an additional 35 min, and the reaction was then quenched at 0°C with saturated aqueous ammonium chloride (10 mL) and saturated aqueous sodium potassium tartrate (7.5 mL). The resultant mixture was warmed to RT and stirred vigorously for 50 min. After extraction with dichloromethane (x4), the combined dichloromethane extracts were washed with ice-cooled 1M sodium bisulfate (x2), saturated aqueous sodium bicarbonate (x3) and brine (x1), dried over Na_2SO_4 , filtered and evaporated. The residue was purified by FC (silica gel, hexane/AcOEt).

Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-ethyl ester **4a**

According to the general procedure B, ester **3a** (116.0 mg, 0.455 mmol), treated sequentially with DIBALH (0.91 mL, 0.909 mmol), pyridine (108.4 mg, 1.364 mmol), DMAP (113.3 mg, 0.909 mmol) and acetic anhydride (279.8 mg, 2.727 mmol), gave **4a** (109.1 mg, 80 %) as a yellow oil.

TLC (SiO_2 , hexane / AcOEt 1:1): $R_f = 0.51$. **$^1\text{H-NMR}$** (360 MHz, CD_3CN): $\delta(\text{ppm})$ 1.43 (d, $J = 5.0$ Hz, 3H), 1.99 (s, 3H), 3.88 (s, 3H), 3.93 (s, 3H), 4.96 (d, $J = 14.5$ Hz, 1H), 5.01 (d, $J = 15.0$ Hz, 1H), 6.01 (q, $J = 5.0$ Hz, 1H), 7.22 (s, 1H), 7.66 (s, 1H). **$^{13}\text{C-NMR}$** (125 MHz, CD_3CN): $\delta(\text{ppm})$ 20.93, 21.36, 56.89, 56.94, 68.46, 96.74, 109.11, 111.45, 129.85, 140.72, 149.01, 154.65, 171.42. **EI-MS**: m/z (%) 299 (1, M^+), 213 (7), 196 (85), 180 (22), 165 (22), 151 (62), 136 (100), 123 (18), 108 (38), 95 (14), 77 (12), 65 (4), 43 (10). **FT-IR** (CHCl_3): ν_{max} 3030, 3020, 1732, 1584, 1522, 1464, 1329, 1277, 1218, 1167, 1141, 1067, 772, 743, 731, 724 cm^{-1} . **HR-MS** (ESI): 322.09008 (calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_7 + \text{Na}$: 322.08972).

4a

Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-propyl ester **4b**

According to the general procedure B, ester **3b** (122.7 mg, 0.456 mmol), treated sequentially with DIBALH (0.91 mL, 0.911 mmol), pyridine (108.7 mg, 1.367 mmol), DMAP (113.6 mg, 0.911 mmol) and acetic anhydride (280.5 mg, 2.734 mmol), gave **4b** (115.3 mg, 81 %) as a yellow oil.

TLC (SiO₂, hexane / AcOEt 1:1): R_f = 0.56. **¹H-NMR** (500 MHz, CDCl₃): δ (ppm) 1.01 (t, J = 7.6 Hz, 3H), 1.80-1.89 (m, 2H), 2.08 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 5.03 (d, J = 15.3 Hz, 1H), 5.10 (d, J = 15.2 Hz, 1H), 5.93 (t, J = 5.1 Hz, 1H), 7.26 (s, 1H), 7.71 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) 8.26, 21.11, 27.47, 56.33, 56.35, 67.72, 99.33, 107.94, 109.85, 129.67, 139.29, 147.73, 153.55, 170.66. **EI-MS**: m/z (%) 254 (1), 212 (1), 196 (100), 180 (9), 165 (9), 151 (29), 136 (77), 123 (7), 108 (11), 95 (7), 77 (6), 63 (2), 57 (2), 43 (7). **FT-IR (CHCl₃)**: $\nu_{\max}$ 3035, 3025, 2975, 2941, 2850, 1735, 1583, 1522, 1465, 1440, 1373, 1355, 1330, 1277, 1241, 1166, 1148, 1133, 1089, 1068, 1012, 944, 909, 877, 789, 749, 738, 728 cm⁻¹. **HR-MS (ESI)**: 336.10519 (calcd for C₁₄H₁₉NO₇ + Na: 336.10537).

4b

Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-butyl ester **4c**

According to the general procedure B, ester **3c** (130.2 mg, 0.460 mmol), treated sequentially with DIBALH (0.92 mL, 0.919 mmol), pyridine (109.6 mg, 1.379 mmol), DMAP (114.6 mg, 0.919 mmol) and acetic anhydride (282.9 mg, 2.758 mmol), gave **4c** (105.1 mg, 70 %) as a yellow oil.

TLC (SiO₂, hexane / AcOEt 1:1): R_f = 0.64. **¹H-NMR** (360 MHz, CDCl₃): δ (ppm) 0.96 (t, J = 7.3 Hz, 3H), 1.46 (sext, J = 7.3 Hz, 2H), 1.79 (quint, J = 6.8 Hz, 2H), 2.07 (s, 3H), 3.95 (s, 3H), 3.99 (s, 3H), 5.02 (d, J = 15.4 Hz, 1H), 5.09 (d, J = 15.4 Hz, 1H), 5.99 (t, J = 5.5 Hz, 1H), 7.25 (s, 1H), 7.70 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) 13.78, 17.36, 21.09, 36.25, 56.31

(2C), 67.71, 98.34, 107.91, 109.87, 129.62, 139.27, 147.70, 153.52, 170.61. **EI-MS:** m/z (%) 327 (1), 212 (1), 196 (100), 180 (12), 165 (10), 151 (33), 136 (86), 123 (10), 109 (12), 95 (7), 84 (6), 77 (4), 63 (2), 43 (8). **FT-IR (CHCl₃):** $\nu_{\max}$ 3037, 3027, 3020, 2965, 2939, 2877, 1735, 1584, 1522, 1465, 1358, 1330, 1277, 1237, 1221, 1208, 1166, 1143, 1070, 1012, 988, 920, 876, 789, 778, 761, 749, 739, 729, 669 cm⁻¹. **HR-MS (ESI):** 350.1218 (calcd for C₁₅H₂₁NO₇ + Na: 350.1210).

4c

Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-pentyl ester **4d**

According to the general procedure B, ester **3d** (130.5 mg, 0.439 mmol), treated sequentially with DIBALH (0.88 mL, 0.878 mmol), pyridine (104.7 mg, 1.317 mmol), DMAP (109.4 mg, 0.878 mmol) and acetic anhydride (270.2 mg, 2.634 mmol), gave **4d** (97.4 mg, 65 %) as a yellow oil.

TLC (SiO₂, hexane / AcOEt 1:1): R_f = 0.62. **¹H-NMR** (360 MHz, CDCl₃): δ (ppm) 0.92 (t, J = 7.3 Hz, 3H), 1.33-1.47 (4H), 1.75-1.90 (m, 2H), 2.08 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 5.03 (d, J = 15.0 Hz, 1H), 5.10 (d, J = 15.4 Hz, 1H), 5.98 (t, J = 5.5 Hz, 1H), 7.26 (s, 1H), 7.72 (s, 1H).

¹³C-NMR (125 MHz, CDCl₃): δ (ppm) 13.96, 21.15, 22.38, 26.20, 33.98, 56.33, 56.37, 67.73, 98.60, 107.95, 109.89, 129.69, 139.31, 147.74, 153.56, 170.66. **EI-MS:** m/z (%) 341(1), 196 (85), 180 (12), 165 (11), 151 (39), 136 (100), 123 (10), 108 (11), 95 (8), 77 (4), 69 (2), 43 (4).

FT-IR (CHCl₃): $\nu_{\max}$ 3037, 3028, 3020, 2962, 2939, 2865, 1735, 1583, 1522, 1465, 1440, 1357, 1330, 1277, 1240, 1166, 1143, 1109, 1069, 1012, 989, 937, 876, 790, 762, 749, 736, 726 cm⁻¹.

HR-MS (ESI): 364.13704 (calcd for C₁₆H₂₃NO₇ + Na: 364.13667).

4d

Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-hexyl ester 4e

According to the general procedure B, ester **3e** (142.0 mg, 0.456 mmol), treated sequentially with DIBALH (0.91 mL, 0.912 mmol), pyridine (108.8 mg, 1.368 mmol), DMAP (113.7 mg, 0.912 mmol) and acetic anhydride (280.8 mg, 2.737 mmol), gave **4e** (107.3 mg, 66 %) as a yellow oil.

TLC (SiO₂, hexane / AcOEt 1:1): R_f = 0.69. **¹H-NMR** (360 MHz, CDCl₃): δ (ppm) 0.89 (t, J = 6.8 Hz, 3H), 1.30-1.34 (4H), 1.42-1.47 (m, 2H), 1.75-1.87 (m, 2H), 2.08 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 5.02 (d, J = 15.4 Hz, 1H), 5.10 (d, J = 15.4 Hz, 1H), 5.98 (t, J = 5.4 Hz, 1H), 7.26 (s, 1H), 7.71 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) 13.91, 21.14, 22.50, 23.71, 31.42, 34.22, 56.32, 56.36, 67.72, 98.59, 107.94, 109.87, 129.68, 139.29, 147.73, 153.55, 170.65. **EI-MS**: m/z (%) 355 (1), 196 (90), 180 (15), 165 (11), 151 (41), 136 (100), 123 (11), 108 (11), 95 (6), 77 (4), 43 (4). **FT-IR (CHCl₃)**: $\nu_{\max}$ 3033, 2960, 2937, 2862, 1734, 1583, 1522, 1465, 1440, 1373, 1357, 1330, 1277, 1247, 1166, 1142, 1113, 1069, 1012, 940, 877, 788, 754, 738, 667, 606 cm⁻¹. **HR-MS (ESI)**: 378.15218 (calcd for C₁₇H₂₅NO₇ + Na: 378.15232).

Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-dodecyl ester 4f

According to the general procedure B, ester **3f** (147.3 mg, 0.372 mmol) in CH₂Cl₂ (25 mL, instead of 2.2 mL due to the poor solubility of the ester **3f** in CH₂Cl₂ at -78°C), treated sequentially with DIBALH (0.74 mL, 0.745 mmol), pyridine (88.8 mg, 1.117 mmol), DMAP (92.9 mg, 0.745 mmol) and acetic anhydride (229.3 mg, 2.235 mmol), gave **4f** (118.5 mg, 72 %) as a yellow oil.

TLC (SiO₂, hexane / AcOEt 2:1): R_f = 0.58. **¹H-NMR** (360 MHz, CDCl₃): δ (ppm) 0.88 (t, J = 6.8 Hz, 3H), 1.22-1.38 (16H), 1.39-1.47 (m, 2H), 1.74-1.90 (m, 2H), 2.08 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 5.02 (d, J = 15.0 Hz, 1H), 5.10 (d, J = 15.4 Hz, 1H), 5.98 (t, J = 5.4 Hz, 1H), 7.26 (s, 1H), 7.72 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) 14.10, 21.17, 22.67, 24.06, 29.27, 29.32, 29.50, 29.60, 31.88, 34.26, 56.33, 67.71, 98.59, 107.88, 109.78, 129.72, 139.22, 147.67, 153.52, 170.67. **EI-MS**: m/z (%) 196 (100), 180 (21), 165 (12), 151 (64), 136 (100), 123 (9), 108

(10), 95 (5), 43 (6). **FT-IR (CHCl₃):** $\nu_{\max}$ 3035, 2957, 2928, 2856, 1736, 1583, 1520, 1465, 1441, 1357, 1330, 1277, 1243, 1167, 1121, 1069, 1011, 936, 876, 789, 763, 747, 729 cm⁻¹. **HR-MS (ESI):** 462.24606 (calcd for C₂₃H₃₇NO₇ + Na: 462.24622).

Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-2-phenyl-ethyl ester 4g

According to the general procedure B, ester **3g** (148.1 mg, 0.447 mmol), treated sequentially with DIBALH (0.89 mL, 0.894 mmol), pyridine (106.6 mg, 1.341 mmol), DMAP (111.4 mg, 0.894 mmol) and acetic anhydride (275.2 mg, 2.682 mmol), gave **4g** (151.5 mg, 90 %) as a yellow oil.

TLC (SiO₂, hexane / AcOEt 3:1): R_f = 0.27. **¹H-NMR** (360 MHz, CDCl₃): δ (ppm) 2.08 (s, 3H), 3.13 (d, J = 5.4 Hz, 2H), 3.80 (s, 3H), 3.94 (s, 3H), 4.97 (d, J = 15.4 Hz, 1H), 5.13 (d, J = 15.4 Hz, 1H), 6.16 (t, J = 5.4 Hz, 1H), 7.05 (s, 1H), 7.22-7.33 (5H), 7.68 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) 21.11, 40.88, 56.27, 56.31, 67.74, 98.35, 107.75, 109.50, 126.86, 128.40, 129.53, 129.81, 135.34, 138.98, 147.56, 153.54, 170.52. **EI-MS:** m/z (%) 283 (2), 270 (3), 254 (3), 241 (8), 224 (4), 206 (11), 196 (100), 180 (14), 165 (23), 151 (50), 136 (48), 125 (10), 108 (10), 91 (26), 77 (5), 65 (5), 43 (5). **FT-IR (CHCl₃):** $\nu_{\max}$ 3034, 3012, 2969, 2940, 2908, 2851, 1736, 1584, 1523, 1464, 1440, 1354, 1330, 1277, 1240, 1167, 1130, 1069, 1012, 939, 877, 788, 752, 729 cm⁻¹. **HR-MS (ESI):** 398.12106 (calcd for C₁₉H₂₁NO₇ + Na: 398.12102).

Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-3-methylsulfanyl-propyl ester 4h

According to the general procedure B, ester **3h** (141.8 mg, 0.450 mmol), treated sequentially with DIBALH (0.90 mL, 0.899 mmol), pyridine (107.2 mg, 1.349 mmol), DMAP (112.1 mg, 0.899 mmol) and acetic anhydride (276.8 mg, 2.698 mmol), gave **4h** (124.4 mg, 77 %) as a yellow oil.

TLC (SiO₂, hexane / AcOEt 2:1): R_f = 0.35. **¹H-NMR** (360 MHz, CDCl₃): δ (ppm) 2.09-2.18 (m, 2H), 2.09 (s, 3H), 2.12 (s, 3H), 2.62 (t, J = 7.3 Hz, 2H), 3.96 (s, 3H), 4.00 (s, 3H), 5.04 (d, J = 14.5 Hz, 1H), 5.12 (d, J = 15.0 Hz, 1H), 6.10 (t, J = 5.0 Hz, 1H), 7.23 (s, 1H), 7.71 (s, 1H). **¹³C-NMR** (125 MHz, CDCl₃): δ (ppm) 15.56, 21.12, 28.57, 33.83, 56.36, 56.41, 68.13, 97.28, 107.94, 109.99, 129.18, 139.35, 147.80, 153.52, 170.52. **EI-MS**: m/z (%) 300 (7), 253 (8), 225 (4), 213 (6), 206 (6), 196 (100), 180 (75), 165 (29), 151 (49), 136 (91), 123 (19), 103 (17), 95 (11), 75 (14), 61 (6), 43 (6). **FT-IR (CHCl₃)**: $\nu_{\max}$ 3034, 3028, 3018, 3004, 2972, 2940, 2920, 2850, 2838, 1736, 1583, 1523, 1465, 1441, 1375, 1358, 1330, 1277, 1245, 1168, 1129, 1067, 1046, 1012, 942, 875, 775, 767, 746, 734 cm⁻¹. **HR-MS (ESI)**: 382.09326 (calcd for C₁₅H₂₁NO₇S + Na: 382.09309).

(3R)-Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-3,7-dimethyl-oct-6-enyl ester 4i

According to the general procedure B, ester **3i** (144.9 mg, 0.397 mmol), treated sequentially with DIBALH (0.79 mL, 0.793 mmol), pyridine (94.6 mg, 1.190 mmol), DMAP (98.9 mg, 0.793 mmol) and acetic anhydride (244.1 mg, 2.379 mmol), gave **4i** (115.6 mg, 71 %) as a yellow oil.

TLC (SiO₂, hexane / AcOEt 3:1): R_f = 0.34. **¹H-NMR** (360 MHz, CDCl₃): mixture of diastereoisomers δ (ppm) 0.96-0.98 (3H), 1.17-1.27 (1H), 1.33-1.44 (1H), 1.53-1.74 (2H), 1.59 (3H), 1.66 (3H), 1.80-2.02 (2H), 2.07 (3H), 3.96-3.99 (6H), 5.00-5.13 (3H), 6.06-6.09 (1H), 7.26-7.27 (1H), 7.71 (1H). **¹³C-NMR** (125 MHz, CDCl₃): mixture of diastereoisomers δ (ppm) 17.61, 19.55, 19.90, 21.13, 21.17, 25.24, 25.28, 25.67, 28.56, 28.62, 36.97, 37.19, 41.14, 41.26, 56.27, 56.33, 67.74, 67.82, 97.59, 97.66, 107.87, 109.75, 109.81, 124.28, 124.32, 129.63, 129.67, 131.49, 139.19, 147.66, 153.52, 170.55, 170.63. **EI-MS**: m/z (%) 332 (2), 304 (2), 286 (14), 234

(2), 212 (27), 196 (79), 180 (100), 165 (24), 153 (43), 136 (89), 121 (30), 109 (64), 95 (25), 81 (16), 69 (24), 55 (6), 43 (11). **FT-IR** (CHCl_3): ν_{max} 3030, 3018, 2967, 2938, 2854, 1732, 1583, 1519, 1464, 1441, 1376, 1330, 1276, 1245, 1167, 1129, 1069, 1011, 927, 876, 781, 761, 746, 729 cm^{-1} . **HR-MS** (ESI): 432.19916 (calcd for $\text{C}_{21}\text{H}_{31}\text{NO}_7 + \text{Na}$: 432.19927).

1-But-1-enyloxymethyl-4,5-dimethoxy-2-nitrobenzene 5

Compound **4c** (34.0 mg, 0.104 mmol) was heated in a Kugelrohr apparatus at 200°C for 4 hours. Enol ether **5** (14.1 mg, 51 %) was obtained as a mixture of isomers (*Z/E* 3:2).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ (ppm) 1.00 (t, $J = 7.4$ Hz, 1.3H), 1.04 (t, $J = 7.4$ Hz, 1.7H), 1.98 (quint d, $J = 7.4, 1.4$ Hz, 0.8H), 2.23 (quint d, $J = 7.4, 1.4$ Hz, 1.2H), 3.97-4.00 (6H), 4.51 (q, $J = 7.2$ Hz, 0.6H), 5.03 (dt, $J = 12.7, 7.2$ Hz, 0.4H), 5.15 (s, 0.8H), 5.23 (1.2H), 5.99 (dt, $J = 6.1, 1.4$ Hz, 0.6H), 6.35 (dt, $J = 12.6, 1.4$ Hz, 0.4H), 7.25-7.26 (1H), 7.74-7.75 (1H). **$^{13}\text{C-NMR}$** (125 MHz, CDCl_3): δ (ppm) 14.43, 15.17, 17.65, 21.05, 56.28, 56.36, 56.43, 68.04, 70.77, 107.81, 107.88, 108.20, 109.09, 109.33, 110.04, 130.04, 130.67, 138.79, 144.13, 144.84, 147.61, 153.83, 153.88. **EI-MS**: m/z (%) 267 (2, M^+), 250 (3), 241 (3), 222 (8), 212 (5), 196 (100), 180 (43), 165 (32), 151 (21), 138 (37), 136 (40), 123 (25), 109 (10), 95 (17), 77 (8), 69 (6).

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-ethyl ester 4a

In a quartz NMR tube, a solution of **4a** (9.4 mg, 0.031 mmol) and an internal standard (tetradecane, olefin free, 1.2 mg, 6 μmol) in CD_3CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the $^1\text{H-NMR}$ spectra showed acetaldehyde **6a** (yield: 58

%) and acetic acid. **¹H-NMR** (360 MHz, CD₃CN): δ(ppm) 2.11 (d, *J* = 2.7 Hz, 3H), 9.69 (q, *J* = 2.7 Hz, 1H).

6a

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitro-benzyloxy)-propyl ester 4b

In a quartz NMR tube, a solution of **4b** (10.0 mg, 0.032 mmol) in CD₃CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the ¹H-NMR spectra showed propionaldehyde **6b** (yield: 79 %) and acetic acid. **¹H-NMR** (360 MHz, CD₃CN): δ(ppm) 1.02 (t, *J* = 7.3 Hz, 3H), 2.43 (q, *J* = 7.3 Hz, 2H), 9.71 (s, 1H).

6b

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-butyl ester 4c

In a quartz NMR tube, a solution of **4c** (15.3 mg, 0.047 mmol) in CD₃CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the ¹H-NMR spectra showed butyraldehyde **6c** (yield: 70 %) and acetic acid. **¹H-NMR** (360 MHz, CD₃CN): δ(ppm) 0.92 (t, *J* = 7.7 Hz, 3H), 1.60 (sext, *J* = 7.3 Hz, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 9.68 (s, 1H).

6c

Photolysis of 1-but-1-enyloxymethyl-4,5-dimethoxy-2-nitrobenzene 5

In a quartz NMR tube, a solution of **5** (8.8 mg, 0.033 mmol) in CD₃CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the ¹H-NMR spectra showed butyraldehyde **6c** as the major product among another minor product.

6c

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-pentyl ester 4d

In a quartz NMR tube, a solution of **4d** (11.6 mg, 0.034 mmol) in CD₃CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the ¹H-NMR spectra showed pentanal **6d** (yield: 74 %) and acetic acid. ¹H-NMR (360 MHz, CD₃CN): δ(ppm) 0.90 (t, *J* = 7.3 Hz, 3H), 1.27-1.39 (m, 2H), 1.56 (quint, *J* = 7.3 Hz, 2H), 2.40 (td, *J* = 7.3, 1.4 Hz, 2H), 9.69 (s, 1H).

6d

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-hexyl ester 4e

In a quartz NMR tube, a solution of **4e** (15.4 mg, 0.043 mmol) in CD₃CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the ¹H-NMR spectra showed hexanal **6e** (yield: 57 %) and acetic acid. ¹H-NMR (360 MHz, CD₃CN): δ(ppm) 0.89 (t, *J* = 6.8 Hz, 3H), 1.25-1.35 (4H), 1.53-1.62 (m, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 9.68 (s, 1H).

6e

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-dodecyl ester 4f

In a quartz NMR tube, a solution of **4f** (11.8 mg, 0.027 mmol) in CD₃CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the ¹H-NMR spectra showed dodecanal **6f** (yield: 69 %) and acetic acid. ¹H-NMR (360 MHz, CD₃CN): δ(ppm) 0.88 (t, *J* = 6.8 Hz, 3H), 1.15-1.40 (16H), 1.56 (m, *J* = 6.8 Hz, 2H), 2.38 (td, *J* = 7.3, 1.4 Hz, 2H), 9.67 (t, *J* = 1.3 Hz, 1H).

6f

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-2-phenyl-ethyl ester 4g

In a quartz NMR tube, a solution of **4g** (14.7 mg, 0.039 mmol) and an internal standard (tetradecane, olefin free, 1.6 mg, 8 μ mol) in CD₃CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the ¹H-NMR spectra showed phenylacetaldehyde **6g** (yield: 62 %) and acetic acid. **¹H-NMR** (360 MHz, CD₃CN): δ (ppm) 3.72 (d, J = 1.4 Hz, 2H), 7.22-7.39 (5H), 9.71 (t, J = 1.8 Hz, 1H).

6g

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-3-methylsulfanyl-propyl ester 4h

In a quartz NMR tube, a solution of **4h** (13.2 mg, 0.037 mmol) and an internal standard (tetradecane, olefin free, 1.5 mg, 7 μ mol) in CD₃CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the ¹H-NMR spectra showed methional **6h** (yield: 53 %) and acetic acid. **¹H-NMR** (360 MHz, CD₃CN): δ (ppm) 2.07 (s, 3H), 2.68-2.77 (4H), 9.68 (s, 1H).

6h

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-dodecyl ester 4i

In a quartz NMR tube, a solution of **4i** (12.6 mg, 0.031 mmol) in CD₃CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the ¹H-NMR spectra showed (*R*)-citronellal **6i** (yield: 73 %) and acetic acid. **¹H-NMR** (360 MHz, CD₃CN): δ (ppm) 0.93 (d, J = 6.8 Hz, 3H), 1.18-1.38 (m, 2H), 1.60 (s, 3H), 1.67 (s, 3H), 1.99-2.06 (3H), 2.17-2.24 (m, 1H), 2.36-2.42 (m, 1H), 5.11 (t, J = 6.8 Hz, 1H), 9.68 (t, J = 1.8 Hz, 1H).

6i