Morita-Baylis-Hillman Adducts as Effective Dipolarophiles in Cu(I)-Catalyzed 1,3-Dipolar Cycloaddition with Azomethine Ylides: Asymmetric Construction of Pyrrolidine Derivatives Containing Quaternary Stereogenic Center

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Supporting Information

Table of Contents

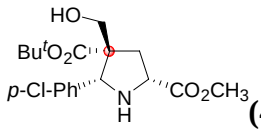
General Remarks.

^{1}H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quarte, m = multiple or unresolved, brs = broad single, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a VARIAN Mercury 100 MHz spectrometer in chloroform-d3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Diastereomeric ratios were determined from crude ^{1}H NMR or HPLC analysis. Enantiomeric ratios were determined by HPLC, using a chiralcel AD-H column, a chiralpak AS-H column with hexane and *i*-PrOH as solvents. Ligands **1a-e** were prepared according to the literature procedure reported by us.[1] Morita-Baylis-Hillman Adducts were prepared according to the literature procedure.[2] The racemic adducts were attained by using racemic AgOAc/PPh_3 as the catalyst. The absolute configuration of **5** was determined unequivocally according to the X-ray diffraction analysis, and those of other adducts were deduced on the basis of these results.

General Procedure for Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylides with Morita-Baylis-Hillman Adducts Catalyzed by Cu(I)/(*S*)-TF-BiphamPhos Complex in the Presence of Et_3N as Base

Under argon atmosphere (*S*)-TF-BiphamPhos **1e**（5.3 mg, 0.0066 mmol) and $Cu(CH_3CN)_4BF_4$ (1.9 mg, 0.006 mmol) were dissolved in 2 mL DCM, and stirred at room temperature for about 1h at room temperature. Then, imine substrate (0.40 mmol), Et_3N (0.03 mmol) were added sequentially, the misture was dropped to -20^{o}C and Morita-Baylis-Hillman Adducts (0.20 mmol) was added. Once starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness, the residue was purified by column chromatography to give the corresponding cycloaddition product, which was then

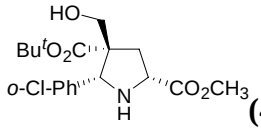
directly analyzed by chiral HPLC to determine the enantiomeric excess.



(4ba)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 5-(4-chlorophenyl)-4-(hydroxymethyl)-pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 88% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_D$ = +1.8 (*c* 2.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 4.31 (s, 1H), 3.98 (t, *J* = 8.4 and 10.2 Hz, 1H), 3.89 (d, *J* = 11.4 Hz, 1H), 3.82 (s, 3H), 3.77 (d, *J* = 11.4 Hz ,1H), 2.64 (br, 1H), 2.58 (m, 2H), 2.32 (m, 1H) ,1.09 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.38, 37.02, 52.24, 58.56, 60.56, 66.00, 66.90, 81.91, 128.11, 129.01, 133.27, 138.02, 172.31, 173.58; IR (KBr) ν 3675, 3616, 3019, 2977, 2400, 1737, 1216, 757 cm^{-1}. HRMS Calcd. For $C_{18}H_{24}ClNO_5$ + H^+: 370.1416, found 370.1411. The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm); t_r = 18.76 and 32.26 min.

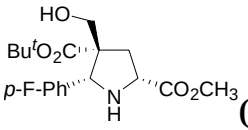


(4bb)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 5-(2-chlorophenyl)-4-(hydroxymethyl)-pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 85% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_D$ = -26.2 (*c* 1.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.15-7.35 (m, 3H), 4.86 (s, 1H), 4.12-4.00 (m, 2H), 3.80 (s,, 3H), 3.75 (d, *J* = 11.1 Hz, 1H), 2.62 (t, *J* = 11.4 Hz, 1H), 2.38-2.46 (m, 2H), 1.06 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.28, 35.58, 52.20, 58.45, 61.94, 65.91, 81.59, 126.90, 128.60, 129.09, 129.84, 133.65, 138.50, 171.31, 173.91; IR (KBr) ν 3683, 3621,

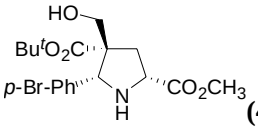
3019, 2977, 2400, 1736, 1216, 757 cm^{-1}. HRMS Calcd. For $C_{18}H_{24}ClNO_5$ + H^+: 370.1416, found 370.1416. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralcel AS-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 210 nm); t_r = 11.40 and 20.42 min.



(4bc)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 5-(4-fluorophenyl)-4-(hydroxymethyl)-pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 72% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_D$ = +1.2 (*c* 0.79, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.36 (m, 2H), 6.99 (t, *J* = 8.7 Hz and 8.4 Hz, 2H), 4.28 (s, 1H), 3.97-3.86 (m, 2H), 3.80 (s, 3H), 3.74 (d, *J* = 11.7 Hz, 1H), 2.68 (br, 1H), 2.54 (m, 1H), 2.32 (m, 1H), 1.08 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.75, 37.43, 52.57, 58.93, 60.86, 66.66, 67.38, 82.28, 115.05, 115.33, 129.53, 129.64, 172.79, 173.88; IR (KBr) v 3684, 3620, 3019, 2896, 2400, 1737, 1217, 758 cm^{-1}. HRMS Calcd. For $C_{18}H_{24}FNO_5$ + H^+: 354.1711, found 354.1713. The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralcel AS-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 210 nm); t_r = 11.29 and 15.97 min.

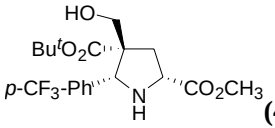


(4bd)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 5-(4-bromophenyl)-4-(hydroxymethyl)-pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 80% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_D$ = -3.0 (*c* 1.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.43 (d, *J* = 8.1 Hz 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 4.27 (s, 1H), 3.96 (m, 1H), 3.88 (d, *J* = 11.1 Hz, 1H), 3.81 (s, 3H), 3.75 (d, *J* = 11.1 Hz ,1H), 2.73 (br, 1H), 2.54 (m, 1H), 2.32 (m, 1H), 1.09

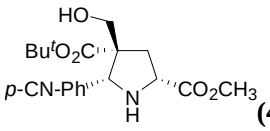
(s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.53, 37.20, 52.40, 58.72, 60.78, 66.34, 67.15, 82.15, 121.54, 129.51, 131.21, 138.70, 172.50, 173.68; IR (KBr) v 3684, 3620, 3019, 2976, 2400, 1737, 1217, 741 cm^{-1}. HRMS Calcd. For $C_{18}H_{24}BrNO_5$ + H^+: 414.0911, found 414.0912. The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralcel AS-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 210 nm); t_r = 11.27 and 16.96 min.



(4be)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 4-(hydroxymethyl)-5-(4-(trifluoromethyl)phenyl) pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 88% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_D$ = +2.5 (*c* 1.05, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.57 (s, 4H), 4.42 (s, 1H), 4.01 (t, *J* = 9.0 Hz and 8.7Hz, 1H), 3.90 (d, *J* = 11.7 Hz, 1H), 3.82 (s, 3H), 3.80 (d, *J* = 11.7 Hz ,1H), 2.90 (br, 1H), 2.57 (m, 1H), 2.32 (m, 1H), 1.04 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.78, 37.39, 52.80, 59.16, 61.09, 66.69, 67.46, 82.61, 125.41, 128.60, 144.40, 172.77, 174.01; IR (KBr) v 3684, 3620, 3019, 2977, 2400, 1738, 1216, 757 cm^{-1}. HRMS Calcd. For $C_{19}H_{24}F_3NO_5$ + H^+: 404.1679, found 404.1682. The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralcel AS-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 210 nm); t_r = 9.21 and 12.88 min.

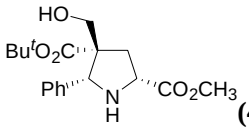


(4bf)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 5-(4-cyanophenyl)-4-(hydroxymethyl) pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 65% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_D$ = +6.4 (*c* 0.57, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.56 (s, 4H), 4.42

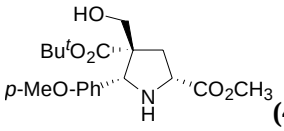
(s, 1H), 4.00 (m, 1H), 3.86 (d, *J* = 11.7 Hz, 1H), 3.82 (s, 3H), 3.79 (d, *J* = 11.7 Hz ,1H), 2.73 (br, 1H), 2.55 (m, 1H), 2.32 (m, 1H), 1.06 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.69, 36.87, 52.63, 58.85, 60.77, 66.38, 67.08, 82.53, 111.45, 119.01, 128.97, 132.07, 145.96, 172.43, 173.77; IR (KBr) v 3423, 3055, 2985, 1720, 1265, 739 cm^{-1}. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralcel AD-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 230 nm); t_r = 25.38 and 29.42 min.



(4bg)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 4-(hydroxymethyl)-5-phenyl pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 65% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_D$ = +6.4 (*c* 0.57, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.39-7.24 (m, 5H), 4.28 (s, 1H), 4.02-3.94 (m, 2H), 3.82 (s, 3H), 3.75 (d, *J* = 11.7 Hz ,1H), 2.86 (br, 1H), 2.55 (m, 1H), 2.36 (m, 1H), 1.06 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.07, 37.25, 51.97, 58.51, 60.54, 66.11, 67.57, 81.43, 127.24, 127.35, 127.85, 138.88, 172.24, 173.33; IR (KBr) v 3683, 3621, 3019, 2976, 1710, 1216, 776 cm^{-1}. HRMS Calcd. For $C_{19}H_{24}F_3NO_5$ + H^+: 336.1806, found 336.1815. The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralcel AS-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 210 nm); t_r = 10.46 and 16.22min.

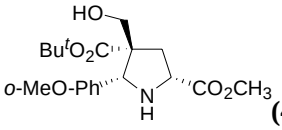


(4bh)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 4-(hydroxymethyl)-5-(4-methoxyphenyl) pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 70% yield. It was purified by flash chromatography to afford colorless oil.

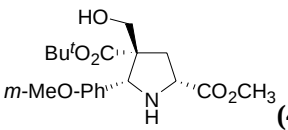
$[\alpha]^{25}_{D}$ = +6.3 (*c* 0.51, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.29 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.22 (s, 1H), 4.00-3.91 (m, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.73 (d, *J* = 11.1 Hz, 1H), 2.82 (br, 1H), 2.54 (m, 1H), 2.35(m, 1H), 1.10 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.32, 37.34, 52.09, 55.10, 58.56, 60.64, 66.26, 67.38, 81.57, 108.63, 113.30, 128.50, 131.06, 158.92, 172.48; IR (KBr) v 3684, 3620, 3019, 2976, 2400, 1737, 1516, 1217, 743 cm^{-1}. HRMS Calcd. For $C_{19}H_{24}F_3NO_5$ + H^+: 366.1911, found 366.1915. The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralcel OD-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 210 nm); t_r = 19.42 and 26.06 min.



(4bi)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 4-(hydroxymethyl)-5-(2-methoxyphenyl) pyrrolidine-2,4-dicarboxylate

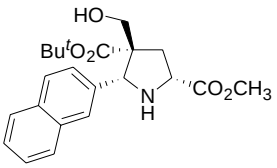
The title compound was prepared according to the general procedure as described above in 68% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_{D}$ = -32.1 (*c* 0.55, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 12 Hz and 7.8 Hz, 1H), 6.94 (t, *J* = 7.2 Hz and 7.5 Hz, 1H), 6.82 (d, *J* = 12.9 Hz, 1H), 4.55 (s, 1H), 4.02-3.90 (m, 2H), 3.79 (s, 6H), 3.65 (d, *J* = 11.1 Hz, 1H), 2.66-2.46 (m, 3H), 1.08 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.28, 37.38, 51.98, 54.95, 58.60, 61.14, 65.45, 80.99, 110.01, 120.36, 126.80, 128.41, 156.68, 172.23, 173.59; IR (KBr) v 3423, 3055, 2985, 1720, 1265, 739 cm^{-1}. The product was analyzed by HPLC to determine the enantiomeric excess: 86% ee (Chiralcel OD-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 210 nm); t_r = 13.83 and 21.54 min.



(4bj)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 4-(hydroxymethyl)-5-(3-methoxyphenyl) pyrrolidine-2,4-dicarboxylate

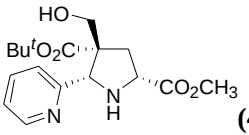
The title compound was prepared according to the general procedure as described above in 72% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_{D}$ = +5.6 (*c* 0.55, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.27-7.18 (m, 1H), 6.94 (m, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 4.26 (s, 1H), 3.97-3.92 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.74 (d, *J* = 11.4 Hz, 1H), 2.64-2.35 (m, 3H), 1.08 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.90, 37.99, 52.77, 55.70, 59.26, 61.29, 66.92, 68.27, 82.24, 113.62, 113.70, 120.29, 129.60, 141.49, 159.86, 173.11, 174.22; IR (KBr) v 3423, 3055, 2985, 1720, 1265, 739 cm^{-1}. The product was analyzed by HPLC to determine the enantiomeric excess: 86% ee (Chiralcel AS-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 210 nm); t_r = 15.10 and 19.92 min.



(4bk)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 4-(hydroxymethyl)-5-(3-methoxyphenyl) pyrrolidine-2,4-dicarboxylate

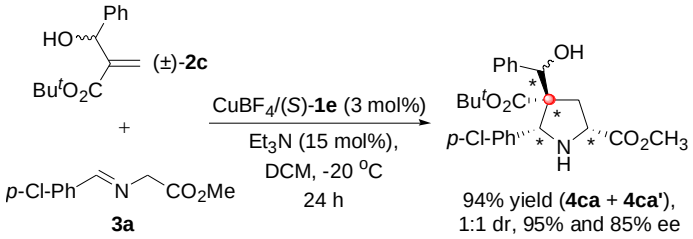
The title compound was prepared according to the general procedure as described above in 72% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_{D}$ = +3.3 (*c* 1.12, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.84-7.75 (m, 4H), 7.46 (m, 3H), 4.53 (s, 1H), 4.11 (t, *J* = 8.7 Hz and 8.7 Hz, 1H), 4.00 (d, *J* = 11.4 Hz, 1H), 3.84 (d, *J* = 11.4 Hz, 1H), 3.83 (s, 3H), 2.69-2.60 (m, 2H), 2.41-2.48 (m, 1H), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.27, 37.60, 52.23, 58.77, 60.84, 66.29, 67.94, 80.70, 125.69, 125.78, 126.04, 126.22, 127.43, 127.64, 127.82, 132.80, 132.95, 136.55, 172.56, 173.65; IR (KBr) v 3683, 3620, 3019, 2976, 2400, 1736, 1522, 1216, 751 cm^{-1}. The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralcel AS-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 254 nm); t_r = 11.89 and 21.25 min.



(4bl)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 4-(hydroxymethyl)-5-(pyridin-2-yl) pyrrolidine-2,4-dicarboxylate

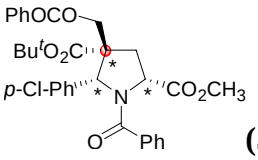
The title compound was prepared according to the general procedure as described above in 41% yield. It was purified by flash chromatography to afford colorless oil. $[\alpha]^{25}_{D}$ = +0.1 (*c* 0.55, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 8.65 (s, 1H), 8.51 (d, *J* = 3.6 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.27 (s, 1H), 4.42 (s, 1H), 4.02 (m, 1H), 3.95-3.82 (m, 5H), 2.76 (br, 1H), 2.56 (m, 1H), 2.35 (m, 1H), 1.08 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.64, 36.81, 52.50, 58.88, 60.88, 65.23, 65.91, 82.27, 123.44, 135.71, 148.80, 149.38, 172.32, 173.80; IR (KBr) v 3684, 3620, 3019, 2976, 2400, 1736, 1521, 1218, 1046, 743 cm^{-1}. The product was analyzed by HPLC to determine the enantiomeric excess: 72% ee (Chiralcel AS-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 254 nm); t_r = 15.30 and 18.62 min.



(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 5-(4-chlorophenyl)-4-((*S*)-hydroxy(phenyl) methyl)pyrrolidine-2,4-dicarboxylate 4ca and (2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 5-(4-chlorophenyl)-4-((*R*)-hydroxy(phenyl)methyl) pyrrolidine-2,4-dicarboxylate 4ca'

The title compounds **4ca** and **4ca'**were prepared according to the general procedure as described above and separated by silica gel column as colorless oil, and the absolute configuration of the stereogenic center bearing hydroxyl group has not been determined. For one diastereomer: $[\alpha]^{25}_{D}$ = -4.2 (*c* 0.46, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.46-7.26 (m, 9H), 4.88 (s, 1H), 4.85 (s, 1H), 3.85 (t, *J*=9.3 Hz and

8.1 Hz, 1H), 3.78 (s, 3H), 2.54 (m, 1H), 2.45 (m, 1H), 1.04 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.37, 35.24, 52.32, 58.36, 63.98, 67.89, 76.70, 82.95, 127.38, 128.15, 128.40, 129.74, 133.32, 139.69, 140.44, 172.68, 174.19; IR (KBr) v 3683, 3620, 3019, 2976, 2400, 1736, 1521, 1423, 1217, 759 cm^{-1}. The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralcel AD-H, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 210 nm); t_r = 7.06 and 20.49 min. For the other diastereomer: $[\alpha]^{25}_D$ = -2.9 (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.39-7.26 (m, 9H), 5.21 (s, 1H), 4.84 (s, 1H), 3.83 (m, 1H), 3.76 (s, 3H), 2.72-2.52 (m, 2H), 0.97 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.34, 33.21, 46.20, 52.24, 58.30, 64.23, 66.89, 74.85, 82.02, 89.19, 127.66, 128.23, 129.20, 133.40, 138.03, 140.71, 143.50, 170.91, 174.09; IR (KBr) v 3684, 3620, 3019, 2975, 2400, 1736, 1520, 1422, 1216, 1046, 762 cm^{-1}. The product was analyzed by HPLC to determine the enantiomeric excess: 85% ee (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 210 nm); t_r = 16.39 and 30.48 min.



(5)

(2*R*,4*R*,5*R*)-4-*tert*-butyl 2-methyl 1-benzoyl-4-(benzoyloxymethyl)-5-(4-chlorophenyl)pyrrolidine-2,4-dicarboxylate

Under argon atmosphere **4ba** (369 mg, 1 mmol) was dissolved in 5 mL DCM, and PhCOCl (352 mg, 2.5 mmol), TEA (252 mg, 2.5 mmol) were added sequentially. The mixture was stirred at room temperature for 4h. Once starting material was consumed (monitored by TLC), the residue was purified by column chromatography to give **5** in 94% yield, which was then directly analyzed by chiral HPLC to determine the enantiomeric excess. $[\alpha]^{25}_D$ = -10.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.62-7.01 (m, 13H), 4.74 (m, 2H), 4.55 (s, 1H), 4.43 (m, 1H), 3.88 (s, 3H), 2.88 (t, *J* = 12.9 Hz and 12.0 Hz, 1H), 2.62 (s, 1H), 1.06 (s, 9H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 27.42, 30.52, 52.61, 58.29, 59.66, 66.30, 67.54, 82.61, 126.65, 128.13, 128.44, 128.62, 129.06, 129.63, 129.96, 130.07, 133.62,

134.13, 135.28, 137.31, 165.84, 167.77, 171.50, 172.15; IR (KBr) v 3683, 3620, 3019, 2977, 2400, 1737, 1436, 1370, 1216, 1046, 758 cm^{-1}. The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralcel AD-H, *i*-propanol/hexane = 20/80, flow rate 0.5 mL/min, λ = 210 nm); t_r = 19.86 and 24.18 min.

The absolute configuration of the cycloadduct (2*R*,4*R*,5*R*)-**5 was determined by X-ray diffraction analysis**

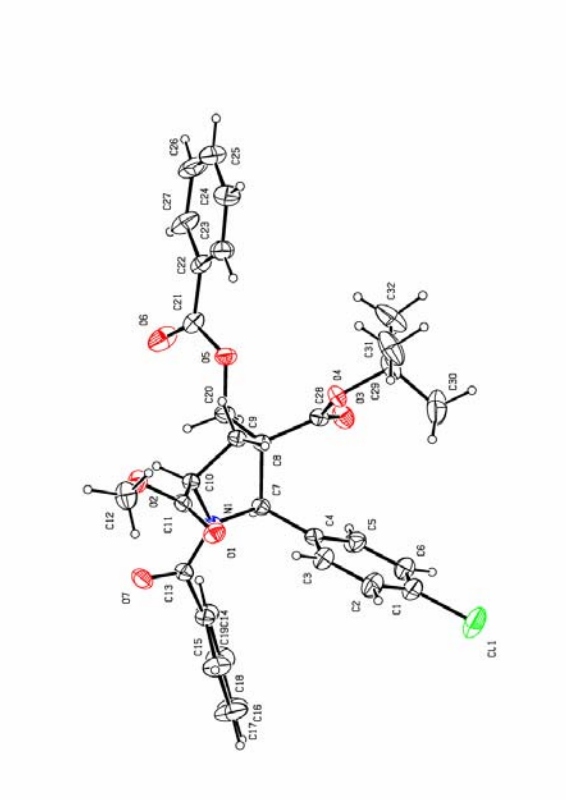


Figure 1. X-ray structure of (2*R*,4*R*,5*R*)-**5**

Crystal data for (2*R*,4*R*,5*R*)-**5**: $C_{32}H_{32}ClNO_7$, M_r = 578.04, T = 293 K, Orthorhombic, space group *P*2(1)2(1)2, a = 19.401(3), b = 24.000(6), c = 6.6143(9) Å, V = 3079.8(7) $Å^3$, Z = 4, 6359 reflections measured, 4817 unique (R_{int} = 0.0412) which were used in all caclculations. The final wR_2 = 0.0844 (all data). Flack χ = 0.03(8). CCDC 813952 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Proposed transition state of the *endo*-selectivity for asymmetric 1,3-dipolar cycloaddition of imino esters with Morita-Baylis-Hillman adduct

Based on the relative and absolute configuration of (2*R*,4*R*,5*R*)-**5** and previous studies,[1,3] a plausible transition state accounting for the observed *endo*-selectivity of the 1,3-DC addition of imino esters with Morita-Baylis-Hillman adduct in the presence of $Cu(CH_3CN)_4BF_4$/(*S*)-TF-BiphamPhos (**1a**) is shown in Figure 2. The *in situ*-formed azomethine ylide is coordinated to the metallic center and oriented in such way because of the steric repulsion between the phenyl group in the ylide and the phenyl ring on the phosphorus atom of the chiral ligand, and the MBH adduct **2** approached the *Si* (C=N) face of the azomethine ylide and forms the *endo*-cycloadduct, which is compatible with the experimental results. The carbonyl group of Morita-Baylis-Hillman adduct could coordinate with the Cu(I) center, which can stabilize the negatively charged oxygen atom in the proposed transition states.[4] It could not rule out the possible hydrogen bond interaction between the carbonyl group of dipolarophile **(2)** and the NH_2 group of the chiral (*S*)-TF-BiphamPhos ligand (**1a**), which also facilitates stabilizing the proposed transition states.[3b,3c] Nevertheless, the real catalytic mechanism still needs further investigation.

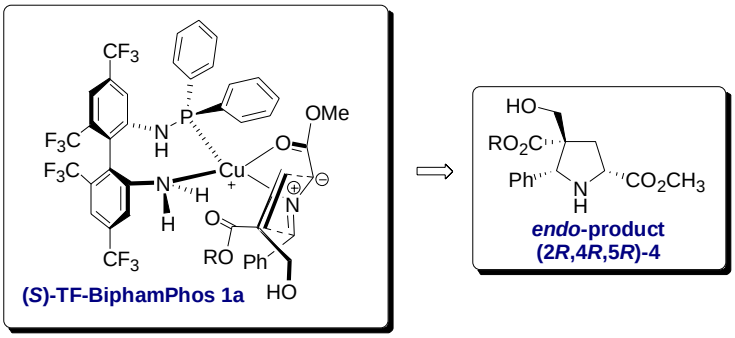


Figure 2. Proposed transition states leading to *endo*-(2*R*,4*R*,5*R*)-cycloadduct while using Morita-Baylis-Hillman adducts as the dipolarophiles.

References

1. a) C.-J. Wang, G. Liang, Z.-Y. Xue, F. Gao, *J. Am. Chem. Soc.* **2008**, *130*, 17250; b) C.-J. Wang, Z.-Y. Xue, G. Liang, Z. Lu, *Chem. Commun.* **2009**, 2905; c) G. Liang, M.-C. Tong, C.-J. Wang, *Adv. Synth. Catal.* **2009**, *351*, 3101; d) Z.-Y. Xue, T.-L. Liu, Z. Lu,; H. Huang, H.-Y. Tao, C.-J. Wang, *Chem. Commun.* **2010**, *46*, 1727.

2. a) H. Huang, X. Liu, J. Deng, M. Qiu and Z. Zheng, *Organic. Letters.,* **2006**, *8*, 3359; b) W. -D. Lee, K. -S. Yang and K. Chen, *Chem. Commun.*, 2001, 1612.

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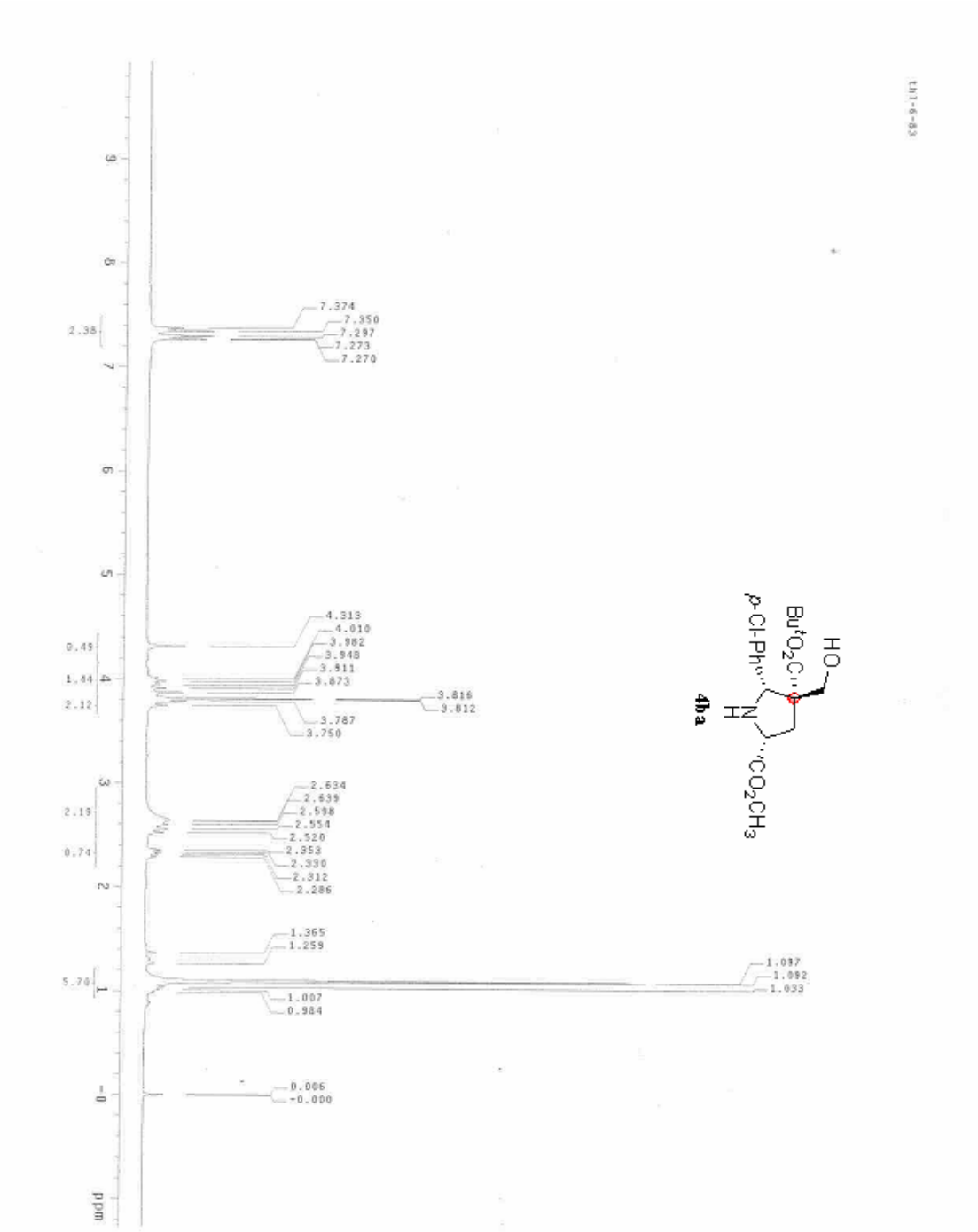
4 X.-X. Yan, Q. Peng, Y. Zhang, K. Zhang, W. Hong, X.-L. Hou, Y.-D. Wu, *Angew. Chem., Int. Ed.* **2006**, *45*, 1979.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3.873
3.816
3.812
3.787
3.750
2.634
2.619
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2.353
2.330
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2.286
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1.259
1.097
1.092
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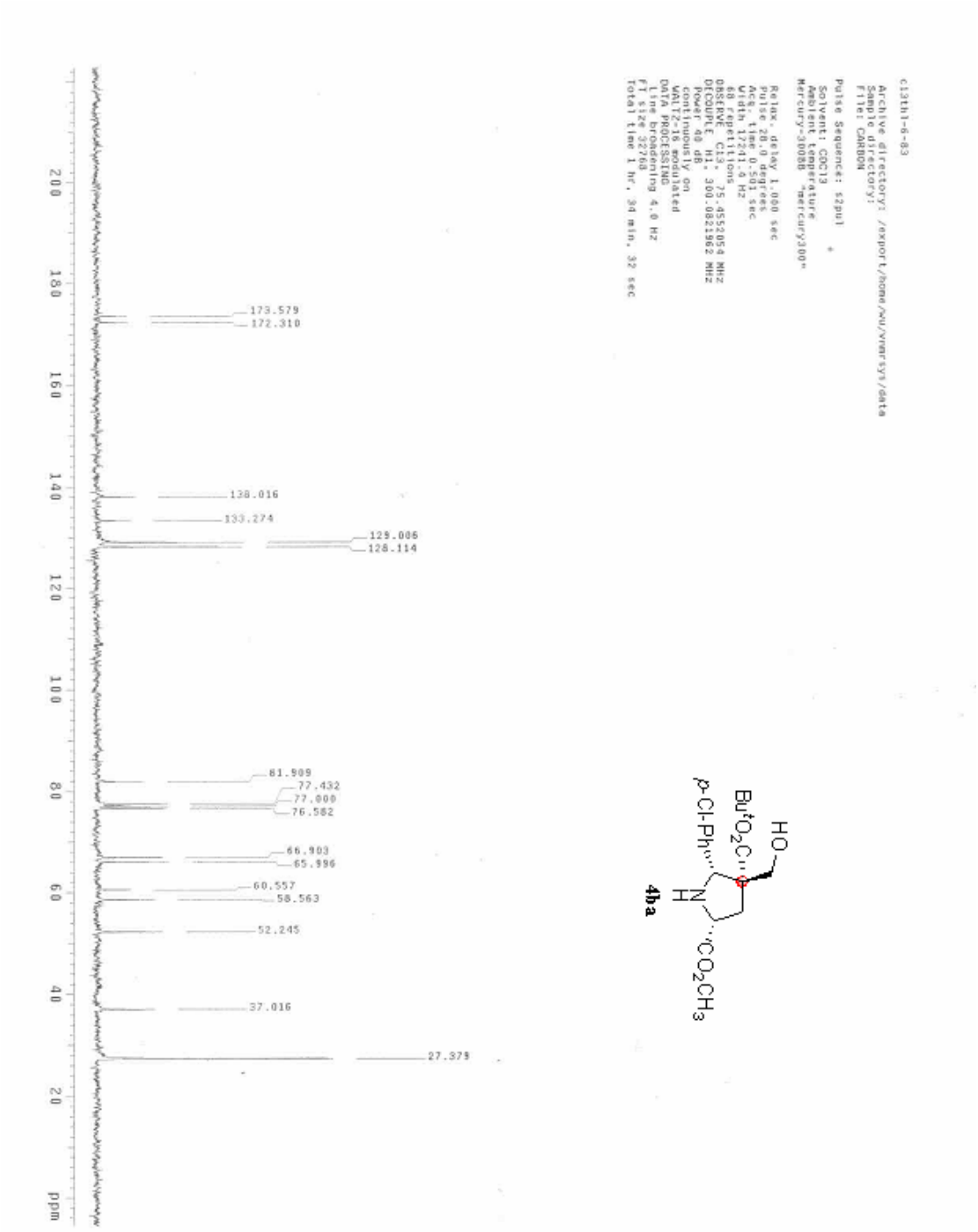
4ba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DATA PROCESSING
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129.006
128.114
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77.432
77.000
76.582
66.903
65.996
60.557
58.563
52.245
37.016
27.379
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180
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140
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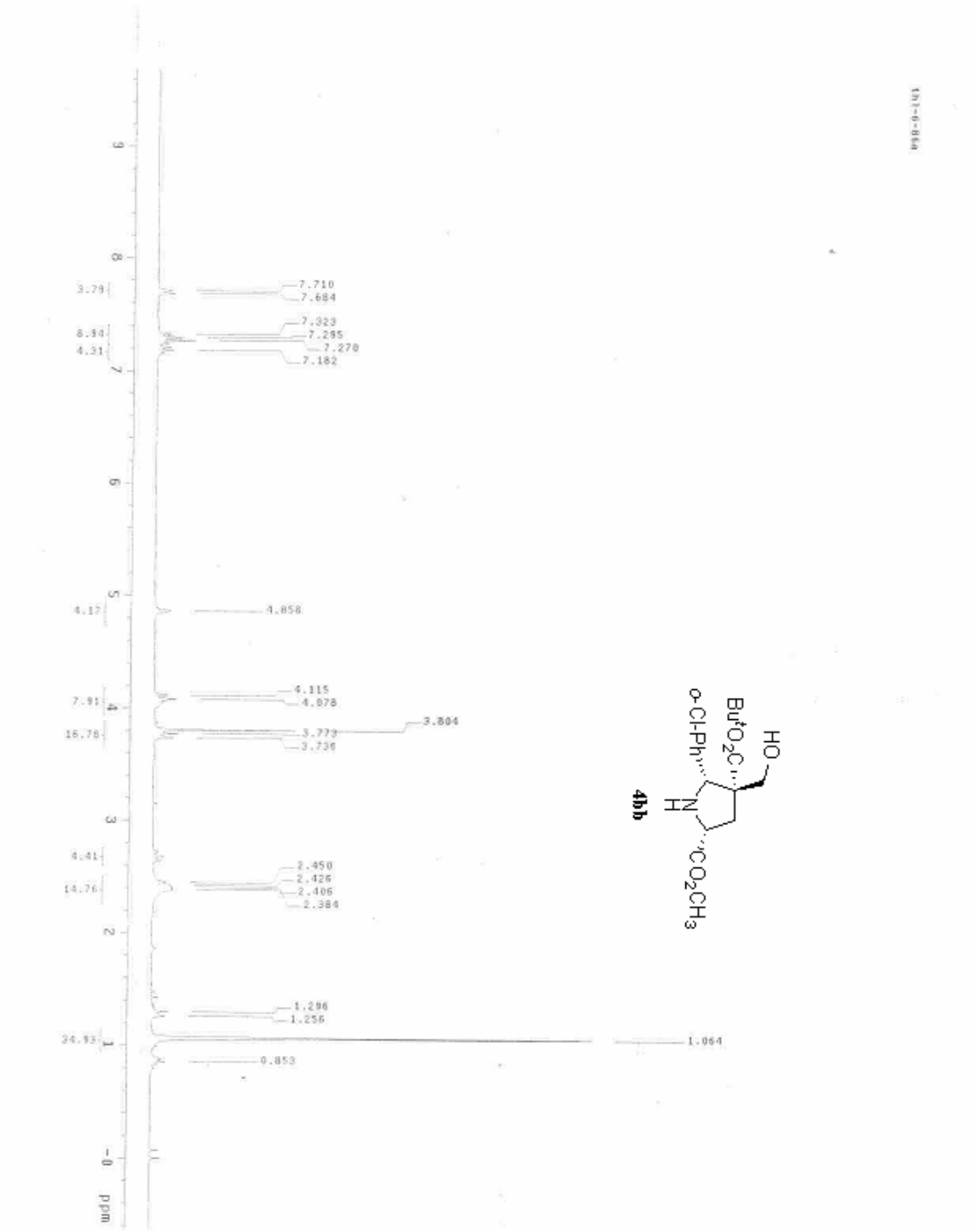
4ba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2.406
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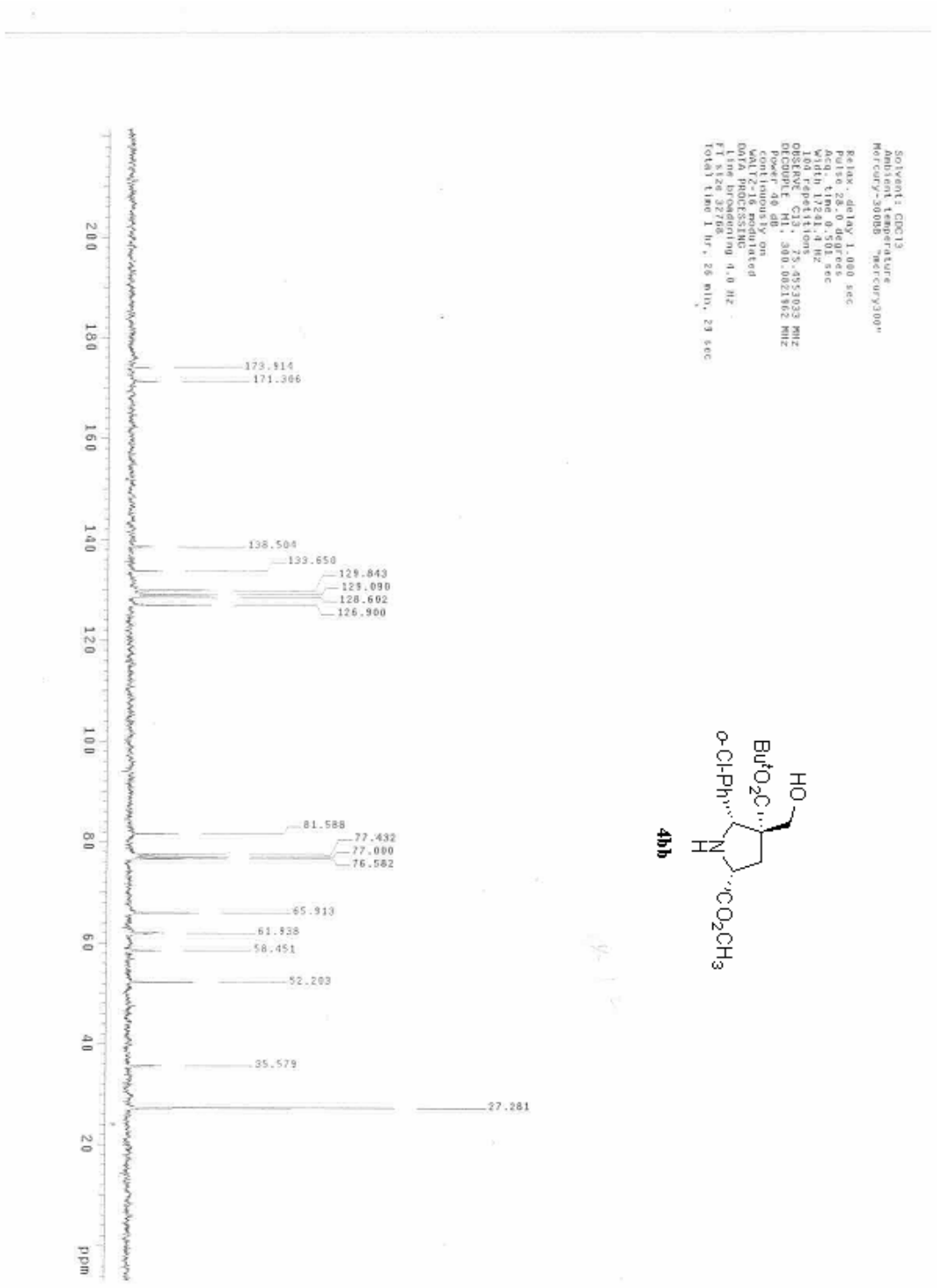
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o-Cl-Ph
N
H
CO$_2$CH$_3$
4bb
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77.000
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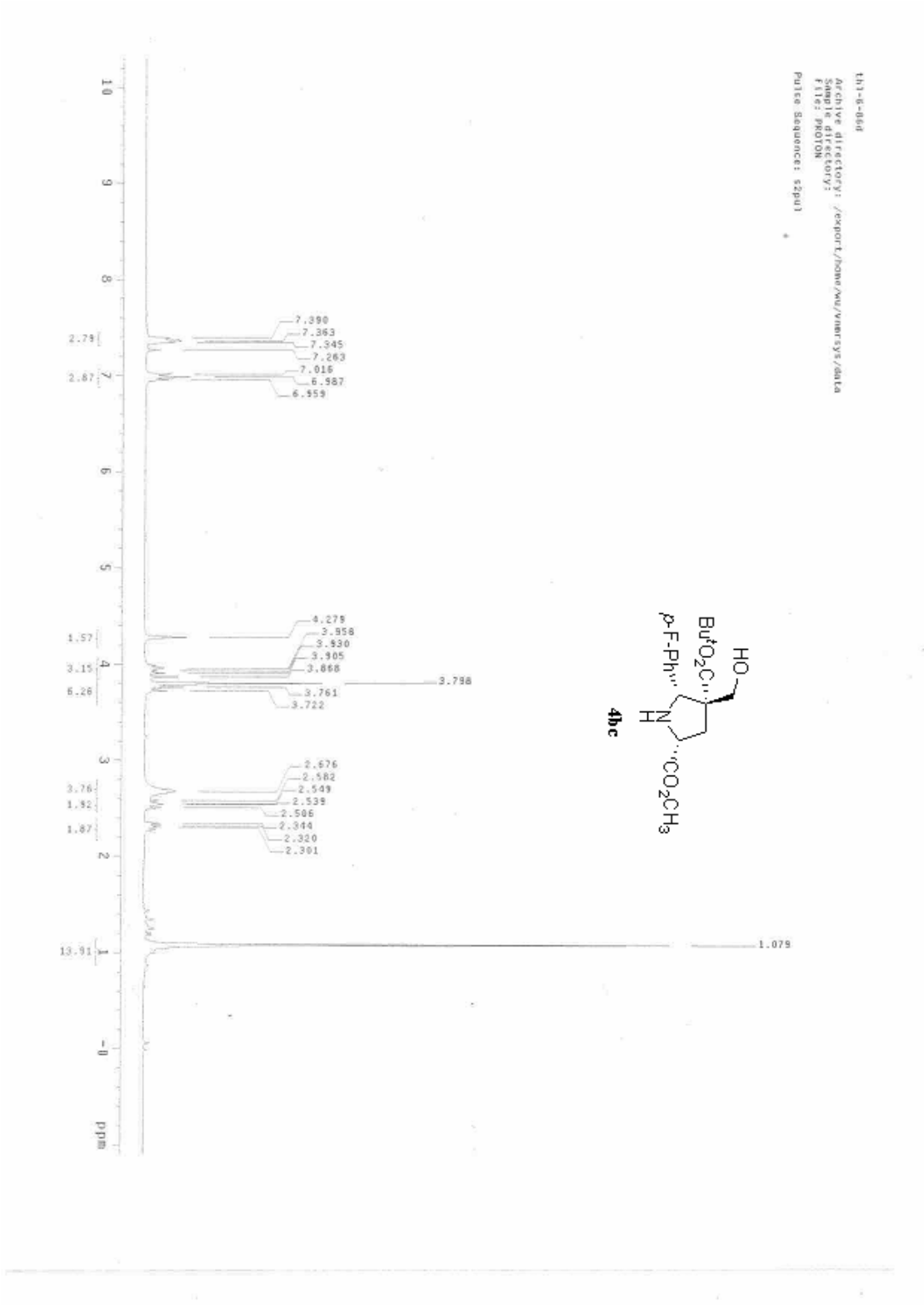
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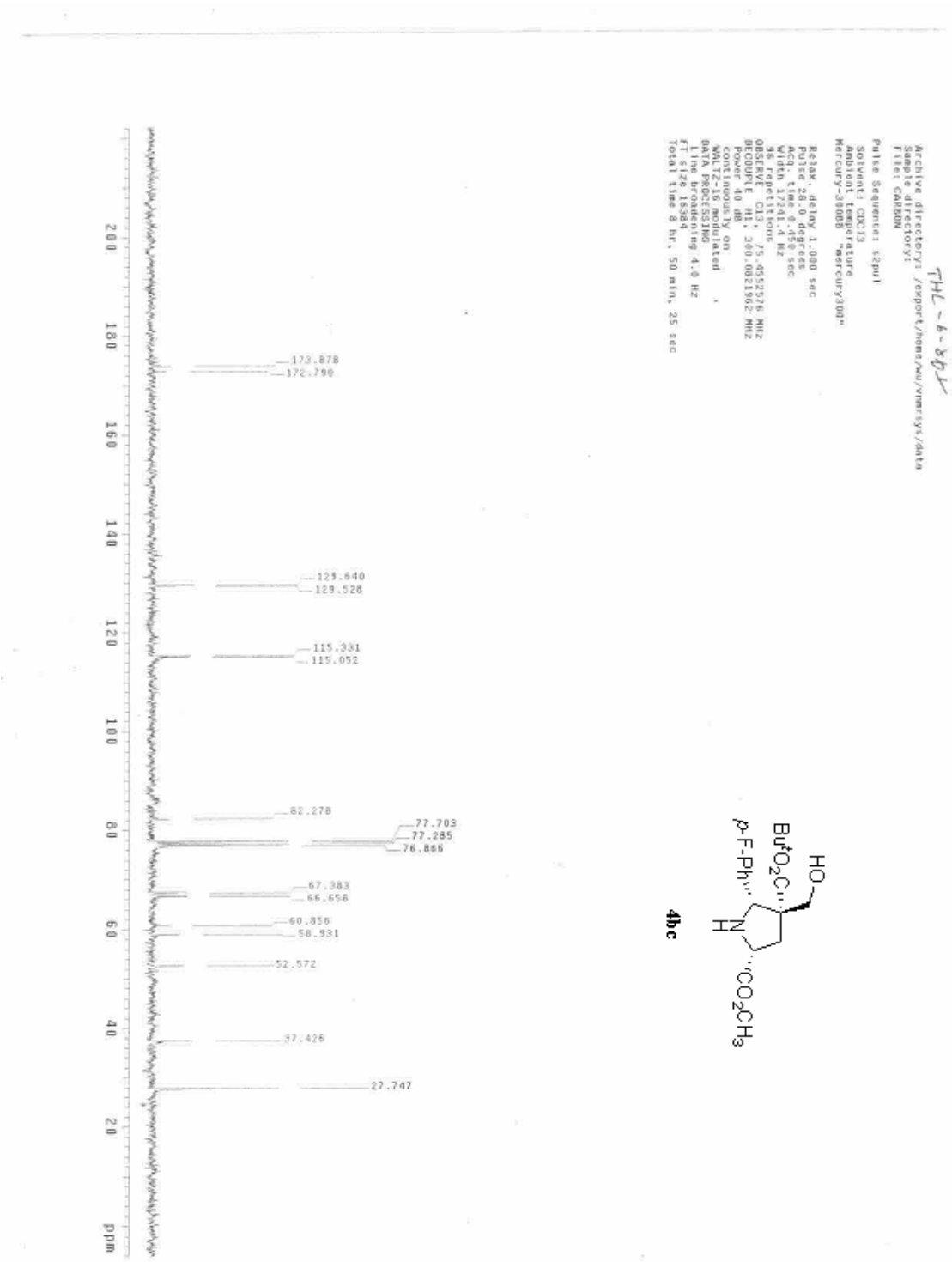
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p-F-Ph
N
H
CO2CH3
4bc
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66.658
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140
120
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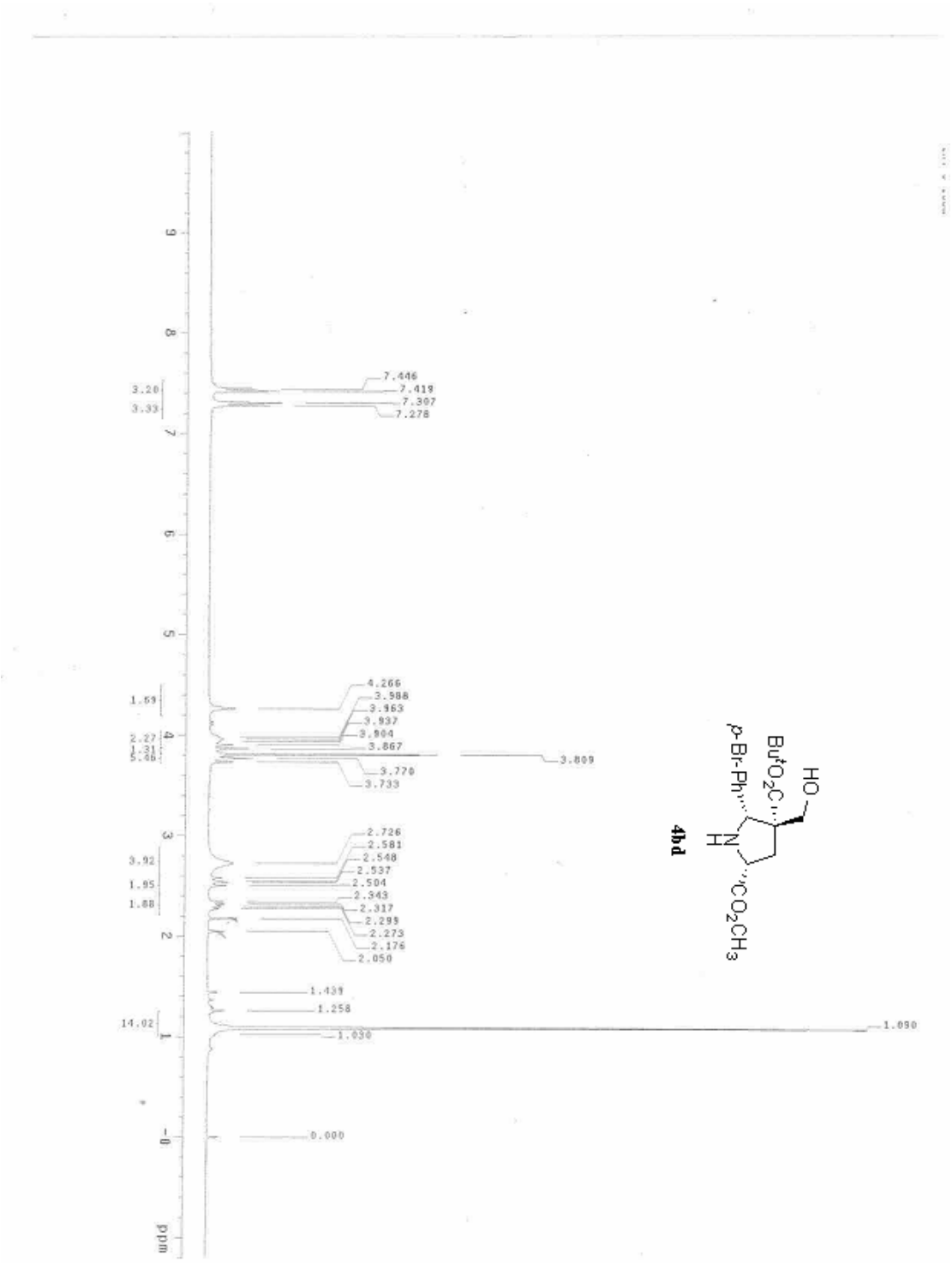
80
60
40
20
ppm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3.33
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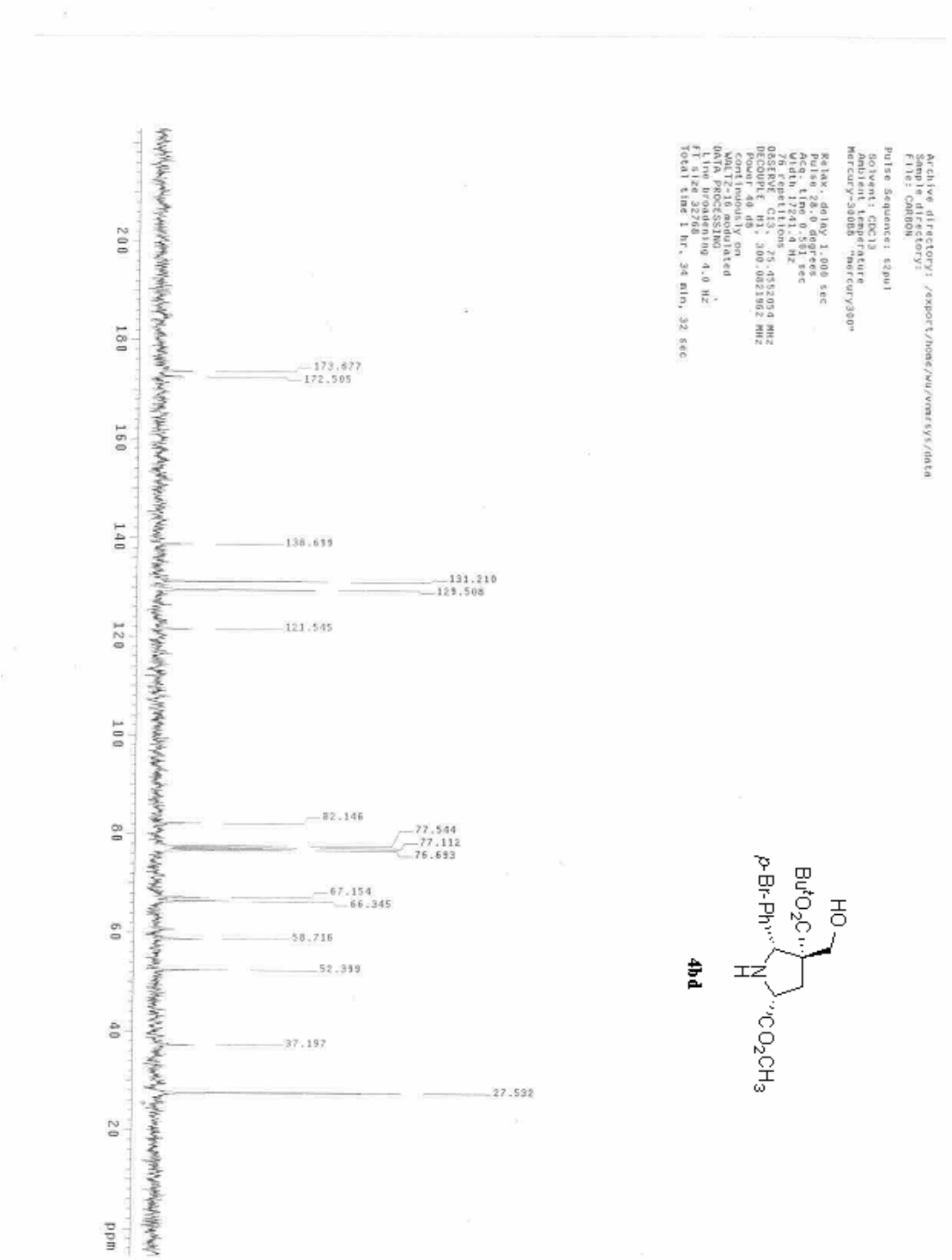
CO$_2$CH$_3$
4bd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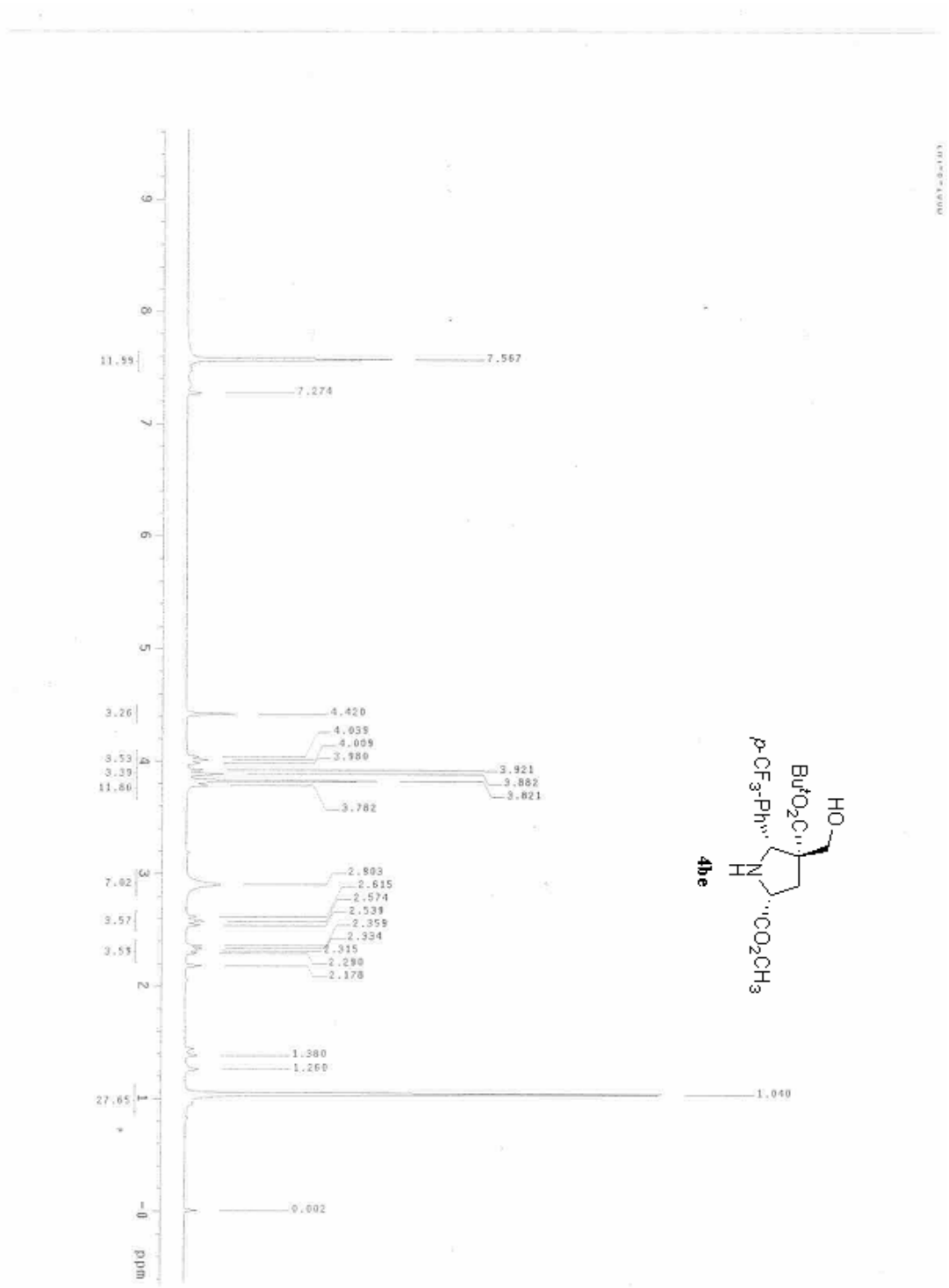
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H
CO$_2$CH$_3$
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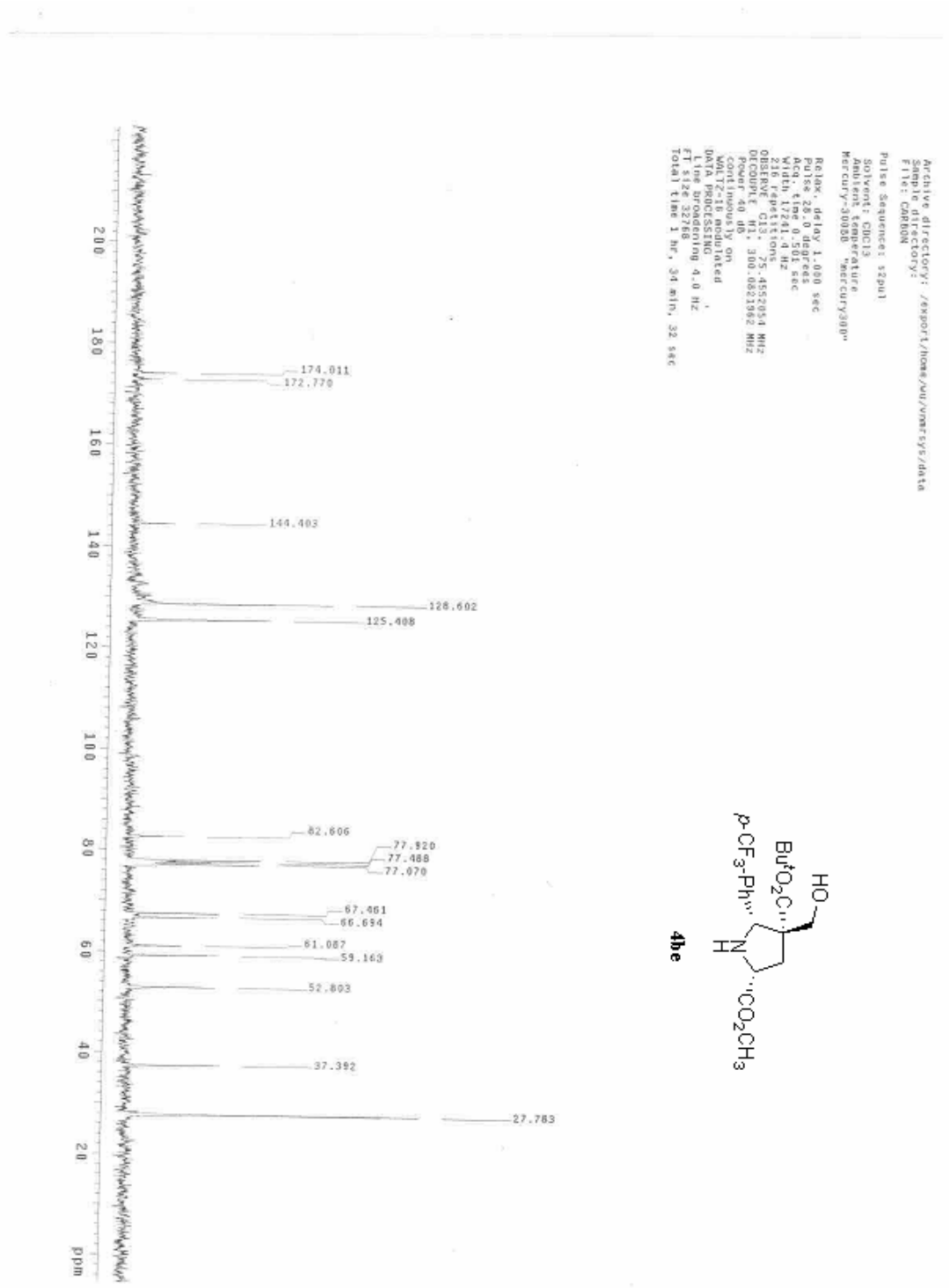
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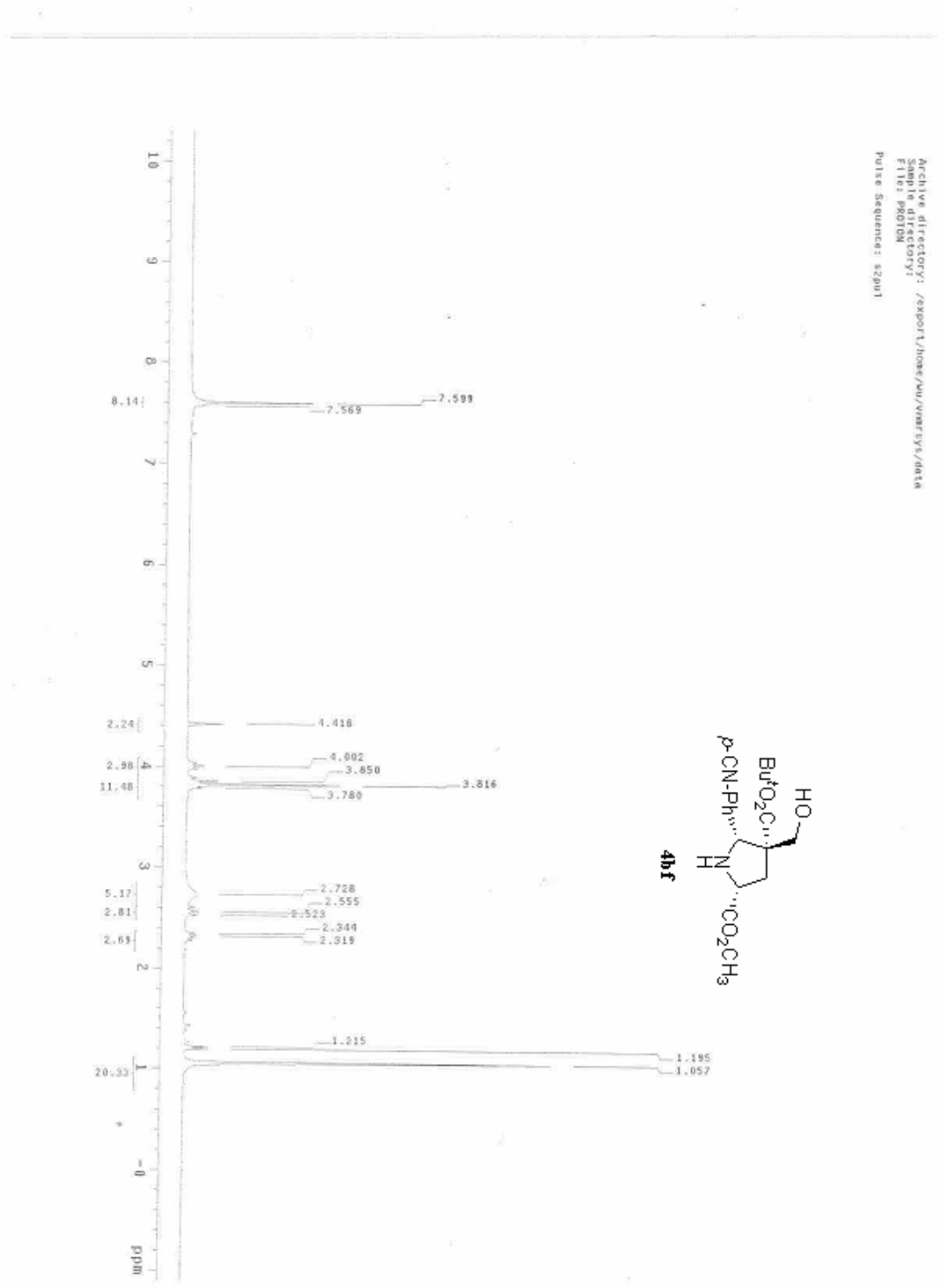
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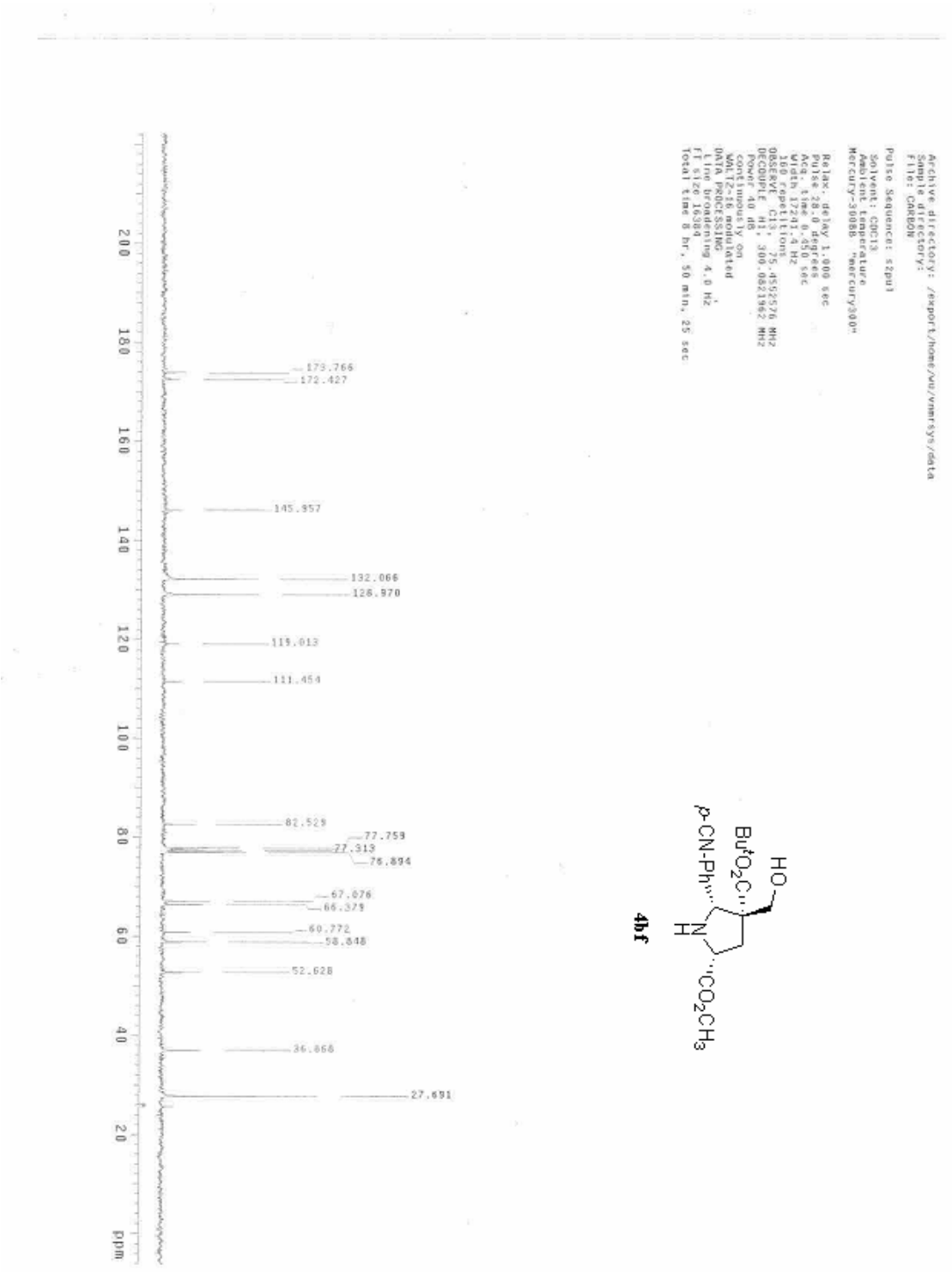
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Power 40 dB
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WALTZ-16 modulated
DATA PROCESSING
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128.970
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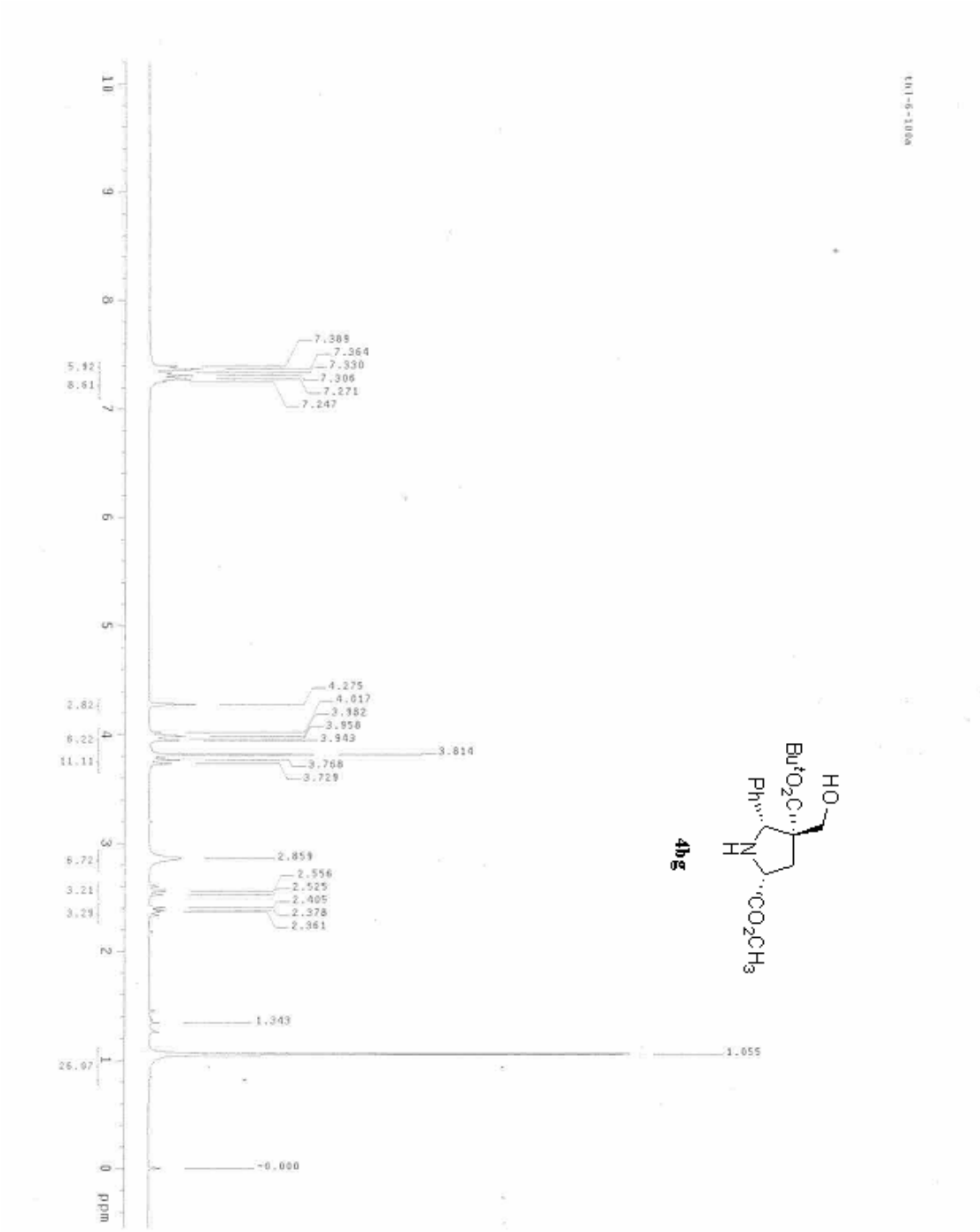
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2.556
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8.61
2.82
6.22
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Bu^{t}O$_2$C
Ph
N
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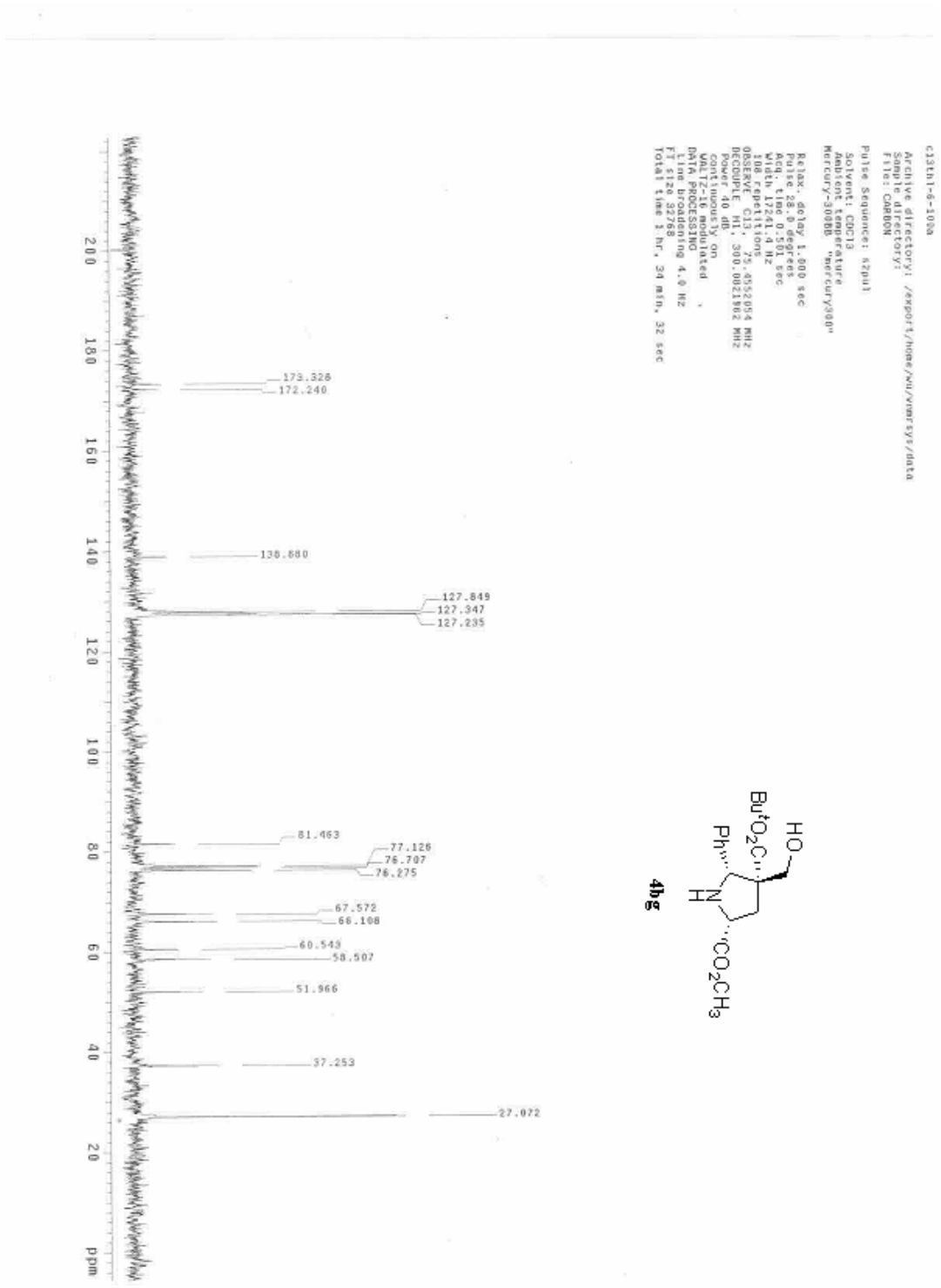
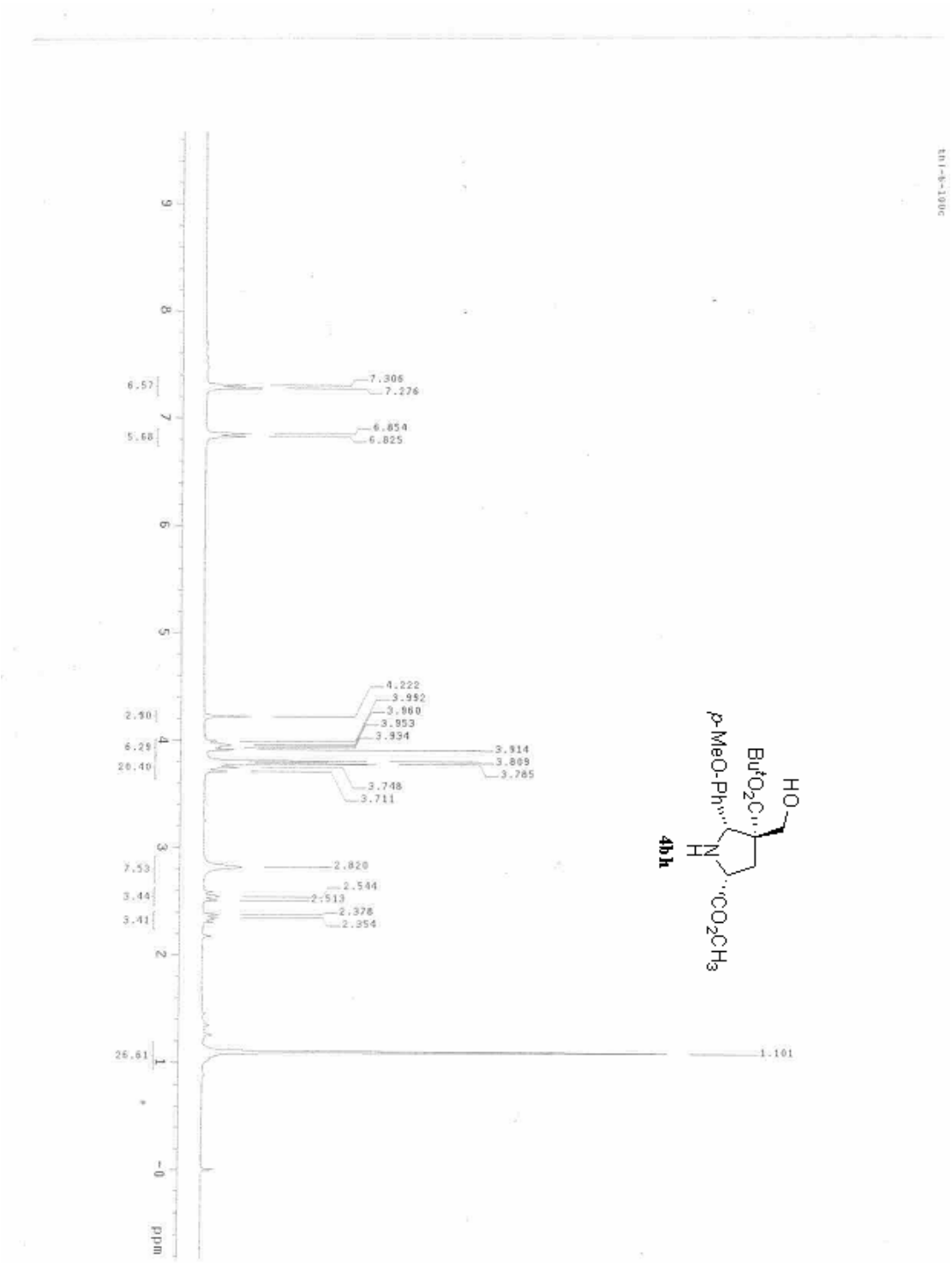
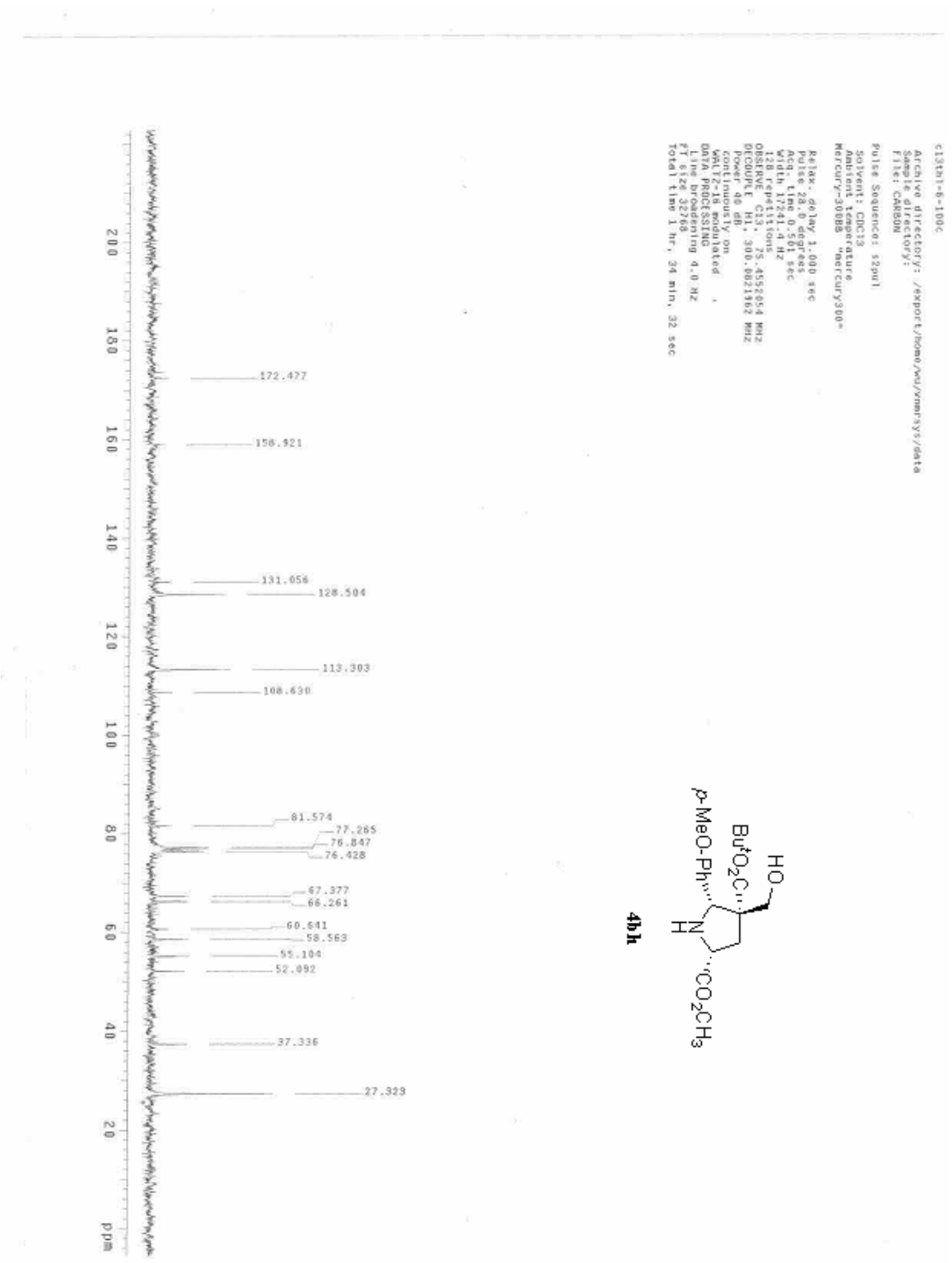
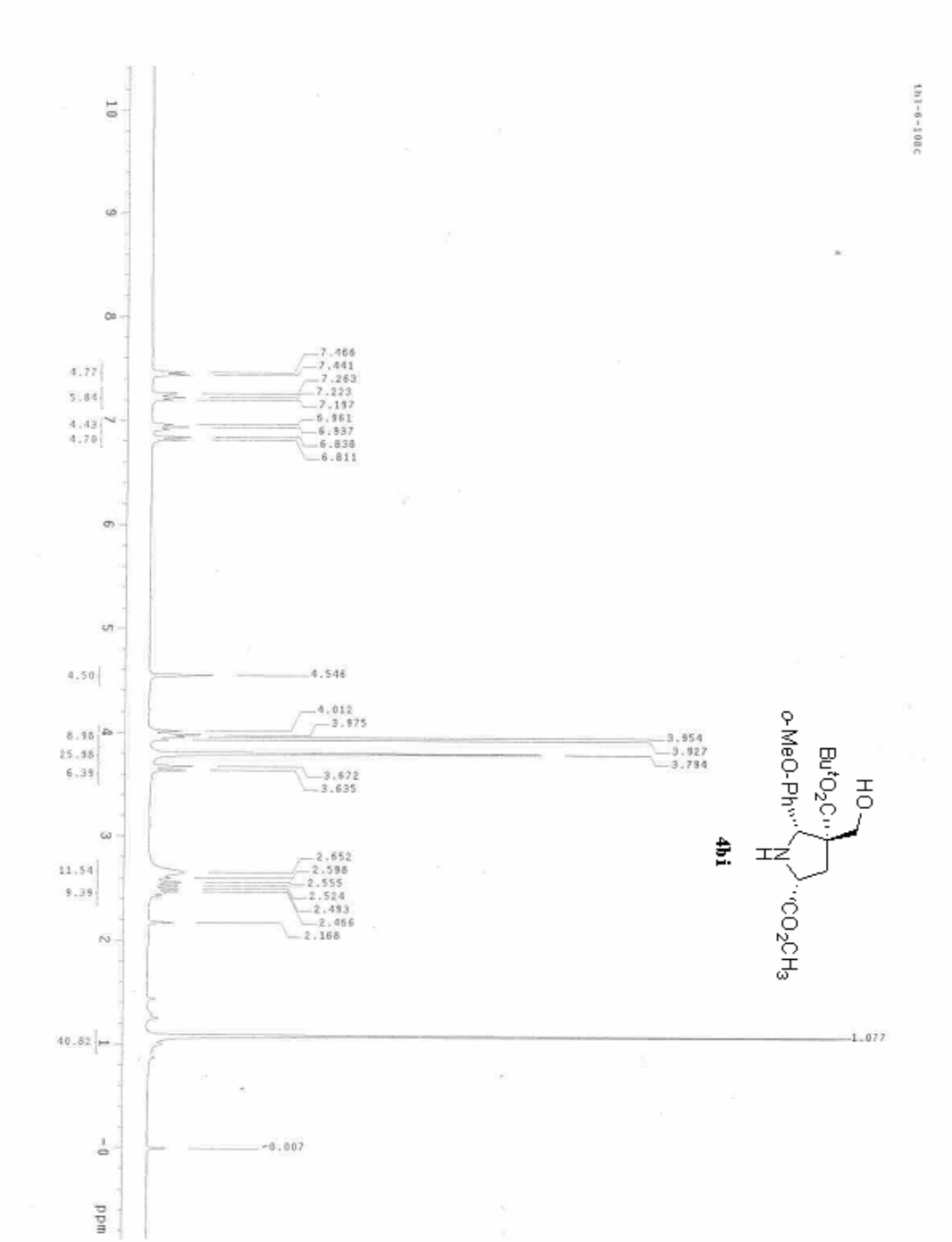
CO$_2$CH$_3$
4bg

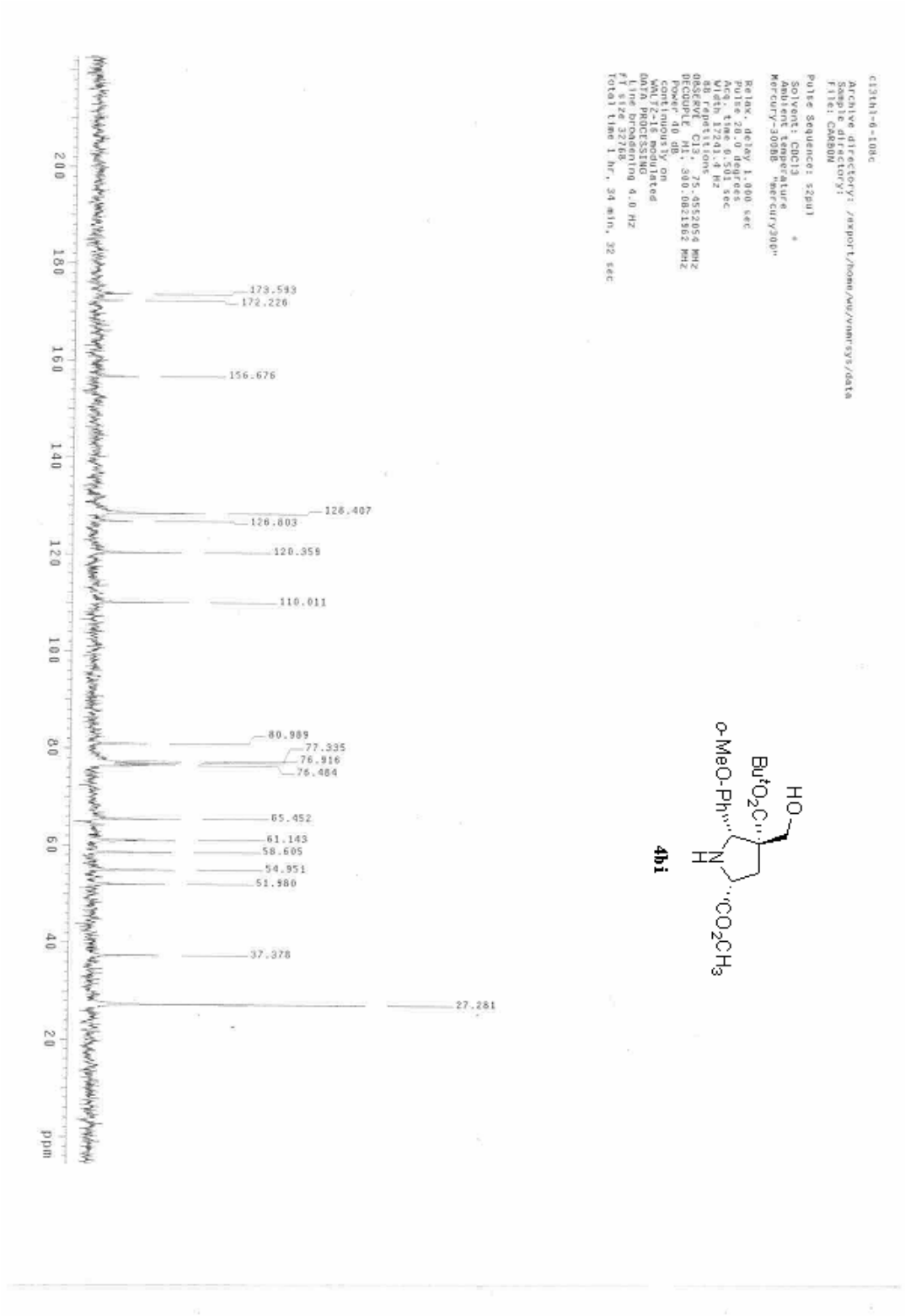

c13th1-6-100a
Archive directory: /export/home/wu/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Pulse 28.0 degrees
Acq. time 0.501 sec
Width 17241.4 Hz
108 repetitions
OBSERVE C13, 75.455204 MHz
DECOUPLE H1, 300.002162 MHz
Power 40 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 1 hr, 34 min, 32 sec
4bg
HO
BuᵗO2C
Ph
N
H
CO2CH3
173.328
172.240
138.880
127.849
127.347
127.235
81.463
77.126
76.707
76.275
67.572
66.108
60.543
58.507
51.966
37.253
27.072
200
180
160
140
120
100
80
60
40
20
ppm

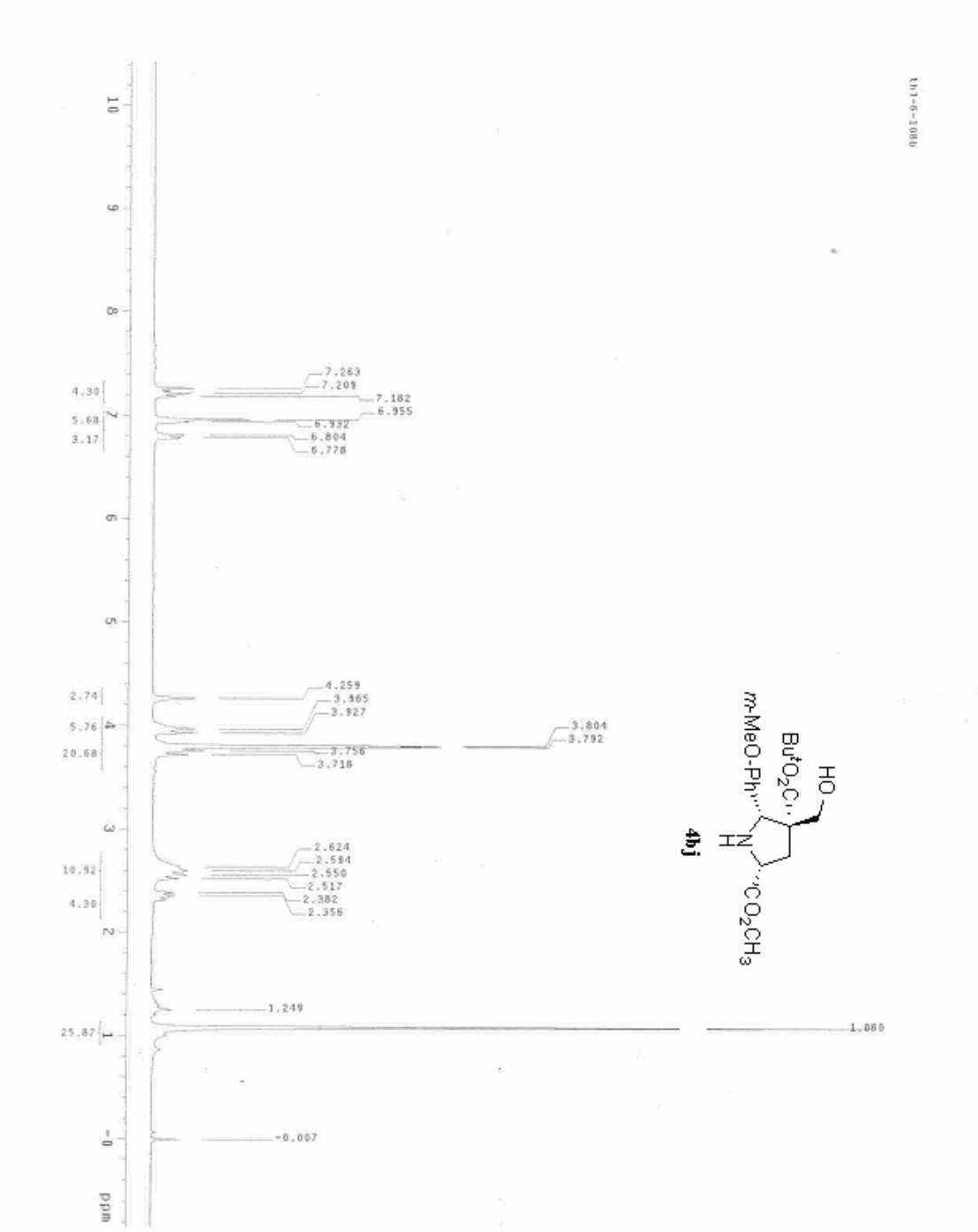

7.306
7.276
6.854
6.825
4.222
3.992
3.960
3.953
3.934
3.914
3.809
3.785
3.748
3.711
2.820
2.544
2.513
2.378
2.354
1.101
6.57
5.68
2.90
6.29
20.40
7.53
3.44
3.41
26.61
ppm
HO
Bu^tO_2C
p-MeO-Ph
N
H
CO_2CH_3
4bh

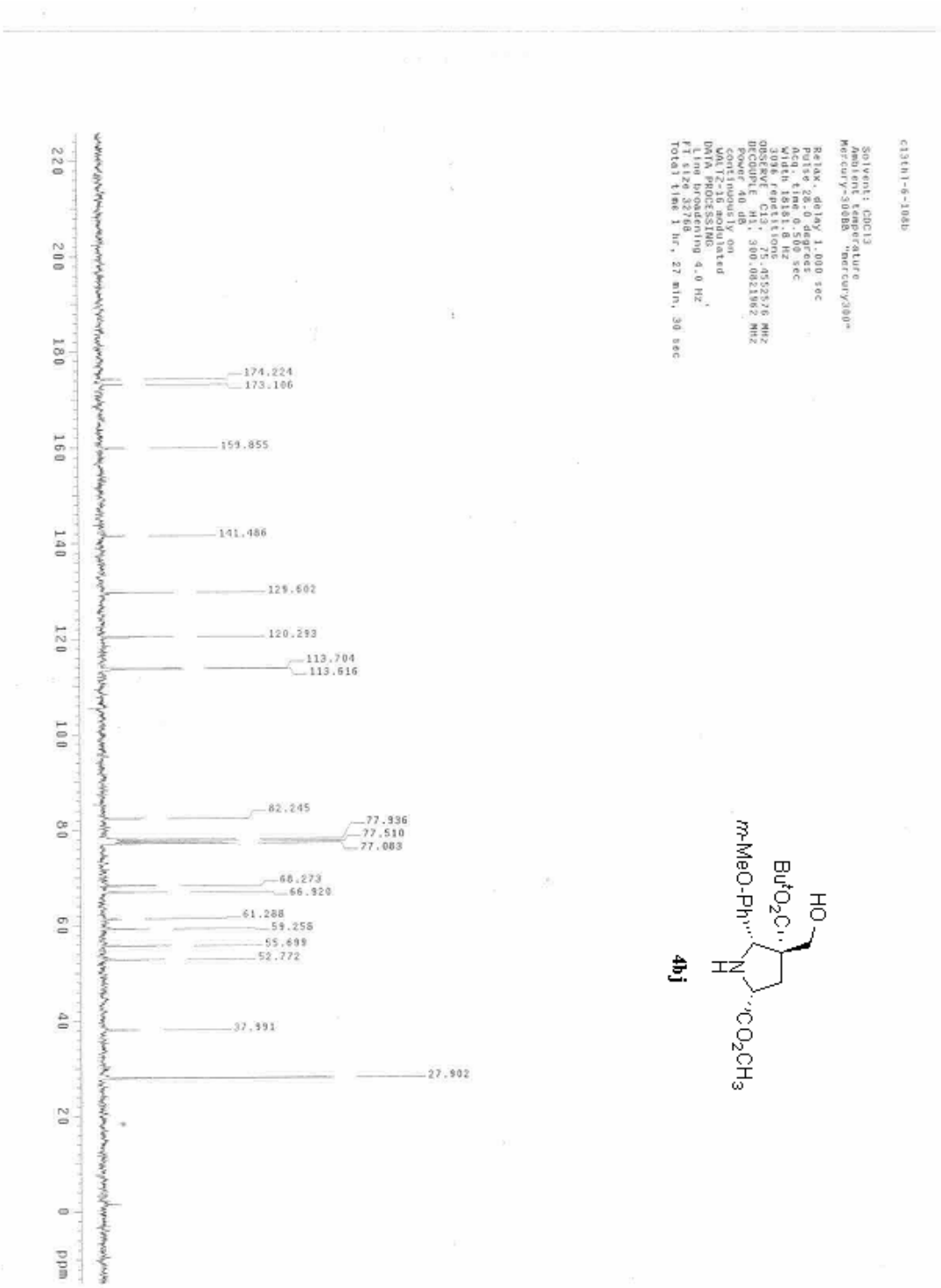

c13th1-6-100c
Archive directory: /export/home0/wu/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Pulse 10.0 degrees
Acq. time 1.000 sec
Width 17241.4 Hz
128 repetitions
OBSERVE C13, 75.4552054 MHz
DECOUPLE H1, 300.0021962 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 1 hr, 34 min, 32 sec
HO
Bu^{t}O$_2$C
p-MeO-Ph
N
H
CO$_2$CH$_3$
4bh
172.477
158.921
131.056
128.504
113.303
108.630
81.574
77.265
76.847
76.428
67.377
66.261
60.641
58.563
55.104
52.092
37.336
27.323
200
180
160
140
120
100
80
60
40
20
ppm

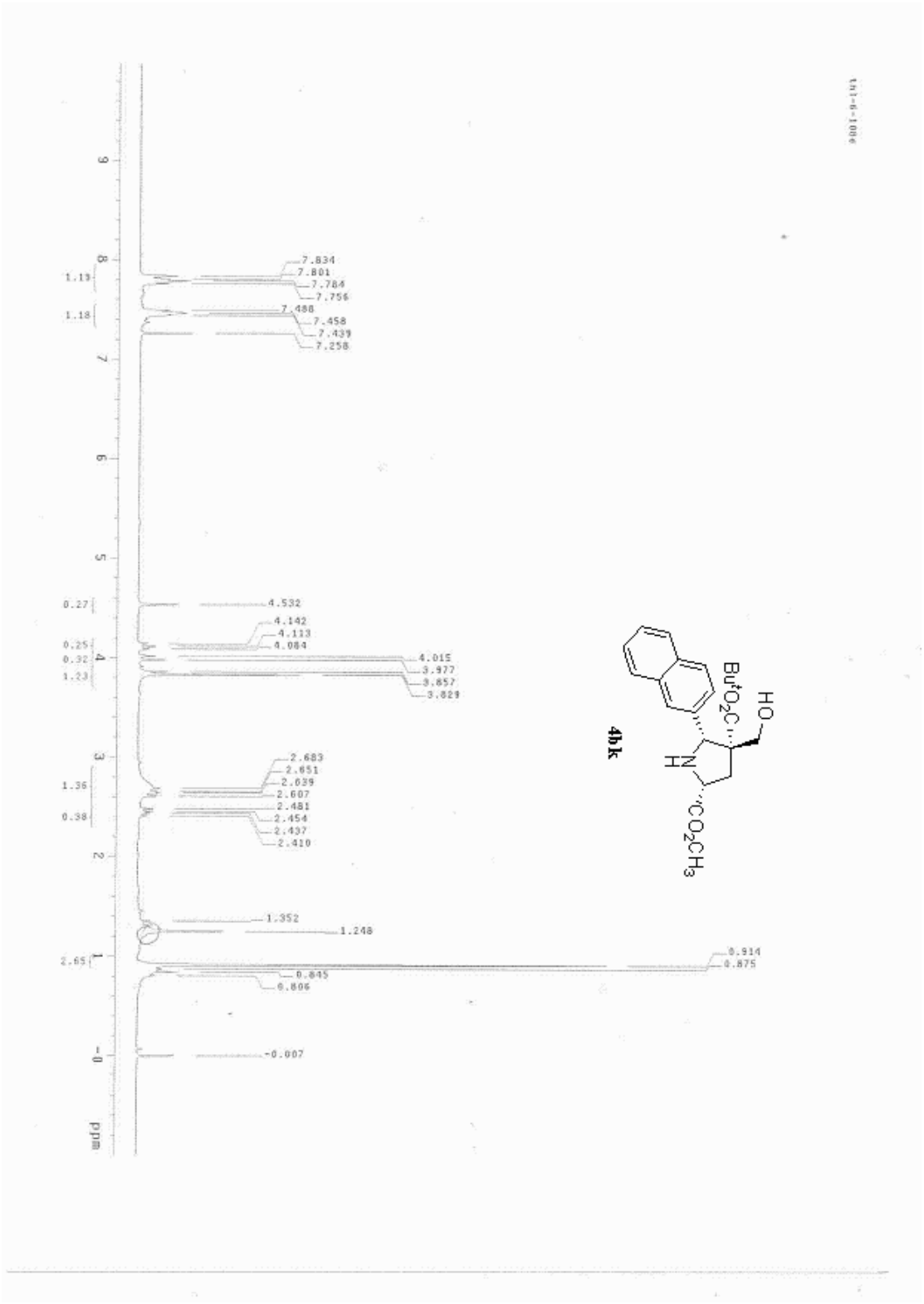

7.466
7.441
7.263
7.223
7.197
6.861
6.837
6.838
6.811
4.546
4.012
3.975
3.954
3.927
3.794
3.672
3.635
2.652
2.598
2.555
2.524
2.493
2.466
2.168
1.077
-0.007
4.77
5.84
4.43
4.70
4.50
8.98
25.98
6.39
11.54
9.39
40.82
ppm
HO
Bu^{t}O$_2$C
o-MeO-Ph
N
H
CO$_2$CH$_3$

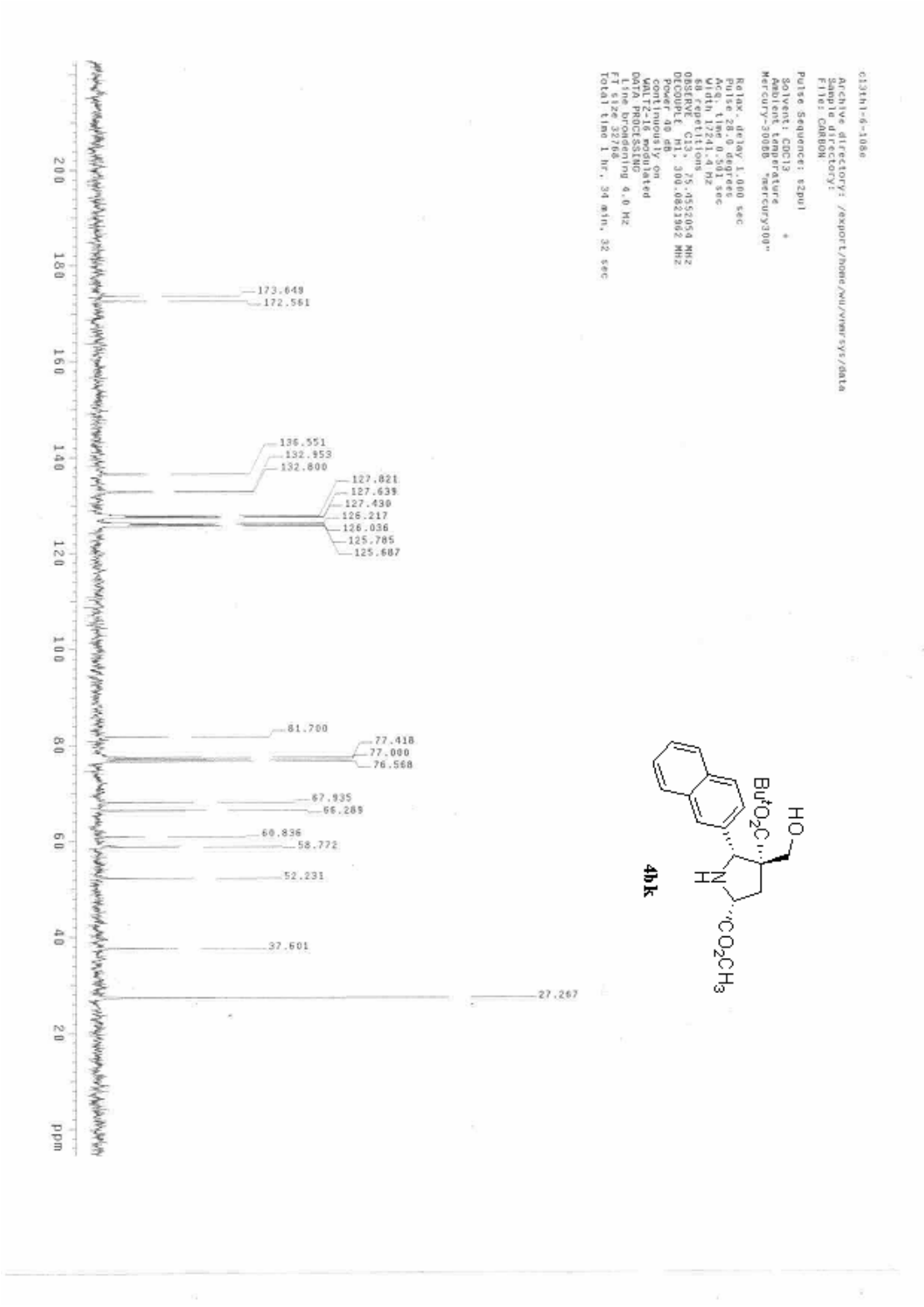
4bi

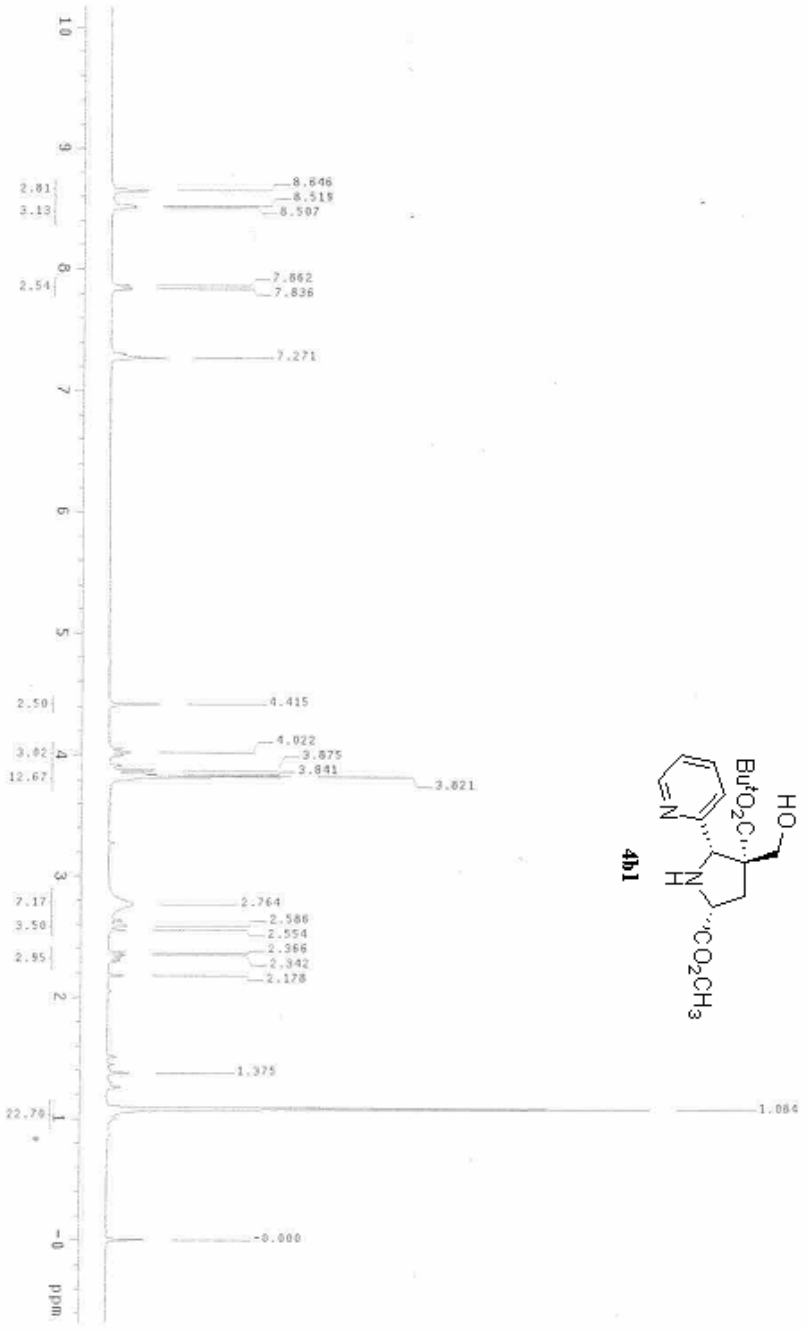

ci3th1-6-10dc
Archive directory: /export/home/ww/vnmrsys/data
Sample directory:
File: CA6B0N
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Pulse 20.0 degrees
Acq. time 0.501 sec
Width 12241.4 Hz
8 repetitions
OBSERVE C13, 75.4552056 MHz
DECOUPLE H1, 300.0021582 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 1 hr, 34 min, 32 sec
173.593
172.226
156.676
128.407
126.803
120.359
110.011
80.989
77.335
76.916
76.484
65.452
61.143
58.605
54.951
51.980
37.378
27.281
ppm
HO
Bu^{t}O$_2$C
o-MeO-Ph
N
H
CO$_2$CH$_3$
4bi


th1-6-108b
7.263
7.205
7.182
6.955
6.932
6.804
6.778
4.259
3.965
3.927
3.804
3.792
3.756
3.718
2.624
2.584
2.550
2.517
2.382
2.356
1.249
1.080
-0.007
4.30
5.68
3.17
2.74
5.76
20.68
10.92
4.30
25.87
ppm
HO
Bu^{t}O$_2$C
m-MeO-Ph
N
H
CO$_2$CH$_3$
4bj

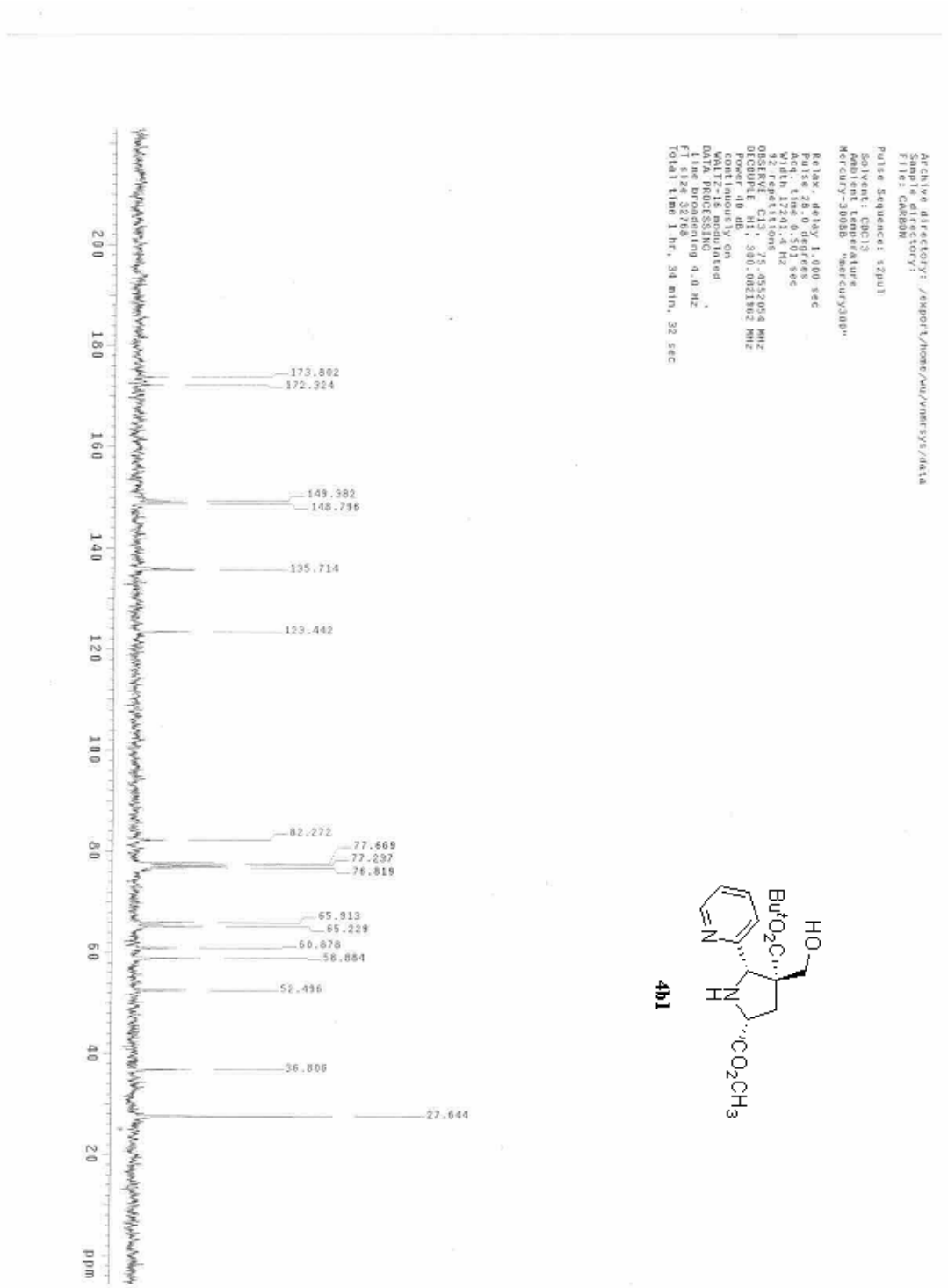

c13th1-6-108b
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Pulse 28.0 degrees
Acq. time 0.852 sec
Width 18868.8 Hz
3096 repetitions
OBSERVE C13, 75.4552576 MHz
DECOUPLE H1, 300.0021962 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 1 hr, 27 min, 30 sec
174.224
173.106
159.855
141.486
129.602
120.293
113.704
113.616
82.245
77.936
77.510
77.083
68.273
66.920
61.288
59.256
55.699
52.772
37.991
27.902
ppm
HO
Bu^{t}O$_2$C
m-MeO-Ph
N
H
CO$_2$CH$_3$
4bj

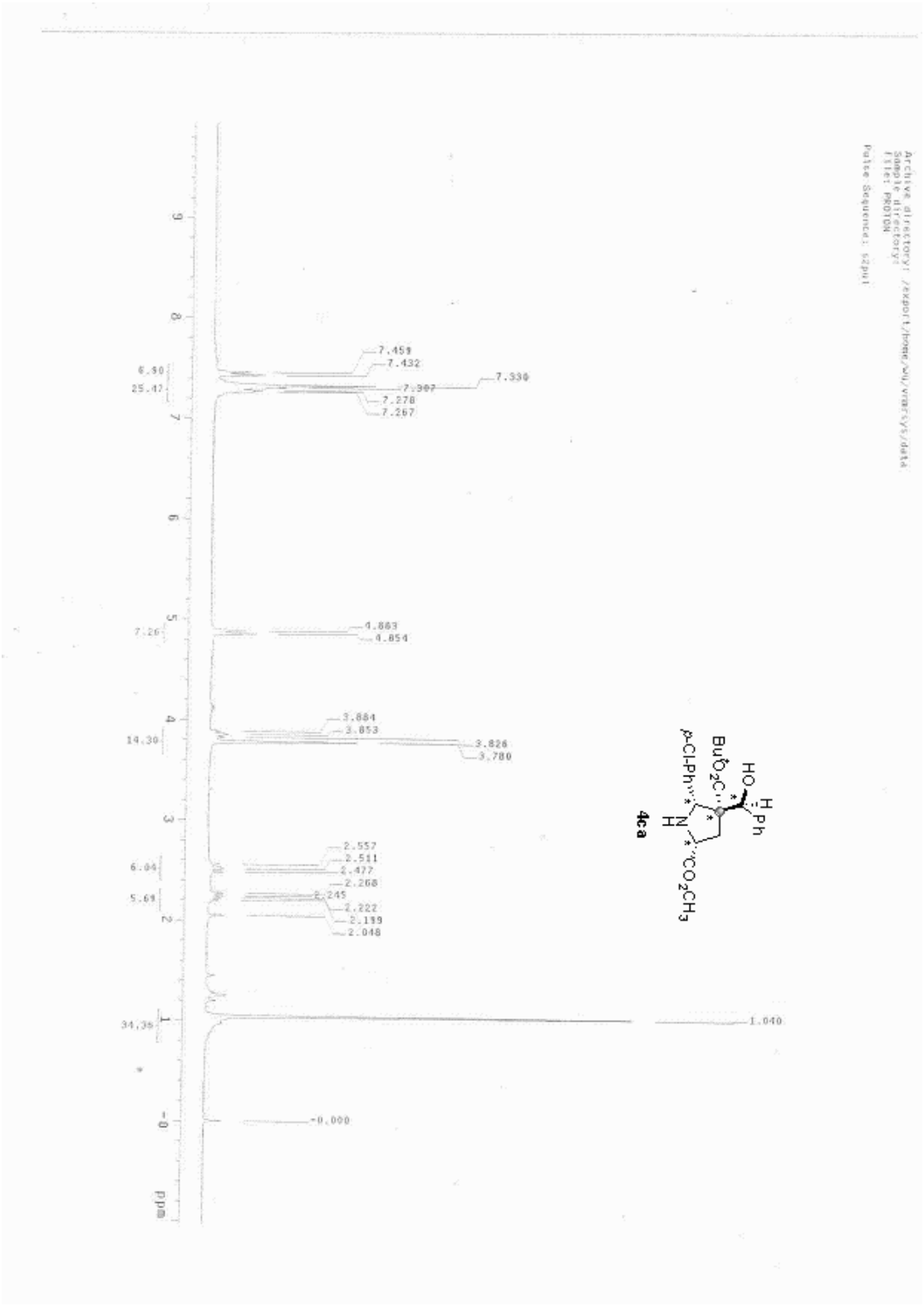

7.834
7.801
7.784
7.756
7.488
7.458
7.439
7.258
4.532
4.142
4.113
4.084
4.015
3.977
3.857
3.829
2.683
2.651
2.639
2.607
2.481
2.454
2.437
2.410
1.352
1.248
0.914
0.875
0.845
0.806
-0.007
1.13
1.18
0.27
0.25
0.32
1.23
1.36
0.38
2.65
ppm
HO
Bu^tO_2C
N
H
CO_2CH_3
4bk

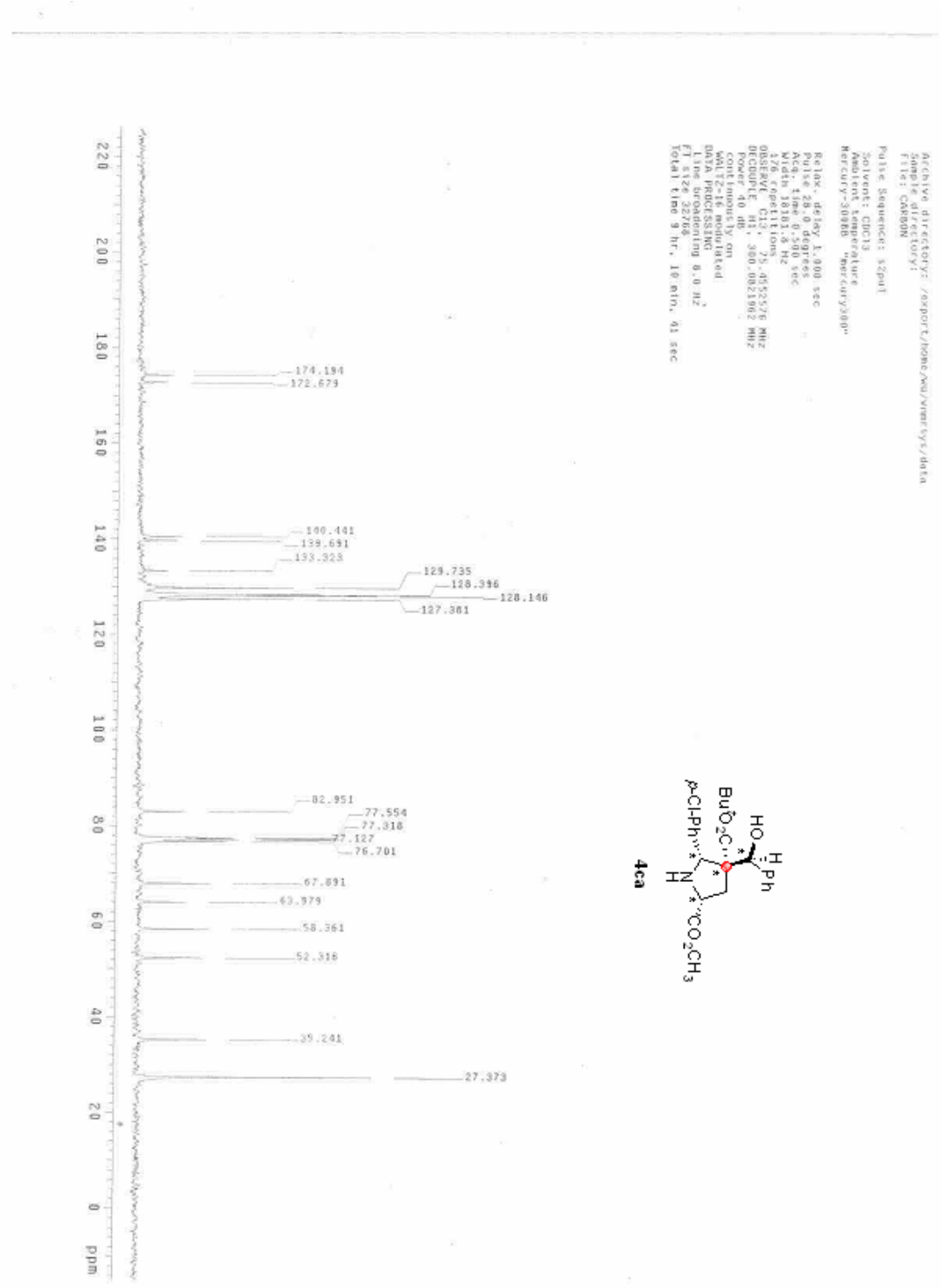

c13thl-6-1a8a
Archive directory: /export/home/wu/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Pulse 28.0 degrees
Acq. time 0.501 sec
Width 12741.4 Hz
8 repetitions
OBSERVE C13, 75.455054 MHz
DECOUPLE H1, 300.0821902 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 1 hr, 34 min, 32 sec
173.649
172.561
136.551
132.953
132.800
127.821
127.639
127.430
126.217
126.036
125.785
125.687
81.700
77.418
77.000
76.568
67.935
66.289
60.836
58.772
52.231
37.601
27.267
200
180
160
140
120
100
80
60
40
20
ppm
HO
ButO2C
N
H
CO2CH3
4bk

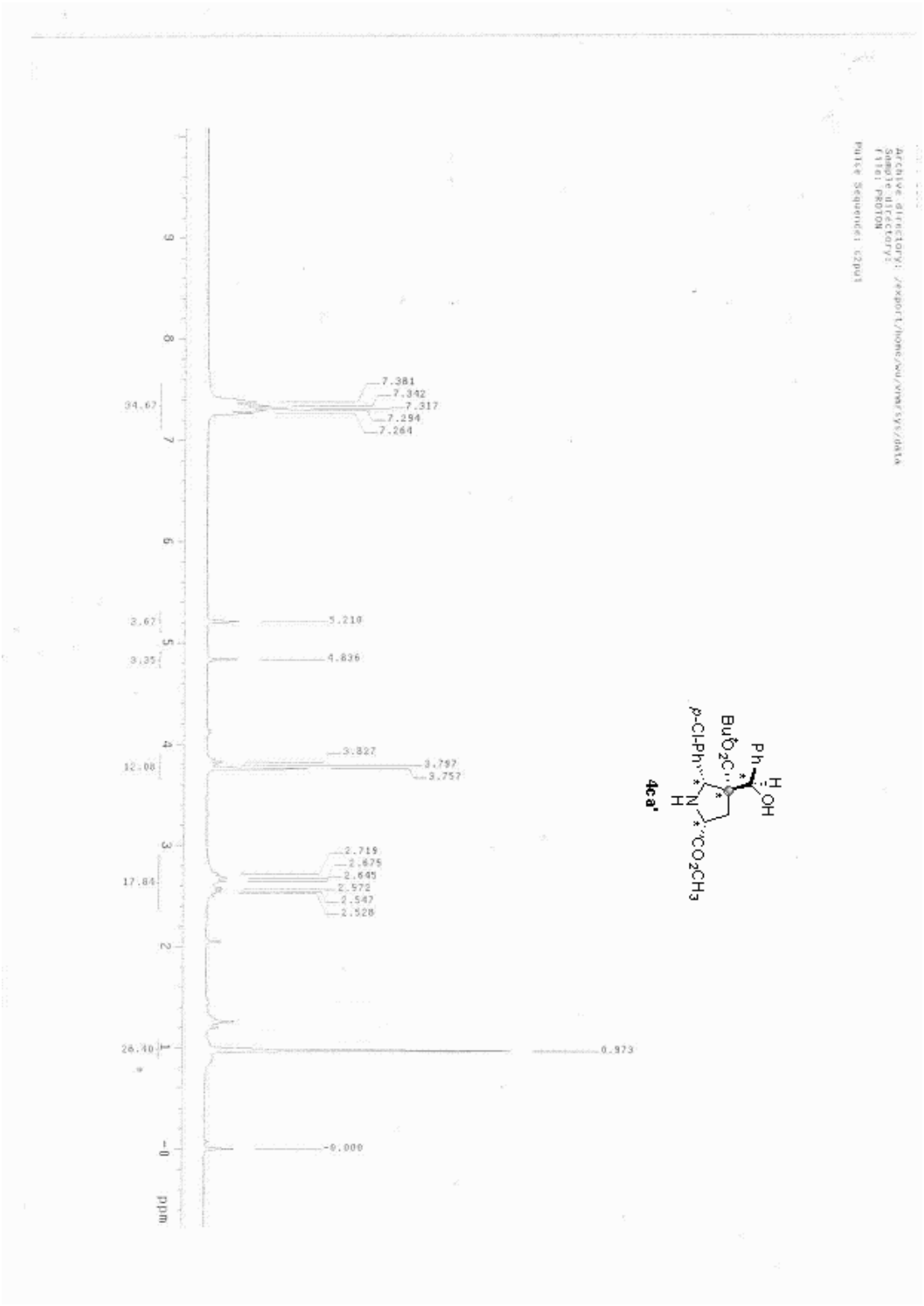

8.646
8.519
8.507
7.862
7.836
7.271
4.415
4.022
3.875
3.841
3.821
2.764
2.586
2.554
2.366
2.342
2.178
1.375
1.084
-0.000
ppm
HO
Bu^tO_2C
CO_2CH_3
N
H

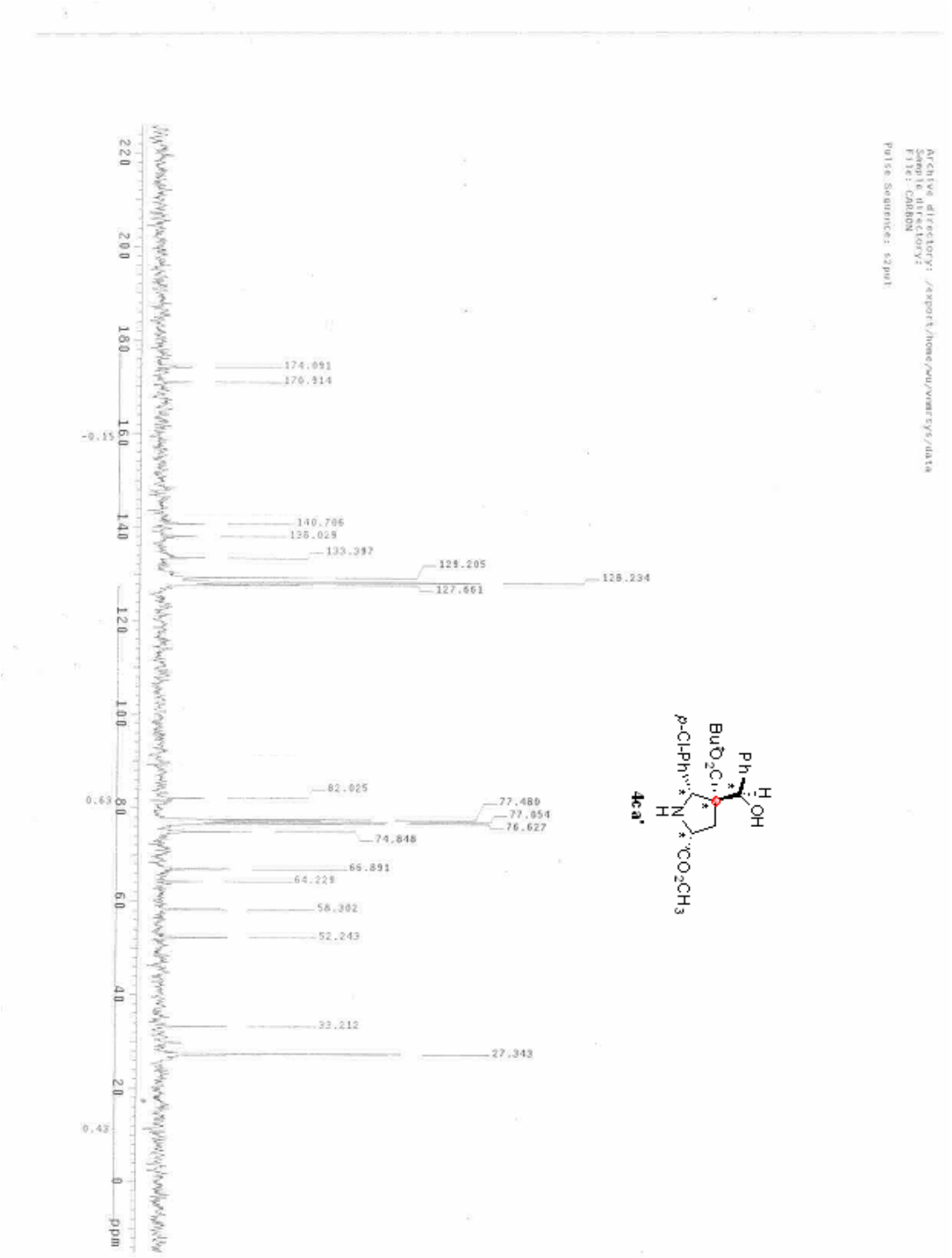
4b1

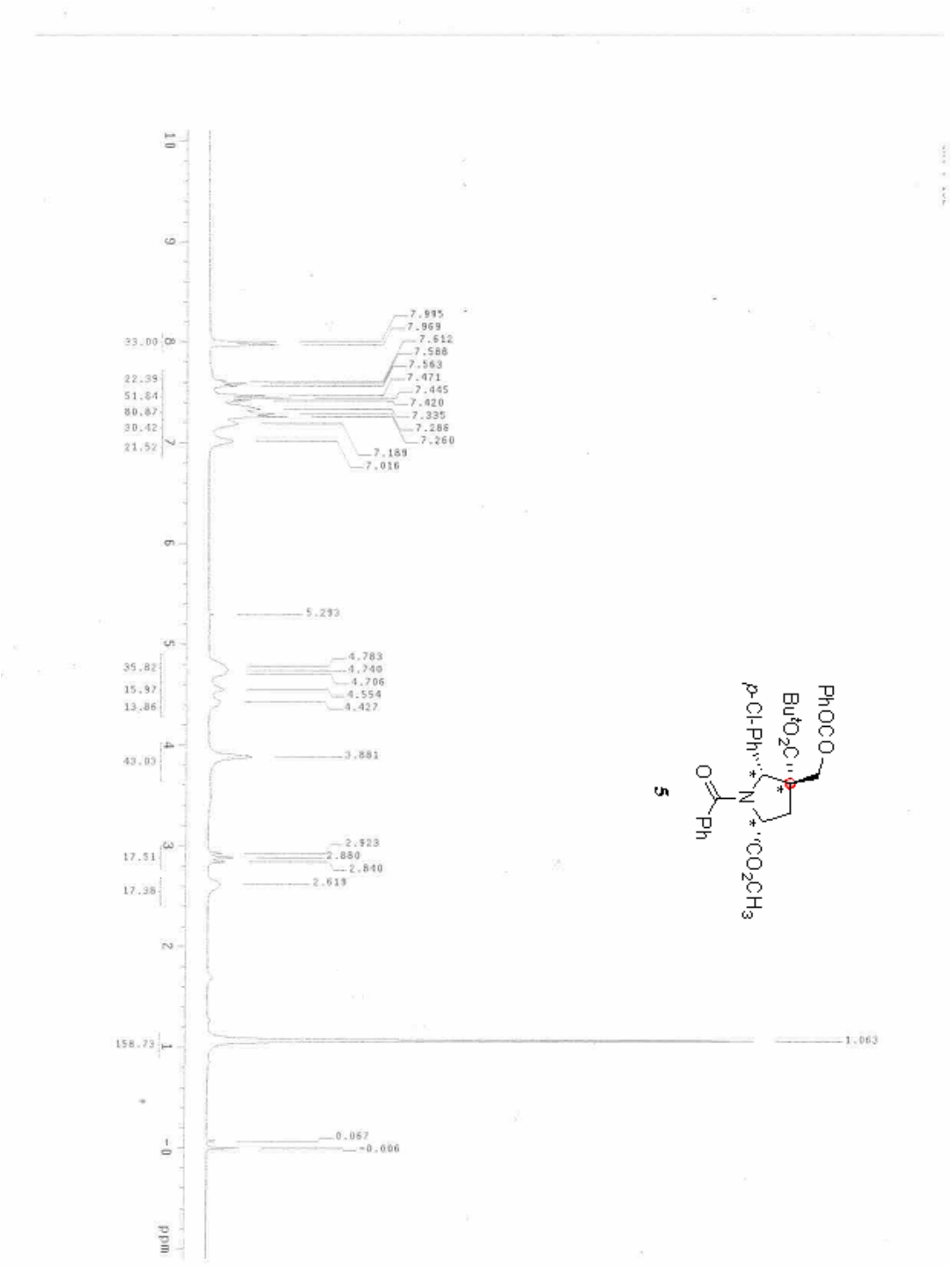

Archive directory: /export/home/wu/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Pulse 28.0 degrees
Acq. time 0.503 sec
Width 22141.4 Hz
32768 repetitions
OBSERVE C13, 75.4552058 MHz
DECOUPLE H1, 300.0021902 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 1 hr, 34 min, 32 sec
173.802
172.324
149.382
148.796
135.714
123.442
82.272
77.669
77.237
76.819
65.913
65.229
60.878
58.884
52.496
36.806
27.644
ppm
HO
Bu^{t}O$_2$C
N
H
CO$_2$CH$_3$
4b1

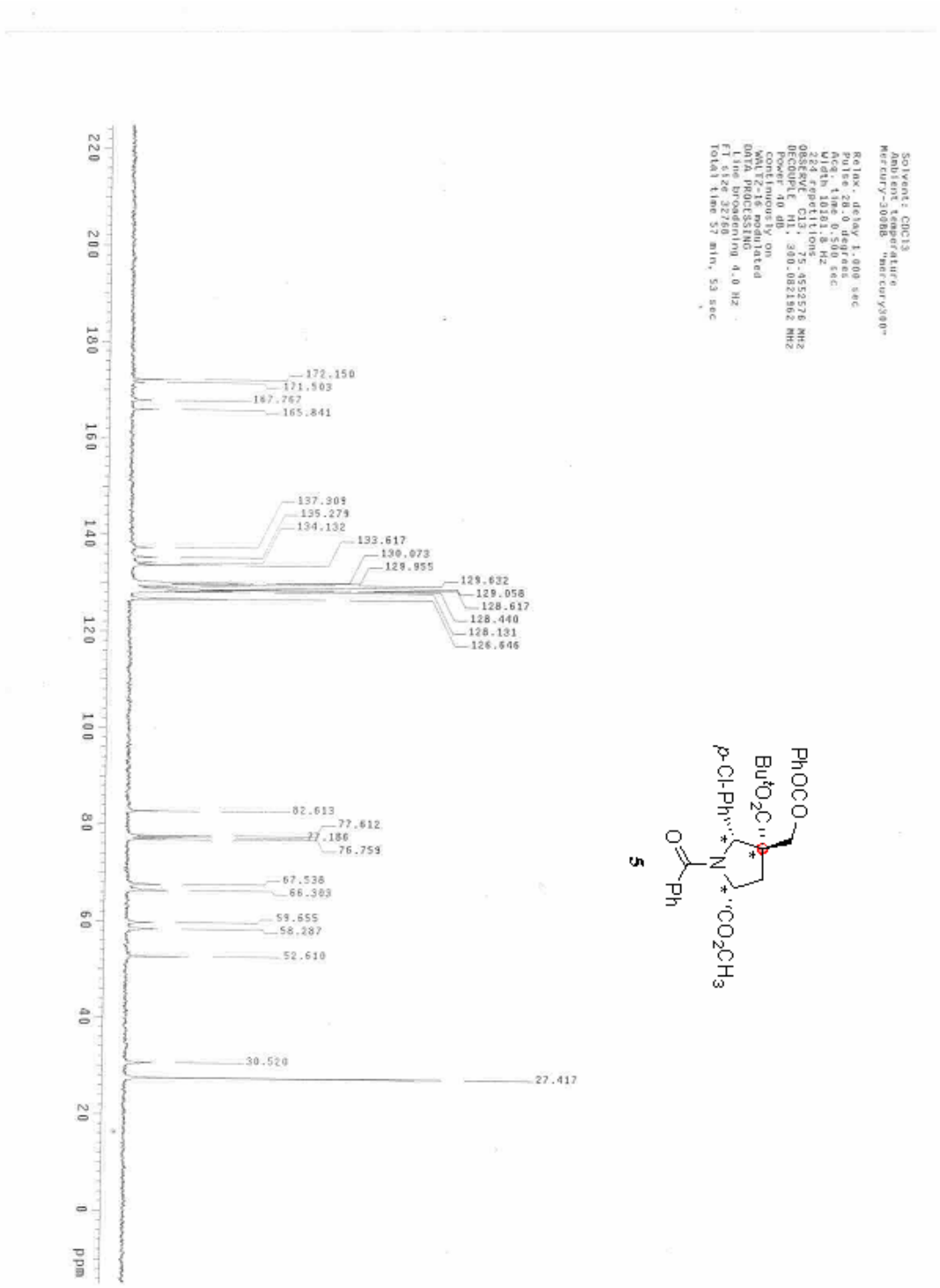

7.459
7.432
7.339
7.307
7.278
7.267
6.50
25.47
4.863
4.854
7.26
3.884
3.853
3.826
3.780
14.30
2.557
2.511
2.477
2.268
2.245
2.222
2.199
2.048
6.04
5.69
1.040
34.35
0.000
ppm
4ca


174.194
172.679
140.441
139.691
133.323
129.735
128.396
128.146
127.361
82.951
77.554
77.318
77.127
76.701
67.891
63.979
58.361
52.318
39.241
27.373
ppm
4ca


7.381
7.342
7.317
7.294
7.264
5.210
4.836
3.827
3.797
3.757
2.719
2.675
2.645
2.572
2.547
2.528
0.973
-0.000
34.67
2.67
3.35
12.08
17.84
28.40
ppm
Ph
OH
BuO2C
p-Cl-Ph
N
H
CO2CH3
4ca'


174.091
170.914
140.706
138.029
133.397
129.205
128.234
127.661
82.025
77.480
77.054
76.627
74.848
66.891
64.229
58.302
52.243
33.212
27.343
ppm
4ca'


7.995
7.969
7.612
7.588
7.563
7.471
7.445
7.420
7.335
7.286
7.260
7.189
7.016
5.293
4.783
4.740
4.706
4.554
4.427
3.881
2.923
2.880
2.840
2.619
1.063
0.067
-0.006
33.00
22.39
51.84
80.87
30.42
21.52
35.82
15.97
13.86
43.03
17.51
17.38
158.73
ppm
PhOCO
Bu^{t}O$_2$C
p-Cl-Ph
N
Ph
O
CO$_2$CH$_3$
5


Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Pulse 28.0 degrees
Acq. time 0.500 sec
Width 10161.8 Hz
224 repetitions
OBSERVE C13, 75.4552576 MHz
DECOUPLE H1, 300.0821562 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 57 min, 53 sec
172.150
171.503
167.767
165.841
137.309
135.279
134.132
133.617
130.073
129.955
129.632
129.058
128.617
128.440
128.131
126.646
82.613
77.612
77.186
76.759
67.538
66.383
59.655
58.287
52.610
30.520
27.417
220
200
180
160
140
120
100
80
60
40
20
0
ppm
PhOCO
Bu^{t}O$_2$C
p-Cl-Ph
N
CO$_2$CH$_3$
O
Ph
5

```
( File D:\LC\THL\DATE\THL-6-120\THL-6-120 2010-12-03 19-09-51\021-0201.D
ile Name: THL-6-120

================================================================
Acq. Operator   : THL                          Seq. Line :   2
Acq. Instrument : Instrument 1                  Location : Vial 21
Injection Date  : 12/3/2010 7:22:11 PM             Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-120\THL-6-120 2010-12-03 19-09-51\ASH-90-10-05ML-
                  210NM-45MIN.M
Last changed    : 12/3/2010 8:01:59 PM by THL
                  (modified after loading)
Analysis Method : D:\LC\THL\DATE\THL-6-120\THL-6-120 2010-12-03 19-09-51\021-0201.D\DA.M (
                  ASH-90-10-05ML-210NM-45MIN.M)
Last changed    : 2/20/2011 2:38:46 PM by LTL
                  (modified after loading)
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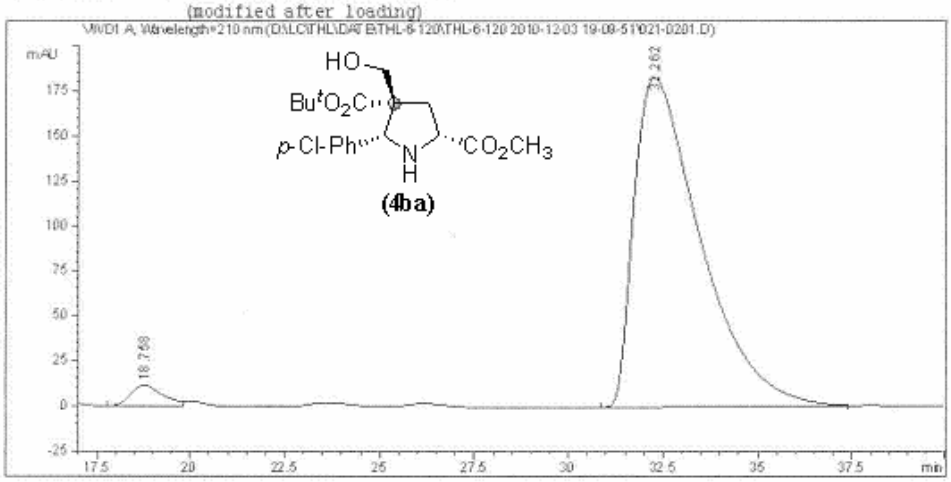



```
================================================================
                      Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  18.758 VV    0.8662  684.00403   11.56460   2.9826
   2  32.262 BB    1.7925 2.22492e4   183.01462  97.0174

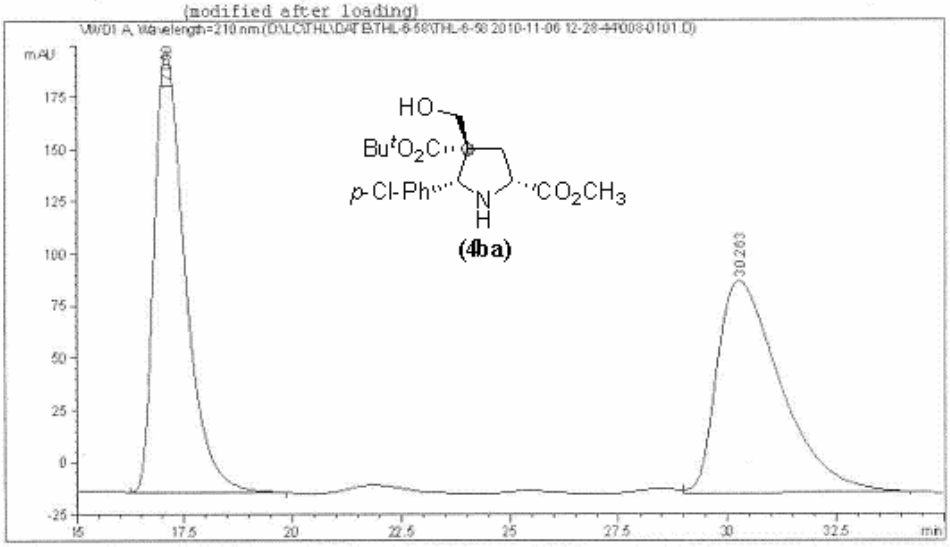
Totals :                  2.29332e4   194.57922

================================================================
                      *** End of Report ***

rument 1 2/20/2011 2:38:50 PM LTL                    Page 1 of 1
```

Data File D:\LC\THL\DATE\THL-6-58\THL-6-58 2010-11-06 12-28-44\008-0101.D
Sample Name: THL-6-48

Acq. Operator	: TMC	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 8
Injection Date	: 11/6/2010 12:30:05 PM	Inj	: 1
		Inj Volume	: 5 µl
Acq. Method	: D:\LC\THL\DATE\THL-6-58\THL-6-58 2010-11-06 12-28-44\ASH-90-10-05ML-210NM-50MIN.M		
Last changed	: 11/6/2010 12:26:41 PM by THL		
Analysis Method	: D:\LC\THL\DATE\THL-6-58\THL-6-58 2010-11-06 12-28-44\008-0101.D\DA.M (ASH-90-10-05ML-210NM-50MIN.M)		
Last changed	: 2/20/2011 2:28:42 PM by LTL (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.090	BB	0.7694	1.06940e4	211.36836	51.1064
2	30.263	VB	1.5143	1.02310e4	101.32860	48.8936
Totals :				2.09251e4	312.69696	

Instrument 1 2/20/2011 2:28:47 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-86\THL-6-86 2010-11-18 15-51-39\012-0201.D
Sample Name: THL-6-86A

```
==================================================================
Acq. Operator   : DXQ                          Seq. Line :   2
Acq. Instrument : Instrument 1                  Location : Vial 12
Injection Date  : 11/18/2010 4:04:00 PM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-86\THL-6-86 2010-11-18 15-51-39\ASH-80-20-05ML-210NM-
                  30MIN.M
Last changed    : 11/18/2010 3:45:02 PM by DXQ
Analysis Method : D:\LC\THL\DATE\THL-6-86\THL-6-86 2010-11-18 15-51-39\012-0201.D\DA.M (ASH-
                  80-20-05ML-210NM-30MIN.M)
Last changed    : 2/20/2011 2:44:43 PM by LTL
                  (modified after loading)
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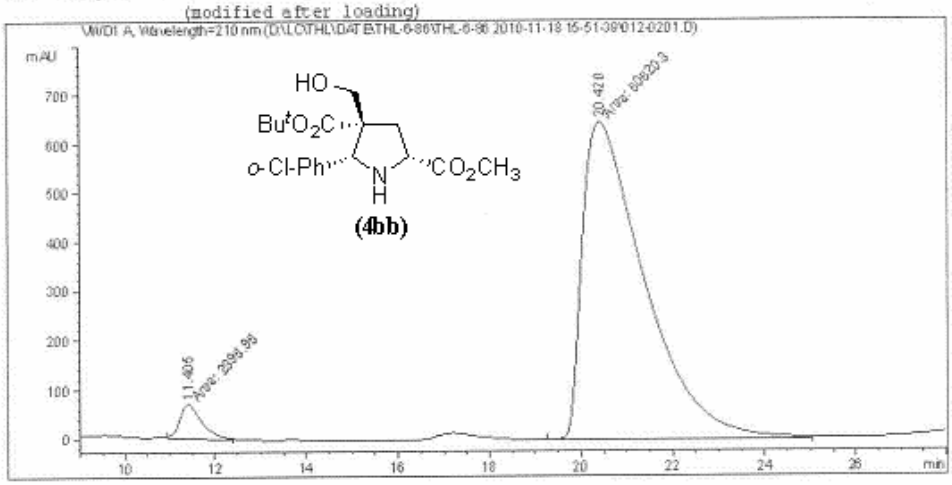



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

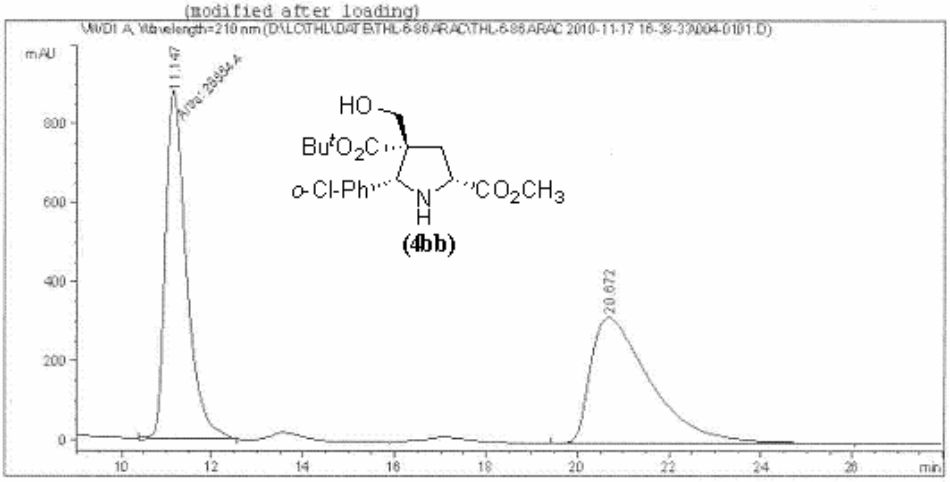
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  11.405 MM    0.5780 2395.95239   69.09161   3.8021
   2  20.420 MM    1.5647 6.06203e4   645.72345  96.1979

Totals :                  6.30162e4   714.81506

==================================================================
                        *** End of Report ***
```

Data File D:\LC\THL\DATE\THL-6-86ARAC\THL-6-86ARAC 2010-11-17 16-38-33\004-0101.D
Sample Name: THL-6-86ARAC

Acq. Operator	: DXQ	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 4
Injection Date	: 11/17/2010 4:39:50 PM	Inj	: 1
		Inj Volume	: 5 µl
Acq. Method	: D:\LC\THL\DATE\THL-6-86ARAC\THL-6-86ARAC 2010-11-17 16-38-33\ASH-80-20-05ML-210NM.M		
Last changed	: 11/6/2010 10:09:43 AM by TMC		
Analysis Method	: D:\LC\THL\DATE\THL-6-86ARAC\THL-6-86ARAC 2010-11-17 16-38-33\004-0101.D\DA.M (ASH-80-20-05ML-210NM.M)		
Last changed	: 2/20/2011 2:42:10 PM by LTL (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

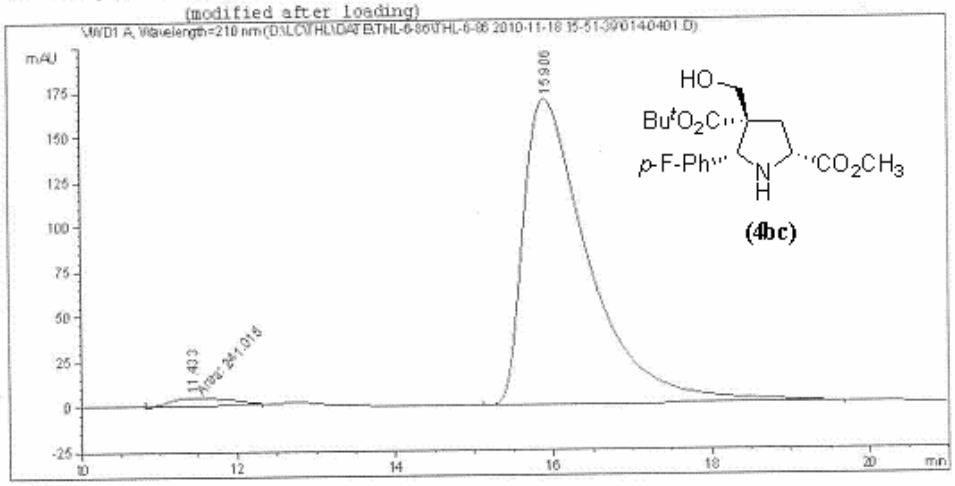
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.147	MM	0.5400	2.85544e4	881.32373	49.8097
2	20.672	VB	1.3519	2.87726e4	317.77271	50.1903
Totals :				5.73271e4	1199.09644	

*** End of Report ***

Data File D:\LC\THL\DATE\THL-6-86\THL-6-86 2010-11-18 15-51-39\014-0401.D
Sample Name: THL-6-86D

Acq. Operator : DXQ
Acq. Instrument : Instrument 1
Injection Date : 11/18/2010 5:02:22 PM
Seq. Line : 4
Location : Vial 14
Inj : 1
Inj Volume : 5 µl

Acq. Method : D:\LC\THL\DATE\THL-6-86\THL-6-86 2010-11-18 15-51-39\ASH-80-20-05ML-210NM-25MIN.M
Last changed : 11/18/2010 3:45:30 PM by DXQ
Analysis Method : D:\LC\THL\DATE\THL-6-86\THL-6-86 2010-11-18 15-51-39\014-0401.D\DA.M (ASH-80-20-05ML-210NM-25MIN.M)
Last changed : 2/20/2011 2:51:21 PM by LTL
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.433	MM	0.8737	241.01488	4.59769	2.4145
2	15.906	BB	0.8614	9741.03906	169.44852	97.5855
Totals :				9982.05394	174.04621	

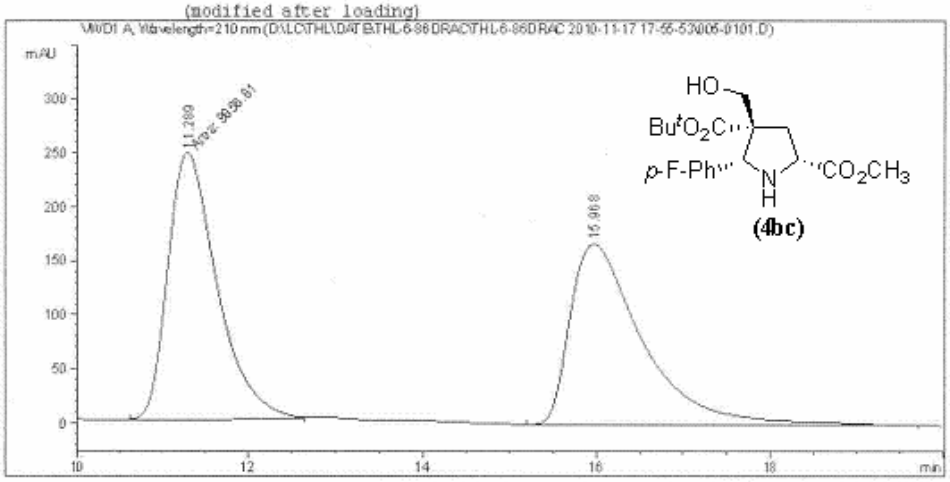
*** End of Report ***

Instrument 1 2/20/2011 2:51:30 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-86DRAC\THL-6-86DRAC 2010-11-17 17-55-53\005-0101.D
Sample Name: THL-6-86DRAC

Acq. Operator	: DXQ	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 5
Injection Date	: 11/17/2010 5:57:11 PM	Inj	: 1
		Inj Volume	: 5 µl
Acq. Method	: D:\LC\THL\DATE\THL-6-86DRAC\THL-6-86DRAC 2010-11-17 17-55-53\ASH-80-20-05ML-210NM.M		
Last changed	: 11/6/2010 10:09:43 AM by TMC		
Analysis Method	: D:\LC\THL\DATE\THL-6-86DRAC\THL-6-86DRAC 2010-11-17 17-55-53\005-0101.D\DA.M (ASH-80-20-05ML-210NM.M)		
Last changed	: 2/20/2011 2:49:43 PM by LTL (modified after loading)		



Area Percent Report

Sorted By	:	Signal
Multiplier	:	1.0000
Dilution	:	1.0000

Use Multiplier & Dilution Factor with ISTDs

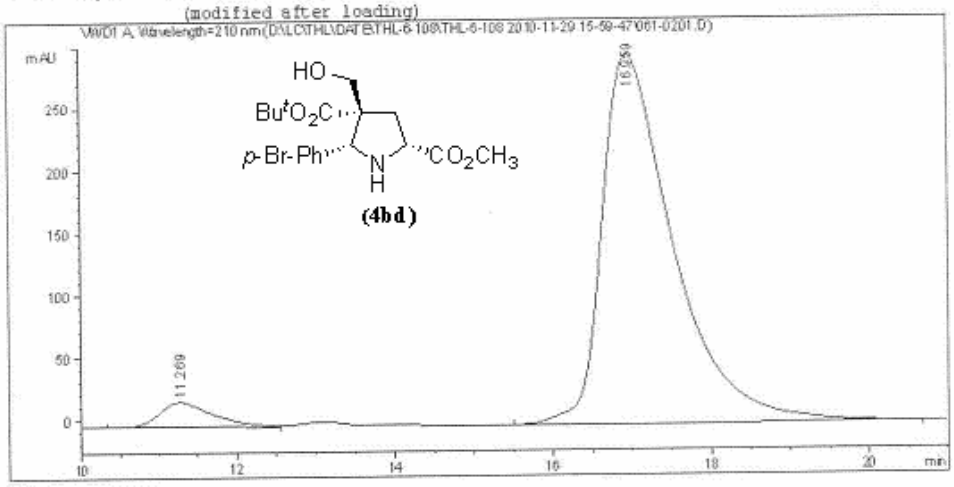
Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.289	MM	0.6647	9856.80762	247.13208	50.3555
2	15.968	VB	0.8718	9717.64160	166.81340	49.6445
Totals :				1.95744e4	413.94548	

*** End of Report ***

Data File D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\061-0201.D
Sample Name: THL-6-108A

Acq. Operator : THL
Acq. Instrument : Instrument 1
Injection Date : 11/29/2010 4:12:24 PM
Seq. Line : 2
Location : Vial 61
Inj : 1
Inj Volume : 5 µl
Acq. Method : D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\ASH-80-20-0SML-210NM-25MIN.M
Last changed : 11/18/2010 3:45:30 PM by DXQ
Analysis Method : D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\061-0201.D\DA.M (ASH-80-20-0SML-210NM-25MIN.M)
Last changed : 2/20/2011 3:16:59 PM by LTL
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

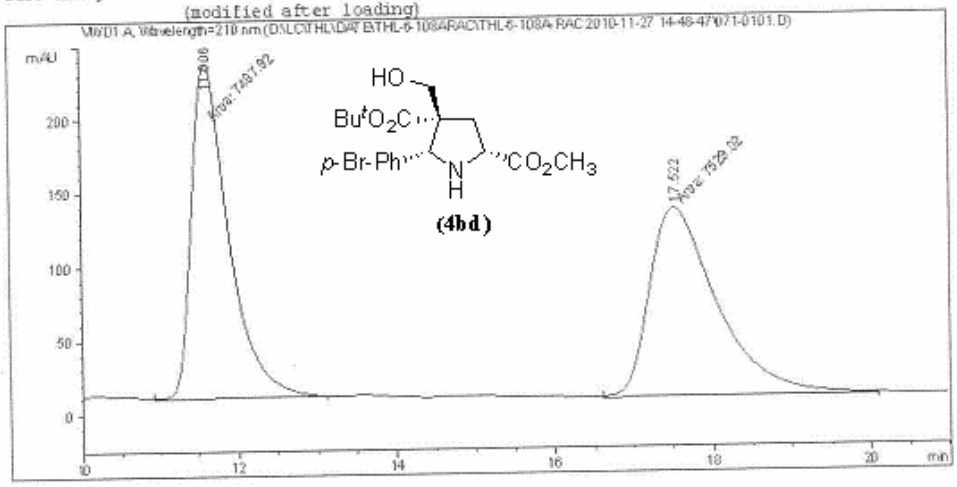
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.269	VV	0.7109	960.58899	19.92666	4.9559
2	16.959	BB	0.9267	1.84223e4	296.13754	95.0441
Totals :				1.93829e4	316.06421	

*** End of Report ***

Data File D:\LC\THL\DATE\THL-6-108ARAC\THL-6-108A-RAC 2010-11-27 14-48-47\071-0101.D
Sample Name: THL-6-108A-RAC

Acq. Operator	: THL	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 71
Injection Date	: 11/27/2010 2:50:14 PM	Inj	: 1
		Inj Volume	: 5 µl

Acq. Method : D:\LC\THL\DATE\THL-6-108ARAC\THL-6-108A-RAC 2010-11-27 14-48-47\ASH-80-20-05ML-210NM-30MIN.M
Last changed : 11/27/2010 2:50:10 PM by THL
(modified after loading)
Analysis Method : D:\LC\THL\DATE\THL-6-108ARAC\THL-6-108A-RAC 2010-11-27 14-48-47\071-0101.D\DA.M (ASH-80-20-05ML-210NM-30MIN.M)
Last changed : 2/20/2011 3:11:27 PM by LTL
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.606	MM	0.5490	7487.92236	227.30307	49.8632
2	17.522	MM	0.9841	7529.01611	127.51185	50.1368
Totals :				1.50169e4	354.81492	

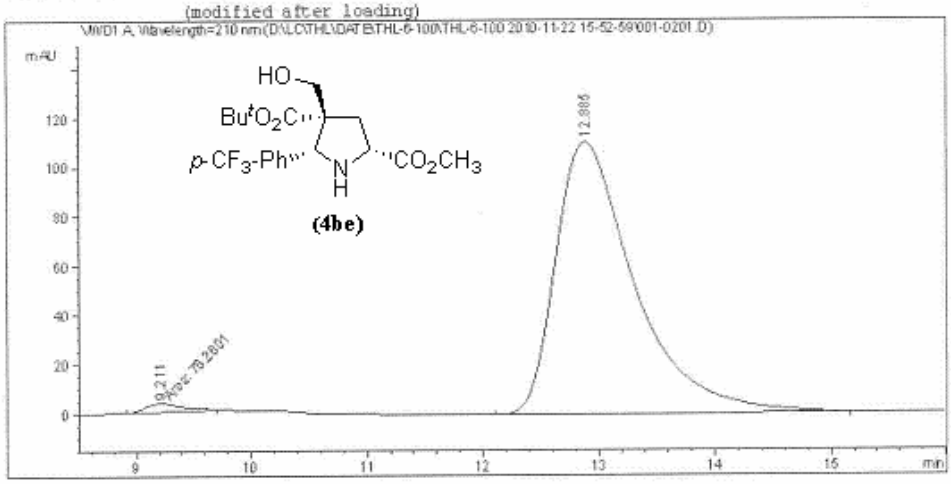
*** End of Report ***

Instrument 1 2/20/2011 3:11:34 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\001-0201.D
Sample Name: THL-6-100B

Acq. Operator : tmc
Seq. Line : 2
Acq. Instrument : Instrument 1
Location : Vial 1
Injection Date : 11/22/2010 4:05:19 PM
Inj : 1
Inj Volume : 5 µl
Acq. Method : D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\ASH-80-20-05ML-210NM-20MIN.M
Last changed : 11/22/2010 3:49:52 PM by tmc
Analysis Method : D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\001-0201.D\DA.M (ASH-80-20-05ML-210NM-20MIN.M)
Last changed : 2/20/2011 3:01:53 PM by LTL
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

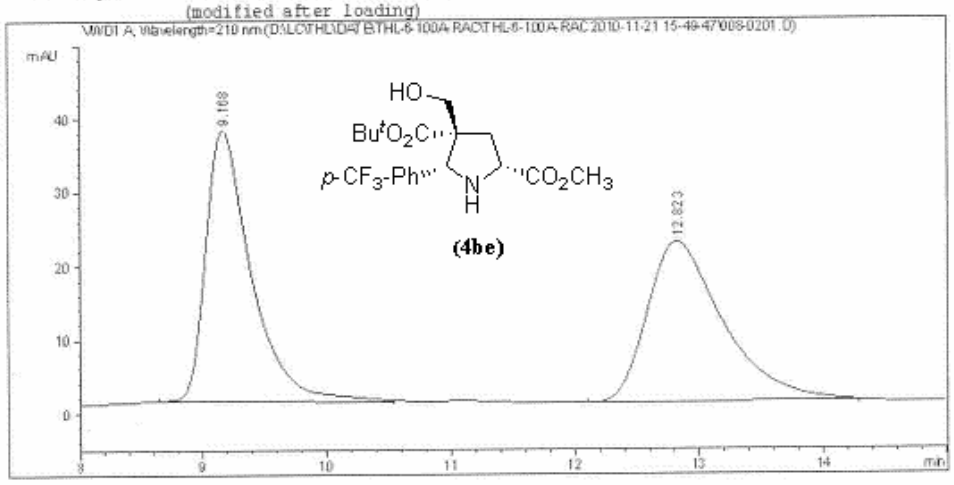
Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.211	MM	0.3874	78.26009	3.36729	1.4803
2	12.885	BB	0.7074	5208.34131	110.45015	98.5197
Totals :				5286.60140	113.81744	

*** End of Report ***

Data File D:\LC\THL\DATE\THL-6-100A-RAC\THL-6-100A-RAC 2010-11-21 15-49-47\008-0201.D
Sample Name: thl-6-100b-rac

Acq. Operator	: THL	Seq. Line	: 2
Acq. Instrument	: Instrument 1	Location	: Vial 8
Injection Date	: 11/21/2010 4:17:40 PM	Inj	: 1
		Inj Volume	: 5 µl
Acq. Method	: D:\LC\THL\DATE\THL-6-100A-RAC\THL-6-100A-RAC 2010-11-21 15-49-47\ASH-80-20-05ML-210NM-30MIN.M		
Last changed	: 11/21/2010 4:16:23 PM by THL (modified after loading)		
Analysis Method	: D:\LC\THL\DATE\THL-6-100A-RAC\THL-6-100A-RAC 2010-11-21 15-49-47\008-0201.D\DA.M (ASH-80-20-05ML-210NM-30MIN.M)		
Last changed	: 2/20/2011 2:56:20 PM by LTL (modified after loading)		



Area Percent Report

Sorted By	:	Signal
Multiplier	:	1.0000
Dilution	:	1.0000

Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

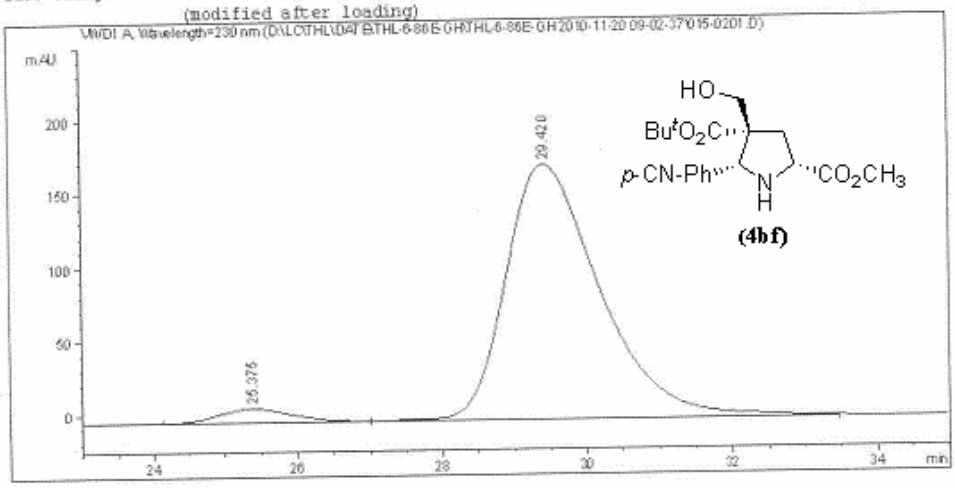
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.168	BB	0.3792	943.40753	36.79168	50.7350
2	12.823	BB	0.6295	916.07239	21.75875	49.2650
Totals :				1859.47992	58.55042	

*** End of Report ***

Data File D:\LC\THL\DATE\THL-6-86E-GH\THL-6-86E-GH 2010-11-20 09-02-37\015-0201.D
Sample Name: THL-6-86E

Acq. Operator : THL
Acq. Instrument : Instrument 1
Injection Date : 11/20/2010 9:14:59 AM
Seq. Line : 2
Location : Vial 15
Inj : 1
Inj Volume : 5 µl

Acq. Method : D:\LC\THL\DATE\THL-6-86E-GH\THL-6-86E-GH 2010-11-20 09-02-37\ADH-80-20-05ML-230NM.M
Last changed : 11/20/2010 9:00:31 AM by THL
Analysis Method : D:\LC\THL\DATE\THL-6-86E-GH\THL-6-86E-GH 2010-11-20 09-02-37\015-0201.D\DA.M (ADH-80-20-05ML-230NM.M)
Last changed : 2/20/2011 2:54:30 PM by LTL
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.375	BV	1.0529	660.96613	9.38834	4.0807
2	29.420	VB	1.3729	1.55366e4	172.69078	95.9193
Totals :				1.61976e4	182.07912	

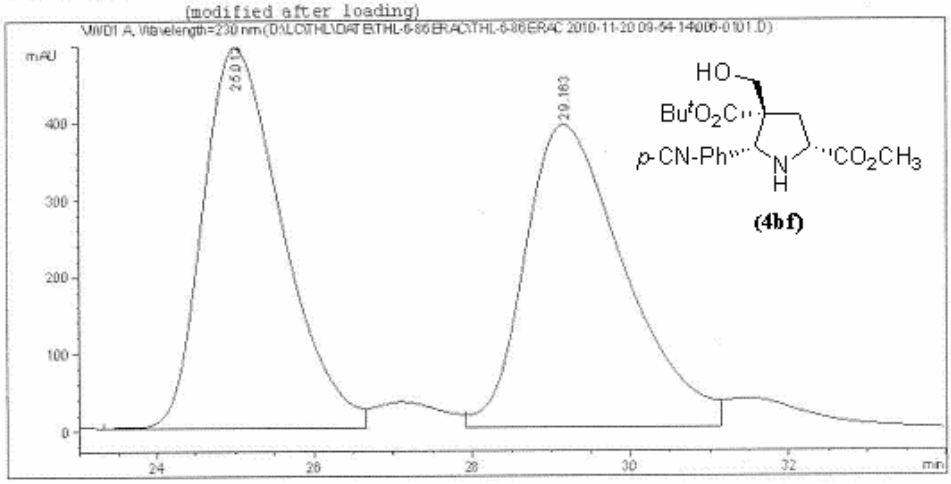
*** End of Report ***

Instrument 1 2/20/2011 2:54:35 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-86ERAC\THL-6-86ERAC 2010-11-20 09-54-14\006-0101.D
Sample Name: THL-6-86ERAC

Acq. Operator	: THL	Seq. Line	: 1
Acq. Instrument	: Instrument 1	Location	: Vial 6
Injection Date	: 11/20/2010 9:55:32 AM	Inj	: 1
		Inj Volume	: 5 µl
Acq. Method	: D:\LC\THL\DATE\THL-6-86ERAC\THL-6-86ERAC 2010-11-20 09-54-14\ADH-80-20-05ML-230NM.M		
Last changed	: 11/20/2010 9:00:31 AM by THL		
Analysis Method	: D:\LC\THL\DATE\THL-6-86ERAC\THL-6-86ERAC 2010-11-20 09-54-14\006-0101.D\DA.M (ADH-80-20-05ML-230NM.M)		
Last changed	: 2/20/2011 2:53:12 PM by LTL (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.013	VV	1.0858	3.44202e4	491.82541	50.0072
2	29.163	VV	1.3377	3.44103e4	392.34802	49.9928
Totals :				6.88305e4	884.17343	

*** End of Report ***

Instrument 1 2/20/2011 2:53:19 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\016-0601.D
Sample Name: THL-6-100A

```
==================================================================
Acq. Operator   : tmc                          Seq. Line :   6
Acq. Instrument : Instrument 1                  Location : Vial 16
Injection Date  : 11/22/2010 5:20:40 PM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\ASH-80-20-05ML-
                  210NM-25MIN.M
Last changed    : 11/18/2010 3:45:30 PM by DXQ
Analysis Method : D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\016-0601.D\DA.M (
                  ASH-80-20-05ML-210NM-25MIN.M)
Last changed    : 2/20/2011 2:59:15 PM by LTL
                  (modified after loading)
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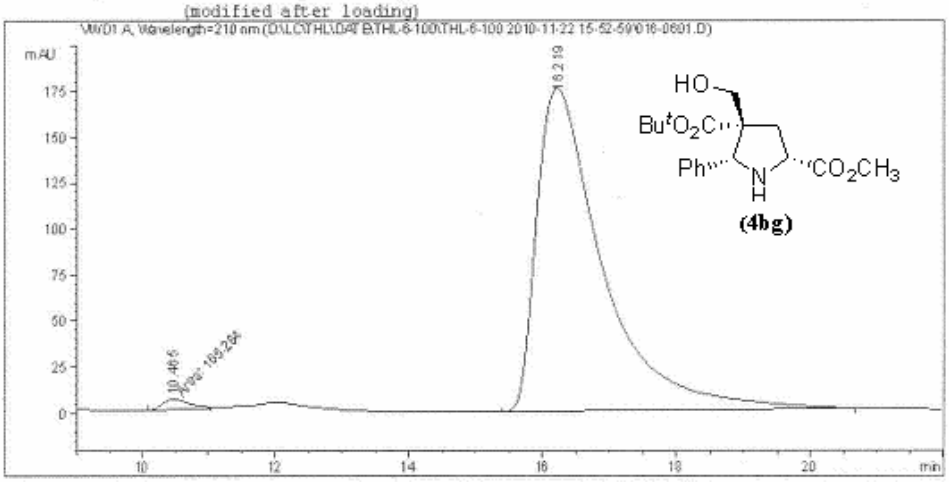


```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|------|----|-------|----------|----------|--------|
   1  10.465 MM    0.4954  165.28436    5.56080   1.3536
   2  16.219 BB    1.0167 1.20450e4   175.71765  98.6464

Totals :*                 1.22103e4   181.27845


==================================================================
                        *** End of Report ***
```

Data File D:\LC\THL\DATE\THL-6-100A-RAC\THL-6-100A-RAC 2010-11-21 15-49-47\007-0101.D
Sample Name: thl-6-100a-rac

```
==================================================================
Acq. Operator   : THL                          Seq. Line :   1
Acq. Instrument : Instrument 1                  Location : Vial 7
Injection Date  : 11/21/2010 3:51:34 PM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-100A-RAC\THL-6-100A-RAC 2010-11-21 15-49-47\ASH-80-
                  20-05ML-210NM-30MIN.M
Last changed    : 11/21/2010 4:04:05 PM by THL
                  (modified after loading)
Analysis Method : D:\LC\THL\DATE\THL-6-100A-RAC\THL-6-100A-RAC 2010-11-21 15-49-47\007-0101.
                  D\DA.M (ASH-80-20-05ML-210NM-30MIN.M)
Last changed    : 2/20/2011 2:57:55 PM by LTL
                  (modified after loading)
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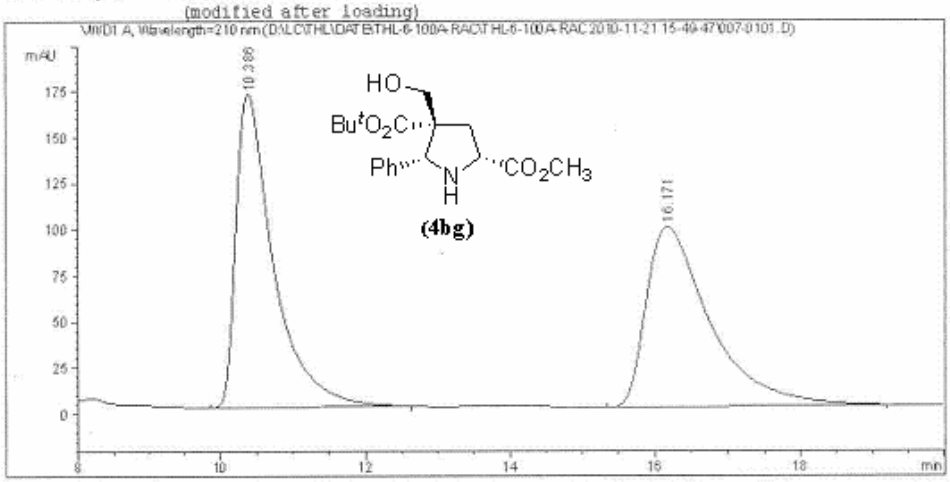



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|------|----|-------|----------|----------|-------|
   1  10.386 BB    0.5292 6128.03027  170.24222  50.7853
   2  16.171 BB    0.9067 5938.50781   97.56725  49.2147

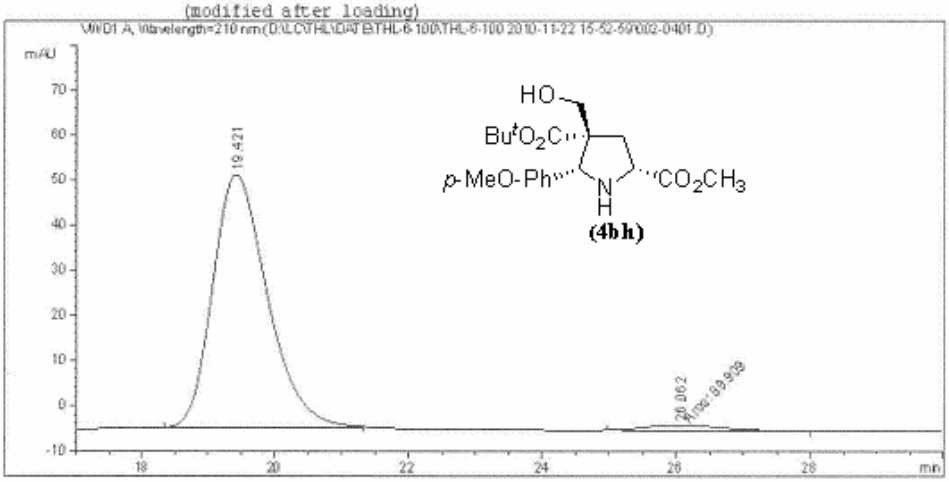
Totals :                  1.20665e4   267.80947


==================================================================
                        *** End of Report ***
```

Instrument 1 2/20/2011 2:57:59 PM LTL

Data File D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\002-0401.D
Sample Name: THL-6-100C

Acq. Operator	: tmc	Seq. Line	: 4
Acq. Instrument	: Instrument 1	Location	: Vial 2
Injection Date	: 11/22/2010 4:37:58 PM	Inj	: 1
		Inj Volume	: 5 µl
Acq. Method	: D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\ODH-80-20-0.5ML-210NM-35MIN.M		
Last changed	: 11/22/2010 5:07:23 PM by tmc (modified after loading)		
Analysis Method	: D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\002-0401.D\DA.M (ODH-80-20-0.5ML-210NM-35MIN.M)		
Last changed	: 2/20/2011 3:05:29 PM by LTL (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.421	BB	0.8741	3174.64624	55.98981	97.2459
2	26.062	MM	1.3586	89.90903	1.10300	2.7541
Totals :				3264.55527	57.09281	

*** End of Report ***

Instrument 1 2/20/2011 3:05:37 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-100C-RAC\THL-6-100C-RAC 2010-11-21 19-45-51\009-0101.D
Sample Name: THL-6-103C-RAC

```
==================================================================
Acq. Operator   : THL                          Seq. Line :   1
Acq. Instrument : Instrument 1                  Location : Vial 9
Injection Date  : 11/21/2010 7:47:22 PM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-100C-RAC\THL-6-100C-RAC 2010-11-21 19-45-51\ODH-80-
                  20-05ML-210NM.M
Last changed    : 11/21/2010 8:18:26 PM by THL
                  (modified after loading)
Analysis Method : D:\LC\THL\DATE\THL-6-100C-RAC\THL-6-100C-RAC 2010-11-21 19-45-51\009-0101.
                  D\DA.M (ODH-80-20-05ML-210NM.M)
Last changed    : 2/20/2011 3:03:33 PM by LTL
                  (modified after loading)
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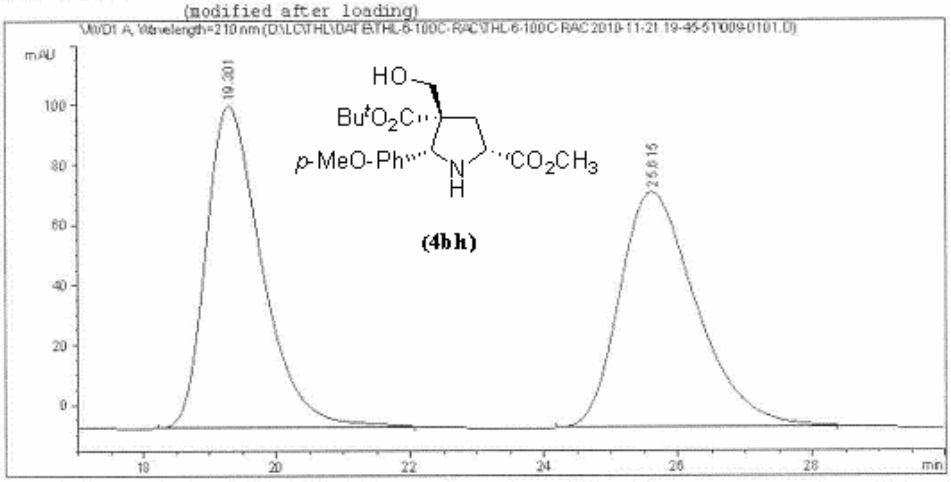



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

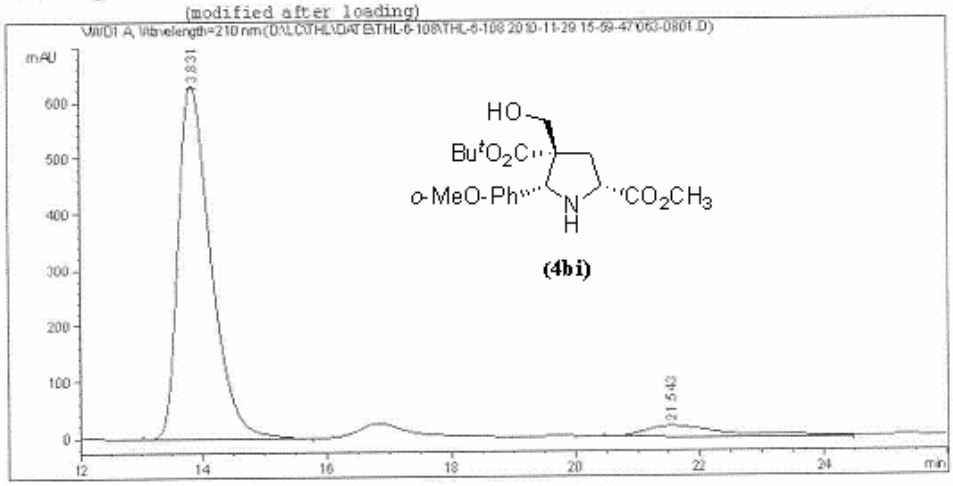
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  19.301 BB    0.8868 6220.93457  107.18763  50.1816
   2  25.615 BB    1.2126 6175.89697   78.07592  49.8184

Totals :                  1.23968e4   185.26355

==================================================================
                        *** End of Report ***
```

Data File D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\063-0801.D
Sample Name: THL-6-108C

Acq. Operator : THL
Acq. Instrument : Instrument 1
Injection Date : 11/29/2010 6:51:22 PM
Seq. Line : 8
Location : Vial 63
Inj : 1
Inj Volume : 5 µl
Acq. Method : D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\ODH-80-20-05ML-210NM-30MIN.M
Last changed : 11/29/2010 8:55:30 AM by THL
Analysis Method : D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\063-0801.D\DA.M (ODH-80-20-05ML-210NM-30MIN.M)
Last changed : 2/20/2011 3:23:52 PM by LTL (modified after loading)



(4bi)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.831	BB	0.5659	2.34379e4	633.10199	92.9419
2	21.543	VV	1.2564	1779.89026	19.89404	7.0581
Totals :				2.52178e4	652.99603	

*** End of Report ***

Instrument 1 2/20/2011 3:23:57 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-108C-RAC\THL-6-108C-RAC 2010-11-29 08-57-25\001-0201.D
Sample Name: THL-6-108CRAC

```
==================================================================
Acq. Operator   : THL                          Seq. Line :   2
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 11/29/2010 9:09:48 AM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-108C-RAC\THL-6-108C-RAC 2010-11-29 08-57-25\ODH-80-
                  20-05ML-210NM-30MIN.M
Last changed    : 11/29/2010 8:55:30 AM by THL
Analysis Method : D:\LC\THL\DATE\THL-6-108C-RAC\THL-6-108C-RAC 2010-11-29 08-57-25\001-0201.
                  D\DA.M (ODH-80-20-05ML-210NM-30MIN.M)
Last changed    : 2/20/2011 3:22:06 PM by LTL
                  (modified after loading)
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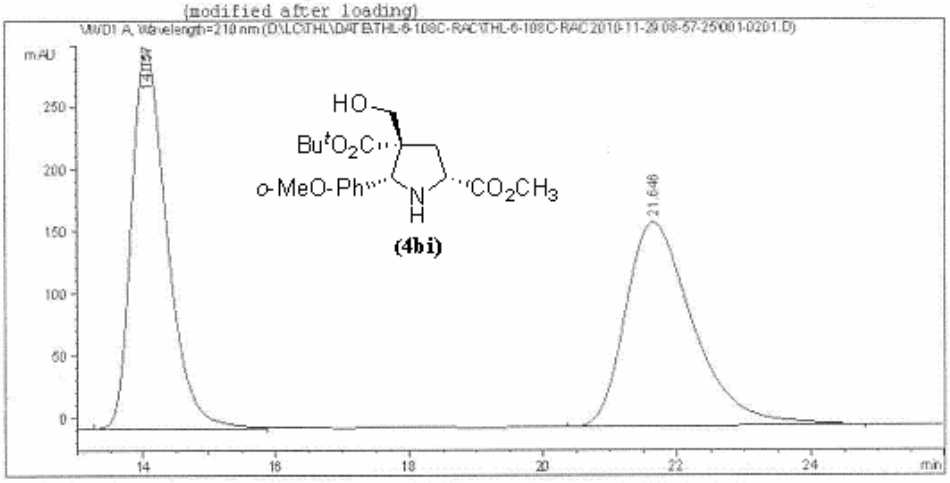



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

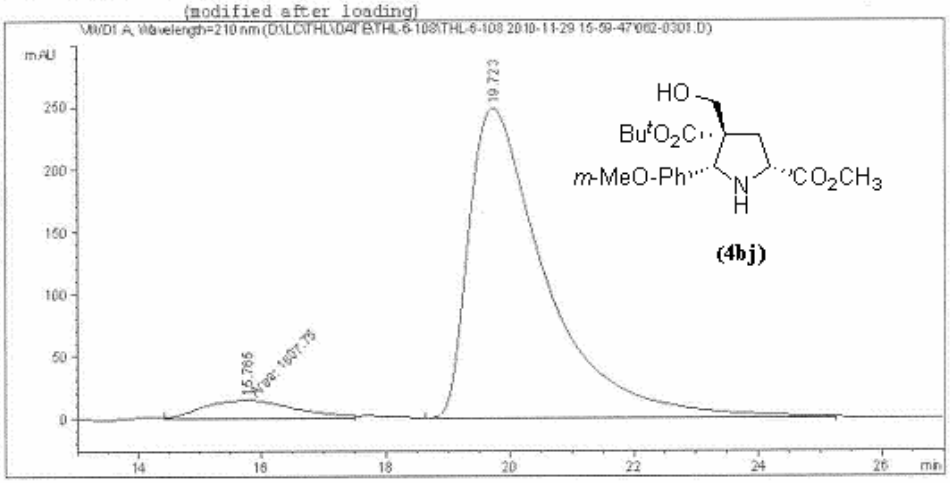
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|------|----|------|---------|----------|-------|
   1  14.057 BB    0.5795 1.14925e4   303.94165  50.2985
   2  21.646 BB    1.0670 1.13561e4   163.11961  49.7015

Totals :                 2.28486e4   467.06126

==================================================================
                        *** End of Report ***
```

Data File D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\062-0301.D
Sample Name: THL-6-106B

```
==================================================================
Acq. Operator   : THL                          Seq. Line :   3
Acq. Instrument : Instrument 1                  Location : Vial 62
Injection Date  : 11/29/2010 4:38:48 PM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\ASH-80-20-05ML-
                  210NM-30MIN.M
Last changed    : 11/18/2010 3:45:02 PM by DXQ
Analysis Method : D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\062-0301.D\DA.M (
                  ASH-80-20-05ML-210NM-30MIN.M)
Last changed    : 2/20/2011 3:18:36 PM by LTL
                  (modified after loading)
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.765 MF    1.7615 1607.74609   15.21164   6.9718
   2  19.723 VB    1.2790 2.14531e4   248.26463  93.0282

Totals :                  2.30608e4   263.47628

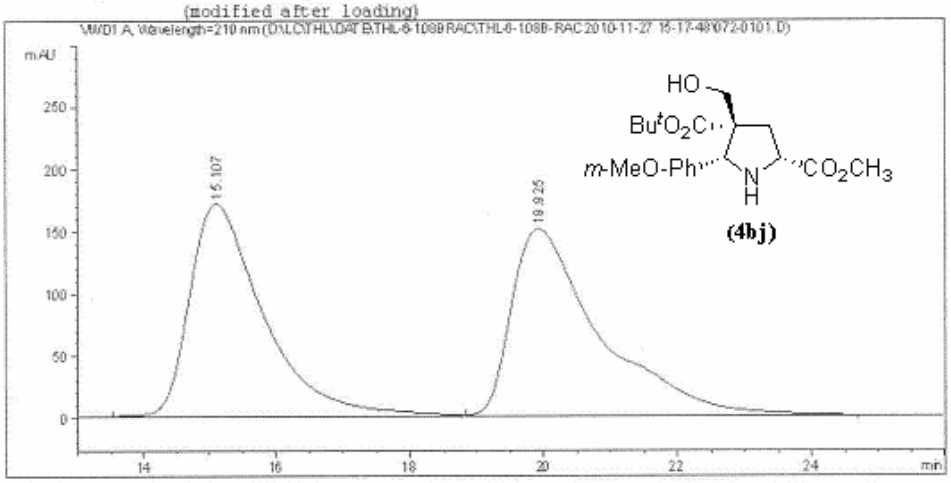
==================================================================
                      *** End of Report ***
```

Instrument 1 2/20/2011 3:18:40 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-108BRAC\THL-6-108B-RAC 2010-11-27 15-17-48\072-0101.D
Sample Name: THL-6-108B-RAC

```
================================================================
Acq. Operator   : THL                          Seq. Line :   1
Acq. Instrument : Instrument 1                  Location : Vial 72
Injection Date  : 11/27/2010 3:19:21 PM             Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-108BRAC\THL-6-108B-RAC 2010-11-27 15-17-48\ASH-80-20-
                  05ML-210NM-30MIN.M
Last changed    : 11/18/2010 3:45:02 PM by DXQ
Analysis Method : D:\LC\THL\DATE\THL-6-108BRAC\THL-6-108B-RAC 2010-11-27 15-17-48\072-0101.
                  D\DA.M (ASH-80-20-05ML-210NM-30MIN.M)
Last changed    : 2/20/2011 3:19:48 PM by LTL
                  (modified after loading)
```




```
================================================================
                      Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  15.107 BB    1.1433 1.30940e4   169.97696  49.0227
   2  19.925 BB    1.3319 1.36160e4   149.71518  50.9773

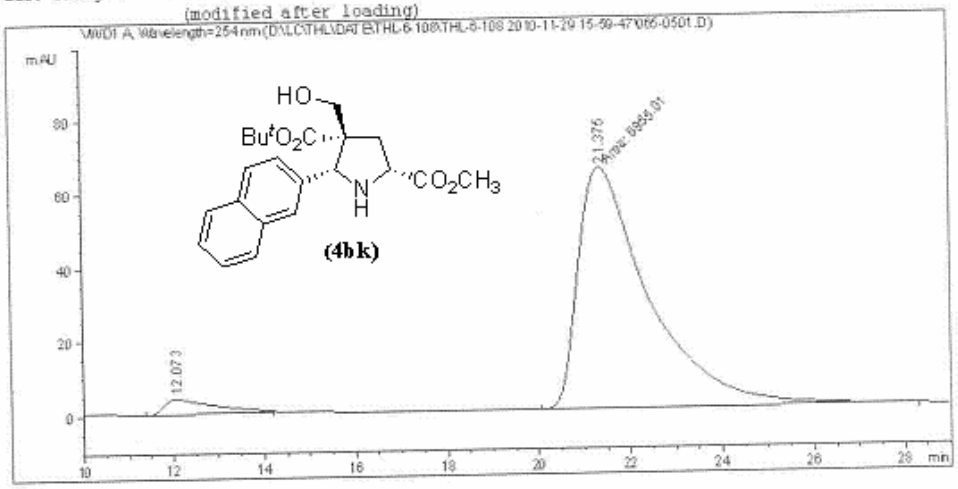
Totals :                 2.67100e4   319.69214

================================================================
                      *** End of Report ***
```

Data File D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\065-0501.D
Sample Name: THL-6-108E

Acq. Operator : THL
Acq. Instrument : Instrument 1
Injection Date : 11/29/2010 5:37:19 PM
Seq. Line : 5
Location : Vial 65
Inj : 1
Inj Volume : 5 µl

Acq. Method : D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\ASH-80-20-05ML-254NM-30MIN.M
Last changed : 11/22/2010 4:59:06 PM by THL
Analysis Method : D:\LC\THL\DATE\THL-6-108\THL-6-108 2010-11-29 15-59-47\065-0501.D\DA.M (ASH-80-20-05ML-254NM-30MIN.M)
Last changed : 2/20/2011 3:25:58 PM by LTL
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.073	BB	1.0069	315.87769	4.18676	4.3444
2	21.375	MM	1.7738	6955.00781	65.34890	95.6556
Totals :				7270.88550	69.53566	

*** End of Report ***

Instrument 1 2/20/2011 3:26:03 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-108C-E\THL-6-108C-E-RAC 2010-11-28 13-34-30\003-0301.D
Sample Name: THL-6-108E-RAC

```
==========================================================================
Acq. Operator   : THL                              Seq. Line :   3
Acq. Instrument : Instrument 1                      Location : Vial 3
Injection Date  : 11/28/2010 2:38:48 PM                 Inj :   1
                                                   Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-108C-E\THL-6-108C-E-RAC 2010-11-28 13-34-30\ASH-80-
                  20-05ML-254NM-30MIN.M
Last changed    : 11/22/2010 4:59:06 PM by THL
Analysis Method : D:\LC\THL\DATE\THL-6-108C-E\THL-6-108C-E-RAC 2010-11-28 13-34-30\003-0301.
                  D\DA.M (ASH-80-20-05ML-254NM-30MIN.M)
Last changed    : 2/20/2011 3:27:10 PM by LTL
                  (modified after loading)
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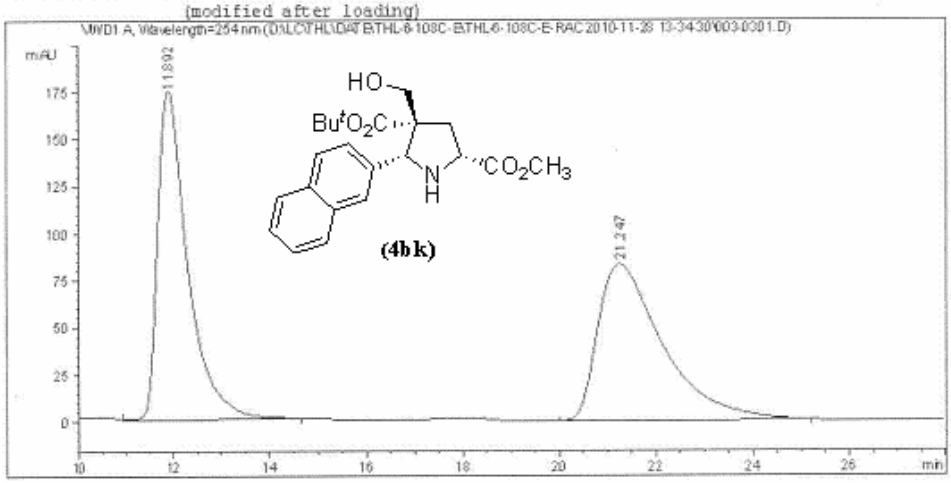



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  11.892 VB    0.6554 7713.11719  174.50972  50.2175
   2  21.247 BB    1.3726 7646.30957   82.71335  49.7825

Totals :                 1.53594e4   257.22307

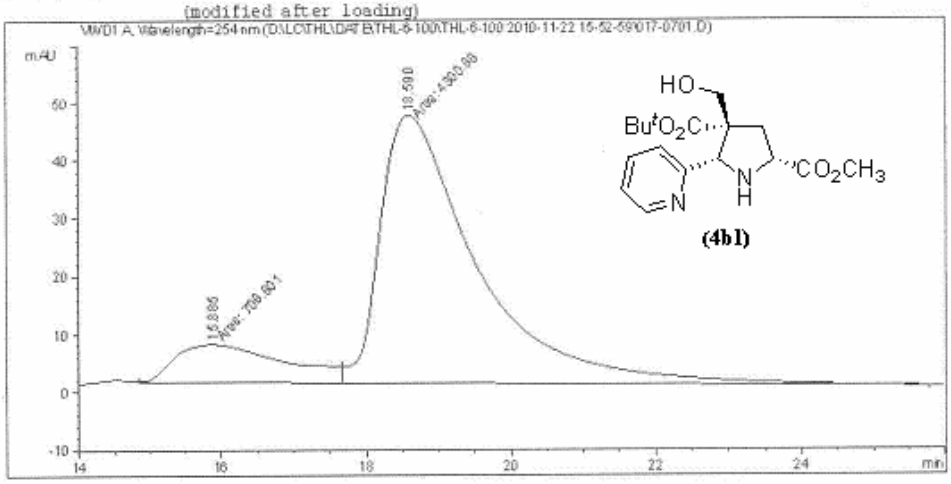
==========================================================================
                        *** End of Report ***
```

Instrument 1 2/20/2011 3:27:14 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\017-0701.D
Sample Name: THL-6-100D

```
Acq. Operator   : tmc                                  Seq. Line :   7
Acq. Instrument : Instrument 1                          Location : Vial 17
Injection Date  : 11/22/2010 5:47:16 PM                    Inj :   1
                                                       Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\ASH-80-20-05ML-
                  254NM-30MIN.M
Last changed    : 11/22/2010 4:59:06 PM by THL
Analysis Method : D:\LC\THL\DATE\THL-6-100\THL-6-100 2010-11-22 15-52-59\017-0701.D\DA.M (
                  ASH-80-20-05ML-254NM-30MIN.M)
Last changed    : 2/20/2011 3:09:34 PM by LTL
                  (modified after loading)
```



(4b1)

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

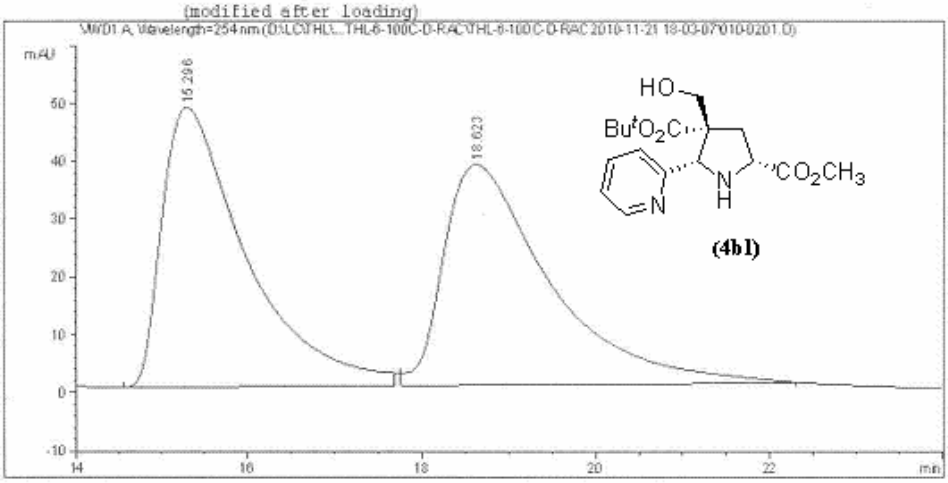
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  15.885 MF    1.7728  708.80109    6.66365  14.1486
   2  18.590 FM    1.5497 4300.87598   46.25590  85.8514

Totals :                 5009.67706   52.91955

                          *** End of Report ***
```

Data File D:\LC\THL\DATE\THL-6-100C-D-RAC\THL-6-100C-D-RAC 2010-11-21 18-03-07\010-0201.D
Sample Name: THL-6-100D-rac

```
=====================================================================
Acq. Operator   : THL                          Seq. Line :   2
Acq. Instrument : Instrument 1                  Location : Vial 10
Injection Date  : 11/21/2010 6:32:17 PM            Inj :   1
                                                Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-100C-D-RAC\THL-6-100C-D-RAC 2010-11-21 18-03-07\ASH-
                  80-20-05ML-254NM.M
Last changed    : 11/21/2010 6:13:57 PM by THL
Analysis Method : D:\LC\THL\DATE\THL-6-100C-D-RAC\THL-6-100C-D-RAC 2010-11-21 18-03-07\010-
                  0201.D\DA.M (ASH-80-20-05ML-254NM.M)
Last changed    : 2/20/2011 3:07:10 PM by LTL
                  (modified after loading)
```



(4b1)

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.296 BB    0.9920 3269.29102   48.30249  50.1562
   2  18.623 BB    1.2401 3248.93408   38.18611  49.8438

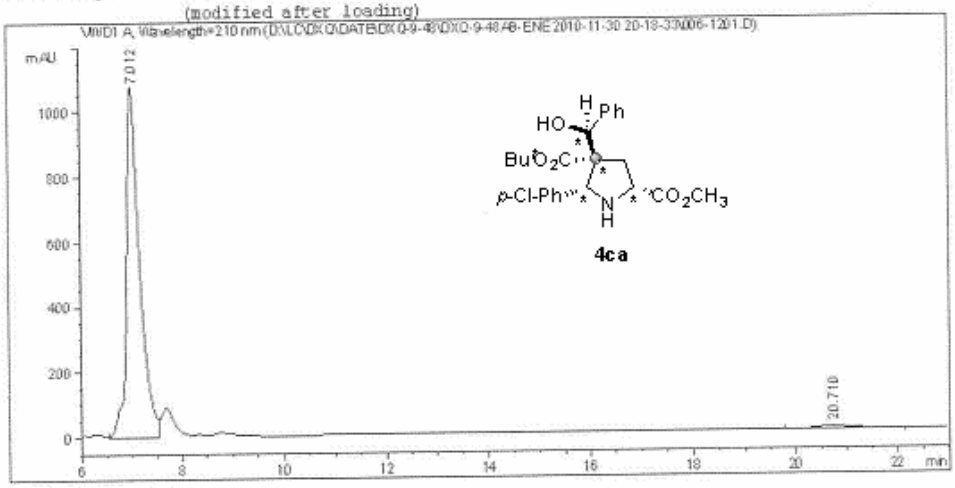
Totals :                 6518.22510   86.48861

=====================================================================
                        *** End of Report ***
```

Data File D:\LC\DXQ\DATE\DXQ-9-48\DXQ-9-48AB-ENE 2010-11-30 20-18-33\006-1201.D
Sample Name: THL-6-116A

Acq. Operator : dxq
Acq. Instrument : Instrument 1
Injection Date : 12/1/2010 1:25:13 AM
Seq. Line : 12
Location : Vial 6
Inj : 1
Inj Volume : 5 µl

Acq. Method : D:\LC\DXQ\DATE\DXQ-9-48\DXQ-9-48AB-ENE 2010-11-30 20-18-33\ADH-70-30-1ML-210NM-25MIN.M
Last changed : 11/28/2010 6:11:42 PM by THL
Analysis Method : D:\LC\DXQ\DATE\DXQ-9-48\DXQ-9-48AB-ENE 2010-11-30 20-18-33\006-1201.D\DA.M (ADH-70-30-1ML-210NM-25MIN.M)
Last changed : 2/20/2011 3:43:39 PM by LTL (modified after loading)



4ca

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.012	VV	0.2698	1.99766e4	1079.10962	97.2547
2	20.710	BB	0.7706	563.88904	10.88027	2.7453
Totals :				2.05405e4	1089.98989	

*** End of Report ***

Instrument 1 2/20/2011 3:43:46 PM LTL

Page 1 of 1

Data File D:\LC\THL\DATE\THL-6-76\THL-6-76 2010-11-12 17-39-05\001-0101.D
Sample Name: THL-6-76AA

```
==================================================================
Acq. Operator   : DXQ                          Seq. Line :   1
Acq. Instrument : Instrument 1                  Location : Vial 1
Injection Date  : 11/12/2010 5:40:21 PM            Inj :   1
                                                Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-76\THL-6-76 2010-11-12 17-39-05\ADH-70-30-1ML210NM-
                  25MIN.M
Last changed    : 11/5/2010 8:32:44 PM by thl
Analysis Method : D:\LC\THL\DATE\THL-6-76\THL-6-76 2010-11-12 17-39-05\001-0101.D\DA.M (ADH-
                  70-30-1ML210NM-25MIN.M)
Last changed    : 2/20/2011 3:39:01 PM by LTL
                  (modified after loading)
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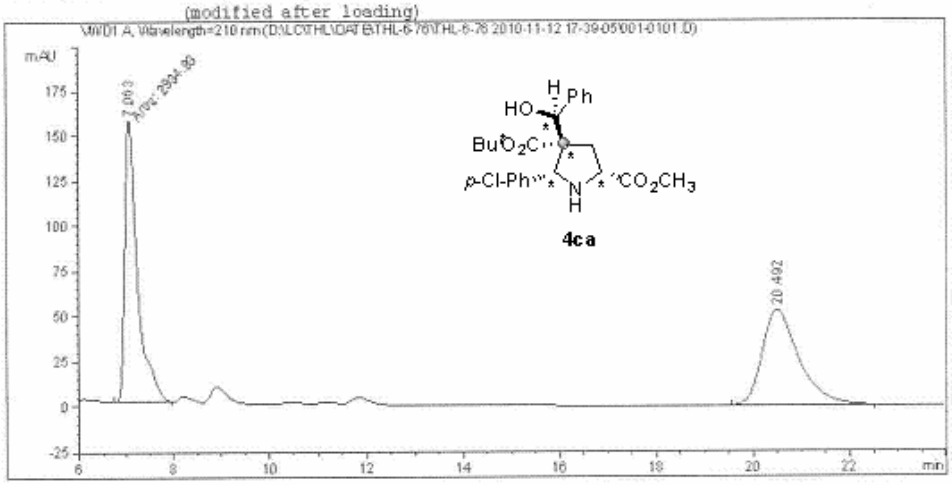


```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.063 MM    0.3138 2934.92993  155.87706  51.5484
   2  20.492 BB    0.7838 2758.60962   52.84193  48.4516

Totals :                  5693.53955  208.71899

==================================================================
                        *** End of Report ***
```

ata File D:\LC\THL\DATE\THL-6-116\THL-6-116 2011-02-21 10-02-32\002-0301.D
ample Name: thl-116b

```
==================================================================
Acq. Operator   : thl                          Seq. Line :   3
Acq. Instrument : Instrument 1                  Location : Vial 2
Injection Date  : 2/21/2011 10:56:27 AM            Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : D:\LC\THL\DATE\THL-6-116\THL-6-116 2011-02-21 10-02-32\ASH-90-10-05ML-
                  210NM-40MIN.M
Last changed    : 2/21/2011 10:55:14 AM by thl
                  (modified after loading)
Analysis Method : D:\LC\THL\DATE\THL-6-116\THL-6-116 2011-02-21 10-02-32\002-0301.D\DA.M (
                  ASH-90-10-05ML-210NM-40MIN.M)
Last changed    : 2/21/2011 12:04:56 PM by LTL
                  (modified after loading)
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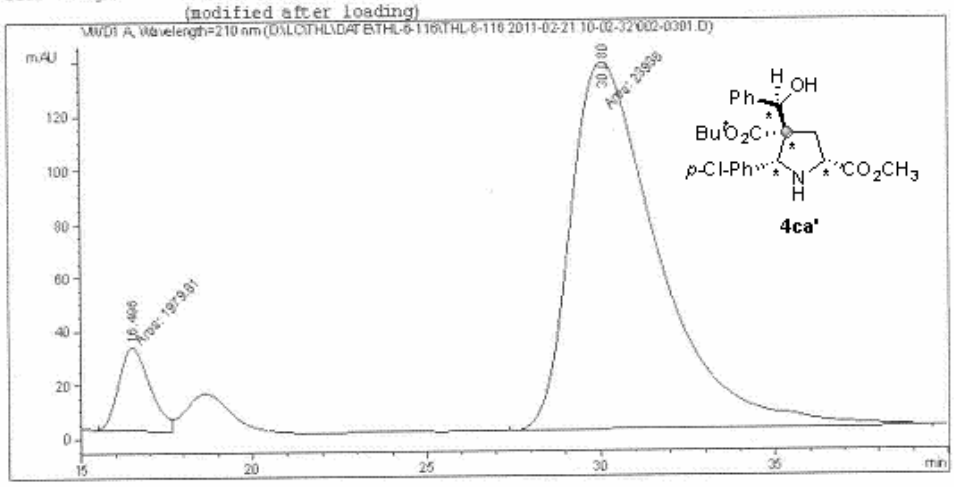



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  16.496 MF    1.0666 1979.80640   30.93568   7.6394
   2  30.080 MM    2.9157 2.39360e4   136.82176  92.3606

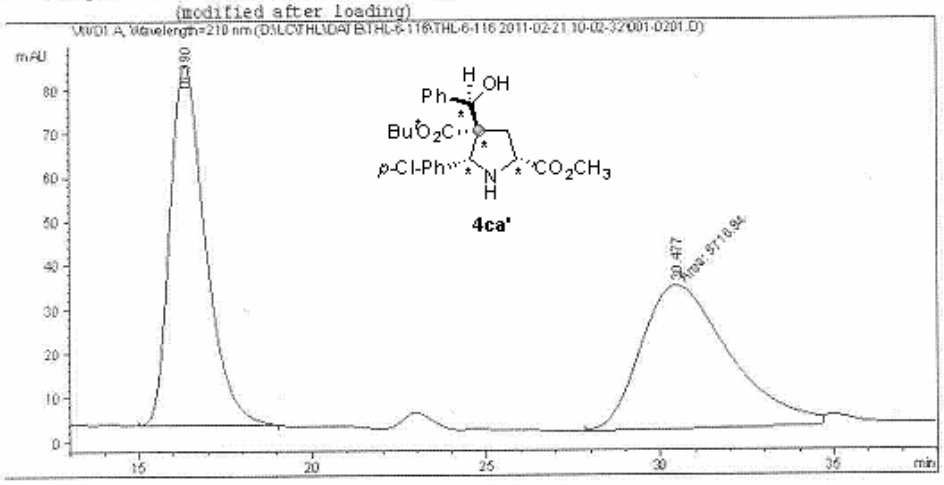
Totals :                  2.59158e4   167.75745

==================================================================
                        *** End of Report ***
```

Instrument 1 2/21/2011 12:05:02 PM LTL Page 1 of 1

File D:\LC\THL\DATE\THL-6-116\THL-6-116 2011-02-21 10-02-32\001-0201.D
e Name: thl-6-116b-rac

Seq. Operator : thl
Seq. Instrument : Instrument 1
Injection Date : 2/21/2011 10:14:58 AM
Seq. Line : 2
Location : Vial 1
Inj : 1
Inj Volume : 5 µl
Seq. Method : D:\LC\THL\DATE\THL-6-116\THL-6-116 2011-02-21 10-02-32\ASH-90-10-05ML-210NM-40MIN.M
Last changed : 2/21/2011 10:51:13 AM by thl
(modified after loading)
Analysis Method : D:\LC\THL\DATE\THL-6-116\THL-6-116 2011-02-21 10-02-32\001-0201.D\DA.M (ASH-90-10-05ML-210NM-40MIN.M)
Last changed : 2/21/2011 11:00:37 AM by LTL
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.390	BB	1.0747	5878.61084	82.04626	50.6971
2	30.477	MF	2.9445	5716.93848	32.35960	49.3029
Totals :				1.15955e4	114.40586	

*** End of Report ***

Document 1 2/21/2011 11:00:43 AM LTL