Supporting Information

Synthesis of 1-Palmitoyl-2-((E) 9- and 10-Nitrooleoyl)-sn-Glycero-3-Phosphatidylcholines

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$^1$H and $^{13}$C NMR spectra
General Remarks: Reaction solvents were dried by standard procedures prior to use when necessary. All reactions including moisture- or air-sensitive reagents were carried out under an argon atmosphere. $^1$H NMR, $^{13}$C NMR and 2D Spectra (COSY, HSQC, HMBD) spectra were recorded at room temperature with a Bruker ARX400, AV400 or AV600 spectrometer in CDCl$_3$ using the signal of residual CHCl$_3$ as internal standard, CD$_2$Cl$_2$, CD$_3$OD, CD$_3$CN, always as indicated. IR spectra were recorded with a Jasco FT/IR-400 plus spectrometer. The high-resolution mass spectra (HRMS) were recorded with a Waters Q ToF Ultima 3 Micromasses spectrometer. Optical rotation was recorded with Perkin-Elmer’s P 241 polarimeter. Column chromatography was performed on MN silica gel 60M from Macherey-Nagel (grain size: 0.040-0.063 mm). Progress of reaction was monitored by thin layer chromatography (TLC) performed on aluminum sheets pre-coated with silica gel 60 F254 silica gel from Merck. Et$_2$O, EA = ethyl acetate, PE = petroleum ether, For HPLC, analytical (4x250 mm) and preparative columns (30 [Gemini] or 32x250 mm and 32x125mm [Nucleosil]) were used. HPLC: RT = peak retention time, k = retention factor = ($RT − t_0$)/$t_0$.

1. Synthesis of 9-nitrooleic acid 1

1.1 8-Oxooctanoic acid methyl ester I:[1]

\[
\begin{align*}
\text{Cyclooctene (26.448 g, 33.14 mL, 240.0 mmol), methanol (144 mL) and sodium carbonate (5.56 g, 61.9 mmol) in CH}_2\text{Cl}_2 (720 mL) were cooled to -78 °C. Then, a stream of ozone/O}_2 was bubbled through the mixture until the pale blue colour of unreacted ozone remained. Excess of ozone was removed by bubbling a stream of argon through the mixture. After raising the temperature to 23 °C, the solids were filtered off and the remaining solution was diluted with toluene (240 mL → viscous liquid) and the volume of the mixture was reduced to 160 mL via vacuum distillation. The resulting viscous solution was diluted with CH$_2$Cl$_2$ (640 mL), cooled to 0 °C and trimethylamine (36.0 g, 49.45 mL, 355.77 mmol) and acetic anhydride (68.26 g, 62.8 mL, 668.63 mmol) were added with stirring. The reaction mixture was stirred for 30 min at 0 °C and at 23 °C overnight. Work-up started by washing the mixture with aq. HCl (2x 480 mL, 0.1 M). After further washing with 10 % aq. NaOH (2x 480 mL) and water (480 mL), the organic layer was dried (MgSO$_4$). The solvent was removed in vacuum and methyl 8-oxo octanoate I (42.66 g, nearly quantitative, residual solvent) was obtained as a pale yellow oil pure enough for the proceeding Henry reaction.
\end{align*}
\]

Data of I: IR ($\tilde{\nu}$ (cm$^{-1}$)): 2937 (m), 2857 (m), 2722 (w), 1736 (vs, br), 1437(m), 1364 (w), 1200 (m), 1173 (m), 1102 (w), 1017 (w). $^1$H-NMR (400 MHz, CDCl$_3$, COSY) δ[ppm]: 9.77 (t, $^3$J$_{HH}$ = 2.2 Hz, 1H, H-8), 3.67 (s, 3H, H-9), 2.44 (dt, $^3$J$_{HH}$ = 2.2 Hz, $^3$J$_{HH}$ = 7.3 Hz, 2H, H-7), 2.32 (t, $^3$J$_{HH}$ = 7.5 Hz, 2 H, H-2), 1.69 – 1.59 (m, 4H, H-3, H-6), 1.39 – 1.32 (m, 4H, H-4, H-5).

For synthesis and further data see ref. [1]

1.2 Methyl 9-nitrononanoate 6:

\[
\begin{align*}
\text{HCO}_2\text{H} \xrightarrow{\text{MeOH-NO}_2} \text{HCO}_2\text{HNO}_2 \xrightarrow{\text{MeOH-NO}_2} \text{O}_2\text{HCO} Me \xrightarrow{\text{MeOH-NO}_2} \text{O}_2\text{HCO} Me
\end{align*}
\]
To a solution of methyl 8-oxo octanoate \( \text{I} \) (41.33 g, 240 mmol) and nitromethane (29.3 g, 25.7 mL, 480 mmol, 2 eq.) in THF/t-BuOH (165 mL, 1:1) at 0 °C was added KO\textsubscript{t}Bu (powder, 1.3546 g, 12.07 mmol). A yellow colour occurred. The mixture was stirred at 23 °C overnight. After dilution with Et\(_2\)O (800 mL) and water (800 mL), the aqueous layer was separated and the organic phase was washed with sat. aq. NaHCO\(_3\) (800 mL) and brine (800 mL). The combined aqueous layers were back-extracted with Et\(_2\)O (2x 1.6 L) and the combined organic phases were dried (MgSO\(_4\)). After removal of the solvents, the crude methyl 8-hydroxy-9-nitro nonanoate \( \text{II} \) remained as yellow oil solidifying upon storing in a fridge. Yield 49.04 g (210.14 mmol, 87.6 %). Selected data of \( \text{II} \):

\[\text{IR}(\text{wavenumber} \text{ (cm}^{-1}): 3491 \text{ (m, br, OH)}, 2937 \text{ (m)}, 2860 \text{ (m)}, 1733 \text{ (s)}, 1552 \text{ (vs)}, 1438 \text{ (m)}, 1380 \text{ (m)}, 1201 \text{ (m)}, 1173 \text{ (m)}, 1108 \text{ (m)}, 885 \text{ (w)}\].

\[\text{\(\text{\text{H}}\text{-NMR}(400 \text{ MHz, CDCl}_3, \text{COSY})\delta[ppm]\}: 4.43 \text{ (dd, } 3J_{HH} = 3.2 \text{ Hz, } 2J_{HH} = 12.7 \text{ Hz, 1H, H-9)}, 4.37 \text{ (dd, } 3J_{HH} = 8.1 \text{ Hz, } 2J_{HH} = 12.7 \text{ Hz, 1H, H-9a)}, 4.34 – 4.27 \text{ (m, 1H, H-8)}, 3.66 \text{ (s, 3H, H-10)}, 2.89 \text{ (s, br, 1H, OH)}, 2.30 \text{ (t, } 3J_{HH} = 7.5 \text{ Hz, 2H, H-2)}, 1.67 – 1.56 \text{ (m, 2H, H-3 from H-3 – H-7)}, 1.55 – 1.45 \text{ (m, 2H, H-7 from H-3 – H-7)}, 1.39 – 1.28 \text{ (m, 6H, H-4-H-6 from H-3 – H-7)}\].

\[\text{MS}\left[\text{ESI}\right]\]: [M+Na]\(^+\) calcd. for C\(_{10}\)H\(_{19}\)NO\(_5\): 256.1153, found: 256.0500.

For synthesis and further data see [1a]

Methyl 8-hydroxy-9-nitro nonanoate \( \text{II} \) (49.04 g, 210.23 mmol), DMAP (1.284 g, 10.51 mmol) and acetic anhydride (23.61 g, 21.72 mL, 231.26 mmol) in dry Et\(_2\)O (540 mL) were stirred at 23 °C for 4 h. Then, the solvent was removed in vacuum and the residue was treated dropwise with a suspension of NaBH\(_4\) (15.907 g, 420.48 mmol) in dry EtOH (430 mL) at 0 °C with stirring (exothermic reaction!). After stirring at 23 °C for 2 h, the reaction mixture was acidified by adding 1 M aq. HCl. The mixture was extracted with Et\(_2\)O (3x 1000 mL) and the combined organic layers were dried (MgSO\(_4\)). The solvent was removed by vacuum distillation affording an oily residue and some solid impurities. After dissolving the organic material in CH\(_2\)Cl\(_2\), filtration of the solids and distillation off the solvent, a pale yellow oil remained. Yield: 45.67 g (nearly quantitative) of methyl 9-nitrononanoate \( \text{6} \) pure enough for the proceeding Henry reaction.

Selected data of \( \text{6} \):

\[\text{IR}(\text{wavenumber} \text{ (cm}^{-1}): 2930 \text{ (m)}, 2858 \text{ (m)}, 1736 \text{ (vs)}, 1551 \text{ (vs)}, 1436 \text{ (m)}, 1380 \text{ (m)}, 1198 \text{ (m)}, 1172 \text{ (m)}, 1107 \text{ (w)}, 1013 \text{ (w)}, 879 \text{ (w)}\].

\[\text{\(\text{\text{H}}\text{-NMR}(400 \text{ MHz, CDCl}_3, \text{COSY})\delta[ppm]\}: 4.39 \text{ (t, } 3J_{HH} = 7.0 \text{ Hz, 2H, H-9)}, 3.69 \text{ (s, 3H, H-10)}, 2.32 \text{ (t, } 3J_{HH} = 7.5 \text{ Hz, 2H, H-2)}, 2.08 – 1.95 \text{ (m, 2H, H-8)}, 1.69 – 1.58 \text{ (m, 2H, H-3)}, 1.44 – 1.27 \text{ (m, 8H, H-4-H-7)}\].

\[\text{MS}\left[\text{ESI-HRMS}\right]\]: calcd. for [M]\(^+\)C\(_{10}\)H\(_{19}\)NO\(_4\): 217.1306, found: 217.1046. [M+H]\(^+\) Calcd. for C\(_{10}\)H\(_{20}\)NO\(_4\): 218.1384, found: 218.1100. [M+Na]\(^+\) Calcd. for C\(_{10}\)H\(_{19}\)NO\(_4\)23Na: 240.1204, found: 240.1300.

For synthesis and further data see [1a]

### 1.3 Methyl 9-nitro-10-hydroxy octadecanoate \( \text{8} \):

Methyl 9-nitrononanoate \( \text{6} \) (9.89 g, 45.52 mmol) and nonanal \( \text{7} \) (6.475 g, 8.24 mL, 45.52 mmol) in t-BuOH/THF (64 mL, 1:1) were treated with KO\textsubscript{t}Bu (powder, 285.5 mg, 2.3 mmol) at 0°C with stirring (orange coloured solution). After stirring for 2 d at 23 °C, a second portion of nonanal (3.236 g, 4.12 mL, 22.76 mmol) and KO\textsubscript{t}Bu (powder, 129.0 mg, 1.15 mmol) were
added and stirring was continued for 1 d. The mixture was diluted with Et₂O (160 mL) and H₂O (160 mL). The organic layer was washed with saturated aq. NaHCO₃ (160 mL) and brine (160 mL). The combined aqueous layers were extracted with Et₂O (2x 320 mL). The combined organic layers were dried (MgSO₄) and the solvent was removed in vacuum affording a yellow oil of crude methyl 9-nitro-10-hydroxyoctadecanoate 8 (20.04 g, excess of nonanal included). Optional: purification via preparative HPLC (nucleosil 50-5, 10 % EtOAc in hexane).

Data of 8 (syn/anti mixture of diastereomers, not completely separated): HPLC: (Nucleosil 50-5, 4x250 mm, 2mL/min, 93 bar): k = 4.5 (10 % EtOAc in Hexane). IR (ν cm⁻¹): 3490 (m, Br, OH), 2927 (s), 2856 (m), 1738 (s), 1573 (s), 1437 (m), 1367 (m), 1200 (m), 91 (w), 744 (m). ¹H-NMR (400 MHz, CDCl₃, COSY) diastereomer 1 [ppm]: 4.46 (ddd, ³JHH = 4.2 Hz, ³JHH = 6.3 Hz, ³JHH = 10.3 Hz, 1H, H-9), 3.88 (ddd, ³JHH = 3.0 Hz, ³JHH = 6.3 Hz, ³JHH = 9.2 Hz, 1H, H-10), 3.68 (s, 3H, H-19), 2.31 (t, ³JHH = 7.5 Hz, 2H, H-2), 2.19 (s, br, 1H, OH), 2.10 – 1.98 (m, 1H), 1.84 – 1.73 (m, 1H), 1.70 – 1.58 (m, 3H), 1.56 – 1.42 (m, 3H), 1.38 – 1.24 (m, 18H), 0.90 (t, ³JHH = 6.9 Hz, 3H, H-18). diastereomer 2 [ppm]: 4.43 (ddd, ³JHH = 3.2 Hz, ³JHH = 4.1 Hz, ³JHH = 10.8 Hz, 1H, H-9), 4.01 (td, ³JHH = 4.1 Hz, ³JHH = 8.3 Hz, 1H, H-10), 3.67 (s, 3H, H-19), 3.96 (s, br, 1H, OH), 2.38 – 2.28 (m, 1H), 2.31 (t, ³JHH = 7.5 Hz, 2H, H-2), 2.17 – 2.04 (m, 1H), 1.85 – 1.74 (m, 1H), 1.66 – 1.42 (m, 4H), 1.39 – 1.32 (m, 19H), 0.89 (t, ³JHH = 7.0 Hz, 3H, H-18). ¹³C-NMR (100 MHz, CDCl₃, HSQC) diastereomer 2 [ppm]: 174.28 (C-1), 92.36 (C-9), 72.36 (C-8), 51.48 (C-19), 33.98, 33.23, 31.80. 29.40, 29.30, 29.18, 29.01, 28.87, 28.83, 27.99, 25.61, 24.78, 22.63, 14.07 (C-18). MS [ESI-HRMS]: [M+Na⁺] calcd. for C₁₉H₂₃NO₃Na: 382.2554, found: 382.2557.

For synthesis and further data see [1]

1.4 Methyl 9-nitro-oleate 9:

Crude methyl 9-nitro-10-hydroxyoctadecanoate 8 (20.04 g, corresponding to pure material: 16.36 g, 45.51 mmol), DMAP (555.9 mg, 4.55 mmol) and acetic anhydride (5.1105 g, 4.7 mL, 50.06 mmol) in dry Et₂O (90 mL) were stirred at 23 °C overnight. Then, the ether was removed by vacuum distillation and the crude acetate 10a was dissolved in CH₂Cl₂ (90 mL). DMAP (6.6711 g, 54.61 mmol) was added at 23 °C with stirring. A red colour occurred. After 2 h, the mixture was diluted with CH₂Cl₂ (2.3 L). The so obtained solution was washed with H₂O (2.3 L). The aqueous phase was extracted with CH₂Cl₂ (2x 2.3 L), the combined organic layers were dried (MgSO₄) and the solvent was removed by vacuum distillation to give a pale brownish oil. Filtration through a short column of silica gel with Et₂O/petroleum ether 1:5 afforded crude methyl 9-nitrooleate 9 (17.62 g) as viscous yellow oil. Purification via preparative HPLC (nucleosil 50-5, 5 % EtOAc in hexanes) afforded pure methyl 9-nitrooleate 9 (3.7178 g, 10.9 mmol, 24 %) and pure methyl 9-nitro-10-acetoxy octadecanoate 10a (0.9766 g, 2.43 mmol, 54. %).

Remark: The reaction sequence Henry reaction, OH group activation and elimination delivered varying yields depending on the scale: Reaction with methyl 9-nitrononanoate 6 (0.88587 g, 3.952 mmol) and nonanal 7 (0.5622 g, 0.7156 mL, 3.952 mmol) following the procedure as described above gave 2.136 g crude 9-nitro-10-hydroxyoctadecanoate 8 (excess of nonanal 7 included). Subsequent acetylation and elimination gave pure methyl 9-nitrooleate 9 (0.73 g, 2.14 mmol, 54.1 %) and pure methyl 9-nitro-10-acetoxy octadecanoate 10a (0.217 g, 0.54 mmol, 13.7 %).

Remark: Elimination starting from methyl 9-nitro-10-hydroxyoctadecanoate 8 (8.2735 g, 23.01 mmol) using trifluoroacetic anhydride (5.317 g, 3.52 mL, 25.31 mmol), DMAP (0.2811 g, 2.0314 mmol - ester formation) and DMAP (3.3737 g, 27.61
mmol – elimination) delivered methyl 9-nitrooleate 9 (1.769 g, mmol, 22.1%), methyl 9-nitro-10-trifluoroacetoxy octadecenoate 10b (2.13 g, mmol, 20.3%) after preparative HPLC purification (nucleosil 50/5, 5% EtOAc in hexane).

Elimination using nitro acetate 10a:
Crude acetate 10a (1.5973 g, 3.978 mmol) and DMAP (0.5832 g, 4.774 mmol) in dry CH₂Cl₂ (10 mL) were stirred at 23 °C for 4 h. A second portion of DMAP (243.5 mg, 1.9935 mmol) was added and stirring was continued for 30 min. Then, the mixture was diluted with CH₂Cl₂ (180 mL). The so obtained solution was washed with H₂O (180 mL), 0.1 Naq. HCl (180 mL) and brine (180 mL). The combined aqueous phases were re-extracted with CH₂Cl₂ (2x 180 mL), the combined organic layers were dried (MgSO₄) and the solvent was removed by vacuum distillation to give a pale oil (1.2699 g). Filtration through a short silica gel column (Et₂O/petroleum ether 1/2) afforded methyl 9-nitrooleate (1.2454 g, mmol). Purification via preparative HPLC (Gemini NX-C18, 5% EtOAc/hexanes) gave methyl 9-nitrooleate 9 (607.23 mg, 1.77 mmol, 44.7%).

Remark: Elimination starting from 9-nitro acetate 10a (2.63 g, 6.55 mmol) using DMAP and DBU delivered mixtures of methyl 9-nitrooleate 9, methyl 9-nitro-(E)-10-octadecenoate 11 (401 mg combined, about 18% yield) and a small amount of methyl 9-oxo-(E)-10-octadecenoate (Nef product) 12 (180 mg, 0.68 mmol, 8.9%).

Remark: Elimination starting from 9-nitro 10-trifluoroacetate 10b (5.0 g, 10.98 mmol) using DMAP delivered mixtures of methyl 9-nitrooleate 9 (5.0 g, and methyl 9-nitro-(E)-10-octadecenoate 11 (1.67 g, 4.89 mmol, 44.5% combined).

Data of methyl 9-nitro 10-acetoxy octadecanoate 10a: R₁ = 0.25 (Et₂O/P: 1:6). HPLC: (Nucleosil 50-5, 4x250 mm, 2mL/min, 127 bar): k = 3.1 (5% EtOAc/hexanes). IR (υ (cm⁻¹)): 2926 (vs), 2856 (s), 1741 (vs), 1701 (vs), 1556 (s), 1436 (m), 1372 (m), 1225 (vs), 1022 (m), 724 (w). ¹H-NMR (400 MHz, CDCl₃, COSY) δ[ppm]: 5.22 (dt, 3JHH = 4.0 Hz, 2JHH = 8.0 Hz, 1H, H-9), 3.61 (s, 3H, H-19), 2.24 (t, 3JHH = 7.5 Hz, 2H, H-2), 1.99 (s, 3H, H-21), 1.97 – 1.82 (m, 1H), 1.67 – 1.43 (m, 6H), 1.35 – 1.12 (m, 19H), 0.82 (t, 3JHH = 6.8 Hz, 3H, H-18). ¹³C-NMR (100 MHz, CDCl₃, HSQC) δ[ppm]: 174.12 (C-1), 156.48 (q, 3JCF = 43.3 Hz, C-20), 114.3 (q, 3JCF = 286.0 Hz, C-21), 90.05 (C-9), 77.16 (C-10), 51.63 (C-19), 33.97, 31.70, 30.28, 29.75, 20.14, 29.06, 29.02, 28.77, 28.73, 28.54, 25.24, 24.71, 24.21, 22.58, 14.02 (C-18). MS [ESI-HRMS]: [M+Na]⁺ calcd. for C₁₉H₁₉F₃NO₆²Na: 478.2392, found: 478.2392.

Data of methyl 9-nitro 10-trifluoroacetoxy octadecanoate 10b: R₁ = 0.6 – 0.7 (Et₂O). HPLC: (Nucleosil 50-5, 4x250 mm, 2mL/min, 155 bar): k = 3.0 (5% EtOAc/hexanes). IR (υ (cm⁻¹)): 2930 (s), 2858 (m), 1741 (vs), 1701 (vs), 1557 (s), 1436 (m), 1378 (w), 1224 (s), 1155 (vs), 913 (w), 742 (w). ¹H-NMR (400 MHz, CDCl₃, COSY) δ[ppm]: 5.48 (dt, 3JHH = 4.0 Hz, 2JHH = 8.0 Hz, 1H, H-10), 4.70 (ddd, 3JHH = 3.6 Hz, 2JHH = 7.9 Hz, 3JHH = 10.5 Hz, 1H, H-9), 3.69 (s, 3H, H-19), 2.33 (t, 3JHH = 7.5 Hz, 2H, H-2), 2.06 – 1.90 (m, 1H), 1.84 – 1.67 (m, 3H), 1.67 – 1.57 (m, 3H), 1.43 – 1.22 (m, 19H), 0.9 (t, 3JHH = 7.0 Hz, 3H, H-18). ¹³C-NMR (100 MHz, CDCl₃, HSQC) δ[ppm]: 174.69 (C-1), 156.48 (q, 3JCF = 43.3 Hz, C-20), 114.3 (q, 3JCF = 286.0 Hz, C-21), 90.05 (C-9), 77.16 (C-10), 51.63 (C-19), 33.97, 31.70, 30.28, 29.75, 20.14, 29.06, 29.02, 28.77, 28.73, 28.54, 25.24, 24.71, 24.21, 22.58, 14.02 (C-18). MS [ESI-HRMS]: [M+Na]⁺ calcd. for C₁₉H₁₉F₃NO₆²Na: 478.2392, found: 478.2392.

For an analogous synthesis see ref. [1a]
Data of methyl 9-nitrooleate 9: Rf = 0.47 (Et2O/PE 1:6). **HPLC**: (Nucleosil 50-5, 4x250 mm, 2mL/min, 127 bar): k = 0.86 (5 % EtOAc/hexanes). **IR** (d, cm⁻¹): 2926 (s), 2856 (m), 1739 (m), 1465 (s), 1336 (s), 1172 (m), 726 (w). 1H-NMR (400 MHz, CDCl3, COSY) δ[ppm]: 7.03 (t, JHH = 7.9 Hz, 1H, H-10), 3.61 (s, 3H, H-19), 2.55 – 2.48 (m, 2H, H-8), 2.28 – 2.21 (m, 2H, H-2), 2.16 (q, br, H-11), 1.63 – 1.51 (m, 2H, 2H, H-1), 1.49 – 1.37 (m, 4H, 4H, H-1), 1.33 – 1.15 (m, 16H, 16H, H-1), 0.83 (t, br, JHH = 7.0 Hz, H-18).

For synthesis and further data see ref. [1a, 2]

For synthesis and further data see ref. [3]

Data of methyl 9-oxo-(E)-10-octadecenoate 11: Rf = 0.35 (Et2O/PE 1:1). **HPLC** (Gemini NX 110-5 C18, 4x250 mm, 2mL/min, 191 bar): k = 1.6 (90 % MeCN/H2O/0.1 % TFA).

1H-NMR (400 MHz, CDCl3, COSY) δ[ppm]: 6.85 (d, JHH = 15.8 Hz, JHH = 6.9 Hz, 1H, H-11), 6.10 (dt, JHH = 15.8 Hz, JHH = 1.6 Hz, 1H, H-10), 3.69 (s, 3H, H-19), 2.54 (t, JHH = 7.5 Hz, 1H, H-8), 2.32 (t, JHH = 7.5 Hz, 2H, H-2), 2.22 (qd, JHH = 6.9 Hz, JHH = 1.6 Hz, 2H, H-12), 1.71 – 1.54 (m, 4H, 4H, H-4), 1.50 – 1.44 (m, 2H, 2H, H-1), 1.40 – 1.13 (m, 14H, 14H, H-14), 0.90 (t, JHH = 7.5 Hz, 3H, 3H, H-18).

For Syntheses and data see ref. [4]:

**1.5 9-Nitro-oleic acid 4:**

Methyl 9-nitrooleate 9 (3.2 g, 9.37 mmol) and 6 M aq. HCl (89 mL) were heated to reflux for 2 d with stirring. After cooling to 23 °C, the mixture was extracted with EtOAc (3x 217 mL). The combined organic layers were washed with H2O (290 mL) and brine (290 mL) and dried (MgSO4). The solvent was removed by vacuum distillation to give a dark brown oil of the crude acid 4 (3.2443 g). After filtration through a short silica gel column (EtOAc), purification by preparative HPLC (Gemini NX-C18, 90% MeCN/H2O, 0.1 % TFA) delivered 9-nitrooleic acid 4 (1.6822 g, 5.14 mmol, 54.8 %) and additional product 4 with some impurities (494.4 mg).

Remark: The standard yield of pure 9-nitrooleic acid 4 varied between 40 and 55 %. However, one run starting with methyl 9-nitrooleate 9 (5.94 g, 17.39 mmol) gave a maximum yield of 9 nitrooleic acid 4 (4.3901 g, 13.41 mmol, 77.1%).

Data of 4: Rf = 0.50 (Et2O/PE 1:1). **HPLC** (Gemini NX 110-5 C18, 4x250 mm, 2mL/min, 127 bar): k = 1.6 (90 % MeCN/H2O/0.1 % TFA). 1H-NMR (400 MHz, CDCl3, COSY) δ[ppm]: 11.47 (s, br, 1H, OH), 7.03 (t, JHH = 7.9 Hz, 1H, H-10), 2.55 – 2.48 (m, 2H, H-8), 2.30 (t, JHH = 7.5 Hz, 2H, H-2), 2.17 (q, JHH = 7.6 Hz, 2H, H-11), 1.63 – 1.52 (m, 2H, 2H, H-1), 1.49 – 1.36 (m, 4H, 4H, H-4), 1.34 – 1.15 (m, 16H, 16H, H-16), 0.83 (t, br, JHH = 6.8 Hz, 3H, 3H, H-18).

For synthesis and further data see ref. [4, 1a, 2, 3]
2. Synthesis of 10-nitrooleic acid 5

2.1 Methyl 9-oxononanoate 13:

Acelaoyl chloride: Azelaic acid (40 g, 212.5 mmol) and thionyl chloride SOCl₂ (101.13 g, 61.67 mL, 850.1 mmol) were heated to reflux (80 °) for 36 h. Then, excess of SOCl₂ was distilled-off at 760 mm and the residue was purified by vacuum distillation to give acelaoyl chloride (47.8 g, 212.5 mmol, nearly 100 %) as a clear liquid, b.p. 137 °C (7 mm). Selected data: 

\[ \text{δ (ppm): 2.91 (t, } J_{HH} = 7.2 \text{ Hz, 4H, H-2, H-8), 1.79 – 1.63 (m, 4H, H-3, H-7), 1.48 – 1.25 (m, 6H, H-4, H-5, H-6).} \]

For syntheses and some data see ref. [5]

Methyl 9-chloro-9-oxononanoate III: Acelaoyl chloride (64.42 g, 286.2 mmol) was treated dropwise with dry MeOH (9.169 g, 11.61 mL, 286.2 mmol) over a period of 105 min. The mixture was stirred at 23 °C overnight. Then, isolation of the product succeeded via vacuum distillation. Yield: Methyl 9-chloro-9-oxononanoate III (37.0 g, 167.8 mmol, 58.6 %), pale yellow liquid. B.p. 174 – 176 °C (25 – 30 mm), 120 – 122 °C (5 mm). Selected data: 

\[ \text{δ (ppm): 3.60 (s, 3H, H-10), 2.83 (td, } J_{HH} = 7.3 \text{ Hz, } J_{HH} = 3.2 \text{ Hz 2H, H-8), 2.24 (td, } J_{HH} = 7.5 \text{ Hz, } J_{HH} = 2.6 \text{ Hz 2H, H-2), 1.71 – 1.59 (m, 2H, H-7), 1.59 – 1.49 (m, 2H, H-3), 1.35 – 1.20 (m, 6H, H-4, H-5, H-6).} \]

For syntheses and further data see ref.[6]

Methyl 9-oxononanoate 13: Rosenmund reduction: Methyl 9-chloro-9-oxononanoate III (10.0 g, 45.3 mmol), 2,6-lutidine (4.856 g, 5.26 mL, 45.3 mmol) and 10% Pd/C (0.675 g, 0.634 mmol) in dry THF (225 mL) were stirred under a H₂ atmosphere (ambient pressure) at 23 °C for 48 h. After removing the THF by vacuum distillation, the residue was dissolved in dry Et₂O (45 mL) and dry pentane (90 mL). The mixture was filtered through Celite (careful washing with Et₂O/pentane 1/2, 2x 23 mL) and the solvents were removed in vacuum. Then, the crude aldehyde was dissolved in a solution of NaHSO₃ (18.72 g) in H₂O (126 mL) and EtOH (84 mL) at about 40 °C with stirring. After stirring overnight at 23 °C, the solution was diluted with H₂O and most of the impurities were removed by extraction with CH₂Cl₂. Then, the aqueous layer was treated with Na₂CO₃ (~19 g) until a basic pH was reached. After stirring at 23 °C for 4 h, the aqueous layer was extracted with CH₂Cl₂. The combined organic phases were washed with brine and dried (MgSO₄), the solvent was distilled-off in vacuum to deliver methyl 9-oxononanoate 13 (3.478 g, 18.67 mmol, 41.2 %) as a clear liquid. Selected data: Rf = 0.23 (Et₂O/PE 1:6) 

\[ \text{δ (ppm): 9.77 (t, } J_{HH} = 1.8 \text{ Hz, 1H, H-9), 3.68 (s, 3H, H-10), 2.43 (td, } J_{HH} = 7.3 \text{ Hz, } J_{HH} = 1.8 \text{ Hz 2H, H-8), 2.31 (t, } J_{HH} = 7.5 \text{ Hz, 2H, H-2), 1.73 – 1.54 (m, 4H, H-3, H-7), 1.41 – 1.26 (m, 6H, H-4, H-5, H-6).} \]
For syntheses and data see ref. [7, 8]

2.2 1-Nitrononane 14:

1-Nitro-2-nonanol IV: To a solution of octanal (5.04 g, 6.14 mL, 39.32 mmol) and nitromethane (4.8 g, 4.21 mL, 78.64 mmol) in THF/t-BuOH (20 mL, 1:1) at 0 °C was added KOTBu (powder, 0.22 g, 2.0 mmol). The mixture was stirred at 23 °C overnight. After dilution with Et₂O (200 mL) and water (200 mL), the aqueous layer was separated and the organic phase was washed with sat. aq. NaHCO₃ (200 mL) and brine (200 mL). The combined aqueous layers were back-extracted with Et₂O (2x 200 mL) and the combined organic phases were dried (MgSO₄). After removal of the solvents, the crude 1-nitro-2-nonanol IV remained as pale yellow oil. Yield 7.46 g (100 %). Selected data of IV: ¹H-NMR (400 MHz, CDCl₃, COSY) δ[ppm]: 4.48 – 4.37 (m, 2H, H-1), 4.37 – 4.29 (m, 1H, H-2), 2.43, (s, br, 1H, OH), 1.62 – 1.44 (m, 3H, of H-3 – H-8), 1.43 – 1.21 (m, 9H, of H-3 – H-8), 0.90 (tr, br, ³JHH = 7.4 Hz, 3H, H-9).

For synthesis and further data see ref.[1a, 9]

1-Nitrononane 14: 1-Nitro-2-nonanol IV (14.88 g, 78.62 mmol), DMAP (0.48 g, 3.92 mmol) and acetic anhydride (10.04 g, 9.24 mL, 98.34 mmol) in dry Et₂O (160 mL) were stirred at 23 °C for 4 h. Then, the solvent was removed in vacuum and the residue was treated dropwise with a suspension of NaBH₄ (5.96 g, 157.54 mmol) in dry EtOH (160 mL) at 0 °C with stirring (exothermic reaction!). After stirring at 23 °C for 2 h, the reaction mixture was acidified by adding 1 M aq. HCl. The mixture was extracted with Et₂O (3x 400 mL) and the combined organic layers were dried (MgSO₄). The solvent was removed by vacuum distillation affording an oily residue and some solid impurities. Dissolving the organic material in Et₂O, filtration of the solids and distillation off the solvent, a pale yellow liquid remained. Yield: 13.06 g (75.38 mmol, 95.9 %) of 1-nitrononane 14 pure enough for the proceeding Henry reaction.

Selected data of nitrononane: Rₓ = 0.73 (Et₂O/PE 1:6). ¹H-NMR (400 MHz, CDCl₃, COSY) δ[ppm]: 4.40 (t, ³JHH = 7.1 Hz, 2H, H-1), 2.03 (p, ³JHH = 7.1 Hz, 2H, H-2), 147 – 1.19 (m, 12H, H-3 – H-8), 0.90 (t, ³JHH = 7.1 Hz, 3H, H-9).

For syntheses and data see [1a, 2, 9a]

2.3 Methyl 9-hydroxy-10-nitro octadecanoate 15:

1-Nitrononane (3.349 g, 19.32 mmol) and methyl 9-oxononanoate 14 (3.6 g, 19.32 mmol) in tBuOH/THF (20 mL, 1:1) were treated with KOTBu (powder, 108.4 mg, 0.9664 mmol) at 0°C with stirring (yellow coloured solution). After stirring for 7 d at 23 °C, the mixture was diluted with Et₂O (120 mL) and H₂O (120 mL). The organic layer was washed with saturated aq.
NaHCO₃ (120 mL) and brine (120 mL). The combined aqueous phases were extracted with Et₂O (2x 240 mL). The combined organic layers were dried (MgSO₄) and the solvent was removed in vacuum affording a yellow oil of crude methyl 9-hydroxy-10-nitro-octadecanoate 15 (9.737 g) including remaining starting materials).

Data of 15 (syn/anti mixture of diastereomers, not separated): Rₛ = 0.32 (Et₂O/PE 1:6). ¹H-NMR (400 MHz, CDCl₃, COSY) δ[ppm]: 4.50 – 4.41 (m, 1H, H-10), 404 – 3.98 and 3.91 – 3.83 (2x m, overall 1H, H-9), 3.68 (s, 3H, H-19), 2.31 (2x t, 3JHH = 7.5 Hz, 2H, H-2), 2.17 (s, br, 1H, OH), 2.15 – 1.98 (m, 2H), 1.85 – 1.74 (m, 1H), 1.68 – 1.58 (m, 3H), 1.56 – 1.40 (m, 3H), 1.40 – 1.22 (m, 17H), 0.89 (t, 3JHH = 6.9 Hz, 3H, H-18.

For synthesis and data see ref. [1a, 10]

2.4 Methyl 10-nitro-oleate 16:

Crude methyl 9-hydroxy-10-nitro-octadecanoate 15 (6.737 g, corresponding to pure material: 6.945 g, 19.32 mmol), DMAP (236.1 mg, 1.932 mmol) and acetic anhydride (2.1706 g, 2.0 mL, 21.26 mmol) in dry Et₂O (38 mL) were stirred at 23 °C overnight. Then, the ether was removed by vacuum distillation and the crude acetate 17 was dissolved in CH₂Cl₂ (38 mL). DMAP (2.8334 g, 23.19 mmol) was added at 23 °C with stirring. After 4 h, the mixture was diluted with CH₂Cl₂ (960 mL). The so obtained solution was washed with H₂O (960 mL), 0.1 N aq. HCl (960 mL) and brine (960 mL). The aqueous phases was extracted with CH₂Cl₂ (2x 960 mL), the combined organic layers were dried (MgSO₄) and the solvent was removed by vacuum distillation to give a pale brownish oil. Filtration through a short column of silica gel with Et₂O/petroleum ether 1:3 afforded crude methyl 10-nitrooleate 16 (8.6 g) as viscous yellow oil. Purification via preparative HPLC (nucleosil 50-5, 10 % EtOAc in hexanes) afforded pure methyl 10-nitrooleate 16 (2.0069 g, 5.877 mmol, 30.4 %) and pure methyl 9-acetoxy-10-nitro-octadecanoate 17 (0.941 g, 2.34 mmol, 12.1 %). Remark: Elimination starting from 10-nitro acetate 17 (0.49 g, 1.22 mmol) using DMAP (0.2 g, 1.64 mmol) in CH₂Cl₂ (3 mL) delivered a mixture of reactant acetate 17 and product nitroalkene 16 after a 4 h of stirring at 23 °C. Dissolving the crude mixture and DMAP (0.2 g, 1.64 mmol) in CH₂Cl₂ and stirring at 23 °C overnight delivered mixtures of methyl 10-nitrooleate 16 (142 mg, 0.416 mmol, 34.1 %, nearly 1:1 mixture with 18), methyl 10-nitro (E)-8-octadecenoate 18 (41 mg, 0. 12 mmol, 10 % yield) and a small amount of methyl 10-oxo-(E)-8-octadecenoate (Nef product) 19 (mixture with impurities).

Data of 17 (syn/anti mixture of diastereomers, not separated): Rₛ = 0.31 (Et₂O/PE 1:6). HPLC (Nucleosil 50-5, 4x250 mm, 2mL/min, 118 bar): k = 1.84 (10 % EtOAc in hexane). ¹H-NMR (400 MHz, CDCl₃, COSY) δ[ppm]: 5.29 (dt, 3JHH = 7.8 Hz, 1H, H-9), 4.60 (ddddd, 3JHH = 10.9 Hz, 3JHH = 7.5 Hz, 3JHH = 3.6 Hz, 1H, H-10), 3.68 (s, 3H, H-19), 2.31 (t, 3JHH = 7.5 Hz, 2H, H-2) 2.06 (s, 3H, H-21), 2.03 – 1.92 (m, 1H), 1.73 – 1.51 (m, 5H), 1.40 – 1.22 (m, 20H), 0.89 (t, 3JHH = 7.1 Hz, 3H, H-18). MS [ESI]: calcd. for [C₂₁H₃₃NO₅²⁺Na]⁺: 424,53, found: 424.34.

For syntheses see ref. [1a, 10]
Data of 16: R_f = 0.45 (Et_2O/PE 1:6). **HPLC** (Nucleosil 50-5, 4x250 mm, 2mL/min, 118 bar): k = 0.44 (10 % EtOAc/hexane).

**1H-NMR** (400 MHz, CDCl_3, COSY) δ [ppm]: 7.08 (t, _J_HH_ = 7.9 Hz, H-9), 3.68 (s, 3H, H-19), 2.58 (t, _J_HH_ = 7.5 Hz, 2H, H-11), 2.32 (t, _J_HH_ = 7.5 Hz, 2H, H-2), 2.23 (q, _J_HH_ = 7.6 Hz, 2H, H-8), 1.70 – 1.60 (m, 2H, H-XX), 1.55 – 1.45 (m, 4H, H-), 1.40 – 1.15 (m, 16H, H-), 0.90 (t, _J_HH_ = 7.0 Hz, 3H, H-18).

**13C-NMR** (100 MHz, CDCl_3, HSQC) δ [ppm]: 174.18 (C-1), 151.94 (C-10), 136.22 (C-9), 51.48 (C-19), 34.01, 31.81, 29.41, 29.27, 29.15, 29.00, 28.96, 28.47, 27.97, 27.91, 26.35, 24.84, 22.64, 14.09 (C-18).

**MS [ESI-HRMS]:** calcd. for C_{19}H_{36}NO_{4}: 342.2644, found: 342.2654.

For synthesis and data see ref. [1]

Data of methyl 10-nitro(1E)-8-octadecenoate 18: R_f = 0.45 (Et_2O/PE 1:6). **HPLC** (Nucleosil 50-5, 4x250 mm, 2mL/min, 150 bar): k = 0.78 (8 % EtOAc in Hexanes). **1H-NMR** (400 MHz, CDCl_3, COSY) δ [ppm]: 5.84 (dt, _J_HH_ = 15.3 Hz, _J_HH_ = 6.7 Hz, 1H, H-8), 5.61 (ddt, _J_HH_ = 15.3 Hz, _J_HH_ = 8.8 Hz, _J_HH_ = 8.8 Hz, 1H, H-9), 4.85 (dt, _J_HH_ = 8.8 Hz, _J_HH_ = 7.2 Hz, 1H, H-10), 3.68 (s, 3H, H-19), 2.31 (t, _J_HH_ = 7.5 Hz, 2H, H-2), 2.08 (q, br, _J_HH_ = 6.9 Hz, 2H, H-7), 1.84 – 1.74 (m, 1H, H-), 1.68 – 1.57 (m, 2H, H-), 1.53 – 1.44 (m, 1H), 1.45 – 1.21 (m, 18H), 0.89 (t, _J_HH_ = 6.8 Hz, 3H, H-18).

**13C-NMR** (100 MHz, CDCl_3, HSQC) δ [ppm]: 174.19 (C-1), 138.71 (C-8), 124.67 (C-9), 90.12 (C-10), 51.46 (C-19), 34.09, 34.00, 32.03, 31.76, 29.23, 29.13, 28.87, 28.85, 28.66, 28.34, 25.55, 24.80, 22.62, 14.07 (C-18).

**2.5 10-Nitrooleic acid 5:**

Methyl 10-nitrooleate 16 (0.8224 g, 2.4082 mmol) and 6 M aq. HCl (26 mL) were heated to reflux for 3 d with stirring. After cooling to 23 °C, the mixture was extracted with EtOAc (3× 60 mL). The combined organic layers were washed with H_2O (80 mL) and brine (80 mL) and dried (MgSO_4). The solvent was removed by vacuum distillation to give a dark brown oil of the crude acid 5 (0.928 g). After filtration through a short silica gel column (EtOAc), purification by preparative HPLC (Gemini NX-C18, 75% MeCN/H_2O, 0.1 % TFA) delivered 10-nitrooleic acid 5 (0.4586 g, 1.40 mmol, 58.2 %) as a yellow oil.

**Data of 5: R_f = 0.29 (Et_2O/PE 1:3).** **HPLC** (Gemini NX 110-5 C18, 4x250 mm, 2mL/min, 116 bar): k = 1.57 (80 % MeCN/H_2O/0.1 % TFA). **1H-NMR** (400 MHz, CDCl_3, COSY) δ [ppm]: 10.35 (s, br, 1H, OH), 7.09 (t, _J_HH_ = 7.9 Hz, 1H, H-9), 2.58 (t, _J_HH_ = 7.6 Hz, H-10), 2.38 (t, _J_HH_ = 7.5 Hz, 2H, H-2), 2.23 (q, br, _J_HH_ = 7.6 Hz, 2H, H-8), 1.71 – 1.61 (m, 2H), 1.55 – 1.45 (m, 4H), 1.41 – 1.24 (m, 16H), 0.90 (t, _J_HH_ = 6.6 Hz, 3H, H-18).

**13C-NMR** (100 MHz, CDCl_3, HSQC) δ [ppm]: 179.61 (C-1), 151.96 (C-10), 136.20 (C-9), 33.89, 31.81, 29.24, 29.23, 29.17, 29.13, 28.98, 28.87, 28.46, 27.97, 27.91, 26.36, 24.56, 22.64, 14.09 (C-18).

**MS [ESI], [M+H]^+:** calcd. for C_{18}H_{34}NO_4: 328.2487., found: 328.2166.

For syntheses and data see ref. [1a, 2, 10]
3. Syntheses of activated nitrooleic acids – syntheses and data

3.1 9-Nitrooleoyl chloride 20a:
Microwave induction: In a microwave tube, 9-nitrooleic acid 4 (100 mg, 0.3054 mmol) in dry CH₂Cl₂ (2 mL) was mixed with dry pyridine (24.2 mg, 25 µl, 0.354 mmol) and cyanuric chloride (56.3 mg, 0.3054 mmol). The mixture was irradiated in a microwave oven (150 W), at 50 °C for 15 min with stirring. After cooling to 23 °C, the white precipitate was filtered-off, the solvent was distilled off in vacuum and the residue was dissolved in dry toluene (11 mL). Cooling to -20 °C for about 20 min induced precipitation of further pyridinium salts, which were removed by filtration. Finally, the solvent was removed in vacuum and 9-nitrooleoyl chloride 20a (104.3 mg, 305.5 mmol, 98.9 %) was isolated as a pale light brown oil pure enough for further use.

Adapted procedure according ref. [11]
Extractive isolation: To a solution of 9-nitrooleic acid 4 (100 mg, 0.3054 mmol) in dry CH₂Cl₂ (10 mL) was added DMAP (37.3 mg, 0.3054 mmol) at 23 °C and the mixture was stirred for 15 min (solution 1). Cyanuric chloride (56.3 mg, 0.3054 mmol) in dry CH₂Cl₂ (10 mL) was treated dropwise with solution 1 at 23 °C with stirring. After a reaction time of about 60 h, the solvent was removed in vacuum and the residue was dissolved in dry acetonitrile. The solution was extracted with heptane and the solvent of the heptane layers was distilled-off in vacuum. 9-Nitrooleoyl chloride 20a (105.6 mg, 305 mmol, nearly 100 %) was isolated as a clear oil pure enough for further use.

Data for 9-nitrooleoyl chloride 20a: IR (ν (cm⁻¹)): 2926 (s), 2855 (m), 1798 (s), 1666 (w), 1511 (s), 1462 (m), 1402 (w), 1334 (s), 1265 (m), 1034 (w), 952 (w), 847 (m), 723 (s). ¹H-NMR (400 MHz, CDCl₃, COSY) δ[ppm]: 7.11 (t, 3JHH = 7.9 Hz, 1H, H-10), 2.91 (t, 3JHH = 7.3 Hz, 2H, H-2), 2.59 (t, br, 3JHH = 8.1 Hz, 2H, H-8), 2.23 (q, 3JHH = 7.6 Hz, 2H, H-11), 1.78 – 1.68 (m, 2H), 1.56 – 1.45 (m, 4H), 1.42 – 1.24 (M, 16H), 0.91 (t, 3JHH = 7.5 Hz, 3H, H-18). ¹³C-NMR (100 MHz, CDCl₃, HSQC) δ[ppm]: 173.93 (C-1), 151.79 (C-9), 136.75 (C-10), 47.16 (C-2), 31.94, 29.48, 29.44, 29.29, 29.06, 28.87, 28.65, 28.40, 28.16, 27.92, 26.41, 25.10, 22.78, 14.23 (C-18). MS [ESI]: calcd. for C₁₈H₃₂ClNO₃H⁺: 346.22, found: 346.22, 346.26.

3.2 10-Nitrooleoyl chloride 21a: Reaction with 10-nitrooleic acid 5 (100 mg, 0.3054 mmol) following the extractive isolation method as described for 9-nitrooleoyl chloride 20a. Yield: 10-Nitrooleoyl chloride 21a (105.6 mg, 0.305 mmol, nearly 100 %) as a clear oil pure enough for further use.
Data for 10-nitrooleoyl chloride 21a: $^1$H-NMR (400 MHz, CDCl$_3$, COSY) $\delta$[ppm]: 7.09 (t, $^3$J$_{HH} = 7.9$ Hz, 1H, H-9), 2.91 (t, $^3$J$_{HH} = 7.2$ Hz, 2H, H-2), 2.59 (t, br, $^3$J$_{HH} = 7.3$ Hz, 2H, H-11), 2.24 (q, br, $^3$J$_{HH} = 7.6$ Hz, 2H, H-8), 1.78 – 1.57 (m, 2H), 1.56 – 1.45 (m, 4H), 1.42 – 1.25 (m, 16H), 0.90 (t, $^3$J$_{HH} = 7.5$ Hz, 3H, H-18). $^{13}$C-NMR, IR and MS data as reported for 20a.

3.3 2,4,6-Trichlorobenzoyl 9-nitrooleate 20b:

To a solution of 9-nitrooleic acid 4 (1.0 g, 3.0538 mmol) in dry THF (30 mL) was added diisopropylethylamine (631.5 mg, 0.83 mL, 4.8861 mmol) at 23 °C and the mixture was stirred for 15 min. 2,4,6-trichlorobenzoyl chloride (893.0 mg, 0.573 mL, 3.6646 mmol) was injected dropwise at 23 °C with stirring. After a reaction time of about 3 h, the solvent was removed in vacuum and the residue was dissolved in dry acetonitrile. The solution was extracted with heptane and the solvent of the heptane layers was distilled-off in vacuum. 2,4,6-Trichlorobenzoyl 9-nitrooleate 20b (1.5096 g, 2.822 mmol, 92.4 %) was isolated as a yellow oil solidifying upon standing.

Data for 2,4,6-trichlorobenzoyl 9-nitrooleate 20b: IR ($\tilde{\nu}$ (cm$^{-1}$)): 3082 (w), 2928 (m), 2857 (w), 1794 (s), 1764 (m), 1575 (s), 1547 (s), 1520 (m), 1433 (w), 1370 (m), 1205 (s), 1152 (w), 1075 (s), 988 (s), 913 (m), 884 (vs), 859 (s), 822 (m), 799 (s), 743 m). $^1$H-NMR (400 MHz, CDCl$_3$, COSY) $\delta$[ppm]: 7.42 (s, 2H, H-22, H-24), 7.11 (t, $^3$J$_{HH} = 7.9$ Hz, 1H, H-10), 2.63 – 2.55 (m, 2H, H-8), 2.47 (t, $^3$J$_{HH} = 7.4$ Hz, 2H, H-2), 2.23 (q, $^3$J$_{HH} = 7.6$ Hz, 2H, H-11), 1.72 – 1.62 (m, 2H, H-), 1.55  – 1.45 (m, 4H, H-), 1.40 – 1.25 (m, 16H, H-), 0.91 (t, br, $^3$J$_{HH} = 7.0$ Hz, 3H, H-18). $^{13}$C-NMR (100 MHz, CDCl$_3$, HSQC) $\delta$[ppm]: 169.49 (C-1), 157.57 (C-19), 151.71 (C-9), 137.61 (C-23), 136.56 (C-10), 133.12 (C-21, C-25), 129.85 (C-20), 128.35 (C-22, C-24), 35.19 (C-2), 31.82 (C-16), 29.35, 29.32, 29.15, 29.00, 28.87, 28.71, 28.53 (C-4), 28.03 (C-12 or C-11), 27.84 (C-11 or C-12), 26.31 (C-8), 24.11 (C-3), 22.65 (C-17), 14.10 (C-18). MS [ESI-HRMS]: [M+Na+H$_2$O]$^+$ calcd. for C$_{25}$H$_{36}$Cl$_3$O$_6$N$_2$: 574.1506, found: 574.1811.

3.4 2,4,6-Trichlorobenzoyl 10-nitrooleate 21b:

Reaction with 10-nitrooleic acid 5 (200 mg, 0.6108 mmol) following the method as described for 2,4,6-trichlorobenzoyl 9-nitrooleate 20b. Yield: 2,4,6-Trichlorobenzoyl 10-nitrooleate 21b (453.7 mg, 0.6108 mmol, nearly 100 % including residual heptane) as a clear oil pure enough for further use.

Data for 2,4,6-trichlorobenzoyl 10-nitrooleate 21b: $^1$H-NMR (400 MHz, CDCl$_3$, COSY) $\delta$[ppm]: 7.43 (s, 2H, H-22, H-24), 7.09 (t, $^3$J$_{HH} = 7.9$ Hz, 1H, H-9), 2.62 – 2.54 (m, 2H, H-11), 2.47 (t, $^3$J$_{HH} = 7.4$ Hz, 2H, H-2), 2.24 (q, $^3$J$_{HH} = 7.6$ Hz, 2H, H-8), 1.73 – 1.63 (m, 2H, H-), 1.60 – 1.45 (m, 4H, H-), 1.41 – 1.24 (m, 16H), 0.90 (t, br, $^3$J$_{HH} = 7.2$ Hz, 3H, H-18). $^{13}$C-NMR, IR and MS data as reported for 20b.
4. P-9-NOPC 1 via one-pot strategies – syntheses and data:

A solution of 9-nitrooleic acid 4 (100 mg, 0.305 mmol), 1-palmitoyl-2-lyso-sn-glycero-3-phosphatidylcholine 3 (302.7 mg, 0.6108 mmol) and DMAP (186.5 mg, 1.527 mmol) in dry CHCl$_3$ (9 mL) was treated slowly with 2,4,6-trichlorobenzoyl chloride (372.4 mg, 0.239 mL, 1.527 mmol) at -40 °C with stirring. The mixture was stirred for 1 h at 23 °C. Then, the reaction mixture was filtered through a short silica gel column (eluent CHCl$_3$/MeOH/H$_2$O 80/18/2). After removal of the solvent, the resulting a colourless foam (1.1422 g) was purified via preparative HPLC (Gemini NX-C18, 99 % MeOH/H$_2$O, 0.05 % TFA). Yield: 1-palmitoyl 2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 (90.6 mg, 0.1125 mmol, 36.9 %) and methyl 9-nitrooleate 9 (65 mg, 0.19 mmol, 62 %).

For data of 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 see chapter 7.
For data of methyl 9-nitrooleate 9 see chapter 1.4

Synthesis adapting ref. [12]

Remark: Replacing 2,4,6-trichlorobenzoyl chloride by N,N'-diisopropylcarbodiimide and dicyclohexylcarbodiimide, respectively, delivered only traces or minor amounts of 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1. In contrast, only 1-palmitoyl-2-(9-nitro-(E)-10-octadecenoyl)-sn-glycero-3-phosphatidylcholine 22 and impure 9-oxo-(E)-10 octadecenoyl and 9-oxo 10-undecenoic acid 12 (acid), respectively, as well as the corresponding methyl ester 12 were found after HPLC separation.

For data of 1-palmitoyl-2-(9-nitro-(E) 10-octadecenoyl)-sn-glycero-3-phosphatidylcholine 22 see chapter 5.1.

Synthesis adapting ref. [13]

5. PNOPC via esterification with nitrooleic acid chloride – syntheses and data

5.1 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1

To a solution of 1-palmitoyl-2-lyso-sn-glycero-3-phosphatidylcholine 3 (151.3 mg, 0.3054 mmol) in dry CHCl$_3$ (4 mL) were added DMAP (74.6 mg, 0.6108 mmol) and 9-nitrooleoyl chloride 20a (211.3 mg, 0.6108 mmol, microwave supported synthesis). The mixture was stirred at 23 °C for 24 h. a white precipitate of ammonium chloride occurred, which was filtered-off. The solvent was removed in vacuum and the residual mixture was separated by preparative HPLC (Nucleosil 50-7, MeOH/CH$_2$Cl$_2$/H$_2$O 50/45/5) or/and (Gemini NX 110-5 C-18, 95 % MeOH in H$_2$O, 0.05 % TFA) to give 1-palmitoyl-2-(9-
nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 (55.0 mg, 0.0683 mmol, 23.4 %) and 1-palmitoyl-3-(9-nitrooleoyl)-sn-glycero-2-phosphatidylcholine 24 (29.0 mg, 0.036 mmol, 11.8 %).

Remark: An alternative experiment with 1-palmitoyl-2-lyso-sn-glycero-3-phosphatidylcholine 3 (302.6 mg, 0.6108 mmol), DMAP (149.2 mg, 1.2216 mmol) and 9-nitrooleoyl chloride 20a (422.6 mg, 0.1.2216 mmol, microwave supported synthesis) and prolonged reaction time of 43 h delivered a mixture of 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 (245.5 mg, 0.3049 mmol, 49.9 %) and 1-palmitoyl-3-(9-nitrooleoyl)-sn-glycero-2-phosphatidylcholine 24 (47.7 mg, 0.059 mmol, 9.7 %).

Remark: Prolonged reaction times in the presence of a base delivered mixtures of 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 and 1-palmitoyl-2-(9-nitro-(E) 10-octadecanooyl)-sn-glycero-3-phosphatidylcholine 22. Stirring such a mixture (about 200 mg) in CH₂Cl₂ (3 mL) and diisopropylethylamine (32.1 mg, 0.041 mL, 0.2484 mmol) for 2 – 8 d, complete isomerization of the 9 alkene 1 to the E 10 alkene 22 could be observed.

Remark: To a solution of 1-palmitoyl-2-lyso-sn-glycero-3-phosphatidylcholine 3 (75.7 mg, 0.1527 mmol) in dry CH₂Cl₂ (5 mL) were added DMAP (37.3 mg, 0.3053 mmol) and 9-nitrooleoyl chloride 20a (105.6 mg, 0.3053 mmol, synthesised via extractive isolation) in dry CH₂Cl₂ (3 mL). The mixture was stirred at 23 °C for 6 d. Then, the solvent was removed in vacuum and the residual mixture was separated by preparative HPLC (Gemini N-X C18, MeOH /H₂O 95/5, 0.05 % TFA) to give 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 (41.3 mg, 0.0513 mmol, 33.6 %) and 1-palmitoyl-3-(9-nitro-(E) 10-octadeconooyl)-sn-glycero-2-phosphatidylcholine (7.7 mg, 0.096 mmol, 6.3 %, impurities, hypothetical structure, not proven).

Data of 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 see chapter 7.

Data of methyl 9-nitrooleate 9 see chapter 1.4

Data of 1-palmitoyl-2-(9-nitro-(E) 10-octadeconooyl)-sn-glycero-3-phosphatidylcholine 22: HPLC (Gemini NX 110-5 C18, 4x250 mm, 2mL/min, 194 bar): k = 5.59 (95 % MeOH/H₂O/0.05 % TFA). ¹H-NMR (400 MHz, CDCl₃, COSY) δ[ppm]: 5.84 (td, ³JHH = 6.8 Hz, ³JHH = 15.3 Hz, 1H, H-33), 5.59 (tdd, ³JHH = 1.6 Hz, ³JHH = 8.5 Hz, ³JHH = 15.3 Hz, 1H, H-32), 5.25 – 5.13 (m, br, 1H, H-2), 4.83 (dt, ³JHH = 6.4 Hz, ³JHH = 8.5 Hz, 1H, H-31), 4.48 – 4.26 (m, 3H, H-5, H-1a), 4.11 (dd, ³JHH = 6.9 Hz, ³JHH = 12 Hz, 1H, H-1b), 4.04 – 3.92 (m, br, 2H, H-3), 3.9 – 3.76 (m, br, 2H, H-4), 3.32 (s, br, 9H, H-6), 2.28 (2x t, ³JHH = 7.8 Hz, H-8, H-24), 2.12 – 1.98 (m, 3H, H-33, H-30a), 1.86 – 1.68 (m, 1H, H-30b), 1.65 – 1.48 (m, 5H), 1.44 – 1.15 (m, 4H), 0.94 – 0.8 (m, 6H, H-22, H-40). ¹³C-NMR (100 MHz, CDCl₃, HSQC, HMBC) δ[ppm]: 173.55 (C-7/23), 173.07 (C-7/23), 140.66 (CH₂), 139.08 (C-33), 124.42 (C-32), 90.20 (C-31), 70.03 (C-2), 66.28 (C-4), 64.14 (C-3), 62.47 (C-1), 59.83 (C-5), 54.54 (C-6), 34.11 (C-8/24/30), 34.07 (C-8/24/30), 34.06 (C-8/24/30), 32.15 (C-34), 31.93, 31.76, 29.72 (3-4x C), 29.68 (2-3x C), 29.54,
Data of 1-palmitoyl-3-(9-nitrooleoyl)-sn-glycero-2-phosphatidylcholine 24: HPLC (Nucleosil 50-5, 4x250 mm, 2mL/min, 116 bar): k = 2.0 (MeOH/CH₂Cl₂/H₂O 50/45/5), (Nucleosil 100-3, 4x120 mm, 2mL/min, 130 bar) k = 0.81 (MeOH/CH₂Cl₂/H₂O 50/45/5). IR (υ (cm⁻¹)): 2923 (s), 2853 (s), 1736 (s), 1648 (w), 1522 (m), 1466 (m), 1336 (m), 1240 (s), 1085 (s), 1061 (s), 978 (m).¹H-NMR (400 MHz, CDCl₃, COSY) δ [ppm]: 7.09 (t, 3JHH = 7.9 Hz, 1H, H-32), 4.56 – 4.47 (m, br, 1H, H-2), 3.39 – 3.30 (m, br, 2H, H-5), 4.27 – 4.21 (m, 4H, H-1, H-3), 3.87 – 3.80 (m, br, 2H, H-4), 3.39 (s, br, 9H, H-6), 2.57 (t, br, 3JHH = 7.8 Hz, 2H, H-30), 2.30 (2x t, 3JHH = 7.6 Hz, 4H, H-8, H-24), 2.22 (q, br, 3JHH = 7.6 Hz, 2H, H-33), 1.63 – 1.53 (m, 4H), 1.53 – 1.42 (m, 2H), 1.37 – 1.21 (m, H), 0.89 (2x t, 3JHH = 6.9 Hz, 6H, H-22, H-40).¹3C-NMR (100 MHz, CDCl₃, HSQC, HMBC) δ [ppm]: 173.46, 173.34 (C-7, C-23), 151.75 (C-31), 136.63 (C-32), 70.54 (C-2), 66.38 (C-4), 62.99, 62.91 (C-1, C-3), 59.46 (C-5), 54.42 (C-6), 34.13, 34.03 (C-8, C-24), 31.92, 31.80, 29.71 (3-4x C), 29.67 (2-3x C), 29.55, 29.37 (2x C), 29.31 (2x C), 29.21, 29.14, 29.02, 28.93, 28.90, 28.52, 28.01 (C-33), 27.86, 26.30 (C-30), 24.89, 24.75, 22.69, 22.63, 14.12, 14.10 (C-22, C-40).

5.2 1-palmitoyl-2-(10-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 2:

Reaction with 10-nitrooleoyl chloride 21a (105.6 mg, 0.305 mmol) and 1-palmitoyl-2-lyso-sn-glycero-3-phosphatidylcholine 3 (75.7 mg, 0.1527 mmol) following the method as described for 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1. Yield: 1-palmitoyl-2-(10-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 2 (19.1 mg, 0.0237 mmol, 15.5 %) and methyl 10-nitrooleate 16 (126.0 mg, 0.369 mmol, 60.4 % MeOH work-up) and 10-nitrooleic acid 5 (12.1 mg, 0.0354 mmol, 11.6 %).

For data of 1-palmitoyl-2-(10-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 2 see chapter 8.

For data of methyl 10-nitrooleate 16 see chapter 2.4, for data of methyl 10-nitrooleate 5 see chapter 2.5
6. Double bond migration, Nef reaction – syntheses and data:

To a mixture of 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 and 1-palmitoyl-2-(9-nitro-(E)-10-octadecenoyl)-sn-glycero-3-phosphatidylcholine 22 (200.0 mg, 0.2484 mmol) in dry CH$_2$Cl$_2$ (3 mL) was added diisopropylethylamine (32.1 mg, 0.041 mL, 0.2484 mmol) at 23 °C with stirring. A red colour occurred. The mixture was stirred at 23 °C for 4 d. Then, the solvent was removed in vacuum and the residue was purified via preparative HPLC (Nucleosil 50-5, MeOH/CH$_2$Cl$_2$/H$_2$O 50/45/5). Complete double bond migration resulted the formation of 1-palmitoyl-2-(9-nitro-E 10-octadecenoyl)-sn-glycero-3-phosphatidylcholine 22 exclusively.

Remark: Stirring for prolonged times and variation of the base did not cause regeneration of the 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine.

For data of 1-palmitoyl-2-(9-nitro-(E) 10-octadecenoyl)-sn-glycero-3-phosphatidylcholine 22 see chapter 5.1.

For data of 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 see chapter 7.

7. P-(9-NO)PC 1 including methyl (E) 9-nitrooleate 9 recycling – synthesis and data:

2,4,6-Trichlorobenzoyl 9-nitrooleate 20b (1.5096 g, 2.822 mmol) was treated with a solution of 1-palmitoyl-2-lyso-sn-glycero-3-phosphatidylcholine 3 (302.7 mg, 0.6108 mmol) and DMAP (379.7 mg, 0.4716 mmol, 77.2 %). Complete double bond migration resulted the formation of 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1 (379.7 mg, 0.4716 mmol, 77.2 %).

Data of 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1: R$_f$ = 0.15 (MeOH/CH$_2$Cl$_2$/H$_2$O 50:45:5).

HPLC (Gemini NX 110-5 C18, 4x250 mm, 2mL/min, 194 bar): k = 6.3 (95 % MeOH/H$_2$O/0.05 % TFA ). [a]$_D$ = 2.2° (c = 1.1, 23°C, CH$_2$Cl$_2$). IR (film, 0 (cm$^{-1}$)): 2923 (s), 2852 (m), 1736 (s), 1648 (w), 1523 (m), 1465 (m), 1335 (m), 1237 (s), 1176 (s), 1088 (s), 1061 (s), 968 (s), 923 (m), 818 (m), 722 (m).

1H-NMR (600 MHz, CDCl$_3$, COSY) δ[ppm]: 7.11 (t, J$_{HH}$ = 7.9 Hz, 1H, H-32), 5.30 – 5.19 (m, br, 1H, H-2), 4.53 – 4.43 (m, br, 2H, H-5), 4.37 (dd, J$_{HH}$ = 3.6 Hz, J$_{HH}$ = 12.0 Hz, 1H, H-1a), 4.15 (dd, J$_{HH}$ = 6.7 Hz, J$_{HH}$ = 12.0 Hz, 1H, H-1b), 4.09 (t, J$_{HH}$ = 6.2 Hz, 2H, H-3), 3.94 – 3.86 (m, br, 2H, H-4), 3.37 (s, br, 9H, H-6), 2.59 (t, J$_{HH}$ = 7.4 Hz, 2H, H-10), 2.34 (t, J$_{HH}$ = 7.4 Hz, 2H, H-8/H-24), 2.31 (t, br, J$_{HH}$ = 7.6 Hz, 2H, H-8/H-24), 2.24 (q, J$_{HH}$ = 7.6 Hz, 2H, H-33), 1.65 – 1.56 (m, 4H), 1.54 – 1.45 (m, 4H), 1.39 -1.23 (m, 40H), 0.91 (t, J$_{HH}$ = 7.0 Hz, 3H, H-22/H-40), 0.90 (t, J$_{HH}$ = 7Hz, 3H, H-22/H-40). 13C-NMR (150 MHz, CDCl$_3$, HSQC, HMBC) δ[ppm]: 173.55
(C-7), 173.10 (C-23), 151.75 (C-31), 136.72 (C-32), 69.93 (C-2), 66.27 (C-4), 64.35 (C-3), 62.32 (C-1), 59.92 (C-5), 54.60 (C-6), 34.09 (C-8), 34.03 (C-24), 31.93, 31.80, 29.71 (2x C), 29.70 (2x C), 29.67 (2x C), 29.53, 29.37, 29.32 (2x C), 29.15 (2x C), 28.98, 28.85, 28.82, 28.51, 28.02 (2x C, C-30/33/34), 27.84 (C-30/33/34), 26.27 (C-30), 24.85 (C-9/C-25), 24.72 (C-9/C-25), 22.69, 22.63, 14.12 (C-22/C40), 14.08 (C-22/C-40).

**FOR DATA OF METHYL 9-NITROOLEATE**

**8. P(10-NO)PC 2 INCLUDING METHYL (E) 10-NITROOLEATE 16 RECYCLING - SYNTHESIS AND DATA:**

Reaction with 2,4,6-Trichlorobenzoyl 10-nitrooleate 21b (453.7 mg, 0.6108 mmol) and 1-palmitoyl-2-lyso-sn-glycero-3-phosphatidylcholine 3 (60.5 mg, 0.1222 mmol) following the method as described for 1-palmitoyl-2-(9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1. Yield: 1-palmitoyl-2-(10-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 2 (43.0 mg, 0.0534 mmol, 43.7 %) and methyl 10-nitrooleate 16 (126.0 mg, 0.369 mmol, 60.4 % from 21b).

Data for 1-palmitoyl-2-((E) 10-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 2: Rₐ = 0.15 (MeOH/CH₂Cl₂/H₂O 50:45:5). HPLC (Gemini NX 110-5 C18, 4x250 mm, 2mL/min, 155 bar): k = 7.55 (95 % MeOH/H₂O/0.1 % TFA), [α]D = 1.5° (c = 0.5, 21°C, CH₂Cl₂). IR (film, ´ʋ (cm⁻¹)): 2925 (s), 2855 (m), 1737 (s), 1522 (m), 1466 (w), 1336 (w), 1163 (s), 1052 (m), 974 (m), 859 (w), 748 (w). ¹H-NMR (400 MHz, CDCl₃, COSY) δ [ppm]: 7.09 (t, ³JHH = 7.8 Hz, 1H, H-31), 5.29 – 5.19 (m, br, 1H, H-2), 4.58 – 4.40 (m, br 2H, H-5), 4.38 (d, br, ²JHH = 11.8 Hz, 1H, H-1a), 4.21 – 4.01 (m, br, 3H, H-1b, H-3), 3.96 – 3.71 (m, 2H, H-4), 3.32 (s, br, 9H, H-6), 2.58 (t, br, ³JHH = 7.4 Hz, 2H, H-33), 2.38 – 2.28 (m, 4H, H-8, H-24), 2.24 (q, ³JHH = 7.5 Hz, H-30), 1.66 – 1.55 (m, 4H, 1.54 – 1.45 (m, 4H), 1.38 – 1.23 (m, 40H), 0.90 (2x t, br, ³JHH = 6.5 Hz, 6H, H-22, H-40). ¹³C-NMR (100 MHz, CDCl₃, HSQC, HMBC) δ [ppm]: 173.59 (C-7), 173.10 (C-23), 151.95 (C-31), 136.31 (C-32), 69.96 (C-2), 66.55 (C-4), 64.26 (C-3), 62.40 (C-1), 59.85 (C-5), 54.72 (C-6), 34.11 (C-8/24), 34.06 (C-8/24), 31.94 (C-20/38), 31.82 (C-20/38), 29.71 (3x C), 29.67 (2x C), 29.54, 29.38, 29.25 (2x C), 29.17 (2x C), 29.09, 29.03, 28.86, 28.46, 27.97 (2x C, C-30/34), 27.92 (C-30/34), 26.37 (C-33), 24.87, 24.74, 22.71 (C-21/39), 22.65 (C-22/C40), 14.14 (C-22/C40). HRMS ESI: [M+H]+: calcd. for C₄₂H₇₆N₂O₁₀P: 805.08, found: 805.09. HRMS ESI: [M+Na]+: calcd. for C₄₂H₇₆N₂O₁₀P²Na: 827.5521, found: 827.5523.

18
9. Syntheses of Nitrooleic acids 4 and 5 from Oleic acid

A direct access to Nitrooleic acids offered the adoption of a procedure published by Maiti. [15] Starting from oleic acid, treatment with silver nitrite and tetramethylpiperidin-N-oxyl (TEMPO) in 1,2-dichloroethane with heating afforded a 3:3:1:1 mixture of (E)-9, (E)-10, (Z)-9 and (Z)-10 nitrooleic acids with about 47% yield overall. (E)-9 nitrooleic acid 4 and (E)-10 nitrooleic acid 5 could be isolated by means of preparative HPLC, the separation of the minor Z-4 and Z-5 nitrooleic acids failed.

Oleic acid (70.6 mg, 0.88 mL, 0.025 mmol, 90 %), silver nitrite (AgNO\(_2\), 153.9 mg, 1 mmol), 2,2,6,6-tetramethylpiperidin-N-oxyl (TEMPO, 78.1 mg, 0.5 mmol) and molsieves (4 Å, 150 mg) in 1,2 dichloroethane (2 mL) were heated to 70 °C for 24 h. After cooling to 23 °C the mixture was passed through a short celite pad (careful washing with 1,2 dichloroethane) and the solvent was removed in vacuuum. The crude mixture of nitrooleic acids (88.4 mg) was purified using preparative HPLC: 1. Gemini NX, 250x30 mm, 70% H\(_3\)CCN/30% H\(_2\)O/0.05% trifluoroacetic acid), 2. Nucleosil 50-7, 250x32 mm, 0.75% isopropanol, 0.05% trifluoroacetic acid in hexane). Yield: 9.2 mg (0.028 mmol, 11 %) (Z)-9 nitrooleic acid Z-4 and (Z)-10 nitrooleic acid Z-5 (1:1), 14.8 mg (0.045 mmol, 18 %) (E) 9 nitrooleic acid 4 and 14.5 mg (0.44 mmol, 18%) (E) 10 nitrooleic acid 4 as colourless oils.

HPLC:
(Nucleosil 50-5, 4x250 mm, 2mL/min, 150 bar, 1 % iPrOH in hexane, 0.1 % TFA): k = 0.89 (Z-4 and Z-5), k = 0.94 (4), k = 1.06 (5). (Nucleosil 50-5, 4x250 mm, 2mL/min, 145 bar, 0.6 % iPrOH in hexane, 0.1 % TFA): k = 2.23 (Z-4 and Z-5), k = 2.50 (4), k = 2.59 (5).
(Gemini NX 110-5 C-18, 4.6x250 mm, 2mL/min, 96 bar, 70 % MeCN in H\(_2\)O, 0.1 % TFA): k = 3.90 (Z-4 and Z-5), k = 3.57 (4), k = 3.43 (5).
For further data see capters 1.5, 2.5 and ref. [1, 2].

10. References


11. Appendix: $^1$H and $^{13}$C NMR-Spectra

8-Oxooctanoic acid methyl ester I (crude)

Methyl 8-hydroxy-9-nitro nonanoate II (crude)
Methyl 9-nitro nonanoate 6 (crude)

Methyl 10-hydroxy-9-nitro octadecanoate 8, predominantly diastereomer 1:
Methyl 10-hydroxy-9-nitro octadecanoate 8, predominantly diastereomer 2:
Methyl 10-acetoxy-9-nitro octadecanoate 10a, predominantly diastereomer 1:
Methyl 9-nitro-10-trifluoracetoxy octadecanoate 10b, predominantly diastereomer 1:
(E) Methyl 9-nitrooleate 9
(E) Methyl 9-Oxo-10-octadecenoate 12 (crude)

(E) 9-Nitrooleic acid 4
Azelaic acid dichloride
Methyl 9-chloro 9-oxo nonanoate III

Methyl 9-oxononanoate 13
1-Nitro-2-nonanol IV

1-Nitrononane 14
Methyl 9-acetoxy-10-nitro octadecanoate 17, predominantly diastereomer 1

(E) Methyl 10-nitrooleate 16
Methyl (E) 10-nitro-8-octadecenoate 18
(E) 10-Nitrooleic acid 5
2,4,6-Trichlorobenzoyl (E) 9-nitrooleate 20b:
(E) 10-Nitro oleoyl chloride 21a

2,4,6-Trichlorobenzoyl (E) 10-nitrooleate 21b:
I-Palmitoyl-2-(9-nitro-(E) 10-octadecenoyl)-sn-glycero-3-phosphatidylcholine 22
HSQC 22
1-Palmitoyl-3-((E) 9-nitrooleoyl)-sn-glycero-2-phosphatidylcholine 24
1-Palmitoyl-2-((E) 9-nitrooleoyl)-sn-glycero-3-phosphatidylcholine 1
COSY I

HSQC I
HMBC 1

$^{31}$P/$^1$H-HMBC 1
Mixture of minor (Z)-9 and (Z)-10 nitrooleic acids. $^1$H NMR spectrum.