Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Chelating Leaving Groups Enabling New Titanium IV Reactions: Applications to Stereoretentive Halogenations and Azidations

Salvatore D. Lepore,* Deboprosad Mondal, Song Ye Li, and Anjan K. Bhunia

Department of Chemistry, Florida Atlantic University, Boca Raton, FL 33431-0991

E-mail: slepore@fau.edu / Fax: 561.297.2759

Supporting Information

General Information. All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring. Purification of reaction products were carried out by flash column chromatography using Flash Silica gel 40-63μ. Analytical thin layer chromatography was performed on 0.25mm silica gel 60-F plates. Visualization was accomplished with UV light and aqueous potassium permanganate solution staining followed by air heating.

^{1}H NMR were recorded on a Varian Mercury400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26ppm). Data are reported as: (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet; coupling constant(s) in Hz, integration). ^{13}C NMR were recorded on Varian Mercury400 (100 MHz) spectrometer. Chemical shifts are reported in ppm trimethylsilane, with solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm). High-resolution mass spectra were obtained from University of Florida Mass Spectrometry Laboratory.

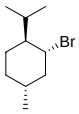
Materials. Stabilized/Certified ACS dichloromethane and anhydrous 1,2-dichloroethane were obtained from commercial sources. All other reagents are also commercially available and were used without further purification.

General procedure for bromination reactions: A cold (-78˚C) solution of quisylate ester (1.0 eq) in dichloromethane (1.5 M) was added to a cold (-78˚C) solution of $TiBr_4$ (2.0 eq) in dichloromethane (0.15 M). Following completion (usually within 15 min), the reaction mixture was quenched with water and extracted three times with dichloromethane. The collected organic extracts were concentrated and the resulting oil was purified by silica gel chromatography (using pure hexane as eluent).

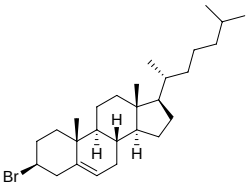
General procedure for azidation reactions: To a room temp solution of TiF_4 (6.0 eq) in 1,2-dichloroethane (0.2 M) was added azidotrimethylsilane (25 eq). After stirring for 30 min, the reaction slurry was cooled (0˚C) followed by the addition of quisylate ester (1.0 eq) as a 2-dichloroethane solution (1.5 M). The reaction was maintained at 0˚C until completion (<8 h). Following completion the reaction mixture was quenched with water and extracted three times with dichloromethane. The collected organic extracts were concentrated and the resulting oil was purified by silica gel chromatography (using pure hexane as eluent).

General Procedure for azidation reactions with mixed Lewis acid: To a room temp solution of TiF_4 (6.0 eq) in dichloromethane (0.5 M) was added trimethylsilyl triflate (9.0 eq). The resulting slurry was stirred for 15 min followed by the addition of azidotrimethylsilane (18.0 eq) which was allowed to stir for an additional 15 min. The reaction slurry was then cooled (0˚C) followed by the addition of quisylate ester (1.0 eq) as a dichloromethane solution (0.2 M). The reaction was maintained at 0˚C until completion (<2 h). Following completion the reaction mixture was quenched with water and extracted three times with dichloromethane. The collected organic extracts were concentrated and the resulting oil was purified by silica gel chromatography (using pure hexane as eluent).

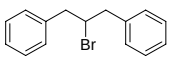
General procedure for iodination reactions: In 1,2-dichloroethane was dissolved TiI_4 (2.0 eq) followed by stirring at room temperature for 30 min. The solution was cooled (0˚C) and to it was added alkylsulfonate ester (1.0 eq) as a solution of 1,2-dichloroethane (1 M). Following completion (usually within 5 h), reaction mixture was quenched with water and extracted three times with dichloromethane. The collected organic extracts were concentrated and the resulting oil was purified by silica gel chromatography (using pure hexane as eluent).



(1*S*, 2*R*, 4*R*)–2-bromo-1-isopropyl-4-methylcyclohexane. ^{1}H NMR (400MHz, $CDCl_3$) δ 4.01-3.94 (td, *J* = 11.44, 4.14 Hz, 1H), 2.42-2.31 (m, 2H), 1.77-1.71 (m, 2H), 1.52-1.41 (m, 2H), 1.07-0.97 (m, 3H), 0.92 (d, *J* = 4.18 Hz, 3H), 0.90 (d, *J* = 3.64 Hz, 3H), 0.75 (d, *J* = 6.93 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 59.3, 50.8, 48.2, 34.8, 34.5, 29.2, 24.9, 22.1, 21.4, 15.1; HRMS (CI+) calc. for $C_{10}H_{18}Br$ $[M-H]^+$: 217.0586. Found: 217.0579. $[\alpha]_D^{25}$ = -49.3 (1.4, EtOH) (NALG); $[\alpha]_D^{25}$ = -49.7 (1.4, EtOH) (quisylate).



3-β –bromo-5-cholestene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34-5.33 (m, 1H), 3.96-3.86 (m, 1H), 2.18-2.11 (m, 1H), 2.05-1.91 (m, 3H), 1.86-1.75 (m, 2H), 1.53-1.19 (m, 14H), 1.15-1.04 (m, 8H), 1.01 (s, 3H), 0.88 (d, *J* = 6.55 Hz, 3H), 0.84 (dd, *J* = 6.62, 1.84 Hz, 6H), 0.66 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 141.7, 122.5, 56.9, 56.3, 52.9, 50.4, 44.5, 42.5, 40.5, 39.9, 39.7, 36.6, 36.4, 36.0, 34.5, 32.0, 31.9, 28.4, 28.2, 24.5, 24.0, 23.1, 22.8, 21.1, 19.5, 18.9, 12.1; HRMS (DIP-CI+) calc. for $C_{27}H_{46}Br$ $[M]^+$: 449.2777. Found: 449.2779. $[\alpha]_D^{25}$ = -21.2 (0.3, $CHCl_3$) (NALG); $[\alpha]_D^{25}$ = -22.5 (2.6, $CHCl_3$) (quisylate).

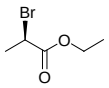


(2-bromopropane-1,3-diyl)dibenzene. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.33-7.29 (m, 4H), 7.26-7.22 (m, 2H), 7.20-7.18 (m, 4H), 4.40-4.33 (m, 1H), 3.22 (dd, *J* = 14.36, 5.77 Hz, 2H), 3.13 (dd, *J* = 14.36, 8.22 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 138.7, 129.4, 128.7, 127.1, 57.3, 45.2; HRMS (CI+) calc. for $C_{15}H_{15}Br$ $[M]^+$: 274.0352. Found: 274.0374.

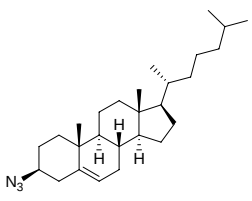
***trans*-1-bromo-2-methycyclohexane** (racemic). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75-3.68 (td, *J* = 11.58, 4.19 Hz, 1H), 2.39-2.33 (m, 1H), 1.90-1.83 (m, 2H), 1.78-1.70 (m, 4H), 1.37-1.28 (m, 2H), 1.12 (d, *J* = 6.47 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 62.3, 41.6, 38.9, 35.4, 27.7, 25.7, 22.1; HRMS (CI+) calc. for $C_7H_{12}Br$ $[M-H]^+$: 175.0117. Found: 175.0122.

Bromocycloheptane. ^{1}H NMR (400MHz, $CDCl_3$) δ 3.36-4.30 (m, 1H), 2.30-2.23 (m, 2H), 2.09-2.00 (m, 2H), 1.73-1.66 (m, 2H), 1.59-1.54 (m, 4H), 1.48-1.40 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 56.8, 40.1, 31.8, 27.8, 25.2, 22.9, 14.3; HRMS (CI+) calc. for $C_7H_{12}Br$ $[M-H]^+$: 175.0117. Found: 175.0107.

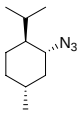
2-adamentylbromide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (m, 1H), 2.35 (m, 1H), 2.32 (m, 1H), 2.15 (m, 2H), 1.98 (m, 1H), 1.96 (m, 1H), 1.88 (m, 4H), 1.76 (m, 2H), 1.64 (m, 1H), 1.61 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 64.2, 38.9, 38.0, 36.6, 31.8, 27.7, 27.1; HRMS (CI+) calc. for $C_{10}H_{14}Br$ $[M-H]^+$: 213.0273. Found: 213.0279.



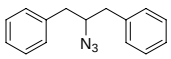
(*R*)-ethyl-2-bromopropanoate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (q, *J* = 6.93 Hz, 1H), 4.22 (dq, *J* = 7.14, 1.68 Hz, 2H), 1.81 (d, *J* = 6.96 Hz, 3H), 1.29 (t, *J* = 7.14 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 170.5, 62.2, 40.5, 21.9, 14.2; HRMS (ESI+) calc. for $C_5H_8BrO_2$ $[M-H]^+$: 180.0278. Found: 180.1040. Measured optical rotation is at $[\alpha]_D^{23}$ = 30.3˚ (1.0, $CHCl_3$). Value from literature (Hanessian, S. ; Kagotani, M. ; Komaglou, K. *Heterocycles* **1989**, *28*, 1115) for the *(R)*-configuration is 32.4˚ (3.93, $CHCl_3$).



3-β –Azido-5-cholestene ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38-5.37 (m, 1H), 3.25-3.16 (m, 1H), 2.29-2.27 (m, 2H), 2.03-1.94 (m, 2H), 1.92-1.78 (m, 2H), 1.61-1.27 (m, 14H), 1.15-1.04 (m, 8H), 0.99 (s, 3H), 0.91 (d, *J* = 6.56 Hz, 3H), 0.86 (dd, *J* = 6.62-1.87 Hz, 6H), 0.67 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 140.0, 122.8, 61.4, 56.9, 56.3, 50.3, 42.5, 39.9, 39.7, 38.3, 37.8, 36.4, 36.1, 32.1, 32.0, 28.5, 28.3, 28.2, 24.5, 24.1, 23.1, 22.8, 21.2, 19.5, 18.9, 12.1; HRMS (ESI+) calc. for $C_{27}H_{46}N$ $[M+H-N_2]^+$: 384.3625. Found: 384.3633. $[\alpha]_D^{25}$ = –5.5 (0.9, $CHCl_3$).



(1*S*, 2*R*, 4*R*) – 2-azido-1-isopropyl-4-methylcyclohexane. ^{1}H NMR (400MHz, $CDCl_3$) δ 3.08-3.02 (td, *J* = 11.25, 4.13 Hz, 1H), 2.14-2.03 (m, 2H), 1.77-1.63 (m, 3H), 1.48-1.37 (m, 1H), 1.22-1.14 (m, 2H), 1.05-0.98 (m, 1H), 0.94 (d, *J* = 6.59 Hz, 3H), 0.91 (d, *J* = 7.05 Hz, 3H), 0.79 (d, *J* = 6.93 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 62.6, 47.4, 40.6, 34.4, 32.1, 27.1, 23.8, 22.5, 21.1, 16.1; HRMS (CI+) calc. for $C_{10}H_{20}N_3$ $[M+H]^+$: 182.1665. Found: 182.1657. $[\alpha]_D^{25}$ = -64.4 (1.6, $CHCl_3$).

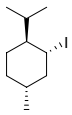


(2-azidopropane-1,3-diyl)Dibenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 4H), 7.29-7.25 (m, 2H), 7.24-7.22 (m, 4H), 3.83-3.76 (m, 1H), 2.92-2.87 (dd, *J* = 13.89, 5.47 Hz, 2H), 2.85-2.80 (dd, *J* = 13.89, 8.19 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 137.9, 129.5, 128.8, 127.0, 65.6, 40.9. HRMS (CI+) calc. for $C_{15}H_{16}N_3$ $[M+H]^+$: 238.1300. Found: 238.1376.

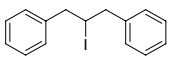
***trans*-1-azido-2-methycyclohexane** (racemic). 1H NMR (400 MHz, $CDCl_3$) δ 2.80-2.74 (td, *J* = 10.61, 3.95 Hz, 1H), 2.05-2.01 (m, 1H), 1.82-1.71 (m, 2H), 1.67-1.62 (m, 2H), 1.56-1.49 (m, 2H), 1.39-1.31 (m, 2H), 1.00 (d, *J* = 6.47 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 67.3, 36.8, 34.2, 31.8, 25.3, 22.5, 19.7. HRMS (CI+) calc. for $C_7H_{14}N_3$ $[M+H]^+$: 140.1200. Found: 140.1188. Compound previously reported (Marino, S. T. *et al. Molecules* **2004**, *9*, 405).

Azidocycloheptane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55-3.49 (m, 1H), 1.97-1.89 (m, 2H), 1.72-1.52 (m, 8H), 1.47-1.38 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 62.8, 34.0, 28.1, 23.0. HRMS (CI+) calc. for $C_7H_{14}N_3$ $[M+H]^+$: 140.1200. Found: 140.1188.

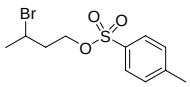
2-adamentylazide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (m, 1H), 2.00-1.97 (m, 4H), 1.91-1.82 (m, 4H), 1.73-1.70 (4H), 1.57-1.55 (m, 1H), 1.54-1.53 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 66.7, 37.5, 36.9, 31.9, 31.8, 27.4, 27.2; HRMS (CI+) calc. for $C_{10}H_{16}N_3$ $[M+H]^+$: 178.1300. Found: 178.1344.



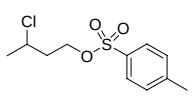
(1*S*, 2*R*, 4*R*) – 2-iodo-1-isopropyl-4-methylcyclohexane. ^{1}H NMR (400MHz, $CDCl_3$) δ 4.16-4.09 (td, *J* = 11.76, 4.02 Hz, 1H), 2.62-2.56 (m, 1H), 2.26-2.18 (m, 1H), 1.83-1.79 (m, 1H), 1.69-1.64 (m, 1H), 1.53-1.40 (m, 2H), 1.12-0.98 (m, 3H), 0.93 (d, *J* = 6.99 Hz, 3H), 0.89 (d, *J* = 6.56 Hz, 3H), 0.71 (d, *J* = 6.91 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 51.3, 51.1, 42.1, 36.5, 34.8, 32.8, 24.8, 21.8, 21.7, 14.8; HRMS (CI+) calc. for $C_{10}H_{18}I$ $[M-H]^+$: 265.0448. Found: 265.0470. $[\alpha]_D^{25}$ = -34.6 (1.84, $CHCl_3$).



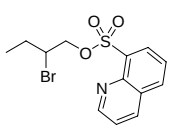
(2-iodopropane-1,3-diyl) Dibenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 4H), 7.27-7.24 (m, 2H), 7.19-7.17 (m, 4H), 4.41 (p, *J* = 4.44 Hz, 1H), 3.22 (d, *J* = 7.23 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 139.9, 129.2, 128.7, 127.1, 46.9, 38.1.



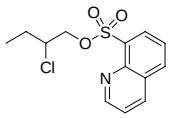
3-bromobutyl-4-methylbenzenesulfonate. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.24 Hz, 2H), 7.07 (d, *J* = 8.07 Hz, 2H), 3.93-3.84 (m, 3H), 2.16 (s, 3H), 1.91-1.83 (m, 1H), 1.78-1.69 (m, 1H), 1.40 (d, *J* = 6.72 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 145.2, 132.9, 130.2, 128.2, 68.6, 46.1, 40.1, 26.6, 21.9; HRMS (DIP-CI+) calc. for $C_{11}H_{15}BrO_3S$ $[M]^+$: 307.0004. Found: 307.0003.



3-chlorobutyl-4-methylbenzenesulfonate. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.26 Hz, 2H), 7.04 (d, *J* = 8.41 Hz, 2H), 3.89-3.86 (dd, *J* = 7.33, 4.65 Hz, 2H), 3.82-3.74 (m, 1H), 2.14 (s, 3H), 1.85-1.76 (m, 1H), 1.65-1.56 (m, 1H), 1.18 (d, *J* = 6.63 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 145.2, 132.9, 130.1, 128.2, 67.7, 54.1, 39.4, 25.5, 21.9; HRMS (DIP-CI+) calc. for $C_{11}H_{15}ClO_3S$ $[M]^+$: 263.0509. Found: 263.0498.



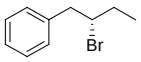
2-bromobutyl quinoline-8 sulfonate. ^{1}H NMR (400MHz, $CDCl_3$) δ 9.15-9.13 (dd, *J* = 4.24, 1.83 Hz, 1H), 8.54-8.52 (dd, *J* = 7.37, 1.35 Hz, 1H), 8.29-8.8.27 (dd, *J* = 8.39, 1.77 Hz, 1H), 8.15-8.12 (dd, *J* = 8.18, 1.27 Hz, 1H), 7.67 (t, *J* = 7.54 Hz, 1H), 7.59-7.56 (dd, *J* = 8.33, 4.26 Hz, 1H), 4.61-4.57 (dd, *J* = 10.6, 5.79 Hz, 1H), 4.50-4.46 (dd, *J* = 10.70, 6.98 Hz, 1H), 4.05-3.99 (m, 1H), 2.02-1.93 (m,1H), 1.72-1.61 (m, 1H), 0.98 (t, *J* = 7.32 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 152.1, 144.2, 136.8, 135.1, 134.1, 133.5, 129.244, 125.576, 122.720, 73.424, 60.073, 27.654, 10.4; HRMS (DIP-CI+) calc. for $C_{13}H_{14}BrNO_3S$ $[M]^+$: 343.9956. Found: 343.9946.



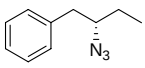
2-chlorobutyl quinoline-8-sulfonate. ^{1}H NMR (400MHz, $CDCl_3$) δ 9.15-9.13 (dd, *J* = 4.26, 1.84 Hz, 1H), 8.54-8.52 (dd, *J* = 7.39, 1.48 Hz, 1H), 8.29-8.27 (dd, *J* = 8.37, 1.8 Hz, 1H), 8.15-8.12 (dd, *J* = 8.22, 1.45 Hz, 1H), 7.68 (t, *J* = 8.07 Hz, 1H, 7.59-7.56 (dd, *J* = 8.31, 4.22 Hz, 1H), 4.61-4.57 (dd, *J* = 10.6, 5.71 Hz, 1H), 4.50-4.46 (dd, *J* = 10.65, 6.98 Hz, 1H), 4.05-3.99 (m, 1H), 2.02-1.92 (m,1H), 1.72-1.61 (m, 1H), 0.98 (t, *J* = 7.36 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 152.1, 144.2, 136.8, 135.1, 134.1, 133.5, 129.2, 125.6, 122.7, 73.4, 60.1, 27.7, 10.4; HRMS (DIP-CI+) calc. for $C_{13}H_{14}ClNO_3S$ $[M]^+$: 300.0461. Found: 300.0478.

4-bromo-2-methypentan-2-ol. ^{1}H NMR (400MHz, $CDCl_3$) δ 4.38-4.30 (m, 1H), 2.23-2.17 (dd, *J* = 15.32, 8.45 Hz, 1H), 2.03-1.98 (dd, *J* = 15.31, 4.53 Hz, 1H), 1.78 (d, *J* = 6.66 Hz, 3H), 1.28 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 71.0, 53.4, 47.1, 30.1, 29.8, 28.6. HRMS (CI+) calc. for $C_6H_{11}Br$ $[M-H_2O]^+$: 163.0600. Found: 163.0122.

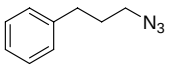
4-chloro-2-methypentan-2-ol. ^{1}H NMR (400MHz, $CDCl_3$) δ 4.30-4.6 (m, 1H), 2.04-1.98 (m, 1H), 1.89-1.85 (m, 1H), 1.55 (d, *J* = 6.57 Hz, 3H), 1.28 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 70.7, 55.5, 52.6, 30.1, 29.7, 27.3.



(S)-(2-bromobutyl)benzene. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 4.17-410 (m, 1H), 3.20-3.09 (m, 2H), 1.92-1.82 (m, 1H), 1.80-1.69 (m, 1H), 1.08 (t, *J* = 7.24 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 138.9, 129.4, 128.7, 127.0, 59.8, 45.6, 31.4, 12.4; HRMS (EI+) calc. for $C_{10}H_{13}Br$ $[M]^+$: 212.0201. Found: 212.0207. $[\alpha]_D^{25}$ = +11.1 (1.8, $CHCl_3$) (NALG); $[\alpha]_D^{25}$ = +10.7 (1.5, $CHCl_3$) (quisylate).

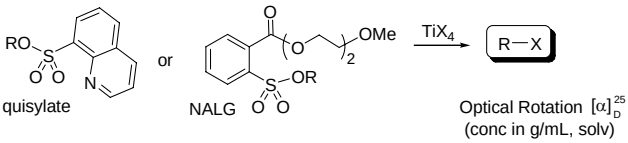


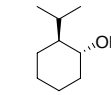
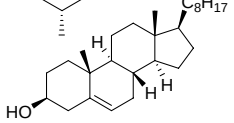
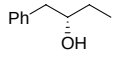
(S)-(2-bromobutyl)benzene. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 3.47-3.41 (m, 1H), 2.81-2.79 (m, 2H), 1.67-1.48 (m, 2H), 1.02 (t, *J* = 7.40 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 138.1, 129.5, 128.8, 126.9, 65.9, 40.8, 27.3, 10.8. $[\alpha]_D^{25}$ = -23.5 (0.6, $CHCl_3$).



3-Phenylpropyl azide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2 H), 7.25-7.18 (m, 3 H), 3.29 (t, J = 6.8 Hz, 2H), 2.71 (t, J = 7.6 Hz, 2H),1.92 (dt, *J* = 15.1, 6.8Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 141.1, 128.74, 128.68, 126.4, 50.9, 33.0, 30.7.

Comparison of Optical Rotations with Reference Compounds - the optical rotation values of examples 1, 2, and 7 (in table 3 of the paper) are included in the table below.

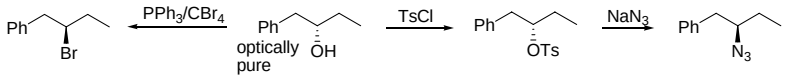


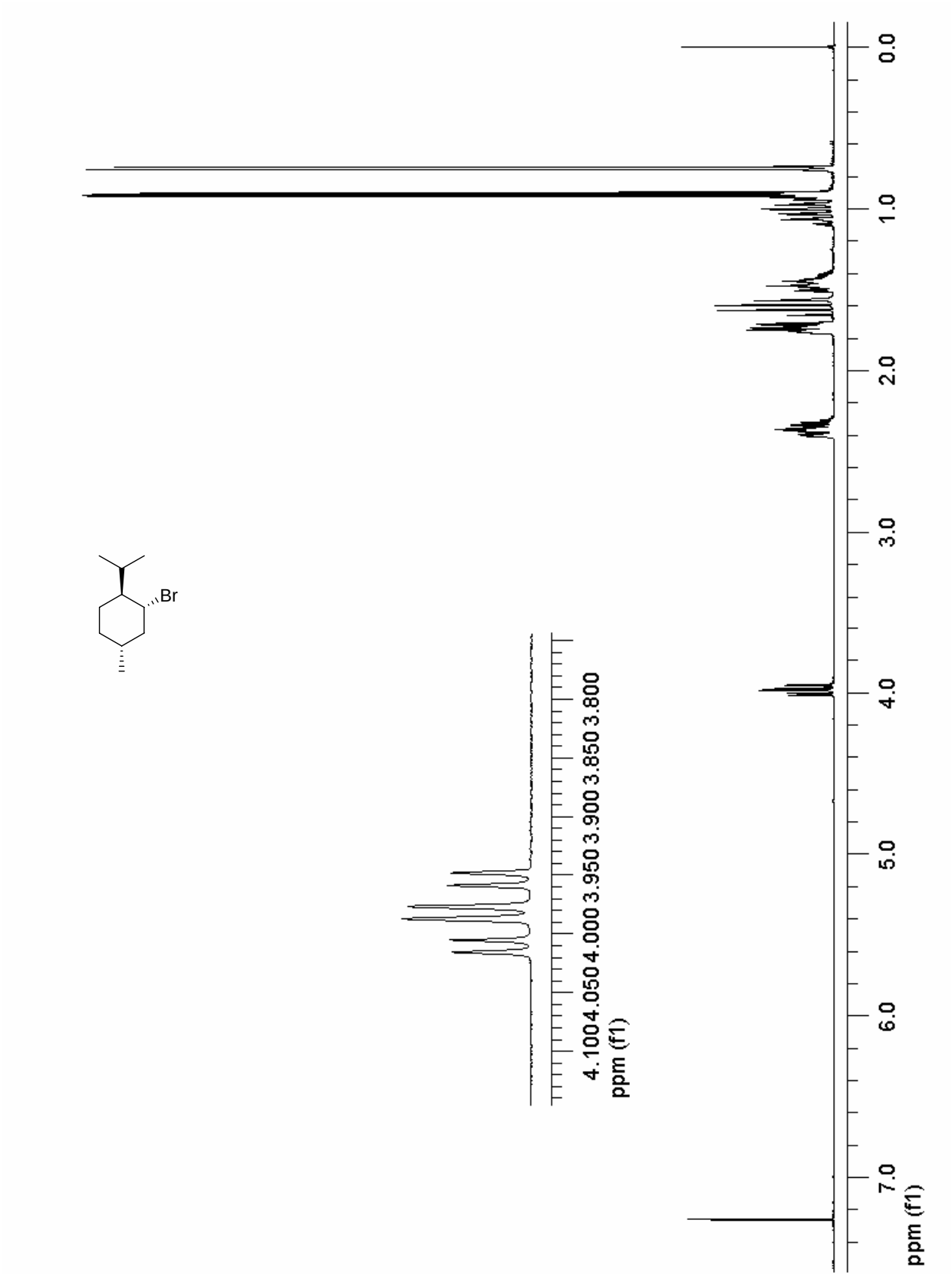
		X = Br			X = N_3	
entry	ROH	ref	NALG	quisylate	ref	quisylate
1		not available	-49.3 (1.4, EtOH)	-49.7 (1.4, EtOH)	-65.7[a] (0.4, $CHCl_3$)	-64.4 (1.6, $CHCl_3$)
2		-22.3[b] (2.92, $CHCl_3$)	-21.2 (0.3, $CHCl_3$)	-22.5 (2.6, $CHCl_3$)	not available	-5.51 (0.9, $CHCl_3$)
7		-12.1[c] (1.4, $CHCl_3$)	11.1 (1.8, $CHCl_3$)	10.7 (1.5, $CHCl_3$)	-26.5[c] (1.2, $CHCl_3$)	+23.5 (0.6, $CHCl_3$)

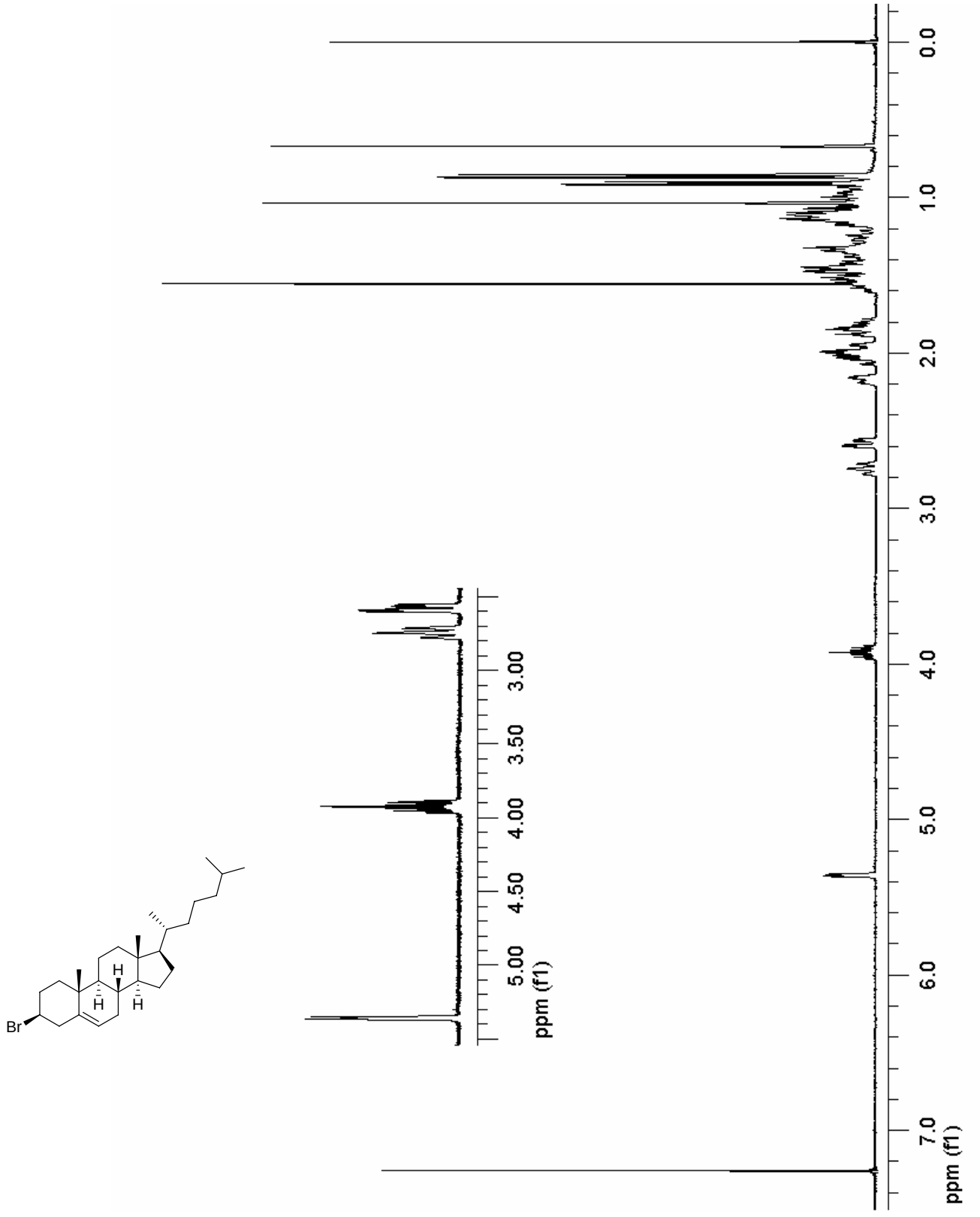
[a] Carmeli, M.; Rozen, S. *J. Org. Chem.* **2006**, *76,* 4585.

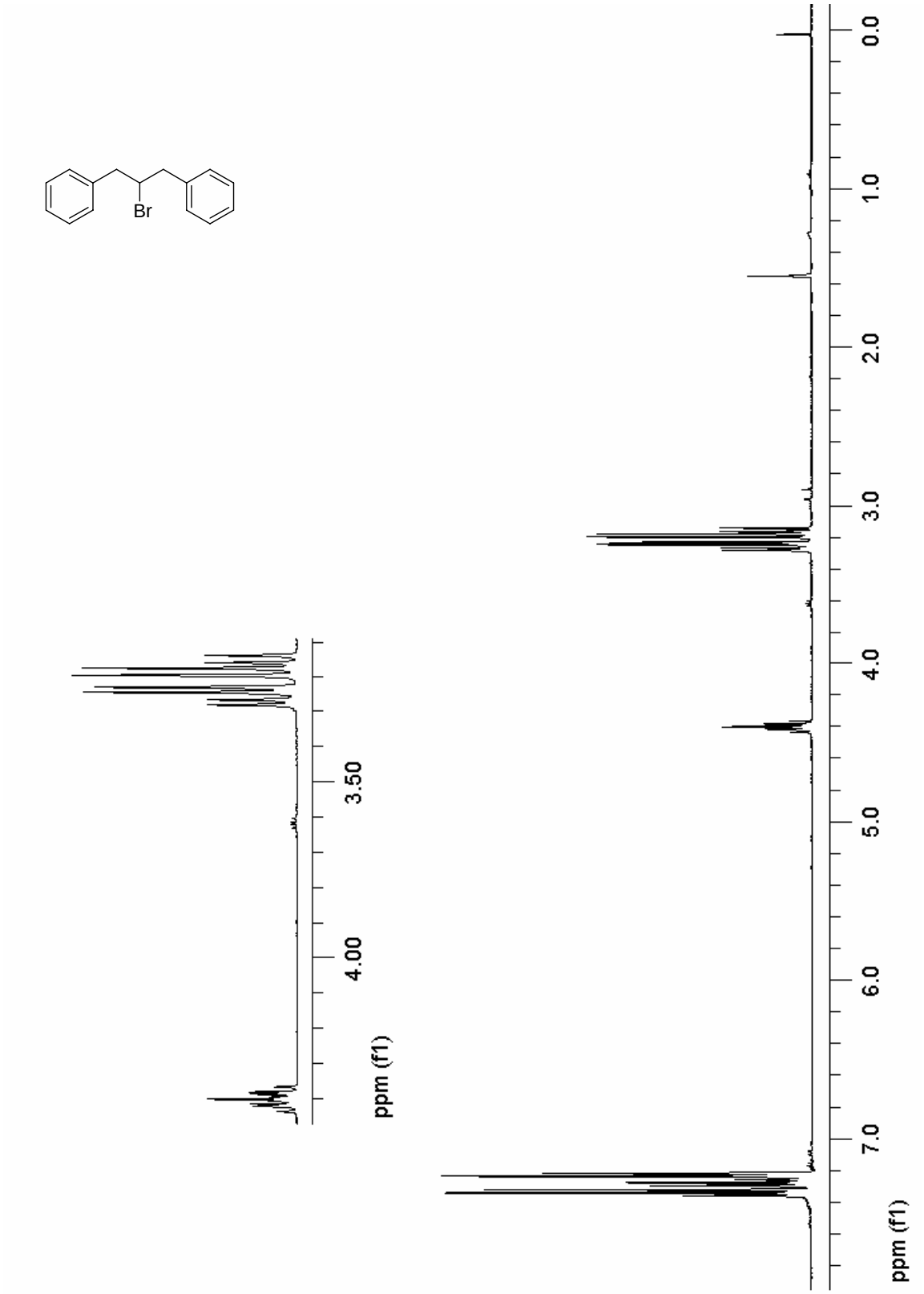
[b] Wagner, A. F.; Wolff, N. R.; Wallis, E. S. *J. Org. Chem.* **1952**, *17,* 529.

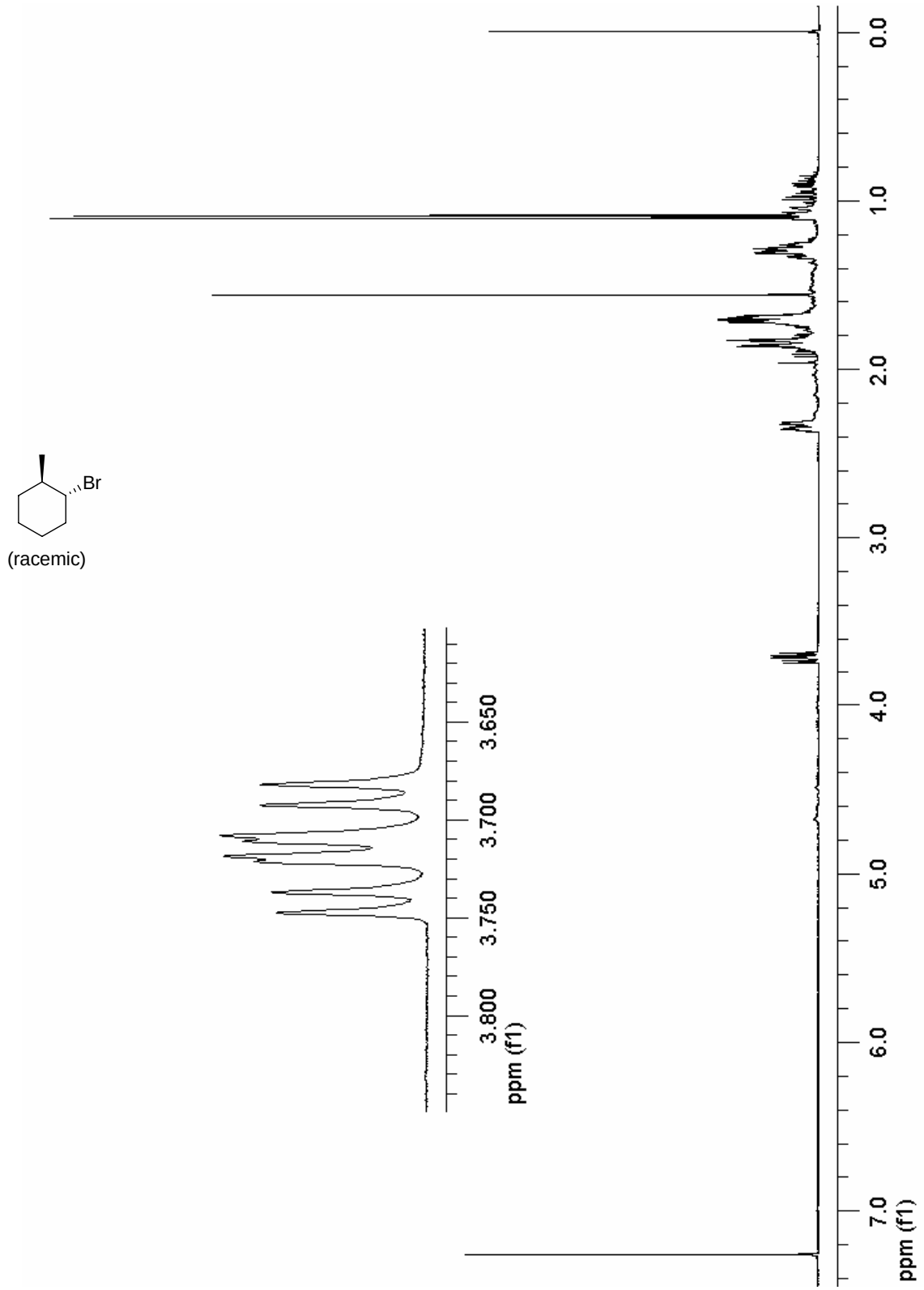
[c] Opposite enantiomer of bromide and azide obtained respectively from S_N2 reaction of (*S*)-1-phenyl-2-butanol with PPh_3/CBr_4 and by conversion of alcohol to the tosylate followed by treatment with NaN_3.

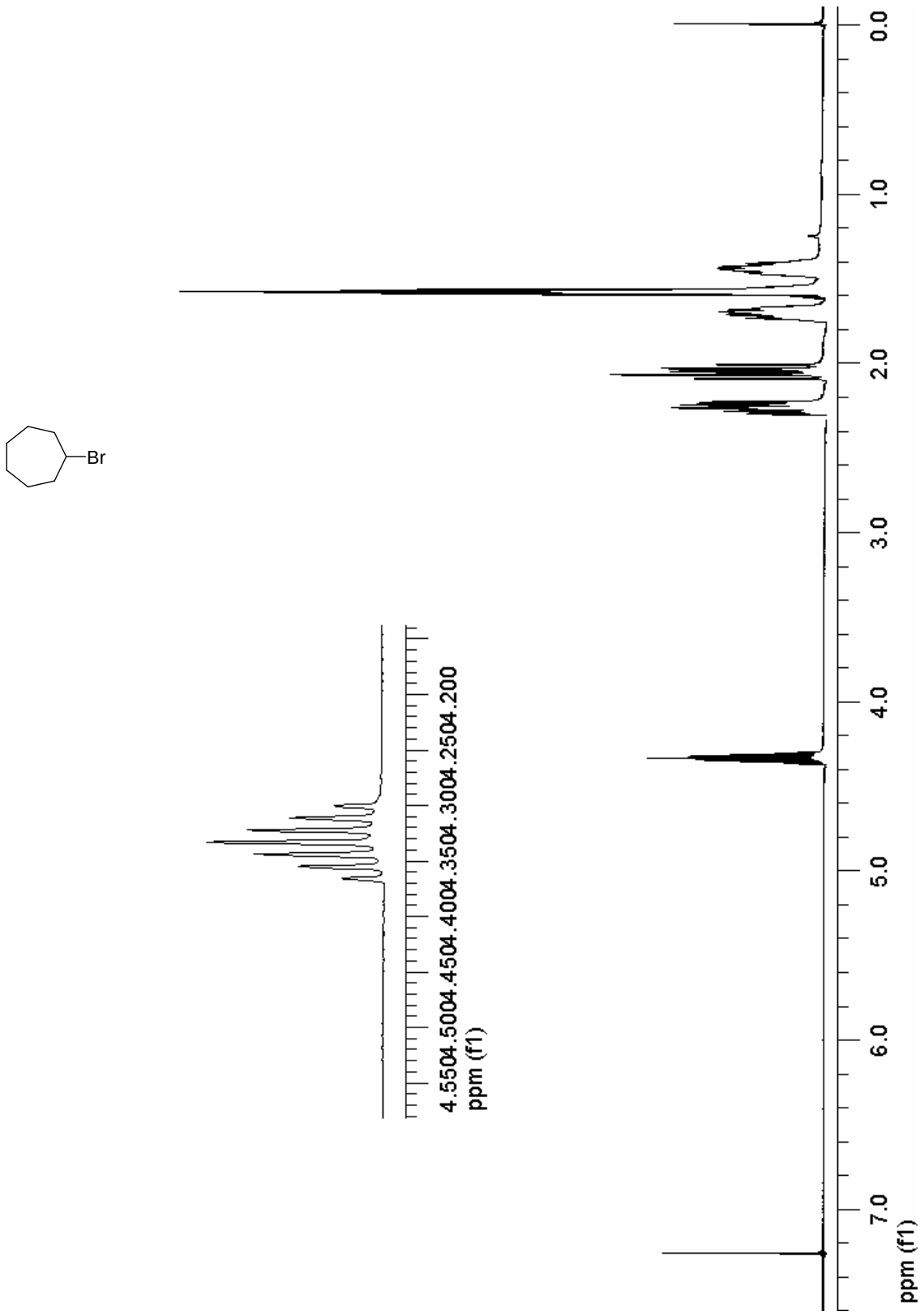


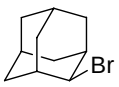

Br
4.100 4.050 4.000 3.950 3.900 3.850 3.800
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

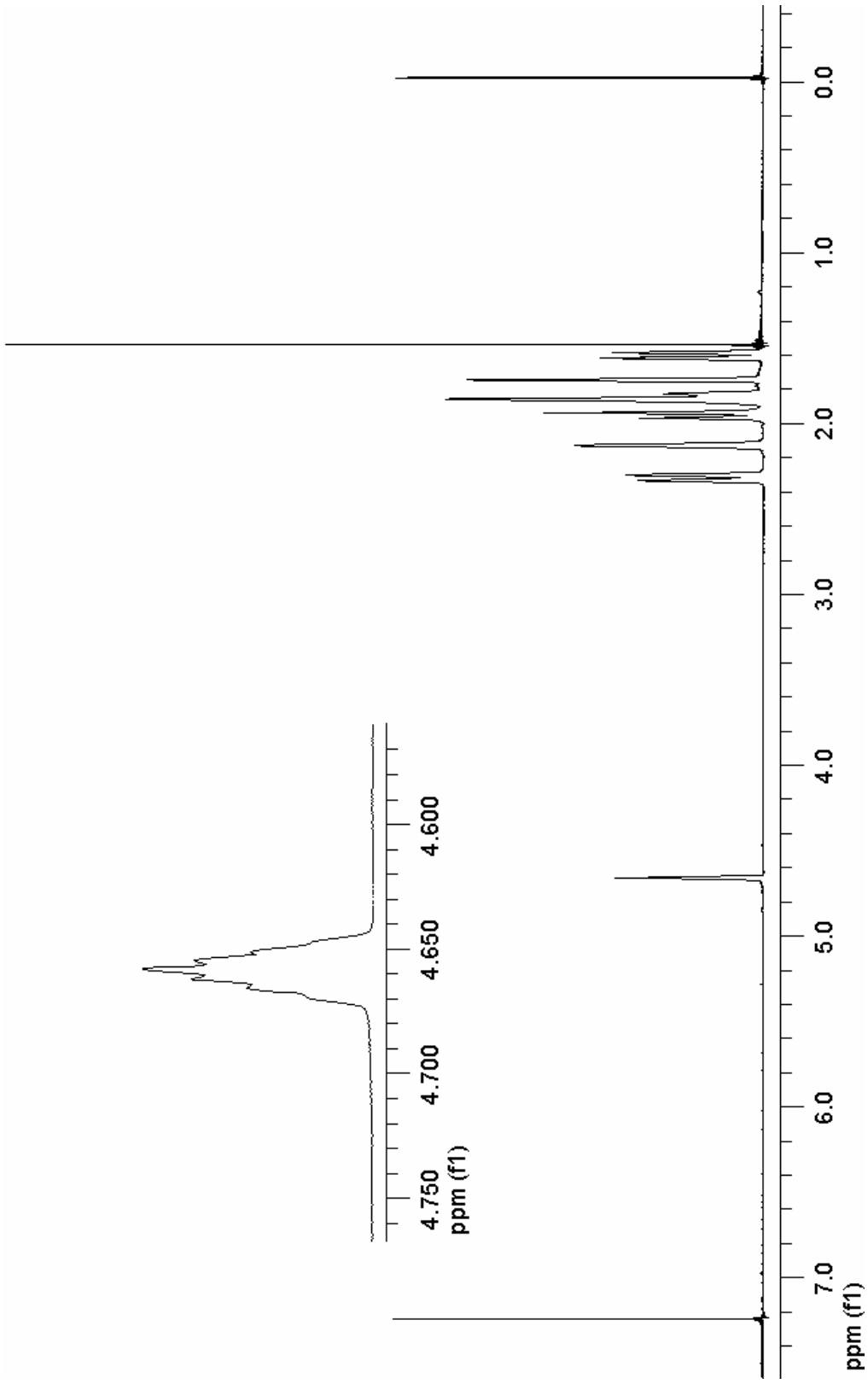

Br
H
H
H
5.00
4.50
4.00
3.50
3.00
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

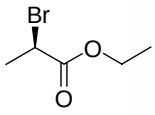

Br
4.00
3.50
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

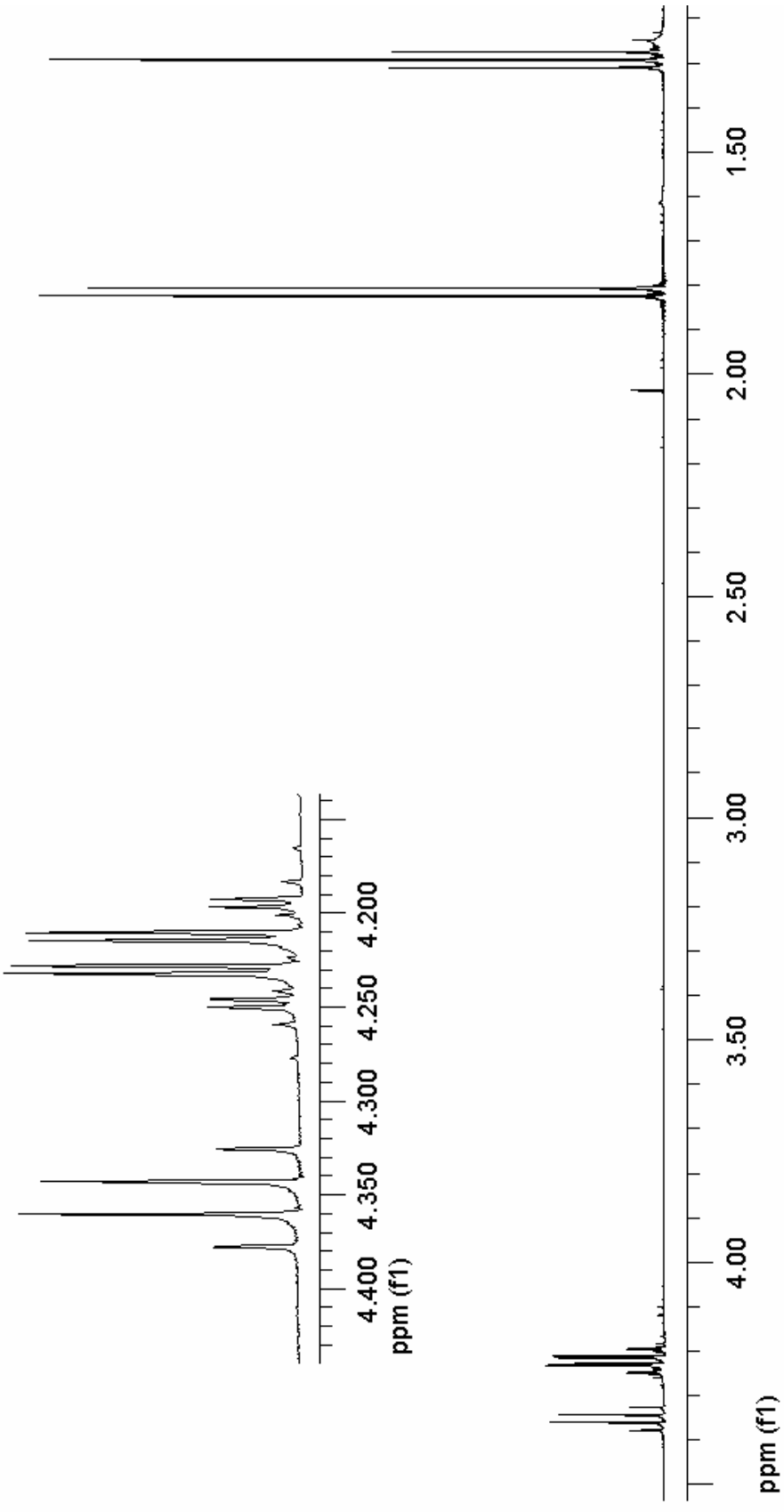

Br
(racemic)
3.800
3.750
3.700
3.650
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

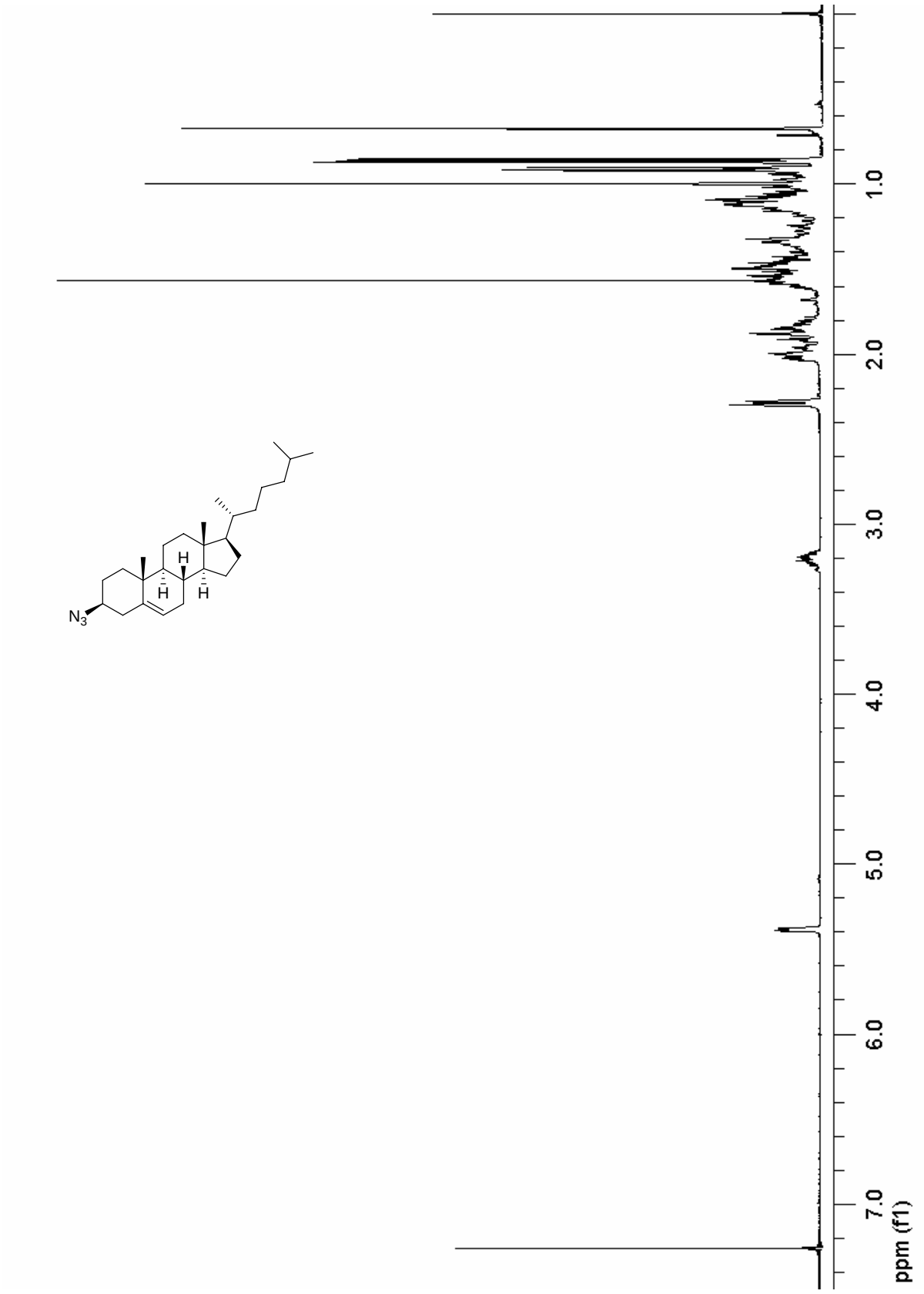

Br
4.550
4.500
4.450
4.400
4.350
4.300
4.250
4.200
ppm (f1)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (f1)

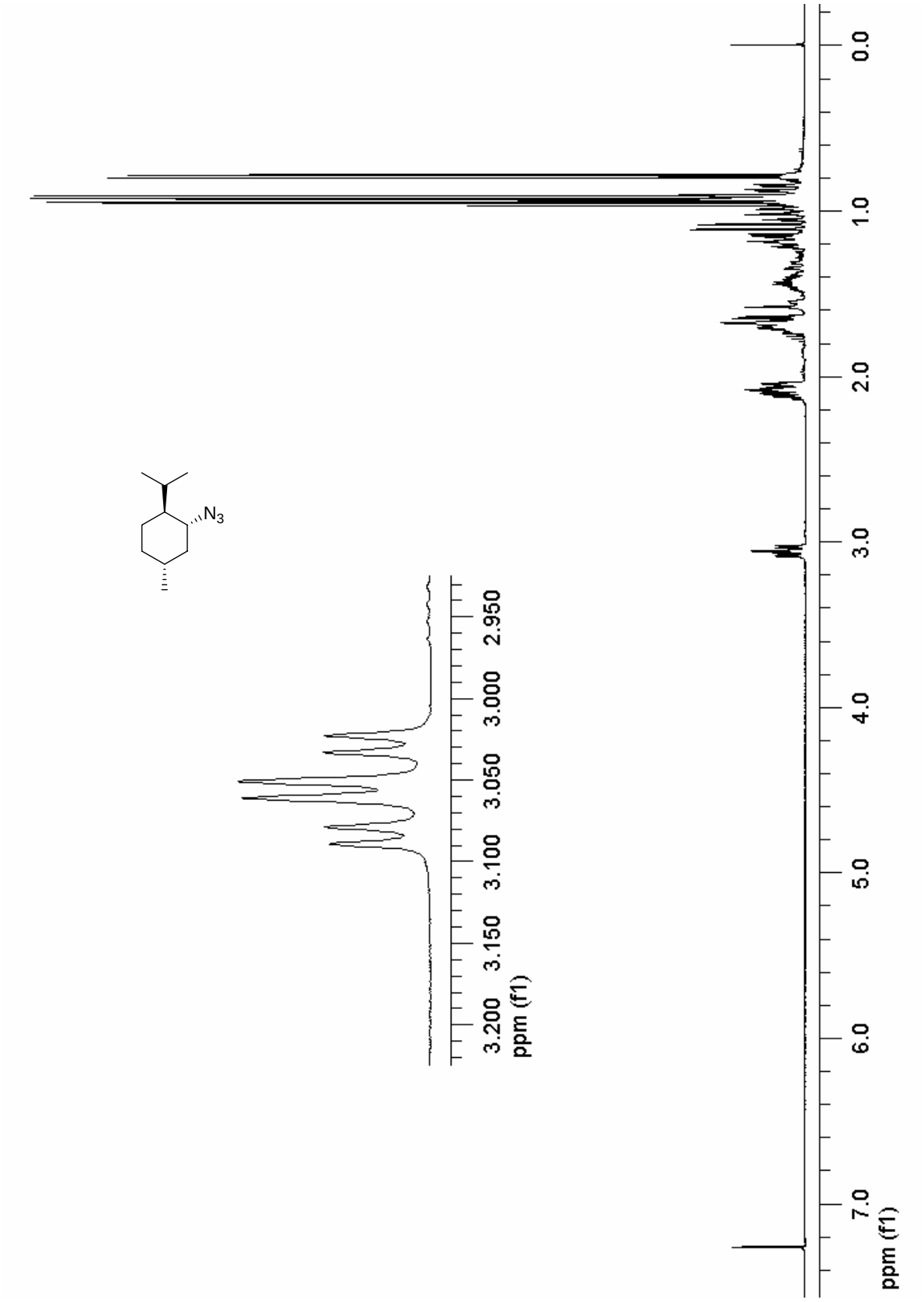

Br

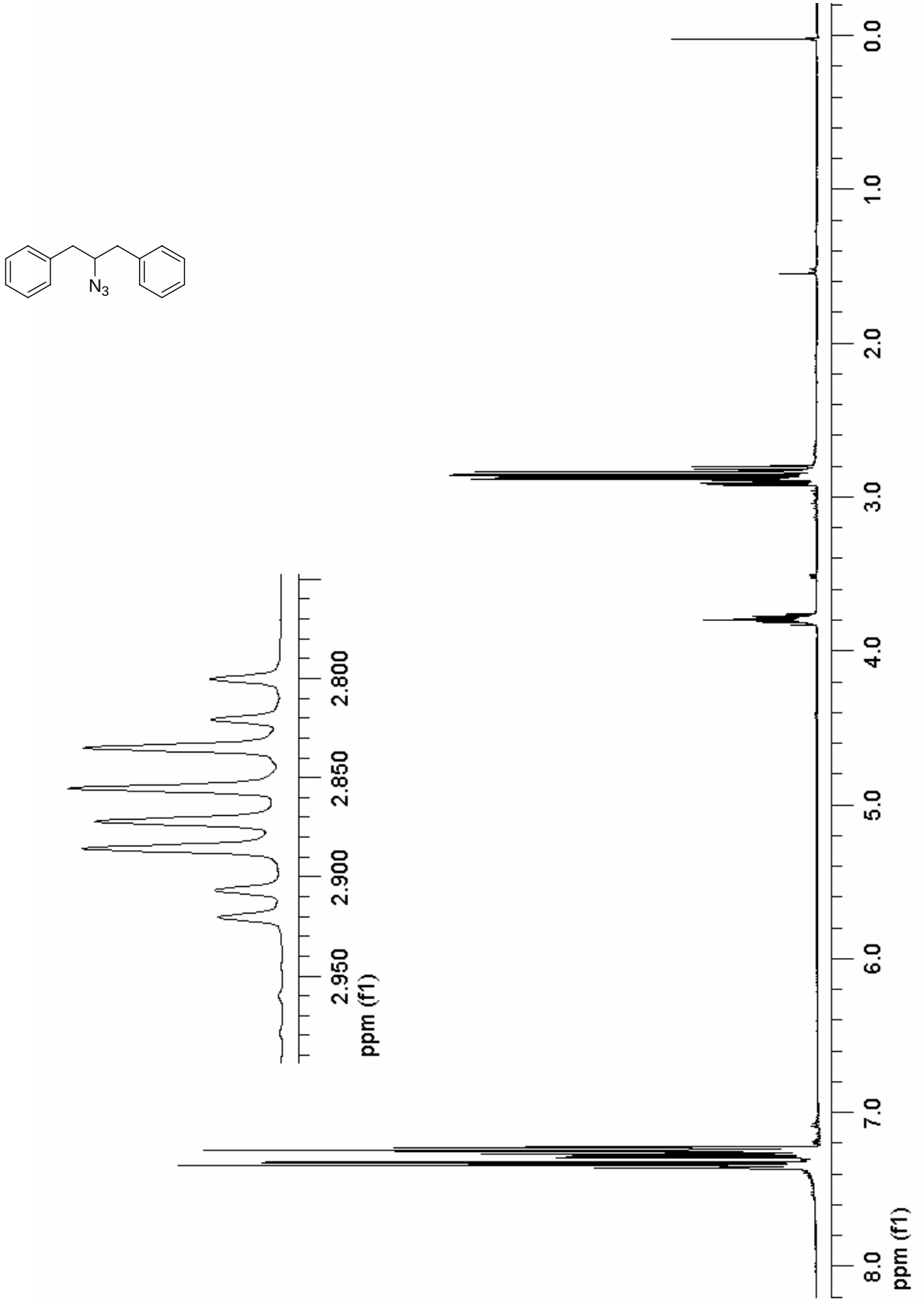

4.750
4.700
4.650
4.600
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

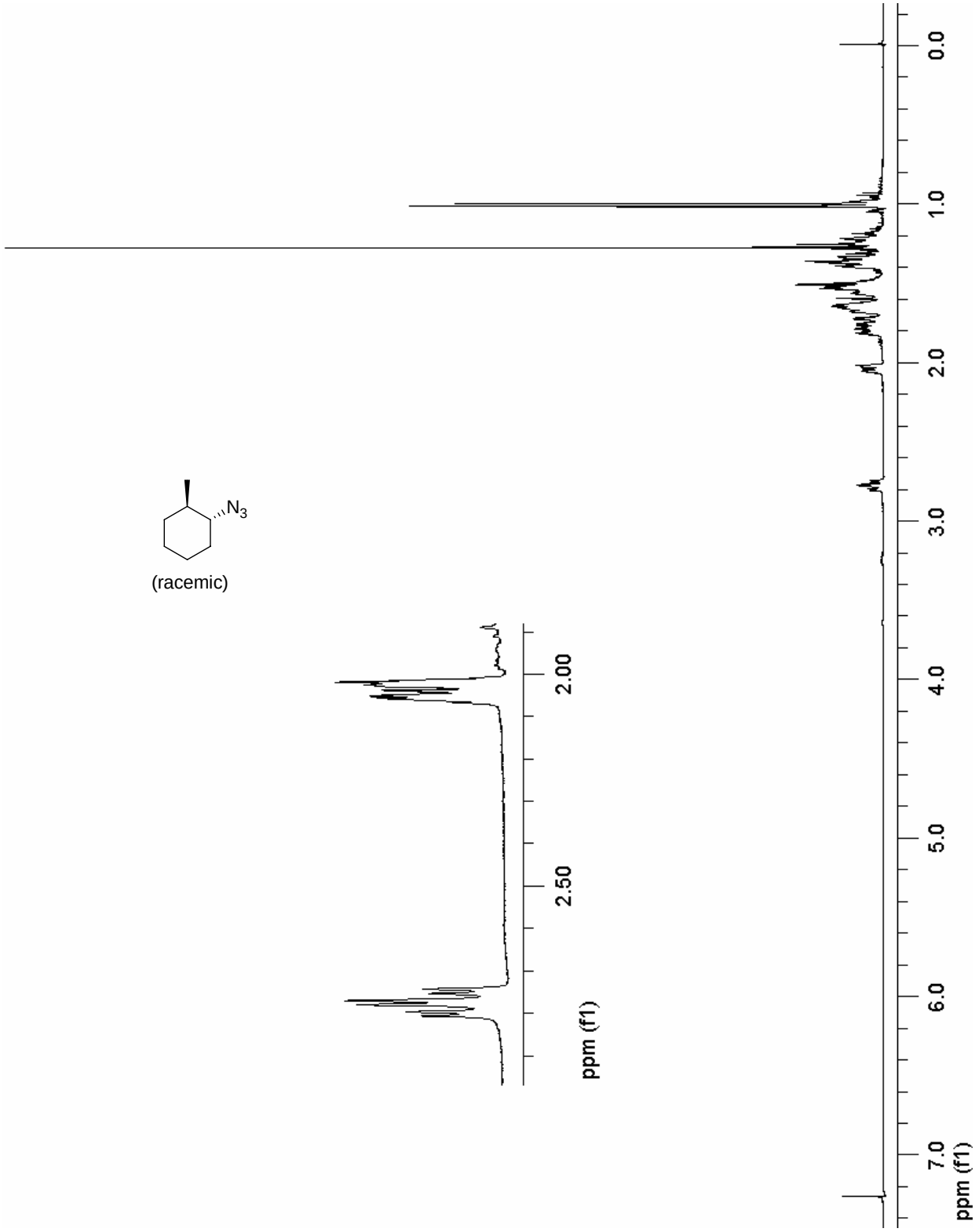

Br
O
O

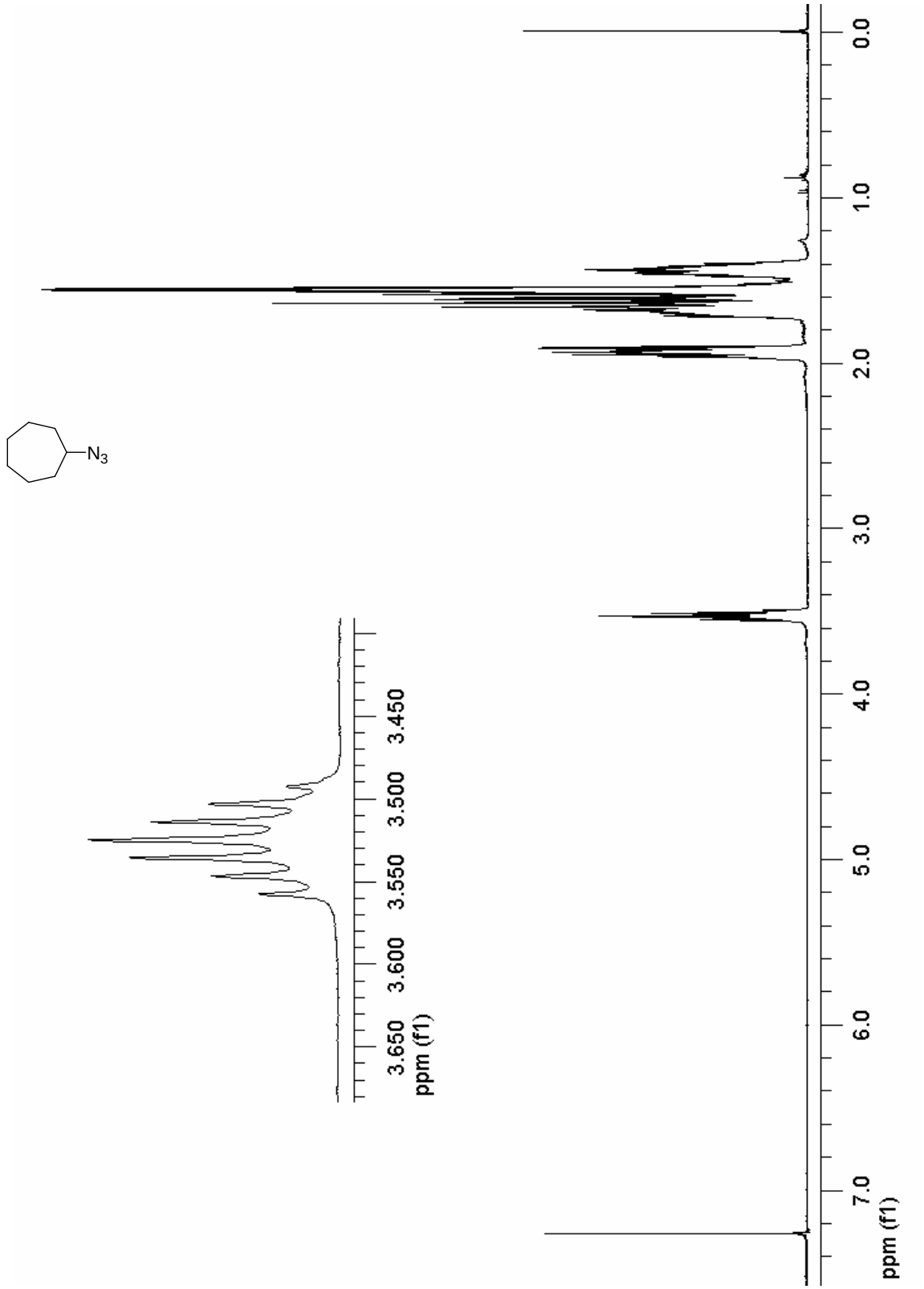

4.400
4.350
4.300
4.250
4.200
ppm (f1)
4.00
3.50
3.00
2.50
2.00
1.50
ppm (f1)

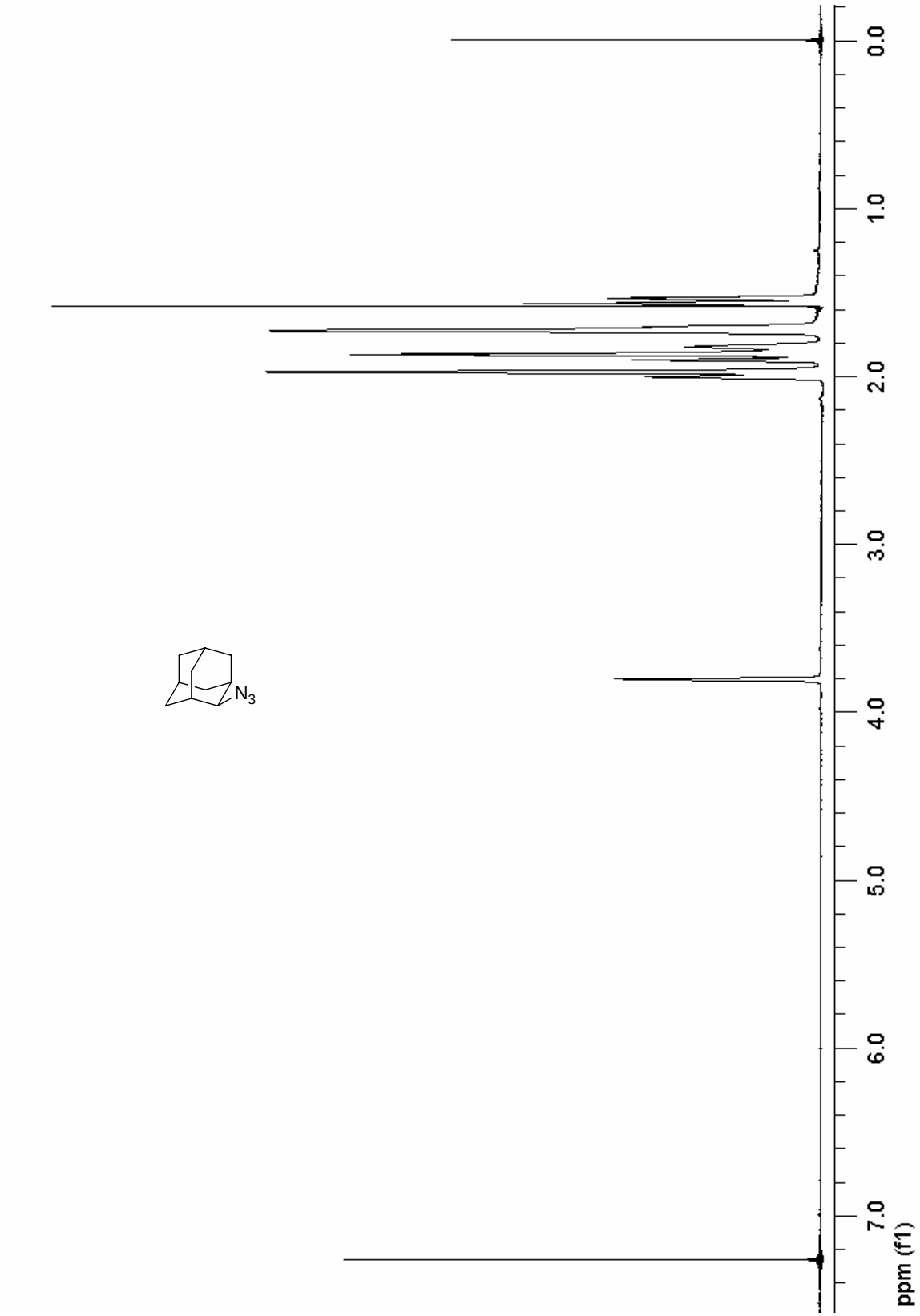

H
H
H
N3
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

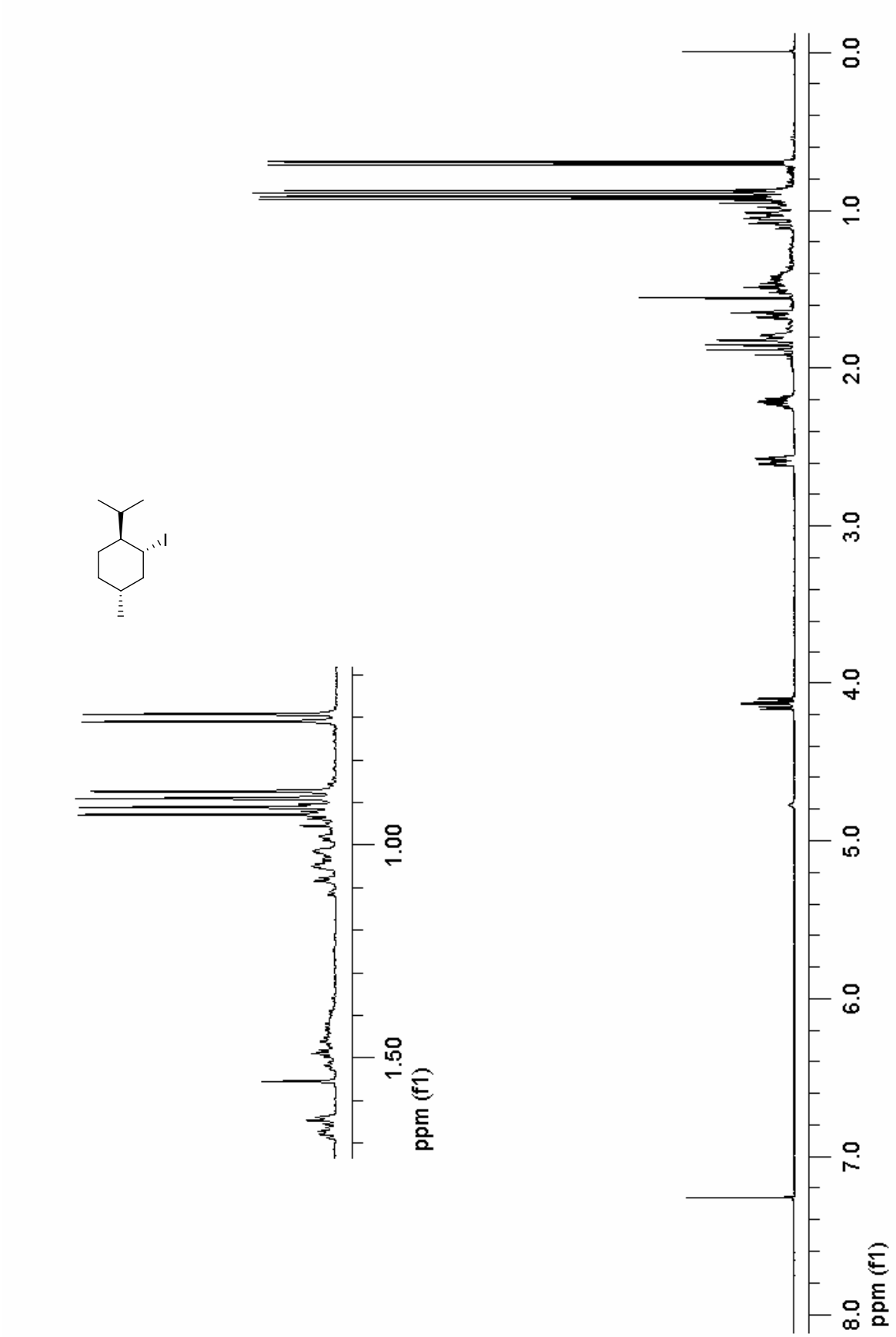

N3
3.200
3.150
3.100
3.050
3.000
2.950
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

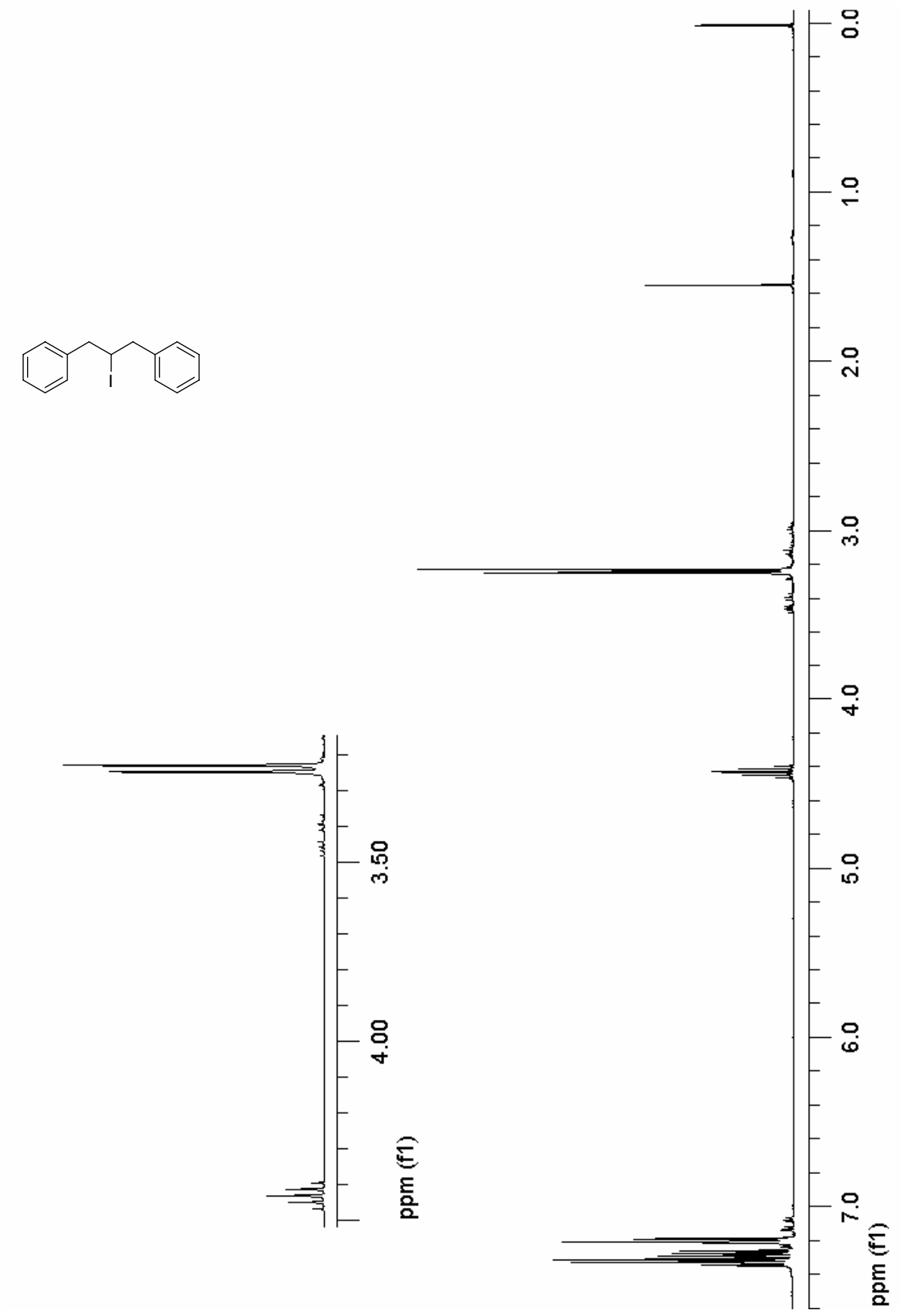

N3
2.950
2.900
2.850
2.800
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

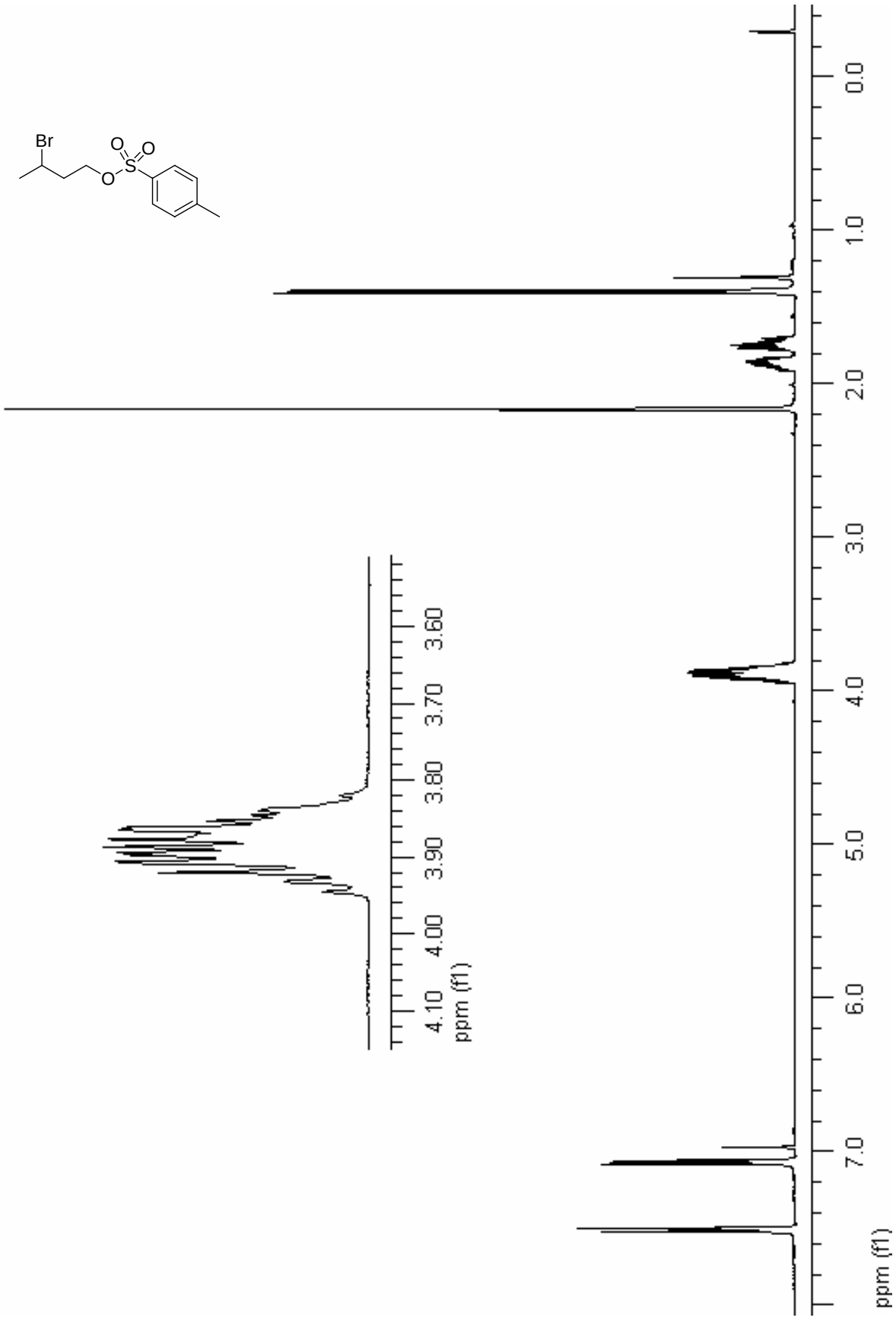

N3
(racemic)
2.00
2.50
ppm (f1)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (f1)

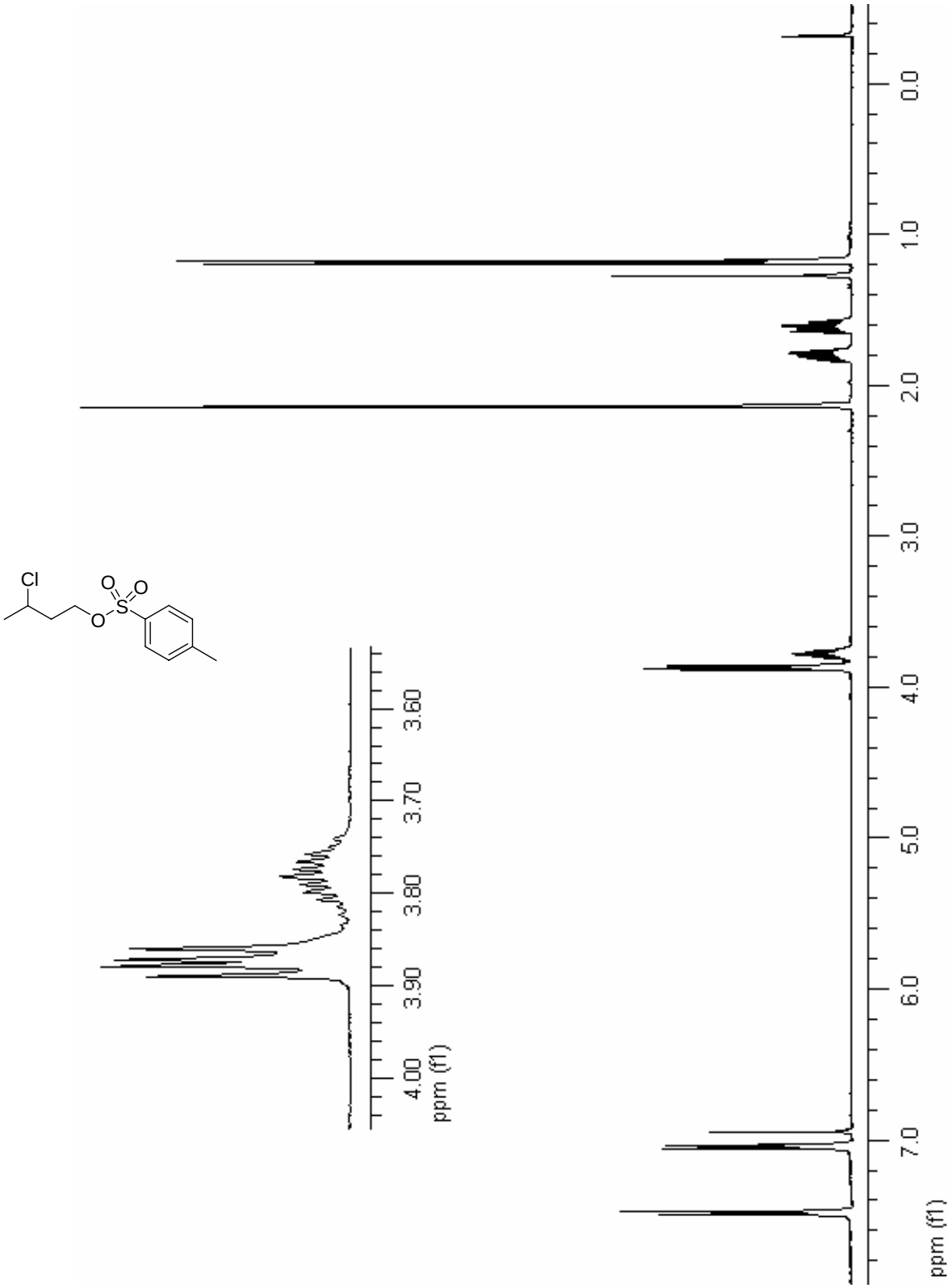

N3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (f1)
3.650
3.600
3.550
3.500
3.450
ppm (f1)

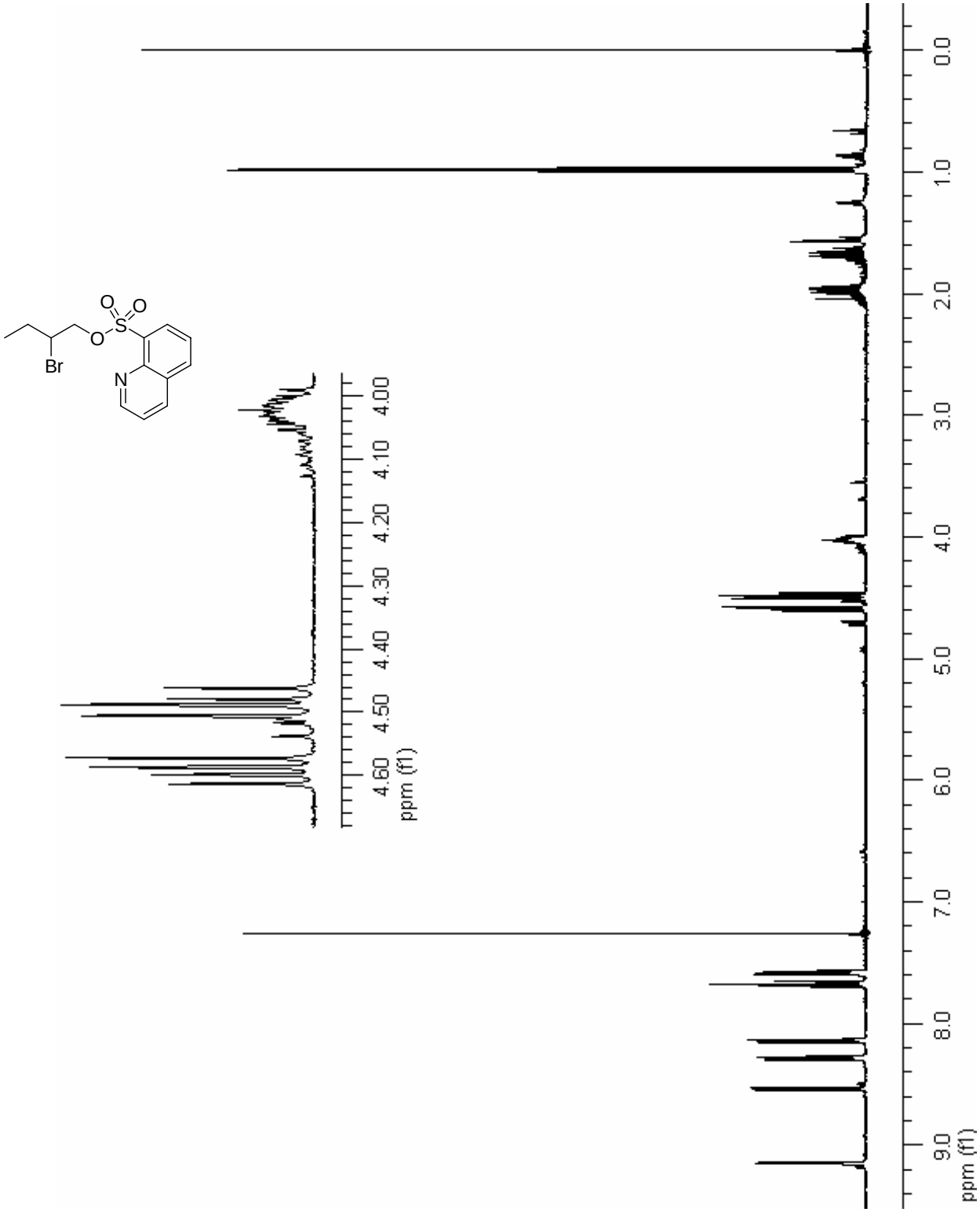

N3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (f1)

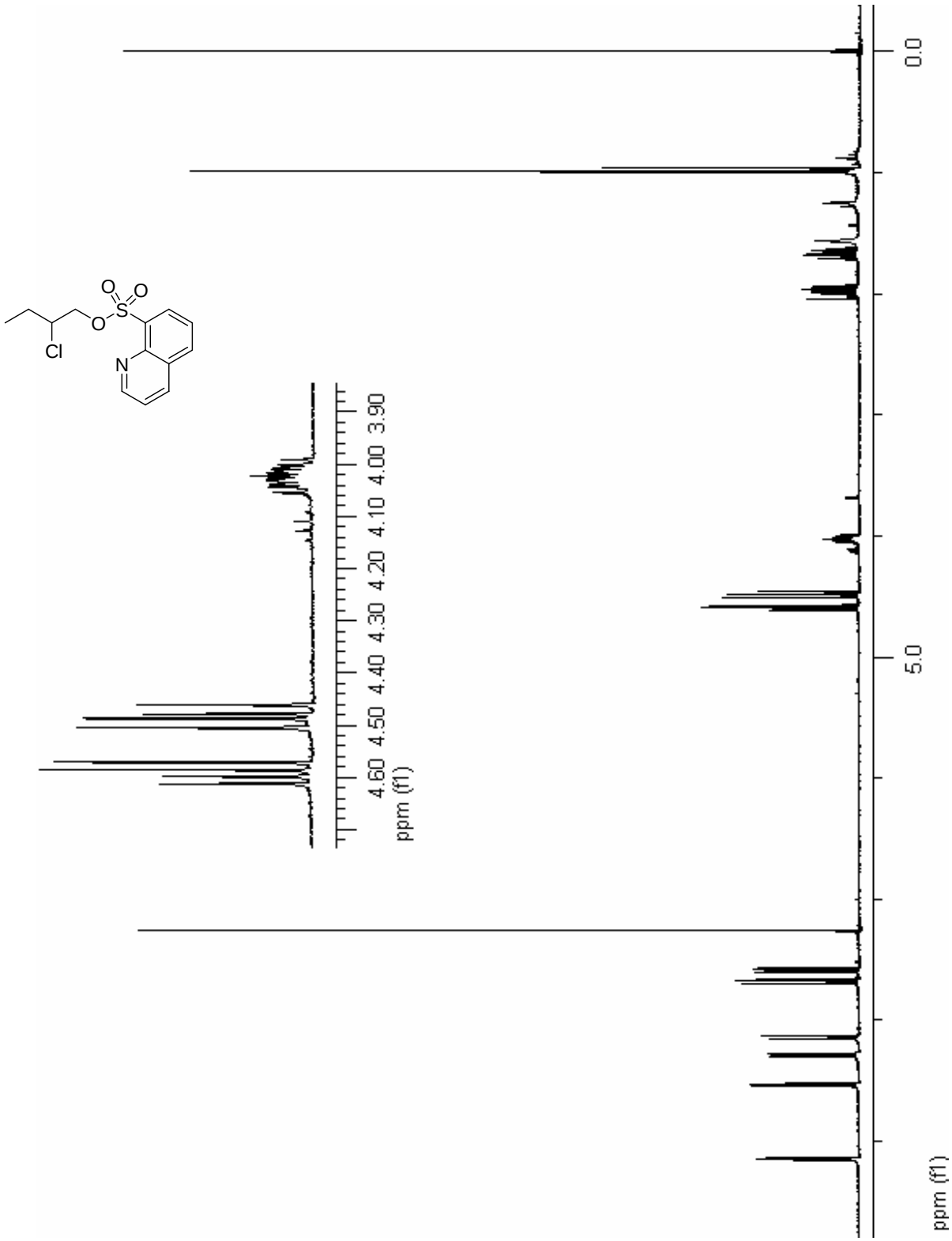

8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
1.50
1.00
ppm (f1)

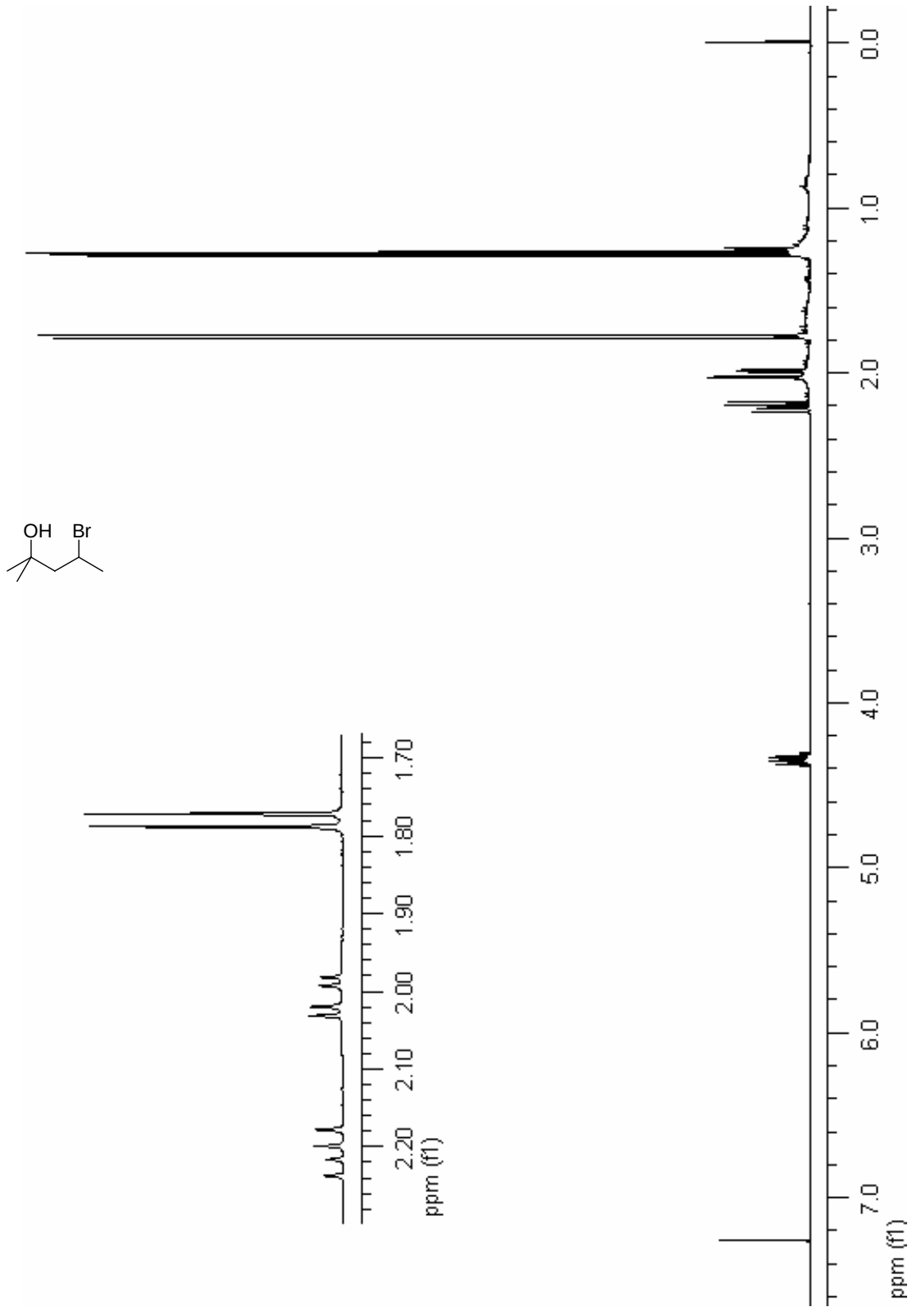

I
4.00
3.50
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

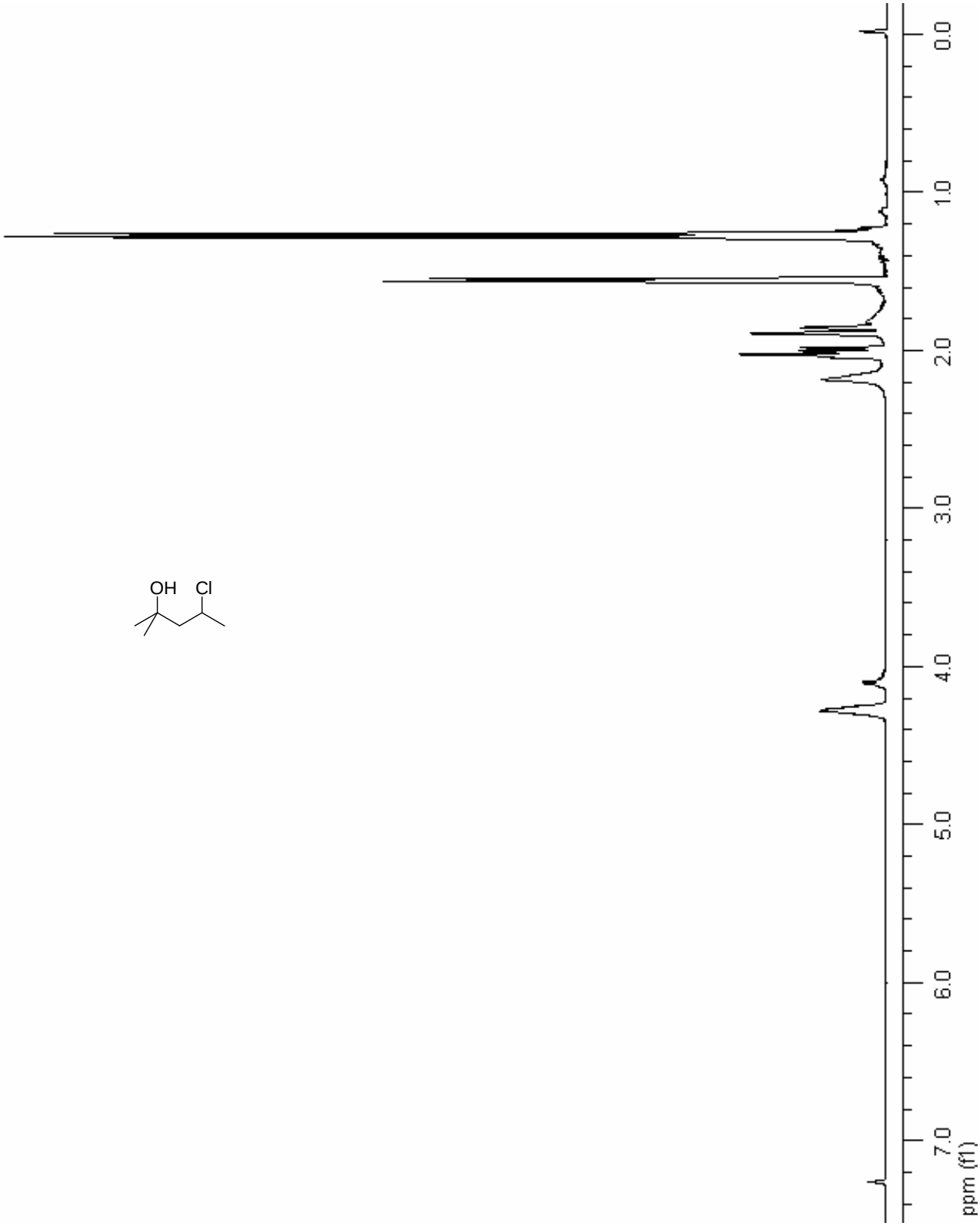

Br
O
O
S
O
O
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
4.10
4.00
3.90
3.80
3.70
3.60
ppm (f1)

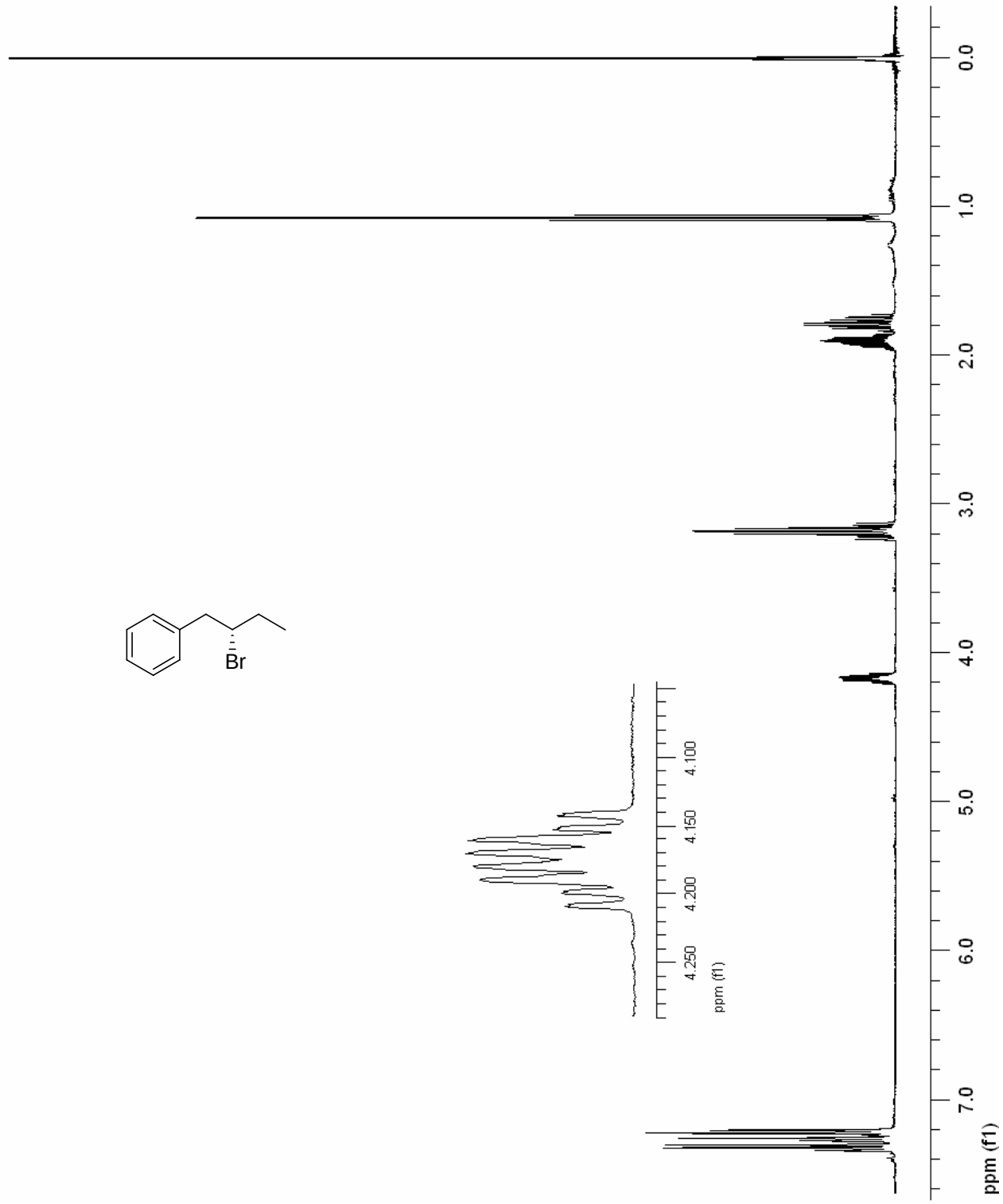

Cl
O
O
S
O
4.00
3.90
3.80
3.70
3.60
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

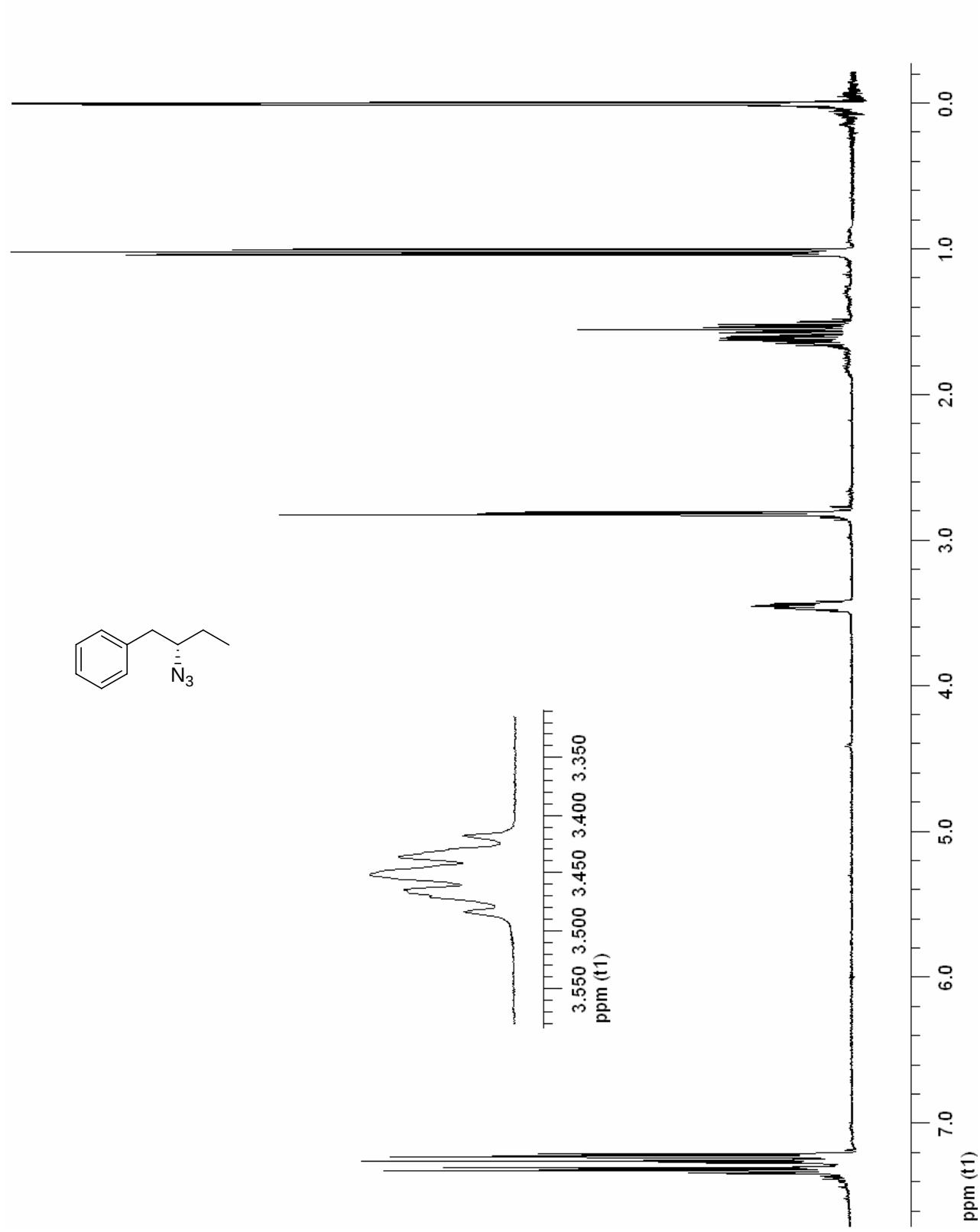

O
O
S
O
Br
N
4.60
4.50
4.40
4.30
4.20
4.10
4.00
ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

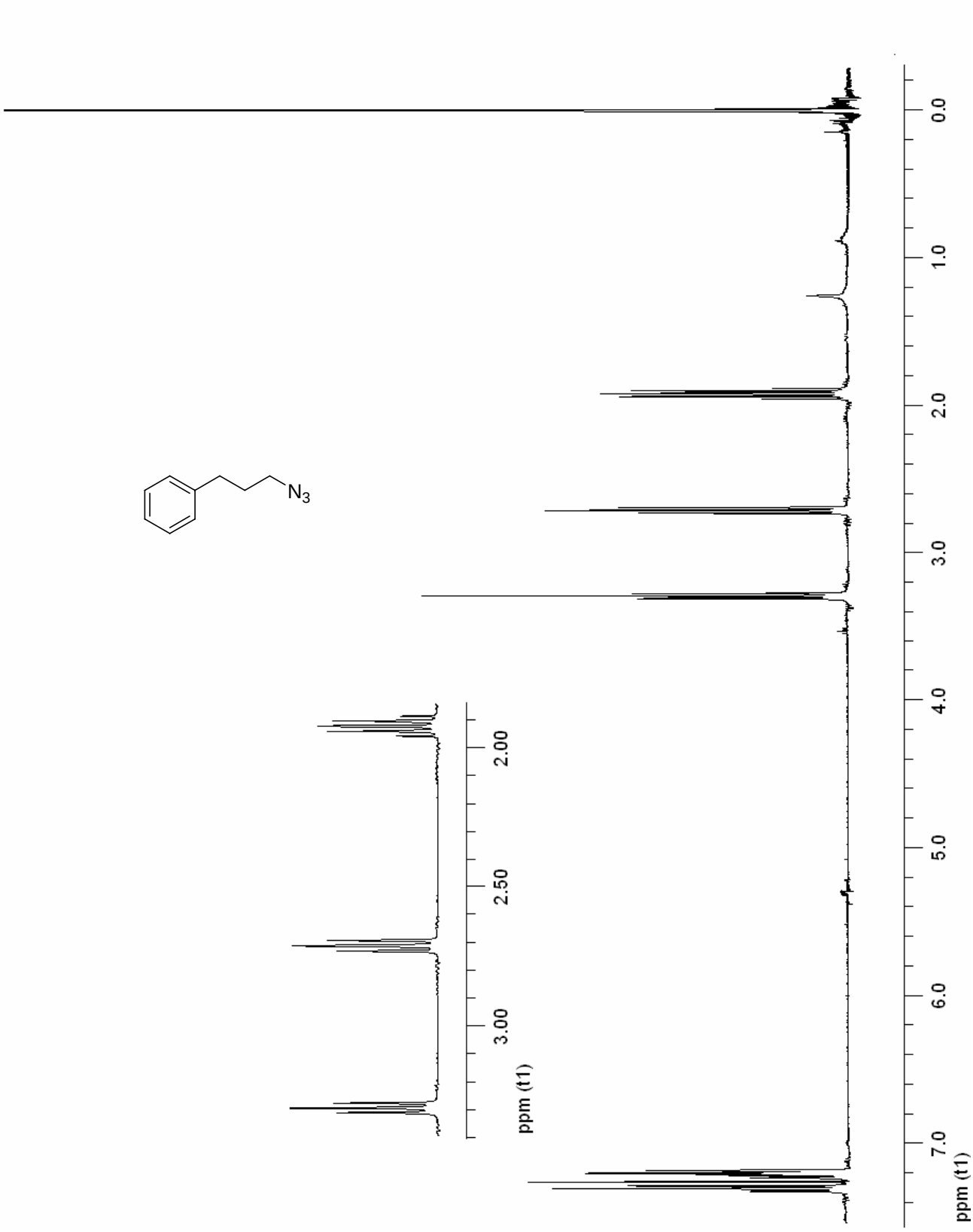

O
O
S
O
Cl
N
4.60 4.50 4.40 4.30 4.20 4.10 4.00 3.90
ppm (f1)
0.0
5.0
ppm (f1)


OH
Br
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
2.20
2.10
2.00
1.90
1.80
1.70
ppm (f1)


OH
Cl
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (f1)


Br
4.250
4.200
4.150
4.100
ppm (f1)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (f1)


N3
3.550 3.500 3.450 3.400 3.350
ppm (t1)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (t1)


N3
ppm (t1)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (t1)
2.00
2.50
3.00