A New Strategy for the Synthesis of γ-Nitro Alcohols from Aliphatic Nitro Compounds

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Abstract: A general method for the synthesis of γ-nitro alcohols **1** via C–C-cross-coupling of nitro compounds **3** with silyl derivatives of nitro compounds **4**, deoximination of resulting substrates and selective reduction of carbonyl group of ketones **2** is elaborated.

Key words: γ-nitro alcohols, aliphatic nitro compounds, new strategy, *N*,*N*-bis(silyloxy)enamines, selective reduction

Aliphatic nitro alcohols constitute a class of useful intermediates. Their utility in the total synthesis of natural products,[1] as well as their ability to serve as precursors to aminoalcohols,[2,3] may explain the growing interest in these compounds. However, different types of nitro alcohols are investigated to varying degrees. Indeed, various aspects of the chemistry of β-nitro alcohols are very well elaborated. At the same time, γ-nitro alcohols **1** are scantily studied, and to date there are no general methods for their synthesis. The occasional examples of the preparation of γ-nitro alcohols usually involve chemoselective reduction of their nearest precursors, corresponding carbonyl compounds **2** obtained from either β-haloketones or α,β-enones (Scheme 1).[4]

However, this approach, which includes different manipulations with functional groups on a fixed carbon skeleton, has quite limited scope owing to difficulties associated with introduction of the nitro group.

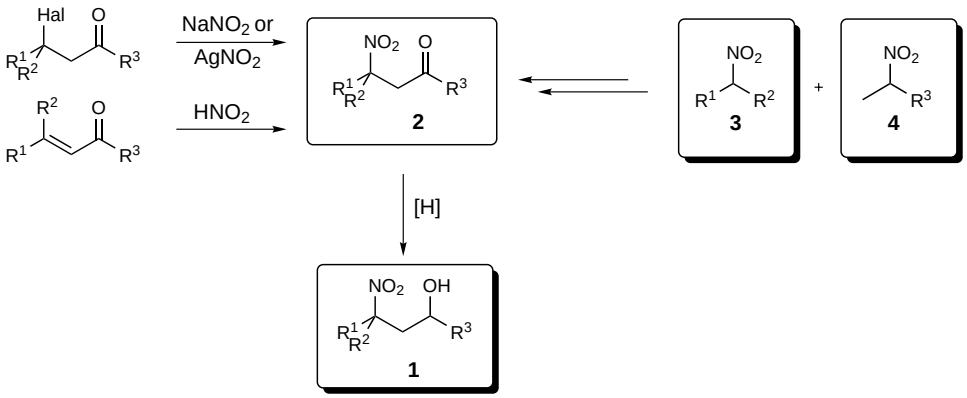
Herein we present a new strategy for the synthesis of γ-nitro alcohols **1** by construction of nitro carbonyl derivatives **2** from two molecules of aliphatic nitro compounds (ANC) (Scheme 1).

ANC **3** can be primary, secondary, or nitro methane. Compound **3** is used as nitro anion **5**, and its nitro group is preserved in the final nitro alcohol **1** (Scheme 2). ANC **4** must possess a methyl group at the α-carbon atom, which is eventually transformed into the methylene group of **1**. In the proposed method the ANC **4** is used as doubly silylated derivatives – *N*,*N*-bis(silyloxy)enamines (BENA) **6**.[5] The nitro group of **4** is finally converted into the hydroxyl group of **1** (Scheme 2).

The proposed strategy towards γ-nitro alcohols includes three steps, namely, the C–C-cross-coupling of anions **5** with BENA **6** affording β-nitrooxymes **7** followed by deoxymination and carbonyl group reduction (Scheme 2, Table 1).

We already studied in detail the first step.[6] In general it proceeds smoothly if *N*,*N*-bis(silyloxy)enamines **6** have a terminal double bond (i.e. the starting ANC **3** has a methyl substitutient).

For the deoximination of compounds **7** we tested several known reagents such as HCl,[7] $[Et_3NH]^+CrClO_3^-$,[8] Bu_4NMnO_4,[9] and levulinic acid,[10] none of which turned out to be generally applicable. For example, while treat-



Scheme 1

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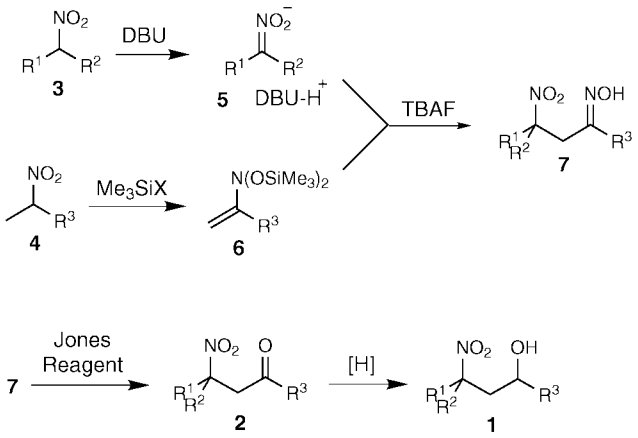


Scheme 2

ment of **7a**,**b** with 6% HCl gave ketones **2a**,**b** in 59% and 89% yields respectively, deoximination of derivative **7c** under the same conditions was accompanied by elimination of HNO_2 from the desired product.

The most suitable reagent for the deoximinaton proved to be CrO_3/H_2SO_4 in aqueous acetone (Jones reagent),[11] which neither caused elimination of HNO_2 nor affected other functional groups present in molecule **7**. Though under these conditions aldoximes were smoothly oxidized to carboxylic acids (for **2h**–**j** R^3 = OH).

The choice of procedure for selective reduction of keto or carboxy group in compounds **2** depends on the type of substrate. In the case of unfunctionalized β-nitro ketones and acids the BH_3·THF worked well leading to desired products without reduction of the nitro group in accordance with literature data.[12] It should be noted that the common reducing agent for ketones – sodium borohydride – is often not applicable to compound **2** owing to facile elimination of HNO_2.

We found that the presence of a nitro function at the β-position to the carbonyl group significantly slows down the reduction of the latter by BH_3·THF. This phenomenon decreases the chemoselectivity of the reduction of corresponding compounds **2**. Thus, reaction of ketone **2e**, having an additional ester group, with BH_3·THF gave rise to desired alcohol **1e**, along with diol **8b**, which can be obtained as the sole product when larger amounts of the reducing agent are used. The reduction of ketones **2k**,**l** with BH_3·THF was even less selective, with the yields of desired alcohols being 31% and 44%, respectively. The reduction of acid **2j** containing the ester function was also non-selective. The latter observation was very surprising,

Table 1 Synthesis of γ-Nitro Alcohols

Entry	R^1	R^2	R^3	ANC **3**	BENA **6**	Oxime **7**	Yield of **7** (%)	Ketone or Acid **2**	Yield of **2** (%)[a]	Alcohol or Diol, **1** or **8**	Yield of **1** or **8** (%)[b,c]
1	Me	Me	Me	**3a**	**6a**	**7a**	72	**2a**	89	**1a**	86 (43)
2	Et	H	Me	**3b**	**6a**	**7b**	72	**2b**	77	**1b**	95 (58)
3	$(CH_2)_2CO_2Me$	H	Me	**3c**	**6a**	**7c**	90	**2c**	80	**1c**	78[d] (51)
4	$(CH_2)_2CO_2Me$	H	Me	**3c**	**6a**	**7c**	90	**2c**	80	**8a**	74 (48)
5	$-(CH_2)_5-$		Me	**3d**	**6a**	**7d**	81	**2d**	90	**1d**	85 (45)
6	$(CH_2)_2CO_2Me$	Me	Me	**3e**	**6a**	**7e**	71	**2e**	91	**1e**	84[d] (47)
7	$(CH_2)_2CO_2Me$	Me	Me	**3e**	**6a**	**7e**	71	**2e**	91	**8b**	74 (48)
8	H	H	Me	**3f**	**6a**	**7f**	64	**2f**	50	**1f**	90
9	Ph	Me	Me	**3g**	**6a**	**7g**	40	**2g**	77	**1g**	85
10	$-(CH_2)_5-$		H	**3d**	**6b**	**7h**	47	**2h**[e]	57	**1h**	62
11	Me	Me	H	**3a**	**6b**	**7i**	55	**2i**[e]	80	**1i**	68
12	$(CH_2)_2CO_2Me$	Me	H	**3e**	**6b**	**7j**	62	**2j**[e]	78	**1j**	54[f]
13	Et	H	$(CH_2)_2CO_2Me$	**3b**	**6c**	**7k**	76	**2k**	86	**1k**	31
14	H	H	$(CH_2)_2CO_2Me$	**3f**	**6c**	**7l**	55	**2l**	58	**1l**	44

[a] Deoximinaton with $CrO_3/H_2O/H_2SO_4$ in aqueous acetone.
[b] Reduction with BH_3·THF if not mentioned otherwise.
[c] The yields in parentheses refer to the procedure [**3** + **6**] → **1** or **8** without purification of intermediate compounds and are given with respect to ANC **3** or BENA **6** (for **1b**).
[d] Reduction with $NaBH_3CN$/HCl in MeOH.
[e] R^3 = OH.
[f] Reduction conditions: 1) $(PhO)_2POCl/Et_3N$; 2) $NaBH_4$/THF.

since acids are known to be much more reactive then esters with respect to BH_3·THF.[12]

The problems outlined above prompted us to find another reducing agents for functionalized substrates **2**. Since there is no general solution, it was necessary to find special conditions for each species. Thus, compounds **2c**,**e** were cleanly reduced by $NaBH_3CN$ in methanol in the presence of HCl[13] (Scheme 3). However, no reduction of ketone **2l** took place with $NaBH_3CN$.

For reduction of acid **2j** we used $(PhO)_2POCl$ to give mixed anhydride which was treated with $NaBH_4$ according to a known procedure[14] (Scheme 4).

γ-Nitro alcohols **1b**,**c**,**e**,**g**,**k** were obtained as a diastereomeric ratio (1:2–1:2.7).

It is of special note that in most cases the whole three-step sequence, [**3** + **6**]→**7**→**2**→**1** (or **8**), can be performed without purification of intermediate compounds in about 50% yield with respect to ANC **3** (see Table 1).

In conclusion, we have demonstrated that γ-nitro alcohols **1** can be assembled simply in a facile manner from two molecules of aliphatic nitro compounds. Our future studies will be aimed at the development of diastereo- and enantioselective approaches toward γ-nitro and γ-aminoalcohols.

NMR spectra were recorded on a Bruker AM-300, WM-250, and AC-200 instruments. Chemical shifts were measured relative to the residual solvent peak (^{1}H, ^{13}C)[15] or external reference ($MeNO_2$, 0 ppm, for ^{14}N). Starting reagents were preparated by literature procedures: TBAF,[6] $(PhO)_2POCl$,[14] BH_3·THF,[12] **ANC 3c,e**,[16] **3g**,[17] BENA **5a**–**c**,[5] and oximes **7a**–**f**,**h**,**j**,**k**,[6] Reductions with BH_3·THF were performed in the atmosphere of dry argon in freshly distilled solvents. Commercially available DBU was distilled from CaH_2 in vacuum and stored under argon.

4-Nitro-4-phenylpentan-2-one Oxime (7g)

To a solution of DBU (0.14 mL, 0.95 mmol) in CH_2Cl_2 (5 mL) at 5 °C was added α-nitroethylbenzene (151 mg, 1 mmol), the reaction mixture was stirred at 5 °C for 5 min, a solution of BENA **6a** (243 mg, 1.05 mmol) in CH_2Cl_2 (3 mL) was added dropwise at 5 °C for 5 min. The reaction mixture was stirred at 5 °C for 1 h. A mixture of NH_4F (39 mg, 1.05 mmol), HOAc (0.07 mL, 1.3 mmol), and MeOH (2.7 mL) was added over 5 min and the reaction mixture was poured into H_2O–Et_2O (1:1, 20 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and evaporated. The residue was recrystallized from petroleum ether–toluene (5:1) to give 88 mg of **7g** (40%, *anti*-isomer); mp 100–105 °C.

^{1}H NMR ($CDCl_3$): δ = 1.44 (s, 3 H, $MeCNO_2$), 1.81 (s, 3 H, CH_3C=NOH), 2.94 (d, 1 H, CH_AH_B, ^2J = 14.8 Hz), 3.27 (d, 1 H, CH_AH_B, ^2J = 14.8 Hz), 7.10–7.32 (m, 5 H, C_6H_5), 9.26 (br, 1 H, OH).

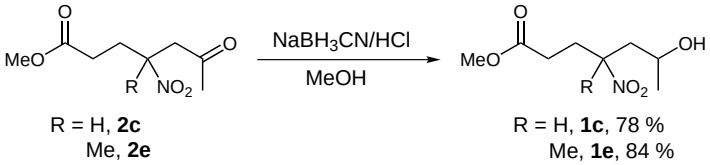
^{13}C NMR ($CDCl_3$): δ = 14.2 (CH_3C=N), 23.4 (CH_3CNO_2), 45.0 (CH_2), 91.4 (CNO_2), 125.0, 128.6 (*o*,*m*-CH_{Ph}), 128.8 (*p*-CH_{Ph}), 139.6 (*i*-C_{Ph}), 152.2 (C=N).

Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.61. Found: C, 59.80; H, 6.37; N, 12.58.

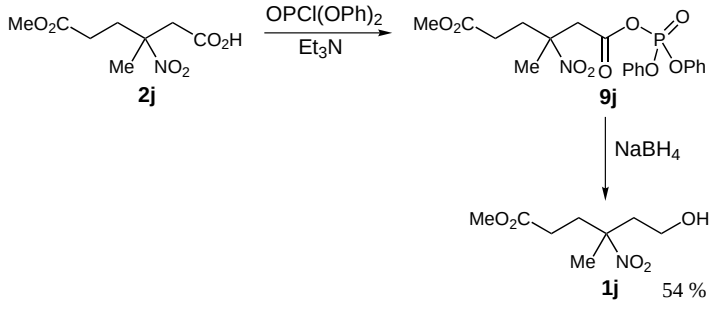
3-Methyl-3-nitrobutanal Oxime (7i)

To a solution of 2-nitropropane (1.35 mL, 15 mmol) in Et_2O (120 mL) at 5 °C was added DBU (2.24 mL, 15 mmol), the reaction mixture was stirred at 5 °C for 5 min, a solution of BENA **5b** (3.285 g, 15 mmol) in mixture of Et_2O–benzene (1:1, 60 mL) was added dropwise at 5 °C over 1 h. The reaction mixture was stirred at 5 °C for 2 h. A mixture of NH_4F (0.555 g, 15 mmol), HOAc (1.29 mL, 22.5 mmol), and MeOH (24 mL) was added and after stirring for 20 min the reaction mixture was poured into H_2O (150 mL). The aqueous layer was extracted with Et_2O (4 × 40 mL), the combined organic layers were washed with brine, dried (Na_2SO_4), and evaporated to give 1.20 g of **7i** (55%, *syn*:*anti*, 1:1), purity >95% (^{1}H NMR); oil.

^{1}H NMR ($CDCl_3$): δ = 1.62, 1.65 (s, 6 H, Me_2C, *syn* and *anti*), 2.78 (d, 2 H, *syn*-CH_2, ^3J = 6.6 Hz,), 3.01 (d, 2 H, *anti*-CH_2, ^3J = 5.4 Hz,), 6.72 (t, 1 H, *anti*-CH=N, ^3J = 5.4 Hz,), 7.35 (t, 1 H, *syn*-CH=N, ^3J = 6.6 Hz,), 8.1–9.1 (br, 1 H, OH).



Scheme 3



Scheme 4

^{13}C NMR ($CDCl_3$): δ = 25.9, 26.1 (Me, *syn* and *anti*), 35.1 (CH_2, *syn*), 39.8 (CH_2, *anti*), 86.2, 86.6 (CNO_2, *syn* and *anti*), 146.1, 146.7 (C=N, *syn* and *anti*).

Methyl 6-Nitro-4-oxyiminohexanoate (7l)

To a solution of $MeNO_2$ (0.81 mL, 15.0 mmol) in CH_2Cl_2 (100 mL) at 5 °C was added DBU (2.23 mL, 15.0 mmol), the reaction mixture was stirred at 5 °C for 5 min and then cooled down to –78 °C. A solution of BENA **6c** (4.54 g, 14.9 mmol) in CH_2Cl_2 (30 mL) and Bu_4NF in THF (4.08 mL 0.73 M, 2.97 mmol) were successively added dropwise at –78 °C. The reaction mixture was stirred at –78 °C for 1 h, then a solution of HOAc (1.8 mL, 30.0 mmol) in Et_2O (10 mL) was added at –78 °C, and stirred for an additional 10 min. The reaction mixture was poured into Et_2O–H_2O (2:1, 300 mL). The aqueous layer was extracted with Et_2O (3 × 30 mL), the combined organic layers were washed with H_2O (20 mL), brine, dried (Na_2SO_4), and evaporated. The residue was subjected to column chromatography (silica gel, $CHCl_3$–Et_2O 3:1) to give 1.67 g of **7l** (55%, *syn*:*anti*, 1:7); oil; R_f (*syn* and *anti*) 0.38 ($CHCl_3$–Et_2O, 2:1).

^{1}H NMR ($CDCl_3$,): *anti*-**7l**: δ = 2.50–2.70 (m, 4 H, CH_2CH_2CO), 2.93 (t, 2 H, C*H*$_2$$CH_2NO_2$, ^3J = 6.7 Hz), 3.67 (s, 3 H, MeO), 4.59 (t, 2 H, CH_2NO_2, ^3J = 6.7 Hz); *syn*-**7l**: δ = 4.65 (t, 2 H, CH_2NO_2, ^3J = 7.4 Hz).

^{13}C NMR ($CDCl_3$): *anti*-**7l**: δ = 29.7 (CH_2*C*H_2CO), 24.0, 31.3 (*C*H_2CN*C*H_2), 52.0 (OMe), 71.0 (CH_2NO_2), 155.4 (C=N), 173.3 (COOMe); *syn*-**7l**: δ = 29.8 (CH_2*C*H_2CO), 27.1, 29.9 (*C*H_2CN*C*H_2), 52.0 (OMe), 70.8 (CH_2NO_2), 154.7 (C=N), 173.2 (COOMe).

Anal. Calcd for $C_{17}H_{12}N_2O_5$: C, 41.18; H, 5.92; N, 13.72. Found: C, 41.39; H, 5.84; N, 13.81.

Preparation of Jones' Reagent[11]

To a solution of CrO_3 (26.67 g, 0.266 mol) in H_2O (27 mL) were added concd H_2SO_4 (22.1 mL) with vigorous stirring and then H_2O up to a total volume of 100 mL.

Deoximination of 7a-l; General Procedure

To a solution of nitrooxime **7a**–**l** (15 mmol) in acetone (70 mL) was added Jones' reagent (**7a**–**g**: 2.66 M, 5.6 mL, 15 mmol; **7h**–**l**: 2.66 M, 11.2 mL, 30 mmol) with vigorous stirring at 20 °C. Two more portions of Jones' reagent (15 mmol each) were added after 1 and 2 h. After additional stirring for 2 h the reaction mixture was poured into Et_2O–H_2O (1:1, 150 mL). The aqueous layer was extracted with Et_2O (4 × 25 mL), the combined organic layers were washed with H_2O (5 × 10 mL), brine (15 mL), dried ($MgSO_4$), and evaporated to give carbonyl compounds **2**.[18]

4-Methyl-4-nitropentan-2-one (2a)[19]

Yield: 89%; oil.

^{1}H NMR ($CDCl_3$): δ = 1.59 (s, 6 H, Me_2C), 2.11 (s, 3 H, MeCO), 3.09 (s, 2 H, CH_2CO).

^{13}C NMR ($CDCl_3$): δ = 26.2 [(*C*H_3)$_2$C], 30.3 (*C*H_3CO), 51.2 (CH_2), 84.5 (CNO_2), 203.6 (CO).

4-Nitrohexan-2-one (2b)

Yield: 77%; oil.

^{1}H NMR spectrum is identical to lit. data.[7]

Methyl 4-Nitro-6-oxoheptanoate (2c)

Yield: 80%; oil.

^{1}H NMR ($CDCl_3$): δ = 2.05–2.20 (m, 2 H, C*H*$_2$$CH_2CO_2$), 2.14 (s, 3 H, MeCO), 2.33–2.43 (m, 2 H, CH_2 C*H*$_2$$CO_2$), 2.74 (dd, 1 H, C*H*$_AH_B$CO, ^2J = 18.8, ^3J = 4.7 Hz), 3.27 (dd, 1 H, CH_AH_BC=O, ^2J = 18.8, ^3J = 9.4 Hz), 3.63 (s, 3 H, OMe), 4.85–4.96 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 28.3, 29.8 (CH_2CH_2), 29.7 (*C*H_3CO), 45.3 (*C*H_2CO), 51.9 (OMe), 81.3 (CNO_2), 172.1 (CO_2), 203.3 (CO).

1-(1-nitrocyclohexyl)propan-2-one (2d)

Yield: 90%; oil.

^{1}H NMR ($CDCl_3$): δ = 1.33–1.77 (m, 6 H, $CH_{2\text{-}3'c\text{-hex}}$, $CH_{2\text{-}4'c\text{-hex}}$), 1.84–2.04 and 2.19–2.34 (m, 4 H, $CH_{2\text{-}2'c\text{-hex}}$), 2.14 (s, 3 H, Me), 3.07 (s, 2 H, CH_2CO).

^{13}C NMR ($CDCl_3$): δ = 22.4 ($CH_{2\text{-}3'c\text{-hex}}$), 24.7 ($CH_{2\text{-}4'c\text{-hex}}$), 31.0 (Me), 34.4 ($CH_{2\text{-}2'c\text{-hex}}$), 49.4 (*C*$H_2$CO), 88.7 ($CNO_2$), 203.7 (CO).

Methyl 4-Methyl-4-nitro-6-oxoheptanoate (2e)

Yield: 91%; oil.

^{1}H NMR ($CDCl_3$): δ = 1.67 (s, 3 H, $MeCNO_2$), 2.17 (s, 3 H, MeCO), 2.20–2.39 (m, 4 H, CH_2CH_2), 2.93 (d, 1 H, C*H*HCO, ^2J = 17.7 Hz), 3.28 (d, 1 H, CH*H*CO, ^2J = 17.7 Hz), 3.67 (s, 3 H, OMe).

^{13}C NMR ($CDCl_3$): δ = 22.6 (*C*$H_3$$CNO_2$), 28.6 (*C*$H_2$$CO_2$Me), 30.6 (*C*$H_3$CO), 34.5 (*C*$H_2$$CNO_2$), 49.9 (*C*$H_2$CO), 51.8 (OMe), 87.0 ($CNO_2$), 172.0 ($CO_2$), 202.3 (CO).

4-Nitrobutan-2-one (2f)

Yield: 50%; oil.

^{1}H NMR spectrum is identical to lit. data.[20]

4-Nitro-4-phenylpentan-2-one (2g)

Yield: 77%; oil.

^{1}H NMR ($CDCl_3$): δ = 2.10, 2.14 (s, 6 H, $MeCNO_2$, MeCO), 3.25 (d, 1 H, C*H*$_A$H$_B$, ^2J = 17.7 Hz), 3.77 (d, 1 H, CH$_A$*H*$_B$, ^2J = 17.7 Hz), 7.34 (br, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 23.8 (*C*$H_3$$CNO_2$), 30.7 (*C*$H_3$CO), 51.6 ($CH_2$), 89.9 ($CNO_2$), 124.7, 129.0 (*o*-, *m*-, *p*-CH_{Ph}), 139.5 (*i*-C_{Ph}), 203.3 (CO).

(1-Nitrocyclohexyl)-acetic Acid (2h)

Yield: 57%; mp 100–104 °C (petroleum ether–toluene, 6:1).

^{1}H NMR ($CDCl_3$): δ = 1.39–1.75 (m, 6 H, 3′-CH_2, 4′-CH_2), 1.84–2.01 and 2.24–2.41 (m, 4 H, 2′-CH_2), 3.01 (s, 2 H, CH_2CO), 10.30–10.71 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 22.3 (3′-CH_2), 24.6 (4′-CH_2), 34.3 (2′-CH_2), 41.8 (*C*H_2CO), 88.2 (CNO_2), 175.3 (CO).

Anal. Calcd for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.57; H, 6.94; N, 7.36.

3-Methyl-3-nitrobutanoic Acid (2i)

Yield: 80%; mp 95–100 °C (petroleum ether–toluene, 7:1)

^{1}H NMR (Acetone-d_6): δ = 1.68 (s, 6 H, Me_2C), 3.08 (s, 2 H, CH_2), 3.69–7.40 (br, 1 H, OH).

^{13}C NMR (Acetone-d_6): δ = 26.5 [(*C*H_3)$_2$C], 43.5 (CH_2), 85.7 (CNO_2), 170.9 (CO).

Anal. Calcd for $C_5H_9NO_4$: C, 40.82; H, 6.17; N, 9.52. Found: C, 40.79; H, 6.18; N, 9.49.

5-Methoxycarbonyl-3-methyl-3-nitropentanoic Acid (2j)

Purified by column chromatography (silica gel, petroleum ether–EtOAc, 1:1); yield 78%; mp 62–65 °C (petroleum ether–toluene, 3:2); R_f 0.48 ($CHCl_3$–Et_2O, 1:1).

^{1}H NMR ($CDCl_3$): δ = 1.71 (s, 3 H, MeCN), 2.21–2.50 (s, 4 H, CH_2CH_2), 2.87 (d, 1 H, C*H*$_A$H$_B$$CO_2$, ^2J = 17.1 Hz), 3.22 (d, 1 H, CH$_A$*H*$_B$$CO_2$, ^2J = 17.1 Hz), 3.68 (s, 3 H, OMe), 8.48–9.17 (br, 1 H, OH).

^{13}C NMR ($CDCl_3$): δ = 22.6 (Me), 28.6, 34.5 (CH_2CH_2), 42.1 (*C*$H_2$$CO_2$H), 52.2 (OMe), 87.0 ($CNO_2$), 172.5, 174.1 ($CO_2$).

Anal. Calcd for $C_8H_{13}NO_6$: C, 43.84; H, 5.98; N, 6.39. Found: C, 44.03; H, 5.89; N, 6.21.

Methyl 6-nitro-4-Oxooctanoate (2k)
Yield: 86%; oil.

^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 3 H, C*H*$_3$CH$_2$, ^3J = 7.4 Hz), 1.74–1.88 (m, 2 H, MeC*H*$_2$), 2.36–2.79 (m, 5 H, $CH_2CH_2CO_2$ and C*H*$_A$H$_B$CO), 3.25 (dd, 1 H, CH$_A$*H*$_B$CO, ^2J = 18.4, ^3J = 9.5 Hz), 3.54 (s, 3 H, OMe), 4.77 (ddt, 1 H, $CHNO_2$, ^3J = 6.5, ^3J = 4.0, ^3J = 9.5 Hz).

^{13}C NMR ($CDCl_3$): δ = 9.7 (C*H*$_3$C), 26.9, 27.5 (*C*H$_2$CO$_2$, *C*H$_2$Me), 36.9 (*C*H$_2$CH$_2$CO$_2$), 44.0 (*C*H$_2$CO), 51.7 (OMe), 83.5 (CNO_2), 172.8 (CO_2), 204.6 (CO).

Methyl 6-Nitro-4-oxohexanoate (2l)
Yield: 58%; oil

^{1}H NMR spectrum is identical to lit. data.[21]

^{13}C NMR ($CDCl_3$): δ = 27.7 (*C*H$_2$CO$_2$), 37.0, 38.5 (*C*H$_2$CO*C*H$_2$), 51.9 (MeO), 69.0 (CH_2NO_2), 173.0 (CO_2), 204.4 (CO).

Reduction of Nitrocarbonyl Compounds 2a,b,d,f–i,k,l with BH_3·THF; General Procedure
To a solution of nitrocarbonyl compound **2** (1 mmol) in THF (1.5 mL) was added the specified amount of BH_3·THF at the specified temperature. The mixture was stirred for the specified time, then MeOH (3.5 mmol for 1 mmol BH_3·THF) was added dropwise, in 5 min the reaction mixture was poured into a mixture of H_2O (4 mL) and concd HCl (0.15 mL). The aqueous layer was extracted with Et_2O (6 × 3 mL), the combined organic layers were washed with brine, dried (Na_2SO_4) and evaporated (for the isolation of nitrodiols **8a,b** from the aqueous layer its continuous extraction with Et_2O over 18 h was required). For some alcohols **1** the reaction mixture was quenched with MeOH (9 mmol per 1 mmol of BH_3·THF) followed by evaporation of the solvent in vacuum and column chromatography.

4-Methyl-4-nitropentan-2-ol (1a)
The reaction was carried out with BH_3·THF (1.4 mmol, 1.86 mL 1.33 M solution in THF) at 20 °C for 3.5 h; yield: 86%; bp 65–67 °C (0.2 Torr).

^{1}H NMR ($CDCl_3$): δ = 1.22 (d, 3 H, Me, ^3J = 6.1 Hz), 1.63, 1.66 [s, 6 H, (C*H*$_3$)$_2$C], 1.96 (dd, 1 H, C*H*$_A$H$_B$, ^2J = 15.3, ^3J = 3.1 Hz), 2.23–2.32 (br, 1 H, OH), 2.22 (dd, 1 H, CH$_A$*H*$_B$, ^2J = 15.3, ^3J = 9.8 Hz), 3.88–4.02 (m, 1 H, C*H*OH).

^{13}C NMR ($CDCl_3$): δ = 24.6, 25.5 and 26.7 (3 × Me), 48.2 (CH_2), 64.2 (CH), 86.9 (CNO_2).

^{14}N NMR ($CDCl_3$): δ = 23.4 (NO_2, $\upsilon_{1/2}$ = 250 Hz).

Anal. Calcd $C_6H_{13}NO_3$: C, 48.97; H, 8.90; N, 9.52. Found: C, 49.08; H, 8.88; N, 9.48.

4-Nitrohexan-2-ol (1b)[7]
The reaction was carried out with BH_3·THF (1.4 mmol, 1.86 mL 1.33 M solution in THF) at 20 °C, for 3.5 h; yield: 95%, minor:major ca. 1:2.7 (^{1}H NMR); bp 66–67 °C (0.15 Torr).

Major Isomer:

^{1}H NMR (DMSO-d_6): δ = 0.96 (t, 3 H, C*H*$_3$CH$_2$, ^3J = 7.4 Hz), 1.23 (d, 3 H, C*H*$_3$CH, ^3J = 7.0 Hz), 1.62–2.28 (m, 4 H, 2 × CH_2), 2.42–2.84 (br, 1 H, OH), 3.81–3.92 (m, 1 H, C*H*OH), 4.51–4.73 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 10.1 (*C*H$_3$CH$_2$), 23.6 (*C*H$_3$CH), 27.3 (Me*C*H$_2$), 42.1 (CH_2), 65.3 (CHOH), 87.8 ($CHNO_2$).

Minor Isomer:

^{1}H NMR (DMSO-d_6): δ = 0.97 (t, 3 H, *C*H$_3$CH$_2$, ^3J = 7.4 Hz), 3.68–3.80 (m, 1 H, C*H*OH), 4.69–4.76 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 10.2 (*C*H$_3$CH$_2$), 23.8 (*C*H$_3$CH), 27.8 (Me*C*H$_2$), 42.2 ($CHOH_2$), 64.2 (CHOH), 87.2 ($CHNO_2$).

^{14}N NMR ($CDCl_3$): δ = 14.9 (NO_2 for two diastereomers, $\upsilon_{1/2}$ = 270 Hz).

Anal. Calcd for $C_6H_{13}NO_3$: C, 48.97; H, 8.90; N, 9.52. Found: C, 49.15; H, 8.76; N, 9.51.

1-(1-Nitrocyclohexyl)-propan-2-ol (1d)
The reaction was carried out with BH_3·THF (1.4 mmol, 1.86 mL 1.33 M solution THF) at 20 °C for 3.5 h; Yield: 85%; bp 89–90 °C (0.2 Torr).

^{1}H NMR ($CDCl_3$): δ = 1.13 (d, 3 H, Me, ^3J = 6.1 Hz), 1.20–1.75 [m, 9 H, OH, 4 × $CH_{2\text{-}c\text{-}Hex}$ except 2 H at -CH(2′)], 1.81 (dd, 1 H, C*H*$_A$H$_B$CHOH, ^2J = 15.0, ^3J = 2.8 Hz), 2.02 (dd, 1 H, CH$_A$*H*$_B$-CHOH, ^2J = 15.0, ^3J = 9.2 Hz), 2.30–2.47 (m, 2 H, -$CH_{2\text{-}2'c\text{-}Hex}$), 3.83–3.98 (m, 1 H, C*H*OH).

^{13}C NMR ($CDCl_3$): δ = 22.2, 22.3 ($CH_{2\text{-}3'\text{-}c\text{-}Hex}$), 24.7 ($CH_{2\text{-}4'\text{-}c\text{-}Hex}$), 24.9 (Me), 34.0, 34.9 ($CH_{2\text{-}2'\text{-}c\text{-}Hex}$), 48.3 (C*H*$_2$CHOH), 63.7 (CHOH), 90.3 (CNO_2).

^{14}N NMR ($CDCl_3$): δ = 19.4 (NO_2, $\upsilon_{1/2}$ = 280 Hz).

Anal. Calcd $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48. Found: C, 57.44; H, 9.10; N, 7.68.

4-Nitrobutan-2-ol (1f)
The reaction was carried out with BH_3·THF (1.2 mmol, 1.60 mL 1.33 M solution in THF) at 20 °C for 1 h; yield: 90%; bp 100–110 °C (7–8 Torr, short-path apparatus), n_d^{20} 1.4448 (lit.[22] n_d^{19} 1.4445).

^{1}H NMR ($CDCl_3$): δ = 1.21 (d, 3 H, Me, ^3J = 5.9 Hz), 1.86–2.25 (m, 2 H, CH_2), 2.31 (br, 1 H, OH), 3.79–3.99 (m, 1 H, C*H*OH), 4.38–4.64 (m, 2 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 23.6 (Me), 35.9 (CH_2), 64.8 (CHOH), 72.6 (CH_2NO_2).

4-Nitro-4-phenylpentan-2-ol (1g)
The reaction was carried out with BH_3·THF (1.4 mmol, 1.86 mL 1.33 M solution in THF) at 20 °C for 3.5 h; yield: 85%, minor:major ca. 1:2.5 (^{1}H NMR); bp 130–145 °C (0.2 Torr, short-path apparatus).

Major Isomer:

^{1}H NMR ($CDCl_3$): δ = 1.23 (d, 3 H, C*H*$_3$COH, ^3J = 5.9 Hz), 1.59 (br, 1 H, OH), 2.10 (s, 1 H, $MeCNO_2$), 2.32–2.47 (m, 1 H, CH$_A$*H*$_B$), 2.75 (dd, 1 H, CH$_A$*H*$_b$, ^2J = 14.7, ^3J = 10.3 Hz), 3.78–3.97 (m, 1 H, C*H*OH), 7.31–7.49 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 23.7, 25.2 (*C*H$_3$CNO$_2$ and *C*H$_3$CHOH), 47.6 (CH_2), 64.6 (CHOH), 92.2 (CNO_2), 125.3 (*p*-CH_{Ph}), 128.8 (*o*-, *m*-CH_{Ph}), 139.9 (*i*- C_{Ph}).

Minor Isomer:

^{1}H NMR ($CDCl_3$): δ = 1.25 (d, 3 H, C*H*$_3$COH, ^3J = 6.6 Hz), 2.07 (s, 1 H, $MeCNO_2$), 2.65 (dd, 1 H, CH$_A$*H*$_B$, ^2J = 15.5, ^3J = 2.2 Hz).

^{13}C NMR ($CDCl_3$): δ = 24.6, 25.3 (*C*H$_3$CNO$_2$ and *C*H$_3$CHOH), 48.4 (CH_2), 65.1 (CHOH), 93.3 (CNO_2), 125.1 (*p*- CH_{Ph}), 128.8 (*o*-, *m*-CH_{Ph}), 140.4 (*i*-C_{Ph}).

^{14}N NMR ($CDCl_3$): δ = 18.9 (NO_2 for two diastereomers, $\upsilon_{1/2}$ = 275 Hz).

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.28; H, 7.23; N, 6.54.

2-(1-Nitrocyclohexyl)-ethanol (1h)
The reaction was carried out with BH_3·THF (2 mmol, 2.66 mL 1.33 M solution in THF) at 20 °C for 2 h; yield: 62%; bp 100–105 °C (0.2 Torr, short-path apparatus).

^{1}H NMR ($CDCl_3$): δ = 1.20–1.72 (m, 8 H, 4 × $CH_{2\text{-}c\text{-}Hex}$ except $CH_{2\text{-}2'\text{-}c\text{-}Hex}$), 2.04 (t, 2 H, C*H*$_2CH_2$OH, ^3J = 6.8 Hz), 2.28–2.43 (m, 2 H, $CH_{2\text{-}2'\text{-}c\text{-}Hex}$), 2.52–2.71 (br, 1 H, OH), 3.59 (t, 2 H, C*H*$_2$OH, ^3J = 6.8 Hz).

^{13}C NMR ($CDCl_3$): δ = 22.3 ($CH_{2\text{-}3'\text{-}c\text{-}Hex}$), 24.7 ($CH_{2\text{-}4'\text{-}c\text{-}Hex}$), 34.3 ($CH_{2\text{-}2'\text{-}c\text{-}Hex}$), 42.1 ($CH_2$), 57.6 ($CH_2OH$), 90.2 ($CNO_2$).

^{14}N NMR ($CDCl_3$): δ = 18.7 (NO_2, $\upsilon_{1/2}$ = 200 Hz).

Anal. Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.50; H, 8.66; N, 8.12.

3-Methyl-3-nitrobutanol (1i)
The reaction was carried out with BH_3·THF (2 mmol, 2.66 mL 1.33 M solution in THF) at 20 °C for 2 h; yield: 62%; bp 46–52 °C (0.2 Torr, short-path apparatus).

^{1}H NMR ($CDCl_3$): δ = 1.52 [s, 6 H, (C*H*$_3$)$_2$C], 2.09 (t, 2 H, CH_2, ^3J = 6.6 Hz), 2.95–3.14 (br, 1 H, OH), 3.57 (t, 2 H, C*H*$_2$OH, ^3J = 6.6 Hz).

^{13}C NMR ($CDCl_3$): δ = 21.7 [(*C*H$_3$)$_2$C)], 38.0 (CH_2), 53.6 (CH_2OH), 82.6 (CNO_2).

^{14}N NMR ($CDCl_3$): δ = 17.5 (NO_2, $\upsilon_{1/2}$ = 200 Hz).

Anal. Calcd for $C_5H_{11}NO_3$: C, 45.10; H, 8.33; N, 10.52. Found: C, 44.98; H, 8.84; N, 10.64.

Methyl 6-Nitro-4-oxyoctanoate (1k)
The reaction was carried out with BH_3·THF (1.2 mmol, 1.6 mL 1.33 M solution in THF) at 0 °C for 2 h, the crude product was purified by column chromatography (silica gel, $CHCl_3$→$CHCl_3$–Et_2O, 3:1); yield: 31%, minor:major ca. 1:2 (^{1}H NMR), bp 121–128 °C (0.2 Torr, short-path apparatus); R_f 0.31 ($CHCl_3$–Et_2O, 2:1).

Major Isomer:

^{1}H NMR ($CDCl_3$): δ = 0.94 (s, 3 H, C*H*$_3$CH$_2$), 1.60–2.27 (m, 6 H, CH$_2$C*H*$_2$, MeC*H*$_2$), 2.37–2.60 (m, 2 H, C*H*$_2$CHOH), 2.65–2.85 (br, 1 H, OH), 3.49–3.78 (m, 1 H, *H*COH),3.66 (s, 3 H, OMe), 4.51–4.66 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 10.0 (*C*H$_3$C), 27.1, 30.3 and 32.2 (CH$_2$CH$_2$ and Me*C*), 40.6 (*C*H$_2$CHOH), 51.9 (OMe), 68.7 (HCOH), 87.5 (CNO_2), 174.4 (CO_2).

Minor Isomer:

^{1}H NMR ($CDCl_3$): δ = 0.95 (s, 3 H, C*H*$_3$CH$_2$), 4.70–4.83 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 10.2 *C*H$_3$C), 27.7, 30.4 and 32.4 (CH$_2$CH$_2$ and Me*C*), 40.7 (*C*H$_2$CHOH), 51.9 (OMe), 67.5 (HCOH), 86.9 (CNO_2), 174.4 (CO_2).

^{14}N NMR ($CDCl_3$): δ = 13.6 (NO_2 for two diastereomers, $\upsilon_{1/2}$ = 260 Hz).

Anal. Calcd $C_9H_{17}NO_5$: C, 49.30; H, 7.82; N, 6.39. Found: C, 49.37; H, 7.63; N, 6.42.

Methyl 6-Nitro-4-oxyhexanoate (1l)
The reaction was carried out with BH_3·THF (1.2 mmol, 1.6 mL 1.33 M solution in THF) at 0 °C for 2 h; the crude product was purified by column chromatography (silica gel, $CHCl_3$–Et_2O, 2:1); yield: 44%; bp 105–115 °C (0.2 Torr, short-path apparatus); R_f 0.17 ($CHCl_3$–Et_2O, 2:1)

^{1}H NMR ($CDCl_3$): δ = 1.68–1.93, 1.94–2.12 and 2.16–2.30 [m, 4 H, C*H*$_2$(CHOH)C*H*$_2$], 2.49 (t, 2 H, C*H*$_2$CO$_2$Me, ^3J = 7.2 Hz), 2.53–2.66 (br, 1 H, OH), 3.68 (s, 3 H, OMe), 3.66–3.83 (m, 1 H, C*H*OH), 4.47–4.68 (m, 2 H, CH_2NO_2).

^{13}C NMR ($CDCl_3$): δ = 30.8, 32.6 and 34.9 (3 × CH_2 except CH_2NO_2), 52.4 (MeO), 68.5 (CHOH), 73.0 (CH_2NO_2), 175.1 (CO_2).

^{14}N NMR ($CDCl_3$): δ = 4.5 (NO_2, $\upsilon_{1/2}$ = 140 Hz).

Anal. Calcd for $C_7H_{13}NO_5$: C, 43.98; H, 6.85; N, 7.33. Found: C, 43.74; H, 6.74; N, 7.23.

4-Nitroheptan-1,6-diol (8a)
The reaction was carried out with BH_3·THF (5 mmol, 6.65 mL 1.33 M solution in THF) at 20 °C for 4 h; yield: 74%; minor:major ca. 1:2.7 (^{1}H NMR); bp 135–137 °C (0.15 Torr).

Major Isomer:

^{1}H NMR ($CDCl_3$): δ = 1.26 (d, 3 H, C*H*$_3$CHOH, ^3J = 6.0 Hz), 1.54–2.27 (m, 8 H, CH$_2$CH$_2$, C*H*$_2$CHOH, 2 × OH), 3.63–3.82 (m, 2 H, C*H*$_2$OH), 3.87–3.96 (m, 1 H, C*H*OH), 4.67–4.77 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 23.6 (*C*H$_3$CHOH), 28.3 and 29.9 (CH$_2$CH$_2$), 42.4 (*C*H$_2$CHOH), 61.2, 65.0 (CH$_2$OH, CHOH), 85.9 ($CHNO_2$).

Minor Isomer:

^{1}H NMR ($CDCl_3$): δ = 1.23 (d, 3 H, C*H*$_3$CHOH, ^3J = 6.4 Hz), 3.63–3.82 (m, 1 H, C*H*OH), 4.83–4.93 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 23.8 (*C*H$_3$CHOH), 28.5, 30.8 (CH$_2$CH$_2$), 42.5 (*C*H$_2$CHOH), 61.2, 64.2 (CH$_2$OH and CHOH), 85.5 ($CHNO_2$).

^{14}N NMR ($CDCl_3$): δ = 16.0, (NO_2 for two diastereomers, $\upsilon_{1/2}$ = 620 Hz).

Anal. Calcd for $C_7H_{15}NO_4$: C, 47.45; H, 8.53; N, 7.90. Found: C, 47.51; H, 8.48; N, 7.91.

4-Methyl-4-nitroheptan-1,6-diol (8b)
The reaction was carried out with BH_3·THF (5 mmol, 6.65 mL 1.33 M solution in THF) at 20 °C for 4 h; yield: 74%; minor:major ca. 1:2 (^{1}H NMR); bp 124–135 °C (0.2 Torr).

Major Isomer:

^{1}H NMR ($CDCl_3$): δ = 1.19 (d, 3 H, C*H*$_3$COH, ^3J = 5.9 Hz), 1.26–1.70, 1.80–2.20 (m, 5 H, CH$_2$CH$_2$ and C*H*$_A$H$_B$CHOH), 1.60 (s, 3 H, MeCNO$_2$), 2.30 (dd, 1 H, CH$_A$*H*$_B$CHOH, ^2J = 15.1, ^3J = 9.8 Hz), 2.38–2.60 (br, 2 H, 2 × OH), 3.54–3.66 (m, 2 H, C*H*$_2$OH), 3.93–4.04 (m, 1 H, C*H*OH).

^{13}C NMR ($CDCl_3$): δ = 21.8, 24.9 (*C*H$_3$CNO$_2$, *C*H$_3$CHOH), 26.8, 36.6 (CH$_2$CH$_2$), 47.5 (*C*H$_2$CHOH), 61.9, 64.1 (*C*H$_2$OH and *C*HOH), 89.9 (*C*NO$_2$).

Minor Isomer:

^{1}H NMR ($CDCl_3$): δ = 1.26–1.70 and 1.80–2.20 (m, 2 H, CH_2), 3.81–3.93 (m, 1 H, C*H*OH).

^{13}C NMR ($CDCl_3$): δ = 23.0, 25.1 (*C*H$_3$CNO$_2$ and *C*H$_3$CHOH), 27.0, 36.0 (CH$_2$CH$_2$), 47.1 (*C*H$_2$CHOH), 61.9, 64.4 (*C*H$_2$OH and *C*HOH), 90.8 ($CHNO_2$).

^{14}N NMR ($CDCl_3$): δ = 18.6, (NO_2 for two diastereomers, $\upsilon_{1/2}$ = 640 Hz).

Anal. Calcd for $C_8H_{17}NO_4$: C, 50.25; H, 8.96; N, 7.32. Found: C, 50.17; H, 8.95; N, 7.41.

Methyl 4-Methyl-4-nitro-6-oxyhexanoate (1j)
To a solution of nitro acid **2j** (205 mg, 1 mmol) in THF (7.5 mL) was added Et_3N (0.14 mL, 1 mmol) followed by $(PhO)_2POCl$ (268.5 mg, 1 mmol) in THF (3.5 mL). The reaction mixture was stirred for 2 h, filtered. Powdered $NaBH_4$ (76 mg, 2 mmol) was added to the filtrate, and after stirring for 2 h the mixture was quenched with AcCl (0.14 mL) in MeOH (4 mL), the solvent was evaporated, and

the residue was subjected to column chromatography (silica gel, petroleum ether–EtOAc, 1:3) to give 110 mg of **1j**; yield: 54%; bp 125–135 °C (0.06 Torr, short-path apparatus); R_f 0.48 (petroleum ether–EtOAc, 1:3)

^{1}H NMR ($CDCl_3$): δ = 1.57 (s, 3 H, $MeCNO_2$), 2.03–2.48 (m, 7 H, CH_2CH_2 and C*H*$_2$CH$_2$O*H*), 3.65 (s, 3 H, MeO), 3.62–3.80 (m, 2 H, C*H*$_2$OH).

^{13}C NMR ($CDCl_3$): δ = 22.1 (*Me*CNO_2), 28.8, 34.5 (CH_2CH_2), 41.2 (*C*H_2COH), 52.1 (CH_2OH), 58.1 (MeO), 89.3 (CNO_2), 172.9 (CO_2).

^{14}N NMR ($CDCl_3$): δ = 18.0 (NO_2, $\upsilon_{1/2}$ = 165 Hz).

Anal. Calcd for $C_8H_{15}NO_5$: C, 46.82; H, 7.37; N, 6.83. Found: C, 46.58; H, 7.09; N, 6.89.

Methyl 4-Nitro-6-oxyheptanoate (1c)

To a solution of ketone **2c** (203 mg, 1 mmol) and $NaBH_3CN$ (94.5 mg, 1.5 mmol) in MeOH (1.7 mL) a solution of AcCl (106 μL, 1.5 mmol) in MeOH (5 mL) was added dropwise over 3 h. To achieve complete conversion (TLC control) the addition of $NaBH_3CN$ and AcCl/MeOH could be repeated, in 24 h the reaction mixture was evaporated and residue was poured into H_2O–Et_2O (1:1, 40 mL), the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried (Na_2SO_4), the solvent evaporated and distilled in a short-path apparatus, to give 160 mg of **1c**; yield: 78%; minor:major ca. 1:2.5 (^{1}H NMR); bp 100–107 °C (0.05 Torr).

Major Isomer:

^{1}H NMR ($CDCl_3$): δ = 1.22 (d, 3 H, C*H*$_3$CHOH, ^3J = 6.0 Hz), 1.82 (ddd, 1 H, C*H*$_A$H$_B$CHOH, ^2J = 14.8, ^3J = 4.7, ^3J = 6.7 Hz), 2.03–2.45 (m, 6 H, CH_2CH_2, CH$_A$*H*$_B$CHO*H*), 3.67 (s, 3 H, OMe), 3.85–3.97 (m, 1 H, C*H*OH), 4.69 (q, 1 H, $CHNO_2$, ^3J = 6.7 Hz).

^{13}C NMR ($CDCl_3$): δ = 23.6 (*C*H$_3$C), 28.2, 29.8 (CH_2CH_2), 42.2 (CH_2), 51.8 (OMe), 64.9 (CHOH), 85.0 ($CHNO_2$), 172.6 (CO).

Minor Isomer:

^{1}H NMR ($CDCl_3$): δ = 1.19 (d, 3 H, C*H*$_3$CHOH, ^3J = 6.0 Hz), 1.72 (ddd, 1 H, C*H*$_A$H$_B$HOH, ^2J = 14.8, ^3J = 3.4, ^3J = 9.4 Hz), 3.70–3.82 (m, 1 H, C*H*OH), 4.79–4.89 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 23.7 (*C*H$_3$C), 29.0, 29.9 (CH_2CH_2), 42.3 (CH_2), 51.8 (OMe), 64.0 (CHOH), 84.6 ($CHNO_2$), 172.3 (CO).

^{14}N NMR ($CDCl_3$): δ = 13.0 (NO_2 for two diastereomers, $\upsilon_{1/2}$ = 380 Hz).

Anal. Calcd for $C_8H_{15}NO_5$: C, 46.82; H, 7.36; N, 6.82. Found: C, 46.89; H, 7.22; N, 6.86.

Methyl 4-Methyl-4-nitro-6-oxyheptanoate (1e)

Nitro ketone **2e** was reduced to **1e** analogously. After concentration of the organic phase the residue was subjected to column chromatography (silica gel, $CHCl_3$–Et_2O, 3:1) to give ester **1e**; yield: 84%, minor:major ca. 1:2 (^{1}H NMR); bp 137–142 °C (0.7 Torr); R_f 0.31 ($CHCl_3$–Et_2O, 3:1)

Major Isomer:

^{1}H NMR ($CDCl_3$): δ= 1.23 (d, 3 H, C*H*$_3$CHOH, ^3J = 6.4 Hz), 1.62 (s, 3 H, $MeCNO_2$), 1.85 (dd, 1 H ^2J = 15.1,^3J = 2.7 Hz, OH), 2.30–2.45 (6 H, 3 × CH_2), 3.67 (s, 3 H, OMe), 3.98–4.06 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 21.6, 25.0 (*C*H_3CNO_2 and *C*H_3CHOH), 28.7, 35.0 (CH_2CH_2), 47.4 (*C*H_2CHOH), 51.9 (OMe), 64.0 (CHOH), 89.1 (CNO_2), 172.7 (CO).

Minor Isomer:

^{1}H NMR ($CDCl_3$): δ = 1.22 (d, 3 H, C*H*$_3$CHOH, ^3J = 6.4 Hz), 1.63 (s, 3 H, $MeCNO_2$), 3.89–3.98 (m, 1 H, $CHNO_2$).

^{13}C NMR ($CDCl_3$): δ = 22.7, 25.2 (*C*H_3CNO_2 and *C*H_3CHOH), 28.9, 34.4 (CH_2CH_2), 47.2 (*C*H_2CHOH), 51.9 (OMe), 64.4 (CHOH), 90.0 (CNO_2), 172.9 (CO).

^{14}N NMR ($CDCl_3$): δ = 18.5 (NO_2 for two diastereomers, $\upsilon_{1/2}$ = 600 Hz).

Anal. Calcd for $C_9H_{17}NO_5$: C, 49.31; H, 7.82; N, 6.39. Found: C, 49.71; H, 7.60; N, 6.48.

Preparation of γ-Nitroalcohols 1a–e and Nitrodiols 9a,b without Purification of Intermediate Compounds

Preparation of 1a,d,e; General Procedure for Secondary ANC

To a solution of DBU (2.78 mL, 18.6 mmol) in Et_2O (180 mL) at 5 °C was added nitrocyclohexane (**3d**) (2.26 mL, 18.6 mmol), the mixture was stirred at 5 °C for 5 min, then a solution of BENA **6a** (4.77 g, 20.46 mmol) in Et_2O (180 mL) was added dropwise at 5 °C for 2 h, the reaction mixture was stirred at 0 °C for 1 h, the mixture of NH_4F (0.69 g, 18.6 mmol), HOAc (1.60 mL, 27.9 mmol), and MeOH (30 mL) was added, the reaction mixture was stirred for an extra 20 min, and poured into H_2O (150 mL). The aqueous layer was extracted with Et_2O (4 × 80 mL), the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated to give **7d** (3.00 g). To a solution of **7d** in acetone (70 mL) Jones' reagent (5.62 mL 2.67 M solution, 15 mmol) was added at 20 °C. Two more portions of Jones' reagent (15 mmol each) were added after 1 and 2 hours. After additional stirring for 2 h the reaction mixture was poured into H_2O–Et_2O (1:1, 150 mL), the aqueous layer was extracted with Et_2O (4 × 25 mL), the combined organic layers were washed with H_2O (4 × 10 mL), brine, dried ($MgSO_4$) and the solvent evaporated, the residue was azeotropically dried with toluene to give 2.59 g of **2d**. To a solution of **2d** in THF (20 mL) at 20 °C was added BH_3·THF (12.5 mL 1.33 M solution in THF, 16.55 mmol). MeOH (2.4 mL, 59 mmol) was added in 3 h, the mixture was poured into HCl (1.7 mL concd HCl and 50 mL H_2O), and extracted with Et_2O (5 × 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and the solvent evaporated, the residue was distilled to give 1.57 g of **1c** (8.4 mmol, yield 45% refers to ANC without purification of intermediate compounds **3d**). Nitroalcohols **1a** and **1e** were obtained analogously (yields are given in Table 1).

Preparation of 1b,c; General Procedure for Primary Nitro Compounds

To a solution of 1-nitropropane **3b** (2 mL, 22.5 mmol) in CH_2Cl_2 (150 mL) at 5 °C was added DBU (3.32 mL, 22.5 mmol), the reaction mixture was stirred at 5 °C for 5 min and then cooled down to –78 °C. A solution of BENA **6a** (5.0 g, 21.4 mmol) in CH_2Cl_2 (49 mL) was added followed by Bu_4NF (5.35 mL 0.8 M solution in THF, 4.28 mmol). The mixture was stirred at –78 °C for 1 h, a solution of HOAc (2.57 mL, 45.0 mmol) in Et_2O (27 mL) was added, kept for additional 10 min, and poured into Et_2O–H_2O (5:3, 400 mL). The aqueous layer was extracted with Et_2O (3 × 50 mL), the combined organic layers were washed with H_2O (30 mL), brine (30 mL), dried (Na_2SO_4) and evaporated to give **7b** (3.25 g). Jones' reagent (6.80 mL 2.66 M solution, 18.0 mmol) was added at 20 °C to a solution of **7b** in acetone (60 mL). Two more portions of Jones' reagent (18 mmol each) were added after 1 and 2 hours. After additional stirring for 2 h the reaction mixture was poured into Et_2O–H_2O (1:1, 130 mL), the aqueous layer was extracted with Et_2O (4 × 40 mL), the combined organic layers were washed with H_2O (4 × 8 mL), brine (10 mL), dried ($MgSO_4$) and the solvent evaporated, the residue was azeotropycally dried with toluene to give **2d** (2.43 g). To a solution of **2d** in THF (22 mL) at 20 °C was added BH_3·THF (14.7 mL, 1.33 M solution in THF, 19.6 mmol), after 3 h MeOH (2.48 mL, 61mmol). The mixture was poured into HCl (from 1.6 mL concd HCl and 47 mL H_2O), the aqueous layer was extracted with Et_2O (5 × 30 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) and evaporated, the residue was distilled to give **1b** (1.81 g, yield 58% refers to BENA **6a**).

Nitroalcohol **1c** was obtained analogously (yield 51% refers to **ANC** without purification of intermediate compounds **3c**).

Preparation of Diols 8a,b without Purification

This was performed analogously to that described above using BH_3·THF (3.2 mmol per 1 mmol of **ANC 3**, 2.4 mL, 1.33 M solution in THF) at 20 °C for 4 h. Yields of target diols are given in Table 1.

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