

*Supporting Information for***Asymmetric Mukaiyama Aldol Reaction of Nonactivated Ketones Catalyzed by *allo*-Threonine-Derived Oxazaborolidinone**

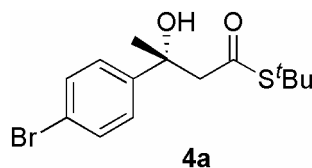
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General. Dichloromethane was dried and distilled over CaH₂. Et₂O and toluene was distilled from sodium benzophenone ketyl. The following compounds were prepared according to a literature procedure; ketone **2d**,¹ *O*-benzoyl-*N*-tosyl-(*L*)-*allo*-threonine,² and silyl ketene acetals **3a**³, **3b**⁴.



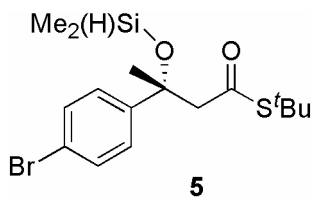
***S*-tert-Butyl (R)-3-(4-Bromophenyl)-3-hydroxybutanethioate (4a)** (Typical Procedure for Asymmetric Aldol Reaction; Table 1, entry 9). To a solution of *O*-benzoyl-*N*-tosyl-(*L*)-*allo*-threonine (75.5 mg, 0.200 mmol) in dry CH₂Cl₂ (2.0 mL) under argon atmosphere at room temperature was added dichlorophenylborane (28.5 μL, 0.22 mmol). After being stirred for 30 min, the mixture was concentrated in vacuo. To a solution of the resulting OXB **1** in dry toluene (0.5 mL) at −10 °C were added *p*-bromoacetophenone (**2a**) (199 mg, 1.00 mmol) and silyl ketene acetal **3b** (306 mg, 1.50 mmol). After being stirred at −10 °C for 48 h, the reaction mixture was quenched by the addition of saturated aqueous NaHCO₃ and filtered. The filtrate was extracted three times with ethyl acetate, dried (Na₂SO₄), and concentrated in vacuo. The residue was dissolved in aqueous 1N HCl (10 mL) and THF (10 mL) at room temperature. After being for 3 h, the mixture was poured into aqueous NaHCO₃ and extracted three times with ethyl acetate. The organic layers were dried (Na₂SO₄) and concentrated in vacuo. Purification of the residue by flash chromatography (SiO₂, 2% ethyl acetate in hexane) gave, in the order of elution, 225 mg (68%) of (*R*)-**4a** (94% ee) and 26.1 mg (13%) of **7** (44% ee). **4a**: [α]_D¹⁸ 28.1 (*c* 1.05, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.36 (9H, s), 1.50 (3H, s), 2.86 (1H, d, *J* = 15.5), 3.02 (1H, d, *J* = 15.4), 4.35 (1H, s), 7.29–7.32 (2H, m), 7.43–7.46 (2H, m); ¹³C NMR (125.8 MHz, CDCl₃) δ 29.5, 30.1, 49.0, 54.9, 73.9, 120.8, 126.6, 131.2, 145.6, 201.3. HRMS (EI) calcd for C₁₄H₁₉BrO₂S 330.0289, found 330.0267. The ee value of **4a** was determined by HPLC analysis using a Chiralcel OD column (1 mL/min, 0.1% *i*-PrOH in hexane); retention times: 34.6 min (major *R*-enantiomer) and 42.6 min (minor *S*-enantiomer).

¹ Percec, V.; Bera, T. K.; De, B. B.; Sanai, Y.; Smith, J.; Holerca, M. N.; Barboiu, B. *J. Org. Chem.* **2001**, *66*, 2104–2117.

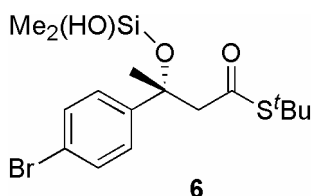
² Wang, X.; Adachi, S.; Iwai, H.; Takatsuki, H.; Fujita, K.; Kubo, M.; Oku, A.; Harada, T. *J. Org. Chem.* **2003**, *68*, 10046–10057.

³ Kita, Y.; Segawa, J.; Haruta, J.; Yasuda, H.; Tamura, Y. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1099–1104.

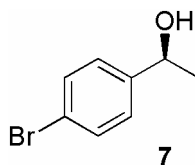
⁴ Harada, T.; Adachi, S.; Wang, X. *Org. Lett.* **2004**, *6*, 4877–4879.



***S*-tert-Butyl (*R*)-3-(4-Bromophenyl)-3-dimethylsilyloxybutanethioate (5):** ^1H NMR (500 MHz, CDCl_3) δ 0.15 (3H, d, $J = 2.8$ Hz), 0.23 (3H, d, $J = 2.8$ Hz), 1.36 (9H, s), 1.79 (3H, s), 2.81 (1H, d, $J = 13.6$ Hz), 2.86 (1H, d, $J = 13.6$ Hz), 4.71 (1H, sept, $J = 2.8$ Hz), 7.25–7.29 (2H, m), 7.42–7.46 (2H, m); ^{13}C NMR (125.8 MHz, CDCl_3) δ 0.2, 0.4, 27.7, 29.5, 48.0, 58.7, 76.1, 120.9, 127.1, 131.0, 145.8, 196.7; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{25}\text{BrO}_2\text{SSi}$ 388.0528, found 388.0528. The ee value (91%; Table 1, entry 2) was determined after transforming (aqueous 1N HCl, THF, room temperature) to **4a** by HPLC analysis using a Chiralcel OD column.



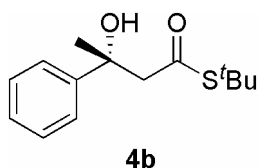
***S*-tert-Butyl (*R*)-3-(4-Bromophenyl)-3-(hydroxydimethylsilyloxy)butanethioate (6):** ^1H NMR (500 MHz, CDCl_3) δ 0.18 (3H, s), 0.19 (3H, s), 1.35 (9H, s), 1.76 (3H, s), 2.91 (1H, d, $J = 13.6$ Hz), 2.93 (1H, d, $J = 13.6$ Hz), 3.15 (1H, s), 7.26–7.29 (2H, m), 7.43–7.46 (2H, m); ^{13}C NMR (125.8 MHz, CDCl_3) δ 0.7, 0.9, 29.5, 29.7, 48.4, 58.4, 76.5, 120.8, 127.0, 131.0, 146.2, 198.4; FT-IR (liquid film) 3409 (br), 1668 cm^{-1} ; HRMS (FAB/*m*-MBA + NaI) calcd for $\text{C}_{16}\text{H}_{25}\text{BrNaO}_3\text{SSi}$ ($\text{M} + \text{Na}^+$) 427.0375, found 427.0388. The ee value (90%; Table 1, entry 2) was determined after transforming (aqueous 1N HCl, THF, room temperature) to **4a** by HPLC analysis using a Chiralcel OD column.



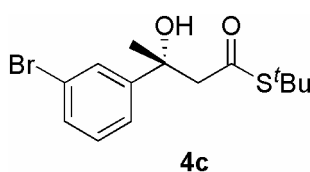
(*S*)-1-(4-Bromophenyl)ethanol (7):⁵ $[\alpha]_{\text{D}}^{21} -20.6$ (c 1.07, MeOH) (44% ee), lit.⁵ $[\alpha]_{\text{D}}^{21} 32.9$ (c 1.39, MeOH) for >99% ee, *R* enantiomer; ^1H NMR (500 MHz, CDCl_3) δ 1.46 (3H, d, $J = 6.5$ Hz), 2.01 (1H, br s), 4.85 (1H, q, $J = 6.5$ Hz), 7.22–7.25 (2H, m), 7.45–7.47 (2H, m); ^{13}C NMR (125.8 MHz, CDCl_3) δ 25.2, 69.7, 121.1, 127.1, 131.5, 144.7. The ee value was determined by GC analysis using a BETA DEXTM

⁵ Mathre, D. J.; Thompson, A. S.; Douglas, A. W.; Hoogsteen, K.; Carroll, J. D.; Corley, E. G.; Grabowski, E. J. J. *J. Org. Chem.* **1993**, 58, 2880–2888.

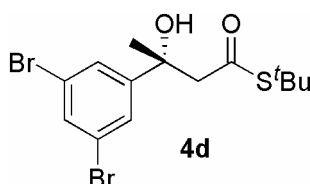
225 (m) column (30 m, 1.8 kg/cm², initial temperature 80 °C, 2 °C/min ramp to 200 °C); retention times: 39.0 min (minor *R*-enantiomer) and 39.4 min (major *S*-enantiomer).



***S*-tert-Butyl (*R*)-3-Hydroxy-3-phenylbutanethioate (4b):** $[\alpha]_{\text{D}}^{18}$ 31.3 (*c* 1.31, CHCl₃) (91% ee); ¹H NMR (500 MHz, CDCl₃) δ 1.35 (9H, s), 1.54 (3H, s), 2.88 (1H, d, *J* = 15.3 Hz), 3.06 (1H, d, *J* = 15.3 Hz), 4.30 (1H, s), 7.22 (1H, br t, *J* = 7.3 Hz), 7.31–7.34 (2H, m), 7.43–7.45 (2H, m); ¹³C NMR (125.8 MHz, CDCl₃) δ 29.5, 30.1, 48.7, 55.3, 74.0, 124.6, 126.7, 128.1, 146.4, 201.3. HRMS (EI) calcd for C₁₄H₂₀O₂S 252.1184, found 252.1187. Anal. calcd for C₁₄H₂₀O₂S: C, 66.63; H, 7.99. Found: C, 66.24; H, 8.32. The ee value was determined by HPLC analysis using a Chiralcel OD column (1 mL/min, 0.1%, *i*-PrOH in hexane); retention times: 17.6 min (major *R*-enantiomer) and 21.6 min (minor *S*-enantiomer). The absolute stereochemistry was determined by correlation (*vide infra*).

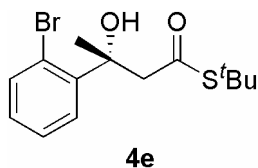


***S*-tert-Butyl (*R*)-3-(3-Bromophenyl)-3-hydroxybutanethioate (4c):** $[\alpha]_{\text{D}}^{18}$ 34.8 (*c* 1.72, CHCl₃) (91% ee); ¹H NMR (500 MHz, CDCl₃) δ 1.36 (9H, s), 1.51 (3H, s), 2.85 (1H, d, *J* = 15.4 Hz), 3.01 (1H, d, *J* = 15.4 Hz), 4.36 (1H, s), 7.19 (1H, t, *J* = 4.1 Hz), 7.33–7.37 (2H, m), 7.61 (1H, t, *J* = 1.9 Hz); ¹³C NMR (125.8 MHz, CDCl₃) δ 29.5, 30.0, 49.0, 54.9, 73.8, 122.5, 123.3, 128.1, 129.7, 129.9, 148.9, 201.2; HRMS (EI) calcd for C₁₄H₁₉BrO₂S 330.0289, found 330.0286. The ee value was determined by HPLC analysis using a Chiralpak AD-H column (1 mL/min, 0.5%, *i*-PrOH in hexane); retention times: 21.9 min (minor *S*-enantiomer) and 23.0 min (major *R*-enantiomer). The absolute stereochemistry was assumed by analogy.

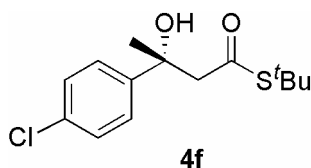


***S*-tert-Butyl (*R*)-3-(3,5-Dibromophenyl)-3-hydroxybutanethioate (4d):** $[\alpha]_{\text{D}}^{16}$ 39.8 (*c* 1.02, CHCl₃) (94% ee); ¹H NMR (500 MHz, CDCl₃) δ 1.38 (9H, s), 1.50 (3H, s), 2.84 (1H, d, *J* = 15.4 Hz), 2.98 (1H, d, *J* = 15.4 Hz), 4.40 (1H, s), 7.52 (2H, d, *J* = 1.7 Hz), 7.54 (1H, t, *J* = 1.7 Hz); ¹³C NMR (125.8 MHz, CDCl₃) δ 29.5, 29.9, 49.3, 54.6, 73.6, 122.9, 127.0, 132.5, 150.6, 201.1; HRMS (EI) calcd for

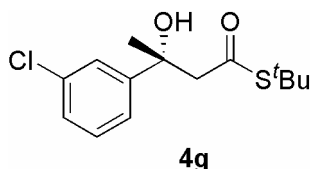
$C_{14}H_{18}Br_2O_2S$ 409.9374, found 409.9374. The ee value was determined by HPLC analysis using a Chiralpak AD-H column (1 mL/min, 0.5%, *i*-PrOH in hexane); retention times: 11.7 min (major *R*-enantiomer) and 16.6 min (minor *S*-enantiomer). The absolute stereochemistry was assumed by analogy.



***S*-tert-Butyl (*R*)-3-(2-Bromophenyl)-3-hydroxybutanethioate (4e):** $[\alpha]_D^{16}$ 100.7 (*c* 1.06, $CHCl_3$) (92% ee); 1H NMR (500 MHz, $CDCl_3$) δ 1.29 (9H, s), 1.62 (3H, s), 3.00 (1H, d, $J = 15.1$ Hz), 3.78 (1H, d, $J = 15.1$ Hz), 4.66 (1H, s), 7.08 (1H, dt, $J = 1.6$ and 7.6 Hz), 7.29 (1H, dd, $J = 1.2$ and 8.3 Hz), 7.56 (1H, dd, $J = 1.2$ and 7.9 Hz), 7.83 (1H, dd, $J = 1.7$ and 8.0 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 26.9, 29.4, 48.6, 52.0, 74.8, 119.9, 127.4, 128.4, 128.7, 134.8, 144.0, 201.8; HRMS (FAB/*m*-NBA) calcd for $C_{14}H_{20}BrO_2S$ ($M+H^+$) 331.0367, found 331.0372. The ee value was determined by HPLC analysis using a Chiralpak AD-H column (1 mL/min, 0.5%, *i*-PrOH in hexane); retention times: 17.2 min (major *R*-enantiomer) and 20.8 min (minor *S*-enantiomer). The absolute stereochemistry was assumed by analogy.

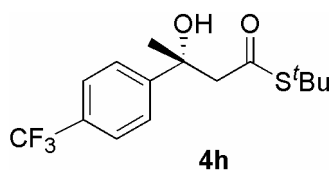


***S*-tert-Butyl (*R*)-3-(4-Chlorophenyl)-3-hydroxybutanethioate (4f):** $[\alpha]_D^{18}$ 23.5 (*c* 1.09, $CHCl_3$) (93% ee); 1H NMR (500 MHz, $CDCl_3$) δ 1.35 (9H, s), 1.50 (3H, s), 2.85 (1H, d, $J = 15.4$ Hz), 3.02 (1H, d, $J = 15.4$ Hz), 4.35 (1H, s), 7.27–7.30 (2H, m), 7.35–7.38 (2H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.5, 30.1, 48.9, 55.0, 73.8, 126.2, 128.2, 132.6, 145.1, 201.2; HRMS (EI) calcd for $C_{14}H_{19}ClO_2S$ 286.0794, found 286.0781. The ee value was determined by HPLC analysis using a Chiralpak AD-H column (1 mL/min, 0.5%, *i*-PrOH in hexane); retention times: 23.1 min (minor *S*-enantiomer) and 30.8 min (major *R*-enantiomer). The absolute stereochemistry was assumed by analogy.

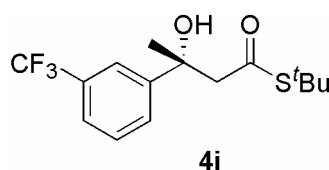


***S*-tert-Butyl (*R*)-3-(3-Chlorophenyl)-3-hydroxybutanethioate (4g):** $[\alpha]_D^{18}$ 26.1 (*c* 1.00, $CHCl_3$) (95% ee); 1H NMR (500 MHz, $CDCl_3$) δ 1.36 (9H, s), 1.51 (3H, s), 2.85 (1H, d, $J = 15.4$ Hz), 3.01 (1H, d, $J = 15.4$ Hz), 4.36 (1H, s), 7.18–7.30 (3H, m), 7.45 (1H, t, $J = 1.9$ Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.4, 30.0, 49.0, 54.9, 73.8, 122.9, 125.2, 127.0, 129.4, 134.1, 148.6, 201.2; HRMS (EI) calcd for

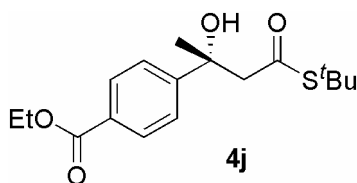
C₁₄H₁₉ClO₂S 286.0794, found 286.0801. The ee value was determined by HPLC analysis using a Chiralpak AD-H column (1 mL/min, 0.5%, *i*-PrOH in hexane); retention times: 17.7 min (minor *S*-enantiomer) and 22.6 min (major *R*-enantiomer). The absolute stereochemistry was assumed by analogy.



***S*-tert-Butyl (*R*)-3-(4-Trifluoromethylphenyl)-3-hydroxybutanethioate (4h):** $[\alpha]_{\text{D}}^{18}$ 28.7 (*c* 1.15, CHCl₃) (92% ee); ¹H NMR (500 MHz, CDCl₃) δ 1.34 (9H, s), 1.53 (3H, s), 2.90 (1H, d, *J* = 15.5 Hz), 3.06 (1H, d, *J* = 15.5 Hz), 4.43 (1H, s), 7.55–7.60 (4H, m); ¹³C NMR (125.8 MHz, CDCl₃) δ 29.4, 30.1, 49.0, 54.8, 74.0, 124.2 (q, *J* = 272 Hz), 125.1 (q, *J* = 4 Hz), 125.2, 129.1 (q, *J* = 32 Hz), 150.5, 201.2; HRMS (EI) calcd for C₁₅H₁₉F₃O₂S 320.1058, found 320.1051. The ee value was determined by HPLC analysis using a Chiralpak AD-H column (1 mL/min, 0.5%, *i*-PrOH in hexane); retention times: 20.4 min (minor *S*-enantiomer) and 23.0 min (major *R*-enantiomer). The absolute stereochemistry was assumed by analogy.

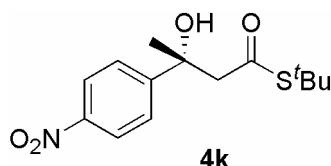


***S*-tert-Butyl (*R*)-3-(3-Trifluoromethylphenyl)-3-hydroxybutanethioate (4i):** $[\alpha]_{\text{D}}^{13}$ 20.4 (*c* 1.01, CHCl₃) (94% ee); ¹H NMR (500 MHz, CDCl₃) δ 1.32 (9H, s), 1.54 (3H, s), 2.88 (1H, d, *J* = 15.3 Hz), 3.05 (1H, d, *J* = 15.3 Hz), 4.45 (1H, s), 7.44 (1H, br t, *J* = 7.7 Hz), 7.49 (1H, br d, *J* = 7.8 Hz), 7.62 (1H, br d, *J* = 7.7 Hz), 7.72 (1H, br s); ¹³C NMR (125.8 MHz, CDCl₃) δ 29.3, 30.0, 48.9, 54.9, 73.9, 121.7 (q, *J* = 4 Hz), 123.7 (q, *J* = 4 Hz), 124.2 (q, *J* = 272 Hz), 128.2, 128.6, 130.4 (q, *J* = 32 Hz), 147.6, 201.2; HRMS (EI) calcd for C₁₅H₁₉F₃O₂S 320.1058, found 320.1054. The ee value was determined by HPLC analysis using a Chiralpak AD-H column (1 mL/min, 0.5%, *i*-PrOH in hexane); retention times: 11.4 min (major *R*-enantiomer) and 14.6 min (minor *S*-enantiomer). The absolute stereochemistry was assumed by analogy.

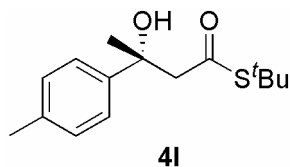


***S*-tert-Butyl (*R*)-3-(4-Ethoxycarbonylphenyl)-3-hydroxybutanethioate (4j):** $[\alpha]_{\text{D}}^{21}$ 17.0 (*c* 1.05, CHCl₃) (94% ee); ¹H NMR (500 MHz, CDCl₃) δ 1.34 (9H, s), 1.39 (3H, t, *J* = 7.1 Hz), 1.52 (3H, s), 2.90

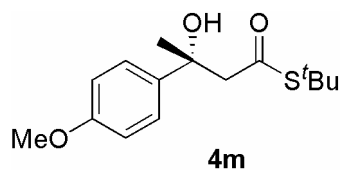
(1H, d, $J = 15.5$ Hz), 3.08 (1H, d, $J = 15.5$ Hz), 4.37 (2H, q, $J = 7.1$ Hz), 4.41 (1H, s), 7.49–7.51 (2H, m), 7.99–8.01 (2H, m); ^{13}C NMR (125.8 MHz, CDCl_3) δ 14.3, 29.5, 30.1, 49.0, 54.8, 60.8, 74.1, 124.7, 129.0, 129.5, 151.5, 166.5, 201.2; HRMS (FAB/ m -NBA) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_4\text{S}$ ($\text{M}+\text{H}^+$) 325.1474, found 325.1466. The ee value was determined by HPLC analysis using a Chiralpak AD-H column (1 mL/min, 4%, i -PrOH in hexane); retention times: 17.0 min (minor S -enantiomer) and 18.6 min (major R -enantiomer). The absolute stereochemistry was assumed by analogy.



***S*-tert-Butyl (*R*)-3-Hydroxy-3-(4-nitrophenyl)butanethioate (4k):** $[\alpha]_{\text{D}}^{18}$ 31.0 (c 1.89, CHCl_3) (98% ee); ^1H NMR (500 MHz, CDCl_3) δ 1.34 (9H, s), 1.53 (3H, s), 2.92 (1H, d, $J = 15.6$ Hz), 3.08 (1H, d, $J = 15.6$ Hz), 4.52 (1H, s), 7.59–7.63 (2H, m), 8.17–8.20 (2H, m); ^{13}C NMR (125.8 MHz, CDCl_3) δ 29.4, 30.1, 49.3, 54.5, 74.1, 123.4, 125.8, 146.9, 153.9, 201.1; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_4\text{S}$ 297.1035, found 297.1030. The ee value was determined by HPLC analysis using a Chiralcel OD column (1 mL/min, 1%, i -PrOH in hexane); retention times: 18.6 min (major R -enantiomer) and 29.9 min (minor S -enantiomer). The absolute stereochemistry was assumed by analogy.

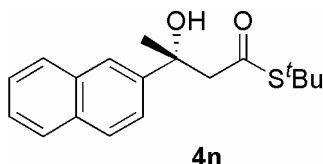


***S*-tert-Butyl (*R*)-3-Hydroxy-3-(4-methylphenyl)butanethioate (4l):** $[\alpha]_{\text{D}}^{21}$ 17.4 (c 1.00, CHCl_3) (92% ee); ^1H NMR (500 MHz, CDCl_3) δ 1.38 (9H, s), 1.53 (3H, s), 2.33 (3H, s), 2.88 (1H, d, $J = 15.4$ Hz), 3.04 (1H, d, $J = 15.4$ Hz), 4.25 (1H, s), 7.13–7.15 (2H, m), 7.32–7.34 (2H, m); ^{13}C NMR (125.8 MHz, CDCl_3) δ 20.9, 29.5, 30.1, 48.7, 55.3, 73.9, 124.5, 128.8, 136.2, 143.6, 201.3. HRMS (EI) calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{S}$ 266.1341, found 266.1340. The ee value was determined by HPLC analysis using a Chiralcel OD column (1 mL/min, 0.1%, i -PrOH in hexane); retention times: 17.2 min (major R -enantiomer) and 20.6 min (minor S -enantiomer). The absolute stereochemistry was assumed by analogy.

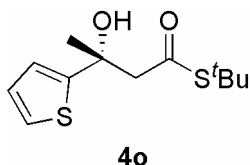


***S*-tert-Butyl (*R*)-3-Hydroxy-3-(4-methoxyphenyl)butanethioate (4m):** $[\alpha]_{\text{D}}^{18}$ 20.2 (c 1.62, CHCl_3) (81% ee); ^1H NMR (500 MHz, CDCl_3) δ 1.37 (9H, s), 1.52 (3H, s), 2.86 (1H, d, $J = 15.4$ Hz), 3.03 (1H, d,

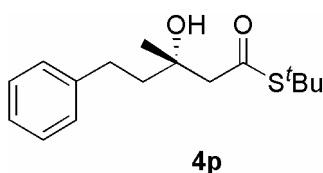
$J = 15.3$ Hz), 3.80 (3H, s), 4.25 (1H, s), 6.85–6.88 (2H, m), 7.34–7.37 (2H, m); ^{13}C NMR (125.8 MHz, CDCl_3) δ 29.5, 30.2, 48.7, 55.2, 55.4, 73.8, 113.4, 125.8, 138.8, 158.3, 201.4; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3\text{S}$ 282.1290, found 282.1286. The ee value was determined by HPLC analysis using a Chiralcel OD column (1 mL/min, 0.5%, *i*-PrOH in hexane); retention times: 15.6 min (major *R*-enantiomer) and 19.1 min (minor *S*-enantiomer). The absolute stereochemistry was assumed by analogy.



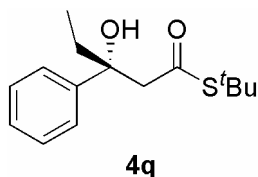
***S*-tert-Butyl (*R*)-3-Hydroxy-3-(2-naphthyl)butanethioate (4n):** $[\alpha]^{19}_{\text{D}} 23.0$ (*c* 1.00, CHCl_3) (97% ee); ^1H NMR (500 MHz, CDCl_3) δ 1.32 (9H, s), 1.63 (3H, s), 2.98 (1H, d, $J = 15.5$ Hz), 3.17 (1H, d, $J = 15.5$ Hz), 4.45 (1H, s), 7.44–7.49 (2H, m), 7.54 (1H, dd, $J = 1.8$ and 8.6 Hz), 7.80–7.86 (3H, m), 7.94 (1H, br s); ^{13}C NMR (125.8 MHz, CDCl_3) δ 29.5, 30.1, 48.9, 55.1, 74.3, 123.2, 123.3, 125.7, 126.0, 127.4, 127.9, 128.2, 132.3, 133.1, 143.9, 201.4; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{S}$ 302.1340, found 302.1349. The ee value was determined by HPLC analysis using a Chiralcel OD column (1 mL/min, 0.1%, *i*-PrOH in hexane); retention times: 7.2 min (major *R*-enantiomer) and 13.9 min (minor *S*-enantiomer). The absolute stereochemistry was assumed by analogy.



***S*-tert-Butyl (*R*)-3-Hydroxy-(2-thienyl)butanethioate (4o):** $[\alpha]^{18}_{\text{D}} 11.7$ (*c* 1.32, CHCl_3) (55% ee); ^1H NMR (500 MHz, CDCl_3) δ 1.40 (9H, s), 1.62 (3H, s), 2.91 (1H, d, $J = 15.4$ Hz), 3.07 (1H, d, $J = 15.4$ Hz), 4.61 (1H, br s), 6.89 (1H, dd, $J = 1.2$ and 3.6 Hz), 6.92 (1H, dd, $J = 3.6$ and 5.0 Hz), 7.17 (1H, dd, $J = 1.2$ and 5.0 Hz); ^{13}C NMR (125.8 MHz, CDCl_3) δ 29.5, 30.8, 48.9, 55.7, 73.2, 122.2, 123.9, 126.6, 151.8, 201.0; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}_2$ 258.0748, found 258.0754. The ee value was determined by HPLC analysis using a Chiralpak AD-H column (1 mL/min, 0.5%, *i*-PrOH in hexane); retention times: 11.6 min (major *R*-enantiomer) and 13.1 min (minor *S*-enantiomer). The absolute stereochemistry was assumed by analogy.

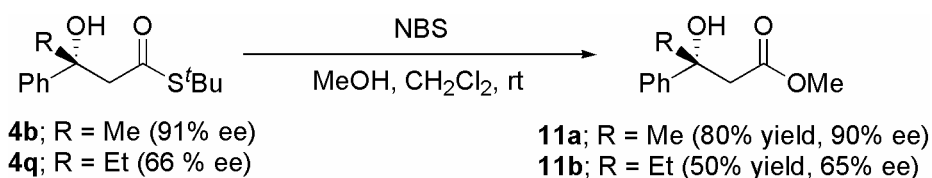


***S*-tert-Butyl (S)-3-Hydroxy-3-methyl-5-phenylpentanethioate (4p)** $[\alpha]_D^{18} -2.6$ (c 1.48, CHCl_3) (52% ee); ^1H NMR (500 MHz, CDCl_3) δ 1.31 (3H, s), 1.50 (9H, s), 1.80–1.86 (2H, m), 2.65 (1H, d, $J = 15.1$ Hz), 2.70–2.74 (3H, m), 3.60 (1H, s), 7.18–7.22 (3H, m), 7.27–7.30 (2H, m); ^{13}C NMR (125.8 MHz, CDCl_3) δ 26.7, 29.6, 30.3, 43.9, 48.7, 53.7, 72.2, 125.7, 128.26, 128.33, 142.2, 201.4; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{S}$ 280.1497, found 280.1490. The ee value was determined by HPLC analysis using a Chiralcel OD column (1 mL/min, 1%, *i*-PrOH in hexane); retention times: 14.2 min (major *S*-enantiomer) and 16.8 min (minor *R*-enantiomer). The absolute stereochemistry was assumed by analogy.



***S*-tert-Butyl (R)-3-Hydroxy-3-phenylpentanethioate (4q):** $[\alpha]_D^{18} 16.3$ (c 1.61, CHCl_3) (for 66% ee); ^1H NMR (500 MHz, CDCl_3) δ 0.76 (3H, t, $J = 7.4$ Hz), 1.32 (9H, s), 1.81 (2H, m), 2.89 (1H, d, $J = 15.3$ Hz), 3.06 (1H, d, $J = 15.3$ Hz), 4.24 (1H, s), 7.22 (1H, m), 7.30–7.33 (2H, m), 7.37–7.39 (2H, m); ^{13}C NMR (125.8 MHz, CDCl_3) δ 7.7, 29.5, 35.5, 48.7, 53.9, 76.7, 125.3, 126.6, 127.9, 144.7, 201.7; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{S}$ 266.1341, found 266.1347. The ee value was determined by HPLC analysis using a Chiralcel OD column (1 mL/min, 0.1%, *i*-PrOH in hexane); retention times: 12.6 min (major *R*-enantiomer) and 14.2 min (minor *S*-enantiomer). The absolute stereochemistry was determined by correlation (*vide infra*).

Absolute Structure Determination of 4b and 4q. Treatment of **4b** (91% ee) with NBS in methanol and dichloromethane⁶ gave **11a** (90% ee) in 80% yield. The absolute configuration of **4b** was determined to be *R* based on the specific rotation of methyl ester **11a**. The *R* stereochemistry of **4q** was established also by transforming it to methyl ester **11b**.



***O*-Methyl (R)-3-Hydroxy-3-phenylbutanoate (11a):** To a solution of **4b** (108 mg, 0.428 mmol, 91% ee) and methanol (0.47 mL, 12 mmol) in CH_2Cl_2 (1.3 mL) at room temperature was added *N*-bromosuccinimide (91.3 mg, 0.513 mmol). After being stirred for 1 h at room temperature, the mixture

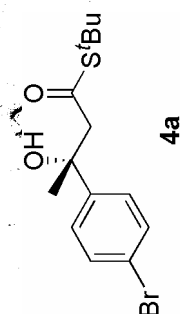
⁶ Minato, H.; Kodama, H.; Miura, T.; Kobayashi, M. *Chem. Lett.* **1977**, 413–416.

was extracted twice with ethyl acetate. The mixture was poured into aqueous NaHCO₃ and extracted three times with ethyl acetate. The organic layers were dried (Na₂SO₄) and concentrated in vacuo. Purification of the residue by flash chromatography (20–50% ethyl acetate in hexane) gave 66.3 mg (80% yield) of (*R*)-**8a**: $[\alpha]^{21}_{\text{D}}$ 6.5 (*c* 1.49, EtOH) (90% ee), lit.⁷ $[\alpha]^{24}_{\text{D}}$ –5.6 (*c* 1.09, EtOH) for 83% ee, *S* enantiomer; ¹H NMR (500 MHz, CDCl₃) δ 1.55 (3H, s), 2.81 (1H, d, *J* = 16.0 Hz), 2.99 (1H, d, *J* = 16.0 Hz), 3.60 (3H, s), 4.33 (1H, br s), 7.24 (1H, m), 7.32–7.35 (2H, m), 7.44–7.46 (2H, m); ¹³C NMR (125.8 MHz, CDCl₃) δ 30.5, 46.1, 51.6, 72.6, 124.3, 126.8, 128.2, 146.8, 173.0. The ee value was determined by HPLC analysis using a Chiralcel OD column (1 mL/min, 1%, *i*-PrOH in hexane); retention times: 13.5 min (major *R*-enantiomer) and 15.6 min (minor *S*-enantiomer).

O-Methyl (*R*)-3-Hydroxy-3-phenylpentanoate (**11b**): The compound was prepared in 52% yield from **4q** (66% ee) according to a procedure similar to that described above. (*R*)-**8b**: $[\alpha]^{21}_{\text{D}}$ –0.97 (*c* 1.03, EtOH) (65% ee), lit.⁸ $[\alpha]^{14}_{\text{D}}$ 1.64 (*c* 0.85, EtOH) for 77% ee, *S* enantiomer; ¹H NMR (500 MHz, CDCl₃) δ 0.76 (3H, t, *J* = 7.4 Hz), 1.77–1.85 (2H, m), 2.81 (1H, d, *J* = 16.0 Hz), 2.98 (1H, d, *J* = 16.0 Hz), 3.57 (3H, s), 4.28 (3H, s), 7.23 (1H, m), 7.31–7.34 (2H, m), 7.38–7.40 (2H, m); ¹³C NMR (125.8 MHz, CDCl₃) δ 7.8, 35.8, 44.7, 51.7, 75.1, 125.1, 126.7, 128.1, 145.1, 173.4. The ee value was determined by HPLC analysis using a Chiralcel OJ column (1 mL/min, 0.7% *i*-PrOH in hexane); retention times: 13.8 min (major *R*-enantiomer) and 16.5 min (minor *S*-enantiomer).

⁷ Denmark, S. E.; Fan, Y.; Eastgate, M. D. *J. Org. Chem.* **2005**, *70*, 5235–5248.

⁸ Oisaki, K.; Zhao, D.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 7164–7165.

¹H NMR (500 MHz, CDCl₃) Spectrum of 4a

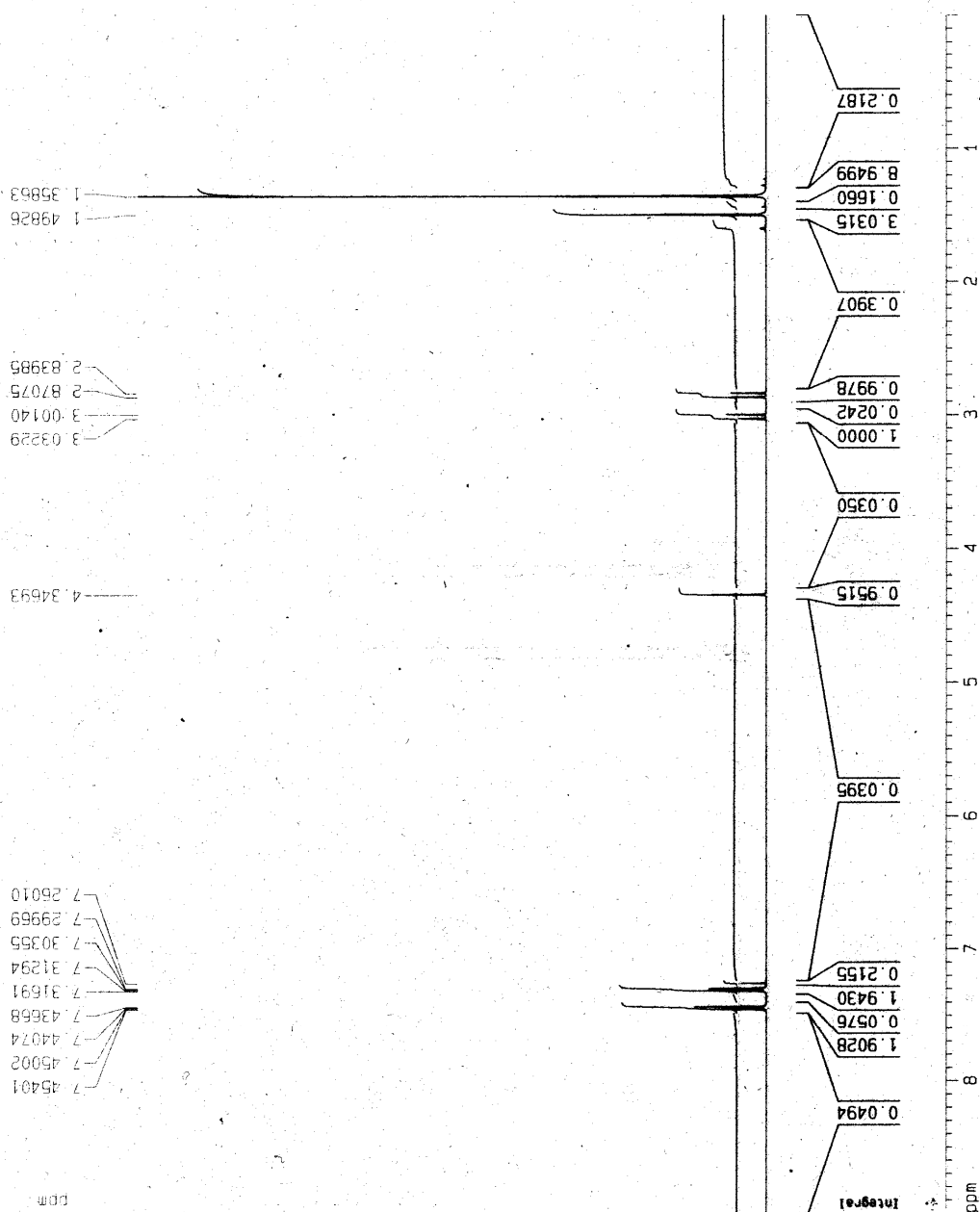
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EXPNO 1
PROCNO 1

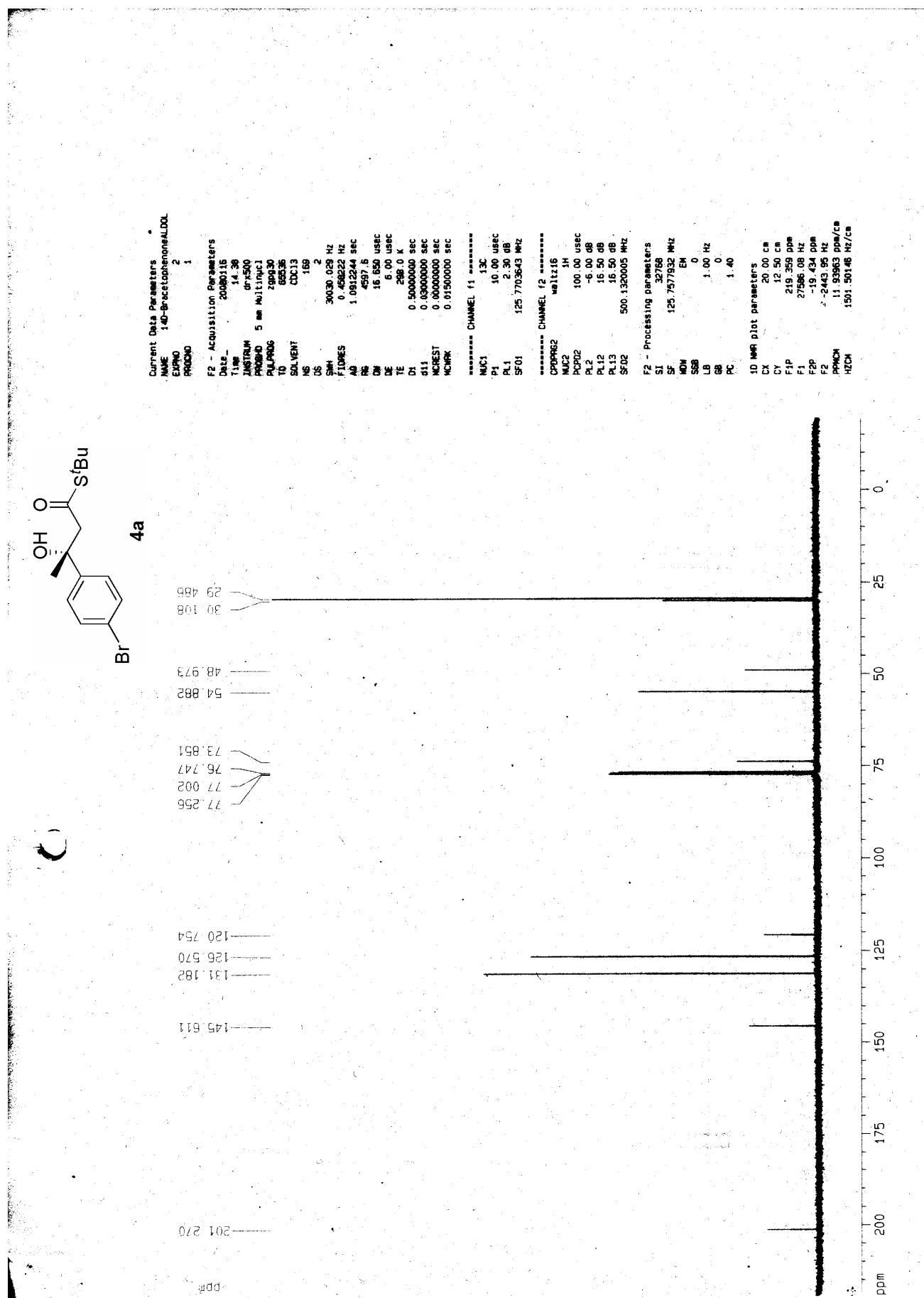
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SWH 10330.578 Hz
FIDRES 0.197632 Hz
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DM 48 400 usec
DE 6.00 usec
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MCWRR 0.01500000 sec

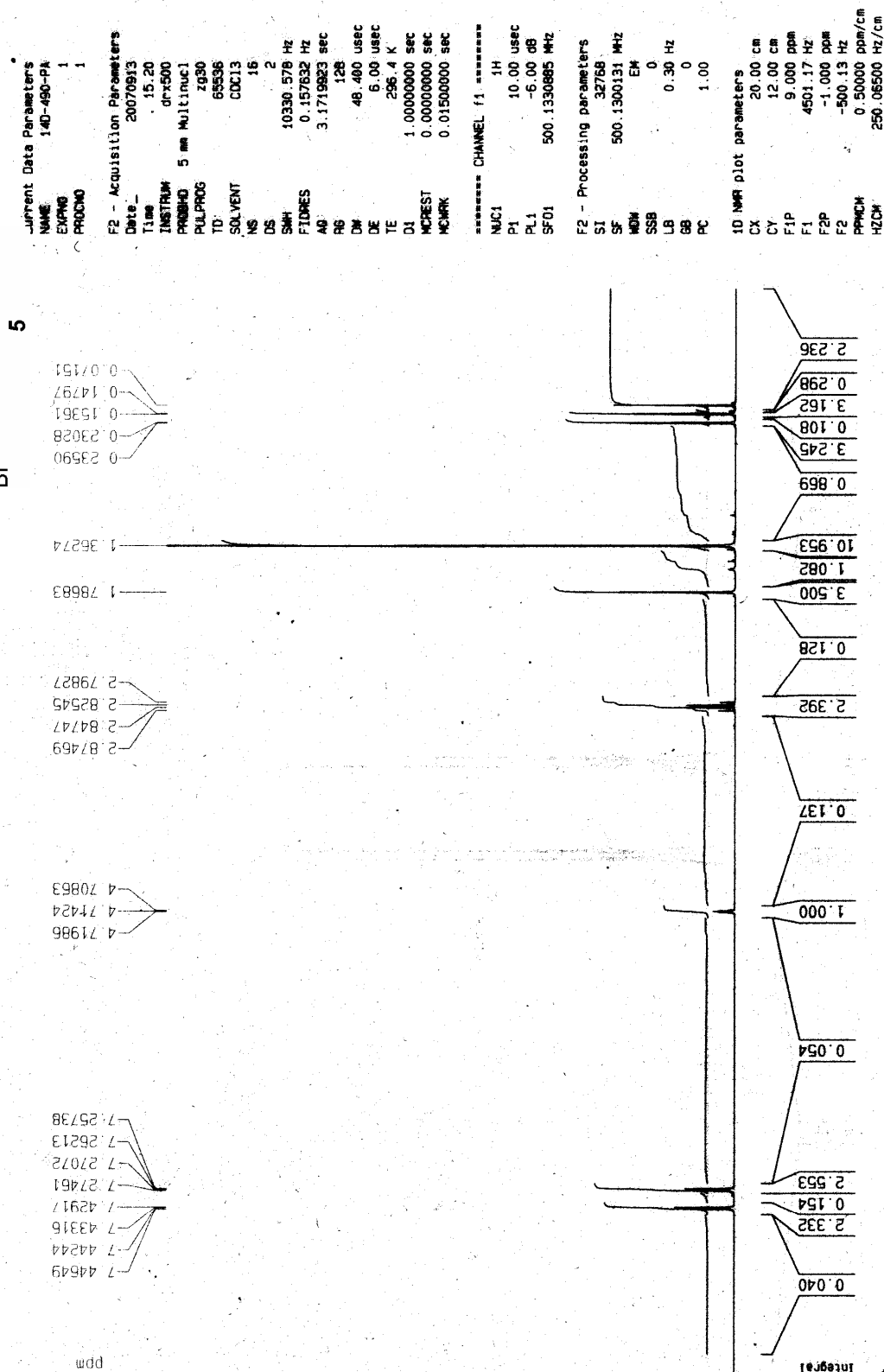
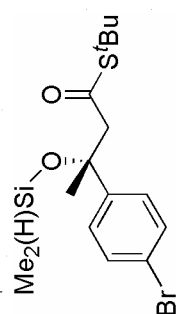
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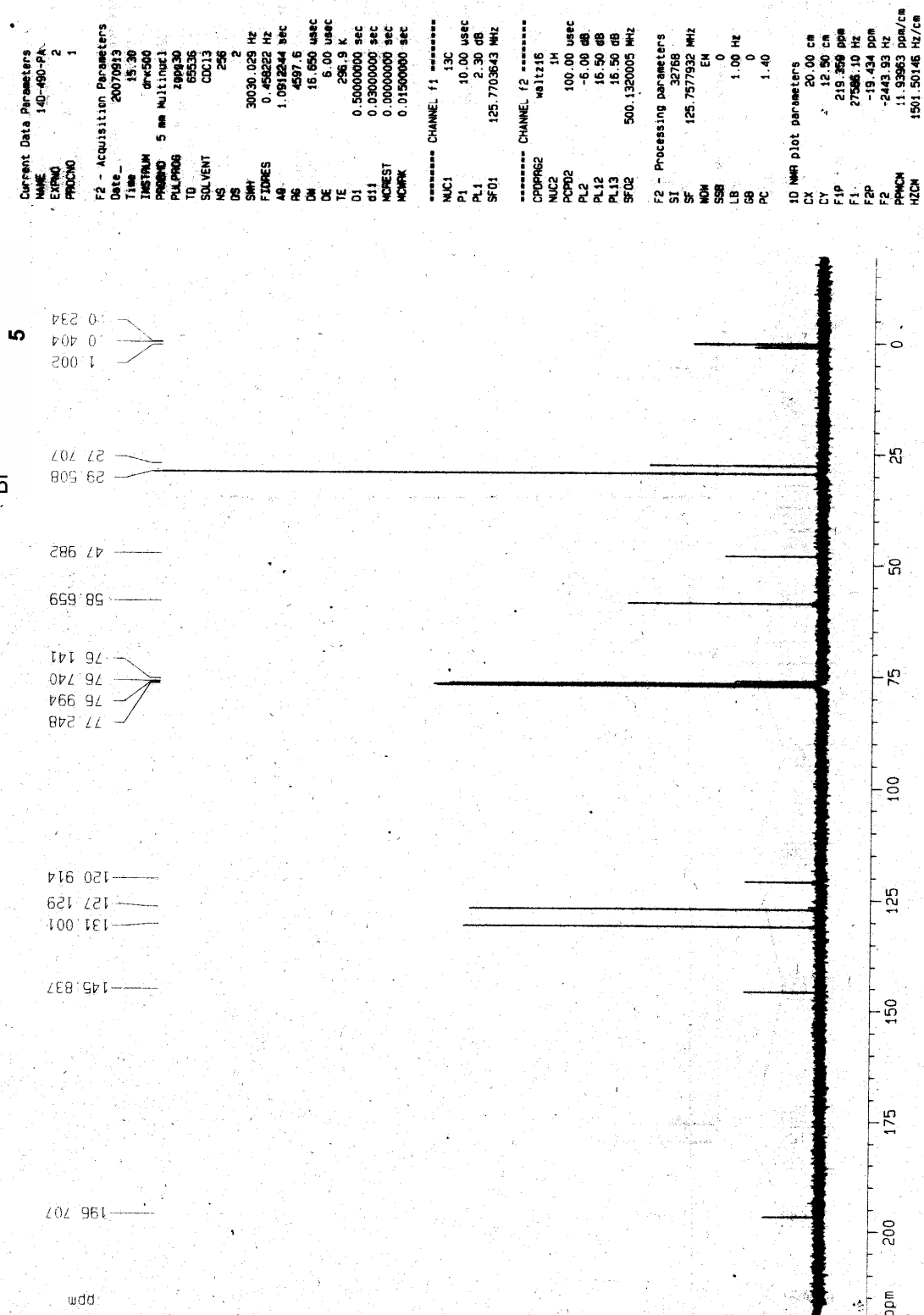
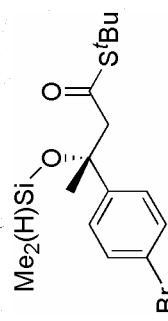
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WDW EM
SSB 0
LB 0.30 Hz
GB 0
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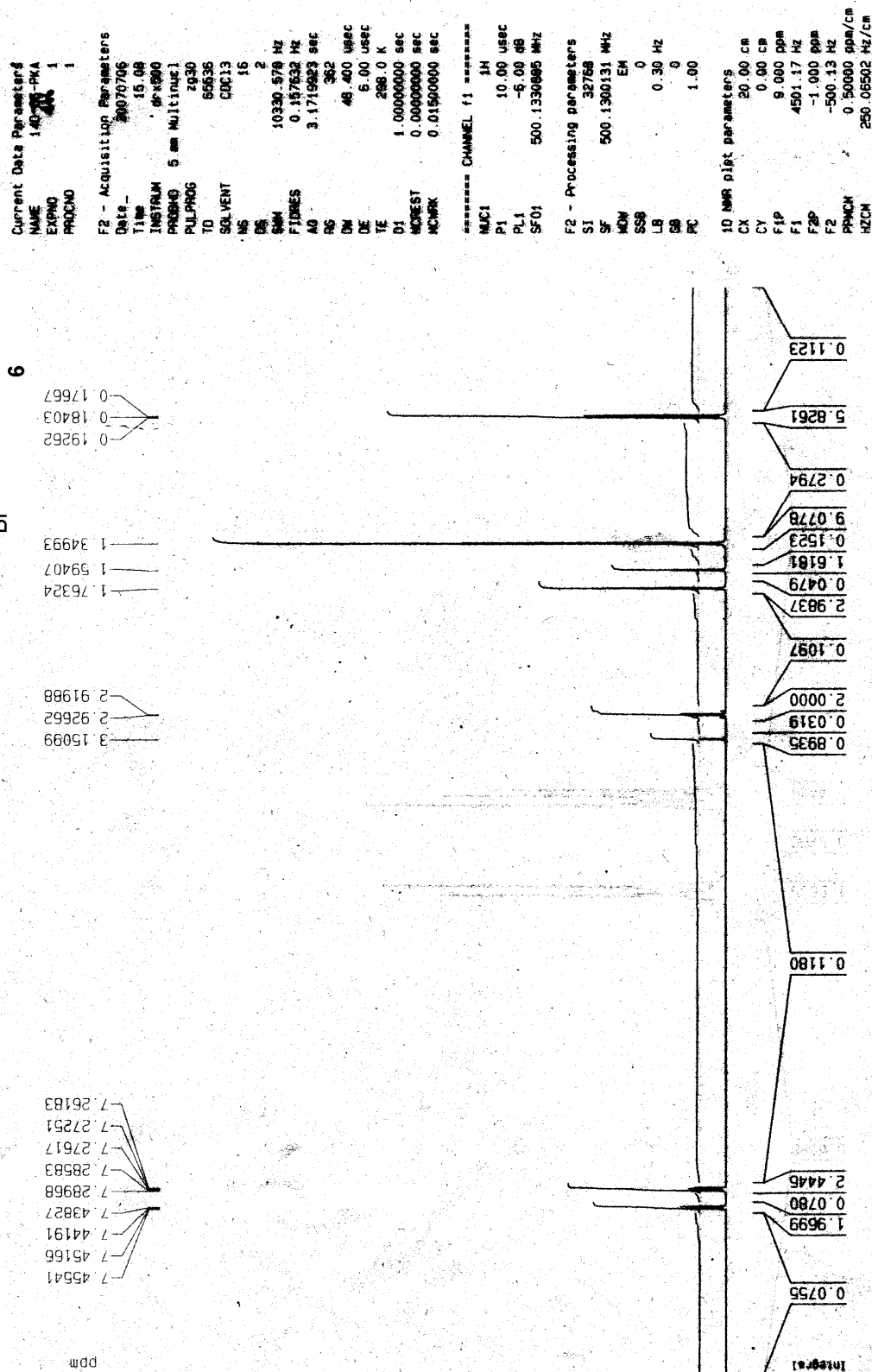
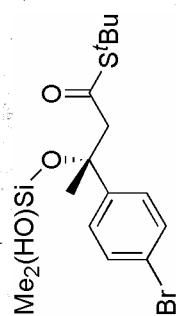
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F1 4501.17 Hz
FAP 0.000 ppm
F2 0.00 Hz
PRGM 0.45000 ppm/cm
HZCN 295.03848 Hz/cm

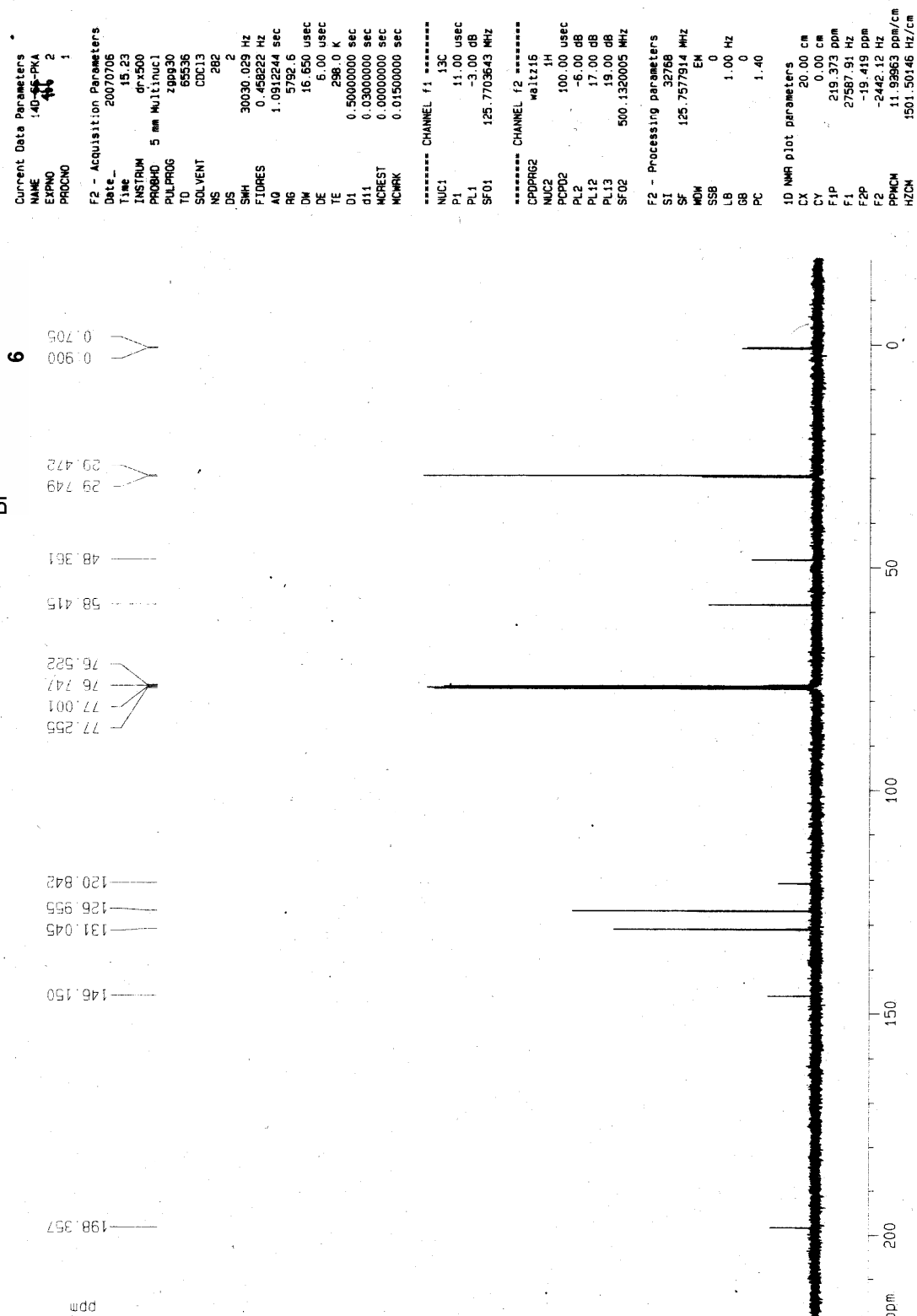
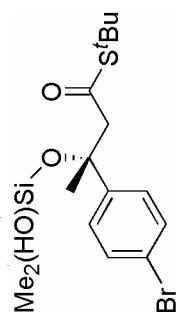


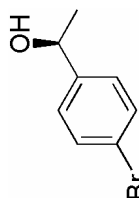
¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4a

¹H NMR (500 MHz, CDCl₃) Spectrum of 5

¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 5

¹H NMR (500 MHz, CDCl₃) Spectrum of 6

¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 6

¹H NMR (500 MHz, CDCl₃) Spectrum of 7

7

Current Data Parameters

NAME 140-00-PK
EXPNO 1
PROCNO 1

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PULPROG zg30
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FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 256
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TE 298.0 K
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MCREST 0.00000000 sec
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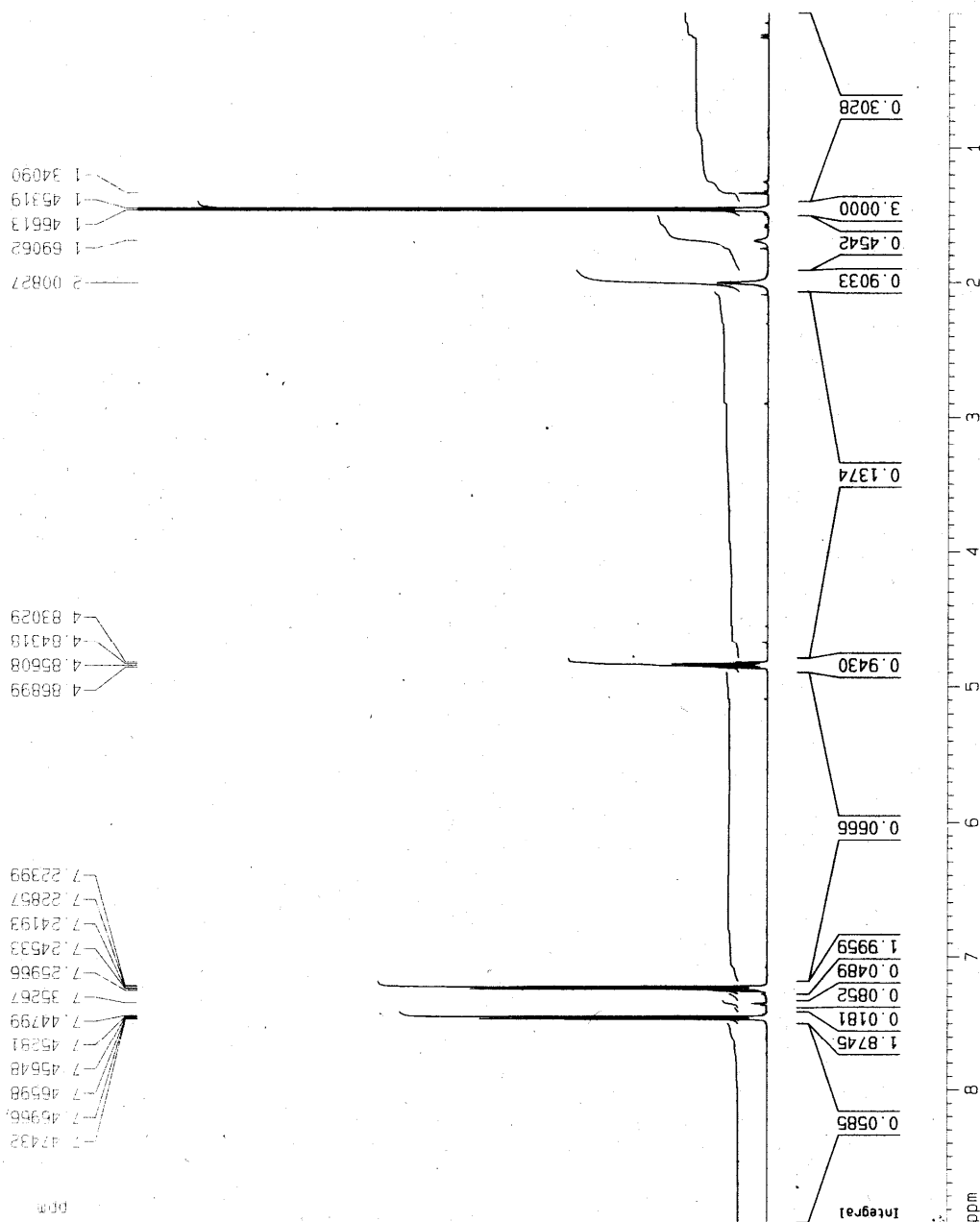
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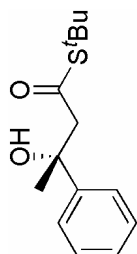
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PC 1.00

10 NMR plot parameters

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FIP 9.000 ppm
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F2 0.000 ppm
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¹H NMR (500 MHz, CDCl₃) Spectrum of 4b

4b

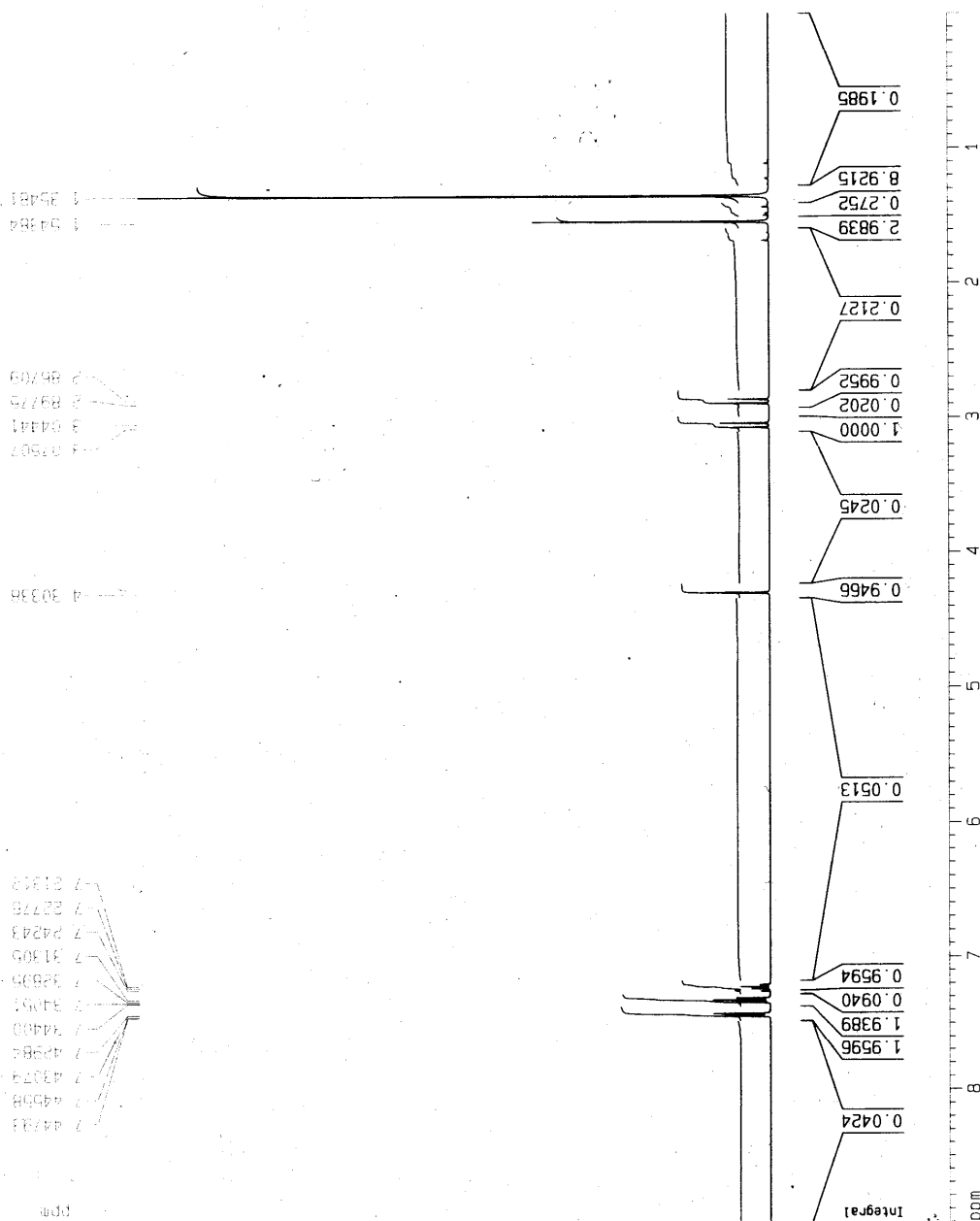
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 PROCNO 1

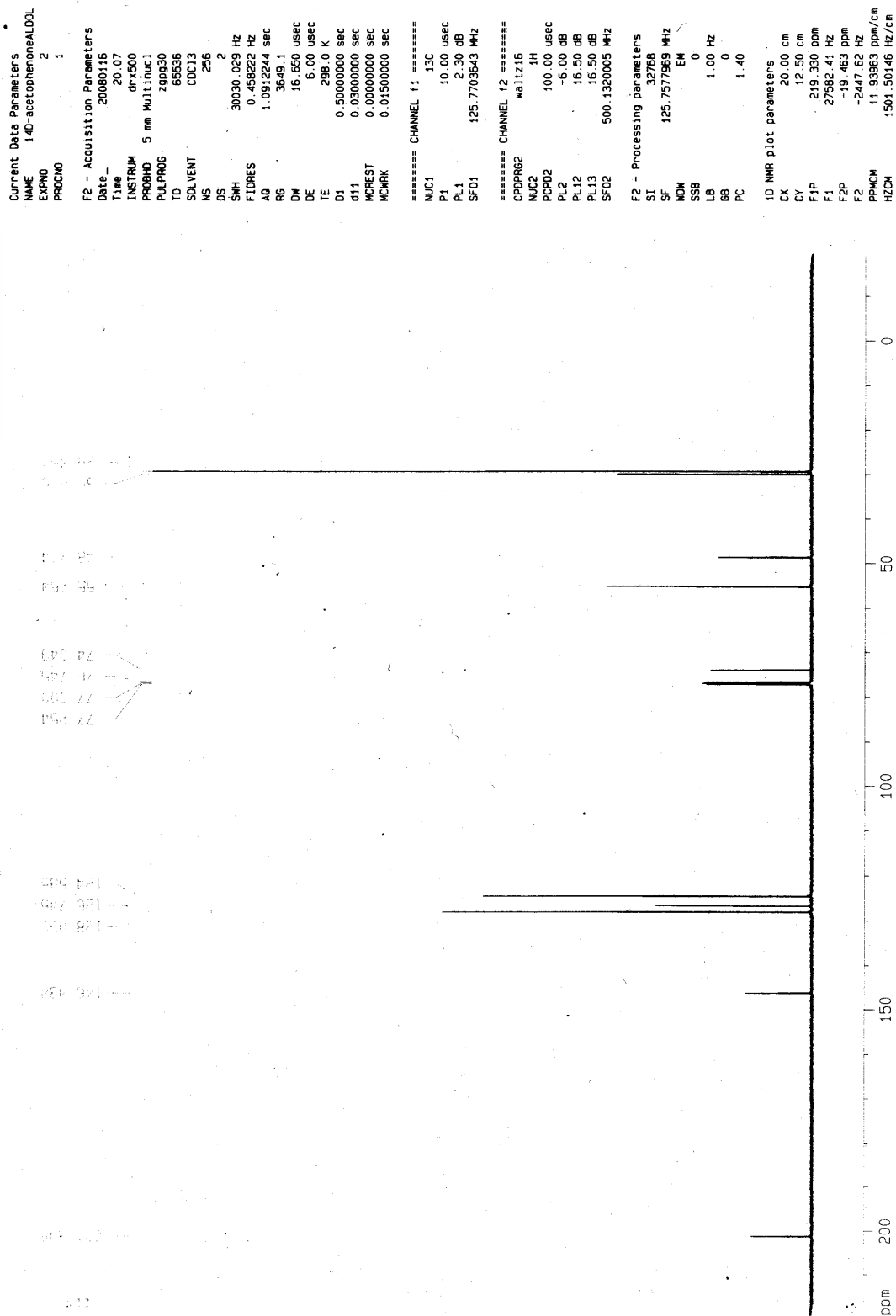
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 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 71.8
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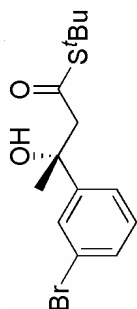
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F2 - Processing parameters
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1D NMR plot parameters
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 F2 0.00 Hz
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 HZCM 225.05849 Hz/cm







4c

```

Current Data Parameters
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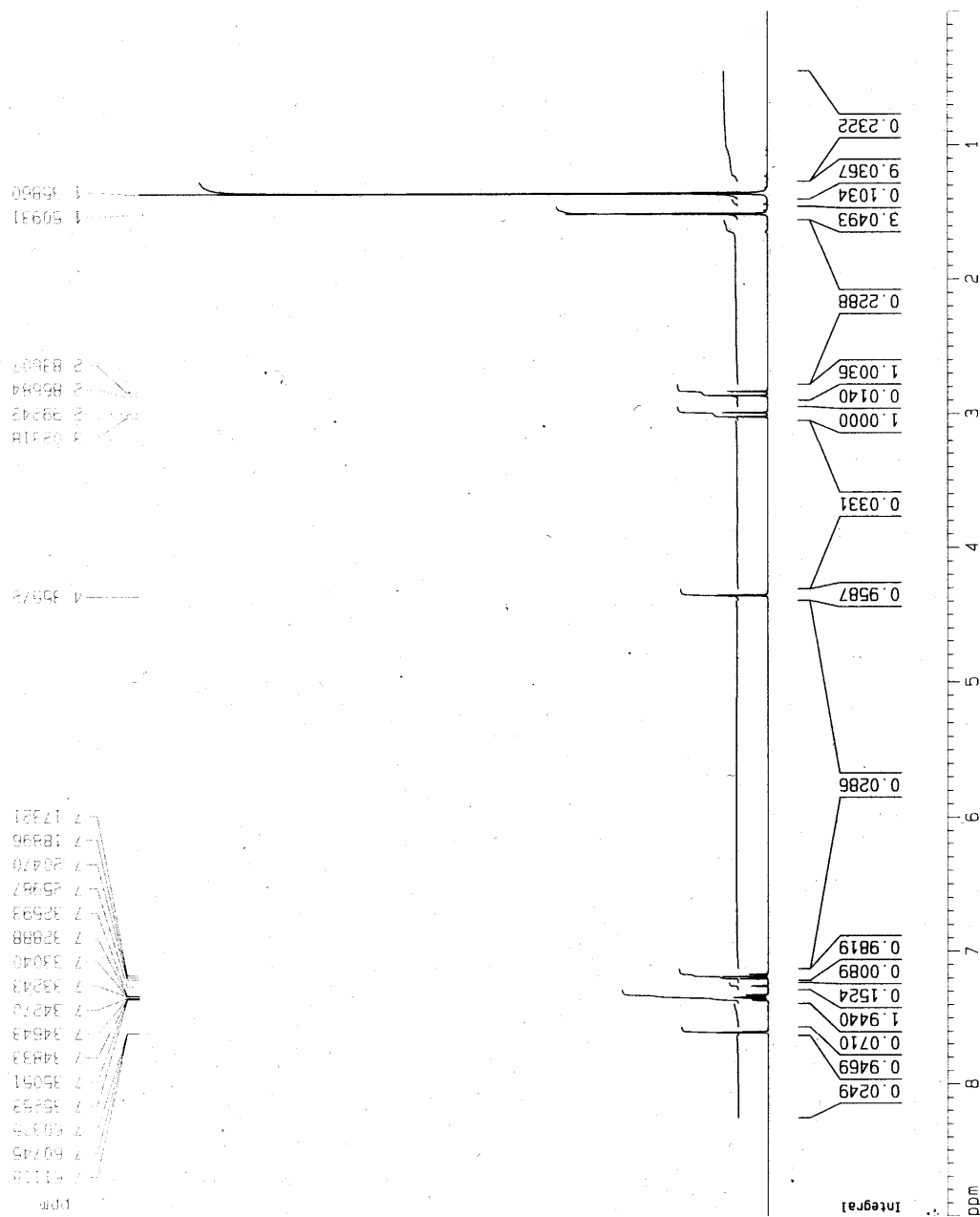
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RG         71.8
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PL1        -6.00 dB
SFO1       500.1330885 MHz

F2 - Processing parameters
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WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

1D NMR plot parameters
=====
CX         20.00 cm
CY         12.50 cm
F1P        9.000 ppm
F1         4501.17 Hz
F2P        0.000 ppm
F2         0.00 Hz
PPMCHM     0.45000 ppm/cm
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```



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4c

Current Data Parameters
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EXPNO 2
PROCNO 1

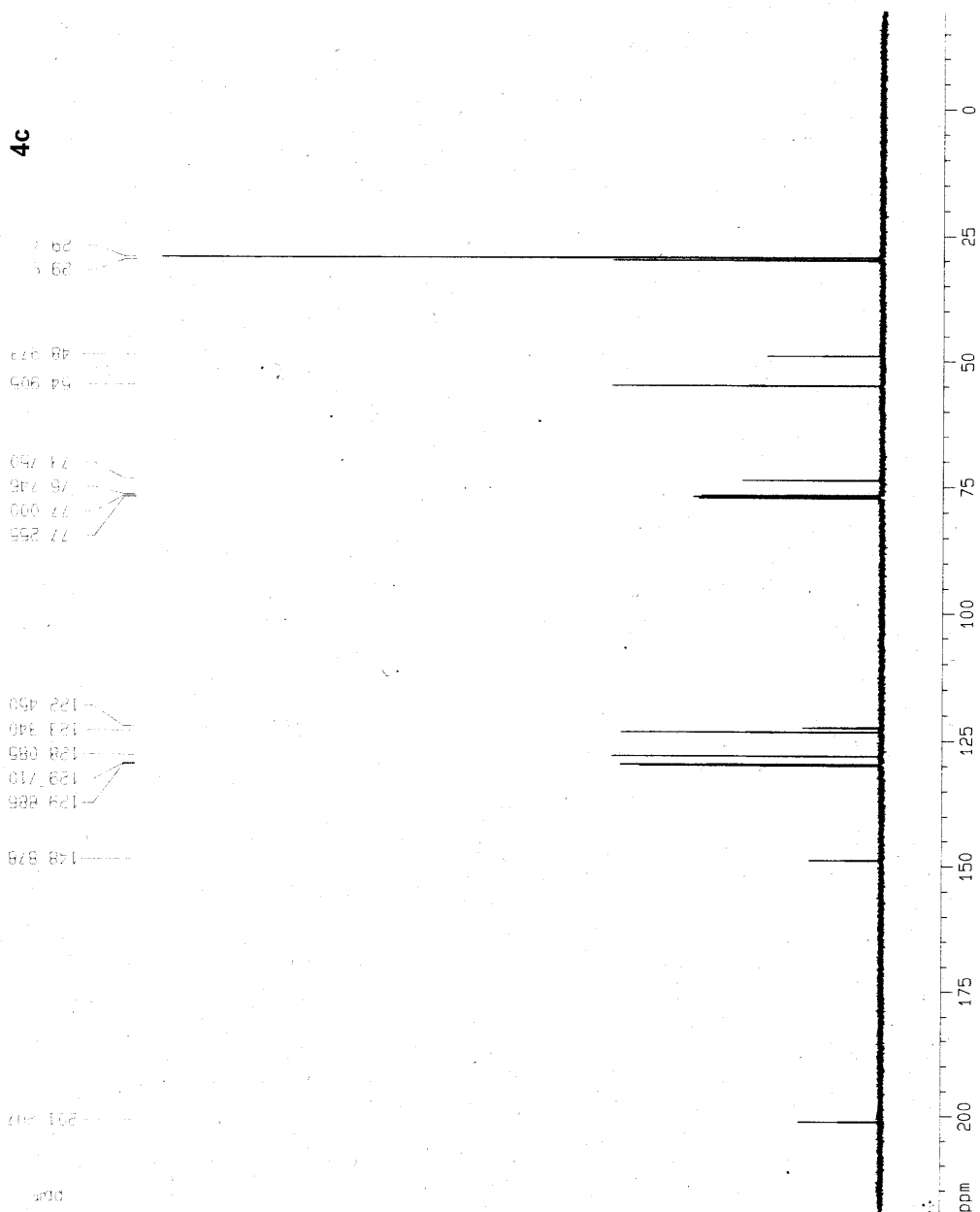
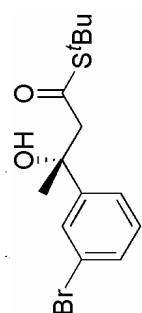
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RG 3649.1
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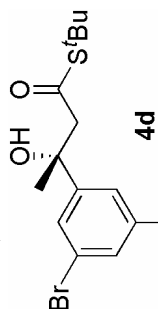
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PL12 16.50 dB
PL13 16.50 dB
SF02 500.1320005 MHz

F2 - Processing parameters
SI 32768
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
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CY 12.50 cm
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¹H NMR (500 MHz, CDCl₃) Spectrum of 4d

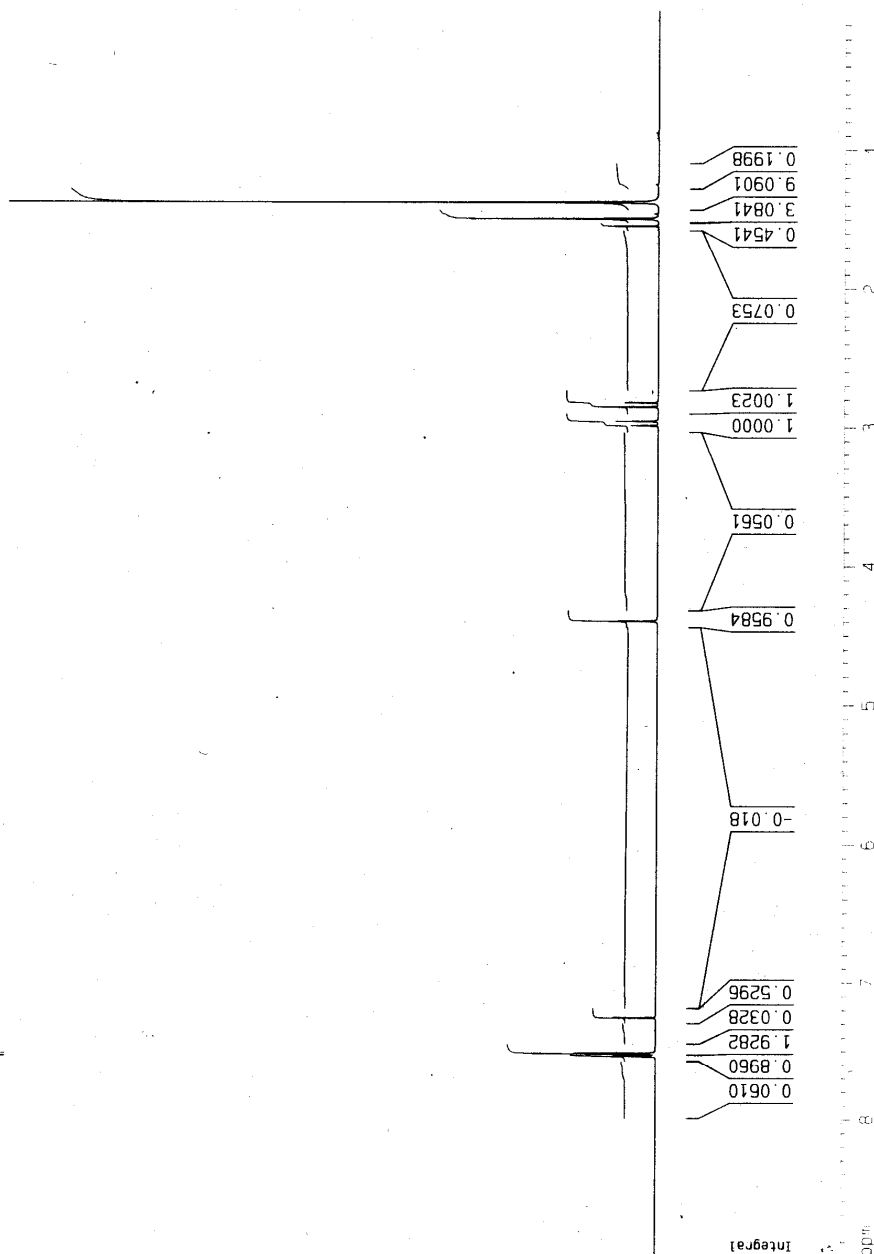
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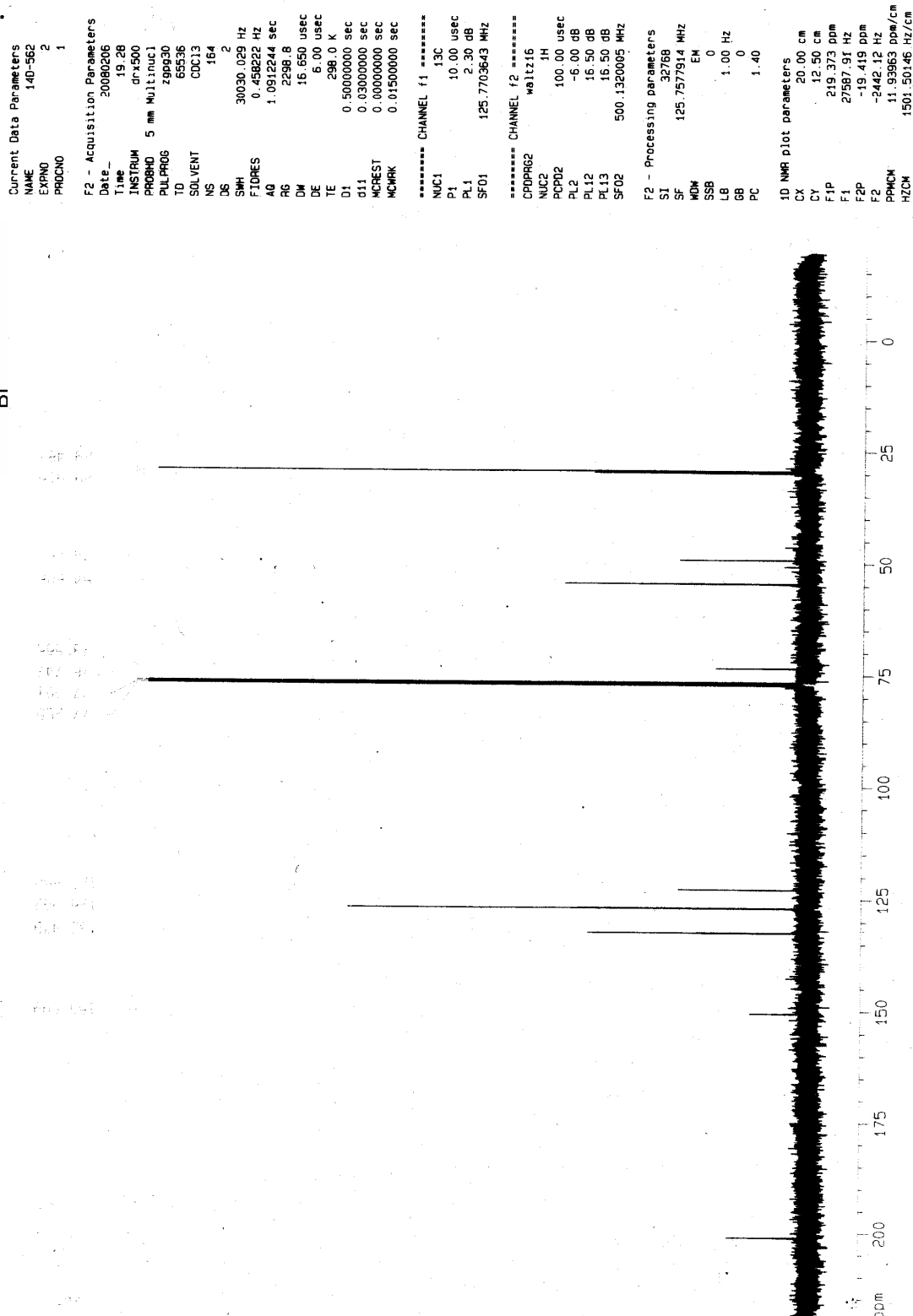
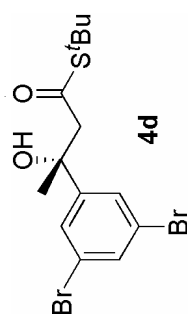
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AQ 3.171923 sec
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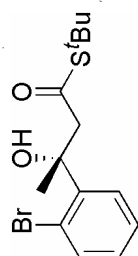
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LB 0.30 Hz
GB 0
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1D NMR plot parameters
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CY 12.50 cm
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F1 4501.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05849 Hz/cm



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4d

¹H NMR (500 MHz, CDCl₃) Spectrum of 4e

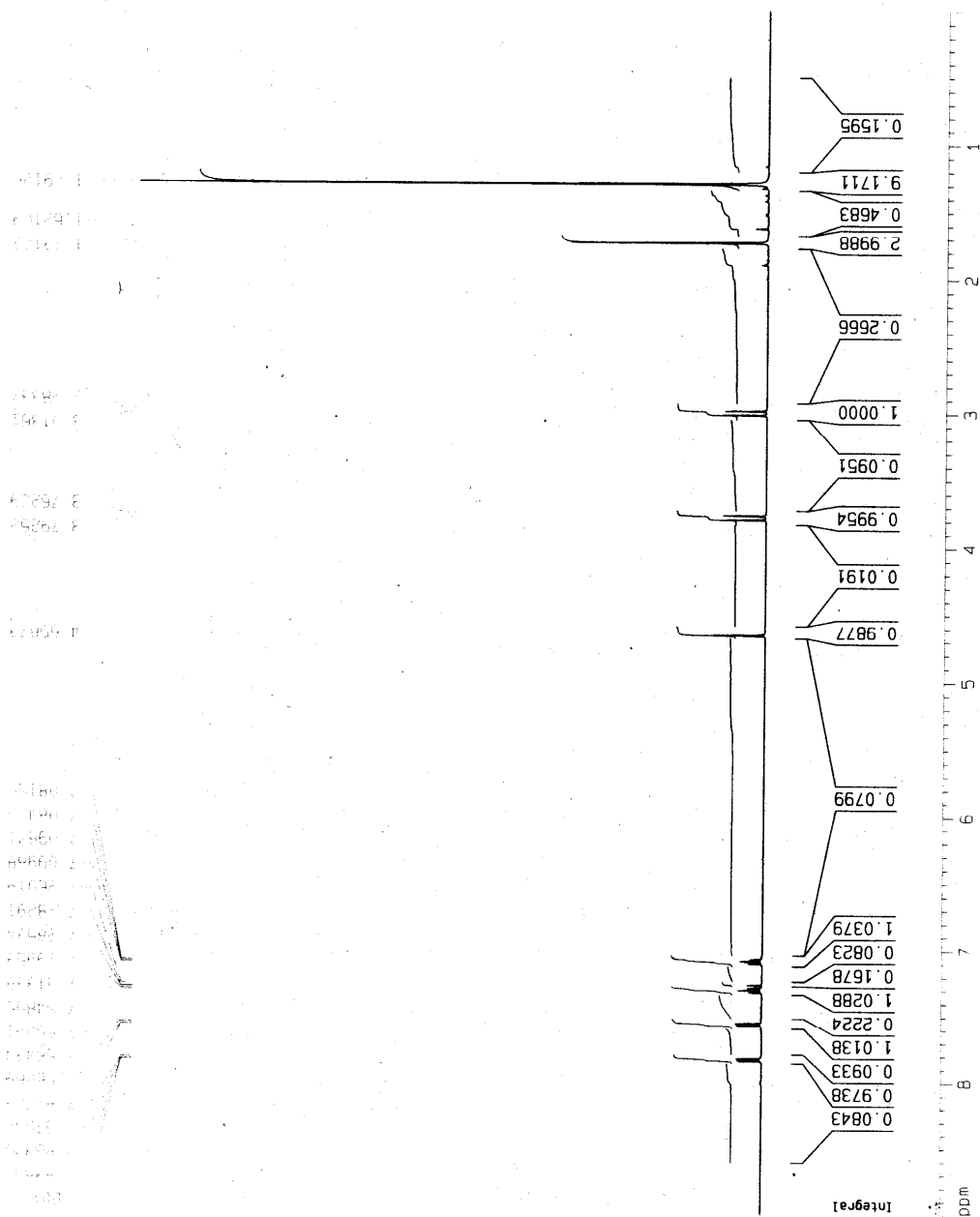
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PROCNO 1

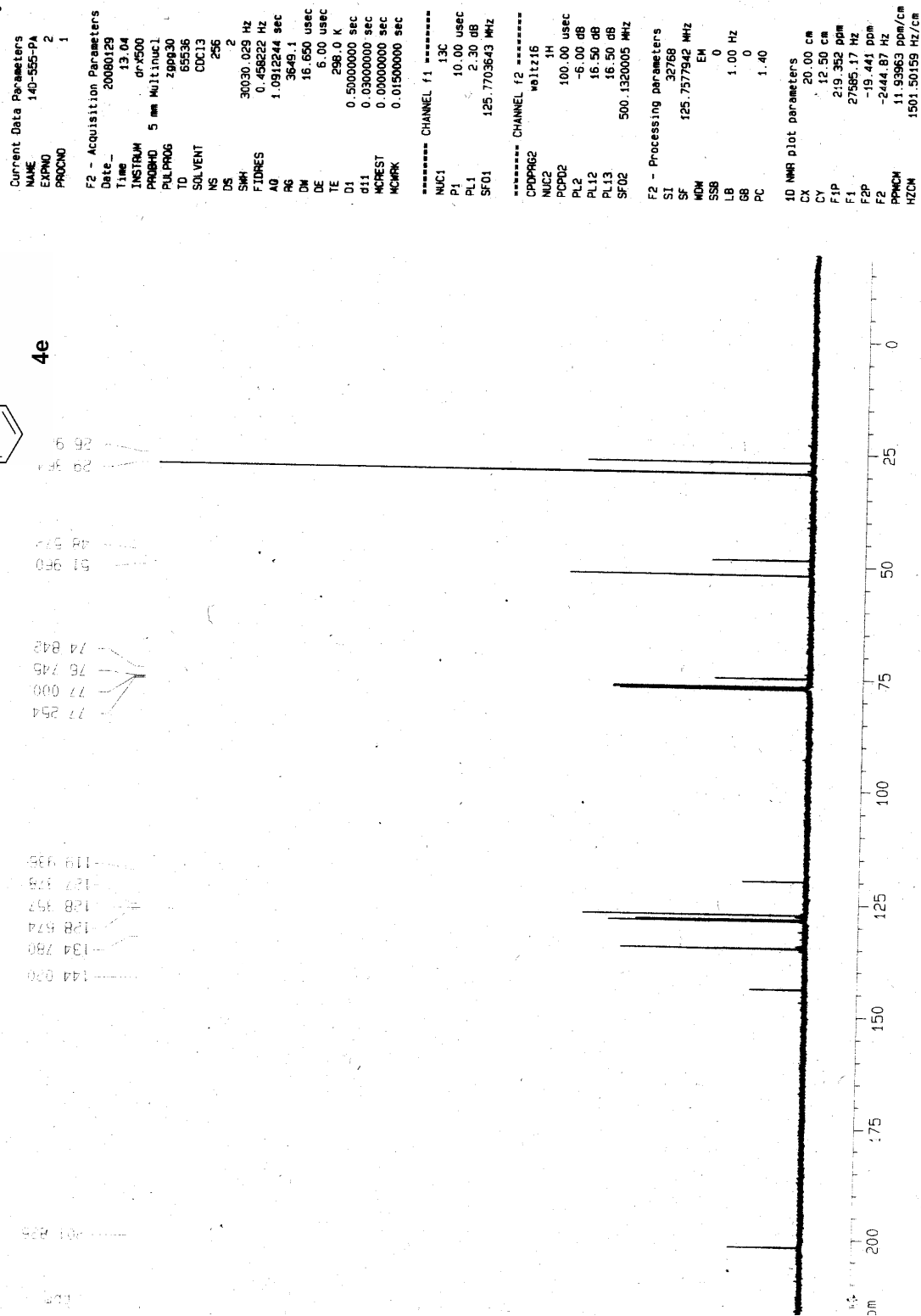
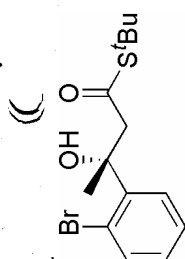
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AQ 3.1719923 sec
RG 114
DM 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWPK 0.01500000 sec

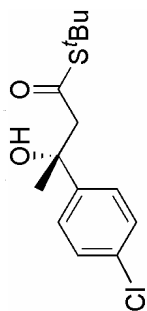
===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -6.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300127 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 9.000 ppm
F1 4501.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05849 Hz/cm



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4e

¹H NMR (500 MHz, CDCl₃) Spectrum of 4f

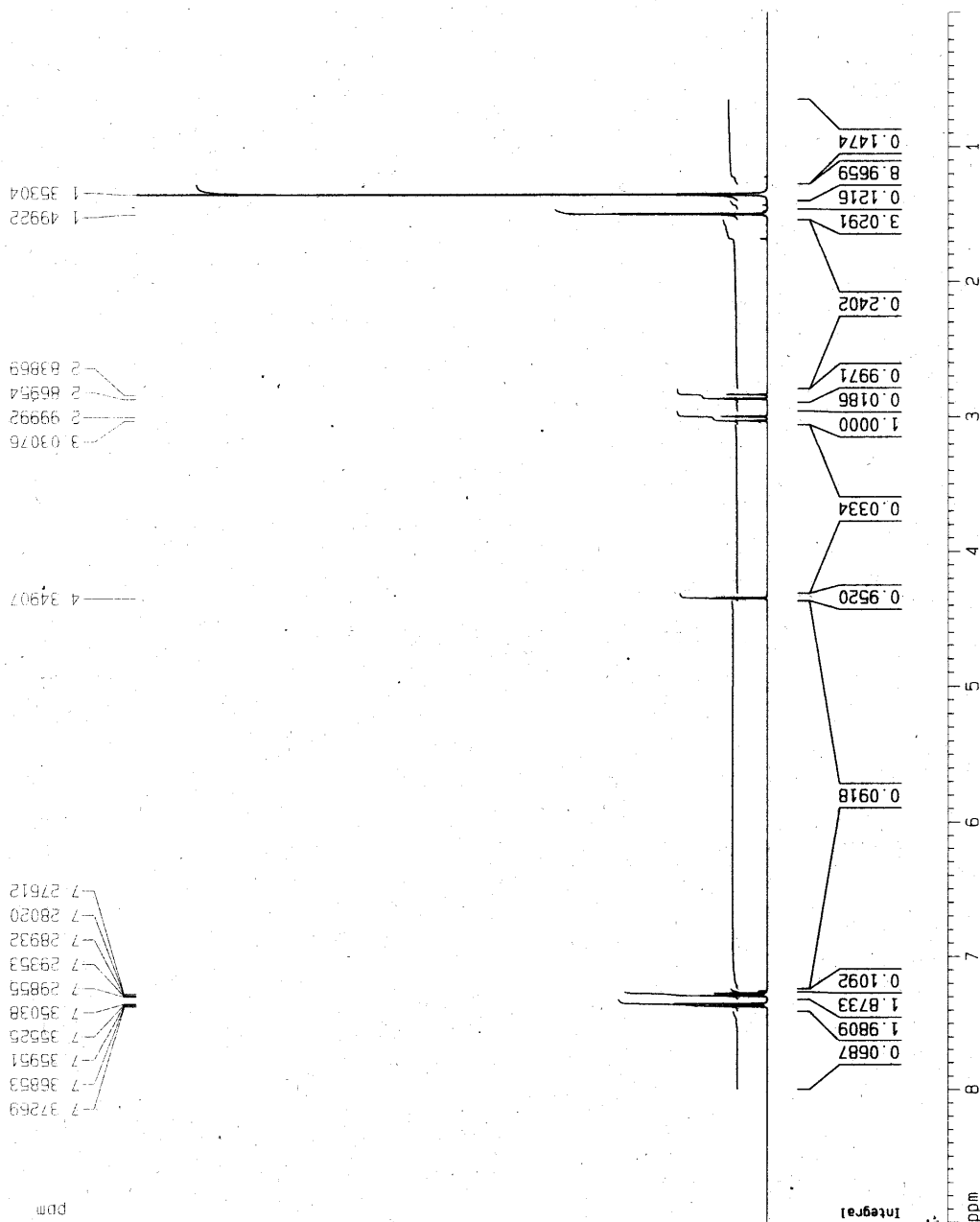
Current Data Parameters
NAME 140-PC1
EXPNO 1
PROCNO 1

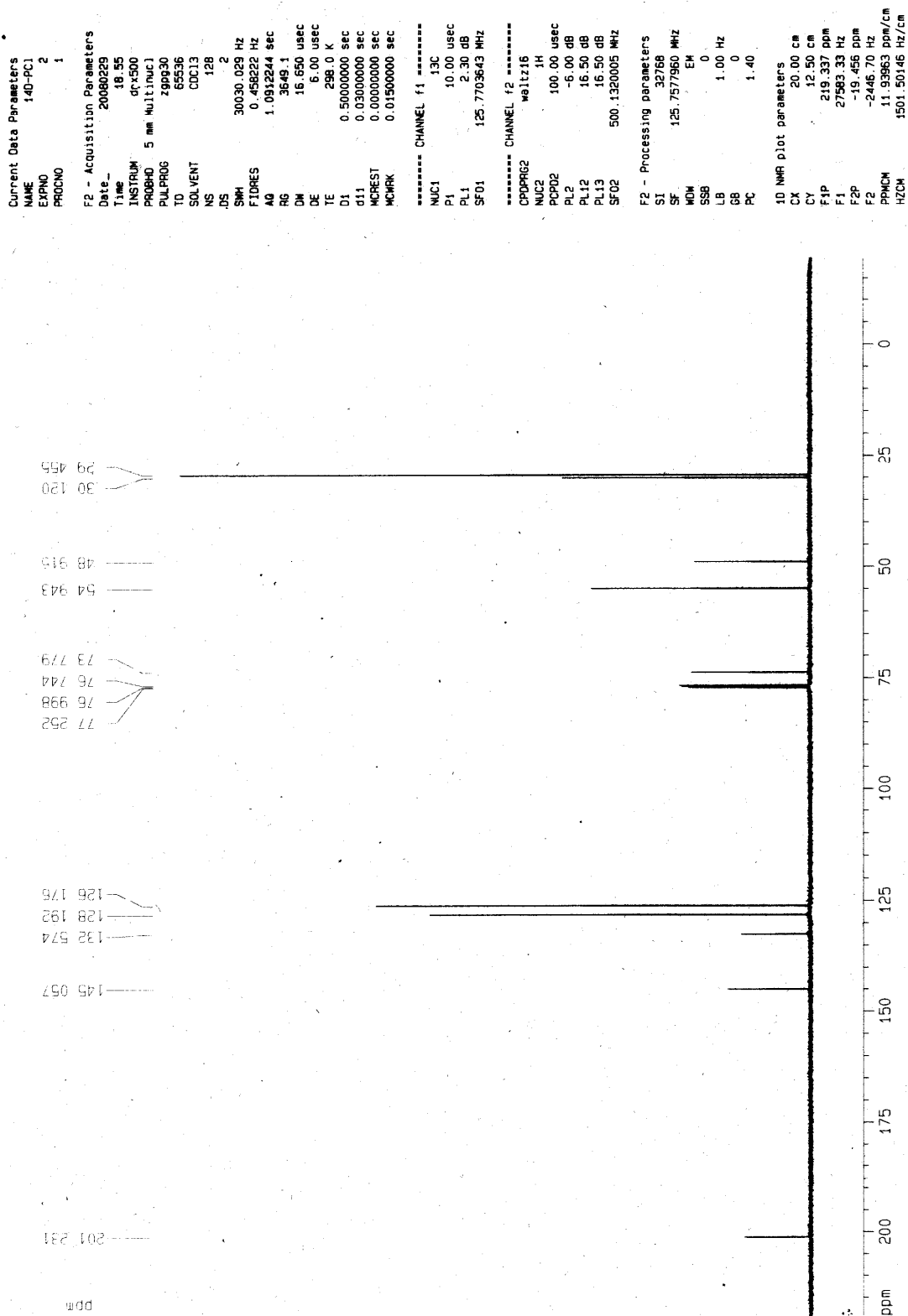
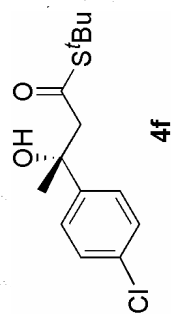
F2 - Acquisition Parameters
Date_ 20080229
Time 18.50
INSTRUM drx500
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl₃
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 71.8
DN 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWPK 0.01500000 sec

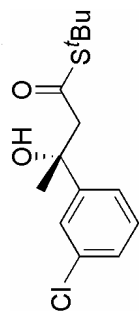
===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -6.00 dB
SF01 500.130885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300137 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
FIP 9.000 ppm
F1 4501.17 Hz
F2 0.000 ppm
F2 0.00 Hz
PPMCH 0.45000 ppm/cm
HZCM 225.05849 Hz/cm



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4f

¹H NMR (500 MHz, CDCl₃) Spectrum of 4g

4g

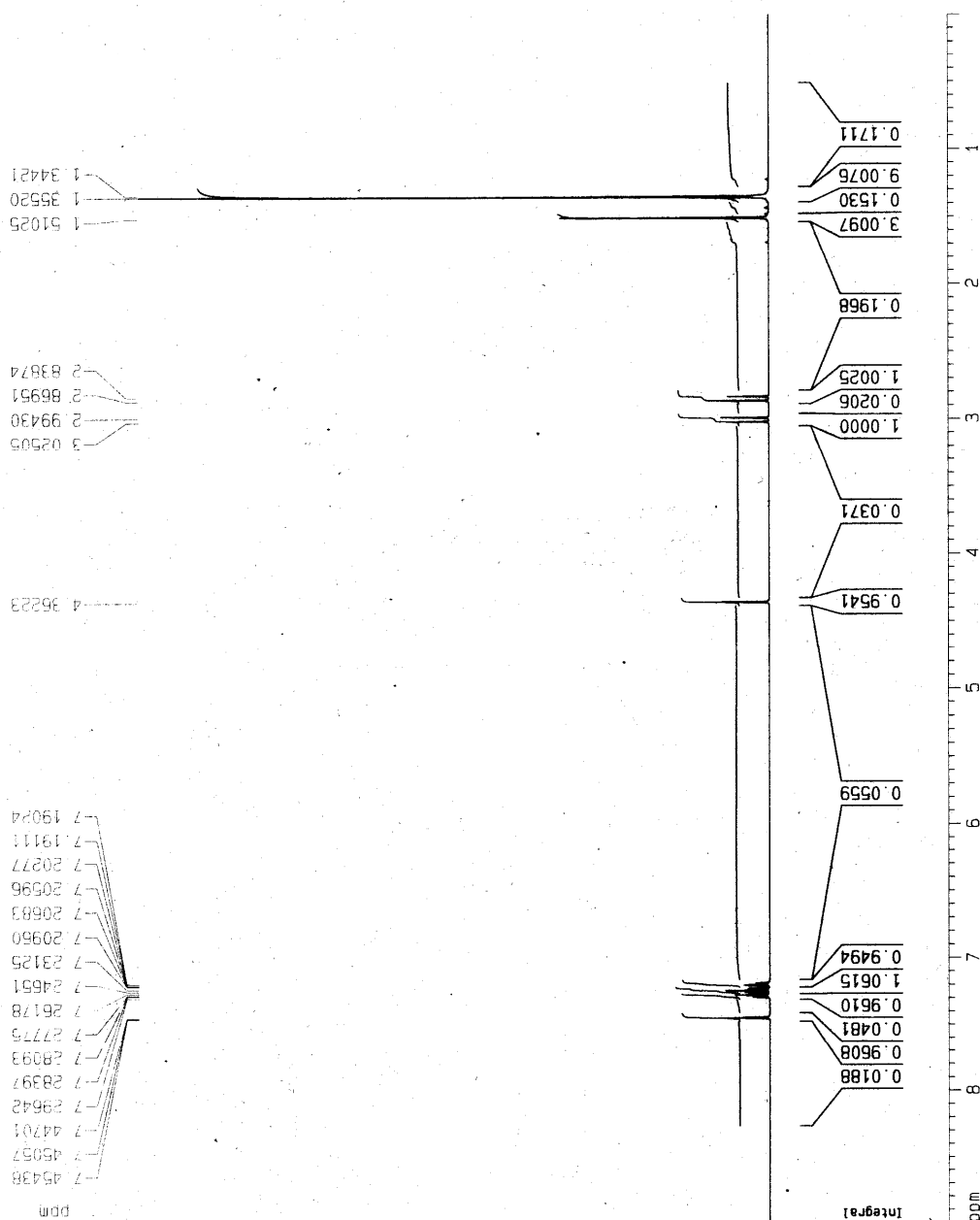
Current Data Parameters
NAME 140-466-BUNSHU
EXPNO 1
PROCNO 1

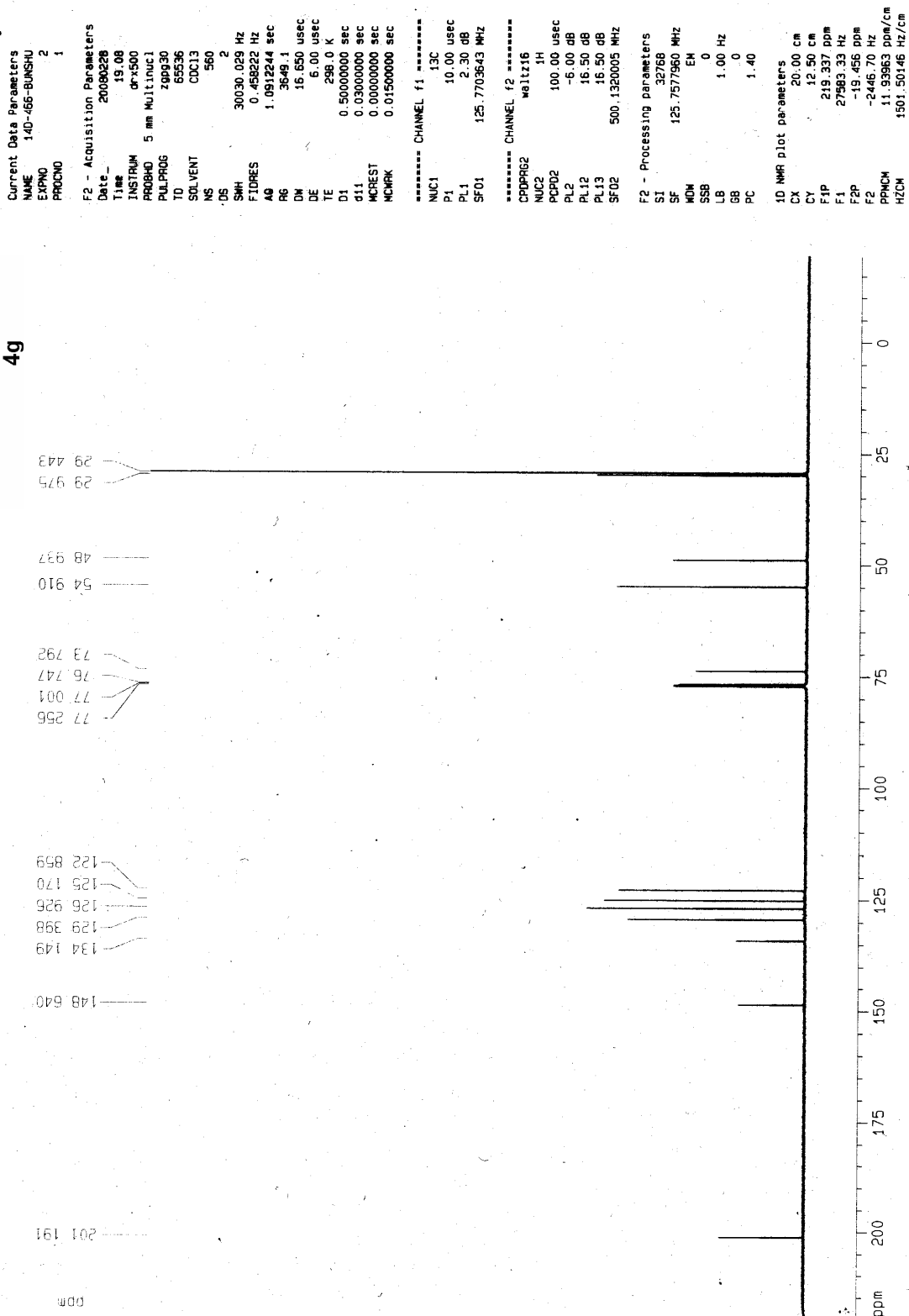
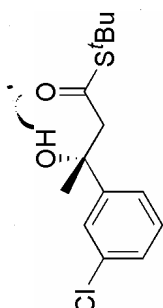
F2 - Acquisition Parameters
Date_ 20080228
Time 19.01
INSTRUM drx500
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 64
DM 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCNMRK 0.01500000 sec

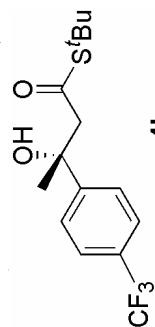
===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -6.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 9.000 ppm
F1 4501.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05849 Hz/cm



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4g

¹H NMR (500 MHz, CDCl₃) Spectrum of 4h

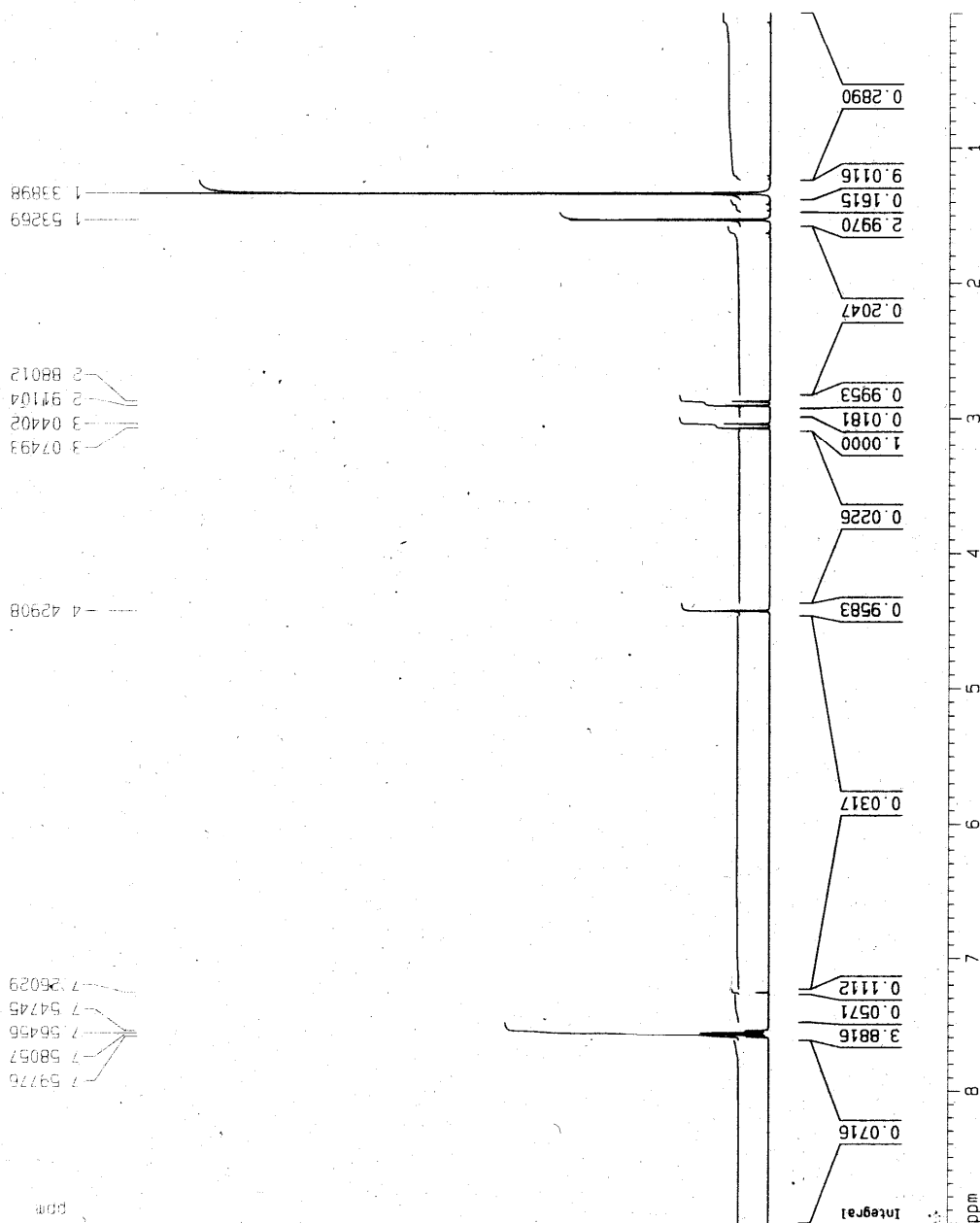
Current Data Parameters
 NAME 140-548-PM
 EXPNO 1
 PROCNO 1

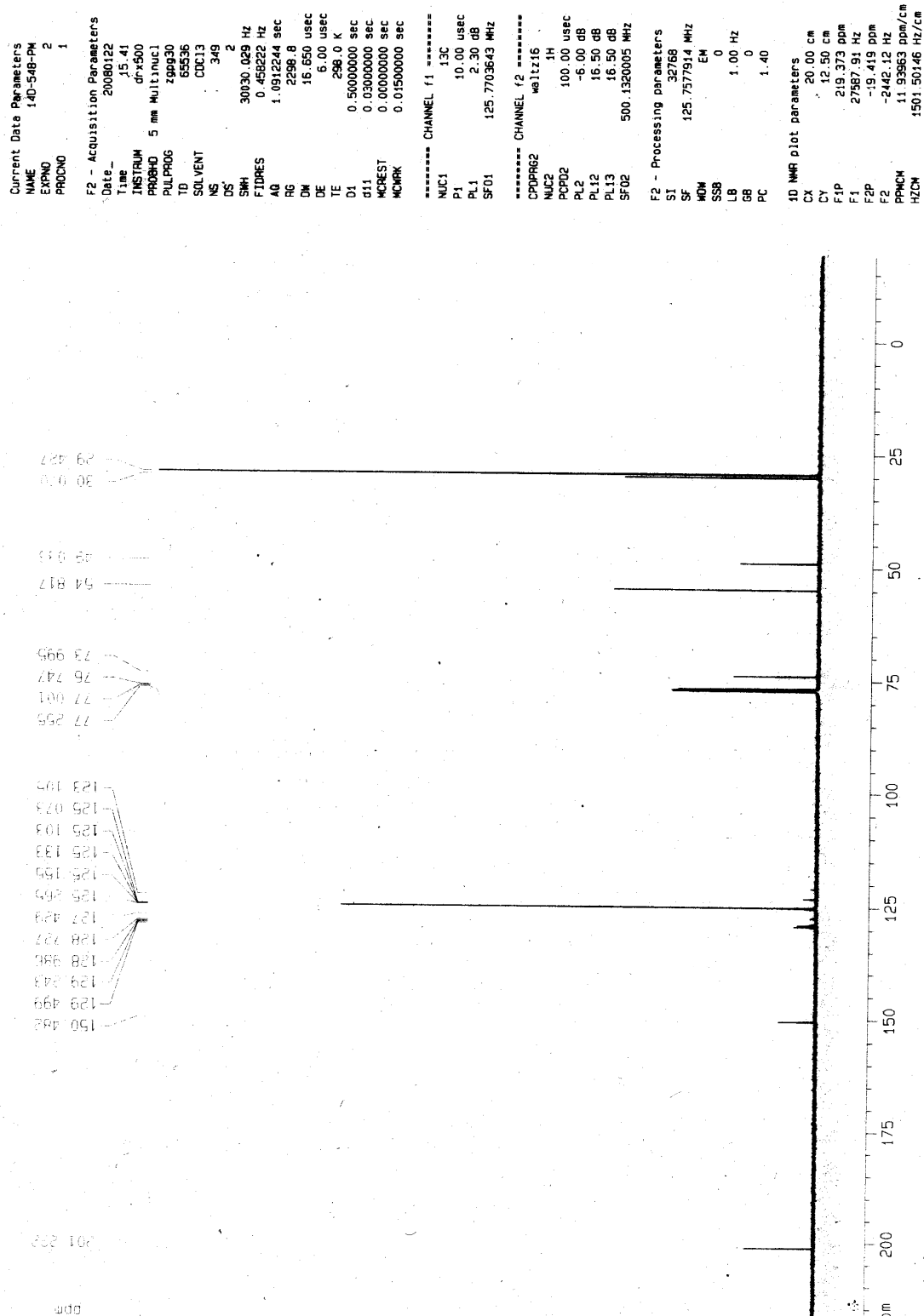
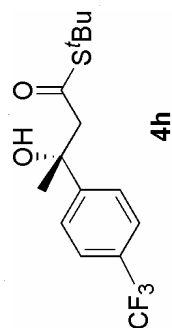
F2 - Acquisition Parameters
 Date_ 20080122
 Time 15.29
 INSTRUM drx500
 PROBHD 5 mm Multinucl
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.171923 sec
 RG 101.5
 DM 48.400 usec
 DE 5.00 usec
 TE 298.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

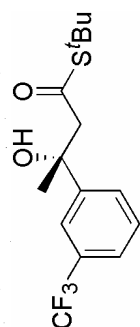
===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PL1 -6.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1330131 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 12.50 cm
 FIP 9.000 ppm
 F1 4501.17 Hz
 F2 0.000 ppm
 F2 0.00 Hz
 PPMCM 0.45000 ppm/cm
 HZCM 225.05849 Hz/cm



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4h

¹H NMR (500 MHz, CDCl₃) Spectrum of 4i

4i

Current Data Parameters

NAME 140-468-BUNSHU
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20080228
Time 18.44
INSTRUM drx500
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl₃
NS 32
DS 2
SMH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.171923 sec
RG 45.3
DM 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.0000000 sec
MCREST 0.0000000 sec
MCWIRK 0.0150000 sec

===== CHANNEL f1 =====

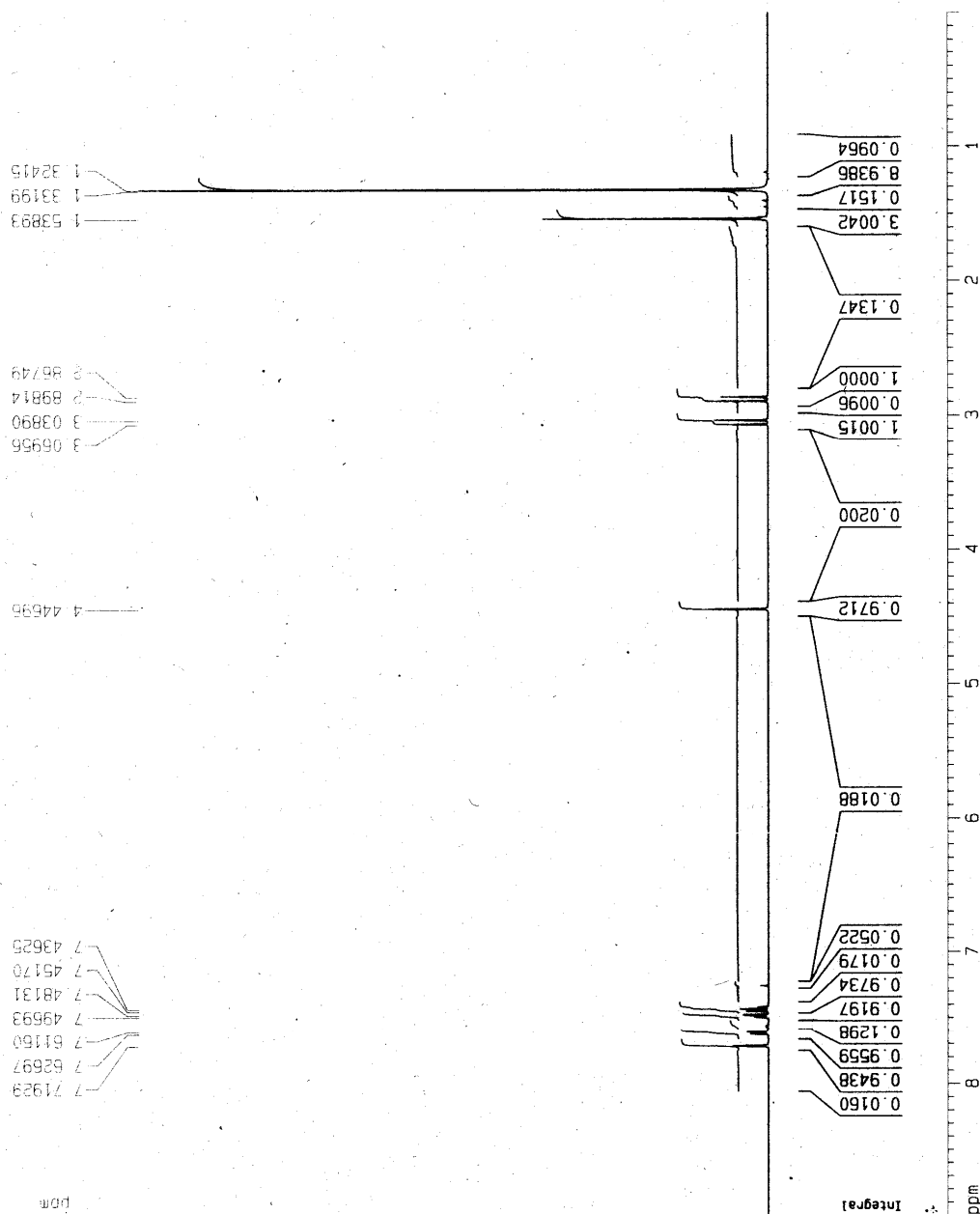
NUC1 1H
P1 10.00 usec
PL1 -6.00 dB
SF01 500.1330885 MHz

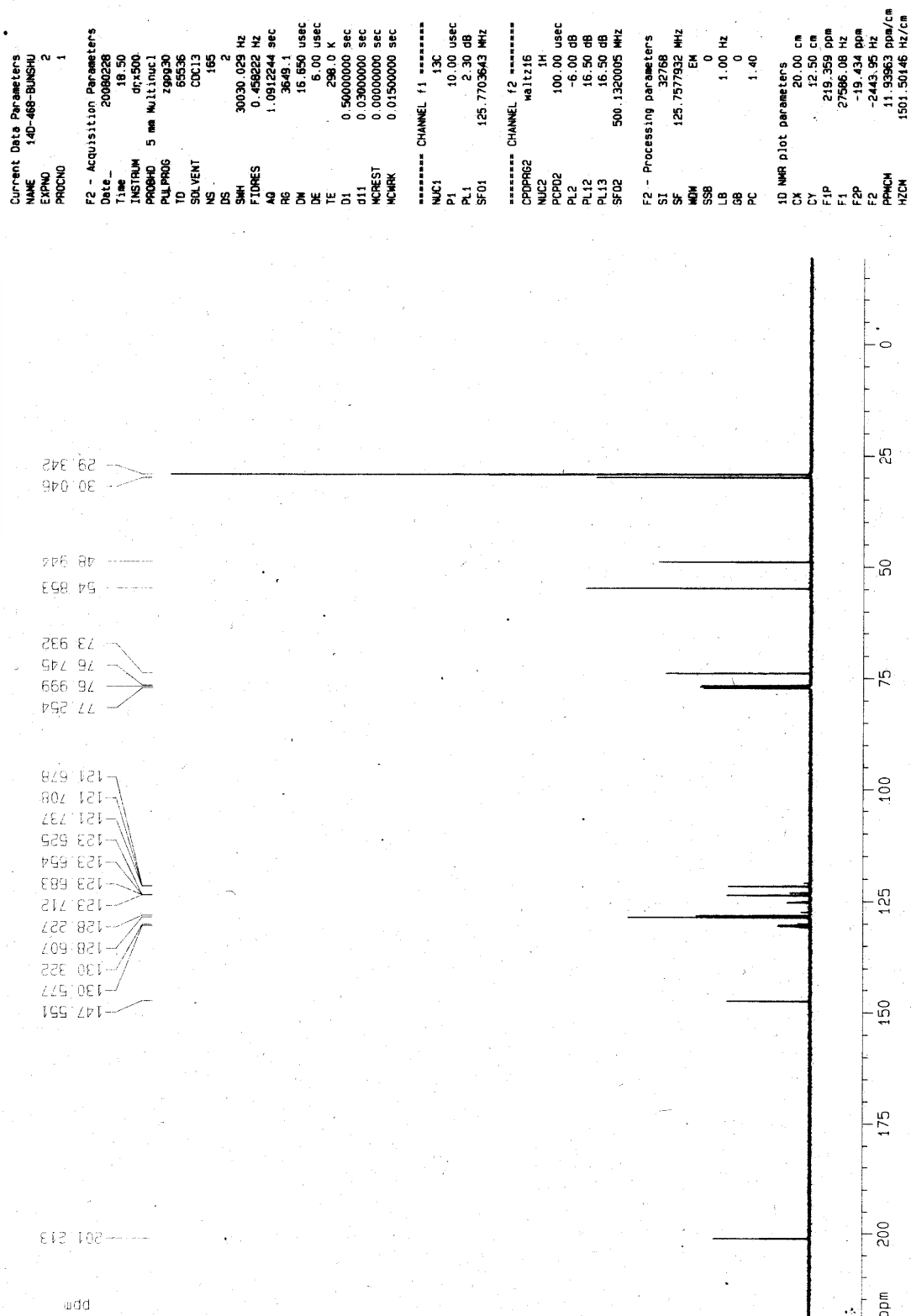
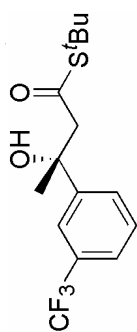
F2 - Processing parameters

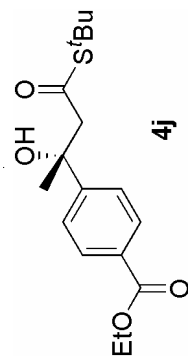
SI 32768
SF 500.1330134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
CY 12.50 cm
F1P 9.000 ppm
F1 4501.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05849 Hz/cm



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4i

¹H NMR (500 MHz, CDCl₃) Spectrum of 4j

4j

Current Data Parameters

NAME 140-571-PA
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20060307
Time 18.58
INSTRUM drx500
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.157532 Hz
AQ 3.1719923 sec
RG 287.4
DM 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCHWK 0.01500000 sec

***** CHANNEL f1 *****

NUC1 1H
P1 10.00 usec
PL1 -6.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters

SI 32768
SF 500.1300137 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
CY 12.50 cm
F1P 9.000 ppm
F1 4501.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05849 Hz/cm

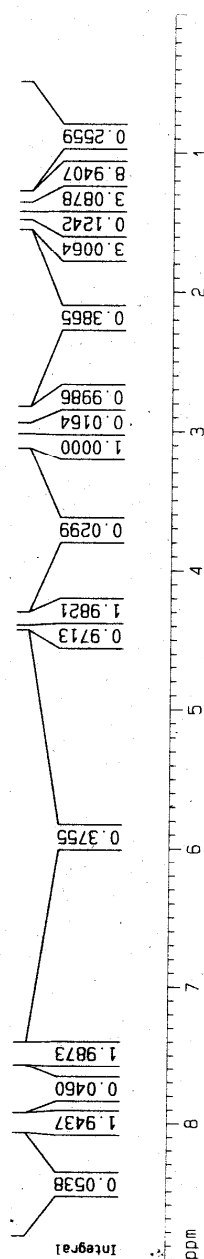
1 34090
1 37372
1 38792
1 40281
1 52491
1 59578

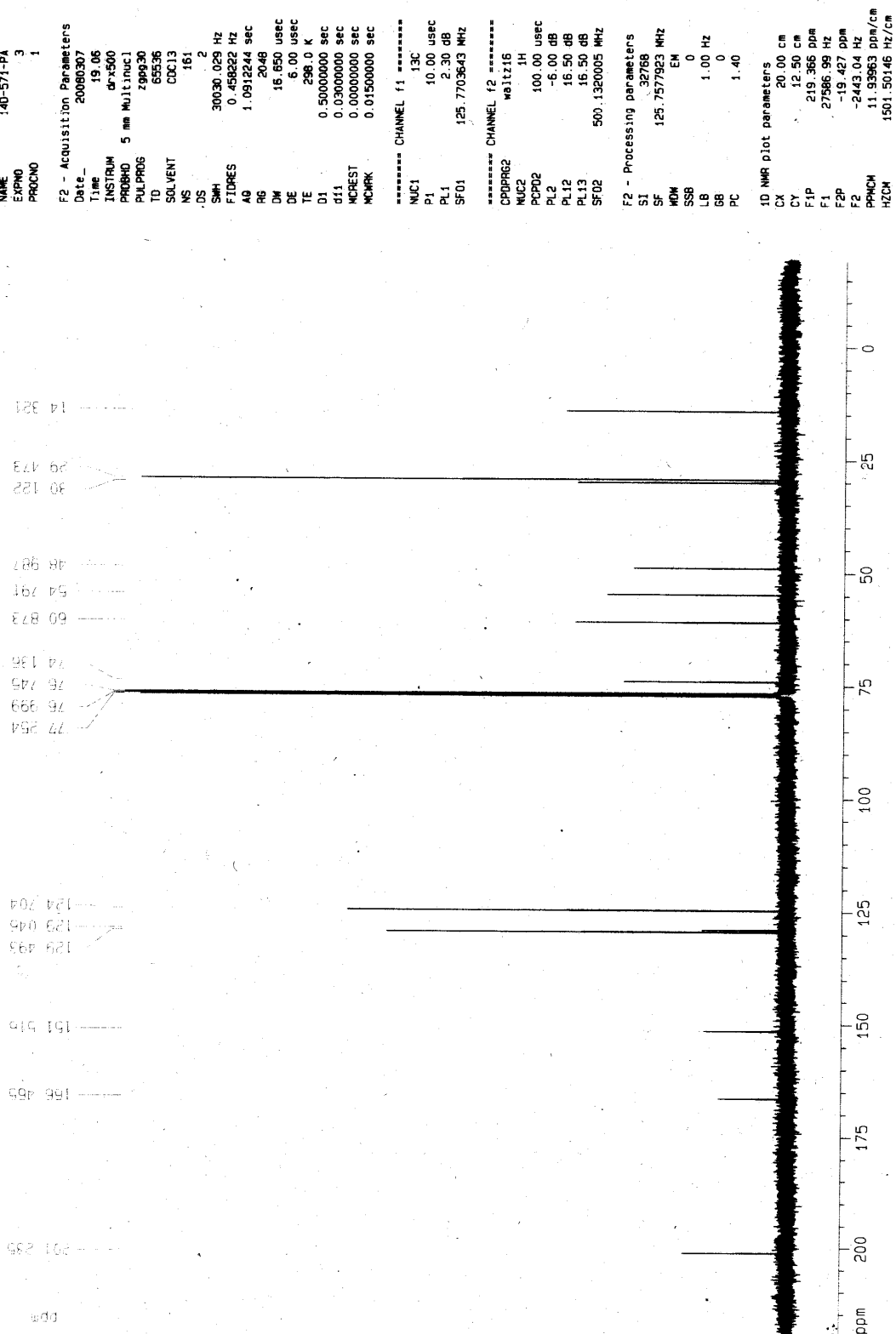
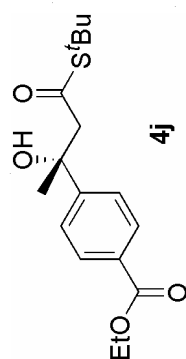
2 88028
2 91128
3 08016
3 09118

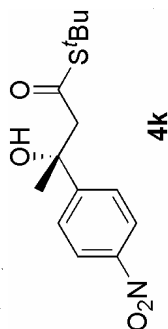
4 41214
4 38889
4 37462
4 36039
4 34512

7 25981
7 49556
7 49885
7 50894
7 51236
7 99620
7 99953
8 00955
8 01329

ppm



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4j

¹H NMR (500 MHz, CDCl₃) Spectrum of 4k

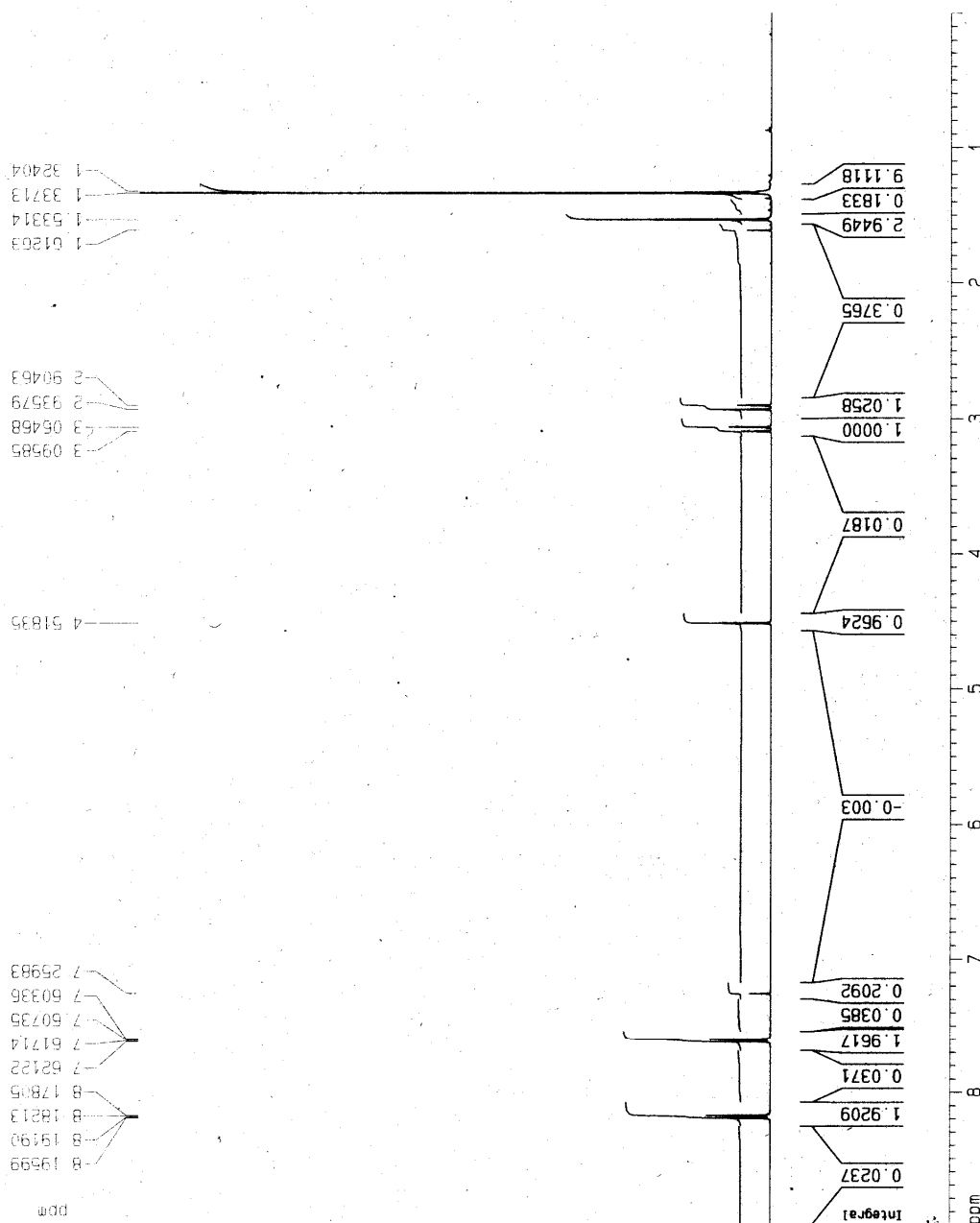
Current Data Parameters
 NAME 140-516-PA
 EXPNO 1
 PROCNO 1

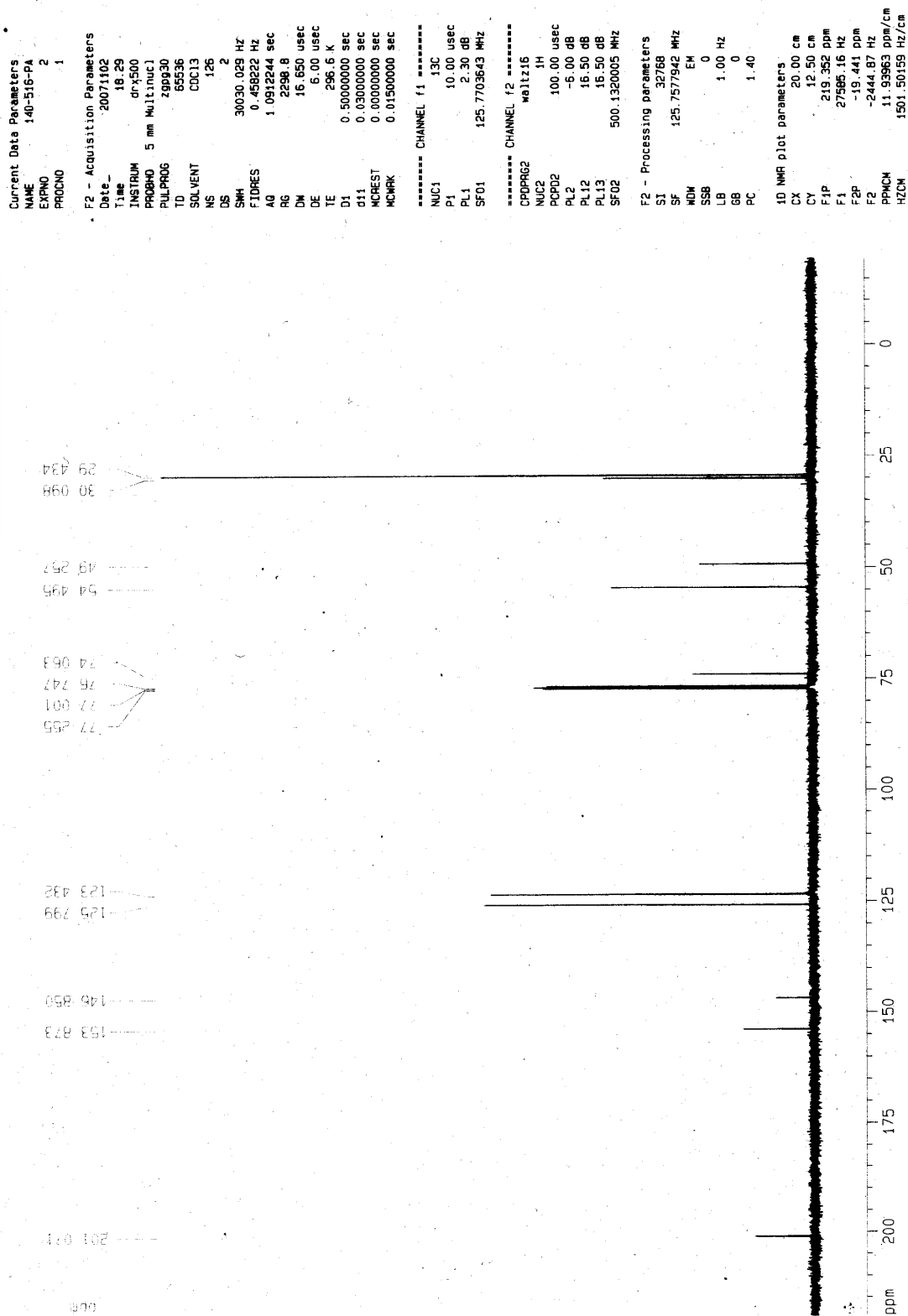
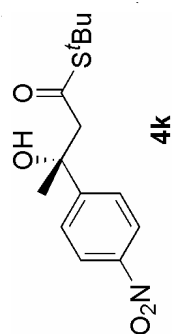
F2 - Acquisition Parameters
 Date_ 20071102
 Time 18.24
 INSTRUM drx500
 PROBHD 5 mm Multinucl
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 16
 DS 2
 SMH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 161.3
 DW 48.400 usec
 DE 6.00 usec
 TE 296.1 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWIRK 0.01500000 sec

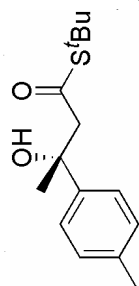
===== CHANNEL f1 =====
 NUC1 ¹H
 P1 10.00 usec
 PL1 -6.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300143 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 12.50 cm
 F1P 9.000 ppm
 F1 4501.17 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCM 0.45000 ppm/cm
 HZCM 225.05852 Hz/cm



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4k

¹H NMR (500 MHz, CDCl₃) Spectrum of 4I

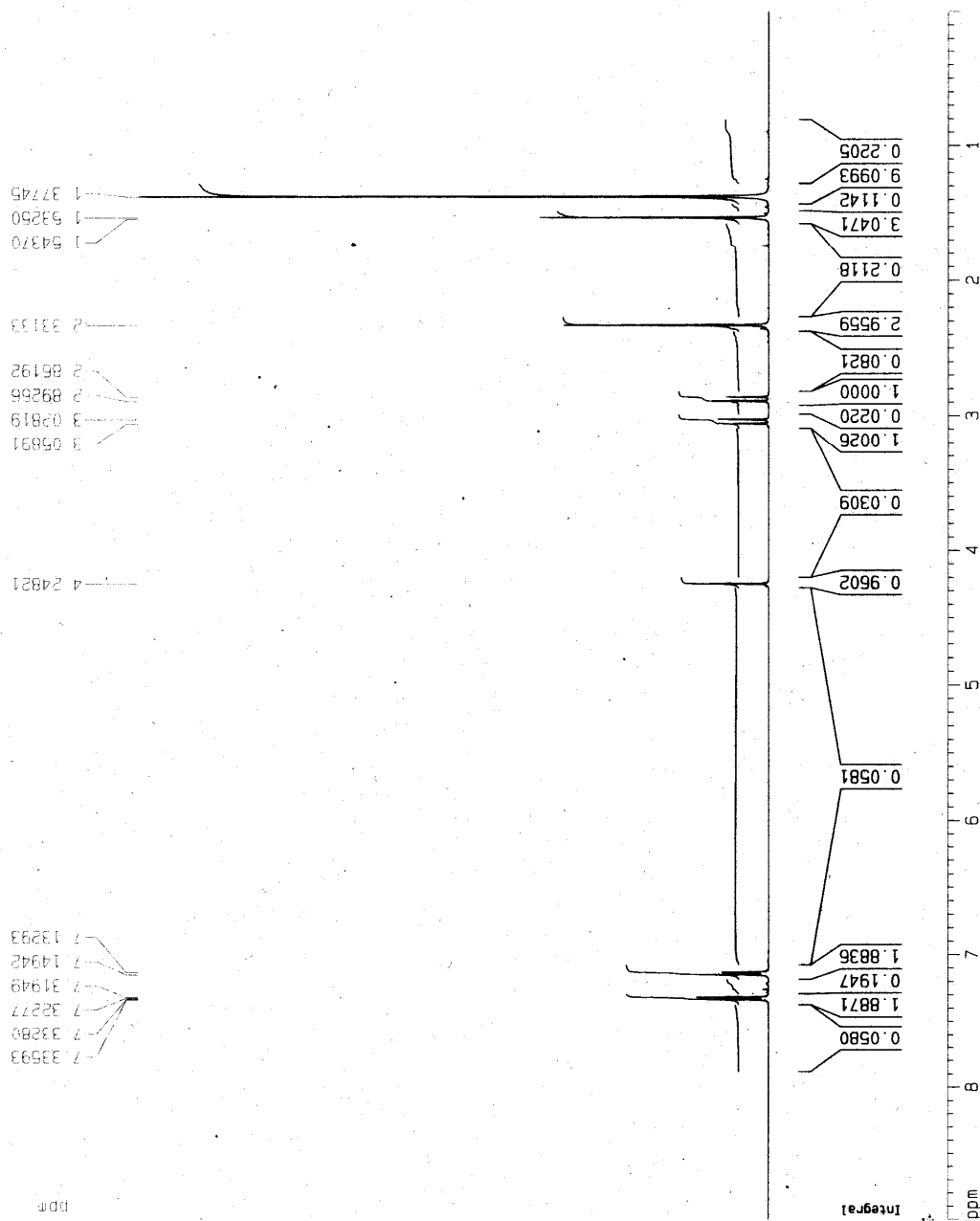
Current Data Parameters
 NAME 140-MePhCDet
 EXPNO 1
 PROCNO 1

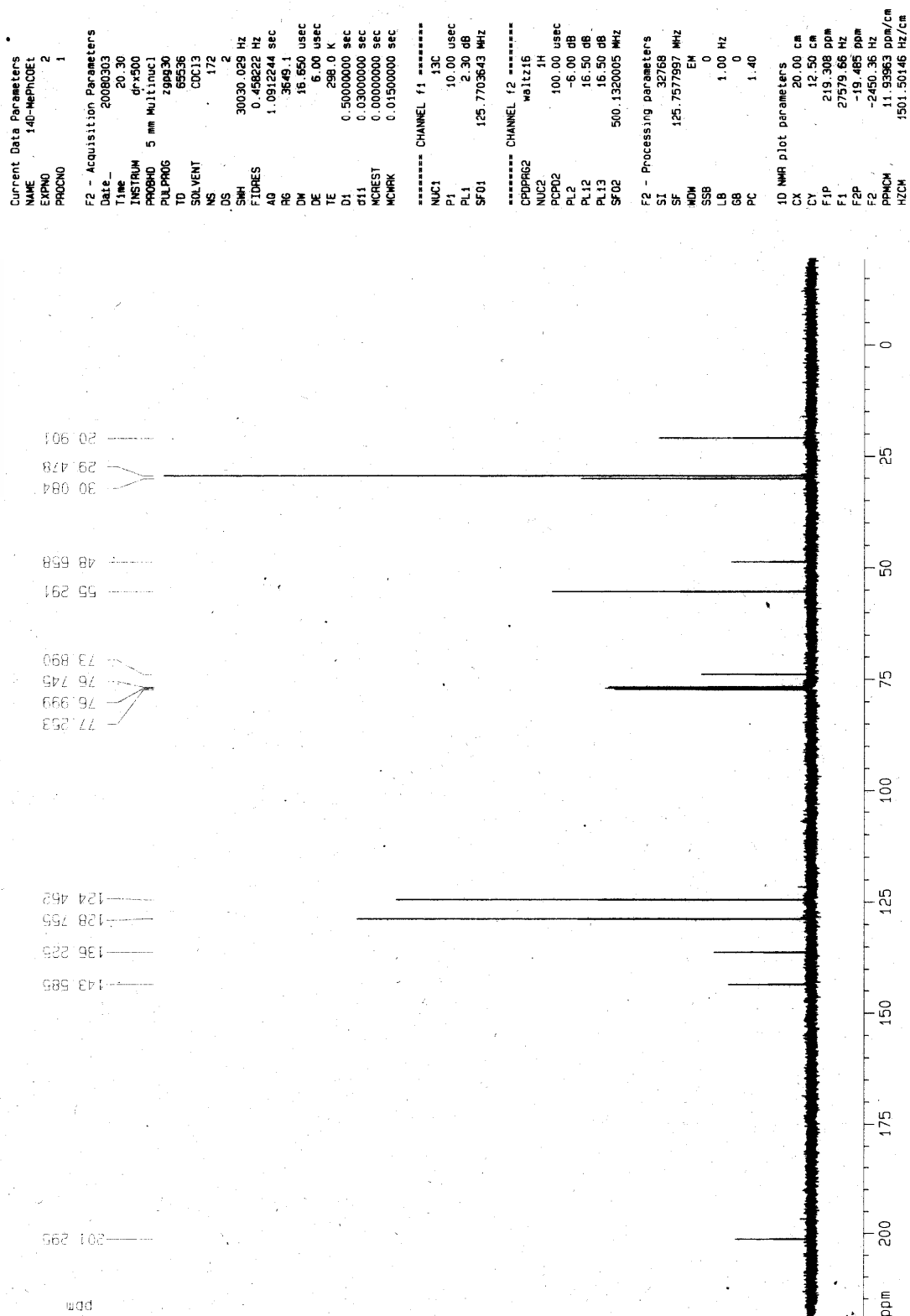
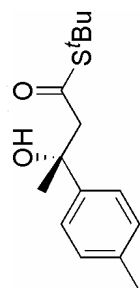
F2 - Acquisition Parameters
 Date_ 20080303
 Time 20.27
 INSTRUM drx500
 PROBHD 5 mm Multinuc1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719823 sec
 RG 45.3
 DW 48.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

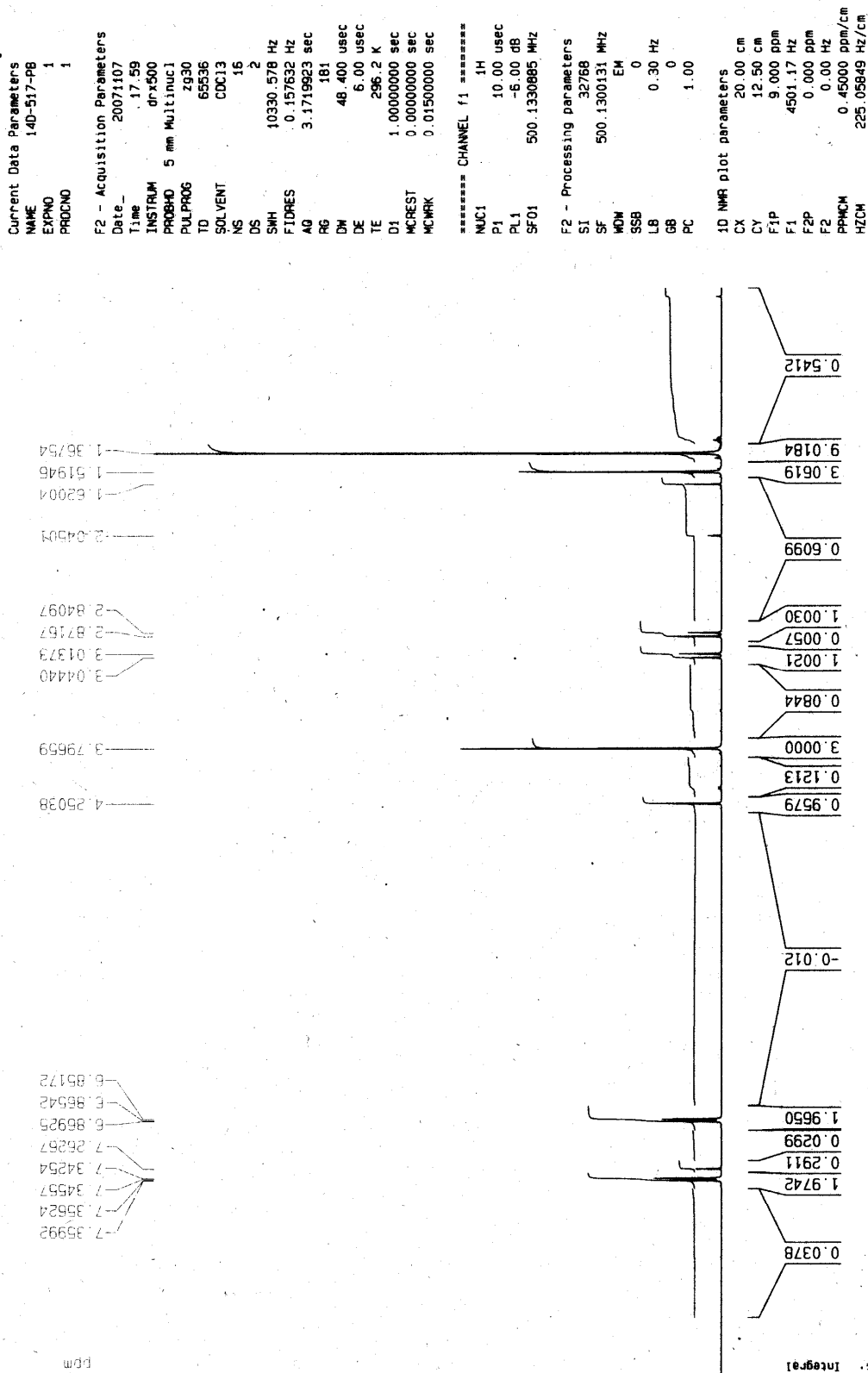
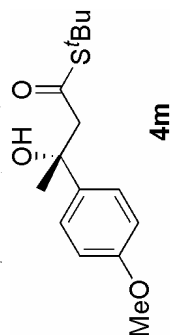
===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PL1 -6.00 dB
 SF01 500.1330885 MHz

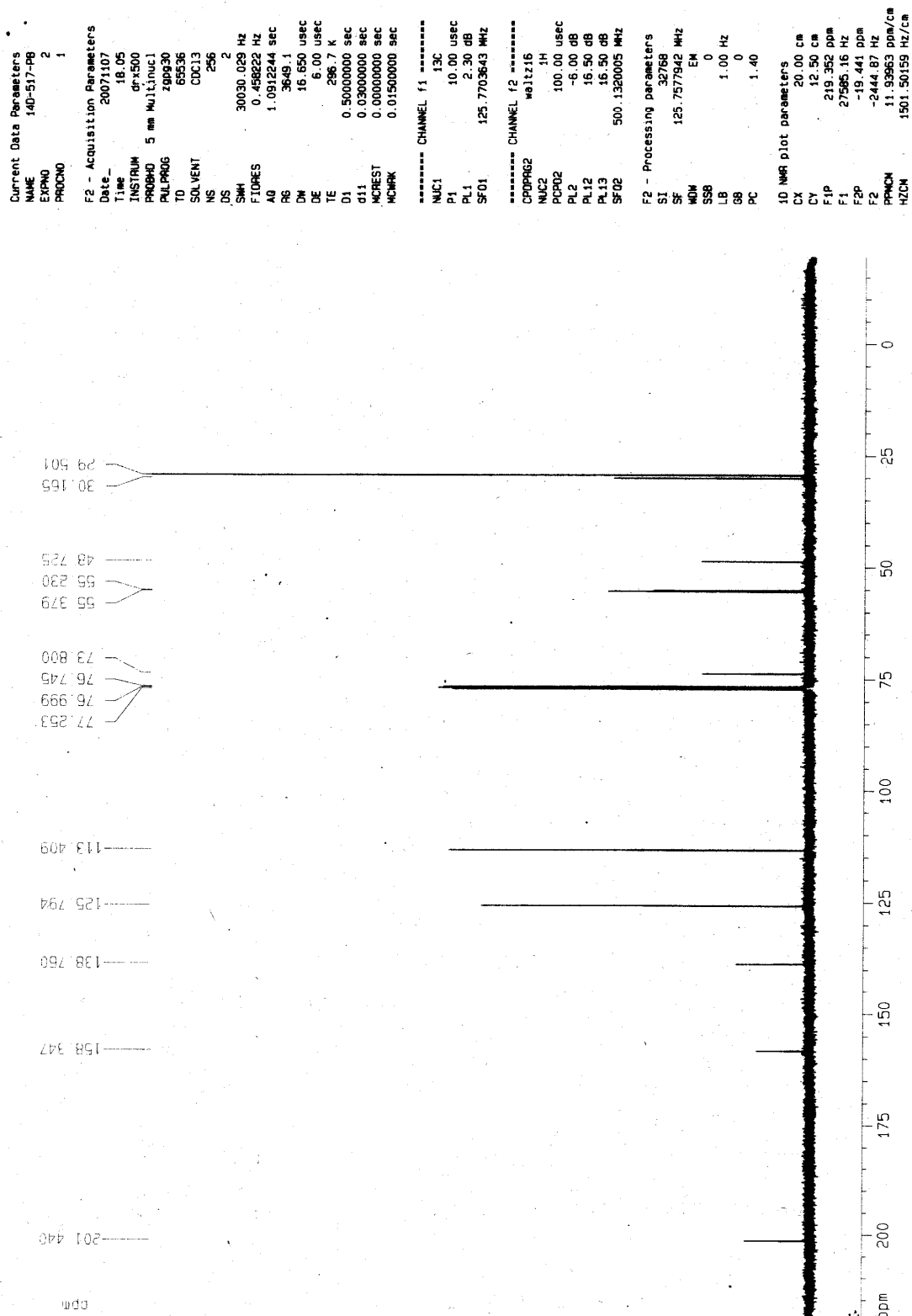
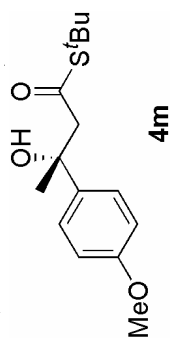
F2 - Processing parameters
 SI 32768
 SF 500.1300134 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

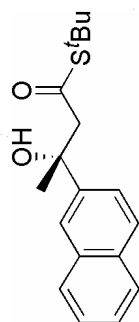
1D NMR plot parameters
 CX 20.00 cm
 CY 12.50 cm
 FIP 9.000 ppm
 F1 4501.17 Hz
 F2 0.000 ppm
 F2 0.00 Hz
 PPMCH 0.45000 ppm/cm
 HZCM 225.05849 Hz/cm



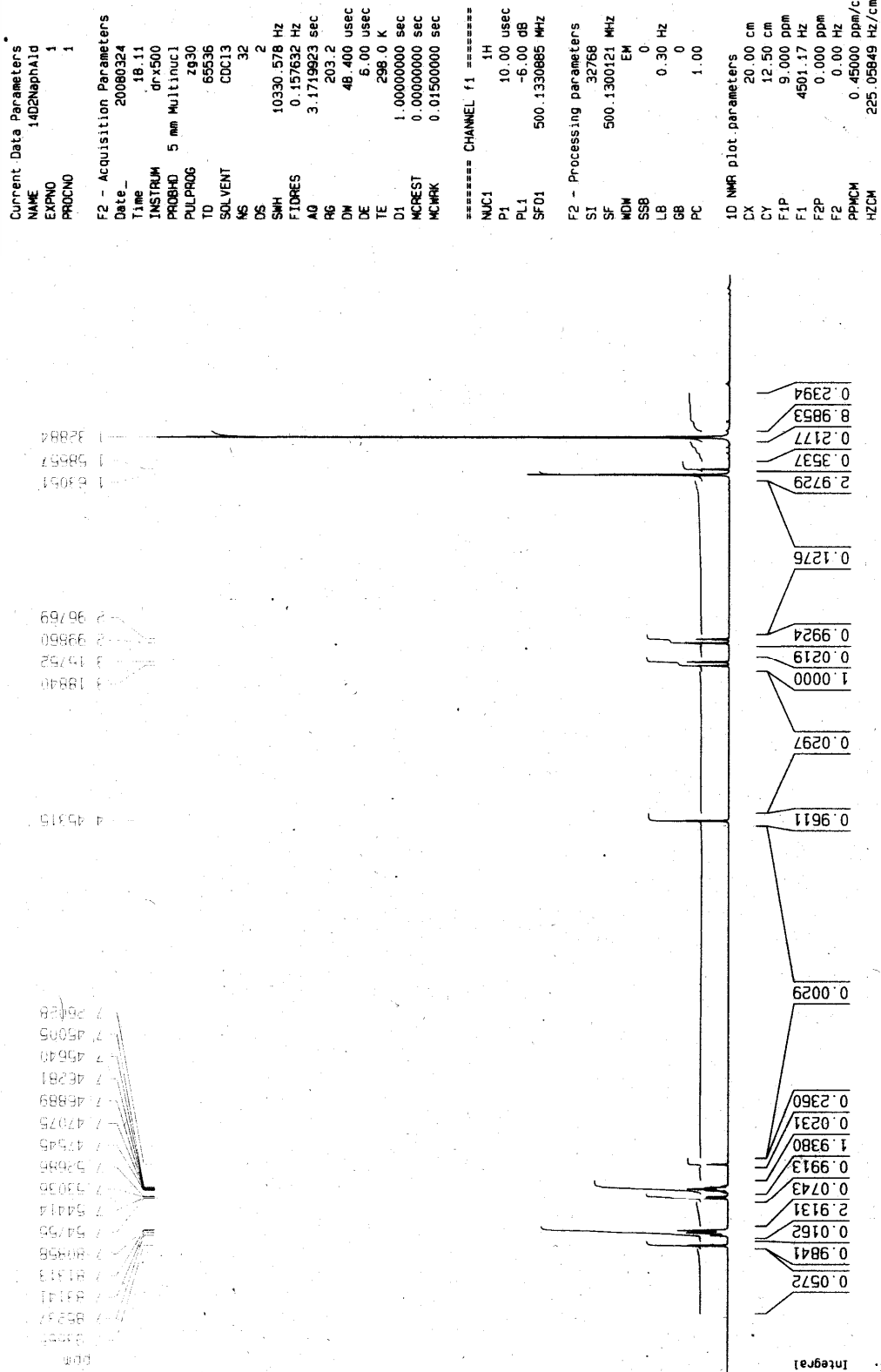
¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4I

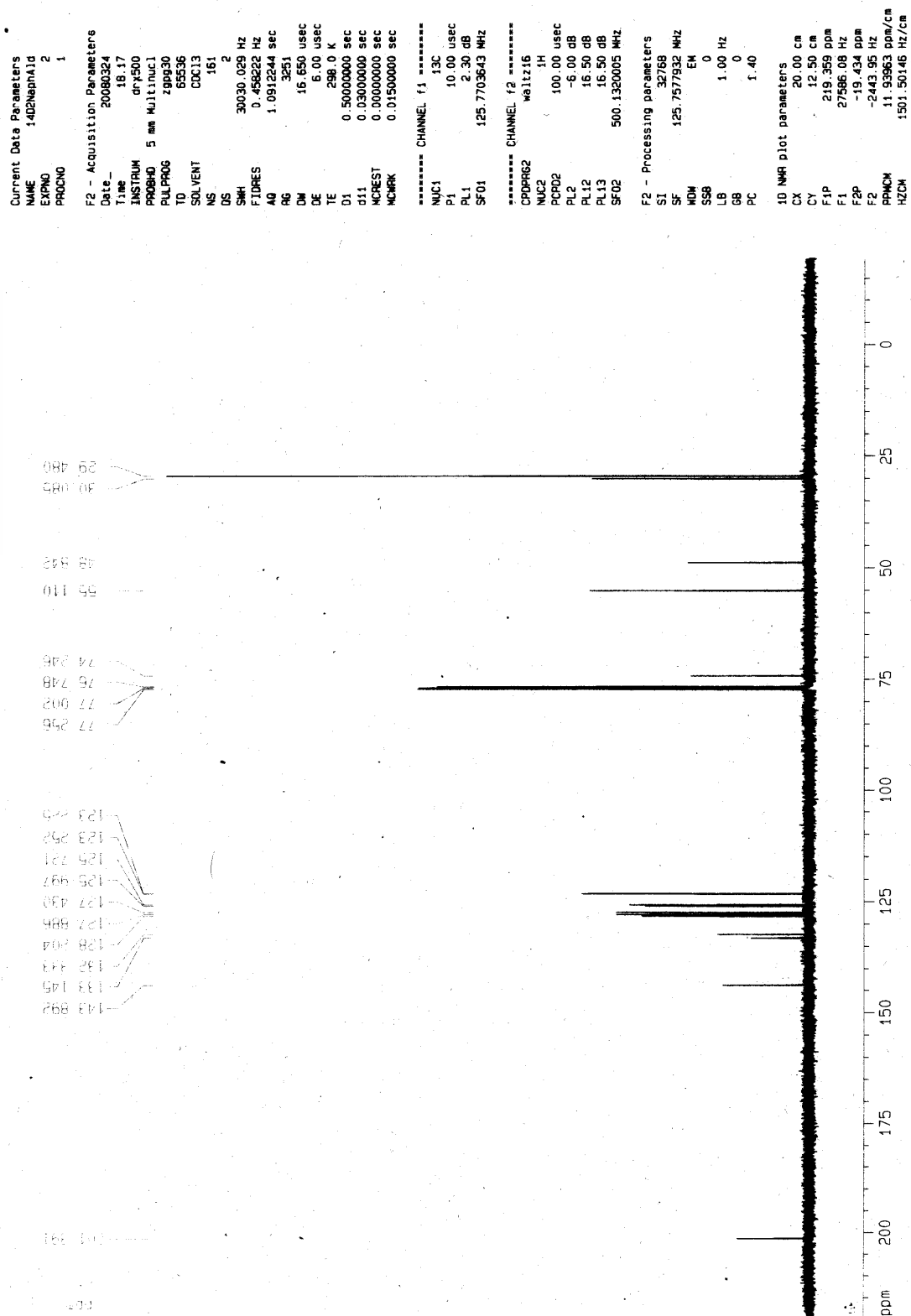
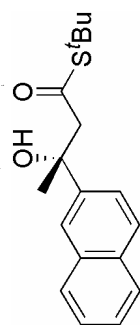
¹H NMR (500 MHz, CDCl₃) Spectrum of 4m

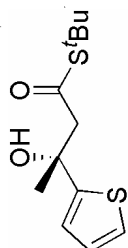
¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4m

¹H NMR (500 MHz, CDCl₃) Spectrum of 4n

4n



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4n

¹H NMR (500 MHz, CDCl₃) Spectrum of 4o

4o

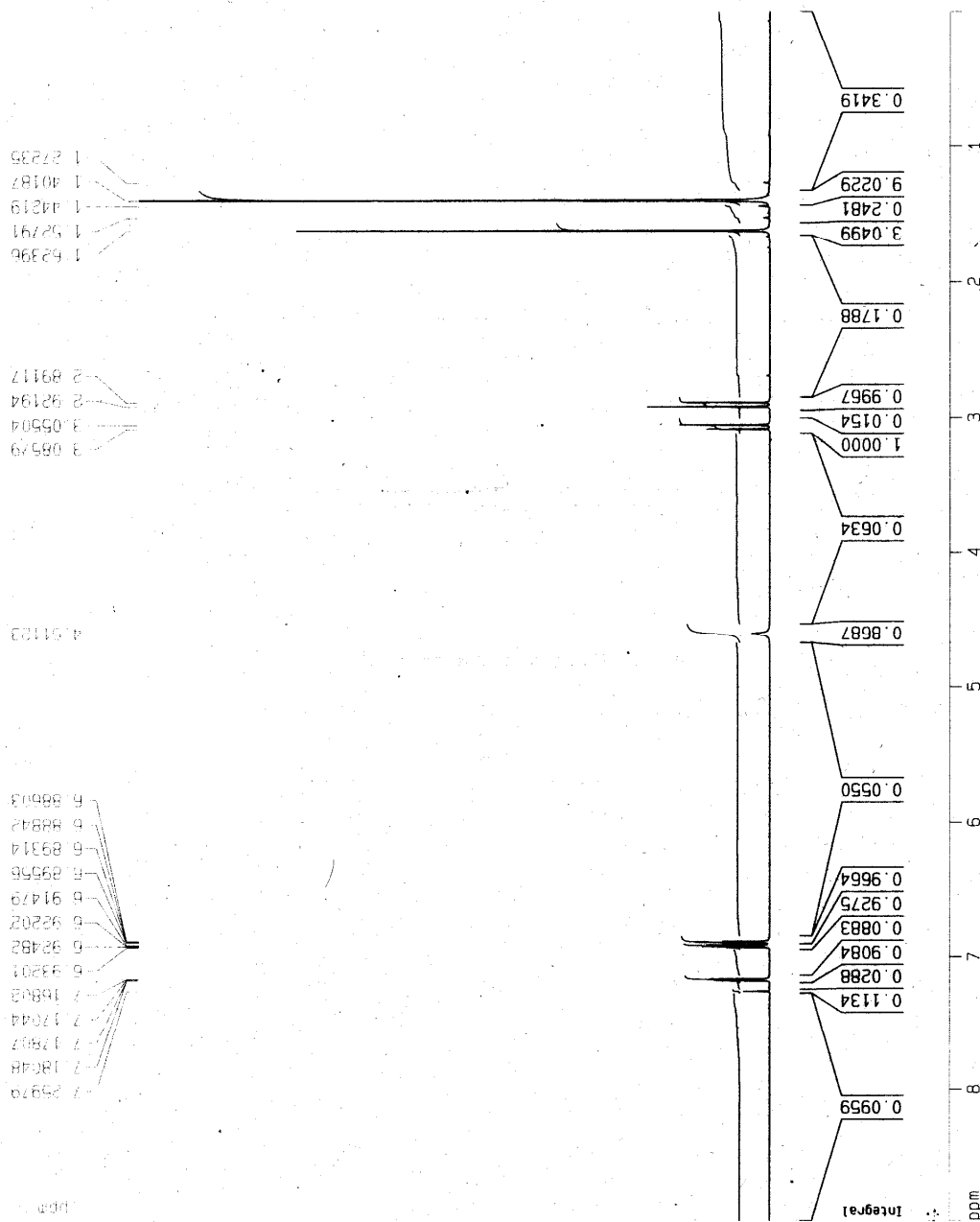
Current Data Parameters
 NAME 14D-528-PA
 EXPNO 1
 PROCNO 1

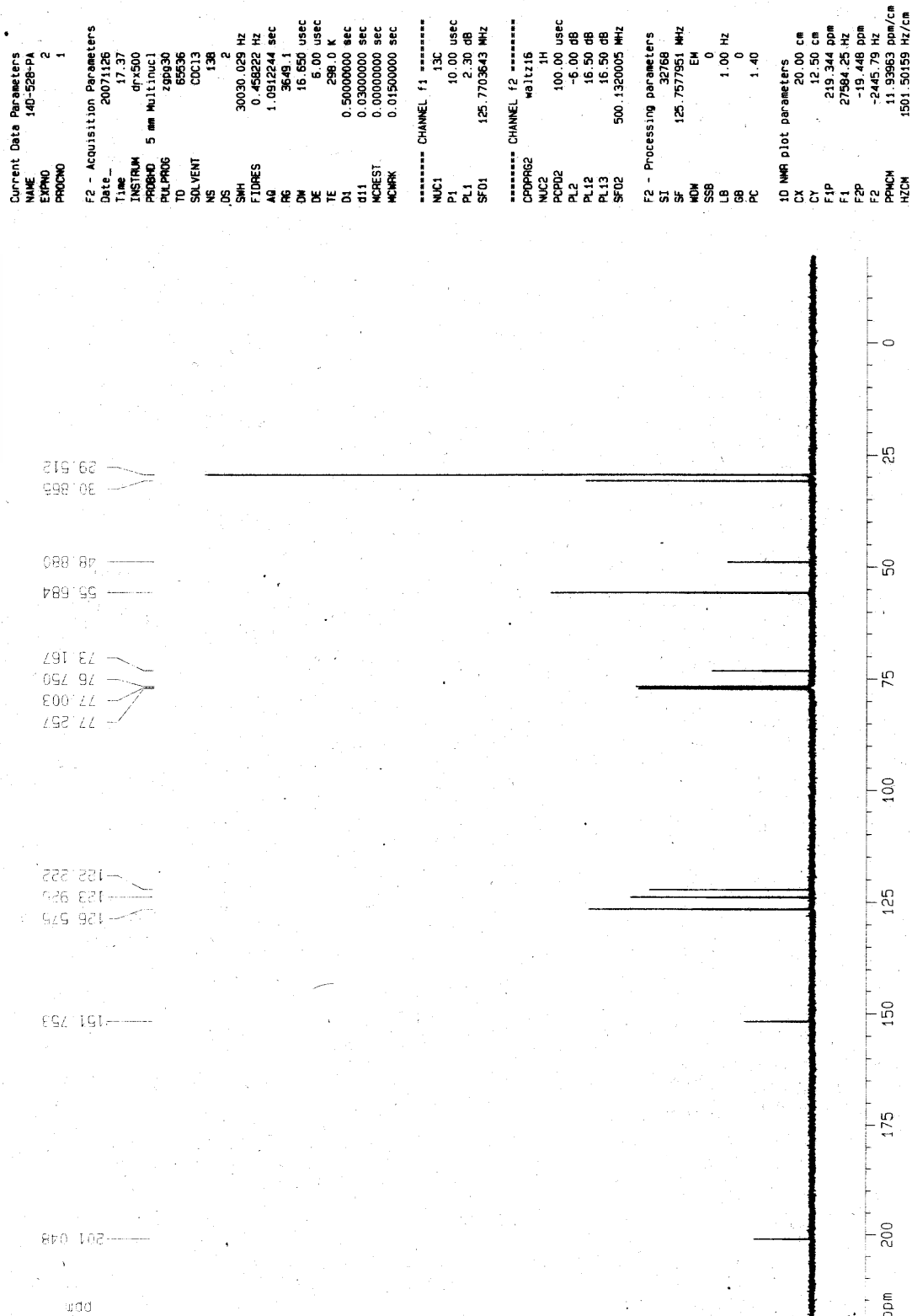
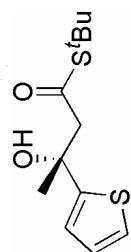
F2 - Acquisition Parameters
 Date_ 20071126
 Time 17.32
 INSTRUM drx500
 PROBD 5 mm Multinuc1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 101.6
 DM 48.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

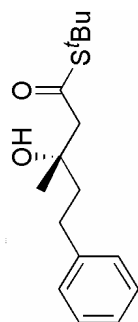
===== CHANNEL f1 =====
 NUC1 ¹H
 P1 10.00 usec
 PL1 -6.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300143 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 0.00 cm
 F1P 9.000 ppm
 F1 4501.17 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCM 0.45000 ppm/cm
 HZCM 225.05849 Hz/cm



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4o

¹H NMR (500 MHz, CDCl₃) Spectrum of 4p

4p

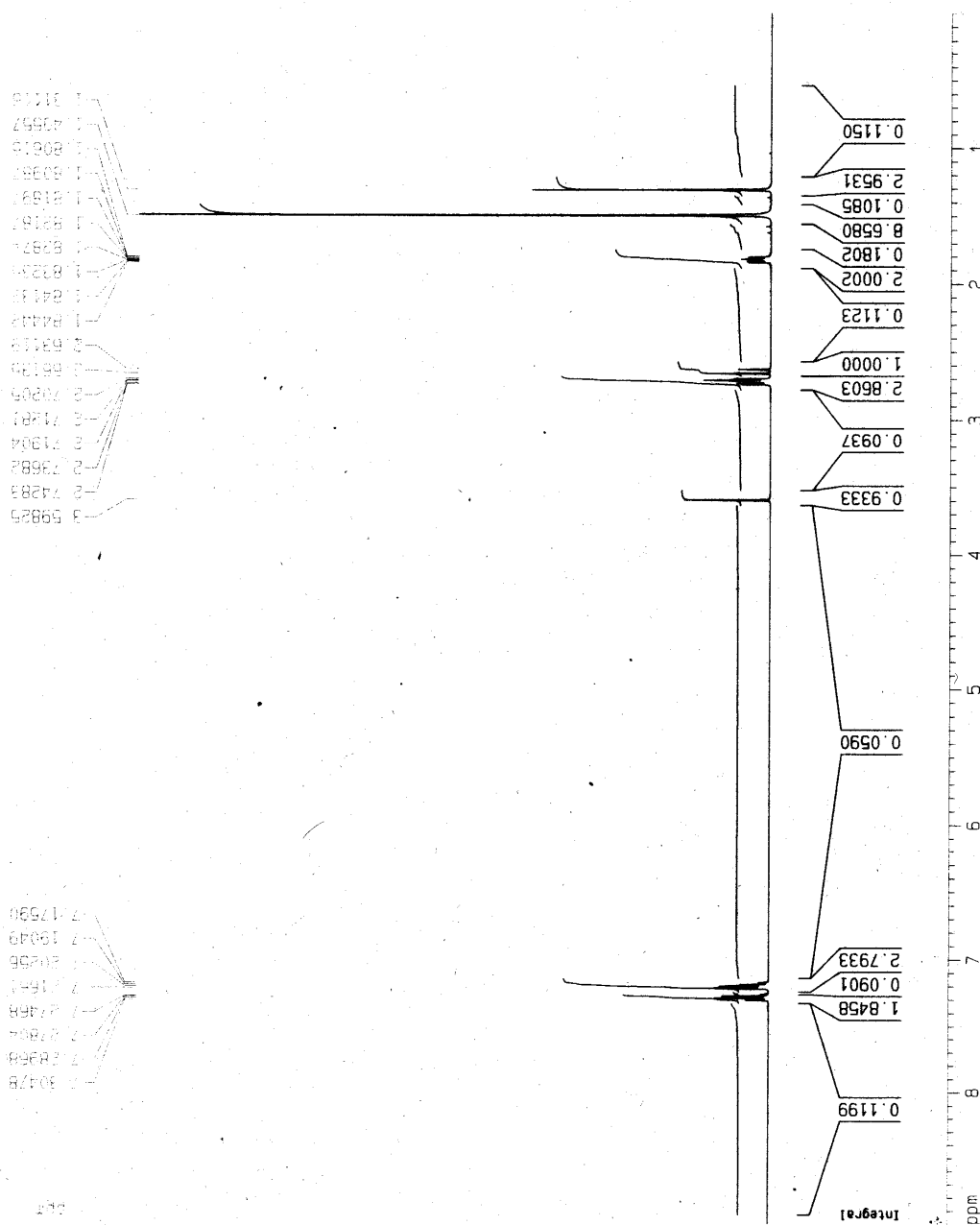
Current Data Parameters
 NAME 140-523-2A
 EXPNO 1
 PROCNO 1

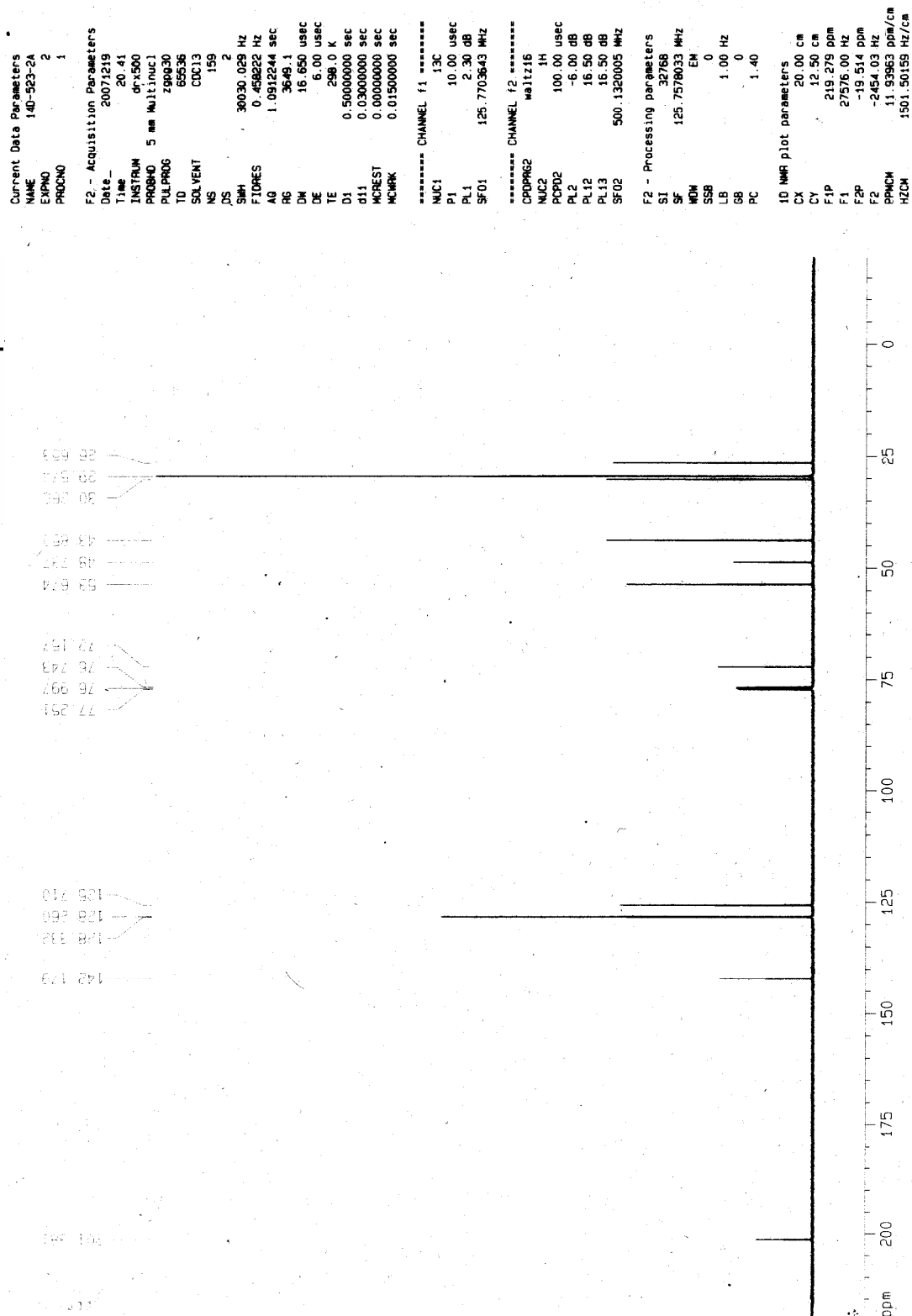
F2 - Acquisition Parameters
 Date_ 20071219
 Time 20:33
 INSTRUM drx500
 PROBO 5 mm Multinucl
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 32
 DS 2
 SMH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 32
 DM 48.400 usec
 DE 6.00 usec
 TE 297.5 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWAK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PL1 -6.00 dB
 SF01 500.1330885 MHz

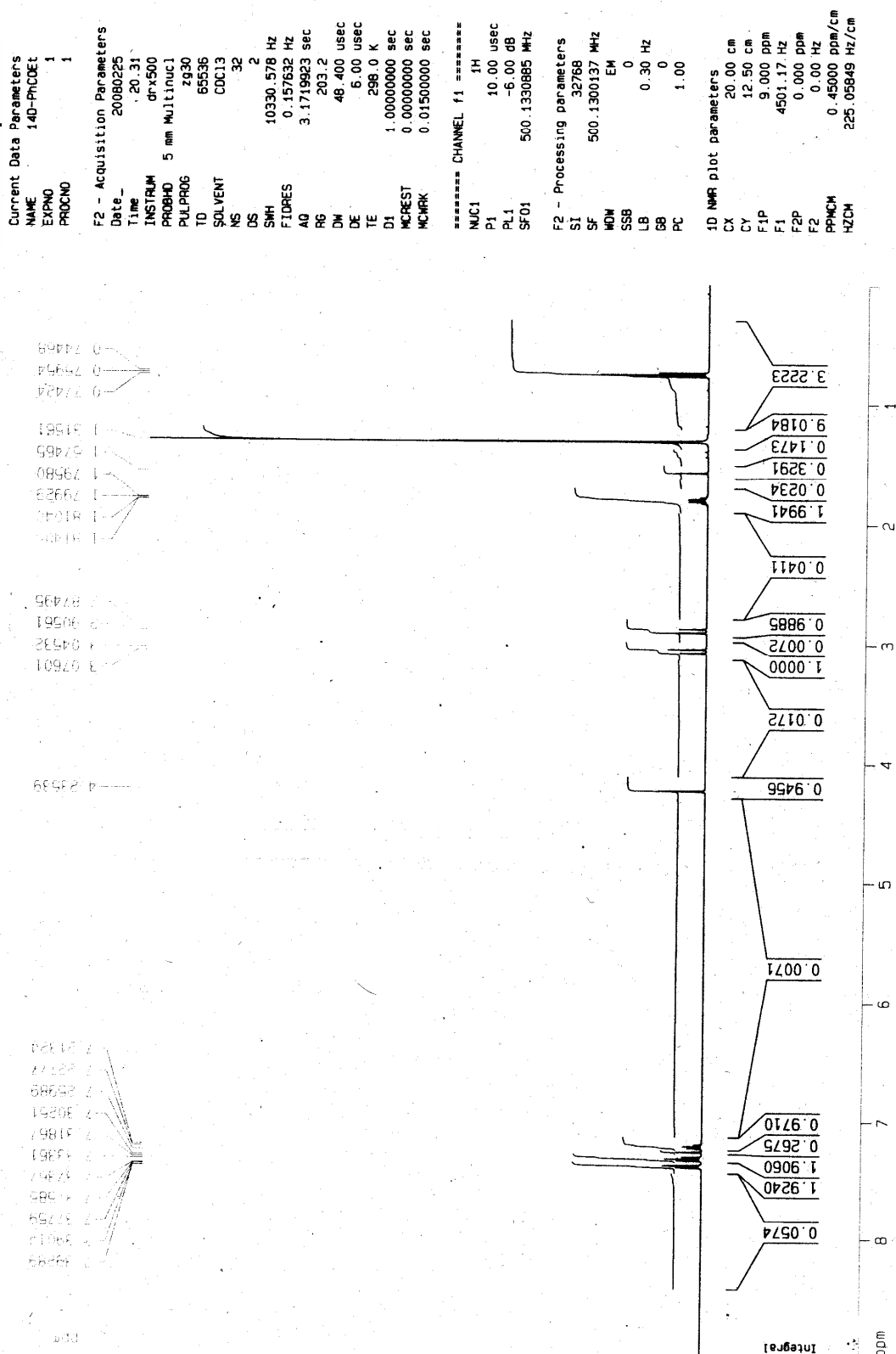
F2 - Processing parameters
 SI 32768
 SF 500.1300143 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

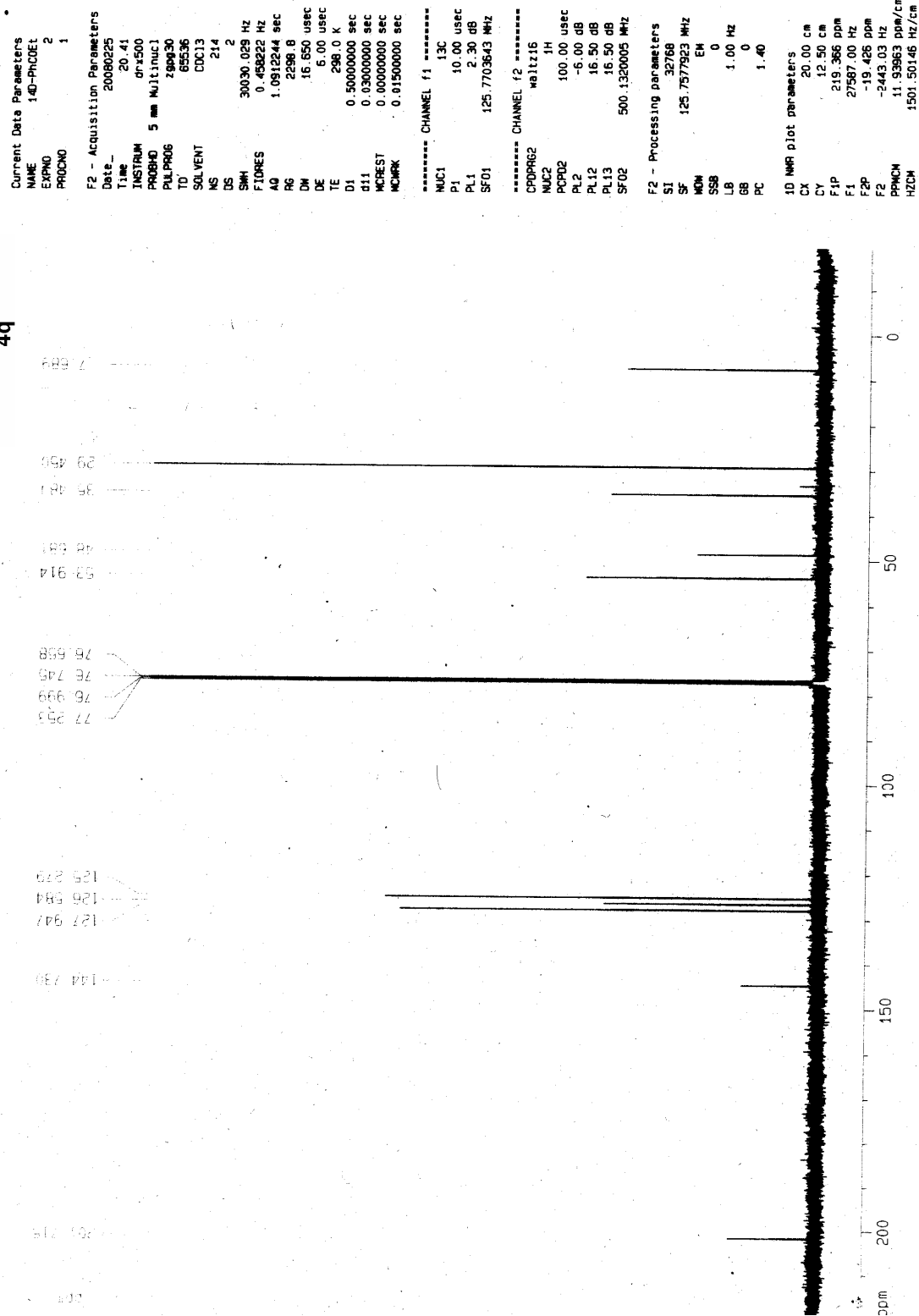
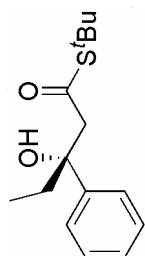
1D NMR plot parameters
 CX 20.00 cm
 CY 12.50 cm
 F1P 9.000 ppm
 F1 4501.17 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCM 0.45000 ppm/cm
 HZCM 225.05849 Hz/cm

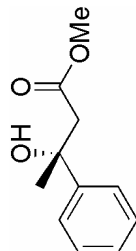




1



¹³C NMR (125.8 MHz, CDCl₃) Spectrum of 4q

¹H NMR (500 MHz, CDCl₃) Spectrum of 11a

11a

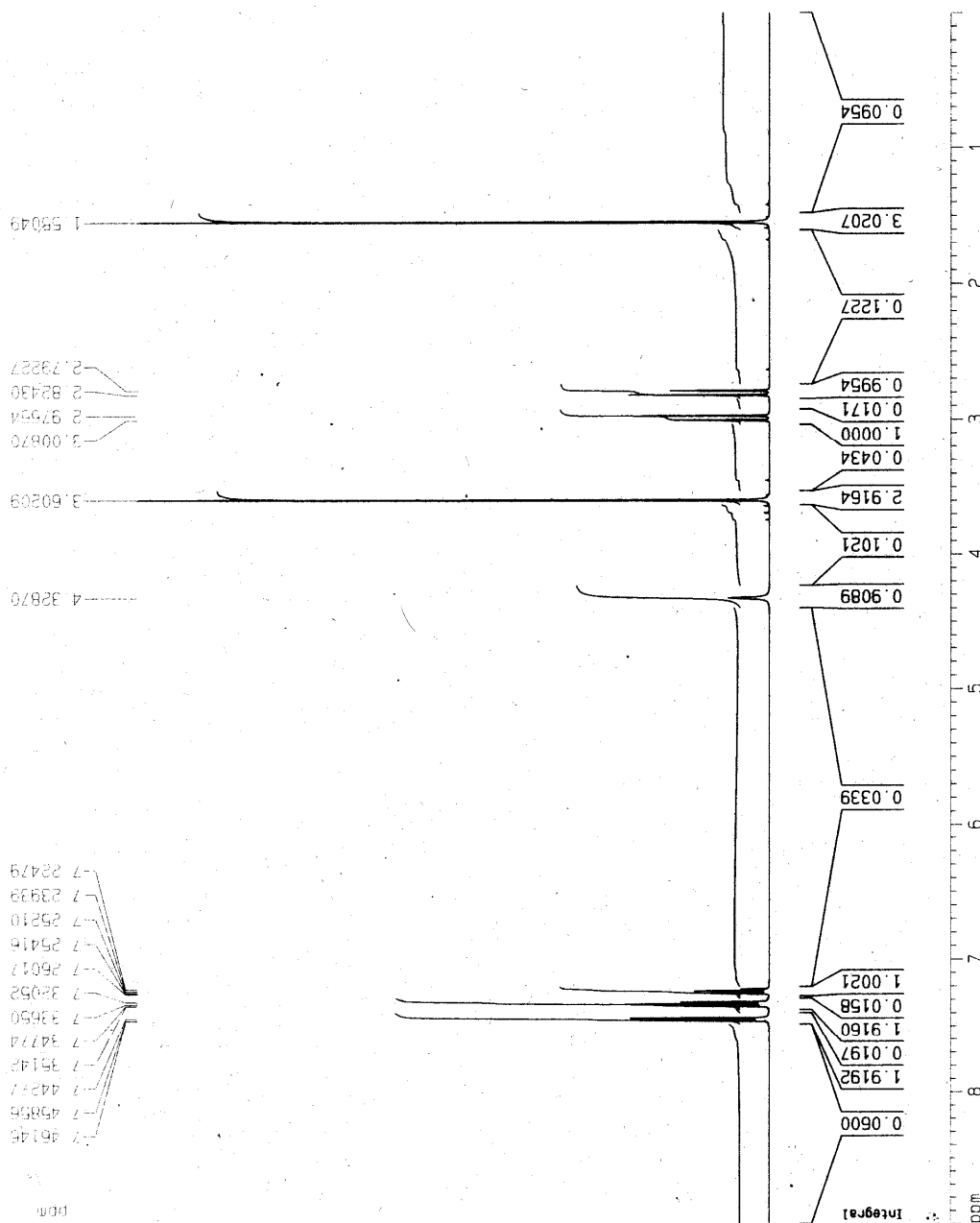
NAME 140-531Me
EXPNO 1
PROCNO 1

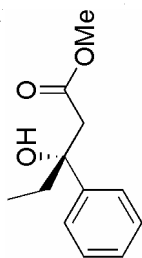
F2 - Acquisition Parameters
Date_ 20071121
Time 18 57
INSTRUM gn500
PROBHD 5 mm Multinuc1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 80.6
DM 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRR 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -6.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300140 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 9.000 ppm
F1 4501.17 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.45000 ppm/cm
HZCM 225.05849 Hz/cm



¹H NMR (500 MHz, CDCl₃) Spectrum of 11b

11b

Current Data Parameters
 NAME 14D-529et
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20071121
 Time 18.43
 INSTRUM drx500
 PROBHD 5 mm Multinuc1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 181
 DM 48.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PL1 -6.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300143 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 12.50 cm
 F1P 9.000 ppm
 F1 4501.17 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCM 0.45000 ppm/cm
 HZCM 225.05849 Hz/cm

