Photochemical release of aldehydes from α-acetoxy nitroveratryl ethers

Jaime Lage Robles and Christian G. Bochet*

Department of Chemistry, University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland.

Christian.Bochet@unifr.ch

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** (SiO$_2$, cyclohexane / AcOEt 1:1): $R_f = 0.52$.  
**m.p.** 160-166°C.  
**$^1$H-NMR** (360 MHz, CDCl$_3$): 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).  
**$^{13}$C-NMR** (125 MHz, CDCl$_3$): 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 (CHCl$_3$):** $\nu_{\text{max}}$ 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 C$_{11}$H$_{13}$NO$_6$ + Na: 278.06350).

![3a](image-url)
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): Rf = 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): νmax 3031, 3018, 1740, 1584, 1524, 1464, 1333, 1278, 1173, 1068, 873, 784, 764, 734, 721 cm⁻¹.

HR-MS (ESI): 292.07945 (calcd for C₁₂H₁₅NO₆ + Na: 292.07915).

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): Rf = 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): νmax 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).
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): ν_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).

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,
CDCl$_3$: 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 (CHCl$_3$):** ν$_{\text{max}}$ 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 C$_{15}$H$_{21}$NO$_6$ + Na: 334.12610).

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

Following the general procedure A, 2-nitoveratrol 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 (SiO$_2$, cyclohexane / AcOEt 2:1):** R$_f$ = 0.61. **m.p.** 76-80°C. **$^1$H-NMR (360 MHz, CDCl$_3$):** 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). **$^{13}$C-NMR (125 MHz, CDCl$_3$):** 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 (CHCl$_3$):** ν$_{\text{max}}$ 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 C$_{21}$H$_{33}$NO$_6$ + 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 CuSO$_4$ solution and brine, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by FC (silica gel, CH$_2$Cl$_2$) giving 3g (275.3 mg, 89 %) as a yellow orange solid.  
TLC (SiO$_2$, CH$_2$Cl$_2$): $R_f$ = 0.68. m.p. 113-116°C. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$(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). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$(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. El-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 (CHCl$_3$): $\nu_{\text{max}}$ 3038, 3022, 3011, 2973, 2940, 2852, 1741, 1584, 1524, 1464, 1441, 1383, 1332, 1279, 1242, 1139, 1068, 1009, 988, 874, 745, 733, 720 cm$^{-1}$. HR-MS (ESI): 354.09478 (calcd for C$_{17}$H$_{17}$NO$_6$ + Na: 354.09480).

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 (SiO$_2$, CH$_2$Cl$_2$): $R_f$ = 0.70. m.p. 79-83°C. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$(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). $^{13}$C-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):** νmax 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).

![3h](image)

**3h**

**3(R)-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):** Rₚ = 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):** νmax 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 Na₂SO₄, 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** (SiO₂, hexane / AcOEt 1:1): Rf = 0.51. **¹H-NMR** (360 MHz, CD₃CN): δ(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). ¹³C-NMR (125 MHz, CD₃CN): δ(ppm) 20.93, 21.36, 56.89, 56.94, 68.46, 96.74, 109.11, 111.45, 129.85, 137.46, 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 (CHCl₃)**: νmax 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 C₁₃H₁₇NO₇ + Na: 322.08972).
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.

\textbf{TLC} (SiO\textsubscript{2}, hexane / AcOEt 1:1): R\textsubscript{f} = 0.56. \textbf{\textsuperscript{1}H-NMR} (500 MHz, CDCl\textsubscript{3}): \(\delta\) (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). \textbf{\textsuperscript{13}C-NMR} (125 MHz, CDCl\textsubscript{3}): \(\delta\) (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. \textbf{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).

\textbf{FT-IR (CHCl\textsubscript{3})}: \(\nu\)\textsubscript{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\textsuperscript{-1}. \textbf{HR-MS (ESI)}: 336.10519 (calcd for C\textsubscript{14}H\textsubscript{19}NO\textsubscript{7} + Na: 336.10537).

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.

\textbf{TLC} (SiO\textsubscript{2}, hexane / AcOEt 1:1): R\textsubscript{f} = 0.64. \textbf{\textsuperscript{1}H-NMR} (360 MHz, CDCl\textsubscript{3}): \(\delta\) (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). \textbf{\textsuperscript{13}C-NMR} (125 MHz, CDCl\textsubscript{3}): \(\delta\) (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 (CHCl\(_3\)):** \( \nu_{\text{max}} \) 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 \( \text{C}_{15}\text{H}_{21}\text{NO}_7 + \text{Na} \)): 350.1210.

![Image](image_url)

**Acetic acid 1-(4,5-dimethoxy-2-nitrobenzyloxy)-penty l 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** (SiO\(_2\), hexane / AcOEt 1:1): \( R_f = 0.62 \). **\(^1\)H-NMR** (360 MHz, CDCl\(_3\)): \( \delta \) (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).

**\(^{13}\)C-NMR** (125 MHz, CDCl\(_3\)): \( \delta \) (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 (CHCl\(_3\)):** \( \nu_{\text{max}} \) 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 \( \text{C}_{16}\text{H}_{23}\text{NO}_7 + \text{Na} \)): 364.13667.
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): Rf = 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), 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, 109.87, 109.94, 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): νmax 3033, 2960, 2937, 2862, 1734, 1583, 1522, 1465, 1440, 1373, 1357, 1330, 1277, 1247, 1166, 1142, 1113, 1069, 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): Rf = 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):** νₚₑₙₛ 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).

![Diagram of 4f]

**Acetic acid 1-(4,5-dimethoxy-2-nitrobenzylxloxy)-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):** Rₐ = 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):** νₚₑₙₛ 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).

![Diagram of 4g]
Acetic acid 1-(4,5-dimethoxy-2-nitrobenzylxoy)-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): Rₖ = 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): νmax 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-nitrobenzylxoy)-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): Rₖ = 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$_3$):** $\nu_{\text{max}}$ 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 C$_{21}$H$_{31}$NO$_7$ + Na: 432.19927).

![Image](https://example.com/image.png)

**4i**

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).

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$(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). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$(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).

![Image](https://example.com/image.png)

**5**

**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$_3$CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the $^1$H-NMR spectra showed acetaldehyde 6a (yield: 58
% and acetic acid. $^1$H-NMR (360 MHz, CD$_3$CN): δ(ppm) 2.11 (d, J = 2.7 Hz, 3H), 9.69 (q, J = 2.7 Hz, 1H).

\[
\begin{align*}
&\text{O} \\
&\text{H} \\
&\text{6a}
\end{align*}
\]

**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 CD$_3$CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the $^1$H-NMR spectra showed propionaldehyde 6b (yield: 79 %) and acetic acid. $^1$H-NMR (360 MHz, CD$_3$CN): δ(ppm) 1.02 (t, J = 7.3 Hz, 3H), 2.43 (q, J = 7.3 Hz, 2H), 9.71 (s, 1H).

\[
\begin{align*}
&\text{O} \\
&\text{H} \\
&\text{6b}
\end{align*}
\]

**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 CD$_3$CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the $^1$H-NMR spectra showed butyraldehyde 6c (yield: 70 %) and acetic acid. $^1$H-NMR (360 MHz, CD$_3$CN): 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).

\[
\begin{align*}
&\text{O} \\
&\text{H} \\
&\text{6c}
\end{align*}
\]

**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 CD$_3$CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the $^1$H-NMR spectra showed butyraldehyde 6c as the major product among another minor product.
Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyl oxy)-pentyl ester 4d
In a quartz NMR tube, a solution of 4d (11.6 mg, 0.034 mmol) in CD$_3$CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the $^1$H-NMR spectra showed pentanal 6d (yield: 74 %) and acetic acid. $^1$H-NMR (360 MHz, CD$_3$CN): 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).

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyl oxy)-hexyl ester 4e
In a quartz NMR tube, a solution of 4e (15.4 mg, 0.043 mmol) in CD$_3$CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the $^1$H-NMR spectra showed hexanal 6e (yield: 57 %) and acetic acid. $^1$H-NMR (360 MHz, CD$_3$CN): 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).

Photolysis of acetic acid 1-(4,5-dimethoxy-2-nitrobenzyl oxy)-dodecyl ester 4f
In a quartz NMR tube, a solution of 4f (11.8 mg, 0.027 mmol) in CD$_3$CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the $^1$H-NMR spectra showed dodecanal 6f (yield: 69 %) and acetic acid. $^1$H-NMR (360 MHz, CD$_3$CN): 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).
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 µmol) in CD$_3$CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the $^1$H-NMR spectra showed phenylacetaldehyde 6g (yield: 62 %) and acetic acid. $^1$H-NMR (360 MHz, CD$_3$CN): $\delta$(ppm) 3.72 (d, $J = 1.4$ Hz, 2H), 7.22-7.39 (5H), 9.71 (t, $J = 1.8$ Hz, 1H).

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 µmol) in CD$_3$CN (0.75 mL) was irradiated at 350 nm for 4 h. The crude residue was not purified, but the $^1$H-NMR spectra showed methional 6h (yield: 53 %) and acetic acid. $^1$H-NMR (360 MHz, CD$_3$CN): $\delta$(ppm) 2.07 (s, 3H), 2.68-2.77 (4H), 9.68 (s, 1H).

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 CD$_3$CN (0.75 mL) was irradiated at 350 nm for 3 h. The crude residue was not purified, but the $^1$H-NMR spectra showed (R)-citronellal 6i (yield: 73 %) and acetic acid. $^1$H-NMR (360 MHz, CD$_3$CN): $\delta$(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).
