Tandem Double Intramolecular [4+2]/[3+2] Cycloadditions of Nitroalkenes

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SUPPORTING INFORMATION

General Experimental

All reactions were performed in oven-dried (140 °C) or flame-dried glassware under an inert atmosphere of dry N_2. The following reaction solvents were distilled from the indicated drying agents: diethyl ether (sodium, benzophenone), toluene (Na), methanol ($Mg(OMe)_2$), triethylamine (CaH_2), *tert*-butyl alcohol was distilled over Na. *n*-Butyllithium solutions were titrated following the method of Gilman.[1] Brine refers to a sat. aq. solution of NaCl. Grignard solutions were titrated using 2,2'-phenanthroline as an indicator.[2]

Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr, or Edwards E050/60 diffusion pump; boiling points (bp) corresponding to uncorrected air-bath temperatures (ABT).

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Unity 400 (400 MHz, ^{1}H; 100 MHz, ^{13}C), Unity 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C). Spectra are referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.0 ppm, ^{13}C) or toluene (δ 7.00 ppm, ^{1}H; δ 20.4 ppm, ^{13}C). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz.

Mass spectroscopy was performed by the University of Illinois Mass Spectrometer Center. Electron impact (EI) and FAB spectra were performed on a Finnigan-MAT CH-5 spectrometer. Data are reported in the form of m/z (intensity relative to base peak = 100).

Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus in sealed tubes and are uncorrected.

Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light and/or PMA and/or Iodide.

Diethyl ether was of reagent grade and used as received; other solvents for chromatography and filtration were technical grade and distilled from the indicated drying agents: hexane; ethyl acetate (K_2CO_3). Column chromatography was performed using EM Science 230-400-mesh silica gel.

All reaction temperature compared to internal temperature measured by Teflon-cooled thermocouples unless other noted.

Commercial Reagents

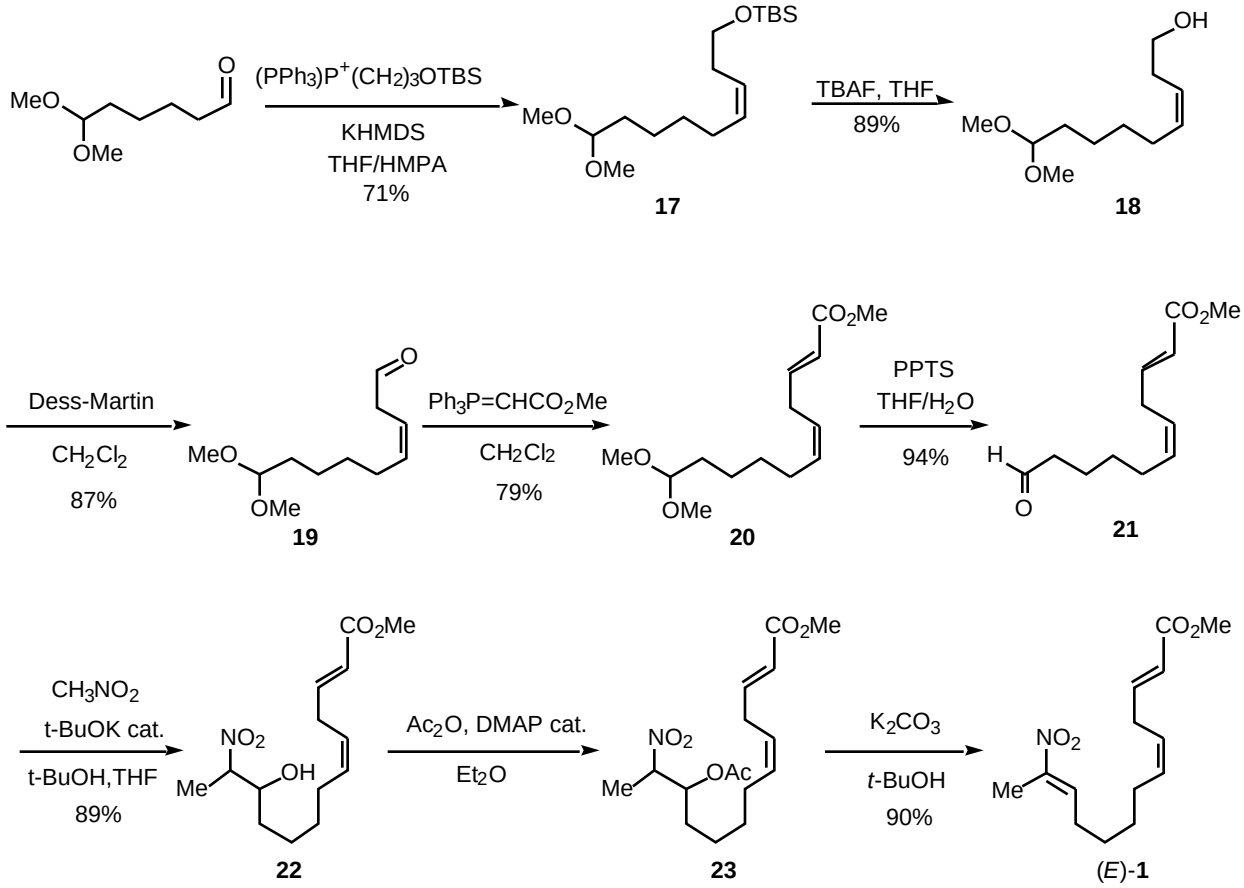
The following chemicals were purchased from the indicated sources: Allyl bromide (Aldrich), *n*-butyllithiun (FMC), *tert*-butyldimethylsily chloride (Gelest), (3-carboxypropyl)triphenylphosphonium bromide (Lancaster), caprolactone (Aldrich), chloromethyl methyl ether (Aldrich), cyclohexene (Aldrich), dimethyl sulfoxide (Aldrich), Magnesium (Aldrich), (methoxycarbonylmethylene)triphenylphosphorane (Lancaster), oxalyl chloride (Aldrich), imidazole (Aldrich), 4-morphilino N-oxide (Aldrich), nitroethane (Aldrich), potassium bis(trimethylsilyl)amide (Aldrich), potassium *tert*-butoxide (Aldrich), Raney nickel (Activated Metals A 5000), sodium hydride (Aldrich), tin (IV) chloride (Aldrich), triphenylphosphine (Acros), tetra-*n*-propylammonium perruthenate (Aldrich), triphenyl phosphonoacetate (Aldrich), tetrabutylammonium fluoride (TBAF•$3H_2O$, Fluka).

Literature Preparations

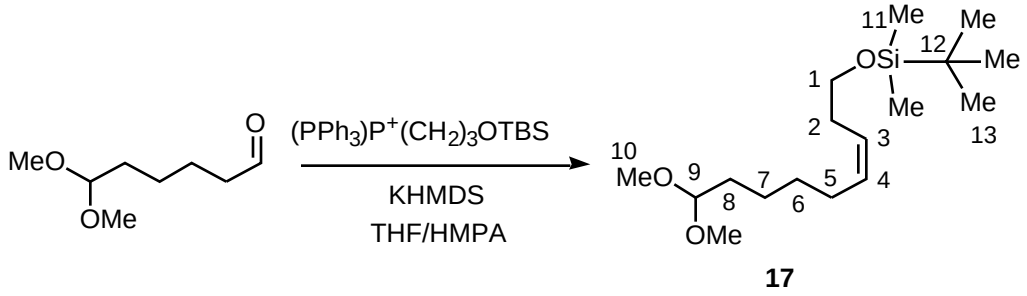
The following compounds were prepared by literature methods: allylmagnesium bromide,[3] methoxymethyltriphenylphosphonium chloride,[4] 6,6-dimethoxyhexanal.[5] bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl)phosphonate,[6] methoxymethyltriphenylphosphine oxide,[7] methyl 6-(O-*tert*-butyldimethylsilyl)hexanoate,[8] anhydrous cerium chloride.[9]

Preparation of Starting Materials

Preparation of Methyl (2*E*,5*Z*,11*E*)-12-Nitrotrideca-2,5,11-trienoate ((*E*)-1)



(3*Z*)-*tert*-Butyl[9,9-dimethoxy-3-nonenyloxy]dimethylsilane (17)



To a cold (–78 °C, internal temperature) solution of (3-*tert*-butyldimethylsilanoxypropyl)triphenylphosphonium bromide (11.5 g, 22.4 mmol, 1.2 equiv) in THF (100 mL) and HMPA (55 mL) was added a solution of KHMDS (0.5 M toluene, 44.8 mL, 22.4 mmol, 1.2 equiv). The mixture was stirred for 1 h at –78 °C then was allowed to warm to 0 °C

over 1.5 h. Upon cooling back to –78 °C, a solution of 6,6-dimethoxyhexanal[7] (3.00 g, 18.7 mmol) in THF (100 mL) was added and the mixture was stirred for 30 min at 0 °C and then was allowed to warm to room temperature for 3 h. The reaction was quenched with sat. aq. NH_4Cl solution (150 mL) and then was diluted with Et_20 (70 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with sat. aq. NH_4Cl solution (100 mL), brine (50 mL) and the combined extracts were dried ($MgSO_4$) and filtered. After removal of the solvent under reduced pressure, the residue was purified by chromatography (silica gel, hexane/EtOAc, 8/1) and distillation to afford 4.55 g (71%) **17** as a colorless oil which constituted of an inseparable mixture of isomers (*Z*/*E*, 91/9 by ^{1}H NMR analysis).

Analytical Data for **17**:

bp: 75 °C (3.0 x 10^{-5} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
5.46-5.33 (m, 2 H, HC(3), HC(4)), 4.34 (t, *J* = 5.5, 1 H, HC(9)), 3.58 (td, *J* = 7.0, 0.5, 2 H, $H_2C(1)$), 3.30 (s, 6 H, 2 $H_3C(10)$), 2.25 (q, *J* = 7.0, 2 H, $H_2C(2)$), 2.06-2.02 (m, 2 H, $H_2C(5)$), 1.62-1.56 (m, 2 H, $H_2C(8)$), 1.35-1.32 (m, 4 H, $H_2C(7)$, $H_2C(6)$), 0.85 (s, 9 H, $H_3C(13)$), 0.04 (s, 6 H, $H_3C(11)$)

^{13}C NMR: (126 MHz, $CDCl_3$)
131.4 (C(3)), 125.7 (C(4)), 104.4 (C(9)), 62.9 (C(1)), 52.50 (C(10)), 32.3 (C(8)), 31.1 (C(2)), 29.5 (C(5)), 27.2 (C(6)), 25.9 (C(13)), 24.3 (C(7)), 18.3 (C(12)), -5.3 (C(11))

IR: ($CHCl_3$)
2950 (s), 2931 (s), 1743 (w), 1463 (w), 1384 (w), 1255 (m), 1097 (s), 1054 (m), 933 (w)

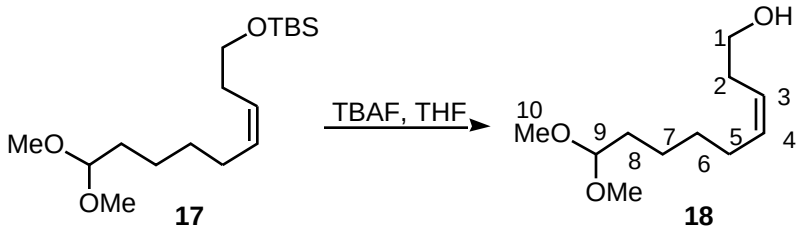
MS: FAB
315 (9, M^+-H), 285 (14), 253 (34), 243 (14), 227 (11), 171 (39), 153 (41), 145 (23), 137 (21), 136 (13), 125 (14), 123 (27), 122 (12), 121 (100), 119 (34), 115 (27)

TLC: R_f 0.28 (silica gel, hexane/EtOAc, 8/1, PMA)

Analysis: $C_{17}H_{36}O_3Si$ (316.56)

Calculated:	C: 64.50;	H: 11.46%
Found:	C: 64.20;	H: 11.45%

(3*Z*)-9,9-Dimethoxy-3-nonen-1-ol (18)



To a cold (0 °C) solution of **17** (2.15 g, 6.80 mmol) in THF (10 mL) was added a solution of tetrabutylammonium fluoride (1 M THF, 10.20 mL, 10.20 mmol, 1.5 equiv) whereupon the mixture was warmed to room temperature. After 3 h, the solution was quenched with water (45 mL) and was diluted with Et_2O (45 mL). The ether layer was separated and the aqueous phase was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (30 mL), brine (25 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 4/1) and distillation to afford 1.22 g (89%) of **18** as a colorless oil which constituted of an inseparable mixture of isomers (*Z*/*E*, 91/9 by ^1H NMR analysis).

Analytical Data for **18**:

bp: 90 °C (7.0×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, $CDCl_3$)
5.57-5.34 (m, 2 H, HC(3), HC(4)), 4.34 (t, J = 5.5, 1 H, HC(9)), 3.63 (q, J = 6.5, 2 H, $H_2C(1)$), 3.30 (s, 6 H, 2 $H_3C(10)$), 2.31 (q, J = 7.0, 2 H, $H_2C(2)$), 2.09-2.05 (m, 2 H, $H_2C(5)$), 1.61-1.57 (m, 2 H, $H_2C(8)$), 1.38-1.34 (m, 4 H, $H_2C(6)$, $H_2C(7)$)

^{13}C NMR: (126 MHz, $CDCl_3$)
132.6 (C(3)), 125.3 (C(4)), 104.3 (C(9)), 62.0 (C(1)), 52.46 (C(10)), 32.2 (C(8)), 30.7 (C(2)), 29.3 (C(5)), 27.0 (C(6)), 24.3 (C(7))

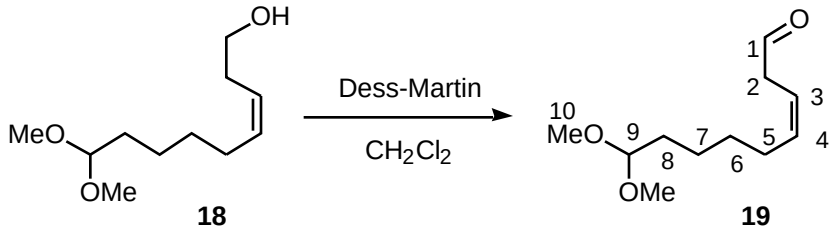
IR: ($CHCl_3$)
3423 (b, m), 3006 (w), 2944 (s), 2859 (m), 2832 (m), 1739 (w), 1461 (w), 1386 (w), 1191 (w), 1130 (s), 1051 (s), 960, (w)

MS: FAB
202 (4, M^+-H), 201 (13), 186 (9), 171 (13), 169 (20), 155 (17), 154 (35), 153 (39), 152 (14), 141 (36), 140 (15), 139 (100), 138 (19), 137 (45), 136 (34), 123 (23), 121 (80), 106 (24)

TLC: R_f 0.38 (silica gel, hexane/EtOAc, 4/1, PMA)

Analysis:	$C_{11}H_{22}O_3$	(202.29)	
	Calculated:	C: 65.31;	H: 10.96%
	Found:	C: 65.08;	H: 11.09%

(3*Z*)-9,9-Dimethoxy-3-nonenal (19)



18 **19**

A solution of alcohol **18** (1.05 g, 5.19 mmol) in CH_2Cl_2 (7 mL) was added to a stirred suspension of 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one (Dess-Martin periodinane, 3.35 g, 7.78 mmol, 1.5 equiv) in CH_2Cl_2 (25 mL) at room temperature. The resulting mixture was stirred for 1 h and then was diluted with Et_2O (100 mL). The reaction was quenched by addition of a sat. aq. $NaHCO_3$ solution (150 mL) containing 15 g of sodium thiosulafte was added and the suspension was stirred 15 min at room temperature. The combined organic layers were washed with water (100 mL), brine (50 mL) and the combined extracts were dried ($MgSO_4$). The solvent was evaporated under reduce pressure to afford **19** 914 mg (87%) as a colorless oil which constituted of an inseparable mixture of isomers (*Z*/*E*, 91/9 by ^{1}H NMR analysis).

Analytical Data for **19**:

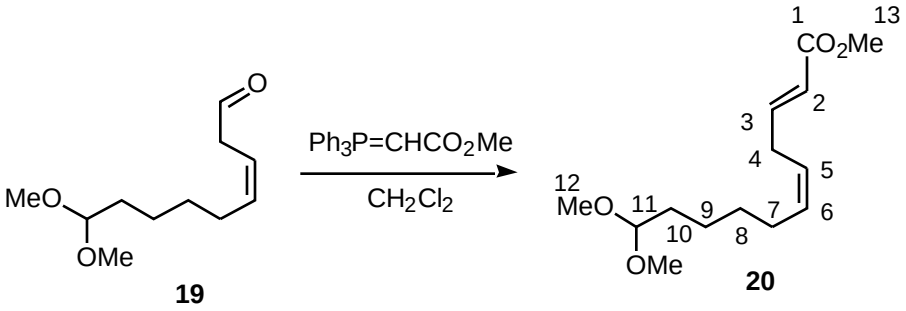
^{1}H NMR: (500 MHz, $CDCl_3$)

9.64 (t, J= 1, 1H, HC(1)), 5.69-5.52 (m, 2 H, HC(3), HC(4)), 4.33 (t, J = 5.5, 1 H, HC(9)), 3.29 (s, 6 H, 2 H_3C(10)), 3.18 (d, J = 7.0, 2 H, H_2C(2)), 2.04 (q, J = 7.0, 2 H, H_2C(5)), 1.60-1.56 (m, 2 H, H_2C(8)), 1.41-1.35 (m, 4 H, H_2C(6), H_2C(7))

^{13}C NMR: (126 MHz, $CDCl_3$)

199.7 (C(1)), 135.0 (C(3)), 118.2 (C(4)), 104.4 (C(9)), 52.46 (C(10)), 42.5 C(2)), 32.3 (C(8)), 29.0 (C(5)), 27.5 (C(6)), 24.1 (C(7))

Methyl (2*E*,5*Z*)-11,11-Dimethoxyundeca-2,5-dienoate (20)



19 **20**

To a solution of **19** (1.05 g, 5.20 mmol) in CH_2Cl_2 (36 mL) was added (methoxycarbonylmethylene)triphenylphosphorane (2.6 g, 7.80 mmol, 1.5 equiv) in one portion. The solution was heated to reflux for 1.5 h. After being cooled to room temperature, the reaction was quenched with water (40 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic extracts were washed with brine (25 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 5/1) and distillation to afford 1.20 g (79%) of **20** as a colorless oil which constituted of an inseparable mixture of isomers (5*Z*/5*E*, 91/9 by ^{1}H NMR analysis).

Analytical Data for **20**:

bp: 80 °C (1.4 x 10^{-4} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
6.96 (td, *J* = 6.4, 16.0, 1 H, HC(3)), 5.82 (td, *J* = 16.0, 1, 1 H, HC(2)), 5.46-5.29 (m, 2 H, HC(5), HC(6)), 4.35 (t, *J* = 6.0, 1 H, HC(11)), 3.72 (s, 3 H, H_3C(13)), 3.30 (s, 6 H, 2 H_3C(12)), 2.93 (t, J = 6.5, 2 H, H_2C(4)), 2.02 (q, J = 7, H_2C(7)), 1.60-1.57 (m, 2 H, H_2C(10)), 1.40-1.32 (m, 4 H, H_2C(9), H_2C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)
167.1 (C(1)), 147.5 (C(3)), 132.57 (C(5)), 124.2 (C(6)), 121.0 (C(2)), 104.4 (C(11)), 52.6 (C(12)), 51.4 (C(13)), 32.6 (C(4)), 29.9 (C(7)), 29.2 (C(10)), 27.1 (C(8)), 24.2 (C(9))

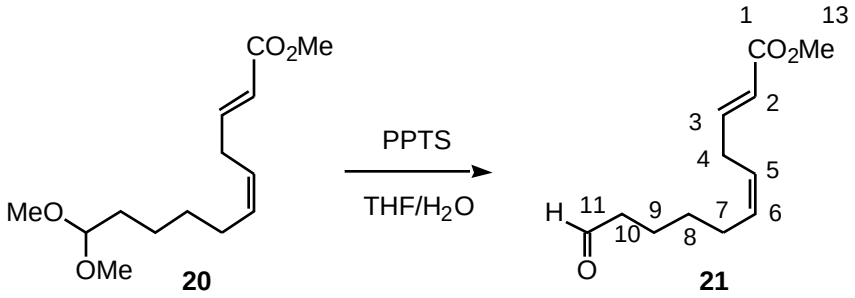
IR: ($CHCl_3$)
2946 (s), 2859 (m), 1724 (s), 1656 (m), 1436 (m), 1330 (m), 1274 (s), 1211 (m), 1128 (m), 1051 (m)

MS: FAB
257 (6, M^++H), 256 (8), 255 (34), 241 (12), 226 (13), 225 (79), 223 (16), 193 (51), 192 (10), 165 (11), 161 (27), 149 (10), 143 (17), 133 (100), 125 (37)

TLC: R_f 0.25 (silica gel, hexane/EtOAc, 5/1, PMA)

Analysis:	$C_{14}H_{24}O_4$	(256.34)	
	Calculated:	C: 65.60;	H: 9.44%
	Found:	C: 65.43;	H: 9.73%

Methyl (2*E*,5*Z*)-11-Oxoundeca-2,5-dienoate (21)



To a solution of **20** (640 mg, 2.5 mmol) in THF/H_2O (1/1, 30 mL) was added pyridinium *p*-toluenesulfonic acid (1.25 g, 5.0 mmol, 2 equiv) at room temperature and the solution was warmed to 45 °C for 5 h. After being cooled to room temperature, the reaction was then diluted with water (10 mL) and with Et_2O (15 mL). The aqueous phase was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (15 mL), brine (10 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 5/1) and distillation to afford 493 mg (94%) of **21** as a colorless oil which constituted of an inseparable mixture of isomers (5*Z*/5*E*, 91/9 by ^{1}H NMR analysis).

Analytical Data for **21**:

bp: 95 °C (9.0×10^{-5} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

9.73 (t, *J* = 1.5, 1 H, HC(11)), 6.95-6.89 (m, 1H, HC(3)), 5.80 (td, *J* = 2.0, 15.5, 1 H, HC(2)), 5.53-5.35 (m, 2 H, HC(5), HC(6)), 3.70 (s, 3 H, H_3C(13)), 2.91 (t, J = 6, 2 H, H_2C(4)), 2.40 (td, *J* = 7.5, 1.5, 2 H, H_2C(10)), 2.04 (q, *J* = 7.5, 2 H, H_2C(7)), 1.64-1.58 (m, 2 H, H_2C(8)), 1.41-1.34 (m, 2 H, H_2C(9))

^{13}C NMR: (126 MHz, $CDCl_3$)

202.7 (C(11)), 167.3 (C(1)), 147.6 (C(3)), 132.3 (C(5)), 124.9 (C(6)), 121.3 (C(2)), 51.7 (C(13)), 43.9 (C(10)), 30.2 (C(4)), 29.1 (C(7)), 27.1 (C(8)), 21.8 (C(9))

IR: ($CDCl_3$)

3014 (w), 2946 (m), 2859 (w), 2723 (w), 1724 (s), 1656 (m), 1436 (m), 1330 (m), 1272 (m), 1211 (m), 1170 (m), 1039 (w), 985 (w)

MS: FAB

211 (100, M^++H), 209 (11), 195 (10), 193 (13), 179 (81), 161 (32), 149 (16), 135 (15), 133 (60), 125 (12), 118 (32)

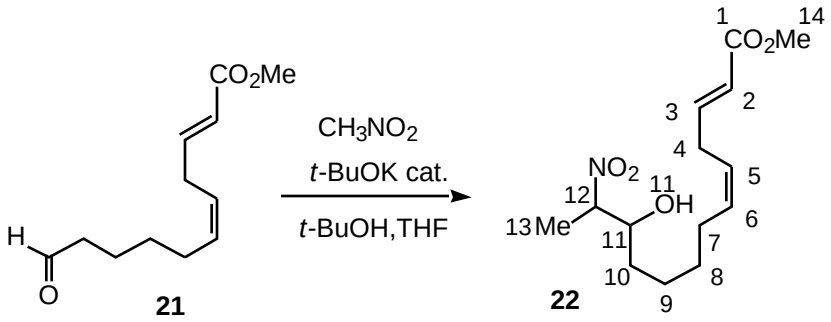
TLC: R_f 0.19 (silica gel, hexane/EtOAc, 5/1, PMA)

Analysis: $C_{12}H_{18}O_3$ (210.27)

Calculated: C: 68.55; H: 8.63%

Found: C: 68.46; H: 8.75%

Methyl (2*E*,5*Z*)-11-Hydroxy-12-nitroundeca-2,5-dienoate (22)



To a solution of aldehyde **21** (320 mg, 1.50 mmol) and nitroethane (328 μL, 4.50 mmol, 3 equiv) in *t*-BuOH/THF (1/1, 3 mL) was added *t*-BuOK (33 mg, 0.03 mmol, 0.2 equiv) at room temperature. After 15 min, the mixture was diluted with EtOAc (20 mL) and water (20 mL). The separated organic layer was washed with brine (20 mL) and the aqueous layers were back-extracted with EtOAc (2 x 25 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 2/1) to afford 380 mg (89%) of **22** as a pale yellow oil which constituted of an inseparable mixture of diastereoisomers (1/1 by ^{1}H NMR analysis).

Analytical Data for **22**:

^{1}H NMR: (500 MHz, $CDCl_3$)

6.95-6.89 (m, 1 H, HC(3)), 5.82-5.78 (m, 1 H, HC(2)), 5.52-5.34 (m, 2 H, HC(5), HC(6)), 4.52-4.43 (m, 1 H, HC(12)), 4.14-4.10 (m, 0.5 H, HC(11)), 3.93-3.85 (m, 0.5 H, HC(11)), 3.69 (s, 3 H, H_3C(14)), 2.91 (t, J = 6.5, 2 H, H_2C(4)), 2.04 (q, *J* = 6.0, 2 H, H_2C(7)), 1.53-1.35 (m, 9 H, H_3C(13)), H_2C(10), H_2C(9), H_2C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)

A: 167.2 (C(1)), 147.5 (C(3)), 132.3 (C(5)), 124.3 (C(6)), 120.9 (C(2)), 86.3 (C(12)), 72.7 (C(11)), 51.4 (C(14)), 32.9 (C(10)), 29.8 (C(4)), 29.0 (C(7)), 26.9 (C(8)), 25.3 (C(9)), 12.3 (C(13))

B: 167.2 (C(1)), 147.5 (C(3)), 132.2 (C(5)), 1214.3 (C(6)), 120.9 (C(2)), 87.7 (C(12)), 71.9 (C(11)), 51.4 (C(14)), 32.7 (C(10)), 29.8 (C(4)), 28.9 (C(7)), 26.8 (C(8)), 24.7 (C(9)), 16.0 (C(13))

IR: ($CHCl_3$)

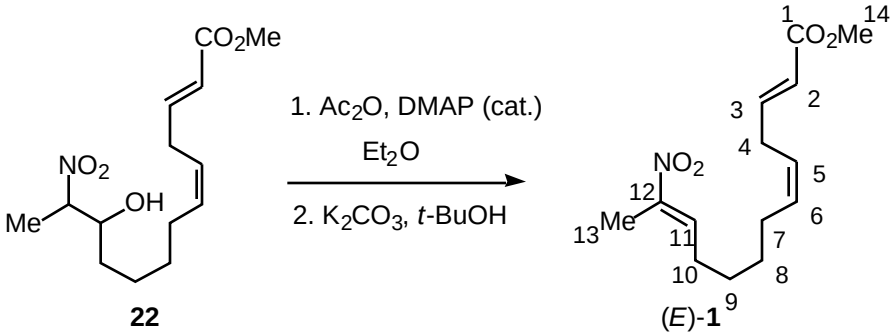
3453 (bm), 3008 (w), 2948 (m), 2859 (w), 1720 (s), 1704 (s), 1650 (m), 1548 (s), 1438 (m), 1392 (w), 1332 (w), 1280 (m), 1000 (w)

MS: FAB

286 (30, M^++H), 256 (29), 254 (28), 211 (13), 207 (13), 199 (11), 195 (15), 185 (10), 179 (28), 167 (19), 165 (20), 153 (30), 147 (27), 135 (87), 131 (21), 123 (25), 121 (50), 118 (100)

TLC: R_f 0.20 (silica gel, hexane/EtOAc, 3/1, PMA)

Methyl (2*E*,5*Z*,11*E*)-12-Nitrotrideca-2,5,11-trienoate ((*E*)-1)



22 (*E*)-**1**

To a cold (0 °C, ice bath) solution of the nitro alcohol **22** (400 mg, 1.40 mmol) and acetic anhydride (150 µL, 1.54 mmol, 1.1 equiv) in Et_2O (9 mL) was added DMAP (28 mg, 0.28 mmol, 0.2 equiv) and the mixture was allowed to warm to room temperature. After 2 h, the mixture was diluted with Et_2O (20 mL) and water (20 mL), and the separated organic layer was washed with sat. aq. $NaHCO_3$ solution (20 mL), sat. aq. NH_4Cl solution (20 mL), and brine (10 mL). The aqueous layers were back extracted with Et_2O (30 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated to afford a pale yellow oil **23** which was used in the next step without further purification.

To a solution of the nitro acetate **23** (442 mg, 1.40 mmol) in *t*-BuOH (10 mL) was added K_2CO_3 (230 mg, 1.68 mmol, 1.2 equiv) at room temperature and then was allowed to warm to

35 °C for 10 h. After being cooled to room temperature, the reaction (orange color) was quenched with water (35 mL) and the product was extracted with Et_2O (2 x 40 mL). The combined organic layers were washed with water (20 mL), brine (20 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 5/1) and distillation to afford 336 mg (90%) of (*E*)-**1** as a pale yellow oil which constituted of an inseparable mixture of isomers (5*Z*/5*E*, 91/9 by ^{1}H NMR analysis).

Analytical Data for (*E*)-**1**:

bp: 115 °C (9.0 x 10^{-5} mmHg, ABT)

^{1}H NMR: (400 MHz, $CDCl_3$)

7.11 (td, *J* = 8.0, 1.0, 1 H, HC(11)), 6.94 (td, *J* = 6.5, 15.5, 1 H, HC(3)), 5.84 (td, *J* = 1.5, 15.5, 1 H, HC(2)), 5.55-5.37 (m, 2 H, HC(5), HC(6)), 3.72 (s, 3 H, H_3C(14)), 2.93 (t, *J* = 6.5, 2 H, H_2C(4)), 2.21 (q, *J* = 7.0, 2 H, H_2C(7)), 2.15 (s, 3 H, H_3C(13)), 2.05 (q, *J* = 7.5, 2 H, H_2C(7)), 1.53-1.47 (m, 2 H, H_2C(9)), 1.43-1.37 (m, 2 H, H_2C(8))

^{13}C NMR: (126 MHz, $CDCl_3$)

167.0 (C(1)), 147.2 (C(12)), 135.9 (C(3)), 132.0 (C(6)), 127.5 (C(11)), 121.1 (C(2)), 51.4 (C(14)), 29.9 (C(8)), 29.0 (C(4)), 27.9 (C(9)), 27.8 (C(7)), 26.8 (C(10)), 12.5 (C(13))

IR: ($CHCl_3$)

3014 (w), 2933 (w), 2858 (w), 1724 (s), 1656 (w), 1519 (s), 1434 (w), 1390 (w), 1332 (s), 1274 (m), 1211 (w), 1168 (m), 1039 (w), 985 (w)

MS: FAB

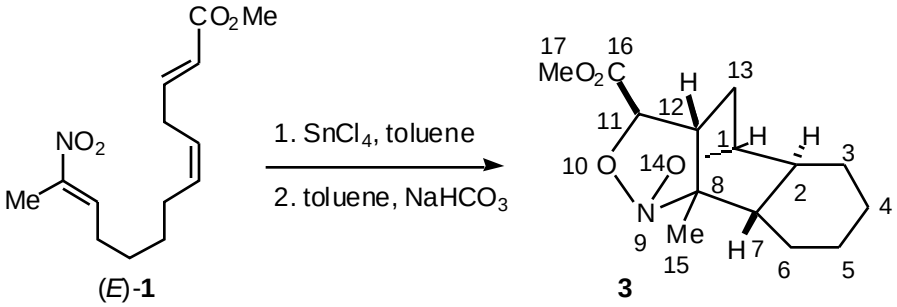
268 (38, M^++H), 195 (16), 155 (57), 152 (30), 134 (43), 118 (100)

TLC: R_f 0.26 (silica gel, hexane/EtOAc, 5/1, PMA, UV)

Analysis: $C_{14}H_{21}NO_4$ (267.32)

Calculated:	C: 62.90;	H: 7.92;	N: 5.24%
Found:	C: 62.92;	H: 8.04;	N: 5.32%

rel-(1_R_,2_S_,7_R_,8_R_,11_S_,12_S_)-8-Methyl-9-aza-10,14-dioxatetracyclo[7.4.1.0^{2,7}.0^{8,12}]tetradecane-11-carboxylate (3)



(*E*)-**1** **3**

To a cold (78 °C, dry ice bath) solution of nitroalkene (*E*)-**1** (268 mg, 1.0 mmol) in toluene (10 mL) was added $SnCl_4$ (234 μL, 2.0 mmol, 2 equiv). After 1 h, the solution was diluted with EtOAc (15 mL) and then was quenched with sat. aq. $NaHCO_3$ solution (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ solution (2 x 25 mL), brine (20 mL), then were dried ($MgSO_4$), filtered and concentrated.

The crude material was dissolved in dry toluene (10 mL), followed by addition of sodium bicarbonate (314 mg, 5.33 mmol, 5 equiv). The suspension was degassed and then was heated at 80 °C. After 1.5 h, the mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography (silica gel, CH_2Cl_2/EtOAc, 9/1) and recrystallization (Et_2O) to afford 219 mg (82%) of **3** as a white crystalline solid.

Analytical Data for **3**:

mp: 109-111 °C (Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)
4.60 (s, 1 H, HC(11)), 3.79 (brs, 4 H, H_3C(17), HC(1)), 2.76 (d, *J* = 8.5, 1 H, HC(12)), 2.16 (dd, J = 8.5, 8.5, 1 H, *H*HC(13)), 2.02 (dd, J = 6.5, 6.0, 1 H, H*H*C(13)), 1.92-1.88 (m, 2 H, *H*HC(3), *H*HC(5)), 1.82-1.80 (m, 1 H, H*H*C(3), *H*HC(6)), 1.71.1.69 (m, 1 H, *H*HC(4)), 1.64 (t, *J* = 12, 1 H, HC(2)), 1.51 (t, *J* = 10, 1 H, HC(7)), 1.42-1.29 (m, 4 H, H_2C(3), H*H*C(4), H*H*C(5), H*H*C(6)), 1.05 (s, 3 H, H_3C(15))

^{13}C NMR: (126 MHz, $CDCl_3$)
171.1 (C(16)), 85.5 (C(11)), 70.7 C(8)), 70.2 (C(1)), 52.5 (C(17)), 46.4 (C(12)), 45.9 (C(2)), 41.3 (C(7)), 31.0 (C(13)), 29.4 (C(4)), 27.8 (C(5)), 27.4 (C(3)), 26.2 (C(6)), 19.2 (C(15))

IR: ($CHCl_3$)
2927 (m), 2856 (m), 1739 (s), 1450 (m), 1373 (w), 1328 (m), 1272 (m), 1243 (s), 1022 (w), 966 (w)

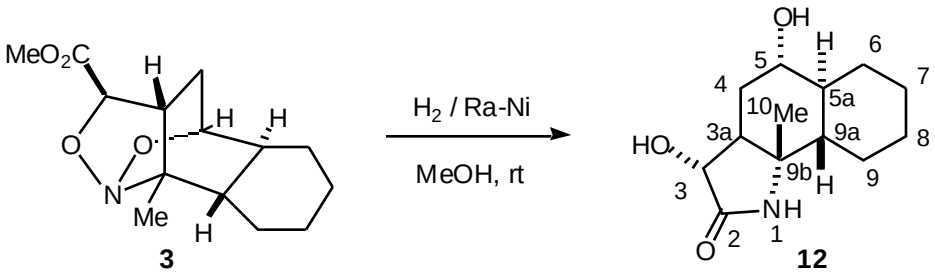
MS: FAB
268 (82, M^++H), 210 (10), 196 (6), 135 (12), 118 (21), 105 (5)

TLC: R_f 0.51 (CH_2Cl_2/EtOAc, 9/1, PMA)

Analysis: $C_{14}H_{21}NO_4$ (281.35)

Calculated:	C: 62.90;	H: 7.92;	N: 5.24%
Found:	C: 62.90;	H: 7.82;	N: 5.37%

rel-(2*R*,6*R*,7*S*,8*R*,9*R*)-3,6-Dihydroxy-9-methyldodecahydrobenzoindol-2-one (12)



To a solution of **3** (267 mg, 1.00 mmol) in MeOH (4 mL) in a glassed-lined, steel autoclave was added A5000 Raney nickel (washed 3 x 10 mL of MeOH). The autoclave was sealed, pressurized to 160 psi with H_2, and the suspension was stirred at room temperature for 12 h. Hydrogen was then carefully released from steel autoclave and the reaction mixture was filtered through a pad of Celite. The filter cake was washed with MeOH (25 mL), and the filtrate was concentrated under reduce pressure. The residue was purified by chromatography (silica gel, CH_2Cl_2/MeOH, 10/1) and recrystallization (EtOAc/MeOH) to afford 170 mg (71%) of **12** as a crystalline solid.

Analytical Data for **12**:

mp: 266-268 °C (EtOAc/MeOH)

^{1}H NMR: (500 MHz, $CDCl_3$ and CD_3OD)
4.38 (d, *J* = 6.5, 1 H, HC(3)), 2.97 (td, *J* = 12.0, 3.5, 1 H, HC(5)), 2.18 (ddd, *J* = 11.5, 6.0, 5.5, 1 H, HC(3a)), 2.00 (dapp, *J* = 13.0, 1 H, *H*HC(8)), 1.66 (m, 2 H, *H*HC(7) *H*HC(4)), 1.52-1.64 (m, 2 H, *H*HC(6), *H*HC(9)), 1.02 (s, 3 H, H_3C(10)), 1.02-0.94 (m, 2 H, H*H*C(7), H*H*C(4)), 0.91-0.77 (m, 4 H, H*H*C(6), HC(9a), HC(5a), *H*HC(9)), 0.63 (m, 1 H, *H*HC(8))

^{13}C NMR: (126 MHz, $CDCl_3$)

177.3 (C(3)), 71.7 (C(5)), 71.3 C(9b)), 56.1 (C(5a)), 47.5 (C(3a)), 45.8 (C(9a)), 43.5 (C(4)), 30.7 (C(8)), 28.5 (C(6)), 26.0 (C(9)), 25.2 (C(10)), 25.1 (C(9)), 24.9 (C(7))

IR: (KBr)

3523 (bs), 3372 (bs), 2964 (m), 2923 (m), 2863 (m), 1660 (s), 1448 (w), 1353 (w), 1253 (w), 1172 (m), 1031 (m)

MS: FAB

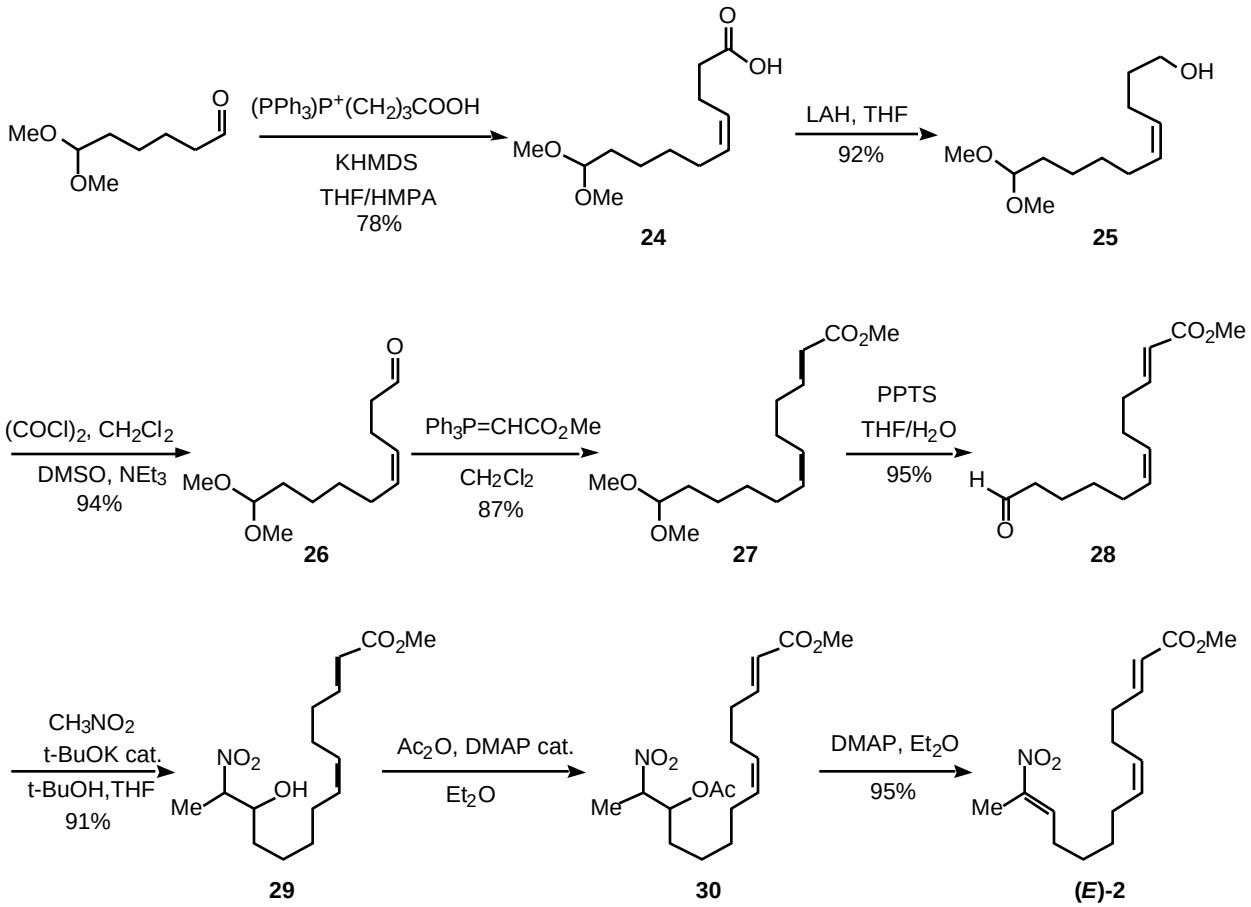
241 (100), 240 (18, M^++H), 224 (10), 223 (29) 205 (33), 195 (15), 155 (12), 152 (10), 135 (21), 127 (11), 118 (61)

TLC: R_f 0.60 (silica gel, CH_2Cl_2/MeOH, 10/1, PMA)

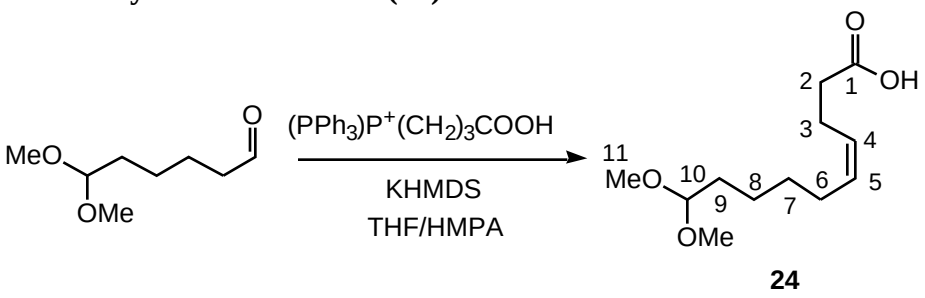
Analysis: $C_{13}H_{21}NO_3$ (239.31)

Calculated:	C: 65.25;	H: 8.84;	N: 5.85%
Found:	C: 65.22;	H: 8.84;	N: 5.96%

Preparation of Methyl (2*E*,6*Z*,12*E*)-13-Nitrotetradeca-2,6,12-trienoate ((*E*)-2)



(4*Z*)-10,10-Dimethoxy-4-decenoic Acid (24)



24

To a cold (–78 °C, internal temperature) solution of (3-carboxypropyl)triphenylphosphonium bromide[3] (8.00 g, 18.75 mmol, 1.5 equiv) in THF (100 mL) and HMPA (55 mL) was added a solution of KHMDS (0.5 M toluene, 82.50 mL, 41.25 mmol, 3.3 equiv). The mixture was stirred for 1 h at –78 °C then was allowed to warm to 0 °C for 1.5 h. Upon cooling back to –78 °C, a solution of 6,6-dimethoxyhexanal[7] (2.00 g, 12.50 mmol) in THF (100 mL) was added and the mixture was stirred for 30 min at 0 °C and then was allowed to warm

to room temperature for 3 h. The reaction was quenched with sat. aq. NH_4Cl solution (150 mL), then was diluted with Et_2O (70 mL) and the pH was adjusted to pH 6 with a solution of hydrochloric acid (0.1 M) and was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (100 mL), brine (50 mL) and the combined extracts were dried ($MgSO_4$). After removal of the solvent under reduced pressure, the residue was purified by chromatography (silica gel, hexane/Et_2O, 2/1) and distillation to afford 2.23 g (78%) **24** as a colorless oil which constituted of an inseparable mixture of isomers (*Z*/*E*, 92/8 by ^1H NMR analysis).

Analytical Data for **24**:

bp: 120 °C (0.65 mmHg, ABT)

^1H NMR: (500 MHz, $CDCl_3$)
5.43-5.31 (m, 2 H, HC(4), HC(5)), 4.36 (t, J = 6.0, 1 H, HC(10)), 3.30 (s, 6 H, 2 H_3C(11)), 2.39-2.34 (m, 4 H, H_2C(6), H_2C(3)), 2.06-2.02 (m, 2 H, H_2C(2)), 1.58 (dt, J = 6.0, 7.5, 2 H, H_2C(9)), 1.32-1.35 (m, 4 H, H_2C(7), H_2C(8))

^{13}C NMR: (126 MHz, $CDCl_3$)
178.8 (C(1)), 131.3 (C(4)), 127.3 (C(5)), 104.4 (C(10)), 52.50 (C(11)), 34.0 (C(2)), 32.2 (C(3)), 29.3 (C(6)), 26.9 (C(9)), 24.1 (C(7)), 22.5 (C(8))

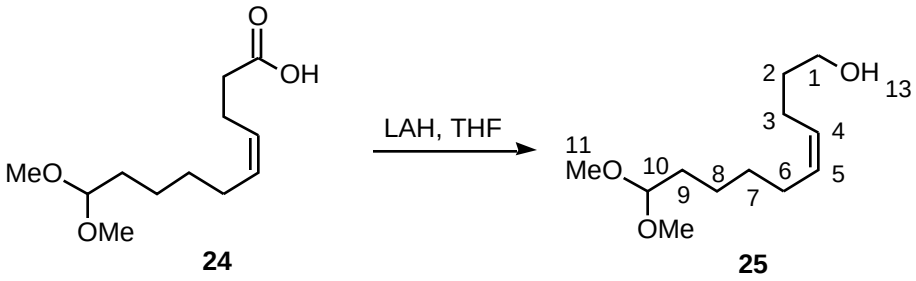
IR: ($CHCl_3$)
2943 (m), 2860 (w), 1710 (s), 1447 (w), 1207 (w), 1127 (m), 1073 (w), 959 (w)

MS: FAB
229 (28, M^+-H), 153 (100), 134 (13), 116 (20)

TLC: R_f 0.28 (silica gel, hexane/Et_2O, 2/1, PMA)

Analysis: $C_{12}H_{22}O_4$ (230.30)
Calculated: C: 62.58; H: 9.63%
Found: C: 62.44; H: 9.65%

(4*Z*)-10,10-Dimethoxy-4-decen-1-ol (25)



24 **25**

To a suspension of lithium aluminum hydride (0.30 g, 5.20 mmol, 1.2 equiv) in THF (10 mL) was added a solution of **24** (1.0 g, 4.34 mmol) in THF (2 mL) at room temperature. The

mixture was stirred for 4 h at room temperature then was cooled to 0 °C and was quenched with sat. aq. NH_4Cl solution (20 mL) and then was diluted with Et_2O (10 mL). The ether layer was separated and the aqueous phase was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (20 mL), brine (20 mL) and the combined extracts were dried ($MgSO_4$). After removal of the solvent under reduced pressure, the residue was purified by chromatography (silica gel, hexane/EtOAc, 3/2) to afford 0.90 g (91%) of **25** as a colorless oil which constituted of an inseparable mixture of isomers (*Z*/*E*, 92/8 by ^1H NMR analysis).

Analytical Data for **25**:

^{1}H NMR: (500 MHz, $CDCl_3$)

5.36-5.37 (m, 2 H, HC(4), HC(5)), 4.33 (t, *J* = 6.0, 1 H HC(10)), 3.61 (t, *J* = 6.5, 2 H, H_2C(1)), 3.28 (s, 6 H, 2 H_3C(11)), 2.11-2.07 (m, 2 H, H_2C(3)), 2.04-2.00 (m, 2 H, H_2C(6)), 1.82 (s, 1 H, HC(13)), 1.62-1.55 (m, 4 H, H_2C(2), HC(9)), 1.35-1.30 (m, 4 H, H_2C(7), H_2C(8))

^{13}C NMR: (126 MHz, $CDCl_3$)

130.1 (C(4)), 129.1 (C(5)), 104.5 (C(10)), 62.30 (C(1)), 52.50 (C(11)), 32.5 (C(2)), 32.2 (C(3)), 29.2 (C(6)), 26.9 (C(9)), 24.1 (C(7)), 23.5 (C(8))

IR: ($CHCl_3$)

3411 (bm), 2934 (m), 2860 (w), 1459 (w), 1266 (m), 1127 (w), 1068 (w)

MS: FAB

185 (28, M^+-31), 153 (100), 135 (70), 84 (26), 71 (54)

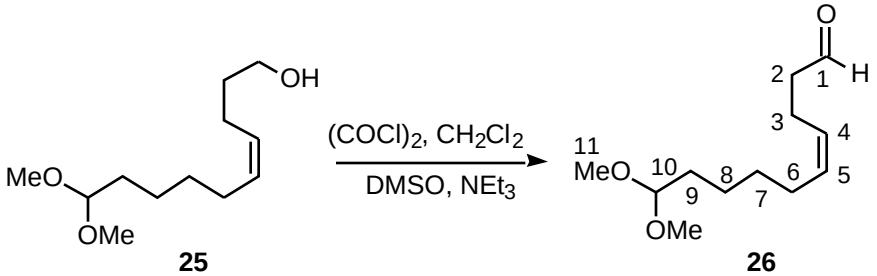
TLC: R_f 0.32 (silica gel, hexane/EtOAc, 3/2, PMA)

Analysis: $C_{12}H_{24}O_3$ (216.32)

Calculated: C: 66.63; H: 11.18%

Found: C: 66.65; H: 10.95%

(4*Z*)-10,10-Dimethoxy-4-decenal (26)



25 **26**

To a cold (–78 °C, dry ice bath) solution of oxalyl chloride (0.601 mL, 6.80 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL) was added a solution of DMSO (0.980 mL, 13.60 mmol, 2.2 equiv) in CH_2Cl_2 (2 mL). After being stirred for 30 min at –78 °C, a solution of **25** (1.38 g, 6.18 mmol) in CH_2Cl_2 (5 mL) was added and the mixture was stirred for 1 h at –78 °C. Then triethylamine (4.12

mL, 28.42 mmol, 4.6 equiv) was added and the reaction was allowed to warm to room temperature for 1 h. The resulting white suspension was quenched with sat. aq. NH_4Cl solution (20 mL). The product was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (20 mL), sat. aq. $NaHCO_3$ solution (20 mL) and brine (20 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 2/1) and distillation to afford 1.20 g (91%) of **26** as a colorless oil which constituted of an inseparable mixture of isomers (*Z*/*E*, 92/8 by ^{1}H NMR analysis).

Analytical Data for **26**:

bp: 65 °C (3.0 x 10^{-5} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
9.74 (t, *J* = 2, 1 H, HC(1)), 5.40-5.29 (m, 2 H, HC(4), HC(5)), 4.32 (t, *J* = 6.0, 1 H, HC(10)), 3.27 (s, 6 H, 2 H_3C(11)), 2.45 (td, *J* = 7.0, 2, 2 H, HC(2)), 2.35-2.31 (m, 2 H, H_2C(3)), 2.03 (q, *J* = 6.0, 2 H, H_2C(6)), 1.56 (q, *J* = 6.0, 2 H, H_2C(9)), 1.36-1.30 (m, 4 H, H_2C(7), H_2C(8))

^{13}C NMR: (126 MHz, $CDCl_3$)
202.1 (C(1)), 131.2 (C(4)), 127.3 (C(5)), 104.4 (C(10)), 52.5 (C(11)), 43.7 (C(2)), 32.3 (C(3)), 29.3 (C(6)), 27.0 (C(9)), 25.0 (C(7)), 19.9 (C(8))

IR: ($CHCl_3$)
2943 (m), 2830 (w), 2720 (w), 1725 (m), 1452 (w), 1387 (w), 1128 (m), 1073 (m), 958 (w)

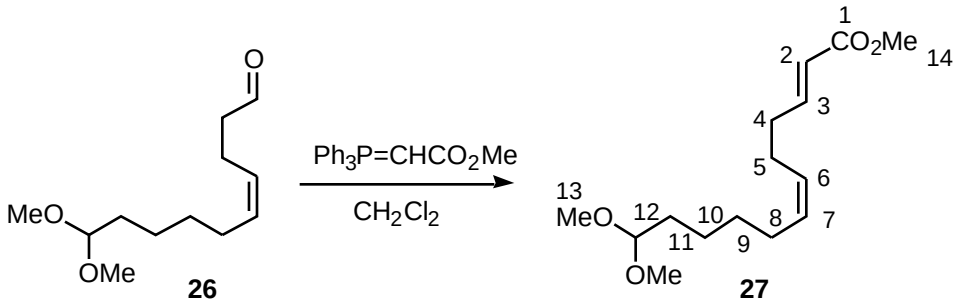
MS: FAB
183 (35, M^+-31), 156 (16), 154 (81), 151 (22), 137 (59), 135 (100), 123 (12), 119 (17), 106 (37)

TLC: R_f 0.21 (silica gel, hexane/EtOAc, 2/1, PMA)

Analysis: $C_{12}H_{22}O_3$ (214.30)

Calculated:	C: 67.26;	H: 10.35%
Found:	C: 67.33;	H: 10.16%

Methyl (2*E*,6*Z*)-12,12-Dimethoxydodeca-2,6-dienoate (27)



To a solution of **26** (1.06 g, 4.95 mmol) in CH_2Cl_2 (45 mL) was added (methoxycarbonylmethylene)triphenylphosphorane (2.5 g, 7.42 mmol, 1.5 equiv) in one portion. The solution was heated to reflux for 2 h. Then another portion of (methoxycarbonylmethylene)triphenylphosphorane (1.6 g, 4.95 mmol, 1.0 equiv) was added and the reaction was heated at reflux for an additional 2 h. After being cooled to room temperature, the reaction was quenched with water (40 mL). The solution was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic extracts were washed with brine (25 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 2/1) and distillation to afford 1.20 g (90%) of **27** as a colorless oil which constituted of an inseparable mixture of isomers (6*Z*/6*E*, 92/8 by ^{1}H NMR analysis).

Analytical Data for **27**:

bp: 105 °C (8.5 x 10^{-5} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
6.96 (td, *J* = 6.5, 15.5, 1 H, HC(3)), 5.82 (td, *J* = 15.5, 1, 1 H, HC(2)), 5.43-5.30 (m, 2 H, HC(6), HC(7)), 4.35 (t, *J* = 6.0, 1 H, HC(12)), 3.72 (s, 3 H, H_3C(4')), 3.30 (s, 6 H, 2 H_3C(13)), 2.27-2.16 (m, 4 H, H_2C(5), H_2C(4)), 2.02 (q, *J* = 6.5, 2 H, H_2C(8)), 1.62-1.57 (m, 2 H, H_2C(11)), 1.36-1.32 (m, 4 H, H_2C(9), H_2C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)
166.7 (C(1)), 148.6 (C(3)), 130.7 (C(6)), 128.4 (C(7)), 121.0 (C(2)), 104.2 (C(12)), 52.0 (C(13)), 51.1 (C(14)), 32.1 (C(4)), 32.0 (C(5)), 29.2 (C(8)), 26.9 (C(11)), 25.5 (C(9)), 24.0 (C(10))

IR: ($CHCl_3$)
2944 (m), 2858 (w), 1726 (s) 1658 (m), 1436 (m), 1271 (m), 1201 (m), 1128 (m), 1051 (m), 965 (w)

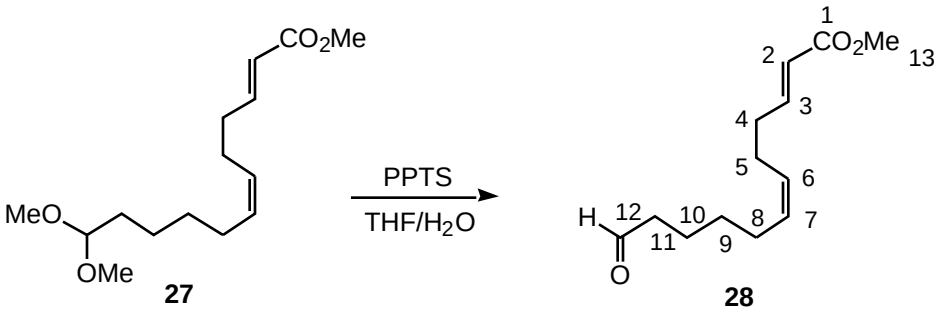
MS: FAB
271 (6, M^++H), 241 (18), 239 (16), 207 (17)

TLC: R_f 0.61 (silica gel, hexane/EtOAc, 2/1, PMA)

Analysis: $C_{15}H_{26}O_4$ (270.37)

Calculated:	C: 66.64;	H: 9.69%
Found:	C: 66.43;	H: 9.86%

Methyl (2*E*,6*Z*)-12-Oxododeca-2,6-dienoate (28)



To a solution of **27** (1.20 g, 4.44 mmol) in THF/H_2O (60 mL) was added pyridinium *p*-toluenesulfonic acid (6.0 g, 22.22 mmol, 5 equiv) at room temperature and the solution was warmed to 45 °C for 3 h. The reaction was then diluted with water (20 mL) and Et_2O (25 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (30 mL), brine (25 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 4/1) and distillation to afford 0.945 g (95%) of **28** as a colorless oil which constituted of an inseparable mixture of isomers (6*Z*/6*E*, 92/8 by 1H NMR analysis).

Analytical Data for 28:

bp: 103 °C (2.4 x 10^{-5} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

9.73 (t, *J* = 1.5, 1 H, HC(12), 6.95-6.89 (m, 1 H, HC(3)), 5.80 (td, *J* = 1.5, 15.5, 1 H, HC(2)), 5.38-5.32 (m, 2 H, HC(6), HC(7)), 3.69 (s, 3 H, H_3C(13)), 2.40 (td, *J* = 7.5, 1.5, 2 H, H_2C(11)), 2.25-2.14 (m, 4 H, H_2C(4), H_2C(5)), 2.01 (q, *J* = 7.0, 2 H, H_2C(8)), 1.63-1.57 (m, 2 H, H_2C(9)), 1.39-1.34 (m, 2 H, H_2C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)

202.3 (C(12)), 166.7 (C(1)), 148.5 (C(3)), 130.2 (C(6)), 128.1 (C(7)), 121.0 (C(2)), 51.1 (C(13)), 43.4 (C(11)), 31.9 (C(4)), 28.7 (C(5)), 26.7 (C(8)), 25.5 (C(9)), 21.3 (C(10))

IR: ($CDCl_3$)

3007 (w), 2942 (m), 2858 (w), 2720 (w), 1724 (s), 1658 (m), 1437 (m), 1273 (m), 1205 (m), 1171 (m), 1040 (w), 977 (w)

MS: FAB

225 (24, M++H), 241 (18), 209 (12), 193 (65), 191 (23), 181 (10), 175 (16), 167 (17), 165 (13), 152 (18), 151 (19), 149 (14), 147 (50), 131 (19), 118 (100)

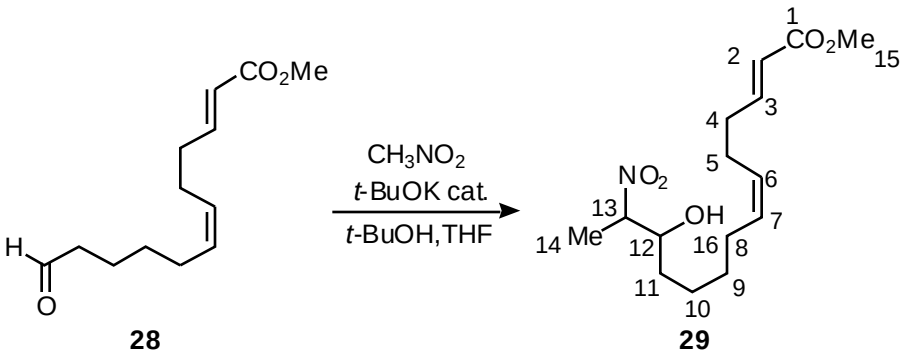
TLC: R_f 0.37 (silica gel, hexane/EtOAc, 4/1, PMA)

Analysis: $C_{13}H_{20}O_3$ (224.30)

Calculated: C: 69.61; H: 8.99%

Found: C: 69.45; H: 8.98%

Methyl (2*E*,6*Z*)-12-Hydroxy-13-nitrododeca-2,6-dienoate (29)



28 **29**

To a solution of aldehyde **28** (770 mg, 3.43 mmol) and nitroethane (740 μL, 10.30 mmol, 3 equiv) in *t*-BuOH/THF (1/1, 7 mL) was added *t*-BuOK (76 mg, 0.68 mmol, 0.2 equiv) at room temperature. After 15 min, the mixture was diluted with EtOAc (30 mL) and water (30 mL). The separated organic layer was washed with brine (20 mL) and the aqueous layers were back-extracted with EtOAc (2 x 25 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 2/1) to afford 950 mg (93%) of **29** as a pale yellow oil which constituted of an inseparable mixture of diastereoisomers (1/1 by ^{1}H NMR analysis).

Analytical Data for **29**:

^{1}H NMR: (500 MHz, $CDCl_3$)

6.94 (td, J = 6.5, 16.0, 1 H, HC(3)), 5.83 (td, J = 1.5, 16.0, 1 H, HC(2)), 5.40-5.31 (m, 2 H, HC(6), HC(7)), 4.56-4.46 (m, 1 H, HC(13)), 4.17-4.13 (m, 0.5 H, HC(12)), 3.93-3.86 (m, 0.5 H, HC(12)), 3.71 (s, 3 H, H_3C(15)), 2.68-2.65 (m, 1 H, HC(16)), 2.29-2.25 (m, 4 H, H_2C(4), H_2C(5)), 2.04 (q, J = 7.0, 2 H, H_2C(8)), 1.54 (d, J = 6.0, 3 H, H_3C(14)), 1.53-1.33 (m, 6 H, H_2C(9), H_2C(10), H_2C(11))

^{13}C NMR: (126 MHz, $CDCl_3$)

Major: 167.3 (C(1)), 149.2 (C(3)), 130.7 (C(6)), 128.2 (C(7)), 121.0 (C(2)), 86.4 (C(13)), 72.6 (C(12)), 51.4 (C(15)), 33.0 (C(11)), 32.0 (C(4)), 29.1 (C(5)), 27.0 (C(8)), 25.6 (C(9)), 25.3 (C(10)), 12.4 (C(14))

Minor: 167.3 (C(1)), 149.2 (C(3)), 130.8 (C(6)), 128.2 (C(7)), 121.0 (C(2)), 87.7 (C(13)), 71.9 (C(12)), 51.3 (C(14)), 32.8 (C(11)), 32.0 (C(4)), 29.1 (C(5)), 29.0 (C(8)), 25.6 (C(9)), 25.8 (C(10)), 16.0 (C(14))

IR: ($CHCl_3$)

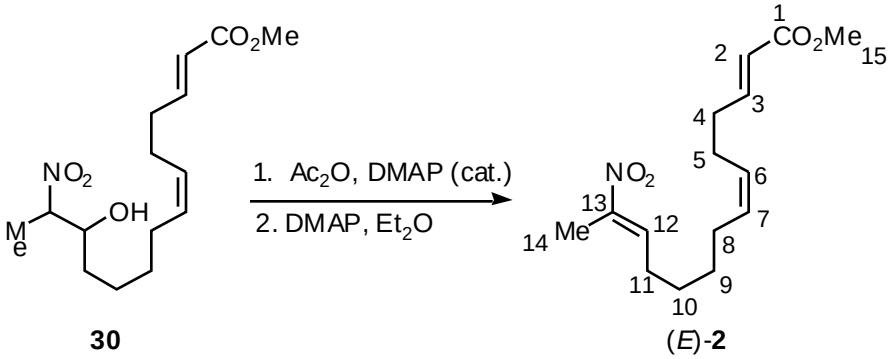
3443 (bm), 3005 (w), 2942 (m), 2858 (w), 1723 (s), 1658 (m), 1549 (s), 1438 (m), 1288 (m), 1207 (m), 1039 (w), 977 (w)

MS: FAB

300 (42, M^++H), 268 (15), 240 (7), 195 (13), 193 (13), 175 (9), 167 (10), 155 (20), 154 (10), 153 (24), 152 (34), 137 (14), 134 (66), 118 (100)

TLC: R_f 0.25 (silica gel, hexane/EtOAc, 2/1, PMA)

Methyl (2*E*,6*Z*,12*E*)-13-nitrotetradeca-2,6,12-trienoate ((*E*)-2)



30 (*E*)-**2**

To a cold (0 °C, ice bath) solution of the nitro alcohol **30** (700 mg, 2.34 mmol) and acetic anhydride (245 µL, 2.57 mmol, 1.1 equiv) in Et_2O (17 mL) was added DMAP (57 mg, 0.46 mmol, 0.2 equiv) and the mixture was allowed to warm to room temperature. After 2 h, the mixture was diluted with Et_2O (20 mL) and water (20 mL), and the separated organic layer was washed with sat. aq. $NaHCO_3$ solution (20 mL), sat. aq. NH_4Cl solution (20 mL), and brine (10 mL). The aqueous layers were back extracted with Et_2O (30 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated to afford a pale yellow oil which was used in the next step without further purification.

To a solution of the nitro acetate **31** (800 mg, 2.34 mmol) in Et_2O (15 mL) was added DMAP (342 mg, 2.76 mmol, 1.2 equiv) at 0 °C (ice water bath) and then was allowed to warm to room temperature. After 8 h, the reaction was quenched with water (20 mL) and the product was

extracted with Et_2O (2 x 25 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (30 mL), brine (20 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 4/1) and distillation to afford 620 mg (95%) of (*E*)-**2** as a pale yellow oil which constituted of an inseparable mixture of isomers (6*Z*/6*E*, 92/8 by ^1H NMR analysis).

Analytical Data for (*E*)-**2**:

bp: 130 °C (8.5×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, $CDCl_3$)

7.11 (td, *J* = 8.0, 1.0, 1 H, HC(12)), 6.94 (td, *J* = 6.5, 16.0, 1 H, HC(3)), 5.82 (td, *J* = 6.5, 16.0, 1 H, HC(2)), 5.39-5.33 (m, 2 H, HC(6), HC(7)), 3.71 (s, 3 H, H_3C(15)), 2.27-2.14 (m, 6 H, H_2C(11), H_2C(5), H_2C(4)), 2.16 (s, 3 H, H_3C(14)), 2.03 (q, *J* = 7.0, 2 H, H_2C(8)), 1.51-1.47 (m, 2 H, H_2C(10)), 1.42-1.37 (m, 2 H, H_2C(9))

^{13}C NMR: (126 MHz, $CDCl_3$)

166.8 (C(1)), 148.5 (C(3)), 147.4 (C(13)), 135.9 (C(12)), 130.2 (C(6)), 128.9 (C(7)), 120.9 (C(2)), 51.1 (C(15)), 31.9 (C(4)), 28.9 (C(5)), 27.8 (C(8)), 27.6 (C(11)), 26.7 (C(9)), 25.5 (C(10)), 12.2 (C(14))

IR: ($CHCl_3$)

2935 (m), 2859 (m), 1723 (s), 1658 (m), 1519 (m), 1436 (w), 1332 (w), 1271 (w), 1204 (w), 974 (w)

MS: FAB

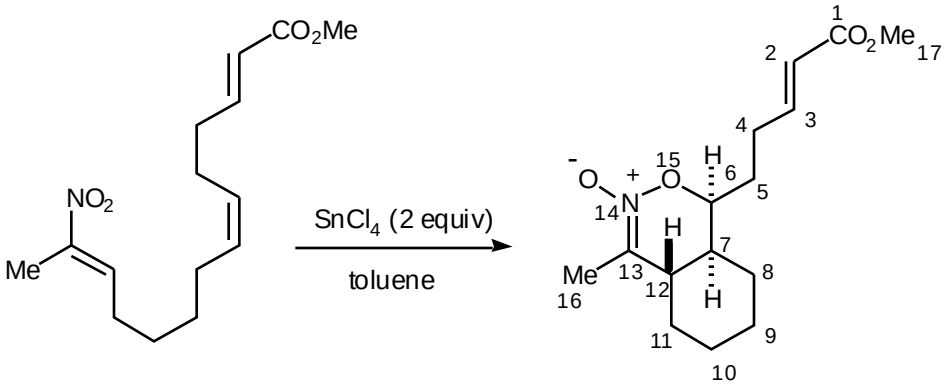
282 (82, M^++H), 250 (100), 175 (13), 155 (14), 152 (45), 147 (30), 137 (11), 134 (57), 121 (25), 118 (65), 112 (10), 106 (26)

TLC: R_f 0.31 (silica gel, hexane/EtOAc, 4/1, PMA)

Analysis: $C_{15}H_{23}NO_4$ (281.35)

Calculated:	C: 64.04;	H: 8.24;	N: 4.98%
Found:	C: 63.89;	H: 8.27;	N: 5.02%

rel-(3a_R_,7a_R_,8_R_)-Methyl-2_E_-5-[8-(3-methyl-2-oxido-3a,4,5,6,7,7a-hexahydro-4_H_-1,2-benzoxazinyl)]-2-pentenoate (4)



(*E*)-**2** **4**

To a cold (–78 °C, dry ice bath) solution of nitroalkene (*E*)-**2** (730 mg, 2.60 mmol) in toluene (20 mL) was added $SnCl_4$ (600 μL, 5.20 mmol, 2 equiv). After 2 h, the solution was diluted with EtOAc (25 mL) and then was quenched with a 1 N solution of triethylamine in MeOH (25 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (2 x 25 mL), brine (20 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, EtOAc) and recrystallization (Et_2O) to afford 720 mg (98%) of **4** as a white, crystalline solid.

Analytical Data for **4**:

mp: 82-83 °C (Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.91 (td, *J* = 6.5, 16, 1 H, HC(3)), 5.85 (td, *J* = 1.0, 16.0, 1 H, HC(2)), 4.22 (td, *J* = 1.0, 11.5, 1 H, HC(6)), 3.69 (s, 3 H, H_3C(17)), 2.60-2.54 (m, 2 H, HC(4)), 2.35 (td, *J* = 15.5, 7.5, 1 H, HC(12)), 2.02-1.98 (m, 2 H, H_2C(5)), 1.99 (s, 3 H, H_3C(16)), 1.91-1.79 (m, 2 H, H_2C(8)), 1.76-1.71 (m, 1 H, *H*HC(11)), 1.71-1.66 (m, 1 H, HC(7)), 1.55-1.49 (m, 1 H, H*H*C(11)), 1.35-1.21 (m, 2 H, *H*HC(9), *H*HC(10)), 1.17-1.10 (m, 1 H, H*H*C(9)), 1.07-1.00 (m, 1 H, H*H*C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)

166.8 (C(1)), 147.6 (C(3)), 123.1 (C(11)), 121.9 (C(2)), 82.7 (C(6)), 51.4 (C(17)), 39.6 (C(12)), 38.0 (C(5)), 29.2 (C(4)), 28.3 (C(5)), 27.7 (C(11)), 25.8 (C(8)), 25.6 (C(10)), 25.4 (C(9)), 15.2 (C(16))

IR: (KBr)
3054 (w), 2936 (m), 2860 (w), 1722 (s), 1658 (m), 1600 (m), 1437 (w), 1268 (m), 1209 (w), 1167 (w), 1122 (w), 983 (w)

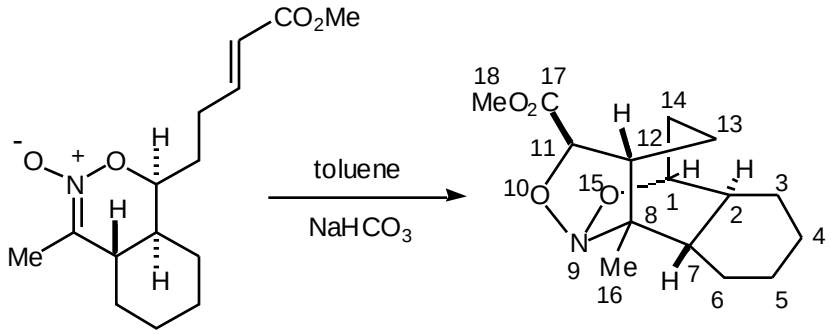
MS: FAB
282 (100, M^++H), 266 (17), 251 (31), 219 (5), 177 (7), 135 (11)

TLC: R_f 0.32 (silica gel, EtOAc, PMA)

Analysis: $C_{15}H_{23}NO_4$ (281.35)

Calculated:	C: 64.04;	H: 8.24%
Found:	C: 63.91;	H: 8.27%

rel-(1_R_,2_S_,7_R_,8_R_,11_S_,12_S_)-8-Methyl-9-aza-10,14-dioxatetracyclo[7.5,1.0^{2,7}.0^{8,12}]pentadecane-11-carboxylate (5)



4 **5**

To a solution of **4** (300 mg, 1.06 mmol) in dry toluene (10 mL) was added sodium bicarbonate (314 mg, 5.33 mmol, 5 equiv). The suspension was degassed and then was heated at 100 °C. After 3 days, the mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography (silica gel, CH_2Cl_2/EtOAc, 9/1) and recrystallization (Et_2O) to afford 132 mg (44%) of **5** as a white solid along with 120 mg (40%) of recovered **4**.

Analytical Data for **5**:

mp: 150-152 °C (Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

4.62 (d, *J* = 5.0, 1 H, HC(11)), 4.02 (q, *J* = 3.0, 1 H, HC(1)), 3.69 (s, 3 H, H_3C(18)), 2.56 (td, *J* = 3.5, 5.0, 1 H, HC(12)), 2.12-2.09 (m, 1 H, HC(2)), 1.95-1.89 (m, 4 H, *H*HC(3), HC(7), *H*HC(13), *H*HC(14)), 1.83-1.81 (m, 2 H, H*H*C(3), *H*HC(6)), 1.78-1.71 (m, 2 H, H*H*C(13), H*H*C(14)), 1.65-1.63 (m, 1 H, H_2C(6)), 1.40-1.27 (m, 3 H, *H*HC(4), H_2C(5)), 1.19 (s, 3 H, H_3C(16)), 1.16-1.13 (m, 1 H, H*H*C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)

171.5 (C(17)), 80.6 (C11)), 74.3 C(1)), 54.9 (C(8)), 52.4 (C(18)), 44.0 (C(12)), 40.4 (C(14)), 30.42 (C(2)), 29.7 (C(7)), 27.6 (C(11)), 27.4 (C(3)), 26.4 (C(13)), 23.9 (C(16)), 23.6 (C(5)), 23.5 (C(4))

IR: ($CHCl_3$)

2917 (m), 2852 (w), 1750 (s), 1438 (w), 1210 (m), 1014 (w), 957 (w)

MS: FAB

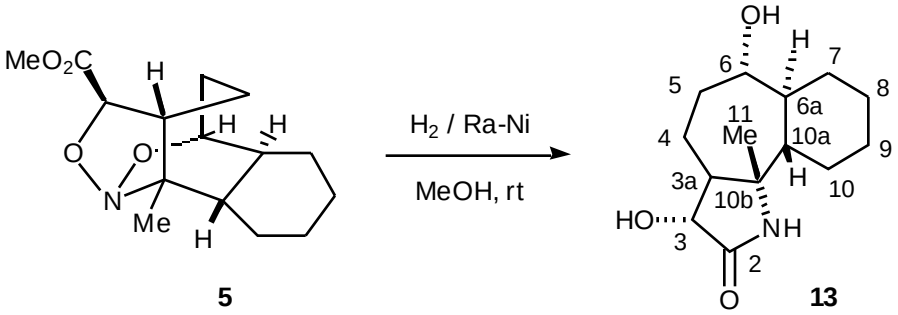
282 (100, M^++H), 135 (7), 132 (90), 119 (7)

TLC: R_f 0.63 (CH_2Cl_2/EtOAc, 9/1, PMA)

Analysis: $C_{15}H_{23}NO_4$ (281.35)

Calculated:	C: 64.04%	H: 8.24%	N: 4.98%
Found:	C: 64.02%	H: 8.44%	N: 5.07%

***rel*-(2*R*,7*R*,7*S*,8*R*,9*R*)-3,7-Dihydroxy-10-methyldodecahydro-1-azabenzoazulen-2-one (13)**



To a solution of **5** (285 mg, 1.01 mmol) in MeOH (5 mL) in a glassed-lined, steel autoclave was added A5000 Raney Nickel (washed 3 x 10 mL MeOH). The autoclave was sealed, pressurized to 160 psi with H_2, and the suspension was stirred at room temperature for 12 h. Hydrogen was then carefully released from steel autoclave and the reaction mixture was filtered through a pad of Celite. The filter cake was washed with MeOH (25 mL), and the filtrate was

concentrated under reduce pressure. The residue was purified by chromatography (silica gel, CH_2Cl_2/MeOH, 10/1) and recrystallization (EtOAc/MeOH) to afford 200 mg (78%) of **13** as a crystalline solid.

Analytical Data for **13**:

mp: 209-211 °C (EtOAc/MeOH)

^{1}H NMR: (500 MHz, $CDCl_3$)
4.44 (d, *J* = 10.5, 1 H, HC(3)), 2.99 (td, *J* = 12.0, 6.0, 1 H, HC(6)), 2.28 (ddd, *J* = 10.5, 5.0, 5.5, 1 H, HC(3a)), 2.21 (dd, *J* = 3.0, 16.0, 1 H, HC(6a)), 1.84 (td, *J* = 16.5, 4.0, 1 H, HC(10a)), 1.76 (ddd, *J* = 11.5, 5.0, 5.5, 1 H, *H*HC(4)), 1.66-1.59 (m, 2 H, *H*HC(5), *H*HC(8)), 1.52 (dd, *J* = 10.5, 5.5, 1 H, *H*HC(7)), 1.42 (td, *J* = 15.0, 5.0, 1 H, *H*HC(10)), 1.35-1.20 (m, 3 H, H*H*C(4), H*H*C(5), *H*HC(9)), 1.10 (s, 3 H, H_3C(11)), 1.10-1.01 (m, 2 H, H*H*C(8), H*H*C(9)), 0.94-0.81 (m, 2 H, H*H*C(7), H*H*C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)
177.5 (C(2)), 77.8 (C(3)), 69.7 C(6)), 61.7 (C(10b)), 49.7 (C(3a)), 43.8 (C(6a)), 41.7 (C(10a)), 31.7 (C(5)), 31.3 (C(4)), 29.1 (C(10)), 27.5 (C(7)), 26.0 (C(9)), 24.0 (C(8)), 19.1 (C(11))

IR: (KBr)
3394 (bm), 3123 (bm), 2935 (m), 2845 (w), 1686 (s), 1447 (m), 1374 (w), 1244 (m), 1040 (m), 949 (w)

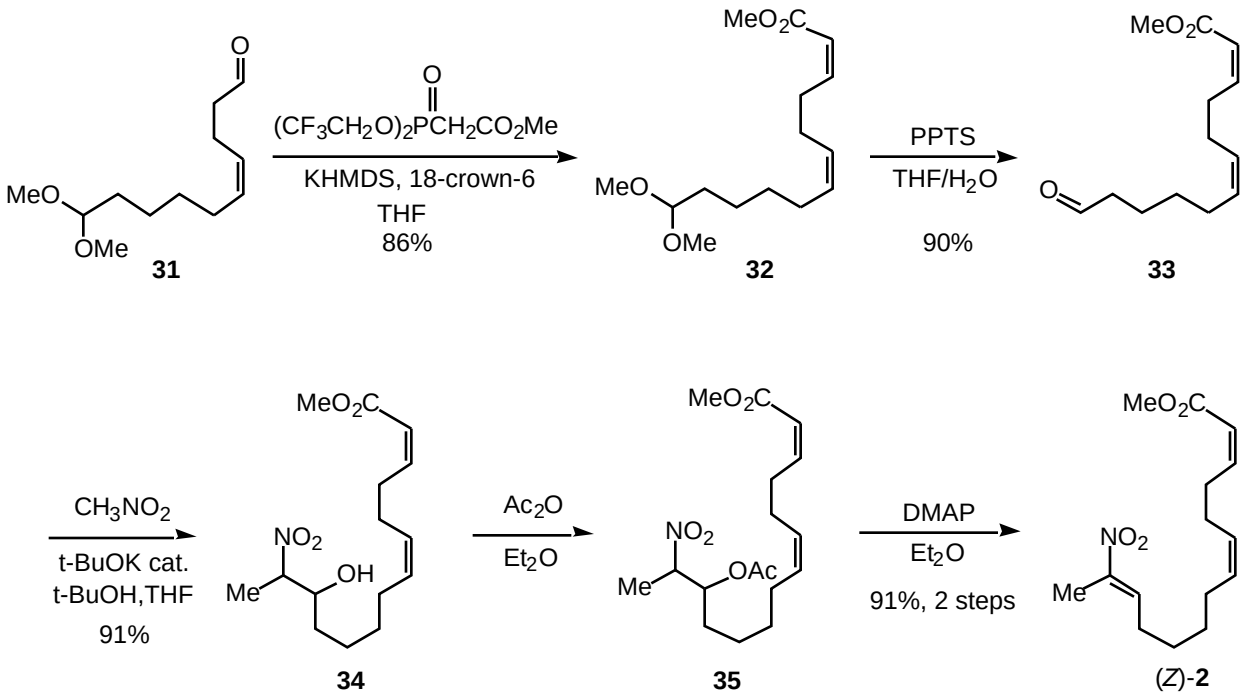
MS: FAB
254 (100, $M+H^+$), 236 (40), 195 (14), 155 (40), 154 (15), 153 (14), 152 (27), 135 (36), 120 (12), 118 (86)

TLC: R_f 0.63 (silica gel, CH_2Cl_2/MeOH, 10/1, PMA)

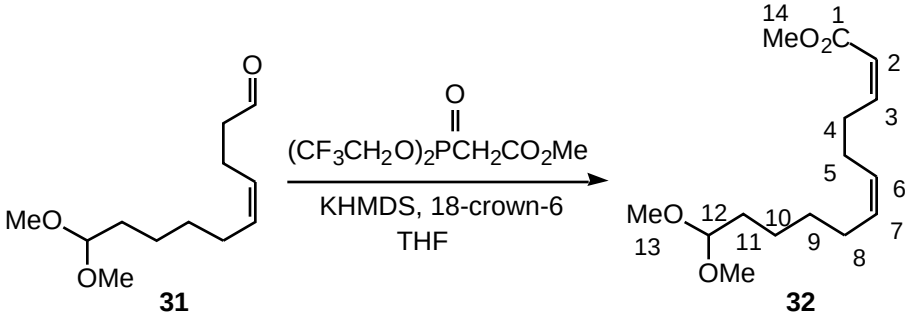
Analysis: $C_{14}H_{23}NO_3$ (253.34)

Calculated:	C: 66.37;	H: 9.15;	N: 5.53%
Found:	C: 66.13;	H: 9.11;	N: 5.60%

Preparation of Methyl (2*Z*,6*Z*,12*E*)-13-Nitrotetradeca-2,6,12-trienoate ((*Z*)-2)



Methyl (2*Z*,6*Z*)-12,12-Dimethoxydodeca-2,6-dienoate (32)



To a cold solution (–78 °C, internal temperature) of bis-(2,2,2-trifluoroethyl)-(methoxycarbonylmethyl)phosphonate (1.45 g, 4.5 mmol, 1.5 equiv), 18-crown-6 (4.00 g, 15 mmol, 5 equiv) in THF (36 mL) was added a solution of KHMDS (0.5 M toluene, 6 mL, 3 mmol, 1 equiv). After 30 min, a solution of aldehyde **31** (650 mg, 3 mmol) in THF (2 mL) was added and the mixture was stirred 2 h at –78 °C (internal temperature). The solution was diluted with Et_2O (40 mL) and quenched with water (25 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 25 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (25 mL), brine (20 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 2/1) to afford 700 mg (86%) of

32 as a colorless oil which constituted of an inseparable mixture of isomers (6*Z*/6*E*, 92/8 by ^{1}H NMR analysis).

Analytical Data for **32**:

bp: 103 °C (2.3 x 10^{-5} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
6.20 (td, *J* = 7.5, 11.5, 1 H, HC(3)), 5.76 (tdd, *J* = 15.0, 11.5, 0.5, 1 H, HC(2)), 5.41-5.32 (m, 2 H, HC(6), HC(7)), 4.33 (t, *J* = 5.5, 1 H, HC(12)), 3.69 (s, 3 H, H_3C(14)), 3.29 (s, 6 H, 2 H_3C(13)), 2.68 (qd, *J* = 7.5, 1.5, 2 H, H_2C(4)), 2.16 (q, *J* = 6.5, 2 H, H_2C(5)), 2.02 (q, *J* = 6.5, 2 H, H_2C(8)), 1.60-1.56 (m, 2 H, H_2C(11)), 1.37-1.31 (m, 4 H, H_2C(9), H_2C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)
166.7 (C(1)), 150.0 (C(3)), 130.7 (C(6)), 128.5 (C(7)), 119.5 (C(2)), 104.4 (C(12)), 52.5 (C(13)), 50.9 (C(14)), 32.3 (C(4)), 29.4 (C(5)), 28.9 (C(8)), 27.1 (C(11)), 26.5 (C(9)), 24.2 (C(10))

IR: ($CHCl_3$)
2946 (m), 2831 (w), 1724 (s) 1645 (m), 1439(m), 1199 (m), 1172 (m), 1128 (m), 1053 (m)

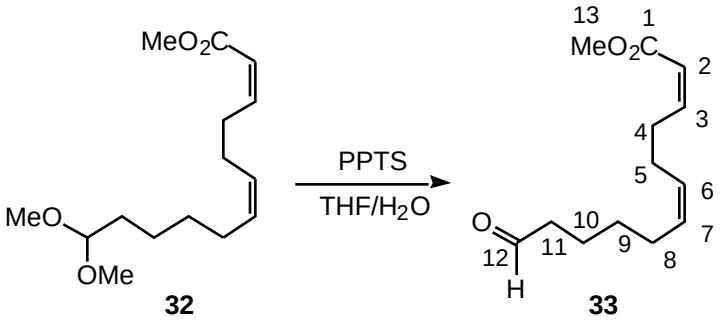
MS: FAB
271 (M^++H, 7), 269 (20), 241 (11), 239 (21), 209 (10), 208 (11), 207 (65), 175 (45), 152 (16), 147 (100), 133 (41)

TLC: R_f 0.60 (silica gel, hexane/EtOAc, 2/1, PMA)

Analysis: $C_{15}H_{26}O_4$ (270.37)

Calculated:	C: 66.64;	H: 9.69%
Found:	C: 66.51;	H: 9.65%

Methyl (2*Z*,6*Z*)-12-Oxododeca-2,6-dienoate (33)



32 **33**

To a solution of **32** (500 mg, 1.84 mmol) in THF/H_2O (1/1, 24 mL) was added pyridinium *p*-toluenesulfonic acid (2.33 g, 9.22 mmol, 5 equiv) at room temperature and the solution was warmed to 45 °C for 3 h. The reaction was then diluted with water (15 mL) and with Et_2O (15 mL). The aqueous phase was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (25 mL), brine (20 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 4/1) and distillation to afford 451 g (90%) of **33** as a colorless oil which constituted of an inseparable mixture of isomers (6*Z*/6*E*, 92/8 by ^{1}H NMR analysis).

Analytical Data for **33**:

bp: 100 °C (2.3 x 10^{-5} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
9.75 (t, *J* = 2.0, 1 H, HC(12)), 6.20 (td, *J* = 7.5, 1H, HC(3)), 5.78 (tdd, *J* = 1.0, 11.5, 0.5, 1 H, HC(2)), 5.38-5.36 (m, 2 H, HC(6), HC(7)), 3.69 (s, 3 H, H_3C(4')), 2.70 (qd, *J* = 7.0, 1.0, 2 H, H_2C(4)), 2.42 (td, *J* = 5.5, 2.0, 2 H, H_2C(11)), 2.18 (q, *J* = 6.0, 2 H, H_2C(8)), 2.04 (q, *J* = 5.5, 2 H, H_2C(10)), 1.65-1.59 (m, 2 H, H_2C(9)), 1.41-1.36 (m, 2 H, H_2C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)
202.7 (C(12)), 166.7 (C(1)), 149.9 (C(3)), 130.1 (C(6)), 128.9 (C(7)), 119.6 (C(2)), 50.9 (C(13)), 43.7 (C(11)), 29.0 (C(4)), 28.9 (C(5)), 26.8 (C(8)), 26.5 (C(9)), 21.6 (C(10))

IR: ($CDCl_3$)
3010 (w), 2947 (m), 2863 (w), 1722 (s), 1654 (m), 1439 (m), 1407 (w), 1201 (m), 1173 (m), 1022 (w)

MS: FAB

225 (15, M^++H), 223 (14), 211 (11), 209 (19), 207 (21), 205 (16), 199 (12), 197 (17), 195 (21), 193 (36), 191 (39), 185 (17), 181 (26), 165 (44), 153 (30), 149 (53), 137 (42), 118 (100)

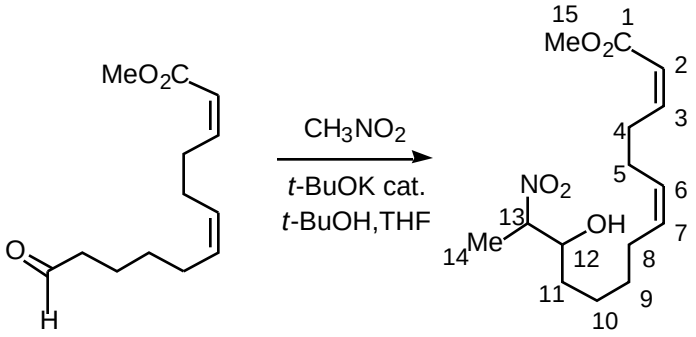
TLC: R_f 0.29 (silica gel, hexane/EtOAc, 4/1, PMA)

Analysis: $C_{13}H_{20}O_3$ (224.30)

Calculated: C: 69.61; H: 8.99%

Found: C: 69.37; H: 8.99%

Methyl (2*Z*,6*Z*)-12-Hydroxy-13-nitrododeca-2,6-dienoate (34)



33 **34**

To a solution of aldehyde **33** (240 mg, 1.10 mmol) and nitroethane (225 μL, 3.30 mmol, 3 equiv) in *t*-BuOH/THF (1/1, 2 mL) was added *t*-BuOK (23 mg, 0.22 mmol, 0.2 equiv) at room temperature. After 15 min, the mixture was diluted with EtOAc (10 mL) and water (10 mL). The separated organic layer was washed with brine (10 mL) and the aqueous layers were back-extracted with EtOAc (2 x 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 2/1) to afford 286 mg (91%) of **34** as a pale yellow oil which constituted of an inseparable mixture of diastereoisomers (1/1 by ^{1}H NMR analysis).

Analytical Data for **34**:

^{1}H NMR: (500 MHz, $CDCl_3$)

6.26-6.20 (m, 1 H, HC(3)), 5.78 (td, *J* = 1.5, 12.0, 1 H, HC(2)), 5.41-5.37 (m, 2 H, HC(6), HC(7)), 4.56-4.47 (m, 1 H, HC(13)), 4.19-4.17 (m, 0.5 H, HC(12)), 3.95-3.90 (m, 0.5 H, HC(12)), 3.69 (s, 3 H, H_3C(15)), 2.70-2.68 (m, 3 H, H_2C(5), OH), 2.19-2.15 (m, 4 H, H_2C(4)), 2.07-2.04 (m, 4 H, H_2C(5)), 1.54 (d, *J* = 4.5, 1.5 H, HC(14)), 1.53 (d, *J* =4.5, 1.5 H, HC(14)), 1.52-1.35 (m, 6 H, H_2C(9), H_2C(10), H_2C(11))

^{13}C NMR: (126 MHz, $CDCl_3$)

Major: 166.9 (C(1)), 150.1 (C(3)), 130.3 (C(6)), 128.7 (C(7)), 119.4 (C(2)), 87.7 (C(13)), 72.7 (C(12)), 51.1 (C(15)), 33.0 (C(11)), 29.11 (C(4)), 28.95 (C(5)), 28.7 (C(8)), 26.4 (C(9)), 24.6 (C(10)), 16.05 (C(14))

Minor: 166.9 (C(1)), 150.1 (C(3)), 130.3 (C(6)), 128.7 (C(7)), 119.3 (C(2)), 86.3 (C(13)), 71.9 (C(12)), 51.0 (C(15)), 32.7 (C(11)), 29.0 (C(4)), 28.9 (C(5)), 28.8 (C(8)), 26.8 (C(9)), 25.2 (C(10)), 12.3 (C(14))

IR: ($CHCl_3$)

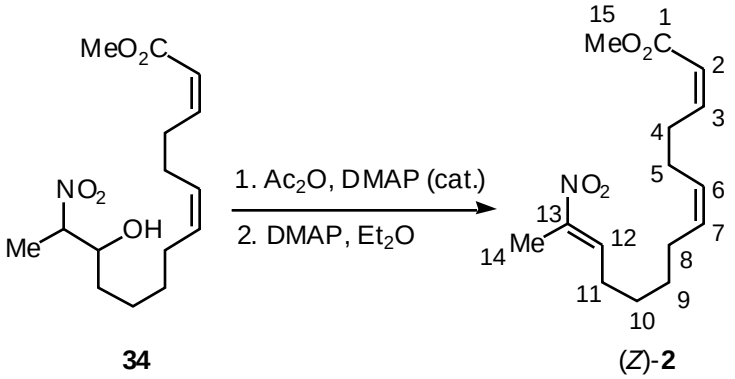
3505 (bm), 2945 (m), 2860 (w), 1721 (s), 1645 (m), 1550 (s), 1440 (m), 1203 (m), 1012 (w)

MS: FAB

300 (29, M^++H), 268 (26), 240 (18), 195 (15), 193 (20), 175 (13), 167 (10), 165 (18), 163 (10), 161 (12), 154 (25), 154 (10), 153 (24), 152 (35), 137 (19), 134 (70), 118 (100).

TLC: R_f 0.23 (silica gel, hexane/EtOAc, 2/1, PMA)

Methyl (2*Z*,6*Z*,12*E*)-13-Nitrotetradeca-2,6,12-trienoate ((Z)-2)



34 (*Z*)-**2**

To a cold (0 °C, ice bath) solution of the nitro alcohol **34** (320 mg, 1.07 mmol) and acetic anhydride (125 µL, 1.17 mmol, 1.1 equiv) in Et_2O (9 mL) was added DMAP (26 mg, 0.21 mmol, 0.2 equiv) and the mixture was allowed to warm to room temperature. After 2 h, the mixture was diluted with Et_2O (10 mL) and water (10 mL), and the separated organic layer was washed with sat. aq. $NaHCO_3$ solution (10 mL), sat. aq. NH_4Cl solution (10 mL), and brine (10 mL). The aqueous layers were back extracted with Et_2O (20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated to afford a pale yellow oil which was used in the next step without further purification.

To a solution of the nitro acetate **35** (365 mg, 1.07 mmol) in Et_2O (8 mL) was added DMAP (156 mg, 1.20 mmol, 1.2 equiv) at 0 °C (ice water bath) and then was allowed to warm to room temperature. After 8 h, the reaction was quenched with water (10 mL) and the product was extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (30 mL), brine (20 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 4/1) and distillation to afford 273 mg (91%) of (*Z*)-**2** as a pale yellow oil which constituted of an inseparable mixture of isomers (6*Z*/6*E*, 92/8 by ^1H NMR analysis).

Analytical Data for (*Z*)-**2**:

bp: 125 °C (9.0×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, $CDCl_3$)
7.12 (td, *J* = 8.0, 1.5, 1 H, HC(12)), 6.22 (td, *J* = 7.5, 12.0, 1 H, HC(3)), 5.78 (td, *J* = 1.5, 12.0, 1 H, HC(2)), 5.41-5.37 (m, 2 H, HC(6), HC(7)), 3.70 (s, 3 H, H_3C(15)), 2.72 (qd, *J* = 7.5, *J* = 2.0, 2 H, H_2C(4)), 2.25-2.12 (m, 4 H, H_2C(11), H_2C(5)), 2.16 (s, 3 H, H_3C(14)), 2.8-2.04 (m, 2 H, H_2C(8)), 1.53-1.48 (m, 2 H, H_2C(10)), 1.43-1.37 (m, 2 H, H_2C(9))

^{13}C NMR: (126 MHz, $CDCl_3$)
166.7 (C(1)), 149.8 (C(3)), 147.3 (C(13)), 136.2 (C(12)), 130.1 (C(6)), 128.9 (C(7)), 119.6 (C(2)), 51.0 (C(15)), 29.2 (C(4)), 28.9 (C(5)), 28.0 (C(8)), 27.8 (C(11)), 26.8 (C(9)), 26.5 (C(10)), 12.5 (C(14))

IR: (KBr)
2945 (m), 2860 (m), 1722 (s), 1645 (m), 1520 (m), 1438 (w), 1333 (w), 1200 (w), 1173 (w)

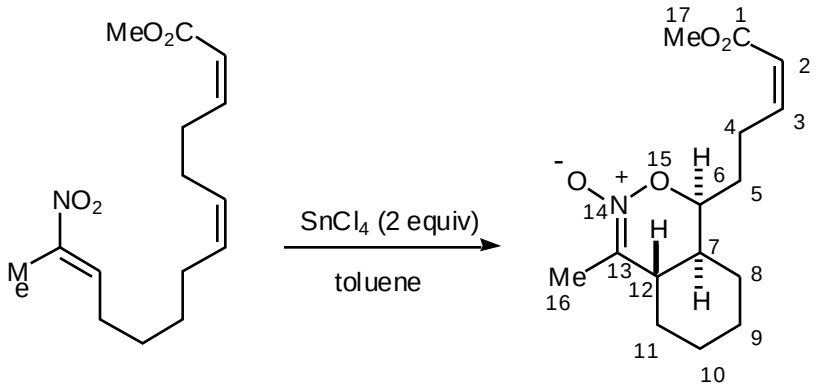
MS: FAB
282 (39, M^++H), 280 (11), 279 (12), 267 (16), 251 (53), 250 (57), 248 (16), 235 (10), 219 (25), 195 (13), 177 (24), 175 (22), 167 (12), 155 (30), 152 (64), 147 (19), 118 (100), 109 (20)

TLC: R_f 0.35 (silica gel, hexane/EtOAc, 4/1, PMA)

Analysis: $C_{15}H_{23}NO_4$ (281.35)

Calculated:	C: 64.04;	H: 8.24:	N: 4.98%
Found:	C: 63.74;	H: 8.14:	N: 4.84%

rel-(3a_R_,7a_R_,8_R_)-Methyl-2_Z_-5-[8-[3-methyl-2-oxido-3a,4,5,6,7,7a-hexahydro-4_H_-1,2-benzoxazinyl]]-2-pentenoate (36)



(*Z*)-**2** **36**

To a cold (–78 °C, dry ice bath) solution of nitroalkene **(*Z*)-2** (270 mg, 1.01 mmol) in toluene (8 mL) was added $SnCl_4$ (125 μL, 2.02 mmol, 2 equiv). After 2 h, the solution was diluted with EtOAc (15 mL) and then quenched with a 1 N solution of triethylamine in MeOH (15 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (2 x 15 mL), brine (15 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, EtOAc) and recrystallization (Et_2O) to afford 220 mg (82%) of **36** as a crystalline solid.

Analytical Data for **36**:

mp: 85-87 °C (Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.30 (td, *J* = 7.5, 12, 1 H, HC(3)), 5.80 (d, *J* = 12.0, 1 H, HC(2)), 4.27 (td, *J* = 1.5, 11.5, 1 H, HC(6)), 3.70 (s, 3 H, H_3C(17)), 2.99 (td, *J* = 16.9, 8.0, 1 H, HC(12)), 2.83-2.80 (m, 2 H, H_2C(4)), 2.45-1.91 (m, 2 H, H_2C(5)), 2.01 (s, 3 H, H_3C(16)), 1.88-1.77 (m, 2 H, H_2C(8)), 1.75-1.69 (m, 1 H, *H*HC(11)), 1.70-1.66 (m, 1 H, HC(7)), 1.56-1.47 (m, 1 H, H*H*C(11)), 1.35-1.21 (m, 2 H, *H*HC(9), H_2C(10)), 1.17-1.10 (m, 1 H, H*H*C(9)), 1.07-1.00 (m, 1 H, H*H*C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)

166.7 (C(1)), 149.7 (C(3)), 124.2 (C(13)), 122.1 (C(2)), 83.2 (C(6)), 49.7 (C(17)), 39.5 (C(12)), 39.1 (C(7)), 26.8 (C(4)), 28.3 (C(5)), 27.8 (C(11)), 25.9 (C(8)), 25.4 (C(10)), 25.2 (C(9)), 15.3 (C(16))

IR: (KBr)
3054 (w), 2936 (m), 2860 (w), 1722 (s), 1658 (m), 1600 (m), 1437 (w), 1268 (m), 1209 (w), 1167 (w), 1122 (w), 983 (w)

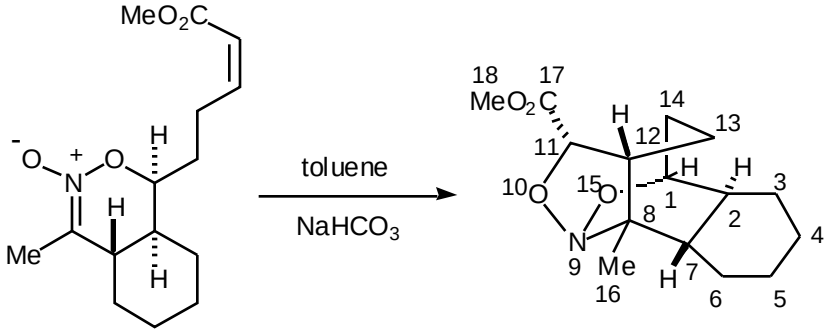
MS: FAB
282 (100, M^++H), 266 (17), 251 (31), 219 (5), 177 (7), 135 (11)

TLC: R_f 0.32 (silica gel, EtOAc, PMA)

Analysis: $C_{15}H_{23}NO_4$ (281.35)

Calculated:	C: 64.04;	H: 8.24%
Found:	C: 63.91;	H: 8.27%

***rel*-(1*R*,2*S*,7*R*,8*R*,11*R*,12*S*)-8-Methyl-9-aza-10,14-dioxatetracyclo[7.5,1.0^{2,7}.0^{8,12}]pentadecane-11-carboxylate (37)**



To a solution of nitronate **36** (220 mg, 0.73 mmol) in dry toluene (8 mL) was added sodium bicarbonate (230 mg, 3.66 mmol, 5 equiv). The suspension was degassed and then was heated at 100 °C. After 3 days, the mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography (silica gel, CH_2Cl_2/EtOAc, 9/1) and recrystallization (Et_2O) to afford 50 mg (23%) of **37** as a crystalline solid along with 150 mg (68%) of recovered **36**.

Analytical Data for **37**:

mp: 151-153 °C (Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

4.93 (d, *J* = 9.5, 1 H, HC(11)), 4.28 (q, *J* = 11.0, 1 H, HC(1)), 3.69 (s, 3 H, HC(18)), 2.93 (td, *J* = 3.5, 5.0, 1 H, HC(12)), 2.34-2.21 (m, 1 H, HC(2)), 2.01-1.97 (m, 4 H, *H*HC(3), HC(7), *H*HC(13), *H*HC(14)), 1.96-1.85 (m, 2 H, H*H*C(3), *H*HC(6)), 1.82-1.71 (m, 2 H, H*H*C(13), H*H*C(14)), 1.69-1.65 (m, 1 H, H*H*C(6)), 1.41-1.27 (m, 3 H, *H*HC(4), H_2C(5)), 2.01 (s, 3 H, H_3C(16)), 1.16-1.12 (m, 1 H, H*H*C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)

171.8 (C(17)), 81.2 (C(11)), 74.5 C(1)), 55.0 (C(8)), 53.1 (C(18)), 44.8 (C(12)), 40.5 (C(14)), 30.4 (C(2)), 29.7 (C(7)), 28.2 (C(6)), 27.4 (C(3)), 26.4 (C(13)), 24.2 (C(16)), 23.6 (C(5)), 23.5 (C(4))

IR: ($CHCl_3$)

2917 (m), 2852 (w), 1750 (s), 1438 (w), 1210 (m), 1014 (w), 957 (w)

MS: FAB

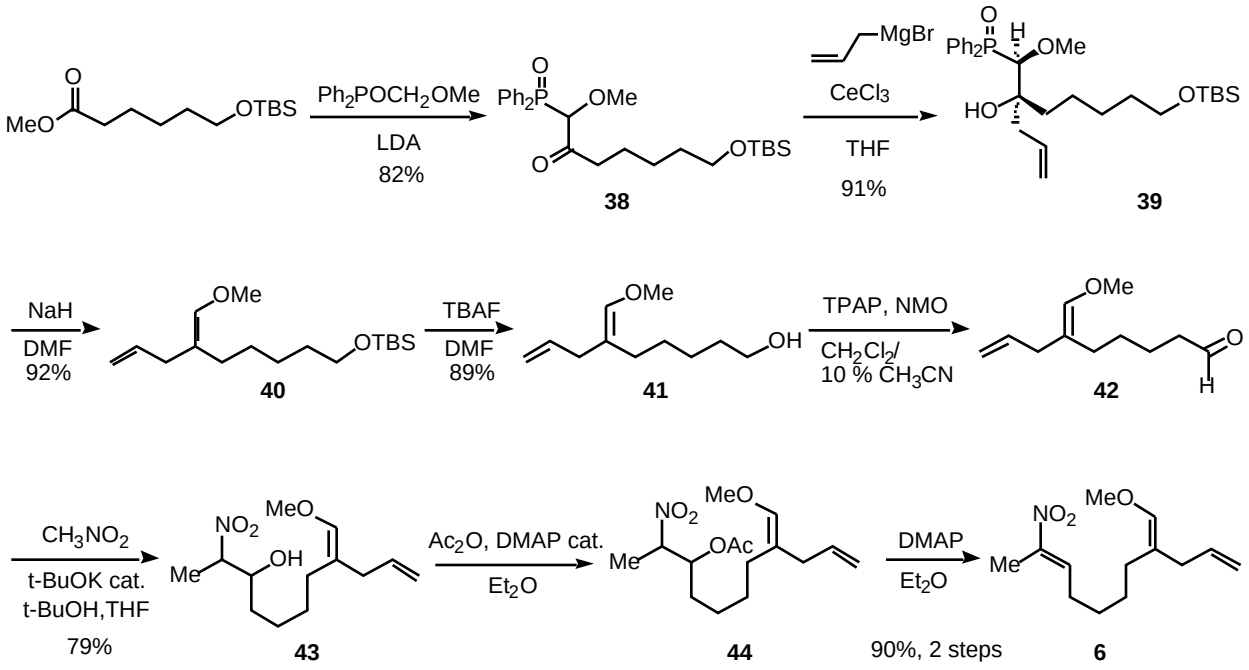
282 (100, M^++H), 280 (75), 279 (15), 278 (48), 266 (19), 237 (12), 236 (51), 234 (19), 207(11), 195 (13), 193 (11), 179 (16), 167 (15), 165(16)

TLC: R_f 0.63 (CH_2Cl_2/EtOAc, 9/1, PMA)

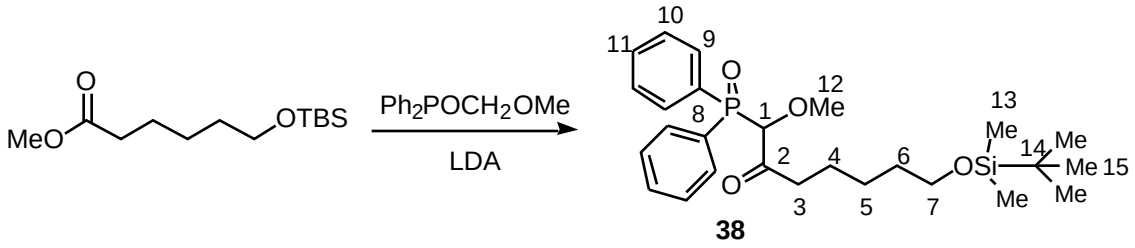
Analysis: $C_{15}H_{23}NO_4$ (281.35)

Calculated:	C: 64.04;	H: 8.24;	N: 4.98%
Found:	C: 63.76;	H: 8.32;	N: 5.06%

Preparation of (9*E*)-4-Methoxymethylene-10-nitroundeca-1,9-diene (6)



7-(*tert*-Butyldimethylsilyloxy)-1-diphenylphosphinyl-1-methoxy-2-heptanone (38)



To a cold (–78 °C, dry ice, *i*-PrOH bath) solution of diisopropylamine (5.41 mL, 38.40 mmol, 2.4 equiv) in THF (40 mL) was added *n*-butyllithium (1.50 M in THF, 26.50 mL, 38.40 mmol, 2.4 equiv). After 1 h at that temperature, the resulting lithium diisopropylamide solution was added to a cold (0 °C internal temperature) solution of methoxymethyltriphenylphosphine oxide (10.40 g, 35.2 mmol, 2.2 equiv) in THF (128 mL). After 10 min, the mixture was cooled to –78 °C (dry ice, internal temperature) and a solution of methyl 6-(O-*tert*-butyldimethylsilyl)hexanoate (4.0 g, 16 mmol) in THF (20 mL) was added dropwise at such a rate that the internal temperature was maintained below –76 °C and the mixture was then stirred for 40 min at –78 °C. The reaction was quenched with sat. aq. NH_4Cl solution (100 mL) and the product was extracted with Et_2O (2 x 75 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (70 mL), brine (50 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by

chromatography (silica gel, hexane/EtOAc, 3/2) and distillation to afford 6.2 g (82%) of **38** as a colorless oil.

Analytical Data for **38**:

bp: 175 °C (1.4×10^{-4} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.88-7.80 (m, 4 H, HC(9)), 7.55-7.52 (m, 2 H, HC(11)), 7.49-7.44 (m, 4 H, HC(10)), 4.62 (d, *J* = 16.0, 1 H, HC(1)), 3.53 (t, *J* = 6.5, 2 H, H_2C(7)), 3.31 (s, 3 H, H_3C(12)), 2.83 (ABt, *J* = 18.0, 7.5, 1 H, H_2C(3)), 2.58 (ABt, *J* = 18.0, 7.5, 1 H, H_2C(3)), 1.56-1.42 (m, 4 H, H_2C(4), H_2C(6)), 1.27-1.20 (m, 2 H, H_2C(5)), 0.89 (s, 9 H, 3 H_3C(15)), 0.01 (s, 6 H, 2 H_3C(13))

^{13}C NMR: (126 MHz, $CDCl_3$)

205.8 (C(2)), 132.4 (d, *J* = 1.9, C(8)), 132.2 (d, *J* = 1.9, C(8)), 131.8 (d, *J* = 9.2, C(10)), 131.4 (d, *J* = 10.2, C(9)), 128.4 (d, *J* = 3.8, C(11)), 128.3 (d, *J* = 3.8, C(11)), 87.8 (d, *J* = 73.8, C(1)), 77.2 (C(12)), 62.9 (C(7)), 41.5 (C(3)), 32.5 (C(6)), 25.9 (C(15)), 25.2 (C(4)), 22.9 (C(5)), 18.2 (C(14)), -5.3 (C(13))

^{31}P NMR: (165 MHz, $CDCl_3$)

25.59

IR: ($CHCl_3$)

2927 (w), 2858 (w), 1718 (s), 1438 (m), 1189 (m), 1120 (m), 1099 (m)

MS: FAB

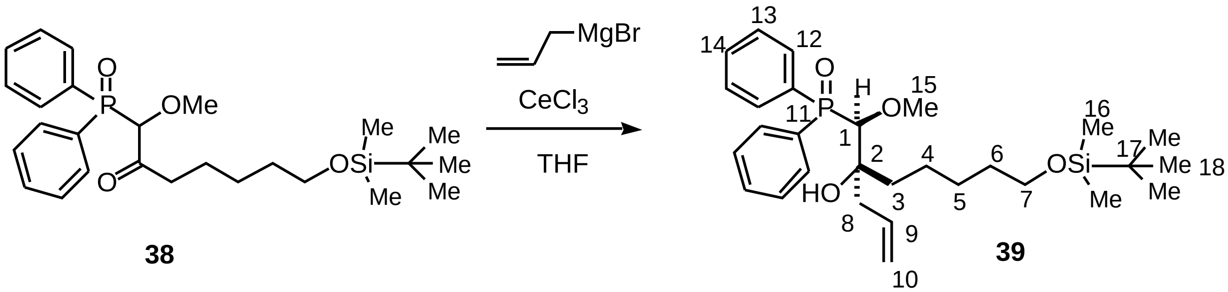
475 (100, M^++H), 417 (17), 343 (7), 275 (7), 246 (7), 231 (19), 219 (16), 215 (10), 203(29), 202 (22), 201 (89), 185 (24), 155 (12), 141(14)

TLC: R_f 0.33 (hexane/EtOAc, 3/2, UV, PMA)

Analysis: $C_{26}H_{39}SiO_4P$ (474.65)

Calculated:	C: 65.79;	H: 8.28;	P: 6.53%
Found:	C: 65.67;	H: 8.36;	P: 5.96%

7-(*tert*-Butyldimethylsilyloxy)-1-(diphenylphosphinyl)-1-methoxy)-2-(2-propenyl)-2-heptanol (39)



Cerium chloride ($CeCl_3.7H_2O$) (3.0 g, 12.6 mmol, 1.5 equiv) was ground to a fine powder and placed in a 250-mL, three-necked flask. The flask was immersed in an oil bath and heated gradually to 140 °C (oil bath) under vacuum (0.15 mmHg) for 1 h. Then a magnetic stirrer bar was placed in the flask and the solid was stirred at that same temperature, and completely dried under vacuum for an additional 12 h. The hot flask was then vented with nitrogen and was cooled to 0 °C (ice bath). THF (54 mL) was added and the mixture was vigorously stirred at room temperature for 1 h. A solution of allylmagnesium bromide (0.6 M in Et_2O, 21 mL, 12.6 mmol, 1.5 equiv) was added dropwise. After 1 h (yellow coloration), a solution of **38** (4.0 g, 8.4 mmol) in THF (24 mL) was added and the mixture was stirred at 0 °C for 1 h. The reaction was then quenched with sat. aq. NH_4Cl solution (100 mL) and was diluted with EtOAc (50 mL). The organic layer was separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (70 mL), brine (50 mL), then were dried ($MgSO_4$), filtered and concentrated. The same procedure was repeated two more times under the same conditions to afford a residue which was purified by chromatography (silica gel, hexane/EtOAc, 2/1) to give 3.62 g (91%) of **39** as a colorless oil which constituted of an inseparable mixture of diastereoisomers (93/7 by ^{1}H NMR analysis).

Analytical Data for **39**:

^{1}H NMR: (500 MHz, $CDCl_3$)

8.12-8.06 (m, 2 H, HC(14)), 7.82-7.79 (m, 2 H, HC(12)), 7.60-7.76 (m, 6 H, HC(12), HC(13)), 6.01 (tdd, J = 17.0, 10.5, 8, 1 H, HC(8)), 5.11 (dd, J = 0.5, 10.5, 1 H, HC(9)), 5.05 (dd, J = 0.5, 17.0, 1 H, HC(9)), 4.06 (d, J = 5.0, 1 H, HC(10)), 3.45 (t, J = 6.5, 2 H, $H_2C(1)$), 3.17 (s, 3 H, $H_3C(15)$), 2.43 (ABd, J = 14.5, 8.0, 1 H, $H_2C(7)$), 2.33 (ABd, J = 14.5, 6.0, 1 H, $H_2C(7)$), 1.50-1.45 (m, 2 H, $H_2C(5)$), 1.34-1.26 (m, 4 H, $H_2C(4)$, $H_2C(2)$), 1.16-1.12 (m, 2 H, $H_2C(3)$), 0.89 (s, 9 H, 3 $H_3C(18)$), 0.04 (s, 6 H, 2 $H_3C(16)$)

^{13}C NMR: (126 MHz, $CDCl_3$)

134.1 (C(8)), 132.6 (d, *J* = 8.3, C(11)), 132.0 (d, *J* = 7.4, C(13)), 130.0 (d, *J* = 9.3, C(12)), 128.6 (d, *J* = 11.0, C(14)), 128.1 (d, *J* = 11.0, C(14)), 117.7 C(9)), 85.6 (d, *J* = 84.0, C(10)), 77.7 (C(15)), 62.9 (C(1)), 61.6 (C(6)), 40.8 (C(7)), 37.8 (C(5)), 32.5 (C(2)), 25.9 (C(4)), 25.8 (C(18)), 22.6 (C(3)), 18.1 (C(17)), -5.5 (C(16))

^{31}P NMR: (165 MHz, $CDCl_3$)

31.04

IR: ($CHCl_3$)

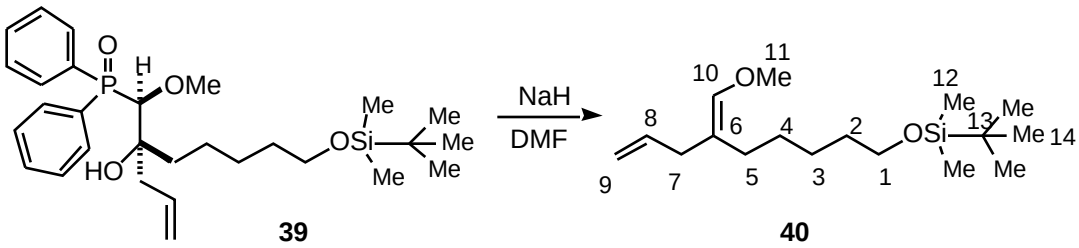
3373 (bm), 3059 (w), 2962 (m), 2858 (m), 1462 (w), 1438 (m), 1254 (w), 1166 (m), 1095 (s)

MS: FAB

517 (38, M^++H), 459 (4), 246 (15), 231 (33), 219 (13), 204 (10), 203 (75), 202 (34), 201 (100), 185 (27), 183 (15), 155(11)

TLC: R_f 0.28 (hexane/EtOAc, 2/1, UV, PMA)

***tert*-Butyl[6-(methoxymethylene)-8-nonenyloxy)dimethylsilane (30)**



39 **40**

To a solution of **39** (2.20 g, 4.25 mmol) in DMF (157 mL) was added NaH (60 % in oil washed with dry hexane, 518 mg, 12.77 mmol, 3 equiv) in one portion at room temperature. The mixture was then warmed to 55 °C for 3 h. The solution was cooled to 0 °C (ice bath) and then quenched with water (100 mL) and diluted with Et_2O (100 mL). The ether layer was separated and the aqueous phase was extracted with Et_2O (3 x 70 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (70 mL), brine (70 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 15/1) and distillation to afford 1.10 g (93%) of **40** as a colorless oil which constituted of an inseparable mixture of isomers (93/7 by ^{1}H NMR analysis).

Analytical Data for **40**:

bp: 69 °C (1.3 x 10^{-4} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

5.76 (s, 1 H, HC(10)), 5.73 (tdd, *J* = 6.8, 11.2, 17.2, 1 H, HC(8)), 5.02 (dd, *J* = 17.2, 1.6, 1 H, HC(9)), 4.98 (dd, *J* = 11.2, 1.6, 1 H, HC(9)), 3.59 (t, *J* = 6.8, 2 H, H_2C(1)), 3.53 (s, 3 H, H_3C(11)), 2.60 (d, *J* = 6.8, 2 H, HC(7)), 2.03 (t, *J* = 7.2, 2 H, H_2C(5)), 1.52 (q, *J* = 6.8, 2 H, H_2C(2)), 1.40-1.21 (m, 4 H, H_2C(3), HC(4)), 0.89 (s, 9 H, 3 H_3C(14)), 0.04 (s, 6 H, 2 H_3C(12))

^{13}C NMR: (126 MHz, $CDCl_3$)

142.9 (C(10)), 137.3 (C(8)), 116.6 (C(9)), 115.4 (C(6)), 63.2 (C(1)), 59.1 (C(11)), 36.1 (C(5)), 32.7 (C(7)), 27.3 (C(5)), 29.6 (C(4)), 25.9 (C(14)), 25.6 (C(3)), 18.3 (C(13)), -5.3 (C(12))

IR: ($CHCl_3$)

2931 (s), 2858 (s), 1730 (w), 1463 (w), 1255 (m), 1101 (s)

MS: FAB

299 (31, M^++H), 298 (28), 297 (14), 283 (12), 255 (12), 242 (18), 241 (100), 209 (5), 185(13), 176 (20), 171 (10), 166 (11), 149 (15), 133 (28), 125 (21), 115 (35), 105 (38)

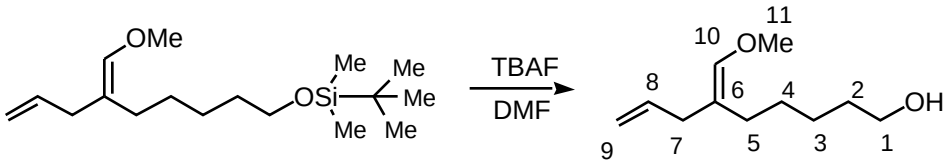
TLC: R_f 0.35 (hexane/EtOAc, 15/1, PMA)

Analysis: $C_{17}H_{34}SiO_2$ (298.54)

Calculated: C: 68.39; H: 11.48%

Found: C: 68.25; H: 11.26%

6-Methoxymethylene-8-nonen-1-ol (41)



40 **41**

To a cold (0 °C) solution of **40** (770 mg, 2.73 mmol) in THF (45 mL) was added a solution of *tetra*-butyl ammonium fluoride (1 M THF, 4 mL, 4 mmol, 1.5 equiv) then the mixture was warmed to room temperature. After 4 h, the solution was quenched with water (30 mL) and diluted with Et_2O (40 mL). The ether layer was separated and the aqueous phase was extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with sat. aq. NH_4Cl solution (30 mL), brine (25 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by

chromatography (silica gel, hexane/EtOAc, 2/1) and distillation to afford 447 mg (89%) of **41** as a colorless oil which constituted of an inseparable mixture of isomers (93/7 by ^{1}H NMR analysis).

Analytical Data for **41**:

bp: 90 °C (2.0 x 10^{-4} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
5.76 (s, 1 H, HC(10)), 5.72 (tdd, *J* = 7.0, 10.0, 17.0, 1 H, HC(8)), 5.02 (dd, *J* = 17.0, 1.5, 1 H, HC(9)), 4.97 (dd, *J* = 10.0, 1.5, 1 H, HC(9)), 3.61 (t, *J* = 6.5, 2 H, H_2C(1)), 3.51 (s, 3 H, H_3C(11)), 2.58 (d, *J* = 7.0, 2 H, HC(7)), 2.03 (t, *J* = 7.0, 2 H, H_2C(5)), 1.56 (q, *J* = 6.5, 2 H, H_2C(2)), 1.54 (br, s, 1H, OH), 1.40-1.29 (m, 4 H, H_2C(3), H_2C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)
142.9 (C(10)), 137.1 (C(8)), 116.6 (C(9)), 115.5 (C(6)), 62.8 (C(1)), 59.2 (C(11)), 36.0 (C(5)), 32.5 (C(7)), 27.1 (C(2)), 26.7 (C(4)), 25.3 (C(3))

IR: ($CHCl_3$)
3393 (bm), 2933 (s), 2859 (s), 1677 (m), 1458 (w), 1208 (m), 1132 (s), 1071 (w), 995 (w)

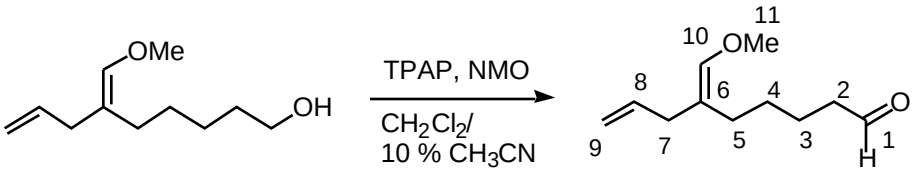
MS: FAB
185 (100, M^++H), 184 (18), 183 (49), 181 (12), 179 (10), 173 (14), 171 (14), 169 (15), 167(28), 165 (20), 155 (15), 153 (22), 149 (32), 137 (28), 134 (78), 118 (20)

TLC: R_f 0.24 (hexane/EtOAc, 2/1, PMA)

Analysis: $C_{11}H_{20}O_2$ (184.28)

Calculated:	C: 71.70;	H: 10.94%
Found:	C: 71.55;	H: 10.95%

6-Methoxymethylene-8-nonenal (42)



41 **42**

To a cold (0 °C) solution of **41** (330 mg, 1.8 mmol) in CH_2Cl_2 (6 mL) and CH_3CN (0.6 mL) was added 4-methylmorpholine *N*-oxide (315 mg, 2.7 mmol, 1.5 equiv), tetra-*n*-propylammonium perruthenate (31 mg, 0.09 mmol, 0.05 equiv), and molecular sieves (4 Å, 561 mg) and the mixture was allowed to warm to room temperature. After 5 h, the mixture was filtered

through a plug of silica gel. The filter cake was washed with hexane/EtOAc, 2/1 (40 mL), and the filtrate was concentrated under reduce pressure to afford **42** 270 mg (82%) as a colorless oil which constituted of an inseparable mixture of isomers (93/7 by ^{1}H NMR analysis). Due to its sensitivity **42** was used directly in the next step without further purification.

Analytical Data for **42**:

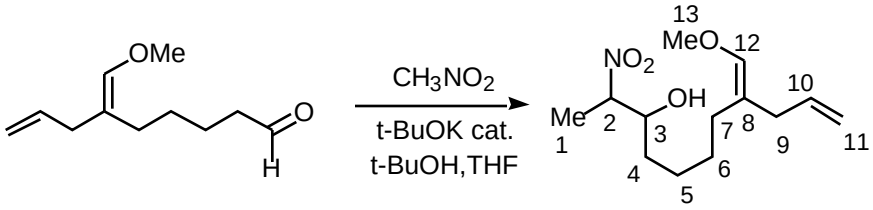
^{1}H NMR: (500 MHz, $CDCl_3$)

9.73 (t, *J* = 2.0, 1 H, HC(1)), 5.77 (s, 1 H, HC(10)), 5.70 (tdd, *J* = 7.0, 10.0, 17.0, 1 H, HC(8)), 5.01 (ddt, *J* = 17.0, 2.0, 1.5, 1 H, HC(9)), 4.96 (ddt, *J* = 10.0, 2.0, 1.0, 1 H, HC(9)), 3.51 (s, 3 H, H_3C(11)), 2.58 (dd, *J* = 7.0, 1.5, 2 H, HC(7)), 2.40 (td, *J* = 7.5, 2.0, 2 H, H_2C(2)), 2.04 (t, *J* = 7.5, 2 H, H_2C(5)), 1.59 (q, *J* = 7.5, 2 H, H_2C(3)), 1.38 (q, *J* = 7.5, 2 H, H_2C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)

202.0 (C(1)), 143.2 (C(10)), 137.0 (C(8)), 115.7 (C(9)), 115.6 (C(6)), 59.2 (C(11)), 43.6 (C(2)), 36.0 (C(5)), 26.7 (C(7), 26.4 (C(4)), 26.3 (C(3))

8-Methoxymethylene-2-nitro-10-undecen-3-ol (43)



42 **43**

To a solution of aldehyde **42** (270 mg, 1.48 mmol) and nitroethane (319 μL, 4.45 mmol, 3 equiv) in *t*-BuOH/THF (1/1, 2.5 mL) was added *t*-BuOK (30 mg, 0.30 mmol, 0.2 equiv) at room temperature. After 20 min, the mixture was diluted with Et_2O (15 mL) and water (15 mL). The separated organic layer was washed with brine (15 mL) and the aqueous layers were back-extracted with Et_2O (2 x 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 4/1) to afford 301 mg (79%) of **43** as a pale yellow oil which constituted of an inseparable mixture of diastereoisomers (1/1 by ^{1}H NMR analysis).

Analytical Data for **43**:

^{1}H NMR: (500 MHz, $CDCl_3$)

5.77 (s, 1 H, HC(12)), 5.68 (tdd, *J* = 7.0, 10.0, 17.0, 1 H, HC(10)), 5.00 (dd, *J* = 17.0, 1.0, 1 H, HC(11)), 4.97 (dd, *J* = 10.0, 1.0, 1 H, HC(11)), 4.53-4.45 (m, 1 H, HC(2)), 4.14-4.13 (m, 0.5 H, HC(3)), 3.88-3.86 (m, 0.5 H, HC(3)), 3.51 (s, 3 H, H_3C(13)), 2.57 (d, *J* = 7.0, 2 H, H_2C(9)), 2.51 (br s, 1H, OH), 2.05-2.01 (m, 2 H, H_2C(7)), 1.53 (d, *J* = 1.5, 1.5 H, H_3C(1)), 1.52 (d, *J* = 1.5, 1.5 H, H_3C(1)), 1.50-1.37 (m, 4 H, H_2C(5), H_2C(6))

^{13}C NMR: (126 MHz, $CDCl_3$)

Major: 143.1 (C(12)), 137.0 (C(10)), 116.2 (C(8)), 115.6 (C(11)), 87.7 (C(2)), 72.0 (C(3)), 59.2 (C(13)), 35.9 (C(7)), 32.6 (C(4)), 26.8 (C(6)), 26.2 (C(9)), 24.7 (C(5)), 16.0 (C(1))

Minor: 143.1 (C(12)), 137.0 (C(10)), 116.2 (C(8)), 115.6 (C(11)), 86.3 (C(2)), 72.8 (C(3)), 59.2 (C(13)), 35.9 (C(7)), 32.4 (C(4)), 26.7 (C(6)), 26.3 (C(9)), 24.2 (C(5)), 12.0 (C(1))

IR: ($CHCl_3$)

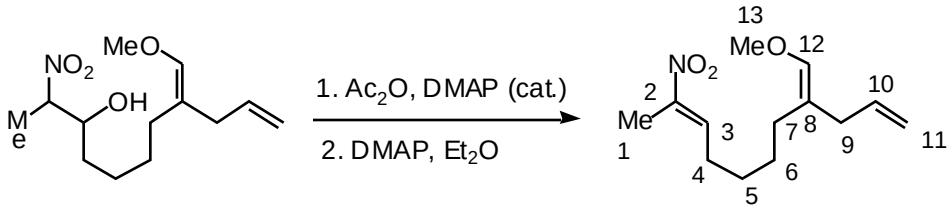
3422 (bm), 2939 (m), 2847 (w), 1679 (w), 1550 (s), 1455 (w), 1391 (w), 1210 (m), 1131 (m), 994 (w), 913 (w)

MS: FAB

258 (32, M^++H), 256 (17), 244 (7), 226 (9), 213 (4), 197 (3), 181 (7), 167 (9), 149 (28), 135 (70), 119 (100), 111 (38)

TLC: R_f 0.48 (hexane/EtOAc, 4/1, PMA)

4-Methoxymethylene-10-nitroundeca-1,9-diene (6)



43 **6**

To a cold (0 °C, ice bath) solution of the nitro alcohol **43** (301 mg, 1.16 mmol) and acetic anhydride (105 µL, 1.27 mmol, 1.1 equiv) in Et_2O (7 mL) was added DMAP (26 mg, 0.23 mmol, 0.2 equiv) and the mixture was allowed to warm to room temperature. After 2 h, the mixture was diluted with Et_2O (10 mL) and water (10 mL), and the separated organic layer was washed with sat. aq. $NaHCO_3$ solution (10 mL), sat. aq. NH_4Cl solution (10 mL), and brine (10 mL). The aqueous

layers were back extracted with Et_2O (20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated to afford a pale yellow oil which was used in the next step without further purification.

To a cold (0 °C) solution of **44** (348 mg, 1.16 mmol) in Et_2O (7 mL) was added DMAP (141 mg, 1.20 mmol, 1.2 equiv) and then was allowed to warm to room temperature. After 8 h, the reaction was quenched with water (10 mL) and the product was extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (30 mL), brine (20 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 5/1) and distillation to afford 250 mg (90%) of **6** as a pale yellow oil.

Analytical Data for **6**:

bp: 125 °C (9.0×10^{-5} mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.13 (t, *J* = 8.0, 1 H, HC(3)), 5.79 (s, 1 H, HC(12)), 5.70 (tdd, *J* = 7.0, 10.0, 17.0, 1 H, HC(10)), 5.02 (dd, *J* = 17.0, 1.5, 1 H, HC(11)), 5.00 (dd, *J* = 17.0, 1.5, 1 H, HC(11)), 3.53 (s, 3 H, H_3C(13)), 2.59 (d, *J* = 7.0, 2 H, H_2C(9)), 2.23 (q, *J* = 8.0, 2 H, H_2C(4)), 2.15 (s, 3 H, H_3C(1)), 2.05 (t, *J* = 7.5, 2 H, H_2C(7)), 1.50-1.39 (m, 4 H, H_2C(5), H_2C(6))

^{13}C NMR: (126 MHz, $CDCl_3$)

147.4 (C(2)), 143.3 (C(12)), 137.0 (C(10)), 136.5 (C(3)), 115.6 (C(11)), 115.4 (C(8)), 59.2 (C(13)), 35.9 (C(7)), 27.7 (C(4)), 27.6 (C(9)), 26.7 (C(5)), 26.2 (C(6)), 12.3 (C(1))

IR: ($CHCl_3$)

3076 (w), 2933 (s), 2859 (m), 1675 (m), 1521 (s), 1454 (w), 1390 (w), 1333 (s), 1027 (m), 1132 (m), 996 (w), 913 (w)

MS: FAB

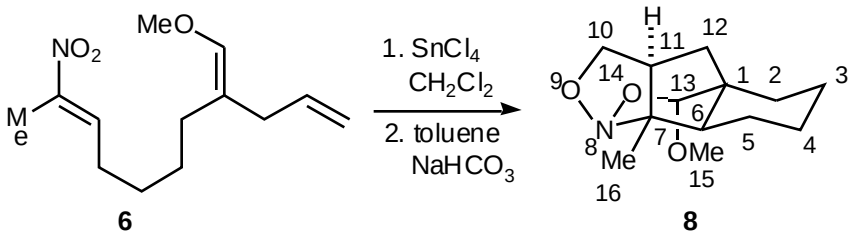
240 (86, M^++H), 239 (12), 238 (51), 224 (29), 213 (13), 208 (40), 194 (20), 192 (22), 180 (25), 177 (18), 167 (31), 165 (39), 161 (21), 159 (21), 155 (15), 149 (62), 137 (45)

TLC: R_f 0.51 (hexane/EtOAc, 5/1, PMA)

Analysis: $C_{13}H_{21}NO_3$ (239.31)

Calculated:	C: 65.25;	H: 8.84;	N: 5.85%
Found:	C: 65.37;	H: 8.94;	N: 5.59%

rel-(1*R*,6*R*,7*R*,11*R*,13*S*)-7-Methyl-13-methoxy-8-aza-9,14-tetracyclo[6.4.2.0^{1,6}.0^{7,11}] tetradecane (8)



6 **8**

To a cold (78 °C, dry ice bath) solution of nitroalkene **6** (250 mg, 1.04 mmol) in CH_2Cl_2 (8.7 mL) was added $SnCl_4$ (122 μL, 1.04 mmol, 1.2 equiv). After 20 min at that temperature, the solution was diluted with CH_2Cl_2 (15 mL) and then quenched with a solution of 1 N triethylamine in MeOH (15 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (2 x 15 mL), brine (15 mL), then were dried ($MgSO_4$), filtered and concentrated. The crude residue, which constituted a mixture of nitronate **7** and nitroso acetal **8** in a 3/2 ratio, was then dissolved in toluene (5 mL). Solid $NaHCO_3$ (420 mg, 5 mmol, 5 equiv) was added and the mixture was stirred at room temperature. After 1 h, the solution was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography (silica gel, CH_2Cl_2/EtOAc, 14/1) and distillation to afford 216 mg (87%) of **8** as colorless oil.

Analytical Data for **8**:

bp: 108 °C (2.2 x 10^{-4} mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

4.40 (dd, *J* = 15.5, 7.5, 1 H, *H*HC(10)), 4.35 (dd, *J* = 7.5, 2.5, 1 H, H*H*C(10)), 4.28 (s, 1 H, HC(13)), 3.47 (s, 3 H, H_3C(15)), 2.53 (tdd, *J* = 3.0, 8.0, 11.0, 1 H, HC(11)), 2.44 (dd, *J* = 5.0, 12.5, 1 H, HC(6)), 2.24 (dd, *J* = 11.0, 14.0, 1 H, *H*HC(12)), 1.79-1.71 (m, 2 H, *H*HC(2), *H*HC(5)), 1.63-1.53 (m, 2 H, H*H*C(2), H*H*C(5)), 1.38 (dd, *J* = 14.0, 2.5, 1 H, H*H*C(12)), 1.32 (dt, *J* = 13.5, 4.0, 1 H, *H*HC(4)), 1.30-1.16 (m, 2 H, *H*HC(3), H*H*C(4)), 1.12 (s, 3 H, H_3C(16)), 0.88 (dq, *J* = 3.0, 13.0, 1 H, H*H*C(3))

^{13}C NMR: (126 MHz, $CDCl_3$)

109.0 (C(13)), 88.2 (C(7)), 78.9 (C(10)), 55.4 (C(15)), 43.3 (C(1)), 38.6 (C(6)), 38.2 (C(11)), 26.1 (C(2)), 25.4 (C(5)), 24.5 (C(4)), 21.1 (C(3)), 21.0 (C(12)), 17.9 (C(16))

IR: ($CHCl_3$)

2936 (s), 2859 (m), 1724 (w), 1452 (m), 1088 (m), 1024 (m)

MS: FAB

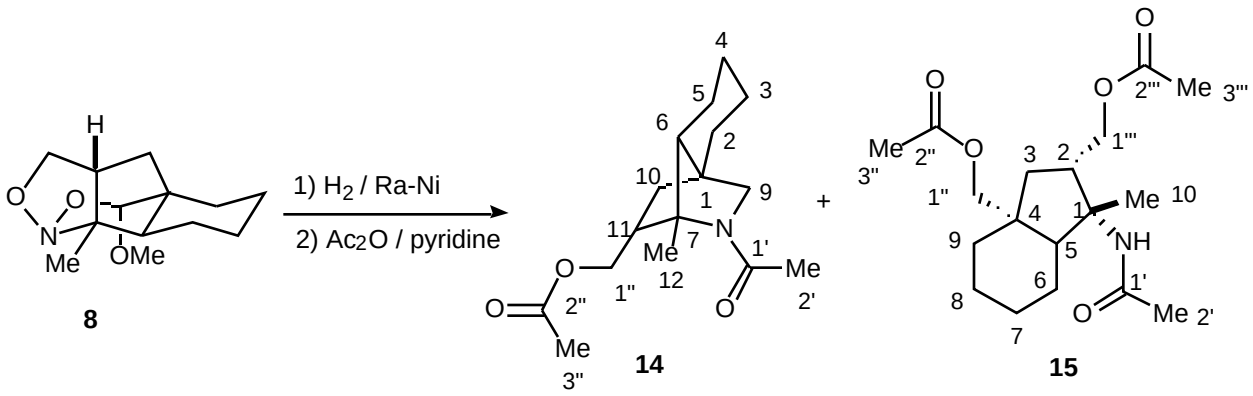
240 (33, M^++H), 220 (6), 209 (8), 155 (25), 154 (100), 149 (12), 147 (14), 138 (29), 137 (54), 136 (65), 120 (11), 106 (19), 104 (11)

TLC: R_f 0.48 (CH_2Cl_2/EtOAc, 14/1, I_2, PMA)

Analysis: $C_{13}H_{21}NO_3$ (239.31)

Calculated:	C: 65.25;	H: 8.84;	N: 5.85%
Found:	C: 65.33;	H: 8.91;	N: 5.81%

***rel*-(1*R*,5*R*,7*S*,11*R*)-N-Acetyl-7-methyl-8-azatricyclo[5.2.2.0^{1,6}]-11-undecylmethyl Acetate (14) and *rel*-(1*R*,2*S*,4*S*,5*S*)-4-acetoxymethyl-1-acetylamino-1-methyloctahydro-2-indenylmethyl Acetate (15)**



To a solution of **8** (86 mg, 0.36 mmol) in MeOH (2 mL) was added A5000 Raney Nickel (washed 3 x 10 mL MeOH). The mixture was placed under 1 atm of H_2, and the suspension was stirred at room temperature for 12 h. The Raney nickel was removed by filtering the reaction mixture through a pad of Celite. The filter cake was washed with MeOH (50 mL) and the filtrate was concentrated under reduced pressure.

The crude material was dissolved in pyridine (2 mL) and acetic anhydride (2 mL) and was stirred at room temperature for 12 h. The solution was diluted with water (10 mL) and CH_2Cl_2 (10 mL). The mixture was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (15 mL), brine (10 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, Et_2O/EtOAc/*t*-BuOH, 14/4/1) and distillation to afford 82 mg (81%) of **14** as a colorless oil and 7 mg (6%) of **15**.

Analytical Data for **14**:

bp: 125 °C (9.5×10^{-5} mmHg, ABT)

^{1}H NMR: (400 MHz, $CDCl_3$)

4.35 (dd, *J* = 6.4, 11.6, 1 H, *H*HC(1")), 4.00 (dd, *J* = 7.6, 11.6, 1 H, H*H*C(1")), 2.54 (dd, *J* = 2.8, 8.0, 1 H, *H*HC(9)), 2.49 (d, *J* = 8.0, 1 H, H*H*C(9)), 2.07-2.10 (m, 1 H, HC(11)), 1.79 (s, 3 H, H_3C(12)), 1.72-1.70 (m, 2H, H_2C(10)), 1.69 (s, 3 H, H_3C(3")), 1.65 (s, 3 H, H_3C(2')), 1.51 (dt, *J* = 13.2, 2.8, 1 H, *H*HC(5)), 1.39-1.28 (m, 2 H, *H*HC(3), H*H*C(5)), 1.22-1.05 (m, 1 H, *H*HC(2)), 1.12-1.01 (m, 1 H, *H*HC(4)), 0.94-0.78 (m, 2 H, H*H*C(2), H*H*C(3)), 0.62-0.55 (m, 2 H, HC(6), H*H*C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)

171.0 (C(1')), 168.7 (C(2")), 70.7 (C(1")), 66.2 (C(7)), 62.7 (C(6)), 57.1 (C(9)), 44.7 (C(11)), 43.5 (C(1)), 28.0 (C(2)), 24.9 (C(4)), 22.8 (C(10)), 21.8 (C(5)), 21.4 (C(3)), 20.8 (C(12)), 20.6 (C(3")), 16.4 (C(2'))

IR: ($CHCl_3$)

2929 (w), 2861 (w), 1739 (s), 1650 (s), 1409 (s), 1367 (m), 1238 (s), 1110 (w), 1033 (m), 973 (w)

MS: FAB

280 (100, M^++H), 278 (8), 264 (3), 238 (16), 220 (26), 178 (22), 161 (19), 159 (6), 137 (54), 149 (7), 147 (11), 104 (5)

TLC: R_f 0.49 (Et_2O/EtOAc/*t*-BuOH, 14/4/1, I_2, PMA)

Analysis: $C_{13}H_{21}NO_3$ (239.31)

Calculated:	C: 68.79;	H: 9.02;	N: 5.01%
Found:	C: 68.60;	H: 9.26;	N: 5.08%

Analytical Data for **15**:

^{1}H NMR: (500 MHz, $CDCl_3$)

5.86 (br, s, 1H, NH), 4.35 (dd, *J* = 5.5, 11.5, 1 H, *H*HC(1")), 4.11 (dd, *J* = 5.5, 11.5, 1 H, H*H*C(1")), 4.06 (d, *J* = 10.5, 1 H, *H*HC(1"')), 3.90 (d, *J* = 10.5, 1 H, H*H*C(1"')), 2.31-1.2.11 (m, 2H, HC(2), HC(5)), 2.09 (s, 3 H, H_3C(3")), 2.06 (s, 3 H, H_3C(3"')), 1.92 (s, 3 H, H_3C(2')), 1.76 (dd, *J* = 11.0, 13.0, 2 H, H_2C(2)), 1.60-1.51 (m, 4 H, *H*HC(6), *H*HC(7), *H*HC(8), *H*HC(9)), 1.50 (s, 3 H, H_3C(10)), 1.49-1.29 (m, 4 H, H*H*C (6), H*H*C(7), H*H*C(8), H*H*C(9))

^{13}C NMR: (126 MHz, $CDCl_3$)

170.5 (C(2")), 169.5 (C(2'")), 161.2 (C(1')), 70.4 (C(1")), 63.7 (C(1"')), 47.6 (C(5)), 46.0 (C(1)), 42.2 (C(2)), 38.3 (C(4)), 29.6 (C(9)), 29.5 (C(7)), 22.7 (C(3)), 21.8 (C(7)), 22.6 (C(8)), 22.4 (C(10)), 21.9 (C(6)), 21.0 (C(2')), 19.0 (C(3")), 14.1 (C(3"')).

IR: ($CHCl_3$)

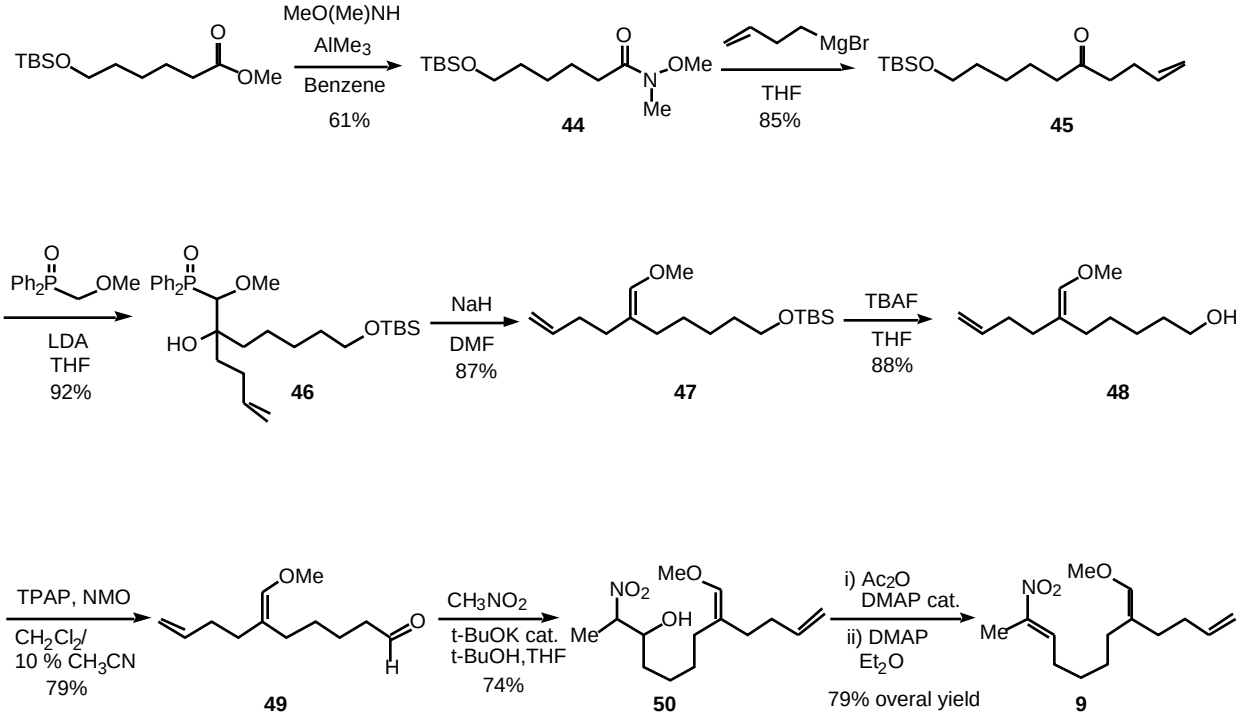
3181 (m), 2925 (s), 2854 (w), 1739 (s), 1658 (m), 1533 (w), 1463 (w), 1367 (w), 1238 (m), 1033 (w), 970 (w)

MS: FAB

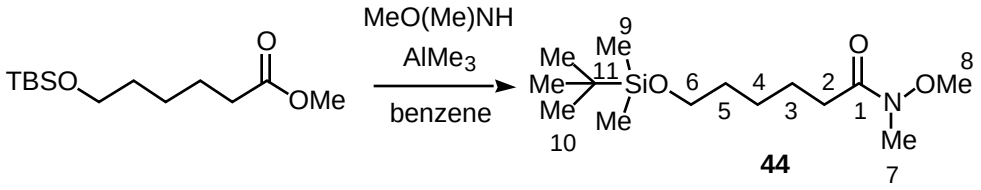
340 (61, $M+H^+$), 282 (100), 264 (3), 153 (7), 220 (26), 178 (22), 118 (100)

TLC: R_f 0.54 (Et_2O/EtOAc/*t*-BuOH, 7/2/0.5, I_2, PMA)

Preparation (10*E*)-5-Methoxymethylene-11-nitrododeca-1,10-diene (9)



6-(*tert*-Butyldimethylsilyloxy)hexanoic Acid Methoxymethylamide (44)



To a cold (0 °C, ice bath) solution of *N*,*O*-dimethylhydroxylamine hydrochloride (940 mg, 9.61 mmol, 2.5 equiv) in benzene (5 mL) was added dropwise a solution of trimethylaluminium (2.0 M toluene, 4.8 mL, 9.61 mmol, 2.5 equiv). After addition was complete, the solution was allowed to warm to room temperature for 1 h, then a solution of methyl-6-(O-*tert*-butyldimethylsilyl)hexanoate[6] (1.0 g, 3.84 mmol) in benzene (10 mL) was added and the mixture was stirred for 12 h at room temperature. The solution was carefully poured into a cold (0 °C, ice bath) aq. HCl (0.5 N, 20 mL) and was diluted with Et_2O (50 mL). The phases were separated and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (20 mL) and then dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 1/1) and distillation to afford 677 mg (61%) of **44** as a pale yellow oil.

Analytical Data for **44**:

bp: 105 °C (0.3 mmHg, ABT)

^{1}H NMR: (400 MHz, $CDCl_3$)
3.60 (s, 3 H, H_3C(8)), 3.58 (t, *J* = 6.0, 2 H, H_2C(6)), 3.10 (s, 3 H, H_3C(7)), 2.39 (t, *J* = 7.2, 2 H, H_2C(2)), 1.62 (q, *J* = 7.2, 2 H, H_2C(3)), 1.52 (q, *J* = 6.0, 2 H, H_2C(5)), 1.38-1.31 (m, 2 H, H_2C(4)), 0.85 (s, 9 H, 3 H_3C(10)), 0.01 (s, 6 H, 2 H_3C(9))

^{13}C NMR: (100 MHz, $CDCl_3$)
174.6 (C(1)), 62.9 (C(6)), 61.1 (C(8)), 32.5 (C(5)), 32.0 (C(7)), 31.8 (C(2)), 25.9 (C(10)), 25.6 (C(4)), 24.4 (C(3)), 18.3 (C(11)), -5.3 (C(9))

IR: ($CHCl_3$)
2933 (w), 2858 (w), 1672 (s), 1463 (w), 1385 (w), 1254 (m), 1101 (s), 1006 (w)

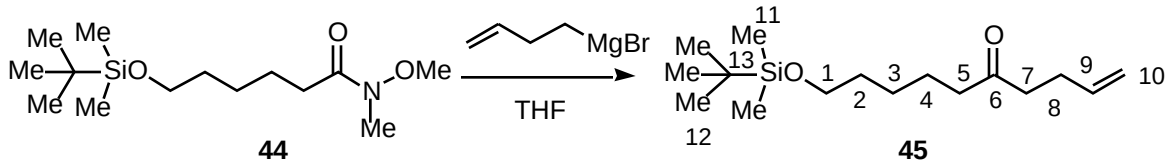
MS: FAB
290 (93, M^++H), 288 (13), 274 (26), 260 (25), 233 (16), 232 (100), 229 (29), 202 (25), 171 (11), 158 (58), 128 (19), 115 (7)

TLC: R_f 0.52 (hexane/EtOAc, 1/1, PMA)

Analysis: $C_{14}H_{31}NO_3Si$ (289.49)

Calculated:	C: 58.09;	H: 10.79;	N: 4.84%
Found:	C: 57.94;	H: 10.89;	N: 4.95%

10-(*tert*-Butyldimethylsilyloxy)-1-decen-5-one (45)



44 **45**

To a cold (–78 °C, internal temperature) solution of **44** (600 mg, 2.07 mmol) in THF (4 mL) was added dropwise a solution of 3-butenylmagnesium bromide (1 M THF, 8.30 mL, 8.28 mmol, 4 equiv). The solution was stirred 1 h at 0 °C (internal temperature), then was quenched with aq. HCl (0.1 N, 10 mL) and was diluted with Et_2O (20 mL). The phases were separated and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (20 mL) and then dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 5/1) and distillation to afford 500 mg (85%) of **45** as a pale yellow oil.

Analytical Data for **45**:

bp: 120 °C (2.5 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)
5.78 (tdd, *J* = 7.5, 17.5, 9.0, 1 H, H_2C(9)), 5.00 (qd, *J* = 1.5, 17.5, 1 H, HC(10)), 4.95 (qd, *J* = 1.5, 9.0, 1 H, HC(10)), 3.57 (t, *J* = 6.5, 2 H, H_2C(1)), 2.48 (t, *J* = 7.0, 2 H, H_2C(7)), 2.39 (t, *J* = 7.5, 2 H, H_2C(5)), 2.30 (dq, *J* = 1.5, 7.0, 2 H, H_2C(8)), 1.57 (t, *J* = 7.5, 2 H, H_2C(5)), 1.50 (q, *J* = 6.5, 2 H, H_2C(2)), 1.32-1.29 (m, 2 H, H_2C(3)), 0.86 (s, 9 H, 3 H_3C(12)), 0.02 (s, 6 H, 2 H_3C(11))

^{13}C NMR: (126 MHz, $CDCl_3$)
210.3 (C(6)), 137.1 (C(9)), 115.1 (C(10)), 62.9 (C(1)), 42.8 (C(7)), 41.7 (C(5)), 32.5 (C(2)), 27.7 (C(8)), 25.9 (C(12)), 25.4 (C(3)), 23.5 (C(4)), 18.3 (C(13)), -5.3 (C(11))

IR: ($CHCl_3$)
2931 (m), 2858 (w), 1717 (s), 1642 (w), 1463 (w), 1361 (w), 1255 (m), 1100 (s), 1004 (w), 912 (w)

MS: FAB

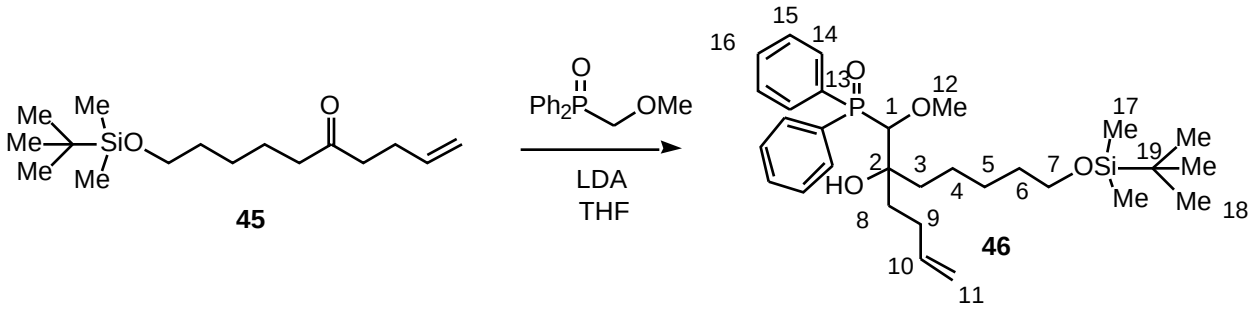
285 (57, M^++H), 229 (84), 227 (17), 199 (29), 187 (15), 183 (10), 173 (15), 169 (21), 157 (21), 153 (100), 151 (29), 149 (34), 143 (24), 135 (20), 133 (51), 131 (75), 129 (41), 127 (36)

TLC: R_f 0.61 (hexane/EtOAc, 5/1, PMA)

Analysis: $C_{16}H_{32}O_2Si$ (284.51)

Calculated:	C: 67.55;	H: 11.34%
Found:	C: 67.83;	H: 11.73%

7-(*tert*-Butyldimethylsilyloxy)-1-diphenylphosphinyl-1-methoxy-2-(3-butenyl)-2-heptanol (46)



To a cold (–78 °C, dry ice, *i*-PrOH bath) solution of diisopropylamine (1.11 mL, 7.88 mmol, 1.1 equiv) in THF (8 mL) was added *n*-butyllithium (1.50 M in THF, 5.40 mL, 7.88 mmol, 1.1 equiv). After 1 h at that temperature, the resulting lithium diisopropylamide solution was added to a cold (0 °C internal temperature) solution of methoxymethyltriphenylphosphine oxide (1.94 g, 7.88 mmol, 1.1 equiv) in THF (44 mL). After 10 min, the mixture was cooled to –78 °C (dry ice, internal temperature), and a solution of 45 (2.04 g, 7.17 mmol) in THF (8 mL) was added dropwise and the mixture was stirred for 3 h at –78 °C. The reaction was quenched with sat. aq. NH_4Cl solution (50 mL) and the product was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (40 mL), brine (40 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 2/1) to afford 3.5 g (92%) of **46** as a colorless oil which constituted of an inseparable mixture of isomers (1/1 by ^{1}H NMR analysis).

Analytical Data for **46**:

^{1}H NMR: (500 MHz, $CDCl_3$)

37 A: 8.11-8.06 (m, 2 H, HC(16)), 7.84-7.80 (m, 2 H, HC(14)), 7.58-7.47 (m, 6 H, HC(14), HC(15)), 5.76 (tdd, *J* = 7.0, 10.5, 17.5, 1 H, H_2C(10)), 4.71 (dd, *J* = 2.0, 10.5, 1 H, HC(11)), 4.62 (dd, *J* = 2.0, 17.5, 1 H, HC(11), 4.02 (d, *J* = 6.0, 1 H, HC(1)), 3.44 (t, *J* = 7.0, 2 H, H_2C(7)), 3.16 (s, 3 H, H_3C(12)), 2.19-2.09 (m, 1 H, H_2C(9)), 2.04-1.98 (m, 1 H, H_2C(9)), 1.71-1.52 (m, 2 H, H_2C(8)), 1.50-1.34 (m, 4 H, H_2C(3), H_2C(6)), 1.29-1.02 (m, 3 H, H_2C(4), H_2C(5)), 1.01-0.99 (m, 1 H, H_2C(4)), 0.88 (s, 9 H, 3 H_3C(19)), 0.22 (s, 6 H, 2 H_3C(17))

37 B: 8.11-8.06 (m, 2 H, HC(16)), 7.84-7.80 (m, 2 H, HC(14)), 7.58-7.47 (m, 6 H, HC(14), HC(15)), 5.42 (tdd, *J* = 6.5, 9.5, 17.0, 1 H, H_2C(10)), 4.95 (dd, *J* = 1.5, 17.0, 1 H, HC(11)), 4.88 (dd, *J* = 1.5, 9.5, 1 H, HC(11)), 4.01 (d, *J* = 5.0, 1 H, HC(1)), 3.55 (t, *J* = 6.5, 2 H, H_2C(7)), 3.18 (s, 3 H, H_3C(12)), 2.19-2.09 (m, 1 H, H_2C(9)), 2.04-1.98 (m, 1 H, H_2C(9)), 1.71-1.52 (m, 2 H, H_2C(8)), 1.50-1.34 (m, 4 H, H_2C(3), H_2C(6)), 1.29-1.02 (m, 3 H, H_2C(4), H_2C(5)), 1.01-0.99 (m, 1 H, H_2C(4)), 0.88 (s, 9 H, 3 H_3C(19)), 0.22 (s, 6 H, 2 H_3C(17))

^{13}C NMR: (126 MHz, $CDCl_3$)

37 A: 138.3 (C(10)), 132.3 (d, *J* = 8.3, C(13)), 131.7 (d, *J* = 8.4, C(15)), 128.4 (d, *J* = 11.0, C(14)), 127.9 (d, *J* = 11.0, C(16)), 113.8 (C(11)), 82.8 (d, *J* = 28.0, C(1)), 77.3 C(12)), 62.7 (C(7)), 61.8 (C(2)), 37.4 (C(9)), 36.1 (C(3)), 35.1 (C(8)), 32.4 (C(6)), 27.1 (C(4)), 25.7 (C(5)), 25.6 (C(19)), 17.9 (C(18)), -5.6 (C(17))

37 B: 138.1 (C(10)), 137.1 (d, *J* = 8.3, C(13)), 131.7 (d, *J* = 8.4, C(15)), 128.4 (d, *J* = 11.0, C(14)), 127.8 (d, *J* = 11.0, C(16)), 113.3 (C(11)), 85.5 (d, *J* = 28.0, C(1)), 77.2 C(12)), 62.7 (C(7)), 61.7 (C(2)), 37.4 (C(9)), 36.2 (C(3)), 35.0 (C(8)), 32.2 (C(6)), 26.9 (C(4)), 25.4 (C(5)), 25.6 (C(19)), 17.9 (C(18)), -5.6 (C(17))

IR: ($CHCl_3$)

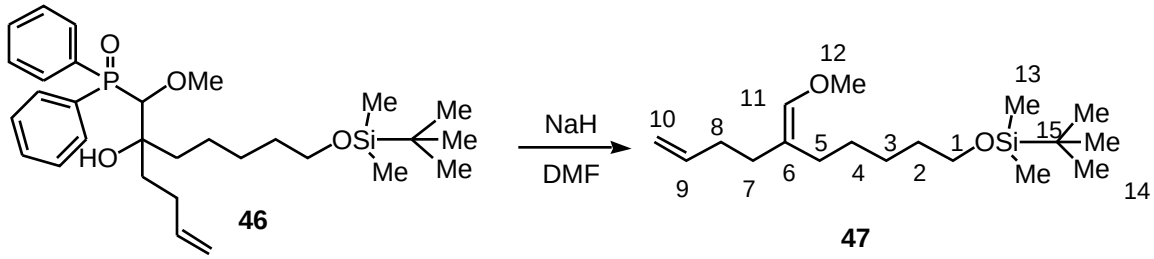
3381 (bm), 3062 (w), 2958 (m), 2864 (m), 1463 (w), 1438 (m), 1262 (w), 1171 (m), 1090 (s)

MS: FAB

531 (43, M^++H), 465 (12), 246 (21), 231 (40), 219 (15), 204 (13), 203 (89), 202 (41), 201 (100), 185 (26), 183 (14), 175 (26), 155 (10), 135 (14), 125 (25)

TLC: R_f 0.62 (hexane/EtOAc, 2/1, UV, PMA)

***tert*-Butyl-(6-methoxymethylene-9-decenyloxy)dimethylsilane (47)**



46 **47**

To a solution of **46** (3.0 g, 5.6 mmol) in DMF (157 mL) was added NaH (60 % in oil, washed with hexane, 680 mg, 17.0 mmol, 3 equiv) in one portion at room temperature. The mixture was then warmed to 55 °C for 3 h. The solution was cooled to 0 °C (ice bath) and then was quenched with water (150 mL) and diluted with Et_2O (150 mL). The ether layer was separated and the aqueous phase was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (70 mL), brine (70 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 15/1) and distillation to afford 1.50 g (87%) of **47** as a colorless oil which constituted of an inseparable mixture of isomers (1/1 by ^1H NMR analysis).

Analytical Data for **47**:

bp: 80 °C (9.0×10^{-5} mmHg, ABT)

^1H NMR: (500 MHz, $CDCl_3$)

5.86-5.75 (m, 2 H, HC(11), HC(9)), 5.03-4.91 (m, 2 H, HC(10)), 3.59 (t, J = 6.5, 2 H, $H_2C(1)$), 3.51 (s, 3 H, $H_3C(12)$), 2.12-2.10 (m, 3 H, $H_2C(5)$, $H_2C(7)$), 2.04 (t, J = 7.0, 2 H, $H_2C(7)$), 1.94 (q, J = 7.0, 1 H, $H_2C(8)$), 1.86 (td, J = 7.0, 1.0, 1 H, $H_2C(8)$), 1.52 (q, J = 7.0, 2 H, $H_2C(2)$), 1.38-1.27 (m, 4 H, $H_2C(3)$, HC(4)), 0.89 (s, 9 H, 3 $H_3C(15)$), 0.04 (s, 6 H, 2 $H_3C(13)$)

^{13}C NMR: (126 MHz, $CDCl_3$)

A: 142.9 (C(11)), 137.9 (C(9)), 117.7 (C(10)), 114.0 (C(6)), 63.3 (C(1)), 59.1 (C(12)), 32.8 (C(7)), 32.0 (C(8)), 31.4 (C(5)), 27.9 (C(2)), 25.9 (C(15)), 25.7 (C(4)), 25.4 (C(3)), 18.3 (C(14)), -5.3 (C(13))

B: 142.3 (C(11)), 138.7 (C(9)), 117.6 (C(10)), 114.4 (C(6)), 63.2 (C(1)), 59.2 (C(12)), 32.7 (C(7)), 32.0 (C(8)), 31.0 (C(5)), 27.5 (C(2)), 26.2 (C(15)), 25.9 (C(4)), 25.7 (C(3), 18.3 (C(14)), -5.3 (C(13))

IR: ($CHCl_3$)

2929 (w), 2858 (w), 1722 (m), 1641 (w), 1463 (m), 1388 (w), 1255 (s), 1101 (s), 1004 (m), 910 (m)

MS: FAB

255 (11, M^++H), 199 (11), 197 (10), 189 (10), 185 (10), 181 (27), 175 (33), 171 (32), 162.(16), 159 (19), 157 (20), 155 (14), 151 (18), 149 (98), 147 (66), 145 (29), 139 (30), 131 (54), 125 (65), 119 (61), 115 (100)

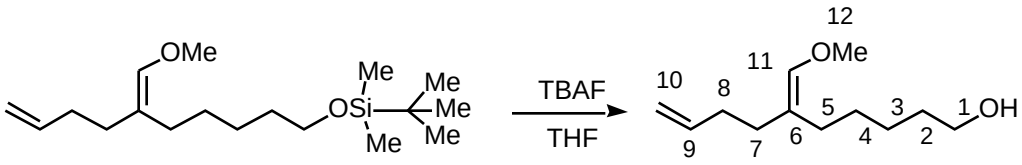
TLC: R_f 0.37 (hexane/EtOAc, 15/1, PMA)

Analysis: $C_{18}H_{36}SiO_2$ (312.57)

Calculated: C: 69.17; H: 11.61%

Found: C: 68.33; H: 11.84%

6-Methoxymethylene-9-decenol (48)



47 **48**

To a cold (0 °C) solution of **47** (1.50 mg, 4.80 mmol) in THF (9 mL) was added a solution of tetrabutylammonium fluoride (1 M THF, 7.20 mL, 7.20 mmol, 1.5 equiv) then the mixture was warmed to room temperature. After 4 h, the reaction was quenched with water (45 mL) and diluted with Et_2O (45 mL). The ether layer was separated and the aqueous phase was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (30 mL), brine (25 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 2/1) and distillation to afford 840 mg (89%) of **48** as a colorless oil which constituted of an inseparable mixture of isomers (1/1 by ^{1}H NMR analysis).

Analytical Data for **48**:

bp: 90 °C (0.02 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

5.85-5.78 (m, 1 H, HC(9)), 5.77 (s, 0.5 H, HC(11)), 5.76 (s, 0.5 H, HC(11)), 5.02 (dd, J = 17.0, 2.0, 1 H, HC(10)), 4.98 (dd, J = 8.0, 2.0, 1 H, HC(10)), 3.63 (t, J = 6.5, 2 H, H_2C(1)), 3.51 (s, 3 H, H_3C(12)), 2.12-2.04 (m, 3 H, H_2C(5), H_2C(7)), 1.96 (t, J = 7.5, 2 H, H_2C(5), H_2C(7)), 1.88 (q, J = 7.5, 1 H, H_2C(8)), 1.85 (t, J = 7.5, 1 H, H_2C(8)), 1.58 (q, J = 7.0, 2 H, H_2C(2)), 1.40-1.21 (m, 4 H, H_2C(3), H_2C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)

A: 142.4 (C(11)), 139.0 (C(9)), 117.7 (C(10)), 114.0 (C(6)), 62.8 (C(1)), 59.2 (C(12)), 32.9 (C(7)), 32.1 (C(8)), 31.4 (C(5)), 27.7 (C(2)), 25.6 (C(4)), 25.3 (C(3))

B: 142.3 (C(11)), 138.7 (C(9)), 117.6 (C(10)), 114.4 (C(6)), 63.0 (C(1)), 59.2 (C(12)), 32.7 (C(7)), 32.0 (C(8)), 31.0 (C(5)), 27.4 (C(2)), 25.8 (C(4)), 25.4 (C(3))

IR: ($CHCl_3$)

2929 (m), 2858 (m), 1725 (s), 1641 (m), 1456 (m), 1371 (w), 1110 (s), 1058 (s), 910 (m)

MS: FAB

199 (81, M^++H), 197 (12), 195 (10), 185 (10), 183 (27), 181 (18), 179 (12), 171.(11), 167 (35), 155 (20), 153 (20), 149 (71), 141 (12), 135 (59), 131 (15), 127 (24), 125 (40), 118 (100)

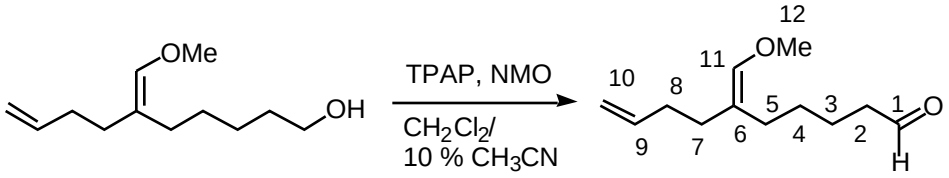
TLC: R_f 0.28 (hexane/EtOAc, 2/1, PMA)

Analysis: $C_{18}H_{36}SiO_2$ (312.57)

Calculated: C: 72.68; H: 11.18%

Found: C: 72.40; H: 11.31%

6-Methoxymethylene-9-decenal (49)



48 **49**

To a solution of **48** (600 mg, 3.0 mmol) in CH_2Cl_2 (10 mL) and CH_3CN (1.0 mL) was added at 0 °C 4-methylmorpholine *N*-oxide (530 mg, 4.5 mmol, 1.5 equiv), tetra-*n*-propylammonium perruthenate (51 mg, 0.15 mmol, 0.05 equiv), and molecular sieves (4 Å, 935 mg) and the mixture was allowed to warm to room temperature. After 5 h, the mixture was filtered through a plug of silica gel. The filter cake was washed with a solution of hexane/EtOAc, 2/1 (60 mL), and the filtrate was concentrated under reduced pressure to afford **49** 480 mg (79%) as a colorless oil which constituted of an inseparable mixture of isomers (1/1 by ^{1}H NMR analysis). Due to its sensitivity, **49** was used directly in the next step without further purification.

Analytical Data for **49**:

^{1}H NMR: (500 MHz, $CDCl_3$)

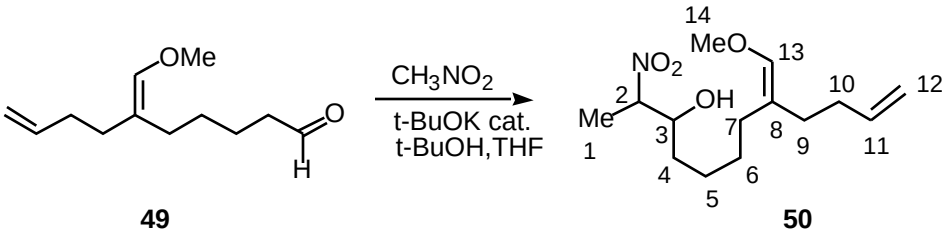
9.68 (t, *J* = 1.0, 1 H, HC(1)), 5.77-5.70 (m, 1 H, HC(9)), 5.72 (s, 0.5 H, HC(11)), 5.70 (s, 0.5 H, HC(11)), 4.96-4.95 (m, 0.5 H, HC(10)), 4.93-4.91 (m, 0.5 H, HC(10)), 4.89-4.85 (m, 1 H, HC(10)), 3.45 (s, 1.5 H, H_3C(12)), 3.46 (s, 1.5 H, H_3C(12)), 2.39-2.35 (m, 2 H, H_2C(2)), 2.06-2.03 (m, 3 H, H_2C(7), H_2C(5)), 2.01 (t, *J* = 7.5, 1 H, H_2C(7)), 1.88 (t, *J* = 7.5, 1 H, H_2C(8)), 1.82 (td, *J* = 7.5, 1.5, 1 H, H_2C(8)), 1.55 (q, *J* = 7.5, 2 H, H_2C(3)), 1.37-1.31 (m, 2 H, H_2C(4))

^{13}C NMR: (126 MHz, $CDCl_3$)

A: 202.7 (C(1)), 142.6 (C(11)), 138.6 (C(9)), 116.5 (C(10)), 114.3 (C(6)), 59.0 (C(12)), 43.5 (C(2)), 32.4 (C(7)), 30.7 (C(5)), 26.7 (C(8)), 25.9 (C(4)), 21.5 (C(3))

B: 202.4 (C(1)), 142.5 (C(11)), 138.4 (C(9)), 116.6 (C(10)), 113.9 (C(6)), 59.0 (C(12)), 43.4 (C(2)), 31.7 (C(7)), 30.9 (C(5)), 27.3 (C(8)), 26.0 (C(4)), 21.4 (C(3))

8-Methoxymethylene-2-nitro-11-dodecen-3-ol (50)



49 **50**

To a solution of aldehyde **49** (480 mg, 2.44 mmol) and nitroethane (525 μL, 7.32 mmol, 3 equiv) in *t*-BuOH/THF (1/1, 4.0 mL) was added *t*-BuOK (48 mg, 0.48 mmol, 0.2 equiv) at room temperature. After 20 min, the mixture was diluted with Et_2O (20 mL) and water (20 mL). The separated organic layer was washed with brine (20 mL) and the aqueous layers were back-extracted with Et_2O (2 x 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 4/1) to afford 500 mg (76%) of **50** as a pale yellow oil which constituted of an inseparable mixture of diastereoisomers.

Analytical Data for **50**:

^{1}H NMR: (500 MHz, $CDCl_3$)

5.84-5.72 (m, 1 H, HC(11)), 5.76 (s, 0.5 H, HC(13)), 5.75 (s, 0.5 H, HC(13)), 5.01-5.00 (m, 0.5 H, HC(12)), 4.97-4.96 (m, 0.5 H, HC(12)), 4.96-4.90 (m, 1 H, HC(12)), 4.53-4.45 (m, 1 H, HC(2)), 4.19-4.12 (m, 0.5 H, H_2C(3)), 3.90-3.85 (m, 0.5 H, H_2C(3)), 3.50 (s, 3 H, H_3C(14)), 2.49 (br s, 1H, OH), 2.11-2.02 (m, 4 H, H_2C(7), H_2C(4)), 1.92 (t, J = 7.0, 2 H, H_2C(9)), 1.86 (t, J = 7.2, 2 H, H_2C(10)), 1.52 (d, J = 6.8, 3 H, H_3C(1)), 1.53-1.33 (m, 4 H, H_2C(5), H_2C(6))

^{13}C NMR: (126 MHz, $CDCl_3$)

142.6 (C(13)), 142.4 (C(13)), 138.8 (C(11)), 138.4 (C(11)), 117.1 (C(8)), 114.4 (C(12)), 114.1 (C(12)), 87.7 (C(2)), 87.6 (C(2)), 86.3 (C(2)), 86.2 (C(2)), 72.7 (C(3)), 72.0 (C(3)), 59.2 (C(14)), 32.8 (C(7)), 32.7 (C(7)), 32.6 (C(7)), 32.5 (C(7)), 31.8 (C(4)), 31.9 (C(4)), 31.8 (C(4)), 32.5 (C(10)), 32.4 (C(10)), 31.1 (C(9)), 30.81 (C(9)), 27.8 (C(6)), 27.7 (C(6)), 26.9 (C(6)), 25.2 (C(5)), 25.0 (C(5)), 24.7 (C(5)), 24.3 (C(5)), 16.1 (C(1)), 12.3 (C(1))

IR: ($CHCl_3$)

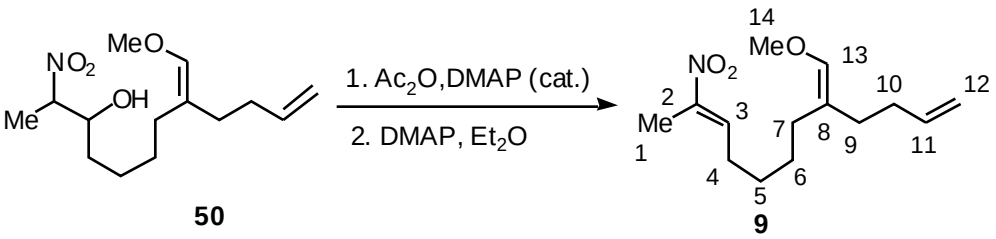
3471 (bm), 2939 (m), 2858 (w), 1735 (m), 1675 (w), 1550 (s), 1454 (w), 1392 (w), 1243 (m), 1243 (m), 1132 (m), 997 (w), 912 (w)

MS: FAB

272 (7, M^++H), 195 (18), 165 (10), 155 (21), 153 (19), 152 (20), 151 (8), 149 (18), 137 (16), 135 (46), 132 (100), 121 (16), 118 (81), 117 (20), 115 (13), 111 (14), 105 (14)

TLC: R_f 0.51 (hexane/EtOAc, 4/1, PMA)

(10*E*)-5-Methoxymethylene-11-nitrododeca-1,10-diene (9)



50 **9**

To a cold (0 °C, ice bath) solution of **50** (500 mg, 1.80 mmol) and acetic anhydride (163 μL, 2.02 mmol, 1.1 equiv) in Et_2O (10 mL) was added DMAP (40 mg, 0.36 mmol, 0.2 equiv) whereupon the mixture was allowed to warm to room temperature. After 2 h, the mixture was diluted with Et_2O (20 mL) and water (20 mL), and the separated organic layer was washed with sat.

aq. $NaHCO_3$ solution (20 mL), sat. aq. NH_4Cl solution (20 mL), and brine (20 mL). The aqueous layers were back extracted with Et_2O (40 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated to afford a pale yellow oil which was used in the next step without further purification.

To a solution of the nitro acetate (565 mg, 1.80 mmol) in Et_2O (13 mL) was added DMAP (250 mg, 2.16 mmol, 1.2 equiv) at 0 °C (ice water bath) and then was allowed to warm to room temperature. After 8 h, the reaction was quenched with water (20 mL) and the product was extracted with Et_2O (2 x 40 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (50 mL), brine (35 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, hexane/EtOAc, 5/1) and distillation to afford 346 mg (79%) of **9** as a pale yellow oil which constituted of an inseparable mixture of isomers (1/1 by ^1H NMR analysis).

Analytical Data for **9**:

bp: 135 °C (0.1 mmHg, ABT)

^1H NMR: (500 MHz, $CDCl_3$)

7.13 (m, 1 H, HC(3)), 5.84-5.74 (m, 1 H, HC(11)), 5.78 (s, 0.5 H, HC(13)), 5.76 (s, 0.5 H, HC(13)), 5.03-5.02 (m, 0.5 H, HC(12)), 5.02-4.98 (m, 0.5 H, HC(12)), 4.96-4.92 (m, 1 H, HC(12)), 3.52 (s, 3 H, H_3C(14)), 2.23 (q, J = 7.5, 2 H, H_2C(4)), 2.16 (s, 1.5 H, H_3C(1)), 2.15 (s, 1.5 H, H_3C(1)), 2.12-2.05 (m, 4 H, H_2C(7), H_2C(9)), 1.95-1.87 (m, 2 H, H_2C(10)), 1.49-1.38 (m, 4 H, H_2C(5), H_2C(6))

^{13}C NMR: (126 MHz, $CDCl_3$)

147.4 (C(2)), 142.8 (C(13)), 142.2 (C(13)), 138.8 (C(11)), 138.4 (C(11)), 136.6 (C(3)), 136.3 (C(3)), 116.8 (C(12)), 116.7 (C(12)), 114.5 (C(8)), 114.2 (C(8)), 59.3 (C(13)), 32.6 (C(7)), 31.9 (C(7)), 31.1 (C(4)), 30.8 (C(4)), 28.0 (C(9)), 27.9 (C(9)), 27.9 (C(10)), 27.8 (C(10)), 27.7 (C(5)), 27.0 (C(5)), 26.7 (C(6)), 26.9 (C(6)), 12.5 (C(1))

IR: ($CHCl_3$)

3076 (w), 2933 (s), 2859 (m), 1675 (m), 1521 (s), 1454 (w), 1390 (w), 1333 (s), 1027 (m), 1132 (m), 996 (w), 913 (w)

MS: FAB

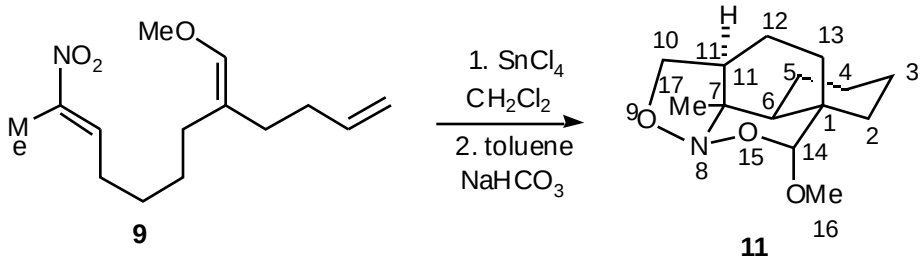
254 (100, M^++H), 152 (19), 240 (15), 238 (18), 224 (30), 223 (13), 222 (40), 208 (13), 206 (12), 195 (11), 194 (19), 192 (11), 191 (11), 163 (34), 161 (33), 149 (18), 135 (66)

TLC: R_f 0.53 (hexane/EtOAc, 5/1, PMA)

Analysis: $C_{14}H_{23}NO_3$ (253.34)

Calculated:	C: 66.37;	H: 9.15;	N: 5.53%
Found:	C: 66.11;	H: 9.28;	N: 5.57%

rel-(1_R_,6_R_,7_R_,11_R_,14_S_)-7-Methyl-14-methoxy-8-aza-9,15-tetracyclo[6.5.2.0^{1,6}.0^{7,11}] tetradecane (11)



9 **11**

To a cold (78 °C, dry ice bath) solution of nitroalkene **9** (260 mg, 1.04 mmol) in CH_2Cl_2 (8.5 mL) was added $SnCl_4$ (117 μL, 1.04 mmol, 1.1 equiv). After 20 min at that temperature, the solution was diluted with CH_2Cl_2 (18 mL) and then quenched with 1 N solution of triethylamine in MeOH (18 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (2 x 15 mL), brine (15 mL), then were dried ($MgSO_4$), filtered and concentrated. The crude residue, which constituted a mixture of nitronate **10** and nitroso acetal **11** in a 5/1 ratio, was then diluted with toluene (3 mL). Solid $NaHCO_3$ (415 mg, 5 mmol, 5 equiv) was added and the mixture was stirred at 100 °C. After 2 h, the solution was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography (silica gel, CH_2Cl_2/EtOAc, 14/1) and distillation to afford 205 mg (79%) of **11** as colorless oil.

Analytical Data for **11**:

bp: 140 °C (0.15 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

4.33 (dd, *J* = 11.5, 7.5, 1 H, HHC(10)), 4.25 (s, 1 H, HC(6)), 4.08 (dd, *J* = 2.0, 7.5, 1 H, HHC(10)), 3.44 (s, 3 H, H_3C(16)), 2.22 (dd, *J* = 12.0, 4.0, 1 H, HC(6)), 2.12 (qd, *J* = 9.0, 1.5, 1 H, HC(11)), 2.04-1.85 (m, 3H, HHC(12), H_2C(13)), 1.76-1.74 (m, 1H, HHC(5)), 1.67-1.65 (m, 1H, HHC(5)), 1.52 (td, *J* = 4.5, 13.5, 1 H, HHC(2)), 1.51-1.42 (m, 1H, HHC(3)), 1.38 (qt, *J* = 13.5, 3.5, 1 H, HHC(2)), 1.27-1.19 (m, 2H, H_2C(4)), 1.18-1.12 (m, 1H, HHC(12)), 1.06-0.99 (m, 1H, HHC(3)), 1.03 (s, 3 H, H_3C(17))

^{13}C NMR: (126 MHz, $CDCl_3$)

108.9 (C(14)), 81.9 (C(7)), 74.4 (C(10)), 55.3 (C(16), 37.9 (C(1)), 36.3 (C(6)), 34.4 (C(11)), 31.3 (C(13)), 28.4 (C(2)), 26.0 (C(12)), 23.1 (C(5)), 22.9 (C(4)), 22.8 (C(3)), 20.7 (C(17))

IR: ($CHCl_3$)

2940 (s), 2867 (m), 1452 (w), 1340 (w), 1191 (w), 1103 (m), 1010 (m), 971 (w)

MS: FAB

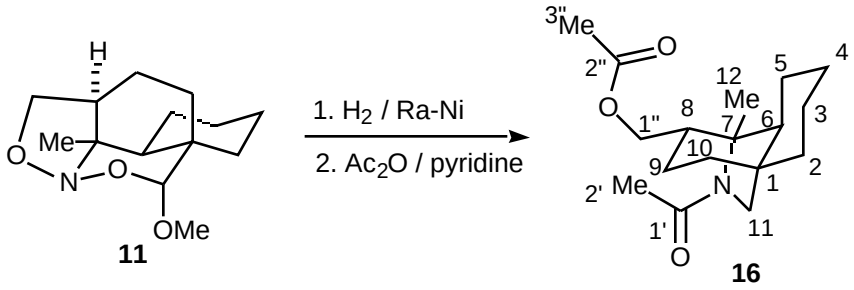
254 (100, M^++H), 252 (17), 224 (21), 223 (24), 222 (75), 194 (30), 193 (18), 192 (18), 191 (20), 178 (9), 173 (10), 164 (14), 163 (69), 161 (52), 136 (32)

TLC: R_f 0.49 (CH_2Cl_2/EtOAc, 14/1, I_2, PMA)

Analysis: $C_{14}H_{23}NO_3$ (253.34)

Calculated:	C: 66.37;	H: 9.15;	N: 5.53%
Found:	C: 66.39;	H: 9.06;	N: 5.59%

r*el*-(1*R*,6*S*,7*R*,8*R*)-*N*-Acetyl-7-methyl-12-azatricyclo[5.3.2.0^{1,6}]dodecylmethyl Acetate (16)



To a solution of nitroso acetal **11** (125 mg, 0.50 mmol) in MeOH (3 mL) was added A5000 Raney nickel (washed 3 x 10 mL of MeOH). The mixture was placed under 1 atm of H_2, and the suspension was stirred at room temperature for 12 h. The Raney nickel was removed by filtering the reaction mixture through a pad of Celite. The filter cake was washed with MeOH (50 mL), and the filtrate was concentrated under reduce pressure.

The crude material was dissolved in pyridine (3 mL) and acetic anhydride (3 mL) and was left to stir at room temperature for 12 h. The solution was diluted with water (15 mL) and CH_2Cl_2 (15 mL). The product was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with sat. aq. NH_4Cl solution (15 mL), brine (10 mL), then were dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (silica gel, CH_2Cl_2/MeOH, 9/1) and distillation to afford 109 mg (75%) of **16** as a colorless oil.

Analytical Data for **16**:

bp: 129 °C (9.5×10^{-5} mmHg, ABT)

^{1}H NMR: (400 MHz, $CDCl_3$)

4.78 (dd, *J* = 4.4, 11.2, 1 H, *H*HC(1")), 4.24 (dd, *J* = 8.8, 11.2, 1 H, H*H*C(1")), 2.68 (d, *J* = 7.6, 1 H, *H*HC(11)), 2.49 (dd, *J* = 1.2, 7.2, 1 H, H*H*C(11)), 1.74 (s, 3 H, H_3C(12)), 1.71-1.64 (m, 1 H, HC(8)), 1.69 (s, 3 H, H_3C(1)), 1.59 (s, 3 H, H_3C(2')), 1.59-1.51 (m, 2 H, *H*HC(9), *H*HC(10)), 1.37-1.14 (m, 4 H, *H*HC(2)), *H*HC(3)), *H*HC(5), HC(6)), 1.03-0.90 (m, 4 H, H*H*C(2), *H*HC(4), H*H*C(5), H*H*C(9)), 0.85-0.79 (m, 2 H, H*H*C(3), H*H*C(4)), 0.70 (dd, *J* = 13.6, 6.0, 1 H, H*H*C(10))

^{13}C NMR: (126 MHz, $CDCl_3$)

169.9 (C(1')), 168.3 (C(2")), 67.7 (C(1")), 65.6 (C(7)), 61.8 (C(11)), 55.7 (C(3)), 40.7 (C(1)), 38.2 (C(8)), 35.5 (C(2)), 27.4 (C(10)), 26.1 (C(4)), 24.9 (C(6)), 23.6 (C(12)), 21.5 (C(5)), 20.9 (C(9)), 20.7 (C(3")), 19.9 (C(2'))

IR: ($CHCl_3$)

2929 (m), 2865 (m), 1737 (s), 1648 (s), 1405 (m), 1236 (m), 1029 (w), 986 (w)

MS: FAB

294 (49, M^++H), 292 (7), 252 (12), 250 (12), 235 (18), 234 (100), 192 (24), 161 (6), 136 (5), 119 (4), 104 (5)

TLC: R_f 0.52 (CH_2Cl_2/MeOH, 9/1, I_2, PMA)

HRMS: calcd for $C_{17}H_{27}NO_3$: 293.19897; found: 293.19896.

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