Experimental Section

General: All the reactions were conducted under an atmosphere of argon. Thin-layer chromatograms (TLC) were performed on precoated silica gel 60 F254 plates (Merck, 0.25 mm.). Flash chromatography separations were performed on silica gel (Merck 60, 230-400 mesh); ^{1}H and ^{13}C NMR chemical shifts **δ** are reported in ppm relative to their standard reference (^{1}H: $CHCl_3$ at 7.27 ppm; ^{13}C: $CDCl_3$ at 77.0 ppm). IR spectra were recorded in wavenumbers (cm^{-1}). Mass spectra (MS) were recorded in the chemical ionization mode. Gas chromatography (GC) separation of compounds 1a, 2a and 3a were performed on a Carlo-Erba ICU 600 with naphthalene as an internal standard. Twenty-five microliters of the 0.4 M reaction mixture were diluted with 1 mL of a 10^{-2} M solution of naphthalene in ethyl acetate, washed with 1.5 mL of water and dried over Na_2SO_4. One microliter of this solution was injected (heating program: T = 105 ºC for 2.5 mns then 10 ºC.mn^{-1} to T = 200 ºC. Retention times: 3.78; 4.40; 5.89 and 7.18 mins for **2a**, **3a**, **1a** and naphthalene respectively). Analytical data for compounds **2c**, **2g** are identical to authentic samples (Aldrich structure index FT-NMR 1 (1), 663C and FT-IR 1 (1), 424D for **2c**; Aldrich structure index FT-NMR 1 (2), 804A) for **2g**).

1-Phenylnitrohexane (1g): Following a modified reported procedure by Seebach.[26] To a solution of nitrobenzyle (18.25 mmol) in THF/HMPA (50:8 mL) at –78 °C was added dropwise a solution of *n*-BuLi in hexane (38.32 mmol). After 2h, bromopentane (18.25 mmol) was added at the same temperature. After 10h, the reaction mixture was neutralized with 100 mL of a saturated solution of NH_4Cl and 5.2 mL of acetic acid. The aqueous layer was extracted several times with ether and the combined organic layers were dried over Na_2SO_4 and concentrated *in* vacuo. Column chromatography of the resulting crude (eluent AcOEt/hexane 6:94) afforded 2.55 g (67%) of pure **1g** as a yellow oil. TLC R_f=0.65 (Hexane/AcOEt 9:1); ^{1}H (200 MHz, $CDCl_3$) δ=0.89 (t, *J* = 7.1 Hz, 3H), 1.31-1.36 (m, 6H), 1.98-2.17 (m, 1H), 2.41-2.60 (m, 1H), 5.47 (dd, *J* = 8.7 Hz, *J* = 7.6 Hz,

1H), 7.38-7.52 (m, 5H); ^{13}C (50 MHz, $CDCl_3$) δ=13.8, 22.2, 25.6, 31.0, 33.8, 91.5, 127.6, 128.9, 129.6, 134.7; IR (CsI) 2958, 2861, 1557, 1456, 1362 cm^{-1}. MS *m/z* 208 $(M + H)^+$, 225 $(M + NH_4)^+$.

5-Nitro-hexan-2-one (1c): Nitroethane (48.85 mmol) and diisopropylamine (24.42 mmol) were successively added to a solution of methylvinylketone (48.85 mmol) in 25 mL of chloroform. The reaction was stirred at reflux for 12h. Water (40 mL) was then added to the reaction mixture and the aqueous layer was extracted several times with AcOEt. Column chromatography of the crude (eluent AcOEt/hexane 20:80 to 25:75) afforded 3.27 g (75%) of pure **1c** as a yellowish oil. TLC R_f=0.40 (Hexane/AcOEt 7:3); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.48 (d, *J* = 6.5 Hz, 3H), 2.02-2.12 (m, 2H), 2.10 (s, 3H), 2.47 (t, *J* = 7.0 Hz, 2H), 4.48-4.64 (m, 1H); ^{13}C (50 MHz, $CDCl_3$) δ=19.2, 28.5, 29.9, 38.8, 82.4, 206.4; IR (CsI) 2993, 2942, 1718, 1550, 1361, 1171 cm^{-1}; MS *m/z* 163 $(M+NH_4)^+$, 180 $(M+NH_3+NH_4)^+$.

5-Nitro-hexan-2-ol (1b): Sodium borohydride (8.96 mmol) was added at 0 ºC to the ketone 1c (6.90 mmol) in solution in 12 mL of methanol. The reaction was stirred at 0 ºC for 20 mns. The methanol was evaporated and 20 mL of water added to the crude. The aqueous layer was extracted several times with AcOEt. The desired product **1b** was obtained quantitatively as a colorless oil after a quick filtration on a pad of silica. TLC R_f=0.40 (Hexane/AcOEt 1:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.19 (d, *J* = 6.1 Hz, 1.7H first dia.), 1.20 (d, *J* = 6.0 Hz, 1.3H second dia.), 1.40-2.20 (m, 4H, H), 1.52 (d, *J* = 8.2 Hz, 1.7H first dia.), 1.53 (d, *J* = 8.2 Hz, 1.3H second dia.), 3.72-3.89 (m, 1H, H_2), 4.51-4.65 (m, 1H, H_5); ^{13}C (50 MHz, $CDCl_3$) δ=19.2, 19.4, 23.7, 23.8, 31.1, 31.6, 34.6, 35.0, 67.0, 67.4, 83.3, 83.7; IR (CsI) 3368, 2970, 2932, 1550, 1391 cm^{-1}. MS *m/z* 148 $(M + H)^+$, 165 $(M + NH_4)^+$.

***tert*-Butyl-dimethyl-(1-methyl-4-nitro-pentyloxy)-silane (1d):** *tert*-Butyldimethyl-silane bromide (0.74 mmol) was added to a solution of imidazole (0.74 mmol) and 1b (0.68 mmol) in 2 mL of dichloromethane. The reaction was refluxed for 4h after which 5 mL of water was added.

The aqueous layer was extracted several times with dichloromethane. Column chromatography of the crude (eluent AcOEt/hexane 20:80) afforded 0.15 g (82%) of pure **1d** as a coloroless oil. TLC R_f=0.85 (hexane/AcOEt 4:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.04, 0.05 (s, 6H), 0.86, 0.88 (s, 6H), 1.12 (d, *J* = 6.3 Hz, 3H), 1.35-1.48 (m, 2H), 1.52 (d, *J* = 6.7 Hz, 3H), 3.75-3.89 (m, 1H), 4.51-4.63 (m, 1H); ^{13}C (50 MHz, $CDCl_3$) δ=-4.8, -4.3, 18.0, 19.2, 19.4, 23.6, 23.8, 25.8, 31.0, 31.5, 35.0, 35.4, 67.4, 67.8, 83.4, 83.8; IR (CsI) 2957, 2930, 2858, 1553, 1256 cm^{-1}. MS *m/z* 262 $(M + H)^+$, 279 $(M + NH_4)^+$.

General Procedure for the Nitrosation of Secondary Nitroalkanes: A solution of the nitroalkane (1 mmol), and sodium nitrite (2 mmol), in DMSO/water (7:1 V:V; 0.4M) was stirred at 65 °C until disappearance of the starting material (TLC). An equal volume of water was then added and the aqueous layer was extracted several times with diethyl ether. The combined organic layers were dried over Na_2SO_4, concentrated and the resulting crude was purified by column chromatography.

5-Hydroxy-hexan-2-one (2b): R_f=0.40 (Hexane/AcOEt 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.19 (d, *J* = 6.0 Hz, 3H), 1.64-1.74 (m, 2H), 2.17 (s, 3H), 2.59 (t, *J* = 7.1 Hz, 2H), 3.72-3.81 (m, 1H).

5-(tert-Butyl-dimethyl-silanyloxy)-hexan-2-one (2d): R_f=0.50 (Hexane-AcOEt 4:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.04, 0.05 (s, 6H), 0.88, 0.90 (s, 6H), 1.12 (d, *J* = 6.3 Hz, 3H), 1.52-1.71 (m, 2H), 2.15 (s, 3H), 2.47 (t, *J* = 7.3 Hz, 2H), 3.75-3.91 (m, 1H); ^{13}C (50 MHz, $CDCl_3$) δ=-4.8, -4.4, 18.0, 23.7, 25.9, 29.7, 29.9, 33.2, 39.8, 67.5, 209.2; IR (CsI) 2957, 2930, 2858, 1720, 1256 cm^{-1}. MS *m/z* 248 $(M + NH_4)^+$, 265 $(M + NH_3 + NH_4)^+$.

2-Hydroxyimino-5-oxo-3,5-diphenyl-pentanoic acid ethyl ester (3e): R_f=0.30 (Hexane-AcOEt 7:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.25 (m, 3H), 3.63 (d, *J* = 5.6 Hz, 0.7H one isomer), 3.69 (d, *J* = 6.0 Hz, 1.3H other isomer), 4.18-4.32 (m, 2H), 5.11-5.17 (m, 1H), 7.21-7.57 (m, 8H), 7.98 (d, *J* =

7.1 Hz, 2H); ^{13}C (75 MHz, $CDCl_3$) δ=13.9, 37.9, 41.4, 61.7, 127.1, 128.1, 128.4, 128.6, 136.4, 139.0, 151.2, 163.3, 198.0; MS *m/z* 326 $(M + H)^+$, 343 $(M + NH_4)^+$.

2-Hydroxyimino-3-methyl-pentanedioic acid 5-benzyl ester 1-ethyl ester (3f): R_f=0.15 (Hexane-AcOEt 4:1); ^1H NMR (300 MHz, $CDCl_3$) δ=1.27-1.32 (m, 6H), 2.69 (ABX, J_{AB} = 16.4 Hz, J_{AX} = 6.8 Hz, 1H), 3.81 (ABX, J_{AB} = 16.4 Hz, J_{AX} = 8.7 Hz, 1H), 3.75-3.85 (m, 1H), 4.25 (q, *J* = 7.5 Hz, 2H), 5.1 (s, 2H), 7.28-7.36 (m, 5H); ^{13}C (75 MHz, $CDCl_3$) δ=14.0, 16.5, 27.8, 37.4, 61.6, 66.4, 128.2, 128.5, 135.8, 154.2, 162.9, 171.9; IR (CsI) 3273, 2980, 2937, 1732 (oxime), 1179 cm^{-1}; MS *m/z* 294 $(M + H)^+$, 311 $(M + NH_4)^+$.