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Supporting Information

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Organocatalytic Asymmetric Domino Reactions: A Michael Addition/Aldehyde α-Alkylation Cascade

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General Methods

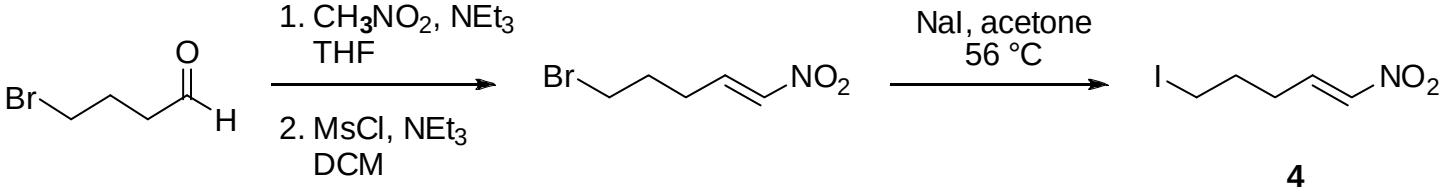
Preparative column chromatography: Merck silica gel 60, particle size 0.040-0.063 mm (230-240 mesh, flash). Analytical TLC: silica gel 60 F_{254} plates from Merck, Darmstadt. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with anisaldehyde or ninhydrin. Optical rotation values were measured on a Perkin-Elmer 241 polarimeter. Microanalyses were performed with a Vario EL element analyser. Mass spectra were acquired on a Finnigan SSQ7000 (EI 70 eV) spectrometer and high resolution mass spectra on a Finnigan MAT 95. IR spectra were taken on a Perkin-Elmer FT-IR 1760. ^{1}H- and ^{13}C- NMR spectra were recorded at ambient temperature on Varian Mercury 300 or Inova 400 with tetramethylsilane as an internal standard. Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases (Chiralcel OD, Chiralcel OJ, Chiralpak AD, Chiralpak AS, Chiralcel IA).

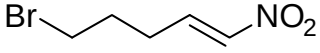
Materials

Unless otherwise noted, all commercially available compounds were used without further purification. Aldehydes were freshly distilled. Dichloromethane was freshly distilled under Ar from calcium hydride. THF was freshly distilled under Ar from natrium. Methanol was freshly distilled under Ar from Mg/I_2. Acetone was freshly distilled under Ar from K_2CO_3. Catalysts **1** and **3** were prepared according to previously described procedures[1,2]. Racemic samples of cyclopentanecarbaldehydes **6a-e** were prepared using pyrrolidine (100 mol%) in DMSO at room temperature.

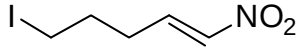
General Procedure and Charaterization

Synthesis of (*E*)-5-iodo-1-nitropent-1-ene (5)





(E)-5-bromo-1-nitropent-1-ene. To a solution of 4-bromobutanal[3] (19.3 g, 127.5 mmol) and nitromethane (77 mL, 1.275 mol) in tetrahydrofuran (125 mL) was added NEt_3 (17.2 mL, 127.5 mmol). The reaction mixture was stirred at room temperature for 24 h. Reaction was then quenched with 1 N HCl (125 mL). The aqueous layer was extracted with Et_2O (3 × 250 mL). The combined organic layers were washed successively with satured $NaHCO_3$ (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. To the solution of the crude product in CH_2Cl_2 (300 mL) was added menthansulfanyl chloride (10.9 mL, 140.3 mmol) at 0 °C. In 15 min NEt_3 (34.4 mL, 255 mmol) was added. The reaction mixture was stirred for 30 min at 0 °C and then 2 h at room temperature. After quenching with H_2O (100 mL) the contents were extracted with CH_2Cl_2 (2 × 250 mL). The combined organic layers were washed successively with satured $NaHCO_3$ (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude procuct was purified by flash chromatography (30:1 pentane/ether) to afford 5-bromonitroalkene as a yellow oil (13.1 g, 53 %). IR (KBr) ν = 3105 (s), 2957 (s), 1651 (vs), 1526 (vs), 1438 (s), 1355 (vs), 1273 (s), 1147 (w), 1080 (w), 956 (vs), 841 (s), 757 (s), 732 (s), 650 (m), 565 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.21 (dt, J = 14.4, 7.2 Hz, 1 H), 7.06 (d, J = 13.2 Hz, 1 H), 3.44 (t, J = 6.4 Hz, 2 H), 2.48 (q, J = 7.6 Hz, 2 H), 2.08 ppm (quin, J = 6.8 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.3 (2 C), 32.0, 30.4, 26.9 ppm; MS (EI, 70 eV): *m/z* (%) 195.00 (0.58) [M^+], 149.0 (17), 147.0 (18), 137.0 (2.7), 135.0 (2.7), 121 (7.7), 119.0 (7.6), 114 (8.9), 109 (26), 107 (27), 97.1 (4.5), 93.0 (4.6), 87.1 (100), 86.1 (99), 70.2 (13), 67.2 (73), 55.4 (27); Anal. Calcd for $C_5H_8BrNO_2$: C, 30.94; H, 4.15; N, 7.22; found: C, 31.04; H, 4.58; N, 7.12.



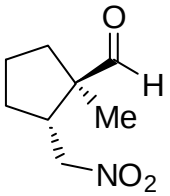
4

(E)-5-iodo-1-nitropent-1-ene (**4**). To a solution of (*E*)-5-bromo-1-nitropent-1-ene (13.1 g, 67.5 mmol) in acetone (125 mL) was added NaI (30.4 g, 202.5 mmol). The reaction mixture was refluxed for 3 h and then cooled to room temperature. After evaporation of acetone under reduced pressure the residue was dissolved in Et_2O (200 mL) and washed with H_2O (50 mL). The aqueous layer was extracted with Et_2O (3 × 200 mL) and the

combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude procuct was purified by flash chromatography (10:1 pentane/ether) to afford 5-iodonitroalkene **4** as a yellow oil (13.0 g, 80 %). IR (KBr) ν = 3103 (m), 2941 (m), 1650 (s), 1524 (vs), 1432 (m), 1353 (vs), 1263 (w), 1213 (m), 1170 (s), 1030 (w), 951 (s), 839 (s), 730 (m), 602 (w), 504 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.19 (dt, J_1 = 13.6, 7.6 Hz, 1 H), 7.06 (d, J = 13.6 Hz, 1 H), 3.22 (t, J = 6.4 Hz, 2 H), 2.43 (q, J = 8 Hz, 2 H), 2.03 ppm (quin, J = 7.6 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.3, 140.1, 30.9, 29.1, 4.7 ppm; MS (EI, 70 eV): *m/z* (%) 241 (2.3) [M^+], 167.0 (1.7), 155.0 (19), 141.0 (2.6), 127.0 (3.4), 114.1 (100), 96.1 (2.5), 87.1 (4.2), 83.1 (2.4), 71.2 (8.4), 67.2 (31), 55.4 (22); Anal. Calcd for $C_5H_8BrNO_2$: C, 24.91; H, 3.35; N, 5.81; found: C, 24.99; H, 3.34; N, 6.17.

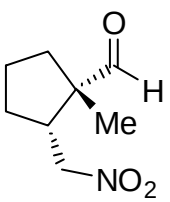
General Procedure for the cyclopentanecarbaldehydes

Catalyst **1** (130 mg, 0.4 mmol) was added to a solution of benzoic acid (244 mg, 2 mmol), aldehydes (**5)** (10 mmol) and (*E*)-5-iodo-1-nitropent-1-en (**4)** (482 mg, 2 mmol) in DMSO (4 mL) at room temperature. The reaction mixture was stirred for 2-7 d and then quenched with satured NH_4Cl (5 mL). Organic materials were extracted three times with ether, and the combined organic phases were washed successively with satured $NaHCO_3$, brine, dried over Na_2SO_4, filtered, and concentrated. The crude procuct was purified by flash chromatography to afford the product as a yellow oil.



trans-**6a**

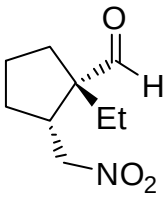
(1R,2R)-1-methyl-2-(nitromethyl)cyclopentanecarbaldehyde (*trans*-**6a**) was isolated after 2 d through flash chromatography (pentane:ether = 12:1) as a yellow oil (140 mg, 41%). The *e.e.* (94 %) was determined by HPLC on a chiral stationary phase [Chiralcel OD, *n*-heptane:*i*PrOH = 9:1, 1.2 mL/min), t_R = 8.95 min (major), 12.43 min (minor)]. $[\alpha]^{20}_D$ = –1.1 (*c* = 1.0, $CHCl_3$); IR (KBr): 2963 (s), 2876 (s), 2819 (w), 2709 (m), 1723 (s), 1552 (s), 1432 (s), 1381 (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.48 (s, 1 H), 4.39 (dd, J = 13.2, 6.4 Hz, 1 H), 4.36 (dd, J = 12.8, 8.8 Hz, 1 H), 2.98-2.93 (m, 1 H), 2.09-2.02 (m, 2 H), 1.89-1.73 (m, 2 H), 1.63-1.51 (m, 2 H), 1.05 ppm (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 202.7, 76.0, 54.9, 41.6, 35.6, 29.0, 22.3, 14.8 ppm; MS (EI, 70 eV): *m/z* (%): 172.0 (0.67) [M^++1], 125 (1.6), 107 (3.0), 95.1 (100), 81.0 (36), 79.0 (21), 77.0 (11), 67.1 (69), 55.0 (59), 53.0 (34), 45.8 (16); Anal. Calcd. for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18; found: C, 56.24; H, 8.03; N, 8.66.



cis-**6a**

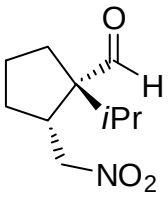
(1S,2R)-1-methyl-2-(nitromethyl)cyclopentanecarbaldehyde (*cis*-**6a**) was isolated after 2 d through flash chromatography (pentane:ether = 12:1) as a yellow oil (72 mg, 21%). The *e.e.* (96 %) was determined by HPLC on a chiral stationary phase [Chiralcel OD, *n*-heptane:*i*PrOH = 9:1,

1.0 mL/min), t_R = 10.55 min (major), 12.87 min (minor)]. $[\alpha]_D^{20}$ = –4.5 (*c* = 1.0 in $CHCl_3$); IR (KBr): 2963 (s), 2875 (s), 2716 (m), 1719 (s), 1552 (s), 1453 (s), 1381 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.52 (s, 1 H), 4.62-4.53 (m, 2 H), 2.52-2.45 (m, 1 H), 2.16-2.04 (m, 2 H), 1.82-1.71 (m, 2 H), 1.69-1.55 (m, 2 H), 1.29 ppm (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 203.9, 76.1, 55.6, 47.0, 35.6, 30.0, 21.8, 20.2 ppm; MS (EI, 70 eV): *m/z* (%): 171.9 (0.39) [M^++1], 124.9 (2.8), 106.9 (4.4), 95.0 (100), 80.9 (33), 78.9 (18), 76.9 (9), 67.0 (56), 55.0 (41), 52.9 (19), 45.8 (8); HRMS (ESI-TOF): calcd. for for $C_8H_{13}NO_3$+H: 172.0975, found: 172.0975.



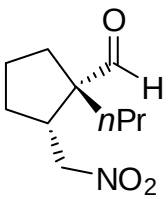
6b

(1S,2R)-1-ethyl-2-(nitromethyl)cyclopentanecarbaldehyde (**6b**) was isolated after 4 d through flash chromatography (pentane:ether = 20:1) as a yellow oil (188 mg, 51 %). The *e.e.* (97 %) was determined by HPLC on a chiral stationary phase [Chiralcel OD, *n*-heptane:*i*PrOH = 97:3, 0.5 mL/min), t_R = 23.22 min (minor), 25.38 min (major)]. $[\alpha]_D^{20}$ = –17.0 (*c* = 0.7 in $CHCl_3$); IR (KBr): 2964 (vs), 2878 (s), 2719 (m), 1722 (vs), 1553 (vs), 1458 (m), 1381 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.59 (s, 1 H), 4.59 (dd, *J* = 12.6, 6.8 Hz, 1 H), 4.51 (dd, *J* = 12.0, 10.5 Hz, 1 H), 2.59-2.55 (m, 1 H), 2.14-2.02 (m, 2 H), 1.94-1.50 (m, 6 H), 0.96 ppm (t, *J* = 8.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.2, 76.8, 59.6, 45.7, 31.8, 30.4, 27.6, 22.1, 9.4 ppm; MS (EI, 70 eV): *m/z* (%): 184.1 (2.8) [M^+-1], 155.0 (13.7), 139.1 (2.4), 125.0 (6.5), 109.1 (100), 95.1 (9.6), 81.1 (13), 67.1 (35), 53.0 (6.5). HRMS (ESI-TOF): calcd. for for $C_9H_{15}NO_3$-H: 184.097368, found: 184.097138.



6c

(1S,2R)-1-isopropyl-2-(nitromethyl)cyclopentanecarbaldehyde (**6c**) was isolated after 7 d through flash chromatography (pentane:ether = 25:1) as a yellow oil (159 mg, 40 %). The *e.e.* (93 %) was determined by HPLC on a chiral stationary phase [Chiralcel OD, *n*-heptane:*i*PrOH = 97:3, 1.0 mL/min), t_R = 6.62 min (major), 7.29 min (minor)]. $[\alpha]_D^{20}$ = –12.9 (*c* = 0.45 in $CHCl_3$); IR (KBr): 2964 (vs), 2877 (s), 2721 (m), 1720 (vs), 1554 (vs), 1466 (m), 1382 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.60 (s, 1 H), 4.63 (dd, *J* = 16.4, 5.2 Hz, 1 H), 4.52 (dd, *J* = 16.4, 13.6 Hz, 1 H), 2.73-2.69 (m, 1 H), 2.21-2.11 (m, 1 H), 2.07-1.95 (m, 2 H), 1.83-1.60 (m, 3 H), 1.52-1.41 (m, 1 H), 1.11 (d, *J* = 9.2 Hz, 3 H), 0.96 ppm (d, *J* = 9.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 206.3, 77.3, 62.4, 43.0, 30.9, 30.6, 28.6, 22.4, 18.6, 17.6 ppm; MS (CI, CH_4): m/z (%): 200.0 (2.3) [M^++1], 169.0 (3.6), 153.1 (78), 139.0 (4.1), 135.0 (27), 123.0 (28),109.1 (100), 95.1 (17), 81.1 (9.8), 67.1 (7.8); HRMS (ESI-TOF): calcd. for for $C_{10}H_{17}NO_3$-NO_2: 153.1275, found: 153.1280.



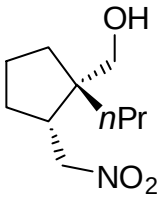
6d

(1S,2R)-1-propyl-2-(nitromethyl)cyclopentanecarbaldehyde (**6c**) was isolated after 4 d through flash chromatography (pentane:ether = 30:1) as a colorless oil (163 mg, 41 %). The *e.e.* (97 %)

was determined by HPLC on a chiral stationary phase [Chiralcel OD, *n*-heptane:*i*PrOH = 97:3, 0.7 mL/min), t_R = 10.73 min (major), 12.00 min (minor)]. $[\alpha]_D^{20}$ = –23.1 (*c* = 0.8 in $CHCl_3$); IR (KBr): 2960 (vs), 2873 (s), 2724 (m), 1720 (vs), 1457 (s), 1382 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.57 (s, 1 H), 4.58 (dd, *J* = 12.6, 4.8 Hz, 1 H), 4.51 (dd, *J* = 12.6, 9.9 Hz, 1 H), 2.58-2.52 (m, 1 H), 2.14-1.98 (m, 2 H), 1.87-1.45 (m, 6 H), 1.37-1.26, (m, 2 H), 0.95 ppm (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.2, 76.9, 59.5, 46.2, 37.5, 32.4, 30.4, 22.1, 18.6, 14.9 ppm; MS (CI, CH_4): m/z (%): 200.0 (8.2) [M^++1], 181.(2.0), 153.1 (100), 139.0 (10), 135.0 (10.7), 123.0 (28), 109.1 (100), 95.1 (14), 81.1 (9.8), 71.1 (28), 67.1 (5.8); HRMS (ESI-TOF): calcd. for for $C_{10}H_{17}NO_3$-CH_2NO_2: 123.117375, found: 123.117440.

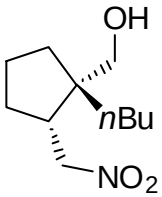
General Procedure for the reduction of cyclopentanecarbaldehydes to cyclopentylmethanols

To a sulotion of cyclopentanecarbaldehydes (1.0 mmol) in methanol was added $NaBH_4$ (244 mg, 2 mmol) at 0 °C. The reaction mixture was stirred for 30 min and then quenched with H_2O (5 mL). Organic materials were extracted three times with ether, and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude procuct was purified by flash chromatography (pentane/ether = 4:1) to afford the product as a colorless oil.



7d

(1S,2R)-1-propyl-2-(nitromethyl)cyclopentyl)methanol (**7d**) was isolated as a colorless oil (187 mg, 93 %). $[\alpha]_D^{20}$ = –14.5 (*c* = 1.0 in $CHCl_3$); IR (KBr): 3576 (m), 3408 (w), 2957 (vs), 2874 (s), 1550 (vs), 1460 (m), 1383 (s), 1045 (s), 482 (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.70 (dd, *J* = 12.0, 4.2 Hz, 1 H), 4.45 (dd, *J* = 12.0, 11.4 Hz, 1 H), 3.51-3.42 (m, 2 H), 2.42-2.35 (m, 1 H), 1.97-1.88 (m, 1 H), 1.72-1.22 (m, 9 H), 0.93 ppm (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 78.3, 65.2, 48.2, 46.7, 36.0, 34.3, 30.1, 26.8, 23.5, 22.2, 14.1 ppm; MS (CI, CH_4): m/z (%): 202.2 (0.52) [M^++1], 184.1 (0.91), 170.2 (1.9), 155.2 (0.95), 137.1 (82), 123.1 (88), 109.1 (7.8), 95.1 (67), 81.1 (100), 67.2 (31); Anal. Calcd. for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.52; N, 6.96; found: C, 59.77; H, 9.53; N, 7.00.



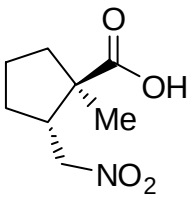
7e

(1S,2R)-1-butyl-2-(nitromethyl)cyclopentyl)methanol (**7e**) was isolated as a colorless oil (155 mg, 36 %) after reduction of **6e,** which was separated from the minor diastereomer after 4 d through flash chromatography (pentane:ether = 30:1). The *e.e.* (97 %) was determined by HPLC on a chiral stationary phase [Chiralcel OD, *n*-heptane:*i*PrOH = 95:5, 0.7 mL/min), t_R = 11.41 min (minor), 14.05 min (major)]. $[\alpha]_D^{20}$ = –13.9 (*c* = 1.3 in $CHCl_3$); IR (KBr): 3572 (m), 3375 (w), 2954 (vs), 2871 (s), 1550 (vs), 1463 (m), 1382 (s), 1046 (s), 467 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.70 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.45 (dd, *J* = 12.0, 11.2 Hz, 1 H), 3.47-3.42 (m, 2 H), 2.38-2.35 (m, 1 H), 1.94-1.88 (m, 1 H), 1.71-1.21 (m, 11 H), 0.95 ppm (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 78.3, 65.2, 48.2,

46.7, 36.0, 34.3, 30.1, 26.8, 23.5, 22.2, 14.1 ppm; MS (CI, CH_4): m/z (%): 216.1 (0.72) [M^++1], 198.1 (2.2), 185.2 (0.56), 167.1 (12), 151.1 (100), 109.1 (52), 95.1 (64), 81.1 (23), 67.2 (5.3); Anal. Calcd. for $C_{11}H_{21}NO_3$: C, 61.37; H, 9.83; N, 6.51; found: C, 61.35; H, 10.29; N, 6.87.

Synthesis of (1*R*,2*R*)-2-(nitromethyl)-1-methylcyclopentanecarboxylic acid (13)

To a sulotion of *(1R,2R)-1-methyl-2-(nitromethyl)cyclopentanecarbaldehyde* (*trans*-**6a**) (80 mg, 0.47 mmol) in H_2O/acetone (1:1, 3 mL) was added successively 2-methylbutene (0.9 mL, 8.43 mmol), KH_2PO_4 (121 mg, 0.89 mmol) and $NaClO_2$ (130 mg, 1.13 mmol) at 0 °C. The reaction mixture was stirred for 40 min at 0 °C. Organic materials were extracted three times with CH_2Cl_2, and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude procuct was purified by flash chromatography (pentane/ether = 4:1to 1:1) to afford the product as a colorless oil (77 mg, 88 %).

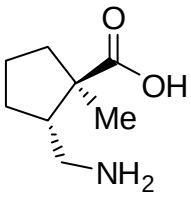


13

(*1R,2R)-2-(nitromethyl)-1-methylcyclopentanecarboxylic acid* (**13**): $[\alpha]_D^{20}$ = –14.4 (*c* = 0.85 in $CHCl_3$); IR (KBr): 3775 (m), 2960 (m), 2921 (m), 2878 (m), 2561 (w), 2296 (m), 1813 (m), 1700 (vs), 1553 (vs), 1435 (vs), 1383 (vs), 1288 (s), 1187 (s), 1151 (s), 1109 (w), 1074 (w), 1024 (m), 934 (vs), 719 (s), 669 (s), 547 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.65 (dd, *J* = 12.4, 5.6 Hz, 1 H), 4.27 (dd, *J* = 12.4, 10.0 Hz, 1 H), 3.10-3.02 (m, 1 H), 2.27-2.20 (m, 1 H), 2.11-2.02 (m, 1 H), 1.85-1.68 (m, 3 H), 1.59-1.49 (m, 1 H), 1.17 ppm (s, 3 H); ^{13}C NMR (101 MHz, D_2O): δ = 183.0, 77.0, 50.3, 44.1, 38.5, 28.7, 21.9, 18.1 ppm; MS (EI, 70 eV): *m/z* (%): 188.0 (0.35) [M^++1], 170.0 (4.6), 142.1 (1.9), 123.0 (2.9), 111.0 (2.3), 95.1 (100), 81.1 (12), 67.1 (22), 55.1 (16), 45.3 (30); HRMS (ESI-TOF): calcd. for for $C_8H_{13}NO_4$-OH: 170.081718, found: 170.081249.

Synthesis of (1*R*,2*R*)-2-(aminomethyl)-1-methylcyclopentanecarboxylic acid (14)

To a solution of (1*R*,2*R*)-2-(nitromethyl)-1-methylcyclopentanecarboxylic acid (**13**) (77 mg, 0.41 mmol) in MeOH (0.41 mL) was added 10 % Pd/C (23 mg) at room temperature and the reaction mixture was stirred for 48 h under H_2 atmosphere at room temperature. The Reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. The crude procuct was purified by flash chromatography (ether to methanol) to afford the product as a white solid (55 mg, 85 %).



14

(*1R,2R)-2-(aminomethyl)-1-methylcyclopentanecarboxylic acid* (**14**): IR (KBr): 3433 (vs), 2965 (vs), 2162 (s), 1639 (s), 1536 (vs), 1460 (m), 1386(m), 1208 (m), 1020 (m); ^{1}H NMR

(300 MHz, D_2O): δ = 2.77 (dd, *J* = 12.8, 7.6 Hz, 1 H), 2.65 (dd, *J* = 12.8, 6.8 Hz, 1 H), 2.09-1.97 (m, 1 H), 1.75-1.57 (m, 2 H), 1.47-1.16 (m, 3 H), 1.14-0.92 (m, 1 H), 0.76 ppm (s, 3 H); ^{13}C NMR (101 MHz, D_2O): δ = 186.6, 52.8, 43.6, 40.6, 38.8, 28.8, 21.4, 19.1 ppm; MS (EI, 70 eV): *m/z* (%): 158.1 (22), 157.1 (21) [M^+], 140.0 (5.0), 124.0 (2.3), 113.1 (5.9), 112.2 (5.7), 111.1(8.1), 110.0 (5.1), 96.1 (17), 95.1 (18), 83.0 (38), 81.1 (34), 67.1 (33), 56.1 (100); HRMS (ESI-TOF): calcd. for for $C_8H_{15}NO_2$: 157.110279, found: 157.110256.

[1] a) J. V. B. Kanth, M. Periasamy, *Tetrahedron* **1993**, *49*, 5127; b) D. Enders, H. Kipphardt, P. Gerdes, L. J. Breña-Valle, V. Bhushan, *Bull*. *Soc*. *Chim*. *Belg*. **1988**, *97*, 691.

[2] M. Marigo, T. Wabnitz, D. Fielenbach, K. A. Jørgensen, *Angew*. *Chem*. **2005**, *117*, 804; *Angew*. *Chem*. *Int*. *Ed*. **2005**, *44*, 794.

[3] D. Enders, H. J. Scherer, J. Runsink, *Chem*. *Ber*. **1993**, *126*, 1929.

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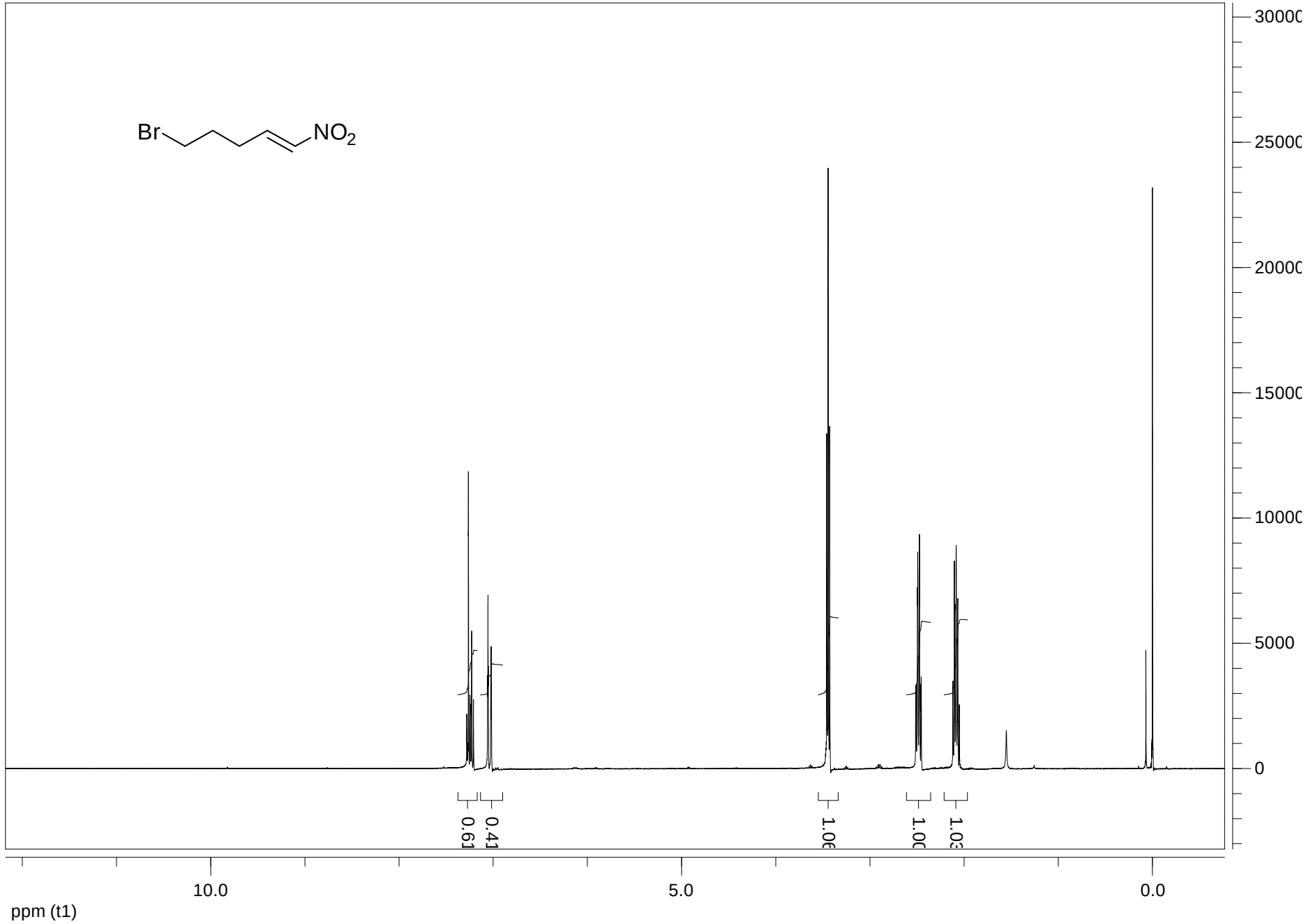


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-5-bromo-1-nitropent-1-ene.

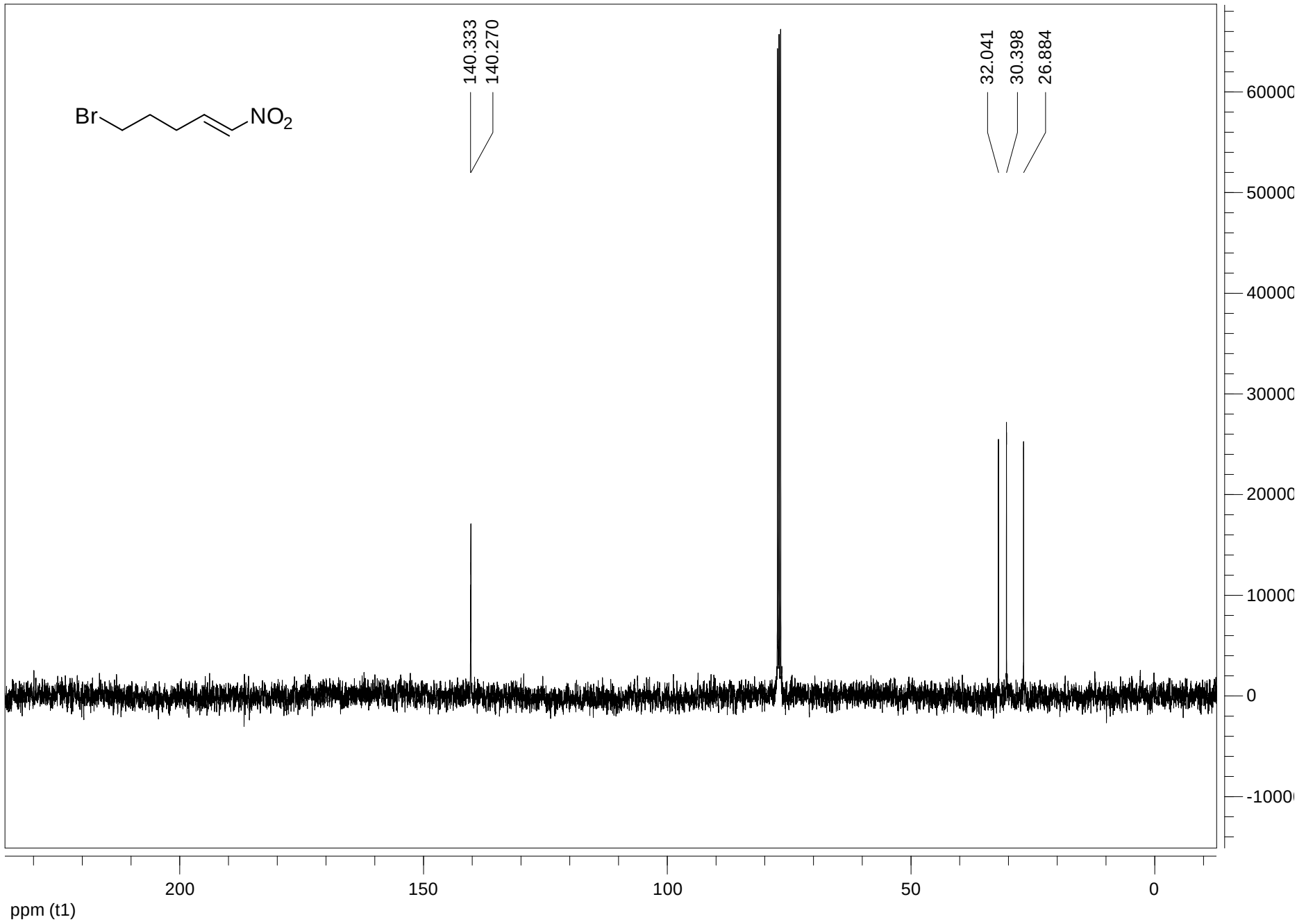


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of (*E*)-5-bromo-1-nitropent-1-ene

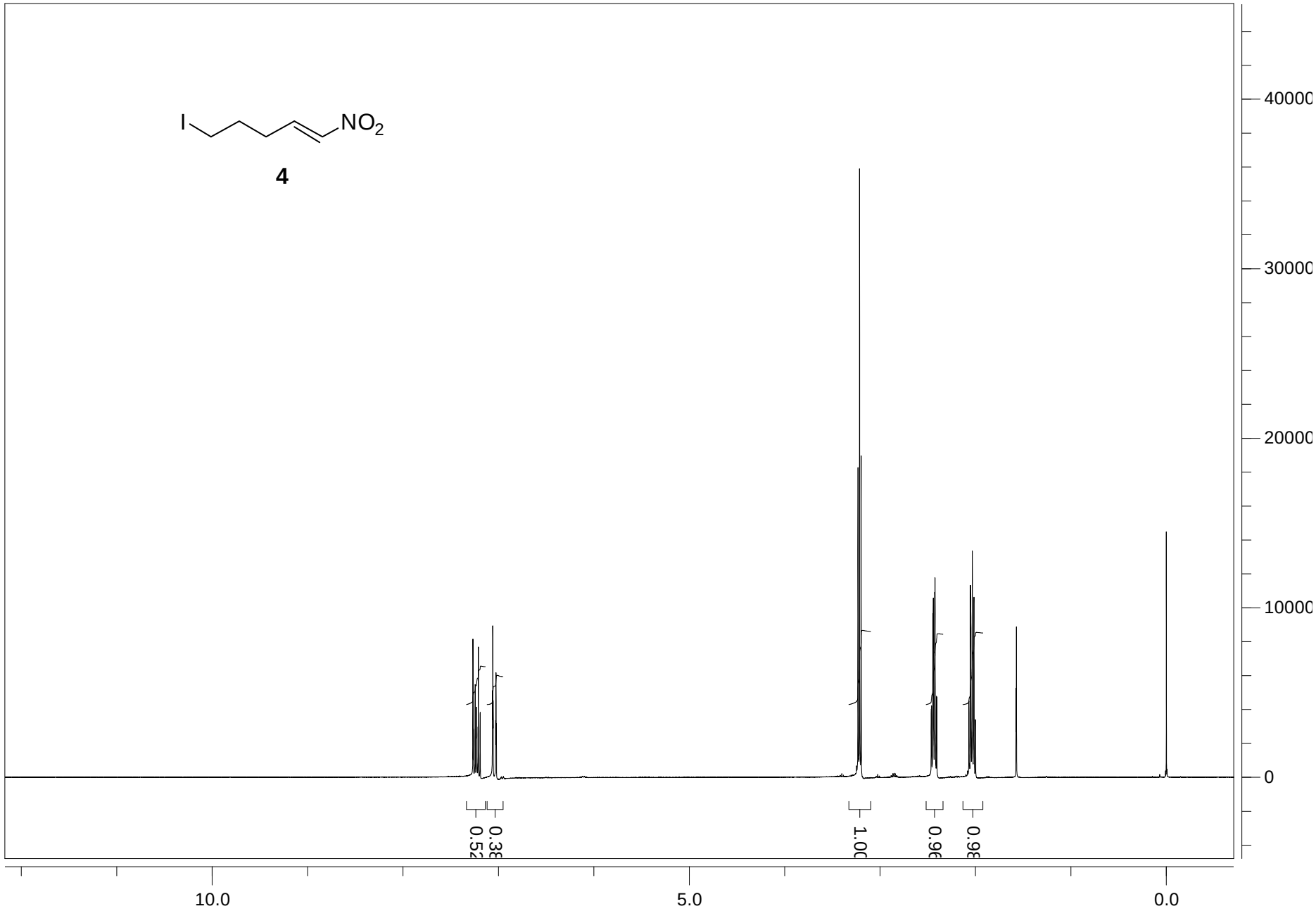


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-5-iodo-1-nitropent-1-ene (**4**)

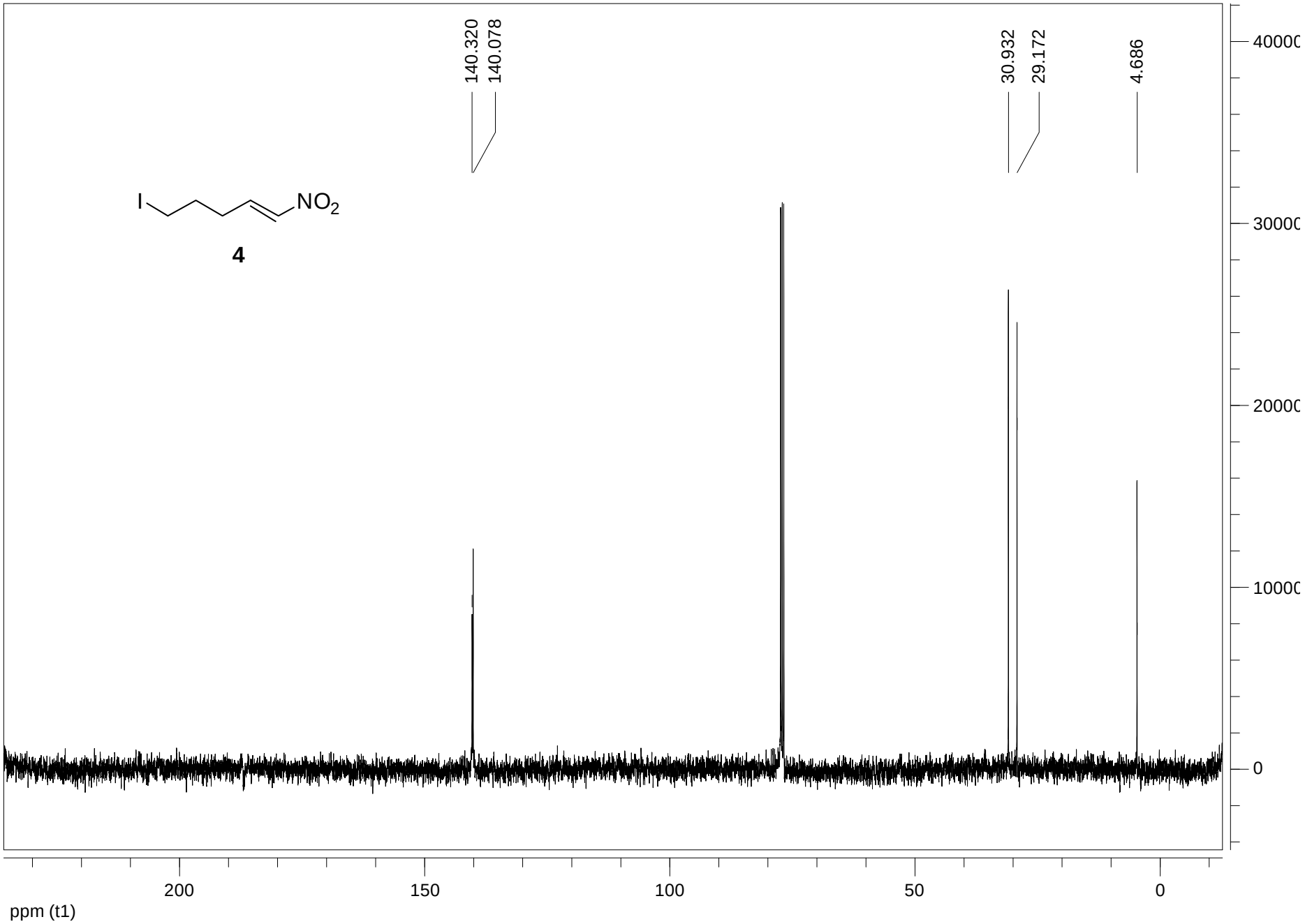


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of (*E*)-5-iodo-1-nitropent-1-ene (**4**)

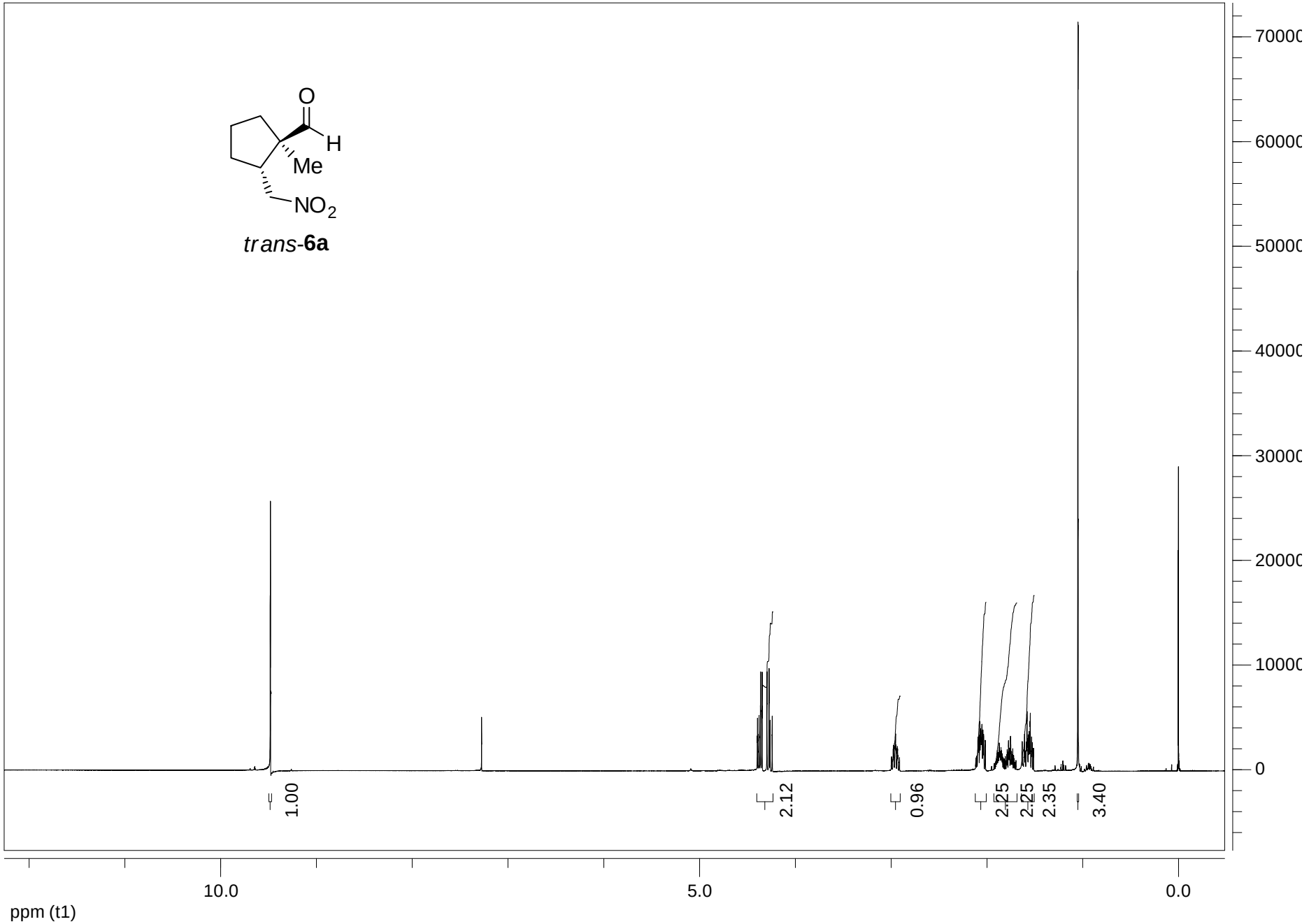


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (1*R*,2*R*)-1-methyl-2-(nitromethyl)cyclopentanecarbaldehyde (*trans*-**6a**)

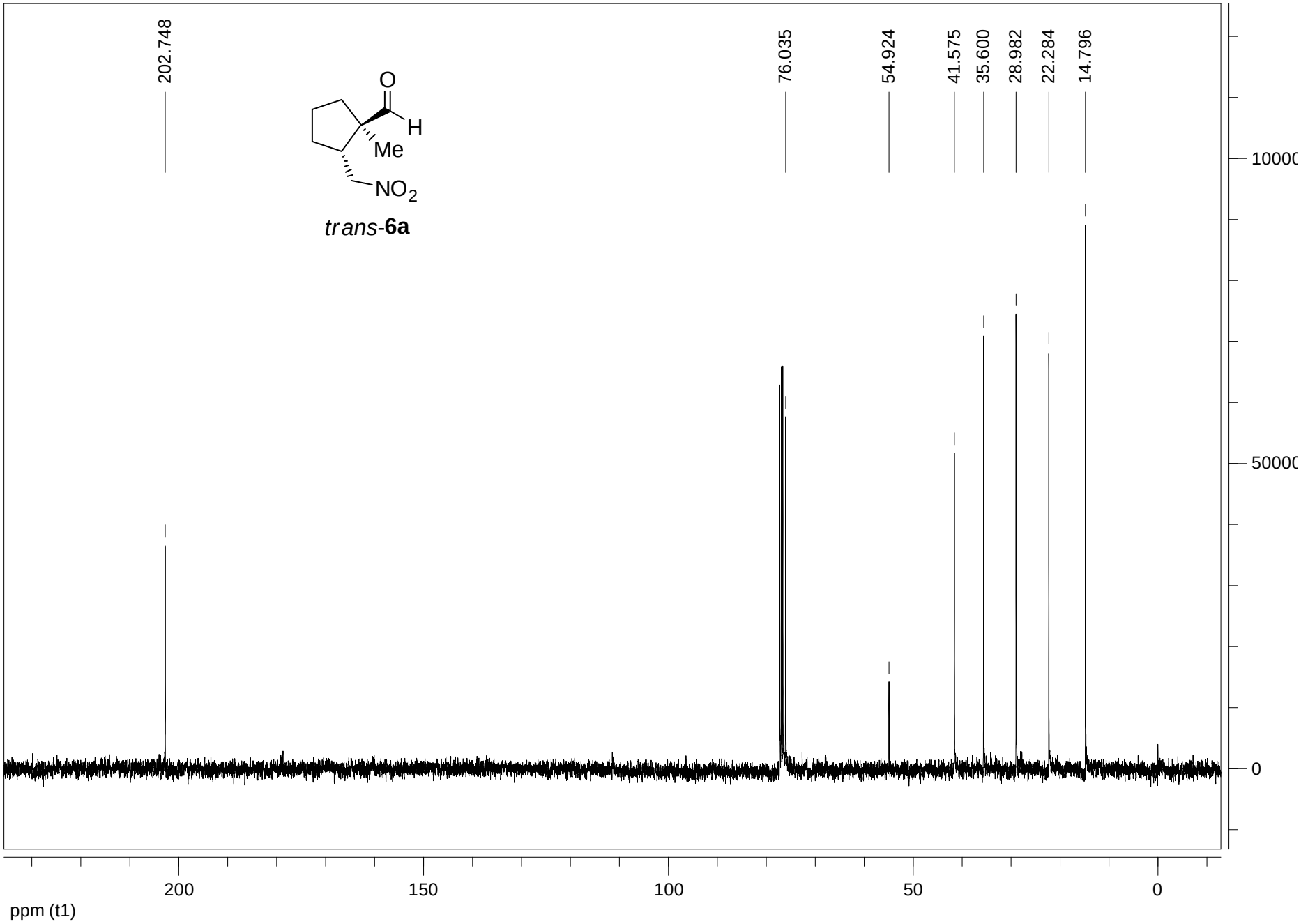
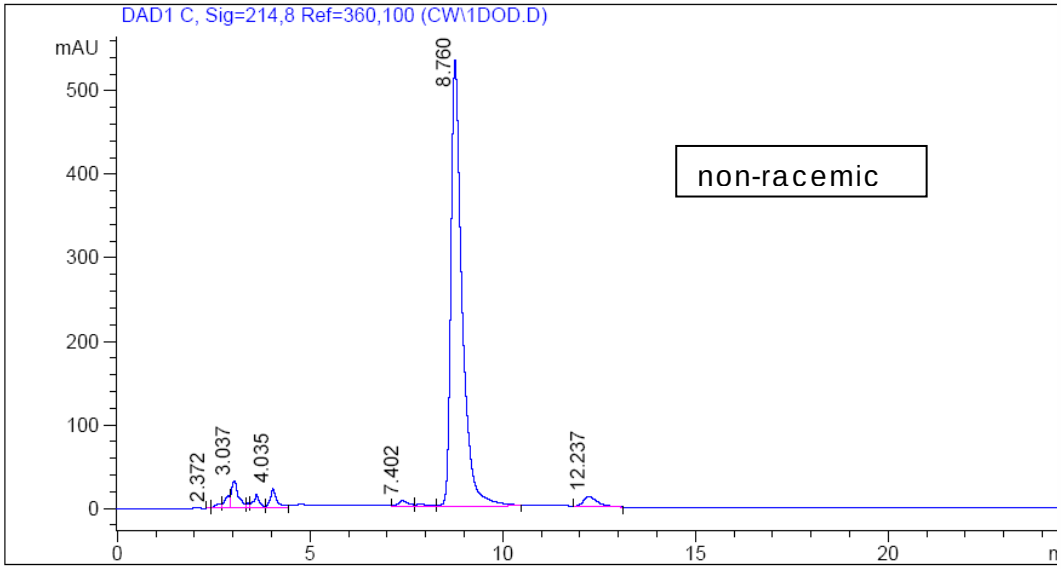
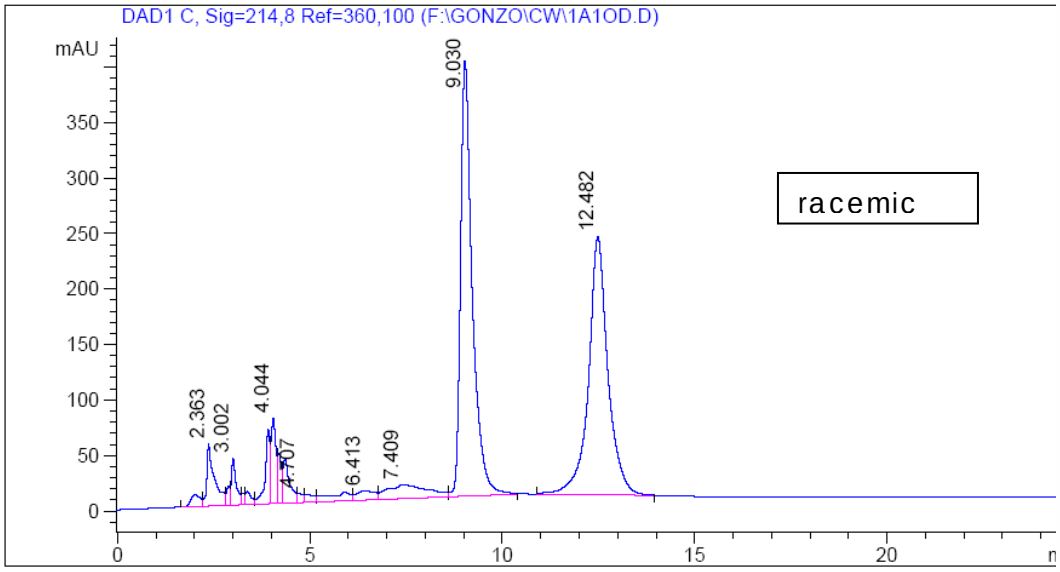


Figure S6. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (1*R*,2*R*)-1-methyl-2-(nitromethyl)cyclopentanecarbaldehyde (*trans*-**6a**)





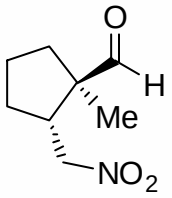
AK Enders - Analytische HPLC

Sample Name: CW 1d
Data file: D:\GONZO\CW\1DOD.D
Sample Info: Laufmittel: n-Heptan/IP 9:1;
Probe im LM gelöst

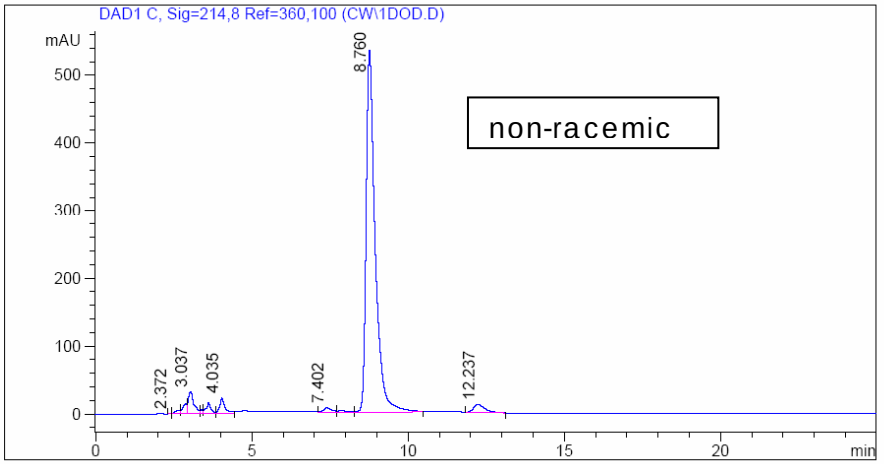
Säule: DAICELOD.M
Säuleninfo: (250x4)mm
Operator: Analytik Labor AKEN

Injektion Time: 13:48:14
Injektion Date: 02.04.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	37.3	38.3
Flow in ml/min:	1.2	1.2



trans-**6a**



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	2.37	0.07	1.04	4.82	0.04
2	2.68	0.17	5.38	65.01	0.53
3	2.88	0.13	14.52	125.33	1.02
4	3.04	0.19	31.94	408.42	3.31
5	3.40	0.08	5.67	31.11	0.25
6	3.61	0.15	15.47	169.66	1.37
7	4.03	0.17	22.76	278.71	2.26
8	7.40	0.27	7.23	141.13	1.14
9	7.87	0.34	2.70	70.51	0.57
10	8.76	0.29	534.63	10733.70	86.98
11	12.24	0.38	12.22	311.92	2.53
Total				12340.32	100.00

Figure S7. HPLC traces of *trans*-**6a**; overlay of racemic and non-racemic (left), non-racemic (right)

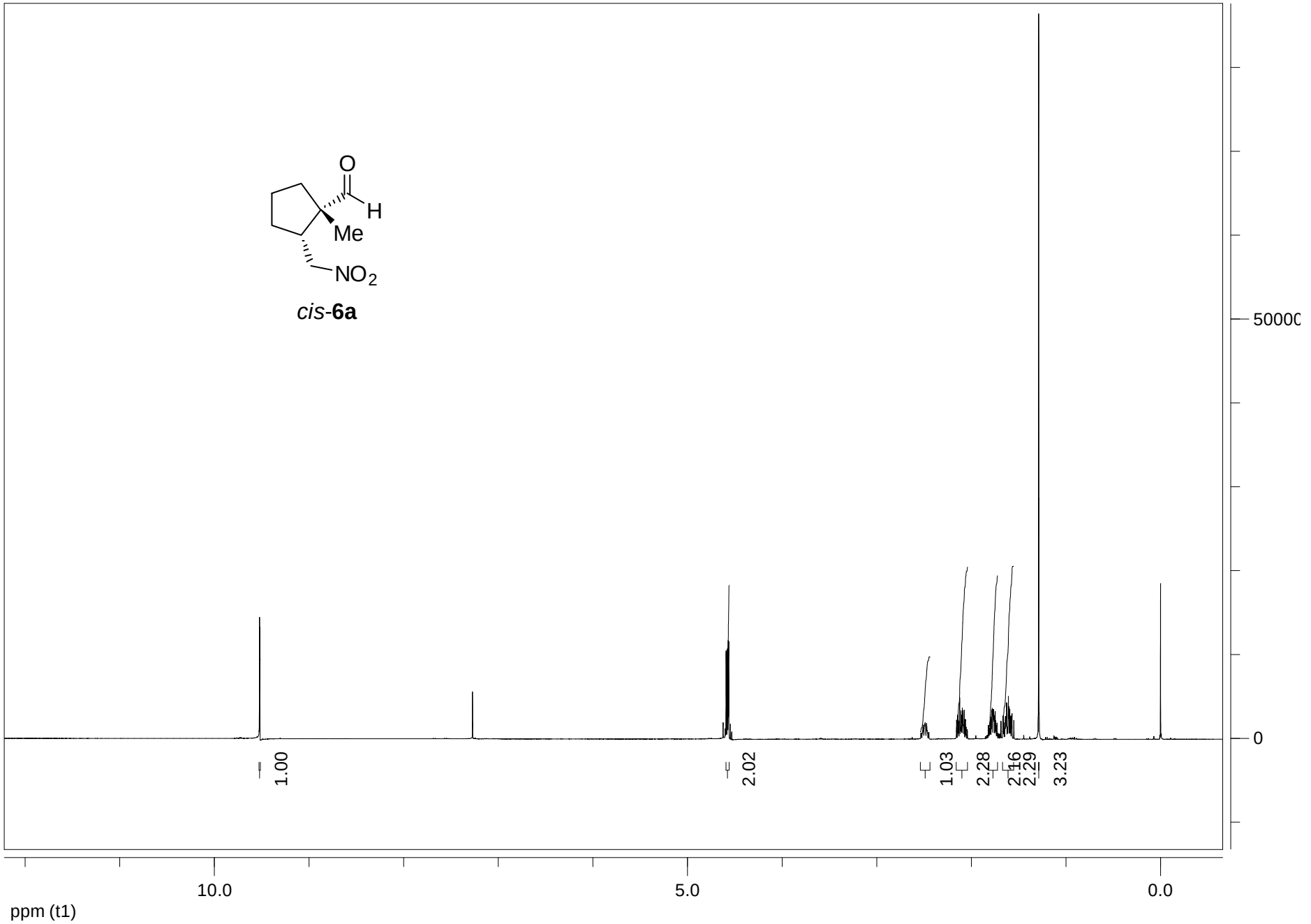


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (1*S*,2*R*)-1-methyl-2-(nitromethyl)cyclopentanecarbaldehyde (*cis*-**6a**).

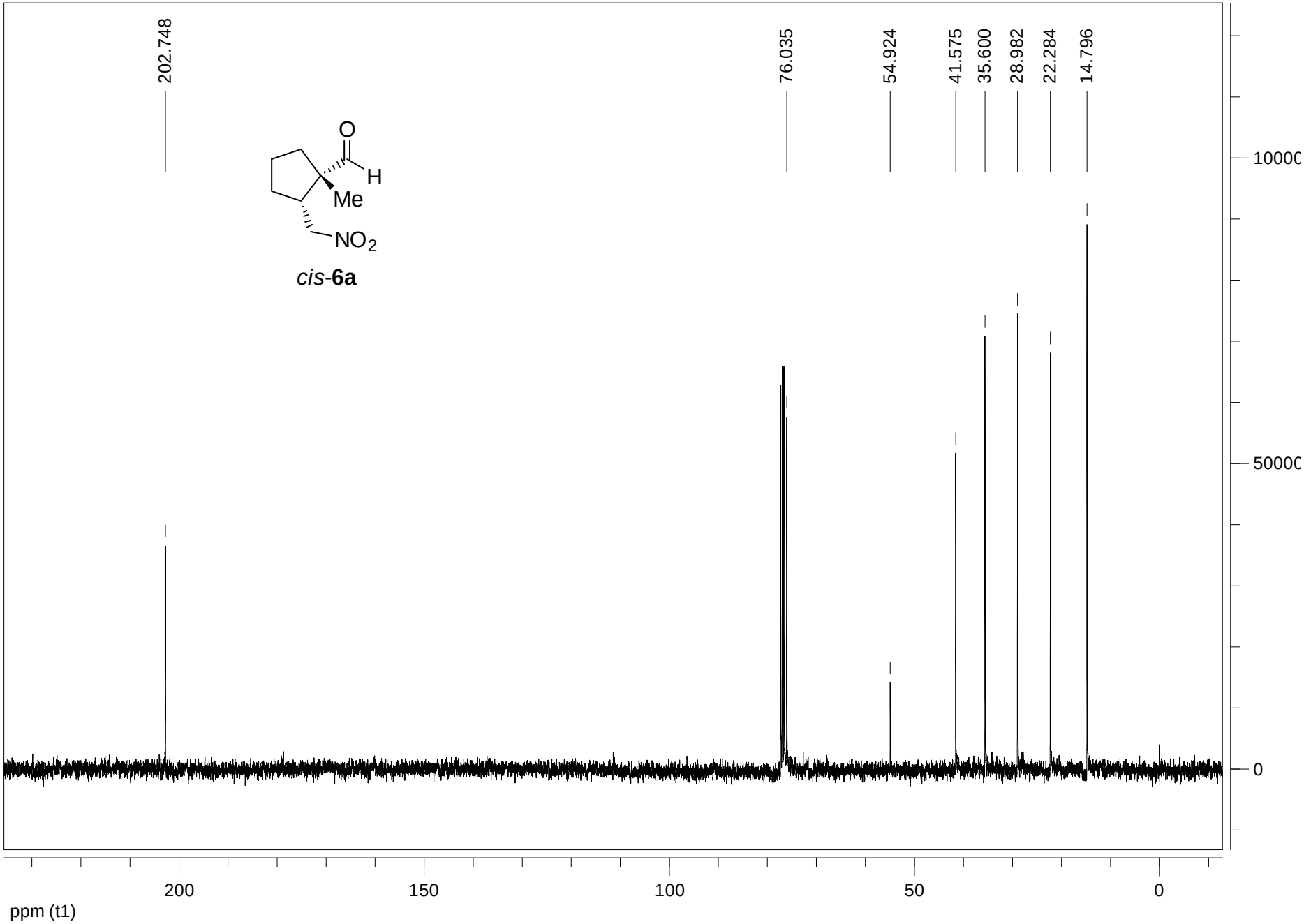
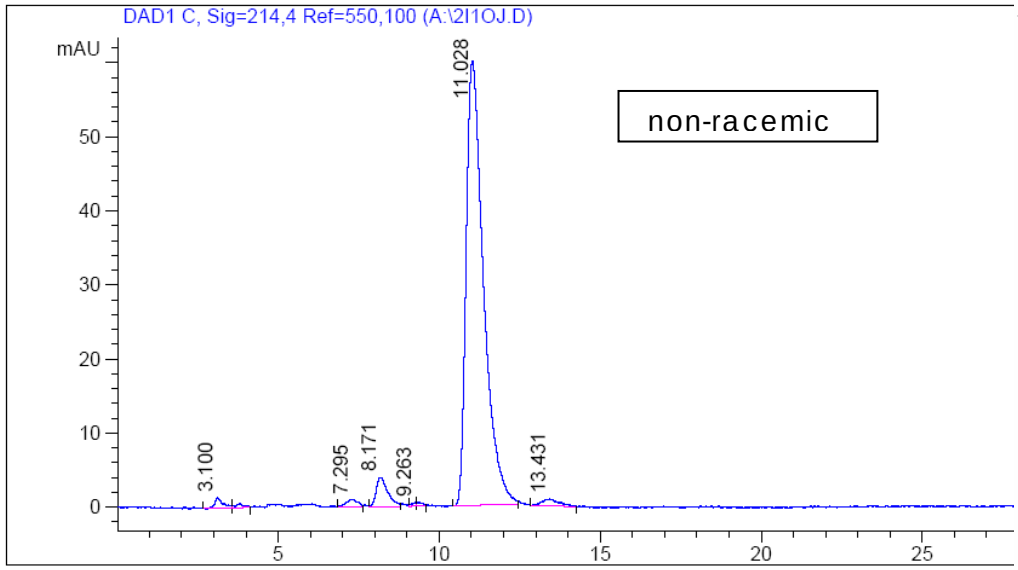
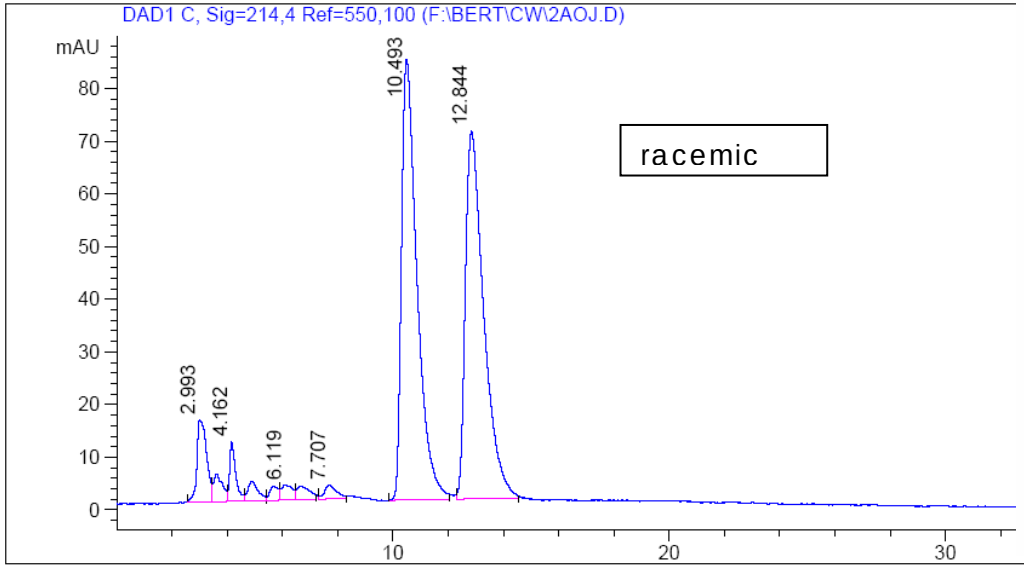


Figure S9. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (1*S*,2*R*)-1-methyl-2-(nitromethyl)cyclopentanecarbaldehyde (*cis*-**6a**)





AK Enders - Analytische HPLC

Sample Name: CW 2 i1
Data file: A:\2I1OJ.D
Sample Info: Laufmittel:n-Heptan/IP 9:1;
Probe im LM gelöst

Säule: DAICELOJ.M
Säuleninfo: (250x4)mm
Operator: Analytik Labor AKEN

Injektion Time: 15:37:50
Injektion Date: 05.05.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	0.0°C	0.0°C
Pressure in bar:	36.4	36.4
Flow in ml/min:	1.0	1.0

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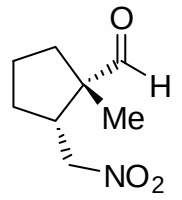
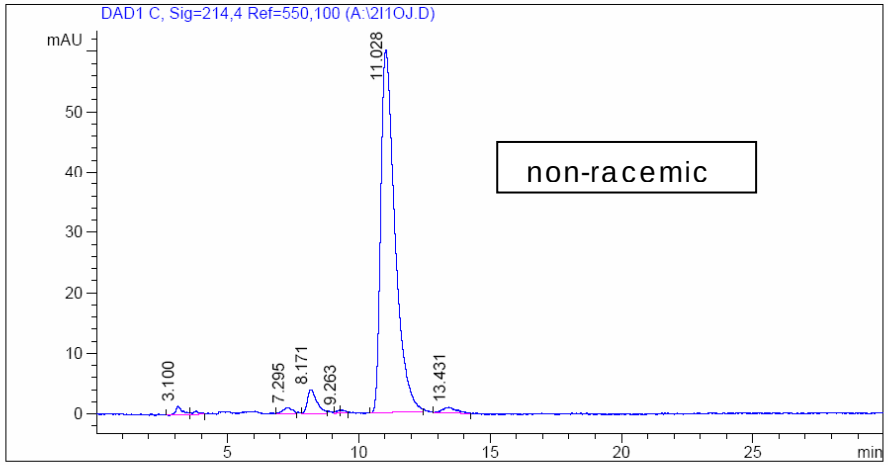


cis-**6a**



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.10	0.20	1.39	22.74	0.93
2	3.79	0.23	0.54	9.54	0.39
3	7.30	0.28	1.00	23.46	0.96
4	8.17	0.32	3.92	98.29	4.02
5	9.26	0.11	0.56	4.88	0.20
6	9.32	0.21	0.54	6.67	0.27
7	11.03	0.53	60.08	2244.49	91.80
8	13.43	0.43	0.96	34.90	1.43
Total				2444.97	100.00

Figure S10. HPLC traces of *cis*-**6a**; overlay of racemic and non-racemic (left), non-racemic (right)

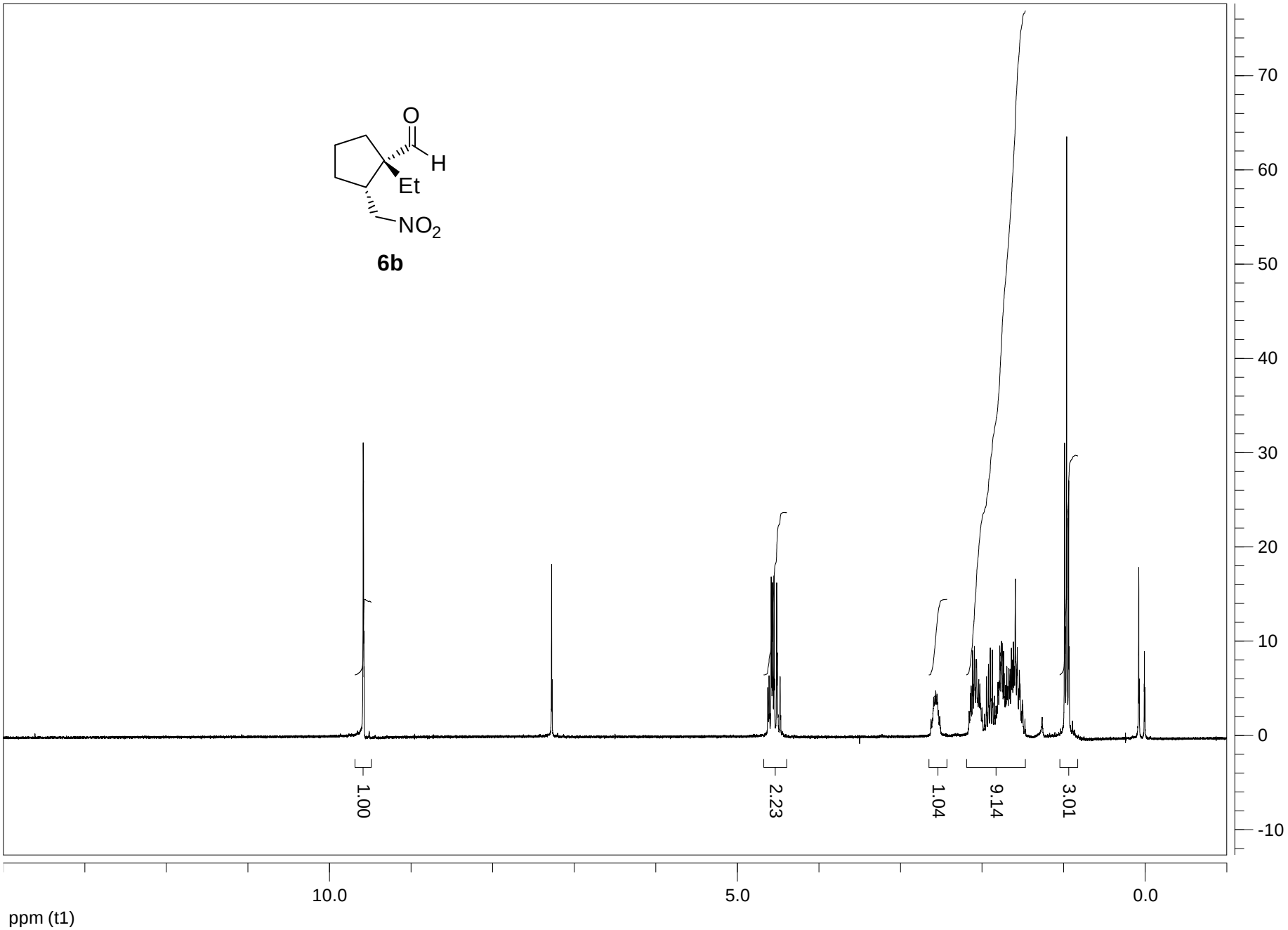


Figure S11. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (1*S*,2*R*)-1-ethyl-2-(nitromethyl)cyclopentanecarbaldehyde (**6b**).

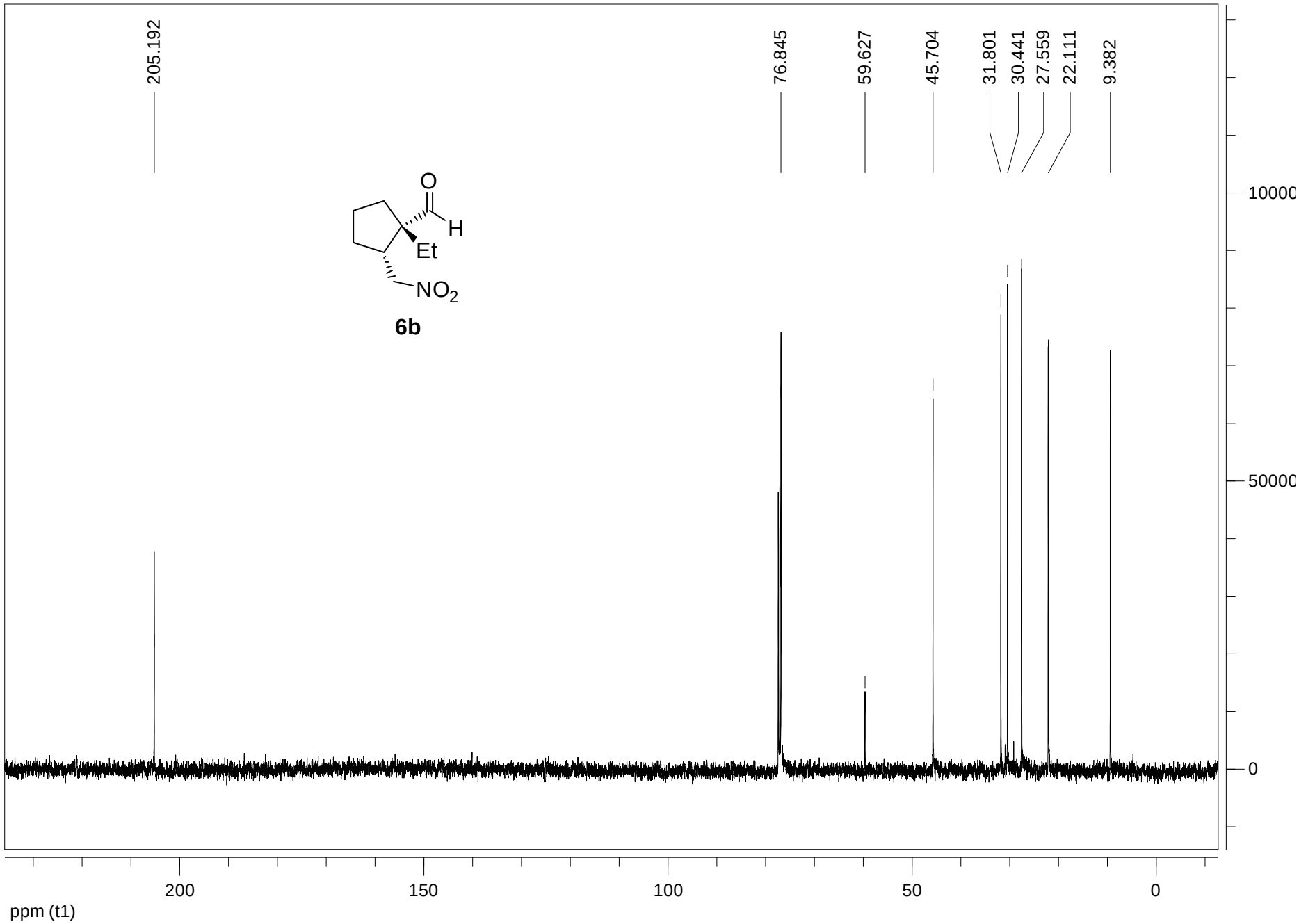
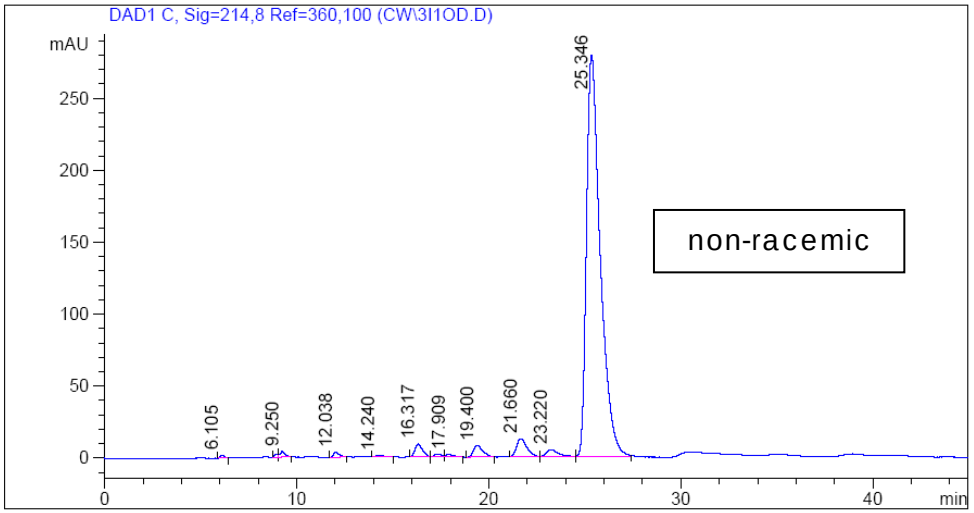
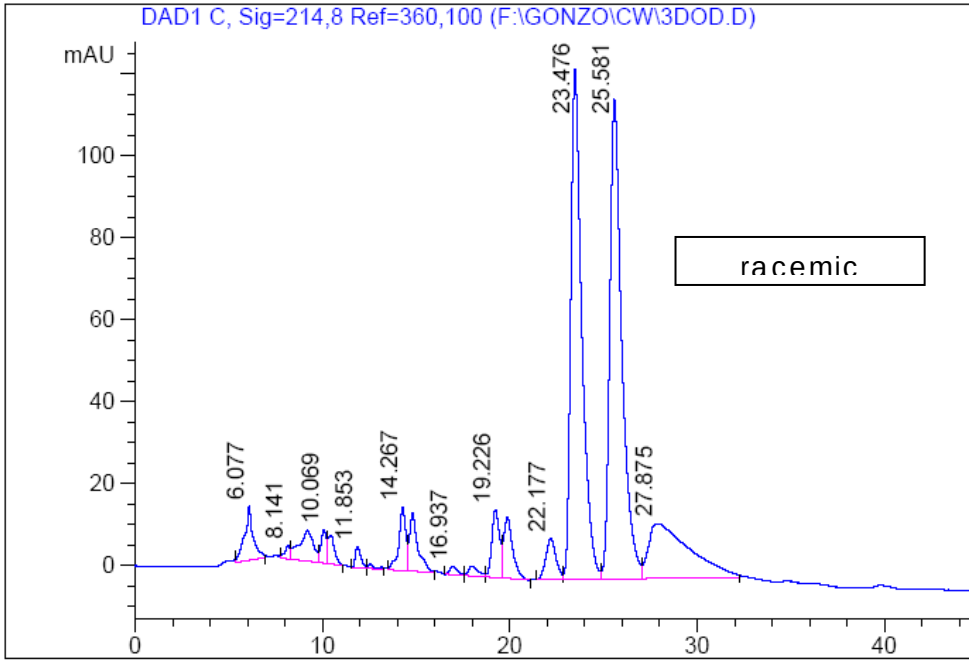


Figure S12. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (1*S*,2*R*)-1-ethyl-2-(nitromethyl)cyclopentanecarbaldehyde (**6b**)





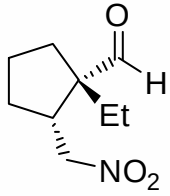
AK Enders - Analytische HPLC

Sample Name: CW 3 i1
Data file: D:\GONZO\CW\3I1OD.D
Sample Info: Laufmittel: n-Heptan/IP 97:3
Probe im LM gelöst

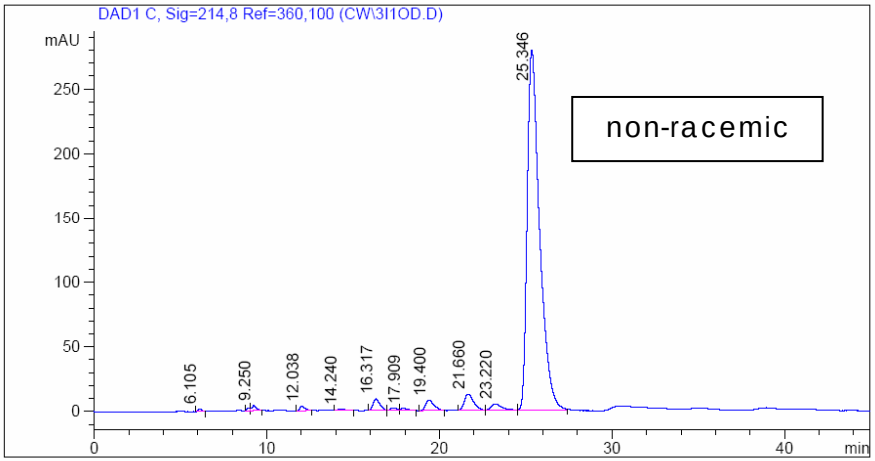
Säule: DAICELOD.M
Säuleninfo: (250x4)mm
Operator: Analytik Labor AKEN

Injektion Time: 08:43:34
Injektion Date: 05.05.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	13.8	14.1
Flow in ml/min:	0.5	0.5



6b



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.11	0.19	2.21	28.03	0.18
2	8.93	0.21	2.24	29.42	0.19
3	9.25	0.26	4.10	77.48	0.50
4	12.04	0.32	3.41	75.59	0.49
5	14.24	0.42	1.15	35.76	0.23
6	16.32	0.42	9.03	258.13	1.67
7	17.33	0.34	2.16	55.60	0.36
8	17.91	0.40	1.77	58.45	0.38
9	19.40	0.52	8.01	273.19	1.77
10	21.66	0.54	12.76	476.25	3.08
11	23.22	0.59	5.00	220.27	1.42
12	25.35	0.73	279.23	13888.12	89.74
Total				15476.28	100.00

Figure S13. HPLC traces of **6b**; overlay of racemic and non-racemic (left), non-racemic (right)

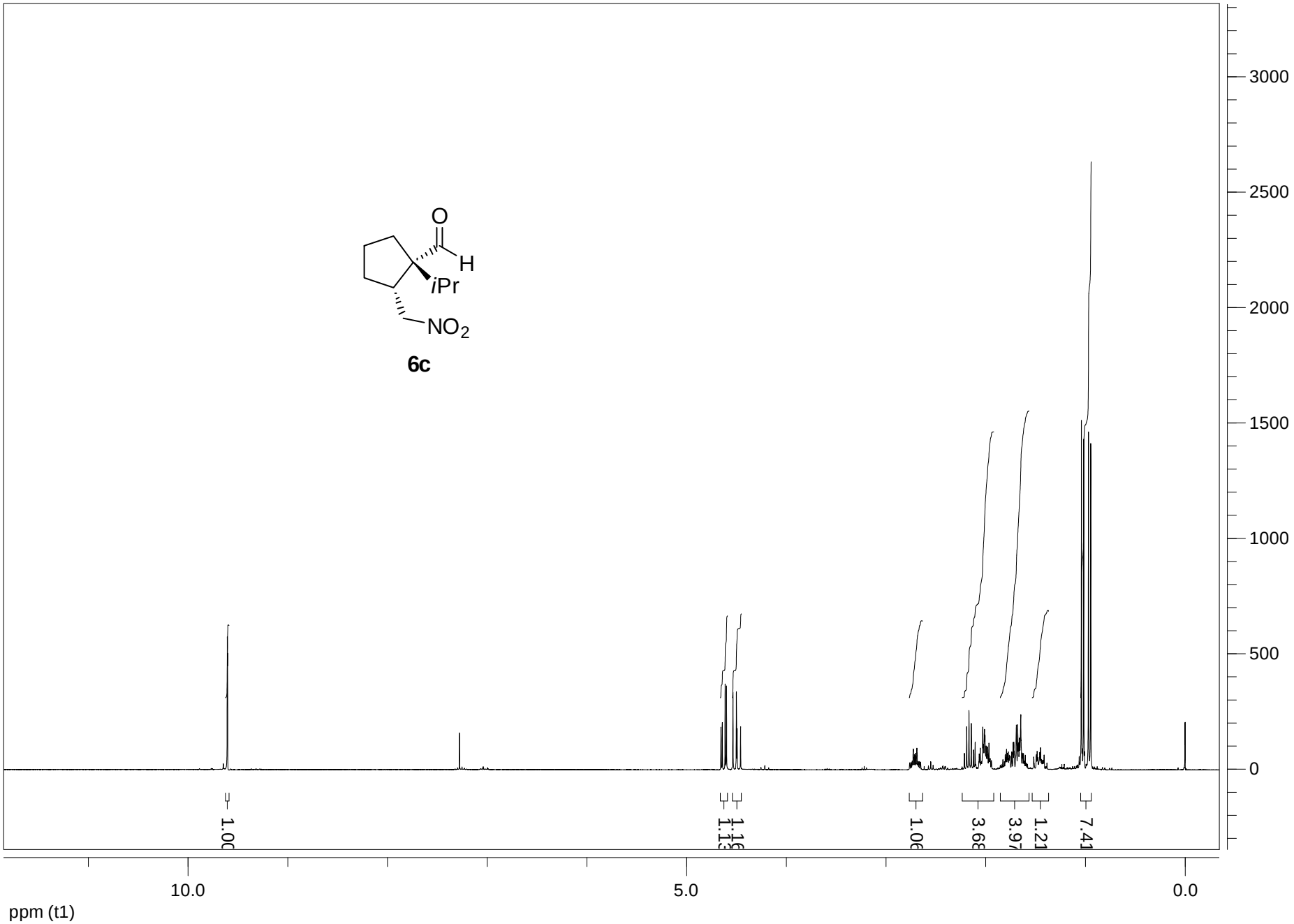


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (1*S*,2*R*)-1-isopropyl-2-(nitromethyl)cyclopentanecarbaldehyde (**6c**).

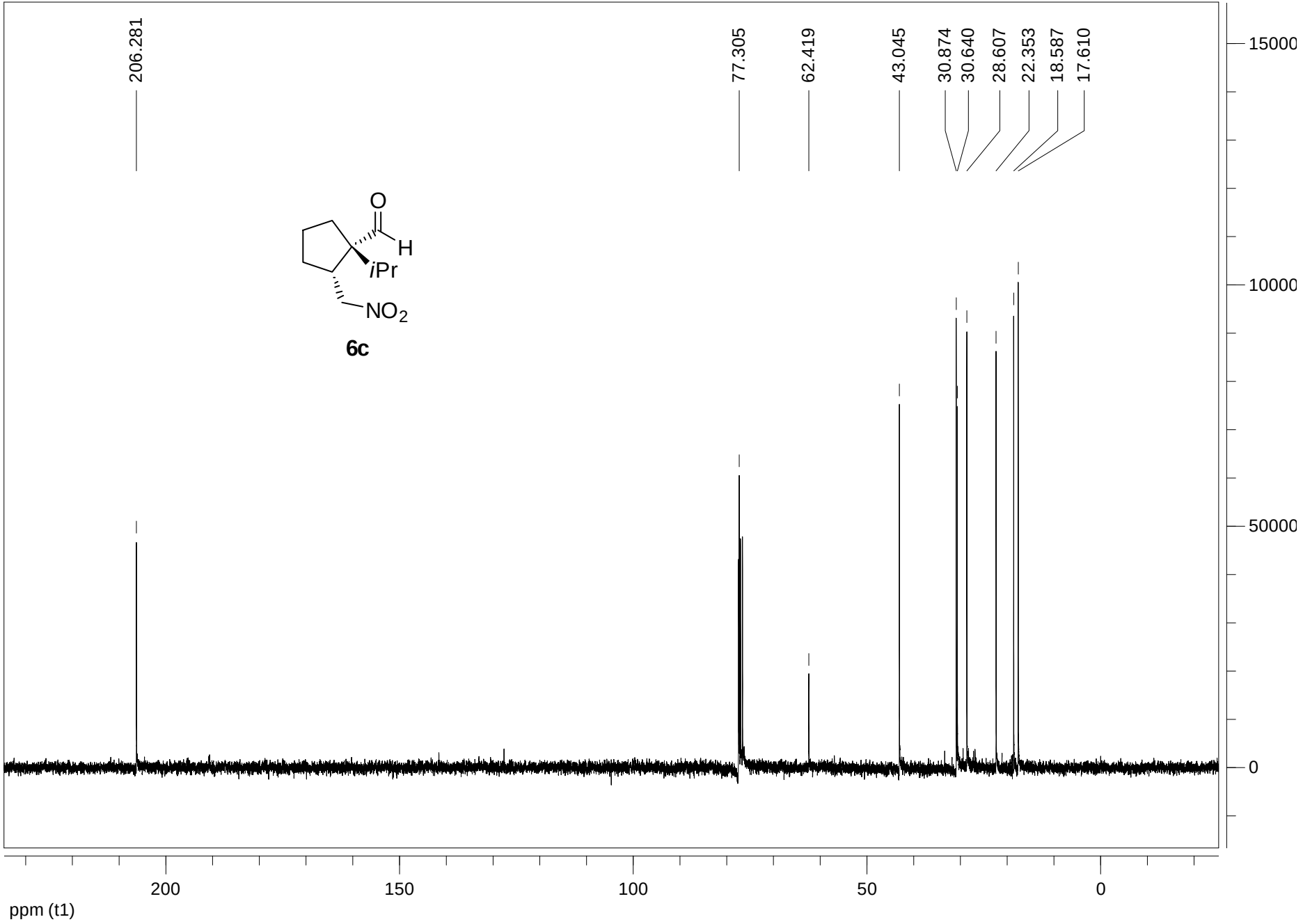
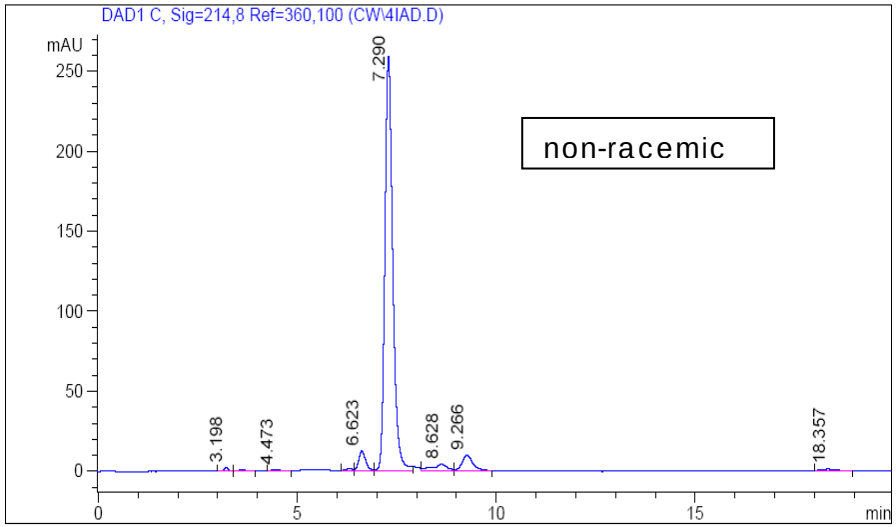
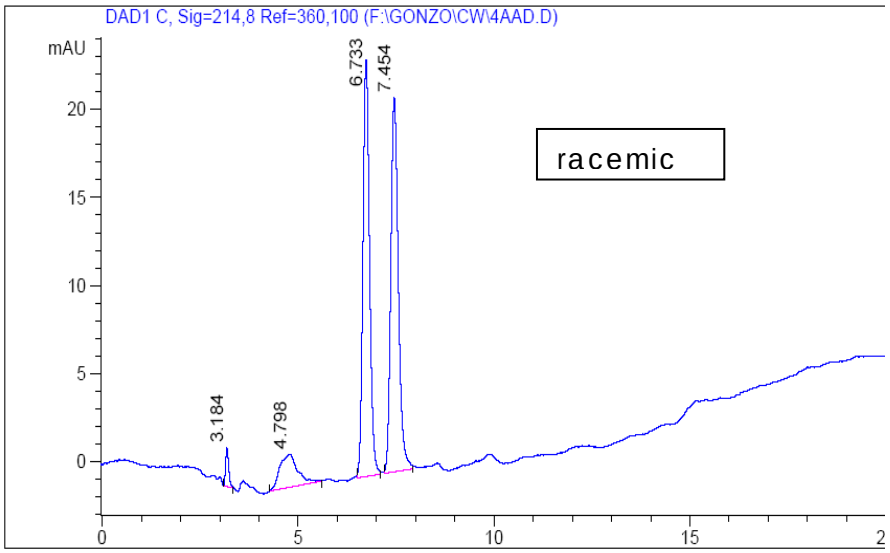


Figure S15. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (1*S*,2*R*)-1-isopropyl-2-(nitromethyl)cyclopentanecarbaldehyde (**6c**)





AK Enders - Analytische HPLC

Sample Name: CW 4i
Data file: D:\GONZO\CW\4IAD.D
Sample Info: Laufmittel: n-Heptan/IP 97:3;
Probe im LM gelöst

Säule: DAICELAD.M
Säuleninfo: (250x4)mm
Operator: Analytik Labor AKEN

Injektion Time: 15:42:27
Injektion Date: 07.05.2008

Instrument Conditions:	At Start	At Stop
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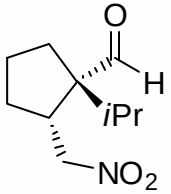
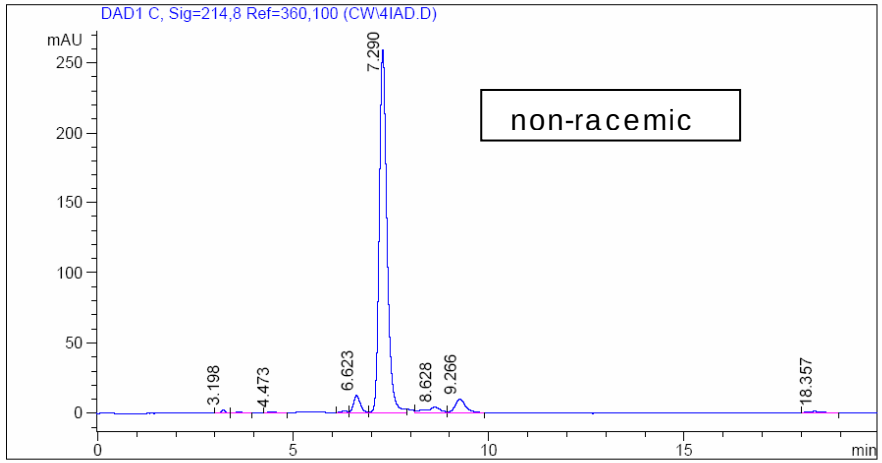
Pressure in bar:	26.8	26.9
Flow in ml/min:	1.0	1.0



6c



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.20	0.11	2.23	16.28	0.40
2	3.63	0.14	0.69	7.85	0.19
3	4.47	0.17	0.84	9.81	0.24
4	6.31	0.15	1.24	12.40	0.31
5	6.62	0.18	12.26	146.24	3.60
6	7.29	0.21	258.95	3548.33	87.38
7	8.63	0.36	3.91	103.40	2.55
8	9.27	0.29	9.52	182.81	4.50
9	18.36	0.36	1.14	33.54	0.83
Total				4060.65	100.00

Figure S16. HPLC traces of **6c**; overlay of racemic and non-racemic (left), non-racemic (right)

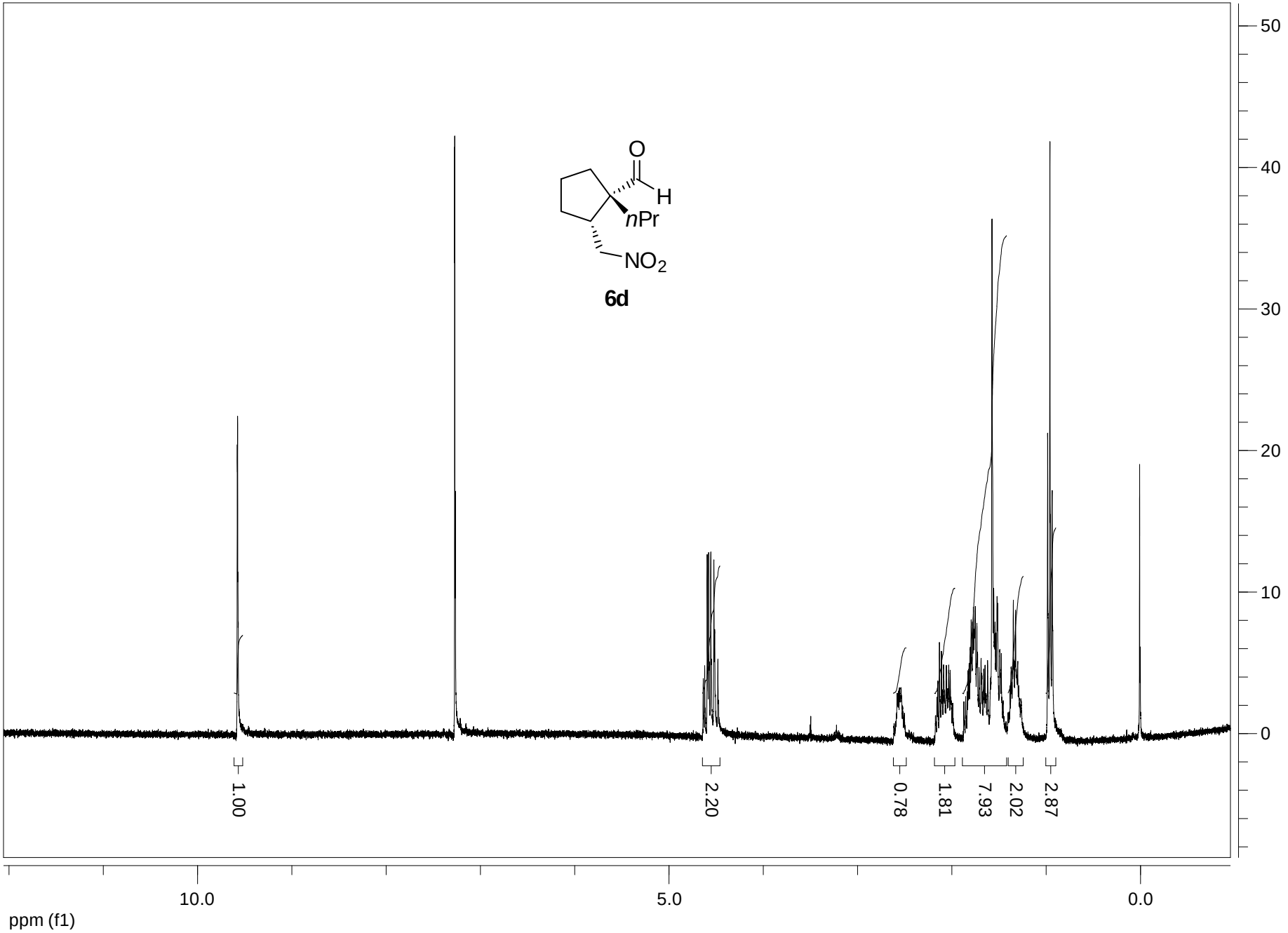


Figure S17. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (1*S*,2*R*)-1-propyl-2-(nitromethyl)cyclopentanecarbaldehyde (**6d**).

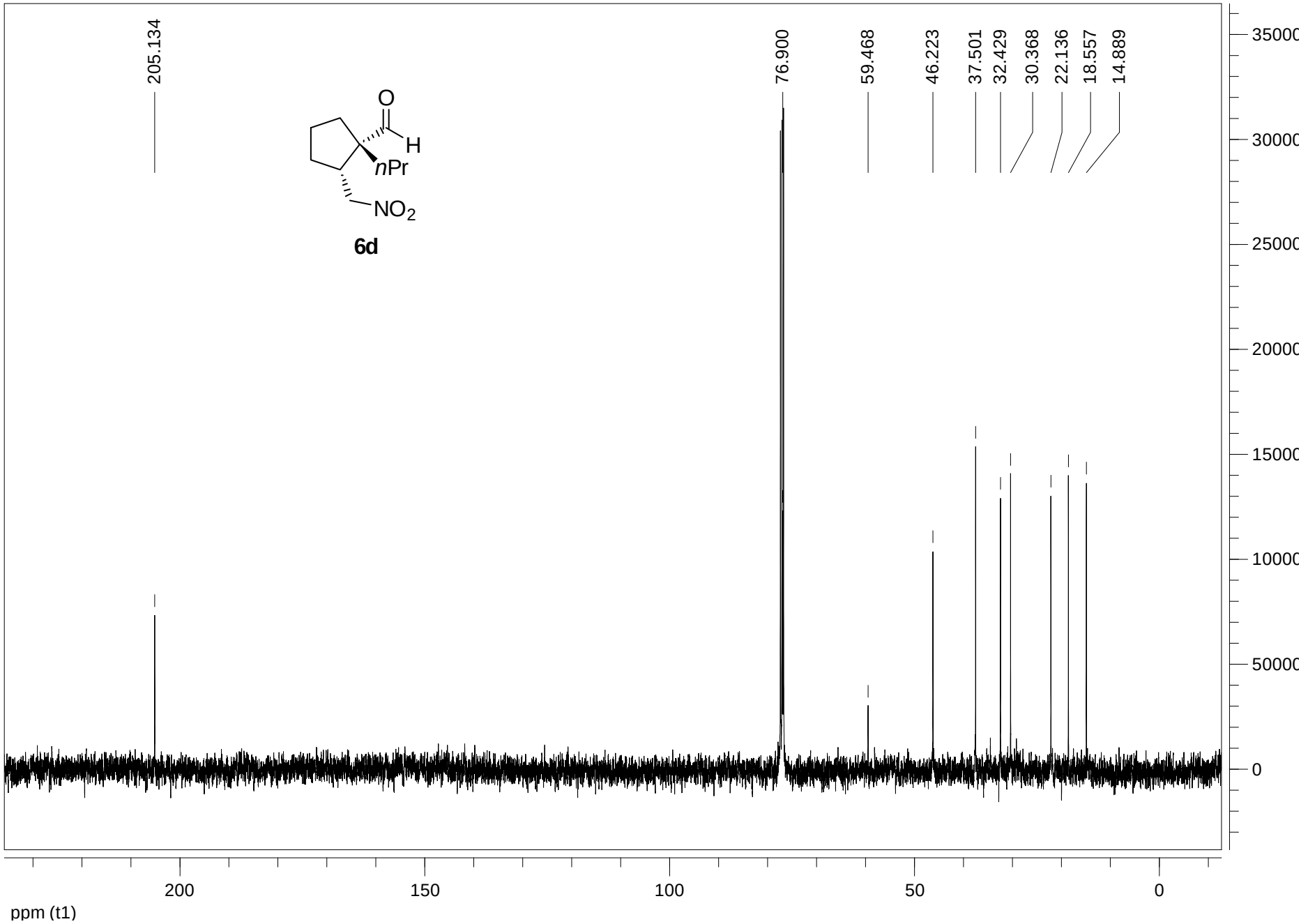
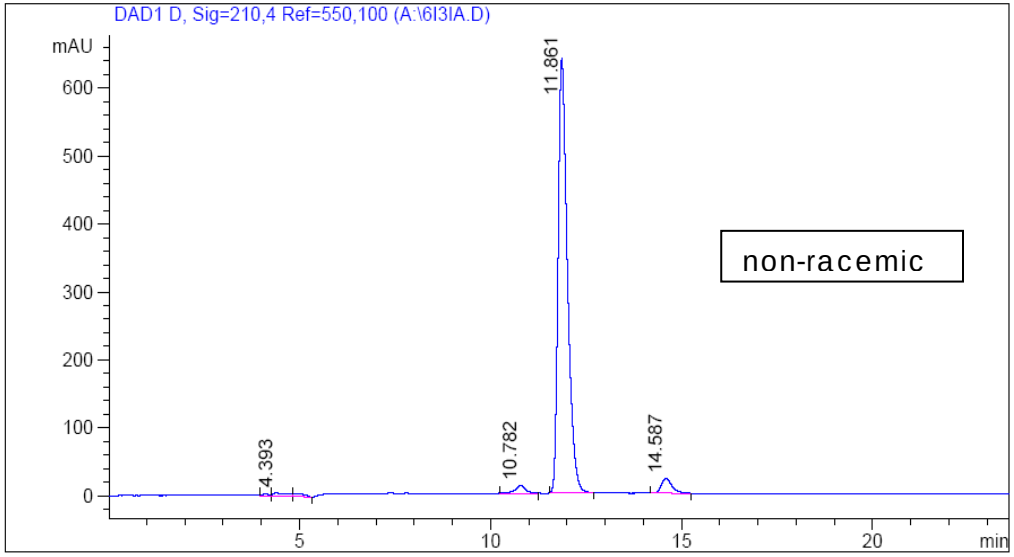
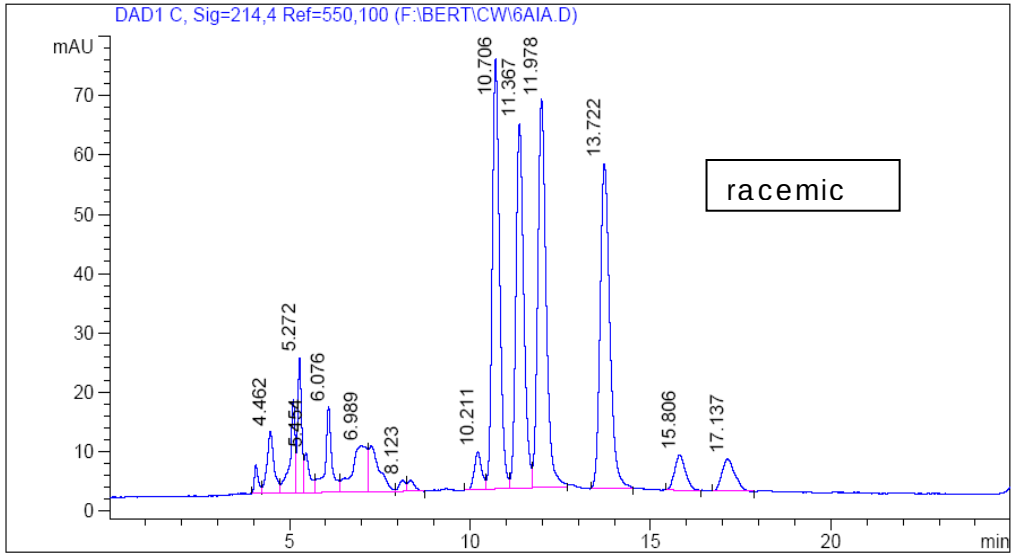


Figure S18. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (1*S*,2*R*)-1-isopropyl-2-(nitromethyl)cyclopentanecarbaldehyde (**6d**).



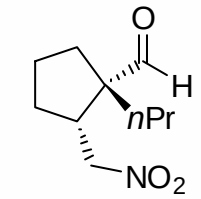


Sample Name: CW 6i3
Data file: A:\6I3IA.D
Sample Info: Laufmittel:n-Heptan/IP 97:3; Probe im LM gelöst

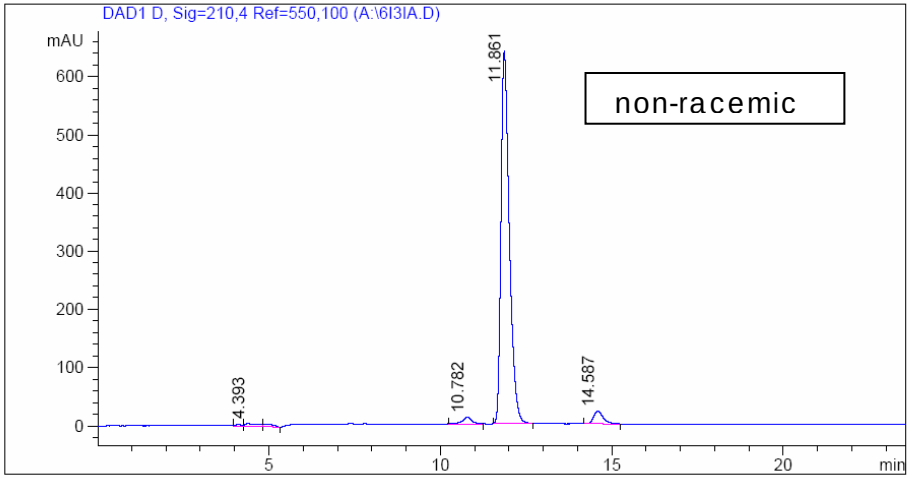
Säule: DAICELIA.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Injektion Time: 15:35:37
Injektion Date: 16.05.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	0.0°C	0.0°C
Pressure in bar:	32.2	32.2
Flow in ml/min:	0.7	0.7



6d



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.09	0.17	2.85	35.75	0.31
2	4.39	0.30	5.01	116.85	1.00
3	4.93	0.24	4.85	88.29	0.75
4	10.78	0.27	11.75	221.70	1.90
5	11.86	0.26	640.53	10808.40	92.42
6	14.59	0.28	21.42	423.67	3.62
Total				11694.66	100.00

Figure S19. HPLC traces of **6d**; overlay of racemic (two diastereomers) and non-racemic (left), non-racemic (right)

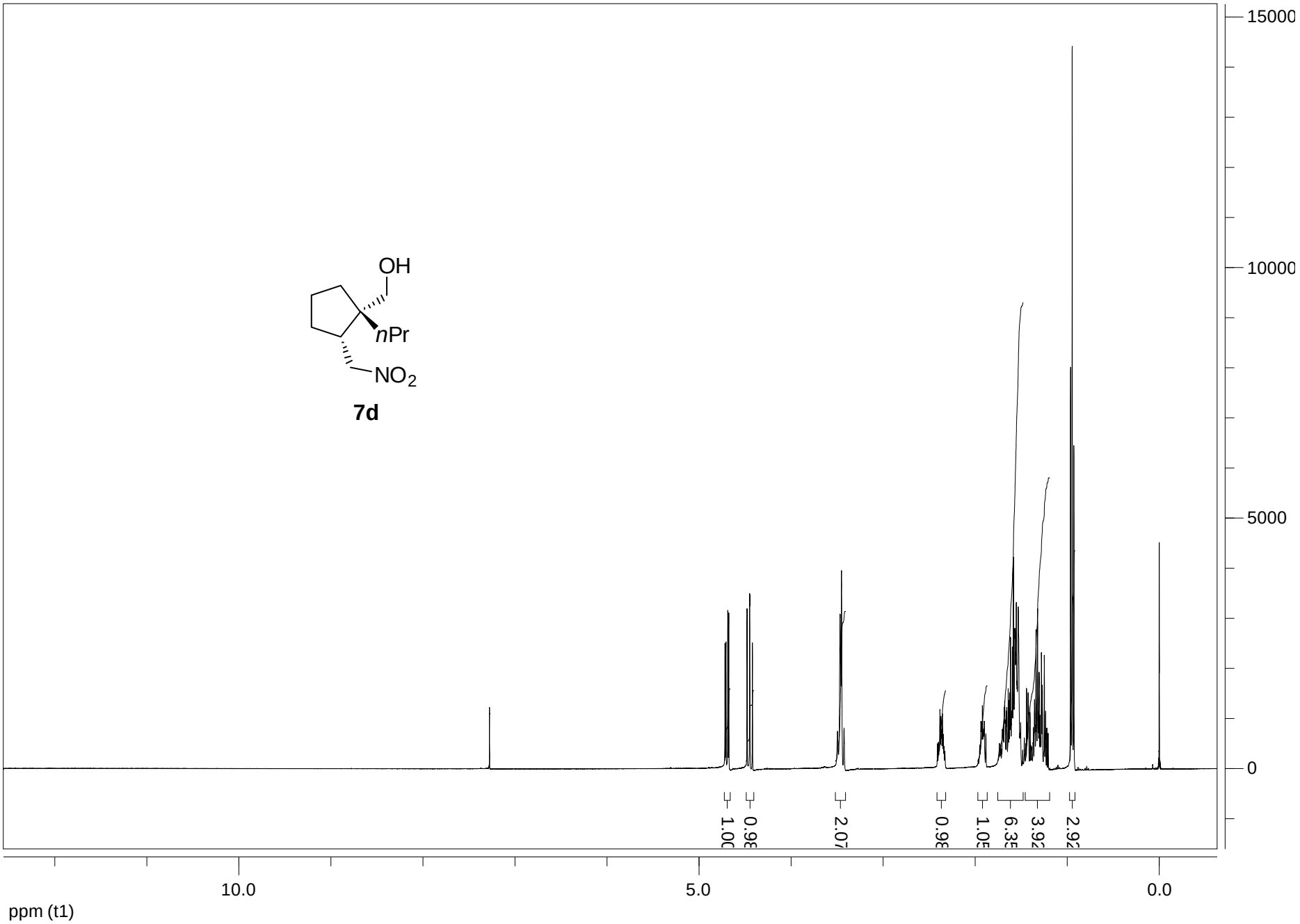


Figure S20. ^{1}H NMR spectrum 300 MHz, $CDCl_3$) of (1*S*,2*R*)-1-propyl-2-(nitromethyl)cyclopentyl)methanol (**7d**)

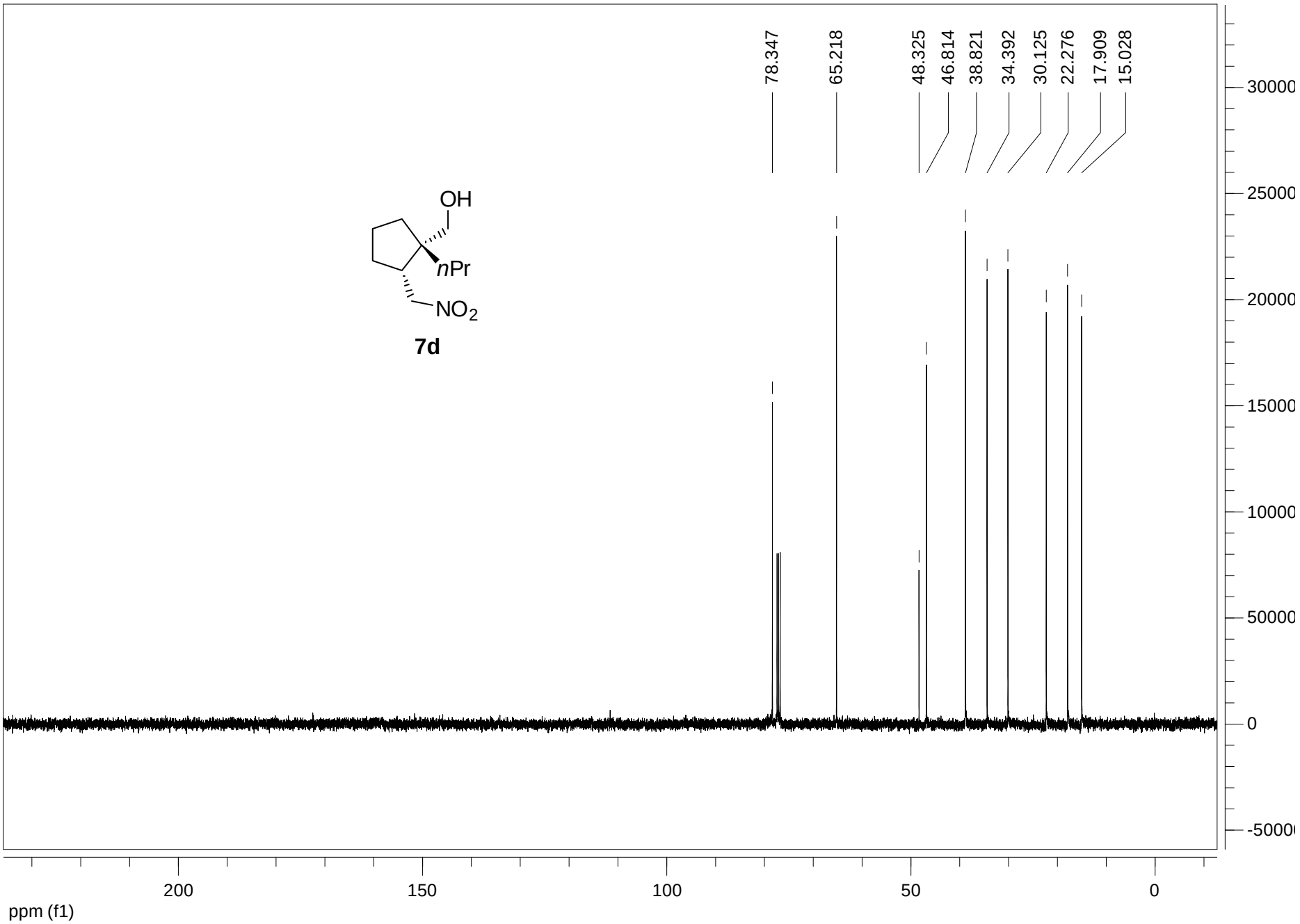


Figure S21. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of (1*S*,2*R*)-1-propyl-2-(nitromethyl)cyclopentyl)methanol (**7d**)

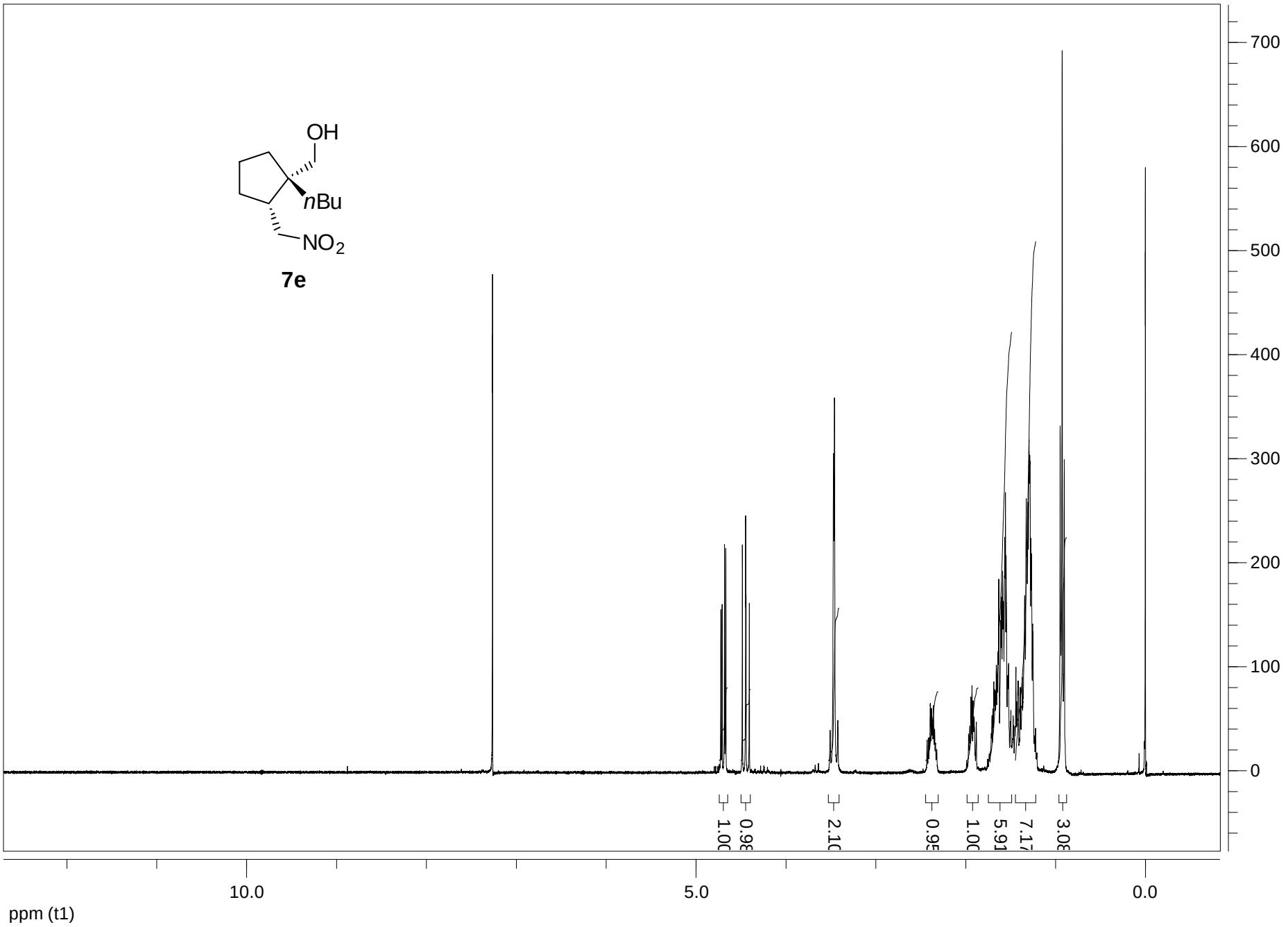


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (1*S*,2*R*)-1-butyl-2-(nitromethyl)cyclopentyl)methanol (**7e**)

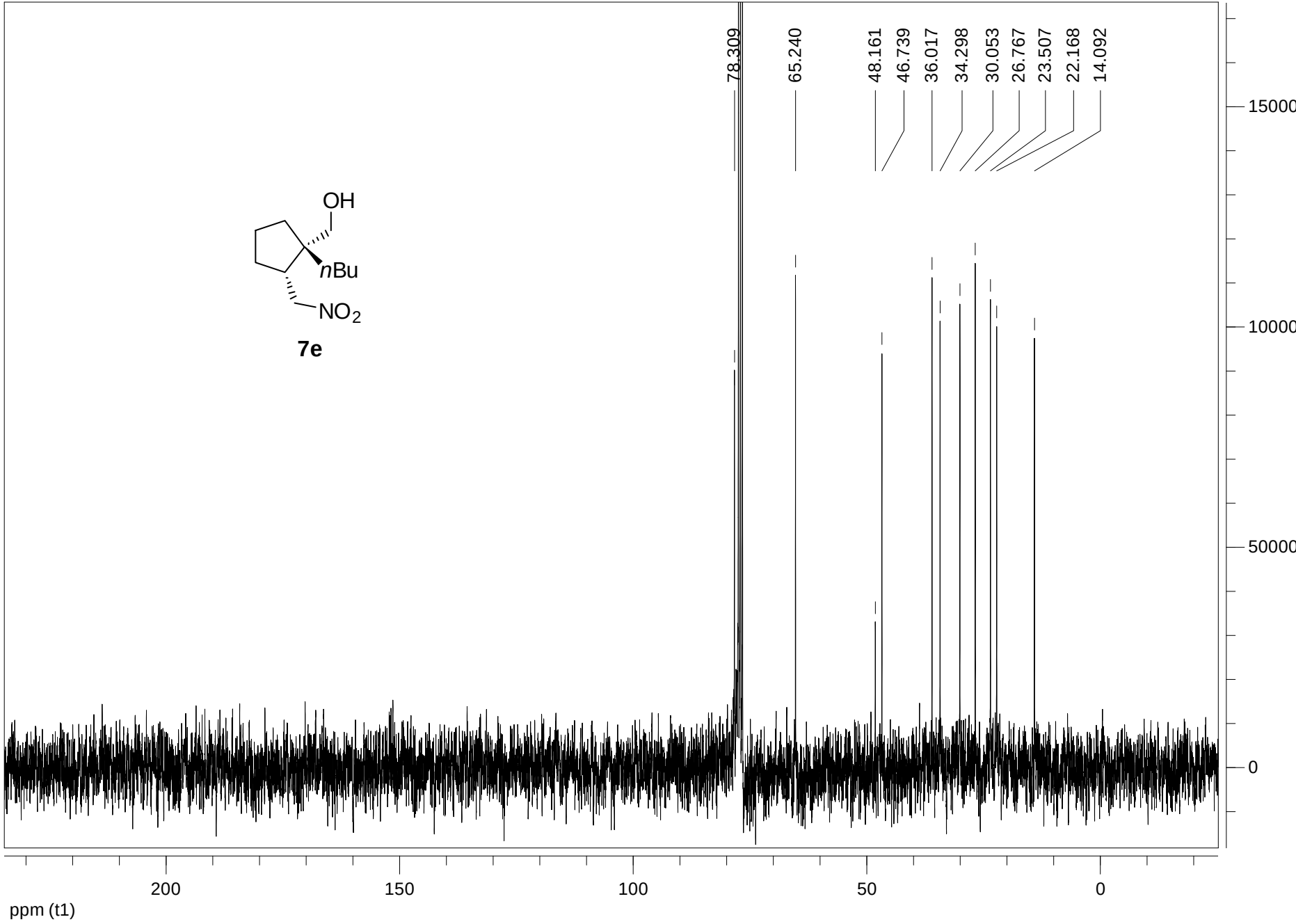
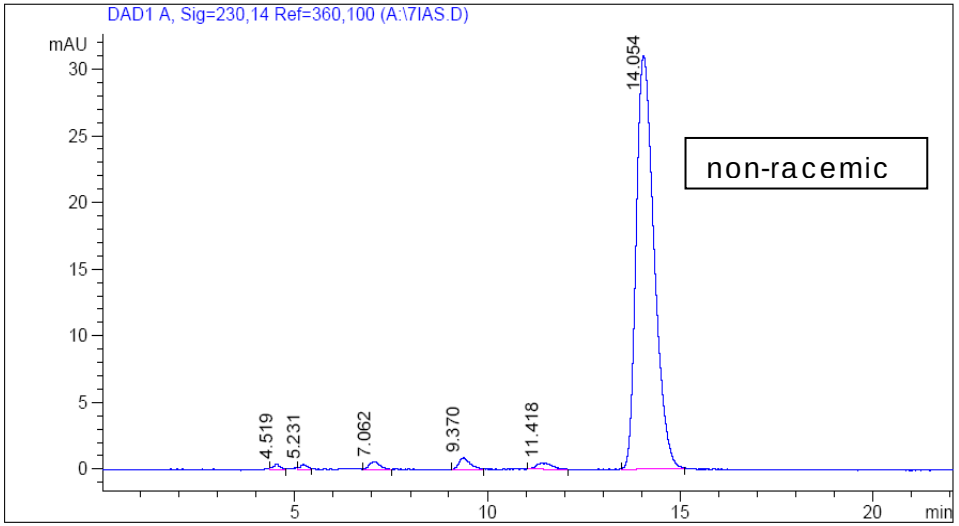
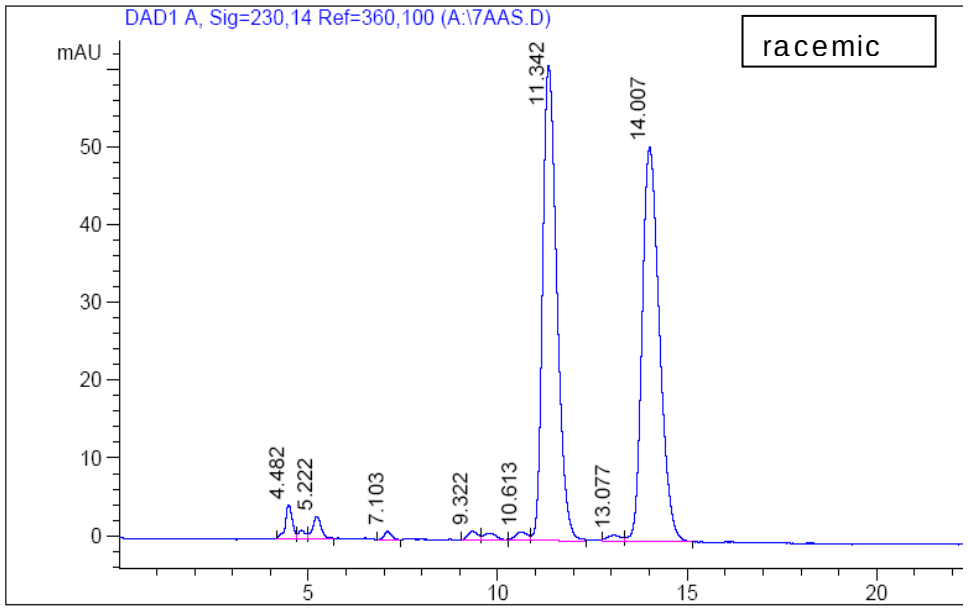


Figure S23. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (1*S*,2*R*)-1-butyl-2-(nitromethyl)cyclopentyl)methanol (**7e**)





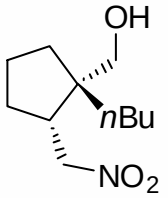
AK Enders - Analytische HPLC

Sample Name: CW 7i
Data file: A:\7IAS.D
Sample Info: Laufmittel:n-Heptan/IP 95:5;
Probe im LM gelöst

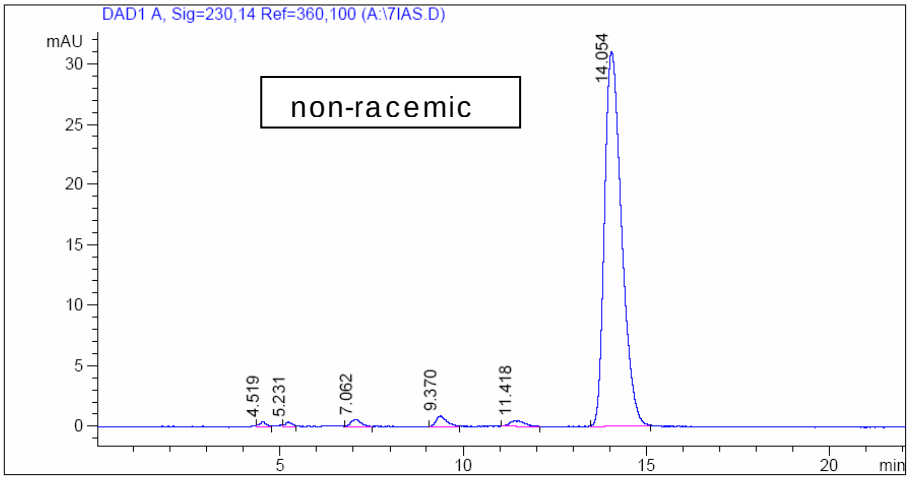
Säule: DAICELAS.M
Säuleninfo: (250x4)mm
Operator: Analytik Labor AKEN

Injektion Time: 16:12:30
Injektion Date: 06.05.2008

Instrument Conditions:	At Start	At Stop
Temperature in°C:	0.0°C	0.0°C
Pressure in bar:	18.6	18.6
Flow in ml/min:	0.7	0.7



7e



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.52	0.17	0.38	4.64	0.44
2	5.23	0.17	0.35	4.47	0.42
3	7.06	0.27	0.57	11.13	1.05
4	9.37	0.29	0.87	17.77	1.68
5	11.42	0.36	0.46	13.35	1.27
6	14.05	0.49	31.06	1003.85	95.13
Total				1055.20	100.00

Figure S24. HPLC traces of **7e**; overlay of racemic and non-racemic (left), non-racemic (right)

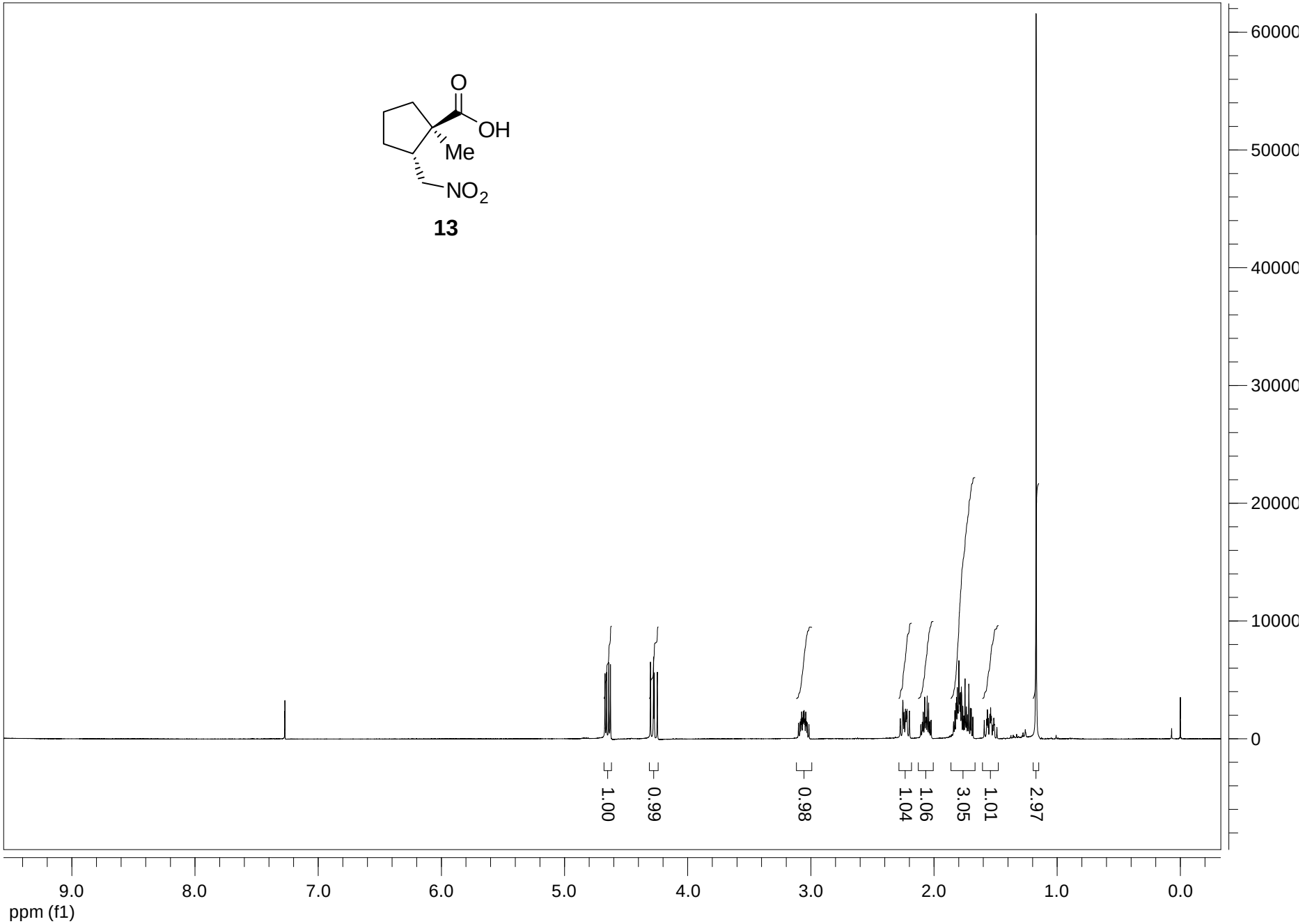


Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (1*R*,2*R*)-2-(nitromethyl)-1-methylcyclopentanecarboxylic acid (**13**).

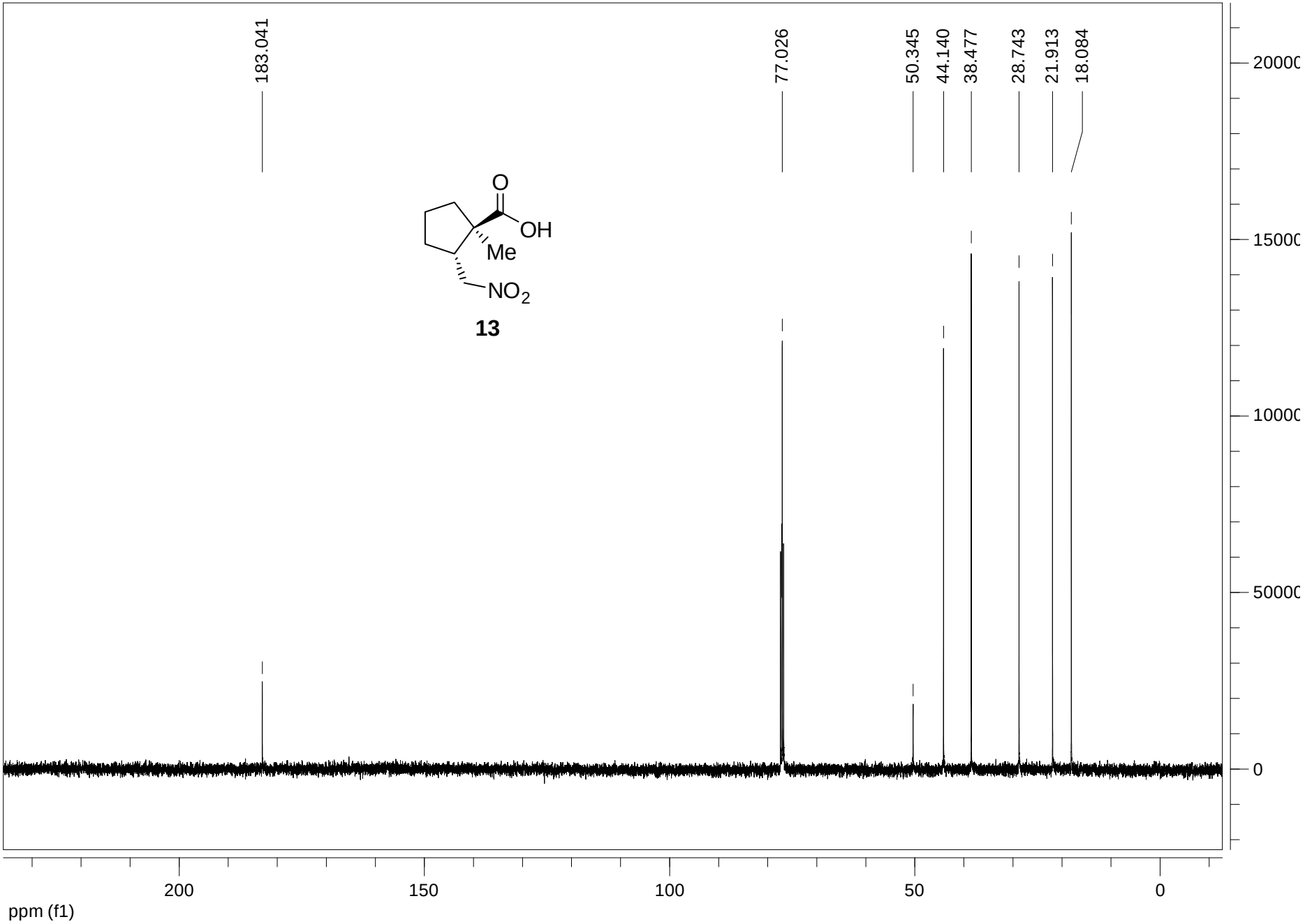


Figure S26. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (1*R*,2*R*)-2-(nitromethyl)-1-methylcyclopentanecarboxylic acid (**13**).

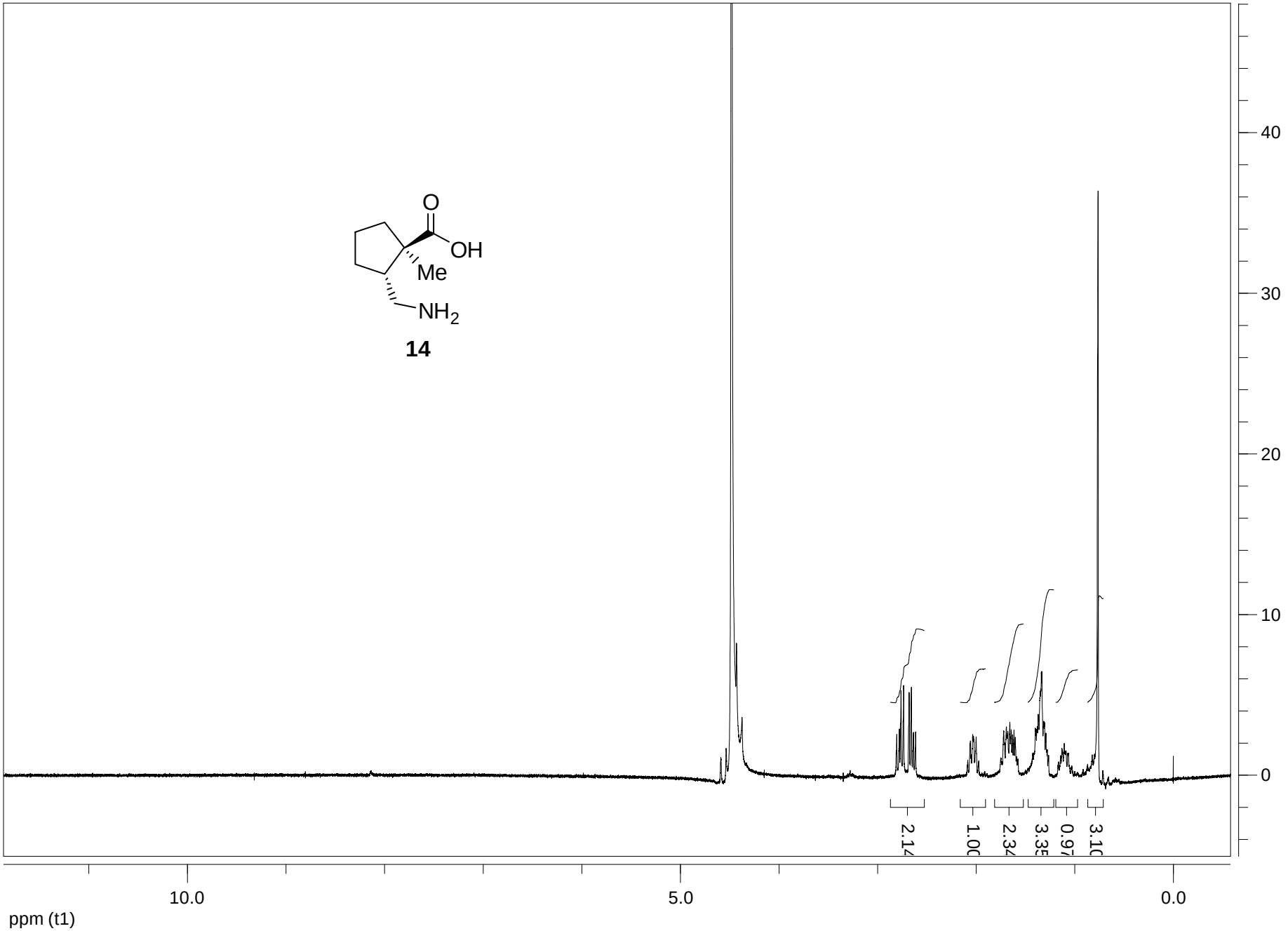


Figure S27. ^{1}H NMR spectrum (300 MHz, D_2O) of (1*R*,2*R*)-2-(aminomethyl)-1-methylcyclopentanecarboxylic acid (**14**).

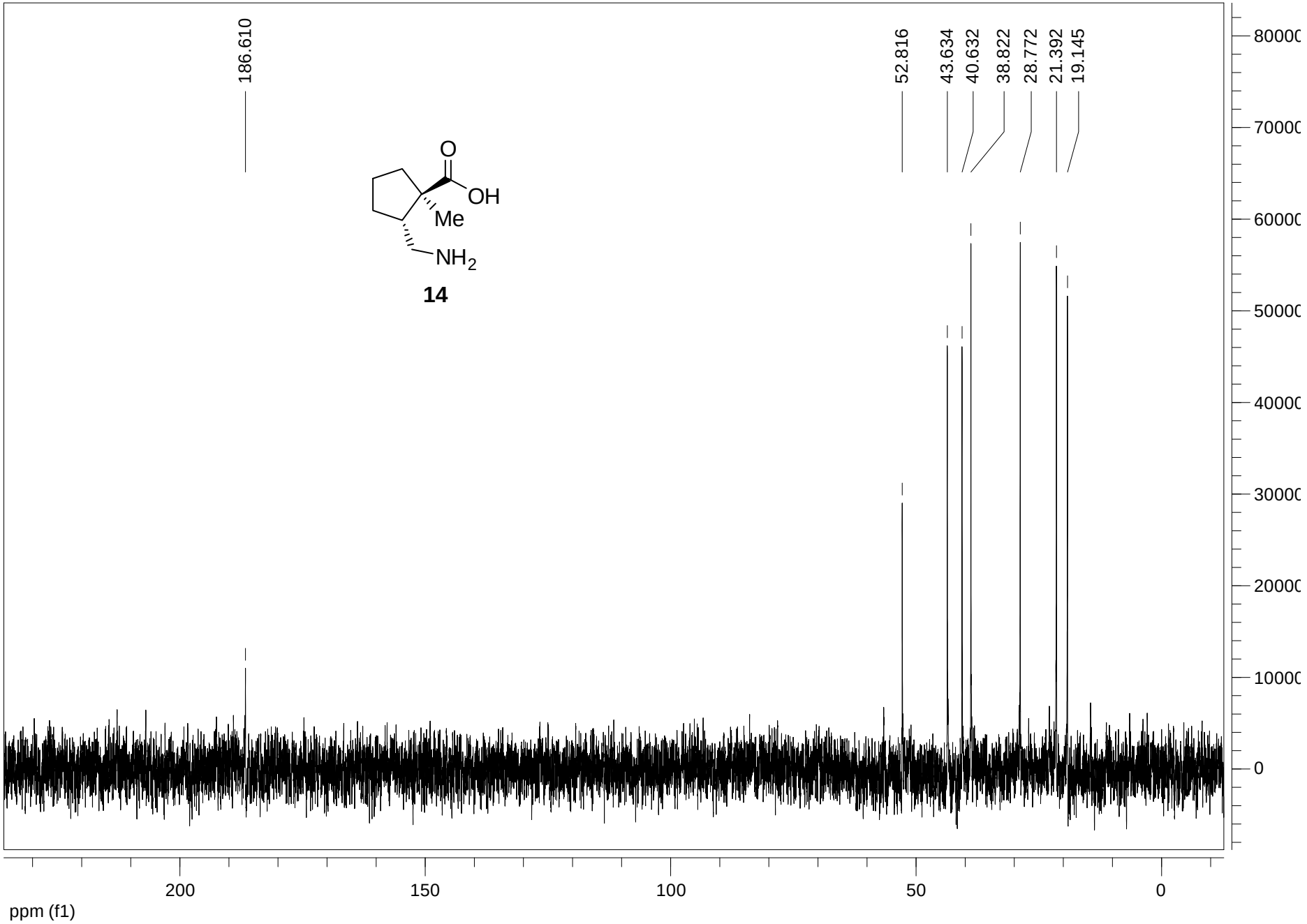


Figure S28. ^{13}C NMR spectrum (101 MHz, D_2O) of (1*R*,2*R*)-2-(aminomethyl)-1-methylcyclopentanecarboxylic acid (**14**).