Experimental Section

General experimental details: Specific rotations were recorded on a JASCO DIP-370 optical polarimeter. Nuclear magnetic resonance spectra were recorded on a Bruker DPX 300 spectrometer. Mass spectra were obtained on a Hewlett Packard 5988A mass spectrometer. Thin layer chromatography (TLC) was performed using Merck GF-254 type 60 silica gel and ethyl acetate/hexane mixtures as eluents; the TLC spots were visualized with Hanessian mixture. Column chromatography was carried out using Merck type 9385 silica gel.

General Procedure for the reaction of indium nitronates and aldehydes. *n*-Butyllithium (1.6 M in Hexane, 2.0 mL, 3.1 mmol) was added to a stirred solution of anhydrous indium trichloride (221 mg, 1.0 mmol) and nitroalkane **1** (3.0 mmol) in THF (4 mL) at -78 ºC. The mixture was stirred for 10 min, after which time aldehyde **2** (2.0 mmol) was added. The reaction mixture was warmed to room temperature and left overnight. The reaction was quenched with 1 M HCl (10 mL), and the product was extracted with diethyl ether (3 x 20 mL). The organic extracts were washed with water and brine, and concentrated. The residue was purified by flash column chromatography in mixtures of ethyl acetate/hexane when necessary to obtain pure compounds shown in Tables 1, 2 and 3.

The products **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3i**, **3k**, **3l**, **3m**, **3n**, **3o**, **3p**, **6a**, **6b** and **6c** are known compounds.

2-Nitro-1-phenylethanol (3a): yellow oil. ^{1}H NMR ($CDCl_3$, ppm): 2.87 (bs, 1 H, –OH), 4.53–4.61 (m, 2 H, H-2), 5.29–5.50 (m, 1 H, H-1), 7.41–7.43 (m, 5 H, 5 x H-Ar).

1-(4-Methoxyphenyl)-2-nitroethanol (3b): yellow oil. ^{1}H NMR ($CDCl_3$, ppm): 2.94 (bs, 1 H, –OH), 3.80 (s, 3 H, $–OCH_3$), 4.45 (dd, 1 H, *J* = 3.5 Hz, *J* = 13.1 Hz, H-2), 4.59 (dd, 1 H, *J* = 9.3 Hz, *J* = 13.1 Hz, H-2'), 5.36–5.40 (m, 1 H, H-1), 6.90 (d, 2 H, *J* = 8.8 Hz, 2 x H-Ar), 7.30 (d, 2 H, *J* = 8.8 Hz, 2 x H-Ar).

1-(4-Cyano)-2-methyl-2-nitropropan-1-ol (3c): yellow oil. ^{1}H NMR ($CDCl_3$, ppm): 4.54-4.60 (m, 2 H, H-2); 5.52-5.56 (m, 1H, H-1); 7.54-7.69 (m, 4H, 4 x H-Ar).

1-(2-Nitro)-2-methyl-2-nitropropan-1-ol (3d): yellow oil. ^{1}H NMR ($CDCl_3$, ppm): 4.66-4.45 (m, 2 H), 5.46 (dd, J = 3.1, 7.8 Hz, 1 H), 7.44-7.27 (m, 4 H, 4 x H-Ar).

1-Nitrononan-2-ol (3e): yellow oil. ^{1}H NMR ($CDCl_3$, ppm): 0.84 (t, 3 H, *J* 6.6 Hz, $–CH_3$), 1.19–1.54 (m, 12 H), 4.22–4.29 (m, 1 H), 4.32–4.39 (m, 2 H).

Ethyl 2-hydroxy-3-nitropropanoate (3f): clear oil. ^{1}H NMR ($CDCl_3$, ppm): 1.29 (t, 3 H, *J* 6.9 Hz, $–OCH_2C\mathit{H}_3$), 3.68 (bs, 1 H, -OH), 4.29 (q, 2 H, *J* 6.9 Hz, $–OC\mathit{H}_2CH_3$), 4.75–4.79 (m, 2 H, H-3), 5.31–5.36 (m, 1 H, H-2).

1-Cyclohexyl-2-nitroethanol (3g): yellow oil. ^{1}H NMR ($CDCl_3$, ppm): 0.90–1.73 (m, 11 H), 4.03–4.11, 4.33–4.45 (m, 3 H, H-1, H-2, H-2').

3-(1-Hydroxy-2-nitroethyl)-4*H*-chromen-4-one (3h): colourless oil. ^{1}H NMR ($CDCl_3$, ppm): 4.69 (dd, 1 H, *J* = 8.1, 13.4 Hz), 4.93 (dd, 1 H, *J* = 4.1, 13.4 Hz), 5.40-5.44 (m, 1 H), 7.44-7.55 8m, 1 H), 7.71-7.78 (m, 1 H), 8.11 (s, 1 H), 8.21 (d, 1 H, *J* = 8.0 Hz).

2-Methyl-2-nitro-1-phenylpropan-1-ol (3i): pale yellow oil. ^{1}H NMR ($CDCl_3$, ppm): 1.41, 1.55 (2 x s, 6 H, 2 x –CH_3), 2.64 (d, 1 H, *J* = 1.4 Hz, –OH), 5.27 (d, 1 H, *J* = 1.4 Hz, H-1), 7.32–7.36 (m, 5 H, 5 x –CHPh).

2-(1-Nitrocyclopentyl)octan-1-ol (3j): Clear oil. ^{1}H NMR ($CDCl_3$, ppm): 0.81 (t, *J* = 6.9 Hz, 3 H, –CH_3), 1.16-1.20 (m, 12 H), 1.62-1.76 (m, 5 H), 2.02-2.12 (m, 1 H), 2.24-2.38 (m, 1 H), 2.46-2.58 (m, 1 H), 3.75 (d, 1 H, *J* = 10.3 Hz, H-1). ^{13}C NMR ($CDCl_3$, ppm): 14.1 (CH_3), 22.6, 24.6, 24.8, 26.3, 29.2, 31.8, 32.5, 33.7, 35.6 (10 x CH_2), 75.9, 103.6 (2 x CH). MS (ESI^+) *m*/*z* (%) 244 ($[M + H]^+$, 40); HRMS (ESI^+) calc. for $[C_{13}H_{26}NO_3]^+$ $[M + H]^+$ 244.1907, found: 244.1925.

(1-Nitrocyclohexyl)methanol (3k): Clear oil. ^{1}H-NMR ($CDCl_3$, ppm): 1.40-1.80 (m, 6 H), 2.24-2.34 (m 4 H), 3.85 (s, 2 H).

1-Phenyl-2-nitropropanol (3l): Clear oil. ^{1}H-NMR ($CDCl_3$, ppm): 1.33 (d, *J* = 6.8 Hz, 1 H, CH_3, *syn*), 1.53 (d, *J* = 6.8 Hz, 1 H, CH_3, *anti*), 2.52 (d, *J* = 3.3 Hz, 1 H, OH, *syn*), 2.66 (d, *J* = 3.5 Hz, 1 H, OH, *anti*), 4.52 (dq, *J* = 6.8 Hz, *J* 3.3 Hz, 1 H, *anti*), 4.78 (dq, *J* = 8.9 Hz, *J* 6.8 Hz, 1 H, *syn*), 5.04 (dd, *J* = 8.9 Hz, *J* = 3.3 Hz, 1 H, *syn*), 5.41 (dd, *J* 3.5 Hz, *J* = 3.3 Hz, 1 H, *anti*), 7.38-7.31 (m, 10 H, HPh, *syn* + *anti*).

1-Cyclohexyl-2-nitropropanol (3m): Clear oil. ^{1}H-NMR ($CDCl_3$, ppm): 1.03 (t, *J* = 7.3 Hz, 3 H, CH_3, *anti*), 1.04 (t, *J* = 7.4 Hz, 3 H, CH_3, *syn*), 1.55 (d, *J* = 6.9 Hz, 3 H, CH_3, *anti*), 1.56 (d, *J* = 6.8 Hz, 3 H, CH_3, *syn*), 1.43-1.65 (m, 4 H, *syn* + *anti*), 2.19 (bs, 1 H, OH, *syn*), 2.28 (bs, 1 H, OH, *anti*), 3.81–3.88 (m, 1 H, *syn*), 4.08-4.11 (m, 1 H, *anti*), 4.53–4.56 (m, 2 H, *syn* + *anti*).

3-(Benzyloxy)-2-nitro-1-phenylpropan-1-ol (3n): Clear oil. ^{1}H-NMR ($CDCl_3$, ppm): 3.43 (dd, *J* = 3.2, 10.7 Hz, 1 H, H-3, *anti*), 3.63 (dd, *J* = 7.6, 10.7 Hz, 1 H, H-3', *anti*), 3.86 (dd, *J* = 3.2, 11.1 Hz, 1 H, H-3, *syn*), 4.05 (dd, *J* = 8.2, 11.1 Hz, 3 H, CH_3, *syn*), 4.27-4.50 (m, 4 H, 2 x CH_2Ph, *syn* + *anti*), 4.76-4.83 (m, 2 H, 2 x H-2, *syn* + *anti*), 5.13 (d, *J* = 8.8 Hz, 1 H, H-1, *anti*), 5.23 (d, *J* = 5.2 Hz, 1 H, H-1, *syn*), 7.08–7.32 (m, 10 H, Ar-H, *syn* + *anti*).

7-Deoxy-1,2:3,4-di-*O*-isopropylidene-7-nitro-D-*glycero*-β-D-*galacto*-heptopyranose (3o): Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.49 (d, *J* = 5.0 Hz, 1 H), 4.78 (apparent d, *J* = 11.2 Hz, 1H), 4.65 (dd, *J* = 8.0, 2.5 Hz, 1 H), 4.51-4.47 (m, 2 H), 4.43 (dd, *J* = 8.0, 2.0 Hz, 1 H), 4.34 (dd, *J* = 4.9, 2.5 Hz, 1 H), 3.73 (dd, *J* = 8.2, 2.0 Hz, 1 H), 2.89 (d, *J* = 5.9 Hz, 1 H), 1.51 (s, 3 H), 1.46 (s, 3 H), 1.37 (s, 3 H), 1.32 (s, 3 H).

3-*O*-Benzyl-6-deoxy-6-nitro-1,2-*O*-isopropyliden-α-D-glucofuranose (3p): Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.49-7.30 (m, 5 H), 5.91 (d, *J* = 3.7 Hz, 1H), 4.76-4.60 (m, 4 H), 4.56-4.42 (m, 2 H), 4.14-4.06 (m, 2 H), 2.58 (d, *J* = 4.9 Hz, 1 H), 1.47 (s, 3 H), 1.32 (s, 3 H).

3-*O*-Benzyl-1,2-*O*-isopropylidene-5-(1-nitrocyclopentanyl)-α-D-xylofuranose (3q): Clear oil. ^{1}H-NMR ($CDCl_3$, ppm): 1.23 (s, 3 H, CH_3, *anti*), 1.26 (s, 3 H, CH_3, *syn*), 1.38 (s, 3 H, CH_3, *anti*), 1.40 (s, 3 H, CH_3, *syn*), 1.54-1.67 (m, 8 H, *syn* + *anti*), 1.85-1.96 (m, 2 H, *syn* + *anti*), 2.10-2.20 (m, 2 H, *syn* + *anti*), 2.35-2.42 (m, 2 H, *syn* + *anti*), 2.54-2.62 (m, 2 H, *syn* + *anti*), 3.96-4.50 (m, 4 H, *syn* + *anti*), 4.25-4.28 (m, 2 H, *syn* + *anti*), 4.36-4.66 (m, 6 H, *syn* + *anti*), 5.84 (d, *J* = 3.8 Hz, 1 H, H-1, *anti*), 5.90 (d, *J* = 3.8 Hz, 1 H, H-1, *syn*), 7.16-7.32 (m, 10 H, Ar-H, *syn* + *anti*). ^{13}C NMR ($CDCl_3$, ppm): 23.8, 24.5 (2 x CH_2), 26.4, 26.8 (2 x CH_3), 33.4, 35.9 (2 x CH_2), 72.2 (CH_2), 72.8, 79.6, 81.4, 82.6 (4 x CH), 102.6 (C), 105.3 (CH), 112.0 (C), 128.0 (2 x CH), 128.4 (CH), 128.8 (2 x CH), 136.9 (C). MS (ESI$^+$) *m*/*z* (%) 394 ([M + H]$^+$, 19); HRMS (ESI$^+$) calc. for $[C_{20}H_{28}NO_7]^+$ [M + H]$^+$ 394,1860, found: 394,1852.

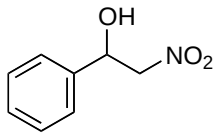
3-*O*-Benzyl-1,2-*O*-isopropylidene-5-(1-nitroethyl)-α-D-xylofuranose (3r): Clear oil. ^{1}H-NMR ($CDCl_3$, ppm): 1.24 (s, 6 H, 2 x CH_3, *syn* + *anti*), 1.38 (s, 6 H, 2 x CH_3, *syn* + *anti*), 1.48 (d, *J* = 6.8 Hz, 3 H, CH_3, *anti*), 1.55 (d, *J* = 6.8 Hz, 3 H, CH_3, *syn*), 3.88-3.94 (m, 2 H, *syn* + *anti*), 4.02-4.07 (m, 2 H, *syn* + *anti*), 4.37-4.72 (m, 6 H, *syn* + *anti*), 5.82 (d, *J* = 3.7 Hz, 1 H, H-1, *anti*), 5.91 (d, *J* = 3.7Hz, 1 H, H-1, *syn*), 7.18-7.32 (m, 10 H, Ar-H, *syn* + *anti*). ^{13}C NMR ($CDCl_3$, ppm) major isomer *anti*: 11.4, 26.3, 26.9 (3 x CH_3), 65.8 (CH), 72.3 (CH_2), 68.5, 79.1, 80.9, 82.1, 83.8, 105.2 (6 x CH), 112.0 (C), 128.0 (2 x CH), 128.4 (CH), 128.8 (2 x CH), 137.1 (C). MS (ESI$^+$) *m*/*z* (%) 354 ([M + H]$^+$, 22); HRMS (ESI$^+$) calc. for $[C_{17}H_{24}NO_7]^+$ [M + H]$^+$ 354,1547, found: 354,1552.

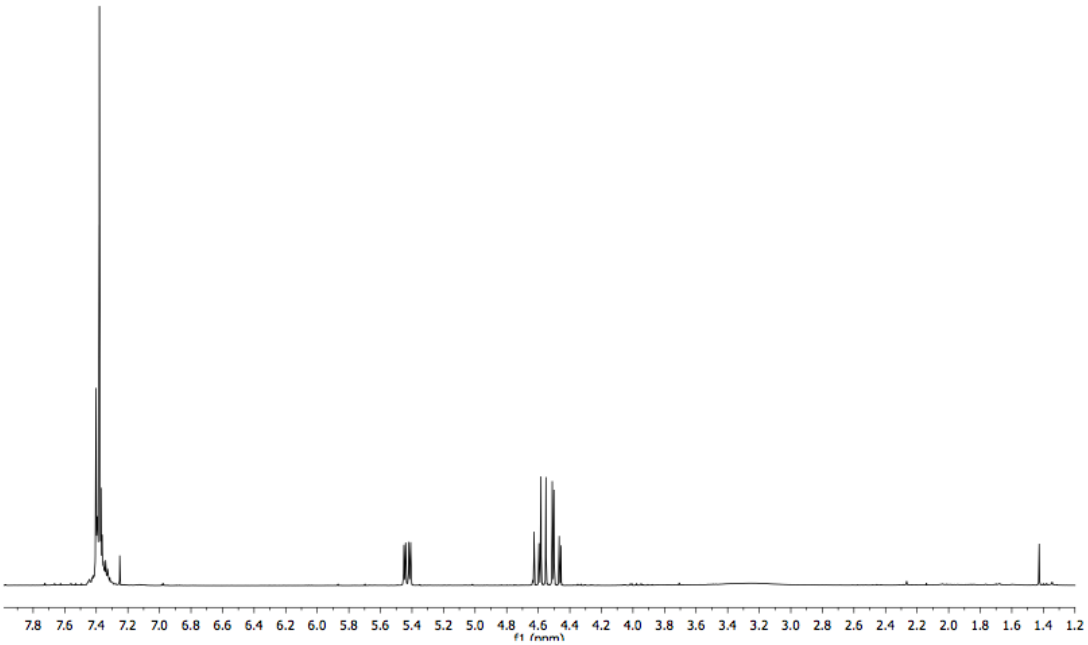
(*E*)-2-(2-Nitrovinyl)phenol (6a): Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.81 (d, *J* = 8.6 Hz, 1 H), 6.88-6.96 (m, 1 H), 7.23-7.38 (m, 2 H), 7.90 (d, *J* = 13.6 Hz, 1 H), 8.06 (d, *J* = 13.6 Hz, 1 H).

(*E*)-5-Chloro-2-(2-Nitrovinyl)phenol (6b): Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.95 (d, *J* = 8.8 Hz, 1 H), 7.24 (dd, *J* = 8.8, 2.6 Hz, 1 H), 7.61 (d, *J* = 2.6 Hz, 1 H), 7.97 (d, *J* = 13.6 Hz, 1 H), 8.05 (d, *J* = 13.6 Hz, 1 H).

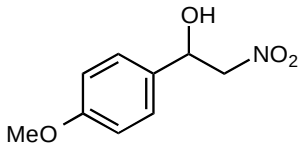
(*E*)-3-Methoxy-2-(2-Nitrovinyl)phenol (6c): Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.86 (s, 3 H), 6.79-6.94 (m, 3 H), 7.87 (d, *J* = 13.6 Hz, 1 H), 8.02 (d, *J* = 13.6 Hz, 1 H).

2-Nitro-1-phenylethan-1-ol (3a)

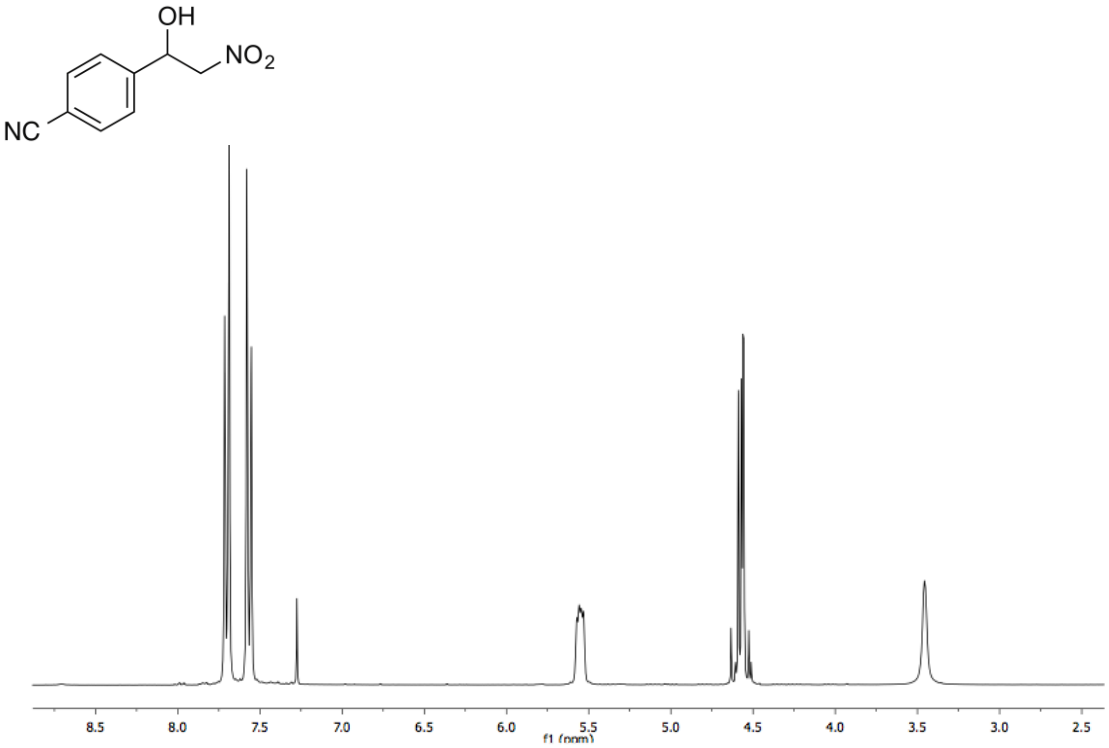




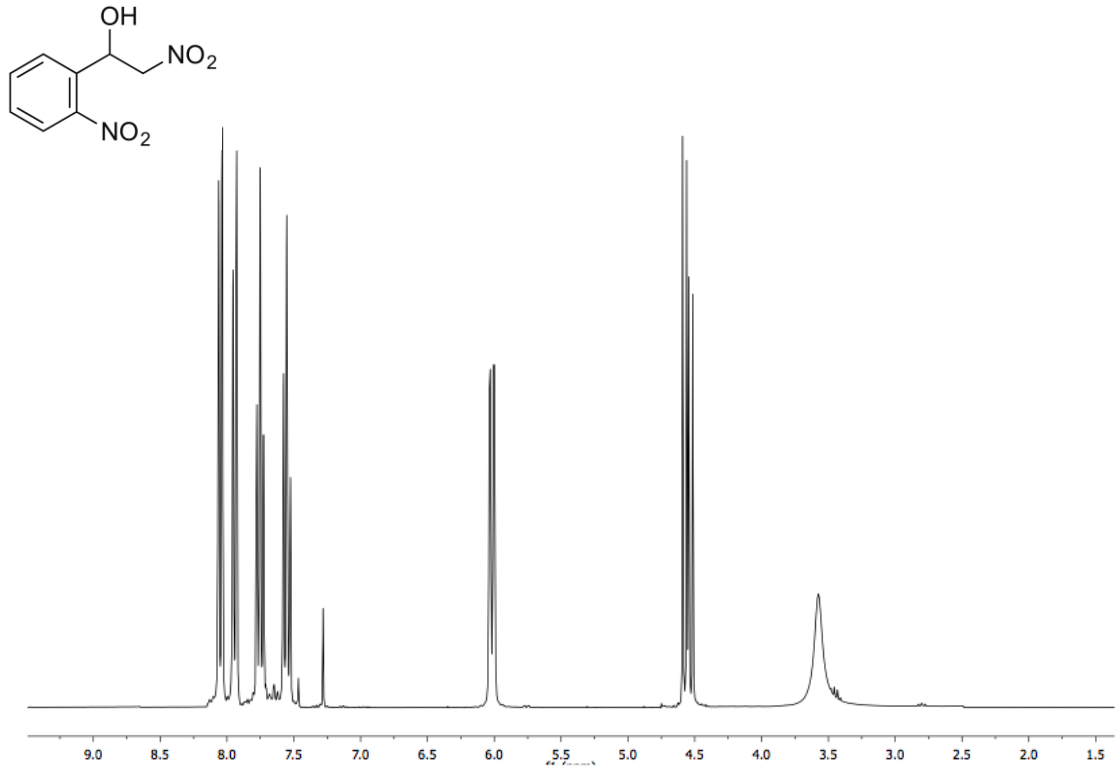
1-(4-Methoxyphenyl)-2-nitroethanol (3b)



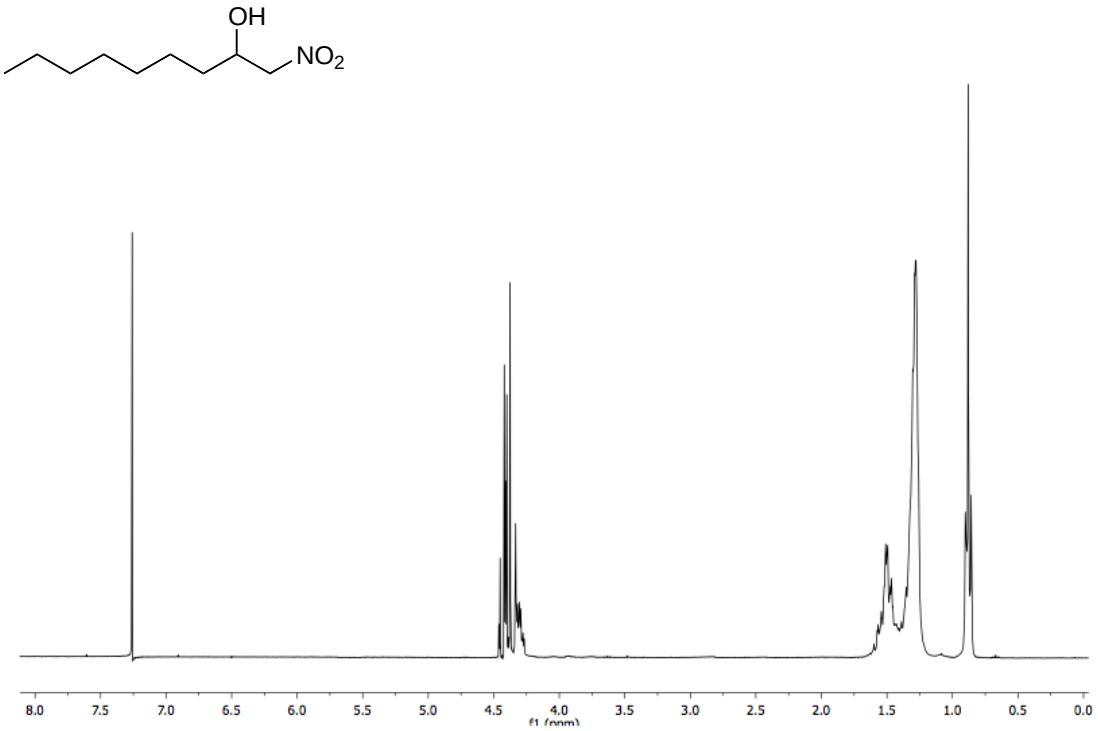
1-(4-Cyano)-2-methyl-2-nitropropan-1-ol (3c)



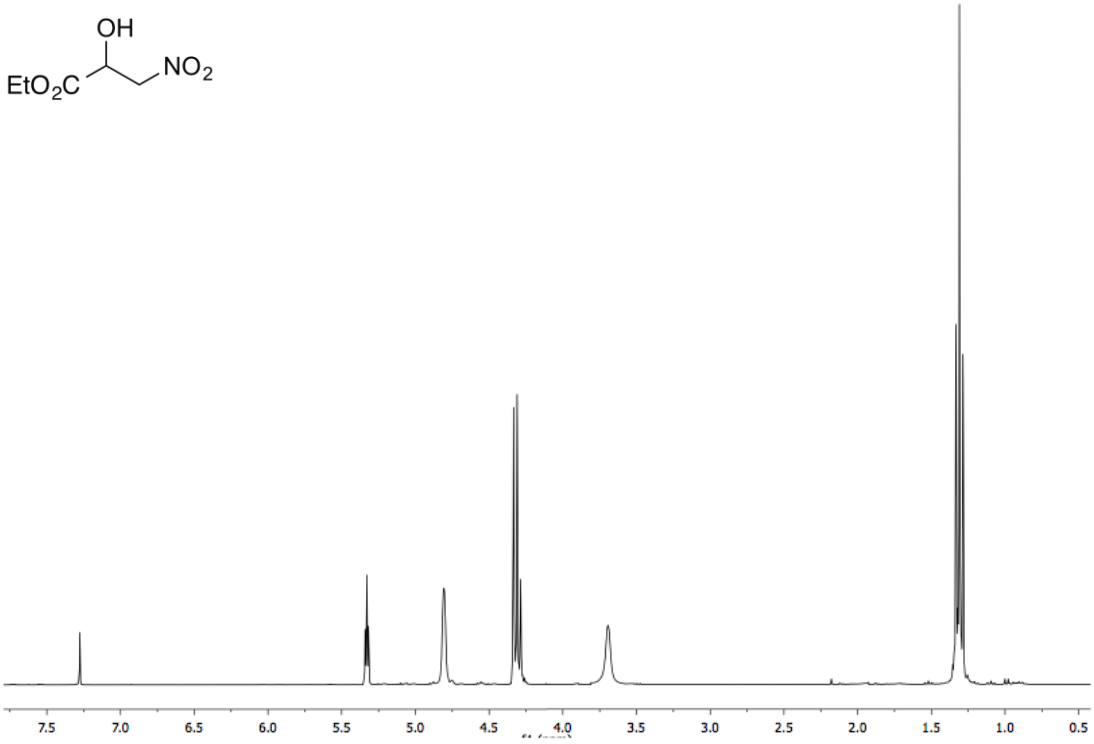
1-(2-Nitro)-2-methyl-2-nitropropan-1-ol (3d)



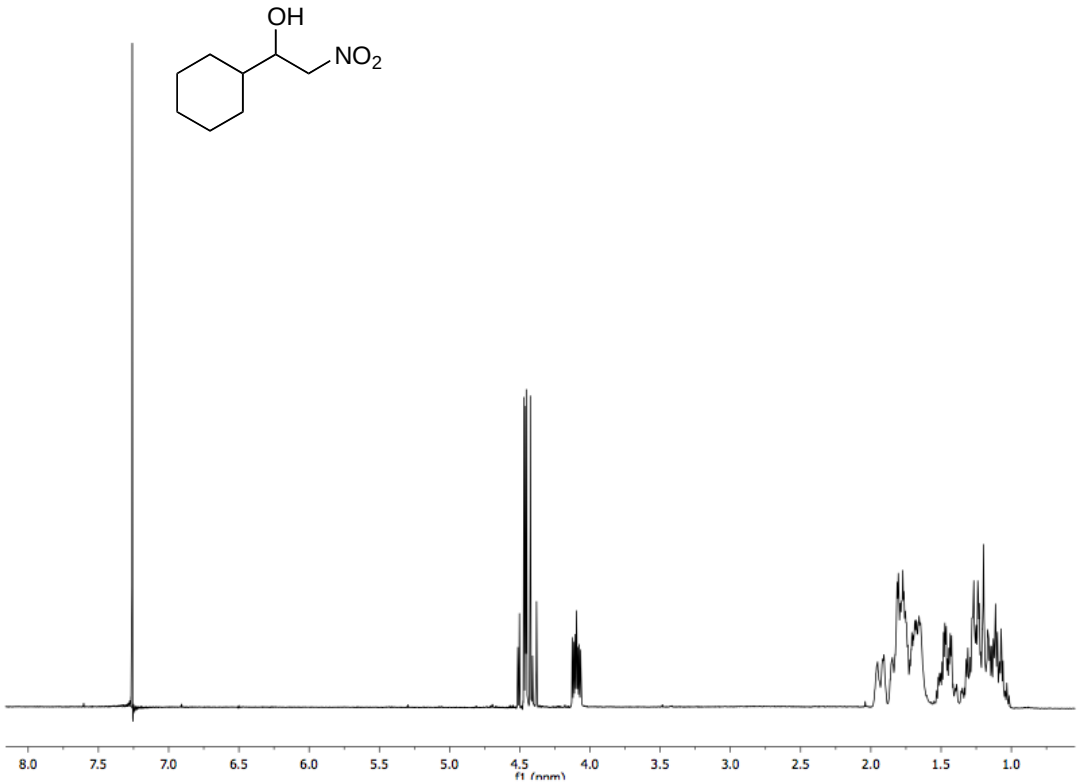
1-Nitrononan-2-ol (3e)



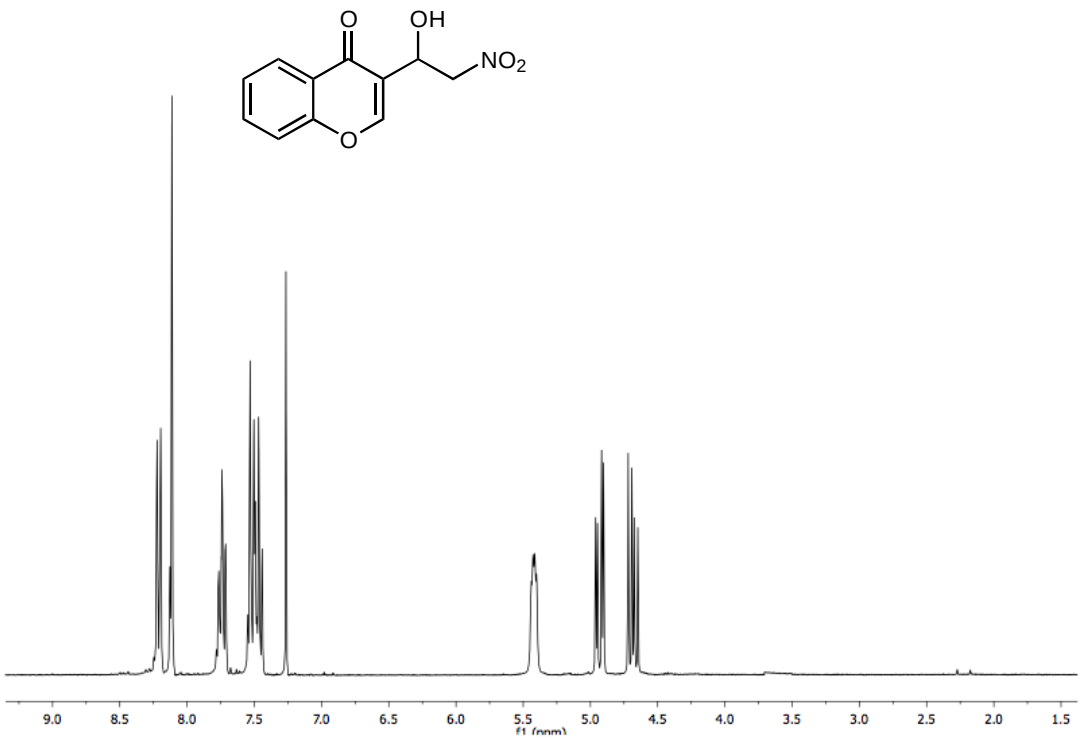
Ethyl 2-hydroxy-3-nitropropanoate (3f)



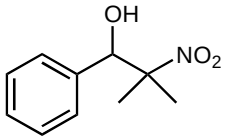
1-Cyclohexyl-2-nitroethanol (3g)

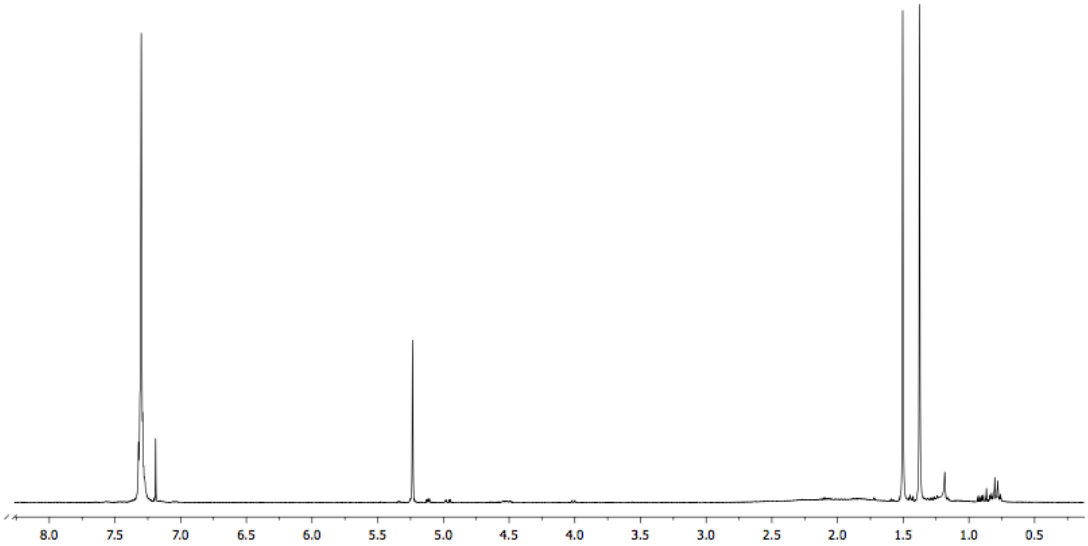


3-(1-Hydroxy-2-nitroethyl)-4*H*-chromen-4-one (3h)

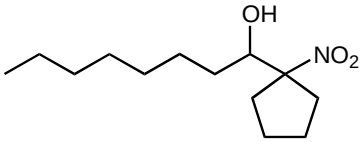


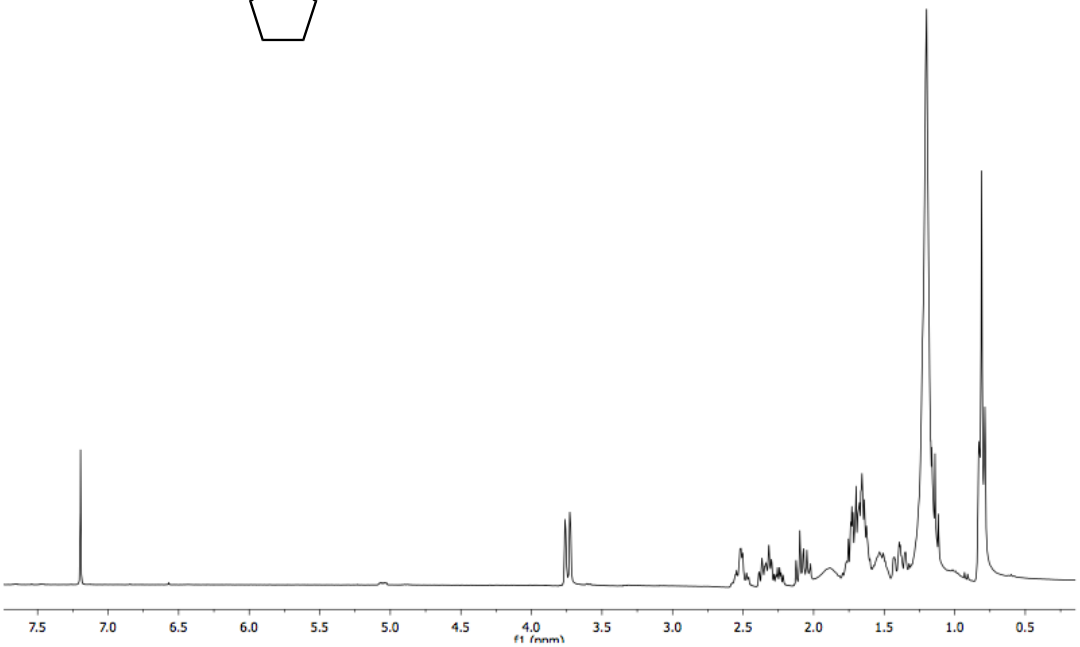
2-Methyl-2-nitro-1-phenylpropan-1-ol (3i)

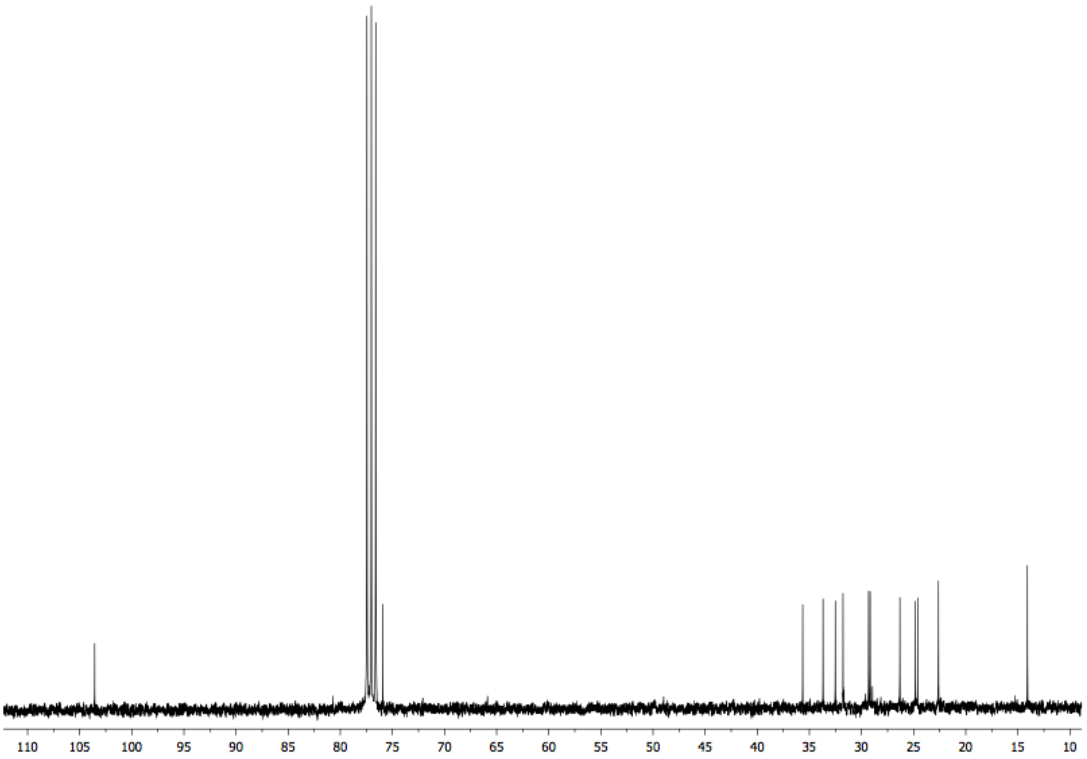




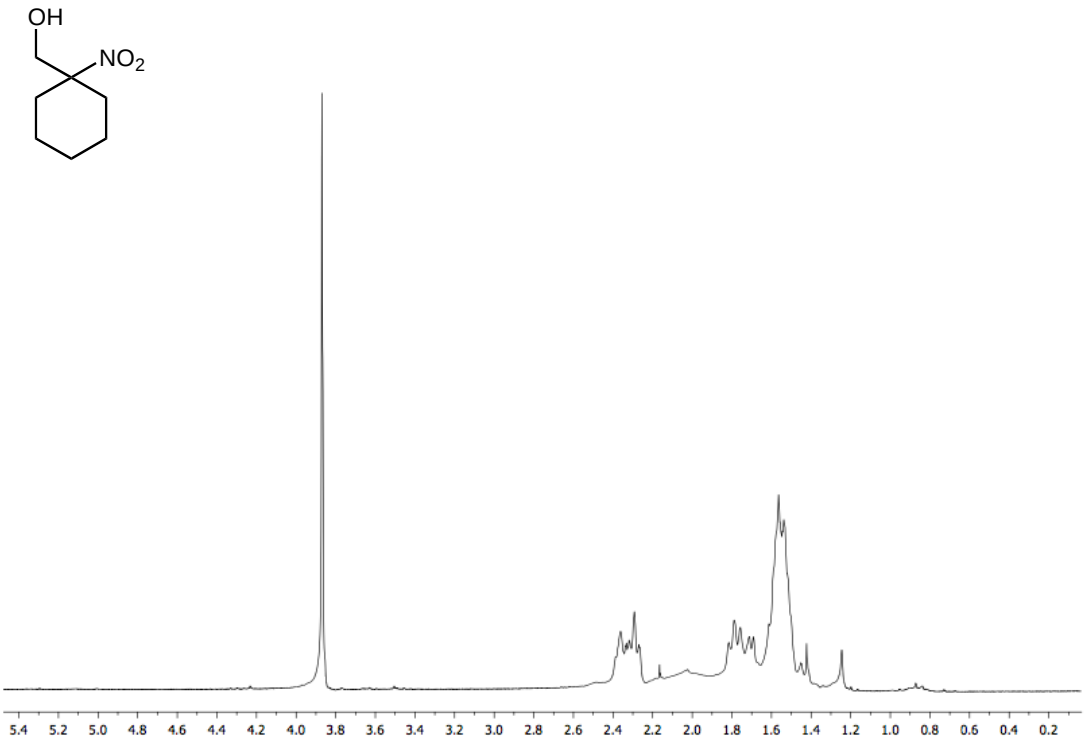
2-(1-Nitrocyclopentyl)octan-1-ol (3j)



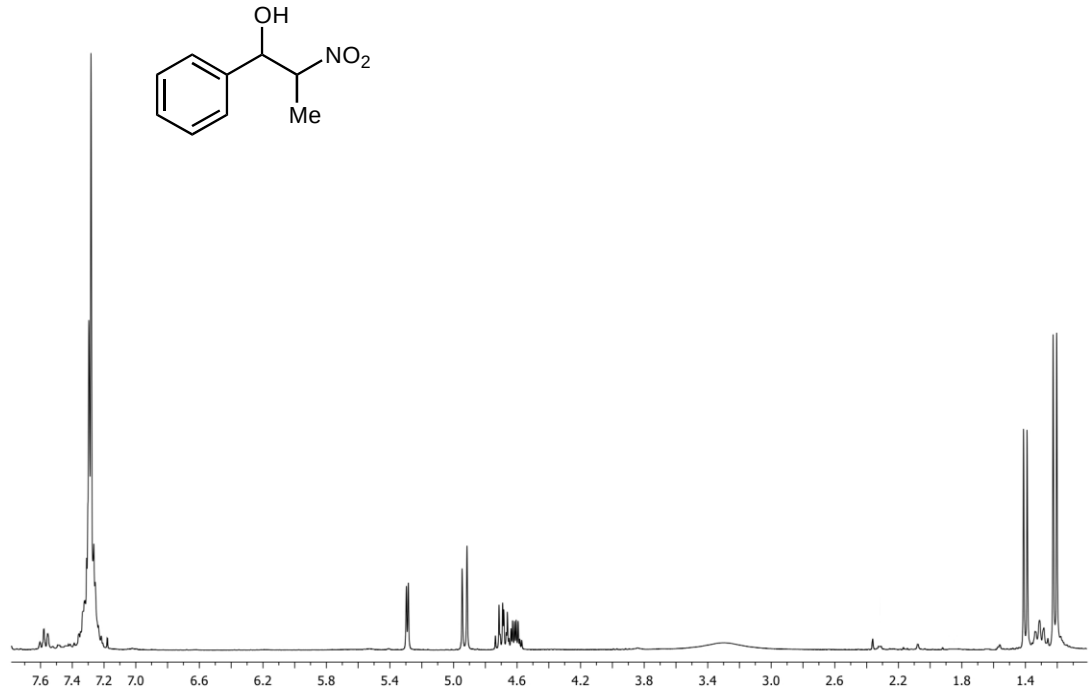




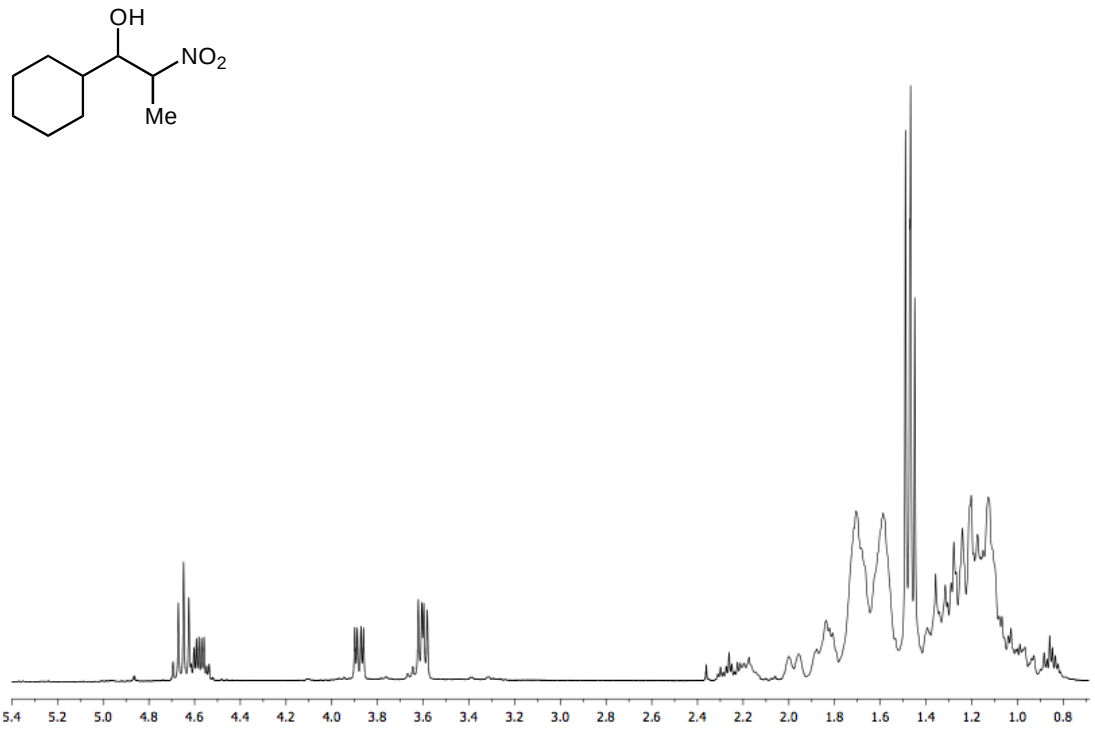
(1-Nitrocyclohexyl)methanol (3k)



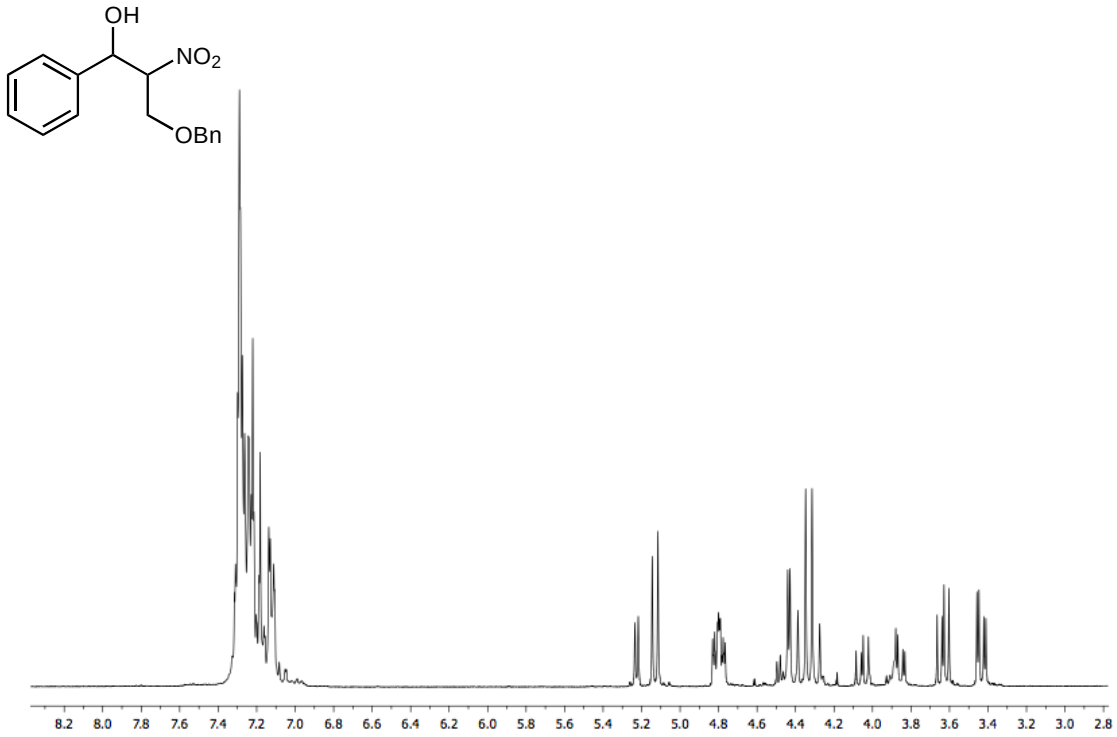
1-Phenyl-2-nitropropanol (3l)



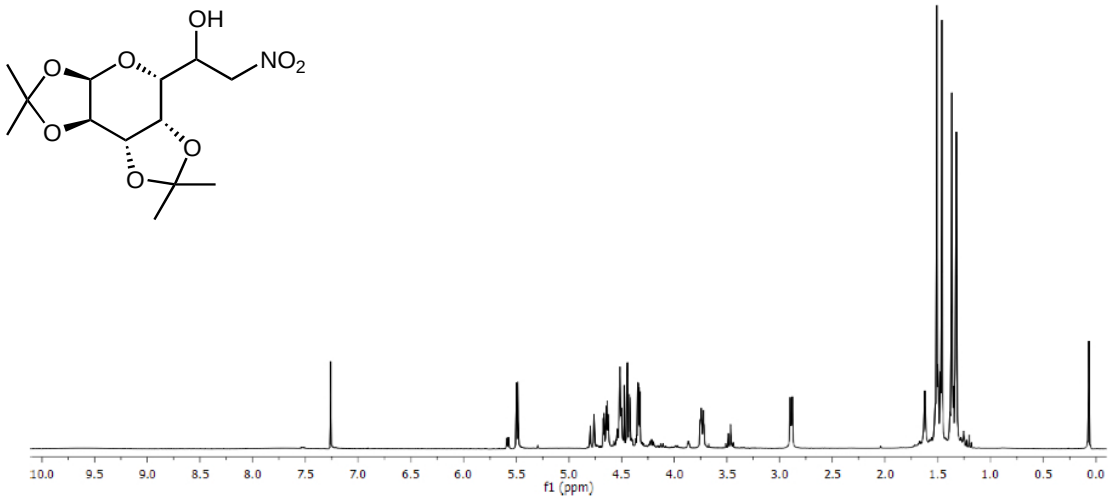
1-Cyclohexyl-2-nitropropanol (3m)



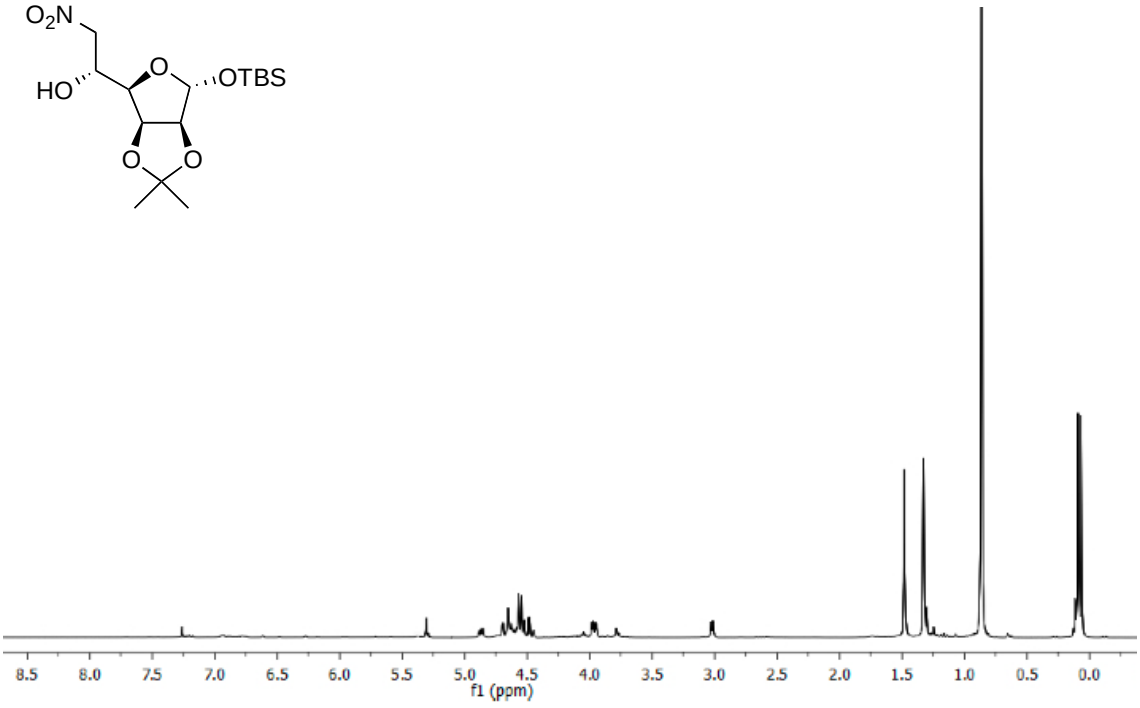
3-(Benzyloxy)-2-nitro-1-phenylpropan-1-ol (3n)



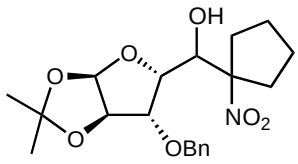
7-Deoxy-1,2:3,4-di-*O*-isopropylidene-7-nitro-D-*glycero*-β-D-*galacto*-heptopyranose (3o)

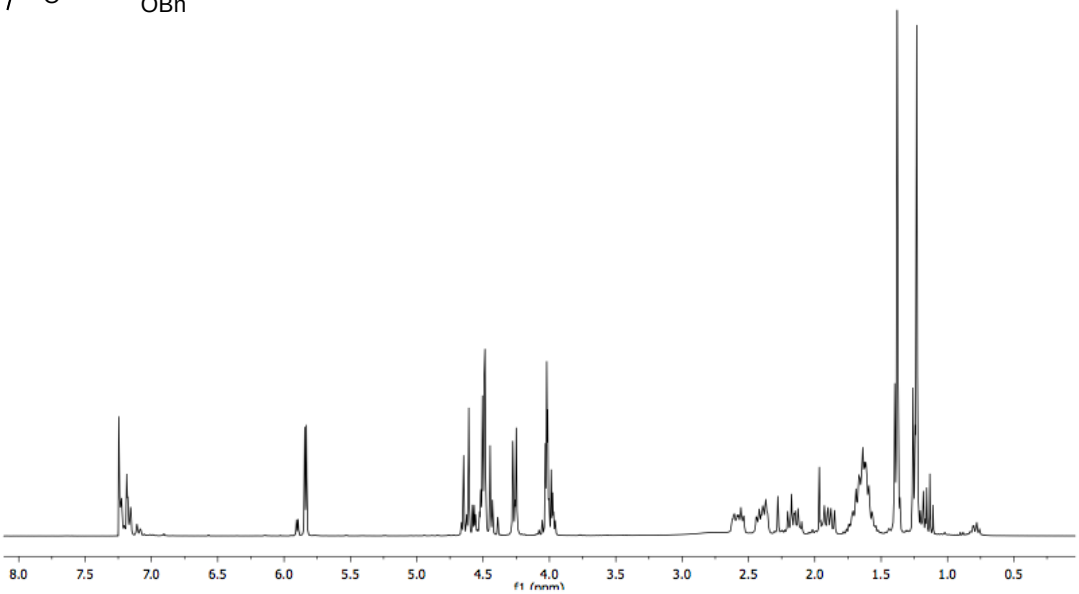


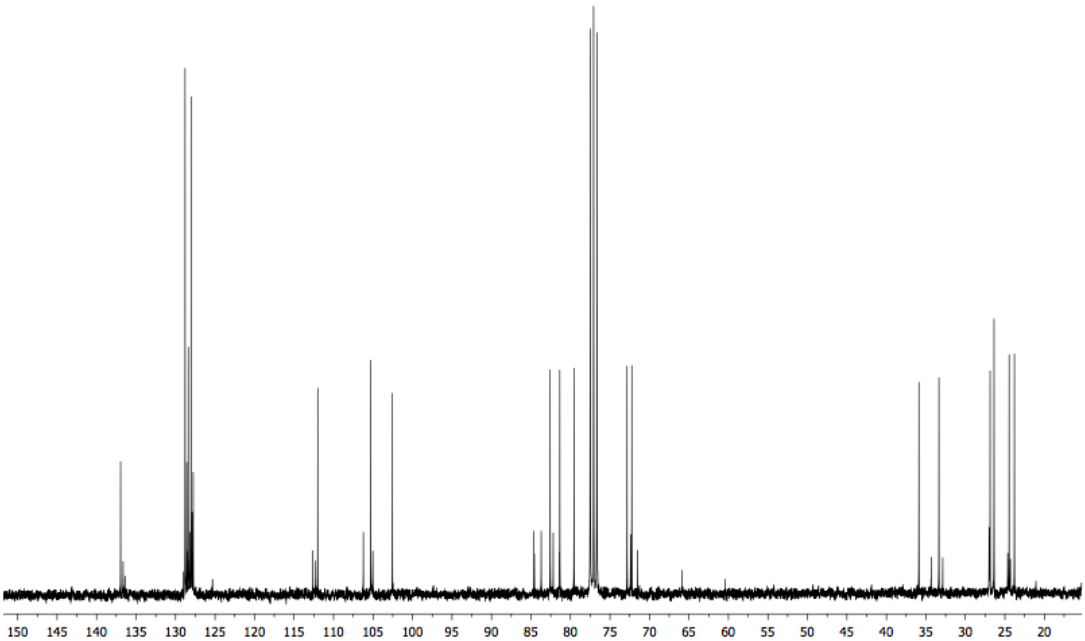
1-*O*-*tert*-Butyldimethylsilyl-6-deoxy-2,3-di-*O*-isopropylidene-6-nitro-α-D-mannofuranose (3p)



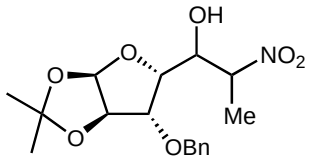
3-*O*-Benzyl-1,2-*O*-isopropylidene-5-(1-nitrocyclopentanyl)-α-D-xylofuranose (3q)

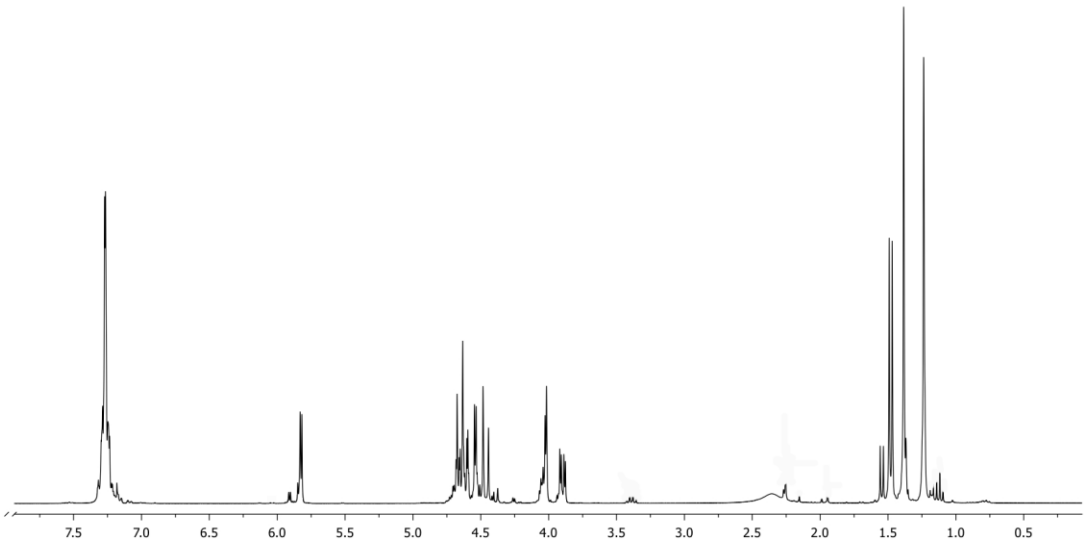


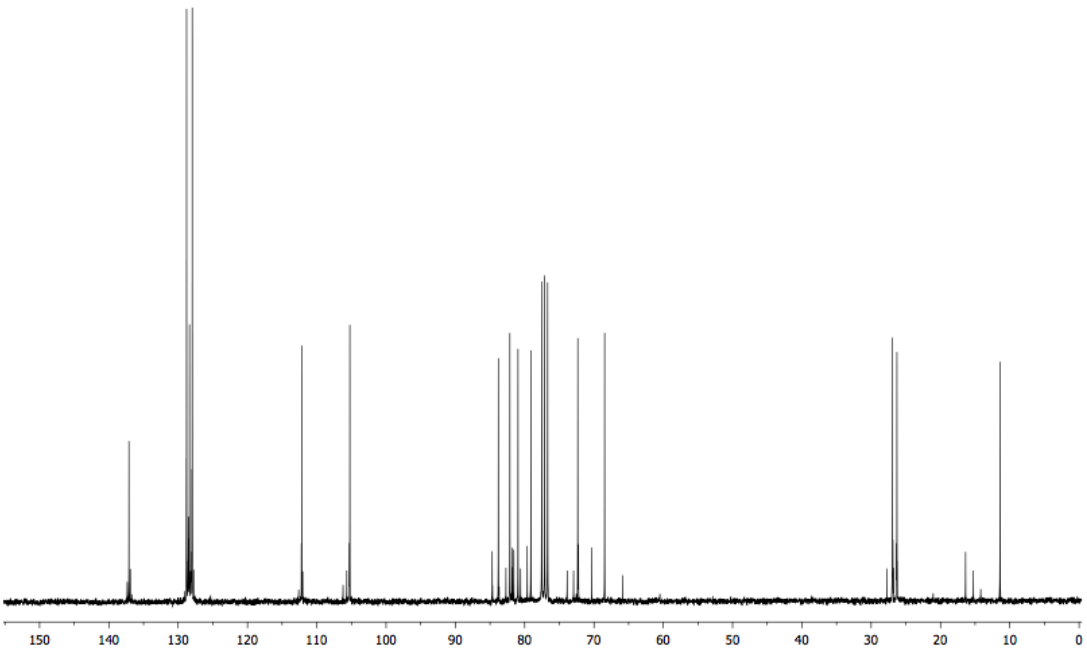




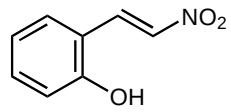
3-*O*-Benzyl-1,2-*O*-isopropylidene-5-(1-nitroethyl)-α-D-xylofuranose (3r)

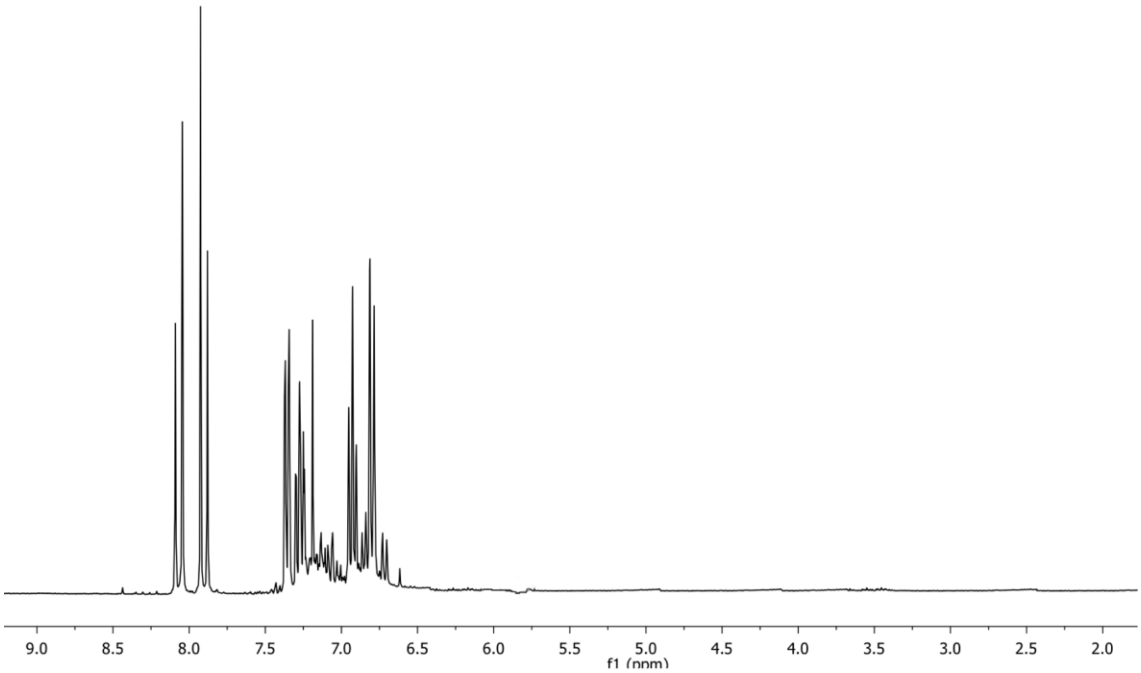




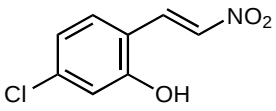


(*E*)-2-(2-Nitrovinyl)phenol (6a)





(*E*)-5-Chloro-2-(2-nitrovinyl)phenol (6b)



(*E*)-2-Methoxy-6-(2-nitrovinyl)phenol (6c)