Organocatalytic Approach to Polysubstituted Piperidines and Tetrahydropyrans

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Supporting Information

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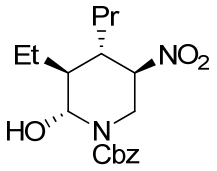
Experimental

General information. For thin-layer chromatography (TLC), Silica gel plates GF254 were used and compounds were visualized by irradiation with UV light, I_2, or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. Optical rotations were measured by used a Perkin–Elmer 241MC polarimeter in the solvent indicated. FT-IR spectra were recorded on an AVATAR-360 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on MERCURY300, Bruker DRX-400, and Bruker AV-500 spectrometers with TMS as the internal standard. HRMS were recorded by using either FTMS-7 or IonSpec 4.7 spectrometers. HPLC was carried out using a Water 515 pump, waters 2487 UV detector, Millennium workstation, Phenomenex (Lux Amylose-2, Lux Cellulose-1, Lux Cellulose-2), Daicel Chiralpak HPLC column. Yields refer to pure compounds, unless otherwise indicated.

General procedure for cascade Michael-aminalization process of aldehydes with substituted nitroalkenes: Aldehyde **2** (0.40 mmol) was added to a suspension of catalyst **1** (0.02-0.03 mmol), nitroalkenes **3** (0.20 mmol) and benzoic acid (0.06-0.09 mmol) in water (0.40 mL) at room temperature. The stirring was continued until complete conversion of **3** (monitored by TLC). The reaction mixture was diluted with ethyl acetate, dried over Na_2SO_4 and concentrated. Purification by flash column chromatography (silica gel, petroleum ether/AcOEt) afforded the the corresponding substituted piperidine. The enantiomeric excess (ee) was determined by HPLC on a chiral phase. *Noteworthy is that these substituted piperidines could isomerize at the chiral center of hemiaminal part during standing in $CDCl_3$, and therefore some additional peaks (for isomer) were observed in ^{13}C NMR spectra if ^{13}C NMR determination took longer time.*

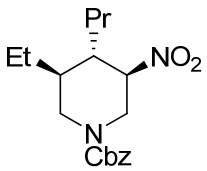
Reduction of 3 with triethylsilane and $BF_3{\cdot}OEt_2$. To a mixture of the above crude product (0.15 mmol) and triethylsilane (72 μL, 0.45 mmol) in CH_2Cl_2 (1.5 mL) was added $BF_3{\cdot}OEt_2$ (23 μL, 0.3 mmol) at 0 °C. The reaction mixture was stirred for 1-3 h.

Purification by flash column chromatography (silica gel, petroleum ether/AcOEt) afforded the reduced product. The enantiomeric excess (ee) was determined by HPLC on a chiral phase.



5a

(2R,3S,4S,5R)-3-Ethyl-2-hydroxy-5-nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester 5a. $[\alpha]_D^{28}$ = -8.4 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 5H), 5.74 (s, 1H), 5.15 (s, 2H), 4.47 (dt, *J* = 4.4, 10.4 Hz, 1H), 4.18 (d, *J* = 10.0 Hz, 1H), 3.78 (t, *J* = 10.8 Hz, 1H), 3.00-2.80（br, 1H）, 2.46-2.39 (m, 1H), 1.63-1.56 (m, 1H), 1.48-1.37 (m, 3H), 1.33-1.21 (m, 3H), 1.00 (t, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.12, 135.89, 128.81, 128.60, 128.27, 85.39, 74.97, 68.07, 42.79, 41.22, 37.59, 30.28, 21.27, 17.17, 14.49, 11.38; IR (neat): ν = 3432 br, 2962 m, 2934 m, 1690 s, 1550 s, 1431 m, 1145 m, 963 m, 748 m, 698 m cm^{-1}; ESI-MS *m/z* 373.4 $(M + Na)^+$, HRMS (MALDI) calcd for $C_{18}H_{26}N_2O_5Na$ $(M + Na)^+$ *m/z* 373.1734, found 373.1733; HPLC: PHENOMENEX LUX AMYLOSE-2 (PA-2) column, hexane/*i*-PrOH = 70:30, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 8.5 min (major), t_R = 7.7 min (minor), *ee*=98%. (*Noteworthy is that some additional peaks (for minor isomer) were observed in* ^{13}C *NMR spectra due to isomerization)*



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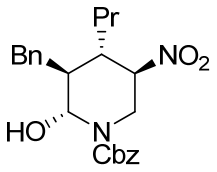
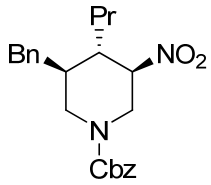
(3S,4S,5R)-3-Ethyl-5-nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester 8. $[\alpha]_D^{28}$ = -40.6 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 5H), 5.20-5.07 (m, 2H), 4.65-4.38 (m, 2H), 4.30-4.10 (m, 1H), 3.30-3.10 (m, 1H),

2.63-2.45 (m, 1H), 1.97 (tt, *J* = 3.2, 10.8 Hz, 1H), 1.70-1.60 (m, 1H), 1.60-1.46 (m, 1H), 1.45-1.35 (m, 1H), 1.35-1.15 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.88, 136.35, 128.72, 128.39, 128.14, 85.57, 67.78, 47.80, 47.16, 43.73, 38.43, 30.37, 22.71, 17.65, 14.56, 10.75; IR (neat): ν = 2962 m, 2875 m, 1694 s, 1546 s, 1440 s, 1222 m, 1146 m, 1098 w, 754 w, 699 m cm-1; ESI-MS m/z 335.2 (M + H)+, 357.3 (M + Na)+, HRMS (ESI) calcd for $C_{18}H_{26}N_2O_4Na$ $(M + Na)^+$ *m/z* 357.1785, found 357.1793; HPLC: PHENOMENEX LUX AMYLOSE-2 (PA-2) column, hexane/*i*-PrOH = 70:30, flow rate 0.7 mL/min, 214 nm, t_R = 12.5 min (major), t_R = 11.0 min (minor), *ee* = 98%.



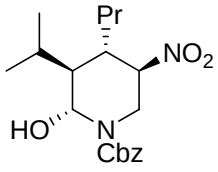
5b

(2R,3S,4S,5R)-3-Benzyl-2-hydroxy-5-nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester 5b. $[\alpha]_D^{27}$ = -8.7 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.31-7.19 (m, 10H), 5.26 (d, *J* = 2.0 Hz, 1H), 5.08-4.98 (m, 2H), 4.50 (dt, *J* = 4.4, 10.4 Hz, 1H), 4.05-4.22 (m, 1H), 3.80 (t, *J* = 10.8 Hz, 1H), 2.91 (dd, *J* = 4.0, 13.6 Hz, 1H), 2.65-2.57 (m, 2H), 1.78 (tt, *J* = 3.6, 14.8 Hz, 1H), 1.61-1.55 (m, 1H), 1.45-1.36 (m, 3H), 0.93 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer: 154.67, 138.93, 135.76, 129.09, 128.78, 128.72, 128.43, 127.92, 126.66, 85.17, 74.73, 67.85, 43.51, 41.17, 37.49, 34.66, 30.39, 17.24, 14.50; IR (neat): ν = 3419 br, 2959 m, 2932 m, 1705 s, 1550 s, 1432 m, 1305 m, 1143 m, 954 w, 737 w, 699 m cm-1; ESI-MS *m/z* 435.5 $(M + Na)^+$, HRMS (MALDI) calcd for $C_{23}H_{28}N_2O_5Na$ $(M + Na)^+$ *m/z* 435.1890, found 435.1889. (*Noteworthy is that some additional peaks (for minor isomer) were observed in ^{13}C NMR spectra due to isomerization)*



reduction product of **5b**

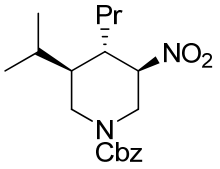
(3S,4S,5R)-3-Benzyl-5-nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester (reduction preoduct of 5b). $[\alpha]_D^{28}$ = -16.8 (*c* 1.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 7H), 7.12-7.06 (m, 3H), 5.10 (d, *J* = 11.2 Hz, 1H), 4.99 (d, *J* = 11.2 Hz, 1H), 4.55-4.45 (m, 2H), 3.95 (d, *J* = 7.2 Hz, 1H), 3.20-3.30 (m, 1H), 3.02 (d, *J* = 11.6 Hz, 1H), 2.54 (t, *J* = 11.6 Hz, 1H), 2.20-2.35 (m, 1H), 2.10-2.04 (m, 1H), 1.76-1.61 (m, 2H), 1.42-1.32 (m, 3H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.65, 138.58, 136.18, 128.91, 128.81, 128.64, 128.18, 127.58, 126.72, 85.23, 67.61, 48.06, 47.06, 44.29, 39.28, 36.76, 30.58, 17.71, 14.56; IR (neat): ν = 2959 m, 2932 m, 2873 m, 1708 s, 1538 s, 1470 m, 1455 m, 1374 m, 1254 m, 1222 s, 1139 s, 736 m, 699 m cm^{-1}; ESI-MS *m/z* 419.4 $(M + Na)^+$, HRMS (ESI) calcd for $C_{23}H_{28}N_2O_4Na$ $(M + Na)^+$ *m/z* 419.1941, found 419.1950; HPLC: PHENOMENEX LUX CELLULOSE-2 (PC-2) column, hexane/*i*-PrOH = 70:30, flow rate 0.7 mL/min, 214 nm, t_R = 14.5 min (major), t_R = 10.6 min (minor), *ee*=99%.



5c

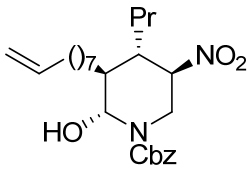
(2R,3S,4S,5R)-2-Hydroxy-3-isopropyl-5-nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester 5c. $[\alpha]_D^{26}$ = -8.6 (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.32-7.30 (m, 5H), 5.82 (s, 1H), 5.12 (s, 2H), 4.51 (dt, *J* = 4.4, 10.0 Hz, 1H), 4.16 (d, *J* = 8.8, Hz, 1H), 3.82 (t, *J* = 11.4, Hz, 1H), 2.73-2.67 (m, 1H), 1.98-1.90 (m, 1H), 1.46-1.43 (m, 1H), 1.42-1.40 (m, 1H), 1.37-1.28 (m, 2H), 1.24-1.16 (m, 1H), 1.09 (d, *J* = 7.2, Hz, 3H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer: 154.90, 135.89, 128.78, 128.55, 128.19, 85.34, 75.46, 67.98, 44.90, 40.97, 35.31, 29.80, 26.62, 20.88, 17.70, 16.39, 14.57; IR (neat): ν = 3437 br, 2962 s, 2934 m, 1702 s, 1552 s, 1429 m, 1266 m, 985 m, 739 s, 702 m

cm^{-1}; ESI-MS *m/z* 387.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{19}H_{28}N_2O_5Na$ $(M + Na)^+$ *m/z* 387.1890, found 387.1883. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



reduction product of **5c**

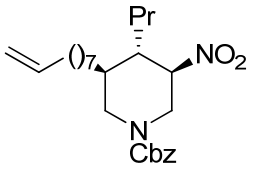
(3S,4S,5R)-3-Isopropyl-5-nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester (reduction product of 5c). $[\alpha]_D^{25}$ = -34.4 (*c* 0.97, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 5H), 5.19-5.09 (m, 2H), 4.54-4.42 (m, 2H), 4.20-4.08 (m, 1H), 3.26-3.14 (m, 1H), 2.68-2.56 (m, 1H), 2.15 (tt, *J* = 3.2, 10.8 Hz, 1H), 2.00-1.92 (m, 1H), 1.54-1.48 (m, 1H), 1.38-1.16 (m, 4H), 1.06-0.98 (m, 3H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.00, 136.37, 128.72, 128.39, 128.11, 85.67, 67.78, 47.28, 43.45, 41.87, 29.85, 25.76, 21.42, 17.12, 15.71, 14.60; IR (neat): ν = 2961 s, 2933 m, 1709 s, 1549 s, 1470 m, 1435 m, 1374 m, 1292 m, 1223 s, 1147 m, 1098 m, 970 w, 745 m, 698 w cm^{-1}; ESI-MS *m/z* 349.3 $(M + H)^+$, 371.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{19}H_{28}N_2O_4Na$ $(M + Na)^+$ *m/z* 397.1734, found 397.1741; HPLC: PHENOMENEX LUX AMYLOSE-2 (PA-2) column, hexane/*i*-PrOH = 50:50, flow rate 0.7 mL/min, 214 nm, t_R = 9.3 min (major), t_R = 8.7 min (minor), *ee*>99%.



5d

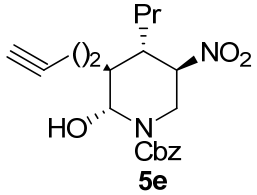
(2R,3S,4S,5R)-2-Hydroxy-5-nitro-3-non-8-enyl-4-propyl-piperidine-1-carboxylic acid benzyl ester 5d. $[\alpha]_D^{25}$ = -13.5 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 5H), 5.84-5.76 (m, 1H), 5.70 (s, 1H), 5.15 (s, 2H), 4.99 (d, *J* = 16.8 Hz, 1H), 4.93 (d, *J* = 10.0 Hz, 1H), 4.46 (dt, *J* = 4.4, 10.4 Hz, 1H), 4.17(d, *J* = 8.4 Hz, 1H), 3.78 (t, *J* = 11.2 Hz, 1H), 2.42 (m, 1H), 2.33 (t, *J* = 7.6 Hz, 1H), 2.06-2.01 (m, 2H), 1.64-1.61 (m, 1H), 1.45-1.26 (m, 16H), 0.90 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 155.15, 139.27, 135.88, 128.81, 128.61, 128.28, 114.34, 85.37, 75.24, 68.09, 41.24, 37.61, 33.90, 30.33, 29.82, 29.53, 29.18, 29.03, 28.30, 26.70, 24.84, 17.21, 14.50; IR (neat): ν = 3448 br, 2928 s, 1686 s, 1551 s, 1336 w, 1143 m, 968 m, 910 m, 697 m cm^{-1}; ESI-MS *m/z* 469.5 $(M + Na)^+$, HRMS (ESI) calcd for $C_{25}H_{38}N_2O_5Na$ $(M + Na)^+$ *m/z* 469.2673, found 469.2682. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



reduction product of **5d**

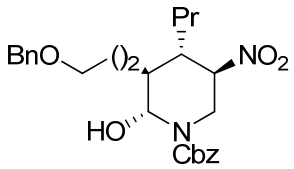
(3R,4S,5S)-3-Nitro-5-non-8-enyl-4-propyl-piperidine-1-carboxylic acid benzyl ester (reduction product of 5d). $[\alpha]_D^{27}$ = -33.7 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 5H), 5.86-5.76 (m, 1H), 5.18-5.10 (m, 2H), 5.00 (dd, *J* = 1.6, 17.2 Hz, 1H), 4.94 (d, *J* = 10.4 Hz, 1H), 4.54-4.38 (m, 2H), 4.27-4.10 (m, 1H), 3.27-3.15 (m, 1H), 2.60-2.45 (m, 1H), 2.04 (q, *J* = 6.8 Hz, 2H), 1.97-1.92 (m, 1H), 1.56-1.50 (m, 2H), 1.39-1.12 (m, 15H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.83, 139.23, 136.35, 128.72, 128.40, 128.13, 114.35, 85.48, 67.79, 48.23, 47.16, 44.11, 37.16, 33.87, 30.42, 29.82, 29.44, 29.12, 29.00, 26.32, 17.68, 14.57; IR (neat): ν = 2928 s, 2855 s, 1710 s, 1550 s, 1467 s, 1433 s, 1376 m, 1290 m, 1221 s, 1142 m, 970 m, 911 m, 754 m, 698 m cm^{-1}; ESI-MS *m/z* 431.5 $(M + H)^+$, 453.5 $(M + Na)^+$, HRMS (MALDI) calcd for $C_{25}H_{38}N_2O_4Na$ $(M + Na)^+$ *m/z* 453.2724, found 453.2719; HPLC: PHENOMENEX LUX AMYLOSE-2 (PA-2) column, hexane/*i*-PrOH = 50:50, flow rate 0.7 mL/min, 214 nm, t_R = 9.2 min (major), t_R = 7.8 min (minor), *ee*>99%.



5e

(2R,3S,4S,5R)-3-But-3-ynyl-2-hydroxy-5-nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester 5e. $[\alpha]_D^{25}$ = -26.2 (*c* 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ

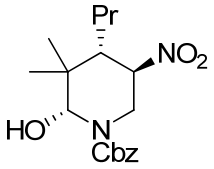
7.38-7.31 (m, 5H), 5.75 (s, 1H), 5.18-5.10 (m, 2H), 4.50 (dt, *J* = 4.0, 10.0 Hz, 1H), 4.11-4.24 (m, 1H), 3.77 (t, *J* = 11.2 Hz, 1H), 2.45 (t, *J* = 10.4 Hz, 1H), 2.35-2.31 (m, 2H), 1.97 (brs, 1H), 1.76-1.66 (m, 3H), 1.48-1.42 (m, 1H), 1.34-1.26 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.13, 135.78, 128.80, 128.61, 128.26, 85.15, 83.27, 74.64, 69.58, 68.13, 41.11, 39.72, 37.30, 30.20, 26.79, 17.05, 15.68, 14.46; IR (neat): ν = 3435 br, 3297 s, 2959 s, 2932 s, 1694 s, 1549 m, 1430 m, 1337 m, 1144 m, 1095 m, 981 s, 698 m, 646 s cm^{-1}; ESI-MS *m/z* 397.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{20}H_{26}N_2O_5Na$ $(M + Na)^+$ *m/z* 397.1734, found 397.1741; HPLC: sino-AD column, hexane/*i*-PrOH = 90:10, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 10.2 min (major), t_R = 12.6 min (minor), *ee*=99%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



5f

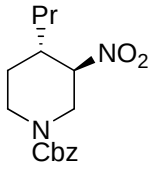
(2R,3S,4S,5R)-3-(3-Benzyloxy-propyl)-2-hydroxy-5-nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester 5f. $[\alpha]_D^{25}$ = -11.7 (*c* 1.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.35-7.29 (m, 10H), 5.71 (s, 1H), 5.12 (s, 2H), 4.47 (s, 2H), 4.43 (dd, *J* = 4.0, 10.0 Hz, 1H), 4.21-4.11 (m, 1H), 3.73 (t, *J* = 11.6 Hz, 1H), 3.47 (t, *J* = 6.0 Hz, 2H), 2.46-2.37 (m, 1H), 1.86-1.75 (m, 1H), 1.61-1.59 (m, 2H), 1.47-1.42 (m, 2H), 1.28-1.24 (m, 4H), 0.88 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer: 154.98, 138.38, 135.87, 128.76, 128.54, 128.49, 128.24, 127.78, 127.74, 85.33, 75.04, 73.05, 70.18, 68.00, 41.13, 37.58, 30.21, 29.78, 26.59, 24.94, 17.15, 14.44; IR (neat): ν = 3418 br, 2958 s, 2931 s, 2872 s, 1705 s, 1549 s, 1455 m, 1337 w, 1102 m, 968 m, 738 s, 698 m cm^{-1}; ESI-MS *m/z* 493.5 $(M + Na)^+$, HRMS (MALDI) calcd for $C_{26}H_{34}N_2O_6Na$ $(M + Na)^+$ *m/z* 493.2309, found 493.2311; HPLC: PHENOMENEX LUX AMYLOSE-2 (PA-2) column, hexane/*i*-PrOH = 70:30, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 18.3 min (major), t_R = 10.5 min (minor),

ee>99%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization).*



5g

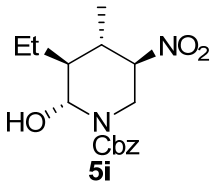
(2R,4S,5R)-2-Hydroxy-3,3-dimethyl-5-nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester 5g. $[\alpha]_D^{28}$ = -8.7 (*c* 0.67, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.40-7.32 (m, 5H), 5.26 (s, 1H), 5.14 (d, *J* = 7.2 Hz, 2H), 4.48 (dt, *J* = 4.8, 11.2 Hz, 1H), 4.39-4.17 (m, 1H), 3.70 (t, *J* = 12.0 Hz, 1H), 2.36-2.32 (m, 1H), 1.82-1.56 (m, 1H), 1.49-1.42 (m, 1H), 1.24-1.18 (m, 2H), 1.10 (s, 3H), 0.85 (t, *J* = 6.8 Hz, 3H), 0.82 (s, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer: 155.30, 135.89, 128.82, 128.62, 128.26, 86.06, 82.44, 68.09, 41.62, 39.25, 30.20, 24.75, 23.24, 19.67, 14.47; IR (neat): ν = 3428 br, 2962 m, 2918 m, 1690 s, 1552 s, 1431 s, 1331 m, 1213 m, 1055 m, 968 m, 739 m, 698 m cm^{-1}; ESI-MS *m/z* 373.4 $(M + Na)^+$, HRMS (MALDI) calcd for $C_{18}H_{26}N_2O_5Na$ $(M + Na)^+$ *m/z* 373.1734, found 373.1741. HPLC: PHENOMENEX LUX CELLULOSE-2 (PC-2) column, hexane/*i*-PrOH = 90:10, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 16.1 min (major), t_R = 9.7 min (minor), *ee* = 90%, minor isomer: t_R = 8.4 min (major), t_R = 11.6 min (minor), *ee* = 92%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



reduction product of **5h**

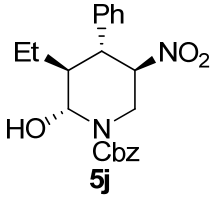
(3R,4S)-3-Nitro-4-propyl-piperidine-1-carboxylic acid benzyl ester (reduction product of 5h). $[\alpha]_D^{29}$ = -17.17 (*c* 0.83, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 5H), 5.14-5.13 (m, 2H), 4.60-4.47 (m, 1H), 4.27-4.23 (m, 1H), 4.20-4.15 (m, 1H), 3.30-3.15 (m, 1H), 2.86 (t, *J* = 11.2 Hz, 1H), 2.14-2.12 (m, 1H), 1.91 (d, *J* = 13.2 Hz, 1H), 1.43-1.34 (m, 2H), 1.25-1.18 (m, 3H), 0.89 (t, *J* = 6.8 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.95, 136.31, 128.75, 128.45, 128.24, 87.06, 67.86, 47.01, 43.65, 39.73, 34.22, 28.61, 19.03, 14.06; IR (neat): ν = 2959 s, 2929 s, 1705 s, 1548 s, 1431 s, 1212 s, 1155 m, 1091 m, 973 m, 751 m, 698 m cm^{-1}; ESI-MS *m/z* 307.3 $(M + H)^+$, 329.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{16}H_{22}N_2O_4Na$ $(M + Na)^+$ *m/z* 329.1472, found 329.1472; HPLC: PHENOMENEX LUX AMYLOSE-2 (PA-2) column, hexane/*i*-PrOH = 80:20, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 20.1 min (major), t_R = 21.7 min (minor), *ee* = 86%.



5i

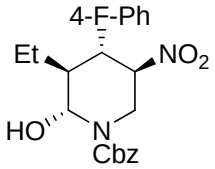
(2R,3S,4S,5R)-3-Ethyl-2-hydroxy-4-methyl-5-nitro-piperidine-1-carboxylic acid benzyl ester 5i. $[\alpha]_D^{29}$ = -26.8 (*c* 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 5H), 5.74 (d, *J* = 2.0 Hz, 1H), 5.14 (s, 2H), 4.27-4.21(m, 2H), 3.67 (t, *J* = 12.0 Hz, 1H), 2.45-2.38 (m, 1H), 1.70-1.63 (m, 1H), 1.46-1.38 (m, 1H), 1.26-1.20 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.06, 135.83, 128.81, 128.62, 128.24, 88.71, 74.91, 68.10, 46.04, 41.27, 33.82, 21.50, 15.25, 11.34; IR (neat): ν = 3466 br, 2962 m, 2929 s, 1698 s, 1669 s, 1549 s, 1536 s, 1472 m, 1439 m, 1337 m, 1246 m, 1149 m, 1019 m, 729 m cm^{-1}; ESI-MS *m/z* 345.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{16}H_{22}N_2O_5Na$ $(M + Na)^+$ *m/z* 345.1421, found 345.1424; HPLC: PHENOMENEX LUX AMYLOSE-2 (PA-2) column, hexane/*i*-PrOH = 70:30, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 10.3 min (major), t_R = 8.2 min (minor), *ee* = 98%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



5j

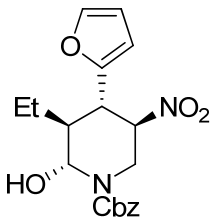
(2R,3S,4R,5R)-3-Ethyl-2-hydroxy-5-nitro-4-phenylpiperidine-1-carboxylic acid benzyl ester 5j. $[\alpha]_D^{25}$ = +33.0 (*c* 1.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H), 7.30-7.23 (m, 3H), 7.15-7.13 (m, 2H), 5.90 (d, *J* = 1.6 Hz, 1H),

5.17 (s, 2H), 4.76 (dt, *J* = 4.8, 11.2 Hz, 1H), 4.42 (d, *J* = 8.0 Hz, 1H), 3.79 (t, *J* = 12.0 Hz, 1H), 3.48 (t, *J* = 11.6 Hz, 1H), 1.80-1.74 (m, 1H), 1.38-1.29 (m, 1H), 1.09-1.03 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.10, 137.49, 135.72, 129.08, 128.83, 128.67, 128.28, 128.01(2C), 87.86, 74.95, 68.23, 46.19, 45.65, 41.56, 22.04, 11.22; IR (neat): ν = 3396 br, 2962 w, 1675 s, 1434 s, 1357 m, 1336 m, 1288 m, 1193 m, 1151 m, 1109 m, 965 m, 765 w, 701w cm^{-1}; ESI-MS *m/z* 407.4 (M + Na)$^+$, HRMS (ESI) calcd for $C_{21}H_{24}N_2O_5Na$ (M + Na)$^+$ *m/z* 407.1577, found 407.1578; HPLC: PHENOMENEX LUX CELLULOSE-2 (PC-2) column, hexane/*i*-PrOH = 70:30, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 11.1 min (major), t_R = 6.7 min (minor), *ee* >99%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



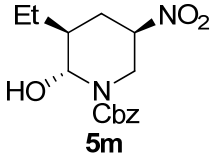
5k

(3S,4R,5R)-3-Ethyl-4-(4-fluorophenyl)-5-nitro-piperidine-1-carboxylic acid benzyl ester 5k. $[\alpha]_D^{23}$ = +27.6 (*c* 1.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 5H), 7.13-7.10 (m, 2H), 7.02-6.97 (m, 2H), 5.90 (s, 1H), 5.17 (s, 2H), 4.70 (dt, *J* = 4.4, 11.2 Hz, 1H), 4.43 (d, *J* = 7.6 Hz, 1H), 3.79 (t, *J* = 11.6 Hz, 1H), 3.48 (t, *J* = 11.6 Hz, 1H), 1.72 (tt, *J* = 2.8, 11.2 Hz, 1H), 1.37-1.29 (m, 1H), 1.07-1.01 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.35 (*J* = 245.7 Hz), 155.10, 135.63, 133.21 (*J* = 3.6 Hz), 129.55, 128.83, 128.69, 128.28, 116.07 (*J* = 21.1 Hz), 87.84, 74.86, 68.28, 45.74, 45.49, 41.49, 21.98, 11.19; ^{19}F NMR (300 MHz, $CDCl_3$) δ -114.50; IR (neat): ν = 3418 br, 1683 s, 1549 s, 1513 m, 1435 m, 1335 m, 1226 m, 833 m, 733 m cm^{-1}; ESI-MS *m/z* 425.2 (M + Na)$^+$, HRMS (ESI) calcd for $C_{21}H_{23}N_2O_5FNa$ (M + Na)$^+$ *m/z* 425.1483, found 425.1501; HPLC: PHENOMENEX LUX CELLULOSE-2 (PC-2) column, hexane/*i*-PrOH = 80:20, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 16.7 min (major), t_R = 8.6 min (minor), *ee*>99%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



5l

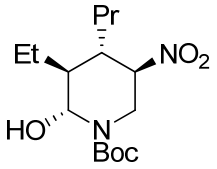
(2R,3S,4S,5R)-3-Ethyl-4-furan-2-yl-2-hydroxy-5-nitro-piperidine-1-carboxylic acid benzyl ester 5l. $[\alpha]_D^{26}$ = +40.0 (*c* 1.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 6H), 6.26 (dd, *J* = 2.0, 2.8 Hz, 1H), 6.15 (d, *J* = 2.8 Hz, 1H), 5.86 (d, *J* = 2.0 Hz, 1H), 5.17 (s, 2H), 4.81 (dt, *J* = 4.8, 11.2 Hz, 1H), 4.40 (d, *J* = 11.6 Hz, 1H), 3.76 (t, *J* = 12.0 Hz, 1H), 3.62 (t, *J* = 11.6 Hz, 1H), 1.92-1.85 (m, 1H), 1.42-1.36 (m, 1H), 1.17-1.10 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.03, 150.48, 142.62, 135.74, 128.85, 128.68, 128.30, 110.41, 109.54, 85.36, 74.93, 68.25, 43.98, 41.14, 40.14, 22.37, 11.18; IR (neat): ν = 3419 s, 2965 m, 1678 s, 1556 s, 1435 w, 1335 w, 1192 m, 1151 m, 965 m, 883 m, 758 s cm^{-1}; ESI-MS *m/z* 397.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{19}H_{22}N_2O_6Na$ $(M + Na)^+$ *m/z* 397.1370, found 397.1370; HPLC: PHENOMENEX LUX CELLULOSE-2 (PC-2) column, hexane/*i*-PrOH = 70:30, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 8.3 min (major), t_R = 6.6 min (minor), *ee*>99%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



5m

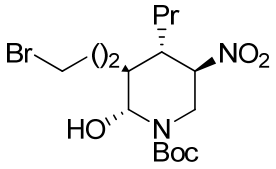
(2R,3S,5R)-3-Ethyl-2-hydroxy-5-nitro-piperidine-1-carboxylic acid benzyl ester 5m. $[\alpha]_D^{29}$ = +0.71 (*c* 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H), 5.87 (s, 1H), 5.16 (s, 2H), 4.43 (tt, *J* = 4.0, 12.0 Hz, 2H), 3.56 (t, *J* = 12.8 Hz, 1H), 2.80-2.60（br s, 1H）, 2.29-2.25 (m, 1H), 2.06 (q, *J* = 12.4 Hz, 1H), 1.58-1.55 (m, 2H), 1.42-1.38 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.26, 135.92, 128.84, 128.64, 128.35, 80.25, 75.69, 68.11, 40.92, 40.59, 29.31, 24.74, 11.38; IR (neat): ν = 3418 br, 2963 m, 2924 m, 1701s, 1545 s, 1328 m, 1268 m, 1164 m, 1004 m, 958 m, 901 m, 751 m, 698 m cm^{-1}; ESI-MS *m/z* 331.3 $(M + Na)^+$, HRMS

(ESI) calcd for $C_{15}H_{20}N_2O_5Na$ $(M + Na)^+$ *m/z* 331.1264, found 331.1270; HPLC: PHENOMENEX LUX AMYLOSE-2 (PA-2) column, hexane/*i*-PrOH = 70:30, flow rate 0.5 mL/min, 214 nm, major isomer: t_R = 10.0 min (major), t_R = 12.0 min (minor), *ee* = 79%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



6a

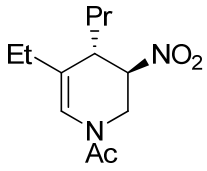
(2R,3S,4S,5R)-3-Ethyl-2-hydroxy-5-nitro-4-propyl-piperidine-1-carboxylic acid *tert*-butyl ester 6a. $[\alpha]_D^{27}$ = -18.4 (*c* 1.88, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.69 (s, 1H), 4.46 (dt, *J* = 4.8, 10.8 Hz, 1H), 4.10 (d, *J* = 10.4 Hz, 1H), 3.70 (t, *J* = 10.8 Hz, 1H), 3.27 (brs, 1H), 2.44-2.39 (m, 1H), 1.62-1.56 (m, 1H), 1.47 (s, 9H), 1.43-1.22 (m, 6H), 1.01 (t, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.43, 85.69, 81.72, 74.35, 42.75, 41.37, 37.66, 30.26, 28.39, 21.28, 17.19, 14.49, 11.32; IR (neat): ν = 3419 s, 2962 m, 2932 m, 1683 s, 1557 m, 1540 m, 1430 m, 1387 w, 1162 s, 1007 w, 884 w cm^{-1}; ESI-MS *m/z* 339.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{15}H_{28}N_2O_3Na$ $(M + Na)^+$ *m/z* 339.1890, found 339.1891; HPLC: sino-AD column, hexane/*i*-PrOH = 90:10, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 7.9 min (major), t_R = 6.5 min (minor), *ee*>99%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



6b

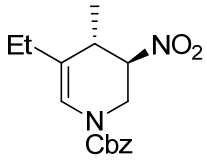
(2R,3S,4S,5R)-3-(3-Bromo-propyl)-2-hydroxy-5-nitro-4-propyl-piperidine-1-carboxylic acid *tert*-butyl ester 6b. $[\alpha]_D^{29}$ = -27.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.61 (s, 1H), 4.47 (dt, *J* = 4.4, 10.4 Hz, 1H), 4.09 (d, *J* = 10.0 Hz, 1H), 3.69 (t, *J* = 12.4 Hz, 1H), 3.46-3.42 (br, 1H), 3.44 (t, *J* = 6.4 Hz, 2H), 2.47-2.42 (m, 1H), 2.11-2.03 (m, 1H), 1.91-1.83 (m, 1H), 1.72-1.66 (m, 1H), 1.62-1.54 (m, 1H), 1.51-1.46 (m, 1H), 1.46 (s, 9H), 1.37-1.23 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 154.37, 85.40, 81.94, 74.48, 41.23, 40.50, 37.45, 33.64, 30.21, 29.70, 28.37, 26.93, 17.14, 14.47; IR (neat): ν = 3445 br, 2959 m, 2932 m, 1678 s, 1557 m, 1538 m, 1472 m, 1389 m, 1165 m, 1006 w, 917 w cm^{-1}; ESI-MS *m/z* 431.4 $(M + Na)^+$, HRMS (ESI) calcd for $C_{16}H_{29}BrN_2O_5Na$ $(M + Na)^+$ *m/z* 431.1152, found 431.1156; HPLC: Chiralpak IC column, hexane/*i*-PrOH = 98:2, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 24.1 min (major), t_R = 19.3 min (minor), *ee*>99%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



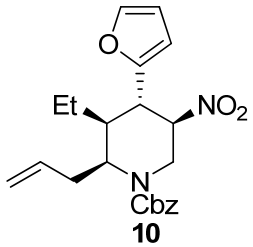
7

1-((3R,4S)-5-Ethyl-3-nitro-4-propyl-3,4-dihydro-2*H*-pyridin-1-yl)-ethanone 7. $[\alpha]_D^{26}$ = +11.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.35 & 7.02 (both s, due to rotamers, 1H), 4.76 & 4.47 (ddd, *J* = 1.6, 3.2, 15.2 Hz, & dd, *J* = 3.2, 13.2 Hz, due to rotamers, 1H), 4.67 & 4.59 (q, *J* = 3.2 Hz & q, *J* = 2.8 Hz, due to rotamers, 1H), 3.51 & 3.67 (dd, *J* = 3.2, 14.8 Hz & dd, *J* = 3.2, 13.6 Hz, due to rotamers, 1H), 2.96 & 3.02 (t, *J* = 4.4 Hz & t , *J* = 4.4 Hz, due to rotamers, 1H), 2.19 &2.23 (both s, due to rotamers, 3H), 2.09 (q, *J* = 7.6 Hz, 2H), 1.69-1.60 (m, 2H), 1.46-1.35 (m, 2H), 1.04 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.32 & 167.59 (due to rotamers), 121.27 & 121.70 (due to rotamers), 119.86 & 118.29 (due to rotamers), 80.83 & 80.89 (due to rotamers), 38.85 & 42.26 (due to rotamers), 38.44 & 37.58 (due to rotamers), 34.74 & 34.93 (due to rotamers), 26.03 & 25.81 (due to rotamers), 21.60 & 22.00 (due to rotamers), 19.98 & 20.04 (due to rotamers), 14.05, 12.57 & 12.55 (due to rotamers); IR (neat): ν = 3418 m, 2964 s, 2934 s, 2875 m, 1652 s, 1549 s, 1410 m, 1316 m, 1210 m, 1179 m, 1017 m, 740 m, 611 m cm^{-1}; ESI-MS *m/z* 241.2 $(M + H)^+$, HRMS (ESI) calcd for $C_{12}H_{20}N_2O_3Na$ $(M + Na)^+$ *m/z* 263.1366, found 263.1372; HPLC: PHENOMENEX LUX AMYLOSE-2 (PA-2) column, hexane/*i*-PrOH = 70:30, flow rate 0.7 mL/min, 214 nm, t_R = 15.2 min (major), t_R = 21.8 min (minor), *ee*=93%.



9

(3R,4S)-5-Ethyl-4-methyl-3-nitro-3,4-dihydro-2*H*-pyridine-1-carboxylic acid benzyl ester 9. To a solution of **4i** (32 mg, 0.10 mol) in 2 mL CH_2Cl_2 was added several drops of TFA at rt. The reation mixture was stirred at this temperature until **4i** was consumed as monitored by TLC. Direct concentration of the reaction mixture gave **9** (30 mg, 100%), which is pure enough for analysis. $[\alpha]_D^{23}$ = +26.5 (*c* 0.83, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 5H), 6.69 &6.58 (both s, due to rotamers, 1H), 5.26-5.16 (m, 2H), 4.50-4.39 (m, 2H), 3.81-3.76 (m, 1H), 3.04 (s, 1H), 2.10-2.02 (m, 2H), 1.17 (d, *J* = 7.2 Hz, 3H), 1.04 & 1.02 (both t, *J* = 7.6 Hz, due to rotamers, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.00 & 152.95 (due to rotamers), 136.05, 128.74, 128.47, 128.26, 120.93 & 120.51, 119.00 & 118.65 (due to rotamers), 83.82 & 83.86 (due to rotamers), 68.07 & 68.12 (due to rotamers), 40.98 & 40.88 (due to rotamers), 33.09 & 33.27 (due to rotamers), 25.37, 18.31 & 18.23 (due to rotamers), 12.54 & 12.67 (due to rotamers); IR (neat): ν = 2918 m, 1708 s, 1546 m, 1215 m, 1139 m, 1029 m, 977 m, 936 m, 692 m, 600 m cm^{-1}; ESI-MS *m/z* 327.2 (M + Na)$^+$, HRMS (ESI) calcd for $C_{16}H_{20}N_2O_4Na$ (M + Na)$^+$ *m/z* 327.1315, found 327.1322.

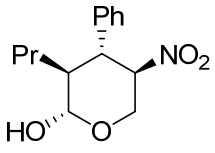


10

(2S,3S,4S,5R)-2-Allyl-3-ethyl-4-furan-2-yl-5-nitro-piperidine-1-carboxylic acid benzyl ester 10. To a solution of **4l** (37 mg, 0.10 mmol) and allyl trimethylsilane (60 μL, 0.5 mmol) in CH_2Cl_2 (2 ml) was added $BF_3{\cdot}OEt_2$ (25 μL, 0.2 mmol) at -78 ^{o}C. The reation mixture was stirred at this temperature until **4l** was consumed as monitored by TLC. Purification by flash column chromatography (silica gel,

petroleum ether/AcOEt 20:1 to 15:1) afforded 37 mg (93%) of **10**. $[\alpha]_D^{23}$ = +31.6 (*c* 0.93, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 6H), 6.29-6.28 (m, 1H), 6.17 (d, *J* = 2.8 Hz, 1H), 5.82-5.72 (m, 1H), 5.17-5.09 (m, 2H), 5.05 (d, *J* = 3.6 Hz, 1H), 5.02 (s, 1H), 4.91-4.88 (m, 1H), 4.60 (d, *J* = 15.6 Hz, 1H), 4.15 (m, 1H), 3.55 (dd, *J* = 6.4, 15.6 Hz, 1H), 3.47 (dd, *J* = 9.2, 11.6 Hz, 1H), 2.46-2.42 (m, 1H), 2.29-2.21 (m, 1H), 1.86-1.79 (m, 1H), 1.44-1.35 (m, 1H), 1.27-1.21 (m, 1H), 0.72 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.74, 151.28, 142.57, 136.34, 133.86, 128.64, 128.27, 128.19, 118.40, 110.64, 109.03, 86.06, 67.82, 54.96, 42.19, 39.77, 39.69, 36.95, 23.53, 9.60; IR (neat): ν = 2964 m, 2933 m, 1703 s, 1552 s, 1424 s, 1243 s, 1114 m, 1011 m, 925 m, 737 s, 598 m cm^{-1}; ESI-MS *m/z* 399.2 $(M + H)^+$, 421.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{22}H_{26}N_2O_5Na$ $(M + Na)^+$ *m/z* 421.1734, found 421.1738.

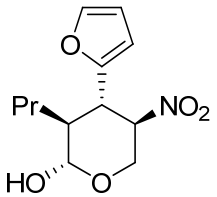
General procedure for cascade Michael-acetalization process of aldehydes with hydroxymethyl substituted nitroolefins: Valeradehyde (0.40 mmol) was added to a suspension of catalyst **1** (20 mol %), hydroxymethyl substituted nitroolefins **11** (0.20 mmol) and benzoic acid (60 mol %) in water (0.40 mL) at room temperature, and stirred until complete conversion of the starting materials (monitored by TLC). The reaction mixture was diluted with ethyl acetate, dried over Na_2SO_4 and concentrated. Purification by flash column chromatography afforded **12.** The enantiomeric excess (ee) was determined by HPLC on a chiral phase.



12a

(2S,3S,4R,5R)-5-Nitro-4-phenyl-3-propyl-tetrahydro-pyran-2-ol 12a. $[\alpha]_D^{28}$ = -8.43 (*c* 0.42, MeOH); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 3H), 7.20-7.18 (m, 2H), 5.31 (s, 1H), 4.87 (dq, *J* = 4.8, 11.2 Hz, 1H), 4.43 (t, *J* = 10.8 Hz, 1H), 4.04 (dd, *J* = 4.8, 10.4 Hz, 1H), 3.52 (t, *J* = 11.6 Hz, 1H), 2.68 (brs, 1H), 2.03-1.98 (m, 1H), 1.36-1.27 (m, 2H), 1.11-1.04 (m, 1H), 0.97-0.90 (m, 1H), 0.75 (t, *J* = 7.2 Hz, 3H); ^1H

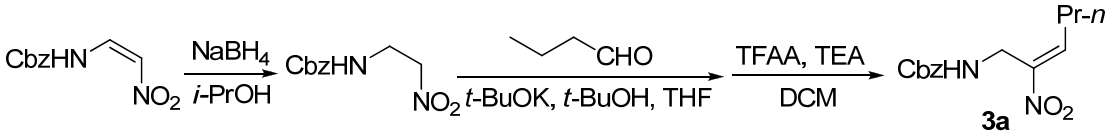
NMR (400 MHz, MeOD) δ 7.35-7.32 (m, 2H), 7.28-7.25 (m, 3H), 5.23 (d, *J* = 2.8 Hz, 1H), 5.03 (dt, *J* = 5.2, 11.2 Hz, 1H), 4.40 (t, *J* = 10.4 Hz, 1H), 4.00 (dd, *J* = 4.8, 10.4 Hz, 1H), 3.48 (t, *J* = 12.0 Hz, 1H), 2.06-2.01 (m, 1H), 1.38-1.25 (m, 2H), 1.11-1.03 (m, 1H), 0.93-0.84 (m, 1H), 0.74 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.55, 129.39, 129.07, 128.10, 127.97, 92.20, 87.76, 60.36, 45.35, 43.35, 30.90, 19.71, 14.13; ^{13}C NMR (100 MHz, MeOD) δ 139.59, 129.76, 128.63, 92.84, 89.11, 61.14, 47.00, 44.81, 32.29, 20.60, 14.43; IR (neat): ν = 3419 br, 2950 m, 1542 s, 1455m, 1352 m, 1059 m, 1033 m, 930 m, 692 m cm^{-1}; EI-MS *m/z* 265 M^+, HRMS (EI) calcd for $C_{14}H_{19}NO_4$ M^+ *m/z* 265.1314, found 265.1319; HPLC: IC column, hexane/*i*-PrOH = 90:10, flow rate 0.7 mL/min, 214 nm, t_R = 8.3 min (major), t_R = 7.5 min (minor), *ee*>99%. (*Noteworthy is that some additional peaks (for isomer) were observed in ^{13}C NMR spectradue to isomerization)*



12b

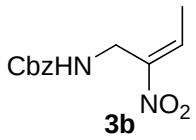
(2S,3S,4S,5R)-4-Furan-2-yl-5-nitro-3-propyl-tetrahydro-pyran-2-ol 12b. $[\alpha]_D^{28}$ = -0.01 (*c* 1.96, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.36 (m, 1H), 6.30-6.26 (m, 1H), 6.18-6.16 (m, 1H), 5.27 (d, *J* = 2.8 Hz, 1H), 4.94 (dt, *J* = 4.8, 11.2 Hz, 1H), 4.37 (t, *J* = 10.8 Hz, 1H), 4.02 (dd, *J* = 4.8, 10.4 Hz, 2H), 3.65 (t, *J* = 11.6 Hz, 1H), 2.13-2.07 (m, 1H), 1.40-1.25 (m, 2H), 1.14-0.97 (m, 2H), 0.81 (t, *J* = 6.8 Hz, 3H); ^{1}H NMR (400 MHz, MeOD) δ 7.44-7.42 (m, 1H), 6.32-6.30 (m, 1H), 6.19-6.18 (m, 1H), 5.18 (d, *J* = 2.8 Hz, 1H), 4.96 (dt, *J* = 5.2, 11.2 Hz, 1H), 4.34 (t, *J* = 10.8 Hz, 1H), 3.97 (dd, *J* = 4.8, 10.4 Hz, 1H), 3.60 (t, *J* = 11.2 Hz, 1H), 2.07-2.01 (m, 1H), 1.39-1.28 (m, 2H), 1.10-1.03 (m, 1H), 1.01-0.93 (m, 1H), 0.71 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 150.55, 142.51, 110.41, 109.35, 92.04, 85.20, 59.97, 41.74, 39.36, 31.30, 19.68, 14.20; ^{13}C NMR (100 MHz, MeOD) δ 152.66, 143.45, 111.20, 109.63, 92.65, 86.71, 60.62, 43.52, 40.82, 32.58, 20.54, 14.48; IR (neat): ν = 3396 br, 2954 m, 2873 w, 1541 s, 1466 w, 1357 w, 1277 w, 1152 m, 1032 w, 1009 m, 928 m, 908 w, 726 m cm^{-1}; EI-MS *m/z* 255 M^+, HRMS (EI) calcd for $C_{12}H_{17}NO_5$ M^+ *m/z*

255.1107, found 255.1113; HPLC: AD-H column, hexane/*i*-PrOH = 95:5, flow rate 0.7 mL/min, 214 nm, major isomer: t_R = 28.0 min (major), t_R = 48.5 min (minor), *ee*>99%. (*Noteworthy is that some additional peaks (for isomer) were observed in* ^{13}C *NMR spectradue to isomerization)*



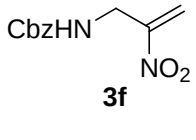
Typical procedure for assembly of 1-protected aminomethyl 2-alkyl substituted nitroalkenes 3a. To a solution of ((*Z*)-2-nitrovinyl)-carbamic acid benzyl ester (2.24 g, 10 mmol) in 50 mL of *i*-PrOH were added $NaBH_4$ (760 mg, 2.0 eq, 20 mmol) at 0 ^oC. The resultant solution was warmed to rt. After stirring at rt for 2 h, 1 mL acetone and 20 mL saturate NH_4Cl aqueous solution was added slowly, the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4 and concentrated to give reduced product as light yellow solid, which was dissolved in 10 mL *t*-BuOH and 10 mL THF. To this solution was added *n*-butylaldehyde (15 mmol, 1.5 equiv.) and *t*-BuOK (112 mg, 1 mmol, 0.1 equiv.) at 0 ^oC. The resultant solution was warmed to rt. After stirring at rt for 5 h, the reaction mixture was diluted with ethyl ether and washed with water, the aqueous phase was extracted with ethyl ether three times. The combined organic phase was washed with brine and dried over Na_2SO_4 and concentrated to give condensation product, which was dissolved in 20 mL CH_2Cl_2. To this solution was added TEA (20 mmol, 2 equiv.) and TFAA (15 mmol) slowly at -20 ^oC. After stirring at -20 ^oC for 1.5 h, the reaction mixture was diluted with CH_2Cl_2 and washed with water. The aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phase was washed with brine and dried over Na_2SO_4 and concentrated. Purification of the residue by flash column chromatography (silica gel, 10:1 petroleum ether/ethyl acetate as eluent) afforded the corresponding (*E*)-2-nitro-hex-2-enyl)carbamic acid benzyl ester **3a** (2.06 g, 74% for 3 steps). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 5.47 (brs, 1H), 5.08 (s, 2H), 4.28 (d, *J* = 6.4 Hz, 2H), 2.50-2.45 (m, 2H), 1.58-1.53 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.17, 148.20, 140.87,

136.25, 128.64, 128.32, 128.15, 67.11, 36.36, 29.96, 21.89, 13.79; IR (neat): ν = 3334 br, 2962 m, 1714 s, 1520 s, 1332 m, 1238 s, 1136 s, 738 m, 698 m cm^{-1}; ESI-MS *m/z* 279.2 $(M + H)^+$, 301.2 $(M + Na)^+$, HRMS (ESI) calcd for $C_{14}H_{18}N_2O_4Na$ $(M + Na)^+$ *m/z* 301.1159, found 301.1164.



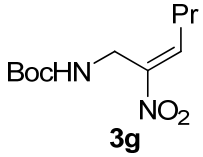
3b

((*E*)-2-Nitrobut-2-enyl)carbamic acid benzyl ester 3b. 49% yield for three steps. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 6H), 5.45 (brs, 1H), 4.99 (s, 2H), 4.18 (d, *J* = 6.4 Hz, 2H), 2.01 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.27, 148.85, 136.34, 136.15, 128.58, 128.26, 128.08, 67.06, 36.01, 13.74; IR (neat): ν = 3333 br, 2956 m, 1714 s, 1515 s, 1341 m, 1241 s, 1137 m, 1080 m, 975 m, 846 m, 777 m, 698 m cm^{-1}; ESI-MS *m/z* 273.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{12}H_{14}N_2O_4Na$ $(M + Na)^+$ *m/z* 273.0846, found 273.0846.



3f

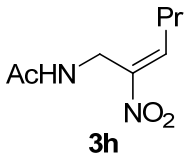
(2-Nitroallyl)carbamic acid benzyl ester 3f. 40% for three steps. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 5H), 6.58 (s, 1H), 5.92 (s, 1H), 5.38 (brs, 1H), 5.11 (s, 2H), 4.27 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.22, 153.90, 136.10, 128.76, 128.52, 128.34, 120.80, 67.41, 40.50; ESI-MS *m/z* 236.1 $(M + H)^+$, 259.1 $(M + Na)^+$.



3g

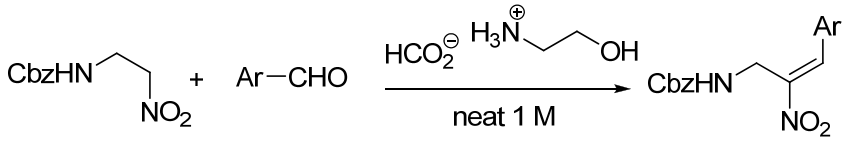
((*E*)-2-Nitrohex-2-enyl)carbamic acid *tert*-butyl ester 3g. Compound **3g** was prepared from ((*Z*)-2-nitrovinyl)carbamic acid *tert*-butyl ester and *n*-butylaldehyde in 59% overall yield according to typical procedure. ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.0 Hz, 1H), 5.19 (b rs, 1H), 4.23 (d, *J* = 6.0 Hz, 2H), 2.48 (q, *J* = 7.6 Hz, 2H), 1.61-1.52 (m, 2H), 1.42 (s, 9H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.50, 148.78, 140.47, 79.99, 35.88, 29.93, 28.40, 21.92, 13.72; IR (neat):

ν = 3419 br, 2966 s, 2935 m, 1716 s, 1526 s, 1367 m, 1332 m, 1249 m, 1167 s, 932 w, 857 w cm^{-1}; ESI-MS *m/z* 267.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{11}H_{20}N_2O_4Na$ $(M + Na)^+$ *m/z* 267.1315, found 267.1319.

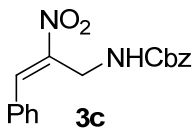


3h

***N*-((*E*)-2-Nitrohex-2-enyl)acetamide 3h.** Compound **3h** was prepared from *N*-((*Z*)-2-nitrovinyl)acetamide and *n*-butylaldehyde in 50% overall yield accoeding to typical procedure. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.0 Hz, 1H), 6.30 (br s, 1H), 4.35 (d, *J* = 6.4 Hz, 2H), 2.50 (q, *J* = 7.6 Hz, 2H), 1.98 (s, 3H), 1.61-1.52 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.18, 148.03, 140.95, 34.65, 29.93, 22.93, 21.80, 13.73; IR (neat): ν = 3255 s, 2962 m, 1668 m, 1644 m, 1516 s, 1338 m, 1288 m, 1095 w, 1075 w, 748 w cm^{-1}; ESI-MS *m/z* 187.1 $(M + H)^+$, 219.2 $(M + Na)^+$, HRMS (MALDI) calcd for $C_8H_{14}N_2O_3Na$ $(M + Na)^+$ *m/z* 209.0897, found 209.0897.



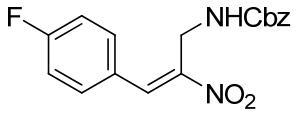
Typical procedure for assembly of 1-protected aminomethyl 2-aryl substituted nitroalkenes. A mixture of (2-nitroethyl)carbamic acid benzyl ester (1 mmol) and arylaldehyde (1 mmol) in 1 mL 2-HEAF was stirred overnight at rt until the starting material disappeared. The mixture was partitioned between water and ethyl acetate. The aqueous phase was extracted with ethyl acetate. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated. Purification of the residue by flash column chromatography (silica gel, 15:1 to 10:1 petroleum ether/ethyl acetate as eluent) afforded the corresponding nitroalkene.



3c

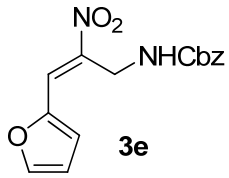
((*E*)-2-Nitro-3-phenylallyl)carbamic acid benzyl ester 3c. 85% yield. ^1H NMR

(400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.72-7.66 (m, 2H), 7.52-7.45 (m, 3H), 7.40-7.30 (m, 5H), 5.50 (brs, 1H), 5.12 (s, 2H), 4.58 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.20, 147.27, 137.21, 136.20, 131.10, 131.00, 130.48, 129.34, 128.70, 128.40, 128.24, 67.29, 37.79; ESI-MS *m/z* 335.3 $(M + Na)^+$, HRMS (MALDI) calcd for $C_{17}H_{16}N_2O_4Na$ $(M + Na)^+$ *m/z* 335.1002, found 335.1004.



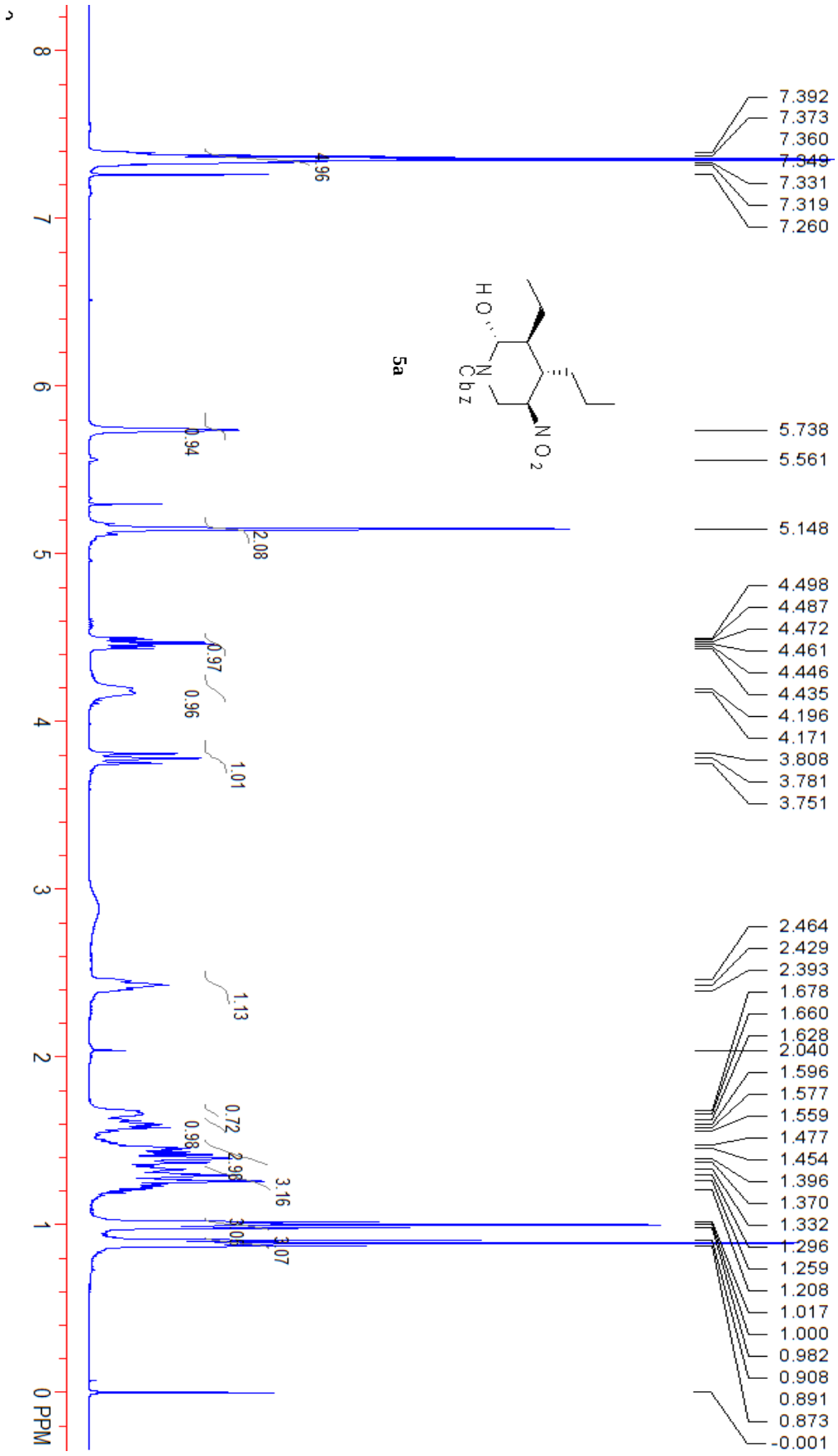
3d

((*E*)-3-(4-Fluorophenyl)-2-nitroallyl)carbamic acid phenethyl ester 3d. 83% yield, ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.78-7.70 (m, 2H), 7.38-7.30 (m, 5H), 7.19-7.15 (m, 2H), 5.55 (brs, 1H), 5.12 (s, 2H), 5.54 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.21 (d, *J* = 252.4 Hz), 156.20, 146.96, 136.06, 135.92, 132.78 (d, *J* = 8.0 Hz), 128.62, 128.24 (d, *J* = 20.0 Hz), 127.03 (d, *J* = 3.7 Hz), 116.55 (d, *J* = 21.8 Hz), 67.25, 37.64; IR (neat): ν = 3249 w, 3144 w, 1728 s, 1600 m, 1516 m, 1407 m, 1347 m, 1242 m, 1033 m, 858 w, 755 w, 696 w cm^{-1}; ESI-MS *m/z* 353.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{17}H_{15}FN_2O_4Na$ $(M + Na)^+$ *m/z* 353.0908, found 353.0907.



3e

((*E*)-3-Furan-2-yl-2-nitroallyl)carbamic acid benzyl ester 3e. 86% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.73 (s, 1H), 7.40-7.27 (m, 5H), 7.13 (s, 1H), 6.62 (s, 1H), 5.44 (brs, 1H), 5.09 (s, 2H), 4.83 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.22, 147.75, 146.82, 143.49, 136.24, 128.59, 128.26, 128.16, 123.09, 121.88, 113.43, 67.08, 37.63; IR (neat): ν = 3318 s, 2922 s, 2851 m, 1686 s, 1498 m, 1311 m, 1269 m, 981 w, 770 m, 699 w cm^{-1}; ESI-MS *m/z* 325.3 $(M + Na)^+$, HRMS (ESI) calcd for $C_{15}H_{14}N_2O_5Na(M + Na)^+$ *m/z* 325.0795, found 325.0799.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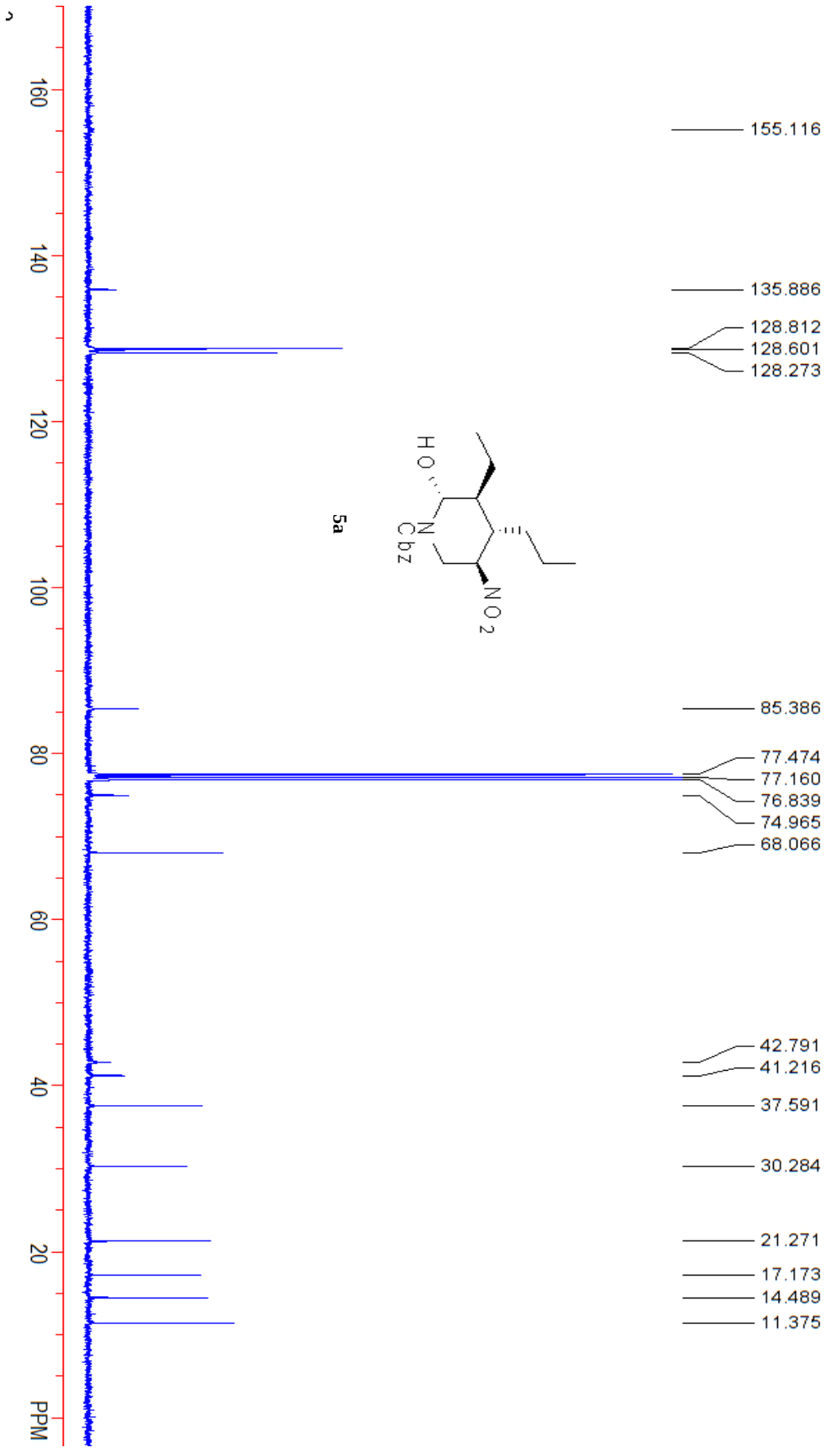
0.72
0.98
2.98
3.16
3.05
3.07
5a
HO
N
Cbz
NO2
8
7
6
5
4
3
2
1
0 PPM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128.812
128.601
128.273
85.386
77.474
77.160
76.839
74.965
68.066
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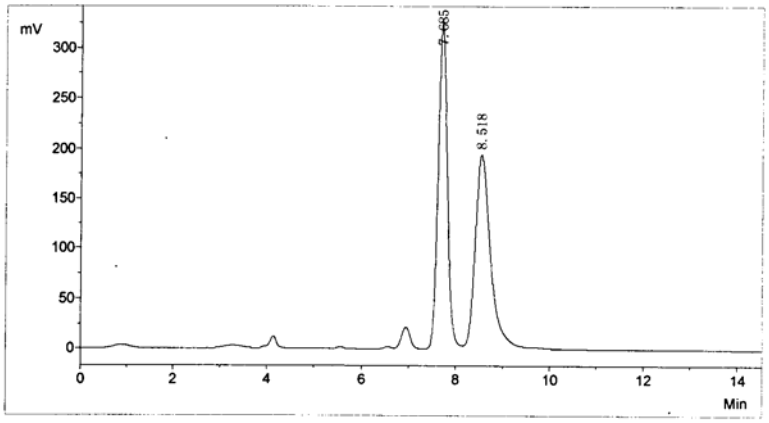
37.591
30.284
21.271
17.173
14.489
11.375
160
140
120
100
80
60
40
20
PPM
HO
N
Cbz
NO2
5a

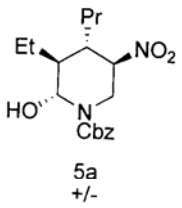
HPLC REPORT

Data File:ZSL-17-41+- PA-2 73 214 0.7.che Sample name:

Date:2010-06-01 Time :09:21

Operator:





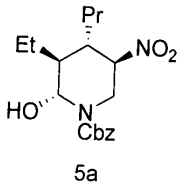
5a
+/-

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		7.685	324496.4	4449265.3	50.8309
2	2		8.518	192347.9	4303805.4	49.1691
Total				516844.3	8753070.6	100.0000

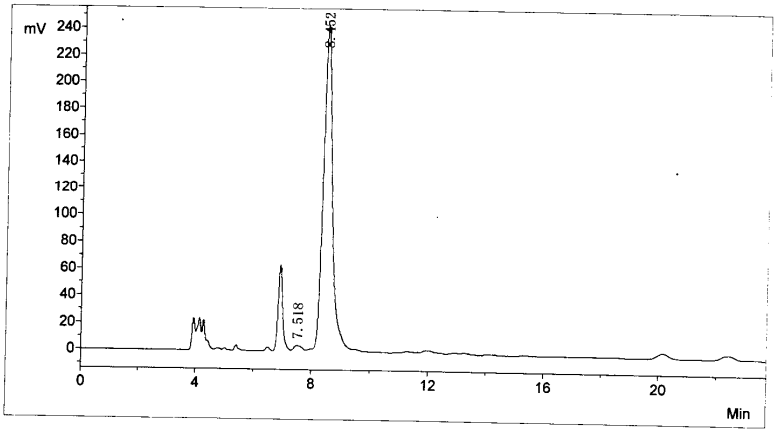
HPLC REPORT

Data File:ZSL-17-40.che
Date:2010-06-01
Operator:

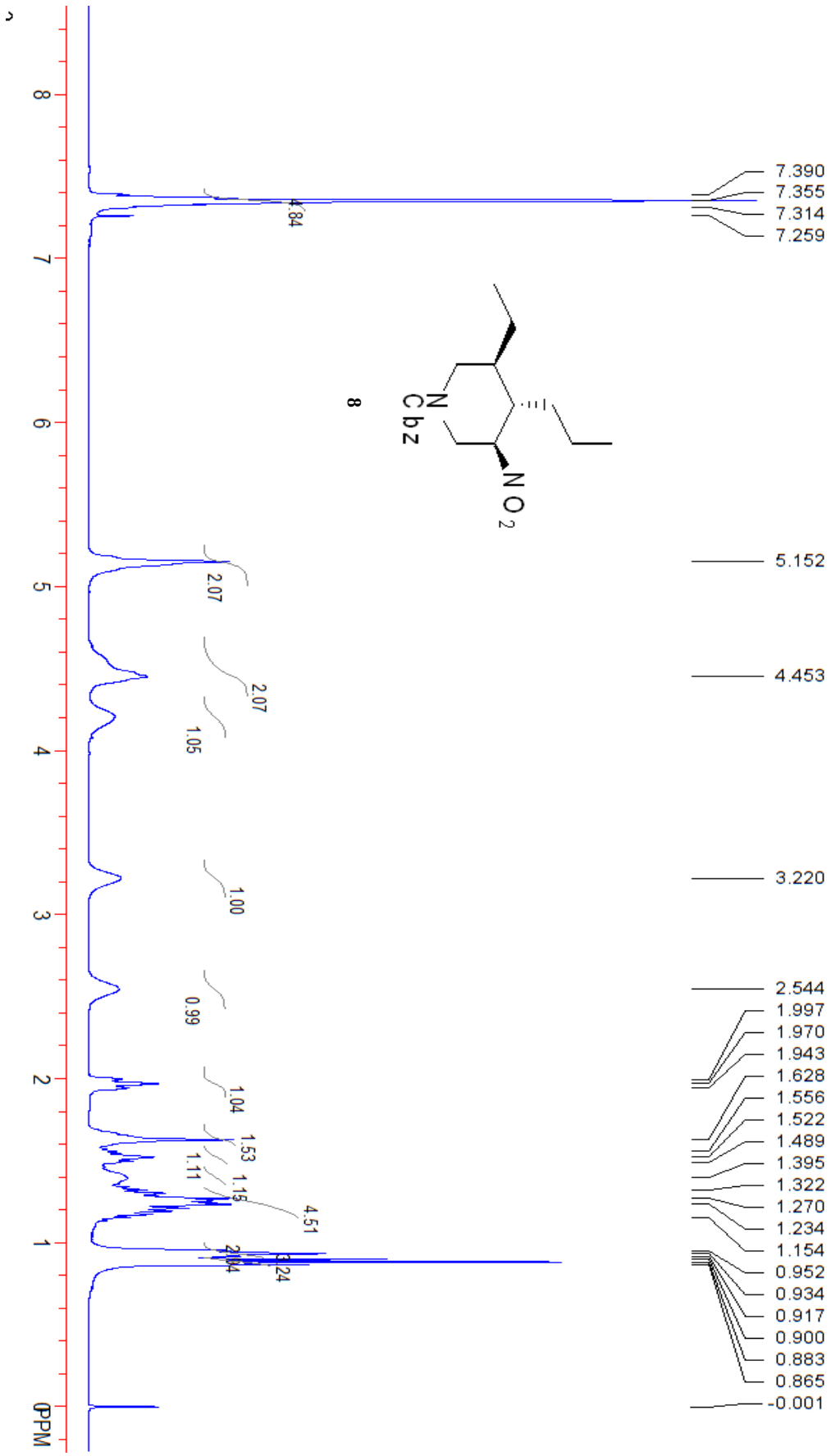
Sample name:
Time :09:46



5a



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		7.518	3392.2	55822.7	1.0677
2	2		8.452	241699.8	5172392.5	98.9323


8
N
Cbz
NO2
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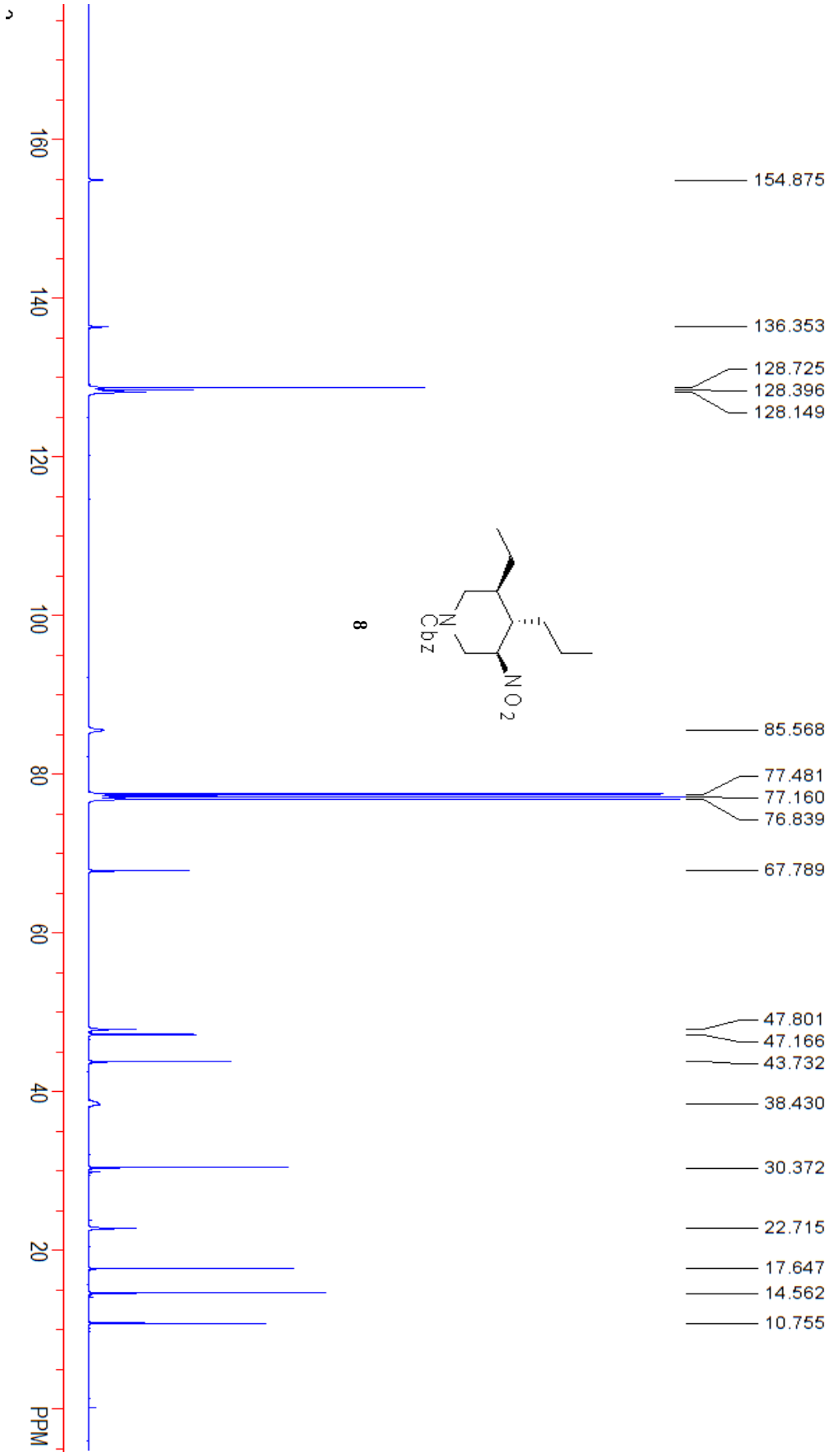
7.355
7.314
7.259
5.152
4.453
3.220
2.544
1.997
1.970
1.943
1.628
1.556
1.522
1.489
1.395
1.322
1.270
1.234
1.154
0.952
0.934
0.917
0.900
0.883
0.865
-0.001
4.84
2.07
2.07
1.05
1.00
0.99
1.04
1.53
1.11
1.15
4.51
2.04
3.24
PPM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128.396
128.149
85.568
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77.160
76.839
67.789
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38.430
30.372
22.715
17.647
14.562
10.755
160
140
120
100
80
60
40
20
PPM
8
N
Cbz
NO2

HPLC Report

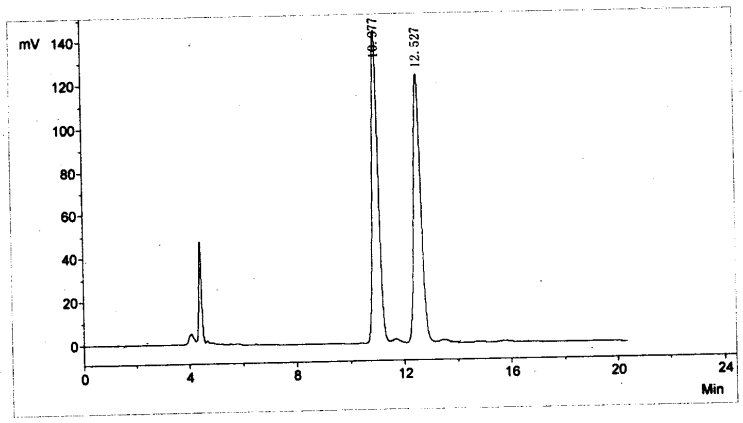
Sample Name:

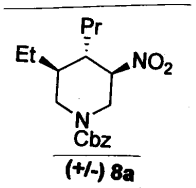
Operator:

Time:13:28

Data File:ZSL6-25+- PA-2730.7214.che

Date:2010-07-07





(+/-) 8a

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	10.977	144556.2	2412167.5	50.9185
2	2	12.527	123530.9	2325147.1	49.0815
Total			268087.1	4737314.6	100.0000

HPLC Report

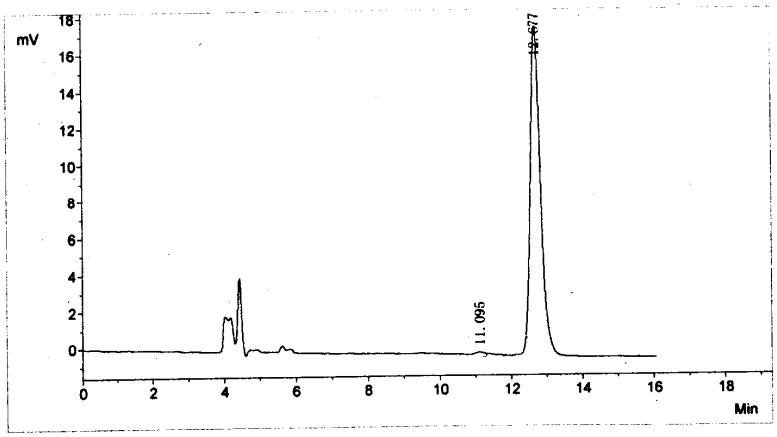
Sample Name:

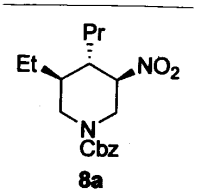
Operator:

Time:14:15

Data File:ZSL6-24-1.che

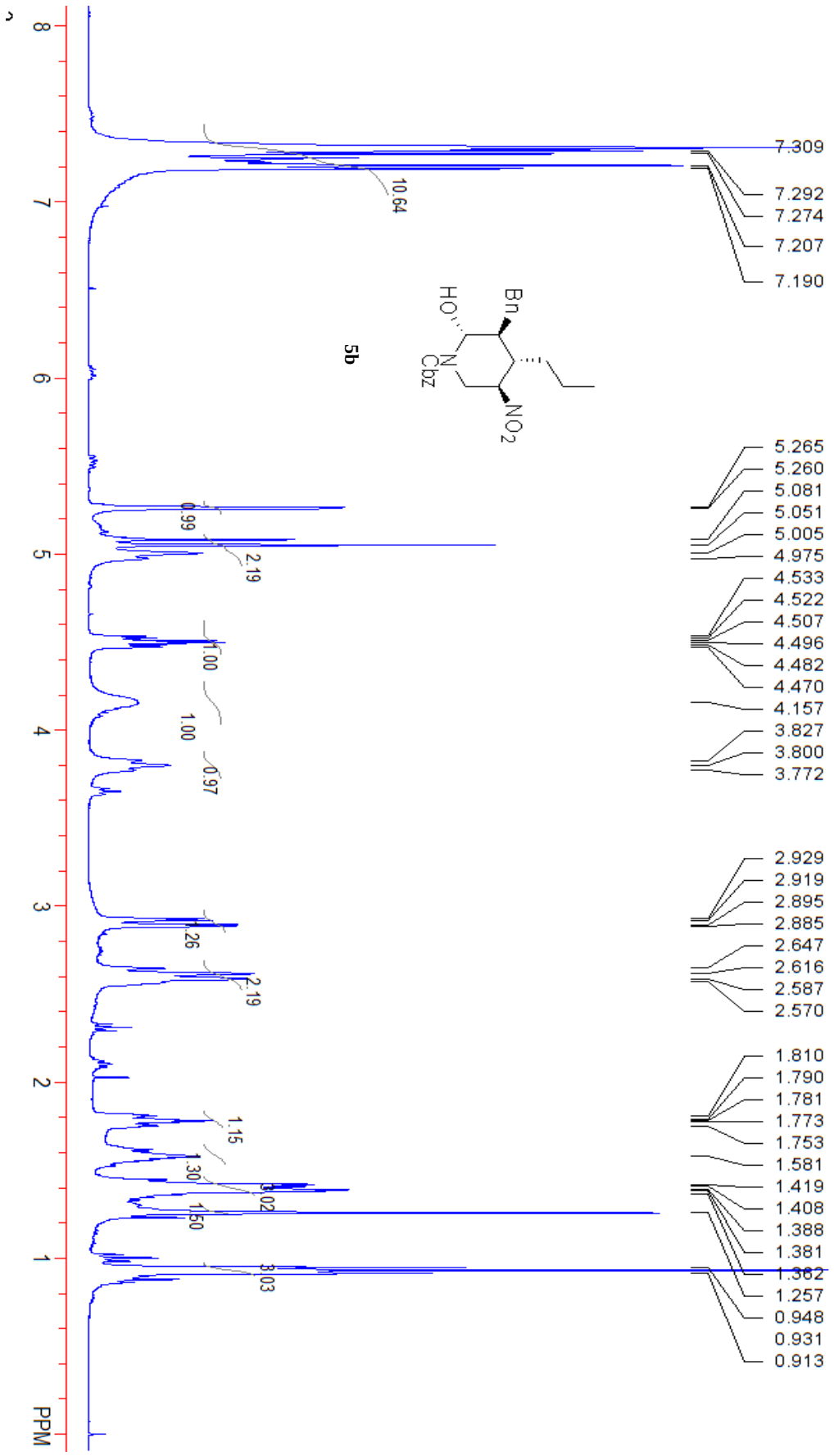
Date:2010-07-07





8a

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	11.095	136.6	2559.5	0.7148
2	2	12.677	17767.1	355502.8	99.2852
Total			17903.7	358062.3	100.0000


5b
Bn
HO
N
Cbz
NO2
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7.292
7.274
7.207
7.190
10.64
5.265
5.260
5.081
5.051
5.005
4.975
4.533
4.522
4.507
4.496
4.482
4.470
4.157
3.827
3.800
3.772
2.929
2.919
2.895
2.885
2.647
2.616
2.587
2.570
1.810
1.790
1.781
1.773
1.753
1.581
1.419
1.408
1.388
1.381
1.362
1.257
0.948
0.931
0.913
0.99
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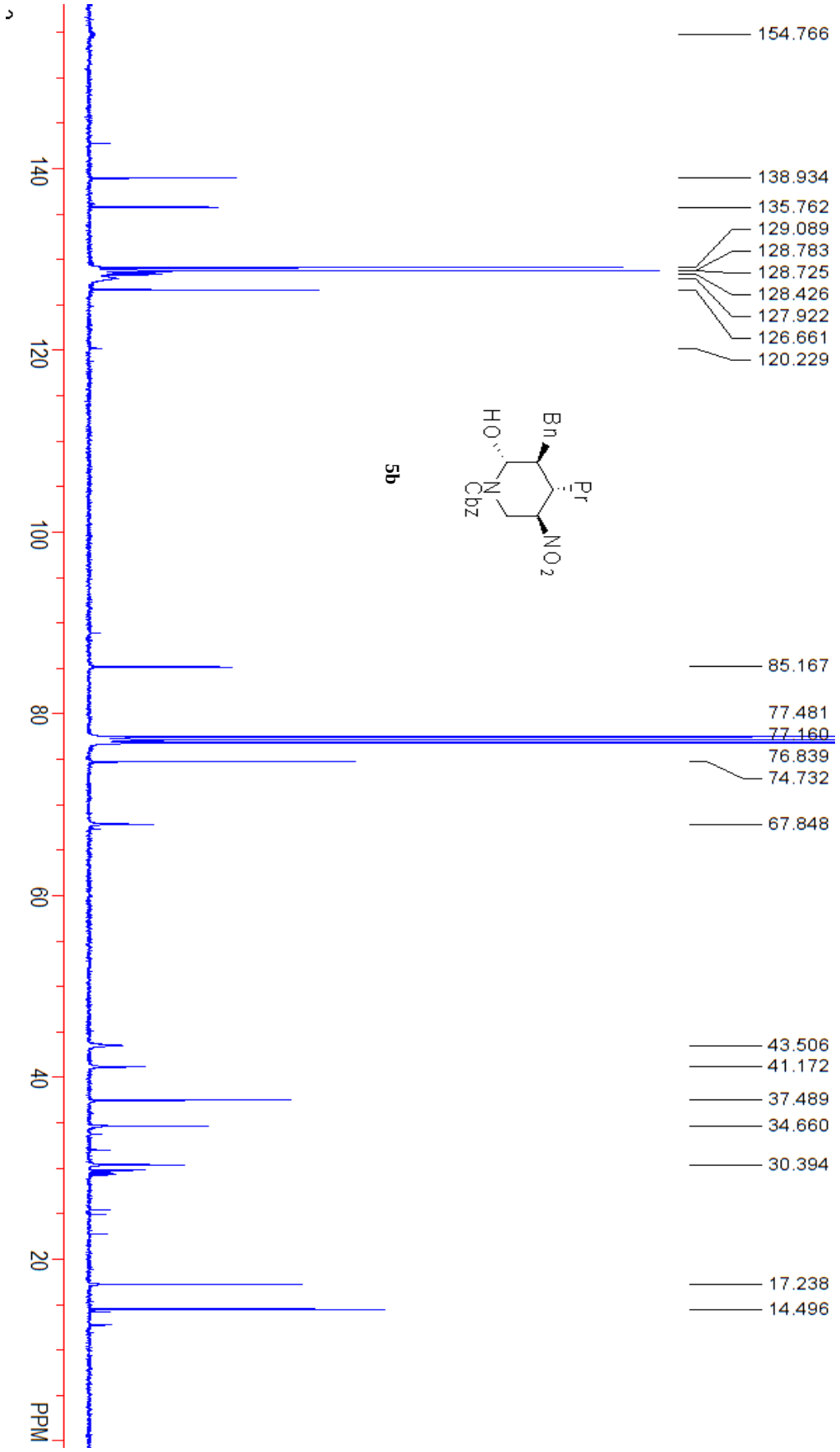
1.00
1.00
0.97
1.26
2.19
1.15
1.30
0.92
1.50
3.03
PPM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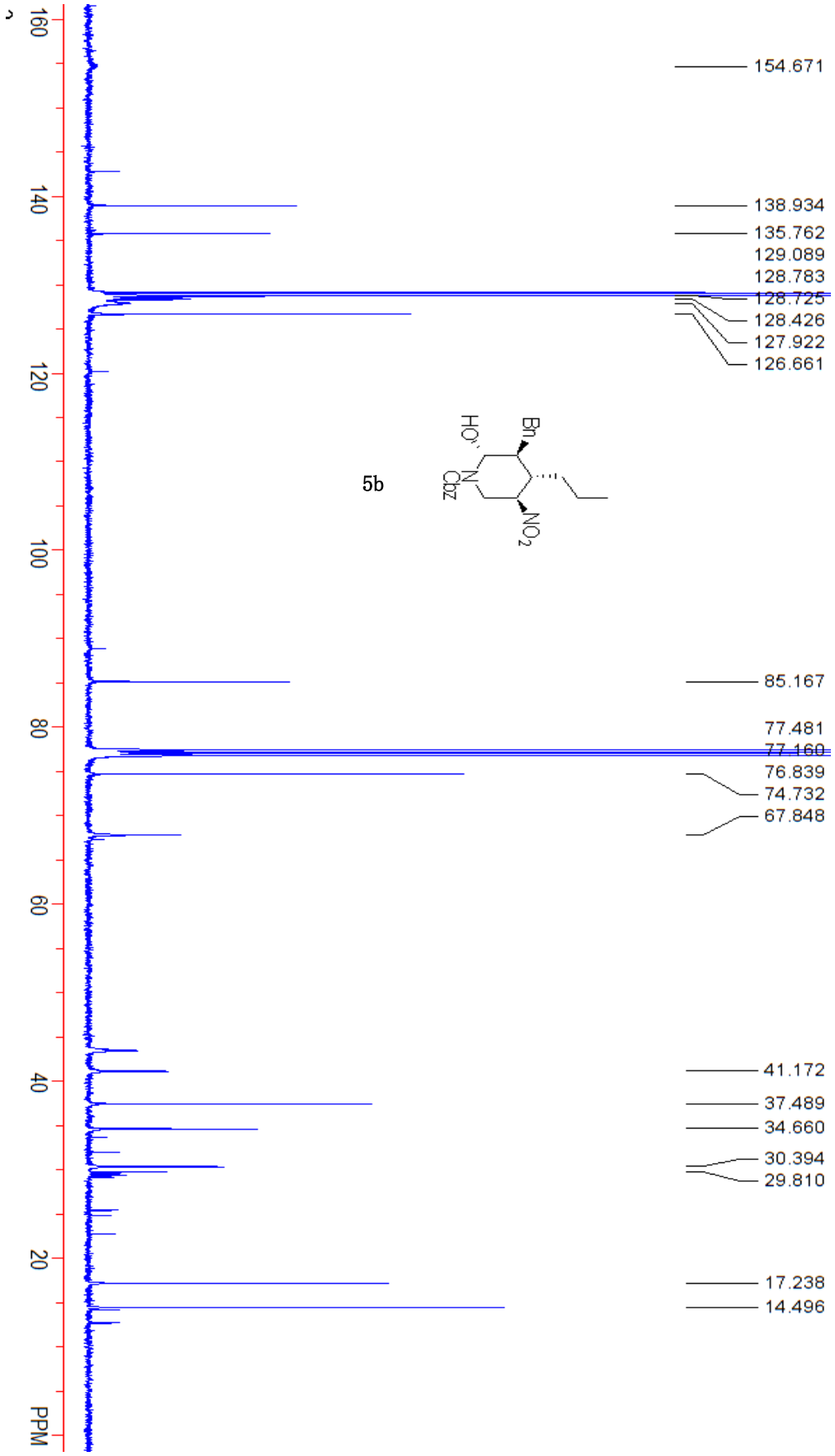
135.762
129.089
128.783
128.725
128.426
127.922
126.661
120.229
85.167
77.481
77.160
76.839
74.732
67.848
43.506
41.172
37.489
34.660
30.394
17.238
14.496
140
120
100
80
60
40
20
PPM
5b
HO
N
Cbz
Bn
Pr
NO2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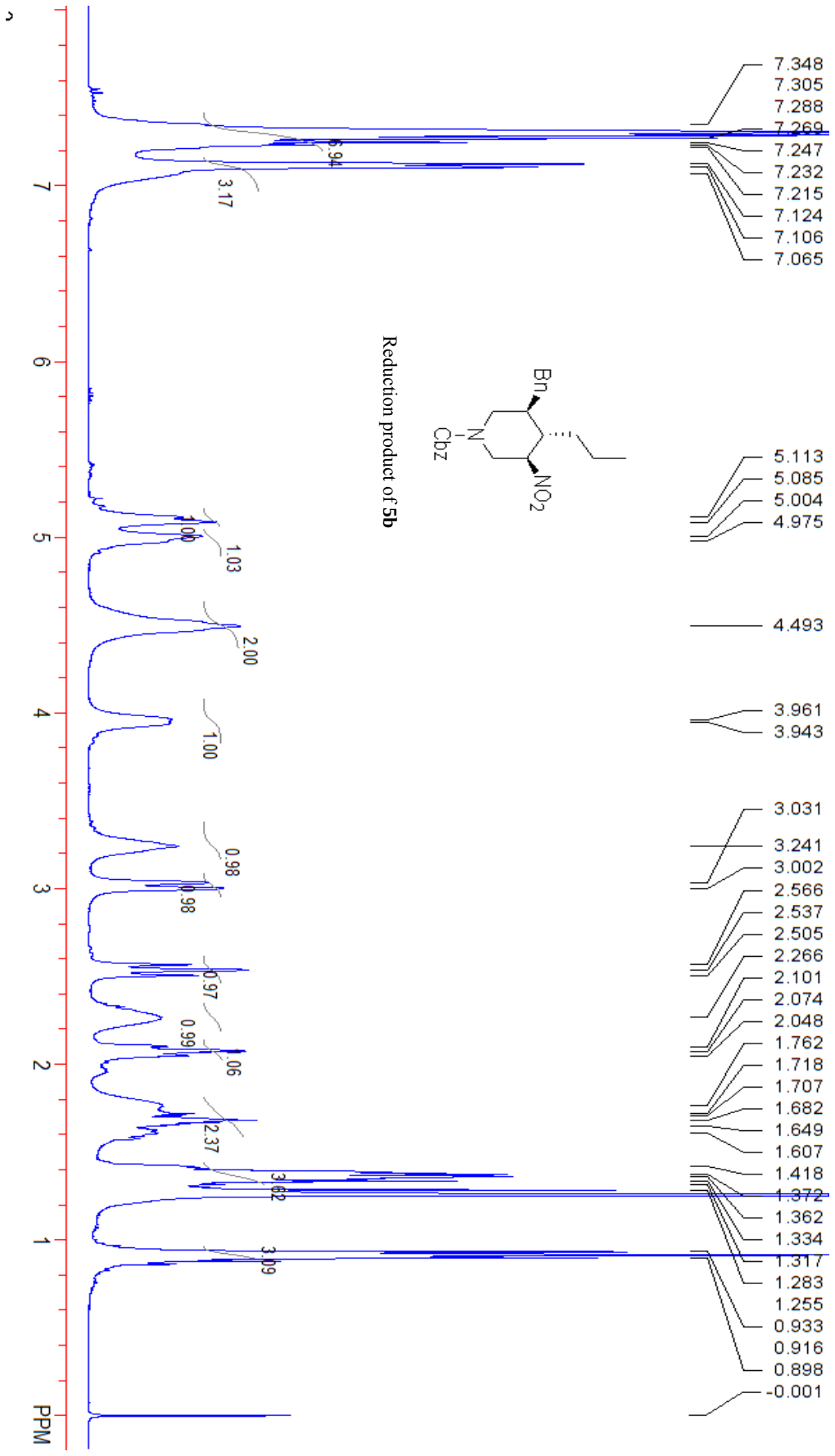
138.934
135.762
129.089
128.783
128.725
128.426
127.922
126.661
85.167
77.481
77.160
76.839
74.732
67.848
41.172
37.489
34.660
30.394
29.810
17.238
14.496
160
140
120
100
80
60
40
20
PPM
5b
HO
N
Cbz
Bn
NO2


Reduction product of 5b
Bn
N
Cbz
NO2
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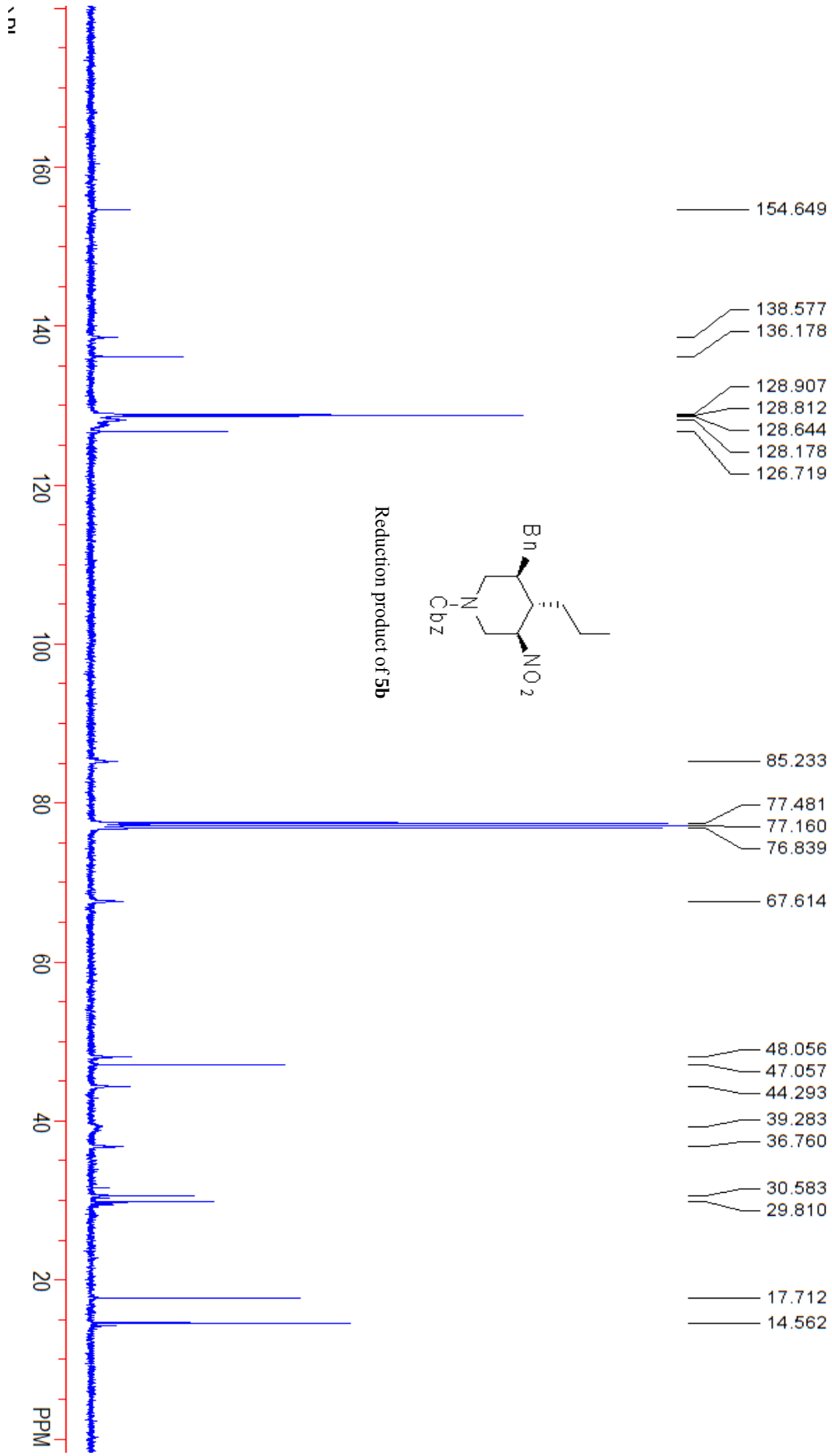
7.269
7.247
7.232
7.215
7.124
7.106
7.065
5.113
5.085
5.004
4.975
4.493
3.961
3.943
3.031
3.241
3.002
2.566
2.537
2.505
2.266
2.101
2.074
2.048
1.762
1.718
1.707
1.682
1.649
1.607
1.418
1.372
1.362
1.334
1.317
1.283
1.255
0.933
0.916
0.898
-0.001
6.94
3.17
1.00
1.03
2.00
1.00
0.98
0.98
0.97
0.99
1.06
2.37
3.62
3.09
PPM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136.178
128.907
128.812
128.644
128.178
126.719
85.233
77.481
77.160
76.839
67.614
48.056
47.057
44.293
39.283
36.760
30.583
29.810
17.712
14.562
PPM
160
140
120
100
80
60
40
20
Reduction product of 5b
Bn
N
Cbz
NO2

HPLC Report

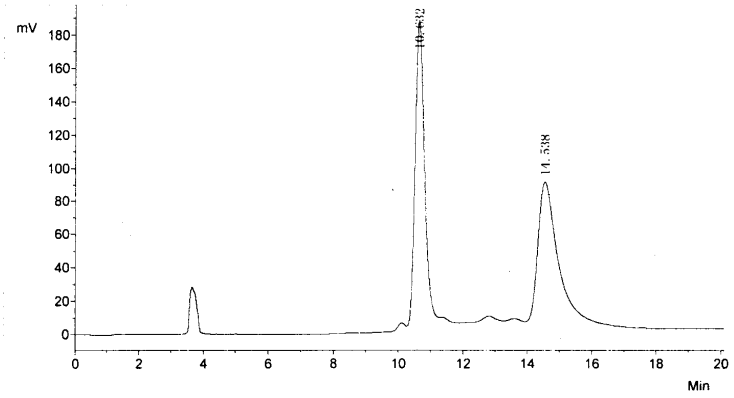
Sample Name:

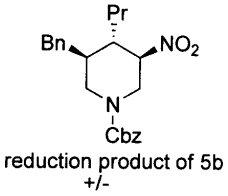
Operator:

Time:13:51

Data File:ZSL17-29-2+-PC-2-730.7214.che

Date:2010-09-07





reduction product of 5b

+/-

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	10.632	181398.8	3576778.5	49.7194
2	2	14.538	74437.0	3617148.2	50.2806
Total			255835.8	7193926.7	100.0000

HPLC Report

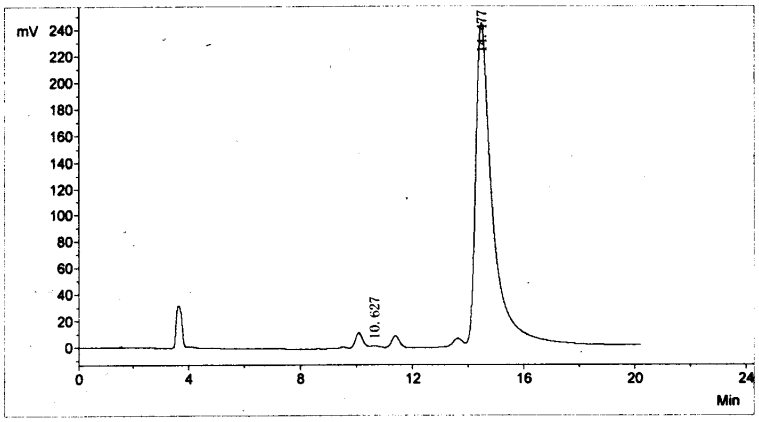
Sample Name:

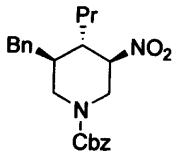
Operator:

Time:14:16

Data File:ZSL6-33-2.che

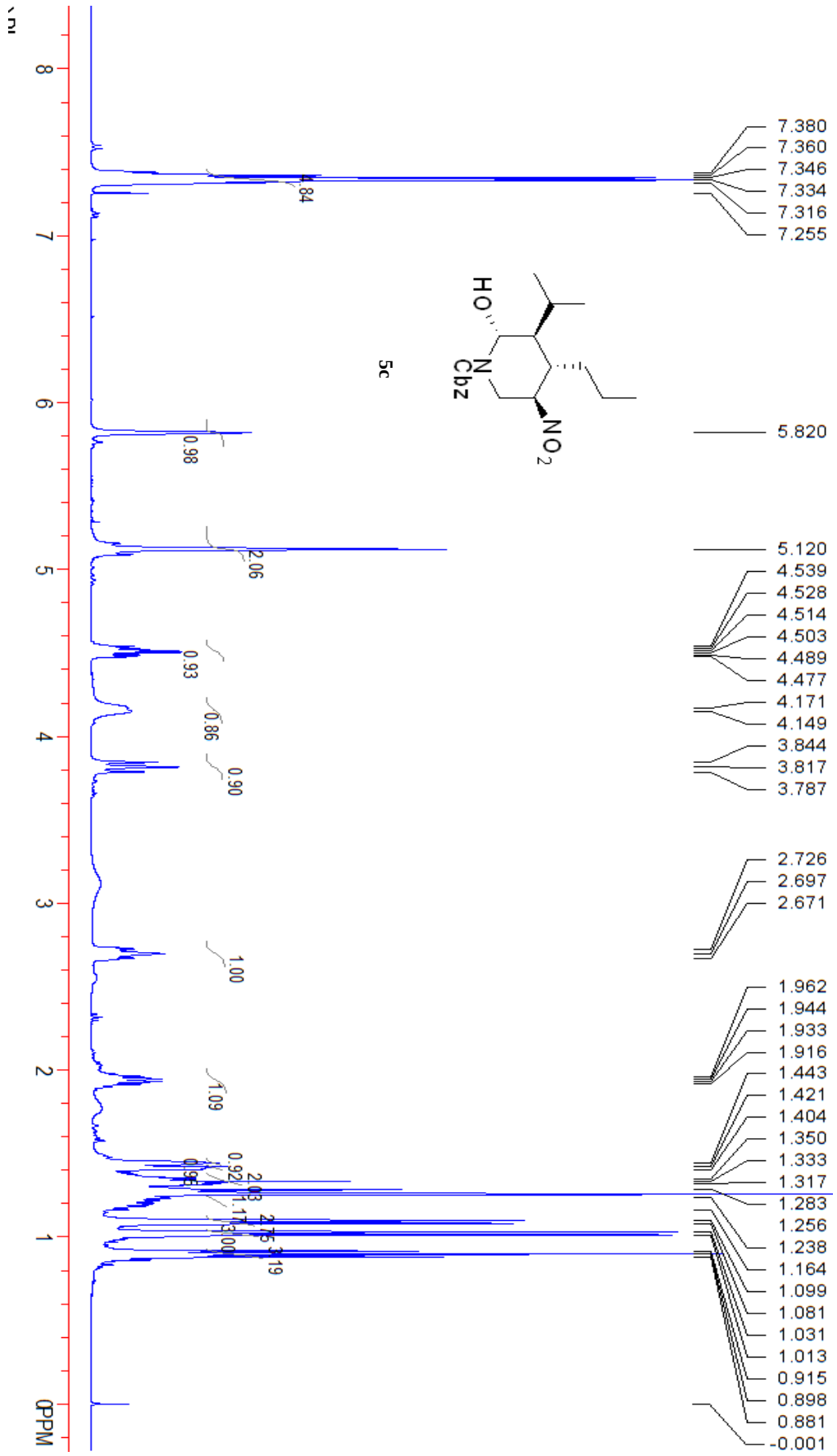
Date:2010-09-07





reduction product of 5b

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	10.627	621.7	8241.4	0.0831
2	2	14.477	241752.0	9907979.4	99.9169
Total			242373.7	9916220.9	100.0000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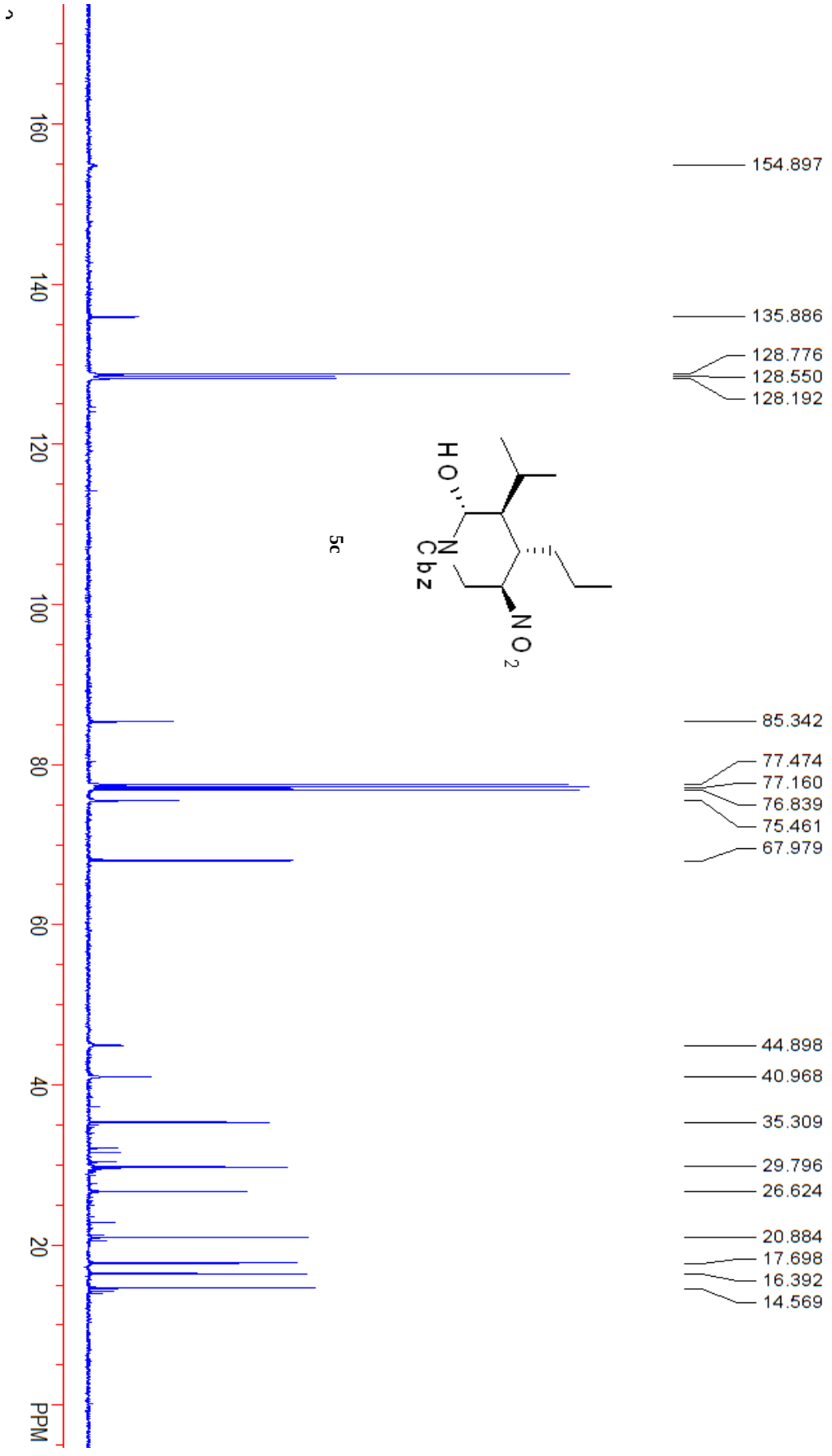
7.255
5.820
5.120
4.539
4.528
4.514
4.503
4.489
4.477
4.171
4.149
3.844
3.817
3.787
2.726
2.697
2.671
1.962
1.944
1.933
1.916
1.443
1.421
1.404
1.350
1.333
1.317
1.283
1.256
1.238
1.164
1.099
1.081
1.031
1.013
0.915
0.898
0.881
-0.001
5c
HO
N
Cbz
NO2
PPM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128.550
128.192
85.342
77.474
77.160
76.839
75.461
67.979
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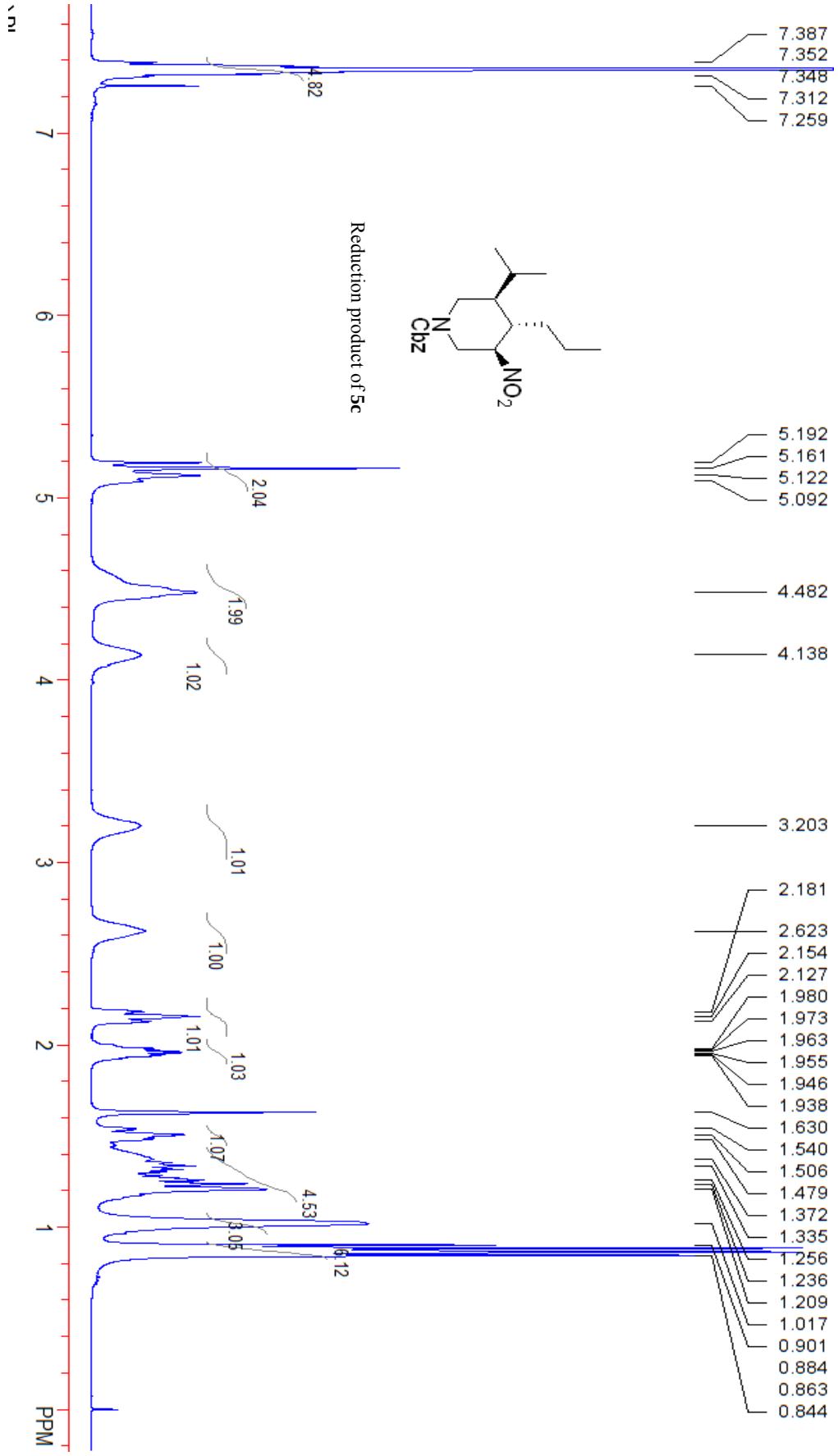
40.968
35.309
29.796
26.624
20.884
17.698
16.392
14.569
160
140
120
100
80
60
40
20
PPM
5c
HO
N
Cbz
NO2


Reduction product of 5c
Cbz
NO2
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7.259
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5.161
5.122
5.092
4.482
4.138
3.203
2.181
2.623
2.154
2.127
1.980
1.973
1.963
1.955
1.946
1.938
1.630
1.540
1.506
1.479
1.372
1.335
1.256
1.236
1.209
1.017
0.901
0.884
0.863
0.844
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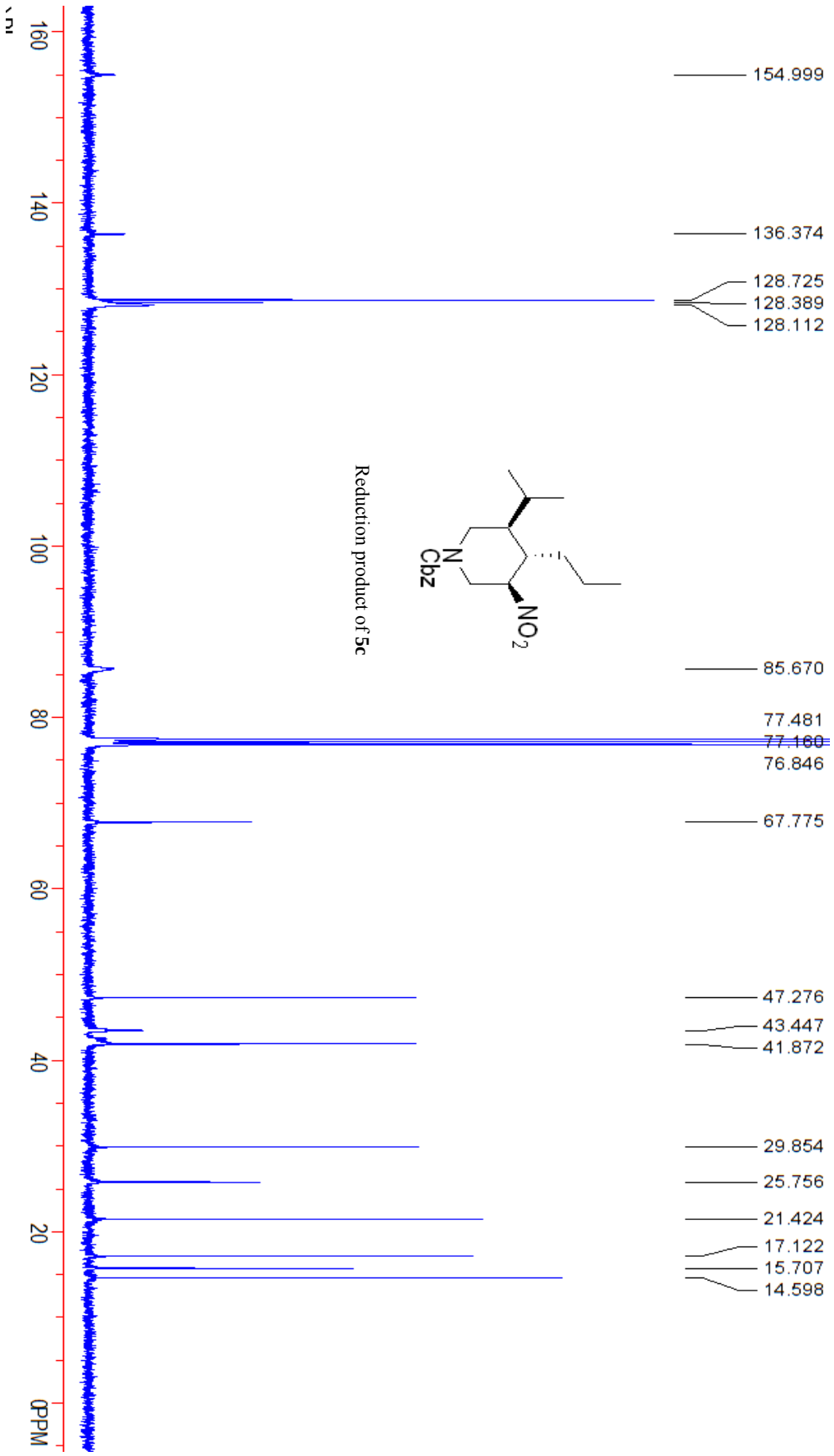
1.03
1.07
4.53
3.05
6.12
PPM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77.160
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67.775
47.276
43.447
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21.424
17.122
15.707
14.598
160
140
120
100
80
60
40
20
0
PPM
Reduction product of 5c
N
Cbz
NO2

HPLC Report

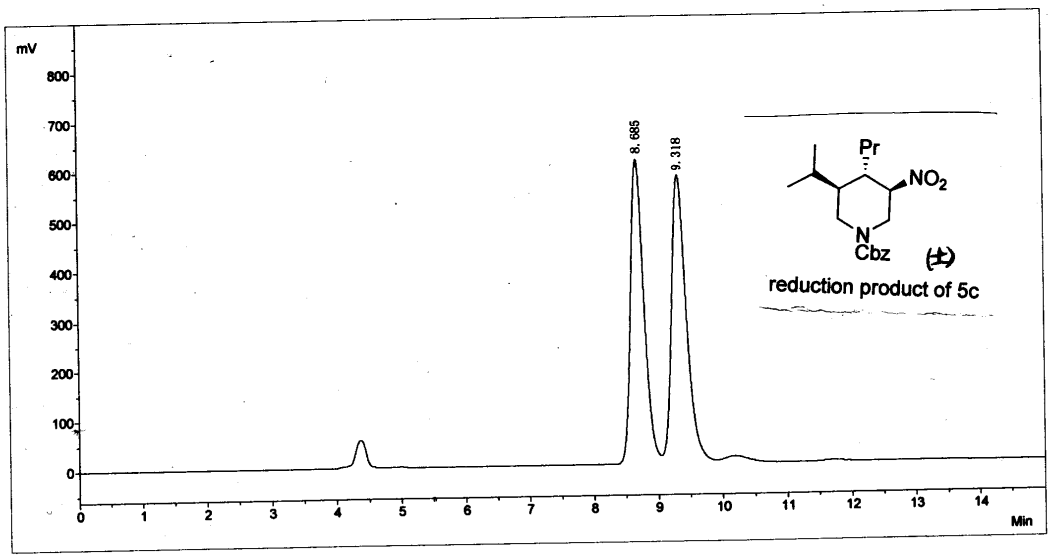
Sample Name:

Operator:

Time:14:01

Data File:ZSL-6-16-2+- PA-2 55 214 0.7.che

Date:2010-07-20



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		8.685	612982.1	8794990.6	49.1811
2	2		9.318	574153.1	9087883.3	50.8189
Total				1187135.2	17882873.9	100.0000

HPLC Report

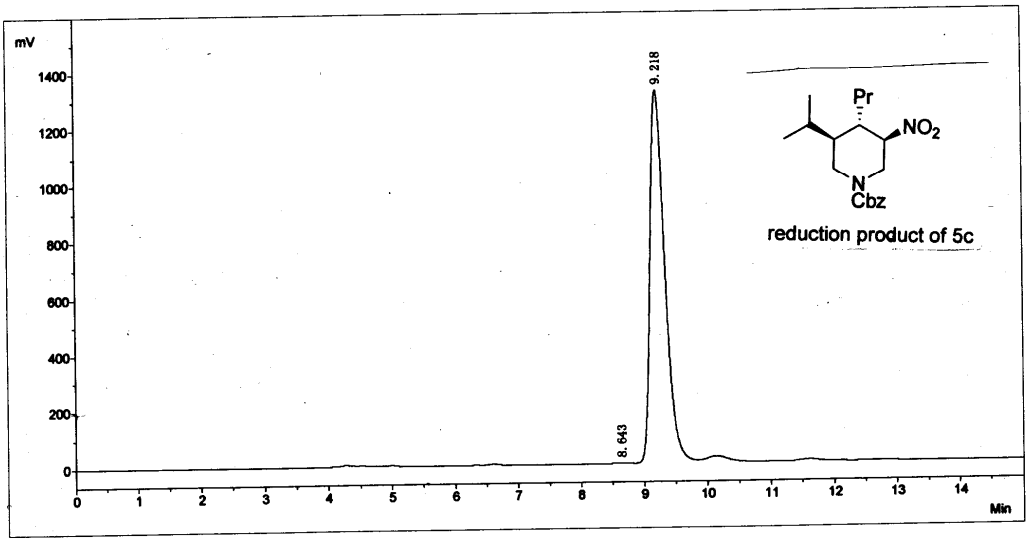
Sample Name:

Operator:

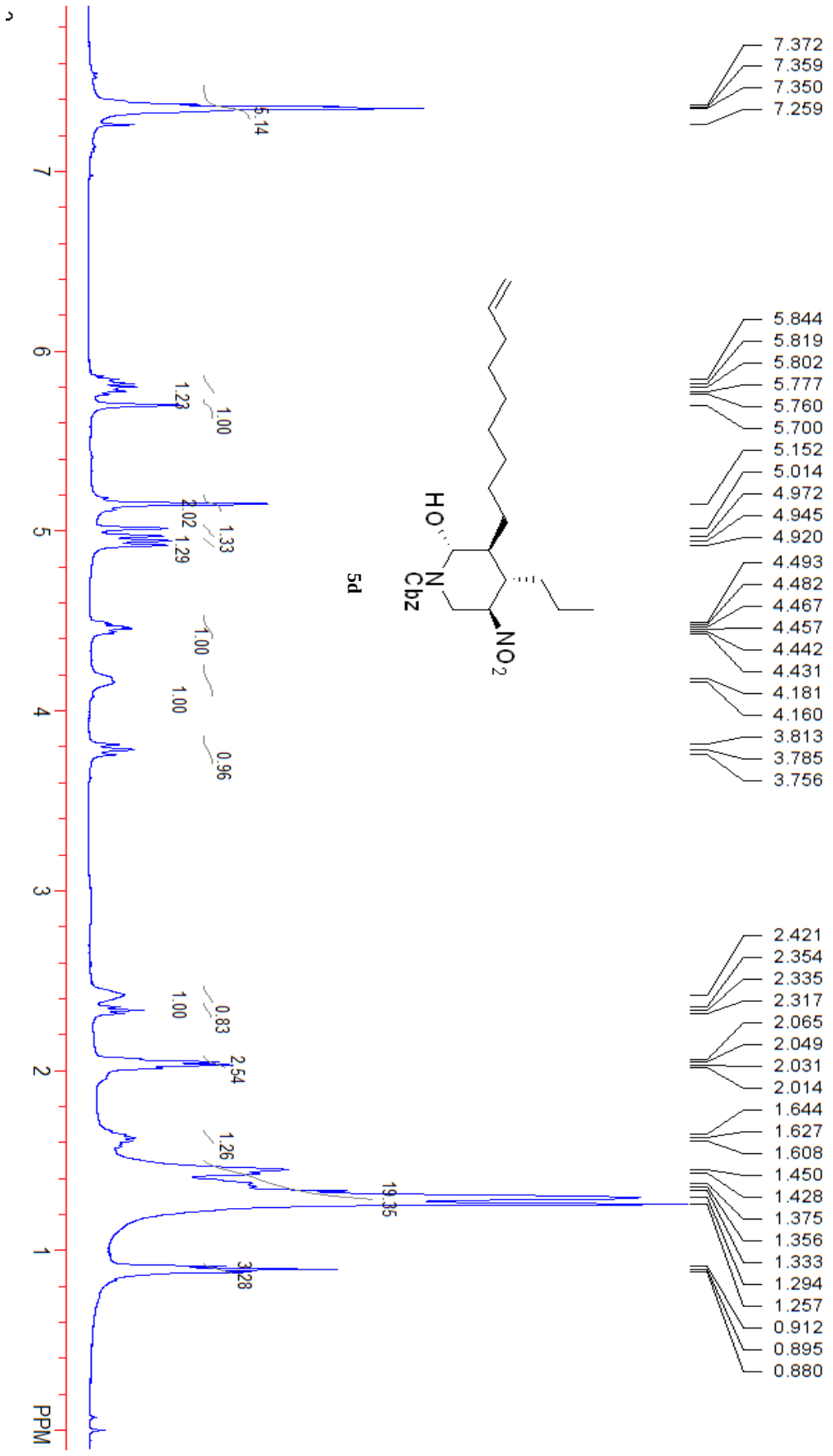
Time:14:27

Data File:ZSL-6-30-2.che

Date:2010-07-20



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		8.643	2207.4	26436.7	0.1249
2	2		9.218	1318725.3	21136472.8	99.8751
Total				1320932.7	21162909.5	100.0000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7.350
7.259
5.844
5.819
5.802
5.777
5.760
5.700
5.152
5.014
4.972
4.945
4.920
4.493
4.482
4.467
4.457
4.442
4.431
4.181
4.160
3.813
3.785
3.756
2.421
2.354
2.335
2.317
2.065
2.049
2.031
2.014
1.644
1.627
1.608
1.450
1.428
1.375
1.356
1.333
1.294
1.257
0.912
0.895
0.880
HO
N
Cbz
NO2
5d
5.14
1.23
1.00
2.02
1.29
1.33
1.00
1.00
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1.00
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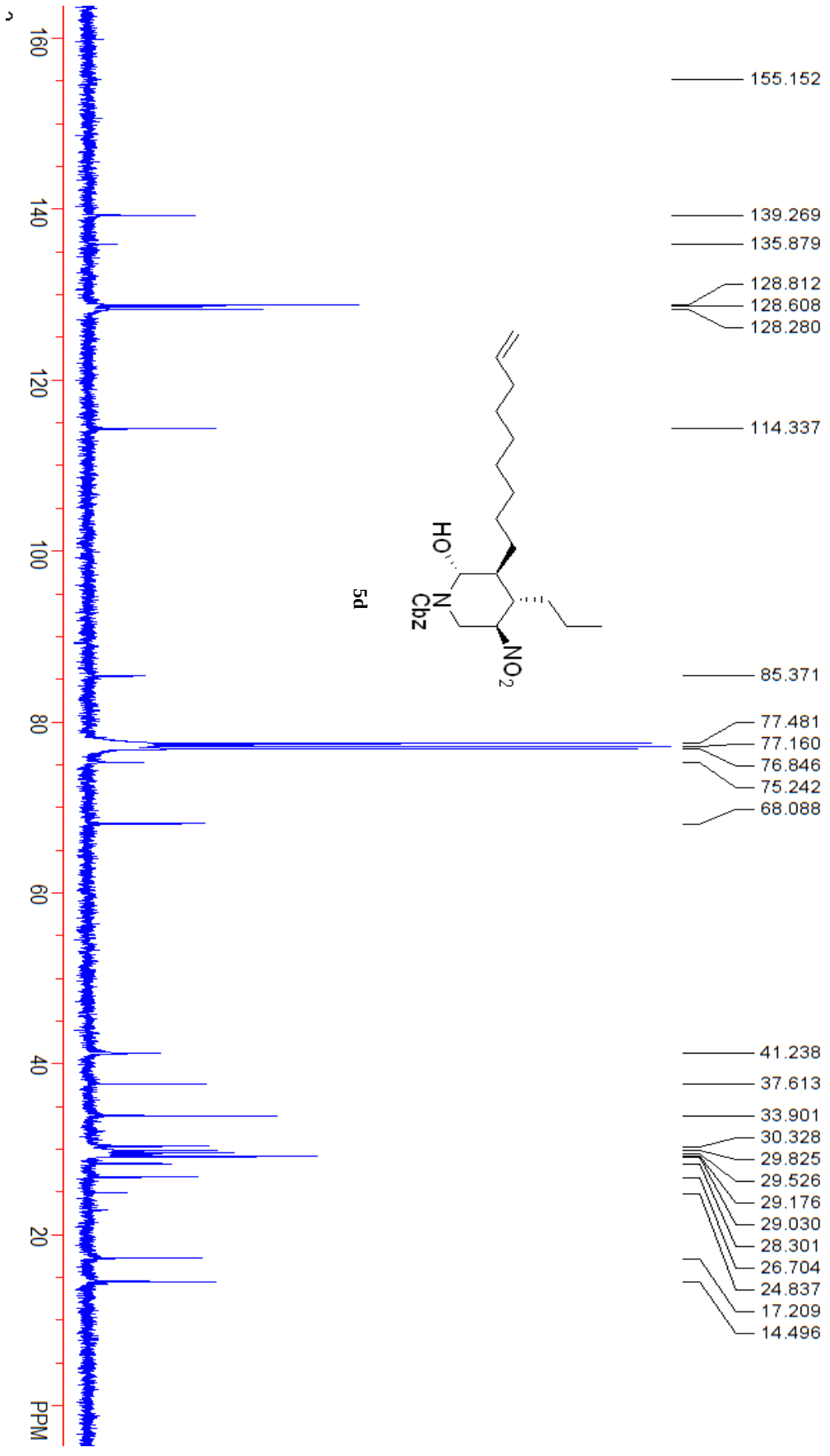
2.54
1.26
19.35
3.28
PPM
7
6
5
4
3
2
1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76.846
75.242
68.088
41.238
37.613
33.901
30.328
29.825
29.526
29.176
29.030
28.301
26.704
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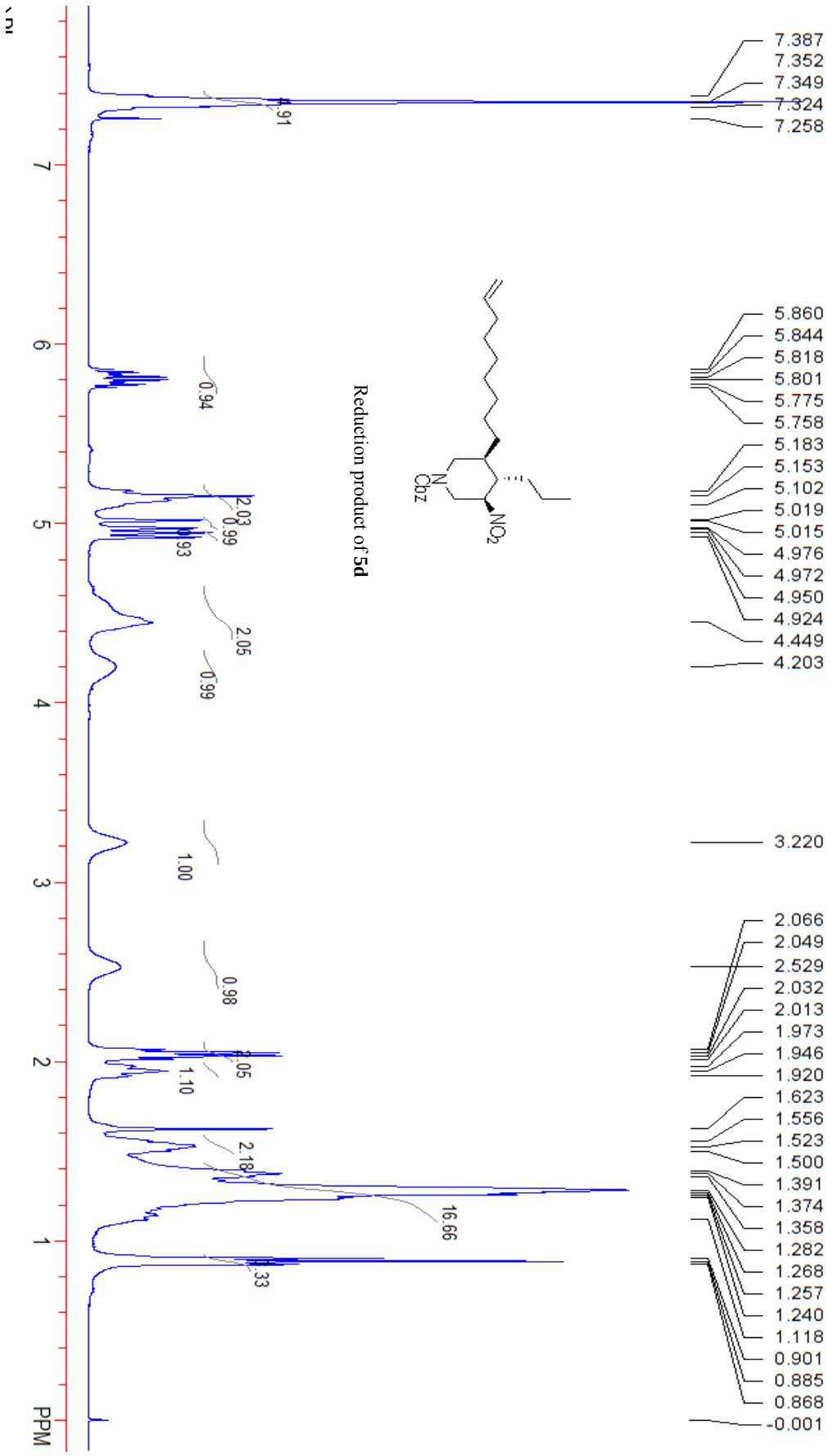
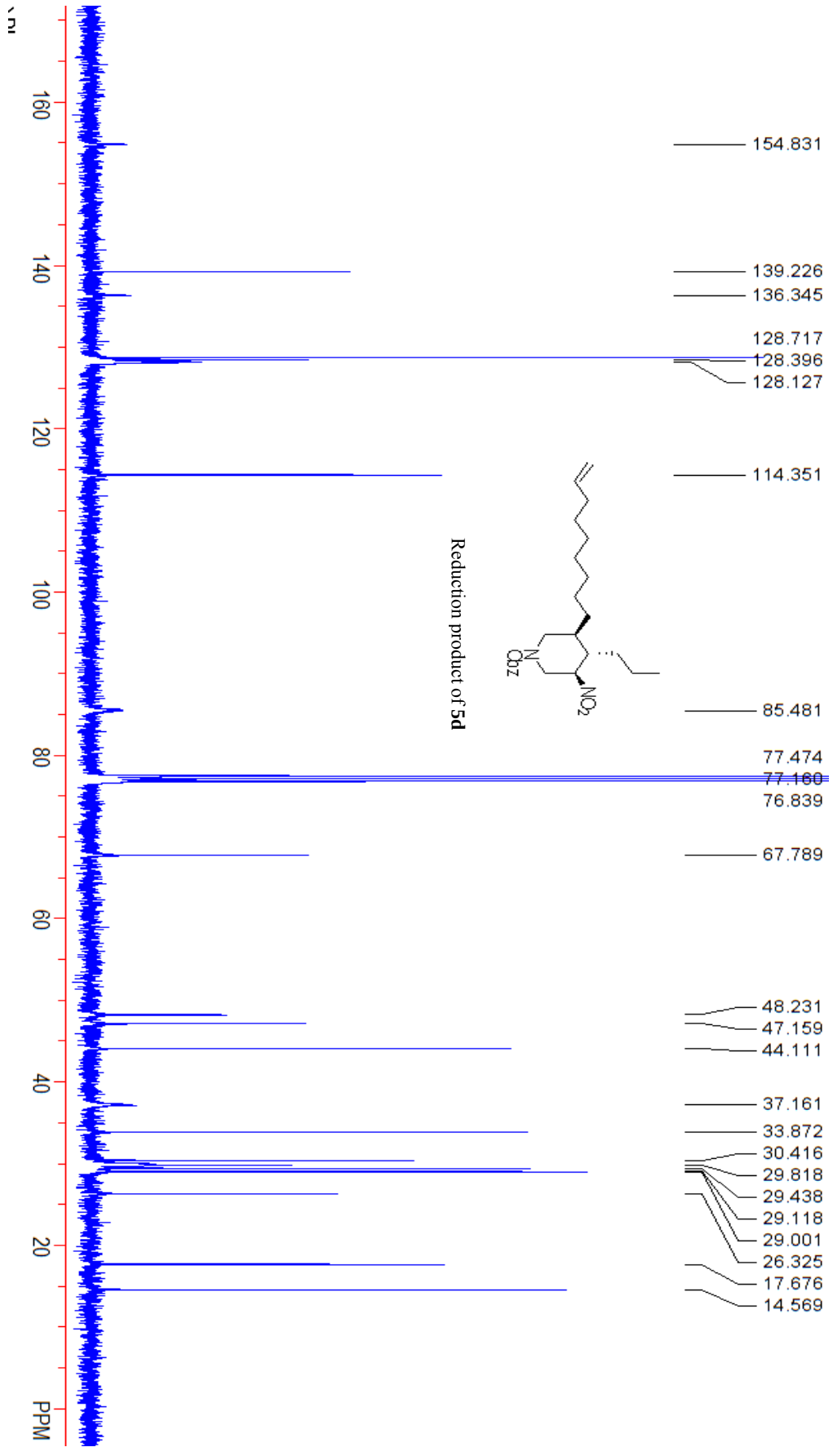
14.496
5d
HO
N
Cbz
NO2
160
140
120
100
80
60
40
20
PPM



Reduction product of **5d**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128.396
128.127
114.351
85.481
77.474
77.160
76.839
67.789
48.231
47.159
44.111
37.161
33.872
30.416
29.818
29.438
29.118
29.001
26.325
17.676
14.569
160
140
120
100
80
60
40
20
PPM
Reduction product of 5d
N
Cbz
NO2

HPLC Report

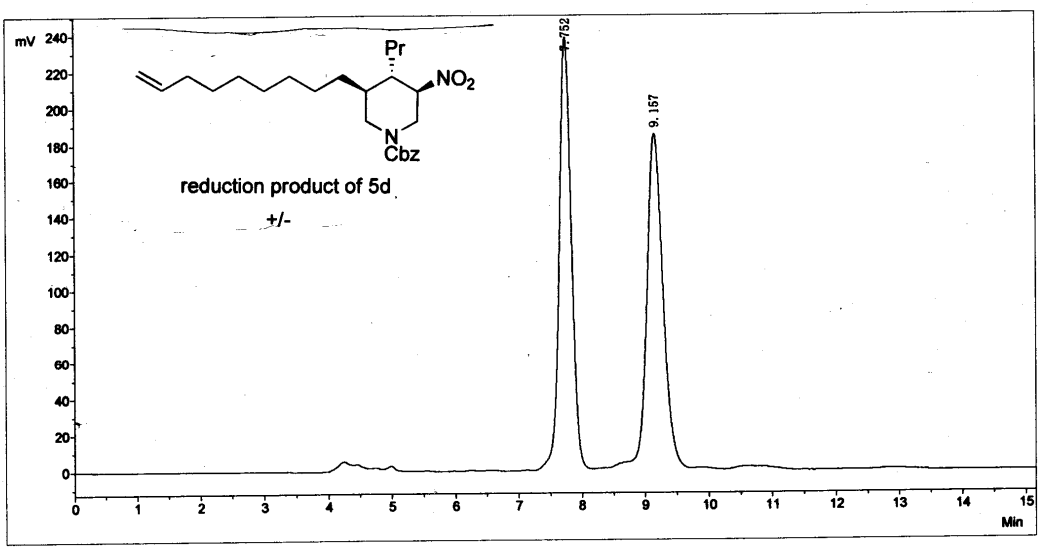
Sample Name:

Operator:

Time:13:25

Data File:ZSL-6-19-2+- PA-2 55 214 0.7.che

Date:2010-07-20



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		7.752	238116.7	3174916.5	50.4255
2	2		9.157	182479.9	3121331.3	49.5745
Total				420596.5	6296247.8	100.0000

HPLC Report

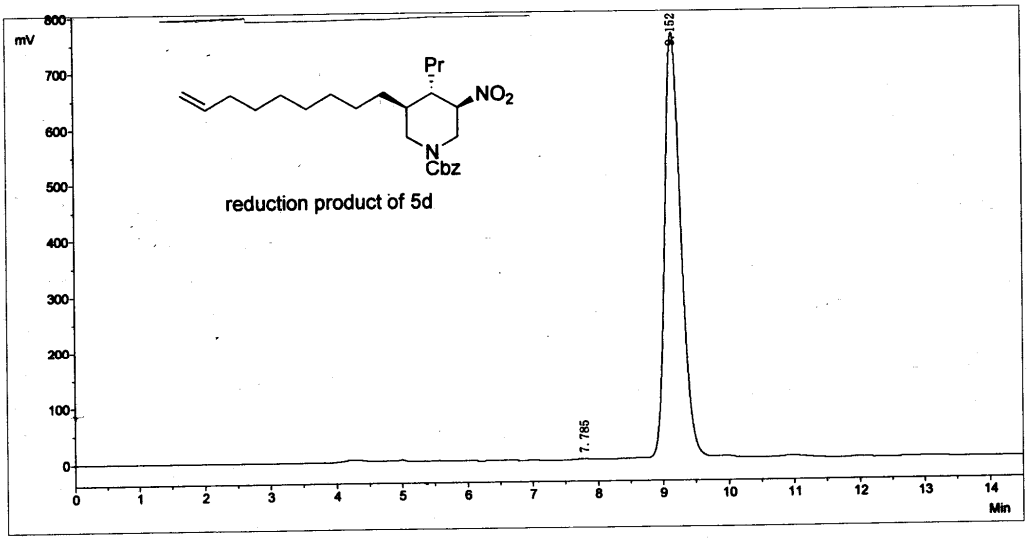
Sample Name:

Operator:

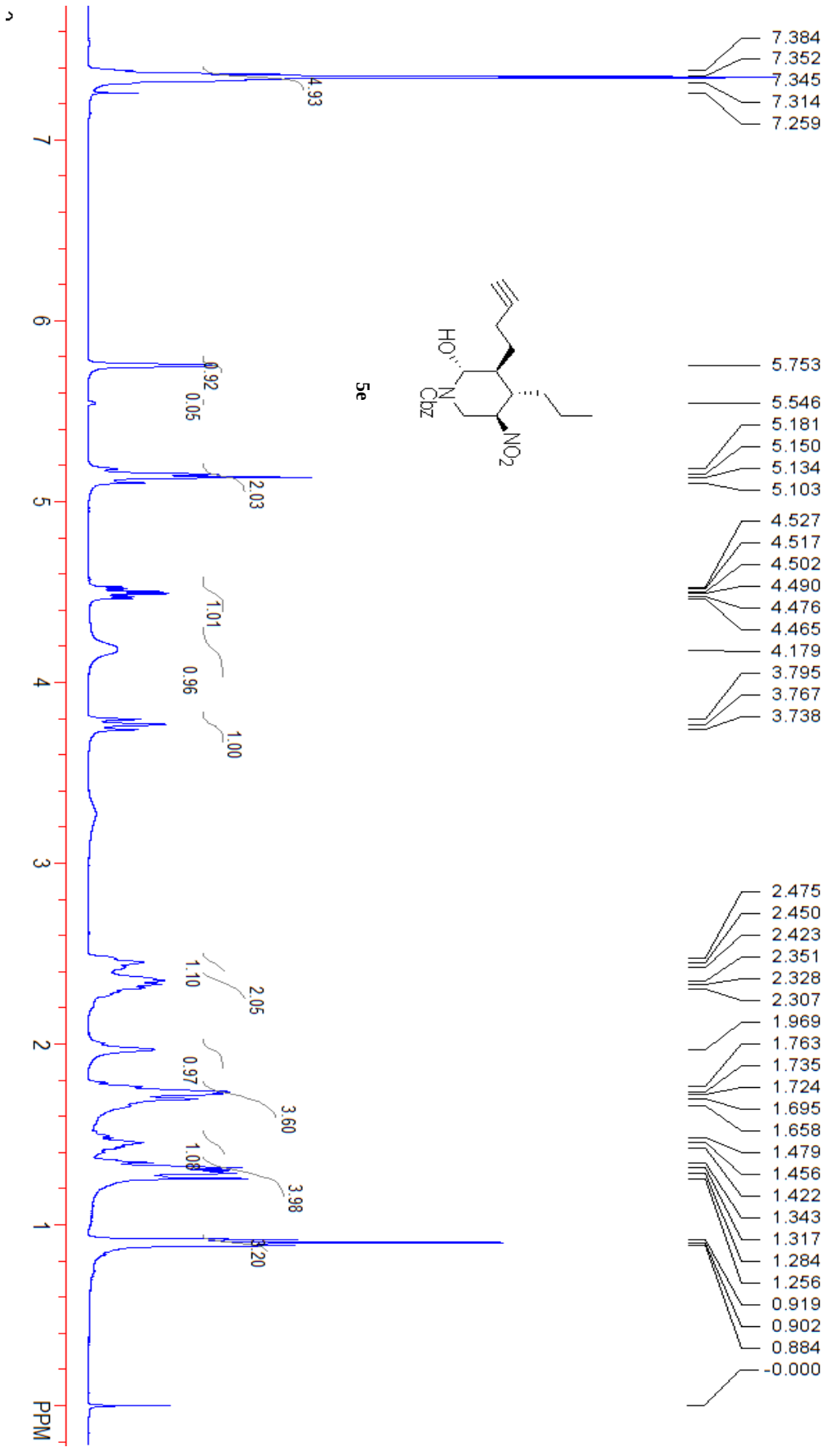
Time:13:43

Data File:ZSL-6-29.che

Date:2010-07-20



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		7.785	1439.2	16491.4	0.1275
2	2		9.152	760472.5	12914286.9	99.8725
Total				761911.7	12930778.3	100.0000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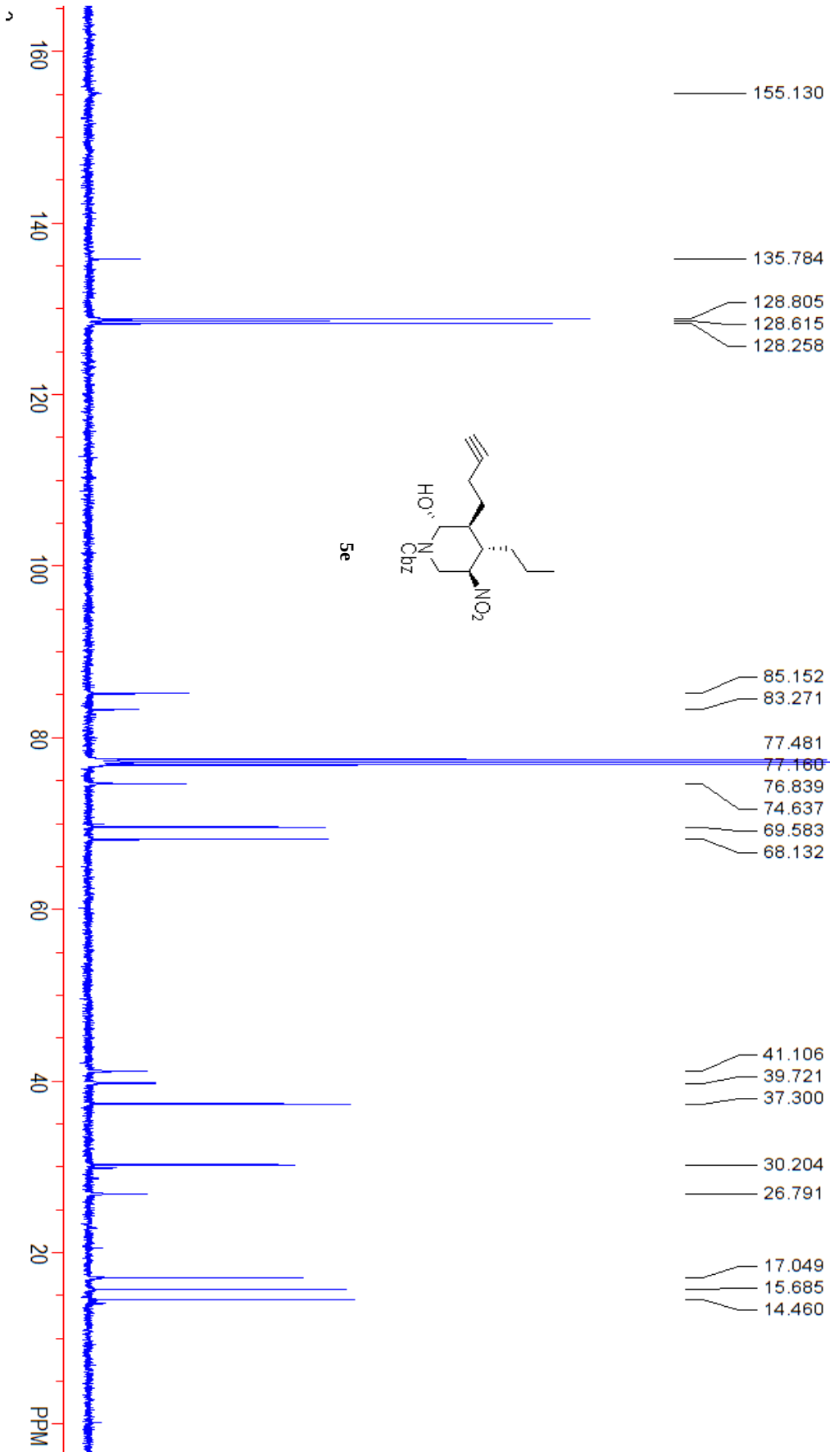
7.259
5.753
5.546
5.181
5.150
5.134
5.103
4.527
4.517
4.502
4.490
4.476
4.465
4.179
3.795
3.767
3.738
2.475
2.450
2.423
2.351
2.328
2.307
1.969
1.763
1.735
1.724
1.695
1.658
1.479
1.456
1.422
1.343
1.317
1.284
1.256
0.919
0.902
0.884
-0.000
4.93
0.92
0.05
2.03
1.01
0.96
1.00
1.10
2.05
0.97
3.60
1.08
3.98
3.20
HO
N
Cbz
NO2
5e
PPM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128.258
85.152
83.271
77.481
77.160
76.839
74.637
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68.132
41.106
39.721
37.300
30.204
26.791
17.049
15.685
14.460
160
140
120
100
80
60
40
20
PPM
5e
HO
N
Cbz
NO2

HPLC Report

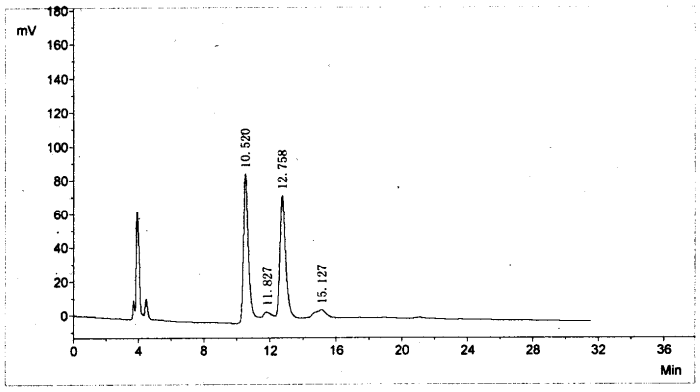
Sample Name:

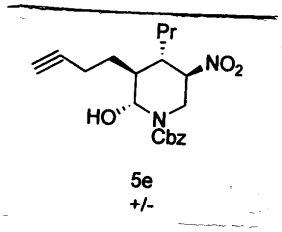
Operator:

Time:09:04

Data File:ZSL6-20+-SINO-AD-910.7214.che

Date:2010-08-19





5e

+/-

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	10.520	86975.5	1719927.1	46.1434
2	2	11.827	2685.0	69032.4	1.8521
3	3	12.758	71819.8	1698966.1	45.5811
4	4	15.127	4827.4	239425.0	6.4235
Total			166307.7	3727350.6	100.0000

HPLC Report

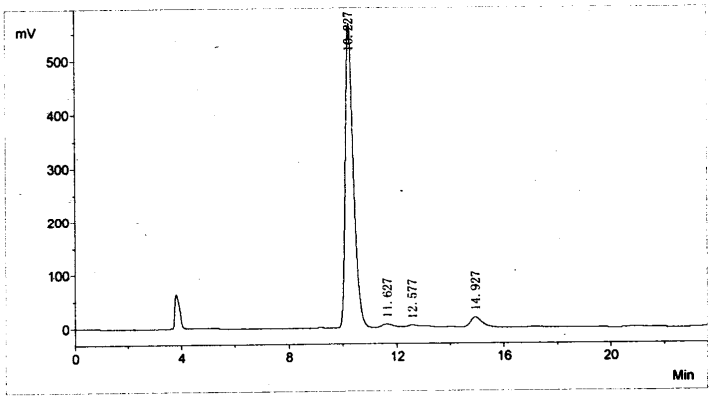
Sample Name:

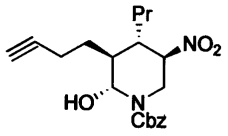
Operator:

Time:09:41

Data File:ZSL6-28.che

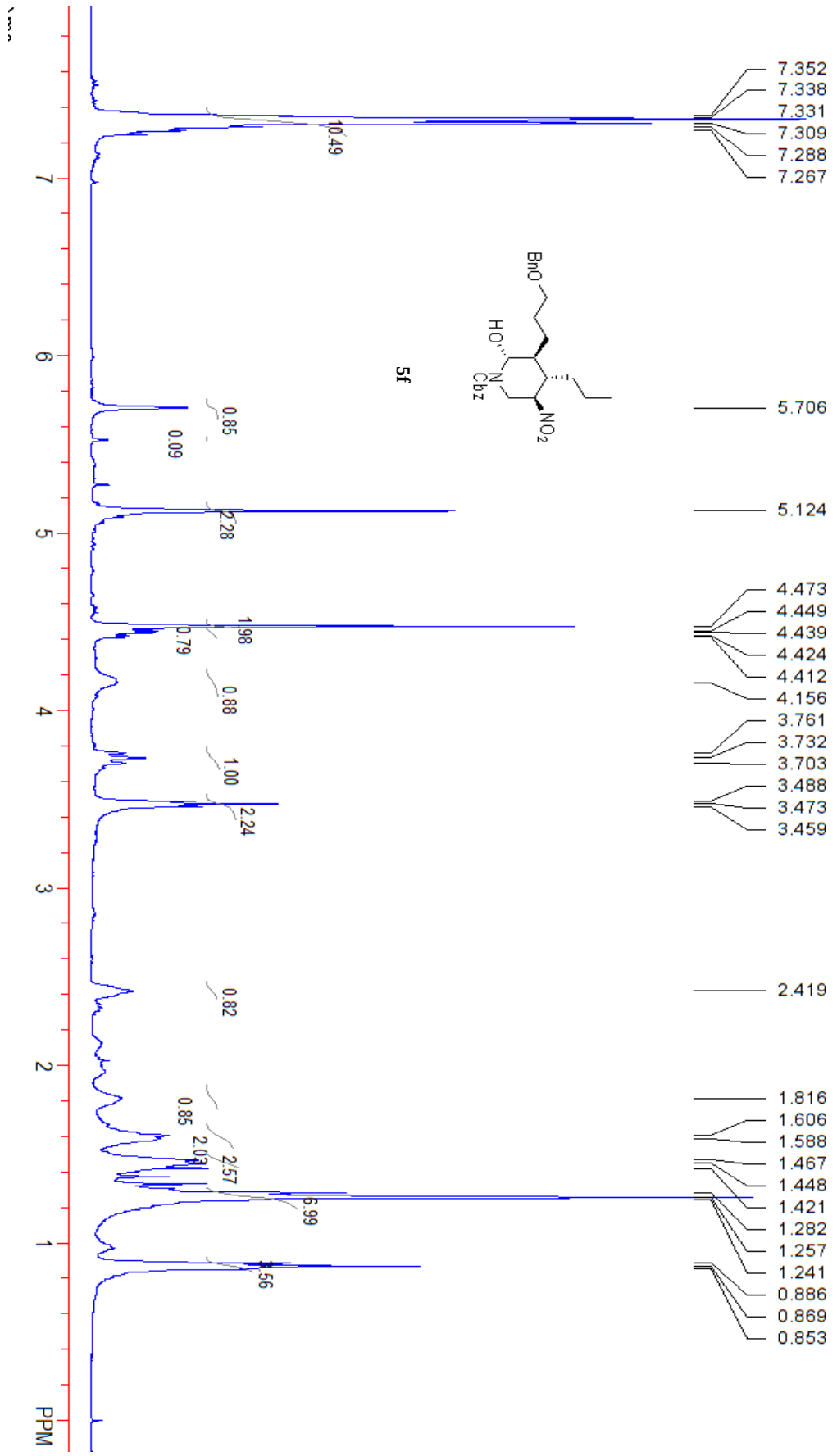
Date:2010-08-19





5e

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	10.227	564408.8	11776232.0	93.7569 ✓
2	2	11.627	5774.7	161741.2	1.2877
3	3	12.577	3127.3	59477.1	0.4735 ✓
4	4	14.927	19044.9	562943.1	4.4819
Total			592355.7	12560393.3	100.0000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5.124
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4.449
4.439
4.424
4.412
4.156
3.761
3.732
3.703
3.488
3.473
3.459
2.419
1.816
1.606
1.588
1.467
1.448
1.421
1.282
1.257
1.241
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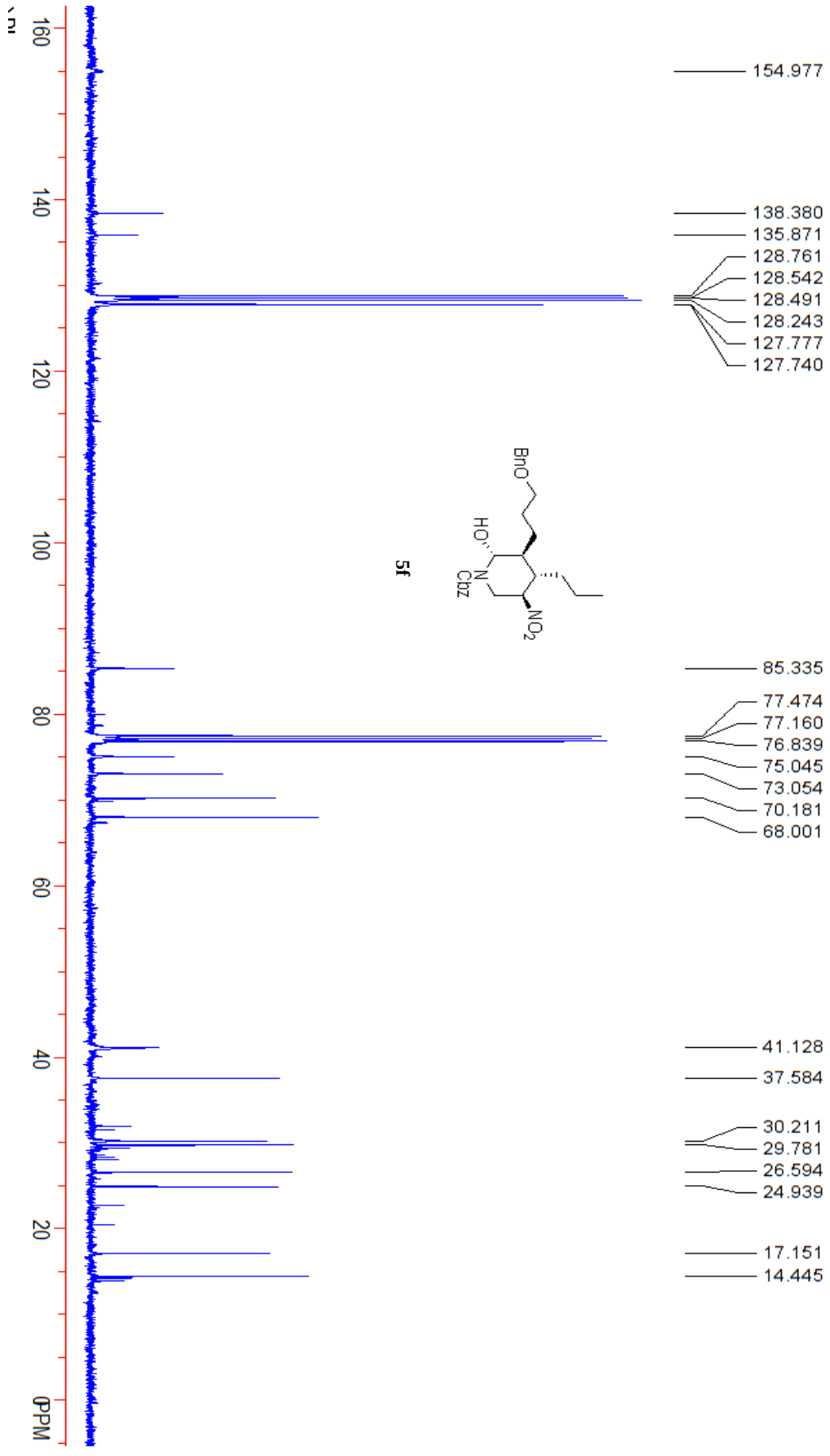
0.869
0.853
10.49
0.85
0.09
2.28
1.98
0.79
0.88
1.00
2.24
0.82
0.85
2.03
2.57
6.99
3.56
5f
BnO
HO
N
Cbz
NO2
PPM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128.243
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HO
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Cbz
NO2
5f
85.335
77.474
77.160
76.839
75.045
73.054
70.181
68.001
41.128
37.584
30.211
29.781
26.594
24.939
17.151
14.445
160
140
120
100
80
60
40
20
0
PPM

HPLC Report

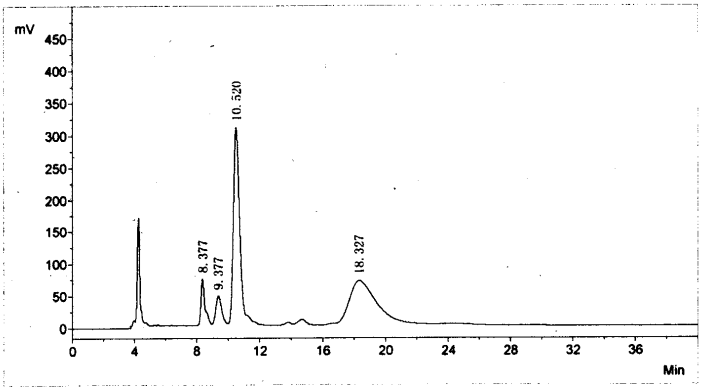
Sample Name:

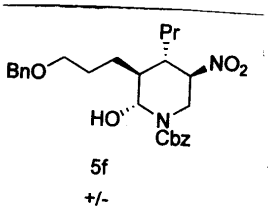
Operator:

Time:16:35

Data File:ZSL-17-49+- PA-2 73 214 0.7.che

Date:2010-08-16





5f

+/-

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.377	72153.0	1264820.3	7.0741
2	2	9.377	44074.8	1111479.7	6.2165
3	3	10.520	300193.5	7770978.7	43.4628
4	4	18.327	66426.7	7732317.3	43.2466
Total			482848.0	17879596.0	100.0000

HPLC Report

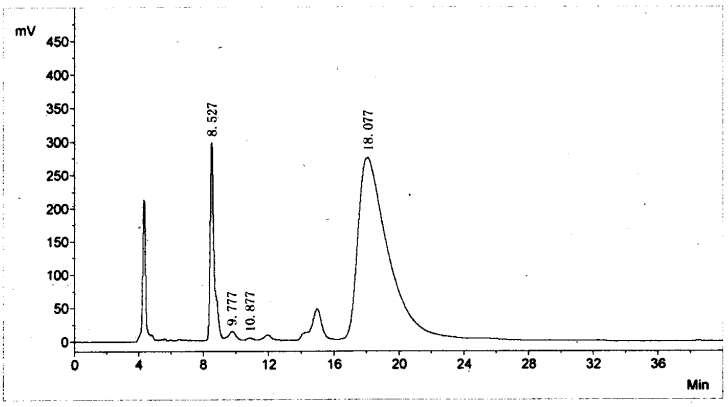
Sample Name:

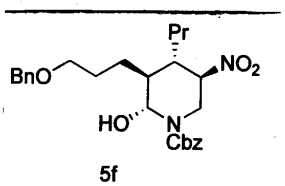
Operator:

Time:17:33

Data File:ZSL-6-32.che

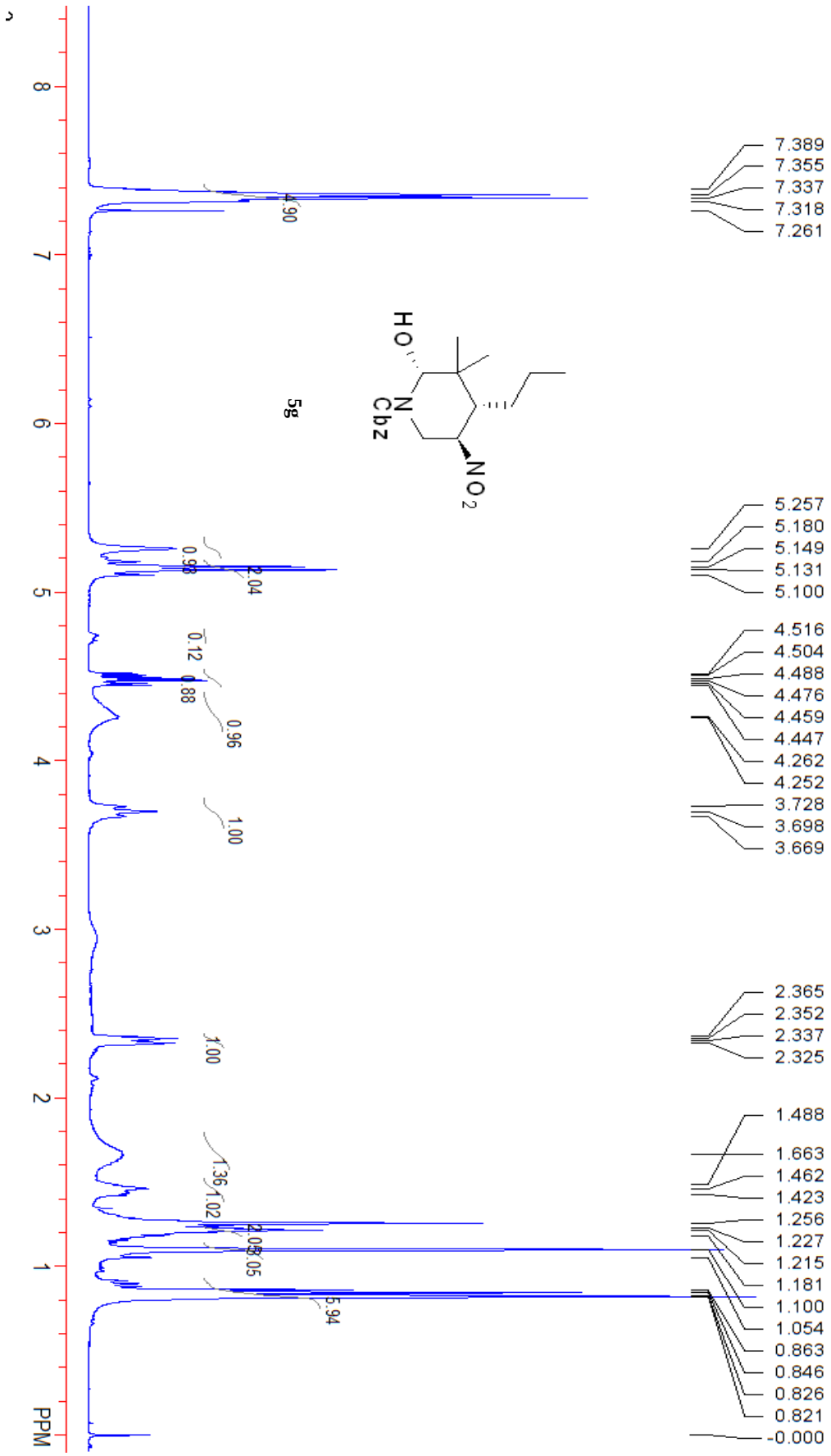
Date:2010-08-16





5f

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.527	297646.4	5204237.6	12.9060
2	2	9.777	13661.7	434562.6	1.0777
3	3	10.877	3312.1	82949.2	0.2057
4	4	18.077	273054.8	34602347.9	85.8106
Total			587675.0	40324097.2	100.0000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5.149
5.131
5.100
4.516
4.504
4.488
4.476
4.459
4.447
4.262
4.252
3.728
3.698
3.669
2.365
2.352
2.337
2.325
1.488
1.663
1.462
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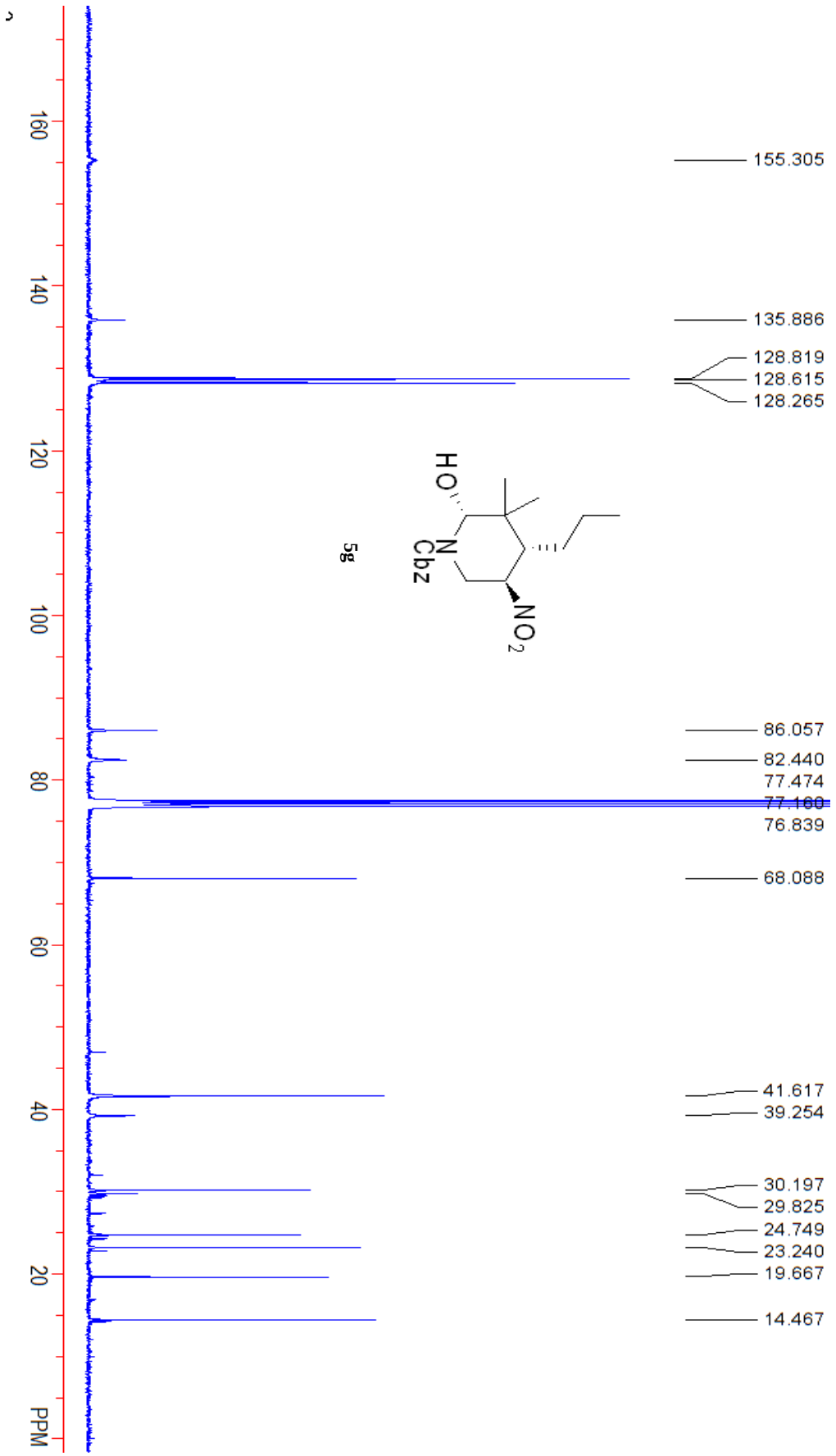
1.256
1.227
1.215
1.181
1.100
1.054
0.863
0.846
0.826
0.821
-0.000
4.90
0.93
2.04
0.12
0.88
0.96
1.00
1.00
1.36
1.02
2.08
3.05
5.94
HO
N
Cbz
NO2
5g
PPM
8
7
6
5
4
3
2
1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128.615
128.265
86.057
82.440
77.474
77.160
76.839
68.088
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39.254
30.197
29.825
24.749
23.240
19.667
14.467
HO
N
Cbz
NO2
5g
160
140
120
100
80
60
40
20
PPM

HPLC Report

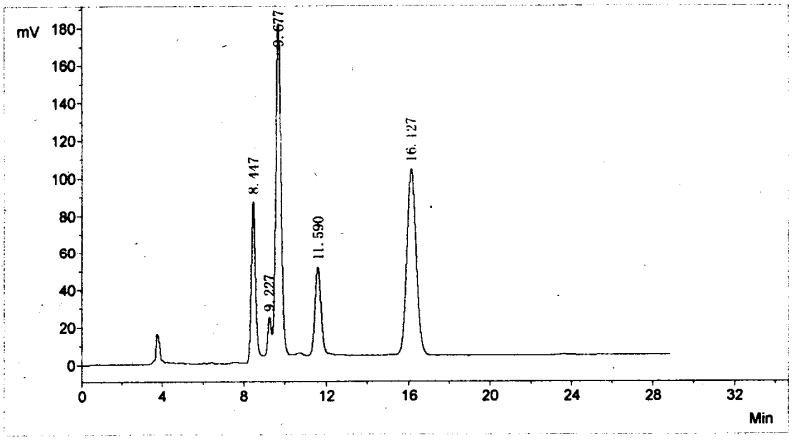
Sample Name:

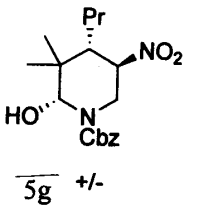
Operator:

Time:10:18

Data File:ZSL-6-12+- PC-2 91 214 0.7.che

Date:2010-09-01





5g +/-

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.447	84949.7	1170842.7	13.4630
2	2	9.227	20003.7	240992.5	2.7711
3	3	9.677	177394.2	3136117.0	36.0608
4	4	11.590	46931.6	957040.2	11.0046
5	5	16.127	99869.3	3191741.0	36.7005
Total			429148.5	8696736.4	100.0000

HPLC Report

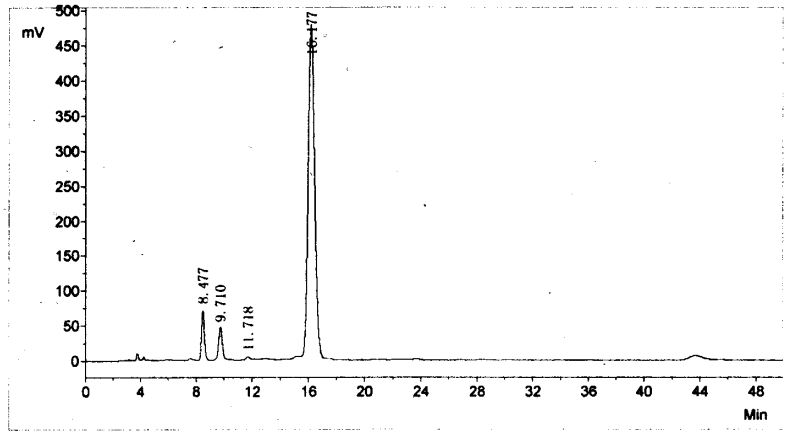
Sample Name:

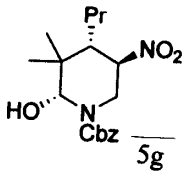
Operator:

Time:10:56

Data File:ZSL-6-58-1.che

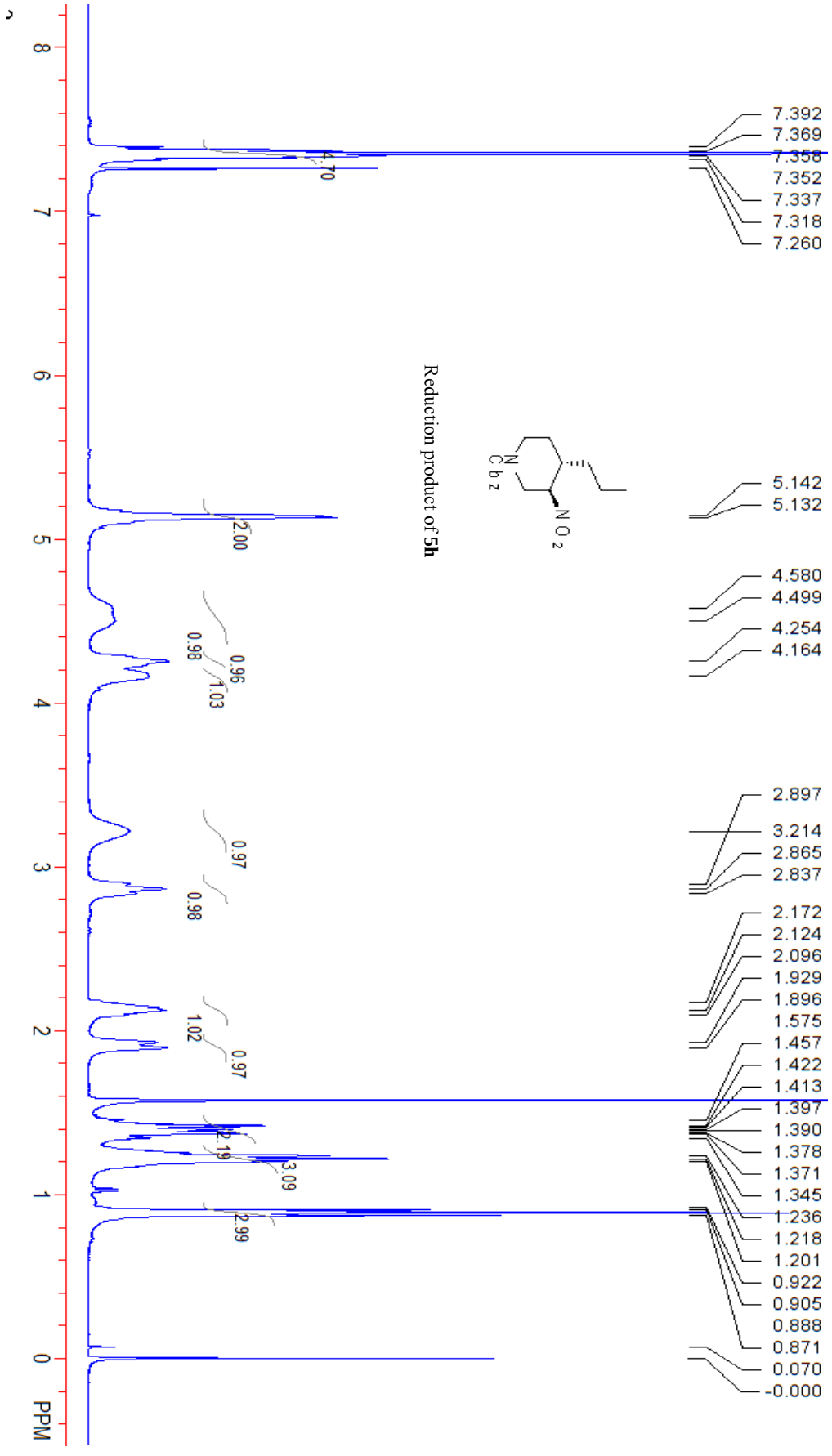
Date:2010-09-01





5g

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.477	71228.2	1025711.5	6.0447
2	2	9.710	43662.8	785706.3	4.6303
3	3	11.718	2788.2	41095.3	0.2422
4	4	16.177	475484.4	15116135.5	89.0827
Total			593163.6	16968648.5	100.0000


Reduction product of 5h
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C b z
N O 2
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7.352
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7.318
7.260
5.142
5.132
4.580
4.499
4.254
4.164
2.897
3.214
2.865
2.837
2.172
2.124
2.096
1.929
1.896
1.575
1.457
1.422
1.413
1.397
1.390
1.378
1.371
1.345
1.236
1.218
1.201
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0.905
0.888
0.871
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4.70
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1.03
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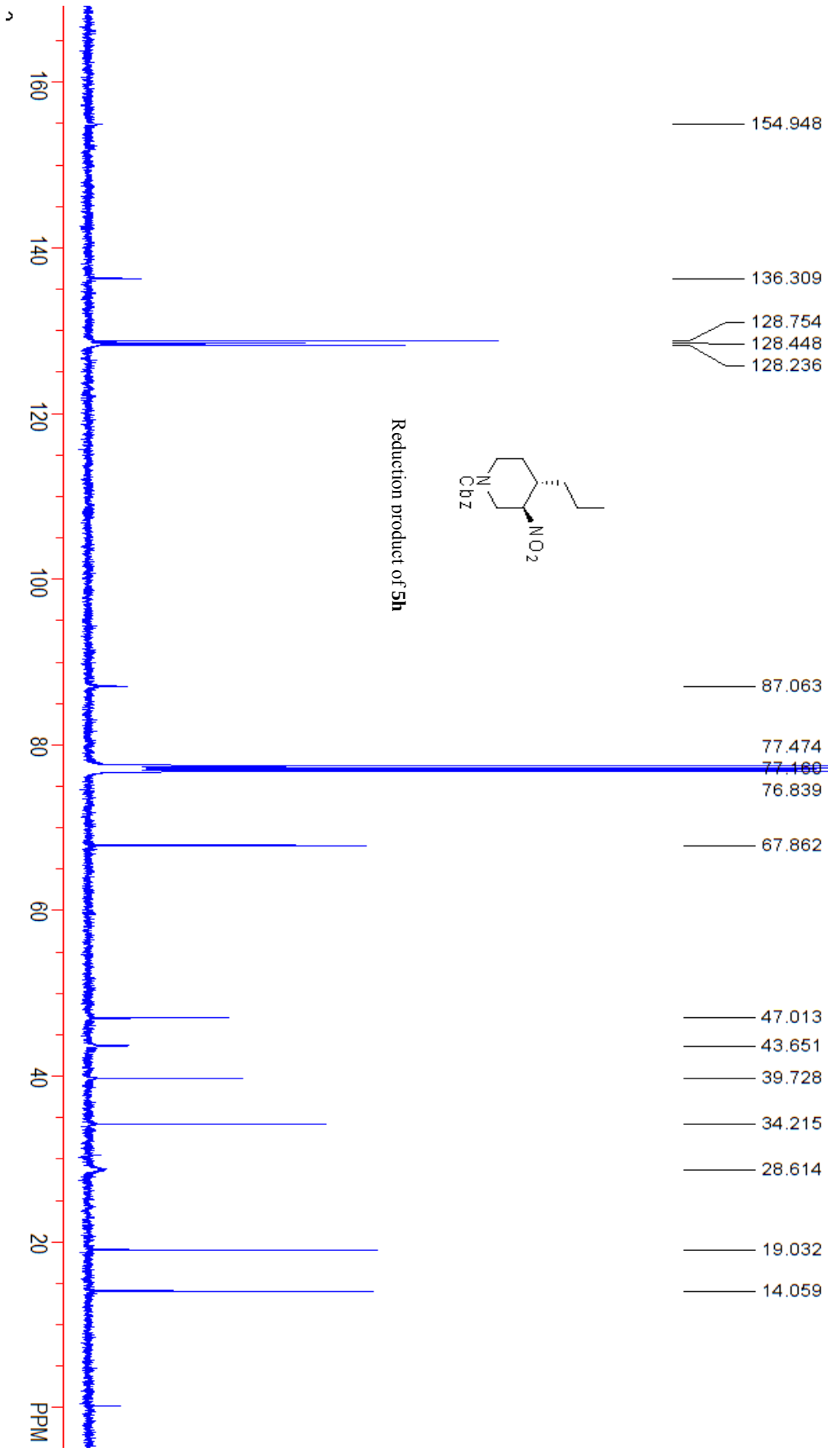
0.97
2.19
3.09
2.99
PPM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67.862
47.013
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39.728
34.215
28.614
19.032
14.059
160
140
120
100
80
60
40
20
PPM
Reduction product of 5h
N
Cbz
NO2

HPLC Report

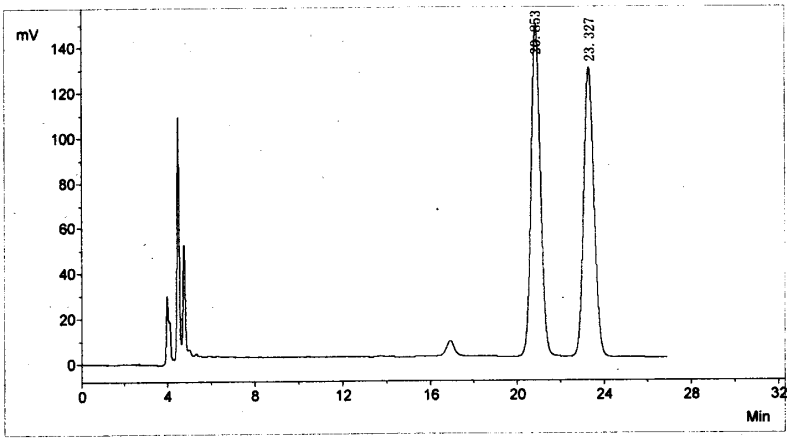
Sample Name:

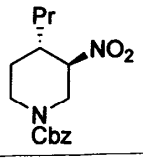
Operator:

Time:08:49

Data File:ZSL6-82+-.che

Date:2010-10-18





reduction product of 5h

+/-

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	20.853	145686.3	4283260.4	50.4646
2	2	23.327	127371.2	4204392.6	49.5354
Total			273057.6	8487652.9	100.0000

HPLC Report

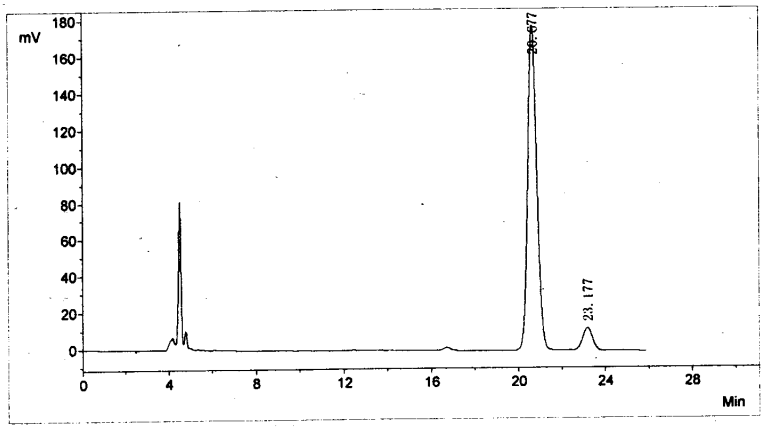
Sample Name:

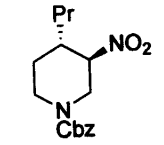
Operator:

Time:09:52

Data File:ZSL6-89.che

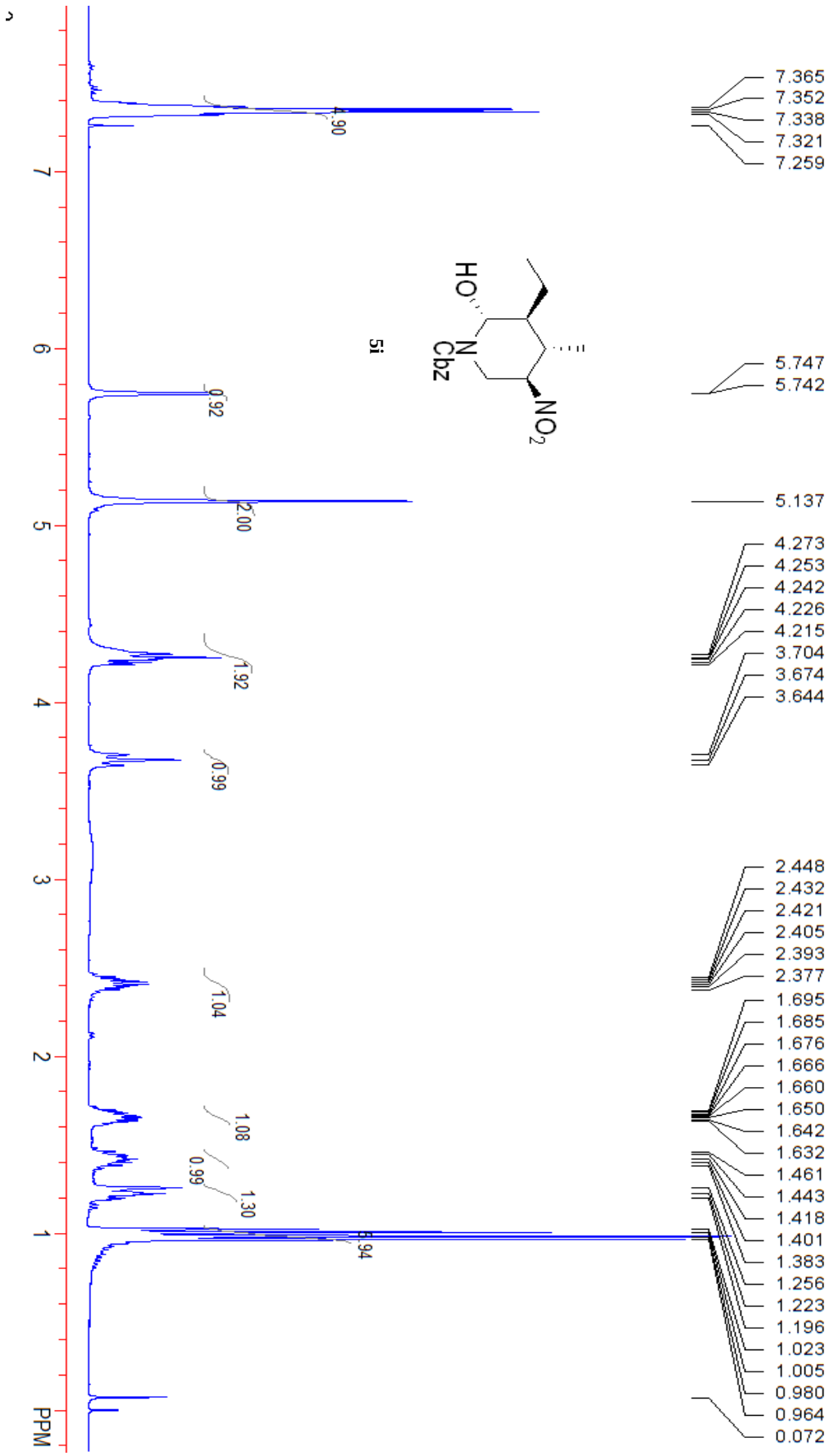
Date:2010-10-18





reduction product of 5h

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	20.677	177490.1	5171404.2	92.9367
2	2	23.177	12366.4	393031.5	7.0633
Total			189856.4	5564435.8	100.0000


5i
HO
N
Cbz
NO2
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5.747
5.742
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4.273
4.253
4.242
4.226
4.215
3.704
3.674
3.644
2.448
2.432
2.421
2.405
2.393
2.377
1.695
1.685
1.676
1.666
1.660
1.650
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1.401
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1.256
1.223
1.196
1.023
1.005
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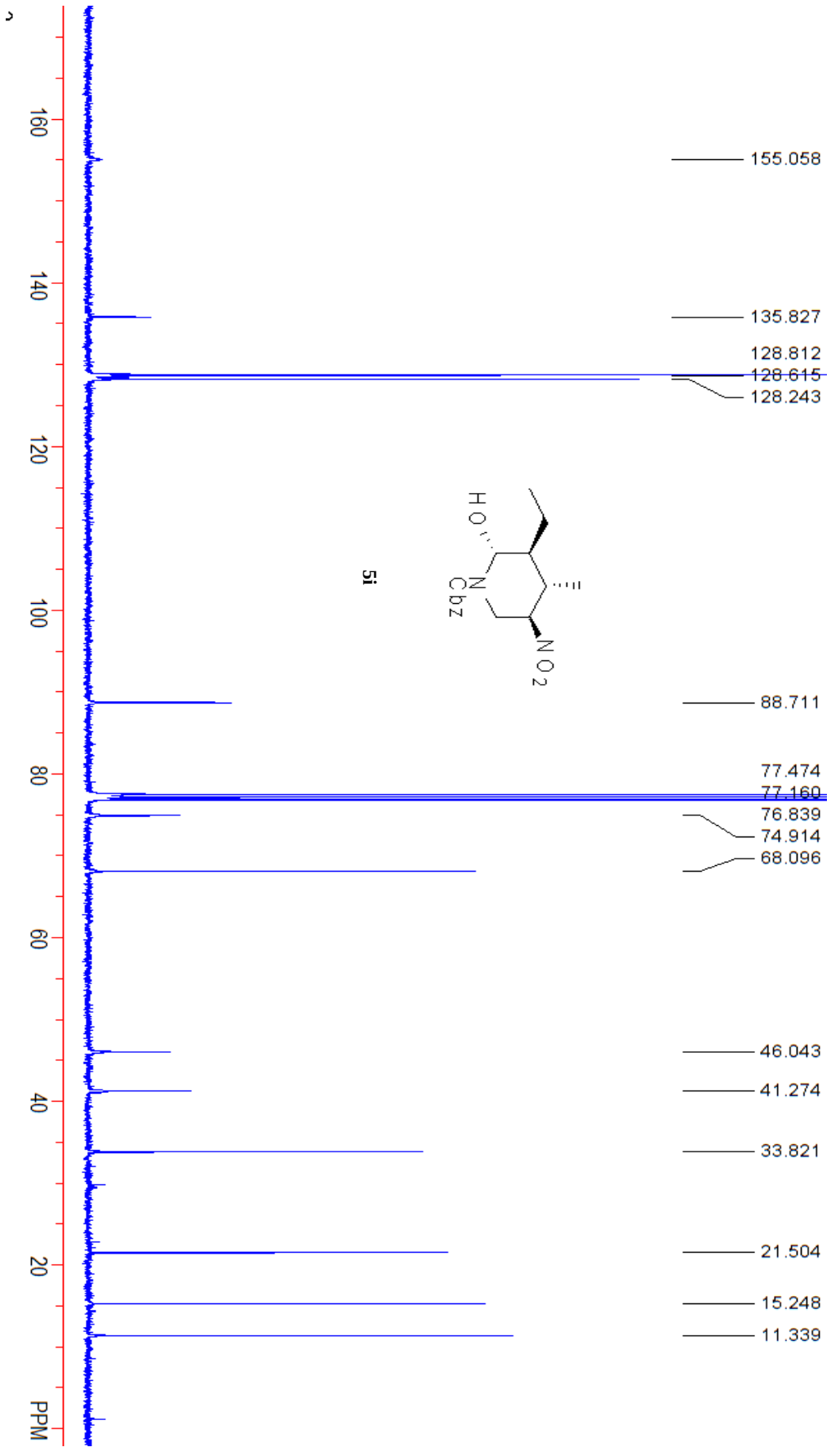
0.99
1.04
1.08
0.99
1.30
8.94
PPM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128.243
88.711
77.474
77.160
76.839
74.914
68.096
46.043
41.274
33.821
21.504
15.248
11.339
160
140
120
100
80
60
40
20
PPM
5i
HO
N
Cbz
NO2

HPLC Report

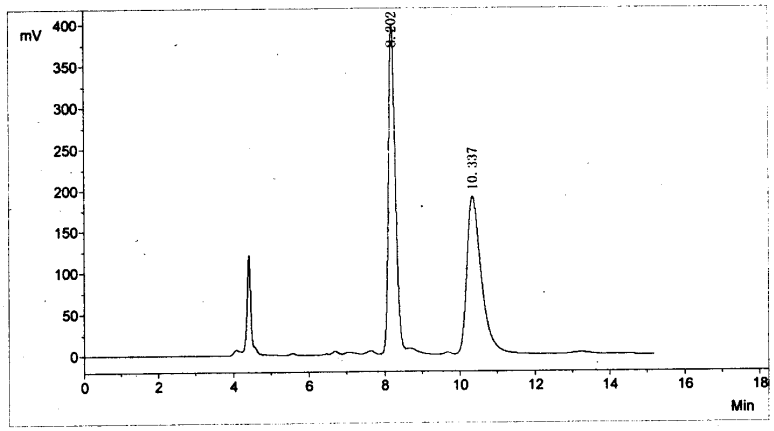
Sample Name:

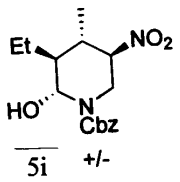
Operator:

Time:13:45

Data File:ZSL6-88+-PA-2730.7214.che

Date:2010-10-20





5i +/-

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.202	390934.8	4789758.2	50.5280
2	2	10.337	187029.8	4689654.3	49.4720
Total			577964.5	9479412.5	100.0000

HPLC Report

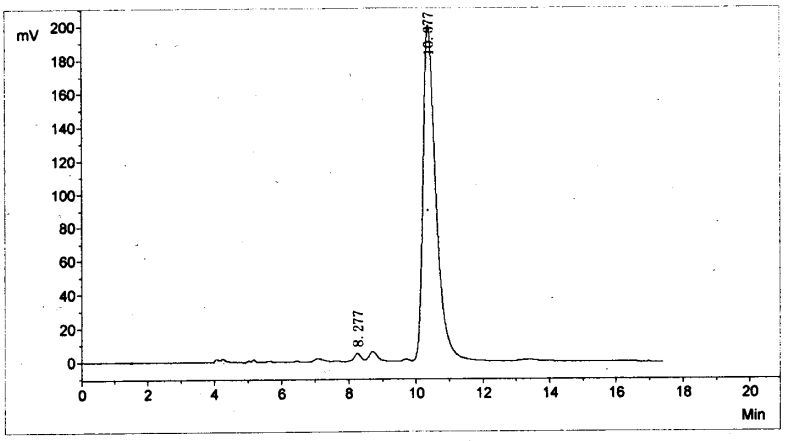
Sample Name:

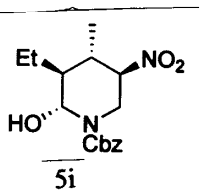
Operator:

Time:14:07

Data File:ZSL6-90.che

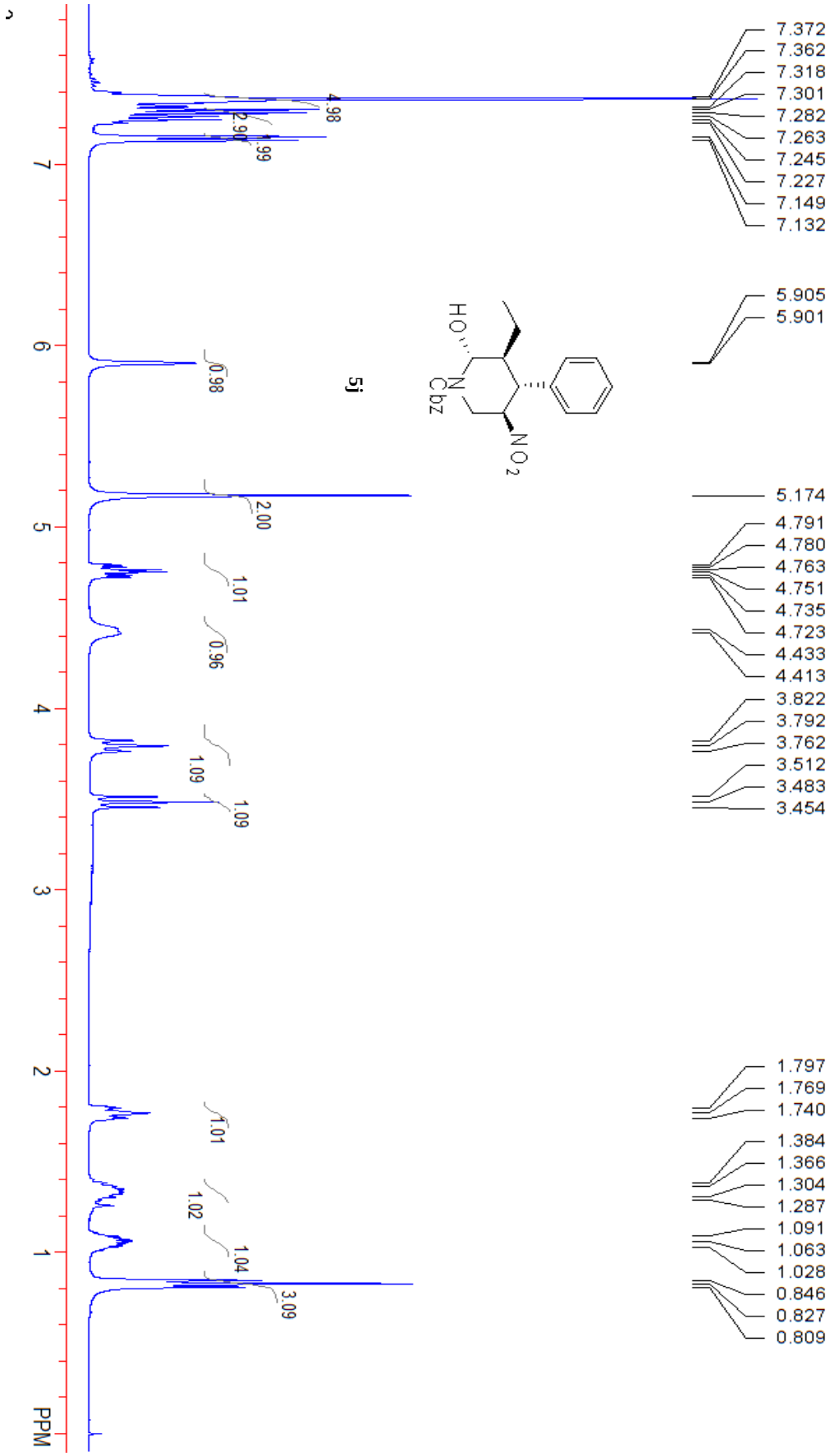
Date:2010-10-20





5i

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.277	4068.2	50828.0	0.9310
2	2	10.377	200075.3	5408880.0	99.0690
Total			204143.6	5459707.9	100.0000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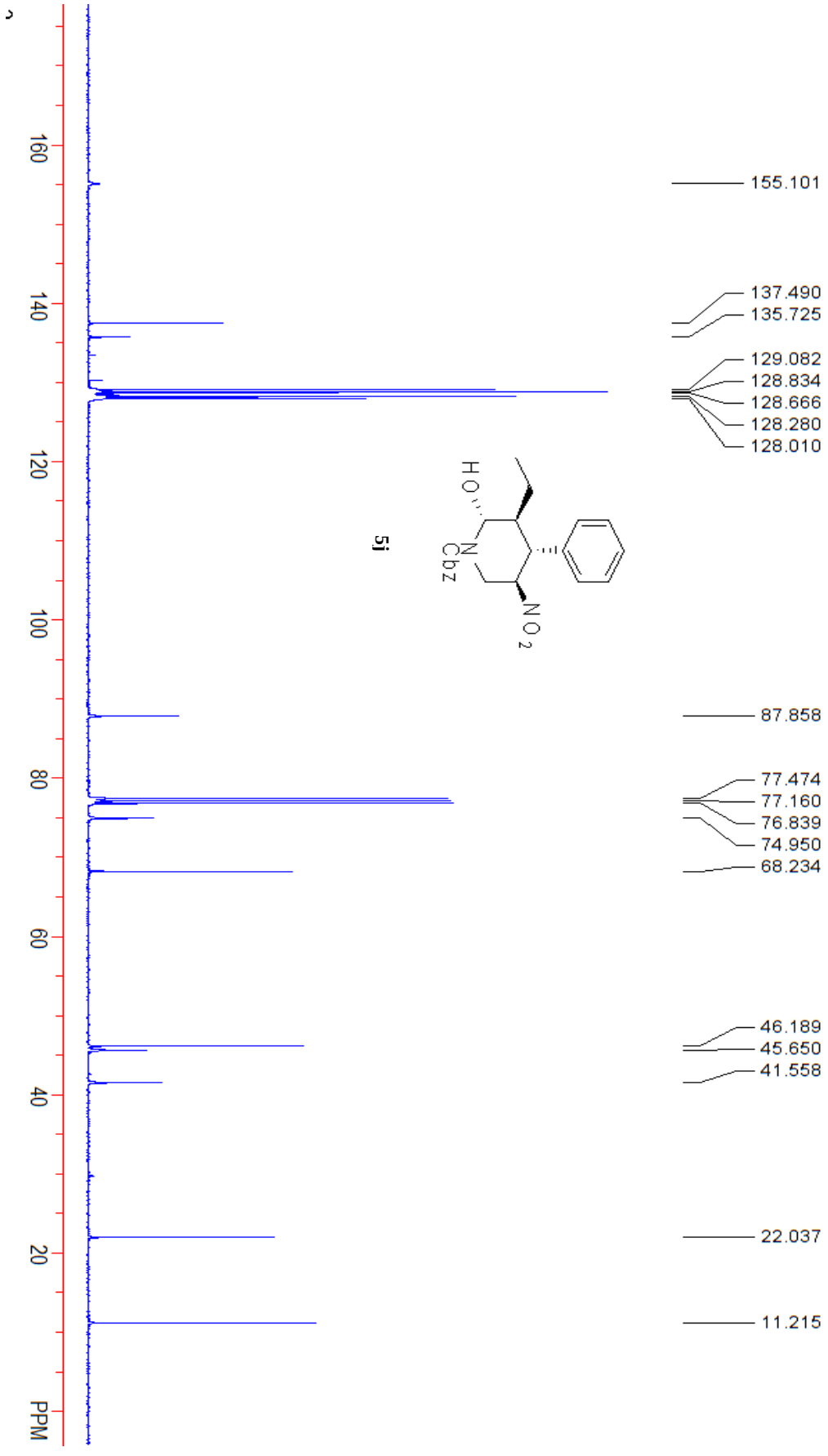
7.301
7.282
7.263
7.245
7.227
7.149
7.132
5.905
5.901
5.174
4.791
4.780
4.763
4.751
4.735
4.723
4.433
4.413
3.822
3.792
3.762
3.512
3.483
3.454
1.797
1.769
1.740
1.384
1.366
1.304
1.287
1.091
1.063
1.028
0.846
0.827
0.809
4.98
2.97
1.99
0.98
2.00
1.01
0.96
1.09
1.09
1.01
1.02
1.04
3.09
5j
HO
N
Cbz
NO2
PPM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135.725
129.082
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128.666
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77.474
77.160
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68.234
46.189
45.650
41.558
22.037
11.215
PPM
160
140
120
100
80
60
40
20
HO
N
Cbz
NO2
5j

HPLC Report

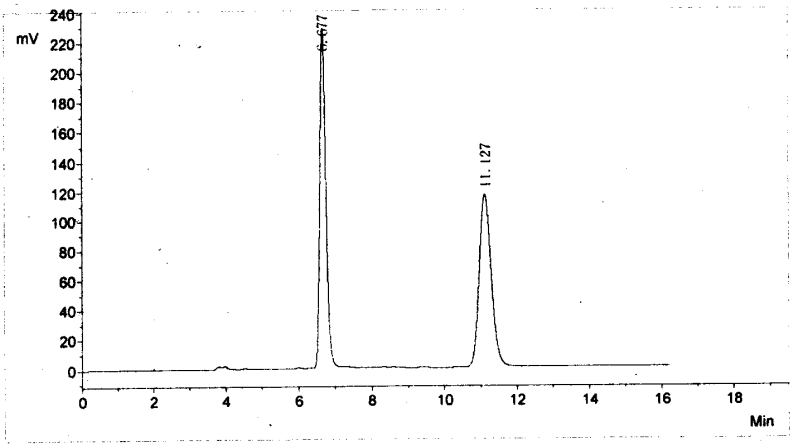
Sample Name:

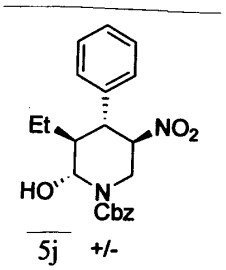
Operator:

Time:09:09

Data File:ZSL6-17+-PC-2730.7214.che

Date:2010-08-25





5j +/-

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	6.677	227041.6	2713102.9	50.0982
2	2	11.127	116279.6	2702463.8	49.9018
Total			343321.3	5415566.6	100.0000

HPLC Report

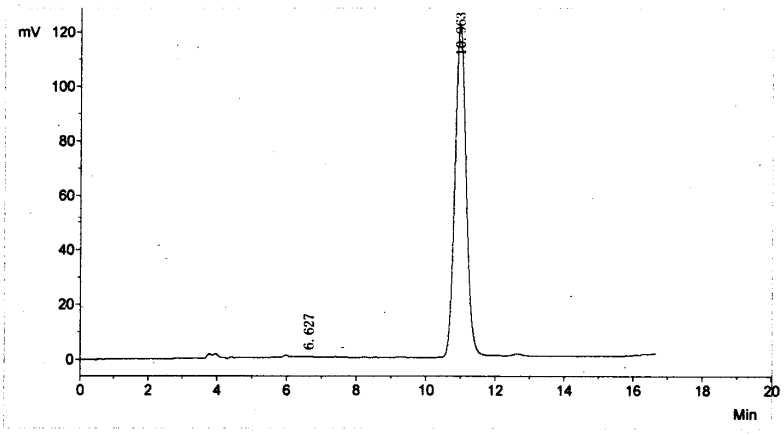
Sample Name:

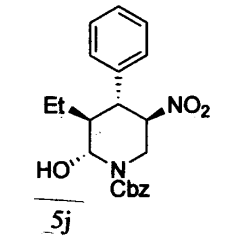
Operator:

Time:09:31

Data File:ZSL6-60.che

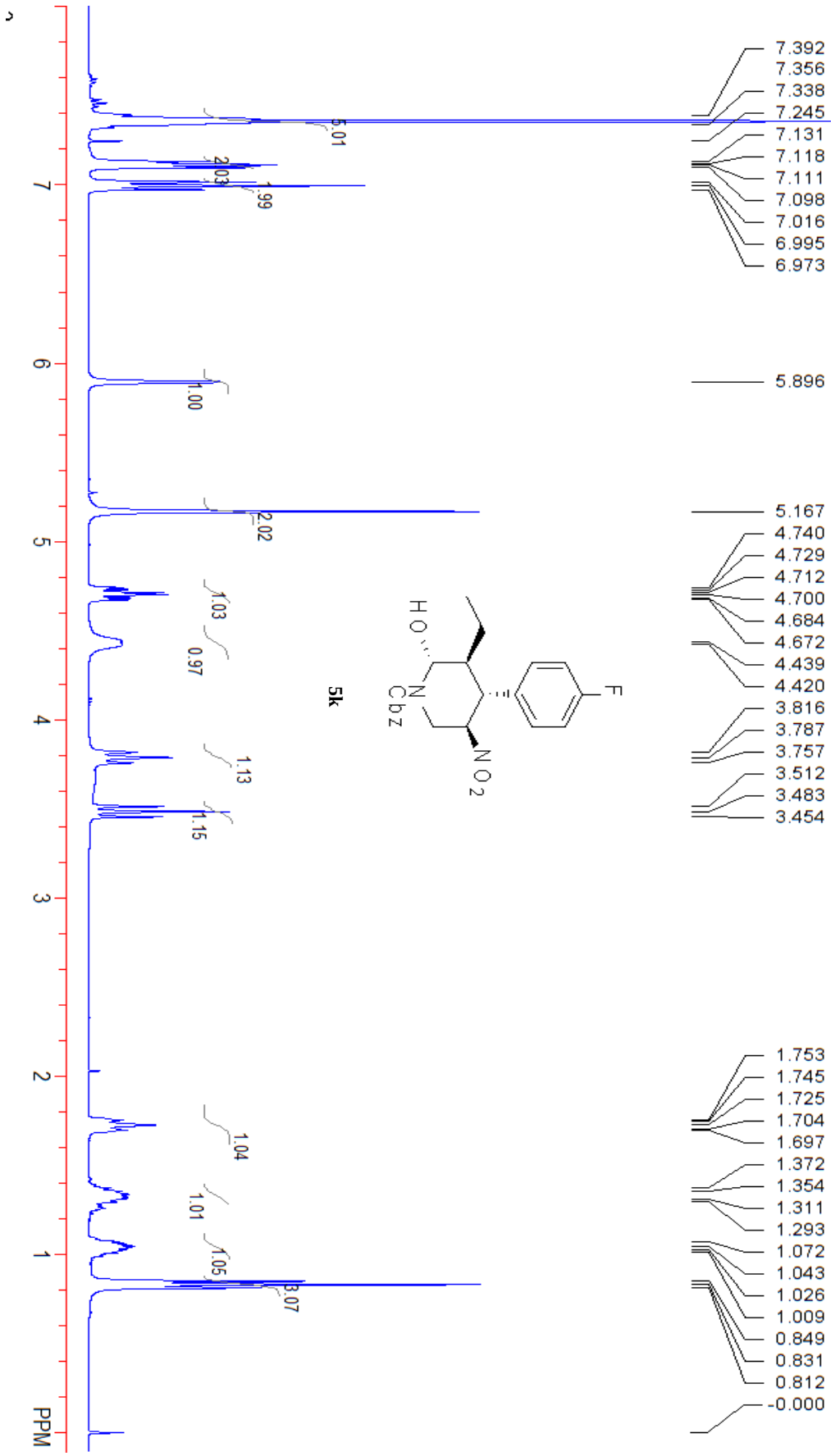
Date:2010-08-25





5j

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	6.627	272.0	5650.9	0.2090
2	2	10.963	121082.4	2698644.4	99.7910
Total			121354.4	2704295.3	100.0000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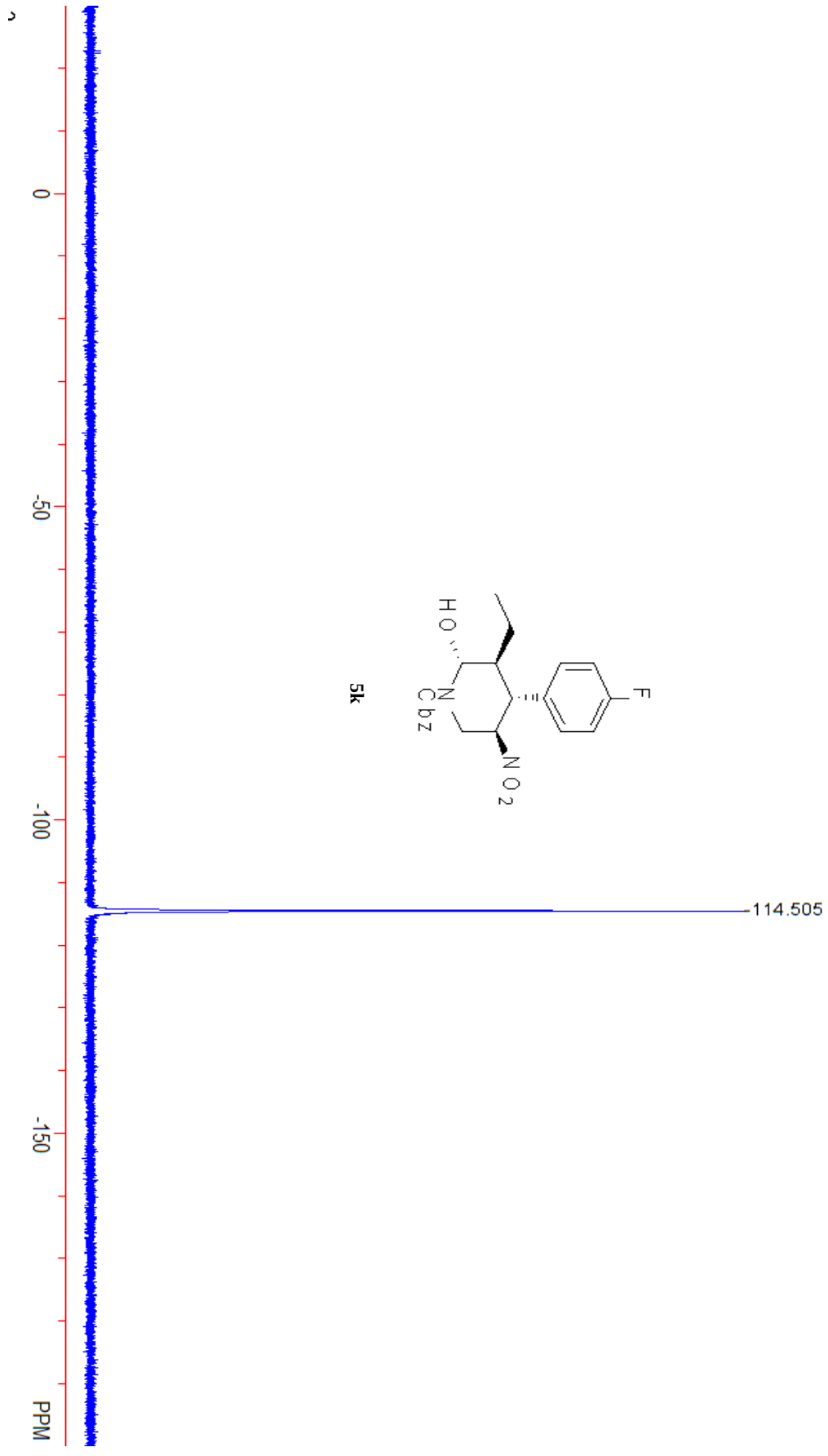
7.245
7.131
7.118
7.111
7.098
7.016
6.995
6.973
5.896
5.167
4.740
4.729
4.712
4.700
4.684
4.672
4.439
4.420
3.816
3.787
3.757
3.512
3.483
3.454
1.753
1.745
1.725
1.704
1.697
1.372
1.354
1.311
1.293
1.072
1.043
1.026
1.009
0.849
0.831
0.812
-0.000
5.01
2.03
1.99
1.00
2.02
1.03
0.97
1.13
1.15
1.04
1.01
1.05
3.07
5k
PPM


0
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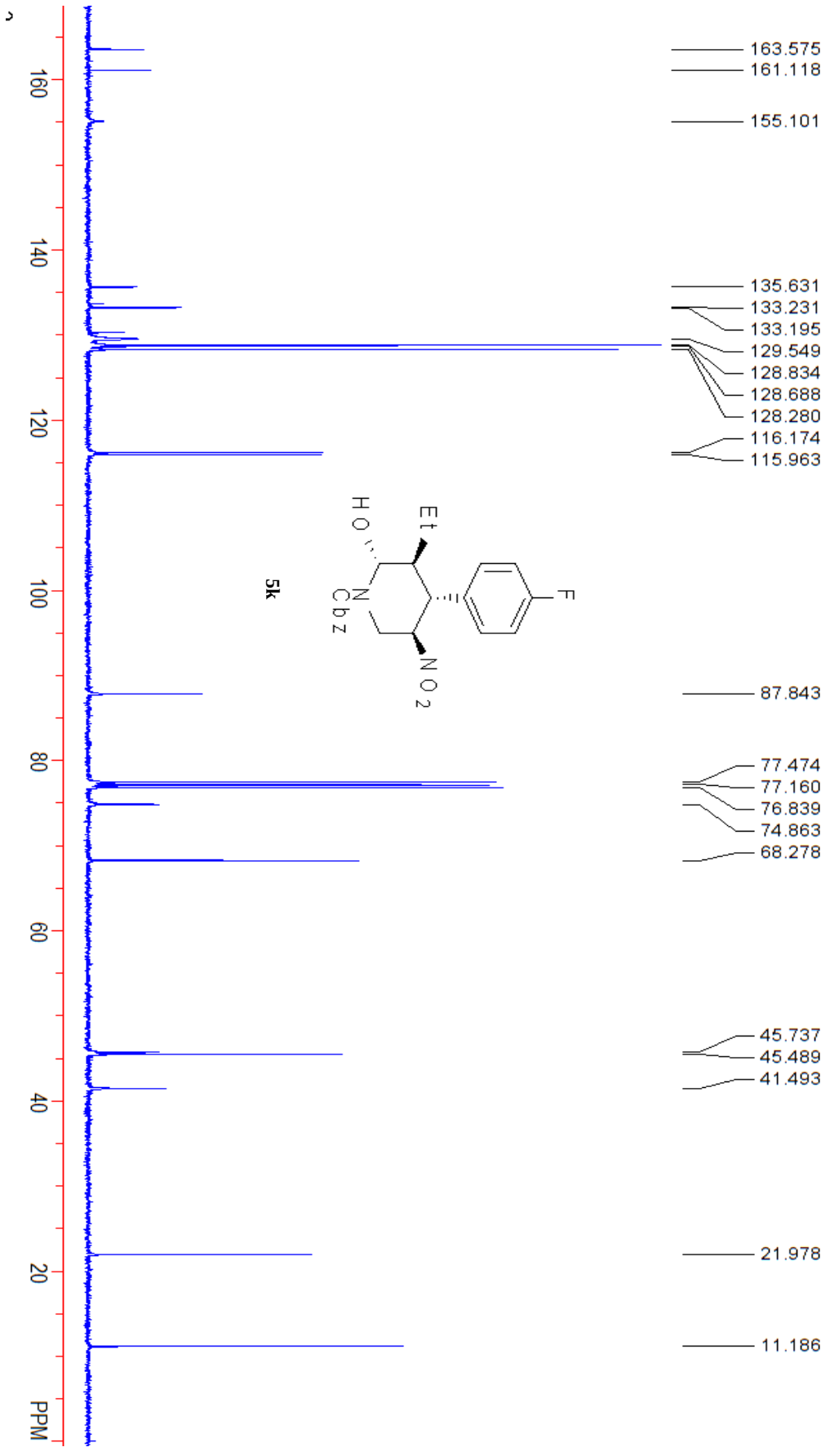
-100
-150
PPM
114.505
5k
HO
N
Cbz
NO2
F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135.631
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133.195
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128.280
116.174
115.963
87.843
77.474
77.160
76.839
74.863
68.278
45.737
45.489
41.493
21.978
11.186
160
140
120
100
80
60
40
20
PPM
5k
HO
Et
N
Cbz
NO2
F

HPLC Report

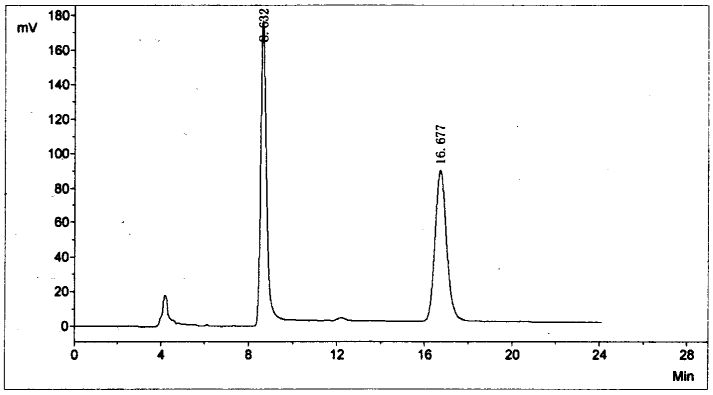
Sample Name:

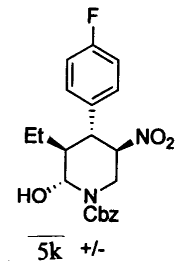
Operator:

Time:13:29

Data File:ZSL6-97+-PC-2820.7214.che

Date:2010-11-23





5k +/-

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.632	174752.3	3111513.3	49.1262
2	2	16.677	87305.2	3222207.0	50.8738
Total			262057.5	6333720.3	100.0000

HPLC Report

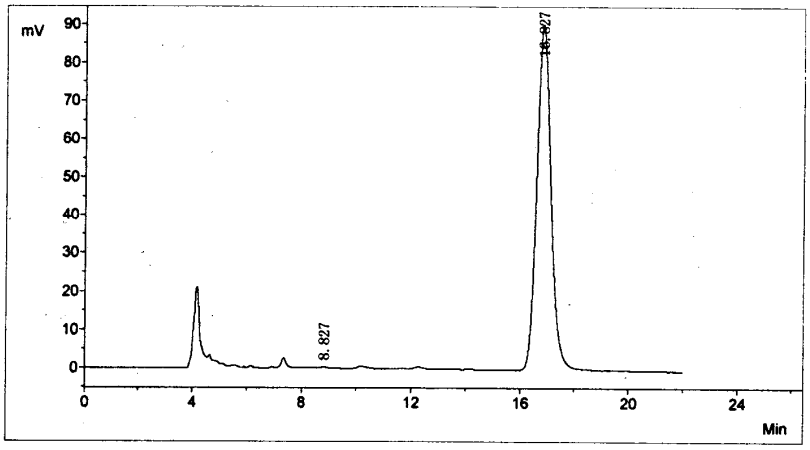
Sample Name:

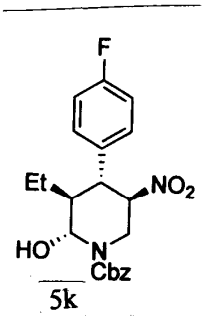
Operator:

Time:13:57

Data File:ZSL6-98.che

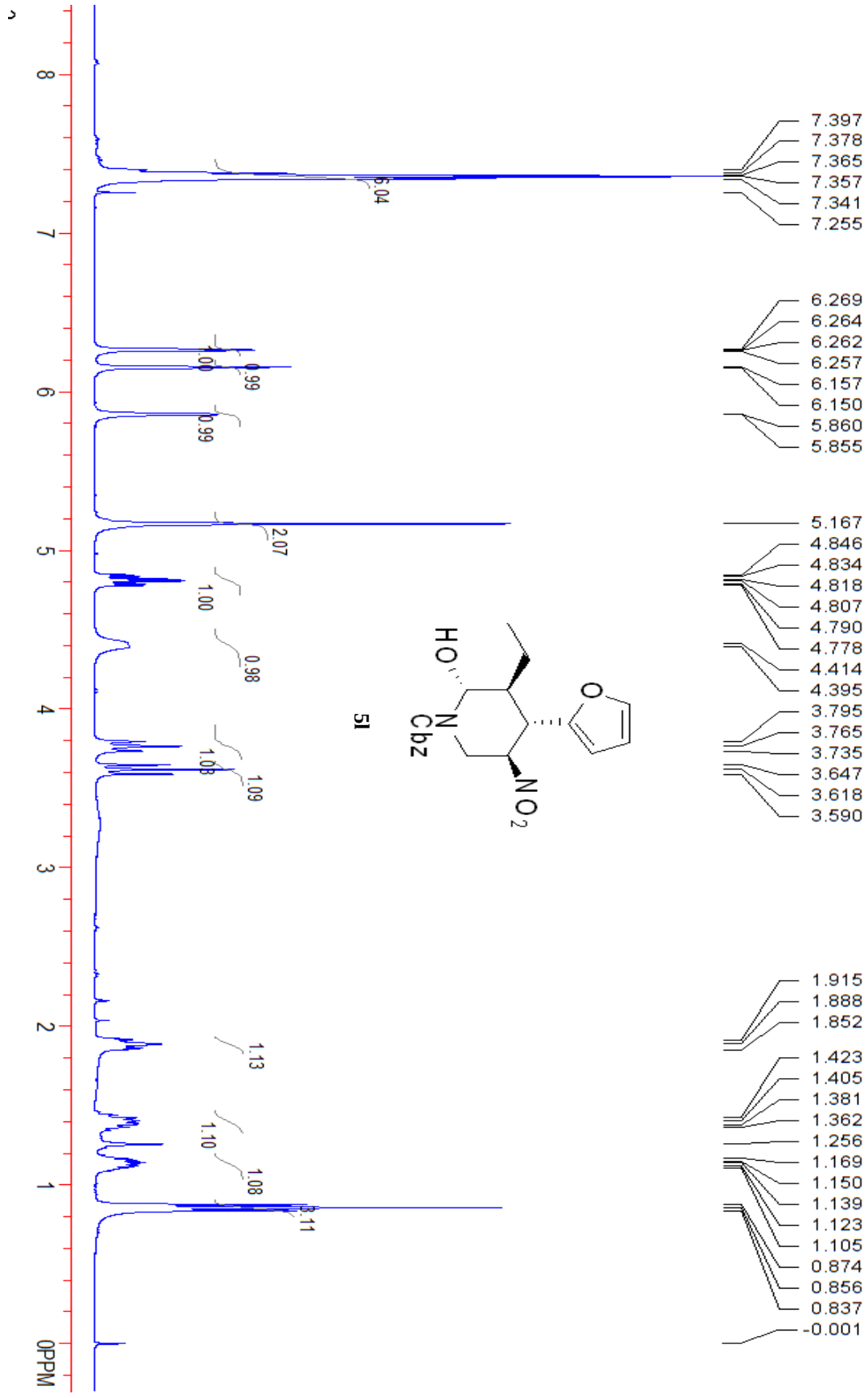
Date:2010-11-23





5k

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	8.827	246.4	1609.5	0.0489
2	2	16.827	90385.6	3292203.7	99.9511
Total			90632.0	3293813.2	100.0000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7.255
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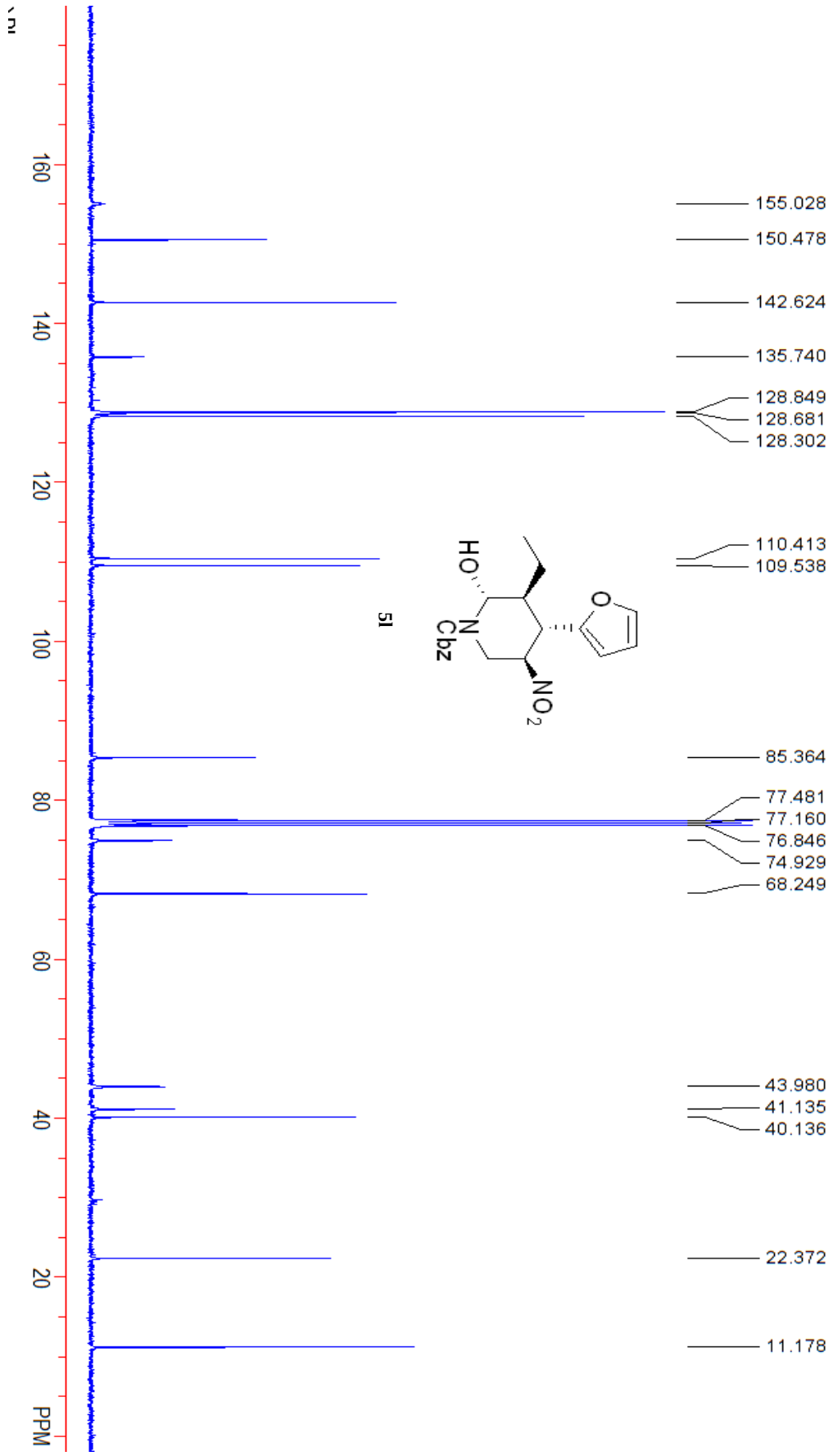
6.264
6.262
6.257
6.157
6.150
5.860
5.855
5.167
4.846
4.834
4.818
4.807
4.790
4.778
4.414
4.395
3.795
3.765
3.735
3.647
3.618
3.590
1.915
1.888
1.852
1.423
1.405
1.381
1.362
1.256
1.169
1.150
1.139
1.123
1.105
0.874
0.856
0.837
-0.001
6.04
1.00
0.99
0.99
2.07
1.00
0.98
1.03
1.09
1.13
1.10
1.08
3.11
HO
N
Cbz
O
NO2
5l
0PPM


155.028
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128.681
128.302
110.413
109.538
85.364
77.481
77.160
76.846
74.929
68.249
43.980
41.135
40.136
22.372
11.178
HO
N
Cbz
O
NO2
51
160
140
120
100
80
60
40
20
PPM

HPLC Report

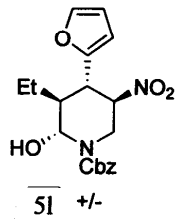
Sample Name:

Operator:

Time:09:32

Data File:ZSL-6-52+- PC-2 73 214 0.7.che

Date:2010-08-20



5l +/-

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		6.562	1039130.9	12968537.7	49.4847
2	2		8.252	783219.4	13238615.3	50.5153
Total				1822350.3	26207153.0	100.0000

HPLC Report

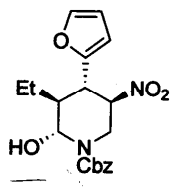
Sample Name:

Operator:

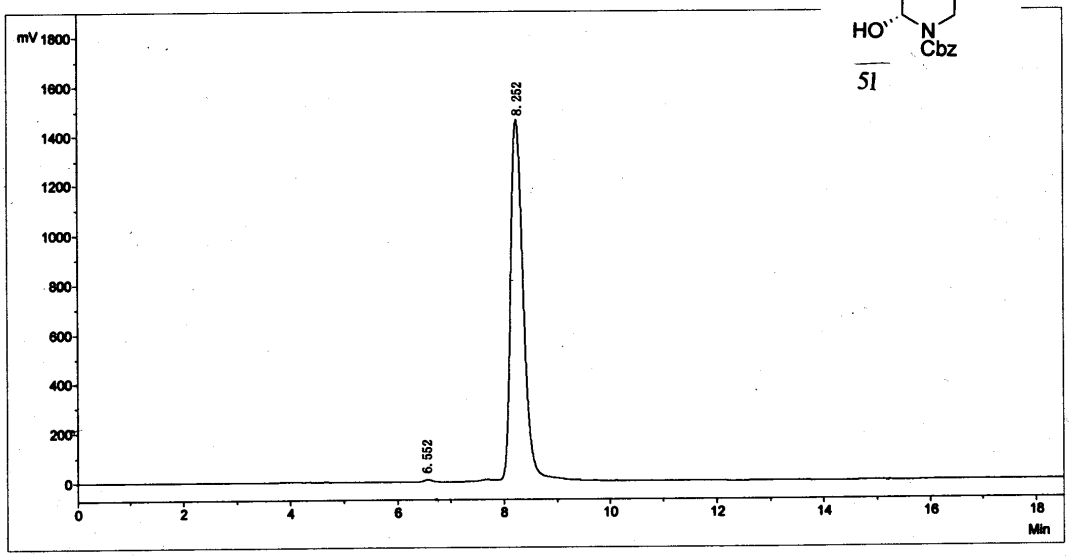
Time:09:53

Data File:ZSL-6-57.che

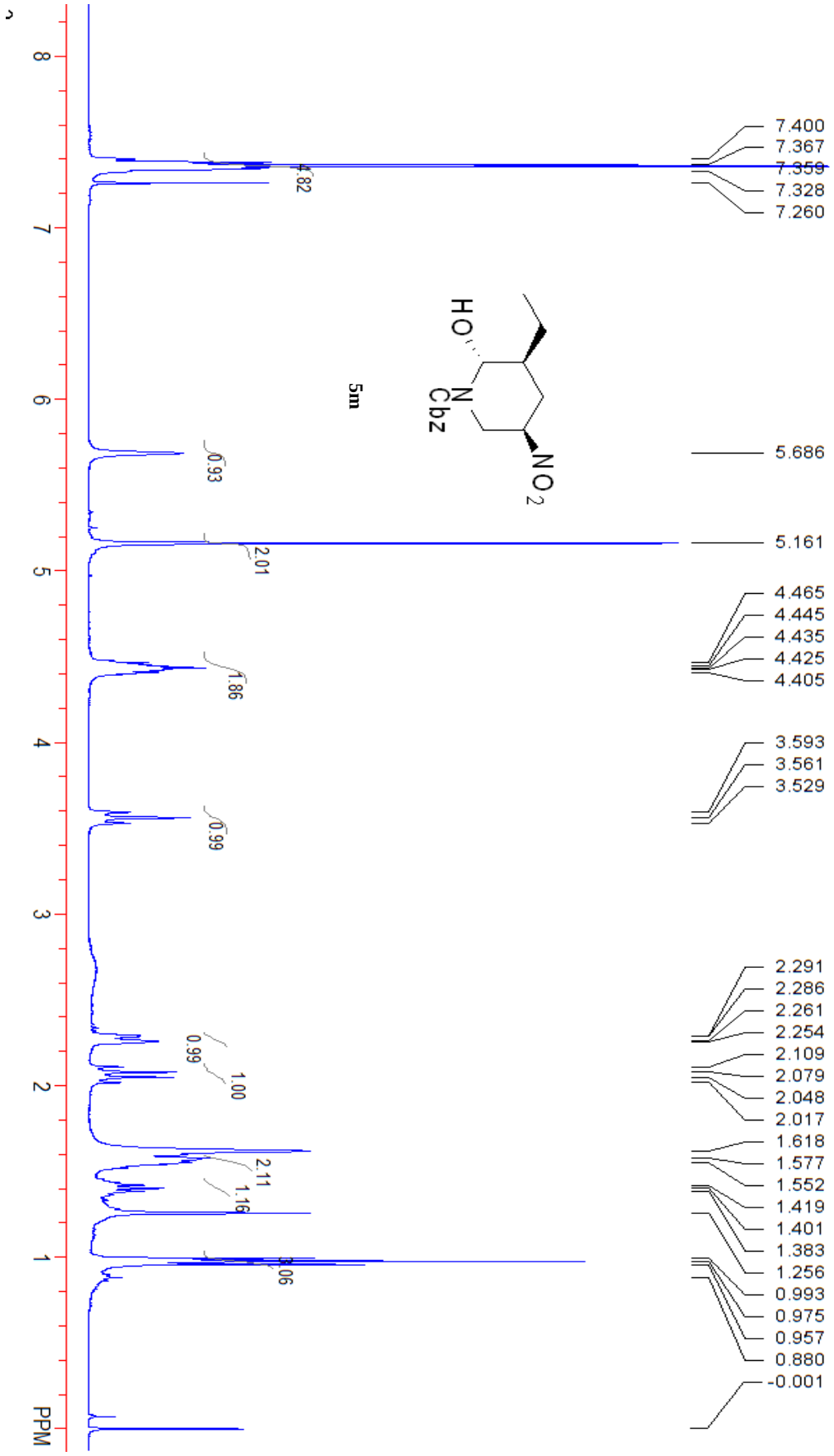
Date:2010-08-20



5l



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		6.552	9232.6	106097.7	0.4436
2	2		8.252	1448408.9	23811995.8	99.5564
Total				1457641.5	23918093.5	100.0000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7.260
5.686
5.161
4.465
4.445
4.435
4.425
4.405
3.593
3.561
3.529
2.291
2.286
2.261
2.254
2.109
2.079
2.048
2.017
1.618
1.577
1.552
1.419
1.401
1.383
1.256
0.993
0.975
0.957
0.880
-0.001
4.82
0.93
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0.99
1.00
2.11
1.16
6.06
5m
HO
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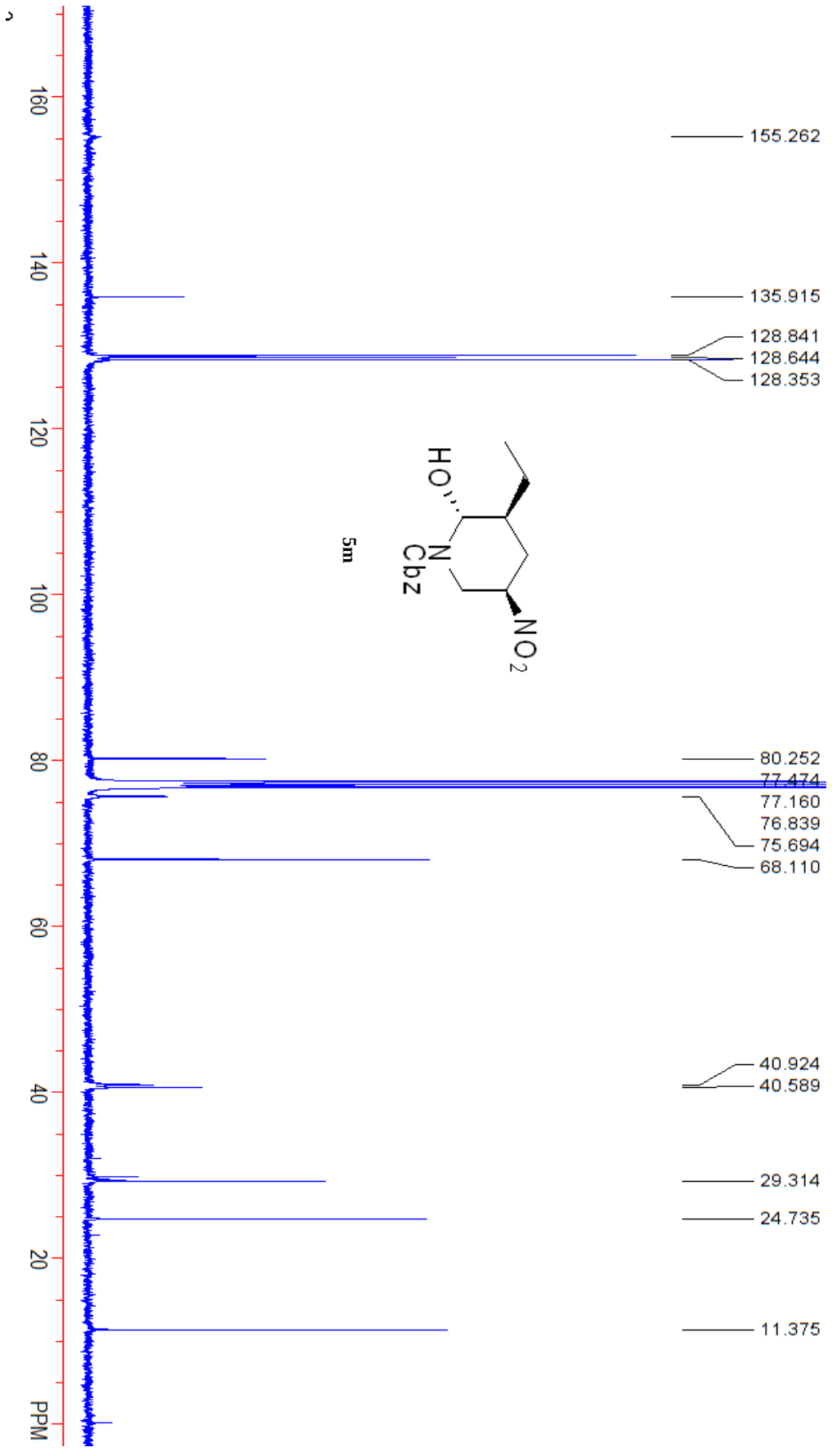
Cbz
NO2
PPM


155.262
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128.841
128.644
128.353
80.252
77.474
77.160
76.839
75.694
68.110
40.924
40.589
29.314
24.735
11.375
PPM
160
140
120
100
80
60
40
20
5m
HO
N
Cbz
NO2

HPLC Report

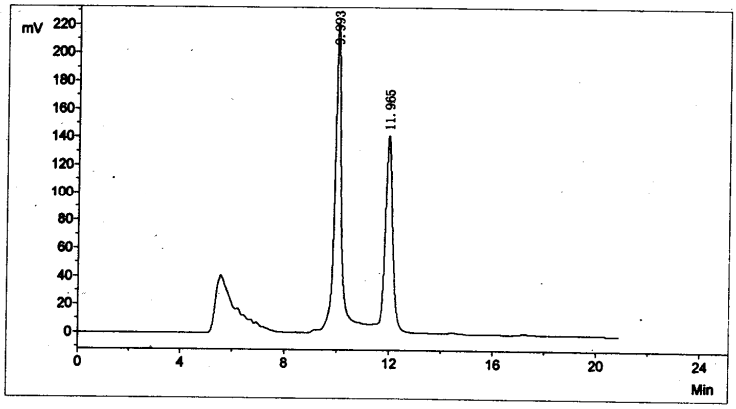
Sample Name:

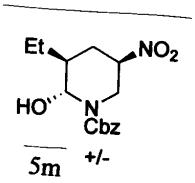
Operator:

Time:10:01

Data File:ZSL6-75+-PA-2730.5214.che

Date:2010-10-13





5m +/-

No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		9.993	215869.9	3477952.2	57.8622
2	2		11.965	136573.4	2532800.5	42.1378
Total				352443.2	6010752.6	100.0000

HPLC Report

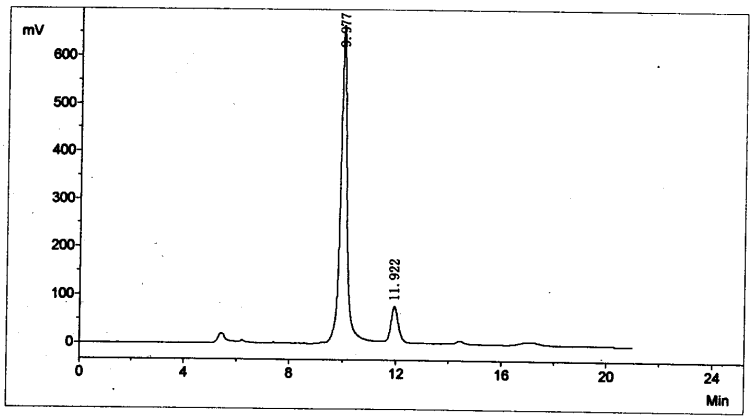
Sample Name:

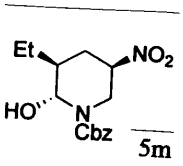
Operator:

Time:10:26

Data File:ZSL6-78.che

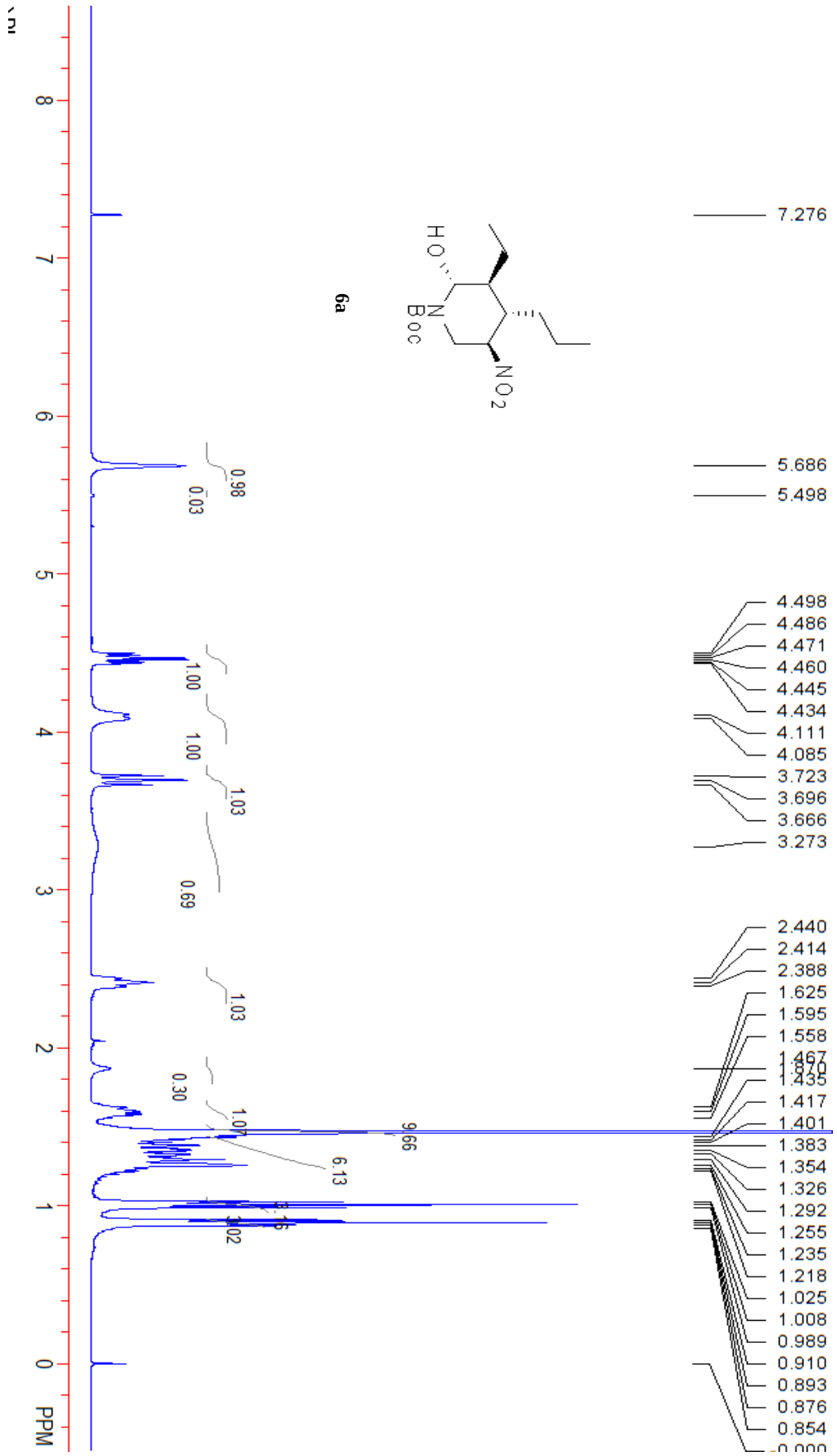
Date:2010-10-13





5m

No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		9.977	659599.3	11319465.2	89.2951
2	2		11.922	71528.3	1357006.8	10.7049
Total				731127.6	12676472.0	100.0000


6a
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Boc
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4.111
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3.723
3.696
3.666
3.273
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2.414
2.388
1.625
1.595
1.558
1.467
1.435
1.417
1.401
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1.354
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1.292
1.255
1.235
1.218
1.025
1.008
0.989
0.910
0.893
0.876
0.854
0.98
0.03
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1.00
1.03
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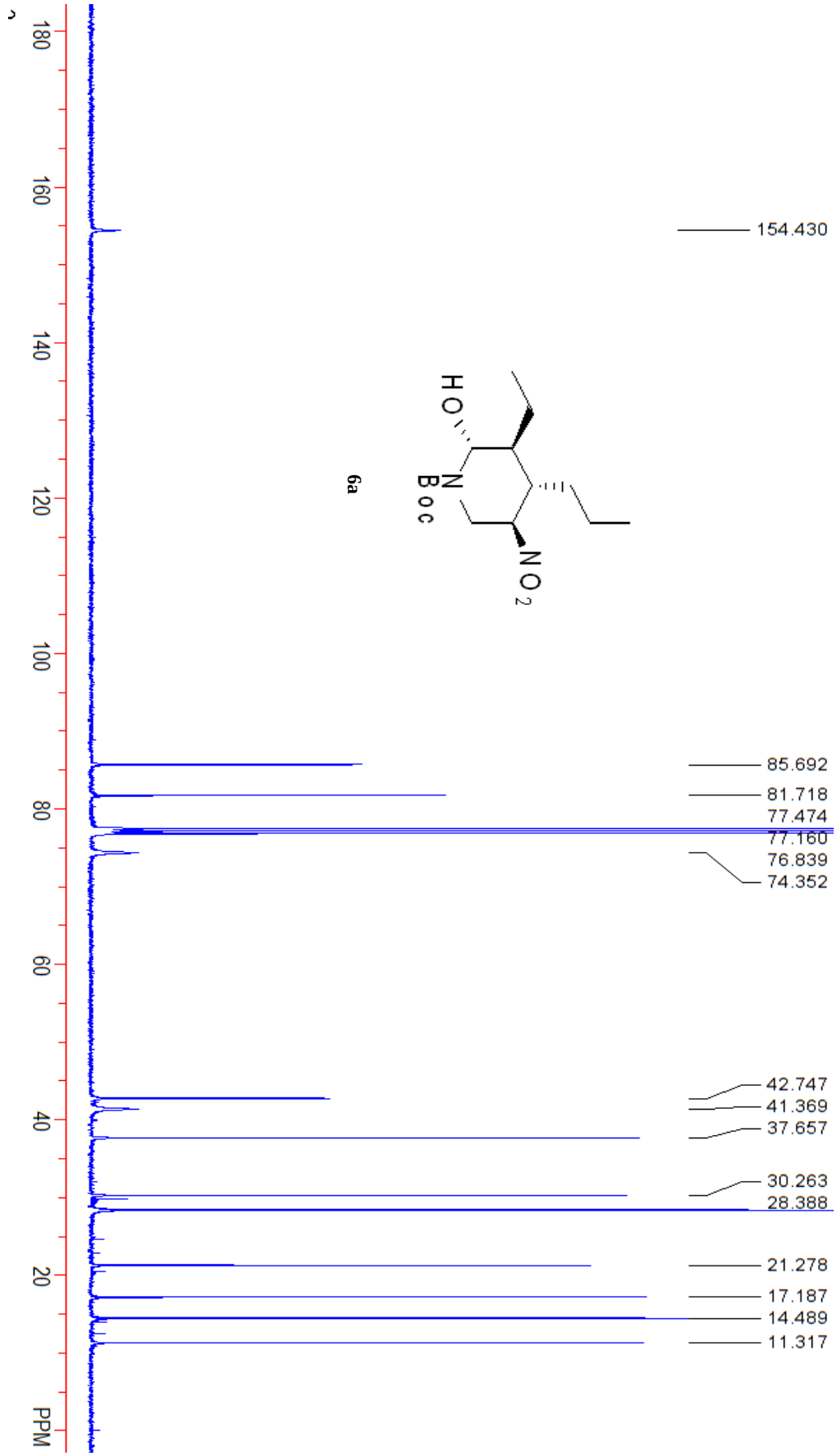
0.30
1.07
9.66
6.13
3.02
PPM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77.160
76.839
74.352
42.747
41.369
37.657
30.263
28.388
21.278
17.187
14.489
11.317
PPM
180
160
140
120
100
80
60
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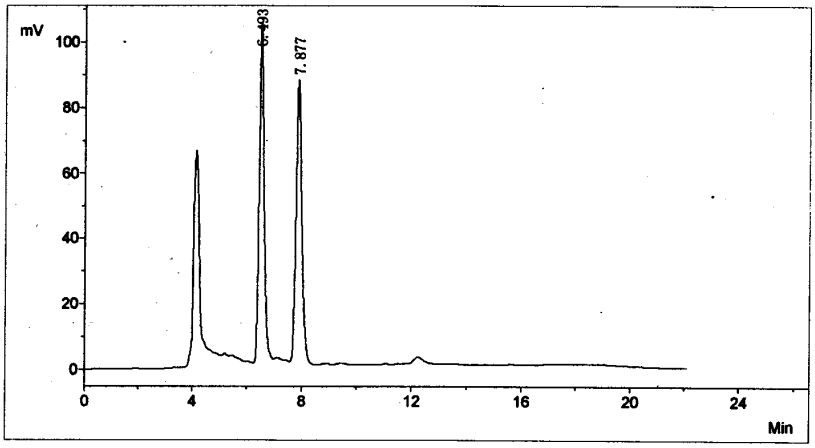
20
HO
N
Boc
NO2
6a

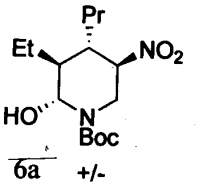
HPLC REPORT

Data File:ZSL6-39-2+-SINO-AD910.7214.che Sample name:

Date:2010-08-26 Time :08:58

Operator;





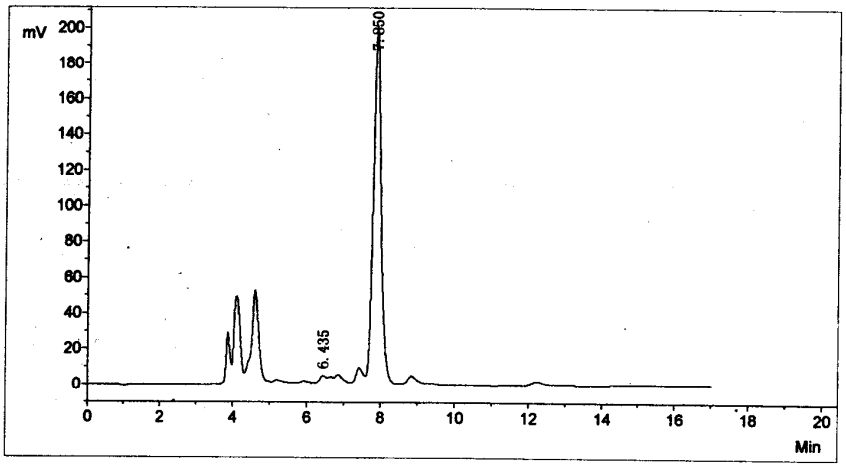
6a +/-

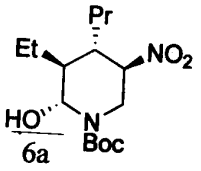
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		6.493	102897.1	1258809.9	50.0411
2	2		7.877	85796.0	1256741.0	49.9589
Total				188693.0	2515550.9	100.0000

HPLC REPORT

Data File:6-41-2.che
Date:2010-08-26
Operator:

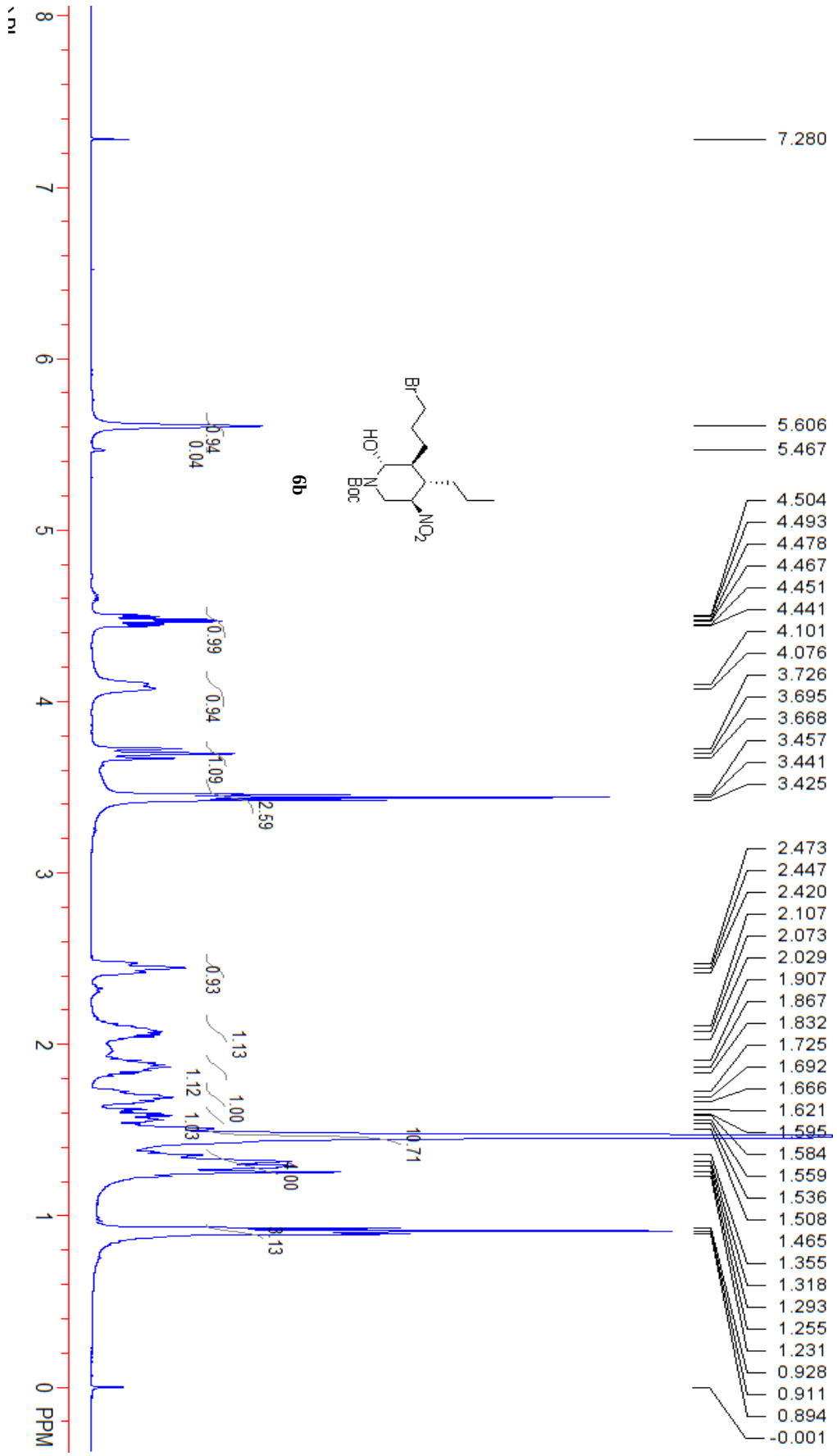
Sample name:
Time :09:27





6a

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		6.435	807.1	3981.3	0.1446
2	2		7.850	196129.3	2748652.6	99.8554
Total				196936.4	2752633.9	100.0000


6b
Br
HO
N
Boc
NO2
7.280
5.606
5.467
4.504
4.493
4.478
4.467
4.451
4.441
4.101
4.076
3.726
3.695
3.668
3.457
3.441
3.425
2.473
2.447
2.420
2.107
2.073
2.029
1.907
1.867
1.832
1.725
1.692
1.666
1.621
1.595
1.584
1.559
1.536
1.508
1.465
1.355
1.318
1.293
1.255
1.231
0.928
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0.894
-0.001
0.94
0.04
0.99
0.94
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2.59
0.93
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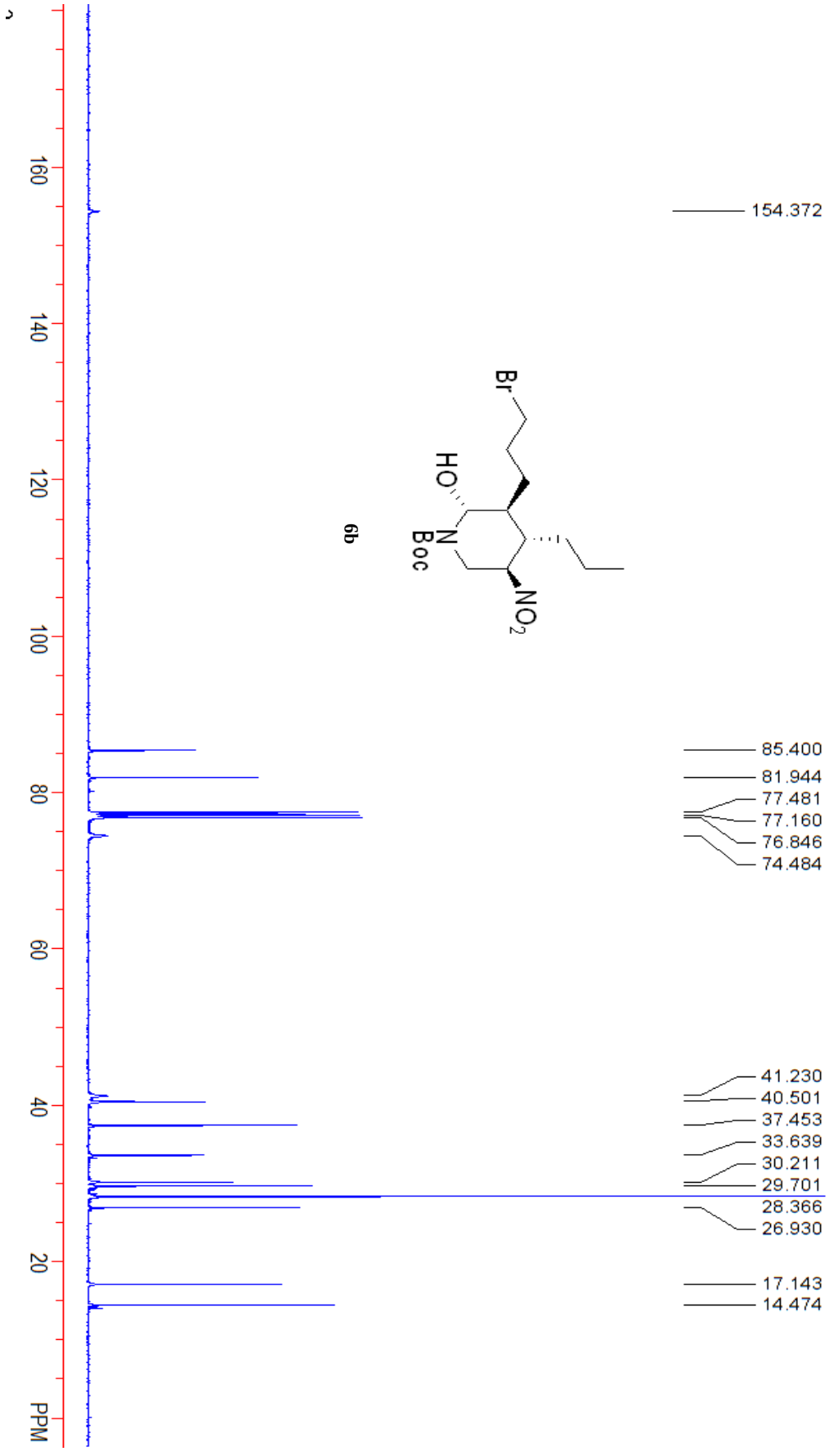
1.00
1.03
10.71
4.00
3.13
0 PPM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37.453
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28.366
26.930
17.143
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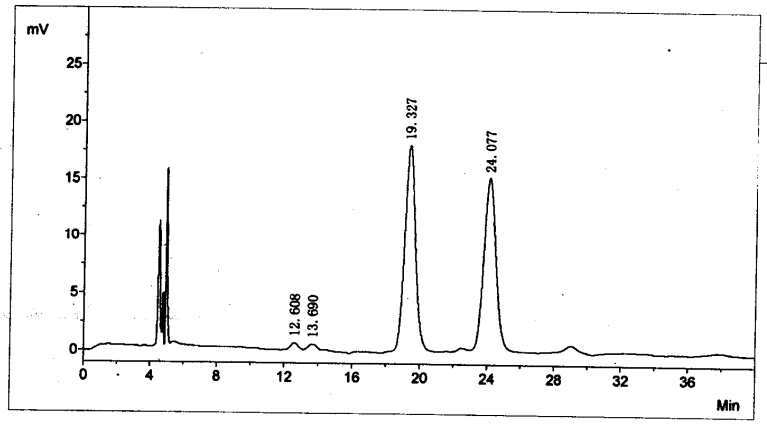
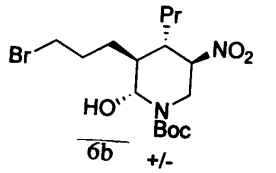
160
140
120
100
80
60
40
20
PPM
6b
Br
HO
N
Boc
NO2

HPLC REPORT

Data File:ZSL-6-44+- IC 982 214 0.7.che
Sample name:
Date:2010-08-16
Time :15:56
Operator:





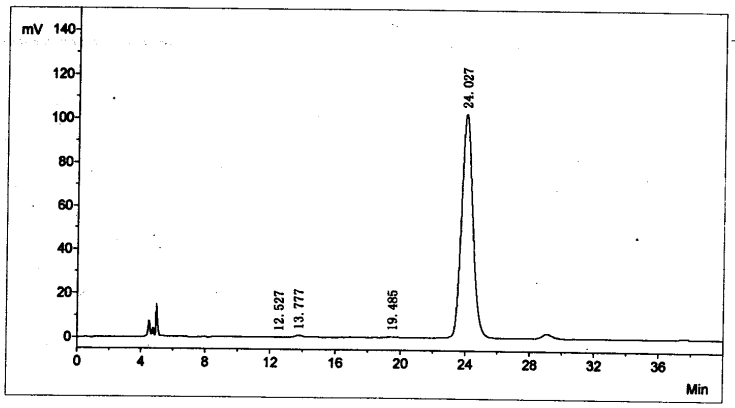
6b +/-

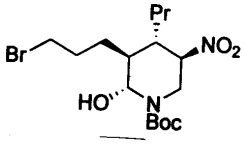
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		12.608	579.8	17664.9	1.1128
2	2		13.690	504.5	16716.8	1.0531
3	3		19.327	18018.8	799430.5	50.3596
4	4		24.077	15054.6	753631.6	47.4745
Total				34157.7	1587443.7	100.0000

HPLC REPORT

Data File:ZSL-6-42.che
Date:2010-08-16
Operator:

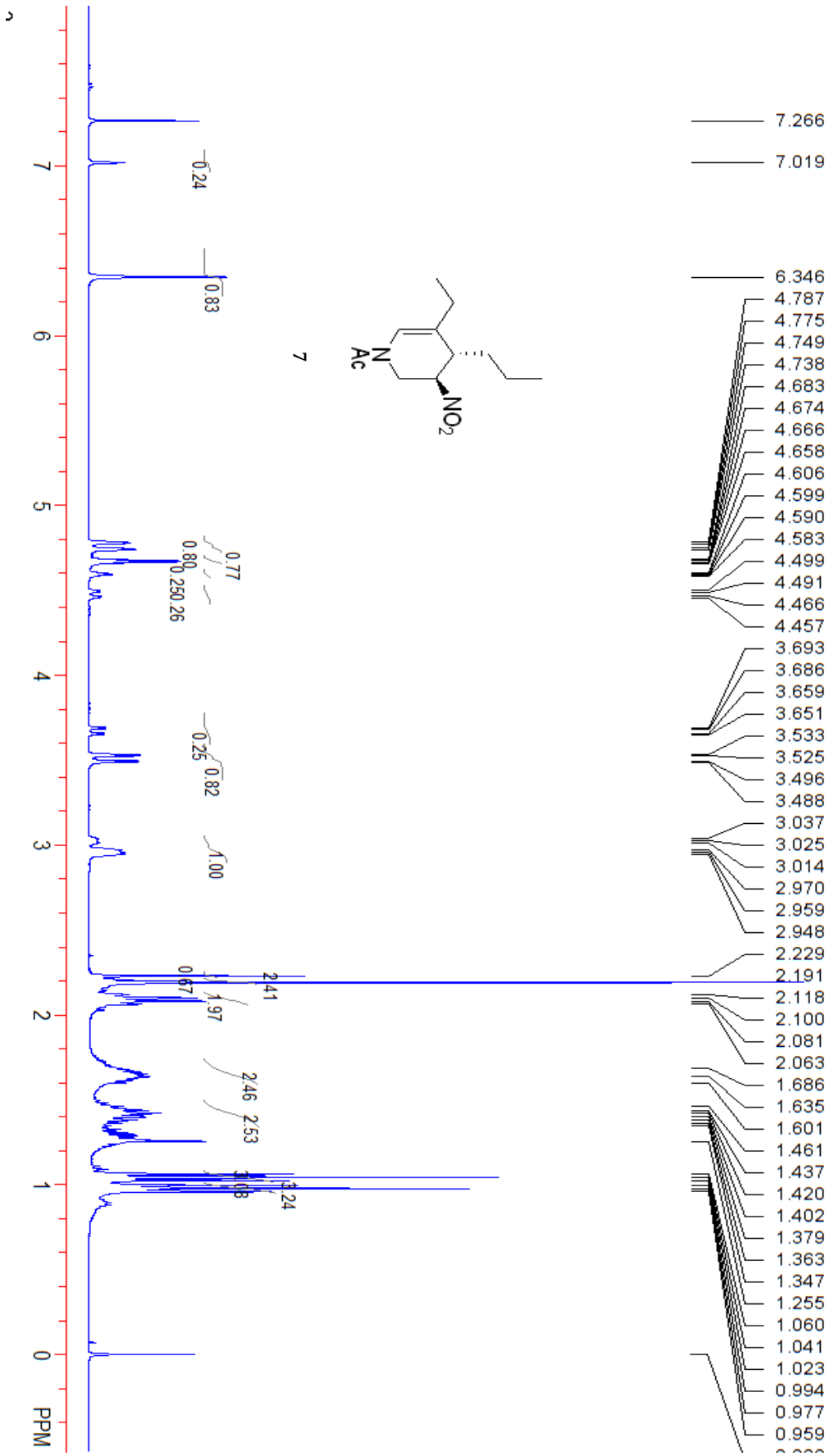
Sample name:
Time :16:40





6b

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		12.527	55.6	1831.4	0.0367
2	2		13.777	817.9	24950.0	0.4996
3	3		19.485	340.9	19602.6	0.3925
4	4		24.027	101902.7	4947892.8	99.0713
Total				103117.1	4994276.8	100.0000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4.683
4.674
4.666
4.658
4.606
4.599
4.590
4.583
4.499
4.491
4.466
4.457
3.693
3.686
3.659
3.651
3.533
3.525
3.496
3.488
3.037
3.025
3.014
2.970
2.959
2.948
2.229
2.191
2.118
2.100
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2.063
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1.420
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1.060
1.041
1.023
0.994
0.977
0.959
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0.83
0.77
0.80
0.25
0.26
0.25
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1.00
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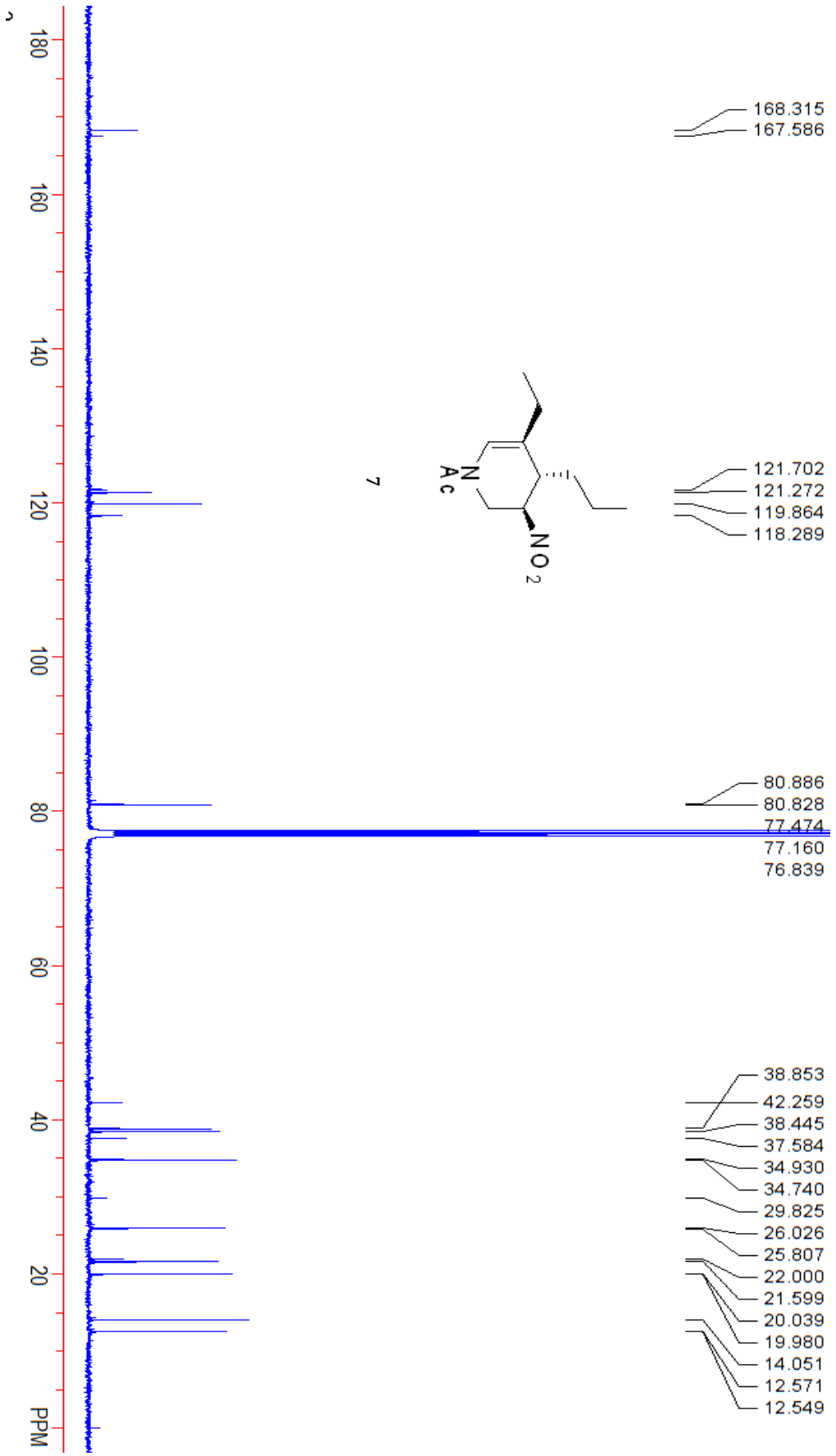
2.41
1.97
2.46
2.53
3.10
3.24
N
Ac
NO2
7
PPM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42.259
38.445
37.584
34.930
34.740
29.825
26.026
25.807
22.000
21.599
20.039
19.980
14.051
12.571
12.549
180
160
140
120
100
80
60
40
20
PPM
N
Ac
NO2
7

HPLC Report

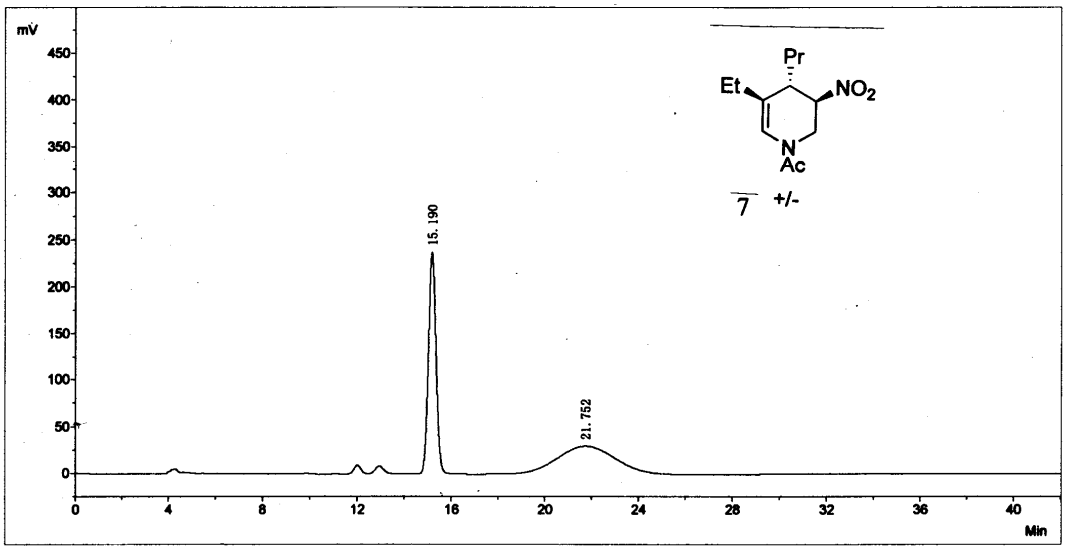
Sample Name:

Operator:

Time:13:53

Data File:ZSL-6-45-0+- PA-2 73 214 0.7.che

Date:2010-08-20



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		15.190	237616.4	5339516.5	50.7161
2	2		21.752	30110.3	5188736.6	49.2839
Total				267726.7	10528253.1	100.0000

HPLC Report

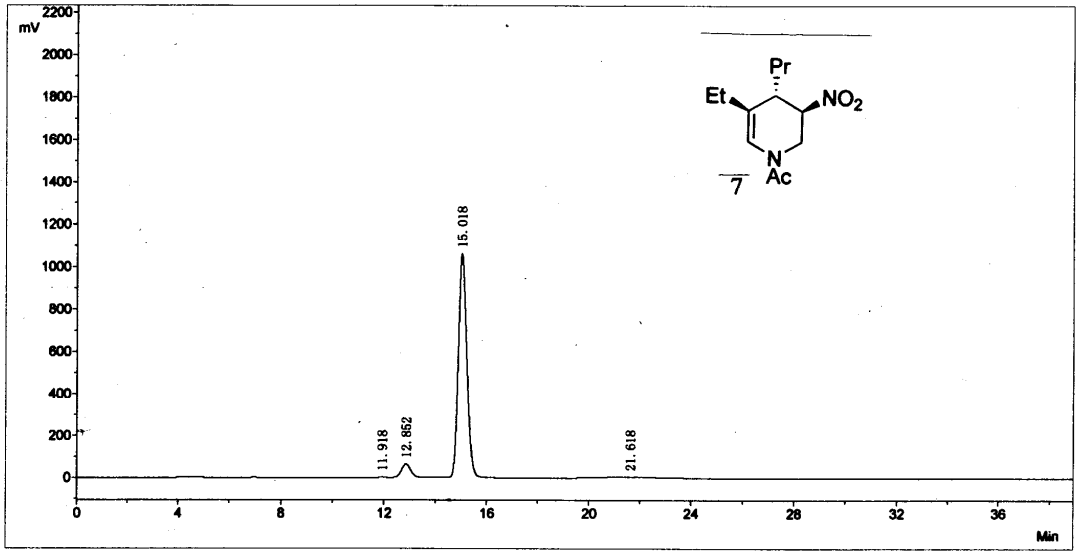
Sample Name:

Operator:

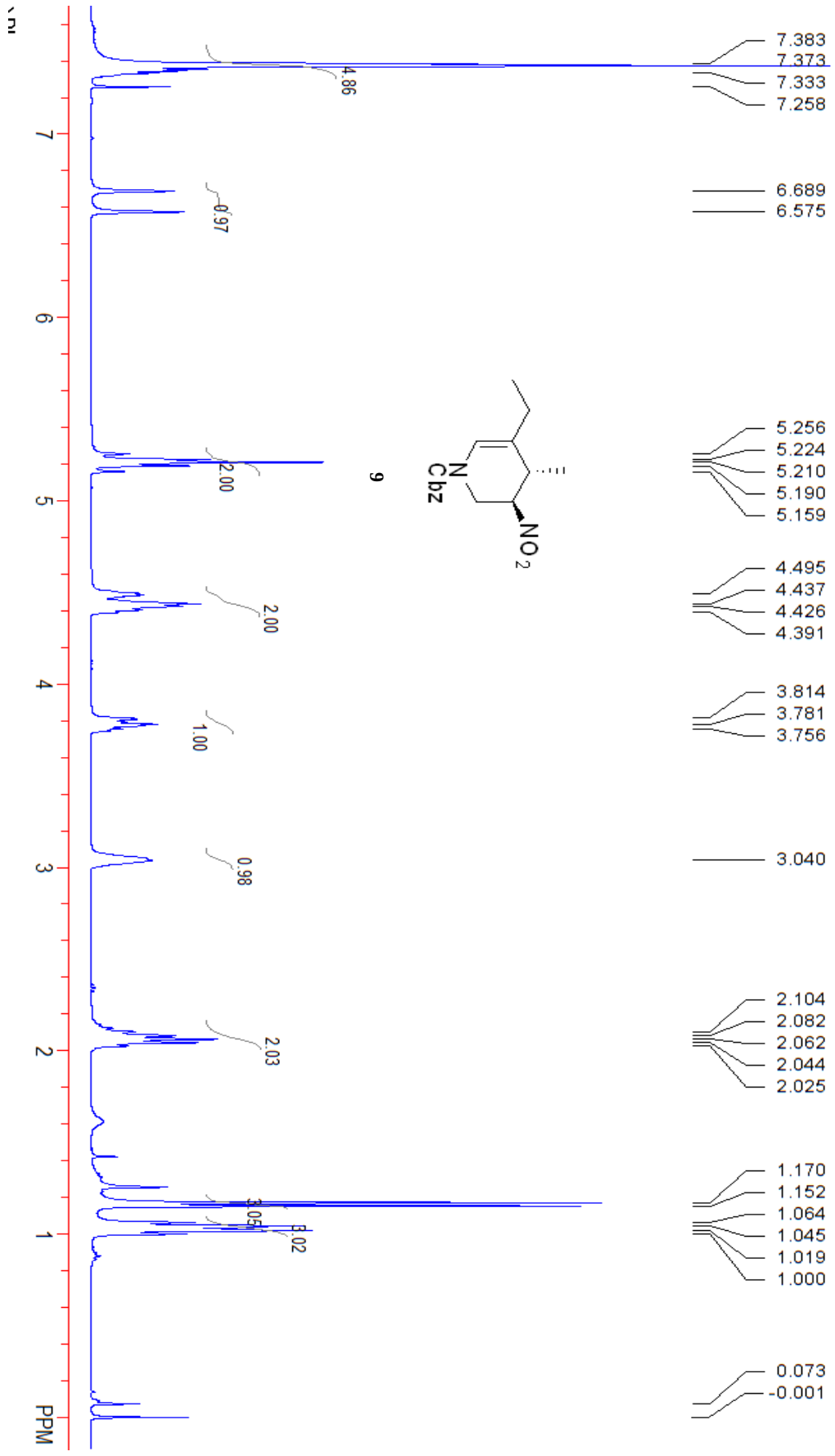
Time:14:37

Data File:ZSL-6-49-0..che

Date:2010-08-20



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		11.918	1116.1	22220.3	0.0819
2	2		12.852	64588.6	1637058.0	6.0356
3	3		15.018	1061127.9	24532317.4	90.4475
4	4		21.618	5505.1	931660.9	3.4349
Total				1132337.8	27123256.6	100.0000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5.159
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4.437
4.426
4.391
3.814
3.781
3.756
3.040
2.104
2.082
2.062
2.044
2.025
1.170
1.152
1.064
1.045
1.019
1.000
0.073
-0.001
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2.00
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1.00
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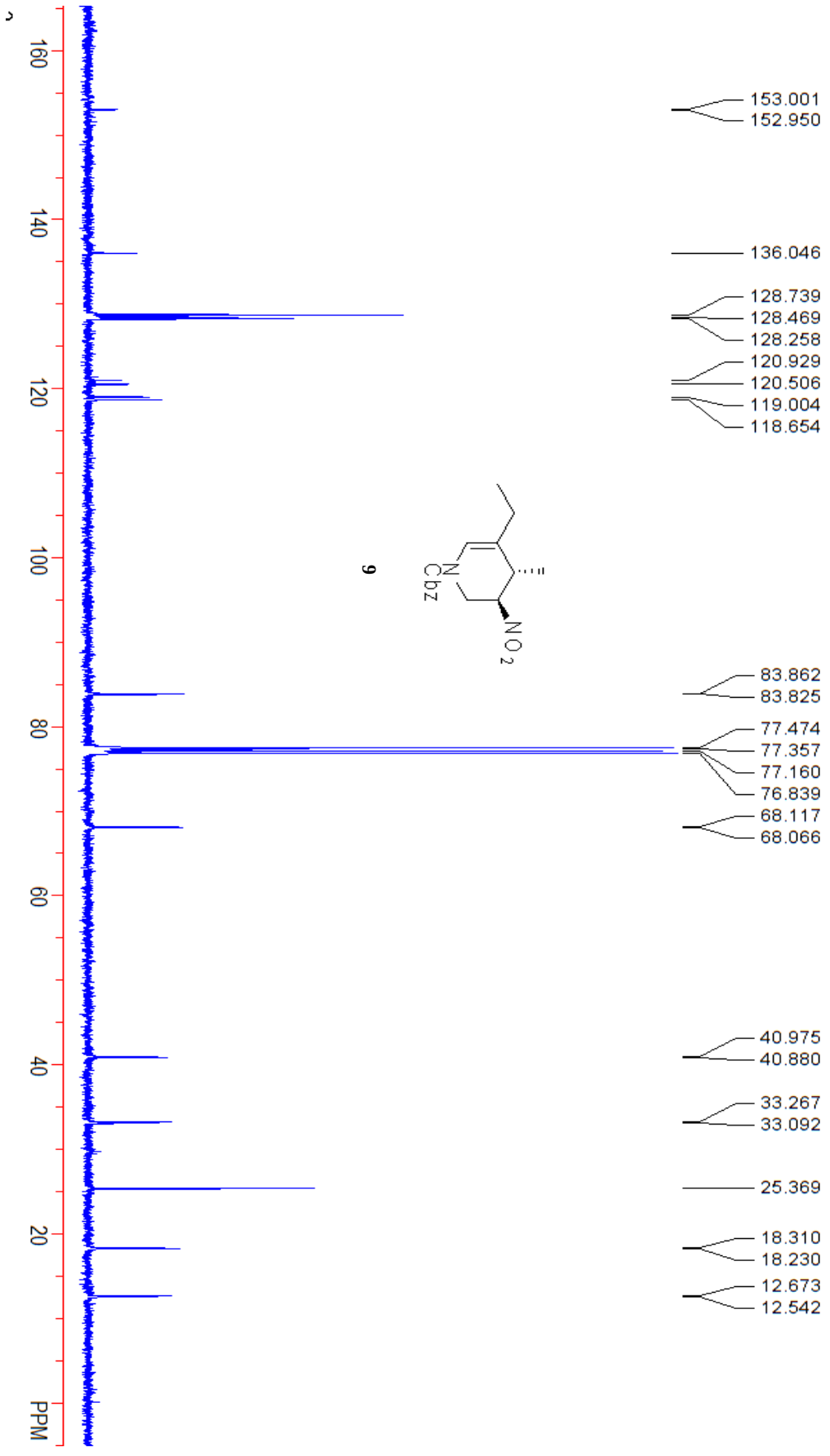
3.05
3.02
9
Cbz
NO2
PPM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77.357
77.160
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40.975
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33.267
33.092
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140
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40
20
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6
Cbz
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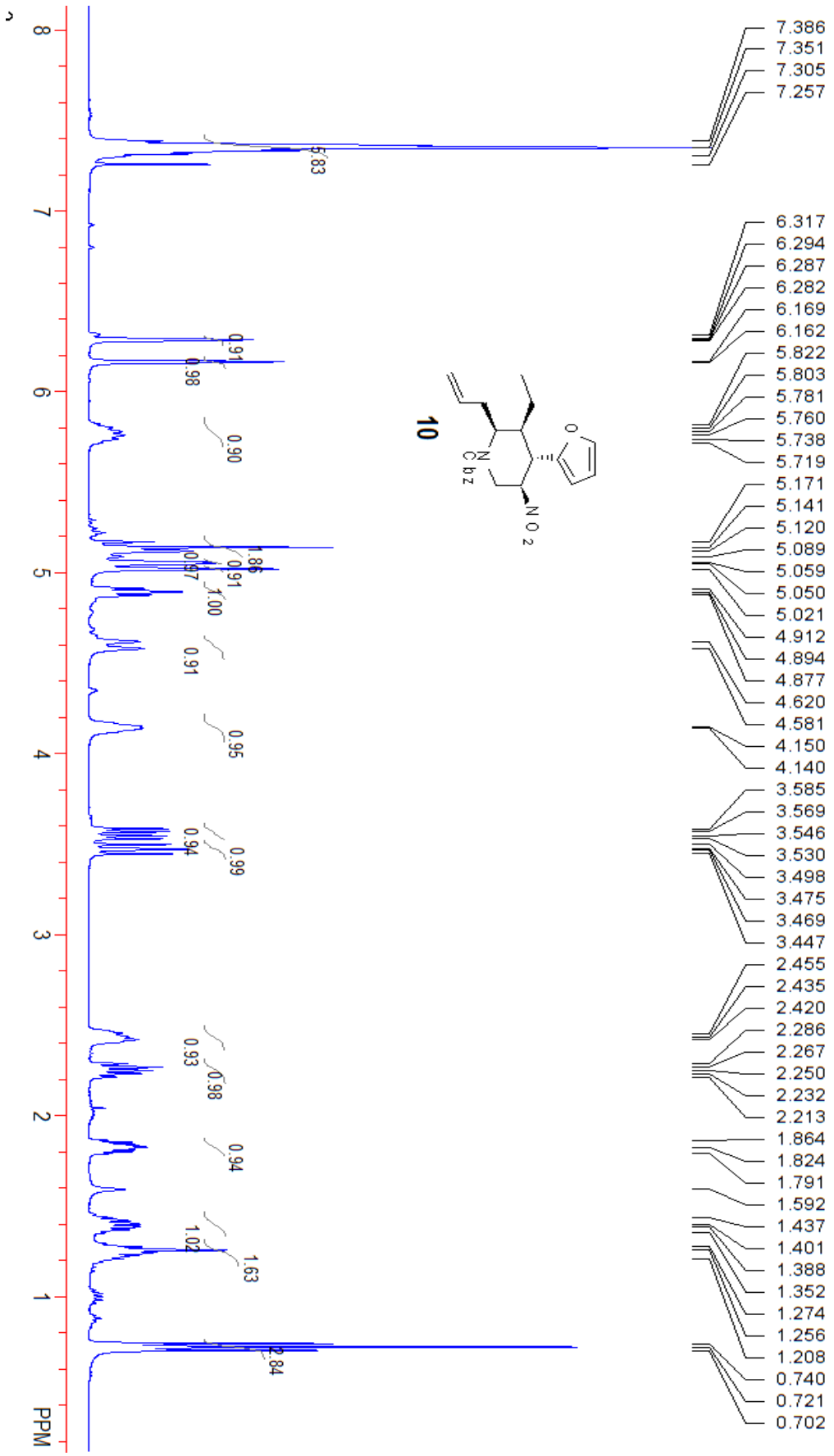
NO2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5.781
5.760
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5.171
5.141
5.120
5.089
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5.050
5.021
4.912
4.894
4.877
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4.581
4.150
4.140
3.585
3.569
3.546
3.530
3.498
3.475
3.469
3.447
2.455
2.435
2.420
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2.250
2.232
2.213
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1.791
1.592
1.437
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1.274
1.256
1.208
0.740
0.721
0.702
10
N
C bz
O
N O 2
5.83
0.91
0.98
0.90
1.86
0.97
0.91
1.00
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0.99
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0.94
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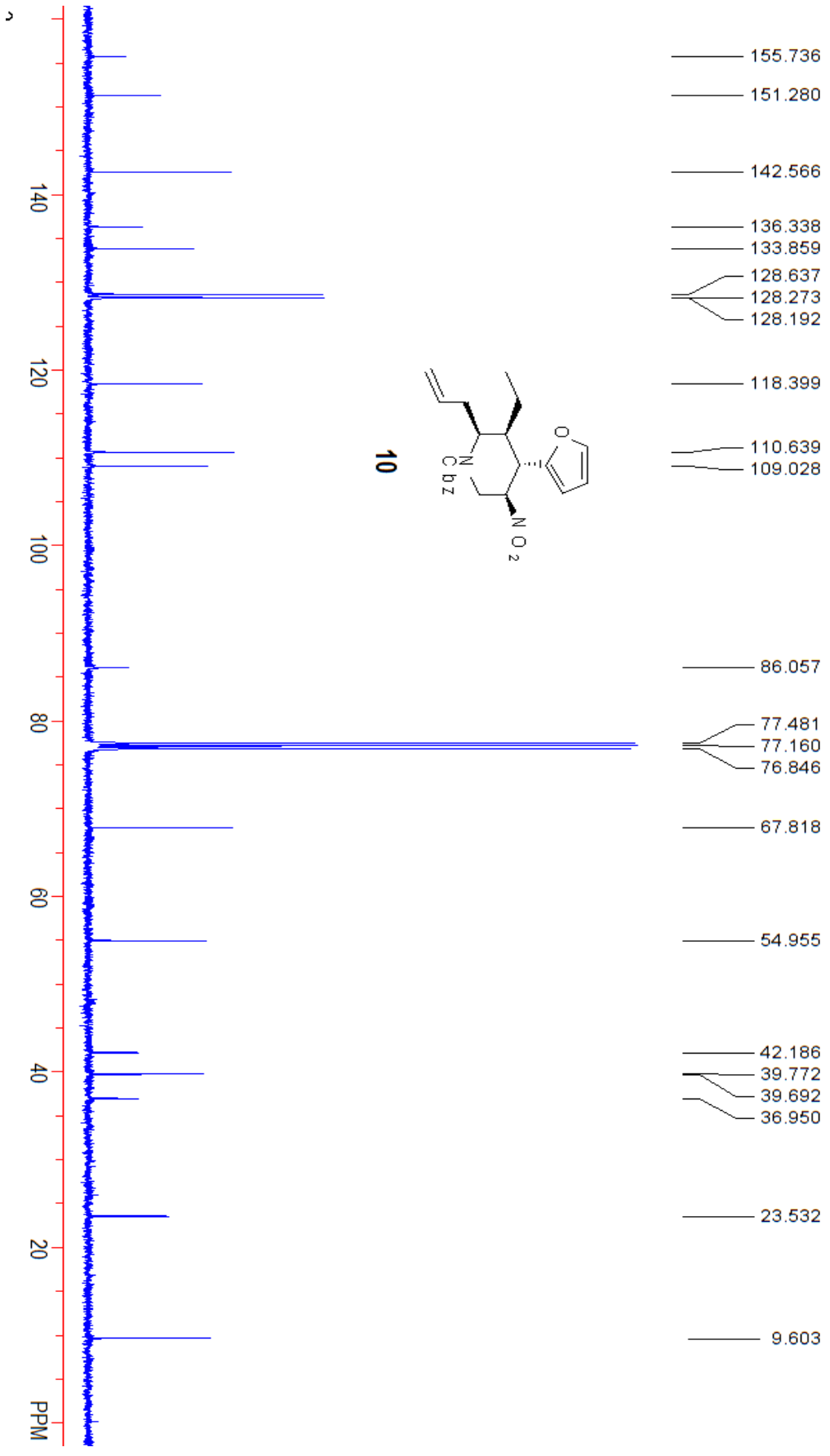
PPM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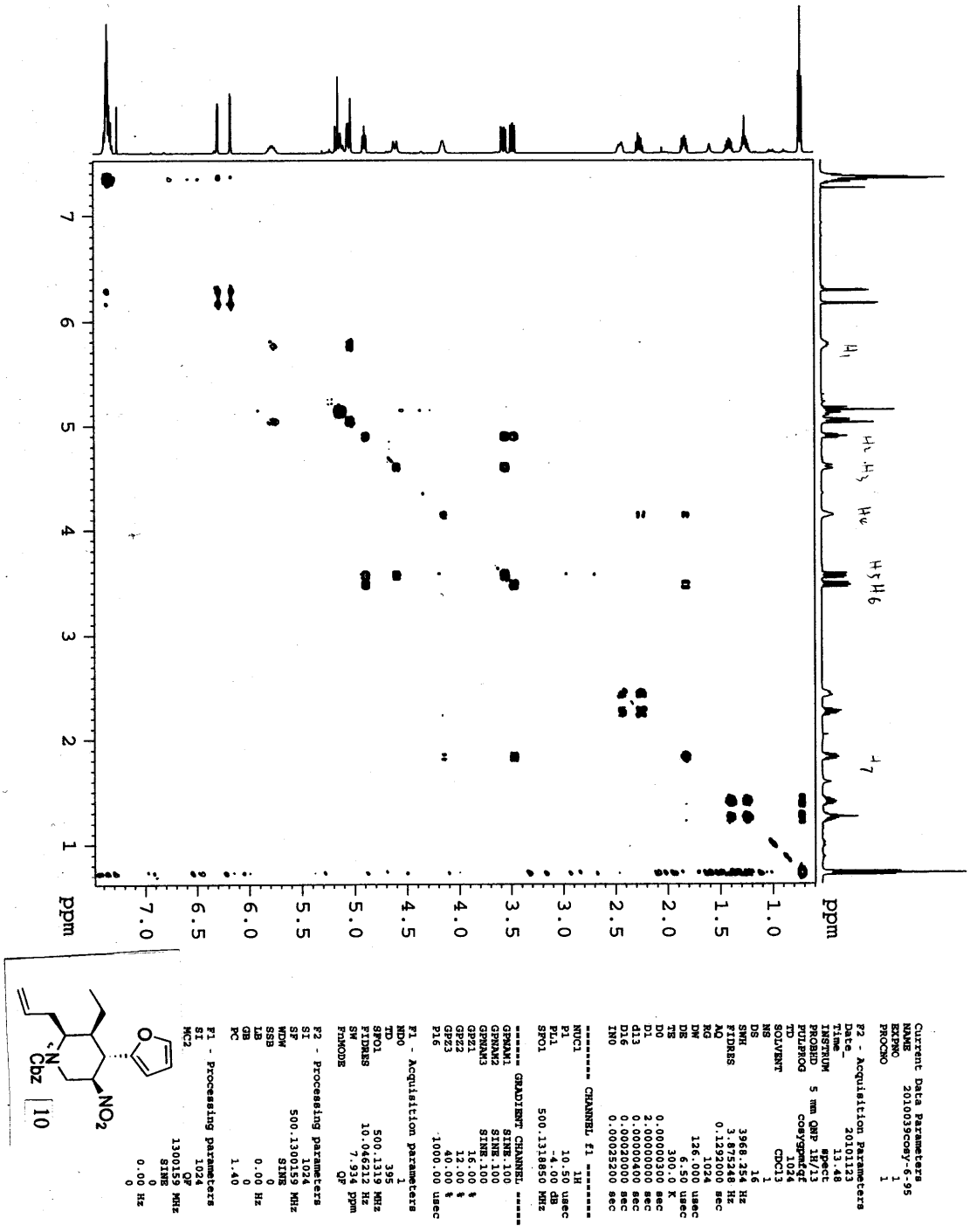
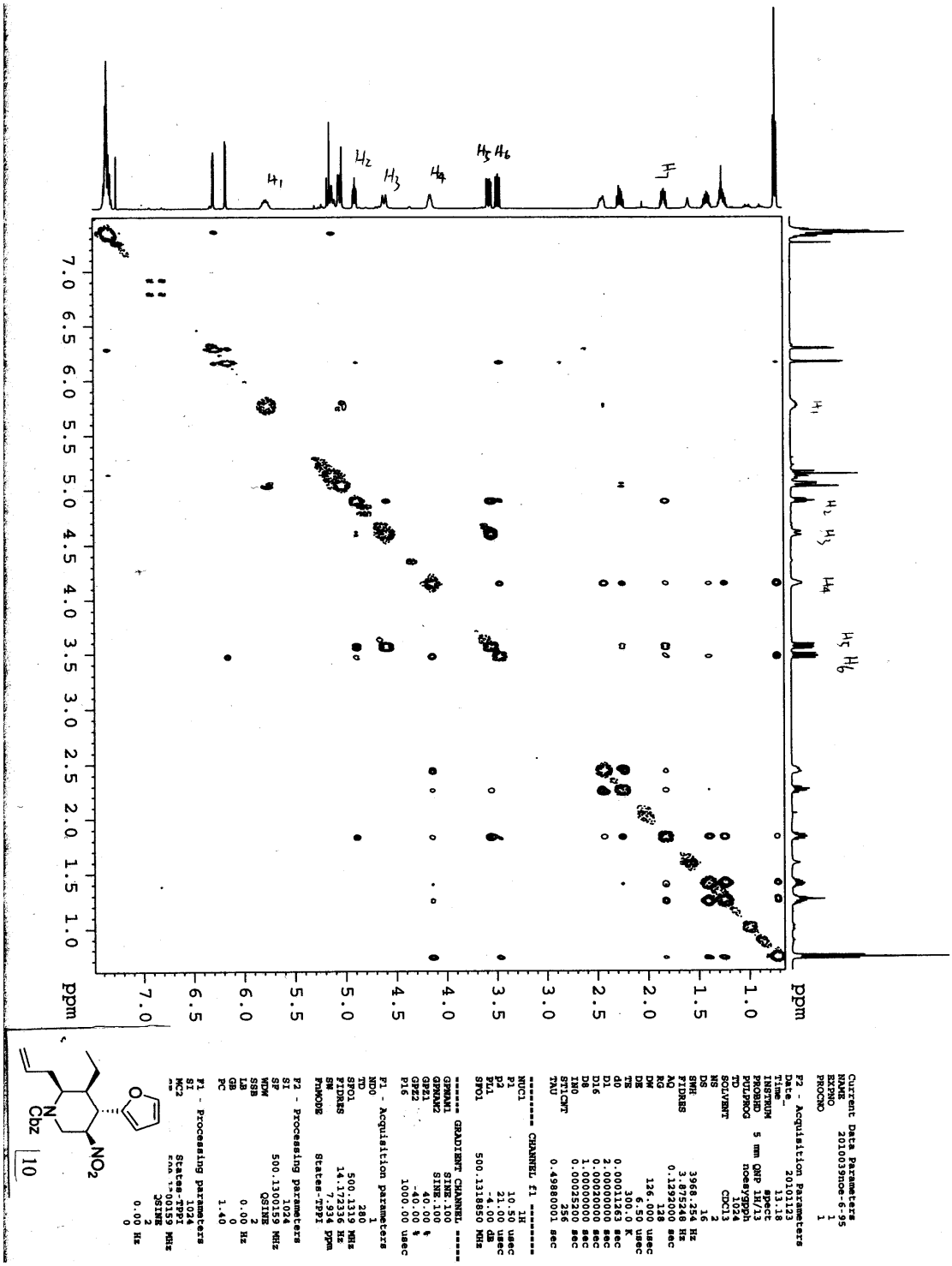
128.273
128.192
118.399
110.639
109.028
86.057
77.481
77.160
76.846
67.818
54.955
42.186
39.772
39.692
36.950
23.532
9.603
140
120
100
80
60
40
20
PPM
10
N
Cbz
O
N O 2




```
Current Data Parameters
NAME          20101039cosy-6-95
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20101123
Time                       13.48
INSTRUM                    spect
PROBHD     5 mm QNP 1H/13
PULPROG                cosygpmfqf
TD                           1024
SOLVENT                    CDCl3
NS                             1
DS                            16
SWH                    3968.254 Hz
FIDRES                 3.875248 Hz
AQ                     0.1292000 sec
RG                           1024
DW                      126.000 usec
DE                        6.50 usec
TE                       300.0 K
D0                     0.00000300 sec
D1                     2.00000000 sec
D13                    0.00000400 sec
D16                    0.00020000 sec
IN0                    0.00035200 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                        10.50 usec
PL1                       -4.00 dB
SFO1           500.1318850 MHz

====== GRADIENT CHANNEL =====
GPNAM1                SINE.100
GPNAM2                SINE.100
GPNAM3                SINE.100
GPZ1                  16.00 %
GPZ2                  12.00 %
GPZ3                  40.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
NDO                          1
TD                         395
SFO1           500.1319 MHz
FIDRES         10.046212 Hz
SW             7.934 ppm
FnMODE                    QF

F2 - Processing parameters
SI                        1024
SF             500.1300159 MHz
WDW                        EM
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.40

F1 - Processing parameters
SI                        1024
                            QF
MC2                       QF
                   1300159 MHz
                        SINE
                           0
                     0.00 Hz
                           0
```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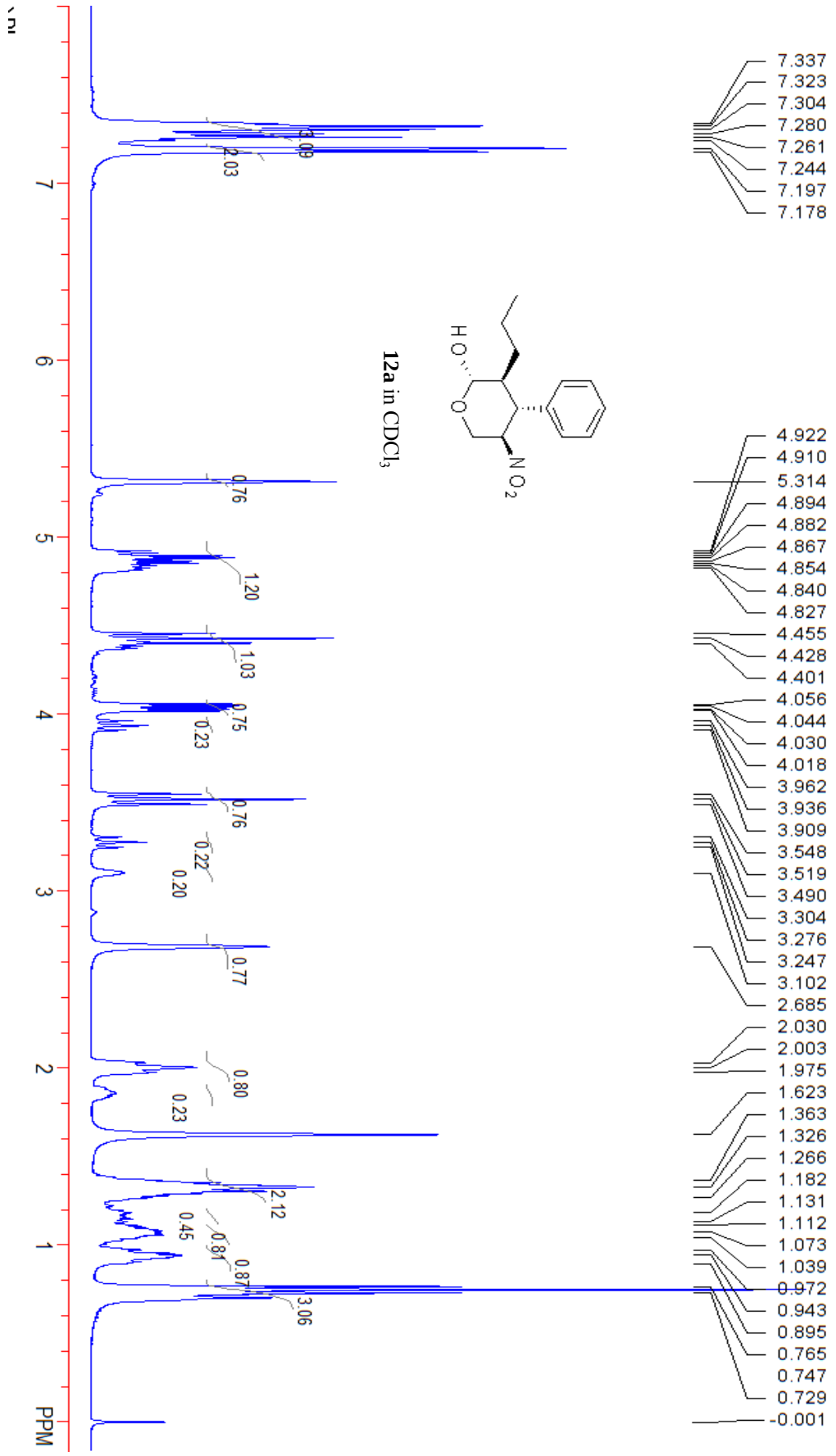
H2
H3
H4
H5 H6
H7
ppm
Cbz
NO2
10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7.304
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7.261
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7.197
7.178
4.922
4.910
5.314
4.894
4.882
4.867
4.854
4.840
4.827
4.455
4.428
4.401
4.056
4.044
4.030
4.018
3.962
3.936
3.909
3.548
3.519
3.490
3.304
3.276
3.247
3.102
2.685
2.030
2.003
1.975
1.623
1.363
1.326
1.266
1.182
1.131
1.112
1.073
1.039
0.972
0.943
0.895
0.765
0.747
0.729
-0.001
1.09
2.03
0.76
1.20
1.03
0.75
0.23
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0.20
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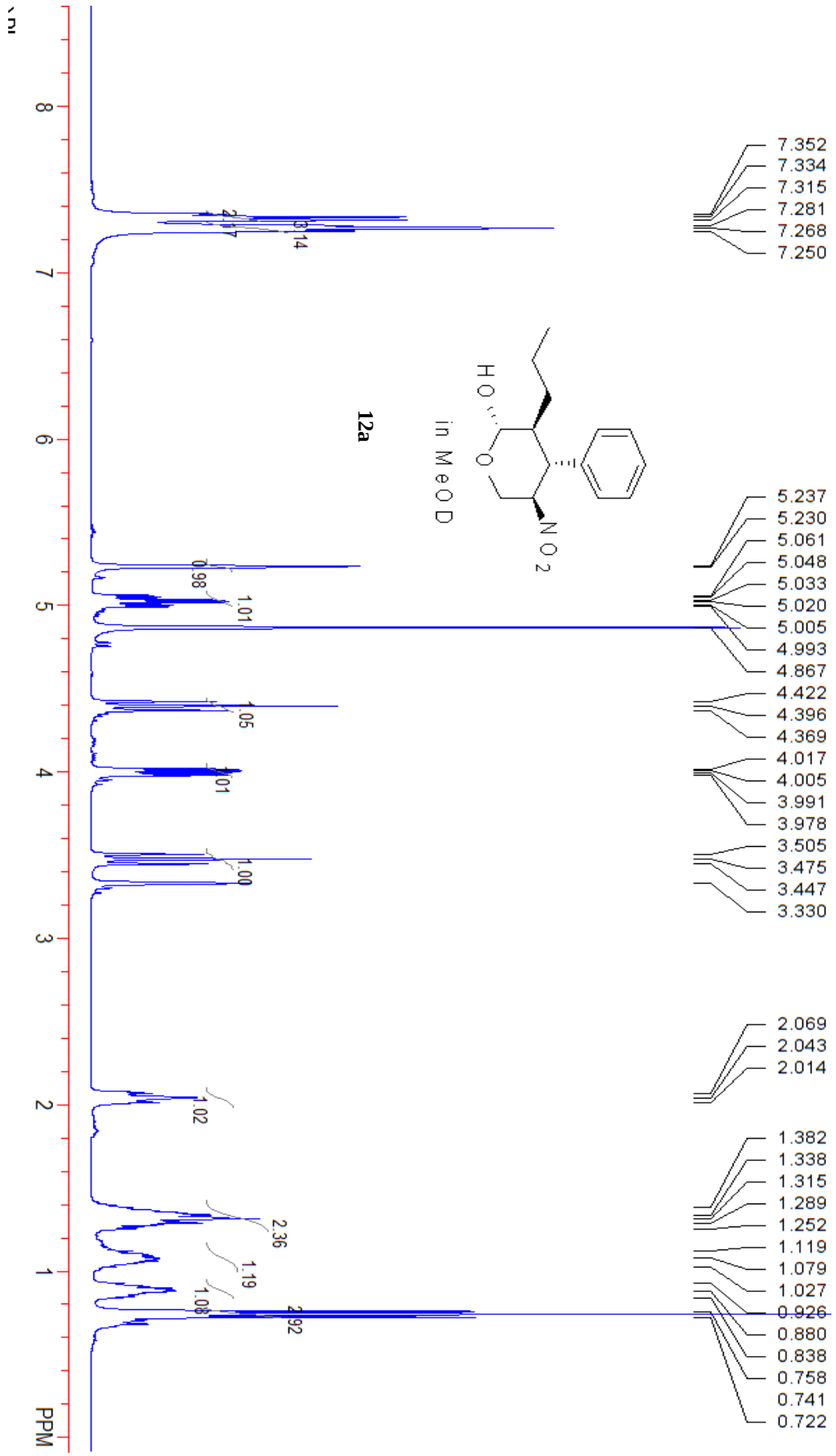
PPM


12a
in MeOD
HO
O
NO2
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7.334
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7.281
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7.250
5.237
5.230
5.061
5.048
5.033
5.020
5.005
4.993
4.867
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4.396
4.369
4.017
4.005
3.991
3.978
3.505
3.475
3.447
3.330
2.069
2.043
2.014
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1.338
1.315
1.289
1.252
1.119
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1.027
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0.838
0.758
0.741
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1.05
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1.00
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2.36
1.19
1.08
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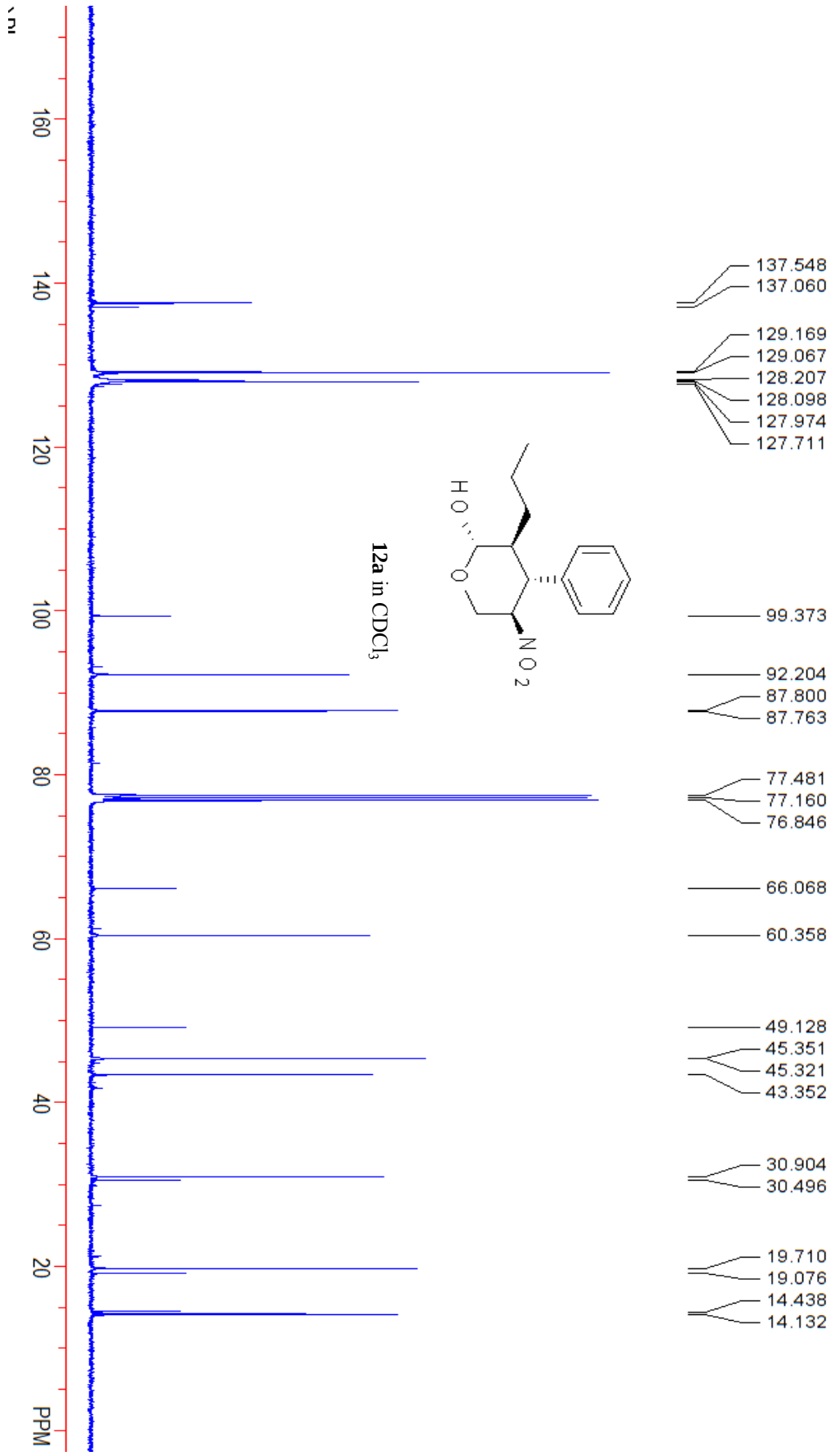
PPM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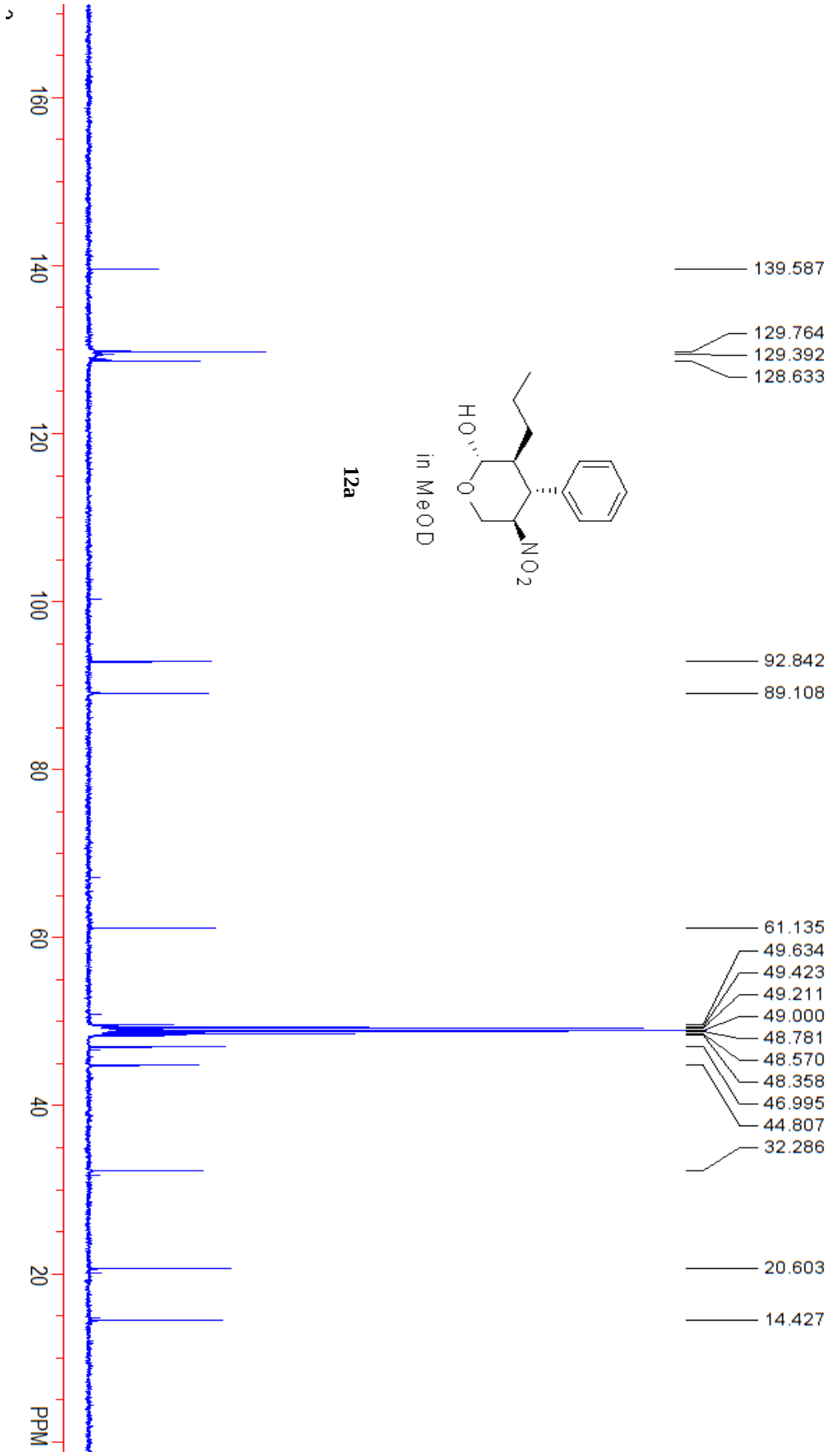
87.763
77.481
77.160
76.846
66.068
60.358
49.128
45.351
45.321
43.352
30.904
30.496
19.710
19.076
14.438
14.132
12a in CDCl3
HO
O
NO2
160
140
120
100
80
60
40
20
PPM


12a
in MeOD
HO
O
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49.000
48.781
48.570
48.358
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44.807
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20.603
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140
120
100
80
60
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20
PPM

HPLC Report

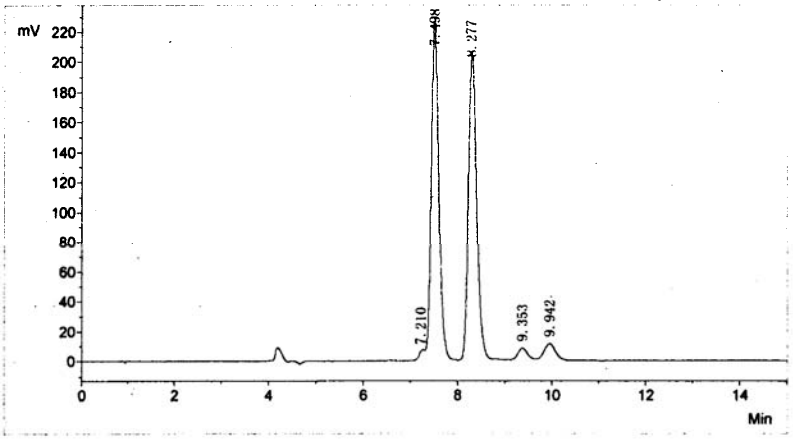
Sample Name:

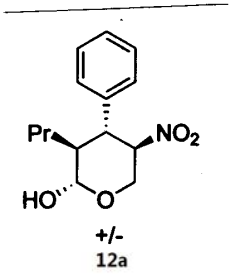
Operator:

Time:14:49

Data File:ZSL-6-56+- IC 91 214 0.7.che

Date:2010-09-09





No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	7.210	89.0	29.2	0.0006
2	2	7.498	217720.6	2319712.6	45.5464
3	3	8.277	198141.8	2522132.3	49.5208
4	4	9.353	7290.2	92011.1	1.8066
5	5	9.942	10316.2	159188.7	3.1256
Total			433557.8	5093073.9	100.0000

HPLC Report

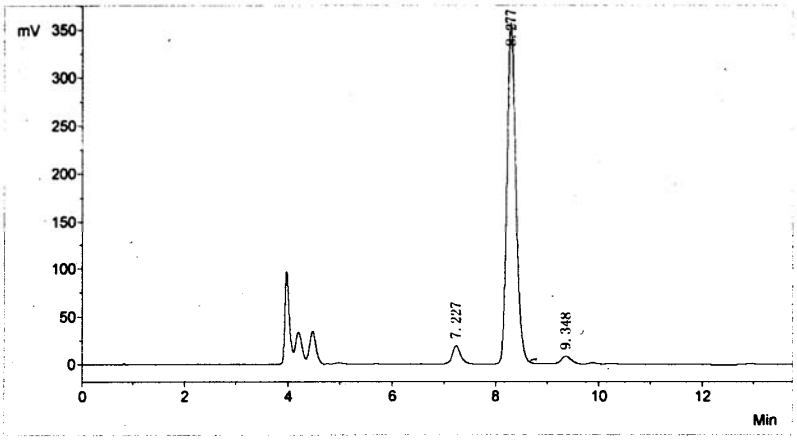
Sample Name:

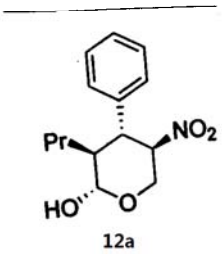
Operator:

Time:15:11

Data File:ZSL-6-54.che

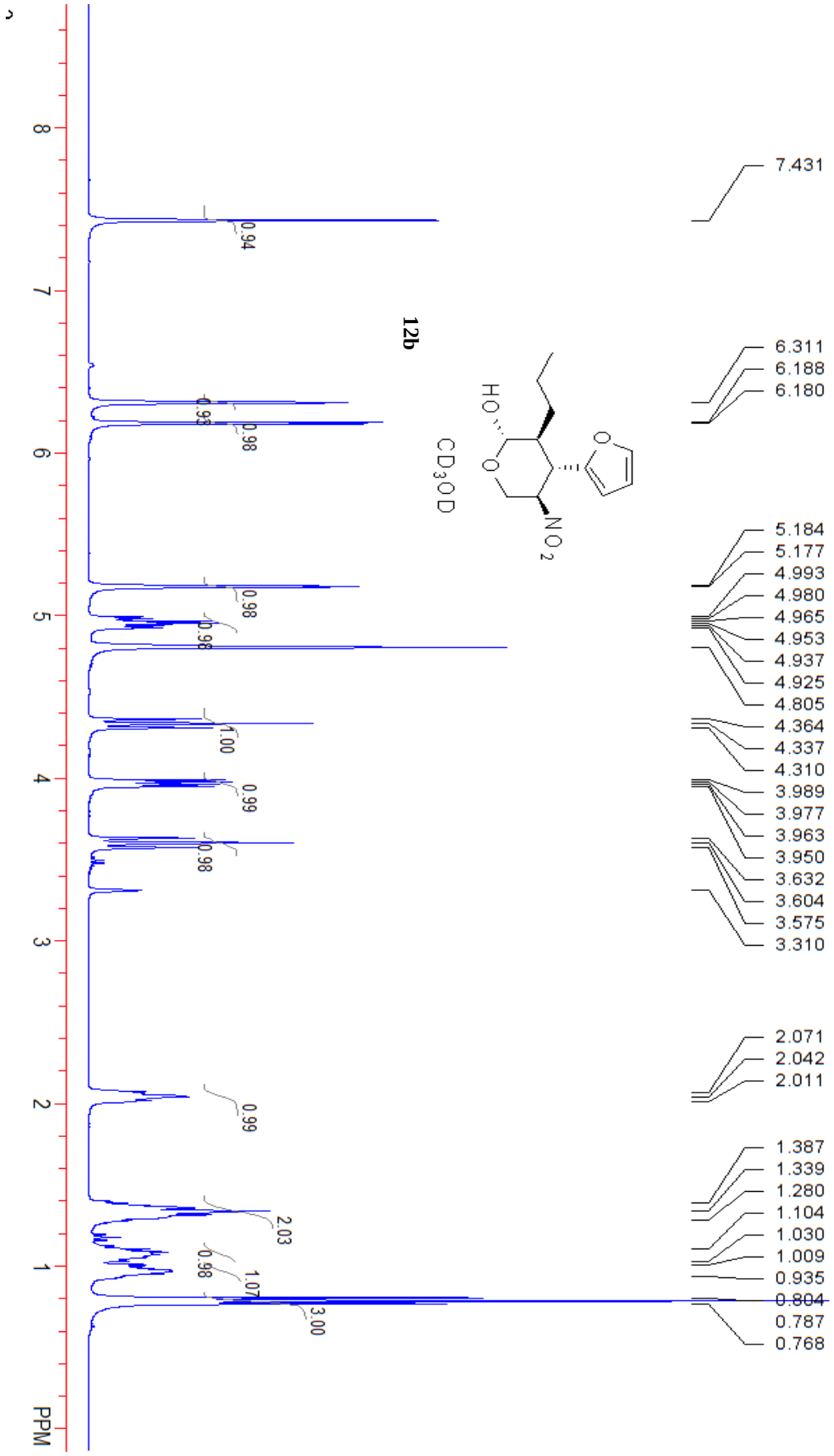
Date:2010-09-09

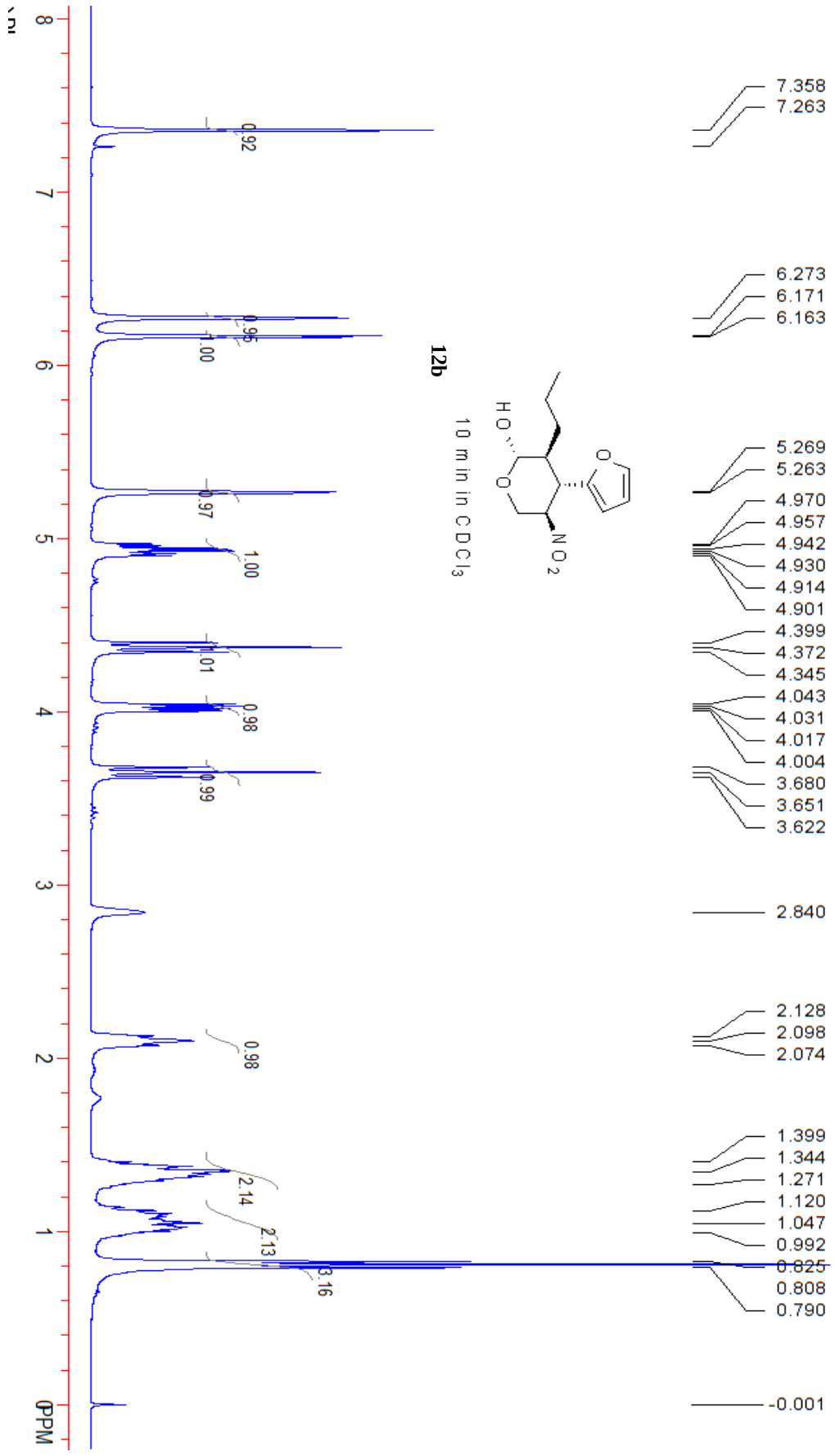




12a

No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	7.227	19627.9	222910.9	4.8456
2	2	8.277	353362.9	4282969.2	93.1032
3	3	9.348	7533.0	94360.6	2.0512
Total			380523.8	4600240.7	100.0000


12b
CD3OD
HO
O
NO2
7.431
6.311
6.188
6.180
5.184
5.177
4.993
4.980
4.965
4.953
4.937
4.925
4.805
4.364
4.337
4.310
3.989
3.977
3.963
3.950
3.632
3.604
3.575
3.310
2.071
2.042
2.011
1.387
1.339
1.280
1.104
1.030
1.009
0.935
0.804
0.787
0.768
0.94
0.98
0.98
0.98
0.98
1.00
0.99
0.98
0.99
2.03
0.98
1.07
3.00
PPM


12b
10 m in in CDCl3
HO
O
O
NO2
7.358
7.263
6.273
6.171
6.163
5.269
5.263
4.970
4.957
4.942
4.930
4.914
4.901
4.399
4.372
4.345
4.043
4.031
4.017
4.004
3.680
3.651
3.622
2.840
2.128
2.098
2.074
1.399
1.344
1.271
1.120
1.047
0.992
0.825
0.808
0.790
-0.001
0.92
0.95
1.00
0.97
1.00
1.01
0.98
0.99
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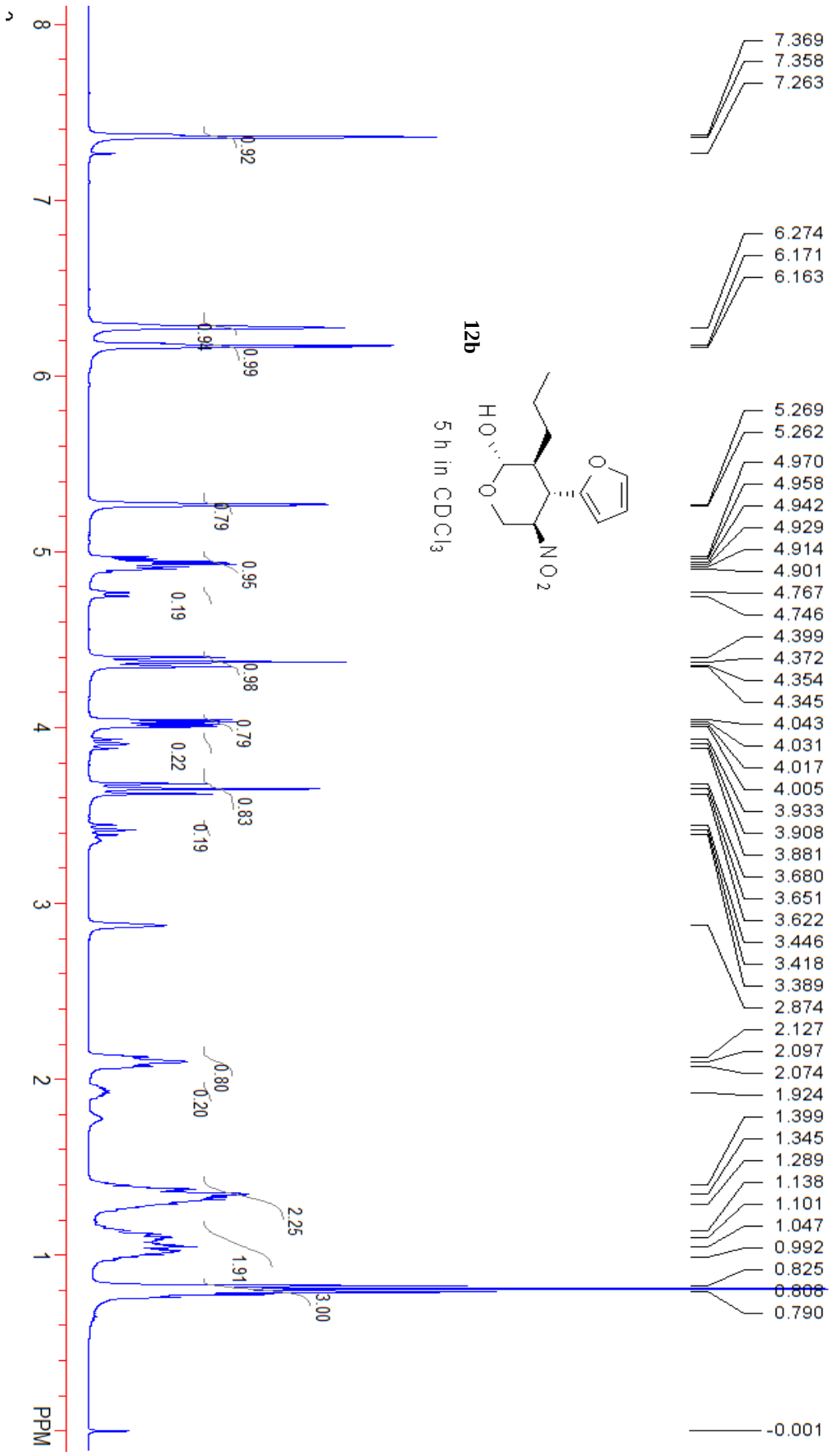
2.14
2.13
3.16
8
7
6
5
4
3
2
1
0
PPM


12b
5 h in CDCl3
HO
O
O
NO2
7.369
7.358
7.263
6.274
6.171
6.163
5.269
5.262
4.970
4.958
4.942
4.929
4.914
4.901
4.767
4.746
4.399
4.372
4.354
4.345
4.043
4.031
4.017
4.005
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3.908
3.881
3.680
3.651
3.622
3.446
3.418
3.389
2.874
2.127
2.097
2.074
1.924
1.399
1.345
1.289
1.138
1.101
1.047
0.992
0.825
0.808
0.790
-0.001
0.92
0.94
0.99
0.79
0.95
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0.98
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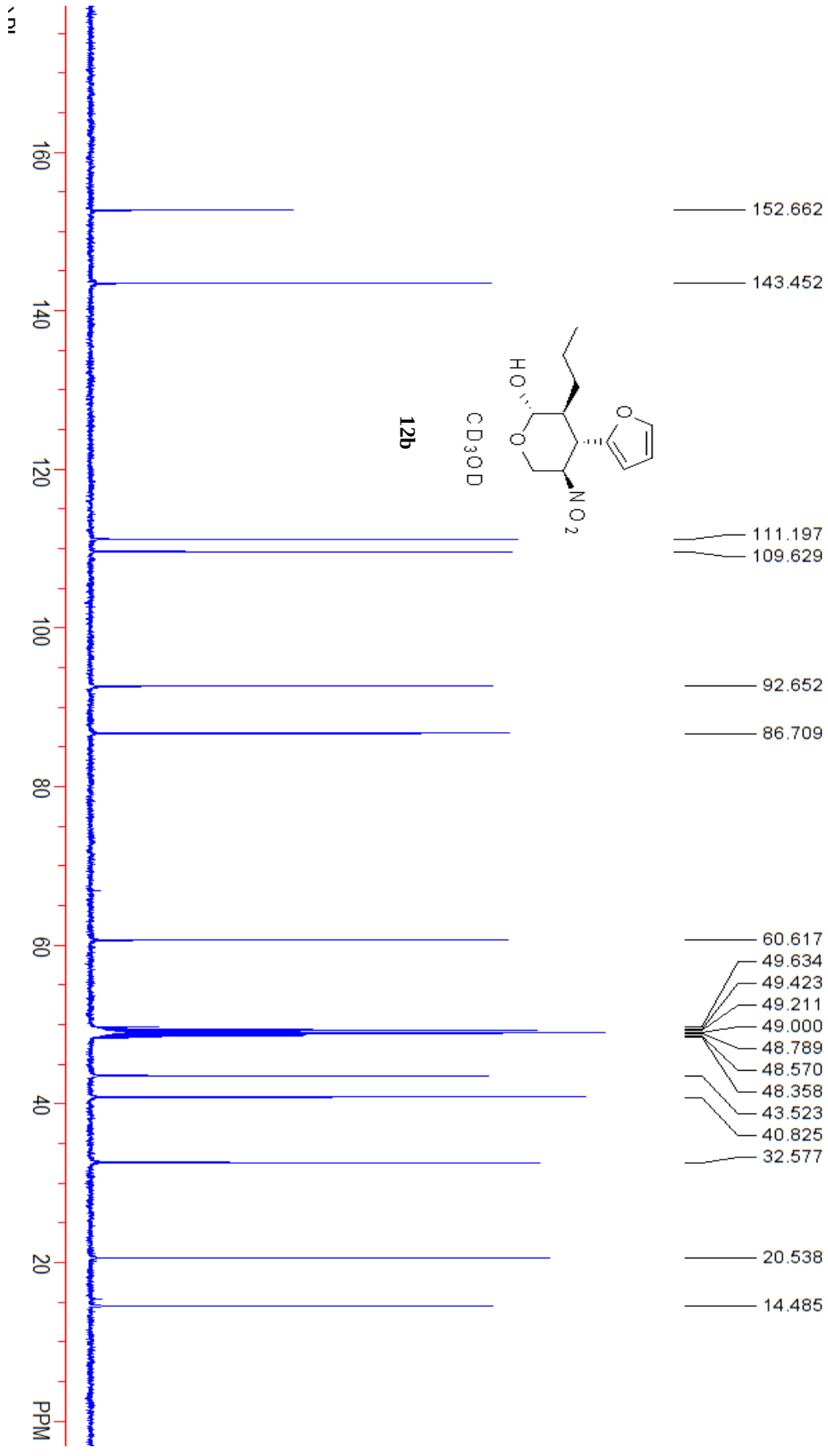
0.80
0.20
2.25
1.91
3.00
PPM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111.197
109.629
92.652
86.709
60.617
49.634
49.423
49.211
49.000
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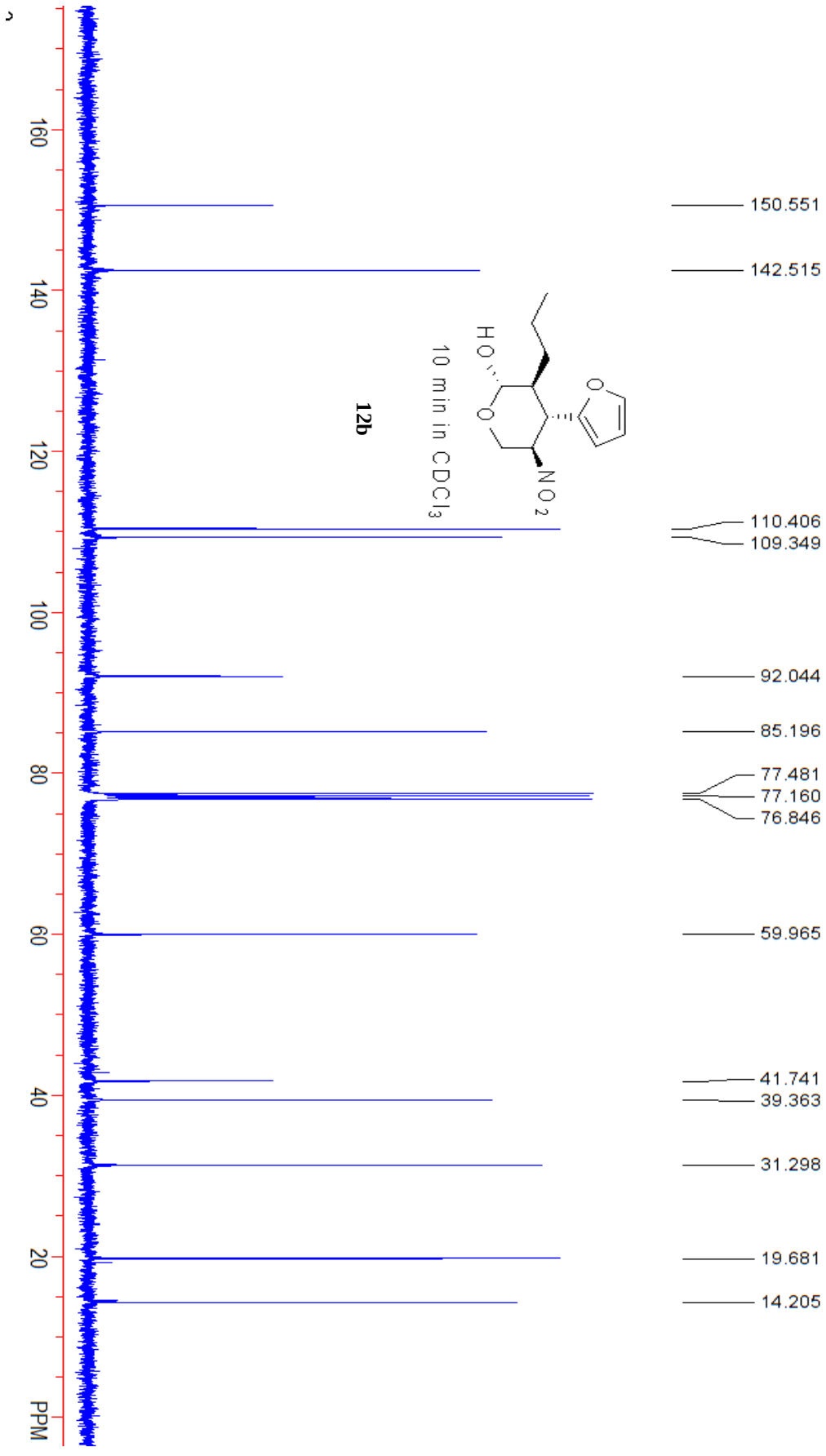
48.570
48.358
43.523
40.825
32.577
20.538
14.485
12b
CD3OD
HO
O
NO2
160
140
120
100
80
60
40
20
PPM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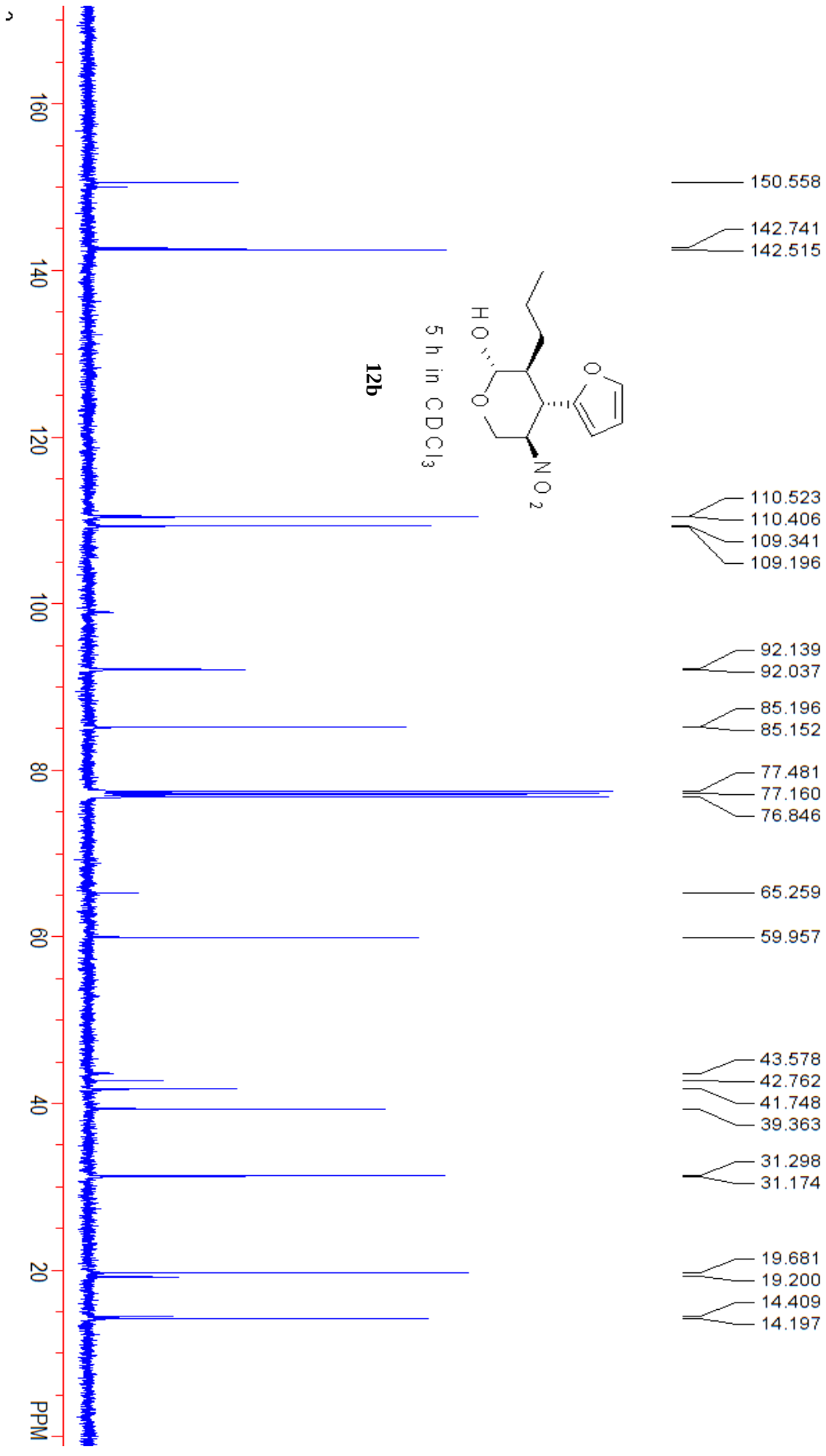
142.515
110.406
109.349
92.044
85.196
77.481
77.160
76.846
59.965
41.741
39.363
31.298
19.681
14.205
160
140
120
100
80
60
40
20
PPM
12b
10 min in CDCl3
HO
O
NO2


12b
5 h in CDCl3
HO
O
O
NO2
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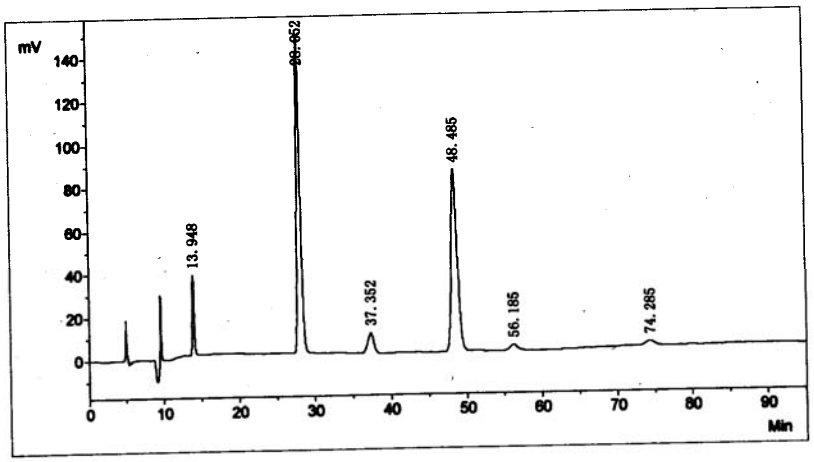
142.741
142.515
110.523
110.406
109.341
109.196
92.139
92.037
85.196
85.152
77.481
77.160
76.846
65.259
59.957
43.578
42.762
41.748
39.363
31.298
31.174
19.681
19.200
14.409
14.197
160
140
120
100
80
60
40
20
PPM

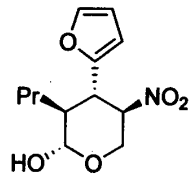
HPLC REPORT

Data File:ZSL-590+- AD-H 95EtOH5 214 0.7.che Sample Name:

Date:2009-09-27 Time:14:54

Operator:





+/-

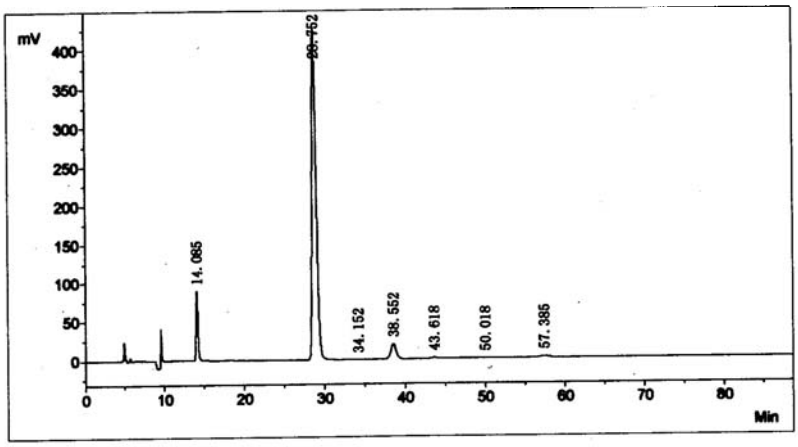
12b

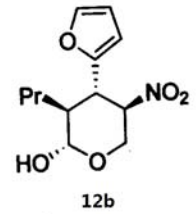
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		13.948	37192.9	627017.1	5.6261
2	2		28.052	147968.1	4884582.5	43.8285
3	3		37.352	9507.6	515955.4	4.6296
4	4		48.485	84533.0	4735838.7	42.4939
5	5		56.185	2813.2	184939.2	1.6594
6	6		74.285	2300.2	196428.4	1.7625
Total				284315.0	11144761.3	100.0000

HPLC REPORT

Data File:ZSL-13-85-2.che
Date:2009-09-27
Operator:

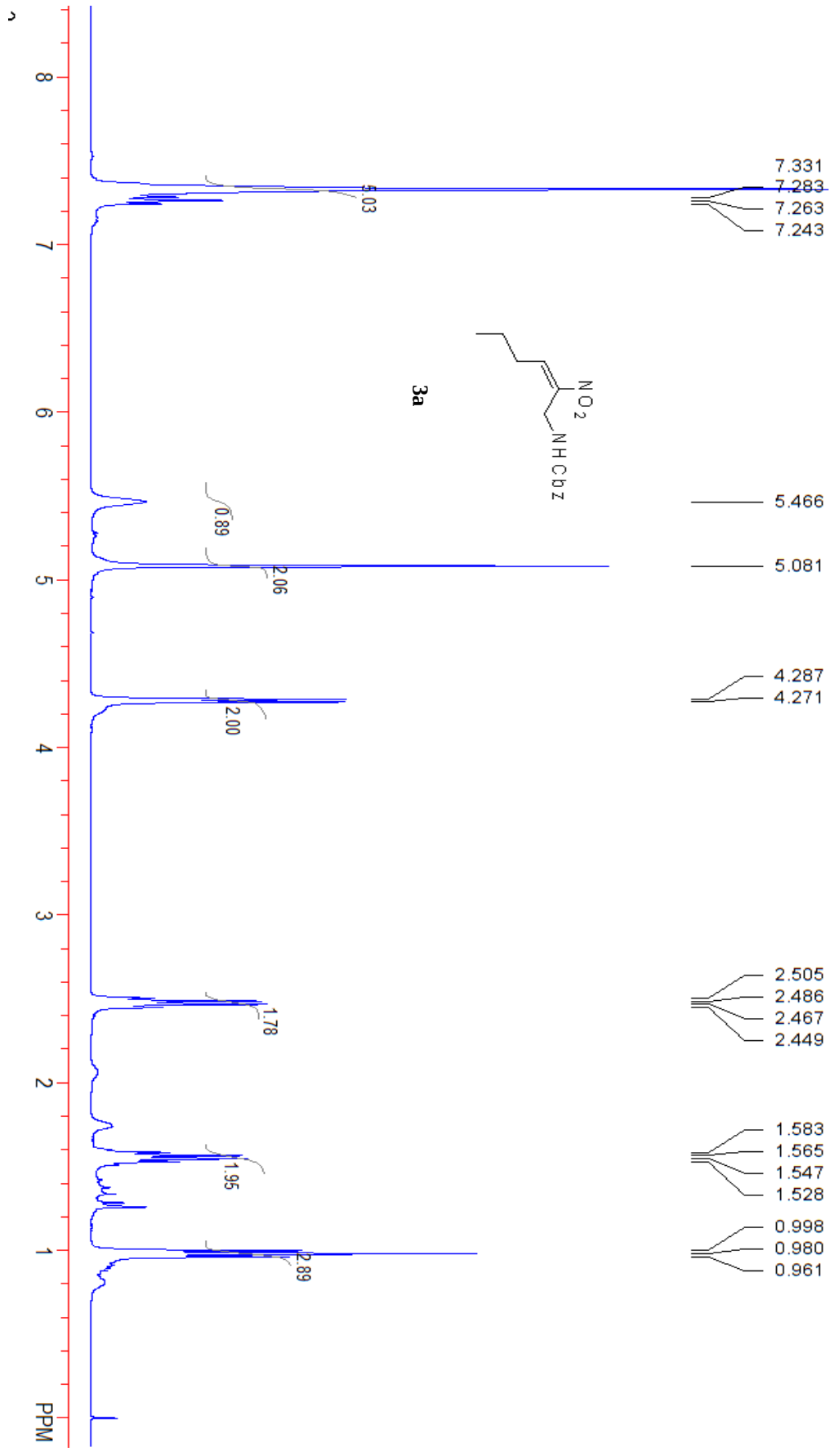
Sample Name:
Time:16:39





12b

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		14.085	89367.0	1549891.6	8.5802
2	2		28.752	426646.6	15416639.9	85.3469
3	3		34.152	164.6	5826.5	0.0323
4	4		38.552	19655.5	905280.1	5.0117
5	5		43.618	1106.2	53651.2	0.2970
6	6		50.018	260.5	14094.0	0.0780
7	7		57.385	1781.9	118127.1	0.6540
Total				538982.3	18063510.3	100.0000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7.283
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5.466
5.081
4.287
4.271
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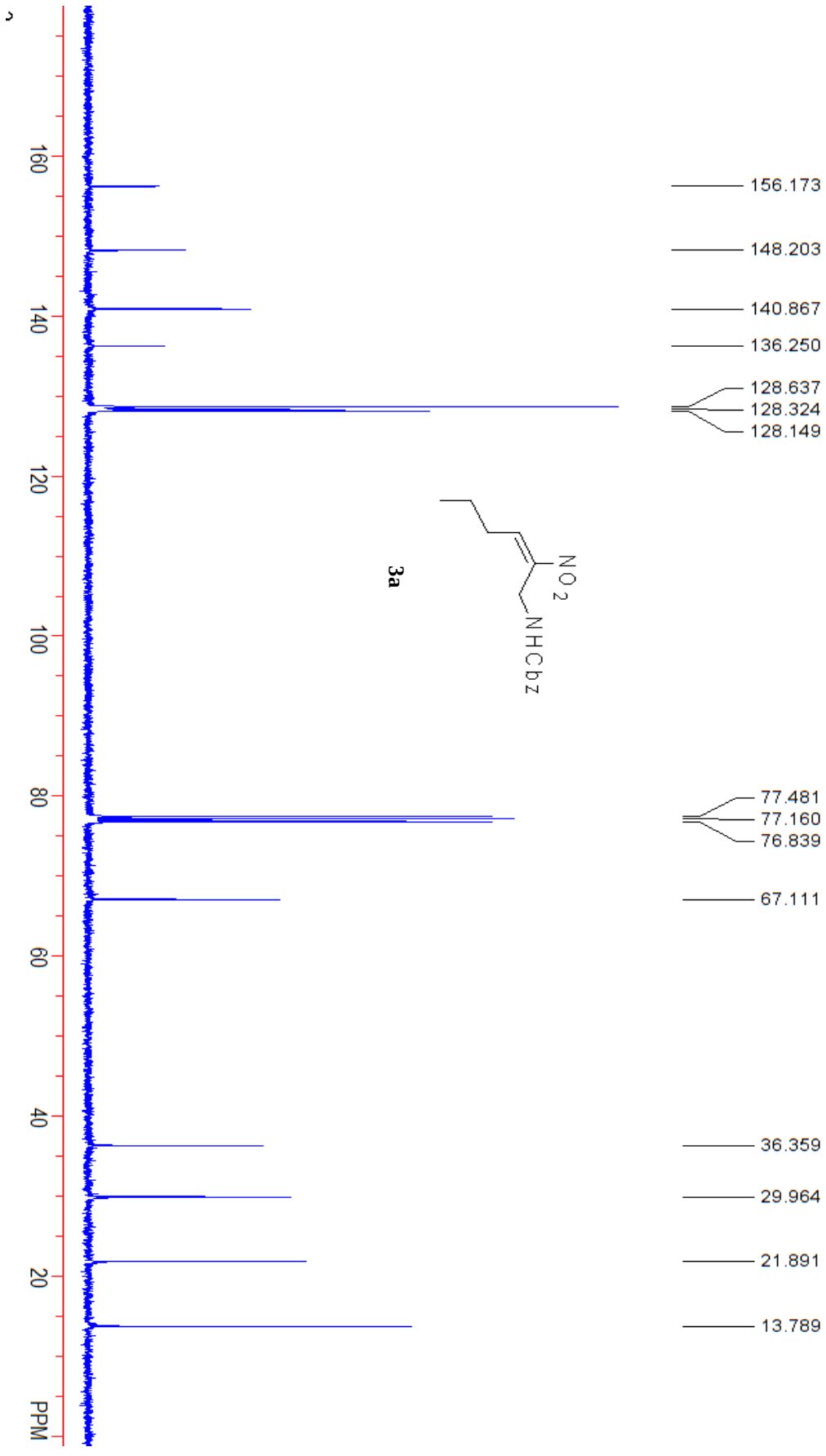
2.486
2.467
2.449
1.583
1.565
1.547
1.528
0.998
0.980
0.961
5.03
0.89
2.06
2.00
1.78
1.95
2.89
3a
NO2
NHCbz
PPM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136.250
128.637
128.324
128.149
77.481
77.160
76.839
67.111
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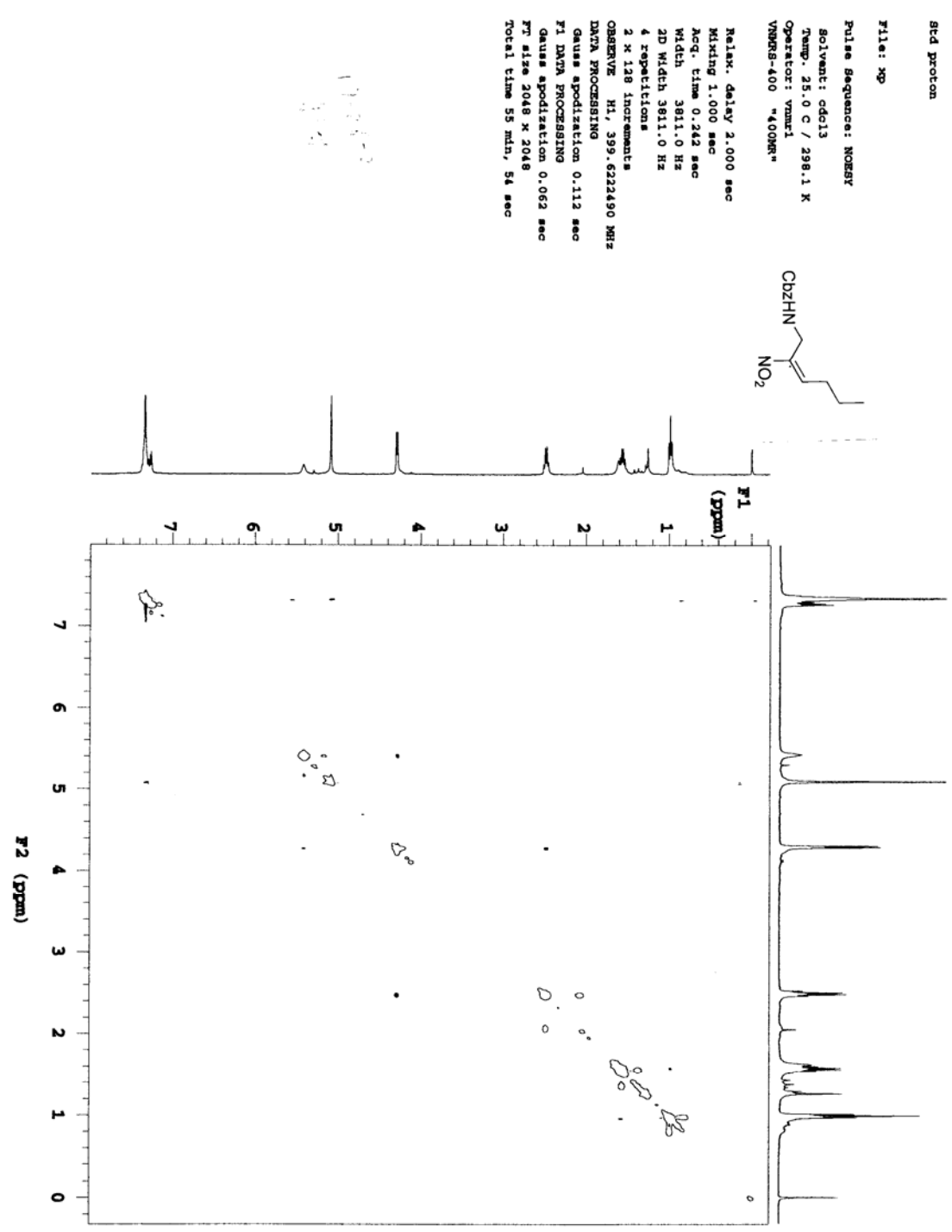
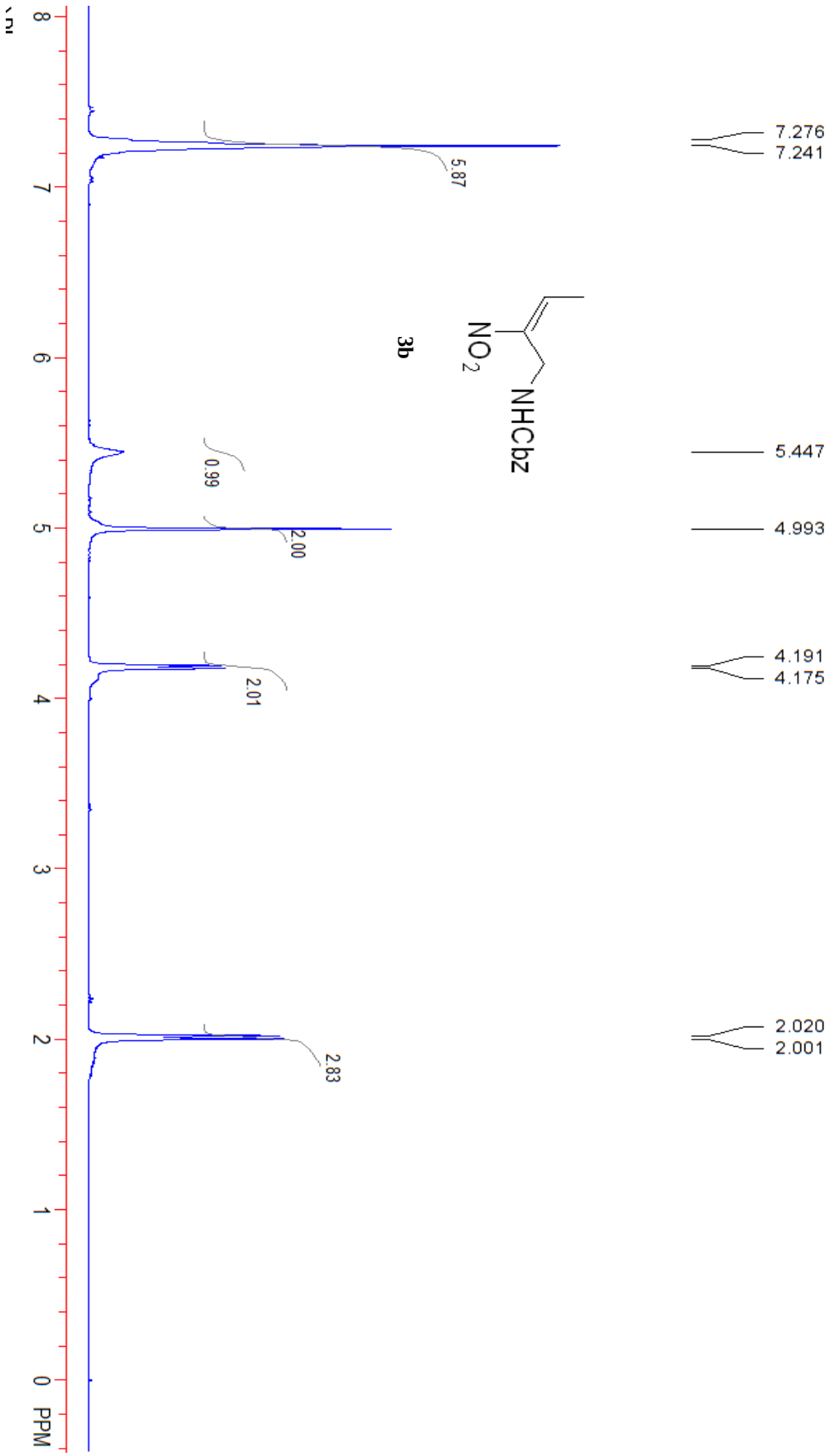
13.789
NO2
NHCbz
3a
160
140
120
100
80
60
40
20
PPM


Std proton
File: xp
Pulse Sequence: NOESY
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: vnmr1
VNMRS-400 "400MR"
Relax. delay 2.000 sec
Mixing 1.000 sec
Acq. time 0.242 sec
Width 3811.0 Hz
2D Width 3811.0 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 399.6222490 MHz
DATA PROCESSING
Gauss apodization 0.112 sec
F1 DATA PROCESSING
Gauss apodization 0.062 sec
FT size 2048 x 2048
Total time 55 min, 54 sec
CbzHN
NO2
F1 (ppm)
F2 (ppm)


3b
NO2
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7.241
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4.191
4.175
2.020
2.001
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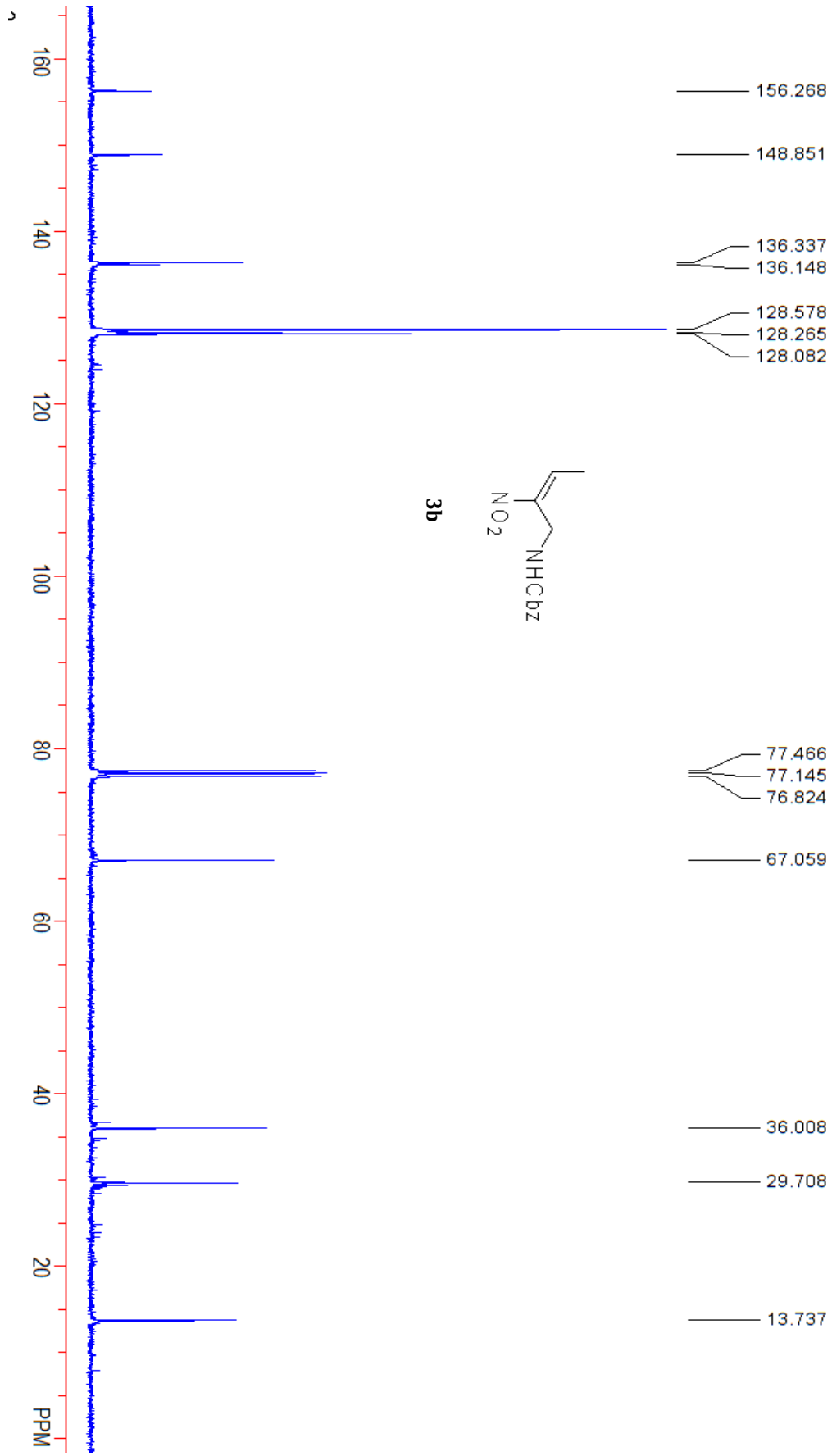
2.00
2.01
2.83
PPM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148.851
136.337
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128.265
128.082
77.466
77.145
76.824
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36.008
29.708
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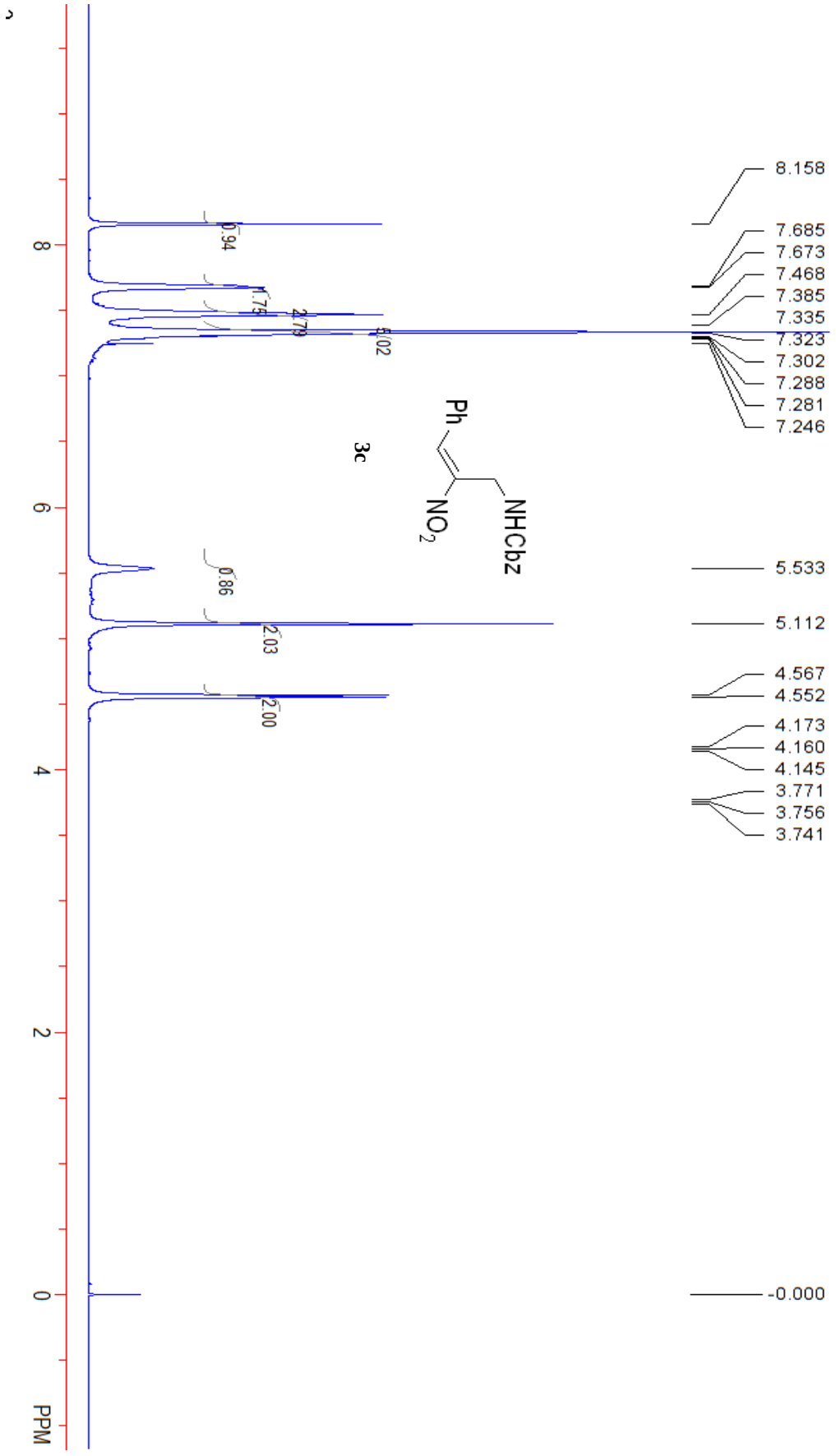
3b
NO2
NHCbz
160
140
120
100
80
60
40
20
PPM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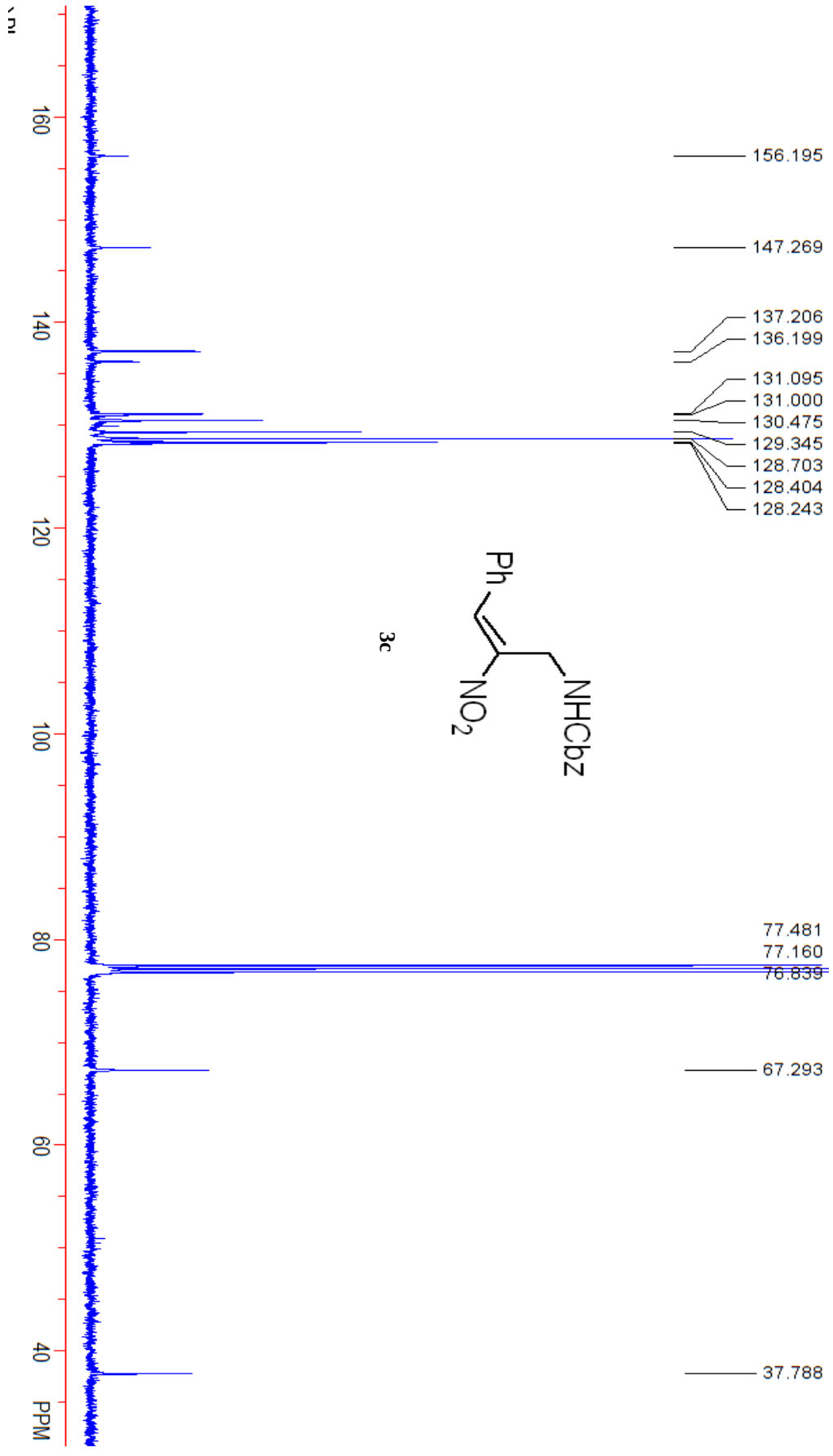
7.281
7.246
5.533
5.112
4.567
4.552
4.173
4.160
4.145
3.771
3.756
3.741
-0.000
0.94
1.75
2.79
6.02
0.86
2.03
2.00
Ph
NO2
NHCbz
3c
PPM
8
6
4
2
0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128.404
128.243
77.481
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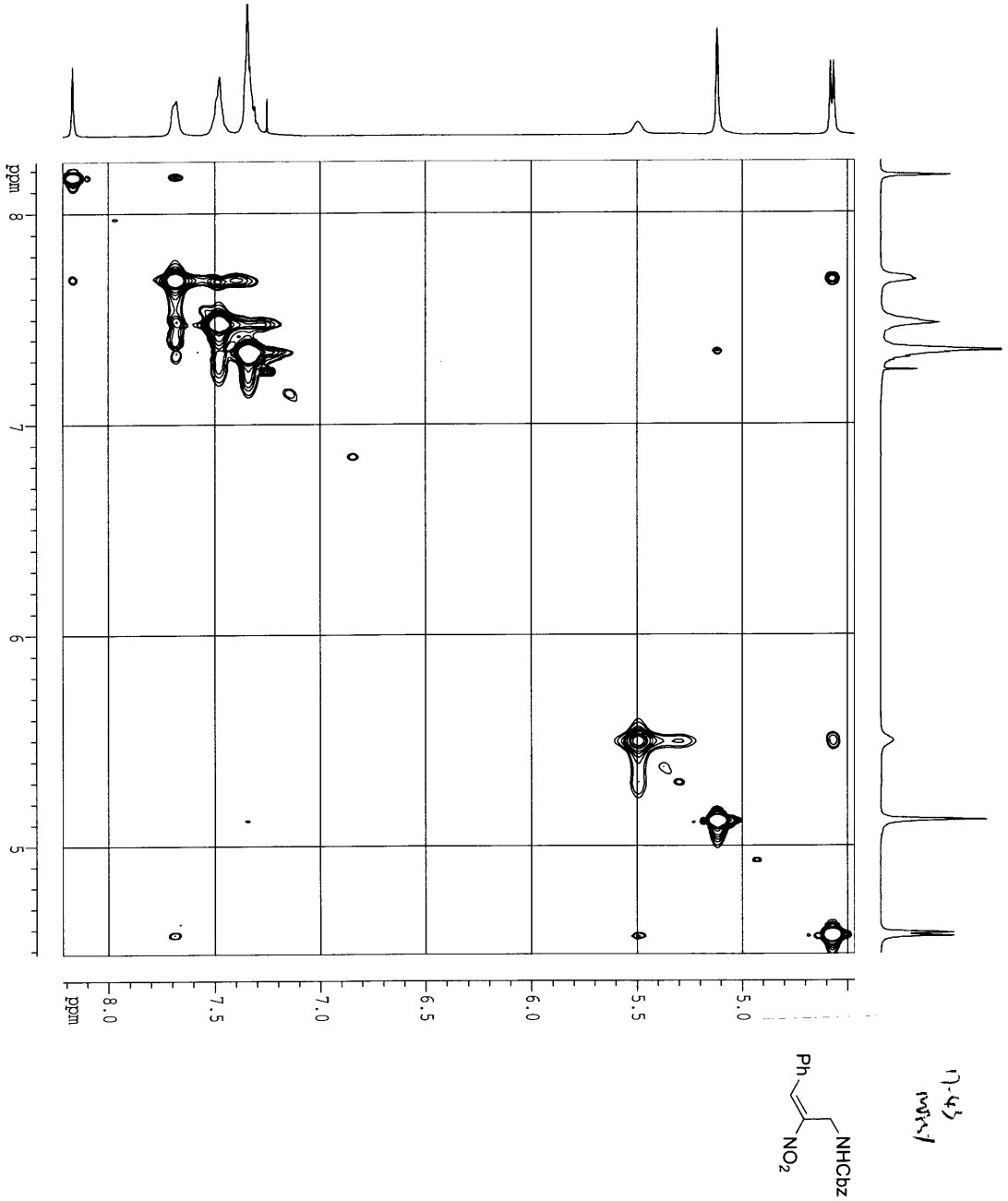
160
140
120
100
80
60
40
PPM
Ph
NO2
NHCbz
3c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8
7
6
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ppm
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7.0
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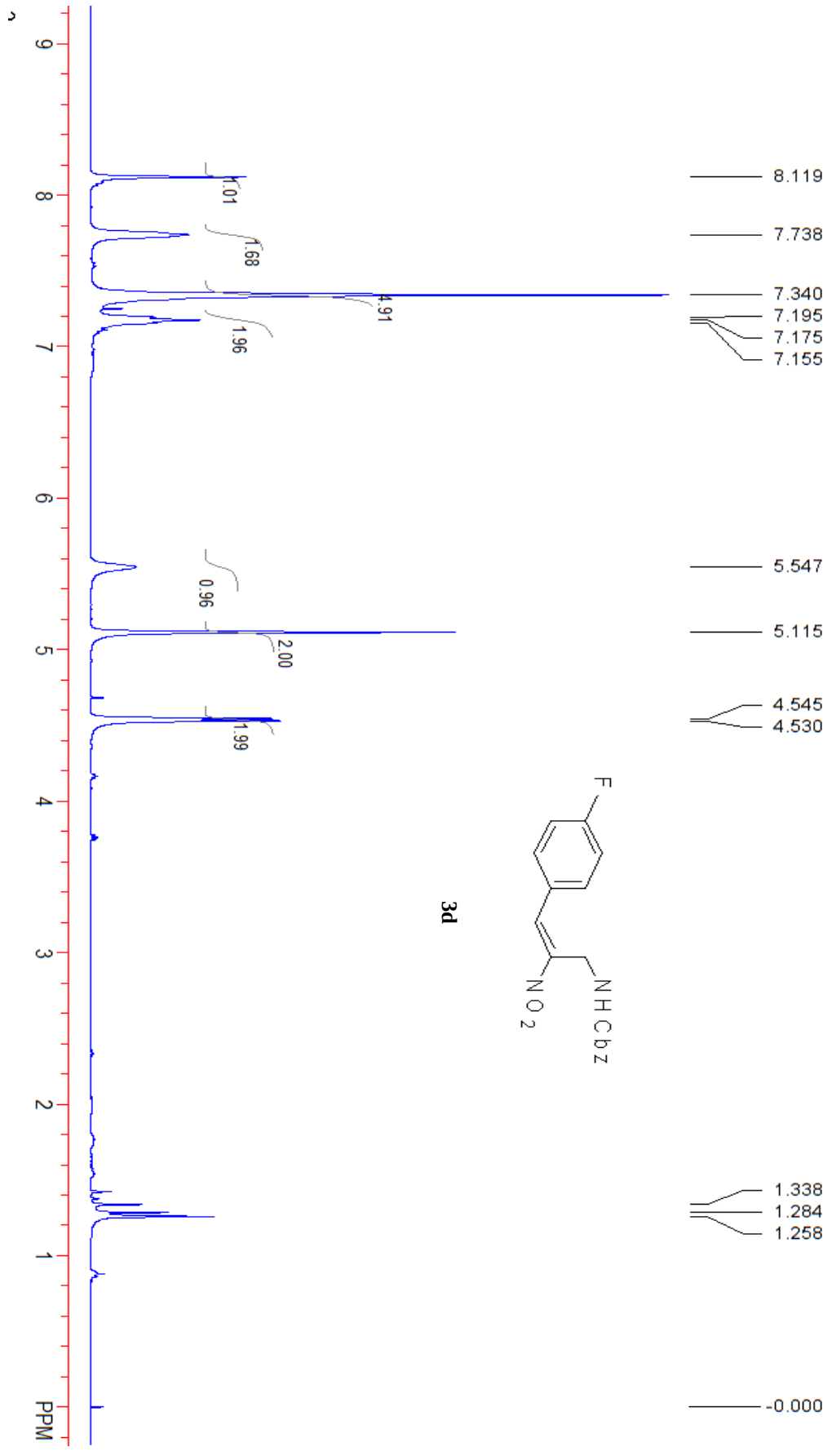
5.5
5.0
Ph
NO2
NHCbz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7.195
7.175
7.155
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5.115
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4.530
1.338
1.284
1.258
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1.68
4.91
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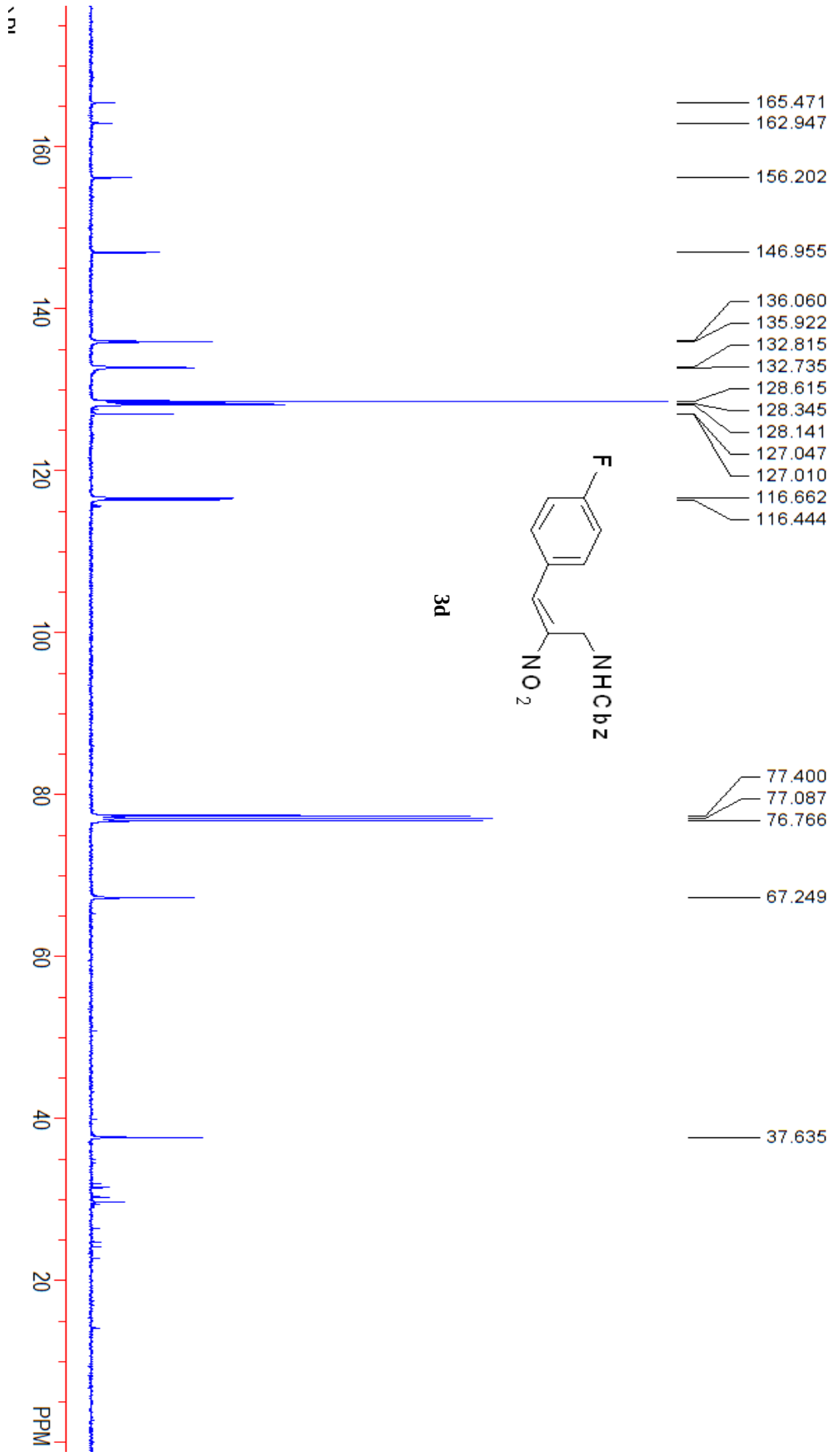
1.99
PPM
F
NHCbz
NO2

3d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132.735
128.615
128.345
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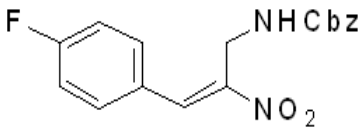
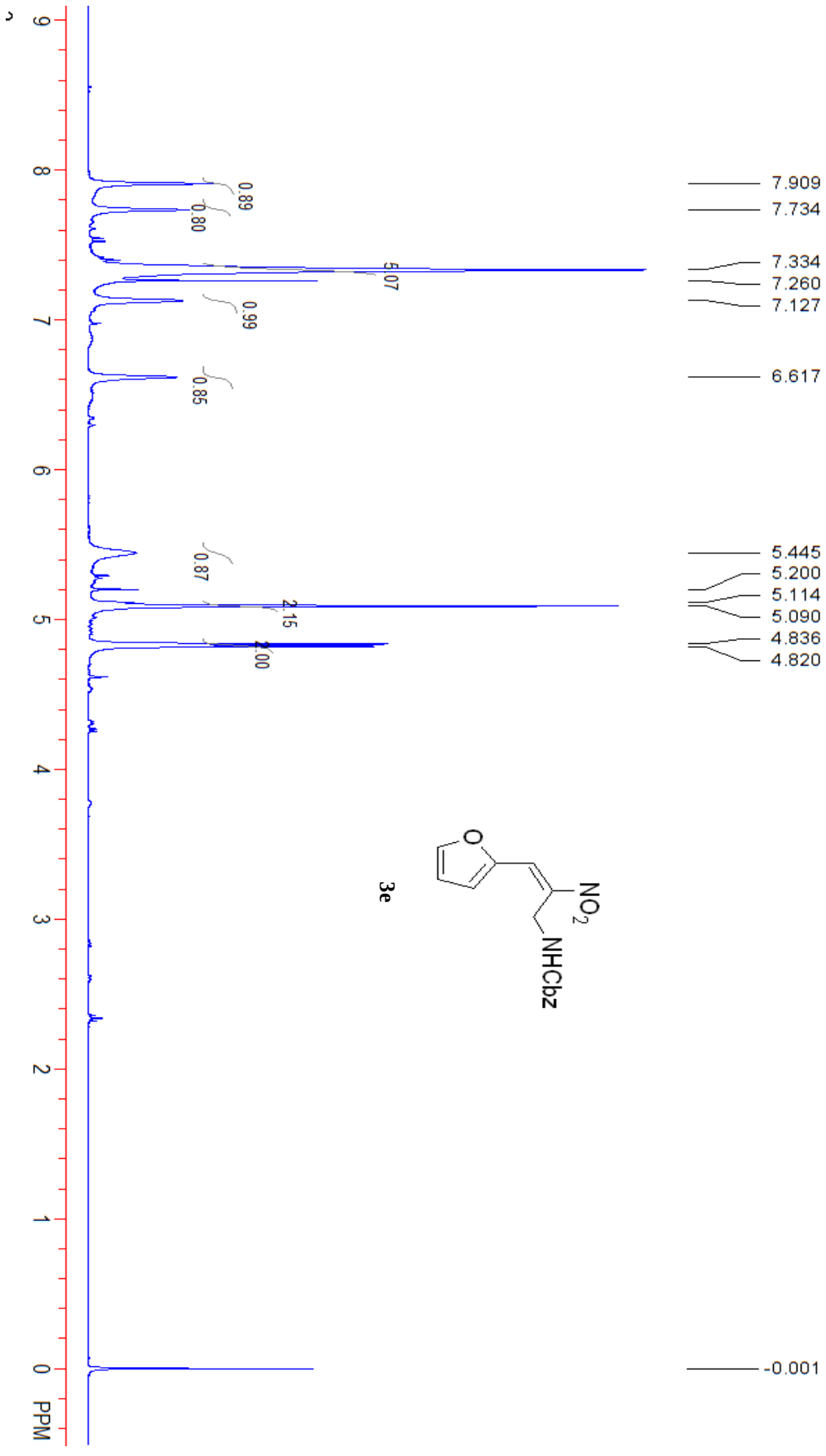
127.010
116.662
116.444
77.400
77.087
76.766
67.249
37.635
3d
F
NO2
NHCbz
160
140
120
100
80
60
40
20
PPM



3d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5.090
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0.80
5.07
0.99
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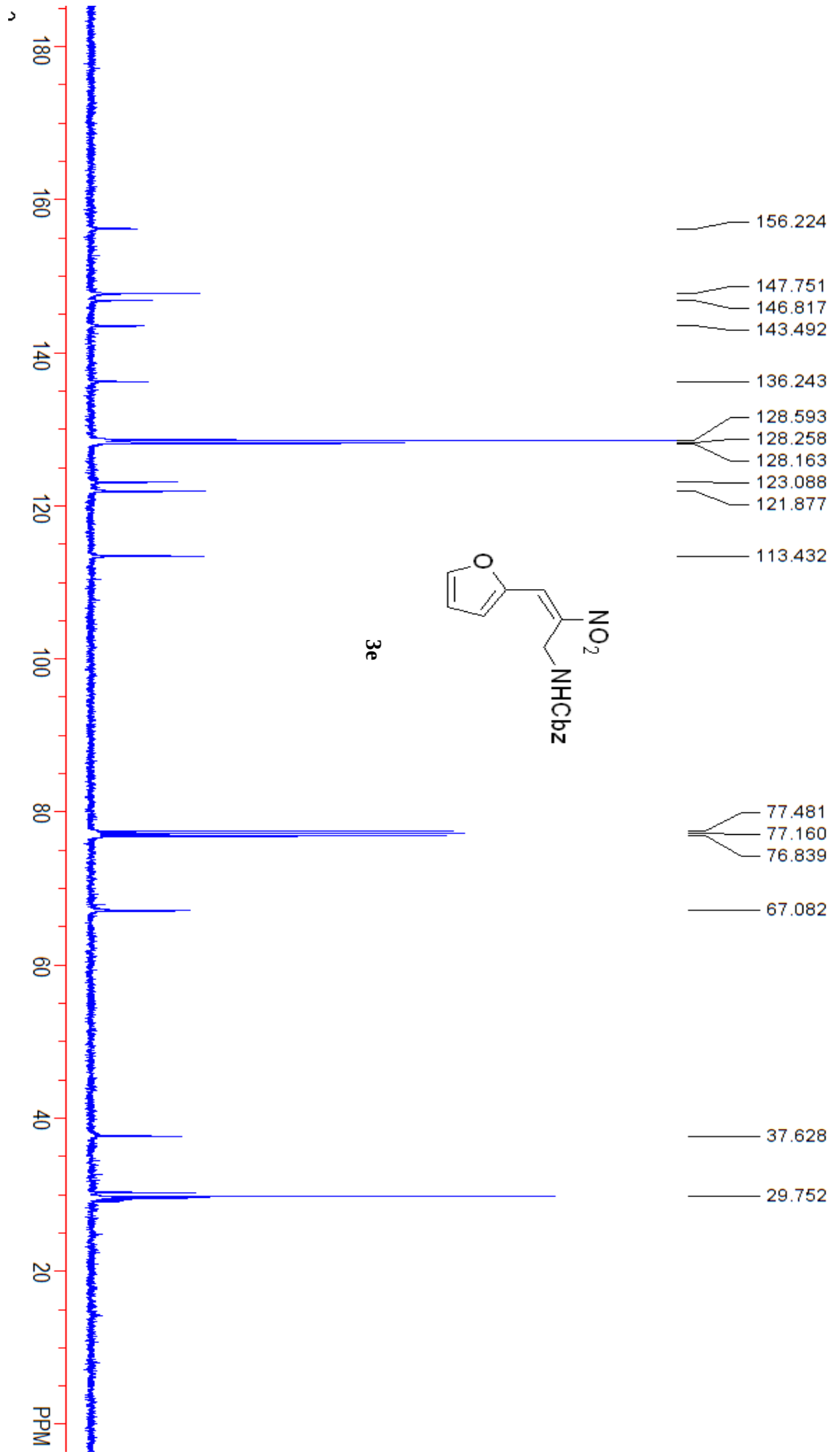
2.00
PPM
3e
NO2
NHCbz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128.163
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121.877
113.432
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77.160
76.839
67.082
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3e
NO2
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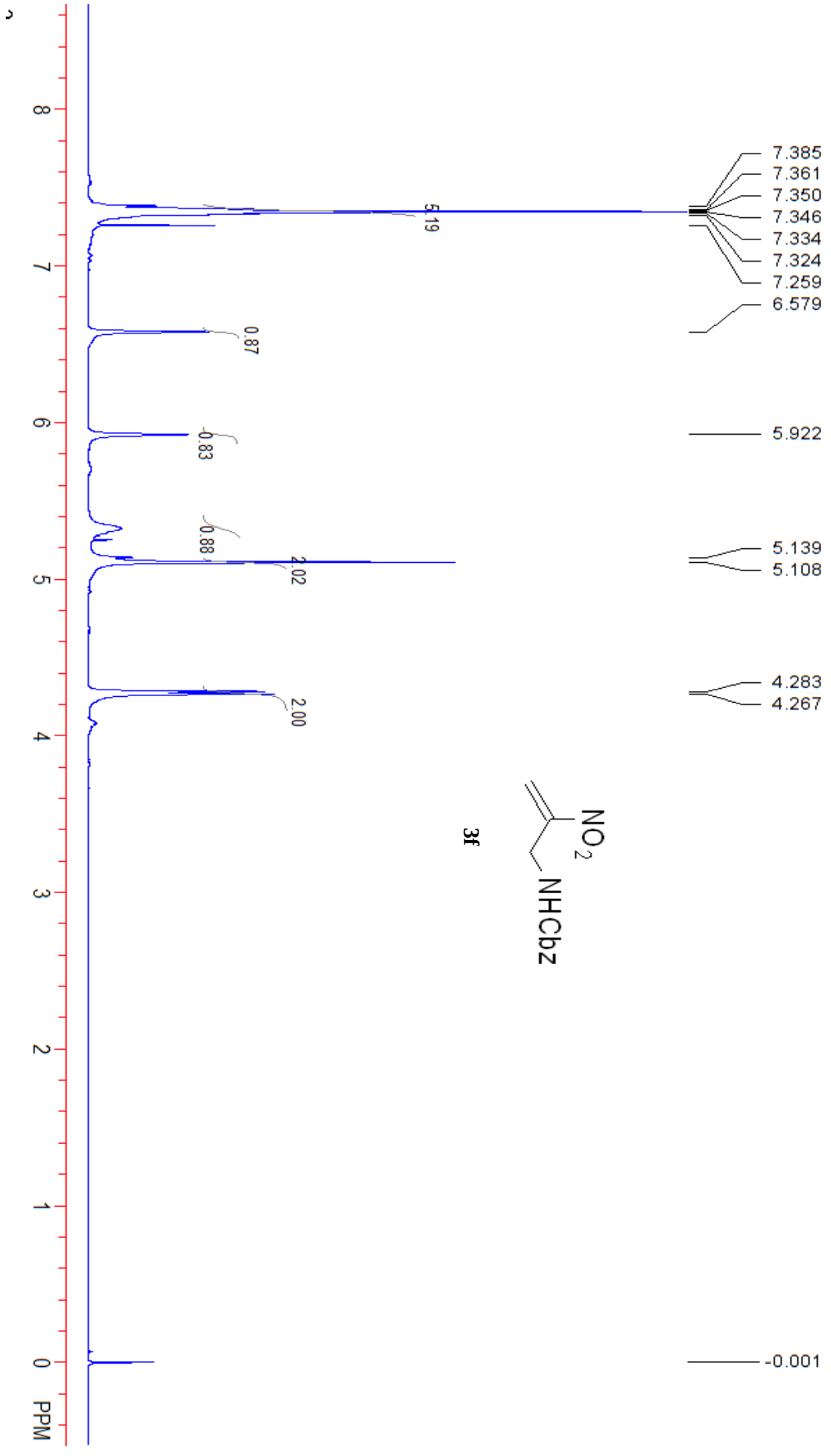
O
180
160
140
120
100
80
60
40
20
PPM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PPM
3f
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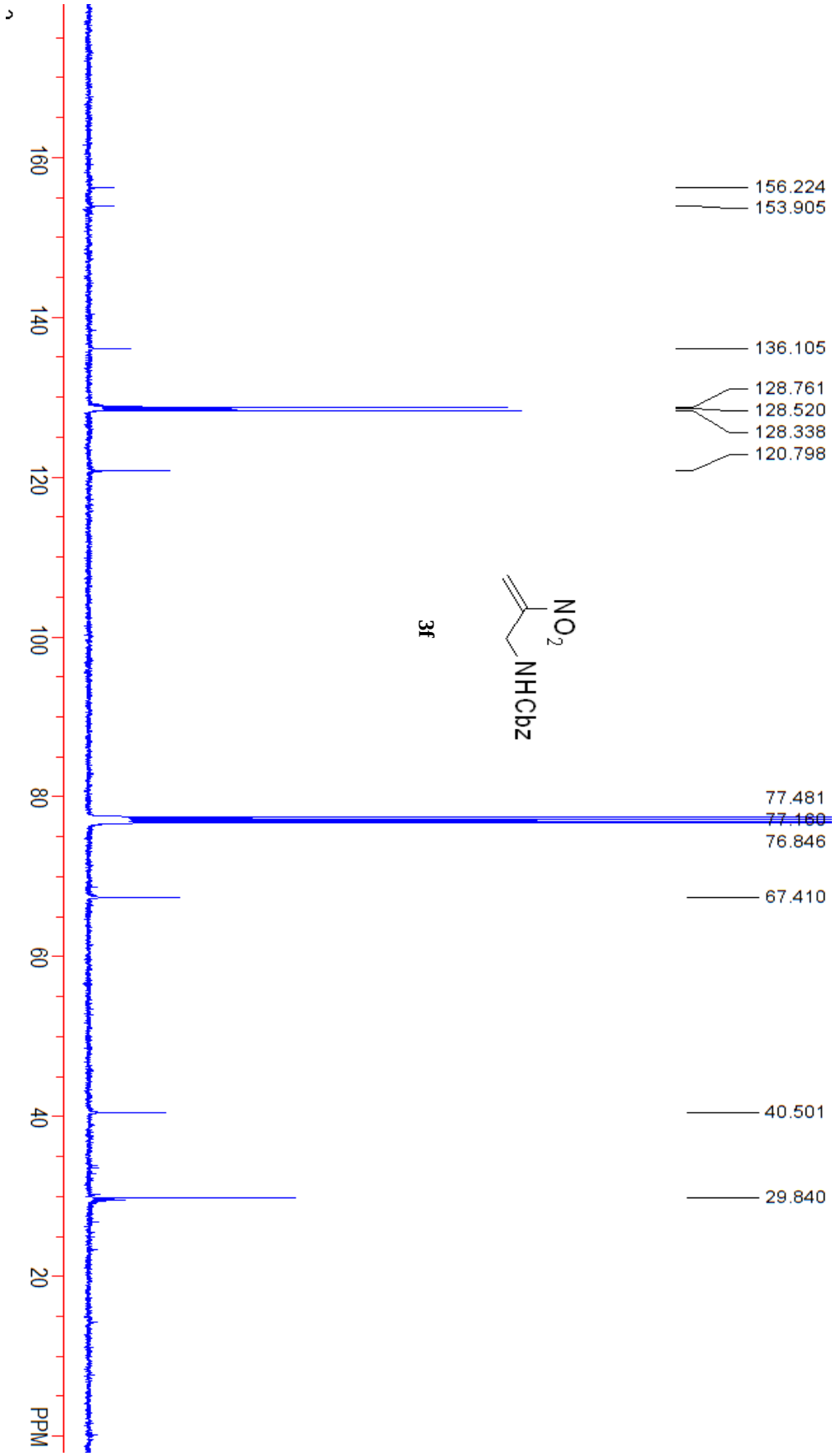
NHCbz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NO2
NHCbz
3f
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120
100
80
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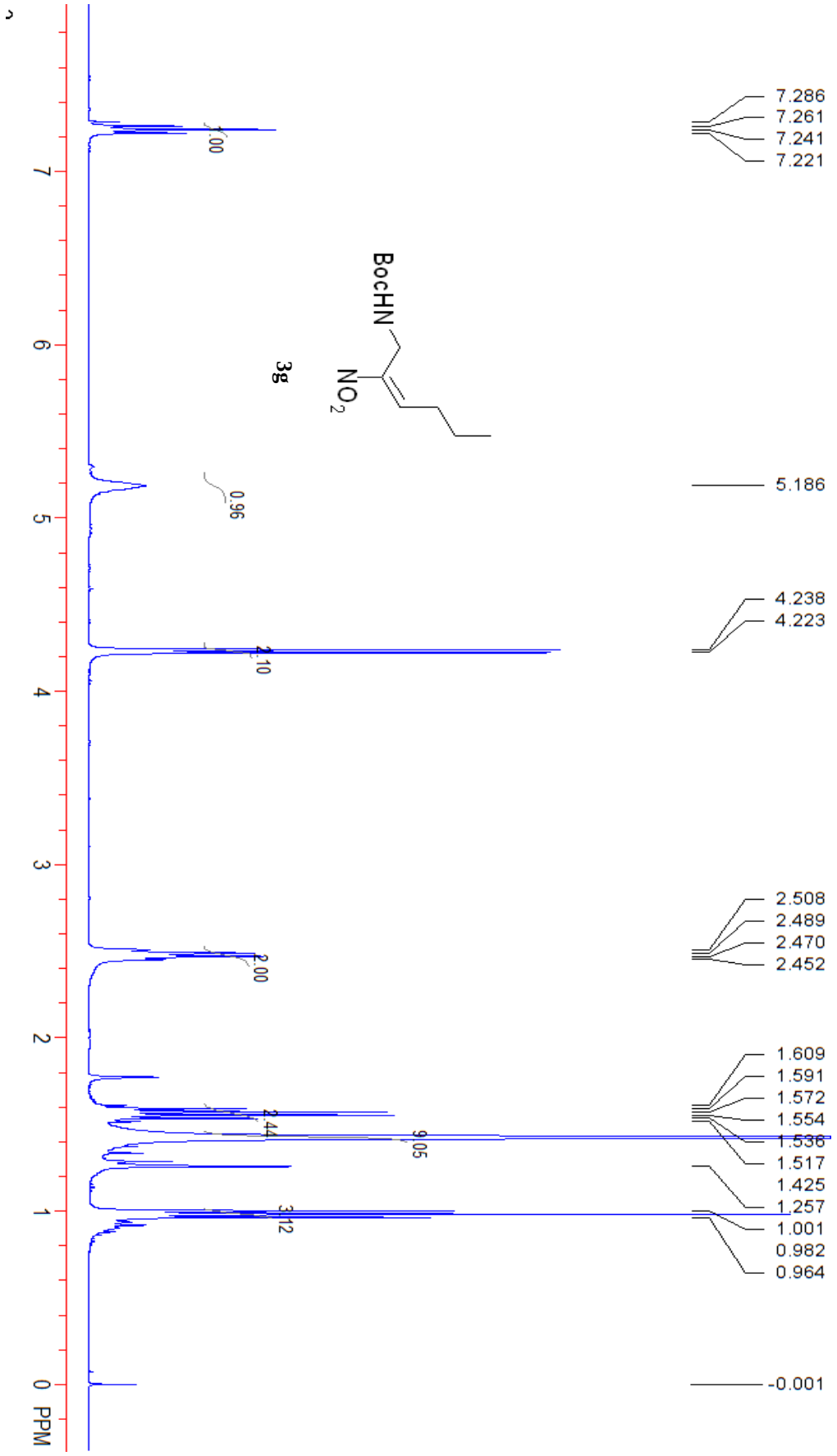
40
20
PPM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1.609
1.591
1.572
1.554
1.536
1.517
1.425
1.257
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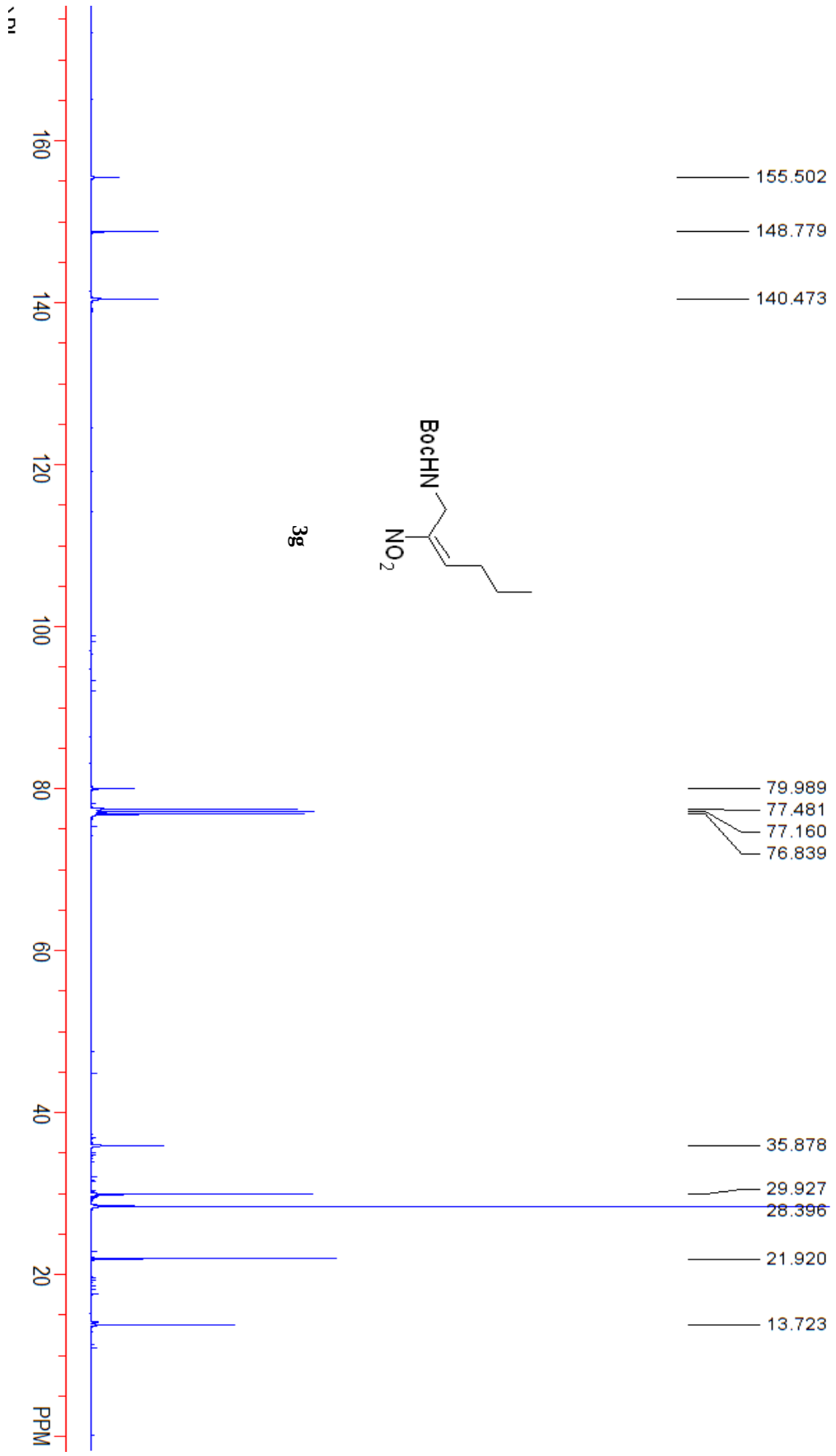
PPM


155.502
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140.473
79.989
77.481
77.160
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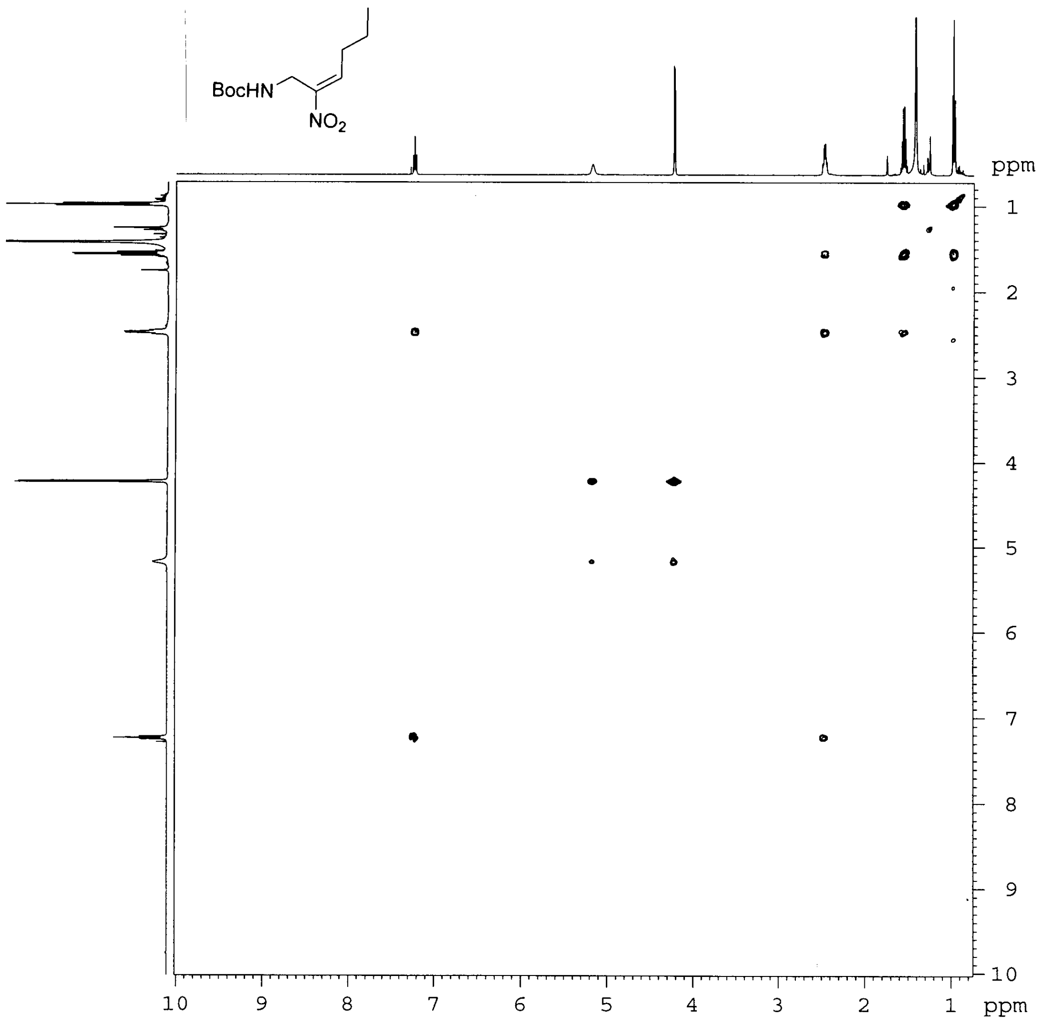
21.920
13.723
160
140
120
100
80
60
40
20
PPM
3g
BocHN
NO2




```
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NAME       2005183cosy-6-38
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20100824
Time                  12.56
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG          cosygpmfqf
TD                     1024
SOLVENT               CDCl3
NS                        1
DS                       16
SWH                5482.456 Hz
FIDRES             5.353961 Hz
AQ                0.0935300 sec
RG                     1024
DW                   91.200 usec
DE                     6.50 usec
TE                    300.0 K
D0               0.00000300 sec
D1               2.00000000 sec
d13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00018240 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    10.50 usec
PL1                   -4.00 dB
SFO1            500.1324200 MHz

====== GRADIENT CHANNEL =====
GPNAM1             SINE.100
GPNAM2             SINE.100
GPNAM3             SINE.100
GPZ1                  16.00 %
GPZ2                  12.00 %
GPZ3                  40.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
ND0                       1
TD                      256
SFO1               500.1324 MHz
FIDRES            21.415844 Hz
SW                   10.962 ppm
FnMODE                   QF

F2 - Processing parameters
SI                     1024
SF              500.1300016 MHz
WDW                    SINE
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.40

F1 - Processing parameters
SI                     1024
MC2                      QF
SF              500.1300016 MHz
WDW                    SINE
SSB                       0
LB                     0.00 Hz
GB                        0
```
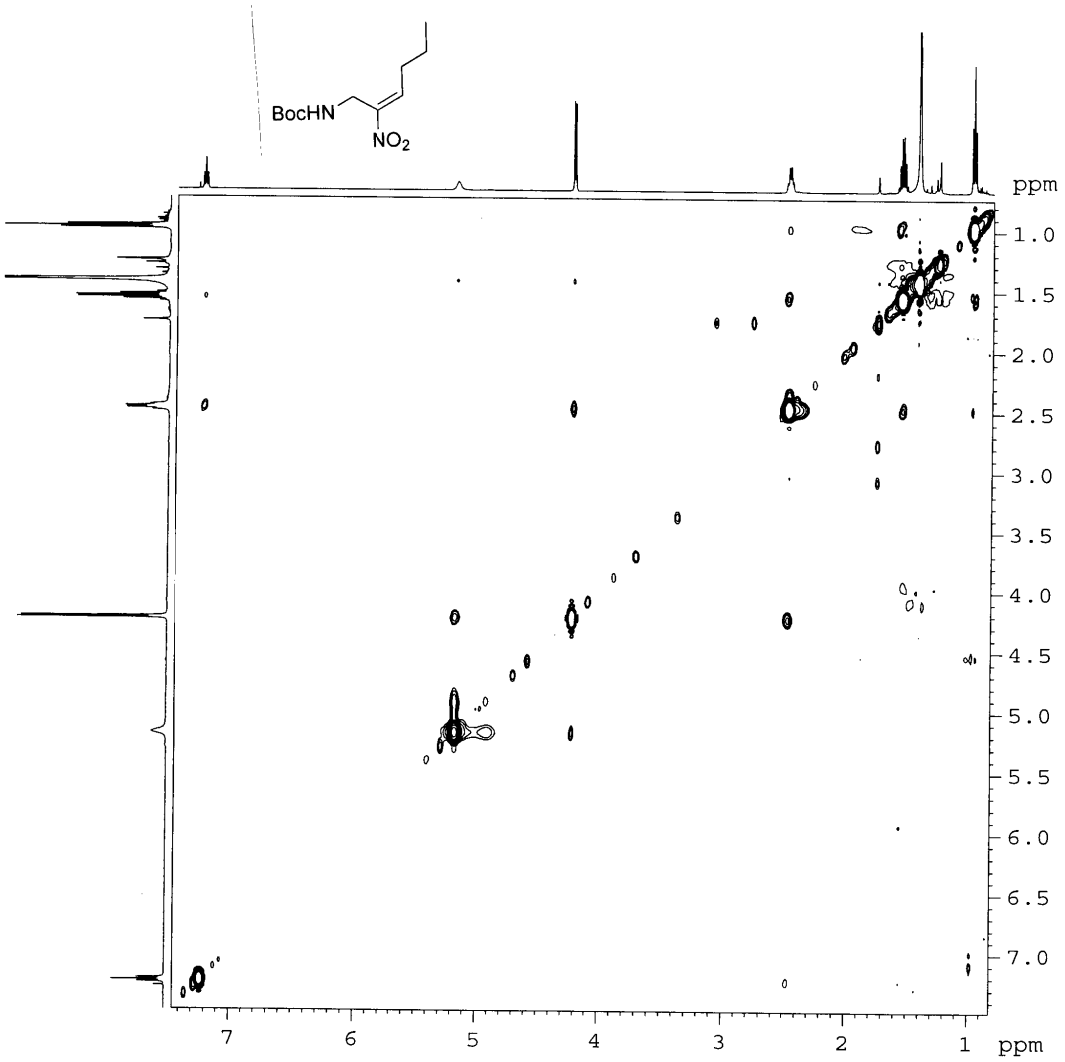
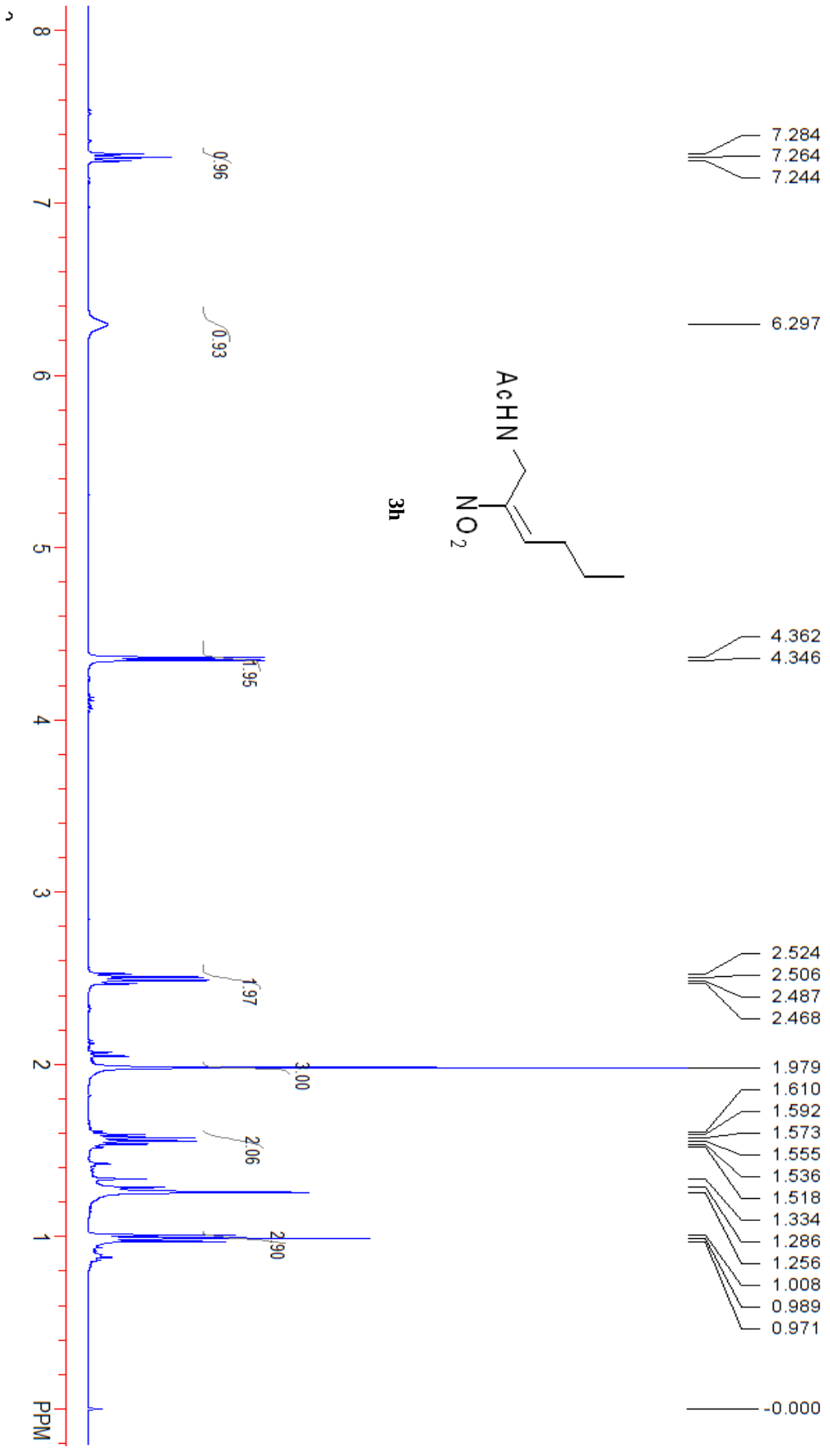
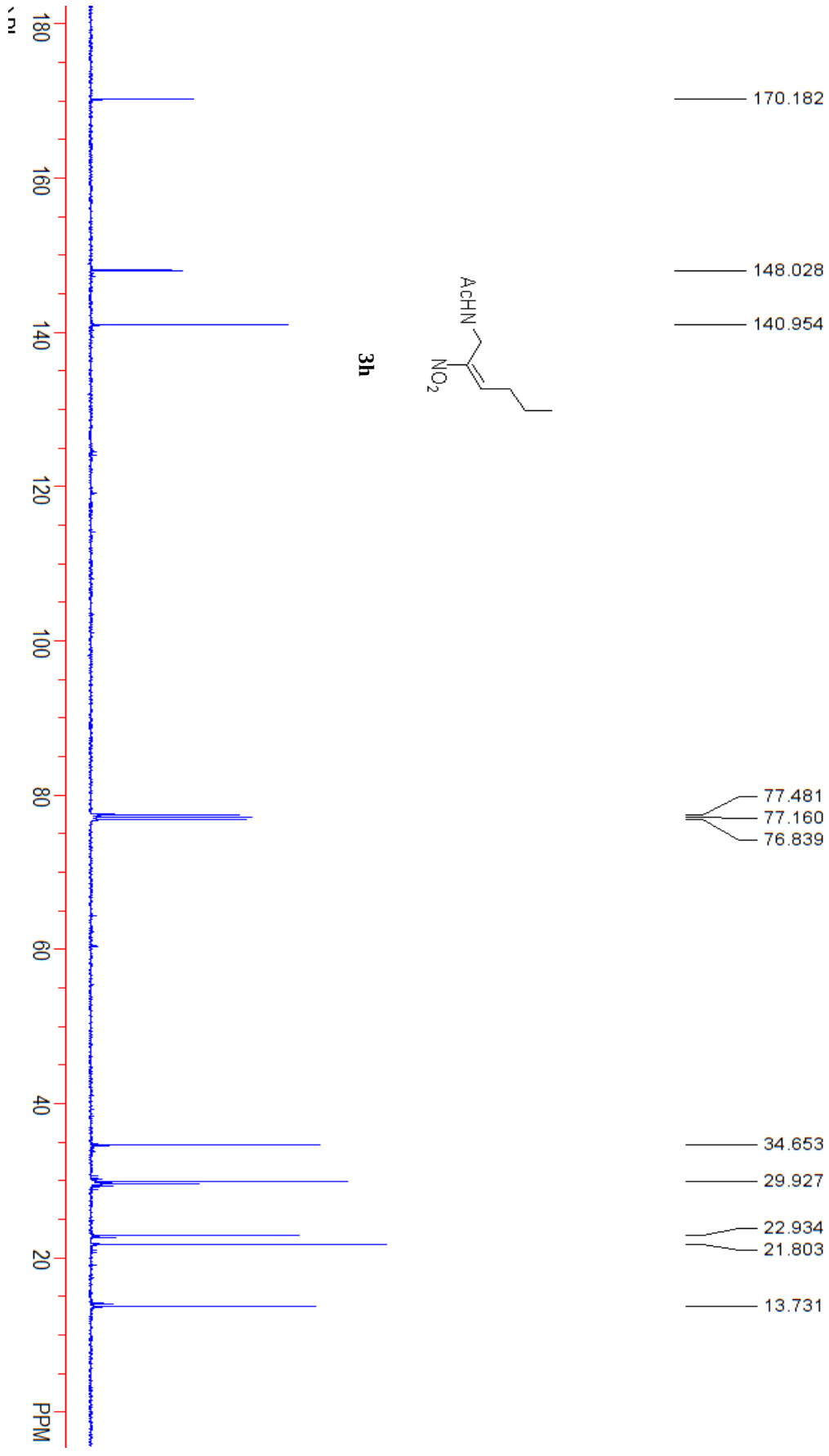




```
Current Data Parameters
NAME      2005183noe-6-38
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20100824
Time                  13.07
INSTRUM               spect
PROBHD    5 mm QNP 1H/13
PULPROG         noesygpph
TD                    1024
SOLVENT               CDCl3
NS                       2
DS                      16
SWH                5482.456 Hz
FIDRES             5.353961 Hz
AQ                 0.0935300 sec
RG                       362
DW                  91.200 usec
DE                   6.50 usec
TE                   300.0 K
d0                0.00007783 sec
D1                2.00000000 sec
D16               0.00020000 sec
D8                1.00000000 sec
IN0               0.00018240 sec
ST1CNT                  256
TAU               0.49880001 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                   10.50 usec
p2                   21.00 usec
PL1                  -4.00 dB
SFO1          500.1324200 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPZ1                40.00 %
GPZ2               -40.00 %
P16                1000.00 usec

F1 - Acquisition parameters
ND0                      1
TD                     256
SFO1            500.1324 MHz
FIDRES          21.415844 Hz
SW                 10.962 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                    1024
SF            500.1300016 MHz
WDW                 QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2          States-TPPI
SF            500.1300016 MHz
WDW                 QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
```


3h
AcHN
NO2
7.284
7.264
7.244
6.297
4.362
4.346
2.524
2.506
2.487
2.468
1.979
1.610
1.592
1.573
1.555
1.536
1.518
1.334
1.286
1.256
1.008
0.989
0.971
-0.000
0.96
0.93
1.95
1.97
3.00
2.06
2.90
PPM


170.182
148.028
140.954
77.481
77.160
76.839
34.653
29.927
22.934
21.803
13.731
AcHN
NO2
3h
PPM